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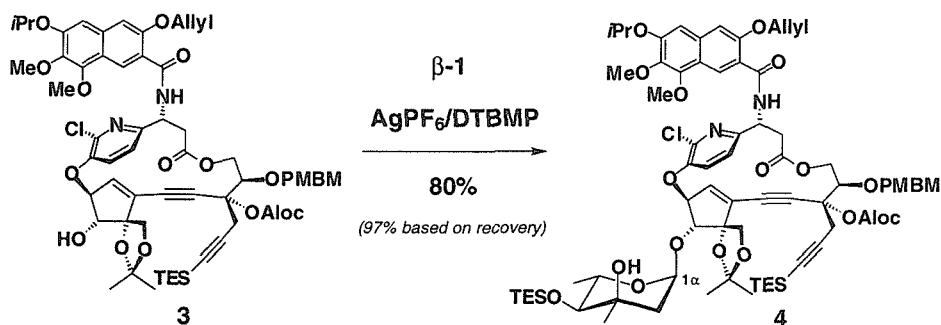
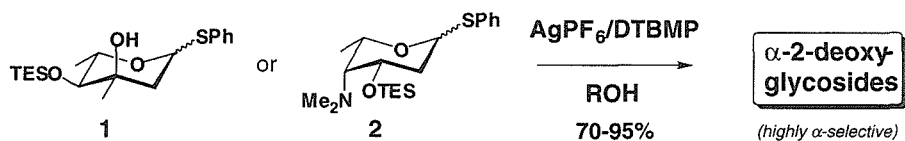
ケダルシジンの2-デオキシ糖のグリコシル化研究

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Concise synthetic routes to the phenyl thioglycosides of the kedarcidin 2-deoxysugars, L-mycarose (1) and L-kedarasamine (2), will be presented together with direct protocols to generate either α - or β -2-deoxyglycosides with high or complete stereochemical control.^{1,2)}

Significantly, a novel and straightforward α -selective protocol has been developed from the unprotected thioglycosides (1, 2) using AgPF₆ and DTBMP (2,6-di-*tert*-butyl-4-methylpyridine) as a remarkably effective activating system.

This potent, yet very mild, method can be applied to sterically hindered alcohols with sensitive functionality and is exemplified in an advanced synthetic study toward the total synthesis of the kedarcidin chromophore (cf. 3 \rightarrow 4).³⁾



1) M. J. Lear, M. Hirama, *Tetrahedron Lett.* **1999**, *40*, 4897.

2) M. J. Lear, F. Yoshimura, M. Hirama, submitted.

3) For recent synthetic work, see: F. Yoshimura, S. Kawata, M. Hirama, *Tetrahedron Lett.* **1999**, *40*, 8281.

"Glycosylation Studies of the 2-Deoxysugars of the Kedarcidin Chromophore"

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Synthetic Study of Norzoanthamine Alkaloid: Asymmetric Synthesis of the ABC-ring Moieties.

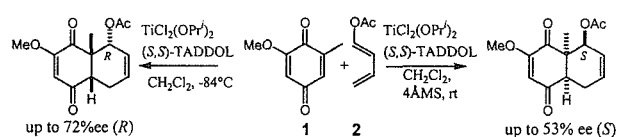
○ Sameh M. Moharram, Go Hirai, Hiroki Oguri and Masahiro Hirama

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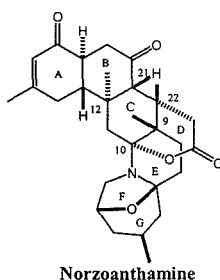
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The marine metabolite norzoanthamine alkaloid, which suppresses the decrease in bone weight and strength in ovariectomized mice, is classified as promising osteoporotic drug.

The stereo-controlled synthesis of racemic C-ring moiety possessing three consecutive quaternary carbon centers has been established.¹ The asymmetric synthesis of C-ring moiety was realized by Diels-Alder reaction of 2-methoxy-6-methyl-1, 4-benzoquinone (1) with 1-acetoxy-1,3-butadiene (2) promoted by (*S,S*)-TADDOL-Ti complex. The enantio-selectivity was significantly affected by the presence of 4Å molecular sieves (Scheme 1).²

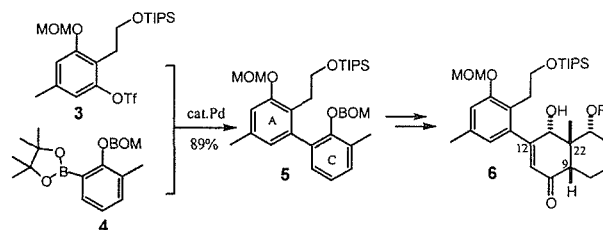


Scheme 1: Asymmetric Diels-Alder reaction.



We demonstrated that the capture of HCl by 4Å MS plays a crucial role for the enantio-face control in the Diels-Alder reaction.

A convergent synthesis of the A-C ring moiety 6 from 3 and 4 was accomplished by applying the Suzuki-Miyaura coupling condition (Scheme 2). The stereo-controlled construction of the quaternary carbon centers (C9, C12 and C22) will be presented.



Scheme 2: Suzuki-Miyaura cross coupling.

1) Hirai, G.; Oguri, H.; Hirama, M. *Chem. Lett.* **1999**, 141-142.

2) Moharram, S. M.; Hirai, G.; Oguri, H.; Hirama, M. *Tetrahedron Lett.* **2000**, *41*, 6669.