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Practical Enantiospecific Synthesis of an Orthogonally Protected 1,4-*trans*-1,5-*cis*- 4,5-Diamino-2-cyclopenten-1-ol Derivative

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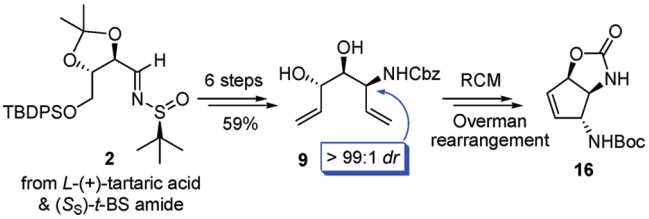

An enantiospecific synthesis of an orthogonally protected 1,4-*trans*-1,5-*cis*-4,5-diamino-2-cyclopenten-1-ol derivative **16** is reported. The *trans*-diamine moiety was established by *anti*-specific vinyl addition to a novel threitol-derived *tert*-butanesulfinylimine **2** and Overman rearrangement. The cyclopentene skeleton was constructed via RCM reaction of a key 1,6-diene intermediate **11**.

Chiral 1,2-amino alcohols are essential structural features in natural products, therapeutics, as well as chiral ligands and auxiliaries.[1] Similarly, chiral 1,2-diamines are also pivotal to these fields.[2] 4,5-Diamino-2-cyclopenten-1-ol (**I**), a cyclic variant incorporating both 1,2-amino alcohol and 1,2-diamine moieties, has been a challenging target due to its dense functionalization, yet its synthetic utility has been highlighted by several total syntheses of the antitumor oroidin alkaloid (−)-agelastatin A.[3] For example, Weinreb's racemic synthesis employed Sharpless−Kresze allylic amination for the introduction of the C-4 amino group.[4a,b] Hale prepared a derivative of **I** in 17 steps starting from D-glucosamine.[4c] [3,3]-Rearrangement of allylic isocyanate was used twice by Ichikawa to deliver an orthogonally protected intermediate in 20 steps from L-arabitol.[4d] Recently, Chida's synthesis featured sequential sigmatropic rearrangement to provide an analogue of **I** in 15 steps from D-tartaric acid.[4e] Focusing on the chemistry of α-chiral amines,[5] herein we report a practical and enantiospecific synthesis of a precursor for 1,4-*trans*-1,5-*cis*-4,5-diamino-2-cyclopenten-1-ol **I**.

We envisaged that Overman rearrangement[6] could be employed not only as an ideal protocol for the chiral allylic amine motif in **I** but also as a strategic solution to the starting material (Scheme 1). In fact, the *trans*-diol moiety of **II** mapped nicely onto the skeleton of L-(+)-tartaric acid, an inexpensive and readily available starting material. Next, the 1,6-diene **III**, a key precursor to the cyclopentene ring via RCM reaction,[7] was to be procured by Wittig methylenation and vinyl addition to a *tert*-butanesulfinylimine.[8] With regard to the latter process, the α-alkoxyl group of imine was expected to favor the desired *anti*- diastereoselectivity. Overall, this approach was totally different from that of Chida and co-workers[4e] in terms of tailoring of the threitol topology.

Since a priori stereochemical prediction for organometallic additions to *N*-*tert*-butanesulfinyl-α-alkoxyaldimines has often been difficult,[9] both (S_S)- and (R_S)-imines were prepared at the outset (Scheme 2). Monosilylated diol **1**[10] underwent Swern oxidation[11] and condensation with (S_S)- and (R_S)-*tert*-butanesulfinamide, respectively, to furnish novel threitol-derived *N*-*t*-BS-imines **2** and **3** in both the same 77% overall yields. $CuSO_4$ and $Ti(OEt)_4$[12] gave comparable results in imine formation, although the former required 2−3 days for complete conversion. Under both conditions, epimerization of imine α-position was not detected.

Subsequent Grignard additions to *t*-BS-imines **2** and **3** revealed some interesting stereochemical outcomes (Table 1).

(1) For excellent reviews, see: (a) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835. (b) Reetz, M. T. *Chem. Rev.* **1999**, *99*, 1121. (c) Bergmeier, S. C. *Tetrahedron* **2000**, *56*, 2561. (d) Burchak, O. N.; Py, S. *Tetrahedron* **2009**, *65*, 7333.

(2) For excellent reviews, see: (a) Kizirian, J.-C. *Chem. Rev.* **2008**, *108*, 140. (b) Viso, A.; de la Pradilla, R. F.; García, A.; Flores, A. *Chem. Rev.* **2005**, *105*, 3167. (c) Kotti, S. R. S. S.; Timmons, C.; Li, G. *Chem. Biol. Drug Des.* **2006**, *67*, 101.

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(6) For an excellent review, see: (a) Overman, L. E.; Carpenter, N. E. *Org. React.* **2005**, *66*, 1. For an improved protocol, see: (b) Nishikawa, T.; Asai, M.; Ohyabu, N.; Isobe, M. *J. Org. Chem.* **1998**, *63*, 188.

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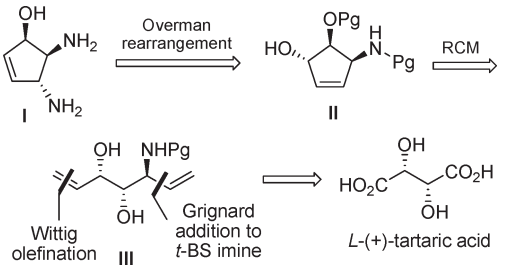
SCHEME 1. Retrosynthetic Plan for I



SCHEME 2. Synthesis of Threitol-Derived *t*-BS-Imines

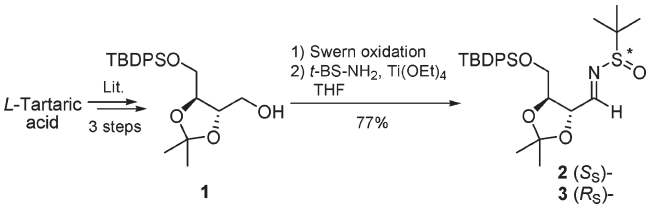
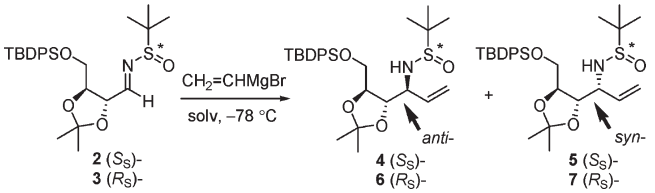


TABLE 1. *Anti*-Selective Vinyl Addition to 2 and 3[a]



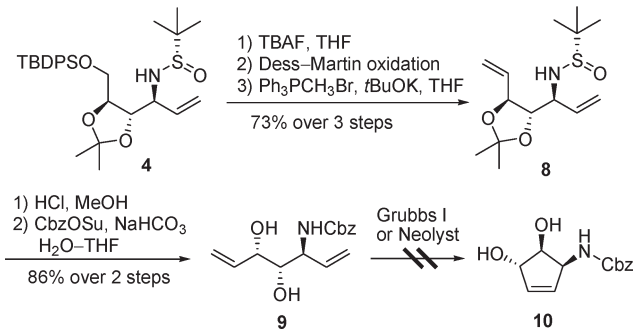
entry	imine	solvent	adduct[b] (%)	anti/syn[c]
1[d]	(S_S)-**2**	THF	**4** + **5**, 86	1.5:1
2	(S_S)-**2**	DCM	**4** only, 94	>99:1
3	(R_S)-**3**	DCM	**6** + **7**, 85	4.8:1
4[d]	(R_S)-**3**	THF	**6** + **7**, 82	7.3:1
5[d]	(R_S)-**3**	DCM	**6** + **7**, 93	9.6:1

[a]Conditions: To a solution of imine (5.0 mmol, 0.2 M) at −78 °C was added dropwise 2.5 equiv of vinylmagnesium bromide, except as indicated otherwise. [b]Isolated yields. [c]Determined by ^{1}H NMR spectroscopy of the crude adducts. [d]The Grignard reagent was precomplexed with TMEDA.

Addition of vinylmagnesium bromide—TMEDA complex[9] to **2** at −78 °C produced inseparable epimers **4** and **5** in a disappointing 1.5:1 ratio. However, this scenario was fundamentally changed by shifting the solvent to DCM and omitting the additive, yielding diastereospecifically a single adduct **4** as judged by the diagnostic olefinic region of the ^{1}H NMR spectroscopy of the crude product (entry 2). On the other hand, using the same protocol, the addition to (R_S)-imine **3** yielded a pair of separable epimers **6**/**7** in a useful 4.8:1 ratio. Interestingly, contrary to the case of **2**, the additive TMEDA enhanced the dr to 9.6:1 for the mismatched substrate **3** under optimized conditions (entry 5). Gratifyingly, the newly formed stereogenic centers in **4** and **6** were unamibiguously determined to be of the desired *S*- configuration, by X-ray analysis of the crystalline desilylation products (see the Supporting Information). Thus, for both imines **2** and **3**, the

(13) Precedences of diastereoconvergent additions to *t*-BS imines are very rare: (a) McMahon, J. P.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 1645. (b) Risseeuw, M. D. P.; Mazurek, J.; van Langenvelde, A.; van der Marel, G. A.; Overkleeft, H. S.; Overhand, M. *Org. Biomol. Chem.* **2007**, *5*, 2311.

SCHEME 3. Synthesis of 1,6-Diene



major vinyl adducts **4** and **6** were *anti*-β-amino alcohols, regardless of the sulfinyl chirality.[13] Nevertheless, it should be emphasized that the unique stabilizing and electron-withdrawing effects of *t*-BS are irreplaceable.[14]

Having one olefin double bond in place, we proceeded to modify the other end of the threitol skeleton. Deblocking the TBDPS group of **4** with TBAF, Dess−Martin oxidation[15] of the resulting primary alcohol, and standard Wittig olefination of the crude aldehyde afforded diene **8** in 73% yield over three steps (Scheme 3). This process demonstrated the compatibility of *t*-BS with the hypervalent iodine reagent Dess−Martin periodinane, which may even qualify it as a protecting group proper in the multistep synthesis of complex molecules. Acidic hydrolysis of both the acetonide and *t*-BS followed by selective *N*-protection with Cbz in one pot provided the RCM precursor **9** in high yield. However, unlike its homologue which cyclized smoothly,[4d] the RCM reaction of diene **9** using Grubbs' first-generation catalyst was sluggish and complex, nor could Neolyst solve the problem. We assumed that intramolecular hydrogen bonding between the polar functionalities might lock **9** in an unfavorble conformation for ring-closure.

To circumvent this difficulty, the diol was acetylated, and diene **11** proved to be an excellent substrate for RCM. With the original Grubbs catalyst (2.5−3.5 mol %) in DCM, a typical gram-scale run furnished cyclopentene **12** in 91% yield, plus 6% unreacted diene, under diluted conditions (Scheme 4). The Ac protections were conveniently removed by mild alcoholysis using a catalytic amount (20 mol %) of K_2CO_3, with concomitant cyclization to yield a carbamate intermediate. In view of its low solubility and potential hydrophilicity, the crude product was used directly without aqueous workup, and its reaction with trichloroacetonitrile proceeded smoothly under conventional conditions. The Overman rearrangement (with Isobe's modification[6b]) of the resulting trichloroacetimidate **13** was uneventful, affording amide **14** with a *trans*- diamine substitution pattern in excellent yields (up to 95%).

Further transformation of the trichloroacetamide turned out to be nontrivial (Scheme 5). Initial attempts at selective removal of this *N*-acyl group in the presence of the carbamate

(14) Analogous *N*-Ts-imines were unstable, while *N*-benzylimines gave lower (35−84%) yields: (a) Cossy, J.; Pévet, I.; Meyer, C. *Eur. J. Org. Chem.* **2001**, 2841. In contrast to *t*-BS imines, the drs for *p*-toluenesulfinylimines were controlled by the sulfur chirality: (b) Zhou, D.; Staake, M.; Patterson, S. E. *Org. Lett.* **2008**, *10*, 2179.

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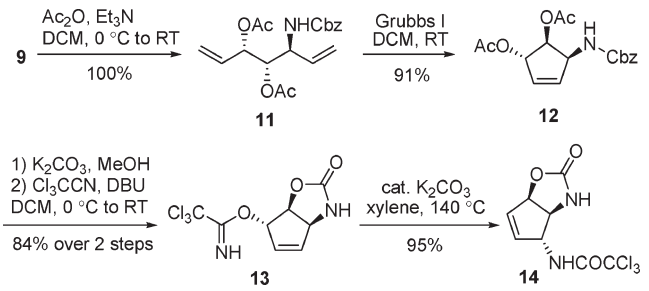
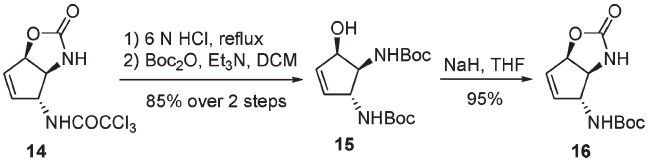
SCHEME 4. Synthesis of 4,5-Diamino-2-cyclopenten-1-ol



SCHEME 5. Functional Group Manipulations



using literature protocols were unsuccessful (aq NaOH, or $NaBH_4$/EtOH) or low yielding (Cs_2CO_3, DMF, 100 °C).[16] Fortuitously, when we turned to acidic hydrolysis (6 N HCl, reflux),[17] a clean global deprotection of both the trichloroacetamide and carbamate was achieved. After evaporation of the volatiles, the resulting diamine bis-HCl salt was neutralized and protected with Boc_2O. To differentiate the two amino groups again, compound **15** was treated with NaH in THF to effect a smooth cyclization, yielding carbamate **16** (95%), whose functionalities were orthogonally protected.

In conclusion, we have developed a practical and enantiospecific access to an orthogonally protected 1,4-*trans*-1,5-*cis*-4,5-diamino-2-cyclopenten-1-ol derivative **16** using inexpensive starting materials such as L-(+)-tartaric acid, (S_S)-*tert*-butanesulfinamide, and accessible reagents and catalysts. The overall yield is 34% from imine **2** in 14 steps, and all operations are convenient. In addition, we have identified a simple protocol for efficient synthesis of chiral β-hydroxy-α-branched allylic amines[18] via a highly diastereoselective vinyl addition to threitol-derived *t*-BS-imines. Other features of the present route include a RCM reaction to construct the cyclopentene ring and an Overman rearrangement to install the C-4 amino group. Finally, the *N*-*tert*-butanesulfinyl auxiliary was shown to be compatible with Dess−Martin oxidation and Wittig olefination.

Experimental Section

(S_S)-*N*-((*S*)-1-((4*S*,5*S*)-5-((*tert*-Butyldiphenylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)allyl)-2-methylpropane-2-sulfinamide (4). Under a N_2 atmosphere, to a cooled (−78 °C) solution of imine **2** (4.445 g, 8.87 mmol) in CH_2Cl_2 (45 mL) was added dropwise vinylmagnesium bromide (0.7 M in THF, 31.7 mL, 22.2 mmol) over 5 min, and the solution was stirred at this temperature for 1 h, quenched by addition of satd aq NH_4Cl, and warmed to rt. The aqueous layer was extracted with ether (2 × 30 mL), and the combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/6 to 1/3) to afford **4** (4.410 g, 94%) as a colorless oil: $[\alpha]^{24}_D$ +30.9 (*c* 1.09, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71−7.65 (m, 4H), 7.45−7.35 (m, 6H), 5.54 (ddd, 1H, *J* = 17.2, 10.4, 8.0 Hz), 5.35 (d, 1H, *J* = 17.2 Hz), 5.23 (d, 1H, *J* = 10.4 Hz), 4.24 (dd, 1H, *J* = 7.9, 3.6 Hz), 4.19 (dt, 1H, *J* = 8.2, 3.0 Hz), 4.11−4.07 (m, 1H), 3.82 (d br, 1H, *J* = 2.4 Hz), 3.81−3.78 (AB-d, 1H, J_{AB} = 11.3 Hz, *J* = 4.0 Hz), 3.71−3.68 (AB-d, 1H, J_{AB} = 11.3 Hz, *J* = 4.2 Hz), 1.42 (s, 3H), 1.41 (s, 3H), 1.21 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6 (4C), 133.7, 133.0 (2C), 129.7 (2C), 127.7 (4C), 120.1, 109.1, 79.6, 77.0, 64.6, 57.6, 55.6, 27.3, 27.0, 26.8 (3C), 22.6 (3C), 19.2; HR-ESI-MS *m*/*z* calcd for $C_{29}H_{44}NO_4SSi$ ($M + H^+$) 530.2760, found 530.2753.

(S_S)-*N*-((*S*)-1-((4*S*,5*S*)-2,2-Dimethyl-5-vinyl-1,3-dioxolan-4-yl)-allyl)-2-methylpropane-2-sulfinamide (8). Compound **4** (7.870 g, 14.88 mmol) in THF (40 mL) was treated with TBAF (1.0 M in THF, 16.4 mL, 16.4 mmol) for 1 h at rt, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/2 to EtOAc) to afford the desilylation product (4.290 g, 99%) as colorless crystals. To a cooled (0 °C) solution of the above alcohol (625 mg, 2.15 mmol) and pyridine (0.34 mL, 4.3 mmol) in CH_2Cl_2 (10 mL) was added Dess−Martin periodinane (1.64 g, 3.87 mmol), and the solution was warmed to rt and stirred at this temperature for 1 h, diluted with ether, quenched with 10% aq $Na_2S_2O_3$ and satd aq $NaHCO_3$, and stirred for 15 min. The aqueous layer was extracted with ether (4 × 30 mL), and the combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Under a N_2 atmosphere, a suspension of methyltriphenylphosphonium bromide (2.30 g, 6.45 mmol) in THF (30 mL) was treated with KHMDS (0.91 M in THF, 6.85 mL, 6.23 mmol) at rt for 1 h and cooled to −78 °C. To the yellow ylide solution was added the above crude aldehyde in THF (6 mL), and the mixture was warmed to room temperature, stirred for 4 h, and then heated at 50 °C for 2 h. The cooled mixture was quenched by addition of satd aq NH_4Cl, the aqueous layer was extracted with ether (2 × 30 mL), and the combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/4 to 1/2) to afford **8** (459 mg, 74%) as a yellow oil: $[\alpha]^{25}_D$ +81.3 (*c* 0.76, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddd, 1H, *J* = 17.3, 10.0, 7.2 Hz), 5.67 (ddd, 1H, *J* = 17.0, 10.2, 8.4 Hz), 5.38 (d, 1H, *J* = 17.3 Hz), 5.38 (d, 1H, *J* = 17.0 Hz), 5.32 (d, 1H, *J* = 10.3 Hz), 5.28 (d, 1H, *J* = 10.5 Hz), 4.39 (t, 1H, *J* = 7.9 Hz), 4.15−4.10 (m, 1H), 3.92 (dd, 1H, *J* = 8.1, 3.8 Hz), 3.78 (d br, 1H, *J* = 2.5 Hz), 1.43 (s, 3H), 1.40 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 133.8, 120.3, 119.3, 109.3, 82.6, 78.0, 57.6, 55.7, 26.9, 26.8, 22.6 (3C); HR-ESI-MS *m*/*z* calcd for $C_{14}H_{26}NO_3S$ ($M + H^+$) 288.1633, found 288.1620.

Benzyl *N*-[(1*S*,4*S*,5*S*)-4,5-Diacetoxy-2-cyclopenten-1-yl]carbamate (12). Under a N_2 atmosphere, to a solution of diene **11** (1.010 g, 2.80 mmol) in DCM (140 mL) was added Grubbs' first-generation catalyst (57 mg, 0.07 mmol, 2.5 mol %) at rt, the solution was stirred overnight, an additional amount (23 mg, 1.0 mol %) of catalyst was added, and stirring was continued for 5 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/3 to 1/2) to recover a small amount of **11** (61 mg, 6%), followed by **12** (848 mg, 91%) as a pale yellow oil which crystallized on standing: mp 63−65 °C; $[\alpha]^{23}_D$ +175.5 (*c* 0.42, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.30 (m, 5H), 6.04−5.98 (m, 1H), 5.98−5.92 (m, 1H), 5.66 (s br, 1H), 5.31−5.27 (m, 1H), 5.15−5.03 (m, 3H), 4.85 (d br, 1H, *J* = 8.4 Hz), 2.06 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4,

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(17) Casara, P. *Tetrahedron Lett.* **1994**, *35*, 3049.

(18) For recent synthetic methods for chiral α-branched allylic amines, see: (a) Ni, C.; Liu, J.; Zhang, L.; Hu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 786. (b) Brak, K.; Ellman, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 3850. (c) Reference 5a.

169.6, 155.7, 136.3, 135.6, 131.5, 128.5 (2C), 128.2 (3C), 81.0, 75.1, 67.0, 55.6, 20.9, 20.6; HR-ESI-MS m/z calcd for $C_{17}H_{19}NNaO_6$ ($M + Na^+$) 356.1110, found 356.1092.

(3a*S*,6*S*,6a*S*)-2-Oxo-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*d*]-oxazol-6-yl 2,2,2-Trichloroacetimidate (13). A solution of **12** (112 mg, 0.34 mmol) in MeOH (5 mL) was treated with K_2CO_3 (10 mg, 0.072 mmol) at rt overnight, and the solvent was completely removed under reduced pressure. To the residue were added DCM (5 mL) and DBU (0.02 mL), the suspension was cooled to 0 °C, and Cl_3CCN (0.15 mL) was added dropwise. The suspension was slowly warmed to rt, stirred for 2 h, and concentrated. The residue was purified by silica gel flash column chromatography (EtOAc/hexane = 2/1) to afford **13** (81 mg, 84%) as white crystals: mp 140−152 °C dec; $[\alpha]^{24}_D$ +233.8 (c 0.81, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 6.60 (s br, 1H), 6.23−6.17 (m, 2H), 5.91 (s, 1H), 5.10 (d, 1H, J = 7.0 Hz), 4.92 (d, 1H, J = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 158.2, 137.4, 130.9, 90.8, 86.4, 82.2, 60.4; HR-ESI-MS m/z calcd for $C_8H_8Cl_3N_2O_3$ ($M + H^+$) 284.9601, found 284.9611.

2,2,2-Trichloro-*N*-((3a*S*,4*R*,6a*R*)-2-oxo-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*d*]oxazol-4-yl)acetamide (14). Under a N_2 atmosphere, a mixture of **13** (372 mg, 1.30 mmol) and K_2CO_3 (28 mg, 0.21 mmol) in xylene (30 mL) was heated at 140 °C for 9 h, cooled to rt, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/1 to 2/1) to afford **14** (355 mg, 95%) as a white foam: mp 179−181 °C; $[\alpha]^{20}_D$ −116.0 (c 0.42, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD) δ 6.16 (dt, 1H, J = 5.8, 1.8 Hz), 6.10−6.07 (m, 1H), 5.73−5.70 (m, 1H), 4.73 (s br, 1H), 4.19 (d, 1H, J = 7.3 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 163.9, 160.5, 134.9, 134.3, 93.6, 86.5, 65.3, 61.7; HR-ESI-MS m/z calcd for $C_8H_8Cl_3N_2O_3$ ($M + H^+$) 284.9601, found 284.9587.

***C*,*C*′-Bis(1,1-dimethylethyl) *N*,*N*′-[(1*R*,2*S*,3*R*)-3-Hydroxy-4-cyclopenten-1,2-diyl]biscarbamate (15).** Compound **14** (665 mg, 2.29 mmol) was suspended in 6 N HCl (15 mL), the mixture was refluxed for 12 h, and the resulting solution was concentrated and dried under high vacuum. The white solid thus obtained was taken up in DCM−MeOH (1:1, 20 mL), Et_3N (0.95 mL, 6.9 mmol) was added follwed by Boc_2O (1.248 g, 5.72 mmol), and the solution was stirred for 4 h at rt. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/2) to afford **15** (622 mg, 85%) as a white solid: mp 145−146 °C; $[\alpha]^{22}_D$ −103.9 (c 0.92, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (s br, 2 × 1H), 5.57−5.33 (m, 1H), 5.17−4.89 (m, 1H), 4.70−4.45 (m, 2H), 3.83−3.71 (m, 1H), 2.70−2.15 (m, 1H), 1.46 (s, 9H), 1.44 (s, 9H); peaks broadened due to rotamers; ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 156.1, 137.7, 132.7, 79.7 (2C), 73.2, 60.3, 59.8, 28.4 (6C); HR-ESI-MS m/z calcd for $C_{15}H_{27}N_2O_5$ ($M + H^+$) 315.1920, found 315.1914.

***tert*-Butyl (3a*S*,4*R*,6a*R*)-2-Oxo-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*d*]oxazol-4-ylcarbamate (16).** Under a N_2 atmosphere, to a cooled (0 °C) solution of **15** (109 mg, 0.35 mmol) in THF (5 mL) was added NaH (60%, 28 mg, 0.70 mmol) in one portion, and the suspension was warmed to rt and stirred overnight, quenched by addition of satd aq NH_4Cl, and extracted with DCM (3 × 10 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/hexane = 1/1 to 2/1) to afford **16** (79 mg, 95%) as a white solid: mp 127−129 °C; $[\alpha]^{25}_D$ −109.6 (c 0.79, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10−6.06 (m, 1H), 6.02 (dd, 1H, J = 5.7, 2.2 Hz), 5.97 (s br, 1H), 5.61 (d, 1H, J = 7.3 Hz), 5.22−4.70 (m, 1H), 4.57−4.40 (m, 1H), 4.10 (d, 1H, J = 7.4 Hz), 1.45 (s, 2 × 9H); peaks broadened due to rotamers; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 155.2, 134.9, 132.8, 84.3, 80.3, 63.8, 61.5, 28.3 (3C); HR-ESI-MS m/z calcd for $C_{11}H_{17}N_2O_4$ ($M + H^+$) 241.1118, found 241.1136.

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Supporting Information Available: Characterization data and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.