JOC Article

N-Vinyl-2-oxazolidinones: Efficient Chiral Dienophiles for the [4 + 2]-Based de Novo Synthesis of New *N*-2-Deoxyglycosides

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Under smooth Eu(fod)$_3$-catalyzed conditions, the inverse-electron demand hetero-Diels−Alder reactions between enantiopure *N*-vinyl-2-oxazolidinones **1a**−**f** and representative β,γ-unsaturated α-ketoesters proceed with a high degree of endo and facial diastereoselectivity. The elucidation of the stereostructure of these adducts, performed by X-ray analysis or chemical correlation, shows that the endo-selective cycloaddition process is facially controlled in favor of the (2*S*,4*S*)-adduct when starting from a (4*S*)-dienophile or vice versa. The specific interest of the adducts **10a**−**e**, derived from (*E*)-4-*tert*-butoxymethylene pyruvic acid methyl ester **9**, has been exemplified by the two-step and highly stereoselective transformation of these adducts into the new and valuable *N*-2-deoxyglycosyl-oxazolidinones **12a**−**e**, isolated in a pure diastereo- and enantiomeric form.

Introduction

The discovery of new cycloreactants is a continuous task in the field of pericyclic reactions. The use of heterosubstituted dienes and dienophiles has provided numerous and powerful asymmetric extensions[1] and is of specific interest for the application of [4 + 2] homo- and hetero-Diels−Alder reactions[2] to the synthesis of natural and biologically active products. Regarding inverse-electron demand [4 + 2] heterocycloaddition methods, aza-substituted dienophiles have been used more rarely than their oxygenated counterparts so far. Contributions in this field have mainly concerned the use of electron-rich enamines.[3−4] Interestingly, the first organocatalytic asymmetric version of an inverse-electron demand hetero-Diels−Alder reaction was recently described, based on the dienophilicity of a transient chiral enamine, generated in situ, toward an activated heterodiene.[5] In contrast, the use of weaker dienophiles such as enamides or enecarbamates was seldom reported. The thermal inverse-electron demand [4 + 2] heterocycloaddition of allenamides derived from lactams, oxazolidinones, and imidazolidinones was described by Hsung's group in 1999.[6] Good levels of stereoselectivity were obtained with the chiral allenamide derived from Close's imidazolidinone toward a range of 1-oxabutadienes.

More recently, we have described the first examples of an inverse-electron demand heterocycloaddition using *N*-vinyl-2-oxazolidinone as the dienophile toward activated heterodienes under appropriate Lewis acid conditions.[7] Therefore, we oriented our work in evaluating the stereochemical potential of 4-substituted and 4,5-disubstituted *N*-vinyl-2-oxazolidinones as new chiral dienophiles in a comparative or complementary way regarding the chiral dienophiles (chiral vinyl ethers),[8] chiral heterodienes,[9] or chiral catalysts[10] previously used for such asymmetric [4 + 2] heterocycloadditions. Having generalized a new mercury-free preparation method of such *N*-vinylamides,[11] we report herewith that these *N*-vinyl-2-oxazolidinones are chiral dienophiles of choice toward

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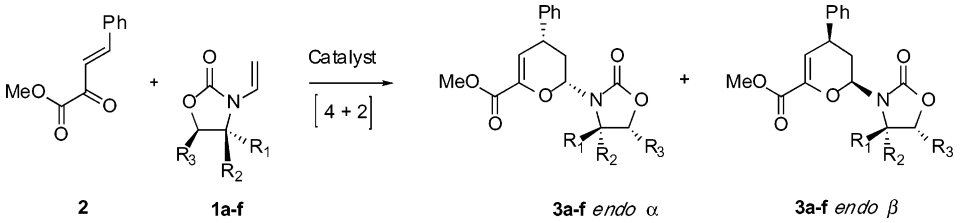
SCHEME 1



β,γ-unsaturated α-ketoesters, leading to heterocycloadducts with high endo and facial selectivities under Eu(fod)$_3$-catalyzed conditions. In addition, we considered in this approach that, if efficient, the oxazolidinyl moiety would act not only as a chiral inducing agent but also as a valuable building block, providing new ways for the stereocontrolled de novo synthesis of *N*-2-deoxyglycosides or even sugar-α-amino acid hybrid[12] derivatives. Therefore, we describe hereby the efficient asymmetric syntheses of common potential precursors of such targets, namely, the new *N*-2-deoxyglycosyl-oxazolidinones **12**.

Results and Discussion

As in the achiral series, we first investigated the cycloaddition of a representative 2-activated heterodiene, the (*E*)-benzylidene pyruvic acid methyl ester **2** (Scheme 1). Our previous study with achiral vinyloxazolidinone showed that the best yields and endo selectivities were obtained with the catalytic use of trivalent lanthanide chelates (Eu-or Yb(fod)$_3$, 5 mol %) in refluxing cyclohexane.[13] Under the same Lewis-acid catalyzed and mild thermal conditions, the chiral *N*-vinyloxazolidinones **1a**−**f**[11] displayed a fluctuating reactivity, depending on the nature of the C-4 substituent. For less bulky dienophiles **1a**, **1d**, and **1e** (R_1 or R_2 = Et, Bn, and Me, respectively), the completion of the cycloaddition occurred in less than 40 h. In contrast, for more bulky dienophiles **1b**, **1c**, and **1f** (R_1 or R_2 = *i*-Bu, Ph), a complete conversion required an extended time period (entries 2, 3, 6, Table 1). Interestingly, apart from the high endo selectivity observed in each case, the level of facial selectivity was noteworthy, being homogeneous and high, ranging from 96/4 to 98/2 or more for the six adducts **3a**−**f** produced. In addition, all heteroadducts except **3c** were obtained as a single endo diastereomer after chromatography and in 77−93% isolated yields.

To determine the absolute configurations of the adducts **3a**−**f**, we used a correlation method previously described in our laboratory for chiral vinyl ether-derived heteroadducts. This method is based on the ozonolytic cleavage of the dihydropyrane ring and subsequent oxidation, thus leading after esterification to known phenyl succinic acid methyl ester **8** (Scheme 2, Table 2).[8b]

Ozonolysis of adducts **3a**−**c** at −78 °C in a methanolic medium, followed by a treatment with acetic anhydride and triethylamine, actually led to different results, depending on the conditions. The use of a large excess of acetic anhydride and triethylamine gave a minor amount of the expected aldehyde-ester **4** (12−15%) as well as a significant amount of *N*,*O*-acylal **5**. With only 1.25 equiv of NEt_3 and 2.5 equiv of Ac_2O, we obtained a 1:1 mixture of the expected aldehyde-ester **4** and of the corresponding *N*,*O*-hemiaminal **6**. In this latter case, a further acidic treatment (4 N H_2SO_4 in acetone) converted the *N*,*O*-hemiaminal **6** into **4** efficiently. Thereby, Jones oxidation of the aldehyde-ester **4** and a final esterification provided the diester **8** in good overall yield (51% from **3b**, entry 2). In the three cases studied, the specific rotation of the latter compound **8** established the absolute configuration at the C-4 center of the corresponding adduct unambiguously. In the case of the adduct **3a**, this attribution was confirmed by X-ray analysis (see Supporting Information) of the corresponding crystalline amido-ester **7a** produced by Jones oxidation of the *N*,*O*-acylal **5a**. Finally, the enantiopurity of **8**, determined in every case by chiral GC, was found to agree with the facial selectivity established by ^{1}H NMR for the corresponding adduct. This chemical correlation established a univocal relationship between the inducing stereogenic center at C-4′ of the oxazolidinyl ring and the two stereogenic centers created on the dihydropyranic ring: the endo-selective cycloaddition process proved to be facially controlled in favor of the (2*R*,4*R*)-adduct **3** when starting from a (4*R*)-dienophile and in favor of the (2*S*,4*S*)-adduct **3** when starting from a (4*S*)-dienophile. Considering the strong

TABLE 1. Eu(fod)$_3$-Catalyzed Heterocycloaddition of 1a−f with 2

	1	R_1	R_2	R_3	time[a]	3	yield (%)[b]	endo/exo[f]	endo α/endo β[f] crude	endo α/endo β[f] purified
1	**1a**	Et	H	H	15 h	**3a**	77[c]	98/2	96/4	>98/2
2	**1b**	H	*i*-Bu	H	6 days	**3b**	92[d]	98/2	3/97	<2/98
3	**1c**	Ph	H	H	9 days	**3c**	90[e]	98/2	96/4	96/4
4	**1d**	Bn	H	H	38 h	**3d**	93	>98/2	>98/2	>98/2
5	**1e**	H	Me	Ph	38 h	**3e**	80	>98/2	<2/98	<2/98
6	**1f**	H	Ph	Ph	4 days	**3f**	80	>98/2	<2/98	<2/98

[a] Reactions run on a 0.5 mmol scale; 1.0 equiv of each cycloreactant was used in all cases with 5 mol % Eu(fod)$_3$ in refluxing cyclohexane. [b] Isolated yields after chromatography. [c] Isolated yield of 75% was obtained on a 7 mmol scale, after 48 h of reaction. [d] Isolated yield of 60% was obtained on a 9 mmol scale, after 7 days of reaction. [e] Isolated yield of 75% was obtained on a 2 mmol scale, after 10 days of reaction. [f] Determined by ^{1}H NMR (400 MHz).

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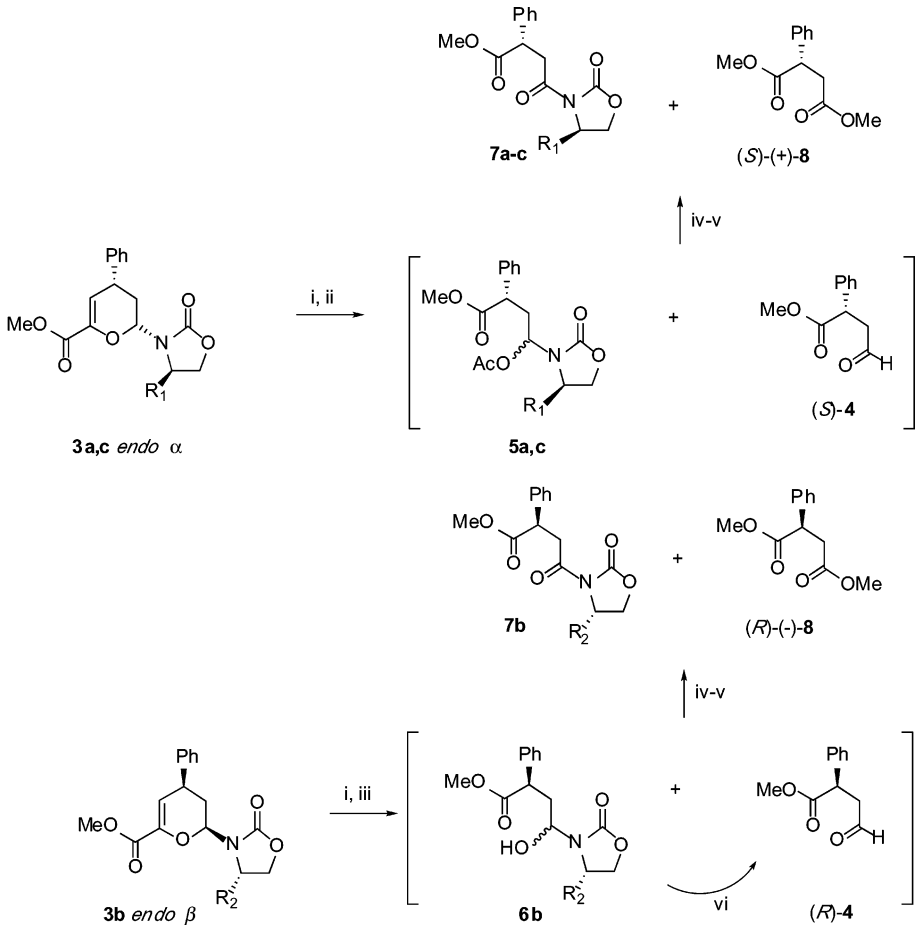
(13) Further experiments using $SnCl_4$ as an alternative Lewis acid confirmed our previous observations in achiral series: reaction proceeded at low temperature with low or without diastereoselectivities.

SCHEME 2[a]



[a] Reagents and conditions: (i) O_3, CH_2Cl_2, MeOH, −78 °C. (ii) Ac_2O (20 equiv), NEt_3 (15 equiv). (iii) Ac_2O (2.5 equiv), NEt_3 (1.5 equiv). (iv) CrO_3−H_2SO_4/acetone. (v) CH_2N_2 or HCl/MeOH. (vi) H_2SO_4/acetone.

TABLE 2. Stereochemical Correlation of Adducts 2a−c with Phenyl Succinic Acid Ester 8

						final products			
						yield[b] (%)			
	starting adduct	R_1	R_2	R_3	method[a]	amide **7**	diester **8**	configuration[c]	**ee**[d]
1	**3a**	Et	H	H	A	42	15	(*S*)-(+)	>98
2	**3b**	H	*i*-Bu	H	B		51	(*R*)-(−)	96
3	**3c**	Ph	H	H	A	56	12	(*S*)-(+)	92

[a] Method A: steps i and ii, NEt_3 (15 equiv), Ac_2O (20 equiv), step iv on the mixture, and then step v (see Scheme 2). Method B: steps i and iii, NEt_3 (1.25 equiv), Ac_2O (2.5 equiv), and then steps vi, iv, and v (see Scheme 2). [b] Isolated yields. [c] Established by specific rotation. [d] Determined by chiral GC.

analogies that prevail between the ^1H NMR data of all adducts **3a**−**f** (see Supporting Information), the configurations of the (major) endo adducts **3d**−**f** were assigned on the assumption of the same relationship (Table 1).

On the basis of these results, the study on heterocycloaddition of chiral *N*-vinyloxazolidinones **1a**−**f** was extended to "prosugar" heterodienes (e.g., 4-alkoxy-substituted). Our previous study with the unsubstituted *N*-vinyloxazolidinone had shown that under the same catalytic conditions, the best results and endo selectivities in this series were obtained with the 4-*tert*-butoxymethylene pyruvic acid ester **9**.[7] Although notably less reactive than its phenylated counterpart **2**, the heterodiene **9** gave rise to the expected cycloadducts with the *N*-vinyloxazolidinones **1a**−**e** (Scheme 3) when using the following modified conditions: reaction time extended to 4−5 days, 2-fold addition of the catalyst, and use of an excess of **9** (Table 3). Under these optimized conditions, adducts **10a**−**e** were obtained in 40−66% isolated yields with a nearly total endo selectivity and a high facial selectivity (from 95/5 to 98/2 or more).

The moderate yields were possibly a consequence of the lack of homogeneity of the reaction medium that prevailed specifically when heterodiene **9** was employed in refluxing cyclohexane. All our attempts to increase the conversion rate by using another solvent (chloroform, dichloromethane, toluene, perfluorocyclohexane) were unsuccessful. Adducts **10a** and **10d** were obtained after chromatography in a pure single diastereomeric form as crystallized compounds, and X-ray analysis allowed the

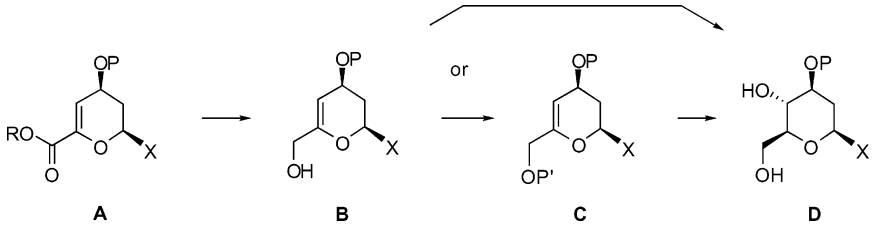


FIGURE 1. Common strategy for the transformation of [4 + 2] heteroadducts into *X*-glycosides.

SCHEME 3

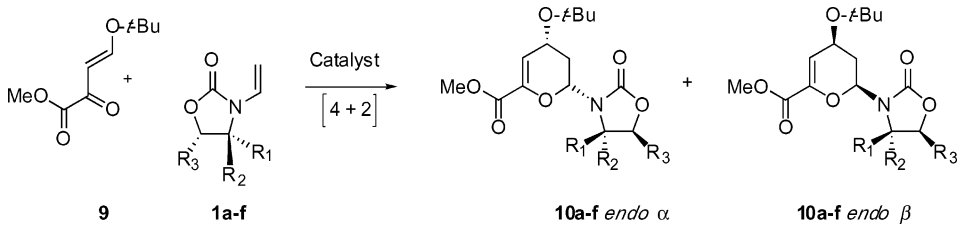


TABLE 3. Eu(fod)$_3$-Catalyzed Heterocycloaddition of 1a−f with 9

entry	**1**	R_1	R_2	R_3	time[a]	**10**[b]	yield (%)[c]	endo/exo	endo α/endo β
1	**1a**	Et	H	H	5 days	**10a**	52	97/3	>98/2
2	**1b**	H	*i*-Bu	H	4 days	**10b**	40	98/2	5/95
3	**1c**	Ph	H	H	4 days	**10c**	54	>98/2	>96/4
4	**1d**	H	Bn	H	4 days	**10d**	42	>98/2	<2/98
5	**1e**	Me	H	Ph	4 days	**10e**	66	>98/2	97/3
6	**1f**	Ph	H	Ph	5 days	**10f**	<20		

[a] Reactions run on 0.5 mmol scale. [b] Reaction conditions: **9/1** ratio = 1.0 for **10a** and 1.5 for **10b**−**f**; catalyst = Eu(fod)$_3$, 2 × 5 mol %; refluxing cyclohexane. [c] Isolated yields after chromatography.

determination of their configuration (see Supporting Information). Not surprisingly, the same relationship between the inducing stereogenic center at C-4′ of the oxazolidinyl ring and the two stereogenic centers created on the dihydropyranic ring was found for adducts **10** when compared to adducts **3**: the endo-selective cycloaddition process proved to be facially biased in favor of the configuration (2*S*,4*S*,4′*S*)- for **10d** and of the configuration (2*R*,4*R*,4′*R*)- for **10a**. Considering the significant analogies that prevail again between the ^{1}H NMR data of all adducts **10a**−**e** (See Supporting Information), the configurations of whole adducts **10** were assigned on the assumption of the same relationship.

In a final part of this work, de novo access to *N*-2-deoxyglycosyl-oxazolidinones **12** was investigated starting from adducts **10**. For this purpose, we envisioned the use of the strategy commonly employed to transform heteroadducts (**A**) derived from other types of heterosubstituted dienophiles (such as vinyl ethers) into X-glycosides (**D**) (*O*-alkyl-2-deoxyglucosides for instance): reduction of the ester function at C-6 (giving **B**), followed by protection of the allylic hydroxyl function (giving **C**) and then regio- and stereoselective hydroboration−oxidation of **C** (or even of **B** in some cases) (Figure 1).

Nevertheless, given the presence of the oxazolidinyl functionality, some modifications were introduced. Indeed, the reduction of the ester function in the first step had to be achieved with convenient chemoselectivity. Our first assays had shown that $LiAlH_4$ (classically used for reduction of type-A adducts) was ineffective in this particular case. In contrast, the application of the reaction conditions described by Gonda and co-workers[14] proved to be convenient: the low-temperature treatment of adducts **10** with an excess of DIBAH in the presence of a stoichiometric amount of BF_3·Et_2O led to the desired crude allylic alcohols **11** in high to quantitative yields and with fair purities (Scheme 4, Table 4). It should be noticed that a significant loss of material and purity was observed in the crude product when the reduction was conducted without the use of a Lewis acid. Attempts to isolate these sensitive allylic alcohols **11** gave tedious results (40−60% yield after chromatography on silicagel), so we employed the crude allylic alcohols **11** in the subsequent steps.

The following hydroboration step was conducted with excess BH_3·Me_2S. Regarding the oxidation of the intermediate organoborane, and given the predictable sensitivity of the carbamate functionality under the harsh basic conditions classically used (6 M NaOH, H_2O_2, refluxing THF), Kabalka's procedure using trimethylamine *N*-oxide dihydrate in refluxing THF[15] was selected. In the relevant literature, de novo access to *O*-glycosides via a classical hydroboration−oxidation sequence is not commonly carried out on the allylic alcohol **B**, but more frequently starting from the corresponding allylic acetate **C** (Figure 1, P′ = Ac). Previous results in our laboratory[8c,16] pointed out that hydroboration−oxidation of the double bond can be performed on unprotected substrates **B** in acceptable yields and without a negative effect on the selectivities. In the present case, due to the modification introduced at the oxidation step by using Kabalka's procedure, the hydroboration−oxidation sequence was then comparatively tested on both the unprotected dihydropyran **11a** (R_1 = Et) and the corresponding allylic acetate **13a** (Scheme 5).

Application of this sequence to the acetate **13a** led to a mixture of **12a** along with the corresponding monoacetate **14a** (Scheme 5). Reacetylation of the mixture under

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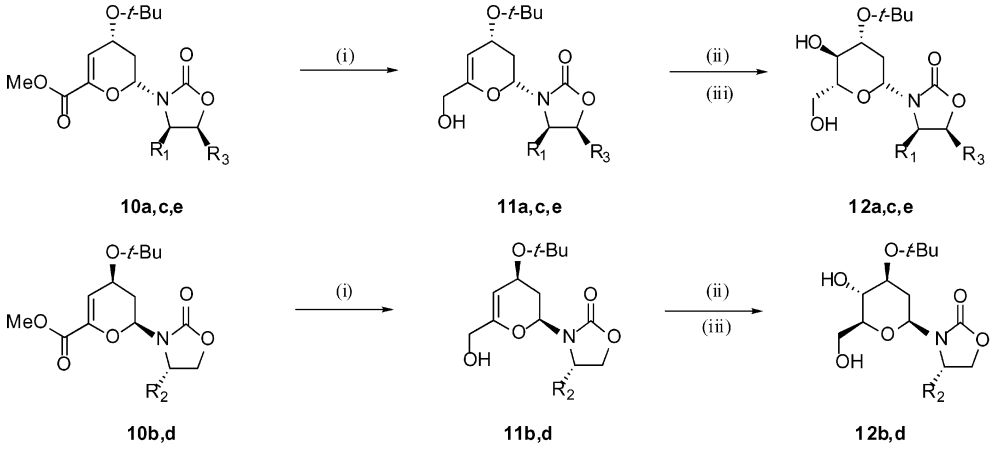
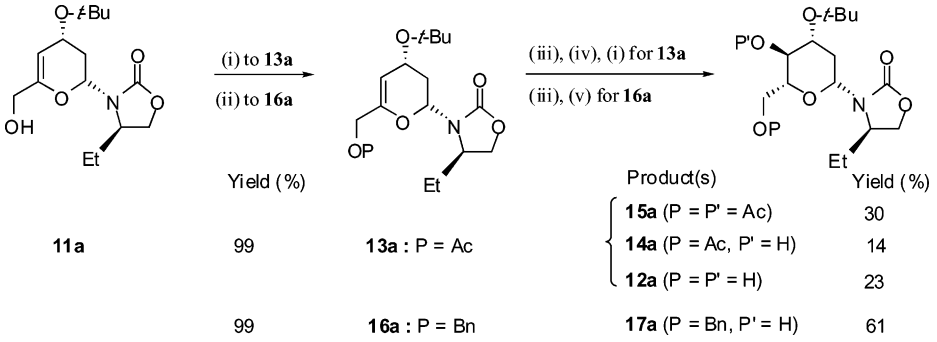
SCHEME 4[a]



[a] Reagents and conditions: (i) DIBAH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −78 °C. (ii) $BH_3{\cdot}Me_2S$, THF, rt. (iii) Me_3NO, diglyme, 110 °C.

SCHEME 5[a]



[a] Reagents and conditions: (i) Ac_2O, DMAP, NEt_3, rt. (ii) NaH, BnBr, DMF, rt. (iii) $BH_3{\cdot}Me_2S$, THF, rt. (iv) Me_3NO, THF, reflux. (v) Me_3NO, diglyme, 110 °C.

TABLE 4. Synthesis of *N*-Glycosyl-oxazolidinones 12a−e

	10	R_1	R_2	R_3	11	crude yield of 11 (%)	12	isolated yield of 12[a] (%)
1	**10a**	Et	H	H	**11a**	>95	**12a**	46
2	**10b**	H	*i*-Bu	H	**11b**	95	**12b**	61
3	**10c**	Ph	H	H	**11c**	71	**12c**	44
4	**10d**	H	Bn	H	**11d**	90	**12d**	52
5	**10e**	Me	H	Ph	**11e**	>95	**12e**	48

[a] Isolated yield of pure diastereomer after chromatography.

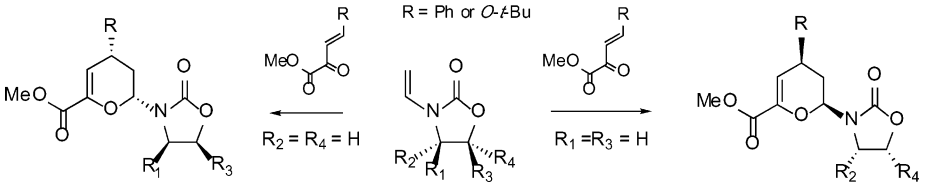
classical conditions failed to provide a single final product: after chromatography, the unprotected *N*-glycoside **12a**, the monoacetate **14a**, and the corresponding diacetate **15a** were isolated in 23, 14, and 30% yields, respectively. In contrast, applying the same hydroboration−oxidation conditions to the free allylic alcohol **11a** led to the desired *N*-glycoside **12a** in a highly stereoselective manner and 40% yield. As a consequence, the hydroboration−oxidation sequence was thus further investigated with unprotected subtrates. According to previous observations,[15] replacing THF with a solvent with a higher boiling point such as diglyme proved to enhance the oxidation rate significantly (Scheme 4, Table 4, entry 1). These conditions were successfully applied to allylic alcohols **11a**−**e**: the expected *N*-glycosyl-oxazolidinones **12a**−**e** were isolated in 32−58% overall yields from the corresponding adducts **10** and in a high state of overall diastereomeric purity (>98% in all cases). Assignment of the common relative configuration for *N*-glycosyl-oxazolidinones **12a**−**e** was established by ^{1}H NMR NOE measurements for **12a** and **12d** and by correlation between ^{1}H NMR data for the other compounds (see Supporting Information).

Considering the limited yields observed in the latter step starting from allylic alcohols **11a**−**e**, other protected analogues of **11a** were finally tested: the allylic *O*-benzyl ether **16a** quantitatively obtained from **11a** proved to be a convenient substrate for this purpose, leading to the orthogonally 4,6-diprotected *N*-glycoside **17a** in a 61% yield in a pure diastereomeric form (Scheme 5).

Conclusion

This study has demonstrated the usefulness and the high potential of *N*-vinyloxazolidinones as new chiral dienophiles in inverse-electron demand [4 + 2] hetero-Diels−Alder reactions.[17] Such heterocycloaddition methods involving β,γ-unsaturated α-ketoesters as the heterodienes were achieved with high, homogeneous diastereoselectivities, weakly dependent on the substitution pattern of the chiral oxazolidinyl moiety. A univocal relationship between the inducing stereogenic center at C-4′ of the oxazolidinyl ring and the two stereogenic centers created on the dihydropyranic ring was established: the endo-selective $Eu(fod)_3$-catalyzed cycloaddition process proved to be facially controlled in favor of

SCHEME 6



the (2*S*,4*S*)-adduct when starting from a (4*S*)-dienophile and in favor of the (2*R*,4*R*)-adduct when starting from a (4*R*)-dienophile (Scheme 6). We have shown not only that these new cycloreactants can act as superior chiral dienophiles but also that they have potential in chiron approaches toward new and valuable targets. A first validation of this strategy was exemplified by the asymmetric synthesis of a series of new *N*-2-deoxyglycosyloxazolidinones. Access to other 2-deoxyglucose-α-amino acid hybrid derivatives by this approach is in progress in our laboratory, together with the evaluation of the potential of the title *N*-vinylic compounds in other asymmetric pericyclic reactions.

Experimental Section

General Preparation of Hetero-adducts 3a−f with Eu(fod)$_3$. A solution of heterodiene **2**[18] (1 equiv, 95 mg, 0.5 mmol), *N*-vinyl-2-oxazolidinone **1a**−**f**[11,17] (1 equiv, 0.5 mmol), and Eu(fod)$_3$ (0.05 equiv, 26 mg, 0.025 mmol) in cyclohexane (5 mL) was refluxed under nitrogen for the time period indicated in Table 1. After removal of solvent, the crude product was chromatographed (silica gel 40/1; cyclohexane/AcOEt 80/20 to 50/50).

(2*R*,4*R*)-2-[(4*R*)-4-Ethyl-2-oxo-1,3-oxazolidin-3-yl]-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 3a. From **1a** (70.5 mg, 0.5 mmol), **3a** (endo/exo 98/2, endo-α/*β* 99/1) was obtained after chromatography as a yellow oil (165 mg, 77%). Major isomer **3a**-*endo*-α: IR (neat) 1757 (C=O), 1645 (C=C), 1423, 1367, 1284, 1216, 1132, 1091, 1032, 762, 731, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.95 (3H, t, *J* = 7.4 Hz), 1.80 (2H, m), 2.12 (1H, dt, *J* = 13.0 and 11.4 Hz), 2.25 (1H, ddt, *J* = 13.0, 6.4 and 1.7 Hz), 3.80 (3H, s), 3.88 (1H, ddd, *J* = 11.4, 6.4 and 2.2 Hz), 3.90 (1H, m), 4.07 (1H, dd, *J* = 8.6 and 5.4 Hz), 4.37 (1H, t, *J* = 8.6 Hz), 5.75 (1H, dd, *J* = 11.2 and 2 Hz), 6.15 (1H, t, *J* = 2 Hz), 7.23 (2H, d, *J* = 6.9 Hz), 7.29 (1H, t, *J* = 7.4 Hz), 7.35 (2H, dd, *J* = 7.4 and 6.9 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) *δ* 7.8 (CH_3), 26.4 (CH_2), 34.1 (CH_2), 39.0 (CH), 52.0 (CH_3), 54.2 (CH), 67.0 (CH_2), 81.3 (CH), 113.6 (CH), 126.9 (CH), 127.1 (CH), 128.7 (CH), 142.0 (C), 143.7 (C), 156.9 (C), 162.4 (C). [α]$^{20}_D$ +11.3 (*c* 0.92, CH_2Cl_2).

(2*S*,4*S*)-2-[(4*S*)-4-Isobutyl-2-oxo-1,3-oxazolidin-3-yl]-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 3b. From **1b** (84.5 mg, 0.5 mmol), **3b** (endo/exo 98/2, endo-*β*/α 99/1) was obtained after chromatography as a yellow oil (165 mg, 92%). Major isomer **3b**-*endo*-*β*: IR (neat) 1759 (C=O), 1737 (C=O), 1643 (C=C), 1282, 1249, 1130 (C−O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.90 (3H, d, *J* = 6.6 Hz), 0.97 (3H, d, *J* = 6.6 Hz), 1.56 (1H, m), 1.67 (1H, ddd, *J* = 14.0, 10.1 and 4.2 Hz), 1.80 (1H, ddd, *J* = 14.0, 9.8 and 3.0 Hz), 2.15 (1H, dt, *J* = 13.0 and 11.1 Hz), 2.26 (1H, ddt, *J* = 13.0, 6.5 and 2 Hz), 3.81 (3H, s), 3.86 (1H, ddd, *J* = 11.1, 6.5 and 2.4 Hz), 3.99 (1H, m), 4.04 (1H, dd, *J* = 8.0 and 6.1 Hz), 4.40 (1H, t, *J* = 8.0 Hz), 5.70 (1H, dd, *J* = 11.1 and 2 Hz), 6.15 (1H, t, *J* = 2 Hz), 7.22 (2H, d, *J* = 6.9 Hz), 7.29 (1H, t, *J* = 7.5 Hz), 7.36 (2H, dd, *J* = 7.5 and 6.9 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) *δ* 21.4 (CH_3), 23.5 (CH_3), 24.6 (CH), 33.9 (CH_2), 39.1 (CH), 42.5 (CH_2), 52.0 (CH), 52.2 (CH_3), 68.0 (CH_2), 81.5 (CH), 113.9 (CH), 126.9 (CH), 127.1 (CH), 128.6 (CH), 141.9 (C), 143.6 (C), 156.8 (C), 162.4 (C); HRMS (EI) calcd for $C_{20}H_{23}NO_4$ [M − H_2O]$^+$ 341.16271, found 341.1608. [α]$^{20}_D$ +1.45 (*c* 1.1, CH_2Cl_2).

(2*R*,4*R*)-2-[(4*R*)-4-Phenyl-2-oxo-1,3-oxazolidin-3-yl]-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 3c. From **1c** (94.5 mg, 0.5 mmol), **3c** (endo/exo 98/2, endo-α/*β* 96/4) was obtained after chromatography as a white foam (170 mg, 90%). Major isomer **3c**-*endo*-α: IR (neat) 1761 (C=O), 1740 (C=O), 1646 (C=C), 1287, 1256, 1130 (C−O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.27 (1H, ddt, *J* = 13.3, 6.1 and 1.7 Hz), 2.56 (1H, dt, *J* = 13.3 and 11.3 Hz), 3.66 (1H, ddd, *J* = 11.3, 6.1 and 2.2 Hz), 3.75 (3H, s), 4.16 (1H, dd, *J* = 8.8 and 8.0 Hz), 4.66 (1H, t, *J* = 8.8 Hz), 5.10 (1H, dd, *J* = 8.8 and 8.0 Hz), 5.23 (1H, dd, *J* = 11.3 and 1.7 Hz), 5.99 (1H, t, *J* = 2 Hz), 7.10−7.50 (10H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) *δ* 33.3 (CH_2), 39.2 (CH), 51.9 (CH_3), 59.2 (CH), 65.7 (CH_2), 82.0 (CH), 113.9 (CH), 127.0−129.0 (CH), 137.4 (C), 141.9 (C), 143.3 (C), 156.7 (C), 162.3 (C); HRMS (EI) calcd for $C_{22}H_{21}NO_5$ [M]$^+$ 379.14197, found 379.1448. [α]$^{20}_D$ −67.9 (*c* 0.96, CH_2Cl_2).

(2*R*,4*R*)-2-[(4*R*)-4-Benzyl-2-oxo-1,3-oxazolidin-3-yl]-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 3d. From **(4*R*)-1d** (102 mg, 0.5 mmol), **3d** (endo/exo > 98/2, endo-α/*β* > 98/2) was obtained after chromatography as a white foam (183 mg, 93%). Major isomer **3d**-*endo*-α: IR (neat) 1760 (C=O), 1734 (C=O), 1641 (C=C), 1424, 1289, 1133, 1093, 1031, 764, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.13 (1H, dt, *J* = 11.6 and 13.0 Hz), 2.30 (1H, ddt, *J* = 2.0, 6.4 and 13.0 Hz), 2.94 (1H, dd, *J* = 8.6 and 14.0 Hz), 3.30 (1H, dd, *J* = 3.9 and 14.0 Hz), 3.81 (3H, s), 3.87 (1H, ddd, *J* = 2.5, 6.4 and 11.6 Hz), 4.10 (1H, dd, *J* = 4.0 and 8.0 Hz), 4.17 (1H, t, *J* = 8.0 Hz), 4.19 (1H, m), 5.78 (1H, dd, *J* = 2.0 and 11.6 Hz), 6.16 (1H, t, *J* = 2.0 Hz), 7.19−7.40 (10H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) *δ* 34.5 (CH_2), 39.3 (CH), 40.0 (CH_2), 52.3 (CH_3), 54.5 (CH), 67.0 (CH_2), 81.7 (CH), 114.0 (CH), 127.2−129.5 (6xCH), 135.7 (C), 142.1 (C), 143.8 (C), 156.9 (C), 162.6 (C); HRMS (EI) calcd for $C_{21}H_{20}NO_3$ [M − CO_2CH_3]$^+$ 334.1443, found 334.1421. [α]$^{25}_D$ −28 (*c* 1.1, CH_2Cl_2).

(2*S*,4*S*)-2-[(4*S*,5*R*)-4-Methyl-2-oxo-5-phenyl-1,3-oxazolidin-3-yl]-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 3e. From **(4*S*,5*R*)-1e** (102 mg, 0.5 mmol), **3e** (endo/exo > 98/2, endo-*β*/α > 98/2) was obtained after chromatography as white crystals (157 mg, 80%). Major isomer **3e**-*endo*-*β*: mp 206−207.5 °C (ether); IR (KBr) 1764 (C=O), 1735 (C=O), 1639 (C=C), 1455, 1419, 1380, 1289, 1239, 1216, 1144, 1088, 1037, 971, 871, 764, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.92 (3H, d, *J* = 6.6 Hz), 2.12 (1H, dt, *J* = 11.3 and 13.0 Hz), 2.35 (1H, ddt, *J* = 2.0, 6.4 and 13.0 Hz), 3.78 (3H, s), 3.89 (1H, ddd, *J* = 2.0, 6.4 and 11.3 Hz), 4.24 (1H, qt, *J* = 6.6 Hz), 5.62 (1H, d, *J* = 7.6 Hz), 5.78 (1H, dd, *J* = 2.0 and 11.3

(17) For efficient uses of chiral *N*-vinyloxazolidinones (i) in asymmetric Pd-promoted carboacylations and alkylations, see: (a) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255. (b) Masters, J. J. M.; Hegedus, L. S.; Tamariz, J. *J. Org. Chem.* **1991**, *56*, 5666. (c) Laidig, G. J.; Hegedus, L. S. *Synlett* **1995**, 527. (ii) In [2 + 2] photocycloadditions, see: (d) Miller, M.; Hegedus, L. S. *J. Org. Chem.* **1993**, *58*, 6779. (e) Bach, T.; Schröder, J.; Brandl, T.; Hecht, J.; Harms, K. *Tetrahedron* **1998**, *54*, 4507. (iii) In asymmetric cyclopropanations, see: (f) Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Akiba, T.; Terashima, S. *Tetrahedron Lett.* **1992**, *33*, 3487. (g) Akiba, T.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Terashima, S. *Tetrahedron* **1994**, *50*, 3905.

(18) Dujardin, G.; Leconte, S.; Bénard, A.; Brown, E. *Synlett* **2001**, 147.

Hz), 6.15 (1H, t, J = 2.0 Hz), 7.21−7.43 (10H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 16.6 (CH_3), 34.8 (CH_2), 39.2 (CH), 52.2 (CH_3), 53.7 (CH), 79.4 (CH), 81.3 (CH), 113.7 (CH), 126.1−128.9 (6 x CH), 134.3 (C), 142.2 (C), 143.9 (C), 156.2 (C), 162.6 (C). Anal. Calcd for $C_{23}H_{23}NO_5$: C, 70.21; H, 5.89; N, 3.56. Found: C, 69.98; H, 5.81; N, 3.31. $[\alpha]^{25}_D$ −9 (*c* 1.03, CH_2Cl_2).

(2*S*,4*S*)-2-[(4*S*,5*R*)-4,5-Diphenyl-2-oxo-1,3-oxazolidin-3-yl]-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 3f. From **(4*S*,5*R*)-1f** (80 mg, 0.3 mmol), **3f** (endo/exo > 98/2, endo-β/α > 98/2) was obtained after chromatography as white crystals (109 mg, 80%). Major isomer **3f**-*endo*-β: mp 190−191 °C; IR (KBr) 1766 (C=O), 1737 (C=O), 1651 (C=C), 1282, 1253, 1142 (C−O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (1H, ddt, J = 1.5, 6.4 and 13.3 Hz), 2.56 (1H, dt, J = 11.3 and 13.3 Hz), 3.69 (1H, ddd, J = 2.0, 6.4 and 11.3 Hz), 3.74 (3H, s), 5.37 (2H, m), 5.87 (1H, d, J = 8.4 Hz), 6.02 (1H, d, J = 1.5 Hz), 6.93−7.33 (15H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 33.9 (CH_2), 39.2 (CH), 52.0 (CH_3), 63.8 (CH), 79.9 (CH), 82.3 (CH), 113.9 (CH), 126.0−128.7 (15 x CH), 134.1 (2 x C), 142.0 (C), 143.4 (C), 156.8 (C), 162.4 (C). Anal. Calcd for $C_{28}H_{25}NO_5$: C, 73.83; H, 5.53; N, 3.08. Found: C, 73.02; H, 5.74; N, 2.76. $[\alpha]^{25}_D$ +51 (*c* 0.87, CH_2Cl_2).

General Procedure for Sequential Transformation of Hetero-adducts 3a−c into Dimethyl Phenylsuccinate 8. (a) Ozonolysis: Procedure A. A cooled mixture at −78 °C under nitrogen of the hetero-adduct **3** (1 equiv, on a 0.3−2.4 mmol scale), with MeOH (2.5 equiv) and $NaHCO_3$ (0.1 equiv) in dichloromethane (20 mL), was treated by ozone (15−20 min) until the persistence of a blue color. After nitrogen stripping of the excess of ozone at −78 °C, triethylamine (2 mL/mmol) and acetic anhydride (2 mL/mmol) were added and the reaction mixture was stirred under nitrogen at room temperature for 16 h. The organic layer was washed with water (3 × 15 mL), dried ($MgSO_4$), and concentrated in vacuo after negative peroxide test. **Procedure B.** The same conditions were applied using triethylamine (1.25 equiv) and acetic anhydride (2.5 equiv). **(b) Oxidation.** To a cooled solution at −10 °C of the crude product of ozonolysis in acetone (20 mL/mmol) was added dropwise Jones reagent (1.3 equiv), and the reaction mixture was stirred at room temperature for 16 h. After elimination of the chromium salts by filtration on Celite, the solvent was removed by concentration. **(c) Esterification: Procedure A.** A solution of the crude product of oxidation in methanol (10 mL/mmol) was treated with diazomethane until the persistence of a yellow color. The excess of diazomethane was canceled by glacial acetic acid, and the reaction mixture was stirred at room temperature for 3 h. After removal of solvent, the crude product was chromatographed (silica gel 30/1; cyclohexane/ether 90/10). **Procedure B.** A solution of the crude product of oxidation in methanol (10 mL/mmol), treated with an anhydrous HCl−methanol solution (0.5 g/10 mL, 10 equiv), was refluxed for 5−10 min. After removal of solvent, the crude product was chromatographed.

Sequential Transformation of Hetero-adduct 3a. (a) After ozonolysis with Procedure A from **3a** (338 mg, 1.02 mmol), a crude mixture (1/9) of aldehyde **4** and diastereoisomeric *N*,*O*-acylals **5a** was obtained.

(2*S*)-4-Acetoxy-4-[(4*R*)-4-ethyl-2-oxo-1,3-oxazolidin-3-yl]-2-phenyl-butyric Acid Methyl Ester 5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ *diastereomer 1*, 0.83 (3H, t, J = 7.4 Hz), 1.99 (3H, s), 1.40−1.80 (2H, m), 2.45 (1H, dt, J = 7.4 and 14.8 Hz), 2.85 (1H, m), 3.64 (2H, m), 3.66 (3H, s), 3.85 (1H, dd, J = 6.1 and 8.4 Hz), 4.04 (1H, t, J = 8.4 Hz), 5.93 (1H, t, J = 7.4 Hz), 7.24−7.40 (5H, m); *diastereomer 2*, 0.87 (3H, t, J = 7.4 Hz), 2.07 (3H, s), 1.40−1.80 (2H, m), 2.59 (1H, dt, J = 7.4 and 14.8 Hz), 2.85 (1H, m), 3.64 (2H, m), 3.67 (3H, s), 3.99 (1H, dd, J = 6.1 and 8.4 Hz), 4.32 (1H, t, J = 8.4 Hz), 5.99 (1H, t, J = 7.4 Hz), 7.24 à 7.40 (5H, m).

(b) After oxidation of the mixture of **4** and **5a**, the crude mixture (18/82) of (*S*)-phenyl succinic acid 1-methyl ester and *N*-acyl oxazolidinone **7a** obtained was esterified using Procedure A. After chromatography, the succinate **(*S*)-8** was obtained as a colorless oil (35 mg, 15% from **3a**) along with **7a** as colorless crystals (130 mg, 42% from **3a**).

(*S*)-(+)-Dimethyl Phenylsuccinate (*S*)-8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (1H, dd, J = 5.1 and 16.7 Hz), 3.21 (1H, dd, J = 10.3 and 16.7 Hz), 3.68 (3H, s), 4.09 (1H, dd, J = 5.1 and 10.3 Hz), 7.25−7.40 (5H, m); $[\alpha]^{20}_D$ +78 (*c* 1.26, MeOH) {lit.[19] $[\alpha]^{20}_D$ +124 (*c* 0.5, MeOH)}; ee > 98%; t_R **(*S*)-8** 141.3 min (>99%), t_R **(*R*)-8** 143.7 min (<1%) (105 °C).

***(2S)*-4-[(4*R*)-4-Ethyl-2-oxo-1,3-oxazolidin-3-yl]-4-oxo-2-phenyl-butyric Acid Methyl Ester 7a:** mp 93.5−95 °C; IR (KBr) 1783 (C=O), 1733 (C=O), 1699 (C=O), 1496, 1453, 1387, 1337, 1270, 1233, 1164, 1124, 1060, 1009, 964, 844, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7.4 Hz), 1.70 (1H, m), 1.82 (1H, m), 3.24 (1H, dd, J = 3.6 and 18.5 Hz), 3.68 (3H, s), 3.81 (1H, dd, J = 11.3 and 18.5 Hz), 4.12 (1H, m), 4.15 (1H, dd, J = 3.6 and 11.3 Hz), 4.41 (2H, m), 7.25−7.35 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 7.9 (CH_3), 24.8 (CH_2), 39.4 (CH_2), 46.3 (CH), 52.1 (CH_3), 54.9 (CH), 66.8 (CH_2), 127.5−128.7 (5xCH), 137.2 (C), 153.5 (C), 171.0 (C), 173.5 (C). Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.93; H, 6.38; N, 4.61. $[\alpha]^{20}_D$ +26 (*c* 1.13, CH_2Cl_2).

Sequential Transformation of Hetero-adduct 3c. (a) After ozonolysis with Procedure A from **3c** (103 mg, 0.27 mmol), a crude mixture (1/4) of aldehyde **4** and diastereoisomeric *N*,*O*-acylals **5c** was obtained.

(2*S*)-4-Acetoxy-4-[(4*R*)-2-oxo-4-phenyl-1,3-oxazolidin-3-yl]-2-phenyl-butyric Acid Methyl Ester 5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ *diastereomer 1*, 1.86 (3H, s), 2.37 (1H, ddd, J = 6.1, 8.6 and 14.5 Hz), 2.95 (1H, ddd, J = 6.4, 8.0 and 14.5 Hz), 3.55 (4H, m), 4.12 (1H, dd, J = 6.9 and 8.9 Hz), 4.36 (1H, t, J = 8.9 Hz), 4.79 (1H, dd, J = 6.9 and 8.9 Hz), 5.50 (1H, dd, J = 6.1 and 8.0 Hz), 7.10−7.40 (10H, m); *diastereomer 2*, 2.08 (3H, s), 2.50 (1H, ddd, J = 6.1, 8.6 and 14.5 Hz), 3.04 (1H, ddd, J = 6.4, 8.0 and 14.5 Hz), 3.56 (4H, m), 4.16 (1H, dd, J = 6.9 and 8.9 Hz), 4.42 (1H, t, J = 8.9 Hz), 4.81 (1H, dd, J = 6.9 and 8.9 Hz), 5.60 (1H, dd, J = 6.1 and 8.0 Hz), 7.10−7.40 (10H, m).

(b) After oxidation of the mixture of **4** and **5c**, the crude mixture (18/82) of (*S*)-phenyl succinic acid 1-methyl ester and *N*-acyl oxazolidinone **7c** obtained was treated with methanol. *N*-Acyl oxazolidinone **7c** was thus isolated as white crystals (53 mg, 56% from **3c**).

(2*S*)-4-Oxo-4-[(4*R*)-2-oxo-4-phenyl-1,3-oxazolidin-3-yl]-2-phenyl-butyric Acid Methyl Ester 7c: mp 179.5−180.5 °C (ether); IR (KBr) 1779 (C=O), 1733 (C=O), 1701 (C=O), 1495, 1454, 1377, 1234, 1167 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (1H, dd, J = 2.6 and 17.7 Hz), 3.65 (3H, s), 3.91 (1H, dd, J = 11.6 and 17.7 Hz), 4.07 (1H, dd, J = 2.6 and 11.6 Hz), 4.29 (1H, dd, J = 3.3 and 8.8 Hz), 4.72 (1H, t, J = 8.8 Hz), 5.42 (1H, dd, J = 3.3 and 8.8 Hz), 7.20−7.40 (10H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 39.4 (CH_2), 46.1 (CH), 52.1 (CH_3), 57.3 (CH), 70.0 (CH_2), 125.7−130 (10 x CH), 137.2 (C), 137.8 (C), 153.5 (C), 170.6 (C), 173.5 (C). Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.98; H, 5.52; N, 3.94. $[\alpha]^{20}_D$ +39.7 (*c* 0.35, CH_2Cl_2).

(c) After esterification of the residual (*S*)-phenyl succinic acid 1-methyl ester with Procedure A, the (*S*)-(+)-dimethyl phenylsuccinate **(*S*)-8** was isolated by chromatography (7 mg, 12% from **3c**): $[\alpha]^{20}_D$ +80 (*c* 0.12, MeOH); ee = 92.3%; t_R **(*S*)-8** 141.3 min (96.2%), t_R **(*R*)-8** 143.7 min (3.9%) (105 °C).

Sequential Transformation of Hetero-adduct 3b. (a) After ozonolysis (20 min) with Procedure B, from **3b** (885 mg, 2.46 mmol), a crude mixture (1/1) of aldehyde **4** and *N*,*O*-hemiaminal **6b** was obtained.

(2*R*)-4-Hydroxy-4-[(4*S*)-4-isobutyl-2-oxo-1,3-oxazolidin-3-yl)-2-phenyl-butyric Acid Methyl Ester 6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, d, J = 6.4 Hz), 0.92 (3H, d, J =

(19) Bettoni, G.; Cellucci, C.; Tortorella, V. *J. Heterocycl. Chem.* **1976**, 1053.

6.4 Hz), 1.35−1.75 (3H, m), 2.20 (1H, ddd, J = 8.9, 4.9 and 13.8 Hz), 2.67 (1H, ddd, J = 6.4, 8.9 and 13.8 Hz), 3.66 (3H, s), 3.78 (1H, dd, J = 6.4 and 8.9 Hz), 3.95 (1H, m), 4.22 (1H, t, J = 8.4 Hz), 4.50 (1H, t, J = 8.4 Hz), 4.93 (1H, dt, J = 4.9 and 8.9 Hz), 5.28 (1H, m), 7.25−7.40 (5H, m).

(b) After oxidation of the mixture of **4** and **6b**, the crude mixture of (*S*)-phenyl succinic acid 1-methyl ester and *N*-acyl oxazolidinone **7b** obtained was esterified with Procedure B. After chromatography, succinate **(*R*)-8** was obtained as a colorless oil (82 mg, 30% from **3b**) along with **7b** as white crystals (157 mg, 38% from **3b**).

(*R*)-(−)-Dimethyl Phenylsuccinate (*R*)-8: $[\alpha]^{20}_D$ −102.5 (*c* 1.19, MeOH); ee = 93%; t_R **(*S*)-8** 141.3 min (3.5%), t_R **(*R*)-8** 143.7 min (96.5%) (105 °C).

(2*R*)-4-[(4*S*)-4-Isobutyl-2-oxo-1,3-oxazolidin-3-yl)-4-oxo-2-phenyl-butyric Acid Methyl Ester 7b: mp 118−119.5 °C; IR (KBr) 1774 (C=O), 1735 (C=O), 1698 (C=O), 1497, 1438, 1399, 1339, 1288, 1231, 1170, 1137, 1084, 1029, 953, 850, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (3H, d, J = 6.4 Hz), 0.95 (3H, d, J = 6.4 Hz), 1.46 (1H, m), 1.60 (1H, m), 1.74 (1H, ddd, J = 3.4, 9.0 and 12.3 Hz), 3.18 (1H, dd, J = 3.4 and 18.7 Hz), 3.68 (3H, s), 3.83 (1H, dd, J = 11.3 and 18.7 Hz), 4.12 (1H, dd, J = 2.5 and 8.8 Hz), 4.15 (1H, dd, J = 3.4 and 11.3 Hz), 4.40 (1H, t, J = 8.8 Hz), 4.49 (1H, m), 7.25−7.35 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 21.5 (CH_3), 23.3 (CH_3), 24.7 (CH), 39.5 (CH_2), 41.2 (CH_2), 46.4 (CH), 52.2 (CH_3), 53.0 (CH), 67.7 (CH_2), 127.5−128.8 (5 x CH), 137.4 (C), 153.5 (C), 170.9 (C), 173.6 (C). Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.64; H, 6.86; N, 4.14. $[\alpha]^{20}_D$ −33.3 (*c* 1.52, CH_2Cl_2).

(d) Variation. After ozonolysis (20 min) with Procedure B, from **3b** (68 mg, 0.19 mmol), the crude mixture (1/1) of aldehyde **4** and *N*,*O*-hemiaminal **6b** obtained was hydrolyzed with 4 M H_2SO_4 (30 μL, 0.12 mmol, 1.3 equiv). After chromatography (cyclohexane/ether 90/10 to 1/1), (4*S*)-4-isobutyl-1,3-oxazolidinone was recovered (28 mg) and the purified aldehyde **(*R*)-4** thus obtained (22 mg, 61%) was oxidized. After esterification of the crude (*R*)-phenyl succinic acid 1-methyl ester with Procedure B and chromatography, the succinate **(*R*)-8** was obtained as a colorless oil (21 mg, 83% from **4**).

(2*R*)-2-(Formylmethyl)phenylacetic Acid Methyl Ester (*R*)-4: ^1H NMR (200 MHz, $CDCl_3$) δ 2.81 (1H, dd, J = 3.9 and 18.7 Hz), 3.41 (1H, dd, J = 9.5 and 18.7 Hz), 3.68 (3H, s), 4.29 (1H, dd, J = 3.9 and 9.5 Hz), 7.20−7.35 (5H, m), 9.80 (1H, s).

(*R*)-Phenyl Succinic Acid 1-Methyl Ester: ^1H NMR (400 MHz, $CDCl_3$) δ 2.72 (1H, dd, J = 5.1 and 17.3 Hz), 3.26 (1H, dd, J = 10.3 and 17.3 Hz), 3.70 (3H, s), 4.09 (1H, dd, J = 5.1 and 10.3 Hz), 7.20−7.35 (5H, m).

(*R*)-(−)-Dimethyl Phenylsuccinate (*R*)-8: ee = 95.5%; t_R **(*S*)-8** 141.3 min (2.25%), t_R **(*R*)-8** 143.7 min (97.75%) (105 °C).

General Preparation of Hetero-adducts 10a−f with Eu(fod)$_3$. A solution of *N*-vinyl-2-oxazolidinone **1** (1 equiv), heterodiene **9**[8d] (1−1.5 equiv, slightly polluted with 8−13 mol % dimethyl oxalate), and Eu(fod)$_3$ (0.05 equiv) in cyclohexane (10 mL per mmol of **1**) was refluxed under nitrogen for 2−3 days. After introduction of additional Eu(fod)$_3$ (0.05 equiv), the mixture was refluxed for the total time indicated in Table 3. After removal of solvent the crude product was chromatographed on silica gel.

(2*R*,4*R*)-4-(*tert*-Butoxy)-2-[(4*R*)-4-ethyl-2-oxo-1,3-oxazolidin-3-yl]-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 10a. From **1a** (900 mg, 6.38 mmol), **9** (1.23 g, 6.38 mmol), and Eu(fod)$_3$ (2 × 165 mg, 0.32 mmol), after chromatography (25/1, cyclohexane/AcOEt 90/10 to 60/40), the hetero-adduct **10a** (endo/exo 97/3, endo-α/β > 98/2) was obtained as colorless crystals (887 mg, 52%). Major isomer **10a**-*endo*-α: mp 133−134 °C (ether); IR (KBr) 1756 (C=O), 1746 (C=O), 1645 (C=C), 1426, 1392, 1367, 1287, 1264, 1146, 768 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (3H, t, J = 7.4 Hz), 1.25 (9H, s), 1.66−1.95 (2H, m), 2.04−2.15 (2H, m), 3.77 (3H, s), 3.94 (1H, m), 4.07 (1H, dd, J = 5.2 and 8.6 Hz), 4.40 (1H, t, J = 8.6 Hz), 4.56 (1H, ddd, J = 2.2, 7.4 and 9.5 Hz, H-3), 5.72 (1H, dd, J = 4.2 and 10.1 Hz), 5.91 (1H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 7.7 (CH_3), 26.3 (CH_2), 27.8 (CH_3), 32.7 (CH_2), 51.9 (CH_3), 54.0 (CH), 63.0 (CH), 66.9 (CH_2), 74.6 (C), 80.3 (CH), 113.9 (CH), 142.9 (C), 156.8 (C), 162.1 (C); HRMS (EI) calcd for $C_{12}H_{17}NO_6$ $[M - C_4H_8]^{+\bullet}$ 271.10559, found 271.1060. Anal. Calcd for $C_{16}H_{25}NO_6$: C, 58.70; H, 7.70; N, 4.28. Found: C, 58.98; H, 7.81; N, 4.01. $[\alpha]^{20}_D$ −6 (*c* 0.9, CH_2Cl_2).

(2*S*,4*S*)-4-(*tert*-Butoxy)-2-[(4*S*)-4-isobutyl-2-oxo-1,3-oxazolidin-3-yl]-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 10b. From **1b** (583 mg, 3.45 mmol), **9** (1.06 g, 5.17 mmol), and Eu(fod)$_3$ (2 × 311 mg, 0.6 mmol), after chromatography (15/1, cyclohexane/AcOEt 8/2), the hetero-adduct **10b** (endo/exo 98/2, endo-β/α 95/5) was obtained as colorless crystals (473 mg, 39%). Major isomer **10b**-*endo*-β: mp 144−147 °C (ether); IR (KBr) 1765 (C=O), 1748 (C=O), 1644 (C=C), 1428, 1393, 1368, 1286, 1262, 1150, 863, 767, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, d, J = 6.6 Hz), 0.94 (3H, d, J = 6.6 Hz), 1.25 (9H, s), 1.62 (2H, m), 1.83 (1H, ddd, J = 3.0, 10.0 and 13.4 Hz), 2.07 (2H, m), 3.78 (3H, s), 4.00 (1H, m), 4.05 (1H, dd, J = 6.1 and 8.0 Hz), 4.40 (1H, t, J = 8.0 Hz), 4.56 (1H, ddd, J 2.3, 8.6 and 10.4 Hz), 5.71 (1H, dd, J = 4.9 and 9.3 Hz), 5.92 (1H, d, J_{4-3} = 2.3 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 23.6 (CH_3), 24.7 (CH), 27.9 (CH_3), 32.9 (CH_2), 42.4 (CH_2), 52.1 and 52.2 (CH_3 + CH), 63.2 (CH), 67.9 (CH_2), 74.8 (C), 80.8 (CH), 114.2 (CH), 143.1 (C), 156.8 (C), 162.2 (C). Anal. Calcd for $C_{18}H_{29}NO_6$: C, 60.83; H, 8.22; N, 3.94. Found: C, 60.59; H, 8.19; N, 3.65. $[\alpha]^{25}_D$ +25.1 (*c* 1.1, CH_2Cl_2).

(2*R*,4*R*)-4-(*tert*-Butoxy)-2-[(4*R*)-2-oxo-4-phenyl-1,3-oxazolidin-3-yl]-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 10c. From **1c** (182.5 mg, 0.96 mmol), **9** (295 mg, 1.44 mmol), and Eu(fod)$_3$ (2 × 87 mg, 0.168 mmol), after chromatography (15/1, cyclohexane/AcOEt 85/15 to 70/30), the hetero-adduct **10c** (endo/exo > 98/2, endo-α/β > 96/4) was obtained as a yellow oil (194 mg, 54%). Major isomer **10c**-*endo*-α: IR (neat) 1762 (C=O), 1743 (C=O), 1648 (C=C), 1436, 1393, 1366, 1281, 1253, 1174, 860, 766, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (9H, s), 2.11 (1H, ddt, J = 2.0, 6.6 and 12.8 Hz), 2.25 (1H, ddd, J = 9.3, 11.5 and 12.8 Hz), 3.68 (3H, s), 4.14 (1H, dd, J = 7.1 and 8.8 Hz), 4.40 (1H, ddd, J = 2.3, 6.6 and 9.3 Hz), 4.64 (1H, t, J = 8.8 Hz), 5.06 (1H, dd, J = 7.1 and 8.8 Hz), 5.48 (1H, dd, J = 2.0 and 11.5 Hz), 5.76 (1H, t, J = 2.0 Hz), 7.31−7.43 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 27.7 (CH_3), 32.5 (CH_2), 51.8 (CH_3), 58.3 (CH), 62.8 (CH), 70.3 (CH_2), 74.5 (C), 80.9 (CH), 113.8 (CH), 127.1 (CH), 128.7 (2xCH), 137.6 (C), 142.7 (C), 156.8 (C), 161.9 (C). Anal. Calcd for $C_{20}H_{25}NO_6$: C, 63.99; H, 6.71; N, 3.73. Found: C, 63.72; H, 6.77; N, 3.54. $[\alpha]^{25}_D$ −82.4 (*c* 1.0, CH_2Cl_2).

(2*S*,4*S*)-2-[(4*S*)-4-Benzyl-2-oxo-1,3-oxazolidin-3-yl]-4-(*tert*-Butoxy)-3,4-dihydro-2*H*-pyran-6-carboxylic Acid Methyl Ester 10d. From **(4*S*)-1d** (650 mg, 3.2 mmol), **9** (982 mg, 4.8 mmol), and Eu(fod)$_3$ (579 mg, 0.56 mmol), after chromatography (15/1, cyclohexane/AcOEt 90/10 to 70/30 with 1% of Et_3N), the hetero-adduct **10d** (endo/exo > 98/2, endo-β/α > 98/2) was obtained as colorless crystals (522 mg, 42%). Major isomer **10d**-*endo*-β: mp 153.5−155 °C (ether); IR (KBr) 1767 (C=O), 1747 (C=O), 1650 (C=C), 1438, 1396, 1365, 1288, 1265, 1189, 867, 767, 749, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (9H, s), 2.16 (1H, ddt, J = 2.1, 6.9 and 12.0 Hz), 2.24 (1H, dt, J = 9.6 and 12.0 Hz), 2.88 (1H, dd, J = 9.8 and 14.0 Hz), 3.33 (1H, dd, J = 3.8 and 14.0 Hz), 3.78 (3H, s), 4.12 (2H, m), 4.20 (1H, m), 4.60 (1H, ddd, J = 2.1, 7.0 and 9.6 Hz), 5.78 (1H, dd, J = 2.1 and 12.0 Hz), 5.96 (1H, t, J = 2.1 Hz), 7.20−7.38 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 27.8 (CH_3), 33.2 (CH_2), 39.4 (CH_2), 52.0 (CH_3), 53.9 (CH), 63.1 (CH), 66.5 (CH_2), 74.7 (C), 80.6 (CH), 114.2 (CH), 126.9 (CH), 128.6 (CH), 129.1 (CH), 135.3 (C), 143.0 (C), 156.6 (C), 162.1 (C). Anal. Calcd for $C_{21}H_{27}NO_6$: C, 64.77; H, 6.99; N, 3.60. Found: C, 65.06; H, 7.03; N, 3.69. $[\alpha]^{25}_D$ +78.4 (*c* 0.74, CH_2Cl_2).

(2*R*,4*R*)-4-(*tert*-Butoxy)-2-[(4*R*,5*S*)-4-methyl-2-oxo-5-phenyl-1,3-oxazolidin-3-yl]-3,4-dihydro-2*H*-pyran-6-car-

boxylic Acid Methyl Ester 10e. From **(4*R*,5*S*)-1e** (1 g, 4.9 mmol), **9** (1.5 g, 7.35 mmol), and $Eu(fod)_3$ (2 × 439 mg, 0.82 mmol), after chromatography (15/1, CH_2Cl_2/AcOEt 100/0 to 98/2), the hetero-adduct **10e** (endo/exo > 98/2, endo-α/β = 97/3) was obtained as colorless crystals (1.17 g, 61%). Major isomer **10c**-*endo*-α: mp 179−180.5 °C (ether); IR (KBr) 1754 (C═O), 1744 (C═O), 1640 (C═C), 1430, 1391, 1366, 1261, 1226, 1156, 861, 767, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, d, *J* = 6.6 Hz), 1.25 (9H, s), 2.11 (1H, dt, *J* = 9.5 and 11.5 Hz), 2.17 (1H, m), 3.74 (3H, s), 4.26 (1H, q_t, *J* = 6.6 Hz), 4.57 (1H, ddd, *J* = 2.2, 7.0 and 9.5 Hz), 5.62 (1H, d, *J* = 7.8 Hz), 5.76 (1H, dd, *J* = 2.4 and 11.5 Hz), 5.91 (1H, t, *J* = 2.2 Hz), 7.29−7.44 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 16.4 (CH_3), 27.9 (CH_3), 33.4 (CH_2), 52.1 (CH_3), 53.5 (CH), 63.1 (CH), 74.7 (C), 79.3 (CH), 80.3 (CH), 113.9 (CH), 125.9 (CH), 128.5 (2 x CH), 134.0 (C), 143.1 (C), 156.3 (C), 162.3 (C). Anal. Calcd for $C_{21}H_{27}NO_6$: C, 64.77; H, 6.99; N, 3.60. Found: C, 64.89; H, 7.11; N, 3.55. $[\alpha]^{25}_D$ +6.5 (*c* 0.76, CH_2Cl_2).

General Procedure for Reduction of Hetero-adducts 10a−e. To a cooled solution of hetero-adduct **10** (1 equiv) in dry dichloromethane (5 mL/mmol) at −78 °C under nitrogen was successively added dropwise $BF_3{\cdot}Et_2O$ (1.2 equiv) and DIBAH (1 M solution in toluene, 3.5−6.5 equiv). The reaction mixture was stirred at −78 °C (with fresh DIBAH) or slowly warmed at −20 °C (with old DIBAH) until complete disappearance of **10** (monitoring by TLC). The excess DIBAH was canceled by slow addition of MeOH (0.2−0.3 mL/mmol of DIBAH), and the reaction mixture was warmed at room temperature. After treatment of aluminum salts with an aqueous solution of potassium sodium tartrate (30 wt %, 1.5−2.5 mL/mmol of DIBAH), the organic layer was separated and the aqueous layer was extracted with dichloromethane or ethyl acetate. The combined organic layers were dried with $MgSO_4$. After removal of solvent, the crude product **11** was used without further purification.

(4*R*)-3-[(2*R*,4*R*)-4-(*tert*-Butoxy)-6-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 11a. From **10a** (160 mg, 0.49 mmol) and DIBAH (2.45 mL, 2.45 mmol) at −78 °C for 1.5 h, allyl alcohol **11a** was obtained as a crude yellow oil (146.5 mg, 100%): ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, t, *J* = 7.5 Hz), 1.23 (9H, s), 1.67 (1H, m), 1.84 (1H, m), 2.05 (2H, m), 3.95 (3H, m), 4.07 (1H, dd, *J* = 4.6 and 8.6 Hz), 4.37 (1H, t, *J* = 8.6 Hz), 4.49 (1H, t, *J* = 8.0 Hz), 4.80 (1H, m), 5.68 (1H, t, *J* = 7.0 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 7.9 (CH_3), 26.5 (CH_2), 28.0 (CH_3), 33.8 (CH_2), 54.1 (CH), 62.1 (CH_2), 63.2 (CH), 67.0 (CH_2), 74.2 (C), 79.9 (CH), 101.8 (CH), 152.9 (C), 157.1 (C).

(4*S*)-3-[(2*S*,4*S*)-4-(*tert*-Butoxy)-6-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-2-yl]-4-isobutyl-1,3-oxazolidin-2-one 11b. From **10b** (449 mg, 1.26 mmol) and DIBAH (6.3 mL, 6.3 mmol) at −78 °C for 1 h, allyl alcohol **11b** was obtained as a crude yellow oil (389 mg, 95%): ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, d, *J* = 6.4 Hz), 0.94 (3H, d, *J* = 6.4 Hz), 1.23 (9H, s), 1.56 (2H, m), 1.82 (1H, ddd, *J* = 3.0, 10.8 and 14.3 Hz), 2.04 (2H, m), 3.91−4.04 (3H, m), 4.05 (1H, dd, *J* = 5.4 and 8.4 Hz), 4.38 (1H, t, *J* = 8.4 Hz), 4.49 (1H, t, *J* = 7.9 Hz), 4.81 (1H, m), 5.66 (1H, dd, *J* = 4.9 and 9.4 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 21.3 (CH_3), 23.6 (CH_3), 24.6 (CH), 28.0 (CH_3), 33.8 (CH_2), 42.5 (CH_2), 52.1 (CH), 62.1 (CH_2), 63.4 (CH), 67.8 (CH_2), 74.3 (C), 80.2 (CH), 102.0 (CH), 153.0 (C), 157.1 (C).

(4*R*)-3-[(2*R*,4*R*)-4-(*tert*-Butoxy)-6-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-2-yl]-4-phenyl-1,3-oxazolidin-2-one 11c. From **10c** (194 mg, 0.52 mmol) and DIBAH (2.6 mL, 2.6 mmol) at −78 °C, with a slow increase in temperature to −20 °C over 2.5 h, allyl alcohol **11c** was obtained as a crude yellow oil (128 mg, 71%): IR (neat) 3453 (OH), 1755 (C═O), 1679 (C═C), 1391, 1367, 1228, 1191, 1056, 1019 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (9H, s), 2.11 (2H, m), 3.62 (2H, broad s), 4.19 (1H, dd, *J* = 6.0 and 8.8 Hz), 4.37 (1H, ddd, *J* = 1.5, 7.9 and 9.6 Hz), 4.60 (1H, m), 4.65 (1H, t, *J* = 8.8 Hz), 4.98 (1H, dd, *J* = 6.0 and 8.8 Hz), 5.63 (1H, dd, *J* = 5.4 and 8.8 Hz), 7.12−7.42 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 27.9 (CH_3), 33.6 (CH_2), 57.7 (CH), 61.8 (CH_2), 63.0 (CH), 70.5 (CH_2), 74.1 (C), 80.3 (CH), 101.4 (CH), 127.0 (CH), 128.7 (4 x CH), 138.7 (C), 152.3 (C), 157,1 (C).

(4*S*)-4-Benzyl-3-[(2*S*,4*S*)-4-(*tert*-butoxy)-6-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-2-yl]-1,3-oxazolidin-2-one 11d. From **10d** (637 mg, 1.64 mmol) and DIBAH (9 mL, 9 mmol) at −78 °C, with a slow increase in temperature to −20 °C over 4 h, allyl alcohol **11d** was obtained as a crude yellow oil (532 mg, 90%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (9H, s), 2.18 (2H, m), 2.76 (1H, dd, *J* = 10.5 and 14.0 Hz), 3.35 (1H, dd, *J* = 3.7 and 14.0 Hz), 4.00 (2H, m), 4.10 (2H, m), 4.17 (1H, m), 4.53 (1H, t, *J* = 8.0 Hz), 4.85 (1H, broad s), 5.74 (1H, dd, *J* = 2.4 and 11.8 Hz), 7.10−7.40 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 28.0 (CH_3), 34.2 (CH_2), 39.7 (CH_2), 54.1 (CH), 62.0 (CH_2), 63.3 (CH), 66.5 (CH_2), 74.3 (C), 80.1 (CH), 102.1 (CH), 126.9 (CH), 128.8 and 129 (4 x CH), 135.5 (C), 153.0 (C), 157.0 (C).

(4*R*,5*S*)-3-[(2*R*,4*R*)-4-(*tert*-Butoxy)-6-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-2-yl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one 11e. From **10e** (1.02 g, 2.63 mmol) and DIBAH (17 mL, 17 mmol) at −78 °C, with a slow increase in temperature to −20 °C over 4.5 h, allyl alcohol **11e** was obtained as a crude yellow oil (953 mg, 100%): IR (neat) 3450 (OH), 1752 (C═O), 1676 (C═C), 1417, 1388, 1365, 1228, 1193, 1174, 1069, 1047, 1018, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, d, *J* = 6.4 Hz), 1.23 (9H, s), 2.05 (1H, td, *J* = 9.8 and 12.3 Hz), 2.14 (1H, ddt, *J* = 2.0, 7.0 and 12.3 Hz), 3.91 and 3.98 (2H, 2d, *J* = 13.7 Hz), 4.25 (1H, dq, *J* = 6.4 and 7.9 Hz), 4.50 (1H, t, *J* = 7.9 Hz), 4.80 (1H, broad s), 5.61 (1H, d, *J* = 7.9 Hz), 5.71 (1H, dd, *J* = 2.0 and 12.3 Hz), 7.28−7.44 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 16.3 (CH_3), 28.0 (CH_3), 34.2 (CH_2), 53.5 (CH), 62.1 (CH_2), 63.2 (CH), 74.2 (C), 79.2 (CH), 79.7 (CH), 101.8 (CH), 125.7 (CH), 128.4 (4 x CH), 133.9 (C), 152.9 (C), 156.7 (C).

(4*R*)-3-[(2*R*,4*R*)-6-(Acetoxymethyl)-4-(*tert*-butoxy)-3,4-dihydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 13a. To a cooled solution at 0 °C under nitrogen of crude allyl alcohol **11a** (75 mg, 0.25 mmol) and DMAP (3 mg, 0.025 mmol) in anhydrous dichloromethane (3 mL) were successively added triethylamine (35 μL, 0.25 mmol) and acetic anhydride dropwise (47 μL, 0.5 mmol), and the reaction mixture was stirred for 1 h at room temperature. The organic layer was successively washed with water and then brine and dried with $MgSO_4$. After removal of solvent, the crude product obtained (84 mg, 99%) was used without further purification: ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.4 Hz), 1.22 (9H, s), 1.68 (1H, m), 1.84 (1H, m), 2.06 (2H, m), 2.23 (3H, s), 3.94 (1H, m), 4.06 (1H, dd, *J* = 4.9 and 8.6 Hz), 4.36 (1H, t, *J* = 8.6 Hz), 4.41 (2H, 2s), 4.48 (1H, t, *J* = 8.0 Hz), 4.83 (1H, broad s), 5.70 (1H, dd, *J* = 5.6 and 8.6 Hz).

(4*R*)-3-[(2*R*,4*R*)-6-(Benzyloxymethyl)-4-(*tert*-butoxy)-3,4-dihydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 16a. To a cooled solution of crude allyl alcohol **11a** (555 mg, 1.85 mmol) in anhydrous dimethylformamide (15 mL) at 0 °C under nitrogen was added NaH (40 wt % dispersion in oil, 167 mg, 2.77 mmol), and the reaction mixture was stirred for 20 min at 0 °C. Benzyl bromide (288 μL, 2.40 mmol) was added dropwise and the reaction mixture was stirred for 3 h at room temperature. After slow addition of methanol (5 mL) at 0 °C, the reaction mixture was stirred for 1 h at room temperature and concentrated under reduced pressure. The residue was recovered with dichloromethane, and the organic layer was successively washed with water and then brine and dried with $MgSO_4$. After removal of solvent, the crude product obtained (720 mg, 100%) was used without further purification: ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.6 Hz), 1.22 (9H, s), 1.65 (1H, m), 1.85 (1H, m), 2.05 (2H, m), 3.87 (2H, s), 3.92 (1H, m), 4.05 (1H, dd, *J* = 4.9 and 8.4 Hz), 4.35 (1H, t, *J* = 8.4 Hz), 4.48 (1H, t, *J* = 8.0 Hz), 4.83 (1H, broad s), 5.69 (1H, dd, *J* = 3.0 and 11.0 Hz), 7.20−7.40 (5H, m).

General Procedure for Preparation of *N*-2-Deoxyglycosyl-oxazolidinones 12. (a) Hydroboration. To a cooled

solution of crude allyl alcohol **11** (1 equiv) in THF (6.7 mL/mmol) at 0 °C under nitrogen was added BH_3·Me_2S (2 M solution in THF, 3.5 equiv), and the reaction mixture was stirred for 1.5 h at 0 °C and then 15 h at room temperature. **(b) Oxidation. Procedure A.** After dilution with THF (6.7 mL/mmol), trimethylamine *N*-oxide dihydrate (3 equiv) was added and the reaction mixture was refluxed for 1 h. After the mixture was cooled, brine (8 mL) was added and the reaction mixture was stirred for 5 min. After removal of THF, the aqueous layer was extracted with ethyl acetate (3 × 8 mL) and the combined organic layers were dried with $MgSO_4$. After removal of solvent, the crude product was chromatographed on silica gel. **Procedure B.** After replacement of THF by diglyme (10 mL/mmol), trimethylamine *N*-oxide dihydrate (3.5 equiv) was added and the reaction mixture was warmed at 110 °C for 4.5−6 h. After the mixture was cooled and diluted with ether, the organic layer was washed with brine (3 × 5 mL); the resulting aqueous layer was extracted with ethyl acetate, and the combined organic layers were dried with $MgSO_4$. After removal of solvent, the crude product was chromatographed.

(4*R*)-3-[(2*R*,4*S*,5*S*,6*S*)-4-(*tert*-Butoxy)-5-hydroxy-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 12a. From **11a** (89 mg, 0.3 mmol), after hydroboration−oxidation (Procedure A), **12a** was obtained after chromatography (silica gel 40 /1, cyclohexane/AcOEt 20/80) as a colorless oil (39 mg, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, t, J = 7.4 Hz), 1.26 (9H, s), 1.63 (1H, m), 1.85 (2H, m), 2.00 (1H, ddd, J = 2.5, 4.5 and 12.3 Hz), 2.44 (1H, d, J = 2.0 Hz), 3.34 (1H, td, J = 2.0 and 9.0 Hz), 3.46 (1H, ddd, J = 3.4, 4.5 and 9.0 Hz), 3.63 (1H, ddd, J = 4.5, 9.0 and 10.8 Hz), 3.76 (1H, dd, J = 4.5 and 11.8 Hz), 3.88 (1H, m) and (1H, dd, J = 3.4 and 11.8 Hz), 4.04 (1H, dd, J = 4.9 and 8.9 Hz), 4.35 (1H, t, J = 8.9 Hz), 5.22 (1H, dd, J = 2.5 and 11.1 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 7.9 (CH_3), 26.8 (CH_2), 28.5 (CH_3), 36.3 (CH_2), 54.2 (CH), 62.8 (CH_2), 66.8 (CH_2), 70.7 (CH), 72.3 (CH), 74.7 (C), 77.1 (CH), 79.7 (CH), 157.1 (C). HRMS (FAB) calcd for $C_{15}H_{27}NO_6Na$ [M + Na]$^+$ 340.1736, found 340.1736; calcd for $C_{15}H_{27}NO_6K$ [M + K]$^+$ 356.1476, found 356.1454. $[\alpha]^{20}_D$ −38 (*c* 0.79, CH_2Cl_2).

(4*S*)-3-[(2*S*,4*R*,5*R*,6*R*)-4-(*tert*-Butoxy)-5-hydroxy-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-2-yl]-4-isobutyl-1,3-oxazolidin-2-one 12b. From **11b** (214 mg, 0.65 mmol), after hydroboration−oxidation (Procedure B, 6 h), **12b** was obtained after chromatography (silica gel 40/1, cyclohexane/AcOEt 50/50 to 30/70) as a colorless oil (138 mg, 61%): IR (neat) 3454 (OH), 1747 (C=O), 1470, 1427, 1394, 1366, 1282, 1256, 1227, 1193, 1127, 1073, 1013, 959, 877, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (3H, d, J = 6.4 Hz), 0.95 (3H, d, J = 6.4 Hz), 1.26 (9H, s), 1.55 (2H, m), 1.75−1.90 (2H, m), 2.00 (1H, ddd, J = 2.0, 4.4 and 12.3 Hz), 2.49 (1H, broad s), 3.33 (1H, td, J = 2.0 and 9.0 Hz), 3.46 (1H, dt, J = 4.4 and 9.0 Hz), 3.62 (1H, ddd, J = 4.4, 9.0 and 10.8 Hz), 3.76 (1H, m), 3.91 (2H, m), 4.02 (1H, dd, J = 5.4 and 8.4 Hz), 4.36 (1H, t, J = 8.4 Hz), 5.19 (1H, d, J = 10.8 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 23.6 (CH_3), 24.6 (CH), 28.6 (CH_3), 36.3 (CH_2), 42.9 (CH_2), 52.2 (CH), 62.8 (CH_2), 67.8 (CH_2), 70.7 (CH), 72.2 (CH), 74.7 (C), 77.5 (CH), 80.0 (CH), 157.1 (C). HRMS (FAB) calcd for $C_{17}H_{31}NO_6Na$ [M + Na]$^+$ 368.20491, found 368.2048; calcd for $C_{17}H_{31}NO_6K$ [M + K]$^+$ 384.17885, found 384.1792. $[\alpha]^{20}_D$ +50.9 (*c* 1.46, CH_2Cl_2).

(4*R*)-3-[(2*R*,4*S*,5*S*,6*S*)-4-(*tert*-Butoxy)-5-hydroxy-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-2-yl]-4-phenyl-1,3-oxazolidin-2-one 12c. From **11c** (101 mg, 0.29 mmol), after hydroboration−oxidation (Procedure B, 4.5 h), **12c** was obtained after chromatography (silica gel 40 /1, cyclohexane/AcOEt 50/50 to 20/80) as white crystals (47 mg, 44%): mp 141.5−142 °C; IR (KBr) 3548, 3432 (OH), 1749 (C=O), 1481, 1460, 1417, 1392, 1361, 1284, 1228, 1192, 1132, 1086, 1032, 972, 870, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (9H, s), 1.90 (1H, dt, J = 11.3 and 12.3 Hz), 2.04 (1H, ddd, J = 2.2, 4.4 and 12.3 Hz), 2.27 (1H, broad s), 3.06 (1H, t, J = 9.1 Hz), 3.21 (1H, dt, J = 3.1 and 9.1 Hz), 3.44−3.58 (3H, m), 4.23 (1H, dd, J = 5.9 and 8.9 Hz), 4.65 (1H, t, J = 8.9 Hz), 4.91 (1H, dd, J = 5.9 and 8.9 Hz), 5.16 (1H, d, J = 11.3 Hz), 7.38 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 28.9 (CH_3), 36.5 (CH_2), 58.1 (CH), 61.8 (CH_2), 69.3 (CH_2), 70.5 (CH), 72.4 (CH), 74.9 (C), 77.5 (CH), 80.4 (CH), 127.5 (CH), 128.9 and 129.1 (4 x CH), 139.6 (C), 157.2 (C); HRMS (FAB) calcd for $C_{19}H_{27}NO_6$-Na [M + Na]$^+$ 388.17361, found 388.1731. $[\alpha]^{20}_D$ −98 (*c* 0.91, CH_2Cl_2).

(4*S*)-4-Benzyl-3-[(2*S*,4*R*,5*R*,6*R*)-4-(*tert*-butoxy)-5-hydroxy-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-2-yl]-1,3-oxazolidin-2-one 12d. From **11d** (150 mg, 0.41 mmol), after hydroboration−oxidation (Procedure B, 4.5 h), **12d** was obtained after chromatography (silica gel 40 /1, cyclohexane/AcOEt 50/50 to 40/60) as white crystals (81 mg, 52%): mp 141−144 °C; IR (KBr) 3505 (OH), 1749 (C=O), 1427, 1400, 1362, 1287, 1267, 1234, 1189, 1127, 1088, 1023, 976, 878, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (9H, s), 2.00 (1H, m), 2.10 (1H, ddd, J = 2.2, 4.3 and 12.3 Hz), 2.52 (1H, broad s), 2.75 (1H, dd, J = 9.8 and 13.7 Hz), 3.31 (1H, dd, J = 3.7 and 13.7 Hz), 3.38 (1H, t, J = 9.0 Hz), 3.50 (1H, ddd, J = 3.7, 4.7 and 9.0 Hz), 3.65 (1H, ddd, J = 4.3, 9.0 and 10.8 Hz), 3.78 (1H, dd, J = 4.7 and 11.8 Hz), 3.91 (1H, dd, J = 3.7 and 11.8 Hz), 4.04−4.20 (3H, m), 5.25 (1H, dd, J = 2.2 and 11.3 Hz), 7.15−7.36 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 28.8 (CH_3), 36.8 (CH_2), 40.2 (CH_2), 54.3 (CH), 62.9 (CH_2), 66.6 (CH_2), 70.9 (CH), 72.4 (CH), 74.9 (C), 77.5 (CH), 80.1 (CH), 127.1 (CH), 128.8 and 129.1 (4 x CH), 135.6 (C), 157.0 (C). HRMS (FAB) calcd for $C_{20}H_{29}NO_6Na$ [M + Na]$^+$ 402.18926, found 402.1896; calcd for $C_{20}H_{29}NO_6K$ [M + K]$^+$ 418.16320, found 418.1635. $[\alpha]^{20}_D$ +55.6 (*c* 1.34, CH_2Cl_2).

(4*R*,5*S*)-3-[(2*R*,4*S*,5*S*,6*S*)-4-(*tert*-Butoxy)-5-hydroxy-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-2-yl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one 12e. From **11e** (72 mg, 0.2 mmol), after hydroboration−oxidation (Procedure B, 6 h), **12e** was obtained after chromatography (silica gel 40/1, cyclohexane/AcOEt 40/60 to 30/70) as white crystals (36 mg, 48%): mp 137−138 °C; IR (KBr) 3473 (OH), 1755 (C=O), 1459, 1429, 1384, 1355, 1290, 1228, 1190, 1143, 1086, 1058, 978, 880, 765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (3H, d, J = 6.4 Hz), 1.27 (9H, s), 1.85 (1H, td, J = 11.3 and 12.3 Hz), 2.11 (1H, ddd, J = 2.0, 4.5 Hz and 12.3 Hz), 2,50 (1H, d, J = 2.0 Hz), 3.32 (1H, td, J = 2.0 and 9.0 Hz), 3.47 (1H, ddd, J = 3.4, 4.7 and 9.0 Hz), 3.65 (1H, ddd, J = 4.5, 9.0 and 10.8 Hz), 3.74 (1H, m), 3.87 (1H, m), 4.19 (1H, m), 5.25 (1H, dd, J = 2.0 and 11.3 Hz), 5.59 (1H, d, J = 7.9 Hz), 7.25−7.45 (5H, m); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 16.7 (CH_2), 28.8 (CH_3), 36.9 (CH_2), 53.7 (CH), 62.8 (C-6), 70.9 (CH), 72.5 (CH), 74.7 (C), 77.4 (CH), 79.1 (CH), 79.9 (CH), 125.9 (CH), 128.4 (4 x CH), 134.3 (C), 156.6 (C). Anal. Calcd for $C_{20}H_{29}NO_6$: C, 63.31; H, 7.70; N, 3.69. Found: C, 63.04; H, 7.75; N, 3.58. $[\alpha]^{20}_D$ +13.9 (*c* 0.36, CH_2Cl_2).

(4*R*)-3-[(2*R*,4*S*,5*S*,6*S*)-6-(benzyloxymethyl)-4-(*tert*-butoxy)-5-hydroxy-tetrahydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 17a. From **16a** (97 mg, 0.25 mmol), after hydroboration−oxidation (Procedure B, 7 h), **17a** was obtained after chromatography (silica gel 30/1, cyclohexane/AcOEt 70/30 to 10/10) as a colorless oil (62 mg, 61%): IR (neat) 3456 (OH), 1746 (C=O), 1424, 1393, 1365, 1272, 1225, 1193, 1077, 1026, 910, 875, 768, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.4 Hz), 1.25 (9H, s), 1.65 (1H, m), 1.87 (2H, m), 1.98 (1H, ddd, J = 2.3, 4.5 and 12.3 Hz), 2.68 (1H, broad s), 3.43 (1H, t, J = 9.3 Hz), 3.52 (1H, dt, J = 3.9 and 9.3 Hz), 3.62 (1H, m), 3.70 (1H, dd, J = 3.9 and 10.8 Hz), 3.79 (1H, dd, J = 4.2 and 10.8 Hz), 3.87 (1H, m), 4.02 (1H, dd, J = 4.9 and 8.6 Hz), 4.33 (1H, t, J = 8.6 Hz), 4.57 (1H, d, J = 4.4 Hz), 5.18 (1H, dd, J = 2.3 and 11.5 Hz); ^{13}C NMR + DEPT 135 (100 MHz, $CDCl_3$) δ 8.0 (CH_3), 26.8 (CH_2), 28.8 (CH_3), 36.4 (CH_2), 54.3 (CH), 66.9 (CH_2), 70.2 (C-6), 71.0 (CH), 72.4 (CH), 73.4 (CH_2), 74.7 (C), 76.5 (CH), 79.8 (CH), 127.4 (2 x CH), 128.2 (2

x CH), 138.1 (C), 157.1 (C); HRMS (FAB) calcd for $C_{22}H_{33}NO_6$-Na $[M + Na]^+$ 430.2206, found 430.2202. $[\alpha]^{20}_D$ −27.4 (*c* 1.015, CH_2Cl_2).

Hydroboration−Oxidation of Allylic Alcohol Acetate 13a. From **13a** (84 mg, 0.24 mmol), after hydroboration−oxidation (Procedure A), partial desacetylation of the crude product was observed (^{1}H NMR). To a cooled solution of the residue and DMAP (3 mg, 0.025 mmol) in anhydrous dichloromethane (3 mL) at 0 °C under nitrogen were successively added triethylamine (70 μL, 0.5 mmol) and acetic anhydride dropwise (94 μL, 1 mmol), and the reaction mixture was stirred for 2 h at room temperature and refluxed for 1 h. The organic layer was successively washed with water and then brine, and the aqueous layer was extracted with AcOEt. After drying ($MgSO_4$) of the combined organic layers, removal of solvent, and chromatography (silica gel 40 /1, cyclohexane/AcOEt 70/30 to 0/100) of the crude product, alcohol **12a** (18 mg, 23%), monoacetate **14a** (13 mg, 14%), and diacetate **15a** (30 mg, 30%) were obtained as colorless oils.

(4*R*)-3-[(2*R*,4*S*,5*S*,6*S*)-6-(Acetoxymethyl)-4-(*tert*-butoxy)-5-hydroxy-tetrahydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 14a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7.4 Hz), 1.26 (9H, s), 1.63 (1H, m), 1.83 (2H, m), 2.00 (1H, ddd, J = 2.5, 4.5 and 12.3 Hz), 2.06 (3H, s), 2.49 (1H, d, J = 2.5 Hz), 3.27 (1H, td, J = 2.5 and 9.5 Hz), 3.54 (1H, dt, J = 3.4 and 9.5 Hz), 3.62 (1H, ddd, J = 4.9, 9.5 and 11.0 Hz), 3.88 (1H, m), 4.03 (1H, dd, J = 4.9 and 8.6 Hz), 4.33 (1H, t, J = 8.6 Hz), 4.34 (2H, m), 5.20 (1H, dd, J = 2.3 and 11.5 Hz).

(4*R*)-3-[(2*R*,4*S*,5*S*,6*S*)-5-Acetoxy-6-(acetoxymethyl)-4-(*tert*-butoxy)-tetrahydro-2*H*-pyran-2-yl]-4-ethyl-1,3-oxazolidin-2-one 15a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 7.6 Hz), 1.18 (9H, s), 1.67 (1H, q_t, J = 7.6 Hz), 1.86 (1H, m), 1.93−2.05 (2H, m), 2.04 (3H, s), 2.08 (3H, s), 3.61 (1H, ddd, J = 2.4, 4.4 and 9.3 Hz), 3.75 (1H, ddd, J = 5.4, 9.3 and 10.3 Hz), 3.89 (1H, m), 4.04 (1H, dd, J = 4.6 and 8.6 Hz), 4.08 (1H, dd, J = 2.4 and 12.3 Hz), 4.17 (1H, dd, J = 4.4 and 12.3 Hz), 4.34 (1H, t, J = 8.6 Hz), 4.82 (1H, t, J = 9.3 Hz), 5.22 (1H, dd, J = 2.5 and 11.3 Hz).

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Supporting Information Available: Crystal structure data of amidoester **7a** and adducts **10a**,**d**; copies of ^{1}H NMR spectra of all new compounds lacking elemental analysis; and tables of ^{1}H NMR correlations between adducts **3a**−**f**, adducts **10a**−**e**, and *N*-glycosides **12a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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