Samarium Iodide-Promoted Asymmetric Reformatsky Reaction of 3-(2-Haloacyl)-2-oxazolidinones with Enals

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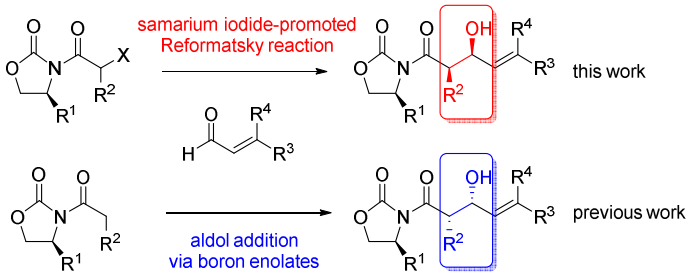
Supporting Information

ABSTRACT: 3-(2-Haloacyl)-2-oxazolidinones were shown to react with enals in an asymmetric SmI_2-promoted Reformatsky reaction to give stereochemically well-defined 3-hydroxy-4-alkenyl- and 3-hydroxy-2-methyl-4-alkenyl imides. Chirality transfer of the Evans (*S*)-oxazolidinone unit via a Zimmerman-Traxler-like transition state resulted in Reformatsky products with a relative *syn*-configuration. The absolute configuration of compounds obtained is opposite to the corresponding products obtained via aldol addition of boron enolates to enals using the same Evans oxazolidinones.

KEYWORDS: asymmetric synthesis, C-C coupling, Reformatsky reaction, Evans auxiliary, samarium

Graphical abstract



■ INTRODUCTION

In 1977 Kagan discovered samarium(II) iodide as a powerful single electron reducing agent, that mediates both radical and ionic reactions.[1] This finding led to its broad applications in organic synthesis. Prominent examples of SmI_2-mediated reactions are pinacol-type couplings, radical alkene-alkyne couplings, aldol-type reactions, Barbier, Grignard and Reformatsky reactions.[2] While Reformatsky reactions of α-bromo esters and α-bromo ketones in the presence of SmI_2 to the corresponding β-hydroxy esters have been already reported by Kagan,[3] the first intramolecular asymmetric variant has been studied by Molander.[4] Much later, the first intermolecular asymmetric samarium Reformatsky reactions were developed by Fukuzawa utilizing α-bromoacetyl-2-oxazolidinones as source of chirality.[5–7] Skrydstrup employed *N*-acyloxazolidinones as acyl radical equivalents in SmI_2-promoted couplings to *N*-acrylamides.[8] In Reformatsky reactions with α-haloacetyl-2-oxazolidinones the substrate scope was further extended by Burke towards α-aminoaldehydes paving the way for pharmacologically relevant isostatine and dolaisoleucine.[9] Despite these impressive results, progress in asymmetric intermolecular samarium Reformatsky reactions is still slow,[10] in particular enals were only rarely employed as electrophilic substrates.[11–13] Such stereoselective cross couplings would be interesting, because the resulting β-hydroxy-γ-alkenyl-ketones (amides, esters or acids) are subunits of natural products such as eremofortin F,[14] stellatolide H,[15] stellettapeptins A and B,[16] mohangic acids,[17] ieodomycin C,[18] or largazole[19] (Figure 1). Furthermore, they are valuable synthetic scaffolds for the synthesis of complex target molecules, as was exemplified in the total synthesis of pleuraspiroketals A, B,[20] (–)-clavosolide A, B,[21] bistramide K,[22] solomonamide,[23] azaspirene,[24] dolatrienoic acid,[7] and ferrulactone.[25] The β-hydroxy-γ-alkenyl-ketone unit has been previously accessed via stereoselective aldol reactions using Evans oxazolidinones.[26–29]

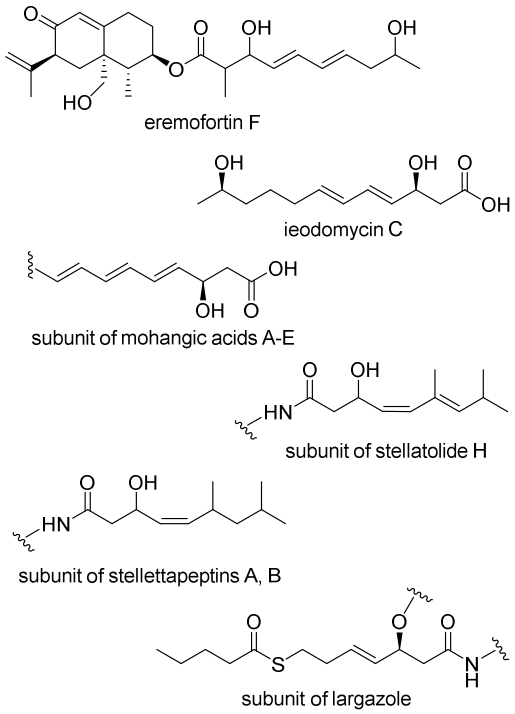


Figure 1. Natural compounds or subunits of natural compounds containing the β-hydroxy-γ-alkenyl-ketone (amide, ester or acid) residue

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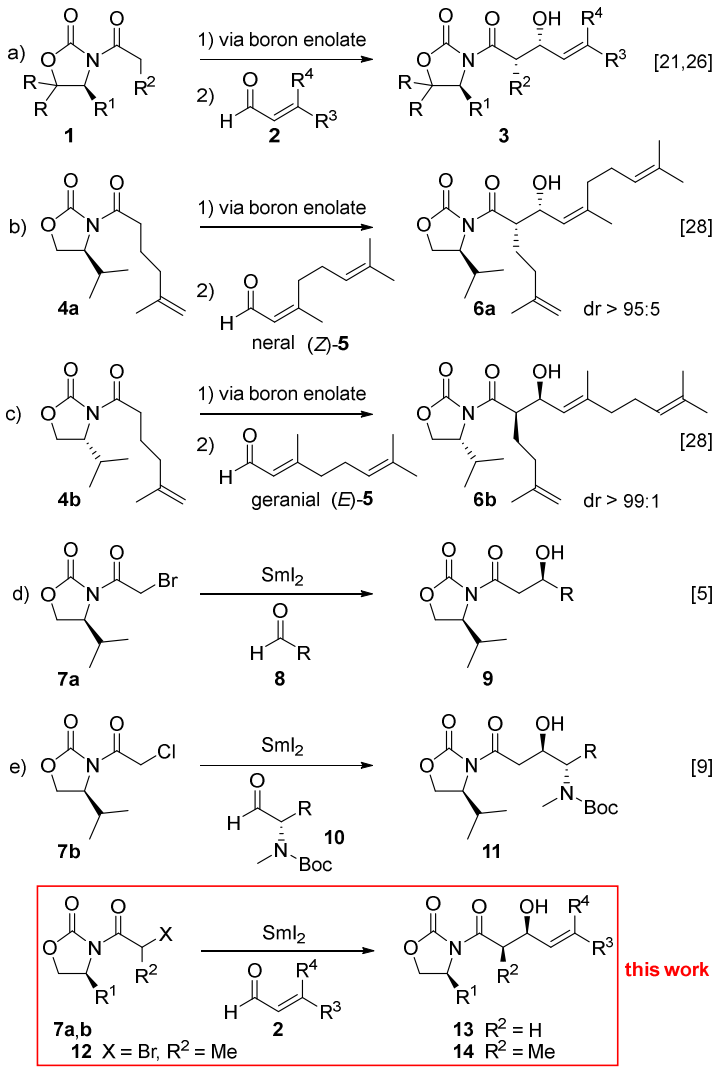
Regarding chirality transfer, these studies revealed that the aldol addition of boron enolates strongly favoured the *syn*-aldol products and the stereogenic centre at C-4 of the oxazolidinone directed the hydroxy group to the opposite face,[21,26,28] while the *E*- or *Z*-configuration of the enal had almost no influence on the stereochemical outcome of the C–C coupling (Scheme 1, routes a-c).[28] In contrast, the samarium Reformatsky reactions reported by Fukuzawa[5] and Burke[9] provided the β-hydroxyimides lacking an α-substituent with the hydroxy group and the stereodirecting isopropyl moiety of the Evans auxiliary positioned on the same side (Scheme 1, routes d,e). Thus, it was our intention to probe the suitability of enals as substrates in such samarium Reformatsky reactions. We were particularly interested in terpene-derived enals, which might enable the C–C coupling with complementary stereocontrol as compared to the boron aldol reaction.[28]

Scheme 1. Selected C–C coupling reactions from the literature and the current work

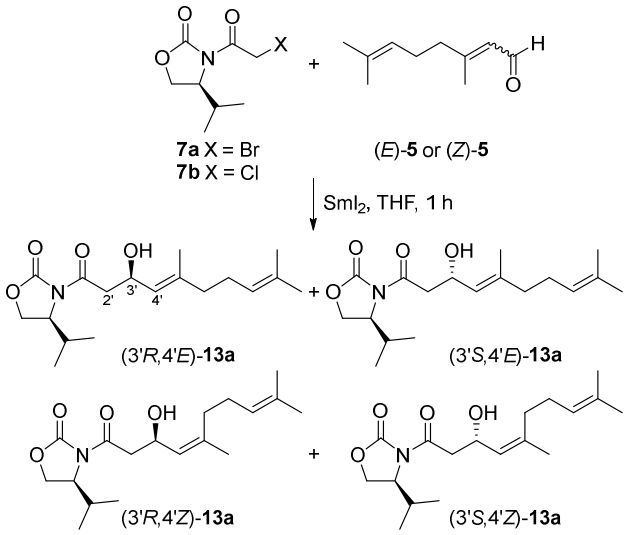


In addition, we were curious about the chirality transfer to the α-substituent in the *N*-acyl chain (C-2'). In the current manuscript we demonstrate the successful implementation of aliphatic and aryl-substituted enals in the SmI_2-promoted Reformatsky reaction and elucidate the stereocontrol at the α-position. Moreover, by using the Evans oxazolidinone auxiliary with the same configuration as in reaction a) in Scheme 1, *syn*-β-hydroxy-γ-alkenyl-imides are obtained, which are stereocomplementary to the boron-enolate-derived aldol products (Scheme 1). The results are discussed below.

■ RESULTS AND DISCUSSION

Reformatsky Reactions of Terpene Enals (*E*)- and (*Z*)-5. Initially, Reformatsky reactions were carried out with 3-(2-haloacetyl)oxazolidinones **7a**,**b**[30,31] and geranial (*E*)-**5** and neral (*Z*)-**5**.[31,32] The results are summarized in Table 1. In a preliminary experiment geranial (*E*)-**5** and 3-(2-bromoacetyl)oxazolidinone **7a** were added simultaneously to a cooled solution of 2.2 equiv SmI_2 in THF at –78 °C, and the reaction mixture was stirred for 1 h (method A). After aqueous workup and chromatographic purification, compound (3'*R*,4'*E*)-**13a** was obtained as a single diastereomer albeit in a low yield of 32% (entry 1). In a similar fashion neral (*Z*)-**5** yielded one diastereomeric product (3'*R*,4'*Z*)-**13a** in 23% yield (entry 2). Monitoring of these reactions by TLC revealed several spots. The ability of SmI_2 to reduce carbonyl compounds and to promote reductive pinacol-type carbonyl couplings or polymerizations is well known.[2] Presumably, reduction of terpene enals and coupling of radical intermediates compete with the SmI_2-mediated Reformatsky reaction leading to the consumption of SmI_2 and formation of byproducts. Hence, the reaction was modified, and a solution of SmI_2 in THF was cooled to –78 °C prior to addition of a solution of 3-(2-bromoacetyl)oxazolidinone **7a** in THF. The resulting mixture was stirred for 5 min in the dark to permit formation of the Sm(III) enolate, followed by slow addition of the enal **5** (method B). After 0.5 h, TLC indicated almost complete conversion. The reaction mixture was stirred for a further 0.5 h followed by workup. Under these conditions the Reformatsky reactions proceeded much cleaner with less byproducts. Geranial (*E*)-**5** gave the diastereomers (3'*R*,4'*E*)-**13a** and (3'*S*,4'*E*)-**13a** in 73% and 6% yield (dr 92 : 8, entry 3), while neral (*Z*)-**5** yielded (3'*R*,4'*Z*)-**13a** and (3'*S*,4'*Z*)-**13a** in 71% and 7% yield (dr 91 : 9, entry 4). Both yields and diastereoselectivities were not affected by the configuration of the enal C=C double bond.

Table 1. SmI_2-Mediated Reformatsky Reaction of 3-(Haloacetyl)oxazolidinones 7a,b with Terpene Enals (*E*)-5 and (*Z*)-5[a,b]



entry	7	enal	*T* (°C)	method	isolated yield	(%)	ratio[c]
1	**7a**	(*E*)-**5**	–78	A	(3'*R*,4'*E*)-**13a**	32	100 : 0
2	**7a**	(*Z*)-**5**	–78	A	(3'*R*,4'*Z*)-**13a**	23	100 : 0
3	**7a**	(*E*)-**5**	–78	B	(3'*R*,4'*E*)-**13a**	73	92 : 8
					(3'*S*,4'*E*)-**13a**	6	
4	**7a**	(*Z*)-**5**	–78	B	(3'*R*,4'*Z*)-**13a**	71	91 : 9
					(3'*S*,4'*Z*)-**13a**	7	
5	**7a**	(*E*)-**5**	–100	B	(3'*R*,4'*E*)-**13a**	59	90 : 10
6	**7a**	(*Z*)-**5**	–100	B	(3'*R*,4'*Z*)-**13a**	54	90 : 10
7	**7b**	(*E*)-**5**	–78	B	(3'*R*,4'*E*)-**13a**	48	89 : 11
8	**7b**	(*Z*)-**5**	–78	B	(3'*R*,4'*Z*)-**13a**	43	90 : 10
9	**7b**	(*E*)-**5**	–100	B	(3'*R*,4'*E*)-**13a**	56	90 : 10
10	**7b**	(*Z*)-**5**	–100	B	(3'*R*,4'*Z*)-**13a**	50	91 : 9

[a]SmI_2 (0.1 M, THF). [b]Method A: simultaneous addition of enal and oxazolidinone to a cooled solution of SmI_2 in THF; method B: 1) addition of oxazolidinone to a cooled solution of SmI_2 in THF; 2) equilibration for 5 min; 3) addition of enal. [c]Diastereomeric ratios were determined by isolation.

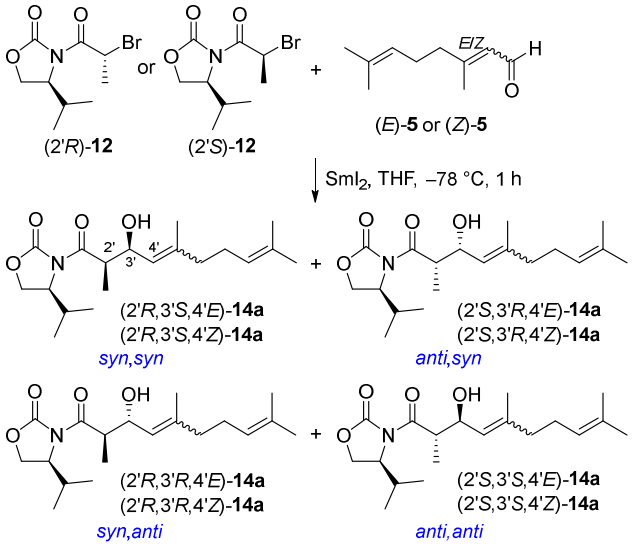
Lowering the temperature to –100 °C led to decreased yields, but comparable diastereomeric ratios, i.e. (3'*R*,4'*E*)-**13a** (59%, dr 90 : 10) and (3'*R*,4'*Z*)-**13a** (54%, dr 90 : 10) (entries 5, 6). The decreased reaction rate is probably due to the poor solubility of the Sm(III) enolate at –100 °C. It should be noted that additives such as HMPA enhance the reduction potential of SmI_2.[2b,d,33] However, we avoided using toxic additives in the reaction. Alternatively, SmI_2 might lead to reductive cleavage of the oxazolidinone auxiliary as recently reported by Frontier.[34]

When the corresponding 3-(2-chloroacetyl)oxazolidinone **7b** was employed under these conditions, yields were generally lower than those with 3-(2-bromoacetyl)oxazolidinone **7a**, but increased with decreasing temperature. The diastereoselectivity, however, remained unchanged (dr ~ 90 : 10) (Table 1, entries 7, 9 and 8, 10).

To investigate the reactivity of secondary halides and the effect of chirality at the halide on the outcome of the Reformatsky reaction, 3-(2-bromopropanoyl)oxazolidinone **12**[31,35] was employed in a series of experiments (Table 2). First, diastereomeric mixtures of **12** (dr 67 : 33) were reacted with geranial (*E*)-**5** and neral (*Z*)-**5**, respectively, under the conditions of method B described above, providing diastereomeric mixtures of (*E*)-**14a** (dr 63 : 21 : 16) and (*Z*)-**14a** (dr 71 : 20 : 9), respectively, from which the major diastereomers (2'*R*,3'*S*,4'*E*)-**14a** and (2'*R*,3'*S*,4'*Z*)-**14a** could be isolated in 55% and 59%, respectively (entries 1 and 2).

Because of the rapid epimerization of 3-(2-bromopropanoyl)oxazolidinone,[35] the diastereomers (2'*R*)-**12** and (2'*S*)-**12** were separated by chromatography and immediately used for the reactions. However, diastereomeric ratios and yields did not change markedly (entries 3–6), suggesting that neither rate nor selectivity forming step is affected by the stereogenic centre at the 2-bromopropanoyl unit.

Table 2. SmI_2-Mediated Reformatsky Reaction of 3-(2-Bromopropanoyl)oxazolidinone 12 with Terpene Enals (*E*)-5 and (*Z*)-5[a,b]



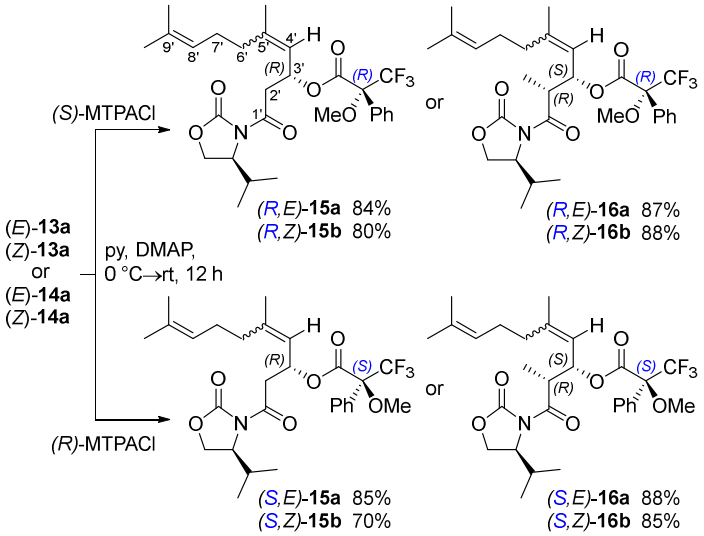
entry	**12**	enal	yield[c]	(%)	ratio	(*R*,*S*):(*S*,*R*):(*R*,*R*)[d]
1	**12** (67:33)	(*E*)-**5**	(2'*R*,3'*S*,4'*E*)-**14a**	55	(*E*)-**14a**	63 : 21 : 16
2	**12** (67:33)	(*Z*)-**5**	(2'*R*,3'*S*,4'*Z*)-**14a**	59	(*Z*)-**14a**	71 : 20 : 9
3	(2'*R*)-**12**	(*E*)-**5**	(2'*R*,3'*S*,4'*E*)-**14a**	52	(*E*)-**14a**	63 : 22 : 15
4	(2'*R*)-**12**	(*Z*)-**5**	(2'*R*,3'*S*,4'*Z*)-**14a**	59	(*Z*)-**14a**	70 : 19 : 11
5	(2'*S*)-**12**	(*E*)-**5**	(2'*R*,3'*S*,4'*E*)-**14a**	53	(*E*)-**14a**	62 : 22 : 16
6	(2'*S*)-**12**	(*Z*)-**5**	(2'*R*,3'*S*,4'*Z*)-**14a**	57	(*Z*)-**14a**	71 : 19 : 10

[a]SmI_2 (0.1 M, THF). [b]Method B: 1) addition of oxazolidinone to a cooled solution of SmI_2 in THF; 2) equilibration for 5 min; 3) addition of enal. [c]Isolated yields; diastereomeric ratios were determined by isolation. [d](2'*S*,3'*S*)-diastereomers were not observed.

Assignment of Relative and Absolute Configuration of Reformatsky Products 13, 14 and Proposed Mechanism. The absolute configuration at the C-3' atom in the Reformatsky products (4'*E*)-**13a** and (4'*Z*)-**13a** was determined by applying Mosher's method.[36] Adopting a procedure reported by Laschat[28] geranial-derived Reformatsky product (4'*E*)-**13a** was esterified with Mosher acyl chloride (*R*)- and (*S*)-MTPACl to afford the corresponding (*S*)- and (*R*)-MTPA esters (*S*)-**15a**

and (*R*)-**15a** in 85 and 84% yield, respectively (Scheme 2). In an analogous fashion (*S*)- and (*R*)-MTPA esters (*S*)-**15b** and (*R*)-**15b** were prepared from neral-derived Reformatsky products (4'*Z*)-**13a** in 70% and 80%, respectively.

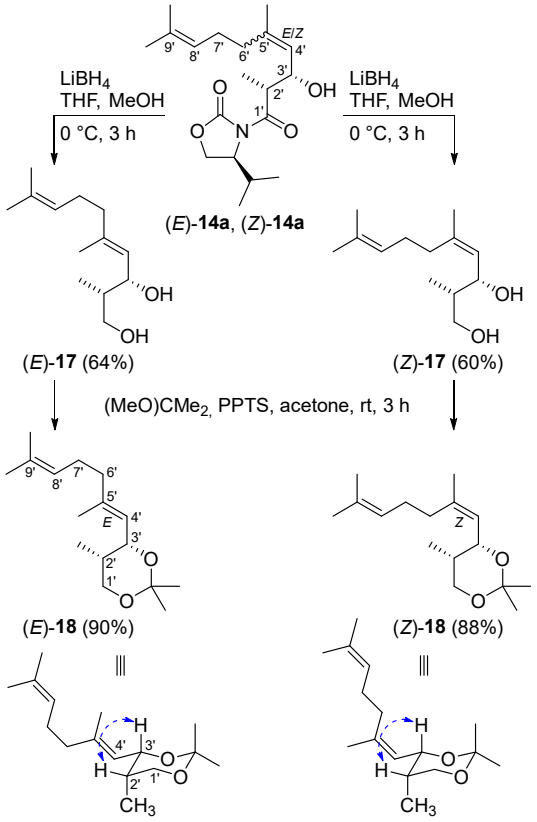
Scheme 2. Conversion of Reformatsky Products 13a and 14a into the Corresponding Mosher Esters (*R*)- and (*S*)-15a,b and (*R*)- and (*S*)-16a,b, respectively



Analysis of the differences in the chemical shifts[36] between (*R*)- and (*S*)-Mosher ester in the ^{1}H NMR indicated the absolute configuration at C-3' as (3'*R*) for both (*E*)-geranial- and (*Z*)-neral-derived Mosher esters (*S*)-**15a**, (*R*)-**15a** and (*S*)-**15b**, (*R*)-**15b** [Table S1, see Supporting Information (SI)]. Following the same procedure, the Mosher esters **16** of diastereomerically pure (*E*)-**14a** and (*Z*)-**14a** were prepared (Scheme 2). From the chemical shift differences between (*R*) and (*S*) Mosher ester the (3'*S*) configuration at C-3' was assigned for (*E*)-geranial- and (*Z*)-neral-derived Mosher esters (*S*)-**16a**, (*R*)-**16a** and (*S*)-**16b**, (*R*)-**16b**, respectively (Table S2, SI).

In order to assign the configuration at C-2', Reformatsky products (*E*)-**14a**, (*Z*)-**14a** were converted into the conformationally locked cyclic acetals (*E*)- and (*Z*)-**18** following a known procedure[28] (Scheme 3).

Scheme 3. Synthesis of Acetals (*E*)- and (*Z*)-18 from Reformatsky Products (*E*)- and (*Z*)-14a



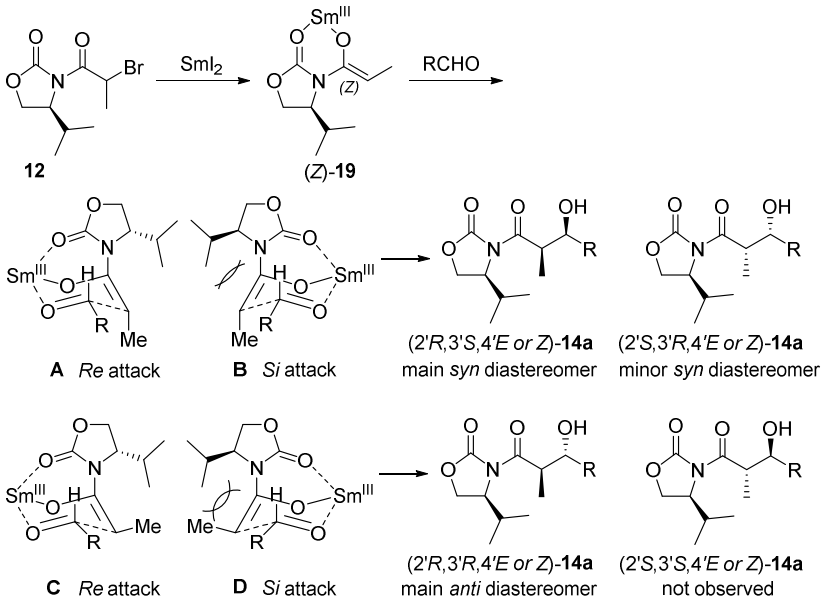
The chiral auxiliary was removed from (*E*)- and (*Z*)-**14a** in a (100 : 1) mixture of THF / MeOH with $LiBH_4$ in THF to yield the respective diols (*E*)- and (*Z*)-**17** in 64% and 60% after workup and chromatographic purification. Diols **17** were then reacted with 2,2-dimethoxypropane and PPTS in acetone followed by workup and chromatography to provide acetals (*E*)- and (*Z*)-**18** in 90% and 88%, respectively (Scheme 3).

NOESY correlations were used to assign the relative configuration at C-2'/C-3'.[28] A strong NOE between 2'-H and 3'-H was observed for acetal (*E*)-**18**, confirming a *syn*-configuration of the stereogenic centers C-2'/C-3'. Analogous results revealed a *syn*-configuration of the stereogenic centers C-2'/C-3' in acetal (*Z*)-**18**. Thus, irrespective of the geometry of the C=C double bond for

both acetals (*E*)- and (*Z*)-**18** a (2'*S*,3'*S*)-configuration was found. Consequently, the major diastereomers (*E*)- and (*Z*)-**14a** are (2'*R*,3'*S*) configurated.

However, this procedure could not be used for minor diastereomers of **14a** because of their very low amounts. Hence, the absolute and relative configuration at C-2'/C-3' for these products was proposed considering the transition state geometries published by Fukuzawa.[5a] In agreement with the evidence reported by Evans and coworkers, enolization of *N*-acyl oxazolidinones leads to the selective formation of (*Z*)-metal enolates.[37] It is therefore reasonable to assume that this geometry is involved also in case of samarium enolates. According to Fukuzawa,[5a] asymmetric samarium(II) iodide-promoted Reformatsky reactions proceed via formation of a chelated transition state. Adapting this model to our reaction we propose that samarium coordinates both the enolate oxygen and the carbonyl group of the oxazolidinone auxiliary as well as the oxygen of the incoming aldehyde (Scheme 4).

Scheme 4. Proposed Mechanism of Diastereomer Formation

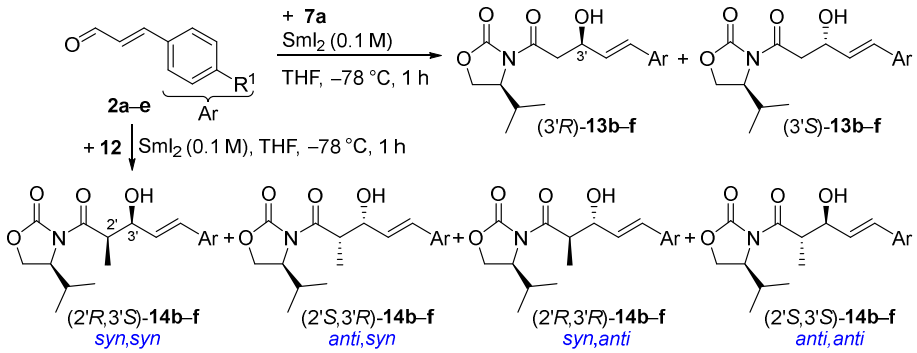


Depending on the geometry of the enolate double bond and the relative topicity of enolate and aldehyde four different transition state geometries **A**–**D** are possible. *Re* face attack at the enal seems to be favoured (transition states **A**, **C**), because steric interactions between the oxazolidinone isopropyl group and the enolate methyl group are minimized as compared to transition states **B**, **D**. The observed stereochemistry of the main diastereomers **14** is fully consistent with this hypothesis. The disfavored *Si* face attack at the enals (transition state **B**) could yield the minor *syn* diastereomers. Magnesium(II) chloride-catalyzed aldol reactions of *N*-acyl oxazolidinones with non-enolizable aldehydes were reported to afford selectively the *anti* adducts. The authors suggest the involvement of a magnesium-chelating boat transition structure.[38] Assuming a similar structure in the case of samarium enolates could lead to the formation of the minor *anti* diastereomer. However, from preliminary DFT calculations a boat transition state seems to be unlikely because in such highly strained geometry the chelating coordination of the samarium enolate by the oxazolidinone carbonyl group is not possible.

The mechanistic proposal is supported by the observation that (2*E*,6*E*)-8-[(4-methoxybenzyl)oxy]-3-(methoxymethyl)-7-methylocta-2,6-dienal **36**[31] carrying an allylic methoxy group did not react with 3-(2-bromoacetyl)oxazolidinone **7a** (Scheme S5, SI). Presumably, the allylic methoxy group in close proximity to the reactive site of the enol interfered with the chelate complex between Sm(III) enolate and the oxazolidinone carbonyl, thus suppressing the C–C bond forming step.

Reformatsky Reaction with Aryl- and Alkyl-substituted Enals. In order to further broaden the scope of the samarium Reformatsky reaction, a series of aryl-substituted enals **2a**–**e**[31,39,40] was investigated using method B described above (Table 3).

Table 3. SmI_2-Mediated Reformatsky Reaction of *N*-(2-Bromoacetyl)- and *N*-(2-Bromopropionyl)oxazolidinone 7a, 12 with Enals 2a–e[a,b]



entry	**7a**, **12**	**2**	Ar R^1	yield [c]	(%)	ratio **13** (*R*):(*S*)	ratio **14** (*R*,*S*):(*S*,*R*):(*R*,*R*):(*S*,*S*)
1	**7a**	**2a**	H	(3'*R*)-**13b**	51	96 : 4	–
2	**7a**	**2b**	OMe	(3'*R*)-**13c**	30	98 : 2	–
3	**7a**	**2c**	Me	(3'*R*)-**13d**	22	99 : 1	–
4	**7a**	**2d**	Cl	(3'*R*)-**13e**	33	94 : 6	–
5	**7a**	**2e**	NO_2	(3'*R*)-**13f**	24	–	–
6	**12**	**2a**	H	(2'*R*,3'*S*)-**14b**	92	–	92 : 5 : 2 : 1
7	**12**	**2b**	OMe	(2'*R*,3'*S*)-**14c**	63	–	85 : 15 : 0 : 0
8	**12**	**2c**	Me	(2'*R*,3'*S*)-**14d**	30	–	93 : 6 : 1 : 0
9	**12**	**2d**	Cl	(2'*R*,3'*S*)-**14e**	34	–	86 : 9 : 3 : 2
10	**12**	**2e**	NO_2	(2'*R*,3'*S*)-**14f**	52	–	94 : 4 : 2 : 0

[a]SmI_2 (0.1 M, THF). [b]Method B: 1) addition of oxazolidinone to a cooled solution of SmI_2 in THF; 2) equilibration for 5 min; 3) addition of enal. [c]Isolated yields; diastereomeric ratios were determined by isolation.

Reaction of 3-(2-bromoacetyl)oxazolidinone **7a** with cinnamic aldehyde **2a** under the conditions described above yielded a (96 : 4) diastereomeric mixture of the Reformatsky products **13b** in 51% yield, from which the major diastereomer was (3'*R*)-**13b** (entry 1). Under similar conditions *p*-substituted cinnamic aldehydes **2b–e** gave poorer yields of 22–33%, but the diastereomeric ratios were only little affected by the electronic influence of the *p*-substituent (dr 94 : 6 up to 99 : 1)

(entries 2–4). The Reformatsky reaction of **2e** proceeded to **13f**, but attempts to separate the diastereomers by HPLC failed (entry 5).

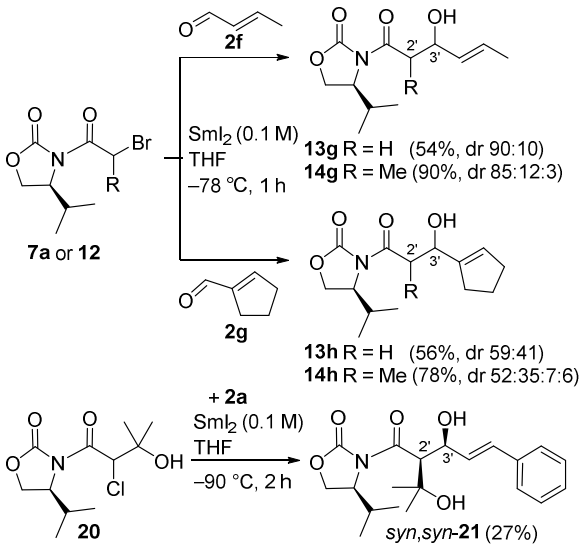
Next, a series of experiments with 3-(2-bromopropionyl)oxazolidinone **12** was carried out. As can be seen from Table 3, cinnamic aldehyde **2a** yielded products **14b** in 92% in a diastereomeric ratio of (92 : 5 : 2 : 1) and the major isomer was assumed to be (2'*R*,3'*S*)-**14b** (entry 6). The other enals **2b–e** gave Reformatsky products **14c–f** in yields of 30–63% (entries 7–10), which were generally higher as compared to **13c–f**. Good diastereoselectivities ranging from (dr 85 : 15 : 0 : 0) up to (94 : 4 : 2 : 0) were obtained for **14c–f**. All diastereomeric ratios for compounds **13b–f** and **14b–f** were determined by analytical HPLC. In the case of derivatives **13d**,**e** and **14c**,**d**, the separation succeeded by HPLC on chiral stationary phases.

The minor *anti* (2'*S*,3'*S*)-diastereomer of **14b** and **14e** could be detected (entries 6 and 9) in contrast to the other products **14c**,**d**,**f** and the terpene enal derived (*E*)- and (*Z*)-**14a** (Table 2).

In an analogous manner to Reformatsky products **14a** (Scheme 2), pure major diastereomer **14b** was reacted with (*R*)- and (*S*)-MTPACl to yield the corresponding (*S*)- and (*R*)-Mosher esters **16c**[31] (Table S3, SI). The NMR analysis confirmed for both (*R*)- and (*S*)-**16c** the (*S*)-configuration at C-3'. NOESY ^{1}H NMR experiments were performed for the assumed major diastereomer (2'*S*,3'*R*)-**14b** revealing a *syn*-configuration (Figure S1, SI), which is in good accordance with the transition state described above and thus, the (*R*)-configuration at C-2' was concluded. The two other diastereomers (2'*S*,3'*S*)-**14b** and (2'*R*,3'*R*)-**14b** could not be isolated and assigned due to their small amount. For the major diastereomers **14c–f** the (2'*R*,3'*S*)-configuration was assumed as well.

When crotonic aldehyde **2f** was reacted with oxazolidinone **7a**, product **13g** was isolated in 54% (dr 90 : 10). Analogously, cyclopentene-1-carbaldehyde **2g** yielded Reformatsky product **13h** in 56% (dr 59 : 41) (Scheme 5).

Scheme 5. SmI_2-Mediated Reformatsky Reaction of Aldehydes 2a,f,g with Oxazolidinones 7a, 12 and 20[a]



[a] The diastereomers of **13** and **14** could not be clearly assigned.

Under the same conditions the Reformatsky reaction of both **2f** and **2g** with oxazolidinone **12** resulted in diastereomeric mixtures **14g** (85 : 12 : 3) and **14h** (52:35:7:6) in isolated yields of 90% and 78%, respectively, which, however, could not be completely separated and assigned by HPLC. To further probe the substrate scope of the Reformatsky reaction 3-(2-chloroacyl)oxazolidinone **20**[31] carrying a quaternary carbon and a free alcohol moiety adjacent to the α-carbon was treated with SmI_2 and cinnamic aldehyde **2a** (Scheme 5). Gratifyingly, the desired product *syn*,*syn*-**21** was isolated as a single diastereomer, albeit in 27% yield. Thus, even under these sterically demanding conditions the *syn*,*syn*-diastereomer was strongly favored.

■ CONCLUSION

Enals have been employed in asymmetric samarium Reformatsky reactions with 3-(2-haloacyl)-2-oxazolidinones **7a**,**b**, **12** providing access to stereochemically well-defined 3-hydroxy-4-alkenyl- and 3-hydroxy-2-methyl-4-alkenyl imides (**13**, **14**). Chirality transfer of the Evans (*S*)-

oxazolidinone unit via a Zimmerman-Traxler-like transition state resulted in the (*R*)-configuration of the hydroxy group in products **13a–f** in case of 3-(2-haloacetyl)oxazolidinones **7a**,**b**. When 3-(2-bromopropionyl)oxazolidinone **12** was employed, the (*S*)-oxazolidinone moiety led to the preferred formation of the (2'*R*,3'*S*)-configuration of the aldol unit, thus giving a relative *syn*-configuration in Reformatsky products **14a–f**. Moreover, their absolute configuration is opposite to the corresponding products obtained via aldol addition of boron enolates to enals using (*S*)-configurated oxazolidinones. Thus, the SmI_2-promoted Reformatsky reaction of enals not only demonstrates the power of the Evans auxiliary to effectively control the stereochemistry of C–C cross coupling reactions, but also provides a complementary entry towards *syn*-3-hydroxy-2-methyl-4-alkenyl imides, yielding the mirror images of boron-enolate-derived aldol products or titanium-enolate derived products.[41] The synthetic utility of this novel methodology can now be further explored in the synthesis of complex target molecules.

■ EXPERIMENTAL SECTION

All reactions were performed under nitrogen atmosphere using common Schlenk technique. All reagents were used as purchased unless otherwise stated. Solvents were purified and dried by standard procedures prior to use. The SmI_2 was purchased in a sealed bottle as a 0.1 M solution in THF and could be stored in the fridge for several weeks after opening without decomposing. NMR spectra were recorded on 300, 400, 500 and 700 MHz spectrometers at room temperature with TMS as an internal standard. Signals in ^1H and ^{13}C NMR spectra were assigned using COSY, HSQC, HMBC, and NOESY techniques. IR spectra were recorded on an FT-IR spectrometer at room temperature. Mass spectra (MS) were recorded using the ESI-TOF technique. Optical rotation was recorded at room temperature (Na-D-line, 589 nm). Diastereomeric ratios were determined by analytical HPLC using a variable wave detector (180–800 nm), performed on a MS-

Analytical Kromasil column (250 × 4.6 mm, 100 Si 5 µm), a Chiralcel OJ-H column (150 × 4.6 mm, 5 µm) or a Chiralcel OD-H column (250 × 4.6 mm, 5 µm). For preparative HPLC a MZ-Analytical Orbit column (250 × 20 mm, 100 Sil 5 µm) was used. Thin layer chromatography was performed on silica gel 60 F_{254} precoated aluminium plates. Column chromatography was carried out using silica gel (40–60 µm) with solvents distilled prior to use.

General Procedure for the Samarium-Mediated Reformatsky Reaction of *N*-Haloacyl-2-oxazolidinones with Enals (GP1). To a solution of SmI_2 (0.1 M in THF, 2.20 equiv) at –78 °C was added dropwise a solution of the respective **7a**,**b**, **12** or **20** (1.0 equiv) in abs. THF (3 mL), and the reaction mixture was stirred for 5 min followed by dropwise addition of a solution of the appropriate enal **5** or **2** (1.2 equiv) in abs. THF (3 mL). The reaction mixture was stirred at –78 °C for 1 h. Then a satd solution of NH_4Cl–H_2O (20 mL) was added at –78 °C, and the reaction mixture was allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with a satd solution of $Na_2S_2O_3$, dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by chromatography on SiO_2.

*(4S)-3-[(3R,4E)- and (3S,4E)-3-Hydroxy-5,9-dimethyldeca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(3'R,4'E)- and (3'S,4'E)-**13a**]*. Chromatography (PE/EtOAc 2:1) afforded (3'*R*,4'*E*)-**13a** (236 mg, 0.73 mmol, 73%, purity 95% ^{1}H NMR, R_f = 0.32) and (3'*S*,4'*E*)-**13a** (20 mg, 60 µmol, 6%, purity 95% ^{1}H NMR, R_f = 0.38) as colorless oils. (3'*R*,4'*E*)-**13a**: $[\alpha]_D^{20}$ = +33.5 (*c* = 1.2 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.92 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.59 (s, 3H, 10-H or 11-H), 1.67 (s, 3H, 10-H or 11-H), 1.71 (s, 3H, 12H), 1.95-2.14 (m, 4H, 6-H, 7-H), 2.32-2.43 (m, 1H, 4'-H), 3.06-3.16 (m, 2H, 2-H), 4.20-4.30 (m, 2H, 2'-H, 3'-H_a), 4.39-4.48 (m, 1H, 3'-H_b), 4.85-4.91 (m, 1H, 3-H), 5.04-5.11 (m,

1H, 8-H), 5.25 (dd, *J* = 8.5 Hz, 1.1 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.9 (C-6'), 16.8 (C-5'), 17.8 (C-12), 18.1 (C-10, C-11), 25.8 (C-10), 26.5 (C-7), 28.6 (C-4'), 39.6 (C-2), 43.0 (C-6), 58.6 (C-3), 63.8 (C-3'), 65.2 (C-2'), 124.0 (C-8), 125.5 (C-4), 131.9 (C-9), 139.5 (C-5), 154.1 (C-1'), 172.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3485 (w), 2964 (m), 2920 (m), 1777 (vs), 1696 (s), 1486 (w), 1441 (w), 1372 (s), 1301 (m), 1202 (s), 1141 (m), 1120 (m), 1104 (m), 1058 (s), 1020 (s), 928 (w), 814 (w), 774 (m), 753 (m), 713 (m), 640 (m), 590 (w), 526 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{29}NO_4Na$ 346.1989; Found 346.1996. (3'*S*,4'*E*)-**13a**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.93 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.59 (s, 3H, 10-H or 11-H), 1.67 (s, 3H, 10-H or 11-H), 1.71 (s, 3H, 12-H), 1.95-2.14 (m, 4H, 6-H, 7-H), 2.32-2.43 (m, 1H, 4'-H), 3.06-3.16 (m, 2H, 2-H), 4.20-4.30 (m, 2H, 2'-H, 3'-H_a), 4.48-4.41 (m, 1H, 3'-H_b), 4.83-4.92 (m, 1H, 3-H), 5.07-5.15 (m, 1H, 8-H), 5.28 (d, *J* = 8.9 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.9 (C-6'), 16.8 (C-5'), 17.8 (C-12), 18.1 (C-10, C-11), 25.8 (C-10), 26.5 (C-7), 28.6 (C-4'), 39.6 (C-2), 43.0 (C-6), 58.6 (C-3), 63.8 (C-3'), 65.2 (C-2'), 124.0(C-8), 125.5 (C-4), 131.9 (C-9), 139.5 (C-5), 154.1 (C-1'), 172.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3495 (w), 2964 (w), 2925 (w), 2976 (w), 1778 (s), 1699 (m), 1447 (w), 1386 (s), 1373 (s), 1302 (m), 1204 (s), 1179 (m), 1143 (w), 1120 (w), 1102 (w), 1058 (m), 1020 (m), 972 (w), 845 (w), 775 (w), 754 (w), 713 (w), 640 (w), 587 (w), 527 (w), 454 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{29}NO_4Na$ 346.1989; Found 346.1973.

*(4S)-3-[(3R,4Z)- and (3S,4Z)-3-Hydroxy-5,9-dimethyldeca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(3'R,4'Z)- and (3'S,4'Z)-**13a**]*. Chromatography (PE/EtOAc 2 : 1) afforded (3'*R*,4'*Z*)-***13a*** (230 mg, 0.71 mmol, 71%, purity 95% ^1H NMR, R_f = 0.32) and (3'*S*,4'*Z*)-**13a** (21 mg, 0.07 mmol, 7%, purity 90% ^1H NMR, R_f = 0.35) as coloress oils. (3'*R*,4'*Z*)-**13a**: $[\alpha]_D^{20}$ = +38.7 (*c* = 1.0 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.92

(d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.60 (s, 3H, 10-H or 11-H), 1.68 (s, 3H, 10-H or 11-H), 1.73 (s, 3H, 12-H), 2.03-2.20 (m, 4H, 6-H, 7-H), 2.33-2.44 (m, 1H, 4'-H), 3.09-3.14 (m, 2H, 2-H), 4.19-4.32 (m, 2H, 2'-H, 3'-H_a), 4.41-4.49 (m, 1H, 3'-H_b), 4.85-4.90 (m, 1H, 3-H), 5.08-5.15 (m, 1H, 8-H), 5.28 (d, *J* = 8.9 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.9 (C-6'), 16.8 (C-5'), 17.8 (C-12), 18.1 (C-10, C-11), 25.8 (C-10), 26.5 (C-7), 28.6 (C-4'), 39.6 (C-2), 43.0 (C-6), 58.6 (C-3), 63.8 (C-3'), 65.2 (C-2'), 124.0 (C-8), 125.5 (C-4), 131.9 (C-9), 139.5 (C-5), 154.1 (C-1'), 172.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3495 (w), 2964 (w), 2925 (w), 2976 (w), 1778 (s), 1699 (m), 1447 (w), 1386 (s), 1373 (s), 1302 (m), 1204 (s), 1179 (m), 1143 (w), 1120 (w), 1102 (w), 1058 (m), 1020 (m), 972 (w), 845 (w), 775 (w), 754 (w), 713 (w), 640 (w), 587 (w), 527 (w), 454 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{29}NO_4Na$ 346.1989; Found 346.1988. (3'*S*,4'*Z*)-**13a**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.93 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.59 (s, 3H, 10-H or 11-H), 1.67 (s, 3H, 10-H or 11-H), 1.71 (s, 3H, 12-H), 1.95-2.14 (m, 4H, 6-H, 7-H), 2.32-2.43 (m, 1H, 4'-H), 3.06-3.16 (m, 2H, 2-H), 4.20-4.30 (m, 2H, 2'-H, 3'-H_a), 4.48-4.41 (m, 1H, 3'-H_b), 4.83-4.92 (m, 1H, 3-H), 5.07-5.15 (m, 1H, 8-H), 5.28 (d, *J* = 8.9 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.9 (C-6'), 16.8 (C-5'), 17.8 (C-12), 18.1 (C-10, C-11), 25.8 (C-10), 26.5 (C-7), 28.6 (C-4'), 39.6 (C-2), 43.0 (C-6), 58.6 (C-3), 63.8 (C-3'), 65.2 (C-2'), 124.0(C-8), 125.5 (C-4), 131.9 (C-9), 139.5 (C-5), 154.1 (C-1'), 172.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3495 (w), 2964 (w), 2925 (w), 2976 (w), 1778 (s), 1699 (m), 1447 (w), 1386 (s), 1373 (s), 1302 (m), 1204 (s), 1179 (m), 1143 (w), 1120 (w), 1102 (w), 1058 (m), 1020 (m), 972 (w), 845 (w), 775 (w), 754 (w), 713 (w), 640 (w), 587 (w), 527 (w), 454 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{29}NO_4Na$ 346.1989; Found 346.2006.

*(4S)-3-[(4E)-3-Hydroxy-2,5,9-trimethyldeca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(E)-**14a**].* Chromatography (PE/EtOAc 2 : 1) afforded (3'*R*,4'*E*)-**14a** (46.1 mg, 0.14 mmol, 14%,

purity 95% ^{1}H NMR, R_f = 0.37), (2'*R*,3'*S*,4'*E*)-**14a** (184 mg, 0.55 mmol, 55%, purity 95% ^{1}H NMR, R_f = 0.28) and (4'*E*)-**14a** (60.6 mg, 0.18 mmol, 18%, purity 90% ^{1}H NMR, R_f = 0.20) as colorless oils. (2'*R*,3'*S*,4'*E*)-**14a**: $[\alpha]_D^{20}$ = +43.6 (*c* = 1.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.86 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.91 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.19 (d, *J* = 6.9 Hz, 3H, 13-H), 1.60 (s, 3H, 10-H or 11-H), 1.68 (s, 3H, 10-H or 11-H), 1.70 (s, 3H, 12-H), 1.96-2.14 (m, 4H, 6-H, 7-H), 2.26-2.42 (m, 1H, 4'-H), 3.94-4.04 (m, 1H, 2-H), 4.17-4.31 (m, 2H, 2'-H, 3'-H_a), 4.16-4.32 (m, 1H, 3'-H_b), 4.42-4.49 (m, 1H, 3-H), 5.01-5.11 (m, 1H, 8-H), 5.22 (dd, *J* = 8.7 Hz, 1.1 Hz, 1H, 4-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 11.9 (C-13), 14.8 (C-6'), 17.0 (C-5'), 17.8 (C-12), 18.1 (C-10, C-11), 25.8 (C-10), 26.5 (C-7), 28.7 (C-4'), 39.9 (C-6), 43.1 (C-2), 58.8 (C-3), 63.4 (C-3'), 69.8 (C-2'), 124.0 (C-8), 125.7 (C-4), 131.9 (C-9), 140.4 (C-5), 154.3 (C-1'), 175.9 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3496 (w), 2965 (m), 2926 (m), 2878 (w), 1775 (vs), 1697 (s), 1487 (w), 1453 (w), 1375 (s), 1300 (m), 1203 (vs), 1143 (w), 1120 (m), 1101 (m), 1054 (w), 1015 (w), 989 (m), 954 (m), 904 (w), 818 (w), 776 (w), 709 (w), 640 (w), 537 (w), 441 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}NO_4Na$ 360.2145; Found 360.2155. (3'*R*,4'*E*)-**14a**: $[\alpha]_D^{20}$ = +42.7 (*c* = 1.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.96 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.08 (d, *J* = 6.9 Hz, 3H, 13-H), 1.60 (s, 3H, 10-H or 11-H), 1.67 (s, 3H, 10-H or 11-H), 1.70 (s, 3H, 12-H), 1.95-2.16 (m, 4H, 6-H, 7-H), 2.34-2.50 (m, 1H, 4'-H), 3.91 (dq, *J* = 13.8 Hz, 6.9 Hz, 1H, 2-H), 4.19-4.32 (m, 2H, 2'-H, 3'-H_a), 4.16-4.32 (m, 1H, 3'-H_b), 4.40-4.51 (m, 1H, 3-H), 5.01-5.12 (m, 1H, 8-H), 5.19 (d, *J* = 8.3 Hz, 4-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.2 (C-13), 14.7 (C-6'), 17.0 (C-5'), 17.8 (C-12), 18.1 (C-10, C-11), 25.8 (C-10), 26.5 (C-7), 28.6 (C-4'), 39.8 (C-6), 44.2 (C-2), 59.1 (C-3), 63.4 (C-3'), 71.9 (C-2'), 124.0 (C-8), 125.7 (C-4), 132.0 (C-9), 140.9 (C-5), 154.5 (C-1'), 176.7 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3501 (w), 2966 (m), 2924 (m), 2878 (w), 1775 (vs), 1698 (s), 1487

(w), 1454 (m), 1383 (vs), 1301 (m), 1251 (m), 1202 (vs), 1142 (m), 1121 (m), 1107 (m), 1081 (m), 1054 (m), 990 (s), 954 (m), 901 (w), 817 (w), 775 (w), 760 (w), 709 (w), 636 (w), 530 (w), 462 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}NO_4Na$ 360.2145; Found 360.2162. (4'*E*)-**14a**: $[\alpha]_D^{20}$ = +38.3 (*c* = 1.2 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.87 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.91 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.10 (d, *J* = 7.0 Hz, 3H, 13-H), 1.58 (s, 3H, 10-H or 11-H), 1.65 (s, 3H, 10-H or 11-H), 1.68 (s, 3H, 12-H), 1.97-2.15 (m, 4H, 6-H, 7-H), 2.29-2.38 (m, 1H, 4'-H), 3.82 (dq, *J* = 14.1 Hz, 7.0 Hz, 1H, 2-H), 4.13-4.30 (m, 2H, 2'-H, 3'-H_a), 4.44-4.58 (m, 2H, 3-H, 3'-H_b), 4.99-5.09 (m, 1H, 8-H), 5.16 (d, *J* = 9.1 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-13), 14.9 (C-6'), 16.9 (C5'), 17.8 (C-12), 18.0 (C-10, C-11), 25.5 (C-10), 26.4 (C-7), 28.7 (C-4'), 39.7 (C-6), 44.5 (C-2), 58.6 (C-3), 63.6 (C-3'), 76.1.8 (C-2'), 123.9 (C-8), 125.2 (C-4), 131.9 (C-9), 140.9 (C-5), 154.0 (C-1'), 176.6 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3445 (w), 2645 (m), 2928 (m), 2878 (w), 1778 (vs), 1696 (s), 1485 (w), 1455 (m), 1382 (vs), 1300 (m), 1256 (s), 1225 (s), 1202 (vs), 1142 (m), 1120 (m), 1104 (m), 1076 (m), 1055 (m), 988 (s), 954 (m), 901 (w), 846 (w), 818 (w), 775 (w), 760 (w), 733,6 (w), 707 (m), 638 (w), 527 (w), 461 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}NO_4Na$ 360.2145; Found 360.2153.

*(4S)-3-[(4Z)-3-Hydroxy-2,5,9-trimethyldeca-4,8-dienoyl)-4-isopropyl-1,3-oxazolidin-2-one [(Z)-**14a**]*. Chromatography (PE/EtOAc 2 : 1) afforded (4'*Z*)-**14a** (25.2 mg, 0.07 mmol, 7%, purity 80% ^1H NMR, R_f = 0.35), (2'*R*,3'*S*,4'*Z*)-**14a** (201 mg, 0.59 mmol, 59%, purity 95% ^1H NMR, R_f = 0.31) and (3'*S*,4'*Z*)-**14a** (56 mg, 0.17 mmol, 17%, purity 95% ^1H NMR, R_f = 0.20) as colorless oils. (2'*R*,3'*S*,4'*Z*)-**14a**: $[\alpha]_D^{20}$ = +26.7 (c = 1.2 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.87 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.91 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.12 (d, *J* = 7.0 Hz, 3H, 13-H), 1.60 (s, 3H, 10-H or 11-H), 1.67 (s, 3H, 10-H or 11-H), 1.74 (s, 3H, 12-H), 1.98-2.22 (m,

4H, 6-H, 7-H), 2.26-2.42 (m, 1H, 4'-H), 3.77-3.88 (m, 1H, 2-H), 4.15-4.31 (m, 2H, 2'-H, 3'-H_a), 4.44-4.56 (m, 2H, 3-H, 3'-H_b), 5.05-5.15 (m, 1H, 8-H), 5.18 (d, J = 9.3 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 15.0 (C-13, C-6'), 17.8 (C-5'), 18.0 (C-12), 23.5 (C-10, C-11), 25.7 (C-10), 26.7 (C-7), 28.7 (C-4'), 32.5 (C-6), 44.3 (C-2), 58.6 (C-3), 63.6 (C-3'), 70.3 (C-2'), 123.9 (C-8), 126.1 (C-4), 132.4 (C-9), 141.4 (C-5), 154.0 (C-1'), 176.6 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3497 (w), 2965 (m), 2926 (m), 2877 (m), 1774 (vs), 1696 (s), 1487 (w), 1454 (m), 1374 (vs), 1300 (m), 1201 (vs), 1142 (m), 1119 (m), 1100 (m), 1054 (m), 1014 (m), 989 (s), 965 (m), 954 (m), 904 (w), 845 (w), 819 (w), 775 (w), 761 (w), 709 (m), 640 (w), 555 (w), 533 (w), 451 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}NO_4Na$ 360.2145; Found 360.2159. (3'*S*,4'*Z*)-**14a**: $[\alpha]_D^{20}$ = +24.6 (*c* = 1.1 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.87 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 0.91 (d, J = 7.0 Hz, 3H, 5'-H or 6'-H), 1.12 (d, J = 7.0 Hz, 3H, 13-H), 1.60 (s, 3H, 10-H or 11-H), 1.67 (s, 3H, 10-H or 11-H), 1.74 (s, 3H, 12-H), 1.98-2.22 (m, 4H, 6-H, 7-H), 2.26-2.42 (m, 1H, 4'-H), 3.77-3.88 (m, 1H, 2'-H), 4.15-4.31 (m, 2H, 2'-H, 3'-H_a), 4.44-4.56 (m, 2H, 3-H, 3'-H_b), 5.05-5.15 (m, 1H, 8-H), 5.18 (d, J = 9.3 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 15.0 (C-13, C-6'), 17.8 (C-5'), 18.0 (C-12), 23.5 (C-10, C-11), 25.7 (C-10), 26.7 (C-7), 28.7 (C-4'), 32.5 (C-6), 44.3 (C-2), 58.6 (C-3), 63.6 (C-3'), 70.3 (C-2'), 123.9 (C-8), 126.1 (C-4), 132.4 (C-9), 141.4 (C-5), 154.0 (C-1'), 176.6 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3469 (w), 2964 (m), 2931 (m), 2977 (w), 1777 (s), 1696 (s), 1455 (m), 1382 (s), 1300 (m), 1255 (m), 1225 (s), 1202 (s), 1143 (w), 1120 (m), 1101 (m), 1055 (m), 988 (s), 954 (m), 901 (w), 848 (w), 819 (w), 775 (w), 707 (m), 638 (w), 595 (w), 528 (w), 449 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}NO_4Na$ 360.2145; Found 360.2161. (4'*Z*)-**14a**: $[\alpha]_D^{20}$ = +30.2 (*c* = 1.2 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) =0.88 (d, J = 7.0 Hz, 3H, 5'-H or 6'-H), 0.90 (d, J = 7.1 Hz, 3H, 5'-H or 6'-H), 1.06 (d, J = 6.9 Hz, 3H, 13-H), 1.58 (s, 3H, 10-H or 11-H), 1.66 (s, 3H, 10-H

or 11-H), 1.73 (s, 3H, 12-H), 2.03-2.19 (m, 4H, 6-H, 7-H), 2.30-2.46 (m, 1H, 4'-H), 3.82-3.95 (m, 1H, 2-H), 4.15-4.34 (m, 3H, 2'-H, 3'-H_a), 4.36-4.51 (m, 2H, 3-H, 3'-H_b), 5.00-5.14 (m, 1H, 8-H), 5.18 (d, J = 9.2 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.4 (C-13), 14.6 (C-6'), 17.9 (C-5'), 18.2 (C-12), 23.4 (C-10, C-11), 25.7 (C-10), 26.6 (C-7), 28.0 (C-4'), 38.6 (C-6), 44.9 (C-2), 59.9 (C-3), 63.3 (C-3'), 71.3 (C-2'), 123.9 (C-8), 126.6 (C-4), 132.3 (C-9), 141.2 (C-5), 154.3 (C-1'), 176.7 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3517 (w), 2965 (m), 2931 (m), 2877 (w), 1776 (vs), 1700 (s), 1487 (w), 1450 (w), 1386 (s), 1373 (s), 1301 (w), 1248 (m), 1205 (s), 1143 (w), 1121 (m), 1056 (m), 1015 (m), 990 (m), 953 (w), 900 (w), 816 (w), 773 (w), 757 (w), 698 (w), 634 (w), 533 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}NO_4Na$ 360.2145; Found 360.2148.

*(4S)-3-[(4E)-3-Hydroxy-5-phenylpent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**13b**).* Chromatography (PE/EtOAc 3 : 1) afforded **13b** (93 mg, 307 µmol, 51%) as a colorless solid. R_f = 0.30. Analytical HPLC (Kromasil, flow 0.8 mL min^{-1}, hexane/isopropanol 90 : 10): t_{R1} = 12.741 min (minor, 4%), t_{R2} = 15.086 min (major, *syn,syn* **13b**, 96%). $[\alpha]_D^{20}$ = + 79.1 (c = 1.1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 0.93 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 2.34–2.43 (m, 1H, 4'-H), 3.01 (s, 1H, OH), 3.22 (dd, J = 17.1 Hz, 8.6 Hz, 1H, 2-H_a), 3.35 (dd, J = 17.1 Hz, 3.4 Hz, 1H, 2-H_b), 4.23 (dd, J = 9.2 Hz, 3.1 Hz, 1H, 3-H_a), 4.28 (dd, J = 9.2 Hz, 8.1 Hz, 1H, 3'-H_b), 4.46 (dt, J = 8.1 Hz, 3.4 Hz, 1H, 2'-H), 4.79–4.87 (m, 1H, 3-H), 6.28 (dd, J = 16.0 Hz, 6.0 Hz, 1H, 4-H), 6.68 (dd, J = 16.0, 1.4 Hz, 1H, 5-H), 7.20–7.28 (m, 1H, *p*-H), 7.27–7.35 (m, 2H, *m*-H), 7.35–7.41 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-6'), 18.0 (C-5'), 28.5 (C-4'), 42.6 (C-2), 58.5 (C-2'), 63.6 (C-3'), 68.8 (C-3), 126.6 (C-*m*), 127.8 (C-*o*), 128.6 (C-*p*), 130.0 (C-4), 130.8 (C-5), 136.5 (C-*i*), 154.1 (C-1'), 171.9 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3465 (w), 3026 (vw), 2963 (w), 2876 (w), 1774 (s), 1696 (s), 1487

(w), 1465 (w), 1449 (w), 1386 (s), 1373 (s), 1301 (m), 1204 (s), 1143 (w), 1119 (m), 1058 (m), 1020 (m), 970 (m), 914 (w), 750 (m), 715 (w), 695 (m), 640 (w), 587 (vw), 543.38 (w), 472 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{21}NO_4Na$ 326.1363; Found: 326.1344.

(4S)-3-[(4E)-3-Hydroxy-5-(4-methoxyphenyl)pent-4-enoyl]-4-isopropyl-1,2-oxazolidin-2-one ***(13c)***. Chromatography (PE/EtOAc 2 : 1) afforded ***13c*** (64 mg, 192 µmol, 30%) as a pale yellow oil. $R_f = 0.21$. Analytical HPLC (Kromasil, flow 0.8 mL min^{-1}, hexane/isopropanol 95 : 5): t_{R1} = 35.312 min (minor, 2%), t_{R2} = 39.530 min (major, *syn,syn* ***13c***, 98%). $[\alpha]_D^{20} = +50.5$ (c = 1.0 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 0.93 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 2.35–2.44 (m, 1H, 4'-H), 2.93 (d, J = 4.5 Hz, 1H, OH), 3.22 (dd, J = 17.1 Hz, 8.7 Hz, 1H, 2-H_a), 3.34 (dd, J = 17.1 Hz, 3.3 Hz, 1H, 2-H_b), 3.81 (s, 3H, OMe), 4.23 (dd, J = 9.1 Hz, 3.0 Hz, 1H, 3'-H_a), 4.29 (dd, J = 9.1 Hz, 8.2 Hz, 1H, 3'-H_b), 4.44–4.49 (m, 1H, 2'-H), 4.76–4.84 (m, 1H, 3-H), 6.14 (dd, J = 15.9 Hz, 6.2 Hz, 1H, 4-H), 6.59–6.64 (m, 1H, 5-H), 6.83–6.87 (m, 2H, *m*-H), 7.29–7.34 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-6'), 18.0 (C-5'), 28.5 (C-4'), 42.7 (C-2), 55.3 (OMe), 58.5 (C-2'), 63.6 (C-3'), 69.0 (C-3), 114.0 (C-*m*), 127.7 (C-4), 127.8 (C-*o*), 129.2 (C-*i*), 130.4 (C-5), 154.1 (C-1'), 159.4 (C-*p*), 172.0 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3490 (w), 2961 (m), 2930 (m), 2837 (w), 1778 (vs), 1698 (s), 1607 (s), 1578 (w), 1511 (vs), 1464 (w), 1387 (s), 1301 (m), 1249 (vs), 1207 (s), 1176 (s), 1143 (w), 1108 (m), 1032 (s), 971 (m), 816 (w), 775 (w), 714 (w), 641 (w), 538 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}NO_5Na$ 356.1468; Found 356.1470.

(4S)-3-[(4E)-3-Hydroxy-5-(4-methylphenyl)pent-4-enoyl]-4-isopropyl-1,2-oxazolidin-2-one ***(13d)***. Chromatography (PE/EtOAc 2.5 : 1) afforded **13d** (36 mg, 113 µmol, 22%) as a pale yellow oil. $R_f = 0.18$. Analytical HPLC (OJ-H, flow 2.0 mL min^{-1}, hexane/isopropanol 85 : 15): t_{R1} = 12.593 min (minor, 1%), t_{R2} = 16.199 min (major, *syn,syn* **13d**, 99%). $[\alpha]_D^{20} = +57.1$ (*c* = 1.0

in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, J = 7.0 Hz, 3H, 5'-H or 6'-H), 0.93 (d, J = 7.0 Hz, 3H, 5'-H or 6'-H), 2.30–2.43 (m, 4H, 4-H, CH_3), 2.96 (s, 1H, OH), 3.22 (dd, J = 17.2 Hz, 8.7 Hz, 1H, 2-H_a), 3.34 (dd, J = 17.2 Hz, 3.3 Hz, 1H, 2-H_b), 4.23 (dd, J = 9.0 Hz, 3.1 Hz, 1H, 3'-H_a), 4.29 (t, J = 9.0 Hz, 1H, 3'-H_b), 4.44–4.49 (m, 1H, 2'-H), 4.79–4.86 (m, 1H, 3-H), 6.22 (dd, J = 15.9 Hz, 6.1 Hz, 1H, 4-H), 6.64 (d, J = 15.9 Hz, 1H, 5-H), 7.09–7.15 (m, 2H, *m*-H), 7.27–7.31 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-6'), 18.0 (C-5'), 21.2 (CH_3), 28.5 (C-4'), 42.6 (C-2), 58.5 (C-2'), 63.6 (C-3'), 68.9 (C-3), 126.5 (C-*o*), 128.8 (C-4), 129.3 (C-*m*), 130.7 (C-5), 133.6 (C-*i*), 137.7 (C-*p*), 154.0 (C-1'), 175.0 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3445 (w), 2961 (m), 2923 (m), 1779 (vs), 1698 (s), 1514 (m), 1485 (w), 1464 (w), 1386 (vs), 1302 (m), 1206 (s), 1143 (w), 1106 (m), 1059 (m), 1020 (m), 971 (m), 802 (m), 775 (w), 715 (w), 641 (w), 529 (w), 464 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}NO_4Na$ 340.1519; Found 340.1529.

(4S)-3-[(4E)-5-(4-Chlorophenyl)-3-hydroxypent-4-enoyl)-4-isopropyl-1,3-oxazolidin-2-one ***(13e)***. Chromatography (PE/EtOAc 3 : 1) afforded **13e** (70 mg, 207 µmol, 33%) as a pale yellow oil. R_f = 0.20. Analytical HPLC (OJ-H, flow 1.0 mL min^{-1}, hexane/isopropanol 85 : 15): t_{R1} = 24.473 min (minor, 6%), t_{R2} = 28.815 min (major, *syn,syn* **13e**, 94%). $[\alpha]_D^{20}$ = + 53.3 (c = 1.0 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 0.94 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 2.34–2.43 (m, 1H, 4'-H), 3.05 (s, 1H, OH), 3.19 (dd, J = 17.2 Hz, 8.8 Hz, 1H, 2-H_a), 3.36 (dd, J = 17.2 Hz, 3.2 Hz, 1H, 2-H_b), 4.24 (dd, J = 9.2 Hz, 3.2 Hz, 1H, 3'-H_a), 4.27–4.32 (m, 1H, 3'-H_b), 4.44–4.49 (m, 1H, 2'-H), 4.79–4.85 (m, 1H, 3-H), 6.25 (dd, J = 15.9 Hz, 5.9 Hz, 1H, 4-H), 6.64 (dd, J = 15.9 Hz, 1.5 Hz, 1H, 5-H), 7.27–7.33 (m, 4H, *o*-H, *m*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-6'), 18.0 (C-5'), 28.5 (C-4'), 42.5 (C-2), 58.5 (C-2'), 63.7 (C-3'), 68.6 (C-3), 127.8 (C-*m*), 128.8 (C-*o*), 129.5 (C-5), 130.5 (C-4), 133.4

(C-*p*), 135.0 (C-*i*), 154.0 (C-1'), 172.1 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3468 (w), 2964 (m), 2162 (w), 2026 (w), 1780 (vs), 1699 (s), 1492 (m), 1387 (s), 1302 (m), 1207 (s), 1092 (m), 1059 (w), 1014 (m), 971 (m), 808 (w), 776 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{20}ClNO_4Na$ 360.0973; Found 360.0975.

(4S)-3-[(4E)-3-Hydroxy-5-(4-nitrophenyl)pent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one ***(13f)***. Chromatography (PE/EtOAc 2.5 : 1) afforded **13f** (51 mg, 146 µmol, 24%) as an orange oil. R_f = 0.30; $[\alpha]_D^{20}$ = + 41.3 (*c* = 1.0 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.90 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.95 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 2.31–2.44 (m, 1H, 4'-H), 3.18 (dd, *J* = 17.4 Hz, 8.9 Hz, 1H, 2-H_a), 3.41 (dd, *J* = 17.4 Hz, 3.2 Hz, 1H, 2-H_b), 4.26 (dd, *J* = 9.2 Hz, 3.0 Hz, 1H, 3'-H_a), 4.31 (dd, *J* = 9.2 Hz, 8.2 Hz, 1H, 3'-H_b), 4.45–4.50 (m, 1H, 2'-H), 4.82–4.93 (m, 1H, 3-H), 6.45 (dd, *J* = 16.0 Hz, 5.3 Hz, 1H, 4-H), 6.78 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H, 5-H), 7.49–7.53 (m, 2H, *o*-H), 8.17–8.21 (m, 2H, *m*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-6'), 18.0 (C-5'), 28.5 (C-4'), 42.4 (C-2), 58.5 (C-2'), 63.7 (C-3'), 68.2 (C-3), 124.0 (C-*m*), 127.1 (C-*o*), 128.4 (C-5), 134.7 (C-4), 143.0 (C-*i*), 147.1 (C-*p*), 154.1 (C-1'), 171.8 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3428 (w), 2963 (m), 2928 (w), 2875 (w), 1777 (vs), 1698 (s), 1597 (m), 1516 (s), 1487 (w), 1466 (w), 1387 (s), 1342 (vs), 1302 (w), 1207 (m), 1143 (w), 1109 (m), 1058 (m), 1019 (m), 973 (m), 863 (w), 824 (w), 800 (w), 773 (m), 717 (w), 692 (w), 640 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{20}N_2O_6Na$ 371.1214; Found 371.1189.

(S)-3-((2'R,3'S,E)- or (S)-3-((2'S,3'R,E)-3-Hydroxy-2-methyl-5-phenylpent-4-enoyl)-4-isopropyloxazolidin-2-one ***(14b)***. Chromatography (PE/EtOAc 3 : 1) afforded **14b** (185 mg, 582 µmol, 92%) as a colorless solid. R_f = 0.27. Analytical HPLC (Kromasil, flow 0.8 mL min^{-1}, hexane/isopropanol 90 : 10): t_{R1} = 7.950 min (minor, 1%), t_{R2} = 8.565 min (minor, 2%), t_{R3} = 9.612 min (minor, *syn,anti* 5%), t_{R4} = 11.212 min (major, *syn,syn* **14b**, 93%). The diastereomers could be

separated via preparative HPLC: *syn,syn* **14b** (170 mg, 536 µmol, 85%) and *anti,syn* **14b** (9.0 mg, 28.4 µmol, 5%). *syn,syn* **14b**: $[\alpha]_D^{20} = +46.6$ ($c = 0.9$ in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.83 (d, $J = 6.9$ Hz, 3H, 5'-H or 6'-H), 0.90 (d, $J = 6.9$ Hz, 3H, 5'-H or 6'-H), 1.22 (d, $J = 6.9$ Hz, 3H, 6-H), 2.28–2.38 (m, 1H, 4'-H), 2.80 (d, $J = 3.1$ Hz, 1H, OH), 4.11 (qd, $J = 6.9$ Hz, 4.1 Hz, 1H, 2-H), 4.22 (dd, $J = 9.2$ Hz, 3.1 Hz, 1H, 3'-H_a), 4.29 (dd, $J = 9.2$ Hz, 8.2 Hz, 1H, 3'-H_b), 4.47 (ddd, $J = 8.2$ Hz, 3.9 Hz, 3.1 Hz, 1H, 2'-H), 4.67 (dddd, $J = 5.9$ Hz, 4.1 Hz, 3.1 Hz, 1.4 Hz, 1H, 3-H), 6.22 (dd, $J = 15.9$ Hz, 5.9 Hz, 1H, 4-H), 6.67 (dd, $J = 15.9$ Hz, 1.4 Hz, 1H, 5-H), 7.21–7.27 (m, 1H, *p*-H), 7.31 (dd, $J = 8.4$ Hz, 6.8 Hz, 2H, *m*-H), 7.36–7.40 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 11.3 (C-6), 14.6 (C-6'), 17.9 (C-5'), 28.6 (C-4'), 42.8 (C-2), 58.7 (C-2'), 63.4 (C-3'), 73.5 (C-3), 126.6 (C-*m*), 127.7 (C-*o*), 128.5 (C-4), 128.6 (C-*o*), 131.7 (C-5), 136.6 (C-*i*), 154.1 (C-1'), 175.8 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3476 (w), 2965 (w), 2933 (w), 2877 (w), 1773 (vs), 1696 (s), 1488 (w), 1451 (w), 1385 (s), 1300 (m), 1203 (s), 1143 (w), 1121 (m), 1055 (w), 1016 (w), 988 (w), 967 (m), 754 (m), 696 (m), 639 (w), 490 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}NO_4Na$ 340.1519; Found 340.1519. *anti,syn* **14b**: ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.79 (d, $J = 6.9$ Hz, 3H, 5'-H or 6'-H), 0.89 (d, $J = 6.9$ Hz, 3H, 5'-H or 6'-H), 1.24 (d, $J = 6.9$ Hz, 3H, 6-H), 2.35 (qd, $J = 7.0$ Hz, 3.9 Hz, 1H, 4'-H), 2.84 (d, $J = 7.7$ Hz, 1H, OH), 4.13 (qd, $J = 7.1$ Hz, $J = 6.8$ Hz, 1H, 2-H), 4.21 (dd, $J = 9.1$ Hz, 3.0 Hz, 1H, 3'-H_a), 4.28 (dd, $J = 9.1$ Hz, 8.3 Hz, 1H, 3'-H_b), 4.39 (dd, $J = 6.8$ Hz, 6.5 Hz, 1H, 3-H), 4.46 (ddd, $J = 8.2$ Hz, 3.9 Hz, 3.0 Hz, 1H, 2'-H), 6.25 (dd, $J = 15.9$ Hz, 6.5 Hz, 1H, 4-H), 6.65 (dd, $J = 15.9$ Hz, 1.3 Hz, 1H, 5-H), 7.25 (d, $J = 9.3$ Hz, 1H, *p*-H), 7.29–7.34 (m, 2H, *m*-H), 7.35–7.40 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 14.5 (C-6), 14.6 (C-6'), 17.9 (C-5'), 28.4 (C-4'), 43.0 (C-2), 58.8 (C-2'), 63.3 (C-3'), 75.8 (C-3), 126.6 (C-*m*), 127.9 (C-*o*), 128.6 (C-*o*), 129.7 (C-4), 132.0 (C-5), 136.4 (C-*i*), 154.2 (C-1'), 176.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3487 (w),

2964 (w), 2925 (w), 2876 (w), 1775 (vs), 1698 (s), 1599 (vw), 1492 (w), 1453 (w), 1383 (s), 1301 (m), 1202 (s), 1143 (w), 1118 (m), 1052 (w), 1016 (m), 988 (m), 966 (m), 906 (w), 846 (w), 802 (w), 749 (m), 694 (m), 635 (w), 555 (w), 459 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}NO_4Na$ 340.1519; Found 340.1525.

*(4S)-3-[(4E)-3-Hydroxy-5-(4-methoxyphenyl)-2-methylpent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**14c**)*. Chromatography (PE/EtOAc 3 : 1 → 2 : 1) afforded **14c** (125 mg, 360 µmol, 63%) as a pale yellow oil. R_f = 0.44 (2 : 1). Analytical HPLC (OJ-H, flow 1.5 mL min^{-1}, hexane/isopropanol 80 : 20): t_{R1} = 19.310 min (major, *syn,syn* **14c**, 85%), t_{R2} = 22.686 min (minor, 15%). $[\alpha]_D^{20}$ = + 23.6 (*c* = 1.0 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.82 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.90 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.22 (d, *J* = 6.9 Hz, 3H, 6-H), 2.27–2.41 (m, 1H, 4'-H), 2.71 (d, *J* = 3.0 Hz, 1H, OH), 3.81 (s, 3H, OMe), 4.05–4.16 (m, 2H, 2-H), 4.22 (dd, *J* = 9.1 Hz, 3.0 Hz, 1H, 3'-H_a), 4.26–4.31 (m, 1H, 3'-H_b), 4.42–4.50 (m, 1H, 2'-H), 4.60–4.68 (m, 1H, 3-H), 6.08 (dd, *J* = 15.9 Hz, 6.2 Hz, 1H, 4-H), 6.58–6.63 (m, 1H, 5-H), 6.82–6.87 (m, 2H, *m*-H), 7.29–7.34 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 11.4 (C-6), 14.6 (C-6'), 18.0 (C-5'), 28.5 (C-4'), 42.9 (C-2), 55.3 (OMe), 58.7 (C-2'), 63.4 (C-3'), 73.7 (C-3), 114.0 (C-*m*), 126.3 (C-4), 127.8 (C-*o*), 129.3 (C-*i*), 131.3 (C-5), 154.1 (C-1'), 159.3 (C-*p*), 175.8 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3469 (w), 2964 (m), 2935 (w), 2878 (w), 2839 (w), 1775 (vs), 1698 (m), 1607 (m), 1512 (s), 1464 (w), 1386 (s), 1301 (m), 1249 (s), 1205 (s), 1176 (m), 1120 (m), 1032 (m), 968 (m), 824 (w), 709 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{25}NO_5Na$ 370.1625; Found 370.1594.

*(4S)-3-[(4E)-3-Hydroxy-2-methyl-5-(4-methylphenyl)pent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**14d**)*. Chromatography (PE/EtOAc 2.5 : 1) afforded **14d** (60 mg, 181 µmol, 30%) as a pale yellow oil. R_f = 0.36. Analytical HPLC (OD-H, flow 1.0 mL min^{-1}, hexane/isopropanol

85 : 15): t_{R1} = 10.968 min (minor, 1%), t_{R2} = 14.111 min (minor, 6%), t_{R3} = 16.710 min (major, *syn,syn* **14d**, 93%). $[\alpha]_D^{20}$ = + 24.9 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.80 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.88 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.21 (d, *J* = 7.0 Hz, 3H, 6-H), 2.27–2.35 (m, 1H, 4'-H), 2.32 (s, 3H, CH_3), 2.84–2.91 (m, 1H, OH), 4.05–4.13 (m, 1H, 2-H), 4.19 (dd, *J* = 9.1 Hz, 3.0 Hz, 1H, 3'-H_a), 4.26 (dd, *J* = 9.1 Hz, 1H, 3'-H_b), 4.42–4.48 (m, 1H, 2'-H), 4.62–4.67 (m, 1H, 3-H), 6.17 (dd, *J* = 15.9 Hz, 6.2 Hz, 1H, 4-H), 6.62 (dd, *J* = 15.9 Hz, 1.4 Hz, 1H, 5-H), 7.08–7.13 (m, 2H, *m*-H), 7.24–7.30 (m, 2H, *o*-H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 11.4 (C-6), 14.6 (C-6'), 17.9 (C-5'), 21.2 (CH_3), 28.5 (C-4'), 42.9 (C-2), 58.6 (C-2'), 63.4 (C-3'), 73.6 (C-3), 126.5 (C-*o*), 127.6 (C-4), 129.2 (C-*m*), 131.6 (C-5), 133.8 (C-*i*), 137.5 (C-*p*), 154.2 (C-1'), 175.7 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3480 (w), 2965 (m), 2924 (m), 2876 (m), 1771 (vs), 1695 (s), 1514 (m), 1486 (w), 1456 (m), 1373 (s), 1300 (m), 1201 (vs), 1119 (m), 1054 (m), 1016 (m), 966 (s), 909 (m), 802 (m), 775 (m), 730 (vs), 710 (s), 647 (w), 510 (w), 476 (w), 433 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{25}NO_4Na$ 354.1676; Found 354.1672.

*(4S)-3-[(4E)-5-(4-Chlorophenyl)-3-hydroxy-2-methylpent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**14e**)*. Chromatography (PE/EtOAc 3 : 1) afforded **14e** (74 mg, 210 µmol, 34%) as a colorless oil. R_f = 0.26. Analytical HPLC (Kromasil, flow 0.8 mL min^{-1}, hexane/isopropanol 95 : 5): t_{R1} = 9.076 min (minor, 2%), t_{R2} = 11.987 min (minor, 3%), t_{R3} = 14.852 min (minor, 9%), t_{R4} = 18.948 min (major, *syn*,*syn* **14e**, 86%). $[\alpha]_D^{20}$ = + 24.4 (c = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.84 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.91 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.21 (d, *J* = 6.9 Hz, 3H, 6-H), 2.30–3.39 (m, 1H, 4'-H), 2.86 (d, *J* = 3.0 Hz, 1H, OH), 4.07–4.15 (m, 1H, 2-H), 4.23 (dd, *J* = 9.2 Hz, 3.0 Hz, 1H, 3'-H_a), 4.27–4.32 (m, 1H, 3'-H_b), 4.45–4.49 (m, 1H, 2'-H), 4.65–4.70 (m, 1H, 3-H), 6.19 (dd, *J* = 15.9 Hz, 5.8 Hz, 1H, 4-H), 6.63 (dd, *J* = 15.9 Hz,

1.5 Hz, 1H, 5-H), 7.27–7.34 (m, 4H, *o*-H, *m*-H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 11.3 (C-6), 14.7 (C-6'), 18.0 (C-5'), 28.6 (C-4'), 42.7 (C-2), 58.7 (C-2'), 63.4 (C-3'), 73.3 (C-3), 127.8 (C-*m*), 128.7 (C-*o*), 129.2 (C-4), 130.4 (C-5), 133.4 (C-*p*), 135.1 (C-*i*), 154.2 (C-1'), 175.8 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3491 (w), 2964 (m), 2935 (w), 2876 (w), 2208 (s), 1776 (vs), 1698 (m), 1656 (w), 1602 (w), 1510 (w), 1491 (w), 1462 (w), 1386 (s), 1299 (m), 1254 (m), 1206 (s), 1173 (w), 1120 (w), 1091 (w), 1033 (m), 968 (w), 837 (w), 756 (w), 702 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{22}ClNO_4Na$ 374.1130; Found 374.1111.

*(4S)-3-[(4E)-3-Hydroxy-2-methyl-5-(4-nitrophenyl)pent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**14f**)*. Chromatography (PE/EtOAc 3 : 1) afforded **14f** (92 mg, 254 µmol, 52%) as an orange oil. R_f = 0.26. Analytical HPLC (Kromasil, flow 0.8 mL min^{-1}, hexane/isopropanol 95 : 5): t_{R1} = 21.884 min (minor, 4%), t_{R2} = 25.025 min (minor, 2%), t_{R3} = 27.798 min (major, *syn* **14f**, 94%). $[\alpha]_D^{20}$ = + 27.8 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.87 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.93 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.21 (d, *J* = 7.0 Hz, 3H, 6-H), 2.30–2.43 (m, 1H, 4'-H), 3.08 (s, 1H, OH), 4.08–4.16 (m, 1H, 2-H), 4.25 (dd, *J* = 9.1 Hz, 2.9 Hz, 1H, 3'-H_a), 4.29–4.35 (m, 1H, 3'-H_b), 4.45–4.51 (m, 1H, 2'-H), 4.72–4.78 (m, 1H, 3-H), 6.40 (dd, *J* = 15.9 Hz, 5.3 Hz, 1H, 4-H), 6.78 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H, 5-H), 7.45–7.58 (m, 2H, *o*-H), 8.16–8.22 (m, 2H, *m*-H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 11.1 (C-6), 14.7 (C-6'), 18.0 (C-5'), 28.6 (C-4'), 42.4 (C-2), 58.8 (C-2'), 63.6 (C-3'), 72.8 (C-3), 124.0 (C-*m*), 127.1 (C-*o*), 129.3 (C-4), 133.4 (C-5), 143.1 (C-*i*), 147.0 (C-*p*), 154.2 (C-1'), 175.7 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3483 (w), 2965 (m), 2877 (w), 1774 (s), 1699 (s), 1596 (m), 1516 (s), 1488 (w), 1462 (w), 1387 (m), 1343 (vs), 1301 (w), 1206 (m), 1110 (m), 1054 (w), 1016, (w), 972 (w), 860 (w), 824 (w), 750 (w), 709 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{22}N_2O_6Na$ 385.1370; Found 385.1344.

*(4S)-3-[(4E)-3-hydroxyhex-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**13g**)*. Chromatography (SiO_2, PE/EtOAc 3 : 1) afforded **13g** (42 mg, 157 µmol, 54%) as a colorless oil. R_f = 0.22. Analytical HPLC (OJ-H, flow 1.0 mL min^{-1}, hexane/isopropanol 90 : 10): t_{R1} = 10.877 min (minor, 10%), t_{R2} = 16.710 min (major, *syn,syn* **13g**, 90%). $[\alpha]_D^{20}$ = + 96.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 0.93 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 1.71 (dt, J = 6.4 Hz, 1.3 Hz, 3H, 6-H), 2.31–2.38 (m, 1H, 4'-H), 2.79 (s, 1H, OH), 3.04–3.14 (m, 1H, 2-H_a), 3.23 (dd, J = 17.1 Hz, 3.3 Hz, 1H, 2-H_b), 4.22 (dd, J = 9.2 Hz, 3.0 Hz, 1H, 3'-H_a), 4.29 (dd, J = 9.2 Hz, 8.1 Hz, 1H, 3'-H_b), 4.45 (dt, J = 8.1 Hz, 3.0 Hz, 1H, 2'-H), 4.53-4.62 (m, 1H, 3-H), 5.56 (ddq, J = 15.3 Hz, 6.6 Hz, 1.6 Hz, 1H, 4-H), 5.70–5.83 (m, 1H, 5-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.9 (C-6'), 17.8 (C-5'), 18.1 (C-6), 28.6 (C-4'), 42.8 (C-2), 58.6 (C-2'), 63.7 (C-3'), 68.9 (C-3), 127.6 (C-5), 131.9 (C-4), 154.3 (C-1), 172.3 (C-1'); FT-IR (ATR): $\tilde{\nu}$ = 3504 (w), 2964 (w), 2922 (w), 2877 (w), 2163 (w), 1990 (w), 1775 (vs), 1697 (s), 1486 (w), 1387 (s), 1373 (s), 1302 (m), 1204 (s), 1143 (m), 1120 (m), 1103 (m), 1058 (m), 1021 (m), 969 (m), 929 (w), 876 (w), 775 (w), 713 (w), 641 (w), 523 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{19}NO_4Na$ 264.1206; Found 264.1195.

*(4S)-3-(3-(Cyclopent-1-en-1-yl)-3-hydroxypropanoyl)-4-isopropyl-1,3-oxazolidin-2-one (**13h**)*. Chromatography (SiO_2, PE/EtOAc 3 : 1) afforded **13h** (89 mg, 333 µmol, 56%) as a colorless oil. R_f = 0.19. Analytical HPLC (Kromasil, flow 0.5 mL min^{-1}, hexane/isopropanol 90 : 10): t_{R1} = 20.094 min (41%), t_{R2} = 21.978 min (59%). $[\alpha]_D^{20}$ = + 102.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, J = 7.0 Hz, 3H, 5'-H or. 6'-H), 0.93 (d, J = 7.0 Hz, 3H, 5'-H or 6'-H), 1.85–1.97 (m, 2H, 7-H), 2.30–2.43 (m, 5H, 4'-H, 6-H, 8-H), 2.84 (s, 1H, OH), 3.18 (dd, J = 17.1 Hz, 9.3 Hz, 1H, 2-H_a), 3.27 (dd, J = 17.1 Hz, 3.1 Hz, 1H, 2-H_b), 4.23 (dd, J = 9.1 Hz, 3.0 Hz, 1H, 3'-H_a), 4.29 (dd, J = 9.1 Hz, 8.3 Hz, 1H, 3'-H_b), 4.44–4.49 (m, 1H, 2'-H), 4.75 (d,

J = 9.3 Hz, 1H, 3-H), 5.65–5.73 (m, 1H, 5-H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-6'), 18.0 (C-5'), 23.3 (C-7), 28.05 (C-4'), 31.8 (C-6), 32.3 (C-8), 41.5 (C-2), 58.5 (C-2'), 63.6 (C-3'), 67.4 (C-3), 126.0 (C-5), 144.9 (C-4), 154.1 (C-1'), 172.4 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3531 (w), 2962 (m), 2876 (w), 1779 (vs), 1702 (vs), 1487 (w), 1467 (w), 1375 (s), 1342 (w), 1304 (s), 1207 (s), 1151 (m), 1118 (m), 1063 (m), 1040 (m), 1017 (m), 984 (w), 969 (m), 825 (w), 774 (m), 731 (w), 642 (w), 621 (m), 594 (w), 528 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{21}NO_4$ 290.1363; Found 290.1349.

*(4S)-3-[(4E)-3-Hydroxy-2-methylhex-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**14g**)*. Chromatography (SiO_2, PE/EtOAc 3 : 1) afforded **14g** (137 mg, 537 µmol, 90%) as a colorless oil. R_f = 0.25. Analytical HPLC (OJ-H, flow 0.5 mL min^{-1}, hexane/isopropanol 85 : 15): t_{R1} = 12.997 min (major, *syn*,*syn* **14g**, 85%), t_{R2} = 15.642 min (minor, 12%), t_{R3} = 17.602 min (minor, 3%). $[\alpha]_D^{20}$ = + 73.3 (c = 0.9 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.90 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 0.92 (d, J = 6.9 Hz, 3H, 5'-H or 6'-H), 1.16 (d, J = 6.9 Hz, 3H, 7-H), 1.68–1.74 (m, 3H, 6-H), 2.30–2.39 (m, 1H, 4'-H), 2.56 (s, 1H, OH), 3.99 (qd, J = 6.9 Hz, 4.5 Hz, 1H, 2-H), 4.22 (dd, J = 9.2 Hz, 3.0 Hz, 1H, 3'-H_a), 4.25-4.32 (m, 1H, 3'-H_b), 4.37–4.43 (m, 1H, 2'-H), 4.43–4.50 (m, 1H, 3-H), 5.46–5.55 (m, 1H, 4-H), 5.70–5.82 (m, 1H, 5-H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) = 11.4 (C-7), 14.7 (C-6'), 17.8 (C-5'), 17.9 (C-6), 28.6 (C-4'), 42.7 (C-2), 58.6 (C-2'), 63.4 (C-3'), 73.8 (C-3), 128.6 (C-5), 130.2 (C-4), 154.2 (C-1), 175.8 (C-1'); FT-IR (ATR): $\tilde{\nu}$ = 3499 (w), 2965 (w), 2937 (w), 2878 (w), 1770 (vs), 1694 (s), 1487 (w), 1454 (w), 1372 (s), 1300 (m), 1200 (s), 1142 (m), 1120 (m), 1101 (m), 1055 (w), 11051 (m), 989 (m), 965 (s), 926 (w), 860 (w), 818 (w), 775 (w), 708 (s), 638 (w), 534 (w), 460 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{21}NO_4Na$ 278.1363; Found 278.1335.

*(4S)-3-(3-Cyclopent-1-en-1-yl-3-hydroxy-2-methylpropanoyl)-4-isopropyl-1,3-oxazolidin-2-one (**14h**)*. Chromatography (SiO_2, PE/EtOAc 3 : 1) afforded **14h** (132 mg, 469 µmol, 78%) as a colorless oil. $R_f = 0.35$. Analytical HPLC (Kromasil, flow 0.8 mL min^{-1}, hexane/isopropanol 90 : 10): $t_{R1} = 8.604$ min (minor, 7%), $t_{R2} = 9.774$ min (35%), $t_{R3} = 10.871$ min (52%), $t_{R4} = 11.529$ min (6%). $[\alpha]_D^{20} = +58.2$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, $J = 7.0$ Hz, 3H, 5'-H or 6'-H), 0.92 (d, $J = 7.0$ Hz, 3H, 5'-H or 6'-H), 1.12 (d, $J = 7.0$ Hz, 3H, 9-H), 1.86–1.93 (m, 2H, 7-H), 2.26–2.41 (m, 5H, 4-H, 6-H, 8-H), 2.47 (s, 1H, OH), 4.05 (qd, $J = 7.0$ Hz, 3.8 Hz, 1H, 2-H), 4.22 (dd, $J = 9.1$ Hz, 3.2 Hz, 1H, 3'-H_a), 4.26–4.31 (m, 3'-H_b), 4.42–4.51 (m, 1H, 2'-H), 4.62–4.67 (m, 1H, 3-H), 5.68–5.74 (m, 1H, 5-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 10.3 (C-9), 14.7 (C-6'), 17.9 (C-5'), 23.4 (C-7), 28.5 (C-4'), 32.3 (C-6), 32.4 (C-8), 41.1 (C-2), 58.5 (C-2'), 63.3 (C-3'), 71.8 (C-3), 126.4 (C-5), 144.2 (C-4), 153.8 (C-1'), 176.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 3500 (w), 2963 (m), 2849 (w), 1776 (vs), 1700 (s), 1487 (w), 1459 (w), 1386 (s), 1301 (m), 1204 (vs), 1145 (w), 1120 (m), 1102 (m), 1055 (m), 1015 (m), 989 (m), 953 (w), 774 (w), 697 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{23}NO_4Na$ 304.1519; Found 304.1510.

*(4S)-3-[(2S,3S,4E)-3-hydroxy-2-(1-hydroxy-1-methylethyl)-5-phenylpent-4-enoyl]-4-isopropyl-1,3-oxazolidin-2-one (**21**)*. Chromatography on SiO_2 with PE/EtOAc (10 : 1 → 1 : 1) gave **21** (93.0 mg, 0.27 mmol, 27%) as a yellowish oil. $R_f = 0.11$ (PE/EtOAc 4 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.49 (d, $J = 7.0$ Hz, 3H, 1-H), 0.79 (d, $J = 7.0$ Hz, 3H, 2-H), 1.32 (s, 3H, 11-H), 1.46 (s, 3H, 10-H), 2.12–2.25 (m, 1H, 3-H), 4.13 (dd, $J = 2.7$ Hz, 9.2 Hz, 1H, 5-H_a), 4.21 (dd, $J = 8.5$ Hz, 9.2 Hz, 1H, 5-H_b), 4.42 (d, $J = 3.6$ Hz, 1H, 8-H), 4.48–4.53 (m, 1H, 4-H), 4.95–5.02 (m, 1H, 12-H), 6.30 (dd, $J = 4.4$ Hz, 16.0 Hz, 1H, 13-H), 6.70 (dd, $J = 1.6$ Hz, 16.0 Hz, 1H, 14-H), 7.18–7.36 (m, 5H, Ph-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.1 (C-1), 17.9 (C-2), 27.4 (C-10),

28.4 (C-3), 29.8 (C-11), 53.7 (C-8), 58.8 (C-4), 63.1 (C-5), 71.3 (C-12), 73.1 (C-9), 126.5 (C-*m*-Ph), 127.6 (C-*p*-Ph), 128.5 (C-*o*-Ph), 129.3 (C-13), 130.4 (C-14), 136.5 (C-*i*-Ph), 154.2 (C-6), 174.2 (C-7); FT-IR (ATR): $\tilde{\nu}$ = 3452 (w, b), 3027 (w), 2967 (w), 2875 (w), 1773 (m), 1750 (m), 1686 (vs), 1601 (w), 1494 (w), 1466 (w), 1450 (w), 1363 (s), 1300 (m), 11253 (m), 1200 (s), 1143 (m), 1097 (m), 1059 (m), 1027 (m), 973 (m), 915 (w), 856 (w), 770 8w), 750 (m), 731 (w), 697 (m), 620 (w), 607 (w), 526 (w), 486 (w), 425 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{27}NaNO_5Na$ 384.1781; Found 384.1800.

General Procedure for the Synthesis of Mosher Esters (GP2). To a solution of the respective alcohol **13** or **14** (1.0 equiv) in abs. CH_2Cl_2 (2 mL) at 0 °C were successively added anhyd pyridine (2.2 equiv), a solution of (*R*)- or (*S*)-MTPACl (1.3 equiv) in abs. CH_2Cl_2 (1 mL) and DMAP (0.55 equiv). The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and the residue was purified by chromatography on SiO_2.

*(1R,2E)-1-{2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(S)-**15a**]*. Purification by chromatography (PE/EtOAc 6 : 1) gave (*S*)-**15a** (27.5 mg, 0.05 mmol, 85%, purity 90% ^{1}H NMR) as a colorless oil. R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.86 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.91 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.59 (s, 3H, 10-H or 11-H), 1.66 (s, 3H, 10-H or 11-H), 1.86 (s, 3H, 12-H), 1.96-2.11 (m, 4H, 6-H, 7-H), 2.30-2.41 (m, 1H, 4'-H), 3.16 (dd, *J* = 17.1 Hz, 3.7 Hz, 1H, 2-H), 3.44 (dd, *J* = 17.1 Hz, 9.4 Hz, 1H, 2-H), 3.52 (s, 3H, OCH_3), 4.16-4.26 (m, 2H, 3'-H), 4.33-4.39 (m, 1H, 2'-H), 5.03-5.09 (m, 2H, 4-H, 8-H), 6.21 (td, *J* = 9.5 Hz, 3.7 Hz, 1H, 3-H), 7.34-7.41 (m, 3H, *m*-H, *p*-H), 7.46-7.49 (m, 2H, *o*-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.7 (C6'), 17.1 (C-5'), 17.8 (C-12), 18.1 (C-10 or C-11), 25.8 (C-10 or C-11), 26.4 (C-7), 29.8 (C-4'), 39.6 (C-6), 40.4 (C-2), 55.7 (OCH_3), 58.7 (C-2'), 63.6 (C-3'), 70.5 (C-3), 120.5

(CF_3), 122.6 (C-8), 123.6 (C-*o*), 124.2 (C-4), 127.7 (C-m), 128.3 (C-p), 132.1 (C-9), 132.6 (C-5), 143.5 (C-i), 154.1 (C-1'), 165.6 (COO), 169.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2960 (m), 2924 (m), 2854 (w), 1782 (vs), 1746 (s), 1703 (s), 1488 (w), 1452 (w), 1452 (m), 1387 (s), 1301 (m), 1269 (s), 1238 (s), 1169 (vs), 1121 (s), 1080 (m), 1018 (m), 991 (m), 920 (w), 831 (w), 766 (w), 719 (m), 641 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{36}F_3NO_6Na$ 562.2387; Found 562.2372.

*(1R,2E)-1-{2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(R)-**15a**]*. Purification by chromatography (PE/EtOAc 6 : 1) gave (*R*)-**15a** (27.2 mg, 0.05 mmol, 84%, purity 95% ^1H NMR) as a colorless oil. R_f = 0.35. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.84 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.88 (d, *J* = 7.9 Hz, 3H, 5'-H or 6'-H), 1.60 (s, 3H, 10-H or 11-H), 1.66 (s, 3H, 10-H or 11-H), 1.87 (s, 3H, 12-H), 1.99-2.12 (m, 4H, 6-H, 7-H), 2.27-2.36 (m, 1H, 4'-H), 3.03 (dd, *J* = 16.9 Hz, 3.8 Hz, 1H, 2-H_a), 3.49-3.54 (m, 1H, 2-H_b), 3.54 (s, 3H, OCH_3), 4.07-4.22 (m, 3H, 2'-H, 3'-H), 5.03-5.09 (m, 1H, 8-H), 5.23 (d, *J* = 9.6 Hz, 1H, 4-H), 6.26 (td, *J* = 9.5 Hz, 3.8 Hz, 1H, 3-H), 7.33-7.39 (m, 3H, *m*-H, *p*-H), 7.49-7.54 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-5' or C6'), 17.1 (C-5' or C6'), 17.8 (C-12), 18.1 (C-10 or C-11), 25.8 (C-10 or C-11), 26.4 (C-7), 28.5 (C-4'), 39.6 (C-6), 40.1 (C-2), 55.6 (OCH_3), 58.6 (C-2'), 63.6 (C-3'), 70.4 (C-3), 120.6 (CF_3), 123.5 (C-8), 124.3 (C-*o*), 127.6 (C-4), 128.3 (C-*m*), 129.5 (C-*p*), 132.2 (C-9), 132.8 (C-5), 143.9 (C-*i*), 154.1 (C-1'), 165.4 (COO), 169.0 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2964 (w), 2925 (w), 2854 (w), 1780 (s), 1747 (s), 1703 (s), 1488 (w), 1451 (w), 1386 (s), 1258 (s), 1237 (s), 1204 (s), 1167 (vs), 1120 (s), 1106 (s), 1080 (m), 1017 (s), 989 (s), 971 (s), 914 (m), 824 (w), 765 (m), 731 (s), 717 (s), 697 (s), 642 (m), 579 (w), 553 (w), 510 (w), 442 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{36}F_3NO_6Na$ 562.2387; Found 562.2375.

*(1R,2Z)-1-{2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(S)-**15b**]*. Purification by chromatography (PE/EtOAc 5 : 1) gave (*S*)-**15b** (22.7 mg, 0.04 mmol, 70%, purity 80% ^{1}H NMR) as a colorless oil. R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.86 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.92 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.61 (s, 3H, 10-H or 11-H), 1.66 (s, 3H, 10-H or 11-H), 1.73 (s, 3H, 12-H), 2.04-2.12 (m, 1H, 7-H), 2.12-2.21 (m, 2H, 6-H), 2.32-2.42 (m, 1H, 4'-H), 3.07 (dd, *J* = 17.4 Hz, 3.3 Hz, 1H, 2-H), 3.47 (dd, *J* = 17.4, 9.7 Hz, 1H, 2-H), 3.51 (s, 3H, OCH_3), 4.18-4.24 (m, 2H, 3'-H), 4.32-4.38 (m, 1H, 2'-H), 5.04-5.11 (m, 1H, 4-H), 5.11-5.16 (m, 1H, 8-H), 6.16-6.24 (m, 1H, 3-H), 7.34-7.41 (m, 3H, *m*-H, *p*-H), 7.45-7.50 (m, 2H, *o*-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.3 (C-5' or C-6'), 14.7 (C-5' or C-6'), 17.8 (C-12), 18.1 (C-10 or C-11), 25.8 (C-10 or C-11), 26.6 (C-7), 28.8 (C-4'), 32.6 (C-6), 40.5 (C-2), 55.7 (OCH_3), 58.7 (C-2'), 63.6 (C-3'), 70.0 (C-3), 121.4 (CF_3), 124.0 (C-*o*), 127.7 (C-4), 128.3 (C-*m*), 129.6 (C-*p*), 132.6 (C-9), 132.8 (C-5), 143.3 (C-*i*), 154.1 (C-1'), 165.5 (COO), 169.3 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2962 (m), 2924 (m), 2854 (w), 1782 (vs), 1747 8s), 1702 (s), 1591 (w), 1487 (w), 1451 (w), 1387 (s), 1270 (s), 1238 (s), 1206 (s), 1183 8vs), 1169 (vs), 1121 (s), 1107 (m), 1080 (m), 1019 (m), 991 (m), 972 (m), 919 (w), 823 (w), 765 (w), 719 (m), 641 (w), 600 (w), 559 (w), 502 (w), 450 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{36}F_3NO_6Na$ 562.2387; Found 562.2358.

*(1R,2Z)-1-{2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(R)-**15b**]*. Purification by chromatography (PE/EtOAc 6 : 1) gave (*R*)-**15b** (25.9 mg, 0.05 mmol, 80%, purity 90% ^{1}H NMR) as a colorless oil. R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.83 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 0.89 (d, *J* = 7.0 Hz, 3H, 5'-H or 6'-H), 1.61 (s, 3H, 10-H or 11-H), 1.65 (s, 3H, 10-H or 11-H), 1.76 (s, 3H, 12-H), 2.02-2.22 (m, 4H, 6-H, 7-H), 2.27-2.38 (m, 1H, 4'-H), 2.94 (dd, *J* =

17.2 Hz, 3.4 Hz, 1H, 2-H), 3.54 (s, 3H, OCH_3), 3.50-3.59 (m, 1H, 2-H), 4.05-4.20 (m, 3H, 2'-H, 3'-H), 5.10-5.16 (m, 1H, 8-H), 5.24 (d, *J* = 9.8 Hz, 1H, 4-H), 6.27 (td, *J* = 9.8 Hz, 3.4 Hz, 3-H), 7.35-7.38 (m, 3H, *m*-H, *p*-H), 7.49-7.53 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-5' or C6'), 17.1 (C-5' or C6'), 17.8 (C-12), 18.1 (C-10 or C-11), 25.8 (C-10 or C-11), 26.6 (C-7), 28.5 (C-4'), 32.6 (C-6), 40.2 (C-2), 55.6 (OCH_3), 58.6 (C-2'), 63.6 (C-3'), 70.0 (C-3), 121.4 (CF_3), 123.9 (C-*o*), 127.7 (C-4), 128.3 (C-*m*), 129.4 (C-*p*), 132.4 (C-9), 132.9 (C-5), 143.6 (C-*i*), 154.1 (C-1'), 165.3 (COO), 168.9 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2965 (w), 2925 (w), 2854 (w)1780 (vs), 1748 (s), 1703 (s), 1487 (w), 1451 (w), 1386 (s), 1237 (s), 1168 (vs), 1120 (s), 1106 (s), 1080 (m), 1018 (s), 989 (s), 971 8s), 917 (w), 825 (w), 765 (m), 718 (s), 697 (m), 642 (w), 581 (w), 553 8w), 507 (w), 452 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{36}F_3NO_6Na$ 562.2387; Found 562.2399.

*(1S,2E)-1-{(1R)-2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-1-methyl-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(S)-**16a**]*. Purification by chromatography (PE/EtOAc 6 : 1) gave (*S*)-**16a** (29.2 mg, 0.05 mmol, 88%, purity 90% ^1H NMR) as a colorless oil. R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.79 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.87 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 1.23 (d, *J* = 6.8 Hz, 3H, 13-H), 1.59 (s, 3H, 10-H or 11-H), 1.65 (s, 3H, 10-H or 11-H), 1.84 (s, 3H, 12-H), 1.94-2.09 (m, 5H, 6-H, 7-H), 2.15-2.23 (m, 1H, 4'-H), 2.15-2.23 (m, 1H, 2-H), 3.55 (s, 3H, OCH_3), 4.14-4.28 (m, 2H, 2'-H, 3'-H), 4.38-4.44 (m, 1H, 3'-H), 5.02-5.06 (m, 1H, 8-H), 5.09 (dd, *J* = 9.6 Hz, 0.8 Hz, 1H, 4-H), 5.99 (dd, *J* = 9.6 Hz, 7.1 Hz, 1H, 3-H), 7.34-7.40 (m, 3H, *m*-H, *p*-H), 7.45-7.51 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.2 (C-13), 14.3 (C-5' or C-6'), 14.5 (C-5' or C-6'), 17.2 (C-12), 17.8 (C-10 or C-11), 18.0 (C-10 or C-11), 25.8 (C-7), 26.4 (C-4'), 28.4 (C-6), 39.8 (C-2), 41.9 (OCH_3), 55.7 (2'), 58.6 (C-3'), 63.2 (C-3), 75.3 (C(OMe)CF_3), 119.4 (CF_3), 122.6 (C-8), 123.7

(C-*o*), 124.2 (C-4), 127.6 (C-*m*), 128.4 (C-*p*), 129.6 (C-9), 132.4 (C-5), 144.5 (C-*i*), 153.8 (C-1'), 165.9 (COO), 173.1 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2965 (w), 2925 (w), 2855 (w), 1778 (s), 1744 (s), 1700 (s), 1488 (w), 1452 (m), 1385 (s), 1299 (m), 1260 (s), 1229 (s), 1184 (vs), 1120 (s), 1104 (s), 1081 (m), 1056 (m), 1014 (vs), 990 (s), 965 (m), 910 (s), 803 (m), 765 (m), 731 (vs), 719 (vs), 697 (s), 648 (m), 550 (w), 521 (w), 445 (w), 411 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{38}F_3NO_6Na$ 576.2543; Found 576.2560.

*(1S,2E)-1-{(1R)-2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-1-methyl-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(R)-**16a**]*. Purification by chromatography (PE/EtOAc 6 : 1) gave (*R*)-**16a** (28.9 mg, 0.05 mmol, 87%, purity: 90% ^{1}H NMR) as a colorless oil. R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.81 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.88 (d, *J* = 7.1 Hz, 5'-H or 6'-H), 1.08 (d, *J* = 6.8 Hz, 13-H), 1.58 (s, 3H, 10-H or 11-H), 1.64 (s, 3H, 10-H or 11-H), 1.83 (s, 3H, 12-H), 1.96-2.11 (m, 5H, 6-H, 7-H), 2.15-2.25 (m, 1H, 4'-H), 3.54 (s, 3H, OCH_3), 4.15-4.26 (m, 2H, 2'-H, 3'-H), 4.34-4.45 (m, 1H, 3'-H), 4.98-5.07 (m, 1H, 8-H), 5.24 (d, *J* = 9.7 Hz, 1H, 4-H), 5.96 (dd, *J* = 9.5 Hz, 8.3 Hz, 1H, 3-H), 7.33-7.41 (m, 3H, *m*-H, *p*-H), 7.49-7.55 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.4 (C-13), 14.3 (C-5' or C-6'), 14.5 (C-5' or C-6'), 17.2 (C-12), 17.8 (C-10 or C-11), 18.0 (C-10 or C-11), 25.8 (C-7), 26.4 (C-4'), 28.4 (C-6), 39.8 (C-2), 41.9 (C-OCH_3), 55.6 (C-2'), 58.6 (C-3'), 63.2 (C-3), 75.2 (C(OMe)CF_3), 123.6 (CF_3), 124.3 (C-8), 127.4 (C-*o*), 128.4 (C-4), 129.6 (C-*m*), 132.2 (C-*p*), 132.7 (C-5), 144.9 (C-*i*), 153.8 (C-1'), 165.8 (COO), 173.5 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2964 (w), 2924 (w), 2853 (w), 1778 (s), 1746 (s), 1699 (s), 1488 (w), 1452 (m), 1384 (s), 1299 (m), 1268 (s), 1229 (s), 1168 (vs), 1120 (s), 1104 (s), 1081 (m), 1055 (m), 1014 (vs), 989 (s), 964 (m), 932 (m), 910 (s), 805 (m), 765 (m), 731 (vs), 719 (vs), 697 (s), 648 (m), 577 (w), 553 (w), 520 (w),

444 (w), 414 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{38}F_3NO_6Na$ 576.2543; Found 562.2542.

*(1S,2Z)-1-{(1R)-2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-1-methyl-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(S)-**16b**]*. Purification by chromatography (PE/EtOAc 5 : 1) gave (*S*)-**16b** (28.2 mg, 0.05 mmol, 85%, purity 90% ^1H NMR) as a colorless oil. R_f = 0.38. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.80 (d, *J* = 6.9 Hz, 3H, 5'-H or 6'-H), 0.87 (d, *J* = 7.4 Hz, 5'-H or 6'-H), 1.23 (d, *J* = 6.8 Hz, 3H, 13-H), 1.64 (s, 3H, 10-H or 11-H), 1.69 (s, 3H, 10-H or 11-H), 1.88 (s, 3H, 12-H), 2.02-2.33 (m, 5H, 4'-H, 6-H, 7-H), 3.55 (s, 3H, OCH_3), 4.13-4.29 (m, 2H, 2'-H, 3'-H), 4.37-4.45 (m, 1H, 3'-H), 5.10 (dd, *J* = 23.9, 7.9 Hz, 4-H), 5.13-5.22 (m, 1H, 8-H), 6.03 (dd, *J* = 9.7, 7.4 Hz, 1H, 3-H), 7.34-7.41 (m, 3H, *m*-H, *p*-H), 7.46-7.50 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.5 (C-13), 14.3 (C-5', C-6'), 17.7 (C-12), 18.1 (C-10, C-11), 25.8 (C-7), 26.5 (C-4'), 28.3 (C-6), 29.7 (C-2), 41.9 (OCH_3), 55.7 (C-2'), 58.6 (C-3'), 63.1 (C-3), 74.7 ($C(OMe)CF_3$), 120.2 (CF_3), 124.2 (C-8), 127.7 (C-*o*), 128.3 (C-4), 129.6 (C-*m*), 132.0 (C-*p*), 132.4 (C-5), 144.6 (C-*i*), 153.8 (C-1'), 165.8 (COO), 173.6 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2965 (m), 2925 (m), 2876 (w), 2854 (w), 1779 (vs), 1745 (s), 1700 (s), 1488 (w), 1452 (m), 1384 (s), 1300 (m), 1261 (s), 1232 (s), 1184 (vs), 1121 (s), 1105 (s), 1081 (m), 1056 (m), 1014 (s), 990 (s), 965 (m), 909 (m), 803 (m), 765 (m), 731 (s), 718 (s), 697 (m), 648 (w), 517 (w), 449 (w), 412 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{38}F_3NO_6Na$ 576.2543, found 562.2538.

*(1S,2Z)-1-{(1R)-2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-1-methyl-2-oxoethyl}-3,7-dimethylocta-2,6-dienyl (2R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(R)-**16b**]*. Purification by chromatography (PE/EtOAc 5 : 1) gave (*R*)-**16b** (28.2 mg, 0.05 mmol, 88%, purity 90% ^1H NMR) as a colorless oil. R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.81 (d, *J* = 6.8 Hz, 3H,

5'-H or 6'-H), 0.88 (d, *J* = 6.8 Hz, 5'-H or 6'-H), 1.07 (d, *J* = 6.8 Hz, 3H, 13-H), 1.62 (s, 3H, 10-H or 11-H), 1.66 (s, 3H, 10-H or 11-H), 1.72 (s, 3H, 12-H), 2.03-2.11 (m, 2H, 7-H), 2.19-2.33 (m, 3H, 4'-H, 6-H), 3.54 (s, 3H, OCH_3), 4.15-4.26 (m, 3H, 3'-H), 4.37-4.42 (m, 1H, 2'-H), 5.12-5.18 (m, 1H, 8-H), 5.27 (d, *J* = 9.9 Hz, 4-H), 6.02 (dd, *J* = 9.8 Hz, 8.4 Hz, 1H, 3-H), 7.32-7.41 (m, 3H, *m*-H, *p*-H), 7.49-7.56 (m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.6 (C-13), 14.4 (C-5', C-6'), 17.7 (C-12), 18.1 (C-10 or C-11), 23.6 (C-10 or C-11), 25.8 (C-7), 26.5 (C-4'), 28.2 (C-6), 32.7 (C-2), 42.0 (OCH_3), 55.6 (C-2'), 58.6 (C-3'), 63.1 (C-3), 74.6 (C(OMe)CF_3), 120.5 (CF_3), 124.1 (C-8), 127.5 (C-*o*), 128.4 (C-4), 129.6 (C-*m*), 132.1 (C-*p*), 132.8 (C-5), 145.0 (C-*i*), 153.8 (C-1'), 165.7 (COO), 173.6 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2965 (m), 2923 (m), 2877 (w), 2854 (w), 1778 (vs), 1746 (s), 1699 (s), 1488 (w), 1452 (m), 1383 (s), 1299 (m), 1232 (vs), 1167 (vs), 1120 (s), 1103 (s), 1080 (s), 1055 (s), 1014 (vs), 989 (vs), 964 (s), 931 (s), 909 (s), 803 (s), 765 (m), 730 (s), 718 (vs), 697 (s), 648 (m), 595 (w), 554 (w), 509 (w), 450 (w), 408 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{38}F_3NO_6Na$ 576.2543; Found 576.2545.

*(1S,2E)-1-{2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-1-methyl-2-oxoethyl}-3-phenylpro-2-enyl (2S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(S)-**16c**]*. Purification by chromatography (PE/EtOAc 5 : 1) gave (*S*)-**16c** (41 mg, 0.076 mmol, 76%, purity 95% ^1H NMR) as a colorless solid. R_f = 0.35. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.68 (d, *J* = 6.8 Hz, 3H, 5'-H or 6'-H), 0.83 (d, *J* = 7.1 Hz, 3H, 5'-H or 6'-H), 1.26 (d, *J* = 6.9 Hz, 3H, 6-H), 2.18 (tt, *J* = 6.9 Hz, 3.5 Hz, 1H, 4'-H), 3.61 (s, 3H, OMe), 4.16–4.30 (m, 3H, 2-H, 3'-H, 2-H), 4.43 (dt, *J* = 8.4 Hz, 3.2 Hz, 1H, 2'-H), 6.02 (ddd, *J* = 6.8 Hz, 5.4 Hz, 1.1 Hz, 1H, 3-H), 6.12 (dd, *J* = 15.9 Hz, 7.0 Hz, 1H, 4-H), 6.54 (d, *J* = 15.9 Hz, 1H, 5-H), 7.21–7.32 (m, 5H, o-H, m-H), 7.32–7.42 (m, 3H, p-H, m-H), 7.51 (dd, *J* = 7.1 Hz, 1.8 Hz, 2H, o-H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 10.8 (C-6), 13.1 (C-6'), 16.9 (C-5'), 27.1 (C-4'), 40.9 (C-2), 54.8 (OCH_3), 57.6 (C-2'), 62.2 (C-3'), 76.3

(C-3), 83.5 (q, J = 27.7 Hz, C-8), 122.2 (q, J = 280 Hz, CF_3), 122.7 (C-4), 125.7 (C-o), 126.4 (C-o), 127.2 (C- p), 127.3 (C-m), 127.5 (C-m), 128.5 (C-p), 131.3 (C-i), 133.6 (C-5), 134.7 (C-i), 152.9 (C-1'), 164.7 (C-7), 172.1 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2965 (w), 2254 (vw), 1773 (s), 1747 (s) 1700 (s), 1488 (w), 1451 (w), 1360 (m), 1299 (w), 1249 (m), 1228 (m), 1167 (s), 1120 (m), 1103 (m), 1081 (w), 1056 (w), 1014 (m), 989 (m), 966 (m) 909 (m), 834 (vw), 804 (w), 729 (s), 718 (s), 694 (s), 648 (w), 510 (vw), 459 (vw), 439 (vw) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{30}F_3NO_6Na$ 556.1917; Found 556.1931.

*(1S,2E)-1-{2-[(4S)-4-Isopropyl-2-oxo-1,3-oxazolidin-3-yl]-1-methyl-2-oxoethyl}-3-phenylpro-2-enyl (2R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(R)-**16c**]*. Purification by chromatography (PE/EtOAc 5 : 1) gave (*R*)-**16c** (45 mg, 0.084 mmol, 84%, purity 90% ^{1}H NMR) as a colorless solid. R_f = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.65 (d, J = 6.8 Hz, 3H, 5'-H or 6'-H), 0.81 (d, J = 7.1 Hz, 3H, 5'-H or 6'-H), 1.13 (d, J = 6.8 Hz, 3H, 6-H), 2.19 (qd, J = 7.0 Hz, 3.6 Hz, 1H, 4'-H), 3.54 (s, 3H, OMe), 4.17 (dd, J = 9.1 Hz, 3.0 Hz, 1H, 2-H), 4.20–4.28 (m, 2H, 3'-H), 4.40 (dt, J = 8.3 Hz, 3.2 Hz, 1H, 2'-H), 5.97 (ddd, J = 7.6 Hz, 6.5 Hz, 0.9 Hz, 1H, 3-H), 6.26 (dd, J = 16.0 Hz, 7.6 Hz, 1H, 4-H), 6.74 (d, J = 15.9 Hz, 1H, 5-H), 7.22–7.45 (m, 8H, o-H, m-H, p-H), 7.48–7.56 (m, 2H, o-H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 11.3 (C-6), 13.1 (C-6'), 16.9 (C-5'), 27.1 (C-4'), 40.9 (C-2), 54.5 (OCH_3) 57.6 (C-2'), 62.2 (C-3'), 76.8 (C-3), 83.5 (q, J = 27.7 Hz, C-8),122.4 (q, J = 280 Hz, CF_3) 122.8 (C-4), 125.7 (C-o), 126.4 (C-o), 127.3 (C-p), 127.4 (C-m), 127.6 (C-m), 128.6 (C-p), 131.3 (C-i), 134.5 (C-5), 134.6 (C-i), 152.8 (C-1'), 164.7 (C-7), 172.0 (C-1); FT-IR (ATR): $\tilde{\nu}$ = 2964 (w), 2257 (vw), 2165 (vw), 1774 (s), 1749 (s), 1700 (s), 1488 (w), 1451 (w), 1386 (m), 1299 (m), 1230 (s), 1168 (s), 1120 (s) 1104 (s), 1081 (m), 1056 (w), 1014 (s), 988 (s), 966 (s), 909 (s), 834 (vw), 803 (w), 729 (s), 694 (s), 648 (m), 556

(vw), 518 (w), 488 (w), 437 (vw) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{30}F_3NO_6Na$ 556.1917; Found 556.1928.

*(2S,3S,4E)-2,5,9-Trimethyldeca-4,8-diene-1,3-diol [(E)-**17**]*. To a solution of (*E*)-**14a** (100 mg, 0.30 mmol) in abs. THF/abs. MeOH (5 : 0.05 mL) at 0 °C was added dropwise $LiBH_4$ (4 M in THF, 222 µL, 0.89 mmol), and the reaction mixture was stirred for 3 h. A satd solution of $NaHCO_3$ (10 mL) was added, the layers were separated, and the aqueous layer was extracted with EtOAc (3×15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by chromatography on SiO_2 (PE/EtOAc 2 : 1) to give (*E*)-**17** (40.2 mg, 0.19 mmol, 64%, ^1H NMR purity >95%) as a colorless oil. $R_f = 0.19$. $[\alpha]_D^{20} = +65.2$ (*c* = 1.0 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.86 (d, *J* = 7.0 Hz, 3H, 11-H), 1.59 (s, 6H, 10-H, 13-H), 1.66 (s, 3H, 12-H), 1.85-1.99 (m, 1H, 2-H), 1.98-2.16 (m, 4H, 6-H, 7-H), 2.52 (s, 2H, OH), 3.57 (dd, *J* = 10.8 Hz, 4.6 Hz, 1H, 1-H_a), 3.68 (dd, *J* = 10.7 Hz, 7.6 Hz, 1H, 1-H_b), 4.50 (dd, *J* = 9.0 Hz, 4.1 Hz, 1H, 3-H), 4.99-5.11 (m, 1H, 8-H), 5.29 (dd, *J* = 9.0 Hz, 1.1 Hz, 1H, 4-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 11.9 (C-12), 16.8 (C-10 or C-13), 17.8 (C-10 or C-13), 25.8 (C-11), 26.5 (C-7), 39.9 (C-6), 40.6 (C-2), 66.3 (C-1), 71.9 (C-3), 124.0 (C-8), 124.9 (C-4), 131.9 (C-9), 139.4 (C-5); FT-IR (ATR): $\tilde{\nu}$ = 3338 (m), 2965 (m), 2921 (m), 2064 (w), 1731 (w), 1669 (w), 1669 (w), 1449 (m), 1376 (m), 1261 (w), 1106 (m), 1082 (m), 1030 (s), 970 (s), 816 (w), 562 (w), 447 (w), 419 (w) cm^{-1}; MS (EI) m/z: $[M^+]$ Calcd for $C_{13}H_{24}O_2$ 212.1776; Found 212.1776.

*(2S,3S,4Z)-2,5,9-Trimethyldeca-4,8-diene-1,3-diol [(Z)-**17**]*. As described above from (*Z*)-**14a** (100 mg, 0.30 mmol) and $LiBH_4$ (4 M in THF, 222 µL, 0.89 mmol), chromatography (PE/EtOAc 2 : 1), yield: 38.1 mg, 0.18 mmol, 60%, ^1H NMR purity >95%, colorless oil. $R_f = 0.22$. $[\alpha]_D^{20} = +68.6$ (*c* = 1.2 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (d, *J* = 7.0 Hz, 3H, 11-H),

1.59 (s, 3H, 10-H or 13-H), 1.67 (s, 3H, 10-H or 11-H), 1.75 (s, 3H, 12-H), 1.81-1.96 (m, 1H, 2-H), 1.98-2.20 (m, 4H, 6-H, 7-H), 2.39 (s, 2H, OH), 3.52-3.64 (m, 1H, 1-H), 3.68 (dd, J = 10.8 Hz, 7.2 Hz, 1H, 1-H), 4.47 (dd, J = 9.3 Hz, 4.3 Hz, 1H, 3-H), 5.02-5.15 (m, 1H, 8-H), 5.34 (d, J = 9.2 Hz, 1H, 4-H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 11.7 (C-12), 17.6 (C-11), 23.5 (C-10 or C-13), 25.6 (C-10 or C-13), 26.5 (C-7), 32.2 (C-6), 40.2 (C-2), 66.3 (C-1), 71.2 (C-3), 123.9 (C-8), 125.5 (C-4), 132.4 (C-9), 139.9 (C-5); FT-IR (ATR): $\tilde{\nu}$ = 3346 (m), 2965 (m), 2916 (m), 2876 (m), 1994 (w), 1972 (w), 1726 (w), 1665 (w), 1449 (m), 1376 (m), 1262 (w), 1104 (m), 1080 (m), 1031 (s), 968 (s), 857 (w), 820 (w), 731 (w), 596 (m), 453 (w) cm^{-1}; MS (EI) m/z: $[M^+]$ Calcd for $C_{13}H_{24}O_2$ 212.1776; Found 212.1768.

*(4S,5S)-4-[(1E)-2,6-Dimethylhepta-1,5-dienyl]-2,2,5-trimethyl-1,3-dioxane [(E)-**18**]*. To a solution of (*E*)-**17** (20 mg, 0.09 mmol) in abs. acetone (1 mL) at room temperature were added dimethoxypropane (99.0 µL, 83.4 mg, 0.8 mmol) and PPTS (1 mg, 3.0 µmol). The reaction mixture was stirred for 3 h, and then the solvent was removed under vacuum. The residue was purified by chromatography on SiO_2 (PE/EtOAc 10 : 1 and 1 v/v Et_3N) to give (*E*)-**18** (20.5 mg, 0.08 mmol, 90%, ^{1}H NMR purity >95%) as a colorless oil. R_f = 0.38. $[\alpha]_D^{20}$ = +52.8 (c = 1.1 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.11 (d, J = 6.9 Hz, 3H, 8-H), 1.42 (s, 6H, 7a-H, 7b-H), 1.44-1.49 (m, 1H, 5-H), 1.50 (s, 3H, 7'-H or 9'-H), 1.66 (s, 3H, 7'-H or 9'-H), 1.67 (s, 3H, 8'-H), 1.96-2.18 (m, 4H, 3'-H, 4'-H), 3.59 (dd, J = 11.5 Hz, 1.7 Hz, 1H, 6-H), 4.15 (dd, J = 11.5 Hz, 2.9 Hz, 1H, 6-H), 4.75 (dd, J = 7.7 Hz, 2.8 Hz, 1H, 4-H), 5.02-5.13 (m, 1H, 5'-H), 5.21 (dd, J = 7.7 Hz, 1.2 Hz, 1H, 1'-H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 11.3 (C-8), 17.0 (C-7' or C-9'), 17.8 (C-7' or C-9'), 19.3 (C-8), 25.8 (C-7a or C-7b), 26.5 (C-7a or C-7b), 29.9 (C-3'), 32.9 (C-4'), 39.8 (C-5), 66.7 (C-6), 69.3 (C-4), 98.8 (C-2), 124.0 (C-5'), 124.2 (C-1'), 131.8 (C-6'), 138.3 (C-2'); FT-IR (ATR): $\tilde{\nu}$ = 3411 (w), 2965 (m), 2925 (m), 2858 (m), 2125 (w), 1671

(w), 1450 (m), 1378 (m), 1270 (m), 1239 (m), 1195 (m), 1166 (m), 1137 (m), 1102 (m), 1087 (m), 1008 (s), 983 (m), 963 (m), 914 (m), 862 (m), 843 (m), 817 (m), 753 (w), 540 (w), 517 (m), 433 (w) cm^{-1}; MS (EI) m/z: [M^+] Calcd for $C_{16}H_{28}O_2$ 252.2089; Found 252.2097.

*(4S,5S)-4-[(1Z)-2,6-Dimethylhepta-1,5-dienyl]-2,2,5-trimethyl-1,3-dioxane [(Z)-**18**]*. As described above, from (*Z*)-**17** (20 mg, 0.09 mmol), dimethoxypropane (99.0 µL, 83.4 mg, 0.8 mmol) and PPTS (1 mg, 3.0 µmol), chromatography (PE/EtOAc 10 : 1 and 1 v/v Et_3N), yield: 19.9 mg, 0.08 mmol, 88%, ^1H NMR purity >95%), colorless oil. $R_f = 0.40$. $[\alpha]_D^{20} = +57.7$ (c = 1.1 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.13 (d, *J* = 6.9 Hz, 3H, 8-H), 1.41 (s, 3H, 7a-H or 7b-H), 1.42-1.47 (m, 1H, 5-H), 1.49 (s, 3H, 7a-H or 7b-H), 1.61 (s, 3H, 7'-H or 9'-H), 1.68 (s, 3H, 7'-H or 9'-H), 1.75 (s, 3H, 8'-H), 1.95-2.22 (m, 4H, 3'-H, 4'-H'), 3.59 (dd, *J* = 11.5 Hz, 1.7 Hz, 1H, 6-H), 4.13 (dd, *J* = 11.5 Hz, 2.9 Hz, 1H, 6-H), 4.74 (dd, *J* = 8.2 Hz, 2.7 Hz, 1H, 4-H), 5.04-5.17 (m, 1H, 5'-H), 5.24 (dd, *J* = 8.2 Hz, 1.1 Hz, 1H, 1'-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 11.3 (C-8'), 17.0 (C-7' or C-9'), 17.8 (C-7' or C-9'), 19.3 (C-8), 25.8 (C-7a or C-7b), 26.5 (C-7a or C-7b), 29.9 (C-4'), 32.9 (C-3'), 39.8 (C-5), 66.7 (C-6), 69.3 (C-4), 98.8 (C-2), 124.0 (C-5'), 124.2 (C-1'), 131.8 (C-6'), 138.3 (C-2'); FT-IR (ATR): $\tilde{\nu}$ = 3359 (w), 2962 (m), 2925 (m), 2856 (m), 2168 (w), 2071 (w), 2037 (w), 2026 (w), 1734 (w), 1455 (m), 1377 (m), 1261 (w), 1104 (w), 1034 (m), 967 (m), 512 (w), 451 (w), 422 (w), 407 (w) cm^{-1}; MS (EI) m/z: [M^+] Calcd for $C_{16}H_{28}O_2$ 252.2089; Found 252.2080.

*(4S)-4-Isopropyl-3-(3-methylbut-2-enoyl)-1,3-oxazolidin-2-one (**23**).*[31] To a solution of **22** (2.00 g, 15.5 mmol) in THF (60 mL) at –78 °C was slowly added dropwise a 1.7 M solution of *t*-BuLi in *n*-pentane (9.70 mL, 16.5 mmol). Then 3-methylbut-2-enoyl chloride, which was prepared from 3,3-dimethylacrylic acid (1.65 g, 16.5 mmol) in abs. CH_2Cl_2 (15 mL) at 0 °C by dropwise addition of $(COCl)_2$ (1.46 mL, 2.16 g, 17.0 mmol) over 5 min followed by stirring for 3 h

at 0 °C, removal of the solvent, repeated take up in $CHCl_3$ (1 mL) and concentration under vacuum, was slowly added dropwise, the reaction mixture stirred at –78 °C for 2 h and allowed to warm to room temperature overnight. After cooling to 0 °C, a satd solution of $NaHCO_3$–H_2O (2 mL) was added followed by addition of a satd solution of NH_4Cl–H_2O (3 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL) and THF (2 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed under vacuum. The residue was purified by column chromatography on SiO_2 (PE/EtOAc 10:1) to give **23** (1.85 g, 8.77 mmol, 57%) as a yellow oil. R_f = 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.88 (d, J = 7.0 Hz, 3H, 1-H), 0.92 (d, J = 7.0 Hz, 3H, 2-H), 1.99 (s, 3 H, 10-H), 2.17 (s, 3H, 11-H), 2.40 (d sept, J = 7.0 Hz, 3.9 Hz, 1H, 3-H), 4.19 (dd, J = 9.0, 3.1 Hz, 1H, 5-H_a), 4.25 (dd, J = 9.0, 8.5 Hz, 1H, 5-H_b), 4.48 (ddd, J = 8.5, 3.9, 3.1 Hz, 1H, 4-H), 6.95 (m, 1H, 8-H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ (ppm) = 14.7 (C-1), 18.1 (C-2), 21.4 (C-10), 28.1 (C-11), 28.6 (C-3), 58.6 (C-5), 63.1 (C-4), 115.9 (C-8), 154.1 (C-9), 159.1 (C-6), 165.1 (C-7); FT-IR (ATR): $\tilde{\nu}$ = 2965 (w), 2877 (w), 1772 (vs), 1679 (m), 1632 (m), 1487 (w), 1447 (b), 1386 (m), 1362 (m), 1300 (w), 1256 (s), 1209 (m), 1185 (s), 1141 (w), 1121 (w), 1101 (w), 1082 (w), 1056 (w), 1024 (w), 1005 (w), 977 (w), 851 (b), 775 (w), 754 (w), 715 (w), 632 (w) cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{17}NO_3Na$ 234.1101; Found 234.1109.

*(4S)-3-(2-Chloro-3-hydroxy-3-methylbutanoyl)-4-isopropyl-1,3-oxazolidin-2-one (**20**).*[31] To a solution of **23** (250 mg, 1.18 mmol) in CH_2Cl_2 (1 mL) were added $Ca(OCl)_2$ (118 mg, 0.83 mmol) and H_2O (2 mL). After cooling to 0 °C, glacial HOAc (0.95 mL, 99.5 mg, 1.66 mmol) was added with stirring and the reaction mixture stirred for a further 15 min prior to addition of CH_2Cl_2 (20 mL) and H_2O (30 mL). The layers were separated and the organic layer was successively washed with a half concd solution of $NaHCO_3$–H_2O (2 × 10 mL) and H_2O (10 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure to give **20** (250 mg) as a (1:1) diastereomeric mixture

(denoted as a and b in NMR spectra), which could not be purified by chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89–0.98 (m, 6H, $1_{a,b}$-H, $2_{a,b}$-H), 1.37 (a) + 1.38 (b) (s, s, 3H, 10-H), 1.41 (b) + 1.44 (a) (s, s, 3H, 11-H), 2.34–2.47 (m, 1H, $3_{a,b}$-H), 4.25–4.32 (m, 1H, $5_{a,b}$-H_a), 4.33–4.43 (m, 1H, $5_{a,b}$-H_b), 4.50–4.57 (m, 1H, $4_{a,b}$-H), 5.69 (b) + 5.74 (a) (s, s, 1H, 8-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.6 (C-1_b), 14.7 (C-1_a), 17.7 (C-2_b), 17.8 (C-2_a), 24.7 (C-10_a), 25.3 (C-10_b), 27.5 (C-11_b), 27.8 (C-11_a), 28.0 (C-3_b), 28.5 (C-3_a), 58.4 (C-4_a), 59.1 (C-8_b), 59.2 (C-8_a), 59.3 (C-4_b), 63.6 (C-5_b), 63.8 (C-5_a), 72.2 (C-9_b), 72.7 (C-9_a), 153.4 (C-6_b), 153.9 (C-6_a), 168.7 (C-7_a), 169.2 (C-7_b); FT-IR (ATR): $\tilde{\nu}$ = 3507 (w, b), 2969 (w), 2876 (w), 1759 (m), 1698 (vs), 1467 (w), 1358 (s), 1300 (m), 1260 (m), 1202 (s), 1123 (m), 1100 (m), 1057 (w), 1025 (m), 972 (w), 930 (w), 892 (w), 878 (w), 848 (w), 814 (w), 763 (m), 737 (w), 709 (m), 633 (w), 598 (w), 549 (w), 490 (w), 429 (w) cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{19}ClNO_3$ 264.0997; Found 264.0995; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{18}ClNO_4Na$ 286.0817; Found 286.0813.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Synthetic schemes, procedure for precursor aldehyde **36**, data of Mosher esters **15**, **16**, NOESY spectra of diastereomers **14b** and analytical data (NMR, HPLC) (pdf).

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Notes

The authors declare no competing financial interest.

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