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Title:	Synthesis of β -cyanoalanine and enantiomerically enriched aspartate derivatives via the Zn- or In-mediated nucleophilic addition to α -imino esters
Authors:	Sudha, A.J. (/jspui/browse?type=author&value=Sudha%2C+A.J.) Aslam, N.A. (/jspui/browse?type=author&value=Aslam%2C+N.A.) Sandhu, Akshey (/jspui/browse?type=author&value=Sandhu%2C+Akshey) Babu, S.A. (/jspui/browse?type=author&value=Babu%2C+S.A.)
Keywords:	β -cyanoalanine Aspartic acid derivatives Stereoselective synthesis Unnatural amino acids Reformatsky/Barbier-type reaction
Issue Date:	2020
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Abstract:	We report the synthesis of β -cyanoalanine derivatives and enantiomerically enriched aspartates. The zinc-mediated addition of α -bromoacetonitrile to α -imino esters afforded various β -cyanoalanine derivatives 3a-l and 5a-d in satisfactory to good yields. The zinc- or indium-mediated addition of α -bromoacetonitrile or ethyl 2-bromoacetate to enantiopure N-tert-butanefulfinyl α -imino esters gave the corresponding products 3m-p in satisfactory yields and diastereoselectivity. Notably, the indium-mediated addition of alkyl 4-bromocrotonates to enantiopure N-tert-butanefulfinyl α -imino esters gave the corresponding enantiomerically enriched β -vinyl aspartates 10c-e (aspartic acid derivatives) with high diastereoselectivity (syn isomers). The stereochemistry of the vicinal stereocenters of the compounds 10c-e (major isomers) were assigned based on the X-ray structure of a derivative 11d which was obtained from 10c. To show the utility of β -cyanoalanine and β -vinyl aspartate derivatives, representative β -cyanoalanine compounds 3a/3b, 5d and aspartic acid derivative 10c were subjected to selected synthetic transformations.
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