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Stereoselective Transformation of 1-Alkenyl Ether ($R^1CH=CHOMe$) into Alkene ($R^1CH=CHR^2$) Based on Stereospecific Elimination of the *Vicinal* Iodo(methoxy)alkane

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Abstract: Treatment of alkenyl methyl ether with ICl rapidly gave 1-chloro-2-iodo-1-methoxyalkane quantitatively. Without isolation, this dihalide was treated with Et_3Al to afford *anti*-iodo(methoxy)alkane in good yield with high stereoselectivity. The stereochemistry of the starting alkenyl ether did not affect the stereochemical outcome of the product. The use of alkynylaluminum ($(RC\equiv C)_2AlEt$) resulted in alkynylation of the α-chloro-β-iodoether. *Anti*-iodo(methoxy)alkane was converted into (*Z*)-alkene upon treatment with *n*-BuLi in hexane-ether at –78 °C. On the other hand, the reaction of the same *anti*-iodo(methoxy)alkane with allylsilane–$TiCl_4$ provided (*E*)-alkene.

The carbon–carbon double bond is a basic structural unit in organic chemistry, and numerous reports have been published on the syntheses and chemical reactivities of alkene.[1] However, it is still desirable to explore more facile and more efficient routes to stereoselective syntheses of alkene. Very recently, we have developed a stereospecific method for alkene synthesis based on stereospecific elimination of the *vicinal* iodomethoxyalkane with butyllithium[2] or allylsilane-$TiCl_4$.[3] Whereas the treatment of an iodomethoxyalkane with butyllithium in hexane–ether (1:1) afforded an olefin stereospecifically via a *syn* elimination of an iodine–methoxy moiety, an *anti* elimination proceeded with the allylsilane–titanium tetrachloride system (Scheme 1). Herein we wish to disclose a stereoselective transformation of 1-alkenyl ether into alkene by a three-step process: (1) an addition of ICl to 1-alkenyl ether, (2) a stereoselective alkylation of α-chloro-β-iodoether, and (3) a stereospecific elimination of the *vicinal* iodo(methoxy)alkane.

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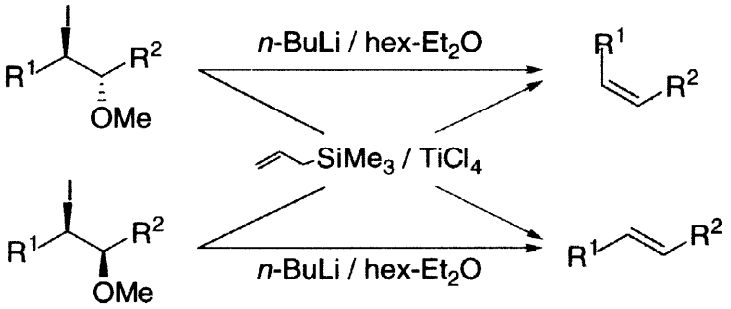
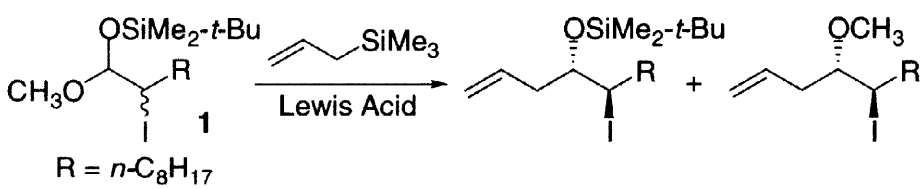
Scheme 1



First of all, we tried to find a general procedure for the stereoselective synthesis of *vicinal* iodo(methoxy)alkanes. We have already reported that a Lewis acid-induced reaction of 2-iodo-1-methoxy-1-siloxyalkanes **1** with allyltrimethylsilane proceeded with high stereoselectivity to provide an allylated *vicinal* iodo(methoxy)alkane (Scheme 2).[4] There were, however, inherent limitations to the reaction and it could be applied only to allylation. An alkylation of **1** with various organometallic reagents could not give a satisfactory result. For instance, treatment of **1** with Et_3Al or Et_2AlCl afforded only a trace amount of the desired alkylated product along with an unidentified complex mixture. Then, it was anticipated that 1-chloro-2-iodo-1-methoxyalkane **3** would be a more suitable compound in order to obtain *vicinal* iodo(methoxy)alkanes by means of organometallic reagents.[5] Indeed, this was the case and alkenyl methyl ethers could be easily transformed into *vicinal* iodo(methoxy)alkanes through 1-chloro-2-iodo-1-methoxyalkanes. Treatment of 1-alkenyl ether **2**[6,7] (*E*/*Z* = 20/80) with ICl[8] at −78 °C in toluene gave 1-chloro-2-iodo-1-methoxyalkane **3** quantitatively. The chloroiodoalkane **3** was used for further reaction without isolation because **3** was not so stable as to allow purification by silica-gel column chromatography. Treatment of **3** with diethylaluminum chloride afforded *anti*-iodo(methoxy)alkane **4** with high stereoselectivity (*anti*/*syn* = >95/<5).[9]

Scheme 2

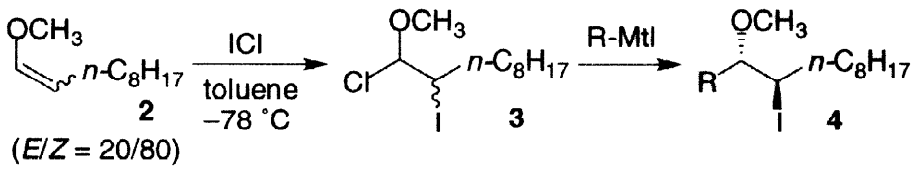


$TiCl_4$	85% (>99/1)	trace
Me_3SiOTf	trace	89% (96/4)

The representative results are shown in Table 1. Several comments are worth noting. (1) The stereochemistry of the starting alkenyl ether did not affect the stereochemical outcome of the product. (2) The use of trialkylaluminum such as Et_3Al or Me_3Al instead of Et_2AlCl also provided the corresponding alkylated iodomethoxyalkanes **4a** or **4b**. In the case of *i*-Bu_3Al, the yield of **4c** decreased. (3) A dialkylzinc reagent was as effective as alkylaluminum reagents to give alkylation product **4** with high

stereoselectivity. (4) Treatment of **3** with ethyldi(1-alkynyl)aluminum ($(RC{\equiv}C)_2AlEt$, R = *n*-C_6H_{13}, Me_3Si, or Ph) resulted in formation of the corresponding alkynylation[10] products **4d**, **4e**, or **4f**. The stereoselectivity was slightly low compared to the reaction with trialkylaluminum. The use of ethyl(1-alkynyl)aluminum chloride gave ethylated product **4a** in 8% yield in addition to the alkynylated product **4d** (82%).

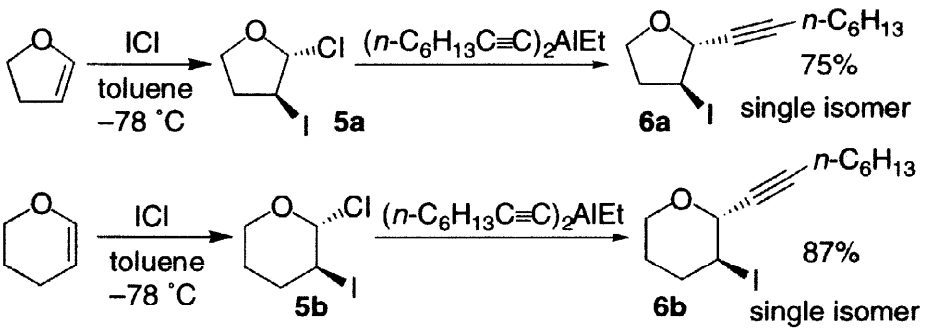
Table 1 Synthesis of *Vicinal* Iodomethoxyalkane from 1-Alkenyl ether



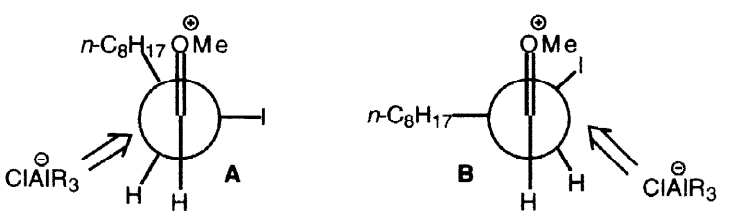
Entry	R-Mtl	Product	Yield(%)	(*anti*/*syn*)
1	Et_2AlCl	**4a**	87	>95/<5
2	Et_3Al	**4a**	84	>95/<5
3	$EtAlCl_2$	**4a**	67	>95/<5
4	Me_3Al	**4b**	84	>95/<5
5	*i*-Bu_3Al	**4c**	51	95/5
6	Et_2Zn	**4a**	74	>95/<5
7	(*n*-$C_6H_{13}C{\equiv}C)_2AlEt$	**4d**	92	88/12
8	*n*-$C_6H_{13}C{\equiv}CAlEtCl$	**4d**	82	88/12
9	$(Me_3SiC{\equiv}C)_2AlEt$	**4e**	94	93/7
10	$(PhC{\equiv}C)_2AlEt$	**4f**	94	91/9

Starting from cyclic 1-alkenyl ethers, such as dihydrofuran and dihydropyran, the reaction with ICl followed by an addition of 1-octynylaluminum provided *trans* 3-iodo-2-octynylfuran **6a** or *trans* 3-iodo-2-octynylpyran **6b** exclusively in good yields (Scheme 3).

Scheme 3

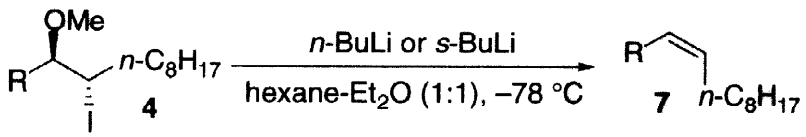


The stereoselective formation of the *anti* alkylated or alkynylated product could be explained as follows. An oxocarbenium ion can possibly be formed by the abstraction of the chlorine atom from α-chloroether. The stereochemistry is determined by the Felkin–Anh model[11] of two possible conformers, **A** and **B**, which give the *anti* and *syn* products, respectively. Due to the electronic and steric effect of the iodine atom, conformer **A** is considered to be more preferable and the *anti* isomer is formed selectively. The decrease of stereoselectivity observed in alkynylation can be attributed to the smaller steric demand of the linear alkynyl group.



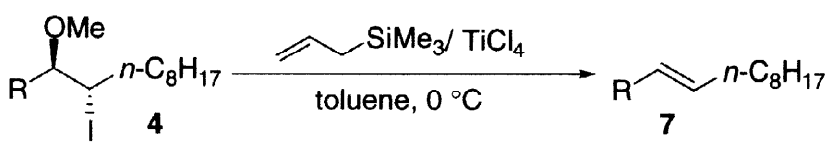
Anti-iodo(methoxy)alkanes **4** thus obtained were converted into (*Z*)-alkene upon treatment with *n*-BuLi or *s*-BuLi in hexane-ether (1:1) at −78 °C via *syn* elimination of an iodine–methoxy moiety (Table 2).[2] In the preparation of enynes from propargyl ether derivatives **4d**, **4e**, and **4f**, the reaction with *n*-BuLi resulted in decrease of stereoselectivities and the use of *s*-BuLi afforded (*Z*)-enynes with better selectivities. In contrast, the reaction of **4** with $TiCl_4$ in the presence of allyltrimethylsilane caused *anti* elimination to provide (*E*)-alkenes without loss of stereoselectivity (Table 3).[3, 12] Therefore, by changing the reagents, both (*Z*)- and (*E*)-alkene could be prepared selectively from the same *anti*-iodo(methoxy)alkane.

Table 2 *Syn* elimination into (*Z*)-Alkenes with butyllithium



Entry	R		(*anti*/*syn*)	condition	Product	Yield(%)	(*E*/*Z*)
1	Et	**4a**	>95/<5	*n*-BuLi	**7a**	59	8/92
2	n-$C_6H_{13}C{\equiv}C$	**4d**	88/12	*n*-BuLi	**7d**	56	22/78
3	n-$C_6H_{13}C{\equiv}C$	**4d**	88/12	*s*-BuLi	**7d**	54	16/84
4	$Me_3SiC{\equiv}C$	**4e**	93/7	*n*-BuLi	**7e**	75	23/77
5	$Me_3SiC{\equiv}C$	**4e**	93/7	*s*-BuLi	**7e**	75	13/87
6	$PhC{\equiv}C$	**4f**	91/9	*s*-BuLi	**7f**	70	14/86

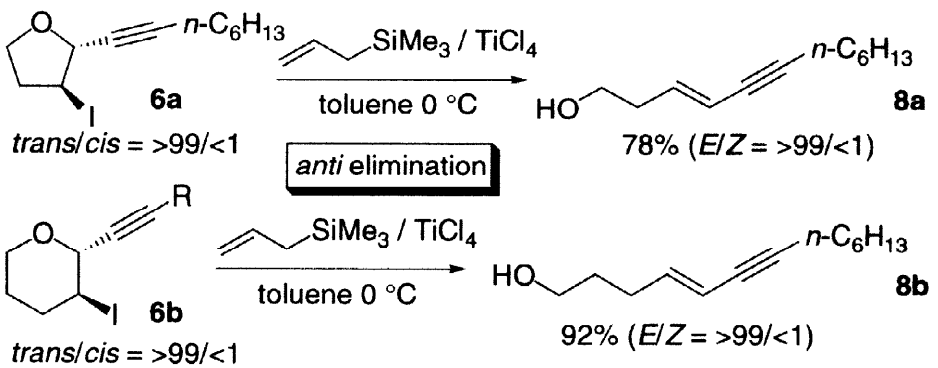
Table 3 *Anti* elimination into (*E*)-Alkenes with Allylsilane–$TiCl_4$



Entry	R		(*anti*/*syn*)	Product	Yield(%)	(*E*/*Z*)
1	Et	**4a**	>95/<5	**7a**	89	>99/<1
2	*i*-Bu	**4c**	95/5	**7c**	90	95/5
3	n-$C_6H_{13}C{\equiv}C$	**4d**	88/12	**7d**	83	85/15
4	$Me_3SiC{\equiv}C$	**4e**	93/7	**7e**	74	90/10
5	$PhC{\equiv}C$	**4f**	91/9	**7f**	84	90/10

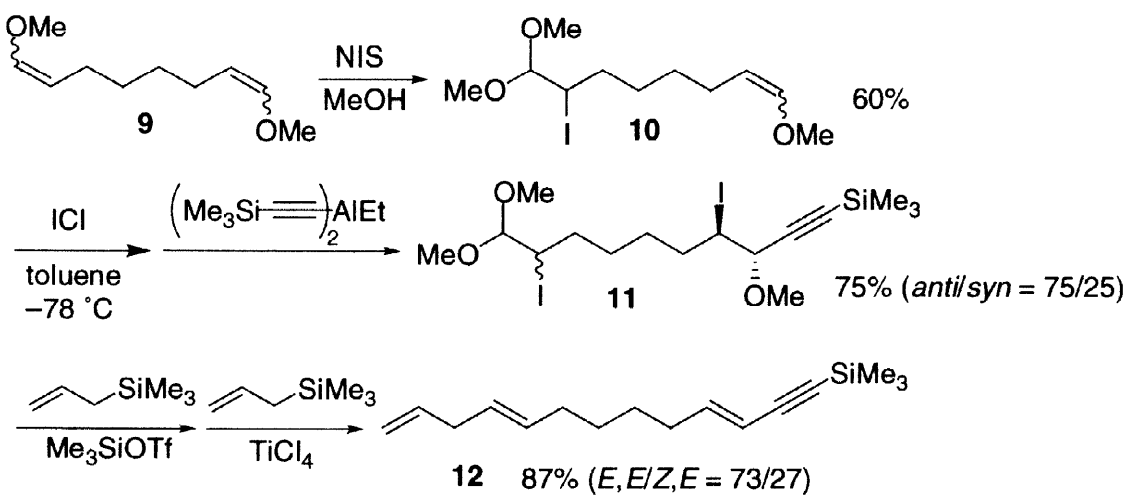
Treatment of pyran derivative **6b** with *s*-BuLi provided the corresponding enynol **8b** in 91% yield without stereoselectivity (*E*/*Z* = 51/49). In this case, *syn* elimination from **6b** might be sterically unfavorable. On the contrary, elimination in *anti* fashion from **6a** or **6b** with a $TiCl_4$-allylsilane system smoothly proceeded to afford (*E*)-enynol **8a** or **8b** in good yields exclusively (Scheme 4).

Scheme 4



Finally, two-directional synthesis[13] from 1,8-dimethoxy-1,7-octadiene **9** was performed (Scheme 5). An addition of *N*-iodosuccinimide (3.0 mmol) and methanol (2.75 mmol) to a solution of **9** (3.0 mmol) provided mono iodo acetal **10**. Exposure of **10** to aluminum acetylide gave alkynylated iodo(methoxy)alkane **11**. Treatment of **11** with allylsilane in the presence of Me_3SiOTf[14] resulted in allylation of iodo acetal. Successive elimination of two iodine–methoxy moieties by an allylsilane-$TiCl_4$ system provided trienyne **12** which contains both 1,3-enyne and 1,4-diene moieties.

Scheme 5



Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian GEMINI 300 spectrometer, $CDCl_3$ was used as a solvent, and chemical shifts are given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Dichloromethane was dried with molecular sieves 4A. Diethyl ether and toluene was dried over a slice of sodium. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. The starting 1-alkenyl methyl ethers were prepared according to the reported procedures.[6,15]

General Procedure for Alkylation of Chloroether. To a precooled toluene solution (6 mL) of 1-methoxy-1-decene (**2**, 0.17 g, 1.0 mmol) at –78 °C was added a dichloromethane solution of ICl (1.0 M, 1.0 mL, 1.0 mmol) dropwise. After 5 min, a hexane solution of Et_2AlCl (1.0 M, 1.1 mL, 1.1 mmol) was added at –78 °C and the mixture was stirred for another 30 min at that temperature. Extractive workup (hexane–aqueous 1 N HCl) followed by silica gel column chromatography provided an ethylated product *anti*-4-iodo-3-methoxydodecane (**4a**) in 87% yield. IR (neat) 2922, 2850, 1459, 1378, 1341, 1294, 1188, 1140, 1094, 929, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.6 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 1.11–1.40 (m, 11H), 1.49–1.68 (m, 4H), 1.68–1.84 (m, 1H), 2.68 (dt, *J* = 5.3, 5.3 Hz, 1H), 3.36 (s, 3H), 4.21 (ddd, *J* = 9.9, 5.3, 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.59, 13.92, 22.48, 25.81, 28.72, 29.08, 29.25, 29.76, 31.68, 35.45, 41.22, 57.73, 85.57. Found: C, 47.86; H, 8.34%. Calcd for $C_{13}H_{27}IO$: C, 47.86; H, 8.34%.

***anti*-3-iodo-2-methoxyundecane (4b)**: IR (neat) 2920, 2848, 1460, 1377, 1325, 1194, 1148, 1096, 905, 419 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 3H), 1.19–1.40 (m, 11H), 1.49–1.65 (m, 2H), 1.67–1.84 (m, 1H), 2.77 (dq, *J* = 3.9, 6.0 Hz, 1H), 3.32 (s, 3H), 4.22 (ddd, *J* = 9.9, 3.9, 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.94, 17.80, 22.50, 28.73, 29.08, 29.25, 29.59, 31.69, 35.98, 43.60, 56.25, 79.24. Found: C, 46.25; H, 8.27%. Calcd for $C_{12}H_{25}IO$: C, 46.16; H, 8.07%.

***anti*-5-iodo-4-methoxy-2-methyltridecane (4c)**: IR (neat) 2918, 2852, 1459, 1368, 1321, 1195, 1144, 1098, 985, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.0 Hz, 3H), 0.92 (d, *J* = 6.0 Hz, 3H), 1.18–1.40 (m, 12H), 1.46–1.64 (m, 3H), 1.66–1.90 (m, 2H), 2.66 (dt, *J* = 9.3, 3.0 Hz, 1H), 3.36 (s, 3H), 4.31 (dt, *J* = 9.3, 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.17, 22.54, 23.47, 24.29, 28.78, 29.12, 29.28, 29.83, 31.73, 35.72, 42.35, 57.27, 81.96. Found: C, 51.02; H, 8.82%. Calcd for $C_{15}H_{31}IO$: C, 50.85; H, 8.82%.

General Procedure for Alkynylation. To a toluene solution (20 mL) of 1-octynyllithium prepared from 1-octyne (12.0 mmol) and butyllithium (12.0 mmol) was added a hexane solution of $EtAlCl_2$ (1.0 M, 6.0 mL, 6.0 mmol) at 0 °C. At –78 °C, the resulting solution was added to a toluene solution (20 mL) of 2-chloro-3-iodopyran (**5b**) prepared from 3,4-dihydropyran (0.42 g, 5.0 mmol) and ICl (5.0 mmol). The whole mixture was stirred for 30 min. Extractive workup (hexane–aqueous 1 N HCl) followed by silica gel column chromatography provided *trans*-3-iodo-2-(1-octynyl)-1-oxacyclohexane (**6b**) in 92% yield. IR (neat) 2924, 2850, 2254, 1462, 1435, 1356, 1262, 1143, 1092, 1069, 1019, 931, 687 cm^{-1}; ^{1}H NMR

($CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 3H), 1.20–1.80 (m, 10H), 2.09 (dddd, J = 4.5, 10.2, 10.2, 14.1 Hz, 1H), 2.25 (dt, J = 1.9, 6.9 Hz, 2H), 2.47 (dddd, J = 3.9, 4.5, 4.5, 14.1 Hz, 1H), 3.57 (ddd, J = 3.0, 9.8, 11.7 Hz, 1H), 4.09 (ddd, J = 3.9, 3.9, 11.7 Hz, 1H), 4.18 (ddd, J = 3.9, 8.6, 10.2 Hz, 1H), 4.30 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.94, 18.51, 22.42, 27.61, 28.22, 28.41, 30.93, 31.19, 35.56, 67.09, 73.99, 77.57, 87.38. Found: C, 48.87; H, 6.80%. Calcd for $C_{13}H_{21}IO$: C, 48.76; H, 6.61%.

***anti*-10-iodo-9-methoxy-7-octadecyne (4d)**: IR (neat) 2922, 2850, 2228, 1461, 1378, 1331, 1312, 1190, 1125, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–0.95 (m, 6H), 1.17–1.60 (m, 20H), 1.69–1.94 (m, 2H), 2.22 (dt, J = 2.1, 6.8 Hz, 2H), 3.42 (s, 3H), 3.82 (dt, J = 4.2, 2.1 Hz, 1H), 4.11 (ddd, J = 9.0, 4.2, 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.87, 13.91, 18.52, 22.39, 22.48, 28.27, 28.31, 28.60, 29.06, 29.18, 29.32, 31.12, 31.68, 35.32, 38.79, 56.57, 75.69, 76.58, 88.34. Found: C, 56.44; H, 8.61%. Calcd for $C_{19}H_{35}IO$: C, 56.16; H, 8.68%.

***anti*-4-iodo-3-methoxy-1-trimethylsilyl-1-dodecyne (4e)**: IR (neat) 2922, 2850, 2164, 1466, 1251, 1107, 1005, 846, 759, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H), 1.20–1.42 (m, 11H), 1.48–1.62 (m, 1H), 1.72–1.94 (m, 2H), 3.47 (s, 3H), 3.90 (d, J = 4.2 Hz, 1H), 4.14 (ddd, J = 4.2, 4.2, 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –0.41, 13.94, 22.50, 28.53, 29.07, 29.16, 29.27, 31.70, 35.08, 37.37, 56.87, 76.04, 92.71, 101.81. Found: C, 49.00; H, 8.19%. Calcd for $C_{16}H_{31}IOSi$: C, 48.72; H, 7.92%.

***anti*-4-iodo-3-methoxy-1-phenyl-1-dodecyne (4f)**: IR (neat) 2920, 2850, 2225, 1600, 1490, 1460, 1444, 1333, 1314, 1094, 754, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 6.8 Hz, 3H), 1.16–1.46 (m, 11H), 1.50–1.66 (m, 1H), 1.78–2.02 (m, 2H), 3.52 (s, 3H), 4.10 (d, J = 4.2 Hz, 1H), 4.22 (ddd, J = 4.2, 4.2, 9.3 Hz, 1H), 7.26–7.35 (m, 3H), 7.43–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.54, 28.64, 29.12, 29.25, 29.40, 31.74, 35.45, 38.06, 57.01, 76.14, 85.82, 87.40, 122.30, 128.38, 128.76, 131.93. Found: C, 57.18; H, 6.73%. Calcd for $C_{19}H_{27}IO$: C, 57.29; H, 6.83%.

***trans*-3-iodo-2-(1-octynyl)-1-oxacyclopentane (6a)**: IR (neat) 2850, 2244, 1461, 1360, 1297, 1150, 1024, 958, 901, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.18–1.40 (m, 6H), 1.40–1.52 (m, 2H), 2.16 (dt, J = 1.8, 6.9 Hz, 2H), 2.24 (dddd, J = 13.8, 7.2, 6.0, 6.0 Hz, 1H), 2.59 (dddd, J = 13.8, 7.2, 7.2, 6.9 Hz, 1H), 3.92–4.05 (m, 2H), 4.13 (ddd, J = 7.2, 6.9, 4.8 Hz, 1H), 4.70 (dt, J = 4.8, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.85, 18.55, 22.32, 24.49, 28.17, 28.28, 31.08, 37.69, 66.98, 76.63, 78.26, 87.47. Found: C, 47.20; H, 6.29%. Calcd for $C_{12}H_{19}IO$: C, 47.07; H, 6.25%.

***trans*-3-dodecen-5-yn-1-ol (8a)**: IR (neat) 3298, 2926, 2854, 2210, 1467, 1430, 1378, 1328, 1047, 954, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 6.6 Hz, 3H), 1.16–1.40 (m, 6H), 1.47 (tt, J = 6.9, 7.2 Hz, 2H), 1.82 (bs, 1H), 2.23 (dt, J = 1.8, 6.9 Hz, 2H), 2.30 (dt, J = 7.2, 6.3 Hz, 2H), 3.62 (t, J = 6.3 Hz, 2H), 5.52 (dt, J = 15.9, 1.8 Hz, 1H), 5.97 (dt, J = 15.9, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.87, 19.15, 22.39, 28.44, 28.58, 31.21, 36.15, 61.49, 78.69, 89.70, 112.89, 138.63. HRMS Found: 180.1520. Calcd for $C_{12}H_{20}O$: M, 180.1514.

***trans*-4-tridecen-6-yn-1-ol (8b)**: IR (neat) 3296, 2926, 2854, 1466, 1378, 1328, 1059, 955, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.18–1.40 (m, 6H), 1.47 (tt, J = 6.6, 7.5 Hz, 2H), 1.61 (tt, J = 6.9, 7.2 Hz, 2H), 1.68 (bs, 1H), 2.13 (dt, J = 7.2, 7.5 Hz, 2H), 2.23 (dt, J = 1.5, 7.1 Hz, 2H), 3.60 (t, J =

6.6 Hz, 2H), 5.45 (dt, J = 15.9, 1.5 Hz, 1H), 6.00 (dt, J = 15.9, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.88, 19.17, 22.39, 28.45, 28.64, 29.07, 31.22, 31.58, 62.04, 78.88, 89.14, 110.57, 142.20. HRMS Found: 194.1679. Calcd for $C_{13}H_{22}O$: M, 194.1671.

One-Pot Procedure for the Synthesis of (*E*)-Enyne. To a toluene solution (6 mL) of 2-phenylethynyllithium prepared from phenylacetylene (2.4 mmol) and butyllithium (2.4 mmol) was added a hexane solution of $EtAlCl_2$ (1.0 M, 1.2 mL, 1.2 mmol) at 0 °C. At –78 °C, the resulting solution was added to a toluene solution (4 mL) of 1-chloro-2-iodo-1-methoxyalkane **2**. After being stirred for 30 min, the reaction mixture was warmed to 0 °C. Then, allyltrimethylsilane (2.4 mmol) and a toluene solution of $TiCl_4$ (1.0 M, 3.6 mL, 3.6 mmol) were added successively and the whole was stirred for further 1 h at 0 °C. Extractive workup (hexane–aqueous 1 N HCl) followed by silica gel column chromatography provided an enyne **7f** in 81% yield (*E*/*Z* = 87/13).

Two-Direction Synthesis of Trienyne 12. The starting 1,8-dimethoxy-1,7-octadiene **9** was prepared through the Wittig-type olefination of 1,6-hexanedial[16] according to the reported procedure.[15] To a solution of **9** (0.51 g, 3.0 mmol) and methanol (0.1 mL, 2.75 mmol) in dichloromethane (10 mL) was added *N*-iodosuccinimide (0.56 g, 2.5 mmol) at –78 °C. After being stirred for 30 min at that temperature, hexane (20 mL) was added and a white precipitate was formed. The mixture was filtered through a short alumina layer. Concentration and purification by silica-gel column chromatography afforded mono iodo acetal **10** (0.47 g, 1.5 mmol) in 60% yield. To a toluene solution (4 mL) of 1-octynyllithium (4.5 mmol) was added a hexane solution of $EtAlCl_2$ (1.0 M, 2.25 mL, 2.25 mmol) at 0 °C. At –78 °C, the resulting solution was added to a toluene solution (6 mL) of α-chloro-β-iodoether which was prepared from mono iodo acetal **10** (0.47 g, 1.5 mmol) and ICl (1.5 mmol). The whole mixture was stirred for 30 min. Extractive workup (hexane–aqueous 1 N HCl) followed by silica gel column chromatography provided an alkynylated iodo acetal **11** (0.60 g, 1.13 mmol, diastereomeric mixture of four isomers, 7,8-*anti*/*syn* = 75/25) in 75% yield; IR (neat) 2928, 2824, 2166, 1460, 1346, 1370, 1250, 1189, 1113, 1005, 957, 844, 759, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.24–1.48 (m, 2H), 1.48–1.69 (m, 2H), 1.69–1.94 (m, 4H), 3.37 (s, 3H), 3.38 (s, 3H), 3.40 (s, 0.75H), 3.41 (s, 2.25H), 3.86 (d, J = 4.2 Hz, 0.75H), 3.95 (d, J = 5.7 Hz, 0.25H), 3.98–4.12 (m, 2H), 4.21 (d, J = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –0.41, 28.32, 28.37, 28.46, 28.55, 28.65, 33.49, 33.56, 33.72, 34.67, 34.80, 34.91, 34.96, 35.65, 36.27, 36.33, 37.01, 37.04, 54.99, 56.79, 56.87, 75.90, 75.96, 76.17, 76.21, 92.85, 92.92, 101.12, 101.63, 106.69. HRMS Found: 552.0068. Calcd for $C_{16}H_{30}I_2O_3Si$: M, 552.0054. Treatment of a solution of **11** (0.60 g, 1.13 mmol) with allyltrimethylsilane (1.1 mL, 6.76 mmol) in the presence of TMSOTf (0.22 mL, 1.24 mmol) followed by an addition of a toluene solution of $TiCl_4$ (1.0 M, 2.48 mL, 2.48 mmol) afforded 1-trimethylsilyl-trideca-3,9,12-triene-1-yne (**12**, 0.24 g, 0.98 mmol) in 87% yield as a diastereomeric mixture (*E,E*/*Z,E* = 73/27): B.p. 83 °C (0.5 torr); IR (neat) 3018, 2852, 2134, 1639, 1434, 1250, 1085, 955, 913, 841, 758, 654 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 6.57H), 0.17 (s, 2.43H), 1.29–1.42 (m, 4H), 1.92–2.12 (m, 3.46H), 2.24-2.35 (m, 0.54H), 2.68–2.75 (m, 2H), 4.93–5.04 (m, 2H), 5.37–5.43 (m, 2H), 5.47 (dt, J = 15.9, 1.7 Hz, 1H), 5.73–5.87 (m, 1H), 5.92 (dt, J = 10.8, 7.5 Hz, 0.27H), 6.19 (dt, J = 15.9 Hz, 7.1 Hz, 0.73H); ^{13}C NMR ($CDCl_3$) major isomer δ 0.17, 27.97, 28.75, 32.22, 32.83, 36.64, 92.56, 104.19, 109.69, 114.86, 127.98, 131.37, 137.49, 146.30. Found: C, 78.20; H, 10.90%. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63%.

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References and Notes

1. *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: New York, 1964; *The Chemistry of Alkenes*; Zabicky, J., Ed.; Interscience: New York, 1968; Vol. 2; Kelly, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I. Eds.; Pergamon Press: New York, 1991; Vol. 1, Chapter 3.1 p. 729; Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers: New York, 1989; p. 105.
2. Maeda, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1996**, *61*, 6770.
3. Yachi, K.; Maeda, K.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **1997**, *38*, 5161.
4. Maeda, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1997**, *62*, 6429.
5. Alkylation of α,β-dihaloethers, see: Militzer, H. -C.; Schömenauer, S.; Otte, C.; Puls, C.; Hain, J.; Bräse, S.; Meijere, A. *Synthesis*, **1993**, 998; Crombie, L.; Rainbow, L. J. *J. Chem. Soc. Perkin. Trans. 1.* **1994**, 673.
6. Barbot, F.; Miginiac, P. *Helv. Chim. Acta.* **1979**, *62*, 1451.
7. Treatment of 7-methoxy-6-tridecene with ICl followed by an addition of Et_2AlCl mainly afforded 7-tridecanone and there was no ethylated product in the reaction mixture.
8. Cambie, R. C.; Noall, W. I.; Potter, G. J.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc. Perkin. Trans. 1*, **1977**, 226; Abd Elall, E. H. M.; Ashmawy, M. I.; Mellor, J. M. *Chem. Commun.* **1987**, 1577; Brisbois, R. G.; Wanke, R. A. *Iodine Monochloride* in *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L., Ed.; Eiley: Chichester, **1995**; p 2811.
9. The use of dichloromethane as a reaction solvent in place of toluene gave a similar result and **4a** was obtained in 89% yield (*anti*/*syn* = >95/<5). In ether, an elimination reaction of chloroiodoalkane **2** with Et_2AlCl into the starting 1-alkenyl ether **3** proceeded and no ethylation product was observed in the reaction mixture. Therefore, it is important to use ether-free organometallics for this alkylation reaction.
10. Alkynylation of alkyl halides by alkynylaluminum compounds, see. Negishi, E.; Baba, S. *J. Am. Chem. Soc.* **1975**, *97*, 7385.
11. Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199; Anh, N. T. *Topics Curr. Chem.* **1980**, *88*, 145.
12. This *anti* elimination reaction could be performed in one-pot. For example, treatment of 1-chloro-2-iodo-1-methoxyalkane **2** with $(PhC{\equiv}C)_2AlEt$ followed by an addition of allyltrimethylsilane (2.4 equivalent) and $TiCl_4$ (3.6 equivalent) afforded **7f** in 81% yield (*E*/*Z* = 87/13).
13. Poss, C. S.; Schreiber, S. L. *Acc. Chem. Res.* **1994**, 27, 9.
14. Tsunoda, T.; Suzuki, M.; Noyori, R.; *Tetrahedron Lett.* **1980**, *21*, 71; Murata, S.; Suzuki, M.; Noyori, R.; *J. Am. Chem. Soc.* **1980**, *102*, 3248.
15. Schlude, H. *Tetrahedron*, **1975**, 31, 89.
16. Daumas, M.; Vo-Quang, Y.; Vo-Quang, L.; Goffic, F. L. *Synthesis*, **1989**, 64.