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Asymmetric Syntheses of New Phosphonotaxoids

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Asymmetric Syntheses of New Phosphonotaxoids

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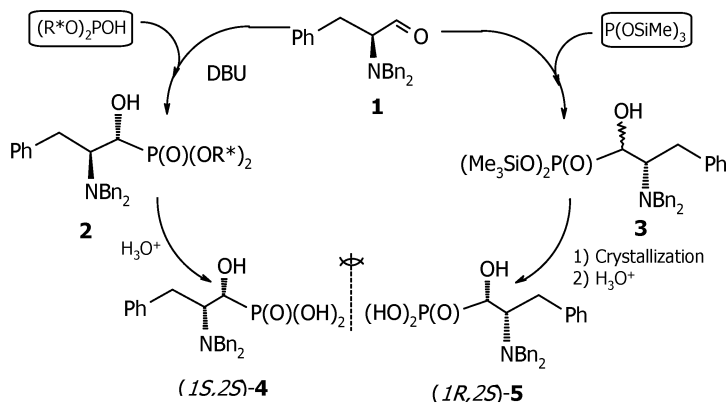
Chiral 1-hydroxy-2-aminophosphonic acids were used for modification of Baccatin III in the synthesis of new taxoids.

Keywords Asymmetric synthesis; chiral hydroxyphosphonates; multistereoselectivity; taxoids

The multiple asymmetric induction (multistereoselectivity) is an efficient method for increasing the stereoselectivity of the phospho-aldol reaction by employing more than one chiral auxiliary. For example, chiral dialkylphosphites react with chiral aldehydes under the control by two chiral auxiliaries, which reinforced one another, to yield the diastereomers **2** with very good *de*. Chiral aldehydes **1** reacted with the (1*R*, 2*S*, 5*R*)-dimenthylphosphite or di-*endo*-bornylphosphite with the formation of either chiral (1*S*, 2*S*)- or (1*R*, 2*S*)-1-hydroxy-2-aminophosphonic acids **4**. The reaction of dibenzylphenylalanyl **1** with *tris*(trimethylsilyl)phosphite afforded the (1*R*, 2*S*)-1-hydroxy-2-aminoalkylphosphonic acid **5**, which was purified by recrystallisation. The stereoselectivity of the reaction depended on the solvent, the nature of the bases and temperature. The absolute configuration of the addition product was proved by NMR spectroscopy and X-ray analysis.

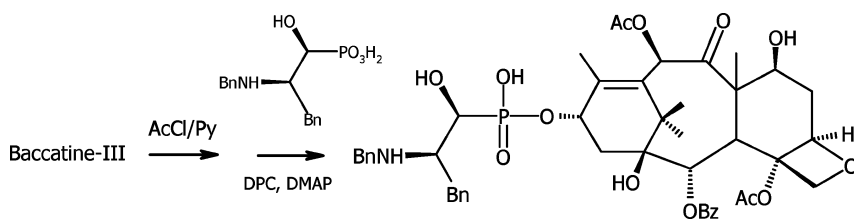
The chiral 1-hydroxy-2-aminophosphonic acids were used for modification of Baccatin III in the synthesis of new taxoids—potential anti-cancer agents

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$R^* = (1R,2S,5R)$ -Mnt (80% ee), Brn (80% ee)

SCHEME 1



SCHEME 2

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