

Studies on the Selectivity Between Nickel-Catalyzed 1,2-*Cis*-2-Amino
Glycosylation of Hydroxyl Groups of Thioglycoside Acceptors with C(2)-Substituted
Benzylidene *N*-Phenyl Trifluoroacetimidates and Intermolecular Aglycon Transfer of
the Sulfide Group

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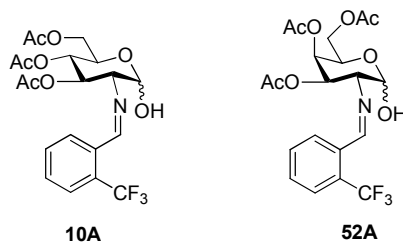
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Methods and Reagents. All reactions were performed in oven-dried Schlenk flasks fitted with glass stoppers under a positive pressure of argon. Organic solutions were concentrated by rotary evaporation below 40 °C at 25 torr. Analytical thin-layer chromatography (TLC) was routinely used to monitor the progress of the reactions and performed using pre-coated glass plates with 230-400 mesh silica gel impregnated with a fluorescent indicator (250 nm). Visualization was achieved using UV light, iodine, or ceric ammonium molybdate. Flash chromatography was performed and employed 230-400 mesh silica gel. Dichloromethane were distilled from calcium hydride under an argon atmosphere at 760 torr. All of the nickel catalysts were prepared according to the literature procedure.¹ All other chemicals were obtained from commercial vendors and used without further purification.

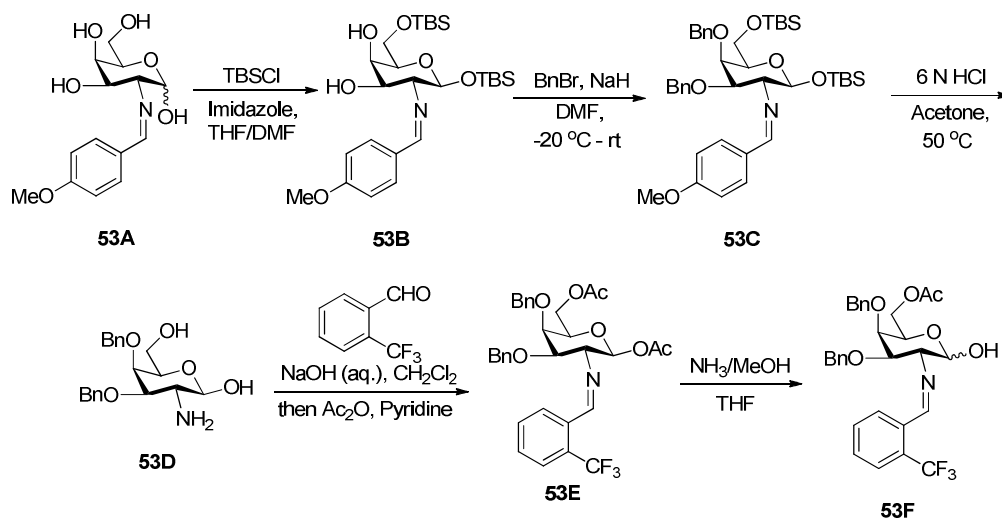
Instrumentation. All proton (¹H) nuclear magnetic resonance spectra were recorded on 400 MHz spectrometer. All carbon (¹³C) nuclear magnetic resonance spectra were recorded on 100 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (CDCl₃: δ 7.26 ppm, δ 77.00 ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and brs = broad singlet), integration, and coupling constant in hertz (Hz). Infrared (IR) spectra were reported in cm⁻¹. High resolution TOF mass spectrometry utilizing electrospray ionization in positive mode or electron ionization was performed to confirm the identity of the compounds.

A) Trichloroacetimidate donors **1** and **2** were prepared according to our reported procedure.

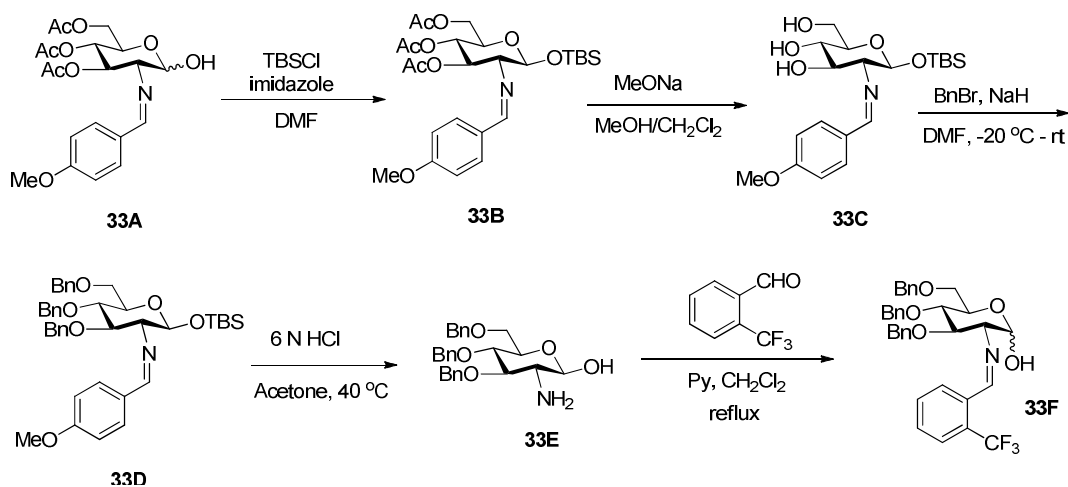
B) D-Glucosamine and Galactosamine Hemiacetals **10A** and **52A** were prepared according to our reported procedure.



C) Synthetic Scheme of 6-*O*-Acetyl-3,4-di-*O*-Benzyl-D-Galactosamine Hemiactal **53F**



D) Synthesis of 3,4,6-*O*-tri-*O*-Benzyl-D-Glucosamine Hemiactal **33F**



(1) (a) Bomfim, J. A. S.; de Souza, F. P.; Filgueiras, C. A. L.; de Sousa, A. G.; Gambardella, M. T. P. *Polyhedron* **2003**, 22, 1567. (b) Qian H.; Pei, T.; Widenhoefer, R. A. *Organometallics* **2005**, 24, 287.