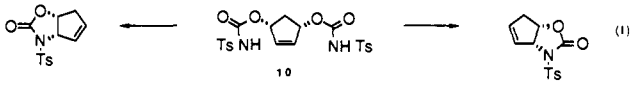
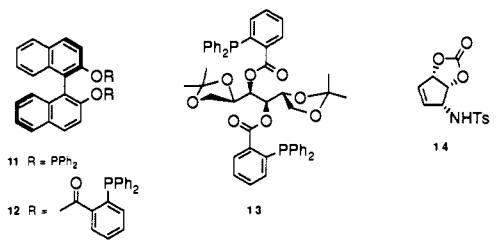
as a consequence of oxazolidin-2-one synthesis[12] via cyclization of the bis-urethane derived from diol **3**[13] (eq 1). In contrast to

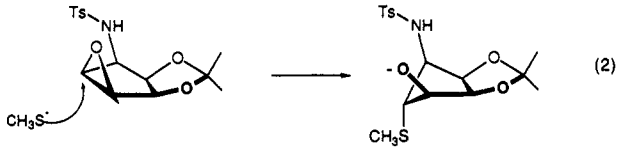




our synthetic efforts directed toward allosamizoline,[14] the Pd-catalyzed cyclization with BINAPO (**11**) as ligand gave only 28% ee. Interestingly, the conformationally less rigid diester ligand **12** (S-BDPBB) enhanced the selectivity to 41%, $[\alpha]^{25}_D$ -56.9 (*c* 3.92, CH_2Cl_2). *Gratifyingly, the c_2 symmetric diester* ***13*** *((+)-BIBDPBM), an example of a new class of very simply derived asymmetric ligands, jumps the ee to 65%,* $[\alpha]^{25}_D$ *+90.7 (c 2.49, CH_2Cl_2) (5 mol % $(dba)_3Pd_2{\cdot}CHCl_3$, 15 mol % **13**, THF, -8 to 20 °C, quantitative yield), of the 1R,2S enantiomer as determined by the O-methylmandelate ester NMR shifts*! The feasibility of an asymmetric synthesis having been demonstrated, biological considerations induced us to focus initially on racemic mannostatin.

Allylic oxidation without rearrangement of the double bond required strenuous conditions using selenium dioxide in which quartz sand was added to maintain dispersion of the reactants (mechanical stirring recommended). Since the resultant alcohol was frequently admixed with considerable quantities of the ketone, the mixture was normally directly oxidized. Of a horde of oxidants, only reaction with MnO_2[15] and the Dess-Martin periodinane[16] proceeded cleanly, the latter being preferred since the reaction went to completion. The third asymmetric center was then set by reduction.[17] The correctness of the stereochemistry was readily apparent by the facility with which the alcohol **6** isomerized to the carbonate **14**. Various attempts to hydroxysulfenylate **6** or **7a** failed due to the lack of reactivity of the double bond. On the other hand, the diol **7a** smoothly succumbed to epoxidation with trifluoroperacetic acid (CH_2Cl_2, Na_2CO_3, 86%) to give a single epoxide tentatively assigned as all-cis on the basis of the high level of directionality observed in the reactions of this reagent with allylic alcohols and ethers.[18]

With the stereochemistry all set, the last issue was the regioselective introduction of the methylthio group. Various attempts to promote regioselective opening by coordination with oxyphilic Lewis acids led to mixtures at best. For example, coordination of **8a** with titanium tetraisopropoxide[19] followed by lithium thiomercaptide led to a 1:1 regioisomeric mixture from which the desired thioether **9** (R = H, R′ = Ts) could be isolated in 21% yield. *On the other hand, the acetonide **8b** generates a 4.6:1 ratio of the two regioisomers in favor of our desired product **9a***! A possible explanation for this remarkable regioselectivity may derive from a Fürst-Plattner type stereoelectronic control[20] in which attack at the desired position involves a conformationally more favorable transition state as depicted in eq 2.[21] Completion of



the synthesis involves detosylation and hydrolysis to give mannostatin A. Passing an aqueous solution of the trifluoroacetate salt through the base form of an IRA 400 ion-exchange resin gives racemic mannostatin A as the free base. Comparison of the spectral data to that of an authentic sample indicated their identity. This route provides mannostatin A in 27% overall yield in 10 steps.

This strategy should prove to be a powerful approach to these types of cyclopentane analogues of carbohydrates. The synthetic intermediates readily available provide great flexibility to vary the regio- and diastereoplacement of the functionality. Furthermore, the ready incorporation of a phosphine ligand into asymmetric alcohols by esterification with the readily available 2-(diphenylphosphino)benzoic acid[22] should prove useful for asymmetric catalysis.

Acknowledgment. We thank the National Institutes of Health for their generous support of our programs. This material is based upon work supported by a National Science Foundation graduate fellowship. We thank Professor Takaaki Aoyagi for comparison data and a sample of mannostatin B. Mass spectra were provided by the Mass Spectrometry Facility, University of California—San Francisco, supported by the NIH Division of Research Resources.

Supplementary Material Available: Characterization data for **1** and **4-9** (2 pages). Ordering information is given on any current masthead page.

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α-Cyano-α-fluorophenylacetic Acid (CFPA): A New Reagent for Determining Enantiomeric Excess That Gives Very Large ^{19}F NMR Δδ Values

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Rapid progress has been made in the development of methods for asymmetric synthesis and in their application in the construction of complex natural products. Consequently, the determination of enantiomeric excess (ee) is an indispensable process for evaluating the efficiency of those methods. Herein we describe a unique multifunctional chiral tertiary fluoride,[1] α-cyano-α-fluorophenylacetic acid (CFPA, **1**), which has remarkable efficacy for determining ee, surpassing MTPA (**2**) in reactivity and ^{19}F NMR Δδ values.

CFPA (**1**) MTPA (**2**)

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(1) (a) Takeuchi, Y.; Asahina, M.; Nagata, K.; Koizumi, T. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2203. (b) Takeuchi, Y.; Asahina, M.; Murayama, A.; Hori, K.; Koizumi, T. *J. Org. Chem.* **1986**, *51*, 955.

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Scheme I

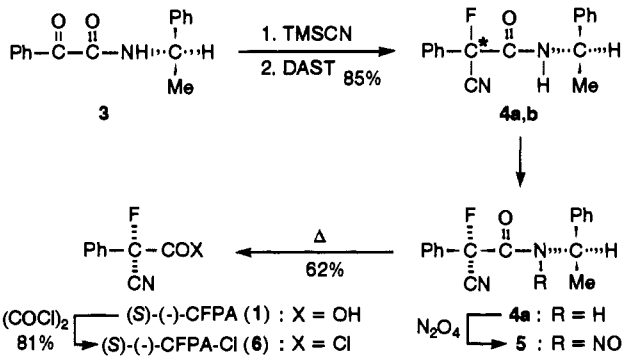


Table I. ^{19}F NMR Chemical Shift Difference $\Delta\delta$(in Hertz) of Some CFPA and MTPA Derivatives by 254-MHz ^{19}F NMR

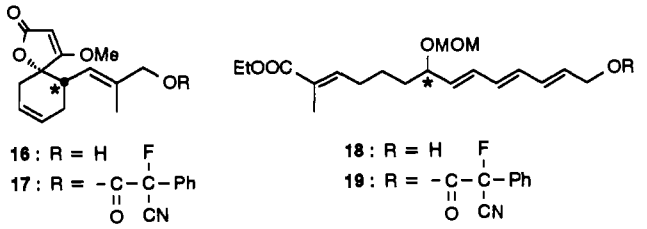
run	chiral compd (HR)	PhCF(CN)COR (CFPA deriv)	PhC(CF_3)(OMe)COR (MTPA deriv)
1	HOCH(Ph)Me	273.9 (**7**)	51.5
2	HOCH(^{t}Bu)Me	305.2 (**8**)	22.0
3	HOCH(Ph)CF_3	292.3 (**9**)	9.2
4	H_2NCH(Me)^{t}Bu	159.9 (**10**)	29.5
5	H_2NCH(Ph)COOEt	316.2 (**11**)	68.0
6	H_2NCH$_2$CH(Ph)Me	794.1 (**12**)	7.3
7	HOCH$_2$CH(Ph)Me	158.2 (**13**)	12.9
8	HOCH$_2$CH$_2$CH(Ph)Me	57.0 (**14**)	ND[a]
9	H_2N(CH$_2$)$_4$CH(OEt)Me	23.9 (**15**)	ND

[a] ND: not detectable.

Among the various methods for ee determination,[2] including several recently reported,[3,4] Mosher's derivative[5] using MTPA (**2**) is currently the most widely employed. The main reasons for the popularity of Mosher's derivative are the availability of ^1H and ^{19}F NMR probes and the large chemical shift range and higher relative NMR sensitivity of the ^{19}F nucleus[6] when compared to other methods using ^{13}C,[7] ^{31}P,[8] and ^{77}Se[4] nuclei. However, many instances have been reported where ee determination by this method failed either because of small chemical shift differences between the two diastereomers ($\Delta\delta$) observed by ^{19}F NMR or because of insufficient reactivity of the chloride (MTPA-Cl). Our ongoing studies of the synthesis and properties of novel organofluorines[1] led us to the rational design[9] of CFPA (**1**) as a new chiral derivatizing reagent.

(*R*)-α-Phenylethylamide **3** was converted to its cyanohydrin derivative (Me_3SiCN) and then subjected to fluorination (DAST, 85%) to afford **4a,b** ($\Delta\delta$ 255.5 Hz). Each diastereomer was obtained by fractional recrystallization from EtOAc/hexane, thus providing optically active **4a** (45%, mp 174 °C, $[\alpha]^{24}_D$ +109.0°) and **4b** (33%, mp 101 °C, $[\alpha]^{24}_D$ +106.3°). The absolute configuration of **4a** was determined by X-ray analysis[10] to be that shown in Scheme I. Amide **4a** was treated with N_2O_4 (NaOAc, 0 °C, 2 h) to produce the *N*-nitroso derivative **5**, which was subjected, without isolation, to thermal decomposition (40 °C, 30 min, 62%),[11] giving (*S*)-CFPA (**1**) ($[\alpha]^{23}_D$ −24.5°). The chloride (CFPA-Cl), (*S*)-**6** ($[\alpha]^{24}_D$ −23.5°),[12] was obtained after distillation (81%).

The $\Delta\delta$ values in the ^{19}F NMR spectra for the diastereomers **7**–**15**, prepared by the condensation of **6**[13] with chiral nucleophiles, are shown in Table I. The merits of the CFPA method can be summarized as follows. First, **6** reacts with secondary alcohols and hindered amines much faster than MTPA-Cl,[14] suggesting that the reaction of **6** with chiral compounds induces potentially less kinetic resolution[15] than that of MTPA-Cl. Second, the ^{19}F signals of CFPA-Cl and CFPA (−136.7 and −147.8 ppm, respectively) appear out of the region of those of CFPA derivatives (from −143.0 to −146.9 ppm),[16] allowing the fluorine signals of the diastereomers of interest to be easily distinguished in the ^{19}F NMR spectrum of a crude sample, even if CFPA-Cl is used in excess.[15] Finally, we used the new reagent to determine the ee of **16** and **18**, which have remotely disposed stereogenic centers.[17] The corresponding CFPA derivatives **17** and **19** gave $\Delta\delta$ values of 44.1 and 6.1 Hz, respectively, whereas the $\Delta\delta$ values of the MTPA derivatives were not detectable.



16 : R = H
17 : R = −C(=O)−C(F)(CN)−Ph

18 : R = H
19 : R = −C(=O)−C(F)(CN)−Ph

MTPA[5] and other ee-determining reagents[3,4] generate a $\Delta\delta/w_{1/2}$ ratio of ca. 0–10, whereas this ratio for CFPA derivatives varies from 7 to 50. This fact, in addition to the relatively high reactivity of CFPA-Cl and the ability of the CFPA moiety to determine the ee of chiral centers remote from the derivatized functionality (runs 6–9), warrants consideration of CFPA in assaying the ee of intermediates and products of modern complex chiral syntheses.

Acknowledgment. We are grateful to Prof. E. Yoshii (Toyama Medical & Pharmaceutical University) for a generous gift of samples of **16** and **18**. This work was partially supported by a Grant-in-Aid (No. 02670949) for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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(10) Compound **4a**, $C_{17}H_{15}FN_2O$ (M_r = 282.32), gave monoclinic crystals with space group $P2_1$, a = 8.367 (1) Å, b = 17.006 (1) Å, c = 5.253 (1) Å, β = 105.3 (1)°, V = 720.9 (2) Å^3, Z = 2, D_{calcd} = 1.300 Mg m^{-3}, λ(Cu Kα$_1$) = 1.540 50 Å, μ = 0.761 mm^{-1}, F(000) = 296, T = 295 K. Crystallographic data were collected on a Rigaku AFC-5 diffractometer. The structures were solved by the direct method and refined by full-matrix least-squares calculations assuming anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms. R = 0.049 and R_w = 0.048 for 1096 reflections above 3σ(F).

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(12) Bp 40–41 °C/0.4 Torr. The optical purity of (*S*)-**6** was determined to be greater than 99% by application of the Eu(hfc)$_3$ method to the (*S*)-CFPA methyl ester.

(13) CFPA-Cl (**6**) was used under almost the same conditions as MTPA-Cl.[5]

(14) For example, reactions of CFPA-Cl with PhCH(OH)CF_3 and ^{t}BuCH(OH)Me (Pyr/CCl_4, room temperature) are complete within 10 min, whereas reactions of MTPA-Cl take more than 10 h for completion.[5]

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(16) The ^{19}F NMR chemical shifts of MTPA-Cl and MTPA (−70.5 and −71.7 ppm, respectively) are within the region of those of diastereomeric MTPA derivatives (from −69.2 to −72.5 ppm). Upfield shifts from $CFCl_3$ are quoted as negative.

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Supplementary Material Available: Experimental details for the preparation and physical and spectral data of **4a,b**, **1** and its sodium salt, and **6**, general procedure for the preparation of CFPA derivatives, all X-ray crystallographic data for compound **4a**, and tables of atomic coordinates and anisotropic thermal parameters (6 pages); observed and calculated structure factors for **4a** (4 pages). Ordering information is given on any current masthead page.

Total Synthesis of Vineomycinone B_2 Methyl Ester via Double Bradsher Cyclization[1]

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Received April 8, 1991

Vineomycin B_2[2] is a secondary metabolite of *Streptomyces matensis* subsp. *vineus* and displays potent antitumor/antibiotic activity with a pharmacologic profile similar to that of the clinically important anthracyclines.[3] Its chemical degradation[2] in acidic methanol yields an aglycon subunit, vineomycinone B_2 methyl ester (**1**), bearing several salient structural features shared in part by other anthraquinone antibiotics,[4] inter alia, an olivose-type β-C-glycoside and a 3(*R*)-hydroxyisovaleryl side chain situated on opposing sides of an anthrarufin nucleus. Accordingly, vineomycin B_2 has engendered much synthetic interest[5] and provided a forum for the demonstration of new methodology resulting in recent total syntheses[6,7] of the aglycon moiety **1**. Herein, we describe a conceptually distinct approach to **1** utilizing a convergent strategy of consecutive Bradsher cycloadditions[8] of the electron-rich dienophiles **2** and **4** with the heterodienes implicit in **3** (eq 1).

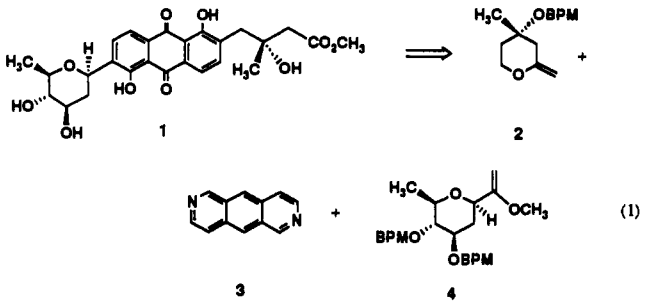
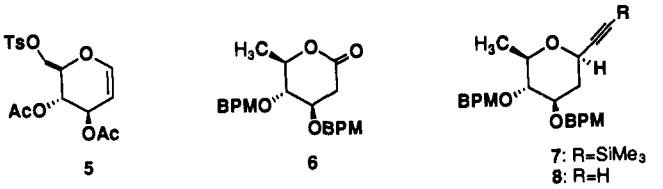
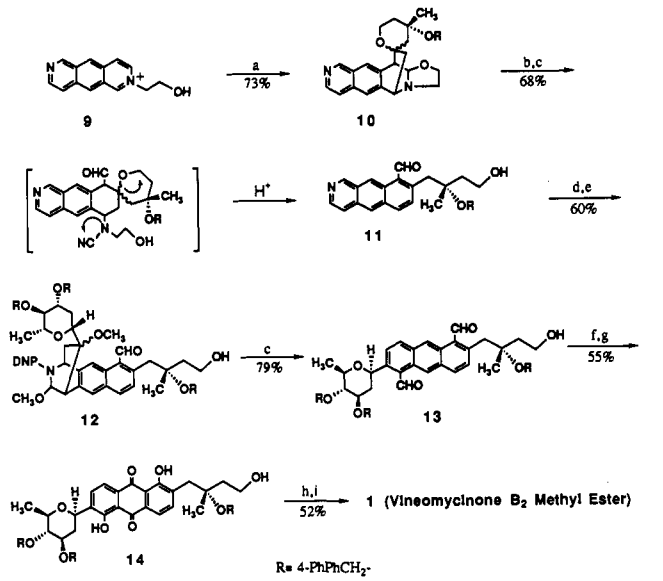


Chart I



Scheme I[a]



[a] (a) **2**, $CaCO_3$, $MeOH/CH_2Cl_2$, 24 °C, 2 h; (b) CNBr, $NaHCO_3$, MeOH, 0 °C, 0.5 h; (c) 3 N HCl/THF, 40 °C, 12 h; (d) DNP-Br, CH_3CN, 65 °C, 10 h; (e) **4**, $CaCO_3$, MeOH, 10 °C, 6 h; (f) $PhSeO_2H$, H_2O_2, H_2O/CH_2Cl_2, 25 °C, 20 h; NH_4OH; (g) $^1O_2$, CH_2Cl_2; $NaBH_4$, MeOH; O_2 (workup); (h) PDC, DMF, 25 °C, 10 h; CH_2N_2; (i) H_2 (1 atm), 5% Pd/C, EtOAc, 6 h.

As envisaged above, the acyclic side chain is introduced in the latent form embodied in **2**,[9] readily available from the vinylidene analogue[10] of (*S*)-mevalonolactone by etherification of the tertiary alcohol with *p*-biphenylmethyl (BPM) bromide[11] (72%). Access to the β-C-glycoside precursor **4** from glucal **5**[12] (Chart I) was realized by sequential lithium aluminum hydride reduction in Et_2O (80%), protection of the liberated C(3) and C(4) alcohols as BPM ethers (86%), and pyridinium chlorochromate oxidation of the cyclic enol ether[13] (76%). Addition of the cerium(III) chloride salt[14] of (trimethylsilyl)acetylide to the resultant lactone **6** (mp 118-120°C) at -78 °C in tetrahydrofuran (THF) provided an anomeric mixture of hemiketals (90%), which was reduced[15] with excess $Et_3SiH/BF_3{\cdot}Et_2O$ (10 equiv each) in CH_3CN/CH_2Cl_2 (1:1) at -40 °C. Chromatographic purification on silica gel (ethyl acetate/hexane, 1:4) afforded **7** and its α-epimer (89%, 3:1), R_f ~ 0.56 and 0.49, respectively. Desilylation[14] to **8** (90%, mp 91 °C) and methoxymercuration/demercuration according to Hudrlik[16] furnished **4** (58%, mp 70-71 °C).

Attachment of both appendages to the polycyclic core and final elaboration to **1** are summarized in Scheme I. Facile[17] Bradsher

(1) (a) Presented at the 199th National Meeting of the American Chemical Society, Boston, MA, 1990. (b) Taken in part from the Ph.D. Thesis of V.B., Universite Louis Pasteur, Strasbourg, France.
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