A NOVEL PATHWAY TO ALKENYL (TRIFLUOROMETHANESULFONATES). APPLICATION TO THE CONVERSION OF SUGAR LACTONES INTO VERSATILE CHIRONS

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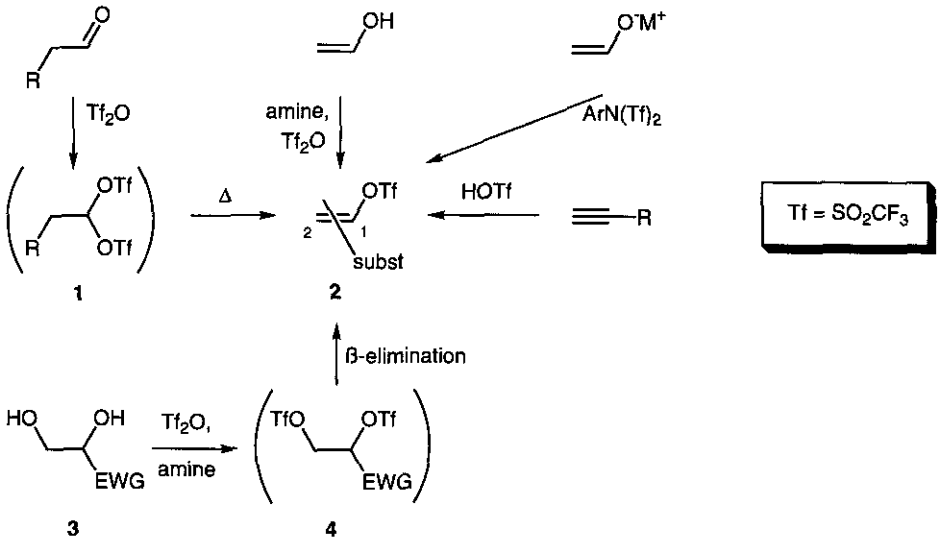
Dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday in deep appreciation of the excitement about Organic Chemistry which he let two of us (I. K., R. B.) share with him.

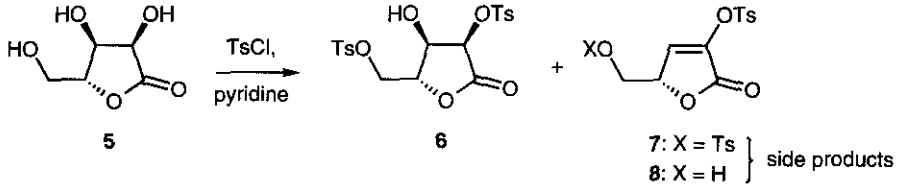
Abstract - Treatment of sugar-γ-lactone monoacetonides with triflic anhydride and pyridine provided monotriflates (**18**, *ent*-**18**, **33**, and *ent*-**33**) or led to alkenyl triflates (**17**, *ent*-**17**, **32**, and *ent*-**32**) depending on the stoichiometry. One-step conversions of these triflates into various enantiopure chirons are described.

Alkenyl (trifluoromethanesulfonates) ("alkenyl triflates", **2**) represent synthetic intermediates of ever increasing importance.[1] They are usually prepared either from enols, a tertiary amine, and trifluoromethanesulfonic acid anhydride ("triflic anhydride", Tf_2O),[2] or from enolates and aniline bis(trifluoromethanesulfonamide)[3] or 2-pyridyl amine bis(trifluoromethanesulfonamide).[4] A less frequently practiced synthesis of alkenyl triflates is the addition of trifluoromethanesulfonic acid to alkynes.[5] Last but not least, alkenyl triflates without an alkyl substituent in the 1-position were prepared *via* ß-elimination of aldehyde hydrate bistriflates (**1**).[6] In the present paper we describe another route to alkenyl triflates. As starting materials glycols (**3**) equipped with an electron withdrawing group ("EWG") are employed. These glycols can be converted - presumably *via* the corresponding bistriflates (**4**) and *in-situ* β-elimination - into alkenyl triflates (**2**) with an acceptor substituent in the 1-position.

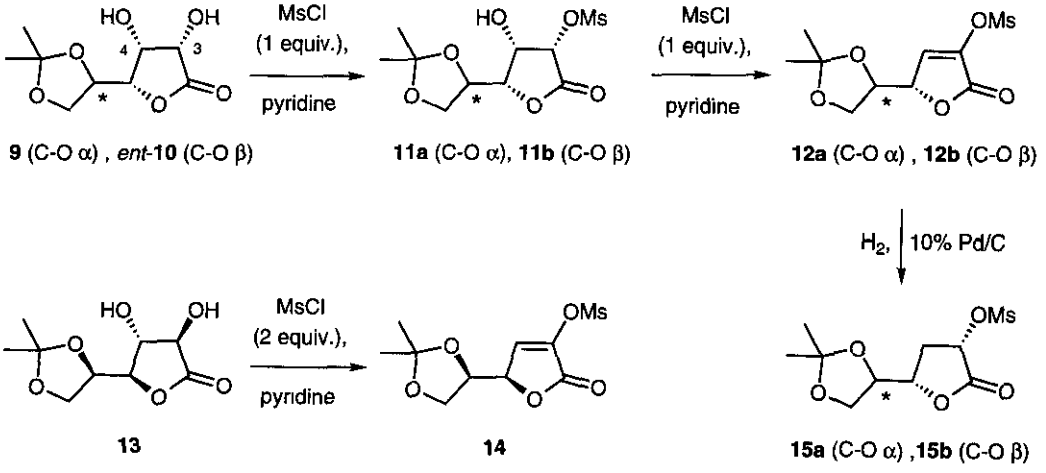
This novel route was specifically applied to sugar-derived γ-lactones as a particular class of EWG-contain-



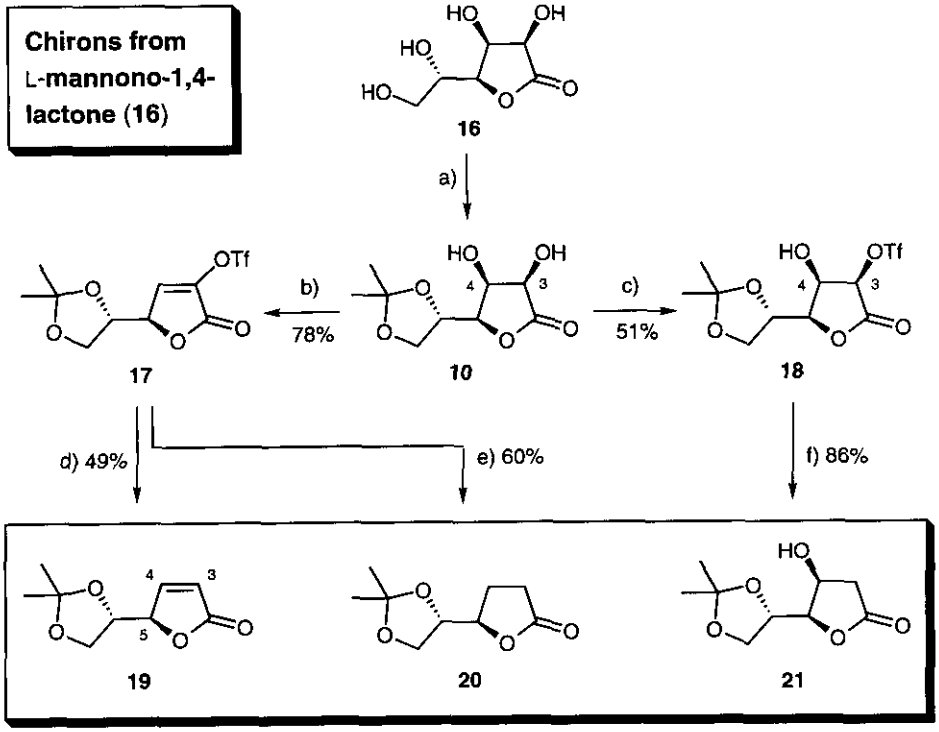
ing glycols. This was done because the corresponding alkenyl triflates constitute interesting chiral synthons ("chirons"), for example through their role als progenitors of other chirons. The importance of commercially available or easily preparable chirons for the synthesis of enantiopure compounds can hardly be overestimated.[7]



We are aware of two previous reports about the conversion of sugar-derived γ-lactones into alkenyl sulfonates. The first is by Barton *et al.*[8] who isolated the alkenyl tosylates (**7**) and (**8**) as side products when treating D-ribonolactone (**5**) in pyridine with excess tosyl chloride. Compounds (**7**) and (**8**) must stem from overall *cis*-eliminations of *vic*-ditosylate intermediates.



According to the second pertinent literature precedence,[9] overall *cis*-eliminations of the *vic*-dimesylates obtained *in-situ* from the lactone monomesylates (**11a**) and (**11b**) and mesyl chloride / pyridine were effected by purpose. They delivered the alkenyl mesylates (**12a**) and (**12b**) in fair yields. In the conversion of *trans*-glycol lactone (**13**) into alkenyl mesylate (**14**),[9] an analogous overall *trans*-elimination took place.



*Scheme 1: a) As described for the enantiomer ent-**10** in ref [10].- b) Tf_2O (2.4 equiv.), pyridine (4 equiv.), CH_2Cl_2, -78°C, 20 min; → -20°C, 2.5 h.- c) Tf_2O (1.2 equiv.), pyridine (2.4 equiv.), CH_2Cl_2, -78°C, 4 h.- d) Me_3SnH[11] (3.3 equiv.), LiCl (3.0 equiv.), CsF (1.3 equiv.), $Pd(PPh_3)_4$[12] (16 mol-%), THF, room temperature, 4 h.- e) H_2 (4 bar), iPr_2NEt (1.9 equiv.), Pd (10% on C), AcOEt, room temperature, 3.3 h.- f) H_2 (4.5 bar), iPr_2NEt (5.5 equiv.), Pd (10% on C), AcOEt, room temperature, 4.5 h.*

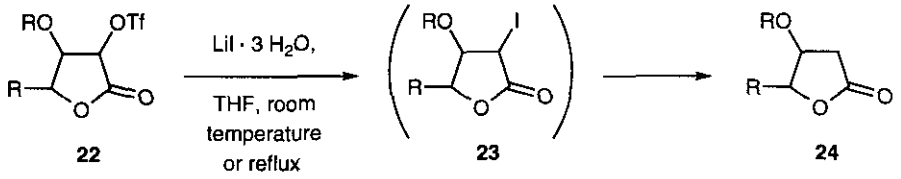
We treated monoacetonide (**10**) of L-mannonic acid γ-lactone (**16**) *with* >2 equiv. Tf_2O in CH_2Cl_2 / pyridine first at -78°C and then at -20°C (Scheme 1). After flash chromatography on silica gel,[13] alkenyl triflate (**17**) was isolated in 78% yield. Compound (**17**) was readily identified by a ^{1}H-nmr doublet for the olefinic proton at very low field (δ 7.41, J_{vic} = 1.8 Hz).

Reductions of alkenyl triflates to alkenes have been described with the reagent combinations $HCOO^- R_3NH^+$ / cat. $Pd(OAc)_2(PPh_3)_2$ / DMF,[14] Bu_3SnH / LiCl / cat. $Pd(PPh_3)_4$,[15] and Et_3SiH / LiCl / cat. $Pd(PPh_3)_4$.[15] The first of them, when applied to triflate (**17**), led to a plethora of unidentified products. The concomitant action of Bu_3SnH, LiCl, and a considerable albeit substoichiometric amount of $Pd(PPh_3)_4$ transformed triflate (**17**) into a tiny amount of the desired reduction product (**19**) (Scheme 1). Varying these conditions, Me_3SnH in combination with LiCl, CsF, and 16 mol-% of $Pd(PPh_3)_4$ was found suitable for hydro-

genolyzing alkenyl triflate (**17**) to butenolide (**19**) at room temperature in 49% yield. Compound (**19**) exhibited two olefinic ^{1}H-nmr resonances: one dd with $J_{3,4}$ = 5.5 Hz and $^4J_{3,5}$ = 1.7 Hz for 3-H at δ 5.62 and one ddd with $J_{4,3}$ = 5.7 Hz, $J_{4,5}$ = 1.5 Hz, and $^4J_{4,4'}$ = 0.8 Hz for 4-H at δ 6.78.

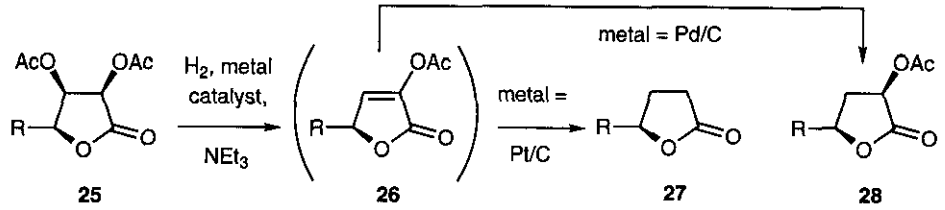
Reductions of alkenyl triflates to alkanes are also known. They employ H_2 as the reductant and Pd, Pt or Ru on charcoal as heterogenous catalysts.[16] We used Pd-C for the transformation of alkenyl triflate (**17**) into γ-lactone (**20**) (Scheme 1; 60% yield) and trapped the liberated triflic acid with added iPr_2NEt. Interestingly, under the influence of H_2 / Pd-C the alkenyl *mesylate* analogue (**12b**) of triflate (**17**) experiences a hydrogenation but *no* hydrogenolysis according to Godefroi and coworkers;[9] thereby, it provides the saturated mesylate (**15b**). This difference illustrates the superior leaving group quality of triflate vs. mesylate groups.

Godefroi *et al.* had also been able to monomesylate the hydroxy group at C-3 of the L-gulono-γ-lactone acetonide (**9a**) (→ **11a**) and of the D-mannono-γ-lactone acetonide *ent*-(**10**) (→ **11b**) without too much interference of the second hydroxy group at C-4.[9] Likewise, sulfonylation of L-mannono-γ-lactone acetonide (**10**) with 1.2 equiv. of Tf_2O / pyridine occurred preferentially at 3-OH and affected 4-OH - before or thereafter - sufficiently little so that we could isolate monotriflate (**18**) in 51% yield (Scheme 1). The location of the triflate group at C-3 rather than at C-4 of this molecule follows from the lowfield shift of the only doublet which the 300 MHz ^{1}H-nmr spectrum of monotriflate (**18**) displays (δ 5.37 vs. 4.47 in the precursor (**10**); $J_{3,4}$ = 2.9 Hz). Interestingly, the cleavage of the C-OTf bond of monotriflate (**18**) could be achieved by H_2 (4.5 bar) in the presence of Pd-C, too (Scheme 1). Thus, we obtained 86% of acetonide (**21**) of a 2-deoxygenated sugar lactone.



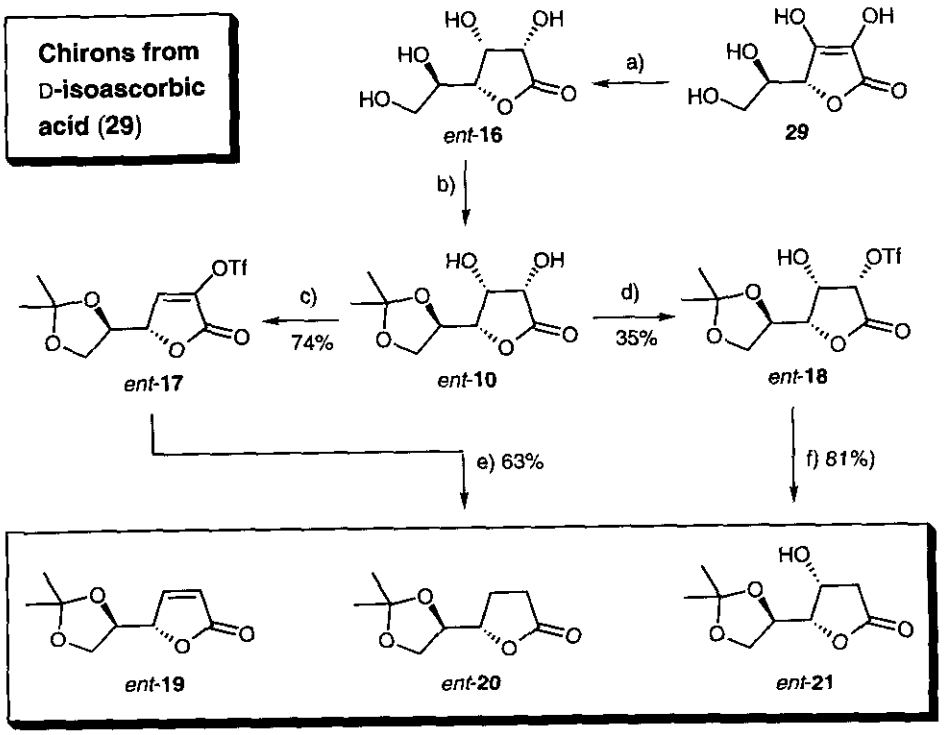
22 **23** **24**

To the best of our knowledge the hydrogenolysis of an *alkyl* triflate has not been described before.[17] Instead, sugar lactones (**22**) with a triflate group α to the C=O bond - i.e., substrates analogous to monotriflate (**18**) - were reduced[18] (→ **24**) by an adaptation of Paulsen's iodide reduction of α-brominated sugar lactones.[19] α-Iodinated lactones (**23**) are the likely intermediates. The dideoxygenation of bis(acetoxylated) lactones (**25**) *via in-situ* formed butenolides (**26**) into lactones (**27**) in the presence of H_2 and Pt[20] were mechanistically analogous to our triflate hydrogenolysis if they proceeded from **26** first to the saturated intermediate (**28**); type-**28** compounds are obtained from butenolides akin to **26** and H_2 / Pd exclusively.[21]



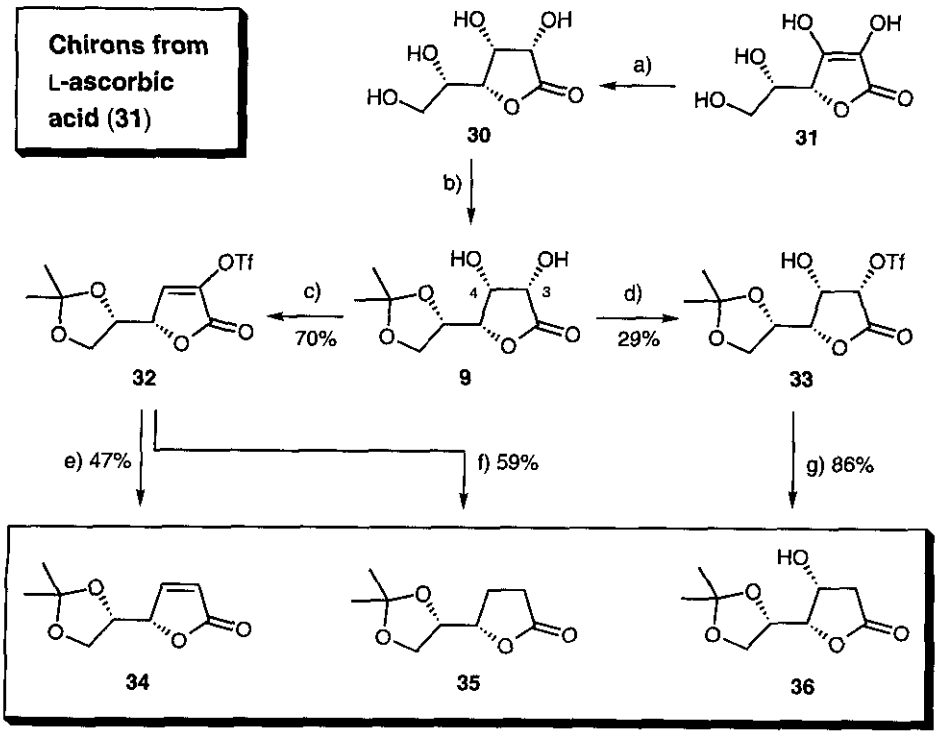
25 **26** **27** **28**

Starting from D-isoascorbic acid (**29**) we next prepared the monoacetonide (*ent*-**10**) of D-mannono lactone (Scheme 2), i.e., the enantiomer of the key intermediate (**10**) of Scheme 1. Accordingly, by applying the reaction conditions detailed above, we proceeded from there *via* butenolide triflate (*ent*-**17**) (74%) and the saturated monotriflate (*ent*-**18**) (35%) to the chirons (*ent*-**20**) (63%) and (*ent*-**21**) (81%), respectively. In summary, the novel preparation of alkenyl triflates makes compounds (**19**), (**20**), and (**21**) accessible from L-mannono lactone in three steps and their enantiomers *ent*-**19**, *ent*-**20**, and *ent*-**21** accessible from D-isoascorbic acid in four steps.



Scheme 2: a) Ref.[22]*.- b) Ref.*[10]*.- c) Tf_2O (2.4 equiv.), pyridine (4 equiv.), CH_2Cl_2, -78°C, 25 min; → -20°C, 3 h.- d) Tf_2O (1.2 equiv.), pyridine (2.4 equiv.), CH_2Cl_2, -78°C, 3 h.- e) H_2 (4 bar), iPr_2NEt (1.9 equiv.), Pd (10% on C), AcOEt, room temperature, 3 h.- f) H_2 (4 bar), iPr_2NEt (5.5 equiv.), Pd (10% on C), AcOEt, room temperature, 3 h.*

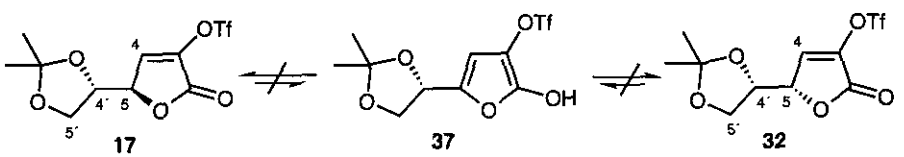
Scheme 3 shows the application of the same set of reactions to L-ascorbic acid (**31**) as the starting lactone. The corresponding alkenyl triflate (**32**) and the saturated monotriflate (**33**), respectively, were converted under the earlier described conditions into butenolide (**34**) (47% from **32**; this compound was contaminated in a 1:14 ratio with the dihydro derivative (**35**), the 2,3-dideoxy-sugar derived lactone (**35**) (59% from **32**), and the 2-deoxy-sugar based lactone (**36**) (86% from **33**). These lactones are chirons which represent diastereomers of the ones depicted in Schemes 1 and 2. The enantiomeric dideoxy (*ent*-**35**) and monodeoxy lactone (*ent*-**36**) were similarly prepared (Scheme 4) from D-gulono-γ-lactone (*ent*-**30**).



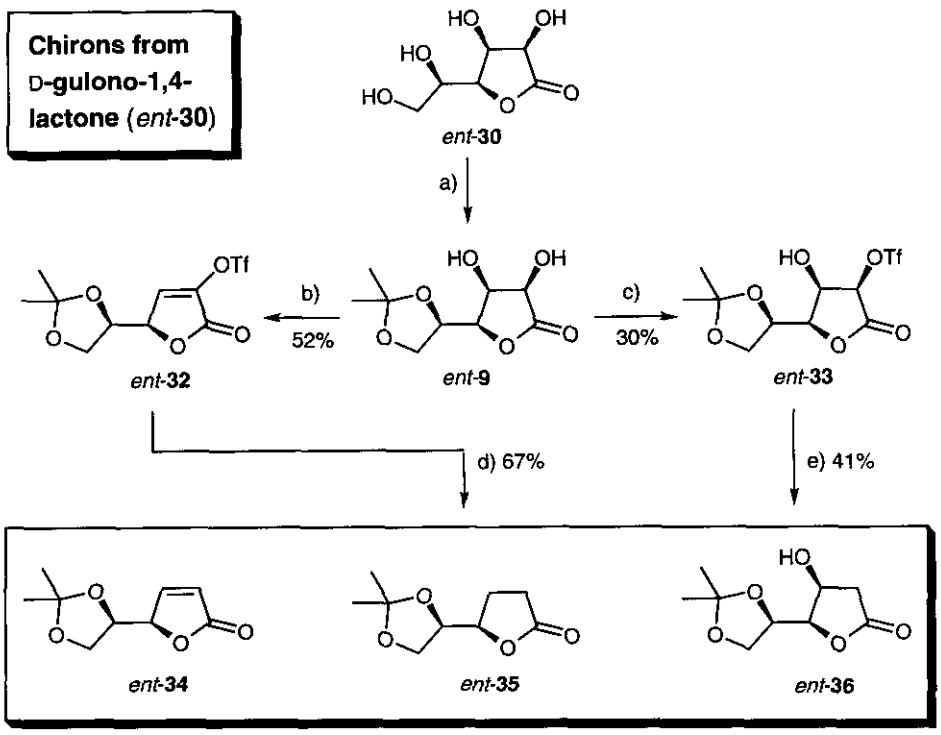
*Scheme 3: a) Ref.[22].- b) Ref.[10].- c) Tf_2O (2.4 equiv.), pyridine (4 equiv.), CH_2Cl_2, -78°C, 10 min; → -20°C, 3.5 h.- d) Tf_2O (1.2 equiv.), pyridine (2.4 equiv.), CH_2Cl_2, -78°C, 4 h.- e) Me_3SnH[11] (3.6 equiv.), LiCl (3.0 equiv.), CsF (1.3 equiv.), $Pd(PPh_3)_4$[12] (30 mol-%), THF, room temperature, 7 h; 50% of a 14:1 mixture of **34** and **35**.- f) H_2 (4 bar), iPr_2NEt (2.0 equiv.), Pd (10% on C), AcOEt, room temperature, 3.7 h.- g) H_2 (4.5 bar), iPr_2NEt (5.4 equiv.), Pd (10% on C), AcOEt, room temperature, 4.5 h.*

Our bis(sulfonylations) / β-eliminations of diols (**10**) and (**9**) had given the alkenyl triflates (**17**) and (**32**), respectively, stereospecifically. They were not contaminated with each other as proven by their ^{1}H-nmr spectra (Table 1). This means that the triflate group does not acidify these butenolides to such an extent that they epimerize *via* the hydroxyfuran tautomer (**37**).

Table 1: ^{1}H-Nmr data (300 MHz) of alkenyl triflates (17) and (32)



17	δ in $CDCl_3$	17	J_{vic} / Hz	32	δ in $CDCl_3$	32	J_{vic} / Hz
4-H	7.41	$J_{4,5}$ =	1.8	4-H	7.26	$J_{4,5}$ =	1.7
5-H	4.91	$J_{5,4'}$ =	7.6	5-H	5.15	$J_{5,4'}$ =	3.3
4'-H	4.02	$J_{4';5'-H(1)}$ =	3.3	4'-H	4.46	$J_{4';5'-H(1)}$ =	5.0
5'-H(1)	4.12	$J_{4';5'-H(2)}$ =	6.1	5'-H(1)	3.90	$J_{4';5'-H(2)}$ =	6.8
5'-H(2)	4.19			5'-H(2)	4.15		



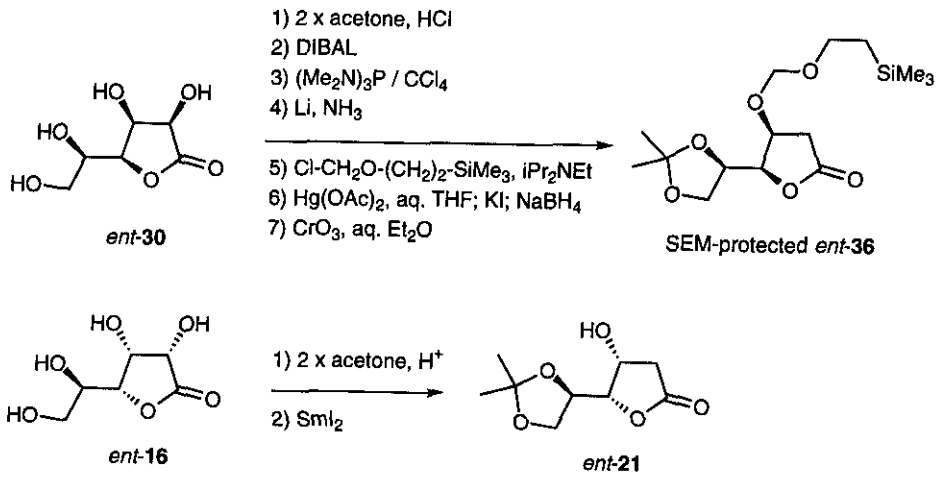
Scheme 4: a) As described for the enantiomer **9** *in ref.*[10]*.- b)* Tf_2O *(2.4 equiv.), pyridine (4 equiv.),* CH_2Cl_2*, -78°C, 15 min; → -25°C, 3 h.- c)* Tf_2O *(1.0 equiv.), pyridine (2.0 equiv.),* CH_2Cl_2*, -78°C, 2 h.- d)* H_2 *(4 bar),* iPr_2NEt *(3.2 equiv.), Pd (10% on C), AcOEt, room temperature, 2 h.- e)* H_2 *(4.5 bar),* iPr_2NEt *(2 0 equiv.), Pd (10% on C), AcOEt, room temperature, 2.5 h.*

Given the many facets of alkenyl triflate chemistry,[1] the novel alkenyl triflates (**17**, **32**) and their enantiomers constitute synthons of promising potential. The here described synthetic paths from sugar-derived triflates

(a) to butenolides are of similar efficiency as existing ways[23] but are less preferable for large-scale preparations because of the high costs of Me_3SnH and $Pd(PPh_3)_4$;

(b) to 2,3-dideoxy sugar lactones are more straightforward than the hitherto practiced preparations *via* butenolides and their hydrogenation; on the other hand, they are more expensive (Tf_2O) than Inanaga's hydrogenation / hydrogenolysis reaction **25** → **27**;

(c) to 2-deoxy sugar based lactones are much shorter than an older route by Heathcock *et al.*[24] (*ent*-**30** → SEM-protected *ent*-**36** required 7 steps); nonetheless, the so far modest yields of the monotriflate formations (29-51%) decrease the efficiency compared with Hanessian's procedure[25] by which the transformation *ent*-**16** → *ent*-**21** is realized in two high-yielding steps.



ACKNOWLEDGMENT

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Experimental

All reactions were performed in oven-dried (100°C) glassware under N_2. THF and Et_2O were freshly distilled from K/Na; CH_2Cl_2 and pyridine from CaH_2; EtOAc was dried with P_2O_5 before distillation. Products were purified by flash chromatography[13] on Merck silica gel 60 (particle size 0.040 - 0.063 mm, 230 - 240 mesh ASTM; eluents given in brackets). Yields refer to analytically pure samples. ^1H and ^{13}C nmr (tetramethylsilane or $CHCl_3$ as internal standard in $CDCl_3$): Bruker AMX 300 and Varian VXR 500S; integrals in accord with assignments; coupling constants in Hz; AB spectra: H_A refers to high- and H_B to low-field resonance; ^{13}C-nmr spectra: δ values refer to δ ($^{13}\underline{C}DCl_3$) = 77.00; ^{13}C APT spectra: "+" for CH or CH_3, "–" for CH_2 or C. - IR: Perkin-Elmer FT-IR 1600. - Optical rotation: Perkin-Elmer 241 Polarimeter. - Combustion analyses: M. Beller, Institute of Organic Chemistry, University of Göttingen. - Mass spectra: G. Remberg, Institute of Organic Chemistry, University of Göttingen.

(+)-(4'*S*,5*R*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2(5*H*)-furanon-3-yl] trifluoromethanesulfonate (17) [Representative procedure for the preparation of enol triflates from 5,6-isopropylidene-2,3-dihydroxy-

1,4-lactone derivatives]. Trifluoromethanesulfonic anhydride ('Tf_2O', freshly distilled over P_4O_{10}; 150 µl, 251 mg, 0.89 mmol, 2.4 equiv.) *in* CH_2Cl_2 (3.5 ml) was added *dropwise to* **10** (82 mg, 0.376 mmol) and pyridine (122 µl, 119 mg, 1.51 mmol, 4.0 equiv.) in CH_2Cl_2 (3.5 ml) under N_2 at –78°C. After stirring at –78°C for 15 min the mixture was warmed to –25°C over a period of 3 h, poured into chilled Et_2O (50 ml), filtered, and concentrated *in vacuo* at ice-bath temperature. Flash chromatography of the crude product on silica gel [50% CH_2Cl_2/50% petroleum ether - ^{t}BuOMe (5:1)] furnished **17** (98 mg, 78%) as a colorless solid; $[\alpha]_D^{22}$ = +77° (*c* 1.0, $CHCl_3$); mp 52-53°C; ^{1}H nmr (300 MHz, $CDCl_3$, TMS): δ = 1.36 and 1.47 [2s, 2'-$(CH_3)_2$], 4.02 (ddd, $J_{4',5}$ = 7.5, $J_{4',5'\text{-H(B)}}$ = 6.1, $J_{4',5'\text{-H(A)}}$ = 3.3, 4'-H), AB signal (δ_A = 4.12, δ_B = 4.19, J_{AB} = 9.5, in addition split by $J_{A,4'}$ = 3.2, $J_{B,4'}$ = 6.0, 5'-H_2), 4.91 (dd, $J_{5,4'}$ = 7.7, $J_{5,4}$ = 1.7, 5-H), 7.41 (d, $J_{4,5}$ = 1.9, 4-H); ir (film): ν = 3125, 2995, 1780, 1660, 1435, 1250, 1215, 1135, 1105 cm^{-1}; Anal. Calcd for $C_{10}H_{11}O_7F_3S$: C, 36.15, H 3.34. Found: C, 36.52; H, 3.43.

(–)-(4'*R*,5*S*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2(5*H*)-furanon-3-yl] trifluoromethanesulfonate (*ent*-17). *ent*-**10** (252 mg) in CH_2Cl_2 (17 ml) furnished *ent*-**17** (284 mg, 74%); $[\alpha]_D^{19}$ = –78° (*c* 1.0, $CHCl_3$); mp 51-53°C.

(–)-(3*R*,4*R*,4'*S*,5*R*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanon-3-yl] trifluoromethanesulfonate (18) [Representative procedure for the preparation of monotriflates from 5,6-isopropylidene-2,3-dihydroxy-1,4-lactone derivatives]. A solution of Tf_2O (freshly distilled over P_4O_{10}; 448 µl, 751 mg, 2.66 mmol, 1.2 equiv.) in CH_2Cl_2 (2 ml) was added to **10** (500 mg, 2.29 mmol) and pyridine (442 µl, 432 mg, 5.46 mmol, 2.4 equiv.) in CH_2Cl_2 (28 ml) under N_2 at –78°C over a period of 5 min. After stirring at –78°C for 4 h the mixture was poured into chilled Et_2O (300 ml), filtered, and concentrated *in vacuo* at ice-bath temperature. Flash chromatography of the crude product (once for **18** and *ent*-**18**, twice for **33** and *ent*-**33**) on silica gel [petroleum ether - ^{t}BuOMe (3:1)] gave 18 (408 mg, 51%) as a colorless solid; $[\alpha]_D^{17}$ = –24° (*c* 1.0, Et_2O); mp 118-119°C (decomp.); ^{1}H nmr (300 MHz, $CDCl_3$, TMS): δ = 1.38 and 1.46 [2s, 2'-$(CH_3)_2$], 2.92 (br. s, 4-OH), AB signal (δ_A = 4.07, δ_B = 4.19, J_{AB} = 9.6, in addition split by $J_{A,4'}$ = 3.4, $J_{B,4'}$ = 5.7, 5'-H_2), 4.30 (dd, $J_{5,4'}$ = 8.6, $J_{5,4}$ = 3.0, 5-H), 4.46 (ddd, $J_{4',5}$ = 8.9, $J_{4',5'\text{-H(B)}}$ = 5.7, $J_{4',5'\text{-H(A)}}$ = 3.2, 4'-H), 4.79 (ddd, $J_{4,3} \approx J_{4,5} \approx J_{4,OH}$ = 2.5, 4-H), 5.37 (d, $J_{3,4}$ = 2.9, 3-H); ms (DCI/200 eV): *m*/*z* = 718.4 (5%, 2xM + NH_4^+), 385.2 (16%, M + NH_3 + NH_4^+), 368.2 (100%, M + NH_4^+), 220.2 (40%, M – SO_3CF_3 + NH_4^+); HRms (EI/70 eV): *m*/*z* = 335.0048 (M^+ – 2'-Me); ir (film): ν = 3375, 2990, 1800, 1775, 1425, 1250, 1215, 1135, 1065 cm^{-1}; due to the instability of the monotriflate under the microanalysis conditions a high resolution mass spectrogram was recorded in lieu; $C_9H_{10}O_8F_3S$ (M^+ – 2'-Me): calcd. 335.0048; the molecular mass (±2 ppm; *R* = 10000) was checked by EI HRms (70 eV) of the exact mass.

(+)-(3*S*,4*S*,4'*R*,5*S*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanon-3-yl] trifluoromethanesulfonate (*ent*-18). *ent*-**10** (155 mg) in CH_2Cl_2 (10 ml) furnished *ent*-**18** (86 mg, 35%); $[\alpha]_D^{19}$ = +25° (*c* 1.0, Et_2O); mp 116-117°C (decomp.).

(+)-(4'*S*,5*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2(5*H*)-furanone (19) [Representative procedure for the hydrogenolysis of enol triflates]. Me_3SnH (166 mg, 1.00 mmol, 3.3 equiv.) was added dropwise to a mixture of **17** (100 mg, 0.301 mmol), LiCl (38 mg, 0.90 mmol, 3.0 equiv.), CsF (62 mg, 0.41 mmol, 1.4 equiv.), and $Pd(PPh_3)_4$ (53 mg, 0.047 mmol, 0.16 equiv.) in THF (3.2 ml). After stirring for 2 h under N_2 at room temperature another portion of Me_3SnH (54 mg, 0.33 mmol, 1.0 equiv.) was added and stirring was continued for 2 h. The reaction mixture was diluted with CH_2Cl_2 (10 ml), filtered, and concentrated *in vacuo*. Flash chromatography of the crude product on silica gel [50% CH_2Cl_2/ 50% petroleum ether - ^tBuOMe (5:1)] gave **19** (27 mg, 49%); $[\alpha]_D^{18}$ = +146° (*c* 0.33, CH_2Cl_2) [lit.,[10] (*ent*-**19**) $[\alpha]_D^{20}$ = −154° (*c* 1.01, $CHCl_3$)]; mp 31-32°C [lit.,[10] (*ent*-**19**) 33-34°C]; ^1H nmr (300 MHz, C_6D_6): δ = 1.14 and 1.29 [2s, 2'-$(CH_3)_2$], 3.33-3.39 (m, 4'-H), AB signal (δ_A = 3.65, δ_B = 3.71, J_{AB} = 9.0, in addition split by $J_{A,4'}$ = 6.1, $J_{B,4'}$ = 4.5, 5'-H_2), 4.21 (ddd only resolved as br. d, $J_{5,4'}$ = 7.6, 5-H), 5.62 (dd, $J_{3,4}$ = 5.5, $^4J_{3,5}$ = 1.7, 3-H), 6.78 (ddd, $J_{4,3}$ = 5.7, $J_{4,5}$ = 1.5, $^4J_{4,4'}$ = 0.8, 4-H); ^{13}C nmr (125.7 MHz, C_6D_6): δ = 24.90 and 26.68 [2'-$(CH_3)_2$], 66.88, 76.34, 82.66 (C-5, C-4', C-5'), 110.06 (C-2'), 122.24 (C-3), 153.85 (C-4), 171.55 (C-2); ms (EI/70 eV): *m*/*z* = 169 (84%, M^+ − 2'-Me), 109 (54%), 101 (85%, dimethyldioxolanyl cation), 43 (100%, C_2H_3O); ir (film): ν = 3095, 2990, 2885, 1755, 1590, 1380, 1255, 1220, 1160, 1055 cm^{-1}; $C_8H_9O_4$ (M^+ − 2'-Me): calcd. 169.0500; the molecular mass (±2ppm; *R* = 10000) was checked by EI HRms (70 eV) of the exact mass; Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.58; H, 6.63.

20 ((−)-(4'*S*,5*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-2(3*H*)-furanone (20). **17** (95 mg) in AcOEt (9 ml) furnished 32 mg, 60%); $[\alpha]_D^{21}$ = −6° (*c* 1.0, $CHCl_3$); ^1H nmr (500 MHz, $CDCl_3$, TMS): δ = 1.36 and 1.44 [2q only resolved as d, $^4J \approx 0.5$, 2'-$(CH_3)_2$], AB signal (δ_A = 2.18, δ_B = 2.37, J_{AB} = 13.2, in addition split by $J_{A,3\text{-}H(B)}$ = 10.1, $J_{A,3\text{-}H(A)}$ = 7.3, $J_{A,5}$ = 6.0, $J_{B,3\text{-}H(A)}$ = 9.7, $J_{B,5}$ = 7.4, $J_{B,3\text{-}H(B)}$ = 6.4, 4-H_2), AB signal (δ_A = 2.53, δ_B = 2.60, J_{AB} = 17.8, in addition split by $J_{A,4\text{-}H(B)}$ = 9.7, $J_{A,4\text{-}H(A)}$ = 7.6, $J_{B,4\text{-}H(A)}$ = 9.8, $J_{B,4\text{-}H(B)}$ = 6.4, 3-H_2), 3.87 and 4.13 (2m_c, 5'-H_2), 4.17 (ddd, $J_{4',5} = J_{4',5'\text{-}H(1)}$ = 6.5, $J_{4',5'\text{-}H(2)}$ = 4.5, 4'-H), 4.42 (ddd, $J_{5,4\text{-}H(B)}$ = 7.5, $J_{5,4'} = J_{5,4\text{-}H(A)}$ = 6.3, 5-H); ir (film): ν = 2985, 2940, 1780, 1455, 1380, 1370, 1265, 1210, 1180, 1060 cm^{-1}; Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.81; H, 7.55. An H,H-COSY experiment was used to verify unambiguously the assignment of 5-H, 4'-H, 5'-H^1, and 5'-H^2: the signal at δ = 4.42 (5-H) exhibits cross-peaks with 2.18 (4-H_A), 2.37 (4-H_B), and 4.17 (4'-H), the signal at δ = 4.17 (4'-H) exhibits cross-peaks with 3.87 (5'-H^1), 4.13 (5'-H^2), and 4.42 (5-H), the signal at δ = 3.87 (5'-H^1) exhibits cross-peaks with 4.13 (5'-H^2) and 4.17 (4'-H), and the signal at δ = 4.13 (5'-H^2) exhibits cross-peaks with 3.87 (5'-H^1) and 4.17 (4'-H).

(+)-(4'*R*,5*S*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-2(3*H*)-furanone (*ent*-**20**). *ent*-**17** (105 mg) in AcOEt (10 ml) furnished *ent*-**20** (37 mg, 63%); $[\alpha]_D^{19}$ = +6° (*c* 1.0, $CHCl_3$).

(–)-(4*S*,4'*S*,5*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanone (21) [Representative procedure for the hydrogenolysis of monotriflates]. $^iPr_2NEt$ (720 µl, 534 mg, 4.06 mmol, 5.5 equiv.) and Pd-C (10%, 62 mg) were added to a solution of monotriflate(**18**)(259 mg, 0.74 mmol) in AcOEt (20 ml). The resulting mixture was stirred vigorously under H_2 (4.5 bar) for 4.5 h. Filtration, concentration *in vacuo*, and flash chromatography on silica gel [petroleum ether - ^{t}BuOMe (1:1)] furnished **21** (128 mg, 86%) as a colorless solid; $[\alpha]_D^{16}$ = –35° (*c* 1.0, $CHCl_3$); mp 55-57°C; ^{1}H nmr (300 MHz, $CDCl_3$, TMS): δ = 1.38 and 1.45 [2s, 2'-$(CH_3)_2$], AB signal (δ_A = 2.60, δ_B = 2.80, J_{AB} = 17.9, in addition split by $J_{A,4} \approx 0.7$, $J_{B,4}$ = 5.6, 3-H_2), 2.76-2.78 (OH), AB signal (δ_A = 4.05, δ_B = 4.20, J_{AB} = 9.1, in addition split by $J_{A,4'}$ = 4.2, $J_{B,4'}$ = 6.1, 5'-H_2), 4.26 (dd, $J_{5,4'}$ = 8.7, $J_{5,4}$ = 3.8, 5-H), 4.41 (ddd, $J_{4',5}$ = 8.7, $J_{4',5'\text{-H(B)}}$ = 6.0, $J_{4',5'\text{-H(A)}}$ = 4.2, 4'-H), 4.63-4.69 (m, 4-H); ir (film): ν = 3445, 2990, 2935, 1770, 1385, 1255, 1210, 1150, 1065 cm^{-1}; Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.36; H, 6.98.

(+)-(4*R*,4'*R*,5*S*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanone (*ent*-**21**). *ent*-**18** (150 mg) in AcOEt (20 ml) furnished *ent*-**21** (70 mg, 81%); $[\alpha]_D^{19}$ = +36° (*c* 1.0, $CHCl_3$) [lit.,[25] $[\alpha]_D^{25}$ = +37.1° (*c* 0.95, $CHCl_3$)]; mp 61-62°C (lit.,[25] 62-64°C).

(–)-(4'*S*,5*S*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2(5*H*)-furanon-3-yl] trifluoromethanesulfonate (32). **9** (400 mg) in CH_2Cl_2 (28 ml) furnished **32** (427 mg, 70%); $[\alpha]_D^{22}$ = –35° (*c* 1.0, $CHCl_3$); mp 67-69°C (decomp.).

(+)-(4'*R*,5*R*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2(5*H*)-furanon-3-yl] trifluoromethanesulfonate (*ent*-**32**). *ent*-**9** (310 mg) in CH_2Cl_2 (19 ml) furnished *ent*-**32** (246 mg, 52%); $[\alpha]_D^{22}$ = +34° (*c* 1.9, $CHCl_3$); mp 64-66°C (decomp.); ^{1}H nmr (300 MHz, $CDCl_3$): δ = 1.35 and 1.41 [2s, 2'-$(CH_3)_2$], AB signal (δ_A = 3.91, δ_B = 4.14, J_{AB} = 9.1, in addition split by $J_{A,4'}$ = 5.3, $J_{B,4'}$ = 6.8, 5'-H_2), 4.46 (ddd, $J_{4',5'\text{-H(A)}}$ = 4.9, $J_{4',5'\text{-H(B)}}$ = 7.0, $J_{4',5'}$ = 3.2, 4'-H), 5.16 (dd, $J_{4',5}$ = 2.6, $J_{4,5}$ = 2.3, 5-H), 7.27 (d, $J_{4,5}$ = 1.5, 4-H); ^{13}C nmr (APT spectrum, 125.7 MHz, $CDCl_3$): δ = '+' 24.78 and '+' 25.73 [2'-$(CH_3)_2$], '–' 64.45 (C-5'), '+' 73.73 and '+' 77.55 (C-5, C'-4), '–' 110.88 (C-2'), '–' 118.50 (q, $^1J_{C,F}$ = 321.2, CF_3), '+' 135.02 (C-4), '–' 138.23 (C-3), '–' 163.41 (C-2); ms (EI/70 eV): *m/z* = 317 (82%, M^+ – 2'-Me), 101 (100%, dimethyldioxolanyl cation), 69 (24%, CF_3), 43 (69%, C_2H_3O); ir (film): ν = 3120, 2990, 1775, 1655, 1435, 1255, 1220, 1135, 1105 cm^{-1}; Anal. Calcd for $C_{10}H_{11}O_7F_3S$: C, 36.15; H, 3.34. Found: C, 36.38; H, 3.26.

(+)-(3*S*,4*S*,4'*S*,5*S*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanon-3-yl] trifluoromethanesulfonate (33). **9** (146 mg) in CH_2Cl_2 (10 ml) furnished **33** (69 mg, 29%); $[\alpha]_D^{21}$ = +27° (*c* 1.0, EtOAc); mp 104°C (decomp.); ^{1}H nmr (300 MHz, $CDCl_3$, TMS): δ = 1.41 and 1.48 [2s, 2'-$(CH_3)_2$], 3.74 (d, $J_{OH,4}$ = 4.5, 4-OH), AB signal (δ_A = 4.07, δ_B = 4.22, J_{AB} = 9.0, in addition split

by $J_{A,4'}$ = 5.7, $J_{B,4'}$ = 6.8, 5'-H_2), 4.49 (dd, $J_{5,4}$ = 4.2, $J_{5,4'}$ = 3.7, 5-H), 4.59 (ddd, $J_{4',5'\text{-H(B)}}$ = 6.8, $J_{4',5'\text{-H(A)}}$ = 5.7, $J_{4',5}$ = 4.5, 4'-H), 4.78 (ddd, $J_{4,3} \approx J_{4,5} \approx J_{4,OH}$ = 4.3, 4-H), 5.31 (d, $J_{3,4}$ = 5.3, 3-H); ^{13}C nmr (APT spectrum, 125.7 MHz, $CDCl_3$/MeOH): δ = '+' 24.96 and '+' 26.34 [2'-$(CH_3)_2$], '+' 50.31 (MeOH), '–' 64.75 (C-5'), '+' 68.33, '+' 74.49, '+' 79.29, '+' 81.60 (C-3, C-4, C-5, C-4'), '–' 110.60 (C-2'), '–' 118.37 (q, $^1J_{C,F}$ = 320.3, CF_3), '–' 166.99 (C-2); ms (DCI/200 eV): *m/z* = 718.3 (4%, 2xM + NH_4^+), 385.2 (50%, M + NH_3 + NH_4^+), 368.2 (100%, M + NH_4^+), 220.2 (75%, M – SO_3CF_3 + NH_4^+); (EI/70 eV): *m/z* = 335 (100%, M^+ – 2'-Me), 217 (6%, M^+ – SO_2CF_3), 149 (25%, SO_3CF_3), 125 (54%), 101 (46%, dimethyldioxolanyl cation), 69 (18%, CF_3), 57 (25%, C_3H_5O), 43 (52%, C_2H_3O); ir (film): ν = 3410, 2950, 1795, 1780, 1430, 1215, 1135, 1055 cm^{-1}; due to the instability of the monotriflate under the microanalysis conditions a high resolution mass spectrogram was recorded in lieu; $C_9H_{10}O_8F_3S$ (M^+ – 2'-Me): calcd. 335.0048; the molecular mass (±2 ppm; *R* = 10000) was checked by EI HRms (70 eV) of the exact mass.

(–)-(*3R,4R,4'R,5R*)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(*3H*)-furanon-3-yl] trifluoromethanesulfonate (*ent*-**33**). *ent*-**9** (114 mg) in CH_2Cl_2 (3.4 ml) furnished *ent*-**33** (56 mg, 30%); $[\alpha]_D^{19}$ = –29° (*c* 0.5, EtOAc); mp 105°C (decomp.).

(–)-(*4'S,5S*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2(*5H*)-furanone (**34**). **32** (100 mg) in THF (3.2 ml) furnished **19** (27 mg, 49%); Me_3SnH (87 mg, 0.53 mmol, 3.6 equiv.) was added dropwise to a mixture of **32** (49 mg, 0.147 mmol), LiCl (35 mg, 0.83 mmol, 5.6 equiv.), CsF (30 mg, 0.20 mmol, 1.4 equiv.), and $Pd(PPh_3)_4$ (35 mg, 0.030 mmol, 0.2 equiv.) in THF (1.6 ml). After stirring for 4 h under N_2 at room temperature another portion of $Pd(PPh_3)_4$ (18 mg, 0.016 mmol, 0.1 equiv.) was added and stirring was continued for 3 h. The reaction mixture was diluted with CH_2Cl_2 (5 ml), filtered, and concentrated *in vacuo*. Flash chromatography of the crude product on silica gel [50% CH_2Cl_2/ 50% petroleum ether - ^{t}BuOMe (5:1)] gave **34** (13.6 mg, 43%), as well as the saturated compound (**35**) (*ca.* 7%, evaluated by ^{1}H nmr spectroscopy); $[\alpha]_D^{22}$ = –117° (*c* 0.33, CH_2Cl_2) [lit.,[10] $[\alpha]_D^{20}$ = –132° (*c* 1.09, $CHCl_3$)]; mp 35-37°C (lit.,[10] 37.5-38.5°C); ^{1}H nmr (500 MHz, $CDCl_3$): δ = 1.35 and 1.43 [2q only resolved as d, $^4J \approx 0.5$, 2'-$(CH_3)_2$], AB signal (δ_A = 3.83, δ_B = 4.08, J_{AB} = 8.9, in addition split by $J_{A,4'}$ = 5.4, $J_{B,4'}$ = 6.8, 5'-H_2), 4.42 (ddd, $J_{4',5'\text{-H(B)}}$ = 6.6, $J_{4',5'\text{-H(A)}}$ = 5.5, $J_{4',5}$ = 3.8, 4'-H), 5.09 (ddd, $J_{5,4'}$ = 3.8, $J_{5,4} = {}^4J_{5,3}$ = 1.9, 5-H), 6.24 (dd, $J_{3,4}$ = 5.8, $^4J_{3,5}$ = 2.1, 3-H), 7.46 (dd, $J_{4,3}$ = 5.7, $J_{4,5}$ = 1.6, 4-H); ^{13}C nmr (APT spectrum, 125.7 MHz, $CDCl_3$): δ = '+' 25.41 and '+' 25.98 [2'-$(CH_3)_2$], '–' 64.72, '+' 74.40, '+' 81.31 (C-5, C-4', C-5'), '–' 110.15 (C-2'), '+' 122.81 (C-3), '+' 152.62 (C-4), 172.37 (C-2); ms (EI/70 eV): *m/z* = 169 (100%, M^+ – 2'-Me), 109 (64%), 101 (82%, dimethyldioxolanyl cation), 43 (72%, C_2H_3O); ir (film): ν = 3095, 2985, 2935, 1755, 1380, 1260, 1220, 1160, 1070 cm^{-1}; $C_8H_9O_4$ (M^+ – 2'-Me): calcd. 169.0500; the molecular mass (±2 ppm; *R* = 10000) was checked by EI HRms (70 eV) of the exact mass; Anal. Calcd for $C_9H_{12}O_4$: *C*, 58.69; H, 6.57. Found: C, 58.77; H, 6.70.

(+)-(4'*S*,5*S*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-2(3*H*)-furanone (35). **32** (184 mg) in AcOEt (17 ml) furnished **35** (61 mg, 59%); $[\alpha]_D^{19}$ = +20° (*c* 1.0, $CHCl_3$).

(-)-(4'*R*,5*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-2(3*H*)-furanone (*ent*-35) [Representative procedure for the hydrogenation/ hydrogenolysis of enol triflates]. $^iPr_2NEt$ (85 µl, 63 mg, 0.48 mmol, 3.2 equiv.) and Pd-C (10%, 9 mg) were added to a solution of enol triflate (*ent*-**32**) (85 mg, 0.15 mmol) in AcOEt (9 ml). The resulting mixture was stirred vigorously under H_2 (4 bar) for 2 h. Filtration, concentration *in vacuo*, and flash chromatography on silica gel [^{t}BuOMe - petroleum ether (5:2)] gave *ent*-**35** (32 mg, 67%) as a colorless oil; $[\alpha]_D^{19}$ = –20° (*c* 1.0, $CHCl_3$); ^{1}H nmr (300 MHz, $CDCl_3$, TMS): δ = 1.38 and 1.40 [2s, 2'-$(CH_3)_2$], 2.14-2.53 (m, 3-H^1, 4-H_2), 2.67 (B part of AB signal, J_{AB} = 17.3, in addition split by $J_{B,4\text{-}H(1)}$ = 10.2, $J_{B,4\text{-}H(2)}$ = 7.2, 3-H^2), AB signal (δ_A = 3.93, δ_B = 4.08, J_{AB} = 8.3, in addition split by $J_{A,4'}$ = 6.8, $J_{B,4'}$ = 6.7, 5'-H_2), 4.20 (ddd, $J_{4',5'\text{-}H(A)}$ = $J_{4',5'\text{-}H(B)}$ = 6.8, $J_{4',5}$ = 3.0, 4'-H), 4.53 (ddd, $J_{5,4\text{-}H(1)}$ = 7.9, $J_{5,4\text{-}H(2)}$ = 5.0, $J_{5,4'}$ = 2.9, 5-H); ^{13}C nmr (APT spectrum, 125.7 MHz, $CDCl_3$): δ = '–' 24.25 and '–' 27.94 (C-3, C-4), '+' 25.50 and '+' 25.86 [2'-$(CH_3)_2$], '–' 65.25 (C-5'), '+' 77.55 and '+' 77.96 (C-5, C-4'), '–' 110.07 (C-2'), '–' 177.18 (C-2); ir (film): ν = 2985, 1775, 1460, 1370, 1260, 1210, 1165, 1065 cm^{-1}; Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.16; H, 7.51.

(+)-(4*R*,4'*S*,5*S*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanone (36). **33** (212 mg) in AcOEt (40 ml) furnished **36** (105 mg, 86%); $[\alpha]_D^{18}$ = +45° (*c* 1.0, $CHCl_3$); mp 64-66°C; ^{1}H nmr (300 MHz, $CDCl_3$, TMS): δ = 1.41 and 1.45 [2s, 2'-$(CH_3)_2$], AB signal (δ_A = 2.62, δ_B = 2.82, J_{AB} = 17.7, in addition split by $J_{A,4}$ = 4.6, $J_{B,4}$ = 7.2, 3-H_2), 3.16 (br. s, 4-OH), AB signal (δ_A = 4.04, δ_B = 4.18, J_{AB} = 8.5, in addition split by $J_{A,4'}$ = $J_{B,4'}$ = 6.8, 5'-H_2), 4.48 (dd, $J_{5,4'}$ = 5.7, $J_{5,4'}$ = 3.4, 5-H), 4.54 (ddd, $J_{4',5'\text{-}H(A)}$ = $J_{4',5'\text{-}H(B)}$ = 6.8, $J_{4',5}$ = 3.4, 4'-H), 4.72 (br. ddd, $J_{4,3\text{-}H(A)} \approx J_{4,3\text{-}H(B)} \approx J_{4,5}$ ≈ 5.7, 4-H); ^{13}C nmr (APT spectrum, 125.7 MHz, $CDCl_3$): δ = '+' 25.51 and '+' 25.85 [2'-$(CH_3)_2$], '–' 38.55 (C-3), '–' 65.34 (C-5'), '+' 68.98, '+' 74.12, '+' 80.48 (C-4, C-5, C-4'), '–' 110.65 (C-2'), '–' 174.32 (C-2); ir (film): ν = 3445, 2990, 1785, 1375, 1260, 1210, 1150, 1065 cm^{-1}. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.58; H, 7.09.

(–)-(4*S*,4'*R*,5*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-4-hydroxy-2(3*H*)-furanone (*ent*-36). *ent*-**33** (56 mg) in AcOEt (5 ml) furnished *ent*-**36** (13 mg, 41%); $[\alpha]_D^{20}$ = –47° (*c* 0.5, $CHCl_3$); mp 67-69°C.

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