Diastereoselectivity in the OsO_4-Catalyzed Dihydroxylation of 5-(*p*-Toluenesulfonamido)-3-hexen-2-ol Derivatives

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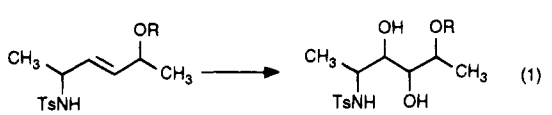
The stereochemistry in dihydroxylation of 5-(*p*-toluenesulfonamido)-3-hexen-2-ol derivatives was studied. The product configuration was assigned by NMR.

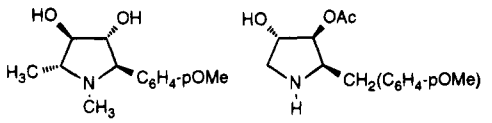
The palladium-catalyzed 1,4-chloroacetoxylation of conjugated dienes[1] offers useful levels of 1,4-stereocontrol in both cyclic and acyclic systems.[2–8] With this approach stereodefined 4-amino-2-alken-1-ol derivatives[9] have been prepared and explored as intermediates in natural product synthesis.[2–4] In previous studies the stereoselectivity of epoxidation of 5-(*p*-toluenesulfonamido)-3-alken-2-ol derivatives (**1**) was investigated.[5] We have now studied the stereoselectivity of the corresponding dihydroxylation[10] of intermediates **1** (eq 1).



(1)

1 R=H, Ac **2**

Stereodefined triol derivatives of type **2** are important intermediates for the synthesis of naturally occurring dihydroxypyrrolidines such as *Anisomycin*[11] and *Codonopsinine*.[12] Since the dihydroxylation of amino alcohol



Codonopsinine Anisomycin

derivatives similar to **1** is one of the key steps in the synthesis of these compounds, information about the stereoselectivity of this reaction is highly desirable. To our knowledge only a few studies of dihydroxylation of acyclic olefins have been performed where two sterically demanding electronegative hetero atom groups are present in both allylic positions.[13,14]

Osmium-catalyzed vicinal dihydroxylation of olefins with a stereodirective substituent in the allylic position has found wide application in organic synthesis.[13–15] OsO_4/NMO (*N*-morpholine oxide) oxidations[10] are often high yielding and can be highly stereoselective for multifunctionalized substrates. The versatility of the reaction was further enhanced when Sharpless introduced the asymmetric, chiral ligand controlled modification of this reaction.[16]

In the racemic reactions the selectivity is often slightly improved using stoichiometric amounts of OsO_4 instead of the preferred catalytic system.[17a] It is known that the bulk of the substituents in the allylic position has a large effect on the stereodifferentiation in the oxidation step. Alkoxy and hydroxy groups have a repulsive effect toward the OsO_4 molecule.[14,17] Furthermore, the diastereoselectivity is sometimes improved by lowering the temperature of the reaction.[18]

Results and Discussion

anti- and *syn*-amido alcohol derivatives **3** and **4** were obtained from (2*E*,4*E*)-hexadiene by the route described

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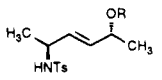
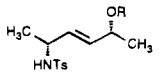
Table 1. Diastereoselectivity in Dihydroxylation of 3 and 4

	R	Temp.[b]	Yield[c]	OH OR / OH (5a[a])	OH OR / OH (6a[a])
	**3a**			**5a**[a]	**6a**[a]
	H	RT	84 %	4	1
		0-RT	83 %	6.5	1
	3b			**5b**[a]	**6b**[a]
	Ac	RT	90 %	2	1
		0-RT	87 %	3	1
	**4a**			**7a**[a]	**7b**[a]
	H	RT	87 %	2	1
		0	84 %	5	1
	4b			**8a**[a]	**8b**[a]
	Ac	RT	78 %	2	1
		0-RT	90 %	2	1
		0	91 %	2	1

[a] The diastereomeric ratios were determined by integration of corresponding well separated signals of the isomers in the crude product ^{1}H NMR spectra. [b] All rt reactions were run in a 5:2 mixture of acetone:H_2O, and the low temperature reactions were performed in acetone:H_2O 20:1. [c] All yields are given for crude product mixtures of dihydroxy compounds.

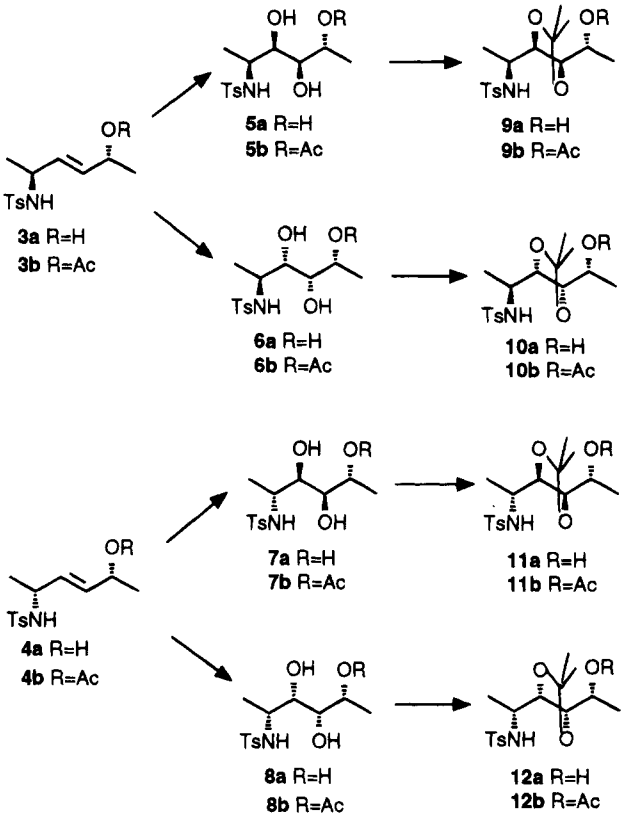
in ref 2. Compounds **3** and **4** were dihydroxylated at different temperatures. Diastereomeric product mixtures were obtained in high yields, and the results are summarized in Table 1. The best diastereomeric ratios were obtained for the amido alcohols **3a** and **4a**. Selectivities up to 6.5:1 were obtained, and the yields were in the range of 78−91%. The acyclic dihydroxylation product mixtures were transformed into acetonides, and the stereochemistry was determined by NMR spectroscopy (*vide infra*).

The results are in accordance with what is expected; i.e., the approach of the osmium complex trans to the preexisting hydroxy or acetoxy group is favored. The stereoselectivity was always higher for the allylic alcohols compared to the allylic acetates. For these substrates the bulk and electronic effects of the NHTs substituent seem to be of minor importance in the stereodifferentiation of the two π-faces.

Stereochemical Assignment. The dihydroxylated products were transformed to acetonides by treatment with acetone and a catalytic amount of acid. For the triols (products from **3a** and **4a**) only the acetonide over C_3-C_4 was formed. This was established by a complete assignment of all ^{1}H NMR signals of acetonides **9a**, **10a**, **11a**, and **12a**.[19] Formation of acetonide from the corresponding diol acetate products proceeded in high selectivity without any observable acetate migration (Scheme 1).

In the empirical method developed by Hoffmann and Landmann[20] the ^{1}H NMR chemical shift for the hydroxy group in the 1-hydroxy-2,3-acetonide is significant for a certain diastereoisomer. The chemical shift of the isomer with a syn relationship between the hydroxy oxygen and the acetonide oxygen is always higher than that for the anti isomer. The difference in chemical shifts for the two

Scheme 1. Dihydroxylation of 5-(*p*-Toluenesulfonamido)-3-alken-2-ol, Followed by Acetonidization



stereoisomers is explained by the differences in ability to form an intramolecular hydrogen bond between the two groups (Figure 1).

Due to a shorter distance between the oxygens the syn isomer has a higher degree of intramolecular hydrogen bonding than the anti isomer, which in turn gives a higher hydroxy proton chemical shift. The O*H* chemical shift for **9a** and **10a** was 1.89 and 2.4 ppm, respectively. According to the discussion above, this would imply that **10a** is intramolecularly hydrogen bonded to a larger extent than **9a** and must therefore be the syn isomer (Figure 1). For **11a** and **12a** the chemical shift difference was less accentuated, being 1.97 and 1.99 ppm, respectively.

The hydrogen bond between the hydroxy group and the vicinal acetonide oxygen was proven to exist by adding a small amount of methanol-d_4 to a $CDCl_3$ solution of the hydroxy acetonide. The resulting changes of the coupling constants for the C*H*OH proton imply the presence of a hydrogen-bonded conformer.

The major isomers obtained from the dihydroxylation of **3a** and **4a** were assigned as the 2,3-anti isomers **5a** and **7a**, respectively. These isomers have a 2,3-erythro relationship. The coupling constants J_{23} of the corresponding acetonide derivatives **9a** and **11a** were 6.5 and 3.1 Hz, respectively. The corresponding coupling constants of the minor 2,3-syn-isomers **10a** and **12a** (2,3-threo relationship) were 8.4 and 6.0 Hz, respectively, and in each case larger than the value of the corresponding major isomer. The larger value for the threo isomers when there is an intramolecular hydrogen bond in these kinds of compounds is well documented and follows from the Karplus equation.[21] Only the threo isomer will have a hydrogen-bonded conformation with an anti relation

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(19) The CHO*H* proton (at C-2) was unambiguously assigned by saturation transfer from the water signal. The C*H*OH proton (at C-2) showed a doublet of a quartet for **9a**, **10a**, and **12a**. For **11a** this proton was partly concealed. In addition, for all four acetonide alcohols **9a**, **10a**, **12a**, and **11a** the C*H*O proton assigned to C-3 (by COSY) showed in each case a sharp doublet of a doublet. For **9a** and **11a** the C*H*O proton assigned to C-4 (by COSY) in each case was a sharp doublet of a doublet. (For **10a** and **12a** this proton was concealed).

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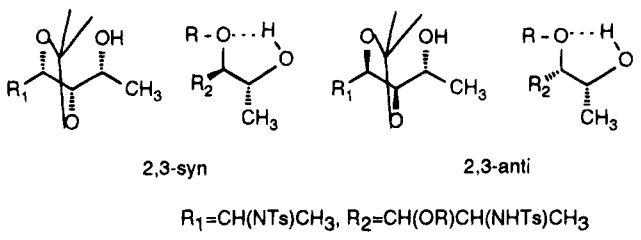
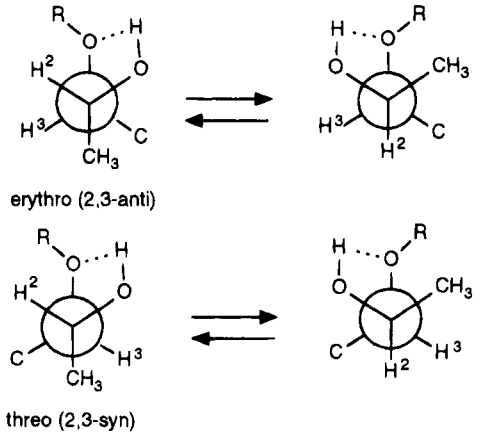
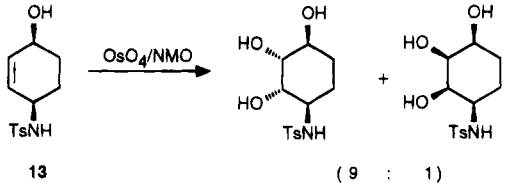


Figure 1.

Scheme 2



Scheme 3



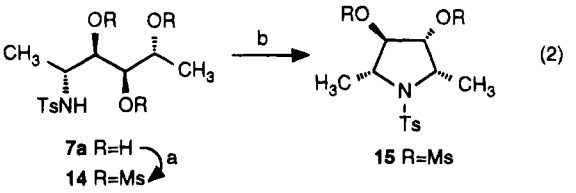
between H-2 and H-3 (Scheme 2). In conclusion, the observed coupling constants provide additional independent confirmation of the stereochemical assignment deduced from the O*H* chemical shifts.

With the assignment of the 2,3-relative stereochemistry in our hand and knowing the relative stereochemical relationship between C*H*NH and C*H*OH, the 5-(*p*-toluenesulfonamido)hexane-2,3,4-triols obtained from **3a** and **4a** were stereochemically assigned (Table 1).

The acetates **9b**, **10b**, **11b**, and **12b** were hydrolyzed to the corresponding alcohols by treatment with K_2CO_3 in aqueous MeOH.[22] By comparison of the ^1H NMR spectra of the hydrolyzed products with those of the acetonides of the 5-(*p*-toluenesulfonamido)hexane-2,3,4-triols the stereochemical assignments of the acetoxy acetonides (**9b**, **10b**, **11b**, and **12b**) were secured.

Preliminary results from a dihydroxylation study of the corresponding cyclic substrates implies that higher selectivities can be obtained in more rigid systems.[14] For *cis*-4-(*p*-toluenesulfonamido)-2-cyclohexen-1-ol (**13**) a ratio of 9:1 was detected (Scheme 3). However, for the *trans*-compounds selectivities similar to those of the acyclic compounds were obtained.

Cyclization Reactions. The major product (**7a**) from dihydroxylation of **4a** was trimesylated to **14** and cyclized (eq 2). Pyrrolidine **15** was isolated as a single product.



a) MsCl, Et_3N, THF. b) K_2CO_3, MeOH.

Compound **15** serves as a model for the naturally occurring *trans*-3,4-dihydroxypyrrolidines mentioned in the Introduction.

Experimental Section

General Comments. ^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions at 400 and 100.6 MHz, respectively. Isomeric ratios were determined by integration of corresponding well-separated signals of the two isomers in the crude spectra. Pure samples of the components of the diastereomeric acetonide mixtures were prepared by HPLC using mixtures of hexane/ethyl acetate as the mobile phase. Flash chromatography was run using Merck silica gel 60 (340–400 mesh). Commercially available chemicals were used as delivered. Solvents were dried according to standard procedures. All salt solutions were saturated, unless stated otherwise. The OsO_4 was supplied by Aldrich as a 2.5 wt % solution in 2-methyl-2-propanol.

(*R,*R**)-2-Acetoxy-5-chloro-3-hexene.** (*E*,*E*)-2,4-Hexadiene was chloro-acetoxylated according to the procedure described in ref 1.

(*E*)-(*R,*R**)-5-(*p*-Toluenesulfonamido)-3-hexen-2-ol (3a)** and **(*E*)-(*R**,*S**)-5-(*p*-Toluenesulfonamido)-3-hexen-2-ol (4a).** The chloroacetate was substituted with NaNHTs and hydrolyzed according to Bäckvall.[2]

Dihydroxlation. All reactions were run with a catalytic amount of OsO_4 and 2 equiv of NMO. The concentration of the substrate was ca. 0.2 M. The reactions were all run ca. 24 h under air atmosphere. Workup followed standard procedures.[18]

Formation of Acetonides. The crude product mixtures from dihydroxylation (100 mg, 0.33 mmol) were dissolved in acetone (6 mL), and a catalytic amount of H_2SO_4 (concd) was added. The mixture was stirred at rt overnight. EtOAc (15 mL) was added, and the mixture was washed with $NaHCO_3$ (3 × 7 mL). Drying and concentration afforded clean acetonides. No starting material was detected by NMR.

Mesylation of Triols. The triol (100 mg, 0.33 mmol) was dissolved in THF (5 mL) under N_2 atmosphere, and Et_3N (280 μL, 3.1 mmol) was added. The mixture was cooled to 0 °C by an ice bath, and MsCl (140 μL, 1.8 mmol) was added dropwise. The cloudy solution was stirred at 0 °C for 1 h and at rt for 3 h before workup. The reaction mixture was partitioned between ether and brine, dried, and concentrated.

Cyclization. The crude mesylates were dissolved in MeOH (5 mL), and K_2CO_3 (200 mg, 1.44 mmol) was added. The reaction was stirred for 12 h at rt. Concentration, dilution with water, and extraction with EtOAc (3 × 10 mL) followed by drying and concentration afforded a thick pale yellow oil. Chromatography on silica using 80/20 hexane/EtOAc as mobile phase afforded pure products.

Hydrolysis of Acetates. The acetates (ca. 50 mg) were dissolved in a 2:1 mixture of MeOH:H_2O. K_2CO_3 (15 mg, 0.11 mmol) was added and the mixture stirred at rt for 2 h. The methanol was evaporated, and water (2 mL) was added. The aqueous solution was extracted twice with EtOAc (2 mL). Drying and concentration afforded clean alcohol.

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Dihydroxylation Products from 3a (*R,*S**-Isomer).** The triols obtained were characterized as their 3,4-acetonides (**9a** and **10a**).

9a. ^{1}H NMR: δ 7.75 (2 H, Ts), 7.27 (2 H, Ts), 4.89 (d, *J* = 9.5 Hz, 1 H, N*H*), 3.79 (dd, *J* = 7.8, 1.8 Hz, 1 H, C*H*OR N-side), 3.75 (dq, *J* = 6.5, 6.8 Hz, 1 H, C*H*OH), 3.70 (dd, *J* = 7.8, 6.5 Hz, 1 H, C*H*OR O-side), 3.57 (ddq, *J* = 1.8, 9.5, 6.2 Hz, 1 H, C*H*NH), 2.41 (s, 3 H, Ts), 1.89 (s, 1 H, O*H*), 1.39 (s, 3 H, acetonide), 1.33 (s, 3 H, acetonide), 1.20 (d, *J* = 6.2 Hz, 3 H, CH_3 N-side), 1.03 (d, *J* = 6.8 Hz, 3 H, CH_3 O-side). ^{13}C NMR: δ 143.5, 138.2, 129.8, 127.0, 108.7, 81.2, 80.1, 68.5, 49.7, 27.1, 27.0, 21.5, 20.1, 19.6.

10a. ^{1}H NMR: δ 7.74 (2 H), 7.27 (2 H), 5.17 (d, *J* = 9.5 Hz, 1 H), 4.02 (dq, *J* = 8.4, 6.4 Hz, 1 H, C*H*OH), 3.51 (dd, *J* = 8.4, 2.0 Hz, 1 H, C*H*OR O-side), 3.31 (m, 1 H), 3.29 (m, 1 H), 2.4 (s, 3 H), 2.4 (s, 1 H, O*H*), 1.39 (s, 3 H), 1.33 (s, 3 H), 1.18 (d, *J* = 6.4 Hz, 3 H), 1.07 (d, *J* = 5.5 Hz, 3 H). Anal. Calcd for $C_{16}H_{25}NSO_5$: C, 55.96; H, 7.34. Found: C, 56.18; H, 7.06.

Dihydroxylation Products from 3b (*R,*S**-Isomer).** The diols obtained were characterized as their 3,4-acetonides (**9b** and **10b**).

9b. ^{1}H NMR: δ 7.75 (2 H, Ts), 7.31 (2 H, Ts), 4.91 (dq, *J* = 6.2, 5.5 Hz, 1 H, C*H*OAc), 4.73 (d, *J* = 9.1 Hz, 1 H, N*H*), 3.76 (dd, *J* = 7.7, 2.2 Hz, 1 H, C*H*OR, N-side), 3.72 (dd, *J* = 7.7, 5.5 Hz, 1 H, C*H*OR O-side), 3.45 (ddq, *J* = 9.1, 6.8, 2.2 Hz, 1 H, C*H*NH), 2.42 (s, 3 H, Ts), 2.08 (s, 3 H, O*Ac*), 1.38 (s, 3 H, acetonide), 1.35 (s, 3 H, acetonide), 1.19 (d, *J* = 6.2 Hz, 3 H, CH_3 O-side), 1.15 (d, *J* = 6.8 Hz, 3 H, CH_3 N-side). ^{13}C NMR: δ 170.2, 143.5, 138.1, 129.7, 127.1, 109.8, 81.1, 78.7, 70.8, 49.9, 27.2, 26.9, 21.5, 21.2, 19.7, 16.3.

10b. ^{1}H NMR: δ 7.75 (2 H), 7.27 (2 H), 5.03 (dq, *J* = 3.5, 6.5 Hz, 1 H, C*H*OAc), 4.86 (d, *J* = 9.0 Hz, 1 H), 3.78 (dd, *J* = 7.8, 3.5 Hz, 1 H), 3.57 (dd, *J* = 7.8, 6.2 Hz, 1 H), 3.43 (ddq, *J* = 9.0, 6.3, 6.2 Hz, 1 H), 2.41 (s, 3 H), 2.05 (s, 3 H), 1.36 (s, 3 H), 1.33 (s, 3 H), 1.22 (d, *J* = 6.5 Hz, 3 H), 1.06 (d, *J* = 6.3 Hz, 3 H). ^{13}C NMR: δ 170.8, 147.4, 143.5, 129.8, 127.0, 109.6, 80.7, 79.0, 69.6, 51.8, 27.2, 26.7, 21.5, 21.2, 17.7, 16.6.

Dihydroxylation Products from 4a (*R,*R**-Isomer).** The triols obtained were characterized as their 3,4-acetonides.

11a. ^{1}H NMR: δ 7.78 (2 H), 7.32 (2 H), 4.69 (d, *J* = 9.1 Hz, 1 H), 3.79 (dd, *J* = 7.8, 2.0 Hz, 1 H, C*H*OR N-side), 3.69 (dd, *J* = 7.8, 3.1 Hz, 1 H, C*H*OR O-side), 3.66 (m, 1 H, C*H*OH) 3.40 (ddq, *J* = 9.1, 2.0, 6.8 Hz, 1 H), 2.42 (s, 3 H), 1.97 (d, *J* = 7.2 Hz, 1 H, O*H*), 1.32 (s, 3 H), 1.31 (s, 3 H), 1.14 (d, *J* = 6.2 Hz, 3 H), 1.09 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR: δ 143.6, 138.1, 129.8, 127.0, 109.2, 80.5, 79.7, 66.3, 48.9, 27.2, 27.1, 21.5, 20.0, 19.9.

12a. ^{1}H NMR: δ 7.75 (2 H), 7.27 (2 H), 5.33 (d, *J* = 7.5 Hz, 1 H), 3.81 (dd, *J* = 6.8, 6.0 Hz, 1 H, C*H*OR O-side), 3.74 (dq, *J* = 6.0, 6.8 Hz, 1 H, C*H*OR), 3.40 (m, 1 H), 3.38 (m, 1 H), 2.42 (s, 3 H), 1.99 (s, 1 H, O*H*), 1.32 (s, 3 H), 1.31 (s, 3 H), 1.22 (d, *J* = 6.8 Hz, 3 H), 1.16 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR: δ 143.5, 138.0, 129.7, 127.2, 109.5, 82.2, 81.8, 69.4, 52.3, 27.0, 26.8, 21.6, 20.4, 17.6. Anal. Calcd for $C_{16}H_{25}NSO_5$: C, 55.96; H, 7.34. Found: C, 56.02; H, 7.31.

Dihydroxylation Products from 4b (*R,*R**-Isomer).** The diols obtained were characterized as their 3,4-acetonides.

11b. ^{1}H NMR: δ 7.75 (2 H), 7.27 (2 H), 4.89 (dq, *J* = 6.5, 3.5 Hz, 1 H, C*H*OAc), 4.66 (d, *J* = 9.0 Hz, 1 H), 3.79 (dd, *J* = 8.1, 3.5 Hz, 1 H), 3.57 (dd, *J* = 8.1, 1.9 Hz, 1 H), 3.51 (ddq, *J* = 9.0, 1.9, 6.0 Hz, 1 H), 2.42 (s, 3 H), 2.05 (s, 3 H), 1.34 (s, 3 H), 1.33 (s, 3 H), 1.20 (d, *J* = 6.5 Hz, 3 H), 1.10 (d, *J* = 6.0 Hz, 3 H).

12b. ^{1}H NMR: δ 7.75 (2 H), 7.27 (2 H), 4.81 (dq, *J* = 6.3, 6.0 Hz, 1 H, C*H*OAc), 4.64 (d, *J* = 8.8 Hz, 1 H), 3.78 (dd, *J* = 7.3, 3.9 Hz, 1 H), 3.74 (dd, *J* = 7.3, 6.3 Hz, 1 H), 3.43 (ddq, *J* = 8.8, 3.9, 6.8 Hz, 1 H), 2.42 (s, 3 H), 2.05 (s, 3 H), 1.36 (s, 3 H), 1.33 (s, 3 H), 1.17 (d, *J* = 6.0 Hz, 3 H), 1.12 (d, *J* = 6.8 Hz, 3 H).

Trimesylate 14. ^{1}H NMR: δ 7.72 (2 H), 7.35 (2 H), 5.75 (d, *J* = 8.4 Hz, 1 H), 4.94 (dd, *J* = 8.0, 2.3 Hz, 1 H), 4.88 (dd, *J* = 6.7, 2.3 Hz, 1 H), 4.73 (dd, *J* = 8.0, 2.5 Hz, 1 H), 3.47 (m, 1 H), 3.22 (s, 3 H), 3.18 (s, 3 H), 3.11 (s, 3 H), 2.42 (s, 3 H), 1.39 (d, *J* = 6.7 Hz, 3 H), 1.11 (d, *J* = 7.0 Hz, 3 H).

Pyrrolidine 15. ^{1}H NMR: δ 7.72 (2 H), 7.35 (2 H), 4.78 (dd, *J* = 3.0, 4.1 Hz, 1 H), 4.69 (dd, *J* = 4.1, 6.5 Hz, 1 H), 3.96 (dq, *J* = 6.5, 6.9 Hz, 1 H), 3.83 (dq, *J* = 3.0, 6.9 Hz, 1 H), 3.09 (s, 3 H), 2.89 (s, 3 H), 2.42 (s, 3 H), 1.54 (d, *J* = 6.9 Hz, 3 H), 1.45 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR: δ 144.3, 129.9, 127.7, 133.5, 83.5, 80.4, 60.2, 56.9, 38.4, 38.3, 21.5, 21.0, 17.0.

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Supplementary Material Available: Copies of ^{1}H-NMR and ^{13}C-NMR spectra of **9a**, **9b**, **10b**, **11a**, **11b**, **12a**, and **12b** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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