DOI: 10.1002/asia.201100497

# The Influence of Exocyclic Stereochemistry on the Tethered Aminohydroxylation Reaction

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**Abstract:** A new strategy that employs an exocyclic stereocenter to effect diastereocontrol in the tethered aminohydroxylation (TA) reaction is applied to the stereoselective synthesis of a range of amino alcohols in good to excellent yields, and with *anti* selectivities of up to 20:1. The influence of the reaction conditions and substrate parameters on the level of diastereocontrol is described. Furthermore, an "inside alkoxy" model is employed to rationalize the sense and degree of stereoselectivity observed in these systems.

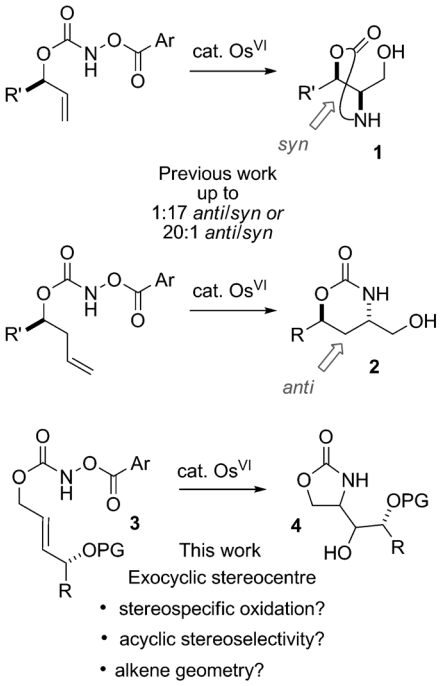
**Keywords:** allylic compounds · aminohydroxylation · chirality · heterocycles · stereoselectivity

## Introduction

The 1,2-amino alcohol motif is present in a wide range of natural products, bioactive compounds, and chiral reagents.[1] Whereas the Sharpless asymmetric aminohydroxylation (AA) reaction remains the most powerful method for the *syn*-stereospecific generation of vicinal amino alcohols directly from alkenes,[2] the low regioselectivity observed with some classes of unsymmetrical olefins has fueled research into alternative methods for the synthesis of this important functional group.[3]

One such method is the tethered aminohydroxylation (TA) reaction, in which a nitrogen source is attached to one end of the olefin, thus securing the regiochemical outcome of the osmium-catalyzed transformation.[4,5] Recent developments obviate the need for generating in situ reoxidants (typically *N*-halocarbamates) by employing bench-stable mesitoyloxycarbamates as starting materials, in which the nitrogen is introduced at the correct oxidation state to complete the catalytic cycle, thus delivering higher-yielding, cleaner reactions with lower catalyst loadings.[6–8]

Although chiral ligands do not induce enantioselectivity in the TA, the stereochemical course of the reaction can be directed by a stereocenter in the starting material. This strategy has been applied successfully in the highly diastereoselective formation of amino alcohols from both cyclic and acyclic carbamates[9,10] and amides[8] in which the stereogenic center in the starting material is positioned on the




Scheme 1. Comparison of previous and current approaches to acyclic stereocontrol in the TA reaction.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201100497.

tether between the olefin and the nitrogen source (Scheme 1).

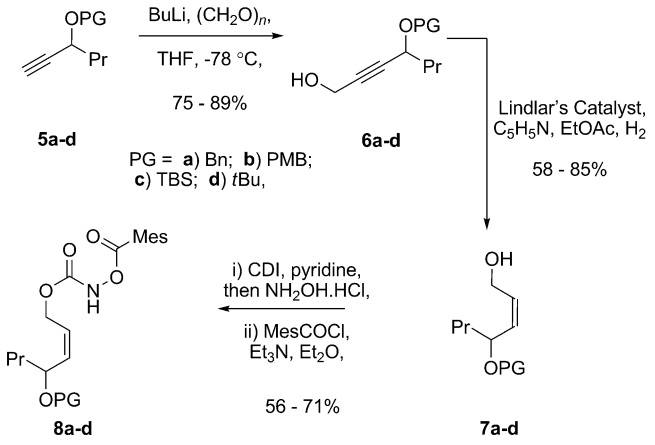
When oxidizing carbamates derived from allylic or homoallylic alcohols were used, we were able to obtain stereochemically defined amino alcohols with good levels of *syn* (**1**) or *anti* (**2**) stereoselectivity. By using these principles, the TA reaction has been used as a key step in the stereoselective synthesis of a range of biologically active compounds and natural products that uses aspects of both cyclic[11–16] and acyclic stereocontrol.[17–20]

Attention was then turned to the possibility of inducing diastereoselectivity by using a stereocenter that is located outside (*exo*) of the heterocycle formed in the reaction (see **3**→**4**). We report herein the results of this investigation, which reveal for the first time that a range of chiral allylic ethers can be oxidized into the corresponding amino alcohols in high yields and with up to 20:1 *anti*/*syn* stereoselectivity.

## Results and Discussion

### Influence of the Protecting Group Identity on the Diastereoselectivity

Preliminary investigations focused on the effect of the character of the protecting group on the diastereoselectivity in the TA reaction to form five-membered carbamates. The requisite mesitoyloxycarbamate precursors **8a–d** were synthesized in five steps from the corresponding commercially available propargylic alcohol (Scheme 2), which was protected, deprotonated, and treated with paraformaldehyde to generate alcohols **6a–d**. Reduction of the alkyne functionality using Lindlar's catalyst gave allyl alcohols **7a–d** as the *Z* isomers, as evidenced by the $^1$H NMR spectra and the observation of coupling constants in the range 10.5–11.5 Hz between the newly introduced olefinic protons. These alcohols were then rapidly transformed into the desired mesitoyloxycarbamates by a protocol previously developed by Donohoe et al.[7,21] Extra protected carbamates **8e–h** were prepared by a different route (see the Supporting Information for details).

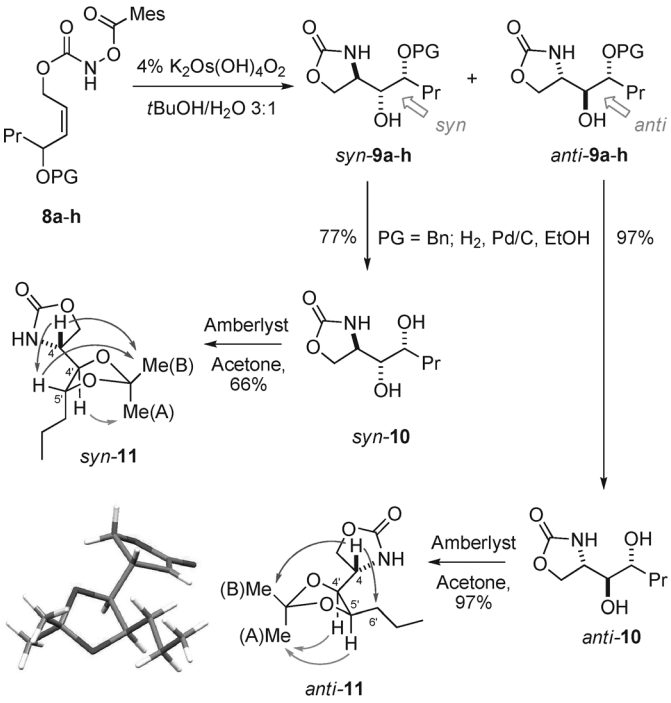



Scheme 2. Synthesis of mesitoyloxycarbamate precursors for the TA reaction. CDI = *N*,*N*′-carbonyldiimidazole, Mes = Mesityl = $Me_3C_6H_2$.

Submission of mesitoyloxycarbamates **8a–h** to the typical TA reaction conditions of 4% $K_2Os(O)_2OH_4$ in *t*BuOH/$H_2O$ (3:1) delivered the desired carbamates **9a–h** as a mixture of diastereomers in ratios determined by $^1$H NMR spectroscopy or HPLC analysis of the crude product (Table 1). Benzyl-protected amino alcohols *syn*-**9a** and *anti*-**9a** were separated by flash column chromatography before being hydrogenated to reveal the corresponding diols *syn*-**10** and *anti*-**10**, which were readily transformed into acetonides *syn*-**11** and *anti*-**11**.

The acetonide derived from the major isomer was then subjected to nuclear Overhauser effect (NOE) experiments

Table 1. TA reaction of acyclic mesitoyloxycarbamate precursors that bear a range of protecting groups. PMB = *para*-methoxybenzyl, SM = starting material, PG = protecting group.




| Entry | SM | OPG | Yield [%][a] | *syn*/*anti*[b] |
|---|---|---|---|---|
| 1 | **8a** | OBn | 74 (**9a**) | 1:3 |
| 2 | **8b** | OPMB | 79 (**9b**) | 1:3 |
| 3 | **8c** | OTBS | 78 (**9c**) | 1:3 |
| 4 | **8d** | O*t*Bu | 93 (**9d**) | 1:3 |
| 5 | **8e** | OAc | –[c] (**9e**) | 1:1.5 |
| 6 | **8f** | OC(O)Mes | 80 (**9f**) | 1:1.5[d] |
| 7 | **8g** | OMe | 82 (**9g**) | 1:3[d] |
| 8 | **8h** | OH | 68 (**9h**) | 1:1.5 |

[a] Combined yield of both diastereomers before separation. [b] Ratios were determined by HPLC analysis or by analysis of crude $^1$H NMR spectra. [c] Decomposition of this carbamate occurred during silica gel chromatography, but analysis of the crude $^1$H NMR spectrum shows >95% conversion. Relative stereochemistry could not be determined but was tentatively assigned as 1:1.5 *syn*/*anti*. [d] Deprotection conditions led to decomposition of the substrate, therefore the relative stereochemistry could not be determined. However, the major isomer was tentatively assigned as *anti*.

to confirm that the reaction proceeds with *anti*-selective addition of the tethered imido osmium species to the olefin. Evidence for this assignment can be seen in the strong enhancement observed in the signal from acetonide *anti*-**11** Me(A) when either C(4′)H or C(5′)H was irradiated, thereby suggesting that they are on the same face of the five-membered ring. Furthermore, irradiation of C(4)H leads to the enhancement of both C(6′)$H_2$ and Me(B), which is consistent with the *anti* structure proposed. Further confirmation of this assignment was provided by an X-ray crystal structure of *anti*-**11**.

Moreover, NOE spectroscopic analysis also revealed that the acetonide derived from the minor amino alcohol diastereomer (*syn*-**11**) possessed the complementary *syn* stereochemistry; irradiation of C(4′)H led to an enhancement in Me(A), whereas irradiation of C(5′)H led to an enhancement in Me(B). This assignment was further confirmed by the observation that irradiation of C(4)H leads to an enhancement in both C(5′)H and Me(B). The relative stereochemistry of carbamates **9b–d** and **9h**, which bear alternative alkoxy substituents, was then confirmed by comparison of $^1$H NMR spectra of the diols formed following deprotection with the $^1$H NMR spectra of diols *syn*-**10** and *anti*-**10** synthesized en route to fully characterized acetonides *syn*-**11** and *anti*-**11**.

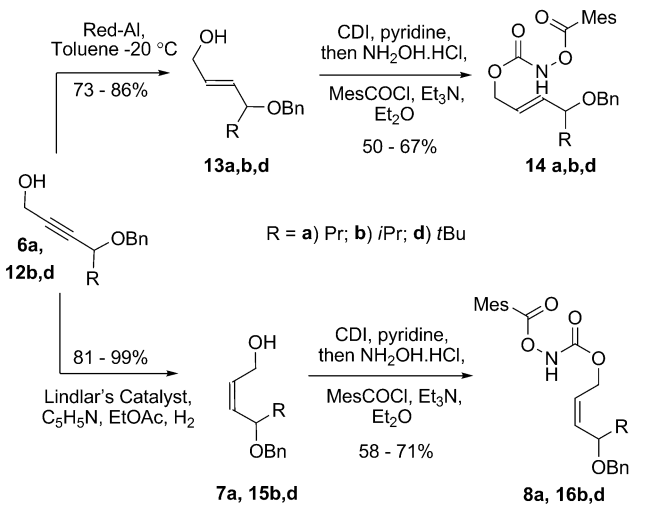
In results that parallel observations in the related osmium-catalyzed dihydroxylation of chiral allylic ethers,[22] it was concluded that changing the steric bulk of the protecting groups had very little effect on the diastereoselectivity of the reaction (Table 1, compare entries 4 and 7 in which both displayed 3:1 *anti* diastereoselectivity). Meanwhile the use of acyl protecting groups (Table 1, entries 5 and 6) or free alcohols (Table 1, entry 8) to direct the stereochemical course of the reaction resulted in reduced levels of *anti* diastereoselectivity.

It was also observed that the reaction proceeded with similar diastereoselectivities at all temperatures in the range between reflux (80 °C) and freezing (0 °C),[23] and that application of different solvent systems did not lead to a significant change either in diastereoselectivity or in the range of temperatures at which the reaction could operate. Furthermore, employment of ligands for osmium such as Hünig's base, hydroquinidine(anthraquinone-1,4-diyl) diether ((DHQD)$_2$AQN), and citric acid (not shown) did not significantly alter the sense or degree of diastereoselectivity in this transformation.[4]

### Influence of the Allylic Substituent on the Diastereoselectivity

Next it was decided to investigate the influence of the allylic substituent (R) on the diastereoselectivity of the reaction.[24,25] The benzyl ether was chosen as a common (and easily removed) standard as it was hoped that this would allow the diastereomeric ratios to be determined conveniently by HPLC.

At first, (*E*)-allylic alcohols **13a**, **13b**, and **13d** were accessed by the stereoselective reduction of the corresponding alkynes **6a** and **12b** and **12d** with sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al; Scheme 3), as confirmed in the $^1$H NMR spectrum by the observation of coupling constants in the range of 15.4–15.7 Hz between the newly introduced olefinic protons; these values were significantly larger than the values obtained for the analogous *Z* isomers. On exposure to the reaction conditions, the (*E*)-mesitoyloxycarbamates **14a–d** underwent the key TA transformation to generate the corresponding carbamates in good yields with good to excellent diastereoselectivity (Table 2). Although the diastereoisomeric amino alcohols were no longer separable, the relative stereochemistry of the major isomers was once again assigned as *anti* by carrying out NOE analysis on the corresponding acetonide derivative formed after deprotection. Correlation was also made to acetonide *anti*-**18a**, the structure of which was proven by X-ray crystallography after being separated from the minor isomer using flash column chromatography.

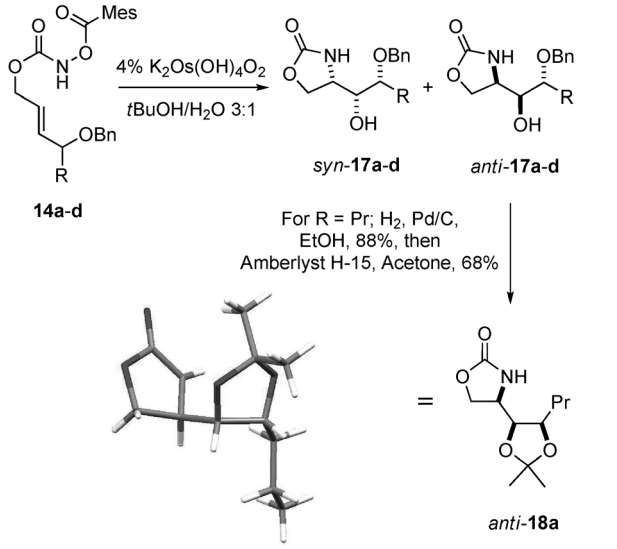



Scheme 3. Synthesis of mesitoyloxycarbamate precursors for the TA reaction. Red-Al = sodium bis(2-methoxyethoxy)aluminumhydride. Compounds **14c** and **16c** (R = Ph) were prepared through a different route; see the Supporting Information for details.

Although there is a clear trend towards increased diastereoselectivity as the steric bulk of the R substituent increases, phenyl appears to be anomalous as it has a larger *A* value ($A$(Ph) = 2.9 kcal mol$^{-1}$) than *i*Pr ($A$(*i*Pr) = 2.15 kcal mol$^{-1}$) yet exhibits lower diastereoselectivity than Pr ($A$(Pr) = 1.8 kcal mol$^{-1}$). This trend can be explained by the uneven distribution of steric bulk about the C–Ph axis, which allows a phenyl to twist to adopt the conformation that minimizes steric repulsion, with the result that the *A* value does not always reflect its true steric bulk.[26] The same anomaly was reported by Houk et al. following studies in the related cycloaddition of nitrile oxides with chiral allylic ethers.[27]

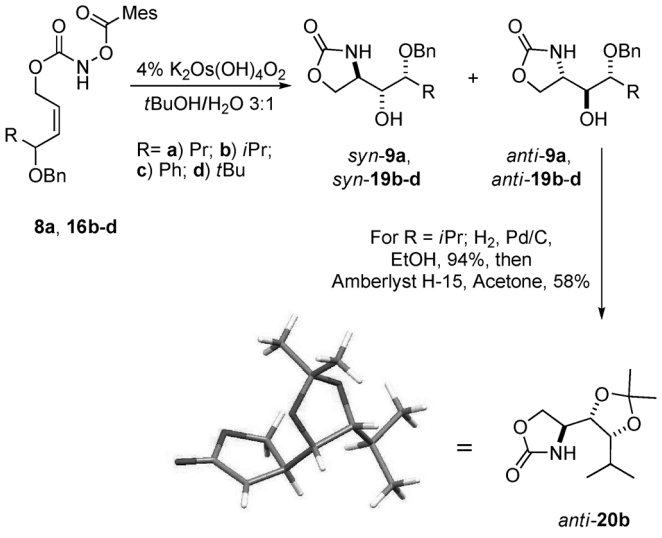
Table 2. TA reaction of acyclic mesitoyloxycarbamate precursors that bear allylic substituents.




| Entry | R | SM | Yield [%] | *syn*/*anti* |
|---|---|---|---|---|
| 1 | Pr | **14a** | 79 (**17a**) | 1:5[a] |
| 2 | *i*Pr | **14b** | 71 (**17b**) | 1:7[a] |
| 3 | Ph | **14c** | 81 (**17c**) | 1:1.5[b] |
| 4 | *t*Bu | **14d** | 90 (**17d**) | <1:20[a] |

[a] Ratios were determined by HPLC analysis or by analysis of the crude $^1$H NMR spectra. [b] Ratio was determined by analysis of the crude $^{13}$C NMR spectrum. Relative stereochemistry could not be determined but was tentatively assigned as 1:1.5 *syn*/*anti*.

Table 3. TA reaction of acyclic mesitoyloxycarbamate precursors that bear allylic substituents.




| Entry | R | SM | Yield [%] | *syn*/*anti*[a] |
|---|---|---|---|---|
| 1 | Pr | **8a** | 74 (**9a**) | 1:3[b] |
| 2 | *i*Pr | **16b** | 85 (**19b**) | 1:4[b] |
| 3 | Ph | **16c** | 88 (**19c**) | 1:2 |
| 4 | *t*Bu | **16d** | 95 (**19d**) | 1:6 |

[a] Ratios were determined by HPLC analysis or by analysis of crude $^1$H NMR spectra. The relative stereochemistry was assigned in all cases by NOE spectroscopy of the acetonide that was formed following removal of the benzyl group from the major diastereomer. [b] In these cases, the relative stereochemistry was also assigned by NOE spectroscopy of the acetonide that was formed following removal of the benzyl group from the minor diastereomer.

Interestingly, the corresponding (*Z*)-mesitoyloxycarbamate precursors **16b–d** also underwent the desired TA transformation to generate the corresponding carbamates in good yields, albeit with slightly lower levels of diastereoselectivity (Table 3). Transformation of the major and minor diastereomers into the corresponding acetonides provided evidence that these TA reactions also proceed with *anti* selectivity; NOE studies closely paralleled those previously performed on acetonides *anti*-**11** and *syn*-**11** (Table 1). Subsequent attainment of the X-ray structure of acetonide *anti*-**20b** lent further weight to this stereochemical assignment. In line with results obtained with the *E* alkenes, there is a clear trend towards increasing *anti* selectivity as the steric bulk of the R group increases, although the phenyl group is once again anomalous. The results obtained so far revealed good levels of *anti* diastereoselectivity and, as expected, regioselectivity and *syn* stereospecificity for aminohydroxylation across the alkene.

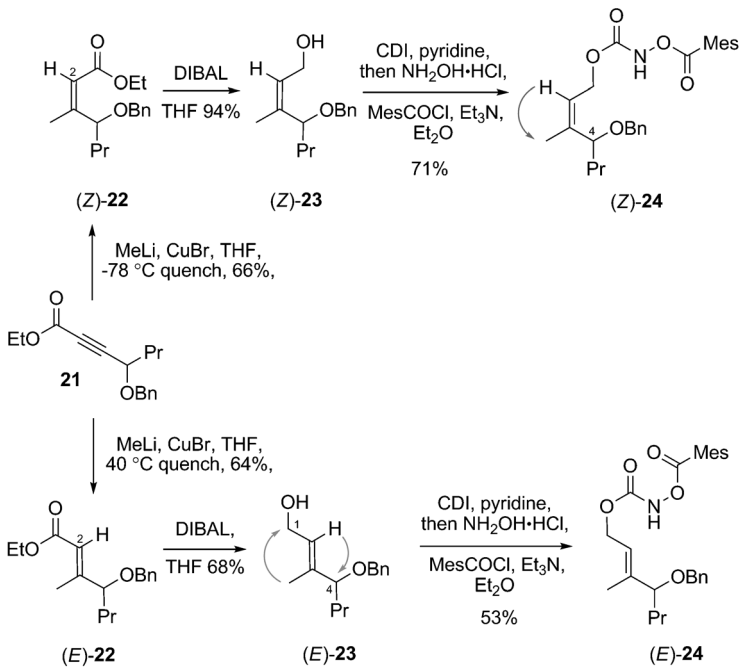
### Alternative Olefin Substitution Patterns

The synthesis of trisubstituted alkenes equipped with the mesitoyloxycarbamate moiety was undertaken next to investigate the diastereoselectivity of the TA reaction with more highly substituted olefins. It was found that the addition of lithium dimethyl cuprate to ester **21** selectively delivered esters (*Z*)-**22** and (*E*)-**22** when quenched at at −78 and 40 °C, respectively (Scheme 4).[28] Reduction afforded the corresponding allylic alcohols (*Z*)-**23** and (*E*)-**23**, which were subsequently converted into the desired reaction precursors (*Z*)-**24** and (*E*)-**24**.

The stereodivergence that resulted from the 1,4-cuprate addition to alkyne **21** was confirmed by NOE spectroscopy; irradiation of the olefinic signal in mesitoyloxycarbamate (*Z*)-**24** delivered an enhancement in the methyl signal but not in the signal that originates from C(4)H, thus establishing that *syn* carbocupration had occurred. Meanwhile, NOE analysis of alcohol (*E*)-**23** strongly suggested that the 1,4-cuprate addition had occurred with overall *anti* selectivity, as irradiation of the alkene proton led to an enhancement in C(4)H, whereas irradiation of the methyl substituent led to a strong enhancement in C(1)H$_2$. Meanwhile, the regioselectivity of this transformation was confirmed by COSY $^1$H NMR spectroscopy of esters (*Z*)-**22** and (*E*)-**22**, in which the characteristic vinyl protons C(2)H at $\delta = 5.83$ and 5.87 ppm do not couple to C(4)H.

Submission of (*Z*)-**24** and (*E*)-**24** to the TA reaction conditions delivered carbamates in good yields and with a similar degree of *anti* diastereoselectivity to that observed with the analogous disubstituted systems (Table 4). The sense of diastereoselectivity was once again confirmed by NOE spectroscopy of acetonide derivatives; amino alcohols *anti*-(*Z*)-




Scheme 4. Synthesis of trisubstituted mesitoyloxycarbamate precursors for the tethered aminohydroxylation reaction. DIBAL = diisobutylaluminium hydride.

**25** and *syn*-(*Z*)-**25** were separated by flash column chromatography and transformed into the acetonides *anti*-(*Z*)-**26** and *syn*-(*Z*)-**26** by using the procedure previously developed for disubstituted analogues.

Once again, NOE analysis of the major *Z* diastereomer *anti*-(*Z*)-**26** confirmed that the active osmium species in the TA reaction undergoes cycloaddition to the *anti* face of 1,1,2-trisubstituted olefin (*Z*)-**24**. Irradiation of C(5′)H delivers a strong enhancement in both Me(A) and Me(C), whereas irradiation of C(4)H delivers an enhancement of Me(B) and the alkyl side-chain protons. Meanwhile, the minor acetonide *syn*-(*Z*)-**26** exhibited NOE spectra consistent with *syn* stereochemistry, as a strong enhancement was observed in both Me(B) and C(4)H upon irradiation of C(5′)H. Further confirmation of this assignment was provided by irradiation of Me(C), which delivers an enhancement only in the alkyl side-chain protons and Me(A).

Although carbamates *anti*-(*E*)-**25** and *syn*-(*E*)-**25** could not be separated, NOE analysis of the major acetonide derivative *anti*-(*E*)-**26** established that the major product was that which resulted from addition of the osmium species *anti* to the existing stereogenic center; irradiation of C(5′)H delivered a strong enhancement in both Me(A) and Me(C), whereas irradiation of C(4)H gave an enhancement both in Me(B) and also in protons on the alkyl side chain.

### Analysis of Trends in Diastereoselectivity

The *anti* selectivity observed in the tethered aminohydroxylation of *E* olefins (Table 2) can be rationalized by the direct application of a model developed by Houk et al. for the related osmium tetroxide-mediated dihydroxylation of chiral allylic ethers,[27,29,30] in which "inside alkoxy" transition state **TS1** is lower in energy than the lowest-energy *syn*-selective transition state **TS2** (Scheme 5).

Furthermore, this model offers a plausible mechanistic rationale for the rise in *anti* diastereoselectivity as the steric bulk of R increases; the *syn* transition state will become increasingly disfavored with respect to the *anti* transition state as a result of the increasing steric repulsion between the incoming osmium oxo ligand and the R group.

Application of Houk and coworkers' model for the osmium-mediated dihydroxylation of chiral (*Z*)-allylic ethers to the TA reaction rationalizes the *anti* selectivity of (*Z*)-olefinic substrates (Table 3); there are two transition states that deliver *anti* stereochemistry at a lower energy than the lowest-energy *syn* transition state **TS5** (Scheme 6).

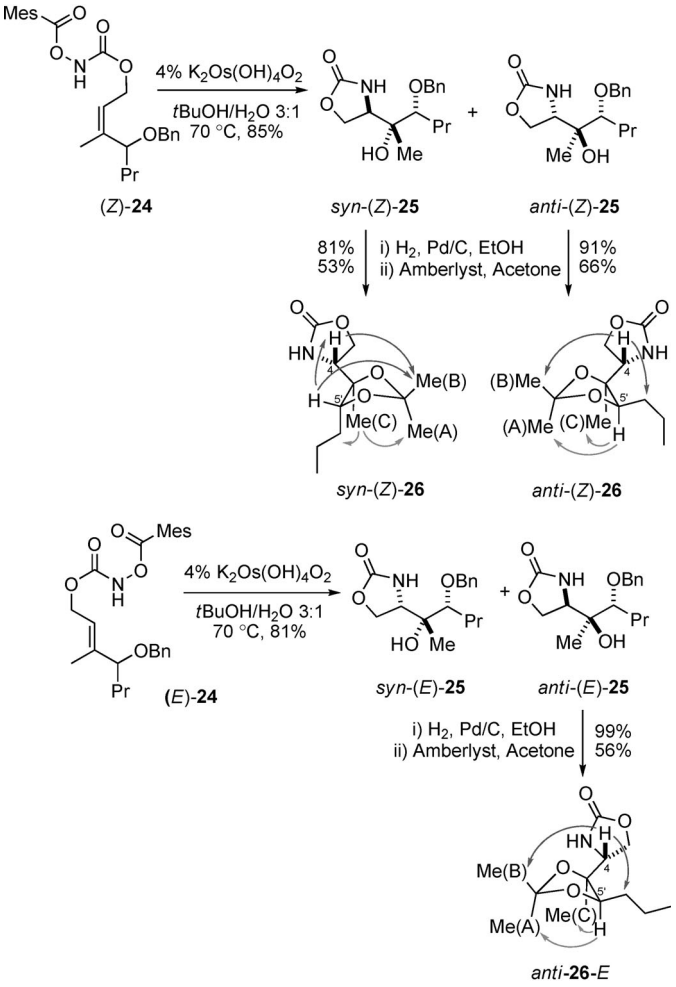
Considering these models provide an explanation for the observed rise in the *anti* diastereoselectivity in the TA reaction that accompanies the increasing bulk of R. Whereas **TS3** and **TS5** experience increasing steric repulsion between the incoming osmium oxo ligand and the R group, *anti*-selective **TS4** will become the most stable, and *anti* products will be increasingly favored.

The less pronounced increase in *anti* diastereoselectivity as R increases in size in *Z* olefins compared to the analogous *E* substrates may also be explained by this model: as R increases in steric bulk in the *Z* system, the two *anti*-selective transition states **TS3** and **TS4** are affected differently. **TS3** will become less stable whereas **TS4** becomes more stable relative to *syn*-selective **TS5**. As a result, the rise in diastereoselectivity that accompanies the increasing steric bulk of the allylic substituent in *Z* alkenes is not as pronounced as in *E* alkenes.

In each case, the trisubstituted double bond gave similar *anti* stereoselectivity to the disubstituted examples, which is consistent with results from the laboratory of Stork et al. for dihydroxylation of trisubstituted alkenes.[31] This observation suggests that the additional $A^{1,2}$ strain incurred upon introduction of a methyl group does not significantly influence the relative energies of transition states that lead to *anti* and *syn* transition states in the TA of either *E* or *Z* olefins.

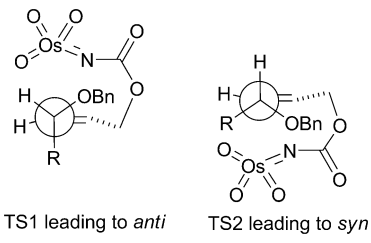
  

Table 4. Tethered aminohydroxylation reaction of acyclic mesitoyloxycarbamate precursors that bear allylic substituents.




| Entry | *E*/*Z* | SM | Yield [%] | *syn*/*anti* |
|---|---|---|---|---|
| 1 | *Z* | (*Z*)-**24** | 85 ((*Z*)-**25**) | 1:2[a] |
| 2 | *E* | (*E*)-**24** | 81 ((*E*)-**25**) | 1:4[b] |

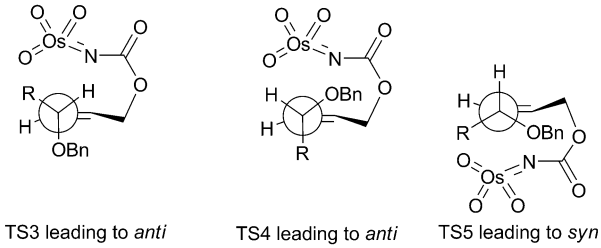
[a] Ratios were determined by HPLC analysis. [b] Ratios were determined by analysis of the crude $^1$H NMR spectrum.




Scheme 5. Lowest-energy transition states leading to *anti* and *syn* products in *E* alkenes from Houk and co-workers' model of diastereoselectivity in the dihydroxylation of chiral allylic ethers.

## Conclusion

A new strategy for the control of diastereoselectivity in the tethered aminohydroxylation reaction has been developed, which proceeds with high yields and *anti* selectivities of up to 20:1 (all with complete regioselectivity and *syn* stereospecificity) by placing a stereogenic center *exo* to the newly forming ring. An adaptation of Houk and co-workers' inside alkoxy effect has been applied to rationalize the stereochemical outcome of the reaction. It is hoped that these developments will lead to the further application of this methodology in the stereoselective synthesis of chiral amino alcohols in complex molecular settings.




Scheme 6. Lowest-energy transition states leading to *anti* and *syn* products in *Z* alkenes from Houk and co-workers' model of diastereoselectivity in the dihydroxylation of chiral allylic ethers.

## Experimental Section

*General*

Tetrahydrofuran and dichloromethane were purified prior to use by filtration through two activated alumina columns (activated basic aluminium oxide, Brockmann I, standard grade, ≈150 mesh, 58 Å). Reagents obtained from Acros, Aldrich, Avocado, Fluka, and Lancaster fine chemicals suppliers were used directly. Flash column chromatography was carried out using silica gel 60 (0.040–0.063 mm; Merck) using head pressure by means of head bellows. Thin-layer chromatography was performed on commercially available precoated aluminum-backed plates (0.25 mm silica gel with fluorescent indicator UV254). Visualization was achieved by either the quenching of UV fluorescence, $KMnO_4$, or vanillin stain. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AVANCE AV400 (400 and 100.6 MHz), Bruker DPX400 (400 and 100.6 MHz), or a Bruker AVANCE AV500 (500 and 125.7 MHz) spectrometer. Signal positions were recorded in ppm with the abbreviations s, d, t, q, qu, br, app, and m denoting singlet, doublet, triplet, quartet, quintet, broad, apparent, and multiplet, respectively. All NMR spectroscopic chemical shifts ($\delta$) were referenced to residual solvent peaks or to $SiMe_4$ as an internal standard. All coupling constants ($J$) are quoted in Hz. Infrared spectra were recorded with a Bruker Tensor 27 FTIR spectrometer. Spectra were analyzed either as thin films between NaCl plates, KBr disks, or in a chloroform solution cell. Mass spectra ($m/z$) and HRMS were recorded under the conditions of electrospray (ESI), chemical (CI), and field (FI) ionization. Melting points were obtained with a Leica VMTG heated-stage microscope and are uncorrected. "Petrol" refers to the fraction of petroleum ether boiling in the range 40–60 °C unless otherwise stated, and "ether" refers to diethyl ether.

*General Procedure for Mesitoyloxycarbamate Formation*

*N*,*N*′-Carbonyldiimidazole (3 equiv) was added to a stirred solution of alcohol in pyridine (2 mL mmol$^{-1}$) at 40 °C. After TLC analysis indicated that complete consumption of the starting material had occurred, the mixture was cooled to 0 °C, and hydroxylamine hydrochloride (10 equiv) was added. After warming to room temperature, the reaction was quenched with 1 M HCl (10 mL mmol$^{-1}$), and the aqueous layer was extracted with diethyl ether (10 mL mmol$^{-1}$) and ethyl acetate (10 mL mmol$^{-1}$). The combined organic layers were then washed with water (10 mL mmol$^{-1}$) and brine (10 mL mmol$^{-1}$), dried over $Na_2SO_4$, and

filtered before the solvents were azeotropically removed with toluene. Triethylamine (0.9 equiv) was then added to a solution of the resultant crude product in diethyl ether (5 mL mmol$^{-1}$) at 0 °C under argon, and trimethylbenzoyl chloride (0.9 equiv) was added dropwise. After warming to room temperature overnight, the reaction was quenched with 1 M HCl (10 mL mmol$^{-1}$), and the aqueous layer was extracted with $Et_2O$ (10 mL mmol$^{-1}$ × 2). The combined organic layers were then washed sequentially with water (10 mL mmol$^{-1}$), an aqueous saturated solution of $NaHCO_3$ (10 mL mmol$^{-1}$), and brine (10 mL mmol$^{-1}$) before being dried over $Na_2SO_4$, filtered, and concentrated in vacuo to afford the crude product.

*General Procedure for TA Reaction*

Potassium osmate dihydrate (4 mol%) in water (0.5 mL mmol$^{-1}$) was added to a stirred solution of mesitoyloxycarbamate in *tert*-butanol/water (3:1, 20 mL mmol$^{-1}$). After TLC analysis indicated that complete consumption of the starting material had occurred, the reaction was quenched by addition of $Na_2SO_3$ (200 mg mmol$^{-1}$) and the resulting solution was left to stir for 30 min. The solvents were then azeotropically removed with toluene to afford the crude product.

*(±)(R)-4-[(1′R,2′S)-2′-(Benzyloxy)-1′-hydroxypentyl]oxazolidin-2-one (anti-**9a**)*

M.p. 97–103 °C; $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.96 (t, $J$ = 7.2 Hz, 3H), 1.34–1.70 (m, 4H), 3.44 (app q, $J$ = 5.4 Hz, 1H), 3.67 (dd, $J$ = 5.4, 3.7 Hz, 1H), 4.05 (ddd, $J$ = 8.7, 5.9, 3.7 Hz, 1H), 4.24 (app t, $J$ = 8.7 Hz, 1H), 4.42 (dd, $J$ = 8.7, 5.9 Hz, 1H), 4.53 (d, $J$ = 11.4 Hz, 1H), 4.59 (d, $J$ = 11.4 Hz, 1H), 7.26–7.40 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 13.6, 18.1, 32.2, 54.1, 66.4, 72.2, 72.6, 80.1, 127.8, 128.2, 128.4, 138.7, 161.6 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3386 (br s), 3031 (w), 2958 (s), 2468 (w), 1746 (s), 1454 (m), 1408 (m), 1243 (m), 1093 (m), 698 cm$^{-1}$ (m); HRMS (ESI): $m/z$ calcd for $C_{15}H_{21}NNaO_4$: 302.1363; found: 302.1363 (−0.16 ppm).

*(±)(R)-4-[(1′R,2′R)-2′-(Benzyloxy)-1′-hydroxypentyl]oxazolidin-2-one (syn-**9a**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.97 (t, $J$ = 7.3 Hz, 3H), 1.35–1.51 (m, 2H), 1.59–1.73 (m, 2H), 3.49 (app td, $J$ = 6.7, 2.6 Hz, 1H), 3.64 (dd, $J$ = 5.3, 2.6 Hz, 1H), 4.00 (app dt, $J$ = 8.7, 5.3 Hz, 1H), 4.38 (app t, $J$ = 8.8 Hz, 1H), 4.48 (dd, $J$ = 8.8, 5.8 Hz, 1H), 4.51 (d, $J$ = 11.4 Hz, 1H), 4.63 (d, $J$ = 11.4 Hz, 1H), 7.25–7.41 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.6, 20.0, 32.9, 55.9, 68.4, 73.0, 73.5, 80.8, 128.8, 129.2, 129.4, 139.9, 162.5 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3384 (br s), 3031 (w), 2958 (s), 2872 (s), 1743 (s), 1496 (s), 1454 (s), 1409 (s), 1243 (s), 1093 (s), 943 (w), 736 cm$^{-1}$ (s); HRMS (ESI): $m/z$ calcd for $C_{15}H_{21}NNaO_4$: 302.1363; found: 302.1363 (−0.3 ppm).

*Diastereomeric Mixture of Major Isomer anti-**9b** and Minor Isomer syn-**9b***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.95 (s, $J$ = 7.3 Hz, 3H), 1.21–1.76 (m, 4H), 3.42 (app q, $J$ = 5.6 Hz, 1H), 3.60–3.66 (m, 1H), 3.79 (s, 3H), 4.02 (ddd, $J$ = 8.7, 5.4, 4.0 Hz, 1H), 4.22 (app t, $J$ = 8.7 Hz, 1H), 4.32–4.43 (m, 1H), 4.45 (d, $J$ = 11.4 Hz, 1H), 4.51 (d, $J$ = 11.4 Hz, 1H), 6.91 (d, $J$ = 8.5 Hz, 2H), 7.27 ppm (d, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 13.7, 18.1, 32.5, 54.1, 54.7, 66.4, 71.8, 72.7, 79.6, 113.8, 129.9, 130.7, 159.9, 161.6 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3396 (br s), 2959 (s), 1747 (s), 1612 (w), 1514 (m), 1465 (s), 1249 (s), 1175 (m), 1032 cm$^{-1}$ (s); HRMS (ESI): $m/z$ calcd for $C_{16}H_{23}NNaO_5$: 332.1468; found: 332.1466 (0.8 ppm).

*(±)(R)-4-[(1′R,2′S)-2′-[(tert-Butyldimethylsilyl)oxy]-1′-hydroxypentyl]oxazolidin-2-one (anti-**9c**)*

M.p. 124–126 °C; $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.10 (m, 6H), 0.88–0.98 (m, 12H), 1.31–1.53 (m, 3H), 1.53–1.69 (m, 1H), 3.60 (dd, $J$ = 4.9, 3.3 Hz, 1H), 3.72 (app q, 1H), 4.07 (ddd, $J$ = 8.6, 6.1, 3.3 Hz, 1H), 4.35 (app t, $J$ = 8.6 Hz, 1H), 4.50 ppm (dd, $J$ = 8.6, 5.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = −5.3, −5.3, 13.7, 17.9, 20.2, 25.4, 35.9, 53.7, 66.3, 73.4, 74.0, 161.7 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3300 (br w), 2930 (s), 1741 (s), 1513 (s), 1249 (s), 1095 cm$^{-1}$ (s); HRMS (ESI): $m/z$ calcd for $C_{14}H_{29}NNaO_4Si$: 326.1758; found: 326.1760 (−0.61 ppm).

*(±)(R)-4-[(1′R,2′R)-2′-(tert-Butyldimethylsilyloxy)-1′-hydroxypentyl]oxazolidin-2-one (syn-**9c**)*

M.p. 111–115 °C; $^1$H NMR (400 MHz, $CD_3OD$): 0.11–0.16 (m, 6H), 0.95 (m, 12H), 1.30–1.50 (m, 4H), 3.57 (dd, $J$ = 5.0, 3.0 Hz, 1H), 3.77 (td, $J$ = 6.0, 3.0 Hz, 1H), 4.02 (dt, $J$ = 8.5, 5.0 Hz, 1H), 4.45 (app t, $J$ = 8.5 Hz, 1H), 4.50 ppm (dd, $J$ = 8.8, 5.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = −4.3, −4.1, 14.5, 19.0, 20.2, 26.4, 36.3, 55.2, 68.2, 74.5, 74.8, 162.4 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3385 (br m), 2930 (m), 1742 (s), 1472 (m), 1254 (m), 1099 (m), 1028 (m), 965 (m), 936 (m), 835 (w), 776 cm$^{-1}$ (w); HRMS (ESI): $m/z$ calcd for $C_{14}H_{29}NNaO_4Si$: 326.1758; found: 326.1757 (0.4 ppm).

*Diastereomeric Mixture of Major Isomer anti-**9d** with Minor Isomer syn-**9d***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.90–1.00 (t, $J$ = 7.3 Hz, 3H), 1.18–1.25 (m, 9H), 1.29–1.64 (m, 4H), 3.54–3.66 (m, 2H), 4.02 (ddd, $J$ = 9.6, 5.8, 4.0 Hz, 1H), 4.39 (t, $J$ = 8.8 Hz, 1H), 4.51 ppm (dd, $J$ = 8.8, 5.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 13.8, 18.4, 28.1, 34.9, 53.8, 67.1, 73.1, 73.7, 74.2, 161.7 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3386 (br s), 3031 (w), 2958 (s), 2468 (w), 1746 (s), 1454 (m), 1408 (m), 1243 (m), 1093 (m), 698 cm$^{-1}$ (m); HRMS (ESI): $m/z$ calcd for $C_{12}H_{23}NNaO_4$: 268.1519; found: 268.1518 (0.3 ppm).

*Diastereomeric Mixture of Major Isomer anti-**9e** with Minor Isomer syn-**9e***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 1.00 (t, $J$ = 7.3 Hz, 3H), 1.36–1.62 (m, 2H), 1.63–1.87 (m, 2H), 2.22–2.25 (s, 3H), 3.82 (t, $J$ = 4.0 Hz, 1H), 4.04 (ddd, $J$ = 9.0, 5.6, 4.0 Hz, 1H), 4.34 (app t, $J$ = 9.0 Hz, 1H), 4.47 (dd, $J$ = 9.0, 5.6 Hz, 1H), 5.20 ppm (td, $J$ = 8.3, 4.3 Hz, 1H); $^{13}$C NMR (63 MHz, $CD_3OD$): $\delta$ = 13.1, 18.7, 19.9, 32.6, 54.4, 66.1, 72.7, 74.1, 161.2, 171.7 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3382 (br s), 2960 (s), 1740 (s), 1375 (m), 1241 cm$^{-1}$ (w); HRMS (ESI): $m/z$ calcd for $C_{10}H_{17}NNaO_5$: 254.0999; found: 254.1000 (−0.2 ppm).

*Diastereomeric Mixture of Major Isomer anti-**9f** with Minor Isomer syn-**9f***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 1.00 (t, $J$ = 6.5 Hz, 3H), 1.37–1.62 (m, 2H), 1.65–1.89 (m, 2H), 2.26–2.29 (m, 3H), 2.30 (s, 6H), 3.82 (app t, $J$ = 4.5 Hz, 1H), 4.04 (ddd, $J$ = 9.1, 5.1, 4.5 Hz, 1H), 4.35 (app t, $J$ = 9.1 Hz, 1H), 4.47 (dd, $J$ = 9.1, 5.1 Hz, 1H), 5.20 (ddd, $J$ = 8.3, 4.5, 4.3 Hz, 1H), 6.90 ppm (s, 2H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 14.3, 19.9, 20.1, 21.2, 33.1, 54.9, 67.3, 73.3, 76.7, 129.5, 132.3, 136.0, 140.7, 162.5, 171.5 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3374 (br s), 2961 (s), 1727 (s), 1611 (w), 1427 (s), 1261 (m), 1170 (s), 1077 (w), 800 cm$^{-1}$ (w); HRMS (ESI): $m/z$ calcd for $C_{18}H_{25}NNaO_5$: 358.1625; found: 358.1625 (0.0 ppm).

*Diastereomeric Mixture of Major Isomer anti-**9g** with Minor Isomer syn-**9g***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.97 (t, $J$ = 7.1 Hz, 3H), 1.32–1.67 (m, 4H), 3.20 (q, $J$ = 5.3 Hz, 1H), 3.37 (s, 3H), 3.61 (dd, $J$ = 5.3, 4.0 Hz, 1H), 4.03 (ddd, $J$ = 9.0, 6.0, 4.0 Hz, 1H), 4.41 (app t, $J$ = 9.0 Hz, 1H), 4.48 ppm (dd, $J$ = 9.0, 6.0 Hz, 1H); $^{13}$C NMR (126 MHz, $CD_3OD$): $\delta$ = 14.6, 19.1, 33.3, 55.3, 58.3, 67.7, 73.6, 83.7, 162.7 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 2923 (m), 1684 (s), 1609 (m), 1434 (m), 1292 (s), 1178 (w), 1097 (w), 856 cm$^{-1}$ (w); HRMS (ESI): $m/z$ calcd for $C_9H_{17}NNaO_4$: 226.1050; found: 226.1059 (−4.3 ppm).

*(±)(R)-4-[(1′R,2′S)-1′,2′-Dihydroxypentyl]oxazolidin-2-one (anti-**9h**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.97 (t, $J$ = 7.1 Hz, 3H), 1.28–1.47 (m, 2H), 1.50–1.71 (m, 2H), 3.39–3.48 (m, 2H), 4.13 (ddd, $J$ = 8.8, 5.8, 3.0 Hz, 1H), 4.41 (app t, $J$ = 8.8 Hz, 1H), 4.48 ppm (dd, $J$ = 8.8, 5.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 13.4, 18.7, 35.9, 54.4, 66.2, 72.3, 74.7, 161.7 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3375 (br s), 2921 (s), 1738 (s), 1416 (w),

1258 (w), 1041 $cm^{-1}$ (m); HRMS (ESI): *m/z* calcd for $C_8H_{15}NNaO_4$: 212.0893; found: 212.0893 (0.04 ppm).

*(±)(R)-4-[(1′R,2′R)-1′,2′-Dihydroxypentyl]oxazolidin-2-one (anti-**9h**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.98 (t, $J$ = 7.3 Hz, 3H), 1.34–1.64 (m, 4H), 3.46 (dd, $J$ = 5.7, 2.2 Hz, 1H), 3.56 (ddd, $J$ = 7.9, 5.0, 2.2 Hz, 1H), 4.01 (appdt, $J$ = 8.8, 5.7 Hz, 1H), 4.46 (appt, $J$ = 8.8 Hz, 1H), 4.52 ppm (dd, $J$ = 8.8, 6.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 14.4, 20.1, 36.8, 56.0, 68.6, 72.2, 75.2, 162.6 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3375 (brs), 2921 (s), 1738 (s), 1416 (w), 1258 (m), 1041 $cm^{-1}$ (m); HRMS (ESI): *m/z* calcd for $C_8H_{15}NNaO_4$: 212.0893; found: 212.0894 (−0.3 ppm).

*Diastereomeric Mixture of Major Isomer anti-**17a** with Minor Isomer syn-**17a***

Data are given for the major isomer. M.p. 88–91 °C; $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.96 (t, $J$ = 7.3 Hz, 3H), 1.34–1.57 (m, 2H), 1.58–1.79 (m, 2H), 3.40–3.51 (m, 2H), 4.10 (ddd, $J$ = 9.0, 6.1, 4.0 Hz, 1H), 4.24 (dd, $J$ = 9.0, 6.1 Hz, 1H), 4.43 (appt, $J$ = 9.0 Hz, 1H), 4.52 (d, $J$ = 11.4 Hz, 1H), 4.61 (d, $J$ = 11.4 Hz, 1H), 7.25–7.40 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 14.7, 18.4, 33.4, 55.8, 69.3, 73.0, 74.0, 81.3, 128.8, 129.1, 129.4, 139.9, 162.8 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3343 (brm), 2925 (s), 1747 (s), 1415 (m), 1259 (m), 1093 $cm^{-1}$ (s); HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NNaO_4$: 279.1477; found: 279.1471 (2.3 ppm).

*Diastereomeric Mixture of Major Isomer anti-**17b** with Minor Isomer syn-**17b***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 1.00 (d, $J$ = 7.0 Hz, 3H), 1.08 (d, $J$ = 7.0 Hz, 3H), 2.20–2.12 (m, 1H), $J$ = 7.0, 3.3 Hz, 1H), 3.30–3.37 (m, 1H), 3.47 (dd, $J$ = 8.3, 3.8 Hz, 1H), 4.08 (ddd, $J$ = 8.8, 5.9, 3.8 Hz, 1H), 4.22 (dd, $J$ = 8.8, 5.9 Hz, 1H), 4.38 (appt, $J$ = 8.8 Hz, 1H), 4.62 (d, $J$ = 11.1 Hz, 1H), 4.65 (d, $J$ = 11.1 Hz, 1H), 7.24–7.44 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 15.9, 19.3, 29.6, 54.9, 68.4, 72.2, 74.8, 85.4, 127.8, 127.9, 128.4, 138.9, 161.8 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3385 (brs), 2957 (m), 1741 (s), 1634 (m), 1463 (m), 1393 (m), 1190 (m), 1026 $cm^{-1}$ (m); HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NNaO_4$: 302.1363; found: 302.1363 (0.0 ppm).

*Diastereomeric Mixture of Major Isomer anti-**17c** with Minor Isomer syn-**17c***

Data are given for the major isomer. M.p. 161–164 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.96 (brs, 1H), 3.47–3.53 (m, 1H), 3.65–3.75 (m, 1H), 3.92–4.12 (m, 1H), 4.17–4.37 (m, 2H), 4.43–4.55 (m, 2H), 6.53 (s, 1H), 7.20–7.50 ppm (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 53.8, 67.1, 70.7, 75.9, 82.1, 127.3, 127.6, 128.1, 128.2, 128.6, 129.0, 137.3, 137.7, 160.2 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3423 (brs), 2975 (m), 1736 (s), 1637 (m), 1535 (m), 1401 (m), 1203 (m), 978 $cm^{-1}$ (s); HRMS (ESI): *m/z* calcd for $C_{18}H_{19}NNaO_4$: 336.1206; found: 336.1211 (−1.5 ppm).

*(±)(R)-4-[(1′S,2′R)-[2′-(Benzyloxy)-1′-hydroxy-3′,3′-dimethylbutyl]]oxazolidin-2-one (anti-**17d**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 1.04 (s, 9H), 3.18 (d, $J$ = 6.7 Hz, 1H), 3.64 (appt, $J$ = 6.7 Hz, 1H), 4.05 (ddd, $J$ = 8.8, 6.7, 6.3 Hz, 1H), 4.11 (dd, $J$ = 8.8, 6.3 Hz, 1H), 4.29 (appt, $J$ = 8.8 Hz, 1H), 4.66 (s, 2H), 7.27–7.40 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 26.0, 35.7, 56.0, 68.6, 74.1, 76.3, 90.2, 127.7, 127.8, 128.5, 138.6, 161.5 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3356 (brs), 2957 (s), 1743 (s), 1396 (m), 1246 (m), 1067 (m), 939 (m), 698 $cm^{-1}$ (m); HRMS (ESI): *m/z* calcd for $C_{16}H_{23}NNaO_4$: 316.1519; found: 316.1523 (−1.2 ppm).

*(±)(R)-4-[(1′R,2′S)-[2′-(Benzyloxy)-1′-hydroxy-2′-methylbutyl]]oxazolidin-2-one (anti-**19b**)*

$^1$H NMR (400 MHz): $\delta$ = 1.00 (d, $J$ = 6.8 Hz, 3H), 1.03 (d, $J$ = 6.8 Hz, 3H), 2.10–1.90 (m, 1H), $J$ = 6.8, 5.9 Hz, 1H), 3.23 (t, $J$ = 5.9 Hz, 1H), 3.76 (dd, $J$ = 5.9, 2.5 Hz, 1H), 4.06 (ddd, $J$ = 9.0, 6.2, 2.5 Hz, 1H), 4.20 (t, $J$ = 9.0 Hz, 1H), 4.47 (dd, $J$ = 9.0, 6.1 Hz, 1H), 4.57 (d, $J$ = 11.4 Hz, 1H), 4.61 (d, $J$ = 11.4 Hz, 1H), 7.24–7.39 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 17.1, 19.0, 30.1, 54.3, 66.1, 71.5, 74.7, 85.8, 127.8, 128.2, 128.5, 138.8, 161.7 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3251 (brs), 2975 (s), 2870 (s), 1742 (s), 1520 (m), 1433 (m), 1267 (m), 1065 (m), 1026 $cm^{-1}$ (s); HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NNaO_4$: 302.1363; found: 302.1364 (0.4 ppm).

*(±)(R)-4-[(1′R,2′R)-[2′-(Benzyloxy)-1′-hydroxy-2′-methylbutyl]]oxazolidin-2-one (syn-**19b**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 1.02 (d, $J$ = 6.8 Hz, 3H), 1.07 (d, $J$ = 6.8 Hz, 3H), 2.04–2.18 (m, 1H), 3.21 (dd, $J$ = 7.2, 2.4 Hz, 1H), 3.70 (dd, $J$ = 5.6, 2.3 Hz, 1H), 3.98 (dt, $J$ = 8.8, 5.6 Hz, 1H), 4.37 (appt, $J$ = 8.8 Hz, 1H), 4.49 (dd, $J$ = 8.8, 5.8 Hz, 1H), 4.58 (d, $J$ = 11.3 Hz, 1H), 4.69 (d, $J$ = 11.3 Hz, 1H), 7.25–7.43 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 18.4, 18.5, 30.0, 55.2, 67.5, 72.5, 74.2, 84.8, 127.7, 128.0, 128.4, 139.1, 161.6 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3248 (brs), 2956 (s), 2886 (s), 1745 (s), 1260 (m), 1069 $cm^{-1}$ (m); HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NNaO_4$: 302.1363; found: 302.1363 (0.1 ppm).

*Diastereomeric Mixture of Major Isomer anti-**19c** and Minor Isomer syn-**19c***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.98–2.38 (brs, 1H), 3.77 (t, $J$ = 6.3 Hz, 1H), 3.95 (ddd, $J$ = 7.8, 6.3, 6.1 Hz, 1H), 4.22 (d, $J$ = 11.6 Hz, 1H), 4.30 (dd, $J$ = 9.3, 7.8 Hz, 1H), 4.26–4.31 (m, 1H), 4.40 (dd, $J$ = 9.3, 6.1 Hz, 1H), 4.51 (d, $J$ = 11.6 Hz, 1H), 5.68 (brs, 1H), 7.20–7.53 ppm (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 54.0, 66.2, 70.8, 74.6, 82.2, 127.5, 127.7, 128.1, 128.6, 128.8, 128.9, 137.4, 137.9, 160.5 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3385 (brs), 2875 (s), 2796 (s), 1737 (s), 1512 (m), 1430 (w), 1256 (w), 977 $cm^{-1}$ (s); HRMS (ESI): *m/z* calcd for $C_{18}H_{19}NNaO_4$: 336.1206; found: 336.1210 (−1.1 ppm).

*Diastereomeric Mixture of Major Isomer anti-**19d** with Minor Isomer syn-**19d***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 1.02 (s, 9H), 3.24 (d, $J$ = 3.4 Hz, 1H), 3.89 (t, $J$ = 3.6 Hz, 1H), 4.12 (ddd, $J$ = 9.1, 6.1, 3.5 Hz, 1H), 4.28 (t, $J$ = 9.1 Hz, 1H), 4.51 (dd, $J$ = 9.1, 6.1 Hz, 1H), 4.63 (d, $J$ = 11.1 Hz, 1H), 4.66 (d, $J$ = 11.1 Hz, 1H), 7.23–7.45 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 26.1, 35.7, 55.1, 66.8, 72.5, 76.2, 91.0, 127.7, 127.8, 128.4, 138.7, 161.5 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3383 (brm), 2956 (m), 1742 (s), 1396 (m), 1246 $cm^{-1}$ (m); HRMS (ESI): *m/z* calcd for $C_{16}H_{23}NNaO_4$: 316.1526; found: 316.1519 (−2.2 ppm).

*(±)(R)-4-[(2′R,3′R)-[3′-(Benzyloxy)-2′-hydroxyhexan-2-yl]]oxazolidin-2-one (anti-(Z)-**26**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.96 (t, $J$ = 7.1 Hz, 3H), 1.18 (s, 3H), 1.28–1.76 (m, 4H), 3.27–3.43 (m, 1H), 3.98 (dd, $J$ = 9.1, 6.1 Hz, 1H), 4.22 (dd, $J$ = 9.1, 8.8 Hz, 1H), 4.51 (dd, 1H), 4.63 (m, 2H), 7.25–7.43 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 14.8, 20.0, 21.7, 34.2, 59.3, 67.6, 75.2, 75.6, 85.2, 128.8, 129.2, 129.5, 139.9, 162.8 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3415 (brs), 2958 (s), 1747 (s), 1454 (s), 1410 (m), 1248 (m), 1108 (m), 942 $cm^{-1}$ (w); HRMS (ESI): *m/z* calcd for $C_{16}H_{23}NNaO_4$: 316.1516; found: 316.1519 (1.0 ppm).

*(±)(R)-4-[(2′R,3′S)-[3′-(Benzyloxy)-2′-hydroxyhexan-2-yl]]oxazolidin-2-one (syn-(Z)-**26**)*

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.94–1.00 ($J$ = 7.3 Hz, 3H), 1.18 (s, 3H), 1.33–1.72 (m, 4H), 3.35 (dd, $J$ = 7.8, 3.0 Hz, 1H), 4.08 (dd, $J$ = 9.1, 5.3 Hz, 1H), 4.36 (appt, $J$ = 9.1 Hz, 1H), 4.51 (dd, $J$ = 9.1, 5.3 Hz, 1H), 4.64 (d, $J$ = 11.8 Hz, 1H), 4.67 (d, $J$ = 11.8 Hz, 1H), 7.23–7.43 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 13.7, 18.6, 20.2, 32.6, 57.0, 66.7, 74.3, 75.3, 84.0, 127.7, 128.0, 128.4, 138.9, 161.6 ppm; IR (thin film): $\tilde{\nu}_{max}$ = 3414 (brs), 2959 (s), 2872 (s), 1748 (s), 1454 (m), 1409 (s), 1248 (s), 1108 (s), 986 (s), 942 (m), 736 $cm^{-1}$ (s); HRMS (ESI): *m/z* calcd for $C_{16}H_{23}NNaO_4$: 316.1516; found: 316.1519 (1.0 ppm).

*Diastereomeric Mixture of Major Isomer anti-(E)-**26** with Minor Isomer syn-(E)-**26***

Data are given for the major isomer. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.99 (t, $J$ = 7.1 Hz, 3H), 1.07 (s, 3H), 1.39–1.83 (m, 4H), 3.41 (dd, $J$ = 7.8, 3.3 Hz, 1H), 4.08 (dd, $J$ = 9.1, 7.1 Hz, 1H), 4.33–4.40 (m, 2H), 4.63 (m,

$J$=11.0 Hz, 1H), 4.66 (d, $J$=11.0 Hz, 1H), 7.25–7.41 ppm (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=14.8, 17.6, 21.8, 34.0, 59.6, 67.7, 75.0, 75.2, 85.4, 128.7, 128.8, 129.5, 140.0, 162.7 ppm; IR (thin film): $\tilde{\nu}_{max}$=3386 (brs), 3031 (w), 2958 (s), 2468w, 1746 (s), 1454 (m), 1408 (m), 1243 (m), 1093 (m), 698 $cm^{-1}$ (m); HRMS (ESI): $m/z$ calcd for $C_{16}H_{23}NNaO_4$: 316.1516; found: 316.1519 (0.9 ppm).

## Acknowledgements

We thank the EPSRC and GSK for funding this project, Oxford Chemical Crystallography Service for the use of their instrumentation, and Dr. Barbara Odell of Oxford University NMR Service for NOE spectroscopic analysis.

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Received: May 30, 2011
Published online: September 14, 2011

  