Title:	Diastereoselective Construction of 3-Aminooxindoles with Adjacent Stereocenters: Stereocontrolled Addition of γ-Substituted Allylindiums to Isatin Ketimines
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Abstract:	The diastereoselective construction of 3-allyl-3-aminooxindoles that have two adjacent stereocenters has been achieved by the In-promoted Barbier-type addition of γ-substituted allylic halides to the C=N bond of isatin ketimines. The reactions of cinnamyl-, crotyl-, and geranylindium compounds with isatin ketimines proceeded in either aqueous or alcohol solution. The addition of a cyclohexenylindium species to an isatin ketimine was carried out in N,N-dimethylformamide (DMF), and the addition of ethyl 4-bromocrotonate to an isatin ketimine in EtOH gave oxindole-based β-amino acid scaffolds. In all of these processes, the reaction conditions were screened to obtain the respective 3-allyl-3-aminooxindoles with very high stereoselectivity. In addition, plausible TS models are proposed, and representative synthetic transformations were carried out by using the oxindole-based β-amino acid scaffolds. Furthermore, the stereochemistry of representative compounds were unequivocally established by single-crystal X-ray structure analysis. A synthetic protocol for the diastereoselective indium-mediated Barbier-type C-C bond formation has been developed. The addition of γ-substituted allylic reagents to the C=N bond of isatin ketimines was employed for the synthesis of several new 3-aminooxindoles that have two contiguous stereocenters.
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