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Highly Diastereoselective Reactions of Isoxazolidine-4,5-diols with Grignard Reagents: A New Approach to *anti*,*syn*-γ-Amino-α,β-diols

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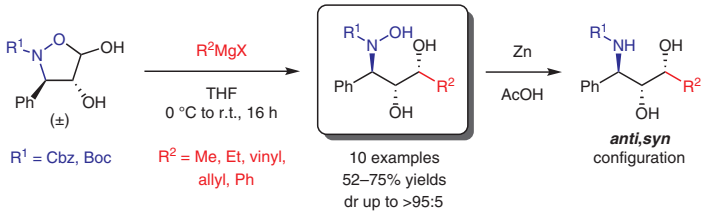

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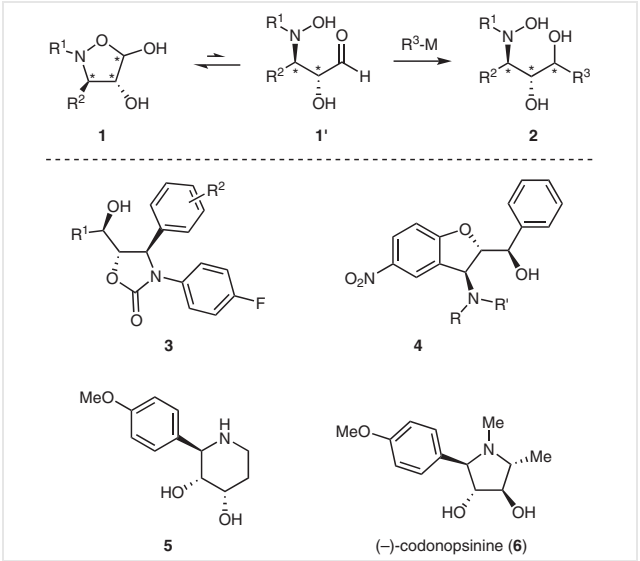
Abstract An investigation of the reaction of 3,4-*trans*-isoxazolidine-4,5-diols with Grignard reagents is described for the first time. Their resemblance to five-membered cyclic hemiacetals allows them to react as α-hydroxy-β-(hydroxyamino)aldehydes in a highly stereoselective manner, providing *anti*,*syn*-γ-(hydroxyamino)-α,β-diols in moderate yields and with good to excellent *syn*-diastereoselectivities, which can be improved by the addition of anhydrous cerium chloride. The obtained (hydroxyamino)diols serve as suitable precursors of *anti*,*syn*-γ-amino-α,β-diols that represent valuable scaffolds for the synthesis of various biologically active compounds.

Key words, isoxazolidines, amino diols, Grignard reaction, diastereoselectivity, crystal structure

While functionalized 4- and 5-hydroxyisoxazolidines constitute a well-known and important class of substrates for the synthesis of many complex organic molecules, including new drug candidates and bioactive natural products and their analogues,[1,2] isoxazolidine-4,5-diols have been recently designed and prepared in our group for the first time by employing highly stereoselective dihydroxylation and epoxidation reactions of 4,5-unsubstituted 2,3-dihydroisoxazoles.[3] Their *O*-benzoylated derivatives have been demonstrated to be powerful anomeric electrophiles in Lewis acid catalyzed nucleophilic substitutions.[4]

In connection with our research program aimed at the utilization of 3,4-*trans*-isoxazolidine-4,5-diols **1** in the synthesis of hydroxylated nitrogen compounds, we envisioned that the resemblance of isoxazolidine-4,5-diols to five-membered cyclic hemiacetals would allow them to react as α-hydroxy-β-(hydroxyamino)aldehydes **1′** in stereoselective nucleophilic additions of organometallic reagents (Scheme 1, top). The obtained highly substituted γ-(hydroxyamino)-α,β-diols **2**, so far mainly achieved starting from nitrones,[5] constitute suitable precursors for the preparation of biologically important linear γ-amino-α,β-diols with three contiguous stereogenic centers.[6]



Scheme 1 General route for the synthesis of γ-(hydroxyamino)-α,β-diols **2**, and bioactive derivatives **3–6** containing a γ-amino-α,β-diol subunit

Although aryl-substituted linear vicinal amino diols alone rarely represent target bioactive molecules, this subunit can often be found in various natural and unnatural

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cyclic products, including oxazolidinones **3**,[7a,b] 3-amino-2,3-dihydrobenzofuran derivatives **4**,[7c] hydroxylated piperidines **5**,[8a] and pyrrolidines **6** (Scheme 1, bottom).[8b,c] Additionally, the phenyl group has been utilized as a carboxyl synthon in the synthesis of polyoxamic acid[9a,b] and phytosphingosine.[9c] While the additions of organometallic reagents to suitably protected β-amino-α-hydroxy aldehydes have already been well-documented,[10] to the best of our knowledge, the literature describes only one example of the reaction of Grignard reagents with 4-unsubstituted 5-hydroxyisoxazolidines [β-(hydroxyamino)aldehydes].[11]

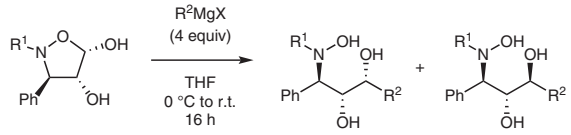
Herein, we report the first results on the stereoselective nucleophilic additions of Grignard reagents directly to O-unprotected isoxazolidine-4,5-diols to obtain the desired γ-(hydroxyamino)-α,β-diols.

Two 3-phenyl-substituted 3,4-*trans*-isoxazolidine-4,5-diols, **7** and **8**, which were prepared by acid-catalyzed hydrolysis of the corresponding isoxazolidinyl epoxides (see the Supporting Information),[3c] were selected as model substrates (Table 1). To investigate their reactivity in nucleophilic additions with Grignard reagents, we first attempted the reaction between diol **7** and methylmagnesium iodide. After dropwise addition of MeMgI (3 equiv) in Et_2O to a cooled solution of **7** in anhydrous THF at –20 °C, the resulting mixture was stirred for 2 hours. However, the reaction proceeded very slowly, even after raising the reaction temperature to 0 °C. This problem was overcome by allowing the reaction mixture to warm to room temperature over several hours (16 h). Increasing the amount of MeMgI (to 4 equiv) was also necessary to bring the reaction to completion. After aqueous work-up, the a mixture of epimeric (hydroxyamino)diols **9a**,**b** was obtained in 57% combined yield with good diastereoselectivity (Table 1, entry 1). Variation of the halide in the Grignard reagent (MeMgCl, MeMgBr) induced no significant change in the diastereoselectivity.

Based on the above-mentioned results, the optimum reaction conditions were next applied for additions of other commercially available Grignard reagents (entries 2, 4, 6–9, 11, 12 and 14). Depending on the bulkiness of the Grignard reagent used, the reactions proceeded with good to excellent stereoselectivity (from 75:25 to >95:5), always in favor of the *anti*,*syn*-isomers. The corresponding (hydroxyamino)diols **10**–**18** were obtained in moderate to good combined yields (52–75%). The effect of Lewis acids on chelation-controlled diastereofacial selectivity was also examined.[9a] To our delight, when the reactions were carried out in the presence of a slight excess of anhydrous $CeCl_3$, excellent *syn*-selectivity was obtained (>95:5), with the yields almost unchanged (entries 3, 5, 10 and 13).[12] It is worth noting that the use of other Lewis acids such as $ZnCl_2$ and $ZnBr_2$ did not affect the stereoselectivity in a positive manner. As the structures are acyclic, it was problematic to determine the stereochemistry of the (hydroxyamino)diols, and therefore, 1D NOESY experiments were out of the question. All attempts to convert the (hydroxyamino)diols into cyclic 1,3-dioxolanes or carbonates failed. Fortunately, we succeeded in preparing a good quality single crystal of one major isomer, *anti*,*syn*-**12a**. Its X-ray crystallographic analysis unambiguously confirmed the relative *syn*-configuration of the diol fragment (Figure 1). The configurations of the other major isomers **9a**–**11a** and **13a**–**18a** were assigned by comparison of their ^{1}H NMR spectra with that recorded for **12a**. To distinguish between the major *anti*,*syn*- and the minor *anti*,*anti*-isomers, the values of vicinal J_{2H-3H} coupling constants were taken into consideration. For the major isomers, the J_{2H-3H} values range from 0.8 Hz to 1.8 Hz, while the minor isomers have larger couplings in the range of 3.5–4.5 Hz. Additionally, the 2-H proton signals of the *anti*,*syn*-isomers are shifted upfield (4.00–4.27 ppm) when compared to those of the *anti*,*anti*-isomers (4.30–4.41 ppm).

The prevalent *syn*-selectivity can be clearly rationalized by the Cram α-chelation-controlled model.[13] In addition, we propose that the presence of $CeCl_3$ as an effective Lewis acid improves the stereochemical outcome of the reactions, possibly due to the formation of a rigid complex structure

Table 1 Reaction Conditions for the Preparation of γ-(Hydroxyamino)-α,β-diols



(±)-**7**, R^1 = Cbz
(±)-**8**, R^1 = Boc

anti,*syn*
(±)-**9a**–**18a**

anti,*anti*
(±)-**9b**–**18b**

Entry	Product	R^1	R^2	Yield (%)[a]	*anti*,*syn*/*anti*,*anti*[b]
1	**9**	Cbz	Me	57	75:25
2	**10**	Cbz	Et	61	85:15
3	**10**	Cbz	Et	60	>95:5[c]
4	**11**	Cbz	vinyl	55	80:20
5	**11**	Cbz	vinyl	59	>95:5[c]
6	**12**	Cbz	allyl	54	75:25
7	**13**	Cbz	Ph	57	>95:5
8	**14**	Boc	Me	61	75:25
9	**15**	Boc	Et	75	85:15
10	**15**	Boc	Et	72	>95:5[c]
11	**16**	Boc	vinyl	70	85:15
12	**17**	Boc	allyl	71	80:20
13	**17**	Boc	allyl	72	>95:5[c]
14	**18**	Boc	Ph	52	>95:5

[a] Isolated combined yield.
[b] Diastereomeric ratios were determined from the ^{1}H NMR spectra of the crude product mixture.
[c] Commercially available anhydrous $CeCl_3$ (1.5 equiv, Aldrich) was used without drying.

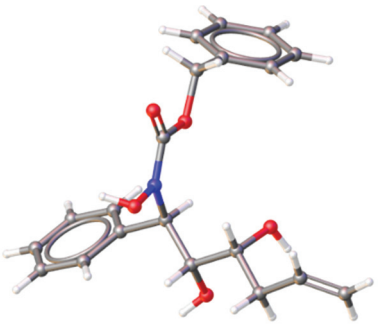


Figure 1 The molecular structure of γ-(hydroxyamino)-α,β-diol *anti*,*syn*-**12a**, as confirmed by X-ray crystallographic analysis

between the oxophilic cerium center, the aldehyde group, and the α-alkoxide group (a 5-membered chelate), and even between the deprotonated β-hydroxyamino group (a 7-membered chelate) (Figure 2).[14]

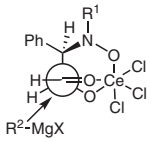
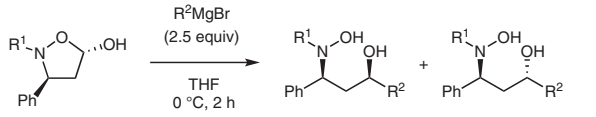


Figure 2 A rationale for the *syn*-diastereoselectivity in the addition of Grignard reagents to isoxazolidine-4,5-diols in the presence of $CeCl_3$

To definitively prove the important role of the 4-hydroxy group in achieving the *syn*-selectivity, two 4-unsubstituted 5-hydroxyisoxazolidines **19** and **20** were prepared[3c] and subjected to the reaction with phenyl and ethylmagnesium bromide at 0 °C. Not surprisingly, the epimeric γ-hydroxyamino alcohols **21**–**24** were invariably obtained with only modest diastereoselectivity, although the combined yields were considerably higher (Table 2). Similarly, comparable or worse selectivities were observed when Grignard reagents were reacted with α-unsubstituted β-amino aldehydes.[15]

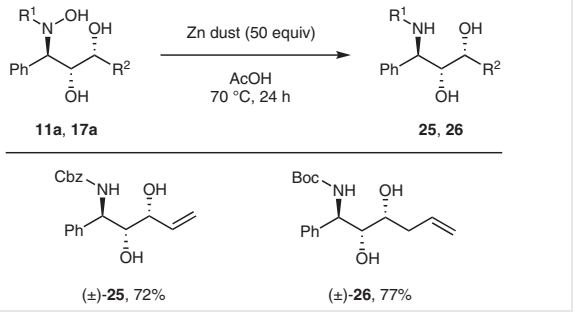
To demonstrate the utility of (hydroxyamino)diols in the synthesis of linear γ-amino-α,β-diols, representative adducts **11a** and **17a** were subjected to reductive cleavage of the N–O bond using zinc in acetic acid.[16] The *N*-Cbz- and *N*-Boc-protected amino diols **25** and **26** were isolated in good yields of 72% and 77%, respectively (Scheme 2). Even though compounds **25** and **26** are racemic, their importance rests in the versatility of the vinyl and allyl groups which can undergo a variety of further synthetic transformations. Additionally, the effective asymmetric organocatalytic conjugate additions provide access to enantiomerically pure isoxazolidin-5-ols,[17] which, if needed, can be easily converted into single enantiomers of the corresponding γ-amino-α,β-diols by employing the above-mentioned strategy.

Table 2 Reactions of Grignard Reagents with 4-Unsubstituted 5-Hydroxyisoxazolidines[a]



Entry	Product	R^1	R^2	Yield (%)[b]	*syn*/*anti*[c]
1	**21**	Cbz	Ph	90	70:30[d]
2	**22**	Cbz	Et	80	70:30
3	**23**	Boc	Ph	89	70:30
4	**24**	Boc	Et	94	70:30

[a] The respective 5-hydroxyisoxazolidines occur as predominant 3,5-*trans*-isomers (*trans*/*cis*, 9:1).
[b] Isolated combined yield.
[c] Diastereomeric ratios were determined from the ^{1}H NMR spectra of the crude product mixture.
[d] The γ-(hydroxyamino)-α,β-diols **21a**,**b** were individually converted into known γ-amino alcohols by hydrogenolysis of the N–O bond to assign their relative configurations (see the Supporting Information).



Scheme 2 Synthesis of *N*-Cbz- and *N*-Boc-protected amino diols **25** and **26**

In summary, we have studied the additions of Grignard reagents to 3-phenyl-substituted 3,4-*trans*-isoxazolidine-4,5-diols that are able to react as α-hydroxy-β-(hydroxyamino)aldehydes due to their hemiacetal character. The reactions provided γ-(hydroxyamino)-α,β-diols in moderate yields and with good to excellent *syn*-selectivity in favor of the *anti*,*syn*-isomers, improved by the addition of anhydrous cerium chloride. This study shows that the presence of an unprotected 4-OH group plays an important role in the stereochemical outcome by participation in the α-chelation-controlled addition. Two representative *N*-Cbz- and *N*-Boc-protected *anti*,*syn*-γ-(hydroxyamino)-α,β-diols were subjected to reductive cleavage of the N–O bond to demonstrate their synthetic utility as precursors of *anti*,*syn*-γ-amino-α,β-diols with three contiguous stereogenic centers. We believe that the presented method will provide a fast and stereoselective approach towards versatile, highly substituted amino diols as valuable scaffolds for the synthesis of bioactive molecules. Further applications of *syn*-dia-

stereoselective reactions for the preparation of hydroxylated nitrogen-containing heterocycles will be reported in due course.

All solvents used were dried and distilled according to conventional methods. Compounds **19** and **20** were synthesized according to the published procedure.[3c] Flash column chromatography (FCC) was carried out with a Büchi system (Pump Manager C-615 and Fraction Collector C-660) using Normasil 60 silica gel (0.040–0.063 mm; VWR). Thin-layer chromatography (TLC) analysis was carried out using TLC silica gel 60 F254 (aluminum sheets, Merck), and plates were visualized with UV light or by treatment with permanganate solution followed by heating. Melting points were obtained using a Melting Point B-540 (Büchi) instrument. Infrared (IR) spectra were recorded as neat samples with a Nicolet 5700 FTIR spectrometer with an ATR Smart Orbit Diamond adapter (Thermo Electron Corporation). NMR spectra were recorded with a Varian INOVA-300 spectrometer (^{1}H, 299.95 MHz, and ^{13}C, 75.42 MHz) and a Varian VNMRS-600 instrument (^{1}H, 599.75 MHz, and ^{13}C, 150.81 MHz) in $CDCl_3$ (using tetramethylsilane as the internal standard) or CD_3OD. Chemical shifts are reported in parts per million (ppm). HRMS analysis was carried out with an Orbitrap Velos Pro spectrometer (Thermo Fisher Scientific).

Synthesis of γ-(Hydroxyamino)-α,β-diols

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylbutyl)carbamate (9); Typical Procedure (TP1)

To a stirred solution of diol **7** (95 mg, 0.30 mmol) in anhydrous THF (3 mL) under argon at 0 °C was added MeMgI (0.4 mL, 1.21 mmol, 3 M solution in Et_2O) dropwise over 5 min. The reaction mixture was allowed to slowly warm to room temperature over 16 h. When TLC showed that the reaction was complete (CH_2Cl_2/MeOH/NH_3, 94.7:5:0.3), the reaction mixture was quenched with sat. aq NH_4Cl (15 mL), diluted with Et_2O (15 mL) and vigorously stirred at room temperature for 5 min. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by FCC (CH_2Cl_2/acetone, 9:1) to give pure major diastereoisomer *anti*,*syn*-**9a** along with a mixture of both diastereoisomers *anti*,*syn*-**9a** and *anti*,*anti*-**9b** (15 mg, 0.05 mmol, 17%, pale yellow sticky oil). For analytical purposes, pure compound **9b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-9a

Yield: 40 mg (0.12 mmol, 40%); white solid; mp 121–123 °C; R_f = 0.13 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3369, 3165, 2918, 1687, 1393, 1275, 1120, 1092, 1062, 692, 601, 570 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.47–7.44 (m, 2 H, H-Ph), 7.34–7.25 (m, 8 H, H-Ph), 5.22 (d, *J* = 10.0 Hz, 1 H, 1-H), 5.18 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 5.08 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 4.11–4.00 (m, 2 H, 2-H, 3-H), 1.28 (d, *J* = 6.5 Hz, 3 H, 4-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.9 (C=O), 139.7 (C-Ph), 137.7 (C-Ph), 130.3 (CH-Ph), 129.4 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.9 (CH-Ph), 128.6 (CH-Ph), 73.7, 67.3 (C-2, C-3), 68.7 (O*C*H$_2$Ph), 64.5 (C-1), 20.1 (C-4).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}NO_5$: 332.1493; found: 332.1494; *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{21}NNaO_5$: 354.1312; found: 354.1314.

Data for *anti*,*anti*-9b

Colorless sticky oil; R_f = 0.09 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3375, 3032, 2933, 1694, 1454, 1403, 1276, 1072, 992, 695, 622, 570 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.49–7.44 (m, 2 H, H-Ph), 7.34–7.26 (m, 8 H, H-Ph), 5.17 (d, AB, *J* = 12.3 Hz, 1 H, OC*H*$_2$Ph), 5.11 (d, AB, *J* = 12.3 Hz, 1 H, OC*H*$_2$Ph), 5.01 (d, *J* = 9.1 Hz, 1 H, 1-H), 4.33 (dd, *J* = 9.1, 3.8 Hz, 1 H, 2-H), 3.94 (dq, *J* = 6.4, 3.9 Hz, 1 H, 3-H), 1.20 (d, *J* = 6.4 Hz, 3 H, 4-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.4 (C=O), 139.2 (C-Ph), 137.7 (C-Ph), 130.3 (CH-Ph), 129.5 (CH-Ph), 129.2 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.7 (CH-Ph), 74.5, 68.8 (C-3, C-2), 68.7 (O*C*H$_2$Ph), 65.1 (C-1), 16.7 (C-4).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{21}NNaO_5$: 354.1312; found: 354.1312.

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpentyl)carbamate (10)

TP1 described above was applied using diol **7** (120 mg, 0.38 mmol), EtMgBr (0.51 mL, 1.53 mmol, 3 M solution in Et_2O) and anhydrous THF (4 mL). FCC (CH_2Cl_2/acetone, 9:1) gave pure major diastereoisomer *anti*,*syn*-**10a** along with a mixture of both diastereoisomers *anti*,*syn*-**10a** and *anti*,*anti*-**10b** (10 mg, 0.03 mmol, 8%, pale yellow sticky oil). For analytical purposes, pure compound **10b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-10a

Yield: 70 mg (0.20 mmol, 53%); white solid; mp 129–130 °C; R_f = 0.20 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3350, 3113, 2926, 1694, 1409, 1281, 1123, 1107, 1028, 733, 692, 571 cm^{-1}.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.48–7.45 (m, 2 H, H-Ph), 7.35–7.25 (m, 8 H, H-Ph), 5.24 (d, *J* = 10.1 Hz, 1 H, 1-H), 5.19 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 5.08 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 4.20 (dd, *J* = 10.1, 1.2 Hz, 1 H, 2-H), 3.72 (ddd, *J* = 8.1, 5.7, 1.1 Hz, 1 H, 3-H), 1.75–1.52 (m, 2 H, 4-H), 1.01 (t, *J* = 7.4 Hz, 3 H, 5-H).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.9 (C=O), 139.7 (C-Ph), 137.7 (C-Ph), 130.3 (CH-Ph), 129.4 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.9 (CH-Ph), 128.5 (CH-Ph), 72.8, 72.3 (C-2, C-3), 68.7 (O*C*H$_2$Ph), 64.4 (C-1), 27.8 (C-4), 10.9 (C-5).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{24}NO_5$: 346.1649; found: 346.1650; *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{23}NNaO_5$: 369.1469; found: 369.1470.

Data for *anti*,*anti*-10b

Colorless sticky oil; R_f = 0.10 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3453, 3031, 2970, 1738, 1364, 1217, 1088, 973, 731, 695, 622, 569 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.49–7.45 (m, 2 H, H-Ph), 7.34–7.26 (m, 8 H, H-Ph), 5.16 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 5.12 (d, *J* = 8.4 Hz, 1 H, 1-H), 5.11 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 4.31 (dd, *J* = 8.5, 4.5 Hz, 1 H, 2-H), 3.58 (ddd, *J* = 9.8, 4.5, 2.6 Hz, 1 H, 3-H), 1.75–1.62 (m, 1 H, 4-H), 1.57–1.41 (m, 1 H, 4-H), 0.97 (t, *J* = 7.4 Hz, 3 H, 5-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.4 (C=O), 139.3 (C-Ph), 137.7 (C-Ph), 130.3 (CH-Ph), 129.5 (CH-Ph), 129.2 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.7 (CH-Ph), 74.8, 74.6 (C-2, C-3), 68.7 (OCH_2Ph), 65.0 (C-1), 24.6 (C-4), 10.7 (C-5).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{23}NNaO_5$: 368.1469; found: 368.1470.

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpent-4-en-1-yl)carbamate (11)

TP1 described above was applied using diol **7** (120 mg, 0.38 mmol), vinyl-MgBr (1.52 mL, 1.52 mmol, 1 M solution in THF) and anhydrous THF (4 mL). FCC (hexanes/EtOAc, 6:4) gave pure major diastereoisomer *anti*,*syn*-**11a** along with a mixture of both diastereoisomers *anti*,*syn*-**11a** and *anti*,*anti*-**11b** (15 mg, 0.04 mmol, 10%, pale yellow sticky oil). For analytical purposes, pure compound **11b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-11a

Yield: 60 mg (0.17 mmol, 45%); white solid; mp 102–103 °C; R_f = 0.18 (*n*-hexane/EtOAc, 1:1).

IR (ATR): 3325, 3032, 2929, 2501, 1690, 1408, 1279, 1108, 750, 695, 593 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.48–7.44 (m, 2 H, H-Ph), 7.35–7.25 (m, 8 H, H-Ph), 6.06 (ddd, *J* = 17.3, 10.5, 5.8 Hz, 1 H, 4-H), 5.35 (dt, *J* = 17.3, 1.7 Hz, 1 H, 5-H_a), 5.26 (d, *J* = 9.9 Hz, 1 H, 1-H), 5.19 (dt, *J* = 10.5, 1.6 Hz, 1 H, 5-H_b), 5.18 (d, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.09 (d, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 4.36 (dq, *J* = 5.8, 1.6 Hz, 1 H, 3-H), 4.27 (dd, *J* = 9.9, 1.8 Hz, 1 H, 2-H).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.7 (C=O), 140.2 (C-4), 139.5 (C-Ph), 137.7 (C-Ph), 130.3 (CH-Ph), 129.4 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.9 (CH-Ph), 128.6 (CH-Ph), 115.9 (C-5), 73.4, 73.1 (C-2, C-3), 68.7 (OCH_2Ph), 64.3 (C-1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{22}NO_5$: 344.1493; found: 344.1495; *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{21}NNaO_5$: 366.1312; found: 366.1314.

Data for *anti*,*anti*-11b

Colorless sticky oil; R_f = 0.11 (*n*-hexane/EtOAc, 1:1).

IR (ATR): 3386, 3032, 2925, 2515, 1697, 1409, 1277, 1218, 1077, 749, 695, 609 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.47–7.44 (m, 2 H, H-Ph), 7.33–7.28 (m, 8 H, H-Ph), 6.03 (ddd, *J* = 17.4, 10.4, 7.1 Hz, 1 H, 4-H), 5.27–5.16 (m, 2 H, 5-H), 5.14 (d, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.08 (d, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 4.97 (d, *J* = 9.5 Hz, 1 H, 1-H), 4.41 (dd, *J* = 9.5, 3.5 Hz, 1 H, 2-H), 4.29 (tdd, *J* = 7.1, 3.5, 1.1 Hz, 1 H, 3-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.5 (C=O), 139.2 (C-Ph), 137.7 (C-Ph), 137.4 (C-4), 130.3 (CH-Ph), 129.5 (CH-Ph), 129.2 (CH-Ph), 129.1 (2 × CH-Ph), 128.7 (CH-Ph), 118.1 (C-5), 74.8, 74.2 (C-2, C-3), 68.7 (OCH_2Ph), 64.9 (C-1).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{21}NNaO_5$: 366.1312; found: 366.1313.

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylhex-5-en-1-yl)carbamate (12)

TP1 described above was applied using diol **7** (150 mg, 0.48 mmol), allyl-MgBr (1.13 mL, 1.92 mmol, 1.7 M solution in THF), and anhydrous THF (5 mL). FCC (CH_2Cl_2/acetone, 9:1) gave pure major diastereoisomer *anti*,*syn*-**12a** along with a mixture of both diastereoisomers *anti*,*syn*-**12a** and *anti*,*anti*-**12b** (15 mg, 0.04 mmol, 8%, pale yellow sticky oil). For analytical purposes, pure compound **12b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-12a

Yield: 80 mg (0.22 mmol, 46%); white solid; mp 111–113 °C; R_f = 0.19 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3369, 3088, 2899, 1684, 1417, 1281, 1116, 1080, 750, 695, 574 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.49–7.43 (m, 2 H, H-Ph), 7.34–7.25 (m, 8 H, H-Ph), 5.99–5.86 (m, 1 H, 5-H), 5.26 (d, *J* = 10.1 Hz, 1 H, 1-H), 5.18 (d, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.17–5.04 (m, 2 H, 6-H), 5.08 (d, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 4.22 (dd, *J* = 10.1, 1.2 Hz, 1 H, 2-H), 3.89 (ddd, *J* = 7.6, 6.2, 1.1 Hz, 1 H, 3-H), 2.48–2.31 (m, 2 H, 4-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.9 (C=O), 139.7 (C-Ph), 137.7 (C-Ph), 136.7 (C-5), 130.3 (CH-Ph), 129.4 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.9 (CH-Ph), 128.6 (CH-Ph), 117.3 (C-6), 72.1, 70.9 (C-2, C-3), 68.7 (OCH_2Ph), 64.4 (C-1), 39.8 (C-4).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{24}NO_5$: 358.1649; found: 358.1652; *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{23}NNaO_5$: 380.1469; found: 380.1472.

Data for *anti*,*anti*-12b

Colorless sticky oil; R_f = 0.10 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3383, 3033, 2950, 1698, 1407, 1277, 1094, 1055, 733, 696, 606, 568 cm^{-1}.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.48–7.47 (m, 2 H, H-Ph), 7.33–7.26 (m, 8 H, H-Ph), 5.91 (tdd, *J* = 17.1, 10.1, 7.0 Hz, 1 H, 5-H), 5.17 (d, AB, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.14 (d, *J* = 8.5 Hz, 1 H, 1-H), 5.11 (d, AB, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.07–5.04 (m, 1 H, 6-H), 5.03–5.01 (m, 1 H, 6-H), 4.33 (dd, *J* = 8.5, 4.5 Hz, 1 H, 2-H), 3.74 (ddd, *J* = 9.6, 4.4, 2.8 Hz, 1 H, 3-H), 2.44–2.40 (m, 1 H, 4-H_a), 2.30–2.24 (m, 1 H, 4-H_b).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.4 (C=O), 139.2 (C-Ph), 137.7 (C-Ph), 137.1 (C-5), 130.3 (CH-Ph), 129.5 (CH-Ph), 129.2 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.7 (CH-Ph), 117.1 (C-6), 74.7, 72.8 (C-2, C-3), 68.7 (OCH_2Ph), 65.0 (C-1), 36.7 (C-4).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{23}NNaO_5$: 380.1469; found: 380.1468.

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1,3-diphenylpropyl)-carbamate (13)

TP1 described above was applied using diol **7** (160 mg, 0.51 mmol), PhMgBr (2 mL, 2 mmol, 1 M solution in THF) and anhydrous THF (5 mL). FCC (hexanes/EtOAc, 6:4) gave single diastereoisomer *anti*,*syn*-**13a** (115 mg, 0.29 mmol, 57%) as a white solid.

Mp 113–114 °C; R_f = 0.14 (*n*-hexane/EtOAc, 6:4).

IR (ATR): 3305, 3030, 2937, 2507, 1682, 1452, 1387, 1278, 1104, 1047, 700, 608, 501 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.49–7.43 (m, 4 H, H-Ph), 7.36–7.19 (m, 11 H, H-Ph), 5.34 (d, *J* = 9.8 Hz, 1 H, 1-H), 5.20 (d, AB, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.10 (d, AB, *J* = 12.4 Hz, 1 H, O*CH*$_2$Ph), 5.00 (br s, 1 H, 3-H), 4.41 (dd, *J* = 9.8, 1.6 Hz, 1 H, 2-H).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.9 (C=O), 144.6 (C-Ph), 139.6 (C-Ph), 137.7 (C-Ph), 130.3 (CH-Ph), 129.5 (CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.9 (2 × CH-Ph), 128.5 (CH-Ph), 127.9 (CH-Ph), 127.6 (CH-Ph), 74.9, 73.2 (C-2, C-3), 68.7 (OCH_2Ph), 64.8 (C-1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_5$: 394.1649; found: 394.1652; *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{23}NNaO_5$: 416.1469; found: 416.1472.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylbutyl)carbamate (14)

TP1 described above was applied using diol **8** (250 mg, 0.89 mmol), MeMgI (1.2 mL, 3.56 mmol, 3 M solution in Et_2O) and anhydrous THF (9 mL). FCC (CH_2Cl_2/acetone, 9:1) gave pure major diastereoisomer *anti*,*syn*-**14a** along with a mixture of both diastereoisomers *anti*,*syn*-**14a** and *anti*,*anti*-**14b** (50 mg, 0.17 mmol, 19%, pale yellow sticky oil). For analytical purposes, pure compound **14b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-14a

Yield: 110 mg (0.37 mmol, 42%); white solid; mp 133–134 °C; R_f = 0.15 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3337, 3171, 2981, 1683, 1394, 1148, 1053, 999, 868, 733, 695, 580 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.47 (m, 2 H, H-Ph), 7.35–7.23 (m, 3 H, H-Ph), 5.12 (d, *J* = 10.0 Hz, 1 H, 1-H), 4.10–4.01 (m, 2 H, 2-H, 3-H), 1.43 (s, 9 H, *t*-Bu), 1.29 (d, *J* = 6.5 Hz, 3 H, 4-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.5 (C=O), 140.1 (C-Ph), 130.3 (CH-Ph), 128.9 (CH-Ph), 128.4 (CH-Ph), 82.5 (*C*Me$_3$), 73.9, 67.3 (C-2, C-3), 64.5 (C-1), 28.6 (C*Me*$_3$), 20.1 (C-4).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{23}NNaO_5$: 320.1469; found: 320.1468.

Data for *anti*,*anti*-14b

Colorless sticky oil; R_f = 0.06 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3377, 2975, 2932, 1687, 1368, 1163, 1102, 1073, 992, 728, 697, 622 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.47 (m, 2 H, H-Ph), 7.36–7.24 (m, 3 H, H-Ph), 4.93 (d, *J* = 9.1 Hz, 1 H, 1-H), 4.32 (dd, *J* = 9.1, 3.8 Hz, 1 H, 2-H), 3.97 (dq, *J* = 6.4, 3.8 Hz, 1 H, 3-H), 1.42 (s, 9 H, *t*-Bu), 1.25 (d, *J* = 6.4 Hz, 3 H, 4-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.0 (C=O), 139.6 (C-Ph), 130.2 (CH-Ph), 129.0 (CH-Ph), 128.6 (CH-Ph), 82.6 (*C*Me$_3$), 74.7, 68.8 (C-2, C-3), 65.2 (C-1), 28.6 (C*Me*$_3$), 16.7 (C-4).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{23}NNaO_5$: 320.1469; found: 320.1468.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpentyl)carbamate (15)

TP1 described above was applied using diol **8** (250 mg, 0.89 mmol), EtMgBr (1.19 mL, 3.56 mmol, 3 M solution in Et_2O) and anhydrous THF (9 mL). FCC (CH_2Cl_2/acetone, 9:1) gave pure major diastereoisomer *anti*,*syn*-**15a** along with a mixture of both diastereoisomers *anti*,*syn*-**15a** and *anti*,*anti*-**15b** (40 mg, 0.13 mmol, 15%, pale yellow sticky oil). For analytical purposes, pure compound **15b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-15a

Yield: 165 mg (0.53 mmol, 60%); white solid; mp 120–121 °C; R_f = 0.15 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3325, 3206, 2933, 1674, 1392, 1337, 1138, 1108, 1064, 743, 699, 575 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.47 (m, 2 H, H-Ph), 7.35–7.23 (m, 3 H, H-Ph), 5.14 (d, *J* = 10.1 Hz, 1 H, 1-H), 4.17 (dd, *J* = 10.1, 1.1 Hz, 1 H, 2-H), 3.74 (ddd, *J* = 8.1, 5.6, 1.0 Hz, 1 H, 3-H), 1.76–1.54 (m, 2 H, 4-H), 1.42 (s, 9 H, *t*-Bu), 1.03 (t, *J* = 7.4 Hz, 3 H, 5-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.6 (C=O), 140.2 (C-Ph), 130.3 (CH-Ph), 128.9 (CH-Ph), 128.4 (CH-Ph), 82.5 (*C*Me$_3$), 72.8, 72.4 (C-2, C-3), 64.5 (C-1), 28.6 (C*Me*$_3$), 27.9 (C-4), 10.9 (C-5).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{25}NNaO_5$: 334.1625; found: 334.1625.

Data for *anti*,*anti*-15b

Colorless sticky oil; R_f = 0.07 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3379, 2971, 2933, 1687, 1367, 1164, 1089, 972, 731, 699, 622 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.47 (m, 2 H, H-Ph), 7.35–7.24 (m, 3 H, H-Ph), 5.03 (d, *J* = 8.5 Hz, 1 H, 1-H), 4.30 (dd, *J* = 8.5, 4.4 Hz, 1 H, 2-H), 3.61 (ddd, *J* = 9.7, 4.4, 2.6 Hz, 1 H, 3-H), 1.80–1.67 (m, 1 H, 4-H$_a$), 1.63–1.46 (m, 1 H, 4-H$_b$), 1.42 (s, 9 H, *t*-Bu), 1.04 (t, *J* = 7.4 Hz, 3 H, 5-H).

^{13}C NMR (75 MHz, CD_3OD): δ = 157.9 (C=O), 139.7 (C-Ph), 130.2 (CH-Ph), 129.0 (CH-Ph), 128.6 (CH-Ph), 82.5 (*C*Me$_3$), 75.0, 74.5 (C-2, C-3), 65.1 (C-1), 28.6 (C*Me*$_3$), 24.5 (C-4), 10.8 (C-5).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{25}NNaO_5$: 334.1625; found: 334.1625.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpent-4-en-1-yl)carbamate (16)

TP1 described above was applied using diol **8** (200 mg, 0.71 mmol), vinyl-MgBr (2.84 mL, 2.84 mmol, 1 M solution in THF) and anhydrous THF (7 mL). FCC (CH_2Cl_2/acetone, 9:1) gave pure major diastereoisomer *anti*,*syn*-**16a** along with a mixture of both diastereoisomers *anti*,*syn*-**16a** and *anti*,*anti*-**16b** (25 mg, 0.08 mmol, 11%, pale yellow sticky oil). For analytical purposes, pure compound **16b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-16a

Yield: 130 mg (0.42 mmol, 59%); white solid; mp 86–87 °C; R_f = 0.19 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3317, 2972, 2923, 1738, 1675, 1367, 1229, 1122, 864, 725, 699, 567 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.47 (m, 2 H, H-Ph), 7.34–7.23 (m, 3 H, H-Ph), 6.08 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1 H, 4-H), 5.38 (dt, *J* = 17.2, 1.7 Hz, 1 H, 5-H$_a$), 5.20 (dt, *J* = 10.5, 1.7 Hz, 1 H, 5-H$_b$), 5.16 (d, *J* = 9.8 Hz, 1 H, 1-H), 4.38 (dq, *J* = 5.8, 1.6 Hz, 1 H, 3-H), 4.24 (dd, *J* = 9.9, 1.7 Hz, 1 H, 2-H), 1.43 (s, 9 H, *t*-Bu).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.3 (C=O), 140.4 (C-4), 140.0 (C-Ph), 130.2 (CH-Ph), 128.9 (CH-Ph), 128.5 (CH-Ph), 115.8 (C-5), 82.5 (*C*Me$_3$), 73.5, 73.1 (C-2, C-3), 64.4 (C-1), 28.6 (C*Me*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{23}NNaO_5$: 332.1469; found: 332.1470.

Data for *anti*,*anti*-16b

Colorless sticky oil; R_f = 0.07 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3376, 2978, 1687, 1368, 1253, 1160, 1113, 927, 756, 698, 562 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.50–7.46 (m, 2 H, H-Ph), 7.35–7.24 (m, 3 H, H-Ph), 6.08 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1 H, 4-H), 5.33 (ddd, *J* = 17.2, 2.1, 1.1 Hz, 1 H, 5-H_a), 5.29 (ddd, *J* = 10.3, 2.1, 1.0 Hz, 1 H, 5-H_b), 4.89 (d, *J* = 9.5 Hz, 1 H, 1-H), 4.40 (dd, *J* = 9.5, 3.5 Hz, 1 H, 2-H), 4.33 (tdd, *J* = 7.0, 3.5, 1.0 Hz, 1 H, 3-H), 1.41 (s, 9 H, *t*-Bu).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.0 (C=O), 139.5 (C-Ph), 137.6 (C-4), 130.2 (CH-Ph), 129.0 (CH-Ph), 128.6 (CH-Ph), 118.0 (C-5), 82.5 (*C*Me_3), 74.8, 74.4 (C-2, C-3), 65.1 (C-1), 28.6 (*CMe*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{23}NNaO_5$: 332.1469; found: 332.1470.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylhex-5-en-1-yl)carbamate (17)

TP1 described above was applied using diol **8** (250 mg, 0.89 mmol), allyl-MgBr (2.1 mL, 3.57 mmol, 1.7 M solution in THF) and anhydrous THF (9 mL). FCC (CH_2Cl_2/acetone, 9:1) gave pure major diastereoisomer *anti*,*syn*-**17a** along with a mixture of both diastereoisomers *anti*,*syn*-**17a** and *anti*,*anti*-**17b** (50 mg, 0.15 mmol, 17%, pale yellow sticky oil). For analytical purposes, pure compound **17b** was obtained by repeated preparative TLC (CH_2Cl_2/MeOH/NH_3, 19:1:0.1).

Data for *anti*,*syn*-17a

Yield: 155 mg (0.48 mmol, 54%); white solid; mp 133–134 °C; R_f = 0.22 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3302, 2922, 1738, 1674, 1367, 1216, 1168, 1115, 988, 864, 739, 699, 572 cm^{-1}.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.50–7.48 (m, 2 H, H-Ph), 7.33–7.25 (m, 3 H, H-Ph), 5.94 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H, 5-H), 5.16 (ddd, *J* = 17.2, 3.6, 1.5 Hz, 1 H, 6-H_a), 5.14 (d, *J* = 10.1 Hz, 1 H, 1-H), 5.07 (tdd, *J* = 10.2, 2.2, 1.1 Hz, 1 H, 6-H_b), 4.19 (dd, *J* = 10.1, 0.8 Hz, 1 H, 2-H), 3.91 (pseudo t, *J* = 7.0, 6.9 Hz, 1 H, 3-H), 2.46–2.34 (m, 2 H, 4-H), 1.41 (s, 9 H, *t*-Bu).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.6 (C=O), 140.2 (C-Ph), 136.8 (C-5), 130.3 (CH-Ph), 128.9 (CH-Ph), 128.4 (CH-Ph), 117.2 (C-6), 82.5 (*C*Me_3), 72.2, 70.9 (C-2, C-3), 64.5 (C-1), 39.8 (C-4), 28.6 (*CMe*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NNaO_5$: 346.1625; found: 346.1626.

Data for *anti*,*anti*-17b

Colorless sticky oil; R_f = 0.11 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3416, 2977, 1688, 1368, 1163, 1109, 1054, 875, 731, 698, 614 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.47 (m, 2 H, H-Ph), 7.36–7.24 (m, 3 H, H-Ph), 5.97 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1 H, 5-H), 5.13 (ddt, *J* = 17.1, 2.3, 1.5 Hz, 1 H, 5-H_a), 5.07 (ddt, *J* = 10.2, 2.3, 1.1 Hz, 1 H, 5-H_b), 5.05 (d, *J* = 8.5 Hz, 1 H, 1-H), 4.33 (dd, *J* = 8.5, 4.3 Hz, 1 H, 2-H), 3.78 (ddd, *J* = 9.5, 4.3, 3.0 Hz, 1 H, 3-H), 2.51–2.42 (m, 1 H, 4-H_a), 2.37–2.25 (m, 1 H, 4-H_b), 1.42 (s, 9 H, *t*-Bu).

^{13}C NMR (75 MHz, CD_3OD): δ = 157.9 (C=O), 139.6 (C-Ph), 137.2 (C-5), 130.2 (CH-Ph), 129.0 (CH-Ph), 128.6 (CH-Ph), 117.1 (C-6), 82.5 (*C*Me_3), 74.8, 72.7 (C-2, C-3), 65.0 (C-1), 36.5 (C-4), 28.6 (*CMe*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NNaO_5$: 346.1625; found: 346.1625.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1,3-diphenylpropyl)carbamate (18)

TP1 described above was applied using diol **8** (100 mg, 0.36 mmol), PhMgBr (1.44 mL, 1.44 mmol, 1 M solution in THF) and anhydrous THF (4 mL). FCC (hexanes/EtOAc, 6:4) gave single diastereoisomer *anti*,*syn*-**18a** (68 mg, 0.19 mmol, 52%) as a white solid.

Mp 158–159 °C; R_f = 0.17 (CH_2Cl_2/acetone, 9:1).

IR (ATR): 3426, 2970, 2534, 1739, 1667, 1370, 1217, 1106, 724, 697, 598, 564 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.51–7.46 (m, 4 H, H-Ph), 7.36–7.20 (m, 6 H, H-Ph), 5.24 (d, *J* = 9.8 Hz, 1 H, 1-H), 5.01 (br s, 1 H, 3-H), 4.39 (dd, *J* = 9.8, 1.6 Hz, 1 H, 2-H), 1.44 (s, 9 H, *t*-Bu).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.5 (C=O), 144.8 (C-Ph), 140.1 (C-Ph), 130.3 (CH-Ph), 128.9 (2 × CH-Ph), 128.4 (CH-Ph), 127.9 (CH-Ph), 127.6 (CH-Ph), 82.5 (*C*Me_3), 75.2, 73.2 (C-2, C-3), 64.9 (C-1), 28.6 (*CMe*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{25}NNaO_5$: 382.1625; found: 382.1625.

Synthesis of γ-(Hydroxyamino)-α,β-diols with the Use of Anhydrous $CeCl_3$

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpent-4-en-1-yl)carbamate (11a); Typical Procedure (TP2)

A reaction flask containing diol **7** (100 mg, 0.32 mmol) and anhydrous $CeCl_3$ (120 mg, 0.49 mmol) was sealed with a rubber septum, evacuated, and filled with argon. Anhydrous THF (3 mL) was added, and the stirred mixture was cooled to 0 °C. Vinyl-MgBr (1.28 mL, 1.28 mmol, 1 M solution in THF) was added dropwise over 5 min. The reaction mixture was allowed to slowly warm to room temperature over 16 h. When TLC showed that the reaction was complete (CH_2Cl_2/MeOH/NH_3, 94.7:5:0.3), the reaction was quenched with 1 M HCl (20 mL), and the product was extracted into Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by FCC (CH_2Cl_2/acetone, 9:1) to give single diastereoisomer *anti*,*syn*-**11a** (65 mg, 0.19 mmol, 59%) as a white solid with physical and spectral data consistent with those described above.

Benzyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpentyl)carbamate (10a)

TP2 described above was applied using diol **7** (100 mg, 0.32 mmol), anhydrous $CeCl_3$ (120 mg, 0.49 mmol), EtMgBr (0.42 mL, 1.27 mmol, 3 M solution in Et_2O) and anhydrous THF (3 mL). FCC (CH_2Cl_2/acetone, 9:1) gave single diastereoisomer *anti*,*syn*-**10a** (66 mg, 0.19 mmol, 60%) as a white solid with physical and spectral data consistent with those described above.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylpentyl)carbamate (15a)

TP2 described above was applied using diol **8** (100 mg, 0.36 mmol), anhydrous $CeCl_3$ (133 mg, 0.54 mmol), EtMgBr (0.48 mL, 1.44 mmol, 3 M solution in Et_2O) and anhydrous THF (4 mL). FCC (CH_2Cl_2/acetone, 9:1) gave single diastereoisomer *anti*,*syn*-**15a** (80 mg, 0.26 mmol, 72%) as a white solid with physical and spectral data consistent with those described above.

tert-Butyl (±)-*N*-Hydroxy-*N*-(2,3-dihydroxy-1-phenylhex-5-en-1-yl)carbamate (17a)

TP2 described above was applied using diol **8** (100 mg, 0.36 mmol), anhydrous $CeCl_3$ (133 mg, 0.54 mmol), allyl-MgBr (0.85 mL, 1.44 mmol, 1.7 M solution in THF) and anhydrous THF (4 mL). FCC (CH_2Cl_2/acetone, 9:1) gave single diastereoisomer *anti*,*syn*-**17a** (85 mg, 0.26 mmol, 72%) as a white solid with physical and spectral data consistent with those described above.

Synthesis of γ-(Hydroxyamino) Alcohols

Benzyl (±)-*N*-Hydroxy-*N*-(3-hydroxy-1,3-diphenylpropyl)carbamate (21); Typical Procedure (TP3)

To a stirred solution of 5-hydroxyisoxazolidine **19** (140 mg, 0.47 mmol) in anhydrous THF (5 mL) under argon at 0 °C was added PhMgBr (1.17 mL, 1.17 mmol, 1 M solution in THF) dropwise over 5 min. The reaction mixture was then stirred at the same temperature for 2 h. When the starting material had disappeared (TLC, CH_2Cl_2/MeOH, 98:2), the reaction was quenched with sat. aq NH_4Cl (25 mL). The mixture was diluted with Et_2O (25 mL), warmed to room temperature and stirred for an additional 5 min. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by FCC (hexanes/EtOAc, 7:3) to give two single diastereoisomers, *syn*-**21a** and *anti*-**21b**, along with a mixture of **21a** and **21b** (50 mg, 0.13 mmol, 28%, yellowish sticky oil).

Data for *syn*-21a

Yield: 80 mg (0.21 mmol, 45%); yellowish sticky oil; R_f = 0.14 (*n*-hexane/EtOAc, 1:1).

IR (ATR): 3273, 3030, 2929, 1692, 1454, 1403, 1304, 1102, 1058, 749, 695, 572 cm^{-1}.

^1H NMR (300 MHz, CD_3OD): δ = 7.38–7.23 (m, 15 H, H-Ph), 5.13 (d, *J* = 7.9 Hz, 1 H, 1-H), 5.12 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 5.07 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 4.53 (dd, *J* = 7.8, 6.2 Hz, 1 H, 3-H), 2.55 (dt, *J* = 13.8, 8.0 Hz, 1 H, 2-H$_a$), 2.24 (ddd, *J* = 13.8, 7.2, 6.2 Hz, 1 H, 2-H$_b$).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.8 (C=O), 145.9 (C-Ph), 141.1 (C-Ph), 137.7 (C-Ph), 129.4 (3 × CH-Ph), 129.1 (CH-Ph), 129.0 (CH-Ph), 128.8 (CH-Ph), 128.7 (CH-Ph), 128.5 (CH-Ph), 127.1 (CH-Ph), 72.5 (C-3), 68.5 (OCH_2Ph), 61.2 (C-1), 42.5 (C-2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_4$: 378.1700; found: 378.1703; *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{23}NNaO_4$: 400.1520; found: 400.1523.

Data for *anti*-21b

Yield: 30 mg (0.08 mmol, 17%); yellowish sticky oil; R_f = 0.16 (*n*-hexane/EtOAc, 1:1).

IR (ATR): 3309, 2924, 1681, 1414, 1301, 1218, 1102, 915, 748, 694, 547 cm^{-1}.

^1H NMR (600 MHz, CD_3OD): δ = 7.38–7.24 (m, 15 H, H-Ph), 5.43 (dd, *J* = 10.5, 4.6 Hz, 1 H, 1-H), 5.19 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 5.11 (d, AB, *J* = 12.4 Hz, 1 H, OC*H*$_2$Ph), 4.71 (dd, *J* = 9.5, 3.7 Hz, 1 H, 3-H), 2.52 (ddd, *J* = 14.2, 10.5, 3.7 Hz, 1 H, 2-H$_a$), 2.11 (ddd, *J* = 14.2, 9.5, 4.6 Hz, 1 H, 2-H$_b$).

^{13}C NMR (150 MHz, CD_3OD): δ = 159.2 (C=O), 146.3 (C-Ph), 141.6 (C-Ph), 137.7 (C-Ph), 129.5 (CH-Ph), 129.3 (2 × CH-Ph), 129.1 (CH-Ph), 128.9 (CH-Ph), 128.7 (CH-Ph), 128.5 (CH-Ph), 128.3 (CH-Ph), 126.9 (CH-Ph), 71.6 (C-3), 68.6 (OCH_2Ph), 60.4 (C-1), 42.4 (C-2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_4$: 378.1700; found: 378.1703; *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{23}NNaO_4$: 400.1520; found: 400.1523.

Benzyl (±)-*N*-Hydroxy-*N*-(3-hydroxy-1-phenylpentyl)carbamate (22)

TP3 described above was applied using 5-hydroxyisoxazolidine **19** (340 mg, 1.14 mmol), EtMgBr (0.93 mL, 2.80 mmol, 3 M solution in Et_2O) and anhydrous THF (11 mL). FCC (CH_2Cl_2/MeOH, 99:1) gave an inseparable mixture of two diastereoisomers, *syn*-**22a** and *anti*-**22b** (300 mg, 0.91 mmol, 80%, **22a**/**22b**, 70:30), as a yellowish sticky oil.

R_f = 0.18 (CH_2Cl_2/MeOH, 99:1).

^1H NMR (300 MHz, CD_3OD): δ (70:30 mixture of diastereoisomers) = 7.42–7.23 (m, 10 H, H-Ph), 5.46 (dd, *J* = 11.3, 3.7 Hz, 0.25 H, 1-H), 5.33 (dd, *J* = 8.8, 6.7 Hz, 0.75 H, 1-H), 5.22–5.08 (m, 2 H, OC*H*$_2$Ph), 3.64–3.55 (m, 0.25 H, 3-H), 3.33–3.25 (m, 0.75 H, 3-H), 2.38 (ddd, *J* = 14.3, 11.3, 2.6 Hz, 0.25 H, 2-H$_a$), 2.18 (ddd, *J* = 13.9, 8.8, 3.9 Hz, 0.75 H, 2-H$_a$), 2.05 (ddd, *J* = 13.9, 8.8, 6.6 Hz, 0.75 H, 2-H$_b$), 1.68 (ddd, *J* = 14.3, 9.8, 3.7 Hz, 0.25 H, 2-H$_b$), 1.59–1.36 (m, 2 H, 4-H), 0.97 (t, *J* = 7.4 Hz, 0.75 H, 5-H), 0.89 (t, *J* = 7.4 Hz, 2.25 H, 5-H).

^{13}C NMR (150 MHz, CD_3OD): δ (70:30 mixture of diastereoisomers) = 159.3, 158.7, 142.2, 141.1, 137.8 (2 C), 129.4 (2 C), 129.3 (2 C), 129.1 (3 C), 128.9 (2 C), 128.6, 128.5, 128.4, 71.0, 70.5, 68.6, 68.5, 61.2, 60.3, 40.2, 40.0, 31.6, 31.4, 10.4, 10.1.

MS (ESI + APCI): *m*/*z* = 330.2 ($C_{19}H_{24}NO_4$) [M + H]$^+$.

tert-Butyl (±)-*N*-Hydroxy-*N*-(3-hydroxy-1,3-diphenylpropyl)carbamate (23)

TP3 described above was applied using 5-hydroxyisoxazolidine **20** (200 mg, 0.75 mmol), PhMgBr (1.9 mL, 1.9 mmol, 1 M solution in THF) and anhydrous THF (8 mL). FCC (CH_2Cl_2/MeOH, 98:2) gave a mixture of two diastereoisomers, *syn*-**23a** and *anti*-**23b** (230 mg, 0.67 mmol, 89%, **23a**/**23b**, 70:30), as a yellowish sticky oil. For analytical purposes, pure compounds **23a** and **23b** were obtained by repeated preparative TLC (hexanes/acetone, 9:1).

Data for *syn*-23a

Colorless sticky oil; R_f = 0.15 (*n*-hexane/acetone, 8:2).

IR (ATR): 3460, 2971, 1738, 1600, 1366, 1217, 1163, 1106, 851, 762, 697, 576 cm^{-1}.

^1H NMR (300 MHz, CD_3OD): δ = 7.39–7.24 (m, 10 H, H-Ph), 4.98 (dd, *J* = 8.4, 7.1 Hz, 1 H, 1-H), 4.57 (dd, *J* = 7.5, 6.6 Hz, 1 H, 3-H), 2.56 (ddd, *J* = 13.7, 8.5, 7.6 Hz, 1 H, 2-H$_a$), 2.24–2.15 (m, 1 H, 2-H$_b$), 1.38 (s, 9 H, *t*-Bu).

^{13}C NMR (75 MHz, CD_3OD): δ = 158.4 (C=O), 146.0 (C-Ph), 141.6 (C-Ph), 129.4 (CH-Ph), 129.3 (CH-Ph), 128.8 (CH-Ph), 128.5 (2 × CH-Ph), 127.3 (CH-Ph), 82.3 (*C*Me$_3$), 72.6 (C-3), 61.2 (C-1), 42.7 (C-2), 28.6 (C*Me*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{25}NNaO_4$: 366.1676; found: 366.1676.

Data for *anti*-23b

Colorless sticky oil; R_f = 0.17 (*n*-hexane/acetone, 8:2).

IR (ATR): 3222, 2977, 1681, 1454, 1367, 1161, 1106, 1056, 750, 698, 571 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.41–7.22 (m, 10 H, H-Ph), 5.32 (dd, *J* = 10.3, 4.8 Hz, 1 H, 1-H), 4.71 (dd, *J* = 9.3, 3.8 Hz, 1 H, 3-H), 2.48 (ddd, *J* = 14.1, 10.3, 3.9 Hz, 1 H, 2-H_a), 2.11 (ddd, *J* = 14.1, 9.3, 4.8 Hz, 1 H, 2-H_b), 1.42 (s, 9 H, *t*-Bu).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.8 (C=O), 146.5 (C-Ph), 142.0 (C-Ph), 129.3 (2 × CH-Ph), 128.7 (CH-Ph), 128.4 (CH-Ph), 128.3 (CH-Ph), 126.9 (CH-Ph), 82.3 (*C*Me$_3$), 71.7 (C-3), 60.5 (C-1), 42.6 (C-2), 28.6 (C*Me*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{25}NNaO_4$: 366.1676; found: 366.1675.

tert-Butyl (±)-*N*-Hydroxy-*N*-(3-hydroxy-1-phenylpentyl)carbamate (24)

TP3 described above was applied using 5-hydroxyisoxazolidine **20** (940 mg, 3.54 mmol), EtMgBr (2.95 mL, 8.85 mmol, 3 M solution in Et_2O) and anhydrous THF (35 mL). FCC (CH_2Cl_2/MeOH, 98:2) gave an inseparable mixture of two diastereoisomers, *syn*-**24a** and *anti*-**24b** (980 mg, 3.32 mmol, 94%, **24a**/**24b**, 70:30), as a yellowish sticky oil.

R_f = 0.14 (CH_2Cl_2/MeOH, 98:2).

^{1}H NMR (600 MHz, CD_3OD): δ (70:30 mixture of diastereoisomers) = 7.44–7.38 (m, 2 H, H-Ph), 7.33–7.22 (m, 3 H, H-Ph), 5.36 (dd, *J* = 11.3, 3.7 Hz, 0.4 H, 1-H), 5.23 (dd, *J* = 8.8, 6.7 Hz, 0.6 H, 1-H), 3.64–3.60 (m, 0.4 H, 3-H), 3.32–3.28 (m, 0.6 H, 3-H), 2.36 (ddd, *J* = 14.3, 11.3, 2.6 Hz, 0.4 H, 2-H_a), 2.14 (ddd, *J* = 13.9, 8.9, 4.0 Hz, 0.6 H, 2-H_a), 2.05 (ddd, *J* = 13.9, 8.9, 6.7 Hz, 0.6 H, 2-H_b), 1.67 (ddd, *J* = 14.3, 9.7, 3.8 Hz, 0.4 H, 2-H_b), 1.59–1.44 (m, 2 H, 4-H), 1.43 (s, 3.6 H, *t*-Bu), 1.41 (s, 5.4 H, *t*-Bu), 0.99 (t, *J* = 7.5 Hz, 1.2 H, 5-H), 0.91 (t, *J* = 7.4 Hz, 1.8 H, 5-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (70:30 mixture of diastereoisomers) = 159.0, 158.3, 142.7, 141.6, 129.2 (2 C), 129.0 (2 C), 128.5, 128.2, 82.2 (2 C), 71.0, 70.5, 61.3, 60.3, 40.4, 40.2, 31.6, 31.4, 28.6 (2 C), 10.3, 10.2.

MS (ESI + APCI): *m*/*z* = 296.2 ($C_{16}H_{26}NO_4$) [M + H]$^+$.

Reductive Cleavage of the N–O Bond in γ-(Hydroxyamino)-α,β-diols

Benzyl (±)-(2,3-Dihydroxy-1-phenylpent-4-en-1-yl)carbamate (25); Typical Procedure (TP4)

To a stirred solution of (hydroxyamino)diol **11a** (100 mg, 0.29 mmol) in acetic acid (2 mL) was added zinc dust (0.76 g, 11.6 mmol), and the reaction mixture was stirred at 70 °C. The reaction progress was monitored by TLC (hexanes/EtOAc, 1:1). After stirring for 12 h, another portion of zinc dust (0.19 g, 2.9 mmol) was added, and stirring was continued at the same temperature for an additional 12 h. After this time, the reaction mixture was cooled to r.t., diluted with 0.1 M NaOH solution (10 mL) and CH_2Cl_2 (10 mL), and the resulting slurry was vigorously stirred for 10 min. Insoluble solids were removed by filtration through a pad of Celite and washed with 0.1 M NaOH solution (10 mL) and CH_2Cl_2 (10 mL). After phase separation, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The product was isolated by FCC (hexanes/EtOAc, 65:35) to give *N*-Cbz-protected amino diol **25** (70 mg, 0.21 mmol, 72%) as a colorless oil.

R_f = 0.11 (*n*-hexane/EtOAc, 65:35).

IR (ATR): 3388, 3033, 2518, 1692, 1423, 1349, 1217, 1026, 929, 737, 697, 597 cm^{-1}.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.41–7.22 (m, 10 H, H-Ph), 5.95 (ddd, *J* = 17.3, 10.6, 6.2 Hz, 1 H, 4-H), 5.21 (dt, *J* = 17.3, 1.3 Hz, 1 H, 5-H_a), 5.14 (dt, *J* = 10.5, 1.3 Hz, 1 H, 5-H_b), 5.08 (d, *J* = 12.5 Hz, 1 H, O*CH*$_2$Ph), 5.02 (d, *J* = 12.5 Hz, 1 H, O*CH*$_2$Ph), 4.83 (d, *J* = 6.8 Hz, 1 H, 1-H), 4.05–4.00 (m, 1 H, 3-H), 3.72 (dd, *J* = 6.8, 3.1 Hz, 1 H, 2-H).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.2 (C=O), 141.7 (C-Ph), 139.8 (C-4), 138.2 (C-Ph), 129.4 (CH-Ph), 129.2 (CH-Ph), 129.0 (CH-Ph), 128.8 (2 × CH-Ph), 128.3 (CH-Ph), 116.4 (C-5), 76.6, 73.3 (C-2, C-3), 67.6 (O*CH*$_2$Ph), 59.2 (C-1).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{21}NNaO_4$: 350.1363; found: 350.1364.

tert-Butyl (±)-(2,3-Dihydroxy-1-phenylhex-5-en-1-yl)carbamate (26)

TP4 described above was applied using (hydroxyamino)diol **17a** (100 mg, 0.31 mmol), acetic acid (2 mL), zinc dust (0.81 g, 12.4 mmol + 0.20 g, 3.1 mmol). FCC (hexanes/EtOAc, 75:25) gave *N*-Boc-protected amino diol **26** (75 mg, 0.24 mmol, 77%) as a white solid.

Mp 104–105 °C; R_f = 0.16 (*n*-hexane/EtOAc, 7:3).

IR (ATR): 3359, 2922, 1679, 1504, 1368, 1245, 1167, 1061, 914, 753, 701, 599 cm^{-1}.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.35–7.30 (m, 4 H, H-Ph), 7.25–7.21 (m, 1 H, H-Ph), 5.77 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1 H, 5-H), 5.08–5.02 (m, 1 H, 6-H_a), 5.02–4.98 (m, 1 H, 6-H_b), 4.77 (d, *J* = 7.3 Hz, 1 H, 1-H), 3.65–3.58 (m, 2 H, 3-H, 2-H), 2.34–2.26 (m, 2 H, 4-H), 1.42 (s, 9 H, *t*-Bu).

^{13}C NMR (150 MHz, CD_3OD): δ = 158.0 (C=O), 142.2 (C-Ph), 136.3 (C-5), 129.3 (CH-Ph), 128.4 (CH-Ph), 128.1 (CH-Ph), 117.4 (C-6), 80.4 (*C*Me$_3$), 75.0, 71.0 (C-2, C-3), 59.1 (C-1), 39.7 (C-4), 28.8 (C*Me*$_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{25}NNaO_4$: 330.1676; found: 330.1676.

Crystallography[18]

Data collection and cell refinement on **12a** were performed using a Stoe StadiVari diffractometer at 100 K using a Pilatus3R 300K HPAD detector and a microfocused Xenocs Genix3D Cu HF (CuKα radiation λ = 1.54186 Å) source. The diffraction intensities were corrected for Lorentz and polarization factors. The structure was solved using the Sir11 program[19] and refined by the full-matrix least-squares procedure with ShelXL (version 2018/3).[20] Multi-scan absorption corrections were applied using Stoe LANA software. Geometrical analyses were performed with ShelXL. The structures were drawn with the OLEX2 package.[21] The Supporting Information contains the Hirshfeld surface analysis. CrystalExplorer[22] was used to calculate the Hirshfeld surface and associated fingerprint plots.[23]

Compound 12a

Empirical formula: $C_{20}H_{23}NO_5$; formula weight = 357.39; crystal system: monoclinic, space group $P2_1/c$ (no. 14), *a* = 21.1672(5) Å, *b* = 11.2461(2) Å, *c* = 15.3097(3) Å, β = 94.813(2), *V* = 3631.60(13) Å^3, *Z* = 8, *T* = 100 K, μ(CuKα) = 0.772 mm^{-1}, *D*calc = 1.307 g/cm^3, 43652 reflections measured (8.384 ≤ 2θ ≤ 143.564), 6976 unique (R_{int} = 0.0197, R_{sigma} = 0.0138) which were used in all calculations. The final R_1 was 0.0305 [$I > 2\sigma(I)$] and wR_2 was 0.0751 (all data).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1706543.

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