(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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(*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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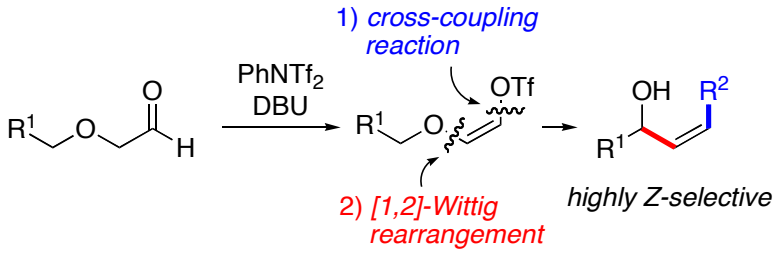


ABSTRACT: The stereoselective transformation of α-alkoxyacetoaldehydes to the corresponding (*Z*)-vinyl triflates was achieved by treatment with phenyl triflimide and DBU. The stereochemistry was explained by the "*syn*-effect," which was attributed primarily to an $\sigma \rightarrow \pi^*$ interaction. 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.

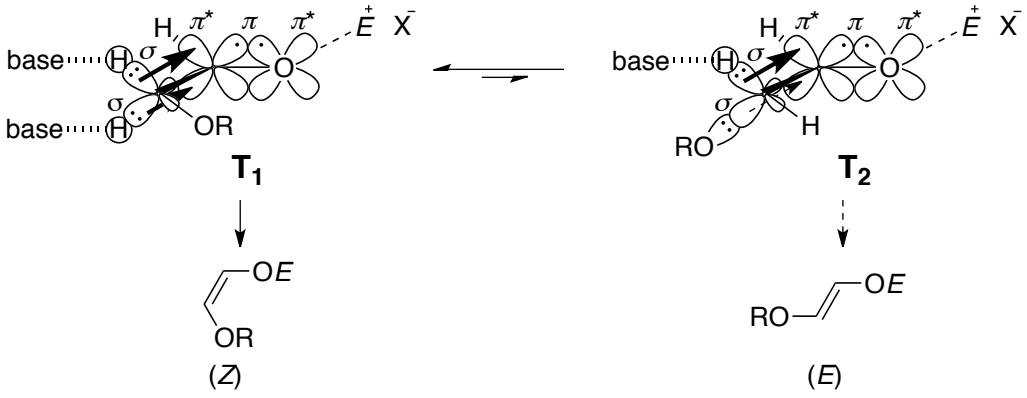
INTRODUCTION

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.[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.[2d,5] Chelation-controlled preparation of (*Z*)-vinyl triflates from α-alkoxy ketones also has been reported.[6] Recently, Cu-catalyzed electrophilic vinyl triflation of alkynes was reported to afford (*Z*)-triflates.[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_2O) and 4-methyl-2,6-(di-*t*-butyl)pyridine (DTBMP).[8] Alternatively, trimethylsilyl enol ethers could be converted to vinyl triflates by treatment with methyllithium and Tf_2O,[9] however, (*Z*)-selective preparation of trimethylsilyl enol ethers from an aldehyde is then an issue.[10]

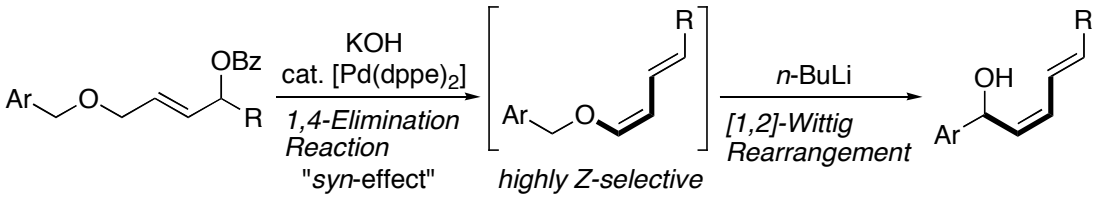
Previously, a series of isomerization reactions and elimination reactions using a base were performed to investigate the stereochemistry of the isomerized and eliminated products. The results showed that sterically unfavorable (*Z*)-alkenes were formed predominantly. These results were explained by the action of a "*syn*-effect,"[11] caused primarily by $\sigma \rightarrow \pi^*$ interactions.[12,13] Oxygen-substituted substrates always produced excellent *Z*-selectivities. For example, conformation $\mathbf{T_1}$ was preferred to conformation $\mathbf{T_2}$ during deprotonation of α-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.[12b]

Scheme 1. Transition State Model for Deprotonation of α-Alkoxyacetoaldehydes in the Presence of Triisopropylsilyl Triflate (*E* = *i*-Pr_3Si, X = OTf)[12b]



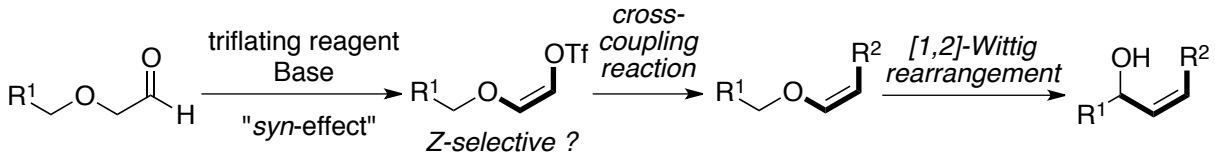
Furthermore, [1,2]-Wittig rearrangement[14] of the resulting (*Z*)-vinyl ethers proceeded after the initial 1,4-eliminative ring opening reaction of vinyl oxiranes and 1,4-elimination of allylic sulfones and allylic benzoates to give (2*Z*)-2,4-pentadien-1-ol derivatives in a highly stereoselective manner (Scheme 2).[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[12f]



Investigation of isomerization reactions revealed that α-alkoxyacetoaldehydes were converted to the corresponding (*Z*)-β-alkoxy silyl enol ethers with excellent *Z*-selectivity.[12b,15] Thus, a (*Z*)-β-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 α-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

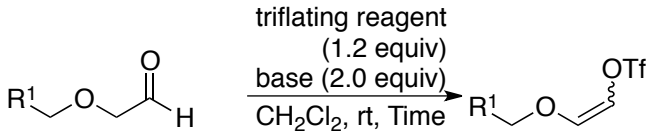


RESULTS AND DISCUSSION

First, the enol triflation reaction of (α-benzyloxy)acetoaldehyde (**1A**) using triflic anhydride (Tf_2O) (1.2 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) was conducted in CH_2Cl_2 under reflux conditions for 2 d.[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 CH_2Cl_2 at rt (Entry 2). When phenyl triflimide ($PhNTf_2$) was used instead of Tf_2O,[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 Et_3N. Other β-benzyloxy-type vinyl triflates **2B**-**2D** were also obtained stereoselectively from the corresponding α-alkoxyacetoaldehydes **1B**-**1D** (Entries 4–6). Furthermore, α-(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 α-Alkoxyacetoaldehydes 1



1 **2**

Entry	R^1		triflating reagent	base	Time	Yield/%	*Z*/*E*[a]
1[b]	Ph	**A**	Tf_2O	DTBMP	2 d	trace	--
2			Tf_2O	DBU	12 h	--	--
3			$PhNTf_2$	DBU	10 min	84	95/5
4	2-MeC_6H_4	**B**	$PhNTf_2$	DBU	10 min	84	95/5
5	4-$(MeO)C_6H_4$	**C**	$PhNTf_2$	DBU	10 min	82	95/5
6	4-ClC_6H_4	**D**	$PhNTf_2$	DBU	10 min	88	94/6
7	*i*-$Pr_3SiC{\equiv}C$	**E**	$PhNTf_2$	DBU	10 min	37	92/8
8[c]			$PhNTf_2$	DBU	10 min	71	95/5

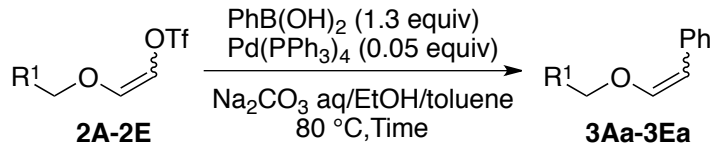
[a]The ratios were determined by 400 MHz ^{1}H NMR spectra.

[b]DTBMP (1.2 equiv) under CH_2Cl_2 reflux.

[c]DBU (2.5 equiv).

Next, the cross-coupling reaction was investigated using (*Z*)-β-alkoxy vinyl triflate **2**. Introduction of a phenyl group was accomplished *via* Suziki-Miyaura coupling with $PhB(OH)_2$ and using $Pd(PPh_3)_4$ as a catalyst[17] to give the β-alkoxy styrenes with retention of *Z*-stereochemistry as shown in Table 2.

Table 2. Coupling Reactions of Vinyl Triflates 2



2A-2E **3Aa-3Ea**

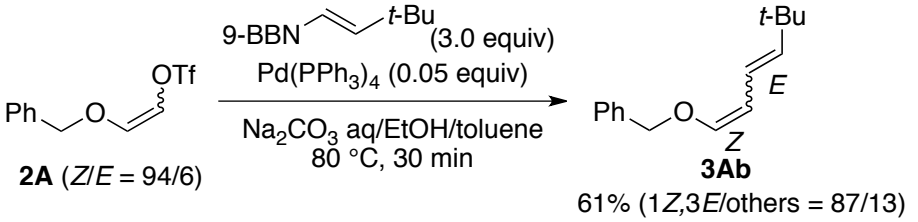
Entry	R^1	**2** (*Z*/*E*)[a]	Time	**3**	Yield/%	*Z*/*E*[a]
1[b]	Ph	**A** (94/6)	40 min	**Aa**	69	95/5
2	2-MeC_6H_4	**B** (94/6)	30 min	**Ba**	49	93/7
3	4-$MeOC_6H_4$	**C** (94/6)	1 h	**Ca**	74	95/5
4	4-ClC_6H_4	**D** (97/3)	20 min	**Da**	65	95/5
5[c]	*i*-$Pr_3SiC{\equiv}C$	**E** (95/5)	45 min	**Ea**	79	97/3

[a]The ratios were determined by 400 MHz ^{1}H NMR spectra.

[b]$Pd(PPh_3)_4$ (0.03 equiv).

[c]$Pd(PPh_3)_4$ (0.10 equiv) at a reaction temperature of 60 °C.

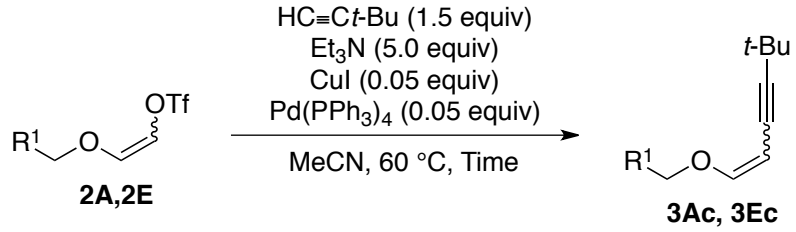
Suzuki-Miyaura coupling reaction of vinylic borane compounds generated *in situ* was performed as shown in Eq. 1.[18] The diene **3Ab** was obtained with nearly full retention of stereochemistry.[19]



(1)

Sonogashira coupling was also examined (Table 3).[20] 3,3-Dimethyl-1-butyne 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



2A,2E **3Ac, 3Ec**

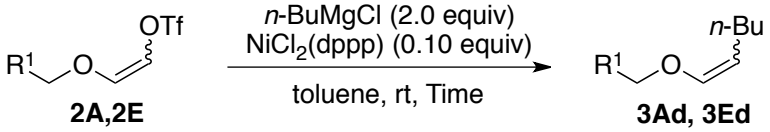
Entry	R^1	**2** $(Z/E)^a$	Time	**3**	Yield/%	Z/E^a
1	Ph	**A** (95/5)	20 min	**Ac**	88	95/5
2[b]	*i*-$Pr_3SiC{\equiv}C$	**E** (95/5)	1 h	**Ec**	98	96/4

[a]The ratios were determined by 400 MHz ^{1}H NMR spectra.

[b]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.[21] 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 $NiCl_2$(dppp)[22] 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



2A,2E **3Ad, 3Ed**

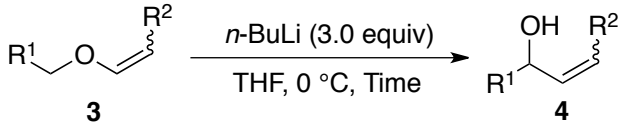
Entry	R^1	**2** $(Z/E)^a$	Time	**3**	Yield/%	Z/E^a
1	Ph	**A** (94/6)	15 min	**Ad**	81	91/9
2	*i*-$Pr_3SiC{\equiv}C$	**E** (95/5)	2 h	**Ed**	38	68/32

[a]The ratios were determined by 400 MHz ^{1}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 **3A**c the rearrangement proceeded to give the

corresponding (*Z*)-allylic alcohols stereoselectively (Table 5, Entries 1, 2, 4, 6, and 7). In the case of 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



3 **4**

Entry	R^1	R^2	**3**	$(Z/E)^a$	Time	Yield/%	Z/E^a
1	Ph	Ph	**Aa**	(95/5)	15 min	86	98/ 2
2	2-MeC_6H_4	Ph	**Ba**	(>98/2)	4 min	54	>98/ 2
3[b,c]	4-$MeOC_6H_4$	Ph	**Ca**	(95/5)	10 min	47	97/ 3
4	4-ClC_6H_4	Ph	**Da**	(96/4)	4 min	63	97/ 3
5	*i*-$Pr_3SiC{\equiv}C$	Ph	**Ea**	(>98/2)	4 min	56	>98/ 2
6	Ph	*t*-BuCH=CH	**Ab**	(87/13)[d]	4 min	85	95/ 5
7	Ph	*t*-Bu$C{\equiv}C$	**Ac**	(93/7)	3 min	49	93/ 7
8	*i*-$Pr_3SiC{\equiv}C$	*t*-Bu$C{\equiv}C$	**Ec**	(96/4)	4 min	31	>98/ 2
9[b,c]	Ph	*n*-Bu	**Ad**	(91/9)	10 min	81	89/11

[a]The ratios were determined by 400 MHz ^{1}H NMR spectra.

[b]*n*-BuLi (8 equiv) and TMEDA (1 equiv) were added.

[c]Temperature was adjusted from –78 °C to rt over 10 min.

[d]Ratio of (1*Z*,3*E*)-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.[23,24] 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.[25]

EXPERIMENTAL SECTION

General Method. ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts δ 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 $CDCl_3$ (δ = 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_2Cl_2 was distilled and stored over drying agents. Anhydrous CH_3CN 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_4NI (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_2O. The combined organic extracts were washed with brine, dried over Na_2SO_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): calcd for $C_{10}H_{14}O_2Na$ [$(M+Na)^+$] 189.0891, found 189.0887.

2-((2-Methylbenzyl)oxy)acetaldehyde (1B). To a solution of oxalyl chloride (1.27 mL, 15 mmol) in CH_2Cl_2 (50 mL) was added DMSO (1.42 ml, 20 mmol) in CH_2Cl_2 (3 mL) at –78 °C. After 5 min of stirring, 2-((2-methylbenzyl)oxy)ethanol (1.66 g, 10 mmol) in CH_2Cl_2 (3 mL) was added dropwise. After 15 min, the reaction mixture was added Et_3N (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): calcd for $C_{10}H_{12}O_2Na$ [$(M+Na)^+$] 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_2SO_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): calcd for $C_{16}H_{30}O_3Si$ [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 N_2 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 Et_2O. The combined organic extracts were washed with brine and dried over Na_2SO_4 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. ^{1}H NMR (400 MHz, $CDCl_3$): 1.07 (s, 21H), 4.21 (s, 2H), 4.35 (s, 2H), 9.77 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{14}H_{26}O_2Si$ [M^+] 254.1702, found 254.1706.

(*Z*)-2-(Benzyloxy)vinyl Trifluoromethanesulfonate (2A). To a solution of **1A** (597 mg, 4.0 mmol) in CH_2Cl_2 (35 mL), DBU (1.21 g, 8.0 mmol) in CH_2Cl_2 (5 mL) and $PhNTf_2$ (1.71 g, 4.8 mmol) in CH_2Cl_2 (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 Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, 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 ^{1}H NMR) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 4.94 (s, 2H), 6.00 (d, *J* = 3.2 Hz, 1H), 6.04 (d, *J* = 3.2 Hz, 1H), 7.27–7.42 (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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{10}H_9F_3O_4S$ [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 $PhNTf_2$ (1.29 g, 3.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{11}H_{11}F_3O_4S$ [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 $C_{11}H_{11}F_3O_5S$ [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 $C_{10}H_8ClF_3O_4S$ [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 $C_{15}H_{25}F_3O_4SSi$ [M^+] 386.1195, found: 386.1169.

(*Z*)-(2-(Benzyloxy)vinyl)benzene (3Aa).[30] 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 Na_2CO_3 (15 mL). After $Pd(PPh_3)_4$ (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.[17b] 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 Et_2O. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, 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. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and $PhB(OH)_2$ (79 mg, 0.65 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{16}H_{16}O$ [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), $Pd(PPh_3)_4$ (51 mg, 0.04 mmol), and $PhB(OH)_2$ (139 mg, 1.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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, 2933, 2836, 1650, 1613, 1513, 1447, 1366, 1250, 1174, 1031, 823, 780, 696 cm^{-1}. HRMS (EI): calcd for $C_{16}H_{16}O_2$ [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), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and $PhB(OH)_2$ (95 mg, 0.78 mmol). ^1H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{15}H_{13}ClO$ $[M^+]$ 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), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 10 mol%), and $PhB(OH)_2$ (48 mg, 0.39 mmol). ^1H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{20}H_{30}OSi$ $[M^+]$ 314.2066, found 314.2070.

((((1*Z*,3*E*)-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 Na_2CO_3 (5 mL) and **2A** (141 mg, 0.5 mmol, *Z*/*E* = 94/6) in THF (1 mL), and $Pd(PPh_3)_4$ (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 Et_2O. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and solvent was evaporated. The crude product was purified by silica gel column chromatography (hexane/benzene = 1/1) to give **3Ab** (59 mg, 61%, 1*Z*,3*E*/*others* = 87/13) as an oil. ^1H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{15}H_{20}O$ $[M^+]$ 216.1514, found 216.1509.

(*Z*)-(((5,5-Dimethylhex-1-en-3-yn-1-yl)oxy)methyl)benzene (3Ac). To a solution of Et_3N (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.[20b] 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_3N (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.[22d] The reaction was quenched with a satd aq solution of NH_4Cl and insoluble substance was filtered off through a bed of Celite. The aqueous layer of the filtrate was separated and extracted with Et_2O. The combined organic extracts were washed with water and brine, dried over Na_2SO_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, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 13.9, 22.3, 23.7, 31.9, 73.5, 108.0, 127.2, 127.7, 128.4, 137.8, 144.3. IR (neat): 3065, 3031, 2956, 2926, 2871, 1668, 1463, 1362, 1271, 1209, 1129, 1095, 1027, 732, 695 cm^{-1}. HRMS (EI): calcd for $C_{13}H_{18}O$ [M^+] 190.1358, found 190.1362.

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), $NiCl_2$(dppp) (11 mg, 0.02 mmol) and *n*-BuMgCl (0.43 mL of 0.94 M solution in THF, 0.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 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).^{13}C NMR (100 MHz, $CDCl_3$): (*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 $C_{18}H_{34}OSiNa$ [$(M+Na)^+$] 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 Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, 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. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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, 997, 870, 770, 751 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O$: 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). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100MHz, $CDCl_3$): 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 $C_{15}H_{13}ClO$ [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). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{20}H_{30}OSi$ [M^+] 314.2066, found 314.2068.

(2*Z*,4*E*)-6,6-Dimethyl-1-phenylhepta-2,4-dien-1-ol (4Ab). Compound **4Ab** (47 mg, 85%, 2*Z*,4*E*/2*E*,4*E* = 95/5) was obtained as an oil from **3Ab** (55 mg, 0.25 mmol, 1*Z*,3*E*/others = 87/13) and *n*-BuLi (0.45 mL of 1.65 M solution in hexane, 0.75 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100MHz, $CDCl_3$): 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 $C_{15}H_{20}O$ [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). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{15}H_{18}O$ [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). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 11.1, 18.6, 28.2, 30.8, 60.7, 74.2, 86.3, 105.8, 106.4, 112.0, 139.4. IR (neat): 3383, 2945, 2865, 2212, 2170, 1616, 1463, 1385, 1363, 1266, 1038, 883, 678 cm^{-1}. HRMS (EI): calcd for $C_{20}H_{34}OSi$ [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 Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, 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. ^{1}H NMR (400 MHz, $CDCl_3$): 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).[32] ^{13}C NMR (100 MHz, $CDCl_3$): 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* = 89/11) was obtained as an oil from **3Ad** (70 mg, 0.37 mmol, *Z*/*E* = 91/9), TMEDA (54 μL, 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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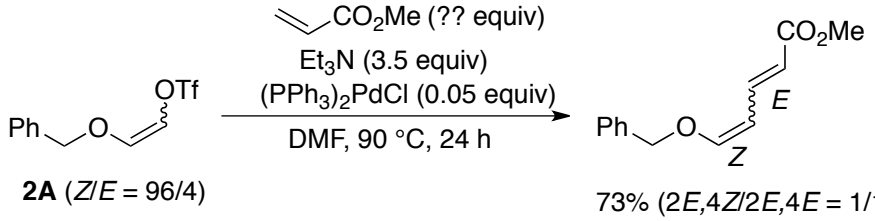

2A (*Z*/*E* = 96/4)

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

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