(S)-(−)-1-Amino-2-methoxypyrrolidine (SAMP) and (R)-(+)1-Amino-2-methoxypyrrolidine (RAMP) as Versatile Chiral Auxiliaries

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Recently SAMP/RAMP chiral auxiliaries was efficiently used as chiral auxiliaries in various important reactions, which includes the palladium catalyzed allylic substitution, asymmetric synthesis of substituted β-formyl δ-lactones and furofuran lactones, diastereo- and enantioselective synthesis of syn-2,3-disubstituted, 1,4-diketones, diastereoselective electrophilic fluorination of enantiopure α-silylketones, recemization free cleavage of ketones SAMP hydrazones, diastereo-and enantioselective synthesis of various 1,2-anti tert-butyl sulfanyl amines, asymmetric synthesis of γ-amino nitriles and γ-amino ketones etc.

Abstracts

(A) An efficient method has recently been developed for the diastero- and enantioselective Michael addition of metalated lactones-SAMP hydrazones to enolates. The lactone esters (S/R,S)-2 were synthesized in good overall yields (37–61%, two steps, high de, ee) by 1,2-addition of metalated lactone SAMP hydrazones to enolate Michael acceptors 2 and subsequent oxidative cleavage of the product of the hydrazones by ozonolysis. The present method represents a bifunctional building block for further synthetic applications.10
(B) Enders et al.\textsuperscript{11} reported the short diastereo- and enantioselective synthesis of cis-4,5-disubstituted oxazolidin-2-ones using SAMP chiral auxiliary in a four step reaction sequence – α-alkylation, 1,2-addition with subsequent carbamate protection, cyclization and concluding with cleavage of the auxiliary. The title compounds are obtained in moderate yields and in excellent de and ee. The use of RAMP as auxiliary gave cis-(4\textit{R},5\textit{S}) the enantiomer of SAMP gave cis-(4\textit{S},5\textit{R}).

(C) SAMP/RAMP was used in the first asymmetric synthesis of (S)- and (R)-Stigmolane. The stereogenic centre at the C-5 position of the pheromone was generated via SAMP/RAMP hydrazine methodology with high enantiomeric purity.\textsuperscript{12}

(D) Very recently the asymmetric synthesis of protected 2-keto-1,3-diols and 1,2,3 triols bearing a quaternary stereogenic center starting from 2,2-dimethyl-1,3-dioxan-5-one was reported.\textsuperscript{13} The stereogenic centers are generated by sequential α-alkylation using SAMP/RAMP hydrazine methodology and stereoselective reduction of the ketone generated with L-selectride. The key step in the synthesis was a subsequent third metalation and alkylation of intermediate to install the quaternary stereocentre. The products are obtained in good yields and high de and ee.

References


