

## Asymmetric Synthesis of 2,3-Dihydrofurans by Reaction of Rhodium-Stabilized Vinylcarbenoids with Vinyl Ethers

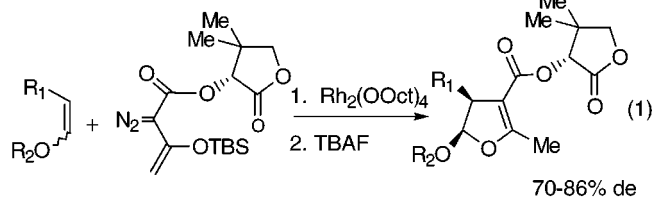
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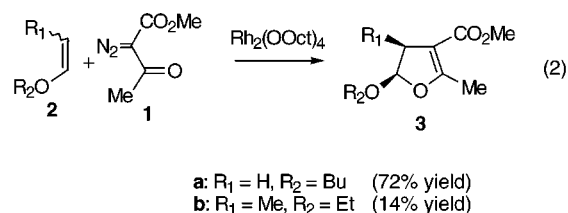
Rhodium(II) octanoate catalyzed decomposition of 2-diazo-3-siloxybutenoates, containing (*R*)-pantolactone as a chiral auxiliary, in the presence of vinyl ethers results in the diastereoselective synthesis of cyclopropanes with high asymmetric induction. Treatment of the cyclopropanes with tetrabutylammonium fluoride results in desilylation and ring expansion of the resulting acylcyclopropanes to 2,3-dihydrofurans with retention of stereochemistry.

The reaction of metal-stabilized carbenoid intermediates with electron rich  $\pi$ -bonds often results in the formation of products that are derived from zwitterionic intermediates.<sup>1–3</sup> A particularly useful example of this chemistry is dihydrofuran formation from the reaction of vinyl ethers with  $\alpha$ -ketocarbenoids such as those derived from diazoacetates or diazopyruvates.<sup>1</sup> In this paper a method is described for the asymmetric synthesis of 2,3-dihydrofurans by reaction of vinyl ethers with carbenoids containing (*R*)-pantolactone<sup>4,5</sup> as a chiral auxiliary (eq 1). This method represents a further illustration of the effectiveness of (*R*)-pantolactone as a chiral auxiliary for asymmetric vinylcarbenoid cyclopropanations.<sup>4,5</sup>



Previous studies have shown that the copper-catalyzed decomposition of methyl diazoacetate **1** in the pres-

ence of vinyl ethers is an effective method for the synthesis of dihydrofurans.<sup>1</sup> Similar results were obtained in this current study using rhodium(II) octanoate as catalyst. Decomposition of methyl diazoacetate **1** with rhodium(II) octanoate in the presence of butyl vinyl ether **2a** resulted in the formation of the dihydrofuran **3a** in 72% yield (eq 2). Repeating the reaction, however, with the more highly substituted vinyl ether **2b** resulted in a much lower yield (14%) of dihydrofuran **3b**, again paralleling the earlier results using copper catalysis.<sup>1a</sup> The *cis* stereochemistry for **3b** was readily determined by NOE difference studies.



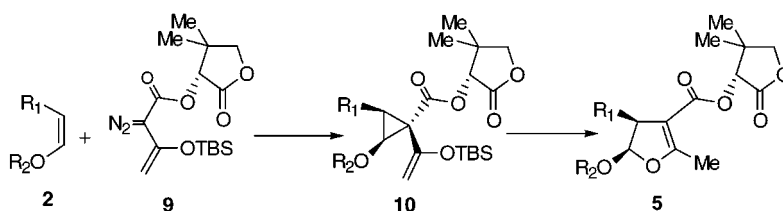
Attempts at extension of this chemistry to asymmetric transformations by using a diazoacetate derivative containing (*R*)-pantolactone as a chiral auxiliary met with limited success. Rhodium(II) octanoate catalyzed decomposition of the diazoacetate **4** in the presence of vinyl ether **2a** resulted in the formation of two products, the dihydrofuran **5a** in 49% yield and the tricyclic product **6a** in 44% yield (eq 3). Furthermore, the desired dihydrofuran **5a** was produced in a meager 11% de. At first sight, the tricyclic product **6a** appears rather unusual, but it is simply the 1,3-dipolar cycloadduct<sup>6</sup> between the vinyl ether and the ylide formed by reaction of the pantolactone carbonyl with the carbenoid. The interaction between the carbenoid and the pantolactone carbonyl is considered to be a critical element for asymmetric cyclopropanation using this chiral auxiliary.<sup>4,5</sup> In the example shown in eq 3, the highly electrophilic carbenoid derived from **4** interacts strongly with the pantolactone carbonyl, and consequently, ylide chemistry<sup>6</sup> dominates over the cyclopropanation chemistry.<sup>7</sup> No improvement

(6) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263.

(7) For a discussion on the delicate balance that exists between ylide and cyclopropanation chemistry for these type of systems, see ref 4a.

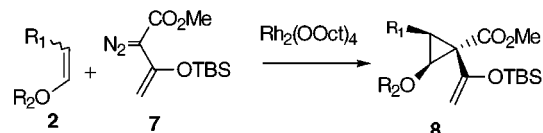
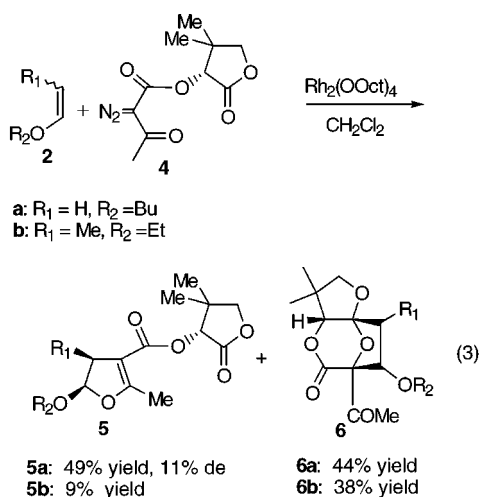
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- (4) (a) Davies, H. M. L.; Huby, N. J. S.; Cantrell, W. R., Jr.; Olive, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 9468. (b) Davies, H. M. L.; Huby, N. J. S., *Tetrahedron Lett.* **1992**, *33*, 6935. (c) Davies, H. M. L.; Ahmed, G.; Churchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774. (d) Davies, H. M. L.; Matasi, J. J.; Hodges, L. M.; Huby, N. J. S.; Thornley, C.; Kong, N.; Houser, J. H. *J. Org. Chem.* **1997**, *62*, 1095.
- (5) (a) Landais, Y.; Planchenault, D. *Tetrahedron* **1997**, *53*, 2855. (b) Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1994**, *53*, 9549. (c) He, M.; Tanimori, S.; Ohira, S.; Nakayama, M. *Tetrahedron* **1997**, *53*, 13307. (d) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630.

Table 1



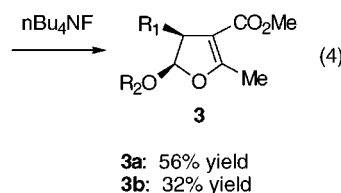
R <sub>1</sub>	R <sub>2</sub>	cyclopropane	yield, %	de, %	dihydrofuran	yield, %	de, %
H	Bu	<b>10a</b>	76	71	<b>5a</b>	56	70
Me	Et	<b>10b</b>	76	ND	<b>5b</b>	77	86
	cyclo-C <sub>2</sub> H <sub>4</sub>	<b>10c</b>	94	68	<b>5c</b>	82	67
Ph	Me	<b>10d</b>	79	71	<b>5d</b>	81	71
4-ClPh	Me	<b>10e</b>	73	80	<b>5e</b>	80	78

was seen in the reaction of **4** with the more highly substituted vinyl ether **2b**. The reaction gave a multitude of products from which **5b** (9% yield) and the tricyclic product **6b** (38% yield) were isolated.



**a**: R<sub>1</sub> = H, R<sub>2</sub> = Bu  
**b**: R<sub>1</sub> = Me, R<sub>2</sub> = Et

**8a**: 46% yield  
**8b**: 32% yield



In contrast to the results seen with the diazoacetate derivatives **1** and **4**, the reactions of the silylated derivatives **7** and **9** resulted in a much more general approach for the asymmetric synthesis of dihydrofuran derivatives. Rhodium(II) octanoate catalyzed decomposition of the vinyl diazomethane **7** in the presence of excess vinyl ether **2a** generated the cyclopropane **8a** in 46% yield (eq 4).<sup>8</sup> Treatment of **8a** with tetrabutylammonium fluoride at  $-78\text{ }^{\circ}\text{C}$  resulted in the formation of the dihydrofuran **3a**. Presumably, the donor-acceptor cyclopropane **8a** that would be formed after desilylation of **8a** undergoes a facile ring expansion to the dihydrofuran.

A more challenging test for **7** is the reaction with the more highly substituted vinyl ether **2b**. Even though the vinyl ether **2b** consisted of a 1:1 mixture of geometrical isomers, the rhodium-catalyzed decomposition of **7** in the presence of excess **2b** generated a single diastereomer of the cyclopropane **8b** in 32% yield. The stereochemical result is consistent with the established lack of reactivity of vinylcarbenoids toward trans alkenes in intermolecular cyclopropanations and the high diastereoselectivity of vinylcarbenoid cyclopropanations.<sup>10</sup> Treatment of **8b** with tetrabutylammonium fluoride at  $-78\text{ }^{\circ}\text{C}$  resulted in the formation of the cis-dihydrofuran **3b**. The cis stereochemistry of **3b** indicates that the ring expansion of **8b** occurs without loss of stereochemistry of the migrating group.

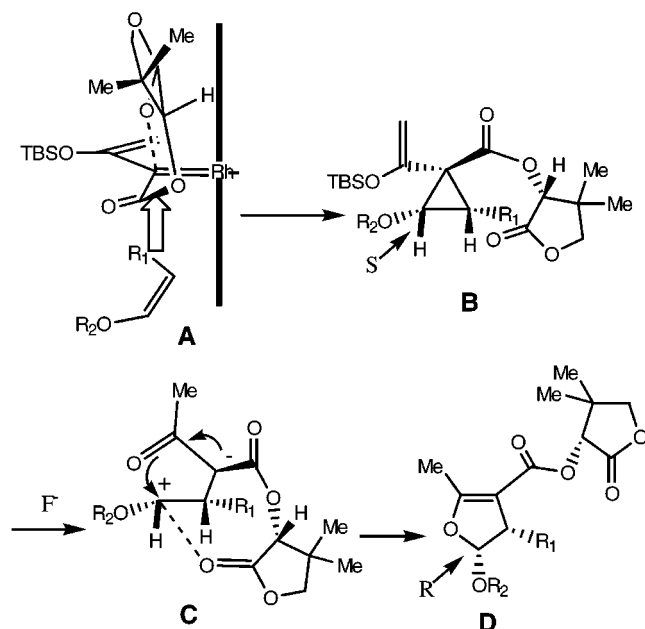
The two-step reaction sequence described above could be extended to the (*R*)-pantolactone derivative **9**, and this resulted in the synthesis of the dihydrofurans with high asymmetric induction. Furthermore, the yields for **9** were much higher than were obtained for the methyl ester derivative **7**.<sup>11</sup> Rhodium(II) octanoate catalyzed decomposition of **9** in the presence of **2a** resulted in the formation of the cyclopropane **10a** in 76% yield and 72% de (Table 1). In this case, no evidence of side-products derived from ylide chemistry were observed. Desilylation of **10a** at  $-78\text{ }^{\circ}\text{C}$  resulted in the formation of **5a** in 56% yield and 70% de. The two diastereomers of the dihydrofuran **5a** were readily separated by column chromatography, to give **5a** of greater than 98% de. The reaction was also successful with the vinyl ether **2b**. Decomposition of **9** in the presence of **2b** generated the cyclopropane **10b** in 76% yield. Desilylation of **10b** at  $-78\text{ }^{\circ}\text{C}$  resulted in the formation of the cis-dihydrofuran **5b** in 77% yield and 86% de. Further examples of this chemistry are shown in Table 1. In each case, the dihydrofuran is formed with virtually the same de as the original cyclopropane, and furthermore, chromatographic purification

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(10) Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203.

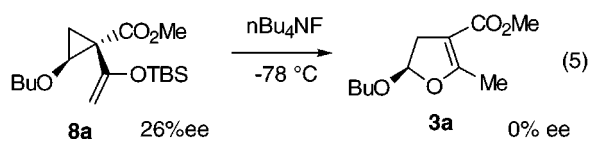
(11) For previous examples of yield enhancement in vinylcarbenoid reactions by using auxiliaries based on  $\alpha$ -hydroxy esters instead of a methyl group, see refs 4d and Davies, H. M. L.; Matasi, J. J.; Thornley, C. *Tetrahedron Lett.* **1995**, *36*, 7205.



**Figure 1.**

of the dihydrofurans readily resolves the major diastereomer to greater than 98% de.

A control experiment was carried out to determine if the (*R*)-pantolactone auxiliary played a role in the stereocontrol of the rearrangement of the cyclopropanes to the dihydrofurans. The cyclopropane **8a** was prepared in 26% ee by  $\text{Rh}_2(\text{DOSP})_4$  catalyzed decomposition of **7** in the presence of vinyl ether **2a**. Tetrabutylammonium fluoride induced rearrangement of **8a** to the dihydrofuran **3a** resulted in complete racemization of the product (eq 5). Comparison of this result with that observed for the rearrangement of **10a** to **5a** would indicate that the (*R*)-pantolactone plays a role not only as the chiral auxiliary in the original cyclopropanation, but also, in retaining the diastereoselectivity during the ring expansion to the dihydrofuran.



On the basis of the fairly extensive studies using (*R*)-pantolactone as a chiral auxiliary for vinylcarbenoid transformations, we have proposed a model in which the carbonyl auxiliary interacts with the re-face of the carbenoid such that preferential attack of the alkene occurs on the si-face of the carbenoid (structure **A**, Figure 1).<sup>4</sup> On the basis of this model, the (2*S*)-2-alkoxycyclopropane (structure **B**) should be preferentially formed. Assuming that the ring expansion to the dihydrofuran occurs with retention of stereochemistry, presumably because of neighboring group participation by the pantolactone carbonyl as shown in structure **C**, the (5*R*)-dihydrofuran (structure **D**) would be predicted to be the major product. The absolute stereochemistry of the dihydrofuran **5d** was unambiguously determined by

X-ray crystallography and was found to be consistent with the predicted absolute stereochemistry. On the basis of the stereochemical model and by analogy to **5d**, the stereochemistry of the major diastereomers of **5a–c** and **5e** are assigned as (5*R*).

In summary, the rhodium(II) octanoate catalyzed reaction between vinyl ethers and (2-siloxyvinyl)diazomethane **9** represents an attractive method for the asymmetric synthesis of dihydrofurans.<sup>13</sup> This method is a further illustration of the effectiveness of (*R*)-pantolactone as a chiral auxiliary for asymmetric vinylcarbenoid cyclopropanations. Furthermore the results of this study underscore the difference in reactivity between vinylcarbenoids and the more traditional carbenoids derived from diazoacetates. A particularly interesting aspect of this chemistry is that the ring expansion of acylcyclopropanes to dihydrofurans was achieved with retention of stereochemistry.

## Experimental Section

**General Methods.** Hexane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Dichloromethane and acetonitrile were distilled from calcium hydride. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 300, 400, or 500 MHz NMR spectrometers. Column chromatography was carried out on silica gel 60 (230–400 mesh). Thin-layer chromatography (TLC) was performed on Whatman (TLC) paper. Vinyl ethers were purchased from Aldrich Chemical Co. and filtered through  $\text{MgSO}_4$  and silica before use. Diazo compounds **1**, **4**, **7**, and **9** were prepared by the literature methods.<sup>4</sup>

**2-*n*-Butoxy-4-(methoxycarbonyl)-5-methyl-2,3-dihydrofuran (**3a**).** Method A: A solution of **1** (0.50 g, 3.52 mmol) in hexane (50 mL) was added dropwise over 30 min to a refluxing solution of rhodium(II) octanoate (0.075 g, 0.096 mmol) and **2a** (0.85 g, 8.50 mmol) in hexane (50 mL) under argon. The resulting solution was refluxed for a further 30 min, the solvent was removed, and the residue was purified by column chromatography on silica gel using  $\text{Et}_2\text{O}$ /hexane (1:19) as solvent to give **3a** as colorless oil (0.54 g, 72% yield). Method B: Tetrabutylammonium fluoride (1 M in THF) was added to a stirring solution of **8a** (0.107 g, 0.33 mmol) in THF (10 mL) at  $-78^\circ\text{C}$  under argon. The resulting solution was allowed to stir for 1 h at  $-78^\circ\text{C}$ . It was quenched with dil aq  $\text{NH}_4\text{Cl}$  solution, and the aqueous layer was extracted with ether (2  $\times$  50 mL). The combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ), the solvent was removed, and the residue was purified by column chromatography on silica gel using  $\text{Et}_2\text{O}$ /hexane (1:19) as solvent to give **3a** as colorless oil (0.40 g, 56% yield). IR (neat) 1706, 1653  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.51 (dd,  $J = 3.0, 7.5$  Hz, 1 H), 3.79 (td,  $J = 6.7, 9.5$  Hz, 1 H), 3.69 (s, 3 H), 3.50 (td,  $J = 6.7, 9.5$  Hz, 1 H), 2.99 (qdd,  $J = 1.8, 7.5, 15.9$  Hz), 2.71 (qdd,  $J = 1.8, 3.0, 15.9$  Hz, 1 H), 2.22 (t,  $J = 1.8$  Hz, 3 H), 1.62–1.52 (m, 2 H), 1.42–1.30 (m, 2 H), 0.91 (t,  $J = 7.4$  Hz, 3 H); <sup>13</sup>C NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 166.3, 105.3, 101.3, 68.5, 50.8, 36.3, 31.5, 19.1, 14.0, 13.7; HRMS calcd for  $\text{C}_{16}\text{H}_{24}\text{O}_6$ : 214.1205; found: 214.1213.

**3,5-Dimethyl-2-ethoxy-4-(methoxycarbonyl)-2,3-dihydrofuran (**3b**).** Prepared from **1** (0.21 g, 1.47 mmol) and **2b** as described in method A for **3a** (14% yield), or it was prepared from **8b** (1.14 g, 3.63 mmol) as described in method B for **3a** (32% yield): IR (neat) 1701, 1646  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.49 (d,  $J = 7.2$  Hz, 1 H), 3.87 (dq,  $J = 7.0$  and 9.6 Hz, 1 H), 3.69 (s, 3 H), 3.58 (dq,  $J = 7.0$  and 9.6 Hz, 1 H), 3.18 (dq,  $J = 1.8$  and 7.2 Hz, 1 H), 2.18 (d,  $J = 1.8$  Hz, 3 H), 1.24 (t,  $J = 7.0$  Hz, 3 H), 1.15 (d,  $J = 7.2$  Hz, 3 H); <sup>13</sup>C NMR

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(13) **Note added in proof:** Since submission of this paper, a chiral catalysis approach to dihydrofurans has been reported: Ishitani, H.; Achiwa, K. *Heterocycles* **1997**, *46*, 153.

(75 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 166.3, 107.6, 107.1, 65.5, 50.6, 39.9, 14.8, 14.3, 11.3. Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>: C, 59.98; H, 8.05. Found: C, 59.99; H, 8.13.

**2-*n*-Butoxy-4-[(3*R*)-3-(4,4-dimethyl-2-oxotetrahydrofuran-2-ylideneoxy)carbonyl]-5-methyl-2,3-dihydrofuran (5a) and 7-Acetyl-8-*n*-butoxy-3,3-dimethyl-7,9a-epoxy-2,3,4-trihydrofuro[2,3-*f*]-6-oxepanone (6a).** Prepared from **4** (0.50 g, 2.08 mmol) and **2a** in dichloromethane as described in method A for **3a** (**5a**: 49% yield, 11% de; **6a**: 44% yield), or **5a** was prepared from **10a** (0.58 g, 1.36 mmol) as described in method B for **3a** (56% yield, 70% de); diastereomeric excess was determined from the ratio of the signals for one of the 3-dihydrofuran protons of the two isomers in the <sup>1</sup>H NMR of the crude reaction mixture. **5a**: IR (neat) 1791, 1708, 1647 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.56 (dd, *J* = 3.1, 7.6 Hz, 1 H), 5.44 (s, 1 H), 4.05 (d, *J* = 9.0 Hz, 1 H), 4.02 (d, *J* = 9.0 Hz, 1 H), 3.81 (td, *J* = 6.6, 9.6 Hz, 1 H), 3.52 (td, *J* = 6.6, 9.6 Hz, 1 H), 3.10 (qdd, *J* = 1.8, 7.6, 15.6 Hz, 1 H), [minor isomer 3.10 (qdd, *J* = 1.8, 7.6, 15.6 Hz, 1 H), 2.72 (qdd, *J* = 1.8, 3.3, 15.6 Hz, 1 H), 2.25 (dd, *J* = 1.8, 1.8 Hz, 3 H), 1.58 (m, 2 H), 1.37 (m, 2 H), 1.20 (s, 3 H), 1.10 (s, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  173.1, 168.9, 164.1, 105.8, 100.1, 76.1, 74.0, 68.8, 40.1, 35.9, 31.4, 22.8, 19.9, 19.0, 14.2, 13.6. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>6</sub>: C, 61.52; H, 7.74. Found: C, 61.44; H, 7.74. **6a**: IR (neat) 1760, 1731 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.37 (d, *J* = 8.8 Hz, 1 H), 4.29 (s, 1 H), 4.01 (d, *J* = 8.7 Hz, 1 H), 3.79 (d, *J* = 8.7 Hz, 1 H), 3.58 (dt, *J* = 6.7, 9.3 Hz, 1 H), 3.47 (dt, *J* = 6.7, 9.3 Hz, 1 H), 2.35 (dd, *J* = 8.8, 13.1 Hz, 1 H), 2.30 (s, 3 H), 2.03 (d, *J* = 13.1 Hz, 1 H), 1.47 (quintet, *J* = 6.7 Hz, 2 H), 1.29 (m, 2 H), 1.28 (s, 3 H), 1.23 (s, 3 H), 0.87 (t, *J* = 7.3 Hz, 3 H)]; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  198.5, 164.0, 108.3, 90.0, 88.3, 80.5, 77.1, 70.8, 41.1, 39.8, 31.5, 26.5, 26.1, 20.8, 19.1, 13.8. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>6</sub>: C, 61.52; H, 7.74. Found: C, 61.58; H, 7.73. HRMS calcd for C<sub>16</sub>H<sub>24</sub>O<sub>6</sub>: 312.1572; found: 312.1560.

**3,5-Dimethyl-4-[(3*R*)-3-(4,4-dimethyl-2-oxotetrahydrofuran-2-ylideneoxy)carbonyl]-2-ethoxy-2,3-dihydrofuran (5b) and 7-Acetyl-8-ethoxy-3,3,9-trimethyl-7,9a-epoxy-2,3,4-trihydrofuro[2,3-*f*]-6-oxepanone (6b).** Prepared from **4** (0.48 g, 2 mmol) and **2b** in dichloromethane as described in method A for **3a** (**5b**: 9% yield; **6b**: 38% yield), or **5b** was prepared from **10b** (0.50 g, 1.21 mmol) as described in method B for **3a** (77% yield, 86% de); diastereomeric excess was determined from the ratio of the signals for the 3-methylidihydrofuran protons of the two isomers in the <sup>1</sup>H NMR of the crude reaction mixture: IR (neat) 1790, 1705, 1635 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.54 (d, *J* = 7.1 Hz, 1 H), 5.46 (s, 1 H), 4.05 (d, *J* = 9.1 Hz, 1 H), 4.02 (d, *J* = 9.1 Hz, 1 H), 3.89 (qd, *J* = 7.1, 9.6 Hz, 1 H), 3.60 (qd, *J* = 7.1, 9.6 Hz, 1 H), 3.27 (quintet, *J* = 1.5, 7.1 Hz, 1 H), 2.22 (d, *J* = 1.5 Hz, 3 H), [minor isomer 2.21 (d, *J* = 1.5 Hz, 3 H)], 1.24 (t, *J* = 7.1 Hz, 3 H), 1.22 (s, 3 H), 1.18 (d, *J* = 7.1 Hz, 3 H), 1.12 (s, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  173.2, 169.1, 164.4, 108.1, 105.9, 76.1, 74.2, 65.7, 40.3, 39.5, 23.0, 20.2, 14.8, 14.7, 12.0. Anal. Calcd for C<sub>15</sub>H<sub>22</sub>O<sub>6</sub>: C, 60.39; H, 7.43. Found: C, 60.32; H, 7.47. **6b** (major isomer): IR (neat) 1765, 1734 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.21 (s, 1 H), 3.96 (d, *J* = 8.8 Hz, 1 H), 3.91 (s, 1 H), 3.73 (d, *J* = 8.8 Hz, 1 H), 3.70–3.45 (m, 2 H), 2.27 (s, 3 H), 2.17 (q, *J* = 7.3 Hz, 1 H), 1.23 (s, 3 H), 1.18 (s, 3 H), 1.11–1.13 (m, 6 H)]; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  198.9, 164.4, 108.8, 88.8, 88.3, 84.7, 79.9, 66.3, 45.2, 41.0, 26.1, 25.9, 20.4, 14.8, 13.4; HRMS calcd for C<sub>15</sub>H<sub>22</sub>O<sub>6</sub>: 298.1411; found: 298.1416.

***cis*-3-[(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuran-2-ylideneoxy)carbonyl]-2-methyl-1,7-dioxabicyclo[3.3.0]oct-2-ene (5c).** Prepared from **10c** (0.55 g, 1.38 mmol) as described in method B for **3a** (82% yield, 67% de); diastereomeric excess was determined from the ratio of the signals for the proton at C-8 of the two isomers in <sup>1</sup>H NMR of the crude reaction mixture: [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -213.0° (*c* 1.5, CHCl<sub>3</sub>); IR (neat) 1788, 1706, 1639 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.11 (d, *J* = 6.3 Hz, 1 H), [minor isomer 6.09 (d, *J* = 6.3 Hz, 1 H)], 5.44 (s, 1 H), 4.04 (m, 1 H), 4.03 (s, 2 H), 3.78 (m, 1 H), 3.68 (m, 1 H), 2.22 (d, *J* = 1.5 Hz, 3 H), 2.04 (m, 2 H), 1.20 (s, 3 H), 1.09 (s, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  172.9, 171.1, 163.8, 110.2, 102.3, 76.0,

74.2, 66.9, 46.5, 40.1, 31.4, 22.8, 20.0, 14.3. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>6</sub>: C, 59.57; H, 6.43. Found: C, 59.65; H, 6.47.

***cis*-4-[(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuran-2-ylideneoxy)carbonyl]-2-methoxy-5-methyl-3-phenyl-2,3-dihydrofuran (5d).** Prepared from **10d** (0.32 g, 0.69 mmol) as described in method B for **3a** (81% yield, 71% de); diastereomeric excess was determined from the ratio of the signals for the 2-dihydrofuran proton of the two isomers in the <sup>1</sup>H NMR of the crude reaction mixture: mp 120–21 °C (ether/hexane); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -161.1° (*c* 1.6, CHCl<sub>3</sub>); IR (neat) 1790, 1709, 1640 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 (d, *J* = 7.6 Hz, 2 H), 7.19 (m, 3 H), 5.64 (d, *J* = 7.9 Hz, 1 H), [minor isomer 5.62 (d, *J* = 7.9 Hz, 1 H)], 5.24 (s, 1 H), 4.48 (qd, *J* = 1.5, 7.9 Hz, 1 H), 3.85 (d, *J* = 8.8 Hz, 1 H), 3.78 (d, *J* = 8.8 Hz, 1 H), 3.39 (s, 3 H), 2.39 (d, *J* = 1.5 Hz, 3 H), 0.80 (s, 3 H), 0.35 (s, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  173.1, 170.8, 164.0, 136.8, 129.2, 127.9, 127.0, 108.6, 104.8, 76.1, 73.9, 57.5, 51.2, 39.7, 22.1, 18.7, 14.2. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>O<sub>6</sub>: C, 65.88; H, 6.40. Found: C, 66.00; H, 6.47.

***cis*-3-(4-Chlorophenyl)-4-[(3*R*)-3-(4,4-dimethyl-2-oxotetrahydrofuran-2-ylideneoxy)carbonyl]-2-methoxy-5-methyl-2,3-dihydrofuran (5e).** Prepared from **10e** (0.42 g, 0.84 mmol) as described in method B for **3a** (80% yield, 78% de); diastereomeric excess was determined from the ratio of the signals for the 3-dihydrofuran proton of the two isomers in <sup>1</sup>H NMR of the crude reaction mixture: IR (neat) 1789, 1708, 1639 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 5.61 (d, *J* = 7.9 Hz, 1 H), 5.25 (s, 1 H), 4.45 (dq, *J* = 1.4, 7.9 Hz, 1 H), [minor isomer 4.41 (dq, *J* = 1.4, 7.9 Hz, 1 H)], 3.88 (d, *J* = 8.9 Hz, 1 H), 3.82 (d, *J* = 8.9 Hz, 1 H), 3.39 (s, 3 H), 2.38 (d, *J* = 1.4 Hz, 3 H), 0.86 (s, 3 H), 0.41 (s, 3 H)]; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  173.0, 171.1, 163.8, 135.5, 132.8, 130.6, 128.1, 108.2, 104.6, 76.1, 74.1, 57.5, 50.7, 39.8, 22.3, 18.8, 14.3. Anal. Calcd for C<sub>19</sub>H<sub>21</sub>O<sub>6</sub>Cl: C, 59.92; H, 5.56. Found: C, 60.02; H, 5.62. HRMS calcd for C<sub>19</sub>H<sub>21</sub>O<sub>6</sub>Cl 380.1027; found: 380.1047.

**Methyl 1-*n*-Butoxy-2-[1-((1,1-dimethylethyl)dimethylsiloxy)ethene]cyclopropane-2-carboxylate (8a).** Prepared from **7** (0.93 g, 3.63 mmol) and **2a** in hexane as described in method A for **3a** (46% yield): IR (neat) 1729, 1636 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.33 (s, 1 H), 4.32 (s, 1 H), 3.79 (t, *J* = 6.2 Hz, 1 H), 3.77–3.70 (m, 1 H), 3.66 (s, 3 H), 3.58–3.51 (m, 1 H), 1.56–1.47 (m, 2 H), 1.44 (d, *J* = 6.2 Hz, 2 H), 1.32 (sextet, *J* = 7.5 Hz, 2 H), 0.91 (s, 9 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 0.22 (s, 3 H), 0.21 (s, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  127.8, 153.2, 94.3, 71.5, 64.2, 51.7, 35.6, 25.4, 21.1, 19.0, 17.8, 13.7, -4.6, -5.9. Anal. Calcd for C<sub>15</sub>H<sub>28</sub>O<sub>4</sub>Si: C, 62.15; H, 9.82. Found: C, 62.00; H, 9.80.

**Methyl 2-[1-((1,1-dimethylethyl)dimethylsiloxy)ethene]-1-ethoxy-3-methylcyclopropane-2-carboxylate (8b).** Prepared from **7** (0.93 g, 3.63 mmol) and **2b** in hexane as described in method A for **3a** (32% yield): IR (neat) 1719, 1636 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.31 (s, 1 H), 4.20 (s, 1 H), 3.70 (dq, *J* = 7.3, 9.1 Hz, 1 H), 3.63 (s, 3 H), 3.59 (dq, *J* = 7.3, 9.1 Hz, 1 H), 3.56 (d, *J* = 7.3 Hz, 1 H), 1.70 (quintet, *J* = 7.3 Hz, 1 H), 1.19 (t, *J* = 7.3 Hz, 3 H), 1.16 (d, *J* = 7.3 Hz, 3 H), 0.88 (s, 9 H), 0.19 (s, 3 H), 0.18 (s, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 173.0, 149.8, 95.5, 66.7 (2 C), 51.4, 36.0, 25.3, 25.1, 17.7, 14.8, 7.7, -5.1, -5.5. Anal. Calcd for C<sub>16</sub>H<sub>30</sub>O<sub>4</sub>Si: C, 61.11; H, 9.61. Found: C, 61.27; H, 9.58.

**(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuran-2-ylideneoxy)-1-*n*-Butoxy-2-[1-((1,1-dimethylethyl)dimethylsiloxy)ethene]cyclopropane-2-carboxylate (10a).** Prepared from **9** (0.89 g, 2.51 mmol) and **2a** in hexane as described for **3a** in method A (76% yield, 72% de); diastereomeric excess was determined from the ratio of the signals for the 5-tetrahydrofuran proton of the two isomers in <sup>1</sup>H NMR of the crude reaction mixture: IR (neat) 1793, 1743, 1624 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.28 (s, 1 H), [minor isomer 5.29 (s, 1 H)], 4.38 (d, *J* = 1.5 Hz, 1 H), 4.37 (d, *J* = 1.5 Hz, 1 H), 4.01 (d, *J* = 8.9 Hz, 1 H), 3.96 (d, *J* = 8.9 Hz, 1 H), 3.90 (dd, *J* = 5.5, 6.4 Hz, 1 H), 3.71 (td, *J* = 6.6, 9.2 Hz, 1 H), 3.52 (td, *J* = 6.6, 9.2 Hz, 1 H), 1.52 (m, 2 H), 1.30 (m, 2 H), 1.15 (s, 3 H), 1.05 (s, 3 H), 0.89 (s, 9 H), 0.87 (t, *J* = 7.2 Hz, 3 H), 0.19 (s, 3 H), 0.18 (s, 3 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  172.3, 170.6, 152.1, 95.4, 76.1, 74.9,

71.4, 64.4, 40.0, 35.8, 31.5, 25.6, 22.9, 21.3, 19.6, 19.0, 17.9, 13.7, -4.9, -5.1. Anal. Calcd for  $C_{22}H_{38}O_6Si$ : C, 61.94; H, 8.98. Found: C, 61.91; H, 9.07.

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**Supporting Information Available:** Experimental data for **5d**, **5e**, and **10b-e**, copies of  $^1H$  NMR spectra of **3a** and **6b**, NOE data for **3b**, and X-ray crystallographic data for **5d** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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