Heteroannelations with Pinane-Type Chiral $\beta$-Enaminoaldehyde

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$\alpha$-Pinene is among the most wide spread natural monoterpenes. Our study was planned to outwork synthetic approaches towards heterocyclic derivatives of $\alpha$-pinene which are of interest from the viewpoint of biological activity. Pinane-type $\beta$-enaminoaldehyde 3 derived from the readily accessible isoxazole 2 was found to be a source for series of chiral heterocycles containing pyridine and pyrimidine moieties.

Because of steric hindrance arises from bicyclic structure with gem-dimethylcyclobutane moiety, $\beta$-enaminoaldehyde 3 is quite stable compound towards addition reaction, and heteroannelations of 3 needs generally more rigid conditions than it has been reported for $\alpha$-aminobenzaldehyde. Acid-catalyzed reaction of 3 with cyclic ketones results in formation of pyridine-annelated products 4 in very good yields. Acylation of 3 and subsequent treatment with hydroxylamine affords the annelated pyrimidine-N-oxides 5 in excellent yields. 2-Amino- and 2-H-substituted pyrimidines 6 were also obtained in the reaction of 3 with cyanamide and formamide correspondingly.

New fused heterocyclic compounds 4-6 are prospective as potential biologically active molecules as well as chiral auxiliary.

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