Organo-phosphorus compounds

S 0080 20- 176 Studies on Organophosphorus Compounds. Part 135. A Facial Chemoenzymatic Method for the Preparation of Chiral 1,2-Dihydroxy-3,3,3-trifluoropropanephosphonates. — A convenient and effective method for the preparation of the chiral isomers by enzymatic kinetic resolution of racemic (VII) is described. — (YUAN\*, C.; LI, J.; ZHANG, W.; J. Fluorine Chem. 127 (2006) 1, 44-47; State Key Lab. Bioorg. Nat. Prod. Chem., Shanghai Inst. Org. Chem., Acad. Sin., Shanghai 200032, Peop. Rep. China; Eng.) — D. Singer

$$F_{3}C \xrightarrow{O} Et \xrightarrow{H_{3}C-PO(O-Et)_{2}} (II), BuLi, THF$$

$$F_{3}C \xrightarrow{PO(O-Et)_{2}} + F_{3}C \xrightarrow{PO(O-Et)_{2}} III IV$$

III and IV 
$$\frac{\text{NaBH}_4, \text{ H}_2\text{O/Et-OH (1:1)}}{\text{0 -> 25°C}} \text{F}_3\text{C} \xrightarrow{\text{OH}} \text{PO(0-Et)}_2$$

$$V \xrightarrow{\text{Mes-CI, NEt}_3, CH_2CI_2} F_3C \xrightarrow{\text{PO}(0-\text{Et})_2} \frac{\text{KMnO}_4, H_2O}{0 \rightarrow 25^{\circ}\text{C}} F_3C \xrightarrow{\text{OH}} F_3C \xrightarrow$$

$$(\pm)-\text{VII} \xrightarrow{\begin{array}{c} 2 \text{ equiv. CI} \\ \text{COOH (VIII)} \\ \text{2.4 equiv. DCC} \\ \text{DMAP (cat.), CH}_2\text{CI}_2 \\ \text{0 -> 25°C} \end{array}} \begin{array}{c} \text{CI} \\ \text{F}_3\text{C} \\ \text{O} \\ \text{O} \\ \text{(+)-IX 90\%} \end{array}$$

$$(\pm)-\mathrm{IX} \xrightarrow{\text{lipase B (Candida antarctica)} \atop \text{BuOH, benzene}} + F_3C \xrightarrow{\text{CI}} PO(O-\mathrm{Et})_2 \\ (-)-\mathrm{IX}^* \ 38\% \qquad (-)-\mathrm{IX}^* \ 39\%$$

$$(-)-X^* \xrightarrow{A)} F_3C \xrightarrow{QH} PO(O-Et)_2 \\ (-)-VII^* \\ 88\% (78\% \text{ e.e.})$$

$$(-)-IX^* \xrightarrow{A)} F_3C \xrightarrow{QH} PO(O-Et)_2 \\ OH \\ (+)-VII^* \\ 90\% (75\% \text{ e.e.})$$

A): aq. NH<sub>3</sub>, MeOH, 25°C, [3 h]