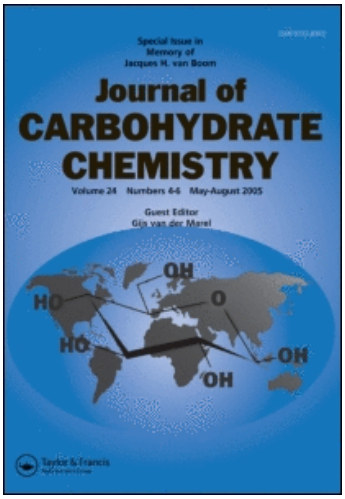

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Highly Deoxygenated Sugars. II. Synthesis of Chiral Cyclopentenes via Novel Carbocyclization of C-4 Branched Deoxysugars

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Highly Deoxygenated Sugars. II. Synthesis of Chiral Cyclopentenes via Novel Carbocyclization of C-4 Branched Deoxysugars[†]

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ABSTRACT

Tri-*O*-acetyl-D-glucal (**1**) was converted via Ferrier type II rearrangement with high α-selectivity to 2,3-unsaturated methyl glycosides **2a** and **2b** using ferric chloride as the catalyst. Palladium induced allylic substitution with sodium *tert*-butylacetoacetate as a nucleophile leads to C-4 branched sugars. Subsequent hydrogenation followed by treatment with trifluoroacetic acid affords the highly functionalized chiral cyclopentene derivative **5a** as a versatile chiral building block for cyclopentanoids.

Key Words: Deoxygenated sugars; Ferrier type II rearrangement; Pd-catalyzed allylic substitution; Carbocyclization; Cyclopentene.

[†]Dedicated to Professor Dr. Hans Paulsen on the occasion of his 80th birthday.

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INTRODUCTION

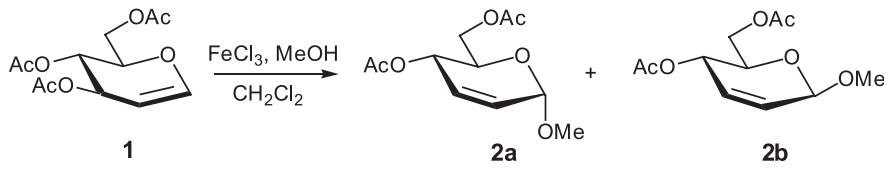
In a first communication on the utilization of sugars as chiral building blocks, we synthesized highly deoxygenated carbohydrate derivatives starting from commercially available tri-*O*-acetyl-D-glucal (**1**).[1] In the present study, we wanted to investigate a new type of carbocyclization in an aldol-type reaction of the protected anomeric aldehyde with reactive functional groups, attached to the deoxygenated sugar core.

RESULT AND DISCUSSION

To achieve deoxygenation in only a few steps, we started from glucal acetate (**1**), which was converted to a mixture of the 2,3-deoxygenated α,β-methyl-*O*-glycosides **2a** and **2b**,[2] employing the ferric chloride catalyzed Ferrier type II rearrangement.[3] Using this catalyst, much milder reaction conditions were possible than with the previously used boron trifluoride etherate[4] or other catalysts (review [5]). In addition, the yields were much better (91%) and the α,β-ratio (8:1) was shifted in favor of the α-anomer **2a** (Scheme 1). It was possible to purify the α-anomer **2a** to a factor of ca. 50:1 by flash chromatography on silica gel.

The key step in the attachment of a keto ester at C-4 was the palladium-catalyzed allylic substitution starting from **2a**. Palladium-catalyzed allylic substitutions are widely employed in organic synthesis, particularly in carbon-carbon bond formation (reviews [6,7]). In carbohydrate chemistry for instance, Baer and Hanna used the reaction in the synthesis of aminated and alkylated 2,3-unsaturated sugars with amines or reactive methylene compounds such as sodium dimethyl malonate as the nucleophiles.[8] Surprisingly, β-keto esters have not yet been employed to attach carbon side chains at C-4 of sugars. In contrast to the malonate alkylation, a new stereogenic center is formed at the C-H acidic center of the keto ester, with little stereoselectivity expected in the formation of this new chiral center. However, this stereochemical problem was not relevant because the stereogenic center was removed later in the sequence by decarboxylation of the β-keto ester to a ketone.

More important concerns of the palladium catalyzed allylic substitution were the stereoselectivity of the incoming nucleophile and the regioselectivity of the process, e.g. α- or γ-addition with respect to the two allylic leaving groups in **2a**. The assumed transition state **A** of the process is shown in Scheme 2. In the initial step, the allylic acetate forms intermediate π-allylpalladium complexes in the presence of tetrakis(triphenylphosphine) palladium. The reactive catalyst is regenerated after substitution of the leaving group by the nucleophile in the presence of excess triphenylphosphine.



Scheme 1. Ferric chloride-catalyzed α-selective Ferrier type II reaction of tri-*O*-acetyl-D-glucal (**1**).

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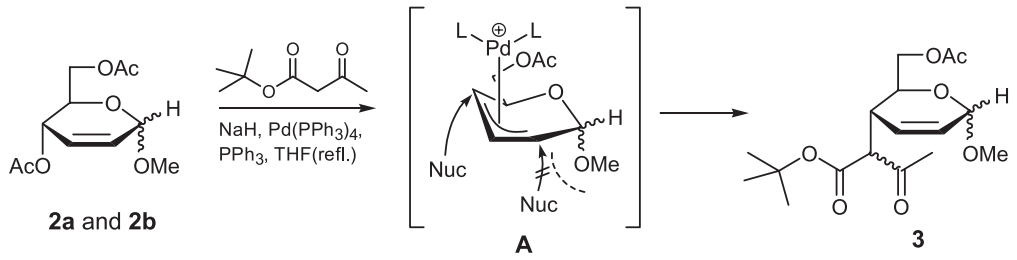


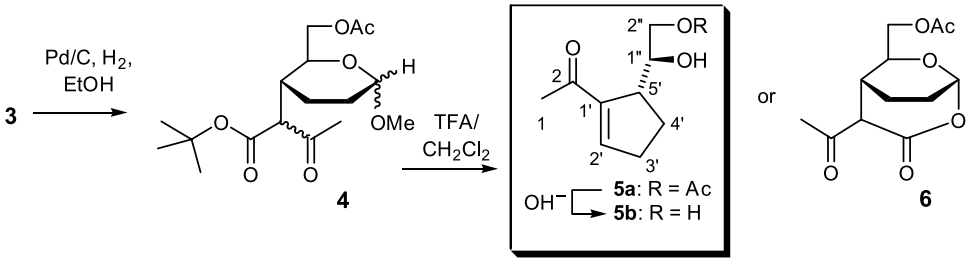
Scheme 2. Regio- and stereoselectivity of the palladium-catalyzed allylic substitution starting from allylic acetate **2**.

Both the regioselectivity and stereoselectivity of the nucleophile addition depend on the formation of the η^3-palladium-allyl complex.

In the present case, the nearly pure α-anomer **2a** was reacted in the initial experiments with sodium *tert*-butylacetoacetate as the nucleophile and tetrakis(triphenylphosphine)palladium/triphenylphosphine as the catalyst (Scheme 2). In later reactions, the 8:1 mixture of **2a** and **2b** was also used without any losses in selectivity or yield. The resulting keto ester **3**, with the keto ester attached to a deoxygenated sugar moiety, was obtained in 88% yield. As expected, an approximately 1:1 ratio of diastereomers was formed at the C-H acidic keto ester function as deduced from the NMR spectra of **3**. However, the reaction was entirely stereoselective with respect to the attack of the nucleophile at C-4 of the η^3-palladiumallyl complex **A**. In addition, the completely regioselective α-substitution was secured by the better leaving group capability of the acetate versus the anomeric methoxy group. These results are in agreement with literature precedence as described in a review by Frost et al.[9]

In the next step, the C-4 alkylated unsaturated sugar derivative **3** was hydrogenated under standard conditions with 5% Pd/C and hydrogen in ethanol to obtain the saturated branched deoxy sugar **4** in 95% yield (Scheme 3).

Five transformations were still needed to arrive at the anticipated cyclization product via aldol-type reaction starting from **4**: saponification and decarboxylation of the ester group, cleavage of the anomeric methyl glycoside, and aldol reaction followed by water elimination of the terminal methyl ketone with the aldehyde at the anomeric center. All these reactions might proceed under acidic catalysis and, therefore,



Scheme 3. Acid-catalyzed transformation of keto ester **4** to either the cyclopentene **5a** or the lactone **6**.

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compound **4** was treated for 30 minutes with trifluoroacetic acid in dichloromethane solution (Scheme 3). To our delight, only two major products were formed in this multistep sequence: the chiral cyclopentene **5a** and the bridged seven-membered lactone **6**. Evidently, cleavage of the *tert*-butyl ester in **4** was the initial step, followed by the decarboxylation and subsequent aldol condensation with the intermediate aldehyde, derived from cleavage of the methyl glycoside **4**.

In a systematic study to improve the yields of either cyclopentene **5a** or lactone **6**, we found that the reaction at room temperature afforded the desired cyclopentene **5a** as essentially the only product in 71% yield. At lower temperatures (0°C), the rate of decarboxylation was apparently slower than the opening of the hemiacetal and the bicyclic lactone **6** was formed predominantly (68%). It has to be stressed that the five membered carbocycle **5a** has two clearly defined chiral centers determined by the stereochemistry of the sugar core. One stereogenic center is located at the ring position and the other one in the side chain. The compound possesses an array of highly condensed functional groups and the primary hydroxyl group is selectively protected as an acetate. These functional groups can all be easily used for further transformations. For instance, saponification of the primary acetate proceeds quantitatively to yield the diol **5b**, opening the way to an aldehyde functionality after periodate glycol cleavage. To the best of our knowledge, this is the first example, possibly extendable to other sugar glycals, in which a keto side chain and the anomeric aldehyde are condensed in an aldol-type condensation to form a cyclopentene. The product may prove to be an easily available chiral starting material for cyclopentanoid natural products of biological importance which have been synthetic targets over the years (e.g. prostaglandins, thromboxanes).[10,11]

In summary, this paper describes the synthesis of the chiral cyclopentene **5a** in only four steps and 54% overall yield, starting from commercially available glucal acetate **1**. A separation of stereoisomeric intermediates is not required at any stage of the synthesis.

EXPERIMENTAL

General remarks and instrumentation. Silica gel 60 F_{254} coated plates from Merck AG Darmstadt were used for TLC. Spots were detected by UV light (λ = 254 and 366 nm), spraying and heating with 8% ethanolic sulfuric acid or the cerium(IV)molybdato phosphoric acid reagent (Merck AG). Preparative LC was performed using silica gel plates (1 mm) from Macherey and Nagel. Melting points were recorded with a Gallenkamp Melting Point apparatus (uncorrected); IR spectra: NICOLET 510 P; optical rotations: Perkin-Elmer polarimeter 241 (589 nm); elemental analyses: Perkin-Elmer Elementar Analysator 240; mass spectra: FINNEGAN MAT 8200 and FISON MD 800, relative intensities in brackets; NMR spectra: Bruker ARX 200 (200/50 MHz) and Bruker AMX 300 (300/75 MHz) spectrometer. GC: Hewlett Packard 5890 Series II, column: FS-SE-52.

α- and β-Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (2a and 2b).[2] To a solution of 3,4,6-tri-*O*-acetyl-D-glucal (2.00 g, 7.3 mmol) and methanol (1.1 equiv) in dried CH_2Cl_2 was added a 0.1 M solution of $FeCl_3$ (0.01 equiv in CH_2Cl_2).[3] The reaction was monitored by TLC [pentane: ethyl acetate = 7:3; ca. 30 min] and then quenched by addition of saturated aqueous $NaHCO_3$ solution (120 mL).

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The phases were separated, the aqueous phase was extracted twice with CH_2Cl_2, and the combined organic phases were washed with brine (50 mL), dried ($MgSO_4$), and the solvent removed under reduced pressure. The crude mixture was analyzed by GC (130°C to 200°C; 10°C/min) to show an 8:1 ratio of the anomeric isomers. The mixture was filtered over a short column of silica gel to afford the methyl-4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside **2a** and **2b** in 91% yield (α/β ratio 8:1). ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of anomers): δ = 2.02, 2.03 (2 × s, 2 × 3 H, 2 × Ac-CH_3), 3.37 (s, 3 H, OCH_3), 3.94–4.04 (m, 1 H, 5-H), 4.06–4.23 (m, 2 H, 2 × 6-H), 4.85–4.96 (m, 1 H, 1-H), 5.08–5.25 (m, 1 H, 4-H), 5.77–5.90 (m, 2 H, 2-H, 3-H). ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of anomers): δ = 20.6, 20.8 (2 × q, 2 × Ac-CH_3), 55.7 (q, OCH_3), 62.8 (t, C-6), 65.1, 66.7 (2 × d, C-4, C-5), 95.2 (d, C-1), 127.5, 129.06 (2 × d, C-2, C-3), 170.1, 170.6 (2 × s, 2 × Ac-C=O).

Methyl 6-*O*-acetyl-2,3,4-trideoxy-4-[acetyl(*tert*-butoxycarbonyl)methyl]-α-D-*erythro*-hex-2-enopyranoside (3) (mixture of isomers). *tert*-Butyl acetoacetate (6.3 mL, 38 mmol) was deprotonated under argon at 0°C in dry THF (50 mL) by addition of sodium hydride (2.8 g, 42 mmol). The clear solution of the anion was added dropwise under argon via a Teflon tube into a flask containing **2a** and **2b** (6.18 g, 25.3 mmol), triphenylphosphine (0.17 g, 0.63 mmol) and tetrakis(triphenylphosphine)palladium (0.07 g, 0.06 mmol, 1/400 equiv) in dry THF (100 mL). The solution was refluxed for 8 h (TLC and GC and monitoring). The reaction was then quenched by addition of ammonium chloride (100 mL), the aqueous phase was extracted with CH_2Cl_2 (3 × 60 mL), the combined organic layers were washed with brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (PE:EtOAc = 9:1 to 3:1) to yield the branched sugar **3** (7.6 g, 88%) as a 1:1 mixture of diastereomers. $[\alpha]_D$ = + 103.9°, (*c* 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$) (mixtures of isomers): δ = 1.37–1.46 (m, 9 H, $OC(CH_3)_3$), 1.94–2.06, 2.15–2.20 (2 × m, 6 H, Ac-CH_3, 3 × 4′-H), 2.79–2.98, 3.28–3.48 (2 × m, 5 H, 4-H, 1-OCH_3, 2′-H), 3.84–4.40 (m, 3 H, 5-H, 2 × 6-H), 4.48–4.97 (m, 1 H, 1-H), 5.62–5.91 (m, 2 H, 2-H, 3-H). ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of isomers): δ = 20.5 (q, Ac-CH_3), 27.6 (3 × s, $OC(CH_3)_3$), 29.1 (d, C-4′), 33.6 (d, C-4), 54.9 (q, OCH_3), 58.3 (d, C-2′), 63.6 (t, C-6), 66.4 (d, C-5), 82.7 (q, $OC(CH_3)_3$), 95.1 (d, C-1), 125.3 (d, C-2), 129.5 (d, C-3), 167.0 (s, C-1′), 170.6 (s, Ac-C=O), 201.1 (s, C-3′). IR (Film): ν = 2979 cm^{-1} (m, C–H), 2938 (m, C–H), 2829 (w, C–H), 1740 (s, C=O, ester), 1716 (s, C=O, ketone), 1654 (w, C=C), 1629 (w, C=C), 1454 (m, C–H), 1394 (m, C–H), 1369 (s, C–H), 1241 (s, C–O), 1147 (s, C–O), 1049 (s, C–O), 966 (m), 843 (w). MS (CI, isobutane): *m/z* (%) = 343 (1) [M^+ + H], 311 (18), 269 (4), 255 (100), 237 (11), 213 (9), 195 (16), 151 (5), 103 (3), 57 (43) [$C_3H_5O^+$], 43 (10) [CH_3CO^+].

Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65. Found: C, 59.14; H, 7.79.

Methyl 6-*O*-acetyl-2,3,4-trideoxy-4-[acetyl(*tert*-butoxycarbonyl)methyl]-α-D-*erythro*-hexopyranoside (4) (mixture of isomers). A solution of **3** (2.04 g, 5.97 mmol) in ethanol was hydrogenated with 5% Pd/C (0.07 mg, 0.5 mol, 1 atm hydrogen pressure). After 5 h, the catalyst was filtered off and the solvent of the filtrate was evaporated. Compound **4** was isolated as a colorless oil (1.95 g, 95%). $[\alpha]_D$ = +89.6°, (*c* 1.15, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of isomers): δ = 1.30–1.75 (m, 13 H, $OC(CH_3)_3$, 2 × 2-H, 2 × 3-H), 1.97–2.04, 2.10–2.41 (2 × m, 7 H, Ac-CH_3, 3 × 4′-H, 4-H), 3.24–3.32 m, 3 H, 1-OCH_3), 3.36–3.50 (m, 1 H, 2′-H), 3.59–4.66 (m, 4 H, 5-H, 2 × 6-H, 1-H). ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of isomers): δ = 19.8

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(t, C-3), 20.4 (q, Ac-CH_3), 27.5 (3 × s, OC(CH_3)$_3$), 29.1 (d, C-4′), 29.2 (t, C-2), 34.5 (d, C-4), 53.9 (q, OCH_3), 59.7 (d, C-2′), 64.1 (t, C-6), 68.6 (d, C-5), 82.1 (q, O*C*(CH_3)$_3$), 97.6 (d, C-1), 167.5 (s, C-1′), 170.4 (s, Ac-C=O), 201.3 (s, C-3′). IR (Film): ν = 2976 cm^{-1} (s, C–H), 2936 (s, C–H), 2833 (m, C–H), 1740 (s, C=O, ester), 1721 (s, C=O, ketone), 1630 (m, C=C), 1456 (m, C–H), 1393 (m, C–H), 1369 (s, C–H), 1238 (s, C–O), 1147 (s, C–O), 1131 (s, C–O), 1055 (s, C–O), 964 (m), 865 (w). MS (CI, isobutane): *m/z* (%) = 345 (1) [M^+ + H], 313 (13), 271 (2), 257 (73), 239 (5), 213 (11), 197 (3), 195 (3), 153 (3), 103 (2), 57 (100) [$C_3H_5O^+$], 43 (36) [CH_3CO^+].

Anal. Calcd for $C_{17}H_{28}O_7$: C, 59.29; H, 8.12. Found: C, 59.16; H, 8.12.

1″(*R*), 5′(*R*)-1-[5-(2-Acetoxy-1-hydroxyethyl)-cyclopent-1-enyl]-ethanone (5a). Compound **4** (128 mg, 0.38 mmol) was treated at 0°C with a mixture of CH_2Cl_2/TFA (2:1, 3 mL). After the addition, the solution was allowed to warm up to room temperature within 5 min, and after 30 min at 20°C it was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL), the combined organic layers were washed twice with brine (each 5 mL), dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Chromatography on silica gel (PE:EtOAc = 7:3 to 1:1) afforded the carbocycle **5a** (57 mg, 71%). $[\alpha]_D$ = + 41.5°, (*c* 0.6, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71–1.88 (m, 1 H, 4′-H_a), 2.00 (s, 3 H, Ac-CH_3), 2.03–2.21 (m, 1 H, 4′-H_b), 2.32 (s, 3 H, 3 × 2-H), 2.42–2.64 (m, 2 H, 2 × 3′-H), 3.14–3.26 (m, 1 H, 5′-H), 3.76 (dd, *J* = 11.7 Hz, *J* = 8.7 Hz, 1 H, 1″-H), 3.95–4.00 (m, 2 H, 2 × 2″-H), 6.87–6.91 (m, 1 H, 2′-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9 (q, Ac-CH_3), 25.7 (t, C-4′), 27.0 (q, C-2), 32.6 (t, C-3′), 48.1 (d, C-5′), 66.7 (t, C-2″), 71.1 (d, C-1″), 145.0 (s, C-1′), 149.9 (d, C-2′), 171.3 (s, Ac-C=O), 198.7 (s, C-1). IR (Film): ν = 3430 cm^{-1} (s, O–H), 2951 (m, C–H), 2921 (m, C–H), 2848 (w, C–H), 1735 (s, C=O, Ester), 1659 (s, C=O, α,β-unsaturated ketone), 1631 (w, C=C), 1431 (m, C–H), 1373 (s, C–H), 1242 (s, C–O), 1040 (s, C–O). MS (CI, isobutane): *m/z* (%) = 213 (37) [M^+ + H], 195 (100) [M^+ + H–H_2O], 153 (15), 135 (8), 125 (3), 110 (2), 91 (2), 57 (30) [$C_3H_5O^+$], 43 (17) [CH_3CO^+].

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60 Found: C, 61.44; H, 7.79.

1″(*R*), 5′(*R*)-1-[5-(1,2-Dihydroxyethyl)-cyclopent-1-enyl]-ethanone (5b). Carbocycle **5a** (140 mg, 0.66 mmol) was dissolved in absolute methanol (10 mL) and to this solution a small piece of sodium was added. After 4 h the mixture was neutralized to pH = 7 with Amberlite 120. The resin was filtered off and the solvent was evaporated to afford the crude product, which was passed over silica to yield **5b** (105 mg, 0.62 mmol) in 95% yield. $[\alpha]_D$ = + 38.3°, (*c* 0.6, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.95–2.05 (m, 2 H, 4′-H), 2.37 (s, 3 H, 3 × 2-H), 2.50–2.66 (m, 2 H, 2 × 3′-H), 3.05–3.16 (m, 1 H, 5′-H), 3.31–3.51 (m, 2 H, 2 × 2″-H), 3.81–3.91 (m, 1 H, 1″-H), 4.28 (br, 2 × OH), 26.97–6.99 (m, 1 H, 2′-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.3 (t, C-4′), 27.1 (q, C-2), 3.1 (t, C-3′), 47.0 (d, C-5′), 65.0 (t, C-2″), 72.9 (d, C-1″), 145.7 (s, C-1′), 150.2 (d, C-2′), 199.4 (s, C-1). IR (Film): ν = 3394 cm^{-1} (s, O–H), 2929 (m, C–H), 2921 (m, C–H), 1651 (s, C=O, α,β-unsaturated ketone), 1629 (w, C=C), 1429 (m, C–H), 1377 (s, C–H), 1289 (s, C–O), 1067 (s, C–O).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29 Found: C, 62.70; H, 8.33.

4-Acetyl-6-acetoxymethyl-2,7-dioxabicyclo[3.2.2]nonan-3-one (6). Keto ester **4** (256 mg, 0.76 mmol) was dissolved at 0°C in a mixture of CH_2Cl_2/TFA (2:1, 6 mL).

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The mixture was stirred at 0°C for 2 h and then a saturated solution of $NaHCO_3$ (20 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL), the combined organic layers were washed with brine, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Chromatography (PE:EtOAc = 7:3 to 1:1) afforded the lactone **7** (113 mg, 58%); mp = 51°C. $[\alpha]_D$ = + 55.5°, (*c* 0.93, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.37–1.56, 1.83–1.94 (2 × m, 4 H, 2 × 8H, 2 × 9H), 2.03 (s, 3 H, $AcCH_3$), 2.42 (s, 3 H, 3 × 2′-H), 2.84–2.92 (m, 1 H, 5-H), 3.62 (d, *J* = 11.6 Hz, 1 H, 4-H), 3.65–3.73 (m, 1 H, 6-H), 3.95–4.11 (m, 2 H, 2 × 1″-H), 5.46 (d, *J* = 4.0 Hz, 1 H, 1-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8 (q, $AcCH_3$), 21.2, 21.7 (2 × t, C-8, C-9), 30.1 (q, C-2′), 35.4 (d, C-5), 52.7 (d, C-4), 65.8 (t, C-1″), 72.7 (d, C-6), 98.4 (d, C-1), 170.8, 171.3 (2 × s, C-3, Ac-C=O), 199.9 (s, C-1′). IR (Film): ν = 2950 cm^{-1} (s, C–H), 2867 (m, C–H), 1786 (s, C=O, lactone), 1793 (s, C=O, ester), 1734 (s, C=O, ketone), 1377 (m, C–H), 1248 (s, C–O), 1160 (s, C–O), 1098 (s, C–O), 1036 (s, C–O). MS (EI, 70 eV): *m/z* (%) = 214 (5) [M^+], 213 (10) [M^+–H], 196 (26) [M^+-H_2O], 154 (18), 136 (8), 123 (24), 107 (15), 67 (6), 43 (100) [CH_3CO^+].

Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59 Found: C, 56.22; H, 6.52.

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