

# Selective Synthesis of Z-Silyl Enol Ethers via Ni-Catalyzed Remote Functionalization of Ketones

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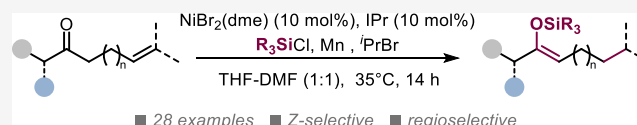


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**ABSTRACT:** We report a remote functionalization strategy, which allows the Z-selective synthesis of silyl enol ethers of (hetero)aromatic and aliphatic ketones via Ni-catalyzed chain walking from a distant olefin site. The positional selectivity is controlled by the directionality of the chain walk and is independent of thermodynamic preferences of the resulting silyl enol ether. Our mechanistic data indicate that a Ni<sup>(II)</sup> dimer is formed under these conditions, which serves as a catalyst resting state and, upon reaction with an alkyl bromide, is converted to [Ni<sup>(III)</sup>-H] as an active chain-walking/functionalization catalyst, ultimately generating a stabilized η<sup>3</sup>-bound Ni<sup>(III)</sup> enolate as the key selectivity-controlling intermediate.



## INTRODUCTION

An emerging strategy in the synthetic chemist's toolbox is chain walking coupled with remote functionalization, in which a functionality is installed at a certain distance from the original reaction center.<sup>1–5</sup> Such approaches have gained increasing popularity and significance, as they allow installing functionalities in a fundamentally different manner, and as such, they can potentially unlock compatibility with different functional groups and enable the use of alternative starting materials or even mixtures of olefin precursors.<sup>6–8</sup> While numerous elegant transformations have been developed, especially C–C,<sup>9</sup> C–Si,<sup>10</sup> and C–B<sup>11</sup> bond formations or redox events (e.g., OH to carbonyl)<sup>12,13</sup> as terminating functionalization in this context, to date, there is no precedence of remote functionalization of ketones.<sup>14–16</sup>

If realizable, such a process could enable the synthesis of silyl enol ethers, which have gained prominence as a powerful synthon for carbon–carbon bond formation and stereo-selective synthesis.<sup>17–20</sup> However, access to silyl enol ethers under positional and stereochemical control is not free of challenges. The commonly pursued direct deprotonation of ketones, followed by silylation of the corresponding enolate, is incompatible with ketones that contain base-sensitive functional groups or that contain two alkyl substituents of similar steric and electronic properties, which will compromise the overall positional selectivity of the double bond (see Figure 1A).<sup>21–23</sup> The alternative approach from α,β-unsaturated ketones, followed by reductive conjugate addition, is amenable for cyclic systems,<sup>24–27</sup> whereas hydrosilylation using Rh, Pd, Pt, or Co catalysis has been predominantly applied to aromatic ketones (Figure 1B).<sup>28–31</sup> Alternative α-C–H bond activations of ketones followed by silylation may give rise to competing over-reductions.<sup>32,33</sup> Indirect synthetic strategies, e.g., via rearrangements or

multicomponent couplings, have therefore also been explored.<sup>34–38</sup>

In the context of remote functionalization (Figure 1D), so far only prefunctionalized silyl ethers with distant double bonds were shown to undergo precious-metal-catalyzed (Ir, Ru, Pd) double-bond migrations to yield silyl enol ethers (Figure 1C).<sup>39,40</sup> The majority of these reports made aldehyde-derived silyl enol ethers resulting from single-bond olefin migration;<sup>41–44</sup> those examples with greater substitution (i.e., ketone-derived) were generated with non-uniform E/Z selectivities, which were highly dependent on the α-substituent.<sup>5,39,41,42</sup>

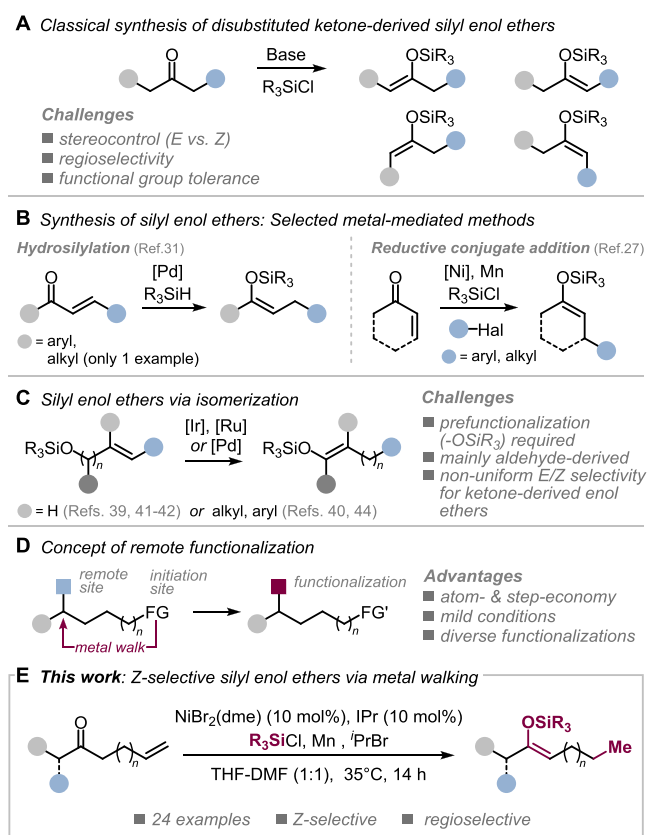
## RESULTS AND DISCUSSION

As part of our ongoing research in metal-catalyzed olefin migrations,<sup>45,46</sup> we set out to explore the possibility of developing a nonprecious Ni-catalyzed chain walking for the regio- and stereoselective functionalization of remote ketones to the corresponding silyl enol ethers (Figure 1E). Such a transformation of silyl ketone olefins requires not only the migration of a double bond and silylation but formally also a net addition of a “H”. We hypothesized that this might be possible through the generation of a [Ni–H] species whose “H” ultimately remains in the product. This in turn would require a stoichiometric amount of H-source that ensures a continuous regeneration of [Ni–H]. Alkyl bromides have

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**Figure 1.** (A) Base-mediated silyl enol ether formations; (B) metal-mediated silyl enol ether formation; (C, D) silyl enol ethers via isomerization and remote functionalization; (E) this work: remote functionalization of ketones.

previously been shown to be suited for this endeavor,<sup>9,47–49</sup> and we set out to explore suitable conditions.

To our delight, we identified that a catalytic amount of  $NiBr_2(dme)$  along with IPr (1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) ligand,  $iPrBr$ , and Mn powder allowed for the selective functionalization of ketone **1** with  $Et_3SiCl$  to yield **2** (Figures 2 and 3).

The omission of either Mn,  $Et_3SiCl$ , or  $Ni^{(II)}/IPr$  from the reaction mixture left the starting ketone **1** untouched. The employment of  $PhMe_2SiH$  instead of  $Et_3SiCl$  and  $iPrBr$  gave rise to a net reductive silylation of ketone without olefin migration.

Given nickel's propensity to form dinuclear  $Ni^{(I)}$  complexes with IPr ligands,<sup>50–52</sup> we investigated the likely speciation of the  $Ni^{(II)}$  precatalyst under these reductive conditions. Indeed, we observed that the subjection of Mn and IPr to a solution of  $NiBr_2(dme)$  in THF resulted in the formation of  $Ni^{(I)}$  dimer  $[Ni(\mu-Br)(IPr)]_2$  as the major product within 15 min at 35 °C. Our crystallization of the mixture resulted in ~91% of  $[Ni(\mu-Br)(IPr)]_2$  (green crystals) along with minor amounts of  $NiBr_2(IPr)_2$  (red crystals; ~9%) (see Figure 2A).<sup>53</sup> In line with these observations and suggesting that the initial reduction to  $Ni^{(I)}$  is mechanistically critical, we found that an initial premixing of  $NiBr_2(dme)$ , IPr, and Mn in THF for 15 min prior to the addition of the substrate and remaining reagents led to optimal conversion to the products. For example, **2** was formed in 89% yield and high Z-selectivity (Z:E 96:4, shown in Figure 3), while it formed in only 60% yield without premixing. Moreover, when we used

the dimer  $[Ni(\mu-Br)(IPr)]_2$  as (pre)catalyst instead of  $Ni^{(II)}/IPr$  under otherwise identical conditions, product **2** was obtained with the same yield (89%).

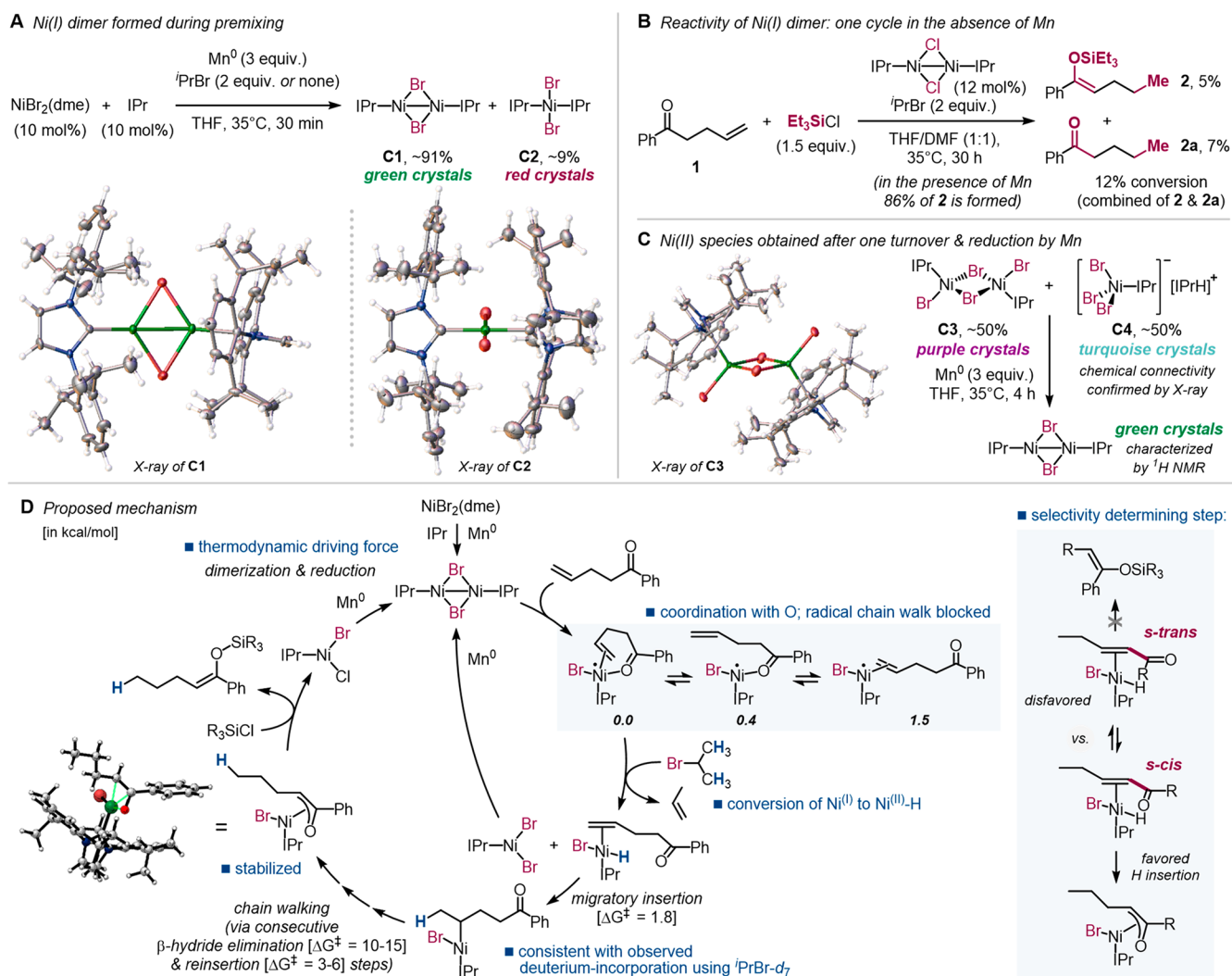
In the absence of Mn, but otherwise unaltered reaction conditions with 12 mol %  $Ni^{(I)}$  dimer, a combined yield of 12% of product **2** and its desilylated form **2a** is generated (see Figure 2B, details in SI), which indicates that one cycle per nickel dimer was undergone and that the role of Mn is likely primarily to regenerate the  $Ni^{(I)}$  dimer. To examine this further, we analyzed the resulting Ni species that is formed in the reaction under  $Ni^{(I)}$  dimer catalysis in the absence of Mn (Figure 2B) by crystallization of the resulting reaction mixture. X-ray crystallographic analysis indicated that two  $Ni^{(II)}$  species had formed: the dimeric  $[Ni(\mu-Br)(Br)(IPr)]_2$  (purple crystals; ~50%) and monomeric  $[NiBr_3(IPr)]$  (turquoise crystals; ~50%) (Figure 2C). However, the latter monomeric  $Ni^{(II)}$  salt potentially forms from fragmentation of the  $Ni^{(II)}$  dimer in solution. By analogy,  $[FeCl_3(SIPr)]$ - $[SIPrH]$  salts have been shown to form from  $[Fe(\mu-Cl)(Cl)(SIPr)]_2$ .<sup>54</sup> We further discovered that the subsequent subjection of Mn (3 equiv) to this mixture of  $Ni^{(II)}$  species in THF gives rise to the formation of the  $Ni^{(I)}$  dimer  $[Ni(\mu-Br)(IPr)]_2$ , as judged by  $^1H$  NMR analysis (Figure 2C). These data indicate that the  $Ni^{(I)}$  dimer is a key species in this transformation. The role of Mn is to regenerate the  $Ni^{(I)}$  dimer after each cycle.

Research in the field of dinuclear metal complexes of oxidation state I with palladium has shown that the precise catalytic role and mechanistic involvement of such dinuclear metal complexes is highly dependent on the type of transformation, the reaction conditions, and especially the additives that are present.<sup>55</sup> In this context, we previously showed that a  $Ni^{(I)}$  dimer can give rise to  $Ni^{(I)}$  metalloradical reactivity with olefins.<sup>45</sup> However, our previous work also indicated that ketones would—if not blocked by a Lewis acid—inhibit such radical reactivity.<sup>45</sup> As such, the radical species may also be converted to an alternative species, if suitable reagents are present in the mixture. In this context, the alkyl bromide likely funnels the “inhibited”  $Ni^{(I)}$  metalloradical to a  $[Ni^{(II)}-H]$ ,<sup>9,47–49</sup> as illustrated in Figure 2D. In line with this proposal, the employment of fully deuterated  $iPrBr$  gave rise to deuterium incorporation at the terminal site, which is consistent with the initial addition of a  $[Ni^{(II)}-D]$  species (see SI for details). Ultimately, upon chain walking, a stabilized  $\eta^3$ -bound enolate is formed.

Our computational studies<sup>57,58</sup> suggest that the  $\eta^3$ -coordination is likely the origin of positional selectivity and stereoselectivity, as it fixes the enol geometry and impedes further chain walking (see Figure 2D). After silylation the formed  $Ni^{(II)}$  is reduced with Mn to (re)form the  $Ni^{(I)}$  dimer.

With the mechanism identified, we subsequently explored the scope of the transformation (Figure 3) using conditions that allow using commercially available catalyst components, i.e., those that start from  $Ni^{(II)}$ , and that efficiently generate the  $Ni^{(I)}$  dimer *in situ* after prestirring.

We reacted our model substrate **1** with different chlorosilane sources, which gave the corresponding silyl enol ethers ( $-OSiMe_3$  (**3**),  $-OSi(iPr)Me_2$  (**4**)) in good yields and excellent Z-selectivities, indicating that different silyl chloride sources are equally efficient in the transformation. With this in mind, we subsequently evaluated the functional group tolerance using  $Et_3SiCl$ . We studied various



**Figure 2.** (A) Formation of Ni(I) dimer, (B) reactivity in the absence of Mn, (C) re-formation of the Ni(I) dimer, (D) proposed mechanism. Free energies calculated at SMD (THF) M06L/def2-TZVP// $\omega$ B97XD/6-31G(d)(SDD for Ni) in kcal/mol.<sup>21</sup> IPr refers to 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene.

aromatic as well as aliphatic ketones with different chain lengths (up to four-carbon).

We found that electron-rich aromatic (*p*-OMe (5), *p*-N(Me)<sub>2</sub> (6), *m*-CH<sub>3</sub> (9)) as well as electron-deficient (*p*-Cl (7), *m*-CF<sub>3</sub> (10)) aromatic ketones reacted equally efficiently. Similarly, biphenyl (11) and polyaromatic ketones (naphthalene (12) or anthracene (13)) as well as heterocyclic examples (1,3-benzodioxole (14), furan (15), or indole (16)) were converted to the corresponding silyl enol ethers in high yields.<sup>59</sup> Nonaromatic acyclic ketones were equally effective (17), tolerating even a bulky adamantyl group (18). Notable in this context is the selective formation of silyl enol ether 19, for which no further isomerization to the thermodynamically favored, alternative conjugated silyl enol ether was observed.

Beyond these two-carbon chain walks, three- or four-carbon chain walks were similarly efficient, although four-carbon walks needed longer reaction times (48 h). Products 20 and 21, which possess a diphenyl acetyl group, were obtained exclusively after three-carbon chain walking without further isomerization to the conjugated enol (21). Notably, a methyl group could be tolerated along the walk (23), and once again fully regio- and stereoselective formation of the

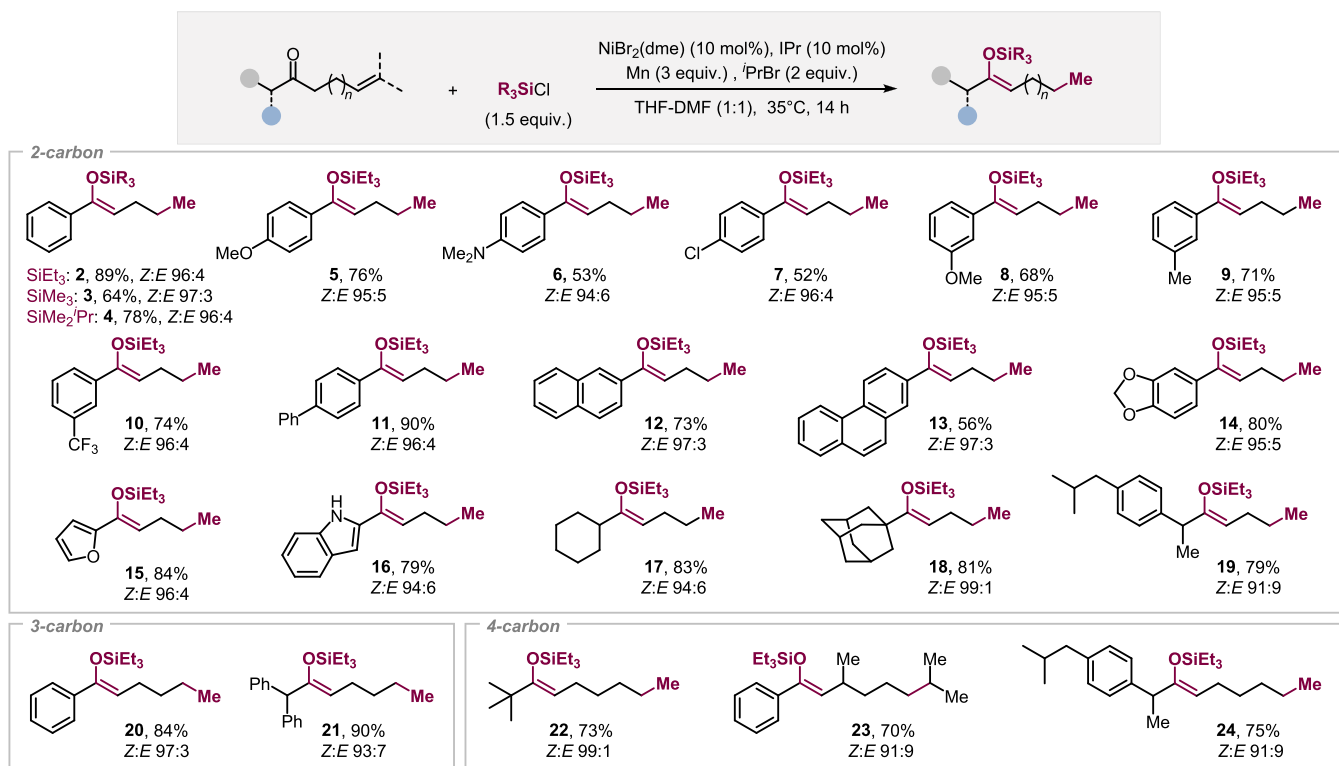
silyl enol ether was observed, which is especially notable for product 24, where a rather acidic benzylic proton is present (Figure 3).

We also tested the feasibility of using an internal rather than a terminal alkene as a starting material (Figure 4). An internal alkene (*Z*:*E* 5:95) separated from the ketone by a two-carbon chain afforded product 20 efficiently. Also using a 50:50 mixture of terminal and internal alkene isomers in a three- and two-carbon distance from the ketone, respectively, led to the same product (20) in high yield. The analogous reaction outcome was observed for the aliphatic analogue 25 and also in the case of 26, for which the starting olefin was stabilized by conjugation. Lastly, formation of the corresponding cyclic silyl enol ethers was also possible (27, 28). Given the sterically and electronically similar substituents of the ketones, the selective formation of 28 showcases that the positional selectivity is dictated solely by the directionality of the chain walk.

## CONCLUSION

In conclusion, the first remote functionalization of ketones has been developed, which enabled the regio- and stereo-





**Figure 3.** Scope of the reaction.<sup>56</sup> Method A: Premix NiBr<sub>2</sub>dme (10 mol %), IPr (10 mol %), <sup>i</sup>PrBr (2 equiv), and Mn (3 equiv) in THF (1.0 M) for 15 min. Method B: Without premixing, add [Ni( $\mu$ -Br)(IPr)]<sub>2</sub> (5 mol %), Mn (3 equiv), <sup>i</sup>PrBr (2 equiv), and THF (1.0 M) in a vial; then add ketone (1.0 equiv) in DMF (1.0 M) and chlorosilane (1.5 equiv). Substrates 7, 19, 22, and 24 were synthesized using method B; all other substrates were synthesized using method A. The reaction was carried out in a glovebox, based on a 0.3 mmol scale unless otherwise stated (see SI). Isolated yields. Z:E ratios are based on GC-MS analysis.

selective synthesis of Z-silyl enol ethers in high yields via Ni-catalyzed chain walking. The methodology is operationally simple and compatible with aliphatic as well as (hetero)-aromatic ketones and is independent of the employed silyl chloride or the distal olefin (terminal or E/Z internal). Mechanistic studies indicate the formation of a Ni<sup>(I)</sup> dimer as a key intermediate, which ultimately converts to a Ni<sup>(II)</sup>-H upon reaction with an alkyl bromide and undergoes the chain walk.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c01797>.

Experimental details, characterization data of compounds, crystallographic data, and computational details (PDF)

### Accession Codes

CCDC 2009557–2009560 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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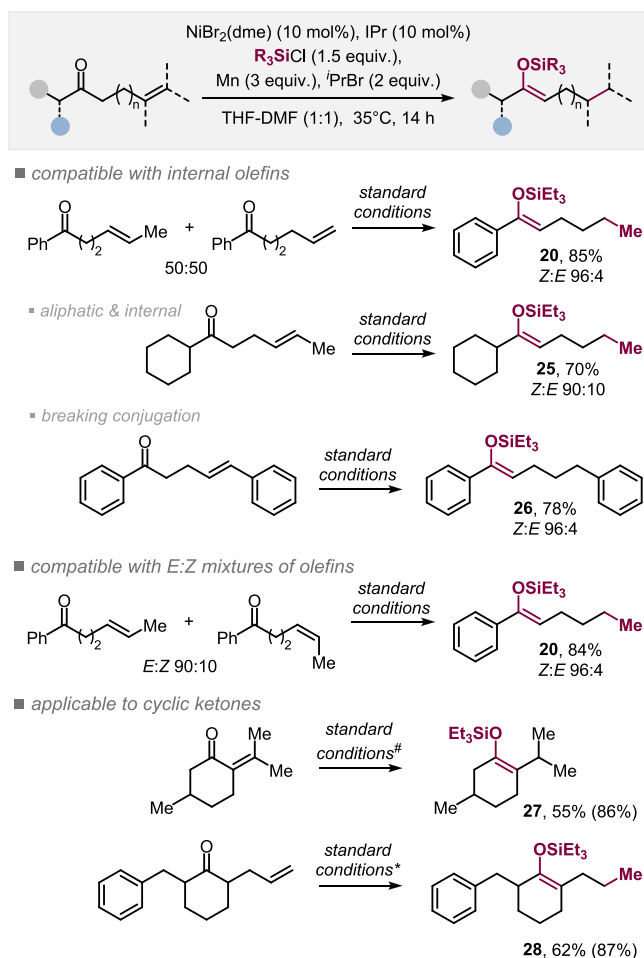
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## Notes

The authors declare no competing financial interest.

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**Figure 4.** Compatibility of the method with internal olefins, E:Z mixtures, and cyclic ketones. Isolated yields are given ( $^1\text{H}$  NMR yields vs internal standard in parentheses). Z:E ratios are based on GC-MS analysis<sup>56</sup> (\*3 h reaction time; <sup>#</sup>92% purity of starting material).

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