Double Diastereoselection in Anti Aldol Reactions Mediated by Dicyclohexylchloroborane between An L-Erythrulose Derivative and Chiral Aldehydes

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Supporting Information

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General Features. NMR spectra were recorded at 500 MHz (\(^1\)H NMR) and 125 MHz (\(^{13}\)C NMR) in CDCl\(_3\) solution at 25 °C, if not otherwise indicated, with the solvent signals as internal reference. \(^{13}\)C NMR signal multiplicities were determined with the DEPT pulse sequence. Mass spectra were run in the EI (70 eV), the FAB (m-nitrobenzyl alcohol matrix) or the electrospray (ESMS) mode. IR data, which were measured as films on NaCl plates (oils) or as KBr pellets (solids), are given only when relevant functions (C=O, OH) are present. Optical rotations were measured at 25 °C. Reactions which required an inert atmosphere (all except those involving water in the reaction medium) were carried out under dry N\(_2\) with flame-dried glassware. Commercial reagents were used as received. THF and Et\(_2\)O were freshly distilled from sodium-benzophenone ketyl. Dichloromethane was freshly distilled from CaH\(_2\). Toluene was freshly distilled from sodium wire. Tertiary amines were freshly distilled from KOH. Unless detailed otherwise, "work-up" means pouring the reaction mixture into brine, followed by extraction with the solvent indicated in parenthesis. If the reaction medium was acidic, an additional washing of the organic layer with 5% aq NaHCO\(_3\) was performed. If the reaction medium was basic, an additional washing with aq NH\(_4\)Cl was performed. Where solutions were filtered through a Celite pad, the pad was additionally washed with the same solvent used, and the washings incorporated to the main organic layer. The latter was dried over anhydrous Na\(_2\)SO\(_4\) and the solvent was eliminated under reduced pressure. Column chromatography of the residue on a silica gel column (60-200 μm) was performed with elution with the indicated solvent mixture.
General reaction scheme

$15 \overset{(R)-3a,b}{\rightarrow} \text{Complex mixtures (+ decomp.)}$

$15_b \overset{(S)-3a,b}{\rightarrow} \text{d.r. > 95:5}$

$15_b \overset{(R)-4a,b}{\rightarrow} \text{d.r. > 95:5}$

$15_b \overset{(S)-4a,b}{\rightarrow} \text{Complex mixtures (+ decomp.)}$

$15_b \overset{(R)-9a,b,c}{\rightarrow} \text{d.r. > 95:5}$

$15_b \overset{(S)-9a,b,c}{\rightarrow} \text{d.r. > 95:5}$

S-3
**General experimental procedures**

**Experimental procedure for the one-pot aldolization/reduction.** Procedure as described in the main text up to aldehyde addition. After stirring for 5 h at −78°C, the solution was treated dropwise with a 2 M solution of LiBH₄ in THF (1.5 mL, 3 mmol). The stirring was then continued at −78°C for 2 h. The reaction was quenched with pH 7 phosphate buffer (6 mL) and MeOH (6 mL), followed by a 30% aq H₂O₂ solution (3 mL). After stirring for 1 h at room temperature, the mixture was poured into satd. aq NaHCO₃ and worked up as above. Removal of volatiles under reduced pressure and column chromatography of the residue on silica gel (hexanes-EtOAc mixtures) afforded the desired 1,3-diols. Yields are indicated in each case (see below).

**O-Methylation of alcohols with Meerwein salt.** The appropriate alcohol (1 mmol) was dissolved under N₂ in anhydrous CH₂Cl₂ and treated with trimethyloxonium tetrafluoroborate (5 mmol per hydroxyl group) and 1,8-bis(N,N-dimethylamino)naphthalene (5 mmol per hydroxyl group). The mixture was stirred at room temp. for 24 h. Work-up (extraction with CH₂Cl₂) and column chromatography on silica gel (hexanes-EtOAc mixtures) gave the desired O-methylated derivative. Yields are indicated in each case (see below).

**Formation of acetonides from 1,3-diols.** The 1,3-diol (1 mmol) and p-toluenesulfonic acid (19 mg, 0.1 mmol) were dissolved in a 4:1 acetone / 2,2-dimethoxypropane (2,2-DMP) mixture (5 mL). The mixture was then stirred at room temperature until consumption of the starting material (TLC monitoring). After adding Et₃N (0.1 mL), all volatiles were removed under reduced pressure and the residue was chromatographed on silica gel (hexanes-EtOAc mixtures).

**Formation of cyclic diol carbonates.** A solution of the diol (1 mmol) in anhydrous toluene (8 mL) was treated with CDI (carbonyl-1,1´-diimidazole, 325 mg, 2 mmol). The reaction mixture was stirred at reflux until consumption of the starting material (several hours, TLC monitoring). Removal of volatiles under reduced pressure was followed by column chromatography of the residue on silica gel (hexanes-EtOAc mixtures) to afford the cyclic carbonate. Yields are indicated in each case (see below).

**Formation of TPS derivatives.** A solution of the alcohol (1 mmol) and imidazole (170 mg, 2.5 mmol) in dry CH₂Cl₂ (4 mL) was treated dropwise under Ar with a solution of TPS chloride (1.5 mmol) in dry CH₂Cl₂ (2 mL). The reaction mixture was stirred overnight at room temp., then diluted with CH₂Cl₂ and worked up. Column chromatography on silica gel (hexanes-EtOAc mixtures) afforded the desired silyl derivative.

**Desilylation of silyl derivatives.** The silyl derivative (1 mmol) was dissolved under Ar in dry THF (3 mL). Tetra-n-butylammonium fluoride trihydrate (TBAF, 315 mg, 1.2 mmol) dissolved in dry THF (1 mL) was then added. The reaction mixture was stirred at room temp. until consumption of the starting material. After addition of an aqueous satd. NH₄Cl solution (0.1 mL), the mixture was stirred for 5 min.
and evaporated under reduced pressure. The residue was then chromatographed on silica gel (hexanes-EtOAc mixtures).

**Saponification of benzoates.** A solution of the ester (1 mmol) en MeOH (50 mL) was treated with K₂CO₃ (10 mmol) and stirred for 24 h at room temperature. After removal of volatiles under reduced pressure, the residue was diluted with water (50 mL) and extracted with Et₂O. The organic layer was dried over anhydrous Na₂SO₄ and the volatiles were eliminated under reduced pressure. Column chromatography of the residue on silica gel (hexanes-EtOAc mixtures) furnished the desired alcohol.
Chemical correlations

Aldols from $\alpha$-methyl aldehydes (S)-3a and (S)-3b

The stereostructures of aldols 17a and 17b, obtained in the aldol reactions of 15 with aldehydes (S)-3a and (S)-3b (page S-3), were established indirectly by means of chemical correlations.

Aldol 17a

In the case of the aldol reaction of 15 with (S)-3a, the intermediate boron aldolate was reduced in situ with LiBH$_4$ to yield diol 21, which was then converted into acetonide 22 (for reaction conditions, see pages S-4/S-5). The relative configuration of stereocentres C3 and C5 was established as anti-1,3 on the basis of the $^{13}$C NMR shifts of the methyl and acetal carbons in 22. The coupling constants involving H3, H4 and H5 (see below) further indicate the stereochemical relations within this carbon chain (see references in page S-27).

Oil: $[\alpha]_D +44.5$ (c 3.3; CHCl$_3$).
IR $\nu_{max}$ (cm$^{-1}$): 3470 (br, OH), 1722 (C=O).

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HR EIMS \( m/z \) (% rel. int.) 723.3597 (\( M^+-tBu \), 1), 269 (42), 105 (100). Calcd. for \( \text{C}_{43}\text{H}_{68}\text{O}_{7}\text{Si}_3-tBu \), 723.3568.

\(^1\)H NMR (500 MHz) \( \delta \) 8.16 (2H, br d, \( J \sim 7.5 \) Hz; aromatic), 7.60-7.30 (13H, br m; aromatic), 5.53 (1H, t, \( J = 6, 2.5 \) Hz; H-2), 4.10-4.05 (3H, m; H-3/H-5/OH), 3.98 (1H, dd, \( J = 10.2, 6 \) Hz; H-1), 3.94 (1H, dd, \( J = 8.6, 3.5 \) Hz; H-4), 3.87 (1H, dd, \( J = 10.2, 6 \) Hz; H-1’), 3.72 (2H, dd, \( J = 10, 3 \) Hz; H-7 overlapped by OH broad singlet), 3.60 (1H, dd, \( J = 10, 4 \) Hz; H-7’), 1.88 (1H, m; H-6), 1.02 (3H, d, \( J = 7 \) Hz; \( \text{Me}_2\text{C}_6 \)), 0.96 (9H, s; \( \text{Me}_3\text{CSi} \)), 0.89 (9H, s; \( \text{Me}_3\text{CSi} \)), 0.88 (9H, s; \( \text{Me}_3\text{CSi} \)), 0.16 (3H, s; \( \text{MeSi} \)), 0.09 (3H, s; \( \text{MeSi} \)), 0.06 (3H, s; \( \text{MeSi} \)), 0.04 (3H, s; \( \text{MeSi} \)).

\(^{13}\)C NMR (125 MHz) \( \delta \) 165.9, 132.8, 132.6, 129.6, 19.1, 18.3, 18.0 (quat C), 135.7 (x 2), 135.5 (x 2), 129.8 (x 4), 129.7, 128.3 (x 2), 127.7 (x 4), 77.1, 72.8, 72.5, 70.6, 35.0 (CH), 69.9, 62.4 (CH\(_2\)), 26.8 (x 3, \( \text{Me}_3\text{CSi} \)), 25.9 (x 6, 2 \( \text{Me}_3\text{CSi} \)), 9.2 (\( \text{Me}_2\text{C}_6 \)), −3.9 (\( \text{MeSi} \)), −4.7 (\( \text{MeSi} \)), −5.5 (x 2) (\( \text{MeSi} \)).

Oil: [\( \alpha \)]\(_D\) +1.8 (c 1.15; CHCl\(_3\)).

IR \( \nu_{max} \) (cm\(^{-1}\)): 1720 (C=O).

HR EIMS \( m/z \) (% rel. int.) 763.3949 (\( M^+-tBu \), 2), 179 (100), 105 (63). Calcd. for \( \text{C}_{46}\text{H}_{72}\text{O}_{7}\text{Si}_3-tBu \), 763.3881.

\(^1\)H NMR (500 MHz) \( \delta \) 8.08 (2H, br d, \( J \sim 7.5 \) Hz; aromatic), 7.70 (4H, m; aromatic), 7.54 (1H, br t, \( J \sim 7.5 \) Hz; aromatic), 7.45-7.35 (8H, br m; aromatic), 5.33 (1H, dt, \( J = 9, 2 \) Hz; H-2), 4.19 (1H, dd, \( J = 9, 2.2 \) Hz; H-3), 4.09 (1H, dd, \( J = 4.6, 2.2 \) Hz; H-4), 4.05 (1H, dd, \( J = 4.6, 1.8 \) Hz; H-5), 4.02 (1H, dd, \( J = 12, 2 \) Hz; H-1), 3.97 (1H, dd, \( J = 12, 2 \) Hz; H-1’), 3.66 (1H, t, \( J = 9.5 \) Hz; H-7), 3.50 (1H, dd, \( J = 9.5, 6 \) Hz; H-7’), 2.11 (1H, m; H-6), 1.37 (3H, s; acetonide Me), 1.29 (3H, s; acetonide Me), 1.07 (9H, s; \( \text{Me}_3\text{CSi} \)), 0.96 (9H, s; \( \text{Me}_3\text{CSi} \)), 0.89 (3H, d, \( J = 7 \) Hz; \( \text{Me}_2\text{C}_6 \)), 0.88 (9H, s; \( \text{Me}_3\text{CSi} \)), 0.18 (3H, s; \( \text{MeSi} \)), 0.15 (3H, s; \( \text{MeSi} \)), 0.01 (6H, s; 2 \( \text{MeSi} \)).

\(^{13}\)C NMR (125 MHz) \( \delta \) 166.2, 133.8, 133.7, 130.9, 100.4, 19.2, 18.3, 18.2 (quat C), 135.7 (x 4), 132.6, 129.5 (x 4), 128.2 (x 2), 127.6 (x 4), 74.4, 73.6, 71.8, 70.2, 38.3 (CH), 65.7, 61.7 (CH\(_2\)), 26.9 (x 3, \( \text{Me}_3\text{CSi} \)), 26.0 (x 3, \( \text{Me}_3\text{CSi} \)), 25.7 (x 3, \( \text{Me}_3\text{CSi} \)), 25.4 (acetonide Me), 23.7 (acetonide Me), 9.7 (\( \text{Me}_2\text{C}_6 \)), −2.8 (\( \text{MeSi} \)), −4.5 (\( \text{MeSi} \)), −5.4 (\( \text{MeSi} \)), −5.5 (\( \text{MeSi} \)).
The chemical shift values of the methyl acetonide carbons (25.4, 23.7 ppm) and of the acetal carbon (100.4 ppm) indicate that compound 22 is the acetonide of an anti-1,3-diol. NOE measurements, including the absence of NOE between H-3 and H-5, are consistent with this stereochemical assignment. The coupling constant values in the C3-C4-C5 segment support the configuration assignments at these stereocentres.

\[
\begin{align*}
\text{H-3} & \: \delta 4.19 \text{ (dd, } J_{2,3} = 9, J_{3,4} = 2.2 \text{ Hz)} \\
\text{H-4} & \: \delta 4.09 \text{ (dd, } J_{3,4} = 2.2 \text{ Hz, } J_{4,5} = 4.6 \text{ Hz)} \\
\text{H-5} & \: \delta 4.05 \text{ (dd, } J_{5,6} = 1.8 \text{ Hz, } J_{4,5} = 4.6 \text{ Hz)}
\end{align*}
\]

NOEs indicate that H-3 and H-5 are on opposite sides of the ring.

Compound 21, obtained as described above (page S-6), was methylated with Meerwein salt to 23 and then debenzoylated by means of alkaline hydrolysis (for reaction conditions, see pages S-4/S-5). The intermediate alcohol was desilylated with TBAF and then selectively resilylated at the two primary alcohol functions to give diol 24, which was subsequently converted into acetonide 25. The relative configuration of stereocentres C2 and C4 in the latter compound was established as syn-1,3 on the basis of the $^{13}$C NMR shifts of the methyl and acetal carbons. The coupling constants involving H2, H3 and H4 further indicate the stereochemical relations within this carbon chain.
Oil: \([\alpha]_D^0 +9.2 \text{ (c 1.68; CHCl}_3\).\

IR \(\nu_{\text{max}} \text{ (cm}^{-1}\)) 1724 (C=O).

HR EIMS \(m/z \) (% rel. int.) 751.3941 (M\(^+\)–tBu, 8), 179 (74), 105 (100). Calcd. for C\(_{45}\)H\(_{72}\)O\(_7\)Si\(_3\)–tBu, 751.3881.

\(^1\)H NMR (500 MHz) \(\delta 8.12 \text{ (2H, br d, } J \sim 8 \text{ Hz; aromatic), 7.70 \text{ (4H, br t, } J \sim 6 \text{ Hz; aromatic), 7.56 \text{ (1H, br t, } J \sim 7.3 \text{ Hz; aromatic), 7.45-7.35 \text{ (8H, br m; aromatic), 5.40 \text{ (1H, apparent q, } J \sim 5.3 \text{ Hz; H-2), 4.02 \text{ (1H, t, } J = 5.5 \text{ Hz; H-4), 3.92 \text{ (1H, dd, } J = 10.3, 6 \text{ Hz; H-1), 3.88 \text{ (1H, dd, } J = 10.3, 5.6 \text{ Hz; H-1’), 3.65 \text{ (2H, m; H-3/H-7), 3.55-3.50 \text{ (2H, m; H-5/H-7), 3.54 \text{ (3H, s; OMe), 3.33 \text{ (3H, s; OMe), 2.19 \text{ (1H, m; H-6), 1.10 \text{ (9H, s; Me}_3\text{CSi), 0.96 \text{ (9H, s; Me}_3\text{CSi), 0.93 \text{ (3H, d, } J = 7 \text{ Hz; Me-C6), 0.89 \text{ (9H, s; Me}_3\text{CSi), 0.16 \text{ (3H, s; MeSi), 0.09 \text{ (3H, s; MeSi), 0.06 \text{ (3H, s; MeSi), 0.05 \text{ (3H, s; MeSi).}}}

\(^{13}\)C NMR (125 MHz) \(\delta 165.8, 133.9 \text{ (x 2), 130.5, 19.3, 18.5, 18.1 \text{ (quat C), 135.7 \text{ (x 2), 135.6 \text{ (x 2), 132.8, 129.8 \text{ (x 2), 129.5 \text{ (x 2), 128.3 \text{ (x 2), 127.7 \text{ (x 4), 81.3, 79.8, 75.2, 72.5, 37.2 \text{ (CH), 66.7, 61.3 \text{ (CH}_2\), 61.2 \text{ (OMe), 59.5 \text{ (OMe), 26.9 \text{ (x 3, Me}_3\text{CSi), 26.2 \text{ (x 3, Me}_3\text{CSi), 25.8 \text{ (x 3, Me}_3\text{CSi), 11.4 \text{ (Me-C6), -3.8 \text{ (MeSi), -4.0 \text{ (MeSi), -5.5 \text{ (x 2) (MeSi).}}}}

Oil: \([\alpha]_D^0 +4.1 \text{ (c 0.8; CHCl}_3\).

IR \(\nu_{\text{max}} \text{ (cm}^{-1}\)) 3460 (br, OH).

HR FABMS \(m/z \) 715.3877 (M+H\(^+\)). Calcd. for C\(_{42}\)H\(_{59}\)O\(_6\)Si\(_2\), 715.3844.

\(^1\)H NMR (500 MHz) \(\delta 7.75-7.70 \text{ (8H, br m; aromatic), 7.50-7.35 \text{ (12H, br m; aromatic), 3.97 \text{ (1H, apparent quint, } J \sim 4.5 \text{ Hz; H-2), 3.85-3.80 \text{ (2H, m; H-1/H-1’), 3.75-3.65 \text{ (3H, br m; H-4/H-7/H-7’), 3.63 \text{ (5H, br s; OMe signal overlapping the signals of H-3 and H-5), 3.48 \text{ (3H, s; OMe), 2.80 \text{ (1H, br d, } J = 4\) \text{ Hz; OH).}}}

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Hz; OH), 2.70 (1H, br s; OH), 2.24 (1H, m; H-6), 1.11 (9H, s; Me3Si), 1.10 (9H, s; Me3Si), 0.88 (3H, d, J = 7 Hz; Me-C6).

13C NMR (125 MHz) δ 133.7, 133.6, 133.2, 133.1, 19.2 (x 2) (quat C), 135.6 (x 4), 135.5 (x 4), 129.8 (x 2), 129.6 (x 2), 127.7 (x 4), 127.6 (x 4), 79.9, 78.6, 74.0, 72.1, 36.5 (CH), 66.3, 64.4 (CH2), 60.8 (OMe), 59.9 (OMe), 26.9 (x 3, Me3Si), 26.8 (x 3, Me3Si), 10.1 (Me-C6).

Oil: [α]D +12.2 (c 0.9; CHCl3).

HR EIMS m/z (% rel. int.) 739.3869 (M+–tBu, 2), 213 (100). Calcd. for C45H62O6Si2–tBu, 739.3850.

1H NMR (500 MHz) δ 7.75-7.65 (8H, br m; aromatic), 7.45-7.35 (12H, br m; aromatic), 3.93 (1H, br dd, J ~ 9, 8.3 Hz; H-1), 3.88 (1H, br dd, J ~ 8.3, 4.8 Hz; H-2), 3.80 (1H, br d, J ~ 8.5 Hz; H-5), 3.75-3.70 (2H, m; H-1’/H-7), 3.64 (1H, br d, J ~ 8.5 Hz; H-4), 3.60 (1H, m; H-7’), 3.58 (3H, s; OMe), 3.48 (3H, s; OMe), 3.45 (1H, br s; H-3), 2.21 (1H, m; H-6), 1.36 (3H, s; acetone Me), 1.30 (3H, s; acetone Me), 1.09 (9H, s; Me3Si), 1.08 (9H, s; Me3Si), 0.85 (3H, d, J = 7 Hz; Me-C6).

13C NMR (125 MHz) δ 134.1, 133.9, 133.5, 133.4, 98.5, 19.3, 19.2 (quat C), 135.7 (x 4), 135.6 (x 4), 129.7 (x 2), 129.5 (x 2), 127.7 (x 4), 127.6 (x 4), 78.2, 73.5, 72.1, 71.3, 36.1 (CH), 66.5, 62.8 (CH2), 60.6 (OMe), 60.0 (OMe), 29.5 (acetone Me), 26.9 (x 6, 2 Me3Si), 18.7 (acetone Me), 10.1 (Me-C6).

The chemical shift values of the methyl acetonide carbons (29.5, 18.7 ppm) and of the acetal carbon (98.5 ppm) indicate that compound 25 is the acetonide of an syn-1,3-diol. The observed NOEs confirm this conclusion.
**Aldol 17b**

In the case of the aldol reaction of 15 with (S)-3b, the intermediate boron aldolate was reduced in situ with LiBH₄ to yield diol 26, which was then converted into cyclic carbonate 27 through reaction with CDI (for reaction conditions, see pages S-4/S-5). The relative configuration of stereocentres C3, C4 and C5 in 27 was established as depicted on the basis of the coupling constants involving H3/H4/H5.

Oil: [α]D +32.5 (c 0.4; CHCl₃).
IR ν_{max} (cm⁻¹): 3470 (br, OH), 1723 (C=O).
HR FABMS m/z 633.3638 (M+H⁺). Calcd. for C₃₄H₅₇O₇Si₂, 633.3642.

**¹H NMR (500 MHz)** δ 8.12 (2H, br d, J ~ 8 Hz; aromatic), 7.52 (1H, br t, J ~ 7.5 Hz; aromatic), 7.42 (2H, br t, J ~ 7.5 Hz; aromatic), 7.30-7.25 (3H, br m; aromatic), 7.12 (2H, m; aromatic), 5.46 (1H, br td, J ~ 5.5, 3.5 Hz; H-2), 4.28, 4.24 (2H, AB system, J = 11.7 Hz; benzyl CH₂), 4.07 (1H, br dt, J ~ 9.2, 3.5 Hz; H-3), 4.00-3.90 (5H, br m; H-1/H-4/H-5/2 OH), 3.85 (1H, dd, J = 10.2, 5.5 Hz; H-1’), 3.45 (2H, m; H-7/H-7’), 1.97 (1H, m; H-6), 1.02 (3H, d, J = 7 Hz; Me-C6), 0.90 (9H, s; Me₃Si), 0.88 (9H, s; Me₃Si), 0.14 (3H, s; MeSi), 0.09 (3H, s; MeSi), 0.06 (3H, s; MeSi), 0.04 (3H, s; MeSi).

**¹³C NMR (125 MHz)** δ 166.1, 137.8, 130.6, 18.3, 18.0 (quat C), 132.9, 129.8 (x 2), 128.4 (x 2), 128.3 (x 2), 127.6, 127.4 (x 2), 77.0, 72.8, 72.6, 70.6, 34.0 (CH), 76.3, 73.4, 62.4 (CH₂), 25.9 (x 6, 2 Me₃Si), 9.9 (Me-C6), −3.9 (MeSi), −4.7 (MeSi), −5.5 (x 2) (MeSi).
Oil: \([\alpha]_D +50\) (c 1; CHCl₃).

IR \(\nu_{\text{max}}\) (cm\(^{-1}\)): 1765, 1728 (C=O).

HR FABMS \(m/z\) 659.3420 (M+H\(^+\)). Calcd. for C\(_{35}\)H\(_{55}\)O\(_8\)Si\(_2\), 659.3435.

\(^1\)H NMR (500 MHz) \(\delta\) 7.99 (2H, br d, \(J \approx 8\) Hz; aromatic), 7.48 (1H, br t, \(J \approx 7.5\) Hz; aromatic), 7.36 (2H, br t, \(J \approx 7.5\) Hz; aromatic), 7.25-7.20 (3H, br m; aromatic), 7.07 (2H, m; aromatic), 5.48 (1H, dt, \(J = 6.5, 4.5\) Hz; H-2), 4.83 (1H, br t, \(J \approx 4.5\) Hz; H-3), 4.47 (1H, dd, \(J = 6.8, 4.4\) Hz; H-5), 4.27 (1H, dd, \(J = 6.8, 4.5\) Hz; H-4), 4.20, 4.14 (2H, AB system, \(J = 12\) Hz; benzyl CH\(_2\)), 3.90 (1H, dd, \(J = 10.3, 6.5\) Hz; H-1), 3.83 (1H, dd, \(J = 10.3, 4.5\) Hz; H-1'), 3.35-3.25 (2H, m; H-7/H-7'), 2.04 (1H, m; H-6), 0.96 (3H, d, J = 7 Hz; Me-C6), 0.88 (9H, s; Me\(_3\)Si), 0.87 (9H, s; Me\(_3\)Si), 0.08 (3H, s; MeSi), 0.06 (3H, s; MeSi), 0.03 (6H, s; 2 MeSi).

\(^{13}\)C NMR (125 MHz) \(\delta\) 165.1, 148.4, 137.8, 129.4, 18.3, 17.9 (quat C), 133.3, 129.8 (x 2), 128.4 (x 2), 128.3 (x 2), 127.5, 127.3 (x 2), 81.7, 75.8, 71.1, 62.5, 35.0 (CH), 73.0, 71.2, 60.2 (CH\(_2\)), 25.8 (x 3, Me\(_3\)Si), 25.6 (x 3, Me\(_3\)Si), 10.5 (Me-C6), −4.4 (MeSi), −4.6 (MeSi), −5.5 (x 2) (MeSi).

The absence of NOE between H-3 and H-5 suggests that compound 27 is the carbonate of an \textit{anti}-1,3-diol. This conclusion is further supported by the NOEs between the hydrogen pairs H-2/H-5 and H-3/H-6. The coupling constant values in the C3-C4-C5 segment are consistent with this conclusion\(^3\) and indicate the relative configurations at these three stereocentres.
**Aldols from α-oxygenated aldehydes**

The stereostructures of the aldols 18a and 18b, generated in the reactions of 15 with α-oxygenated aldehydes (R)-4a and (R)-4b (page S-3), were determined by means of a combination of chemical correlations and X-ray diffraction analyses.

- Aldol reaction of 15 and (R)-4a followed by reduction in situ with LiBH₄ (for reaction conditions, see pages S-4/S-5) gave diol 28. The diol was crystalline and could be analyzed by means of X-ray diffraction. This established the absolute configuration of aldol 18a in an unambiguous way.
- Aldol reaction of 15 and (R)-4b followed by reduction in situ with LiBH₄ (page S-4) gave diol 28. Treatment of the latter with CDI (for reaction conditions, see pages S-4/S-5) afforded the crystalline carbonate 30, which was analyzed by means of X-ray diffraction. This established the absolute configuration of aldol 18b in an unambiguous way.
Solid: mp 83-84 °C (CHCl₃/CH₂Cl₂); [α]₀ +43.5 (c 1.05; CHCl₃).

IR ν_max (cm⁻¹): 3500 (br, OH), 1722 (C=O).

HR FABMS m/z 767.4191 (M+H⁺). Calcd. for C₄₂H₆₇O₇Si₃, 767.4194.

¹H NMR (500 MHz) δ 8.16 (2H, br d, J ~ 7.5 Hz; aromatic), 7.60-7.30 (13H, br m; aromatic), 5.46 (1H, dt, J = 6, 2.5 Hz; H-2), 4.05-3.95 (2H, m; H-6/OH), 3.93 (1H, dd, J = 10, 7 Hz; H-4), 3.90-3.80 (4H, br m; H-1/H-1’/H-3/H-5), 2.90 (1H, br s; OH), 0.97 (3H, d, J = 6.5 Hz; H-7), 0.88 (9H, s; Me₃CSi), 0.85 (9H, s; Me₃CSi), 0.74 (9H, s; Me₃CSi), 0.07 (6H, s; 2 Me₂Si), 0.05 (3H, s; MeSi), −0.12 (3H, s; MeSi).

¹³C NMR (125 MHz) δ 165.7, 134.8, 134.1, 130.4, 18.9, 18.4, 17.8 (quat C), 135.7 (x 4), 133.0, 129.8 (x 4), 128.3 (x 2), 127.7 (x 2), 127.5 (x 2), 77.3, 72.3 (x 2), 70.5, 69.8 (CH), 61.8 (CH₂), 26.8 (x 3, Me₃CSi), 25.9 (x 3, Me₃CSi), 25.7 (x 3, Me₃CSi), 15.3 (C7), −3.9 (MeSi), −4.9 (MeSi), −5.4 (MeSi), −5.5 (MeSi).

The definitive assignment came from an X-ray diffraction analysis (data deposited at the Cambridge Crystallographic Data Centre; deposition number: CCDC-880798).

Two views of the molecule of compound 28
Oil: $[\alpha]_D +21.2$ (c 1.5; CHCl$_3$).

IR $\nu_{\text{max}}$ (cm$^{-1}$): 3490 (br, OH), 1722 (C=O).

HR FABMS $m/z$ 619.3492 (M+H$^+$$)$. Calcd. for C$_{33}$H$_{55}$O$_7$Si$_2$, 619.3486.

$^1$H NMR (500 MHz) $\delta$ 8.12 (2H, br d, $J \sim 7.5$ Hz; aromatic), 7.57 (1H, br t, $J \sim 7.5$ Hz; aromatic), 7.43 (2H, br t, $J \sim 7.5$ Hz; aromatic), 7.30-7.25 (3H, br m; aromatic), 7.15 (2H, m; aromatic), 5.44 (1H, apparent q, $J \sim 5$ Hz; H-2), 4.43 (1H, d, $J = 11.5$ Hz; benzyl CH$_2$), 4.33 (1H, d, $J = 11.5$ Hz; benzyl CH$_2$), 4.12 (1H, dt, $J = 9$, 3.5 Hz; H-3), 3.98 (1H, dd, $J = 6.5$, 3.5 Hz; H-4), 3.95-3.90 (2H, m; H-1/H-5), 3.83 (1H, dd, $J = 10.5$, 5.5 Hz; H-1’), 3.67 (1H, apparent quint, $J \sim 6$ Hz; H-6), 3.60 (1H, d, $J = 9$ Hz; 3-OH), 2.90 (1H, d, $J = 3$ Hz; 5-OH), 1.22 (3H, d, $J = 6$ Hz; H-7), 0.90 (9H, s; Me$_3$CSi), 0.87 (9H, s; Me$_3$CSi), 0.13 (3H, s; MeSi), 0.08 (3H, s; MeSi), 0.04 (3H, s; MeSi), 0.02 (3H, s; MeSi).

$^{13}$C NMR (125 MHz) $\delta$ 166.2, 138.2, 130.4, 18.3, 18.1 (quat C), 133.0, 129.8 (x 2), 128.4 (x 4), 127.6 (x 3), 75.4, 75.0, 73.4, 72.0, 70.8 (CH), 70.4, 62.4 (CH$_2$), 25.9 (x 6, 2 Me$_3$CSi), 13.9 (C7), −4.1 (MeSi), −4.5 (MeSi), −5.4 (x 2) (MeSi).

Solid: mp 121-122 ºC (from Et$_2$O-pentane); $[\alpha]_D +33$ (c 2; CHCl$_3$).

IR $\nu_{\text{max}}$ (cm$^{-1}$): 1768, 1723 (C=O).

HR FABMS $m/z$ 645.3275 (M+H$^+$$)$. Calcd. for C$_{34}$H$_{53}$O$_8$Si$_2$, 645.3279.

$^1$H NMR (500 MHz) $\delta$ 8.05 (2H, br d, $J \sim 7.5$ Hz; aromatic), 7.57 (1H, br t, $J \sim 7.5$ Hz; aromatic), 7.44 (2H, br t, $J \sim 7.5$ Hz; aromatic), 7.35-7.20 (5H, br m; aromatic), 5.42 (1H, dt, $J \sim 6.5$, 3 Hz; H-2), 5.10
(1H, dd, $J \sim 6.5, 3$ Hz; H-3), 4.60 (1H, d, $J = 11.5$ Hz; benzyl CH$_2$), 4.46 (1H, d, $J = 11.5$ Hz; benzyl CH$_2$), 4.46 (1H, H-4, signal overlapped by benzyl CH), 4.28 (1H, dd, $J = 5, 3.3$ Hz; H-5), 4.00 (1H, dd, $J = 11.5, 4$ Hz; H-1), 3.93 (1H, dd, $J = 11.5, 3$ Hz; H-1’), 3.67 (1H, apparent quint, $J \sim 6$ Hz; H-6), 1.30 (3H, d, $J = 6.5$ Hz; H-7), 0.92 (9H, s; Me$_3$Si), 0.84 (9H, s; Me$_3$CSi), 0.14 (6H, s; 2 MeSi), −0.01 (3H, s; MeSi), −0.02 (3H, s; MeSi).

$^{13}$C NMR (125 MHz) $\delta$ 165.6, 147.9, 137.5, 129.8, 18.2, 18.0 (quat C), 133.2, 129.8 (x 2), 128.4 (x 4), 127.6 (x 3), 85.0, 77.3, 74.1, 73.1, 61.9 (CH), 71.6, 61.0 (CH$_2$), 25.6 (x 6, 2 Me$_3$Si), 15.5 (C7), −4.1 (MeSi), −4.5 (MeSi), −5.4 (x 2) (MeSi).

The absence of NOE between H-3 and H-5 suggests that 30 is the carbonate of an anti-1,3-diol. This is confirmed by the NOEs between H-3 and H-6. The coupling constant values in the C3-C4-C5 segment support this conclusion and indicate the relative configurations at these stereocentres. The definitive assignment came from an X-ray diffraction analysis (data deposited at the Cambridge Crystallographic Data Centre; deposition number: CCDC-762867).

Two views of the molecule of compound 30
Aldols from \( \alpha \)-amino aldehydes

The stereostructures of the aldols 19a-c and 20a-c, generated in the reactions of 15 with \( \alpha \)-amino aldehydes (R)- and (S)-9a,b,c (page S-3), respectively, were determined by means of a combination of chemical correlations and X-ray diffraction analyses.

Aldol reactions with aldehydes (R)-9a,b,c

- Reduction of aldol 19a with LiBH₄ (page S-4) yielded a 1,3-diol as a mixture of diastereoisomers. The chromatographic separation of the mixture proved difficult but gave a fraction from which diol 31 could be crystallized and then analyzed by means of X-ray diffraction. This unambiguously establishes the absolute configuration of 19a.

- Reduction of aldol 19b with LiBH₄ (page S-4) yielded the crystalline 1,3-diol 32, which was analyzed by means of X-ray diffraction. This unambiguously establishes the absolute configuration of 19b.
Aldol reaction of 15 and (R)-9c followed by reduction in situ with LiBH₄ (page S-4) gave a major 1,3-diol as an inseparable mixture with a minor diastereoisomer. Treatment of the mixture with CDI (page S-5) followed by chromatographic separation afforded carbonate 33. No crystalline derivatives could be obtained in this case for X-ray diffraction analysis. However, NOE measurements in 33 (see below) indicate the same relative configuration within the C3-C4-C5 segment, which strongly suggests that the steric course of this aldol reaction is the same demonstrated for the other cases. This establishes the absolute configuration of aldol 19c.
Solid: mp 102-103 °C (from MeOH/Et₂O/CH₂Cl₂); [α]₀ +28.1 (c 3; CHCl₃).
IR: 3470 (br, OH), 1721 (C=O) cm⁻¹
HR ESMS m/z 708.4117 (M+H+). Calcd. for C₄₀H₆₂NO₆Si₂, 708.4115.

¹H NMR (500 MHz) δ 8.20 (2H, br d, J ~ 8 Hz; aromatic), 7.60 (1H, br t, J ~ 7.5 Hz; aromatic), 7.49 (2H, br t, J ~ 7.5 Hz; aromatic), 7.30-7.20 (10H, br m; aromatic), 5.44 (1H, m; H-2), 4.10-3.70 (6H, br m; H-1/H-1’/H-3/H-4/H-5/OH), 3.60, 3.55 (5H, AB system, J = 14 Hz; benzyl CH₂ signal overlapping an OH signal), 2.98 (1H, m; H-6), 1.20 (3H, d, J = 6.8 Hz; H-7), 0.90 (9H, s; Me₃Si), 0.82 (9H, s; Me₂C), 0.09 (3H, s; MeSi), 0.07 (3H, s; MeSi), 0.05 (3H, s; MeSi), −0.08 (3H, s; MeSi).

¹³C NMR (125 MHz) δ 166.3, 140.2 (x 2), 130.3, 18.1, 18.0 (quat C), 133.1, 129.8 (x 2), 128.5 (x 4), 128.3 (x 4), 128.2 (x 2), 126.6 (x 2), 75.6, 73.5, 73.3, 71.0, 53.9 (CH), 64.1, 54.3 (x 2) (CH₂), 25.7 (x 6, 2 Me₂C), 8.5 (C7), −4.5 (MeSi), −4.7 (MeSi), −5.5 (x 2) (MeSi).

The definitive stereochemical assignment of 31 came from an X-ray diffraction analysis (data deposited at the Cambridge Crystallographic Data Centre; deposition number: CCDC 766571).

Two views of the molecule of compound 31
Solid: mp 50-51 ºC (from Et2O/CH2Cl2); [α]D +10.2 (c 0.4; CHCl3).

IR: 3450 (br, OH), 1723 (C=O) cm⁻¹

HR FABMS m/z 784.4427 (M+H+). Calcd. for C₄₆H₆₆NO₆Si₂, 784.4428.

¹H NMR (500 MHz) δ 8.25 (2H, br d, J ~ 8 Hz; aromatic), 7.65 (1H, br t, J ~ 7.5 Hz; aromatic), 7.54 (2H, br t, J ~ 7.5 Hz; aromatic), 7.40-7.10 (11H, br m; aromatic), 6.90 (4H, m; aromatic), 5.50 (1H, m; H-2), 4.30 (1H, br d, J = 8 Hz; OH), 4.15 (1H, br s; OH), 4.13 (1H, dd, J = 11.4, 3 Hz; H-1), 4.10 (1H, m; H-3), 3.95 (1H, m; H-5), 3.91 (1H, dd, J = 11.4, 4 Hz; H-1'), 3.88 (1H, dd, J = 7.8, 4 Hz; H-4), 3.70 (2H, d, J = 14.5 Hz; benzyl CH₂), 3.25 (2H, d, J = 14.5 Hz; benzyl CH₂), 3.20-3.15 (2H, m; H-6/H-7), 2.95 (1H, br d, J = 11.3 Hz; H-7'), 0.91 (9H, s; Me₃CSi), 0.81 (9H, s; Me₃CSi), 0.08 (6H, s; 2 MeSi), 0.06 (3H, s; MeSi), −0.17 (3H, s; MeSi).

¹³C NMR (125 MHz) δ 166.2, 140.6, 140.2 (x 2), 130.2, 18.2, 18.0 (quat C), 133.3, 130.1 (x 2), 130.0 (x 2), 128.5 (x 6), 127.9 (x 6), 126.4 (x 2), 125.7, 75.3, 72.0, 71.7, 71.2, 58.6 (CH), 65.5, 53.9 (x 2), 31.4 (CH₂), 25.9 (x 3, Me₃CSi), 25.7 (x 3, Me₃CSi), −4.4 (MeSi), −4.6 (MeSi), −5.6 (x 2) (MeSi).

The definitive stereochemical assignment of 32 came from an X-ray diffraction analysis (data deposited at the Cambridge Crystallographic Data Centre; deposition number: CCDC 764882).

Two views of the molecule of compound 32
Oil: [α]D +22 (c 1.35; CHCl₃).

IR: 1767, 1730 (C=O) cm⁻¹

HR ESMS m/z 988.5032 (M+H⁺). Calcd. for C₅₇H₇₈NO₈Si₃, 988.5035.

¹H NMR (500 MHz) δ 8.16 (2H, br d, J ~ 7.5 Hz; aromatic), 7.76 (2H, br d, J ~ 7 Hz; aromatic), 7.67 (2H, br d, J ~ 7 Hz; aromatic), 7.60 (1H, br t, J ~ 7.5 Hz; aromatic), 7.50-7.40 (9H, m; aromatic), 7.20 (5H, m; aromatic), 7.10 (4H, br m; aromatic), 5.69 (1H, ddd, J = 7.8, 5.8, 2.5 Hz; H-2), 4.72 (1H, dd, J = 7.3, 3 Hz; H-5), 4.66 (1H, dd, J = 7.3, 4.8 Hz; H-4), 4.63 (1H, dd, J = 4.8, 2.5 Hz; H-3), 4.20 (1H, dd, J = 10.7, 7.3 Hz; H-7), 4.02 (1H, dd, J = 10.7, 5 Hz; H-7'), 3.95 (1H, dd, J = 9.8, 7.8 Hz; H-1), 3.86 (1H, dd, J = 9.8, 5.8 Hz; H-1'), 3.60 (2H, d, J = 14.3 Hz; benzyl CH₂), 3.39 (2H, d, J = 14.3 Hz; benzyl CH₂), 3.10 (1H, m; H-6), 1.11 (9H, s; Me₃CSi), 0.91 (9H, s; Me₃CSi), 0.87 (9H, s; Me₃CSi), 0.13 (3H, s; MeSi), 0.09 (3H, s; MeSi), −0.03 (3H, s; MeSi), −0.29 (3H, s; MeSi).

¹³C NMR (125 MHz) δ 165.0, 147.5, 139.1 (x 2), 132.8, 132.4, 129.8, 19.1, 18.3, 17.8 (quat C), 135.6 (x 2), 135.5 (x 2), 133.5, 130.0 (x 3), 129.8, 128.7 (x 2), 128.3 (x 4), 128.1 (x 4), 128.0 (x 2), 127.8 (x 2), 126.9 (x 2), 80.3, 75.4, 70.7, 62.3, 58.5 (CH), 60.5, 60.1, 54.6 (x 2) (CH₂), 26.9 (x 3, Me₃CSi), 25.8 (x 6, 2 Me₃CSi), −4.7 (MeSi), −4.8 (MeSi), −5.4 (MeSi), −5.5 (MeSi).

The absence of NOE between H-3 and H-5 suggests that 33 is the carbonate of an anti-1,3-diol. This conclusion is further supported by the NOEs between the hydrogen pairs H-2/H-5 and H-3/H-6. The coupling constant values in the C₃-C₄-C₅ segment are consistent with this conclusion and indicate the relative configurations at these three stereocentres.
Aldol reactions with aldehydes (S)-9a,b,c

- Aldol reaction of 15 and (S)-9a followed by reduction in situ with LiBH₄ (for reaction conditions, see pages S-4/S-5) gave diol 34. Treatment of the latter with CDI (for reaction conditions, see pages S-4/S-5) afforded the crystalline carbonate 35, which was analyzed by means of X-ray diffraction. This unambiguously establishes the absolute configuration of aldol 20a.

- Aldol reaction of 15 and (S)-9b followed by reduction in situ with LiBH₄ gave diol 36. Treatment of the latter with CDI afforded the crystalline carbonate 37, which was analyzed by means of X-ray diffraction. This unambiguously establishes the absolute configuration of aldol 20b.

- An analogous aldolization-reduction-carbonylation sequence was performed in the case of the reaction of 15 with (S)-9c to yield first diol 38 and then cyclic carbonate 39. Unfortunately, no crystalline derivatives could be obtained in this case for X-ray diffraction analysis. However, NOE measurements (see below) indicate the same relative configuration within the C3-C4-C5 segment, which strongly suggests that the steric course of this aldol reaction is the same demonstrated for the other cases. This establishes the absolute configuration of aldol 20c.
Oil: $[\alpha]_D^{11.1}$ (c 1; CHCl$_3$).

IR: 3480 (br, OH), 1721 (C=O) cm$^{-1}$

HR FABMS $m/z$ 708.4111 (M+H$^+$). Calcd. for C$_{40}$H$_{62}$NO$_6$Si$_2$, 708.4115.

$^1$H NMR (500 MHz) $\delta$ 8.21 (2H, br d, $J \sim 8$ Hz; aromatic), 7.57 (1H, br t, $J \sim 7.5$ Hz; aromatic), 7.45-7.30 (12H, br m; aromatic), 5.36 (1H, td, $J \sim 6$, 3 Hz; H-2), 5.20 (1H, br s; OH), 4.00-3.95 (3H, m; H-1/H-1/ H-3), 3.90 (1H, br s; OH), 3.80 (3H, H-4, signal overlapped by benzyl CH$_2$), 3.40 (2H, d, $J = 13.7$ Hz; benzyl CH$_2$), 3.65 (1H, dd, $J = 9.2$, 4 Hz; H-5), 2.88 (1H, dq, $J = 9.2$, 6.8 Hz; H-6), 1.20 (3H, s; Me$_7$), 0.96 (9H, s; Me$_3$CSi), 0.95 (9H, s; Me$_3$CSi), 0.14 (3H, s; MeSi), 0.12 (3H, s; MeSi), 0.10 (3H, s; MeSi), −0.09 (3H, s; MeSi).

$^{13}$C NMR (125 MHz) $\delta$ 166.1, 138.4 (x 2), 130.5, 18.3, 18.0 (quat C), 132.7, 129.8 (x 2), 129.1 (x 4), 128.5 (x 4), 128.1 (x 2), 127.4 (x 2), 74.2, 73.8, 73.3, 70.3, 55.9 (CH), 61.6, 53.3 (x 2) (CH$_2$), 25.9 (x 3, Me$_3$CSi), 25.8 (x 3, Me$_3$CSi), 9.9 (C7), −4.5 (MeSi), −4.7 (MeSi), −5.5 (x 2) (MeSi).

Solid: mp 125-126 °C (from Et$_2$O-pentane); $[\alpha]_D^{18.1}$ (c 1; CHCl$_3$).

IR: 1763, 1723 (C=O) cm$^{-1}$

HR FABMS $m/z$ 734.3918 (M+H$^+$). Calcd. for C$_{41}$H$_{60}$NO$_7$Si$_2$, 734.3908.

$^1$H NMR (500 MHz) $\delta$ 8.06 (2H, br d, $J \sim 8$ Hz; aromatic), 7.59 (1H, br t, $J \sim 7.5$ Hz; aromatic), 7.50-7.25 (12H, br m; aromatic), 5.35 (1H, dt, $J \sim 7.5$, 3 Hz; H-2), 4.51 (1H, br d, $J = 7.7$ Hz; H-3), 4.39 (1H, br d, $J = 9.2$ Hz; H-5), 4.14 (1H, br s; H-4), 3.98 (1H, dd, $J = 12$, 2.5 Hz; H-1), 3.90 (1H, dd, $J = 12$, 2.5 Hz; H-1).
Hz; H-1”), 3.89 (2H, d, J = 13.5 Hz; benzyl CH₂), 3.61 (2H, d, J = 13.5 Hz; benzyl CH₂), 3.03 (1H, dq, J = 9.2, 6.8 Hz; H-6), 1.14 (3H, d, J = 6.8 Hz; H-7), 0.93 (9H, s; Me₃CSi), 0.80 (9H, s; Me₃CSi), 0.13 (6H, s; 2 MeSi), −0.03 (3H, s; MeSi), −0.07 (3H, s; MeSi).

¹³C NMR (125 MHz) δ 165.6, 147.5, 139.3 (x 2), 129.9, 18.0, 17.9 (quat C), 133.2, 129.8 (x 2), 128.8 (x 4), 128.5 (x 4), 128.3 (x 2), 127.1 (x 2), 85.2, 76.9, 73.6, 63.6, 54.1 (CH), 61.4, 54.0 (x 2) (CH₂), 25.7 (x 6, 2 Me₃CSi), 12.2 (C7), −4.0 (MeSi), −4.6 (MeSi), −5.5 (MeSi), −5.6 (MeSi).

The definitive stereochemical assignment of 35 came from an X-ray diffraction analysis (data deposited at the Cambridge Crystallographic Data Centre; deposition number: CCDC-762868).

Two views of the molecule of compound 35
Oil: $[\alpha]_D +0.5 \text{ (c 1.2; CHCl}_3\text{)}$.

IR: 3420 (br, OH), 1722 (C=O) cm$^{-1}$

HR FABMS $m/z$ 784.4438 (M+H$^+$). Calcd. for C$_{46}$H$_{66}$NO$_6$Si$_2$, 784.4428.

$^1$H NMR (500 MHz) $\delta$ 8.11 (2H, br d, $J$ ~ 8 Hz; aromatic), 7.52 (1H, br t, $J$ ~ 7.5 Hz; aromatic), 7.40-7.10 (17H, br m; aromatic), 5.29 (1H, m; H-2), 5.10 (1H, br s; OH), 3.85-3.75 (6H, br m; H-1/H-1'/H-3/H-5/benzyl CH$_2$), 3.64 (1H, br dd, $J$ ~ 8, 4 Hz; H-4), 3.30 (2H, d, $J = 13$ Hz; benzyl CH$_2$), 3.15 (1H, m; H-6), 3.05 (1H, dd, $J = 14.3$, 4 Hz; H-7), 2.90 (1H, dd, $J = 14.3$, 9.8 Hz; H-7'), 1.60 (1H, br s; OH), 0.84 (9H, s; Me$_3$Si), 0.83 (9H, s; Me$_3$Si), 0.04 (3H, s; MeSi), 0.00 (6H, s; 2 MeSi), $-0.12$ (3H, s; MeSi).

$^{13}$C NMR (125 MHz) $\delta$ 166.2, 139.5, 138.6 (x 2), 130.6, 18.2, 18.1 (quat C), 132.8, 129.8 (x 2), 129.5 (x 2), 129.2 (x 4), 128.6 (x 2), 128.5 (x 4), 128.2 (x 2), 127.3 (x 2), 126.5, 74.9, 73.6 (x 2), 70.5, 61.1 (CH), 61.9, 54.1 (x 2), 34.8 (CH$_2$), 26.0 (x 3, Me$_2$CSi), 25.8 (x 3, Me$_3$CSi), $-4.1$ (MeSi), $-4.4$ (MeSi), $-5.4$ (x 2) (MeSi).

Solid: mp 68-69 °C; $[\alpha]_D +43.4$ (c 1.05; CHCl$_3$).

IR: 1764, 1730 (C=O) cm$^{-1}$

HR FABMS $m/z$ 810.4231 (M+H$^+$). Calcd. for C$_{47}$H$_{64}$NO$_7$Si$_2$, 810.4221.

$^1$H NMR (500 MHz) $\delta$ 8.08 (2H, br d, $J$ ~ 7.5 Hz; aromatic), 7.63 (1H, br t, $J$ ~ 7.5 Hz; aromatic), 7.50 (2H, br t, $J$ ~ 7.5 Hz; aromatic), 7.40-7.25 (10H, br m; aromatic), 7.15 (3H, m; aromatic), 7.04 (2H, m; aromatic), 5.48 (1H, m; H-2), 4.97 (1H, dt, $J = 6.2$, 3 Hz; H-3), 4.17 (1H, m; H-5), 4.10 (2H, br d, $J =$ S-25
13.6 Hz; benzyl CH₂), 3.99 (1H, m; H-4), 3.92 (1H, br dd, J = 11.2, 4.2 Hz; H-1), 3.82 (1H, br dd, J = 11.2, 5.2 Hz; H-1´), 3.68 (2H, br d, J = 13.6 Hz; benzyl CH₂), 3.04 (1H, m; H-6), 3.00-2.95 (2H, m; H-7/H-7´), 0.84 (9H, s; Me₃CSi), 0.71 (9H, s; Me₃CSi), 0.04 (3H, s; MeSi), 0.03 (3H, s; MeSi), −0.15 (3H, s; MeSi), −0.47 (3H, s; MeSi).

¹³C NMR (125 MHz) δ 165.3, 148.4, 138.6 (x 2), 138.4, 129.3, 18.3, 17.7 (quat C), 133.2, 130.0 (x 2), 129.3 (x 2), 129.1 (x 4), 128.6 (x 2), 128.5 (x 4), 128.3 (x 2), 127.4 (x 2), 126.5, 84.6, 77.2, 72.4, 65.0, 61.6 (CH), 61.0, 55.7 (x 2), 31.5 (CH₂), 25.8 (x 3, Me₃CSi), 25.5 (x 3, Me₃CSi), −4.6 (MeSi), −4.8 (MeSi), −5.3 (x 2) (MeSi).

The definitive stereochemical assignment of 37 came from an X-ray diffraction analysis (data deposited at the Cambridge Crystallographic Data Centre; deposition number: CCDC-764883).

Two views of the molecule of compound 37
Oil: $\alpha_D +0.4$ (c 1; CHCl$_3$).

IR: 3450 (br, OH), 1722 (C=O) cm$^{-1}$

HR FABMS $m/z$ 962.5234 (M+H$^+$). Calcd. for C$_{56}$H$_{80}$NO$_7$Si$_3$, 962.5242.

$^1$H NMR (500 MHz) $\delta$ 8.09 (2H, br d, $J \sim 8$ Hz; aromatic), 7.72 (4H, m; aromatic), 7.50-7.20 (19H, br m; aromatic), 5.30 (1H, br s; OH), 5.25 (1H, td, $J = 6.2$, 3 Hz; H-2), 3.96 (1H, dd, $J = 11.3$, 3.5 Hz; H-7), 3.85-3.75 (6H, m; H-1/H-1'/H-7'/benzyl CH$_2$/OH), 3.66 (3H, d, $J = 13.3$ Hz; benzyl CH$_2$ overlapping signal from H-3), 3.51 (1H, br t, $J \sim 5$ Hz; H-4), 3.42 (1H, br dd, $J \sim 8.2$, 5 Hz; H-5), 3.00 (1H, td, $J = 8.2$, 3.5 Hz; H-6), 1.16 (9H, s; Me$_3$Si), 0.82 (9H, s; Me$_3$Si), 0.74 (9H, s; Me$_3$Si), 0.01 (3H, s; MeSi), −0.01 (3H, s; MeSi), −0.10 (3H, s; MeSi), −0.28 (3H, s; MeSi).

$^{13}$C NMR (125 MHz) $\delta$ 166.0, 138.9 (x 2), 133.1, 132.9, 130.6, 19.2, 18.3, 18.0 (quat C), 136.0 (x 2), 135.9 (x 2), 132.7, 130.0, 129.9 (x 2), 129.8 (x 3), 129.2 (x 4), 128.6 (x 4), 128.2 (x 2), 127.8 (x 3), 127.3, 74.4, 74.0, 70.8, 68.6, 61.2 (CH), 63.2, 61.7, 54.6 (x 2) (CH$_2$), 27.2 (x 3, Me$_3$Si), 26.0 (x 3, Me$_3$Si), 25.8 (x 3, Me$_3$Si), −4.4 (MeSi), −4.8 (MeSi), −5.4 (x 2) (MeSi).

Oil: $\alpha_D +16.2$ (c 1; CHCl$_3$).

IR: 1769, 1729 (C=O) cm$^{-1}$

HR FABMS $m/z$ 988.5076 (M+H$^+$). Calcd. for C$_{57}$H$_{78}$NO$_8$Si$_3$, 988.5035.

$^1$H NMR (500 MHz) $\delta$ 8.04 (2H, br d, $J \sim 8$ Hz; aromatic), 7.60 (4H, m; aromatic), 7.55 (1H, br t, $J \sim 7.5$ Hz; aromatic), 7.50-7.40 (8H, br m; aromatic), 7.30-7.20 (10H, br m; aromatic), 5.60 (1H, apparent q, $J \sim 5$ Hz; H-2), 4.80 (1H, dd, $J = 6$, 3.3 Hz; H-3), 4.71 (1H, dd, $J = 4.5$, 3.3 Hz; H-5), 4.14 (1H, br t, $J \sim 3.3$ Hz; H-4), 3.96 (1H, dd, $J = 11.3$, 3.5 Hz; H-7), 3.85-3.75 (6H, m; H-1/H-1'/H-7'/benzyl CH$_2$/OH), 3.66 (3H, d, $J = 13.3$ Hz; benzyl CH$_2$ overlapping signal from H-3), 3.51 (1H, br t, $J \sim 5$ Hz; H-4), 3.42 (1H, br dd, $J \sim 8.2$, 5 Hz; H-5), 3.00 (1H, td, $J = 8.2$, 3.5 Hz; H-6), 1.16 (9H, s; Me$_3$Si), 0.82 (9H, s; Me$_3$Si), 0.74 (9H, s; Me$_3$Si), 0.01 (3H, s; MeSi), −0.01 (3H, s; MeSi), −0.10 (3H, s; MeSi), −0.28 (3H, s; MeSi).

$^{13}$C NMR (125 MHz) $\delta$ 166.0, 138.9 (x 2), 133.1, 132.9, 130.6, 19.2, 18.3, 18.0 (quat C), 136.0 (x 2), 135.9 (x 2), 132.7, 130.0, 129.9 (x 2), 129.8 (x 3), 129.2 (x 4), 128.6 (x 4), 128.2 (x 2), 127.8 (x 3), 127.3, 74.4, 74.0, 70.8, 68.6, 61.2 (CH), 63.2, 61.7, 54.6 (x 2) (CH$_2$), 27.2 (x 3, Me$_3$Si), 26.0 (x 3, Me$_3$Si), 25.8 (x 3, Me$_3$Si), −4.4 (MeSi), −4.8 (MeSi), −5.4 (x 2) (MeSi).
Hz; H-4), 4.06 (3H, d, J = 13.7 Hz; benzyl CH₂ overlapping the signal from H-1 or H-7), 3.90-3.85 (2H, br m; H-1 or H-1’/H-7 or H-7’), 3.81 (1H, dd, J = 11, 5 Hz; H-1 or H-7’), 3.52 (2H, d, J = 13.7 Hz; benzyl CH₂), 3.02 (1H, dt, J = 5, 4.5 Hz; H-6), 1.01 (9H, s; Me₃CSi), 0.86 (9H, s; Me₃CSi), 0.80 (9H, s; Me₃CSi), 0.00 (3H, s; MeSi), −0.01 (3H, s; MeSi), −0.03 (3H, s; MeSi), −0.08 (3H, s; MeSi).

13C NMR (125 MHz) δ 165.4, 148.3, 138.9 (x 2), 132.9, 132.7, 129.6, 19.1, 18.2, 17.9 (quat C), 135.6 (x 2), 135.5 (x 2), 133.2, 130.0, 129.9, 129.6 (x 3), 129.0 (x 4), 128.5 (x 4), 128.4 (x 2), 127.8 (x 3), 127.3 (x 2), 83.1, 76.9, 72.4, 64.6, 60.7 (CH), 60.9, 60.1, 55.7 (x 2) (CH₂), 26.9 (x 3, Me₃CSi), 25.8 (x 3, Me₃CSi), 25.6 (x 3, Me₃CSi), −4.2 (MeSi), −4.5 (MeSi), −5.4 (x 2) (MeSi).

The absence of NOE between H-3 and H-5 suggests that 39 is the carbonate of an anti-1,3-diol. This conclusion is further supported by the NOEs between the hydrogen pairs H-2/H-5 and H-3/H-6. The coupling constant values in the C3-C4-C5 segment are consistent with this conclusion and indicate the relative configurations at these three stereocentres.

References