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Vinylsiloxanes as Alkenylating Agents in Nickel-Catalyzed Difunctionalization of Vinylarenes

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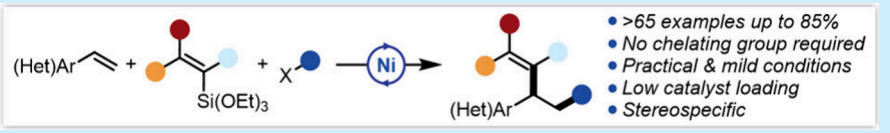

ABSTRACT: We report the first directing-group-free nickel-catalyzed difunctionalization of vinylarenes using bench-stable vinylsiloxanes as alkenylating agents. This mild, scalable and stereospecific method provides regioselective access to functionalized disubstituted alkenes with broad scope, low catalyst loadings, and minimal *Z*-isomerization, establishing vinylsiloxanes as versatile alkenyl transfer partners in multicomponent nickel catalysis.

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Intermolecular transition-metal-catalyzed alkene difunctionalization has emerged as a powerful strategy in modern synthetic chemistry, enabling the simultaneous formation of two new bonds across an olefin in a single operation.[1] These transformations enable rapid construction of molecular complexity from abundant and readily accessible alkene feedstocks, affording structurally diverse molecular architectures. Among the transition metals employed for alkene difunctionalization, nickel stands out due to its ability to engage in diverse mechanistic manifolds, including single-electron transfer (SET) pathways, while showing a comparatively low propensity for β-hydride elimination.[2] These features render nickel complexes well-suited for the catalysis of radical-mediated transformations and three-component coupling processes.

In such multicomponent difunctionalization reactions, precise control over regioselectivity and chemoselectivity is key and often requires directing groups. In this context, the chelating-group-assisted strategy has become widely used, and a variety of strongly coordinating auxiliaries have been developed to guide site-selective bond formation (Figure 1A).[3] Despite the broad substrate scope and high efficiency, this strategy typically requires installation and subsequent removal of the directing group, when feasible. These additional steps diminish atom economy and overall efficiency, thereby limiting synthetic applicability and flexibility.

More recently, to move beyond directing groups, difunctionalization approaches exploiting intrinsically electron-deficient alkenes have been developed, thereby broadening the accessible chemical space (Figure 1B).[4] In contrast, despite their inherent ability to govern regioselectivity through benzylic stabilization, radical-mediated difunctionalizations of vinylarenes remain underdeveloped, despite strong synthetic potential. A notable contribution was reported by Giri in 2018,[5] describing a nickel-catalyzed alkylarylation of vinylarenes that enables access to 1,1-diarylalkanes using organozinc reagents and alkyl iodides as coupling partners (Figure 1C).

Despite the substantial advances, most transformations remain largely confined to (difluoro)alkylation and arylation processes. In contrast, three-component alkenylation reactions—which enable direct installation of synthetically versatile alkenyl motifs—remain underexplored. To the best of our knowledge, only three reports describe alkenylative variants of this transformation (Figure 1D).[6] The first example was disclosed by Zhao in 2018,[6a] reporting a nickel-catalyzed alkenylative difunctionalization using organoboronic acids and organic halides in conjunction with an *N*-allylpyrimidin-2-amine directing group. This method enabled either 1,3-arylalkenylation or 1,2-alkenylarylation depending on the coupling partners. However, the substrate scope was limited, largely restricted to styrenyl derivatives and providing only moderate yields. In 2024, Molander and Nevado[6b] reported an enantioselective difunctionalization platform enabled by photochemical aliphatic C−H activation. While conceptually innovative, this approach includes few alkenylation examples and is mainly limited to styrenyl bromides. In the same year, Xu and Wang[6c] described a dicarbofunctionalization protocol using alkenyl boronic acids and alkyl halides, leveraging native functional groups as directing elements. Despite a broad substrate scope, this strategy relies on a chelating-group-assisted manifold, and alkenylation occurs exclusively at the

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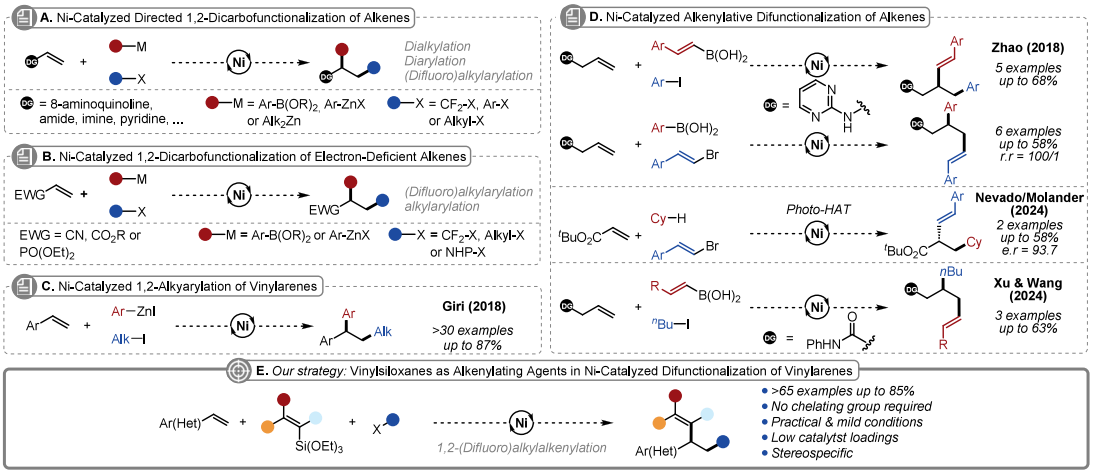


Figure 1. Overview of nickel-catalyzed alkene difunctionalization strategies, including (A) directed approaches, (B) the use of electron-deficient alkenes or (C) the use of vinylarenes, (D) three-component alkenylation reactions, and (E) our strategy.

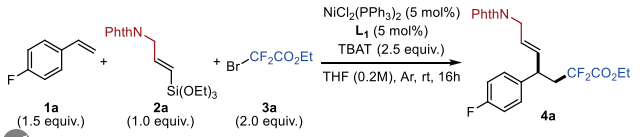
terminal position, with only three examples involving styrenyl derivatives.

Building on these recent advances and acknowledging the current limitations, we envisioned that vinylsiloxanes — which we previously showed to be versatile, stereodefined organosilicon building blocks[7] — could serve as readily available, bench-stable alkenylating agents in nickel-catalyzed difunctionalizations of vinylarenes without the need for a directing group. In contrast to commonly employed alkenylmetal reagents, these user-friendly alkenylating agents exhibit tolerance toward moisture and oxygen. Moreover, all isomers with diverse substitution patterns and defined stereochemistry can be prepared in a divergent and straightforward manner via hydrosilylation of the corresponding alkyne.[8] Herein, we report the successful development of this novel three-component transformation, along with an exhaustive investigation of its scope.

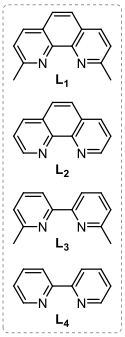
We initiated our studies with a comprehensive evaluation of the difluoroalkylalkenylation of styrene **1a** with β-(*E*)-vinylsiloxane **2a** and ethyl bromodifluoroacetate **3a** which were selected as model substrates. Preliminary systematic variation of key reaction parameters—including the nature of the nickel precatalyst, ligand, solvent, and stoichiometry of the coupling partners—enabled identification of optimal conditions (see the Supporting Information for details) that delivered the desired product **4a** in 85% isolated yield without detectable double-bond isomerization (Table 1, entry 1). The optimized protocol is operationally straightforward, employing 5 mol % of nickel catalyst in THF at room temperature with air- and bench-stable reagents. Activation of vinylsiloxane **2a** was accomplished using tetrabutylammonium triphenyldifluorosilicate (TBAT, 2.5 equiv), which proved essential for productive reactivity.[7] Increasing the catalyst loading to 20 mol % provided only marginal improvement, whereas reducing the loading maintained comparable efficiency yields (Table 1, entries 2 and 3), highlighting the robustness of the catalytic system. Control experiments established the critical role of both nickel precatalysts and ligand $\mathbf{L_1}$, as omission of either component completely suppressed product formation (Table 1, entries 4 and 5).

The nature of the electrophile exerted minimal influence on reaction efficiency, since switching to chloro or iodo difluoroacetates furnished product **4a** in similarly high yields

Table 1. Optimization of the Reaction Conditions[a]



entry	variation	yield (%)[b]
1	none	87, 85[c]
2	20 mol% Ni/$\mathbf{L_1}$	93, 92[c]
3	2.5 mol% Ni/$\mathbf{L_1}$	83
4	w/o Ni/$\mathbf{L_1}$	n.d
5	w/o $\mathbf{L_1}$	n.d
6	Cl-CF_2CO_2Et	82
7	I-CF_2CO_2Et	79
8	w/o TBAT	n.d.
9	TBAF[d]	n.d
10	1.0 equiv. **1a**	77
11	1.0 equiv. **3a**	66
12	under air	32
13	50 mol% H_2O	78
14	$\mathbf{L_2}$	n.d
15	$\mathbf{L_3}$	70
16	$\mathbf{L_4}$	25



[a]All reactions performed on a 0.20 mmol scale. [b]^{19}F NMR yield using 2,2,2-trifluoro-*N*,*N*-dimethylacetamide as an internal standard. [c]Yield of isolated product after purification by flash chromatography. [d]5.0 equiv. n.d. = not determined.

(Table 1, entries 6 and 7). In contrast, omission of TBAT or substitution with tetrabutylammonium fluoride (TBAF) entirely inhibited the reaction (Table 1, entries 8 and 9), underscoring the unique role of TBAT in facilitating transmetalation to nickel,[7] the lower efficiency of TBAF being most certainly due to the detrimental presence of water systematically contaminating this fluoride source. Precise control over reagent stoichiometry was also important, as reducing either styrene **1a** or difluoroacetate **3a** to 1.0 equiv resulted in diminished yields (Table 1, entries 10 and 11). Although an inert atmosphere was required, the transformation tolerated low levels of adventitious water (Table 1, entries 12 and 13). Finally, the nature of the ligand proved decisive for catalytic performance. In particular, 2,2′-dimethyl substitution on the phenanthroline scaffold was essential for high efficiency,

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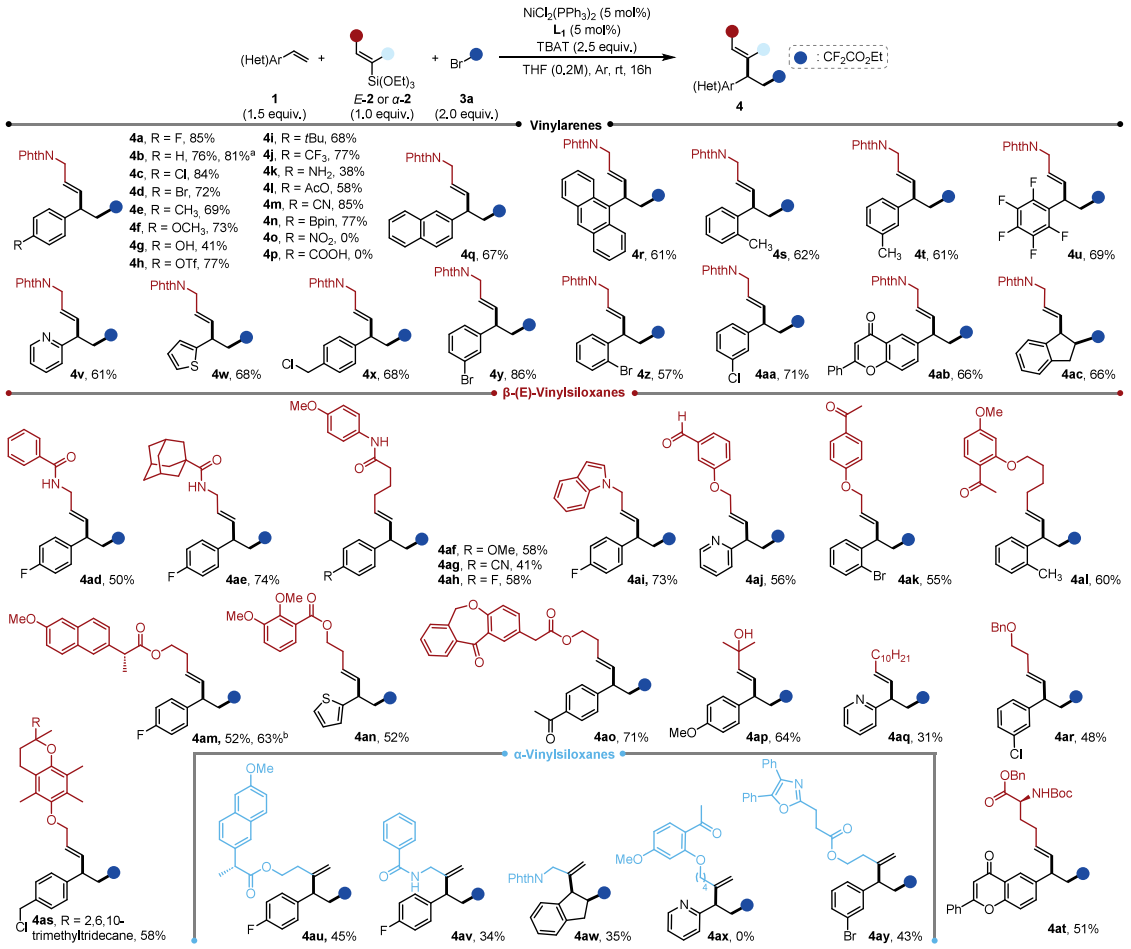

Figure 2. Substrate scope of vinylarenes, β-(*E*)-vinylsiloxanes and α-vinylsiloxanes. Reactions were carried out on a 0.20 mmol scale. [a]Gram-scale on 5 mmol. [b]20 mol % Ni/$\mathbf{L_1}$.

whereas alternative ligands led to substantially reduced reactivity (Table 1, entries 14−16).

With the optimized conditions in hand, we next examined the scope of the transformation, initially focusing on the influence of the vinylarene component using a representative β-(*E*)-vinylsiloxane. As shown in the top panel of Figure 2, a broad range of vinylarenes bearing diverse functional groups proved compatible with the reaction conditions, delivering the desired products in yields ranging from 41% to 85%. Electron-neutral, electron-rich and electron-deficient substituents on the arene were all well-tolerated, underscoring the robustness of the protocol toward electronic variation. Halogen substituents such as chloro (**4c**, **4aa**), fluoro (**4a**), and bromo (**4d**, **4y**−**4z**) groups are preserved, providing handles for downstream diversification through cross-coupling chemistry. Strongly electron withdrawing groups including trifluoromethyl (**4j**), cyano (**4m**), and related motifs are likewise compatible, generally affording the corresponding adducts in very good yields. More sensitive functionalities, such as aryl triflate (**4h**), a boronic ester (**4n**), and a benzylic chloride (**4x**), were all found to be perfectly compatible with the reaction conditions, highlighting the surgical precision of the nickel catalyst and providing additional opportunities for product diversification. Heteroaromatic substrates (**4v**−**4w**) participate smoothly, demonstrating that even coordinating heteroarenes such pyridines or thiophenes do not significantly interfere with the nickel catalyst. With respect to steric effects on the vinylarene, only a moderate impact was observed, *ortho*-substituted vinylarenes (**4s**, **4z**) furnishing slightly diminished yields compared to their *para*-substituted analogues (**4d**, **4e**), consistent with increased steric congestion around the reactive alkene. A cyclic alkene (indene) also proved to be a competent substrate delivering the desired product (**4ac**) in a synthetically useful 66% yield. Notably, the reaction was successfully conducted on a 5 mmol scale, affording 1.68 g of product (**4b**) in comparable yield, thereby confirming the operational robustness and preparative potential of the method. An extension to other activated alkenes such as acrylates or vinylsulfones as well as substituted vinylarenes was also evaluated but was not met with success (see the Supporting Information for details).

Having established the broad scope with respect to the vinylarene component, we next evaluated the influence of the β-(*E*)-vinylsiloxane partner. As summarized in the bottom panel of Figure 2, an equally broad substrate scope was observed, further highlighting the generality of this three-component coupling. The transformation accommodates a wide array of functional groups, including amides (**4ad**−**5ah**), ketones (**4ak**−**4al**) and an aldehyde (**4aj**), delivering the desired products in satisfactory yields without detectable isomerization of the sensitive alkene moiety. Importantly, no protecting groups were required for these potentially labile functionalities, underscoring the mildness of the reaction conditions. For more demanding substrates, increasing the

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catalyst loading to 20 mol % resulted in a 10% improvement in yield for substrate (**4am**), illustrating the tunability of the catalytic system. The protocol also enables late-stage functionalization of structurally complex scaffolds derived from pharmaceuticals and natural products. Isoxepac derivative (**4ao**), vitamin E analogue (**4as**), and glutamic acid derivative (**4at**) were efficiently converted, highlighting the synthetic utility of this platform for diversity-oriented synthesis. As a note, a lower yield was observed when the starting vinylsiloxane (**4aq**) lacked a heteroatom, which suggests that the heteroatom plays a subtle role in the catalytic cycle, likely stabilizing certain nickel intermediates through chelation.

Under the same optimized conditions, α-vinylsiloxanes (**4au**−**4ay**) also underwent alkylalkenylation, albeit in more moderate yields (34%−45%), likely reflecting the increased steric hindrance imposed by the branched siloxane substituent proximal to the reactive olefin. The lower efficiency observed with α-vinylsiloxanes also resulted in a narrower substrate scope; for instance, 2-vinylpyridine failed to react with these alkenylating agents (**4ax**).

Encouraged by these results, we next turned to the more challenging difunctionalization using β-(*Z*)-vinylsiloxanes.

To the best of our knowledge, this transformation constitutes the first example of the direct incorporation of a geometrically strained (*Z*)-alkene into a styrene framework, thereby providing access to this distinctive structural motif (Figure 3). Despite the well-documented propensity of (*Z*)-

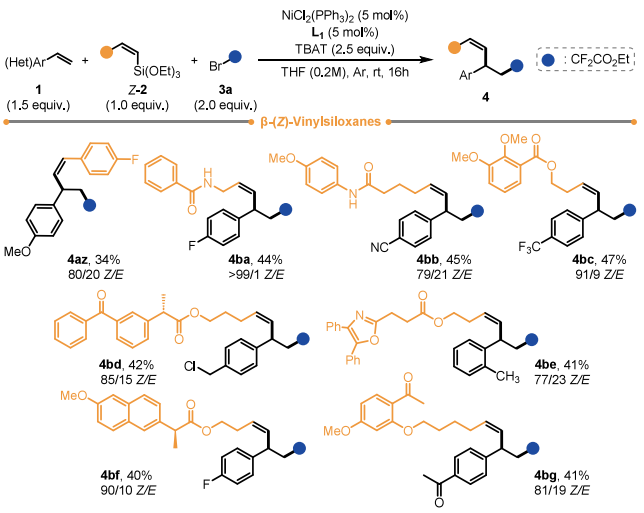

Figure 3. Substrate scope of β-(*Z*)-vinylsiloxanes. Reactions were carried out on a 0.20 mmol scale.

alkenes to undergo isomerization under transition-metal catalysis, the reaction proceeds in synthetically useful yields (34%−47%) across a representative set of β-(*Z*)-vinylsiloxanes (**4az**−**4bg**). Importantly, high levels of stereoretention are observed, with substrate-dependent *Z*/*E* ratios ranging from 77:23 to >99:1. The extent of isomerization appears to correlate with substrate structure, suggesting that reversible β-hydride elimination from a key nickel intermediate may be operative in the most challenging cases under the reaction conditions. Nevertheless, the substantial preservation of the (*Z*)-configuration in several cases underscores the ability of the catalytic system to minimize double-bond scrambling, even under a radical manifold.

Finally, to demonstrate that the electrophile is not restricted to ethyl bromodifluoroacetate (**3a**), a diverse set of electrophiles known to generate radicals under nickel catalysis was evaluated without further optimization (Figure 4). As

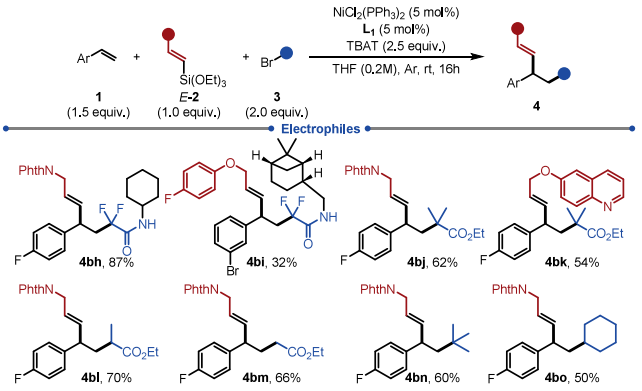

Figure 4. Substrate scope of electrophiles. Reactions were carried out on a 0.20 mmol scale.

anticipated, difluoroalkylated products (**4bh**) and (**4bi**) were obtained efficiently under the standard conditions. Importantly, replacement of the fluorinated substituents with methyl groups furnished the corresponding alkylated products (**4bj**) and (**4bk**) in synthetically useful yields, indicating that fluorine is not required for reactivity. The method is also not restricted to tertiary radical precursors, as secondary alkyl electrophiles participated smoothly, delivering products **4bl** and **4bm** in 70% and 66% yield, respectively. Moreover, electron-withdrawing groups on the electrophile are not necessary. Simple *tert*-butyl and cyclohexyl iodides underwent efficient alkylalkenylation to afford **4bn** and **4bo**, highlighting the broad radical compatibility and generality of the transformation.

Based on literature precedents on nickel catalysis and cross-coupling reactions involving vinylsiloxanes, the catalytic cycle depicted in Figure 5 can reasonably be proposed. Activation of

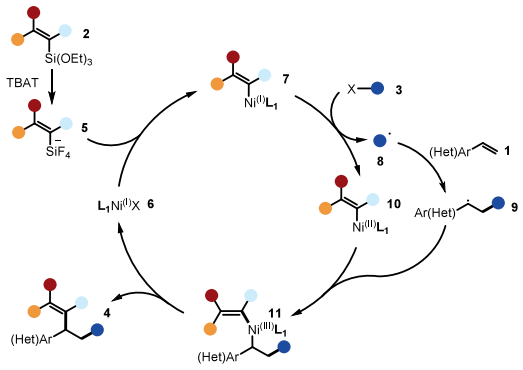

Figure 5. Proposed catalytic cycle.

the starting vinylsiloxane **2** by TBAT generates a fluorosilicate **5**[9] that undergoes stereospecific transmetalation with the L_1-ligated $Ni^{(I)}$ species to furnish vinylnickel complex **7**. Single-electron transfer from **7** to alkyl bromide **3** then produces an alkyl radical together with a $Ni^{(II)}$ species **10**; addition of the former to the starting vinylarene **1** delivers the transient benzylic radical species **9**. The stabilized nature of radical species **9** might result in a sufficient lifetime of vinylnickel intermediate **10** to undergo reversible β-hydride elimination to

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a Ni−H species and reinsertion to the thermodynamically favored (*E*)-vinylnickel isomer, thereby accounting for the erosion of the *E*/*Z* ratio observed starting from some (*Z*)-siloxanes. Subsequent radical capture of **9** by complex **10** forms a $Ni^{(III)}$ intermediate **11**, which then undergoes reductive elimination to deliver the difunctionalized product **4** and regenerate the $Ni^{(I)}$ catalyst **6**. As a note, addition of 1 equiv of TEMPO to the reaction mixture using the model substrates utilized for the optimization totally inhibited the reaction, which is consistent with the intermediacy of radical species.

In conclusion, we report a directing-group-free, nickel-catalyzed difunctionalization of vinylarenes that enables installation of an alkyl chain and a functionalized double bond in a single, operationally simple step. The transformation shows broad scope for both vinylarene and vinylsiloxane partners, tolerates diverse functional groups, and accommodates radical precursors beyond difluoroalkyl electrophiles. Notably, the method enables incorporation of stereodefined alkenyl fragments, including challenging β-(Z)-vinylsiloxanes, with substantial retention of alkene geometry. Overall, this strategy expands alkene difunctionalization by allowing direct incorporation of synthetically versatile alkenyl fragments from bench-stable vinylsiloxanes, increasing access to densely functionalized alkenes and enhancing the utility of organosilicon reagents. The operational simplicity, functional-group tolerance, and stereochemical fidelity of this process make it a valuable platform for rapid assembly of highly substituted alkenes.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.6c01252.

Experimental procedures, optimization study, graphics, spectroscopic data, and NMR spectra (PDF)

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Logan Salamone: Conceptualization, Methodology, Investigation, Scope, Visualization, Original draft, Funding Acquisition. **Qihang Tan:** Conceptualization, Methodology, Investigation, Review and Editing. **Gwilherm Evano:** Conceptualization, Methodology, Project Administration, Supervision, Review and Editing, Funding Acquisition. **Olivier Riant**: Conceptualization, Methodology, Project Administration, Supervision, Review and Editing, Funding Acquisition. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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