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(Z)-Selective Enol Triflation of α-Alkoxyacetoaldehydes: Application to Synthesis of (Z)-Allylic Alcohols via Cross-Coupling Reaction and [1,2]-Wittig Rearrangement

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ABSTRACT: The stereoselective transformation of α-alkoxyacetoaldehydes to the corresponding (Z)-vinyl triflates was achieved by treatment with phenyl triflimide and DBU. The stereochemistry was explained by the “syn-effect,” which was attributed primarily to an σ→π* interaction. The β-alkoxy vinyl triflates obtained were applied to the stereoselective synthesis of structurally diverse (Z)-allylic alcohols via transition metal-catalyzed cross-coupling reaction and [1,2]-Wittig rearrangement.

INTRODUCTION
Stereoselective synthesis of alkenes has been studied extensively. The (Z)-alkenes, especially, are versatile two-carbon units present in many biologically active compounds and are useful starting materials for chemical transformations, although their preparation is usually more difficult than that for the E-isomers. One reason is that (Z)-alkenes are generally thermodynamically less stable.1
Cross-coupling reaction is quite useful method to prepare alkenes stereospecifically from the corresponding vinyl halides. Vinyl triflates have been also used as synthetic intermediates toward transition metal-mediated cross-coupling reactions in addition to vinyl cation and alkylidene carbene precursors.\textsuperscript{2,3,4} For cross-coupling reactions, stereoselective preparation of (Z)-vinyl triflates is essential for the subsequent transformation to (Z)-alkenes. For 1,3 dicarbonyl compounds, Z-selective preparation of vinyl triflates was achieved.\textsuperscript{2d,5} Chelation-controlled preparation of (Z)-vinyl triflates from \(\alpha\)-alkoxy ketones also has been reported.\textsuperscript{6} Recently, Cu-catalyzed electrophilic vinyl triflation of alkynes was reported to afford (Z)-triflates.\textsuperscript{7} For preparation of vinyl triflates from aldehydes, a mixture of (Z)- and (E)-vinyl triflates was formed through the use of triflic anhydride (Tf\(_2\)O) and 4-methyl-2,6-(di-\(t\)-butyl)pyridine (DTBMP).\textsuperscript{8} Alternatively, trimethylsilyl enol ethers could be converted to vinyl triflates by treatment with methyllithium and Tf\(_2\)O,\textsuperscript{9} however, (Z)-selective preparation of trimethylsilyl enol ethers from an aldehyde is then an issue.\textsuperscript{10}

Previously, a series of isomerization reactions and elimination reactions using a base were performed to investigate the stereochemistry of the isomerized and eliminated products. The results showed that sterically unfavorable (Z)-alkenes were formed predominantly. These results were explained by the action of a “\textit{syn-effect},”\textsuperscript{11} caused primarily by \(\sigma\rightarrow\pi^*\) interactions.\textsuperscript{12,13} Oxygen-substituted substrates always produced excellent Z-selectivities. For example, conformation \(T_1\) was preferred to conformation \(T_2\) during deprotonation of \(\alpha\)-alkoxyacetoaldehyde due to the low donor ability of the C-O bond compared with the C-H bond, affording the corresponding (Z)-vinyl ethers predominantly as shown in Scheme 1.\textsuperscript{12b}

\textbf{Scheme 1. Transition State Model for Deprotonation of \(\alpha\)-Alkoxyacetalddehydes in the Presence of Triisopropylsilyl Triflate (\(E = \textit{i}-\text{Pr}_3\text{Si}, X = \text{OTf}\))}\textsuperscript{12b}
Furthermore, [1,2]-Wittig rearrangement\textsuperscript{14} of the resulting (Z)-vinyl ethers proceeded after the initial 1,4-eliminative ring opening reaction of vinyl oxiranes and 1,4-elimination of allylic sulfones and allylic benzoates to give (2Z)-2,4-pentadien-1-ol derivatives in a highly stereoselective manner (Scheme 2).\textsuperscript{12c,12e,12f} These results demonstrate that the greatest Z-selectivity based on the “syn-effect” for oxygen-substituted substrates could be applied to stereoselective C–C bond formation.

**Scheme 2. Previous Example of Stereoselective Transformation by the Combination of “Syn-Effect” and [1,2]-Wittig Rearrangement**\textsuperscript{12f}

Investigation of isomerization reactions revealed that \(\alpha\)-alkoxyacetoaldehydes were converted to the corresponding (Z)-\(\beta\)-alkoxy silyl enol ethers with excellent Z-selectivity.\textsuperscript{12b,15} Thus, a (Z)-\(\beta\)-alkoxy vinyl triflate could be prepared if the enolate is trapped by a triflic-cationic species instead of a silyl cation. In addition, the resulting (Z)-vinyl triflate should be accompanied by sequential stereoselective C–C bond formation via cross-coupling reaction in combination with [1,2]-Wittig rearrangement (Scheme 3). The present report describes the stereoselective enol triflation of \(\alpha\)-alkoxyacetoaldehydes, followed by cross-coupling reaction and [1,2]-Wittig rearrangement to afford various (Z)-allylic alcohols stereoselectively.

**Scheme 3. Strategy toward Synthesis of (Z)-Allylic Alcohols**

**RESULTS AND DISCUSSION**

First, the enol triflation reaction of (\(\alpha\)-benzyloxy)acetoaldehyde (1A) using triflic anhydride (\(\text{TF}_2\text{O}\)) (1.2 equiv) and 2,6-di-tert-butyl-4-methylpyridine (DTBMP) was conducted in \(\text{CH}_2\text{Cl}_2\) under reflux conditions for 2 d.\textsuperscript{8c} However, very little of the desired vinyl triflate was obtained, while 48% of 1A
was recovered (Table 1, Entry 1). The desired vinyl triflate also was not obtained when DBU (2.0 equiv) was used as the base in CH₂Cl₂ at rt (Entry 2). When phenyl triflimide (PhNTf₂) was used instead of Tf₂O,¹⁶ the reaction proceeded rapidly. The stereoselectivity of the resulting vinyl triflate was high ($Z/E = 95/5$) (Entry 3). DBU was chosen as the base because no reaction occurred using other bases such as DTBMP and Et₃N. Other $\beta$-benzyloxy-type vinyl triflates 2B-2D were also obtained stereoselectively from the corresponding $\alpha$-alkoxyacetoaldehydes 1B-1D (Entries 4–6). Furthermore, $\alpha$-(propargyloxy)acetoaldehyde 1E could be stereoselectively transformed into the corresponding vinyl triflate 2E stereoselectively (Entry 7); using 2.5 equiv of DBU improved the chemical yield (Entry 8).

**Table 1. Enol Triflation of $\alpha$-Alkoxyacetoaldehydes 1**

<table>
<thead>
<tr>
<th>Entry</th>
<th>$R^1$</th>
<th>triflating reagent</th>
<th>base</th>
<th>Time</th>
<th>Yield/%</th>
<th>$Z/E^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>A Tf₂O</td>
<td>DTBMP</td>
<td>2 d</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Tf₂O</td>
<td>DBU</td>
<td>12 h</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>PhNTf₂</td>
<td>DBU</td>
<td>10 min</td>
<td>84</td>
<td>95/5</td>
</tr>
<tr>
<td>4</td>
<td>2-MeC₆H₄</td>
<td>B PhNTf₂</td>
<td>DBU</td>
<td>10 min</td>
<td>84</td>
<td>95/5</td>
</tr>
<tr>
<td>5</td>
<td>4-(MeO)C₆H₄</td>
<td>C PhNTf₂</td>
<td>DBU</td>
<td>10 min</td>
<td>82</td>
<td>95/5</td>
</tr>
<tr>
<td>6</td>
<td>4-ClC₆H₄</td>
<td>D PhNTf₂</td>
<td>DBU</td>
<td>10 min</td>
<td>88</td>
<td>94/6</td>
</tr>
<tr>
<td>7</td>
<td>$i$-Pr₃SiC≡C</td>
<td>E PhNTf₂</td>
<td>DBU</td>
<td>10 min</td>
<td>37</td>
<td>92/8</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>PhNTf₂</td>
<td>DBU</td>
<td>10 min</td>
<td>71</td>
<td>95/5</td>
</tr>
</tbody>
</table>

$^a$The ratios were determined by 400 MHz $^1$H NMR spectra.

$^b$DTBMP (1.2 equiv) under CH₂Cl₂ reflux.

$^c$DBU (2.5 equiv).

Next, the cross-coupling reaction was investigated using (Z)-$\beta$-alkoxy vinyl triflate 2. Introduction of a phenyl group was accomplished via Suzuki-Miyaura coupling with PhB(OH)₂ and using Pd(PPh₃)₄ as a catalyst¹⁷ to give the $\beta$-alkoxy styrenes with retention of $Z$-stereochemistry as shown in Table 2.
Table 2. Coupling Reactions of Vinyl Triflates 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>2 (Z/E)ᵃ</th>
<th>Time</th>
<th>3</th>
<th>Yield/%</th>
<th>Z/Eᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵇ</td>
<td>Ph</td>
<td>A (94/6)</td>
<td>40 min</td>
<td>Aa</td>
<td>69</td>
<td>95/5</td>
</tr>
<tr>
<td>2</td>
<td>2-MeC₆H₄</td>
<td>B (94/6)</td>
<td>30 min</td>
<td>Ba</td>
<td>49</td>
<td>93/7</td>
</tr>
<tr>
<td>3</td>
<td>4-MeOC₆H₄</td>
<td>C (94/6)</td>
<td>1 h</td>
<td>Ca</td>
<td>74</td>
<td>95/5</td>
</tr>
<tr>
<td>4</td>
<td>4-ClC₆H₄</td>
<td>D (97/3)</td>
<td>20 min</td>
<td>Da</td>
<td>65</td>
<td>95/5</td>
</tr>
<tr>
<td>5ᶜ</td>
<td>i-Pr₃SiC≡C</td>
<td>E (95/5)</td>
<td>45 min</td>
<td>Ea</td>
<td>79</td>
<td>97/3</td>
</tr>
</tbody>
</table>

ᵃThe ratios were determined by 400 MHz ¹H NMR spectra.
ᵇPd(PPh₃)₄ (0.03 equiv).
ᶜPd(PPh₃)₄ (0.10 equiv) at a reaction temperature of 60 °C.

Suzuki-Miyaura coupling reaction of vinylic borane compounds generated in situ was performed as shown in Eq. 1.¹⁸ The diene 3Ab was obtained with nearly full retention of stereochemistry.¹⁹

Sonogashira coupling was also examined (Table 3).²⁰ 3,3-Dimethyl-1-butylene was used as a substrate for the transformation to give Z-enynes 3Ac and 3Ec in high chemical yield with high stereoselectivity.
Table 3. Sonogashira Coupling Reaction of Vinyl Triflates 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>2 (Z/E)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Time</th>
<th>3 Yield/%</th>
<th>Z/E&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>A (95/5)</td>
<td>20 min</td>
<td>Ac</td>
<td>88 95/5</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>i-Pr&lt;sub&gt;3&lt;/sub&gt;Si=C≡C</td>
<td>E (95/5)</td>
<td>1 h</td>
<td>Ec</td>
<td>98 96/4</td>
</tr>
</tbody>
</table>

<sup>a</sup>The ratios were determined by 400 MHz <sup>1</sup>H NMR spectra.

<sup>b</sup>i,3,3-Dimethyl-1-butyne (2 equiv); CuI (0.1 equiv).

Next, an alkyl group was introduced via alkyl boron reagent generated in situ from styrene and 9-BBN.<sup>21</sup> However, the reaction was sluggish and a mixture of the desired product, benzyl vinyl ether, and inseparable byproducts was obtained in poor yield. After intensive investigation, Kumada-Tamao-Corriu coupling reaction of 2A using n-BuMgCl in the presence of NiCl<sub>2</sub>(dppp)<sup>22</sup> resulted in the addition of a primary alkyl group. Although slight isomerization was observed, the corresponding vinyl ether 3Ad was obtained with high Z-selectivity (Table 4, Entry 1). In contrast, the coupling reaction of propargyloxy triflate 1E underwent extensive isomerization to give a ca. 2/1 mixture of 3Ed (Entry 2).

Table 4. Introduction of an Alkyl Group via Kumada-Tamao-Corriu Coupling

<table>
<thead>
<tr>
<th>Entry</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>2 (Z/E)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Time</th>
<th>3 Yield/%</th>
<th>Z/E&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>A (94/6)</td>
<td>15 min</td>
<td>Ad</td>
<td>81 91/9</td>
</tr>
<tr>
<td>2</td>
<td>i-Pr&lt;sub&gt;3&lt;/sub&gt;Si=C≡C</td>
<td>E (95/5)</td>
<td>2 h</td>
<td>Ed</td>
<td>38 68/32</td>
</tr>
</tbody>
</table>

<sup>a</sup>The ratios were determined by 400 MHz <sup>1</sup>H NMR spectra.

After establishing a procedure for addition of substituents via cross-coupling reaction of vinyl triflates 2, the [1,2]-Wittig rearrangement of vinyl ethers 3 was investigated. For benzyl-type ethereal substrates 3Aa, 3Ba, 3Da, 3Ab, and 3Ac the rearrangement proceeded to give the
corresponding (Z)-allylic alcohols stereoselectively (Table 5, Entries 1, 2, 4, 6, and 7). In the case of (4-methoxyphenyl)methyl ether 3Ca, a specific reaction conditions were required. When the 3Ca was treated with n-BuLi (3.0 equiv) in THF, the rearrangement did not proceed cleanly and yielded the allylic alcohol 4Ca in low yield of 19% with 92/8 selectivity. By the addition of N,N,N',N’-tetraethylenediamine (TMEDA) using an excess amount of n-BuLi, 4Ca was obtained in enhanced chemical yield (Entry 3). Although the reaction of propargylic ethers 3Ea and 3Ec provided rearranged alcohols at slightly lower chemical yields, excellent Z-stereoselectivity was realized (Entries 5 and 8). Using a vinyl ether with a primary alkyl group at the β-position, treatment with n-BuLi gave a complex mixture. In this case, the addition of TMEDA using an excess amount of n-BuLi was also effective to realize the rearrangement affording (Z)-allylic alcohol 4Ad in good chemical yield (Entry 9).

Table 5. [1,2]-Wittig rearrangement of vinyl ethers 3 to allylic alcohols 4

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>R²</th>
<th>3 (Z/E)a</th>
<th>Time</th>
<th>Yield/%</th>
<th>Z/Ea</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Ph</td>
<td>Aa (95/5)</td>
<td>15 min</td>
<td>86</td>
<td>98/2</td>
</tr>
<tr>
<td>2</td>
<td>2-MeC₆H₄</td>
<td>Ph</td>
<td>Ba (&gt;98/2)</td>
<td>4 min</td>
<td>54</td>
<td>&gt;98/2</td>
</tr>
<tr>
<td>3b,c</td>
<td>4-MeOC₆H₄</td>
<td>Ph</td>
<td>Ca (95/5)</td>
<td>10 min</td>
<td>47</td>
<td>97/3</td>
</tr>
<tr>
<td>4</td>
<td>4-ClC₆H₄</td>
<td>Ph</td>
<td>Da (96/4)</td>
<td>4 min</td>
<td>63</td>
<td>97/3</td>
</tr>
<tr>
<td>5</td>
<td>i-Pr₃SiC≡C</td>
<td>Ph</td>
<td>Ea (&gt;98/2)</td>
<td>4 min</td>
<td>56</td>
<td>&gt;98/2</td>
</tr>
<tr>
<td>6</td>
<td>Ph</td>
<td>t-BuCH=CH</td>
<td>Ab (87/13)</td>
<td>4 min</td>
<td>85</td>
<td>95/5</td>
</tr>
<tr>
<td>7</td>
<td>Ph</td>
<td>t-BuC≡C</td>
<td>Ac (93/7)</td>
<td>3 min</td>
<td>49</td>
<td>93/7</td>
</tr>
<tr>
<td>8</td>
<td>i-Pr₃SiC≡C</td>
<td>t-BuC≡C</td>
<td>Ec (96/4)</td>
<td>4 min</td>
<td>31</td>
<td>&gt;98/2</td>
</tr>
<tr>
<td>9b,c</td>
<td>Ph</td>
<td>n-Bu</td>
<td>Ad (91/9)</td>
<td>10 min</td>
<td>81</td>
<td>89/11</td>
</tr>
</tbody>
</table>

aThe ratios were determined by 400 MHz ¹H NMR spectra. 
b n-BuLi (8 equiv) and TMEDA (1 equiv) were added. 
cTemperature was adjusted from –78 °C to rt over 10 min. 
dRatio of (1Z,3E)-isomer/other isomers was 87/13.
In summary, a useful synthetic scheme for (Z)-allylic alcohols was established based on the novel (Z)-selective vinyl-triflation of α-alkoxyacetoaldehydes followed by cross-coupling and [1,2]-Wittig rearrangement. This synthetic scheme allowed the preparation of a wide array of structurally diverse (Z)-allylic alcohols in a stereoselective manner. These (Z)-allylic alcohols are versatile synthetic intermediates for stereospecific transformations such as Katsuki-Sharpless and related epoxidations and Simmons-Smith cyclopropanation. The synthetic method presented here can be used in place of the technique using (Z)-allylic alcohols with triple bonds, which could not be prepared by conventional Lindlar reduction of diynols.

**EXPERIMENTAL SECTION**

**General Method.** $^1$H NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts $\delta$ are reported in ppm using TMS as an internal standard. Data are reported as follows: chemical shift, multiplicity ($s =$ singlet, $d =$ doublet, $t =$ triplet, $q =$ quartet, $m =$ multiplet), coupling constant ($J$) and integration. $^{13}$C NMR spectra were recorded on a 100 MHz NMR spectrometer. The chemical shifts are reported relative to CDCl$_3$ ($\delta = 77.0$ ppm). The wavenumbers of maximum absorption peaks in IR spectra are presented in cm$^{-1}$. HRMS (EI positive, ESI-TOF) spectra were measured with quadrupole and TOF mass spectrometers. All of the melting points were measured with a micro melting point apparatus. THF was freshly distilled from sodium diphenylketyl. CH$_2$Cl$_2$ was distilled and stored over drying agents. Anhydrous CH$_3$CN was purchased and stored over drying agents.

**2-((2-Methylbenzyl)oxy)ethanol.** To a suspension of NaH (2.4 g, 60% in mineral oil, 60 mmol) in THF (160 mL) was added ethylene glycol (10.0 mL, 180 mmol) in THF (40 mL) at 0 °C under N$_2$ atmosphere. After 30 min of stirring, 1-(chloromethyl)-2-methylbenzene (9.66 g 60 mmol) in THF (40 mL) and $n$-Bu$_4$NI (1.11 g, 1.2 mmol) were added, and the mixture was refluxed for 1 d. Water was added and aqueous layer was separated and extracted with Et$_2$O. The combined organic extracts were washed with brine, dried over Na$_2$SO$_4$ and solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 3/1) to give 2-((2-methylbenzyl)oxy)ethanol (7.08 g, 64%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$): 2.24 (s, 3H), 2.42 (brs, 2H), 3.46–3.49 (m, 2H), 3.62 (dd, $J = 9.2$, 5.5 Hz, 1H), 4.44 (s, 2H), 7.05–
7.14 (m, 3H), 7.19–7.22 (m, 1H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 18.7, 61.7, 71.4, 71.5, 125.7, 127.9, 128.6, 130.2, 135.7, 136.6. IR (neat): 3421, 2865, 1459, 1355, 1102, 893, 745 cm\(^{-1}\). HRMS (ESI-TOF): calcld for C\(_{10}\)H\(_{14}\)O\(_2\)Na [(M+Na\(^+\)] 189.0891, found 189.0887.

2-((2-Methylbenzyl)oxy)acetaldehyde (1B). To a solution of oxalyl chloride (1.27 mL, 15 mmol) in CH\(_2\)Cl\(_2\) (50 mL) was added DMSO (1.42 ml, 20 mmol) in CH\(_2\)Cl\(_2\) (3 mL) at –78 °C. After 5 min of stirring, 2-((2-methylbenzyl)oxy)ethanol (1.66 g, 10 mmol) in CH\(_2\)Cl\(_2\) (3 mL) was added dropwise. After 15 min, the reaction mixture was added Et\(_3\)N (7.0 mL, 50 mmol) and allowed to warm to rt. After 1 h of stirring, the insoluble substrate in the reaction mixture was filtered off through a bed of Celite and solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/AcOEt = 3/1) to give 1B (1.16 g, 71%) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 2.28 (s, 3H), 4.00 (d, \(J = 0.9\) Hz, 2H), 4.54 (s, 2H), 7.06–7.17 (m, 3H), 7.20–7.23 (m, 1H), 9.61 (t, \(J = 0.9\) Hz, 1H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 18.7, 71.9, 75.2, 125.8, 128.3, 128.9, 130.4, 134.7, 136, 9, 200.5. IR (neat): 3029, 2867, 1736, 1492, 1460, 1376, 1104, 746 cm\(^{-1}\). HRMS (ESI-TOF): calcld for C\(_{10}\)H\(_{12}\)O\(_2\)Na [(M+Na\(^+\)] 187.0735, found 187.0740.

In a similar manner, 2-alkoxyacetoaldehyde 1A,\(^{26}\) 1C,\(^{27}\) and 1D\(^{28}\) were prepared from ethylene glycol.

**Ethyl 2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)acetate.** To a solution of 3-(triisopropylsilyl)prop-2-yn-1-ol\(^{29}\) (3.19 g, 15 mmol) and HMPA (10.4 mL, 60 mmol) in THF (15 mL) was added MeMgBr (15 mL of 1.0 M solution in THF, 15 mmol) dropwise at 0 °C under N\(_2\) atmosphere. After 10 min of stirring, ethyl bromoacetate (2.51 g, 15 mmol) in THF (5 mL) was added, and the resulting solution was warmed 50 °C, and stirred for 1 h. The reaction mixture was quenched with a satd aq solution of NaHCO\(_3\) (5 mL). After insoluble substance was filtered off through a bed of Celite, the organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 20/1) to give ethyl 2-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)acetate (1.92 g, 49 %) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.00 (s, 21H), 1.23 (t, \(J = 6.8\) Hz, 3H), 4.16 (s, 2H), 4.17 (q, \(J = 6.8\) Hz, 2H), 4.29 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 11.0, 14.1, 18.5, 58.9, 60.9, 65.7, 89.1, 101.7, 170.0. IR (neat): 2944, 2865, 2171, 1754, 1463, 1204, 1121, 1000, 883, 677 cm\(^{-1}\). HRMS (EI): calcld for C\(_{16}\)H\(_{30}\)O\(_3\)Si [M\(^+\)] 298.1964, found 298.1981.
2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)acetaldehyde (1E). To a solution of ethyl 2-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)acetate (1.92 g, 7.4 mmol) in toluene (50 mL) was added DIBAL-H (7.4 mL of 1.0 M solution in toluene, 7.4 mmol) dropwise over 5 min at –78 °C under N₂ atmosphere. After 5 min, MeOH (7 mL) was added and the reaction mixture was warmed to room temperature. A satd aq solution of potassium sodium tartrate was added and the resulting mixture was stirred for 3 h. After insoluble substance was filtered off through a bed of Celite, the aqueous layer was separated and extracted with Et₂O. The combined organic extracts were washed with brine and dried over Na₂SO₄ and the solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 6/1) to give 1E (1.00 g, 53 %) as an oil. ¹H NMR (400 MHz, CDCl₃): 1.07 (s, 21H), 4.21 (s, 2H), 4.35 (s, 2H), 9.77 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): 11.0, 18.5, 59.5, 74.3, 89.5, 101.6, 200.1. IR (neat): 2943, 2891, 2865, 2716, 1739, 1463, 1382, 1366, 1242, 1114, 1009, 883, 678 cm⁻¹. HRMS (EI): calcd for C₁₄H₂₆O₂Si [M⁺] 254.1702, found: 254.1706.

(Z)-2-(Benzyloxy)vinyl Trifluoromethanesulfonate (2A). To a solution of 1A (597 mg, 4.0 mmol) in CH₂Cl₂ (35 mL), DBU (1.21 g, 8.0 mmol) in CH₂Cl₂ (5 mL) and PhNTf₂ (1.71 g, 4.8 mmol) in CH₂Cl₂ (10 mL) were added at rt under Ar atmosphere. After reaction completion (monitored by TLC), the reaction was quenched with a phosphate buffer solution (pH 7). The aqueous layer was separated and extracted with Et₂O. The combined organic extracts were washed with brine, dried over Na₂SO₄, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 6/1) to give 2A (948 mg, 84%, Z/E = 95/5 mixture from ¹H NMR) as an oil. ¹H NMR (400 MHz, CDCl₃): 4.94 (s, 2H), 6.00 (d, J = 3.2 Hz, 1H), 6.04 (d, J = 3.2 Hz, 1H), 6.27–7.42 (m, 5 H). Selected data of (E)-isomer; 4.77 (s, 2H), 6.57 (d, J = 10.1 Hz, 1H), 7.01 (d, J = 10.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 75.3, 118.6 (J = 320.7 Hz), 118.9, 123.7, 127.7, 128.7, 129.7, 138.5. IR (neat): 3134, 3067, 3035, 2938, 2883, 1684, 1497, 1421, 1211, 1141 987, 847, 698 cm⁻¹. HRMS (EI): calcd for C₁₀H₈F₃O₄S [M⁺] 282.0174, found: 282.0170.

In a similar manner, (Z)-vinyl triflates 2B–2E were obtained from 1B–1E.

(Z)-2-((2-Methylbenzyl)oxy)vinyl Trifluoromethanesulfonate (2B). Compound 2B (749 mg, 84%, Z/E = 95/5) was obtained as an oil from 1B (493 mg, 3.0 mmol), DBU (913 mg, 6.0 mmol), and PhNTf₂ (1.29 g, 3.6 mmol). ¹H NMR (400 MHz, CDCl₃): 2.36 (s, 3H), 4.95 (s, 2H), 5.99 (d, J
= 3.2 Hz, 1H), 6.05 (d, J = 3.2 Hz, 1H), 7.20–7.30 (m, 4H). Selected data of (E)-isomer; 2.33 (s, 3H), 4.77 (s, 2H), 6.60 (d, J = 10.5 Hz, 1H), 7.01 (d, J = 10.5 Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 18.7, 74.0, 118.6 (J = 320.7 Hz), 118.9, 126.0, 128.9, 129.0, 130.7, 133.4, 137.1, 138.3. IR (neat): 3136, 3025, 2956, 2890, 1683, 1421, 1352, 1221, 1141, 986, 744, 693 cm\(^{-1}\). HRMS (EI): calcd for C\(_{11}\)H\(_{11}\)F\(_3\)O\(_4\)S [M+] 296.0330, found: 296.0336.

(Z)-2-((4-Methoxybenzyl)oxy)vinyl Trifluoromethanesulfonate (2C). Compound 2C (244 mg, 82%, Z/E = 95/5) was obtained as an oil from 1C (180 mg, 1.0 mmol), DBU (304 mg, 2.0 mmol), and PhNTf\(_2\) (429 mg, 1.2 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 3.82 (s, 3H), 4.86 (s, 2H), 5.97 (d, J = 3.2 Hz, 1H), 6.03 (d, J = 3.2 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H). Selected data of (E)-isomer; 4.69 (s, 2H), 6.55 (d, J = 10.1 Hz, 1H), 6.99 (d, J = 10.1 Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 55.2, 75.1, 114.1, 118.6 (J = 320.7 Hz), 118.8, 127.6, 129.6, 138.3, 159.9. IR (neat): 3135, 3005, 2941, 2840, 1684, 1614, 1517, 1420, 1246, 1211, 1142, 825, 692 cm\(^{-1}\). HRMS (EI): calcd for C\(_{11}\)H\(_{11}\)F\(_3\)O\(_5\)S [M+] 312.0279, found: 312.0282.

(Z)-2-((4-Chlorobenzyl)oxy)vinyl Trifluoromethanesulfonate (2D). Compound 2D (139 mg, 88%, Z/E = 94/6) was obtained as an oil from 1D (92 mg, 0.5 mmol), DBU (152 mg, 1.0 mmol), and PhNTf\(_2\) (214 mg, 0.6 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 4.91 (s, 2H), 6.01 (d, J = 3.7 Hz, 1H), 6.02 (d, J = 3.7 Hz, 1H), 7.26–7.42 (m, 4H). Selected data of (E)-isomer; 4.74 (s, 3H), 6.56 (d, J = 10.1 Hz, 1H), 6.99 (d, J = 10.1 Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 74.5, 118.6 (J = 320.7 Hz), 119.2, 128.9, 129.0, 129.7, 134.0, 138.4. IR (neat): 3321, 3134, 2942, 2884, 1684, 1600, 1495, 1211, 1142, 966, 812, 693 cm\(^{-1}\). HRMS (EI): calcd for C\(_{10}\)H\(_{8}\)ClF\(_3\)O\(_4\)S [M+] 315.9784, found: 315.9786.

(Z)-2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)vinyl Trifluoromethanesulfonate (2E). Compound 2E (82 mg, 71%, Z/E = 95/5) was obtained as an oil from 1E (76 mg, 0.3 mmol), DBU (114 mg, 0.75 mmol), and PhNTf\(_2\) (129 mg, 0.36 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.07 (s, 21H), 4.55 (s, 2H), 6.10 (d, J = 3.2 Hz, 1H), 6.23 (d, J = 3.2 Hz, 1H). Selected data of (E)-isomer; 4.47 (s, 2H), 6.66 (d, J = 10.1 Hz, 1H), 6.96 (d, J = 10.1 Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 11.0, 18.4, 61.1, 91.4, 99.9, 118.7 (J = 320.7 Hz), 119.6, 136.9. IR (neat): 3137, 2946, 2868, 2170, 1685, 1425, 1245, 1117, 1045, 1009, 951, 883, 845, 706, 681 cm\(^{-1}\). HRMS (EI): calcd for C\(_{13}\)H\(_{25}\)F\(_3\)O\(_4\)SSi [M+] 386.1195, found: 386.1169.
(Z)-(2-(Benzyloxy)vinyl)benzene (3Aa). To a solution of 2A (282 mg, 1.0 mmol, Z/E = 94/6) in toluene (15 mL) and EtOH (2.5 mL) was added 2 M aq solution of Na₂CO₃ (15 mL). After Pd(PPh₃)₄ (37 mg, 0.03 mmol), and PhB(OH)₂ (156 mg, 1.3 mmol) were added, the reaction mixture was stirred at 80 °C for 30 min under Ar atmosphere. The reaction mixture was cooled to rt and insoluble substance was filtered off through a bed of Celite. The aqueous layer of the filtrate was separated and extracted with Et₂O. The combined organic extracts were washed with water and brine, dried over Na₂SO₄, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 20/1) to give 3Aa (144 mg, 69%, Z/E = 95/5) as an oil.

1H NMR (400 MHz, CDCl₃): 5.00 (s, 2H), 5.27 (d, J = 6.9 Hz, 1H), 6.29 (d, J = 6.9 Hz, 1H), 7.06–7.39 (m, 8H), 7.63 (d, J = 7.3 Hz, 2H). Selected data of (E)-isomer; 4.91 (s, 2H), 5.96 (d, J = 12.8 Hz, 1H), 7.08 (d, J =12.8 Hz, 1H). 13C NMR (100 MHz, CDCl₃): 74.9, 106.3, 125.8, 127.2, 128.0, 128.2, 128.3, 128.6, 135.8, 137.2, 146.2.

In a similar manner, (Z)-vinyl ethers 3Ba–3Ea were obtained from 2B–2E.

(Z)-1-Methyl-2-((styryloxy)methyl)benzene (3Ba). Compound 3Ba (55 mg, 49%, Z/E = 93/7) was obtained as an oil from 2B (148 mg, 0.50 mmol, Z/E = 94/6), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and PhB(OH)₂ (79 mg, 0.65 mmol). 1H NMR (400 MHz, CDCl₃): 2.38 (s, 3H), 4.99 (s, 2H), 5.26 (d, J = 7.4 Hz, 1H), 6.30 (d, J = 7.4 Hz, 1H), 7.12–7.38 (m, 7H), 7.61 (d, J = 7.4 Hz, 2H). Selected data of (E)-isomer; 2.33 (s, 3H), 4.89 (s, 2H), 5.98 (d, J = 12.8 Hz, 1H). 13C NMR (100 MHz, CDCl₃): 18.9, 73.6, 106.1, 125.7, 126.0, 128.18, 128.22, 128.27, 128.29, 130.4, 135.1, 135.9, 136.5, 146.2. IR (neat): 3024, 2927, 1650, 1493, 1447, 1365, 1265, 1120, 1086, 779, 746, 694 cm⁻¹. HRMS (EI): calcd for C₁₆H₁₆O [M⁺] 224.1201, found 224.1200.

(Z)-1-Methoxy-4-((styryloxy)methyl)benzene (3Ca). Compound 3Ca (156 mg, 74%, Z/E = 95/5) was obtained as an oil from 2C (260 mg, 0.88 mmol, Z/E = 94/6), Pd(PPh₃)₄ (51 mg, 0.04 mmol), and PhB(OH)₂ (139 mg, 1.14 mmol). 1H NMR (400 MHz, CDCl₃): 3.81 (s, 3H), 4.92 (s, 2H), 5.25 (d, J = 7.3 Hz, 1H), 6.28 (d, J = 7.3 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 7.12–7.46 (m, 5H), 7.60 (d, J = 8.7 Hz, 2H). Selected data of (E)-isomer; 3.78 (s, 3H), 4.83 (s, 2H), 5.95 (d, J = 12.8 Hz, 1H). 13C NMR (100 MHz, CDCl₃): 55.3, 74.6, 106.1, 113.9, 125.7, 128.16, 128.24, 129.0, 129.2, 135.9, 146.1, 159.5. IR (neat): 3031, 2927, 2836, 1650, 1613, 1513, 1447, 1366, 1250, 1174, 1031, 823, 780, 696 cm⁻¹. HRMS (EI): calcd for C₁₆H₁₆O₂ [M⁺] 240.1150, found 240.1143.
**(Z)-1-Chloro-4-((styryloxy)methyl)benzene (3Da).** Compound **3Da** (79 mg, 65%, Z/E = 95/5) was obtained as an oil from **2D** (190 mg, 0.60 mmol, Z/E = 97/3), Pd(PPh₃)₄ (35 mg, 0.03 mmol), and PhB(OH)₂ (95 mg, 0.78 mmol).¹H NMR (400 MHz, CDCl₃): 4.93 (s, 2H), 5.28 (d, J = 7.3 Hz, 1H), 6.23 (d, J = 7.3 Hz, 1H), 7.13–7.36 (m, 7H), 7.60 (d, J = 7.3 Hz, 2H). Selected data of (E)-isomer: 4.87 (s, 2H), 5.95 (d, J = 12.8 Hz, 1H), 7.05 (d, J = 12.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 74.1, 106.7, 125.9, 127.1, 128.2, 128.3, 128.5, 128.8, 133.8, 135.6, 145.9. IR (neat): 3085, 3031, 2928, 2972, 1651, 1600, 1492, 1447, 1403, 1365, 1266, 1200, 1088, 1014, 806, 779, 695 cm⁻¹. HRMS (EI): calcd for C₁₅H₁₃ClO [M⁺] 244.0655, found 244.0656.

**(Z)-Triisopropyl(3-(styryloxy)prop-1-yn-1-yl)silane (3Ea).** Compound **3Ea** (74 mg, 79%, 97/3) was obtained as an oil from **2E** (116 mg, 0.3 mmol, Z/E = 95/5), Pd(PPh₃)₄ (35 mg, 0.03 mmol, 10 mol%), and PhB(OH)₂ (48 mg, 0.39 mmol).¹H NMR (400 MHz, CDCl₃): 1.07 (s, 21H), 4.56 (s, 2H), 5.34 (d, J = 6.8 Hz, 1H), 6.37 (d, J = 6.8 Hz, 1H), 7.13–7.16 (m, 1H), 7.24–7.36 (m, 2H), 7.58–7.61 (m, 2H). Selected data of (E)-isomer; 4.54 (s, 2H), 5.99 (d, J = 12.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 11.1, 18.5, 60.4, 89.4, 101.8, 107.3, 125.9, 128.1, 128.4, 135.6, 144.6. IR (neat): 2942, 2864, 2725, 2174, 1652, 1493, 1462, 1450, 1356, 1274, 1086, 1034, 999, 883, 777, 693, 678, 666 cm⁻¹. HRMS (EI): calcd for C₂₀H₃₀OSi [M⁺] 314.2066, found 314.2070.

**(((1Z,3E)-5,5-Dimethylhexa-1,3-dien-1-yl)oxy)methyl)benzene (3Ab).** To a solution of 3,3-dimethyl-1-butyne (123 mg,1.5 mmol) in THF (1 mL) was added 9-BBN (3.0 mL of 0.5 M solution in THF, 1.5 mmol) and stirred 1 d.¹⁸ To the solution, 2 M aq solution of Na₂CO₃ (5 mL) and **2A** (141 mg, 0.5 mmol, Z/E = 94/6) in THF (1 mL), and Pd(PPh₃)₄ (29 mg, 0.025 mmol,) in EtOH (1 mL) were added and the reaction mixture was stirred at 80 °C for 30 min. The reaction mixture was cooled to rt and insoluble substance was filtered off through a bed of Celite. The aqueous layer of the filtrate was separated and extracted with Et₂O. The combined organic extracts were washed with water and brine, dried over Na₂SO₄, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/benzene = 1/1) to give **3Ab** (59 mg, 61%, 1Z,3/E/others = 87/13) as an oil.¹H NMR (400 MHz, CDCl₃): 1.04 (s, 9H), 4.85 (s, 2H), 5.07 (dd, J = 6.0, 11.0 Hz, 1H), 5.60 (d, J = 15.6 Hz, 1H), 5.96 (d, J = 6.0 Hz, 1H), 6.36, (dd, J = 11.0, 15.6 Hz, 1H), 7.24–7.35 (m, 5H).¹³C NMR (100 MHz, CDCl₃): 29.7, 33.2, 74.0, 108.0, 117.6, 127.4, 127.9, 128.5, 137.4, 142.7, 144.0. IR (neat): 3034, 2959, 2863, 1654, 1615, 1455, 1365, 1285, 1267, 1194, 1131, 1090, 1071, 975, 734 cm⁻¹. HRMS (EI): calcd for C₁₅H₂₀O [M⁺] 216.1514, found 216.1509.
(Z)-((5,5-Dimethylhex-1-en-3-yn-1-yl)oxy)methyl)benzene (3Ac). To a solution of Et$_3$N (252 mg, 2.5 mmol), 3,3-dimethyl-1-butyne (62 mg, 0.75 mmol) and 2A (141 mg, 0.5 mmol, Z/E = 95/5) in MeCN (1 mL) was added Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol) in MeCN (1 mL) and CuI (5 mg, 0.026 mmol) at rt under Ar atmosphere and the reaction mixture was stirred at 60 °C for 20 min. The reaction mixture was cooled to rt and insoluble substance was filtered off through a bed of Celite and solvent of the filtrate was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 10/1) to give 3Ac (94 mg, 88%, Z/E = 95/5) as an oil. $^1$H NMR (400 MHz, CDCl$_3$): 1.27 (s, 9H), 4.55 (d, $J = 6.4$ Hz, 1H), 4.97 (s, 2H), 6.29 (d, $J = 6.4$ Hz, 1H), 7.28–7.36 (m, 5H). Selected data of (E)-isomer; 1.23 (s, 9H), 4.78 (s, 2H), 5.01 (d, $J = 12.8$ Hz, 1H), 6.83 (d, $J = 12.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): 28.2, 31.1, 72.9, 74.0, 86.8, 102.1, 127.2, 127.9, 128.5, 137.0, 153.2. IR (neat): 3065, 3034, 2967, 2927, 2866, 2222, 1632, 1455, 1364, 1264, 1123, 1051, 730, 696 cm$^{-1}$. HRMS (EI): calcd for C$_{15}$H$_{18}$O [M+] 214.1358, found 214.1359.

In a similar manner, (Z)-vinyl ethers 3Ec was obtained from 2E.

(Z)-(3-((5,5-Dimethylhex-1-en-3-yn-1-yl)oxy)prop-1-yn-1-yl)triisopropylsilane (3Ec). Compound 3Ec (88 mg, 98%, Z/E = 96/4) was obtained as an oil from 2E (116 mg, 0.3 mmol, Z/E = 95/5), Et$_3$N (152 mg, 1.5 mmol), 3,3-dimethyl-1-butyne (49 mg, 0.6 mmol), Pd(PPh$_3$)$_4$ (20 mg, 0.017 mmol), and CuI (6 mg, 0.03 mmol). $^1$H NMR (400 MHz, CDCl$_3$): 1.07 (s, 21H), 1.26 (s, 9H), 4.54 (s, 2H), 4.61, (d, $J = 6.4$ Hz, 1H), 6.45 (d, $J = 6.4$ Hz, 1H). Selected data of (E)-isomer; 4.42 (s, 2H), 5.03, (d, $J = 12.8$ Hz, 1H), 6.76 (d, $J = 12.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): 11.0, 18.5, 28.2, 31.1, 60.1, 72.6, 87.4, 89.7, 101.3, 102.2, 151.5. IR (neat): 3043, 2965, 2944, 2866, 2726, 2230, 2176, 1634, 1564, 1462, 1359, 1264, 1229, 1115, 1028, 998, 883, 727, 678 cm$^{-1}$. HRMS (EI): calcd for C$_{20}$H$_{34}$OSi [M$^+$] 318.2379, found 318.2370.

(Z)-(Hex-1-en-1-yloxy)methyl)benzene (3Ad). To a solution of 2A (141 mg, 0.5 mmol, Z/E = 94/6) in toluene (3 mL), NiCl$_2$(dppp) (28 mg, 0.05 mmol) and n-BuMgCl (1.1 mL of 0.91 M solution in THF, 1.0 mmol) were added and the reaction mixture was stirred at rt for 30 min under Ar atmosphere. The reaction was quenched with a satd aq solution of NH$_4$Cl and insoluble substance was filtered off through a bed of Celite. The aqueous layer of the filtrate was separated and extracted with Et$_2$O. The combined organic extracts were washed with water and brine, dried over Na$_2$SO$_4$, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 10/1) to give 3Ad (77 mg, 81%, Z/E = 91/9) as an oil. $^1$H NMR
(400 MHz, CDCl₃): 0.87–0.91 (m, 3H), 1.25–1.37 (m, 4H), 2.09–2.15 (m, 2H), 4.39 (dt, J = 6.0, 7.3 Hz, 1H), 4.79 (s, 2H), 6.00 (dt, J = 6.0, 1.4 Hz, 1H), 7.26–7.36 (m, 5H). Selected data of (E)-isomer; 1.90–1.95 (m, 2H), 4.71 (s, 2H), 4.88 (dt, J = 12.8, 7.3 Hz, 1H), 6.32 (d, J = 12.8 Hz, 1H).

13C NMR (100 MHz, CDCl₃): 13.9, 22.3, 23.7, 31.9, 73.5, 108.0, 127.2, 127.7, 128.4, 137.8, 144.3.


In a similar manner, vinyl ethers 3Ed were obtained from 2E.

(3-(Hex-1-en-1-yloxy)prop-1-yn-1-yl)triisopropylsilane (3Ed). Compound 3Ed (44 mg, 38%, Z/E = 68/32) was obtained as an oil from 2E (77 mg, 0.2 mmol, Z/E = 95/5), NiCl₂(dppp) (11 mg, 0.02 mmol) and n-BuMgCl (0.43 mL of 0.94 M solution in THF, 0.4 mmol). 1H NMR (400 MHz, CDCl₃): 0.86–0.91 (m, 3H), 1.07 (s, 21H), 1.30–1.35 (m, 4H), 2.05–2.11 (m, 2H), 4.38 (s, 2H), 4.48 (dt, J = 6.4, 7.4 Hz, 1H), 6.06 (d, J = 6.4 Hz, 1H). Selected data of (E)-isomer; 1.89–1.95 (m, 2H), 4.37 (s, 2H), 4.92 (dt, J = 12.4, 7.4 Hz, 1H), 6.24 (d, J = 12.4 Hz, 1H). 13C NMR (100 MHz, CDCl₃): (Z)-isomer; 11.1, 13.9, 18.5, 22.3, 23.6, 31.9, 59.5, 88.3, 102.6, 109.1, 143.0; (E)-isomer; 11.1, 13.9, 18.5, 22.0, 27.3, 32.6, 57.4, 88.2, 102.3, 106.3, 144.3; IR (neat) 3035, 2943, 2865, 2175, 1666, 1617, 1463, 1382, 1353, 1274, 1134, 1092, 997, 919, 883, 731, 677 cm⁻¹. HRMS (ESI-TOF): calcd for C₁₈H₃₄OSiNa [(M+Na)+] 317.2277, found 317.2268.

(Z)-1,3-Diphenylprop-2-en-1-ol (4Aa).³¹ To a solution of 3Aa (63 mg, 0.3 mmol, Z/E = 95/5) in THF (3 mL) was added n-BuLi (0.56 mL of 1.62 M solution in hexane, 0.9 mmol) at 0 °C under Ar atmosphere and the reaction mixture was stirred at 0 °C for 10 min. The reaction was quenched with water. The aqueous layer was separated and extracted with Et₂O. The combined organic extracts were washed with brine, dried over Na₂SO₄, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 6/1) to give 4Aa (48 mg, 86%, Z/E = 98/2) as an oil. 1H NMR (400 MHz, CDCl₃): 1.97 (brs, 1H), 5.64 (d, J = 9.2 Hz, 1H), 5.94 (dd, J = 11.4, 9.2 Hz, 1H), 6.70 (d, J = 11.4 Hz, 1H), 7.26–7.47 (m, 10H). Selected data of (E)-isomer: 5.40 (d, J = 6.9 Hz 1H), 6.39 (dd, J = 16.0, 6.9 Hz, 1H). 13C NMR (100 MHz, CDCl₃): 70.0, 126.3, 127.5, 127.8, 128.3, 128.7, 128.8, 131.4, 133.2, 136.3, 143.1.

In a similar manner, (Z)-allylic alcohols 4Ba, 4Da, 4Ea, 4Ab, 4Ac, and 4Ec were obtained from the corresponding (Z)-vinyl ethers 3Ba, 3Da, 3Ea, 3Ab, 3Ac, and 3Ec, respectively.
(Z)-3-Phenyl-1-(o-tolyl)prop-2-en-1-ol (4Ba). Compound 4Ba (28 mg, 54%, Z/E = >98/2) was obtained as a solid from 3Ba (52 mg, 0.23 mmol, Z/E = >98/2) and n-BuLi (0.42 mL of 1.65 M solution in hexane, 0.69 mmol). Mp 84–86 °C (from AcOEt). ¹H NMR (400 MHz, CDCl₃): 1.89 (d, J = 4.1 Hz, 1H), 2.11 (s, 3H), 5.72 (dd, J = 4.1, 9.2 Hz, 1H), 5.89 (dd, J = 9.2, 11.4 Hz, 1H), 6.66 (d, J = 11.4 Hz, 1H), 7.13–7.37 (m, 8H), 7.58 (d, J = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 18.9, 67.6, 125.4, 126.3, 127.4, 127.6, 128.3, 128.7, 130.6, 131.5, 132.6, 135.6, 136.4, 141.5. IR (KBr): 3274, 3022, 2925, 1492, 1458, 1209, 1039, 977, 870, 770, 751 cm⁻¹. Anal. Calcd for C₁₆H₁₆O: C, 85.68; H, 7.19. Found: C, 85.59; H, 7.33.

(Z)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol (4Da). Compound 4Da (50 mg, 63%, Z/E = 97/3) was obtained as an oil from 3Da (80 mg, 0.33 mmol, Z/E = 96/4) and n-BuLi (0.61 mL of 1.65 M solution in hexane, 1.0 mmol). ¹H NMR (400 MHz, CDCl₃): 1.98 (d, J = 3.2 Hz, 1H), 5.62 (dd, J = 9.2, 3.2 Hz, 1H), 5.87 (dd, J = 11.5, 9.2 Hz, 1H), 6.71 (d, J = 11.5 Hz, 1H), 7.26–7.39 (m, 9H). Selected data of (E)-isomer; 6.33 (dd, J = 16.0, 6.8 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H). ¹³C NMR (100MHz, CDCl₃): 69.4, 127.6, 127.7, 128.4, 128.70, 128.73, 131.8, 132.7, 133.4, 136.1, 141.5. IR (neat): 3337, 3057, 3023, 2927, 1597, 1491, 1446, 1408, 1213, 1091, 1046, 1013, 867, 827, 801, 771, 701 cm⁻¹. HRMS (EI): Calcd for C₁₅H₁₃ClO [M⁺]: 244.0655. Found: 244.0652.

(Z)-1-Phenyl-5-(triisopropylsilyl)pent-1-en-4-yn-3-ol (4Ea). Compound 4Ea (40 mg, 56%, >98/2)) was obtained as an oil from 3Ea (72 mg, 0.23 mmol, >98/2)) and n-BuLi (0.42 mL of 1.65 M solution in hexane, 0.69 mmol). ¹H NMR (400 MHz, CDCl₃): 1.01 (s, 21H), 1.97 (d, J = 5.0 Hz, 1H), 5.17 (dd, J =5.0, 8.7 Hz, 1H), 5.76 (dd, J =8.7, 11.0 Hz, 1H), 6.55 (d, J =11.0 Hz, 1H), 7.22–7.30 (m, 5H). Selected data of (E)-isomer: 1.02 (s, 9H), 5.96 (dd, J = 15.6, 10.6 Hz, 1H), 6.26 (dd, J = 15.6, 11.0 Hz, 1H). ¹³C NMR (100MHz, CDCl₃): 11.1, 18.6, 59.5, 86.9, 107.3, 127.6, 128.3, 129.0, 130.9, 131.2, 136.0. IR (neat): 3343, 3059, 3025, 2942, 2864, 2170, 1494, 1462, 1383, 1026, 883, 701, 677 cm⁻¹. HRMS (EI): Calcd for C₂₀H₃₀OSi [M⁺]: 314.2066, found 314.2068.

(2Z,4E)-6,6-Dimethyl-1-phenylhepta-2,4-dien-1-ol (4Ab). Compound 4Ab (47 mg, 85%, 2Z,4E/2E,4E = 95/5) was obtained as an oil from 3Ab (55 mg, 0.25 mmol, 1Z,3E/others = 87/13) and n-BuLi (0.45 mL of 1.65 M solution in hexane, 0.75 mmol). ¹H NMR (400 MHz, CDCl₃): 1.06 (s, 9H), 1.88 (brs, 1H), 5.51 (dd, J = 10.6, 9.2 Hz, 1H), 5.72 (d, J = 9.2, Hz, 1H), 5.83 (d, J = 15.6 Hz, 1H), 6.11 (dd, J = 11.0, 10.6 Hz, 1H), 6.40 (dd, J = 15.6, 11.0 Hz, 1H), 7.26–7.42 (m, 5 H). Selected data of (E,E)-isomer: 1.02 (s, 9H), 5.96 (dd, J = 15.6, 10.6 Hz, 1H), 6.26 (dd, J = 15.6, 11.0 Hz, 1H). ¹³C NMR (100MHz, CDCl₃): 29.4, 33.5, 69.9, 119.5, 125.8, 127.4, 128.5, 130.6,
130.9, 143.4, 149.0. IR (neat): 3340, 3030, 2959, 2901, 2864, 1650, 1602, 1452, 1389, 1362, 1037, 1020, 985, 950, 743, 698 cm⁻¹. HRMS (EI): calcd for C₁₅H₂₀O [M⁺] 216.1514, found: 216.1515.

(Z)-6,6-Dimethyl-1-phenylhept-2-en-4-yn-1-ol (4Ac). Compound 4Ac (21 mg, 49%, Z/E = 93/7) was obtained as an oil from 3Ac (43 mg, 0.20 mmol, Z/E = 93/7) and n-BuLi (0.36 mL of 1.65 M solution in hexane, 0.6 mmol). ¹H NMR (400 MHz, CDCl₃): 1.29 (s, 9H), 2.18 (d, J = 3.2 Hz, 1H), 5.59 (dd, J = 10.5, 0.9 Hz, 1H), 5.79 (dd, J = 8.2, 3.2 Hz, 1H), 5.99 (J = 10.5, 8.2 Hz, 1H), 7.26–7.46 (m, 5H). Selected data of (E)-isomer: 1.22 (s, 9H), 5.22–5.24 (m, 1H), 6.19 (dd, J = 15.6, 6.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 28.2, 30.9, 72.0, 75.1, 104.8, 110.4, 125.7, 127.6, 128.5, 142.67, 142.71. IR (neat): 3342, 2968, 2928, 2866, 2213, 1602, 1493, 1475, 1453, 1362, 1266, 1036, 1003, 854, 744, 698 cm⁻¹. HRMS (EI): calcd for C₁₅H₁₈O [M⁺] 214.1358, found: 214.1355.

(Z)-8,8-Dimethyl-1-(triisopropylsilyl)nona-4-en-1,6-diyn-3-ol (4Ec). Compound 4Ec (14 mg, 31%, Z/E = >98/2) was obtained as an oil from 3Ec (45 mg, 0.15 mmol, Z/E = 96/4) and n-BuLi (0.27 mL of 1.65 M solution in hexane, 0.45 mmol). ¹H NMR (400 MHz, CDCl₃): 1.07 (s, 21H), 1.26 (s, 9H), 2.08 (d, J = 5.0 Hz, 1H), 5.37 (dd, J = 8.3, 5.0 Hz, 1H), 5.61 (dd, J = 10.6, 0.9 Hz, 1H), 5.93 (dd, J = 10.6, 8.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 28.2, 30.9, 72.0, 75.1, 104.8, 110.4, 125.7, 127.6, 128.5, 142.67, 142.71. IR (neat): 3342, 2968, 2928, 2866, 2213, 1602, 1493, 1475, 1453, 1362, 1266, 1203, 1036, 1003, 854, 744, 698 cm⁻¹. HRMS (EI): calcd for C₂₀H₃₄OSi [M⁺] 318.2379, found 318.2384.

(Z)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol (4Ca). To a solution of 3Ca (21 mg, 0.09 mmol, Z/E = 95/5) and N,N,N',N'-tetraethylenediamine (TMEDA) (15 µL, 0.09 mmol) in THF (1 mL) was added n-BuLi (0.45 mL of 1.60 M solution in hexane, 0.72 mmol) at −78 °C under Ar atmosphere and the reaction mixture was warmed to rt over 10 min. The reaction was quenched with water. The aqueous layer was separated and extracted with Et₂O. The combined organic extracts were washed with brine, dried over Na₂SO₄, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 8/1) to give 4Ca (10 mg, 47%, Z/E = 97/3) as an oil. ¹H NMR (400 MHz, CDCl₃): 3.82 (s, 3H), 5.60 (d, J = 9.2 Hz, 1H), 5.95 (dd, J = 11.4, 9.2 Hz, 1H), 6.67 (d, J = 11.4 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 7.26–7.38 (m, 7H), the signal of OH proton was not clearly observed. Selected data of (E)-isomer; 5.25 (d, J = 6.9 Hz, 1H), 6.27 (dd, J = 13.8, 6.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 55.3, 69.7, 114.0, 127.4, 127.6, 128.3, 128.8, 130.9, 133.4, 135.4, 136.4, 159.2. IR (neat): 3371, 3057, 3021, 2956, 2934,
2835, 1610, 1509, 1463, 1302, 1247, 1173, 1032, 831, 699 cm\(^{-1}\). HRMS (EI): Calcd for C\(_{16}\)H\(_{16}\)O\(_2\) [M\(^+\)]: 240.1150. Found: 240.1148.

In a similar manner, (Z)-allylic alcohol 4Ad was obtained from the corresponding (Z)-vinyl ether 3Ad.

(Z)-1-Phenylhept-2-en-1-ol (4Ad).\(^{25}\) Compound 4Ad (57 mg, 81%, Z/E = 91/9) was obtained as an oil from 3Ad (70 mg, 0.37 mmol, Z/E = 91/9), TMEDA (54 \(\mu\)L, 0.36 mmol) and \(n\)-BuLi in hexane (1.76 mL, 1.65 M solution in hexane, 2.9 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.92 (t, \(J = 6.9\) Hz, 3H), 1.30–1.43 (m, 4H), 1.81 (d, \(J = 2.7\) Hz, 1H), 2.14–2.30 (m, 2H), 5.52–5.59 (m, 3H), 7.24–7.80 (m, 5H). Selected data of (E)-isomer: 2.03–2.09 (m, 2H), 5.17 (d, \(J = 6.9\) Hz, 1H), 5.67 (dd, \(J = 15.6, 6.9\) Hz, 1H), 5.77 (dt, \(J = 15.6, 6.4\) Hz, 1H).\(^{33}\) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 13.9, 22.3, 27.4, 31.7, 69.7, 125.9, 127.4, 128.5, 131.8, 132.4, 143.7.

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

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REFERENCES AND NOTES


(11) The “syn-effect” is herein defined as an effect which stabilizes the syn-conformation against the steric hindrance at the transition state.


(19) Although the Heck reaction of the vinyl triflate 2A with methyl acrylate was examined, the serious isomerization occurred to give a ca. 1/1 mixture of the product.35

![Chemical structure](image)

2A (Z/E = 96/4) → CO₂Me (?? equiv)

Et₃N (3.5 equiv)

(PPh₃)₂PdCl (0.05 equiv)

DMF, 90 °C, 24 h

73% (2E,4Z/2E,4E = 1/1)


