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Highly Regioselective Rearrangement of 2-Substituted Vinylepoxides Catalyzed by Gallium(III) Triflate

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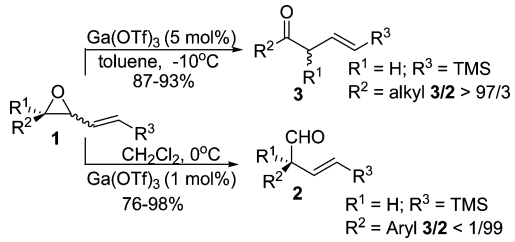
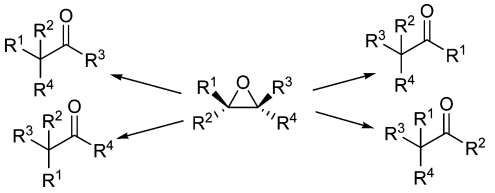


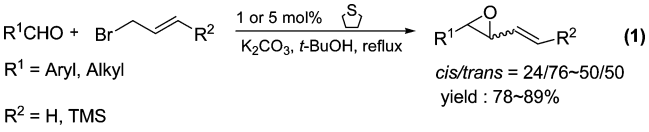
Gallium(III) triflate catalyzed the rearrangement of 2-substituted vinylepoxides into β,γ-unsaturated carbonyl compounds with high regio- and chemoselectivity (>97/3) in low catalyst loading (1−5 mol %). The alkyl-substituted trimethylsilylvinyl epoxides gave β,γ-unsaturated ketone, but aryl-substituted vinylepoxides gave the aldehydes instead.

Lewis acid promoted rearrangement of epoxides into carbonyl compounds is one of the most useful tools in organic synthesis[1] and has been widely applied to the preparation of various biologically active natural and non-natural products.[2] As involved in chemoselectivity and regioselectivity, the product distribution of the rearrangement of epoxides depends on promoter/catalyst and substrates as well as reaction conditions.[1,3] Of the substrates investigated, aryl-, alkyl-, and acyloxy-substituted epoxides are well-studied.[4−6] However, few reports[7] on the Lewis acid catalyzed rearrangement of vinylepoxides appeared in the literature except for a few examples of those related to trisubstituted ones[8] promoted by stoichiometric Lewis acids.[9] In this paper, we wish to report a highly chemoselective and regioselective rearrangement of 2-substituted vinylepoxides into β,γ-unsaturated carbonyl compounds catalyzed by $Ga(OTf)_3$ (Scheme 1).

SCHEME 1



In a previous study on ylide chemistry,[10] we developed a highly efficient ylide epoxidation of aldhydes with allylic bromide (eq 1),[11] providing an easy access to 2-substituted vinylepoxides but as a mixture of *cis* and *trans* isomers. Very recently, we found that these mixed



epoxides could be chemo- and regioselectively transformed into β,γ-unsaturated carbonyl compounds, potentially useful intermediates in organic synthesis. This

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(2) For a review, see: Silva, L. F., Jr. *Tetrahedron* **2002**, *58*, 9137. Selected references: (a) Kita, Y.; Higuchi, K.; Yoshida, Y.; Iio, K.; Kitagaki, S.; Uede, K.; Akai, S.; Fujioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 3214. (b) Grellepois, F.; Chorki, F.; Crousse, B.; Ourévitch, M.; Bonnet-Delpon, D.; Bégué, J. P. *J. Org. Chem.* **2002**, *67*, 1253. (c) Kimura, T.; Yamamoto, N.; Suzuki, Y.; Kawano, K.; Norimine, Y.; Ito, K.; Nagato, S.; Iimura, Y.; Yonaga, M. *J. Org. Chem.* **2002**, *67*, 6228. (d) Tønder, J. E.; Tanner, D. *Tetrahedron* **2003**, *59*, 6937.

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(4) See, for example, the following. Organoaluminum reagent: (a) Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 6431. (b) Maruoka, K.; Ooi, T.; Nagahara, S.; Yamamoto, H. *Tetrahedron* **1991**, *47*, 6983. (c) Maruoka, K.; Ooi, T.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 3303. (d) Maruoka, K.; Murase, N.; Bureau, R.; Ooi, T.; Yamamoto, H. *Tetrahedron* **1994**, *50*, 3663. (e) $B(C_6F_5)_3$: Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1995**, 721. (f) Pd(0) catalyst: Kulasegaram, S.; Kulawiec, R. J. *J. Org. Chem.* **1994**, *59*, 7195. (g) $LiClO_4$: Sudha, R.; Narasimhan, K. M.; Saraswathy, V. G.; Sankararaman, S. *J. Org. Chem.* **1996**, *61*, 1877. (h) $InCl_3$: Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212. (i) $BiOClO_4{\cdot}xH_2O$: Anderson, A. M.; Blazek, J. M.; Garg, P.; Payne, B. J.; Mohan, R. S. *Tetrahedron Lett.* **2000**, *41*, 1527. (j) $Bi(OTf)_3{\cdot}xH_2O$: Bhatia, K. A.; Eash, K. J.; Leonard, N. M.; Oswald, M. C.; Mohan, R. S. *Tetrahedron Lett.* **2001**, *42*, 8129. (k) $VO(OEt)Cl_2$: Martínez, F.; Campo, C.; Llama, E. F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1749. (l) $Er(OTf)_3$: Procopio, A.; Dalpozzo, R.; Nino, A. D.; Nardi, M.; Sindona, G.; Tagarelli, A. *Synlett* **2004**, 2633.

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(6) For recent acid-catalyzed rearrangement of enol ester epoxides, see: (a) Zhu, Y.; Manske, K. J.; Shi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4080. (b) Feng, X.; Shu, L.; Shi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11002. (c) Zhu, Y.; Shu, L.; Tu, Y.; Shi, Y. *J. Org. Chem.* **2001**, *66*, 1818. (d) Feng, X.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, *67*, 2831.

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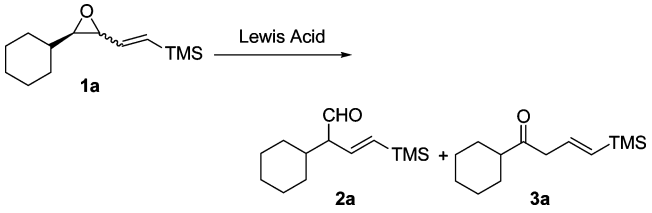
TABLE 1. Effects of Reaction Conditions on the Rearrangement of Epoxide 1a



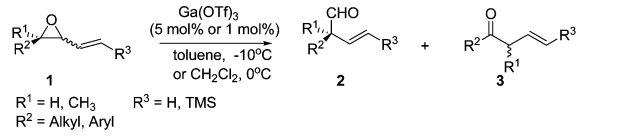
entry	Lewis acid (mol %)	reaction conditions	**2a/3a**[a]	yield[b] (%)
1	$SnCl_4$ (100)	CH_2Cl_2/45 min/−78 °C		*c*
2	$Ti(OPr^i)_4$ (10)	CH_2Cl_2/24 h/−78 °C → reflux		0
3	LiOTf (10)	CH_2Cl_2/18 h/25 °C → reflux		0
4	$Mg(OTf)_2$ (10)	CH_2Cl_2/18 h/25 °C → reflux		0
5	$Y(OTf)_3$ (10)	CH_2Cl_2/18 h/25 °C → reflux	13/87	48
6	$Ga(OTf)_3$ (10)	CH_2Cl_2/30 min/25 °C	33/67	68
7	$Ga(OTf)_3$ (5)	CH_2Cl_2/1.5 h/0 °C	8/92	80
8	$Ga(OTf)_3$ (5)	$ClCH_2CH_2Cl$/1.5 h/0 °C	9/91	78
9	$Ga(OTf)_3$ (5)	toluene/1.5 h/0 °C	6/94	92
10	$Ga(OTf)_3$ (5)	toluene/2 h/−10 °C	3/97	87

[a] Determined by ^1H NMR. [b] Isolated yield. [c] Complicated.

transformation proved Lewis acid and solvent dependent. As shown in Table 1, the rearrangement of 2-cyclohexylsilylvinylepoxide **1a** in the presence of stoichiometric $SnCl_4$ gave disordered products in dichloromethane (entry 1, Table 1). Attempts using a catalytic amount (10 mol %) of commonly used Lewis acids such as $Ti(OPr^i)_4$, LiOTf, and $Mg(OTf)_2$ failed in dichloromethane, and no desired products were obtained (entries 2−4, Table 1). $Y(OTf)_3$ (10 mol %)could promote the reaction under reflux in CH_2Cl_2 to afford a mixture of aldehyde **2a** and ketone **3a** with a ratio of 13:87 (entry 5) in 48% yield. Fortunately, 10 mol % of $Ga(OTf)_3$ catalyzed the rearrangement well to give the desired products in reasonable yields at room temperature, although the regioselectivity was not good. Further studies showed that the ratio of **3a** and **2a** could be improved from 33/67 to 8/92 by lowering the reaction temperature from 25 to 0 °C and even the catalyst loading was reduced to 5 mol % (entries 6 and 7). Replacement of the solvent with toluene gave better results (entries 9 and 10) compared with those in CH_2Cl_2. In our screened conditions, the best result was achieved using gallium(III) triflate as the catalyst and toluene as the solvent at −10 °C. In this case, the rearrangement gave the aldehyde in 87% yield with excellent chemo- and regioselectivity (**2a/3a**, 3/97, entry 10).

To study the generality of the rearrangement, a variety of 1,2-disubstitued trimethylsilylvinyl epoxides and trisubstituted trimethylsilylvinyl epoxide were examined under the optimal conditions. As summarized in Table 2, the regioselectivity was substrate dependent. 2-Alkyl-substituted trimethylsilylvinyl epoxides regioselectively gave β,γ-unsaturated ketone **3**, via a hydrogen migration, as major products in high yields (entries 1 and 2, Table 2) while aryl-substituted vinylepoxides gave the aldehydes **2** in lieu of ketones as single products in high yields (entries 3−8, Table 2). In addition, aryl-substituted vinyl epoxides proved more active than alkyl-substituted ones, and the loading of $Ga(OTf)_3$ could be reduced to 1 mol %. In the case of aryl-substituted vinylepoxides used, the reactions were very clean and the purification procedure

TABLE 2. $Ga(OTf)_3$-Catalyzed Rearrangement of Vinyl Epoxides



Entry		Substrate	Product	**2/3**[a]	Yield(%)[b]
1[d]	**1a**	c-C_6H_{11} TMS (56/44)[a,c]	c-C_6H_{11} TMS **3a**	3/97	87
2[d]	**1b**	n-C_9H_{19} TMS (57/43)[a,c]	n-C_9H_{19} TMS **3b**	1/99	93
3[e]	**1c**	p-Cl-C_6H_4 TMS (73/27)[a,c]	p-Cl-C_6H_4 CHO TMS **2c**	>99/1	98
4[e]	**1d**	Ph TMS (76/24)[a,c]	Ph CHO TMS **2d**	>99/1	95
5[e]	**1e**	p-Br-C_6H_4 TMS (78/22)[a,c]	p-Br-C_6H_4 CHO TMS **2e**	>99/1	95
6[e]	**1f**	p-MeO-C_6H_4 TMS (72/28)[a,c]	p-MeO-C_6H_4 CHO TMS **2f**	>99/1	93
7[e]	**1g**	1-Naphthyl TMS (72/28)[a,c]	1-Naphthyl CHO TMS **2g**	>99/1	98
8[e]	**1h**	H_3C, p-F-C_6H_4 TMS (53/47)[a,c]	H_3C, p-F-C_6H_4 CHO TMS **2h**	>99/1	76
9[e]	**1i**	p-Cl-C_6H_4 (66/34)[a,c]	p-Cl-C_6H_4 CHO CH_3 **4i**	77/23[f]	61[g]
10[e]	**1j**	p-MeO-C_6H_4 (60/40)[a,c]	p-MeO-C_6H_4 CHO CH_3 **4j**	91/9[f]	65[g]

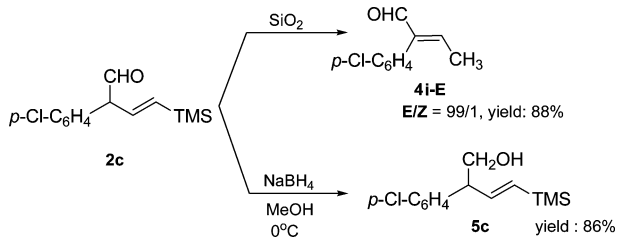
[a] Determined by ^1H NMR. [b] Isolated yields. [c] The ratio for *trans* and *cis* isomers. [d] 5 mol % of $Ga(OTf)_3$ in toluene at −10 °C. [e] 1 mol % of $Ga(OTf)_3$ in CH_2Cl_2 at 0 °C. [f] Ratio for *E* and *Z* isomers. [g] Isolated total yield of *Z* and *E* isomers.

was very simple (entries 3−8, Table 2). The pure product could be obtained just by filtering the catalyst off by a short silica gel column followed by concentration. The substitution on the aryl ring has almost no effects on both yields and selectivity. Trisubstituted oxirane **1h** also worked well and afforded quaternary aldehyde (entry 8, Table 2). Noticeably, *the stereochemistry of the product is substrate independent.* In all cases investigated (entries 1−8, Table 2), a mixture of *cis* and *trans* isomers of epoxides gave β,γ-unsaturated carbonyl compounds with high *E* stereoselectivity. Unlike that the silylvinyl-substituted epoxides were transformed into β,γ-unsaturated aldehydes, simple vinyl-substituted epoxides gave a mixture of *E*- and *Z*-α,β-unsaturated aldehydes **4i** and **4j** (entries 9 and 10, Table 2) as the final products under the same reaction conditions, demonstrating trimethylsilyl in the vinyl group inhibited the isomerization of β,γ-unsaturated aldehydes into α,β-unsaturated aldehydes and was important to control the stereoselectivity of the products.

The β,γ-unsaturated aldehydes with a vinlysilane group[12] prepared by the current method should be synthetically useful. For example, aldehyde **2c** could be readily transformed into trisubtituted olefin **4i-E** in the

(12) For reviews on transformation of vinylsilane, see: (a) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlage: Berlin, 1983. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1983.

SCHEME 2



presence of silica gel (Scheme 2), providing an easy access to *E*-trisubstitued α,*β*-unsaturated aldehydes with high stereoselectivity (*E*/*Z* > 50/1). The aldehyde **2c** could also be converted to homoallylic alcohol **5c** by reduction with $NaBH_4$.

In summary, we developed an efficient gallium triflate catalyzed rearrangement of 2-substituted vinyl epoxides into *β*,*γ*-unsaturated carbonyl compounds with high regio- and chemoselectivity (>97/3). The low catalyst loading (1−5 mol %), the mild conditions, the multifunctionalized products, and in particular, the use of readily available *cis*/*trans*-vinyl epoxides as materials make the current method useful for practical use in organic synthesis.

Experimental Section

General Procedure for Rearrangement of Alkylvinyl Epoxides. To a solution of the epoxide (0.45 mmol) in toluene (3 mL) was added $Ga(OTf)_3$ (11.6 mg, 5 mol %). The resulting mixture was stirred at −10 °C under N_2 atmosphere. After the reaction was complete (monitored by TLC), it was washed with water followed by sodium bicarbonate aqueous solution and saturated brine solution. The organic layer was collected and dried by anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by flash chromatography to give the pure product.

(1) (*E*)-1-Cyclohexyl-4-(trimethylsilyl)but-3-en-1-one (3a). Yield: 87%. IR (film) ν/cm^{-1}: 2931 (s), 2854 (s), 1710 (s), 1615 (w), 1450 (m), 1247 (m), 863 (s), 838 (s). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 6.10 (dt, J = 6.6, 12.3 Hz, 1H), 5.74 (dt, J = 1.5, 17.4 Hz, 1H), 3.25 (dd, J = 1.2, 6.9 Hz, 2H), 2.40−2.32 (m, 1H), 1.85−1.62 (m, 5H), 1.34−1.16 (m, 5H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 211.8, 138.3, 134.9, 50.5, 48.6, 28.3, 25.8, 25.6, −1.4. MS (EI, *m*/*z*, rel intensity): 223 (M^+, 1.96), 209 (18.23), 208 (77.02), 134 (49.27), 111 (19.76), 83 (25.47), 75 (15.09), 73 (100.00). HRMS: calcd for $C_{13}H_{24}OSi$ 224.1596, found 225.1669 (M + H^+).

(2) (*E*)-1-(Trimethylsilyl)tridec-1-en-4-one (3b). Yield: 93%, IR (film) ν/cm^{-1}: 2955 (s), 2926 (s), 2855 (s), 1718 (s), 1248 (s), 863 (s), 839 (s). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 6.06 (dt, J = 6.6, 12.6 Hz, 1H), 5.76 (dt, J = 1.5, 17.4 Hz, 1H), 3.21 (dd, J = 1.5, 6.6 Hz, 2H), 2.41 (t, J = 6.6 Hz, 2H), 1.60−1.50 (m, 2H), 1.35−1.18 (m, 12H), 0.86 (t, J = 6.6 Hz, 3H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 209.1, 138.0, 135.2, 50.8, 42.4, 31.8, 29.40, 29.39, 29.24, 29.16, 23.7, 22.6, 14.1, −1.4.. MS (EI, *m*/*z*, rel intensity): 269 (M^+, 12.12), 169 (42.88), 156 (33.80), 155 (100.00), 85 (43.98), 73 (45.05), 71 (61.00), 43 (72.67). HRMS: calcd for $C_{16}H_{32}OSi$ 268.2222, found 269.2295 (M + H^+).

General Procedure for Rearrangement of Arylvinyl Epoxides. To a solution of the epoxide (0.5 mmol) in CH_2Cl_2 (2.5 mL) was added $Ga(OTf)_3$ (2.6 mg, 1 mol %). The resulting mixture was stirred at 0 °C under N_2 atmosphere. After the reaction was completed (monitored by TLC), the mixture was diluted with CH_2Cl_2 and rapidly filtered through a glass funnel with a thin layer of silica gel (eluted with CH_2Cl_2). The filtrate was collected and concentrated under reduced pressure to give the pure product.

(3) (*E*)-2-(4-Chlorophenyl)-4-(trimethylsilyl)but-3-enal (2c). Yield: 98%. IR (film) ν/cm^{-1}: 2956 (m), 1726 (s), 1607 (w), 1492 (m), 1249 (m), 867 (m), 840 (m). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.66 (d, J = 2.4 Hz, 1H), 7.38−7.34 (m, 2H), 7.16−7.13 (m, 2H), 6.23 (dd, J = 6.0, 18.6 Hz, 1H), 5.85 (dd, J = 1.5, 18.9 Hz, 1H), 4.28 (dt, J = 1.8, 6.6 Hz, 1H), 0.09 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 198.0, 139.3, 136.8, 133.8, 133.5, 130.2, 129.1, 64.2, −1.5. MS (EI, *m*/z, rel intensity): 252 (M^+, 19.92), 237 (11.65), 223 (14.03), 115 (24.14), 75 (14.69), 73 (100), 45 (13.48). HRMS: calcd for $C_{13}H_{17}ClOSi$ 252.0737, found 253.0810 (M + H^+).

(4) (*E*)-2-Phenyl-4-(trimethylsilyl)but-3-enal (2d). Yield: 95%. IR (film) ν/cm^{-1}: 2955 (m), 1726 (s), 1600 (m), 1493 (w), 1453 (w), 1248 (m), 868 (m), 839 (m), 755 (w), 699 (m). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.68 (d, J = 2.4 Hz, 1H), 7.44−7.31 (m, 3H), 7.25−7.22 (m, 2H), 6.30 (dd, J = 6.0, 18.9 Hz, 1H), 5.87 (dd, J = 1.5, 18.9 Hz, 1H), 4.30 (dt, J = 1.8, 4.2 Hz, 1H), 0.10 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 198.5, 139.9, 136.2, 135.4, 129.0, 128.9, 127.6, 65.0, −1.4. MS (EI, *m*/z, rel intensity): 218 (M^+, 2.58), 189 (13.36), 129 (8.01), 105 (10.10), 75 (13.46), 74 (9.79), 73 (100.0), 45 (8.41). HRMS: calcd for $C_{13}H_{18}OSi$ 218.1127, found 219.1200 (M + H^+).

(5) (*E*)-2-(4-Bromophenyl)-4-(trimethylsilyl)but-3-enal (2e). Yield: 95%. IR (film) ν/cm^{-1}: 2955 (m), 1725 (s), 1683 (m), 1488 (s), 1248 (s), 866 (s), 840 (s). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.66 (d, J = 2.4 Hz, 1H), 7.54−7.50 (m, 2H), 7.11−7.07 (m, 2H), 6.22 (dd, J = 6.6, 18.9 Hz, 1H), 5.85 (dd, J = 1.5, 18.9 Hz, 1H), 4.26 (dt, J = 1.8, 6.3 Hz, 1H), 0.09 (s, 9H). ^{13}C NMR (75 MHz, CDCl3): 197.9, 139.2, 136.9, 134.3, 132.1, 130.6, 121.7, 64.2, −1.4. MS (EI, *m*/*z*, rel intensity): 292 (M^+, 2.20), 131 (100.0), 115 (25.07), 103 (53.39), 102 (52.54), 84 (26.98), 75 (40.64), 73 (85.61). HRMS: calcd for $C_{13}H_{17}BrOSi$ 296.0232, found 297.0305 (M + H^+).

(6) (*E*)-2-(4-Methoxyphenyl)-4-(trimethylsilyl)but-3-enal (2f). Yield: 93%. IR (film) ν/cm^{-1}: 2955 (s), 1724 (s), 1611 (m), 1512 (s), 1250 (m), 867 (m), 839 (m). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.63 (d, J = 2.1 Hz, 1H), 7.12 (dd, J = 2.1, 6.0 Hz, 2H), 6.92 (dd, J = 2.1, 6.6 Hz, 2H), 6.25 (dd, J = 6.0, 18.9 Hz, 1H), 5.81 (dd, J = 1.5, 18.6 Hz, 1H), 4.22 (dt, J = 2.1, 6.3 Hz, 1H), 3.79 (s, 3H), 0.07 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 198.8, 159.0, 140.2, 135.8, 129.9, 127.2, 114.4, 64.0, 55.2, −1.4. MS (EI, *m*/z, rel intensity): 248 (M^+, 29.98), 162 (29.31), 161 (26.77), 147 (20.54), 131 (26.60), 121 (26.63), 73 (95.14). HRMS: calcd for $C_{14}H_{20}O_2Si$ 248.1233, found 249.1305 (M + H^+).

(7) (*E*)-2-(Naphthalen-1-yl)-4-(trimethylsilyl)but-3-enal (2g). Yield: 98%. IR (film) ν/cm^{-1}: 3049 (w), 2955 (m), 1724 (s), 1248 (m), 867 (m), 840 (m). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.78 (d, J = 1.8 Hz, 1H), 7.97−7.86 (m, 3H), 7.56−7.51 (m, 3H), 7.43 (dd, J = 1.2, 6.9 Hz, 1H), 6.54 (dd, J = 5.4, 18.6 Hz, 1H), 5.88 (dd, J = 1.5, 18.6 Hz, 1H), 5.00 (dt, J = 1.5, 5.4 Hz, 1H), 0.13 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 199.0, 140.0, 135.9, 134.1, 131.7, 128.9, 128.5, 127.2, 126.5, 125.9, 125.5, 123.5,61.1, −1.4. MS (EI, *m*/z, rel intensity): 268 (M^+, 4.79), 181 (66.00), 165 (43.02), 153 (91.03), 152 (100), 151 (35.0), 147 (33.26), 75 (25.65), 73 (66.66). HRMS: calcd for $C_{17}H_{20}OSi$ 268.1283, found 291.1176 (M + Na^+).

(8) (*E*)-2-(4-Fluorophenyl)-2-methyl-4-(trimethylsilyl)-but-3-enal (2h). Yield: 76%. IR (film) ν/cm^{-1}: 2956 (s), 1729 (s), 1604 (m), 1509 (s), 1249 (s), 866 (s), 839 (s). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.55 (s, 1H), 7.21−7.04 (m, 4H), 6.29 (d, J = 19.2 Hz, 1H), 5.87 (d, J = 19.2 Hz, 1H), 1.49 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$). 199.2, 162.0 (d, J_{C-F} = 245.6 Hz), 144.7, 136.1 (d, J_{C-F} = 2.8 Hz), 134.0, 129.2 (d, J_{C-F} = 8.2 Hz), 115.8 (d, J_{C-F} = 21.2 Hz), 58.9, 20.6, −1.3. MS (EI, *m*/z, rel intensity): 250 (M^+, 5.41), 221 (18.84), 139 (15.48), 129 (28.24), 127 (16.39), 75 (16.76), 73 (100), 43 (13.65). Anal. Calcd for $C_{14}H_{19}FOSi$: C, 67.16; H, 7.65. Found: C, 66.78; H, 7.86.

(9) (*E*)-2-(4-Chlorophenyl)but-2-enal (4i-E).[13] The total yield of *E* and *Z* isomers (*E*/*Z* = 77/23) was 61%. ^{1}H NMR (300

(13) Dana, G.; Thuan, S. L. T.; Gharbi-Benarous, J. *Bull. Soc. Chim. Fr.* **1974**, 2089.

MHz, $CDCl_3$/TMS) for *E*-isomer δ: 9.59 (s, 1H), 7.41−7.36 (m, 2H), 7.13−7.10 (m, 2H), 6.87 (q, J = 7.2 Hz, 1H), 2.01 (d, J = 6.9 Hz, 3H).

(10) (*E*)-2-(4-Methoxyphenyl)but-2-enal (4j-E). The total yield of *E* and *Z* isomers (*E*/*Z* = 91/9) was 65%. IR (film) ν/cm^{-1} for *E*-isomer: 2956 (w), 2837 (w), 1688 (s), 1607 (m), 1514 (s), 1463 (w), 1249 (s), 842 (m), 805 (m). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 9.56 (s, 1H), 7.11−7.08 (m, 2H), 6.94−6.90 (m, 2H), 6.77 (q, J = 7.2 Hz, 1H), 3.79 (s, 3H), 1.99 (d, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 193.8, 159.1, 151.0, 144.3, 130.6, 124.2, 113.6, 55.1, 15.9. MS (EI, *m*/*z*, rel intensity) 176 (M^+, 100), 147 (61.78), 135 (32.07), 132 (21.39), 117 (20.60), 115 (31.33), 91 (37.19), 77 (23.23). HRMS: calcd for $C_{11}H_{12}O_2$ 176.0837, found 199.0730 ($M + Na^+$).

(11) Synthesis of (*E*)-2-(4-chlorophenyl)but-2-enal[13] (4i-E). Aldehyde **2c** was chromatographed on silica gel to give pure product. Total yield of *E* and *Z* isomers (*E*/*Z* > 50/1) was 88%.

(12) Synthesis of (*E*)-2-(4-Chlorophenyl)-4-(trimethylsilyl)but-3-en-1-ol (5c). To a solution of aldehyde **2c** (126.4 mg, 0.5 mmol) in MeOH (10 mL) at 0 °C was added $NaBH_4$ (20 mg). After 15 min, the reaction mixture was acidified slowly by addition of hydrogen chloride solution (2 N) to PH = 4. To the resulting mixture was added 10 mL of water, and the mixture was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography to give **5c** as white solid. Yield: 86%. Mp: 75−77 °C. IR (KBr) ν/cm^{-1}: 3268 (w, br), 2953 (m), 1608 (w), 1491 (m), 1246 (s), 866 (s), 836 (s). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.34−7.29 (m, 2H), 7.18−7.15 (m, 2H), 6.11 (dd, J = 6.9, 18.6 Hz, 1H), 5.81 (dd, J = 1.2, 18.6 Hz, 1H), 3.85−3.75 (m, 2H), 3.55 (dd, J = 6.3, 13.8 Hz, 1H), 1.52 (s, br, 1H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 144.9, 139.2, 133.3, 132.5, 129.4, 128.7, 65.7, 54.1, −1.3. MS (EI, *m*/z, rel intensity): 254 (M^+, 1.02), 225 (10.39), 224 (16.17), 223 (22.31), 129 (12.39), 115 (18.79), 75 (27.44), 73 (100.00). Anal. Calcd for $C_{13}H_{19}ClOSi$: C, 61.27; H, 7.52. Found: C, 61.37; H, 7.55.

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Supporting Information Available: NMR spectra of new compounds and experimental details for the preparation of vinyloxiranes **2g** and **2h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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