Stereodivergent Hetero-Diels–Alder Reactions of Chiral 1-Oxa-1,3-butadienes through a Conformational Switch induced by Lewis Acids

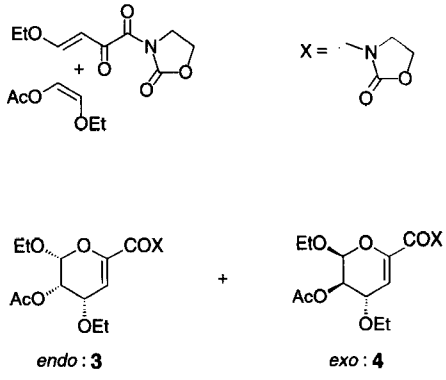
Abstract: The stereodivergent asymmetric hetero-Diels–Alder reaction of achiral and chiral 1-oxa-1,3-butadienes carrying an oxazolidine moiety with various enol ethers in the presence of different Lewis acids is described as a highly stereoselective and efficient approach to dihydropyrans, which can be used for the synthesis of carbohydrates. In the cycloaddition of the achiral oxabutadiene very good *endo*/*exo* selectivity was possible, and with the chiral oxabutadienes excellent 1,6-asymmetric induction was additionally observed. In the processes a reversal of facial selectivity occurs by changing the Lewis acid, allowing the synthesis of both enantiomers of the dihydropyrans with the same auxiliary. Thus, cycloaddition of **1** to **2** in the presence of Me_2AlCl gives predominantly the *endo* product **3** (**3**:**4** = 10:1), whereas with $SnCl_4$ the *exo* product **4** is obtained (**3**:**4** = 1:15). The reaction of **7** and **1a** in the presence of Me_2AlCl as promoter nearly exclusively yields the *endo*-I adduct **16a** (**16a**+**17a**:**18a**+**19a** = > 50:1; **16a**:**17a** = 60:1), whereas with TMS-OTf the *endo*-II-product **17a** was obtained as the main component (**16a**+**17a**:**18a**+**19a** = > 50:1; **16a**:**17a** = 1:7.9). The use of $SnCl_4$ leads to a mixture of *endo* and *exo*, again, however, with excellent induced selectivity. A similarly good induction was obtained with the oxabutadiene **9** containing the new auxiliary **8**. Also, other enol ethers **1b–g** were used, some of which afforded excellent induction. Mechanistic considerations are used to explain the results.

Keywords: asymmetric syntheses · Diels–Alder reactions · dihydropyrans · Lewis acids · oxabutadienes

Introduction

The Diels–Alder reaction is one of the most fundamental C–C bond-forming reactions available to synthetic chemists. Its potential has been demonstrated by numerous natural product syntheses. In addition, heteroanalogues of this process have evolved as an important tool for the synthesis of heterocycles.[1] The use of 1-oxa-1,3-butadienes especially has been pursued for carbohydrate synthesis.[2] These oxabutadienes react with enol ethers in an inverse electron-demand fashion to give rise to dihydropyrans, which can easily be converted into carbohydrates in a short reaction sequence.[2] Electron-withdrawing substituents at the oxabutadiene,[1] Lewis acid promotion[1, 2] and high pressure[3] considerably accelerate the reaction. However, so far the utility of this process has been badly hampered by the lack of feasible methods to obtain a high induced diastereoselectivity.[4]

Recently we showed that the achiral oxabutadiene **2**, which contains an acyl oxazolidinone moiety, undergoes cycloaddition with enol ethers in the presence of different Lewis acids to give either the *endo* or *exo* adduct preferentially. Strong Lewis acids like $TiCl_4$ or $SnCl_4$ resulted in high *exo* selectivity with (*Z*)-1-acetoxy-2-ethoxyethylene (**1a**) to give **4**, while silyl triflates and Me_2AlCl predominantly afforded the *endo* isomer **3** (Scheme 1, Table 1).[5a]



Scheme 1. Hetero-Diels–Alder reaction of achiral 1-oxa-1,3-butadiene **2** and the enol ether **1a**.

Promoter	*T* (°C)	*t* (h)	*endo*:*exo* **3**:**4** [a]	Yield (%) **3**/**4** [b]
Me_2AlCl	−78	48	10: 1	82
$SnCl_4$	−78	0.5	1:15	86
TMS-OTf	−78	24	7.1: 1	77

In this paper we describe the hetero-Diels–Alder reaction of oxabutadienes **7** and **9**, which contain a chiral oxazolidinone moiety, with enol ethers **1a–g** to give enantiopure dihydropy-

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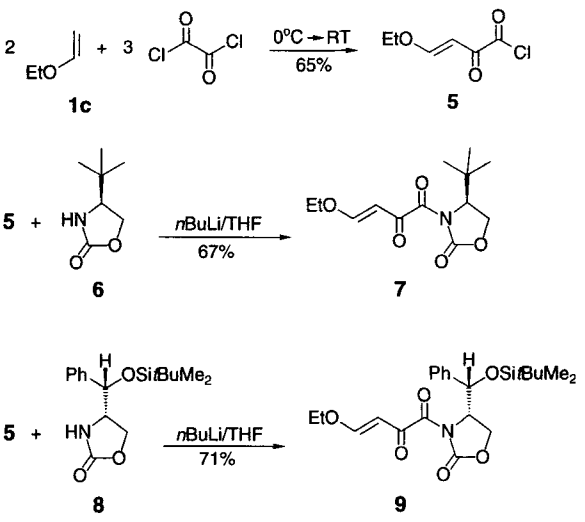
rans in both enantiomeric forms.[5b] We have already published a short and efficient de novo synthesis of enantiopure ethyl β-D- and β-L-mannopyranoside that uses this method.[6]

Results

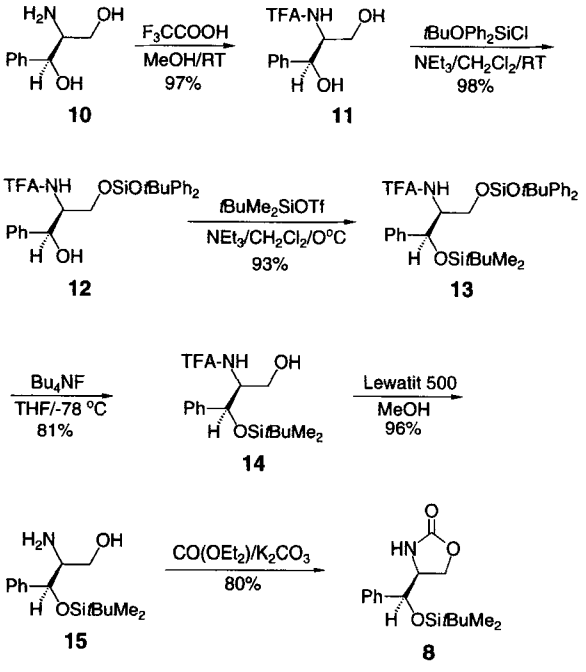
The oxazolidinone moiety derived from enantiopure amino acids was introduced by Evans in 1981 as a chiral control element and has been used since then in numerous enolate-based transformations.[7, 8] It has been shown to provide excellent levels of diastereofacial selectivities. In the hetero-Diels–Alder reaction of **7** and **9** it was expected that Lewis acids would accelerate the reaction and lock the heterodiene in a specific conformation which would allow the selective attack of the enol ether from one face only.

The heterodienes **7** and **9** were readily prepared in a two-step procedure from ethyl vinyl ether, oxalyl chloride and the oxazolidinones **6** and **8**, respectively, analogous to procedures of Effenberger[9] and Evans[7] (Scheme 2). Care should be taken when distilling the intermediate α-keto acid chloride **5**, which easily decomposes at higher temperatures to form the decarbonylated acryloyl chloride.[10] We envisaged the oxazolidinone **8** as an attractive new auxiliary that bears a silyloxy group on the side chain, thus providing an additional coordination site for a Lewis acid. The synthesis of **8**, starting from the purchasable (1*S*,2*S*)-2-amino-1-phenylpropan-1,3-diol **10**, proceeds in a 6-step sequence with an overall yield of 60% via the intermediates **11**–**15** (Scheme 3). The enol ethers **1** used in this study were either commercially available or prepared according to literature precedent.[2c, 11] The hetero-Diels–Alder reactions were generally performed with 1.0 equivalent of the oxabutadiene, 2.0 equivalents of the enol ether and 1.5 equivalents of the promoter at temperatures between −30 °C and −78 °C. Several Lewis acids and silylating agents, monodentate as well as bidentate, were screened as activating agents; of these, only Me_2AlCl, $SnCl_4$ and TMS-OTf were used for the whole study, based on the preliminary results. Separate experiments with the Lewis acids and the silyl triflates confirmed that the starting materials were configurationally stable under the reaction conditions. All of the reactions investigated proceeded very cleanly and in high yield; the diastereomeric ratios were determined on the crude reaction mixtures by gas chromatography or ^{13}C NMR spectroscopy. In the first study we investigated the cycloadditions of oxabutadiene **7** and the enol ethers **1a** and **1b**. The results are listed in Table 2.

In the cycloaddition the four diastereomers **16**–**19** with three new stereogenic centres were expected to be formed (Scheme 4).



Scheme 2. Synthesis of the chiral 1-oxa-1,3-butadienes **7** and **9**.



Scheme 3. Synthesis of the new chiral oxazolidinone **8**.

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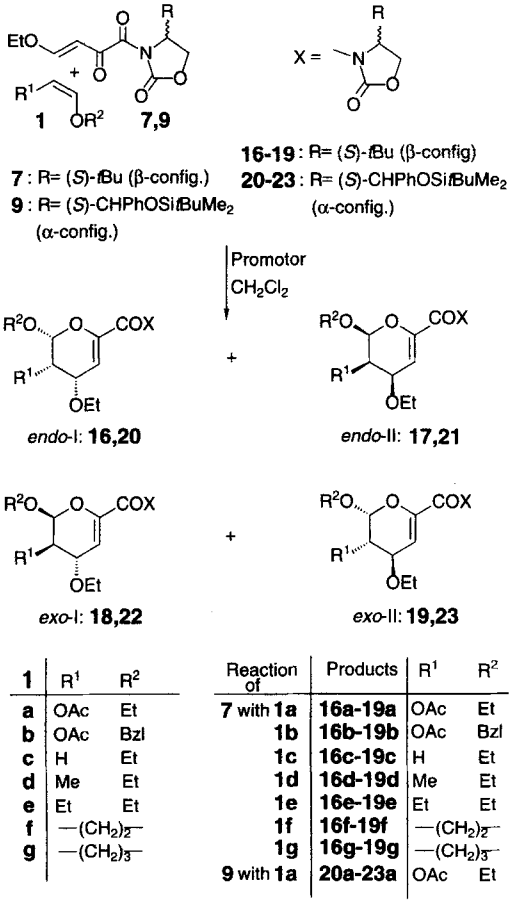
Table 2. Hetero-Diels–Alder reactions of the chiral oxabutadiene **7** with enol ethers **1a** and **1b** in CH_2Cl_2 to yield cycloadducts **16a–19a** and **16b–19b**, respectively.

Enol ether	Promoter	T (°C)	t (h)	$\sum endo/\sum exo$ [a] **16+17/18+19**	*endo-I/endo-II* [a] **16/17**	Yield [b] (%) **16–19**
1a	Me_2AlCl	−40	24	>50:1	60:1	84
1a	TMS-OTf	−78	48	>50:1	1:7.9	90
1a	$SnCl_4$	−78	1	1:1	50:1 (12:1) [c]	41 (37) [c]
1b	Me_2AlCl	−35	15	>50:1	30:1	94 (86) [d]
1b	TMS-OTf	−78	72	30:1 [e]	1:8 [e]	50 [f] (40) [g]
1b	$SnCl_4$	−78	2	1:4 [e]	>50:1 (25:1) [e,h]	94

[a] Determined by capillary gas chromatography of the crude product. [b] Isolated yield of **16**, **17**, **18** and **19**. [c] **18a**/**19a** in parentheses. [d] Isolated yield of **16b** in parentheses. [e] Determined by ^{13}C NMR spectroscopic analysis of the crude product. [f] 82% yield based on conversion. [g] Isolated yield of **17b** in parentheses. [h] In parentheses **18b**/**19b**, 49% epimerization at C-2 of **18b**.



1	R^1	R^2
a	OAc	Et
b	OAc	Bzl
c	H	Et
d	Me	Et
e	Et	Et
f	$-(CH_2)_2-$	
g	$-(CH_2)_3-$	

Reaction of	Products	R^1	R^2
7 with **1a**	**16a-19a**	OAc	Et
1b	**16b-19b**	OAc	Bzl
1c	**16c-19c**	H	Et
1d	**16d-19d**	Me	Et
1e	**16e-19e**	Et	Et
1f	**16f-19f**	$-(CH_2)_2-$	
1g	**16g-19g**	$-(CH_2)_3-$	
9 with **1a**	**20a-23a**	OAc	Et

Scheme 4. Hetero-Diels–Alder reactions of the chiral 1-oxa-1,3-butadienes **7** and **9** with the enol ethers **1a–g**.

However, the Me_2AlCl- and TMS-OTf-initiated reactions were completely *endo*-selective ($\sum endo:\sum exo > 50:1$). Here, the *endo* selectivity was even higher than found for the reaction with the achiral heterodiene **2**. In addition, when Me_2AlCl was the promoter, an excellent induced diastereoselectivity was also found with **16a** and **16b**, the main products formed in 84 and 86% yield, respectively. The asymmetric induction amounted to 60:1 (**16a**:**17a**) and 30:1 (**16b**:**17b**), which was remarkably high, especially considering the distance of the inducing and the newly formed stereogenic centres (1,6-induction). In contrast, employing TMS-OTf as promoter for the cycloaddition of **7** to **1a** and **1b**, the other *endo* isomers (**17a** and **17b**, respectively) were formed predominantly, albeit with lower selectivity (**16a**:**17a** = 1:7.9; **16b**:**17b** = 1:8.0). The diastereofacial selectivity in the cycloaddition with **7** can therefore be controlled simply by varying the promoter whilst leaving the auxiliary unchanged.[12]

$SnCl_4$ as promoter for the cycloaddition of **7** to **1a** did not produce the significant *exo* preference that was observed for the achiral heterodiene **2**. Here a 1:1 mixture of *endo* and *exo* adducts was obtained. Apparently, the bulky substituent on the oxazolidinone disfavours the *exo* transition state. However, with the enol ether **1b** a good *exo* selectivity was again observed ($\sum endo/\sum exo = 1:4$). In both cycloadditions (**7** to **1a** and **1b** with $SnCl_4$) the induced diastereoselectivity was excellent, not only for the *endo* products with **16a** and **16b** as the main products, respectively (50:1 and >50:1), but also for the *exo* adducts (12:1 and 25:1) where **18a** and **18b**, respectively, are formed predominantly. It should be noted, however, that **18b** partially isomerized into the C-2 epimer under the reaction conditions (Table 2).

The Me_2AlCl-promoted cycloaddition of the oxabutadiene **9**, containing the new chiral oxazolidinone, to **1a** displayed a slightly reduced *endo* selectivity compared with the reaction of **7**, but the asymmetric induction is only moderate (50% *de*). The use of the silyl triflates TMS-OTf and TBDMS-OTf, however, gave rise to more selective transformations (Table 3). Whereas

Table 3. Hetero-Diels–Alder reactions of the chiral heterodiene **9** with enol ether **1a** in CH_2Cl_2 to yield cycloadducts **20a–23a**.

Promoter	T (°C)	t (h)	$\sum endo/\sum exo$ [a] **20a+21a/22a+23a**	*endo-I/endo-II* [a] **20a/21a**	Yield [b] (%) **20a–23a**
Me_2AlCl	−30	24	16:1	1:3.2	73
TMS-OTf	−8	1	30:1	17:1	88
TBDMS-OTf [c]	−8	72	17:1	23:1	81

[a] Determined by ^{13}C NMR spectroscopic analysis of the crude product. [b] Isolated yield of **20a**, **21a**, **22a** and **23a**. [c] TBDMS = $SitBuMe_2$.

the *endo* selectivity was nearly as good as found for **7**, the asymmetric induction went up from 8:1, obtained for **7**, to 17:1 with TMS-OTf and even to 23:1 with TBDMS-OTf. Since heterodiene **9** has the opposite configuration at the stereogenic centre to that of heterodiene **7**, the major *endo* product **20a** formed in the silyl triflate-promoted reaction of heterodiene **9** has the same absolute configuration at the dihydropyran moiety as the cycloadduct **16a** obtained predominantly in the Me_2AlCl-promoted reaction of heterodiene **7**. With regard to selectivity, yield and ease of preparation, heterodiene **9** compared favourably with heterodiene **7**.

In an attempt to investigate scope and limitations of the hetero-Diels–Alder reaction of the chiral oxabutadienes **7** and **9** we also looked at the cycloadditions of **7** to the enol ethers **1c–g** (Table 4). The reactions of the cyclic enol ethers dihydrofuran

Table 4. Hetero-Diels–Alder reactions of the chiral heterodiene **7** with enol ethers **1c–g** in CH_2Cl_2.

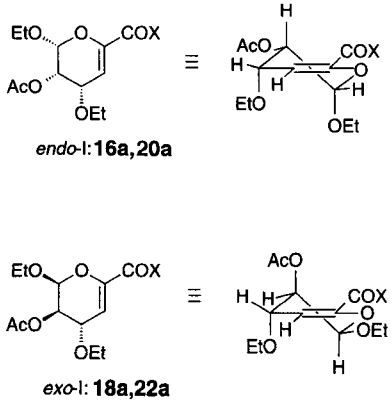
Enol ether	Promoter	T (°C)	t (h)	$\sum endo/\sum exo$ [a] **16+17/18+19**	*endo-I/endo-II* [a] **16/17**	Yield [b] (%) **16–19**
1c	Me_2AlCl	−78	24	7:1	2:1	89
1d	Me_2AlCl	−78	24	24:1	6:1	81 (67) [c]
1d	$SnCl_4$	−78	24	1:4.4	12:1 [d] (8:1) [e]	85
1e	Me_2AlCl	−78	15	9:1 [f]	4:1 [f]	79
1f	Me_2AlCl	−78	18	>50:1	1.6:1	85
1g	Me_2AlCl	−78	15	>50:1	2.9:1	84

[a] Determined by capillary gas chromatography of the crude product. [b] Isolated yield of **16**, **17**, **18** and **19**. [c] Isolated yield of **16d** in parentheses. [d] 41% epimerization at C-2 of *endo*-I isomer **16d**. [e] In parentheses **18d**/**19d**. [f] Determined by ^{13}C NMR spectroscopic analysis of the crude product.

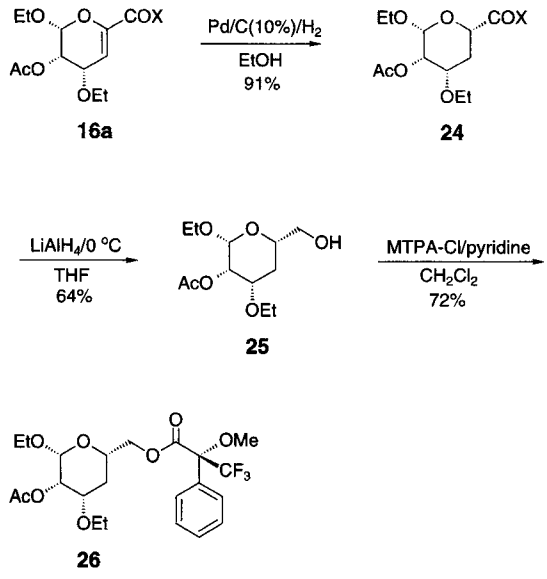
1f and dihydropyran **1g** with **7** were highly *endo* selective (>50:1) affording the *endo* isomers **16f** and **17f** in high yield, however, the diastereofacial selectivity was only low. The three acyclic enol ethers **1c–e** reveal a similar trend with Me_2AlCl as promoter: useful levels of *endo* selectivity and moderate levels of diastereofacial selectivity ranging from 2:1 to 12:1. Here the reaction of **7** and the ethyl vinyl ether **3c** showed the lowest simple and induced selectivity, whereas with ethyl propenyl ether **3d** a more selective formation of the *endo*-I cycloadduct **16d** was obtained (**16d**:**17d** = 6:1), which was isolated after chromatography on silica gel in 67% yield. Interestingly, with $SnCl_4$ as promoter a pronounced preference for the formation of the *exo* product **18d** with good induced selectivity was again observed (**18d**:**19d** = 8:1).

Structure Elucidation of Diels–Alder Products: Structural assignment of the cycloadducts was based on ^1H and ^{13}C NMR data and on three X-ray structures,[13] which ultimately confirm the relative as well as the absolute configuration of the cycloadducts. In the ^1H NMR spectra the 2-H, 3-H, 4-H and 5-H signals of the cycloadducts could be used to determine the relative configuration and conformation. For the *endo* products **16a** and **20a** the 2-H signal appears at $\delta = 5.08$ and 5.28, respectively, with coupling constants of $J_1 = 1.0$ and $J_2 = 0.5$ Hz, from which J_1 is a long-range ^4J coupling to 4-H. This *W* coupling clearly indicates that both the 2-H and 4-H are in pseudoequatorial positions and is in agreement with previous studies on dihydropyrans.[3] Since the (*Z*)-enol ether **1a** and the products were configurationally stable under the reaction conditions the 3-OAc group has to have a *syn* relationship to the 2-OEt group. Apparently, the destabilizing 1,3-diaxial interaction between 2-OEt and 4-OEt is attenuated by the anomeric and vinylogous anomeric effect. An X-ray structure analysis of the parent *endo* product **3** confirms this assignment.[13]

In the ^1H NMR spectra of the *exo* products **18a** and **22a** significant changes are found for the signals of 2-H and 4-H. The 2-H signal is shifted downfield to $\delta = 5.58$ and shows only a doublet with $J = 1.5$ Hz. There is no *W* coupling between the 2-H and 4-H, suggesting that at least one of the protons occupies an axial or pseudoaxial position. In the ^{13}C NMR spectra of the *exo* products the C-3 signal is shifted by about 4 ppm downfield relative to the corresponding signal of the *endo* products, while no other resonances are significantly changed. This suggests a reversed configuration at C-2 and C-3. The relative configuration and conformation is depicted in Scheme 5 and is confirmed by an X-ray structure of the *exo* product **4**. Unfortunately we were not able to obtain suitable crystals of the cycloadducts with the chiral oxabutadienes **7** and **9** to determine the absolute configuration of the dihydropyran moiety. Therefore **16a** was selectively hydrogenated to give **24** as a single product, then reduced to afford **25**, which was finally transformed into the crystalline Mosher ester **26** (Scheme 6). An X-ray structure determination revealed the absolute configuration of the dihydropyran moiety in **16a**, to which all other hetero-Diels–Alder adducts are referred under the assumption of identical pathways.



Scheme 5. Configuration and conformation of the cycloadducts **16a**, **18a**, **19a** and **22a**.



Scheme 6. Transformation of the cycloadduct **16a** into the Mosher ester **26**.

In the mass spectra the *endo* and *exo* products reveal an interesting and diagnostic difference which especially helps to distinguish between *endo* and *exo* products in the GC-MS measurements. The fragment $m/z = 169$, which arises by loss of OAc and the carboximide group, consistently shows up for the *exo* products in an intensity of 60–90% relative to $m/z = 99$, which is usually the base peak, while it is diminished to less than 10% for the *endo* products.

The relative configuration of the cycloadducts **16d** and **18d** was unambigously determined after transformation into the saturated tetrahydropyrans by hydrogenation. The ^1H NMR spectrum of the reduced major *endo* product displays a signal at $\delta = 2.22$ with three large coupling constants of $J = 12.0$ Hz belonging to one geminal coupling of the 4-H and two diaxial couplings of $J_{3-H/4-H}$ and $J_{4-H/5-H}$. Since a large coupling constant is not present in the 2-H signal, which only shows a doublet of doublets with $J_{2-H/3-H} = 2.0$ Hz and $J_{3-H/4-H} = 4.5$ Hz, 2-H must be in an equatorial position. 1-H has to have a *cis* relationship to 2-H; thus 1-H is in the axial position. The *endo*-I product **16d** can be epimerized at C-2 upon exposure to $SnCl_4$ at −78 °C.

The ^1H NMR spectra of the Diels–Alder products **16f** and **16g** do not display diagnostic signals or coupling constants. The nonexistence of a *W* coupling between 1a-H and 6-H and the similar resonance of 1a-H at $\delta = 5.65$ and 5.59, respectively, compared with $\delta = 5.58$ in **18a** indicates that 1a-H is in a pseudoaxial position. In the ^{13}C NMR spectra the C-1a signals appear at $\delta = 98.31$ and 98.75, respectively, which is in good agreement with a β-alkoxy group and an axial 1a-H. For these reasons and by analogy with published data for similar hetero-Diels–Alder products[14] we assign **16f** and **16g** the relative *endo* configuration and the conformation which is depicted in Scheme 7.

Mechanistic Considerations: In an effort to explain the course of the cycloaddition and, in particular, the reversal of selectivity between the reactions promoted by Me_2AlCl and TMS-OTf, we developed the following model.[15] The ^{13}C NMR spectrum taken from a solution of the achiral heterodiene **2** and two equivalents of TMS-OTf in dichloromethane at −78 °C clearly

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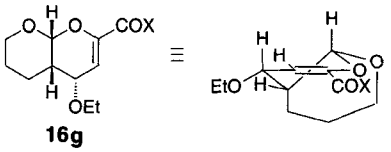
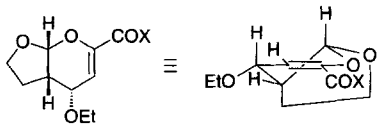


16g

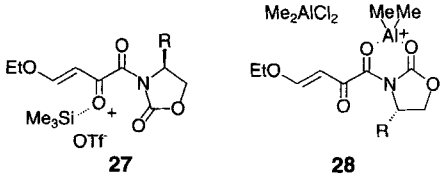


16f

Scheme 7. Configuration and conformation of the cycloadducts **16f** and **16g**.

shows that TMS-OTf binds to the oxygen atom of the oxabutadiene moiety and not to the carbonyl groups of the imide moiety [$\Delta\delta$(2′-CO) = 0, $\Delta\delta$(1-CO) = 0, $\Delta\delta$(2-CO) = 20 ppm]. Semiempirical calculations (AM1 and PM3)[16] conducted on the ground state of **2** and of the oxonium ion **27a** obtained by silylation at the 2-CO group reveal that the *anti* arrangement of the carbonyl groups of the imide moiety is the more stable conformation in both cases (ΔH_f *anti*-**2**: −7.53 and ΔH_f *syn*-**2**: −9.20 kJ mol^{-1}; ΔH_f *anti*-**27a**: −30.96 and ΔH_f *syn*-**27a**: −35.98 kJ mol^{-1}). It is therefore to be expected that the heterodiene **7** favours conformation **27b** in the transition state of the reaction promoted by TMS-OTf (nonchelate control).

With Me_2AlCl as promoter the chelate **28b** (Scheme 8) should be formed; Evans et al.[8a, b] and later Castellino et al.[17] have shown that such a chelate exists in the Diels–Alder reaction



27 **28**

27/28a: R = H

27/28b: R = *t*Bu

Scheme 8. Proposed intermediates in the Diels–Alder reaction of **7** using TMS-OTf and Me_2AlCl.

of *N*-acryloyloxazolidinones promoted by R_2AlCl. Unfortunately, we were not able to confirm the existence of complex **28a** by low-temperature ^{13}C NMR measurements on a mixture of **2** and Me_2AlCl and thus failed to obtain any information concerning the preferred coordination site of the Lewis acid at the heterodiene. However, **28b** should be the preferred conformation in the transition structure of the Me_2AlCl-promoted reaction (chelate control). The facial differentiations of conformations **27b** and **28b** are opposite. This means that the attack by the enol ethers is preferentially directed to opposite faces of the heterodiene, thus inducing the opposite absolute configuration in the dihydropyran unit of the cycloadduct.

Experimental Procedure

^1H NMR and ^{13}C NMR: Varian XL-200, Bruker AMX-300 and Varian XL-500; multiplicities were determined with APT pulse sequence. MS: Varian MAT 311A, high resolution: Varian MAT 731. IR: Bruker IFS 25. UV/Vis: Perkin–Elmer Lambda 2 and Lambda 9. Melting points: Kofler hot stage or Mettler FP61. Elemental analyses were carried out in the analytical laboratory of the university. GC analytical: Varian 3700 (Machery, Nagel; 50 m fused silica capillary SE-30, carrier gas N_2). All solvents were distilled prior to use. Reagents and materials were obtained from commercial suppliers and were used without further purification. All reactions were carried out under a positive pressure of nitrogen or argon and monitored by TLC (Machery, Nagel; Alugram SIL G/UV_{254}). Products were isolated by column chromatography on silica gel (silica gel 60, particle size 0.04–0.063 nm, Merck).

(*E*)-4-Ethoxy-2-oxo-3-butenoyl chloride (5): Ethyl vinyl ether **1c** (9.56 mL, 0.10 mol) was added dropwise with stirring to oxalyl chloride (12.9 mL, 0.15 mol). While stirred for 2 h at 0 °C, the reaction mixture was allowed to warm to room temperature and then stirred for a further 15 h. The excess oxalyl chloride was removed in vacuo (15 Torr, oil bath temperature 70–80 °C) and the residue fractionally distilled (b.p. 55 °C/0.5 Torr, oil bath temperature 80–90 °C) to yield 10.5 g (65%) of **5**. Care should be taken when distilling **5**, which easily decomposes at higher temperatures (oil bath temperature >100 °C) to form the decarbonylated acryloyl chloride. B.p. 55 °C/0.5 Torr; ^1H NMR (80 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.0 Hz, 3H, CH_3), 4.13 (q, J = 7.0 Hz, 2H, OCH_2), 6.03 (d, J = 12.8 Hz, 1H, 3-H), 7.87 (d, J = 12.8 Hz, 1H, 4-H).

(1*S*,2*S*)-1-Phenyl-2-trifluoroacetamidopropan-1,3-diol (11): To a solution of (1*S*,2*S*)-2-amino-1-phenylpropan-1,3-diol (**10**) (10.0 g, 59.8 mmol) in dry methanol (70 mL) was slowly added at 0 °C ethyl trifluoroacetate (7.85 mL, 65.8 mmol). After stirring for 15 h at 0 °C, the mixture was concentrated in vacuo and purified by chromatography (300 g SiO_2, ethyl acetate/petroleum ether, 2:1) to give **11** (15.2 g, 97%) as a colourless solid. R_f = 0.29; M.p. 99–100 °C (ethyl acetate); $[\alpha]_D^{20}$ = +11.0 (c = 1 in chloroform); ^1H NMR (80 MHz, [D_6]acetone): δ = 2.82 (s, 1H, OH), 3.50–3.85 (m, 2H, 3-H_2), 3.95–4.28 (m, 1H, 2-H), 4.70 (d, J = 5.0 Hz, 1H, OH), 5.05 (dd, J = 5.0, 5.0 Hz, 1H, 1-H), 7.28–7.47 (m, 5H, aromatic H), 7.70 (s, 1H, NH); MS (70 eV, EI): m/z (%): 245 (5) [$M^+ - H_2O$], 227 (6) [$M^+ - 2H_2O$], 139 (72) [$F_3CCOCHCH_2$], 107 (100) [PhCHOH]; $C_{11}H_{12}NO_3F_3$ (263.2): calcd C 50.19, H 4.59, found C 50.01, H 4.58.

(1*S*,2*S*)-3-*tert*-Butoxydiphenylsiloxy-1-phenyl-2-trifluoroacetamidopropan-1-ol (12): A mixture of **11** (1.70 g, 6.50 mmol) and triethylamine (1.36 mL, 9.75 mmol) in dry dichloromethane (60 mL) was treated at 0 °C with *tert*-butoxydiphenylsilyl chloride and stirred for 45 min at 23 °C. The reaction mixture was diluted with brine (50 mL) and extracted with ether (3 × 70 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by column chromatography (150 g, SiO_2, ethyl acetate/petroleum ether, 1:5) to yield **12** (3.30 g, 98%). R_f = 0.38; M.p. 75–76 °C (ethyl acetate/petroleum ether); $[\alpha]_D^{20}$ = +19.4 (c = 1 in chloroform); IR (KBr): $\tilde{\nu}$ = 3426 (NH, OH), 2976, 2932, 2882 (CH), 1724 (C=O) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 193 nm (4.922); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.30 (s, 9H, SiO*t*Bu), 2.80 (s, 1H, OH), 3.88 (dd, J = 10.5, 4.0 Hz, 1H, 3-H), 3.96 (dd, J = 10.5, 5.0 Hz, 1H, 3-H), 4.22 (m_c, 1H, 2-H), 5.14 (d, J = 3.4 Hz, 1H, 1-H), 6.86 (br d, J = 7.0 Hz, 1H, NH), 7.30–7.70 (m, 15H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.91 (SiO*t*Bu-*C*H_3), 56.18 (C-2), 62.63 (C-3), 72.33 (C-1), 74.41 (SiO*t*Bu-*C*), 115.7 (CF_3), 125.7, 127.9, 128.0, 128.1, 128.6, 130.4, 133.6, 133.7, 134.8, 134.9, 140.2 (aromatic C), 157.2 (CO); MS (70 eV, EI): m/z (%): 440 (9) [M^+ − Ph], 257 (55) [Si*t*BuPh$_2$ +2], 199 (100) [SiPh$_2$O +1]; $C_{27}H_{30}NO_4F_3Si$ (517.6): calcd C 62.65, H 5.84, found C 62.64, H 5.87.

(1*S*,2*S*)-*tert*-Butoxydiphenylsiloxy-1-*tert*-butyldimethylsilyloxy-1-phenyl-2-trifluoroacetamidopropane (13): An ice-cold solution of **12** (1.51 g, 2.93 mmol) and triethylamine (0.61 mL, 4.39 mmol) in dry dichloromethane (30 mL) was treated with TBDMS-OTf (0.74 mL, 3.22 mmol) and stirred under nitrogen for 30 min at 23 °C. The mixture was diluted with saturated aqueous sodium bicarbonate solution (50 mL) and extracted with ether (3 × 70 mL). The organic layer was dried ($MgSO_4$), evaporated in vacuo and chromatographed (100 g SiO_2, ethyl acetate/petroleum ether, 1:15) to give **13** (1.72 g, 93%). R_f = 0.49; $[\alpha]_D^{20}$ = +19.0 (c = 1 in chloroform); IR (film): $\tilde{\nu}$ = 3430 (NH), 2974, 2956, 2932, 2886 (CH), 1734 (C=O) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 193.5 nm (4.970); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3H, SiMe), 0.22 (s, 3H, SiMe), 1.06 (s, 9H, Si*t*Bu), 1.49 (s, 9H, SiO*t*Bu), 3.96 (d, J = 5.8 Hz, 2H, 3-H_2), 4.28 (m_c, 1H, 2-H), 5.25 (d, J = 3.8 Hz, 1H, 1-H), 6.84 (br d, J = 7.0 Hz, 1H, NH), 7.35–7.87 (m, 15H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = −5.07, −4.38 (2 × SiMe), 18.00 (Si*t*-Bu-*C*), 25.69 (Si*t*Bu-*C*H_3), 31.91 (SiO*t*Bu-*C*H_3), 57.58 (C-2), 60.98 (C-3), 71.87 (C-1), 74.18 (SiO*t*Bu-C), 115.8 (CF_3), 126.0, 127.8, 127.9, 128.3, 130.2, 134.1, 134.8, 141.0 (aromatic C), 156.7 (CO); MS (70 eV, EI): m/z (%): 574 (3) [M^+ − *t*Bu], 517 (12) [M^+ − Si*t*BuMe$_2$], 439 (17), [M^+ − Si*t*BuMe$_2$Ph], 221 (100) [PhCHOSi*t*-BuMe$_2$], 199 (49) [SiPh$_2$O +1], 73 (86) [O*t*Bu]; $C_{33}H_{44}NO_4F_3Si_2$ (631.9): calcd C 62.73, H 7.02, found C 62.63, H 6.98.

(1*S*,2*S*)-1-*tert*-Butyldimethylsilyloxy-1-phenyl-2-trifluoroacetamidopropan-3-ol (14): To a solution of **13** (335 mg, 0.53 mmol) in dry tetrahydrofuran (5 mL) was added with stirring at −78 °C a solution of tetra-*n*-butylammoniumfluoride in 1 mL tetrahydrofuran. After stirring at −78 °C for 30 min, the cold reaction mixture was then filtered through SiO_2 (2 g, ethyl acetate) and the filtrate concentrated in vacuo. The residue was purified by chromatography (20 g SiO_2, ethyl acetate/petroleum ether, 1:5) to yield **14** (167 mg, 83%); R_f = 0.27; $[\alpha]_D^{20}$ = +15.2 (c = 1 in chloroform); IR (film): $\tilde{\nu}$ = 3424 (NH, OH), 2956, 2932, 2890, 2860 (CH), 1722 (C=O) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 191 nm (4.608); ^1H NMR (200 MHz,

$CDCl_3$): δ = 0.02 (s, 3H, SiMe), 0.25 (s, 3H, SiMe), 1.07 (s, 9H, Si*t*Bu), 2.20 (s, 1H, OH), 3.87 (d, J = 5.5 Hz, 2H, 3-H_2), 4.18 (m_c, 1H, 2-H), 5.17 (d, J = 3.7 Hz, 1H, 1-H), 6.99 (br d, J = 7.0 Hz, 1H, NH), 7.38–7.55 (m, 5H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = – 5.40, –4.71 (2 × SiMe), 18.01 (Si*t*Bu-*C*), 25.67 (Si*t*Bu-*C*H_3), 58.19 (C-2), 61.29 (C-3), 72.21 (C-1), 115.8 (CF_3), 125.9, 128.1, 128.4, 140.7 (aromatic C), 157.3 (CO); MS (70 eV, EI): m/z (%): 320 (24) [M^+ – *t*Bu], 290 (70) [M^+ – *t*BuMe_2], 221 (100) [PhCHOSi*t*BuMe_2], 105 (65) [PhCHO – 1], 73 (100) [$SiMe_3$]; $C_{17}H_{26}NO_3F_3Si$: calcd 377.1634, found 377.1634 (MS).

(1*S*,2*S*)-2-Amino-1-*tert*-butyldimethylsilyloxy-1-phenylpropan-1-ol (15): Amberlyst A-27 (1.24 g) was added to a solution of **14** (211 mg, 0.56 mmol) in dry methanol (3 mL) and stirred while sonicated until completion (TLC). The resin was removed by filtration and washed with ethyl acetate and methanol (3 × 10 mL). The filtrate was concentrated in vacuo and the residue was purified by column chromatography (20 g SiO_2, ethyl acetate/methanol, 10:1) to yield **15** (151 mg, 96%); R_f = 0.38; M.p. 30–31 °C; $[\alpha]_D^{20}$ = + 63.2 (c = 0.842 in chloroform); IR (film): $\tilde{\nu}$ = 3366 (NH, OH), 2954, 2930, 2888, 2858 (CH) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 192.5 nm (4.436); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.00 (s, 3H, SiMe), 0.25 (s, 3H, SiMe), 1.10 (s, 9H, Si*t*Bu), 2.40 (s, 3H, NH_2 and OH), 3.09 (ddd, J = 7.0, 4.7, 4.5 Hz, 1H, 2-H), 3.57 (dd, J = 10.5, 7.0 Hz, 1H, 3-H), 3.73 (dd, J = 10.5, 4.5 Hz, 1H, 3-H), 4.82 (d, J = 4.7 Hz, 1H, 1-H), 7.45–7.58 (m, 5H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = – 5.16, –4.55 (2 × SiMe), 18.11 (Si*t*Bu-*C*), 25.81 (Si*t*Bu-*C*H_3), 59.66 (C-2), 63.47 (C-3), 75.85 (C-1), 126.4, 127.5, 128.2, 142.1 (aromatic C); MS (70 eV, EI): m/z (%): 266 (1) [M^+ – CH_3], 224 (14) [M^+ – *t*Bu], 221 (62) [PhCHOSi*t*BuMe_2], 132 (31) [OSi*t*BuMe_2 + 1], 73 (99) [$SiMe_3$], 60 (100) [H_2NCHCH_2OH]; $C_{15}H_{27}NO_2Si$ (281.5): calcd C 64.01, H 9.67, found C 64.00, H 9.73.

Synthesis of Oxazolidinone 6 and 8—General Procedure I: A dry 250 mL 3-necked round-bottomed flask equipped with a thermometer and a 10 cm Vigreux column with a distillation head was charged with the amino alcohol (0.10 mol), dry potassium carbonate (1.38 g, 0.01 mol) and diethyl carbonate (29.5 g, 0.25 mol). The mixture was carefully heated to 130–140 °C and ethanol was allowed to distill as it was formed. After 2 h the suspension was cooled to ambient temperature, diluted with dichloromethane (50 mL) and filtered to remove most of the remaining potassium carbonate. The filtrate was washed with saturated aqueous sodium bicarbonate solution (3 × 60 mL), dried ($MgSO_4$) and evaporated in vacuo. Crystallization from ethyl acetate/petroleum ether afforded **6** and **8**, respectively.

(4*S*)-*tert*-Butyloxazolidin-2-one (6): Reaction of (2*S*)-2-amino-3,3-dimethylbutan-1-ol (1.30 g, 11.1 mmol) with diethyl carbonate (6.50 g, 55.0 mmol) and potassium carbonate (0.20 g, 1.50 mmol) according to general procedure I yielded **6** (1.36 g, 86%) as white needles. M.p. 120 °C (ethyl acetate/petroleum ether); $[\alpha]_D^{20}$ = – 18.0 (c = 0.50 in ethanol); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (s, 9H, *t*Bu), 3.60 (ddd, J = 8.8, 5.8, 1.0 Hz, 1H, 4-H), 4.20 (dd, J = 8.8, 5.8 Hz, 1H, 5-H), 4.37 (dd, J = 8.8, 8.8 Hz, 1H, 5-H), 6.43 (s, 1H, NH).

(4*S*,1′*S*)-(1′-*tert*-Butyldimethylsilyloxy-1′-phenyl)-methyloxazolidin-2-one (8): According to general procedure I, **15** (1.59 g, 5.54 mmol) was treated with diethyl carbonate (2.68 mL, 11.1 mmol) and potassium carbonate (153 mg, 1.11 mmol) to afford **8** (1.36 g, 80%) as colourless crystals. R_f = 0.52 (ethyl acetate/petroleum ether); M.p. 83–85 °C (ethyl acetate/petroleum ether); $[\alpha]_D^{20}$ = + 88.6 (c = 1 in chloroform); IR (film): $\tilde{\nu}$ = 3302 (NH), 2956, 2932, 2894 (CH), 1754 (C=O) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 192.5 nm (4.508), 205 nm (3.985); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3H, SiMe), 0.26 (s, 3H, SiMe), 1.09 (s, 9H, Si*t*Bu), 4.07–4.19 (m, 1H, 4-H), 4.30 (dd, J = 8.5, 5.0 Hz, 1H, 5-H), 4.38 (dd, J = 8.5, 8.5 Hz, 1H, 5-H), 4.74 (d, J = 6.7 Hz, 1H, 1′-H), 5.55 (s, 1H, NH), 7.50–7.62 (m, 5H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = – 5.64, –4.87 (2 × SiMe), 17.90 (Si*t*Bu-*C*), 25.57 (Si*t*Bu-*C*H_3), 58.84 (C-4), 66.23 (C-5), 77.00 (C-1′), 126.6, 128.5, 128.6, 139.3 (aromatic C), 159.2 (CO); MS (70 eV, EI): m/z (%): 250 (10) [M^+ – *t*Bu], 221 (75) [PhCHOSi*t*BuMe_2], 176 (6) [M^+ – OSi*t*BuMe_2], 105 (40) [PhCHO – 1], 73 (100) [$SiMe_3$]; $C_{16}H_{25}NO_3Si$ (307.5): calcd C 62.50, H 8.20, found C 62.74, H 8.16.

Synthesis of chiral heterodiene 7 and 9—General Procedure II: A solution of oxazolidinone [**6** (1.43 g, 10 mmol) or **8** (3.07 g, 10 mmol)] in anhydrous tetrahydrofuran (30 mL) was treated with *n*-butyllithium in hexane (10.5 mmol) and stirred at –78 °C under nitrogen for 30 min. **5** (1.71 g, 10.5 mmol) was slowly added to the reaction mixture and stirring was continued for 1 h. The solution was quenched with saturated aqueous sodium bicarbonate solution (30 mL) and extracted with ether (2 × 40 mL) and ethyl acetate (1 × 40 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, and the resulting residue was purified by chromatography or crystallization to give **7** or **9**, respectively.

(4*S*)-4-*tert*-Butyl-3-[(*E*)-4′ethoxy-2′-oxo-3′-butenoyl]-oxazolidin-2-one (7): According to general procedure II a solution of **6** (1.04 g, 7.30 mmol) in dry tetrahydrofuran (25 mL) was treated with *n*-butyllithium in hexane (7.50 mmol) and **5** (1.22 g, 7.50 mmol). Flash chromatography (50 g SiO_2, ethyl acetate/petroleum ether, 1:2) and recrystallization (ether) afforded **7** as white crystals; R_f = 0.44; M.p. 100–102 °C (ether); $[\alpha]_D^{20}$ = + 69.8 (c = 1.05 in chloroform); IR (KBr): $\tilde{\nu}$ = 2970, 2898 (CH), 1778 (C=O, urethane), 1696 (C=O, amide), 1656 (C=O, conjugated), 1618 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 204.5 nm (3.793), 251.5 nm (4.118); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.01 (s, 9H, *t*Bu), 1.39 (t, J = 7.0 Hz, 3H, CH_3), 4.04 (q, J = 7.0 Hz, 2H, OCH_2), 4.30–4.43 (m, 3H, 4-H, 5-H_2), 5.71 (d, J = 12.8 Hz, 1H, 3′-H), 7.55 (d, J = 12.8 Hz, 1H, 4′-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.32 (CH_3), 25.59 (*t*Bu-*C*H_3), 36.00 (*t*Bu-*C*), 60.85 (C-4), 66.77, 67.81 (OCH_2, C-5), 103.5 (C-3′), 154.0 (C-2), 166.5 (C-4′), 166.9 (C-2′), 186.9 (C-1′); MS (70 eV, EI): m/z (%): 269 (1) [M^+], 99 (100) [EtOCH=CHCO], 71 (51) [EtOCH=CH]; $C_{13}H_{19}NO_5$ (269.3): calcd C 57.98, H 7.11, found C 58.05, H 7.24.

(4*S*,1″*S*)-4-(1″-*tert*-Butyldimethylsilyloxy-1″-phenyl)-methyl-3-[(*E*)-4′-ethoxy-2′-oxo-3′-butenoyl]-oxazolidin-2-one (9): Reaction of **8** (1.12 g, 3.64 mmol) with *n*-butyllithium in hexane (3.80 mmol) and **5** (0.62 g, 3.80 mmol) according to general procedure II yielded **9** (1.12 g, 71%) as a colourless oil. R_f = 0.75 (ethyl acetate/petroleum ether, 1:2); $[\alpha]_D^{20}$ = – 116.4 (c = 1 in chloroform); IR (film): $\tilde{\nu}$ = 2954, 2930, 2892 (CH), 1796 (C=O, urethane), 1688 (C=O, amide), 1656 (C=O, conjugated), 1618 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 190.5 nm (4.553), 206 nm (4.034), 251 nm (4.012); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3H, SiMe), 0.15 (s, 3H, SiMe), 0.93 (s, 9H, Si*t*Bu), 1.41 (t, J = 7.0 Hz, 3H, CH_3), 4.05 (q, J = 7.0 Hz, 2H, OCH_2), 4.39 (dd, J = 9.5, 8.5 Hz, 1H, 5-H), 4.62–4.74 (m, 2H, 4-H, 5-H), 5.34 (d, J = 4.0 Hz, 1H, 1″-H), 5.69 (d, J = 12.8 Hz, 1H, 3′-H), 7.30–7.42 (m, 5H, aromatic H), 7.56 (d, J = 12.8 Hz, 1H, 4′-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = – 5.16, –4.55 (2 × SiMe), 14.33 (CH_3), 18.12 (Si*t*Bu-*C*), 25.71 (Si*t*Bu-*C*H_3), 57.27 (C-4), 64.27, 67.83 (C-5, OCH_2), 70.44 (C-1″), 103.1 (C-3′), 126.4, 128.6, 128.8, 137.2 (aromatic C), 152.5 (C-2), 166.4 (C-4′), 166.6 (C-2′), 186.2 (C-1′); MS (70 eV, EI): m/z (%): 433 (1) [M^+], 376 (16) [M^+ – *t*Bu], 221 (100) [PhCHOSi*t*BuMe_2], 147 (12), 99 (68) [EtOCH=CHCO], 71 (31) [EtOCH=CH]; $C_{22}H_{31}NO_6Si$ (433.6): calcd C 60.94, H 7.21, found C 61.09, H 7.38.

Synthesis of the Dihydropyrans 16a–19a, 16b–19b and 20a–23a by a Lewis acid promoted Diels–Alder reaction—General Procedure III: Reaction of oxabutadiene **7** with the enol ethers **1a** and **1b** and oxabutadiene **9** with enol ether **1a**: A solution of **7** or **9** (0.20 mmol) in dry dichloromethane (2 mL) was treated with **1a** or **1b** (0.40 mmol). The mixture was cooled to –78 °C and a 1 M solution of the Lewis acid in dichloromethane (0.30 mmol) was added dropwise. Stirring was continued at this temperature, after which the reaction was quenched by addition of saturated aqueous sodium bicarbonate solution (1–5 mL) and extracted with ether (3 × 10 mL). After drying ($MgSO_4$), the organic layer was concentrated in vacuo and the residue was purified by chromatography to give **16a–19a**, **16b–19b** and **20a–23a**, respectively.

Synthesis of the Dihydropyrans 16a–19a, 16b–19b and 20a–23a by a triflate-promoted Diels–Alder reaction—General Procedure IV: Reaction of heterodiene **7** with the enol ethers **1a** and **1b** and heterodiene **9** with enol ether **1a**: To a solution of **7** or **9** (0.20 mmol) in dry dichloromethane (2 mL), enol ether **1a** or **1b** (0.30 mol) was added. The reaction mixture was cooled to –78 °C and slowly treated with TMS-OTf or TBDMS-OTf. The solution was stirred at –78 °C until completion of the reaction and quenched by the addition of 1 mL of a mixture of triethylamine/ethanol (1:1) and filtered (5 g SiO_2, ethyl acetate). The filtrate was washed with saturated aqueous sodium bicarbonate solution (3 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was then chromatographed to yield **16a–19a**, **16b–19b** and **20b–23b**, respectively.

Reaction of 2 and 1a: Following general procedures III and IV, a mixture of **2** (43.0 mg, 0.20 mmol) and **1a** (52.0 mg, 0.40 mmol) in dry dichloromethane (2 mL) was treated at –78 °C with the 1 M Lewis acid in dichloromethane (0.30 mL, 0.30 mmol) or TMS-OTf (58.0 mL, 0.30 mmol), to yield after chromatography (10 g SiO_2, ethyl acetate/petroleum ether, 1:1) **3** and **4**.

(2*SR*,3*RS*,4*SR*)-3-Acetoxy-2,4-diethoxy-6-(carbonyloxazolidin-2′-one)-3,4-dihydro-2*H*-pyran (4, *exo* isomer): R_f = 0.42; M.p. 116 °C (ether); IR (KBr): $\tilde{\nu}$ = 2978, 2932, 2876 (CH), 1790 (C=O, urethane), 1744 (C=O, OAc), 1694 (C=O, amide), 1658 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 212 nm (3.675), 240 nm (3.639); ^{1}H NMR (200 MHz, C_6D_6): δ = 1.04 (t, J = 7.0 Hz, 3H, CH_3), 1.08 (t, J = 7.0 Hz, 3H, CH_3), 1.65 (s, 3H, OAc), 2.72–3.08 (m, 4H, 4′-H_2, 5′-H_2), 3.44 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.54 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.65 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.96 (dd, J = 4.2, 3.0 Hz, 1H, 4-H), 4.09 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 5.50 (d, J = 1.5 Hz, 1H, 2-H), 5.53 (ddd, J = 3.0, 1.5, 1.2 Hz, 1H, 3-H), 5.84 (dd, J = 4.2, 1.2 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.20 (CH_3), 15.58 (CH_3), 20.53 (OAc), 42.55 (C-4′), 62.02 (C-5′), 64.72, 66.23 (2 × OCH_2), 70.03 (C-3), 71.98 (C-4), 98.31 (C-2), 106.2 (C-5), 147.4 (C-6), 152.1 (C-2′), 163.7 (C-7), 169.8 (OAc); MS (70 eV; EI), m/z (%): 343 (1) [M^+], 214 (86) [retro-Diels–Alder (RDA), diene + 1], 169 (62) [M^+ – OAc – carboximide], 99 (90) [RDA, EtOCH=CHCO], 88 (100) [RDA, enol ether – Ac + 1]; $C_{15}H_{21}NO_8$ (343.3): calcd C 52.47, H 6.17, found C 52.68, H 6.14.

(2*SR*,3*RS*,4*SR*)-3-Acetoxy-2,4-diethoxy-6-(carbonyloxazolidin-2′-one)-3,4-dihydro-2*H*-pyran (3, *endo* isomer): R_f = 0.35; M.p. 57–59 °C (ether); IR (KBr): $\tilde{\nu}$ = 2980, 2930, 2908 (CH), 1790 (C=O, urethane), 1744 (C=O, OAc), 1694 (C=O, amide), 1658 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 211 nm (3.821), 250.5 nm (3.691); ^{1}H NMR (500 MHz, C_6D_6): δ = 1.08 (t, J = 7.0 Hz, 3H, CH_3), 1.12 (t, J = 7.0 Hz, 3H, CH_3), 1.74 (s, 3H, OAc), 2.68–2.73 (m, 1H, 5′-H), 2.86–2.93 (m,

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1H, 5'-H), 2.94–2.98 (m, 2H, 4'-H_2), 3.17 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.55 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.69 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.85 (ddd, J = 4.5, 2.5, 1.0 Hz, 1H, 4-H), 4.04 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 5.16 (dd, J = 1.0, 0.5 Hz, 1H, 2-H), 5.58 (ddd, J = 4.5, 1.7, 0.5 Hz, 1H, 3-H), 5.72 (dd, J = 2.5, 1.7 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.20 (CH_3), 15.47 (CH_3), 20.63 (OAc), 42.54 (C-4'), 62.16 (C-5'), 65.06 (C-3), 65.41, 65.88 (2 × OCH_2), 72.04 (C-4), 100.6 (C-2), 108.6 (C-5), 146.0 (C-6), 152.5 (C-2'), 163.3 (C-7), 170.1 (OAc); MS (70 eV; EI): m/z (%): 343 (1) [M^+], 214 (28) [RDA, diene +1], 169 (1) [M^+ − OAc − carboximide], 130 (11) [RDA, enol ether], 43 (100) [Ac]; $C_{15}H_{21}NO_8$ (343.3): calcd C 52.47, H 6.17, found C 52.49, H 6.24.

Reaction of 7 and 1a: A solution of **7** (54.0 mg, 0.20 mmol) and **1a** (52.0 mg, 0.40 mmol) in dry dichloromethane was treated according to general procedures III and IV with a 1 M solution of the Lewis acid in dichloromethane (0.30 mL, 0.30 mmol) or with TMS-OTf (58.0 mL, 0.30 mmol), respectively, to give after chromatography (10 g SiO_2, ethyl acetate/petroleum ether, 1:2) **16a–19a**.

(2*S*,3*R*,4*S*,4'*S*)-3-Acetoxy-2,4-diethoxy-6-(carbonyl-4'-*tert*-butyl-oxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (18a, *exo*-I product): R_f = 0.46; $[\alpha]_D^{20}$ = − 32.7 (c = 0.63 in chloroform); IR (film): $\tilde{\nu}$ = 2972, 2940, 2896 (CH), 1788 (C=O, urethane), 1744 (C=O, OAc), 1702 (C=O, amide), 1656 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 241.5 nm (3.716); ^{1}H NMR (200 MHz, C_6D_6): δ = 0.60 (s, 9H, *t*Bu), 1.03 (t, J = 7.0 Hz, 3H, CH_3), 1.08 (t, J = 7.0 Hz, 3H, CH_3), 1.62 (s, 3H, OAc), 3.17 (dd, J = 9.0, 8.5 Hz, 1H, 5'-H), 3.22 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.44 (dd, J = 9.0, 2.0 Hz, 1H, 5'-H), 3.48–3.76 (m, 2H, 2 × OCH), 3.91 (dd, J = 4.5, 2.5 Hz, 1H, 4-H), 4.02 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 4.06 (dd, J = 8.5, 2.0 Hz, 1H, 4'-H), 5.54 (ddd, J = 2.5, 1.5, 1.5 Hz, 1H, 3-H), 5.58 (d, J = 1.5 Hz, 1H, 2-H), 5.89 (dd, J = 4.5, 1.5 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.03 (CH_3), 15.45 (CH_3), 21.11 (OAc), 25.33 (*t*Bu-CH_3), 35.99 (*t*Bu-*C*), 60.52 (C-4'), 64.77, 65.22, 66.15 (2 × OCH_2, C-5'), 69.73 (C-3), 71.35 (C-4), 97.60 (C-2), 106.7 (C-5), 147.0 (C-6), 153.0 (C-2'), 164.7 (C-7), 170.4 (OAc); MS (70 eV, EI): m/z (%): 270 (100) [RDA, diene +1], 169 (17) [M^+ − carboximide − OAc], 130 (8) [RDA, enol ether], 99 (70) [RDA, EtOCH=*C*HCO]; $C_{19}H_{29}NO_8$ (399.4): calcd C 57.13, H 7.32, found C 57.04, H 7.37.

(2*R*,3*S*,4*S*,4'*S*)-3-Acetoxy-2,4-diethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (16a, *endo*-I isomer): R_f = 0.40; $[\alpha]_D^{20}$ = + 30.2 (c = 1 in chloroform); IR (KBr): $\tilde{\nu}$ = 2974, 2908 (CH), 1786 (C=O, urethane), 1746 (C=O, OAc), 1704 (C=O, amide), 1656 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 252 nm (3.681); ^{1}H NMR (200 MHz, C_6D_6): δ = 0.60 (s, 9H, *t*Bu), 1.07 (t, J = 7.0 Hz, 3H, CH_3), 1.13 (t, J = 7.0 Hz, 3H, CH_3), 1.72 (s, 3H, OAc), 3.17 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.19 (dd, J = 9.0, 8.5 Hz, 1H, 5'-H), 3.46 (dd, J = 9.0, 2.2 Hz, 1H, 5'-H), 3.54 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.69 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.86 (ddd, J = 4.5, 2.5, 1.0 Hz, 1H, 4-H), 4.00 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 4.06 (dd, J = 8.5, 2.2 Hz, 1H, 4'-H), 5.28 (dd, J = 1.0, 0.5 Hz, 1H, 2-H), 5.58 (ddd, J = 4.5, 1.7, 0.5 Hz, 1H, 3-H), 5.76 (dd, J = 2.5, 1.7 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 16.04 (CH_3), 16.25 (CH_3), 21.45 (OAc), 25.86 (*t*Bu-CH_3), 36.54 (*t*Bu-*C*), 61.21 (C-4'), 65.56, 66.24, 66.58 (2 × OCH_2, C-5'), 65.91 (C-3), 72.88 (C-4), 101.6 (C-2), 110.1 (C-5), 147.3 (C-6), 154.3 (C-2'), 165.3 (C-7), 170.9 (OAc); MS (70 eV, EI): m/z (%): 270 (16) [RDA, diene +1], 169 (1) [M^+ − carboximide − OAc], 130 (6) [RDA, enol ether], 99 (46) [RDA, EtOCH=CHCO], 43 (100); $C_{19}H_{29}NO_8$ (399.4): calcd C 57.13, H 7.32, found C 57.23, H 7.45.

(2*S*,3*R*,4*R*,4'*S*)-3-Acetoxy-2,4-diethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (17a, *endo*-II isomer): R_f = 0.39; $[\alpha]_D^{20}$ = + 34.8 (c = 1 in chloroform); IR (KBr): $\tilde{\nu}$ = 2976, 2932, 2880 (CH), 1792 (C=O, urethane), 1746 (C=O, OAc), 1704 (C=O, amide), 1660 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 200 nm (3.868), 247.5 nm (3.424); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.63 (s, 9H, *t*Bu), 1.07 (t, J = 7.0 Hz, 3H, CH_3), 1.13 (t, J = 7.0 Hz, 3H, CH_3), 1.76 (s, 3H, OAc), 3.17 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.26 (dd, J = 7.0, 7.0 Hz, 1H, 5'-H), 3.28 (dd, J = 7.0, 4.0 Hz, 1H, 5'-H), 3.45–3.73 (m, 3H, 4'-H, 2 × OCH), 3.92 (ddd, J = 4.5, 2.5, 1.0 Hz, 1H, 4-H), 4.02 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 5.08 (dd, J = 1.0, 0.5 Hz, 1H, 2-H), 5.56 (ddd, J = 4.5, 1.5, 0.5 Hz, 1H, 3-H), 5.62 (dd, J = 2.5, 1.5 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.22 (CH_3), 15.45 (CH_3), 20.59 (OAc), 25.69 (*t*Bu-CH_3), 35.61 (*t*Bu-*C*), 62.98 (C-4'), 65.12 (C-3), 65.35, 65.65, 65.82 (2 × OCH_2, C-5'), 72.03 (C-4), 100.3 (C-2), 108.1 (C-5), 145.8 (C-6), 154.1 (C-2'), 163.3 (C-7), 170.0 (OAc); MS (70 eV, EI): m/z (%): 270 (8) [RDA, diene +1], 169 (3) [M^+ − carboximide − OAc], 131 (42) [RDA, enol ether +1], 99 (89) [RDA, EtOCH=CHCO]; $C_{19}H_{29}NO_8$: calcd 399.1893, found 399.1893 (MS).

(2*S*,3*S*,4*S*,4'*S*)-3-Acetoxy-2,4-diethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (*endo*-I epimerized isomer): R_f = 0.43; IR (KBr): $\tilde{\nu}$ = 2974, 2936, 2898, 2876 (CH), 1794 (C=O, urethane), 1746 (C=O, OAc), 1704 (C=O, amide), 1658 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 212.5 nm (3.667), 248 nm (3.433); ^{1}H NMR (200 MHz, C_6D_6): δ = 0.62 (s, 9H, *t*Bu), 1.02 (t, J = 7.0 Hz, 3H, CH_3), 1.12 (t, J = 7.0 Hz, 3H, CH_3), 1.76 (s, 3H, OAc), 3.23 (dd, J = 9.5, 8.5 Hz, 1H, 5'-H), 3.24 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.36 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.39 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.47 (dd, J = 9.5, 2.5 Hz, 1H, 5'-H), 4.01 (dd, J = 8.5, 2.5 Hz, 1H, 4'-H), 4.14 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 4.40 (dd, J = 4.0, 2.7 Hz, 1H, 4-H), 5.23 (d, J = 4.0 Hz, 1H, 2-H), 5.50 (ddd, J = 4.0, 4.0, 1.5 Hz, 1H, 3-H), 5.89 (dd, J = 2.7, 1.5 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.08 (CH_3), 15.54 (CH_3), 20.54 (OAc), 25.26 (*t*Bu-CH_3), 35.69 (*t*Bu-*C*), 61.13 (C-4'), 64.67, 65.04, 65.60 (2 × OCH_2, C-5'), 66.11 (C-3), 69.00 (C-4), 99.16 (C-2), 108.2 (C-5), 145.3 (C-6), 153.0 (C-2'), 164.5 (C-7), 170.0 (OAc); MS (70 eV, EI): m/z (%): 399 (5) [M^+], 270 (99) [RDA, diene +1], 169 (19) [M^+ − carboximide − OAc], 130 (71) [RDA, enol ether], 103 (33), 99 (99) [RDA, EtOCH=CHCO]; $C_{19}H_{29}NO_8$: calcd 399.1893, found 399.1893 (MS).

Reaction of 7 and 1b: According to general procedures III and IV, a mixture of **7** (50.0 mg, 0.19 mmol) and **1b** (71.4 mg, 0.37 mmol) in dry dichloromethane (2 mL) was treated at −78 °C with a 1 M solution of the Lewis acid in dichloromethane (0.28 mL, 0.28 mmol) or TMS-OTf (50.0 mL, 0.28 mmol), respectively, to yield after chromatography (10 g SiO_2) **16b–19b**.

(2*R*,3*S*,4*S*,4'*S*)-3-Acetoxy-2-benzyloxy-4-ethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (16b, *endo*-I isomer): R_f = 0.18 (ethyl acetate/petroleum ether, 2:5); $[\alpha]_D^{20}$ = − 6.8 (c = 0.5 in chloroform); IR (KBr): $\tilde{\nu}$ = 3446 (aromatic CH), 2970, 2880 (CH), 1784 (C=O, urethane), 1746 (C=O, OAc), 1704 (C=O, amide), 1654 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 207.5 nm (4.042), 251.5 nm (3.675); ^{1}H NMR (200 MHz, C_6D_6): δ = 0.59 (s, 9H, *t*Bu), 1.11 (t, J = 7.0 Hz, 3H, CH_3), 1.73 (s, 3H, OAc), 3.12 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.35 (dd, J = 9.5, 8.5 Hz, 1H, 5'-H), 3.43 (m, 1H, OCH), 3.44 (dd, J = 9.5, 2.5 Hz, 1H, 5'-H), 3.68 (ddd, J = 4.5, 2.5, 1.0 Hz, 1H, 4-H), 4.07 (dd, J = 8.5, 2.5 Hz, 1H, 4'-H), 4.88 (d, J = 12.5 Hz, 1H, OCHPh), 5.06 (d, J = 12.5 Hz, 1H, OCHPh), 5.42 (s, 1H, 2-H), 5.60 (ddd, J = 4.5, 1.7, 0.5 Hz, 1H, 3-H), 5.77 (dd, J = 2.5, 1.7 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.44 (CH_3), 20.59 (OAc), 25.05 (*t*Bu-CH_3), 35.71 (*t*Bu-*C*), 60.46 (C-4'), 56.65 (C-3), 64.72, 65.38, 70.94 (2 × OCH_2, C-5'), 71.87 (C-4), 99.67 (C-2), 99.67 (C-5), 128.3, 128.8, 137.7 (aromatic C), 146.3 (C-6), 153.5 (C-2'), 164.4 (C-7), 170.1 (OAc); MS (70 eV, EI): m/z (%): 461 (2) [M^+], 270 (40) [RDA, diene +1], 91 (100) [$C_7H_7^+$]; $C_{24}H_{31}NO_8$ (461.5): calcd C 62.46, H 6.77, found C 62.57, H 6.95.

(2*S*,3*R*,4*R*,4'*S*)-3-Acetoxy-2-benzyloxy-4-ethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (17b, *endo*-II isomer): R_f = 0.21 (ethyl acetate / petroleum ether, 2:5); $[\alpha]_D^{20}$ = + 84.4 (c = 0.25 in chloroform); IR (KBr): $\tilde{\nu}$ = 3412 (aromatic CH), 2972, 2942 (CH), 1790 (C=O, urethane), 1746 (C=O, OAc), 1700 (C=O, amide), 1662 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 204 nm (4.196), 242 nm (3.670); ^{1}H NMR (200 MHz, C_6D_6): δ = 0.62 (s, 9H, *t*Bu), 1.12 (t, J = 7.0 Hz, 3H, CH_3), 1.75 (s, 3H, OAc), 3.09 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.30 (dd, J = 9.0, 7.5 Hz, 1H, 5'-H), 3.42–3.60 (m, 2H, OCH, 5'-H), 3.72 (dd, J = 7.5, 1.5 Hz, 1H, 4'-H), 3.78 (m, 1H, 4-H), 4.82 (d, J = 12.5 Hz, 1H, OCHPh), 5.00 (d, J = 12.5 Hz, 1H, OCHPh), 5.21 (s, 1H, 2-H), 5.57 (ddd, J = 4.5, 1.7, 0.5 Hz, 1H, 3-H), 5.65 (dd, J = 2.5, 1.7 Hz, 1H, 5-H); ^{13}C NMR (75 MHz, C_6D_6): δ = 15.44 (CH_3), 20.59 (OAc), 25.66 (*t*Bu-CH_3), 35.58 (*t*Bu-*C*), 63.08 (C-4'), 65.15 (C-3), 65.27, 65.77, 70.99 (2 × OCH_2, C-5'), 71.69 (C-4), 99.10 (C-2), 108.4 (C-5), 128.5, 128.6, 128.7, 137.7 (aromatic C), 145.7 (C-6), 154.2 (C-2'), 163.2 (C-7), 170.0 (OAc); MS (70 eV, EI): m/z (%): 461 (2) [M^+], 270 (42) [RDA, diene +1], 91 (100) [$C_7H_7^+$]; $C_{24}H_{31}NO_8$: calcd 461.2049, found 461.2049 (MS).

(2*S*,3*R*,4*S*,4'*S*)- and (2*R*,3*S*,4*R*,4'*S*)-3-Acetoxy-2-benzyloxy-4-ethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (18b and **19b**, *exo*-I and *exo*-II isomer): R_f = 0.20 (ethyl acetate/petroleum ether, 2:5); IR (KBr): $\tilde{\nu}$ = 3412 (aromatic CH), 2972, 2942 (CH), 1790 (C=O, urethane), 1746 (C=O, OAc), 1700 (C=O, amide), 1662 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 204 nm (4.196), 242 nm (3.670); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.52 (s, 9H, *t*Bu), 0.93 (t, J = 7.0 Hz, 3H, CH_3), 1.56 (s, 3H, OAc), 3.10 (dd, J = 9.0, 9.0 Hz, 1H, 5'-H), 3.33 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.38 (dd, J = 9.0, 2.5 Hz, 1H, 5'-H), 3.45 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.88 (dd, J = 4.2, 2.8 Hz, 1H, 4-H), 4.01 (dd, J = 8.5, 2.5 Hz, 1H, 4'-H, *exo*-I isomer), 4.05 (dd, J = 8.0, 3.0 Hz, 1H, 4'-H, *exo*-II isomer), 4.67 (d, J = 12.5 Hz, 1H, OCHPh, *exo*-I isomer), 4.71 (d, J = 12.5 Hz, 1H, OCHPh, *exo*-II isomer), 4.89 (d, J = 12.5 Hz, 1H, OCHPh, *exo*-II isomer), 5.01 (d, J = 12.5 Hz, 1H, OCHPh, *exo*-I isomer), 5.51 (m, 1H, 3-H), 5.64 (d, J = 1.2 Hz, 1H, 2-H), 5.79 (dd, J = 3.0, 1.0 Hz, 1H, 5-H, *exo*-II isomer), 5.86 (dd, J = 4.5, 1.0 Hz, 1H, 5-H, *exo*-I isomer); ^{13}C NMR (75 MHz, C_6D_6): δ = 15.51 (CH_3), 20.43 (OAc), 25.09 (*t*Bu-CH_3), 35.72 (*t*Bu-*C*), 60.49 (C-4', *exo*-I isomer), 60.59 (C-4', *exo*-II isomer), 64.66, 64.74, 71.91 (2 × OCH_2, C-5'), 70.04 (C-3, *exo*-I isomer), 70.32 (C-3, *exo*-II isomer), 72.17 (C-4, *exo*-I isomer), 75.09 (C-4, *exo*-II isomer), 98.00 (C-2, *exo*-I isomer), 101.3 (C-2, *exo*-II isomer), 107.2 (C-5, *exo*-I isomer), 109.7 (C-5, *exo*-II isomer), 127.8, 128.3, 128.5, 137.8 (aromatic C), 147.6 (C-6), 153.2 (C-2'), 164.8 (C-7), 169.8 (OAc); MS (70 eV; EI): m/z (%): 270 (18) [RDA, diene +1], 91 (100) [$C_7H_7^+$], 99 (18) [RDA, EtOCH=CHCO]; $C_{24}H_{31}NO_8$ (461.5): calcd C 62.46, H 6.77, found C 62.57, H 6.95.

(2*R*,3*R*,4*S*,4'*S*)-3-Acetoxy-2-benzyloxy-4-ethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (*exo*-I epimerized isomer): R_f = 0.27 (ethyl acetate/petroleum ether, 2:5); $[\alpha]_D^{20}$ = +193.6 (c = 0.5 in chloroform); IR (KBr): $\tilde{\nu}$ = 3412 (aromatic CH), 2972, 2942 (CH), 1790 (C=O, urethane), 1746 (C=O, OAc), 1700 (C=O, amide), 1662 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 204 nm (4.196), 242 nm (3.670); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.64 (s, 9H, *t*Bu), 1.00 (t, J = 7.0 Hz, 3H, CH_3), 1.65 (s, 3H, OAc), 3.21 (dd, J = 9.0, 7.5 Hz,

1H, 5'-H), 3.38–3.43 (m, 2H, 2 × OCH), 3.45 (dd, J = 9.0, 1.8 Hz, 1H, 5'-H), 3.86 (dd, J = 7.5, 1.8 Hz, 1H, 4'-H), 4.18 (dd, J = 4.8, 3.5 Hz, 1H, 4-H), 4.66 (d, J = 12.0 Hz, 1H, OCHPh), 5.14 (d, J = 12.0 Hz, 1H, OCHPh), 5.51 (d, J = 2.0 Hz, 1H, 2-H), 5.54 (dd, J = 4.8, 2.0 Hz, 1H, 3-H), 5.88 (d, J = 3.5 Hz, 1H, 5-H); ^{13}C NMR (75 MHz, C_6D_6): δ = 15.54 (CH_3), 20.39 (OAc), 25.46 (*t*Bu-CH_3), 35.65 (*t*Bu-C), 62.15 (C-4'), 64.47, 65.19, 71.87 (2 × OCH_2, C-5'), 70.18 (C-3), 71.57 (C-4), 97.82 (C-2), 107.09 (C-5), 127.9, 128.5, 137.9 (aromatic C), 146.6 (C-6), 153.5 (C-2'), 164.1 (C-7), 169.7 (OAc); MS (70 eV): m/z (%): 461 (2) [M^+], 270 (42) [RDA, diene +1], 91 (100) [$C_7H_7^+$]; $C_{24}H_{31}NO_8$ (461.5): calcd C 62.46, H 6.77, found C 62.66, H 6.67.

Reaction of 9 and 1a: A solution of **9** (87.0 mg, 0.20 mmol) and **1a** (52.0 mg, 0.40 mmol) in dry dichloromethane was treated according to general procedures III and IV with a 1 M solution of the Lewis acid in dichloromethane (0.30 mL, 0.30 mmol) or TMS-OTf (58.0 mL, 0.30 mmol), to give after chromatography (10 g SiO_2, ethyl acetate/petroleum ether, 2:7) **20a–23a**.

(2*R*,3*S*,4*S*,4'*S*,1''*S*)-3-Acetoxy-2,4-diethoxy-6-[carbonyl-4'-(1''-*tert*-butyldimethylsiloxy-1''-phenylmethyl)-oxazolidin-2'-one]-3,4-dihydro-2*H*-pyran (20a, *endo*-I isomer): R_f = 0.47; $[\alpha]_D^{20}$ = −65.0 (c = 1 in chloroform); IR (film): $\tilde{\nu}$ = 2976, 2956, 2932, 2886, 2880 (CH), 1792 (C=O, urethane), 1746 (C=O, OAc), 1700 (C=O, amide), 1662 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 191 nm (4.696), 253 nm (3.628); ^{1}H NMR (200 MHz, C_6D_6): δ = −0.22 (s, 3H, SiMe), 0.07 (s, 3H, SiMe), 0.91 (s, 9H, *t*Bu), 1.08 (t, J = 7.0 Hz, 3H, CH_3), 1.12 (t, J = 7.0 Hz, 3H, CH_3), 1.80 (s, 3H, OAc), 3.12–3.66 (m, 5H, 4 × OCH, 5'-H), 3.84–3.94 (m, 1H, 4-H), 3.99 (dd, J = 9.0, 4.0 Hz, 1H, 5'-H), 4.41 (ddd, J = 9.0, 4.5, 4.0 Hz, 1H, 4'-H), 5.04 (d, J = 4.5 Hz, 1H, 1''-H), 5.20 (dd, J = 1.0, 0.5 Hz, 1H, 2-H), 5.58 (ddd, J = 4.5, 1.7, 0.5 Hz, 1H, 3-H), 5.66 (dd, J = 2.5, 1.7 Hz, 1H, 5-H), 7.00–7.35 (m, 5H, aromatic H); ^{13}C NMR (50 MHz, C_6D_6): δ = −5.26 (SiMe), −4.93 (SiMe), 15.05 (CH_3), 15.47 (CH_3), 18.26 (*t*Bu-*C*), 20.71 (OAc), 25.88 (*t*Bu-CH_3), 57.34 (C-4'), 62.86 (C-5'), 65.07 (C-3), 65.43, 65.54 (2 × OCH_2), 71.17 (SiOCH), 72.21 (C-4), 100.4 (C-2), 108.0 (C-5), 127.2, 128.3, 128.7, 138.1 (aromatic C), 146.2 (C-6), 152.3 (C-2'), 163.4 (C-7), 170.0 (OAc); MS (70 eV, EI): m/z = 506 (23) [M^+ − *t*Bu], 434 (67) [RDA, diene], 169 (9) [M^+ − carboximide − OAc], 130 (15) [RDA, enol ether], 99 (60) [RDA, EtOCH=CHCO], 71 (62) [RDA, EtOCH=CH]; $C_{28}H_{41}NO_9Si$ (563.7): calcd C 59.66, H 7.33, found C 59.60, H 7.47.

(2*S*,3*R*,4*R*,4'*S*,1''*S*)-3-Acetoxy-2,4-diethoxy-6-[carbonyl-4'-(1''-*tert*-butyldimethylsiloxy-1''-phenylmethyl)oxazolidin-2'-one]-3,4-dihydro-2*H*-pyran (21a, *endo*-II isomer): R_f = 0.45; $[\alpha]_D^{20}$ = −99.6 (c = 1 in chloroform); IR (KBr): $\tilde{\nu}$ = 2976, 2956, 2932, 2896, 2860 (CH), 1796 (C=O, urethane), 1746 (C=O, OAc), 1694 (C=O, amide), 1660 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 190.5 nm (4.696), 256 nm (3.680); ^{1}H NMR (300 MHz, C_6D_6): δ = −0.09 (s, 3H, SiMe), 0.02 (s, 3H, SiMe), 0.88 (s, 9H, *t*Bu), 1.08 (t, J = 7.0 Hz, 6H, 2 × CH_3), 1.76 (s, 3H, OAc), 3.17 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.41 (dd, J = 9.0, 8.0 Hz, 1H, 5'-H), 3.54 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.59 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.78 (ddd, J = 4.5, 2.5, 1.0 Hz, 1H, 4-H), 3.94 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.95 (ddd, J = 8.0, 4.5, 2.0 Hz, 1H, 4'-H), 4.23 (dd, J = 9.0, 2.0 Hz, 1H, 5'-H), 5.04 (dd, J = 1.0, 0.5 Hz, 1H, 2-H), 5.52 (ddd, J = 4.5, 2.0, 0.5 Hz, 1H, 3-H), 5.60 (d, J = 4.5 Hz, 1H, 1''-H), 5.77 (dd, J = 2.5, 2.0 Hz, 1H, 5-H), 6.98–7.12 (m, 3H, aromatic H), 7.27–7.33 (m, 2H, aromatic H); ^{13}C NMR (50 MHz, C_6D_6): δ = −5.21 (SiMe), −4.91 (SiMe), 15.13 (CH_3), 15.45 (CH_3), 18.26 (*t*Bu-*C*), 20.60 (OAc), 25.86 (*t*Bu-CH_3), 59.58 (C-4'), 62.97 (C-5'), 65.01 (C-3), 65.38, 65.85 (2 × OCH_2), 70.71 (SiOCH), 72.06 (C-4), 100.5 (C-2), 109.1 (C-5), 126.4, 128.3, 128.6, 138.0 (aromatic C), 146.0 (C-6), 152.1 (C-2'), 163.9 (C-7), 169.9 (OAc); MS (70 eV; EI): m/z (%): 506 (16) [M^+ − *t*Bu], 434 (31) [RDA, diene], 221 (100) [PhCHOSi*t*BuMe_2], 169 (8) [M^+ − carboximide − OAc], 99 (78) [RDA, EtOCH=CHCO]; $C_{28}H_{41}NO_9Si$ (563.7): calcd C 59.66, H 7.33, found C 59.60, H 7.47.

Synthesis of the Dihydropyrans 16c–19c, 16d–19d, 16e–19e, 16f–19f and 16g–19g by a Lewis acid promoted Diels–Alder reaction—General Procedure V: Reaction of heterodiene **7** with the enol ethers **1c**, **1d**, **1e**, **1g** and **1g**: A solution of **7** (0.20 mmol) in dry dichloromethane (2 mL) was treated with one of **1c–g** (0.40 mmol) at −78 °C. After stirring for 3 min at −78 °C, a 1 M solution of the Lewis acid in dichloromethane (0.30 mmol) was added dropwise. The solution was stirred at −78 °C until completion of the reaction, quenched by the addition of saturated aqueous sodium bicarbonate solution (1–5 mL) and extracted with ethyl acetate (3 × 10 mL). After drying ($MgSO_4$), the organic layer was concentrated in vacuo and the residue was purified by chromatography to give **16c–19c**, **16d–19d**, **16e–19e**, **16f–19f** and **16g–19g**, respectively.

Reaction of 7 and 1c: A mixture of **7** (26.9 mg, 0.10 mmol) and **1c** (28 mL, 0.30 mmol) in dry dichloromethane (2 mL) was treated according to general procedure V with a 1 M solution of Me_2AlCl in dichloromethane (0.15 mL, 0.15 mmol) at −78 °C to afford after chromatography (8 g SiO_2, ethyl acetate/petroleum ether, 1:2) **16c–19c**.

(2*R*,4*R*,4'*S*)- and (2*S*,4*S*,4'*S*)-2,4-Diethoxy-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (16c and **17c**, *endo*-I and *endo*-II isomer): R_f = 0.43; IR (film): $\tilde{\nu}$ = 2972, 2940, 2876 (CH), 1786 (C=O, urethane), 1702 (C=O, amide), 1656 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 254.5 nm (3.651); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 and 0.95 (s, 9H, *t*Bu, *endo*-I and *endo*-II isomer), 1.16–1.24 (4 × t, J = 7.0 Hz, 12H, 4 × CH_3), 1.95 (dt, J = 13.0, 10.0 Hz, 1H, 3-H_{ax}, *endo*-I isomer), 1.99 (dt, J = 13.0, 9.5 Hz, 1H, 3-H_{ax}, *endo*-II isomer), 2.27 (ddt, J = 13.0, 6.8, 1.5 Hz, 1H, 3-H_{eq}, *endo*-II isomer), 2.31 (ddt, J = 13.0, 7.0, 1.5 Hz, 1H, 3-H_{eq}, *endo*-I isomer), 3.48–3.66 (6 × dq, J = 9.0, 7.0 Hz, 6H, 6 × OCH), 3.83–3.91 (2 × dq, J = 9.0, 7.0 Hz, 2H, 2 × OCH), 4.26–4.31 (m, 4H, 2 × 5'-H_2), 4.32–4.37 (m, 2H, 2 × 4-H), 4.47 (dd, J = 7.0, 3.5 Hz, 1H, 4'-H, *endo*-I isomer), 5.07 (dd, J = 8.5, 2.0 Hz, 1H, *exo*-I isomer), 5.09 (dd, J = 9.5, 2.0 Hz, 1H, 2-H, *endo*-II isomer), 5.18 (dd, J = 10.0, 1.5 Hz, 1H, 2-H, *endo*-I isomer), 5.57 (dd, J = 2.5, 1.5, 1H, 5-H, *endo*-II isomer), 5.63 (dd, J = 2.5, 1.5 Hz, 1H, 5-H, *endo*-I isomer), 5.66 (dd, J = 4.5, 1.0 Hz, 1H, 5-H, *exo*-I isomer); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 15.12, 15.45 (2 × CH_3), 25.23, 25.71 (2 × *t*Bu-CH_3), 34.08, (C-3, *endo*-II isomer), 34.52 (C-3, *endo*-I isomer), 35.87, 35.97 (2 × *t*Bu-*C*), 60.54, 62.37 (2 × C-4'), 62.37, 63.53, 63.63, 65.10 (4 × OCH_2, 2 × C-5'), 69.78 (C-4, *endo*-II isomer), 70.10 (C-4, *endo*-I isomer), 98.81 (C-2, *exo*-I isomer), 100.6 (C-2, *endo*-II isomer), 101.4 (C-2, *endo*-I isomer), 106.9 (C-5, *exo*-I isomer), 108.9 (C-5, *endo*-II isomer), 109.7 (C-5, *endo*-I isomer), 145.6, 146.4 (2 × C-6), 153.3, 153.8 (2 × C-2'), 163.9, 165.1 (2 × C-7); MS (70 eV, EI): m/z (%): 341 (1) [M^+], 99 (100) [RDA, EtOCH=CHCO], 71 (18) [RDA, EtOCH=CH]; $C_{17}H_{27}NO_6$ (341.4): calcd C 59.81, H 7.91, found C 60.07, H 7.96.

Reaction of 7 and 1d: A solution of **7** (53.8 mg, 0.20 mmol) and **1d** (66 ml, 0.60 mmol) in dry dichloromethane was treated according to general procedure V with a 1 M solution of the Lewis acid in dichloromethane (0.30 mL, 0.30 mmol). The crude mixture was chromatographed on 10 g SiO_2 (ethyl acetate/petroleum ether, 2:9) to give **16d–19d**.

Reaction of 7 and 1d promoted by Me_2AlCl: Chromatography on 10 g SiO_2 (ethyl acetate/petroleum ether, 2:9) provided an overall yield of 81% of **16d–19d**.

Fraction I: 8.5 mg (12%) of **17d** and **18d**.
(2*S*,3*R*,4*S*,4'*S*)- and (2*S*,3*R*,4*R*,4'*S*)-2,4-Diethoxy-3-methyl-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (17d and **18d**, *endo*-II and *exo*-I isomer): R_f = 0.23; IR (film): $\tilde{\nu}$ = 2974, 2936, 2878 (CH), 1794 (C=O, urethane), 1702 (C=O, amide), 1658 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 195.5 nm (3.793), 249.5 nm (3.540); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.62 (s, 9H, *t*Bu), 1.02, 1.14 (2 × t, J = 7.0 Hz, 6H, 2 × CH_3), 1.34 (d, J = 7.0 Hz, 3H, 3-CH_3), 2.20 (m, 1H, 3-H), 3.06–3.18 (m, 2H, 2 × OCH), 3.24 (dd, J = 9.0, 7.5 Hz, 1H, 5'-H, *endo*-II isomer), 3.34 (dq, J = 9.5, 7.0 Hz, 1H, OCH, *exo*-I isomer), 3.42 (dd, J = 9.0, 2.0 Hz, 1H, 5'-H, *exo*-I isomer), 3.43 (dd, J = 9.0, 1.5 Hz, 1H, 5'-H, *endo*-II isomer), 3.52 (dq, J = 9.5, 7.0 Hz, 1H, OCH, *exo*-I isomer), 3.60 (dq, J = 10.0, 7.0 Hz, 1H, OCH, *endo*-II isomer), 3.78 (dd, J = 7.5, 1.5 Hz, 1H, 4'-H, *endo*-II isomer), 3.88 (dd, J = 5.0, 4.0 Hz, 1H, 4-H, *exo*-I isomer), 3.93 (dd, J = 8.0, 2.0 Hz, 1H, 4'-H, *exo*-I isomer), 4.04 (dq J = 10.0, 7.0 Hz, 1H, OCH, *endo*-II isomer), 4.08 (dd, J = 6.5, 2.5 Hz, 1H, 4-H, *endo*-II isomer), 5.06 (d, J = 6.5 Hz, 1H, 2-H, *exo*-I isomer), 5.08 (d, J = 1.8 Hz, 1H, 2-H, *endo*-II isomer), 5.70 (dd, J = 2.5, 1.5 Hz, 1H, 5-H, *endo*-II isomer), 5.88 (d, J = 4.0 Hz, 1H, 5-H, *exo*-I isomer); ^{13}C NMR (75 MHz, C_6D_6): δ = 6.334 (3-CH_3), 15.31, 15.49 (CH_3), 25.56 (*t*Bu-CH_3), 35.42 (C-3), 35.59 (*t*Bu-*C*), 61.44 (C-4', *exo*-I isomer), 62.42 (C-4', *endo*-II isomer), 64.01 (OCH_2), 65.27, 65.44 (OCH_2, C-5'), 71.08 (C-4, *exo*-I isomer), 73.62 (C-4, *endo*-II isomer), 103.4 (C-2), 107.4 (C-5, *exo*-I isomer), 108.5 (C-5, *endo*-II isomer), 145.7 (C-6, *endo*-II isomer), 146.2 (C-6, *exo*-I isomer), 153.8 (C-2'), 164.1 (C-7, *endo*-II isomer), 164.9 (C-7, *exo*-I isomer); MS (70 eV, EI): m/z (%): 355 (2) [M^+], 270 (38) [RDA, diene +1], 86 (100) [enol ether]; $C_{18}H_{29}NO_6$: calcd 355.1994, found 355.1994 (MS).

Fraction II: 47.6 mg (67%) of **16d**.
(2*R*,3*S*,4*R*,4'*S*)-2,4-Diethoxy-3-methyl-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (16d, *endo*-I isomer): R_f = 0.18; $[\alpha]_D^{20}$ = +19.6 (c = 0.5 in chloroform); IR (film): $\tilde{\nu}$ = 2974, 2942, 2876 (CH), 1786 (C=O, urethane), 1704 (C=O, amide), 1652 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 259.0 nm (3.652); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.62 (s, 9H, *t*Bu), 1.04, 1.14 (2 × t, J = 7.0 Hz, 6H, 2 × CH_3), 1.31 (d, J = 7.0 Hz, 3H, 3-CH_3), 2.25 (m, 1H, 3-H), 3.12–3.22 (m, 3H, 2 × OCH, 5'-H), 3.46 (dd, J = 9.0, 2.0 Hz, 1H, 5'-H), 3.71 (dq, J = 10.0, 7.0 Hz, 1H, OCH), 4.02–4.07 (m, 2H, OCH, 4'-H), 4.08 (dd, J = 6.0, 2.5 Hz, 1H, 4-H), 5.32 (d, J = 1.5 Hz, 1H, 2-H), 5.84 (dd, J = 2.5, 1.0 Hz, 1H, 5-H); ^{13}C NMR (75 MHz, C_6D_6): δ = 6.260 (3-CH_3), 15.38, 15.53 (CH_3), 25.11 (*t*Bu-CH_3), 35.41 (C-3), 35.81 (*t*Bu-*C*), 60.47 (C-4'), 64.05 (OCH_2), 64.63 (C-5'), 65.41 (OCH_2), 73.86 (C-4), 103.9 (C-2), 109.6 (C-5), 146.2 (C-6), 153.3 (C-2'), 165.1 (C-7); MS (70 eV, EI): m/z (%): 355 (3) [M^+], 270 (28) [RDA, diene +1], 86 (100) [enol ether]; $C_{18}H_{29}NO_6$ (355.43): calcd C 60.83, H 8.22, found C 61.15, H 8.35.

Reaction of 7 and 1d promoted by $SnCl_4$: Chromatography on 10 g SiO_2 (ethyl acetate/petroleum ether, 2:9) provided an overall yield of 85% of **16–19d**.

Fraction I: 50.0 mg (70%) of **18d** and **19d**.
(2*S*,3*R*,4*R*,4'*S*)- and (2*R*,3*S*,4*S*,4'*S*)-2,4-Diethoxy-3-methyl-6-(carbonyl-4'-*tert*-butyloxazolidin-2'-one)-3,4-dihydro-2*H*-pyran (18d and **19d**, *exo*-I and *exo*-II isomer): R_f = 0.26; IR (film): $\tilde{\nu}$ = 2972, 2934, 2878 (CH), 1790 (C=O, urethane), 1702 (C=O, amide), 1656 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 241.0 nm (3.582), 245.0 nm (3582); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.62 (s, 9H, *t*Bu), 1.00, 1.15

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(2 × t, J = 7.0 Hz, 6H, 2 × CH_3), 1.18 (d, J = 7.0 Hz, 3H, 3-CH_3), 2.16 (m, 1H, 3-H), 3.10 (dq, J = 8.5, 6.5 Hz, 1H, OCH), 3.21 (dd, J = 8.5, 7.5 Hz, 1H, 5′-H), 3.34 (dq, J = 8.5, 6.5 Hz, 1H, OCH), 3.44 (dd, J = 8.5, 2.0 Hz, 1H, 5′-H), 3.51 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.88 (dd, J = 5.0, 4.0 Hz, 1H, 4-H), 3.93 (dd, J = 7.5, 2.0 Hz, 1H, 4′-H), 4.09 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 5.05 (d, J = 6.5 Hz, 1H, 2-H, *exo*-I isomer), 5.20 (d, J = 7.5 Hz, 1H, 2-H, *exo*-II isomer), 5.87 (d, J = 4.0 Hz, 1H, 5-H, *exo*-I isomer), 5.97 (d, J = 4.0 Hz, 1H, 5-H, *exo*-II isomer); ^{13}C NMR (50 MHz, C_6D_6): δ = 10.69 (3-CH_3), 15.30, 15.59 (CH_3), 25.38 (*t*Bu-CH_3), 35.71 (*t*Bu-*C*), 36.14 (C-3), 61.46 (C-4′), 64.11, 64.86, 65.06 (2 × OCH_2, C-5′), 71.08 (C-4, *exo*-I isomer), 74.58 (C-4, *exo*-II isomer), 103.1 (C-2, *exo*-II isomer), 103.2 (C-2, *exo*-II isomer), 106.8 (C-5, *exo*-II isomer), 107.4 (C-5, *exo*-I isomer), 146.2 (C-6), 153.2 (C-2′), 164.9 (C-7); MS (70 eV, EI): *m/z* (%): 355 (2) [M^+], 270 (75) [RDA, diene +1], 86 (100) [enol ether]; $C_{18}H_{29}NO_6$ (355.4): calcd C 60.83, H 8.22, found C 61.15, H 8.35.

Fraction II: 7.80 mg (11%) of **16d** and the C-2-epimerized **16d**.

(2*S*,3*S*,4*R*,4′*S*)- and (2*R*,3*S*,4*R*,4′*S*)-2,4-Diethoxy-3-methyl-6-(carbonyl-4′-*tert*-butyloxazolidin-2′-one)-3,4-dihydro-2*H*-pyran (16d epimerized and **16d**, *endo*-I epimerized (ep) and *endo*-I isomer): R_f = 0.20; IR (film): $\tilde{\nu}$ = 2972, 2934, 2878 (CH), 1790 (C=O, urethane), 1702 (C=O, amide), 1656 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 241.0 nm (3.582), 245.0 nm (3582); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.63 and 0.64 (2 × s, 18H, 2 × *t*Bu), 1.02, 1.15 (2 × t, J = 7.0 Hz, 6H, 2 × CH_3, *endo*-I isomer), 1.05, 1.08 (2 × t, J = 7.0 Hz, 6H, 2 × CH_3, *endo*-I-ep isomer), 1.06 (d, J = 7.0 Hz, 3H, 3-CH_3), 2.25 (m, 1H, 3-H, *endo*-I isomer), 2.30 (m, 1H, 3-H, *endo*-I-ep isomer), 3.18 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.19 (dd, J = 9.0, 8.5 Hz, 1H, 5′-H), 3.34 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.45 (dd, J = 9.0, 2.2 Hz, 1H, 5′-H, *endo*-I-ep isomer), 3.47 (dd, J = 9.0, 2.2 Hz, 1H, 5′-H, *endo*-I isomer), 3.55 (dd, J = 4.1, 3.2 Hz, 1H, 4-H, *endo*-I-ep isomer), 3.63 (dq, J = 10.0, 7.0 Hz, 1H, OCH, *endo*-I-ep isomer), 3.71 (dq, J = 10.0, 7.0 Hz, 1H, OCH, *endo*-I isomer), 4.03 (dq, J = 10.0, 7.0 Hz, 1H, OCH, *endo*-I-ep isomer), 4.07 (dd, J = 2.5, 1.5 Hz, 1H, 4-H, *endo*-I isomer), 4.10 (dd, J = 8.5, 2.2 Hz, 1H, 4′-H), 5.32 (d, J = 1.5 Hz, 1H, 2-H, *endo*-I isomer), 5.42 (d, J = 2.0 Hz, 1H, 2-H, *endo*-I isomer), 5,84 (dd, J = 2.5, 1.5 Hz, 1H, 5-H, *endo*-I isomer), 5,93 (dd, J = 4.0, 1.0 Hz, 1H, 5-H, *endo*-I-ep isomer); ^{13}C NMR (125 MHz, C_6D_6): δ = 6.250 (3-CH_3, *endo*-I isomer), 10.69 (3-CH_3, *endo*-I-ep isomer), 15.34, 15.37, 15.52, 15.74 (4 × CH_3), 25.14 (*t*Bu-CH_3), 35.37 (C-3, *endo*-I isomer), 35.81 (*t*Bu-*C*), 37.59 (C-3, *endo*-I-ep isomer), 61.45 (C-4′), 63.56, 64.03, 64.49, 64.60, 65.41 (4 × OCH_2, 2 × C-5′), 73.85 (C-4, *endo*-I isomer), 75.20 (C-4, *endo*-I-ep isomer), 101.7 (C-2, *endo*-I-ep isomer), 103.9 (C-2, *endo*-I isomer), 107.4 (C-5, *endo*-I-ep isomer), 109.6 (C-5, *endo*-I isomer), 147.4 (C-6), 152.9 (C-2′), 165.5 (C-7); MS (70 eV, EI): *m/z* (%): 270 (38) [RDA, diene +1], 99 (42) [RDA, EtOCH=CHCO], 86 (100) [enol ether]; $C_{18}H_{29}NO_6$: calcd 355.1994, found 355.1994 (MS).

Reaction of 7 and 1e: According to general procedure V, a mixture of **7** (53.8 mg, 0.20 mmol) and **1e** (60.0 mg, 0.60 mmol) in dry dichloromethane (2 mL) was treated at −78 °C with a 1 M solution of Me_2AlCl in dichloromethane (0.30 mL, 0.30 mmol) to give after chromatography (10 g SiO_2, ethyl acetate/petroleum ether, 2:9) an overall yield of 79% of **16e–19e**.

Fraction I: 5.9 mg (8.0%) of **18e** and **19e**.

(2*S*,3*R*,4*R*,4′*S*)- and (2*R*,3*S*,4*S*,4′*S*)-2,4-Diethoxy-3-ethyl-6-(carbonyl-4′-*tert*-butyloxazolidin-2′-one)-3,4-dihydro-2*H*-pyran (18e and **19e**, *exo*-I and *exo*-II isomer): R_f = 0.27; IR (film): $\tilde{\nu}$ = 2970, 2932, 2876 (CH), 1786 (C=O, urethane), 1702 (C=O, amide), 1656 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 194.0 nm (3.826); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.66 (s, 9H, *t*Bu), 0.92, 1.03, 1.12 (3 × t, J = 7.0 Hz, 9H, 3 × CH_3), 1.75–2.02 (m, 3H, 3-CH_2), 3.10 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.23 (dd, J = 9.0, 8.0 Hz, 1H, 5′-H), 3.44 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.45 (dd, J = 9.0, 2.0 Hz, 1H, 5′-H), 3.55 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.83 (t, J = 4.5 Hz, 1H, 4-H, *exo*-II isomer), 3.90 (t, J = 4.5 Hz, 1H, 4-H, *exo*-I isomer), 3.94 (dd, J = 8.0, 2.0 Hz, 1H, 4′-H), 4.07 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 5.23 (d, J = 7.5 Hz, 1H, 2-H, *exo*-I isomer), 5.35 (d, J = 7.5 Hz, 1H, 2-H, *exo*-II isomer), 5.90 (d, J = 4.5 Hz, 1H, 5-H, *exo*-I isomer), 6.00 (d, J = 4.5 Hz, 1H, 5-H, *exo*-II isomer); ^{13}C NMR (75 MHz, C_6D_6): δ = 11.81, 15.34, 15.64 (3 × CH_3), 17.90 (3-CH_2, *exo*-I isomer), 18.00 (3-CH_2, *exo*-II isomer), 25.17 (*t*Bu-CH_3, *exo*-I isomer), 25.46 (*t*Bu-CH_3, *exo*-II isomer), 30.21 (*t*Bu-*C*, *exo*-II isomer), 35.73 (*t*Bu-*C*, *exo*-I isomer), 43.50 (C-3, *exo*-I isomer), 44.48 (C-3, *exo*-II isomer), 60.55 (C-4′, *exo*-I isomer), 61.72 (C-4′, *exo*-II isomer), 63.91, 64.93, 65.24 (2 × OCH_2, C-5′), 69.09 (C-4, *exo*-I isomer), 69.33 (C-4, *exo*-II isomer), 102.3 (C-2), 106.8 (C-5, *exo*-I isomer), 108.2 (C-5, *exo*-II isomer), 147.1 (C-6), 153.3 (C-2′), 164.9 (C-7); MS (70 eV, EI): *m/z* (%): 369 (1) [M^+], 270 (78) [RDA, diene +1], 100 (100) [enol ether], 99 (45) [RDA, EtOCH=CHCO]; $C_{19}H_{31}NO_6$: calcd 369.2151, found 369.2151 (MS).

Fraction II: 51.2 mg (70%) of **16e** and **17e**.

(2*R*,3*S*,4*R*,4′*S*)- and (2*S*,3*R*,4*S*,4′*S*)-2,4-Diethoxy-3-ethyl-6-(carbonyl-4′-*tert*-butyloxazolidin-2′-one)-3,4-dihydro-2*H*-pyran (16e and **17e**, *endo*-I and *endo*-II isomer): R_f = 0.21; IR (film): $\tilde{\nu}$ = 2972, 2938, 2876 (CH), 1788 (C=O, urethane), 1704 (C=O, amide), 1654 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 254.0 nm (3.6.29); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.66 (s, 9H, *t*Bu), 1.04, 1.11, 1.12 (3 × t, J = 7.0 Hz, 9H, 3 × CH_3), 1.80–2.05 (m, 3H, 3-CH_2), 3.10–3.30 (m, 3H, 2 × OCH, 5′-H), 3.49 (dd, J = 9.0, 2.5 Hz, 1H, 5′-H), 3.60 (dq, J = 10.0, 7.0 Hz, 1H, OCH), 3.94 (dq, J = 10.0, 7.0 Hz, 1H, OCH), 4.00 (dd, J = 6.0, 3.0 Hz, 1H, 4-H), 4.11 (dd, J = 8.5, 2.5 Hz, 1H, 4′-H), 5.06 (d, J = 1.5 Hz, 1H, 2-H, *endo*-II isomer), 5.25 (d, J = 1.5 Hz, 1H, 2-H, *endo*-I isomer), 5.84 (d, J = 3.5 Hz, 1H, 5-H, *endo*-II isomer), 5.90 (dd, J = 3.0, 1.0 Hz, 1H, 5-H, *endo*-I isomer); ^{13}C NMR (125 MHz, C_6D_6): δ = 13.45, 15.24, 15.68 (3 × CH_3, *endo*-II isomer), 14.04, 15.33, 15.59 (3 × CH_3, *endo*-I isomer), 16.58 (3-CH_2, *endo*-I isomer), 17.34 (3-CH_2, *endo*-II isomer), 25.12 (*t*Bu-CH_3, *endo*-I isomer), 25.49 (*t*Bu-CH_3, *endo*-II isomer), 35.66 (*t*Bu-*C*, *endo*-II isomer), 35.81 (*t*Bu-*C*, *endo*-I isomer), 42.46 (C-3, *endo*-I isomer), 42.89 (C-3, *endo*-II isomer), 60.44 (C-4′, *endo*-I isomer), 61.84 (C-4′, *endo*-II isomer), 64.36, 64.60, 65.32 (2 × OCH_2, C-5′), 71.33 (C-4, *endo*-II isomer), 72.69 (C-4, *endo*-I isomer), 102.3 (C-2, *endo*-II isomer), 103.5 (C-2, *endo*-I isomer), 108.7 (C-5, *endo*-II isomer), 109.2 (C-5, *endo*-I isomer), 146.3 (C-6), 153.3 (C-2′), 165.4 (C-7); MS (70 eV, EI): *m/z* (%): 369 (1) [M^+], 270 (32) [RDA, diene +1], 100 (100) [enol ether], 99 (57) [RDA, EtOCH=CHCO]; $C_{19}H_{31}NO_6$: calcd 369.2151, found C 369.2151 (MS).

Reaction of 7 and 1f: A solution of **7** (53.8 mg, 0.20 mmol) and **1f** (45 mL, 0.60 mmol) in dry dichloromethane was treated according to general procedure V with a 1 M solution of the Lewis acid in dichloromethane (0.30 mL, 0.30 mmol). The crude mixture was chromatographed on 10 g SiO_2 (ethyl acetate/petroleum ether, 2:5) to give an overall yield of 85% of **16f** and **17f**.

(1a*R*,4a*S*,5*S*,4′*S*)- and (1a*S*,4a*R*,5*R*,4′*S*)-4′-*tert*-Butyl-7-(carbonyloxazolidin-2′-one)-5-ethoxy-tetrahydrofurano[2,3-b]3,4-dihydro-2*H*-pyran (16f and **17f**, *endo*-I and *endo*-II isomer): R_f = 0.24; IR (film): $\tilde{\nu}$ = 2970, 2904 (CH), 1788 (C=O, urethane), 1704 (C=O, amide), 1679 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 204.5 nm (3.672); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.60, 0.62 (2 × s, 18H, 2 × *t*Bu), 1.03, 1.04 (2 × t, J = 7.0 Hz, 6H, 2 × CH_3), 1.66–1.75 (m, 4H, 2 × 4-H), 2.12–2.20 (m, 3H, 4-H (*endo*-I isomer), 2 × 4-Ha), 2.40–2.49 (m, 1H, 4-H, *endo*-II isomer), 3.06–3.17 (4 × dq, J = 9.0, 7.0 Hz, 4H, 4 × OCH), 3.18–3.22 (m, 2H, 2 × 5′-H), 3.42 (dd, J = 9.5, 2.0 Hz, 1H, 5′-H, *endo*-II isomer), 3.44 (dd, J = 9.5, 2.0 Hz, 1H, 5′-H, *endo*-I isomer), 3.59–3.65 (m, 1H, 3-H, *endo*-I isomer), 3.65–3.72 (m, 1H, 3-H, *endo*-II isomer), 3.92 (dd, J = 8.0, 2.0 Hz, 1H, 4′-H, *endo*-II isomer), 4.02 (dd, J = 8.0, 2.0 Hz, 1H, 4′-H, *endo*-I isomer), 4.08 (2 × dd, J = 6.5, 2.5 Hz, 2H, 2 × 5-H), 4.09–4.12 (m, 1H, 3-H, *endo*-I isomer), 4.32–4.37 (m, 1H, 3-H, *endo*-II isomer), 5.59 (d, J = 3.3 Hz, 1H, 1-Ha, *endo*-II isomer), 5.64 (dd, J = 2.5, 1.0 Hz, 1H, 6-H, *endo*-II isomer), 5.67 (dd, J = 2.5, 1.0 Hz, 1H, 6-H, *endo*-I isomer), 5.87 (d, J = 3.3 Hz, 1H, 1-Ha, *endo*-I isomer); ^{13}C NMR (75 MHz, C_6D_6): δ = 15.59 (CH_3), 23.88 (C-4, *endo*-II isomer), 24.06 (C-4, *endo*-I isomer), 25.26 (*t*Bu-CH_3, *endo*-I isomer), 25.38 (*t*Bu-CH_3, *endo*-II isomer), 35.76 (*t*Bu-*C*), 43.14 (C-4a, *endo*-II isomer), 43.39 (C-4a, *endo*-I isomer), 60.77 (C-4′, *endo*-I isomer), 61.32 (C-4′ isomer, *endo*-II isomer), 63.96, 64.08, 64.77, 64.88, 68.52, 68.81 (2 × C-5′, 2 × OCH_2, 2 × C-3), 70.98 (C-5, *endo*-I isomer), 71.06 (C-5, *endo*-II isomer), 102.9 (C-1a, *endo*-II isomer), 103.7 (C-1a, *endo*-I isomer), 104.6 (C-6, *endo*-II isomer), 105.3 (C-6, *endo*-I isomer), 145.9 (C-7, *endo*-II isomer), 146.2 (C-7, *endo*-I isomer), 153.2 (C-2′), 164.9 (C-8); MS (70 eV, EI): *m/z* (%): 270 (80) [RDA, diene +1], 99 (100) [RDA, EtOCH=CHCO], 70 (23) [RDA, enol ether]; $C_{15}H_{25}NO_6$ (315.4): calcd C 57.13, H 7.99, found C 57.01, H 7.80.

Reaction of 7 and 1g: A mixture of **7** (53.8 mg, 0.20 mmol) and **1g** (0.10 ml, 1.10 mmol) in dry dichloromethane (2 mL) was treated at −78 °C according to general procedure V with a 1 M solution of Me_2AlCl in dichloromethane (0.30 mL, 0.30 mmol) to give after chromatography (10 g SiO_2, ethyl acetate/petroleum ether, 1:2) an overall yield of 84% of **16g** and **17g**.

(1a*R*,5a*S*,6*S*,4′*S*)- and (1a*S*,5a*R*,6*R*,4′*S*)-4′-*tert*-Butyl-7-(carbonyloxazolidin-2′-one)-5-ethoxytetrahydropyrano[2,3-b]3,4-dihydro-2*H*-pyran (16g and **17g**, *endo*-I and *endo*-II): R_f = 0.47; IR (film): $\tilde{\nu}$ = 2970, 2936, 2872 (CH), 1788 (C=O, urethane), 1704 (C=O, amide), 1658 (C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 203.5 nm (3.671), 257.5 nm (3.539); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.64 (s, 9H, *t*Bu), 1.03 (t, J = 7.0 Hz, 3H, CH_3), 1.20–2.00 (m, 5H, 4-H_2, 5-H_2, 5-Ha), 3.08, 3.09 (2 × q, J = 7.0 Hz, 4H, 2 × OCH_2), 3.24 (dd, J = 9.0, 8.0 Hz, 1H, 5′-H), 3.46, 3.48 (2 × dd, J = 9.0, 2.0 Hz, 2H, 2 × 5′-H), 3.56–3.64 (m, 1H, 3-H), 3.97 (dd, J = 6.0, 2.0 Hz, 1H, 6-H), 3.98–4.08 (m, 1H, 3-H), 4.02 (dd, J = 8.0, 2.0 Hz, 1H, 4′-H), 5.63–5.69 (m, 2H, 1a-H, 7-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.52 (CH_3), 17.57, 18.03 (2 × C-4), 24.79, 24.94 (2 × C-5), 25.30 (*t*Bu-CH_3), 35.81 (*t*Bu-*C*), 36.58, 36.86 (2 × C-5a) 60.87, 61.08 (2 × C-4′), 61.82, 62.01, 63.98, 64.77 (2 × C-5′, 2 × OCH_2, 2 × C-3), 72.97, 73.17 (2 × C-6), 98.31, 98.75 (2 × C-1a), 107.0, 107.2 (2 × C-7), 146.2 (C-8), 153.2 (C-2′), 164.7, 164,9 (C-9); MS (70 eV, EI): *m/z* (%): 353 (1) [M^+], 270 (72) [RDA, diene +1], 99 (100) [RDA, EtOCH=CHCO], 84 (73) [RDA, enol ether]; $C_{18}H_{27}NO_6$: calcd 353.1838, found 353.1838 (MS).

(1*R*,2*S*,3*S*,5*S*,4′*S*)-2-*O*-Acetyl-4,5-didesoxy-2,4-*O*-diethyl-5-(carbonyl-4′-*tert*-butyloxazolidin-2′-one)-β-D-mannopyranoside (24): A stirred suspension of **16a** (200 mg, 0.5 mmol) and 10% palladium on carbon (50.0 mg) in ethanol (5 mL) was hydrogenated at 1 atm H_2 for 15 h. The catalyst was filtered off and the filtrate concentrated in vacuo. The residue was purified by column chromatography (20 g SiO_2, ethyl acetate/petroleum ether, 1:2) to yield **24** (182 mg, 91%). R_f = 0.15; $[\alpha]_D^{20}$ = −32.0 (*c* = 0.54 in chloroform); IR (KBr): $\tilde{\nu}$ = 2972, 2876 (CH), 1782 (C=O, urethane), 1740 (C=O, OAc), 1724 (C=O, amide) cm^{-1}; UV (acetonitrile): λ_{max} (lgε) = 205.5 nm (3.859); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.64 (s, 9H, *t*Bu), 1.14 (t, J = 7.0 Hz, 3H, CH_3), 1.16 (t, J = 7.0 Hz, 3H, CH_3), 1.76 (s, 3H, OAc), 1.95

(dddd, J = 12.5, 4.8, 2.0, 1.0 Hz, 1H, 4-H_{eq}), 2.49 (q, J = 12.5 Hz, 1H, 4-H_{ax}), 3.14 (ddd, J = 12.0, 4.8, 3.0 Hz, 1H, 3-H), 3.22 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 3.26 (dd, J = 9.0, 8.0 Hz, 1H, 5'-H), 3.48 (dd, J = 9.0, 1.5 Hz, 1H, 5'-H), 3.69 (dq, J = 8.5, 7.0 Hz, 1H, OCH), 4.01 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 4.03 (dd, J = 8.0, 1.5 Hz, 1H, 4'-H), 4.44 (d, J = 1.5 Hz, 1H, 1-H), 4.79 (dd, J = 12.0, 2.0 Hz, 1H, 5-H), 5.62 (d, J = 3.0 Hz, 1H, 2-H); ^{13}C NMR (50 MHz, C_6D_6): δ = 15.37 (CH_3), 15.56 (CH_3), 20.73 (OAc), 25,29 (*t*Bu-CH_3), 28.91 (C-4), 35.85 (*t*Bu-*C*), 60.54 (C-4'), 64.16, 64.84, 65.37 (2 × OCH_2, C-5'), 67.34 (C-2), 70.41 (C-5), 75.17 (C-3), 100,5 (C-1), 153.3 (C-2'), 169.0 (C-6), 169.9 (OAc); MS (200 eV, DCI/NH_3): m/z (%): 419 (100) $[M + NH_4]^+$; $C_{19}H_{31}NO_8$ (401.2): calcd C 56.88, H 7.73, found C 56.94, H 7.77

(1*R*,2*S*,3*S*,5*S*)-2-*O*-Acetyl-4-desoxy-1,3-*O*-diethyl-β-D-mannopyranoside (25): To a solution of **24** (144 mg, 0.36 mmol) in dry tetrahydrofuran (4 mL) was added at −78 °C lithium aluminium hydride (27.2 mg, 0.72 mmol) and stirring was continued for 1 h. After careful addition of saturated aqueous sodium bicarbonate solution (1 mL), the salts were removed by filtration. The filtrate was concentrated in vacuo, and chromatography (6 g SiO_2, ethyl acetate/petroleum ether/ethanol, 10:20:1.5) of the residue afforded **25** (60.4 mg, 64%) as a colourless oil. R_f = 0.20; $[\alpha]_D^{20}$ = − 80.8 (c = 0.5 in chloroform); IR (film): $\tilde{\nu}$ = 2976, 2932, 2847 (CH), 1742 (C=O, OAc) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, J = 7.0 Hz, 3H, CH_3), 1.26 (t, J = 7.0 Hz, 3H, CH_3), 1.66–1.74 (m, 2H, 4-H_2), 2.10 (dd, J = 8.5, 4.5 Hz, 1H, OH), 2.19 (s, 3H, OAc), 3.42 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.54 (ddd, J = 11.0, 6.5, 3.0 Hz, 1H, 3-H), 3.58–3.66 (m, 2H, OCH, 5-H), 3.66–3.76 (m, 2H, 6-H_2), 3.95 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 4.50 (d, J = 1.0 Hz, 1H, 1-H), 5.48 (dd, J = 3.0, 1.0 Hz, 1H, 2-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.02 (CH_3), 15.21 (CH_3), 21.01 (OAc), 28.76 (C-4), 64.06 (C-6), 65.22 (OCH_2), 65.32 (OCH_2), 67.04 (C-2), 73.14 (C-5), 74.74 (C-3), 99.19 (C-1), 170.5 (OAc); MS (200 eV, DCI/NH_3): m/z = 280 $[M + NH_4]^+$; $C_{12}H_{22}O_6$ (262.1): calcd C 54.98, H 8.39, found C 55.18, H 8.53.

(1*R*,2*S*,3*S*,5*S*)-2-*O*-Acetyl-4-desoxy-1,3-diethyl-6-*O*-[(*R*)-α-methoxy-α-trifluoromethylphenylacetyl]-β-D-mannopyranoside (26): To a solution of (*S*)-(+)-α-methoxy-α-trifluoromethylphenylacetylchloride (110 mg, 0.43 mmol) in dry pyridine (0.93 mL) was added at 23 °C a solution of **25** in dichloromethane (2 mL). After stirring for 2 h, the reaction mixture was quenched with 3-dimethylamino-1-propylamine (70 μL, 0.62 mmol) and diluted with ether (10 mL). The organic layer was washed with 1 N HCl (1 × 10 mL) and saturated aqueous sodium bicarbonate solution (2 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by chromatography (10 g SiO_2, ethyl acetate/petroleum ether, 3:1) and cyrstallization to give **26** (107 mg, 72%) as white needles. R_f = 0.21; $[\alpha]_D^{20}$ = + 2.4 (c = 0.5 in chloroform); IR (KBr): $\tilde{\nu}$ = 3068 (aromatic CH), 2982, 2936, 2876 (CH), 1750 (C=O), 1628 (aromatic C=C) cm^{-1}; UV (acetonitrile): λ_{max} (lg ε) = 205 nm (3.924); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (t, J = 7.0 Hz, 3H, CH_3), 1.20 (t, J = 7.0 Hz, 3H, CH_3), 1.70–1.80 (m, 2H, 4-H_{ax}, 4-H_{eq}), 2.10 (s, 3H, OAc), 3.40 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.46–3.51 (m, 1H, 3-H), 3.52 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 3.57 (s, 3H, OMe), 3.68 (dq, J = 9.0, 7.0 Hz, 1H, OCH), 3.73–3.79 (m, 1H, 5-H), 3.84 (dq, J = 9.5, 7.0 Hz, 1H, OCH), 4.38 (dd, J = 11.5, 6.5 Hz, 1H, CHO), 4.44 (d, J = 1.0 Hz, 1H, 1-H). 4.49 (dd, J = 11.0, 5.0, 4.0 Hz, 1H, CHO), 5.45 (dd, J = 3.0, 1.0 Hz, 1H, 2-H), 7.40 (m, 3H, aromatic H), 7.57 (m, 2H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.99 (CH_3), 15.18 (CH_3), 20.96 (OAc), 29.10 (C-4), 55.44 (OMe), 64.15 (OCH_2), 65.17 (OCH_2), 66.72 (C-2), 67.47 (C-6), 69.81 (C-5), 74.57 (C-3), 99.03 (C-1), 121.3 (C-2'),125.1 (CF_3), 127.4, 128.4, 129.6, 132.1 (aromatic C), 166.3 (C-1'), 170.5 (OAc); MS (200 eV, DCI/NH_3): m/z (%): 496 (100) $[M + NH_4]^+$; $C_{22}H_{29}O_8F_3$ (478.2): calcd C 55.25, H 6.06, found C 55.33, H 6.02.

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