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High enantio- and diastereoselective induction of BINOL- and TADDOL-modified vinyloxy ethoxides in C–C coupling reactions with aldehydes

Peter Maier, Hartmut Redlich* and Jessica Richter

Westfälische Wilhelms-Universität, Organisch-Chemisches Institut, Corrensstraße 40, 48149 Münster, Germany

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Abstract—The basic reagent vinyloxyethoxy titanium trisisopropyloxide, easily modified by replacing two of the isopropyloxides with the optically active diol (*R*)- or (*S*)-BINOL, reacts with simple, prochiral aldehydes to give chiral β-hydroxy-1,3-dioxolanes with enantiomeric ratios up to 99:1. The same reagents, (*R*)- or (*S*)-configured, react with the chiral 2,3-*O*-isopropylidene-D-glyceraldehyde to give the corresponding open chain pentose derivatives. The main components have opposite descriptors at the newly created stereogenic center, indicating strong reagent control. A comparable system, modified by (*R*,*R*)- or (*S*,*S*)-TADDOL shows a weaker induction with the chiral aldehyde, but now with the same product configuration for both reagents, indicating predominant substrate control.

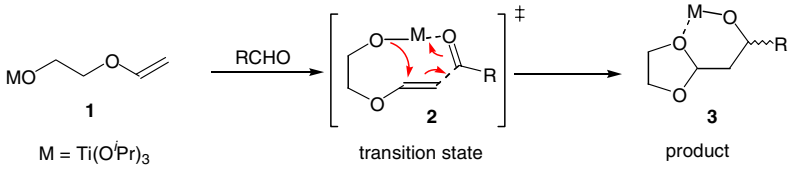
1. Introduction

Vinyloxy ethoxides with a Lewis acidic and/or coordinating counter ion react with aldehydes to yield β-hydroxy-1,3-dioxolanes (Scheme 1).

Experimental and also theoretical considerations of this new reaction principle are in agreement with the idea, that the reaction proceeds via a transition state, in which the metal coordinates the educts to a cyclic nine-membered arrangement, resulting in C–C and C–O σ-bond formation.[1,2] The stereochemical course of the reaction can be affected independently by chiral induction from an aldehyde,[2] by (*E*/*Z*)-configurations in the vinyloxy moiety,[2] and by C_2-symmetry[3] in the underlying diols of the reagent. We now report the observation that (*R*)- or (*S*)-BINOL[4] and (*R*,*R*)- or (*S*,*S*)-TADDOL[5] modified trisisopropyloxy titanium$^+$ exhibits a fourth independent very simple possibility to influence the stereochemical course of the reaction.

Scheme 2 describes the formal generation of the reagents. While the reaction of $ClTi(O^iPr)_3$ with sodium vinyloxy ethoxide **8** generates the basic reagent **1**, now in a separate step, the chiral diols (*R*)- or (*S*)-BINOL or (*R*,*R*)- or (*S*,*S*)-TADDOL are set into equilibrium with the chloro titanium alcoholate. Molecular sieves promote faster equilibration of the reaction mixture. This solution is then treated in the usual way.

The structure of the chiral reagents, described as monomers in Scheme 2 is not proven, due to the dynamic equilibrium, titanium alcoholates may undergo. Also dimeric structures for Ti-species as described here have



Scheme 1. General scheme for the reaction of vinyloxy ethoxides with aldehydes.

* Corresponding author. Tel.: +49 251 83 33251; fax: +49 251 83 36504; e-mail: redlich@uni-muenster.de

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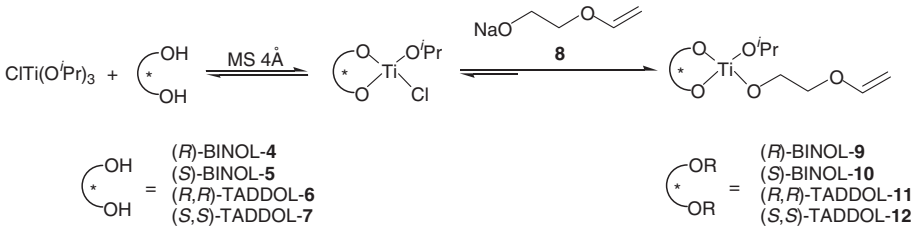


Scheme 2. Formation of the reagents **9**–**12**.

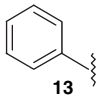
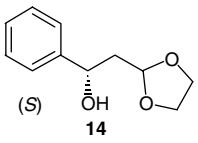
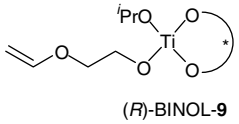
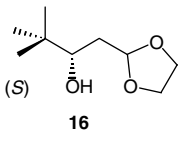
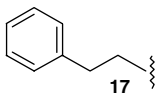
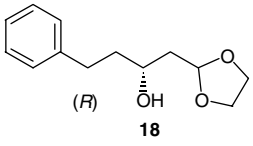
been proposed.[6] The structures of the reagent in Scheme 2 may be regarded as proposals, derived from the stoichiometric composition of the solution.

2. Results and discussion

(*R*)-BINOL **4** reacts with the prochiral benzaldehyde **13** to the corresponding β-hydroxy-1,3-dioxolane **14** (Table 1). The enantiomeric ratio is 92.5:7.5 in favor for the (*S*)-configuration at C-3. With 2,2-dimethylpropanal **15**, bearing the bulky *tert*-butyl group, the e.r. is 95.5:4.5 also with (*S*)-configuration at C-3 for the main compound **16**. 3-Phenylpropanal **17** shows the best stereochemical result with an e.r. of 99:1. The descriptor of the main product **18** is now (*R*) at C-3, according to the CIP-rules, but the absolute configuration is the same as in the examples given before, D with regard to 1,3-dioxolane.

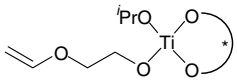
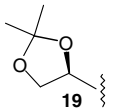
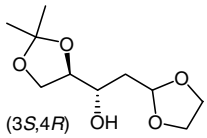
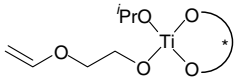
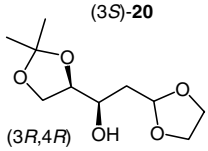
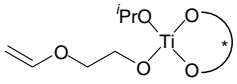
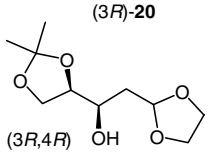
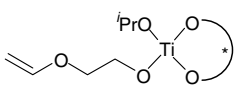
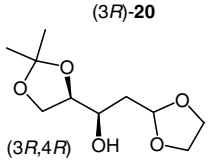
The reaction of the chiral 2,3-*O*-isopropylidene-D-glyceraldehyde **19** with the reagent modified with (*R*)-BINOL **4** leads in an excellent yield of 95% to the corresponding diastereomers with a diastereomeric ratio of 94:6 in favor of the (3*S*)-configured open chain 2-deoxypentose derivative (3*S*)-**20** (Table 2). Nearly the same d.r. of 93:7 is found, now with (3*R*)-configuration at C-3 of (3*R*)-**20**, when (*S*)-BINOL **5** is applied, indicating strong reagent control for the C–C and C–O bond forming process to yield the β-hydroxy-1,3-dioxolane. The reactions of (*R*,*R*)- or (*S*,*S*)-TADDOL-**11**, respectively, -**12** with the glyceraldehyde derivative **19** are lower in yield (77%, respectively, 85%) and induction (d.r. 82:18 for (*R*,*R*)-TADDOL-**11** and 71:29 for (*S*,*S*)-TADDOL-**12**). Interestingly for both enantiomeric reagents they show the same configuration (3*R*) for the predominant stereoisomer (3*R*)-**20**. Figure 1 describes the assumed situation leading to the transition state. The bulky phenyl substituents shield the Ti^{4+}-cation in such a strong way, that the aldehyde function of **19** can only contact the Ti^{4+} by approaching with the less hindered side to one of the phenyl groups (see arrows). As a consequence of this, the mobile vinyloxy moiety has to enter the C–C bond forming trajectory from the opposite side. The stereochemical situation is nearly identical for both TADDOLato-configurations. There should be a slight difference, due to the fact, that for the (*R*,*R*)-TADDOL-**11** the destabilizing interactions with the aldehyde **19** should be lower, than for the (*S*,*S*)-TADDOL-**12** (compare red bonds in Fig. 1). This might be reflected in the small differences for the diastereomeric ratios, found experimentally. Here, straight substrate control seems to operate.

Table 1. Results of the enantioselective C–C coupling reactions

Chiral Ti-reagent[a]	R	Products[b,c]		Yield (%)[d]
	 **13**	 (*S*) OH **14**	e.r. 92.5:7.5	70
 (*R*)-BINOL-**9**	 **15**	 (*S*) OH **16**	e.r. 95.5:4.5	54
	 **17**	 (*R*) OH **18**	e.r. 99:1	62

[a] BINOL: 1,1′-Binaphthyl-2,2′-diol.
[b] Enantiomeric ratios determined by GC-analysis of the crude product.
[c] The assignments of the configurations were established by chiroptical methods (CD of the corresponding methyl xanthogenate).[7,8]
[d] Isolated yield.

Table 2. Results of the diastereoselective C–C coupling reactions

Chiral Ti-reagent[a]	R	Products[b,c]	Yield (%)
 (*R*)-BINOL-**9**	 **19**	 d.r. 94:6 (3*S*,4*R*) (3*S*)-**20**	95[d]
 (*S*)-BINOL-**10**	**19**	 d.r. 93:7 (3*R*,4*R*) (3*R*)-**20**	95[e]
 (*R*,*R*)-TADDOL-**11**	**19**	 d.r. 82:18 (3*R*,4*R*) (3*R*)-**20**	77[e]
 (*S*,*S*)-TADDOL-**12**	**19**	 d.r. 71:29 (3*R*,4*R*) (3*R*)-**20**	85[e]

[a] BINOL: 1,1′-Binaphthyl-2,2′-diol, TADDOL: 2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol.
[b] Diastereomeric ratios determined by GC-analysis of the crude product.
[c] The absolute configurations are correlated with authentic samples from 2-deoxy-D-*erythro*-pentose (2-deoxy-D-ribose).
[d] Isolated yield.
[e] Yield determined by GC-calibration with an internal standard.

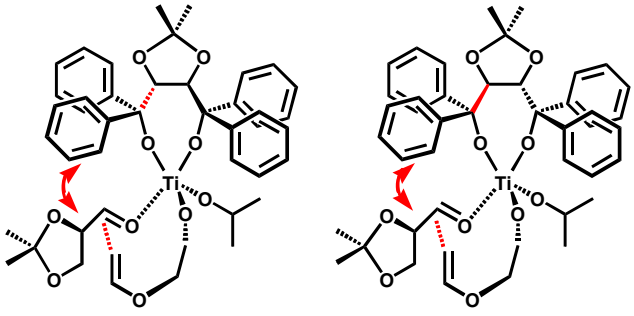


Figure 1. Assumed transition state model, leading for the reaction of (*R*,*R*)-TADDOL-**11** and (*S*,*S*)-TADDOL-**12** with **19** both to the predominant (3*R*)-configurated **20**.

3. Conclusion

In conclusion, the facile modification of the non-chiral basic reagent system vinyloxyethoxy trisisopropyloxide **1** with the C_2-symmetric diols (*R*)- or (*S*)-BINOL **4** or **5**, respectively TADDOL **6** or **7** to highly inducing chiral reagents offers a very simple new route for the stereoselective synthesis of chiral β-hydroxy-1,3-dioxolanes. In the case of the (*R*)- or (*S*)-BINOL modified reagents **9** or **10**, high enantiomeric ratios are observed with the prochiral aldehydes **13**, **15**, and **17**. Their reaction with the enantiomerically pure 2,3-*O*-isopropylidene-D-glyceraldehyde **19** shows such strong reagent control, that the inherent induction of the glyceraldehyde derivative **19**, which leads to a 78:22 distribution in favor of the (3*S*)-configurated compound with the basic, not chiral modified reagent **1**, essentially remains without influence.[2] For both enantiomeric reagent systems (*R*,*R*)-TADDOL-**11** and (*S*,*S*)-TADDOL-**12** the main compound—with slightly different distributions—is (*R*)-configured in the reaction with the chiral aldehyde **19** yielding (3*R*)-**20**. This result better fits the idea, that a very bulky reagent such as TADDOLato-modified **11** or **12** might, independent from its stereochemical assignment, approach the substrate predominantly from a less hindered side, in other words, is subjected to substrate control.

4. Experimental

4.1. General

Chemicals and solvents were either purchased (puriss. p. A.) from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (25 g), $Ce(SO_4)_2{*}H_2O$ (10 g), concd H_2SO_4 (60 mL), and H_2O (940 mL) followed by heating. Medium pressure chromatography was performed using silica gel Merck 60 (particle size 230–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker WM 300 or Bruker AMX 400. Chemical shifts are given in δ relative to tetramethylsilane (TMS); the coupling con-

stants (J) are given in Hertz. Spectra were recorded in C_6D_6 as solvent at room temperature. TMS served as internal standard ($\delta = 0$ ppm) for ^{1}H NMR, and C_6D_6 as internal standard (δ (C_6D_6) = 128.39) for ^{13}C NMR. GC was carried out using a HP 6890 GC Instrument. For determination of enantiomeric ratios a GC-14A (Shimadzu) with a chiral GC-column was used (FS Hydrodex β-PM, 50 m × 0.25 mm). Optical rotations were recorded on a Perkin Elmer 241 Polarimeter ($d = 589$ nm, 1 dm cell). Elemental analyses were carried out with a CHN-RAPID of Hereaus. Mass spectra were measured after ESI method (electron spray ionization) on a QUATTRO LCZ (Waters-Micromass, Manchester, UK) with nanospray inlet.

4.2. General procedure for C–C coupling reactions

In an argon atmosphere molecular sieves (1 g, 4 Å) and 1,1′-binaphthyl-2,2′-diol **4/5** or 2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol **6/7** (1.0 mmol) were dissolved in 10 mL of toluene. At room temperature chlorotitanium trisisopropyloxide (1.0 mmol, 1 M solution in hexane) was added and the mixture was stirred for 1 h. In a second reaction flask, 2-vinyloxyethanol (1.0 mmol) was dissolved in 10 mL of toluene. To the solution stirring at 0 °C, sodium hydride (1.1 mmol, 60% in paraffin oil) was added. The generated sodium vinyloxy ethoxide **8** was added with a syringe to the first reaction flask. The reaction mixture was allowed to warm to room temperature and the aldehyde was added (0.5–1.1 mmol). After completion of the reaction the mixture was poured into an ice cold saturated solution of sodium hydrogen carbonate (10 mL) in diethylether (100 mL). The residue was removed by filtration over celite and the filtrate treated with water. After separation of the organic layer, the aqueous layer was washed with diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated in vacuo. All products were purified by silica gel column chromatography (cyclohexane/EtOAc).

4.3. 2-(1,3-Dioxolane-2-yl)-1-phenylethanol 14

Compound **14** was obtained by the addition of 2-vinyloxyethanol to benzaldehyde **13** according to the general procedure for C–C coupling reactions. By using 2-vinyloxyethanol (196 mg, 2.2 mmol), sodium hydride (91 mg, 2.3 mmol), (*R*)-BINOL **4** (629 mg, 2.2 mmol), a 1 M solution of chlorotitanium trisisopropyloxide in hexane (2.3 mL, 2.3 mmol) and benzaldehyde **13** (128 mg, 1.2 mmol), 160 mg (70%) of compound **14** was obtained: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.01 (1H, ddd, $^3J = 3.8$ Hz, $^3J = 4.8$ Hz, $^3J = 14.4$ Hz, CH_2CHOH), 2.11 (1H, ddd, $^3J = 4.8$ Hz, $^3J = 9.2$ Hz, $^3J = 14.4$ Hz, CH_2CHOH), 3.75–3.99 (4H, m, dioxolane-CH_2), 4.93 (1H, dd, $^3J = 3.8$ Hz, $^3J = 9.2$ Hz, CHOH), 4.97 (1H, t, $^3J = 4.8$ Hz, CHO$_2$), 7.18–7.37 (m, 5H, C$H_{ar.}$); ^{13}C NMR (C_6D_6, 75 MHz): δ 43.18 (CH_2, CH_2CHOH), 64.28, 64.45 (2 × CH_2, dioxolane-CH_2), 70.18 (CH, CHOH), 103.00 (CH, CHO$_2$), 125.74, 127.02, 127.36 (3 × CH, 5 × CH$_{ar.}$), 144.75 (C, $C_{ar.}$); $[\alpha]_D^{20} = -10.0$ (c 1.0, CH_3OH); HRMS (ESI): m/z calcd for $[M+Na]^+$: 217.0835; found: 217.0842; elemental analysis calcd (%) for $C_{11}H_{14}O_3$ (194.2): C 68.02, H 7.27; found: C 67.78, H 7.36.

4.4. 1-(1,3-Dioxolane-2-yl)-3,3-dimethyl-butane-2-ol 16

Compound **16** was obtained by the addition of 2-vinyloxyethanol to 2,2-dimethylpropanal **15** according to the general procedure for C–C coupling reactions. By using 2-vinyloxyethanol (305 mg, 3.5 mmol), sodium hydride (142 mg, 3.6 mmol), (*R*)-BINOL **4** (1 g, 3.5 mmol), a 1 M solution of chlorotitanium trisisopropyloxide in hexane (3.6 mL, 3.6 mmol), and 2,2-dimethylpropanal **15** (154 mg, 1.8 mmol), 166 mg (54%) of compound **16** was obtained: ^{1}H NMR (C_6D_6, 300 MHz, TMS): δ 0.94 (s, 9H, 3 × CH_3), 1.70 (ddd, 1H, $^3J = 5.3$ Hz, $^3J = 10.4$ Hz, $^2J = 14.2$ Hz, CH_2CHOH), 1.91 (ddd, 1H, $^3J = 1.5$ Hz, $^3J = 3.7$ Hz, $^2J = 14.2$ Hz, CH_2-CHOH), 2.89 (s, 1H, OH), 3.20–3.29 (m, 2H, dioxolane-CH_2), 3.36–3.45 (m, 2H, dioxolane-CH_2), 3.60 (dd, 1H, $^3J = 1.5$ Hz, $^3J = 10.4$ Hz, CHOH), 4.87 (dd, 1H, $^3J = 3.7$ Hz, $^3J = 5.3$ Hz, CHO$_2$); ^{13}C NMR (C_6D_6, 75 MHz): δ 26.25 (CH_3, C(CH_3)$_3$), 35.01 (C, C(CH$_3$)$_3$), 36.23 (CH_2, CH_2CHOH), 64.90, 65.24 (2 × CH_2, dioxolane-CH_2), 75.69 (CH, CHOH), 106.07 (CH, CHO$_2$); $[\alpha]_D^{20} = -33.3$ (c 0.98, CH_3OH); HRMS (ESI): m/z calcd for $[M+Na]^+$: 197.1148; found: 197.1115; elemental analysis calcd (%) for $C_9H_{18}O_3$ (174.2): C 62.04, H 10.41; found: C 62.32, H 10.51.

4.5. 1-(1,3-Dioxolane-2-yl)-4-phenyl-butane-2-ol 18

Compound **18** was obtained by the addition of 2-vinyloxyethanol to 3-phenylpropanal **17** according to the general procedure for C–C coupling reactions. By using 2-vinyloxyethanol (740 mg, 8.9 mmol), sodium hydride (365 mg, 9.1 mmol), (*R*)-BINOL **4** (2.5 g, 8.9 mmol), a 1 M solution of chlorotitanium trisisopropyloxide in hexane (9.0 mL, 9.0 mmol), and 3-phenylpropanal **17** (591 mg, 4.4 mmol) 606 mg (62%) of compound **18** was obtained: ^{1}H NMR (C_6D_6, 300 MHz, TMS): δ 1.52–1.88 (m, 4H, CH_2CH(OH)CH_2), 2.67 (ddd, 1H, $^3J = 6.6$ Hz, $^3J = 9.8$ Hz, $^3J = 13.8$ Hz, CH_2Ph), 2.81 (ddd, 1H, $^3J = 5.6$ Hz, $^3J = 10.2$ Hz, $^3J = 13.8$ Hz, CH_2Ph), 3.24–3.50 (m, 4H, dioxolane-CH_2), 3.92 (tt, 1H, $^3J = 4.2$ Hz, $^3J = 8.2$ Hz, CHOH), 4.84 (t, 1H, $^3J = 4.5$ Hz, CHO$_2$), 7.04–7.22 (m, 5H, C$H_{ar.}$). ^{13}C NMR (C_6D_6, 75 MHz): δ 32.15 (CH_2, CH_2Ph), 39.56 (CH_2, CH_2CH$_2$Ph), 40.99 (CH_2, CH_2CHO$_2$), 64.55, 64.77 (2 × CH_2, dioxolane-CH_2), 67.44 (CH, CHOH), 103.63 (CH, CHO$_2$), 125.96–128.83 (CH, CH$_{ar.}$), 142.68 (C, $C_{ar.}$); $[\alpha]_D^{20} = +9.1$ (c 0.99, CH_3OH); MS (GC/MS): m/z (%) = 221 (3) $[M^+-H]$, 204 (10) $[M^+-H_2O]$, 160 (15), 142 (11), 117 (26) $[M^+-C_8H_9]$, 105 (18) $[C_8H_9^+]$, 99 (19), 91 (81) $[C_7H_7^+]$, 73 (100) $[C_3H_5O_2^+]$, 65 (19) $[C_5H_5^+]$, 51 (7) $[C_6H_5^+-C_2H_2]$, 45 (43) $[C_2H_5O^+]$; elemental analysis calcd (%) for $C_{13}H_{18}O_3$ (222.3): C 70.24, H 8.16; found: C 70.37, H 8.37.

4.6. 2-Deoxy-4,5-*O*-isopropylidene-D-*erythrolthreo*-pentose-ethyleneglycol-acetal 20

Compound **20** was obtained by the addition of 2-vinyloxyethanol to 2,3-*O*-isopropylidene-D-glyceraldehyde **19**

according to the general procedure for C–C coupling reactions. By using 2-vinyloxyethanol (187 mg, 2.1 mmol), sodium hydride (95 mg, 2.3 mmol), (*R*)-BINOL **4** or (*S*)-BINOL **5** (600 mg, 2.1 mmol) or (*R*,*R*)-TADDOL **6** or (*S*,*S*)-TADDOL **7** (980 mg, 2.1 mmol), a 1 M solution of chlorotitanium trisisopropyloxide in hexane (2.1 mL, 2.1 mmol) and 2,3-*O*-isopropylidene-D-glyceraldehyde **19** (311 mg, 2.4 mmol) compound **20** was obtained. The diastereomers were separated by column chromatography (cyclohexane/EtOAc 8/1). (3*S*)-**20**: $R_f = 0.23$ (CH/EE = 1:1); ^{1}H NMR (C_6D_6, 300 MHz, TMS): δ 1.26, 1.35 (2 × s, 2 × 3H, ^{i}Pr-CH_3), 1.82 (ddd, 1H, $^3J = 4.6$ Hz, $^3J = 9.3$ Hz, $^3J = 14.6$ Hz, H-2), 2.17 (ddd, 1H, $^3J = 2.2$ Hz, $^3J = 4.6$ Hz, $^3J = 14.6$ Hz, H-2′), 2.99 (s, 1H, O*H*), 3.16–3.30 (m, 2H, dioxolane-CH_2), 3.31–3.44 (m, 2H, dioxolane-CH_2), 3.84–4.08 (m, 4H, H-3, H-4, H-5, H-5′), 4.87 (t, 1H, $^3J = 4.6$ Hz, H-1); ^{13}C NMR (C_6D_6, 75 MHz): δ 25.51 (CH_3, ^{i}Pr-*C*H$_3$), 26.89 (CH_3, ^{i}Pr-*C*H$_3$), 37.72 (CH_2, C-2), 64.64, 64.80 (2 × CH_2, dioxolane-*C*H$_2$), 66.84 (CH_2, C-5), 69.33 (CH, C-3), 78.90 (CH, C-4), 103.47 (CH, C-1), 109.30 (C, ^{i}Pr-*C*); $[\alpha]_D^{20} = +9.6$ (*c* 1.00, CH_3OH); (3*R*)-**20**: $R_f = 0.29$ (CH/EE = 1:1); ^{1}H NMR (C_6D_6, 300 MHz, TMS): δ 1.24, 1.34 (2 × s, 2 × 3H, ^{i}Pr-CH_3), 1.78 (ddd, 1H, $^3J = 3.0$ Hz, $^3J = 5.4$ Hz, $^3J = 14.2$ Hz, H-2), 1.97 (ddd, 1H, $^3J = 4.2$ Hz, $^3J = 9.0$ Hz, $^3J = 14.2$ Hz, H-2′), 2.58 (s, 1H, O*H*), 3.23–3.34 (m, 2H, dioxolane-CH_2), 3.36–3.50 (m, 2H, dioxolane-CH_2), 3.73 (m, 2H, H-5, H-5′), 3.80–3.94 (m, 2H, H-3, H-4), 5.04 (dd, 1H, $^3J = 4.2$ Hz, $^3J = 5.4$ Hz, H-1); ^{13}C NMR (75 MHz, C_6D_6): δ 26.39, 26.73 (2 × CH_3, ^{i}Pr-*C*H$_3$), 37.91 (CH_2, C-2), 64.65, 64.84 (CH_2, dioxolane-*C*H$_2$), 65.86 (CH_2, C-5), 68.78 (CH, C-3), 79.19 (CH, C-4), 102.90 (CH, C-1), 109.37 (C, ^{i}Pr-*C*); $[\alpha]_D^{20} = +8.4$ (*c* = 1.00, CH_3OH); HRMS (ESI): *m*/*z* calcd for $[M+Na]^+$: 241.1046; found: 241.1060; elemental analysis calcd (%) for $C_{10}H_{18}O_5$ (218.3): C 55.03, H 8.31; found: C 55.27, H 8.49.

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