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TETRAHEDRON

First Enantioselective Synthesis of (+)-(3*R*,3a*S*,6a*S*)-3-Hydroxy-3,3a,4,6a-tetrahydrocyclopenta[b]furan-2-one - a Versatile Chiral Heterocyclic Building Block

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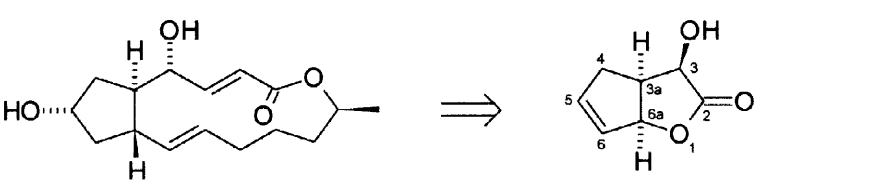
***Abstract**: Asymmetric Pd-catalyzed allylic alkylations of 2-acetoxymalonates with 2-cyclopentenyl chloride are described. With the cymantrene based phosphinooxazoline **2** as chiral ligand enantiomeric excess of > 99 % and > 90 % yield were obtained. Alkylation products were transformed in three steps to (+)-(3R,3aS,6aS)-3-hydroxy-3,3a,4,6a-tetrahydrocyclopenta[b]furan-2-one (**1a**) in up to 52 % yield.* © 1998 Elsevier Science Ltd. All rights reserved.

The bicyclic lactone **1a** (Scheme 1) is a versatile building block for syntheses of a variety of important natural products, e.g. brefeldin A,[1,2] mevinolin,[3] aristeromycin and carbodine,[4] 5'-*homo*-carbocyclic nucleosides,[5] carbocyclic analogs of polyoxins and nikkomycins,[6] the anti-HIV agent carbovir[7] and the antitumor agents sesbanimide A and B.[8] The key building block **1a** has so far been prepared by enzyme catalyzed kinetic resolution of the racemic compound which was obtained *via* Diels-Alder reaction of cyclopentadiene and glyoxylic acid.[9] In view of the importance of the lactone **1a** a catalytic asymmetric synthesis appears highly desirable.



Brefeldin A (+)-(3*R*,3a*S*,6a*S*)-**1a**

Scheme 1

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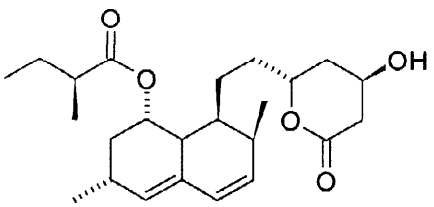
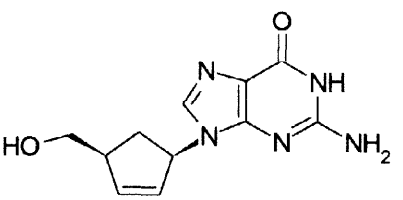
We have now worked out an enantioselective access to (+)-**1a** using as key step a palladium complex catalyzed allylic substitution of a cyclopentene derivative with the acetoxymalonates **3** (Scheme 2).[10] In our original plan subsequent reactions according to Scheme 3 were envisaged on the basis of the expectation that diastereoselectivity in favor of **1b** would be provided by base-catalyzed epimerization. However, serendipity gave rise to **1a** because its precursor **7a** was the main diastereoisomer after iodolactonization of a mixture of the hydroxyacids (*R*,*R*)-**6** and (*R*,*S*)-**6**.



Mevinolin



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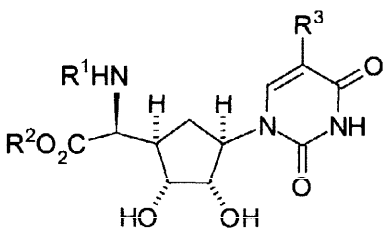
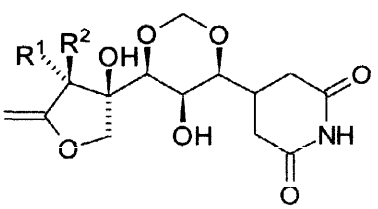


Polyoxin and Nikkomycin Analogs

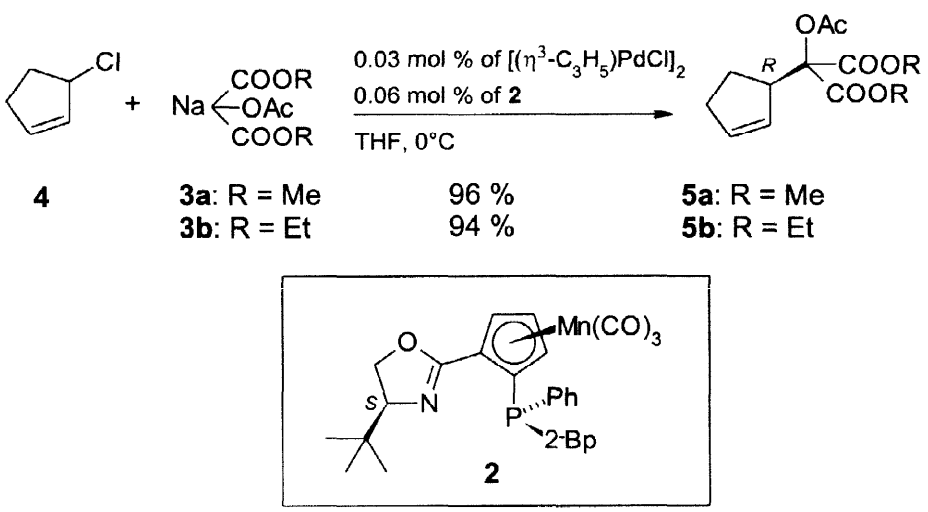


Sesbanimides

As chiral ligand in the allylic substitution the recently introduced cymantrene-based phosphinooxazoline **2**[11] was used (Scheme 2). Generally, ligands[12,13] of this type form chelate complexes in which the donor atoms P and N exhibit different electronic properties. In the case of **2** the ligand framework provides a concave moiety for the allylic system. Enantiomeric excess of 93-99 % ee with dimethyl sodiomalonate as nucleophile could be obtained in the case of five-, six- and seven-membered cyclic substrates.[11] However, high enantioselectivity does not necessarily imply practicability. With the normally used cycloalkenyl acetates or carbonates as substrates amounts of 1-3 mol % of the catalyst are required which is prohibitively high for preparative applications on a 100 g scale. With the more reactive cyclopentenyl chloride **4** as substrate down

to ca. 0.05 mol % of catalyst sufficed. However, with this substrate proper reaction conditions had to be worked out in order to avoid interference by the non-catalyzed substitution reaction.

Optimal conditions involved running the reaction at a temperature of 0 °C with *freshly distilled* starting materials and *dropwise* addition of a solution of the nucleophile in THF to a solution of the substrate **4** and the catalyst (molar ratio of substrate to catalyst: 1:0.0006). The reaction rate was very high, and complete conversion was reached after addition of the nucleophile. The products (+)-(*R*)-**5a** and (+)-(*R*)-**5b** were obtained in > 90 % yields with enantiomeric excesses of 98.5 and 99.5 %, respectively. Enantiomeric excess was determined by GC on a Chrompack Permethyl β-CD column. Baseline separations were achieved at 120 °C (**5a**) and 115 °C (**5b**), respectively. Enantiomeric products (-)-(*S*)-**5a** and (-)-(*S*)-**5b** were prepared by employing the enantiomeric ligand *ent*-**2**.

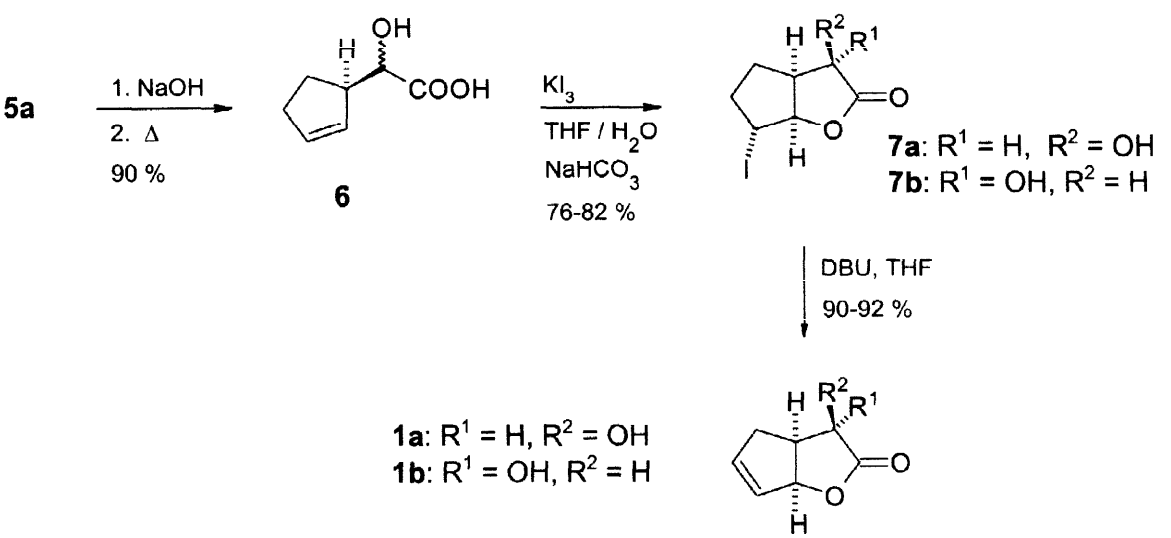


Scheme 2

The ester (+)-(*R*)-**5a** was saponified by heating it for 6 h under reflux with 3 N aqueous NaOH (Scheme 3). Fast heating of the resultant crude dicarboxylic acid to 190-200 °C effected decarboxylation to give the monoacid **6** after distillation in 90 % yield as mixture of the epimers (*R,S*)-**6**:(*R,R*)-**6** in ratios varying from 1:1.1 to 1:1.4 (^{1}H NMR), respectively. After treating these mixtures with KI_3 in H_2O/THF 3:2 as solvent at room temperature, mixtures of the epimeric iodolactones **7a** and **7b** were obtained in 76-82 % yield with

epimer ratios between 2.2:1 and 3.8:1 (NMR), respectively. ^{1}H NMR monitoring of the iodolactonization showed that (*R,R*)-**6** was consumed during a period of 60 minutes to give **7a** whereas (*R,S*)-**6** was transformed to **7b** much slower and was still present in the reaction mixture after 30 h. Subsequent elimination of HI with 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) in THF gave the hydroxylactones **1a** and **1b** in a 1.9:1 to 3.7:1 ratio (NMR) in 90-92 % yield. Separation of the diastereoisomers was carried out by column chromatography:[9] (+)-**1a**, $[\alpha]_D^{20}$ = +109.7 (c = 1.41, $CHCl_3$), mp 83-85 °C; (+)-**1b**, $[\alpha]_D^{20}$ = +79.8 (c = 1.03, $CHCl_3$) [lit.[2b]: $[\alpha]_D^{20}$ = +79 ($CHCl_3$, c = 1)]. The major diastereoisomer (+)-**1a** was obtained pure in 61 % yield also by recrystallization from diethyl ether.[7a]

In order to obtain the thermodynamically more stable isomer **1b** a solution of **1a** and the Schwesinger base *tert*-butyliminotris(dimethylamino)phosphorane (P_4-*t*Bu)[14] (10 mol %) in THF was heated to reflux for 6 h to give a 1:2.6 mixture of **1a** and **1b**; **1b** yielded a 1:2.8 mixture of **1a** and **1b** under the same reaction conditions. These experiments prove that **1b** is the more stable isomer. However, it is also demonstrated that epimerization of the lactones **1** does not lead to preparatively useful enrichment of **1b**.



Scheme 3

In conclusion, we have developed an enantioselective synthesis of the enantiomerically pure lactone (+)-**1a** via palladium complex catalyzed allylic substitution. High reactivity and selectivity induced by the phosphinooxazoline ligand **2** in the catalytic step makes an economic and straightforward access possible: over four steps a mixture of the epimeric lactones **1a** and **1b** can be obtained in 59-66 % and, in the best case, pure **1a** in up to 52 % overall yield by chromatographic separation of the epimers.

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

General. Melting points were not corrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer [300 MHz (^1H), 75.46 MHz (^{13}C), $CDCl_3$] and mass spectra on a JEOL JMS 700 instrument. Optical rotations were determined with a Perkin Elmer 241 Polarimeter with $CHCl_3$ as solvent. For flash chromatography ICN Kieselgel S (0.032-0.063 mm) was used. Gas chromatography was carried out on a Hewlett Packard HP 5890 A instrument equipped with a Chrompack Permethyl β-CD, 50 m x 0.25 mm, column.

(+)-(*R*)-2-Acetoxy-2-(cyclopent-2-enyl)-malonic acid dimethyl ester (5a). Solution A: Under an argon atmosphere 34.20 g of **3a** (0.180 mol) were added to a suspension of 4.08 g (0.170 mol) of sodium hydride in 450 ml of anhydrous THF. Upon stirring for 2 h at room temperature the suspension turned into a yellow solution. Solution B: A solution of 23.25 mg (0.0630 mmol) of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and 82.95 mg (0.1410 mmol) of **2** in 50 ml of anhydrous THF was stirred for 10 min at room temperature, then 16.5 g (0.161 mol) of *freshly distilled* 2-cyclopentenyl chloride (**4**) were added. Solution B was cooled to 0 °C and solution A was added dropwise during 2 h. Then aqueous NH_4Cl was added and the mixture was extracted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4. The solvents were evaporated and the residue distilled *in vacuo* (110 °C/1 *torr*) to give 39.54 g (96 %) of **5a** as colorless oil (98.5 % ee). $[\alpha]_D^{20}$ = +79.1 (c = 0.31, $CHCl_3$); ^1H NMR: δ = 1.94 (m, 2H, CH_2), 2.12 (s, 3H, O_2CCH_3), 2.32 (m, 2H,

CH_2), 3.51 (m, 1H, C=C-CH), 3.74 (s, 6H, CO_2CH_3), 5.59 (dd, J = 5.5 Hz, J = 2.3 Hz, 1H, CH=), 5.86 (dd, J = 5.5 Hz, J = 2.1 Hz, 1H, CH=); ^{13}C NMR: δ = 21.00 (q, CH_3), 24.53 (t, CH_2), 32.38 (t, CH_2), 52.14 (d, C=C-CH), 53.22, 53.30 (2q, O-CH_3), 84.24 [s, C($COOCH_3$)$_2$], 128.71, 135.00 (2d, CH=), 167.24 (s, $COOCH_3$), 170.35 (s, CH_3CO); GC: Permethyl β-CD, 120 °C, t_R[(+)-(*R*)- **5a**] = 32.2 min, t_R[(-)-(*S*)-**5a**] = 33.2 min; HRMS Calcd for $C_{12}H_{16}O_6$: 256.0947. Found: 256.0970; Anal. Calcd for $C_{12}H_{16}O_6$: C 56.25, H 6.25. Found: C 56.09, H 6.44.

(+)-(*R*)-2-Acetoxy-2-(cyclopent-2-enyl)-malonic acid diethyl ester (5b). 39.24 g (0.180 mol) of **3b** were reacted with 16.5 g (0.161 mol) of **4** under exactly the same conditions as described above for **3a** in the synthesis of **5a**. After distillation (142 °C/3.8 *torr*) 42.95 g (94 %) of **5b** were obtained as colorless oil (99.5 % ee). $[\alpha]_D^{20}$ = +77.0 (c = 1.37, $CHCl_3$); ^{1}H NMR: δ = 1.25 (t, J = 7.2 Hz, 6H, CH_2CH_3), 1.93 (m, 2H, CH_2), 2.12 (s, 3H, O_2CCH_3), 2.30 (m, 2H, CH_2), 3.54 (m, 1H, C=C-CH), 4.22 (m, 4 H, CH_2CH_3), 5.63 (ddd, J = 7.8 Hz, J = 4.6 Hz, J = 2.2 Hz, 1H, CH=), 5.84 (ddd, J = 7.7 Hz, J = 4.3 Hz, J = 2.1 Hz, 1H, CH=); ^{13}C NMR: δ = 13.76 (q, CH_2CH_3), 20.38 (q, $COCH_3$), 23.89 (t, CH_2), 31.77 (t, CH_2), 51.40 (d, C=C-CH), 61.69, 61.73 (2q, O-CH_2), 83.66 [s, C($COOCH_3$)$_2$], 128.57, 134.29 (2d, CH=), 166.09 (s, $COOCH_2$), 169.55 (s, CH_3CO); GC: Permethyl β-CD, 115 °C, t_R[(+)-(*R*)-**5a**] = 66.9 min, t_R[(-)-(*S*)-**5a**] = 68.0 min; HRMS-FAB (M+1) Calcd for $C_{14}H_{21}O_6$: 285.1338. Found: 285.1328; Anal. Calcd for $C_{12}H_{20}O_6$: C 59.15, H 7.04. Found: C 59.14, H 7.15.

2-[(1*R*)-Cyclopent-2-enyl]-hydroxyacetic acid (6). A vigorously stirred emulsion of 21.0 g (0.082 mol) of (+)-(*R*)-**5a** in 75 ml of 3 N aqueous NaOH was heated to reflux for 6 h. The resultant solution was extracted with 20 ml of diethyl ether and the organic layer was discarded. The aqueous solution was acidified with 6 N HCl and concentrated *in vacuo*. The solid residue was extracted six times with 100 ml of ethyl acetate. The solvent was removed by evaporation, the solid residue was dried *in vacuo* and for decarboxylation heated very fast to 190-200 °C for 20 min. It is important to rise the temperature quickly in order to obtain epimer (*R,R*)-**6** preferentially. Distillation (150 °C/0.5 *torr*) gave 9.5 g (90 %) of a mixture of the epimers of **6** in a 1.35:1 ratio (^{1}H NMR). Colorless oil; ^{1}H NMR: δ = 1.79 (m, 1H, CH_2), 1.92 (m, 2H, CH_2), 2.11 (m, 1H, CH_2), 2.35 (m, 4H, CH_2) 3.22 (m, 2H, OH), 4.19 (d, J = 4.2 Hz, 1H, C=C-CH), 4.32 (d, J = 4.0 Hz, 1H, C=C-CH), 5.52 [(*R,S*)-**6**, dd, J = 5.7 Hz, J = 2.2 Hz, 1H, CH=), 5.65 [(*R,S*)-**6**, dd, J = 5.7 Hz, J = 2.2 Hz, 1H, CH=), 5.93 [(*R,R*)-**6**, dd, J = 5.8 Hz, J = 2.3 Hz, 1H, CH=), 5.97 [(*R,R*)-**6**, dd, J = 5.7 Hz, J = 2.2 Hz, 1H, CH=]; ^{13}C NMR: δ = 23.19, 25.83, 32.17, 32.29 (4t, CH_2), 49.36, 49.48 (2d, CH=CH-CH), 71.99, 72.73 (2d, HO-CH), 127.25, 129.49, 134.34, 135.75 (4d, CH=), 177.90, 178.38 (2s, COOH); HRMS-FAB (M+1) Calcd for $C_7H_{11}O_3$: 143.0708. Found: 143.0724.

(+)-(3*R*,3a*S*,6*R*,6a*R*)-3-Hydroxy-6-iodo-hexahydro-cyclopenta[b]furan-2-one (7a). A solution of 22.6 g (0.089 mol) of I_2 and 44.5 g (0.268 mol) of KI in 100 ml of water was added to a solution of 6.21 g (0.0437 mol) of **6** [1.35:1 mixture of (*R*,*R*)-**6**:(*R*,*S*)-**6**] in 120 ml of THF and 80 ml of a saturated aqueous $NaHCO_3$ solution. The mixture was stirred over night at room temperature and then a saturated aqueous $Na_2S_2O_3$ solution was added until the reaction mixture became colorless. The mixture was then extracted four times with 150 ml of ethyl acetate, the organic layer dried with Na_2SO_4 and evaporated down. Column chromatography on silica gel (8 x 5 cm) using hexane/ethyl acetate 1:1 as eluent gave 9.01 g (77 %) of a 3.8:1 mixture of **7a** and **7b**. From a solution of the epimers in hexane/ethyl acetate 6.13 g (52 %) of pure diastereomer (+)-**7a** crystallized as colorless needles. **7a**: mp 126-127 °C; $[\alpha]_D^{20}$ = +3.1 (c = 7.2, $CHCl_3$); ^{1}H NMR of **7a**: δ = 2.03 [(m, 4H (and 2H of **7b**), CH_2], 3.00 (m, 1H, OH), 3.32 (m, 1H, OH-CH-C<u>H</u>), 4.42 (d, *J* = 3.5 Hz, 1H, I-CH), 4.57 (d, *J* = 9.0 Hz, 1H, CH-O-CO), 5.06 (d, *J* = 5.1 Hz, 1H, C<u>H</u>-OH), 5.28 (**7b**, d, *J* = 6.1 Hz, 1H, C<u>H</u>-OH); ^{13}C NMR of **7a**: δ = 21.04 (t, CH_2), 28.43 (d, CH), 34.76 (t, CH_2), 41.60 (d, CH), 68.80 (d, CH), 89.15 (d, CH), 176.98 (s, CO); ^{13}C NMR of **7b**: δ = 27.44 (t, CH_2), 28.24 (d, CH), 34.87 (t, CH_2), 44.80 (d, CH), 74.41 (d, CH), 91.50 (d, CH), 176.23 (s, CO); HRMS-FAB (M+1) Calcd for $C_7H_{10}IO_3$: 268.9675. Found: 268.9684; Anal. Calcd for $C_7H_9IO_3$: C 31.34, H 3.36. Found: C 31.45, H 3.41.

(+)-(3*R*,3a*S*,6a*S*)-3-Hydroxy-3,3a,4,6a-tetrahydro-cyclopenta[b]furan-2-one (1a) and (+)-(3*S*,3a*S*, 6a*S*)-3-Hydroxy-3,3a,4,6a-tetrahydro-cyclopenta[b]furan-2-one (1b). A mixture of 3.96 g (26.05 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-en and 3.00 g (11.2 mmol) of **7** (**7a**:**7b** = 3.8:1) in 100 ml of anhydrous THF was stirred and heated to reflux for 4 h. The resultant solution was cooled to room temperature and 1 N HCl was added until the mixture became acidic. Then it was extracted four times with 50 ml of ethyl acetate. The organic layer was washed with 1 N HCl, water and brine. After drying over Na_2SO_4 the solvents were removed *in vacuo* to give 1.44 g (92 %) of a 3.7:1 mixture of **1a** and **1b**. Chromatography on silica gel (8 x 40 cm) using hexane/ethyl acetate 9:1 as eluent gave 1.12 g (72 %) of **1a** and 0.27 g (17 %) of **1b**. 0.18 g (6 %) of **7** were recovered. From a solution of the 3.7:1 mixture of epimers in diethyl ether pure (+)-**1a** crystallized in 61 % yield.

(+)-1a: Colorless needlelike prisms, mp 83-85 °C; $[\alpha]_D^{20}$ = +109.7 (c = 1.41, $CHCl_3$); ^{1}H NMR: δ = 2.44 (dd, *J* = 18.5 Hz, *J* = 9.5 Hz, 1H, CH_2), 2.74 (dd, *J* = 18.2 Hz, *J* = 5.9 Hz, 1H, CH_2), 3.18 (m, 1H, OH-CH-C<u>H</u>), 3.39 (s, 1H, OH), 4.71 (d, *J* = 9.4 Hz, 1H, C<u>H</u>-OH), 5.31 (dd, *J* = 6.4 Hz, *J* = 2.3 Hz, 1H, CH-O-CO), 5.91 (dd, *J* = 5.7 Hz, *J* = 2.3 Hz, 1H, CH=), 6.24 (dd, *J* = 5.4 Hz, *J* = 2.2 Hz, 1H, CH=); ^{13}C NMR: δ = 30.60 (t, CH_2), 40.36 (d, HO-CH-<u>C</u>H), 69.03, 86.30 (2d, CH), 127.39, 140.89 (2d, CH=), 177.07 (s, CO); HRMS-FAB (M+1) Calcd for $C_7H_9O_3$: 141.0551. Found: 141.0545; Anal. Calcd for $C_7H_8O_3$: C 60.00, H 5.75. Found: C 60.02, H 5.79.

(+)-1b: Colorless oil; $[\alpha]_D^{20}$ = +79.8 (c = 1.03, $CHCl_3$); ^1H NMR: δ = 2.55 (d, *J* = 17.5 Hz, 1H, CH_2), 2.75 (ddd, *J* = 17.8 Hz, *J* = 7.3 Hz, *J* = 2.1 Hz, 1H, CH_2), 3.04 (m, *J* = 7.4 Hz, 1H, OH-CH-C<u>H</u>), 4.12 (d, *J* = 7.2 Hz, 1H, C<u>H</u>-OH), 4.28 (s, 1H, OH), 5.52 (d, *J* = 7.7 Hz, 1H, CH-O-CO), 5.89 (dd, *J* = 5.6 Hz, *J* = 2.1 Hz, 1H, CH=), 6.07 (d, *J* = 5.5 Hz, 1H, CH=); ^{13}C NMR: δ = 36.50 (t, CH_2), 43.96 (d, HO-CH-<u>C</u>H), 74.25, 87.18 (2d, CH), 129.28, 136.45 (2d, CH=), 177.46 (s, CO); HRMS-FAB (M+1) Calcd for $C_7H_9O_3$: 141.0551. Found: 141.0550; Anal. Calcd for $C_7H_8O_3$: C 60.00, H 5.75. Found: C 60.05, H 5.75.

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