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Supporting Information

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Enantioselective Synthesis of Cyclic Ethers through a Vanadium-Catalyzed Resolution-Oxidative Cyclization

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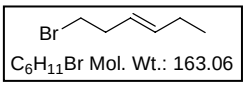
Experimental Section:

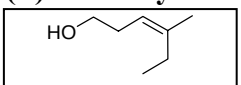
General Information: Unless otherwise noted, all reagents were obtained commercially and used without further purification. Extracts were dried over $MgSO_4$ or Na_2SO_4 and solvents were removed *in vacuo via* a rotary evaporator at aspirator pressure. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates which were visualized with $KMnO_4$, *p*-anisaldehyde, or molybdophosphoric acid/$Ce(SO_4)_2$,$4H_2O$. Flash Chromatography (FC) was carried out on ICN SiliTech 32-63 D 60 Å silica gel. ^1H and ^{13}C NMR spectra were recorded with Bruker DRX-500, AVB-400, AVQ-400, and AV-300 spectrometers and referenced to $CDCl_3$ (7.26 ppm) unless otherwise noted. A *Gemini FT-IR* was used to record IR spectra (in $CHCl_3$ or neat). Enantiomeric excess was determined by chiral Gas Chromatography or chiral High Preformance Liquid Chromatography. Analytic GC was carried out with Hewlett Packard HP 6850 GC equipped with a Chiraldex G-TA (30 m x 0.25 mm) column. Analytical chiral HPLC was performed with a Shimadzu VP Series Chiral HPLC with UV detection using Chiralcel OJ and OD columns. $[\alpha]^{T°C}_D$ (*c* = g/mL, in $CHCl_3$) were measured on *Perkin-Elmer 241 polarimeter* using a quartz cell (l = 10 cm), with high-pressure sodium lamp (λ = 589 nm). Mass spectral and microanalysis data were obtained from the Micro-Mass Facility operated by the College of Chemistry, University of California, Berkeley.

(*E*)-1-Bromohex-3-ene (I). (*E*)-3-Hexen-1-ol (1.8 g, 18 mmol) and PBr_3 (570 µL, 6 mmol) were mixed in dry Et_2O overnight under N_2. Water was carefully added and the mixture was extracted with pentane. The combined organic layers were washed with 1N HCl, 1N NaOH and water, dried over Na_2SO_4 and evaporated (Caution: volatile product). Filtration of the crude mixture through a pad of silica gel (Pentane) gave **I** (1.4 g, 48 %) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.4 Hz, 3 H), 2.03 (quint, *J* = 7.8 Hz, 2 H), 2.54 (q, *J* = 7.1 Hz, 2 H), 3.67 (t, *J* = 7.2 Hz, 2 H), 5.35-5.62 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 25.5, 33.0, 36.0, 125.4, 135.5.



$C_6H_{11}Br$ Mol. Wt.: 163.06

(*Z*)-4-Methylhex-3-en-1-ol (II).[1] Hex-3-yn-1-ol (4.4 g, 45 mmol) was carefully added at 0°C on a solution of $AlMe_3$ (50 mL, 0.1 mol) in 150 mL of CH_2Cl_2 (Caution: methane formation). The resulting mixture was cooled down at -78°C and a solution of $TiCl_4$ (4.3 g, 45 mmol) in 100 mL of CH_2Cl_2 at -78°C was then transferred via canula into this mixture. The reaction was stirred at -78°C for 8 h and then quenched via addition of precooled methanol at 0°C. An aqueous 1N HCl solution saturated with NaCl (100 mL) was then added. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. FC (Hexane/EtOAc 5-20 %) gave **II** (3.2 g, 62 %) as a colorless oil (Ratio Z/E >95/5): TLC *Rf* 0.27 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3367, 2965, 2933, 2875, 1451, 1376, 1113, 1048, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.6 Hz, 3 H), 1.55 (br, -OH, 1 H), 1.71 (s, 3 H), 2.06 (q, *J* = 7.5 Hz, 2 H), 2.27

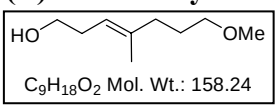


$C_7H_{14}O$ Mol. Wt.: 114.19

[1] See: Ewing, J. C.; Ferguson, G. S.; Moore, D. W.; Schultz, F. W.; Thompson, D. W. *J. Org. Chem.* **1985**, *50*, 2124-2128.

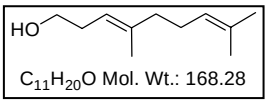
(q, *J* = 6.5 Hz, 2 H), 3.60 (t, *J* = 6.6 Hz, 2 H), 5.08 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 12.8, 23.0, 24.8, 31.2, 62.6, 119.5, 140.9; MS (EI) *m/z* (%) 114 (20, $M^{+\cdot}$), 83 (35), 70 (17), 55 (100); HR-MS 114.1045 ($C_7H_{14}O$ calcd 114.1044).

(*E*)-7-Methoxy-4-methylhept-3-en-1-ol (III).[2] A solution of *tert*-butyllithium in 1.7 M pentane (28.3 mL, 48 mmol) was added dropwise to a solution of 2,3-dihydrofuran (4.3 mL, 56 mmol) in dry THF (15 mL) cooled to -78°C under N_2. The resulting yellow suspension was allowed to warm to 0°C (colorless solution). The mixture was then cooled to -20°C and a solution of 1-iodo-3-methoxypropane (8 g, 40 mmol, obtained from commercially available 3-methoxy-1-propanol via tosylation follow by Finkelstein reaction) in dry THF (5 mL) was added over 10 min. The mixture was allowed to warm to room temperature and was refluxed for 2 h. The mixture obtained was cooled to 0°C and poured into a solution of saturated NH_4Cl. The organic products were extracted with Et_2O. The combined extracts were washed with $Na_2S_2O_3$ satd solution, brine, dried over $MgSO_4$ and evaporated to leave the substituted 2,3-dihydrofuran as a pale yellow oil (5.7 g, quantitative reaction): ^{1}H NMR (400 MHz, acetone-d_6) δ 1.67 (quint, *J* = 7.0 Hz, 2 H), 2.09 (t, *J* = 7.7 Hz, 2 H), 2,53 (t, *J* = 9.4 Hz, 2 H), 3.23 (s, 3 H), 3.32 (t, *J* = 6.4 Hz, 2 H), 4.21 (t, *J* = 9.4 Hz, 2 H), 4.56 (m, 1 H). The crude mixture was directly used.



A solution of MeMgBr 3 M in ether (28.3 mL, 84 mmol) was added dropwise to a stirred suspension of bis(triphenylphosphe)nickel(II) dichloride (1.3 g, 2 mmol) in dry benzene (30 mL) under N_2. The resulting dark-red solution was stirred at room temperature for 20 min. The bulk of solvent was then removed. The dark residue was suspended in dry benzene (70 mL) and a solution of 2,3-dihydro-5-(3-methoxypropyl)furan (5.7 g, 40 mmol) in dry benzene (30 mL) was added. The mixture was heated to reflux for 45 min, cooled to 0°C, and poured into saturated ammonium chloride solution with vigorous stirring. The mixture was stirred until decolorized and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. FC (Hexane/EtOAc 25-40 %) gave **III** (5.75 g, 91 %) as a colorless oil: TLC *Rf* 0.11 (Hexane/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 3 H), 1.66 (quint, *J* = 7.1 Hz, 2 H), 1.93 (br, -OH, 1 H), 2.04 (t, *J* = 7.7 Hz, 2 H), 2.25 (q, *J* = 6.6 Hz, 2 H), 3.29 (s, 3 H), 3.33 (t, *J* = 6.5 Hz, 2 H), 3.58 (t, *J* = 6.6 Hz, 2 H), 5.13 (t, *J* = 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 16.0, 27.7, 31.4, 36.2, 58.5, 62.3, 72.4, 120.1, 138.0.

(*E*)-4,8-Dimethylnona-3,7-dien-1-ol (IV).[2] A solution of *tert*-butyllithium in 1.7 M pentane (11.1 mL, 18.9 mmol) was added dropwise to a solution of 2,3-dihydrofuran (1.26 g, 18 mmol) in dry THF (10 mL) cooled to -78°C under N_2. The resulting yellow suspension was allowed to warm to 0°C and was stirred for a further 30 min. The mixture was then cooled to -30°C and a solution of l-iodo-4-methylpent-3-ene (3 g, 14.3 mmol, obtained from commercially available l-bromo-4-methylpent-3-ene via Finkelstein reaction) in dry THF (10 mL) was added. The mixture was allowed to warm to room temperature and was stirred for 18 h. The mixture obtained was poured into a solution of saturated NH_4Cl and



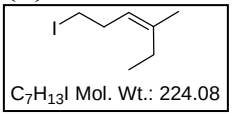
[2] For a complete characterization see: a) Kocienski, P.; Wadman, S.; Cooper, K. *J. Org. Chem.* **1989**, *54*, 1215-1217.; b) Kocienski, P. J.; Pritchard, M.; Wadman, S. N.; Whitby, R. J.; Yeates, C. L. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3419-3429.

the organic products were extracted with Et_2O. The combined extracts were washed with brine, dried briefly ($MgSO_4$) and evaporated to leave a pale yellow oil (2.2 g, quantitative reaction): ^{1}H NMR (400 MHz, acetone-d_6) δ 1.57 (s, 3 H), 1.63 (s, 3 H), 2.00-2.15 (m, 4 H), 2,54 (t, *J* = 7.5 Hz, 2 H), 4.21 (t, *J* = 6.5 Hz, 2 H), 4.55 (s, 1 H), 5.09 (t, *J* = 7.2 Hz, 1 H). The crude mixture of 5-(4-methylpent-3-enyl)-2,3-dihydrofuran was used directly.
A solution of MeMgBr 3 M in ether (9.5 mL, 28.5 mmol) was added to a stirred suspension of bis(triphenylphosphe)nickel(II) dichloride (468 mg, 0.71 mmol) in dry benzene (20 mL) under N_2. The resulting dark-red solution was stirred at room temperature for 20 min, and a solution of 5-(4-methylpent-3-enyl)-2,3-dihydrofuran (2.2 g, 14.3 mmol) in dry benzene (20 mL) was then added. The mixture was heated to reflux for 40 min, cooled to room temperature, and poured into saturated ammonium chloride solution with vigorous stirring. The mixture was stirred until decolorized and the organic material was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. FC (Hexane/EtOAc 10 %) gave **IV** (1.64 g, 68 %) as a colorless oil (Ratio Z/E >95/5): TLC *Rf* 0.27 (Hexane/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (br, -OH, 1 H), 1.60 (s, 3 H), 1.64 (s, 3 H), 1.68 (s, 3 H), 2.00-2.10 (m, 4 H), 2.28 (q, *J* = 6.7 Hz, 2 H), 3.60 (t, *J* = 6.4 Hz, 2 H), 5.05-5.14 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 16.1, 17.7, 25.7, 26.5, 31.4, 39.8, 62.3, 119.8, 124.1, 131.7, 138.9.

<u>General procedure 1</u>: Preparation of unsaturated halide.

The homoallylic alcohol (10 mmol) was treated with tosyl chloride (TsCl, 15 mmol) in dry CH_2Cl_2 in presence of pyridine (20 mmol) at 0°C. The mixture was stirred for 2 h and warm up to room temperature. MeOH was then added to quench excess of TsCl. The mixture was poured into ice cold water and extracted with Et_2O. The combined organic layers were washed with HCl 1N, saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$ and evaporated. The ^{1}H NMR spectrum of the crude mixture showed a complete conversion. The tosylate was directly converted in halide compound.
<u>Iodo compound</u>: The crude tosylate was taken up in acetone and sodium iodide (NaI, 20 mmol) was added. The mixture was vigorously stirred at 50°C for 3 h (precipitate of NaOTs). The mixture was then cooled and filtered. Acetone was removed and the residue was partitioned between pentane and water. The organic phase was washed with water, saturated sodium thiosulfate solution ($Na_2S_2O_3$), brine and dried over $MgSO_4$. The crude mixture was purified by filtration through a pad of silica gel (Pentane).
<u>Bromo compound</u>: The crude tosylate was taken up in DMF and sodium bromide (NaBr, 50 mmol) was added. The mixture was vigorously stirred at 50°C for 3 h and then diluted with water, extracted with pentane. The organic phase was washed with brine, dried over $MgSO_4$ and evaporated. The crude mixture was purified by filtration through a pad of silica gel (Pentane).

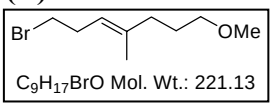
(*Z*)-1-Iodo-4-methylhex-3-ene (V). Following the *<u>general procedure 1</u>*, from alcohol **II**



(1.14 g, 10 mmol), the unsaturated halide **V** (1.5 g, 67 %) was obtained as a colorless oil (Caution volatile product): TLC *Rf* 0.64 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 2965, 2932, 2874, 1642, 1450, 1424, 1376, 1246, 1165, 1072, 1021 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.6 Hz, 3 H), 1.69 (s, 3 H), 2.02 (q, *J* = 7.6 Hz, 2 H), 2.57 (q, *J* = 7.4 Hz, 2 H), 3.09 (t, *J* = 7.5

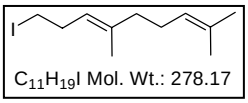
Hz, 2 H), 5.05 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 6.2, 12.8, 22.9, 24.9, 32.2, 122.6, 140.2; MS (EI) *m/z* (%) 224 (6, $M^{+\cdot}$), 128 (8), 97 (82), 81 (12), 67 (10), 55 (100); HR-MS 224.0024 ($C_7H_{13}I$ calcd 224.0062).

(*E*)-1-Bromo-7-methoxy-4-methylhept-3-ene (VI). Following the *general procedure 1*, from alcohol **III** (3.16 g, 20 mmol), the unsaturated halide **VI** (4 g, 90 %) was obtained as a pale yellow oil: TLC *Rf* 0.55 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 2977, 2922, 2894, 2869, 2829, 1448, 1385, 1267, 1206, 1184, 1119 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 3 H), 1.67 (quint, *J* = 7.1 Hz, 2 H), 2.05 (t, *J* = 7.6 Hz, 2 H), 2.57 (q, *J* = 7.2 Hz, 2 H), 3.32-3.37 (m, 7 H), 5.14 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 16.2, 27.8, 31.6, 32.9, 36.0, 58.6, 72.3, 121.2, 138.1; MS (EI) *m/z* (%) 188 (8), 162 (7), 140 (22), 109 (65), 95 (57), 81 (53), 67 (59), 58 (100); HR-MS 188.0200 (C_9H_{17}BrO-MeOH calcd 188.0200); Anal. calcd for C_9H_{17}BrO: C, 48.88; H, 7.75; found C, 48.63; H, 8.01.



C_9H_{17}BrO Mol. Wt.: 221.13

(*E*)-9-Iodo-2,6-dimethylnona-2,6-diene (VII).[2] Following the *general procedure 1*, from alcohol **IV** (1.6 g, 9.5 mmol), the unsaturated halide **VII** (2.1 g, 79 %) was obtained as a colorless oil: TLC *Rf* 0.71 (Hexane/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 6 H), 1.68 (s, 3 H), 1.97-2.12 (m, 4 H), 2.58 (q, *J* = 7.3 Hz, 2 H), 3.11 (t, *J* = 7.5 Hz, 2 H), 5.09 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 6.1, 16.3, 17.7, 25.7, 26.4, 32.4, 39.6, 122.9, 124.0, 131.5, 138.1.

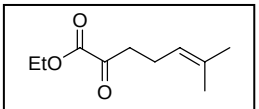


$C_{11}H_{19}$I Mol. Wt.: 278.17

<u>General procedure 2</u>: Preparation of bishomoallylic α-ketoesters.[3]

To a dry flask containing magnesium (25 mmol) was added a solution of the unsaturated halide (20 mmol) in THF or Et_2O with vigorous agitation. The Grignard reagent was added dropwise to a mixture of diethyl or dimethyl oxalate (20 mmol) in THF and ether (1/1) at -78°C and the solution was stirred for 5 h. The reaction was quenched by addition of NH_4Cl satd. The mixture was then partitioned with ether. The aqueous phase was extracted and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The crude mixture was purified by FC (Hexane/EtOAc).

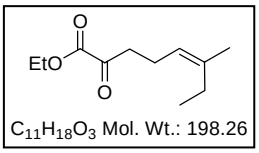
Ethyl 6-methyl-2-oxohept-5-enoate (2b). Following the *general procedure 2*, the Grignard reagent obtained from commercially available 5-bromo-2-methylpent-2-ene (2.09 g, 12.8 mmol) was added on diethyl oxalate (1.87 g, 12.8 mmol). Purification gave the α-ketoester **2b** (1.85 g, 78 %) as a colorless oil: TLC *Rf* 0.45 (Hexane/EtOAc 4/1); IR (neat) ν_{max} 2980, 2929, 1729, 1447, 1399, 1376, 1299, 1277, 1248, 1177, 1108, 1072, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.2 Hz, 3 H), 1.60 (s, 3 H), 1.67 (s, 3 H), 2.30 (q, *J* = 7.2 Hz, 2 H), 2.85 (t, *J* = 7.3 Hz, 2 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 5.06 (t, *J* = 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 17.6, 21.7, 25.6, 39.5, 62.3, 68.7, 121.8, 133.4, 161.0, 194.4; MS (EI) *m/z* (%) 182 (16, $M^{+\cdot}$), 166 (2), 155 (2), 111 (27), 83 (18), 69 (100); HR-MS 184.1098 ($C_{10}H_{16}O_3$ calcd 184.1099).



$C_{10}H_{16}O_3$ Mol. Wt.: 184.23

[3] Macritchie, J. A.; Silcock, A.; Willis, C. L. *Tetrahedron: Asymmetry* **1997**, *8*, 3895-3902.

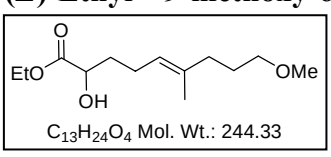
(*Z*)-Ethyl 6-methyl-2-oxooct-5-enoate (3a). Following the *general procedure 2*, the



$C_{11}H_{18}O_3$ Mol. Wt.: 198.26

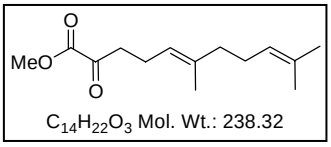
Grignard reagent obtained from V (630 mg, 2.8 mmol) was added on diethyl oxalate (412 mg, 2.8 mmol). Purification gave the α-ketoester **3a** (270 mg, 49 %) as a colorless oil: TLC *Rf* 0.48 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 2967, 2935, 2876, 1728, 1449, 1400, 1375, 1297, 1279, 1246, 1173, 1113, 1072, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.6 Hz, 3 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 1.65 (s, 3 H), 2.01 (q, *J* = 7.6 Hz, 2 H), 2.30 (q, *J* = 7.6 Hz, 2 H), 2.83 (t, *J* = 7.4 Hz, 2 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 5.03 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 12.7, 13.9, 21.3, 22.8, 24.7, 39.7, 62.3, 121.4, 139.1, 161.0, 194.3; MS (EI) *m/z* (%) 198 (40, $M^{+\cdot}$), 180 (27), 169 (19), 152 (5), 142 (9), 125 (62), 107 (10), 97 (24), 83 (100), 55 (73); HR-MS 198.1254 ($C_{11}H_{18}O_3$ calcd 198.1255).

(*E*)-Ethyl 9-methoxy-6-methyl-2-oxonon-5-enoate (5a). Following the *general procedure 2*, the Grignard reagent obtained from **VI** (2 g, 9 mmol) was added on diethyl oxalate (1.3 g, 9 mmol). Purification gave the α-ketoester **5a** (1.4 g, 64 %) as a colorless oil: TLC *Rf* 0.27 (Hexane/EtOAc 7/3); IR (neat) ν_{max} 2980, 2937, 2870, 2831, 1729, 1448, 1387, 1298, 1280, 1247, 1181, 1119, 1074, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.6 Hz, 3 H), 1.59 (s, 3 H), 1.61 (quint, *J* = 7.3 Hz, 2 H), 1.99 (t, *J* = 7.7 Hz, 2 H), 2.31 (q, *J* = 7.2 Hz, 2 H), 2.85 (t, *J* = 7.3 Hz, 2 H), 3.29 (s, 3 H), 3.31 (t, *J* = 6.5 Hz, 2 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 5.08 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 13.9, 15.8, 21.6, 27.7, 35.9, 58.5, 62.3, 72.2, 121.9, 136.5, 161.0, 194.2; MS (EI) *m/z* (%) 242 (2, $M^{+\cdot}$), 192 (11), 169 (9), 137 (32), 126 (12), 109 (15), 95 (100); HR-MS 242.1514 ($C_{13}H_{22}O_4$ calcd 242.1518). Anal. calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15; found C, 64.45; H, 9.34.



$C_{13}H_{24}O_4$ Mol. Wt.: 244.33

(*E*)-Methyl 6,10-dimethyl-2-oxoundeca-5,9-dienoate (7a). Following the *general procedure 2*, the Grignard reagent obtained from **VII** (2 g, 7.2 mmol, incomplete formation of the Grignard) was added on dimethyl oxalate (850 mg, 7.2 mmol). Purification gave the α-ketoester **7a** (900 mg, 44 %) as a colorless oil (and 640 mg of recovered **VII**): TLC *Rf* 0.44 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 2962, 2919, 2857, 1733, 1440, 1399, 1379, 1281, 1250, 1200, 1161, 1072, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3 H), 1.61 (s, 3 H), 1.66 (s, 3 H), 1.90-2.10 (m, 4 H), 2.32 (q, *J* = 7.2 Hz, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 3.85 (s, 3 H), 5.05 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 16.0, 17.6, 21.6, 25.6, 26.5, 39.5, 39.6, 52.9, 121.6, 124.1, 131.5, 137.1, 161.4, 193.9; MS (EI) *m/z* (%) 238 (3, $M^{+\cdot}$), 220 (2), 195 (4), 136 (22), 109 (13), 81 (24), 69 (100); HR-MS 238.1566 ($C_{14}H_{22}O_3$ calcd 238.1569).

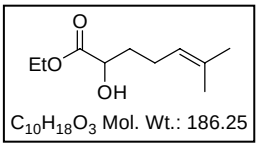


$C_{14}H_{22}O_3$ Mol. Wt.: 238.32

General procedure 3: Preparation of bishomoallylic α-hydroxyesters.[3]

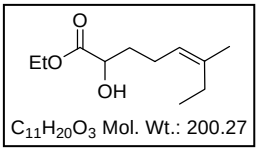
Sodium cyanoborohydride ($NaBH_3CN$, 10 mmol) was added to a solution of α-ketoester (10 mmol) in ethanol and acetic acid (7.5/1). The mixture was stirred at room temperature for 1h. The solution was then acidified with HCl 1N, stirred for 1h and extracted with ether. The combined organic layers were washed with saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$ and evaporated. The crude mixture was purified by FC (Hexane/EtOAc).

Ethyl 2-hydroxy-6-methylhept-5-enoate (1). Following the *general procedure 3*, the α-ketoester **1b** (1.5 g, 8.15 mmol) was reduced with $NaBH_3CN$ (510 mg, 8.15 mmol). Purification gave the α-hydroxyester **1** (1.2 g, 79 %) as a colorless oil: TLC *Rf* 0.42 (Hexane/EtOAc 4/1); IR (neat) ν_{max} 3485, 2969, 2926, 2859, 1730, 1447, 1376, 1267, 1210, 1167, 1113, 1096, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 3 H), 1.60 (s, 3 H), 1.78 (s, 3 H), 1.65-2.20 (m, 4 H), 2.80 (br, -OH, 1 H), 4.16 (dd, *J* = 7.2, 4.2 Hz, 1 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 5.09 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2, 17.6, 23.3, 25.7, 34.3, 61.6, 70.0, 123.1, 132.8, 175.4; MS (EI) *m/z* (%) 186 (10, $M^{+\cdot}$), 168 (2), 140 (3), 113 (6), 104 (100), 95 (53), 89 (19), 76 (52); HR-MS 186.1255 ($C_{10}H_{18}O_3$ calcd 186.1255).



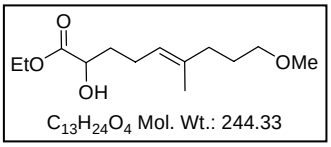
$C_{10}H_{18}O_3$ Mol. Wt.: 186.25

(*Z*)-Ethyl 2-hydroxy-6-methyloct-5-enoate (3). Following the *general procedure 3*, the α-ketoester **3a** (200 mg, 1 mmol) was reduced with $NaBH_3CN$ (63 mg, 1 mmol). Purification gave the α-hydroxyester **3** (159 mg, 79 %) as a colorless oil: TLC *Rf* 0.38 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3481, 2965, 2934, 2874, 1734, 1447, 1374, 1300, 1266, 1210, 1165, 1117, 1096, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.6 Hz, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.67 (s, 3 H), 1.65-1.90 (m, 2 H), 2.05 (q, *J* = 6.9 Hz, 2 H), 2.14 (m, 2 H), 2.79 (d, -OH, *J* = 5.6 Hz, 1 H), 4.15 (dd, *J* = 7.4, 4.1 Hz, 1 H), 4.22 (dq, *J* = 7.2, 2.5 Hz, 2 H), 5.06 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 12.7, 14.2, 22.8, 22.9, 24.7, 34.6, 33.8, 61.6, 69.9, 122.6, 138.5, 175.4; MS (EI) *m/z* (%) 200 (29, $M^{+\cdot}$), 154 (10), 127 (20), 109 (54), 104 (79), 97 (24), 83 (37), 76 (57), 67 (38), 55 (100); HR-MS 200.1414 ($C_{11}H_{20}O_3$ calcd 200.1412); Anal. calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07; found C, 65.68; H, 10.44.



$C_{11}H_{20}O_3$ Mol. Wt.: 200.27

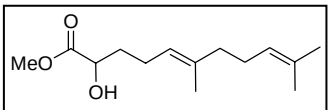
(*E*)-Ethyl 2-hydroxy-9-methoxy-6-methylnon-5-enoate (5). Following the *general procedure 3*, the α-ketoester **5a** (500 mg, 2.06 mmol) was reduced with $NaBH_3CN$ (130 mg, 2.06 mmol). Purification gave the α-hydroxyester **5** (460 mg, 91 %) as a colorless oil: TLC *Rf* 0.27 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3453, 2979, 2930, 2869, 1738, 1448, 1386, 1370, 1266, 1242, 1207, 1164, 1117, 1025, 864 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3 H), 1.60 (s, 3 H), 1.62-1.88 (m, 4 H), 1.98-2.20 (m, 4 H), 2.67 (br, -OH, 1 H), 3.31 (s, 3 H), 3.33 (t, *J* = 6.6 Hz, 2 H), 4.14 (dd, *J* = 7.7, 4.2 Hz, 1 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 5.12 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.2, 15.8, 23.2, 27.8, 34.4, 36.0, 58.5, 61.6, 69.9, 72.4, 123.2, 135.9, 175.4; MS (EI) *m/z* (%) 244 (16, $M^{+\cdot}$), 212 (10), 180 (6), 166 (8), 139 (21), 121 (30), 104



$C_{13}H_{24}O_4$ Mol. Wt.: 244.33

(100), 95 (72); HR-MS 244.1670 ($C_{13}H_{24}O_4$ calcd 244.1674). Anal. calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90; found C, 63.26; H, 9.97.

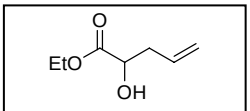
(*E*)-Methyl 2-hydroxy-6,10-dimethylundeca-5,9-dienoate (7). Following the *general procedure 3*, the α-ketoester **7a** (330 mg, 1.38 mmol) was reduced with $NaBH_3CN$ (87 mg, 1.38 mmol). Purification gave the α-hydroxyester **7** (271 mg, 82 %) as a colorless oil:



$C_{14}H_{24}O_3$ Mol. Wt.: 240.34

TLC *Rf* 0.33 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3480, 2953, 2921, 2856, 1738, 1441, 1377, 1269, 1216, 1166, 1108, 987 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 3 H), 1.61 (s, 3 H), 1.67 (s, 3 H), 1.68 (m, 1 H), 1.80 (m, 1 H), 1.95-2.25 (m, 6 H), 2.21 (d, *J* = 5.6 Hz, -OH, 1 H), 3.78 (s, 3 H), 4.18, (m, 1 H), 5.09 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 16.0, 17.6, 23.2, 25.6, 26.6, 34.4, 39.7, 52.4, 69.9, 122.8, 124.2, 131.4, 136.6, 175.9; MS (EI) *m/z* (%) 240 (1, $M^{+\cdot}$), 197 (61), 171 (17), 123 (21), 111 (48), 93 (71), 69 (100); HR-MS 240.1723 ($C_{14}H_{24}O_3$ calcd 240.1725).

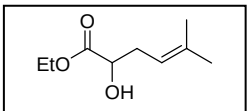
Ethyl 2-hydroxypent-4-enoate (9a). To a mixture of indium powder 100 mesh (5 g, 43.5 mmol) in distillated water (300 mL) was added a solution of ethyl glyoxalate 50 % in toluene (8.24 mL, 43.2 mmol) and allyl bromide (5.75 g, 47.2 mmol). The mixture was stirred at room temperature for 24 h (formation of a white precipitated). EtOAc and 1N HCl solution were added and the mixture was stirred for 1 h. The aqueous phase was extracted several times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. After FC (Hexane/EtOAc 10-25 %), **9a** (5.5 g, 88 %) was obtained as a colorless oil:



$C_7H_{12}O_3$ Mol. Wt.: 144.17

TLC *Rf* 0.29 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3470, 3078, 2982, 2939, 2912, 1738, 1729, 1642, 1466, 1438, 1370, 1298, 1269, 1212, 1136, 1086, 1028, 919 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3 H), 2.38-2.61 (m, 2 H), 2.76 (s, -OH, 1 H), 4.18-4.28 (m, 3 H), 5.10-5.18 (m, 2 H), 5.80 (ddt, *J* = 17.1, 10.0, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.2, 38.7, 61.7, 69.9, 118.6, 132.5, 174.4; MS (EI) *m/z* (%) 144 (1, $M^{+\cdot}$), 126 (11), 103 (50), 98 (19), 76 (49), 71 (100); HR-MS 144.0785 ($C_7H_{12}O_3$ calcd 144.0786); Anal. calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39; found C, 58.52; H, 8.59.

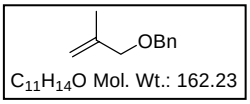
Ethyl 2-hydroxy-5-methylhex-4-enoate (9). Homoallylic alcohol **9a** (400 mg, 2,77 mmol) and 2-methyl-2-butene (7.5 mL) were simultaneously added via syringe to Grubbs catalyst 2nd generation (23.5 mg, 0.027 mmol) under N_2. After 16 h of stirring, the solvent was removed and the residue was directly purified. FC (Hexane/EtOAc 25 %) gave **9** (470 mg, 98 %) as a yellow oil:



$C_9H_{16}O_3$ Mol. Wt.: 172.22

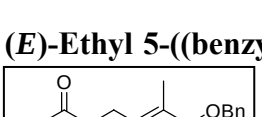
TLC *Rf* 0.18 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3476, 2980, 2916, 2860, 1734, 1446, 1377, 1298, 1269, 1208, 1092, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3 H), 1.61 (s, 3 H), 1.70 (s, 3 H), 2.36-2.53 (m, 2 H), 2.78 (s, -OH, 1 H), 4.18-4.23 (m, 3 H), 5.13 (t, *J* = 6.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 17.9, 25.8, 33.1, 61.5, 70.4, 117.8, 135.6, 174.7; MS (EI) *m/z* (%) 172 (1, $M^{+\cdot}$), 154 (31), 139 (11), 104 (22), 81 (39), 76 (22), 69 (100); HR-MS 172.1097 ($C_9H_{16}O_3$ calcd 172.1099); Anal. calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36; found C, 62.60; H, 9.62.

1-((2-Methylallyloxy)methyl)benzene (11a). β-Methallyl alcohol (4.23 mL, 50 mmol) in dry THF (100 mL) at 0°C was treated with NaH (1.32 mg, 55 mmol) and the mixture was stirred at 0°C for 1 h. Benzyl bromide (6.53 mL, 55 mmol) was then added. The reaction was stirred at 0°C for 3 h. The conversion was monitored by TLC. Saturated $NaHCO_3$ solution was added and the mixture was partitioned with ether. The aqueous phase was extracted and combined organic layers were washed with HCl 10 % and brine, dried over $MgSO_4$ and evaporated. After FC (Hexane/EtOAc 5 %), **11a** (8 g, 98 %) was obtained as a colorless oil: TLC *Rf* 0.60 (Hexane/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 3 H), 3.95 (s, 3 H), 4.51 (s, 3 H), 4.94 (s, 1 H), 5.02 (s, 1 H), 7.29-7.41 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) 19.5, 71.8, 74.1, 112.3, 127.5, 127.6, 128.3, 128.4, 129.0, 138.4, 142.2.



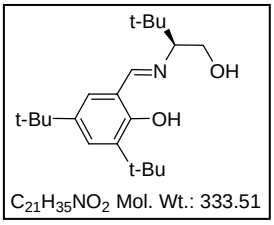
$C_{11}H_{14}O$ Mol. Wt.: 162.23

(*E*)-Ethyl 5-((benzyloxy)methyl)-2-hydroxyhex-4-enoate (11). Homoallylic alcohol **9a** (340 mg, 2.35 mmol) and benzyl ether **11a** (1.15 g, 7.09 mmol) were simultaneously added via syringe to Grubbs catalyst 2nd generation (100 mg, 0.117 mmol) in dry CH_2Cl_2 (10 mL) under N_2. After 16 h of stirring, the solvent was removed and the residue was directly purified. FC (Hexane/EtOAc 10 %) gave **11** (150 mg, 23 %, E/Z ratio 88/12 by ^{1}H NMR) as colorless oil: TLC *Rf* 0.22 (Hexane/EtOAc 3/1); IR (neat) ν_{max} 3462, 3063, 3030, 2980, 2915, 2856, 2850, 1736, 1496, 1453, 1368, 1298, 1268, 1207, 1092, 1072, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) for the *trans* product δ 1.26 (t, *J* = 7.2 Hz, 3 H), 1.70 (s, 3 H), 2.43-2.62 (m, 2 H), 2.83 (d, *J* = 5.6 Hz, -OH, 1 H), 3.91 (s, 3 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.44 (s, 3 H), 5.49 (t, *J* = 7.3 Hz, 1 H), 7.25-7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) for the *trans* product 14.1, 14.2, 32.7, 61.7, 70.1, 75.8, 121.5, 127.5, 127.7, 128.3, 135.9, 138.4, 174.6; MS (EI) *m/z* (%) 278 (1, $M^{+\cdot}$), 202 (2), 117 (16), 91 (100); HR-MS 278.1515 ($C_{16}H_{22}O_4$ calcd 278.1518).



$C_{16}H_{22}O_4$ Mol. Wt.: 278.34

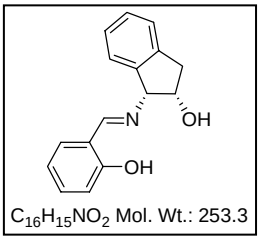
2-[((*S*)-1-Hydroxy-3,3-dimethylbutan-2-ylimino)methyl]-4,6-di-tert-butylphenol (L1).[4] 3,5-Di-*tert*-butylsalicylaldehyde (2.34 g, 10 mmol) and (*S*)-*tert*-leucinol (1.17 g, 10 mmol) were mixed in MeOH in presence of anhydrous $MgSO_4$ for 16 h. The mixture was then filtered twice and MeOH was evaporated. The crude residue was dissolved in CH_2Cl_2. After evaporation, ligand **L1** (3.1 g, 93 %) was obtained as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 9 H), 1.32 (s, 9 H), 1.46 (s, 9 H), 2.93 (d, *J* = 9.5 Hz, 1 H), 3.75 (t, *J* = 10.3 Hz, 1 H), 3.92 (d, *J* = 11.2 Hz, 1 H), 7.14 (s, 1 H), 7.41 (s, 1 H), 8.37 (s, 1 H), 13.61 (br, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 27.1, 29.4, 31.5, 33.2, 34.1, 35.0, 62.5, 81.4, 117.6, 126.2, 127.0, 136.7, 140.1, 158.1, 167.1.



$C_{21}H_{35}NO_2$ Mol. Wt.: 333.51

[4] For a complete characterization see: Liu, G.; Cogan, D. A.; Ellman, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 9913-9914.

(*1R,2S*)-1-(2-Hydroxybenzylideneamino)-2,3-dihydro-1H-inden-2-ol (L2). (*1R,2S*)-(+)-*cis*-1-Amino-2-indanol (298 mg, 2 mmol) and salicylaldehyde (245 mg, 2 mmol) were mixed in EtOH in presence of anhydrous $MgSO_4$ for 16 h. The mixture was then filtered twice and EtOH was evaporated. The crude residue was dissolved in CH_2Cl_2. After evaporation, ligand **L2** (500 mg, 98 %) was obtained as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (br, 1 H), 3.08 (dd_{ab}, J = 15.6, 5.2 Hz, 1 H), 3.25 (dd_{ab}, J = 16.0, 6.1 Hz, 1 H), 4.70 (q, J = 8.1 Hz, 1 H), 4.81 (d, J = 5.4 Hz, 1 H), 6.90-7.55 (m, 8 H), 8.60 (s, 1 H), 12.86 (br, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 39.6, 75.2, 75.5, 117.2, 118.6, 118.8, 124.8, 125.5, 127.1, 128.6, 131.9, 132.9, 140.7, 140.1, 161.2, 166.8.



$C_{16}H_{15}NO_2$ Mol. Wt.: 253.3

<u>General procedure 4</u>: Vanadium(V) complex catalyzed tandem kinetic resolution-oxidative cyclization of bishomo- and homoallylic α-hydroxyesters.

To a 25 mL round bottom flask equipped with magnetic stir bar was added ligand **L1** (36.7 mg, 0.11 mmol, 11 mol%) followed by acetone (2.5 mL) at room temperature. $VO(OiPr)_3$ (24 μL, 0.1 mmol, 10 mol%) was then added, and the resulting dark solution was stirred under an atmosphere of oxygen for 15 min. CAUTION: organic solvents under oxygen atmosphere are extremely flammable. The racemic alcohol (1 mmol) was then added via syringe as a solution in 2.5 mL of acetone with an inert internal standard (5 mg, hexamethylbenzene) and the reaction was heated at 30°C. After a given time (*Table 2*), an aliquot of the reaction mixture was removed via syringe. The aliquot (0.1 mL) was filtered through a short pad of silica gel (Et_2O), and the filtrate was analyzed by GC and HPLC to monitor for percent conversion and enantiomeric excess. Upon completion of the reaction (~ 50 % conversion), the acetone was removed to form a thick slurry, which was dissolved in $CHCl_3$ (5 mL). The resulting mixture was stirred under nitrogen for 15 min. TBHP (1.1 mmol, 5.5 M in decane) was then added and the mixture was stirred for 24 to 72 h at 0°C to room temperature (for homoallylic alcohols 5 mol% of CSA was added after 3 h to complete the cyclization). The conversion was monitored by TLC. The solvent was removed and the crude mixture was filtered through a pad of silica gel (Et_2O). Regioselectivity and diastereoselectivity were determined by ^{1}H NMR experiment (*Table 3*); relative configuration by 2D-NOESY NMR experiment. The crude mixture was purified by FC (Hexane/EtOAc).

Table 1: **Influence of the solvent on the resolution of bishomoallylic α-hydroxyester 1.**

Entry	Catalyst	Solvent	Time	Conv.	ee
1	10 mol%	acetone	24h	45 %	75 %ee
2	10 mol%	acetone	40h	57 %	38 % Yield 99 %ee
3	10 mol%	CH_2Cl_2	24h	5 %	11 %ee
4[a]	10 mol%	$CHCl_3$	24h	7 %	12 %ee
5	10 mol%	EtOAc	24h	25 %	36 %ee

[a] After 24h, chloroform was removed and acetone was added + 48h: 60 %conv 93 %ee.

Table 2: **Methods for the determination of percent conversion and enantiomeric excess.**

Kinetic Resolution				Oxidative Cyclization			
Alcohol	**Method**	**Retention Time (min)**	**GC Conversion (time) / *ee* / *s*[a]**	**Product**	**Method**	**Retention Time (min)**	**Enantiomeric Excess[d]**
1	GC Chiraldex GT-A 90°C 0 min, 2°C/min to 110°C, 15 min	13.53 (major *R*) 13.69 (minor *S*)	56 % (24h) 95 %*ee* *s* = 35	**2**	GC Chiraldex GT-A 90°C 0 min, 10°C/min to 105°C, 60 min	51.98 (major *R*) 54.06 (minor *S*)	99 %*ee*
3	GC Chiraldex GT-A 90°C, 50 min	43.61 (major *R*) 44.88 (minor *S*)	52 % (36h) 99 %*ee* *s* = >100	**4**	GC Chiraldex GT-A 90°C 0 min, 10°C/min to 110°C, 75 min	60.32 (major *R*) 63.02 (minor *S*)	99 %*ee*
5[b]	GC Chiraldex GT-A 90°C 0 min, 10°C/min to 105°C, 75 min	71.32 (major *R*) 73.68 (minor *S*)	48 % (24h) 98 %*ee* *s* = >100	**6**	-	-	-
7	HPLC Chiralcel OJ Hexane/*i*PrOH 1 % 1 mL/min	8.90 (major *R*) 9.93 (minor *S*)	52 %[c] (22h) 97 %*ee* *s* = 55	**8**	-	-	-
9[b]	GC Chiraldex GT-A 90°C 0 min, 2°C/min to 110°C, 15 min	5.88 (major *R*) 6.12 (minor *S*)	50 % (30h), 93 %*ee* *s* = 94	**10**	GC Chiraldex GT-A 90°C 0 min, 2°C/min to 110°C, 30 min	18.74 (major *R*) 23.15 (minor *S*)	92.5 %*ee*
11	HPLC Chiralcel OD Hexane/*i*PrOH 2 % 1 mL/min	18.08 (minor *S*) 22.43 (major *R*)	51 %[c] (46h), 89 %*ee* *s* = 38	**12**	-	-	-

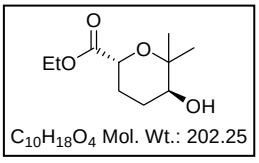
[a] Stereoselectivity factor $s = k_{rel(fast/slow)} = \ln[(1-c)(1-ee)]/\ln[(1-c)(1+ee)]$: Luukas, T. O.; Girard, C.; Fenwick, D. R.; Kagan, H. B. *J. Am. Chem. Soc.* **1999**, *121*, 9299-9306.;[b] *ee* was measured on the CF_3CO-derivative.;[c] conversion was measured by ^1H NMR.;[d] *ee* after purification by FC.

***Table 3*:**

Entry	Regioselectivity: THF/THP[a]	Diastereoselectivity *cis*/*trans*[a]	Product	Recovered Ketone
1	22/78	5/>95	**2**	**1b** 41 %
2	15/85	5/95	**4**	**3a** 26 %
3	31/69	12/88	**6**	**5a** 27 %
4	11/89	5/>95	**8**	**7a** 38 %
5[b]	-	>95/5	**10**	-[c]
6[b]	-	77/23	**12**	-[c]

[a] determinated by NMR ^1H.; [b] homoallylic alcohols.; [c] no trace of ketone was recovered for homoallylic alcohols presumably due to the instable enol form.

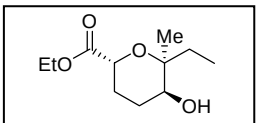
(-)-(*2R,5S*)-Ethyl 5-hydroxy-6,6-dimethyltetrahydropyran-2-carboxylate (2).



$C_{10}H_{18}O_4$ Mol. Wt.: 202.25

Following the *general procedure 4*, alcohol **1** (184 mg, 1 mmol) gave after purification by FC (Hexane/EtOAc 10-50%) **2** (55 mg, 30 %, 99 %*ee*) as a colorless oil: TLC *Rf* 0.11 (Hexane/EtOAc 3/2); $[\alpha]^{25}_D$ = -4° (*c* 1.04, $CHCl_3$); IR (neat) ν_{max} 3476, 2980, 2940, 2873, 1740, 1640, 1464, 1445, 1377, 1335, 1294, 1216, 1199, 1164, 1146, 1105, 1032, 957 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 1.36 (s, 3 H), 1.65 (m, 3 H), 1.89 (m, 1 H), 2.01 (d, *J* = 6.6 Hz, 1 H), 3.49 (dd, *J* = 11.0, 4.9 Hz, 1 H), 4.12 (dd, *J* = 11.7, 2.6 Hz, 1 H), 4.18 (q, *J* = 7.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.4, 16.3, 28.1, 28.2, 29.2, 61.3, 69.8, 73.6, 76.5, 172.0; MS (EI) *m/z* (%) 203 (12, $MH^{+\cdot}$), 185 (100), 144 (20), 129 (53), 116 (21), 101 (25), 88 (47), 73 (43); HR-MS 203.1287 ($C_{10}H_{18}O_4$+H calcd 203.1238).

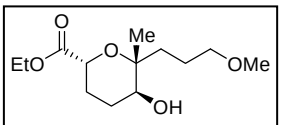
(-)-(*2R,5S,6S*)-Ethyl 6-ethyl-5-hydroxy-6-methyltetrahydropyran-2-carboxylate (4).



$C_{11}H_{20}O_4$ Mol. Wt.: 216.27

Following the *general procedure 4*, alcohol **3** (160 mg, 0.8 mmol) gave after purification by FC (Hexane/EtOAc 10-50%) **4** (61 mg, 35 %, 99 %*ee*) as a colorless oil: TLC *Rf* 0.2 (Hexane/EtOAc 3/2); $[\alpha]^{25}_D$ = -13° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} 3464, 2975, 2940, 2880, 1740, 1638, 1464, 1446, 138, 1339, 1285, 1208, 1191, 1158, 1106, 1072, 1029, 999, 926 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.5 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.28 (s, 3 H), 1.40 (m, 1 H), 1.70 (m, 3 H), 1.86 (m, 2 H), 1.99 (m, 1 H), 3.56 (dd, *J* = 10.8, 4.8 Hz, 1 H), 4.12 (dd, *J* = 11.4, 2.5 Hz, 1 H), 4.18 (q, *J* = 7.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 6.0, 14.1, 19.3, 23.9, 27.4, 28.6, 60.9, 69.0, 74.3, 77.5, 171.6; MS (EI) *m/z* (%) 216 (1, $M^{+\cdot}$), 199 (100), 181 (7), 143 (13), 125 (18), 113 (10), 88 (15), 73 (26); HR-MS 216.1284 ($C_{11}H_{20}O_4$ calcd 215.1238).

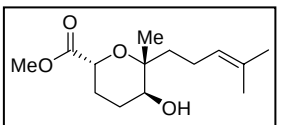
(-)-(*2R,5S,6R*)-Ethyl 5-hydroxy-6-(3-methoxypropyl)-6-methyl-tetrahydropyran-2-carboxylate (6).



$C_{13}H_{24}O_5$ Mol. Wt.: 260.33

Following the *general procedure 4*, alcohol **5** (100 mg, 0.41 mmol) gave after purification (FC Hex/EtOAc 25-40 %) **6** (28 mg, 26 %) as a pale yellow oil: TLC *Rf* 0.09 (Hexane/EtOAc 1/1); $[\alpha]^{25}_D$ = -15° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} 3451, 2979, 2939, 2872, 1741, 1462, 1447, 1377, 1294, 1197, 1108, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 1.74-2.10 (m, 8 H), 2.10 (br, -OH, 1 H), 3.32 (s, 3 H), 3.41 (m, 2 H), 3.56 (dd, *J* = 10.9, 4.7 Hz, 1 H), 4.09 (dd, *J* = 11.5, 2.5 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 14.8, 22.6, 27.5, 28.8, 36.6, 58.5, 60.8, 69.3, 70.9, 73.3, 77.4, 171.7; MS (EI) *m/z* (%) 187 (6), 185 (5), 169 (11), 153 (9), 144 (11), 117 (52), 101 (30), 85 (100), 73 (35); HR-MS 185.1176 ($C_{13}H_{24}O_5$-$C_3H_7O_2$ calcd 185.1177).

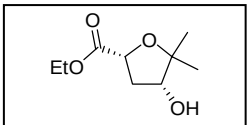
(-)-(*2R,5S,6R*)-Methyl 5-hydroxy-6-methyl-6-(4-methylpent-3-enyl)tetrahydropyran-2-carboxylate (8).



$C_{14}H_{24}O_4$ Mol. Wt.: 256.34

Following the *general procedure 4*, alcohol **7** (256 mg, 1 mmol) gave after purification (FC Hex/EtOAc 10-25 %) **8** (52 mg, 20 %) as a colorless oil: TLC *Rf* 0.31 (Hexane/EtOAc 3/2); $[\alpha]^{25}_D$ = -23° (*c* 0.95, $CHCl_3$); IR (neat) ν_{max} 3444, 2965, 2954, 2874, 1743, 1648, 1441, 1377, 1364, 1275, 1204, 1174, 1107, 1070, 990 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 3 H), 1.62 (s, 3 H), 1.68 (s, 3 H), 1.74-2.10 (m, 8 H), 3.57 (dd, *J* = 11.1, 4.8 Hz, 1 H), 3.73 (s, 3 H), 4.13 (dd, *J* = 11.6, 2.5 Hz, 1 H), 5.14 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 16.8, 19.1, 19.6, 22.6, 25.0, 25.6, 33.8, 52.2, 71.3, 75.3, 79.8, 126.8, 131.4, 170.9; MS (EI) *m/z* (%) 256 (2, $M^{+\cdot}$), 237 (6), 219 (4), 174 (33), 156 (49), 129 (41), 109 (58), 84 (83), 69 (100); HR-MS 256.1669 ($C_{14}H_{24}O_4$ calcd 256.1674).

(-)-(*2R,4R*)-Ethyl 4-hydroxy-5,5-dimethyltetrahydrofuran-2-carboxylate (10).

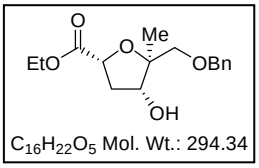


$C_9H_{16}O_4$ Mol. Wt.: 188.22

Following the *general procedure 4*, alcohol **9** (690 mg, 4 mmol) gave after purification (FC Hex/EtOAc 10-25 %) **10** (286 mg, 38 %, 92.5 %*ee*) as a colorless oil: TLC *Rf* 0.05 (Hexane/EtOAc 3/1); $[\alpha]^{25}_D$ = -52° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} 3431, 2980, 2938, 1746, 1640, 1462, 1447, 1386, 1374, 1279, 1218, 1181, 1127, 1100, 1075, 1020, 959 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 3 H), 1.28 (t, *J* = 7.3 Hz, 3 H),

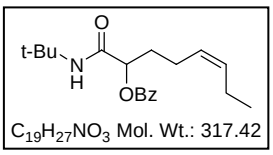
1.38 (s, 3 H), 2.09 (dd, *J* = 14.1, 3.0 Hz, 1 H), 2.65 (ddd, *J* = 14.1, 9.6, 5.3 Hz, 1 H), 3.03 (br, -OH, 1 H), 3.89 (dd, *J* = 6.8, 2.0 Hz, 1 H), 4.20 (m, 2 H), 4.48 (dd, *J* = 9.6, 3.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2, 22.1, 26.5, 38.3, 61.6, 74.9, 86.5, 175.0; MS (EI) *m/z* (%) 189 (6, $MH^{+\cdot}$), 171 (6), 130 (42), 115 (77), 101 (81), 84 (15), 71 (100); HR-MS 189.1126 ($C_9H_{16}O_4$+H calcd 189.1126).

(-)-(*2R*,*4R*,*5S*)-Ethyl 5-((benzyloxy)methyl)-4-hydroxy-5-methyltetrahydro-furan-2-carboxylate (12). Following the *general procedure 4*, alcohol **11** (100 mg, 0.36 mmol) gave after purification (FC Hex/EtOAc 10-25 %) **12** (33 mg, 31 %) as a pale yellow oil: TLC *Rf* 0.27 (Hexane/EtOAc 3/1); $[\alpha]^{25}_D$ = -35° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} 3479, 3087, 3062, 3030, 2981, 2934, 2907, 2863, 1732, 1688, 1496, 1453, 1372, 1269, 1212, 1154, 1095, 1029, 910, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3 H), 1.35 (s, 3 H), 2.09 (dt, *J* = 13.7, 3.1 Hz, 1 H), 2.67 (ddd, *J* = 13.7, 9.2, 5.9 Hz, 1 H), 2.95 (br, -OH, 1 H), 3.33 (d, J_{ab} = 9.6 Hz, 1 H), 3.38 (d, J_{ab} = 9.5 Hz, 1 H), 4.15-4.25 (m, 3 H), 4.52-4.55 (m, 3 H), 7.27-7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 18.6, 38.6, 61.5, 73.5, 74.9, 75.9, 76.1, 87.9, 127.5, 127.7, 128.4, 138.0, 174.9; MS (EI) *m/z* (%) 294 (1, $M^{+\cdot}$), 221 (7), 203 (3), 191 (14), 173 (74), 99 (47), 91 (100); HR-MS 294.1463 ($C_{16}H_{22}O_5$ calcd 294.1467).



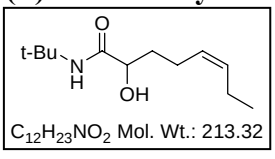
$C_{16}H_{22}O_5$ Mol. Wt.: 294.34

(*Z*)-1-(*tert*-Butylcarbamoyl)hept-4-enyl benzoate (13a). A mixture of isonitrile (600 µL, 5 mmol), commercially available *cis*-4-hepten-1-al (660 µL, 5 mmol) and benzoic acid (610 mg, 5 mmol) in THF was stirred at room temperature over night. The mixture was diluted with EtOAc, washed with water and brine, dried over $MgSO_4$ and evaporated. The residue was purified by FC (Hexane/EtOAc 25 %) to give **13a** (1.6 g, 99 %) as a white solid: mp 99°C; TLC *Rf* 0.4 (Hexane/EtOAc 3/1); IR ($CHCl_3$) ν_{max} 3619, 3019, 2975, 2934, 2895, 1757, 1725, 1678, 1520, 1476, 1423, 1216, 1106, 1094, 1044, 928 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.4 Hz, 3 H), 1.35 (s, 9 H), 1.93-2.18 (m, 6 H), 5.27-5.40 (m, 3 H), 5.90 (br, -NH, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 8.07 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.2, 20.4, 22.5, 28.6, 31.8, 51.3, 74.4, 127.2, 128.6, 129.4, 129.6, 132.9, 133.5, 165.3, 168.8; MS (EI) *m/z* (%) 317 (7, $M^{+\cdot}$), 235 (28), 212 (8), 195 (18), 139 (11), 130 (30), 122 (8), 105 (100); HR-MS 317.1993 ($C_{19}H_{27}NO_3$ calcd 317.1990); Anal. calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57; N, 4.41; found C, 71.95; H, 8.78; N, 4.33.



$C_{19}H_{27}NO_3$ Mol. Wt.: 317.42

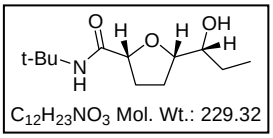
(*Z*)-*N*-*tert*-Butyl-2-hydroxyoct-5-enamide (13). Benzoate **13a** (635 mg, 2 mmol) and NaOH (8 mg, 0.2 mmol) were stirred in MeOH at room temperature for 1 h. The solvent was removed and the crude residue was purified by FC (Hexane/EtOAc 10-25 %) to afford **13** (400 mg, 94 %) as a colorless oil: TLC *Rf* 0.11 (Hexane/EtOAc 3/1); GC Chiraldex GT-A 90°C 0 min, 10°C/min to 140°C, 25 min, R_{t1} = 17.66 min (*R*), R_{t2} = 18.59 min (*S*); IR ($CHCl_3$) ν_{max} 3383, 3003, 2964, 2932, 2873, 1657, 1530, 1478, 1455, 1393, 1364, 1283, 1230, 1130, 1090 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3 H), 1.35 (s, 9 H), 1.61-1.90 (m, 2 H), 2.04 (quint, *J* = 7.2 Hz, 2 H), 2.15 (m, 2 H), 3.33 (br, -OH, 1 H), 3.97 (dd, *J* = 7.7, 3.6 Hz, 1 H), 5.37 (m, 2 H), 6.38 (br, -NH, 1



$C_{12}H_{23}NO_2$ Mol. Wt.: 213.32

H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.3, 20.5, 22.7, 28.7, 34.7, 50.9, 72.0, 127.9, 132.9, 173.1; MS (EI) *m/z* (%) 213 (9, $M^{+\cdot}$), 156 (16), 131 (98), 113 (6), 95 (40), 75 (100); HR-MS 213.1729 ($C_{12}H_{23}NO_2$ calcd 213.1728); Anal. calcd for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.87; N, 6.57; found C, 67.89; H, 11.13; N, 6.84.

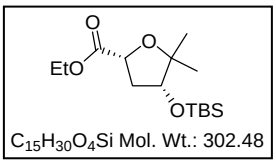
(*2R*,5S)-*N-tert*-butyl-tetrahydro-5-((*R**)-1-hydroxypropyl)furan-2-carboxamide (14).** Hydroxyenamide **13** (130 mg, 0.6 mmol) , periodic acid (178 mg, 0.78 mmol) and rhenium(VII) oxide (145 mg, 0.3 mmol) were mixed in dry CH_2Cl_2 at room temperature overnight. $NaHSO_3$ (10 equiv.) in water was added. The resulting mixture was stirred for 1 h and then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. After FC (Hexane/EtOAc 1/1), **14** (95 mg, 69 %) was obtained as thin colorless needles: relative configuration was determined by Xray structure; mp 101°C; TLC *Rf* 0.08 (Hexane/EtOAc 3/2); IR ($CHCl_3$) ν_{max} 3392, 3297, 2968, 2932, 2878, 1650, 1553, 1535, 1457, 1455, 1393, 1364, 1306, 1270, 1227, 1167, 1078 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.6 Hz, 3 H), 1.34 (s, 9 H), 1.35-1.57 (m, 2 H), 1.67 (br, -OH, 1 H), 1.71-1.87 (m, 2 H), 2.10-2.29 (m, 2 H), 3.85 (m, 1 H), 3.98 (m, 1 H), 4.27 (dd, *J* = 8.8, 3.3 Hz, 1 H), 7.00 (br, -NH, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 10.4, 23.2, 26.9, 28.7, 31.0, 50.7, 73.0, 78.7, 83.9, 173.1; MS (EI) *m/z* (%) 229 (1, $M^{+\cdot}$), 221 (12), 171 (35), 143 (17), 129 (64), 111 (34), 83 (66), 69 (51), 57 (100); HR-MS 229.1681 ($C_{12}H_{23}NO_3$ calcd 229.1678); Anal. calcd for $C_{12}H_{23}NO_3$: C, 62.85; H, 10.11; N, 6.11; found C, 62.52; H, 10.32; N, 6.04.



$C_{12}H_{23}NO_3$ Mol. Wt.: 229.32

Synthesis of (-)-pantofuranoid E [5]

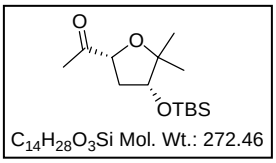
(-)-(*2R,4R*)-Ethyl 4-*tert*-butyldimethylsilyloxy-5,5-dimethyltetrahydrofuran-2-carboxylate (10a). *cis*-Tetrahydrofuran **10** (345 mg, 2 mmol) and 2,6-lutidine (580 μL, 5 mmol) were stirred in dry CH_2Cl_2 at 0°C and TBSOTf (690 μL, 3 mmol) was then added. The reaction was stirred at 0°C for 30 min. The mixture was quenched with $NaHCO_3$ satd and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. FC (Hexane/EtOAc 5 %) gave **10a** (575 mg, 95 %) as a colorless oil: TLC *Rf* 0.17 (Hexane/EtOAc 9/1); $[\alpha]^{25}_D$ = -27.5° (*c* 1.03, $CHCl_3$); IR (neat) ν_{max} 2956, 2931, 2898, 2857, 1757, 1730, 1464, 1370, 1254, 1198, 1131, 1086, 1038, 876, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6 H), 0.86 (s, 9 H), 1.19 (s, 3 H), 1.23 (s, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 2.14 (dt, *J* = 13.0, 5.5 Hz, 1 H), 2.48 (ddd, *J* = 14.4, 8.7, 5.7 Hz, 1 H), 3.88 (t, *J* = 5.5 Hz, 1 H), 4.17 (m, 2 H), 4.44 (dd, *J* = 8.7, 5.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) -5.1, -4.8, 14.1, 17.9, 22.4, 25.6, 26.9, 38.3, 60.9, 74.2, 84.6, 85.2, 173.2; MS (EI) *m/z* (%) 302 (1, $M^{+\cdot}$), 287 (4), 245 (100), 229 (20), 215 (8), 199 (23), 187 (10), 171 (20), 159 (12), 145 (15); HR-MS 302.1864 ($C_{15}H_{30}O_4Si$ calcd 302.1913); Anal. calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.00; found C, 59.21; H, 10.29.



$C_{15}H_{30}O_4Si$ Mol. Wt.: 302.48

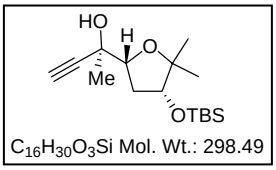
[5] Cueto, M.; Darias, J. *Tetrahedron* **1996**, *52*, 5899-5906.

(-)-1-((*2R,4R*)-4-*tert*-Butyldimethylsilyloxy-5,5-dimethyltetrahydrofuran-2-yl)-ethanone (15). To a mixture of *cis*-tetrahydrofuran **10a** (450 mg, 1.5 mmol) and Me(MeO)NH·HCl (220 mg, 2.25 mmol) was slowly added a solution of MeMgBr 3 M in ether (1.5 mL, 4.5 mmol) at -30°C. The reaction was stirred for 1.5 h during which the temperature rose 0°C. The mixture was cooled down to -78°C and an excess of MeMgBr was added (3.3 mL, 10 mmol). After the addition, the resulting mixture was stirred at 0°C for 3 h, quenched by addition of NH_4Cl satd and extracted with Et_2O. Combined organic layers were washed with water and brine, dried over $MgSO_4$ and evaporated. FC (Hexane/EtOAc 10 %) gave **15** (310 mg, 76 %) as a colorless oil (Caution: the product is unstable at room temperature and was directly used after purification for the next reaction): TLC *Rf* 0.40 (Hexane/EtOAc 3/1); $[\alpha]^{25}_D$ = -3° (*c* 1.05, $CHCl_3$); IR (neat) ν_{max} 2956, 2931, 2887, 2858, 1782, 1718, 1464, 1362, 1256, 1171, 1132, 1093, 1062, 1038, 875, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 3 H), 0.04 (s, 3 H), 0.86 (s, 9 H), 1.17 (s, 3 H), 1.28 (s, 3 H), 2.14 (dt, *J* = 13.4, 4.0 Hz, 1 H), 2.27 (s, 3 H), 2.51 (ddd, *J* = 14.4, 9.6, 4.8 Hz, 1 H), 3.85 (dd, *J* = 4.8, 2.8 Hz, 1 H), 4.44 (dd, *J* = 9,6, 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) -5.2, -4.9, 18.0, 22.7, 25.6, 26.0, 26.8, 39.1, 77.3, 81.6, 85.5, 213.5; MS (EI) *m/z* (%) 273 (8, $MH^{+\cdot}$), 255 (10), 245 (15), 229 (40), 215 (48), 187 (19), 157 (8), 145 (75), 129 (16), 101 (26), 75 (100); HR-MS 273.1887 ($C_{14}H_{28}O_3Si$+H calcd 273.1885).



$C_{14}H_{28}O_3Si$ Mol. Wt.: 272.46

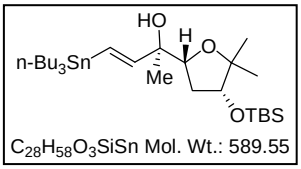
(-)-(*R*)-2-((*2R,4R*)-4-*tert*-Butyldimethylsilyloxy-5,5-dimethyltetrahydrofuran-2-yl)but-3-yn-2-ol (16). Anhydrous cerium(III) chloride powder (620 mg, 2.5 mmol) was stirred in THF (5 mL) for 2 h. THF was removed in vacuo, and the flask was back-filled with N_2 and cooled to -78°C. A 1:1 mixture of diethyl ether/triethylamine (5 mL) was added. In a separate flask, *n*-butyllithium (2.5 M in hexanes, 1 mL) was added to trimethylsilylacetylene (360 μL, 2.5 mmol) in diethyl ether/triethylamine (1:1, 5 mL) at -78°C, stirred for 30 min, then warmed to 0°C. The lithium trimethylsilylacetylide solution thus formed was transferred via cannula to the cerium(III) chloride suspension. The whole mixture was warmed to 0°C, stirred for 20 min and then recooled to -78°C. An solution of methyl ketone **15** (230 mg, 0.83 mmol) in 1:1 diethyl ether/triethylamine (5 mL) was added, and the whole mixture was stirred at -78°C for 2 h. Satd NH_4Cl solution was then added, and the mixture was warmed to room temperature. Diethyl ether and water were added, and the mixture was separated. The aqueous layer was extracted with diethyl ether, and combined extracts were washed with brine and dried over $MgSO_4$ and evaporated. The mixture of crude propargylic alcohol was dissolved in 5 mL of methanol. Potassium carbonate (345 mg, 2.5 mmol) was added, and the mixture was stirred for 2 h. The mixture was quenched with satd NH_4Cl solution, diluted with diethyl ether, and separated. The aqueous layer was extracted with diethyl ether, and the combined extracts were washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by FC (Hexane/EtOAc 5-10 %) to give alcohol **16** (150 mg, 60 %, *dr* 4/1) as a white solid: mp 59°C; TLC *Rf* 0.37 (Hexane/EtOAc 3/1); $[\alpha]^{25}_D$ = -38° (c 0.63, $CHCl_3$); IR (neat) ν_{max} 3433, 3312, 2955, 2930, 2885, 2858, 2113, 1463, 1384, 1366, 1257, 1220, 1188, 1129, 1077, 1052, 994, 876, 837, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.19 (s, 3 H), 1.22



$C_{16}H_{30}O_3Si$ Mol. Wt.: 298.49

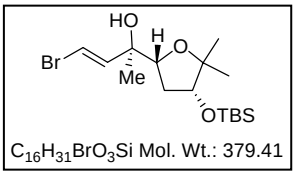
(s, 3 H), 1.39 (s, 3 H), 1.88 (ddd, *J* = 11.5, 6.8, 4.5 Hz, 1 H), 2.22 (ddd, *J* = 13.4, 7.8, 5.8 Hz, 1 H), 3.19 (br, -OH, 1 H), 3.92 (t, *J* = 5.2 Hz, 1 H), 4.04 (t, *J* = 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) -5.1, -4.8, 18.0, 22.8, 25.6, 25.6, 25.7, 34.9, 68.0, 70.8, 77.6, 81.2, 83.6, 87.2; MS (EI) *m/z* (%) 281 (14), 265 (3), 241 (15), 229 (68), 223 (35), 199 (9), 171 (35), 155 (67), 145 (22), 129 (12), 115 (29), 101 (15), 73 (100); HR-MS 281.1937 ($C_{16}H_{30}O_3Si$-OH calcd 281.1936). Anal. calcd for $C_{16}H_{30}O_3Si$: C, 64.38; H, 10.13; found C, 64.11; H, 10.75.

(-)-(*R,E*)-2-((*2R,4R*)-4-Butyldimethylsilyloxy-5,5-dimethyltetrahydrofuran-2-yl)-4-(tributylstannyl)but-3-en-2-ol (17). To a solution of propargyl alcohol **16** (100 mg, 0.335 mmol) in CH_2Cl_2 (7 mL) at 0°C was added bis(triphenylphosphine) palladium(II) chloride (23.5 mg, 0.0335 mmol). Tributyltinhydride (134 µL, 0.5 mmol) was added dropwise over 3 min; the reaction mixture was then stirred at 0°C for 15 min and warmed to room temperature (30 min). Concentration and FC (Hexane/EtOAc 5 %, 1 % Et_3N was added to the eluent) afforded vinyl stannane **17** as a colorless oil (163 mg, 82 %, *E*/*Z* ratio >95/5): TLC *Rf* 0.11 (Hexane/EtOAc 5 %); $[\alpha]^{25}_D$ = -16° (*c* 0.89, $CHCl_3$); IR (neat) ν_{max} 3468, 2956, 2927, 2870, 2856, 1599, 1462, 1363, 1252, 1128, 1075, 1045, 992, 876, 836, 775 cm^{-1}; ^{1}H NMR (400 MHz, Benzene-d_6) δ -0.03 (s, 3 H), 0.01 (s, 3 H), 0.92 (s, 9 H), 0.90-1.00 (m, 15 H), 1.07 (s, 3 H), 1.20 (s, 3 H), 1.26 (s, 3 H), 1.37 (sext, *J* = 7.4 Hz, 6 H), 1.55-1.67 (m, 6 H), 1.88-2.04 (m, 2 H), 2,47 (s, -OH, 1 H), 3.76 (t, *J* = 6.3 Hz, 1 H), 3.80 (dd, *J* = 8.6, 6.8 Hz, 1 H), 6.28 (d, J_{ab} = 19.3 Hz, 1 H), 6.36 (d, J_{ab} = 19.2 Hz, 1 H); ^{13}C NMR (100 MHz, Benzene-d_6) -4.4, -4.0, 10.3, 14.6, 18.8, 24.1, 24.9, 26.5, 26.8, 28.2, 30.1, 36.4, 75.3, 79.2, 81.9, 83.2, 124.6, 154.9; MS (EI) *m/z* (%) 533 (100), 291 (28), 267 (9), 249 (21), 229 (36), 169 (52); HR-MS 533.2464 ($C_{28}H_{58}O_3Si^{120}Sn$-*t*Bu calcd 533.2472). Anal. calcd for $C_{28}H_{56}O_3SiSn$: C, 57.04; H, 9.92; found C, 57.13; H, 9.90.



$C_{28}H_{58}O_3SiSn$ Mol. Wt.: 589.55

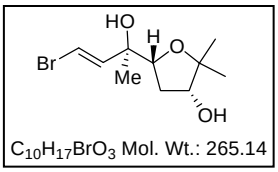
(-)-(*R,E*)-4-bromo-2-((*2R,4R*)-4-Butyldimethylsilyloxy-5,5-dimethyltetrahydrofuran-2-yl)but-3-en-2-ol (18). *N*-Bromosuccinimide (40 mg, 0.224 mmol) was added to a cold solution of vinyl stannane **17** (120 mg, 0.203 mmol) in dry CH_2Cl_2 (2.5 mL). Upon completion (TLC, 1 h), the reaction was quenched by the addition of satd aqueous solution of $Na_2S_2O_3$ (1 mL). The aqueous phase extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by FC (Hexane/EtOAc 10 %) to afford vinyl bromide **18** (67 mg, 87 %) as a colorless oil: TLC *Rf* 0.48 (Hexane/EtOAc 3/1); $[\alpha]^{25}_D$ = -30° (*c* 0.57, $CHCl_3$); IR (neat) ν_{max} 3468, 2955, 2930, 2884, 2858, 1619, 1462, 1383, 1364, 1325, 1256, 1219, 1197, 1130, 1077, 1046, 1006, 993, 876, 836, 776 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 3 H), 0.07 (s, 3 H), 0.89 (s, 9 H), 1.13 (s, 3 H), 1.16 (s, 3 H), 1.17 (s, 3 H), 1.88 (ddd, *J* = 10.8, 6.6, 4.2 Hz, 1 H), 2.21 (ddd, *J* = 13.4, 7.7, 6.0 Hz, 1 H), 2,95 (br, -OH, 1 H), 3.87 (t, *J* = 7.4 Hz, 1 H), 3.90 (t, *J* = 4.4 Hz, 1 H), 6.28 (d, J_{ab} = 13.6 Hz, 1 H), 6.35 (d, J_{ab} = 13.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) -5.1, -4.8, 18.1, 22.8, 23.8, 25.4, 25.7, 35.3, 74.3, 77.5, 80.7, 83.6, 105.9, 142.6; MS (EI) *m/z* (%) 363 (9), 229 (84), 185 (6), 171 (13), 161 (13), 145



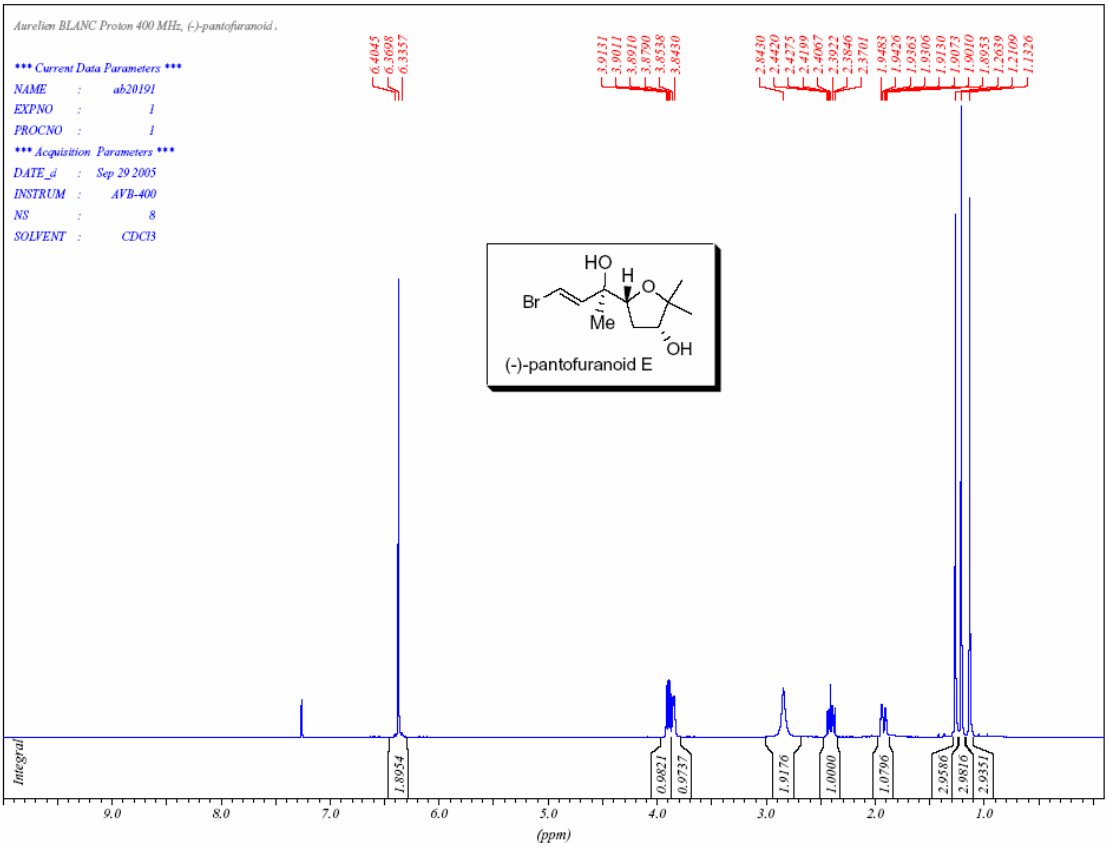
$C_{16}H_{31}BrO_3Si$ Mol. Wt.: 379.41

(26), 133 (35), 115 (23), 95 (20), 71 (100); HR-MS 363.1171 ($C_{16}H_{31}{}^{81}BrO_3Si$-OH calcd 363.1177). Anal. calcd for $C_{16}H_{31}BrO_3$: C, 50.65; H, 8.24; found C, 50.98; H, 8.65.

(-)-Pantofuranoid E.[5] To a solution of TBS-protected *cis*-tetrahydrofuran **18** (95 mg, 0.25 mmol) in dry THF (2.5 mL) under N_2 was added tetrabutylammonium fluoride in THF 1.0 M (0.5 mL, 0.5 mmol) at room temperature. After stirring for 1 h, the reaction mixture was treated with saturated aqueous sodium chloride and the solution was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. FC (Hexane/EtOAc 25 %) gave pantofuranoid E (63 mg, 94 %, 95%*ee* after recrystallization in hexane) as a white solid: mp 82°C; TLC *Rf* 0.04 (Hexane/EtOAc 3/1); HPLC Chiralcel OD, Hexane/*i*PrOH 2%, 1 mL/min, retention time: minor 22.1 min, major 24.4 min; $[\alpha]^{25}_D$ = -52° (*c* 1.03, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3618, 3433, 3011, 2976, 2934, 2884, 2890, 1617, 1449, 1320, 1256, 1219, 1148, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 3 H), 1.22 (s, 3 H), 1.27 (s, 3 H), 1.93 (ddd, *J* = 14.2, 4.9, 2.2 Hz, 1 H), 2.41 (ddd, *J* = 14.3, 8.8, 5.7 Hz, 1 H), 2,62 (br, -OH, 2 H), 3.86 (dd, *J* = 5.8, 2.1 Hz, 1 H), 3.90 (dd, *J* = 8.9, 4.9 Hz, 1 H), 6.37 (d, J_{ab} = 13.7 Hz, 1 H), 6.39 (d, J_{ab} = 13.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 22.0, 23.9, 25.1, 35.2, 74.6, 76.6, 81.0, 84.4, 106.6, 142.2; MS (EI) *m/z* (%) 247 (1), 231 (2), 162 (12), 149 (23), 115 (87), 97 (18), 71 (100); HR-MS 247.0337 ($C_{10}H_{17}{}^{79}BrO_3$-OH calcd 247.0333). Anal. calcd for $C_{10}H_{17}BrO_3$: C, 45.30; H, 6.46; found C, 45.44; H, 6.69.



$C_{10}H_{17}BrO_3$ Mol. Wt.: 265.14


Aurelien BLANC Proton 400 MHz, (-)-pantofuranoid .
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PROCNO : 1
*** Acquisition Parameters ***
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6.3357
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3.9011
3.8910
3.8790
3.8538
3.8430
2.8430
2.4420
2.4275
2.4199
2.4007
2.3922
2.3846
2.3701
1.9483
1.9426
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1.9306
1.9130
1.9073
1.9010
1.8953
1.2639
1.2169
1.1326
HO
H
O
Br
Me
OH
(-)-pantofuranoid E
Integral
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0.9737
1.9176
1.0000
1.0790
2.9586
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4.0
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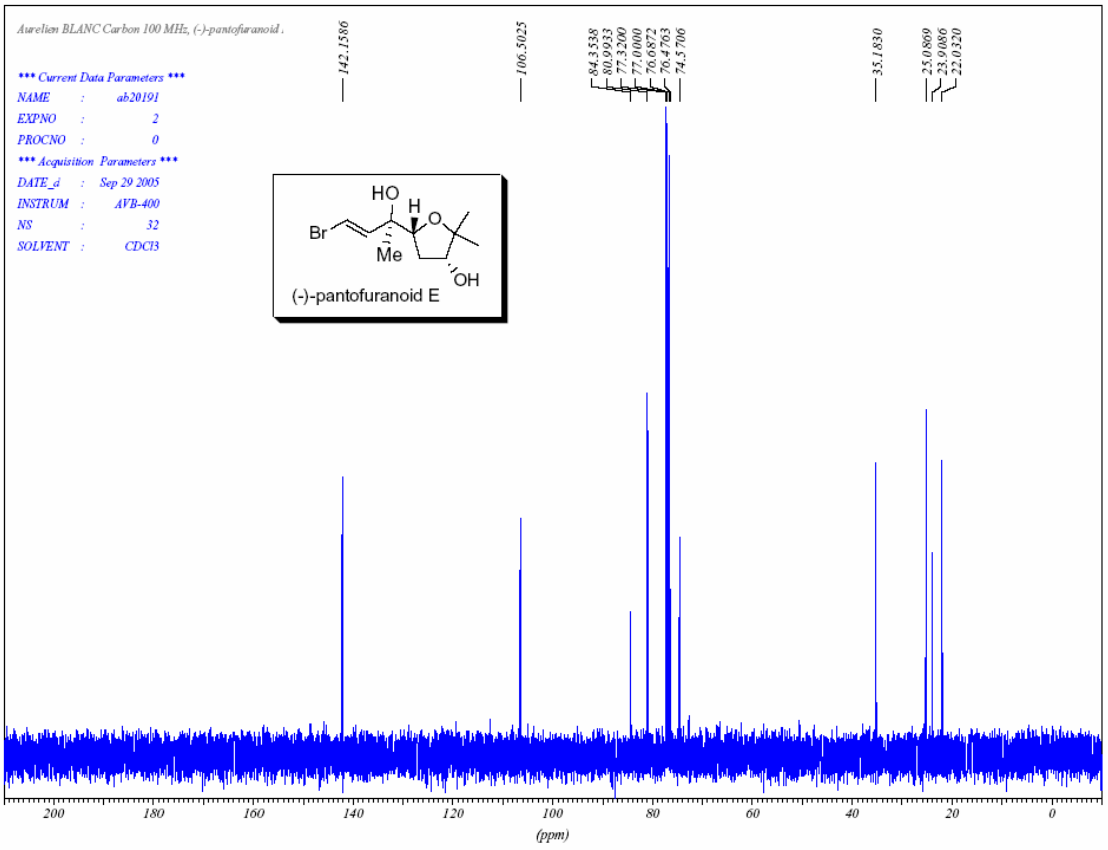
(ppm)


Aurelien BLANC Carbon 100 MHz, (-)-pantofuranoid .
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23.0086
22.0320
HO
H
O
Br
Me
OH
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140
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100
80
60
40
20
0
(ppm)

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                                                Inj Volume : 1 µl
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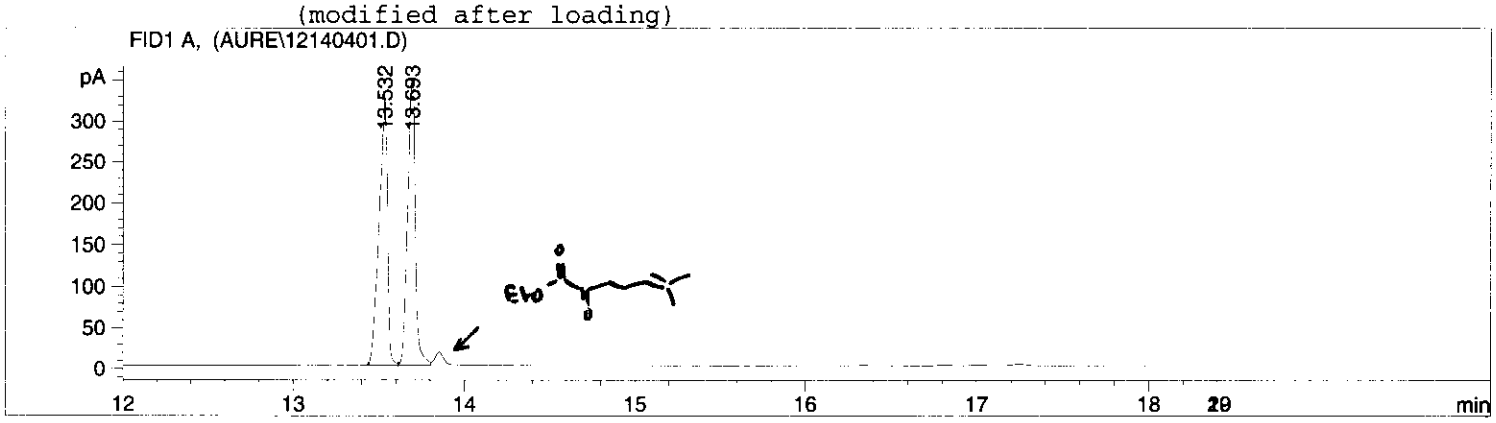


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Dilution              :      1.0000


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   1  13.532 BV    0.0495 1089.04492  321.44409 49.76799
   2  13.693 VV    0.0460 1099.19885  346.41229 50.23201

Totals :                  2188.24377  667.85638

 Results obtained with enhanced integrator!
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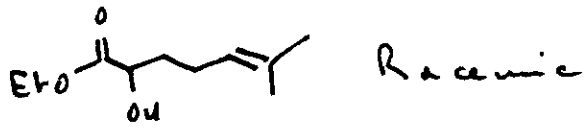

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                                                Inj Volume : 1 µl
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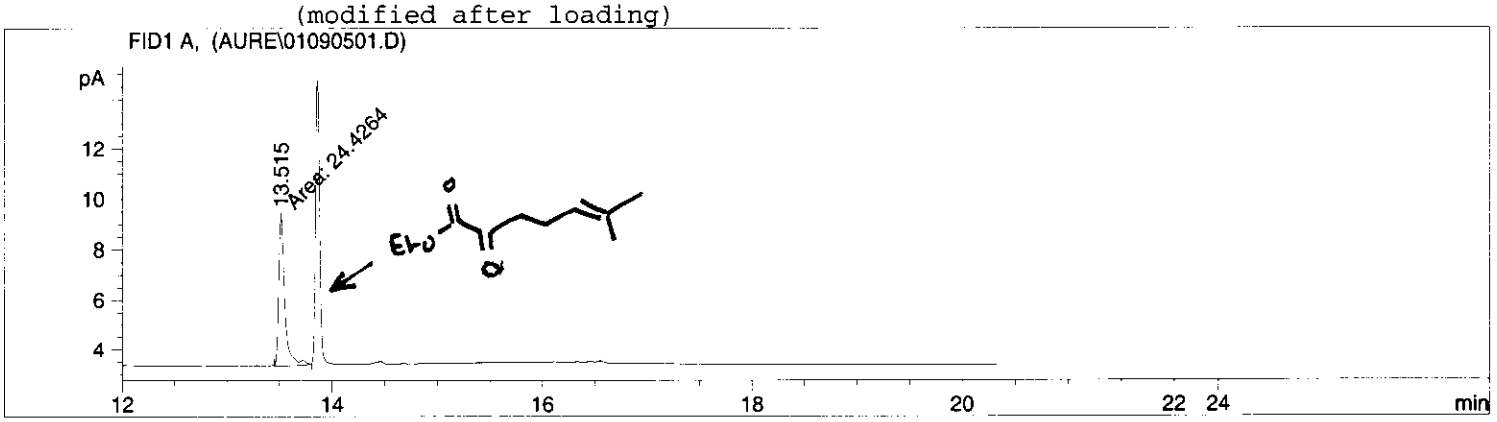


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Dilution              :      1.0000

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Totals :                    24.42636    6.09701
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1 Both peaks

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 Results obtained with enhanced integrator!
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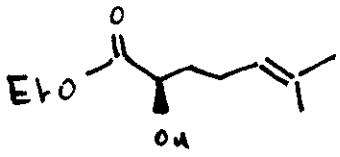

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                                           Inj Volume : 1 µl

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Analysis Method : D:\HPCHEM\1\METHODS\SULFOXID.M
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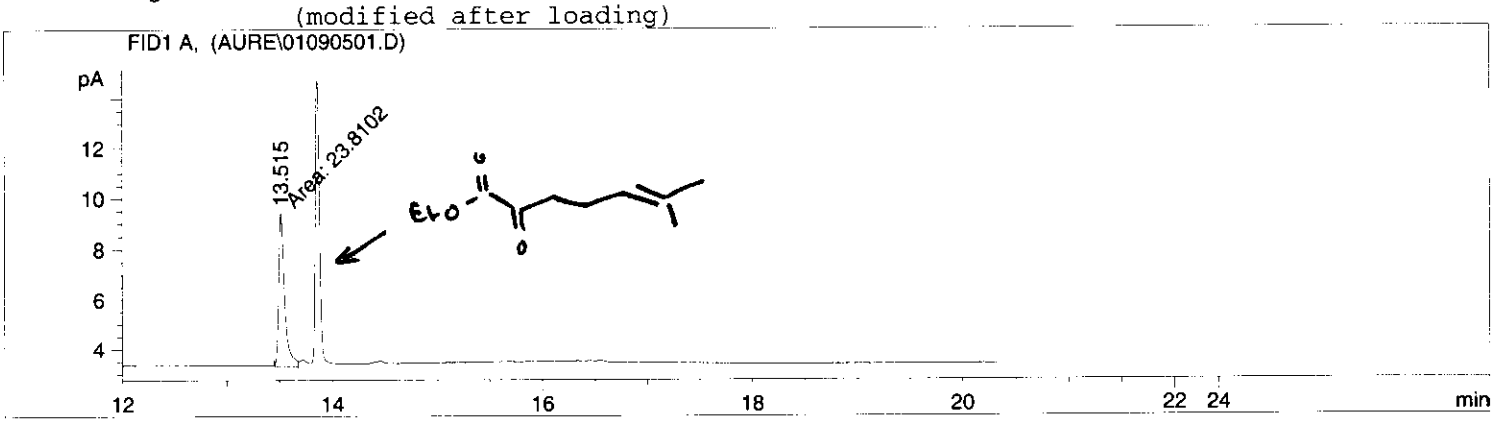


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Dilution              :      1.0000

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Totals :                    23.81016    6.13988   ) Major Peak

 Results obtained with enhanced integrator!
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                        *** End of Report ***
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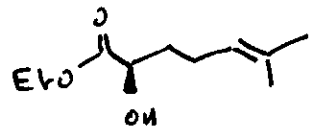

Major: Area = 23.8101
Minor: Area = 0.6162
) 95% e.e

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                                                 Inj Volume : 1 µl
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Last changed    : 6/6/05 6:12:53 PM by aurelien_blanc
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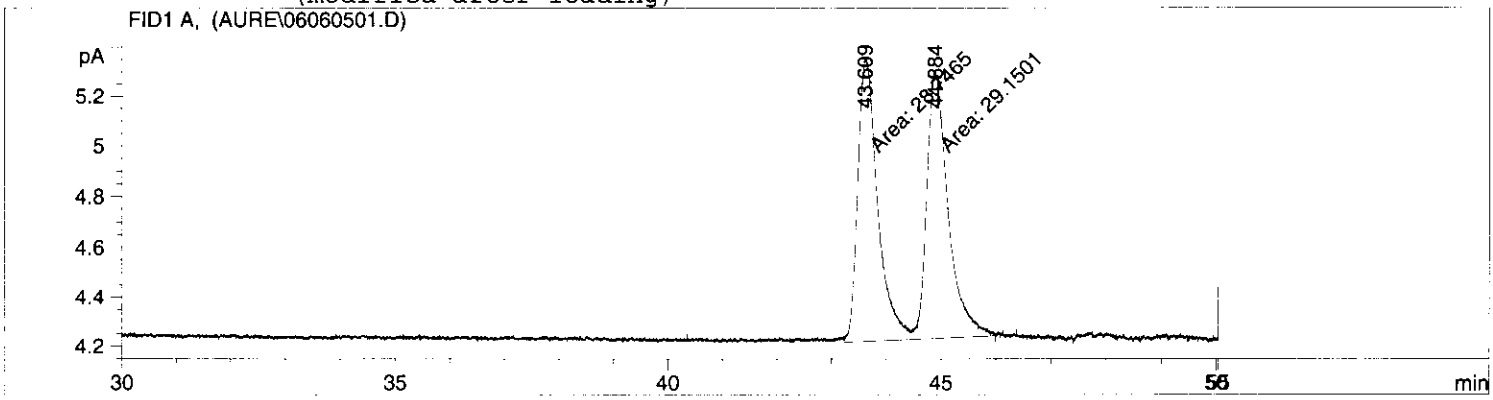


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Dilution              :      1.0000

Signal 1: FID1 A,

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   2  44.884 FM    0.4539   29.15005    1.07045 50.34848

Totals :                    57.89660    2.20764

 Results obtained with enhanced integrator!
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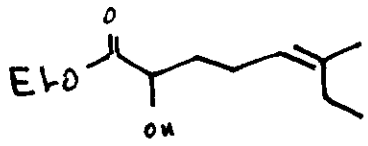
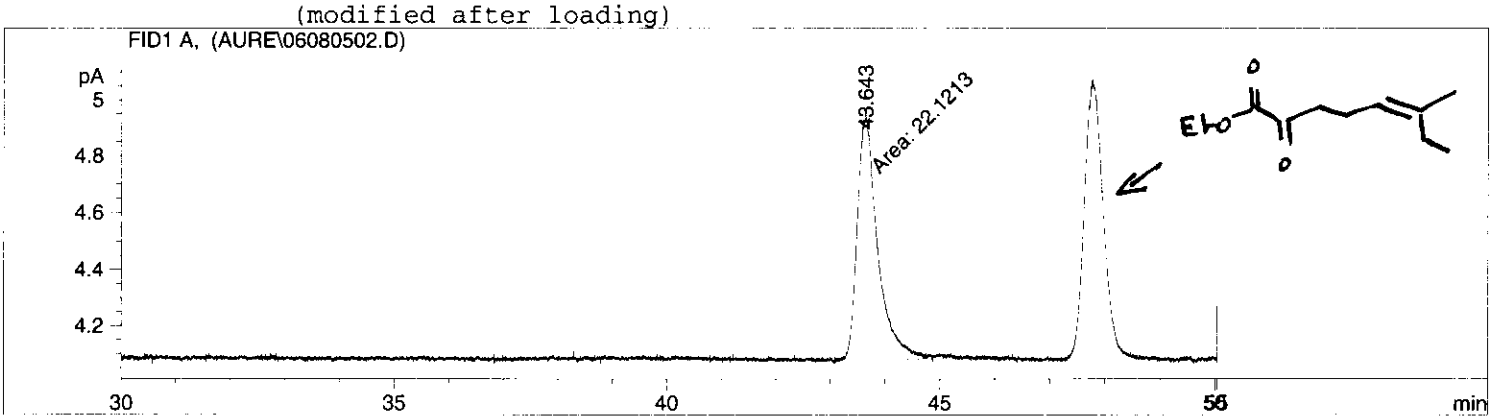
                          *** End of Report ***
```



Racemic

3

```
==========================================================================
Injection Date  : 6/8/05 11:58:12 AM            Seq. Line :   2
Sample Name     : ab159_ee_36h                       Vial :   2
Acq. Operator   : aurelien                           Inj :   1
                                               Inj Volume : 1 µl
Acq. Method     : D:\HPCHEM\1\METHODS\AURE9.M
Last changed    : 6/7/05 9:21:11 AM by aurelien_blanc
Analysis Method : D:\HPCHEM\1\METHODS\AURE10.M
Last changed    : 6/8/05 12:59:24 PM by aurelien_blanc
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

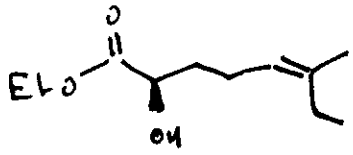
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  43.643 MM    0.4176   22.12132 8.82820e-1 1.000e2

Totals :                    22.12132 8.82820e-1

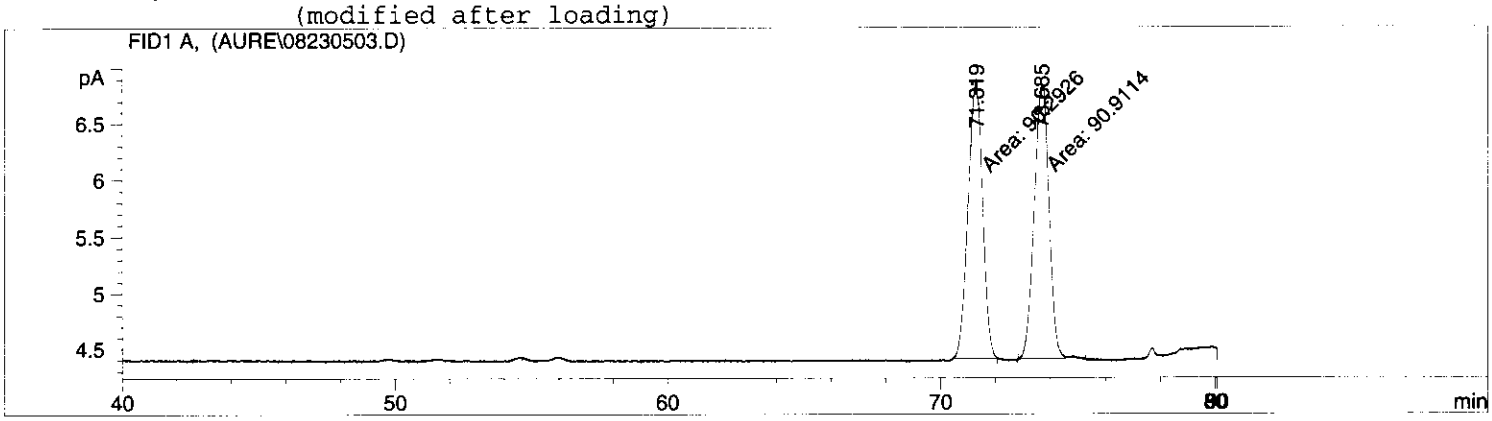
 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```



99% ee

```
==========================================================================
Injection Date  : 8/23/05 5:57:10 PM            Seq. Line :   1
Sample Name     : ab202_racCF3                       Vial :   1
Acq. Operator   : Aurelien                           Inj :   1
                                                Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\AURE12.M
Last changed    : 6/8/05 1:50:56 PM by aurelien_blanc
Analysis Method : D:\HPCHEM\1\METHODS\AURE12.M
Last changed    : 8/23/05 7:22:14 PM by MPW
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

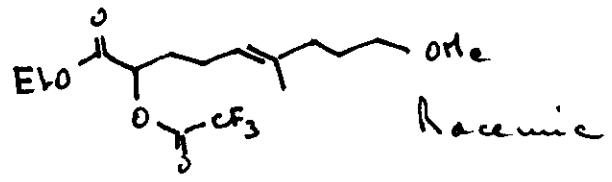
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

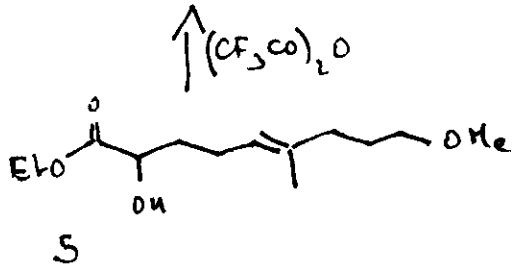
Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  71.319 MM    0.6026   90.29260    2.49737 49.82926
   2  73.685 MM    0.6181   90.91139    2.45126 50.17074

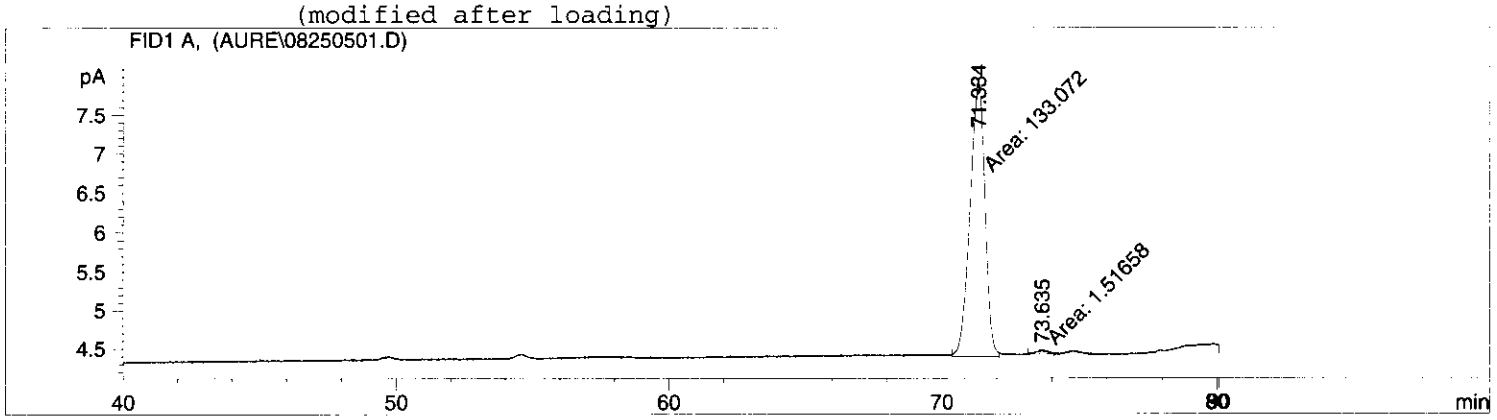
Totals :                   181.20399    4.94863

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```





```
==========================================================================
Injection Date  : 8/25/05 10:30:17 AM          Seq. Line :   1
Sample Name     : ab204_eeCF3                       Vial :   1
Acq. Operator   : Aurelien                          Inj :   1
                                             Inj Volume : 1.5 µl
Acq. Method     : D:\HPCHEM\1\METHODS\AURE12.M
Last changed    : 8/25/05 10:27:06 AM by MPW
Analysis Method : D:\HPCHEM\1\METHODS\AURE12.M
Last changed    : 8/25/05 11:57:13 AM by MPW
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

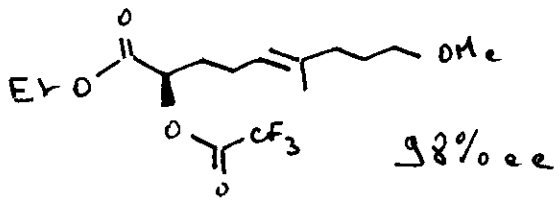
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  71.334 MM    0.6182  133.07161    3.58764 98.87317
   2  73.635 MM    0.3895    1.51658 6.48919e-2  1.12683

Totals :                   134.58819    3.65253

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

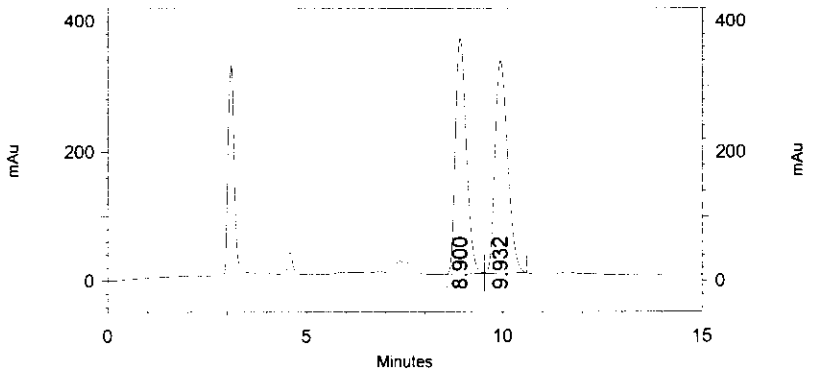


Sample ID: **ab184_rac1**

Filename:
C:\EZStart\Projects\Default\Data\ab184_rac1OJ9901IP.met8-8-2005 6-25-41 PM.dat

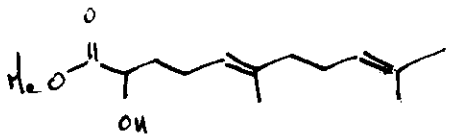
Method:
C:\EZStart\Projects\Default\Method\OJ\OJ9901IP.met

Injection volume: 5 uL



3: 216 nm, 4 nm Results

Retention Time	Area	Area Percent
8.900	7042486	49.177
9.932	7278314	50.823



Racemic

7

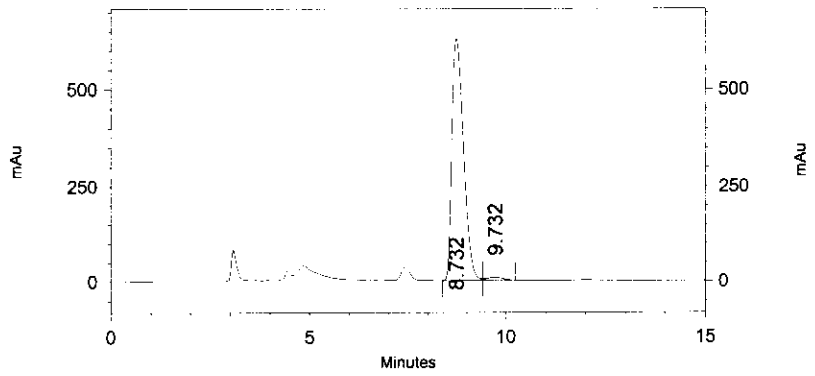
8/8/2005 6:27:19 PM

Sample ID: **ab184_ee_fc**

Filename:
C:\EZStart\Projects\Default\Data\aure\ab184_ee_fcOJ9901IP.met8-11-2005 6-30-09 PM.dat

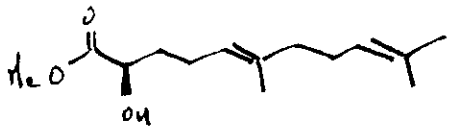
Method:
C:\EZStart\Projects\Default\Method\OJ\OJ9901IP.met

Injection volume: 5 uL



3: 216 nm, 4 nm Results

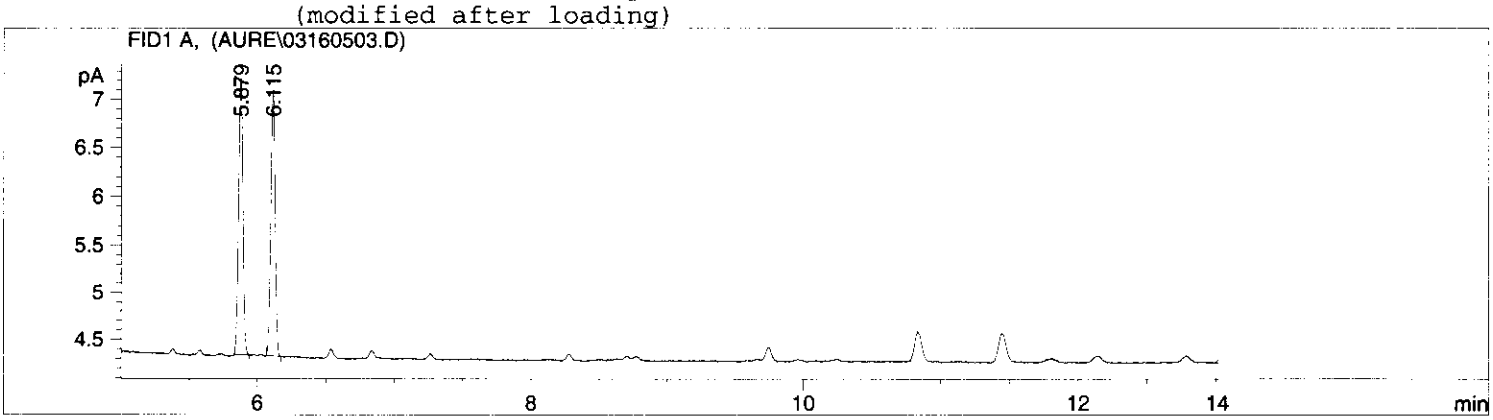
Retention Time	Area	Area Percent
8.732	13125492	98.335
9.732	222246	1.665



97% ee

8/11/2005 6:31:50 PM

```
==========================================================================
Injection Date  : 3/16/05 8:54:58 AM            Seq. Line :   1
Sample Name     : test                               Vial :   1
Acq. Operator   : aurelien                           Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : D:\HPCHEM\1\METHODS\AURE5.M
Last changed    : 1/22/05 5:49:59 PM by Alex
Analysis Method : D:\HPCHEM\1\METHODS\SULFOXID.M
Last changed    : 10/19/05 4:04:48 PM by KAN
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

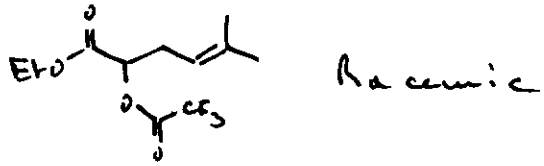
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   5.879 BB    0.0349    6.40785    2.88627 51.03478
   2   6.115 BB    0.0349    6.14800    2.76955 48.96522

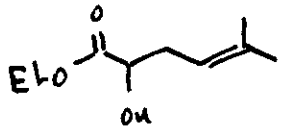
Totals :                    12.55585    5.65582

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```



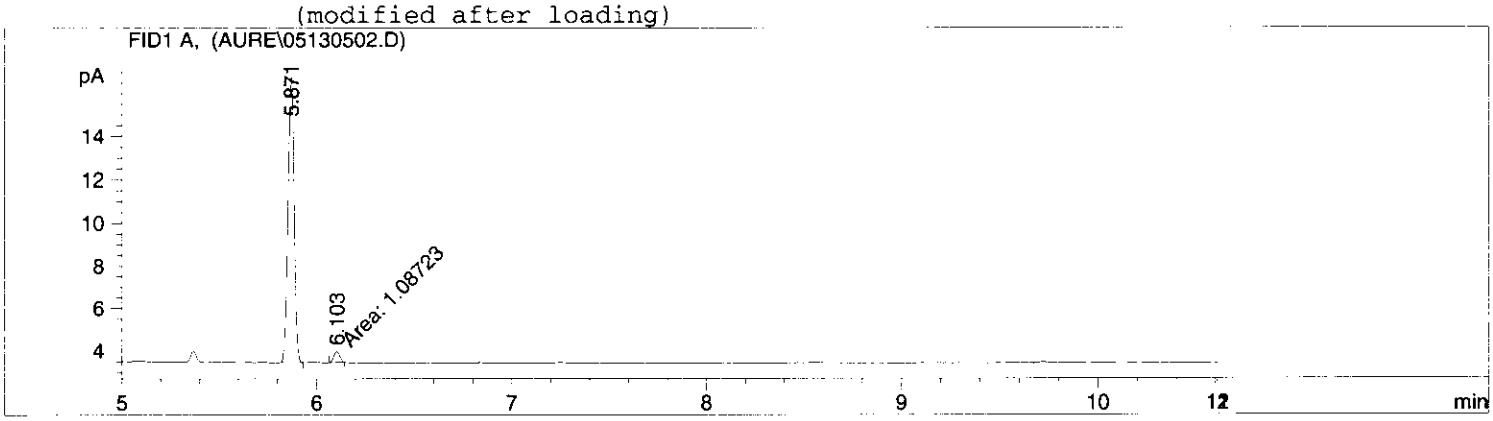
Racemic

↑ $(CF_3CO)_2O$



9

```
==========================================================================
Injection Date  : 5/13/05 12:09:58 PM          Seq. Line :   1
Sample Name     : ab139_ee                          Vial :   2
Acq. Operator   : aurelien_blanc                     Inj :   1
                                              Inj Volume : 1 µl
Acq. Method     : D:\HPCHEM\1\METHODS\AURE5.M
Last changed    : 1/22/05 5:49:59 PM by Alex
Analysis Method : D:\HPCHEM\1\METHODS\AURE5.M
Last changed    : 5/13/05 1:22:06 PM by aurelien_blanc
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

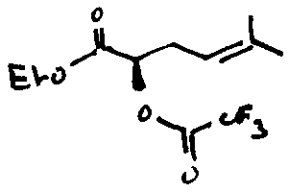
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   5.871 BP    0.0344   28.85992   13.27787 96.36950
   2   6.103 MM    0.0358    1.08723 5.06126e-1  3.63050

Totals :                    29.94715   13.78400

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```



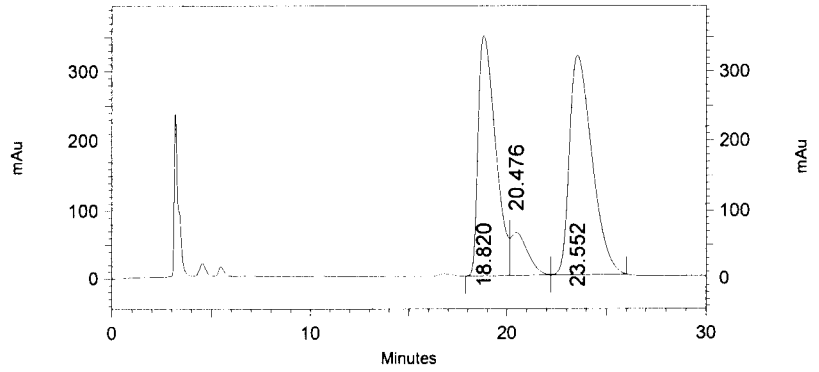
93% ee

Sample ID: ab199_II_rac5

Filename:
C:\EZStart\Projects\Default\Data\aure\ab199_II_rac5OD9802IP.met10-18-2005 8-35-42 AM.dat

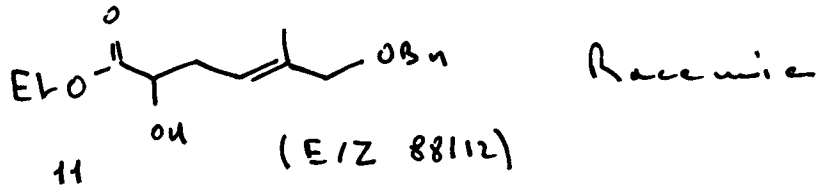
Method:
C:\EZStart\Projects\Default\Method\OD\OD9802IP.met

Injection volume: 5 uL



3: 215 nm, 4 nm Results

Retention Time	Area	Area Percent
18.820	21555896	42.701
20.476	3764473	7.457
23.552	25161018	49.842



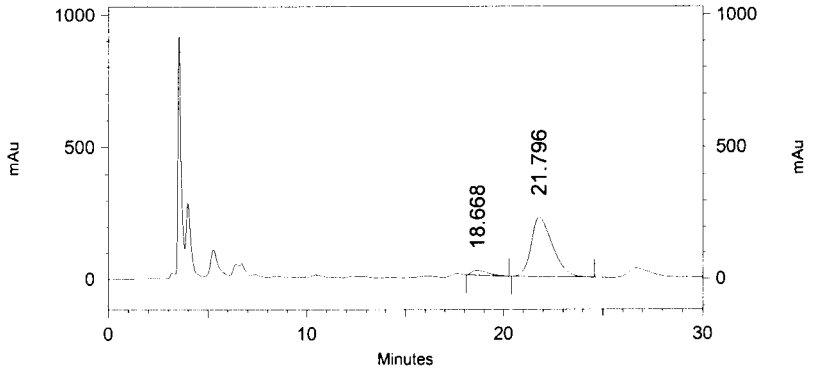
11

Racemic

(E/Z 88:12)

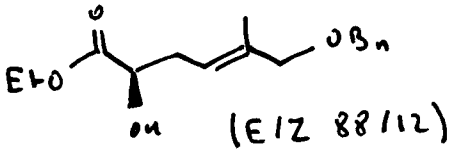
10/18/2005 8:37:19 AM

Sample ID: **ab199_II_ee_48h**
Filename:
C:\EZStart\Projects\Default\Data\aure\ab199_II_ee_48hOD9802IP.met10-20-2005 9-57-19 AM.dat Method:
C:\EZStart\Projects\Default\Method\OD\OD9802IP.met
Injection volume: 5 uL



3: 215 nm, 4 nm Results

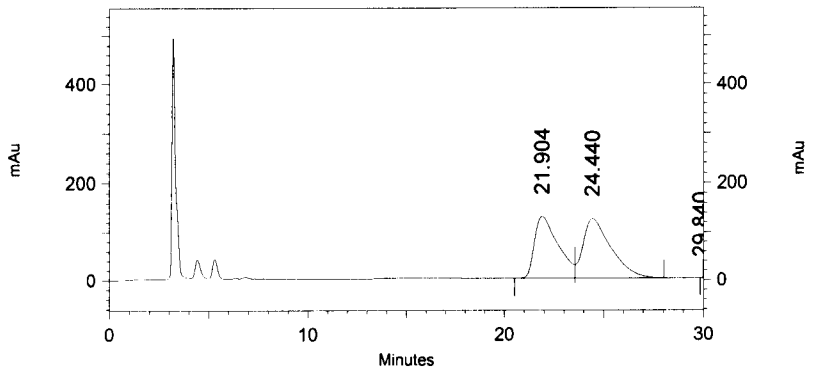
Retention Time	Area	Area Percent
18.668	1024243	5.710
21.796	16912953	94.290



(E/Z 88/12)

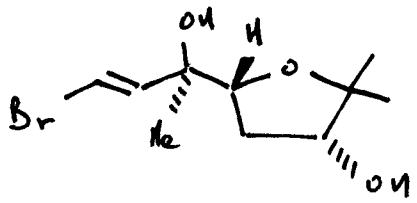
89% ee

Sample ID: **ab7_II_rac10**
Filename:
C:\EZStart\Projects\Default\Data\aure\ab7_II_rac10OD9802IP.met10-6-2005 5-43-56 PM.dat Method:
C:\EZStart\Projects\Default\Method\OD\OD9802IP.met
Injection volume: 5 uL



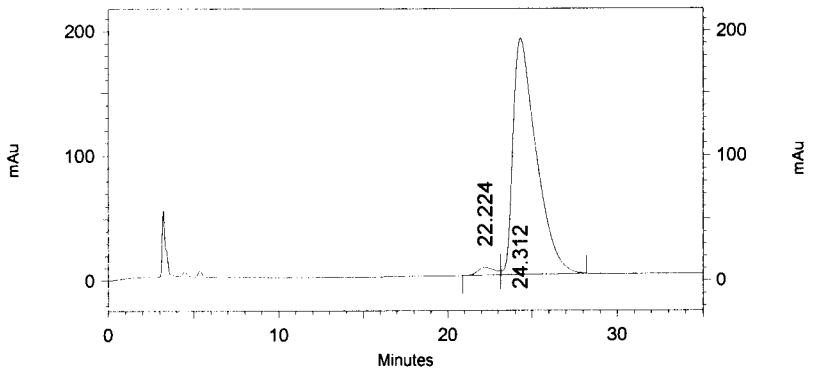
3: 212 nm, 4 nm Results

Retention Time	Area	Area Percent
21.904	10537703	46.795
24.440	11980762	53.204
29.840	192	0.001



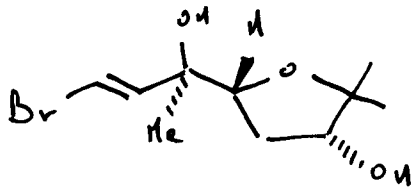
Racemic

Sample ID: **ab7_II_ee5**
Filename:
C:\EZStart\Projects\Default\Data\aure\ab7_II_ee5OD9802IP.met10-6-2005 9-27-41 AM.dat Method:
C:\EZStart\Projects\Default\Method\OD\OD9802IP.met
Injection volume: 5 uL



3: 212 nm, 4 nm Results

Retention Time	Area	Area Percent
22.224	429264	2.338
24.312	17932468	97.662



(-)-pantofuranoid E
95% ee