1999 alkaloids

alkaloids U 0600 08 - 239

Asymmetric Synthesis of Alkaloid (-)-(2S,4S) SS 20846 A and Its C-4 Epimer. — Ongoing interest in the stereoselective synthesis of polysubstituted piperidines leads to the development of a methodology to generate piperidines such as (V) and (-)-(VI). The latter is transformed to the title compound (-)-(XI). The C-4-epimer is easily obtained from (+)-(IX). The starting material (-)-(I) is obtained via the reaction of the corresponding sorbic ester with $Fe(CO)_5$ and chromatographic separation of the diastereomers. — (RIPOCHE, I.; CANET, J.-L.; ABOAB, B.; GELAS, J.; TROIN, Y.; J. Chem. Soc., Perkin Trans. 1 [old] (1998) 20, 3485-3492; Ec. Natl. Super. Chim. Clermont-Ferrand, F-63174 Aubiere, Fr.; EN)

Fe(CO)₃
Me

CO-O-Me

(-)-I*

$$\frac{1. \text{ KOH, MeOH } (79\%)}{2. \text{ KOH, H}_2\text{O/EtOH } (1:1) (83\%)}}{2. \text{ KOH, H}_2\text{O/EtOH } (1:1) (83\%)}$$
Fe(CO)₃
Me

(-)-II*

$$\frac{1. (\text{CO-Cl})_2, \text{ CH}_2\text{Cl}_2}{2. (\text{PPh}_3)_2\text{CuBH}_4, \text{ acetone}}}$$
Me

COOH

(-)-II*

Fe(CO)₃

Me

CHO

(-)-III*

$$\begin{array}{c} \text{Fe}(\text{CO})_3 \\ \text{Fmoc-Cl} \quad (\text{VII}), \; (\text{iPr})_2 \text{N-Et}, \; \text{CH}_2 \text{Cl}_2 \; (89\%) \\ \hline 2. \; 40\% \; \text{aq}, \; \text{TFA}, \; \; \text{CH}_2 \text{Cl}_2 \; (96\%) \\ \hline \\ \text{(-)-VIII*} \end{array}$$

$$(+)-X^*$$
 $\xrightarrow{\text{Me}_3N^+-D^-, acetone}$ $\xrightarrow{\text{Me}}$ $\xrightarrow{\text{Me}}$ $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{OH}}$ $(-)-XI^*$ 50% (100% e.e.)