A New Route to Vitamin E Key-Intermediates by Olefin Cross-Metathesis

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Dedicated to Professor *Günther Wilke* on the occasion of his 80th birthday

Ru-Catalyzed olefin cross-metathesis (CM) has been successfully applied to the synthesis of several phytyl derivatives (**2b**, **2d**–**f**, **3b**) with a trisubstituted C=C bond, as useful intermediates for an alternative route to α-tocopheryl acetate (vitamin E acetate; **1b**) (*Scheme 1*). Using the second-generation *Grubbs* catalyst $RuCl_2(C_{21}H_{26}N_2)(CHPh)PCy_3$ (Cy = cyclohexyl; **4a**) and *Hoveyda–Grubbs* catalyst $RuCl_2(C_{21}H_{26}N_2)\{CH\text{-}C_6H_4(O\text{-}^iPr)\text{-}2\}$ (**4b**), the reactions were performed with various *C*-allyl (**5a**–**f**, **7a,b**) and *O*-allyl (**8a**–**d**) derivatives of trimethylhydroquinone-1-acetate as substrates. 2,6,10,14-Tetramethylpentadec-1-ene (**6a**) and derivatives **6c**–**e** of phytol (**6b**) as well as phytal (**6f**) were employed as olefin partners for the CM reactions (*Schemes 2* and *5*). The vitamin E precursors could be prepared in up to 83% isolated yield as (*E*/*Z*)-mixtures.

Introduction. – Vitamin E, an essential food ingredient, is of high economic interest because of its biological activity and antioxidant properties [1]. From the family of vitamin E compounds, the naturally occuring α-tocopherol (**1a**) with (2*R*,4′*R*,8′*R*)-configuration is the biologically most-valuable representative [1a][1b][2]. Synthetic, fully racemic α-tocopherol ((all-*rac*)-**1a**) has achieved the greatest commercial importance (*Scheme 1*) [3]. It is produced on a scale of over 25000 tons per year worldwide, mainly for application in feed industry, followed by the pharmaceutical, food, and cosmetic markets. The acetate derivative (all-*rac*)-**1b** is the major sales form, since it is more stable towards oxidation and, therefore, more convenient to handle compared to α-tocopherol. It is usually produced by the reaction of trimethylhydroquinone with isophytol, phytol, or a derivative thereof in the presence of a *Lewis* or *Brønsted* acid catalyst, followed by acetylation [4].

A disadvantage of such procedures is often the formation of salts (waste material) and by-products such as benzofurans or other impurities, which are rather difficult to separate from **1a** or **1b**. Regarding construction of the tocopherol skeleton, it has been reported that the phytylhydroquinones (2′*E*,7′*R*,11′*R*)-**2a** and (all-*rac*, *E*/*Z*)-**2a** are open-chain precursors in biosynthetic [5] as well as chemical [6] routes to tocopherols, respectively (*Scheme 1*). Furthermore, it has been shown that the phytyl ether **3c** can be transformed into the vitamin E precursor **2c** by a [1,3] rearrangement, and sub-

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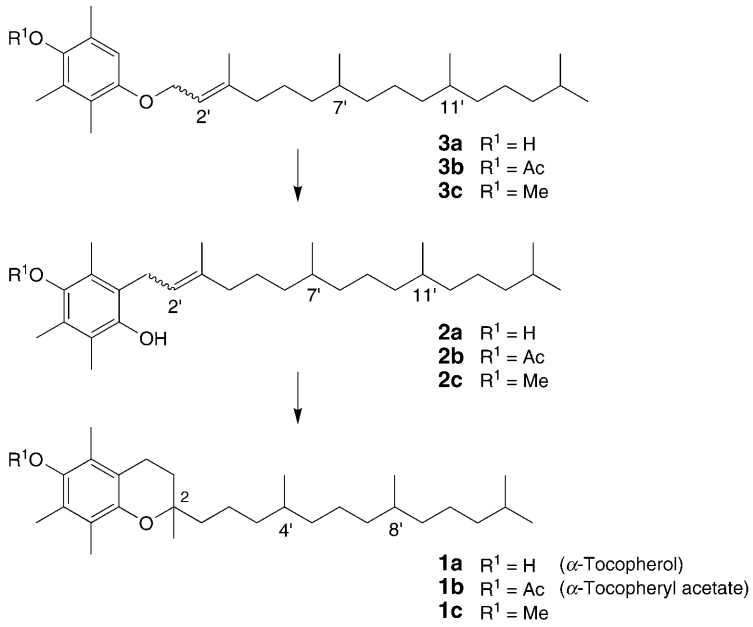
Scheme 1



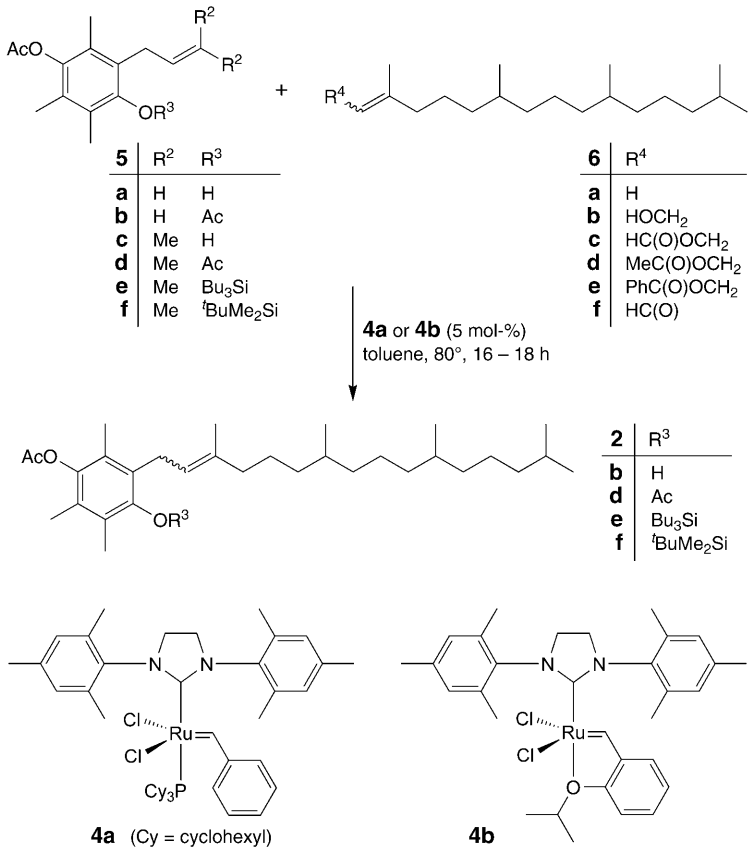
sequently cyclized to **1c** [7]. Thus, compounds **2** and **3** (particularly **2a**,**b** and **3a**,**b**) are considered as key intermediates for an alternative route to vitamin E (**1a**,**b**) preventing the formation of by-products usually obtained by classical syntheses.

Among the many types of transition-metal-catalyzed carbon–carbon bond-forming reactions, olefin metathesis has attracted widespread attention from the synthetic community in recent years, and has become a powerful tool for organic chemists [8]. As a consequence, and in our continual effort to develop alternative methods in the field of tocopherol chemistry, we wish to describe hereafter the successful application of the ruthenium (Ru)-catalyzed olefin cross-metathesis (CM) reaction for the synthesis of the vitamin E intermediates **2b**, **3b**, and the related compounds **2d**–**f** [9].

Results and Discussion. – The Ru alkylidenes **4a** (second-generation *Grubbs* catalyst) and **4b** (*Hoveyda–Grubbs* catalyst), which are commercially available, have proved to be very efficient for the preparation of alkenes. Many applications have been reported, mainly dealing with ring-closing metathesis (RCM) and the construction of more or less unhindered C=C bonds [10]. The synthesis of sterically congested olefins, however, is a more-demanding task. Not many examples for the efficient preparation of tri- or even tetrasubstituted alkenes with Ru catalysts had been described at the beginning of our project, most of them aiming at cyclic products, *i.e.*, again using RCM [11]. We decided to investigate catalysts **4a**,**b** in the synthesis of compounds **2b**, **2d**–**f**, and **3b**, which contain a trisubstituted C=C bond.

Our studies were first based on the six *C*-allyl derivatives **5a**–**f** of 2,3,6-trimethylhydroquinone-1-acetate as substrates for the synthesis of compounds **2b** and **2d**–**f**

Scheme 2



(*Scheme 2*). We also chose to employ the terminal disubstituted olefin 2,6,10,14-tetramethylpentadec-1-ene (**6a**) and compounds **6c**–**f**, easily derived from 3,7,11,15-tetramethylhexadec-2-en-1-ol (phytol; **6b**), as CM partners[3]). Preferred conditions were the following: reactions were carried out under an inert atmosphere in toluene[4]) at 80° using the Ru catalyst **4a** (5 mol-% based on substrates **5**). The ratio **5**/**6** was 1:2. Tridecane (same amount as **5**) was used as internal GLC standard to have an estimation (no calibration was done) of the amount of the compounds present in the reaction mixture. The results obtained for the synthesis of compounds **2b** and **2d**–**f** are summarized in *Table 1*.

Our initial work began with the CM reaction of the terminal olefins **5a** or **5b** with **6a**. Unfortunately, with **5a**, the expected product **2b** was not formed (*Entry 1* in *Table 1*), and **2d** was formed in low yield (12%) from **5b** (*Entry 3*). Interestingly, in both cases,

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[3]) In preliminary experiments, CM reactions between **5d** and phytyl methyl ether or phytyl *tert*-butyl(dimethyl)silyl ether gave very low yields (<5%).

[4]) In preliminary experiments, poor yields (0–20%) were obtained with CH_2Cl_2 or THF as solvent.

Table 1. *Experimental Results of Cross-Methathesis with* C*-Allyl Substrates* **5** *or* **7**. Conditions: substrate (0.2 mmol), metathesis partner (0.4 mmol), catalyst **4a** (10 μmol), toluene (5 ml), 80° for 16–18 h (unless noted otherwise); tridecane was used as internal GLC standard. The abbreviations n.m. and n.d. refer to 'not measured' and 'not detected', resp.

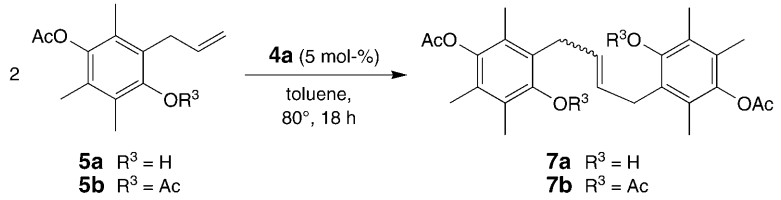
Entry	Substrate	Metathesis partner	Product	Isolated yield [%]	(*E*/*Z*)-Ratio[a])	Remaining substrate [%][b])	Dimer (yield [%])[b])
1	**5a**	**6a**	**2b**	n.d.	–	n.d.	**7a**[c])
2	**7a**	**6a**	**2b**	n.d.	–	–	**7a**[c])
3	**5b**	**6a**	**2d**	12	n.m.	5	**7b** (11)
4	**7b**	**6a**	**2d**	26	72:28	–	**7b** (38)
5	**5c**	**6a**	**2b**	34	67:33	64	**7a** (n.m.)
6	**5d**	**6a**	**2d**	69	72:28	15	**7b** (3)
7[d])	**5d**	**6a**	**2d**	60	70:30	27	n.d.
8	**5d**	(all-*rac*, *E*/*Z*)-**6b**	**2d**	n.d.	–	n.m.	n.d.
9	**5d**	(all-*rac*, *E*/*Z*)-**6c**	**2d**	31	69:31	85	n.d.
10	**5d**	(all-*rac*, *E*/*Z*)-**6d**	**2d**	46	68:32	48	**7b** (4)
11	**5d**	(all-*rac*, *E*/*Z*)-**6e**	**2d**	50	67:33	34	**7b** (2)
12	**5e**	**6a**	**2e**	60	74:26	82	n.m.
13	**5e**	(all-*rac*, *E*/*Z*)-**6d**	**2e**	49[e])	70:30	n.d.	n.m.
14	**5f**	**6a**	**2f**	70	73:27	50	n.m.
15[d])	**5f**	**6a**	**2f**	5	72:28	39	n.m.
16	**5f**	(all-*rac*, *E*/*Z*)-**6c**	**2f**	42	68:32	82	n.m.
17	**5f**	(all-*rac*, *E*/*Z*)-**6d**	**2f**	52[e])	68:32	42	n.m.
18	**5f**	(*R*,*R*,*E*)-**6d**	**2f**	54[e])	66:34	45	n.m.
19	**5d**	**6f**	**2d**	0	–	97	n.d.
20[f])	**5d**	**6a**	**2d**	35	68:32	51	n.d.

[a]) Determined by GLC (**2b**, **2e**, **2f**) or ^{1}H-NMR (**2d**). [b]) Determined by GLC rel. to tridecane. [c]) Presence shown by TLC. [d]) At 33 mbar without solvent, 3 h. [e]) Yield determined by GLC due to separation problems. [f]) With catalyst **4b** in toluene (3 ml) at 120° for 46 h.

we observed by TLC or GLC the homodimerization (self-metathesis) of the substrates **5a** and **5b** to the disubstituted products **7a** and **7b**, respectively (*Scheme 3*), due to the high reactivity of these terminal olefins towards CM. The formation of the dimers **7a** and **7b** is a possible explanation for the low yields obtained when the monosubstituted terminal olefins **5a** or **5b** were used as substrates. Compounds **7a** and **7b** were synthesized from **5a** and **5b**, respectively, in toluene at room temperature in good yields (81 and 77%). Compound **7b** was readily isolated from the reaction mixture by precipitation with Et_2O. Both dimers were fully characterized, but, their configurations could not be determined since the analyses (NMR, GLC, HPLC) did not afford any indication of a separation of the signals or peaks of the (*E*)- and (*Z*)-isomers.

Grubbs and co-workers reported an innovative strategy for avoiding undesired self-metathesis products [12]. In a two-step procedure, a terminal olefin was first homodimerized in a CM reaction, and the internal olefinic product was then treated with a second terminal olefin in the presence of a Ru catalyst to give cross-coupled products in good yields. According to this method, dimers **7a** and **7b** were also used as starting materials (*Entries 2* and *4* in *Table 1*). Compound **7a** did not lead to the formation of

Scheme 3



5a R^3 = H
5b R^3 = Ac

7a R^3 = H
7b R^3 = Ac

the wanted product **2b**, but dimer **7b** gave **2d** with a better yield than in the case where the monomer **5b** had been used as substrate (26 *vs.* 12%). In both cases, the major part of the starting dimer remained in solution, as shown by TLC and GLC analyses.

The homodimerization of **5a** and **5b** prompted us to investigate the use of trisubstituted olefins as more-convenient substrates, since they should not undergo self-metathesis, the formation of the tetrasubstituted 2,3-dimethylbut-2-ene as by-product being disfavored. However, in all the cases, the starting substrate remained unaffected, as indicated by GLC analyses, and no or only traces of dimer were detected. As expected, compounds **5c**–**f** proved to be better substrates for the studied CM reactions. Indeed, when **6a** was chosen as the metathesis partner, the isolated yields (34–70%) with the above four substrates were always higher compared to the results with **5a** and **5b**, (*Entries 5*, *6*, *12*, and *14* in *Table 1*). In the particular case of **5c** (*Entry 5*), the low yield of 34% could be due to chelation of the OH moiety of **5c** to Ru during the catalytic cycle under subsequent deactivation of the catalyst [13]. Although recent reports have described efficient metathesis reactions in the presence of an allylic OH group [14], we observed a negative effect with the allylic alcohol **6b**. Indeed, reaction between **5d** and **6b** failed, and **5d** remained in solution (*Entry 8*). In reference experiments, addition of phytol ((all-*rac*, *E*/*Z*)-**5b**) to solutions of complex **4a** in (D_8)toluene did not result in a shift of the ^{31}P-NMR signal of the phosphane ligand (δ(P) 29.44 ppm)[5]. In addition to a possible nonproductive coordination of the OH group, which would deactivate the catalyst, and according to the literature [15], a second reason could be isomerization of the allylic alcohol **6b** to the corresponding saturated aldehyde. Careful GLC analysis of the crude mixture obtained after 18 h showed only traces of phytanaldehyde, and phytol (**6b**) remained the major compound.

The phenoxy-protected compounds **5d**–**f** bearing a trisubstituted C=C bond were the best substrates, especially when the terminal olefin **6a** was the partner, (60–70% yield; *Entries 6*, *12*, and *14*). Furthermore, since the allylic alcohol **6b** gave no conversion (*Entry 8*), we employed allylic esters, which proved to be better. For example, reaction of **5d** with **6c**, **6d** or **6e** afforded **2d** in respective yields of 31, 46, and 50% (*Entries 9*, *10*, and *11*), and **2f** was prepared in 52% yield starting from **5f** and (*E*,*Z*)-(all-*rac*)-**6d** (*Entry 17*). The corresponding α,β-unsaturated aldehyde, phytal (**6f**), gave also no conversion (*Entry 19*). Finally, application of the *Hoveyda–Grubbs* catalyst **4b** instead of **4a** did not result in a better yield (35%; *Entry 20*).

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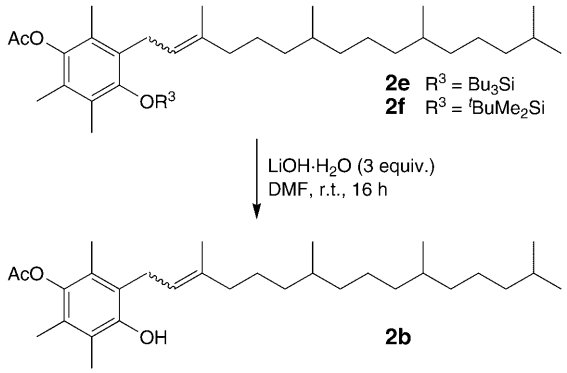
[5]) Reported value in CD_2Cl_2: δ(P) 31.41 [11b].

With all the substrates tested, the moderate (*E*/*Z*)-selectivity was always in favor of the (*E*)-isomer and comprised ratios between 66 : 34 and 74 : 26, as expected for a thermodynamic equilibrium. This selectivity is similar to that obtained from the reaction of geminal disubstituted olefins with terminal olefins [11a]. Higher selectivities in CM ((*E*/*Z*) > 20 : 1) could be achieved with terminal olefins and α,β-unsaturated compounds (esters, aldehydes, ketones), as shown by *Grubbs* and co-workers [11c]. In fact, the (*E*/*Z*)-selectivity in CM depends on different factors such as solvent, temperature, catalyst, or substituents on the substrates [16]. The use of the nearly isomerically pure metathesis partner (*R*,*R*,*E*)-**6d** ((*E*/*Z*) 99.7 : 0.3) instead of an (*E*/*Z*)-mixture [(all-*rac*, *E*/*Z*)-**6d**; (*E*/*Z*) 72 : 28] did not change considerably the (*E*/*Z*)-ratio of the product **2f** (68 : 32 and 66 : 34; *Entries 17* and *18*, resp.), and **6d**, remaining in solution after 18 h of exposure showed an (*E*/*Z*)-ratio of 67 : 33. Furthermore, we found no indication that one of the isomers ((*E*) or (*Z*)) reacted faster than the other.

Test reactions were also carried out under both solvent-free and *in vacuo* conditions, as already employed with success by *Grubbs* and co-workers for the synthesis of symmetrical disubstituted olefins [17]. The CM reaction performed between **6a** and **5d** afforded **2d** in a yield of 60% (*Entry 7*), without detection of dimer, and reaction of **5f** with **6a** gave **2f** in a similar yield of 56% (*Entry 15*). Compared to the reactions achieved under standard conditions (toluene at ambient pressure), the yields obtained under these particular conditions were somewhat lower. Performing the experiment under vacuum should have the benefit of removing isobutene, the gaseous by-product of the reaction, therefore driving the reaction toward completion.

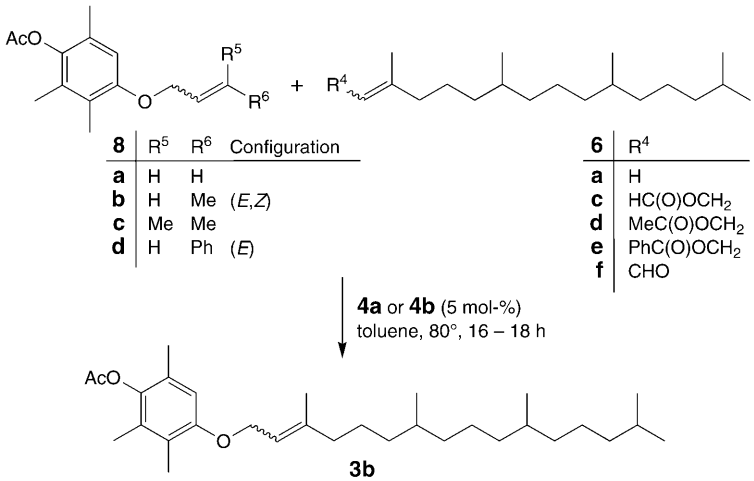
Finally, the silyl-protected CM products **2e** and **2f** were easily transformed into the vitamin E intermediate **2b** using 3.0 equiv. of LiOH in DMF at room temperature overnight (according to *Ankala* and *Fenteany* [18]), with yields of 74 and 69%, respectively (*Scheme 4*).

Scheme 4



On the basis of the above results, we next applied the Ru-catalyzed CM reaction to the synthesis of the vitamin E intermediate **3b**. The reaction conditions were the same as those described above, with toluene as solvent, tridecane as internal GLC standard, and **4a** (5 mol-%) as catalyst. We employed three different *O*-allyl substrates possessing a mono- (**8a**), a di- (**8b**), or a trisubstituted (**8c**) olefin moiety (*Scheme 5*). The same CM

Scheme 5



8	R^5	R^6	Configuration
a	H	H	
b	H	Me	(*E*,*Z*)
c	Me	Me	
d	H	Ph	(*E*)

6	R^4
a	H
c	$HC(O)OCH_2$
d	$MeC(O)OCH_2$
e	$PhC(O)OCH_2$
f	CHO

partners as before were used, except the allylic alcohol **6b** which proved to be inefficient. The ratio **8**/**6** was 1:2.

The results for the synthesis of **3b** are presented in *Table 2*. Reaction between the allyl ether **8a** and the olefin **6a** led to the phytyl ether **3b** in only 29% yield (*Entry 1* in *Table 2*), probably due to the concomitant formation of dimer **9** (*ca.* 33% by GLC), as it has already been the case with substrates **5a** and **5b**. The dimer **9** was also prepared for reference from **8a** in the presence of 5 mol-% of **4a** in toluene at room temperature (*Scheme 6*) which gave rise to a yield of 30%. Product **9** was fully characterized as a mixture of two isomers. The observed ratio of 63:37 (by GLC) was assumed to be in favor of the (*E*)-isomer, but has not been confirmed yet.

When the disubstituted olefin **8b** was employed (*Entry 2*), the yield increased to 51%, and the formation of **9** was low (*ca.* 6%), with a large amount of unreacted starting material (*ca.* 50%) remaining in the reaction mixture. As expected, the allyl ether **8c** (*Entry 3*) proved to be the most-convenient substrate since it did not dimerize (**9** < 1%), affording the desired product in 73% yield, when **6a** was used as metathesis partner. Increasing the amount of catalyst to 10 mol-%, or increasing the overall concentration by a factor of four, did not afford better yields (68% in both cases; *Entries 4* and *5*). We also tested **8c** with the other olefin partners derived from phytol[6]). When starting from **6c**–**e**, yields ranged from 57 to 67% (*Entries 8–11*), the best results being obtained with the phytyl formiate **6c** (*Entry 8*). Here again, the formation of dimer **9** was not observed, which probably explains why the formation of **3b** was favored.

Interestingly, a yield of 67% (*Entry 6*) was reached by performing the reaction between **8c** and **6a** without solvent, and the isolated yield could be improved up to 83% by applying vacuum (33 mbar) during the reaction (*Entry 7*), with no dimerization

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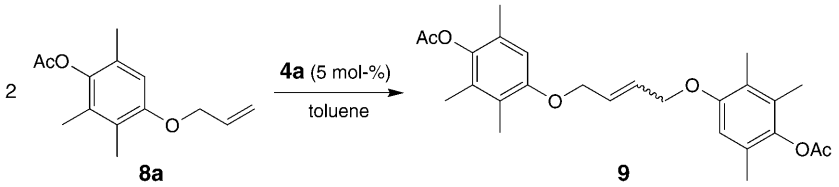
[6]) In preliminary tests, CM reactions between **8c** and phytyl methyl ether or phytyl *tert*-butyl(dimethyl)silyl ether gave yields below 40%.

Table 2. *Experimental Results of Cross-Methathesis with* O-*Allyl Substrates* **8**. For reaction conditions, see *Table 1*. The abbreviations n.m. and n.d. refer to 'not measured' and 'not detected', resp.

Entry	Substrate	Metathesis partner	**3b** [%]	(*E*/*Z*)-Ratio[a])	Remaining substrate [%][b])	**9** [%][b])
1	**8a**	**6a**	29	72:28	8	33
2	(*E*,*Z*)-**8b**	**6a**	51	66:34	50	6
3	**8c**	**6a**	73	67:33	27	<1
4[c])	**8c**	**6a**	68	67:33	26	n.d.
5[d])	**8c**	**6a**	68	68:32	32	2
6[e])	**8c**	**6a**	67	64:36	35	n.d.
7[f])	**8c**	**6a**	83	67:33	n.d.[g])	n.d.
8	**8c**	(all-*rac*,*E*/*Z*)-**6c**	67	70:30	n.m.[g])	n.d.
9	**8c**	(all-*rac*,*E*/*Z*)-**6d**	59	69:31	37	n.d.
10	**8c**	(*R*,*R*,*E*)-**6d**	57	70:30	40[h])	n.d.
11	**8c**	(all-*rac*,*E*/*Z*)-**6e**	58	66:34	34	n.d.
12	**8d**	**6a**	0	–	n.m.[i])	1.4
13[j])	**8c**	**6a**	0	–	45	n.d.

[a]) Determined by GLC or ^{1}H-NMR. [b]) Determined by GLC rel. to tridecane. [c]) With 20 μmol catalyst. [d]) At fourfold concentration of all reactants. [e]) Without solvent (neat). [f]) At 33 mbar without solvent, 2 h. [g]) Absence/presence shown by TLC. [h]) After 16 h, the (*E*/*Z*)-ratio was 67:33 for unreacted **6d**. [i]) Decomposing under GLC conditions. [j]) With 10 μmol **4b**, 115 h)

Scheme 6



occurring. This result is of particular interest for conducting larger-scale experiments, and also in terms of solvent handling and recycling.

The use of the cinnamyl ether **8d** [19] (prepared from trimethylhydroquinone-1-acetate and cinnamyl bromide) did not afford **3b** (*Entry 12*). Also, the application of the *Hoveyda–Grubbs* catalyst **4b** was unsuccessful in this case (*Entry 13*).

Concerning stereoselectivity, the (*E*/*Z*)-ratio of the phytyl ether **3b** was always moderate (*ca.* 67:33). As already observed when **5f** was employed (*Entries 17* and *18* in *Table 1*), using the isomerically nearly pure metathesis partner (*R*,*R*,*E*)-**6d** ((*E*/*Z*) 99.7:0.3) instead of an (*E*/*Z*)-mixture [(all-*rac*, *E*/*Z*-**6d**; (*E*/*Z*) 72:28] did not change the selectivity ((*E*/*Z*) 70:30 instead of 69:31; *Entries 9 vs. 10*), and the olefin **6d**, remaining in solution for 16 h, gave rise to (*E*/*Z*) 67:33. This suggests that (*E*/*Z*)-isomerisation (*via* metathesis equilibrium) was faster than CM.

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Experimental Part

General. All reactions were carried out under Ar atmosphere in dried glassware. Reactions at room temperature (r.t.) refer to 21–23°. Toluene, DMF, CH_2Cl_2, and THF (over molecular sieves), solvents for extraction and chromatography, (all-*rac*, *E*/*Z*)-phytol (all-*rac*, *E*/*Z*)-**6b**) with (*E*/*Z*) 72:28), $BF_3 \cdot Et_2O$, NaH (55–65%, in mineral oil), *tert*-butyl(dimethyl)chlorosilane, tributylchlorosilane, tridecane, Et_3N, diethylazodicarboxylate (DEAD), K_2CO_3, $LiOH \cdot H_2O$, Ph_3P, pyridine, Ac_2O, benzoic anhydride, HCO_2H, 4-(dimethylamino)pyridine (DMAP), 3-methyl-but-2-en-1-ol, and cinnamyl bromide were all purchased from *Fluka*, and used as received. The Ru catalysts **4a** and **4b** were purchased from *Strem* and *Aldrich*, resp., and stored under Ar. (*E*,*Z*)-4-Bromobut-2-ene, 4-bromo-2-methylbut-2-ene, and imidazole were purchased from *Aldrich*, and used without further purification. 2,3,6-Trimethylhydroquinone-1-acetate (TMHQA; >99%) was synthesized at *F. Hoffmann-La Roche* (Kilolab). Compounds **5a** [20], **6a** [21], and **8a** [22] were synthesized according to literature procedures. 3-(Prop-2-enyl)-2,5,6-trimethylhydroquinone-1,4-diacetate (**5b**) was prepared in 97% yield by acetylation of **5a** with Ac_2O in CH_2Cl_2 in the presence of DMAP (10 mol-%) (m.p. 92–94°, 98.5% pure by GLC). This compound can also be obtained according to [20]. Natural phytol was obtained from *Nippon Roche* from natural sources (purity: 90.8%; GLC); (*E*/*Z*) 98.7:1.3), and was purified by flash chromatography (FC) [SiO_2 (1 kg for 70 g phytol); hexane/Et_2O 2:1; R_f 0.57, and 0.48 for (*Z*)- and (*E*)-**6b**, resp.] to give (*E*,*R*,*R*)-**6b** (purity: 92.5% (GLC; (*E*/*Z*) 99.7:0.3) [23]. (all-*rac*)-Phytal (**6f**), was prepared from phytol (**6b**) as described earlier [24]. Flash chromatography (FC; excess Ar pressure ≤0.2 bar) was performed on *Merck* silica gel *60* (0.063–0.200 mm), and thin layer chromatography (TLC) was performed on *Merck* silica gel *F254* plates; detection by UV (254, 366 nm) and by spraying with phosphomolybdic acid followed by heating with a heat gun. Gas–liquid chromatography (GLC) was carried out with a gas chromatograph *HP 6890* [capillary column *Restek XTI* (fused silica); 30 m × 0.32 mm, film 0.25 μm, 1.8 ml/min He flux, T = 50–290° (30°/min), then 290° for 21 min)] equipped with an autosampler *HP 7683*, split injector, and FID; t_R in min. High-performance liquid chromatography (HPLC) was carried out with an *HP 1100* apparatus; t_R in min; given values in area %. HPLC Conditions for **3b**: column *Spherisorb S3-W* (3 μm, 150 × 4.6 mm), hexane/(20% AcOEt/1% 2-methoxyethanol/0.1% Et(i-Pr)$_2$N) 95:5 at 1.5 ml/min, UV detection at 280 nm. HPLC Conditions for **2b**: column *Spherisorb S5-W* (3 μm, 150 × 4.6 mm), 3% isopropylacetate/0.1% AcOH in hexane at 2 ml/min. UV detection at 220 nm. HPLC Conditions for **7a**, **7b**, and **8d**: column *ProC18* (150 × 3 mm), MeCN/H_2O/0.01% methanesulfonic acid at 0.5 ml/min, UV detection at 210 nm. Melting points (m.p.) are uncorrected. IR Spectra: microscopic infrared (MIR), *Nicplan FT-IR* microscope (*Spectratech*)); as film or in nujol: *20SX FT-IR* or *Magna 750 FT-IR* spectrometer; in cm^{-1}. Optical rotations were measured on a *Perkin-Elmer* polarimeter. ^1H-, ^{13}C-, and ^{31}P-NMR Spectroscopy: at 298 K on *Bruker DPX-400* or *Advance-300* spectrometers with $CDCl_3$ as solvent; chemical shifts δ in ppm rel. to Me_4Si, coupling constants, J in Hz. EI-MS: *Finnigan MAT*, *SSQ7000* (70 eV). ESI-MS: *API 300 Triple Quadrupole*, NH_4OAc in H_2O/MeCN as solvent; in *m*/*z* (rel. %). Microanalyses were carried out at *Solvias AG*, Basel.

4-Hydroxy-2,3,6-trimethyl-5-(3-methylbut-2-en-1-yl)phenyl Acetate (**5c**). To a soln. of TMHQA (100 g, 670 mmol) and 3-methylbut-2-en-1-ol (57.7 g, 70 ml, 670 mmol) in anh. CH_2Cl_2 (1 l) was added dropwise a soln. of 48% $BF_3 \cdot Et_2O$ (32.5 ml, 260 mmol) during 2 h at 0°. After another 30 min, the mixture was poured into 5% aq. $NaHCO_3$ soln. (1 l), and stirred for 1 h at r.t. The org. phase was extracted with CH_2Cl_2 (2 × 200 ml), and washed with sat. aq. $NaHCO_3$ soln. and brine. The org. layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was recrystallized from boiling hexane to give **5c** (95.3 g, 69%). Colorless, crystalline solid. Purity: 99.6% (GLC). M.p. 110–112°. GLC: t_R (TMHQA) 6.17, t_R (**5c**) 7.56. IR (MIR): 3506*m*, 2992*m*, 2962*m*, 2927*m*, 1732*s*, 1619*w*, 1574*w*, 1449*m* (br.), 1380*m*, 1365*s*, 1301*m*, 1256*s*, 1228*s*, 1197*s*, 1157*s*, 1073*s*, 1056*s*, 1019*s*, 989*m*, 937*m*, 868*w*, 838*s*. ^1H-NMR (300 MHz): 1.73 (*d*, *J* = 1.1, Me); 1.81 (*s*, Me); 2.03 (*s*, Ar*Me*); 2.06 (*s*, Ar*Me*); 2.06 (*s*, Ar*Me*); 2.33 (*s*, Ac); 3.35 (*d*, *J* = 6.8, =CHC*H*$_2$); 5.03 (*s*, O*H*); 5.12 (m_c, =CH). EI-MS: 263.1 (5, $[M+H]^+$),

262.1 (27, M^+), 221.1 (14, $[M-COCH]^+$), 220.1 (88, $[M-COCH_2]^+$), 165.0 (66, $[M-COCH-CH_2-CMe_2]^+$), 164.0 (100, $[M-COCH_2-CH_2CMe_2]^+$). Anal. calc. for $C_{16}H_{22}O_3$ (262.35): C 73.25, H 8.45; found: C 72.92, H 8.58.

2,3,5-Trimethyl-6-(3-methylbut-2-en-1-yl)benzene-1,4-diyl Diacetate (**5d**). A soln. of **5c** (500 mg, 1.90 mmol), Ac_2O (540 µl, 5.72 mmol) and DMAP (23.2 mg, 0.19 mmol) in CH_2Cl_2 (5 ml) was stirred for 16 h at 20–21°. Then, 5% aq. HCl (10 ml) was added to the colorless soln. The org. phase was extracted with Et_2O (3×10 ml), neutralized with sat. aq. $NaHCO_3$ soln. (15 ml), washed with H_2O (2×10 ml), and dried (Na_2SO_4). After filtration, the solvent was removed *in vacuo* to give a colorless oil which was crystallized at r.t. from boiling hexane (5 ml). After 5 h, **5d** was isolated as a colorless powder (490 mg, 85%). Purity: 99.8% (GLC). M.p. 93–95°. GLC: t_R (**5c**) 7.56, t_R (**5d**) 7.77. IR (MIR): 2933*w*, 1746*s*, 1432*w*, 1384*w*, 1368*m*, 1244*m*, 1204*s*, 1169*w*, 1080*w*, 1053*m*, 1012*w*, 943*w*, 911*m*, 840*w*. ^{1}H-NMR (300 MHz): 1.66 (*d*, *J*=1.2, Me); 1.72 (*s*, Me); 2.03 (*s*, Ar*Me*); 2.04 (*s*, 6 H, Ar*Me*); 2.31 (*s*, Ac); 2.33 (*s*, Ac); 3.20 (br. *s*, =CHCH_2); 4.95 (m_c, =CH). EI-MS: 305.2 (6, $[M+H]^+$), 304.2 (24, M^+), 262.1 (14, $[M-COCH_2]^+$), 261.1 (27, $[M-COMe]^+$), 221.1 (16, $[M-2(COCH_2)+H]^+$), [220.1 (100, $[M-2(COCH_2)]^+$), 165.1 (29, $[M-2(COCH_2)-CHCMe_2]^+$), 164.0 (56, $[M-2(COCH_2)-CH_2CMe_2]^+$). Anal. calc. for $C_{18}H_{24}O_4$ (304.39): C 71.03, H 7.95; found: C 71.14, H 7.92.

2,3,6-Trimethyl-5-(3-methylbut-2-en-1-yl)-4-[(tributylsilyl)oxy]phenyl Acetate (**5e**). To a soln. of **5c** (515 mg, 2.0 mmol) in anh. THF (6 ml) were added dropwise Et_3N (0.280 ml, 2.0 mmol) and Bu_3SiCl (0.335 ml, 2.0 mmol) successively. The resulting soln. was heated to 50° while a colorless precipitate was rapidly formed. After 18 h at 50°, the solvent was removed *in vacuo*, and the crude product was purified by FC (SiO_2 (50–60 g); Et_2O/hexane 1:9; R_f (**5c**) 0.10, R_f (**5e**) 0.30) to afford **5e** (510 mg, 55%). Colorless oil. Purity: 99.3% (GLC). GLC: t_R (**5c**) 7.56, t_R (Bu_3SiOH) 5.21, t_R (**5e**) 9.37. IR (film): 2958*s*, 2925*s*, 2872*s*, 1763*s*, 1572*w*, 1458*s*, 1416*s*, 1368*s*, 1329*m*, 1291*m*, 1247*m*, 1206*s*, 1001*m*, 963*w*, 910*m*, 887*m*, 770*m*, 722*m*. ^{1}H-NMR (400 MHz): 0.69–0.74 (*m*, 6 H, SiCH_2); 0.83–0.89 (*m*, 9 H, Si(CH$_2$)$_3$*Me*); 1.27–1.33 (*m*, 12 H, SiCH$_2$(CH_2)$_2$Me); 1.65 (*d*, *J*=1.2, C=CMe); 1.71 (*s*, C=CMe); 1.98 (*s*, Ar*Me*); 2.00 (*s*, Ar*Me*); 2.12 (*s*, Ar*Me*); 2.30 (*s*, Ac); 3.28 (m_c, =CHCH_2); 4.97 (m_c, =CH). EI-MS: 460.4 (28, M^+), 418.3 (100, $[M-CH_2CO]^+$). Anal. calc. for $C_{28}H_{48}O_3Si$ (460.77): C 72.99, H 10.50; found: C 72.69, H 10.42.

4-{[(1,1-Dimethylethyl)(dimethyl)silyl]oxy}-2,3,6-trimethyl-5-(3-methylbut-2-en-1-yl)phenyl Acetate (**5f**). A soln. of **5c** (1.31 g, 5.0 mmol), ^{t}BuMe$_2$SiCl (1.13 g, 7.1 mmol), and imidazole (1.02 g, 15.0 mmol) in anh. DMF (5 ml) was stirred at r.t. for 16 h. Then, Et_2O (40 ml) and 10% aq. HCl (15 ml) were added, and the org. phase was extracted with Et_2O (3×15 ml). The org. layer was washed with sat. aq. $NaHCO_3$ soln. (30 ml), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting crude oil was purified by FC (SiO_2 (120 g); Et_2O/hexane 1:4; R_f (**5c**) 0.25, R_f (**5f**) 0.66) to give **5f** (1.84 g, 98%). Yellow oil that solidified on standing at r.t. Purity: 99.6% (GLC). M.p. 63–65°. GLC: t_R (**5c**) 7.56, t_R (**5f**) 8.29. IR (nujol): 2926*s*, 2855*s*, 1765*s*, 1567*w*, 1463*s*, 1414*w*, 1375*s*, 1324*m*, 1257*s*, 1206*s*, 1100*s*, 1060*s*, 998*m*, 910*s*, 873*s*, 840*s*, 825*m*, 811*m*, 781*s*, 754*m*, 673*m*. ^{1}H-NMR (400 MHz): 0.00 (*s*, 6 H, SiMe$_2$); 0.88 (*s*, 9 H, *t*-Bu); 1.49 (*d*, *J*=1.6, =CMe); 1.55 (*s*, =CMe); 1.84 (*s*, Ar*Me*); 1.85 (*s*, Ar*Me*); 1.97 (*s*, Ar*Me*); 2.17 (*s*, Ac); 3.18 (m_c, =CHCH_2); 4.86 (m_c, =C*H*). EI-MS: 376.2 (24, M^+), 334.2 (38, $[M+H-COMe]^+$), 263.2 (60, $[M+H-SiMe_2CMe_3]^+$), 221.2 (100, $[M+2\,H-SiMe_2(CMe)-COMe]^+$). Anal. calc. for $C_{22}H_{36}SiO_3$ (376.61): C 70.16, H 9.63, Si 7.46; found: C 70.45, H 9.75, Si 7.81.

*4-[(2*E,*Z)-But-2-en-1-yloxy]-2,3,6-trimethylphenyl Acetate* (**8b**). To a suspension of NaH (450 mg, 10.3–12.2 mmol; 55–65% suspension in mineral oil) in THF (10 ml) was added portionwise TMHQA (1.94 g, 10.0 mmol) at 2–3° under gas evolution. After 30 min, (*E*,*Z*)-4-bromobut-2-ene (1.7 ml, 14.0 mmol) was added dropwise, and the yellow mixture was stirred at 2–3° for 1 h. The mixture was allowed to warm to r.t., filtered after 18 h over a glass frit, and concentrated *in vacuo*. The crude residue was purified by FC (SiO_2 (120 g); Et_2O/hexane 1:4; R_f (TMHQA) 0.12, R_f (**8b**) 0.50) to give **8b** (1.74 g, 7.0 mmol, 70%). Colorless oil that solidified on standing at r.t. Purity: 97.7% (GLC). M.p. 38–40°. GLC: t_R (TMHQA) 6.17, t_R ((*E*)-**8b**) 6.86, t_R ((*Z*)-**8b**) 6.89 ((*E*/*Z*) 89:11). IR (MIR): 2917*w*, 2864*w*, 1748*s*, 1617*w*, 1586*w*, 1484*m*, 1372*s*, 1325*s*, 1218*s*, 1218*s*, 1189*s*, 1105*s*, 1077*s*, 1004*s*, 968*s*, 909*s*, 827*s*. ^{1}H-NMR (300 MHz): 4.05 (*dd*, *J*=6.0, 1.1, =CMe); 2.04 (*s*, Ar*Me*); 2.11 (*s*, Ar*Me*); 2.14 (*s*, Ar*Me*); 2.32 (*s*, Ac); 4.40 (*d*, *J*=5.5, =CCH_2O, (*E*)-isomer); 4.54 (*d*, *J*=3.7, =CCH_2CO, (*Z*)-isomer); 5.66–5.88 (*m*, C*H*=

C*H*); 6.56 (*s*, arom. H, (*E*)-isomer), 6.58 (*s*, arom. H, (*Z*)-isomer). EI-MS: 248.2 (28, M^+), 206.2 (20, $[M+H-CH_2CO]^+$), 194.1 (3, $[M-C_4H_6]^+$), 152.1 (100, $[C_6H(OH)_2Me_3]^+$), 151.1 (39, $[C_6H(OH)_2Me_3-H]^+$). Anal. calc. for $C_{15}H_{20}O_3$ (248.32) : C 72.55, H 8.12; found: C 72.58, H 8.16.

3,3,6-Trimethyl-4-[(3-methylbut-2-en-1-yl)oxy]phenyl Acetate (**8c**). TMHQA (1.94 g, 10.0 mmol) was added portionwise at 22–23° to a suspension of NaH (450 mg, 10.3–12.2 mmol) in THF (10 ml) under gas evolution. After 15 min, 4-bromo-2-methylbut-2-ene (1.7 ml, 14.1 mmol) was added *via* syringe, and the yellow mixture was stirred overnight at 22–23°. After 18 h, H_2O (30 ml) was added to the mixture, and the org. phase was extracted with Et_2O (3×50 ml), and dried (Na_2SO_4). After filtration and evaporation of the solvent, the resulting yellow oil was purified by FC (SiO_2 (130 g); Et_2O/hexane 1:4; R_f (TMHQA) 0.13, R_f (**8c**) 0.55). Compound **8c** was isolated as a yellow liquid (1.82 g, 69%) containing an unknown impurity (*ca.* 7%). A pure anal. sample of **8c** (477 mg, 18%), was obtained by two crystallizations from hexane (5 ml) at −40°, starting from impure **8c** (1.29 g, 4.9 mmol). Furthermore, after FC, starting TMHQA was partly recovered (415 mg, 21%) as well as 3-(3-methylbuten-2-yl)-2,5,6-trimethylhydroquinone-1-acetate (**5c**) (yellow powder; 200 mg, 7%) Characterization data given were obtained. *Data of pure* **8c**. Purity: 99.9% (GLC). Colorless crystals. M.p. 25–27°. GLC: t_R (TMHQA) 6.18, t_R (**8c**) 7.18, t_R (**4c**) 7.57. IR (MIR): 2964*w*, 2927*w*, 2866*w*, 1746*s*, 1615*w*, 1586*w*, 1483*m*, 1441*m*, 1378*s*, 1371*s*, 1326*m*, 1224*s*, 1196*s*, 1106*s*, 1081*s*, 1054*m*, 1036*m*, 1008*s*, 926*m*, 903*m*, 851*s*, 785*s*. ^{1}H-NMR (400 MHz): 1.72 (*s*, =CMe); 1.78 (*d*, J=0.8, =CMe); 2.04 (*s*, Ar*Me*); 2.12 (*s*, Ar*Me*); 2.13 (*s*, Ar*Me*); 2.32 (*s*, Ac); 4.46 (*d*, J=6.4, =CCH_2O); 5.49 (m_c, =CH); 6.58 (*s*, arom. H). EI-MS: 262.2 (7, M^+), 220.2 (3, $[M-CH_2CO]^+$), 194.1 (21, $[M-C_5H_8]^+$), 152.1 (100, $[M-C_5H_8-CH_2CO]^+$). Anal. calc. for $C_{16}H_{22}O_3$ (262.35): C 73.25, H 8.45; found: C 73.20, H 8.38.

Alternative Synthesis of **8c**. To a soln. of TMHQA (1.94 g, 10.0 mmol), 3-methyl-2-buten-1-ol (1.50 ml, 15.0 mmol), and Ph_3P (3.41 g, 13.0 mmol) in anh. THF (100 ml) cooled to −10° to −15° was added over 25 min diethyl azodicarboxylate (DEAD; 2.49 ml, 16.0 mmol) dissolved in THF (8 ml). The resulting yellow soln. was stirred at this temp. for 2 h, and then allowed to warm to r.t. After 20 h, the soln. was concentrated *in vacuo*, and the crude residue was purified by FC (SiO_2 (120 g); Et_2O/hexane 1:4; R_f ($OPPh_3$) 0.00, R_f (TMHQA) 0.12, R_f (**8c**) 0.55) to give **8c** (2.25 g, 83%). Pale-yellow oil. Purity: 94.1% (GLC). GLC: t_R (3-methyl-buten-1-ol) 4.98, t_R (TMHQA) 6.17, t_R (**8c**) 7.18, t_R ($OPPh_3$) 9.16.

*2,3,6-Trimethyl-4-{[(2*E*)-3-phenylprop-2-en-1-yl]oxy}phenyl Acetate* ((*E*)-**8d**). A solution of TMHQA (1.94 g, 10.0 mmol) in anh. DMF (10 ml) was added dropwise over 20 min to a stirred suspension of NaH (524 mg, 12.0–14.2 mmol) in DMF (15 ml) at 2–3° (ice bath) under gas evolution. After another 30 min, cinnamyl bromide (2.76 g, 14.0 mmol) dissolved in anh. DMF (10 ml) was added dropwise over 10 min to the mixture at 2–3°. The resulting paste was stirred at this temp. for an additional 30 min, and allowed to warm to r.t. over 14 h. The reaction was quenched by addition of cold H_2O (50 ml), and the resulting mixture was extracted with Et_2O (3×30 ml). The combined org. phases were washed with 50 ml each of a 2M aq. NaOH soln., H_2O, and brine. The org. phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo* to afford the crude product as a yellow solid (3.26 g), which was purified by FC (SiO_2 (120 g); Et_2O/hexane 1:4; R_f (TMHQA) 0.12, R_f (**8d**) 0.30, R_f (cinnamyl bromide) 0.62) to afford **8d** (2.72 g, 88%). Colorless needles. Purity: 98.3% (HPLC). M.p. 107–108° (lit. 104–107° [19]). HPLC: t_R 23.4 (dec. under GLC conditions). IR (nujol): 2923*s*, 2854*s*, 1742*s*, 1663*w*, 1586*m*, 1576*m*, 1485*s*, 1458*s*, 1412*m*, 1372*s*, 1329*m*, 1277*w*, 1223*s*, 1203*s*, 1117*s*, 1084*s*, 1037*m*, 1002*m*, 969*s*, 907*m*, 849*m*, 833*m*, 748*s*, 694*s*. ^{1}H-NMR (300 MHz): 2.06 (*s*, Ar*Me*); 2.12 (*s*, Ar*Me*); 2.18 (*s*, Ar*Me*); 2.33 (*s*, Ac); 4.65 (*dd*, J=1.3, 5.5, OCH_2); 6.43 (*dt*, J=5.5, 16.0, OCH_2CH=), 6.62[7]) (*s*, arom. H); 6.73 (*d*, J=16.0, OCH_2CH=C*H*), 7.23–7.28 (*m*, arom. H); 7.31–7.36 (*m*, arom. H), 7.41–7.44 (*m*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 12.1; 13.0; 16.6; 20.5; 69.4; 111.7; 125.1; 126.5; 127.1; 127.8; 128.6; 129.7; 132.2; 136.6; 154.2; 169.4. EI-MS: 310 (3, M^+), 268 (7, $[M-CH_2CO]^+$), 151 (6, $[C_6H(OH)_2Me_3]^+$), 117 (100, $[C_6H_5CH{=}CHCH_2]^+$). Anal. calc. for $C_{20}H_{22}O_3$ (310.39): C 77.39, H 7.14, O 15.46; found: C 77.40, H 7.26, O 15.52.

*(all-*rac*,* E*/*Z*)-Phytyl Formiate* (**6c**). A mixture of (all-*rac*, *E*/*Z*)-**6b** (3.11 g, 10.0 mmol; (*E*/*Z*) 72:28) and HCO_2H (4.60 g, 100 mmol) was vigorously stirred at 60° for 2.5 h. Then, H_2O (30 ml) was added to

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[7]) It is assumed that the value of 5.63 given in [19] is a typing error.

the mixture, and the org. phase was extracted with Et_2O (2×30 ml). The org. layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude residue was purified by FC (SiO_2 (100 g); Et_2O/hexane 5:95; R_f ((*E*/*Z*)-**6b**) 0.10, R_f ((*E*)-**6c**) 0.43, R_f ((*Z*)-**6c**) 0.48) to give (*E*/*Z*)-**6c**. Colorless oil (2.92 g, 90%). Purity: 91.5% (GLC; dec.). GLC: t_R ((*Z*)-**6b**) 7.69, t_R ((*E*)-**6b**) 7.76, t_R ((*Z*)-**6c**) 7.78, t_R ((*E*)-**6c**) 7.87 ((*E*/*Z*) 65:35). IR (nujol): 2954*m*, 2925*m*, 2866*m*, 1728*s*, 1670*w*, 1462*m*, 1377*m*, 1366*m*, 1273*w*, 1156*s* (br.). ^{1}H-NMR (300 MHz): 0.85–0.88 (*m*, 4 Me); 1.00–1.60 (*m*, 19 H, CH, CH_2); 1.71 (*s*, =CMe, (*E*)-isomer); 1.76 (*d*, *J*=1, =CMe, (*Z*)-isomer); 2.01 (*t*, *J*=7.6, =(Me)CH_2, (*E*)-isomer); 2.10 (*t*, *J*=7.5, =(Me)CH_2, (*Z*)-isomer); 4.66 (*d*, *J*=7.5, OCH_2, (*Z*)-isomer); 4.69 (*d*, *J*=7.6, OCH_2, (*E*)-isomer); 5.36 (m_c, =CH); 8.06 (*s*, OCHO). EI-MS: 324.4 (4, M^+), 278.3 (27, $[M-HCOOH]^+$), 123.1 (100, $[C_9H_{15}]^+$). Anal. calc. for $C_{21}H_{40}O_2$ (324.55): C 77.72, H 12.42; found: C 77.72, H 12.42.

*(all-*rac,E/Z*)-Phytyl Acetate* (all-*rac*,*E*/*Z*)-**6d**). A mixture of (all-*rac*,*E*/*Z*)-**5b** (6.23 g, 20.0 mmol; (*E*/*Z*) 72:28), pyridine (1.98 g, 25.0 mmol), Ac_2O (2.04 g, 20.0 mmol), and hexane (5 ml) was stirred at r.t. for 18 h. Then, H_2O (30 ml) was added, and the resulting mixture was extracted with Et_2O (3×50 ml). The org. phases were combined and washed with 10% aq. HCl (3×30 ml), neutralized with sat. aq. $NaHCO_3$ soln. (50 ml), washed with brine (50 ml) and H_2O (50 ml), and dried (Na_2SO_4). After filtration, the solvent was removed *in vacuo*, and the crude residue was purified by FC (SiO_2 (120 g); Et_2O/hexane 1:4; R_f ((*E*,*Z*)-**6b**) 0.15, R_f ((*E*,*Z*)-**6d**) 0.66) to give (*E*,*Z*)-(all-*rac*)-**6d**. Colorless oil (5.62 g, 16.6 mmol, 83%). Purity: 98.2% (GLC). GLC: t_R ((*Z*)-**5b**) 7.69, t_R ((*E*)-**5b**) 7.76, t_R ((*Z*)-**5d**) 7.97 min, t_R ((*E*)-**5d**) 8.06 min ((*E*/*Z*) 71:29). IR (MIR): 2952*m*, 2926*m*, 2868*m*, 1742*s*, 1673*w*, 1462*m* (br.), 1378*m*, 1365*m*, 1228*s*, 1020*m*. ^{1}H-NMR (400 MHz): 0.84–0.88 (*m*, 4 Me); 1.00–1.60 (*m*, 19 H, CH, CH_2); 1.69 (*s*, =CMe, (*E*)-isomer); 1.75 (*d*, *J*=0.8, =CMe; (*Z*)-isomer); 2.00 (*t*, *J*=7.2, =C(Me)CH_2, (*E*)-isomer); 2.04 (*s*, Ac); 2.08 (*t*, *J*=7.0, =C(Me)CH_2, (*Z*)-isomer); 4.56 (*d*, *J*=7.0, OCH_2, (*Z*)-isomer); 4.58 (*d*, *J*=7.2, OCH_2, (*E*)-isomer); 5.35 (m_c, =C*H*). EI-MS: 278.3 (47, $[M-H-AcO]^+$), 123.1 (100, $[C_9H_{15}]^+$). Anal. calc. for $C_{22}H_{42}O_2$ (338.57): C 78.05, H 12.50; found: C 78.20, H 12.61.

*(*R,R,E*)-Phytyl Acetate* ((*R*,*R*,*E*)-**6d**). Obtained from (*R*,*R*,*E*)-**6b** ((*E*/*Z*) 99.7:0.3) by the same procedure as described above. Yield: 61%. Purity: 96.5% ((*E*/*Z*) 99.7:0.3 (GLC)). $[\alpha]_D^{20} = -0.57$ (*c*=1.04, CH_2Cl_2).

*(all-*rac,E/Z*)-Phytyl Benzoate* (**6e**). A mixture of (all-*rac*,*E*/*Z*)-**6b** (15.02 g, 48.6 mmol; (*E*/*Z*) 72:28), benzoic anhydride (11.56 g, 51.1 mmol), and DMAP (300 mg, 2.4 mmol) in hexane (30 ml) was stirred at r.t. for 20 h. Then, H_2O (50 ml) was added, and the org. phase was extracted with Et_2O (3×50 ml). The org. layer was washed with 10% aq. HCl (3×15 ml), neutralized with sat. aq. $NaHCO_3$ soln. (50 ml), washed with brine (50 ml) and H_2O (50 ml), and dried (Na_2SO_4). After filtration, the solvent was removed *in vacuo*, and the crude residue was purified by FC (SiO_2 (140 g); AcOEt/hexane 5:95; R_f ((*E*/*Z*)-**6b**) 0.17, R_f ((*E*/*Z*)-**6e**) 0.74) to give **6e** (14.8 g, 76%). Purity: 99.5% (GLC). GLC: t_R ((*Z*)-**6b**) 7.69, t_R ((*E*)-**6b**) 7.76, t_R ((*Z*)-**6e**) 9.89, t_R ((*E*)-**6e**) 10.08 ((*E*/*Z*) 68:32). IR (MIR): 2952*m*, 2926*m*, 2867*m*, 1720*s*, 1602*w*, 1586*w*, 1461*m*, 1451*m*, 1377*m*, 1314*m*, 1267*s* (br.), 1175*m*, 1106*m*, 1097*m*, 1069*m*, 1027*m*. ^{1}H-NMR (400 MHz): 0.82–0.95 (*m*, 4 Me); 0.99–1.60 (*m*, 19 H, CH, CH_2); 1.75 (*s*, =CMe); 1.78 (*d*, *J*=0.8, =CMe); 2.03 (*t*, *J*=7.6, =CMeCH_2, (*E*)-isomer); 2.13 (*t*, *J*=7.6, =CMeCH_2, (*Z*)-isomer); 4.81 (*d*, *J*=7.6, OCH_2, (*Z*)-isomer); 4.84 (*d*, *J*=6.8, OCH_2, (*E*)-isomer); 5.46 (m_c, =CH); 7.43 (*dd*, *J*=8.0, 8.4, 2 arom. H); 7.54 (*t*, *J*=8.4, 1.3, arom. H); 8.05 (*dd*, *J*=8.0, 1.3, 2 arom. H). EI-MS: 278.3 (3, $[M-H-C_6H_5COO]^+$), 123 (33, $[C_9H_{15}]^+$), 105 (100, $[C_6H_5CO]^+$). Anal. calc. for $C_{27}H_{44}O_2$ (400.64): C 80.94, H 11.07; found: C 80.97, H 11.07.

General Procedure for Ru-Catalyzed Reactions. a) *Reactions in Toluene at Ambient Pressure.* A *Schlenk* tube placed under Ar and equipped with a magnetic stirring bar was charged with **4a** (8.4 mg, 0.01 mmol) (or **4b**), tridecane (36.8 mg, 0.2 mmol), and anh. toluene (2 ml). Then, a soln. of substrate **5**, **7**, or **8** (0.2 mmol) and metathesis partner **6** (0.4 mmol) dissolved in toluene (4 ml) was added at r.t. The resulting brown soln. was stirred at r.t. for 10 min, and then at 80° for 16–18 h. The progress of the reaction was monitored by GLC: t_R (tridecane) 4.77, t_R (**5a**) 6.85, t_R (**5b**) 7.16, t_R (**5c**) 7.56, t_R (**5d**) 7.77, t_R (**5e**) 9.37, t_R (**5f**) 8.29, t_R (**7a**) 15 (br.), t_R (**7b**) 14.65, t_R (**8a**) 6.46, t_R ((*E*)-**8b**) 6.86, t_R ((*Z*)-**8b**) 6.89, t_R (**8c**) 7.18, t_R (**6a**) 6.49, t_R ((*Z*)-**6b**) 7.69, t_R ((*E*)-**6b**) 7.76, t_R ((*Z*)-**6c**) 7.78, t_R ((*E*)-**6c**) 7.87, t_R ((*Z*)-**6d**) 7.97, t_R ((*E*)-**6d**) 8.06, t_R ((*Z*)-**6e**) 9.89, t_R ((*E*)-**6e**) 10.08, t_R ((*Z*)-**2b**) 12.96, t_R ((*E*)-**2b**) 13.14, t_R ((*E*,*Z*)-**2d**) 13.49, t_R ((*Z*)-**2e**) 19.59, t_R ((*E*)-**2e**) 20.51, t_R ((*Z*)-**2f**) 14.73, t_R ((*E*)-**2f**) 15.07, t_R ((*Z*,*E*)-**3b**) 9.5 (br.)), t_R ((*E*)-**9**) 12.44, t_R ((*Z*)-**9**) 12.65; **8d** decomposed under GLC conditions. After 16–18 h,

the soln. (always orange, except when **5a**, **5c**, **6b**, or **7a** were used (green)) was cooled to r.t., and the solvent was evaporated *in vacuo*. The crude residue was purified by FC (SiO_2 (60 g); elution: *1*) Et_2O/hexane 1:4 when **5a**,**b**,**d**, **7a**,**b**, or **8a**,**b** were used as substrate [R_f (**5a**) 0.25, R_f (**5b**) 0.25, R_f (**5d**) 0.22, R_f (**7a**) 0.05, R_f (**7b**) 0.05, R_f (**8a**) 0.50, R_f (**8b**) 0.50, R_f (**8d**) 0.30, R_f (**6a**) 0.90, R_f ((*E*,*Z*)-**6b**) 0.15, R_f ((*E*,*Z*)-**6c**) 0.86, R_f ((*E*,*Z*)-**6d**) 0.70, R_f ((*E*,*Z*)-**6e**) 0.74, R_f ((*E*,*Z*)-**2b**) 0.42, R_f ((*E*,*Z*)-**2d**) 0.42, R_f ((*E*,*Z*)-**3b**) 0.70, R_f ((*E*,*Z*)-**9**) 0.10]; *2*) Et_2O/hexane 5:95 for **5e**,**f** or **8c** as substrate [R_f (**5e**) 0.29, R_f (**5f**) 0.23, R_f (**8c**) 0.22, R_f (**6a**) 0.90, R_f ((*E*,*Z*)-**6c**) 0.52, R_f ((*E*,*Z*)-**6d**) 0.40, R_f ((*E*,*Z*)-**6e**) 0.45, R_f ((*E*,*Z*)-**2e**) 0.34, R_f ((*E*,*Z*)-**2f**) 0.35, R_f ((*E*,*Z*)-**3b**) 0.35]. The expected products (*cf. Tables 1* and *2*) were obtained as colorless oils. For the reaction between **8c** and **6a** at 4-fold concentration (*Table 2*, *Entry 5*), the same procedure as above was used, except that the amount of all the reactants was multiplied by a factor of two, and the volume of toluene was divided by the same factor. For the reaction between **5e** and **6d** (*Table 11*, *Entry 13*), we were not able to separate by FC **2e** from **6d**; the yield of 49% was determined by GLC. The mixture **2e**/**6d** was isolated by FC (SiO_2, (60 g); Et_2O/hexane 5:95; R_f ((*E*,*Z*)-**6d**) 0.40, R_f ((*E*,*Z*)-**2e**) 0.34). Then, the mixture was dissolved in DMF (2 ml), and $LiOH \cdot H_2O$ (10 mg, 0.24 mmol) was added to the soln., which was stirred for 16 h at r.t. The solvent was evaporated *in vacuo*, and the crude residue was purified by FC (SiO_2 (50 g); Et_2O/hexane 1:4; R_f ((*E*,*Z*)-**6d**) 0.70, ((*E*,*Z*)-**2b**) 0.42) to give (*E*,*Z*)-**2b** (26 mg, 50% based on starting **2e**) as a colorless oil. The same procedure was used for the reaction between (*E*,*Z*)-**6d** and **5f** to isolate (*E*,*Z*)-**2b** (*Table 1*, *Entries 17* and *18*).

b) *Reactions without Solvent* in vacuo. A mixture of **5d**, **5f** or **8c** (0.8 mmol), **6a** (1.6 mmol), and catalyst **4** (0.04 mmol) was vigorously stirred under vacuum (33 mbar) at 80° for 2 h (**8c**) or 3 h (**5d** or **5f**). The crude mixture was purified by FC (SiO_2 (60 g)), to give the expected products as colorless oils.

c) *Reaction without Solvent at Ambient Pressure.* The same procedure as described above, but with **8c** and **6a** (*Table 2*, *Entry 6*) was followed, except that the reaction was run under an Ar atmosphere for 18 h.

*Data of 4-Hydroxy-2,3,6-trimethyl-5-(all-*rac,E/Z*)-3,7,11,15-tetramethylhexadec-2-en-1-yl]phenyl Acetate* (**2b**). Data collected from different samples. Colorless oil. Purity: 99.1% (HPLC), 95.8% (GLC). R_f (SiO_2; Et_2O/hexane 1:4) 0.42. HPLC: t_R 4.47 (*Z*), 4.80 (*E*). GLC: t_R 12.96 (*Z*), 13.14 (*E*). IR (film): 3502*s*, 2953*s*, 2927*s*, 2868*s*, 1761*s*, 1744*s*, 1577*w*, 1462*s*, 1368*s*, 1302*w*, 1225*s*, 1209*s*, 1075*m*, 908*w*, 834*w*. ^{1}H-NMR (400 MHz): 0.81–0.91 (*m*, 4 Me); 1.00–1.58 (*m*, 19 H, CH, CH_2); 1.72 (m_c, =CMe, (*Z*)-isomer); 1.80 (*d*, *J* = 1.2, =CMe, (*E*)-isomer); 1.98 (*t*, *J* = 7.4, =MeCH_2, (*E*)-isomer); 2.04 (*s*, Ar*Me*); 2.06 (*s*, Ar*Me*); 2.14 (*s*, Ar*Me*); 2.19 (*t*, *J* = 7.4, =MeCH_2, (*Z*)-isomer); 2.33 (*s*, Ac); 3.36 (*d*, *J* = 6.8, ArCH_2); 5.03 (*s*, OH, (*Z*)-isomer); 5.05 (*s*, OH, (*E*)-isomer); 5.13 (*t*, *J* = 6.8, =CH). EI-MS: 472.3 (7, M^+), 430.3 (100, $[M - CH_2CO]^+$), 207.1 (16, $[M - C_{19}H_{37}]^+$), 165.1 (57, $[M - C_{19}H_{37} - CH_2CO]^+$). Anal. calc. for $C_{31}H_{52}O_3$ (472.75): C 78.76, H 11.09; found: C 78.66, H 11.04.

Data of (*R*,*R*,*E*/*Z*)-**2b**. Prepared by the selective deprotection of (*R*,*R*,*E*/*Z*)-**2f** (see below) obtained from the reaction between **5f** and (*R*,*R*,*E*)-**6d** (*Table 1*, *Entry 18*). The anal. data were almost identical to those of (all-*rac*,*E*/*Z*)-**2b**. (*E*/*Z*) 65:35. Optical rotation not determined.

*Data of 2,3,5-Trimethyl-6-[(all-*rac,E/Z*)-3,7,11,15-tetramethylhexadec-2-en-1-yl]benzene-1,4-diyl Diacetate* (**2d**). Sample obtained from the reaction between **5d** and **6a**. Colorless oil. R_f (SiO_2; Et_2O/hexane 1:4) 0.42. Purity: > 99.9% (GLC). GLC: t_R 13.45. The (*E*/*Z*)-ratio was determined by ^{1}H-NMR. IR (MIR): 2925*s*, 2867*m*, 1760*s*, 1461*m*, 1366*s*, 1244*w*, 1187*s*, 1079*s*, 1052*s*, 1009*m*, 908*m*. ^{1}H-NMR (400 MHz): 0.85–0.90 (*m*, 4 Me); 0.95–1.60 (*m*, 19 H, CH, CH_2); 1.64 (*d*, *J* = 1.6, =CMe, (*Z*)-isomer); 1.71 (*s*, =CMe, (*E*)-isomer); 1.90 (m_c, =CMeCH_2, (*E*)-isomer); 2.03 (*s*, Ar*Me*); 2.04 (*s*, Ar*Me*); 2.05 (*s*, Ar*Me*); 2.10 (m_c, =CH_2, (*Z*)-isomer); 2.30 (*s*, Ac); 2.33 (*s*, Ac); 3.20 (br. *s*, ArCH_2); 4.95 (m_c, =CH). EI-MS: 514.5 (10, M^+), 472.4 (24, $[M - CH_2CO]^+$), 430.4 (100, $[M - 2(CH_2CO)]^+$). Anal. calc. for $C_{33}H_{54}O_4$ (514.79): C 77.00, H 10.57; found: C 76.99, H 10.55.

*Data of 2,3,6-Trimethyl-5-[(all-*rac,E/Z*)-3,7,11,15-tetramethylhexadec-2-en-1-yl]-4-[(tributylsilyl)-oxy]phenyl Acetate* (**2e**). Sample obtained from the reaction between **5e** and **6a**. Colorless oil. R_f (SiO_2, Et_2O/hexane 5:95) 0.34. Purity: 96.3% (GLC). GLC: t_R 19.59 (*Z*), 20.51 (*E*), ((*E*/*Z*) 74:26). IR (MIR): 2955*m*, 2923*m*, 2857*m*, 1762*m*, 1461*m* (br.), 1415*w*, 1366*m*, 1329*w*, 1296*w*, 1246*w*, 1203*s*, 1108*w*, 1075*m*, 1000*w*, 910*m*. ^{1}H-NMR (400 MHz): 0.65–0.75 (*m*, 6 H, $SiCH_2$); 0.80–0.90 (*m*, 7 Me); 0.95–1.60 (*m*, 31 H, CH_2, CH); 1.64 (*d*, *J* = 1.2, =CMe, (*Z*)-isomer); 1.69 (*s*, =CMe, (*E*)-isomer); 1.92

(m_c, =CMeCH$_2$, (*E*)-isomer); 1.97 (*s*, Ar*Me*); 2.00 (*s*, Ar*Me*); 2.09 (m_c, =CMeC*H*$_2$, (*Z*)-isomer); 2.12 (*s*, Ar*Me*); 2.30 (*s*, 2 Ac); 3.29 (br. *s*, ArC*H*$_2$); 4.98 (m_c, =C*H*). EI-MS: 670.7 (40, M^+), 628.6 (100, $[M-CH_2CO]^+$). Anal. calc. for $C_{43}H_{78}O_3Si$ (671.17) : C 76.95, H 11.71; found: C 76.47, H 11.39.

*Data of 4-{[(1,1-Dimethylethyl)(dimethyl)silyl]oxy}-2,3,6-trimethyl-5-[(all-*rac,E/Z*)-3,7,11,15-tetramethylhexadec-2-en-1-yl]phenyl Acetate* (**2f**). Sample obtained from the reaction between **5f** and **6a**. Colorless oil. Purity: 96.5% (GLC). R_f (SiO_2; Et_2O/hexane 5:95) 0.35. GLC: t_R 14.73 (*Z*), 15.07 (*E*), ((*E*/*Z*) 73:27). IR (MIR): 2952*m*, 2927*m*, 2858*m*, 1763*m*, 1462*m*, 1366*m*, 1326*w*, 1252*m*, 1203*s*, 1102*w*, 1060*m*, 1005*w*, 911*m*, 872*m*, 838*s*, 778*s*. ^{1}H-NMR (400 MHz): 0.14 (*s*, SiMe$_2$); 0.80–0.90 (*m*, 4 Me); 1.02 (*s*, *t*-Bu); 1.00–1.55 (*m*, 19 H, CH, CH$_2$); 1.62 (*s*, =CCH); 1.67 (*d*, *J* = 0.8, =CMe, (*E*)-isomer); 1.92 (m_c, =CMeC*H*$_2$, (*E*)-isomer); 1.98 (*s*, Ar*Me*); 2.00 (*s*, Ar*Me*); 2.09 (m_c, =CMeC*H*$_2$, (*Z*)-isomer); 2.11 (*s*, Ar*Me*); 2.31 (*s*, Ac); 3.30 (m_c, ArC*H*$_2$); 4.97 (m_c, =CH). EI-MS: 586.5 (24, M^+), 544.5 (62, $[M-CH_2CO]^+$). Anal. calc. for $C_{37}H_{66}O_3Si$ (587.01): C 75.71, H 11.33, Si 4.78; found: C 75.67, H 11.33, Si 4.80.

*Data of 2,3,6-Trimethyl-4-{[(all-*rac,E/Z*)-3,7,11,15-tetramethylhexadec-2-en-1-yl]oxy}phenyl Acetate* (**3b**). Data collected from different samples. Colorless oil. Purity: 99.6% (HPLC). R_f (Et_2O/hexane 5:95) 0.35. HPLC: t_R 5.39 (*Z*), 6.29 (*E*), ((*E*/*Z*) 70:30). IR (film): 2927*s*, 2868*s*, 1763*s*, 1462*s*, 1368*s*, 1223*s*, 1197*s*, 1112*s*, 1081*s*. ^{1}H-NMR (400 MHz): 0.83–0.87 (*m*, 4 Me); 1.05–1.56 (*m*, 19 H, CH, CH$_2$); 1.70 (*s*, =CMe, (*E*)-isomer); 1.77 (*s*, =CMe, (*Z*)-isomer); 2.03 (m_c, C=CCH$_2$); 2.04 (*s*, Ar*Me*); 2.11 (*s*, Ar*Me*); 2.13 (*s*, Ar*Me*); 2.32 (*s*, Ac); 4.45 (*d*, *J* = 7.2, OCH$_2$, (*Z*)-isomer); 4.48 (*d*, *J* = 6.4, OCH$_2$, (*E*)-isomer); 5.48 (*t*, *J* = 6.4, =CH, (*E*)-isomer); 5.50 (*t*, *J* = 7.2, =CH, (*Z*)-isomer); 6.57 (*s*, arom. H). EI-MS: 472.4 (2, M^+), 430.4 (2, $[M-CH_2CO]^+$), 194.2 (26, $[M-C_{20}H_{39}]^+$), 152.2 (100, $[M-C_{20}H_{39}-CH_2CO]^+$). Anal. calc. for $C_{31}H_{52}O_3$ (472.75): C 78.76, H 11.09; found: C 78.50, H 11.08.

Data of (*R*,*R*,*E*/*Z*)-**1b**. Obtained from the reaction between **8c** and (*R*,*R*,*E*)-**6d**. The anal. data were almost identical to those of (all-*rac*,*E*/*Z*)-**1b**. (*E*/*Z*) 70:30.

*Synthesis of (E/Z)-***2b** *by Selective Deprotection of (E/Z)-***2e**. A mixture of (*E*/*Z*)-**2e** (50.0 mg, 0.074 mmol; (*E*/*Z*) 73:27) and LiOH·H$_2$O (9.4 mg, 0.223 mmol) in DMF (0.2 ml) was vigorously stirred at r.t. After 16 h, the solvent was removed *in vacuo*, and the crude oil was purified by FC (SiO_2 (25 g); Et_2O/hexane 1:4; R_f ((*E*/*Z*)-**2e**) 0.23, R_f (*E*/*Z*)-**2b** 0.42) to give (*E*/*Z*)-**2b** (26.1 mg, 74%). Colorless oil. Purity: 92.1% (GLC). GLC: t_R ((*Z*)-**2b**) 12.96, t_R ((*E*)-**2b**) 13.14, ((*E*/*Z*) 72:28). For anal. data, see above.

*Synthesis of (E/Z)-***2b** *by Selective Deprotection of (E/Z)-***2f**. A mixture of (*E*/*Z*)-**2f** (33.0 mg, 0.056 mmol) and LiOH·H$_2$O (7.1 mg, 0.17 mmol) in DMF (2 ml) was vigorously stirred at r.t. for 16 h. The solvent was removed *in vacuo*, and the crude oil was purified by FC (SiO_2 (25 g); Et_2O/hexane 1:4; R_f ((*E*/*Z*)-**2f**) 0.33, R_f ((*E*/*Z*)-**2b**) 0.42) to give (*E*/*Z*)-**2b** (20.0 mg, 69%). Colorless oil. Purity: 94.2% (GLC). GLC: t_R ((*Z*)-**2b**) 12.96, t_R ((*E*)-**2b**) 13.14, ((*E*/*Z*) 68:32). For anal. data, see above.

But-2-ene-1,4-diylbis(4-hydroxy-2,5,6-trimethylbenzene-3,1-diyl) Diacetate (**7a**). A soln. of **5a** (238 mg, 1.0 mmol) and catalyst **4a** (43 mg, 0.05 mmol) in anh. toluene (5.5 ml) was stirred at r.t. A white precipitate (probably **7a**) appeared after 1 h. After 18 h, the solvent was removed *in vacuo* to afford a green powder, which was purified by FC (SiO_2, (50 g); CH_2Cl_2/Et_2O 9:1; R_f (**4a**) 0.72, R_f (**7a**) 0.21) to give a pale-green powder, which was subjected to a second purification by FC (SiO_2 (50 g); CH_2Cl_2/Et_2O 9:1) to give **7a** (107 mg, 49%). Colorless powder. Purity: 97.0% (HPLC). M.p. 212–213° (decomp.). HPLC: t_R (**7a**) 20.79. GLC: t_R (**5a**) 6.85, t_R (**7a**) *ca.* 15 (br.). IR (nujol): 3469*s* (br.), 2925*s*, 2855*s*, 1736*s*, 1573*w*, 1461*s*, 1374*s*, 1340*w*, 1302*m*, 1251*s*, 1225*s*, 1166*m*, 1094*w*, 1074*s*, 1052*s*, 1041*s*, 1012*w*, 969*s*, 942*m*, 909*m*. ^{1}H-NMR (400 MHz): 2.01 (*s*, Me); 2.04 (*s*, Me); 2.14 (*s*, Me); 2.32 (*s*, Ac); 3.35 (br. *s*, ArCH$_2$); 4.78 (*s*, OH); 5.58 (m_c, =CH). ESI-MS: 458.4 (100, $[M+NH_4]^+$), 441.5 (7, $[M+H]^+$). Anal. calc. for $C_{26}H_{32}O_6 \cdot H_2O$ (458.55): C 68.11, H 7.47; found: C 68.19, H 7.06.

But-2-ene-1,4-diylbis(3,5,6-trimethylbenzene-2,1,4-triyl) Tetraacetate (**7b**). A brown soln. of **5b** (299 mg, 1.0 mmol) and catalyst **4** (43 mg, 0.05 mmol) in anh. toluene (5.5 ml) was stirred at r.t. A white precipitate (**7b**) appeared after 10 min. After 18 h, Et_2O (5 ml) was added to the green mixture. After filtration over a glass frit and washing with Et_2O (5 ml), a white precipitate was isolated. The filtrate was evaporated *in vacuo*, the residue was dissolved in CH_2Cl_2 (2 ml), and Et_2O (10 ml) was layered over this soln., which led to a white precipitate after 2 d. Then, both precipitates were combined, and washed with toluene (2 ml) and Et_2O (3 ml) to give **7b** (212 mg, 81%), which is insoluble in hexane or Et_2O. Colorless powder. Purity: 97.7% (HPLC). M.p. >235°. HPLC: t_R (**7b**) 22.65. GLC: t_R (**4b**) 7.16, t_R (**7b**) 14.58.

IR (nujol): 2924*s*, 2854*s*, 1752*s*, 1461*s*, 1377*s*, 1343*w*, 1247*m*, 1241*m*, 1214*s*, 1195*s*, 1082*m*, 1066*m*, 1047*m*, 975*w*, 945*w*, 911*m*, 825*m*. ^{1}H-NMR (400 MHz): 2.00 (*s*, Ar*Me*); 2.02 (*s*, Ar*Me*); 2.05 (*s*, Ar*Me*); 2.26 (*s*, Ac); 2.33 (*s*, Ac); 3.18 (br. *s*, $ArCH_2$); 5.31 (m_c, =CH). ESI-MS: 542.5 (100, $[M+NH_4]^+$). Anal. calc. for $C_{30}H_{36}O_8 \cdot 0.5\ H_2O$ (533.62): C 67.53, H 6.99; found: C 67.86, H 6.77.

(E/Z)-But-2-ene-1,4-diylbis(oxy-2,3,6-trimethylbenzene-4,1-diyl) Diacetate (**9**). A soln. of **8a** (238 mg, 1.0 mmol) and catalyst **4a** (43 mg, 0.05 mmol) in anh. toluene (3 ml) was stirred at r.t. After 75 h, GLC analysis showed peaks at t_R 6.46 (24%, **8a**) , 6.38 (31%), 6.41 (12%), 12.46 (8%), and 12.67 (5%). According to a GLC/MS analysis, t_R 6.38 and 6.41 were assigned to the (*E*)- and (*Z*)-isomers of 2,3,6-trimethyl-4-(prop-1-enyloxy)phenyl acetate (M^+ at *m*/*z* 234), a regioisomer of **8a**. Furthermore, GLC/MS analysis showed that t_R 12.46 and 12.67 probably corresponded to the (*E*)- and (*Z*)–isomers of **9** (M^+ at *m*/*z* 440). The brown soln. was evaporated *in vacuo*, and the crude oil was purified by FC (SiO_2 (60 g); 1. Et_2O/hexane 1:4; R_f (**9**) 0.10, R_f (**8a** + other isomers) 0.52; 2. CH_2Cl_2/Et_2O 9:1) to give (*E*/*Z*)-**9** as a beige powder (67 mg, 30%). Colorless crystals could be obtained after a few days by layering hexane (20 ml) over a soln. of (*E*,*Z*)-**9** in CH_2Cl_2 (2 ml). Purity: 92.2% (GLC). M.p. 143–145°. GLC: t_R (**9**) 12.46 and 12.67 ((*E*/*Z*) or (*Z*/*E*) 63:37), t_R (**8a**) 6.46, t_R (isomers of **8a**) 6.38 and 6.41. IR (nujol): 2925*s*, 2855*s*, 1753*s*, 1662*w*, 1617*w*, 1584*m*, 1490*m*, 1463*s*, 1377*s*, 1325*m*, 1276*w*, 1227*s*, 1204*s*, 1157*w*, 1114*s*, 1104*m*, 1098*m*, 1031*w*, 1006*m*, 990*w*, 971*m*, 930*w*, 905*w*, 832*s*. ^{1}H-NMR (400 MHz): 2.05 (*s*, Me); 2.11 (*s*, Me); 2.16 (*s*, Me); 2.32 (*s*, 2 Ac); 4.53 (*d*, *J* = 2.8, OCH_2), 6.08 (m_c, =CH); 6.57 (*s*, arom. H). EI-MS: 440.2 (26, M^+), 398.2 (56, $[M-CH_2CO]^+$), 247.2 (49, $[M-Me_3C_6HO(OCOMe)]^+$), 205.1 (100, $[M-Me_3C_6HO(OCOMe)-CH_2CO]^+$). Anal. calc. for $C_{26}H_{32}O_6$ (440.53): C 70.89, H 7.32; found: C 70.45, H 7.19.

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