

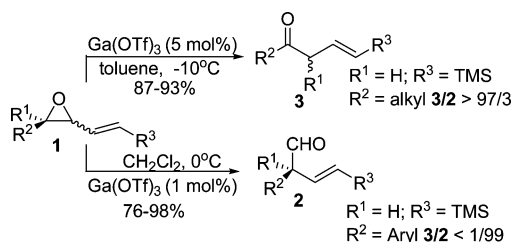
## Highly Regioselective Rearrangement of 2-Substituted Vinylepoxides Catalyzed by Gallium(III) Triflate

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

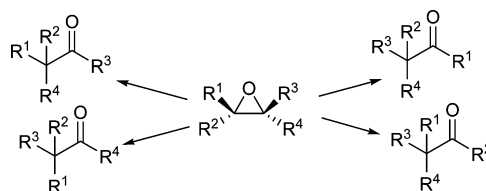
Lewis acid promoted rearrangement of epoxides into carbonyl compounds is one of the most useful tools in organic synthesis<sup>1</sup> and has been widely applied to the preparation of various biologically active natural and non-natural products.<sup>2</sup> As involved in chemoselectivity and regioselectivity,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

(1) For reviews, see: (a) Parker, R. E.; Issacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (b) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. (c) Smith, J. G. *Synthesis* **1984**, 629.

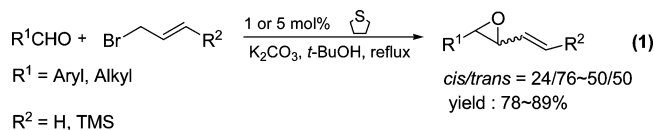
(2) For a review, see: Silva, L. F., Jr. *Tetrahedron* **2002**, *58*, 9137. Selected references: (a) Kita, Y.; Higuchi, K.; Yoshida, Y.; Iio, K.; Kitagaki, S.; Uede, K.; Akai, S.; Fujioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 3214. (b) Grellepous, F.; Chorki, F.; Crousse, B.; Ourévitich, M.; Bonnet-Delpon, D.; Bégue, 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.

(3) For a review, see: Rickborn, B. *Acid-catalyzed Rearrangements of Epoxides in Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 3.3, pp 733–775.

### SCHEME 1



In a previous study on ylide chemistry,<sup>10</sup> we developed a highly efficient ylide epoxidation of aldehydes with allylic bromide (eq 1),<sup>11</sup> 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  $\beta,\gamma$ -unsaturated carbonyl compounds, potentially useful intermediates in organic synthesis. This

(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<sub>6</sub>F<sub>5</sub>)<sub>3</sub>: 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<sub>4</sub>: Sudha, R.; Narasimhan, K. M.; Saraswathy, V. G.; Sankararaman, S. *J. Org. Chem.* **1996**, *61*, 1877. (h) InCl<sub>3</sub>: Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212. (i) Bi(OTf)<sub>3</sub>: Anderson, A. M.; Blazek, J. M.; Garg, P.; Payne, B. J.; Mohan, R. S. *Tetrahedron Lett.* **2000**, *41*, 1527. (j) Bi(OTf)<sub>3</sub>:xH<sub>2</sub>O: Bhatia, K. A.; Eash, K. J.; Leonard, N. M.; Oswald, M. C.; Mohan, R. S. *Tetrahedron Lett.* **2001**, *42*, 8129. (k) VO(OEt)<sub>2</sub>: Martínez, F.; Campo, C.; Llama, E. F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1749. (l) Er(OTf)<sub>3</sub>: Procopio, A.; Dalpozzo, R.; Nino, A. D.; Nardi, M.; Sindona, G.; Tagarelli, A. *Synlett* **2004**, 2633.

(5) For metalloporphyrin-catalyzed rearrangement, see the following: (a) Fe(TPP)OTf: Takanami, T.; Hirabe, R.; Ueno, M.; Hino, F.; Suda, K. *Chem. Lett.* **1996**, 1031. (b) Fe(TPP)ClO<sub>4</sub>: Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. *Tetrahedron Lett.* **1999**, *40*, 7243. (c) Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. *Chem. Commun.* **2002**, 2570. (d) Cr(TPP)OTf: Suda, K.; Kikkawa, T.; Nakajima, S.; Takanami, T. *J. Am. Chem. Soc.* **2004**, *126*, 9554.

(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.

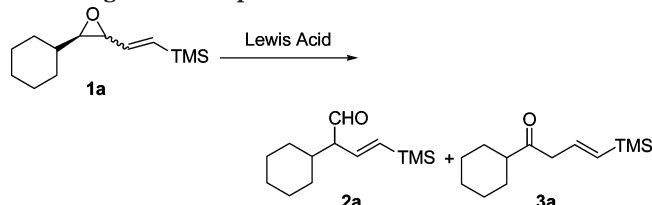
(7) Rosenberger, M.; Jackson, W.; Saucy, G. *Helv. Chim. Acta* **1980**, *63*, 175.

(8) Stoichiometric BF<sub>3</sub>-promoted rearrangements of vinyl epoxides: (a) Jung, M. E.; D'Amico, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 7379. (b) Jung, M. E.; Anderson, K. L. *Tetrahedron Lett.* **1997**, *38*, 2605. (c) Jung, M. E.; Marquez R. *Tetrahedron Lett.* **1999**, *40*, 3129.

(9) For rearrangement catalyzed by Pd(0), see: (a) Gilloir, F.; Malacria, M. *Tetrahedron Lett.* **1992**, *33*, 3859. (b) Bideau, F. L.; Aubert, C.; Malacria, M. *Tetrahedron: Asymmetry* **1995**, *6*, 697. (c) Bideau, F. L.; Gilloir, F.; Nilson, Y.; Aubert, C.; Malacria, M. *Tetrahedron* **1996**, *52*, 7487. (d) Courillon, C.; Fol, R. L.; Vandendriess, E.; Malacria, M. *Tetrahedron Lett.* **1997**, *38*, 5493.

(10) (a) Huang, Z.-Z.; Ye, S.; Xia, W.; Tang, Y. *Chem. Commun.* **2001**, 1384. (b) Ye, S.; Huang, Z.-Z.; Xia, C.-A.; Tang, Y.; Dai, L.-X. *J. Am. Chem. Soc.* **2002**, *124*, 2432. (c) Liao, W.-W.; Li, K.; Tang, Y. *J. Am. Chem. Soc.* **2003**, *125*, 13030. (d) Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, *67*, 3096. (e) Huang, Z.-Z.; Tang, Y. *J. Org. Chem.* **2002**, *67*, 5320.

(11) (a) Li, K.; Huang, Z.-Z.; Tang, Y. *Tetrahedron Lett.* **2003**, *44*, 2605. (b) Li, K.; Deng, X.-M.; Tang, Y. *Chem. Commun.* **2003**, 2074.

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

| entry | Lewis acid (mol %)                      | reaction conditions                                   | 2a/3a <sup>a</sup> | yield <sup>b</sup> (%) |
|-------|---|---|--------------------|------------------------|
| 1     | SnCl <sub>4</sub> (100)                 | CH <sub>2</sub> Cl <sub>2</sub> /45 min/-78 °C        |                    | c                      |
| 2     | Ti(OPr <sup>i</sup> ) <sub>4</sub> (10) | CH <sub>2</sub> Cl <sub>2</sub> /24 h/-78 °C → reflux |                    | 0                      |
| 3     | LiOTf (10)                              | CH <sub>2</sub> Cl <sub>2</sub> /18 h/25 °C → reflux  |                    | 0                      |
| 4     | Mg(OTf) <sub>2</sub> (10)               | CH <sub>2</sub> Cl <sub>2</sub> /18 h/25 °C → reflux  |                    | 0                      |
| 5     | Y(OTf) <sub>3</sub> (10)                | CH <sub>2</sub> Cl <sub>2</sub> /18 h/25 °C → reflux  | 13/87              | 48                     |
| 6     | Ga(OTf) <sub>3</sub> (10)               | CH <sub>2</sub> Cl <sub>2</sub> /30 min/25 °C         | 33/67              | 68                     |
| 7     | Ga(OTf) <sub>3</sub> (5)                | CH <sub>2</sub> Cl <sub>2</sub> /1.5 h/0 °C           | 8/92               | 80                     |
| 8     | Ga(OTf) <sub>3</sub> (5)                | ClCH <sub>2</sub> CH <sub>2</sub> Cl/1.5 h/0 °C       | 9/91               | 78                     |
| 9     | Ga(OTf) <sub>3</sub> (5)                | toluene/1.5 h/0 °C                                    | 6/94               | 92                     |
| 10    | Ga(OTf) <sub>3</sub> (5)                | toluene/2 h/-10 °C                                    | 3/97               | 87                     |

<sup>a</sup> Determined by <sup>1</sup>H NMR. <sup>b</sup> Isolated yield. <sup>c</sup> 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<sub>4</sub> 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<sup>i</sup>)<sub>4</sub>, LiOTf, and Mg(OTf)<sub>2</sub> failed in dichloromethane, and no desired products were obtained (entries 2–4, Table 1). Y(OTf)<sub>3</sub> (10 mol %) could promote the reaction under reflux in CH<sub>2</sub>Cl<sub>2</sub> 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)<sub>3</sub> 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<sub>2</sub>Cl<sub>2</sub>. 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-disubstituted 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 vinyl epoxides 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)<sub>3</sub> could be reduced to 1 mol %. In the case of aryl-substituted vinyl epoxides used, the reactions were very clean and the purification procedure

**TABLE 2. Ga(OTf)<sub>3</sub>-Catalyzed Rearrangement of Vinyl Epoxides**

Reaction scheme showing the Ga(OTf)<sub>3</sub>-catalyzed rearrangement of vinyl epoxide **1** to aldehyde **2** or ketone **3**.

R<sup>1</sup> = H, CH<sub>3</sub>    R<sup>3</sup> = H, TMS  
R<sup>2</sup> = Alkyl, Aryl

| Entry           | Substrate   | Product  | 2/3 <sup>a</sup>   | Yield(%) <sup>b</sup> |
|-----------------|---|--|--------------------|-----------------------|
| 1 <sup>d</sup>  | <b>1a</b> (c-C <sub>6</sub> H <sub>11</sub> ) (56/44) <sup>a,c</sup>    | <b>3a</b> (c-C <sub>6</sub> H <sub>11</sub> )    | 3/97               | 87                    |
| 2 <sup>d</sup>  | <b>1b</b> (n-C <sub>8</sub> H <sub>19</sub> ) (57/43) <sup>a,c</sup>    | <b>3b</b> (n-C <sub>8</sub> H <sub>19</sub> )    | 1/99               | 93                    |
| 3 <sup>e</sup>  | <b>1c</b> (p-Cl-C <sub>6</sub> H <sub>4</sub> ) (73/27) <sup>a,c</sup>  | <b>2c</b> (p-Cl-C <sub>6</sub> H <sub>4</sub> )  | >99/1              | 98                    |
| 4 <sup>e</sup>  | <b>1d</b> (Ph) (76/24) <sup>a,c</sup>                                   | <b>2d</b> (Ph)                                   | >99/1              | 95                    |
| 5 <sup>e</sup>  | <b>1e</b> (p-Br-C <sub>6</sub> H <sub>4</sub> ) (78/22) <sup>a,c</sup>  | <b>2e</b> (p-Br-C <sub>6</sub> H <sub>4</sub> )  | >99/1              | 95                    |
| 6 <sup>e</sup>  | <b>1f</b> (p-MeO-C <sub>6</sub> H <sub>4</sub> ) (72/28) <sup>a,c</sup> | <b>2f</b> (p-MeO-C <sub>6</sub> H <sub>4</sub> ) | >99/1              | 93                    |
| 7 <sup>e</sup>  | <b>1g</b> (1-Naphthyl) (72/28) <sup>a,c</sup>                           | <b>2g</b> (1-Naphthyl)                           | >99/1              | 98                    |
| 8 <sup>e</sup>  | <b>1h</b> (p-F-C <sub>6</sub> H <sub>4</sub> ) (53/47) <sup>a,c</sup>   | <b>2h</b> (p-F-C <sub>6</sub> H <sub>4</sub> )   | >99/1              | 76                    |
| 9 <sup>e</sup>  | <b>1i</b> (p-Cl-C <sub>6</sub> H <sub>4</sub> ) (66/34) <sup>a,c</sup>  | <b>4i</b> (p-Cl-C <sub>6</sub> H <sub>4</sub> )  | 77/23 <sup>f</sup> | 61 <sup>g</sup>       |
| 10 <sup>e</sup> | <b>1j</b> (p-MeO-C <sub>6</sub> H <sub>4</sub> ) (60/40) <sup>a,c</sup> | <b>4j</b> (p-MeO-C <sub>6</sub> H <sub>4</sub> ) | 91/9 <sup>f</sup>  | 65 <sup>g</sup>       |

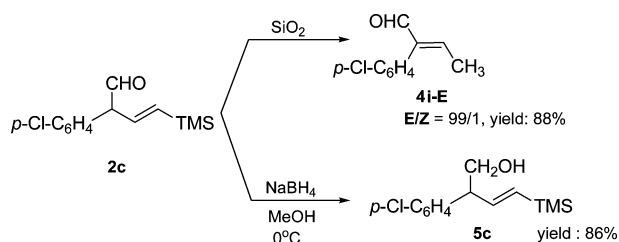
<sup>a</sup> Determined by <sup>1</sup>H NMR. <sup>b</sup> Isolated yields. <sup>c</sup> The ratio for *trans* and *cis* isomers. <sup>d</sup> 5 mol % of Ga(OTf)<sub>3</sub> in toluene at -10 °C. <sup>e</sup> 1 mol % of Ga(OTf)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. <sup>f</sup> Ratio for *E* and *Z* isomers. <sup>g</sup> 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 vinylsilane group<sup>12</sup> prepared by the current method should be synthetically useful. For example, aldehyde **2c** could be readily transformed into trisubstituted 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-Verlag: 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*-trisubstituted  $\alpha,\beta$ -unsaturated aldehydes with high stereoselectivity ( $E/Z > 50/1$ ). The aldehyde **2c** could also be converted to homoallylic alcohol **5c** by reduction with  $\text{NaBH}_4$ .

In summary, we developed an efficient gallium triflate catalyzed rearrangement of 2-substituted vinyl epoxides into  $\beta,\gamma$ -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  $\text{Ga}(\text{OTf})_3$  (11.6 mg, 5 mol %). The resulting mixture was stirred at  $-10^\circ\text{C}$  under  $\text{N}_2$  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  $\text{Na}_2\text{SO}_4$  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)  $\nu/\text{cm}^{-1}$ : 2931 (s), 2854 (s), 1710 (s), 1615 (w), 1450 (m), 1247 (m), 863 (s), 838 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 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  $\text{C}_{13}\text{H}_{24}\text{OSi}$  224.1596, found 225.1669 ( $\text{M} + \text{H}^+$ ).

**(2) (*E*)-1-(Trimethylsilyl)tridec-1-en-4-one (3b).** Yield: 93%. IR (film)  $\nu/\text{cm}^{-1}$ : 2955 (s), 2926 (s), 2855 (s), 1718 (s), 1248 (s), 863 (s), 839 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 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  $\text{C}_{16}\text{H}_{32}\text{OSi}$  268.2222, found 269.2295 ( $\text{M} + \text{H}^+$ ).

**General Procedure for Rearrangement of Arylvinyl Epoxides.** To a solution of the epoxide (0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL) was added  $\text{Ga}(\text{OTf})_3$  (2.6 mg, 1 mol %). The resulting mixture was stirred at  $0^\circ\text{C}$  under  $\text{N}_2$  atmosphere. After the reaction was completed (monitored by TLC), the mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and rapidly filtered through a glass funnel with a thin layer of silica gel (eluted with  $\text{CH}_2\text{Cl}_2$ ). 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)  $\nu/\text{cm}^{-1}$ : 2956 (m), 1726 (s), 1607 (w), 1492 (m), 1249 (m), 867 (m), 840 (m).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 19.92), 237 (11.65), 223 (14.03), 115 (24.14), 75 (14.69), 73 (100), 45 (13.48). HRMS: calcd for  $\text{C}_{13}\text{H}_{17}\text{ClOSi}$  252.0737, found 253.0810 ( $\text{M} + \text{H}^+$ ).

**(4) (*E*)-2-Phenyl-4-(trimethylsilyl)but-3-enal (2d).** Yield: 95%. IR (film)  $\nu/\text{cm}^{-1}$ : 2955 (m), 1726 (s), 1600 (m), 1493 (w), 1453 (w), 1248 (m), 868 (m), 839 (m), 755 (w), 699 (m).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 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  $\text{C}_{13}\text{H}_{18}\text{OSi}$  218.1127, found 219.1200 ( $\text{M} + \text{H}^+$ ).

**(5) (*E*)-2-(4-Bromophenyl)-4-(trimethylsilyl)but-3-enal (2e).** Yield: 95%. IR (film)  $\nu/\text{cm}^{-1}$ : 2955 (m), 1725 (s), 1683 (m), 1488 (s), 1248 (s), 866 (s), 840 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 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  $\text{C}_{13}\text{H}_{17}\text{BrOSi}$  296.0232, found 297.0305 ( $\text{M} + \text{H}^+$ ).

**(6) (*E*)-2-(4-Methoxyphenyl)-4-(trimethylsilyl)but-3-enal (2f).** Yield: 93%. IR (film)  $\nu/\text{cm}^{-1}$ : 2955 (s), 1724 (s), 1611 (m), 1512 (s), 1250 (m), 867 (m), 839 (m).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 29.98), 162 (29.31), 161 (26.77), 147 (20.54), 131 (26.60), 121 (26.63), 73 (95.14). HRMS: calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Si}$  248.1233, found 249.1305 ( $\text{M} + \text{H}^+$ ).

**(7) (*E*)-2-(Naphthalen-1-yl)-4-(trimethylsilyl)but-3-enal (2g).** Yield: 98%. IR (film)  $\nu/\text{cm}^{-1}$ : 3049 (w), 2955 (m), 1724 (s), 1248 (m), 867 (m), 840 (m).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 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 ( $\text{M}^+$ , 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  $\text{C}_{17}\text{H}_{20}\text{OSi}$  268.1283, found 291.1176 ( $\text{M} + \text{Na}^+$ ).

**(8) (*E*)-2-(4-Fluorophenyl)-2-methyl-4-(trimethylsilyl)but-3-enal (2h).** Yield: 76%. IR (film)  $\nu/\text{cm}^{-1}$ : 2956 (s), 1729 (s), 1604 (m), 1509 (s), 1249 (s), 866 (s), 839 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 199.2, 162.0 (d,  $J_{\text{C-F}} = 245.6$  Hz), 144.7, 136.1 (d,  $J_{\text{C-F}} = 2.8$  Hz), 134.0, 129.2 (d,  $J_{\text{C-F}} = 8.2$  Hz), 115.8 (d,  $J_{\text{C-F}} = 21.2$  Hz), 58.9, 20.6,  $-1.3$ . MS (EI,  $m/z$ , rel intensity): 250 ( $\text{M}^+$ , 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  $\text{C}_{14}\text{H}_{19}\text{FOSi}$ : C, 67.16; H, 7.65. Found: C, 66.78; H, 7.86.

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

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

MHz, CDCl<sub>3</sub>/TMS) for *E*-isomer  $\delta$ : 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)  $\nu/\text{cm}^{-1}$  for *E*-isomer: 2956 (w), 2837 (w), 1688 (s), 1607 (m), 1514 (s), 1463 (w), 1249 (s), 842 (m), 805 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/TMS)  $\delta$ : 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). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sup>+</sup>, 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<sub>11</sub>H<sub>12</sub>O<sub>2</sub> 176.0837, found 199.0730 (M + Na<sup>+</sup>).

**(11) Synthesis of (*E*)-2-(4-chlorophenyl)but-2-enal<sup>13</sup> (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<sub>4</sub> (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<sub>2</sub>SO<sub>4</sub> and con-

centrated under reduced pressure. The residue was purified by flash chromatography to give **5c** as white solid. Yield: 86%. Mp: 75–77 °C. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3268 (w, br), 2953 (m), 1608 (w), 1491 (m), 1246 (s), 866 (s), 836 (s). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/TMS):  $\delta$  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). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sup>+</sup>, 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<sub>13</sub>H<sub>19</sub>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 vinylloxiranes **2g** and **2h**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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