Supporting Information

Catalytic and Asymmetric Vinylogous Mukaiyama Reactions on Aliphatic Ketones: Formal Asymmetric Synthesis of Taurospingin

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General. Unless otherwise specified, the reactions were carried out in oven-dried glassware under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively in CDCl_3 as solvent: chemical shifts are given in ppm. Column chromatography was performed on silica-gel 230-400 mesh. THF was distilled from sodium / benzophenone. Dichloromethane, diisopropylamine and chlorotrimethylsilane were distilled over CaH_2 prior to use. Elemental analyses were carried out by "laboratoire de micro-analyse ICSN - Gif/Yvette". IR Spectra were recorded with an FTIR spectrometer. Mass spectra were recorded by Navigator LC/MS (source AQA) for electrospray ionisation. Optical rotations were determined operating at the sodium D line.

(1Z)-(1-ethoxy-buta-1,3-dienyloxy)-trimethyl-silane (1). To a solution of DIPA (1.5 mL, 11 mmol) in anhydrous THF (20 mL) at -50°C were added dropwise *n*-BuLi (7 mL, 11 mmol). The mixture was stirred 30 min, cooled to -78°C and DMPU (1.4 mL, 11 mmol) were added dropwise. The solution was stirred 30 min and *trans*-ethyl crotonate (1.26 mL, 10 mmol) were added. The mixture was stirred 30 min and a solution of TMSCl (2 mL) in anhydrous THF (2 mL) were added over a period of 15 min. The solution was warmed to

room temperature and stirred 2h. The solvent was removed under reduce pressure, the residue was taken up in pentane (50 mL) and filtered. The solvent was removed under reduce pressure and the crude material was distilled with a Kugel-Rohr (45°C, 1 mm Hg) to provide **2** (1.3 g, 70% yield) as an inseparable mixture *Z/E* 90/10. ¹H NMR (CDCl₃, 300 MHz) δ 0.24 (s, 8.1H), 0.27 (s, 0.9H), 1.25 (t, J = 7.1 Hz, 0.3H), 1.31 (t, J = 7.0 Hz, 2.7H), 3.81 (q, J = 7.0 Hz, 1.8H), 3.92 (q, J = 7.1 Hz, 0.2H), 4.46 (d, J = 10.4 Hz, 0.9H), 4.54 (d, J = 10.4 Hz, 0.1H), 4.59 (dd, J = 1.8 Hz ; J = 10.4 Hz, 1H), 4.83 (dd, J = 1.8 Hz ; J = 17.2 Hz, 1H), 6.51 (dt, J= 10.4 Hz ; J = 17.2 Hz, 1H) ; ¹³C NMR (CDCl₃, 75 MHz) δ 14.0, 62.4, 80.4, 106.9, 131.7, 157.2.

General procedure of the preparation of lactones (3a-j). A solution of Cu(OTf)₂ (11 mg, 0.027 mmol) and (*R or S*)-tol-BINAP (20.5 mg, 0.03 mmol) in anhydrous THF (5 mL) was stirred for 30 min at room temperature. A solution of TBAT (30 mg, 0.054 mmol) in anhydrous THF (2 mL) was added and the stirring was maintained for an additional 15 min. Dienolate **1** (100 mg, 0.54 mmol) was added dropwise followed by the ketone **2** (0.27 mmol). The solution was stirred overnight at room temperature and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography to provide the desired lactone **3**.

(6*S*)-6-methyl-6-phenyl-3,4-dihydro-pyran-2-one (3a). The lactone **3a** was obtained according to the general procedure from acetophenone **2a** and (*S*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3a** (71% yield). The enantiomeric purity was 80% ee by chiral HPLC (CHIRAPACK AD, hexane/iPrOH 98:2). $[\alpha]_D^{25} = -33.2$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.70 (s, 3H), 2.77 (ddd, $J = 2.2$ Hz ; $J = 3.6$ Hz ; $J = 18.4$ Hz, 1H), 2.95 (ddd, $J = 1.6$ Hz ; $J = 5.1$ Hz ; $J = 18.4$ Hz, 1H), 5.97 (ddd, $J = 1.6$ Hz ; $J = 2.2$ Hz ; $J = 9.8$ Hz, 1H), 6.73 (ddd, $J = 3.6$ Hz ; $J = 5.1$ Hz ; $J = 9.8$ Hz, 1H), 7.30 (m, 5H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.2, 35.4, 83.2, 121.8, 124.5, 127.6, 128.6, 143.6, 143.9, 164.0 ; IR (KCl, cm^{-1}) ν 1062, 1261, 1380, 1641, 1710, 2980 ; ESI-MS m/z 211.1 ($\text{M}+\text{Na}^+$), 189.1 ($\text{M}+\text{H}^+$) ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2$: 189.0916 ; Found: 189.0917.

(6*R*)-6-methyl-6-*p*-methoxyphenyl-3,4-dihydro-pyran-2-one (3b). Lactone **3b** was obtained according to the general procedure from 4'-methoxyacetophenone **2b** and (*R*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3b** (39% yield). 59% ee chiral HPLC (Chiracel OD, hexane/iPrOH 95:5). $[\alpha]_D^{25} = +4.4$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.72 (s, 3H), 2.77 (ddd, $J = 2.3$ Hz ; $J = 3.5$ Hz ; $J = 18.4$ Hz, 1H), 2.95 (ddd, $J = 1.5$ Hz ; $J = 5.1$ Hz ; $J = 18.4$ Hz, 1H), 3.80 (s, 3H), 6.01 (ddd, $J = 1.5$ Hz ; $J = 2.3$ Hz ; $J = 9.8$ Hz, 1H), 6.76 (ddd, $J = 3.5$ Hz ; $J = 5.1$ Hz ; $J = 9.8$ Hz, 1H), 6.87 (d, $J = 8.9$ Hz, 2H), 7.30 (d, $J = 8.9$ Hz, 2H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.3, 35.4, 55.3, 83.0, 113.8, 121.8, 125.8, 135.9, 143.5, 158.9, 164.0 ; IR (KCl, cm^{-1}) ν 1065, 1380, 1515, 1715, 2979 ; MS (IE) m/z 218.0 (M, 30%), 135.0 (100%), 77.0 (55%), 68.0 (90%).

(6*R*)-6-methyl-6-*p*-bromophenyl-3,4-dihydro-pyran-2-one (3c). Lactone **3c** was obtained according to the general procedure from 4'-bromoacetophenone **2c** and (*R*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3c** (58% yield). 81% ee chiral HPLC (CHIRAPACK AD, hexane/iPrOH 98:2). $[\alpha]_D^{25} = +30.9$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.71 (s, 3H), 2.80 (ddd, $J = 2.2$ Hz ; $J = 3.7$ Hz ; $J = 18.4$ Hz, 1H), 2.92 (ddd, $J = 1.6$ Hz ; $J = 5.0$ Hz ; $J = 18.4$ Hz, 1H), 6.07 (ddd, $J = 1.6$ Hz ; $J = 2.2$ Hz ; $J = 9.8$ Hz, 1H), 6.76 (ddd, $J = 3.7$ Hz ; $J = 5.0$ Hz ; $J = 9.8$ Hz, 1H), 7.27 (d, $J = 8.7$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.0, 35.4, 82.8, 121.8, 122.0, 126.5, 131.8, 143.2, 143.3, 163.6 ; IR (KCl, cm^{-1}) ν 1064, 1258, 1379, 1714, 2980 ; ESI-MS m/z 291.0 ($\text{M} + \text{Na}^+$), 289.0 ($\text{M} + \text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{11}\text{BrO}_2\text{Na}$: 288.9795 ; Found: 288.9805.

(6R)-6-methyl-6-*p*-nitrophenyl-3,4-dihydro-pyran-2-one (3d). Lactone **3d** was obtained according the general procedure from 4'-nitroacetophenone **2d** and (*R*)-Tol-Binap. The crude material was purified by flash chromatography (2/1 heptane/ethyl acetate) to provide **3d** (19% yield). 75% ee chiral HPLC (Chiracel OD, hexane/iPrOH 90:10). $[\alpha]_{\text{D}}^{25} = + 31.8$, (*c* = 1, CHCl₃) ; ¹H NMR (CDCl₃, 300 MHz) δ 1.77 (s, 3H), 2.87 (ddd, *J* = 2.0 Hz ; *J* = 4.0 Hz ; *J* = 18.4 Hz, 1H), 2.97 (ddd, *J* = 1.7 Hz ; *J* = 4.6 Hz ; *J* = 18.4 Hz, 1H), 6.07 (ddd, *J* = 1.7 Hz ; *J* = 2.0 Hz ; *J* = 9.8 Hz, 1H), 6.76 (ddd, *J* = 4.0 Hz ; *J* = 4.6 Hz ; *J* = 9.8 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 2H), 8.24 (d, *J* = 9.0 Hz, 2H) ; ¹³C NMR (CDCl₃, 75 MHz) δ 29.5, 35.2, 82.5, 121.9, 123.9, 125.8, 143.0, 147.3, 151.1, 162.9 ; IR (KCl, cm⁻¹) ν 1066, 1261, 1350, 1514, 1641, 1710, 2982 ; MS (IE) *m/z* 233.0 (M, 5%), 218.0 (15%), 150.0 (20%), 68.0 (100%).

(5R)- 5-Hydroxy-5-(4-nitro-phenyl)-hex-2-enoic acid ethyl ester (4d). "linear" product **4d** was obtained as the major product, in 39% yield, from 4'-nitroacetophenone. <10% ee chiral HPLC (Chiracel OD, hexane/iPrOH 90:10). ¹H NMR (CDCl₃, 300 MHz) δ 1.27 (t, *J* = 7.1 Hz, 3H), 1.64 (s, 3H), 2.19 (bs, 1H), 2.72 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 5.86 (td, *J* = 1.4 Hz ; *J* = 15.6 Hz, 1H), 6.80 (td, *J* = 7.7 Hz ; *J* = 15.6 Hz, 1H), 7.63 (d, *J* = 9.9 Hz, 2H), 8.21 (d, *J* = 9.9 Hz, 2H) ; ¹³C NMR (CDCl₃, 75 MHz) δ 14.3, 30.1, 46.7, 60.6, 74.2, 123.8, 125.8, 126.0, 142.6, 147.1, 154.4, 166.0 ; IR (KCl, cm⁻¹) ν 855, 1184, 1348, 1518, 1656, 1702, 2920, 2980 ; MS (IE) *m/z* 279.0 (M, 20%), 149.0 (30%), 57.0 (100%), 43.0 (100%).

(6S)-6-methyl-6-phenylethyl-3,4-dihydro-pyran-2-one (3e). Lactone **3e** was obtained according the general procedure from benzylacetone **2e** and (*S*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3e** (70% yield). 87% ee chiral HPLC (CHIRAPACK AD, hexane/iPrOH 97:3). $[\alpha]_{\text{D}}^{25} = + 38.7$, (*c* = 1, CHCl₃) ; ¹H NMR (CDCl₃, 300 MHz) δ 1.52 (s, 3H), 2.04 (m, 2H), 2.37 (ddd, *J* = 1.9 Hz ; *J* =

4.9 Hz ; J = 18.5 Hz, 1H), 2.57 (ddd, J = 2.1 Hz ; J = 3.7 Hz ; J = 18.5 Hz, 1H), 2.77 (m, 2H), 6.07 (ddd, J = 1.9 Hz ; J = 2.1 Hz ; J = 9.8 Hz, 1H), 6.79 (ddd, J = 3.7 Hz ; J = 4.9 Hz ; J = 9.8 Hz, 1H), 7.25 (m, 5H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.3, 30.0, 34.1, 42.8, 81.9, 121.1, 126.1, 128.4, 128.6, 141.4, 143.5, 163.8 ; IR (KCl, cm^{-1}) ν 1061, 1379, 1714, 2922 ; ESI-MS m/z 239.1 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Na}$: 239.1048 ; Found: 239.1063.

(6S)-6-methyl-6-butenyl-3,4-dihydro-pyran-2-one (3f). The lactone **3f** was obtained according to the general procedure from 5-hexen-2-one **2f** and (S)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3f** (40% yield). 90% ee chiral HPLC (CHIRAPACK AD, hexane/iPrOH 99:1). $[\alpha]_{\text{D}}^{25} = + 35.9$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.43 (s, 3H), 1.81 (m, 2H), 2.18 (m, 2H), 2.33 (ddd, J = 2.0 Hz ; J = 4.9 Hz ; J = 18.5 Hz, 1H), 2.52 (ddd, J = 2.0 Hz ; J = 3.7 Hz ; J = 18.5 Hz, 1H), 4.97 (bd, J = 10.2 Hz, 1H), 5.03 (bd, J = 16.8 Hz, 1H), 5.80 (tdd, J = 6.5 Hz ; J = 10.2 Hz ; J = 16.8 Hz, 1H), 6.03 (td, J = 2.0 Hz ; J = 9.9 Hz, 1H), 6.76 (ddd, J = 3.7 Hz ; J = 4.9 Hz ; J = 9.9 Hz, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.3, 28.0, 34.0, 40.0, 82.1, 115.2, 121.1, 137.7, 143.5, 163.8 ; IR (KCl, cm^{-1}) ν 1068, 1382, 1641, 1719, 2922 ; ESI-MS m/z 189.1 ($\text{M}+\text{Na}^+$), 167.1 ($\text{M}+\text{H}^+$) ; HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2$: 167.1072 ; Found: 167.1067.

(6R)-6-methyl-6-*i*-butyl-3,4-dihydro-pyran-2-one (3g). Lactone **3g** was obtained according to the general procedure from 4-methyl-2-pentanone **2g** and (R)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3g** (81% yield). 93% ee chiral HPLC (CHIRAPACK AD, hexane/iPrOH 98/2). $[\alpha]_{\text{D}}^{25} = - 8.6$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.94 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 1.42 (s, 3H), 1.54 (dd, J = 5.7 Hz ; J = 14.5 Hz, 1H), 1.67 (dd, J = 6.2 Hz ; J = 14.5 Hz, 1H), 1.83 (m, 1H), 2.30 (ddd, J = 2.0 Hz ; J = 4.7 Hz ; J = 18.5 Hz, 1H), 2.49 (ddd, J = 2.0 Hz ; J =

3.9 Hz ; J = 18.5 Hz, 1H), 6.01 (td, J = 2.0 Hz ; J = 9.8 Hz, 1H), 6.74 (ddd, J = 3.9 Hz ; J = 4.7 Hz ; J = 9.8 Hz, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 24.2, 24.5, 24.6, 25.8, 34.7, 49.2, 82.8, 121.2, 143.5, 163.9 ; IR (KCl, cm^{-1}) ν 1044, 1251, 1383, 1718, 2956 ; ESI-MS m/z 191.1 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Na}$: 191.1027 ; Found: 191.1033.

(6*R*)-6-methyl-6-*t*-butyl-3,4-dihydro-pyran-2-one (3h). Lactone **3h** was obtained according to the general procedure from 3,3-dimethyl-2-butanone **2h** and (*R*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3h** (39% yield). 92% ee chiral HPLC (CHIRAPACK AD, hexane/*i*PrOH 99:1). $[\alpha]_{\text{D}}^{25} = +46.9$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.03 (s, 9H), 1.40 (s, 3H), 2.16 (dd, J = 6.5 Hz ; J = 18.7 Hz, 1H), 2.72 (bd, J = 18.7 Hz, 1H), 6.02 (bdd, J = 2.9 Hz ; J = 9.8 Hz, 1H), 6.78 (m, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 20.0, 24.9, 29.8, 37.8, 86.5, 120.6, 144.1, 163.8 ; IR (KCl, cm^{-1}) ν 1073, 1383, 1718, 2963 ; ESI-MS m/z 191.1 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Na}$: 191.1027 ; Found: 191.1036.

(6*R*)-6-methyl-6-styryl-3,4-dihydro-pyran-2-one (3i). Lactone **3i** was obtained according to the general procedure from *trans*-4-phenyl-3-buten-2-one **2i** and (*R*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3i** (17% yield). 24% ee chiral HPLC (CHIRAPACK AD, hexane/*i*PrOH 90:10). ^1H NMR (CDCl_3 , 300 MHz) δ 1.62 (s, 3H), 2.63 (dd, J = 1.7 Hz ; J = 4.2 Hz, 2H), 6.06 (dt, J = 1.7 Hz ; J = 9.8 Hz, 1H), 6.21 (d, J = 16.1 Hz, 1H), 6.61 (dt, J = 4.2 Hz ; J = 9.8 Hz, 1H), 6.77 (d, J = 16.1 Hz, 1H), 7.29-7.37 (m, 5H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 27.7, 34.8, 81.4, 121.6, 126.5, 128.1, 128.7, 129.8, 131.4, 135.9, 143.0, 163.9 ; IR (KCl, cm^{-1}) ν 1060, 1248, 1380, 1713, 2929 ; ESI-MS m/z 237.1 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{Na}$: 237.0891 ; Found: 237.0909.

(6*R*)-6-ethyl-6-phenyl-3,4-dihydro-pyran-2-one (3j). Lactone **3j** was obtained according to the general procedure from propiophenone **2j** and (*R*)-Tol-Binap. The crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide **3j** (73% yield). 39% ee chiral HPLC (CHIRAPACK AD, hexane/iPrOH 99:1). $[\alpha]_D^{25} = +13.5$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.82 (t, $J = 7.4$ Hz, 3H), 2.02 (m, 2H), 2.83 (ddd, $J = 2.5$ Hz ; $J = 3.2$ Hz ; $J = 18.3$ Hz, 1H), 2.94 (ddd, $J = 1.2$ Hz ; $J = 5.5$ Hz ; $J = 18.3$ Hz, 1H), 5.96 (ddd, $J = 1.2$ Hz ; $J = 2.5$ Hz ; $J = 9.8$ Hz, 1H), 6.79 (ddd, $J = 3.2$ Hz ; $J = 5.5$ Hz ; $J = 9.8$ Hz, 1H), 7.25 (bs, 5H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 7.8, 33.5, 35.7, 85.9, 121.9, 125.2, 127.5, 128.4, 142.2, 164.1 ; IR (KCl, cm^{-1}) ν 1035, 1256, 1381, 1716, 2937 ; ESI-MS m/z 225.1 ($\text{M} + \text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Na}$: 225.0891 ; Found: 225.0878.

Formal enantioselective synthesis of taurospongins A

(6S)-6-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-6-methyl-3,4-dihydro-pyran-2-one

(3k). A solution of Cu(OTf)₂ (110 mg, 0.27 mmol) and (*R*)-tol-BINAP (205 mg, 0.3 mmol) in anhydrous THF (60 mL) was stirred for 30 min at room temperature. A solution of TBAT (300 mg, 0.54 mmol) in anhydrous THF (6 mL) was added and the stirring was maintained for an additional 15 min. The dienolate **1** (1010 mg, 5.4 mmol) was added dropwise followed by a solution of ketone **2k** (545 mg, 2.7 mmol) in anhydrous THF (4 mL). The solution was stirred overnight at room temperature and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (4/1 heptane/ethyl acetate) to provide **3k** (525 mg, 72% yield). 88% ee chiral HPLC (Chiracel OD (10 °C), hexane/iPrOH 98:2). $[\alpha]_D^{25} = +16.0$, (*c* = 1, CHCl₃) ; ¹H NMR (CDCl₃, 300 MHz) δ 0.07 (s, 6H), 0.90 (s, 9H), 1.47 (s, 3H), 1.98 (m, 2H), 2.36 (ddd, *J* = 1.8 Hz ; *J* = 4.7 Hz ; *J* = 18.6 Hz, 1H), 2.72 (ddd, *J* = 2.2 Hz ; *J* = 3.9 Hz ; *J* = 18.6 Hz, 1H), 3.79 (m, 2H), 6.03 (dt, *J* = 2.0 Hz ; *J* = 9.8 Hz, 1H), 6.77 (ddd, *J* = 3.9 Hz ; *J* = 4.7 Hz ; *J* = 9.8 Hz, 1H) ; ¹³C NMR (CDCl₃, 75 MHz) δ -5.3, 18.3, 25.9, 26.0, 34.4, 42.9, 58.8, 81.9, 120.9, 143.9, 163.9 ; IR (KCl, cm⁻¹) ν 836, 1094, 1255, 1383, 1721, 2856, 2929 ; ESI-MS *m/z* 293.1 (M+Na⁺) ; Anal. Calcd for C₁₄H₂₆O₃Si: C 62.18, H 9.69. Found: C 62.07, H 9.72.

(6R)-6-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-6-methyl-tetrahydro-pyran-2-one (5).

To a solution of lactone **3k** (525 mg, 1.94 mmol) in EtOAc (24 mL) at 0°C were added Pd/C (41.3 mg, 0.39 mmol). The solution was stirred for 3h at room temperature under a H₂ balloon atmosphere (1 atm). The crude material was filtered over silica gel to provide **5** (528 mg, quantitative yield). $[\alpha]_D^{25} = +4.6$, (*c* = 1, CHCl₃) ; ¹H NMR (CDCl₃, 300 MHz) δ 0.06 (s, 6H), 0.89 (s, 9H), 1.41 (s, 3H), 1.74 (m, 1H), 1.89 (m, 5H), 2.47 (m, 2H), 3.75 (dt, *J* = 1.6 Hz ; *J* = 6.5 Hz, 2H) ; ¹³C NMR (CDCl₃, 75 MHz) δ -5.3, 16.7, 18.3, 26.0, 26.8, 29.4, 32.6, 44.0, 58.8,

83.9, 171.3 ; IR (KCl, cm^{-1}) ν 835, 1093, 1251, 1732, 2856, 2929, 2953 ; ESI-MS m/z 295.1 ($\text{M}+\text{Na}^+$) ; Anal.Calcd for $\text{C}_{14}\text{H}_{28}\text{NO}_3\text{Si}$: C 61.72, H 10.36 ; Found: C 61.34, H 10.57.

(5*R*)-7-(*tert*-butyl-dimethyl-silanyloxy)-5-hydroxy-5-methyl-heptanoic acid methoxy-methyl-amide (5'). To a solution of lactone **5** (520 mg, 1.91 mmol) in anhydrous THF (12 mL) were added $\text{NH}(\text{OMe})(\text{Me})\cdot\text{HCl}$ (560 mg, 5.73 mmol) at 0°C. A solution of *i*PrMgCl (5.74 mL, 11.46 mmol) in Et_2O (2M) was then added dropwise. After warming up to rt, the solution was further stirred 3h. Saturated aqueous NH_4Cl was added and the mixture was diluted in Et_2O . The layers were separated and the aqueous layer was washed with Et_2O . The combined organic layers were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the crude material **5'** was used in the next step without further purification.

(5*R*)-7-(*tert*-butyl-dimethyl-silanyloxy)-5-methyl-5-(triethyl-silanyloxy)-heptanoic acid methoxy-methyl-amide (6). To a solution of the crude material **5'** in CH_2Cl_2 (19 mL) at 0°C were added dropwise 2,6-lutidine (1.11 mL, 9.55 mmol) and TESOTf (2.16 mL, 9.55 mmol). The solution was warmed up to room temperature and stirred overnight. Saturated aqueous NH_4Cl was added and the mixture was diluted in CH_2Cl_2 . The layers were separated and the aqueous layer was washed with CH_2Cl_2 . The combined organic layers were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the crude material was purified by flash chromatography (5/1 heptane/ethyl acetate) to provide the desired compound **6** (550 mg, 64% yield (over 2 steps)). $[\alpha]_{\text{D}}^{25} = +1.6$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.05 (s, 6H), 0.57 (q, $J = 7.9$ Hz, 6H), 0.89 (s, 9H), 0.95 (t, $J = 7.9$ Hz, 9H), 1.22 (s, 3H), 1.48 (m, 2H), 1.67 (m, 2H), 1.73 (m, 2H), 2.40 (bt, $J = 7.5$ Hz, 2H), 3.18 (s, 3H), 3.68 (s, 3H), 3.72 (t, $J = 7.4$ Hz, 2H) ; ^{13}C NMR (CDCl_3 , 75 MHz) -5.3, 7.0, 7.3,

18.3, 19.7, 26.0, 28.1, 32.4, 42.8, 44.7, 59.8, 61.2, 74.7, 174.5 ; IR (KCl, cm^{-1}) ν 836, 1006, 1062, 1091, 1253, 1462, 1673, 2877, 2955 ; ESI-MS m/z 470.3 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{49}\text{NO}_4\text{Si}_2\text{Na}$: 470.3093 ; Found: 470.3098.

(5*R*)-7-(tert-butyl-dimethyl-silanyloxy)-5-methyl-5-(triethyl-silanyloxy)-heptanal (6').

To a solution of compound **6** (380 mg, 0.85 mmol) in CH_2Cl_2 (8.5 mL) at -78°C were added dropwise a solution of Dibal-H (1.3 mL, 1.3 mmol) in THF (1M). The mixture was stirred 30 min at -78°C and a solution of aqueous HCl (1M) was added. The stirring was maintained for an additional 15 min. The layers were separated and the aqueous layer was washed with CH_2Cl_2 . The combined organic layers were washed with brine and dried over MgSO_4 . The crude material was purified by flash chromatography (5/1 heptane/ethyl acetate) to provide aldehyde **6'** (260 mg, 79 % yield). ^1H NMR (CDCl_3 , 300 MHz) δ 0.06 (s, 6H), 0.57 (q, $J = 7.9$ Hz, 6H), 0.90 (s, 9H), 0.95 (t, $J = 7.9$ Hz, 9H), 1.23 (s, 3H), 1.46 (m, 2H), 1.68 (m, 2H), 1.74 (m, 2H), 2.42 (m, 2H), 3.71 (t, $J = 7.1$ Hz, 2H), 9.77 (s, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ - 5.2, 7.0, 7.2, 17.2, 18.4, 26.1, 28.2, 42.5, 44.4, 48.8, 59.8, 74.6, 202.7.

(4*S*,8*R*)-10-(tert-butyl-dimethyl-silanyloxy)-8-methyl-8-(triethyl-silanyloxy)-dec-1-en-4-ol (7). A suspension of (*R*)-BINOL (57.4 mg, 0.2 mmol) in CH_2Cl_2 (670 μL) was stirred until the BINOL was completely dissolved. Powered 4A molecular sieves (267 mg) was added. To the resultant suspension was added dropwise a solution of $\text{Ti}(\text{O}i\text{Pr})_4$ (60 μL , 0.2 mmol) in CH_2Cl_2 (200 μL). The red-orange suspension was heated at reflux for 1h. The mixture was cooled to room temperature and a solution of aldehyde **6'** (260 mg, 0.67 mmol) in CH_2Cl_2 (100 μL) was added dropwise. The resulting mixture was stirred 5 min at room temperature then cooled at -78°C and allyltributylstannane (622 μL , 2 mmol) was added dropwise. The mixture was kept in a freezer at -20°C for 60h without stirring. Saturated

aqueous NaHCO_3 was added and the mixture was diluted in CH_2Cl_2 . The molecular sieves was removed by filtration through a pad of Celite. The layers were separated and the aqueous layer was washed with CH_2Cl_2 . The combined organic layers were washed with brine and dried over MgSO_4 . The crude material was purified by flash chromatography (15/1 heptane/ethyl acetate) to provide **7** (233 mg, 81% yield and 90% ee (Mosher's esterification)). $[\alpha]_{\text{D}}^{25} = -3.1$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.06 (s, 6H), 0.57 (q, $J = 7.9$ Hz, 6H), 0.90 (s, 9H), 0.95 (t, $J = 7.9$ Hz, 9H), 1.21 (s, 3H), 1.45 (bm, 6H), 1.60 (bs, 1H), 1.72 (bm, 2H), 2.15 (m, 1H), 2.32 (m, 1H), 3.66 (bm, 1H), 3.72 (t, $J = 7.4$ Hz, 2H), 5.15 (bd, $J = 15.3$ Hz, 1H), 5.84 (m, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) -5.3, 6.9, 7.1, 18.3, 20.5, 26.0, 28.1, 37.4, 41.9, 43.1, 44.6, 59.8, 70.6, 74.7, 118.0, 134.8 ; IR (KCl, cm^{-1}) ν 774, 836, 1006, 1053, 1092, 1255, 1462, 1641, 2931, 2954, 3077, 3364 ; ESI-MS m/z 453.4 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{50}\text{O}_3\text{Si}_2\text{Na}$: 453.3208 ; Found: 453.3196.

(1S)-carbonic acid *tert*-butyl ester 1-[(4R)-6-(*tert*-butyl-dimethyl-silanyloxy)-4-methyl-4-(triethyl-silanyloxy)-hexyl]-but-3-enyl ester (8). To a solution of **7** (120 mg, 0.28 mmol) in CH_2Cl_2 (4 mL) were added Boc_2O (243 mg, 1.12 mmol), NEt_3 (50 μL , 0.36 mmol) and DMAP (7 mg, 0.06 mmol). The mixture was stirred overnight at room temperature and quenched with a solution of KHSO_4 (5%). The layers were separated and the aqueous layer was washed with CH_2Cl_2 . The combined organic layers were washed with brine and dried over MgSO_4 . The crude material was purified by flash chromatography (20/1 heptane/ethyl acetate) to provide **8** (120 mg, 81% yield). $[\alpha]_{\text{D}}^{25} = -3.6$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.06 (s, 6H), 0.57 (q, $J = 7.9$ Hz, 6H), 0.91 (s, 9H), 0.95 (t, $J = 7.9$ Hz, 9H), 1.20 (s, 3H), 1.40 (m, 4H), 1.50 (s, 9H), 1.55 (bm, 2H), 1.71 (bm, 2H), 2.36 (bt, $J = 6.6$ Hz, 2H), 3.72 (t, $J = 7.4$ Hz, 2H), 4.71 (m, 1H), 5.09 (bd, $J = 10.1$ Hz, 1H), 5.11 (bd, $J = 17.1$ Hz, 1H), 5.80 (m, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) -5.3, 6.7, 7.3, 18.4, 20.3, 26.1, 28.0, 28.2, 34.3,

38.9, 43.0, 44.9, 59.8, 59.9, 74.7, 81.7, 117.8, 134.7, 153.5 ; IR (KCl, cm^{-1}) ν 1093, 1169, 1254, 1279, 1739, 2877, 2954 ; ESI-MS m/z 553.4 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{28}\text{H}_{58}\text{O}_5\text{Si}_2\text{Na}$: 553.3178 ; Found: 553.3121.

(1*S*,2*S*,6*R*)-8-(*tert*-butyl-dimethyl-silanyloxy)-6-methyl-1-oxiranyl-6-(triethyl-silanyloxy)-octan-2-ol (9). To a solution of compound **8** (32mg, 0.06 mmol) in toluene (500 μL) at -78°C was added a solution of IBr (72 μL , 0.072 mmol) in CH_2Cl_2 (1M). The resulting mixture was stirred 1h at -78°C and warmed at room temperature. An aqueous $\text{NaHCO}_3/\text{Na}_2\text{S}_2\text{O}_3$ (1/1) was added and the mixture was diluted in Et_2O . The layers were separated and the aqueous layer was washed with Et_2O . The combined organic layers were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the crude material was used for the next step without further purifications.

To a solution of the crude product **8'** in MeOH (500 μL) were added propylene oxide (12 μL , 0.18 mmol) and anhydrous K_2CO_3 (25 mg, 0.18 mmol). The mixture was stirred overnight at room temperature. Saturated aqueous NaHCO_3 was added and the mixture was diluted in Et_2O . The layers were separated and the aqueous layer was washed with Et_2O . The combined organic layers were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the crude material was purified by flash chromatography (7/3 heptane/ethyl acetate) to provide the desired compound **9** (13.6 mg, 51% yield (over 2 steps)) in an inseparable mixture of diastereoisomers *syn/anti* 9/1. $[\alpha]_{\text{D}}^{25} = -1.7$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.06 (s, 6H), 0.57 (q, $J = 7.9$ Hz, 6H), 0.90 (s, 9H), 0.95 (t, $J = 7.9$ Hz, 9H), 1.21 (s, 3H), 1.46 (bm, 6H), 1.54 (m, 1H), 1.72 (m, 2H), 1.86 (dt, $J = 3.9$ Hz ; 14.4 Hz, 1H), 2.07 (bs, 1H), 2.51 (dd, $J = 2.7$ Hz ; $J = 4.9$ Hz, 1H), 2.80 (dd, $J = 4.0$ Hz ; $J = 4.9$ Hz, 1H), 3.10 (m, 1H), 3.71 (t, $J = 7.3$ Hz, 2H), 3.89 (bm, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) -5.3, 6.9, 7.1, 18.3, 20.3, 26.0, 28.1, 38.0, 39.7, 43.0, 44.6, 46.6, 50.6, 59.8, 70.5, 74.7 ; IR (KCl,

cm^{-1}) ν 835, 1006, 1054, 1091, 1254, 2876, 2953, 3510 ; ESI-MS m/z 469.3 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{50}\text{O}_4\text{Si}_2\text{Na}$: 469.3129 ; Found: 469.3145.

(1*S*, 5*R*)-acetic acid 7-(*tert*-butyl-dimethyl-silanyloxy)-3-[(3*S*)-methyl-1-oxiranylmethyl]-5-(triethyl-silanyloxy)-heptyl ester (10). To a solution of **9** (14 mg, 0.03 mmol) in CH_2Cl_2 (300 μL) were added Ac_2O (15 μL , 0.15 mmol), NEt_3 (7 μL , 0.045 mmol) and DMAP (1 mg, 30%mol). The mixture was stirred 1h at room temperature and the solvent was removed with toluene under reduce pressure. The crude material was purified by flash chromatography (20/1 heptane/ethyl acetate) to provide **10** (13 mg, 85% yield). $[\alpha]_{\text{D}}^{25} = +9.4$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.05 (s, 6H), 0.56 (q, $J = 7.9$ Hz, 6H), 0.90 (s, 9H), 0.94 (t, $J = 7.9$ Hz, 9H), 1.19 (s, 3H), 1.28-1.39 (m, 4H), 1.52-1.58 (m, 2H), 1.62-1.68 (m, 2H), 1.73-1.82 (m, 2H), 2.07 (s, 3H), 2.44 (dd, $J = 2.7$ Hz ; $J = 4.8$ Hz, 1H), 2.75 (dd, $J = 4.3$ Hz ; $J = 4.8$ Hz, 1H), 2.98 (m, 1H), 3.70 (t, $J = 7.4$ Hz, 2H), 5.07 (m, 1H) ; ^{13}C NMR (CDCl_3 , 75 MHz) -5.2, 7.0, 7.3, 18.4, 20.2, 21.3, 26.1, 28.2, 34.8, 37.4, 42.9, 45.0, 46.4, 49.4, 59.9, 72.3, 74.7, 170.9 ; IR (KCl, cm^{-1}) ν 835, 1017, 1090, 1239, 1740, 2954 ; ESI-MS m/z 511.3 ($\text{M}+\text{Na}^+$) ; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{52}\text{O}_5\text{Si}_2\text{Na}$: 511.3179 ; Found : 511.3251.

(1*S*,5*R*)-acetic acid 7-(*tert*-butyl-dimethyl-silanyloxy)-1-[(2*S*)-2-hydroxy-propyl]-5-methyl-5-(triethyl-silanyloxy)-heptyl ester (10'). To a solution of the compound **10** (8 mg, 0.016 mmol) in MeOH (100 μL) were added Pd/C (en) (1mg, 12.5 %wt). The mixture was stirred 24 h under H_2 atmosphere (3 bars). The solvent was evaporated under reduce pressure and the crude material was purified by flash chromatography (6/1 heptane/ethyl acetate) to provide **10'** (4 mg, 50% yield) and starting material **10** (3.4 mg, 42%).

(1*S*,5*R*)-acetic acid 7-(*tert*-butyl-dimethyl-silanyloxy)-1-[(2*S*)-2-(*tert*-butyl-dimethyl-silanyloxy)-propyl]-5-methyl-5-(triethyl-silanyloxy)-heptyl ester (11).¹

To a solution of **10'** (4 mg, 0.08 mmol) in CH₂Cl₂ (135 µL) were added 2,6-lutidine (2.5 µL, 0.01 mmol) and TBSOTf (1.6 µL, 0.012 mmol). The mixture was stirred 1h at 0°C and filtered through silica gel. The crude material was purified by flash chromatography (2% ethyl acetate in heptane) to provide **11** (3.2 mg, 65% yield). $[\alpha]_D^{25} = +5.2$, ($c = 1$, CHCl₃) ; ¹H NMR (CDCl₃, 300 MHz) δ 0.06 (bs, 12H), 0.57 (q, $J = 7.9$ Hz, 6H), 0.90 (s, 18H), 0.95 (t, $J = 7.9$ Hz, 9H), 1.16 (d, $J = 6.0$ Hz, 3H), 1.18 (s, 3H), 1.32-1.43 (m, 4H), 1.51-1.60 (m, 3H), 1.67-1.73 (m, 2H), 1.78-1.84 (m, 1H), 2.03 (s, 3H), 3.71 (m, 2H), 3.80-3.85 (m, 1H), 4.92-4.97 (m, 1H) ; ¹³C NMR (CDCl₃, 75 MHz) -5.3, -4.8, -4.4, 6.9, 7.2, 18.1, 18.4, 20.0, 21.2, 23.5, 25.9, 26.0, 28.0, 35.1, 43.0, 44.2, 44.9, 59.8, 65.7, 71.9, 74.6, 171.0 ; IR (KCl, cm⁻¹) ν 835, 1093, 1247, 1741, 2356, 2854, 2925 ; ESI-MS m/z 627.3 (M+Na⁺).

Determination of the absolute configuration: (6*S*)-6-methyl-6-phenyl-pyran-2-one (12).

To a solution of lactone **3a** (15 mg, 0.08 mmol, obtained from (*S*)-tolBinap) in EtOH (1 mL) were added Ni/Raney (1.5 mg, 10%wt). The suspension was stirred 2h at room temperature under H₂ atmosphere (1 atm.). The mixture was filtered through a pad of Celite and the solvent removed under reduce pressure. The crude material was purified by flash

¹ Lebel, H.; Jacobsen, E. N. *J. Org. Chem.* **1998**, 63, 9624.

chromatography (7/3 heptane/ethyl acetate) to provide **12**² (7 mg, 38% yield) and started material **1a** (9 mg). $[\alpha]_D^{25} = -33.0$, ($c = 1$, CHCl_3) ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.51-1.66 (m, 1H), 1.69 (s, 3H), 1.73-1.88 (m, 1H), 2.02 (ddd, $J = 4.3$ Hz ; $J = 11.3$ Hz ; $J = 14.1$ Hz, 1H), 2.33 (~dt, $J = 5.1$ Hz ; $J = 14.1$ Hz, 1H), 2.47 (m, 2H), 7.33 (m, 5H) ; ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.2, 35.4, 83.2, 121.8, 124.5, 127.6, 128.6, 143.6, 143.9, 164.0.

A rotation of -33.0 ($c = 1$, CHCl_3 , for 81% e. e.) compares favourably with the rotation of $+39.8$ ($c = 1.01$, CHCl_3 , 90% e. e.) obtained for the known (*R*) lactone². Consequently, lactones **3** obtained with $\text{CuF}(\text{S})\text{-Tol-Binap}$ were tentatively assigned to the following configuration:

² Date, M.; Tamai, Y.; Hattori, T.; Takayama, H.; Kamikubo, Y.; Miyano, S.; *J. Chem. Soc. Perkin Trans. 1* **2001**, 645.

6-methyl-6-phenyl-5,6-dihydropyran-2-one (3a)

Peak Results			
Name	RT	Area	%Area
1	23.454	66833308	52.15
2	50.512	61325434	47.85

bb194v Rac
hex/iproh 98/2
isocratic
débit: 1 ml/min
colonne: Chiralpak AD
210

Peak Results			
Name	RT	Area	%Area
1	22.740	31377830	90.10
2	42.401	3446566	9.90

bb193v
hex/iproh 98/2
isocratic
débit: 1 ml/min
colonne: Chiralpak AD
210

6-(4-methoxyphenyl)-6-methyl-5,6-dihydropyran-2-one (3b)

Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name:	xm347 Fac TOBNA.P 95/5 n/iso	Date Acquired:	17/10/2003 11:17:21
Vial:	1	Proc. Chnl. Descr.:	FDA 275.0 nm
Injection Volume:	10.00 uI

RT	Area	Height	% Area
1	14.479	879452	32143
2	17.036	871082	28325

Colonne OD
Hexane/isopropanol 95/5
Débit 1ml/min

018

Report Method: xavier

Printed 11:43:40

17/10/2003

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Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name:	xm382 (R) TOBNA.P 95/5 n/iso	Date Acquired:	17/10/2003 11:40:04
Vial:	2	Proc. Chnl. Descr.:	FDA 275.0 nm
Injection Volume:	10.00 uI

RT	Area	Height	% Area
1	14.505	1285583	47911
2	17.077	334283	10341

Colonne OD
Hexane/isopropanol 95/5
Débit 1ml/min

Report Method: xavier

Printed 12:02:27

17/10/2003

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6-(4-bromophenyl)-6-methyl-5,6-dihdropyran-2-one (3c)

Empower

xavier

Reported by User: Eudiant

Project Name: moreau

Sample Name: xmr345 Rac TolBMAP 95/5 H/iso Date Acquired: 15/10/2003 11:28:32
Vial: 4 Proc. Chnl. Descr.: FDA 212.2 nm
Injection Volume: 10.00 uI

	RT	Area	Height	% Area
1	20.821	11292889	347424	50.33
2	23.344	11144000	309338	49.67

Colonne AD
Hexane/isopropanol 98/2
Debit l/min

19

Report Method: xavier

Printed 12:05:05

15/10/2003

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Empower

xavier

Reported by User: Eudiant

Project Name: moreau

Sample Name: xmr373 (R) TolBMAP 98/2 H/ISO Date Acquired: 15/10/2003 12:33:37
Vial: 6 Proc. Chnl. Descr.: FDA 212.2 nm
Injection Volume: 10.00 uI

	RT	Area	Height	% Area
1	18.674	4375929	160422	9.17
2	21.086	43352549	1061462	90.83

Colonne AD
Hexane/isopropanol 98/2
Debit l/min

Report Method: xavier

Printed 14:18:00

15/10/2003

Page: 1 of 1

6-methyl-6-(4-nitrophenyl)-5,6-dihydropyran-2-one (3d)

Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name: xm352 Rec TolBNA.P 90/10 n/iso
Vial: 1
Injection Volume: 10.00 ul
Date Acquired: 14/10/2003 13:35:28
Proc. Chnl. Descr.: PDA 292.0 nm

RT	Area	Height	% Area
1 18.256	3628241	121230	50.67
2 21.155	3531857	92397	49.33

Colonne AD
Hexane/isopropanol 90/10
Débit 1ml/min

S20

Report Method: xavier

Printed 14:12:17

14/10/2003

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Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name: xm353 (R) TolBNA.P 90/10 n/iso
Vial: 2
Injection Volume: 10.00 ul
Date Acquired: 14/10/2003 14:29:58
Proc. Chnl. Descr.: PDA 292.0 nm

RT	Area	Height	% Area
1 17.620	361558	13058	12.36
2 20.119	2564482	76394	87.64

Colonne AD
Hexane/isopropanol 90/10
Débit 1ml/min

Report Method: xavier

Printed 14:55:19

14/10/2003

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6-methyl-6-phenethyl-5,6-dihydropyran-2-one (3e)

Empower

xavier

Reported by: User: Eudiant

Project Name: moreau

SAMPLE INFORMATION

Sample Name:	xm320 rac 97/3 hex/isop	Acquired By:	Eudiant
Sample Type:	Unknown	Date Acquired:	17/04/2003 18:14:06
Vial:	3	Acq. Method Set:	ad
Injection #:	1	Date Processed:	17/04/2003 18:32:38
Injection Volume:	20.00 uL	Processing Method:	xavier
Run Time:	80.0 Minutes	Channel Name:	W/in Ch1
Sample Set Name:		Proc. Chnl. Descr.:	PDA 209.6 nm

Peak Results

Name	RT	Area	Height	% Area
1	14.656	4760328	182715	50.72
2	15.962	4625826	152276	49.28

021

Report Method: xavier

Printed 18:33:04

17/04/2003

Page: 1 of 1

Empower

xavier

Reported by: User: Eudiant

Project Name: moreau

SAMPLE INFORMATION

Sample Name:	xm321 (R) ToBINAP 97/3 hex/isop	Acquired By:	Eudiant
Sample Type:	Unknown	Date Acquired:	17/04/2003 18:35:13
Vial:	4	Acq. Method Set:	ad
Injection #:	1	Date Processed:	17/04/2003 18:57:38
Injection Volume:	10.00 uL	Processing Method:	xavier
Run Time:	80.0 Minutes	Channel Name:	W/in Ch1
Sample Set Name:		Proc. Chnl. Descr.:	PDA 209.6 nm

Peak Results

Name	RT	Area	Height	% Area
1	14.383	29886686	1044224	93.80
2	15.825	1975054	77461	6.20

Report Method: xavier

Printed 18:57:59

17/04/2003

Page: 1 of 1

6-methyl-6-butenyl-3,4-dihydro-pyran-2-one (3f)

Empower

Reported by User: Etudiant

Project Name: moreau

xavier

Sample Name:	xm329 (Fac) ToBINAP 98/2 n/so	Date Acquired:	10/06/2003 11:43:34
Vial:	4	Proc. Chnl. Descr.:	PDA 212,2 nm
Injection Volume:	5,00 ul

	RT	Area	Height	% Area
1	12.089	2226649	134077	48,90
2	12.921	2326833	131354	51,10

Colonne AD
Hexane/isopropanol 98/2
Débit 1ml/min

S22

Report Method: xavier

Printed 14:35:42

10/06/2003

Page: 1 of 1

Empower

Reported by User: Etudiant

Project Name: moreau

xavier

Sample Name:	xm335 (S) ToBINAP 98/2 n/so	Date Acquired:	10/06/2003 13:08:20
Vial:	3	Proc. Chnl. Descr.:	PDA 212,2 nm
Injection Volume:	5,00 ul

	RT	Area	Height	% Area
1	12.601	9289114	518722	94,64
2	14.256	526222	31089	5,36

Colonne AD
Hexane/isopropanol 98/2
Débit 1ml/min

Report Method: xavier

Printed 14:32:24

10/06/2003

Page: 1 of 1

6-methyl-6-i-butyl-3,4-dihydro-pyran-2-one (3g)

Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name: xrm339 Rac TolBMAP 98/2 h/iso Date Acquired: 10/06/2003 14:28:14
Vial: 6 Proc. Chnl. Descr.: PDA 212.2 nm
Injection Volume: 5.00 ul

	RT	Area	Height	% Area
1	10.508	1890721	232616	51.41
2	11.662	1787258	126190	48.59

Colonne AD
Hexane/isopropanol 98/2
Débit 1ml/min

S23

Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name: xrm340 (S) TolBMAP 98/2 h/iso Date Acquired: 10/06/2003 14:43:34
Vial: 7 Proc. Chnl. Descr.: PDA 212.2 nm
Injection Volume: 5.00 ul

	RT	Area	Height	% Area
1	10.677	4010927	482797	96.24
2	11.862	156576	13084	3.76

Colonne AD
Hexane/isopropanol 98/2
Débit 1ml/min

6-methyl-6-t-butyl-3,4-dihydro-pyran-2-one (3h)

Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name:	xm370 Rac TolBNA.P 99/1 h/iso	Date Acquired:	25/09/2003 14:50:02
Vial:	3	Proc. Cntl. Descr.:	FDA 212.2 nm
Injection Volume:	5.00 ul

RT	Area	Height	% Area
1 15.692	1834056	213019	50.84
2 16.771	1773556	78800	49.16

Colonne A/D
Hexane/isopropanol 99/1
Débit 1ml/min

624

Report Method: xavier

Printed 16:36:43 25/09/2003

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Empower

xavier

Reported by User: Etudiant

Project Name: moreau

Sample Name:	xm368 (R) TolBNA.P 99/1 h/iso	Date Acquired:	25/09/2003 15:11:29
Vial:	4	Proc. Cntl. Descr.:	FDA 212.2 nm
Injection Volume:	10.00 ul

RT	Area	Height	% Area
1 17.376	379096	14385	4.10
2 19.813	8858063	163124	95.90

Colonne A/D
Hexane/isopropanol 99/1
Débit 1ml/min

Report Method: xavier

Printed 16:05:48 25/09/2003

Page: 1 of 1

6-methyl-6-styryl-3,4-dihydro-pyran-2-one (3i)

Empower

xavier

Reported by User: equipe56

Project Name: xavier

Spectrum Index Plot

SampleName cinnamyl lactone Rac 90/10; Date Acquired 11/05/2004 10:39:43; Processed Channel Descr: PDA 250.0 nm

Peak Results		
RT	Area	%Area
1 9.179	7645592	55.07
2 11.380	6238389	44.93

Colonne AD
Hexane/isopropanol
90/10

S25

Report Method: xavier

Printed 10:57:42

11/05/2004

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Empower

xavier

Reported by User: equipe56

Project Name: xavier

Spectrum Index Plot

SampleName xrn440 (R) ToBINAP 90/10; Date Acquired 11/05/2004 10:57:08; Processed Channel Descr: PDA 250.0 nm

Peak Results		
RT	Area	%Area
1 9.165	9663686	62.25
2 11.359	5861330	37.75

Colonne AD
Hexane/isopropanol
90/10

Report Method: xavier

Printed 11:27:16

11/05/2004

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sans nom

Reported by User: assistant

Project Name: XAVIER

SAMPLE INFORMATION

Sample Name:	XM608rac AD 982hex/iproh	Acquired By:	assistant
Sample Type:	Unknown	Date Acquired:	27/03/2003 16:46:20
Vial:	1	Acq. Method Set:	AD
Injection #:	1	Date Processed:	27/03/2003 17:33:32
Injection Volume:	10.00 ul	Processing Method:	xav
Run Time:	120.0 Minutes	Channel Name:	WIn Ch1
Sample Set Name:		Proc. Chnl. Descr.:	PDA 208.3 nm

Auto-Scaled Chromatogram

Empower

Reported by User: etudiant

Project Name: xavier

xavier

Spectrum Index Plot

SampleName xm398 RacTolBinap 98/2 h/iso, Date Acquired 29/01/2004 18:39:29, Processed Channel Descr. PDA 207.0 nm

Peak Results		
RT	Area	% Area
1 11.229	7877889	48.43
2 12.178	8397656	51.57

Colonne OD (10°C)
Hexane/Isopropanol
98/2

S27

Empower

Reported by User: etudiant

Project Name: xavier

xavier

Spectrum Index Plot

SampleName xm399 (S) TolBinap 98/2 h/iso, Date Acquired 29/01/2004 18:59:45, Processed Channel Descr. PDA 207.0 nm

Peak Results		
RT	Area	% Area
1 11.137	20461330	94.18
2 12.153	1284835	5.82

Colonne OD (10°C)
Hexane/Isopropanol
98/2