

## オキシインドール型磁気異方性試薬によるキラル第一級アミン類の絶対配置の決定

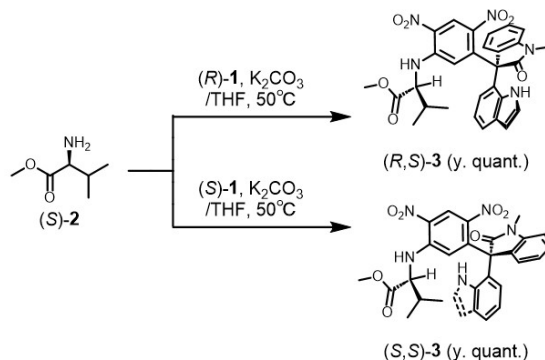
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Determination of the Absolute Configurations of Chiral Primary Amines by Oxyindole-Type Chiral Derivatizing Agents (<sup>1</sup>*Department of Chemistry and* <sup>2</sup>*Research Center for Materials with Integrated Properties, Toho University,* <sup>3</sup>*Department of Chemistry, Education Center, Chiba Institute of Technology*) ○Haruki Kumagai,<sup>1</sup> Ryosuke Kimura,<sup>1</sup> Mari Ikeda,<sup>3</sup> Yoichi Habata,<sup>1,2</sup> Shirai Tomohiko,<sup>1</sup> Shunsuke Kuwahara<sup>1,2</sup>

A convenient method for determining the absolute configuration of chiral amines is to use a chiral derivatizing agent (CDA)<sup>1)</sup>. Recently we reported the synthesis of new oxyindole derivatives (*R*)-, (*S*)-**1** and the determination of the absolute configuration of aliphatic chiral primary amines. In this study, (*R*)-, (*S*)-**1** was applied to chiral primary amines, amino alcohols, and amino acid esters. Chiral primary amines and amino alcohols reacted with (*R*)- and (*S*)-**1** in THF in the presence of potassium carbonate in 1 hour at room temperature. On the other hand, the amino acid ester (*S*)-**2** reacted slowly with (*R*)- and (*S*)-**1** at room temperature, but when the temperature was raised to 50°C, the reaction was completed in about 3 hours, and the conjugates (*R,S*)-**3** and (*S,S*)-**3** were quantitatively obtained. We also report the determination of the absolute configurations of (*S*)-**2** by the differences in the chemical shifts ( $\Delta\delta^{RS}$ ) of (*R,S*)-**3** and (*S,S*)-**3** in <sup>1</sup>H NMR spectra.

Keywords : Chiral derivatizing agent; Determination of the absolute configuration; Chiral primary amine; Oxindole

キラルアミンの簡便な絶対配置の決定法として、磁気異方性試薬を用いる方法がある<sup>1)</sup>。近年我々は、新規オキシインドール誘導体(*R*)-, (*S*)-**1**を合成し、脂肪族キラルアミンの絶対配置を決定したことを報告した。今回(*R*)-, (*S*)-**1**とキラルアミノアルコール、アミノ酸エステル類を炭酸カリウム存在下 THF 中で混合し、種々の連結体を得た。脂肪族アミンおよびアミノアルコールは(*R*)-, (*S*)-**1**と室温下1時間程度で反応した。一方、アミノ酸エステル(*S*)-**2**は(*R*)-, (*S*)-**1**と室温下では反応が遅かったが、50°Cに昇温したところ3時間程度で反応が完結し、連結体(*R,S*)-**3**, (*S,S*)-**3**を定量的に得た。<sup>1</sup>H NMRにおける(*R,S*)-**3**, (*S,S*)-**3**の化学シフト差 ( $\Delta\delta^{RS}$ )による絶対配置決定についても報告する。



1) Kriegelstein, M.; Profous, D.; Lyčka, A.; Trávníček, Z.; Příbylka, A.; Volná, T.; Benická, S.; Cankař, P. *J. Org. Chem.* **2019**, *84*, 11911–11921.