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# An Anomeric Effect Drives the Regiospecific Ring-Opening of 1,3-Oxazolidines under Acetylating Conditions

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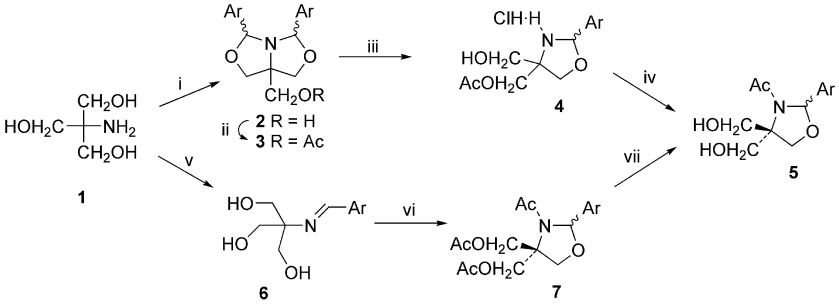
*Dedicated to Professor Vicente Ramos Estrada on the occasion of his retirement*

**Keywords:** Heterocycles / Acylation / Regioselectivity / Anomeric effect

A series of oxazolidines derived from tris(hydroxymethyl)-aminomethane (TRIS; **1**), have been prepared efficiently. Geometries optimized at the B3LYP/6-31G* level of theory, along with the crystal data of compounds **9** and **12** and NOESY correlations, point to a strong *endo* anomeric effect that anchors a preferential conformation and subsequently dictates the completely regioselective ring-opening of the oxazolidine moiety under acetylating conditions to afford imines instead of *N*-acetyloxazolidines. This process was monitored by $^1$H NMR spectroscopy, corroborated by synthesis, and rationalized by the intermediacy of an iminium ion. Oxazolidine–imine equilibria are also described for TRIS and other aminopolyols. The equilibria are shifted to the heterocyclic partner as the number of reactive hydroxy groups increases. The structures of an unprotected imine (**31**) and a per-*O*-acetylated derivative (**43**) have also been established by crystallographic analyses.

## Introduction

Recently, in the course of studies directed towards the preparation of chiral imines from amino sugars, we observed the unexpected formation of *N*-acetyl-1,3-oxazolidines upon acetylation.[1] This transformation most likely occurs via the transient formation of a chiral iminium ion.[2] This protocol, exemplified in Scheme 1 for the imine **6** (Ar = 2-HOC$_6$H$_4$) derived from a structurally simple aminopolyol, tris(hydroxymethyl)aminomethane (usually abbreviated as TRIS; **1**), and salicylaldehyde, points to an advantageous synthesis of unprotected *N*-acetyloxazolidines (**5**) with a significant atom economy relative to the previously described method (**1**→**2**→**3**→**4**→**5**)[3–5] that saves one mmol of aldehyde.




Scheme 1. Reagents and conditions: i) ArCHO (2 mol), $C_6H_6$, Δ; ii) $CH_3COCl$; iii) $H_2O$; iv) aqueous NaOH or $NaHCO_3$; v) ArCHO (1 mol); vi) $Ac_2O$, $C_5H_5N$; vii) $NH_3$, MeOH.

In this paper we report in detail both the formation and stereocontrolled ring-opening of 1,3-oxazolidines derived from TRIS. As we shall see later, it is possible to identify for such heterocycles a strong anomeric effect that dictates their subsequent and regioselective conversion into imines.

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The anomeric effect is a major stereoelectronic effect in organic chemistry. Although theories on the ultimate origin of this curious effect are invariably open, it has long been held that both anomeric and anti-anomeric effects are responsible for conformational preferences in some heterocycles and influence the stereochemical outcome of numerous organic reactions.[6,7]

## Results and Discussion

### Synthesis and Structural Assignment of TRIS-Based Oxazolidines

In the search for environmentally friendly conditions, reactions of TRIS with different monosubstituted benzaldehydes were attempted in water/methanol mixtures at room temperature. However, only aldehydes bearing electron-withdrawing groups led to products that were easily isolated. Thus, instead of the expected imines, racemic mixtures of oxazolidines **8**–**16** were obtained.

The structures attributed to the above-mentioned substances are supported by spectroscopic and analytical data. Moreover, suitable crystals for X-ray diffraction analysis could be grown for oxazolidines **9** and **12** (see Figures 1 and 2).[8] Selected bond lengths, bond angles, and dihedral angles for such derivatives are presented in Table 1. For comparative purposes, empirical data are presented along with theoretical figures obtained at the B3LYP/6-31G* level.[9,10]

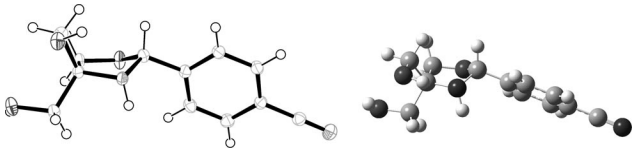


Figure 1. Experimental and calculated geometries for compound **9**.

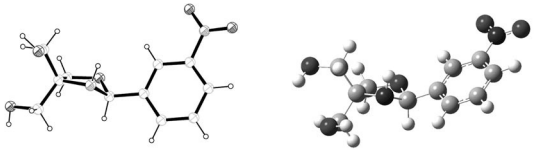


Figure 2. Experimental and calculated geometries for compound **12**.

The spectroscopic data for compounds **8**–**16** have a diagnostic value that rules out alternative isomeric structures. The FTIR spectra reveal stretching bands of the hydroxy groups in the range of 3600–3000 $cm^{-1}$ and of the NH absorption at 3280–3250 $cm^{-1}$, whereas no characteristic bands arising from an imine double bond are observed above 1610 $cm^{-1}$. The NMR spectra show resonances typical of the oxazolidine ring, for example, 2-H (≈ 5.5 ppm) and C-2 (≈ 91 ppm; see Table S1 of the Supporting Information).

The most salient structural feature manifests itself through the coupling constant between the NH group and the 2-H proton (≈ 11 Hz). This value suggests a *trans* or antiperiplanar disposition between these hydrogen atoms, or, in other words, the hydrogen in NH adopts a pseudo-axial orientation in solution.[11a] As evidenced by crystal data, this disposition is also adopted in the solid state and the dihedral angle H–N–C–H has a value of around 160°. The oxazolidine ring exhibits a geometry consistent with either $^2E$ or $E_2$ conformations in which the benzene ring lies in an equatorial arrangement thereby avoiding its interaction with other substituents (see Figures 1 and 2).[11b]

Table 1. Selected bond lengths [Å], angles [°], and torsion angles [°] for compounds **8**, **9**, and **12**.

| | **9** | | **12** | | **8** |
|---|---|---|---|---|---|
| | X-ray | Calcd.[a] | X-ray | Calcd.[a] | Calcd.[a] |
| C4–C5 | 1.5490 | 1.5589 | 1.5570 | 1.5598 | 1.5591 |
| N–C2 | 1.4496 | 1.4677 | 1.4619 | 1.4671 | 1.4672 |
| N–C4 | 1.4779 | 1.4883 | 1.4885 | 1.4883 | 1.4885 |
| O1–C2 | 1.4488 | 1.4242 | 1.4298 | 1.4231 | 1.4240 |
| O1–C5 | 1.4382 | 1.4264 | 1.4394 | 1.4266 | 1.4266 |
| C2–O1–C5 | 106.10 | 105.028 | 103.48 | 105.104 | 105.037 |
| C2–N–C4 | 104.67 | 104.466 | 103.64 | 104.364 | 104.436 |
| N–C4–C5 | 104.30 | 104.096 | 103.27 | 104.089 | 104.101 |
| O1–C5–C4 | 106.04 | 105.461 | 106.04 | 105.474 | 105.469 |
| O1–C2–N | 105.94 | 106.375 | 105.34 | 106.405 | 106.423 |
| H–N–C2–H2 | 161.50 | 160.83 | 170.21 | 161.42 | 178.12 |

[a] Calculated at the B3LYP/6-31G* level of theory.

The relative disposition between the 2-H and NH protons is likewise supported by NOEs determined by NOESY correlations measured for compound **8** (Table S2 and Figure S1 in the Supporting Information).

### Anomeric Effect in TRIS-Based Oxazolidines

This particular geometry of the oxazolidine ring could have its origin in a strong *endo* anomeric effect.[6,7] Thus, on the basis of MO theory, the equatorial lone-pair of the nitrogen atom is placed in a favorable disposition to interact with the σ* orbital of the C2–O1 bond, thus causing an anomeric effect.[12,13] As a result of this interaction there is delocalization of the lone-pair and a partial electron transfer to the σ* orbital, which destabilizes the corresponding σ-bonding orbital, thereby weakening the C2–O1 bond and strengthening the C2–N bond. Overall, this translates into a shorter C2–N bond and a longer C2–O1 bond. Similar conclusions can be inferred from valence bond theory and resonance effects, the greater stability of the conformer with the NH in an axial disposition being accounted for by the hyperconjugation in the canonical form **18** (Figure 3), which is consistent with a higher bond order for C2–N and a lower one for C2–O1.

It is true that the equatorial lone-pair on the oxygen atom may also interact with the σ* orbital of the C2–N bond, thus causing an opposite anomeric effect. However, had this effect been present, it would be weaker due to the higher energy of the σ* orbital of the C2–N bond. That delocalization would be less intense than that of the nitrogen lone-pair; in other words, the nitrogen serves as donor and the oxygen as acceptor. This situation is reflected best

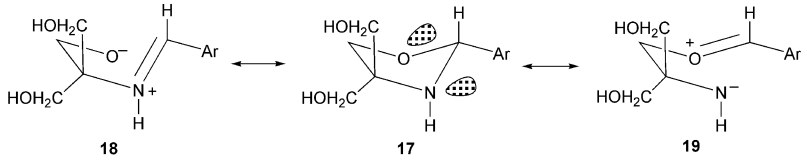



Figure 3. Anomeric effects in 1,3-oxazolidines.

by the delocalization shown in **18** and not in **19**.[13,14] Similar conclusions have been proposed for other 1,3-oxazolidines[15] and 1,3-oxazanes.[16,17]

In summary, the anomeric effect is expected to result in a longer C2–O1 bond and a shorter C2–N bond relative to the regular C5–O1 and C4–N bonds that are not affected by the anomeric effect.

A closer inspection of the X-ray data of **9** and **12** (Table 1) reveals further support for the anomeric effect. Thus, the N–C2 bonds are significantly shorter (≈ 0.03 Å) than the corresponding distances for N–C4, which is consistent with the delocalization of the lone-pair on the nitrogen ($\Delta d$ = 0.0283 Å for **9** and $\Delta d$ = 0.0266 Å for **12**). In contrast, the lengths of the C2–O1 bonds do not show any significant variation capable of supporting an anomeric effect by delocalization of the lone-pair on oxygen ($\Delta d$ = –0.0106 Å for **9** and $\Delta d$ = 0.0096 Å for **12**).

## Theoretical Calculations

DFT calculations at the B3LYP/6-31G* level of theory[9,10] were also performed to evaluate the gas-phase geometries of compounds **8**, **9**, and **12**. The results were compared with the crystal data (Table 1, Figures 1 and 2) and showed quite good agreement with the calculated distances reproducing the anomeric effect and showing shorter N–C2 bonds by about 0.02 Å ($\Delta d$ = 0.0206 Å for **9** and $\Delta d$ = 0.0212 Å for **8** and **12**), although these variations are slightly smaller than those measured experimentally.

The stabilization energies associated with n→σ* electronic delocalizations were subsequently obtained from a natural bond orbital (NBO) analysis based on the optimized ground-state geometries of compounds **8**, **9**, and **12**. Table 2 shows selected donor–acceptor natural bond orbital interactions and their second-order perturbational stabilization energies, $E_2$, calculated for the O1–C2–N fragment.

Table 2. Second-order perturbational energies from NBO analysis.

| Compound | Donor NBO | Acceptor NBO | $E_2$ [kcal mol$^{-1}$][a] |
|---|---|---|---|
| **8** | LPN | $\sigma^*_{C2-O1}$ | 8.35 |
| | LPO1 | $\sigma^*_{C2-N}$ | 1.60 |
| | LPO1 | $\sigma^*_{C2-N}$ | 5.82 |
| **9** | LPN | $\sigma^*_{C2-O1}$ | 8.32 |
| | LPO1 | $\sigma^*_{C2-N}$ | 1.60 |
| | LPO1 | $\sigma^*_{C2-N}$ | 5.82 |
| **12** | LPN | $\sigma^*_{C2-O1}$ | 8.34 |
| | LPO1 | $\sigma^*_{C2-N}$ | 1.62 |
| | LPO1 | $\sigma^*_{C2-N}$ | 5.84 |

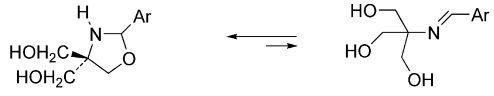
[a] Calculated at the B3LYP/6-31G* level of theory.

The interaction between the nitrogen lone-pair (LPN) as donor and $\sigma^*_{C2-O1}$ as acceptor (≈ 8.34 kcal mol$^{-1}$) is much stronger than that of the O1 lone-pair (LPO1) as donor and $\sigma^*_{C2-N}$ as acceptor (≈ 5.82 kcal mol$^{-1}$).

Remarkably, the structures calculated for **8**, **9**, and **12** invariably show the NH group in an axial disposition with a dihedral angle (H–N–C2–H2) of about 160–180°, which is similar to that determined experimentally (Table 1). We were unable to locate a conformational minimum for the NH group in an equatorial orientation.

## Oxazolidine–Imine Equilibria

When [D$_6$]DMSO solutions of compounds **8**–**16** were kept at room temperature, a partial isomerization could be detected (Scheme 2, Table 3, Figure S2) leading to a mixture in which the starting oxazolidines are largely favored (≈ 89–93%). Maiereanu et al.[15] have also reported an equilibrium for 4-dimethylaminobenzylidene derivatives of TRIS, although both tautomers are present in similar proportions (≈ 1:1). The spectroscopic data for such equilibria show the diagnostic resonances of the corresponding imines




**8** Ar = 4-$NO_2C_6H_4$
**9** Ar = 4-$NCC_6H_4$
**10** Ar = 4-$CF_3C_6H_4$
**11** Ar = 4-$MeO_2CC_6H_4$
**12** Ar = 3-$NO_2C_6H_4$
**13** Ar = 3-$NCC_6H_4$
**14** Ar = 3-$MeO_2CC_6H_4$
**15** Ar = 4-$CH_3$-3-$NO_2C_6H_3$
**16** Ar = 4-$NO_2$-2-$CH_3OC_6H_3$

**20** Ar = 4-$NO_2C_6H_4$
**21** Ar = 4-$NCC_6H_4$
**22** Ar = 4-$CF_3C_6H_4$
**23** Ar = 4-$MeO_2CC_6H_4$
**24** Ar = 3-$NO_2C_6H_4$
**25** Ar = 3-$NCC_6H_4$
**26** Ar = 3-$MeO_2CC_6H_4$
**27** Ar = 4-$CH_3$-3-$NO_2C_6H_3$
**28** Ar = 4-$NO_2$-2-$CH_3OC_6H_3$

Scheme 2.

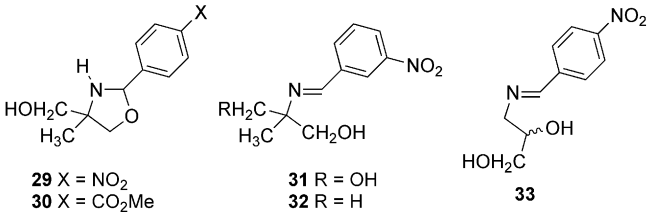
Table 3. Composition and NMR spectroscopic data for the imine group in the oxazolidine–imine equilibria.

| Equilibrium | Ratio [%] | $\delta$ (N=C*H*) [ppm] | $\delta$ (N=*C*H) [ppm] |
|---|---|---|---|
| **8⇄20** | 93:7 | 8.55 | 157.66 |
| **9⇄21** | 91:9 | 8.50 | 158.20 |
| **10⇄22** | 93:7 | 8.51 | 158.57 |
| **11⇄23** | 90:10 | 8.50 | 158.89 |
| **12⇄24** | 91:9 | 8.54 | 157.93 |
| **13⇄25** | 92:8 | 8.45 | 157.91 |
| **14⇄26** | 89:11 | 8.50 | 158.80 |
| **15⇄27** | 91:9 | 8.45 | 157.68 |
| **16⇄28** | 89:11 | 8.80 | 153.61 |
| **29⇄34** | 57:43 | 8.48 | 157.05 |
| **30⇄35** | 50:50 | 8.42 | 157.73 |
| **36⇄31** | 57:43 | 8.59 | 156.81 |
| **37⇄32** | 17:83 | 8.45 | 155.61 |

**20**–**28**: A singlet signal for the imine proton at around 8.50 ppm and a resonance for the unsaturated carbon at around 158 ppm.

Because we wondered whether the formation of an oxazolidine ring would only occur with TRIS, condensation reactions of 2-amino-2-methylpropane-1,3-diol with 4-nitrobenzaldehyde and methyl 4-formylbenzoate were also studied. In these cases, the corresponding oxazolidines **29** and **30** were isolated in good yields. However, the reaction of the aforementioned alcohol or 2-amino-2-methylpropan-1-ol with 3-nitrobenzaldehyde gave rise to imines **31** and **32** in excellent yields. In addition, the imine derivative **33** was obtained from 3-aminopropane-1,2-diol.




**29** X = $NO_2$
**30** X = $CO_2Me$

**31** R = OH
**32** R = H

**33**

The NMR spectroscopic data for compounds **29** and **30** show similar chemical shifts to those of **8**–**16** (doublet at 5.5 ppm and carbon resonances at ca. 91.5 and 91 ppm). However, both the $^1H$ and $^{13}C$ NMR spectra also show duplicated sets of signals. This points to diastereomeric mixtures in a nearly equal ratio as a result of the existence of two chiral centers (C-2 and C-4). Likewise, imines **31**–**33** exhibit IR absorptions at around 1640 $cm^{-1}$ along with NMR shifts at around 8.5 and 156 ppm, characteristic of the imino functional group. In addition, the unequivocal solid-state structure of **31** was elucidated by single-crystal X-ray analysis (Figure 4).[8]

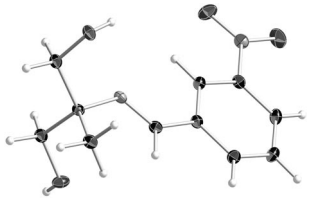
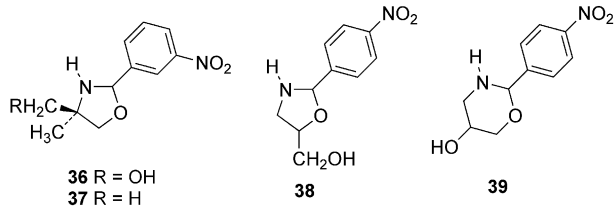


Figure 4. ORTEP diagram for compound **31**.

Oxazolidines **29** and **30** equilibrate in solution with the corresponding imines **34** and **35** (about 57% **29** and ca. 50% **30**), as oxazolidines **36** and **37** do with **31** and **32**, respectively (about 57% **36** and ca. 17% **37**; Table 3). In the particular case of compound **30**, we were able to isolate by fractional crystallization a pure diastereomer (**30b**) as a racemic mixture, which converted in DMSO solution into a mixture of **30a**, **30b**, and **35** in equilibrium (Scheme 3).




**36** R = OH
**37** R = H

**38**

**39**

The configuration (2*R*,4*R*) [or (2*S*,4*S*) for its enantiomer] attributed to **30a** was established on the basis of a NOE between the methyl hydrogens at C-4 and 2-H (Figure S3 in the Supporting Information) measured in the equilibrium mixture (**30a**/**30b**/**35**, 27:23:50).

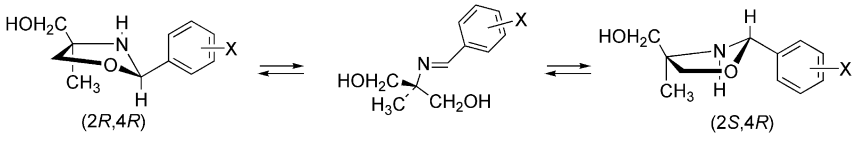
Compound **33** was reluctant to undergo cyclization, although after 2 weeks in solution four carbon signals appeared in the range 92–86 ppm. Such resonances can be attributed to two diastereomeric oxazolidines arising from cyclization of the secondary hydroxy (**38**, diastereomeric ratio 32:68) and to two oxazines resulting from cyclization of the primary hydroxy (**39**, diastereomeric ratio 44:56). Nevertheless, the amount of cyclized products was less than 6% in the whole mixture (**33**/**38**/**39** = 94:4:2).

These results reveal that in such equilibria the percentage of oxazolidines derived from aldehydes with electron-withdrawing substituents increases on increasing the number of available hydroxy groups: ≈20% for derivatives of 2-amino-2-methylpropan-1-ol, ca. 60% for those of 2-amino-2-methylpropane-1,3-diol, and ca. 100% for those based on TRIS. These percentages are related to the statistical probability of cyclization with the number of hydroxy groups present.

The Hammett plot for $\log K_{ring-chain}$ (= [ring]/[chain]) against $\sigma$ values gave a linear relationship although with a rather poor fit ($r$ = 0.62). Nevertheless, the negative value of $\rho$ (–0.35) suggests that electron-withdrawing substituents favor oxazolidine formation.

### Acetylation of 2-Aryl-4,4-bis(hydroxymethyl)oxazolidines

Oxazolidines **40** are in principle good candidates to prepare the corresponding *N*-acetyloxazolidines because they already contain the heterocyclic unit. Thus, one would have expected the easy formation of such substances by conventional treatment with acetic anhydride in pyridine. However, this protocol failed to give the desired compounds **41**, yielding only the per-*O*-acetylated imines **42** instead (Scheme 4).



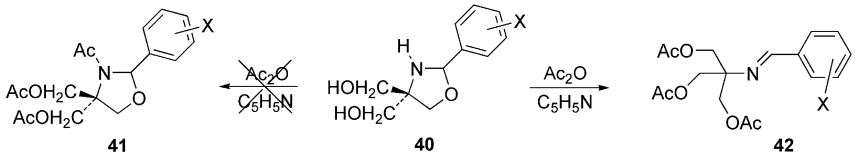

**29a** X = 4-$NO_2$
**30a** X = 4-$CO_2Me$
**36a** X = 3-$NO_2$

**34** X = 4-$NO_2$
**35** X = 4-$CO_2Me$
**31** X = 3-$NO_2$

**29b** X = 4-$NO_2$
**30b** X = 4-$CO_2Me$
**36b** X = 3-$NO_2$

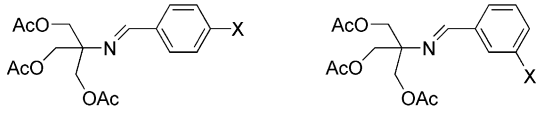
Scheme 3.



Scheme 4.

Accordingly, starting from the parent oxazolidines **8**–**14** the corresponding imines **43**–**49** were isolated with yields approaching 70%. Their structures were again corroborated by analytical and spectroscopic data. FTIR spectra showed stretching bands at ca. 1650 $cm^{-1}$ (C=N bond) and NMR resonances at ca. 8.4 and ca. 159 ppm, proving the existence of an imino group. The solid state of **43** was also established by single-crystal X-ray analysis (Figure 5).[8] Structures attributed to **44**–**49** were also correlated with that found for **43**.



**43** X = $NO_2$
**44** X = CN
**45** X = $CF_3$
**46** X = $CO_2Me$



**47** X = $NO_2$
**48** X = CN
**49** X = $CO_2Me$

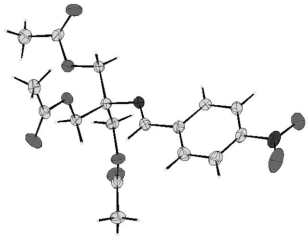


Figure 5. ORTEP diagram for per-*O*-acetyl imine **43**.

## Acetylation Mechanism

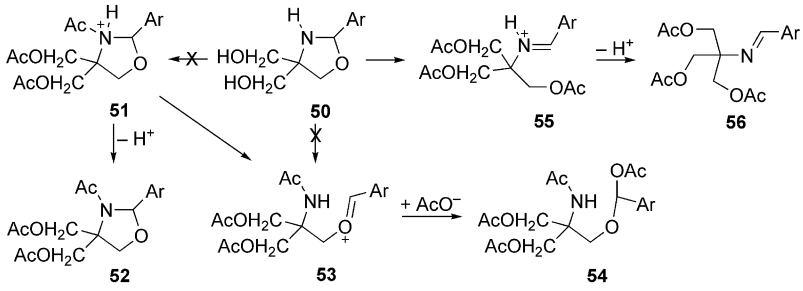
Three possible pathways can be envisaged (Scheme 5). Attack of the acetylating species on the nitrogen atom of the starting oxazolidine **50** would yield tetrahedral intermediate **51**, which could either evolve into *N*-acetyloxazolidine **52** (canonical form **17**, Figure 3) after deprotonation or into **54** (canonical form **19**) by ring-opening. The third alternative involves attack on the endocyclic oxygen atom plus ring-opening (canonical form **18**) leading to per-*O*-acetylimine **56**.

Further studies were undertaken to shed light on the mechanism of this acetylation. To this end, the reactions of **8**–**16** with hexadeuteriated acetic anhydride, $(CD_3CO)_2O$, in pentadeuteriated pyridine, $C_5D_5N$, were monitored in an NMR tube. The evolution of the NMR spectra over time is depicted in Figure 6 (see also Figures S4 and S5 in the Supporting Information).

For compound **8** the rapid formation of its mono- (**57** and **58**) and di-*O*-acetyl (**59**) derivatives can be observed. This transformation occurs rapidly and, within 15 min, the prevalent compound is essentially the di-*O*-acetylated oxazolidine **59**, which disappears slowly to give exclusively **43** after 24 h (Scheme 6).

This rationale is also supported by the preparation of **59** by acetylation of **8**. The process was quenched after 15 min and **59** was isolated in 62% yield. The structure of this oxazolidine was confirmed again by FTIR (absorption of the NH group at 3287 $cm^{-1}$, absence of bands in the range between 1740 and 1606 $cm^{-1}$) and NMR spectroscopic data (signal at 5.60 ppm for 2-H and a carbon resonance at 91.08 ppm for C-2). The large coupling constant $J_{NH,2\text{-}H}$ that **59** exhibits in [$D_6$]DMSO suggests an axial disposition of the NH group, in a similar way to compounds **8**–**16**. When **59** was subjected to the same acetylation conditions, its complete transformation into **43** was observed. Similar results were obtained in the acetylation of compounds **9**–**16**.

The fate of this transformation is most likely influenced by the anomeric effect present in oxazolidines **8**–**16**. The important contribution of canonical form **18** (Figure 3) accounts for the observed reactivity as the most nucleophilic center should be the oxygen atom of the ring and not the nitrogen. The nucleophilic site would attack acetic anhydride and/or pyridinium acetate (**60**→**61**), thus enabling



Scheme 5.

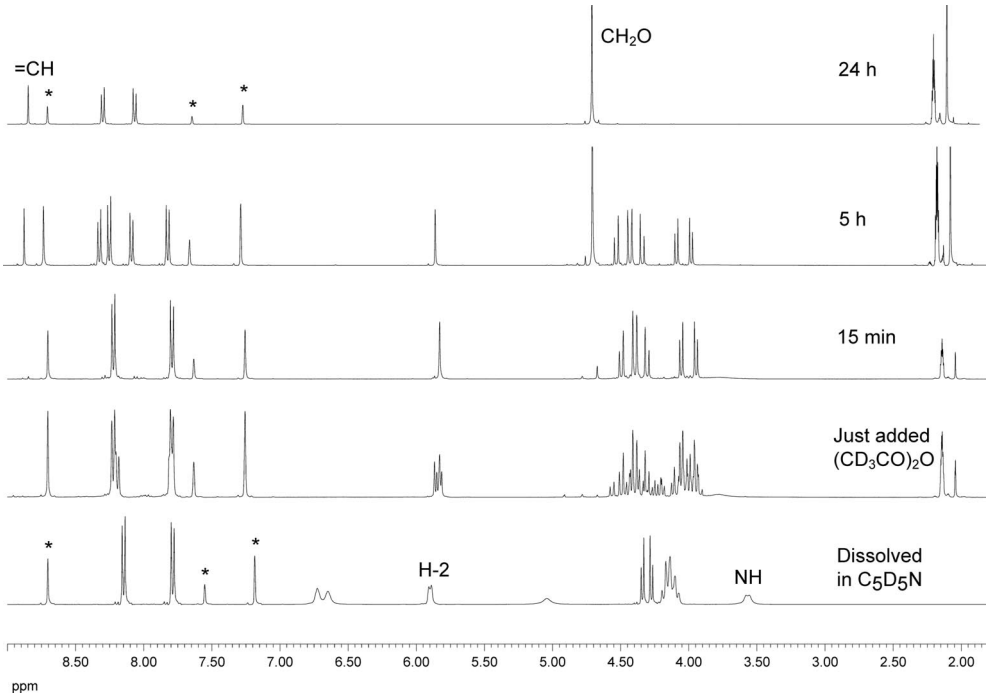
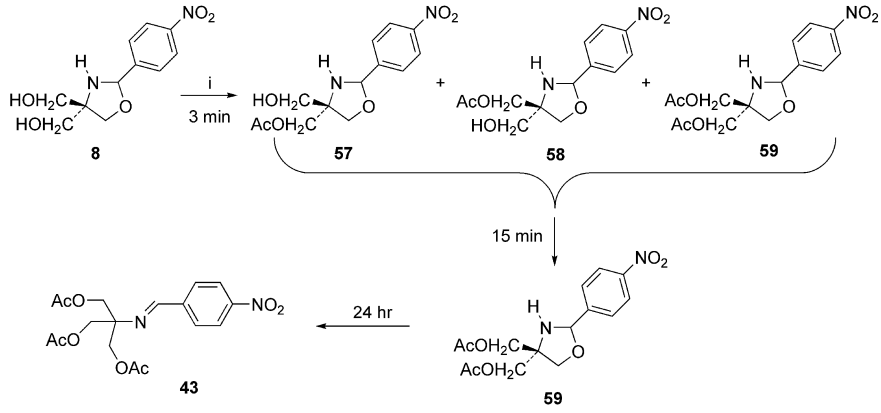
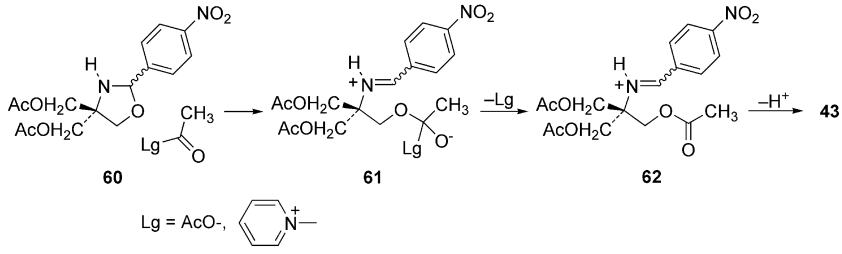



Figure 6. Evolution with time of the NMR spectra of compound **8** after acetylation (* denotes pyridine signals).




Scheme 6. Reagents: i) $(CD_3CO)_2O$, $C_5D_5N$.




Scheme 7. Proposed mechanism for the acetylation of oxazolidines.

ring-opening to produce an iminium ion (**62**), which could subsequently be deprotonated leading to an imine (**43**; Scheme 7).

## Conclusions

Oxazolidines derived from TRIS that exhibit a strong *endo* anomeric effect have been described and fully characterized. DFT calculations predict such an anomeric effect, in excellent agreement with X-ray crystal data. This stereoelectronic effect directs the conformational bias of the heterocyclic ring and facilitates its regiospecific ring-opening under acetylating conditions to give per-*O*-acetyl imines. Oxazolidine–imine equilibria have been evaluated not only for TRIS derivatives but also for 2-amino-2-methylpropane-1,3-diol, 2-amino-2-methylpropan-1-ol, and 3-aminoprop-

ane-1,2-diol. The results show that the amount of oxazolidine increases as the number of potential hydroxy groups capable of participating in the cyclization step increases.

## Experimental Section

**General Methods:** Melting points were determined with Gallenkamp and Electrothermal apparatuses. IR spectra were recorded in the range of 4000–600 $cm^{-1}$ with a FTIR THERMO spectrophotometer. Solid samples were recorded as KBr (Merck) pellets. NMR spectra were recorded with a Bruker 400 AC/PC instrument in different solvent systems. Assignments were confirmed by homo- and hetero-nuclear double-resonance and DEPT (distortionless enhancement by polarization transfer). TMS was used as the internal standard ($\delta$ = 0.00 ppm) and all $J$ values are given in Hz. Microanalyses were determined with a Leco 932 analyzer. High-resolution mass spectra (chemical ionization) were recorded with an Autospec-Q spectrometer by the Servicio de Espectrometría de Masas de la Universidad de Sevilla (Spain).

**General Procedure for the Synthesis of 2-Aryl-4,4-bis(hydroxymethyl)oxazolidines:** A solution of the corresponding aldehyde (16.5 mmol) in a small volume of methanol was slowly added to a solution of α,α,α-tris(hydroxymethyl)methylamine (2.0 g, 16.5 mmol) in water (16 mL). The mixture was stirred at room temperature to produce a precipitate within a few minutes. When the mixture did not precipitate spontaneously, it was evaporated in vacuo to give a solid on standing or on cooling. The resulting product was collected by filtration, washed successively with cold water, ethanol, and diethyl ether, and recrystallized from ethanol or methanol.

**4,4-Bis(hydroxymethyl)-2-(4-nitrophenyl)oxazolidine (8):** Yield 2.85 g, 68%; m.p. 108–109 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3500–3100 (OH), 1604, 1515 (arom.) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.23 (d, $J$ = 8.4 Hz, 2 H, H arom.), 7.70 (d, $J$ = 8.4 Hz, 2 H, H arom.), 5.55 (d, $J_{2\text{-H,NH}}$ = 10.8 Hz, 1 H, 2-H), 4.81 (t, $J$ = 5.6 Hz, 2 H, OH), 3.74 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.70 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.46 (d, $J_{CH2,OH}$ = 5.6 Hz, 2 H, $CH_2$), 3.42 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 3.32 (dd, $J_{CH2,OH}$ = 5.8, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 2.99 (d, $J_{NH,2\text{-H}}$ = 10.8 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 148.5, 147.8, 128.1, 123.9 (C arom.), 90.9 (C-2), 69.7 (C-5), 67.9 (C-4), 63.2, 62.9 (2 C, $CH_2$) ppm. $C_{11}H_{14}N_2O_5$ (254.24): calcd. C 51.97, H 5.55, N 11.02; found C 51.67, H 5.72, N 11.10.

**4,4-Bis(hydroxymethyl)-2-(4-cyanophenyl)oxazolidine (9):** Yield 2.13 g, 55%; m.p. 120–121 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3400–3200 (OH), 2225 (C≡N), 1610, 1482, 1467 (arom.) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.84 (d, $J$ = 8.0 Hz, 2 H, H arom.), 7.62 (d, $J$ = 8.0 Hz, 2 H, H arom.), 5.49 (d, $J_{2\text{-H,NH}}$ = 10.8 Hz, 1 H, 2-H), 4.81 (t, $J$ = 6.0 Hz, 1 H, OH), 4.79 (t, $J$ = 6.0 Hz, 1 H, OH), 3.71 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.68 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.44 (d, $J_{CH2,OH}$ = 5.6 Hz, 2 H, $CH_2$), 3.42 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 3.33 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 2.93 (d, $J_{NH,2\text{-H}}$ = 10.8 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 146.5 (C≡N), 132.7, 127.8, 119.2, 111.4 (C arom.), 91.1 (C-2), 69.7 (C-5), 67.9 (C-4), 63.3, 62.9 (2 C, $CH_2$) ppm. $C_{12}H_{14}N_2O_3$ (234.25): calcd. C 61.53, H 6.02, N 11.96; found C 61.42, H 6.24, N 11.86.

**4,4-Bis(hydroxymethyl)-2-(4-trifluoromethylphenyl)oxazolidine (10):** Yield 3.02 g, 66%; m.p. 98–99 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300–3100 (OH), 1623, 1450 (arom.) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.40 (d, $J$ = 8.0 Hz, 2 H, H arom.), 7.66 (d, $J$ = 8.0 Hz, 2 H, H arom.), 5.49 (d, $J_{2\text{-H,NH}}$ = 10.8 Hz, 1 H, 2-H), 4.84 (t, $J$ = 5.6 Hz, 1 H, OH), 4.80 (t, $J$ = 5.6 Hz, 1 H, OH), 3.73 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.70 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.45 (d, $J_{CH2,OH}$ = 5.6 Hz, 2 H, $CH_2$), 3.44 (dd, $J_{CH2,OH}$ = 6.0, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 3.36 (dd, $J_{CH2,OH}$ = 6.0, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 2.90 (d, $J_{NH,2\text{-H}}$ = 10.8 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 145.6, 129.2 (q, $J_{C\text{-F}}$ = 31.5 Hz), 127.5, 127.4 (q, $J_{C\text{-F}}$ = 269.8 Hz), 125.5 (q, $J_{C\text{-F}}$ = 3.7 Hz, C arom.), 91.1 (C-2), 69.6 (C-5), 67.9 (C-4), 63.4, 62.9 (2 C, $CH_2$) ppm. $C_{12}H_{14}F_3NO_3$ (277.09): calcd. C 51.99, H 5.09, N 5.05; found C 51.67, H 4.98, N 5.04.

**4,4-Bis(hydroxymethyl)-2-(4-methoxycarbonylphenyl)oxazolidine (11):** Yield 3.70 g, 84%; m.p. 128–129 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3500–3100 (OH), 1703 (C=O), 1612, 1576, 1513 (arom.) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.96 (d, $J$ = 8.4 Hz, 2 H, H arom.), 7.56 (d, $J$ = 8.4 Hz, 2 H, H arom.), 5.45 (d, $J_{2\text{-H,NH}}$ = 10.0 Hz, 1 H, 2-H), 4.85 (t, $J$ = 5.6 Hz, 1 H, OH), 4.79 (t, $J$ = 5.6 Hz, 1 H, OH), 3.85 (s, 3 H, $OCH_3$), 3.72 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.68 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.44 (d, $J_{CH2,OH}$ = 5.6 Hz, 2 H, $CH_2$), 3.44 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.37 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 2.86 (d, $J_{NH,2\text{-H}}$ = 10.4 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.5 (C=O), 146.1, 129.9, 129.6, 127.1 (C arom.), 91.4 (C-2), 69.5 (C-5), 67.9 (C-4), 63.4, 62.8 (2 C, $CH_2$), 52.6 ($CH_3$) ppm. $C_{13}H_{17}NO_5$ (267.28): calcd. C 58.42, H 6.41, N 5.24; found C 58.28, H 6.47, N 5.47.

**4,4-Bis(hydroxymethyl)-2-(3-nitrophenyl)oxazolidine (12):** Yield 2.64 g, 63%; m.p. 92–93 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300–3100 (OH), 1618, 1586 (arom.), 1529, 1350 ($NO_2$) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.26 (s, 1 H, H arom.), 8.20 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.88 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.68 (t, $J$ = 8.0 Hz, 1 H, H arom.), 5.56 (d, $J_{2\text{-H,NH}}$ = 10.8 Hz, 1 H, 2-H), 4.82 (t, $J$ = 5.6 Hz, 1 H, OH), 4.80 (t, $J$ = 5.6 Hz, 1 H, OH), 3.75 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.70 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.46 (d, $J_{CH2,OH}$ = 5.6 Hz, 2 H, $CH_2$), 3.43 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.33 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.02 (d, $J_{NH,2\text{-H}}$ = 10.8 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 148.1, 143.5, 133.6, 130.3, 123.5, 121.4 (C arom.), 90.7 (C-2), 69.7 (C-5), 67.9 (C-4), 63.3, 63.1 (2 C, $CH_2$) ppm. $C_{11}H_{14}N_2O_5$ (254.24): calcd. C 51.97, H 5.55, N 11.02; found C 51.91, H 5.50, N 11.16.

**4,4-Bis(hydroxymethyl)-2-(3-cyanophenyl)oxazolidine (13):** Yield 2.51 g, 65%; m.p. 129–130 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300–3100 (OH), 2227 (C≡N), 1618, 1451 (arom.) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.85 (s, 1 H, H arom.), 7.81 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.77 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.60 (t, $J$ = 7.6 Hz, 1 H, H arom.), 5.46 (d, $J_{2\text{-H,NH}}$ = 10.4 Hz, 1 H, 2-H), 4.80 (t, $J$ = 6.0 Hz, 1 H, OH), 4.78 (t, $J$ = 5.6 Hz, 1 H, OH), 3.72 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.67 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.44 (d, $J_{CH2,OH}$ = 6.0 Hz, 2 H, $CH_2$), 3.43 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 11.4 Hz, 1 H, $CH_2$), 3.35 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 2.94 (d, $J_{NH,2\text{-H}}$ = 10.8 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 142.8 (C≡N), 132.5, 131.8, 130.4, 130.0, 119.2, 111.7 (C arom.), 90.9 (C-2), 69.7 (C-5), 67.8 (C-4), 63.3, 63.0 (2 C, $CH_2$) ppm. $C_{12}H_{14}N_2O_3$ (234.25): calcd. C 61.53, H 6.02, N 11.96; found C 61.50, H 6.05, N 12.15.

**4,4-Bis(hydroxymethyl)-2-(3-methoxycarbonylphenyl)oxazolidine (14):** Yield 3.44 g, 78%; m.p. 119–120 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3400–3000 (OH), 1719 (C=O), 1604, 1515 (arom.) $cm^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.05 (s, 1 H, H arom.), 7.92 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.70 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.53 (t, $J$ = 7.6 Hz 1 H, H arom.), 5.45 (d, $J_{2\text{-H,NH}}$ = 10.8 Hz, 1 H, 2-H), 4.85 (t, $J$ = 5.6 Hz, 1 H, OH), 4.79 (t, $J$ = 5.6 Hz, 1 H, OH), 3.87 (s, 3 H,

$OCH_3$), 3.72 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.68 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.44 (d, $J_{CH2,OH}$ = 5.6 Hz, 2 H, $CH_2$), 3.44 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.37 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 2.85 (d, $J_{NH,2\text{-}H}$ = 11.2 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.6 (C=O), 141.6, 131.7, 130.1, 129.4, 129.2, 127.3 (C arom.), 91.3 (C-2), 69.5 (C-5), 67.9 (C-4), 63.5, 62.9 (2 C, $CH_2$), 52.7 ($CH_3$) ppm. $C_{13}H_{17}NO_5$ (267.28): calcd. C 58.42, H 6.41, N 5.24; found C 58.45, H 6.40, N 5.31.

**4,4-Bis(hydroxymethyl)-2-(4-methyl-3-nitrophenyl)oxazolidine (15):** Yield 2.57 g, 58%; m.p. 82–83 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3500–2500 (OH, NH), 1621, 1565, 1495 (arom.), 1527, 1340 ($NO_2$) cm$^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.01 (s, 1 H, H arom.), 7.67 (dd, $J$ = 1.2, $J$ = 7.9 Hz, 1 H, H arom.), 7.50 (d, $J$ = 7.9 Hz, 1 H, H arom.), 5.48 (d, $J_{2\text{-}H,NH}$ = 10.6 Hz, 1 H, 2-H), 4.79 (m, 2 H, 2 OH), 3.72 (d, $J$ = 7.9 Hz, 1 H, $CH_2$ ring), 3.67 (d, $J$ = 7.9 Hz, 1 H, $CH_2$ ring), 3.45 (d, $J_{CH2,OH}$ = 4.8 Hz, 2 H, $CH_2$), 3.43 (dd, $J_{CH2,OH}$ = 5.0, $J_{H,H}$ = 13.2 Hz, 1 H, $CH_2$), 3.34 (dd, $J_{CH2,OH}$ = 5.7, $J_{H,H}$ = 11.2 Hz, 1 H, $CH_2$), 2.94 (d, $J_{NH,2\text{-}H}$ = 10.8 Hz, 1 H, NH), 2.52 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 149.1, 140.8, 133.2, 133.0, 131.7, 122.5 (C arom.), 90.6 (C-2), 69.7 (C-5), 67.8 (C-4), 63.63, 63.0 (2 C, $CH_2$), 19.8 ($CH_3$) ppm. $C_{12}H_{16}N_2O_5$ (268.27): calcd. C 53.73, H 6.01, N 10.44; found C 53.68, H 6.17, N 10.55.

**4,4-Bis(hydroxymethyl)-2-(2-methoxy-4-nitrophenyl)oxazolidine (16):** Yield 3.47 g, 74%; m.p. 121–122 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3400–3200 (OH), 1618, 1488 (arom.), 1521, 1360 ($NO_2$) cm$^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.85 (d, $J$ = 8.4 Hz, 1 H, H arom.), 7.72 (m, 2 H, H arom.), 5.56 (d, $J_{2\text{-}H,NH}$ = 9.6 Hz, 1 H, 2-H), 4.84 (t, $J$ = 4.8 Hz, 1 H, OH), 4.78 (t, $J$ = 4.6 Hz, 1 H, OH), 3.92 (s, 3 H, $CH_3$), 3.76 (d, $J$ = 7.8 Hz, 1 H, $CH_2$ ring), 3.68 (d, $J$ = 7.8 Hz, 1 H, $CH_2$ ring), 3.46 (m, 4 H, 2 $CH_2$), 2.86 (d, $J_{NH,2\text{-}H}$ = 9.6 Hz, 1 H, NH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 157.8, 148.8, 136.2, 128.2, 115.9, 106.1 (C arom.), 86.4 (C-2), 69.4 (C-5), 67.7 (C-4), 63.2, 62.9 (2 C, $CH_2$), 56.6 ($CH_3$) ppm. $C_{12}H_{16}N_2O_6$ (284.27): calcd. C 50.70, H 5.67, N 9.85; found C 50.60, H 5.68, N 9.85.

**4-Hydroxymethyl-4-methyl-2-(4-nitrophenyl)oxazolidine (29):** From 2-amino-2-methylpropane-1,3-diol, and prepared following the same procedure as used for the synthesis of **8**, compound **29** was isolated (2.71 g, 69%) as a mixture of diastereomers **29a** and **29b** (1:1). IR (KBr): $\tilde{\nu}_{max}$ = 3300–3100 (OH), 1519, 1346 ($NO_2$), 1605, 1482, 1450 (arom.) cm$^{-1}$. $C_{11}H_{14}N_2O_4$ (238.24): calcd. C 55.46, H 5.92, N 11.76; found C 55.63, H 5.94, N 11.92. Data for **29a**: $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.21 (d, $J$ = 8.8 Hz, 2 H, H arom.), 7.70 (d, $J$ = 8.8 Hz, 2 H, H arom.), 5.57 (d, $J_{2\text{-}H,NH}$ = 11.2 Hz, 1 H, 2-H), 4.98 (t, $J$ = 5.6 Hz, 1 H, OH), 3.80 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.42 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.27 (d, $J$ = 5.2 Hz, 2 H, $CH_2$), 3.03 (d, $J_{NH,2\text{-}H}$ = 11.2 Hz, 1 H, NH), 1.15 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 149.0, 147.7, 128.1, 123.8 (C arom.), 91.1 (C-2), 73.4 (C-5), 65.6 ($CH_2$), 63.8 (C-4), 22.7 ($CH_3$) ppm. Data for **29b**: $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.21 (d, $J$ = 8.8 Hz, 2 H, H arom.), 7.70 (d, $J$ = 8.8 Hz, 2 H, H arom.), 5.57 (d, $J_{2\text{-}H,NH}$ = 9.6 Hz, 1 H, 2-H), 4.94 (t, $J$ = 5.6 Hz, 1 H, OH), 3.80 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.42 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.40 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.32 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.12 (d, $J_{NH,2\text{-}H}$ = 10.4 Hz, 1 H, NH), 1.08 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 148.6, 147.6, 128.0, 123.7 (C arom.), 90.5 (C-2), 73.4 (C-5), 66.0 ($CH_2$), 63.8 (C-4), 22.2 ($CH_3$) ppm.

**(2*R*,4*S*)- and (2*S*,4*R*)-4-Hydroxymethyl-4-methyl-2-(4-methoxycarbonylphenyl)oxazolidine (30b):** From 2-amino-2-methylpropane-1,3-diol, and prepared following the same procedure as used for the synthesis of **11**, compound **30** was isolated (3.44 g, 83%) as a mixture of diastereomers **30a** and **30b** (1:2.3). Recrystallization of this mixture in ethanol gave rise to compound **30b**; yield 2.07 g, 50%; m.p. 106–107 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300–3100 (OH), 1724 (C=O), 1613, 1572, 1511 (arom.) cm$^{-1}$. $^1$H NMR (400 MHz, [D$_6$]-DMSO): $\delta$ = 7.94 (d, $J$ = 8.0 Hz, 2 H, H arom.), 7.58 (d, $J$ = 8.0 Hz, 2 H, H arom.), 5.49 (d, $J_{2\text{-}H,NH}$ = 12.0 Hz, 1 H, 2-H), 4.85 (t, $J$ = 5.6 Hz, 1 H, OH), 3.85 (s, 3 H, $OCH_3$), 3.79 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.41 (d, $J$ = 7.6 Hz, 1 H, $CH_2$ ring), 3.40 (dd, $J_{CH2,OH}$ = 6.0, $J_{H,H}$ = 10.1 Hz, 1 H, $CH_2$), 3.32 (dd, $J_{CH2,OH}$ = 5.2, $J_{H,H}$ = 10.4 Hz, 1 H, $CH_2$), 2.95 (d, $J_{NH,2\text{-}H}$ = 10.4 Hz, 1 H, NH), 1.12 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.5 (C=O), 146.5, 129.6, 129.4, 127.2 (C arom.), 91.6 (C-2), 73.4 (C-5), 66.2 ($CH_2$), 63.9 (C-4), 52.6 ($OCH_3$), 22.7 ($CH_3$) ppm. $C_{13}H_{17}NO_4$ (251.28): calcd. C 62.14, H 6.82, N 5.57; found C 62.08, H 6.71, N 5.80.

**2-Methyl-2-(3-nitrobenzylideneamino)propane-1,3-diol (31):** From 2-amino-2-methylpropane-1,3-diol, compound **31** was obtained following the same procedure as used for the synthesis of **12**; yield 3.54 g, 90%; m.p. 116–117 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1639 (C=N), 1534, 1349 ($NO_2$) cm$^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.59 (s, 1 H, H arom.), 8.48 (s, 1 H, CH=N), 8.26 (d, $J$ = 7.6 Hz, 1 H, H arom.), 8.18 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.72 (t, $J$ = 7.8 Hz, 1 H, H arom.), 4.62 (t, $J$ = 5.2 Hz, 2 H, 2 OH), 3.53 (dd, $J$ = 5.6, $J$ = 10.0 Hz, 2 H, $CH_2$), 3.46 (dd, $J$ = 6.2, $J$ = 10.2 Hz, 2 H, $CH_2$), 1.18 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 156.8 (C=N), 148.5, 139.0, 134.8, 130.6, 125.0, 122.1 (C arom.), 66.2 ($CH_2$), 65.9 (C-N), 18.7 ($CH_3$) ppm. $C_{11}H_{14}N_2O_4$ (238.24): calcd. C 55.46, H 5.92, N 11.76; found C 55.23, H 5.88, N 11.91.

**2-Methyl-2-(3-nitrobenzylideneamino)propan-1-ol (32):** From 2-amino-2-methylpropan-1-ol, compound **32** was obtained following the same procedure as used for the synthesis of **12**; yield 3.63 g, 99%; m.p. 127–128 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300 (OH), 1641 (C=N), 1532, 1351 ($NO_2$) cm$^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.58 (s, 1 H, H arom.), 8.45 (s, 1 H, CH=N), 8.25 (dd, $J$ = 7.6, $J$ = 7.8 Hz, 1 H, H arom.), 8.18 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.72 (t, $J$ = 7.8 Hz, 1 H, H arom.), 4.71 (t, $J$ = 5.8 Hz, 1 H, OH), 3.39 (dd, $J$ = 5.6 Hz, 2 H, $CH_2$), 1.20 (s, 6 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 155.6 (C=N), 148.5, 138.9, 134.7, 130.7, 125.1, 122.1 (C arom.), 69.8 ($CH_2$), 62.1 (C-N), 24.4 ($CH_3$) ppm. $C_{11}H_{14}N_2O_3$ (222.24): calcd. C 59.45, H 6.35, N 12.60; found C 59.09, H 6.32, N 12.59.

**3-(4-Nitrobenzylideneamino)propane-1,2-diol (33):** From 3-aminopropane-1,2-diol, compound **33** was obtained following the same procedure as used for the synthesis of **8**; yield 3.26 g, 88%; m.p. 94–95 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3400–3100 (OH), 1643 (C=N), 1523, 1343 ($NO_2$) cm$^{-1}$. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.45 (s, 1 H, CH=N), 8.29 (d, $J$ = 8.8 Hz, 2 H, H arom.), 8.00 (d, $J$ = 8.8 Hz, 2 H, H arom.), 4.72 (d, $J$ = 5.2 Hz, 1 H, OH), 4.64 (t, $J$ = 5.6 Hz, 1 H, OH), 3.85 (ddd, $J$ = 11.6, $J$ = 4.2, $J$ = 1.3 Hz, 1 H, $CH_2N$), 3.78 (m, 1 H, C*H*OH), 3.50 (dd, $J$ = 12.0, $J$ = 6.8 Hz, 1 H, $CH_2N$), 3.43 (d, $J$ = 5.6 Hz, 2 H, C$H_2$OH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]-DMSO): $\delta$ = 160.8 (C=N), 148.9, 142.3, 129.3, 124.3 (C arom.), 71.5 (CH), 64.7, 64.6 (2 C, 2 $CH_2$) ppm. $C_{10}H_{12}N_2O_4$ (224.21): calcd. C 53.57, H 5.39, N 12.49; found C 53.25, H 5.29, N 12.26.

**Oxazolidine–Imine Equilibria:** Oxazolidines **8**–**16**, **29** and **30** and imines **31**–**33** form equilibria in DMSO solution with the corresponding imines **20**–**28**, **34**, and **35**, oxazolidines **36**–**38**, and oxazine **39**.

**Spectroscopic Data for 20:** $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.55 (s, 1 H, CH=N), 8.29 (d, $J$ = 8.8 Hz, 2 H, H arom.), 8.04 (d,

$J$ = 8.8 Hz, 2 H, H arom.), 4.52 (t, $J$ = 5.6 Hz, 3 H, OH), 3.62 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 157.7 (C=N), 148.2, 142.5, 128.8, 123.7 (C arom.), 68.4 (C-N), 61.6 (3 C, $CH_2$) ppm.

**Spectroscopic Data for 21:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.50 (s, 1 H, CH=N), 7.96 (d, $J$ = 8.0 Hz, 2 H, H arom.), 7.89 (d, $J$ = 8.0 Hz, 2 H, H arom.), 4.88 (t, $J$ = 5.6 Hz, 3 H, OH), 3.61 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 158.2 (C=N), 140.9 (C≡N), 132.6, 128.6, 118.9, 112.4 (C arom.), 68.3 (C-N), 61.7 (3 C, $CH_2$) ppm.

**Spectroscopic Data for 22:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.51 (s, 1 H, CH=N), 7.99 (d, $J$ = 8.0 Hz, 2 H, H arom.), 7.79 (d, $J$ = 8.0 Hz, 2 H, H arom.), 4.52 (t, $J$ = 5.6 Hz, 3 H, OH), 3.63 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 158.6 (C=N), 141.0, 130.6 (q, $J_{C\text{-}F}$ = 11.3 Hz), 128.9, 125.8 (q, $J_{C\text{-}F}$ = 3.8 Hz, C arom.), 68.5 (C-N), 62.2 ($CH_2$) ppm.

**Spectroscopic Data for 23:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.50 (s, 1 H, CH=N), 8.02 (d, $J$ = 7.6 Hz, 2 H, H arom.), 7.91 (d, $J$ = 8.0 Hz, 2 H, H arom.), 4.50 (t, $J$ = 5.6 Hz, 3 H, OH), 3.87 (s, 3 H, $OCH_3$), 3.62 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.5 (C=O), 158.9 (C=N), 141.5, 131.2, 129.8, 128.5 (C arom.), 68.5 (C-N), 62.2 (3 C, $CH_2$) ppm.

**Spectroscopic Data for 24:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.61 (s, 1 H, H arom.), 8.54 (s, 1 H, CH=N), 8.27 (dd, $J$ = 2.4, $J$ = 8.0 Hz, 1 H, H arom.), 7.87 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.74 ($J$ = 8.0 Hz, 1 H, H arom.), 4.54 (t, $J$ = 5.6 Hz, 3 H, OH), 3.62 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 157.9 (C=N), 148.6, 139.1, 134.9, 130.6, 125.1, 122.0 (C arom.), 68.6 (C-N), 62.2 (3 C, $CH_2$) ppm.

**Spectroscopic Data for 25:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.45 (s, 1 H, CH=N), 8.26 (s, 1 H, H arom.), 8.08 (d, $J$ = 8.0 Hz, 1 H, H arom.), 7.89 (d, $J$ = 8.0 Hz, 1 H, H arom.), 7.65 (t, $J$ = 8.0 Hz, 1 H, H arom.), 4.52 (t, $J$ = 5.6 Hz, 3 H, OH), 3.59 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 157.9 (C=N), 138.5 (C≡N), 134.0, 132.9, 131.6, 130.2, 119.1, 112.1 (C arom.), 68.4 (C-N), 62.1 (3 C, $CH_2$) ppm.

**Spectroscopic Data for 26:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.50 (s, 1 H, CH=N), 8.37 (s, 1 H, H arom.), 8.01 (d, $J$ = 7.6 Hz, 2 H, H arom.), 7.60 (t, $J$ = 7.6 Hz, 1 H, H arom.), 4.49 (t, $J$ = 5.6 Hz, 3 H, OH), 3.88 (s, 3 H, $OCH_3$), 3.62 (d, $J$ = 5.6 Hz, 6 H, $CH_2$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.6 (C=O), 158.8 (C=N), 137.9, 133.3, 131.1, 130.3, 129.5, 128.4 (C arom.), 68.3 (C-N), 62.2 (3 C, $CH_2$) ppm.

**Spectroscopic Data for 27:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.45 (s, 1 H, CH=N), 8.36 (s, 1 H, H arom.), 7.98 (m, 1 H, H arom.), 7.56 (d, $J$ = 7.6 Hz, 1 H, H arom.), 4.50 (t, $J$ = 5.4 Hz, 3 H, OH), 3.61 (d, $J$ = 4.8 Hz, 6 H, $CH_2$), 2.55 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 157.7 (C=N), 149.6, 136.9, 134.8, 133.5, 132.8, 123.3 (C arom.), 68.4 (C-N), 62.18 (3 C, $CH_2$), 20.0 ($CH_3$) ppm.

**Spectroscopic Data for 28:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.80 (s, 1 H, CH=N), 8.14 (d, $J$ = 9.2 Hz, 1 H, H arom.), 7.85 (m, 2 H, H arom.), 7.72 (m, 1 H, H arom.), 4.51 (t, $J$ = 5.6 Hz, 3 H, OH), 3.62 (d, $J$ = 5.2 Hz, 6 H, $CH_2$), 2.09 (s, 3 H, $OCH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 153.6 (C=N), 158.9, 149.9, 131.1, 127.9, 115.8, 107.2 (C arom.), 69.0 (C-N), 62.3 (3 C, $CH_2$), 31.2 ($OCH_3$) ppm.

**Spectroscopic Data for 34:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.48 (s, 1 H, CH=N), 8.28 (d, $J$ = 8.4 Hz, 2 H, H arom.), 8.03 (d, $J$ = 8.4 Hz, 2 H, H arom.), 4.62 (m, 3 H, 2 OH), 3.54 (dd, $J$ = 5.4, $J$ = 10.6 Hz, 2 H, $CH_2$), 3.45 (dd, $J$ = 6.0, $J$ = 10.8 Hz, 2 H, $CH_2$), 1.17 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 157.1 (C=N), 148.8, 142.9, 129.3, 124.2 (C arom.), 66.2 (C-N), 66.1 ($CH_2$), 18.7 ($CH_3$) ppm.

Compound **30b** equilibrated in DMSO solution with its diastereoisomer **30a** and imine **35**.

**Spectroscopic Data for 30a**: $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.97 (d, $J$ = 8.4 Hz, 2 H, H arom.), 7.58 (d, $J$ = 8.4 Hz, 2 H, H arom.), 5.50 (d, $J_{2\text{-}H,NH}$ = 11.6 Hz, 1 H, 2-H), 4.97 (t, $J$ = 5.6 Hz, 1 H, OH), 3.86 (s, 3 H, $OCH_3$), 3.79 (d, $J$ = 7.2 Hz, 1 H, $CH_2$ ring), 3.41 (d, $J$ = 7.2 Hz, 1 H, $CH_2$ ring), 3.30 (d, $J$ = 4.8 Hz, 2 H, $CH_2$), 2.91 (d, $J_{NH,2\text{-}H}$ = 11.2 Hz, 1 H, NH), 1.14 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.5 (C=O), 146.3, 129.6, 129.4, 127.0 (C arom.), 91.0 (C-2), 73.2 (C-5), 65.5 ($CH_2$), 63.9 (C-4), 52.6 ($OCH_3$), 22.4 ($CH_3$) ppm.

**Spectroscopic Data for 35:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.42 (s, 1 H, CH=N), 8.02 (d, $J$ = 8.4 Hz, 2 H, H arom.), 7.90 (d, $J$ = 8.4 Hz, 2 H, H arom.), 4.59 (t, $J$ = 5.6 Hz, 2 H, OH), 3.87 (s, 3 H, $OCH_3$), 3.52 (dd, $J$ = 10.8, $J$ = 5.6 Hz, 2 H, $CH_2$), 3.43 (dd, $J$ = 10.8, $J$ = 5.6 Hz, 2 H, $CH_2$), 1.16 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 166.4 (C=O), 157.7 (C=N), 141.4, 131.2, 129.8, 128.5 (C arom.), 65.8 ($CH_2$), 65.5 (C-N), 52.7 ($OCH_3$), 18.8 ($CH_3$) ppm.

**Spectroscopic Data for 36a:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.27 (m, 1 H, H arom.), 8.18 (m, 1 H, H arom.), 7.87 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.66 (m, 1 H, H arom.), 5.59 (d, $J_{2\text{-}H,NH}$ = 10.8 Hz, 1 H, 2-H), 4.94 (t, $J$ = 5.6 Hz, 1 H, OH), 3.82 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.43 (m, 1 H, $CH_2$ ring), 3.28 (d, $J$ = 5.6 Hz, 2 H, $CH_2$), 3.07 (d, $J_{NH,2\text{-}H}$ = 11.2 Hz, 1 H, NH), 1.17 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 148.1, 143.6, 133.5, 130.3, 123.5, 121.3 (C arom.), 90.3 (C-2), 73.4 (C-5), 65.6 ($CH_2$), 63.9 (C-4), 22.7 ($CH_3$) ppm.

**Spectroscopic Data for 36b:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.27 (m, 1 H, H arom.), 8.18 (m, 1 H, H arom.), 7.87 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.66 (m, 1 H, H arom.), 5.59 (d, $J_{2\text{-}H,NH}$ = 10.8 Hz, 1 H, 2-H), 4.89 (t, $J$ = 5.6 Hz, 1 H, OH), 3.80 (d, $J$ = 8.0 Hz, 1 H, $CH_2$ ring), 3.43 (m, 1 H, $CH_2$ ring), 3.40 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.33 (dd, $J_{CH2,OH}$ = 5.6, $J_{H,H}$ = 10.8 Hz, 1 H, $CH_2$), 3.18 (d, $J_{NH,2\text{-}H}$ = 10.4 Hz, 1 H, NH), 1.10 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 148.1, 143.8, 133.7, 130.2, 123.3, 121.5 (C arom.), 90.9 (C-2), 73.4 (C-5), 66.0 ($CH_2$), 63.8 (C-4), 22.3 ($CH_3$) ppm.

**Spectroscopic Data for 37:** $^1H$ NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 8.27 (dd, $J$ = 2.2, $J$ = 8.1 Hz, 1 H, H arom.), 8.18 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.88 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.66 (t, $J$ = 7.9 Hz, 1 H, H arom.), 5.60 (d, $J_{2\text{-}H,NH}$ = 11.2 Hz, 1 H, 2-H), 3.55 (d, $J$ = 7.2 Hz, 1 H, $CH_2$), 3.48 (d, $J$ = 7.6 Hz, 1 H, $CH_2$), 3.20 (d, $J_{NH,2\text{-}H}$ = 11.2 Hz, 1 H, H arom.), 1.21 (s, 3 H, $CH_3$), 1.15 (s, 3 H, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 148.0, 143.8, 133.7, 130.1, 123.3, 121.4 (C arom.), 90.7 (C-2), 77.4 (C-5), 59.9 (C-4), 26.3, 26.0 (2 C, $CH_3$) ppm.

**Spectroscopic Data for 38:** Diastereomeric ratio 1:2.1. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 128.1, 128.0, 123.6, 123.5 (C arom.), 87.1, 86.8 (C-2), 72.5, 71.9 ($CH_2OH$), 62.7, 62.6 (CH), 51.6, 49.9 ($CH_2N$) ppm.

**Spectroscopic Data for 39:** Diastereomeric ratio 1:1.3. $^{13}C$ NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 91.8, 91.3 (C-2), 77.9, 77.5 ($CH_2O$), 63.5, 63.2 (CH), 49.1, 48.4 ($CH_2N$) ppm.

**General Procedure for the Synthesis of Per-*O*-acetyl Imines Derived from TRIS:** Acetic anhydride (6.5 mL) was added to a solution of

the corresponding oxazolidine (5.0 mmol) in pyridine (6.7 mL). The reaction mixture was kept at 0 °C for 24 h and then poured into ice–water. When the resulting product was an oil, it was extracted with chloroform (3 × 50 mL) and the organic layer was washed sequentially with 1 N HCl (2 × 50 mL), a saturated solution of $NaHCO_3$ (2 × 50 mL), and distilled water (2 × 50 mL). The organic layer was dried ($MgSO_4$) and the solvents evaporated. Solid substances were collected by filtration, washed with distilled water, and dried under vacuum.

**1,3-Diacetoxy-2-acetoxymethyl-2-(4-nitrobenzylideneamino)propane (43):** This compound was obtained from **8**; yield 1.33 g, 70%; m.p. 85–86 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1738 (C=O), 1649 (C=N), 1601, 1516, 1471 (arom.) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.47 (s, 1 H, CH=N), 8.29 (d, $J$ = 8.8 Hz, 2 H, H arom.), 7.93 (d, $J$ = 8.8 Hz, 2 H, H arom.), 4.40 (s, 6 H, $CH_2$), 2.08 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.5 (C=O), 158.7 (C=N), 149.4, 141.2, 129.1, 123.9 (C arom.), 64.2 (C-N), 63.4 ($CH_2$), 20.8 (3 C, $CH_3$, OAc) ppm. $C_{17}H_{20}N_2O_8$ (380.35): calcd. C 53.68, H 5.30, N 7.37; found C 53.77, H 5.39, N 7.58.

**1,3-Diacetoxy-2-acetoxymethyl-2-(4-cyanobenzylideneamino)-propane (44):** This compound was obtained from **9**; yield 1.30 g, 72%; m.p. 65–66 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2228 (C≡N), 1738 (C=O), 1649 (C=N), 1601, 1472 (arom.) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.41 (s, 1 H, CH=N), 7.86 (d, $J$ = 8.8 Hz, 2 H, H arom.), 7.73 (d, $J$ = 8.8 Hz, 2 H, H arom.), 4.38 (s, 6 H, $CH_2$), 2.07 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.4 (C=O), 159.1 (C=N), 139.7 (C≡N), 132.5, 128.8, 118.4, 114.6 (C arom.), 64.1 (C-N), 63.4 ($CH_2$), 20.8 (3 C, $CH_3$, OAc) ppm. $C_{18}H_{20}N_2O_6$ (360.36): calcd. C 59.99, H 5.59, N 7.77; found C 60.00, H 5.59, N 7.82.

**1,3-Diacetoxy-2-acetoxymethyl-2-(4-trifluorobenzylideneamino)-propane (45):** This compound was obtained from **10** as an oil; yield 1.41 g, 70%. IR (NaCl): $\tilde{\nu}_{max}$ = 1745 (C=O), 1646 (C=N), 1544, 1466 (arom.), 1232 (C–O) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.41 (s, 1 H, CH=N), 7.87 (d, $J$ = 8.0 Hz, 2 H, H arom.), 7.69 (d, $J$ = 8.4 Hz, 2 H, H arom.), 4.38 (s, 6 H, $CH_2$), 2.06 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 171.8, 170.9, 170.5 (C=O), 159.5 (C=N), 129.9, 128.6, 126.1, 125, 6 (C arom.), 63.5 ($CH_2$), 60.2 (C-N), 20.8 (3 C, $CH_3$, OAc) ppm. HRMS (CI): calcd. $C_{18}H_{20}F_3NO_6$ $[M + H]^+$ 404.1321; found 404.1321.

**1,3-Diacetoxy-2-acetoxymethyl-2-(4-methoxycarbonylbenzylidene-amino)propane (46):** This compound was obtained from **11**; yield 1.20 g, 61%; m.p. 66–67 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1732, 1720 (C=O), 1646 (C=N), 1602, 1471 (arom.) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.43 (s, 1 H, CH=N), 8.10 (d, $J$ = 7.6 Hz, 2 H, H arom.), 7.82 (d, $J$ = 7.6 Hz, 2 H, H arom.), 4.39 (s, 6 H, $CH_2$), 3.95 (s, 3 H, $OCH_3$), 2.07 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.5 (C=O), 166.6 (C=O), 159.9 (C=N), 139.8, 132.4, 129.9, 128.3 (C arom.), 63.8 (C-N), 63.6 ($CH_2$), 52.4 ($OCH_3$), 20.8 (3 C, $CH_3$, OAc) ppm. $C_{19}H_{23}NO_8$ (393.39): calcd. C 58.01, H 5.89, N 3.56; found C 57.95, H 5.83, N 3.47.

**1,3-Diacetoxy-2-acetoxymethyl-2-(3-nitrobenzylideneamino)propane (47):** This compound was obtained from **12**; yield 1.64 g, 86%; m.p. 74–76 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1748 (C=O), 1649 (C=N), 1612, 1469 (arom.) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.59 (t, $J$ = 1.8 Hz, 1 H, H arom.), 8.46 (s, 1 H, CH=N), 8.31 (dd, $J$ = 2.2, $J$ = 8.2 Hz, 1 H, H arom.), 8.11 (d, $J$ = 7.6 Hz, 1 H, H arom.), 7.64 (t, $J$ = 7.8 Hz, 1 H, H arom.), 4.39 (s, 6 H, $CH_2$), 2.08 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.5 (C=O), 158.4 (C=N), 148.6, 137.6, 133.8, 129.8, 125.7, 123.2 (C arom.), 63.7 (C-N), 63.5 ($CH_2$), 20.8 (3 C, $CH_3$, OAc) ppm. $C_{17}H_{20}N_2O_8$ (380.35): calcd. C 53.68, H 5.30, N 7.37; found C 53.60, H 5.31, N 7.45.

**1,3-Diacetoxy-2-acetoxymethyl-2-(3-cyanobenzylideneamino)-propane (48):** This compound was obtained from **13**; yield 1.12 g, 62%; m.p. 94–96 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2227 (C≡N), 1742 (C=O), 1645 (C=N), 1598, 1580, 1477 (arom.) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.39 (s, 1 H, CH=N), 8.08 (s, 1 H, H arom.), 8.00 (dt, $J$ = 1.2, $J$ = 1.2, $J$ = 7.6 Hz, 1 H, H arom.), 7.76 (dt, $J$ = 1.2, $J$ = 1.2, $J$ = 7.6 Hz, 1 H, H arom.), 7.58 (t, $J$ = 7.6 Hz, 1 H, H arom.), 4.39 (s, 6 H, $CH_2$), 2.09 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.5 (C=O), 158.6 (C=N), 137.0 (C≡N), 134.4, 132.4, 131.9, 129.6, 118.2, 113.2 (C arom.), 63.9 (C-N), 63.5 ($CH_2$), 20.8 (3 C, $CH_3$, OAc) ppm. $C_{18}H_{20}N_2O_6$ (360.36): calcd. C 59.99, H 5.59, N 7.77; found C 59.75, H 5.72, N 7.67.

**1,3-Diacetoxy-2-acetoxymethyl-2-(3-methoxycarbonylbenzylidene-amino)propane (49):** This compound was obtained from **14** as an oil; yield 1.59 g, 81%). IR (NaCl): $\tilde{\nu}_{max}$ = 1742 (C=O), 1649 (C=N), 1604, 1587 (arom.) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.42 (s, 1 H, CH=N), 8.37 (s, 1 H, H arom.), 8.13 (d, $J$ = 7.6 Hz, 1 H, H arom.), 8.00 (d, $J$ = 8.0 Hz, 1 H, H arom.), 7.52 (t, $J$ = 7.6 Hz, 1 H, H arom.), 4.38 (s, 6 H, $CH_2$), 3.95 (s, 3 H, $OCH_3$), 2.07 (s, 9 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.6 (C=O), 166.6 (C=O), 159.8 (C=N), 136.4, 132.2, 131.1, 130.7, 129.9, 128.9 (C arom.), 63.6 (C-N), 63.6 ($CH_2$), 52.4 ($OCH_3$), 20.9 (3 C, $CH_3$, OAc) ppm. HRMS (CI): calcd. for $C_{19}H_{23}NO_8$ $[M + H]^+$ 394.1502; found 394.1504.

**4,4-Bis(acetoxymethyl)-2-(4-nitrophenyl)oxazolidine (59):** Acetic anhydride (6.5 mL) was added to a solution of oxazolidine **8** (5.0 mmol) in pyridine (6.7 mL). The reaction mixture was kept at 0 °C for 15 min and then it was poured into ice–water. The resulting product was extracted with chloroform (3 × 50 mL) and the organic layer was washed sequentially with 1 N HCl (2 × 50 mL), a saturated solution of $NaHCO_3$ (2 × 50 mL), and distilled water (2 × 50 mL). The organic layer was dried ($MgSO_4$) and evaporated; yield 1.05 g, 62%; m.p. 69–70 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1738 (C=O), 1606, 1520, 1465 (arom.), 1249 (C–O) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.24 (d, $J$ = 8.8 Hz, 2 H, H arom.), 7.67 (d, $J$ = 8.8 Hz, 2 H, H arom.), 5.60 (s, 1 H, 2-H), 4.27 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 4.21 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 4.16 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 4.08 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 3.90 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 3.80 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 2.55 (s, 1 H, NH), 2.14, 2.07 (s, 6 H, OAc) ppm. $^1H$ NMR (400 MHz, $[D_6]$DMSO): $\delta$ = 8.24 (d, $J$ = 8.8 Hz, 2 H, H arom.), 7.71 (d, $J$ = 8.8 Hz, 2 H, H arom.), 5.63 (d, $J_{2\text{-H,NH}}$ = 9.5 Hz, 1 H, 2-H), 4.16 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 4.09 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 4.01 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 3.97 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 3.78 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 3.70 (d, $J$ = 11.2 Hz, 1 H, $CH_2$), 3.68 (d, $J_{NH,2\text{-H}}$ = 9.5 Hz, 1 H, NH), 2.06, 1.99 (s, 6 H, OAc) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.8, 170.7 (C=O), 148.2, 145.8, 127.2, 123.8 (C arom.), 91.1 (C-2), 70.6 (C-5), 65.2, 64.9 ($CH_2$), 64.4 (C-4), 20.9, 20.8 (3 C, $CH_3$, OAc) ppm. $C_{15}H_{18}N_2O_7$ (338.31): calcd. C 53.25, H 5.36, N 8.28; found C 53.06, H 5.36, N 8.25.

**Supporting Information** (see also the footnote on the first page of this article): Tables S1 and S2, Figures S1–S5, $^1H$ and $^{13}C$ NMR spectra, and computational data.

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