Addition of 2-Fluoro-2,2-dinitroethanol to 1,3-Butadiene (Products 7 and 8). A Paar pressure bottle charged with 40 mL of CCl_4 was cooled in an ice bath before 4.2 g (7.8 mmol) of 1,3-butadiene was bubbled into the solvent. Next, 3.08 (2.0 mmol) of 2-fluoro-2,2-dinitroethanol and 100 mg of $HgSO_4$ were added to the Paar bottle. The bottle, stoppered with a Teflon-brand wrapped rubber stopper, was shaken at 55 °C for 16 h. The reaction product was then washed through 23 g of alumina (pH = 7.2) with CCl_4. The CCl_4 was removed; the product was again filtered through 23 g of alumina with a CCl_4 wash. CCl_4 removal provided 4.05 g of light reddish brown oil. Vacuum distillation (6-in. Vigreaux column) at 35 °C/0.10 mm gave 2.19 g (53%) of light yellow oil. The distillate contained mainly the 1,2-adduct 7 with some 1,4-adduct 8. Distillation (51.0–51.5 °C/1.6 mm) (12-in. glass bead column) provided nearly pure (90%) 1,2-adduct 7; the 1,4-adduct would not distill even with a diethyl succinate pot chaser. Analytical samples of the two adducts were obtained by preparative GLPC (8 ft. by $^1/_2$ in. 20% Dow 710 silicon oil column) at 148 °C. **1,2-Adduct 7**: NMR (m, 5.55, 3 H), (dd, 4.48, 2 H) with $J_{vic\text{-}HF}$ = 18 Hz, (pent, 4.02, 1 H), (d, 1.25, 3 H); IR (cm^{-1}) 3090 (=CH), 2990, 2930, 2890 (sat. CH), 1600, 1310 (NO_2). Anal. Calcd for $C_5H_9N_2O_5F$: C, 34.6; H, 4.36; N, 13.5; F, 9.13. Found: C, 34.85; H, 4.39; N, 13.3; F, 9.16. **1,4-Adduct 8**: NMR (m, 5.62, 2 H), (dd, 4.49, 2 H) with $J_{vic\text{-}HF}$ = 18 Hz, (d, 1.76, 3 H); IR (cm^{-1}) 3010 (=CH), 2985, 2960, 2920, 2870 (sat. CH), 1600, 1315 (NO_2). Anal. Calcd for $C_5H_9N_2O_5F$: C, 34.6; H, 4.36; N, 13.5; F, 9.13. Found: C, 34.85; H, 4.39; N, 13.6; F, 8.71.

Addition of 2-Fluoro-2,2-dinitroethanol to Divinyl Ether (Products 9 and 10). **(a)** A flask charged with 1.05 g (15 mmol) of divinyl ether (DVE), 25 mL of CH_2Cl_2, 3.08 g (20 mmol) of FDNEOH, and 200 mg of $HgSO_4$ was stirred under reflux for 16 h. Short-path vacuum distillation (43.2–43.4 °C/0.3 mmHg) of the isolated oil afforded 0.4 g (12%) of monoadduct **9**. The pot residue was taken up in CCl_4 and passed through a short alumina (pH = 7.2) column. CCl_4 removal gave 2.20 g (58%) of pure diadduct 10, density = 1.42 g/mL. Diadduct **10**: NMR (pent, 5.07, 2 H), (dd, 4.57, 4 H) with $J_{vic\text{-}HF}$ = 18 Hz, (d, 1.39, 6 H); IR (cm^{-1}) 3000, 2940 (sat. CH), 1600, 1310 (NO_2); mass spectrum, characteristic m/e 181 (higher GLPC diastereomer), 147, 133, 119, 105, 91, 75, 73, 45 (base), 44, 30, 29. Anal. Calcd for $C_6H_{12}N_4O_{11}F_2$: C, 25.4; H, 3.20; N, 14.8; F, 10.1. Found: C, 25.6; H, 3.20; N, 14.7; F, 10.0.

(b) DVE (2.10 g, 30.0 mmol), FDNEOH (2.31 g, 15.0 mmol), and 200 mg of $HgSO_4$ in 25 mL of CH_2Cl_2 refluxed 16 h produced 3.28 g of crude oil product. GC/MS analysis revealed the following crude product distribution: **11** (6%), **9** (70%), **4** (3%), **5** (1%), and **10** (20%). Prolonged or gradual heating during distillation causes apparent polymerization of **9**.

(c) A flask charged with 2.0 g (28.6 mmol) of DVE, 60 mL of CH_2Cl_2, 2.2 g (14.3 mmol) of FDNEOH, and 750 mg of Hg_2SO_4 was stirred under reflux for 26 h. Workup produced 2.63 g of crude oil containing both monoadduct **9** and diadduct **10**. Short-path vacuum distillation afforded 1.29 g (40%) of monoadduct **9**. The pot residue was dissolved in CH_2Cl_2 and eluted through a short alumina column. CH_2Cl_2 removal gave 0.91 g (34%) of diadduct **11**. **Monoadduct 9**: NMR (dd, 6.36, 1 H), (q, 5.14, 1 H), (dd, 4.62, 2 H) with $J_{vic\text{-}HF}$ = 18 Hz, (m, 4.50, 2 H), d, 1.40, 3 H); IR (cm^{-1}) 3120, 3070 (=CH), 3000, 2945 (sat. CH), 1645 (C=C), 1600, 1315 (NO_2); mass spectrum, characteristic m/e 181, 134, 105, 91, 87, 71, 45 (base), 44, 43, 30, 29. Anal. Calcd for $C_5H_9N_2O_6F$: C, 32.2; H, 4.05; N, 12.5, F, 8.48. Found: C, 32.0; H, 3.98; N, 12.5; F, 8.31.

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Registry No. 1, 88934-30-9; 2, 124618-93-5; 3, 124618-94-6; 4, 124618-95-7; 5, 124618-96-8; 6, 88934-26-3; 7, 88934-28-5; 8, 88934-29-6; 9, 88934-27-4; (±)-10, 124618-97-9; *meso*-10, 124618-98-0; 11, 52483-76-8; FDNEOH, 17003-75-7; DVE, 109-93-3; H_2C=CHOFDNE, 52483-76-8; EtOC≡CH, 927-80-0; EtOCH=CH_2, 109-92-2; H_2C=C(Me)$CH_2CH_2CH_3$, 763-29-1; H_2C=CH-H=CH_2, 106-99-0; $Hg(OAc)_2$, 1600-27-7; $HgSO_4$, 7783-35-9; Hg_2SO_4, 7783-36-0; HgO, 21908-53-2; 3,4-dihydropyran, 110-87-2.

A Short Enantiodivergent Synthesis of the Geissman–Waiss Lactone[1]

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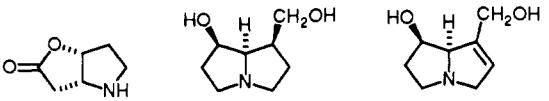
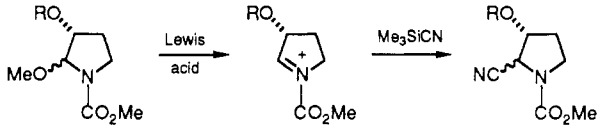
The Geissman–Waiss lactone (1) has been shown to be a useful intermediate in the synthesis of pyrrolizidine alkaloids such as retronecine.[2] In recent years, (+)-1 (with absolute stereochemistry as depicted in 1) has been used



1 2 3

in the chirospecific synthesis of a number of pyrrolizidine alkaloids such as (−)-platynecine (2) and (+)-retronecine (3).[3] The enantioselective synthesis of (+)-1 from an optically active starting material has been achieved by several groups.[4] We here report a short synthesis of both (+)- and (−)-1[5] from a common intermediate, thus making it possible to synthesize both enantiomers of various pyrrolizidine alkaloids.

We recently reported on the preparation and reactivity of the *N*-acyliminium ion **5** (generated in situ from the electrochemically prepared α-methoxylated carbamate **4**).[6]



4b; R = Ac
c; R = TBDMS

5 **6**

It was shown that, on reaction with Me_3SiCN, the stereoselectivity could be controlled to give **6** in cis:trans ratios varying from 86:14 to 42:58 by using different O-protective groups. In addition, amidoalkylation occurred without racemization at C(3).[7,8] The synthon **5** incorporates the same absolute stereochemistry at C(3) as (+)-1, and in addition, C(2) is easily functionalized via reaction with a nucleophile. Thus, intermediate **5** is an ideal starting point for the enantioselective synthesis of (+)-1.

The introduction of the carbon chain at C(2) in **5** was achieved by using allyltrimethylsilane as the nucleophile[8,9] (Scheme I). Control of the stereoselectivity was again possible by using different O-protective groups. The cis:trans ratios varied from 77:23 (R = TBDMS) to 21:79 (R = Ac). Only very small effects on the stereoselectivity were observed when the temperature and the Lewis acid were changed (see Table I). The separation and identification[10] of the different allyl compounds were carried out

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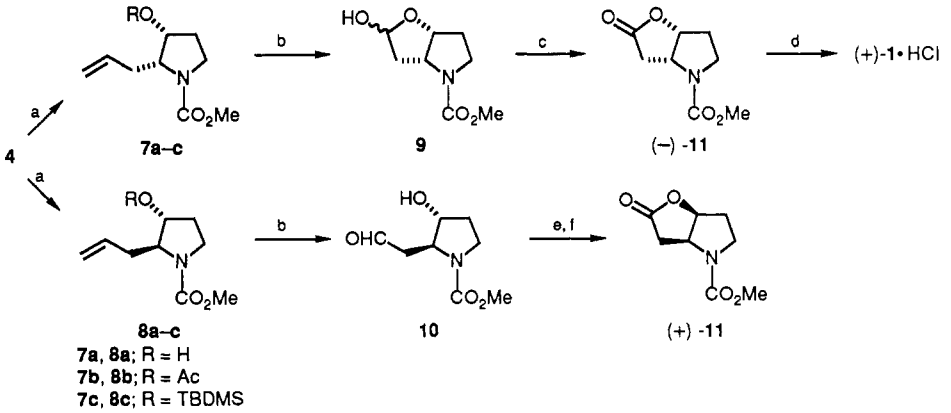
Scheme I[a]



[a] (a) Allyltrimethylsilane, CH_2Cl_2, $BF_3{\cdot}Et_2O$; (b) O_3, CH_2Cl_2, followed by Me_2S; (c) Ag_2CO_3 on Celite; (d) 6 M aqueous HCl, reflux; (e) PtO_2/O_2; (f) Ph_3P, DEAD, THF.

Table I. Stereoselectivity in the Allylation of 4[a]

substrate	Lewis acid[b]	temp, °C	cis:trans ratio[c]
4b	$BF_3{\cdot}Et_2O$	20	20:80
4b	$BF_3{\cdot}Et_2O$	−78	21:79
4b	$TiCl_4$	20	22:78
4c	$BF_3{\cdot}Et_2O$	20	69:31
4c	$BF_3{\cdot}Et_2O$	−78	77:23

[a] Isolated yields were always ≥90%. [b] Two equivalents of acid and 4 equiv of silane were used. [c] Determined by GLC analysis.

on the free alcohols **7a** and **8a** and by interconversion as in the earlier work.[6]

Ozonolysis of the cis allyl alcohol **7a**, obtained after hydrolysis (Bu_4NF, THF, 69% from **4c**) of **7c**, followed by reductive workup with dimethyl sulfide (DMS) gave the crude hemiacetal **9**,[11] which was oxidized by Ag_2CO_3 on Celite[12] to the lactone (−)-**11** (94% from **7a**). Spectral data were in agreement with those reported for racemic **11**.[13] Finally, acidic hydrolysis of (−)-**11** gave (+)-**1** as the hydrochloride salt ($[\alpha]^{25}_D$ +47.9° (lit.[4b] $[\alpha]^{25}_D$ +48.8°)).

In our synthesis of (+)-**11**, we used the possibility of controlling the stereochemistry of the allylation. Thus, the trans allyl alcohol **8a**, prepared from **8b** by hydrolysis (K_2CO_3, MeOH, 64% from **4b**), was ozonized to the aldehyde **10**. Further oxidation to the acid was carried out with PtO_2/O_2. Finally, the stereochemistry at C(3) was inverted by employing an intramolecular Mitsunobu[14] reaction, which gave the lactone (+)-**11**. These three steps (from **8a** to (+)-**11**) were carried out without purification of intermediates in 75% overall yield. (−)-**11** and (+)-**11** were spectroscopically identical except for the sign of the optical rotation, and thus, the formal synthesis of (−)-**1** is completed.

In conclusion, we have presented a brief enantioselective synthesis of the Geissman–Waiss lactone (+)-**1** with an overall yield of 15% (starting from (*S*)-*trans*-4-hydroxyproline). In addition, an equally efficient synthesis of (−)-**1** has been described, using the possibility of controlling the stereoselectivity of the allylation of the *N*-acyliminium ion **5**.

Experimental Section

General Methods. All chemicals used were of the highest commercial quality and were used without further purification. Petroleum ether (60–80 °C) and ethyl acetate, used for chromatography, were distilled before use. $BF_3{\cdot}Et_2O$ was distilled before use and stored under an atmosphere of argon. Gas chromatographic analyses were performed on a Varian 3400 gas chromatograph equipped with a Varian 4270 integrator on a 25 m × 0.25 mm OV 1701 column. Flash chromatography was performed on TLC grade silica gel according to Taber.[15] Optical rotations were determined on a Perkin-Elmer 241 MC polarimeter. ^1H NMR spectra were recorded on a Varian XL 300 instrument; δ are in parts per million downfield from $SiMe_4$ as an internal standard. Mass spectra were recorded on a Finnigan 4021 mass spectrometer at 70 eV, direct inlet. Elementary analysis was performed by Dornis und Kolbe, Mülheim, FRG.

(2*R*,3*R*)-2-Allyl-3-hydroxy-1-(methoxycarbonyl)-pyrrolidine (7a). Compound **4c** (3.73 g, 12.91 mmol) and allyltrimethylsilane (8.22 mL, 51.7 mmol) were dissolved in CH_2Cl_2 (100 mL) in a dry flask under an argon atmosphere. The mixture was cooled to −70 °C, and $BF_3{\cdot}Et_2O$ (3.25 mL, 25.85 mmol) was slowly added. After 5 min, the cooling bath was removed, and the mixture was stirred for 1.5 h. The organic phase was washed once with saturated $NaHCO_3$ (aqueous) and once with water and dried over $MgSO_4$. After evaporation, a clear oil was obtained, which was dissolved in dry THF (100 mL) in a dry flask under an argon atmosphere. The solution was cooled to 0 °C, and a solution of Bu_4NF in THF (1 M, 13 mL) was added dropwise. After 5 h, the reaction mixture was evaporated and chromatographed, with EtOAc/petroleum ether (2:1) as the eluant, which gave 1.65 g (69%) of **7a** as a colorless oil: $[\alpha]^{25}_D$ −59.0° (*c* 1.0, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ 5.84–5.97 (1 H, m,

(1) Synthetic Applications of Electrochemically Produced α-Methoxy Amides. 5. Part 4: Ludwig, C.; Wistrand, L.-G. *Acta Chem. Scand.* **1989**, *43*, 676.
(2) Geissman, T. A.; Waiss, A. C. *J. Am. Chem. Soc.* **1962**, *27*, 139.
(3) See, for example: Rüeger, H.; Benn, M. *Heterocycles* **1983**, *20*, 1331.
(4) For recent examples of the enantioselective synthesis of (+)-**1**, see: (a) Rüeger, H.; Benn, M. *Heterocycles* **1982**, *19*, 23. (b) Shishido, K.; Sukegawa, Y.; Fukumoto, K.; Kametani, K. *J. Chem. Soc., Perkin Trans. 1* **1987**, 993. (c) Ikota, N.; Hanaki, A. *Heterocycles* **1988**, *27*, 2535.
(5) For a recent enantioselective synthesis of (−)-**1**, see: Cooper, J.; Gallagher, P. T.; Knight, D. W. *J. Chem. Soc., Chem. Commun.* **1988**, 509.
(6) Thaning, M.; Wistrand, L.-G. *Acta Chem. Scand.* **1989**, *43*, 290.
(7) In similar intramolecular cases, Hart and Chamberlin have both reported a retained stereochemistry α to an *N*-acyliminium ion; see: Hart, D. J.; Yang, T. K. *J. Org. Chem.* **1985**, *50*, 235. Chamberlin, A. R.; Chung, J. Y. L. *J. Org. Chem.* **1985**, *50*, 4425.
(8) Thaning, M.; Wistrand, L.-G. *Helv. Chim. Acta* **1986**, *69*, 1711.
(9) Kraus, G. A.; Neuenschwander, K. *J. Chem. Soc., Chem. Commun.* **1982**, 134.
(10) The assignment of the stereochemistry of **7a** and **8a** was based on the vicinal coupling constant (J_{vic}) between H-C(2) and H-C(3). In our earlier work on similar systems,[6,8] we concluded that the trans coupling is usually 0–1 Hz, while for the corresponding cis-substituted compound, J_{vic} is ~5 Hz. Similar coupling constants were observed for **7a** and **8a**, and thus, the stereochemistry was assigned accordingly. These assignments were verified by the formation of hemiacetal from **7a** but not from **8a**.
(11) The tentative structural assignment of **9** is based only on the absence of an aldehyde proton in its ^1H NMR spectrum.
(12) McKillop, A.; Young, D. W. *Synthesis* **1979**, 401.
(13) Tamaru, Y.; Hojo, M.; Yoshida, Z. *J. Org. Chem.* **1988**, *53*, 5731.
(14) Mitsunobu, O. *Synthesis* **1981**, 1.
(15) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

CH_2=C*H*CH_2) 5.12–5.22 (1 H, 2 br s, C*H*$_2$=CHC*H*$_2$), 5.08 (1 H, ddt, J_d = 10.1, 2.0 Hz, J_t = 1.1 Hz, C*H*$_2$=CHC*H*$_2$), 4.41 (1 H, p, J = 5.5 Hz, H-C(3)) 3.84–3.91 (1 H, m, H-C(2)), 3.69 (3 H, s, CH_3OCO), 3.39–3.58 (2 H, m, H-C(5)), 2.50–2.95 (1 H, br m, CH_2=CHC*H*$_2$), 2.40–2.50 (1 H, m, CH_2=CHC*H*$_2$), 1.38–2.08 (2 H, m, H-C(4)). Anal. Calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 57.89; H, 8.22; N, 7.41.

(2*S*,3*R*)-2-Allyl-3-hydroxy-1-(methoxycarbonyl)-pyrrolidine (8a). Compound **4b** (1.027 g, 4.73 mmol) and allyltrimethylsilane (3.00 mL, 18.93 mmol) were dissolved in CH_2Cl_2 (50 mL) in a dry flask under an argon atmosphere. The mixture was cooled to −70 °C, and BF_3·Et_2O (1.19 mL, 9.47 mmol) was added dropwise. After 5 min, the cooling bath was removed, and the mixture was stirred for 1.5 h. Na_2CO_3·$10H_2O$ (5.0 g, 17.5 mmol) was added, and the mixture was stirred for 30 min. The solid material was removed by filtering the mixture through a Celite pad, and the filtrate was evaporated, giving the crude product as an inseparable mixture of cis and trans isomers in the ratio of 20:80. The acetyl group was removed by treating the crude product with K_2CO_3 (1.22 g, 8.80 mmol) in methanol (25 mL). After stirring for 1 h, the mixture was filtered through a silica pad. Evaporation and chromatography (EtOAc/petroleum ether, 2:1) gave 0.56 g of pure **8a** (64%) as a colorless oil: $[\alpha]^{25}_D$ + 28.7° (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67–5.88 (1 H, m, CH_2=C*H*CH_2), 5.00–5.10 (1 H, m, C*H*$_2$=CHC*H*$_2$), 5.10–5.15 (1 H, m, C*H*$_2$=CHC*H*$_2$), 4.20 (1 H, d, J = 2.7 Hz, H-C(3)), 3.72–3.85 (1 H, m, H-C(2)), 3.68 (3 H, s, CH_3OCO), 3.37–3.65 (2 H, m, H-C(5)), 2.35–2.60 (1 H, m, CH_2=CHC*H*$_2$), 1.74–2.22 (3 H, m, 2H-C(4), CH_2=CHC*H*$_2$). Anal. Calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56: Found: C, 58.29; H, 8.08; N, 7.58.

(1*R*,5*R*)-6-(Methoxycarbonyl)-2-oxa-6-azabicyclo[3.3.0]-octan-3-one ((−)-11). Compound **7a** (500 mg, 2.70 mmol) was dissolved in methanol (25 mL) in a dry flask under an argon atmosphere. The mixture was cooled to −70 °C, treated with a stream of oxygen/ozone until the blue color persisted, and then purged with an argon stream until colorless. DMS (1.25 mL) was added, and after stirring overnight at ambient temperature, the reaction mixture was evaporated, leaving the crude hemiacetal **9**. The hemiacetal was dissolved in benzene (10 mL) and added to a slurry of freshly prepared Ag_2CO_3/Celite (15.4 g, approximately 10 equiv) in benzene (125 mL) which had previously been refluxed in a Dean–Stark apparatus to remove traces of water. After refluxing for 30 min, the reagent was removed by filtering through a Celite pad. The filtrate was evaporated and chromatographed, with EtOAc as the eluant, which gave (−)-**11** (470 mg, 94%) as a colorless oil: $[\alpha]^{25}_D$ −159° (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$, 60 °C) δ 5.06 (1 H, t, J = 4.6 Hz), 4.48 (1 H, dd, J = 4.6, 4.0 Hz), 3.78 (1 H, br s), 3.72 (3 H, s, CH_3OCO), 3.40 (1 H, dt, J_t = 11.1 Hz, J_d = 6.3 Hz), 2.79 (2 H, br s), 2.30 (1 H, dd, J = 14.1, 6.3 Hz), 2.04 (1 H, dddd, J = 14.1, 11.1, 8.9, 4.6 Hz); mass spectrum, *m*/*e* (relative intensity) 185 (8), 143 (13), 126 (12), 70 (28), 59 (34), 42 (100). Anal. Calcd for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.56. Found: C, 51.17; H, 6.20; N, 7.43.

(1*S*,5*S*)-6-(Methoxycarbonyl)-2-oxa-6-azabicyclo[3.3.0]-octan-3-one ((+)-11). Compound **8a** (160 mg, 0.87 mmol) dissolved in methanol (8 mL) was ozonized in a manner similar to that described above, whereupon DMS (0.4 mL) was added. After stirring overnight at ambient temperature, the mixture was evaporated, and the colorless residue (pure **10** could be obtained by column chromatography of this material in 92% yield) dissolved in water (10 mL, doubly distilled), was added to a vigorously stirred slurry of prereduced Adams' catalyst[16] (200 mg) in water (10 mL). $NaHCO_3$ (73 mg, 0.87 mmol) was added, and the mixture was treated with an oxygen stream for 2.6 h. After removal of the catalyst by filtration through a Celite pad, the filtrate was evaporated to ca. 3 mL. The remaining aqueous phase was acidified to pH 4 with 0.05 M hydrochloric acid, evaporated to dryness, and triturated several times with dry ether. The ether phase was evaporated, leaving a colorless glass (180 mg), which was dissolved in dry THF (10 mL) in a dry flask under an argon atmosphere. Triphenylphosphine (245 mg, 0.93 mmol) was added, and the solution was cooled to 0 °C. Diethyl azodicarboxylate (DEAD; 148 μL, 0.95 mmol) was added dropwise, and the mixture was stirred overnight. The reaction mixture was evaporated and the residue chromatographed, with EtOAc as the eluant, giving (+)-11 (120 mg, 75%) as a colorless oil: $[\alpha]^{25}_D$ +159° (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$, 60 °C) spectrum was identical with the one described for the (−) isomer. Anal. Calcd for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.56. Found: C, 51.15; H, 6.23; N, 7.42. Compound **10**: $[\alpha]^{25}_D$ +10° (*c* 1.0, MeOH); ^{1}H NMR (300 MHz $CDCl_3$) δ 9.79 (1 H, s, CHO), 4.04–4.19 (2 H, br s), 3.70 (3 H, s, CH_3OCO), 3.27–3.70 (2 H, m), 3.07 (0.5 H, br d, J = 17.5 Hz), 2.92 (0.5 H, br d, J = 17.5 Hz), 2.46 (1 H, dd, J = 17.5, 8.5 Hz), 1.86–2.12 (2 H, m).

(1*R*,5*R*)-2-Oxa-6-azabicyclo[3.3.0]octan-3-one Hydrochloride ((+)-1·HCl). Compound (−)-**11** (210 mg, 1.13 mmol) was refluxed in 6 M aqueous hydrochloric acid (7 mL) overnight and evaporated to dryness. The off-white residue was recrystallized twice from ethanol, to afford (+)-1·HCl (130 mg, 70%) as fine white needles: mp 185–188 °C (lit.[4b] mp 185–186 °C); $[\alpha]^{25}_D$ +47.9° (*c* 1.5, MeOH) (lit.[4b] $[\alpha]^{25}_D$ +48.8° (*c* 0.20, MeOH)); ^{1}H NMR (300 MHz, D_2O) δ 5.41 (1 H, dt, J_t = 5.7 Hz, J_d = 1.2 Hz, H-C(1)), 4.68 (1 H, ddd, J = 8.9, 5.7, 1.7 Hz, H-C(5)), 3.56 (1 H, ddd, $^1/_2$ AB, J = 12.0, 7.9, 3.5 Hz, H-C(7)), 3.45 (1 H, ddd, $^1/_2$ AB, J = 12.1, 10.6, 6.7 Hz, H-C(7)), 3.31 (1 H, dd, $^1/_2$ AB, J = 19.7, 8.9 Hz, H-C(4)), 2.99 (1 H, dd, $^1/_2$ AB, J = 19.7, 1.7 Hz, H-C(4)), 2.28–2.54 (2 H, m, H-C(8)).

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Registry No. (±)-1·HCl, 95530-39-5; **4b**, 124155-25-5; **4c**, 124155-24-4; **7a**, 124155-27-7; *cis*-**7b**, 82259-12-9; *cis*-**7c**, 124155-26-6; **8a**, 124175-09-3; *trans*-**8b**, 82259-15-2; *trans*-**8c**, 124155-30-2; **9**, 124155-28-8; **10**, 124155-29-9; (−)-**11**, 124223-42-3; (+)-11, 124223-43-4; H_2C=$CHCH_2Si(CH_3)_3$, 762-72-1.

(16) Haines, A. H. In *Methods for the Oxidation of Organic Compounds*; Academic Press: London, 1988; p 160.