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Tetrahedron 62 (2006) 11350–11359
Tetrahedron

Nickel-catalyzed coupling of terminal allenes, aldehydes, and silanes

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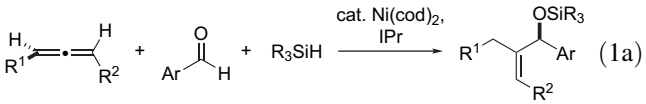
Received 16 February 2006; revised 1 May 2006; accepted 4 May 2006
Available online 26 May 2006

Abstract—The development of a nickel-catalyzed coupling of terminal allenes, aldehydes, and silanes is described. This transformation selectively provides 1,1-disubstituted allylic alcohols, protected as a silyl ether. The choice of the reducing agent is essential for achieving selectivity in this coupling process. A trialkylphosphine (Cyp_3P) and an *N*-heterocyclic carbene (IPr) are complementary in this reaction.

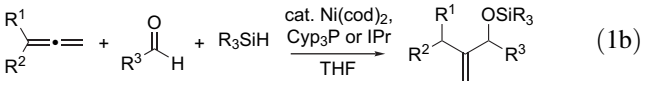
1. Introduction

Nickel is a versatile metal that catalyzes several important transformations, such as, Ziegler–Natta polymerization, hydrogenation, cross coupling, hydrometallation, and multicomponent coupling reactions.[1] We and others have developed several nickel-catalyzed coupling reactions that provided synthetically useful alcohol and amine derivatives.[2] The most effort has been directed toward coupling reactions of aldehydes with either an alkyne or a 1,3-diene, and an organophosphine has often served as a supporting ligand. Also, in these reactions a third coupling partner provides either a hydrogen atom (reductive coupling) or an organic substituent (alkylative coupling), and organozinc and organoboron are the most common such reagents. More recently, organosilanes and *N*-heterocyclic carbene (NHC) ligands have also been reported to be useful alternatives in nickel-catalyzed alkyne–aldehyde (Montgomery)[2g] and 1,3-diene–aldehyde (Mori)[2w–bb] reductive coupling reactions.

We have found the silane/NHC combination to be useful in related allene–aldehyde coupling reactions as well. When employed in nickel-catalyzed coupling of chiral 1,3-disubstituted allenes and aldehydes, *Z*-trisubstituted allylic alcohols are afforded with high selectivity and with complete chirality transfer (Eq. 1a).[2r,s] Herein, we summarize our work on nickel-catalyzed coupling reactions of terminal allenes, aldehydes, and silanes, a process that affords allylic alcohols that differ from those obtained in the allene coupling reactions that were described previously in high regioselectivity and site selectivity (Eq. 1b).



(1a)



(1b)

Allylic alcohols are often prepared by reactions that involve the addition of an alkenyl metal reagent to an aldehyde or a ketone. Two examples are the Nozaki–Hiyama–Kishi reaction[3] and the addition of alkenyl zinc species to aldehydes.[4] The use of transition metals in these two methods allows coordination of chiral ligands to induce asymmetric addition to the carbonyl, providing enantiomerically enriched allylic alcohols.[3g–j,4] The nickel-catalyzed reductive coupling of allenes and aldehydes described in this work is distinct from these strategies since the preparation of a vinyl halide or a vinyl metal species is not required.

Most intramolecular and intermolecular coupling reactions of allenes and aldehydes afford homoallylic alcohols, in which one of the sp^2-hybridized carbons of the allene is the site of C–C bond formation.[5] Catalyzed by several transition metals, cyclization of allenylaldehydes provided homoallylic alcohols in high diastereoselectivity.[5a–j] Transition metal-catalyzed intermolecular couplings of allenes and aldehydes also provided homoallylic alcohols in most cases.[5k–w,2r–t] Other methods of intermolecular and intramolecular coupling of allenes and aldehydes include the single electron transfer process from Pattenden and Crandall,[6a–c] as well as the recently developed SmI_2 mediated reductive coupling from Gillmann, Reissig, and Molander.[6d–f] The

keywords: Allene; Allylic alcohol; *N*-Heterocyclic carbene; Nickel; Silane.
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doi:10.1016/j.tet.2006.05.006

SmI_2 mediated process gave either allylic or homoallylic alcohols, depending on the nature of the substrates.

The three-component couplings of allenes, aldehydes, and silanes described herein are differentiated from the others in that an *allylic* alcohol derivative is the major product, where C–C bond formation occurs at the sp-hybridized carbon of the allene.[2r,s]

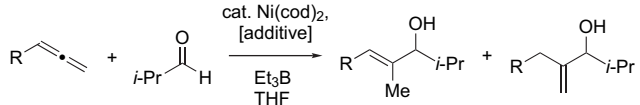
2. Results

Triethylborane (Et_3B) has emerged as an efficient and functional group-tolerant reducing agent in several nickel-catalyzed reactions developed by our group and by others, such as reductive coupling reactions of a diene, an alkyne, or an enyne with an aldehyde, ketone, epoxide, or imine.[7] Thus the starting point for our investigations of the reductive coupling reactions between allenes and aldehydes commenced with a $Ni(cod)_2/Et_3B$ system. A mixture of allene **1a**, isobutyraldehyde, $Ni(cod)_2$, an additive, and Et_3B provided two major coupling products, **2a** and **3a′** (Table 1). Certain additives improved the yield significantly. Phosphines Cyp_3P and $(o\text{-anis})_3P$ provided slightly better yields (entries 3 and 5) than tributylphosphine and NMDPP (entries 2 and 4). Dropwise addition of the allene further increased the yield, possibly due to a minimization of oligomerization of the allene (entries 8 and 9). Without this mode of addition, a substantial amount of **1b** oligomerized under the reaction conditions, affording **2k** in <5% yield (entries 6 and 7). Allylic alcohol **2** predominated over **3′** in all cases regardless of the presence of additives (entries 1–9).

In contrast to these cases using Et_3B, those in which triethylsilane (Et_3SiH) was employed afforded geminally disubstituted allylic alcohol as the exclusive three-component coupling product, along with a product corresponding to hydrosilylation of the allene (Table 2, entry 1). Remarkably, trisubstituted allylic alcohol **2a** was not observed in an NMR spectrum of any of the crude reaction mixtures. Several commercially available silanes were examined next. With Cyp_3P as the supporting ligand, Et_3SiH and *tert*-butyldimethylsilane ($t\text{-BuMe}_2SiH$) provided moderate yields of **3a** (Table 2, entries 1 and 2). Triisopropylsilane afforded **3a** only upon heating (entry 3). Under similar conditions other silanes did not provide **3a** in significant yields (entries 4–7). Diethylzinc in ether did not provide the desired reductive coupling (entry 8).

Solvent and ligand effects were briefly examined (Tables 3 and 4). Although toluene, ethyl acetate, and methanol could also be used, tetrahydrofuran (THF) was found to be the best

Table 1. Additive effects in the $Ni(cod)_2/Et_3B$ system[a]



1a : R = Cy
1b : R = Ph

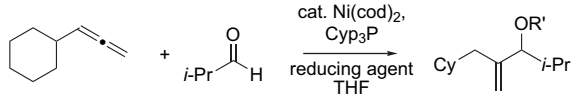
2a : R = Cy
2k : R = Ph

3a' : R = Cy
3k' : R = Ph

Entry	Allene	Additive	Yield (%)[b] **2**+**3′**	**2**:**3′**
1	**1a**	None	9	n.d.
2	**1a**	Bu_3P	10	n.d.
3	**1a**	Cyp_3P[c]	25	6:1
4	**1a**	NMDPP[c]	15	n.d.
5	**1a**	$(o\text{-Anis})_3P$	26	2:1
6	**1b**	$(o\text{-Anis})_3P$	<5	n.d.
7	**1b**	Cyp_3P	<5	n.d.
8[d]	**1b**	Cyp_3P	24	n.d.
9[d]	**1a**	Cyp_3P	50	8:1

[a] General procedure: to a mixture of $Ni(cod)_2$ (20 mol %) and an additive (40 mol %) in THF were added the aldehyde, Et_3B, and the allene at room temperature under argon. The reaction was stirred for 18 h at room temperature.
[b] Isolated yield of **2** and **3′**.
[c] Cyp=cyclopentyl. NMDPP=neomenthyldiphenylphosphine.
[d] The allene was dissolved in THF and added to the reaction mixture via a syringe pump over 1–3 h.

Table 2. Examination of reducing agents[a]

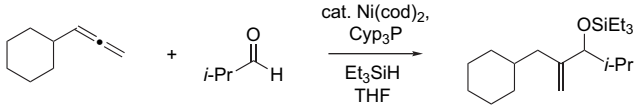


1a **3a**

Entry	Reducing agent	Yield (%)[b]	**3a**:**2a**
1	Et_3SiH	51[h]	>95:5
2[c]	$t\text{-BuMe}_2SiH$	53	>95:5
3[d,e]	$i\text{-Pr}_3SiH$[f]	24	>95:5
4[d]	Ph_2MeSiH[f]	<5	n.d.
5[d]	Me_2PhSiH[f]	<5	n.d.
6	$(EtO)_3SiH$	<5	n.d.
7	Ph_2SiH2	<5	n.d.
8[g]	Et_2Zn[f]	<5	n.d.

[a] General procedure: to a solution of $Ni(cod)_2$ (10 mol %) and Cyp_3P (10 mol %) were added the reducing agents (200 mol %) and the aldehyde (200 mol %). Allene **1a** (100 mol %) in THF was added to the reaction mixture over 8–12 h. The reaction mixture was stirred for 18 h at room temperature.
[b] Isolated yield.
[c] Cyp_3P (20 mol %) was used instead of 10 mol %.
[d] Cyclohexanecarboxaldehyde (300 mol %) was used instead of isobutyraldehyde.
[e] The reaction was heated to 50 °C in toluene.
[f] Reducing agent (300 mol %) was used.
[g] Diethylether was used as the solvent.
[h] Average of two runs.

Table 3. Ligand ratio and solvent effects[a]

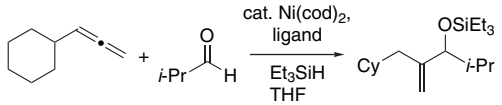


1a **3a**

Entry	Ligand (mol %)	Solvent	Yield (%)[b]
1	None	THF	<5
2	10	THF	51[c]
3	20	THF	50
4	10	EtOAc	40
5	20	EtOAc	21
6	10	MeOH	36
7	20	MeOH	27
8	10	Toluene	46

[a] General procedure: to a solution of $Ni(cod)_2$ (10 mol %) and Cyp_3P were added Et_3SiH (200 mol %) and the aldehyde (200 mol %). Allene **1a** (100 mol %) in THF was added to the reaction mixture over 4 h. The reaction mixture was stirred for 18 h at room temperature.
[b] Isolated yield.
[c] Average of two runs.

Table 4. Ligand screen[a]

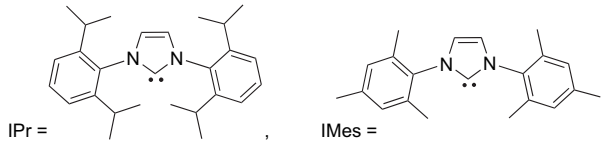


1a **3a**

Entry	Ligand	Yield (%)[b]
1	Cyp_3P	51[c]
2	Cy_3P	41
3	Bu_3P	<10
4	$(o\text{-Anis})_3P$	<10
5	Ph_3P	<10
6	NMDPP	<10
7	BINAP	<10

[a] General procedure: to a solution of $Ni(cod)_2$ (10 mol %) and ligand (10 mol %) were added Et_3SiH (200 mol %) and the aldehyde (200 mol %). Allene **1a** (100 mol %) in THF was added to the reaction mixture over 4 h. The reaction mixture was stirred for 18 h at room temperature.
[b] Isolated yield.
[c] Average of two runs.

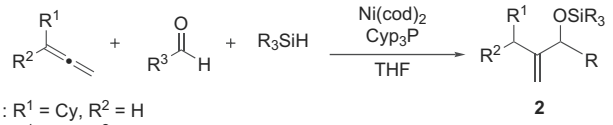
solvent for this coupling reaction (Table 3, entry 2). The nickel/ligand ratio was also found to be an important variable. A 1:1 ratio of $Ni(cod)_2$ and Cyp_3P was optimal, regardless of the choice of solvent (Table 3, entries 2–7). Most strikingly, among phosphines examined, only large and electron donating ones such as Cy_3P and Cyp_3P were compatible with the Ni/Et_3SiH system (Table 4, entries 1 and 2). The *N*-heterocyclic carbene IPr, which is also large and is also a strong electron donor, was also an excellent ligand for this coupling reaction (vide infra). Smaller phosphines such as Bu_3P and Ph_3P and bidentate ligand BINAP only afforded a trace amount of coupling product **3a** (Table 4, entries 3–7). Finally, increasing the amount of aldehyde and silane to 300 mol % further increased the yield (Table 5).



The catalyst system derived from $Ni(cod)_2$ and Cyp_3P was found to promote the coupling of **1a**, **1b**, and **1c** with various aliphatic and aromatic aldehydes in good yield and excellent regioselectivity when a silane was employed as a reducing agent (Table 5). In all cases, carbon–carbon bond formation occurred at the sp-hybridized carbon (rather than the sp^2-hybridized carbons) of the allenes (regioselectivity). No trace of homoallylic alcohol product was observed in any case. Also noteworthy was the fact that the more hindered double bond reacted with the aldehyde, rather than the less substituted double bond. This site selectivity was not affected by the steric bulk around the allene. Allene **1c**, possessing two geminal alkyl substituents, also underwent coupling with aliphatic aldehydes with the same sense of site selectivity as **1a** and **1b** (Table 5, entries 7–9).

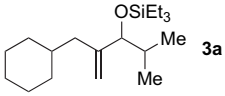
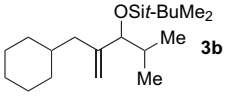
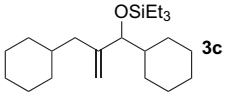
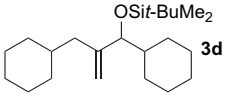
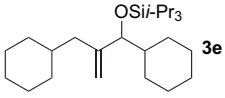
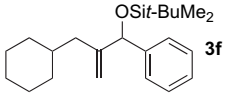
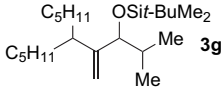
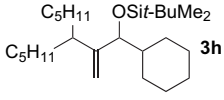
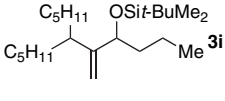
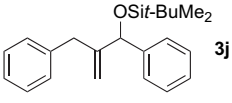
The size of the silane, in contrast, did affect the yield of the coupling product significantly. Switching from *t*-$BuMe_2SiH$ to Et_3SiH lowered the yield substantially (Table 5, entries 1–4) due to competing hydrosilylation of the allene and more hydrosilylation of allene was observed in the latter

Table 5. Reaction scope[a]



1a : R^1 = Cy, R^2 = H
1b : R^1 = Ph, R^2 = H
1c : R^1 = R^2 = n-C_5H_{11}

2

Entry	Allene	Aldehyde	Silane	Product	Yield (%)[b]
1	**1a**	*i*-Pr	Et_3SiH	 **3a**	52
2	**1a**	*i*-Pr	*t*-$BuMe_2SiH$	 **3b**	71
3	**1a**	Cy	Et_3SiH	 **3c**	46
4	**1a**	Cy	*t*-$BuMe_2SiH$	 **3d**	73
5	**1a**	Cy	*i*-Pr_3SiH	 **3e**	24
6	**1a**	Ph	*t*-$BuMe_2SiH$	 **3f**	86[c]
7	**1c**	*i*-Pr	*t*-$BuMe_2SiH$	 **3g**	75
8	**1c**	Cy	*t*-$BuMe_2SiH$	 **3h**	68
9	**1c**	*n*-Bu	*t*-$BuMe_2SiH$	 **3i**	35
10[d]	**1b**	Ph	*t*-$BuMe_2SiH$	 **3j**	56 (5)[e]

[a] General procedure: to a solution of $Ni(cod)_2$ (10 mol %) and Cyp_3P (10 mol %) were added Et_3SiH (300 mol %) and the aldehyde (300 mol %). Allene **1a** (100 mol %) in THF was added to the reaction mixture over 5–9 h. The reaction mixture was stirred for 18 h at room temperature.
[b] Isolated yield.
[c] Cyp_3P was replaced by IPr, and the reaction mixture was cooled to −78 °C before the addition of allene **1a** in one portion. The reaction was warmed to room temperature over 8 h.
[d] The general procedure was followed except that Cyp_3P was replaced by IPr.
[e] Cyp_3P was employed as the ligand. Yield was determined by NMR of the crude mixture versus DMF as an external standard.

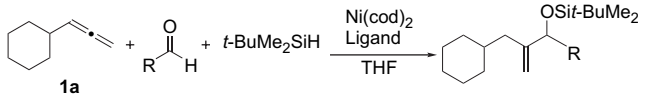
case. This phenomenon might be related to the relative size of those two organosilanes. Triisopropylsilane (*i*-Pr_3SiH), however, appeared to be too bulky for either the coupling or hydrosilylation to occur efficiently (entry 5).

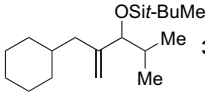
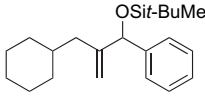
With Cyp_3P as the supporting ligand, oligomerization of **1b** was pronounced, and **3j** was obtained in only 5% yield (entry 10). Nevertheless, this problem was alleviated when Cyp_3P was replaced by IPr (entry 10), and the same regioselectivity and site selectivity were observed as with Cyp_3P.

We have recently reported the nickel-catalyzed coupling of chiral 1,3-disubstituted allenes and aromatic aldehydes using the $Ni(cod)_2/Et_3SiH$ system.[2r,s] While *N*-heterocyclic carbene IPr provided similar site selectivity and regioselectivity as Cyp_3P, only IPr provided complete chirality transfer from an enantiomerically enriched allene to the product. Moreover, it was also found that slow addition of these 1,3-disubstituted allenes was not necessary as long as the allene was added to the reaction mixture at −78 °C. Accordingly, a set of experiments were conducted to determine whether Cyp_3P or IPr was the better ligand for the coupling of terminal allenes and aldehydes and whether the mode of addition affected the yield of the reaction (Table 6).

Cyp_3P was the more efficient ligand for the coupling of terminal allenes and aliphatic aldehydes (Table 6, entries 1–4). The *N*-heterocyclic carbene IPr, however, was the ligand of choice for the coupling with aromatic aldehydes (entries 5–8). Slow addition of cyclohexylallene **1a** to the reaction mixture allowed coupling with isobutyraldehyde to proceed smoothly to afford **3b** in good yield when Cyp_3P was the ligand (entry 1). Under the same condition IPr afforded **3b** only in 12% yield (entry 3). Starting the reaction at −78 °C did not improve the yield of the coupling with aliphatic aldehydes, regardless of whether Cyp_3P or IPr was used (entries 2 and 4). On the other hand, IPr was an excellent ligand for the coupling of allenes and aromatic aldehydes. Slow addition of **1a** to the reaction mixture resulted in smooth coupling with benzaldehyde, giving **3b** in 65% yield (entry 7). Furthermore, in contrast to the results obtained with aliphatic aldehydes, slow addition of **1a** was unnecessary. When **1a** was added to the reaction system in one portion at −78 °C, an increase in yield was observed (entry 8). In fact, in this case the reaction could also be conducted at 0 °C without the use of dropwise addition, but a slight decrease in yield was observed (entry 9).

Table 6. Comparison of Cyp_3P and IPr as ligands



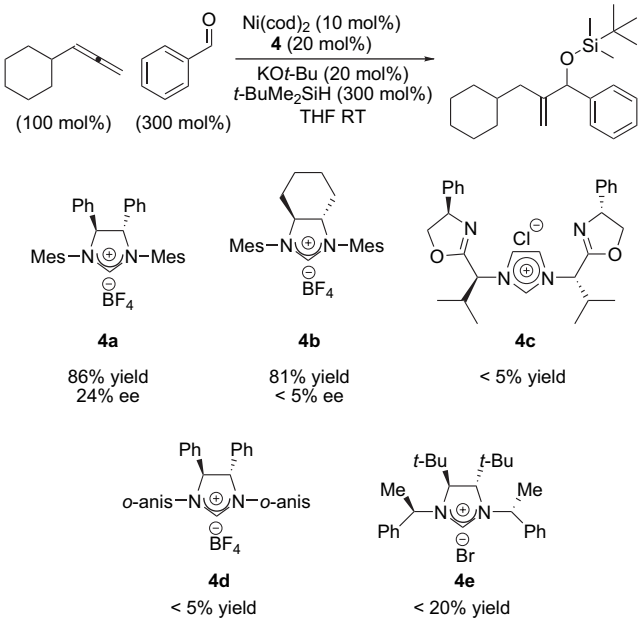
Entry	R (aldehyde)	Ligand	Condition[a]	Product	Yield (%)[b]
1	*i*-Pr	Cyp_3P[c]	A	 **3b**	70
2	*i*-Pr		B		<5
3	*i*-Pr	IPr[d]	A		12
4	*i*-Pr		B		8
5	Ph	Cyp_3P[c]	A	 **3f**	23
6	Ph		B		<5
7	Ph	IPr[d]	A		65
8	Ph		B		86
9	Ph		C		71

[a] Condition A: allene was diluted in THF and added to the reaction over 4 h at room temperature and the reaction mixture continued to stir for 12 h. Condition B: silane, aldehyde, and allene were each added consecutively in one portion to the catalyst mixture at −78 °C. The reaction was slowly warmed to room temperature over 15 h. Condition C: same as condition B except that the allene was added to the reaction mixture at 0 °C instead of −78 °C.

[b] Yield was determined by NMR of the crude mixture versus DMF as an external standard.

[c] $Ni(cod)_2$: $PCyp_3$ ratio was 1:1.

[d] $Ni(cod)_2$: IPr ratio was 1:2.



Scheme 1. Evaluation of chiral *N*-heterocyclic carbene ligands.

3. Discussion

Since the first stable *N*-heterocyclic carbene (NHC) was isolated by Arduengo,[8] derivatives of NHCs were developed and applied extensively as ligands on transition metals and as organocatalysts.[9,10] As ligands on metal catalysts, NHCs are electron rich σ donors, enabling processes such as the oxidative addition of aryl chlorides[9d,e] and providing more reactive and stable olefin metathesis catalysts.[9d] The Ni/NHC system catalyzed several transformations such as reduction of aryl halides and imines,[12a,b] polymerization,[12c,d] Heck reaction,[12e] and cycloaddition[12f] and annulation.[12g]

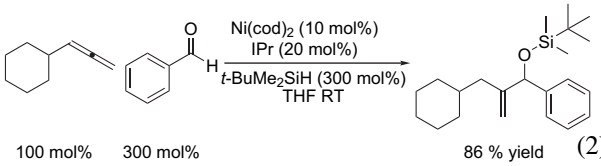
N-Heterocyclic carbene ligands have also been used in other Ni-catalyzed reactions. In the nickel-catalyzed reductive coupling of 1,3-diene and aldehydes, Mori and Sato showed that regioselectivity can be tuned by using either a phosphine ligand or an *N*-heterocyclic carbene.[2w–bb] Montgomery demonstrated that the *N*-heterocyclic carbene IMes had a broad substrate scope of alkynes in the nickel-catalyzed coupling

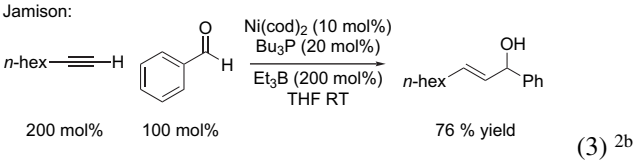
of alkynes, aldehydes, and silanes.[2g] However, the same reaction was sluggish when IMes was replaced by Bu_3P. A crossover experiment indicated that different mechanisms were operating in these two cases and also explained the difference in reactivity.

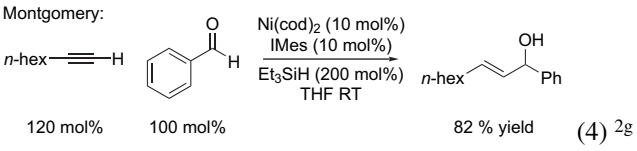
The nickel-catalyzed coupling of allenes and aldehydes described herein demonstrated that phosphines and *N*-heterocyclic carbenes are complementary as supporting ligands for nickel, depending on the nature of the aldehyde coupling partner (aliphatic vs aromatic). In the nickel-catalyzed coupling of allenes and aldehydes, *N*-heterocyclic carbene IPr had a larger substrate scope with respect to the allene, enabling the coupling of alkyl allenes **1a** and **1c** and aryl allene **1b**. Although Cyp_3P did not tolerate aryl allene **1b**, it did promote coupling reactions with aliphatic aldehydes with allenes bearing one aliphatic substituent (**1a** and **1c**). The reduced yield that was observed with aliphatic aldehydes when IPr was employed may have its origins in the basicity of this supporting ligand. Being more basic than Cyp_3P, it is possible that IPr was inactivated by deprotonation of the α-protons of aliphatic aldehydes.[11] More experiments are necessary to confirm this hypothesis, however, since there are examples of aliphatic aldehydes being tolerated in reactions using NHC ligands.[13]

The nickel-catalyzed allene–aldehyde coupling described herein is complementary also to the nickel-catalyzed coupling reactions of alkynes and aldehydes (Scheme 2). The allene–aldehyde coupling provides a different type of disubstituted allylic alcohol product (geminal, Eq. 2) from the alkyne–aldehyde couplings (vicinal, Eqs. 3 and 4). For example, the reductive coupling of the terminal alkyne 1-octyne with benzaldehyde affords a *trans*-1,2-disubstituted allylic alcohol with high selectivity using either the $Ni(cod)_2/Bu_3P$–Et_3B system developed in our group (Eq. 3) or the $Ni(cod)_2$/NHC–Et_3SiH system developed by Montgomery (Eq. 4). In contrast, the allene–aldehyde coupling described here provided 1,1-disubstituted allylic alcohol (Eq. 2). The same substitution pattern is obtained in a related nickel-catalyzed coupling of alkenes, aldehydes, and silyl triflates that we recently reported.[2u]

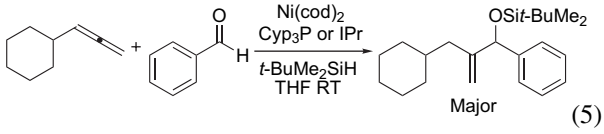
A further distinguishing characteristic is that the regioselectivity and site selectivity of the nickel-catalyzed coupling of allenes and aldehydes are distinctly different among the R_3SiH, Et_3B, and R_2Zn systems (Scheme 3). C–C bond formation occurred between the sp-hybridized carbon of the allene and the aldehyde in the R_3SiH and Et_3B systems (Scheme 3, Eqs. 5 and 6). These two systems, however, have the opposite site selectivity. Whereas in the R_3SiH system addition occurs across the internal double bond, the less substituted double bond reacts in the Et_3B system. The organozinc system developed by Montgomery also affords C–C bond formation between the less substituted sp^2-hybridized carbon of the allene and the aldehyde, but homoallylic alcohols are obtained (Scheme 3, Eq. 7). A related process, the nickel-catalyzed dicarboxylation of an allene by Mori and Sato C–C bond formation occurs between the sp-hybridized carbon of the allene and CO_2 (Scheme 3, Eq. 8). Given these observations, it appears that R_3SiH, Et_3B, and R_2Zn each direct the allene–aldehyde coupling through different mechanisms. The formation of a nickellacycle has been proposed as the first step in the catalytic cycle in all of these examples, and thus R_3SiH, Et_3B, and R_2Zn may play a large role in directing the formation and subsequent reactions of such a nickellacycle species. One possibility is that Et_3B and R_2Zn, being more Lewis acidic than R_3SiH, interact with the aldehyde, giving a larger species that may be accommodated in the nickellacycle in a very different arrangement than the aldehyde itself. More studies are required to further understand the mechanism of these nickel-catalyzed coupling reactions of allenes and aldehydes.[14]

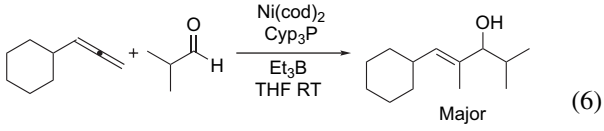


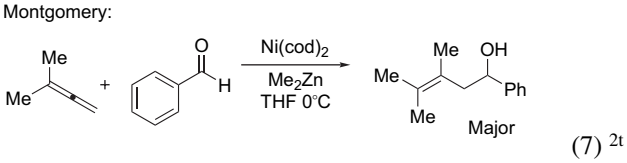


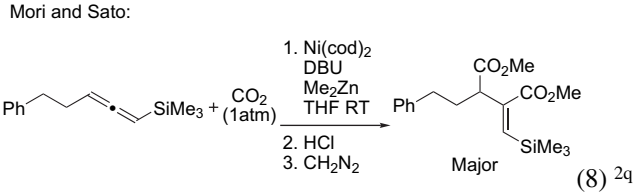


Scheme 2. Comparison between allene–aldehyde coupling and alkyne–aldehyde coupling.









Scheme 3. Nickel-catalyzed allene couplings.

4. Conclusion

In summary, the nickel-catalyzed coupling of allenes, aldehydes, and silanes provides 1,1-disubstituted allylic alcohols with high regioselectivity and high site selectivity. The optimal ligand, however, is different for aliphatic (Cyp_3P) and aromatic (IPr) aldehydes. These transformations are complementary to other allene–aldehyde coupling reactions. Carbon–carbon bond formation occurs between the sp-hybridized carbon of allene and aldehyde, regardless of ligand type, as long as a silane is used as the reducing agent. The use of chiral NHCs resulted in low enantiomeric excess to the coupling product, but nevertheless represents the first example of an enantioselective, nickel-catalyzed coupling of allene and aldehyde.[14] Applications to natural product synthesis and further investigations to develop a highly enantioselective version of this reaction are ongoing.

5. Experimental

5.1. General

Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of nitrogen or argon with rigid exclusion of moisture from reagents and glassware. Tetrahydrofuran was distilled from a blue solution of sodium benzophenone ketyl. Triethylsilane, triisopropylsilane, and *tert*-butyldimethylsilane were purchased from Aldrich Chemical Co. and were saturated with nitrogen before use. Benzaldehyde was purchased from Aldrich Chemical Co. and was distilled before use. All aliphatic aldehydes were distilled over magnesium sulfate under argon before use. Bis(*cyclo*-octadienyl)nickel(0) ($Ni(cod)_2$) and tricyclopentylphosphine were purchased from Strem Chemicals, Inc., stored under nitrogen atmosphere, and used without further purification. 1,3-Bis-(2,6-di-isopropylphenyl)imidazol-2-ylidene (NHC-IPr) was prepared according to literature procedure.[15]

Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F_{254} plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Silicycle silica gel (230–400 mesh). ^1H and ^{13}C NMR spectra were recorded on Varian 300 MHz, Varian 500 MHz or Bruker 400 MHz spectrometer in $CDCl_3$, unless otherwise noted. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in parts per million from the central peak of $CDCl_3$ (77.23 ppm) on the δ scale. Infrared (IR) spectra were recorded on a Perkin–Elmer 2000 FTIR. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer by Dr. Li Li of the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility. Chiral GC analysis was performed on a Varian CP-3800 gas chromatograph fitted with Chiraldex B-PH, B-DA, and G-TA capillary columns. Chiral HPLC analysis was performed on a Hewlett-Packard 1100 chromatograph equipped with a variable wavelength detector and Chiralcel OD or OD-H columns. Specific rotations ($[\alpha]_D$) were measured on a Perkin–Elmer 241 polarimeter at 589 nm.

5.2. Preparation of allenes

5.2.1. Propa-1,2-dienyl-cyclohexane (1a). Prepared by the method of Brandsma.[16] Cyclohexyl-magnesium chloride (50 mL, 100 mmol, 2 M in ether) was dissolved in anhydrous THF (80 mL) and cooled to −78 °C under argon. After 10 min of cooling, a THF (8 mL) solution of anhydrous lithium bromide (2 g) and anhydrous copper(I) bromide (1 g) was added to the Grignard solution in one portion. The reaction mixture was stirred for 20 min at −78 °C. Propargyl bromide (13.4 mL, 120 mmol) was dissolved in anhydrous THF (10 mL) in an oven-dried round bottom flask and was cooled at −78 °C for 15 min. The propargyl bromide solution was taken up by a 50 mL syringe and added to the reaction mixture over 30 min. During this time the reaction mixture was kept below −50 °C with rigorous stirring. After the addition was complete the reaction mixture was stirred for 30 min at −78 °C. The dry ice/acetone bath was removed and the reaction was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was poured into an aqueous NH_4Cl solution (10 g NH_4Cl, 100 mL). The mixture was extracted with 200 mL pentane. The aqueous layer was extracted again with 100 mL pentane. The combined pentane solution was washed repeatedly with water and finally with brine. The solution was dried with $MgSO_4$ and pentane was removed in rotovap. Purification via flash chromatography on silica followed by distillation afforded **1a** as a colorless oil (7.9 g, 65% yield). ^1H NMR (500 MHz, $CDCl_3$, δ): 5.10 (q, J=6.4 Hz, 1H), 4.69 (dd, J=6.7, 3.4 Hz, 2H), 1.99 (m, 1H), 1.80–1.02 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 207.6, 96.3, 75.6, 36.8, 33.2, 26.4, 26.2. IR (NaCl, thin film): 2925, 2852, 2662, 1955, 1445, 839.

5.2.2. Propa-1,2-dienyl-benzene (1b). Prepared according to the method of Myers.[17] Triphenylphosphine (5 g, 15 mmol) was dissolved in THF (20 mL). The solution was cooled in a MeOH/ice bath, and diethylazodicarboxylate (DEAD) (2.4 mL, 15 mmol) was added to the solution over 1 min. The solution was stirred for 10 min below −10 °C. 1-Phenyl-2-propyn-1-ol (1.22 mL, 10 mmol) in THF (10 mL) was added. THF (5 mL) was used to rinse the rest of the alcohol into the reaction mixture. The mixture was stirred for 10 min, and *o*-nitrobenzenesulfonylhydrazine[17b] (3.3 g, 15 mmol in 20 mL THF) was added. The mixture was kept below 0 °C for 2 h and was allowed to warm to room temperature and stirred for 16 h. The reaction was diluted with pentane (300 mL) and washed five times with ice cold water to remove THF. The mixture was dried with $MgSO_4$. Column chromatography in pentane afforded **1b** as a colorless oil (250 mg, 21% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.40–7.28 (m, 4H), 7.25–7.16 (m, 1H), 6.18 (t, J=6.8 Hz, 1H), 5.16 (d, J=6.8 Hz, 2H).

5.2.3. 6-Vinylidene-undecane (1c). 2-Octyn-1-ol (4.3 mL, 30 mmol) and triethylamine (17 mL, 120 mmol) were

dissolved in anhydrous dichloromethane (35 mL) in a 100 mL round bottom flask. The reaction mixture was stirred for 10 min at −78 °C. Methanesulfonyl chloride (7 mL, 90 mmol) was added dropwise. After the addition was complete the reaction was stirred for 2 h at −78 °C. The dry ice/acetone bath was replaced by a sodium chloride/ice slush bath. The reaction mixture was stirred for 90 min at −10 °C. The reaction mixture was poured into water (50 mL). The organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined dichloromethane solution was washed with water and dried with $MgSO_4$. Purification via flash chromatography on silica afforded methanesulfonic acid oct-2-ynyl ester. In an oven-dried 50 mL round bottom flask magnesium turning (0.56 g) was stirred in anhydrous THF (4 mL). A few drops of 1,2-dibromoethane were added. Gentle heating was applied to initiate the reaction. *n*-Pentylbromide (2.84 mL, 23 mmol) was added slowly at a rate that caused and maintained a gentle reflux. When most of the magnesium vanished more *n*-pentylbromide (1 mL) was added. The solution was cooled down to slightly warm (pentylmagnesium bromide was not soluble in cold THF). Meanwhile anhydrous CuBr (3.44 g, 24 mmol) and anhydrous LiBr (2.08 g, 24 mmol) were dissolved in anhydrous THF (40 mL) in an ice bath and stirred vigorously. Once the mixture became homogeneous, the warm pentylmagnesium bromide solution was added via a syringe with a thick needle. The reaction mixture was stirred rigorously for 20 min at 0 °C. The reaction mixture was cooled to −78 °C. Methanesulfonic acid oct-2-ynyl ester in anhydrous THF (30 mL) was added to the reaction mixture dropwise via a syringe pump over 30 min. Once the addition was complete, the dry ice/acetone bath was allowed to warm back to room temperature and stirred for 12 h. The reaction mixture was quenched with ice cold saturated NH_4Cl (80 mL) and extracted with 250 mL hexane. The aqueous layer was extracted again with hexane until the aqueous layer became blue. The combined hexane solution was then washed two times with saturated NH_4Cl, once with water (50 mL), and finally with brine (50 mL). Purification via flash column chromatography on silica afforded 6-vinylidene-undecane **1c** (2.54 g, 47% from 2-octyn-1-ol). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.64 (p, J=3.0 Hz, 2H), 1.96–1.90 (m, 4H), 1.46–1.39 (m, 4H), 1.35–1.26 (m, 8H), 0.94–0.87 (t, J=7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 205.9, 103.6, 75.4, 32.3, 31.8, 27.5, 22.8, 14.3. IR (thin film NaCl): 2957, 2929, 2873, 2859, 1958, 843.

5.3. Nickel-catalyzed couplings of allenes and aldehydes

5.3.1. Standard procedure A. A 25 mL round bottom flask and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (28 mg, 0.1 mmol, 10 mol %) and tricyclopentylphosphine (28 μL, 0.1 mmol, 10 mol %) were added to the flask. The flask was sealed with a septum and electrical tape. The sealed flask was brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in THF (2 mL) at room temperature under argon and stirred for 10 min at room temperature. Silane (3 mmol, 300 mol %) was added in one portion. Aldehyde (3 mmol, 300 mol %) was added in one portion. Finally allene (1 mmol, 100 mol %) in THF (8 mL) was added into the reaction mixture at room temperature via a syringe pump over 8 h. The reaction was stirred at room temperature for another 12 h. THF and other volatiles were removed under reduced pressure. The crude mixture was diluted in hexane. Purification via flash chromatography on silica afforded the allylic alcohol coupling product.

5.3.2. Standard procedure B. A 10 mL round bottom flask and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (7 mg, 0.025 mmol, 10 mol %) and tricyclopentylphosphine (7 μL, 0.025 mmol, 10 mol %) were added to the flask. The flask was sealed with a septum and electrical tape. The sealed flask was brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in THF or toluene (0.5 mL) at room temperature under argon and stirred for 10 min at room temperature. Silane (0.75 mmol, 300 mol %) was added in one portion. Aldehyde (0.75 mmol, 300 mol %) was added in one portion. Finally allene (0.25 mmol, 100 mol %) in THF or toluene (2 mL) was added into the reaction mixture at room temperature via a syringe pump over 3.5 h. The reaction was stirred at room temperature for another 12 h. THF and other volatiles were removed under reduced pressure. The crude mixture was diluted in hexane. Purification via flash chromatography on silica afforded the allylic alcohol coupling product.

5.3.3. Standard procedure C. A 10 mL round bottom flask and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (10 mg, 0.036 mmol, 15 mol %) and tricyclopentylphosphine (10 μL, 0.036 mmol, 15 mol %) were added to the flask. The flask was sealed with a septum and electrical tape. The sealed flask was brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in THF (0.5 mL) at room temperature under argon and stirred for 10 min at room temperature. Silane (0.75 mmol, 300 mol %) was added in one portion. Aldehyde (0.75 mmol, 300 mol %) was added in one portion. Finally allene (0.25 mmol, 100 mol %) in THF or toluene (3 mL) was added into the reaction mixture at room temperature via a syringe pump over 5 h. The reaction was stirred at room temperature for another 12 h. THF and other volatiles were removed under reduced pressure. The crude mixture was diluted in hexane. Purification via flash chromatography on silica afforded the allylic alcohol coupling product.

5.3.4. (1-Cyclohexylmethyl-1-isopropyl-allyloxy)-triethylsilane (3a). The reaction of propa-1,2-dienyl-cyclohexane (**1a**) (148 μL, 1 mmol) and isobutyraldehyde (272 μL, 3 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and triethylsilane (480 μL, 3 mmol) in THF following the standard procedure A described above afforded **3a** in 52% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.98 (m, 1H), 4.80 (m, 1H), 3.72 (d, J=6.1 Hz, 1H), 2.00–1.00 (m, 14H), 0.96 (t, J=8.0 Hz, 9H), 0.85 (t, J=6.32 Hz, 6H), 0.59 (q, J=7.98 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 149.0, 111.0, 82.0, 39.4, 35.9, 34.1, 33.7, 31.8, 26.9, 26.7, 26.6, 20.1, 17.6, 7.3, 5.2; IR (NaCl, thin film): 3077, 2955, 2923, 2877, 2853, 1811, 1646, 1459, 1449, 1414, 1063, 1007, 904, 834, 740, 725; HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{38}OSi$, 333.2584; found, 333.2593.

5.3.5. *tert*-Butyl-(2-cyclohexylmethyl-1-isopropyl-allyloxy)-dimethylsilane (3b). The reaction of propa-1,2-dienyl-cyclohexane (**1a**) (148 μL, 1 mmol) and isobutyraldehyde

(272 μL, 3 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and *tert*-butyldimethylsilane (498 μL, 3 mmol) in THF following the standard procedure A described above afforded **3b** in 71% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.98 (m, 1H), 4.80 (m, 1H), 3.70 (d, J=5.8 Hz, 1H), 1.98–1.60 (m, 9H), 1.58–1.40 (m, 1H), 1.38–1.10 (m, 4H), 0.92 (s, 9H), 0.843 (dd, J=6.9, 6.6 Hz, 6H), 0.04 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 148.8, 111.1, 81.5, 39.7, 35.7, 34.2, 33.6, 31.7, 26.9, 26.7, 26.6, 26.2, 20.3, 18.5, 17.3, −4.1, −4.8; IR (NaCl, thin film): 3077, 2957, 2927, 2855, 1647, 1463, 1251, 1057, 863, 838, 774; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{38}OSi$, 333.2584; found, 333.2590.

5.3.6. (1-Cyclohexyl-2-cyclohexylmethyl-allyloxy)-triethylsilane (3c). The reaction of propa-1,2-dienyl-cyclohexane (**1a**) (148 μL, 1 mmol) and cyclohexanecarboxaldehyde (361 μL, 3 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and triethylsilane (480 μL, 3 mmol) in THF following the standard procedure A described above afforded **3c** in 46% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.93 (m, 1H), 4.79 (m, 1H), 3.72 (d, J=6.7 Hz, 1H), 2.00–0.80 (m, 24H), 0.96 (t, J=7.6 Hz, 9H), 0.59 (q, 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 148.6, 111.1, 81.8, 41.5, 39.0, 35.6, 34.1, 33.7, 30.4, 28.4, 26.9, 26.9, 26.7, 26.7, 26.6, 26.5, 7.3, 5.2; IR (NaCl, thin film): 3076, 2923, 2876, 2852, 1809, 1644, 1449, 1239, 1063, 1008, 898, 827, 740; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{42}OSi$, 373.2897; found, 373.2892.

5.3.7. *tert*-Butyl-(1-cyclohexyl-2-cyclohexylmethyl-allyloxy)-dimethylsilane (3d). The reaction of propa-1,2-dienyl-cyclohexane (**1a**) (148 μL, 1 mmol) and cyclohexanecarboxaldehyde (361 μL, 3 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and *tert*-butyldimethylsilane (498 μL, 3 mmol) in THF following the standard procedure A described above afforded **3d** in 73% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.94 (m, 1H), 4.80 (m, 1H), 3.70 (d, J=6.1 Hz, 1H), 2.00–0.80 (m, 24H), 0.91 (s, 9H), 0.03 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 148.4, 111.2, 81.4, 41.5, 39.3, 35.6, 34.2, 33.7, 30.7, 28.1, 26.9, 26.9, 26.7, 26.7, 26.6, 26.6, 26.2, 18.5, −4.1, −4.7; IR (NaCl, thin film): 3076, 2926, 1645, 1450, 1251, 1061, 900, 837, 774; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{42}OSi$, 373.2897; found, 373.2893.

5.3.8. (1-Cyclohexyl-2-cyclohexylmethyl-allyloxy)-triisopropylsilane (3e). The reaction of propa-1,2-dienyl-cyclohexane (**1a**) (37 μL, 0.25 mmol) and cyclohexanecarboxaldehyde (90 μL, 0.75 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and triisopropylsilane (154 μL, 0.75 mmol) in toluene following the standard procedure B described above (except that 1 mL toluene was used to dissolve $Ni(cod)_2$ and tricyclopentylphosphine) afforded **3e** in 24% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.96 (m, 1H), 4.82 (m, 1H), 3.95 (d, J=5.8 Hz, 1H), 2.00–0.80 (m, 25H), 1.10 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.6, 110.9, 81.9, 42.8, 39.5, 35.6, 34.2, 33.8, 30.2, 28.6, 26.9, 26.8, 26.8, 26.7, 26.6, 18.5, 13.1; IR (NaCl, thin film): 3079, 2924, 2865, 2852, 1645.71, 1449, 1086, 1062, 883; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{25}H_{48}OSi$, 415.3367; found, 415.3366.

5.3.9. *tert*-Butyl-(2-cyclohexylmethyl-1-phenyl-allyloxy)-dimethylsilane (3f). A 7 mL vial and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (7 mg, 0.025 mmol, 10 mol %) and IPr (19 mg, 0.05 mmol, 20 mol %) were added to the flask. The vial was sealed with a septum and electrical tape. The sealed vial was brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in THF (3 mL) at room temperature under argon and stirred for 10 min at room temperature. The mixture was cooled to −78 °C. *t*-$BuMe_2SiH$ (125 μL, 0.75 mmol, 300 mol %) was added in one portion. Benzaldehyde (76 μL, 0.75 mmol, 300 mol %) was added in one portion. Finally allene (37 μL, 0.25 mmol, 100 mol %) was added. The reaction was stirred for 2 h at −78 °C. The dry ice/acetone bath was then covered with aluminum foil and the temperature was slowly raised to room temperature. The reaction was stirred for a total of 15 h. THF and other volatiles were removed under reduced pressure. Purification via flash chromatography on silica afforded **3f** in 86% yield as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.35–7.20 (m, 5H), 5.24 (s, 1H), 5.10 (s, 1H), 4.83 (s, 1H), 1.80 (m, 1H), 1.70 (m, 6H), 1.45 (m, 1H), 1.15 (m, 3H), 0.92 (s, 9H), 0.75 (m, 2H), 0.07 (s, 3H), −0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.0, 143.7, 128.1, 127.1, 126.7, 110.9, 78.4, 39.5, 35.8, 33.7, 33.480, 26.8, 26.6, 26.5, 26.1, 18.5, −4.7, −4.7; IR (NaCl, thin film): 2926, 2854, 1472, 1449, 1252, 1090, 1065, 867, 835, 776, 699. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{38}OSi$, 367.2428; found, 367.2431.

5.3.10. *tert*-Butyl-(1-isopropyl-2-methylene-3-pentyl-octyloxy)-dimethylsilane (3g). The reaction of 6-vinylidene-undecane (**1c**) (57 μL, 0.25 mmol) and isobutyraldehyde (68 μL, 0.75 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and *tert*-butyldimethylsilane (125 μL, 0.75 mmol) in THF following the standard procedure C described above afforded **3g** in 75% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, δ): 5.10 (m, 1H), 4.83 (m, 1H), 3.79 (br s, 1H), 1.80–1.68 (m, 2H), 1.46–1.18 (m, 22H), 0.97 (d, J=6.7 Hz, 3H), 0.94 (s, 9H), 0.93–0.85 (m, 6H), 0.76 (d, J=6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 154.7, 108.3, 79.7, 41.4, 36.2, 34.0, 32.5, 32.5, 30.9, 27.5, 26.7, 26.2, 22.9, 22.9, 21.4, 18.5, 14.9, 14.4, 14.3, −3.9, −4.8; IR (NaCl, thin film): 2958, 2929, 2858, 1647, 1463, 1250, 1056, 902, 865, 839, 774. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{48}OSi$, 391.3367; found, 391.3365.

5.3.11. *tert*-Butyl-(1-cyclohexyl-2-methylene-3-pentyl-octyloxy)-dimethylsilane (3h). The reaction of 6-vinylidene-undecane (**1c**) (57 μL, 0.25 mmol) and cyclohexanecarboxaldehyde (90 μL, 0.75 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and *tert*-butyldimethylsilane (125 μL, 0.75 mmol) in THF following the standard procedure B described above afforded **3h** in 68% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, δ): 5.06 (m, 1H), 4.83 (m, 1H), 3.76 (br s, 1H), 1.90–1.00 (m, 28H), 0.94 (s, 9H), 0.90 (m, 6H), 0.03 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 154.2, 108.4, 79.8, 41.2, 41.1, 36.2, 34.2, 32.5, 32.5, 32.1, 27.4, 27.1, 27.0, 26.8, 26.6, 26.3, 25.5, 22.9, 22.925, 18.5, 14.4, 14.3, −3.9, −4.7; IR (NaCl, thin film): 2929, 2856, 1647, 1463, 1251, 1103, 902, 835, 774. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{26}H_{52}OSi$, 431.3680; found, 431.3700.

5.3.12. *tert*-Butyl-dimethyl-(2-methylene-3-pentyl-1-propyl-octyloxy)-silane (3i). The reaction of 6-vinylideneundecane (**1c**) (57 μL, 0.25 mmol) and *n*-butyraldehyde (68 μL, 0.75 mmol) with $Ni(cod)_2$, tricyclopentylphosphine, and *tert*-butyldimethylsilane (125 μL, 0.75 mmol) in THF following the standard procedure C described above afforded **3i** in 35% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.09 (br s, 1H), 4.76 (br s, 1H), 3.97 (t, J=4.9 Hz, 1H), 1.90–1.82 (m, 1H), 1.55–1.20 (m, 23H), 0.92 (s, 9H), 0.88 (m, 6H), 0.05 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 156.0, 107.6, 75.8, 40.7, 39.1, 35.9, 34.7, 32.5, 27.4, 26.9, 26.2, 22.9, 18.8, 18.5, 14.4, 14.3, −4.2, −4.7. IR (NaCl, thin film): 2958, 2930, 2858, 1646, 1463, 1255, 1085, 902, 836, 774. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{23}H_{48}OSi$, 391.3367; found, 391.3350.

5.3.13. (2-Benzyl-1-phenyl-allyloxy)-*tert*-butyldimethylsilane (3j). The reaction of phenylallene (**1b**) (121 μL, 1 mmol) and benzaldehyde (305 μL, 3 mmol) with $Ni(cod)_2$, IPr (78 mg, 0.2 mmol), and *tert*-butyldimethylsilane (498 μL, 3 mmol) in THF following the standard procedure A (described above except that tricyclopentylphosphine was replaced by IPr) afforded **3j** in 56% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.43–7.33 (m, 4H), 7.30 (t, J=7.4 Hz, 3H), 7.22 (t, J=7.3 Hz, 1H), 7.10 (d, J=7.0 Hz, 2H), 5.35 (s, 1H), 5.19 (s, 1H), 4.71 (d, J=1.4 Hz, 1H), 3.39 (d, J=16.1 Hz, 1H), 3.05 (d, J=16.1 Hz, 1H), 0.97 (s, 9H), 0.09 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.8, 143.3, 139.7, 129.6, 128.4, 128.2, 127.3, 126.6, 126.1, 112.1, 77.8, 37.6, 26.1, 18.5, −4.7, −4.8; IR (NaCl, thin film): 3028, 2956, 2929, 2857, 1648, 1602, 1494, 1251, 1091, 1067, 868, 835, 776, 699. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{22}H_{30}OSi$, 361.1958; found, 361.1959.

Acknowledgements

Support for this work was provided by the National Institute of General Medical Sciences (GM-063755). We also thank the NIGMS (GM-072566), NSF (CAREER CHE-0134704), Amgen, Boehringer-Ingelheim, Bristol Myers-Squibb, GlaxoSmithKline, Johnson & Johnson, Merck Research Laboratories, Pfizer, the Sloan Foundation, Wyeth, and the Deshpande Center (MIT) for generous financial support. We are grateful to Dr. Li Li for obtaining mass spectrometric data for all compounds (MIT Department of Chemistry Instrumentation Facility, which is supported in part by the NSF (CHE-9809061 and DBI-9729592) and the NIH (1S10RR13886-01)).

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