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Chiral 2- and 8-Functionalised 1,7-Dioxaspiro[5.5]Undecanes *via* Asymmetric Dihydroxylation

Sandrine Sauret, Annie Cuer, Jean-Gabriel Gourcy and Georges Jeminet*

Université Blaise Pascal Clermont-Ferrand
Laboratoire de Synthèse et Etude de Systèmes à Intérêt Biologique (URA 485 du CNRS)
63177 Aubière Cedex (France)

Abstract : Asymmetric dihydroxylation with AD-mix-α [or AD-mix-β] carried out on an appropriate ketodiene precursor afforded (2S, 6S, 8S) [or (2R, 6R, 8R)] 2,8-dihydroxymethyl-1,7-dioxaspiro[5.5]undecane. Subsequent synthesis of (+)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane (insect pheromone) and (+)-2-iodomethyl-8-acetyloxymethyl-1,7-dioxaspiro[5.5]undecane are described.

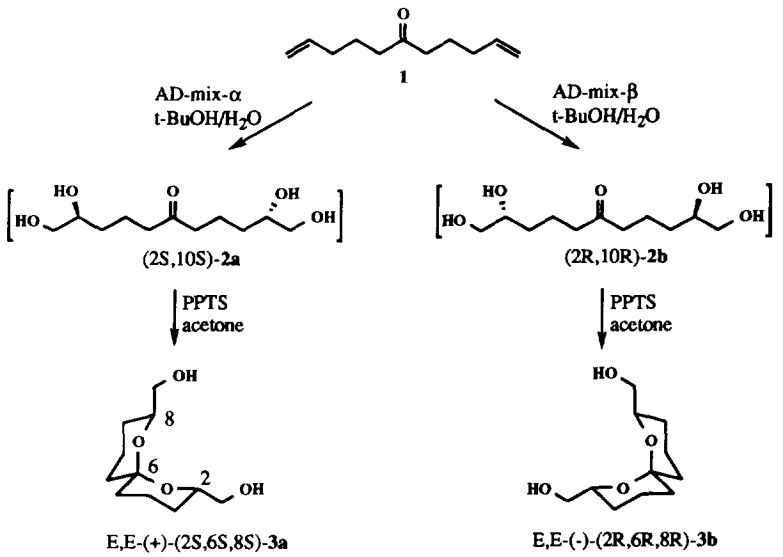
Natural products containing a spiroacetal form a very large class of biologically active molecules. They include antiparasitic agents (avermectins and milbemycins), polyether antibiotics (e.g. calcimycin, ...) and many volatile spiroacetals that are insect pheromones[1].

In pioneering work Sondheimer and coworkers[2] developed a method to prepare spiroacetals using a hydroxy-bromo addition on undeca-1,10-diene-6-one. This starting material was used more recently for the same target system using oxymercuration reaction[3], for the synthesis of a biomimetic model of calcimycin[4], and to study lipase-catalysed hydrolysis of dibutyl esters prepared *via* 2,8-diiodomethyl-1,7-dioxaspiro [5.5]undecane[5].

The discovery of catalytic asymmetric dihydroxylation (AD) and its tremendous possibilities for the synthesis of enantiomerically pure compounds has attracted much attention[6]. In early work Sharpless and coworkers[7] extended the reaction to terminal olefins with long chains.

This prompted us to apply AD to undeca-1,10-diene-6-one. Cyclisation of the tetraol obtained should give preferentially a 1,7-dioxaspiro[5.5]undecane skeleton, with E,E stereochemistry (for identical configurations in positions 2 and 8) or E,Z stereochemistry (for different configurations), as already reported by us for a similar cyclisation in the spiro-bidioxanes series[8]. If the AD reaction took place with high enantioselectivity the formation of a chiral E,E spiroacetal could be expected, with possibly a small amount of easily separated E,Z isomer.

We report here that the synthesis of the enantiomers (2S, 6S, 8S) and (2R, 6R, 8R) of 2,8-dihydroxy-1,7-dioxaspiro[5.5]undecane **3a** and **3b** (scheme 1) can be conveniently achieved by this approach. The absolute configuration of **3a** was established *via* the corresponding dimethyl derivative, which is a known insect pheromone[9]. We subsequently prepared the spiroacetal (+)-2-iodomethyl-8-acetyloxymethyl with two different arms, as a useful synthon for the synthesis of calcimycin analogs and other related molecules.

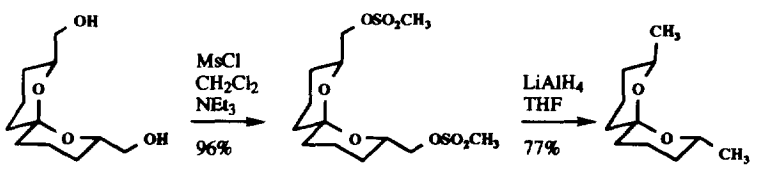


Scheme 1

The reaction of ketodiene **1**[2] with AD-mix-α (or AD-mix-β) and methanesulfonamide in a 1:1 mixture of t-butyl alcohol:water at 4°C (cold room) gave, after 24 h, the olefins **2a** (or **2b**) which were not isolated due to their high water solubility and resulting difficulties for purification in high yield. Also, we observed that the optical rotation fell during its measurement in MeOH (the tetraols are insoluble in non-polar solvents).

After careful solvent evaporation in vacuum, the intramolecular cyclisation on the crude product was carried out in wet acetone with pyridinium p-toluenesulfonate. In these conditions, the tetraol **2a** led almost exclusively to the spiroacetal **3a**, and **2b** to the corresponding **3b**. ^{1}H and ^{13}C NMR analysis showed that molecules had a C2 axis of symmetry corresponding to an E,E structure. The e.e. values were determined by NMR, (±)-**3** prepared for that purpose gave duplicate resonance signals (^{1}H spectra) for H2 and H8 protons in the presence of the chiral shift reagent $Eu(hfc)_3$, allowing e.e. determination for (+)-**3a** and (-)-**3b**. In both experiments e.e. were found ≥ 95 %. The overall yield for both series of reaction was 56%; by-products were not studied.

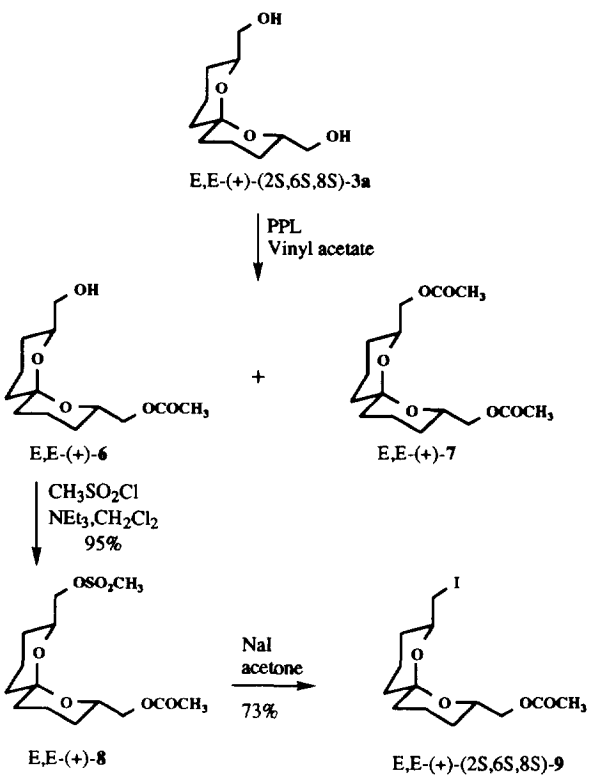
The absolute configuration of (+)-**3a** was determined by chemical correlation with the well-known pheromone **5**[10], which had a closely related structure (scheme 2).



Scheme 2

The preparation of **5** was straightforward from **3a** via the dimesylate **4**, obtained in high yield. As already reported by Mori and coworkers[10], Solladié and coworkers[11], pheromone **5** is a highly volatile liquid for which accurate measurement of the optical rotation is difficult. Nevertheless, the value which we determined : $[\alpha]_J^{25}$ = + 51 (pentane, c= 0.026) led us to conclude unambiguously that compound **3a** had the structure E,E-(+)-(2S, 6S, 8S), and therefore **3b** : E,E-(-)-(2R, 6R, 8R).

Hence asymmetric dihydroxylation with commercial AD-mix-α carried out on product **1** installed predominantely (2S, 10S) configurations at the newly created secondary alcohol centres in tetraol **2a**, and with AD-mix-β we obtained formation of tetraol (2R, 10R)-**2b**. These results agreed with experiments described for long chain terminal olefins[7], and also with recent works using similar approach[12,13]. We observed the formation of traces of E,Z isomer only if MeOH was used as solvent for the cyclisation.



Scheme 3

As already described in the racemic series[4,5], the synthesis of a calcimycin analog from compound (+)-**3a** needed to differentiate between functions in 2 and 8 positions, this was achieved here by a chemo-enzymatic approach (scheme 3), using in the first step porcine pancreatic lipase (PPL) as a simple reagent[8] which allowed a monotransesterification in vinyl acetate to be monitored.

In our experimental conditions, we obtained 56 % of product **6** and 13 % of product **7**. The corresponding mesylate (+)-**8** and iodo derivative (+)-**9** were obtained in moderate to high yields.

In conclusion, AD reaction applied to the ketodiene **1** led us to obtain seven new chiral 2- and 8-funtionalised 1,7-dioxaspiro[5.5]undecanes, fully characterised, in a small number of steps. This method opens the way to the synthesis of skeletons incorporating the spiroacetal unit in a chiral form, and so to the full asymmetric synthesis of calcimycin model and other ionophore antibiotics.

EXPERIMENTAL

Optical rotation values were measured on a Perkin-Elmer 141 polarimeter for the mercury J line (λ = 578 nm) at 25°C (c in g/mL). Infrared (IR) spectra were obtained using a Perkin-Elmer 881 spectrometer and bands are expressed in frequency units (ν cm^{-1}). NMR spectra were recorded at 400 MHz for ^1H and 100 MHz for ^{13}C on a Bruker MSL 400 spectrometer. All signals are expressed in ppm and were assigned by 2D ^1H-^1H experiments. The following abbreviations are used : singlet (s), doublet (d), triplet (t), multiplet (m), axial (a), equatorial (e). Satisfactory analytical data were obtained for all new compounds (± 0,3 %) at the Service Central d'Analyse du CNRS, Solaize, France. Tris-[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]-europium III ($Eu(hfc)_3$), was used as a shift reagent for enantiomeric excess determination. Merck silica gel (40-63 μ) was used for column chromatography and commercial Kieselgel 60F254 plates were used for thin layer chromatography (TLC). Porcine Pancreas Lipase (PPL) was purchased from Sigma (ref. 3126, Lot 34F-0035) and was used without any purification.

E,E-(2S, 6S, 8S)-(+)-2,8-dihydroxymethyl-1,7-dioxaspiro[5.5]undecane 3a and E,E-(2R, 6R, 8R)-(-)-2,8-dihydroxymethyl-1,7-dioxaspiro [5.5] undecane 3b.

A well stirred solution of AD-mix-α (21 g) (or AD-mix-β), $CH_3SO_2NH_2$ (1.14 g, 12 mmol) in 1:1 tert-butyl alcohol-water (80 mL) was cooled to 4°C (cold room) and the undeca-1,10-diene-6-one (2.03 g, 12 mmol) was added. The mixture was stirred at 4°C overnight, then 12 g of Na_2SO_3 was added and stirring continued at room temperature for 1 hour. The AD-mix was filtered ; tert-butanol and water were evaporated.

At the tetraol was added 100 ml of acetone and a catalytic amount of pyridinium paratoluene sulfonate (100 mg). The mixture was refluxed for 24 h. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with cyclohexane/ethylacetate: 30/70, and obtained in 56 % in two steps (1.453 g) yield.

$[\alpha]_J^{25}$ = + 65 (c = 0,042, $CHCl_3$) for **3a** and $[\alpha]_J^{25}$ = - 65 (c = 0.038, $CHCl_3$) for **3b**. IR: 3400, 2950, 1230, 1080, 1050, 980 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_4$ (216): C 61.11, H 9.26. Found: C 60.87, H 9.21.^1H-NMR ($CDCl_3$) δ: 3.74 (dddd, 2H, H2a and H8a, $J_{2a,3eA}$ 2.4 Hz, $J_{2a,12A}$ 3.3Hz, $J_{2a,12B}$ 6.9 Hz, $J_{2a,3aB}$ 11.7 Hz); 3.60 (dd, 2H,H12A and H12'A,$J_{12A,2a}$ 3.3 Hz, $J_{12A,12B}$ 11.3 Hz) ; 3.51 (dd, 2H, H12B and H12'B, $J_{12B,2a}$ 6.9 Hz, $J_{12B,12A}$ 11.3 Hz) ; 2.21 (s, 2H, OH) ; 1.89 (m, 2H, H4aA and H10aA, $J_{4aA,3eA}$ = $J_{4aA,5eA}$ 4.1 Hz, $J_{4aA,3aB}$ = $J_{4aA,4eB}$ = $J_{4aA,5aB}$ 13.2 Hz) ; 1.64 (m, 2H, H5eA and H11eA, $J_{5eA,4eB}$ 1.3 Hz, $J_{5eA,4aA}$ 4.1 Hz, $J_{5eA,5aB}$ 13.2 Hz) ; 1.59 (m, 2H, H4eB and H10eB, $J_{4eB,3eA}$ = $J_{4eB,5eB}$ 1.3 Hz, $J_{4eB,3aB}$ 4.1 Hz, $J_{4eB,5aB}$ 4.5 Hz, $J_{4eB,4aA}$ 13.2 Hz) ; 1.50 (dddd, 2H, H3eA and H9eA, $J_{3eA,4eB}$ 1.3 Hz, $J_{3eA,2a}$ 2.4 Hz, $J_{3eA,4aA}$ 4.1 Hz, $J_{3eA,3aA}$ 13.2 Hz) ; 1.41 (ddd, 2H, H5aB and H11aB, $J_{5aB,4eB}$ 4.5 Hz, $J_{5aB,4aA}$ = $J_{5aB,5eA}$ 13.2 Hz) ; 1.29 (dddd, 2H, H3aB and H9aB, $J_{3aB,4eB}$ 4.1 Hz, $J_{3aB,2a}$ 11.7 Hz, $J_{3aB,3eA}$ = $J_{3aB,4aA}$ 13.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 18.3 (C_4-C_{10}) ; 26.5 (C_3-C_9) ; 35.3 (C_5-C_{11}) ; 66.2 (C_{12}-$C_{12'}$) ; 69.8 (C_2-C_8) ; 96.1 (C_6).

E,E-(+)-2,8-mesyloxy methyl-1,7-dioxaspiro[5.5]undecane 4.

To a solution of diol **3a** (198.5 mg, 0.92 mmol) in CH_2Cl_2 (6 mL), freshly distilled triethylamine (0.5 mL) was added. The mixture was stirred and cooled to 0-5°C. Freshly distilled methane sulfonyl chloride (1.4 mL) was then added dropwise. The reaction was stirred at room temperature for 2 h. The organic phase was washed with brine, dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel with cyclohexane/ethylacetate: 70/30 and the compound **4** was obtained in 97 % (331 mg) yield.

$[\alpha]_J^{25}$ = + 25 (c = 0.062, $CHCl_3$). IR: 2950, 1350, 1180, 1000-960 cm^{-1}. Anal. Calcd. for $C_{13}H_{24}O_8S_2$ (372): C 41.93, H 6.45, S 17.20. Found: C 42.21, H 6.38, S 17.11. ^1H-NMR ($CDCl_3$) δ: 4.30 (dd, 2H, H12A and H12'A, $J_{12A,2a}$ 3.4 Hz, $J_{12A,12B}$ 10.9 Hz) ; 4.24 (dd, 2H, H12B and H12'B, $J_{12B,2a}$ 6.3 Hz, $J_{12B,12A}$

10.9Hz) ; 4.01 (dddd, 2H, H2a and H8a, $J_{2a,3eA}$ 2.3 Hz, $J_{2a,12A}$ 3.4 Hz, $J_{2a,12B}$ 6.3 Hz, $J_{2a,3aB}$ 11.8 Hz) ; 3.02 (s, 6H, H14 and H14') ; 1.98 (m, 2H, H4aA and H10aA, $J_{4aA,3eA}$ = $J_{4aA,5eA}$ 4.5 Hz, $J_{4aA,3aB}$ = $J_{4aA,4eB}$ = $J_{4aA,5aB}$ 13.4 Hz) ; 1.70 (m, 6H, H3e, H4e, H5e) ; 1.50 (ddd, 2H, H5aB and H11aB, $J_{5aB,4eB}$ 4.5 Hz, $J_{5aB,4aA}$ = $J_{5aB,5eA}$ 13.4 Hz) ; 1.40 (dddd, 2H, H3aB and H9aB, $J_{3aB,4eB}$ 4.1 Hz, $J_{3aB,2a}$ 11.8 Hz, $J_{3aB,3eA}$ = $J_{3aB,4aA}$ 13.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 18.1 (C_4-C_{18}) ; 26.2 (C_3-C_9) ; 34.7 (C_5-C_{11}) ; 37.5 (SO_2CH_3) ;67.5 (C_2-C_8) ; 72.7 (C_{12}-$C_{12'}$) ; 96.6 (C_6).

E,E-(+)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane 5.

The dimesylate **4** (121 mg, 0.32 mmol) was dissolved in 4 mL anhydrous THF and 6 mg of LAH was added at 0°C. The resulting mixture was refluxed for 2 h. Excess LAH was hydrolysed while cooling with an ice bath. After filtration of the solution, the cake was washed with THF. The combined organic layers were dried over $MgSO_4$ and were evaporated under vacuum. The residue was chromatographed on silica gel with cyclohexane/ethylacetate: 80/20 and the compound **5** was obtained in 50 % (30 mg) yield.
$[\alpha]_J^{25}$ = + 51 (c = 0.026, pentane). ^{1}H and ^{13}C-NMR spectra ($CDCl_3$) were in agreement with those described[9].

E,E-(+)-8-acetyloxymethyl-2-hydroxymethyl-1,7-dioxaspiro[5.5]undecane 6 and 2,8-diacetyloxymethyl-1,7-dioxaspiro [5.5] undecane 7.

A solution of diol **3a** (0.926 g ; 4.3 mmol) in 43 mL of vinylacetate was treated with Porcine Pancreas Lipase (1.15 g). The suspension was stirred at room temperature for 5 h. After filtration of the lipase, the residue was chromatographed on silica gel with cyclohexane/ethylacetate: 50/50. The product **7** was first collected in 13 % yield and the product **6** in 56 % yield.

Data for E,E-(+)-**6**: $[\alpha]_J^{25}$ = + 41 (c = 0.026, $CHCl_3$). IR: 3450, 2950, 1740, 1240, 1050, 980 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_5$ (258): C 60.46, H 8.53. Found: C 60.19, H 8.70. ^{1}H-NMR ($CDCl_3$) δ: 4.00 (dd, 1H, H12'A, $J_{12'A,,8a}$ 6,8 Hz, $J_{12'A,12'B}$ 11,2 Hz) ; 3.93 (dd, 1H, H12'B, $J_{12'B,8a}$ 4,0 Hz, $J_{12'B,12'A}$ 11,2 Hz) ; 3.77 (dddd, 1H, H8a, $J_{8a,9eA}$ 2.3 Hz, $J_{8a,12"B}$ 4,0 Hz, $J_{8a,12'A}$ 6..8 Hz, $J_{8a,9aB}$ 11.7 Hz) ; 3.65 (dddd, 1H, H2a, $J_{2a,3eA}$ 2.4 Hz, $J_{2a,12A}$ 3.3 Hz, $J_{2a,12B}$ 6.8 Hz, $J_{2a,3aB}$ 11..8 Hz) ; 3.51 (dd, 1H, H12A, $J_{12A,2a}$ 3.3 Hz, $J_{12A,12B}$ 11.2 Hz) ; 3.43 (dd, 1H, H12B, $J_{12B,2a}$ 6.8 Hz, $J_{12B,12A}$11.2 Hz) ; 2.20 (s, 1H, OH) ; 2.03 (s, 3H, H14') ; 1.82 (m, 2H, H4aA and H10aA, $J_{4aA,3eA}$ = $J_{4aA,5eA}$ 4.1 Hz, $J_{4aA,3aB}$ = $J_{4aA,4eB}$ = J 4aA,5aB 13.3 Hz) ; 1.53 (m, 5H, H4eB, H5eA, H9eA, H10eB, H11eA) ; 1.42 (m, 1H, H3e) ; 1.34 (ddd, 1H, H5aB,$J_{5aB,4eB}$ 4.3 Hz, $J_{5aB,5eA}$ = $J_{5aB,4aA}$ 13.0 Hz) ; 1.30 (ddd, 1H, H11aB,$J_{11aB,10eB}$ 4.1 Hz, $J_{11aB,11eA}$ = $J_{11aB,10aA}$ 13.0 Hz) ; 1.17 (dddd, 2H, H3aB and H9aB). ^{13}C-NMR ($CDCl_3$) δ: 18.4 (C_4-C_{10}); 20.9 ($C_{14'}$) ; 26.5-27 (C_3-C_9) ; 35.0-35.2 (C_5-C_{11}) ; 66.3 (CH_2OH) ; 67.3 ($C_{12'}$) ; 69.3 (C_2-C_8) ; 96.1 (C_6) ; 171.0 ($C_{13'}$).

Data for E,E-(+)-**7**: $[\alpha]_J^{25}$ = + 46 (c = 0.022, $CHCl_3$). IR: 2950, 1745, 1235, 1050 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_6$ (300): C 60.00, H 8.00. Found: C 59.96, H 8.06. ^{1}H-NMR ($CDCl_3$) δ: 4.01 (d, 4H, H12A, H12B and H12'A, H12'B, $J_{12A,2a}$ = $J_{12B,2a}$ 5.5 Hz) ; 3.77 (tdd, 2H, H2a and H8a, $J_{2a,3eA}$ 2.2 Hz, $J_{2a,12}$ 5.5 Hz, $J_{2a,3aB}$ 11.7 Hz) ; 2.03 (s, 6H, H14 and H14') ; 1.84 (m, 2H, H4aA and H10aA, $J_{4aA,3eA}$ = $J_{4aA,5eA}$ 4.3 Hz, $J_{4aA,3aB}$ = $J_{4aA,4eB}$ = $J_{4aA,5aB}$ 13.7 Hz) ; 1.55 (m, 6H, H3e, H4e, H5e,H9e, H10e,H11e) ; 1.36 (ddd, 2H, H5aB and H11aB, $J_{5aB,4eB}$ 4.5 Hz, $J_{5aB,4aA}$ = $J_{5aB,5eA}$ 13.4 Hz) ; 1.20 (dddd, 2H, H3aB and H9aB, $J_{3aB,4eB}$ 4.25 Hz, $J_{3aB,2a}$ 11.7 Hz, $J_{3aB,3eA}$ = $J_{3aB,4aA}$ 13.7 Hz).^{13}C-NMR ($CDCl_3$) δ: 18.4 (C_4-C_{10}) ; 20.9 (C_{14}- $C_{14'}$) ; 27.0 (C_3-C_9) ; 34.9 (C_5-C_{11}) ; 67.3 (C_{12}-$C_{12'}$) ; 67.6 (C_2-C_8) ; 96.2 (C_6) ; 171.0 (C_{13}-$C_{13'}$).

E,E-(+)-8-acetyloxymethyl-2-mesyloxymethyl-1,7-dioxaspiro[5.5]undecane 8.

A solution of NEt_3 (0.45 mL) and the product **6** (0,455 g, 1.76 mmol) in methylene chloride (10 mL) was stirred at 0°C. Methane sulfonyl chloride (0.347 g, 3,03 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 2 h. The solution was washed with brine, dried over $MgSO_4$ and concentrated. The residue underwent column chromatography on silica gel with cyclohexane/ethylacetate: 60/40, to give **8** in 96 % (0.57 g) yield.
$[\alpha]_J^{25}$ = + 28 (c = 0.024, $CHCl_3$). IR: 2950, 1740, 1360, 1240, 1230, 1180, 1000, 960 cm^{-1}. Anal. Calcd for

$C_{14}H_{24}O_7S$ (336): C 50.00, H 7.15, S 9.52. Found: C 49.81, H 7.20, S 9.78. ^{1}H-NMR ($CDCl_3$) δ: 4.22 (dd, 1H, H12A, $J_{12A,2a}$ 3.5 Hz, $J_{12A,12B}$ 10.9Hz) ; 4.16 (dd, 1H, H12B, $J_{12B,2a}$ 6.2 Hz, $J_{12B,12A}$ 10.9 Hz) ; 4.09 (dd, 1H, H12'A, $J_{12'A,8a}$ 7.0 Hz, $J_{12'A,12'B}$ 11.6 Hz) ; 4.01 (dd, 1H, H12'B, $J_{12'B,8a}$ 3.9 Hz, $J_{12'B,12'A}$ 11.6 Hz) ; 3.89 (dddd, 1H, H2a, $J_{2a,3eA}$ 2.2 Hz, $J_{2a,12A}$ 3.5 Hz, $J_{2a,12B}$ 6.2 Hz, $J_{2a,3aB}$ 11.6 Hz) ; 3.83 (dddd, 1H, H8a, $J_{8a,9eA}$ 2.4 Hz, $J_{8a,12'A}$ 3.9 Hz, $J_{8a,12'B}$ 7.0 Hz, $J_{8a,9aB}$ 11.4 Hz) ; 3.06 (s, 3H, H14) ; 2.08 (s, 3H, H14') ; 1.91 (m, 1H, H4aA, $J_{4aA,3eA}$ = $J_{4aA,5eA}$ 4.3 Hz, $J_{4aA,3aB}$ = $J_{4aA,4eB}$ = $J_{4aA,5aB}$ 13.8 Hz) ; 1.86 (m, 1H, H10aA, $J_{10aA,9eA}$ = $J_{10aA,11eA}$ 4.1 Hz, $J_{10aA,9aB}$ = $J_{10aA,10eB}$ = $J_{9aA,11aB}$ 13.3 Hz) ; 1.62 (m, 6H, H3eA H4eB, H5eA, H9eA, H10eB, H11eA) ; 1.33 (m, 2H, H5aB and H11aB) ; 1.20 (m, 2H, H3aB and H9aB).^{13}C-NMR ($CDCl_3$) δ: 18.1-18.3 (C_4-C_{10}) ; 21.0 ($C_{14'}$) ;26.4-26.8 (C_3-C_9) ; 34.8 (C_5-C_{11}) ; 37.5 (SO_2CH_3) ; 67.1 ($C_{12'}$) ; 67.4 (C_2-C_8) ; 72.7 (C_{12}) ; 96.4 (C_6) ; 171.0 ($C_{13'}$).

E,E-(+)-8-acetyloxymethyl-2-iodomethyl-1,7-dioxaspiro[5.5]undecane 9.

A solution of **8** (0.33 g, 1 mmol) in acetone (2.2 mL) and 0.77 g (5.13 mmol, 4.5 equivalent) of NaI was refluxed for 24 h. The solution was treated with 10 % aqueous K_2SO_3 (1 mL). The organic phase was dried over $MgSO_4$ and concentrated to give a residue which underwent column chromatography on silica gel with cyclohexane/ethylacetate: 70/30 to give the compound **9** in 73 % (0.27 g) yield.

$[\alpha]_J^{25}$ = + 58 (c = 0.038, $CHCl_3$). IR: 2950, 1740, 1230, 990 cm^{-1}. Anal. Calcd. for $C_{13}H_{21}O_4I$ (368): C 42.39, H 5.70, I 34.51. Found: C 42.54, H 5.98, I 34.32. ^{1}H-NMR ($CDCl_3$) δ: 4.05 (m, 1H, H8a) ; 4.00 (d, 2H, H12'A and H12'B) ; 3.68 (m, 1H, H2a, $J_{2a,3eA}$ 2.3 Hz, $J_{2a,12A}$ 4.1 Hz, $J_{2a,12B}$ 8.6 Hz, $J_{2a,3aB}$ 11.1 Hz) ; 3.18 (dd, 1H, H12A, $J_{12A,2a}$ 4.1 Hz, $J_{12A,12B}$ 10.1 Hz) ; 3.12 (dd, 1H, H12B, $J_{12B,2a}$ 8.6 Hz, $J_{12B,12A}$ 10.1 Hz) ; 2.07 (s, 1H, H14') ; 2.00 (m, 1H, H10aA, $J_{10aA,9eA}$ = $J_{10aA,11eA}$ 3.4 Hz, $J_{10aA,9aB}$ = $J_{10aA,10eB}$ = $J_{10aA,11aB}$ 11.4 Hz) ; 1.88 (m, 1H, H4aA, $J_{4aA,3eA}$ = $J_{4aA,5eA}$ 3.6 Hz, $J_{4aA,3aB}$ = $J_{4aA,4eB}$ = $J_{4aA,5aB}$ 11.7 Hz) ; 1.78 (m, 1H, H3eA) ; 1.58 (m, 5H, H4eB, H5eA, H9eA, H10eB, H11eA) ; 1.40(ddd, 1H, H11aB) ; 1.36 (m, 1H, H5aB) ; 1.17 (m, 2H, H3aB and H9aB).^{13}C-NMR ($CDCl_3$) δ: 9.95 (C_{12}) ; 18.2-18.7 (C_4-C_{10}) ; 20.9 ($C_{14'}$) ; 26.9-31 (C_3-C_9) ; 34.7-34.9 (C_5-C_{11}) ; 67.2-67.5 (C_2-C_8) ; 69.3 ($C_{12'}$) ; 96.7 (C_6) ; 170.8 ($C_{13'}$).

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