Supporting informations for :

The First Asymmetric Synthesis of α-Sulfanylphosphonates.

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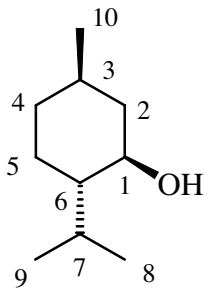
(*l*)-Menthol (purity 99 %) was used for the synthesis of di-(*l*)menthylphosphite. Following numbering was used for NMR data. Prime notation was used to differentiate non equivalent protons and carbons of the two menthyl groups.



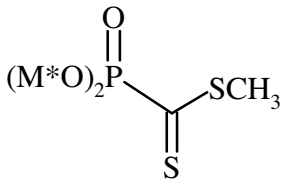
-(*l*)-menthol

^{13}C {^{1}H} NMR, ^{1}H NMR, ^{31}P {^{1}H} NMR were recorded with a Brüker AC 250 (250 MHz / ^{1}H, 62.9 MHz / ^{13}C, 101.2 MHz / ^{31}P) or a Brüker AC 400 MHz (400 MHz / ^{1}H, 100.62 MHz / ^{13}C, 161.9 MHz / ^{31}P) spectrometer in $CDCl_3$ using TMS as internal standart. Chemical shifts (δ) are given in ppm and coupling constants ($^{n}J_{CP}$) in Hz. Conventional abbreviations are used. The infra-red spectra were recorded with a Perkin-Elmer 16 PC spectrometer on the liquid film, ν (cm^{-1}) are given. Mass spectra were recorded with a Nermag R 10 10H spectrometer in electronic impact at 70 eV, m / z and relative abundance are given.

Methyl di-(*l*)-menthylphosphono)methyldithioate 1

At 0°C, under a nitrogen flux, the di-(*l*)-menthylphosphite (3.96 g, 0.011 mol.) in dry THF (10 x mL) was added slowly to a suspension of potassium hydride (2.25 g, 1.1 equiv., 20-25% in oil, washed with pentane) in dry THF (35 mL). The pale yellow mixture was stirred for 3 h and then added slowly under nitrogen onto a solution of carbon disulfide (4.201 g, 3.33 mL, 0.055 mol., 5 5 equiv.) in 10 mL of THF (previously cooled at 0°C). The brown solution was stirred at room temperature for 2 h and methyl iodide (2.06 mL, 3 equiv.) was added.

The resulting dark red solution was stirred over night at room temperature and then poured into an aqueous solution of 10 % hydrochloric acid. The product was extracted twice with 100 mL of petroleum ether. Organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude oil was purified over silica gel and elution with petroleum ether-AcOEt (99 : 1). Yield : 82 %



1

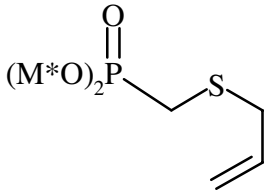
^{1}H NMR : ($CDCl_3$, 400 MHz) : 0.62 (d, 3H, $^3J_{HH}$ = 6.87, 3 $H_{8/9}$) ; 0.81 (d, 3H, $^3J_{HH}$ = 6.8, 3 $H_{8/9}$) ; 0.82 (d, 3H, $^3J_{HH}$ = 6.97, 3 $H_{8/9}$) ; 0.86 (d, 3H, $^3J_{HH}$ = 6.56, 3 $H_{8/9}$) ; 0.9 (d, 6H, $^3J_{HH}$ = 6.45, 3 H_{10} and 3 $H_{10'}$) ; 1.12-1.23 (m, 3H) ; 1.28-1.42 (m, 5H) ; 1.60-1.63 (m, 5H) ; 1.90-2.01 (m, 1H) ; 2.08-2.30 (m, 3H) ; 2.30-2.40 (m, 1H) ; 2.60 (s, 3H, SCH_3) ; 4.20-4.32 (m, 1H, POCH) ; 4.32-4.42 (m, 1H, POCH).

^{31}P NMR : ($CDCl_3$, 101 MHz) : -3.76.

^{13}C NMR : ($CDCl_3$, 100,6 MHz) : 15.86 (s, $C_{8/9}C_{8'/9'}$) ; 19.51 (d, $^3J_{CP}$ = 3.35, SCH_3) ; 21.10 (s, $C_{9/8}C_{9'/8'}$) ; 22.01 (s, $C_{10}C_{10'}$) ; 22.85 (s, $C_5C_{5'}$) ; 25.74 and 25.56 (2s, $C_7C_{7'}$) ; 31.68 (s, $C_3C_{3'}$) ; 34.08 (s, $C_4C_{4'}$) ; 42.79 and 43.56 (2s, $C_2C_{2'}$) ; 48.62 (d, $^3J_{CP}$ = 5.33, $C_6C_{6'}$) ; 80.19 and 80.43 (2d, $^2J_{CP}$ = 7.31 and $^2J_{CP}$ = 7.25, $C_1C_{1'}$) ; 231.12 (d, $^1J_{CP}$ = 176.39, C=S). **Mass** : (70 eV): (m/z): 448 (4.3 %), [$M^{+\cdot}$] ; 310 (20.7 %), [(MenthO)P(OH)$OCS_2CH_3^{+\cdot}$] ; 263 (10.4 %), [(MenthO)P(OH)OCS^+] ; 173 (34.4%), [$(OH)_3PCS_2CH_3^+$)] ; 139 (23.2%), [$C_{10}H_{19}^+$] ; 138 (25.4 %), [$C_{10}H_{18}^+$] ; 137 (22.8 %), [$C_{10}H_{17}^+$] ; 95 (52.2 %), [$C_7H_{13}^+$] ; 84 (64.9 %) ; 83 (58.1 %) ; 43 (100 %) . **IR** (NaCl, cm^{-1}) : 1254 ; 992 ; 1100 ; 2868 ; 2954 ; 2926. $[\alpha]_D$ = -120 ° (c= 1, $CHCl_3$). **Anal.** Calcd. % C, 58.89 ; H, 9.21 Found C, 58.89 ; H, 9.06.

Di-(*l*)-menthyl (allylsulfanyl)methylphosphonate 2.

The phosphonodithioformate **1** (4.41 g, 1 equiv. in 50 mL of absolute ethanol) was added slowly at 0°C under nitrogen to a suspension of sodium borohydride (1.5 g, 4 equiv. in 100 mL of absolute ethanol). After addition the mixture was heated up to 70°C for 5 h. The homogenous solution was then cooled at 0°C and 3 equiv. of allyl bromide (2.8 mL) were added. The solution was stirred overnight at room temperature under nitrogen flux. The reaction was quenched by a solution of hydrochloric acid (10 % in water) and extracted twice with petroleum ether (150 mL). Organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residual oil was diluted in pentane (8-10 mL) and filtered twice. The solvent was removed and the residual viscous oil (4.13 g) was used in crude form or purified by chromatography over silica gel, elution with petroleum ether-Et_2O (70 : 30). Yield : 95 %.



2

^{1}H NMR : ($CDCl_3$, 250 MHz) : 0.78 (d, 6H, $^3J_{HH}$ = 6.9, 3 $H_8H_{8'}$) ; 0.92 (d, 12H, $^3J_{HH}$ = 6.9, 3 H_9 and 3 $H_{9'}$, 3 H_{10} and 3 $H_{10'}$) ; 0.96-1.43 (m, 8H, 1 H_6 and 1 $H_{6'}$, 2 H_4 and 2 $H_{4'}$, 1 H_3 and 1 $H_{3'}$) ; 1.63 (broad d, 4H, 2 H_5 and 2 $H_{5'}$) ; 2.13-2.17 (m, 6H, 1 H_7 and 1 $H_{7'}$, 2 H_2 and 2 $H_{2'}$) ; 2.58 (d, 1H, $^2J_{HP}$ = 13.3, PCH<u>H</u>) ; 2.59 (d, 1H, $^2J_{HP}$ = 13.2, PCH<u>H</u>) ; 3.27 (ddd, 2H, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = $^4J_{HH}$ = 1, SCH_2) ; 4.19 (m, 2H, 2 CHOP) ; 5.15 (ddd, 1H_{trans}, $^4J_{HH}$ = 1, $^3J_{HH}$ = 16, H<u>H</u>C=) ; 5.16 (ddd, 1H_{cis}, $^4J_{HH}$ = 1, $^3J_{HH}$ = 10.9, H<u>H</u>C=) ; 5.70 (ddt, 1H, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 10, $^3J_{HH}$ = 16.1, HC=).

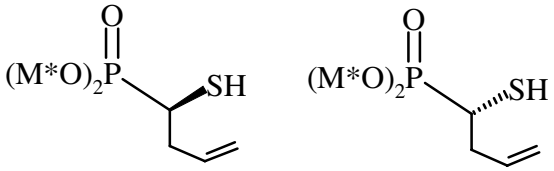
^{31}P NMR : ($CDCl_3$, 101 MHz) : 24.51.

^{13}C NMR : ($CDCl_3$, 100.6 MHz) : 15.8 (s, C_8, $C_{8'}$) ; 21.0 (s, C_9, $C_{9'}$) ; 21.9 (s, C_{10}, $C_{10'}$) ; 22.7 (s, C_5) ; 22.8 (s, $C_{5'}$) ; 24.8 (d, $^1J_{CP}$ = 151.7, PCH_2) ; 25.3 (s, C_7) ; 25.4 (s, $C_{7'}$) ; 31.5 (s, C_3, $C_{3'}$) ; 34 (s, C_4) ; 34.1 (s, $C_{4'}$) ; 35.7 (d, $^3J_{CP}$ = 4.5, SCH_2) ; 43.1 (s, C_2) ; 43.7 (s, $C_{2'}$) ; 48.6 (2d, $^3J_{CP}$ = 7.6 and $^3J_{C'P}$ = 7.2, C_6, $C_{6'}$) ; 77.7 (d, $^2J_{CP}$ = 7.18, C_1) ; 77.8 (d, $^2J_{CP}$ = 8.08, $C_{1'}$) ; 118.1 (s, CH_2=) ; 133.3 (S, HC=). **Mass** : (70 eV): 444 (1.56%), [$M^{+\cdot}$] ; 306 (5.51%), [(MenthO)P(OH)OCH_2Sallyl$^+$]; 168 (100%), [$(OH)_2POCH_2$Sallyl$^+$] ; 96 (41%) ; 81 (46%) ; 69 (36.6%). **IR** (NaCl, cm^{-1}) : 1008 ; 1024 ; 1252 ; 2868 ; 2926 ; 2954 ; 3080 $[\alpha]_D$ = -83.12 ° (c = 2.72, $CHCl_3$). **Anal.** Calcd. % C, 64.82 ; H, 10.2 ; S, 7.21 Found C, 64.89 ; H, 9.95 ; S, 7.16.

Di-(*l*)-menthyl (1-mercaptobut-3-enyl)phosphonate (3a / 3b).

In a dry two necked round bottom flask, under nitrogen, was introduced freshly distillated THF (20 mL) then HMPA (1.37 mL, 5 equiv., 7.88 mmol) . The solution was stirred vigourously and cooled at -40°C. A solution of sec-BuLi (1.3 M in cyclohexane, 6.2 mL, 5.1 equiv.) was then added and the yellow solution was stirred for 30 mn. at -40 / -50 °C. The solution was cooled at -78°C and the sulfide **2** (1 equiv., 700 mg, 1.57 mmol) in 2.5 mL of THF was slowly added over ca 10 mn.

After addition the temperature of the vigourously stirred solution was raised to -70 / -72 °C over 10 mn and the reaction mixture was stirred for 1 h at this temperature. The reaction was quenched by adding a 10 % aqueous solution of hydrochloric acid (10 mL) . The mixture was extracted with petroleum ether (2x50mL) . Organic layers were dried and filtered. The solvent was removed under reduced pressure (without heating). The residual oil was stored in the dark, under nitrogen and used in crude form for the next step. Yield : 98 %.



3a major **3b minor**

^{1}H NMR : ($CDCl_3$, 250 MHz) : 0.74 (d, 3H, $^3J_{HH}$ = 6.9, 3 H_8) ; 0.75 (d, 3H, $^3J_{HH}$ = 6.9, 3 $H_{8'}$) ; 0.85 (d, 12H, $^3J_{HH}$ = 6.9, 3 H_9 and 3 $H_{9'}$, 3 H_{10} and 3 $H_{10'}$) ; 0.89-1.61 (m, 12H, 1 H_6 and 1 $H_{6'}$, 2 H_5 and 2 $H_{5'}$, 2 H_4 and 2 $H_{4'}$, 1 H_3 and 1 $H_{3'}$) ; 1.92 (dd 1H, $^3J_{HH}$ = 7.6, $^3J_{HP}$ = 10.6, SH) ; 2.05-2.28 (m, 6H, 1 H_7 and 1 $H_{7'}$, 2 H_2 and 2 $H_{2'}$) ; 2.78 (m, 3H, PC<u>H</u> and C<u>H</u>2) ; 4.16 (m, 2H, 2 CHOP) ; 5.07 (m, 2H, =CH_2) ; 5.80 (m, 1H, HC=).

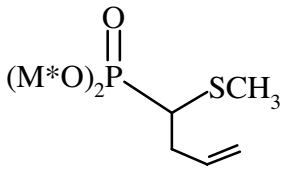
^{31}P NMR : ($CDCl_3$, 101 MHz) : 24.60 (major) ; 24.52 (minor).

^{13}C NMR : ($CDCl_3$, 100.6 MHz) : 14.8 (s, CO<u>C</u>H3) ; 15.8 and 15.9 (2s, C_8, $C_{8'}$) ; 21.15 and 21.20 (2s, C_9, $C_{9'}$) ; 21.90 (2s, C_{10}, $C_{10'}$) ; 22.70 (s, C_5) ; 22.80 (s, $C_{5'}$) ; 25.30 (s, C_7) ; 25.40 (s, $C_{7'}$) ; 31.50 (2s, C_3,

$C_{3'}$) ; 34.00 (s, C_4) ; 34.10 (s, $C_{4'}$) ; 35.10 (d, $^1J_{CP}$ = 149.9, PCH) ; 37.02 (s, PCH$\underline{C}H_2$) ; 43.10 (s, C_2) ; 43.70 (s, $C_{2'}$) ; 48.60 (2d, $^3J_{CP}$ = 7.6 and $^3J_{CP}$ = 7.2, C_6, $C_{6'}$) ; 77.70 (d, $^2J_{CP}$ = 7.18, C_1) ; 77.80 (d, $^2J_{CP}$ = 8.08, $C_{1'}$) ; 118.10 (s, CH_2=) ; 134.70 (d, $^3J_{CP}$ = 14.2, CH=).

Di-(*l*)-menthyl [1-(methylsulfanyl)but-3-enyl]phosphonate 4.

The reaction was carried out as for the synthesis of the thiol **3** by using 120 mg (0.27 mmol) of sulfide **2** and 5.1 equivalents of a lithiated base. The reaction mixture was treated with methyl iodide (1.1 equiv.) and after 10 mn it was quenched with a solution of 10 % hydrochloric acid . The mixture was extracted with petroleum ether (120 mL) and the organic layers were washed with brine, dried and filtered. The solvent was removed under reduced pressure.The crude oil was purified by chromatography over silica gel, elution with petroleum ether - Et_2O (70 / 30) . Yield 75 %.



4a and 4b

^{1}H NMR : ($CDCl_3$, 250 MHz) : 0.74 (d, 3H, $^3J_{HH}$ = 6.9, 3 H_8) ; 0.75 (d, 3H, $^3J_{HH}$ = 6.8, 3 $H_{8'}$) ; 0.84 (d, 12H, $^3J_{HH}$ = 7.1, 3 H_9 and 3 $H_{9'}$, 3 H_{10} and 3 $H_{10'}$) ; 0.90-1.70 (m, 12H, 1 H_6 and 1 $H_{6'}$, 2 H_4, 2 $H_{4'}$, 1 H_3 and 1 $H_{3'}$, 2 H_5 and 2 $H_{5'}$) ; 2.10-2.40 (m, 6H, 1 H_7, 1 $H_{7'}$, 2 H_2 and 2 $H_{2'}$) ; 2.18 (s, 3H, SCH_3) ; 2.40-2.70 (m, 3H, PC$\underline{H}$ and PCHC$\underline{H}_2$) ; 4.20 (m, 2H, 2 CHOP) ; 5.10 (m, 2H, H_2C=) ; 5.90 (m, 1H, HC=).

^{31}P NMR : ($CDCl_3$, 101 MHz) : 24.80.

^{13}C NMR : ($CDCl_3$, 62.9 MHz) : 15.80 and 15.90 (2s, C_8, $C_{8'}$) ; 16.20 (s, SCH_3) ; 21.21 and 21.26 (2s, C_9, $C_{9'}$) ; 22.07 (s, $C_{10}C_{10'}$) ; 22.87 (s, $C_5C_{5'}$) ; 24.90 (d, $^1J_{CP}$ = 167, PCH) ; 25.28 and 25.36 (2s, $C_7C_{7'}$) ; 31.60 and 31.70 (2s, C_3, $C_{3'}$) ; 34.20 and 34.60 (2s, $C_4C_{4'}$) ; 43.30 (s, C_2) ; 43.90 (s, $C_{2'}$) ; 45.20 (s, PCH$\underline{C}$H2) ; 48.90 (d, $^3J_{CP}$ = 6.3, C_6, $C_{6'}$) ; 77.80 (m, 2 x CHOP) ; 117.06 (s, H_2C=) ; 135.40 (d, $^3J_{CP}$ = 14.02, HC=). **Anal.** calcd % S, 6.99 Found S, 7.09.

Di-(*l*)-menthyl [1-(acetylsulfanyl)-but-3-enyl]phosphonate 6a or 6b.

6b major product by method A (Mitsunobu reaction) .

Diethyl azodicarboxylate (DEAD) (174 mg, 1 mmol, 2 equiv.) was added dropwise at 0°C onto a solution of triphenylphosphine (262 mg, 1mmol, 2 equiv) in anhydrous THF (25 mL). The mixture was stirred at 0°C for 30 min. then the phosphonate **5** of *R* configuration at Cα (de = 92 %, 215 mg, 0.5 mmol, 1 equiv.) in THF (10 mL) was added slowly. The solution was stirred for 1 h at 0°C and thiolacetic acid (2 equiv., 1 mmol) was added. The solution was stirred for 24 h at room temperature and filtered twice. The crude mixture was hydrolysed with 10 mL of a 5 % solution of hydrochloric acid. The product was extracted with petroleum ether (75 mL). The organic layers were dried over MgSO4 and filtered. The solvent was removed under reduced pressure. The residual oil (mainly **6b**) was purified by chromatography over silica gel, elution with petroleum ether - Et_2O (80 / 20). Yield 25 %, de = 92 %.

H NMR: ($CDCl_3$, 250 MHz) : 0.73 (d, 3H, $^3J_{HH}$ = 6.9, CH_3) ; 0.76 (d, 3H, $^3J_{HH}$ = 6.8, CH_3) ; 0.84 (d, 12H, $^3J_{HH}$ = 6.3, 4 CH_3) ; 0.91-1.70 (m, 10H) ; 1.80-2.20 (m, 8H) ; 2.29 (s, 3H, $SCOCH_3$) ; 2.70-2.90 (m, 2H) ; 3.70 (m, 1H, PCH) ; 4.10 (m, 2H, 2 CHOP) ; 4.90 (dd, 2H, $^3J_{HH}$ = 9.1 and $^3J_{HH}$ = 17.2, H_2C=) ; 5.70 (m, 1H, HC=).

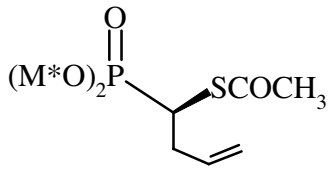
^{31}P NMR : ($CDCl_3$, 101 MHz) : 24.83.

^{13}C NMR : ($CDCl_3$, 100.6 MHz) : 15.63 and 15.78 (2s, C_8, $C_{8'}$) ; 21.09 (s, $C_{10}C_{10'}$) ; 21.95 and 21.97 (2s, C_9, $C_{9'}$) ; 22.66 (s, $C_5C_{5'}$) ; 25.23 and 25.33 (2s, $C_7C_{7'}$) ; 31.50 and 31.54 (2s, C_3, $C_{3'}$) ; 33.9 (s, CH_2) ; 34.00 (s, $C_4C_{4'}$) ; 38.6 (d, $^1J_{CP}$ = 157, PCH) ; 43.03 and 43.65 (2s, $C_2C_{2'}$) ; 48.54 and 48.61 (2d, $^3J_{CP}$ = 5.66 and $^3J_{CP}$ = 6.9, C_6, $C_{6'}$) ; 78.05 (d, $^2J_{CP}$ = 7.16,C_1) ; 78.41 (d, $^2J_{CP}$ = 78.11,$C_{1'}$) ; 117.74 (s, H_2C) ; 134.10 (d, $^3J_{CP}$ = 10.06, HC=) ; 193.33 (d, $^3J_{CP}$ = 2.64, CO).

6a major product by methode B (acetylation of the thiol **3**) .

α-Mercaptophosphonate **3** (219 mg, 0.49 mmol, 1 equiv.) diluted in THF (10 mL) was added slowly at 0°C onto a solution of acetic anhydride (1.5 equiv., 75 mg) in anhydrous THF (10 mL) . After about 5 min., triethylamine (2 equiv., 100 mg) was added. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by 10 mL of a 10 % solution of hydrochloric acid.

The product was extracted twice with petroleum ether (2x30 mL). The organic layers were collected, washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. Yield 94 %, *de* = 88 %,, purity 90 % (by ^{31}P NMR).



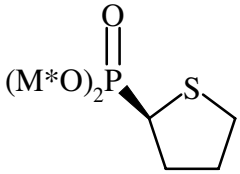
6a

^{31}P NMR : ($CDCl_3$, 101 MHz) : 24.91.

2-(Di-(*l*)-menthylphosphono)thiolane 7.

Anhydrous THF (60 mL) and AIBN (25 mg) were introduced in a quartz flask under nitrogen. The flask was irradiated using an 150W UV lamp (fitted at ~ 7 cm of the flask) for 20 min. The thiol **3** (1.5 mmol, 665 mg) in anhydrous THF (50mL) was added by portion (10 mL every 15 mn) under irradiation. After complete addition, irradion was maintained for 35 min then the solution was concentrated (50-60%) under reduced pressure and quenched by a 5 % solution (25 mL) of hydrochloric acid. The solution was extracted with petroleum ether (3x60 mL). The organic layers were dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The residual oil was purified by chromatography over silica gel, elution with petroleum ether - Et_2O (75 / 25). Yield 60 %.

Crystalization of the phosphonothiolane **7** (320 mg, *de* = 75 %) was performed at -60°C / -65°C in pentane (4-5 mL) under nitrogen. After elimination of the mother liquor, the 2-phosphonothiolane **7** (mainly **7a**)was obtained as a white solid, with a diastereoisomeric excess of 96 % (yield = 30 %).



7a

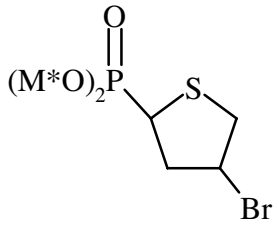
^{1}H NMR : ($CDCl_3$, 250 MHz) : 0.82 (d, 3H, $^3J_{HH}$ = 6.8, 3 H_8) ; 0.83 (d, 3H, $^3J_{HH}$ = 6.8, 3 $H_{8'}$) ; 0.90 (d, 12H, $^3J_{HH}$ = 6.96, 3 H_9, 3 $H_{9'}$, 3 H_{10} and 3 $H_{10'}$) ; 0.98-1.50 (m, 8H, 1 H_6 and 1 $H_{6'}$, 2 H_4, 2 $H_{4'}$, 1 H_3 and 1 $H_{3'}$) ; 1.64 (broad d, 4H, 2 H_5 and 2 $H_{5'}$) ; 1.89 (m, 2H, $SCH_2C\underline{H}_2$) ; 2.12-2.37 (m, 8H, 1 H_7, 1 $H_{7'}$, 2 H_2 and 2 $H_{2'}$, $PCHC\underline{H}_2$) ; 2.90 (dd, 2H, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 5.16, SCH_2) ; 3.42 (q = dt, 1H, $^2J_{HP}$ = $^3J_{HH}$ = 7.35, PCH) ; 4.22 (m, 2H, 2 CHOP).

^{31}P NMR : ($CDCl_3$, 101 MHz) : 26.04 (**7a** major) ; 25.96 (**7b** minor).

^{13}C NMR : ($CDCl_3$, 62.9 MHz) : 16.0 (s, $C_8C_{8'}$) ; 21.2 (s, C_9) ; 21.3 (s, $C_{9'}$) ; 22.0 (s, C_{10}) ; 22.1 (s, $C_{10'}$); 22.9 (s, $C_5C_{5'}$) ; 25.4 (s, C_7) ; 25.5 (s, $C_{7'}$) ; 31.4 (d, $^2J_{CP}$ = 9.87, PCH<u>C</u>H_2) ; 31.6 (s, $C_3C_{3'}$) ; 32.4 (d, $^3J_{CP}$ = 3.59, SCH_2<u>C</u>H_2) ; 33.2 (d, $^3J_{CP}$ = 3.59, SCH_2) ; 34.2 (s, $C_4C_{4'}$) ; 42.4 (d, $^1J_{CP}$ = 156.18, PCH) ; 43.2 (s, C_2) ; 43.9 (s, $C_{2'}$) ; 48.8 and 48.9 (2d, $^3J_{CP}$ = 6.28 and $^3J_{C'P}$ = 7.18, $C_6C_{6'}$) ; 77.7 (d, $^2J_{CP}$ = 7, C_1) ; 78.2 (d, $^2J_{CP}$ = 8.07, $C_{1'}$). Mp : 86 °C, de = 96 %. $[\alpha]_D$ = -44.4 ° (c = 0.7, $HCCl_3$). **Anal.** calcd. % S, 7.21 Found 7.34.

4-Bromo-2-(di-(*l*)-menthylphosphono)thiolane 8.

The α-mercaptophosphonate **3** (600 mg, 1.35 mmol, 1 equiv.) diluted in chloroform (20 mL) was added for 5 mn, under nitrogen, to a suspension of NBS (1 equiv., 241 mg) in chloroform (30 mL) at - 50°C. the mixture was stirred for 2 h at -50°C, then the temperature was allowed to rise at room temperature overnight. The reaction was quenched by an aqueous solution of sodium thiosulfate. Organic layers were collected, washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure (without heating). The residual yellow oil was purified by chromatography over neutral alumina (AcOEt). Yield 65 %.



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^{1}H NMR : ($CDCl_3$, 250 MHz) : 0.81 (d, 3H, $^3J_{HH}$ = 6.76, CH_3) ; 0.83 (d, 3H, $^3J_{HH}$ = 6.73, CH_3) ; 0.92 (d, 6H, $^3J_{HH}$ = 6.85, 2 CH_3) ; 0.93 (d, 6H, $^3J_{HH}$ = 6.61, 2 CH_3) ; 1.20-3.00 (m, 18H) ; 2.61 (m, 1H, CH<u>H</u>) ; 2.80-2.90 (m, 1H, CH<u>H</u>) ; 3.10-3.30 (m, 2H, CH_2) ; 3.40 (m, 1H, PCH) ; 4.05-4.40 (m, 3H, 2 CHOP and CHBr).

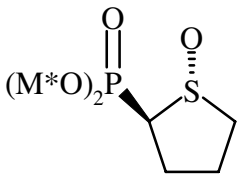
^{31}P NMR: ($CDCl_3$, 101.2 MHz) : 24.3.

^{13}C NMR: ($CDCl_3$, 62.9 MHz) : 16.04 and 16.15 (2s, C_8, $C_{8'}$) ; 21.39 and 21.44 (2s, C_9, $C_{9'}$) ; 22.33 and 22.37 (2s, $C_{10}C_{10'}$) ; 23.13 (s, $C_5C_{5'}$) ; 25.74 and 25.84 (2s, $C_7C_{7'}$) ; 31.91 (s, C_3, $C_{3'}$) ; 34.38 (s, $C_4C_{4'}$) ; 37.30 (d, $^1J_{CP}$ = 160, PCH) ; 40.27 (d, $^2J_{CP}$ = 2.70, CH_2) ; 40.97 (s, CH_2) ; 43.13 (s, $C_2C_{2'}$) ; 45.83 (d, $^3J_{CP}$ = 13.58, CHBr) ; 48.95 (d, $^3J_{CP}$ = 6.41, C_6) ; 49.02 (d, $^3J_{CP}$ = 7.19, $C_{6'}$) ; 78.56 (d, $^2J_{CP}$ = 7.98, CHOP) ; 79.09 (d, $^2J_{CP}$ = 7.17, CHOP). **Anal.** calcd. % C, 55.06 ; H, 8.47 ; S, 6.12 Found C, 55.70 ; H, 8.52 ; S, 5.80.

2-[Di(*l*)-menthyloxyphosphonyl]-thiolane-S-oxide 9.

The phosphonothiolane **7** (94% of **7a**, 1 equiv., 420 mg, 0.946 mmol) diluted in THF (5 mL) was added slowly at -78°C to a solution of mCPBA (1 equiv., 251 mg) in THF (15 mL). the reaction mixture was stirred overnight, allowing the temperature to increase slowly (up to r. t.). The reaction was quenched by addition of a 5 % aqueous solution of $NaHCO_3$ (30 mL). The product was extracted with diethyl ether (75 mL). Organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure.

The sulfoxyde was purified by chromatography over silica gel, elution with CH_2Cl_2 - EtOH (95 / 5) or over neutral alumina, elution with AcOEt. Yield 85 %.



9a

^{1}H NMR (major) : ($CDCl_3$, 250 MHz) : 0.81 (d, 3H, J = 6.71, CH_3) ; 0.82 (d, 3H, J = 6.70, CH_3) ; 0.90 (d, 12H, J = 6.17, 4 CH_3) ; 1.00-1.70 (m, 12H, 1 H_6 and 1 $H_{6'}$, 2 H_4 and 2 $H_{4'}$, 1 H_3 and 1 $H_{3'}$, 2 H_5 and 2 $H_{5'}$) ; 2.00-2.40 (m, 8H, 1 H_7 and 1 $H_{7'}$, 2 H_2 and 2 $H_{2'}$ and PCHC$\underline{H}_2$) ; 2.50-2.80 (m, 3H, SOCH$\underline{H}$ and SOCH_2C$\underline{H}_2$) ; 3.00-3.20 (m, 2H, PC$\underline{H}$ and SOCH$\underline{H}$) ; 4.20 (m, 2H, 2 CHOP).

^{31}P NMR : ($CDCl_3$, 101.2 MHz) : 20.26 (**9a**, 94%) and 20.42 (**9b**, 6%).

^{13}C NMR : ($CDCl_3$, 62.9 MHz) : **9a** : 15.5 and 15.8 (2s, $C_8C_{8'}$) ; 21.0 and 21.1 (2s, $C_9C_{9'}$) ; 21.9 (s, $C_{10}C_{10'}$) ; 22.69 and 22.73 (2s, $C_5C_{5'}$) ; 25.4 (s, C_7) ; 25.5 (s, $C_{7'}$) ; 26.6 (d, $^{3}J_{CP}$ = 8.3, $\underline{C}H_2CH_2SO$) ; 28.5 (d, $^{2}J_{CP}$ = 2.7, PCH$\underline{C}H_2$) ; 31.6 and 36.1 (2s, $C_3C_{3'}$) ; 33.90 and 33.94 (2s, $C_4C_{4'}$) ; 43.0 and 43.60 (2s, $C_2C_{2'}$) ; 48.5 and 48.6 (2d, $^{3}J_{CP}$ = 6.9 and $^{3}J_{CP}$ = 6.9, C_6, $C_{6'}$) ; 54.5 (d, $^{3}J_{CP}$ = 4.0, $SOCH_2$) ; 68.6 (d, $^{1}J_{CP}$ = 143.0, PCH) ; 78.5 (d, $^{2}J_{CP}$ = 7.8, C_1) ; 78.9 (d, $^{2}J_{CP}$ = 7.7, $C_{1'}$).

^{13}C NMR : ($CDCl_3$, 62.9 MHz) : **9b** : 15.6 and 15.7 (2s, $C_8C_{8'}$) ; 21.05 and 21.06 (2s, $C_9C_{9'}$) ; 21.8 (s, $C_{10}C_{10'}$) ; 22.69 and 22.70 (2s, $C_5C_{5'}$) ; 25.3 (s, C_7) ; 25.4 (s, $C_{7'}$) ; 26.7 (d, $^{3}J_{CP}$ = 7.8, $\underline{C}H_2CH_2SO$) ; 28.4 (d, $^{2}J_{CP}$ = 1.71, PCH$\underline{C}H_2$) ; 31.5 (m, C_3 and $C_{3'}$) ; 33.88 and 33.89 (2s, $C_4C_{4'}$) ; 43.1 and 43.7 (2s, $C_2C_{2'}$) ; 48.5 (m, C_6 and $C_{6'}$) ; 54.5 (d, $^{3}J_{CP}$ = 3.4, $SOCH_2$) ; 67.8 (d, $^{1}J_{CP}$ = 142.6, PCH) ; 78.4 (d, $^{2}J_{CP}$ = 7.77, C_1) ; 78.9 (d, $^{2}J_{CP}$ = 7.7, $C_{1'}$).

Anal. calcd. % C, 62.57 ; H, 9.84 Found C, 62.26 ; H, 9.82.