OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Synthesis of Allylsilanes via Nickel-Catalyzed Cross-Coupling of Silicon Nucleophiles with Allyl Alcohols

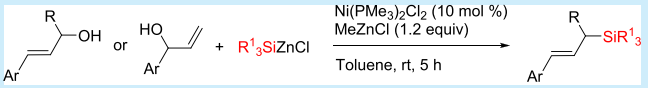
Bo Yang[†] and Zhong-Xia Wang*[,†,‡]

[†]CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

[‡]Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, People's Republic of China

Supporting Information

ABSTRACT: $NiCl_2(PMe_3)_2$-catalyzed reaction of allyl alcohols with silylzinc reagents, including $PhMe_2SiZnCl$, $Ph_2MeSiZnCl$, and $Ph_3SiZnCl$, was performed, achieving allylsilanes in high yields. Aryl- and heteroaryl-substituted allyl alcohols, (*E*)-3-arylprop-2-en-1-ols, 1-aryl-prop-2-en-1-ols, and (*E*)-1-phenylpent-1-en-3-ol can be employed in the transformation. A range of functional groups as well as heteroaryl groups were tolerated. Reaction exhibited high regioselectivity and *E*/*Z*-selectivity when 1- or 3-aryl-substituted allyl alcohols were used as the substrates. Reaction of chiral allyl alcohol, (*S*,*E*)-1-phenylpent-1-en-3-ol, yielded a configuration-inversion product (*R*,*E*)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane.



Allylsilanes are important building blocks in view of the reactivity of both alkenes and metal-allyl reagents, which have been widely applied in organic synthesis and materials science.[1] A range of methods for synthesis of allylsilanes have been developed. Among them, silylation of allylic substrates with silicon nucleophilic reagents such as silylzinc,[2] silylmagnesium,[3] silyltin,[4] and silylboron[5] reagents, as well as disilanes,[4,6] under palladium or copper catalysis, has attracted great attention. The allylic substrates were mainly allyl halides and allyl alcohol derivatives such as allylic ethers, allylic carboxylates, allylic carbonates, and allylic phosphates. Allyl alcohols themselves as electrophiles have seldom been reported, because of poor leaving ability of the hydroxyl group and the presence of an acidic proton.[5e,6f,g] However, allyl halides and allyl alcohol derivatives are often prepared from allyl alcohols. Hence, direct silylation of allyl alcohols is more step- and atom-economical.

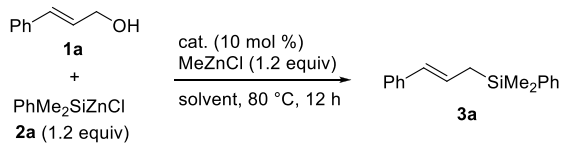
We recently developed a method for construction of $C_{(allyl)}-C_{(aryl/alkenyl)}$ bonds by nickel-catalyzed cross-coupling of allyl alcohols with arylzinc or alkenylzinc reagents.[7] The reaction showed high regioselectivity and *E*/*Z*-selectivity, giving linear and *E* configuration products in most cases. This methodology was expected to extend to the synthesis of allylsilanes from allyl alcohols. For this purpose, we explored reaction of allyl alcohols with silylzinc reagents. Herein, we report the results.

The reaction of cinnamyl alcohol (**1a**) with $PhMe_2SiZnCl$ (**2a**) was employed to optimize the reaction conditions. Because of the presence of the acidic proton, excess organozinc reagent or a strong base was required to convert the cinnamyl alcohol to its salts prior to performing the reaction. We used 1.2 equiv of MeZnCl to grab the proton, in view of our previous report.[7] In the absence of a transition-metal catalyst, the cross-coupling cannot occur in tetrahydrofuran (THF) at 80 °C (Table 1, entry 1). According to the reports in the literature, copper or palladium can catalyze the cross-coupling of allyl alcohol derivatives with silicon-based nucleophiles.[2−5] However, the reaction of **1a** with **2a** did not occur in the presence of CuI or $[Pd(\pi\text{-allyl})Cl]_2$ (see Table 1, entries 2 and 3). This probably results from a difficult oxidation addition process of copper or palladium with a metal salt of allylic alcohol, whereas nickel can catalyze the reactions of alkoxide salts or phenoxide salts via the C−O bond cleavage.[7,8] Hence, nickel catalysts were tested next. When $NiCl_2$(dppe) was used as the catalyst, the reaction gave the expected product **3a** in 29% yield (Table 1, entry 4). This positive result motivated us to examine other nickel catalysts. $NiCl_2$(dppp), $NiCl_2$(dppf), and $NiCl_2(PPh_3)_2$ exhibited a similar catalytic activity to $NiCl_2$(dppe) (Table 1, entries 5−7). While $NiCl_2(PCy_3)_2$ was ineffective (Table 1, entry 8). Further tests showed that $NiCl_2(PMe_3)_2$ was a more effective catalyst than those mentioned above. In the presence of 10 mol % $NiCl_2(PMe_3)_2$, the reaction of **1a** with **2a** gave the desired product in 88% yield (Table 1, entry 9). We also found that phosphorus-ligand-free nickel complexes such as $NiCl_2$(DME) and $NiBr_2$(glyme) were inefficient (Table 1, entries 10 and 11). Extending the reaction time did not improve the yield (Table 1, entry 12). Increasing the loading of **2a** to 1.5 equiv led to the increase of **3a** yield (Table 1, entry 13). When the reaction was performed in other solvents such as THF/toluene (3:1), nBu_2O/toluene (1:3), and toluene, a loading of 1.2 equiv of **2a** was sufficient. Among the alternative solvents, both toluene and toluene/nBu_2O (3/1) were more suitable for this transformation (Table 1, entries 14−16). When 5 mol % $NiCl_2(PMe_3)_2$ was used, the reaction gave a slightly lower yield (Table 1, entry 17). Finally, we demonstrated that the reaction can go to completion at room temperature within 5 h. The

Received: August 19, 2019

DOI: 10.1021/acs.orglett.9b02946
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	yield[b] (%)
1	–	THF	none
2	CuI	THF	none
3[c]	$[Pd(\pi\text{-allyl})Cl]_2$	THF	none
4	$NiCl_2(dppe)$	THF	29
5	$NiCl_2(dppp)$	THF	34
6	$NiCl_2(dppf)$	THF	24
7	$NiCl_2(PPh_3)_2$	THF	31
8	$NiCl_2(PCy_3)_2$	THF	trace
9	$NiCl_2(PMe_3)_2$	THF	88
10	$NiCl_2(DME)$	THF	10
11	$NiBr_2(glyme)$	THF	5
12[d]	$NiCl_2(PMe_3)_2$	THF	88
13[e]	$NiCl_2(PMe_3)_2$	THF	92
14	$NiCl_2(PMe_3)_2$	THF/toluene (3/1)	92
15	$NiCl_2(PMe_3)_2$	toluene/nBu$_2$O (3/1)	97
16	$NiCl_2(PMe_3)_2$	toluene	97
17[c]	$NiCl_2(PMe_3)_2$	toluene	93
18[f]	$NiCl_2(PMe_3)_2$	toluene	97 (90[g])

[a]Unless otherwise specified, the reactions were performed on a 0.2 mmol scale, according to the conditions indicated by the above equation. [b]Isolated yield. [c]5 mol % catalyst was employed. [d]The reaction was run for 18 h. [e]1.5 equiv of **2a** was employed. [f]The reaction was performed at room temperature for 5 h. [g]2 mmol scale.

reaction on a 2 mmol scale also proceeded well under the conditions (Table 1, entry 18).

With the optimized conditions in hand, we explored the scope of allyl alcohols using $PhMe_2SiZnCl$ (**2a**) as the nucleophilic reagent (see Table 2). Thus, allyl alcohols was first treated with MeZnCl. The reaction with $PhMe_2SiZnCl$ then was run in toluene at room temperature for 5 h, using $Ni(PMe_3)Cl_2$ (10 mol %) as a catalyst. A range of 3-(substituted phenyl)prop-2-en-1-ols were tested and demonstrated to be suitable for the transformation. The allyl alcohols with either electron-rich or electron-poor substituted phenyl gave excellent product yields (Table 2, entries 1–9 and 11–17). It seems that the electron effect of the substituents on the phenyl rings makes no difference to the reaction. The coupling of (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol was also performed on a 4 mmol scale and gave **3c** in 87% isolated yield (Table 2, entry 2). Functional groups on the phenyl rings, including *p*-*t*Bu, *p*-OMe, *p*-NMe_2, *p*-SMe, *p*-CF_3, *p*-OCF_3, *p*-$OCHF_2$, *p*-F, *p*-Cl, *p*-CO_2Me, *p*-$CONEt_2$, *m*-OMe, *m*-OPh, *m*-CF_3, *o*-Ph, and *o*-F, were tolerated.

However, the bromo substituent in (*E*)-3-(4-bromophenyl) prop-2-en-1-ol (**1k**) cannot be tolerated. Reaction of **1k** with $PhMe_2SiZnCl$ under the standard conditions afforded (*E*)-3-(4-(dimethyl(phenyl)silyl)phenyl)prop-2-en-1-ol (**3k**) in 72% yield, along with (*E*)-(3-(4-(dimethyl(phenyl)silyl)phenyl)-allyl)dimethyl(phenyl)silane (**3ka**) in 27% yield (Table 2, entry 10). It seems that the bromo substituent is more reactive than the hydroxy group in **1k** under the standard conditions. When 2 equiv of $PhMe_2SiZnCl$ were used, the reaction resulted in **3ka** in 99% yield. Other 3-arylprop-2-en-1-ols, such as (*E*)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)prop-2-en-1-ol (**1s**), (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)prop-2-en-1-ol (**1t**), (*E*)-3-(naphthalen-2-yl)prop-2-en-1-ol (**1u**), and (*E*)-3-(naphthalen-1-yl)prop-2-en-1-ol (**1v**), displayed reactivity similar to that of (*E*)-3-phenylprop-2-en-1-ol (Table 2, entries 18–21). We also examined the reactivity of (*E*)-4-phenylbut-3-en-2-ol (**1w**) and (*E*)-1,3-diphenylprop-2-en-1-ol (**1x**). Their reaction required longer time and gave excellent product yields (Table 2, entries 22 and 23). (*E*)-2-Methyl-3-phenylprop-2-en-1-ol (**1y**) showed relatively low reactivity. Its reaction with **2a** was performed at 80 °C and led to the desired product in 56% yield, as a mixture of *Z* and *E* isomers (Table 2, entry 24). The catalytic system was also used to perform the transformation of alkyl-substituted allyl alcohols. Reaction of these substrates required longer time and higher temperature. For example, reaction of (*E*)-6-(4-methoxyphenyl)hex-2-en-1-ol (**1z**) and (*E*)-3-(tetrahydro-2*H*-pyran-4-yl)prop-2-en-1-ol (**1za**) with **2a** at 80 °C for 24 h resulted in the mixtures of linear and branched coupling products in 86% and 80% total yields, respectively (Table 2, entries 25 and 26) (see the mechanism discussion section below).

Several heteroaryl-substituted allyl alcohols were also examined under the optimized conditions. As shown in Scheme 1, furan-2-yl-, thiophen-2-yl-, pyridin-2-yl-, benzo[*b*]-thiophen-3-yl-, and 1-methyl-1*H*-indol-5-yl-substituted allyl alcohols were demonstrated to be suitable substrates for the coupling, leading to the desired products in excellent yields. Reaction of (*E*)-3-(thiophen-2-yl)prop-2-en-1-ol with **2a** required a longer reaction time and gave the desired product in 85% yield, as a mixture of *Z* and *E* isomers.

Reactivity of 1-arylprop-2-en-1-ols was also examined using $PhMe_2SiZnCl$ as the nucleophilic reagent (see Scheme 2). A mixture of toluene and nBu$_2$O (3:1) were demonstrated to be superior to toluene as a solvent, and the reaction time was prolonged to 24 h to ensure the complete consumption of the 1-arylprop-2-en-1-ols. Linear allylsilanes were formed in each case. Reaction of 1-phenylprop-2-en-1-ol and 1-(4-substituted phenyl)prop-2-en-1-ols with electron-donor groups on the phenyl rings gave the products in yields of 83%–86%. Reaction of 1-(4-substituted phenyl)prop-2-en-1-ols with electron-withdrawing groups on the phenyl rings resulted in slightly lower product yields.

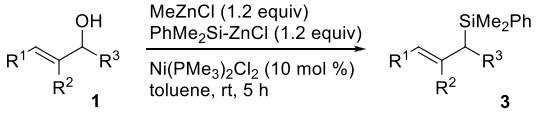
Other silicon nucleophiles were also tested. Both $Ph_2MeSiZnCl$ and $Ph_3SiZnCl$ exhibited excellent reactivity. Their reaction with cinnamyl alcohol afforded the corresponding products in yields of 99% and 91%, respectively (see Scheme 3). Reaction of $Ph_3SiZnCl$ required a longer reaction time to make the alcohol convert completely.

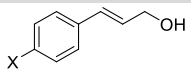
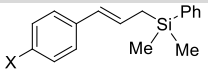
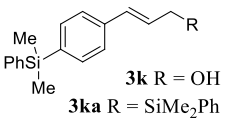
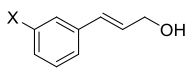
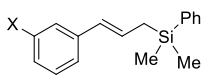
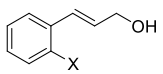
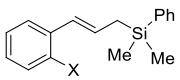
We also examined the potential use of the allylsilanes produced in this work. It was demonstrated that the resultant allylsilane, cinnamyldimethyl(phenyl)silane, can be utilized as an allylating agent with high regioselectivity when reacted with Ph_2CHOH in the presence of $InCl_3$ (see Scheme 4).[9]

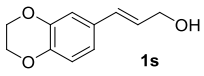
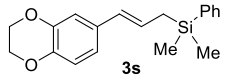
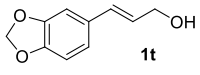
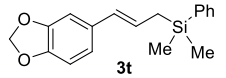
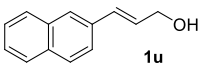
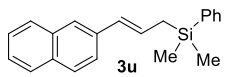
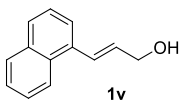
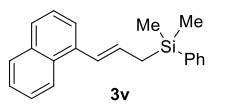
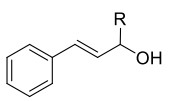
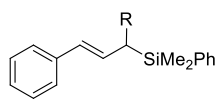
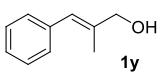
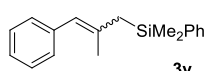
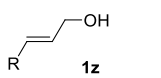
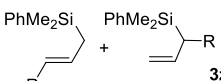
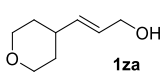
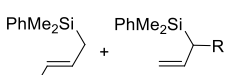
Preliminary experiments to evaluate the plausible reaction mechanism were performed (see Scheme S9 in the Supporting Information). The reaction of cinnamyl alcohol (**1a**) with $PhMe_2SiZnCl$ (**2a**) was not affected by (1-cyclopropylvinyl)-benzene additive. When 1.0 equiv of (1-cyclopropylvinyl)-benzene was added to the reaction system, the catalytic process gave the desired coupling product in 97% yield, along with recovery of (1-cyclopropyl-vinyl)benzene in 94% yield (see Scheme S9a in the Supporting Information). This is inconsistent with a free radical process. The combination of $Ni(COD)_2$ and PMe_3 exhibited almost the same catalytic

DOI: 10.1021/acs.orglett.9b02946
Org. Lett. XXXX, XXX, XXX–XXX

Table 2. Scope of Allyl Alcohols[a]



entry	allyl alcohol	product	yield (%)[b]
			
1	**1b**, X = *t*Bu	**3b** X = *t*Bu	90
2	**1c**, X = OMe	**3c** X = OMe	91 (87[c])
3	**1d**, X = NMe_2	**3d** X = NMe_2	90
4	**1e**, X = SMe	**3e**, X = SMe	95
5	**1f**, X = CF_3	**3f** X = CF_3	99
6	**1g**, X = OCF_3	**3g** X = OCF_3	99
7	**1h**, X = $OCHF_2$	**3h** X = $OCHF_2$	93
8	**1i**, X = F	**3i** X = F	93
9	**1j**, X = Cl	**3j** X = Cl	95
10	**1k**, X = Br	 **3k** R = OH **3ka** R = $SiMe_2Ph$	72 (27[d]) (99[e])
11	**1l**, X = CO_2Me	**3l**, X = CO_2Me	99
12[f]	**1m**, X = $CONEt_2$	**3m**, X = $CONEt_2$	85
			
13	**1n**, X = OMe	**3n**, X = OMe	96
14	**1o**, X = OPh	**3o**, X = OPh	99
15	**1p**, X = CF_3	**3p**, X = CF_3	99
			

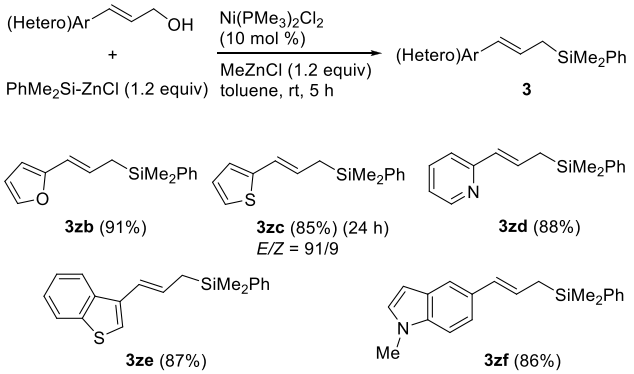
entry	allyl alcohol	product	yield (%)[b]
16	**1q**, X = Ph	**3q**, X = Ph	92
17	**1r**, X = F	**3r**, X = F	91
18	 **1s**	 **3s**	90
19	 **1t**	 **3t**	91
20	 **1u**	 **3u**	98
21	 **1v**	 **3v**	99
			
22[g]	**1w**, R = Me	**3w**, R = Me	95
23[g]	**1x**, R = Ph	**3x**, R = Ph	99
24[h]	 **1y**	 **3y** *E*/*Z* ~ 72/28	56
25[g,h]	 **1z** R = *p*-$MeOC_6H_4(CH_2)_3$	 **3z** R = *p*-$MeOC_6H_4(CH_2)_3$ linear:branched = 33:67	86
26[g,h]	 **1za**	 **3za** R = tetrahydro-2*H*-pyran-4-yl linear:branched = 39:61	80

[a]Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b]Isolated yield. [c]4 mmol scale. [d]The yields of **3k** and **3ka** were 72% and 27%, respectively. [e]2.0 equiv of **2a** were used. [f]The reaction was performed in THF at 80 °C. [g]Reaction time was 24 h. [h]Reaction temperature was 80 °C.

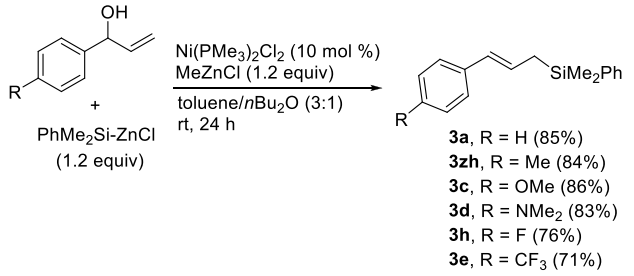
activity as $NiCl_2(PMe_3)_2$ (see Scheme S9b in the Supporting Information). Furthermore, a small amount of $PhMe_2Si$-$SiMe_2Ph$ was detected when $NiCl_2(PMe_3)_2$ was employed as the catalyst (5.1% based on cinnamyl alcohol). The fact that the isolated $PhMe_2Si$-$SiMe_2Ph$ was less than the theoretical amount might be because a portion of $NiCl_2(PMe_3)_2$ was reduced by the unconsumed MeZnCl. These experimental facts imply the reaction might proceed through a Ni(0)/Ni(II) cycle. Next, we found that the reaction of racemic (*E*)-1-phenylpent-1-en-3-ol (*rac*-**1zo**) with $PhMe_2SiZnCl$ under standard conditions gave racemic (*E*)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane (*rac*-**3zo**) in 91% yield. Whereas reaction of (*S*)-**1zo** with **2a** produced (*R*)-**3zo** (see Schemes S9c and S9d in the Supporting Information). Hence, we inferred that the reaction might involve a SN2 process. On the basis of the above experimental facts and the related reports in the literature,[2b,10] a plausible catalytic cycle is outlined in Scheme 5. Thus, allylic alcohol was first converted to the corresponding salt **A**. Meanwhile, $NiCl_2(PMe_3)_2$ was reduced to active Ni(0) species **B** by $R_3SiZnCl$ along with the formation of R_3Si-SiR_3. Oxidative addition with inversion of the Ni(0) species with **A** results in a [σ, π]-type Ni(II) intermediate **C**. Subsequently, transmetalation of **C** with $R_3SiZnCl$ forms complex **D**. When R is a aryl group, **D** prefers to directly undergo reductive elimilation to give α-silylated product **E** with the inversion of configuration. When R′ is a aryl group, **D** prefers to isomerize to form a more stable [σ, π]-type Ni(II) intermediate **G** via a π-allyl Ni(II) intermediate **F**. Reductive elimilation of **G** leads to γ-silylated product **H**. If both R and R′ are alkyl groups or protons, the

DOI: 10.1021/acs.orglett.9b02946
Org. Lett. XXXX, XXX, XXX−XXX

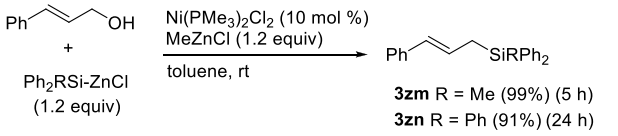
Scheme 1. Reaction of Heteroaryl Allyl Alcohols with $PhMe_2SiZnCl$



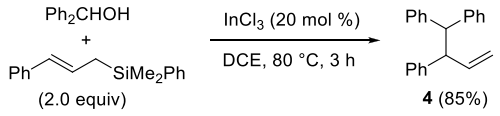
Scheme 2. Reaction of 1-Arylprop-2-en-1-ols with $PhMe_2SiZnCl$



Scheme 3. Reaction of (*E*)-3-Phenylprop-2-en-1-ol with $Ph_2MeSiZnCl$ and $Ph_3SiZnCl$



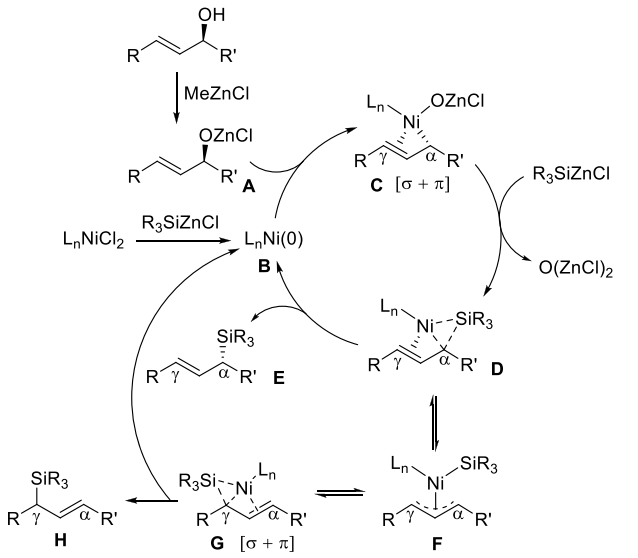
Scheme 4. Reaction of Cinnamyldimethyl(phenyl)silane with Diphenylmethanol



reaction leads to the products with poor regioselectivity, because none of the intermediates **D** and **G** is dominant (see Table 2, entries 25 and 26).

In summary, we developed a synthetic method of allylic silanes via $NiCl_2(PMe_3)_2$-catalyzed reaction of allyl alcohols with silylzinc reagents under mild conditions. The method suits for a broad scope of substrates. $PhMe_2SiZnCl$, $Ph_2MeSiZnCl$ and $Ph_3SiZnCl$ are suitable nucleophilic species. Aryl and heteroaryl-substituted allyl alcohols, (*E*)-3-arylprop-2-en-1-ols, 1-aryl-prop-2-en-1-ols, and (*E*)-1-phenylpent-1-en-3-ol are suitable electrophilic substrates. A range of functional groups were tolerated. Reaction also showed high regioselectivity and *E*/*Z*-selectivity when 1- or 3-aryl-substituted allyl alcohols were used as the substrates. Reaction of chiral allyl alcohol, (*S*,*E*)-1-phenylpent-1-en-3-ol, yielded a configuration-inversion product (*R*,*E*)-dimethyl(phenyl)(1-phenylpent-1-en-3-yl)silane. Preliminary mechanism studies showed that the

Scheme 5. Proposed Catalytic Cycle



reaction might proceed via a Ni(0)/Ni(II) catalytic cycle and [σ, π]-type allyl nickel intermediates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02946.

Experimental procedures, full analysis data for new compounds, and copies of NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zxwang@ustc.edu.cn.

ORCID

Bo Yang: 0000-0003-0612-5712

Zhong-Xia Wang: 0000-0001-8126-8778

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 21772186) and the National Basic Research Program of China (Grant No. 2015CB856600). We thank Y.-Y. Kong for her help in performing additional experiments.

■ REFERENCES

(1) (a) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293. (b) Fleming, I.; Barbero, A.; Walter, A. D. *Chem. Rev.* **1997**, *97*, 2063. (c) Brook, M. A. Silicon in organic, organometallic and polymer chemistry; John Wiley & Sons, Ltd., Chichester, 2000. (d) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (e) Barbero, A.; Pulido, F. J. *Acc. Chem. Res.* **2004**, *37*, 817. (f) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, *2004*, 3173. (g) Nielsen, L.; Skrydstrup, T. *J. Am. Chem. Soc.* **2008**, *130*, 13145. (h) Franz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388. (i) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2013**, *113*, 5595. (j) Denmark, S. E.; Ambrosi, A. *Org. Process Res. Dev.* **2015**, *19*, 982.

DOI: 10.1021/acs.orglett.9b02946
Org. Lett. XXXX, XXX, XXX−XXX

(2) (a) Oestreich, M.; Auer, G. *Adv. Synth. Catal.* **2005**, *347*, 637. (b) Schmidtmann, E. S.; Oestreich, M. *Chem. Commun.* **2006**, 3643. (c) Vyas, D. J.; Oestreich, M. *Chem. Commun.* **2010**, *46*, 568. (d) Hensel, A.; Oestreich, M. *Chem. - Eur. J.* **2015**, *21*, 9062.
(3) Xue, W.-C.; Oestreich, M. *Synthesis* **2019**, *51*, 233.
(4) (a) Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993**, *58*, 3607. (b) Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. *J. Org. Chem.* **1996**, *61*, 5779.
(5) (a) Vyas, D. J.; Oestreich, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8513. (b) Delvos, L. B.; Vyas, D. J.; Oestreich, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 4650. (c) Takeda, M.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2013**, *78*, 5007. (d) Hazra, C. K.; Irran, E.; Oestreich, M. *Eur. J. Org. Chem.* **2013**, *2013*, 4903. (e) Xuan, Q.-Q.; Zhong, N.-J.; Ren, C.-L.; Liu, L.; Wang, D.; Chen, Y.-J.; Li, C.-J. *J. Org. Chem.* **2013**, *78*, 11076. (f) Delvos, L. B.; Hensel, A.; Oestreich, M. *Synthesis* **2014**, *46*, 2957. (g) Delvos, L. B.; Oestreich, M. *Synthesis* **2015**, *47*, 924.
(6) (a) Hayashi, T.; Ohno, A.; Lu, S.-J.; Matsumoto, Y.; Fukuyo, E.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 4221. (b) Macsári, I.; Hupe, E.; Szabó, K. J. *J. Org. Chem.* **1999**, *64*, 9547. (c) Kabalka, G. W.; Venkataiah, B.; Dong, G. *Organometallics* **2005**, *24*, 762. (d) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (e) Moser, R.; Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 28. (f) Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409. (g) Larsson, J. M.; Szabó, K. J. *J. Am. Chem. Soc.* **2013**, *135*, 443.
(7) Yang, B.; Wang, Z.-X. *J. Org. Chem.* **2017**, *82*, 4542.
(8) (a) Yu, D.-G.; Wang, X.; Zhu, R.-Y.; Luo, S.; Zhang, X.-B.; Wang, B.-Q.; Wang, L.; Shi, Z.-J. *J. Am. Chem. Soc.* **2012**, *134*, 14638. (b) Yu, D.-G.; Li, B.-J.; Zheng, S.-F.; Guan, B.-T.; Wang, B.-Q.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4566.
(9) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1414.
(10) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 6863. (c) Pound, S. M.; Watson, M. P. *Chem. Commun.* **2018**, *54*, 12286. (d) Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *Chem. Rev.* **2015**, *115*, 9587. (e) Srinivas, H. D.; Zhou, Q.; Watson, M. P. *Org. Lett.* **2014**, *16*, 3596. (f) Cobb, K. M.; Rabb-Lynch, J. M.; Hoerrner, M. E.; Manders, A.; Zhou, Q.; Watson, M. P. *Org. Lett.* **2017**, *19*, 4355.

DOI: 10.1021/acs.orglett.9b02946
Org. Lett. XXXX, XXX, XXX−XXX