

Enantioselective syntheses

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Dynamic Kinetic Asymmetric Allylic Amination and Acyl Migration of Vinyl Aziridines with Imido Carboxylates. — Palladium-catalyzed reaction of vinylaziridines (I) with diacylamines (II) in the presence of a bidentate ligand (BNAC) provides access towards chiral vicinal diamines (III). The reaction proceeds with excellent re-

dines (I) with diacylamines (II) in the presence of a bidentate ligand (BNAC) provides access towards chiral vicinal diamines (III). The reaction proceeds with excellent regioselectivity and is accompanied by N-acyl migration. This step depends on the electronic and steric properties of the acyl residues. The amination—acyl migration product (IIIf) is transformed to azepine (VII), a key precursor of balanol (VIII), and its epimer (XI). — (TROST*, B. M.; FANDRICK, D. R.; BRODMANN, T.; STILES, D. T.; Angew. Chem., Int. Ed. 46 (2007) 32, 6123-6125; Dep. Chem., Stanford Univ., Stanford, CA 94305, USA; Eng.) — Mischke

(+)-X*

(-)-XI*



$$Io \xrightarrow{\text{Pht-H } (\text{XII}), \text{ Pd}_2\text{Cl}_2(\text{aliyl})_2/(\text{R,R})-\text{BNAC}/\text{Et}_3\text{N } (\text{cot.})} \\ CH_2\text{Cl}_2, \text{ 25°C, [sealed tube]} \xrightarrow{\text{Pht}} H_2\text{C} \xrightarrow{\text{NH-Bn}} \text{NH-Bn} \text{ Pht: -N} \\ (\text{R,R})-\text{BNAC:} \xrightarrow{\text{NH-Bn}} H_2\text{C} \xrightarrow{\text{Phph}_2} Ph_2\text{Ph}_2} \xrightarrow{\text{Phph}_2} Ph_2\text{Ph}_2 Ph_2\text{Ph}_2} \\ H_2\text{C} \xrightarrow{\text{O}} \xrightarrow{\text{A}} H_2\text{C} \xrightarrow{\text{EiOH}} H_2\text{C} \xrightarrow{\text{NH-Boc}} H_2\text{C} \xrightarrow{\text{NH-Boc}} H_2\text{C} \xrightarrow{\text{NH-Boc}} \text{NH-Boc} \\ \text{XIV} \xrightarrow{\text{R}} (\text{R})-(+)-\text{XV} \\ 72\% (\text{90\% e.e.}) \xrightarrow{\text{R}} (\text{R}) \xrightarrow{\text{R}} (\text{R}) \xrightarrow{\text{R}} (\text{R}) \xrightarrow{\text{NH-Bn}} (\text{R}) \xrightarrow{\text{R}} (\text{R}) \xrightarrow{\text{R$$