Diastereo-Face Selectivity in the Aldol Reaction of Boryl Enolate Derived from Oppolzer's Sultam

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In the Oppolzer aldol reaction, aldehyde reacts exclusively on the *Si* face (C(α)-*Si* attack) of the double bond of the boryl enolate 2 derived from (1*S*,2*R*)-*N*-propionylbornane-10,2-sultam (1), providing only 3a stereoselectively. Hexafluoroacetone (4) caused complete reversal of the diastereo-face selectivity, reacting exclusively on the *Re* face (C(α)-*Re* attack) of 2 to give only 5. Trifluoroacetaldehyde (8) and 2,2-difluoro-5-phenylpentanal (9) caused partial reversal of the diastereo-face selectivity, giving significant amounts of unexpected and unusual *syn*- (12c, 13c) and *anti*- (12d, 13d) aldols along with the normal *syn*-aldol (12a, 13a). This finding was applied to the reactions of the boryl enolate with phenylglyoxal (10) and ethyl glyoxylate (11).

Key words diastereo-face selectivity; aldol reaction; boryl enolate; Oppolzer's sultam

The synthesis of chiral fluoroorganic compounds is important in biological and medicinal chemistry, in view of the influence of fluorine on biological activity.[1] In addition, these compounds have potential application to electronic materials, such as liquid crystals.[2] In the preparation of fluorine-containing molecules with unexpected and generally unusual reactivity, methodologies for synthesizing nonfluorinated chiral compounds are frequently impractical, giving rise to the term "flustrate" by Seebach.[3]

The Evans aldol reaction in which aldehydes react exclusively on the *Re* face of the double bond of boryl enolate is a very effective means for synthesizing chiral "Evans" *syn* aldols and is useful for the preparation of biologically active molecules. Unexpected and unusual *Si* face attack was previously reported in reactions with fluorine-containing carbonyl compounds such as trifluoroacetaldehyde (CF_3CHO), phenylglyoxal and ethyl glyoxylate (Chart 1).[4] This paper describes the diastereo-face selectivity in the aldol reaction of boryl enolates derived from Oppolzer's sultam with α,α-difluoro- and α,α,α-trifluorocarbonyl compounds. Applications of this finding to phenylglyoxal and ethyl glyoxylate are discussed.[5]

Results and Discussion

In the Oppolzer aldol reaction, aldehyde reacts exclusively on the *Si* face (C(α)-*Si* attack) of the double bond of the boryl enolate **2** derived from (1*S*,2*R*)-*N*-propionylbornane-10,2-sultam (**1**), providing only the *syn* aldol **3a** stereoselectively.[6] The use of $TiCl_4$ completely eliminated the ability of the enolate to generate **3a**, giving the *anti* aldol **3d** exclusively (Chart 2).[7] We examined the

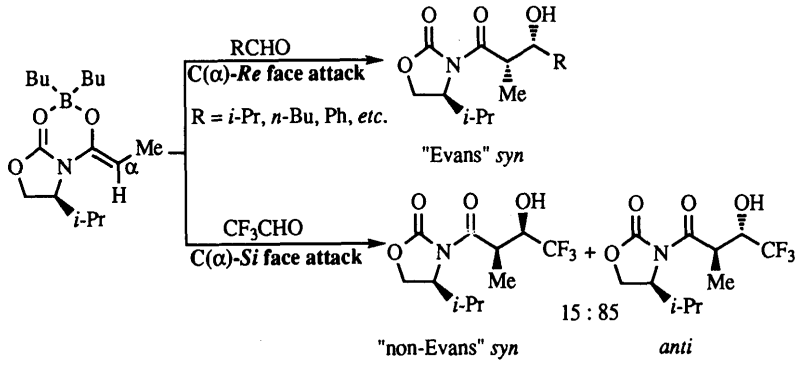

Chart 1

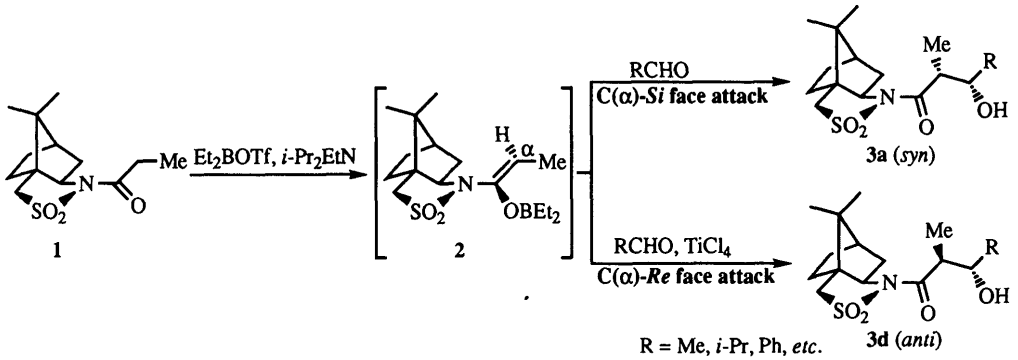

Chart 2

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reactions of **2** with fluorine-containing carbonyl compounds such as hexafluoroacetone and trifluoroacetaldehyde, as well as phenylglyoxal and ethyl glyoxylate, in the absence of Lewis acids such as $TiCl_4$.

Reversal of Stereochemistry with Hexafluoroacetone (4) Reaction of **2** with **4** was examined by the standard procedure of Oppolzer *et al.*[6] Boryl enolate **2**, prepared from *N*-propionylsultam **1**, diethylboryl triflate (Et_2BOTf) and *N*,*N*-diisopropylethylamine (iso-Pr_2EtN), was treated with gaseous **4** at −78 °C. The reaction system was warmed to 5 °C over 90 min and left at the same temperature for 30 min to give the aldol **5** stereoselectively in 93% yield. Compound **5** was found to have the *S*-configuration by conversion to stereochemically known **7** as follows. Treatment of **5** with chloromethyl methyl ether (MOMCl) and *iso*-Pr_2EtN and then reduction of the resulting MOM ether **6** with $LiAlH_4$ gave the (*R*)-alcohol **7**, which was identical with an authentic sample obtained according to the literature.[8] Hexafluoroacetone (**4**) reacted selectively on the *Re* face of the double bond of **2**.

Reversal of Stereochemistry with Aldehydes (8—11) Aldehydes **8**—**11** were allowed to react with boryl enolate **2** and the results are summarized in Table 1. Interestingly, trifluoroacetaldehyde (**8**) caused complete reversal of the diastereo-face selectivity in the Evans aldol reaction (Chart 1),[4] while reaction of **8** with Oppolzer's sultam **1** brought about partial reversal, giving the normal *syn*-aldol **12a** as the major product (entry 1). Thus, the reaction system was warmed from −78 °C to 5 °C over 90 min and stirred at this temperature for 30 min to give the aldol **12** in 96% yield. The **12a**—**d** ratio was 73 : 1 : 19 : 7. As shown in Chart 4, the major product, the normal *syn*-aldol **12a**, was formed through C(α)-*Si* face attack on **2** and the minor production of **12c** and **12d** indicated partial reversal of the diastereo-face selectivity. The addition of $TiCl_4$[7] to **2** prior to **8** resulted in complete reversal to give **12d** exclusively (entry 2). Since the α,α-difluoro aldehyde **9**, phenylglyoxal (**10**) and ethyl glyoxylate (**11**) readily undergo self-condensation, these aldehydes were added to **2** at −5 °C. The α,α-difluoro aldehyde **5** gave the aldol **13** in 86% yield (entry 3). The **13a**—**d** ratio was 21 : 0 : 49 : 30. In the case of **10**, the aldol **14** was obtained in 78% yield and the normal *syn* adduct **14a** was formed in only a small amount (entry 4). The **14a**—**d** ratio was 17 : 0 : 25 : 58. Ethyl

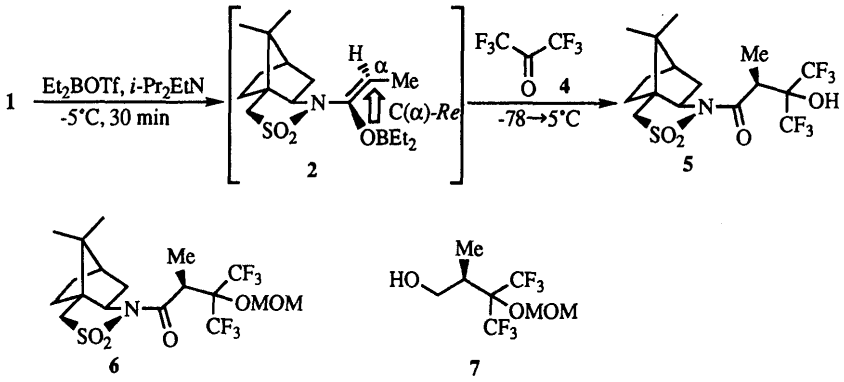


Chart 3

Table 1. Aldol Reactions of Boryl Enolate **2** with Aldehydes

Entry	Aldehyde R	(RCHO)	Conditions Temperature (time, min)	Yield (%)[a]	Product a : b : c : d[b]
1	CF_3	(**8**)	−78 to 5 °C (90), then 5 °C (30)	96 (100)	73 : 1 : 19 : 7 (**12**)
2[c]	CF_3	(**8**)	−78 °C (90), then −78 to −30 °C (15)	89 (96)	0 : 0 : 1 : 99 (**12**)
3	$Ph(CH_2)_3CF_2$	(**9**)	−5 to 0 °C (120)	86 (99)	21 : 0 : 49 : 30 (**13**)
4	PhCO	(**10**)	−5 °C (50)	78	17 : 0 : 25 : 58 (**14**)
5	EtOCO	(**11**)	−5 to 0 °C (180)	66 (100)	33 : 2 : 50 : 15 (**15**)

a) All yields are those of isolated compounds. Values in parentheses are conversion yields. *b*) Ratios were determined by capillary GLC. Relative and absolute stereochemical assignments were made based on conversion to stereochemically confirmed compounds. *c*) The reaction was carried out in the presence of $TiCl_4$.

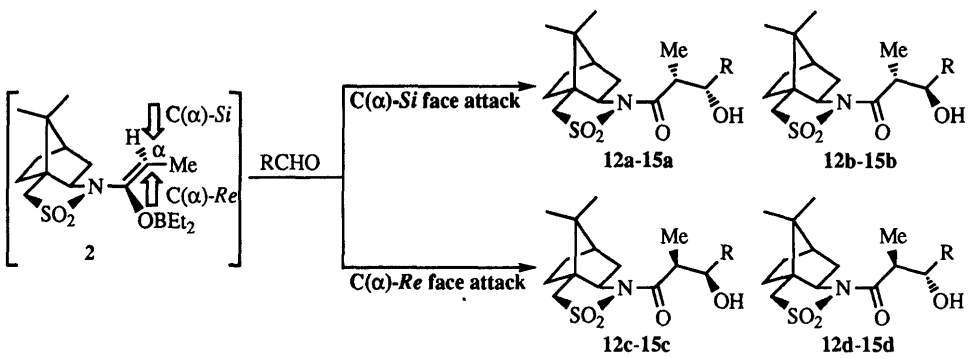
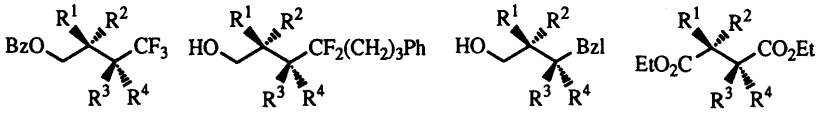


Chart 4



16 17 18 19

a: R^1 = H, R^2 = Me, R^3 = H, R^4 = OH, b: R^1 = H, R^2 = Me, R^3 = OH, R^4 = H,
c: R^1 = Me, R^2 = H, R^3 = OH, R^4 = H, d: R^1 = Me, R^2 = H, R^3 = H, R^4 = OH

Chart 5

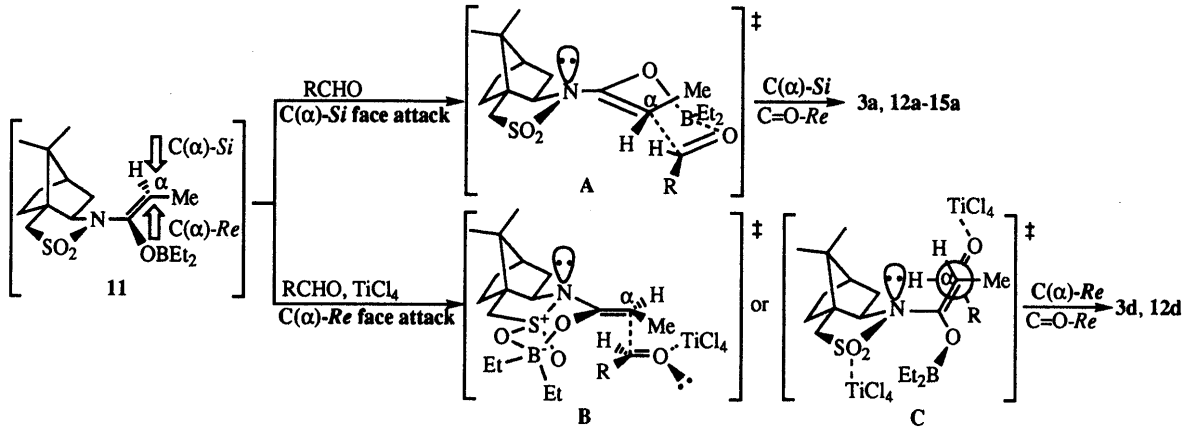


Chart 6

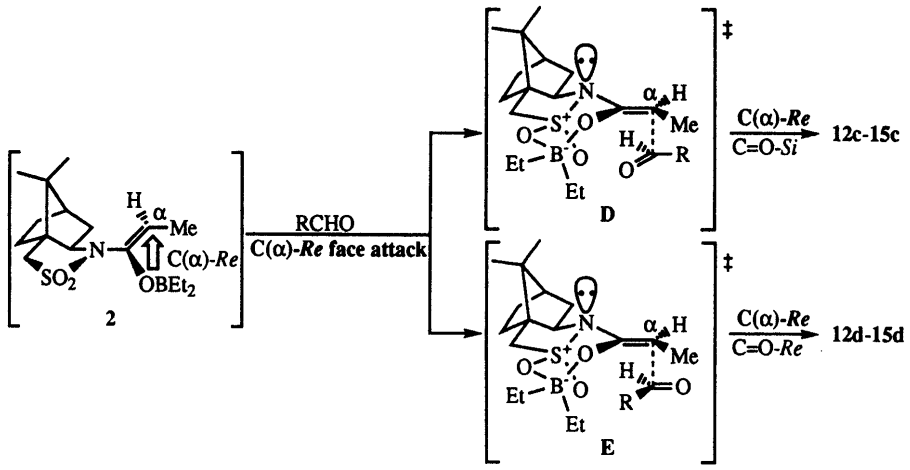


Chart 7

glyoxylate (**11**), gave the aldol **15** in 66% yield with a (**15a** and **15b**)–(**15c** and **15d**) ratio of 35 : 65 (entry 5). In both **10** and **11**, reversal of π-facial selectivity was predominant.

The relative and absolute stereochemical assignments of the aldols **12**—**15** were confirmed based on conversion to stereochemically known compounds (Chart 5). The reduction of the aldol **12d** with $LiAlH_4$ followed by benzoylation of the resulting diol gave the benzoate **16d** ($[\alpha]_D^{24}$ +18.4° (c=0.47, $CHCl_3$)) which was identical with **16b**, except for optical rotation ($[\alpha]_D^{25}$ −18.5° (c=0.39, $CHCl_3$)).[4] In the same manner, **12a** and **12c** were converted to **16a** and **16c**, respectively.[4] The aldol **13c** was reduced with $LiAlH_4$ and converted to **17c** ($[\alpha]_D^{25}$ −15.0° (c=0.99, $CHCl_3$)), which was identical with **17a**, except for optical rotation ($[\alpha]_D^{25}$ +14.3° (c=0.69, $CHCl_3$)).[4] In the same manner, **13d** and **13a** were converted to **17d** and **17a**, respectively, and the stereochemistry of the products was determined by comparison with authentic samples.[4] The aldols **14a**, **14c** and **14d** were converted to **18a**, **18c** and **18d**, respectively, by reduction ($LiAlH_4$), acetylation (Ac_2O, pyridine), hydrogenolysis (H_2, Pd–C) and deacetylation (K_2CO_3 in MeOH).[4] Ethanolysis of **15c** and **15d** with NaH in EtOH at 0 °C gave **19c** ($[\alpha]_D^{24}$ −1.6° (c=0.63, ether)) and **19d** ($[\alpha]_D^{24}$ +12.2° (c=0.63, ether)), respectively, which were identical with **19a** and **19b** except for optical rotation.[4] In the same manner, the aldols **15a** and **15b** were converted to **19a** and **19b**, respectively.

Mechanism Oppolzer and Lienard proposed that reactions of boryl enolate **2** with aldehydes proceed exclusively *via* the closed transition state A (C(α)-*Si*/C=O-*Re* attack) to give only **3a** and reactions in the presence of $TiCl_4$ occur *via* the open transition state B or C (C(α)-*Re*/C=O-*Re* attack) to yield **3d** selectively (Chart

Table 2. *Ab Initio* Calculations for Carbonyl Compounds Using the RHF/6-31G** Basis Set[9]

Carbonyl compound	MO energy level LUMO (hartree)	Mulliken atomic charge O (C=O)	Diastereofacial selectivity [C(α)]	
			Oppolzer aldol reaction	Evans aldol reaction
CH_3CHO	0.1561	−0.4909	*Si* only	*Re* only
PhCHO	0.0817	−0.5257	*Si* only	*Re* only
CF_3COCF_3 (**4**)	0.0590	−0.4145	*Re* only	*Si* only
CF_3CHO (**8**)	0.0957	−0.4259	*Re*:*Si* (26:74)	*Si* only
$Ph(CH_2)_3CF_2CHO$ (**9**)	0.1169	−0.4685	*Re*:*Si* (79:21)	*Si*:*Re* (94: 6)
PhCOCHO (**10**)	0.0442	−0.4740	*Re*:*Si* (83:17)	*Si*:*Re* (96: 4)
EtOCOCHO (**11**)	0.0743	−0.4351	*Re*:*Si* (65:35)	*Si*:*Re* (79:21)

6).[7] The present C(α)-*Re* face selectivity with hexafluoroacetone (**4**) and aldehydes **8**—**11** would imply the mechanism shown in Chart 7. Aldols **12c**—**15c** and **12d**—**15d** would appear to be derived from the aldehydes by C(α)-*Re*/C=O-*Si* and C(α)-*Re*/C=O-*Re* attacks, this being consistent with the open transition states, D and E, respectively. Trifluoroacetaldehyde (**8**) may react with **2** preferentially through the closed transition state A and partially through transition states D and E. The reaction of **8** in the presence of $TiCl_4$ may proceed exclusively *via* the open transition state B. With the α,α-difluoro aldehyde **9**, phenylglyoxal (**10**) and ethyl glyoxylate (**11**), the open transition states D and E are predominant.

The complete or partial facial selectivity of the enolate **2** may possibly bear some relation to the low Lewis basicity and high electrophilicity of the carbonyl of hexafluoroacetone (**4**) and the aldehydes **8**—**11**. As shown in Table 2, these carbonyl compounds, except for **8** and **9**, have lower LUMO levels (higher electrophilicity) and lower negative charges of carbonyl oxygen (lower Lewis basicity), respectively, than aldehydes (CH_3CHO and PhCHO) showing C(α)-*Si* face attack. Hexafluoroacetone, showing complete reversal of diastereo-face selectivity in both the Oppolzer and Evans aldol reactions, has the lowest negative charge of carbonyl oxygen. The low Lewis basicity may prevent carbonyl oxygen from coordinating with the boron of **2** and the high electrophilicity may promote the reaction *via* the open transition states D and E, even without activation of the carbonyl (enhancement of electrophilicity) by coordination with the boron of **2** or a Lewis acid such as $TiCl_4$.

Experimental

General Reactions were run under an argon atmosphere with magnetic stirring in oven-dried glassware. CH_2Cl_2 was distilled from CaH_2 immediately before use. Tetrahydrofuran (THF) and Et_2O were freshly distilled from sodium diphenylketyl. Other solvents and reagents were used as supplied or purified. Anhydrous magnesium sulfate was used as the drying agent. Silica gel 60 (Merck, 230—400 mesh) was used for column chromatography. Analytical gas-liquid chromatography (GLC) was carried out using a GL Science (30 m × 0.25 mm) Neutrabond-1 capillary column 1.5 μm in thickness. GLC data were obtained for mixtures of diastereomers. Melting points are uncorrected. Optical rotation was measured at 589 nm using a 1.0-dm cell with a total volume of 1 ml. Infrared spectra were obtained either neat or in KBr pellets, and absorption is expressed in reciprocal centimeters (cm^{-1}). ^{1}H-NMR spectra were recorded at 200 MHz and expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) as the internal standard (δ). ^{19}F-NMR spectra were measured at 188 MHz and values are given in parts per million (ppm) upfield from CCl_3F as the internal standard. Coupling constants are indicated in hertz (Hz). $CDCl_3$ served as the solvent for ^{1}H- and ^{19}F-NMR. Low- and high-resolution MS analyses were performed under 70 eV electron-impact (EI) conditions. Elemental analyses were conducted at the Toray Research Center Inc., Tokyo. *N*-Propionylbornane-10,2-sultam **1** was prepared by the reported method.[6]

General Procedure for Aldol Condensation. (1*S*,2*R*,2′*S*)-*N*-[4′,4′,4′-Trifluoro-3′-hydroxy-2′-methyl-3′-(trifluoromethyl)butanoyl]bornane-10,2-sultam (5) CF_3SO_3H (326 μl, 3.68 mmol) was added to Et_3B (1.0 M solution in hexane, 3.7 ml, 3.70 mmol) at room temperature and the mixture was stirred at 40 °C until gas evolution ceased. Solutions of propionylsultam **1** (501 mg, 1.85 mmol) in CH_2Cl_2 (7 ml) and iso-Pr_2EtN (680 μl, 3.90 mmol) in CH_2Cl_2 (3.9 ml) were successively added to the resulting Et_2BOTf at −5 °C and stirring at the same temperature for 30 min gave a solution of **2**. The boryl enolate solution was cooled to −78 °C and gaseous **4** (2 ml at −78 °C, 15.9 mmol) was added *via* a cannula. The mixture was warmed to 5 °C over 90 min and left at the same temperature for 30 min, then the reaction was quenched with phosphate buffer (pH 7) and the whole was extracted with Et_2O. The combined extracts were washed with saturated aqueous NH_4Cl and brine, dried and filtered. Following evaporation of the solvent, chromatography of the residue with hexane–CH_2Cl_2 gave **5** (755 mg, 93.5%) and the starting material **1** (20 mg, 4.0%). **5**: colorless needles (hexane), mp 140.8—141.6 °C, $[\alpha]_D^{25}$ −38.2° (*c*=0.51, $CHCl_3$). IR (KBr): 3229, 1654, 1283, 1219 cm^{-1}. ^{1}H-NMR δ: 0.99 (3H, s), 1.13 (3H, s), 1.29—1.54 (5H, m), 1.84—2.22 (5H, m), 3.49 (1H, d, *J*=13.8 Hz), 3.59 (1H, d, *J*=13.8 Hz), 3.69 (1H, dd, *J*=14.3, 7.4 Hz), 3.89 (1H, dd, *J*=7.8, 5.7 Hz), 6.31 (1H, s). ^{19}F-NMR δ: 72.9 (3F, dd, *J*=22.1, 10.5 Hz), 76.0 (3F, dd, *J*=22.1, 11.2 Hz). MS *m/z*: 437 (M^+), 418, 223, 175, 151, 125, 108, 69. HRMS Calcd for $C_{16}H_{21}F_6NO_4S$ (M^+): 437.110. Found: 437.109. *Anal.* Calcd for $C_{16}H_{21}F_6NO_4S$: C, 43.9; H,4.8; N, 3.2. Found: C, 43.8; H, 4.7; N, 3.2.

(1*S*,2*R*)-*N*-(4′,4′,4′-Trifluoro-3′-hydroxy-2′-methylbutanoyl)bornane-10,2-sultam (12) Gaseous **8** (2 ml at −78 °C, 31.9 mmol) was added at −78 °C to a solution of **2** in CH_2Cl_2, prepared from **1** (1002 mg, 3.7 mmol) according to the general procedure. The reaction system was warmed to 5 °C over 90 min and left at the same temperature for 30 min prior to quenching. Chromatography with hexane–CH_2Cl_2 and hexane–AcOEt as eluents gave **12a** (911 mg, 66.8%), **12d** (92 mg, 6.7%), a mixture of **12c** and **12a** (205 mg, 15.0%), a mixture of **12a**, **12b** and **12c** (104 mg, 7.6%) and the starting material **1** (38 mg, 3.8%). **12d**: colorless needles (hexane), mp 136.1—137.4 °C, $[\alpha]_D^{24}$ −44.9° (*c*=0.20, $CHCl_3$). IR (KBr): 3489, 1690, 1331, 1138 cm^{-1}. ^{1}H-NMR δ: 0.98 (3H, s), 1.14 (3H, s), 1.29—1.54 (3H, m), 1.45 (3H, d, *J*=6.8 Hz), 1.80—2.22 (4H, m), 3.46 (1H, d, *J*=14.5 Hz), 3.56 (1H, d, *J*=14.5 Hz), 3.48—3.60 (1H, m), 3.84—4.06 (2H, m), 4.44 (1H, d, *J*=11.0 Hz). ^{19}F-NMR δ: 78.0 (d, *J*=7.5 Hz). MS *m/z*: 369 (M^+), 305, 271, 151, 108, 67. HRMS Calcd for $C_{15}H_{22}F_3NO_4S$ (M^+): 369.122. Found: 369.122. *Anal.* Calcd for $C_{15}H_{22}F_3NO_4S$: C, 48.8; H, 6.0; N, 3.8. Found: C, 48.5; H, 5.9; N, 3.8. **12a**: colorless needles (hexane–CH_2Cl_2), mp 177.8—179.0 °C, $[\alpha]_D^{24}$ −88.4° (*c*=0.79, $CHCl_3$). IR (KBr): 3444, 1685, 1333, 1143 cm^{-1}. ^{1}H-NMR δ: 0.99 (3H, s), 1.15 (3H, s), 1.40 (3H, dd, *J*=7.1, 1.4 Hz), 1.22—1.51 (3H, m), 1.86—2.10 (4H, m), 3.40 (1H, d, *J*=4.0 Hz), 3.46 (1H, d, *J*=10.7 Hz), 3.55 (1H, d, *J*=10.7 Hz), 3.45—3.56 (1H, m), 3.90 (1H, t, *J*=6.6 Hz), 4.35—4.49 (1H, m). ^{19}F-NMR δ: 76.7 (d, *J*=6.7 Hz). MS *m/z*: 369 (M^+), 349, 305, 151, 108, 67. HRMS Calcd for $C_{15}H_{22}F_3NO_4S$ (M^+): 369.122. Found: 369.121. *Anal.* Calcd for $C_{15}H_{22}F_3NO_4S$: C, 48.8; H, 6.0; N, 3.8. Found: C, 48.7; H, 6.1; N, 3.6. A mixture of **12c** and **12a** (84:16): a colorless oil. IR (neat) 1685 cm^{-1}. ^{1}H-NMR δ: 0.97 (2.5H, s), 0.99 (0.5H, s), 1.14 (2.5H, s), 1.15 (0.5H, s), 1.19—1.57 (5H, m), 1.78—2.11 (5H, m), 3.37—3.61 (3H, m), 3.90 (1H,

t, J=6.6 Hz), 4.07—4.49 (2H, m). ^{19}F-NMR δ: 76.7 (0.5F, d, J=6.7 Hz), 77.2 (2.5F, d, J=6.4 Hz). MS m/z: 369 (M^+), 349, 305, 151, 108, 67.

Reaction with 8 in the Presence of $TiCl_4$ A solution of **2** was prepared from **1** (502 mg, 1.85 mmol) and to this was added $TiCl_4$ (5.6 ml, 51.1 mmol) at −78 °C. The mixture was stirred at this temperature for 10 min, then gaseous **8** (7 ml at −78 °C) was added. Stirring was continued at −78 °C for 90 min then the mixture was warmed to −30 °C over 15 min prior to quenching to give **12c** (6 mg, 0.9%), **12d** (599 mg, 87.9%) and the starting material **1** (40 mg, 7.9%).

(1*S*,2*R*)-*N*-[4′,4′-Difluoro-3′-hydroxy-2′-methyl-7′-phenylheptanoyl]-bornane-10,2-sultam (13) A solution of **9** (546 mg, 2.75 mmol) in CH_2Cl_2 (5 ml) was added over 5 min at −5 °C to a solution of **2** prepared from **1** (502 mg, 1.85 mmol). The reaction system was warmed to 0 °C over 2 h prior to quenching. Chromatography with hexane–CH_2Cl_2–AcOEt (10 : 10 : 1) gave **13a** (154 mg, 17.8%), **13d** (224 mg, 25.7%), **13c** (372 mg, 42.8%) and the starting material **1** (65 mg, 12.9%). **13c**: colorless needles (hexane–Et_2O), mp 138.0—139.2 °C, $[\alpha]_D^{26}$ −31.2° (c=0.90, $CHCl_3$). IR (KBr): 3482, 1694, 1604, 1456 cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, s), 1.14 (3H, s), 1.32 (3H, d, J=6.7 Hz), 1.34—1.43 (2H, m), 1.79—2.17 (9H, m), 2.19 (1H, d, J=7.0 Hz), 2.59—2.70 (2H, m), 3.77—3.43 (1H, m), 3.43 (1H, d, J=13.8 Hz), 3.50 (1H, d, J=13.8 Hz), 3.88 (1H, dd, J=7.7, 5.0 Hz), 4.01—4.08 (1H, m), 7.16—7.18 (3H, m), 7.26—7.29 (2H, m). ^{19}F-NMR δ: 105.8—107.4 (1F, m), 110.3—111.9 (1F, m). MS m/z: 469 (M^+), 300. HRMS Calcd for $C_{24}H_{33}F_2NO_4S$ (M^+): 469.210. Found: 469.209. *Anal.* Calcd for $C_{24}H_{33}F_2NO_4S$: C, 61.4; H, 7.1; N, 3.0. Found: C, 61.3; H, 7.2; N, 3.0. **13d**: a colorless oil, $[\alpha]_D^{26}$ −25.7° (c=0.84, $CHCl_3$). IR (neat): 3440, 1664, 1604, 1455 cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, s), 1.15 (3H, s), 1.31—1.40 (2H, m), 1.42 (3H, d, J=7.0 Hz), 1.78—2.15 (9H, m), 2.65 (2H, t, J=7.7 Hz), 3.44 (1H, d, J=13.8 Hz), 3.50—3.55 (1H, m), 3.51 (1H, d, J=13.8 Hz), 3.63—3.71 (1H, m), 3.86 (1H, dd, J=7.8, 4.9 Hz), 4.29 (1H, d, J=10.4 Hz), 7.16—7.19 (3H, m), 7.27—7.29 (2H, m). ^{19}F-NMR δ: 108.7—110.3 (1F, m), 110.9—112.5 (1F, m); MS m/z: 469 (M^+), 300. HRMS Calcd for $C_{24}H_{33}F_2NO_4S$ (M^+): 469.210. Found 469.210. **13a**: a colorless oil, $[\alpha]_D^{26}$ −68.3° (c=1.10, $CHCl_3$). IR (neat): 3464, 1690, 1604, 1456 cm^{-1}. ^{1}H-NMR δ: 0.98 (3H, s), 1.15 (3H, s), 1.36 (3H, d, J=7.1 Hz), 1.34—1.44 (2H, m), 1.82—2.10 (9H, m), 2.61—2.72 (2H, m), 2.95 (1H, d, J=4.4 Hz), 3.44 (1H, d, J=13.8 Hz), 3.50 (1H, d, J=13.8 Hz), 3.49—3.54 (1H, m), 3.86 (1H, dd, J=6.9, 5.7 Hz), 4.12 (1H, dq, J=18.5, 3.9 Hz), 7.16—7.18 (3H, m), 7.26—7.28 (2H, m). ^{19}F-NMR δ: 107.5—109.1 (1F, m), 111.6—113.2 (1F, m). MS m/z: 469 (M^+), 300. HRMS Calcd for $C_{24}H_{33}F_2NO_4S$ (M^+): 469.210. Found: 469.211.

(1*S*,2*R*)-*N*-(3′-Hydroxy-2′-methyl-4′-oxo-4′-phenylbutanoyl)bornane-10,2-sultam (14) A solution of **10** (550 mg, 4.10 mmol) in CH_2Cl_2 (5 ml) was added over 5 min at −5 °C to a solution of **2** prepared from **1** (504 mg, 1.86 mmol). The reaction system was stirred at −5 °C for 50 min prior to quenching. Chromatography with benzene–AcOEt (10 : 1) gave **14a** (185 mg, 24.6%), **14c** (129 mg, 17.1%) and **14d** (274 mg, 36.3%). **14c**: colorless needles (hexane–AcOEt), mp 192.5—193.5 °C, $[\alpha]_D^{23}$ +21.7° (c=0.86, $CHCl_3$). IR (KBr): 3430, 1701, 1678, 1597, 1448 cm^{-1}. ^{1}H-NMR δ: 0.83 (3H, d, J=6.7 Hz), 1.00 (3H, s), 1.26 (3H, s), 1.35—1.45 (2H, m), 1.90—2.00 (3H, m), 2.06 (1H, dd, J=14.0, 7.8 Hz), 2.11—2.17 (1H, m), 3.51 (1H, d, J=13.7 Hz), 3.51—3.59 (1H, m), 3.57 (1H, d, J=13.7 Hz), 3.90 (1H, d, J=6.4 Hz), 3.98 (1H, dd, J=7.8, 4.8 Hz), 5.66 (1H, dd, J=6.4, 3.7 Hz), 7.49—7.53 (2H, m), 7.61—7.64 (1H, m), 8.15—8.18 (2H, m). MS (FAB) m/z: 406 (M+1). HRMS (FAB) Calcd for $C_{21}H_{28}NO_5S$ (M+H): 406.169. Found: 406.170. *Anal.* Calcd for $C_{21}H_{27}NO_5S$: C, 62.2; H, 6.7; N, 3.5. Found: C, 62.1; H, 6.8; N, 3.5. **14d**: a colorless oil, $[\alpha]_D^{24}$ −57.4° (c=0.72, $CHCl_3$). IR (neat): 3441, 1683, 1598, 1450 cm^{-1}. ^{1}H-NMR δ: 0.95 (3H, s), 1.15 (3H, s), 1.31 (3H, d, J=6.9 Hz), 1.34—1.40 (2H, m), 1.87—1.92 (3H, m), 2.04 (1H, dd, J=13.9, 7.9 Hz), 2.18—2.23 (1H, m), 3.39 (1H, d, J=13.7 Hz), 3.44 (1H, d, J=13.7 Hz), 3.48—3.54 (1H, m), 3.87 (1H, dd, J=7.9, 5.0 Hz), 3.89 (1H, d, J=10.7 Hz), 5.10 (1H, dd, J=10.7, 5.5 Hz), 7.47—7.50 (2H, m), 7.58—7.62 (1H, m), 7.96—7.99 (2H, m). MS (FAB) m/z: 406 (M+1). HRMS (FAB) Calcd for $C_{21}H_{28}NO_5S$ (M+H): 406.169. Found: 406.169. **14a**: colorless needles (hexane–EtOAc), mp 202.0—203.0 °C, $[\alpha]_D^{23}$ −86.7° (c=0.75, $CHCl_3$). IR (KBr): 3462, 1691, 1676, 1597, 1450 cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, s), 1.12 (3H, s), 1.13 (3H, d, J=7.0 Hz), 1.33—1.45 (2H, m), 1.85—1.95 (2H, m), 2.08 (1H, d, J=6.3 Hz), 3.46 (1H, d, J=9.5 Hz), 3.49 (1H, d, J=9.5 Hz), 3.59 (1H, dq, J=7.0, 2.8 Hz), 3.80 (1H, d, J=5.0 Hz), 3.93 (1H, t, J=6.3 Hz), 5.50—5.60 (1H, m), 7.47—7.50 (2H, m), 7.58—7.60 (1H, m), 8.00—8.02 (2H, m). MS (FAB) m/z: 406 (M+1). HRMS (FAB) Calcd for $C_{21}H_{28}NO_5S$ (M+H): 406.169. Found: 406.168. *Anal.* Calcd for $C_{21}H_{27}NO_5S$: C, 62.2; H, 6.7; N, 3.5. Found: C, 62.0; H, 6.8; N, 3.4.

(1*S*,2*R*)-*N*-[3′-(Ethoxycarbonyl)-3′-hydroxy-2′-methylpropionyl]-bornane-10,2-sultam (15) A solution of **11** (800 mg, 7.84 mmol) in CH_2Cl_2 (10 ml) was added over 5 min at −5 °C to a solution of **2** prepared from **1** (501 mg, 1.85 mmol). The reaction system was warmed to 0 °C over 3 h prior to quenching. Chromatography of the residue with hexane–AcOEt (4 : 1) gave **15a** (150 mg, 21.8%), **15b** (12 mg, 1.7%), a mixture of **15c** and **15d** (123 mg, 17.8%), **15c** (128 mg, 18.6%), **15d** (41 mg, 5.9%) and the starting material **1** (174 mg, 34.7%). **15c**: a colorless oil, $[\alpha]_D^{25}$ −53.4° (c=0.82, $CHCl_3$). IR (neat): 3475, 1736, 1699, 1458 cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, s), 1.15 (3H, d, J=6.8 Hz), 1.18 (3H, s), 1.32 (3H, t, J=7.1 Hz), 1.35—1.43 (2H, m), 1.85—1.95 (3H, m), 2.05—2.12 (2H, m), 2.96 (1H, d, J=5.3 Hz), 3.45 (2H, q, J=7.1 Hz), 3.52—3.57 (1H, m), 3.91 (1H, dd, J=7.6, 4.9 Hz), 4.24—4.34 (2H, m), 4.65 (1H, dd, J=4.9, 4.0 Hz). MS m/z: 373 (M^+), 328, 300, 271. HRMS Calcd for $C_{17}H_{27}NO_6S$ (M^+): 373.156. Found: 373.157. **15d**: a colorless oil, $[\alpha]_D^{25}$ −54.3° (c=0.90, $CHCl_3$). IR (neat): 3499, 1738, 1694, 1456 cm^{-1}. ^{1}H-NMR δ: 0.95 (3H, s), 1.16 (3H, s), 1.28 (3H, t, J=7.2 Hz), 1.29 (3H, d, J=6.8 Hz), 1.32—1.43 (2H, m), 1.86—1.92 (3H, m), 2.05 (1H, dd, J=14.0, 7.9 Hz), 2.15—2.20 (1H, m), 3.39 (1H, d, J=10.0 Hz), 3.44 (1H, d, J=13.8 Hz), 3.42—3.51 (1H, m), 3.50 (1H, d, J=13.8 Hz), 3.88 (1H, dd, J=7.9, 4.9 Hz), 4.13—4.26 (2H, m), 4.29 (1H, dd, J=10.0, 5.6 Hz). MS m/z: 373 (M^+), 328, 300, 271. HRMS Calcd for $C_{17}H_{27}NO_6S$ (M^+): 373.156. Found: 373.155. **15a**: colorless needles (hexane), mp 103.8—104.6 °C, $[\alpha]_D^{24}$ −100.4° (c=0.89, $CHCl_3$). IR (KBr): 3468, 1728, 1686, 1456 cm^{-1}. ^{1}H-NMR δ: 0.98 (3H, s), 1.15 (3H, s), 1.30 (3H, t, J=7.1 Hz), 1.35 (3H, d, J=7.2 Hz), 1.35—1.41 (2H, m), 1.88—1.95 (3H, m), 2.00—2.10 (2H, m), 3.24 (1H, d, J=4.0 Hz), 3.44 (1H, d, J=14.0 Hz), 3.50 (1H, d, J=14.0 Hz), 3.48—3.53 (1H, m), 3.89 (1H, t, J=6.5 Hz), 4.26 (2H, q, J=7.1 Hz), 4.48 (1H, dd, J=5.1, 4.0 Hz). MS m/z: 373 (M^+), 328, 300, 271. HRMS Calcd for $C_{17}H_{27}NO_6S$ (M^+): 373.156. Found: 373.157. *Anal.* Calcd for $C_{17}H_{27}NO_6S$: C, 54.7; H, 7.3; N, 3.8. Found: C, 54.7; H, 7.3; N, 3.8. **15b**: a colorless oil. IR (neat): 3492, 1744, 1695, 1458 cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, s), 1.14 (3H, s), 1.28 (3H, t, J=7.1 Hz), 1.41 (3H, d, J=7.2 Hz), 1.30—1.50 (2H, m), 1.85—1.95 (3H, m), 2.05—2.06 (2H, m), 3.44 (1H, d, J=14.0 Hz), 3.47 (1H, d, J=14.0 Hz), 3.48—3.56 (1H, m), 3.58 (1H, d, J=10.6 Hz), 3.90 (1H, t, J=6.5 Hz), 4.17 (1H, dd, J=10.6, 5.0 Hz), 4.22 (2H, q, J=7.1 Hz). MS m/z: 373 (M^+), 328, 300, 271. HRMS Calcd for $C_{17}H_{27}NO_6S$ (M^+): 373.156. Found: 373.157.

Stereochemical Assignments of 5 A solution of **5** (744 mg, 1.70 mmol), iso-Pr_2EtN (2.1 ml, 12.1 mmol) and MOMCl (935 μl, 12.3 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 3 h and diluted with Et_2O and H_2O. The organic layer was washed with 2 M aqueous HCl, saturated aqueous $NaHCO_3$ and brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with hexane–AcOEt (4 : 1) gave (1*S*,2*R*,2′*S*)-*N*-[4′,4′,4′-trifluoro-3′-methoxymethoxy-2′-methyl-3′-(trifluoromethyl)butanoyl]bornane-10,2-sultam (**6**, 785 mg, 95.6%): colorless needles (hexane), mp 71.9—72.3 °C. IR (KBr): 1702 cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, s), 1.16 (3H, s), 1.22—1.56 (5H, m), 1.77—2.09 (5H, m), 3.48 (3H, s), 3.44 (1H, d, J=14.1 Hz), 3.54 (1H, d, J=14.1 Hz), 3.80—3.93 (2H, m), 5.07 (2H, m). ^{19}F-NMR δ: 69.17 (3F, dd, J=20.9, 10.4 Hz), 68.17 (3F, dd, J=20.9, 10.4 Hz). MS m/z: 481 (M^+), 480, 450, 421, 180, 87. A solution of **6** (359 mg, 746 μmol) in Et_2O (5 ml) was added to a suspension of $LiAlH_4$ (40 mg, 1.05 mmol) in Et_2O (2 ml) at 0 °C. After 18 h at room temperature, the reaction was quenched with successive additions of H_2O (45 μl), 15% aqueous NaOH (45 μl) and H_2O (135 μl) and the whole was filtered. The residue was washed with Et_2O, and the combined filtrates were dried and filtered. After evaporation of the solvent, chromatography of the residue with hexane–AcOEt (2 : 1) gave (*R*)-4,4,4-trifluoro-3-methoxymethoxy-2-methyl-3-(trifluoromethyl)butan-1-ol (**7**, 78 mg, 39.0%): $[\alpha]_D^{24}$ −8.4° (c=1.48, $CHCl_3$). This compound was identical with an authentic sample ($[\alpha]_D^{26}$ −7.8° (c=0.95, $CHCl_3$)) prepared according to the literature.[8]

Stereochemical Assignments of 12 A solution of the aldol **12d** (71 mg, 191 μmol) in THF (3 ml) was added to a suspension of $LiAlH_4$ (29 mg, 764 μmol) in THF (1 ml) at 0 °C. The reaction mixture was stirred at room temperature for 18 h, followed by the addition of H_2O (110 μl). Stirring was continued at room temperature for 15 min, then the mixture was filtered and the residue was washed with Et_2O. The combined filtrates were dried and filtered. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (1.8 ml) followed by the addition of pyridine (25 μl, 309 μmol) and benzoyl chloride (26 μl, 224 μmol). The mixture was stirred

at room temperature for 18 h, diluted with Et_2O, washed with 2 M aqueous HCl, saturated aqueous $NaHCO_3$ and brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with hexane–AcOEt (10:1) gave (2*R*,3*R*)-4,4,4-trifluoro-3-hydroxy-2-methylbutyl benzoate (**16d**, 17 mg, 33.8%): a colorless oil, $[\alpha]_D^{24}$ +18.4° (c=0.47, $CHCl_3$). IR (neat): 3457, 1704, 1602 cm^{-1}. ^{1}H-NMR δ: 1.23 (3H, dq, J=7.0, 1.3 Hz), 2.28—2.45 (1H, m), 2.90 (1H, d, J=6.0 Hz), 3.86—4.03 (1H, m), 4.41 (1H, dd, J=11.3, 4.1 Hz), 4.58 (1H, dd, J=11.3, 4.7 Hz), 7.40—7.65 (3H, m), 8.00—8.05 (2H, m). ^{19}F-NMR δ: 76.28 (d, J=7.0 Hz). MS m/z: 262 (M^+), 244, 193, 164, 123, 105, 77, 69. In the same manner, **12a** (200 mg, 541 mmol) was converted to (2*S*,3*R*)-4,4,4-trifluoro-3-hydroxy-2-methylbutyl benzoate (**16a**, 82 mg, 58.0%): a colorless oil, $[\alpha]_D^{23}$ +23.9° (c=0.44, $CHCl_3$). IR (neat): 3473, 1704, 1602 cm^{-1}. ^{1}H-NMR δ: 1.12 (3H, dq, J=7.0, 1.0 Hz), 2.38—2.50 (1H, m), 2.57 (1H, d, J=6.4 Hz), 4.08—4.24 (1H, m), 4.24 (1H, dd, J=11.1, 5.2 Hz), 4.43 (1H, dd, J=11.1, 9.0 Hz), 7.41—7.63 (3H, m), 8.01—8.06 (2H, m). ^{19}F-NMR δ: 76.33 (d, J=7.0 Hz). MS m/z: 262 (M^+), 244, 193, 164, 123, 105, 77, 69. A mixture of **12c** and **12a** (84:14, 293 mg, 794 μmol) was converted to a mixture of **16c** and **16a** (63 mg, 30.2%): a colorless oil, $[\alpha]_D^{24}$ −14.8° (c=0.41 $CHCl_3$). The stereochemistry of **20a**, **20c** and **20d** was determined by comparison with authentic samples prepared according to the literature.[4]

Stereochemical Assignments of 13 The aldol **13c** (107 mg, 229 μmol) was reduced with $LiAlH_4$ according to the procedure for the reduction of **6** to give (2*R*,3*S*)-4,4-difluoro-2-methyl-7-phenylheptane-1,3-diol (**17c**, 47 mg, 80.0%): a colorless oil, $[\alpha]_D^{25}$ −15.0° (c=0.99, $CHCl_3$). IR (neat): 3300, 1604 cm^{-1}. ^{1}H-NMR δ: 1.01 (3H, d, J=7.0 Hz), 1.63 (1H, t, J=5.1 Hz), 1.83—2.09 (5H, m), 2.35 (1H, d, J=6.6 Hz), 2.67 (2H, t, J=7.6 Hz), 3.68 (2H, t, J=5.4 Hz), 3.92—3.99 (1H, m), 7.17—7.20 (3H, m), 7.26—7.30 (2H, m). ^{19}F-NMR δ: 108.92—109.55 (1F, m), 110.56—11.19 (1F, m). MS m/z: 258 (M^+), 244, 181, 161, 147, 91, 77. In the same manner, the aldol **13d** (115 mg, 245 μmol) was converted to (2*R*,3*R*)-4,4-difluoro-2-methyl-7-phenylheptane-1,3-diol (**17d**, 27 mg, 43.2%): a colorless oil, $[\alpha]_D^{25}$ +1.0° (c=0.79, $CHCl_3$). IR (neat): 3300, 1603 cm^{-1}. ^{1}H-NMR δ: 1.07 (3H, d, J=7.1 Hz), 1.84—2.15 (6H, m), 2.68 (2H, t, J=7.6 Hz), 3.49 (1H, d, J=6.3 Hz), 3.61—3.70 (2H, m), 3.95 (1H, d, J=10.5 Hz), 7.17—7.20 (3H, m), 7.26—7.30 (2H, m). ^{19}F-NMR δ: 107.63—108.26 (1F, m), 111.67—111.80 (1F, m). MS m/z: 258 (M^+), 244, 181, 161, 147, 91, 77. The aldol **13a** (101 mg, 215 μmol) was converted to (2*S*,3*R*)-4,4-difluoro-2-methy-7-phenylheptane-1,3-diol (**17a**, 45 mg, 80.6%). These diols, **17a**, **21c** and **21d**, were identical with authentic samples prepared according to the literature.[4]

Stereochemical Assignments of 14 The aldol **14c** (93 mg, 230 μmol) was reduced with $LiAlH_4$ using the same procedure as for **13** to give crude (2*S*,3*R*)-3-methyl-1-phenylbutane-1,2,4-triol. A solution of the triol in pyridine (2 ml) was treated with Ac_2O (250 ml, 2.6 mmol) and 4-dimethylaminopyridine (1.5 mg) at room temperature. The reaction mixture was stirred at the same temperature for 18 h, poured into ice water and extracted with Et_2O. The combined extracts were washed with 2 M aqueous HCl, saturated aqueous $NaHCO_3$ and brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with hexane–AcOEt (6:1) gave the corresponding triacetate (46 mg, 62.6%): a colorless oil. IR (neat): 1737 cm^{-1}. ^{1}H-NMR δ: 1.00 (3H, d, J=7.0 Hz), 1.86 (3H, s), 2.03 (3H, s), 2.10 (3H, s), 2.13—2.28 (1H, m), 3.91 (2H, d, J=6.8 Hz), 5.39 (1H, dd, J=7.4, 3.5 Hz), 5.90 (1H, d, J=7.4 Hz), 7.30—7.40 (5H, m). MS m/z: 263 (M−59), 220, 202, 173, 107, 91, 77. A mixture of the triacetate (46 mg, 143 mmol) and 5% Pd–C (100 mg) in AcOH (1 ml) was stirred under H_2 (1 atm) at room temperature for 40 h. The Pd–C catalyst was filtered off and washed with AcOEt. The combined filtrates were washed with saturated aqueous $NaHCO_3$ and brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with hexane–AcOEt (10:1) gave (2*R*,3*R*)-2-methyl-4-phenylbutane-1,3-diyl diacetate (13 mg, 35.3%) which was dissolved in MeOH (1 ml) and then treated with anhydrous K_2CO_3 (34 mg, 246 μmol). The reaction mixture was stirred at room temperature for 1 h, then diluted with CH_2Cl_2, washed with H_2O and brine, dried and filtered. Following evaporation of the solvent, chromatography of the residue with hexane–AcOEt (1:1) afforded (2*R*,3*R*)-2-methyl-4-phenylbutane-1,3-diol (**18c**, 7.0 mg, 27.2%): a colorless oil, $[\alpha]_D^{25}$ +17.0° (c=0.65, $CHCl_3$). IR (neat): 3346, 1605 cm^{-1}. ^{1}H-NMR δ: 1.04 (3H, d, J=7.1 Hz), 1.79—1.96 (1H, m), 2.11 (1H, d, J=3.3 Hz), 2.25 (1H, t, J=5.3 Hz), 2.78 (2H, d, J=6.9 Hz), 3.74 (2H, t, J=5.3 Hz), 4.04—4.14 (1H, m), 7.21—7.38 (5H, m). MS m/z: 162 (M−18), 121, 103, 91, 77. In the same manner, the aldol **14d** (233 mg, 575 mmol) was converted to (2*R*,3*S*)-2-methyl-4-phenylbutane-1,3-diol (**18d**, 4.8 mg, 4.6% in four steps): a colorless oil, $[\alpha]_D^{25}$ −47.9° (c=0.24, $CHCl_3$). IR (neat): 3329, 1602 cm^{-1}. ^{1}H-NMR δ: 1.01 (3H, d, J=7.0 Hz), 1.76—1.86 (1H, m), 2.20 (1H, s), 2.64 (1H, dd, J=13.7, 9.5 Hz), 2.82 (1H, s), 3.00 (1H, dd, J=13.7, 3.3 Hz), 3.64—3.81 (3H, m), 7.20—7.38 (5H, m). MS m/z: 180 (M^+), 121, 103, 91, 77. The aldol **14a** (110 mg, 271 μmol) was converted to (2*S*,3*S*)-2-methyl-4-phenylbutane-1,3-diol (**18a**, 6.2 mg, 11.6% in four steps). These diols, **18a**, **18c** and **18d**, were identical with authentic samples prepared according to the literature.[4]

Stereochemical Assignments of 15 A solution of **15c** (104 mg, 280 μmol) in EtOH (2 ml) was added to a solution of NaH (60%, 58 mg, 1.4 mmol) in EtOH (2 ml) at 0 °C. After 30 min at 0 °C, the reaction mixture was poured into saturated aqueous NH_4Cl and extracted with Et_2O. The combined extracts were washed with brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with hexane–AcOEt (6:1) gave diethyl (2*S*,3*S*)-2-hydroxy-3-methylsuccinate (**19c**, 39 mg, 68.0%): a colorless oil, $[\alpha]_D^{24}$ −1.6° (c=0.63, Et_2O). IR (neat): 3350, 1737 cm^{-1}. ^{1}H-NMR δ: 1.17 (3H, d, J=7.2 Hz), 1.28 (3H, t, J=7.1 Hz), 1.31 (3H, t, J=7.1 Hz), 2.92 (1H, dq, J=7.2, 3.6 Hz), 3.05 (1H, d, J=5.4 Hz), 4.19 (2H, d, J=5.4 Hz), 4.28 (2H, q, J=7.1 Hz), 4.60 (1H, dd, J=5.4, 3.6 Hz). MS m/z: 204 (M^+), 131, 113, 85. In the same manner, the aldol **15d** (40 mg, 107 μmol) was converted to diethyl (2*R*,3*S*)-2-hydroxy-3-methylsuccinate (**19d**, 15 mg, 68.3%): a colorless oil, $[\alpha]_D^{24}$ +12.2° (c=0.63, Et_2O). IR (neat): 3400, 1737 cm^{-1}. ^{1}H-NMR δ: 1.25 (3H, t, J=7.2 Hz), 1.29 (3H, d, J=7.3 Hz), 1.30 (3H, t, J=7.2 Hz), 3.02 (1H, dq, J=7.3, 3.5 Hz), 3.15 (1H, d, J=6.4 Hz), 4.15 (2H, q, J=7.2 Hz), 4.20—4.33 (3H, m). MS m/z: 204 (M^+), 131, 113, 85. The aldols **15a** (50 mg, 134 μmol) and **15b** (5.2 mg, 13.9 μmol) were converted to the enantiomers of **19c** and **19d**, diethyl (2*R*,3*R*)-2-hydroxy-3-methylsuccinate (**19a**, 19 mg, 68.5%) and diethyl (2*S*,3*R*)-2-hydroxy-3-methylsuccinate (**19b**, 1.5 mg, 53%), respectively. These diesters, **19a—d**, were identical with authentic samples prepared according to the literature.[4]

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References

1) "Biomedical Aspects of Fluorine Chemistry," ed. by Filler R., Kobayashi Y., Kodansha Ltd. and Elsevier Biomedical Press, Tokyo and Amsterdam, 1982; Welch J. T., *Tetrahedron*, **43**, 3123—3197 (1987); Bravo P., Resnati G., *Tetrahedron: Asymm.*, **1**, 661—692 (1990); Welch J. T., Eswarakrishnan S., "Fluorine in Bioorganic Chemistry," John Wiley and Sons, Inc., New York, 1991; "Selective Fluorination in Organic and Bioorganic Chemistry," ed. by Welch J. T., American Chemical Society, Washington, 1991; "Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications," ed. by Filler R., Kobayashi Y., Yagupolskii L. M., Elsevier: Amsterdam, 1993; Resnati G., *Tetrahedron*, **49**, 9385—9445 (1993); Iseki K., Kobayashi Y., *Yuki Gosei Kagaku Kyokai Shi*, **52**, 40—48 (1994).
2) Arakawa S., Nito K., Seto J., *Mol. Cryst. Liq. Cryst.*, **204**, 15—25 (1991); Bömelburg J., Heppke G., Ranft A., *Z. Naturforsch*, 1127—1131 (1989); Buchecker R., Kelly S. M., Fünfschilling J., *Liquid Cryst.*, **8**, 217—227 (1990).
3) Seebach D., *Angew. Chem. Int. Ed. Engl.*, **29**, 1320—1367 (1990).
4) Iseki K., Oishi S., Taguchi T., Kobayashi Y., *Tetrahedron Lett.*, **34**, 8147—8150 (1993); Iseki K., Oishi S., Kobayashi Y., *Tetrahedron*, **52**, 71—84 (1996).
5) Our preliminary communication: Iseki K., Oishi S., Kobayashi Y., *Chem. Lett.*, **1994**, 1135—1138.
6) Oppolzer W., Blagg J., Rodriguez I., Walther E., *J. Am. Chem. Soc.*, **112**, 2767—2772 (1990).
7) Oppolzer W., Lienard P., *Tetrahedron Lett.*, **34**, 4321—4324 (1993).
8) Iseki K., Oishi S., Namba H., Taguchi T., Kobayashi Y., *Chem. Pharm. Bull.*, **43**, 1897—1901 (1995).
9) Calculations were performed with GAUSSIAN 92, Revision A: Frisch M. J., Trucks G. W., Head-Gordon M., Gill P. M. W., Wong M. W., Foresman J. B., Johnson B. G., Schlegel H. B., Robb M. A., Replogle E. S., Gomperts R., Andres J. L., Raghavachari K., Binkley J. S., Gonzalez C., Martin R. L., Fox D. J., Defrees D. J., Baker J., Stewart J. J. P., Pople J. A., Gaussian, Inc., Pittsburgh PA, 1992.