Diastereoreactivity of a Chiral Oxathiane Derived from 5-Hydroxy-1-tetralone

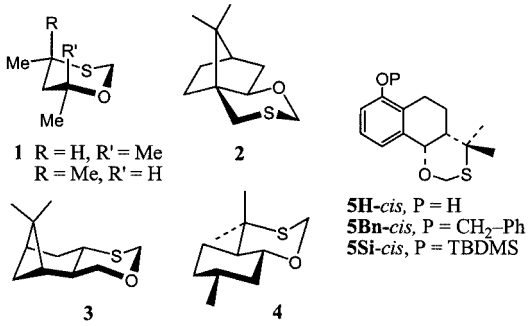
Arlette Solladié-Cavallo,*[a] Milan Balaz,[a] and Marta Salisova*[b]

Keywords: Diastereoreactivity / Lithiation / 1,3-Oxathiane

The diastereoreactivity at the CH_2 bridge of a *cis*-oxathiane derived from 5-hydroxy-1-tetralone (unprotected and protected at the OH) was studied, and it appeared that all reactions at C-2 provided *equatorial* substitution. It was also found that: i) reductions of the *equatorial* benzoyl derivative with selectrides provided high diastereoselectivities at C-2′ while LAH did not. Methyl Grignard addition was less selective and the selectivity of the propanoyl analogue was smaller; ii) condensation of aldehydes and/or ketones with the lithio derivative provided high *equatorial* diastereoselectivities at C-2 but low or nil diastereoselectivities at C-2′; iii) lithiation at C-2 was possible only with the oxathiane unsubstituted at C-2 (CH_2) and not possible with derivatives substituted at C-2 (CHR), perhaps due to the conformational rigidity of this oxathiane in the lithiation transition state and to the equatorial demand of all substituents at C-2, including lithium.

Introduction

The chiral 1,3-oxathianes **1**,[1] **2**,[2] **3**,[3] and **4**[4] have been used since 1978 as CH_2-bridge chiral auxiliaries for enantioselective syntheses of bioactive compounds, and in 1992 we showed that oxathiane **4** could also be successfully used at the sulfur atom as a chiral sulfide[5] for asymmetric synthesis of monoaryl epoxides, *trans*-diaryl epoxides,[6] and *trans*-cyclopropanes.[7]



Oxathianes **2**, **3**, and **4**, however, being derived from natural products, are each available only as a single enantiomer. Moreover, a drawback of these syntheses is the need to separate the chiral auxiliaries **2**–**4** (used in stoichiometric amounts) or some corresponding intermediate/precursor **I**[8] (formed during hydrolysis) from the desired products by chromatography. We thus decided to look for a chiral oxathiane that would be available as both enantiomers and which could either be grafted onto a solid support (to be separated by filtration) or be derivatized with a polyfluoro group (to be separated by extraction with a fluorous phase). Oxathiane **5H-*cis*** was therefore synthesized and resolved, and its structure and absolute configuration were determined.[9]

Here we report the diastereoreactivity at the CH_2 bridge of unprotected and protected oxathiane **5H-*cis***, **5Bn-*cis***, and **5Si-*cis***.

Results and Discussion

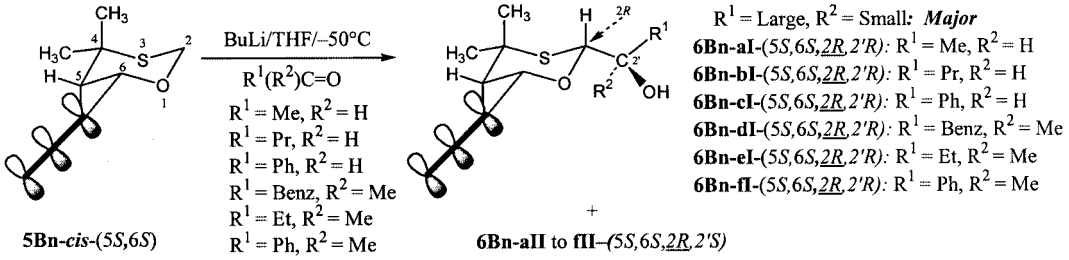
Addition of Carbonyl Compounds to Lithio Derivative 5Bn-Li

Condensation of lithiated oxathiane **5Bn-Li** with aldehydes and/or ketones exclusively afforded equatorial products **6Bn** (Scheme 1), but with low diastereoselectivity at C-2′, consistent with the results obtained with Eliel's oxathiane **1**.[10] The results are collected in Table 1.

The larger 70:30 and 80:20 diastereoselectivities observed with benzaldehyde and with acetophenone, respectively (Table 1, lines 3, 6) are interesting, but attempts to increase these diastereoselectivities by changes in the solvent or addition of salts and/or HMPA to **5Bn-Li** before addition of benzaldehyde and/or acetophenone in fact resulted in more complex mixtures in which at least three of the four possible diastereomers could be detected.

After Eliel's work[11] pointing out the important equatorial preference of lithium in lithiodithianes, Seebach and Dunitz[12] showed that 2-lithio-2-methyl-1,3-dithiane had a sul-

[a] Département de Chimie Organique Fine, ECPM/Université Louis Pasteur,
67087 Strasbourg, France
E-mail: cavallo@chimie.u-strasbg.fr
[b] Department of Organic Chemistry, Comenius University,
84215 Bratislava, Slovakia
E-mail: salisova@fns.uniba.sk



Scheme 1

Table 1. Condensation of carbonyl compounds with the lithio derivative 5Bn-Li (*: from Table 2)

Electrophile	R^1	R^2	Compound conversion	**6Bn I/II**	Compound	Absol. config. of **I***
Acetaldehyde	Me	H	85%	50:50	**6Bn-a**	
Butyraldehyde	Pr	H	83%	57:43	**6Bn-b**	
Benzaldehyde	Ph	H	87%	70:30	**6Bn-c**	(*R*)
Benzyl methyl ketone	$PhCH_2$	Me	79%	53:47	**6Bn-d**	
Butanone	Et	Me	89%	58:42	**6Bn-e**	
Acetophenone	Ph	Me	83%	80:20	**6Bn-f**	(*R*)

fur-bridged dimeric structure in the solid state (single-crystal X-ray diffraction). NMR studies[13] of 2-lithio-1,3-dithiane and 2-lithio-2-methyl-1,3-dithiane then showed that these lithio derivatives were either monomeric or dimeric (sulfur-bridged) in THF solution at low temperature (−100 °C), and cryoscopic measurements then indicated that 2-lithio-2-methyl-1,3-dithiane was largely monomeric in THF.[14] Moreover, more recent NMR studies by Reich[15] of 2-lithio-1,3-dithiane and of 2-*tert*-butyl-2-lithio-1,3-dithiane and 2-lithio-2-phenyl-1,3-dithiane have shown that all are monomeric contact ion pairs (CIPs) in THF/Et_2O mixtures (concentration of about 0.17 M), becoming separated ion pairs (SIPs) in the presence of excess HMPA.

Therefore, speculating that 1,3-oxathianes might behave similarly, we postulate that the lithium atom was equatorial and that **5Bn-Li** is monomeric at these reaction concentrations (about 0.05 M in THF), the coordination sphere of the lithium atom being completed by solvent molecules. Consequently, exclusive formation of the equatorial isomer (at C-2) could be explained through approach **A**, and the poor stereoselectivity at C-2′ could then be explained by the fact that the carbonyl group may approach from both faces (Figure 1), with **AI** slightly preferred or identical to **AII**.

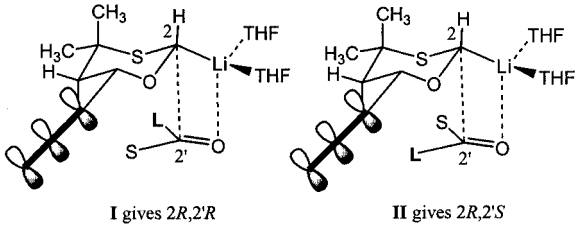


Figure 1. Approach **A**

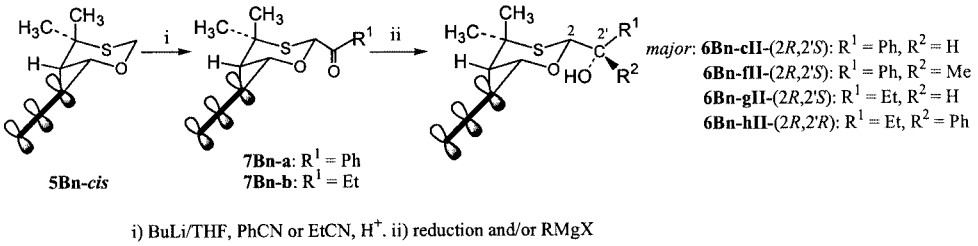
On the other hand, it is reasonable to suppose that the hybridization of C-2 should change from sp^3-type to sp^2-type in the transition (upon addition of salts and/or of HMPA) from contact ions to separated ions (in which the role of lithium should decrease), also making approach from the upper face of the oxathiane possible, and thus resulting in the potential formation of the two other diastereomers, which would explain the more complex mixtures obtained under these conditions.

Oxo Derivatives 7Bn: Synthesis, Reductions, and Grignard Additions

The oxo derivatives **7Bn-a** and **7Bn-b** were synthesized in 80% and 38% isolated yields by addition of benzonitrile and propionitrile, respectively, to the lithio derivative **5Bn-Li**, followed by hydrolysis.[16] A better preparation of enolisable oxo derivatives might be to treat the desired R−CO−Cl with the lithium cuprate **$5Bn_2$-CuLi**, but that method, although attractive, is difficult to perform, as mentioned by the authors themselves.[17]

It should be noted that the introduced CO−R groups have equatorial orientations (Scheme 2).

Reduction of compounds **7Bn-a** (Scheme 2) provided the corresponding product **6Bn-c** with high diastereoselectivity, but only when selectrides were used (Table 2, lines 1, 2), and it is worth noting that DIBAL provided a smaller and reversed diastereoselectivity (as already observed by Eliel with oxathiane **4**[18,19]). In contrast to Eliel's results[4] with oxathiane **4**, however, methyl Grignard addition to compound **7Bn-a** proceeded with low diastereoselectivity. Reduction of compound **7Bn-b** with K-selectride gave a lower diastereoselectivity than that from compound **7Bn-a** (compare lines 2 and 6, Table 2), and phenyl Grignard addition



Scheme 2

Table 2. Reduction of and Grignard addition to oxo derivatives 7Bn [*: deduced from Cram's model (see ref.[10,18])]

Reagent	R^1	R^2	Comp. (%)	6Bn **I/II**	Absol. config. of **II***
L-selectride	Ph	H	**6Bn-c** (100)	3:97	(*S*)
K-selectride	Ph	H	**6Bn-c** (100)	< 1:> 99	(*S*)
$LiAlH_4$	Ph	H	**6Bn-c** (100)	12:88	(*S*)
DIBAL	Ph	H	**6Bn-c** (100)	77:23	(*R*)
MeMgI	Ph	Me	**6Bn-f** (60)	20:80	(*S*)
K-selectride	Et	H	**6Bn-g** (100)	16:84	(*S*)
PhMgBr	Et	Ph	**6Bn-h** (59)	40:60	(*R*)

was still worse (with a 40:60 diastereomeric ratio). It is clear that the selectivity in the ethyl ketone system **7Bn-b** is less than in the phenyl analogue **7Bn-a**, as has often been observed during reductions and Grignard additions.[4,18,19]

It is worth noting that while diastereomers **I** of products **6Bn-c** and **6Bn-f** were preferred on addition of benzaldehyde and acetophenone to **5Bn-Li**, diastereomers **II** (**6Bn-cII** and **6Bn-fII**) were preferred by reduction of or methyl Grignard addition to ketone **7Bn-a**.

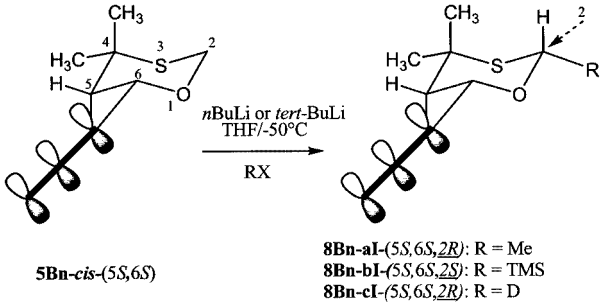
By Eliel's conclusions[10,18] concerning oxathianes **1** and **4**, these additions follow Cram's rule (open or rigid model) and the (*S*) configuration should be expected at C-2′ for diastereomers **II** (**6Bn-cII** and **6Bn-fII**). The (*S*) and (*R*) configurations were consequently assigned to **6Bn-g** and **6Bn-h**, respectively (Table 2). Moreover, diastereomers **I** (**6Bn-cI** and **6Bn-f**) could then be assigned the (*R*) configuration at C-2′, consistently with approach **AI** (Figure 1).

Alkylation and Quenching of Lithio Derivative 5Bn-Li

Addition of methyl iodide and quenching with TMSCl or D_2O exclusively afforded the equatorial diastereomers **8Bn-aI**, **8Bn-bI**, and **8Bn-cI**, with high percentage conversions (Table 3 and Scheme 3). Addition of *isopropyl* iodide, however, resulted in an unidentified product, and 50% of starting material was recovered.

Table 3. Alkylation and quenching of lithio derivative **5Bn-Li** to give compounds **8Bna-c**

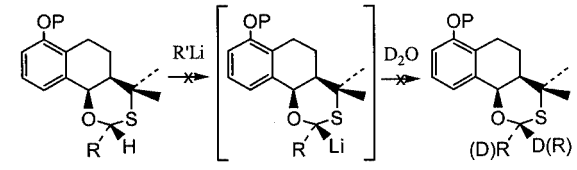
Electrophile	R	Conversion	Diastereomer. **I** (equatorial)
Methyl iodide	Me	90%	**8Bn-aI** 100%
TMSCl	TMS	97%	**8Bn-bI** 100%
D_2O	D	98%	**8Bn-cI** 100%



Scheme 3

Reactivity of 8 Towards Alkyllithium Bases

Any attempts to form the lithio derivatives of compounds **8** with an equatorial substituent present at C-2 failed (Scheme 4 and Table 4), and no deuterium could be incorporated at C-2 after quenching with D_2O. The non-deuterated starting substrates were quantitatively recovered in all cases except for those of benzyl- or TMS-protected compounds at 0 °C (Table 4, lines 4, 8).



	8Bn-aI	**8Bn-bI**	**8Si-aI**	**8Si-gI**	**8H-aI**	**8H-gI**
P	Bn	Bn	TBDMS	TBDMS	H	H
R	Me	TMS	Me	Ph	Me	Ph

Scheme 4

It is worth noting that this treatment of **8Bn-bI**, after isolation, gave 15% of deprotected compound (**8H-bI**) and 57% of non-deuterated recovered **8Bn-bI** (the remaining 28% being non-isolated and undetermined products), while that of **8Bn-aI** gave, in 71% isolated yield, a mixture corresponding to 39% deuteration at the benzyl protecting group, 43% Wittig rearrangement, and 18% deprotection, but with no starting material (deuterated or non-deuterated) being recovered, the remaining 29% also being lost and unidentified (Scheme 5).

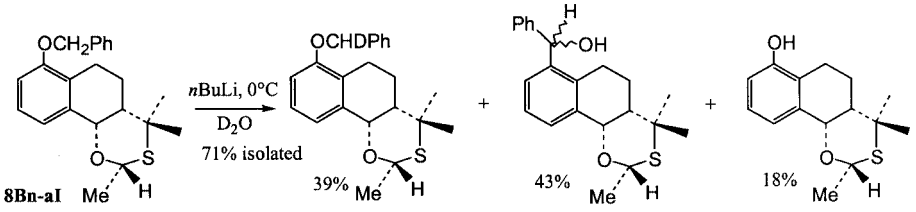
Direct Preparation of Type 8 Compounds

It is worth noting that compounds of type **8** with an equatorial substituent at C-2, when not accessible through

Table 4. Attempted deuteration of equatorially substituted compounds **8**

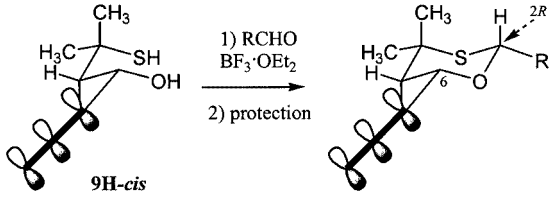
	R	Base	Solvent	Temp.	Deuterated **8**	Non-deuterated starting **8**
8Bn-aI	Me	*t*BuLi	THF	−50 °C	0%	≥ 98%
	Me	*n*BuLi	Et_2O	−50 °C	0%	≥ 98%
	Me	*n*BuLi	THF	−30 °C	0%	≥ 98%
	Me	*n*BuLi	THF	0 °C	0%[a]	0%
8Bn-bI	TMS	*t*BuLi	THF	−50 °C	0%	≥ 98%
	TMS	*n*BuLi	Et_2O	−50 °C	0%	≥ 98%
	TMS	*n*BuLi	THF	−30 °C	0%	≥ 98%
	TMS	*n*BuLi	THF	0 °C	0%[b]	57%
8Si-aI	Me	*s*BuLi	THF	0 °C	0%	97%
8Si-aI	Me	*t*BuLi	THF	0 °C	0%	≥ 98%
8Si-gI	Ph	*s*BuLi	THF	0 °C	0%	97%
8Si-gI	Ph	*t*BuLi	THF	0 °C	0%	≥ 98%
8H-aI	Me	PhLi[c]	THF	−50 °C	0%	≥ 98%
	Me	*t*BuLi[c]	THF/HMPA[d]	−50 °C	0%	≥ 98%
8H-gI	Ph	*t*BuLi[c]	THF	0 °C	0%	≥ 98%

[a] No starting **8Bn-aI** (deuterated or non-deuterated) was recovered (cf. Scheme 5). [b] 57% of starting **8Bn-bI** (non deuterated) and 14% of deprotected **8H-bI** were recovered. [c] 2.3 equiv. used. [d] 1 equiv. of HMPA.



Scheme 5

alkylation of the lithio derivatives (cf. above), can be directly obtained in high yields (80−100%) by condensation of the desired unprotected hydroxy thiol **9H-*cis*** with the corresponding aldehydes with a subsequent protection step (allowing the introduction of various protecting groups as desired, Scheme 6). Again, all type **8** compounds obtained have the new substituent at C-2 in an equatorial position.



8Bn-aI-(5*S*,6*S*,2*R*): P = Bn, R = Me
8Si-aI-(5*S*,6*S*,2*R*): P = TBDMS, R = Me
8Bn-dI-(5*S*,6*S*,2*R*): P = Bn, R = *i*Pr
8Bn-eI -(5*S*,6*S*,2*R*): P = Bn, R = Hexyl
8Bn-fI -(5*S*,6*S*,2*R*): P = Bn, R = Cyclohex.
8Si-gI -(5*S*,6*S*,2*R*): P = TBDMS, R = Ph

Scheme 6

NMR Determination of the Configuration at C-2

The equatorial orientations of the "large" substituent in compounds **6**, **7**, and **8** were determined by 2D NMR spectroscopy. The NOESY spectra showed correlations between the proton at C-2, one of the methyl groups at C-4, and the proton at C-6.

Conclusion

It was found that:

1. All reactions at C-2 of oxathiane **5Bn** provide equatorial substitution at C-2.

2. Reductions of equatorial oxo derivative **7Bn-a** with selectrides provide high diastereoselectivities at C-2′, but methyl Grignard addition is less selective.

3. Condensation of aldehydes and/or ketones with the lithio derivative **5Bn-Li** provides high equatorial diastereoselectivities at C-2 but low or nil diastereoselectivities at C-2′.

4. The *major* configuration at C-2′ is inverted on going from condensation products (Table 1) to reduction/Grignard addition products (Table 2).

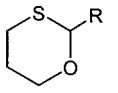
5. Lithiation at C-2 is possible only with the starting **5Bn** (CH_2) and impossible with **8Bn** derivatives substituted at C-2 (CHR).

6. The selectivity with the ethyl ketone **7Bn-b** is less than with the phenyl analogue **7Bn-a**, as has often been observed during reductions and Grignard additions.[4,18,19]

Concerning points 1−4, oxathiane **5Bn**, although possessing a *cis* junction, has a reactivity at C-2 similar to that of oxathianes **2**, **3**, and **4**, which each possess a rigid *trans* junction, and even to that of oxathiane **1**, which is flexible.

However, differences in behavior arise where lithiation is concerned (point 5). While lithiation of oxathianes **1**,[1] **4**,[4] and **5Bn** occurred readily with use of *n*Buli, lithiation of oxathianes **2**[2] and **3**[3] was not possible with *n*BuLi, although *s*BuLi allowed lithiation of oxathiane **2**.

Attempted lithiation of oxathianes **5** substituted at C2 (**8Bn**, **8Si**, **8 H**) with *n*BuLi, *s*BuLi, and *t*BuLi all failed, while lithiation of oxathianes **10**−**12**, substituted at C-2, worked readily (*s*BuLi/THF, −78 °C).[20−22]

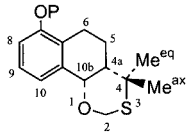


10: R = $SiMe_3$
11: R = CH=CHMe
12: R = Ph

From the observation that the equatorial position is the only one accepted at C-2 (even for Li) it is reasonable to postulate that flexibility is necessary for lithiation of C-2-substituted oxathianes.

Experimental Section

General: All reactions involving organolithium reagents were carried out under argon in flame-dried glassware. THF was dried under argon by distillation from sodium/benzophenone. *n*BuLi, *t*BuLi, and *s*BuLi were purchased from Aldrich and Fluka. ^1H and ^{13}C NMR spectra were recorded with Bruker AC 200 (200 MHz) or Bruker Avance (400 MHz) spectrometers with $CDCl_3$ as solvent. Chemical shifts (δ) are reported in ppm downfield from TMS. TLCs were performed on Merck glass plates with 63 F_{254} silica gel, and PLC (preparative layer chromatography) on Merck glass plates with 60 F_{254} silica gel (2 mm). Si 60 silica gel (40−60 μm) from Merck was used for chromatographic purifications. Usual IR spectra were recorded with a Perkin−Elmer Spectrum one.



General Procedures for the Treatment of Oxathiane 5Bn with Electrophiles: *n*BuLi (1.6 M solution in hexanes, 0.12 mL, 0.19 mmol, 1.3 equiv.) was added dropwise by syringe at −50 °C and under argon to a solution of **5Bn** (50 mg, 0.15 mmol, 1 equiv.) in anhydrous THF (3.5 mL). After the mixture had been stirred for 40 min, the desired electrophile (0.22 mmol, 1.5 equiv.) was added dropwise. After being stirred at −50 °C for 90 min, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (2 mL). The mixture was extracted with diethyl ether (4 × 5 mL), dried (Na_2SO_4), and, after filtration, concentrated under vacuum to afford an oil that was analyzed by TLC and ^1H NMR before being purified by preparative layer chromatography PLC.

Acetaldehyde

6Bn-aI: ^1H NMR ($CDCl_3$): δ = 1.22 (d, ^3J = 6.5 Hz, 3 H, CH_3), 1.35 (s, 3 H, Me^{eq}), 1.45 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.67 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.14 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.57 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 2.77 (d, ^3J = 2.5 Hz, 1 H, OH), 3.13 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 3.83 (dquint, ^3J = ^3J = ^3J = ^3J = 7, ^3J = 2.5 Hz, 1 H, 2′-H), 4.76 (s, 1 H, 10b-H), 4.88 (d, ^3J = 7 Hz, 1 H, 2-H), 5.08 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 6.87 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.93 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.19 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.28−7.47 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.9 (CH_2), 18.2 (CH_3), 23.8 (CH_2), 29.2 (Me), 29.6 (Me), 43.0 (CH), 43.4 (C), 69.7 (C-2′), 69.8 (CH_2O), 74.5 (C-10b), 84.4 (C-2), 110.9 (CH), 123.3 (CH), 126.6 (CH), 127.0 (C), 127.0 (CH), 127.8 (CH), 128.5 (CH), 136.7 (C), 137.2 (C), 156.2 (C) ppm. IR: ν_{OH} = 3436 cm^{-1}.

6Bn-aII: ^1H NMR ($CDCl_3$): δ = 1.25 (d, ^3J = 5 Hz, 3 H, CH_3), 1.36 (s, 3 H, Me^{eq}), 1.44 (dt, ^3J = 12, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.67 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.16 (dq, ^2J = ^3J = ^3J = 12, J = 6 Hz, 1 H, 5-H^{ax}), 2.25 (d, ^3J = 5 Hz, 1 H, OH), 2.55 (ddd, ^2J = 18.5, ^3J = 12, ^3J = 6 Hz, 1 H, 6-H^{ax}), 3.12 (ddd, ^2J = 18.5, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 3.99 (m, 1 H, 2′-H), 4.79 (s, 1 H, 10b-H), 5.08 (s, 2 H, CH_2O), 5.13 (d, ^3J = 3.5 Hz, 1 H, 2-H), 6.86 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.91 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.3−7.5 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.9 (CH_2), 18.3 (CH_3), 23.8 (CH_2), 29.4 (2 × Me), 43.0 (C), 43.3 (CH), 69.5 (C-2′), 69.8 (CH_2O), 74.8 (C-10b), 84.2 (C-2), 110.9 (CH), 123.3 (CH), 126.4 (CH), 127.1 (C), 127.0 (CH), 127.8 (CH), 128.5 (CH), 136.9 (C), 137.3 (C), 156.2 (C) ppm. IR: ν_{OH} = 3421 cm^{-1}.

Butyraldehyde

6Bn-bI: ^1H NMR ($CDCl_3$): δ = 0.92 (t, ^3J = 6 Hz, 3 H, CH_3), 1.35 (s, 3 H, Me^{eq}), 1.4−1.6 (m, 5 H, 4a-H + CH_2CH_2), 1.67 (s, 3 H, Me^{ax}), 1.9 (m, 1 H, 5-H^{eq}), 2.12 (dq, ^2J = ^3J = ^3J = 12, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.57 (ddd, ^2J = 18, ^3J = 12, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 2.6 (1 H, OH, overlap), 3.12 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 3.68 (dt, ^3J = ^3J = 7, ^3J = 2.5 Hz, 1 H, 2′-H), 4.75 (s, 1 H, 10b-H), 4.95 (d, ^3J = 6.5 Hz, 1 H, 2-H), 5.08 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 6.86 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.92 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.26−7.45 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 17.9 (CH_2), 18.4 (CH_2), 23.8 (CH_2), 29.2 (Me), 29.5 (Me), 34.4 (CH_2), 43.1 (C), 43.3 (CH), 69.8 (CH_2), 73.0 (CH), 74.6 (C-10b), 83.3 (C-2), 110.9 (CH), 123.3 (CH), 126.6 (CH), 127.0 (C), 127.1 (CH), 127.8 (CH), 128.5 (CH), 136.7 (C), 137.3 (C), 156.2 (C) ppm. IR: ν_{OH} = 3436 cm^{-1}.

6Bn-bII: ^1H NMR ($CDCl_3$): δ = 0.92 (t, ^3J = 6.5 Hz, 3 H, CH_3), 1.36 (s, 3 H, Me^{eq}), 1.25−1.6 (m, 5 H, 4a-H + CH_2CH_2), 1.43 (dt, ^3J = 12, ^3J = ^3J = 2 Hz, 1 H, 4a-H), 1.67 (s, 3 H, Me^{ax}), 1.9 (m, 1 H, 5-H^{eq}), 2.16 (dq, ^2J = ^3J = ^3J = 12, J = 6 Hz, 1 H, 5-H^{ax}), 2.16 (1 H, OH), 2.57 (ddd, ^2J = 18, ^3J = 12, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.12 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 3.83 (m, 1 H, 2′-H), 4.79 (s, 1 H, 10b-H), 5.08 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 5.15 (d, ^3J = 3.5 Hz, 1 H, 2-H), 6.86 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.91 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.26−7.45 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 18.0 (CH_2), 18.9 (CH_2), 23.8 (CH_2), 29.4 (2 × Me), 34.3 (CH_2), 42.9 (C), 43.3 (CH), 69.8 (CH_2O), 73.1 (CH), 74.8 (C-10b), 83.7

(C-2), 110.8 (CH), 123.4 (CH), 126.4 (CH), 127.0 (CH), 127.1 (C), 127.8 (CH), 128.5 (CH), 136.9 (C), 137.3 (C), 156.2 (C) ppm. IR: ν_{OH} = 3431 cm^{-1}.

6Bn-cI: ^1H NMR ($CDCl_3$): δ = 1.28 (s, 3 H, Me^{eq}), 1.44 (dt, ^3J = 12.5, ^3J = ^3J = 2 Hz, 1 H, 4a-H), 1.56 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.19 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.58 (ddd, ^2J = 18.5, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 3.15 (dd, ^2J = 18.5, ^3J = 6 Hz, 1 H, 6-H^{eq}), 3.26 (s, 1 H, OH), 4.67 (d, ^3J = 8 Hz, 1 H, 2′-H), 4.81 (s, 1 H, 10b-H), 5.09 (s, 2 H, CH_2O), 5.12 (d, ^3J = 8 Hz, 1 H, 2-H), 6.89 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.96 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.28−7.48 (m, 10 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_2), 24.0 (CH_2), 29.5 (Me), 43.2 (CH), 43.8 (CH), 70.1 (CH_2O), 74.8 (C-10b), 76.7 (CH), 84.1 (C-2), 111.2 (CH), 123.6 (CH), 126.5 (CH), 126.8 (CH), 127.3 (CH), 127.5 (CH), 128.0 (CH), 128.5 (CH), 128.7 (CH), 136.8 (C), 137.5 (C), 138.7 (C), 139.0 (C), 156.5 (C) ppm. IR: ν_{OH} = 3555 cm^{-1}.

6Bn-cII: ^1H NMR ($CDCl_3$): δ = 1.30 (s, 3 H, Me^{eq}), 1.42 (dt, ^3J = 12, ^3J = ^3J = 2 Hz, 1 H, 4a-H), 1.57 (s, 3 H, Me^{ax}), 1.91 (m, 1 H, 5-H^{eq}), 2.16 (dq, ^2J = ^3J = ^3J = 12, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.58 (ddd, ^2J = 18, ^3J = 12, ^3J = 6 Hz, 1 H, 6-H^{ax}), 2.82 (s, 1 H, OH), 3.13 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.84 (s, 1 H, 10b-H), 5.06 (d, ^3J = 4 Hz, 1 H, 2′-H), 5.09 (s, 2 H, CH_2O), 5.35 (d, ^3J = 4 Hz, 1 H, 2-H), 6.87 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.90 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.21 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.26−7.48 (m, 10 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_2), 24.0 (CH_2), 29.3 (Me), 43.2 (C), 43.3 (CH), 70.1 (CH_2O), 75.1 (C-10b), 75.4 (CH), 84.9 (C-2), 111.1 (CH), 123.6 (CH), 126.6 (CH), 126.8 (CH), 127.2 (CH), 127.4 (CH), 128.0 (CH), 128.3 (CH), 128.7 (CH), 136.9 (C), 137.5 (C), 138.7 (C), 139.0 (C), 156.4 (C) ppm. IR: ν_{OH} = 3431 cm^{-1}.

Benzyl Methyl Ketone

6Bn-dI: ^1H NMR ($CDCl_3$): δ = 1.23 (s, 3 H, CH_3), 1.36 (s, 3 H, Me^{eq}), 1.40 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.59 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.16 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.57 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 2.63 (br. s, 1 H, OH), 2.89 (AB, J_{AB} = 14 Hz, 2 H, CH_2Ph), 3.12 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 4.71 (s, 1 H, 10b-H), 4.88 (s, 1 H, 2-H), 5.08 (s, 2 H, CH_2O), 6.87 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.92 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.20−7.47 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.0 (CH_2), 23.4 (CH_3), 23.8 (CH_2), 29.2 (Me), 29.3 (Me), 43.2 (CH), 43.4 (C), 44.2 (CH_2), 69.8 (CH_2O), 74.4 (C-2′), 74.9 (C-10b), 85.1 (C-2), 110.8 (CH), 123.4 (CH), 126.4 (CH), 127.1 (CH), 127.2 (C), 127.8 (CH), 127.9 (CH), 128.5 (CH), 130.7 (CH), 136.9 (C), 137.1 (C), 137.3 (C), 156.2 (C) ppm. IR: ν_{OH} = 3560 cm^{-1}.

6Bn-dII: ^1H NMR ($CDCl_3$): δ = 1.17 (s, 3 H, CH_3), 1.38 (s, 3 H, Me^{eq}), 1.42 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.65 (s, 3 H, Me^{ax}), 1.91 (m, 1 H, 5-H^{eq}), 2.17 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.32 (br. s, 1 H, OH), 2.58 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 2.92 (AB, J_{AB} = 14 Hz, 2 H, CH_2Ph), 3.12 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.75 (s, 1 H, 10b-H), 5.00 (s, 1 H, 2-H), 5.09 (s, 2 H, CH_2O), 6.88 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.92 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.19 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.20−7.45 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_2), 23.2 (CH_3), 24.1 (CH_2), 29.6 (Me), 29.6 (Me), 43.4 (CH), 43.6 (C), 43.7 (CH_2), 70.1 (CH_2O), 74.8 (C-2′), 75.2 (C-10b), 86.8 (C-2), 111.0 (CH), 123.6 (CH), 126.6 (CH), 126.6 (CH), 127.3 (CH), 127.4 (C), 128.0 (CH), 128.2 (CH), 128.7 (CH), 131 (CH), 137.2 (C), 137.4 (C), 137.5 (C), 156.4 (C) ppm. IR: ν_{OH} = 3555 cm^{-1}.

Butanone

6Bn-eI: ^1H NMR ($CDCl_3$): δ = 0.96 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 1.20 (s, 3 H, CH_3), 1.35 (s, 3 H, Me^{eq}), 1.42 (d, ^3J = 12 Hz, 1 H, 4a-H), 1.61 (m, 2 H, CH_2CH_3), 1.62 (m, 2 H, CH_2), 1.67 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.13 (dq, ^2J = ^3J = ^3J = 12, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.50 (s, 1 H, OH), 2.59 (ddd, ^2J = 18, ^3J = 12, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.13 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.76 (s, 1 H, 10b-H), 5.01 (s, 1 H, 2-H), 5.08 (s, 2 H, CH_2O), 6.89 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.93 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.20 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.32−7.50 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 7.6 (CH_3), 18.0 (CH_2), 22.3 (CH_3), 23.9 (CH_2), 29.3 (Me), 29.4 (Me), 31.2 (CH_2), 43.2 (CH + C), 69.8 (CH_2), 74.4 (C-2′), 75.0 (C-10b), 85.8 (C-2), 110.8 (CH), 123.3 (CH), 126.4 (CH), 127.1 (CH), 127.1 (C), 127.8 (CH), 128.5 (CH), 137.0 (C), 137.3 (C), 156.2 (C) ppm. IR: ν_{OH} = 3552 cm^{-1}.

6Bn-eII: ^1H NMR ($CDCl_3$): δ = 0.91 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 1.22 (s, 3 H, CH_3), 1.35 (s, 3 H, Me^{eq}), 1.42 (d, ^3J = 12 Hz, 1 H, 4a-H), 1.60 (m, 2 H, CH_2CH_3), 1.63 (m, 2 H, CH_2), 1.67 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.09 (dq, ^2J = ^3J = ^3J = 12, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.33 (s, 1 H, OH), 2.59 (ddd, ^2J = 18, ^3J = 12, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.13 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.76 (s, 1 H, 10b-H), 5.01 (s, 1 H, 2-H), 5.08 (s, 2 H, CH_2O), 6.89 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.93 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.20 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.32−7.50 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 7.7 (CH_3), 18.0 (CH_2), 22.6 (CH_3), 23.9 (CH_2), 29.3 (Me), 29.4 (Me), 29.9 (CH_2), 43.2 (CH + C), 69.8 (CH_2), 75.0 (C-10b), 76.6 (C-2′), 87.1 (C-2), 110.8 (CH), 123.3 (CH), 126.4 (CH), 127.1 (CH), 127.1 (C), 127.8 (CH), 128.5 (CH), 137.0 (C), 137.3 (C), 156.2 (C) ppm. IR: ν_{OH} = 3560 cm^{-1}.

Acetophenone

6Bn-fI: ^1H NMR ($CDCl_3$): δ = 1.35 (s, 3 H, Me^{eq}), 1.44 (dt, ^3J = 12.5, ^3J = ^3J = 2 Hz, 1 H, 4a-H), 1.62 (s, 3 H, CH_3), 1.67 (s, 3 H, Me^{ax}), 1.93 (m, 1 H, 5-H^{eq}), 2.16 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.61 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.16 (dd, ^2J = 18, ^3J = 6 Hz, 6-H^{eq}), 3.21 (s, 1 H, OH), 4.79 (s, 1 H, 10b-H), 5.12 (s, 2 H, CH_2O), 5.25 (s, 1 H, 2-H), 6.80 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.90 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.25−7.60 (m, 10 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_2), 23.9 (CH_3), 24.0 (CH_2), 29.4 (Me), 29.4 (Me), 43.2 (CH), 43.6 (C), 69.9 (CH_2), 75.0 (C-10b), 76.1 (C-2′), 87.4 (C-2), 110.8 (CH), 123.5 (CH), 125.3 (CH), 126.0 (CH), 126.5 (CH), 127.2 (CH), 128.0 (CH), 128.0 (CH), 128.7 (CH), 136.9 (C), 137.4 (C), 143.9 (C), 156.2 (C) ppm. IR: ν_{OH} = 3550 cm^{-1}.

6Bn-fII: ^1H NMR ($CDCl_3$): δ = 1.31 (s, 3 H, Me^{eq}), 1.44 (dt, ^3J = 12.5, ^3J = ^3J = 2 Hz, 1 H, 4a-H), 1.62 (s, 3 H, CH_3), 1.71 (s, 3 H, Me^{ax}), 1.88 (m, 1 H, 5-H^{eq}), 2.16 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.61 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 2.87 (s, 1 H, OH), 3.17 (dd, ^2J = 18, ^3J = 6 Hz, 6-H^{eq}), 4.89 (s, 1 H, 10b-H), 5.14 (s, 2 H, CH_2O), 5.33 (s, 1 H, 2-H), 6.93 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.95 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.23 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.25−7.60 (m, 10 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_2), 23.9 (CH_3), 24.0 (CH_2), 29.4 (Me), 29.4 (Me), 43.0 (CH), 43.4 (C), 69.9 (CH_2), 75.2 (C-10b), 75.8 (C-2′), 87.2 (C-2), 110.6 (CH), 123.5 (CH), 125.4 (CH), 126.0 (CH), 126.5 (CH), 127.5 (CH), 128.1 (CH), 128.3 (CH), 128.7 (CH), 136.9 (C), 137.4 (C), 143.5 (C), 156.3 (C) ppm. IR: ν_{OH} = 3556 cm^{-1}.

Methyl Iodide

8Bn-aI: ^1H NMR ($CDCl_3$): δ = 1.34 (s, 3 H, Me^{eq}), 1.44 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.52 (d, ^3J = 6 Hz, 3 H, CH_3),

1.69 (s, 3 H, Me^{ax}), 1.93 (m, 1 H, 5-H^{eq}), 2.23 (dq, $^2J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.61 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 3.15 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.79 (s, 1 H, 10b-H), 5.10 (AB, J_{AB} = 12 Hz, 2 H, CH_2OH), 5.25 (q, ^3J = 6 Hz, 1 H, 2-H), 6.86 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.96 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.20 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.31−7.48 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.4 (CH_2), 22.2 (CH_3), 24.3 (CH_2), 29.6 (Me), 30.0 (Me), 43.1 (C), 43.7 (CH), 70.3 (CH_2O), 75.2 (CH), 76.2 (CH), 111.3 (CH), 123.8 (CH), 126.9 (CH), 127.5 (CH), 128.2 (C), 128.9 (CH), 137.6 (C), 137.8 (C), 156.7 (C) ppm.

Chlorotrimethylsilane

8bn-bI: ^{1}H NMR ($CDCl_3$): δ = 0.14 [s, 9 H, $Si(CH_3)_3$], 1.36 (s, 3 H, Me^{eq}), 1.43 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2 Hz, 1 H, 4a-H), 1.70 (s, 3 H, Me^{ax}), 1.91 (m, 1 H, 5-H^{eq}), 2.24 (dq, $^2J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.59 (ddd, ^2J = 18.5, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.12 (dd, ^2J = 18.5, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.63 (s, 1 H, 10b-H), 5.00 (s, 1 H, 2-H), 5.14 (AB, J_{AB} = 13 Hz, 2 H, CH_2O), 6.87 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.91 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.19 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.33−7.49 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = −3.3 [$(CH_3)_3Si$], 18.5 (CH_2), 24.6 (CH_2), 28.9 (Me), 29.8 (Me), 42.0 (C), 44.5 (CH), 70.2 (CH_2), 73.7 (CH), 76.0 (CH), 110.8 (CH), 124.0 (CH), 126.5 (CH), 127.5 (CH), 128.2 (CH), 128.9 (CH), 137.9 (C), 138.6 (C), 156.6 (C) ppm.

Deuterated Water

8Bn-cI: ^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 3 H, Me^{eq}), 1.49 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2.5 Hz, 1 H, 4a-H), 1.72 (s, 3 H, Me^{ax}), 1.97 (m, 1 H, 5-H^{eq}), 2.31 (dq, $^2J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.61 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.18 (ddd, ^2J = 18, ^3J = 6, ^3J = 1.5 Hz, 1 H, 6-H^{eq}), 4.74 (t, $^3J = {}^4J$ = 2 Hz, 1 H, 10b-H), 5.11 (AB, J_{AB} = 12 Hz, 2 H, CH_2OH), 5.24 (s, 1 H, H^{2ax}), 6.88 (dd, ^3J = 8, ^4J = 1 Hz, 1 H, H^{ar}), 6.95 (dd, ^3J = 8, ^4J = 1 Hz, 1 H, H^{ar}), 7.20 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.33−7.49 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_2), 23.9 (CH_2), 28.5 (Me), 29.5 (Me), 42.2 (C), 43.9 (CH), 67.9 (t, C-2-HD), 69.9 (CH_2O), 74.3 (C-10b), 111.0 (CH), 123.3 (CH), 126.7 (CH), 127.1 (CH), 127.9 (C), 128.7 (CH), 137.1 (C), 137.5 (C), 156.3 (C) ppm.

General Procedures for the Condensation of Hydroxy Thiol with Aldehydes. Direct Preparation of Type 8 Compounds: Boron trifluoride−diethyl ether (0.21 mmol, 0.5 equiv.) was added under argon to a cooled (ice bath), well-stirred solution of hydroxy thiol (100 mg, 0.42 mmol, 1 equiv.) and aldehyde (1.26 mmol, 3 equiv.) in dry dichloromethane (5 mL). After 15 min, the reaction mixture was loaded directly onto a silica gel column and eluted with chloroform to give the oxathiane as a clear oil. The obtained oxathiane was protected with benzyl bromide or TBDMSCl by standard procedures.[9,23]

Acetaldehyde

8Si-aI: ^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 6 H, 2 × CH_3Si), 1.04 [s, 9 H, $(CH_3)_3$], 1.34 (s, 3 H, Me^{eq}), 1.40 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2.5 Hz, 1 H, 4a-H), 1.52 (d, ^3J = 6 Hz, 3 H, CH_3), 1.69 (s, 3 H, Me^{ax}), 1.92 (m, 1 H, 5-H^{eq}), 2.21 (dq, $^2J = {}^3J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.53 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 3.03 (ddd, ^2J = 18, ^3J = 6, ^3J = 1.5 Hz, 1 H, 6-H^{eq}), 4.76 (t, $^3J = {}^4J$ = 2 Hz, 1 H, 10b-H), 5.24 (q, ^3J = 6 Hz, 1 H, 2-H), 6.75 (dd, ^3J = 7.5, ^4J = 1 Hz, 1 H, H^{ar}), 6.93 (dd, ^3J = 7.5, ^4J = 1 Hz, 1 H, H^{ar}), 7.11 (t, ^3J = 7.5 Hz, 1 H, H^{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = −4.1 (CH_3Si), −4.0 (CH_3Si), 18.2 (CH_2), 18.4 (CSi), 21.9 (CH_3), 24.7 (CH_2), 25.9 (3 × CH_3), 29.2 (Me), 29.7 (Me), 42.8 (CH), 43.3 (C), 74.9 (CH), 75.8 (CH), 117.6 (CH), 123.7 (CH), 126.4 (CH), 129.0 (C), 137.6 (C), 153.5 (C) ppm.

2-Methylpropionaldehyde

8Bn-dI: ^{1}H NMR ($CDCl_3$): δ = 1.08 (d, ^3J = 7 Hz, 3 H, CH_3), 1.12 (d, ^3J = 7 Hz, 3 H, CH_3), 1.40 (s, 3 H, Me^{eq}), 1.46 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2.5 Hz, 1 H, 4a-H), 1.73 (s, 3 H, Me^{ax}), 1.95 (m, 1 H, 5-H^{eq}), 2.03 (1 H, quint, ^3J = 6.5 Hz, CH), 2.23 (dq, $^2J = {}^3J = {}^3J$ = 12.5, ^3J = 5.5 Hz, 1 H, 5-H^{ax}), 2.64 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.19 (dd, ^2J = 18, ^3J = 5.5 Hz, 1 H, 6-H^{eq}), 4.78 (s, 1 H, 10b-H), 4.93 (d, ^3J = 6 Hz, 1 H, 2-H), 5.13 (AB, J_{AB} = 11.5 Hz, 2 H, CH_2OH), 6.90 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.98 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.23 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.35−7.55 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.5 (CH_2), 19.2 (CH_3), 19.4 (CH_3), 24.4 (CH_2), 29.9 (Me), 30.0 (Me), 34.0 (CH), 43.3 (C), 43.6 (CH), 70.2 (CH_2O), 75.2 (CH), 86.5 (CH), 111.1 (CH), 123.9 (CH), 126.8 (CH), 127.5 (CH), 128.2 (CH), 128.9 (CH), 137.9 (C), 156.7 (C) ppm.

Hexanal

8Bn-eI: ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, ^3J = 7 Hz, 3 H, CH_3CH_2), 1.25−1.57 (m, 8 H), 1.34 (s, 3 H, Me^{eq}), 1.44 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2.5 Hz, 1 H, 4a-H), 1.8 (m, 1 H), 1.69 (s, 3 H, Me^{ax}), 1.84 (m, 1 H), 1.92 (m, 1 H, 5-H^{eq}), 2.20 (dq, $^2J = {}^3J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.59 (ddd, ^2J = 18.5, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.14 (dd, ^2J = 18.5, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.75 (t, $^3J = {}^4J$ = 1.5 Hz, 1 H, 10b-H), 5.09 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 5.10 (dd, ^3J = 7, ^3J = 5.5 Hz, 1 H, 2-H), 6.86 (dd, ^3J = 8, ^4J = 1 Hz, 1 H, H^{ar}), 6.93 (dd, ^3J = 8, ^4J = 1 Hz, 1 H, H^{ar}), 7.19 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.30−7.47 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.5 (CH_3), 18.4 (CH_2), 23.0 (CH_2), 24.3 (CH_2), 26.0 (CH_2), 29.4 (CH_2), 29.6 (Me), 30.0 (Me), 32.1 (CH_2), 36.2 (CH_2), 43.5 (C), 43.5 (CH), 70.2 (CH_2O), 75.1 (CH), 80.6 (CH), 111.1 (CH), 123.8 (CH), 126.8 (CH), 127.4 (CH), 128.1 (CH), 128.9 (CH), 137.7 (C), 137.8 (C), 156.7 (C) ppm.

Cyclohexanecarbaldehyde

8Bn-fI: ^{1}H NMR ($CDCl_3$): δ = 1.30−1.60 (m, 8 H), 1.36 (s, 3 H, Me^{eq}), 1.45 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2.5 Hz, 1 H, 4a-H), 1.70 (m, 1 H), 1.71 (s, 3 H, Me^{ax}), 1.83−1.98 (m, 2 H, 5-H^{eq}+H), 2.03 (m, 1 H), 2.22 (dq, $^2J = {}^3J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.61 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 2.95 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}), 4.77 (br. s, 1 H, 10b-H), 5.11 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 5.12 (1 H, overlapped, 2-H), 6.87 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.96 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.21 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.30−7.50 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.2 (CH), 18.4 (CH_2), 22.7 (CH_2), 24.1 (CH_2), 25.8 (CH_2), 29.2 (CH_2), 29.4 (Me), 29.7 (Me), 31.8 (CH_2),35.9 (CH_2), 43.2 (CH), 43.3 (C), 69.9 (CH_2), 74.8 (CH), 80.3 (CH), 110.8 (CH), 123.5 (CH), 126.6 (C), 127.1 (CH), 127.9 (CH), 128.6 (CH), 137.3 (C), 137.5 (C), 156.4 (C) ppm.

Benzaldehyde

8Si-gI: ^{1}H NMR ($CDCl_3$): δ = 0.27 (s, 3 H, CH_3Si), 0.28 (s, 3 H, CH_3Si), 1.06 [s, 9 H, $(CH_3)_3$], 1.37 (s, 3 H, Me^{eq}), 1.50 (dt, ^3J = 12.5, $^3J = {}^3J$ = 2.5 Hz, 1 H, 4a-H), 1.81 (s, 3 H, Me^{ax}), 1.99 (m, 1 H, 5-H^{eq}), 2.39 (dq, $^2J = {}^3J = {}^3J$ = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.59 (ddd, ^2J = 18.5, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 3.09 (ddd, ^2J = 18.5, ^3J = 6, ^3J = 2 Hz, 1 H, 6-H^{eq}), 4.94 (s, 1 H, 10b-H), 6.16 (s, 1 H, 2-H), 6.76 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.93 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.08 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.25−7.35 (m, 3 H, H^{Ph}), 7.50 (dd, ^3J = 8, ^4J = 1 Hz, 2 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = −3.7 (CH_3Si), 18.7 (CH_2), 25.1 (CH_2), 26.2 (3 ×

CH_3), 29.4 (Me), 29.8 (Me), 43.3 (CH), 44.8 (C), 75.7 (CH), 81.6 (CH), 118.0 (CH), 124.3 (CH), 126.6 (CH), 127.0 (CH), 128.7 (CH), 129.4 (C), 137.9 (C), 139.7 (C), 153.7 (C).

Typical Procedure for the Preparation of Oxo Derivatives 7Bn: *t*BuLi (1.7 M in pentane, 0.23 mL, 0.38 mmol, 1.3 equiv.) was added dropwise by syringe under argon at −50 °C to oxathiane **5Bn** (100 mg, 0.29 mmol, 1 equiv.) in dry THF (6 mL). After the mixture had been stirred for 15 min, PhCN (39 μL, 0.38 mmol, 1.3 equiv.) was added dropwise by syringe. Stirring at −50 °C was continued for 60 min, 2 M HCl (1 mL) was added, and the mixture was stirred briefly at room temperature until two clear phases appeared. The organic layer was separated, and the aqueous layer was extracted four times with diethyl ether (15 mL each). The combined organic solutions were washed with water, dried with Na_2SO_4, and concentrated under vacuum to yield 150 mg of an oil. Purification by PLC with 10% of acetone in hexane gave 106 mg (80%) of the desired ketone **7Bn-a**.

7Bn-a: ^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 3 H, Me), 1.57 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.84 (s, 3 H, Me), 2.00 (m, 1 H, 5-H^{eq}), 2.32 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.64 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 3.19 (ddd, ^2J = 18, ^3J = 6, ^3J = 1.5 Hz, 1 H, 6-H^{eq}), 4.99 (d, ^3J = 1.5 Hz, 1 H, 10b-H), 5.1 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 6.44 (s, 1 H, 2-H), 6.86 (dd, ^3J = 8, ^4J = 1 Hz, 1 H, H^{ar}), 6.98 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.3−7.6 (m, 8 H, H^{Ph}), 8.14 (dd, ^3J = 8, ^4J = 1 Hz, 2 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.3 (CH_2), 24.0 (CH_2), 29.1 (Me), 29.2 (Me), 43.2 (CH), 44.7 (C), 69.9 (CH_2O), 75.8 (C-10b), 82.6 (C-2), 111.1 (CH), 123.7 (CH), 126.6 (CH), 127.2 (CH), 127.4 (C), 127.9 (CH), 128.5 (CH), 128.7 (CH), 129.8 (CH), 133.7 (CH), 134.2 (C), 136.3 (C), 137.4 (C), 156.3 (C), 192.8 (C=O) ppm. IR: ν_{CO} = 1694 cm^{-1}.

7Bn-b: ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, ^3J = 7 Hz, 3 H, CH_3), 1.36 (s, 3 H, Me), 1.46 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.70 (s, 3 H, Me), 1.91 (m, 1 H, 5-H^{eq}), 2.18 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.59 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 2.70 (dq, ^3J = 7, J = 3 Hz, 2 H, CH_2), 3.14 (ddd, ^2J = 18, ^3J = 6, ^3J = 1.5 Hz, 1 H, 6-H^{eq}), 4.78 (t, ^3J = 2 Hz, 1 H, 10b-H), 5.09 (s, 2 H, CH_2O), 5.63 (s, 1 H, 2-H), 6.90 (t, ^3J = 8 Hz, 2 H, H^{ar}), 7.18 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.3−7.55 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 7.2 (CH_3), 18.0 (CH_2), 23.9 (CH_2), 29.2 (2 × Me), 31.4 (CH_2), 42.9 (CH), 44.1 (C), 69.9 (CH_2O), 74.7 (C-10b), 83.6 (C-2), 111.0 (CH), 123.5 (CH), 126.6 (CH), 127.2 (CH), 127.9 (CH), 128.6 (CH), 136.6 (C), 137.4 (C), 156.3 (C), 206.8 (C=O) ppm. IR: ν_{CO} = 1720 cm^{-1}.

Typical Procedure for the Reduction of Oxo Derivatives 7Bn-a with Selectrides: A well-stirred solution of ketone (22 mg, 0.05 mmol) in dry toluene (1 mL) was treated at −78 °C with L-selectride® (1.0 M solution in THF, 0.1 mL 0.1 mmol, 2 equiv.). After the mixture had been stirred for 5 h at the same temperature, the excess reducing agent was quenched at −78 °C with NaOH in MeOH (1 M, 1 mL). The mixture was allowed to warm, and was extracted with diethyl ether (4 × 5 mL) and concentrated under vacuum to afford an oil that was analyzed by TLC and ^{1}H NMR before being purified by PLC.

Typical Procedure for the Reduction of Oxo Derivatives 7Bn-a with $LiAlH_4$: A well-stirred solution of ketone (24 mg, 0.05 mmol) in dry THF/Et_2O (1:1, 2 mL) was treated at −78 °C with $LiAlH_4$ (5 mg 0.1 mmol, 2 equiv.). After the mixture had been stirred for 3 h at the same temperature, the excess reducing agent was quenched at −78 °C with 1 mL of saturated aqueous NH_4Cl solution. The mixture was allowed to warm, and was extracted with diethyl ether (4 × 5 mL) and concentrated under vacuum to afford an oil that was analyzed by TLC and ^{1}H NMR before being purified by PLC.

6Bn-gII: ^{1}H NMR ($CDCl_3$): δ = 1.00 (t, ^3J = 7.5 Hz, 2 H, CH_3), 1.38 (s, 3 H, Me^{eq}), 1.46 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.5−1.7 (m, 2 H, CH_2), 1.70 (s, 3 H, Me^{ax}), 1.93 (m, 1 H, 5-H^{eq}), 2.18 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.20 (br. s, 1 H, OH), 2.60 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 3.15 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 3.76 (m, 1 H, 2′-H), 4.81 (t, ^3J = ^4J = 2 Hz, 1 H, 10b-H), 5.11 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 5.19 (d, ^3J = 4 Hz, 1 H, 2-H), 6.88 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.93 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.20 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.32−7.48 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 18.4 (CH_2), 24.3 (CH_2), 25.8 (CH_2), 29.6 (Me), 29.9 (Me), 43.3 (C), 43.7 (CH), 70.3 (CH_2O), 74.8 (CH), 75.2 (CH), 83.9 (C-2), 111.3 (CH), 123.8 (CH), 126.8 (CH), 127.4 (C), 128.2 (CH), 128.9 (CH), 137.3 (C), 137.7 (C), 156.7 (C) ppm. IR: ν_{OH} = 3412 cm^{-1}.

6Bn-gI: ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, ^3J = 7.5 Hz, 2 H, CH_3), 1.37 (s, 3 H, Me^{eq}), 1.47 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.5−1.7 (m, 2 H, CH_2), 1.70 (s, 3 H, Me^{ax}), 1.93 (m, 1 H, 5-H^{eq}), 2.17 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.60 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 2.66 (br. s, 1 H, OH), 3.14 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 3.64 (dt, ^3J = ^3J = 7.5, ^3J = 4 Hz, 1 H, 2′-H), 4.78 (br. s, 1 H, 10b-H), 5.00 (d, ^3J = 7 Hz, 1 H, 2-H), 5.11 (AB, J_{AB} = 12 Hz, 2 H, CH_2O), 6.89 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.95 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.21 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.32−7.48 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.9 (CH_3), 18.4 (CH_2), 24.2 (CH_2), 25.8 (CH_2), 29.6 (Me), 29.9 (Me), 43.3 (C), 43.5 (CH), 70.3 (CH_2O), 75.0 (CH), 75.3 (CH), 83.4 (C-2), 111.3 (CH), 123.8 (CH), 127.0 (CH), 127.5 (C), 128.2 (CH), 128.9 (CH), 137.2 (C), 137.7 (C), 156.6 (C) ppm. IR: ν_{OH} = 3426 cm^{-1}.

Typical Procedure for the Grignard Addition to Oxo Derivatives 7Bn-a: A well-stirred solution of ketone (58 mg, 0.13 mmol) in dry THF (3 mL) was treated at −78 °C with MeMgI in dry Et_2O (0.52 M, 1 mL, 0.52 mmol, 4 equiv.). After the mixture had been stirred for 5 h at the same temperature, it was quenched with 2 mL of saturated aqueous NH_4Cl solution and allowed to warm to room temperature. The mixture was extracted with diethyl ether (4 × 5 mL) and concentrated under vacuum to afford an oil that was analyzed by TLC and ^{1}H NMR spectroscopy.

6Bn-hII: ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, ^3J = 7 Hz, 3 H, CH_3), 1.35 (s, 3 H, Me^{eq}), 1.42 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.63 (s, 3 H, Me^{ax}), 1.90 (m, 1 H, 5-H^{eq}), 2.05 (m, 2 H, CH_2), 2.12 (dq, ^2J = ^3J = ^3J = 12.5, ^3J = 6 Hz, 1 H, 5-H^{ax}), 2.57 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6 Hz, 1 H, 6-H^{ax}), 2.95 (s, 1 H, OH), 3.13 (ddd, ^2J = 18, ^3J = 6, ^3J = 1 Hz, 1 H, 6-H^{eq}), 4.75 (t, ^3J = ^4J = 2 Hz, 1 H, 10b-H), 5.10 (s, 2 H, CH_2O), 5.28 (s, 1 H, 2-H), 6.72 (d, ^3J = 8 Hz, 1 H, H^{ar}), 6.86 (d, ^3J = 8 Hz, 1 H, H^{ar}), 7.14 (t, ^3J = 8 Hz, 1 H, H^{ar}), 7.32−7.55 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 7.6 (CH_3), 18.1 (CH_2), 24.0 (CH_2), 29.4 (2 × Me), 30.4 (CH_2), 43.3 (CH), 43.5 (C), 69.9 (CH_2O), 75.2 (C-10b), 87.4 (C-2), 110.8 (CH), 123.4 (CH), 125.9 (CH), 126.5 (CH), 127.1 (CH), 127.8 (CH), 128.0 (CH), 128.7 (CH), 136.9 (C), 137.4 (C), 142.4 (C), 156.2 (C) ppm. IR: ν_{OH} = 3405 cm^{-1}.

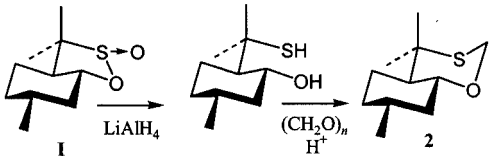
6Bn-hI: ^{1}H NMR ($CDCl_3$): δ = 0.66 (t, ^3J = 7 Hz, 3 H, CH_3), 1.26 (s, 3 H, Me^{eq}), 1.42 (dt, ^3J = 12.5, ^3J = ^3J = 2.5 Hz, 1 H, 4a-H), 1.62 (s, 3 H, Me^{ax}), 1.90 (m, 2 H, 5-H^{ax} + CH_2), 2.20 (m, 2 H, 5-H^{ax} + CH_2), 2.57 (ddd, ^2J = 18, ^3J = 12.5, ^3J = 6.5 Hz, 1 H, 6-H^{ax}), 2.63 (s, 1 H, OH), 3.14 (dd, ^2J = 18, ^3J = 6 Hz, 1 H, 6-H^{eq}),

4.89 (t, $^3J = {}^4J = 2$ Hz, 1 H, 10b-H), 5.15 (s, 2 H, CH_2O), 5.37 (s, 1 H, 2-H), 6.89 (d, $^3J = 8$ Hz, 1 H, H^{ar}), 6.94 (d, $^3J = 8$ Hz, 1 H, H^{ar}), 7.22 (t, $^3J = 8$ Hz, 1 H, H^{ar}), 7.28−7.48 (m, 5 H, H^{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 7.6 (CH_3), 18.1 (CH_2), 24.0 (CH_2), 29.3 (Me), 29.5 (CH_3), 32.3 (CH_2), 43.1 (CH), 43.3 (C), 69.9 (CH_2O), 75.1 (C-10b), 87.1 (C-2), 110.9 (CH), 123.5 (CH), 125.9 (CH), 126.5 (CH), 127.2 (CH), 127.4 (C), 127.9 (CH), 128.0 (CH), 128.7 (CH), 136.9 (C), 137.4 (C), 141.2 (C), 156.3 (C) ppm. IR: ν_{OH} = 3410 cm^{-1}.

Acknowledgments

We are grateful to the French Government (Sous-Direction des Boursiers Etrangers et des Affaires Internationales) for a grant to M. B. (No. 19991885), the Ambassade de France à Bratislava − Service de Coopération et d'Action Culturelle (M. B. Paqueteau) for encouragement and financial support to M. B. and M. S., and to M. Schmitt for NMR spectral assistance.

[1] E. L. Eliel, J. K. Koskimies, B. Lohri, *J. Am. Chem. Soc.* **1978**, *100*, 1614.
[2] E. L. Eliel, W. J. Frazee, *J. Org. Chem.* **1979**, *44*, 3598.
[3] F. Martinez-Ramos, M. E. Vargas-Diaz, L. Chacon-Garcia, J. Tamariz, P. Joseph-Nathan, L. G. Zepeda, *Tetrahedron: Asymmetry* **2001**, *12*, 3095.
[4] J. E. Lynch, E. L. Eliel, *J. Am. Chem. Soc.* **1984**, *106*, 2943.
[5] A. Solladié-Cavallo, A. Adib, *Tetrahedron* **1992**, *48*, 2453.
[6] [6a] A. Solladié-Cavallo, A. Diep-Vohuule, *J. Org. Chem.* **1995**, *60*, 3494. [6b] A. Solladié-Cavallo, A. Diep-Vohuule, V. Sunjic, V. Vinkovic, *Tetrahedron: Asymmetry* **1996**, *7*, 1783.
[7] A. Solladié-Cavallo, A. Diep-Vohuule, T. Isarno, *Angew. Chem. Int. Ed.* **1998**, *37*, 1689.
[8] As an example, compound **I**, isolated upon hydrolysis of oxathiane derivatives **4**, can be retransformed into the desired starting oxathiane



[9] A. Solladié-Cavallo, M. Balaz, M. Salisova, C. Suteu, L. Nafie, X. Cao, T. B. Freedman, *Tetrahedron: Asymmetry* **2001**, *12*, 2605.
[10] E. L. Eliel, S. Morris-Natschke, *J. Am. Chem. Soc.* **1984**, *106*, 2937.
[11] E. L. Eliel, A. A. Hartmann, A. G. Abatjoglou, *J. Am. Chem. Soc.* **1974**, *96*, 1807.
[12] R. Amstutz, D. Seebach, P. Seiler, B. Schweizer, J. D. Dunitz, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 53.
[13] D. Seebach, J. Gabriel, R. Hässig, *Helv. Chim. Acta* **1984**, *67*, 1083.
[14] W. Bauer, D. Seebach, *Helv. Chim. Acta* **1984**, *67*, 1972.
[15] H. J. Reich, J. P. Borst, R. R. Dykstra, *Tetrahedron* **1994**, *50*, 5869.
[16] E. L. Eliel, X. Bai, A. F. Abdel-Magid, R. O. Hutchins, *J. Org. Chem.* **1990**, *55*, 4951.
[17] J. Wei, R. O. Hutchins, J. Prol, Jr., *J. Org. Chem.* **1993**, *58*, 2920.
[18] S. V. Frye, E. L. Eliel, *J. Am. Chem. Soc.* **1988**, *110*, 484.
[19] K. Y. Ko, W. J. Frazee, E. L. Eliel, *Tetrahedron* **1984**, *40*, 1333.
[20] K. Fuji, M. Ueda, K. Sumi, E. Fujita, *J. Org. Chem.* **1985**, *50*, 662.
[21] R. Bellato, A. Gatti, P. Venturello, *Tetrahedron* **1992**, *48*, 2501.
[22] H. Perrier, G. Huyer, R. N. Young, *Tetrahedron Lett.* **1992**, *33*, 725.
[23] N. Watanabe, H. Kobayashi, M. Azami, M. Matsumoto, *Tetrahedron* **1999**, *55*, 6831.

Received July 29, 2002
[O02429]