

[*Tetrahedron Lett.*, **39**, 5799-5802 (1998)]

[Lab. of Pharm. Synthetic Chemistry]

**Unprecedented Polymer-supported  $\pi$ -Acid: Synthesis and Its Application as a Promoter to the Monothioacetalization of Acetals**

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A novel polymer was synthesized by copolymerization of styrene monomer bearing dicyanoketene acetal functionality and ethylene glycol dimethacrylate, and used successfully as a recyclable  $\pi$ -acid catalyst in monothioacetalization of aromatic, aliphatic, acyclic, and cyclic acetals with thiophenol and phenylthiotrimethylsilane.

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[Lab. of Pharm. Synthetic Chemistry]

**Selective Acceleration for Deprotection of Benzyl Ethers with Ti-HMS**

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Ti-HMS, a Ti-loaded hexagonal mesoporous silica, was found to accelerate deprotection of benzyl ethers under hydrogenolytic conditions with palladium catalyst. Such acid-sensitive functional groups as silyl ether and acetal moieties in the molecule were little affected by Ti-HMS, which possesses Lewis-acid sites due to Ti-atom.

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[Lab. of Pharm. Synthetic Chemistry]

**Chiral  $C_2$ -Symmetric 2,5-Disubstituted Pyrrolidine Derivatives as Catalytic Chiral Ligands in the Reactions of Diethylzinc with Aryl Aldehydes**

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Two kinds of chiral  $C_2$ -symmetric 2,5-disubstituted pyrrolidines having a  $\beta$ -aminoalcohol moiety have been successfully synthesized and their catalytic abilities of chiral induction have been examined in the reactions of diethylzinc with substituted benzaldehydes. The production of *sec*-alcohols having (*R*)-configuration could be achieved in very high chemical yields (85—95%) and enantiomeric excess (ee) (70—96%) when *N*-(2',2'-diphenyl-2'-hydroxyethyl)-(2*R*,5*R*)-bis(methoxymethyl)pyrrolidine was used as a chiral ligand. On the other hand, when an *N*-methyl-(2*R*,5*R*)-bis(diarylhydroxymethyl)pyrrolidine was used as a chiral ligand, the ee of the corresponding *sec*-alcohols decreased to 20—45% and an interesting inversion of the enantioselectivity was observed in the reaction of several halogen-substituted benzaldehydes.

[*Thin Solid Films*, **316**, 158-164 (1998)]

[Lab. of Pharm. Physical Chemistry]

**Plasma-induced Free Radicals of Polycrystalline Dicarbohyrates Studied by Electron Spin Resonance.**

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We report here special features of plasma-induced free radicals of dicarbohyrates, such as maltose and cellobiose, on its comparison with those of amylose and cellulose. The simulated spectra disclosed that the observed spectra of maltose consist of four kinds of spectral components, two isotropic spectra [doublet (I) and triplets (II)], both being assigned to hydroxylalkyl radicals and an anisotropic spectrum [doublet of doublets (IV)], assigned to an acylalkyl radical, and a smeared-out single line spectrum (V), assigned to an immobilized dangling-bond site (DBS) at the surface cross-linked region. On the other hand, those of cellobiose consist of five kinds of spectral components, I, II, IV, V and triplet spectrum (III) different in hyperfine splitting constant (HSC) from II, but assignable to the other hydroxylalkyl radicals.