# Synthesis of α-Allyloxy-Substituted α,β-Unsaturated Esters via Aldol Condensation. Convenient Access to Highly Substituted Allyl Vinyl Ethers

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**Abstract**:  $\alpha$ -Allyloxy-substituted  $\alpha$ , $\beta$ -unsaturated esters **1a**-**r** have been prepared in 5 steps from commercially available starting materials. The key sequence of the synthesis is an aldol addition between an  $\alpha$ -allyloxy-substituted ester **2a**-**i** and an aldehyde R<sup>1</sup>CHO followed by mesylation and DBU mediated elimination to afford the 2-alkoxycarbonyl-substituted allyl vinyl ethers **1a**-**r**. The *E*/*Z* ratio of the newly generated vinyl ether double bond is apparently determined by the steric bulk of the vinyl ether double bond substituent R<sup>1</sup>. *Z:E* ratios from 3:2–9:1 were obtained.

Key words: allyl vinyl ethers, aldol reactions, eliminations, esters

Without doubt, sigmatropic rearrangements create one of the most important classes of synthetic transformations. Several striking examples have proven the utility of sigmatropic rearrangements for the stereoselective synthesis of organic compounds.<sup>1</sup> In an ongoing effort to further increase the synthetic efficiency, much work is devoted to extend the scope of classical sigmatropic rearrangements.<sup>2</sup> In this regard, we are engaged in a research program which focuses on the development of metal catalyzed Claisen rearrangements and pericyclic domino reactions which are triggered by a dienolate [2,3]-Wittig rearrangement. The starting materials for both processes are  $\alpha$ -allyloxy-substituted  $\alpha$ , $\beta$ -unsaturated esters **1**.

Particularly, we were able to show that the 2-alkoxycarbonyl-substituted allyl vinyl ether **1f** can be transformed to an  $\alpha$ -keto ester diastereoselectively employing a combination of Pd(II)-catalysis and thermal reaction conditions (Scheme 1).<sup>3</sup>





Furthermore, when treated with an appropriate base  $\alpha$ -allyloxy-substituted  $\alpha$ , $\beta$ -unsaturated esters **1** can be transformed to the corresponding dienolates which undergo a dienolate [2,3]-Wittig rearrangement to 3-alkoxycarbonyl-3-hydroxy-substituted 1,5-hexadienes.<sup>4</sup> These compounds are substrates for a domino 3-oxy-Cope rearrangement/type II carbonyl ene reaction affording substituted carbocycles (Scheme 2).<sup>5</sup>





Finally, we have recently established first examples for a domino ester dienolate [2,3]-Wittig/anionic 3-oxy Cope rearrangement to afford the corresponding  $\alpha$ -keto esters (Scheme 3).<sup>6</sup>



Scheme 3

Obviously, it was indispensable to develop a reliable, flexible and efficient synthetic access to  $\alpha$ -allyloxy-sub-

stituted  $\alpha$ , $\beta$ -unsaturated esters **1** to be in the position to study the scope and limitations of the newly developed synthetic processes. At the outset, an aldol condensation strategy seemed to be an ideal approach with respect to synthetic convergence and substrate availability (Scheme 4).





The general access to 2-allyloxy-substituted esters **2** was well established (etherification followed by esterification)<sup>7</sup> and an example for a chemoselective aldol addition of an ester enolate from **2** with an aldehyde was also found in the literature.<sup>8</sup> The transformation of the  $\beta$ -hydroxy ester **3** to the desired unsaturated ester **1** via an E<sub>2</sub>-like elimination would be straightforward with the inherent possibility of a stereoselective double bond generation via E<sub>2</sub> elimination of a diastereomerically pure  $\beta$ -hydroxy ester **3**. We report here, for the first time, detailed synthetic procedures, and spectroscopic data for the synthesis and characterization of the  $\alpha$ -allyloxy-substituted  $\alpha$ , $\beta$ -unsaturated esters **1a**–**r**.

The 2-allyloxy-substituted esters  $2\mathbf{a}-\mathbf{i}$  were prepared utilizing a modified literature procedure for the etherification of bromoacetic acid with allylic alcohols (see experimental). The esterification was conveniently realized employing the DCC/DMAP method (Scheme 5, Table 1).<sup>7</sup> The acids and the esters  $2\mathbf{a}-\mathbf{i}$  can be purified by kugelrohr distillation.





# **Table 1** Synthesis of Allyloxy-acetic acid Esters **2a-i**

Cpd.	R <sup>ester</sup>	$\mathbb{R}^2$	R <sup>3</sup>	$\mathbf{R}^{E}$	R <sup>z</sup>	Yield (%)
2a	Me	Н	Н	<i>n</i> -Pr	Н	63
2b	Me	Me	Н	Н	Н	69
2c	Me	Н	Н	Н	<i>n</i> -Pr	62
2d	<i>i</i> -Pr	Me	Н	Н	Н	56
2e	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	69
2f	<i>i</i> -Pr	Н	Н	Н	<i>n</i> -Pr	78
2g	<i>i</i> -Pr	Н	Н	Me	Me	64
2h	<i>i</i> -Pr	Н	Me	Н	Н	65
2i	MeOEt <sup>a</sup>	Н	Н	<i>n</i> -Pr	Н	64

<sup>a</sup> MeOEt: methoxyethyl.

The aldol addition was realized by treating the esters  $2\mathbf{a}-\mathbf{i}$  with LDA at -78 °C followed by the addition of an aldehyde at -78 °C to provide the desired  $\beta$ -hydroxy-esters  $3\mathbf{a}-\mathbf{r}$  in good yield but low diastereoselectivity (Scheme 6, Table 2). The diastereoselectivity was determined for the corresponding mesylates  $4\mathbf{a}-\mathbf{p}$  (Table 3). The relative configuration was not assigned. A deprotonation time of 5 to 10 minutes proved to be sufficient. By utilizing these reaction conditions, we were able to suppress the enolate [2,3]-Wittig rearrangement of the lithium ester enolates generated from the 2-allyloxy-acetic acid esters  $2\mathbf{a}-\mathbf{i}$ .<sup>9</sup>



## Scheme 6

The transformation of the  $\beta$ -hydroxy esters  $3\mathbf{a}-\mathbf{r}$  to the desired  $\alpha,\beta$ -unsaturated esters  $1\mathbf{a}-\mathbf{r}$  was realized by a two-step procedure. The  $\beta$ -hydroxy ester  $3\mathbf{a}-\mathbf{r}$  was mesylated and, following an aqueous work-up the crude mesylate  $4\mathbf{a}-\mathbf{r}$  was treated with DBU in THF to provide the  $\alpha,\beta$ -unsaturated esters  $1\mathbf{a}-\mathbf{r}$  in high yield as an inseparable mixture of double bond isomers (Schemes 6 and 7, Table 3). The assignment of the double bond configuration is based on NOESY experiments.

The diastereoselectivity for the aldol addition, determined by integration of the <sup>1</sup>H NMR signal of the OSO<sub>2</sub>CH<sub>3</sub> group of the mesylates **4a**–**q**, was in the range of 7:3 for all  $\beta$ -hydroxy esters **3a–r** (Table 3). Based on an E<sub>2</sub>-like

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<b>Table 2</b> Synthesis of β-Hydroxy Esters
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Prod- uct	$\mathbb{R}^1$	R <sup>ester</sup>	R <sup>2</sup>	R <sup>3</sup>	$\mathbf{R}^{E}$	R <sup>Z</sup>	Yield (%)
3a	Me	Me	Н	Н	<i>n</i> -Pr	Н	84
3b	Me	Me	Me	Н	Н	Н	55
3c	Et	Me	Н	Н	Н	<i>n</i> -Pr	64
3d	Et	Me	Н	Н	<i>n</i> -Pr	Н	75
3e	Me	MeOEt <sup>a</sup>	Н	Н	<i>n</i> -Pr	Н	77
3f	Et	MeOEt <sup>a</sup>	Н	Н	<i>n</i> -Pr	Н	62
3g	Et	<i>i</i> -Pr	Н	Н	Me	Me	92
3h	Me	<i>i</i> -Pr	Н	Н	Me	Me	84
3i	Me	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	88
3j	Me	<i>i</i> -Pr	Н	Н	Н	<i>n</i> -Pr	88
3k	Et	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	95
31	Me	<i>i</i> -Pr	Н	Me	Н	Н	79
3m	<i>i</i> -Pr	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	77
3n	Ph	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	89
30	Bn	<i>i</i> -Pr	Н	Н	Me	Me	78
3р	Bn	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	95
3q	Bn	<i>i</i> -Pr	Me	Н	Н	Н	64
3r	Bn	<i>i</i> -Pr	Н	Me	Н	Н	80

<sup>a</sup> MeOEt: methoxyethyl.



Scheme 7

elimination process, one would assume that the diastereomeric ratio of the mesylates 4a-r would be transferred into the E/Z ratios of the elimination products 1a-r(Scheme 8). That is obviously not the case. The Z/E ratios vary roughly from 3:2 ( $R^1 = Me$ ) to 7:3 ( $R^1 = Et$ ) to >9:1  $(R^1 = i$ -Pr, Ph, Bn). Other substituents besides  $R^1$  have apparently no significant influence on the observed Z/E ratios in 1a-r. We assume that the Z configured esters 1a**r** are thermodynamically more stable and an increasing steric bulk of the substituent R<sup>1</sup> favors the formation of the Z configured esters 1a-r. We suggest a nucleophilic 1,4addition/elimination process with DBU acting as a nucleophile in order to explain the proposed equilibration between the E and Z configured  $\alpha,\beta$ -unsaturated esters 1a-r (Scheme 8). It should be noted that the DBU mediated elimination of the mesylates 40-r (R<sup>1</sup> = Bn) led to the formation of a minor amount of the corresponding  $\beta$ ,  $\gamma$ unsaturated esters 60-r which were easily separated by column chromatography (Table 3, Scheme 8).

Table 3 Synthesis of 2-Allyloxy-Substituted α,β-Unsaturated Esters 1a-r

	Substr	ate					Produc	:t			
Entry	Cpd	dr <sup>a</sup>	Cpd.	$R^1$	R <sup>ester</sup>	R <sup>2</sup>	R <sup>3</sup>	$\mathbf{R}^{E}$	R <sup>Z</sup>	Yield (%) from <b>3</b>	$Z:E^{\mathrm{b}}$
1	4a	71:29	1a	Me	Me	Н	Н	<i>n</i> -Pr	Н	91	59:41
2	<b>4b</b>	с	1b	Me	Me	Me	Н	Н	Н	51 <sup>d</sup>	с
3	4c	70:30	1c	Et	Me	Н	Н	Н	<i>n</i> -Pr	81	69:31
4	<b>4d</b>	72:28	1d	Et	Me	Н	Н	<i>n</i> -Pr	Н	83	72:28
5	4e	78:22	1e	Me	MeOEte	Н	Н	<i>n</i> -Pr	Н	81	60:40
6	<b>4f</b>	76:24	1f	Et	MeOEte	Н	Н	<i>n</i> -Pr	Н	95	73:27
7	4g	73:27	1g	Et	<i>i</i> -Pr	Н	Н	Me	Me	71	67:33
8	4 <b>h</b>	70:30	1ĥ	Me	<i>i</i> -Pr	Н	Н	Me	Me	89	61:39
9	<b>4i</b>	70:30	1i	Me	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	93	64:36
10	4j	72:28	1j	Me	<i>i</i> -Pr	Н	Н	Н	<i>n</i> -Pr	88	61:39
11	4k	69:31	1k	Et	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	77	76:24
12	41	70:30	11	Me	<i>i</i> -Pr	Н	Me	Н	Н	82	59:41
13	4m	71:29	1m	<i>i</i> -Pr	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	52 (42) <sup>f</sup>	91:9
14	4n	60:40	1n	Ph	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	78 <sup>g</sup>	>95:5
15	<b>4</b> o	75:25	10	Bn	<i>i</i> -Pr	Н	Н	Me	Me	61 (10) <sup>h</sup>	96:4
16	4p	76:24	1p	Bn	<i>i</i> -Pr	Н	Н	<i>n</i> -Pr	Н	80 (10) <sup>h</sup>	97:3
17	4q	с	1q	Bn	<i>i</i> -Pr	Me	Н	Н	Н	34 <sup>g</sup>	>95:5
18	4 <b>r</b>	83:17 <sup>i</sup>	1r	Bn	<i>i</i> -Pr	Н	Me	Н	Н	77 (12) <sup>h</sup>	96:4

<sup>a</sup> Determined from <sup>1</sup>H NMR spectra, configuration not assigned.

<sup>b</sup> Determined from <sup>1</sup>H NMR spectra, configuration assigned based on NOESY experiments.

<sup>d</sup> Spectra in CDCl<sub>3</sub> show a 1:1 mixture with the corresponding Claisen rearrangement product.

<sup>e</sup> MeOEt: methoxyethyl.

 $^{\rm f}$  In parentheses: % yield of recovered mesylate 4m.

<sup>g</sup> Spectra in CDCl<sub>3</sub> show a contamination with the corresponding Claisen rearrangement product.

<sup>h</sup> In parentheses: % yield of the corresponding  $\beta$ , $\gamma$ -unsaturated ester.

<sup>i</sup> Determined from the <sup>1</sup>H NMR spectrum of the  $\beta$ -hydroxy ester **3r**.

<sup>&</sup>lt;sup>c</sup> Not determined.





Except for the compounds **1b**, **1n** and **1q**, all allyl vinyl ethers **1a**-**r** are stable colorless oils which can be stored at 0 °C for weeks without significant decomposition. Generally, the allyl vinyl ethers **1a**-**r** are vulnerable to the thermal Claisen rearrangement affording the corresponding  $\alpha$ -keto esters **5a**-**r**. The thermal Claisen rearrangement proceeds slowly at or above room temperature for most of the ethers **1a**-**r**. Allyl vinyl ethers **1b**, **1q** (R<sup>2</sup> = methyl) and **1n** (R<sup>1</sup> = phenyl) are significantly more reactive with respect to the Claisen rearrangement so that only a mixture of the allyl vinyl ethers **1b**, **1r**, **1n** and the  $\beta$ -keto esters **5b**, **5r** and **5n** were detected by NMR in CDCl<sub>3</sub> at room temperature. A detailed study of the thermal and metal catalyzed Claisen rearrangement of the allyl vinyl ethers **1a**-**r** will be reported elsewhere.<sup>10</sup>

In conclusion, we present a reliable, variable and efficient general access to  $\alpha$ -allyloxy-substituted  $\alpha$ , $\beta$ -unsaturated esters **1a**-**r**. Unfortunately, the outlined procedure does not allow general stereocontrol over the vinyl ether double bond configuration. Nevertheless, bulky substituents (R<sup>1</sup> = *i*-Pr, Bn, Ph) on the vinyl ether double bond give access to *Z* configured allyl vinyl ethers stereoselectively (**1m**-**r**, *Z*:*E* >9:1). Even as a mixture of double bond isomers, the esters **1** have already been utilized as starting

materials for diastereoselective sequential pericyclic reactions and for a metal catalyzed Claisen rearrangement.<sup>3,4,5</sup> Further work aimed at exploiting the synthetic potential of the 2-alkoxycarbonyl-substituted allyl vinyl ethers **1** is currently under way.

All reactions were performed in septum-sealed flame-dried flasks under an Ar atm. Solvents, reagents, and substrates were transferred by the means of syringes. All solvents were dried by standard methods. Reagents were used as purchased unless otherwise noted. All aldehydes were freshly distilled prior to use for the aldol addition. MeOH, *i*-PrOH and 2-methoxy-ethanol were dried by standard methods and stored over molecular sieves. Commercial *n*-BuLi solutions in hexanes were titrated following the procedure of Kofron.<sup>11</sup> Crude products were purified by column chromatography employing silica gel (0.040–0.063 mm) and mixtures from EtOAc and heptane. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC 300 or a DRX 500 in CDCl<sub>3</sub>. IR spectra were obtained on a Carlo Erba CHN-S analyzer.

## 2-Allyloxy-Substituted Acetic Acids; General Procedure

NaH (100 mmol, 60% suspension in mineral oil) was suspended in THF (250 mL). Under vigorous stirring, the allylic alcohol (50 mmol) was added at r.t. and stirring was continued until the gas extrusion was finished. To this suspension was added a solution of bromo-acetic acid (50 mmol) in THF (10 mL) at r.t. The reaction mixture was stirred over night and the reaction was then quenched by the addition of aq KOH (3 N, 75 mL). The phases were separated and the organic phase was extracted with aq KOH (3 N,  $2 \times 75$  mL). The combined aqueous phases were acidified by the addition of concd HCl (pH<4), an organic phase was formed. The acidic aqueous layer was extracted with CHCl<sub>3</sub> ( $3 \times 100$  mL), the combined organic phases were separated and dried (MgSO<sub>4</sub>). The solvents were evaporated at reduced pressure to afford the crude product which was purified by kugelrohr distillation (bp, depending on substituents 80–110 °C,  $5 \times 10^{-2}$  mbar).

# 2-Allyloxy-Substituted Acetic Acid Esters 2a-i; General Procedure

To a stirred solution of the 2-allyloxy-substituted acid (1 equiv) in  $CH_2Cl_2$  (2.5 mL/mmol of the acid) at 0 °C were successively added DMAP (0.05 equiv), DCC (1.1 equiv), and the alcohol (2 equiv). The reaction mixture was allowed to warm to r.t. overnight. The precipitate was then removed by filtration and washed with EtOAc. The solvents were then evaporated at reduced pressure and the crude product was purified by kugelrohr distillation (bp, depending on substituents 80–110 °C, 1 mbar).

#### Aldol Addition to 3a-r; General Procedure

To a stirred solution of LDA [prepared in situ from diisopropylamine (1.3 equiv) and *n*-BuLi (1.2 equiv)] in THF (2 mL/mmol of the ester) was added a cooled (-78 °C) solution of the ester (1 equiv) in THF (2.5 mL/mmol of the ester) at -78 °C. The solution was stirred for 10 to 15 min and then the aldehyde (1.3–2.0 equiv) was added either neat or as a solution in THF (benzaldehyde, phenyl-acetaldehyde). The reaction mixture was stirred 30 min at -78 °C and then quenched by the addition of sat. NH<sub>4</sub>Cl at -78 °C. The solution was diluted with H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>, the layers were then separated and the organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×). The combined organic phases were dried (MgSO<sub>4</sub>) and concentrated to afford the crude product oil which was purified by column chromatography (EtOAc/heptane) to afford the  $\beta$ -hydroxy esters **3a–r** as colorless oils (Table 4–6).

Substrate		Product	Yield	IR			tal Analysis	analysis		
Ester	Aldehyde		g	in substance			Four	ıd	Calcul	ated
g (mmol)	R <sup>1</sup> CHO		%	$v (cm^{-1})$	Formula	MW	С	Н	С	Н
<b>2a</b> 2.0 (11.4)	MeCHO	3a	2.1 84	3475, 2960– 2875, 1750	$C_{11}H_{20}O_4$	216.3	60.75	9.51	61.09	9.32
<b>2b</b> 3.0 (20.8)	MeCHO	3b	2.1 55	3490, 2980– 2900, 1745	$C_9H_{16}O_4$	188.2	57.56	8.77	57.43	8.57
<b>2c</b> 2 5 (14 3)	EtCHO	3c	2.1 64	3485, 2960–2875, 1750	$C_{12}H_{22}O_4$	230.3	63.06	9.76	62.58	9.63
2a 49(28.8)	EtCHO	3d	5.0 75	3470, 2935– 2875, 1745	$C_{12}H_{22}O_4$	230.3	62.28	9.88	62.58	9.63
2i 3 8 (17 5)	MeCHO	3e	3.5 76	3470, 2940– 2880, 1745	$C_{13}H_{24}O_5$	260.3	59.63	9.39	59.98	9.29
<b>2i</b>	EtCHO	3f	1.2 62	3470, 2960– 2880, 1750	$C_{14}H_{26}O_5$	274.4	61.31	9.57	61.29	9.55
<b>2g</b> 2.4 (12.9)	EtCHO	3g	2.9 92	3470, 2980– 2880, 1740	$C_{13}H_{24}O_4$	244.3	63.98	10.28	63.91	9.90
<b>2g</b> 2.2 (11.8)	MeCHO	3h	2.3 84	3470, 2980– 2880, 1740	$C_{12}H_{22}O_4$	230.3	62.04	9.90	62.58	9.63
2e 30(150)	MeCHO	3i	3.1 88	3475, 2980– 2875, 1740	$C_{13}H_{24}O_4$	244.3	63.74	10.11	63.91	9.90
2f 2 8 (14)	MeCHO	3ј	3.0 88	3470, 2980– 2875, 1745	$\mathrm{C}_{13}\mathrm{H}_{24}\mathrm{O}_4$	244.3	63.84	10.12	63.91	9.90
<b>2e</b> 24 (11.8)	EtCHO	3k	2.7	3480, 2965– 2875, 1740	$C_{14}H_{26}O_4$	258.4	64.73	10.34	65.09	10.14
2h 2 5 (14 5)	MeCHO	31	2.5 79	3470, 2980– 2880, 1740	$C_{11}H_{20}O_4$	216.3	60.70	9.49	61.09	9.32
<b>2e</b> 2.0 (10)	iPrCHO	3m	2.1 77	3475, 2985– 2885, 1745	$C_{15}H_{28}O_4$	272.4	66.01	10.52	66.14	10.36
<b>2e</b> 2.0 (10)	PhCHO	3n	2.8 89	3475, 2980– 2875, 1740	$C_{18}H_{26}O_4$	306.4	70.53	8.67	70.56	8.55
<b>2g</b> 2.9 (15)	BnCHO	30	3.7 78	3475, 2980– 2880, 1740	$C_{18}H_{26}O_4$	306.4	71.15	8.67	70.56	8.55
2e 3.1 (15.5)	BnCHO	3p	4.6 95	3480, 2980– 2875, 1745	$C_{19}H_{28}O_4$	320.4	70.64	9.05	71.22	8.81
2d 2.1 (12)	BnCHO	3q	2.6 64	3480, 2980– 2880, 1740	$C_{17}H_{24}O_4$	292.4	71.54	8.56	69.84	8.27
<b>2h</b> 2.3 (13.4)	BnCHO	3r	3.1 80	3480, 2980– 2880, 1735	$C_{17}H_{24}O_4$	292.4	69.86	8.41	69.84	8.27

**Table 4** Synthesis of  $\beta$ -Hydroxy Esters **3a**- $\mathbf{r}^{a}$ 

<sup>a</sup> Colorless oils, isolated as a mixture of diastereomers, ratio see table 3.

# Mesylation/Elimination to the Allyl Vinyl Ethers 1a-r; General Procedure

To a solution of the  $\beta$ -hydroxy esters 3a-r (1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL/mmol of the  $\beta$ -hydroxy ester) at 0 °C was added successively Et<sub>3</sub>N (1.3 equiv) and methanesulfonic acid chloride (1.2 equiv). The reaction was allowed to warm to ambient temperature over night. The reaction was then quenched by the addition of sat. NaHCO<sub>3</sub>. The phases were separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×). The organic phase was dried (MgSO<sub>4</sub>) and concentrated in vacuum to afford the crude mesylate which was dissolved in THF (2 mL/mmol of the mesylate). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 3 equiv) was added at r.t., and the reaction mixture was stirred at ambient temperature until TLC indicated complete consumption of the starting material. The reaction was then quenched by the addition of H<sub>2</sub>O (2 mL/mmol of the mesylate), the phases

were separated, and the aqueous layer was extracted with  $CH_2Cl_2$  (2×). The combined organic phases were dried (MgSO<sub>4</sub>), and the solvent was removed under reduced pressure to afford the crude product which was purified by column chromatography (EtOAc/heptane) (Tables 7–9).

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# Table 5 <sup>1</sup>H NMR Data of $\beta$ -Hydroxy Esters **3a**-r,<sup>a</sup> 300 MHz, CDCl<sub>3</sub>

Compound	δ, <i>J</i> (Hz)
3a	0.90 (t, $J = 7.3, 3$ H), 1.21 (d, $J = 6.5, 3$ H <sup>major</sup> ), 1.22 (d, $J = 6.5, 3$ H <sup>minor</sup> ), 1.41 (qt, $J_1 = J_2 = 7.4, 2$ H), 2.03 (td, $J_1 = J_2 = 7.4, 2$ H), 2.43 (br d, $J = 6.5, 1$ H <sup>major</sup> ), 2.55 (br d, $J = 4.9, 1$ H <sup>minor</sup> ), 3.74 (d, $J = 5.5, 1$ H <sup>minor</sup> ), 3.77 (s, 3H <sup>minor</sup> ), 3.78 (s, 3H <sup>major</sup> ), 3.88–4.21 (m, 4H <sup>major</sup> , 3H <sup>minor</sup> ), 5.48–5.61 (m, 1 H), 5.65–5.77 (m, 1H)
<b>3b</b> <sup>b</sup>	1.17–1.24 (m, 3 H), 1.28–1.35 (m, 3 H), 2.36–2.49 and 2.56–2.61 (br m, 1 H), 3.725 and 3.734 and 3.77 (s, 3 H), 3.82–4.10 (m, 3 H), 5.08–5.24 (m, 3 H), 5.58–5.87 (m, 1 H)
3c	0.90 (t, $J = 7.5$ , 3 H), 0.99 (t, $J = 7.5$ , 3 H), 1.39 (qt, $J_1 = J_2 = 7.4$ , 2 H), 1.47–1.62 (m, 2 H), 2.03 (dt, $J_1 = J_2 = 7.3$ , 2 H), 2.31 (br s, 1 H), 3.70–3.84 (m, partially covered, 1 H), 3.78 (s, 3 H), 3.84 (d, $J = 4.6$ , 1H <sup>minor</sup> ), 3.95 (d, $J = 4.9$ , 1H <sup>major</sup> ), 4.01–4.11 (m, 1 H), 4.19–4.29 (m, 1 H), 5.48–5.70 (m, 1 H)
3d	0.90 (t, $J = 7.5$ , 3 H), 0.98 (t, $J = 7.5$ , 3H <sup>minor</sup> ), 0.99 (t, $J = 7.5$ , 3H <sup>major</sup> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 1 H), 1.47–1.60 (m, 2 H), 2.03 (td, $J_1 = J_2 = 7.0$ , 2 H), 2.36 (d, $J = 7.0$ , 1 H), 3.77 (s, 3 H), 3.71–3.97 (m, 3 H), 4.11–4.22 (m, 1 H), 5.47–5.60 (m, 1 H), 5.64–5.77 (m, 1 H)
3e	0.898 (t, $J = 7.3$ , $3H^{\text{minor}}$ ), 0.903 (t, $J = 7.3$ , $3H^{\text{major}}$ ), 1.22 (d, $J = 6.5$ , $3H^{\text{minor}}$ ), 1.23 (d, $J = 6.4$ , $3H^{\text{major}}$ ), 1.42–1.47 (m, 2 H), 2.30 (td, $J_1 = J_2 = 7.4$ , 2 H), 2.62–2.64 (br m, 1 H), 3.376 (s, $3H^{\text{minor}}$ ), 3.381 (s, $3H^{\text{major}}$ ), 3.60–3.63 (m, 2 H), 3.79–3.81 and 3.90–4.78 (m, 6 H), 5.55–5.59 (m, 1 H), 5.66–5.76 (m, 1 H)
3f	0.87 (t, $J = 7.4$ , 3 H), 0.92–0.98 (m, 3 H), 1.37 (qt, $J_1 = J_2 = 7.4$ , 2 H), 1.46–1.62 (m, 2 H), 2.01 (dt, $J_1 = J_2 = 6.9$ , 2 H), 2.37 (d, $J = 7.3$ , 1H <sup>minor</sup> ), 2.45 (d, $J = 6.2$ , 1H <sup>major</sup> ), 3.34 (s, 3H <sup>major</sup> ), 3.35 (s, 3H <sup>minor</sup> ), 3.59 (ddd, $J_1 = J_2 = J_3 = 4.8$ , 2 H), 3.72–3.80 (m, 1 H), 3.87–3.92 (m, 2 H), 4.09–4.18 (m 1 H), 4.23–4.40 (m, 2 H), 5.46–5.56 (m, 1 H), 5.63–5.72 (m, 1 H)
3g	0.98 (t, $J = 7.5$ , 3H <sup>major</sup> ), 1.02 (t, $J = 7.5$ , 3H <sup>major</sup> ), 1.29 (d, $J = 6.2$ , 6 H), 1.45–1.63 (m, 2 H), 1.67 (s, 3 H), 1.76 (s, 3 H), 2.31 (d, $J = 6.2$ , 1H <sup>major</sup> ), 2.37 (d, $J = 6.2$ , 1H <sup>minor</sup> ), 3.68–3.88 (m, 2H), 3.92–4.03 (m, 1 H), 4.13–4.23 (m, 1 H), 5.13 (sept, $J = 6.3$ , 1 H), 5.30–5.39 (m, 1 H)
3h	1.208 (d, $J = 6.5$ , $3H^{major}$ ), 1.214 (d, $J = 6.2$ , $3H^{minor}$ ), 1.29 (d, $J = 6.5$ , 6 H), 1.68 (s, 3 H), 1.76 (s, 3H), 2.48 (d, $J = 6.8$ , $1H^{major}$ ), 2.62 (d, $J = 4.9$ , $1H^{minor}$ ), 3.65 (d, $J = 6.2$ , $1H^{minor}$ ), 3.84 (d, $J = 4.6$ , $1H^{major}$ ), 3.91–4.24 (m, 3 H), 5.13 (sept, $J = 6.3$ , 1 H), 5.35 (m, 1 H)
3i	0.90 (t, $J = 7.3, 3$ H), 1.21 (d, $J = 6.5, 3$ H <sup>major</sup> ), 1.22 (d, $J = 6.2, 3$ H <sup>minor</sup> ), 1.28 (d, $J = 6.2, 6$ H), 1.41 (qt, $J_1 = J_2 = 7.4, 2$ H), 2.03 (dt, $J_1 = J_2 = 7.3, 2$ H), 2.38 (d, $J = 7.1, 1$ H <sup>major</sup> ), 2.54 (d, $J = 5.2, 1$ H <sup>minor</sup> ), 3.67 (d, $J = 5.5, 1$ H <sup>minor</sup> ), 3.86 (d, $J = 4.6, 1$ H <sup>major</sup> ), 3.88–4.22 (m, 3 H), 5.12 (sept, $J = 6.3, 1$ H), 5.49–5.61 (m, 1 H), 5.64–5.76 (m, 1 H)
3ј	0.90 (t, $J = 7.3, 3$ H), 1.21 (d, $J = 6.5, 3$ H <sup>major</sup> ), 1.22 (d, $J = 6.5, 3$ H <sup>minor</sup> ), 1.29 (d, $J = 6.5, 6$ H), 1.39 (qt, $J_1 = J_2 = 7.4, 2$ H), 2.04 (td, $J_1 = J_2 = 7.3, 2$ H), 2.49–2.55 (br m, 1H <sup>major</sup> ), 2.60–2.65 (br m, 1H <sup>minor</sup> ), 3.67 (d, $J = 5.8, 1$ H <sup>minor</sup> ), 3.86 (d, $J = 4.6, 1$ H <sup>major</sup> ), 3.92–4.11 and 4.19–4.30 (m, 3H), 5.13 (sept, $J = 6.3, 1$ H), 5.49–5.70 (m, 1 H)
3k	0.90 (t, $J = 7.5$ , 3 H), 0.98 (t, $J = 7.5$ , 3H <sup>minor</sup> ), 0.99 (t, $J = 7.5$ , 3H <sup>minor</sup> ), 1.28 (d, $J = 6.2$ , 6H <sup>minor</sup> ), 1.28 (d, $J = 6.5$ , 6H <sup>major</sup> ), 1.41 (qt, $J_I = J_2 = 7.4$ , 2 H), 1.47–1.62 (m, 2 H), 2.03 (td, $J_I = J_2 = 7.0$ , 2 H), 2.27–2.37 (m, 1 H), 3.69–3.84 and 3.87–3.96 (m, 3 H), 4.11–4.20 (m, 1 H), 5.12 (sept, $J = 6.3$ , 1 H), 5.48–5.60 and 5.64–5.76 (m, 2 H)
31	1.23 (d, $J = 6.5$ , $3H^{\text{major}}$ ), 1.24 (d, $J = 6.2$ , $3H^{\text{minor}}$ ), 1.28 (d, $J = 6.2$ , $3H$ ), 1.29 (d, $J = 6.2$ , $3H$ ), 1.77 (s, $3H$ ), 2.40 (br d, $J = 6.2$ , $1H^{\text{major}}$ ), 2.54 (br d, $J = 5.5$ , $1H^{\text{minor}}$ ), 3.69 (d, $J = 5.5$ , $1H^{\text{minor}}$ ), 3.82–3.90 (m, $2H^{\text{major}}$ , $1H^{\text{minor}}$ ), 4.03–4.18 (m, 2 H), 4.93 (br s, 1 H), 4.98 (br s, 1 H), 5.13 (sept, $J = 6.3$ , 1 H)
3m	0.75-1.01 (m, 9 H), $1.28$ (d, $J = 7.1$ , 6 H), $1.35-1.47$ (m, 2 H), $1.79-1.93$ (m, 1 H), $1.99-2.06$ (m, 2 H), $2.20$ (d, $J = 7.6$ , 1H <sup>minor</sup> ), $2.34$ (d, $J = 4.6$ , 1H <sup>major</sup> ), $3.49$ (m, 1H <sup>minor</sup> ), $3.61$ (m, 1H <sup>major</sup> ), $3.86-3.93$ (m, 2 H), $4.09-4.29$ (m, 1 H), $5.07-5.19$ (m, 1 H), $5.48-5.58$ (m, 1 H), $5.65-5.75$ (m, 1 H)
3n	0.89 (t, $J = 7.3, 3$ H), 0.97 (d, $J = 6.5, 3$ H <sup>minor</sup> ), 1.08 (d, $J = 6.2, 3$ H <sup>major</sup> ), 1.16 (d, $J = 6.2, 3$ H <sup>major</sup> ), 1.17 (d, $J = 6.5, 3$ H <sup>minor</sup> ), 1.38 (qt, $J_1 = J_2 = 7.4, 2$ H), 1.99 (td, $J_1 = J_2 = 7.3, 2$ H), 3.09 (br s, 1 H), 3.82–3.97 and 4.02–4.13 (m, 2 H), 3.97 (d, $J = 6.5, 1$ H <sup>minor</sup> ), 4.07 (d, $J = 5.8, 1$ H <sup>major</sup> ), 4.84–5.03 (m, 2 H), 5.35–5.50 and 5.57–5.69 (m, 2 H), 7.23–7.41 (m, 5 H)
30	1.23 (d, $J = 6.2$ , $3H^{\text{minor}}$ ), 1.27 (d, $J = 6.2$ , $3H^{\text{minor}}$ ), 1.30 (d, $J = 6.2$ , $6H^{\text{major}}$ ), 1.67 (s, 3 H), 1.76 (s, 3 H), 2.30 and 2.40 (br s, 1 H), 2.73–2.83 and 2.86–2.98 (m, 2 H), 3.72 (d, $J = 3.9$ , $1H^{\text{minor}}$ ), 3.86 (d, $J = 5.2$ , $1H^{\text{major}}$ ), 3.92–4.03 and 4.06–4.25 (m, 2 H), 5.10 (sept, $J = 6.3$ , $1H^{\text{minor}}$ ), 5.14 (sept, $J = 6.3$ , $1H^{\text{major}}$ ), 5.32–5.41 (m, 1 H), 7.19–7.33 (m, 5 H)
3р	0.90 (t, $J = 7.3, 3$ H), 1.30 (d, $J = 6.2, 6$ H), 1.33–1.47 (m, 2 H), 1.96–2.07 (m, 2 H), 2.28 (d, $J = 5.8, 1$ H <sup>major</sup> ), 2.37 (d, $J = 7.5, 1$ H <sup>minor</sup> ), 2.73–2.97 (m, 2 H), 3.72–3.76 and 3.84–3.96 (m, 2 H), 4.06–4.23 (m, 2 H), 5.06–5.19 (m, 1 H), 5.49–5.76 (m, 2 H), 7.18–7.35 (m, 5 H)
3q <sup>b</sup>	1.22–1.38 (m, 9 H), 2.14–2.44 (br m, 1 H), 2.30–2.36 and 2.39–2.45 and 2.68–3.00 (br m, 1 H), 3.73–3.76 and 3.85–4.15 (m, 3 H), 5.04–5.22 (m, 3 H), 5.59–5.73 and 5.75–5.90 (m, 1 H), 7.16–7.39 (m, 5 H)
3r	1.27 (d, $J = 7.1$ , $3H^{\text{minor}}$ ), 1.30 (d, $J = 6.2$ , $3H^{\text{major}}$ ), 1.76 (s, $3H^{\text{major}}$ ), 1.81 (s, $3H^{\text{minor}}$ ), 2.26 (br s, $1H^{\text{major}}$ ), 2.37 (br s, $1H^{\text{minor}}$ ), 2.75–2.85 and 2.87–3.00 (m, 2 H), 3.77 (d, $J = 3.6$ , $1H^{\text{minor}}$ ), 3.84 (br s, $1H^{\text{minor}}$ ), 3.88 (d, $J = 4.9$ , $1H^{\text{major}}$ ), 3.88 (br s, $1H^{\text{major}}$ ), 4.07–4.19 (br m, 2 H), 4.92 (br s, $1H^{\text{major}}$ ), 4.95 (br s, $1H^{\text{minor}}$ ), 4.97 (br s, $1H^{\text{major}}$ ), 5.01 (br s, $1H^{\text{minor}}$ ), 5.14 (sept, $J = 6.3$ , 1H), 7.16–7.34 (m, 5 H)
a Dotormino	d form a minture of 2 diostanoanam. Diostanoanamia asticulas Table 2. The terms Humior and Humior are used to indiaste astronated

<sup>a</sup> Determined from a mixture of 2 diastereomers. Diastereomeric ratio: see Table 3. The terms H<sup>major</sup> and H<sup>minor</sup> are used to indicate separated proton resonance for the major or the minor diastereomer.

<sup>b</sup> Mixture of 4 diastereomers.

Table 6	<sup>13</sup> C NMR Data of	β-Hydroxy Esters 3a	<b>-r</b> , <sup>a</sup> 75.5 MHz, 0	$CDCl_3, \delta$
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Com	pound <sup>b</sup>	C-1	C-2	C-3	C-1′	Other Signals
3a	major	171.4	81.2	68.3	71.8	13.6, 18.3, 22.1, 34.3, 51.9, 125.3, 136.1
	minor	171.6	81.8	68.4	71.8	13.6, 18.7, 22.1, 34.3, 51.9, 125.2, 136.4
3b	4 dia-	18.4, 19	.0, 20.5,	21.4, 51	.7, 51.77	, 51.78, 51.9, 68.31, 68.34, 68.41, 77.0, 77.1, 78.8, 79.2, 79.3, 79.6, 80.7, 81.9, 116.6,
	stereomers	116.5, 1	17.7, 11	7.8, 138.	7, 138.9,	139.3, 139.4, 171.6, 171.8, 171.9, 172.0
3c	major	171.4	80.8	73.6	66.3	10.0, 13.6, 22.6, 25.4, 29.5, 51.8, 124.9, 134.8
	minor	171.8	80.0	73.8	66.2	9.9, 13.6, 22.6, 25.4, 26.2, 51.9, 124.8, 135.0
3d	major	171.5	80.5	73.6	71.8	10.0, 13.6, 22.0, 25.4, 34.2, 51.8, 125.3, 136.1
	minor	171.9	79.7	73.8	71.8	9.9, 13.6, 22.4, 26.1, 34.2, 51.9, 125.3, 136.3
3e	major	170.9	81.4	68.3	63.4	13.6, 18.4, 22.0, 34.2, 58.7, 70.1, 71.6, 125.4, 136.0
	minor	171.0	81.6	68.4	63.5	13.6, 18.7, 22.0, 34.2, 58.7, 70.1, 71.6, 125.2, 136.2
3f	major	171.0	80.6	73.6	63.3	10.0, 13.6, 22.1, 25.5, 34.3, 58.8, 70.2, 71.6, 125.3, 136.0
	minor	171.4	79.7	73.8	63.6	10.0, 13.6, 22.1, 26.1, 34.3, 58.8, 70.2, 71.6, 125.3, 136.2
3g	major	170.6	81.5	73.7	67.0	10.0, 18.0, 21.8, 25.3, 25.5, 68.6, 120.1, 138.4
	minor	171.0	80.2	73.7	66.9	9.8, 18.0, 21.8, 25.5, 26.1, 68.6, 120.0, 138.6
3h	major	170.5	81.2	68.3	67.1	18.0, 18.2, 21.8, 25.7, 68.6, 120.1, 138.4
	minor	170.7	82.3	68.3	67.0	18.2, 18.6, 21.8, 25.7, 68.6, 119.9, 138.6
3i	major	170.3	81.2	68.1	71.6	13.6, 18.2, 21.7, 22.0, 34.2, 68.5, 125.5, 135.8
	minor	170.6	82.0	68.2	71.6	13.6, 18.6, 21.7, 22.0, 34.2, 68.5, 125.3, 136.1
3j	major	170.3	81.3	68.2	66.1	13.6, 18.2, 21.7, 22.5, 29.5, 68.5, 125.1, 134.7
•	minor	170.5	82.2	68.3	66.0	13.6, 18.6, 21.7, 22.5, 29.5, 68.6, 124.9, 134.8
3k	major	170.5	80.5	73.7	71.6	10.1, 13.6, 21.8, 22.1, 25.4, 34.3, 68.6, 125.5, 135.9
	minor	170.9	80.0	73.7	71.6	9.9, 13.6, 21.8, 22.1, 26.1, 34.3, 68.6, 125.4, 136.1
31	major	170.1	81.5	68.4	74.7	18.3, 19.5, 21.8, 68.7, 113.4, 141.3
	minor	170.4	82.3	68.5	74.8	18.3, 18.8, 21.8, 68.7, 113.8, 141.1
3m	major	170.9	79.0	76.9	71.3	13.6, 17.1, 19.3, 21.8, 22.1, 29.7, 34.3, 68.6, 125.4, 135.9
	minor	171.1	78.3	77.6	71.4	13.6, 17.9, 19.3, 21.7, 22.1, 30.6, 34.3, 68.5, 125.4, 136.1
3n	major	170.2	81.8	74.0	71.7	13.6, 21.5, 21.7, 22.0, 34.2, 68.6, 125.3, 126.7, 127.7, 128.1, 136.2, 139.6
	minor	170.0	82.4	74.9	71.7	13.6, 21.3, 21.7, 22.0, 34.2, 68.6, 125.1, 126.9, 127.9, 128.1, 136.2, 138.9
30	major	170.6	80.3	73.2	67.0	18.0, 21.8, 25.8, 38.9, 68.7, 120.1, 126.4, 128.4, 129.5, 137.9, 138.4
	minor	170.9	78.9	73.5	66.9	18.0, 21.8, 25.8, 39.7, 68.7, 120.1, 126.4, 128.4, 129.3, 137.8, 138.4
3p	major	170.4	80.1	73.3	71.6	13.7, 21.9, 22.1, 34.3, 38.9, 68.8, 125.4, 126.5, 128.4, 129.5, 136.1, 137.9
-	minor	170.8	79.0	73.6	71.6	13.7, 21.8, 22.1, 34.3, 39.7, 68.8, 125.4, 126.5, 128.4, 129.4, 136.1, 137.8
3q	4 dia-	20.5, 20	.6, 21.5,	21.7, 21	.8, 39.1, 3	39.5, 39.9, 68.6, 68.7, 73.4, 73.5, 77.1, 77.2, 78.5, 78.7, 79.0, 79.2, 79.9, 116.4, 117.6,
•	stereomers	117.9, 1	26.4, 12	6.5, 128.	4, 128.5,	129.3, 129.4, 137.8, 138.0, 138.1, 138.8, 139.6
3r	major	170.2	80.6	73.4	74.7	19.5, 21.8, 39.0, 68.8, 113.4, 126.5, 128.4, 129.5, 137.9, 141.2
	minor	170.5	79.7	73.6	74.7	19.7, 21.8, 39.8, 68.8, 113.5, 126.5, 128.4, 129.3, 137.8, 141.2

<sup>a</sup> Determined from a mixture of diastereomers. Diasteromeric ratio: see Table 3.

<sup>b</sup> Though determined from the mixture of diastereomers, the chemical shifts for the major and minor the diastereomer are listed separately. Relative configuration not assigned.

#### Table 7 Synthesis of Allyl Vinyl Ethers 1a-r

Substrate	Product <sup>a</sup>	Yield	IR	Formula	MW		Elementa	al Analysis	
Alcohol		g	in substance			Found		Calcu	lated
g (mmol)		(%)	v [cm <sup>-1</sup> ]			С	Н	С	Н
<b>3a</b> 3.9 (17.9)	1a	3.23 91	2960–2875, 1750, 1730	$C_{11}H_{18}O_3$	198.3	67.18	9.27	66.64	9.15
<b>3b</b> 2.1 (11.2)	<b>1b</b> <sup>b</sup>	0.98 51	b	$C_9H_{14}O_3$	170.2	b	b	65.51	8.29
<b>3c</b> 2.0 (8.7)	1c	1.46 79	2965–2875, 1730	$C_{12}H_{20}O_3$	212.3	66.67 (67.85) <sup>c</sup>	9.41 (9.55) <sup>c</sup>	67.89	9.50
<b>3d</b> 4.9 (20.0)	1d	3.53 83	2960–2875, 1730	$C_{12}H_{20}O_{3}$	212.3	67.37	9.64	67.89	9.50
<b>3e</b> 3.5 (13.3)	1e	2.60 81	2960–2875, 1725	$C_{13}H_{22}O_4$	242.3	64.84	9.27	64.44	9.15
<b>3f</b> 0.94 (3.4)	1f	0.88 95	2960–2880, 1750	$C_{14}H_{24}O_4$	256.3	65.32	9.54	65.60	9.44
<b>3g</b> 2.7 (11.1)	1g	1.78 71	2980–2880, 1720	$C_{13}H_{22}O_3$	226.3	66.88	9.71	68.99	9.80
<b>3h</b> 2.3 (10.0)	1h	1.88 89	2940–2880, 1720	$C_{12}H_{20}O_{3}$	212.3	67.24	10.00	67.89	9.50
<b>3i</b> 3.1 (12.8)	1i	2.69 93	2980–2875, 1720	$C_{13}H_{22}O_3$	226.3	68.35	10.04	68.99	9.80
<b>3</b> j 3.0 (12.3)	1j	2.46 88	2980–2875, 1720	$C_{13}H_{22}O_3$	226.3	67.88 (69.14) <sup>d</sup>	9.86 (10.03) <sup>d</sup>	68.99	9.80
<b>3k</b> 0.9 (3.3)	1k	0.61 77	2965–2875, 1720	$C_{14}H_{24}O_3$	240.3	68.23 (70.30) <sup>d</sup>	9.93 (10.58) <sup>d</sup>	69.96	10.06
<b>3l</b> 2.4 (11.1)	11	1.81 82	2980–2880, 1720	$C_{11}H_{18}O_3$	198.3	66.11	9.34	66.64	9.15
<b>3m</b> 2.0 (7.6)	1m	1.0 <sup>e</sup> 52 <sup>e</sup>	2960–2875, 1720	$C_{15}H_{26}O_{3}$	254.4	70.46	10.28	70.83	10.30
<b>3n</b> 2.75 (9.0)	$1n^{\rm f}$	2.01 78	2980–2875, 1725	$C_{18}H_{24}O_3$	288.4	73.82	8.46	74.97	8.39
<b>30</b> 3.6 (11.8)	10 <sup>g</sup>	2.08 61	2980–2880, 1720	$C_{18}H_{24}O_3$	288.4	74.80	8.52	74.97	8.39
<b>3p</b> 2.5 (7.8)	$1\mathbf{p}^{h}$	1.91 81	2980–2875, 1720	$C_{19}H_{26}O_3$	302.4	75.93	8.82	75.46	8.67
<b>3q</b> 2.6 (8.9)	$\mathbf{1q}^{\mathrm{f}}$	0.84 34	f	$C_{17}H_{22}O_3$	274.4	f (74.36) <sup>d</sup>	f (8.41) <sup>d</sup>	74.42	8.08
<b>3r</b> 3.0 (10.3)	$\mathbf{1r}^{\mathrm{i,f}}$	2.18 77	2980–2875, 1720	$C_{17}H_{22}O_3$	274.4	74.63	74.08	74.42	8.08

<sup>a</sup> Colorless oils, isolated as a mixture of double bond isomers as indicated in Table 3.

<sup>b</sup> Spectra in CDCl<sub>3</sub> show a 1:1 mixture with the corresponding Claisen rearrangement product **5b**.

<sup>c</sup> In parentheses: found for the corresponding Claisen rearrangement product 5c.

<sup>d</sup> In parentheses: found for the corresponding dienolate [2,3]-Wittig rearrangement product.

<sup>e</sup> 820 mg (42 %) of the mesylate **4m** isolated.

<sup>f</sup> Spectra in CDCl<sub>3</sub> show a contamination with the corresponding Claisen rearrangement product **5q**.

<sup>g</sup> 350 mg (10 %) of the corresponding *E* configured  $\beta$ , $\gamma$ -unsaturated ester isolated **60**.

<sup>h</sup> 220 mg (19 %) of the corresponding *E* configured  $\beta$ , $\gamma$ -unsaturated ester isolated **6p**.

<sup>i</sup> 340 mg (12 %) of the corresponding *E* configured  $\beta$ , $\gamma$ -unsaturated ester isolated **6r**.

Table 8	<sup>1</sup> H NMR Data	of Allyl	Vinyl Ethers	1a-r, <sup>a</sup> 300 MHz,	$CDCl_3, \delta, J (Hz)$
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Compound	3-Н	4-CH <sub>n</sub>	1'-CH <sub>n</sub>	Other Signals
Z-1a	6.36 (q, <i>J</i> = 7.1, 1H)	1.77 (d, <i>J</i> = 7.1, 3 H, CH <sub>3</sub> )	4.28 (d, <i>J</i> = 5.8, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 2.03 (td, $J_1 = J_2 = 6.9$ , 2 H, 4'-CH <sub>2</sub> ), 3.76 (s, 3 H, OCH <sub>3</sub> ), 5.68 (m, 2H, 2'-H, 3'-H)
<i>E-</i> 1a	5.41 (q, <i>J</i> = 7.5, 1H)	1.97 (d, <i>J</i> = 7.5, 3 H, CH <sub>3</sub> )	4.20 (d, <i>J</i> = 5.8, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 1.97–2.09 (m, 2 H, 4'-CH <sub>2</sub> ), 3.80 (s, 3H, OCH <sub>3</sub> ), 5.56–5.71 (m, 2 H, 2'-H, 3'-H)
<i>Z</i> -1 <b>b</b> <sup>b</sup>	6.36 (q, <i>J</i> = 7.1, 1 H)	1.75 (d, <i>J</i> = 7.1, 3 H, CH <sub>3</sub> )	4.48 (qd, $J_1 = J_2 = 6.6$ , 1 H)	1.36 (d, <i>J</i> = 6.2, 3 H, 1'-CH <sub>3</sub> ), 3.75 (s, 3 H, OCH <sub>3</sub> ), 5.11 (d, <i>J</i> = 9.1, 1 H, 3'-H), 5.15 (d, <i>J</i> = 16.9, 1 H, 3'-H), 5.74–5.90 (m, 1 H, 2'-H)
<i>E</i> -1b °	5.57 (q, <i>J</i> = 7.5, 1 H)	1.95 (d, <i>J</i> = 7.5, 3 H, CH <sub>3</sub> )	4.35 (qd, $J_1 = J_2 = 6.5$ , 1 H)	1.35 (d, <i>J</i> = 6.5, 3 H, 1'-CH <sub>3</sub> ), 3.79 (s, 3 H, OCH <sub>3</sub> ), 5.11 (d, <i>J</i> = 9.1, 1 H, 3'-H), 5.15 (d, <i>J</i> = 16.9, 1 H, 3'-H), 5.74–5.90 (m, 1 H, 2'-H)
Z-1c	6.28 (t, <i>J</i> = 7.6, 1 H)	2.26 (qd, $J_1 = J_2 = 7.56$ , 2 H, CH <sub>2</sub> )	4.38 and 4.43 (AB system, <i>J</i> = 9.7, 2 H)	0.90 (t, $J$ = 7.3, 3 H, 6'-CH <sub>3</sub> ), 1.03 (t, $J$ = 7.5, 3 H, 5-CH <sub>3</sub> ), 1.34 (qt, $J_1$ = $J_2$ = 7.5, 2 H, 5'-CH <sub>2</sub> ), 1.99–2.12 (m, 2 H, 4'-CH <sub>2</sub> ), 3.77 (s, 3 H, OCH <sub>3</sub> ), 5.55–5.69 (m, 2 H, 2'-H, 3 '-H)
<i>E</i> -1c	5.29 (t, <i>J</i> = 7.6, 1 H)	2.47 (qd, $J_1 = J_2 = 7.6$ , 2 H, CH <sub>2</sub> )	4.32 (br d, <i>J</i> = 4.6, 2 H)	0.92 (t, $J = 5.7$ , 3 H, 6'-CH <sub>3</sub> ), 1.04 (t, $J = 7.3$ , 3 H, 5-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.7$ , 2 H, 5'-CH <sub>2</sub> ), 1.99–2.12 (m, 2 H, 4'- CH <sub>2</sub> ), 3.79 (s, 3 H, OCH <sub>3</sub> ), 5.55–5.69 (m, 2 H, 2'-H, 3'-H)
Z-1d	6.27 (t, <i>J</i> = 7.6, 1 H)	2.24 (qd, $J_1 = J_2 = 7.6$ , 2 H, CH <sub>2</sub> )	4.27 (d, <i>J</i> = 6.2, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.02 (t, $J = 7.6$ , 3 H, 5-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 1.99–2.09 (m, 2 H, 4'-CH <sub>2</sub> ), 3.77 (s, 3 H, OCH <sub>3</sub> ), 5.68 (m, 2 H, 2'-H, 3'-H)
<i>E</i> -1d	5.29 (t, <i>J</i> = 7.6, 1 H)	2.46 (qd, $J_1 = J_2 = 7.6$ , 2 H, CH <sub>2</sub> )	5.84 (d, <i>J</i> = 5.8, 2 H)	0.91 (t, $J = 7.5$ , 3 H, 6'-CH <sub>3</sub> ), 1.04 (t, $J = 7.5$ , 3 H, 5-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 1.99–2.09 (m, 2 H, 4'-CH <sub>2</sub> ), 3.80 (s, 3 H, OCH <sub>3</sub> ), 5.68 (m, 2 H, 2'-H, 3'-H)
Z-1e	6.39 (q, <i>J</i> = 7.1, 1 H)	1.76 (d, <i>J</i> = 7.1, 3 H, CH <sub>3</sub> )	4.29 (br d, <i>J</i> = 6.2, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 2.03 (td, $J_1 = J_2 = 7.0$ , 2 H, 4'-CH <sub>2</sub> ), 3.40 (s, 3 H, OCH <sub>3</sub> ), 3.61–3.71 (m, 2 H, 1"-CH <sub>2</sub> ), 4.28–4.34 (m, 2 H, 2"-CH <sub>2</sub> ), 5.63 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-H), 5.73 (dt, $J_1 = 15.4$ , $J_2 = 6.0$ , 1 H, 3'-H)
<i>E</i> -1e	5.44 (q, <i>J</i> = 7.5, 1 H)	1.96 (d, <i>J</i> = 7.5, 3 H, H <sub>3</sub> )	4.20 (br d, <i>J</i> = 6.2, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.5$ , 2 H, 5'-CH <sub>2</sub> ), 1.98–2.08 (m, 2 H, 4'-CH <sub>2</sub> ), 3.40 (s, 3 H, OCH <sub>3</sub> ), 3.61–3.71 (m, 2 H, 1"-CH <sub>2</sub> ), 4.28–4.34 (m, 2 H, 2"-CH <sub>2</sub> ), 5.56–5.80 (m, 2 H, 2'-H, 3'-H)
Z-1f	6.31 (t, <i>J</i> = 7.6, 1 H)	2.24 (qd, $J_1 = J_2 = 7.6$ , 2 H, CH <sub>2</sub> )	4.28 (br d, <i>J</i> = 5.8, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.02 (t, $J = 7.6$ , 3 H, 5-CH <sub>3</sub> ), 1.40 (qt, $J_1 = J_2 = 7.3$ , 2 H, 5'-CH <sub>2</sub> ), 2.03 (td, $J_1 = J_2 = 7.0$ , 2 H, 4'-CH <sub>2</sub> ), 3.40 (s, 3 H, OCH <sub>3</sub> ), 3.62–3.70 (m, 2 H, 1"- CH <sub>2</sub> ), 4.29–4.34 (m, 2 H, 2"-CH <sub>2</sub> ), 5.63 (dt, $J_1 = 15.3$ , $J_2 = 6.2$ , 1 H, 2'-H), 5.73 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 3'-H)
<i>E</i> -1f	5.31 (t, <i>J</i> = 7.6, 1 H)	2.44 (qd, $J_1 = J_2 = 7.6$ , 2 H, CH <sub>2</sub> )	4.20 (br d, <i>J</i> = 5.8, 2 H)	$\begin{array}{l} 0.90 \; ({\rm t}, J=7.3, 3 \; {\rm H}, 6'{\rm -CH_3}),  1.03 \; ({\rm t}, J=7.5, 3 \; {\rm H},  5{\rm -CH_3}), \\ 1.41 \; ({\rm qt}, J_1=J_2=7.7, 2 \; {\rm H},  5'{\rm -CH_2}),  1.98{-}2.08 \; ({\rm m}, 2 \; {\rm H},  4'{\rm -CH_2}),  3.39 \; ({\rm s}, 3 \; {\rm H}, \; {\rm OCH_3}),  3.62{-}3.70 \; ({\rm m}, 2 \; {\rm H},  1''{\rm -CH_2}), \\ 4.29{-}4.34 \; ({\rm m}, 2 \; {\rm H},  2''{\rm -CH_2}),  5.55{-}5.75 \; ({\rm m}, 2 \; {\rm H},  2'{\rm -H},  3'{\rm -H}) \end{array}$
Z-1g	6.23 (t, <i>J</i> = 7.6, 1 H)	2.24 (qd, $J_1 = J_2 = 7.6$ , 2 H, CH <sub>2</sub> )	4.31 (br d, <i>J</i> = 7.5, 2 H)	1.02 (t, $J = 7.6$ , 3 H, 5-CH <sub>3</sub> ), 1.30 (d, $J = 6.2$ , 6 H, Oi-Pr-CH <sub>3</sub> ), 1.70 (br s, 3 H, 4'-CH <sub>3</sub> ), 1.76 (br s, 3 H, 4'-CH <sub>3</sub> ), 5.09 (sept, $J = 6.3$ , 1 H, Oi-Pr-CH), 5.37–5.47 (m, 1 H, 3'-H)
<i>E</i> -1g	5.27 (t, <i>J</i> = 7.8, 1 H)	2.41 (qd, $J_1 = J_2 = 7.6$ , H, CH <sub>2</sub> )	4.23 (br d, <i>J</i> = 6.5, 2 H)	1.03 (t, $J = 7.5$ , 3 H, 5-CH <sub>3</sub> ), 1.32 (d, $J = 5.5$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.68 (br s, 3 H, 4'-CH <sub>3</sub> ), 1.76 (br s, 3 H, 4'-CH <sub>3</sub> ), 5.12 (sept, $J = 6.2$ , 1 H, O <i>i</i> -Pr-CH), 5.37–5.47 (m, 1 H, 3'-H)
Z-1h	6.32 (q, <i>J</i> = 6.3, 1 H)	1.76 (d, <i>J</i> = 7.1, 3 H, CH <sub>3</sub> )	4.33 (d, <i>J</i> = 7.1, 2 H)	1.29 (d, <i>J</i> = 6.5, 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.70 (s, 3 H, 4'-CH <sub>3</sub> ), 1.76 (s, 3 H, 4'-CH <sub>3</sub> ), 5.10 (sept, <i>J</i> = 6.5, 1 H, O <i>i</i> -Pr-CH), 5.37–5.49 (m, partially covered, 1H, 3'-H)

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Table 8 (continued)

Compound	3-Н	4-CH <sub>n</sub>	1'-CH <sub>n</sub>	Other Signals
<i>E</i> -1h	5.40 (q, <i>J</i> = 7.1, 1 H)	1.94 (d, <i>J</i> = 7.1, 3 H, CH <sub>3</sub> )	4.23 (d, <i>J</i> = 6.8, 2 H)	1.32 (d, $J = 6.5$ , 6H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.68 (s, 3H, 4'-CH <sub>3</sub> ), 1.76 (s, 3 H, 4'-CH <sub>3</sub> ), 5.13 (sept, $J = 6.5$ , 1 H, O <i>i</i> -Pr-CH), 5.37–5.49 (m, partially covered, 1H, 3'-H)
<i>E-</i> 1i	6.32 (q, <i>J</i> = 7.14, 1 H)	1.76 (d, <i>J</i> = 7.14, 3 H, CH <sub>3</sub> )	4.27 (br d, <i>J</i> = 5.84, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.29 (d, $J = 6.2$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.40 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 2.03 (dt, $J_1 = J_2 = 6.8$ , 2 H, 4'-CH <sub>2</sub> ), 5.10 (sept, $J = 6.3$ , 1 H, O <i>i</i> -Pr-H), 5.60 (dt, $J_1 = 15.3$ , $J_2 = 6.01$ , 1 H, 2'-H), 5.7 (dt, $J_1 = 15.6$ , $J_2 = 6.2$ , 1 H, 3'-H)
Z-1i	5.40 (q, <i>J</i> = 7.36, 1 H)	1.93 (d, <i>J</i> = 7.47, 3 H, CH <sub>3</sub> )	4.19 (br d, <i>J</i> = 5.84, 2 H)	0.90 (t, $J = 7.3$ , 3H, 6'-CH <sub>3</sub> ), 1.32 (d, $J = 6.2$ , 6 H, Oi-Pr-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.5$ , 2 H, 5'-CH <sub>2</sub> ), 1.99–2.08 (m, 2 H, 4'-CH <sub>2</sub> ), 5.13 (sept, $J = 6.3$ , 1 H, Oi-Pr-H), 5.56–5.79 (m, 2 H, 2'-H, 3'-H)
Z-1j	6.33 (q, <i>J</i> = 7.1, 1 H)	1.77 (d, <i>J</i> = 7.1, 3 H, CH <sub>3</sub> )	4.41 (br d, <i>J</i> = 5.5, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.29 (d, $J = 6.2$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.34–1.45 (m, 2 H, 5'-CH <sub>2</sub> ), 2.05 (m, 2 H, 4'-CH <sub>2</sub> ), 5.13 (sept, $J = 6.5$ , 1 H, O <i>i</i> -Pr-CH), 5.56–5.67 (m, 2 H, 2'-H, 3'-H)
<i>E-</i> 1j	5.40 (q, <i>J</i> = 7.5, 1 H)	1.94 (d, <i>J</i> = 7.5, 3 H, CH <sub>3</sub> )	4.22 (br d, <i>J</i> = 4.2, 2 H)	0.91 (t, $J = 7.5$ , 3 H, 6'-CH <sub>3</sub> ), 1.32 (d, $J = 6.5$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.34–1.45 (m, 2 H, 5'-CH <sub>2</sub> ), 2.05 (m, 2 H, 4'-CH <sub>2</sub> ), 5.10 (sept, $J = 6.5$ , 1 H, O <i>i</i> -Pr-CH), 5.56–5.67 (m, 2 H, 2'-H, 3'-H)
Z-1m	6.0 (d, <i>J</i> = 10.1, 1 H)	2.89 (m <sub>c</sub> , 1 H, CH)	4.26 (br d, <i>J</i> = 5.8, 2 H)	0.90 (t, $J = 7.5$ , 3 H, 6'-CH <sub>3</sub> ), 1.01 (d, $J = 6.25$ , 6 H, 5-CH <sub>3</sub> ), 1.29 (d, $J = 6.3$ , 6 H, Oi-Pr-CH <sub>3</sub> ), 1.41 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 2.03 (dt, $J_1 = J_2 = 7.1$ , 2 H, 4'-CH <sub>2</sub> ), 5.07 (sept, $J = 6.3$ , 1 H, Oi-Pr-CH), 5.61 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-H), 5.72 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 3'-H)
Z-1n	6.97 (s, 1 H)	-	4.43 (d, <i>J</i> = 5.8, 2 H)	0.87 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.32–1.42 (m, partially covered, 2 H, 5'-CH <sub>2</sub> ), 1.35 (d, $J = 6.5$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 2.01 (td, $J_1 = J_2 = 6.9$ , 2 H, 4'-CH <sub>2</sub> ), 5.16 (sept, $J = 6.3$ , 1 H, O <i>i</i> -Pr-CH), 5.60–5.81 (m, 2 H, 2'-H, 3'-H), 7.21–7.40 (m, 3 H, aryl-H), 7.76–7.81 (m, 2 H, aryl-H)
Z-10	6.38 (t, <i>J</i> = 7.6, 1 H)	3.57 (d, <i>J</i> = 7.8, 2 H, CH <sub>2</sub> )	4.41 (d, <i>J</i> = 7.1, 2 H)	1.28 (d, $J = 6.2, 6$ H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.70 (s, 3 H, 4'-CH <sub>3</sub> ), 1.76 (s, 3 H, 4'-CH <sub>3</sub> ), 5.10 (sept, $J = 6.3, 1$ H, O <i>i</i> -Pr-CH), 5.46 (m <sub>c</sub> , 1 H, 2'-H), 7.17–7.33 (m, 5 H, aryl-H)
Z-1p	6.38 (t, <i>J</i> = 6.5, 1 H)	3.56 (d, <i>J</i> = 7.8, 2 H, CH <sub>2</sub> )	4.35 (d, <i>J</i> = 6.3, 2 H)	0.90 (t, $J = 7.3$ , 3 H, 6'-CH <sub>3</sub> ), 1.28 (d, $J = 6.5$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.40 (qt, $J_1 = J_2 = 7.4$ , 2 H, 5'-CH <sub>2</sub> ), 2.03 (td, $J_1 = J_2 = 7.1$ , 2 H, 4'-CH <sub>2</sub> ), 5.08 (sept, $J = 6.3$ , 1 H, O <i>i</i> -Pr-CH), 5.65 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-CH), 5.75 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-CH), 5.75 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-CH), 5.75 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-CH), 5.75 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-CH), 5.75 (dt, $J_1 = 15.3$ , $J_2 = 6.0$ , 1 H, 2'-CH), 5.75 (dt, $J_2 = 15.3$ , $J_$
Z-1q <sup>c</sup>	6.37 (t, <i>J</i> = 7.6, 1 H)	3.55 and 3.56 (d, <i>J</i> = 7.5, 1 H, CH)	4.58 (qd, $J_1 = J_2 = 6.7$ , 1 H)	1.27 (d, $J = 6.2, 6$ H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.40 (d, $J = 6.2, 3$ H, 1'-CH <sub>3</sub> ), 5.07 (sept, $J = 6.3, 1$ H, O <i>i</i> -Pr-CH), 5.13 (d, $J = 10.4, 1$ H, 3'-CH <sub>2</sub> ), 5.18 (d, $J = 17.5, 1$ H, 3' CH <sub>2</sub> ), 5.86 (ddd, $J_1 = 17.4, J_2 = 10.1, J_3 = 7.5, 1$ H, 2'-CH), 7.11–7.34 (m, 5 H, aryl-H)
Z-1r	6.36 (t, <i>J</i> = 7.6, 1 H)	3.59 (d, $J = 7.8, 2$ H, CH <sub>2</sub> )	4.29 (s, 2 H)	1.28 (d, $J = 6.2$ , 6 H, O <i>i</i> -Pr-CH <sub>3</sub> ), 1.86 (s, 3 H, 2'-CH <sub>3</sub> ), 4.96 (br s, 1 H, 3'-CH <sub>2</sub> ), 5.07 (br s, 1 H, 3'-CH <sub>2</sub> ), 5.09 (sept, $J = 6.25$ , 1 H, O <i>i</i> -Pr-CH), 7.17–7.34 (m, 5 H, arvl-H)

<sup>a</sup> Determined from a mixture of double bond isomers as indicated in Table 3, assignment of the double configuration is based on NOESY experiments of selected allyl vinyl ethers. <sup>b</sup> Determined from 1:1 mixture with the corresponding Claisen rearrangement product **5b**.

<sup>c</sup> Contaminated by the corresponding Claisen rearrangement product **5b**, **5q**.

Table 9	<sup>13</sup> C NMR Data of Allyl	Vinyl Ethers	<b>1a−r</b> , <sup>a</sup> 75.5,	CDCl <sub>3</sub> , δ
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Compound	C-1	C-2	C-3	C-1′	Other Signals
Z-1a	164.5	145.3	124.6	72.9	11.4 (4-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 51.7 (OCH <sub>3</sub> ), 125.4 (2'-CH <sub>2</sub> ), 136.1 (3'-CH <sub>2</sub> )
E-1a	164.2	144.9	112.7	69.8	12.5 (4-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 51.7 (OCH <sub>3</sub> ), 124.6 (2'-CH <sub>2</sub> ), 135.7 (3'-CH <sub>2</sub> )
<i>Z</i> -1c	164.5	144.0	131.3	67.5	13.2 (5-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 19.1 (4-CH <sub>2</sub> ), 22.6 (5'-CH <sub>2</sub> ), 29.4, (4'-CH <sub>2</sub> ), 51.7 (OCH <sub>3</sub> ), 124.9 (2'-CH <sub>3</sub> ), 134.5 (3'-CH <sub>3</sub> )
<i>E</i> -1c	164.1	144.0	119.5	64.8	13.6 (6'-CH <sub>3</sub> ), 14.6 (5-CH <sub>3</sub> ), 20.2 (4-CH <sub>2</sub> ), 22.5 (5'-CH <sub>2</sub> ), 29.7, (4'-CH <sub>2</sub> ), 51.7 (OCH <sub>3</sub> ), 124.6 (2'-CH <sub>3</sub> ), 134.0 (3'-CH <sub>3</sub> )
<i>Z</i> -1d	164.6	143.9	131.2	73.0	13.2 (5-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 19.2 (4-CH <sub>2</sub> ), 22.1 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 51.7 (OCH <sub>3</sub> ), 125.4 (2'-CH <sub>2</sub> ), 136.0 (3'-CH <sub>2</sub> )
<i>E</i> -1d	164.2	143.9	119.7	69.8	13.6 (6'-CH <sub>3</sub> ), 14.7 (5-CH <sub>3</sub> ), 20.2 (4-CH <sub>2</sub> ), 22.1 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 51.7 (OCH <sub>3</sub> ), 124.6 (2'-CH <sub>2</sub> ), 135.6 (3'-CH <sub>2</sub> )
Z-1e	163.8	145.1	124.7	72.7	11.4 (4-CH <sub>3</sub> ), 13.5 (6'-CH <sub>3</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.2 (4'-CH <sub>2</sub> ), 58.8 (OCH <sub>3</sub> ), 63.5 (1"-CH <sub>2</sub> ), 70.3 (2"-CH <sub>2</sub> ), 125.4 (2'-CH <sub>3</sub> ), 135.9 (3'-CH <sub>3</sub> )
<i>E</i> -1e	163.8	145.0	113.4	69.9	12.4 (4-CH <sub>3</sub> ), 13.5 (6'-CH <sub>3</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.2 (4'-CH <sub>2</sub> ), 58.8 (OCH <sub>3</sub> ), 63.5 (1"-CH <sub>2</sub> ), 70.1 (2"-CH <sub>2</sub> ), 124.7 (2'-CH <sub>3</sub> ), 135.2 (3'-CH <sub>3</sub> )
Z-1f	164.0	143.8	131.5	72.9	13.1 (5-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 19.2 (4-CH <sub>2</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 58.9 (OCH <sub>3</sub> ), 63.6 (1"-CH <sub>2</sub> ), 70.4 (2"-CH <sub>2</sub> ), 125.4 (2'-CH <sub>2</sub> ), 136.0 (3'-CH <sub>2</sub> )
<i>E</i> -1f	163.8	144.0	120.2	69.9	13.6 (6'-CH <sub>3</sub> ), 14.6 (5-CH <sub>3</sub> ), 19.2 (4-CH <sub>2</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 58.9 (OCH <sub>3</sub> ), 63.6 (1"-CH <sub>2</sub> ), 70.2 (2"-CH <sub>2</sub> ), 124.7 (2'-CH <sub>2</sub> ), 135.3 (3'-CH <sub>2</sub> )
Z-1g	163.8	144.6	130.6	68.2	13.2 (5-CH <sub>3</sub> ), 17.9 (4'-CH <sub>3</sub> ), 19.1 (4-CH <sub>2</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 25.7 (4'-CH <sub>3</sub> ), 68.3 (O <i>i</i> -Pr-CH), 120.1 (2'-CH), 138.5 (3'-C)
E-1g	163.6	144.8	119.2	66.1	14.7 (5-CH <sub>3</sub> ), 18.1 (4'-CH <sub>3</sub> ), 20.3 (4-CH <sub>2</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 25.7 (4'-CH <sub>3</sub> ), 68.2 (O <i>i</i> -Pr-CH), 119.8 (2'-CH), 137.4 (3'-C)
Z-1h	163.6	145.9	123.9	68.2	11.3 (4-CH <sub>3</sub> ), 17.9 (4'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 25.7 (4'-CH <sub>3</sub> ), 68.1 (O <i>i</i> -Pr-CH), 120.1 (2'-CH), 138.5 (3'-C)
<i>E</i> -1h	163.7	145.8	112.4	66.2	12.6 (4-CH <sub>3</sub> ), 18.1 (4'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 25.7 (4'-CH <sub>3</sub> ), 68.3 (O <i>i</i> -Pr-CH), 119.8 (2'-CH), 137.4 (3'-C)
Z-1i	163.5	145.8	123.8	72.8	11.3 (4-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 21.8 (Oi-Pr-CH <sub>3</sub> ), 22.1 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 68.2 (Oi-Pr-CH), 125.6 (2'-CH <sub>2</sub> ), 136.0 (3'-CH <sub>2</sub> )
<i>E</i> -1i	163.6	145.6	113.0	70.2	12.6 (4-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 22.1 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 68.4 (O <i>i</i> -Pr-CH), 125.0 (2'-CH <sub>2</sub> ), 135.2 (3'-CH <sub>2</sub> )
Z-1j	163.4	145.8	124.9	67.2	11.3 (4-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 22.6 (5'-CH <sub>2</sub> ), 29.4 (4'-CH <sub>2</sub> ), 68.1 (O <i>i</i> -Pr-CH), 125.1 (2'-CH <sub>2</sub> ), 134.5 (3'-CH <sub>2</sub> )
E-1j	163.5	145.6	112.6	65.2	12.5 (4-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 21.8 (Oi-Pr-CH <sub>3</sub> ), 22.5 (5'-CH <sub>2</sub> ), 29.7 (4'-CH <sub>2</sub> ), 68.3 (Oi-Pr-CH), 124.9 (2'-CH <sub>2</sub> ), 133.7 (3'-CH <sub>2</sub> )
Z-1k	163.7	144.4	130.5	72.9	13.2 (5-CH <sub>3</sub> ), 13.6 (6'-CH <sub>3</sub> ), 19.1 (4-CH <sub>2</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 22.1 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 68.2 (O <i>i</i> -Pr-CH), 125.5 (2'-CH <sub>2</sub> ), 135.9 (3'-CH <sub>2</sub> )
<i>E</i> -1k	163.7	144.6	119.4	70.0	13.6 (6'-CH <sub>3</sub> ), 14.7 (5-CH <sub>3</sub> ), 20.2 (4-CH <sub>2</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 22.1 (5'-CH <sub>2</sub> ), 34.3 (4'-CH <sub>2</sub> ), 68.4 (O <i>i</i> -Pr-CH), 124.9 (2'-CH <sub>2</sub> ), 135.2 (3'-CH <sub>2</sub> )
Z-11	163.4	146.2	123.3	75.6	11.2 (4-CH <sub>3</sub> ), 19.6 (2'-CH <sub>3</sub> ), 21.8 (Oi-Pr-CH <sub>3</sub> ), 68.2 (Oi-Pr-CH), 113.3 (3'-CH <sub>2</sub> ), 141.6 (2'-C)
<i>E</i> -11	163.5	145.6	112.6	73.0	12.5 (4-CH <sub>3</sub> ), 19.3 (2'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 68.3 (O <i>i</i> -Pr-CH), 112.6 (3'-CH <sub>2</sub> ), 140.8 (2'-C)
Z-1m	163.9	143.2	136.0	73.0	13.6 (6'-CH <sub>3</sub> ), 21.8 (Oi-Pr-CH <sub>3</sub> ), 22.1 (5'-CH <sub>2</sub> ), 22.3 ( <i>i</i> -Pr-CH <sub>3</sub> ), 23.6 (4-CH), 34.3 (4'-CH <sub>2</sub> ), 68.3 (O <i>i</i> -Pr-CH), 125.6 (2'-CH <sub>2</sub> ), 135.6 (3'-CH <sub>2</sub> )
Z-1nº Z-10	164.2 163.5	144.6 145.2	b c	72.5 68.3	13.5 (6'-CH <sub>3</sub> ), 21.9 (Oi-Pr-CH <sub>3</sub> ), 22.0 (5'-CH <sub>2</sub> ), 34.2 (4'-CH <sub>2</sub> ), 68.7 (O- <i>i</i> -Pr-CH) 18.0 (4'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 25.8 (4'-CH <sub>3</sub> ), 31.9 (4-CH <sub>2</sub> ), 68.4 (O <i>i</i> -Pr-CH), 120.1 (2'-
<i>Z</i> -1p	163.4	145.1	136.2	72.9	CH), 126.2, 126.8, 128.4, 128.5, 138.8, 139.4 (aryl-C, 3-C, 3'-C) 13.6 (6'-CH <sub>3</sub> ), 21.8 (Oi-Pr-CH <sub>3</sub> ), 22.1 (5'-CH <sub>2</sub> ), 31.9, 34.3 (4'-CH <sub>2</sub> , 4-CH <sub>2</sub> ), 68.4 (Oi-Pr- CH <sub>2</sub> ), 125.5, 120.2, 120.5, 120.2, (CH <sub>2</sub> ), 21.9, 24.2, (CH <sub>2</sub> ),
Z-1q <sup>b</sup>	163.6	144.1	b	78.5	Cn), 125.5, 120.2, 120.0, 128.4, 128.5, 159.3 (aryl-C, $3$ -Ch <sub>2</sub> , $2$ -Ch <sub>2</sub> ) 20.8 (1'-CH <sub>3</sub> ), 21.8 (Oi-Pr-CH <sub>3</sub> ), 32.1 (4-CH <sub>3</sub> ), 68.4 (Oi-Pr-CH), 116.9 (3'-CH <sub>3</sub> )
Z-1r	163.3	145.4	с	76.0	19.7 (2'-CH <sub>3</sub> ), 21.8 (O <i>i</i> -Pr-CH <sub>3</sub> ), 31.8 (4-CH <sub>2</sub> ), 68.5 (O <i>i</i> -Pr-CH), 113.5 (3'-CH <sub>2</sub> ), 126.2, 126.3, 128.5, 139.3, 141.4 (aryl-C, 2'-C, 3-CH).

<sup>a</sup> Determined from a mixture of double bond isomers as indicated in Table 3.

<sup>b</sup> Only characteristic signals, determined from a 1:1 mixture with the corresponding Claisen rearrangement product 5.

<sup>c</sup> Not unambiguously assignable.

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