Rh 触媒 C-H アミノ化反応を利用する 1,3-二置換アダマンタンの不斉非対称化:アダマンタン母格をもつ光学活性アミノ酸の合成

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Enantioselective Desymmetrization of 1,3-Disubstituted Adamantane Derivatives via Rhodium-Catalyzed C–H Bond Amination: Access to Optically Active Amino Acids Containing Adamantane Core

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In order to synthesize optically active amino acids containing the adamantane core, an enantioselective desymmetrization of adamantanes via rhodium-catalyzed C–H bond amination was examined. After investigating various conditions, it was found that the coupling reaction between disubstituted adamantane and aryloxysulfonamide was catalyzed by Rh₂(S-TCPTTL)₄ to furnish the desired products having up to 85% ee. The synthetic utility of the enantioenriched products as chiral building blocks was demonstrated by transforming one of them into a dipeptide derivative and a Schiff-base ligand. The absolute configuration of one of the amino acid derivatives was determined unambiguously by X-ray single-crystal structure analysis.

Keywords: Adamantanes; Amino Acids; Chiral Building Blocks; Enantioselective Desymmetrization; Rh-catalyzed C–H Amination

1,3-二置換アダマンタンに対してロジウム触媒を利用する C-H アミノ化反応による不斉非対称化を実施した。様々な条件検討を行った結果、 $Rh_2(S-TCPTTL)_4$ を触媒として用いることで、最高 85% ee でアダマンタンを母格にもつ光学活性アミノ酸誘導体を得ることができた。次に、得られた生成物を新たなキラルビルディングブロックとして、ジペプチドやキラル配位子に変換した 1)。

1) R. Yasue, K. Yoshida, Adv. Synth. Catal. 2021, 363, 1662-1671.