Asymmetric Induction and Simple Diastereoselectivity in the [2,3] Wittig Rearrangement of Ester Enolates

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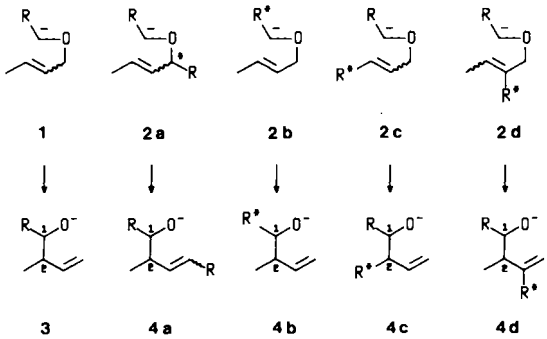
The [2,3] Wittig rearrangements of the lithio enolates of the *cis*-configurated allylic ethers **5a–d** are stereoselective. The *tert*-butyl ester **5d** gives 79% of a single rearrangement product **6d**. The chiral center of the dioxolane controls the configuration at one of the newly formed stereogenic centers through asymmetric induction. The size of the dioxolane is responsible for the concomitant high *syn* selectivity. The [2,3] Wittig rearrangements of the *trans*-configurated allyl esters **20a–d** exhibit moderate stereocontrol through asymmetric induction; the ratio of *syn* (**6**) and *anti* products (**21**) can be tuned from 2:1 as in the case of the *tert*-butyl ester, to 1:3 by choosing the methyl ester.

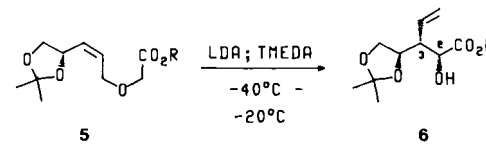
Asymmetrische Induktion und einfache Diastereoselektivität bei der [2,3]-Wittig-Umlagerung von Esterenolaten

Die [2,3]-Wittig-Umlagerungen der Esterenolate der *cis*-konfigurierten Allylether **5a–d** erfolgen stereoselektiv. Aus dem *tert*-Butylester **5** gewinnt man in 79proz. Ausbeute ein einziges Umlagerungsprodukt **6d** ohne die anderen drei Diastereomeren. Das Chiralitätszentrum des Dioxolan-Rings kontrolliert die Konfiguration an einem der neu entstehenden stereogenen Zentren. Die Raumerfüllung des Dioxolan-Rings ist für die gleichzeitig beobachtete hohe *syn*-Selektivität verantwortlich. Die [2,3]-Umlagerungen der *trans*-konfigurierten Allylester **20a–d** unterliegen nur mäßiger Stereokontrolle durch asymmetrische Induktion; das Verhältnis von *syn*- (**6**) zu *anti*-Umlagerungsprodukten (**21**) läßt sich durch die Wahl des Esters von 2:1 (*tert*-Butylester) zu 1:3 (Methylester) verschieben.

The [2,3] Wittig rearrangement **1** → **3** of metalated allylic ethers was discovered in 1960[1]. However, applications in synthesis remained scarce. It was not until two decades later, that studies by Still[2a] and Nakai[2b] spearheaded a revival of this reaction. The Wittig rearrangement became appreciated increasingly as a means of achieving acyclic diastereocontrol in stereoselective synthesis[3]. Control of the *relative configurations* of the newly formed stereogenic centers ("stereocenters") C-1 and C-2 in the rearrangement product **3** highlights the earlier stages of this development.



The *absolute configurations* of Wittig rearrangement products **4** can be controlled starting from chiral ethers **2**. In the formation of **4a**[4] configurational control stems from *chirality transfer*. On the other hand, product types **4b–4d** are enantiomerically enriched through the influence of *asymmetric induction*. Note that in the metalated ether **2a** the chiral center is *part of* the 5-atom backbone involved in the sigmatropic process. In the anions **2b–2d**, however, the chiral center is only *attached to* the backbone in question. No matter *where* the location of the chiral center is in **2b–2d**, it induces the formation of products **4b**, **4c**, and **4d** with defined absolute configurations. Reactions of type **2b** → **4b** were described by Nakai and Katsuki[5]. Stereoselectivity in the **2c** → **4c** class of Wittig rearrangements has been studied by us[6] and applied in the synthesis of a partial structure of amphotericin B[7]. Quite recently, we observed configurational control illustrated by the transformation of **2d** into **4d**[8]. This paper describes [2,3] Wittig rearrangements of chiral ester enolates derived from **5** and **20**, i.e. conversions of type **2c** → **4c**.



only 1 diastereomer

	R	yield	
5a	Me	40%	6a
b	Et	53% *	b
c	iPr	70% *	c
d	tBu	79%	d

* based on recovered starting material

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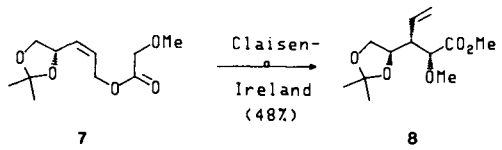
The lithium enolate of the unsaturated methyl ester **5a** is stable in THF solution at −40°C in the absence of tetramethylethylenediamine (TMEDA). In the presence of TMEDA the ionic character of the enolate and hence its reactivity are enhanced, leading to complete conversion within 3 h. Chromatographic workup gave 40% of the Wittig rearrangement product **6a** along with less than 2% of the other three possible stereoisomers[6a].

Although pleased with the high degree of diastereoselectivity found in this reaction, we were worried about the poor mass balance. We argued that the anion derived from **5a** – as any ester enolate – could decompose to an alcoholate ion and a ketene in a yield-lowering sidereaction. It is known that ester enolates are *less* prone to ketene formation with increasing size of their alcoholic constituents[9]. Accordingly, we subjected esters **5** with R = Et, *i*Pr or *t*Bu to the Wittig rearrangement conditions. Indeed, as anticipated, they gave increased yields of **6**, the highest observed for R = *t*Bu (79%). Again, the rearrangement products **6b**–**6d** were diastereomerically pure.



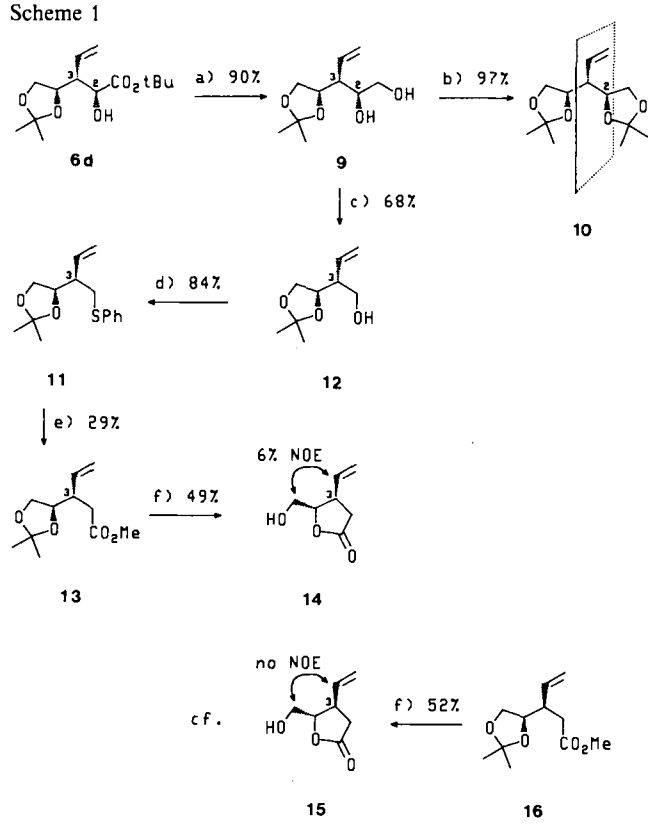
Interestingly, the *Ireland-Claisen rearrangement* of the ester **7** was used by Cha[10] to prepare a compound **8** *stereochemically identical with the Wittig rearrangement product* **6**. In terms of yield and stereoselectivity, however, the stereotriad of compounds **6** and **8** is more advantageously accessible through the [2,3] sigmatropic shift from **5d**.

The configurations at the newly formed stereocenters of the rearranged esters **6** were determined as shown in Scheme 1. The *tert*-butyl ester **6d** was reduced to the diol **9**. The configuration at C-2 of **9** followed after protection as the bisacetonide **10**. **10** was optically inactive and revealed *one* set of signals for the *two* dioxolane rings both in its ^{13}C- and ^{1}H-NMR spectra. Therefore, **10** must contain a plane of symmetry. This proves that the C–O bond at C-2 of the hydroxy ester **6d** is *syn* with respect to the C–O bond at the "heterocyclic stereocenter".

In order to unravel the configuration at C-3 of the diol **9**, the stereocenter at C-2 was removed by oxidative cleavage and subsequent reduction. We thereby obtained the alcohol **12**. After conversion via sulfide **11** and the homologated ester **13** into lactone **14**[11], the missing configuration at C-3 was determined by ^{1}H-NMR spectroscopy. The irradiation of the CH_2–OH resonance of **14** produced a 6% nuclear Overhauser effect (NOE) for the vinylic $-CH=CH_2$ signal. From this we conclude that the vinyl and hydroxymethyl groups of lactone **14** are *syn*. (In the isomeric *trans*-lactone **16**[11], we observed no NOE).

These correlations prove that the *tert*-butyl ester **6d** is the *all-syn* diastereomer shown. The methyl and isopropyl esters

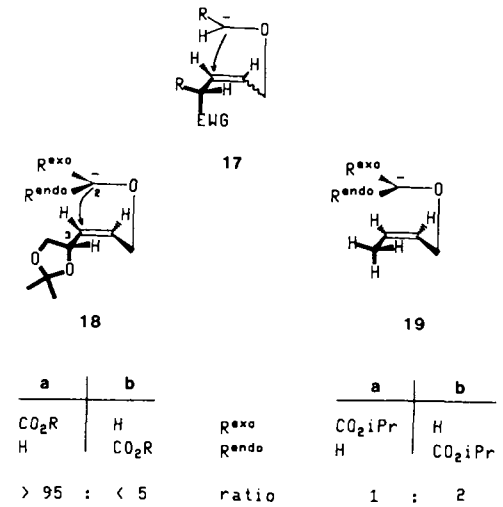
Scheme 1



a) $LiAlH_4$.- b) $H_2C(OMe)_2$, TsOH.- c) $NaIO_4$, aq. MeOH; $NaBH_4$.- d) Ph_2S_2, Bu_3P.- e) LiNaphth; $ClCO_2Me$.- f) H_2SO_4 (ref. 19).

6a and **6c**, respectively, were reduced to the diol **9** already derived from the *tert*-butyl ester **6d**. Hence, their configuration is safely established as well. The stereochemical assignment of the ethyl ester **6b** rests on analogy with NMR-spectroscopic data.

In explaining the stereochemical outcome of the Wittig rearrangements **5** → **6**, two types of stereoselectivity intervene: (1) The chiral dioxolane in the ester enolate controls the configuration at C-3 of the rearrangement products through asymmetric induction. (2) "Simple diastereoselectivity" gives rise to the *syn* orientation of hydroxy and vinyl groups in **6**.

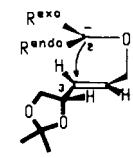


As outlined earlier, the origin of asymmetric induction in Wittig rearrangements of type **2c** → **4c** can be understood with the Houk-like transition state model **17**[6]. In fact, if the ester enolates of **5** react via transition states **18** *derived from* **17**, the vinyl group of **6** will be oriented as observed. The usefulness of the suggested transition state **18** extends to a rationalization of the "simple diastereoselectivity" of the rearrangement. There, this selectivity implies that the reaction proceeds *exclusively* via the *exo* transition state **18a**. Apparently, the corresponding *endo* transition state **18b** is unfavored because of repulsion of the ester function by the dioxolane. This *exo* preference contrasts with literature precedent on "simply diastereoselective" Wittig rearrangements of ester enolates: The anion derived from isopropyl *cis*-crotyloxyacetate reacts with an opposite albeit weak 2:1 preference via an *endo* transition state **19b**[12]. The hindering steric bulk of the dioxolane ring, which in *endo*-**18b** replaces the small methyl group of *endo*-**19b**, readily accounts for the preference of the *exo* transition state as opposed to the *endo* one. That a *branched* residue in the allylic moiety enhances the diastereoselectivity of a [2,3] Wittig rearrangement has not been noticed before. It might encourage respective applications[13].

In fact, we required the *epimeric* rearranged alcohols **21** with the hydroxy group oriented towards the *other* side of the molecule. Inversion of the "simple diastereoselectivity" of Wittig rearrangements by changing the double bond configuration of the starting material is, in general, an established remedy[3]. Unfortunately, this is not applicable in the case of ester enolates[12]. Nevertheless, we resolved to rearrange the *trans* isomers **20** of the previously described *cis*-esters **5**. At least in the *trans* series we expected the *same* asymmetric induction as in *cis*-**5** → **6**. This expectation was based on similar Wittig rearrangements of *cis*/*trans* isomeric propargylic ethers[6b].

We found that the *trans*-esters **20a–d** gave *two* major products, each. These were the already known *all-syn*-esters **6a–d** and their *anti* epimers **21a–d**, respectively. Both products **21** and **6** have *identical* configurations at C-3. This means that in the *trans* series asymmetric induction orients the substituents on C-3 of the rearrangement products in the *same* fashion as in the *cis* series. Asymmetric induction was lower, however: **21**/**6** were invariably accompanied by the two C-3 epimers. 1,3-Allylic strain[14] – due to the more restricted rotational freedom in their transition states – contributes often to higher stereoselectivity in reactions of *cis*- vs. *trans*-olefins. Consequently, less asymmetric induction in the Wittig rearrangements of *trans*- vs. *cis*-allylic ethers comes without surprise[15].

Interestingly, in the *trans* series, the "simple diastereoselectivity" varies with the size of the ester residue: The *anti*/*syn* products **21**/**6** resulted in a 3:1 ratio from the methyl ester **20a**, in a 2:1 ratio from the ethyl ester **20b**, and in equal amounts in the isopropyl case. Only the *tert*-butyl ester **20d** gave less *anti* than *syn* epimer.



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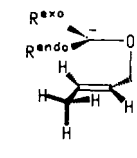
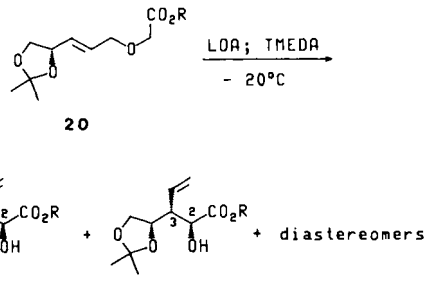


23

	a	b		a	b
R^{exo}	H	CO_2R	R^{exo}	H	CO_2iPr
R^{endo}	CO_2R	H	R^{endo}	CO_2iPr	H

R =				ratio		
Me	3.2	:	1			
Et	1.9	:	1			
iPr	1	:	1			
tBu	1	:	1.8			
				ratio	4.5	: 1

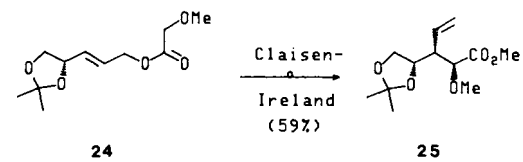
This dependence indicates a previously unrecognized possibility for diastereocontrol in the [2,3] Wittig rearrangement. It is readily understood on the assumption that the transition state of *these* rearrangements is represented by formula **22**. **22** is isomeric to the transition state **18** previously discussed for the Wittig rearrangements of the *cis*-ethers, and it adheres to the electronic requirements of the Houk-like transition state model **17**. In **22** the *anti*/*syn* selectivity can be equalled with the *endo* (**22a**) vs. *exo* (**22b**) transition state ratios. In the absence of other factors, the *endo* transition state should be favored as concluded from the 4.5:1.0 ratio of *endo* (**23a**) vs. *exo* (**23b**) transition states of an analogous Wittig rearrangement[12]. The 3:1 preference for *endo*-**22a** in the case of the methyl ester comes close to this expectation. Larger ester residues, however, yield increasingly to the steric hindrance imposed by the bulky he-



20 **21** **6**

	R	yield	21		6		diast.
a	Me	40% *	63	:	20	:	17
b	Et	54%	54	:	27	:	19
c	iPr	63%	44	:	46	:	10
d	tBu	75%	32	:	57	:	11

* based on recovered starting material



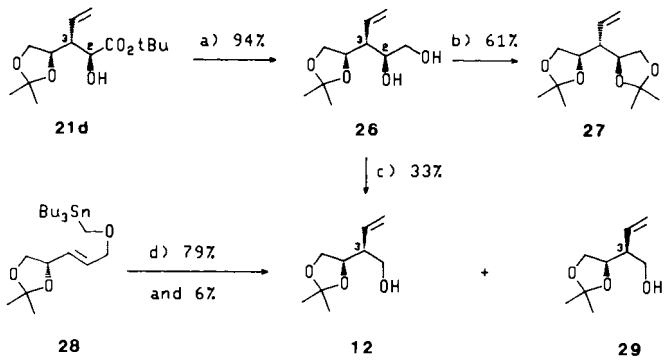
24 **25**

75% (+ 25% of 3 diastereomers)

terocycle "underneath" them. Hence, they react via the *exo* transition state **22b**.

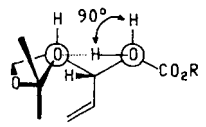
Unfortunately, higher *anti/syn* ratios are accompanied by decreasing overall yields. This makes the Wittig rearrangement of *trans*-esters useless for the preparation of *anti*-α-hydroxyesters **21**. The Claisen-Ireland rearrangement of **24d**[10] serves this purpose better, furnishing the methyl ether **25** corresponding to **21a**. However, the stereotriad contained in **21/25** – attached to a C≡C bond in place of the ester – is far more selectively accessible by the Wittig rearrangement of an allylic propargylic ether[6b].

Scheme 2

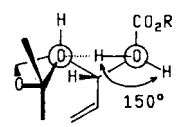


a) $LiAlH_4$.- b) $H_2C(OMe)_2$, TsOH.- c) $NaIO_4$, aq. MeOH; $NaBH_4$.- d) BuLi, THF, -78°C.

The rearrangement products **21a–21c** were assigned the same stereochemistry as **21d** on the basis of similar ^{1}H-NMR spectra. The configuration of **21d** was determined starting from the corresponding diol **26** (Scheme 2). The bisacetonide **27** obtained from **26** does *not* contain a mirror plane, since it is optically active ($[\alpha]_D = +9.0$) and shows *two* sets of ^{1}H- and ^{13}C-NMR signals for its diastereotopic dioxolane rings. The absence of symmetry in **27** proves the configuration at C-2. Oxidative cleavage of diol **26** and reduction of the resulting aldehyde gave an alcohol spectroscopically indistinguishable from the previously prepared **12** (cf. Scheme 1). Since, on the other hand, this alcohol differs spectroscopically from the *epimer* **29**[6a], the configuration at C-3 of **21d** is unambiguously established.



syn-**6**



anti-**21**

6	$J_{OH,H}$	$\Sigma\delta(^{13}C)$	R	**21**	$J_{OH,H}$	$\Sigma\delta(^{13}C)$
a	4.6 Hz	148.2	Me	**a**	8.5 Hz	147.4
b	4.6 Hz	147.9	Et	**b**	8.5 Hz	147.5
c	4.6 Hz	147.6	iPr	**c**	8.5 Hz	147.3
d	4.7 Hz	147.5	tBu	**d**	8.1 Hz	147.3

The vicinal coupling constants $J_{OH,H}$ in the hydroxy esters **6** and **21** deserve comment. In the *syn*-esters **6**, they are by 3.4–3.9 Hz smaller than in the *anti* epimers **21**. This order could be a consequence of H-bridging between the hydroxy groups and an oxygen atom of the dioxolane. The presumably favored conformations of the resulting 6-membered H-bridged rings are shown as Newman projections *syn*-**6** and *anti*-**21**, respectively. The relevant dihedral angles – ca. 90° for *syn*-**6** and ca. 150° for *anti*-**21** – plus a Karplus-type dependence of the $J_{OH,H}$ values therefrom, make them once again[16] a useful criterion for assigning relative configurations to γ-alkoxyalcohols. The established criterion based on the relative magnitudes of the sums of the ^{13}C-NMR shifts of the oxygen-linked *methine* carbons is equivocal for these particular compounds[17].

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Experimental

^{1}H- and ^{13}C-NMR spectra: Bruker AC 300, WH 400; tetramethylsilane or $CHCl_3$ as internal standard in $CDCl_3$; integrals in accord with assignments; coupling constants in Hz. – All reactions were performed in oven-dried (100°C) glassware under dry nitrogen. Compounds were purified by flash chromatography[18] on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh ASTM); eluents given in brackets. Yields refer to analytically pure samples.

cis-(4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol ⟨$[\alpha]_D^{18} = +20.5$ (*c* = 5.4, CH_2Cl_2); ref.[19] $[\alpha]_D = +17.1$ (*c* = 0.34, $CHCl_3$); ref.[20] $[\alpha]_D = +14.0$ (*c* = 4.5, $CHCl_3$)⟩ was prepared in 92% yield by DIBAL reduction of methyl *cis*-(4′*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propenoate. The latter compound was prepared via 1,2:5,6-di-*O*-isopropylidene-D-mannitol[21] and (4*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde[22] by the method of Mulzer[23].

trans-(4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol ⟨$[\alpha]_D^{18} = +30.2$ (*c* = 7.2, CH_2Cl_2); ref.[19] $[\alpha]_D = +26.7$ (*c* = 0.21, $CHCl_3$); ref.[20] $[\alpha]_D = +33.9$ (*c* = 3.6, $CHCl_3$)⟩ was prepared in 95% yield by DIBAL reduction of methyl *trans*-(4′*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propenoate, which was obtained via (4*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (vide supra) according to ref.[24].

cis-(4″S)-[3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-propenyl]oxyacetates **5a–d** *and trans-(4″S)-[3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-propenyl]oxyacetates* **20a–d**: **20a** was prepared in 84% yield as described for **5a**. **5b** (65%), **5c** (61%), **20b** (55%), **20c** (52%), and **20d** (56%) were obtained in the indicated yields following the procedure exemplified for **5d**.

Methyl Ester **5a**: $Na^{\oplus}[DMSO]^{\ominus}$ (1.55 mol/l in DMSO, 4.89 ml, 7.59 mmol, 1.2 equiv.), sodium chloroacetate (0.96 g, 8.22 mmol, 1.3 equiv.), and *cis*-(4′*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol (1.00 g, 6.32 mmol) were allowed to react in DMSO (18 ml) at room temp. for 2.7 h. After dilution with H_2O (80 ml), impurities were extracted with CH_2Cl_2 (3 × 80 ml). The mixture was acidified with satd. aqueous citric acid (15 ml), the crude acid extracted into CH_2Cl_2 (100 ml + 3 × 50 ml), and the solvent exchanged for diethylether. Etherification with ethereal diazomethane gave upon flash chromatography [petroleum ether/ether (3:2)] **5a** (1.30 g, 89% for the two steps). – $[\alpha]_D^{20} = +1.2$ (*c* = 4.0, CH_2Cl_2). – ^{1}H NMR:

δ = 1.38 and 1.41 [2 s; 2″-$(CH_3)_2$], 3.55 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 8.0$; 5″-$H^1$), 3.75 (s; OCH_3), AB signal ($\delta_A = 4.07$, $\delta_B = 4.09$, $J_{A,B} = 16.4$; 2-H), superimposes 4.09 (m_c; 5″-H^2), 4.20 (m_c; 1′-H_2), 4.83 (br. ddd, all J values ca. 7; 4″-H), 5.63–5.68 (m; 3′-H), 5.74–5.79 (m; 2′-H).

$C_{11}H_{18}O_5$ (230.3) Calcd. C 57.38 H 7.88
Found C 57.08 H 7.87

Ethyl Ester **5b**: $[\alpha]_D^{18} = +1.9$ ($c = 4.0$, CH_2Cl_2). – ^{1}H NMR: δ = 1.29 (t, $J = 7.2$; CH_2CH_3), 1.39 and 1.42 [2 s; 2″-$(CH_3)_2$], 3.56 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 8.0$; 5″-$H^1$), AB signal ($\delta_A = 4.07$, $\delta_B = 4.08$, $J_{A,B} = 16.4$; OCH_2CO_2), 4.10 (dd, $J_{gem} = 8.2$, $J_{5''\text{-}H^2,4''} = 6.2$; 5″-$H^2$), 4.21 ($m_c$; 1′-$H_2$, CH_2CH_3), 4.83 (ddd, all J values ca. 6; 4″-H), 5.63–5.80 (m; 2′-H, 3′-H).

$C_{12}H_{20}O_5$ (244.3) Calcd. C 59.00 H 8.25
Found C 59.14 H 8.36

Isopropyl Ester **5c**: $[\alpha]_D^{18} = +1.8$ ($c = 4.5$, CH_2Cl_2). – ^{1}H NMR: δ = 1.27 [d, $J = 6.3$; $CH(CH_3)_2$], 1.39 and 1.43 [2 s; 2″-$(CH_3)_2$], 3.56 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 7.9$; 5″-$H^1$), AB signal ($\delta_A = 4.02$, $\delta_B = 4.05$, $J_{A,B} = 16.3$; OCH_2CO_2), 4.10 (dd, $J_{gem} = 8.2$, $J_{5''\text{-}H^2,4''} = 6.1$; 5″-$H^2$), 4.21 ($m_c$; 1′-$H_2$), 4.85 (dddm, all J values ca. 7; 4″-H), 5.11 [sept, $J = 6.3$; $OCH(CH_3)_2$], 5.62–5.81 (m; 2′-H, 3′-H).

$C_{13}H_{22}O_5$ (258.3) Calcd. C 60.45 H 8.58
Found C 60.30 H 8.32

tert-Butyl Ester **5d**: To the crude *cis*-(4″*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propenyloxyacetic acid – obtained as detailed in the preparation of **5a** – in CH_2Cl_2 (20 ml) were added *t*BuOH (0.515 g, 6.95 mmol, 1.1 equiv.), 4-(dimethylamino)pyridine (0.154 g, 1.26 mmol, 0.20 equiv.), and dicyclohexylcarbodiimide (1.565 g, 7.59 mmol, 1.2 equiv.). The mixture was diluted with satd. aqueous NH_4Cl (20 ml)/H_2O (20 ml), extracted with CH_2Cl_2 (4 × 50 ml), and purified by flash chromatography yielding 1.012 g (59%) of **5d**. – $[\alpha]_D^{26} = +1.6$ ($c = 4.7$, CH_2Cl_2). – ^{1}H NMR: δ = 1.39 and 1.43 [2 s; 2″-$(CH_3)_2$], 1.48 (s; *t*Bu), 3.56 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 8.0$; 5″-$H^1$), AB-signal ($\delta_A = 3.95$, $\delta_B = 3.96$, $J_{A,B} = 16.3$; OCH_2CO_2), 4.10 (dd, $J_{gem} = 8.1$, $J_{5''\text{-}H^2,4''} = 6.2$; 5″-$H^2$), 4.20 ($m_c$; 1′-$H_2$), 4.85 (br. ddd, all J values ca. 6.5; 4″-H), 5.64 (m_c; 3′-H), 5.79 (m_c; 2′-H).

$C_{14}H_{24}O_5$ (272.3) Calcd. C 61.74 H 8.88
Found C 61.73 H 9.10

Methyl Ester **20a**: $[\alpha]_D^{20} = +23.0$ ($c = 3.9$, CH_2). – ^{1}H NMR: δ = 1.38 and 1.41 [2 s; 2″-$(CH_3)_2$], 3.59 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 7.9$; 5″-$H^1$), 3.75 (s; OCH_3), 4.07–4.16 (m; 1′-H_2, 2-H_2, 5″-H^2), 4.52 (ddd, all J values 7.0; 4″-H), 5.74 (m_c; 3′-H), 5.87 (m_c; 2′-H).

$C_{11}H_{18}O_5$ (230.7) Calcd. C 57.38 H 7.88
Found C 57.23 H 7.93

Ethyl Ester **20b**: $[\alpha]_D^{18} = +24.2$ ($c = 4.5$, CH_2Cl_2). – ^{1}H NMR: δ = 1.29 (t, $J = 7.1$; CH_2CH_3), 1.39 and 1.43 [2 s; 2″-$(CH_3)_2$], 3.60 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 7.9$; 5″-$H^1$), 4.06–4.12 (m; 1′-$H_2$, 2-$H_2$, 5″-$H^2$), 4.53 (ddd, all J values 7.0; 4″-H), AB signal ($\delta_A = 5.76$, $\delta_B = 5.89$, $J_{A,B} = 15.5$, in addition split by $J_{A,4''} = 7.0$, $J_{B,1'} = 5.5$; A = 3′-H, B = 2′-H).

$C_{12}H_{20}O_5$ (244.3) Calcd. C 59.00 H 8.25
Found C 59.06 H 8.08

Isopropyl Ester **20c**: $[\alpha]_D^{18} = +23.5$ ($c = 6.0$, CH_2Cl_2). – ^{1}H NMR: δ = 1.26 [d, $J = 6.3$; $CH(CH_3)_2$], 1.39 and 1.43 [2 s; 2″-$(CH_3)_2$], 3.60 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 7.9$; 5″-$H^1$), 4.03 (s; 2-$H_2$), 4.10 ($m_c$; 5″-$H^2$, 1′-$H_2$), 4.53 (ddd, all J values 7.0; 4″-H), 5.10 [sept, $J = 6.3$; $CH(CH_3)_2$], AB signal ($\delta_A = 5.75$, $\delta_B = 5.90$, $J_{A,B} = 15.5$, in addition split by $J_{A,4''} \approx 7.5$, $J_{B,1'} = 5.5$; A = 3′-H, B = 2′-H).

$C_{13}H_{22}O_5$ (258.3) Calcd. C 60.45 H 8.58
Found C 60.52 H 8.70

tert-Butyl Ester **20d**: $[\alpha]_D^{26} = +19.3$ ($c = 5.0$, CH_2Cl_2). – ^{1}H NMR: δ = 1.39 and 1.42 [2 s; 2″-$(CH_3)_2$], 1.48 (s; *t*Bu), 3.60 (dd, $J_{gem} = J_{5''\text{-}H^1,4''} = 7.9$; 5″-$H^1$), 3.96 (s; 2-$H_2$), 4.07–4.12 (m; 1′-$H_2$, 5″-$H^2$), 4.53 (ddd, all J values ca. 7; 4″-H), AB signal ($\delta_A = 5.83$, $\delta_B = 5.91$, $J_{A,B} = 15.5$, in addition split by $J_{A,4''} = 7.1$, $J_{A,1'} = 1.2$, $J_{B,1'} = 5.6$, $J_{B,4''} = 0.6$; A = 3′-H, B = 2′-H).

$C_{14}H_{24}O_5$ (272.3) Calcd. C 61.74 H 8.88
Found C 61.88 H 9.03

Wittig Rearrangements of **5a–d** *and* **20a–d**: The rearrangements of **5b–d** and **20a–d** were effected as described for **5a**, except that after the addition of tetramethylethylenediamine the temperature was raised to –20°C for 5–15 h.

At –78°C, **5a** (1.129 g, 4.90 mmol) in THF (25 ml) was added during 22 min to a solution prepared from diisopropylamine (1.10 ml, 0.794 g, 7.85 mmol, 1.6 equiv.) and *n*BuLi (1.47 mol/l in hexane; 4.17 ml, 6.13 mmol, 1.25 equiv.) in THF (30 ml). Tetramethylethylenediamine (4.00 ml, 3.12 g, 26.85 mmol, 5.5 equiv.) was added 20 min later, and another 20 min later the temp. was allowed to raise to –40°C for 2.7 h. Extractive workup [satd. aqueous NH_4Cl (100 ml)/ether (5 × 100 ml)] and flash chromatography [petroleum ether/ether (2:1)] gave a 4:2:1 mixture of **5a** and two unidentified sideproducts (0.069 g, 6%), and **6a** (0.446 g, 40%).

5b (0.806 g, 3.30 mmol) gave recovered starting material (0.144 g, 18%) and **6b** (0.351 g, 44%). – **5c** (0.829 g, 3.21 mmol) gave recovered starting material (0.079 g, 10%) and **6c** (0.528 g, 64%). – **5d** (0.217 g, 0.80 mmol) gave **6d** (0.171 g, 79%). – **20a** (0.373 g, 1.62 mmol) gave a 1:2 mixture of **A**/recovered **20a** (0.047 g, 13%), a 3:4 mixture of **B**/recovered **20a** (0.010 g, 3%), and a 1:3 mixture of **6a**/**21a** (0.118 g, 32%). – **20b** (0.094 g, 0.39 mmol) gave a 10:1 mixture of **C**/**D** (0.010 g, 10%), **6b** (0.014 g, 15%), and **21b** (0.027 g, 29%). – **20c** (0.094 g, 0.36 mmol) gave a 4:1 mixture of **E**/**F** (0.006 g, 6%), **6c** (0.027 g, 29%), and **21c** (0.026 g, 28%). – **20d** (0.689 g, 2.53 mmol) gave a 6:1 mixture of **G**/**H** (0.042 g, 6%), **6d** (0.207 g, 30%), and **21d** (0.176 g, 26%).

(2R,3R,4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-hydroxy-4-pentenoates **6a–d**

Methyl Ester **6a**: $[\alpha]_D^{20} = -25.7$ ($c = 5.4$, CH_2Cl_2). – ^{1}H NMR: δ = 1.37 and 1.42 [2 s; 2′-$(CH_3)_2$], 2.65 (ddd, $J_{3,4} = 9.4$, $J' = 6.2$, $J'' = 2.6$; 3-H), 3.12 (d, $J = 4.6$; OH), 3.78 (s; OCH_3), 3.85 (dd, $J_{gem} = 8.1$, $J_{5'\text{-}H^1,4'} = 7.1$; 5′-$H^1$), 4.10 (dd, $J_{gem} = 8.2$, $J_{5'\text{-}H^2,4'} = 6.2$; 5′-$H^2$), 4.33–4.39 (m; 2-H, 4′-H), 5.15 (ddd, $J_{trans} = 17.2$, $J_{gem} = 1.7$, $J_{5,3} = 0.7$; *Z*-5-H), 5.25 (dd, $J_{cis} = 10.4$, $J_{gem} = 1.8$; *E*-5-H), 5.87 (ddd, $J_{trans} = 17.2$, $J_{cis} = 10.3$, $J_{4,3} = 9.5$; 4-H). – ^{13}C NMR: δ = 25.47 and 26.47 [2′-$(CH_3)_2$], 50.23 and 52.53 (CO_2CH_3, C-3), 67.26 (C-5′), 72.09 and 76.09 (C-2, C-4′), 109.36 and 119.99 (C-2′, C-5), 132.35 (C-4), 173.81 (C-1).

$C_{11}H_{18}O_5$ (230.3) Calcd. C 57.38 H 7.88
Found C 57.61 H 7.98

Ethyl Ester **6b**: $[\alpha]_D^{22} = -11.4$ ($c = 7.2$, CH_2Cl_2). – ^{1}H NMR: δ = 1.30 (t, $J = 7.1$; OCH_2CH_3), 1.38 and 1.43 [2 s; 2′-$(CH_3)_2$], 2.66 (ddd, $J_{3,4} = 9.5$, $J = 6.7$, $J = 2.6$; 3-H), 3.06 (d, $J_{OH,2} = 4.6$; OH), 3.85 (dd, $J_{gem} = 8.1$, $J_{5'\text{-}H^1,4'} = 7.2$; 5′-$H^1$), 4.10 (dd, $J_{gem} = 8.1$, $J_{5'\text{-}H^2,4'} = 6.2$; 5′-$H^2$), 4.20–4.39 ($OCH_2CH_3$, 2-H, 4′-H), 5.15 (dm, $J_{trans} \approx 17$; *Z*-5-H), 5.25 (dd, $J_{cis} = 10.4$, $J_{gem} = 1.9$; *E*-5-H), 5.86 (ddd, $J_{trans} = 17.2$, $J_{cis} = 10.2$, $J_{4,3} = 9.7$; 4-H). – ^{13}C NMR: δ = 14.26 (CH_2CH_3), 25.52, 26.54 [2′-$(CH_3)_2$], 50.33 (C-3), 61.90 (CH_2CH_3), 67.32 (C-5′), 71.79, 76.10 (C-2, C-4′), 109.33 (C-2′), 119.99 (C-5), 132.40 (C-4), 173.43 (C-1).

$C_{12}H_{20}O_5$ (244.3) Calcd. C 59.00 H 8.25
Found C 59.10 H 8.25

Isopropyl Ester **6c**: $[\alpha]_D^{20} = -4.8$ ($c = 4.8$, CH_2Cl_2). – ^{1}H NMR: δ = 1.26 and 1.28 [2 d, $J = 6.2$; $OCH(CH_3)_2$], 1.38 and 1.43 [2 s;

2′-$(CH_3)_2$], 2.63 (ddd, $J_{3,4}$ = 9.3, J = 6.8, J = 2.5; 3-H), 3.06 (d, $J_{OH,2}$ = 4.6; OH), 3.86 (dd, J_{gem} = $J_{5'\text{-}H^1,4'}$ = 7.6; 5′-H^1), 4.10 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.2; 5′-H^2), 4.26 (dd, $J_{2,OH}$ = 4.6, $J_{2,3}$ = 2.5; 2-H), 4.35 (ddd, $J_{4',5'\text{-}H^1}$ = $J_{4',5'\text{-}H^2}$ = $J_{4',3}$ = 6.6; 4′-H), 5.10 [sept, J = 6.3; OC*H*$(CH_3)_2$], 5.14 (dm, $J_{trans} \approx$ 17; *Z*-5-H), 5.25 (dd, J_{cis} = 10.3, J_{gem} = 1.9; *E*-5-H), 5.85 (ddd, J_{trans} = 17.1, J_{cis} = $J_{4,3}$ = 10.0; 4-H). – ^{13}C NMR: δ = 21.77, 21.78 [CH$(CH_3)_2$], 25.49, 26.53 [2′-$(CH_3)_2$], 50.29 (C-3), 67.29 (C-5′), 69.78 [CO_2*C*H$(CH_3)_2$], 71.48, 76.07 (C-2, C-4′), 109.22 (C-2′), 119.87 (C-5), 132.34 (C-4), 172.94 [*C*O_2CH$(CH_3)_2$].

$C_{13}H_{22}O_5$ (258.3) Calcd. C 60.45 H 8.58
Found C 60.38 H 8.59

tert-Butyl Ester **6d**: $[\alpha]_D^{22}$ = −5.7 (*c* = 4.1, CH_2Cl_2). – ^{1}H NMR: δ = 1.37 and 1.43 [2 s; 2′-$(CH_3)_2$], 1.47 (s; *t*Bu), 2.59 (ddd, $J_{3,4}$ = 9.4, $J_{3,4'}$ = 7.0, $J_{3,2}$ = 2.6; 3-H), 3.03 (d, $J_{OH,2}$ = 4.7; OH), 3.85 (dd, J_{gem} = $J_{5'\text{-}H^1,4'}$ = 7.7; 5′-H^1), 4.10 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.0; 5′-H^2), 4.15 (dd, $J_{2,OH}$ = 4.6, $J_{2,3}$ = 2.5; 2-H), 4.33 (ddd, all *J* values ca. 6–7; 4′-H), 5.17 (ddd, $J_{trans} \approx$ 17, J_{gem} = 1.9, $J_{Z\text{-}5\text{-}H,3}$ = 0.6; *Z*-5-H), 5.25 (dd, J_{cis} = 10.3, J_{gem} = 1.9; *E*-5-H), 5.84 (ddd, J_{trans} = 17.2, J_{cis} = 10.2, $J_{4,3}$ = 9.6; 4-H). – ^{13}C NMR: δ = 25.58, 26.64, 28.11 [2′-$(CH_3)_2$ and C$(CH_3)_3$], 50.45 (C-3), 67.42 (C-5′), 71.38, 76.14 (C-2, C-4′), 82.97 [*C*$(CH_3)_3$], 109.24 (C-2′), 119.80 (C-5), 132.52 (C-4), 172.68 (C-1).

$C_{14}H_{24}O_5$ (272.3) Calcd. C 61.74 H 8.88
Found C 62.14 H 9.01

(2S,3R,4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-hydroxy-4-pentenoates **21a–d**

Methyl Ester **21a**: ^{1}H NMR: δ = 1.35 and 1.40 [2 s; 2′-$(CH_3)_2$], 2.55 (ddd, $J_{3,4}$ = 9.8, $J_{3,4'} \approx J_{3,2} \approx$ 4.9; 3-H), 3.03 (d, $J_{OH,2}$ = 8.5; OH), 3.73 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^1,4'}$ = 7.4; 5′-H^1), 3.76 (s; OCH_3), 4.02 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.4; 5′-H^2), 4.26 (dd, $J_{2,OH}$ = 8.5, $J_{2,3}$ = 5.8; 2-H), 4.31–4.37 [m (superimposed by 4′-H and 2-H of **6a**); 4′-H], 5.19 (dm, $J_{trans} \approx$ 17; *Z*-5-H), 5.27 (dd, J_{cis} = 10.3, J_{gem} = 1.7; *E*-5-H), 5.87 [m_c (superimposed by **6a**); 4-H). – ^{13}C NMR: δ = 25.23, 26.09 [2′-$(CH_3)_2$], 50.56 (C-3), 52.03 (OCH_3), 67.08 (C-5′), 72.80, 74.64 (C-2, C-4′), 109.25 (C-2′), 119.74 (C-5), 132.90 (C-4), 174.05 (CO_2CH_3).

$C_{11}H_{18}O_5$ (230.3) Calcd. C 57.38 H 7.88
Found C 57.70 H 7.93

Ethyl Ester **21b**: $[\alpha]_D^{25}$ = +24.5 (*c* = 3.3, CH_2Cl_2). – ^{1}H NMR: δ = 1.30 (t, *J* = 7.1; OCH_2CH_3), 1.35 and 1.40 [2 s; 2′-$(CH_3)_2$], 2.53 (ddd, $J_{3,4} \approx$ 10, $J_{3,4'} \approx J_{3,2} \approx$ 6; 3-H), 3.07 (d, $J_{OH,2}$ = 8.5; OH), 3.72 (dd, J_{gem} = 8.0, $J_{5'\text{-}H^1,4'}$ = 7.4; 5′-H^1), 4.03 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.5; 5′-H^2), 4.16–4.31 (m; OCH_2CH_3, 2-H), 4.36 (br. ddd, $J_{4',5'\text{-}H^1} \approx J_{4',5'\text{-}H^2} \approx$ 6.5, $J_{4',3}$ = 4.3; 4′-H), 5.19 (dm, $J_{trans} \approx$ 17; *Z*-5-H), 5.27 (dd, J_{cis} = 10.3, J_{gem} = 1.7; *E*-5-H), 5.87 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{4,3}$ = 9.5; 4-H). – ^{13}C NMR: δ = 14.22 (CH_2CH_3), 25.28, 26.14 [2′-$(CH_3)_2$], 50.65 (C-3), 61.44 (CH_2CH_3), 67.16 (C-5′), 72.74, 74.75 (C-2, C-4′), 109.25 (C-2′), 119.73 (C-5), 133.02 (C-4), 173.57 (C-1).

$C_{12}H_{20}O_5$ (244.3) Calcd. C 59.00 H 8.25
Found C 59.99 H 8.81

Isopropyl Ester **21c**: ^{1}H NMR: δ = 1.27 and 1.28 [2 d, *J* = 6.3; $OCH(CH_3)_2$], 1.35 and 1.40 [2 s; 2′-$(CH_3)_2$], 2.51 (br. ddd, $J_{3,4}$ = 9.4, $J_{3,4'} \approx J_{3,2} \approx$ 4.7; 3-H), 2.98 (d, $J_{OH,2}$ = 8.5; OH), 3.72 (dd, J_{gem} = $J_{5'\text{-}H^1,4'}$ = 7.8; 5′-H^1), 4.03 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.4; 5′-H^2), 4.17 (dd, $J_{2,OH}$ = 8.5, $J_{2,3}$ = 6.0; 2-H), 4.34 (ddd, $J_{4',5'\text{-}H^1}$ = 7.2, $J_{4',5'\text{-}H^2}$ = 6.6, $J_{4',3}$ = 4.5; 4′-H), 5.10 [sept, *J* = 6.3; OC*H*$(CH_3)_2$], 5.19 (dd, J_{trans} = 17.0, J_{gem} = 1.7; *Z*-5-H), 5.26 (dd, J_{cis} = 10.4, J_{gem} = 1.7; *E*-5-H), 5.86 (ddd, J_{trans} = 17.2, J_{cis} = $J_{4,3}$ = 10.0; 4-H). – ^{13}C NMR: δ = 21.77, 21.82 [C$(CH_3)_2$], 25.30, 26.15 [2′-$(CH_3)_2$], 50.79 (C-3), 67.18 (C-5′), 69.50, 72.53, 74.74 [C-2, C-4′, $CO_2CH(CH_3)_2$], 109.18 (C-2′), 119.70 (C-5), 133.07 (C-4), 173.06 [$CO_2CH(CH_3)_2$].

$C_{13}H_{22}O_5$ (258.3) Calcd. C 60.45 H 8.58
Found C 60.50 H 8.62

tert-Butyl Ester **21d**: $[\alpha]_D^{20}$ = +23.6 (*c* = 4.2, CH_2Cl_2). – ^{1}H NMR: δ = 1.35 and 1.40 [2 s; 2′-$(CH_3)_2$], 1.48 (s; *t*Bu), 2.47 (ddd, $J_{3,4}$ = 9.3, $J_{3,4'}$ = $J_{3,2}$ = 5.4; 3-H), 2.95 (d, $J_{OH,2}$ = 8.1; OH), 3.72 (dd, J_{gem} = $J_{5'\text{-}H^1,4'}$ = 7.9; 5′-H^1), 4.03 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.3; 5′-H^2*), 4.07 (dd, $J_{2,OH}$ = 8.2, $J_{2,3}$ = 6.0; 2-H*), 4.35 (m_c; 4′-H), 5.15 (dm, $J_{trans} \approx$ 17; *Z*-5-H), 5.26 (dd, J_{cis} = 10.3, J_{gem} = 1.8; *E*-5-H), 5.84 (ddd, J_{trans} = 17.2, J_{cis} = 10.2, $J_{4,3}$ = 9.4; 4-H); * assignments interchangeable. – ^{13}C NMR: δ = 25.42, 26.25 [2′-$(CH_3)_2$], 28.08 [C$(CH_3)_3$], 51.13 (C-3), 67.33 (C-5′), 72.46, 74.87 (C-2, C-4′), 82.80 [*C*$(CH_3)_3$], 109.13 (C-2′), 119.55 (C-5), 133.37 (C-4), 172.76 (C-1).

$C_{14}H_{24}O_5$ (272.3) Cacld. C 61.74 H 8.88
Found C 61.91 H 8.83

(2R,3S,4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-hydroxy-4-pentenoates **A**, **C**, **E**, *and* **G** *and (2S,3S,4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-hydroxy-4-pentenoates* **B**, **D**, **E**, *and* **H**: Spectral data of the minor isomers [methyl (**A**, **B**), ethyl (**C**, **D**), isopropyl (**E**, **F**), and *tert*-butyl (**G**, **H**) esters] are not included for the sake of brevity; their configurations at C-2 are interchangeable.

Stereochemical Assignments

(2R,3R,4′S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-penten-1,2-diol (**9**) *from* **6a**, **6c**, *or* **6d**: At room temp., **6a** (0.436 g, 1.89 mmol) in THF (12 ml) was added to a stirred suspension of $LiAlH_4$ (0.211 g, 5.56 mmol) in THF (30 ml) and refluxed (65 min). The mixture was hydrolyzed at 0°C by slow addition of aqueous K,Na tartrate (1 mol/l, 22 ml) and extracted with ether (8 × 50 ml). Flash chromatography [ether, ether/methanol (20:1)] gave **9** (0.351 g, 92%). – Similarly, **9** was obtained from **6c** (93%) and from **6d** (90%). – $[\alpha]_D^{24}$ = +7.9 (*c* = 2.1, CH_2Cl_2). – ^{1}H NMR: δ = 1.37 and 1.42 [2 s; 2′-$(CH_3)_2$], 2.25 (very broad "t", $J \approx$ 6; 1-OH), 2.32 (ddd, $J_{3,4}$ = 9.7, $J_{3,2}$ = $J_{3,4'}$ = 3.6; 3-H), 2.85 (sharp d, *J* = 3.1; 2-OH), 3.62–3.75 (m; 5′-H^1, 1-H_2), 3.88 (m_c; 2-H), 4.01 (dd, J_{gem} = 8.2, $J_{5'\text{-}H^2,4'}$ = 6.5; 5′-H^2), 4.39 (ddd, $J_{4',5'\text{-}H^1}$ = $J_{4',5'\text{-}H^2}$ = 6.9, $J_{4',3}$ = 3.1; 4′-H), 5.17 (dd, J_{trans} = 17.3, J_{gem} = 1.7; Z-5-H), 5.33 (dd, J_{cis} = 10.3, J_{gem} = 1.9; *E*-5-H), 5.92 (ddd, J_{trans} = 17.3, J_{cis} = $J_{4,3}$ = 10.0; 4-H).

$C_{10}H_{18}O_4$ (202.3) Calcd. C 59.39 H 8.97
Found C 59.49 H 9.07

(3S,4′S,4″R)-3,3-Bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-1-propen (**10**): **9** (0.314 g, 1.55 mmol), TsOH · H_2O (0.011 g, 0.06 mmol, 0.04 equiv.), and 2,2-dimethoxypropane (0.5 ml) were stirred in dry acetone (10 ml) at room temp. (2 h). K_2CO_3 (0.501 g, 3.63 mmol, 2.3 equiv.) was added, the solution filtered, and the filtrate purified by flash chromatography [petroleum ether/ether (6:1)] giving **10** (0.370 g, 97%). – $[\alpha]_D^{20}$ = 0.0 (*c* = 5.1, CH_2Cl_2). – ^{1}H NMR: δ = 1.35 and 1.40 [2 s; 2′-$(CH_3)_2$], 2.37 (ddd, $J_{3,2}$ = 9.2, $J_{3,4'}$ = $J_{3,4''}$ = 5.2; 3-H), 3.76 (dd, J_{gem} = J_{vic} = 7.8; 5′- and 5″-H^1), 4.04 (dd, J_{gem} = 8.1, J_{vic} = 6.2; 5′- and 5″-H^2), 4.21 [ddd, *J* (with 5′-/5″-H^1) = 5.7, *J* (with 5′-/5″-H^2) = *J* (with 3-H) = 5.7; 4′- and 4″-H], 5.17 (dd, J_{trans} = 17.5, J_{gem} = 1.5; *Z*-1-H), 5.28 (dd, J_{cis} = 10.3, J_{gem} = 1.8; *E*-1-H), 5.81 (ddd, J_{trans} = 17.2, J_{cis} = 10.2, $J_{2,3}$ = 9.3; 2-H). – ^{13}C NMR: δ = 25.51 and 26.41 [2′- and 2″-$(CH_3)_2$], 49.11 (C-3), 67.34 (C-5′, C-5″), 75.49 (C-4′, C-4″), 108.94 (C-2′, C-2″), 119.56 (C-1), 133.68 (C-2).

$C_{13}H_{22}O_4$ (242.3) Calcd. C 64.44 H 9.15
Found C 64.33 H 9.25

(3S,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-(phenylthio)-1-butene (**11**): **12** (0.083 g, 0.48 mmol), diphenyldisulfide (0.209 g, 0.96 mmol, 2.0 equiv.), and tributylphosphine (0.236 ml, 0.194 g, 0.96 mmol, 2.0 equiv.) were stirred in $CH_2Cl_2/CDCl_3$ (3:1, 2.5 ml) during 4 h. Extraction from NaOH (1 mol/l, 10 ml) with ether (50 ml) and flash chromatography [petroleum ether/ether (15:1)] gave **11** (0.106 g, 84%). – $[\alpha]_D = +13$ ($c = 2.8$, CH_2Cl_2). – ^{1}H NMR: $\delta = 1.35$ and 1.42 [2 s; 2'-$(CH_3)_2$], 2.43 (m_c; 3-H), AB signal ($\delta_A = 3.01$, $\delta_B = 3.14$, $J_{A,B} = 13.0$, in addition split by $J_{A,3} = 7.8$, $J_{B,3} = 6.5$; 4-H_2), 3.67 (dd, $J_{gem} = J_{5'\text{-}H^1,4'} = 7.7$; 5'-$H^1$), 4.00 (dd, $J_{gem} = 8.1$, $J_{5'\text{-}H^2,4'} = 6.6$, 5'-$H^2$), 4.34 (ddd, $J_{4',5'\text{-}H^1} = J_{4',5'\text{-}H^2} = 6.8$, $J_{4',3} = 4.0$; 4'-H), 5.14 (dm_c, $J_{trans} = 18.0$; *Z*-1-H), 5.25 (dd, $J_{cis} = 10.3$, $J_{1,3} = 1.5$; *E*-1-H), 5.80 (ddd, $J_{trans} = 17.2$, $J_{cis} = 10.2$, $J_{2,3} = 8.5$; 2-H), 7.16–7.36 (m; C_6H_5).

$C_{15}H_{20}O_2S$ (264.4) Calcd. C 68.14 H 7.63
Found C 68.30 H 7.72

Degradations of (2R,3R,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-penten-1,2-diol (**9**) *and (2S,3R,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-penten-1,2-diol* (**26**) *to (2R,4'S)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)-3-buten-1-ol* (**12**): At 0°C, aqueous $NaIO_4$ (0.864 ml of a 0.312 mol/l solution, 0.26 mmol, 1.1 equiv.) and **9** (0.049 g, 0.24 mmol) in 1:1 MeOH/H_2O (4 ml) were stirred during 40 min. After extractive workup [H_2O (12 ml)/ether (5 × 13 ml] and removal of the solvent i.vac., the crude aldehyde was dissolved in MeOH (3 ml) and reduced with $NaBH_4$ (0.058 g, 1.53 mmol). The reaction was worked up after 1 h by the addition of KF · H_2O (0.6 g) in H_2O (5 ml). Extraction with brine (12 ml) and ether (5 × 13 ml) and flash chromatography [petroleum ether/ether (2:3)] furnished **12** (0.028, 68%). – Similarly, **26** (0.024 g, 0.12 mmol) gave **12** (0.007 g, 33%). – $[\alpha]_D^{20} = +13.9$ ($c = 1.3$, $CDCl_3$). – ^{1}H NMR: $\delta = 1.30$ and 1.36 [2 s; 2'-$(CH_3)_2$], 1.89 (dd, $J = 7.0$, $J = 5.0$; OH), 2.39 (m_c; 2-H), 3.59–3.70 (m; 1-H_2, 5'-H^1), 3.97 (dd, $J_{gem} = 8.2$, $J_{5'\text{-}H^2,4'} = 6.4$; 5'-$H^2$), 4.22 (ddd, $J_{4',5'\text{-}H^1} = J_{4',5'\text{-}H^2} = 6.9$, $J_{4',2} = 4.6$; 4'-H), 5.15 (ddd, $J_{trans} = 17.3$, $J_{gem} = 1.7$, $J_{4,2} = 0.8$; *Z*-4-H), 5.22 (dd, $J_{cis} = 10.4$, $J_{gem} = 1.7$; *E*-4-H), 5.75 (ddd, $J_{trans} = 17.3$, $J_{cis} = 10.4$, $J_{3,2} = 8.7$; 3-H).

$C_9H_{16}O_3$ (172.2) Calcd. C 62.77 H 9.36
Found C 63.05 H 9.42

Methyl (3S,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-pentenoate (**13**) *from Orthoester Claisen Rearrangement*[19] *and Methyl (3R,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-pentenoate* (**16**): *cis*-(4'*S*)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol (1.84 g, 11.6 mmol) and trimethyl orthoacetate (14.41 g, 120 mmol) were refluxed in the presence of propionic acid (0.09 g, 1 mmol) in a stream of N_2 for 5 h. Dilution with ether (40 ml), washing with satd. aqueous $NaHCO_3$ (2 × 10 ml), and flash chromatography [petroleum ether/ether (9:1)] led to **16** (0.452 g, 18%), a 2:5 mixture of **16**/**13** (0.709 g, 29%), and **13** (0.308 g, 12%) (total yields: **13**: 33%; **16**: 26%).

13: $[\alpha]_D^{21} = +21$ ($c = 1.3$, $CDCl_3$); ref.[19] $[\alpha]_D = +24$ ($c = 0.20$, $CHCl_3$). – ^{1}H NMR: $\delta = 1.32$ and 1.39 [2 q, $^4J = 0.6$ and 0.5, respectively; 2'-$(CH_3)_2$], AB signal ($\delta_A = 2.39$, $\delta_B = 2.52$, $J_{A,B} = 15.3$, in addition split by $J_{A,3} = 8.8$, $J_{B,3} = 5.7$; 2-H_2), 2.77 (m_c; 3-H), 3.64 (dd, $J_{gem} = 8.2$, $J_{5'\text{-}H^1,4'} = 7.1$; 5'-$H^1$), 3.65 (s; OCH_3), 3.96 (dd, $J_{gem} = 8.2$, $J_{5'\text{-}H^2,4'} = 6.5$; 5'-$H^2$), 4.15 (ddd, $J_{4',5'\text{-}H^1} = J_{4',5'\text{-}H^2} = 6.8$, $J_{4',3} = 4.6$; 4'-H), 5.11 (dm_c, $J_{trans} \approx 17$; *Z*-5-H), 5.14 (dm_c, $J_{cis} \approx 10$; *E*-5-H), 5.73 (ddd, $J_{trans} = 17.1$, $J_{cis} = 10.5$, $J_{4,3} = 8.4$; 4-H).

$C_{11}H_{18}O_4$ (214.3) Calcd. C 61.66 H 8.47
Found C 61.71 H 8.56

16: $[\alpha]_D^{21} = +13.3$ ($c = 1.0$, $CDCl_3$); ref.[19] $[\alpha]_D = +13.5$ ($c = 0.22$, $CHCl_3$). – ^{1}H NMR: $\delta = 1.32$ and 1.39 [2 q, $^4J = 0.6$ and 0.4, respectively; 2'-$(CH_3)_2$], 2.35 (m_c; 1 H), 2.65–2.73 (m; 2 H), 3.64 (s; OCH_3), 3.66–3.69 (m; 1 H), 3.96 (m_c; 2 H), 5.09 (dm_c, $J_{cis} \approx 10.5$; *E*-5-H), 5.13 (dm_c, $J_{trans} \approx 17.5$; *Z*-5-H), 5.62 (ddd, $J_{trans} = 17.2$, $J_{cis} = 10.3$, $J_{4,3} = 8.4$; 4-H).

$C_{11}H_{18}O_4$ (214.3) Calcd. C 61.66 H 8.47
Found C 61.73 H 8.57

Preparation of **13** *from (3S,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-(phenylthio)-1-butene* (**11**): At –78°C, **11** (0.100 g, 0.38 mmol) in THF (1.5 ml) was titrated with lithium naphthalide (1.0 mol/l in THF) until the dark green color persisted. 35 min later the solution was transferred by cannula into a solution of $ClCO_2Me$ (0.088 ml, 0.107 g, 1.14 mmol, 3.0 equiv.) in THF (1.5 ml) and maintained at the same temp. After 20 min, the reaction was quenched with satd. aqueous NH_4Cl (3 ml). Extraction with ether (3 × 30 ml) and flash chromatography [petroleum ether/ether (3:1)] yielded **13** accompanied by an unidentified impurity (0.024 g, ≤29%). The described sample, by its 400-MHz ^{1}H-NMR spectrum and capillary gas chromatography, contained not even trace amounts of the epimer **16**.

(4S,5S)-4,5-Dihydro-5-(hydroxymethyl)-4-vinyl-2(3H)furanon (**14**) was prepared from **13** according to ref.[19] in 49% yield. – $[\alpha]_D^{20} = +54$ ($c = 1.3$, $CDCl_3$); ref.[19] $[\alpha]_D = +43.5$ ($c = 0.31$, $CHCl_3$). – ^{1}H NMR: $\delta = 1.94$ (br. t, $J = 6.0$; OH), 2.62 (d, $J = 9.2$; 3-H_2), 3.32 (br. dddd, all *J* values ca. 8.6; 4-H), AB signal ($\delta_A = 3.77$, $\delta_B = 3.84$, $J_{A,B} = 12.5$, in addition split by $J_{A,5} = J_{A,OH} = 4.9$, $J_{B,OH} = 6.4$, $J_{B,5} = 3.2$; CH_2OH), 4.57 (ddd, $J_{5,4} = 7.9$, $J_{5,CH^1OH} = 4.3$, $J_{5,CH^2OH} = 3.2$; 5-H), 5.21 (dm_c, $J_{cis} \approx 10$; *E*-4-CH=C*H*H), 5.22 (dm_c, $J_{trans} \approx 18$; *Z*-4-CH=C*H*H), 5.89 (ddd, $J_{trans} = 16.9$, $J_{cis} = 10.3$, $J_{CH=,4} = 8.6$, C*H*=CH_2). – Stereochemically relevant NOE's were observed when $\delta = 5.89$ was observed during irradition of $\delta = 2.62$, and vice versa; in the former case, the absorption at $\delta = 5.89$ was increased by 6.4%.

$C_7H_{10}O_3$ (142.2) Calcd. C 59.14 H 7.09
Found C 59.22 H 7.23

(4R,5S)-4,5-Dihydro-5-(hydroxymethyl)-4-vinyl-2(3H)furanon (**15**) was prepared according to ref.[19] from **16** in 52% yield. – $[\alpha]_D^{21} = +86$ ($c = 1.3$, $CDCl_3$); ref.[19] $[\alpha]_D = +83.1$ ($c = 2.19$, $CHCl_3$). – ^{1}H NMR: $\delta = 1.95$ (dd, $J = 7.1$, $J = 6.2$; OH), AB signal ($\delta_A = 2.47$, $\delta_B = 2.75$, $J_{A,B} = 17.6$, in addition split by $J_{A,4} = 10.2$, $J_{B,4} = 8.8$; 3-H_2), 3.13 (br. dddd, all *J* values ca. 8.3; 4-H), 3.67 (ddd, $J_{gem} = 12.5$, $J_{CH,OH} = 7.2$, $J_{CH,5} = 4.3$; HOCH^1), 3.94 (ddd, $J_{gem} = 12.7$, $J_{CH,OH} = 6.0$, $J_{CH,5} = 2.6$; HOCH^2), 4.25 (ddd, $J_{5,4} = 8.3$, $J_{5,CH^1OH} = 4.2$, $J_{5,CH^2OH} = 2.7$; 5-H), 5.18 (dm_c, $J_{cis} = 10.4$; *E*-4-HC=C*H*H), 5.21 (dm_c, $J_{trans} = 17.1$; *Z*-4-HC=C*H*H), 5.75 (ddd, $J_{trans} = 17.1$, $J_{cis} = 10.2$, $J_{CH=,4} = 8.0$; C*H*=CH_2).

$C_7H_{10}O_3$ (142.2) Calcd. C 59.14 H 7.09
Found C 59.11 H 7.12

(2S,3R,4'S)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-penten-1,2-diol (**26**) was obtained from **21d** (0.168 g, 0.62 mmol) as described for the preparation of **9** from **6d** in 94% yield (0.117 g). – $[\alpha]_D^{20} = +37$ ($c = 1.7$, CH_2Cl_2). – ^{1}H NMR: $\delta = 1.36$ and 1.42 [2 s; 2'-$(CH_3)_2$], 2.03 (br. s; 1-OH), 2.38 (ddd, $J_{3,4} = J = 9.1$, $J = 3.5$; 3-H), 2.87 (d, $J = 4.7$; 2-OH), 3.52, 3.72, and 3.84 (3 m_c; 1-H_2, 2-H), in part superimposing 3.74 (dd, $J_{gem} = J_{5'\text{-}H^1,4'} = 7.9$; 5'-$H^1$), 4.03 (dd, $J_{gem} = 8.2$, $J_{5'\text{-}H^2,4'} = 6.5$; 5'-$H^2$), 4.47 (ddd, $J_{4',5'\text{-}H^1} = 7.4$, $J_{4',5'\text{-}H^2} = 6.7$, $J_{4',3} = 3.6$; 4'-H), 5.17 (dd, $J_{trans} = 16.9$, $J_{gem} = 1.7$; *Z*-5-H), 5.25 (dd, $J_{cis} = 10.3$, $J_{gem} = 1.8$; *E*-5-H), 5.70 (ddd, $J_{trans} = 17.2$, $J_{cis} = J_{4,3} = 10.0$; 4-H).

$C_{10}H_{18}O_4$ (202.3) Calcd. C 59.39 H 8.97
Found C 59.40 H 8.86

(4'S,4"S)-3,3-Bis(2,2-dimethyl-1,3-dioxolan-4-yl)-1-propen (**27**) was obtained from **26** (0.014 g, 0.068 mmol) as described for the preparation of **10** from **9** in 61% yield. – $[\alpha]_D^{20} = +9.0$ ($c = 0.8$,

$CHCl_3$). – ^1H NMR: δ = 1.36 (s; 2 CH_3), 1.39 and 1.40 (2 s; 2 CH_3), 2.19 (ddd, $J = J = 9.4$, $J = 4.4$; 3-H), 3.64–3.73 (m; 5′-H^1, 5″-H^1), 3.96 (dd, $J_{gem} = 8.5$, $J_{vic} = 6.1$; 5′-H^{2*}), 4.06 (dd, $J_{gem} = 8.2$, $J_{vic} = 6.4$; 5″-H^{2*}), 4.12 (ddd, $J = 9.3$, $J = J = 6.4$; 4′-H**), 4.37 (ddd, $J = J = 6.8$, $J = 4.4$; 4″-H**), 5.16 (dd, $J_{trans} = 17.1$, $J_{gem} = 1.8$; *Z*-1-H), 5.22 (dd, $J_{cis} = 10.4$, $J_{gem} = 1.8$; *E*-1-H), 5.69 (ddd, $J_{trans} = 17.2$, $J_{cis} = J_{2,3} = 10.0$; 2-H); *,** assignments interchangeable. – ^{13}C NMR: δ = 25.34, 25.68, 26.23 and 26.87 (4 CH_3), 51.81 (C-3), 67.69 and 68.30 (C-5′, C-5″), 75.40 and 75.50 (C-4′, C-4″), 108.68 and 109.38 (C-2′, C-2″), 119.66 (C-1), 133.31 (C-2).

trans-(4′S)-1-(2,2-Dimethyl-1,3-dioxolan-4-yl)-3-[(tributylstannyl)methoxy]-1-propene (**28**): At room temp., iodo(tributylstannyl)-methane (0.640 g, 1.50 mmol, 7.5 equiv.) in THF (1.0 ml) was added to a stirred suspension of KH (0.265 g, 6.60 mmol, 33 equiv.) and *trans*-(4′*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol (0.031 g, 0.20 mmol) in THF (2.0 ml)[25]. After 15 min, the reaction was quenched with satd. aqueous NH_4Cl (1 ml) at –78°C, extracted with H_2O (10 ml) and ether (4 × 10 ml), and flash-chromatographed [petroleum ether/ether (10:1)] to yield **26** (0.055 g, 60%). – $[\alpha]_D^{20} = +11.2$ (*c* = 1.6, CH_2Cl_2). – ^1H NMR: δ = 0.88 (t, J = 7.3; 3 CH_2CH_3), superimposes 0.89 [m_c; 3 $CH_2(CH_2)_2CH_3$], 1.29 (qt, both J values 7.2; 3 CH_2CH_3), 1.38 and 1.42 [2 s; 2′-$(CH_3)_2$], 1.47 (m_c; 3 $CH_2CH_2CH_2$), 3.58 (dd, $J_{gem} = J_{5'-H^1,4'} = 8.0$; 5′-$H^1$), 3.70 (s with superimposing satellite caused by ^{117}Sn and ^{119}Sn couplings $J_{Sn,H} = 14.8$; OCH_2Sn), 3.87 (m_c; 3-H_2), 4.08 (dd, $J_{gem} = 8.1$, $J_{5'-H^2,4'} = 6.1$; 5′-H^2), 4.51 (br. q, $J_{4',5'-H^1} = J_{4',5'-H^2} = J_{4',1} \approx 7$; 4′-H), AB signal ($\delta_A = 5.66$, $\delta_B = 5.83$, $J_{A,B} = 15.6$, in addition split by $J_{A,4'} = 7.4$, $J_{A,3} = 1.4$, $J_{B,3} = 5.2$; A = 1-H, B = 2-H).

$C_{21}H_{42}O_3Sn$ (461.3) Calcd. C 54.68 H 9.18
Found C 54.72 H 9.17

Wittig Rearrangement of **28**: At –78°C, *n*BuLi (1.47 mol/l in hexane, 1.10 ml, 1.62 mmol, 2.0 equiv.) was added dropwise to **26** (0.374 g, 0.81 mmol) in THF (4.0 ml). The reaction was quenched with satd. aqueous NH_4Cl (18 ml) after 1 h. Extraction with ether (4 × 25 ml) and flash chromatography [petroleum ether/ether (3:2)] gave **12** (0.110 g, 79%) along with a 3:2 mixture (0.012 g) of **29** (6%) and (2*E*,4*Z*)-5-methoxy-2,4-pentadien-1-ol (4%) which were not separated.

29: ^1H NMR: δ = 1.37 and 1.43 [2s; 2′-$(CH_3)_2$], 2.42 (m_c; 2-H), 3.66 (d, $J_{gem} = 11.1$; 1-H^1), 3.69 (dd, $J_{gem} = 8.3$, $J_{5'-H^1,4'} = 6.8$; 5′-H^1), 3.82 (dd, $J_{gem} = 11.0$, $J_{1-H^2,2} = 6.8$; 1-H^2), 4.03 (dd, $J_{gem} = 8.3$, $J_{5'-H^2,4'} = 6.2$; 5′-H^2), 4.11 (ddd, $J_{4',2} = 9.0$, $J_{4',5'-H^1} = J_{4',5'-H^2} = 6.4$; 4′-H), 5.18 ($dm_c$, $J_{cis} = 10.3$; *E*-4-H), 5.19 (dm_c, $J_{trans} = 17.4$; *Z*-4-H), 5.59 (ddd, $J_{trans} = 17.3$, $J_{cis} = 10.4$, $J_{3,2} = 8.7$; 3-H); OH signal not visible.

(2E,4Z)-5-Methoxy-2,4-pentadien-1-ol: ^1H NMR: δ = 3.66 (s; OCH_3), 4.16 (dd, $J_{1,2} = 6.2$, $J_{1,3} = 1.0$; 1-H_2), 5.07 (dd, $J_{4,3} = 10.9$, $J_{4,5} = 6.2$; 4-H), 5.72 (dt, $J_{2,3} = 15.5$, $J_{2,1} = 6.2$; 2-H), 5.92 (d, $J_{5,4} = 6.2$; 5-H), 6.56 (dddt, $J_{3,2} = 15.5$, $J_{3,4} = 10.9$, $J_{3,5} = J_{3,1} = 1.0$; 3-H); OH not observed.

CAS Registry Numbers

5a: 112422-97-6 / **5a** (free acid): 118276-29-2 / **5b**: 118276-22-5 / **5c**: 118276-23-6 / **5d**: 118276-24-7 / **6a**: 112422-98-7 / **6b**: 118276-31-6 / **6c**: 118276-32-7 / **6d**: 118276-33-8 / **9**: 118374-64-4 / **10**: 112423-00-4 / **11**: 118276-34-9 / **12**: 112422-95-4 / **13**: 118417-67-7 / **14**: 118374-66-6 / **15**: 118374-67-7 / **16**: 118417-68-8 / **20a**: 118276-25-8 / **20a** (free acid): 118276-30-5 / **20b**: 118276-26-9 / **20c**: 118276-27-0 / **20d**: 118276-28-1 / **21a**: 118374-60-0 / **21b**: 118374-61-1 / **21c**: 118374-62-2 / **21d**: 118374-63-3 / **26**: 118374-68-8 / **27**: 118374-69-9 / **28**: 112422-94-3 / **29**: 112422-96-5 / Bu_4SnCH_2I: 66222-29-5 / (2*E*,4*Z*)-$HOCH_2CH=CHCH=C(Me)OMe$: 118276-35-0 / $ClCH_2CO_2H$ · Na: 3926-62-3 / *cis*-(4′*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol: 80532-35-0 / *trans*-(4′*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-propen-1-ol: 79060-23-4

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