

Division of Synthetic Chemistry - Synthetic Organic Chemistry -

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Visitors

Prof KAGAN, Henri Université de Paris-Sud, France, 11 May 2007
Prof SMITH, Amos B University of Pennsylvania, USA, 3 November 2007

Scope of Research

The research interests of the laboratory include the development of advanced molecular transformation, total synthesis of biologically active products, and molecular recognition. Programs are active in the areas of asymmetric alkylation of carbonyl compounds based on “memory of chirality”, nucleophilic catalysis for fine organic syntheses, synthesis of unusual amino acids and nitrogen heterocycles, visualization of molecular information by functional phenolphthaleins, synthesis and properties of homochiral oligonaphthalenes, and the structural and functional investigation of heterochiral oligomers.

Research Activities (Year 2007)

Publication

Kawabata T, Muramatsu W, Nishio T, Shibata T, Schedel H: A Catalytic One-Step Process for the Chemo- and Regioselective Acylation of Monosaccharides, *J. Am. Chem. Soc.*, **129**, 12890-12895 (2007).

Presentations

Asymmetric Synthesis of Amino Acids with a Tetra-substituted Carbon Center via Memory of Chirality, 233rd ACS National Meeting, Kawabata T, 26 March 2007.

Colorimetric Recognition of Spermidine and Spermine Based on Phenolphthalein Derivatives, Tsubaki K, 21st International Congress for Heterocyclic Chemistry, 17 July 2007.

Kinetic Resolution of (±)-1,1'-Binaphthyl-8,8'-diamines by Chiral PPY Organocatalysts, VALLURU R K, 12th

International Symposium on Novel Aromatic Compounds, 23 July 2007.

Fine Molecular Transformation by Nucleophilic Catalysis, Kawabata T, ICCT-2007, 16 December 2007.

Grants

Kawabata T, Fine Organic Synthesis by Nucleophilic Catalysis, Grant-in-Aid for Scientific Research (A), 1 April 2006–31 March 2009.

Kawabata T, Advanced Molecular Transformation with Functional Carbanions, Grant-in-Aid for Scientific Research on Priority Areas, 1 October 2005–31 March 2009.

Kawabata T, Creation of Novel Binaphthyls with Inner Hydrogen Bonding, Grant-in-Aid for Exploratory Research, 1 April 2007–31 March 2009.

Synthesis and Determination of the Absolute Configuration of Chiral Tetracosanaphthalenes

Oxidative coupling of all-(*R*)-**1** and all (*R*)-**2** gave three diastereomeric 24-mers **3**. The mixture of diastereomers was purified by recycling preparative HPLC to give pure diastereomers (Figure 1, fractions 1-3). In order to determine the absolute configuration of the 24-mers with two unknown axes, tetraphenylporphyrin (TPP) was introduced into four phenolic hydroxy groups to give **4**. Based on the CD spectra of **4** (Figure 2), the diastereomer in fraction 1 with a large positive Cotton effect, the diastereomer in fraction 2 with a weak CD intensity, and the diastereomer in fraction 3 with a large negative Cotton

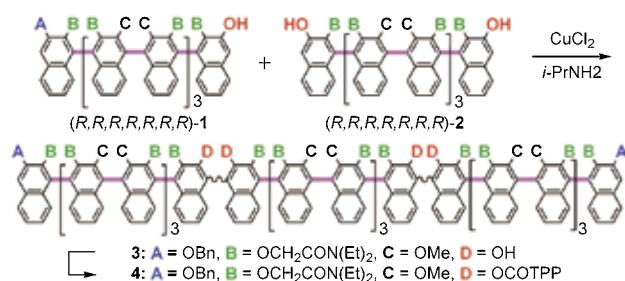


Figure 1.

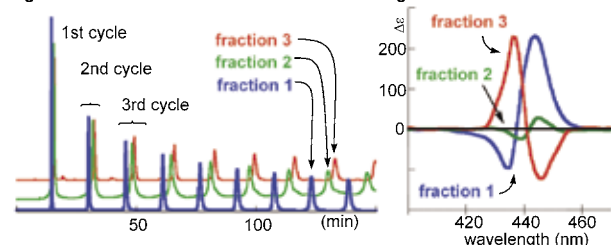


Figure 2.

effect were determined to be (*R,R,R,R,R,R,S,R,R,R,R,R,R,R,S,R,R,R,R,R,R,R,R*), (*R,R,R,R,R,R,R,R,R,R,R,R,R,R,S,R,R,R,R,R,R,R*), and (*R,R*), respectively.

A Novel Binaphthyl Analogue with Inner Hydrogen Bonding

Chiral binaphthyls have been extensively utilized as ligands for asymmetric synthesis. A novel binaphthyl analogue **5** based on inner hydrogen bonding has been created. The N-H of **5** appears at 13.2 ppm in its ¹H NMR spectrum, indicating extremely strong hydrogen bonding. Enantiomers of **5** were stable at the ambient temperature and separable by HPLC with a chiral stationary phase. The half life of racemization of the enantiomer is ≥ six months at 20°C and the barrier for racemization is 27.4 kcal/mol. X-ray crystal analysis of **5** shows that the pseudo-naphthyl skeleton including C=N...H-N is almost completely planar, and the dihedral angle between the pseudo-naphthalene and naphthalene rings is 110°.

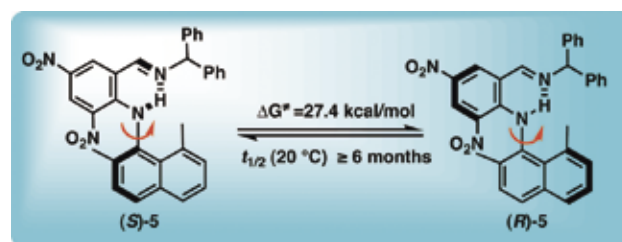


Figure 3. An enantiomerically stable binaphthyl analogue with Inner N-H-N hydrogen bonding.

Tsubaki K, Construction of Molecular Recognition System in Water and Rapid Quantification of Polyamines, Grant-in-Aid for Scientific Research (B), 1 April 2006–31 March 2009.

Tsubaki K, Synthesis and Properties of Optically Active Oligonaphthalene Derivatives, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Awards

Takaishi K, Impressive Presentation Award, Synthesis of Higher Order Oligonaphthalenes and Optical Property of TPP, TPP-Zn Adducts, 2nd Host Guest Chemistry Symposium, 25 May 2007.

Tsubaki K, HGCS Japan Award of Excellence 2007, Colorimetric Recognition Using Functional Phenolphthalein Derivatives, 12 July 2007.

Moriyama K, Best Poster Award, Metal Hydroxide-

Promoted Asymmetric Cyclization via Memory of Chirality at Room Temperature: Construction of Cyclic Amino Acids with a Tetrasubstituted Carbon Center, The 92nd Symposium on Organic Synthesis, Japan, 9 November 2007.

Tomohara K, Best Poster Award, Synthesis of Cyclic Ethers with a Tetrasubstituted Carbon Center via C-O Axially Chiral Enolates, The 27th Seminar on Synthetic Organic Chemistry for Young Scientists, 15 November 2007.

Muramatsu W, ICR Award for Graduate Students, A Catalytic One-Step Process for the Chemo- and Regioselective Acylation of Monosaccharides, 7 December 2007.

Imamura Y, Best Poster Award, Development of Highly Sensitive and Selective Molecules for Detection of Spermidine and Spermine, 1st Symposium on Organic π -Electron Systems, 8 December 2007.