Supporting Information for

Application of cyanobacteria for chiral phosphonates synthesis

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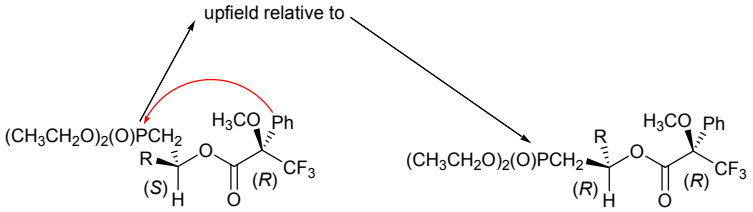
Experimental

Determination of the absolute configuration of diethyl 2-hydroxyphosphonates (1a, 2a, 3a)

This was accomplished according to Mosher's method.[1] Thus, the examined sample consisted of 0.1 mmol of a particular diethyl 2–hydroxyphosphonate (a mixture of both enantiomers, ratio 10:1) dissolved in a mixture of solvents composed of dry dichloromethane (300 µL) and dry pyridine (300 µL), followed by the addition of 0.14 mmol of (*S*)-(+)-MTPA-Cl. The reaction mixture was left for 3 days at room temperature. Then, the excess volume of 3-dimethyl-amino-1-propylamine (0.20 mmol) was added and after 5 min. at room temperature, the mixture was diluted with diethyl ether (10 mL), washed by a cold solution of 5% HCl (10 mL) and water (10 mL), then the organic layer was dried over anhydrous $MgSO_4$. Solid residues were removed by filtration, the ether fraction was evaporated and the final acylated products were purified by means of FPLC (flash column Puriflash C18HP 15µm, 120G). The initial mobile phase composition was 70% water and 30% acetonitrile (v/v). The composition was linearly changed to 100% acetonitrile in 40 min., at a flow rate of 15 mL/min., detection was performed at 220 nm. The retention times of the (*R*)-MTPA diastereoisomers were as follows: **1a**-(*R*)-MTPA 30 min., **2a**-(*R*)-MTPA 34 min., **3a**-(*R*)-MTPA 32 min.
The absolute configuration was determined by ^{1}H and ^{31}P NMR spectroscopic analyses of the resultant Mosher esters (Scheme 1).

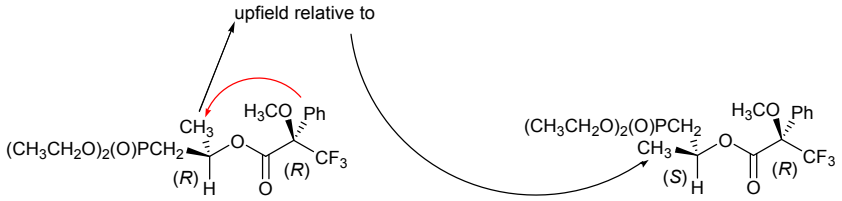
The absolute configuration was confirmed by the measurement of the optical rotation ($[\alpha]_D^{25}$) of the methanol solutions of hydroxyphosphonates (polarimeter PolAAr 31), according to the literature.[2]

A.



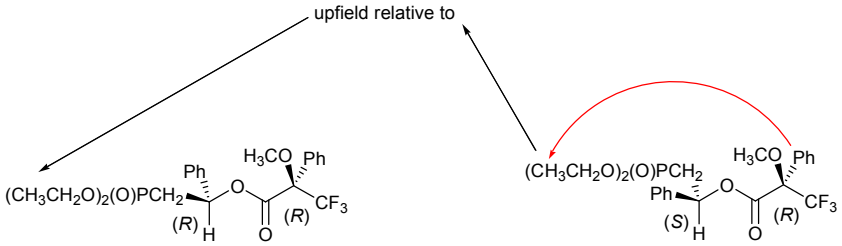
(*R*)-MTPA esters of **1a** R= - CH_3
(*R*)-MTPA esters of **2a** R= - C_6H_5
(*R*)-MTPA esters of **3a** R= - CH_2CH_3

B.



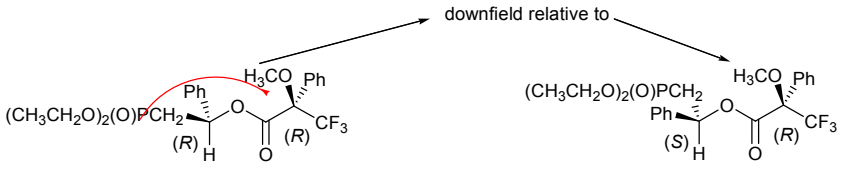
(*R*)-MTPA esters of **1a**

C.



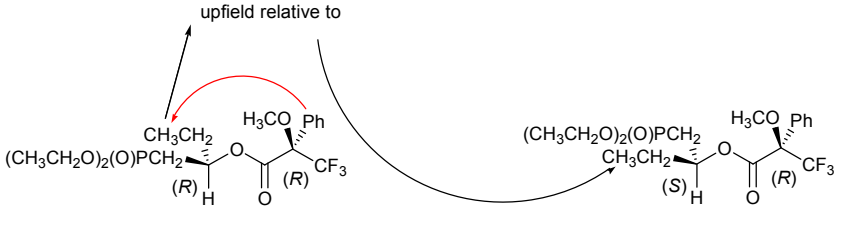
(*R*)-MTPA esters of **2a**

D.



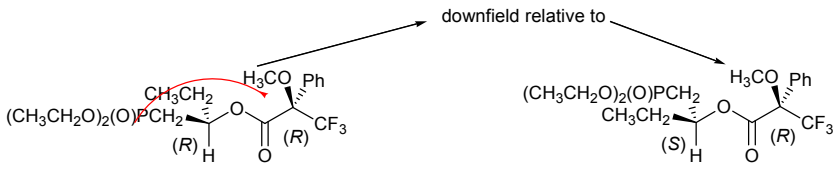
(*R*)-MTPA esters of **2a**

E.



(*R*)-MTPA esters of **3a**

F.



(*R*)-MTPA esters of **3a**

Scheme 1 Configuration correlation models for (*R*)-MTPA esters. A, B, C, E–the effect of the phenyl group of the Mosher's ester. D, F–the effect of the phosphonate group of hydroxyphosphonate.

Spectroscopic data

(*R*)-MTPA esters of 1a

Diastereoizomer (*R*,*R*). ^{31}P NMR (600 MHz, $CDCl_3$) δ (ppm) 25.22; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 1.27-1.37 (m, 6 H, P(O)(OCH_2CH_3)), 1.45 (d, 3 H, *J*=6.1 Hz, CH_3), 2.0-2.3 (m, 2 H, CH_2P), 3.58 (s, 3 H, CH_3O), 4.05-4.18 (m, 4 H, P(O)(OCH_2CH_3)), 5.4-5.5 (m, 1 H, C*H*), 7.4-7.6 (m, 5 H, C_6H_5).

Diastereoizomer (*S*,*R*). ^{31}P NMR (600 MHz, $CDCl_3$) δ (ppm) 25.16; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 1.27-1.37 (m, 6 H, P(O)(OCH_2CH_3)), 1.54 (d, 3 H, *J*=6.1 Hz, CH_3), 2.0-2.3 (m, 2 H, CH_2P), 3.58 (s, 3 H, CH_3O), 4.05-4.18 (m, 4 H, P(O)(OCH_2CH_3)), 5.4-5.5 (m, 1 H, C*H*), 7.4-7.6 (m, 5 H, C_6H_5).

(*R*)-MTPA esters of 2a

Diastereoizomer (*R*,*R*). ^{31}P NMR (600 MHz, $CDCl_3$) δ (ppm) 24.45; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 1.20-1.23 (m, 3 H, P(O)(OCH_2CH_3)), 2.31-2.61 (m, 2 H, CH_2P), 3.54 (s, 3 H, CH_3O), 3.78-4.02 (m, 4 H, P(O)(OCH_2CH_3)), 6.22-6.33 (m, 1 H, C*H*), 7.26-7.43 (m, 10 H, C_6H_5).

Diastereoizomer (*S*,*R*). ^{31}P NMR (600 MHz, $CDCl_3$) δ (ppm) 24.29; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 1.12-1.20 (td, 3 H, , *J*=7.0 Hz, P(O)(OCH_2CH_3)), 2.31-2.61 (m, 2 H, CH_2P), 3.43 (s, 3 H, CH_3O), 3.78-4.02 (m, 4 H, P(O)(OCH_2CH_3)), 6.22-6.33 (m, 1 H, C*H*), 7.26-7.43 (m, 10 H, C_6H_5).

(*R*)-MTPA esters of 3a

Diastereoizomer (*R*,*R*). ^{31}P NMR (600 MHz, $CDCl_3$) δ (ppm) 25.59; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 0.82-0.86 (t, 3 H, J=7.5 Hz, CH_3CH_2C)), 1.29-1.35 (m, 6 H, P(O)(OCH_2CH_3)), 1.67-2.01 (m, 2 H, CH_3CH_2C), 2.02-2.3 (m, 2 H, CH_2P), 3.60 (s, 3 H, CH_3O), 4.05-4.17 (m, 2 H, P(O)(OCH_2CH_3)), 5.26-5.35 (m, 1 H, C*H*), 7.40-7.60 (m, 6 H, C_6H_5).

Diastereoizomer (*S*,*R*). ^{31}P NMR (600 MHz, $CDCl_3$) δ (ppm) 25.52; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 0.95-0.99 (t, 3 H, J=7.5 Hz, C*H*$_3$CH$_2$C)), 1.29-1.35 (m, 6 H, P(O)(OCH$_2$C*H*$_3$)), 1.67-2.01 (m, 2 H, CH$_3$C*H*$_2$C), 2.02-2.3 (m, 2 H, C*H*$_2$P), 3.57 (s, 3 H, C*H*$_3$O), 4.05-4.17 (m, 2 H, P(O)(OC*H*$_2$CH$_3$)), 5.26-5.35 (m, 1 H, C*H*), 7.40-7.60 (m, 6 H, C_6H_5).

References

1. J. A. Dale, H. S. Mosher, *J. Am. Chem. Soc*., 1973, **95**, 512.
2. A. Woschek, W. Lindner, F. Hammerschmidt, *Adv. Synth. Catal*., 2003, **345**, 1287.