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Asymmetric Evans *syn*-Aldol Reactions of Terpene-Derived Enals: Scope and Limitations

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The (*E*)- and (*Z*)-terpene-based aldehydes **6b** and **6c** with a silyl ether function in the γ-position were prepared and investigated in boron-mediated asymmetric Evans aldol reactions. Screening experiments of chiral *N*-acylated oxazolidinones **7**, which are conveniently accessible from 5-methyl-5-hexenoic acid and Evans oxazolidinone auxiliaries, with various boron triflates and terpenoid neral (*Z*)-**6a** as aldehyde component, provided conditions in which highly selective formation of *syn*-aldol adduct **5a** occurred and competing C=C double bond isomerization to **10** was completely suppressed. Applying the optimized conditions to *O*-silylated aldehydes **6b** and **6c** and *N*-acyloxazolidinone derivative (*R*)-**7a** confirmed the *syn*-selectivity and gave the appropriate products *syn*-**5b**,**c** and *syn*-**21b**,**c** in good yields. In the case of neral-derived *syn* adduct **5a**, the configuration of the new stereogenic centers C-2/C-3 could be assigned as (2*R*,3*S*).

Introduction

The discovery of boron enolates[1] and silyl enol ethers[2] and their use in stereocontrolled aldol reactions 40 years ago by Mukaiyama opened a plethora of possibilities in asymmetric C–C coupling reactions and has been successfully implemented as key steps in numerous total syntheses of natural products.[3] In particular, the combination of the Mukaiyama aldol reaction with Evans oxazolidinone auxiliary led to a highly reliable and robust methodology even for complex target molecules.[4]

Although asymmetric aldol reactions with either enals[5] or aldehydes carrying alkenes[6,5a,5b] are known to proceed with a high degree of stereoselectivity, surprisingly little is known about enals derived from terpenes.[7] For these substrates one might worry about competing C=C double bond isomerization. *anti*-Aldol products from acrolein are not accessible through an anti-Evans protocol, but recently a method to overcome these difficulties was reported.[8] During our studies on gephyronic acid, we observed that 2,3,5,6-dienals are particularly sensitive towards double bond isomerization but they could be cleanly converted into the anti-Evans aldol products without any formation of the conjugated dienes.[9] Hence, we intended to install an asymmetric Evans aldol addition as key step in the synthesis of asperdiol precursors. Asperdiol (**1a**) is a 14-membered macrocyclic diterpene that was isolated together with acetate **1b** from the soft corals *Eunicea asperula* and *Eunicea tourneforti* in 1977 by Weinheimer.[10] The natural product **1** and its closely related analogues knightol (**2a**), knightol acetate (**2b**), and knightal (**3**) (Figure 1), which were isolated in 2009 by Tello from the Caribbean sea whip *Eunicea knighti*,[11] have received increasing interest due to their promising cytotoxic and antimicrobial activity.

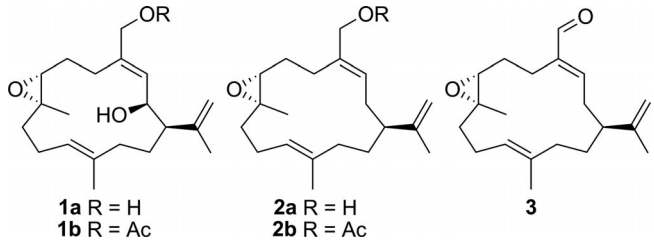

Figure 1. Asperdiol (**1a**), its analogue knightol (**2a**), their acetates **1b**, **2b** and knightal (**3**).

Five total syntheses of asperdiol (**1a**) have been reported by Still,[12] Marshall,[13] and Tius[14] utilizing a Nozaki–Hiyami–Kishi reaction,[12] sulfone alkylation,[13b] [2,3]-Wittig rearrangements[13a] or Horner–Wadsworth–Emmons (HWE) olefinations[14] as key steps for the ring closure. To gain access to potential asperdiol precursors **4**, we envisaged a synthetic strategy that was based on an Evans aldol reaction between terpene-based enals **6** and *N*-acyloxazolidinone derivatives **7**. Variation at the double bond in **6** (*E* or *Z*) and at the stereocenter in **7** (*R* or *S*) should provide different stereoisomers, also those with unnatural configuration, for structure–activity relationship (SAR) studies. A methodological study was therefore undertaken to explore the synthesis of **5** starting from enals **6** and *N*-acyloxazolidinones **7** (Scheme 1). The results are discussed below.

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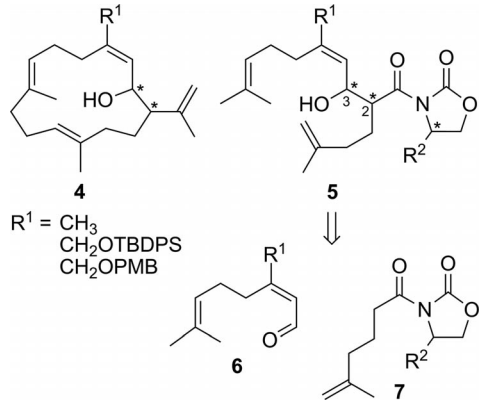


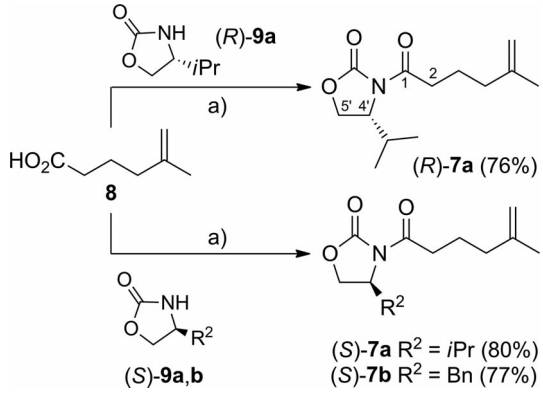
Scheme 1. Evans aldol products **5** based on fragments **6** und **7**.

Results and Discussion

The required chiral *N*-acylated oxazolidin-2-one derivatives **7** were accessible from 5-methylhex-5-enoic acid (**8**)[15] by conversion with pivaloyl chloride[16] and subsequent reaction with auxiliaries (*R*)-**9a**, (*S*)-**9a**, or (*S*)-**9b** to yield the target products (*R*)-**7a**, (*S*)-**7a**, and (*S*)-**7b** in 76, 80, and 77%, respectively (Scheme 2).

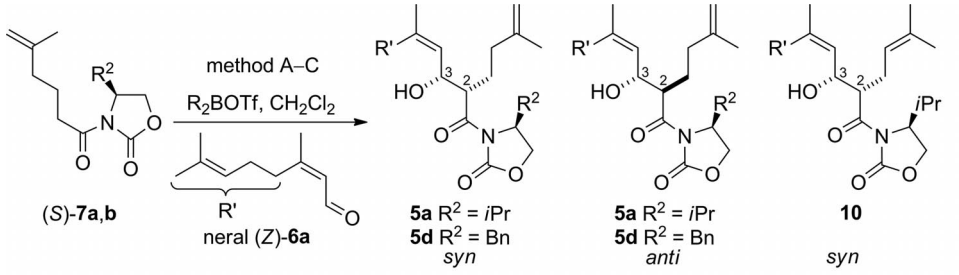
It should be noted that the use of thionyl chloride instead of pivaloyl chloride resulted in the formation of undesired byproducts (see the Supporting Information).

The *N*-acyloxazolidines (*S*)-**7** were first coupled with the terpenoid neral (*Z*)-**6a** in boron-mediated aldol reactions.[3a,17] To find optimal conditions, a series of screening experiments were undertaken; the results thereof are summarized in Table 1. Reactions of oxazolidinone (*S*)-**7b** with Bu_2BOTf and (*Z*)-**6a** at –78 °C provided the aldol addition product **5d** as an almost equimolar mixture of *syn*- and *anti*-diastereomers, and the yield could be improved from 39 to 70% by replacing Et_3N with Hünig's base (iPr_2NEt;



Scheme 2. Synthesis of *N*-acyloxazolidinones **7**. *Reagents and conditions:* (a) 1. PivCl, Et_3N, THF, 0 °C, 30 min; 2. BuLi, **9**; 3. –78 °C, 1 h; 0 °C, 1 h. Numbering for NMR assignment.

Table 1. Asymmetric aldol reactions of *N*-acyloxazolidinones (*S*)-**7a** or (*S*)-**7b** with neral (*Z*)-**6a** under various conditions.[a,b]



method A: 1) **7**, R_2BOTf, –78 °C, 5–60 min (t_1); 2) iPr_2NEt, –78 °C, 1 h; 0 °C, 15 min; 3) **+6a**, –100–0 °C, 2–21 h (t_2)
method B: 1) **7a**, BBNOTf, 0 °C, 30–120 min (t_1); 2) iPr_2NEt, 0 °C, 1 h; 3) **+6a**, 0 °C, 21 h (t_2)
method C: 1) **7a**, iPr_2NEt, 0 °C, 15 min; 2) R_2BOTf, 0 °C, 90 min (t_1); 3) **+6a**, 0 °C, 17–19 h (t_2)
workup method A–C: H_2O_2/pH 7 buffer (1:2), 0 °C, 2 h

								Product			Ratio	Yield [%]
Entry	Method	(*S*)-7	R_2BOTf	t_1 [min]	Enal	*T* [°C]	t_2 [h]	**5**	*syn*/*anti*	Yield [%]	**5a**/**10**	**5a**+**10**[c]
1	A[d]	**7b**	Bu_2BOTf	60	**6a**	–78	2	**5d**	47:53	39	–	–
2	A	**7b**	Bu_2BOTf	30	**6a**	–78	20	**5d**	52:48	70	–	–
3	A	**7a**	Bu_2BOTf	5	**6a**	–78	5.5	**5a**	100:0	69	–	–
4	A	**7a**	Bu_2BOTf	5	**6a**	–15	5.5	**5a**	100:0	70	–	–
5	A	**7a**	Bu_2BOTf	5	**6a**	0	15	**5a**	100:0	72	–	–
6	A	**7a**	Cy_2BOTf	5	**6a**	–100	21	**5a**	100:0	–	71:29	14
7	B	**7a**	BBNOTf	30	**6a**	0	21	**5a**	>95:5	–	30:70	62
8	B	**7a**	BBNOTf	45	**6a**	0	21	**5a**	>95:5	–	20:80	51
9	B	**7a**	BBNOTf	120	**6a**	0	21	**5a**	>95:5	–	6:94	59
10	C	**7a**	BBNOTf	90	**6a**	0	17	**5a**	100:0	86	–	–
11	C	**7a**	Cy_2BOTf	90	**6a**	0	19	**5a**	100:0	48	–	–

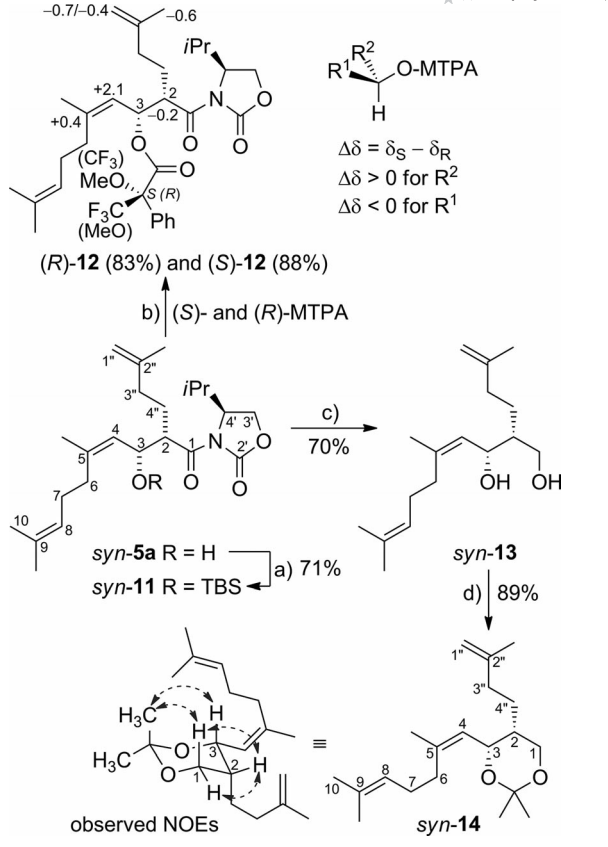
[a] Formation of boron enolate (time t_1), aldol addition (time t_2). [b] The *syn*/*anti* and isomeric ratios **5a**/**10** were determined by ^1H NMR spectroscopic analysis. [c] Compound **10** could not be separated by chromatography and was analyzed as 1,3-diol after removal of the auxiliary (see the Supporting Information). [d] Et_3N was used as base.

entries 1 and 2, method A). In contrast, oxazolidinone (*S*)-**7a** in combination with Bu_2BOTf/Hünig's base underwent a stereoselective aldol reaction with (*Z*)-**6a** affording exclusively the *syn*-aldol product **5a** in 69–72% yield regardless of the reaction temperature (entries 3–5). The use of BBNOTf, however, resulted in the formation of a 20:80 mixture of aldol product **5a** (*syn*/*anti* = 95:5) and byproduct **10** in which isomerization of the terminal double bond had taken place (entry 8, method B). This C=C double bond isomerization could be slightly suppressed by shortening the reaction time of (*S*)-**7a** with the boron reagent BBNOTf (entry 7), whereas reaction time extension promoted isomerization, providing a mixture of **5a**/**10** in a ratio of 6:94, which was isolated in 59% yield (entry 9). The ratio **5a**/**10** could be shifted in favor of **5a** by reacting (*S*)-**7a** with boron triflate Cy_2BOTf at –100 °C for 5 min (entry 6). By using an inverse addition protocol, i.e., first addition of Hünig base to oxazolidinone (*S*)-**7a** followed by addition of the boron reagent BBNOTf (Method C), not only avoided byproduct formation but also led to the selective formation of *syn*-aldol adduct **5a** in 86% yield (entry 10); thus Method C was clearly superior to Method A. Use of the inverse reaction conditions with dicyclohexylboron triflate Cy_2BOTf also gave clean adduct *syn*-**5a**, albeit with a poorer yield of 48% (entry 11).

To check the enantiomeric purity, aldol adduct *syn*-**5a** was converted into the respective TBS ether **11** (Scheme 3), which was submitted to capillary GC analysis with an achiral nonpolar stationary phase. Only a single peak was detected and the diastereoselectivity was determined to be 96% *de* (see the Supporting Information).

All attempts to determine the configuration of aldol product **5a** by X-ray single-crystal structure analysis failed (see the Supporting Information). Therefore, Mosher's method[18] was applied to determine the absolute configuration at carbon atom C-3. For this purpose, *syn*-**5a** was esterified with Mosher acid chloride (*R*)- and (*S*)-MTPA chloride to furnish the corresponding (*S*)- and (*R*)-MTPA esters (*S*)- and (*R*)-**12**, respectively (Scheme 3). Analysis of the ^1H NMR shift differences[18] indicated the absolute configuration at C-3 as *R* (see the Supporting Information for details).

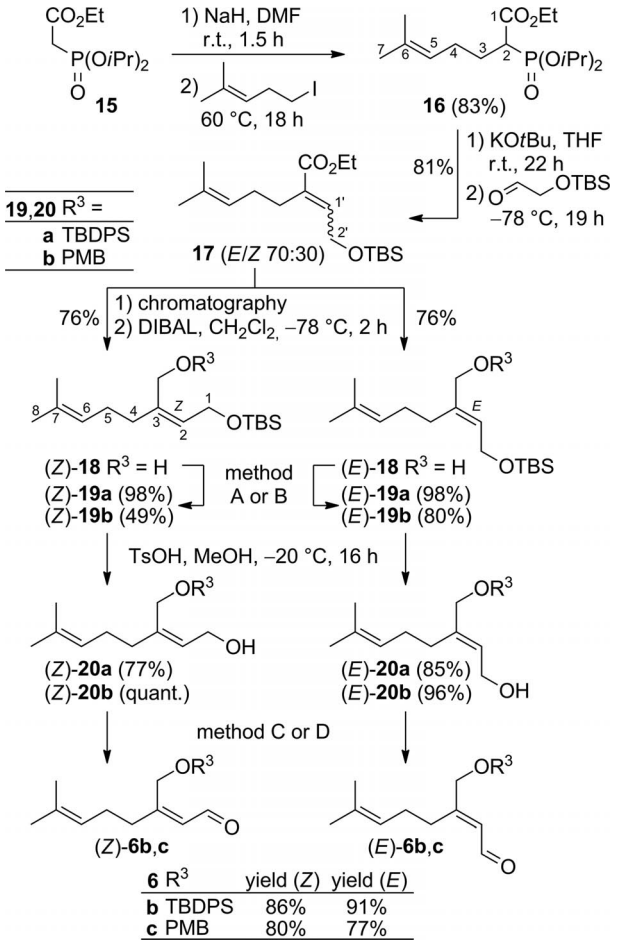
To simplify the assignment of the relative configuration at C-3/C-2, product *syn*-**5a** was converted into the conformationally fixed cyclic acetal **14**. First, **5a** was treated with $LiBH_4$ to remove the auxiliary[5a] and the resulting *syn* diol **13** was isolated in 70% yield. Subsequent reaction with 2,2-dimethoxypropane in the presence of PPTS in acetone afforded acetal **14** in 89% yield (Scheme 3). Coupling constants and NOESY correlations secured the relative stereochemical assignment. A *syn*-configured position of the protons H-2 and H_{ax} of the adjacent CH_2 group is indicated by the small coupling constant (J = 2.9 Hz). NOEs of H-2 with both H_{ax} and H_{eq} of the CH_2 group can be found. Furthermore, a NOE of the axial methyl group with H_{ax} but not H_{eq} of the CH_2 group was observed. A second NOE of the axial CH_3 group with H-3 brings the alkyl chain at C-3 in an equatorial position, thus confirming a *syn*-configuration of the stereogenic centers C-2/C-3. Consequently, a (2*S*,3*R*)-configuration was assumed for *syn*-**5a**.



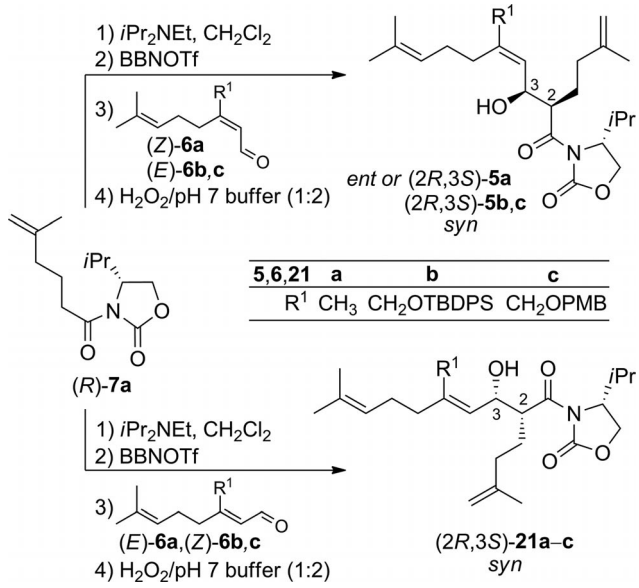
Scheme 3. Assignment of the relative and absolute configuration of aldol product **5a**. *Reagents and conditions:* (a) TBSCl, Et_3N, DMAP, DMF, room temp., 21 h; (b) (*R*)- or (*S*)-MTPACl, py, DMAP, CH_2Cl_2, room temp., 17 h; (c) **5a**, $LiBH_4$, THF/MeOH (100:1), 0 °C, 6 h; (d) $(MeO)_2CMe_2$, PPTS, acetone, room temp., 3 h. (*R*)- and (*S*)-**12** denotes the MTPA configuration; the $\Delta\delta$ values are given in units of 10^{-1} ppm. Numbering in **5a** and **14** for NMR assignment.

The γ-substituted terpene-based aldehydes (*E*)-**6b**,**c**, with oxy functionality, and their corresponding (*Z*)-isomers (*Z*)-**6b**,**c** were obtained starting from phosphonate **15**, which was α-alkylated with 5-iodo-2-methyl-2-pentene as shown in Scheme 4.

The resulting phosphonate **16** was submitted to a HWE olefination with {[*tert*-butyl(dimethyl)silyl]oxy}acetaldehyde in the presence of KO*t*Bu to yield methacrylate **17** as a 70:30 mixture of *E*/*Z* isomers (see Table S1 in the Supporting Information for studies on *E*/*Z* selectivity control). Chromatographic separation followed by DIBAL-mediated reduction provided (*E*)-allylic alcohol (*E*)-**18** or its (*Z*)-analogue (*Z*)-**18**, which were protected with TBDPSCl (Method A) or with PMBBr (Method B) to give derivatives (*E*)-**19a**,**b** and (*Z*)-**19a**,**b**, respectively. Deprotection of the TBS ether in **19** with TsOH gave allylic alcohols (*E*)- and (*Z*)-**20a**,**b**, respectively. Compounds (*E*)-**20a** and (*Z*)-**20a** were finally submitted to Dess–Martin periodinane oxidation to give (*E*)- and (*Z*)-enals **6b** in 91 and 86% yield, respectively. The corresponding PMB derivatives (*E*)- and



Scheme 4. Preparation of enals (*E*)- and (*Z*)-**6b**,**c**. *Reagents and conditions:* Method A: imidazole, TBDPSCl, DMF, room temp., 18 h; Method B: NaH, CH_2Cl_2, 0 °C, (*E*)- or (*Z*)-**18**, room temp., 1 h, PMBBr, 16 h; Method C: DMP, CH_2Cl_2, 0 °C, 1.5 h (**20a**); Method D: NMO, TPAP, CH_2Cl_2, room temp., 4 h (**20b**). Numbering for NMR assignment.



Scheme 5. Aldol reaction of *N*-acyloxazolidinone (*R*)-**7a** with (*E*)- and (*Z*)-enals **6** by following Method C.

Table 2. Boron (BBNOTf)-mediated aldol reactions of *N*-acyloxazolidinone (*R*)-**7a** with enals (*E*)- and (*Z*)-**6a**–**c** in the presence of Hünigs base iPr_2NEt according to Method C.[a]

Entry	Enal	*T* [°C]	*t* [h]	Product	*syn*/*anti*[b]	Yield [%]
1	(*Z*)-**6a**	r.t.	22	(2*R*,3*S*)-**5a**	100:0	73
2	(*E*)-**6a**	r.t.	22	(2*R*,3*S*)-**21a**	100:0	73
3	(*E*)-**6b**	r.t.	22	(2*R*,3*S*)-**5b**	100:0	64
4	(*Z*)-**6b**	r.t.	22	(2*R*,3*S*)-**21b**	85:15[c]	45
5	(*E*)-**6c**	r.t.	22	(2*R*,3*S*)-**5c**	100:0	70
6	(*Z*)-**6c**	r.t.	22	(2*R*,3*S*)-**21c**	100:0	70

[a] For details see Scheme 5 and Table 1. [b] For entries 1–3 and 5, 6 no trace of *anti* product was detected by ^1H NMR spectroscopic analysis. [c] The *syn*/*anti* or (2*R*,3*S*)/(2*S*,3*S*)-ratio of **21b** was determined by ^1H NMR spectroscopic analysis.

(*Z*)-**20b** were oxidized with *N*-methylmorpholine *N*-oxide (NMO) and tetrapropylammonium perruthenate (TPAP) to give substituted enals (*E*)- and (*Z*)-**6c** in 77 and 80%, respectively (Scheme 4).

With fragments **6b**,**c** in hand, we applied the conditions of boron-mediated aldol reaction (Method C) to the *N*-acylated oxazolidinone (*R*)-**7a** in the presence of Hünigs base. For comparison, neral (*Z*)-**6a** and geranial (*E*)-**6a** were also converted (Scheme 5). The results are summarized in Table 2.

Under these conditions, aldol coupling occurred between the boron enolate of oxazolidinone (*R*)-**7a** and both terpenoids neral [(*Z*)-**6a**] and geranial [(*E*)-**6a**] with high selectivity to give the respective (2*R*,3*S*)-aldol products **5a** and **21a** (Table 2, entries 1 and 2). The absolute and relative stereochemistry of the two stereocenters in *ent*-**5a** was assigned as described for its (2*S*,3*R*)-congener **5a** (see the Supporting Information). In the case of carbonyl components **6b**,**c**, the method was modified by slightly changing the proportion of reactants **6b**,**c**, **7a**, and BBNOTf as compared with those in Table 1. Only in the case of TBDPS silyl ether (*Z*)-**6b**, was the *anti*-configured aldol adduct (2*S*,3*S*)-**21b** detected (*syn*/*anti* ratio = 85:15) (entry 4), whereas the reaction of oxazolidinone (*R*)-**7a** with the other silylated enals (*E*)-**6b**,**c** and (*Z*)-**6c** proceeded *syn*-selectively and afforded the corresponding (2*R*,3*S*)-aldol products **5b**,**c** and **21c** in moderate to good yields (entries 3, 5, and 6).

Conclusions

We have documented a directed aldol reaction employing chiral Evans *N*-acyloxazolidinone derivatives (*S*)- and (*R*)-**7** and boron triflates in the presence of iPr_2NEt as the base. The aldol reaction was based on a methodological screening with the aldehyde component neral (*Z*)-**6a**. In addition to neral, its (*E*)-analogue geranial (*E*)-**6a** and the structurally related aldehydes (*E*)- and (*Z*)-**6b**,**c** with *O*-silyl function in the γ-position were studied. The synthesis of the latter was realized by a sequence of alkylation/HWE olefination starting from the commercially available diisopropyl (ethoxycarbonylmethyl)phosphonate **15** to give *E*/*Z*-methacrylate **17**. Chromatographic separation of the

isomers allowed a systematic preparation of both *O*-silylated (*E*)- and (*Z*)-enals **6b**,**c**. The aldol coupling between the boron enolate of **7** and terpene-based enals **6** proceeded with high selectivity to afford the appropriate *syn*-aldol adducts **5** and **21**. Under the optimized reaction conditions, the boron enolate of (*R*)-**7a** coupled with (*E*)-**6b**,**c** and (*Z*)-**6c** *syn*-selectively to give the respective aldol adducts. The aldol reaction between (*R*)-**7a** and (*Z*)-**6b**, however, also produced the *anti* adduct **21b**, with a low *syn*/*anti* ratio (85:15). The absolute and relative configuration of the newly formed stereocenters at C-2/C-3 was established for *syn*-**5a** to be (2*S*,3*R*) by the Mosher method and conversion into the conformationally rigid acetal **14**. The results demonstrate that terpene-derived enals can be submitted to boron-mediated Evans aldol reactions without any competing double bond isomerization or conjugate additions. Thus, the scope of the Evans methodology has been further extended. The obtained aldol addition products **5a**–**c** and **21a**–**c** will be further utilized for the synthesis of unnatural asperdiol derivatives. Work towards this goal is in progress in our laboratory.

Experimental Section

General: NMR spectra were recorded with a Bruker Avance 500 spectrometer with TMS as internal standard. IR spectra were recorded with a Bruker FTIR Vektor 22 spectrometer equipped with an MKII golden gate single reflection Diamant ATR system. Mass spectra were recorded with a Finnigan MAT 95 spectrometer (CI, APCI) with ammonia as carrier gas, a Varian MAT 711 (EI, 70 eV), and a Bruker Daltonics micrOTOF_Q (ESI) with nitrogen as carrier gas. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at 20 °C. Diastereoselectivities were determined by GC with a Trace GC Ultra (Thermo Electron Corporation) using an achiral stationary phase Trace TR-5MS (55 m × 0.32 mm, film thickness 0.25 μm, Thermo Scientific) with hydrogen as carrier gas. Chromatography was performed on silica gel (grain size 40–63 μm, Fluka).

All reactions were performed under nitrogen in oven-dried glassware. All reagents were used as purchased unless otherwise noted. Solvents for chromatography were distilled prior to use. THF and Et_2O were distilled from sodium/benzophenone, CH_2Cl_2, Et_3N, DMF, and pyridine from CaH_2, and MeOH from magnesium. The reactions were monitored by TLC (Macherey–Nagel 60 F_{254} plates) and visualized with an ethanolic solution of *p*-anisaldehyde and sulfuric acid.

(4*R*)-Isopropyl-3-(5-methylhex-5-enoyl)-1,3-oxazolidin-2-one [(*R*)-7a]: To a solution of (*R*)-**9a** (3.06 g, 23.7 mmol) in THF (60 mL) at –70 °C was added dropwise a solution of *n*BuLi (1.6 M in hexane, 14.8 mL, 1.52 g, 23.7 mmol), and the reaction mixture stirred at –70 °C for 30 min. In a second flask, anhydrous Et_3N (3.31 mL, 2.40 g, 23.7 mmol) and pivaloyl chloride (2.92 mL, 2.86 g, 23.7 mmol) were successively added dropwise to a solution of **8** (3.04 g, 23.7 mmol) in anhydrous Et_2O (60 mL) at 0 °C and the resulting suspension was stirred at 0 °C for 50 min. After cooling to –78 °C, the suspension of **9a**/BuLi was added dropwise and the reaction mixture stirred for 4.5 h. A saturated solution of Na_2CO_3 (100 mL) was added and the layers were separated. The aqueous layer was extracted with EtOAc (4 × 100 mL) and the combined organic layers were dried ($MgSO_4$), and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 10:1; R_f = 0.26) to give (*R*)-**7a** (4.30 g, 18.0 mmol, 76%, GC purity 98%) as a colorless oil. $[\alpha]_D^{20}$ = –72.0 (*c* = 1.00, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 and 0.92 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.73 (dd, *J* = 1.3, 1.2 Hz, 3 H, CH_3), 1.75–1.88 (m, 2 H, CH_2), 2.09 (td, *J* = 7.6, 1.3 Hz, 2 H, CH_2), 2.38 [qqd, *J* = 7.0, 7.0, 3.9 Hz, 1 H, $CH(CH_3)_2$], 2.87 (ddd, *J* = 16.9, 8.3, 6.6 Hz, 1 H, 2-H_a), 2.98 (ddd, *J* = 16.9, 8.4, 6.5 Hz, 1 H, 2-H_b), 4.21 (dd, *J* = 9.1, 3.0 Hz, 1 H, 5′-H_a), 4.27 (dd, *J* = 9.1, 8.2 Hz, 1 H, 5′-H_b), 4.44 (ddd, *J* = 8.2, 3.9, 3.0 Hz, 1 H, 4′H), 4.69–4.71 (m, 1 H, =CH_aH_b), 4.72–4.74 (m, 1 H, =CH_aH_b) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.8, 18.1 [$CH(CH_3)_2$], 22.38 (CH_2), 22.39 (CH_3), 28.5 [$CH(CH_3)_2$], 35.1 (C-2), 37.2 (CH_2), 58.5 (C-4′), 63.5 (C-5′), 110.7 (=CH_2), 145.1 (C=), 154.2 (CO), 173.3 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2964 (w), 2876 (w), 1772 (vs), 1698 (s), 1649 (w), 1486 (w), 1450 (w), 1385 (s), 1339 (w), 1301 (m), 1243 (m), 1201 (vs), 1165 (m), 1140 (w), 1121 (w), 1103 (m), 1070 (m), 1020 (m), 972 (w), 888 (m), 816 (w), 774 (w), 754 (w), 693 (w) cm^{-1}. MS (ESI): *m*/*z* = 262.1 [M + Na]$^+$, 240.2 [M + H]$^+$. HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{21}NO_3Na$ [M + Na]$^+$ 262.1414; found 262.1419. $C_{13}H_{21}NO_3$ (239.3): calcd. C 65.25, H 8.84, N 5.85; found C 65.24, H 8.91, N 5.72.

(4*S*)-Isopropyl-3-(5-methylhex-5-enoyl)-1,3-oxazolidin-2-one [(*S*)-7a]: As described above for (*R*)-**7a**, from (*S*)-**9a** (1.01 g, 7.80 mmol) in anhydrous THF (40 mL), BuLi (1.6 M in hexane, 4.68 mL, 480 mg, 7.49 mmol), **8** (1.00 g, 7.80 mmol) in anhydrous Et_2O (40 mL), Et_3N (1.09 mL, 0.79 g, 7.80 mmol), pivaloyl chloride (0.96 mL, 0.94 g, 7.80 mmol), saturated solution of Na_2CO_3 (50 mL), extraction with EtOAc (4 × 30 mL) and chromatography (R_f = 0.26) gave (*S*)-**7a** (1.26 g, 5.28 mmol, 70%, GC purity 98%) as a colorless oil. $[\alpha]_D^{20}$ = +71.8 (*c* = 1.03, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 and 0.92 [each d, *J* = 7.1 Hz, 3 H, $CH(CH_3)_2$], 1.73 (d, *J* = 0.6 Hz, 3 H, CH_3), 1.75–1.88 (m, 2 H, CH_2), 2.09 (td, *J* = 7.6, 1.2 Hz, 2 H, CH_2), 2.38 [qqd, *J* = 7.1, 7.1, 4.0 Hz, 1 H, $CH(CH_3)_2$], 2.87 (ddd, *J* = 16.9, 8.3, 6.6 Hz, 1 H, 2-H_a), 2.98 (ddd, *J* = 16.9, 8.4, 6.4 Hz, 1 H, 2-H_b), 4.21 (dd, *J* = 9.1, 3.0 Hz, 1 H, 5′-H_a), 4.27 (dd, *J* = 9.1, 8.3 Hz, 1 H, 5′-H_b), 4.44 (ddd, *J* = 8.3, 4.0, 3.0 Hz, 1 H, 4′-H), 4.69–4.71 (m, 1 H, =CH_aH_b), 4.73–4.74 (m, 1 H, =CH_aH_b) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.8, 18.1 [$CH(CH_3)_2$], 22.38 (CH_2), 22.40 (CH_3), 28.5 [$CH(CH_3)_2$], 35.1 (C-2), 37.2 (CH_2), 58.5 (C-4′), 63.5 (C-5′), 110.7 (=CH_2), 145.1 (C=), 154.2 (CO), 173.3 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2964 (w), 2937 (w), 2877 (w), 1776 (vs), 1699 (s), 1650 (w), 1606 (w), 1487 (w), 1450 (w), 1385 (s), 1339 (w), 1301 (m), 1249 (m), 1204 (s), 1167 (m), 1141 (w), 1120 (w), 1103 (w), 1069 (w), 1020 (w), 973 (w), 889 (w), 773 (w), 756 (w) cm^{-1}. MS (ESI): *m*/*z* = 262.1 [M + Na]$^+$, 240.2 [M + H]$^+$, 130.1 [AuxH$_2$]$^+$. HRMS (ESI): calcd. for $C_{13}H_{21}NO_3Na$ [M + Na]$^+$ 262.1414; found 262.1417. $C_{13}H_{21}NO_3$ (239.3): calcd. C 65.25, H 8.84, N 5.85; found C 65.03, H 8.83, N 5.86.

(4*S*)-4-Benzyl-3-(5-methylhex-5-enoyl)-1,3-oxazolidin-2-one [(*S*)-7b]: To a solution of **8** (240 mg, 1.87 mmol) in anhydrous THF (5 mL) at 0 °C were successively added dropwise anhydrous Et_3N (0.26 mL, 189 mg, 1.87 mmol) and pivaloyl chloride (0.23 mL, 226 mg, 1.87 mmol), and the resulting suspension was stirred at 0 °C for 1 h. In a second flask, a solution of *n*BuLi (1.6 M in hexane, 1.17 mL, 120 mg, 1.87 mmol) was added dropwise to a solution of (*S*)-**9b** (332 mg, 1.87 mmol) in THF (10 mL) at –78 °C, and the reaction mixture was stirred at –78 °C for 20 min prior to dropwise addition to the suspension of **8**. The reaction mixture was stirred at –78 °C for 1 h and at 0 °C for a further 1.5 h. A solution of Na_2CO_3 (50 mL) was then added and the layers were separated. The aqueous layer was extracted with EtOAc (4 × 50 mL). The

combined organic layers were dried ($MgSO_4$), and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 10:1) to give (*S*)-**7b** (415 mg, 1.14 mmol, 77%, ^1H NMR purity 95%) as a colorless solid. R_f = 0.21 (hexanes/EtOAc, 20:1); m.p. 46 °C; $[\alpha]_D^{20}$ = +63.9 (*c* = 1.06, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3), 1.80–1.92 (m, 2 H, CH_2), 2.12 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.77 (dd, *J* = 13.4, 6.7 Hz, 1 H, 5′-H_a), 2.90 (ddd, *J* = 17.2, 8.1, 6.8 Hz, 1 H, 2-H_a), 2.98 (ddd, *J* = 17.2, 8.3, 6.6 Hz, 1 H, 2-H_b), 3.30 (dd, *J* = 13.4, 3.3 Hz, 1 H, 5′-H_b), 4.17 (dd, *J* = 9.1, 3.0 Hz, 1 H, C$H_a$$H_b$Ph), 4.20 (dd, *J* = 9.1, 7.5 Hz, 1 H, C$H_a$$H_b$Ph), 4.68 (dddd, *J* = 9.7, 7.5, 3.3, 3.0 Hz, 1 H, 4′-H), 4.72 (br. s, 1 H, =C$H_a$$H_b$), 4.75 (br. s, 1 H, =C$H_a$$H_b$), 7.19–7.23 (m, 2 H, *o*-H), 7.25–7.31 (m, 1 H, *p*-H), 7.31–7.36 (m, 2 H, *m*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.2 (CH_2), 22.4 (CH_3), 35.1 (C-2), 37.2 (CH_2), 38.1 (C-5′), 55.3 (C-4′), 66.3 (*C*H_2Ph), 110.8 (=CH_2), 127.5 (C-*p*), 129.1 (C-*m*), 129.6 (C-*o*), 135.4 (C-*i*), 145.1 (C=), 153.6 (*C*O), 173.4 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3069 (w), 3029 (w), 2933 (w), 2362 (w), 1781 (vs), 1699 (m), 1649 (w), 1497 (w), 1454 (w), 1386 (m), 1352 (m), 1210 (m), 1110 (w), 1076 (w), 1052 (w), 997 (w), 890 (w), 762 (w), 740 (w), 703 (w), 521 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 287.1 (100) $[M]^+$, 269.1 (3), 256.2 (3), 232.1 (21) $[M–Me_2CCH_2]^+$, 219.1 (32) $[M–C_5H_8]^+$, 204.1 (1), 190.1 (7), 178.1 (65) $[AuxH_2]^+$, 160.1 (4), 134.1 (35), 128.0 (26) $[M–C_5H_8 – Bn]^+$, 117.1 (48), 111.1 (100) $[M–Aux]^+$, 91.0 (37) $[Bn]^+$, 69.0 (19), 55.0 (80) $[Me_2CCH_2]^+$, 41.0 (21) $[CH_2CCCH_2]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{21}NO_3Na$ [M + Na]$^+$ 310.1414; found 310.1417. $C_{17}H_{21}NO_3$ (287.35): calcd. C 71.06, H 7.37, N 4.87; found C 70.95, H 7.36, N 4.90.

Ethyl 2-(Diisopropoxyphosphoryl)-6-methylhept-5-enoate (16): In a Schlenk flask, NaH (60% suspension, 1.27 g, 52.8 mmol) was washed with *n*-hexane (2× 10 mL) and the overlaying solvent was removed by using a pipette. After removal of trace amounts of solvent under vacuum, the solid was suspended in anhydrous DMF (20 mL) and cooled to 0 °C. A solution of **15** (14.6 g, 57.9 mmol) in anhydrous DMF (20 mL) was added dropwise (low levels of gas formation), and the reaction mixture was stirred at room temp. for 1.5 h. After addition of a solution of 5-iodo-2-methyl-2-pentene (9.64 g, 45.9 mmol) in anhydrous DMF (10 mL), the reaction mixture was stirred at 60 °C for 18 h and taken up in a mixture of Et_2O (200 mL) and H_2O (100 mL) at room temp. The layers were separated and the aqueous layer was extracted with Et_2O (4× 100 mL). The combined organic layers were successively washed with H_2O and brine (200 mL each), dried ($MgSO_4$), and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 2:1; R_f = 0.20) to give **16** (12.0 g, 35.8 mmol, 78%, GC purity 96%) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.32 [d, *J* = 6.2 Hz, 6 H, $CH(CH_3)_2$], 1.34 [d, *J* = 6.2 Hz, 6 H, $CH(CH_3)_2$], 1.58 (d, *J* = 1.3 Hz, 3 H, 6-CH_3), 1.68 (d, *J* = 1.1 Hz, 3 H, 7-H), 1.79–2.09 (m, 4 H, 3-H, 4-H), 2.88 (ddd, *J* = 22.6, 10.7, 3.2 Hz, 1 H, 2-H), 4.20 (q, *J* = 7.1 Hz, 2 H, O*CH*$_2$CH$_3$), 4.71 [dqq, *J* = 12.3, 6.2, 6.2 Hz, 1 H, C*H*$(CH_3)_2$], 4.72 [dqq, *J* = 12.3, 6.2, 6.2 Hz, 1 H, C*H*$(CH_3)_2$], 5.04–5.08 (m, 1 H, 5-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (OCH_2CH_3), 17.8 (6-CH_3), 23.9 [d, *J* = 5.3 Hz, CH(*C*H$_3$)], 24.0 [d, *J* = 5.2 Hz, CH(*C*H$_3$)], 24.2 [d, *J* = 3.7 Hz, CH(*C*H$_3$)], 24.3 [d, *J* = 3.5 Hz, CH(*C*H$_3$)], 25.9 (C-7), 26.8 (d, *J* = 15.7 Hz, C-3), 27.4 (d, *J* = 4.7 Hz, C-4), 46.0 (d, *J* = 132.0 Hz, C-2), 61.3 (OCH_2CH_3), 71.2 [d, *J* = 6.8 Hz, *C*H$(CH_3)_2$], 71.4 [d, *J* = 6.8 Hz, *C*H$(CH_3)_2$], 122.9 (C-5), 133.4 (C-6), 169.6 (d, *J* = 5.0 Hz, C-1) ppm. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 20.97 ppm. FTIR (ATR): $\tilde{\nu}$ = 2979 (w), 2934 (w), 1734 (m), 1451 (w), 1374 (w), 1332 (w), 1255 (m), 1178 (w), 1143 (m), 1107 (m), 984 (vs), 888 (w), 835 (w), 771 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 334.2 (21) $[M]^+$, 292.2 (7) $[M – i\text{Pr}]^+$, 275.2 (5) $[M–O\text{i}Pr]^+$, 250.1 (27) $[M–Me_2CCHCH_2CH_2]^+$, 233.1 (18), 211.1 (28), 205.1 (22), 181.0 (10), 168.0 (100) $[M–PO(O\text{i}Pr)_2]^+$, 141.0 (9), 135.0 (3), 123.0 (13), 109.0 (6), 96.0 (15), 82.1 (17) $[Me_2CCHCH_2CH_2]^+$, 67.1 (5), 55.0 (6), 41.0 (10). MS (ESI): *m*/*z* (%) = 357.2 [M + Na]$^+$, 335.2 [M + H]$^+$, 251.1 (27) $[M–Me_2CCHCH_2CH_2 – H]^+$, 205.1. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{32}O_5P$ [M + H]$^+$ 335.1975; found 335.1969.

Ethyl (2*E*,*Z*)-2-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethylidene)-6-methylhept-5-enoate (17): A solution of **16** (9.58 g, 28.6 mmol) in anhydrous THF (20 mL) was added dropwise to a solution of freshly sublimated KO*t*Bu (3.51 g, 31.2 mmol) in anhydrous THF (60 mL) at 0 °C in a Schlenk flask, and the reaction mixture was stirred at room temp. for 19 h. After cooling to –78 °C, a solution of {[*tert*-butyl(dimethyl)silyl]oxy}acetaldehyde (4.54 g, 26.0 mmol) in anhydrous THF (20 mL) was added dropwise and the reaction mixture was stirred at –78 °C for 23 h. A saturated solution of NH_4Cl (40 mL) was then added, the layers were separated, and the aqueous layer was extracted with Et_2O (5× 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by flash chromatography on SiO_2 (hexanes/CH_2Cl_2, 5:1→1:1) to give in a first fraction (*Z*)-**17** (2.05 g, 6.29 mmol, 24%, ^1H NMR purity >95%) and in a second fraction (*E*)-**17** (4.79 g, 14.7 mmol, 56%, ^1H NMR purity >95%) as colorless oils.

(*Z*)-**17:** R_f = 0.31 (hexanes/CH_2Cl_2, 2:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.07 [s, 6 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.30 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.58 (d, *J* = 1.1 Hz, 3 H, 6-CH_3), 1.68 (d, *J* = 1.3 Hz, 3 H, 7-H), 2.09–2.15 (m, 2 H, 4-H), 2.25–2.29 (m, 2 H, 3-H), 4.19 (q, *J* = 7.1 Hz, 2 H, O*CH*$_2$CH$_3$), 4.59 (dt, *J* = 4.7, 1.4 Hz, 2 H, 2′-H), 5.10 (tqq, *J* = 7.2, 1.4, 1.4 Hz, 1 H, 5-H), 6.04 (tt, *J* = 4.7, 1.2 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.1 $[Si(CH_3)_2]$, 14.4 (OCH_2CH_3), 17.8 (Me-6), 18.5 $[SiC(CH_3)_3]$, 25.8 (C-7), 26.1 $[SiC(CH_3)_3]$, 27.8 (C-4), 33.9 (C-3), 60.4 (OCH_2CH_3), 62.4 (C-2′), 123.6 (C-5), 130.2 (C-2), 132.4 (C-6), 145.6 (C-1′), 167.4 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2959 (m), 2930 (s), 2858 (m), 2360 (m), 2342 (m), 1714 (vs), 1645 (w), 1463 (w), 1376 (w), 1255 (m), 1221 (m), 1160 (w), 1100 (s), 1061 (w), 836 (vs), 777 (m), 668 (w) cm^{-1}. MS (ESI): *m*/*z* = 349.2 [M + Na]$^+$, 195.1 [M–OTBS]$^+$, 167.1 $[C_{10}H_{15}O_2]^+$, 102.1. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{34}O_3SiNa$ [M + Na]$^+$ 349.2169; found 349.2167.

(***E***)-**17:** R_f = 0.21 (hexanes/CH_2Cl_2, 2:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.30 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.58 (d, *J* = 1.3 Hz, 3 H, 6-CH_3), 1.68 (d, *J* = 1.3 Hz, 3 H, 7-H), 2.05–2.11 (m, 2 H, 4-H), 2.26–2.29 (m, 2 H, 3-H), 4.20 (q, *J* = 7.1 Hz, 2 H, O*CH*$_2$CH$_3$), 4.34 (d, *J* = 5.8 Hz, 2 H, 2′-H), 5.10 (tqq, *J* = 7.4, 1.4, 1.4 Hz, 1 H, 5-H), 6.77 (t, *J* = 5.8 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.1 $[Si(CH_3)_2]$, 14.4 (OCH_2CH_3), 17.7 (6-CH_3), 18.5 $[SiC(CH_3)_3]$, 25.9 (C-7), 26.1 $[SiC(CH_3)_3]$, 27.61 (C-4), 27.65 (C-3), 60.5 (C-2′), 60.7 (OCH_2CH_3), 123.5 (C-5), 131.8 (C-6), 132.7 (C-2), 142.1 (C-1′), 167.6 (C-8) ppm. FTIR (ATR): $\tilde{\nu}$ = 2956 (m), 2929 (m), 2858 (m), 1713 (vs), 1650 (w), 1463 (m), 1365 (m), 1253 (s), 1165 (m), 1096 (s), 1052 (s), 1006 (w), 939 (w), 835 (vs), 776 (s), 738 (m), 672 (w) cm^{-1}. MS (ESI): *m*/*z* = 349.2 [M + Na]$^+$, 195.1 [M–OTBS]$^+$, 167.1 $[C_{10}H_{15}O_2]^+$, 139.1, 121.1. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{34}O_3SiNa$ [M + Na]$^+$ 349.2169; found 349.2162.

(2*Z*)-2-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethylidene)-6-methylhept-5-en-1-ol [(*Z*)-18]: To a solution of (*Z*)-**17** (801 mg, 2.48 mmol) in anhydrous CH_2Cl_2 (20 mL) at –78 °C was added dropwise a solution of DIBAL (1.2 M in toluene, 4.55 mL, 778 mg, 5.45 mmol) and the reaction mixture was stirred for 2 h. A saturated solution of Na/K tartrate (20 mL) was added, the layers were separated, and

the aqueous layer was extracted with Et_2O (3× 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 15:1) to give (*Z*)-**18** (536 mg, 1.88 mmol, 76%, ^1H NMR purity 95%) as a colorless oil. R_f = 0.58 (hexanes/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $SiC(CH_3)_3$], 1.60 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.09–2.17 (m, 4 H, 4-H, 5-H), 2.25 (t, *J* = 4.9 Hz, 1 H, O*H*), 4.11 (dt, *J* = 4.9, 0.7 Hz, 2 H, CH_2OH), 4.24 (d, *J* = 6.4 Hz, 2 H, 1-H), 5.11 (tqq, *J* = 6.7, 1.4, 1.4 Hz, 1 H, 6-H), 5.52 (tt, *J* = 6.4, 0.7 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.0 [$Si(CH_3)_2$], 17.9 (7-CH_3), 18.4 [$SiC(CH_3)_3$], 25.8 (C-8), 26.1 [$SiC(CH_3)_3$], 26.8, 36.0 (C-4, C-5), 59.6 (C-1), 61.3 (CH_2OH), 124.0 (C-6), 126.9 (C-2), 132.1 (C-7), 142.7 (C-3) ppm. FTIR (ATR): $\tilde{\nu}$ = 3379 (br w), 2955 (m), 2928 (m), 2856 (m), 1666 (w), 1462 (m), 1378 (m), 1361 (w), 1254 (m), 1099 (m), 1062 (s), 1006 (m), 939 (w), 833 (vs), 775 (s), 666 (w) cm^{-1}. MS (ESI): *m*/*z* = 323.2 $[M + K]^+$, 307.2 $[M + Na]^+$, 265.1 $[M – H_2O – H]^+$, 209.1 $[M – H_2O – tBu]^+$, 193.1, 167.1, 151.1 $[M – H_2O – TBS]^+$, 135.1 $[M – H_2O – OTBS]^+$, 123.1, 107.1. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{32}O_2SiNa$ $[M + Na]^+$ 307.2064; found 307.2062.

(2*E*)-2-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethylidene)-6-methylhept-5-en-1-ol [(*E*)-18]: As described above for (*Z*)-**18**, from (*E*)-**17** (309 mg, 0.95 mmol) in anhydrous CH_2Cl_2 (10 mL), a solution of DIBAL (1.2 M in toluene, 1.70 mL, 292 mg, 2.05 mmol), a saturated solution of Na/K tartrate (10 mL); chromatography gave (*E*)-**18** (202 mg, 0.71 mmol, 76%, GC purity 98%) as a colorless oil. R_f = 0.52 (hexanes/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.33 (t, *J* = 6.3 Hz, 1 H, O*H*), 1.60 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.04–2.15 (m, 4 H, 4-H, 5-H), 4.06 (dtt, *J* = 6.3, 1.4, 1.1 Hz, 2 H, CH_2OH), 4.24 (dt, *J* = 6.3, 1.1 Hz, 2 H, 1-H), 5.10 (tqq, *J* = 7.0, 1.4, 1.4 Hz, 1 H, 6-H), 5.58 (tt, *J* = 6.3, 1.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.0 [$Si(CH_3)_2$], 17.8 (7-CH_3), 18.6 [$SiC(CH_3)_3$], 25.9 (C-8), 26.1 [$SiC(CH_3)_3$], 27.3 (C-4), 28.6 (C-5), 59.9 (C-1), 66.8 (CH_2OH), 123.8 (C-6), 126.3 (C-2), 132.5 (C-7), 140.3 (C-3) ppm. FTIR (ATR): $\tilde{\nu}$ = 3350 (br w), 2954 (m), 2928 (m), 2856 (m), 1462 (m), 1377 (w), 1361 (w), 1254 (m), 1093 (s), 1062 (s), 1005 (m), 939 (w), 834 (vs), 775 (s), 665 (w) cm^{-1}. MS (ESI): *m*/*z* = 323.2 $[M + K]^+$, 307.2 $[M + Na]^+$, 265.1 $[M – H_2O – H]^+$, 193.1, 169.1, 151.1 $[M – H_2O – TBS]^+$, 135.1 $[M – H_2O – OTBS]^+$, 107.1. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{32}O_2SiNa$ $[M + Na]^+$ 307.2064; found 307.2054.

(6*E*)-2,2,10,10,11,11-Hexamethyl-6-(4-methylpent-3-enyl)-3,3-diphenyl-4,9-dioxa-3,10-disiladodec-6-ene [(*E*)-19a]: To a solution of (*E*)-**18** (197 mg, 0.69 mmol) in anhydrous DMF (10 mL) at 0 °C were successively added imidazole (104 mg, 1.52 mmol) and TBDPSCl (0.20 mL, 209 mg, 0.76 mmol), and the reaction mixture was stirred at room temp. for 18 h. A saturated solution of $NaHCO_3$ (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3× 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 50:1) to give (*E*)-**19a** (354 mg, 0.68 mmol, 98%, GC purity 97%) as a colorless oil. R_f = 0.89 (hexanes/EtOAc, 20:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 0.92 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 1.06 [s, 9 H, $Ph_2SiC(CH_3)_3$], 1.54 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.65 (d, *J* = 1.4 Hz, 3 H, 8-H), 1.94–2.01 (m, 2 H, 5-H), 2.01–2.06 (m, 2 H, 4-H), 4.09 (dt, *J* = 1.6, 1.5 Hz, 2 H, CH_2O), 4.27 (dt, *J* = 6.3, 1.4 Hz, 2 H, 1-H), 5.03 (tqq, *J* = 7.1, 1.4, 1.4 Hz, 1 H, 6-H), 5.68 (tt, *J* = 6.3, 1.6 Hz, 1 H, 2-H), 7.35–7.70 (m, 4 H, *m*-H), 7.40–7.44 (m, 2 H, *p*-H), 7.67–7.70 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.9 [$Si(CH_3)_2$], 17.8 (7-CH_3), 18.5 [$(CH_3)_2SiC(CH_3)_3$], 19.4 [$Ph_2SiC(CH_3)_3$], 25.8 (C-8), 26.1 [$(CH_3)_2SiC(CH_3)_3$], 27.0 [$Ph_2SiC(CH_3)_3$], 27.4 (C-5), 28.6 (C-4), 60.0 (C-1), 66.9 (CH_2O), 124.1 (C-6), 124.9 (C-2), 127.8 (C-*m*), 129.7 (C-*p*), 132.1 (C-7), 133.8 (C-*i*), 135.7 (C-*o*), 139.2 (C-3) ppm. FTIR (ATR): $\tilde{\nu}$ = 3071 (w), 2955 (m), 2929 (m), 2856 (m), 2361 (w), 1590 (w), 1472 (w), 1462 (w), 1428 (m), 1389 (w), 1362 (w), 1253 (m), 1189 (w), 1105 (s), 1053 (s), 1007 (m), 938 (w), 834 (vs), 775 (s), 739 (m), 701 (vs), 666 (w), 614 (w) cm^{-1}. MS (ESI): *m*/*z* = 561.3 $[M + K]^+$, 545.3 $[M + Na]^+$, 391.2 $[M–OTBS]^+$, 313.2, 281.1, 267.2 $[M–OTBDPS]^+$, 211.2, 135.1 $[M–OTBS–OTBDPS]^+$, 107.1. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{50}O_2Si_2Na$ $[M + Na]^+$ 545.3242; found 545.3227.

(6*Z*)-2,2,10,10,11,11-Hexamethyl-6-(4-methylpent-3-enyl)-3,3-diphenyl-4,9-dioxa-3,10-disiladodec-6-ene [(*Z*)-19a]: As described above for (*E*)-**19a**, from (*Z*)-**18** (483 mg, 1.70 mmol) in anhydrous DMF (10 mL), imidazole (254 mg, 3.73 mmol) and TBDPSCl (0.49 mL, 513 mg, 1.87 mmol), stirring for 14 h; a saturated solution of $NaHCO_3$ (15 mL), extraction with CH_2Cl_2 (3× 20 mL), and chromatography gave (*Z*)-**19a** (865 mg, 1.65 mmol, 97%, ^1H NMR purity 95%) as a colorless oil. R_f = 0.88 (hexanes/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = –0.01 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $Me_2SiC(CH_3)_3$], 1.04 [s, 9 H, $Ph_2SiC(CH_3)_3$], 1.59 (d, *J* = 1.1 Hz, 3 H, 7-CH_3), 1.68 (d, *J* = 1.2 Hz, 3 H, 8-H), 2.10–2.16 (m, 2 H, 5-H), 2.17–2.22 (m, 2 H, 4-H), 4.05 (dt, *J* = 6.2, 0.9 Hz, 2 H, 1-H), 4.15 (d, *J* = 1.0 Hz, 2 H, CH_2OSi), 5.11 (tqq, *J* = 6.9, 1.4, 1.4 Hz, 1 H, 6-H), 5.36 (tt, *J* = 6.2, 1.0 Hz, 1 H, 2-H), 7.36–7.45 (m, 6 H, *m*-H, *p*-H), 7.65–7.70 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.0 [$Si(CH_3)_2$], 17.9 (7-CH_3), 18.5 [$Me_2SiC(CH_3)_3$], 19.4 [$Ph_2SiC(CH_3)_3$], 25.9 (C-8), 26.1 [$Me_2SiC(CH_3)_3$], 26.8 (C-5), 26.9 [$Ph_2SiC(CH_3)_3$], 34.7 (C-4), 59.9 (C-1), 61.8 (CH_2OSi), 124.5 (C-6), 126.7 (C-2), 127.8 (C-*m*), 129.8 (C-*p*), 131.6 (C-7), 133.7 (C-*i*), 135.5 (C-*o*), 139.4 (C-3) ppm. FTIR (ATR): $\tilde{\nu}$ = 2929 (m), 2856 (m), 2360 (w), 1471 (w), 1428 (w), 1388 (w), 1361 (w), 1253 (w), 1106 (m), 1058 (s), 1006 (w), 938 (w), 833 (s), 775 (m), 738 (m), 700 (vs), 667 (w), 614 (m) cm^{-1}. MS (ESI): *m*/*z* = 545.3 $[M + Na]^+$, 391.3 $[M–OTBS]^+$, 313.2 $[M–OTBS–Ph]^+$, 281.2, 257.1, 135.1 $[M–OTBS–OTBDPS]^+$, 119.1. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{50}O_2Si_2Na$ $[M + Na]^+$ 545.3242; found 545.3240.

***tert*-Butyl[((2*E*)-3-{[(4-methoxybenzyl)oxy]-methyl}-7-methylocta-2,6-dienyl)oxy]dimethylsilane [(*E*)-19b]:** In a Schlenk flask, NaH (60% suspension, 70.4 mg, 1.76 mmol) was washed with *n*-hexane (2× 4 mL) and the overlaying solvent was removed by using a pipette. After careful removal of trace amounts of solvent under vacuum, the solid was suspended in anhydrous THF (5 mL) and cooled to 0 °C. A solution of (*E*)-**18** (251 mg, 0.88 mmol) in anhydrous THF (10 mL) was added dropwise (low levels of gas formation), and the reaction mixture stirred at room temp. for 1 h. After addition of a solution of *p*-methoxybenzylbromide (355 mg, 1.76 mmol) in anhydrous THF (5 mL), the reaction mixture was stirred for a further 16 h. Water (30 mL) was added and the layers were separated. The aqueous layer was salted out with NaCl and extracted with Et_2O (3× 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 30:1) to give (*E*)-**19b** (284 mg, 0.70 mmol, 80%, GC purity 98%) as a colorless oil. R_f = 0.35 (hexanes/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.58 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.67 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.03–2.13 (m, 4 H, 4-H, 5-H), 3.80 (s, 3 H, OMe), 3.92 (dt, *J* = 1.2, 1.0 Hz, 2 H, CH_2O), 4.26 (tt, *J* = 6.2, 1.0 Hz, 2 H, 1-H), 4.40 (s, 2 H, 1′-H), 5.09 (tqq, *J* = 7.0, 1.4, 1.4 Hz, 1 H, 6-H), 5.59 (tt, *J* = 6.1, 1.2 Hz, 1 H, 2-H), 6.86–6.89 (m, 2 H, 4′-H), 7.24–

7.28 (m, 2 H, 3′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.9 [Si(CH_3)$_2$], 17.8 (7-CH_3), 18.5 [SiC(CH_3)$_3$], 25.9 (C-8), 26.1 [SiC(CH_3)$_3$], 27.1 (C-4), 28.7 (C-5), 55.4 (OMe), 59.9 (C-1), 71.5 (C-1′), 73.7 (CH_2O), 113.9 (C-4′), 124.0 (C-6), 128.6 (C-2), 129.5 (C-3′), 130.7 (C-2′), 132.1 (C-7), 137.3 (C-3), 159.3 (C-5′) ppm. FTIR (ATR): ṽ = 2956 (w), 2928 (m), 2855 (m), 1613 (w), 1513 (m), 1470 (w), 1378 (w), 1360 (w), 1301 (w), 1248 (s), 1172 (w), 1097 (m), 1060 (m), 1037 (m), 1006 (w), 835 (s), 776 (m), 693 (w), 347 (w) cm^{-1}. MS (ESI): *m*/*z* = 443.2 [M + K]$^+$, 427.3 [M + Na]$^+$, 255.2, 121.1 [MeOPhCH$_2$]$^+$. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{40}O_3SiNa$ [M + Na]$^+$ 427.2639; found 427.2631.

***tert*-Butyl[((2*Z*)-3-{[(4-methoxybenzyl)oxy]-methyl}-7-methylocta-2,6-dienyl)oxy]dimethylsilane [(*Z*)-19b]:** As described above for (*E*)-**19b**, from NaH (60% suspension, 182 mg, 4.54 mmol) in anhydrous THF (5 mL), (*Z*)-**18** (542 mg, 1.91 mmol) in anhydrous THF (10 mL) and *p*-methoxybenzylbromide (913 mg, 4.54 mmol) in anhydrous THF (5 mL); chromatography on SiO_2 (hexanes/EtOAc, 30:1) gave (*Z*)-**19b** (378 mg, 0.93 mmol, 49%, GC purity: 95%) as a colorless oil. R_f = 0.37 (hexanes/EtOAc, 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05 [s, 6 H, Si(CH_3)$_2$], 0.89 [s, 9 H, SiC(CH_3)$_3$], 1.59 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.67 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.08–2.15 (m, 4 H, 4-H, 5-H), 3.81 (s, 3 H, OMe), 3.96 (d, *J* = 0.9 Hz, 2 H, CH_2O), 4.21 (d, *J* = 6.3 Hz, 2 H, 1-H), 4.38 (s, 2 H, 1′-H), 5.10 (tqq, *J* = 6.8, 1.4, 1.4 Hz, 1 H, 6-H), 5.52 (tt, *J* = 6.3, 0.9 Hz, 1 H, 2-H), 6.86–6.90 (m, 2 H, 4′-H), 7.24–7.27 (m, 2 H, 3′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.9 [Si(CH_3)$_2$], 17.9 (7-CH_3), 18.5 [SiC(CH_3)$_3$], 25.8 (C-8), 26.1 [SiC(CH_3)$_3$], 26.7 (C-5), 35.4 (C-4), 55.4 (OMe), 59.9 (C-1), 67.3 (CH_2O), 71.8 (C-1′), 113.9 (C-4′), 124.2 (C-6), 129.1 (C-2), 129.5 (C-3′), 130.6 (C-2′), 131.8 (C-7), 137.4 (C-3), 159.3 (C-5′) ppm. FTIR (ATR): ṽ = 2955 (m), 2928 (m), 2855 (m), 1669 (w), 1612 (w), 1586 (w), 1513 (m), 1462 (w), 1441 (w), 1379 (w), 1360 (w), 1302 (w), 1248 (s), 01173 (w), 1099 (m), 1063 (s), 1037 (m), 1006 (w), 835 (s), 776 (m), 666 (w) cm^{-1}. MS (ESI): *m*/*z* = 443.2 [M + K]$^+$, 427.3 [M + Na]$^+$, 371.3, 273.2 [M–OTBS]$^+$, 255.2, 121.1 [MeOPhCH$_2$]$^+$. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{40}O_3SiNa$ [M + Na]$^+$ 427.2639; found 427.2625.

General Procedure for the Deprotection of the TBS Ethers: To a solution of the respective silyl ether **19** (1.0 equiv.) in anhydrous MeOH at –10 °C was added *p*TsOH·H_2O (0.08 equiv.) and the reaction mixture was stirred for 14–23 h. Anhydrous Et_3N (0.2 mL) was then added and the reaction mixture was stirred for 5 min. The solvent was removed under vacuum and the residue was purified by chromatography on SiO_2 to give products **20**.

(2*E*)-3-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-7-methylocta-2,6-dien-1-ol [(*E*)-20a]: From (*E*)-**19a** (390 mg, 0.76 mmol) in anhydrous MeOH (5 mL) and *p*TsOH·H_2O (11.4 mg, 0.06 mmol), reaction time 14 h; chromatography (hexanes/EtOAc, 6:1) gave (*E*)-**20a** (313 mg, 0.76 mmol, quant., GC purity 98%) as a colorless oil. R_f = 0.33 (hexanes/EtOAc, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 [s, 9 H, SiC(CH_3)$_3$], 1.11 (t, *J* = 5.8 Hz, 1 H, O*H*), 1.53 (d, *J* = 1.3 Hz, 3 H, 7-CH_3), 1.65 (d, *J* = 1.3 Hz, 3 H, 8-H), 1.95–2.01 (m, 2 H, 5-H), 2.05–2.11 (m, 2 H, 4-H), 4.12 (d, *J* = 1.5 Hz, 2 H, CH_2O), 4.18 (1-H), 4.18 (dt, *J* = 7.1, 5.8 Hz, 2 H, 1-H), 5.03 (tqq, *J* = 7.2, 1.3, 1.3 Hz, 1 H, 6-H), 5.74–5.79 (m, 1 H, 2-H), 7.35–7.40 (m, 4 H, *m*-H), 7.40–7.45 (m, 2 H, *p*-H), 7.66–7.70 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.8 (7-CH_3), 19.4 [SiC(CH_3)$_3$], 25.8 (C-8), 26.9 [SiC(CH_3)$_3$], 27.4 (C-5), 28.2 (C-4), 59.0 (C-1), 66.7 (CH_2O), 123.5 (C-2), 123.9 (C-6), 127.8 (C-*m*), 129.8 (C-*p*), 132.6 (C-7), 133.7 (C-*i*), 135.7 (C-*o*), 141.9 (C-3) ppm. FTIR (ATR): ṽ = 3320 (br w), 3071 (w), 3049 (w), 2959 (w), 2929 (w), 2856 (m), 1672 (w), 1589 (w), 1472 (w), 1461 (w), 1427 (m), 1376 (w), 1361 (w), 1188 (w), 1107 (vs), 1090 (s), 999 (m), 822 (m), 739 (m), 700 (vs), 613 (w) cm^{-1}. MS (ESI): *m*/*z* = 431.2 [M + Na]$^+$, 135.1. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{36}O_2SiNa$ [M + Na]$^+$ 431.2377; found 431.2375.

(2*E*)-3-{[(4-Methoxybenzyl)oxy]methyl}-7-methylocta-2,6-dien-1-ol [(*E*)-20b]: From (*E*)-**19b** (277 mg, 0.68 mmol) in anhydrous MeOH (10 mL) and *p*TsOH·H_2O (9.11 mg, 0.05 mmol), reaction time 23 h, Et_3N (0.4 mL); chromatography (hexanes/EtOAc, 2:1; R_f = 0.26) gave (*E*)-**20b** (11.0 mg, 0.04 mmol, 95%, GC purity 98%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 5.4 Hz, 1 H, O*H*), 1.58 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.04–2.10 (m, 2 H, 5-H), 2.14–2.18 (m, 2 H, 4-H), 3.81 (s, 3 H, OMe), 3.94 (s, 2 H, CH_2O), 4.20 (dd, *J* = 7.0, 5.4 Hz, 2 H, 1-H), 4.42 (s, 2 H, 1′-H), 5.09 (tqq, *J* = 7.2, 1.4, 1.4 Hz, 1 H, 6-H), 5.71 (t, *J* = 7.0 Hz, 1 H, 2-H), 6.86–6.90 (m, 2 H, 4′-H), 7.25–7.28 (m, 2 H, 3′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.8 (7-CH_3), 25.8 (C-8), 27.1 (C-5), 28.4 (C-4), 55.4 (OMe), 59.0 (C-1), 71.9 (C-1′), 73.4 (CH_2O), 113.9 (C-4′), 123.9 (C-6), 126.9 (C-2), 129.5 (C-3′), 130.5 (C-2′), 132.7 (C-7), 139.7 (C-3), 159.3 (C-5′) ppm. FTIR (ATR): ṽ = 3382 (br w), 2964 (m), 2928 (m), 2854 (m), 2358 (w), 1671 (w), 1612 (m), 1586 (w), 1513 (vs), 1466 (m), 1441 (m), 1377 (w), 1302 (m), 1248 (vs), 1174 (m), 1091 (m), 1066 (m), 1036 (s), 923 (w), 820 (m), 759 (w) cm^{-1}. MS (ESI): *m*/*z* = 329.2 [M + K]$^+$, 313.2 [M + Na]$^+$, 121.1 [MeOPhCH$_2$]$^+$. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{26}O_3Na$ [M + Na]$^+$ 313.1774; found 313.1766.

(2*Z*)-3-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-7-methylocta-2,6-dien-1-ol [(*Z*)-20a]: From (*Z*)-**19a** (134 mg, 0.26 mmol) in anhydrous MeOH (10 mL) and *p*TsOH·H_2O (3.41 mg, 0.02 mmol), reaction time 23 h; chromatography (hexanes/EtOAc, 20:1→10:1) gave (*Z*)-**19a** (82.0 mg, 0.20 mmol, 76%, GC purity 98%) as a colorless oil. R_f = 0.29 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 [s, 9 H, SiC(CH_3)$_3$], 1.33 (br. s, 1 H, O*H*), 1.58 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.07–2.13 (m, 2 H, 5-H), 2.15–2.20 (m, 2 H, 4-H), 3.96 (d, *J* = 6.9 Hz, 2 H, 1-H), 4.19 (d, *J* = 1.0 Hz, 2 H, CH_2OSi), 5.09 (tqq, *J* = 6.9, 1.4, 1.4 Hz, 1 H, 6-H), 5.46 (tt, *J* = 6.9, 1.0 Hz, 1 H, 2-H), 7.37–7.41 (m, 4 H, *m*-H), 7.42–7.46 (m, 2 H, *p*-H), 7.67–7.70 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (7-CH_3), 19.3 [SiC(CH_3)$_3$], 25.8 (C-8), 26.8 (C-5), 26.9 [SiC(CH_3)$_3$], 35.0 (C-4), 58.9 (C-1), 61.8 (CH_2OSi), 124.1 (C-6), 125.8 (C-2), 127.9 (C-*m*), 129.9 (C-*p*), 131.9 (C-7), 133.5 (C-*i*), 135.8 (C-*o*), 142.1 (C-3) ppm. FTIR (ATR): ṽ = 3323 (br w), 2959 (w), 2929 (m), 2856 (m), 2360 (w), 1589 (w), 1472 (w), 1427 (m), 1389 (w), 1361 (w), 1188 (w), 1110 (s), 1071 (s), 1007 (m), 823 (m), 740 (m), 701 (vs), 615 (m) cm^{-1}. MS (ESI): *m*/*z* = 447.2 [M + K]$^+$, 431.2 [M + Na]$^+$, 391.2 [M–OH]$^+$, 313.2, 135.1, 119.1. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{36}O_2SiNa$ [M + Na]$^+$ 431.2377; found 431.2367.

(2*Z*)-3-{[(4-Methoxybenzyl)oxy]methyl}-7-methylocta-2,6-dien-1-ol [(*Z*)-20b]: From (*Z*)-**19b** (17.0 mg, 0.04 mmol) in anhydrous MeOH (3 mL) and *p*TsOH·H_2O (0.56 mg, 0.03 mmol), reaction time 23 h; chromatography (hexanes/EtOAc, 2:1; R_f = 0.31) gave (*Z*)-**20b** (11.0 mg, 0.04 mmol, 95%, GC purity: 97%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 8-H), 1.78 (br. s, 1 H, O*H*), 2.07–2.16 (m, 4 H, 4-H, 5-H), 3.81 (s, 3 H, OMe), 3.99 (s, 2 H, CH_2O), 4.11–4.15 (m, 2 H, 1-H), 4.43 (s, 2 H, 1′-H), 5.10 (tqq, *J* = 6.9, 1.4, 1.4 Hz, 1 H, 6-H), 5.67 (d, *J* = 7.0 Hz, 1 H, 2-H), 6.86–6.90 (m, 2 H, 4′-H), 7.24–7.28 (m, 2 H, 3′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (7-CH_3), 25.8 (C-8), 26.8 (C-5), 36.1 (C-4), 55.4 (OMe), 58.9 (C-1), 67.7 (CH_2O), 72.3 (C-1′), 114.0 (C-4′), 123.9 (C-6), 128.2 (C-2), 129.6 (C-3′), 130.2 (C-2′), 132.1 (C-7), 140.4 (C-3),

159.4 (C-5′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3395 (br w), 2964 (m), 2926 (m), 2854 (m), 2359 (w), 1736 (w), 1670 (w), 1612 (m), 1585 (w), 1513 (s), 1440 (m), 1377 (w), 1302 (m), 1248 (vs), 1173 (m), 1071 (m), 1035 (s), 923 (w), 820 (m) cm^{-1}. MS (ESI): *m*/*z* = 329.2 $[M + K]^+$, 313.2 $[M + Na]^+$, 121.1 $[MeOPhCH_2]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{26}O_3Na$ $[M + Na]^+$ 313.1774; found 313.1788.

(2*E*)-3-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-7-methylocta-2,6-dienal [(*E*)-6b]: To a solution of (*E*)-**20a** (335 mg, 0.82 mmol) in anhydrous CH_2Cl_2 (10 mL) at 0 °C was added DMP (522 mg, 1.23 mmol) and the reaction mixture was stirred for 1.5 h. The solvent was removed under vacuum and the residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 4:1; R_f = 0.71) to give (*E*)-**6b** (303 mg, 0.75 mmol, 91%, ^1H NMR purity 95%) as a light-yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.08 [s, 9 H, $SiC(CH_3)_3$], 1.50 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.63 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.10 (td, *J* = 7.4, 7.4 Hz, 2 H, 5-H), 2.42 (t, *J* = 7.4 Hz, 2 H, 4-H), 4.24 (d, *J* = 1.9 Hz, 2 H, CH_2O), 5.01 (tqq, *J* = 7.4, 1.4, 1.4 Hz, 1 H, 6-H), 6.38 (dt, *J* = 8.4, 1.9 Hz, 1 H, 2-H), 7.37–7.41 (m, 4 H, *m*-H), 7.43–7.47 (m, 2 H, *p*-H), 7.63–7.67 (m, 4 H, *o*-H), 10.01 (d, *J* = 8.4 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (7-CH_3), 19.4 [$SiC(CH_3)_3$], 25.7 (C-8), 26.9 [$SiC(CH_3)_3$], 28.5 (C-5), 28.6 (C-4), 66.1 (CH_2O), 122.3 (C-6), 124.7 (C-2), 128.0 (C-*m*), 130.1 (C-*p*), 132.9 (C-*i*), 134.1 (C-7), 135.6 (C-*o*), 164.8 (C-3), 191.2 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (w), 2962 (w), 2930 (w), 2857 (m), 2740 (w), 1678 (s), 1472 (w), 1428 (m), 1378 (w), 1190 (w), 1151 (w), 1112 (vs), 938 (w), 854 (w), 824 (m), 804 (w), 741 (w), 703 (m), 622 (w) cm^{-1}. MS (ESI): *m*/*z* = 445.2 $[M + K]^+$, 429.2 $[M + Na]^+$, 389.2 $[M–OH]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{34}O_2SiNa$ $[M + Na]^+$ 429.2220; found 429.2211.

(2*Z*)-3-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-7-methylocta-2,6-dienal [(*Z*)-6b]: As described above for (*E*)-**6b**, from (*Z*)-**20a** (481 mg, 1.18 mmol) and DMP (749 mg, 1.77 mmol); chromatography on SiO_2 (hexanes/EtOAc, 4:1; R_f = 0.71) gave (*Z*)-**6b** (414 mg, 1.02 mmol, 86%, ^1H NMR purity 95%) as a light-yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.06 [s, 9 H, $SiC(CH_3)_3$], 1.58 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.67 (d, *J* = 1.4 Hz, 3 H, 8-H), 2.15–2.21 (m, 2 H, 5-H), 2.32–2.36 (m, 2 H, 4-H), 4.59 (d, *J* = 1.2 Hz, 2 H, CH_2O), 5.06 (tqq, *J* = 7.1, 1.4, 1.4 Hz, 1 H, 6-H), 5.85 (dtt, *J* = 7.8, 1.2, 1.2 Hz, 1 H, 2-H), 7.37–7.42 (m, 4 H, *m*-H), 7.43–7.47 (m, 2 H, *p*-H), 7.64–7.69 (m, 4 H, *o*-H), 9.87 (d, *J* = 7.8 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (7-CH_3), 19.3 [$SiC(CH_3)_3$], 25.8 (C-8), 26.3 (C-5), 26.9 [$SiC(CH_3)_3$], 35.3 (C-4), 62.4 (CH_2O), 122.9 (C-6), 127.7 (C-2), 128.1 (C-*m*), 130.2 (C-*p*), 132.8 (C-*i*), 133.0 (C-7), 135.7 (C-*o*), 163.9 (C-3), 191.2 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (w), 3050 (w), 2961 (w), 2930 (m), 2857 (w), 1722 (w), 1678 (m), 1589 (w), 1472 (w), 1428 (m), 1378 (w), 1262 (w), 1190 (w), 1169 (w), 1113 (s), 1079 (m), 998 (w), 823 (m), 741 (m), 702 (s), 612 (w) cm^{-1}. MS (ESI): *m*/*z* = 445.2 $[M + K]^+$, 429.2 $[M + Na]^+$, 407.2 $[M + H]^+$, 389.2 $[M–OH]^+$, 327.3. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{34}O_2SiNa$ $[M + Na]^+$ 429.2220; found 429.2202.

(2*E*)-3-{[(4-Methoxybenzyl)oxy]methyl}-7-methylocta-2,6-dienal [(*E*)-6c]: To dried and ground (pestle and mortar) molecular sieves 4 Å (500 mg) was added a solution of (*E*)-**20b** (183 mg, 0.63 mmol) in anhydrous CH_2Cl_2 (5 mL) followed by addition of NMO (111 mg, 0.95 mmol) and TPAP (11.1 mg, 0.03 mmol). The suspension was stirred for 4 h and then filtered through Celite. The filter residue was washed with CH_2Cl_2 (200 mL) and the combined filtrates were concentrated under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 10:1; R_f = 0.19) to give (*E*)-**6c** (138 mg, 0.48 mmol, 77%, ^1H NMR purity 95%) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.56 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.67 (dt, *J* = 1.4, 1.4 Hz, 3 H, 8-H), 2.18–2.24 (m, 2 H, 5-H), 2.54 (t, *J* = 7.4 Hz, 2 H, 4-H), 3.81 (s, 3 H, OMe), 4.07 (d, *J* = 1.6 Hz, 2 H, CH_2O), 4.48 (s, 2 H, 1′-H), 5.09 (tqq, *J* = 7.4, 1.4, 1.4 Hz, 1 H, 6-H), 6.17 (dt, *J* = 8.0, 1.6 Hz, 1 H, 2-H), 6.88–6.91 (m, 2 H, 4′-H), 7.25–7.28 (m, 2 H, 3′-H), 9.99 (d, *J* = 8.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (7-CH_3), 25.8 (C-8), 28.1 (C-5), 28.8 (C-4), 55.4 (OMe), 72.0 (CH_2O), 72.6 (C-1′), 114.0 (C-4′), 122.3 (C-6), 126.3 (C-2), 129.5 (C-3′), 129.7 (C-2′), 134.1 (C-7), 159.5 (C-5′), 162.3 (C-3), 191.0 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2965 (w), 2933 (w), 2911 (w), 2856 (w), 2835 (w), 2744 (w), 2361 (w), 1668 (vs), 1636 (w), 1612 (m), 1585 (w), 1512 (s), 1441 (m), 1404 (m), 1378 (w), 1363 (w), 1302 (m), 1246 (vs), 1174 (m), 1149 (m), 1102 (vs), 1034 (s), 951 (w), 886 (w), 850 (m), 818 (s), 759 (w), 576 (w), 522 (w) cm^{-1}. MS (ESI): *m*/*z* = 311.2 $[M + Na]^+$, 281.3 $[M + Na – CHO]^+$, 227.0 $[M – Me_2CCHCH_2CH_2 + Na]^+$, 159.0, 121.1 $[PMB]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{24}O_3Na$ $[M + Na]^+$ 311.1618; found 311.1636.

(2*Z*)-3-{[(4-Methoxybenzyl)oxy]methyl}-7-methylocta-2,6-dienal [(*Z*)-6c]: As described above for (*E*)-**6c**, from (*Z*)-**20b** (254 mg, 0.87 mmol) in anhydrous CH_2Cl_2 (5 mL), NMO (154 mg, 1.31 mmol) and TPAP (15.4 mg, 0.04 mmol); chromatography on SiO_2 (hexanes/EtOAc, 10:1; R_f = 0.19) gave (*Z*)-**6c** (202 mg, 0.70 mmol, 80%, ^1H NMR purity 95%) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 1.4 Hz, 3 H, 7-CH_3), 1.68 (dt, *J* = 1.4, 1.4 Hz, 3 H, 8-H), 2.16–2.21 (m, 2 H, 5-H), 2.30–2.35 (m, 2 H, 4-H), 3.81 (s, 3 H, OMe), 4.39 (d, *J* = 1.2 Hz, 2 H, CH_2O), 4.49 (s, 2 H, 1′-H), 5.07 (tqq, *J* = 7.1, 1.4, 1.4 Hz, 1 H, 6-H), 5.95 (dt, *J* = 7.7, 1.2 Hz, 1 H, 2-H), 6.88–6.91 (m, 2 H, 4′-H), 7.25–7.27 (m, 2 H, 3′-H), 10.05 (d, *J* = 7.7 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (7-CH_3), 25.8 (C-8), 26.2 (C-5), 36.0 (C-4), 55.4 (OMe), 67.6 (CH_2O), 72.7 (C-1′), 114.1 (C-4′), 122.8 (C-6), 129.1 (C-2), 129.55 (C-2′), 129.63 (C-3′), 133.1 (C-7), 159.6 (C-5′), 161.8 (C-3), 191.4 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2966 (w), 2912 (w), 2856 (w), 1721 (w), 1674 (vs), 1612 (m), 1513 (s), 1441 (w), 1377 (w), 1362 (w), 1302 (w), 1247 (vs), 1174 (m), 1113 (m), 1078 (m), 1034 (m), 820 (m), 756 (w), 575 (w), 520 (w) cm^{-1}. MS (ESI): *m*/*z* = 311.2 $[M + Na]^+$, 285.3, 225.1, 209.1, 121.1 $[PMB]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{24}O_3Na$ $[M + Na]^+$ 311.1618; found 311.1634.

General Procedure for the Aldol Reaction of *N*-Acyloxazolidinones 7 with Enals 6. Method A: To a solution of (*S*)- or (*R*)-**7** (1 equiv.) in anhydrous CH_2Cl_2 at –78 °C was added dropwise Bu_2BOTf (1 M in CH_2Cl_2, 1.25 equiv.) followed by addition of iPr_2NEt (1.5 equiv.) after the time given in Table 1. The reaction mixture was stirred at –78 °C for 1 h and at 0 °C for a further 15 min. Then a solution of enal **6** (1.25 equiv.) in anhydrous CH_2Cl_2 was added dropwise, and the reaction mixture was stirred (temperature and time are given in Table 1). A mixture of pH 7 buffer and aqueous H_2O_2 (30%, 2:1) was added at 0 °C, the mixture was stirred for 1 h, and then the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The crude products were purified by column chromatography on SiO_2 (hexanes/EtOAc, 6:1).

Method B: To a solution of (*S*)-**7a** (1 equiv.) in anhydrous CH_2Cl_2 at 0 °C was added dropwise BBNOTf (0.5 M in CH_2Cl_2, 1.25 equiv.) followed by addition of iPr_2NEt (1.5 equiv.) after the time given in Table 1. The reaction mixture was stirred at 0 °C for 2 h. Then a solution of enal **6** (1.25 equiv.) in anhydrous CH_2Cl_2 was added dropwise and the reaction mixture was stirred (temperature and time are given in Table 1). A mixture of pH 7 buffer and aqueous

H_2O_2 (30%, 2:1) was added at 0 °C, the mixture was stirred for 2 h, and then the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The crude products were purified by column chromatography on SiO_2 (hexanes/EtOAc, 6:1).

Method C: To a solution of (*S*)- or (*R*)-**7a** (1 equiv.) in anhydrous CH_2Cl_2 at 0 °C was added dropwise *i*Pr_2NEt (1.5 equiv.) and the mixture was stirred for 10 min. Then BBNOTf (0.5 M in hexane, 1.25 equiv.) was added dropwise at 0 °C. After stirring for 1.5 h, a solution of **6** (1.25 equiv.) in CH_2Cl_2 was added dropwise [in the case of enals (*E*)- and (*Z*)-**6b**,**c**, 1.2 equiv. of (*R*)-**7a**, 1.2 equiv. of BBNOTf and 1 equiv. of the enal was used]. The reaction mixture was stirred (temperature and time are given in Table 1 and Table 2) then a mixture of pH 7 buffer and aqueous H_2O_2 (30%, 2:1) was added at 0 °C. The reaction mixture was stirred for 2 h, then the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The crude products were purified by column chromatography on SiO_2 (hexanes/EtOAc, 6:1).

(4*S*)-3-[(2*S*,3*R*,4*Z*)-3-Hydroxy-5,9-dimethyl-2-(3-methylbut-3-enyl)-deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [*syn*- or (2*S*,3*R*)-5a]: According to Method A, chromatography gave *syn*-**5a** (63%, ^1H NMR purity 95%) as a yellow oil; R_f = 0.26 (hexanes/EtOAc, 4:1). $[\alpha]_D^{20}$ = +18.1 (*c* = 1.05, CH_2Cl_2). ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.87 and 0.91 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.61 (d, *J* = 1.5 Hz, 3 H, 9-CH_3), 1.69 (d, *J* = 1.5 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.5, 0.9 Hz, 3 H, 2′′-CH_3), 1.72 (d, *J* = 1.5 Hz, 3 H, 5-CH_3), 1.81 (dddd, *J* = 13.3, 9.3, 7.2, 4.0 Hz, 1 H, 4′′-H_a), 1.92 (dddd, *J* = 13.3, 9.5, 9.5, 5.8 Hz, 1 H, 4′′-H_b), 1.88–2.17 (m, 7 H, 3′′-H, 6-H, 7-H, OH), 2.32 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 4.12 (ddd, *J* = 9.5, 6.4, 4.0 Hz, 1 H, 2-H), 4.17–4.22 (m, 2 H, 3′-H), 4.41 (ddd, *J* = 6.6, 4.4, 3.8 Hz, 1 H, 4′-H), 4.52 (dd, *J* = 9.1, 6.4 Hz, 1 H, 3-H), 4.66–4.68 (m, 1 H, 1′′-H_b), 4.69–4.71 (m, 1 H, 1′′-H_a), 5.12 (ddqq, *J* = 6.9, 6.9, 1.5, 1.5 Hz, 1 H, 8-H), 5.26 (dq, *J* = 9.1, 1.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 15.0 [$CH(CH_3)_2$], 17.8 (9-CH_3), 18.2 [$CH(CH_3)_2$], 22.4 (2′′-CH_3), 23.6 (5-CH_3), 25.8 (C-10), 27.0 (C-7), 27.1 (C-4′′), 29.0 [$CH(CH_3)_2$], 32.6 (C-6), 35.8 (C-3′′), 48.4 (C-2), 59.2 (C-4′), 63.7 (C-3′), 69.4 (C-3), 110.4 (C-1′′), 124.3 (C-8), 125.5 (C-4), 132.5 (C-9), 140.8 (C-5), 145.9 (C-2′′), 154.5 (C-2′), 174.9 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3495 (br w), 2965 (m), 2929 (w), 1779 (vs), 1695 (s), 1486 (w), 1449 (w), 1384 (s), 1300 (m), 1226 (m), 1201 (s), 1141 (w), 1095 (w), 1056 (w), 1019 (m), 984 (w), 888 (w), 705 (w) cm^{-1}. MS (ESI): *m*/*z* = 414.26 $[M + Na]^+$, 374.3 $[M - H_2O]^+$, 250.1. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{37}NO_4Na$ $[M + Na]^+$ 414.2615; found 414.2626.

(4*S*)-3-[(2*R*,3*R*,4*Z*)-3-Hydroxy-5,9-dimethyl-2-(3-methylbut-3-enyl)-deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [*anti*- or (2*R*,3*R*)-5a]: According to Method A, chromatography gave *anti*-**5a** (21%, 95% ^1H NMR purity) as a yellow oil; R_f = 0.23 (hexanes/EtOAc, 4:1). $[\alpha]_D^{20}$ = +25.3 (*c* = 1.06, CH_2Cl_2). ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.87 and 0.91 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.61 (d, *J* = 1.5 Hz, 3 H, 9-CH_3), 1.66 (d, *J* = 1.4 Hz, 3 H, 5-CH_3), 1.68 (d, *J* = 1.5 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.5, 0.8 Hz, 3 H, 2′′-CH_3), 1.82 (dddd, *J* = 13.3, 9.5, 7.0, 4.0 Hz, 1 H, 4′′-H_a), 1.93 (dddd, *J* = 13.3, 9.5, 9.5, 5.4 Hz, 1 H, 4′′-H_b), 1.98–2.16 (m, 7 H, 3′′-H, 6-H, 7-H, OH), 2.33 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 4.12 (ddd, *J* = 9.5, 6.1, 4.0 Hz, 1 H, 2-H), 4.18 (dd, *J* = 9.1, 4.2 Hz, 1 H, 3′-H_a), 4.20 (dd, *J* = 9.1, 6.9 Hz, 1 H, 3′-H_b), 4.42 (ddd, *J* = 6.9, 4.2, 3.8 Hz, 1 H, 4′-H), 4.55 (dd, *J* = 8.9, 6.1 Hz, 1 H, 3-H), 4.66–4.68 (m, 1 H, 1′′-H_b), 4.69–4.71 (m, 1 H, 1′′-H_a), 5.09 (ddqq, *J* = 6.9, 6.9, 1.5, 1.5 Hz, 1 H, 8-H), 5.24 (dq, *J* = 8.9, 1.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9, 18.2 [$CH(CH_3)_2$], 16.9 (5-CH_3), 17.8 (9-CH_3), 22.4 (2′′-CH_3), 25.8 (C-10), 26.9 (C-7), 27.0 (C-4′′), 28.9 (C-5′), 35.9 (C-3′′), 40.1 (C-6), 48.6 (C-2), 59.2 (C-4′), 63.6 (C-3′), 69.9 (C-3), 110.4 (C-1′′), 124.2 (C-8), 124.9 (C-4), 132.1 (C-9), 140.2 (C-5), 145.8 (C-2′′), 154.5 (C-2′), 175.0 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3492 (br w), 2965 (m), 2922 (m), 1779 (vs), 1695 (m), 1486 (w), 1449 (w), 1384 (s), 1300 (m), 1201 (s), 1141 (w), 1120 (w), 1096 (w), 1056 (w), 1020 (m), 984 (w), 888 (w), 705 (w) cm^{-1}. MS (ESI): *m*/*z* = 414.26 $[M + Na]^+$, 393.3 $[M + 2H]^+$, 374.3 $[M - H_2O]^+$, 250.1. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{37}NO_4Na$ $[M + Na]^+$ 414.2615; found 414.2614.

(4*R*)-3-[(2*R*,3*S*,4*Z*)-3-Hydroxy-5,9-dimethyl-2-(3-methylbut-3-enyl)-deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [*ent*- or (2*R*,3*S*)-5a]: Colorless oil. R_f = 0.33 (hexanes/EtOAc, 4:1). $[\alpha]_D^{20}$ = –19.2 (*c* = 1.00, CH_2Cl_2). ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.87 and 0.91 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.61 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.69 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.4, 0.8 Hz, 3 H, 2′′-CH_3), 1.72 (d, *J* = 1.4 Hz, 3 H, 5-CH_3), 1.78–1.86 (m, 1 H, 4′′-H_a), 1.88–1.97 (m, 2 H, 4′′-H_b, OH), 1.97–2.18 (m, 6 H, 3′′-H, 6-H, 7-H), 2.32 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 4.11 (ddd, *J* = 9.5, 6.3, 3.9 Hz, 1 H, 2-H), 4.17–4.22 (m, 2 H, 3′-H), 4.41 (ddd, *J* = 6.6, 4.6, 3.8 Hz, 1 H, 4′-H), 4.52 (ddd, *J* = 9.2, 6.3, 3.1 Hz, 1 H, 3-H), 4.66–4.68 (m, 1 H, 1′′-H_b), 4.69–4.71 (m, 1 H, 1′′-H_a), 5.12 (ddqq, *J* = 7.0, 7.0, 1.4, 1.4 Hz, 1 H, 8-H), 5.26 (dq, *J* = 9.2, 1.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 15.0, 18.2 [$CH(CH_3)_2$], 17.8 (9-CH_3), 22.4 (2′′-CH_3), 23.6 (5-CH_3), 25.8 (C-10), 27.0 (C-7), 27.1 (C-4′′), 29.0 [$CH(CH_3)_2$], 32.6 (C-6), 35.8 (C-3′′), 48.4 (C-2), 59.2 (C-4′), 63.6 (C-3′), 69.4 (C-3), 110.4 (C-1′′), 124.3 (C-8), 125.5 (C-4), 132.6 (C-9), 140.8 (C-5), 145.9 (C-2′′), 154.5 (C-2′), 174.9 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3495 (br w), 2965 (m), 2933 (w), 1779 (vs), 1695 (s), 1486 (w), 1450 (w), 1385 (s), 1300 (m), 1226 (m), 1200 (vs), 1141 (w), 1120 (w), 1095 (m), 1056 (w), 1018 (m), 983 (m), 887 (m), 774 (w), 756 (w), 705 (w) cm^{-1}. MS (ESI): *m*/*z* = 430.2 $[M + K]^+$, 414.26 $[M + Na]^+$, 374.3 $[M - H_2O]^+$, 250.1. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{37}NO_4Na$ $[M + Na]^+$ 414.2615; found 414.2626.

(4*R*)-3-[(2*R*,3*S*,4*E*)-5-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-3-hydroxy-9-methyl-2-(3-methylbut-3-enyl)deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [(2*R*,3*S*)-5b]: Light-yellow oil; R_f = 0.24. $[\alpha]_D^{20}$ = –22.9 (*c* = 0.99, CH_2Cl_2). ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.87 and 0.91 [each d, *J* = 7.1 Hz, 3 H, $CH(CH_3)_2$], 1.06 [s, 9 H, $SiC(CH_3)_3$], 1.54 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.65 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.4, 1.0 Hz, 3 H, 2′′-CH_3), 1.82–1.89 (m, 1 H, 4′′-H_a), 1.93–2.08 (m, 7 H, 3′′-H, 4′′-H_b, 6-H_a, 7-H, OH), 2.11–2.18 (m, 1 H, 6-H_b), 2.34 [qqd, *J* = 7.1, 7.1, 3.7 Hz, 1 H, $CH(CH_3)_2$], 4.11 (dd, *J* = 9.2, 3.7 Hz, 1 H, 3′-H_a), 4.12 (d, *J* = 1.7 Hz, 1 H, CH_2O), 4.14 (dd, *J* = 9.1, 3.7 Hz, 1 H, 3′-H_b), 4.18 (ddd, *J* = 9.4, 6.0, 3.9 Hz, 1 H, 2-H), 4.39 (ddd, *J* = 7.5, 3.7, 3.7 Hz, 1 H, 4′-H), 4.62 (d, *J* = 9.3, 6.0, 3.4 Hz, 1 H, 3-H), 4.66–4.68 (m, 1 H, 1′′-H_a), 4.69–4.71 (m, 1 H, 1′′-H_b), 5.06 (ddqq, *J* = 7.0, 7.0, 1.4, 1.4 Hz, 1 H, 8-H), 5.67 (dt, *J* = 9.3, 1.7 Hz, 1 H, 4-H), 7.37–7.45 (m, 6 H, *m*-H, *p*-H), 7.65–7.69 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9, 18.2 [$CH(CH_3)_2$], 17.8 (9-CH_3), 19.5 [$SiC(CH_3)_3$], 22.5 (2′′-CH_3), 25.7 (C-10), 27.0 [$SiC(CH_3)_3$], 27.6 (C-7), 28.6 (C-6), 29.0 [$CH(CH_3)_2$], 35.8 (C-3′′), 48.4 (C-2), 59.2 (C-4′), 63.5 (C-3′), 66.9 (CH_2O), 69.1 (C-3), 110.4 (C-1′′), 124.2 (C-4), 124.3 (C-8), 128.1 (C-*m*), 130.08 (C-*p*), 130.10 (C-*p*), 132.6 (C-9), 133.97 (C-*i*), 134.04 (C-*i*), 135.91 (C-*o*),135.92 (C-*o*), 143.1 (C-5), 145.8 (C-2′′), 154.5 (C-2′), 174.8 (C-1) ppm. FTIR (ATR):

$\tilde{\nu}$ = 3500 (br w), 3072 (w), 2963 (w), 2930 (w), 2856 (w), 2359 (w), 1781 (s), 1695 (m), 1649 (w), 1589 (w), 1448 (w), 1427 (w), 1385 (m), 1299 (w), 1226 (m), 1201 (m), 1140 (w), 1110 (s), 1055 (m), 1020 (m), 983 (w), 888 (w), 823 (m), 741 (m), 703 (vs), 611 (w), 503 (m) cm^{-1}. MS (ESI): *m*/*z* = 668.4 $[M + Na]^+$, 628.4 $[M - H_2O]^+$, 372.3, 243.2 $[C_{15}H_{19}OSi]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{39}H_{55}NO_5SiNa$ $[M + Na]^+$ 668.3742; found 668.3721.

(4*R*)-3-((2*R*,3*S*,4*E*)-3-Hydroxy-5-{[(4-methoxybenzyl)oxy]methyl}-9-methyl-2-(3-methylbut-3-enyl)-deca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(2*R*,3*S*)-5c]: Colorless oil. R_f = 0.21 (hexanes/EtOAc, 3:1). $[\alpha]_D^{20}$ = –21.1 (*c* = 1.00, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.85 and 0.88 [each d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$], 1.59 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.4, 0.9 Hz, 3 H, 2′′-CH_3), 1.82–1.89 (m, 1 H, 4′′-H_a), 1.90–2.22 (m, 8 H, 3′′-H, 4′′-H_b, 6-H, 7-H, OH), 2.31 [qqd, *J* = 6.9, 6.9, 3.8 Hz, 1 H, $CH(CH_3)_2$], 3.79 (s, 3 H, OMe), 3.86 (dd, *J* = 12.2, 1.3 Hz, 1 H, CH_aH_bO), 3.93 (dd, *J* = 12.2, 1.3 Hz, 1 H, CH_aH_bO), 4.09 (dd, *J* = 9.1, 3.5 Hz, 1 H, 3′-H_a), 4.12 (dd, *J* = 9.1, 7.6 Hz, 1 H, 3′-H_b), 4.16 (ddd, *J* = 9.5, 6.6, 3.9 Hz, 1 H, 2-H), 4.361 (ddd, *J* = 7.6, 3.8, 3.5 Hz, 1 H, 4′-H), 4.362 (d, *J* = 11.1 Hz, 1 H, OCH_aH_b), 4.39 (d, *J* = 11.1 Hz, 1 H, OCH_aH_b), 4.58 (ddd, *J* = 9.2, 6.6, 3.6 Hz, 1 H, 3-H), 4.66–4.68 (m, 1 H, 1′′-H_a), 4.69–4.71 (m, 1 H, 1′′-H_b), 5. 12 (ddqq, *J* = 7.0, 7.0, 1.4, 1.4 Hz, 1 H, 8-H), 5.52 (ddd, *J* = 9.2, 1.3, 1.3 Hz, 1 H, 4-H), 6.85–6.89 (m, 2 H, Ph), 7.24–7.27 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9, 18.2 $[CH(CH_3)_2]$, 17.8 (9-CH_3), 22.5 (2′′-CH_3), 25.8 (C-10), 27.2 (C-4′′), 27.3 (C-7), 28.8 $[CH(CH_3)_2]$, 29.0 (C-6), 35.8 (C-3′′), 48.5 (C-2), 55.6 (OMe), 59.3 (C-4′), 63.6 (C-3′), 69.3 (C-3), 72.2 (OCH_2), 73.7 (CH_2O), 110.5 (C-1′′), 114.0 (Ph), 124.3 (C-8), 127.5 (C-4), 129.7 (Ph), 131.0 (Ph), 132.7 (C-9), 141.0 (C-5), 145.8 (C-2′′), 154.6 (C-2′), 159.7 (*C*-OMe), 174.7 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3477 (br w), 2965 (w), 2913 (w), 2854 (w), 1778 (vs), 1694 (m), 1649 (w), 1612 (w), 1586 (w), 1513 (m), 1443 (w), 1385 (s), 1300 (m), 1247 (vs), 1173 (m), 1141 (w), 1097 (s), 1056 (m), 1034 (s), 983 (m), 888 (m), 820 (m), 774 (w), 756 (w), 705 (w), 637 (w), 569 (w) cm^{-1}. MS (ESI): *m*/*z* = 550.3 $[M + Na]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{45}NO_6Na$ $[M + Na]^+$ 550.3139; found 550.3142.

(4*R*)-3-[(2*R*,3*S*,4*E*)-3-Hydroxy-5,9-dimethyl-2-(3-methylbut-3-enyl)-deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [(2*R*,3*S*)-21a]: Colorless oil. R_f = 0.43 (hexanes/EtOAc, 2:1). $[\alpha]_D^{20}$ = –40.8 (*c* = 0.98, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.87 and 0.92 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.61 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.66 (d, *J* = 1.4 Hz, 3 H, 5-CH_3), 1.68 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.4, 0.9 Hz, 3 H, 2′′-CH_3), 1.79–1.86 (m, 1 H, 4′′-H_a), 1.89–1.98 (m, 1 H, 4′′-H_b), 1.98–2.13 (m, 7 H, 3′′-H, 6-H, 7-H, OH), 2.33 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 4.12 (ddd, *J* = 9.4, 6.2, 4.1 Hz, 1 H, 2-H), 4.18 (dd, *J* = 9.1, 3.8 Hz, 1 H, 3′-H_a), 4.20 (dd, *J* = 9.1, 6.9 Hz, 1 H, 3′-H_b), 4.43 (ddd, *J* = 6.9, 3.8, 3.8 Hz, 1 H, 4′-H), 4.55 (ddd, *J* = 9.0, 6.2, 3.6 Hz, 1 H, 3-H), 4.66–4.68 (m, 1 H, 1′′-H_a), 4.69–4.71 (m, 1 H, 1′′-H_b), 5.09 (ddqq, *J* = 7.0, 7.0, 1.4, 1.4 Hz, 1 H, 8-H), 5.24 (dt, *J* = 9.0, 1.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9, 18.2 $[CH(CH_3)_2]$, 16.9 (5-CH_3), 17.8 (9-CH_3), 22.4 (2′′-CH_3), 25.8 (C-10), 26.9 (C-7), 27.0 (C-4′′), 29.0 $[CH(CH_3)_2]$, 35.9 (C-3′′), 40.1 (C-6), 48.5 (C-2), 59.2 (C-4′), 63.6 (C-3′), 69.9 (C-3), 110.4 (C-1′′), 124.2 (C-8), 124.9 (C-4), 132.1 (C-9), 140.2 (C-5), 145.9 (C-2′′), 154.5 (C-2′), 175.0 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3498 (br w), 3073 (w), 2965 (m), 2926 (m), 2854 (w), 1779 (vs), 1696 (s), 1486 (w), 1450 (m), 1385 (vs), 1300 (m), 1227 (m), 1201 (vs), 1141 (w), 1121 (w), 1096 (m), 1056 (m), 1019 (m), 983 (m), 887 (m), 774 (w), 756 (w), 705 (w) cm^{-1}. MS (ESI): *m*/*z* = 414.3 $[M + Na]^+$, 374.3 $[M - H_2O]^+$, 250.1. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{37}NO_4Na$ $[M + Na]^+$ 414.2615; found 414.2615.

(4*R*)-3-[(2*R*,3*S*,4*Z*)-5-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-3-hydroxy-9-methyl-2-(3-methylbut-3-enyl)deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [*syn*-(2*R*,3*S*)-21b]: Colorless oil. R_f = 0.21 (hexanes/Et_2O, 2:1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.84 and 0.88 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.58 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.665 (dd, *J* = 1.5, 1.0 Hz, 3 H, 2′′-CH_3), 1.672 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.69–1.75 (m, 1 H, 4′′-H_a), 1.84 (dddd, *J* = 13.5, 9.5, 9.5, 5.9 Hz, 1 H, 4′′-H_b), 1.92–1.97 (m, 2 H, 3′′-H), 1.95 (d, *J* = 3.4 Hz, 1 H, O*H*), 2.01–2.19 (m, 3 H, 6-H_a, 7-H), 2.21–2.27 (m, 1 H, 6-H_b), 2.29 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 4.02 (ddd, *J* = 9.5, 6.4, 4.0 Hz, 1 H, 2-H), 4.11 (dd, *J* = 12.6, 1.1 Hz, 1 H, 5-CH_aH_bO), 4.12–4.16 (m, 2 H, 3′-H), 4.29 (dd, *J* = 12.6, 1.1 Hz, 1 H, 5-CH_aH_bO), 4.33–4.38 (m, 2 H, 4′-H, 3-H), 4.61–4.63 (m, 1 H, 1′′-H_a), 4.65–4.68 (m, 1 H, 1′′-H_b), 5.10 (ddqq, *J* = 6.9, 6.9, 1.4, 1.4 Hz, 1 H, 8-H), 5.31 (ddd, *J* = 8.9, 1.1, 1.1 Hz, 1 H, 4-H), 7.38–7.47 (m, 6 H, *m*-H, *p*-H), 7.66–7.71 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9, 18.1 $[CH(CH_3)_2]$, 17.8 (9-CH_3), 19.5 $[SiC(CH_3)_3]$, 22.4 (2′′-CH_3), 25.8 (C-10), 26.7 (C-4′′), 27.0 $[SiC(CH_3)_3]$, 27.3 (C-7), 28.9 $[CH(CH_3)_2]$, 35.0 (C-6), 35.7 (C-3′′), 48.3 (C-2), 59.1 (C-4′), 61.8 (CH_2O), 63.5 (C-3′), 68.9 (C-3), 110.4 (C-1′′), 124.3 (C-8), 126.6 (C-4), 128.08 (C-*m*), 128.13 (C-*m*), 130.1 (C-*p*), 130.2 (C-*p*), 132.1 (C-9), 133.88 (C-*i*), 133.89 (C-*i*), 136.0 (C-*o*), 136.1 (C-*o*), 142.8 (C-5), 145.7 (C-2′′), 154.4 (C-2′), 174.6 (C-1) ppm.

(4*R*)-3-[(2*S*,3*S*,4*Z*)-5-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-3-hydroxy-9-methyl-2-(3-methylbut-3-enyl)deca-4,8-dienoyl]-4-isopropyl-1,3-oxazolidin-2-one [*anti*-(2*S*,3*S*)-21b]: R_f = 0.21 (hexanes/Et_2O, 2:1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.86 and 0.91 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.07 [s, 9 H, $SiC(CH_3)_3$], 1.64 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.66 (dd, *J* = 1.4, 1.0 Hz, 3 H, 2′′-CH_3), 1.70 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.69–1.75 (m, 1 H, 4′′-H_a), 1.84 (dddd, *J* = 13.5, 9.5, 9.5, 5.9 Hz, 1 H, 4′′-H_b), 1.92–1.97 (m, 2 H, 3′′-H), 1.95 (d, *J* = 3.4 Hz, 1 H, O*H*), 2.01–2.19 (m, 3 H, 6-H_a, 7-H), 2.21–2.27 (m, 1 H, 6-H_b), 2.29 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 3.84–3.89 (m, 1 H, 3-H), 3.96–4.01 (m, 1 H, 2-H), 4.17 (dd, *J* = 9.2, 2.7 Hz, 1 H, 3′-H_a), 4.21 (dd, *J* = 9.2, 7.9 Hz, 1 H, 3′-H_b), 4.11 (dd, *J* = 12.6, 1.1 Hz, 1 H, 5-CH_aH_bO), 4.29 (dd, *J* = 12.6, 1.1 Hz, 1 H, 5-CH_aH_bO), 4.44 (ddd, *J* = 6.8, 3.83, 3.1 Hz, 1 H, 4′-H), 4.61–4.63 (m, 1 H, 1′′-H_a), 4.65–4.68 (m, 1 H, 1′′-H_b), 5.19–5.24 (m, 1 H, 8-H), 5.31 (ddd, *J* = 8.9, 1.1, 1.1 Hz, 1 H, 4-H), 7.38–7.47 (m, 6 H, *m*-H, *p*-H), 7.66–7.71 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9, 18.1 $[CH(CH_3)_2]$, 17.8 (9-CH_3), 19.5 $[SiC(CH_3)_3]$, 22.4 (2′′-CH_3), 25.8 (C-10), 26.7 (C-4′′), 27.0 $[SiC(CH_3)_3]$, 27.3 (C-7), 28.9 $[CH(CH_3)_2]$, 35.0 (C-6), 35.7 (C-3′′), 47.5 (C-2), 59.1 (C-4′), 61.8 (CH_2O), 63.5 (C-3′), 69.6 (C-3), 110.4 (C-1′′), 124.9 (C-8), 126.6 (C-4), 128.21 (C-*m*), 128.25 (C-*m*), 130.1 (C-*p*), 130.2 (C-*p*), 132.0 (C-9), 133.88 (C-*i*), 133.89 (C-*i*), 135.7 (C-*o*), 135.8 (C-*o*), 142.8 (C-5), 145.9 (C-2′′), 154.4 (C-2′), 174.6 (C-1) ppm.

***syn*/*anti*-21b (85:15):** $[\alpha]_D^{20}$ = –17.4 (*c* = 1.00, CH_2Cl_2). FTIR (ATR): $\tilde{\nu}$ = 3495 (br w), 3072 (w), 2963 (w), 2930 (m), 2856 (w), 1782 (s), 1695 (m), 1448 (w), 1427 (w), 1385 (m), 1300 (w), 1261 (w), 1202 (m), 1141 (w), 1111 (s), 1056 (s), 1018 (s), 983 (m), 888 (w), 822 (m), 798 (m), 740 (m), 702 (vs), 613 (w), 503 (s) cm^{-1}. MS (ESI): *m*/*z* = 668.4 $[M + Na]^+$, 628.4 $[M - H_2O]^+$, 561.4, 372.3 $[M - H_2O - OTBDPS]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{39}H_{55}NO_5SiNa$ $[M + Na]^+$ 668.3742; found 668.3731.

(4*R*)-3-((2*R*,3*S*,4*Z*)-3-Hydroxy-5-{[(4-methoxybenzyl)oxy]methyl}-9-methyl-2-(3-methylbut-3-enyl)deca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(2*R*,3*S*)-21c]: Colorless oil. R_f = 0.23 (hexanes/

EtOAc, 3:1). $[\alpha]_D^{20}$ = –33.0 (*c* = 0.98, CH_2Cl_2). ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.85 and 0.87 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.59 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.67 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.70 (dd, *J* = 1.4, 0.8 Hz, 3 H, 2′′-CH_3), 1.77–1.84 (m, 1 H, 4′′-H_a), 1.88–1.96 (m, 1 H, 4′′-H_b), 1.96–2.02 (m, 2 H, 3′′-H), 2.04–2.14 (m, 4 H, 6-H, 7-H), 2.28 [qqd, *J* = 7.0, 7.0, 3.9 Hz, 1 H, $CH(CH_3)_2$], 2.35 (d, *J* = 3.5 Hz, 1 H, O*H*), 3.79 (s, 3 H, OMe), 3.89 (dd, *J* = 11.3, 1.0 Hz, 1 H, CH_aH_bO), 4.06 (dd, *J* = 11.3, 1.0 Hz, 1 H, CH_aH_bO), 4.11 (ddd, *J* = 9.5, 6.5, 3.9 Hz, 1 H, 2-H), 4.13 (dd, *J* = 9.2, 4.0 Hz, 1 H, 3′-H_a), 4.15 (dd, *J* = 9.2, 6.9 Hz, 1 H, 3′-H_b), 4.37 (ddd, *J* = 6.9, 4.0, 3.9 Hz, 1 H, 4′-H), 4.38 (d, *J* = 11.3 Hz, 1 H, OCH_aH_b), 4.41 (d, *J* = 11.3 Hz, 1 H, OCH_aH_b), 4.57 (ddd, *J* = 8.7, 6.5, 3.5 Hz, 1 H, 3-H), 4.65–4.67 (m, 1 H, 1′′-H_a), 4.69–4.71 (m, 1 H, 1′′-H_b), 5.07–5.12 (m, 1 H, 8-H), 5.46 (dt, *J* = 8.7, 1.0 Hz, 1 H, 4-H), 6.85–6.89 (m, 2 H, Ph), 7.24–7.28 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 15.0, 18.1 [$CH(CH_3)_2$], 17.8 (9-CH_3), 22.4 (2′′-CH_3), 25.8 (C-10), 26.9 (C-4′′), 27.1 (C-7), 29.0 [$CH(CH_3)_2$], 35.8 (C-3′′), 36.0 (C-6), 48.4 (C-2), 55.6 (OMe), 59.1 (C-4′), 63.6 (C-3′), 67.9 (CH_2O), 69.2 (C-3), 72.6 (OCH_2), 110.4 (C-1′′), 114.0 (Ph), 124.2 (C-8), 129.0 (C-4), 129.8 (Ph), 130.9 (Ph), 132.2 (C-9), 140.7 (C-5), 145.8 (C-2′′), 154.5 (C-2′), 159.7 (*C*-OMe), 174.7 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3485 (br w), 2965 (w), 2933 (w), 291 (w), 2855 (w), 1778 (vs), 1694 (m), 1612 (w), 1586 (w), 1513 (m), 1486 (w), 1451 (w), 1385 (s), 1300 (m), 1248 (s), 1202 (s), 1174 (m), 1142 (w), 1095 (m), 1034 (m), 984 (w), 888 (w), 822 (w), 774 (w), 756 (w), 705 (w), 642 (w), 566 (w) cm^{-1}. MS (ESI): *m*/*z* = 550.3 $[M + Na]^+$, 510.3 $[M – H_2O]^+$, 492.3, 372.3 [M–AuxCO]$^+$. HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{45}NO_6Na$ $[M + Na]^+$ 550.3139; found 550.3136.

(4*S*)-3-((2*S*,3*R*,4*Z*)-3-{[*tert*-Butyl(dimethyl)silyl]oxy}-5,9-dimethyl-2-(3-methylbut-3-enyl)deca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(2*S*,3*R*)-11]: To a solution of *syn*-**5a** (38.0 mg, 0.10 mmol) in anhydrous DMF (2 mL) at 0 °C were successively added anhydrous Et_3N (0.04 mL, 29.5 mg, 0.29 mmol) and a solution of TBSCl (29.3 mg, 0.19 mmol) in anhydrous DMF (1 mL). After stirring at room temp. for 20 h, a saturated solution of $NaHCO_3$ (10 mL) was added, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 40:1; R_f = 0.27) to give **11** (36.0 mg, 0.07 mmol, 71%, ^1H NMR purity 95%) as a light-yellow oil. $[\alpha]_D^{20}$ = +27.4 (*c* = 1.01, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = –0.41 [s, 3 H, $Si(CH_3)_2$], –0.36 [s, 3 H, $Si(CH_3)_2$], 0.82 [s, 9 H, $SiC(CH_3)_3$], 0.83 and 0.87 [d, *J* = 7.1 Hz, 3 H, $CH(CH_3)_2$], 1.59 (d, *J* = 1.5 Hz, 3 H, 9-CH_3), 1.65 (d, *J* = 1.4 Hz, 3 H, 5-CH_3), 1.66–1.67 (m, 6 H, 2′′-CH_3, 10-H), 1.79–1.87 (m, 2 H, 4′′-H), 1.90–2.06 (m, 6 H, 3′′-H, 6-H, 7-H), 2.27 [qqd, *J* = 7.1, 7.1, 3.9 Hz, 1 H, $CH(CH_3)_2$], 4.09 (ddd, *J* = 8.0, 4.2, 2.8 Hz, 1 H, 2-H), 4.05 (dd, *J* = 9.2, 8.1 Hz, 1 H, 3′-H_a), 4.12 (dd, *J* = 9.2, 2.3 Hz, 1 H, 3′-H_b), 4.28 (ddd, *J* = 8.1, 3.9, 2.4 Hz, 1 H, 4′-H), 4.46 (dd, *J* = 9.4, 8.0 Hz, 1 H, 3-H), 4.60–4.62 (m, 1 H, 1′′-H_b), 4.63–4.65 (m, 1 H, 1′′-H_a), 5.07–5.12 (m, 2 H, 4-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.7 [$Si(CH_3)_2$], –3.9 [$Si(CH_3)_2$], 15.1, 18.2 [$CH(CH_3)_2$], 17.8 (9-CH_3), 18.4 [$SiC(CH_3)_3$], 22.4 (2′′-CH_3), 23.1 (5-CH_3), 25.8 (C-10), 26.0 [$SiC(CH_3)_3$], 26.8 (C-7), 27.8 (C-4′′), 29.3 [$CH(CH_3)_2$], 32.8 (C-6), 35.7 (C-3′′), 49.6 (C-2), 59.4 (C-4′), 63.5 (C-3′), 71.0 (C-3), 110.2 (C-1′′), 124.5 (C-8), 127.5 (C-4), 132.1 (C-9), 137.4 (C-5), 145.9 (C-2′′), 154.2 (C-2′), 174.2 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2960 (m), 2928 (m), 2856 (w), 1781 (s), 1694 (m), 1650 (w), 1449 (w), 1382 (m), 1299 (m), 1248 (m), 1229 (m), 1200 (m), 1057 (s), 985 (m), 940 (w), 887 (m), 834 (vs), 774 (vs), 754 (m), 731 (w), 696 (w), 666 (w), 635 (w) cm^{-1}. MS (ESI): *m*/*z* = 528.4 $[M + Na]^+$, 374.3 $[M–OTBS]^+$, 250.1. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{51}NO_4SiNa$ $[M + Na]^+$ 528.3480; found 528.3462.

(1*R*,2*Z*)-1-((1*S*)-1-{[(4*S*)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]carbonyl}-4-methylpent-4-enyl)-3,7-dimethylocta-2,6-dienyl (2*S*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoate [(*S*)-12]: To a solution of *syn*-**5a** (25.0 mg, 0.06 mmol) in anhydrous CH_2Cl_2 (2 mL) at 0 °C were successively added anhydrous pyridine (0.01 mL, 10.1 mg, 0.13 mmol), a solution of (*R*)-MTPACl (20.2 mg, 0.08 mmol) in anhydrous CH_2Cl_2 (1 mL) and DMAP (3.90 mg, 0.03 mmol). The reaction mixture was warmed to room temp. within 2 h and stirred for a further 15 h. A saturated solution of $NaHCO_3$ (10 mL) was then added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 10:1; R_f = 0.27) to give (*S*)-**12** (34.0 mg, 0.06 mmol, 88%, ^1H NMR purity 95%) as a yellow oil. $[\alpha]_D^{20}$ = +29.3 (*c* = 1.01, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 and 0.91 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.55–1.61 (m, 7 H, 2′′-CH_3, 9-CH_3, 4′′-H_a), 1.66 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.76 (d, *J* = 1.6 Hz, 3 H, 5-CH_3), 1.80–1.90 (m, 1 H, 4′′-H_b), 1.90–1.96 (m, 2 H, 3′′-H), 2.01–2.14 (m, 2 H, 7-H), 2.19–2.25 (m, 2 H, 6-H), 2.33 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 3.54 (s, 3 H, OCH_3), 4.13 (dd, *J* = 9.1, 7.7 Hz, 1 H, 3′-H_a), 4.16 (dd, *J* = 9.1, 3.1 Hz, 1 H, 3′-H_b), 4.34 (ddd, *J* = 7.7, 3.8, 3.1 Hz, 1 H, 4′-H), 4.38 (ddd, *J* = 9.7, 7.6, 3.8 Hz, 1 H, 2-H), 4.56–4.58 (m, 1 H, 1′′-H_b), 4.65–4.67 (m, 1 H, 1′′-H_a), 5.13 (ddqq, *J* = 7.1, 7.1, 1.4, 1.4 Hz, 1 H, 8-H), 5.34 (dq, *J* = 10.0, 1.6 Hz, 1 H, 4-H), 5.97 (dd, *J* = 10.0, 7.6 Hz, 1 H, 3-H), 7.33–7.38 (m, 3 H, *m*-H, *p*-H), 7.48–7.53 (m, 2 H, *o*-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8, 18.2 [$CH(CH_3)_2$], 17.7 (9-CH_3), 22.3 (2′′-CH_3), 23.5 (5-CH_3), 25.8 (C-10), 26.7 (C-7), 26.8 (C-4′′), 28.7 [$CH(CH_3)_2$], 32.6 (C-6), 34.9 (C-3′′), 45.9 (C-2), 55.6 (q, *J* = 1.6 Hz, OCH_3), 59.1 (C-4′), 63.2 (C-3′), 73.8 (C-3), 84.4 (q, *J* = 27.6 Hz, CCF_3), 110.7 (C-1′′), 119.9 (C-4), 123.5 (q, *J* = 288.3 Hz, CF_3), 123.9 (C-8), 127.4 (C-*o*), 128.4 (C-*m*), 129.6 (C-*p*), 132.2 (C-9), 132.7 (C-*i*), 144.65 (C-5), 144.69 (C-2′′), 153.8 (C-2′), 165.6 (*C*O), 172.7 (C-1) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –71.32 ppm. FTIR (ATR): $\tilde{\nu}$ = 2966 (w), 1780 (vs), 1747 (m), 1697 (m), 1488 (w), 1451 (w), 1385 (m), 1299 (m), 1269 (m), 1234 (s), 1169 (vs), 1121 (m), 1081 (m), 1056 (w), 1017 (m), 989 (m), 964 (w), 926 (w), 891 (w), 816 (w), 766 (w), 718 (m), 697 (w), 640 (w) cm^{-1}. MS (ESI): *m*/*z* = 630.3 $[M + Na]^+$, 396.3, 374.3 [M – MPTA]$^+$. HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{44}F_3NO_6Na$ $[M + Na]^+$ 630.3013; found 630.3001.

(1*R*,2*Z*)-1-((1*S*)-1-{[(4*S*)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]carbonyl}-4-methylpent-4-enyl)-3,7-dimethylocta-2,6-dienyl (2*R*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoate [(*R*)-12]: Obtained as described above from *syn*-**5a** (25.0 mg, 0.06 mmol) in anhydrous CH_2Cl_2 (2 mL), anhydrous pyridine (0.01 mL, 10.1 mg, 0.13 mmol), (*S*)-MTPACl (20.2 mg, 0.08 mmol) in anhydrous CH_2Cl_2 (1 mL) and DMAP (3.90 mg, 0.03 mmol) to give (*R*)-**12** (32.0 mg, 0.05 mmol, 83%, ^1H NMR purity 95%) as a yellow oil. R_f = 0.27. $[\alpha]_D^{20}$ = +105.3 (*c* = 1.00, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 and 0.90 [each d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.64 (d, *J* = 1.4 Hz, 3 H, 9-CH_3), 1.67 (d, *J* = 1.4 Hz, 3 H, 2′′-CH_3), 1.69 (d, *J* = 1.4 Hz, 3 H, 10-H), 1.72 (d, *J* = 1.3 Hz, 3 H, 5-CH_3), 1.70–1.75 (m, 1 H, 4′′-H_a), 1.91–2.18 (m, 5 H, 3′′-H, 7-H, 4′′-H_b), 2.19–2.27 (m, 2 H, 6-H), 2.33 [qqd, *J* = 7.0, 7.0, 3.8 Hz, 1 H, $CH(CH_3)_2$], 3.53 (s, 3 H, OCH_3), 4.11 (dd, *J* = 9.1, 8.0 Hz, 1 H, 3′-H_a), 4.15 (dd, *J* = 9.1, 2.7 Hz, 1 H, 3′-H_b), 4.27 (ddd, *J* = 8.0, 3.8, 2.7 Hz, 1 H, 4′-H), 4.40 (ddd, *J* = 9.6, 6.7, 3.7 Hz, 1 H, 2-H), 4.63–4.65 (m, 1 H, 1′′-H_b), 4.69–4.71 (m, 1 H, 1′′-H_a), 5.13 (dq, *J* = 9.8, 1.3 Hz, 1 H, 4-H), 5.16 (ddqq, *J* = 7.1, 7.1, 1.4, 1.4 Hz,

1 H, 8-H), 5.94 (dd, J = 9.8, 6.9 Hz, 1 H, 3-H), 7.34–7.40 (m, 3 H, *m*-H, *p*-H), 7.44–7.48 (m, 2 H, *o*-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9, 18.2 [CH(CH_3)$_2$], 17.8 (9-CH_3), 22.3 (2′′-CH_3), 23.4 (5-CH_3), 25.8 (C-10), 26.6 (C-4′′), 26.7 (C-7), 28.7 [CH(CH$_3$)$_2$], 32.6 (C-6), 35.1 (C-3′′), 45.8 (C-2), 55.7 (q, J = 1.5 Hz, OCH_3), 59.1 (C-4′), 63.3 (C-3′), 74.1 (C-3), 84.8 (q, J = 27.6 Hz, CCF$_3$), 110.8 (C-1′′), 119.6 (C-4), 123.4 (q, J = 288.7 Hz, CF_3), 124.0 (C-8), 127.6 (C-*o*), 128.4 (C-*m*), 129.7 (C-*p*), 132.1 (C-9), 132.4 (C-*i*), 144.4 (C-5), 144.7 (C-2′′), 154.0 (C-2′), 165.7 (CO), 172.6 (C-1) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –71.51 ppm. FTIR (ATR): $\tilde{\nu}$ = 2966 (w), 1779 (vs), 1747 (m), 1697 (m), 1487 (w), 1451 (m), 1385 (m), 1299 (m), 1237 (m), 1169 (vs), 1121 (m), 1082 (w), 1056 (w), 1016 (m), 989 (m), 922 (w), 890 (w), 765 (w), 718 (m), 698 (w), 641 (w) cm^{-1}. MS (ESI): m/z = 630.3 [M + Na]$^+$, 396.3, 374.3 [M–MPTA]$^+$. HRMS (ESI): m/z calcd. for $C_{33}H_{44}F_3NO_6Na$ [M + Na]$^+$ 630.3013; found 630.3007.

(4*Z*)-5,9-Dimethyl-2-(3-methylbut-3-enyl)deca-4,8-diene-1,3-diol (13): To a solution of **5a** (228 mg, 0.58 mmol, *syn*/*anti* = 95:5 by ^{1}H NMR) in anhydrous THF/anhydrous MeOH (10:0.1 mL) at 0 °C was added dropwise a solution of $LiBH_4$ (4 M in THF, 0.44 mL, 38.0 mg, 1.75 mmol) and the reaction mixture was stirred for 3 h. A saturated solution of $NaHCO_3$ (10 mL) was added, the layers were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 4:1) to give a 95:5 *syn*/*anti* mixture of **13** (108 mg, 0.41 mmol, 70%, GC purity 98%) as a colorless oil.

***syn*-13:** R_f = 0.24. $[a]_D^{20}$ = –10.8 (c = 0.99, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.49–1.55 (m, 2 H, 4′′-H), 1.61 (d, J = 1.5 Hz, 3 H, 9-CH_3), 1.69 (d, J = 1.5 Hz, 3 H, 10-H), 1.71 (dd, J = 1.4, 0.9 Hz, 3 H, 2′′-CH_3), 1.77 (d, J = 1.5 Hz, 3 H, 5-CH_3), 1.75–1.82 (m, 1 H, 2-H), 1.97–2.20 (m, 7 H, 3′′-H, 6-H, 7-H, OH), 2.70–2.75 (m, 1 H, CH_2OH), 3.69 (ddd, J = 10.8, 4.9, 3.9 Hz, 1 H, CH_aH_bOH), 3.80 (ddd, J = 10.8, 7.7, 3.5 Hz, 1 H, CH_aH_bOH), 4.58 (ddd, J = 9.3, 4.2, 1.5 Hz, 1 H, 3-H), 4.68–4.70 (m, 1 H, 1′′-H_b), 4.70–4.73 (m, 1 H, 1′′-H_a), 5.12 (ddqq, J = 7.3, 7.3, 1.5, 1.5 Hz, 1 H, 8-H), 5.41 (dq, J = 9.4, 1.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 17.8 (9-CH_3), 22.5 (2′′-CH_3), 23.7 (5-CH_3), 24.3 (C-4′′), 25.8 (C-10), 26.5 (C-7), 32.4 (C-6), 35.7 (C-3′′), 44.5 (C-2), 64.3 (CH_2OH), 71.4 (C-3), 110.3 (C-1′′), 124.0 (C-8), 125.3 (C-4), 132.8 (C-9), 140.4 (C-5), 145.8 (C-2′′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3334 (br m), 3072 (w), 2967 (m), 2934 (m), 2912 (s), 2881 (m), 2858 (m), 2359 (w), 1649 (w), 1451 (s), 1376 (s), 1109 (w), 1094 (w), 1033 (s), 986 (s), 884 (vs), 846 (w), 817 (w), 763 (w) cm^{-1}. MS (EI): m/z (%) = 266.1 (4) [M]$^+$, 248.2 (5) [M – H_2O]$^+$, 235.2 (5) [M – H_2O (×2)]$^+$, 217.2 (6) [M – H_2O – CH_2OH]$^+$, 194.2 (6), 179.1 (5), 153.1 (8) [$C_{10}H_{17}O$]$^+$, 135.1 (21), 128.1 (12) [C_9H_{15}]$^+$, 109.1 (24), 109.1 (24), 95.1 (66) [C_7H_{12}]$^+$, 81.1 (32), 69.1 (100) [Me_2CCHCH_2]$^+$, 59.0 (30), 41.0 (38) [allyl]$^+$. HRMS (EI): m/z calcd. for $C_{17}H_{30}O_2$ [M]$^+$ 266.2246; found 266.2251.

***anti*-13:** R_f = 0.24. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.49–1.55 (m, 2 H, 4′′-H), 1.60 (d, J = 1.1 Hz, 3 H, 9-CH_3), 1.69 (d, J = 1.5 Hz, 3 H, 10-H), 1.71 (dd, J = 1.4, 0.9 Hz, 3 H, 2′′-CH_3), 1.77 (d, J = 1.5 Hz, 3 H, 5-CH_3), 1.82–1.88 (m, 1 H, 2-H), 1.97–2.20 (m, 7 H, 3′′-H, 6-H, 7-H, OH), 2.54–2.59 (m, 1 H, CH_2OH), 3.61–3.66 (m, 1 H, CH_aH_bOH), 3.72–3.78 (m, 1 H, CH_aH_bOH), 4.52–4.57 (m, 1 H, 3-H), 4.68–4.70 (m, 1 H, 1′′-H_b), 4.70–4.73 (m, 1 H, 1′′-H_a), 5.14 (ddqq, J = 7.4, 7.4, 1.4, 1.4 Hz, 1 H, 8-H), 5.41 (dq, J = 9.4, 1.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 17.9 (9-CH_3), 22.5 (2′′-CH_3), 23.7 (5-CH_3), 25.6 (C-4′′), 25.9 (C-10), 26.5 (C-7), 32.3 (C-6), 35.7 (C-3′′), 46.0 (C-2), 64.3 (CH_2OH), 71.0 (C-3), 110.3 (C-1′′), 122.7 (C-8), 125.4 (C-4), 132.8 (C-9), 140.4 (C-5), 145.8 (C-2′′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3334 (br m), 3072 (w), 2965 (m), 2916 (s), 2359 (w), 1649 (w), 1446 (s), 1376 (s), 1274 (w), 1095 (w), 1031 (s), 885 (vs), 844 (w) cm^{-1}.

4-[(1*Z*)-2,6-Dimethylhepta-1,5-dienyl]-2,2-dimethyl-5-(3-methylbut-3-enyl)-1,3-dioxane (14): To a solution of **13** (71.0 mg, 0.27 mmol, *syn*/*anti* = 95:5 by ^{1}H NMR) in anhydrous acetone (3 mL) at room temp. were added dimethoxypropane (0.30 mL, 250 mg, 2.40 mmol) and PPTS (3.35 mg, 0.01 mmol). After stirring for 2 h, the solvent was removed under vacuum and the residue was purified by chromatography on SiO_2 (hexanes/EtOAc, 4:1 and 2 vol.-% Et_3N) to give a 95:5 *syn*/*anti* mixture of **14** (74.0 mg, 0.24 mmol, 91%, GC purity 98%) as a colorless oil.

***syn*-14:** R_f = 0.85 (hexanes/EtOAc, 2:1). $[a]_D^{20}$ = –15.3 (c = 1.03, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.22–1.28 (m, 1 H, 2-H), 1.32 (q, J = 0.8 Hz, 3 H, CH_3-eq), 1.44 (q, J = 0.8 Hz, 3 H, CH_3-ax), 1.61 (d, J = 1.4 Hz, 3 H, 9-CH_3), 1.62–1.67 (m, 1 H, 4′′-H_a), 1.68 (d, J = 1.4 Hz, 3 H, 10-H), 1.71 (dd, J = 1.4, 0.8 Hz, 3 H, 2′′-CH_3), 1.74 (dd, J = 1.5, 0.6 Hz, 3 H, 5-CH_3), 1.82 (dddd, J = 13.7, 9.4, 9.4, 5.3 Hz, 1 H, 4′′-H_b), 1.95 (dddd, J = 14.5, 9.4, 6.7, 1.5 Hz, 1 H, 3′′-H_a), 2.00–2.16 (m, 5 H, 3′′-H_b, 6-H, 7-H), 3.72 (dd, J = 11.8, 1.9 Hz, 1 H, $CH_{eq}H_{ax}O$), 3.98 (ddd, J = 11.8, 2.9, 1.2 Hz, 1 H, $CH_{eq}H_{ax}O$), 4.67–4.68 (m, 1 H, 1′′-H_b), 4.69–4.70 (m, 1 H, 1′′-H_a), 4.75 (ddd, J = 8.0, 2.8, 0.6 Hz, 1 H, 3-H), 5.12 (ddqq, J = 6.9, 6.9, 1.4, 1.4 Hz, 1 H, 8-H), 5.23 (dq, J = 8.0, 1.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 17.8 (9-CH_3), 19.5 (CH_3-ax), 22.3 (C-4′′), 22.5 (2′′-CH_3), 23.5 (5-CH_3), 25.8 (C-10), 27.0 (C-7), 29.9 (CH_3-eq), 33.0 (C-6), 36.1 (C-3′′), 38.5 (C-2), 63.2 (CH_2O), 69.7 (C-3), 98.8 (Me$_2C$), 110.1 (C-1′′), 124.3 (C-8), 125.0 (C-4), 132.2 (C-9), 138.7 (C-5), 146.5 (C-2′′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (w), 2991 (m), 2967 (m), 2936 (m), 2856 (m), 2359 (w), 1670 (w), 1649 (w), 1452 (m), 1378 (s), 1274 (w), 1241 (m), 1196 (vs), 1160 (s), 1129 (s), 1085 (m), 1064 (m), 1035 (w), 982 (m), 917 (m), 885 (s), 839 (w), 741 (w) cm^{-1}. MS (EI): m/z (%) = 306.2 (1) [M]$^+$, 291.2 (1) [M – Me]$^+$, 263.2 (1) [M–CMe_2]$^+$, 248.2 (9) [M–Me_2COH]$^+$, 231.2 (4) [M–Me_2CO_2]$^+$, 205.2 (3), 194.2 (9), 178.1 (6), 168.1 (12), 153.1 (8) [nerol]$^+$, 135.1 (21) [$C_{10}H_{15}$]$^+$, 123.1 (11) [C_9H_{15}]$^+$, 109.1 (31), 95.1 (100) [C_7H_{11}]$^+$, 81.1 (74) [C_6H_9]$^+$, 69.1 (86) [Me_2CCHCH_2]$^+$, 59.0 (49) [Me_2COH]$^+$, 41.0 (40) [allyl]$^+$, 29.0 (6). HRMS (EI): m/z calcd. for $C_{20}H_{34}O_2$ [M]$^+$ 306.2559; found 306.2562.

***anti*-14:** R_f = 0.85 (hexanes/EtOAc, 2:1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.22–1.28 (m, 1 H, 2-H), 1.33 (q, J = 0.8 Hz, 3 H, CH_3-eq), 1.44 (q, J = 0.8 Hz, 3 H, CH_3-ax), 1.64 (d, J = 1.2 Hz, 3 H, 9-CH_3), 1.62–1.67 (m, 1 H, 4′′-H_a), 1.69 (d, J = 1.4 Hz, 3 H, 10-H), 1.71 (dd, J = 1.4, 0.8 Hz, 3 H, 2′′-CH_3), 1.74 (dd, J = 1.5, 0.6 Hz, 3 H, 5-CH_3), 1.82 (dddd, J = 13.7, 9.4, 9.4, 5.3 Hz, 1 H, 4′′-H_b), 1.95 (dddd, J = 14.5, 9.4, 6.7, 1.5 Hz, 1 H, 3′′-H_a), 2.00–2.16 (m, 4 H, 3′′-H_b, 6-H, 7-H_a), 2.44–2.48 (m, 1 H, 7-H_b), 3.65 (dd, J = 11.6, 1.8 Hz, 1 H, $CH_{eq}H_{ax}O$), 3.92 (ddd, J = 11.6, 2.9, 1.3 Hz, 1 H, $CH_{eq}H_{ax}O$), 4.67–4.68 (m, 1 H, 1′′-H_b), 4.69–4.70 (m, 1 H, 1′′-H_a), 4.77 (dd, J = 8.0, 2.8 Hz, 1 H, 3-H), 5.08 (ddqq, J = 7.4, 7.4, 1.4, 1.4 Hz, 1 H, 8-H), 5.23 (dq, J = 8.0, 1.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 17.9 (9-CH_3), 19.4 (CH_3-ax), 22.3 (C-4′′), 22.5 (2′′-CH_3), 23.2 (5-CH_3), 25.9 (C-10), 27.0 (C-7), 30.0 (CH_3-eq), 33.0 (C-6), 36.1 (C-3′′), 39.5 (C-2), 62.9 (CH_2O), 69.4 (C-3), 98.7 (Me$_2C$), 110.1 (C-1′′), 123.6 (C-8), 125.2 (C-4), 133.4 (C-9), 138.6 (C-5), 146.6 (C-2′′) ppm.

Supporting Information (see footnote on the first page of this article): Further experimental results, Mosher method, GC and NOESY spectra for configuration assignment as well as NMR spectra of all new compounds.

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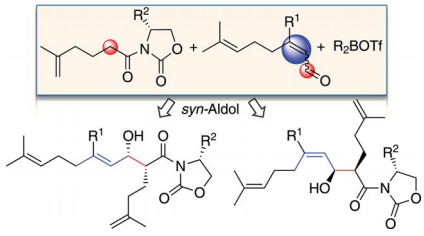
The asymmetric Evans aldol reaction could be successfully applied to terpene-based (*E*)- and (*Z*)-aldehydes and *N*-acyloxazolidinones, giving *syn*-aldol adducts with high selectivity. Isomerization at the double bond was not observed.



Keywords: Aldol reactions / Terpenoids / Boron / C–C coupling / Configuration determination

