Chiral Acetals as Stereoinductors: Diastereoface Selective Alkylation of Dihydrobenzoxazine-Derived Amide Enolates

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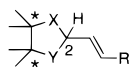
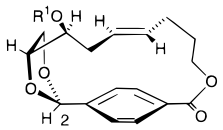
Novel dihydrobenzoxazine-derived acetals of type **3** have been developed for asymmetric C-alkylations of propionyl amide enolates. High stereoselectivities are obtained for amides **15** and **22** which are rationalized in terms of intramolecular metal chelate formation.

Introduction

Chiral acetals of type **1** have been frequently used as stereochemical inductors for additions to adjacent prostereogenic sp²-carbons.[1] However, in preparing these systems stereocontrol of C2 is a problem unless this carbon is chosen to be a chirotopic nonstereogenic center. The necessity to separate C2-anomers was also a main drawback in using chiral ansa acetals such as **2**, which proved quite efficient as stereoinductors for the epoxidation or dihydroxylation of the olefinic double bond.[2]



1 (X, Y = O, NR')



2

In this paper we report on a different combination of an acetal moiety with a rigid benzenoid template to achieve highly diastereoface-controlled sp² additions. Our objective was to construct a rigid and conformationally defined amide system by bringing the aminal nitrogen into resonance interaction with the benzenoid ring. In consequence, *N*-acylated dihydrobenzoxazines such as **3** were envisaged that could bear stereogenic centers at C-2, C-4 and most simply, in the appendage at C-2. These compounds to a certain degree resemble the chiral auxiliaries that have been developed for enolate alkylations (and related reactions) over the past 20 years by several research groups. These efforts were pioneered by Meyers,[3] Evans,[4] and Oppolzer[5] and were, more recently, continued by Myers,[6] Masamune,[7] Seebach,[8] and others.[9] Except for Myers' compounds, the chiral information of these auxiliaries is incorporated in a five-membered heterocyclic ring, and the N−H group is part of a lactam, oxazolidinone, or sultam structure so that an imide is formed on *N*-acylation. Imide enolates **4** and **5** are particularly noteworthy applications of this concept.

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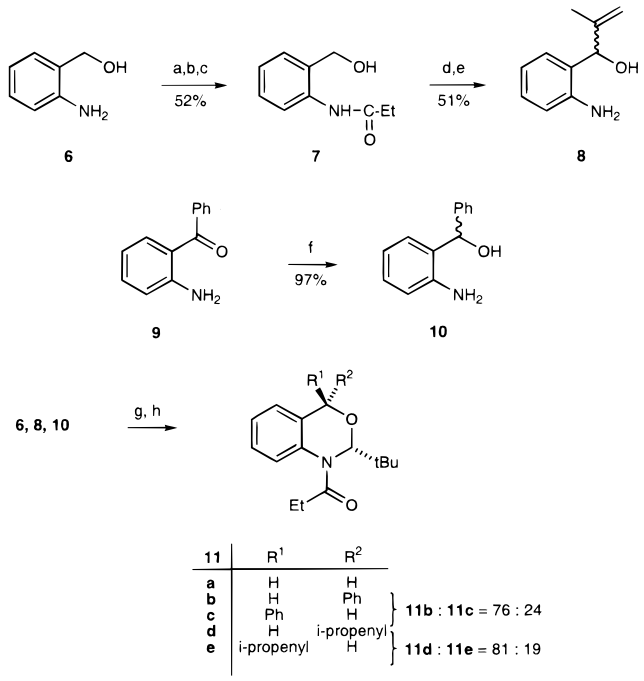
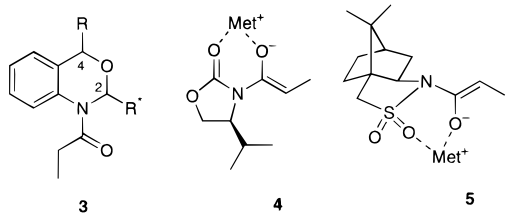
Scheme 1[a]



11	R^1	R^2	
a	H	H	
b	H	Ph	11b : 11c = 76 : 24
c	Ph	H	
d	H	i-propenyl	11d : 11e = 81 : 19
e	i-propenyl	H	

[a] Reagents and conditions: (a) TBDMSCl, DMF, NEt_3, DMAP, 22 °C, 12 h; (b) propionyl chloride, pyridine, DMAP, 22 °C, 12 h; (c) 60% AcOH, 22 °C, 12 h; (d) $COCl)_2$, DMSO, $NiPr_2Et$, -60 °C, then isopropenyl magnesium bromide; (e) LiOH, MeOH, 22 °C, 3d; (f) $LiAlH_4$, THF, 0 °C, 1 h; (g) pivaldehyde, H_2SO_4, CH_2Cl_2, 22 °C, 1 h; (h) MeC(OTMS)═NTMS, CH_2Cl_2, 22 °C, 1 h, then propionyl chloride, 22 °C, 12 h; **11a**, 63%, **11b/c**, 52%; **11d/e**, 45%.

Although it was not our main intention to enlarge this collection of rather mature and well-established chiral auxiliaries, it appeared an attractive idea to test our compounds **3** in comparison with the abovementioned examples.

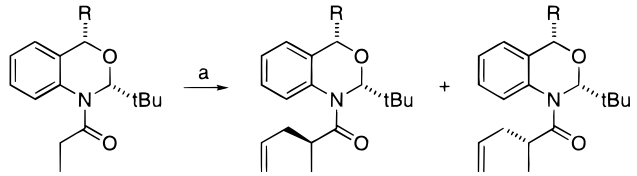


3 **4** **5**

Results and Discussion

Derivatives with stereogenic centers at C2 and C4 were addressed first. Amino alcohol **6** was converted into a racemic mixture of the isopropenyl derivative **8**. The second model system was generated by reduction of commercially available 2-aminobenzophenone (**9**) to racemic amino alcohol **10**. With pivaldehyde all three amino alcohols, **6**, **8**, and **10** were converted into the acetals, which were *N*-silylated and then acylated with propionyl chloride to form the dihydrobenzoxazines **11a**−**e** as shown in Scheme 1. The diastereomers **11b**/**c** (ratio 76:24) and **11d**/**e** (ratio 81:19) were separated by chromatography. The relative configurations of **11b** and **11e** were determined by crystal structure analysis (Figures S1, S2). Remarkably, the dihydrobenzoxazine ring shows a boat conformation due to the amide moiety which forces the C2-tBu residue into a pseudoaxial location by its allylic 1,3-strain effect.[10] Consequently, the C4-substituent adopts a pseudoequatorial position in **11b** and a pseudoaxial one in **11e**. To a certain degree the geometry of our dihydrobenzoxazines is similar to the axially twisted *N*-aryl amides described by Curran.[10c] Both in Curran's and in our auxiliaries the acyl moiety and the aryl ring at the nitrogen are axially twisted. In Curran's systems it is the aryl group that is out of plane and in our work it is both the aryl ring and the MeCH═COMet group.

Scheme 2[a]



11a,b,d **12a-c** **13a-c**

12,13	R	12:13	yield 12 + 13 (%)
a	H	2 : 1	86
b	Ph	4 : 1	85
c	i-propenyl	4 : 1	75

[a] Reagents and conditions: (a) THF, *p*-TsOH, 22 °C, 15 min; (b) MeC(OTMS)═NTMS, CH_2Cl_2, 22 °C, 1 h, then propionyl chloride, 22 °C, 1 h.

Deprotonation of **11a,b,d** and allylation of the resulting enolates proceeded with moderate stereoselectivity (Scheme 2). The main diastereomers were tentatively assigned to have structures **12a**−**c** in analogy with the results obtained later from systems **15** and **22**.

In view of the unsatisfactory stereocontrol observed for amides **11**, we decided to transfer the stereogenic master center from C4 into the side chain. Hence, amino alcohol **6** was treated with the known OTBDPS-lactic aldehyde **14**[11] to form an anomeric mixture of the acetals, which were immediately *N*-acylated to furnish the amides **15a**/**b** in a ratio of 84:16 (Scheme 3).[12]

After chromatographic separation the amides **15a** and **15b** were deprotonated with KHMDS and alkylated with four different alkyl halides (Scheme 4, Table 1). The diastereomers **16**/**17** were obtained in diastereomeric ratios of ≥85:15. For the corresponding pair **18**/**19**, the diastereomeric ratio was demonstrated similar. The configuration of **16d** was determined by X-ray single-crystal diffraction (Figure S3). Allyl adducts **16a**, **17a**, and **18a** were used to demonstrate the facile removal of the dihydrobenzoxazine residue: LAH reduction of **16a** gave (*R*)-2-methyl-pentene-1-ol (***R*-20**),[13] whereas the corresponding reduction of **17a** and **18a** delivered (***S*-20**).

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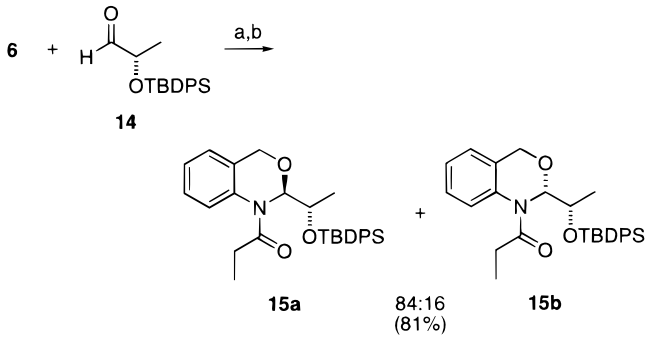
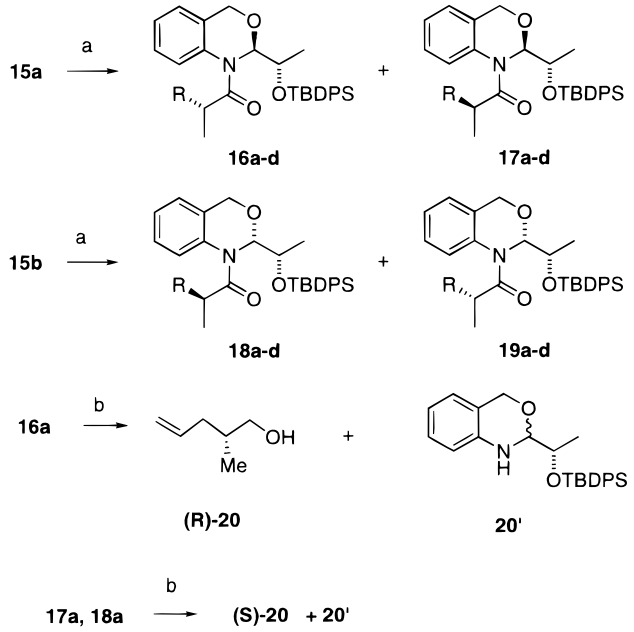
Scheme 3[a]



[a] Reagents and conditions: (a) THF, *p*-TsOH, 22 °C, 15 min; (b) MeC(OTMS)=NTMS, CH_2Cl_2, 22 °C, 1 h, then propionyl chloride, 22 °C, 1 h.

Scheme 4[a]



[a] Reagents and conditions: (a) $KN(SiMe_3)_2$, THF, −78 °C, 1 h, then R-X, to 22 °C, 14 h. (b) $LiAlH_4$, Et_2O, 0 °C, 1 h.

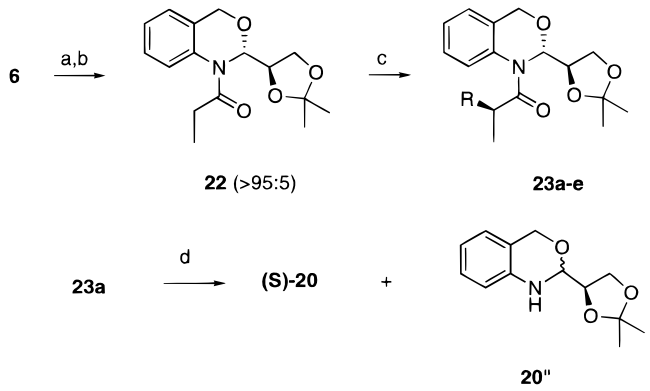
Table 1. Alkylation of 15a/15b with Various Alkyl Halides

products **16**/**17** and **18**/**19**	alkyl halide	ratio of **16**:**17**[a] (**18**/**19**)[a]	% yield **16**[b] (**18**)[b]
a	allyl bromide	93:7 (94:6)	74 (76)
b	ethyl bromide	85:15 (93:7)	73 (69)
c	*n*-propyl iodide	95:5 (93:7)	70 (55)
d	5-bromo-1-pentene	96:4 (93:7)	58 (53)

[a] Determined by HPLC. [b] Yield of pure diastereomer **16**/**18a**−**d** after chromatographic separation.

In both cases the optical purities of the alcohols were determined by Mosher analysis[14] to be >98%. These results also corroborate the initial configurational assignments and demonstrate that the chiral induction is mainly exerted by the acetal center at C2, to the effect that the (*S*) configuration at C2 induces *si*-face attack at the enolate carbon, and vice versa. This means that the enolate alkylation follows a *lk*-topicity.[15] Unfortunately, the benzoxazine template was epimerized to amine **20′** in course of the reduction, which greatly detracts from its applicability as a chiral auxiliary. Still, amine **20′** can be recycled into the acylation step.

Scheme 5[a]



[a] Reagents and conditions: (a) **21**, THF, *p*-TsOH, 22 °C, 15 min; (b) MeC(OTMS)=NTMS, CH_2Cl_2, 22 °C, 1 h, then propionyl chloride, 22 °C, 1 h; (c) $KN(SiMe_3)_2$, THF, 20% (v/v) of additive, −78 °C, 1 h, then R−X, −78 to 22 °C, 14 h; (d) $LiAlH_4$, Et_2O, 0 °C, 1 h.

Table 2. Diastereoselective Alkylation of Amide 22

product **23**	R−X	additive	% yield[a]	dr[b]
a	allyl bromide		81	98:2
b	ethyl bromide	HMPA	22 (35)	>99:1
b	ethyl iodide	HMPA	76	99:1
b	ethyl iodide		37 (8)	99:1
c	propyl iodide	HMPA	76 (8)	99:1
c	propyl iodide		54	99:1
d	benzyl bromide	HMPA	83	98:2
d	benzyl bromide	DMPU	56	98:2
d	benzyl bromide		40	96:4
e	pentyl bromide	HMPA	46 (37)	98:2

[a] In parentheses are the % reisolated starting material. [b] (2*S*,2′*R*,4″*R*):(2*R*,2′*R*,4″*R*), determined by HPLC.

Despite these encouraging results, the overall stereocontrol exerted by system **15** was still unsatisfactory, particularly due to the low selectivity in the acetal forming step (84:16 mixture of **15a**/**b**). To find a system with higher stereocontrol, amino alcohol **6** was ketalized with (*R*)-2,3-*O*-isopropylidene glyceraldehyde (**21**) in place of lactaldehyde **14** (Scheme 5). Acetal amide **22** was formed with >95:5 diastereoselectivity, the deprotonation and enolate alkylation of which furnished diastereomer **23a**−**e** with high selectivities (≥96:4, Table 2). The configuration of the benzyl adduct **23d** was determined by single-crystal diffraction (Figure S4). The removal of the auxiliary from the allyl adduct **23a** was performed as described for **16a**/**17a**/**18a** to give enantiopure (*S*)-**20** (>99% ee according to Mosher analysis). In analogy to amine **20′,** now amine **20″** was recovered as an epimeric mixture. In this case this is no serious drawback, as only one amide diastereomer (**22**) is from **20″** on reacylation.

Remarkably, addition of HMPA as a decomplexing agent increased the yield of the alkylation without affecting the stereoselectivity (Table 2).

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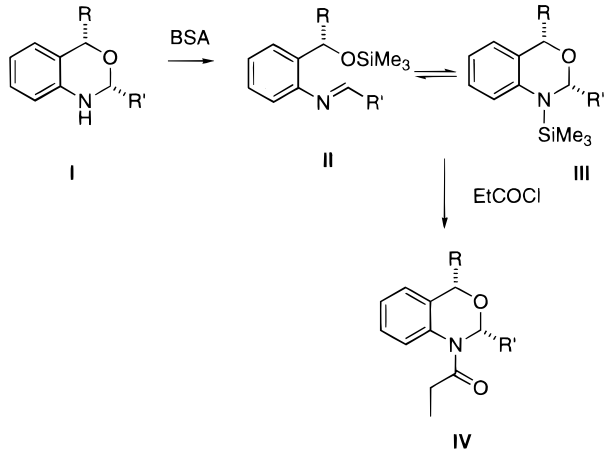
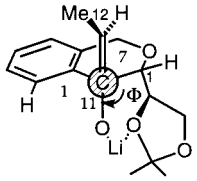
Scheme 6



Discussion

The central question is how chiral information is transferred with the observed *lk*-topicity from the stereogenic center in the C2-appendage to the diastereofaces of the enolate carbon. The first step in this relay is the stereochemical course of the acetal formation. Originally the *N*,*O*-acetals **I** are formed as 1:1 epimeric mixtures, and only in the course of the acylation process is the diastereomeric ratio gradually shifted toward **11b**, **11d**, **15a**, and **22**, respectively. This *N*-acylation obviously occurs via an equilibrium of acyclic (**II**) and cyclic (**III**) nonacylated *O*-silylated intermediates (Scheme 6), and from this equilibrium the most stable amide diastereomer (**IV**) is formed with the highest rate.

The amide enolates could not be trapped with TMSCl, as the resulting silyl enol ethers were too unstable to be isolated. However the enolate geometry may be safely assumed to be (*Z*), in accordance with literature precedence.[16] A crucial issue was to determine the ground state conformation of the metalated dihydrobenzoxazine propionamides, particularly with respect to the rotational barrier around the former CN amide bond. Recent results by Streitweiser indicated a very low barrier (<10 kcal/mol).[17] Direct measurements were unsuccessful in our case. Therefore, semiempirical calculations using MOPAC[18] and the semiempirical Hamiltonian PM3[19] were performed to analyze the energy potential for rotations around the (exocyclic) C−N bond of the lithiated[20] propionamide **24** (Figure 1). The dihedral angle ϕ (Figure 1) is set equal to 0 for a conformation with the enolate side chain coplanar with the benzoxazine ring and the OLi syn to C2. Starting from an unrestrained conformation an energy profile was calculated by restricting ϕ to fixed values (ϕ = 0−360°) in steps of 10° and allowing the rest of the molecule to be minimized. Energies of the resulting minima were recorded. Figure 1 shows a graph



24 (note that ϕ has a negative sign)

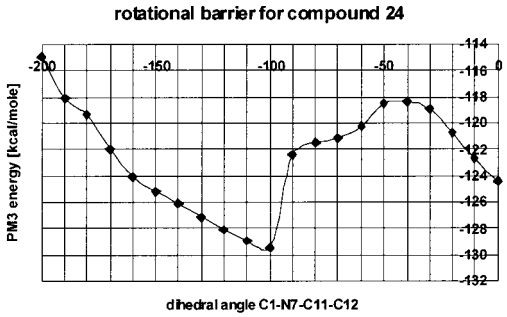


Figure 1. Calculated potential curve[18,19] of amide enolate **24** for varying torsion angles (ϕ).

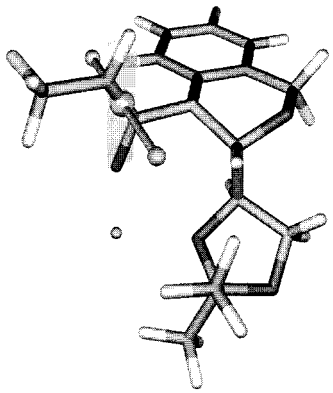


Figure 2. Perspective view of **24** to show the accessibility of the enolate *re*-face.

of the PM3 potential curve thus obtained. The sudden decline of energy in the range between ϕ = −90 and −100° is caused by an inversion of configuration at N. The local minimum is found at ϕ = −100°, which means that the plane of the enolate approximately bisects the oxazine ring. Further rotation from ϕ = −100° toward −200° results in a strong increase in energy due to interactions with the ortho-H combined with the loss of chelate stabilization. The low-energy conformation is shown in projection (Figure 2), which shows that the overall boat conformation of the parent amide has roughly been maintained, although the allylic 1,3-strain around the CN bond is no longer existent. The ortho-H of the benzenoid ring shields the *si*-face of the enolate carbon quite efficiently, so that the attack of the electrophile is directed to the comparatively unhindered *re*-face. The varying degree of diastereofacial selection for amides **11**, **15**, and **22** has then to be attributed to the ability of the C2-residue for chelate formation with the enolate-OK.[21] Thus, the increase of the stereoselectivity in the sequence **22** > **15** > **11** appears reasonable, although the bulkiness of the C2-residues is in opposite order. Remarkably, the presence of HMPA does not interfere with this chelation. Quite consistently, analogous calculations

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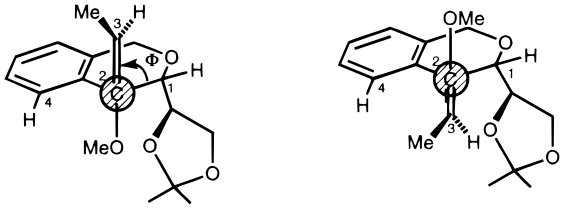
(18) Stewart, J. J. P.; MOPAC: A General Molecular Orbital Package *Quantum Chem. Prog. Exch.* **1990**, 10, 86.

(19) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 210−220. Anders, E.; Koch, R.; Freunscht, P. *Comput. Chem.* **1993**, *14*, 1301−1312.

(20) The experiments were carried out with the potassium enolate; however, potassium was beyond the scope of our calcalutions. Therefore, the lithium enolate was taken as a model system.

for the lithium enolate of **11a** revealed a very low barrier of rotation around the exocyclic N−C bond; two minima were found for dihedral angles of 90° and −100° with nearly identical energy levels. Similarly, calculations performed on enol methyl ether **25** which corresponds to **24** except for chelate formation revealed two energetically similar bisectic ground state conformations **25A** and **25B** (corresponding to dihedral angles of −100° and 95°).

In conclusion, we have shown that in systems such as **22** an almost complete chirality transfer is achieved from an exocyclic sp^3 reference center to an amide enolate sp^2-carbon via a chiral cyclic *N*,*O*-acetal attached to a rigid benzenoid template. This chirality transfer proceeds in a relay which first implies stereoselective acetal formation in favor of an anti-arrangement of the C2- and C5-oxygens and then enolate formation of an enolate whose ground-state conformation is determined by metal chelate formation to C5−O. Research is underway in our laboratory to test a variety of α-chiral aldehydes for ketal formation with amino alcohol **6** in order to increase the applicability of the method.



25A **25B**

Experimental Section

All reaction with air- and moisture-sensitive compounds were performed under an argon atmosphere. Reaction flasks were flame-dried under a stream of argon. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride. Potassium hexamethyldisilazide (KHDMS) was used as a 15% solution in toluene. Preparative column chromatography was performed on silica gel Merck 60, 230−400 mesh. Unless noted otherwise, ^{1}H and ^{13}C NMR spectra were recorded at 270 or 500 MHz in $CDCl_3$. HPLC was performed on Nucleosil 50-5 from Macherey-Nagel. Optical rotations were determined in $CHCl_3$ at 589 nm at 25 °C.

(1″*S*,2′*S*)- and (1″*S*,2′*R*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-propan-1-one (15a/15b) (1*S*,*RS*)-1-(2′,4′-Dihydro-1′H-benzo[*d*][1′,3′]oxazin-2′-yl)-*tert*-butyldimethylsiloxyethanol. 2-Aminobenzyl alcohol (**6**) (13.9 g, 112.7 mmol) in dry THF (150 mL) was treated with *p*-toluenesulfonic acid (*p*-TsOH) (536 mg, 2.82 mmol). The solution was stirred at room temperature and aldehyde **14** (32 g, 102.4 mmol) in dry THF (100 mL) was added. The mixture was concentrated under reduced pressure and purified by column chromatography (ethyl acetate/hexane v/v 1/10) to give the *N*,*O*-acetal (37.5 g, 87%) as a colorless oil (1:1 mixture of diastereomers). ^{1}H NMR: δ 1.16 (s, 9 + 9H), 1.24 (d + d, J = 6 Hz, 3 + 3H), 4.11 (mc, 1H), 4.21 (mc, 1H), 4.43 (mc, 1H), 4.48 (mc, 1H), 4.50 (mc, 1H), 4.67 (mc, 1H), 4.75−5.0 (m, 2 AB systems, 2 + 2H), 6.51 (mc, 1H), 6.71 (mc, 1H), 6.88 (mc, 1 + 1H), 6.92 (mc, 1 + 1H), 7.11 (mc, 1 + 1H), 7.37−7.53 (m, 6 + 6H), 7.69−7.87 (m, 4 + 4H). ^{13}C NMR: δ 16.58, 19.21, 19.31, 19.55, 27.02, 36.53, 67.39, 69.98, 71.45, 85.07, 87.33, 115.84, 116.54, 118.52, 118.97, 121.19, 121.73, 124.65, 127.29, 127.37, 127.59, 127.64, 127.67, 129.75, 133.43, 133.68, 133.79, 135.71, 135.79, 135.89, 141.77, 142.21. HRMS (EI, 80 eV, 100 °C): *m*/*e* calcd for $C_{26}H_{31}NO_2Si$ 417.21241, found 417.21250. Anal. Calcd for $C_{26}H_{31}NO_2Si$: C, 74.78; H, 7.48; N, 3.35. Found: C, 74.52; H, 7.63; N, 3.50.

N,*O*-Bis(trimethylsilyl)acetamide (0.35 mL, 1.44 mmol) was added at 25 °C to the above *N*,*O*-acetal (1.0 g, 2.39 mmol) in dry dichloromethane (5 mL). The solution was stirred for 1 h and then cooled to −78 °C, and propionyl chloride (0.25 mL, 2.87 mmol) was added dropwise. The reaction was warmed to 25 °C overnight. The reaction mixture was filtered, evaporated under reduced pressure, and purified by chromatography (ethyl acetate/hexane 1:5). The diastereomers were separated by HPLC (diisopropyl ether/hexane 3:97) to give **15a** (0.89 g, 78%) and **15b** (0.17 g, 17%) as viscous colorless oils. **15a**: ^{1}H NMR: δ 0.96 (s, 9H), 1.05 (mc, 3H), 1.22 (mc, 3H), 2.69 (mc (br), 2H), 3.78 (mc, 1H), 4.56 (mc, 2H), 5.74 (s, br, 1H), 6.95 (mc, 1H), 7.05−7.57 (m, 13H). ^{1}H NMR (DMSO-d_6, 120 °C, 500 MHz): δ 0.995 (s, 9H), 0.98 (d, J = 6.25 Hz, 3H), 1.07 (t, J = 7.5 Hz, 3H), 2.45 (mc, 1H), 2.63 (mc, 1H), 3.88 (mc, 1H), 4.565 (mc, AB system, 2H), 5.76 (d, J = 7.5 Hz, 1H), 7.11 (mc, 1H), 7.50 (mc, 1H), 7.28 (mc, 1H), 7.385 (mc, 2H), 7.31−7.42 (m, 5H), 7.46 (mc, 2H), 7.545 (mc, 2H). HRMS (EI, 80 eV, 150 °C): *m*/*e* calcd for $C_{28}H_{32}NO_3Si$ = M − CH_3 458.21515, found 458.21502. **15b**: ^{1}H NMR: δ 1.02 (s, 9H), 1.04 (d, 3H), 1.13 (t, J = 7.5 Hz, 3H), 2.49 (mc, 1H), 2.50 (mc, 1H), 3.86 (mc, 1H), 4.21−4.53 (m, AB system, 2H), 5.82 (s, br, 1H), 6.81 (mc, 1H), 7.00−7.19 (m, 3H), 7.24−7.44 (m, 6H), 7.57 (mc, 2H), 7.66 (mc, 2H). ^{1}H NMR (DMSO-d_6, 120 °C, 500 MHz): δ 0.94 (d, J = 6 Hz, 3H), 0.99 (s, 9H), 1.02 (t, J = 7 Hz, 3H), 2.33 (mc, 1H), 2.58 (mc, 1H), 3.78 (mc, 1H), 4.40−4.51 (m, AB system, 2H), 5.79 (d, J = 7 Hz, 1H)), 7.02 (mc, 1H), 7.12 (mc, 1H), 7.19−7.26 (m, 2H), 7.13−7.43 (m, 6H), 7.55 (mc, 2H), 7.61 (mc, 2H). Anal. Calcd for $C_{29}H_{35}NO_3Si$: C, 73.53; H, 7.44; N, 2.96. Found: C, 73.81; H, 7.20; N, 3.05.

Enolate Alkylation. To a solution of KHMDS (15% solution in toluene, 2,39 mL, 1.58 mmol) in THF (3 mL) was added a solution of the amide (0.5 g, 1.06 mmol) **15a** or **15b** in THF (5 mL) at −100 °C and the alkyl halide ((8.48 mmol), allyl bromide (0,72 mL), ethyl bromide (0.63 mL), propyl iodide (0.83 mL), or 5-bromo-1-pentene (1.0 mL) was added. The reaction mixture was warmed to 25 °C overnight, quenched with saturated aqueous NH_4Cl (5 mL) and water (50 mL), and extracted with ether (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated at reduced pressure and purified by chromatography (ethyl acetate/hexane 1:5). The diastereomers were separated by HPLC (ethyl acetate/hexane 3:97) to give **16**/**17** or **18**/**19**. Only the main diastereomers in both series (**16** and **18**) were fully characterized.

(1″*S*,2*R*,2′*S*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methyl-pent-4-en-1-one (16a). Preparative HPLC (ethyl acetate/hexane: 3/97) gave **16a** (390 mg, 73%) as colorless crystals. ^{1}H NMR: δ 0.95 (mc, 12H), 1.30 (d, J = 3 Hz, 3H), 2.00 (s, (br), 1H), 2.32 (s, br, 1H), 3.10 (mc, 1H), 3.85 (mc, 1H), 4.53 (mc, 2H), 4.73−5.24 (s, br, 2H), 5.45 (s, br, 1H), 6.03 (s, br, 1H), 6.64−7,83 (m, 14H). ^{13}C NMR: δ 17.61 (br), 18.99, 19.49 (br), 26.74, 36.69, 38.68 (br), 63.44 (br), 69.26 (br), 84.35 (br), 116.73, 124.79 (br), 125.33 (br), 127.28, 129.36, 134.05 (br), 135.73, 175.92. $[\alpha]^{25}_D$: −123.7° (c = 0.83, $CHCl_3$). Anal. Calcd for $C_{32}H_{39}NO_3Si$: C, 74.81; H, 7.65; N, 2.73. Found: C, 74.70; H, 7.62; N, 2.49.

(1″*S*,2*R*,2′*S*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylbutan-1-one (16b). Preparative HPLC (ethyl acetate/hexane 4:96) gave **16b** (400 mg, 74%) as a viscous colorless oil. ^{1}H NMR: δ 0.5−1.15 (m, 6H), 0.95 (s, 9H), 1.15 (mc, br, 1H), 1.61 (mc, br, 1H), 2.95 (mc, 1H), 3.85 (mc, 1H), 4.53 (mc, 2H), 6.10 (s, br, 1H), 6.65−7.73 (m, 14H). ^{13}C NMR: δ 11.49, 17.60 (br), 18.95, 19.50 (br), 26.52, 26.70, 27.66 (br), 38.19 (br), 63.25 (br), 68.90 (br), 84.11 (br), 124.80 (br), 125.23 (br), 125.47 (br), 127.25, 129.33, 133.99, 134.74, 135.69, 176.71. HRMS (EI, 80 eV, 150 °C): *m*/*e* calcd for $C_{30}H_{36}NO_3Si$ = M − CH_3 486.24645, found 486.24689.

(21) Chelate-induced chirality transfer in the alkylation of potassium amide enolates in the presence of HMPA has also been observed by Evans (e.g., Evans, D. A.; Dow, R. L.; Shih, T. L.; Takacs, J. M.; Zahler, R. *J. Am. Chem. Soc.* **1990**, *112*, 5290−5313). Potassium-induced Birch reduction−alkylation sequences were reported by Schultz (e.g., Schultz, A. G.; Wang, A. *J. Am. Chem. Soc.* **1999**, *120*, 8259−8260 and earlier lit.)

$[\alpha]^{25}_D$: −128 °C (c = 1.1, $CHCl_3$). Anal. Calcd for $C_{31}H_{39}NO_3Si$: C, 74.21; H, 7.89; N, 2.79. Found: C, 74.00; H, 8.13; N, 2.54.

(1″*S*,2*R*,2′*S*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*] [1′,3′]oxazin-1′-yl]-2-methylpentan-1-one (16c). Preparative HPLC (ethyl acetate/hexane 3:97) gave **16c** (380 mg, 70%) as a viscous colorless oil. ^{1}H NMR: δ 0.61 (s, br, 3H), 0.77−1.8 (m, 7H), 1.00 (s, 9H), 1.27 (d, J = 3 Hz, 3H), 3.03 (mc, 1H), 3.85 (mc, 1H), 4.56 (mc, 2H), 6.09 (s, br, 1H), 6.83−7.68 (m, 14H). ^{13}C NMR: δ 13.65 (br), 17.96 (br), 18.94, 19.33 (br), 20.10 (br), 26.67, 36.02 (br), 37.06 (br), 63. 48 (br), 69.10 (br), 83.99 (br), 125.34 (br), 127.23, 129.30, 133.99 (br), 135.68. HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{31}H_{38}NO_3Si$ = M − CH_3 500.26210, found 500.26283. $[\alpha]^{25}_D$: −127° (c = 1.34, $CHCl_3$). Anal. Calcd for $C_{32}H_{41}NO_3Si$: C, 74.52; H, 8.01; N, 2.72. Found: C, 74.34; H, 8.25; N, 2.54.

(1″*S*,2*R*,2′*S*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxy-ethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylhept-6-en-1-one (16d). Preparative HPLC (ethyl acetate/hexane 3:97) gave **16d** (220 mg, 38%) as viscous colorless oil. ^{1}H NMR: δ 0.77−1.44 (m, 4H), 0.95 (s, 9H), 1.29 (d, J = 3 Hz, 3H), 1.43−2.27 (m, br signals, 4H), 3.01 (s, br, 1H), 3.83 (mc, 1H), 4.51 (mc, 2H), 4.85 (mc, 2H), 5.71 (s, very br, 1H), 6.14 (s, br, 1H), 6.83−7.80 (m, 14H). ^{13}C NMR: δ 18.14 (br), 19.02 (q), 19.48 (br), 26.10 (−CH_2−) (br), 26.75, 33.22 (−CH_2−) (br), 34.35 (−CH_2−) (br), 36.03 (br), 63.45 (−CH_2−) (br), 69.00 (br), 84.00 (br), 114.14 (−CH_2−), 125.41 (br), 127.29, 129.37, 135.68, 135.76, 138.28, 176.83 (q) (br). HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{33}H_{40}NO_3Si$ = M − CH_3 526.27775, found 526.27752). $[\alpha]^{25}_D$: −123.6° (c = 0.6, $CHCl_3$). Anal. Calcd for $C_{34}H_{43}NO_3Si$: C, 75.37; H, 8.00; N, 2.59. Found: C, 75.43; H, 7.78; N 2.67.

(1″*S*,2*S*,2′*R*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylpent-4-en-1-one (18a). Preparative HPLC (diisopropyl ether/hexane 3:97) gave **18a** (410 mg, 76%) as a viscous colorless oil. ^{1}H NMR: δ 1.00 (s, 9H), 1.24 (d + d, 3 + 3H), 2.02 (s, br, 1H), 2.33 (s, br, 1H), 3.03 (s, br, 1H), 3.88 (mc, 1H), 4.23−4−53 (m, AB system, low field part br, 2H), 4.88 (mc, br, 2H), 5.48 (s, br, 1H), 5.91 (s, br, 1H), 6.71−7,42 (m, 10H), 7.58 (mc, 2H), 7.67 (mc, 2H). ^{13}C NMR: δ 19.12, 26.75, 29.54, 31.76, 36.36, 38.80, 62.97, 69.08, 84.71, 116.61, 124.86, 125.29, 127.24, 127.30, 129.29, 133.73, 134.36, 135.20, 135.68, 137.71, 175.74. HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{28}H_{30}NO_3Si$ = M − C_4H_9 456.19949, found 456.19950. Anal. Calcd for $C_{32}H_{39}NO_3Si$: C, 74.81; H, 7.65; N, 2.73. Found: C, 75.43; H, 7.78; N, 2.67.

(1″*S*,2*S*,2′*R*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylbutan-1-one (18b). Preparative HPLC (diisopropyl ether/hexane 3:97) gave **18b** (320 mg, 60%) as a viscous colorless oil. ^{1}H NMR: δ 0.71 (s, 3H), 1.03 (s, 12H), 1.21 (d, J = 7.5 Hz, 3H), 1.32 (s, br, 1H), 1.64 (s, br, 1H), 2.89 (mc, br, 1H), 3.83 (mc, 1H, 4.36 (m, AB system, low field part br, 1H), 5.95 (s, br, 1H), 6.74−7.47 (m, 10H), 7.59 (mc, 2H), 7.67 (mc, 2H). ^{13}C NMR: δ 11.57, 17.86, 19.17, 26.81, 27.98, 29.59, 38.04, 62.86, 68.94 (br), 84.60 (br), 124.81 (br), 125.24 (br), 127.05 (br), 127.30, 127.36, 129.35, 133.82, 134.43, 135.77, 176.81. HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{27}H_{30}NO_3Si$ = M − C_4H_9 444.19950, found 444.19948. Anal. Calcd for $C_{31}H_{39}NO_3Si$: C, 74.21; H, 7.89; N, 2.79. Found: C, 74.12; H, 8.01; N, 2.85.

(1″*S*,2*S*,2′*R*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxyethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylpentan-1-one (18c). Preparative HPLC (diisopropyl ether/hexane 3:97) gave **18c** (300 mg, 55%) as a viscous colorless oil. ^{1}H NMR: δ 0.65 (s, br, 3H), 1.02 (s, 12H), 1.23 (d, J = 7.5 Hz, 3H), 0.82−1.35 (m, br, 3H), 1.71 (s, br, 1H), 2.98 (s, br, 1H), 3.83 (mc, 1H), 4.36 (mc, AB system, low field part br, 2H), 5.98 (s, br, 1H), 6.73−7.48 (m, 10H), 7.58 (mc, 2H), 7.68 (mc, 2H). ^{13}C NMR: δ 13.67, 18.14, 19.13, 20.15, 26.76, 35.91 (br), 37.22, 62.86 (br), 68.94 (br), 84.44 br, 124.81, 125.23, 127.02, 127.25, 133.77, 134.82, 135.72, 176.80. HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{28}H_{32}NO_3Si$ = M − C_4H_9 458.21515, found 458.21502. Anal. Calcd for $C_{32}H_{41}NO_3Si$: C, 74.52; H, 8.01; N, 2.72. Found: C, 74.61; H, 7.73; N, 2.44.

(1″*S*,2*S*,2′*R*)-1-[2′-(1″-*tert*-Butyldiphenylsiloxethyl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylhept-6-en-1-one (18d). Preparative HPLC (diisopropyl ether/hexane 3:97) gave **18d** (120 mg, 21%) as a viscous colorless oil. ^{1}H NMR: δ 0.71−1,39 (m, br, 3H), 1.00 (s, 12H), 1.23 (d, J = 3 Hz, 3H), 1.50−1.97 (m, br, 3H), 2.97 (s, br), 3.80 (mc, 1H), 4.36 (mc, AB system, low field part br, 2H), 4.83 (mc, br, 2H), 5.62 (s, br, 1H), 5.97 (s, br, 1H), 6.70−7.45 (m, 10H), 7.56 (mc, 2H), 7.65 (mc, 2H)). ^{13}C NMR: δ 18.24, 19.22, 26.20 (−CH_2−) (br), 26.84, 29.65 (−CH_2−), 33.79 (−CH_2−), 34.50 (br), 36.04 (q), 62.95 (−CH_2−) (br), 69.07 (br), 84.49 (br), 114.47 (−CH_2−), 124.94 (br), 125.35, 127.34, 127.40, 129.39, 133.89 (q), 134.51 (q), 135.83, 176.72 (q) (br). HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{30}H_{34}NO_3Si$ = M − C_4H_9 484.23080, found 484.23067. Anal. Calcd for $C_{34}H_{43}NO_3Si$: C, 75.37; H, 8.00; N, 2.59. Found: C, 75.11; H, 8.12; N, 2.87.

(2′*R*,4″*R*)-[2′-(2″-Dimethyl-[1″, 3″]dioxolan-4″-yl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]propan-1-one (22). 2-Aminobenzyl alcohol (**6**) (11 g, 89 mmol) in absolute THF (100 mL) was treated with p-TsOH (425 mg, 2,23 mmol). Glyceraldehyde **21** obtained from diacetone d-mannitol (23 g) and $NaIO_4$ (53 g) in THF (40 mL) was added. The reaction was quenched after 15 min with aqueous saturated $NaHCO_3$ (150 mL). Workup with ether in the usual way, including column chromatography (ethyl acetate/hexane 1:20), furnished the *N*,*O*-acetals (**20″**) as a 2:1 diastereomeric mixture (19.8 g, 65%). ^{1}H NMR: δ 1.39 (s, 3 + 3H), 1.47 (s, $3H^{major}$), 1.5 (s, $3H^{minor}$), 3.99−4.18 (m, 3 + 3H), 4.32 (mc, $1H^{minor}$), 4.43 (s, br, $1H^{major}$), 4.53 (mc, $1H^{major}$), 4.73 (mc, $1H^{minor}$), 4.77−5.0 (2 AB systems, 4 + 4H): 6.69 (mc, 1 + 1H), 6.78 (mc, 1 + 1H), 6.89 (mc, 1 + 1H), 7.08 (mc, 1 + 1H). ^{13}C NMR: δ 24.8, 25.0, 26.3, 26.7, 64.8, 66.3, 67.4, 67.5, 75.6, 83.1, 84.2, 109.8, 109.9, 116.3, 117.2, 119.2, 119.6, 121.2, 121.9, 124.7, 124.8, 127.4, 127.5, 141.2. MS (60 °C): m/e 235 ($[M]^+$).

The *N*,*O*-acetal mixture obtained above (200 mg, 0.85 mmol) in dichloromethane (10 mL) at −20 °C was treated with propionyl chloride (45 μL, 0.6 mol equiv) and NEt_3 (12 μL). After stirring for 15 min, additional propionyl chloride (45 μL, 0.6 mol equiv) and NEt_3 (12μL) were added until a clear solution was formed. The mixture was stirred at − 20 °C for 5 h, and NEt_3 was added to dissolve any precipitate which was formed. Ether (30 mL) was added and the mixture was treated with saturated aqueous $NaHCO_3$. The organic phase was separated, dried ($MgSO_4$), and chromatographed (ethyl acetate/hexane 1:2) to give amide **22** (180 mg, 73%). ^{1}H NMR: δ 1.15 (t, J = 7 Hz, 3H), 1.26 (s, 3H), 1.44 (s, 3H), 2.45 (mc, 1H, br), 2.63 (mc, 1H), 3.95 (mc, 3H), 4.60 (mc, 2H), 5.98 (s, 1H, br), 7.15 (mc, 1H), 7.23 (mc, 1H), 7.35 (mc, 1H), 7.45 (s, 1H, br). ^{13}C NMR: δ 9.1, 25.0, 26.3, 27.8, 63.6, 65.5, 74.8, 81.1 (br), 109.7, 124.9, 125.8, 125.8, 127.8, 135.4, (br), 173,3. HRMS (EI, 80 eV, 150 °C): m/e calcd for $C_{16}H_{21}NO_4$ 291.14706, found 291.14727. IR (cm^{-1}) 1677 (ss). $[\alpha]^{20}_D$: +92° (c = 0.5, $CHCl_3$). Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C. 66.11; H, 7.12; N, 4.87.

Enolate Alkylations of Amide 22: KHDMS (1.03 g, 5.15 mmol) in THF (5 mL) was cooled to −78 °C under an argon atmosphere and treated dropwise with a solution of **22** (5.0 mL, 0.687 M in THF). After 60 min allyl bromide (1.16 mL, 13.72 mmol) was added next and the mixture was stirred for 14 h without cooling. Phosphate buffer (pH 7) (5 mL) was added, followed by ether (20 mL) and water (10 mL). The organic layer was separated, washed with brine (10 mL), dried ($MgSO_4$), and chromatographed (ethyl acetate/hexane 1:2) to give adduct **23a** (911 mg, 81%) as a colorless crystals of mp 58 °C. The crude product was analyzed by HPLC (ethyl acetate/hexane 15:85, Nucleosil 50−5) and showed a diastereomeric purity of 98:2. The pure diastereomers were obtained by preparative HPLC (ethyl acetate/hexane 10:90).

Similarly the alkylations of **22** with ethyl iodide (**23b**), propyl iodide (**23c**), benzyl bromide (**23d**), and pentyl bromide (**23e**) were performed. Yields and diastereomeric ratios are shown in Table 2.

(2*S*,2′*R*,4″*R*)-[2′-(2″-Dimethyl-[1″,3″]dioxolan-4″-yl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylpent-4-en-1-one (23a). ^{1}H NMR: δ 1.30 (s, 3H), 1.35 (d, J = 8 Hz, 3H), 1.48 (s, 3H),

2.06 (s, 1H, br), 2.33 (s, 1H, br), 3.15 (mc, 1H), 3.95 (s, 3H, br), 4.65 (mc, 2H, br), 4.94 (mc, 2H, br), 5.50 (s, 1H, br), 6.17 (s, 1H, br), 7.12−7.48 (m, 4H). ^{13}C NMR: δ 17,5, 24.8, 26.0, 36.2, 38.2, 63.5, 65.0, 74.9 br, 80.1 br, 109.2, 116.4, 125.0, 125.8, 127.7, 133.0 (br), 134.9 (br), 135.6 (br), 175.3. MS (EI, 80 eV, 150 °C): *m*/*z* 331 $[M]^+$). $[\alpha]^{20}_D$: +177° (*c* = 1.3, $CHCl_3$). Mp: 58 °C. Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.59; H, 7.45; N, 4.83.

(2*S*,2′*R*,4″*R*)-[2′-(2″-Dimethyl-[1″, 3″]dioxolan-4″-yl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylpropan-1-one (23b). ^{1}H NMR: δ 0.78 (s, 3H, br), 1.23 (s, 3H), 1.30 (d, 3H), 1.33 (mc, 1H, br), 1.42 (s, 3H), 1.53 (mc, 1H, br), 2.92 (mc, 1H), 3.94 (s, br, 3H), 4.59 (mc, 2H, AB systems), 6.15 (s, 1H, br), 7.09−7,42 (m, 4H, br). ^{13}C NMR: δ 11.4, 17.7, 25.0, 26.2, 27.5, 38.1, 63.7, 65.3, 75.0 (br), 80.2 (br), 109.3, 125.1 (br), 125.4 (br), 125.9 (br), 127.8, 132.7 (br), 135.8 (br), 176.5. HRMS (EI, 80 eV, 150 °C): *m*/*e* calcd for $C_{18}H_{25}NO_4$ 319.17836, found 319.17830. IR (cm^{-1}): 1674 (ss). $[\alpha]^{20}_D$: +79° (*c* = 1,1, $CHCl_3$). Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.68; H, 7.89; N, 4.39. Found: C, 67.91; H, 7.65; N, 4.33.

(2*S*,2′*R*,4″*R*)-[2′-(2″-Dimethyl-[1″,3″]dioxolan-4″-yl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylpentan-1-one (23c). ^{1}H NMR: δ 0.64 (s, 3H, br), 1.33−168 (m, 4H, br), 1.44 (mc, 6H), 1.42 (s, 3H), 3.03 (mc, 1H), 3.92 (s, 3H, br), 4.59 (mc, 2H, AB systems), 6.15 (s, 1H, br), 7.08−7.42 (m, 4H, br). ^{13}C NMR: δ 13.4, 17.8, 19.9, 24.8, 26.0, 35.8, 36.5, 63.5, 65.1, 74.8 (br), 79.9 (br), 109.3, 125.2 (br), 125.7 (br), 127.7, 132.7 (br), 135.7 (br), 176.3. HRMS (EI, 80 eV, 150 °C): *m*/*e* calcd for $C_{19}H_{27}NO_4$ 333.19407, found 333.19417. IR (cm^{-1}): 1674 (ss). $[\alpha]^{20}_D$: +120° (*c* = 2, $CHCl_3$). Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.21. Found: C, 68.21; H, 7.95; N, 4.37.

(2*S*,2′*R*,4″*R*)-[2′-(2″-Dimethyl-[1″,3″]dioxolan-4″-yl)-4′H-benzo[*d*] [1′,3′]oxazin-1′-yl]-2-methyl-3-phenylpropan-1-one (23d). ^{1}H NMR: δ 1.32 (s, 3H), 1.39 (d, 3H), 1.41 (s, 3H), 2.56 (mc, 1H, br), 2.80 (mc, 1H, br), 3.06 (mc, 1H, br), 3.27 (mc, 1H), 3.77 (mc, 2H), 3.94 (mc, 1H), 4.15 (mc, 1H, br), 5.86 (s, 1H, br), 6.8 (s, 2H, br), 7,0−7,36 (m, 7H). ^{13}C NMR: δ 18.3, 25.0, 26.1, 38.9, 41.0, 63.2, 64.9, 75.3 (br), 80.4 (br), 109.3. 124,9, 125.1, 125.9, 126,0, 127.7, 128.0, 128.6, 134.5 (br), 135.5 (br), 139.1, 175.5. MS (EI, 80 eV, 150 °C): *m*/*z* 381 ($[M]^+$). $[\alpha]^{20}_D$: +218° (c = 1.7, $CHCl_3$). Mp: 98−100 °C. Anal. Calcd for $C_{23}H_{27}NO_4$: C, 72.42; H, 7.13; N, 3.67. Found: C, 72.12; H, 7.12; N, 3.43.

(2*S*,2′*R*,4″*R*)-[2′-(2″-Dimethyl-[1″,3″]dioxolan-4″-yl)-4′H-benzo[*d*][1′,3′]oxazin-1′-yl]-2-methylheptan-1-one (23e). ^{1}H NMR: δ 0.77 (s, 3H, br), 0.88−1.36 (m, 7H, br), 1.24 (s, 3H), 1.27 (d, 3H), 1.42 (s, 3H), 1.58 (mc, 1H, br), 3.0 (mc, 1H), 3.92 (s, 3H, br), 4.59 (mc, AB systems, 2H), 6.15 (s, 1H, br), 7.09−7.42 (m, 4H, br). ^{13}C NMR: δ 13.7, 17.9, 22.1, 24.9, 26.1, 26.5, 26.9, 31.2, 36.1, 63.6, 65.2, 75.0 (br), 80.1 (br), 109.4, 125.0, 125.3, 125.8, 127.8, 132.8 (br), 135.8 (br), 176.5. HRMS (EI, 80 eV, 150 °C): *m*/*e* calcd for $C_{21}H_{31}NO_4$ 361.22531, found 361.22548. $[\alpha]^{20}_D$: +167° (*c* = 0.5, $CHCl_3$). Anal. Calcd for $C_{21}H_{31}NO_4$: C, 69.77; H, 8.65; N, 3.87; Found: C, 70.02; H, 8.82; N, 3.73.

Removal of the Auxiliary. Amide **16a** (10.0 g, 19.5 mmol) in ether (200 mL) at 0 °C was treated with solid lithium aluminum hydride (4.43 g) in small portions and stirred without cooling overnight. For workup the mixture was diluted with moist ether, and water was added until all lithium aluminum hydride was consumed. The organic layer was separated, washed with brine, dried over $MgSO_4$, and distilled under normal pressure. The volatiles were redistilled under normal pressure to furnish alcohol (*R*)-**20** (1.83 g, 70%). The nonvolatile residue was chromatographed to give aminal **20′** (4.81 g, 59%) as a 5:1 diastereomeric mixture.

(2*R*)-2-Methylpenten-4-ol (*R*-20). ^{1}H NMR: δ 0.91 (d, *J* = 7 Hz,3H), 1.70 (mc, 1H), 1.89 (mc, 1H), 2.18 (mc, 1H), 3.17 (br, 1H), 3.47 (mc, 1 H), 5.01 (mc, 1H), 5.79 (mc, 1 H). $[\alpha]^{20}_D$: +2.40° (*c* = 13, $CHCl_3$), lit.[13] $[\alpha]^{20}_D$: +2.60 (*c* = 1.5, $CHCl_3$).

(1S,2′RS)-1-(2′,4′-Dihydro-1′H-benzo[*d*][1′,3′]oxazin-2′-yl)-*tert*-butyldiphenylsiloxyethanol (20′). ^{1}H NMR: δ 1.16 (s,9 + 9H),1.24 (d + d, *J* = 6 Hz, 3 + 3H), 4.11 (mc, 1H), 4.21 (mc,1 H), 4.43 (mc, 1 H), 4.48 (mc, 1H), 4.50 (mc, 1H), 4.67 (mc, 1H), 4.75−5.0 (m, d + d, 2 + 2 H), 6.51 (mc, 1H9, 6.71 (mc, 1H), 6.88 (mc, 1 + 1H), 6.92 (mc, 1 + 1 H), 7.11 (mc, 1 + 1H), 7.37−7.53 (m, 6 + 6H), 7.69−7.87 (m, 4 + 4H). ^{13}C NMR: δ 16.58, 19.21, 19.31, 19.55, 27.02, 27.39, 36.53, 69.98, 71.45, 85.07, 87.33, 115.84, 116.54, 118.52, 118.97, 121.19, 121.73, 124.65, 127.29, 127.37, 127.59, 127.64, 127.67, 129.75, 133.34, 133.68, 133.79, 135.71, 135.79, 135.89, 141.77, 142.21. Anal. Calcd for $C_{26}H_{31}NO_2Si$: C, 74.78; H, 7.48; N, 3.35. Found: C, 74.26; H, 7.31; N, 3.35.

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Supporting Information Available: Experimental details on the preparation and characteristic analytical data of compounds **7, 10**, **11a**−**e**, **12a**−**c**, **13a**−**c**. Drawings, tables of crystal data, atomic coordinates, bond angles and bond lengths, torsion angles, equivalent isotropic displacement parameters, anisotropic thermal parameters, H-atom coordinates and isotropic displacement coefficients for **11b**, **11e**, **16d**. Drawing, table of crystal data, positional parameters and their estinaled standard deviations, general displacement parameters expressions, bond distances, bond angles, torsion angles and least-squares planes for **23d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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