JOC The Journal of Organic Chemistry

Article

Selective Long-Distance Isomerization of Terminal Alkenes via Nondissociative Chain Walking

Yuya Yamasaki, Takaaki Kumagai, Shota Kanno, Fumitoshi Kakiuchi, and Takuya Kochi

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01288 • Publication Date (Web): 19 Jul 2018

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

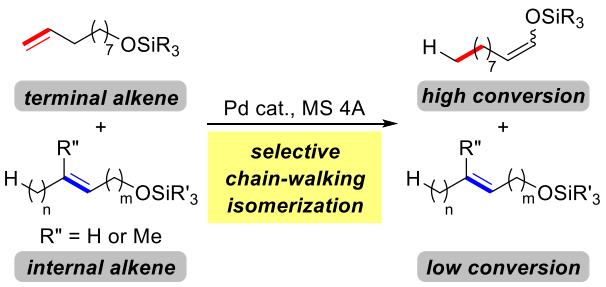
Selective Long-Distance Isomerization of Terminal Alkenes via Nondissociative Chain Walking

Yuya Yamasaki, Takaaki Kumagai, Shota Kanno, Fumitoshi Kakiuchi, and Takuya Kochi*

Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan.

kochi@chem.keio.ac.jp

Table of Contents/Abstract Graphic



Abstract

Selective long-distance isomerization of terminal alkenes to silyl enol ethers proceeded via “nondissociative” chain walking using phenanthroline palladium catalysts. Notable features achieved taking advantage of the nondissociative chain walking mechanism include high efficiency obtained regardless of the chain length, high chemoselectivity toward terminal alkenes over internal ones, and retention of the stereoconfiguration of the stereocenter on the alkyl chain.

Introduction

Selective alkene isomerization is a powerful method to form desired unsaturated functional groups without using oxidants.[1] While most of the studies on the alkene isomerization have focused on those in which double bonds migrates over one carbon, long-distance alkene isomerization[2] has also attracted growing attention as increasing efforts have been directed toward developments of efficient remote functionalization methods.[3]

In general, there are two extreme types of mechanistic pathways considered for the long-distance isomerization. One is the "stepwise" isomerization pathway (Figure 1a), in which alkene exchange processes compete significantly with the isomerization process. In this case, various intermediate alkenes may be formed during the reaction and have to coordinate to the metal center again to complete the desired isomerization process. The other is the "nondissociative" chain walking pathway (Figure 1b),[4-7] in which alkene exchange process is much slower than the isomerization process and substrate alkenes are directly converted to the desired alkenes without releasing intermediate alkenes from the metal center. The mechanisms of the previously-reported long-distance isomerization reactions may be unclear and are probably one of the two pathways or fall between them. For example, Grotjahn and coworkers reported on a long-distance isomerization of terminal alkenes to alcohols using a bifunctional ruthenium catalyst.[2e,f] Their examples include the isomerization over up to 30 carbons, and their results showed that many intermediate alkenes are formed during the reaction. Mazet and coworkers also reported on isomerization reactions using palladium phosphine complexes,[2g,h] and their results on the complete racemization of the stereocenters in the alkyl chain suggest that alkene exchange occurs rapidly during the isomerization. Very recently, Kocen, Brookhart, and Daugulis reported on an isomerization

reaction of terminal alkenes to silyl enol ethers using 2,9-dimethylphenanthroline-palladium catalyst.[2i]

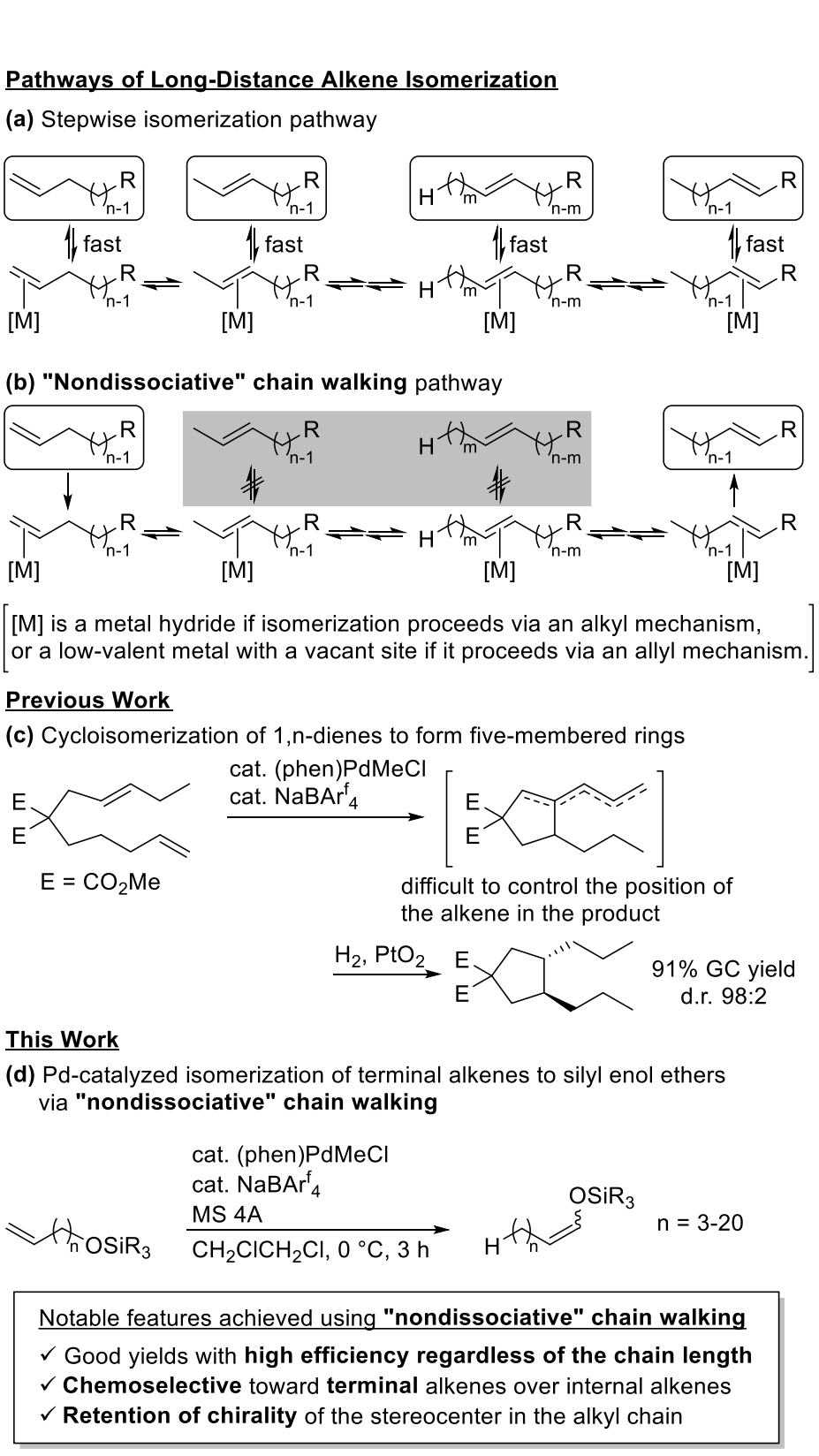


Figure 1. Long-Distance Alkene Isomerizations

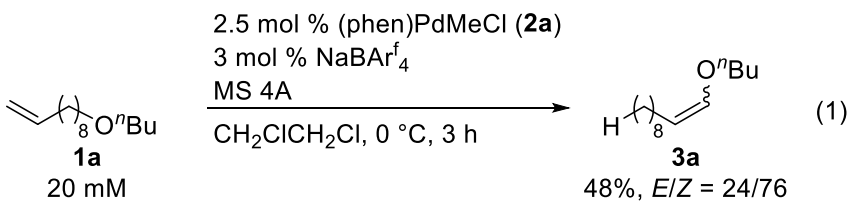
We envisioned that if a long-distance isomerization reaction via the nondissociative chain walking pathway is established, several distinguished features that are difficult to realize with the stepwise isomerization pathway would be achieved. However, none of the previously-reported selective long-distance isomerizations took advantage of the "nondissociative" chain walking pathway to apply for the isomerization reaction that are otherwise difficult to achieve.[8]

Herein we report a palladium-catalyzed selective long-distance isomerization of terminal alkenes to silyl enol ethers via the nondissociative chain walking pathway (Figure 1d).[9] Several notable features were achieved taking advantage of the nondissociative chain walking mechanism such as high efficiency obtained regardless of the chain length, high chemoselectivity toward terminal alkenes over internal ones, and retention of the stereoconfiguration of the stereocenter on the alkyl chain.

Results and Discussion

During the investigation of the chain-walking isomerization of 1,n-dienes using a phenanthroline palladium catalyst,[4] we encountered a challenge in settling the position of the alkene moiety left in the product (Figure 1c). The cycloisomerization reaction is considered to proceed via the nondissociative chain walking pathway, so we decided to search for a functional group that can settle the position of the isomerizing alkene right next to it. Initially we attempted the isomerization of several linear terminal alkenes possessing a functional group at the other terminus. While methoxycarbonyl and phenyl groups failed to form the desired α,β-unsaturated systems, alcohol substrates were mostly recovered with only a trace amount of the isomerization products.[10] But the reaction of a substrate possessing an alkoxy group (**1a**) with 1,10-phenanthroline palladium catalyst **2a** gave an encouraging result that alkenyl ether **3a** was obtained

in 48% yield (eq 1). Long-distance isomerizations of terminal alkenes possessing an alkoxy group at the other terminus have been achieved and utilized in one-pot cross-coupling reactions by Mazet[2j] and Marek.[2k]

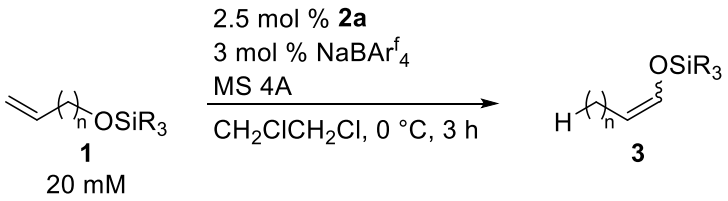


(1)

Then we turned our attention to another class of ethers, silyl ethers, and found that siloxy groups can settle the position of the isomerizing alkenes effectively next to them. The reaction of TES-protected 9-decen-1-ol (**1b**) using 2.5 mol % of **2a** and 3 mol % of $NaBAr^f_4$ (Ar^f = 3,5-$(F_3C)_2C_6H_3$) in 1,2-dichloroethane in the presence of MS 4A at 0 ºC for 3 h under a low-concentration condition (20 mM) provided silyl enol ether **3b** in 77% yield (Table 1, entry 1).[11] The reaction in dichloromethane proceeded similarly, but the yield was decreased to 71% (*E*/*Z* = 27/73). While the reactions of TBDPS- and TBS-protected alcohols (**1c** and **1d**) gave comparable yields of the products, the use of TIPS group further improved the yield to 90% (entry 4). The reaction of TIPS-protected alcohol **1e** also proceeds on a 1 g scale or using 0.12 mol % of **2a** to give 91 and 92% yields of **3e** (Table 1, entry 5 and eq 2). The number of methylenes between vinyl and siloxy groups was then examined (Table 1, entries 6-11), and it was found that the length of the methylene chain had little effect on the yields, and even if the isomerization needs to proceed over 20 carbons, the reaction was completed in 3 h at 0 ºC to give product **3k** in 81% yield (entry 11). Long-distance isomerizations of terminal alkenes possessing a siloxy group at the other terminus have been reported,[2c,e,j] but previous examples required longer reaction times (18-24 h) and/or higher

temperature (>70 ºC) for shorter substrates (isomerization over up to 8 carbons). The high efficiency of the long-distance isomerization described here may be attributed to the nondissociative chain-walking mechanism, where alkene exchange mostly proceeds between silyl enol ether products and small terminal alkene moieties, and it does not require recoordination of bulkier intermediate internal alkenes which competes with product recoordination.

Table 1. Isomerization of ω-Siloxy-α-olefins to Silyl Enol Ethers[a]

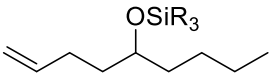
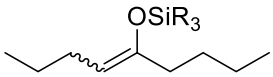
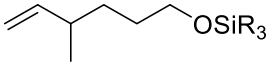
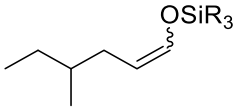
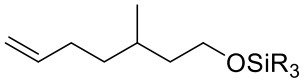
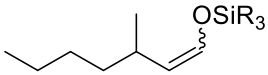


entry	alkene **1** [SiR_3]	n	**3**, isolated yield (%)	*E*/*Z*
1	**1b** [$SiEt_3$]	8	**3b**, 77	25/75
2	**1c** [Si^tBuPh_2]	8	**3c**, 76	15/85
3	**1d** [Si^tBuMe_2]	8	**3d**, 83	28/72
4	**1e** [Si^iPr_3]	8	**3e**, 90	26/74
5[b]	**1e** [Si^iPr_3]	8	**3e**, 91	26/74
6	**1f** [Si^iPr_3]	3	**3f**, 87	26/74
7	**1g** [Si^iPr_3]	4	**3g**, 89	26/74
8	**1h** [Si^iPr_3]	7	**3h**, 90	26/74
9	**1i** [Si^iPr_3]	14	**3i**, 86	26/74
10	**1j** [Si^iPr_3]	18	**3j**, 84	27/73
11	**1k** [Si^iPr_3]	20	**3k**, 81	23/77

[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.0125 mmol), $NaBAr^f_4$ (0.015 mmol), CH_2ClCH_2Cl (25 mL), 0 ºC. [b]Performed using 3.2 mmol (1.0 g) of **1e** with 2.5 mol % of **2a** and 3 mol % of $NaBAr^f_4$ in 160 mL of CH_2ClCH_2Cl.

The long-distance isomerization can also be applied to substrates possessing branches on the chain. The reaction of TIPS-protected secondary alcohol **1l** did not give the corresponding product (Table 2, entry 1),[12] but the use of a smaller TES group provided product **3m** in 61% yield (entry 2). The reaction was also attempted with TES-protected 1-phenyl-6-hepten-2-ol but almost no isomerization was observed. Substrates possessing a methyl branch were also examined. The isomerization of 4-methyl-5-hexen-1-ol derivatives **1n** and **1o** proceeded smoothly to afford **3n** and **3o** in excellent yields (entries 3 and 4). In the case of silyl-protected 3-methyl-6-hepten-1-ol **1p** and **1q**, the reaction became less efficient probably due to the increased steric congestion around the alkene moiety, but products **3p** and **3q** were obtained in 69 and 67% yields, respectively (entries 5 and 6). The reaction of TES-protected 3-phenyl-5-hexen-1-ol was also examined, but no formation of the isomerization product was observed.

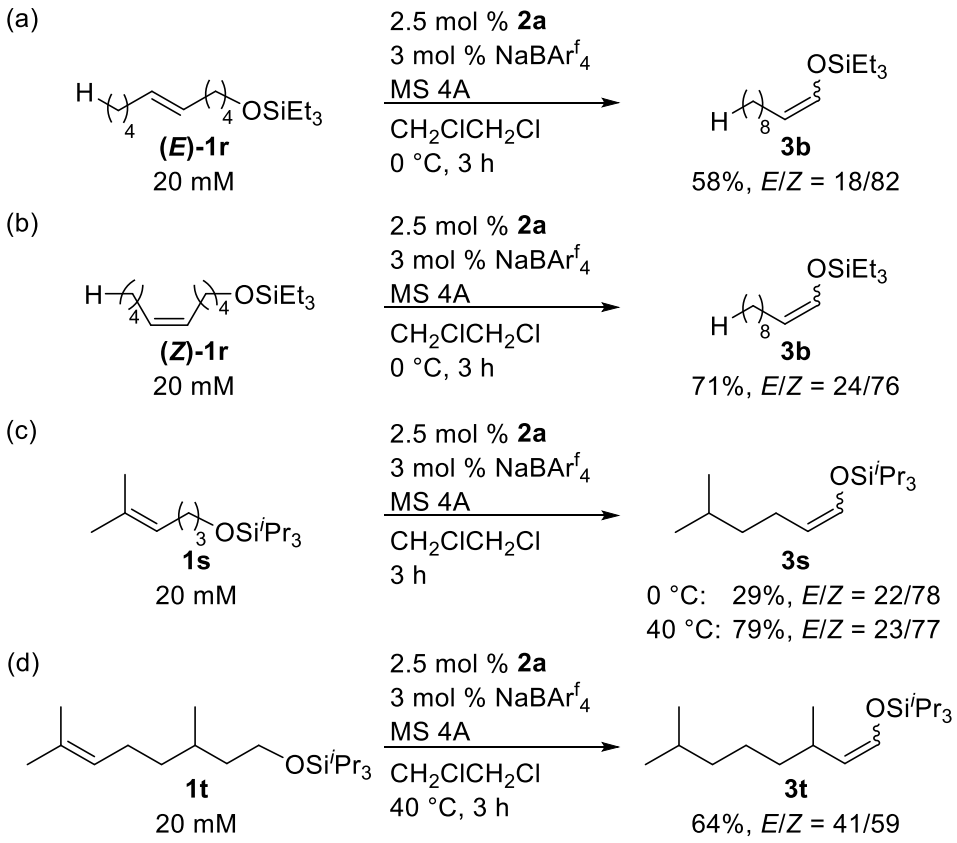
Table 2. Selective Isomerization of Branched Siloxy-α-olefins[a]

entry	alkene **1**	silyl enol ether **3**, isolated yield (%) [*E*/*Z*]
		
1	**1l** (R = ^{i}Pr)	not detected
2	**1m** (R = Et)	**3m**, 61 [15/85]
		
3	**1n** (R = ^{i}Pr)	**3n**, 91 [27/73]
4	**1o** (R = Et)	**3o**, 86 [31/69]
		
5[b]	**1p** (R = ^{i}Pr)	**3p**, 69 [40/60]
6[c]	**1q** (R = Et)	**3q**, 67 [25/75]

[a]Reaction conditions: **1** (1.0 mmol), **2a** (0.025 mmol), $NaBAr^{f}_{4}$ (0.03 mmol), CH_2ClCH_2Cl (50 mL), 0 ºC, 3 h. [b]Performed using 2 mmol of **1p** with 2.5 mol % of **2a** and 3 mol % of $NaBAr^{f}_{4}$ in 100 mL of CH_2ClCH_2Cl. [c]Performed using 0.5 mmol of **1q** with 2.5 mol % of **2a** and 3 mol % of $NaBAr^{f}_{4}$ in 25 mL of CH_2ClCH_2Cl.

Investigation of the reactions of internal alkenes bearing a siloxy group showed that the isomerization proceeded but with lower efficiency. Under the same reaction conditions used in Table 1, the reaction of 1,2-disubstituted alkenes **(*E*)-** and **(*Z*)-1r** produced product **3b** in 58 and 71% yields, respectively (Scheme 1a and 1b). Conversion of trisubstituted alkene **1s** to product **3s** was not efficient at 0 ºC, but the reaction at 40 ºC gave **3s** in 79% yield (Scheme 1c). The isomerization of citronellol derivative **1t** also proceeded at 40 ºC to provide **3t** in 64% yield (Scheme 1d).

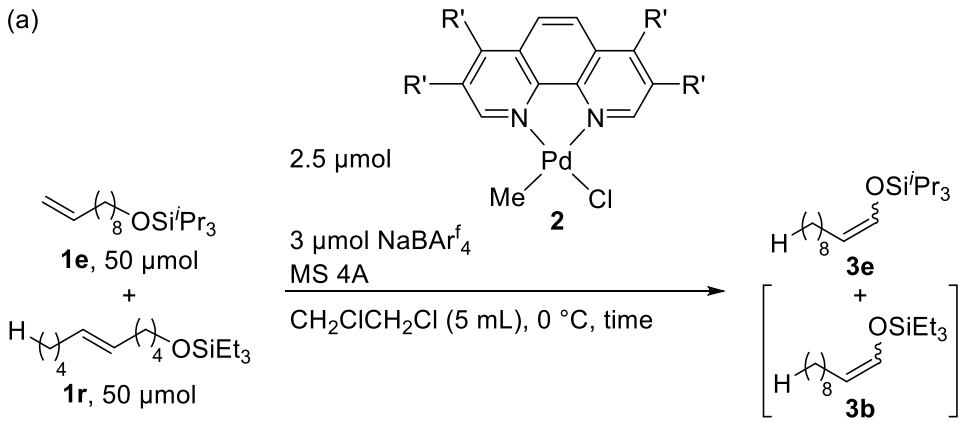
Scheme 1. Isomerization of Internal Alkenes to Silyl Enol Ethers[a]



One of the most striking features of the isomerization via the nondissociative chain walking pathway is that conversion of terminal alkenes to products are completed without forming intermediate internal alkenes. Therefore, if coordination of terminal alkenes to catalysts is much faster than that of internal alkenes, it may be possible to perform chemoselective direct conversion of terminal alkenes to products in the presence of internal alkenes. This type of reaction is very difficult to achieve using the stepwise isomerization pathway, which inherently requires efficient coordination of internal alkenes to catalysts.

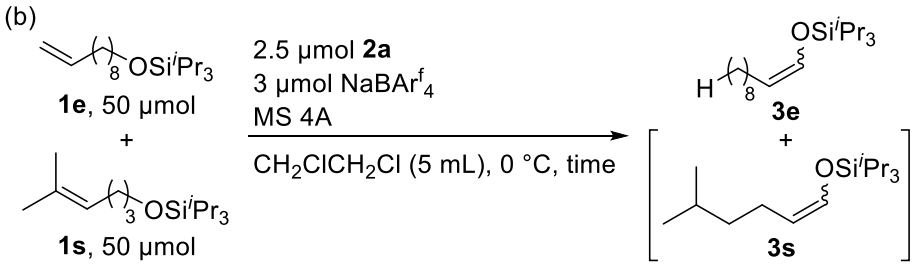
In order to examine the chemoselectivity toward terminal alkenes over internal alkenes, competition experiments between terminal and internal alkene substrates were performed (Table 3). The reaction of a 1:1 mixture of terminal alkene **1e** and 1,2-disubstituted alkene **1r** was first conducted using catalyst **2a** (entries 1-3). The reaction was quite selective initially, and terminal alkene **1e** was converted to product **3e** in 36% GC yield, while only 2% of product **3b** was generated from internal alkene **1r**. The reaction for 30 min gave **3e** in 75% yield, but conversion of **1r** to **3b** was gradually accelerated to form **3b** in 22% yield, as the amount of the remaining **1e** was reduced. Further elongation of the reaction time increased the yield of **3b** rather than **3e** (entry 3). Screening of the reaction conditions revealed that the use of tetramethylphenanthroline palladium catalyst **2b** and the increase of the solvent volume was effective for improving the chemoselectivity (entry 4-6), and the reaction for 30 min gave **3e** in 92% yield while generating only 10 % of **3b** (entry 5). The competition experiment was also performed using terminal alkene **1e** with trisubstituted alkene **1s** (entries 7-9), and in the presence of catalyst **2a**, the reaction for 30 min provided **3e** in 87% GC yield along with only 7% GC yield of **3s** (entry 8).

Table 3. Chemoselective Isomerization of a Terminal Alkene in the Presence of Internal Alkenes[a]



entry	catalyst **2** [R']	time (min)	GC yield of **3e** (%) [E/Z]	GC yield of **3b** (%) [E/Z]
1	**2a** [H]	5	36 [13/87]	2 [20/80]
2	**2a** [H]	30	75 [17/83]	22 [18/82]
3	**2a** [H]	120	80 [17/83]	41 [18/82]
4[b]	**2b** [Me]	5	8 [–][c]	nd[d]
5[b]	**2b** [Me]	30	**92** [15/85]	**10** [16/84]
6[b]	**2b** [Me]	120	94 [16/84]	31 [20/80]

[a]Reaction conditions: **1e** (50 μmol), **1r** (50 μmol), **2** (2.5 μmol), NaBAr$^f_4$ (3 μmol), CH_2ClCH_2Cl (5 mL), 0 °C. [b]Performed in 10 mL of CH_2ClCH_2Cl. [c]Not determined. [d]Not detected.

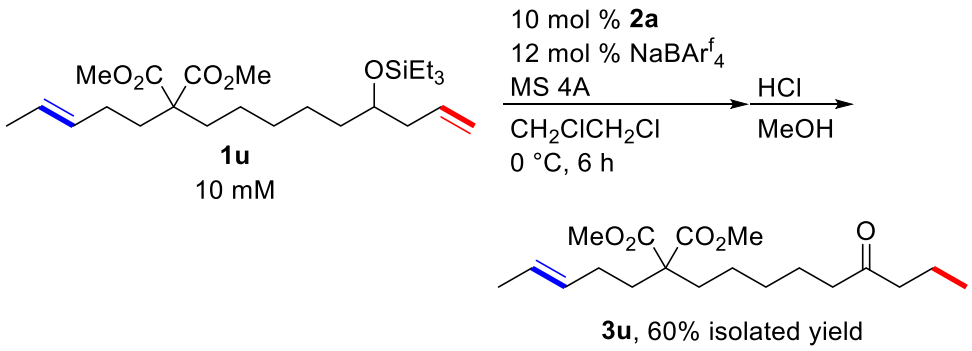


entry	time (min)	GC yield of **3e** (%) [E/Z]	GC yield of **3s** (%) [E/Z]
7	5	7 [–][b]	nd[c]
8	30	87 [20/80]	7 [15/85]
9	120	90 [24/76]	31 [20/80]

[a]Reaction conditions: **1e** (50 μmol), **1s** (50 μmol), **2** (2.5 μmol), $NaBAr^f_4$ (3 μmol), CH_2ClCH_2Cl (5 mL), 0 °C. [b]Not determined. [c]Not detected.

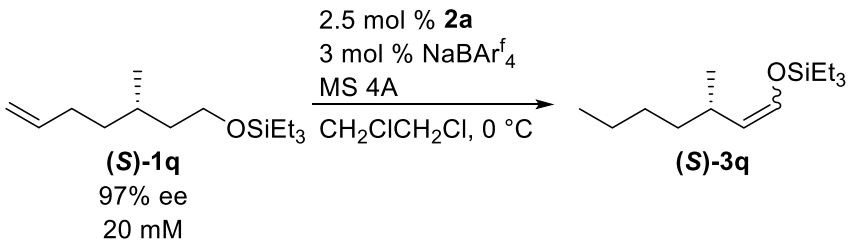
Finally, the chemoselective isomerization of terminal alkenes over internal alkenes was applied to substrate **1u**, which has both terminal and internal alkene moieties. The reaction of **1u** in the presence of 10 mol % of **2a** for 6 h, followed by acid deprotection, provided 60% isolated yield of ketone **3u**, which still possesses the internal alkene moiety without isomerization (Scheme 2).

Scheme 2. Chemoselective Isomerization of a Terminal Alkene Possessing an Internal Alkene Moiety



Another feature of the isomerization via the nondissociative chain walking pathway is that stereoconfiguration of the stereocenter present on the alkyl chain on which metal catalysts migrate should be maintained after the isomerization. This feature has been previously shown in some reactions,[5d,j,l,13] but has not been demonstrated for simple long-distance isomerization reactions. When the reaction of **(*S*)-1q** (97% ee) in the presence of 2.5 mol % of **2a** was performed for 30 min, 38% NMR yield of **(*S*)-3q** was obtained with only 2% degradation of the enantiomeric excess (Table 4, entry 1). Extension of the reaction time to 60 min improved the yield of **(*S*)-3q** to 57% with maintaining the high enantiomeric excess (95% ee) (entry 2). The observed high level of retention of the stereochemistry strongly supports that the reaction mostly proceeds via the nondissociative chain walking pathway. The slight degradation of the enantiomeric excess may be attributed to dissociation of a small amount of trisubstituted alkene intermediates during the reaction. When the reaction of **(*S*)-1q** was performed in 2 mL of dichloroethane instead of 10 mL, the yield of **(*S*)-3q** was decreased with maintaining the similar level of ee, indicating that the alkene exchange was somewhat accelerated at high concentration. The reaction at 40 ºC for 30 min gave **(*S*)-3q** in 78% yield but the ee was decreased to 32%, probably because the isomerization was accelerated significantly, and considerable recoordination/isomerization of the product alkene started to occur to racemize the stereocenter (entry 4).

Table 4. Retention of the Stereoconfiguration at the Stereocenter on the Methylene Chain[a]



entry	time (min)	temp (ºC)	NMR yield of **3q** (%) [E/Z]	ee [es] (%, after deprotection)
1	30	0	38 [21/79]	95 [97]
2	60	0	57 [23/77]	95 [97]
3	30	40	78 [39/61]	32 [33]
4[b]	30	0	27 [26/74]	96 [98]

[a]Reaction conditions: **(*S*)-1q** (0.2 mmol), **2a** (5 μmol), $NaBAr^f_4$ (6 μmol), MS 4A, CH_2ClCH_2Cl (10 mL). [b]Performed in 2 mL of CH_2ClCH_2Cl (100 mM).

Conclusion

Selective long-distance isomerization of alkenes to silyl enol ethers via the "nondissociative" chain walking pathway was developed using phenanthroline palladium catalysts. Various terminal alkenes bearing a siloxy group were efficiently isomerized to silyl enol ethers, and isomerization of a substrate which requires chain walking over 20 carbons can be conducted at 0 ºC within 3 h to obtain the corresponding product in high yield. Highly chemoselective isomerization of terminal alkenes in the presence of internal alkenes and retention of the stereoconfiguration of the stereocenter on the alkyl chain were also achieved by taking advantage of the nondissociative chain walking mechanism. Application of the chain-walking isomerization to other reactions such as cycloisomerization reactions is in progress.

Experimental Section

Unless otherwise noted, all reactions were carried out under nitrogen, and all commercial reagents were used as received. (3,4,7,8-Me_4phen)PdMeCl, (phen)PdMeCl, (bpy)PdMeCl and (1,10-Me_2phen)PdMeCl were prepared by previously-reported methods.[4a] NaH was washed three times with hexane prior to use. Anhydrous DMF and THF were purchased from Kanto Chemical Co. Inc. and used as received. 1,2-Dichloroethane was distilled from P_2O_5. Dichloromethane was purified by passing through a Glass Contour solvent purification system. 3-Methy1-6-hepten-1-ol was synthesized according to the literature procedure.[13] ^{1}H, and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL ECX-400 or AL-400 spectrometer. Gas chromatography (GC) analyses were performed using a CBP-10 capillary column (25 m × 0.22 mm, film thickness 0.25 μm). IR spectra were recorded on a JASCO FT/IR-410 infrared spectrometer. ESI-MS was performed on a JEOL JMS-T100LCS. HPLC analysis was performed on a HITACHI Elite LaChrom Series HPLC with a Chiralpak AY-H (0.46 cm x 25 cm) column with UV detection at 254 nm. Flash column chromatography was carried out with silica gel 60N (Kanto Chemical Co., Inc.) or $AgNO_3$/silica gel prepared before use.[4b,14]

Preparation of Alkyl Ether 1a. To a suspension of NaH (808 mg of 60% oil suspension, washed three times with hexane before use, 20.2 mmol, 2.05 equiv) in DMF (20 mL) was slowly added 9-decen-1-ol (1.54 g, 9.84 mmol) in DMF (5 mL) at 0 °C. A solution of 1-bromobutane (1.51 g, 11.0 mmol) in DMF (5 mL) was added dropwise to the flask and the mixture was stirred 30 min. The solution was gradually warmed to room temperature and stirred overnight. After this period, a saturated aqueous solution of ammonium chloride was introduced to the mixture, which was then extracted five times with EtOAc. Combined organic portions were washed five times with water, quickly dried over $MgSO_4$, filtered, and concentrated. Column chromatography of the

crude material on silica gel (hexane:EtOAc = 20:1) afforded of the desired alkyl ether **1a** (1.04 g, 50% yield) as a colorless oil: IR (neat): 3328 w, 3077 w, 2958 s, 2929 s, 2855 s, 2795 m, 2744 w, 1641 m, 1465 m, 1438 m, 1415 w, 1375 m, 1301 w, 1232 w, 1117 s, 992 m, 910 s, 841 m, 723 w, 635 w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.6 Hz, 3H), 1.23-1.41 (m, 12H), 1.52-1.59 (m, 4H), 2.04 (q, *J* = 7.2 Hz, 2H), 3.40 (td, *J* = 6.8 Hz, 3.6 Hz, 4H), 4.91-5.01 (m, 2H), 5.76-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 19.4, 26.2, 28.9, 29.1, 29.4 (2×1C), 29.8, 31.9, 33.8, 70.6, 71.0, 114.1, 139.2; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{29}O$ 213.2218; Found 213.2209.

General Procedure A for Preparation of Silyl Ethers 1b-h,l-t. To a solution of the alcohol (1 equiv) in CH_2Cl_2 (ca. 10 mL per 3 mmol of alcohol) at 0 °C, was added imidazole (1.10 equiv) and DMAP (0.05 equiv, if any). Stirring was continued for 5 min, and then the silyl chloride (1.20 equiv). The reaction mixture was gradually warmed to room temperature and stirred for 3 h. After this period, a saturated aqueous solution of $NaHCO_3$ was introduced to the mixture and stirred for 30 min, which extracted with CH_2Cl_2 three times. Combined organic portions were washed with brine, quickly dried over $MgSO_4$, filtered, and concentrated. Column chromatography of the crude material on silica gel (hexane/EtOAc) afforded the desired silyl ethers **1**.

Silyl ether 1b. General Procedure A was followed with 803 mg of 9-decen-1-ol and 900 mg of triethylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 20:1) of the crude material afforded 976 mg of **1b** (70% yield) as a colorless oil. The analytical data of **1b** are in good agreement with those reported in literature.[15]

Silyl ether 1c. General Procedure A was followed with 1.41 g of 9-decen-1-ol and 3.59 g of *tert*-butyldiphenylsilyl chloride without using DMAP. Silica gel chromatography (hexane only) of

the crude material afforded 2.87 g of **1c** (81% yield) as a colorless oil. The analytical data of **1c** are in good agreement with those reported in literature.[16]

Silyl ether 1d. General Procedure A was followed with 790 mg of 9-decen-1-ol and 929 mg of *tert*-butyldimethylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 100:1) of the crude material afforded 1.17 g of **1d** (86% yield) as a colorless oil. The analytical data of **1d** are in good agreement with those reported in literature.[17]

Silyl ether 1e. General Procedure A was followed with 783 mg of 9-decen-1-ol and 1.18 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 100:1) of the crude material afforded 1.25 g of **1e** (80% yield) as a colorless oil. IR (neat): 2928 s, 2865 s, 1641 w, 1463 w, 1386 w, 1249 w, 1107 m, 1069 w, 994 w, 909 w, 882 m, 790 w, 681 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.98-1.13 (m, 21H), 1.29-1.39 (m, 10H), 1.50-1.56 (m, 2H), 2.04 (q, J = 8.0 Hz, 2H), 3.67 (t, J = 6.8 Hz, 2H), 4.91-5.02 (m, 2H), 5.76-5.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 25.8, 28.9, 29.1, 29.4, 29.5, 33.0, 33.8, 63.5, 114.1, 139.2; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{41}OSi$ 313.2927; Found 313.2928.

Silyl ether 1f. General Procedure A was followed with 856 mg of 4-penten-1-ol and 2.33 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 2.09 g of **1f** (87% yield) as a colorless oil. The analytical data of **1f** are in good agreement with those reported in literature.[18]

Silyl ether 1g. General Procedure A was followed with 1.02 g of 5-hexen-1-ol and 2.26 g of triisopropylsilyl chloride without using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 2.26 g of **1g** (87% yield) as a colorless oil. The analytical data of **1g** are in good agreement with those reported in literature.[19]

Silyl ether 1h. General Procedure A was followed with 1.43 g of 8-nonen-1-ol and 2.32 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 2.50 g of **1h** (83% yield) as a colorless oil. IR (neat): 3078 w, 2929 s, 2866 s, 2728 w, 1642 m, 1464 s, 1383 m, 1247 w, 1108 s, 1070 m, 1013 m, 995 s, 910 s, 883 s, 794 m, 718 m, 682 s, 668 s, 657 m, 638 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03-1.13 (m, 21H), 1.31-1.40 (m, 8H), 1.50-1.57 (m, 2H), 2.04 (q, *J* = 7.2 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 4.91-5.02 (m, 2H), 5.76-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 25.8, 28.9, 29.1, 29.3, 33.0, 33.8, 63.5, 114.1, 139.2; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{39}OSi$ 299.2770; Found 299.2766.

Silyl ether 1l. General Procedure A was followed with 1.46 g of 1-nonen-5-ol and 2.37 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 184 mg of **1l** (6% yield) as a colorless oil. IR (neat): 3079 w, 2943 s, 2867 s, 2724 w, 1825 w, 1642 m, 1367 w, 1288 w, 1247 w, 1216 w, 1130 m, 1086 s, 1059 s, 1013 m, 996 m, 910 s, 883 s, 881 w, 720 w, 676 s m^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.01-1.12 (m, 21H), 1.26-1.31 (m, 4H), 1.46-1.64 (m, 4H), 2.10 (q, J = 7.2 Hz, 2H), 3.84 (quin, *J* = 5.6 Hz, 1H), 4.92-5.03 (m, 2H), 5.78-5.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.7, 14.1, 18.2, 23.0, 27.1, 29.1, 35.7, 36.3, 71.8, 114.1, 139.1; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{39}OSi$ 299.2770; Found 299.2756.

Silyl ether 1m. General Procedure A was followed with 1.43 g of 1-nonen-5-ol and 2.03 g of triethylsilyl chloride using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 2.03 g of **1m** (79% yield) as a colorless oil. IR (neat): 2957 s, 2876 s, 1642 w, 1459 w, 1414 w, 1378 w, 1238 w, 1134 w, 1057 m, 1011 m, 909 m, 759 s, 743 s, 724 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (q, *J* = 8.0 Hz, 6H), 0.88-0.91 (m, 3H), 0.96 (t, *J* = 8.0 Hz, 9H), 1.28-1.32

(m, 4H), 1.41-1.55 (m, 4H), 2.01-2.17 (m, 2H), 3.66 (quin, J = 6.0 Hz, 1H), 4.93-5.03 (m, 2H), 5.77-5.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.1, 7.0, 14.1, 22.9, 27.5, 29.7, 36.3, 36.9, 71.8, 114.2, 139.0; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{33}OSi$ 257.2301; Found 257.2293.

Silyl ether 1n. General Procedure A was followed with 1.72 g of 4-methyl-5-hexen-1-ol and 3.49 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 100:1) of the crude material afforded 3.69 g of **1n** (91% yield) as a colorless oil. IR (neat): 3079 w, 2958 s, 2943 s, 2894 m, 2867 s, 1640 w, 1464 m, 1383 w, 1247 w, 1107 s, 1070 w, 1014 w, 995 m, 910 m, 882 m, 785 w, 725 w, 687 m, 682 m, 656 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, J = 6.8 Hz, 3H), 1.03-1.13 (m, 21H), 1.31-1.39 (m, 2H), 1.47-1.61 (m, 2H), 2.13 (sep, J = 6.8 Hz, 1H), 3.66 (t, J = 6.8 Hz, 2H), 4.90-4.98 (m, 2H), 5.65-5.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 20.2, 30.7, 32.7, 37.6, 63.5, 112.4, 144.8; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2448.

Silyl ether 1o. General Procedure A was followed with 1.72 g of 4-methyl-5-hexen-1-ol and 2.75 g of triethylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 100:1) of the crude material afforded 2.06 g of **1o** (60% yield) as a colorless oil. IR (neat): 3079 w, 2957 s, 2913 s, 2877 s, 1457 m, 1419 w, 1388 w, 1239 w, 1100 s, 1006 m, 911 m, 793 w, 743 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.59 (q, J = 8.0 Hz, 6H), 0.94-1.00 (m, 12H), 1.27-1.35 (m, 2H), 1.49-1.57 (m, 2H), 2.12 (sep, J = 6.8 Hz, 1H), 3.59 (t, J = 6.8 Hz, 2H), 4.90-4.98 (m, 2H), 5.64-5.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.8, 20.2, 30.6, 32.7, 37.6, 63.0, 112.5, 144.7; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{29}OSi$ 229.1988; Found 229.1994.

Silyl ether 1p. General Procedure A was followed with 1.79 g of 3-methyl-6-hepten-1-ol and 3.26 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 1000:1) of the crude material afforded 638 mg of **1p** (16% yield) as a colorless oil. IR (neat): 3699

w, 3469 w, 3078 w, 2942 s, 2868 s, 2725 w, 1642 w, 1464 s, 1383 w, 1367 w, 1248 w, 1103 s, 1071 m, 1014 m, 995 m, 909 m, 883 s, 803 m, 737 m, 680 s, 658 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, *J* = 6.8 Hz, 3H), 0.98-1.13 (m, 21H), 1.18-1.27 (m, 1H), 1.32-1.46 (m, 2H),1.50-1.65 (m, 2H), 1.98-2.14 (m, 2H), 3.66-3.76 (m, 2H), 4.91-5.03 (m, 2H), 5.76-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 19.6, 29.1, 31.3, 36.3, 40.0, 61.6, 114.0, 139.3; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{37}OSi$ 285.2614; Found 285.2618.

Silyl ether 1q. General Procedure A was followed with 1.31 g of 3-methyl-6-hepten-1-ol and 1.81 g of triethylsilyl chloride using DMAP. Silica gel chromatography (hexane only to hexane:EtOAc = 100:1) of the crude material afforded 2.10 g of **1q** (85% yield) as a colorless oil. IR (neat): 3078 w, 2957 s, 2910 s, 2879 s, 2734 w, 1641 w, 1460 m, 1415 w, 1379 w, 1239 w, 1097 s, 1010 m, 910 m 804 w, 668 w, 637 w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (q, *J* = 8.0 Hz, 6H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 8 Hz, 9H), 1.17-1.26 (m, 1H), 1.31-1.45 (m, 2H), 1.51-1.62 (m, 2H), 1.98-2.14 (m, 2H), 3.58-3.69 (m, 2H), 4.91-5.03 (m, 2H), 5.76-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.8, 19.5, 29.1, 31.3, 36.3, 39.9, 61.1, 114.1, 139.2; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{31}OSi$ 243.2144; Found 243.2132.

Silyl ether (*E*)-1r. General Procedure A was followed with 1.04 g of (*E*)-5-decen-1-ol and 1.38 g of triethylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 150:1) of the crude material afforded 1.00 g of **1r** (56% yield) as a colorless oil. IR (neat): 2957 s, 2935 s, 2876 s, 1700 w, 1653 w, 1457 w, 1414 w, 1386 w, 1240 w, 1103 s, 1007 m, 967 m, 802 w, 740 s, 677 s, 668 w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (q, 8.0 Hz, 6H), 0.89 (d, 7.2 Hz, 3H), 0.96 (t, 8.0 Hz, 9H), 1.28-1.42 (m, 6H), 1.50-1.57 (m, 2H), 1.97-2.01 (m, 4H), 3.60 (t, *J* = 6.8 Hz, 2H), 5.34-5.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.8, 13.9, 22.2, 25.8, 31.8, 32.26, 32.35,

32.4, 62.8, 130.0, 130.6; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2451.

Silyl ether (*Z*)-1r. (*Z*)-5-decen-1-ol was prepared following the procedure reported by Singh et al.[20] General Procedure A was followed with 259 mg of (*Z*)-5-decen-1-ol and 316 mg of triethylsilyl chloride using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 320 mg of **1r** (72% yield) as a colorless oil. IR (neat): 3005 s, 2955 s, 2934 s, 2876 s, 2733 w, 1654 w, 1458 m, 1414 m, 1381 w, 1238 m, 1178 w, 1102 s, 1014 m, 976 m, 893 w, 853 w, 795 m, 776 m, 742 s, 672 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.60 (q, 8.0 Hz, 6H), 0.88-0.91 (m, 3H), 0.96 (t, 8.0 Hz, 9H), 1.30-1.34 (m, 4H), 1.36-1.43 (m, 2H), 1.51-1.58 (m, 2H), 2.00-2.07 (m, 4H), 3.60 (t, *J* = 6.6 Hz, 2H), 5.31-5.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.8, 14.0, 22.3, 26.0, 26.93, 26.97, 31.9, 32.5, 62.8, 129.6, 130.1; HRMS (DART-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2459.

Silyl ether 1s. General Procedure A was followed with 2.29 g of 5-methyl-4-hexen-1-ol and 2.87 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane:EtOAc = 100:1) of the crude material afforded 4.66 g of **1s** (86% yield) as a colorless oil. IR (neat): 2942 s, 2893 m, 2867 s, 1464 m, 1381 w, 1249 w, 1104 m, 1067 w, 1013 w, 996 w, 882 m, 796 w, 720 w, 682 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.99-1.13 (m, 21H), 1.53-1.59 (m, 2H), 1.60 (s, 3H), 1.69 (s, 3H), 2.05 (q, *J* = 7.2 Hz, 2H), 3.67 (t, *J* = 6.4Hz, 2H), 5.11-5.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 17.6, 18.0, 24.3, 25.7, 33.2, 62.9, 124.3, 131.6; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2454.

Silyl ether 1t. General Procedure A was followed with 4.73 g of 3,7-dimethyl-6-octen-1-ol and 6.46 g of triisopropylsilyl chloride using DMAP. Silica gel chromatography (hexane only) of the crude material afforded 4.93 g of **1t** (52% yield) as a colorless oil. IR (neat): 2959 s, 2942 s, 2926

s, 2867 s, 2725 w, 1463 m, 1380 m, 1247 w, 1103 s, 1070 m, 1012 w, 996 w, 918 w, 883 m, 738 w, 681 m, 658 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, *J* = 6.8 Hz, 3H), 1.03-1.23 (m, 22H), 1.29-1.40 (m, 2H), 1.55-1.63 (m, 2H), 1.60 (s, 3H), 1.68 (s, 3H), 1.90-2.05 (m, 2H), 3.66-3.77 (m, 2H), 5.08-5.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 17.6, 18.0, 19.7, 25.5, 25.7, 29.1, 37.2, 40.1, 61.7, 124.9, 131.0; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{41}OSi$ 313.2927; Found 313.2929.

General Procedure B for Preparation of Silyl Ethers 1i-k. Alkenyl esters were prepared following the procedure reported by Riepl et al.[21] To a suspension of magnesium (2 equiv) in THF (ca. 2 mL per 1 mmol of bromoalkane) at rt, was slowly added the bromoalkane (2 equiv). The reaction mixture was refluxed for 30 min and cooled to rt to form a solution of a Grignard reagent.

In a separate flask, CuI (2 equiv) was suspended in THF (ca. 1 mL per 1 mmol of CuI) and cooled to -78 °C. A solution of methyllithium (1.0 M in Et_2O, 2 equiv) was slowly added to the suspension via a syringe. The resulting mixture was stirred at -78 °C for 1 h and allowed to warm to 0 °C to form an orange suspension, which was then cooled to -78 °C. The aforementioned solution of Grignard reagent was then slowly added to the mixture via a cannula. The mixture was stirred at -78 °C for 1 h and then allowed to warm to 0 ºC to form a purple suspension. The mixture was again cooled to -78 °C, and a solution of methyl 11-iodoundecanoate (1 equiv) in THF (ca. 4 mL per 1 mmol of ester) was added to the mixture via a cannula. The reaction mixture was stirred at -78 °C for 1 h and then at room temperature for 2 h, and a saturated aqueous solution of NH_4Cl and Et_2O were added to the resulting mixture. The mixture was filtered through a pad of Celite and the filter cake was washed with Et_2O. The filtrate was extracted three times with Et_2O. The combined organic portions were washed with brine, dried over $MgSO_4$, filtered and concentrated.

Silica gel column chromatography (hexane:EtOAc = 30:1) of the crude material afforded the corresponding alkenyl ester that was used without further purification.

To a solution of the alkenyl ester in THF (2 mL per 1 mmol of ester) at 0 °C, was slowly added a solution of DIBAL-H (1.0 M in toluene, 2.2 equiv), and then allowed to warm to room temperature. The mixture was stirred for 14 h, and then a 15% aqueous solution of NaOH (0.1 mL per 1 mmol of ester) was slowly added to the reaction mixture. Et_2O (0.2 mL per 1 mmol of ester) and water (0.3 mL per 1 mmol of ester) were added to the mixture, which was then warm to room temperature. The mixture was dried over $MgSO_4$ and filtered through a pad of Celite. The filter cake was washed with Et_2O, and the filtrate was concentrated. Silica gel column chromatography (hexane:EtOAc = 5:1) of the crude material afforded the corresponding alcohol that was used without further purification.

Preparation of silyl ethers were conducted following General Procedure A using the aforementioned alcohol. Flash column chromatography was performed using 30% $AgNO_3$/silica gel instead of 100% silica gel (hexane only) to afford the corresponding silyl ethers.

Silyl ether 1i. General Procedure B was followed with 3.27 g of methyl 11-iodoundecanoate. Silica gel chromatography of the crude material afforded 2.07 g of methyl hexadec-15-enoate containing a substantial amount of methyl dodecanoate[10] (ca. 61% yield, ca. 79% purity based on the ratio of the ^{1}H NMR peak areas) as a colorless oil. 283 mg of this mixture was used for the reduction and the silyl protection. Column chromatography of the crude material using 30% $AgNO_3$/silica gel afforded 273 mg of silyl ether **1i** (50% yield over 2 steps) as a colorless oil. IR (neat): 3077 w, 2925 s, 2854 s, 2721 w, 1642 w, 1464 m, 1382 w, 1247 w, 1107 s, 1070 m, 1013 m, 995 m, 909 m, 883 s, 792 w, 720 w, 680 m, 657 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02-1.11 (m, 21H), 1.22-1.39 (m, 22H), 1.50-1.57 (m, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 3.66 (t, *J* = 6.8

Hz, 2H), 4.91-5.02 (m, 2H), 5.76-5.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 25.8, 28.9, 29.2, 29.5-29.7 (8×1C), 33.0, 33.8, 63.5, 114.1, 139.3; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{53}OSi$ 397.3866; Found 397.3877.

Silyl ether 1j. General Procedure B was followed with 2.97 g of methyl 11-iodoundecanoate. Silica gel chromatography of the crude material afforded 1.56 g of methyl methyl henicos-20-enoate containing a substantial amount of methyl dodecanoate[10] (ca. 46% yield, ca. 86% purity based on the ratio of the ^{1}H NMR peak areas) as a white solid. 319 mg of this mixture was used for the reduction and the silyl protection. Column chromatography of the crude material using 30% $AgNO_3$/silica gel afforded 363 mg of silyl ether **1j** (43% yield over 2 steps) as a colorless oil. IR (neat): 3077 w, 2924 s, 2854 s, 2721 w, 1823 w, 1642 w, 1464 s, 1382 w, 1367 w, 1248 w, 1107 s, 1070 m, 1014 m, 995 m, 909 m, 883 s, 791 w, 721 w, 681 s, 658 m, 640 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99-1.15 (m, 21H), 1.21-1.39 (m, 30H), 1.50-1.57 (m, 2H), 2.04 (q, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 4.91-5.02 (m, 2H), 5.76-5.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 25.8, 29.0, 29.2, 29.5-29.7 (12×1C), 33.1, 33.8, 63.5, 114.1, 139.3; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{61}OSi$ 453.4492; Found 453.4487.

Silyl ether 1k. General Procedure B was followed with 1.68 g of methyl 11-iodoundecanoate. Silica gel chromatography of the crude material afforded 1.50 g of methyl tricos-22-enoate containing a substantial amount of methyl dodecanoate[10] (ca. 62% yield, ca. 75% purity calculated by NMR peak area) as a white solid. 346 mg of this mixture was used for the reduction and the silyl protection. Column chromatography of the crude material using 30% $AgNO_3$/silica gel afforded 127 mg of silyl ether **1k** (22% yield over 2 steps) as a colorless oil. IR (neat): 3077 w, 2925 s, 2854 s, 2726 w, 1821 w, 1641 w, 1465 s, 1384 w, 1366 w, 1301 w, 1247 w, 1107 s, 1070 m, 1012 w, 994 m, 909 m, 882 m, 791 w, 719 w, 681m, 658 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 1.01-1.13 (m, 21H), 1.21-1.39 (m, 34H), 1.50-1.56 (m, 2H), 2.04 (q, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 4.91-5.02 (m, 2H), 5.76-5.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 18.0, 25.8, 29.0, 29.2, 29.5-29.7 (14×1C), 33.1, 33.8, 63.5, 114.1, 139.3; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{65}OSi$ 481.4805; Found 481.4793.

Preparation of Terminal Alkene Possessing an Internal Alkene Moiety 1u. 6-(4-Methoxyphenylmethoxy)-1-hexanal[22] and (*E*)-3-penten-1-ol[23] were prepared following the procedures reported in literature.

9-(4-Methoxyphenylmethoxy)-4-triethylsiloxy-1-nonene. The Grignard reaction[24] and the TES-protection of the alcohol[25] were carried out by procedures similar to those reported in literature. To a solution of 6-(4-methoxyphenylmethoxy)-1-hexanal (4.82 g, 20.4 mmol) in Et_2O (100 mL) was added allyl magnesium bromide (1.0 M in Et_2O, 50 mL) at -78 ºC. The reaction mixture was stirred at room temperature for 1.5 h. A saturated solution of ammonium chloride was added to the mixture at 0 ºC The organic layer was separated and the aqueous layer was extracted three times with Et_2O. The combined organic portions were dried over Na_2SO_4 and the volatile materials were removed in vacuo to afford 9-(4-methoxyphenylmethoxy)-1-nonen-4-ol, which was used in the next step without further purification.

To a solution of 9-(4-methoxyphenylmethoxy)-1-nonen-4-ol in CH_2Cl_2 (100 mL) were added imidazole (4.50 g, 66.1 mmol) and TESCl (5.50 mL, 32.8 mmol) at 0 ºC, and the reaction mixture was stirred at room temperature for 2.5 h. A saturated aqueous solution of $NaHCO_3$ was added to the resulting mixture, which was then extracted with EtOAc. The combined organic portions were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Silica gel column chromatography (hexane:EtOAc = 20:1 to 10:1) of the crude material afforded 2.67 g of 9-(4-methoxyphenylmethoxy)-4-triethylsiloxy-1-nonene (6.79 mmol, 33% yield over 2 steps) as a

colorless oil: IR (neat): 3074 w, 2938 s, 2913 s, 2876 s, 1640 w, 1613 m, 1586 w, 1515 s, 1461 m, 1415 w, 1362 w, 1302 w, 1248 s, 1173 w, 1097 s, 1042 m, 1005 m, 911 w, 833 w, 742 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.59 (q, *J* = 8.0 Hz, 6H), 0.95 (t, *J* = 8.0 Hz, 9H), 1.24-1.49 (m, 6H), 1.56-1.63 (m, 2H), 2.20 (t, *J* = 6.0 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.68 (quin, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 4.43 (s, 2H), 5.01 (s, 1H), 5.04 (d, *J* = 7.2 Hz, 1H), 5.75-5.86 (m, 1H), 6.88 (d, *J* = 9.2 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.0, 6.9, 25.2, 26.3, 29.8, 36.8, 42.0, 55.2, 70.1, 71.9, 72.5, 113.7, 116.6, 129.2, 130.8, 135.3, 159.1; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{41}O_3Si$ 393.2825; Found 393.2817.

9-Iodo-4-triethylsiloxy-1-nonene. The PMB-deprotection with DDQ[14] and the conversion to the alkyl iodide[26] were carried out by procedures similar to those reported in literature. To a solution of 9-(4-methoxyphenylmethoxy)-4-triethylsiloxy-1-nonene (7.06 g, 18.0 mmol) in 110 mL (10:1, v/v) of CH_2Cl_2/pH 7 buffer (NaH_2PO_4/Na_2HPO_4) at 0 ºC was added DDQ (5.00 g, 22.0 mmol), and the reaction mixture was stirred at room temperature for 30 min. A saturated aqueous solution of $NaHCO_3$ was added to the mixture. Insoluble materials were filtered off, and the filtrate was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. Column chromatography of the crude material on silica gel (hexane:EtOAc = 5:1, then again with benzene:EtOAc = 8:1 to 3:1) afforded 3.00 g of 6-triethylsiloxy-8-nonen-1-ol (11.0 mmol, 61% yield).

To a solution of 6-triethylsiloxy-8-nonen-1-ol (3.00 g, 11.0 mmol) in benzene (75 mL) were added imidazole (1.36 g, 20.0 mmol), PPh_3 (4.30 g, 16.4 mmol) and I_2 (4.20 g, 16.5 mmol). The reaction mixture was stirred at room temperature for 30 min. A saturated aqueous solution of Na_2SO_3 was added to the mixture, which was then diluted with ether. The organic layer was separated and washed with water and then with brine. The resulting solution was dried over

Na_2SO_4, filtered, and concentrated. Silica gel column chromatography of the crude material (hexane:EtOAc = 50:1) afforded 628 mg of 9-iodo-4-triethylsiloxy-1-nonene (1.64 mmol, 9% yield over 2 steps) as a pale brown oil: IR (neat): 3075 w, 2953 s, 2934 s, 2912 s, 2875 s, 1640 w, 1461 m, 1431 w, 1415 w, 1364 w, 1238 m, 1202 w, 1084 m, 1008 m, 913 m, 741 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.60 (q , *J* = 8.0 Hz, 6H) , 0.96 (t, *J* = 8.0 Hz, 9H), 1.27-1.48 (m, 6H), 1.83 (quin, *J* = 7.2 Hz, 2H), 2.19-2.23 (m, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 3.69 (quin, *J* = 6.0 Hz, 1H), 5.02-5.07 (m, 2H), 5.75-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.0, 6.9, 7.1, 24.3, 30.6, 33.5, 36.6, 42.0, 71.8, 116.8, 135.2; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{32}IOSi$ 383.1267; Found 383.1251.

Dimethyl (*E*)-2-(3-penten-1-yl)malonate: To a solution of (*E*)-3-penten-1-ol (2.32 g, 27.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added pyridine (4.3 mL, 53 mmol), and MsCl (3.4 mL, 44 mmol). The reaction mixture was stirred at 0 °C for 1.5 h. Water was added to the mixture, which was then extracted with CH_2Cl_2. The organic layer was washed with a 2 M hydrochloric acid, a saturated aqueous solution of $NaHCO_3$, and brine. The resulting solution was dried over Na_2SO_4, and concentrated. Volatile materials were further removed in vacuo to afford 4.85 g of (*E*)-3-penten-1-yl methanesulfonate, which was used in the next step without further purification.

A 200 mL three-necked flask was charged with NaH (60% oil suspension, 1.51 g, 37.8 mmol), which was washed three times with hexane, and THF (60 mL). Dimethylmalonate (5.35 g, 40.5 mmol) was added to the suspension at 0 °C. The mixture was gradually warmed to room temperature and stirred for 30 min. (*E*)-3-Penten-1-yl methanesulfonate (4.85 g, 29.5 mmol) was added dropwise to the mixture, and the reaction mixture was refluxed for 14 h. A saturated aqueous solution of ammonium chloride was introduced to the mixture, which was then extracted three times with Et_2O. The combined organic portions were washed with brine, quickly dried over

Na_2SO_4, filtered, and concentrated. Silica gel column chromatography (hexane:EtOAc = 7:1 to 5:1) of the crude material afforded 3.89 g of alkylated dimethyl (*E*)-2-(3-penten-1-yl)malonate (19.4 mmol, 72% yield over 2 steps) as a colorless oil. The analytical data of dimethyl (*E*)-2-(3-penten-1-yl)malonate are in good agreement with those reported in literature.[27]

Dimethyl 2-{(3*E*)-3-penten-1-yl}-2-{6-(triethylsiloxy)-8-nonen-1-yl}malonate (1u). A 200 mL three-necked flask was charged with NaH (60% oil suspension, 160 mg, 4.00 mmol), which was washed three times with hexane, and THF (40 mL). Dimethyl (*E*)-2-(3-penten-1-yl)malonate (815 mg, 4.07 mmol) was added to the suspension at 0 °C. The mixture was gradually warmed to room temperature and stirred for 1 h. 9-Iodo-4-triethylsiloxy-1-nonene (1.56 g, 4.08 mmol) was added dropwise to the mixture, and the reaction mixture was refluxed for 14 h. A saturated aqueous solution of ammonium chloride was introduced to the mixture, which was then extracted twice with Et_2O. The combined organic portions were washed with brine, quickly dried over $MgSO_4$, filtered, and concentrated. Silica gel column chromatography (hexane:EtOAc = 50:1 to 20:1) of the crude material afforded 1.47 g of **1u** (3.22 mmol, 79% yield) as a colorless oil: IR (neat): 3076 w, 2954 s, 2877 m, 1736 s, 1458 m, 1436 m, 1241 m, 1199 m, 1127 w, 1006 w, 965 w, 912 w, 740 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 0.59 (q, *J* = 6.0 Hz, 6H), 0.96 (t, *J* = 6.0 Hz, 9H), 1.09-1.17 (m, 2H), 1.24-1.31 (m, 3H), 1.33-1.46 (m, 3H), 1.63 (d, *J* = 6.0 Hz, 3H), 1.82-1.96 (m, 6H), 2.20 (t, *J* = 6.4 Hz, 2H), 3.64-3.68 (m, 1H), 3.70 (s, 6H), 5.01 (s, 1H), 5.03-5.06 (m, 1H), 5.34-5.49 (m, 2H), 5.75-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.0, 6.9, 17.9, 24.0, 25.1, 27.2, 29.9, 32.2, 32.4, 36.7, 42.0, 52.2, 57.3, 71.9, 116.7, 125.6, 130.0, 135.2, 172.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{25}H_{47}O_5Si$ 455.3193; Found 455.3184.

Isomerization of Terminal Alkene 1a to Enol Ether 3a. To a Schlenk flask charged with of MS 4A (2.5 g) was added 1,2-dichloloethane (25 mL), alkenyl ether **1a** (105 mg, 0.494 mmol),

palladium complex **2a** (4.2 mg, 0.012 mmol), and $NaBAr^f_4$ (13.3 mg, 0.015 mmol), and the mixture was stirred at 0 ºC for 3 h. The resulting mixture was passed through a short column of silica gel (hexane:EtOAc = 10:1) and concentrated. Silica gel column chromatography (hexane:$CHCl_3$ = 5:1) of the crude material afforded 12.0 mg (11% yield) of **(*E*)-3a** and 38.6 mg (37% yield) of **(*Z*)-3a** as a colorless oil (48% combined yield, *E*/*Z* = 24/76). **(*E*)-3a**: IR (neat): 3360 w, 3077 w, 2958 s, 2927 s, 2856 s, 2795 m, 2737 w, 1820 w, 1641 m, 1465 m, 1415 w, 1375 m, 1303 w, 1258 w, 1233 w, 1117 s, 991 m, 909 s, 845 w, 722 w, 640 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.6 Hz, 3 H), 1.26-1.30 (m, 12 H), 1.35-1.44 (m, 2H), 1.57-1.65 (m, 2H), 1.89 (q, *J* = 6.8 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 4.76 (dt, *J* = 12.6 Hz, 7.2Hz, 1H), 6.22 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.1, 19.2, 22.7, 27.8, 29.0, 29.3, 29.5, 30.8, 31.4, 31.9, 68.9, 104.2, 146.1; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{29}O$ 213.2218; Found 213.2213. The analytical data of **(*Z*)-3a** are in good agreement with those reported in literature.[28]

General Procedure C for Isomerization of Alkenes to Silyl Enol Ethers. To a Schlenk flask charged with MS 4A (2.5 g) was added 1,2-dichloroethane (25 mL), silyl ether **1** (0.5 mmol), palladium complex **2a** (4.2 mg, 0.012 mmol), and $NaBAr^f_4$ (13.3 mg, 0.015 mmol), and the mixture was stirred at 0 ºC or 40 ºC for 3 h. The resulting mixture was passed through a short column of silica gel (hexane:EtOAc = 10:1) and concentrated. Silica gel column chromatography of the crude material afforded silyl enol ether product **3**.

Silyl enol ether 3b. The general procedure C was followed with 135 mg (0.499 mmol) of **1b**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 26.4 mg (20% yield) of isomerization product **(*E*)-3b** and 77.6 mg (58%

yield) of **(*Z*)-3b** as a colorless oil (77% combined yield, *E*/*Z* = 25/75). **(*E*)-3b**: IR (neat): 3036 w, 2956 s, 2925 s, 2877 m, 2854 m, 1663 m, 1461 w, 1239 w, 1163 s, 1007 w, 921 w, 826 w, 745 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.66 (q, *J* = 8.0 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.26-1.31 (m, 12H), 1.86 (q, *J* = 6.8 Hz, 2H), 4.99 (dt, *J* = 11.6 Hz, 7.2 Hz, 1H), 6.22 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.5, 14.1, 22.7, 27.3, 29.0, 29.3, 29.4, 30.4, 31.9, 111.7, 139.8; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi_1$ 271.2457; Found 271.2456. **(*Z*)-3b**: IR (neat): 3030 w, 2957 s, 2925 s, 2877 m, 2855 m, 1656 m, 1460 w, 1400 w, 1261 m, 1241 m, 1136 w, 1093 w, 1008 m, 825 w, 743 s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65 (q, *J* = 8.0 Hz, 6H), 0.88 (t, *J* = 6.4 Hz, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.27-1.34 (m, 12H), 2.08 (q, *J* = 6.4 Hz, 2H), 4.44 (td, *J* = 7.2 Hz, 6.0 Hz, 1H), 6.19 (dt, *J* = 6.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.5, 14.1, 22.7, 23.5, 29.31, 29.33, 29.5, 29.7, 31.9, 111.0, 138.2; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2456.

Silyl enol ether 3c. The general procedure C was followed with 197 mg (0.499 mmol) of **1c**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane:$CHCl_3$ = 10:1) of the crude material afforded 150 mg (76% yield) of a mixture of *E*/*Z* isomers of **3c** as a colorless oil (*E*/*Z* = 15/85). IR (neat): 3072 w, 3049 w, 3032 w, 2957 s, 2928 s, 2856 s, 1956 w, 1887 w, 1820 w, 1656 m, 1590 w, 1471 m, 1428 m, 1397 w, 1362 w, 1258 m, 1133 m, 1113 s, 1095 s, 1008 w, 938 w, 822 m, 741 m, 700 s, 634 m, 618 w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85-0.90 (m, 3H, *E*+*Z*), 1.06 (s, 9H, *E*), 1.08 (s, 9H *Z*), 1.20-1.41 (m, 12H, *E*+*Z*), 1.80 (q, *J* = 7.2 Hz, 2H, *E*), 2.24 (q, *J* = 7.2 Hz, 2H, *Z*), 4.44-4.49 (m, 1H, *Z*), 5.05-5.12 (m, 1H, *E*), 6.16-6.18 (m, 1H, *Z*), 6.21-6.25 (m, 1H, *E*), 7.35-7.45 (m, 6H, *E*+*Z*), 7.66-7.70 (m, 4H, *E*+*Z*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11 (*E*), 14.14 (*Z*), 19.2 (*E*), 19.3 (*Z*), 22.68 (*E*), 22.71 (*Z*), 23.8 (*Z*), 26.5 (*E*+*Z*), 27.2

(*E*), 28.9 (*E*), 29.31 (*E*), 29.38 (*Z*), 29.43 (*E*+*Z*), 29.6 (*Z*), 29.7 (*Z*), 30.3 (*E*), 31.88 (*E*), 31.93 (*Z*), 110.7 (*Z*), 112.0 (*E*), 127.67 (*E*), 127.71 (*Z*), 129.76 (*E*), 129.81 (*Z*), 133.06 (*Z*), 133.11 (*E*), 135.4 (*Z*), 135.5 (*E*), 138.7 (*Z*), 140.2 (*E*); HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{39}OSi$ 395.2770; Found 395.2781.

Silyl enol ether 3d. The general procedure C was followed with 134 mg (0.495 mmol) of **1d**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 30.7 mg (23% yield) of **(*E*)-3d** and 80.0 mg (60% yield) of **(*Z*)-3d** as a colorless oil (83% combined yield, *E*/*Z* = 28/72). **(*E*)-3d**: IR (neat): 3031 w, 2957 s, 2926 s, 2856 m, 1660 m, 1464 w, 1256 w, 1163 m, 1093 w, 1006 w, 922 w, 839 m, 782 w, 742 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.12 (s, 6H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.92 (s, 9H), 1.26-1.30 (m, 12H), 1.86 (q, *J* = 6.8 Hz, 2H), 4.98 (dt, *J* = 12.4 Hz, 7.6 Hz, 1H), 6.21 (dt, *J* = 12.0 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.2, 14.1, 18.4, 22.7, 25.7, 27.3, 29.0, 29.3, 29.4, 30.4, 31.9, 111.7, 140.0; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2455. **(*Z*)-3d**: IR (neat): 3031 w, 2957 s, 2927 s, 2856 s, 1657 m, 1464 w, 1401 w, 1257 m, 1135 w, 1094 m, 1007 w, 838 m, 781 w, 743 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.12 (s, 6H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.92 (s, 9H), 1.27-1.34 (m, 12H), 2.04-2.10 (m, 2H), 4.44 (td, *J* = 7.2 Hz, 6.4 Hz, 1H), 6.16 (dt, *J* = 6.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.4, 14.1, 18.3, 22.7, 23.6, 25.6, 29.32, 29.34, 29.5, 29.7, 31.9, 110.9, 138.3; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2455.

Silyl enol ether 3e. The general procedure C was followed with 157 mg (0.502 mmol) of **1e**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 36.9 mg (24% yield) of **(*E*)-3e** and 105 mg (67% yield) of **(*Z*)-3e** as a colorless oil (90% combined yield, *E*/*Z* = 26/74). **(*E*)-3e**: IR (neat): 3034 w, 2958 s, 2925 s, 2867

s, 1664 m, 1464 m, 1384 w, 1259 w, 1169 s, 1070 w, 1016 w, 996 w, 921 m, 882 m, 806 m, 687 m, 661 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.06-1.17 (m, 21H), 1.23-1.30 (m, 12H), 1.87 (q, *J* = 7.2 Hz, 2H), 4.99 (dt, *J* = 11.6 Hz, 7.2 Hz, 1H), 6.30 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.8, 22.7, 27.2, 29.0, 29.3, 29.4, 30.5, 31.9, 111.3, 140.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{41}OSi$ 313.2927; Found 313.2924. **(*Z*)-3e**: IR (neat): 3032 w, 2925 s, 2867 s, 1656 m, 1465 m, 1401 w, 1260 m, 1135 s, 1097 m, 1066 w, 1014 w, 995 w, 883 m, 798 w, 744 w, 684 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.05-1.18 (m, 21H), 1.21-1.35 (m, 12H), 2.09 (q, *J* = 6.8 Hz, 2H), 4.39 (td, *J* = 7.2 Hz, 6.4 Hz, 1H), 6.26 (dt, *J* = 6.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.7, 22.7, 23.6, 29.3, 29.4, 29.5, 29.7, 31.9, 110.0, 138.9; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{41}OSi$ 313.2927; Found 313.2921.

Silyl enol ether 3f. The general procedure C was followed with 124 mg (0.511 mmol) of **1f**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 28.0 mg (23% yield) of **(*E*)-3f** and 79.4 mg (64% yield) of **(*Z*)-3f** as a colorless oil (87% combined yield, *E*/*Z* = 26/74). **(*E*)-3f**: IR (neat): 2958 s, 2945 s, 2894 m, 2868 s, 1731 w, 1663 m, 1465 m, 1384 w, 1256 w, 1173 s, 1014 w, 921 w, 883 m, 810 w, 737 w, 684 m, 668 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.04-1.19 (m, 21H), 1.34 (sext, *J* = 7.2 Hz, 2H), 1.83-1.88 (m, 2H), 5.00 (dt, *J* = 11.7 Hz, 7.3 Hz, 1H), 6.30 (d, *J* = 11.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 13.6, 17.7, 23.5, 29.4, 111.0, 140.6; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{31}OSi$ 243.2144; Found 243.2143. **(*Z*)-3f**: IR (neat): 3034 w, 2959 s, 2945 s, 2894 m, 2868 s, 1734 w, 1700 w, 1696 w, 1685 w, 1675 w, 1653 s, 1635 w, 1465 m, 1437 w, 1419 w, 1399 w, 1255 m, 1227 w, 1144 m, 1087 s, 1071 m, 1015 w, 996 w, 919 w, 883 s, 812 w, 741 w, 692 m, 682 w, 627 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.3

Hz, 3H), 1.05-1.26 (m, 21H), 1.36 (sext, *J* = 7.3 Hz, 2H), 2.05-2.11 (m, 2H), 4.39 (td, *J* = 7.3 Hz, 5.9 Hz, 1H), 6.28 (d, *J* = 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 13.9, 17.7, 22.8, 25.7, 109.8, 139.0; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{31}OSi$ 243.2144; Found 243.2143.

Silyl enol ether 3g. The general procedure C was followed with 129 mg (0.503 mmol) of **1g**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 30.2 mg (23% yield) of **(*E*)-3g** and 84.4 mg (65% yield) of **(*Z*)-3g** as a colorless oil (89% combined yield, *E*/*Z* = 26/74). The analytical data for this product are in good agreement with those reported in literature.[29]

Silyl enol ether 3h. The general procedure C was followed with 151 mg (0.506 mmol) of **1h**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 35.4 mg (23% yield) of **(*E*)-3h** and 101 mg (67% yield) of **(*Z*)-3h** as a colorless oil (90% combined yield, *E*/*Z* = 26/74). **(*E*)-3h**: IR (neat): 3034 w, 2924 s, 2867 s, 2729 w, 1735 w, 1662 s, 1464 s, 1384 m, 1368 w, 1259 m, 1168 s, 1071 m, 1015 m, 996 m, 922 m, 883 s, 801 m, 685 s, 662 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.07-1.19 (m, 21H), 1.26-1.30 (m, 10H), 1.87 (q, *J* = 6.6 Hz, 2H), 5.00 (dt, *J* = 12.0 Hz, 7.6 Hz, 1H), 6.30 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.7, 22.7, 27.2, 29.0, 29.1, 30.5, 31.9, 111.3, 140.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{39}OSi$ 299.2770; Found 299.2759. **(*Z*)-3h**: IR (neat): 3032 w, 2925 s, 2867 s, 2727 w, 1653 s, 1464 s, 1401 m, 1382 w, 1266 m, 1135 m, 1096 s, 1071 m, 1015 m, 996 m, 920 w, 883 s, 809 w, 743 m, 685 s, 668 s, 632 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.07-1.19 (m, 21H), 1.27-1.30 (m, 10H), 2.09 (q, *J* = 6.8 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 1H), 6.26 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 14.1, 17.7, 22.7, 23.5, 29.2, 29.3, 29.7, 31.9, 110.0, 138.9; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{39}OSi$ 299.2770; Found 299.2769.

Silyl enol ether 3i. The general procedure C was followed with 200 mg (0.504 mmol) of **1i**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 45.0 mg (23% yield) of **(*E*)-3i** and 126 mg (63% yield) of **(*Z*)-3i** as a colorless oil (86% combined yield, *E*/*Z* = 26/74). **(*E*)-3i**: IR (neat): 3034 w, 2925 s, 2854 s, 2725 w, 1663 w, 1465 m, 1382 w, 1254 w, 1171 m, 1106 w, 1013 w, 997 w, 921 w, 883 m, 797 w, 684 m, 661 w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.02-1.19 (m, 21H), 1.25-1.32 (m, 24H), 1.87 (q, *J* = 6.8 Hz, 2H), 4.99 (dt, *J* = 12.0 Hz, 7.6 Hz, 1H), 6.30 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.8, 22.7, 27.2, 29.1, 29.4, 29.5, 29.6-29.7 (6×1C), 30.5, 31.9, 111.3, 140.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{53}OSi$ 397.3866; Found 397.3860. **(*Z*)-3i**: IR (neat): 3034 w, 2925 s, 2854 s, 2725 w, 1731 w, 1655 m, 1465 m, 1401 w, 1382 w, 1260 w, 1133 w, 1103 m, 996 m, 921 w, 883 m, 804 w, 744 w, 685 m, 668 w, 625 w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.07-1.19 (m, 21H), 1.22-1.30 (m, 24H), 2.09 (q, *J* = 6.4 Hz, 2H), 4.39 (q, *J* = 6.0 Hz, 1H), 6.26 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.7, 22.7, 23.5, 29.4 (2×1C), 29.5, 29.7 (7×1C), 31.9, 110.0, 138.9; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{53}OSi$ 397.3866; Found 397.3858.

Silyl enol ether 3j. The general procedure C was followed with 227 mg (0.501 mmol) of **1j**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 50.8 mg (22% yield) of **(*E*)-3j** and 139 mg (61% yield) of **(*Z*)-3j** as a colorless oil (84% combined yield, *E*/*Z* = 27/73). **(*E*)-3j**: IR (neat): 3030 w, 2958 m, 2924 s, 2853 s, 2725 w, 1731 w, 1663 w, 1465 m, 1384 w, 1366 w, 1259 w, 1170 m, 1070 w, 1013 w, 996 w, 921 w, 883 m, 804 w, 721 w, 684 w, 668 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.05-1.19 (m, 21H), 1.21-1.32 (m, 32H), 1.87 (q, *J* = 6.8 Hz, 2H), 4.99 (dt, *J* = 11.6 Hz, 7.6 Hz, 1H), 6.29 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.8, 22.7, 27.2,

29.1, 29.4, 29.5, 29.7 (10×1C), 30.5, 31.9, 111.3, 140.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{61}OSi$ 453.4492; Found 453.4490. **(*Z*)-3j**: IR (neat): 3031 w, 2926 s, 2856 s, 2716 w, 1732 w, 1653 m, 1464 s, 1401 w, 1384 w, 1368 w, 1249 m, 1133 m, 1095 m, 1069 m, 1015 m, 996 m, 919 w, 883 m, 802 w, 744 w, 721 w, 685 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.05-1.19 (m, 21H), 1.25-1.30 (m, 32H), 2.09 (q, *J* = 6.8 Hz, 2H), 4.39 (q, *J* = 6.4 Hz, 1H), 6.26 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.7, 22.7, 23.5, 29.4 (2×1C), 29.5, 29.7 (11×1C), 31.9, 110.0, 138.9; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{61}OSi$ 453.4492; Found 453.4488.

Silyl enol ether 3k. The general procedure C was followed with 237 mg (0.493 mmol) of **1k**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 44.9 mg (19% yield) of **(*E*)-3k** and 148 mg (62% yield) of **(*Z*)-3k** as a colorless oil (81% combined yield, *E*/*Z* = 23/77). **(*E*)-3k**: IR (neat): 3020 m, 2924 s, 2854 m, 1727 w, 1659 w, 1467 w, 1430 w, 1215 s, 1174 w, 1013 w, 928 w, 885 w, 756 s, 668 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.05-1.19 (m, 21H), 1.25-1.32 (m, 36H), 1.87 (q, *J* = 6.8 Hz, 2H), 4.99 (dt, *J* = 11.7 Hz, 7.8 Hz, 1H), 6.30 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.8, 22.7, 27.3, 29.1, 29.4, 29.5, 29.7 (12×1C), 30.5, 31.9, 111.3, 140.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{65}OSi$ 481.4805; Found 481.4801. **(*Z*)-3k**: IR (neat): 3018 w, 2962 m, 2924 s, 2852 s, 1727 w, 1652 w, 1464 m, 1386 w, 1215 m, 1098 w, 1065 w, 997 w, 921 w, 883 m, 759 s, 677 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.05-1.18 (m, 21H), 1.25-1.34 (m, 36H), 2.06-2.12 (m, 2H), 4.39 (td, *J* = 7.2 Hz, 6.0 Hz, 1H), 6.26 (dt, *J* = 6.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 17.7, 22.7, 23.6, 29.4 (2×1C), 29.6, 29.7 (13×1C), 31.9, 110.1, 138.9; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{65}OSi$ 481.4805; Found 481.4801.

Silyl enol ether 3m. The general procedure C was followed with 257 mg (1.00 mmol) of **1m**, 8.5 mg of palladium complex **2a** (0.025 mmol), 26.6 mg of $NaBAr^f_4$ (0.030 mmol), 5.0 g of MS 4A, and 50 mL of 1,2-dichloroethane. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 157 mg (61% yield) of a mixture of *E*/*Z* isomers of **3m** as a colorless oil (*E*/*Z* = 15/85). IR (neat): 2957 s, 2934 s, 2876 s, 2734 w, 1718 w, 1672 m, 1460 m, 1415 w, 1378 w, 1362 w, 1333 w, 1240 w, 1184 m, 1122 m, 1097 w, 1062 w, 1007 m, 976 w, 913 w, 889 w, 859 w, 804 w, 742 s, 670 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.66 (q, *J* = 8.0 Hz, 6H, *E*), 0.67 (q, *J* = 8.0 Hz, 6H, *Z*), 0.87-0.92 (m, 6H, *E*+*Z*), 0.95-1.01 (m, 9H, *E*+*Z*), 1.25-1.37 (m, 4H, *E*+*Z*), 1.40-1.49 (m, 2H, *E*+*Z*), 1.90 (q, *J* = 7.6 Hz, 2H, *E*), 1.95-2.02 (m, 4H, *Z*), 2.05 (t, *J* = 7.6 Hz, *E*), 4.40 (t, *J* = 7.2 Hz, 1H, *Z*), 4.58 (t, *J* = 7.6 Hz, 1H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.1 (3×1C, *E*), 5.5 (3×1C, *Z*), 6.78 (3×1C, *E*), 6.80 (3×1C, *Z*), 13.7 (*E*), 13.96 (2×1C, *Z*), 14.01 (*E*), 22.3 (*Z*), 22.5 (*E*), 23.1 (*Z*), 23.8 (*E*), 27.3 (*Z*), 29.0 (*E*), 29.40 (*Z*), 29.41 (*E*), 31.0 (*E*), 36.4 (*Z*), 106.7 (*E*), 107.6 (*Z*), 150.4 (*Z*), 151.7 (*E*); HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{33}OSi$ 257.2301; Found 257.2299.

Silyl enol ether 3n. The general procedure C was followed with 273 mg (1.01 mmol) of **1n**, 8.3 mg of palladium complex **2a** (0.025 mmol), 27.0 mg of $NaBAr^f_4$ (0.030 mmol), 5.0 g of MS 4A, and 50 mL of 1,2-dichloroethane. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 66.2 mg (24% yield) of **(*E*)-3n** and 181 mg (66% yield) of **(*Z*)-3n** as a colorless oil (91% combined yield, *E*/*Z* = 27/73). **(*E*)-3n**: IR (neat): 2960 s, 2946 s, 2868 s, 1662 m, 1463 m, 1382 w, 1254 w, 1172 s, 996 w, 922 m, 883 m, 817 w, 686 m, 662 w, 654 w, 644 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.83-0.88 (m, 6H), 1.06-1.20 (m, 22H), 1.26-1.40 (m, 2H), 1.67-1.75 (m, 1H), 1.84-1.91 (m, 1H), 4.98 (dt, *J* = 11.6 Hz, 8.0Hz, 1H), 6.28 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 12.0, 17.7, 18.9, 28.9,

34.1, 35.2, 109.5, 141.1; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2456. **(*Z*)-3n**: IR (neat): 3034 w, 2960 s, 2942 s, 2868 s, 1655 m, 1651 m, 1463 m, 1402 w, 1260 m, 1140 m, 1091 s, 1014 w, 995 w, 883 m, 808 w, 770 w, 684 m, 668 m, 668 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6H), 1.05-1.19 (m, 22H), 1.31-1.41 (m, 2H), 1.91-1.98 (m, 1H), 2.07-2.14 (m, 1H), 4.39 (td, *J* = 7.2 Hz, 5.6Hz, 1H), 6.31 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 11.9, 17.7, 19.2, 29.2, 30.3, 35.1, 108.2, 139.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2446.

Silyl enol ether 3o. The general procedure C was followed with 230 mg (1.01 mmol) of **1o**, 8.4 mg of palladium complex **2a** (0.025 mmol), 26.5 mg of $NaBAr^f_4$ (0.030 mmol), 5.0 g of MS 4A, and 50 mL of 1,2-dichloroethane. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 61.3 mg (27% yield) of **(*E*)-3o** and 137 mg (60% yield) of **(*Z*)-3o** as a colorless oil (86% combined yield, *E*/*Z* = 31/69). **(*E*)-3o**: IR (neat): 3034 w, 2959 s, 2878 s, 1657 m, 1460 m, 1402 w, 1374 w, 1242 m, 1141 m, 1087 s, 1010 m, 817 w, 741 s, 694 w, 669 w, 668 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.66 (q, *J* = 8.0 Hz, 6H), 0.83-0.88 (m, 6H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.08-1.15 (m, 1H), 1.26-1.38 (m, 2H), 1.68-1.75 (m, 1H), 1.84-1.91 (m, 1H), 4.98 (dt, *J* = 11.7 Hz, 7.8 Hz, 1H), 6.20 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.5, 11.5, 18.9, 28.9, 34.2, 35.2, 110.0, 140.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{29}OSi$ 229.1988; Found 229.1994. **(*Z*)-3o**: IR (neat): 3042 w, 2957 s, 2912 m, 2878 m, 1664 m, 1651 m, 1460 w, 1414 w, 1378 w, 1238 w, 1170 s, 1017 m, 923 w, 817 m, 747 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.65 (q, *J* = 8.4 Hz, 6H), 0.85-0.89 (m, 6H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.11-1.19 (m, 1H), 1.30-1.40 (m, 2H), 1.90-1.97 (m, 1H), 2.05-2.12 (m, 1H), 4.44 (td, *J* = 7.2 Hz, 6.0 Hz, 1H), 6.24 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

4.4, 6.5, 11.6, 19.2, 29.1, 30.3, 35.1, 109.1, 138.7; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{29}OSi$ 229.1988; Found 229.1994.

Silyl enol ether 3p. The general procedure C was followed with 554 mg (1.95 mmol) of **1p**, 16.7 mg of palladium complex **2a** (0.050 mmol), 54.3 mg of $NaBAr^f_4$ (0.061 mmol), 10.0 g of MS 4A, and 100 mL of 1,2-dichloroethane. The reaction was performed at 0 °C, and silica gel column chromatography (hexane only) of the crude material afforded 153 mg (28% yield) of **(*E*)-3p** and 229 mg (41% yield) of **(*Z*)-3p** as a colorless oil (69% combined yield, *E*/*Z* = 40/60). **(*E*)-3p**: IR (neat): 3461 w, 2959 s, 2940 s, 2927 s, 2895 m, 2867 s, 1709 w, 1465 m, 1378 w, 1258 w, 1137 m, 1109 m, 1107 m, 1063 m, 1016 w, 883 m, 804 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85-0.89 (m, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.07-1.28 (m, 27H), 1.95-2.01 (m, 1H), 4.85 (dd, *J* = 12.0 Hz 8.8 Hz, 1H), 6.27 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 14.1, 18.0, 22.0, 22.7, 29.7, 32.4, 37.5, 117.7, 139.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{37}OSi$ 285.2614; Found 285.2613. The analytical data of **(*Z*)-3p** are in good agreement with those reported in literature.[30]

Silyl enol ether 3q. The general procedure C was followed with 121 mg (0.499 mmol) of **1q**. The reaction was performed at 0 °C, and silica gel column chromatography (pentane only) of the crude material afforded 20.3 mg (17% yield) of **(*E*)-3q** and 61.2 mg (51% yield) of **(*Z*)-3q** as a colorless oil (67% combined yield, *E*/*Z* = 25/75). **(*E*)-3q**: IR (neat): 3022 w, 2957 s, 2926 m, 2877 m, 1656 m, 1459 w, 1403 w, 1253 m, 1161 w, 1083 s, 1008 m, 881 w, 746 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.65 (q, *J* = 8.0 Hz, 6H), 0.86-0.89 (m, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.16-1.35 (m, 6H), 2.63-2.70 (m, 1H), 4.22 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 6.15 (dd, *J* = 6.0 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.5, 14.1, 21.3, 22.8, 28.3, 29.7, 37.4, 117.2, 137.1; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{31}OSi$ 243.2144; Found 243.2139.

(*Z*)-3q: IR (neat): 2953 m, 2923 s, 2851 m, 1739 w, 1459 w, 1378 w, 1260 w, 1094 w, 1018 w, 800 w, 741 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.66 (q, *J* = 8.0 Hz, 6H), 0.86-0.89 (m, 3H), 0.94-1.00 (m, 12H), 1.17-1.30 (m, 6H), 1.95-2.00 (m, 1H), 4.85 (dd, *J* = 12.0 Hz, 4.8 Hz, 1H), 6.20 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4, 6.5, 14.1, 22.0, 22.7, 29.6, 32.4, 37.4, 118.2, 138.7; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{31}OSi$ 243.2144; Found 243.2139.

Isomerization of 1r to 3b. The general procedure C was followed with 133 mg (0.492 mmol) of **1r**. The reaction was performed at 0 °C, and silica gel column chromatography (hexane:EtOAc = 200:1) of the crude material afforded 13.8 mg (10% yield) of **(*E*)-3b** and 64.0 mg (48% yield) of **(*Z*)-3b** as a colorless oil (58% combined yield, *E*/*Z* = 18/82).

Silyl enol ether 3s. The general procedure C was followed with 137 mg (0.506 mmol) of **1s**. The reaction was performed at 40 °C, and silica gel column chromatography (hexane only) of the crude material afforded 24.5 mg (18% yield) of **(*E*)-3s** and 83.1 mg (61% yield) of **(*Z*)-3s** as a colorless oil (79% combined yield, *E*/*Z* = 23/77). **(*E*)-3s**: IR (neat): 3034 w, 2946 s, 2868 s, 1664 s, 1467 m, 1385 w, 1367 w, 1278 w, 1173 s, 1071 w, 1015 w, 996 w, 922 m, 883 m, 818 w, 687 m, 668 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (d, *J* = 6.4 Hz, 6H), 1.07-1.23 (m, 23H), 1.55 (sept, *J* = 6.8 Hz, 1H), 1.85-1.91 (m, 2H), 4.99 (dt, *J* = 11.6 Hz, 7.2 Hz, 1H), 6.30 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 17.7, 22.5, 25.1, 27.3, 39.7, 111.4, 140.3; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2465. **(*Z*)-3s**: IR (neat): 3032 w, 2947 s, 2898 m, 2869 s, 1656 m, 1466 m, 1401 w, 1384 w, 1367 w, 1267 m, 1207 w, 1144 m, 1094 s, 1070 w, 998 w, 920 w, 883 m, 816 w, 802 w, 742 w, 684 m, 668 s, 665 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.0 Hz, 3H), 1.05-1.25 (m, 23H), 1.51-1.61 (m, 1H), 2.08-2.14 (m, 2H), 4.38 (td, *J* = 11.6 Hz, 6.0 Hz, 1H), 6.26 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 11.9, 17.7, 21.5, 22.5, 27.6, 38.9, 110.1, 138.8; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{35}OSi$ 271.2457; Found 271.2461.

Silyl enol ether 3t. The general procedure C was followed with 1.56 g (5.02 mmol) of **1t**, 42.5 mg of palladium complex **2a** (0.126 mmol), 134 mg of $NaBAr^f_4$ (0.161 mmol), 20.0 g of MS 4A, and 250 mL of 1,2-dichloroethane. The reaction was performed at 40 °C, and silica gel column chromatography (hexane only) of the crude material afforded 417 mg (27% yield) of **(*E*)-3t** and 588 mg (38% yield) of **(*Z*)-3t** as a colorless oil (64% combined yield, *E*/*Z* = 41/59). **(*E*)-3t**: IR (neat): 3033 w, 2951 s, 2927 s, 2894 s, 2868 s, 2726 w, 1662 s, 1464 m, 1384 m, 1367 m, 1278 m, 1248 w, 1175 s, 1137 m, 1071 m, 1015 m, 996 m, 922 m, 883 s, 813 w, 788 m, 686 s, 685 s, 670 m, 668 m, 568 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (d, *J* = 6.8 Hz, 6H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.07-1.32 (m, 27H), 1.50 (quin, *J* = 6.8 Hz, 1H), 1.94-2.01 (m, 1H), 4.85 (dd, *J* = 12.0 Hz, 8.8 Hz, 1H), 6.27 (d, *J* = 11.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 17.8, 22.0, 22.6 (2×1C), 25.2, 28.0, 32.5, 38.1, 39.1, 117.7, 139.4; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{41}OSi$ 313.2927; Found 313.2915. **(*Z*)-3t**: IR (neat): 3024 w, 2949 s, 2926 s, 2898 s, 2868 s, 2729 w, 1653 s, 1464 s, 1403 m, 1384 m, 1367 w, 1277 w, 1249 m, 1197 w, 1162 m, 1093 s, 1067 s, 1015 m, 996 m, 919 w, 883 s, 779 w, 756 m, 733 w, 684 m, 668 s, 640 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (d, *J* = 6.4 Hz, 6H), 0.93 (d, *J* = 6.8 Hz, 3H), 1.07-1.33 (m, 27H), 1.46-1.54 (m, 1H), 2.66-2.73 (m, 1H), 4.16 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 6.22 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 17.8, 21.3, 22.6, 22.7, 25.3, 28.0, 28.4, 37.9, 39.1, 116.2, 137.8; HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{41}OSi$ 313.2927; Found 313.2920.

Isomerization of a Terminal Alkenes in the Presence of Internal Alkenes. To a Schlenk flask charged with of MS 4A (2.5 g) was added 1,2-dichloroethane (25 mL), terminal alkene **1e** (0.25 mmol), internal alkene **1r** or **1s** (0.25 mmol), palladium complex **2a** or **2b** (0.0125 mmol) and *n*-

docosane (ca. 50 mg, internal standard for GC analysis). Using a syringe, 5 mL of the mixture was transferred to a Schlenk flask and stirred at 0 ºC. $NaBAr^f_4$ (2.7 mg, 3 μ mol) was added to the flask and the reaction mixture was stirred at 0 ºC. The resulting mixture was passed through a short column of silica gel (10:1 hexane/EtOAc) and concentrated. After dissolving the residue with hexane/EtOAc, the solution was subjected to GC analysis.

Chemoselective Isomerization of a Terminal Alkenes Possessing an Internal Alkene Moiety. To a Schlenk flask charged with of MS 4A (3.0 g) was added of 1,2-dichloroethane (30 mL), silyl ether **1u** (137 mg, 0.301 mmol), palladium complex **2a** (10.2 mg, 0.030 mmol), $NaBAr^f_4$ (32.0 mg, 0.036 mmol), and the mixture was stirred at 0 ºC for 6 h. The resulting mixture was passed through a short column of silica gel (hexane:EtOAc = 5:1) and concentrated.

To a solution of the residue in MeOH (30 mL) was added 3 drops of ca. 1% HCl/MeOH. After stirring for 1 h at room temperature, the resulting mixture was concentrated. Silica gel column chromatography (hexane:EtOAc = 5:1) of the crude material, followed by column chromatography using 30% $AgNO_3$/silica gel (hexane:EtOAc = 10:1), afforded 61.7 mg (60% yield) of ketone product **3u** as a colorless oil: IR (neat): 2954 m, 2872 w, 1735 s, 1454 w, 1435 w, 1377 w, 1243 w, 1197 w, 1127 w, 967 w, 890 w, 800 w, 728 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 7.6 Hz, 3H), 1.11-1.19 (m, 2H), 1.25-1.32 (m, 2H), 1.52-1.64 (m, 8H), 1.81-1.95 (m, 6H), 2.37 (td, J = 7.2 Hz, 2.4 Hz, 4H), 3.70 (s, 6H), 5.33-5.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 17.3, 17.9, 23.5, 23.9, 27.2, 29.4, 32.3 (2×1C), 42.6, 44.7, 52.3 (2×1C), 57.3, 125.7, 130.0, 172.2 (2×1C), 211.2; HRMS (DART-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{33}O_5$ 341.2328; Found 341.2341.

Retention of the Stereoconfiguration at the Stereocenter on the Methylene Chain. To a Schlenk flask charged with MS 4A (1.0 g) was added 1,2-dichloroethane (10 mL), silyl ether **(*S*)-1q** (0.2 mmol), palladium complex **2a** (1.7 mg, 0.005 mmol), and $NaBAr^f_4$ (5.3 mg, 0.006 mmol),

and the mixture was stirred at 0 ºC. The resulting mixture was passed through a short column of silica gel (hexane/EtOAc) and concentrated. Silica gel column chromatography (hexane only) of the crude material afforded silyl enol ether **3q**. In order to check the enantiomeric excess, **3q** was converted into dinitrobenzoate **S4** following the procedure reported by Mazet et al.[2g]

Supporting Information

Additional data for optimization of the isomerization conditions, procedures for determination of enantiomeric excesses, and ^{1}H and ^{13}C NMR spectra of new compounds as well as ^{1}H NMR spectra of known compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgements

This work was supported, in part, by JSPS KAKENHI Grant Numbers 25708019 (Grant-in-Aid for Young Scientists (A)), 15KT0069, 18H01985 (Grant-in-Aid for Scientific Research (B)), 16H01040 and 18H04271 (Precisely Designed Catalysts with Customized Scaffolding) and the Asahi Glass Foundation.

References and Notes

(1) (a) Yus, M.; Foubelo, F. Synthesis by Isomerization. *Science of Synthesis*, Georg Thieme Verlag KG: Stuttgart, 2010; Vol. 47b; pp 1067-1094. (b) Uma, R.; Crévisy, C.; Grée, R. Transposition of Allylic Alcohols into Carbonyl Compounds Mediated by Transition Metal Complexes. *Chem. Rev.* **2003**, *103*, 27-52. (c) Krompiec, S.; Krompiec, M.; Penczek, R.; Ignasiak,

H. Double bond migration in N-allylic systems catalyzed by transition metal complexes. *Coord. Chem. Rev.* **2008**, *252*, 1819-1841.

(2) (a) Matsuda, I.; Kato, T.; Sato, S.; Izumi, Y. Regiocontrolled synthesis of allylsilanes by means of rhodium(I) or iridium(I) catalyzed isomerization of olefins. *Tetrahedron Lett*. **1986**, *27*, 5747-5750. (b) Iranpoor, N.; Mottaghinejad, E. Dodecacarbonyl triiron, an efficient catalyst for photochemical isomerization of unsaturated alcohols, ethers and ester to their corresponding carbonyl compounds, enol ethers and esters. *J. Organomet. Chem*. **1992**, *423*, 399-404. (c) Wakamatsu, H.; Nishida, M.; Adachi, N.; Mori, M. Isomerization Reaction of Olefin Using $RuClH(CO)(PPh_3)_3$. *J. Org. Chem*. **2000**, *65*, 3966-3970. (d) Sergeyev, S. A.; Hesse, M. Enamides *via* Long-Distance Migration of Double Bonds. *Helv. Chim. Acta*. **2003**, *86*, 750-755. (e) Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair R.; Sharma, A. Extensive Isomerization of Alkenes Using a Bifunctional Catalyst: An Alkene Zipper. *J. Am. Chem. Soc*. **2007**, *129*, 9592-9593. (f) Larionov, E.; Lin, L.; Guénée, L.; Mazet. C. Scope and Mechanism in Palladium-Catalyzed Isomerizations of Highly Substituted Allylic, Homoallylic, and Alkenyl Alcohols. *J. Am. Chem. Soc*. **2014**, *136*, 16882-16894. (g) Lin, L.; Romano, C.; Mazet. C. Palladium-Catalyzed Long-Range Deconjugative Isomerization of Highly Substituted α,β-Unsaturated Carbonyl Compounds. *J. Am. Chem. Soc*. **2016**, *138*, 10344-10350. (h) Chuc, L. T. N.; Chen, C.-S.; Lo, W.-S.; Shen, P.-C.; Hsuan, Y.-C.; Tsai, H.-H. G.; Shieh, F.-K.; Hou, D.-R. Long-Range Olefin Isomerization Catalyzed by Palladium(0) Nanoparticles. *ACS Omega* **2017**, *2*, 698-711. (i) Kocen, A. L.; Brookhart, M.; Daugulis, O. Palladium-catalysed alkene chain-running isomerization. *Chem. Commun.* **2017**, *53*, 10010-10013. (j) Romano, C.; Mazet, C. Multicatalytic Stereoselective Synthesis of Highly Substituted Alkenes by Sequential Isomerization/Cross-Coupling Reactions. *J. Am. Chem. Soc*. **2018**, *140*, 4743-4750. (k) Ho, G.-M.; Judkele, L.; Bruffaerts, J.; Marek, I.

Metal-Catalyzed Remote Functionalization of ω-Ene Unsaturated Ethers:Towards Functionalized Vinyl Species. *Angew. Chem., Int. Ed*. **2018**, *57*, 8012-8016.

(3) (a) Franzoni, I.; Mazet, C. Recent trends in Pd-catalyzed remote functionalization of carbonyl compounds. *Org. Biomol. Chem.* **2014**, *12*, 233-241. (b) Vasseur, A.; Bruffaerts, J.; Marek, I. Remote functionalization through alkene isomerization. *Nat. Chem.* **2016**, *8*, 209-219. (c) Sommer, H.; Juliá-Hernández, F.; Martin, R.; Marek, I. Walking Metals for Remote Functionalization. *ACS Cent. Sci.* **2018**, *4*, 153-165.

(4) Our previous reports on organic synthesis via long-distance nondissociative chain walking: (a) Kochi, T.; Hamasaki, T.; Aoyama, Y.; Kawasaki, J.; Kakiuchi, F. Chain-Walking Strategy for Organic Synthesis: Catalytic Cycloisomerization of 1,n-Dienes. *J. Am. Chem. Soc.* **2012**, *134*, 16544-16547. (b) Hamasaki, T.; Aoyama, Y.; Kawasaki, J.; Kakiuchi, F.; Kochi, T. Chain Walking as a Strategy for Carbon–Carbon Bond Formation at Unreactive Sites in Organic Synthesis: Catalytic Cycloisomerization of Various 1,n-Dienes. *J. Am. Chem. Soc.* **2015**, *137*, 16163-16171. (c) Hamasaki, T.; Kakiuchi, F.; Kochi, T. Chain-walking Cycloisomerization of 1, n -Dienes Catalyzed by Pyridine–Oxazoline Palladium Catalysts and Its Application to Asymmetric Synthesis. *Chem. Lett.* **2016**, *45*, 297-299.

(5) Representative examples of organic syntheses via chain walking over more than one carbon reported by other groups: (a) Werner, E. W.; Mei, T.-S.; Burckle, A. J.; Sigman, M. S. Enantioselective Heck Arylations of Acyclic Alkenyl Alcohols Using a Redox-Relay Strategy. *Science* **2012**, *338*, 1455-1458. (b) Aspin, S.; Goutierre, A.-S.; Larini, P.; Jazzar, R.; Baudoin, O. Synthesis of Aromatic α-Aminoesters: Palladium-Catalyzed Long-Range Arylation of Primary C-H Bonds. *Angew. Chem., Int. Ed.* **2012**, *51*, 10808-10811. (c) Mei, T.-S.; Werner, E. W.; Burckle, A. J.; Sigman, M. S. Enantioselective Redox-Relay Oxidative Heck Arylations of Acyclic Alkenyl

Alcohols using Boronic Acids. *J. Am. Chem. Soc.* **2013**, *135*, 6830-6833. (d) Mei, T.-S.; Patel, H. H.; Sigman, M. S. Enantioselective construction of remote quaternary stereocentres. *Nature* **2014**, *508*, 340-344. (e) Singh, S.; Bruffaerts, J.; Vasseur, A.; Marek, I. A unique Pd-catalysed Heck arylation as a remote trigger for cyclopropane selective ring-opening. *Nat. Commun*. **2017**, *8*, 14200. (f) He, Y.; Cai, Y.; Zhu, S. Mild and Regioselective Benzylic C–H Functionalization: Ni-Catalyzed Reductive Arylation of Remote and Proximal Olefins. *J. Am. Chem. Soc.* **2017**, *139*, 1061-1064. (g) Julia-Hernandez, F.; Moragas, T.; Cornella, J.; Martin, R. Remote carboxylation of halogenated aliphatic hydrocarbons with carbon dioxide. *Nature* **2017**, *545*, 84-88. (h) Kohler, D. G.; Gockel, S. N.; Kennemur, J. L.; Waller, P. J.; Hull, K. L. Palladium-catalysed anti-Markovnikov selective oxidative amination. *Nat. Chem*. **2018**, *10*, 333-340.

(6) Olefin polymerization via nondissociative chain walking: (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **2000**, *100*, 1169-1204. (b) Johnson, L. K.; Killian, C. M.; Brookhart, M. New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and .alpha.-Olefins. *J. Am. Chem. Soc.* **1995**, *117*, 6414-6415. (c) Johnson, L. K.; Mecking, S.; Brookhart, M. Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium(II) Catalysts. *J. Am. Chem. Soc.* **1996**, *118*, 267-268. (d) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. Chain Walking: A New Strategy to Control Polymer Topology. *Science* **1999**, *283*, 2059-2062. (e) Okada, T.; Park, S.; Takeuchi, D.; Osakada, K. Pd-Catalyzed Polymerization of Dienes that Involves Chain-Walking Isomerization of the Growing Polymer End: Synthesis of Polymers Composed of Polymethylene and Five-Membered-Ring Units. *Angew. Chem., Int. Ed.* **2007**, *46*, 6141-6145. (f) Okada, T.; Takeuchi, D.; Shishido, A.; Ikeda, T.; Osakada, K. Isomerization Polymerization of 4-Alkylcyclopentenes Catalyzed by Pd Complexes: Hydrocarbon Polymers with Isotactic-Type

Stereochemistry and Liquid-Crystalline Properties. *J. Am. Chem. Soc.* **2009**, *131*, 10852-10853. (g) Takeuchi, D. Precise Isomerization Polymerization of Alkenylcyclohexanes: Stereoregular Polymers Containing Six-Membered Rings along the Polymer Chain. *J. Am. Chem. Soc.* **2011**, *133*, 11106-11109.

(7) We decided to use the term "nondissociative chain walking" for this paper instead of just "chain walking", which we used in the previous publications, because "chain walking" has often been used by other researchers to describe both mechanisms shown in Figure 1a and 1b.

(8) Involvement of the chain walking mechanism was described in the isomerization of 1-hexene to (*Z*)-2-hexene: Chen, C.; Dugan, T. R.; Brennessel, W. W.; Weix, D. J.; Holland, P. L. Z-Selective Alkene Isomerization by High-Spin Cobalt(II) Complexes. *J. Am. Chem. Soc.* **2014**, *136*, 945-955.

(9) Most of the work described here was presented in the following presentation: Yamasaki, Y.; Kakiuchi, F.; Kochi, T. Pacifichem 2015, Honolulu, HI, ORGN1036.

(10) Mazet and coworkers reported a similar result using a 2,2'-bypyridine palladium catalyst. See ref 2f.

(11) *Z*-isomers of silyl enol ethers derived from aldehydes are known to be thermodynamically more stable than *E*-isomers: (a) Fielding, A. J.; Roberts, B. P. Radical-chain isomerisation of allyl silyl ethers to silyl enol ethers in the presence of thiols as polarity reversal catalysts. *Tetrahedron Lett*. **2001**, *42*, 4061-4064. (b) Tuokko, S.; Honkala, K.; Pihko, P. M. Pd/C-Catalyzed Hydrosilylation of Enals and Enones with Triethylsilane: Conformer Populations Control the Stereoselectivity. *ACS Catal.* **2017**, *7*, 480-493.

(12) Ida, A.; Hoshiya, N.; Uenishi, J. Alkene migration to the end-terminal carbon bearing a phenyl group over a chiral siloxy carbon center in Heck reaction. *Tetrahedron* **2015**, *71*, 6442-6448.

(13) Yasumoto, K.; Nishigami, A.; Aoi, H.; Tsuchihashi, C.; Kasai, F.; Kusumi, T.; Ooi, T. Isolation and Absolute Configuration Determination of Aliphatic Sulfates as the Daphnia Kairomones Inducing Morphological Defense of a Phytoplankton—Part 2. *Chem. Pharm. Bull*. **2008**, *56*, 129-132.

(14) Li, X.; Burrell, C. E.; Staples, R. J.; Borhan, B. Absolute Configuration for 1,n-Glycols: A Nonempirical Approach to Long-Range Stereochemical Determination. *J. Am. Chem. Soc.* **2012**, *134*, 9026-9029.

(15) Ito, H.; Watanabe, A.; Sawamura M. Versatile Dehydrogenative Alcohol Silylation Catalyzed by Cu(I)−Phosphine Complex. *Org. Lett.* **2005**, *7*, 1869-1871.

(16) Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. Olefin Isomerization and Hydrosilylation Catalysis by Lewis Acidic Organofluorophosphonium Salts. *J. Am. Chem. Soc.* **2013**, *135*, 18308-18310.

(17) Matsushita, M.; Nagaoka, Y.; Hioki, H.; Fukuyama, Y.; Kodama, M. A Simple Method for the Conversion of Primary Alcohols into Terminal Olefins. *Chem. Lett.* **1996**, *25*, 1039-1040.

(18) Phukan, P.; Bauer, M.; Maier, M. E. Facile Generation of Alkenes and Dienes from Tosylates. *Synthesis* **2003**, *2003*, 1324-1328.

(19) Reid, W. B.; Spillane, J. J.; Krause, S. B.; Watson, D. A. Direct Synthesis of Alkenyl Boronic Esters from Unfunctionalized Alkenes: A Boryl-Heck Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 5539-5542.

(20) Jindal, R.; Devi, A.; Kad, G. L.; Singh, J. Synthesis of heneicos-6(*Z*)-en-11-one, dec-5(*Z*)-en-1yl acetate, dec-5(*Z*)-en-1yl-3-methylbutanone (insect sex pheromones). *Indian J. Chem*. **2010**, *49B*, 495-499.

(21) Huber, T.; Firlbeck, D.; Riepl, H. M. Iridium-catalysed isomerising trialkylsilylation of

methyl oleate. *J. Orgnomet. Chem.* **2013**, *744*, 144-148.

(22) Hayashi, Y.; Yamaguchi, H.; Toyoshima, M.; Okado, K.; Toyo, T.; Shoji, M. Formal Total Synthesis of Fostriecin by 1,4-Asymmetric Induction with an Alkyne‐Cobalt Complex. *Chem. Eur. J.* **2010**, *16*, 10150-10159.

(23) Hornyánszky, G.; Rohály, J.; Novák, L. Facile Synthesis of Mill Moth's Sex Pheromone Components. *Synthetic Communications* **2008**, *38*, 1533-1540.

(24) Singh, V.; Das, B.; and Mobin, S. M. Oxidative Dearomatization of o-Hydroxymethylphenol and Intramolecular π4s+π2s Cycloaddition: An Expedient Synthesis of a Tricyclic Intermediate for Platencin. *Synlett* **2013**, *24*, 1583-1587.

(25) Fuwa, H.; Yamagata, N.; Okuaki, Y.; Ogata, Y.; Saito, A.; Sasaki, M. Total Synthesis and Complete Stereostructure of a Marine Macrolide Glycoside, (−)-Lyngbyaloside B. *Chem. Eur. J.* **2016**, *22*, 6815-6829.

(26) Tsukano, C.; Ebine, M.; Sasaki, M. Convergent Total Synthesis of Gymnocin-A and Evaluation of Synthetic Analogues. *J. Am. Chem. Soc.* **2005**, *127*, 4326-4335.

(27) Heidt, T.; Baro, A.; Köhn, A.; Laschat, S. Synthesis of Cembranoid Analogues through Ring-Closing Metathesis of Terpenoid Precursors: A Challenge Regarding Ring-Size Selectivity. *Chem. Eur. J.* **2015**, *21*, 12396-12404.

(28) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. Catalytic Z-selective olefin cross-metathesis for natural product synthesis. *Nature*, **2011,** *471*, 461-466.

(29) Doi, T.; Fukuyama, T.; Minamino, S.; Hussona, G.; Ryu I. An unusual dimerization of primary unsaturated alcohols catalyzed by $RuHCl(CO)(PPh_3)_3$. *Chem. Commun.* **2006**, *17*, 1875-1877.

(30) Tsubouchi, A.; Sasaki, N.; Enatsu, S.; Takeda, T. Regio- and stereoselective preparation of

(*Z*)-silyl enol ethers by three-component coupling using α,β-unsaturated acylsilanes as core building blocks. *Tetrahedron Lett.* **2013**, *54*, 1264-1267.