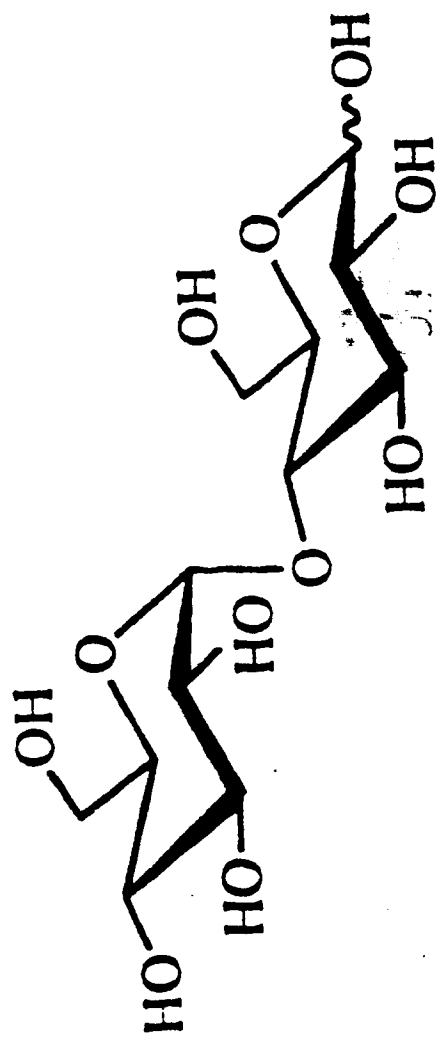
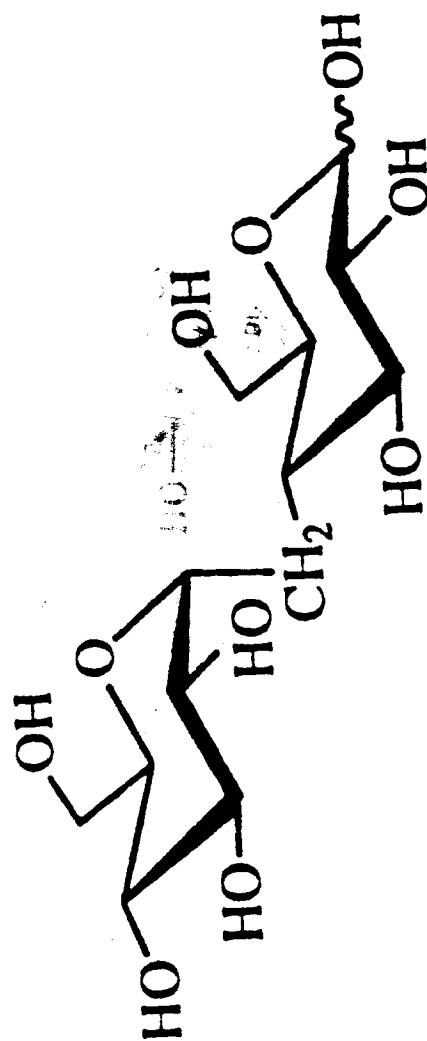
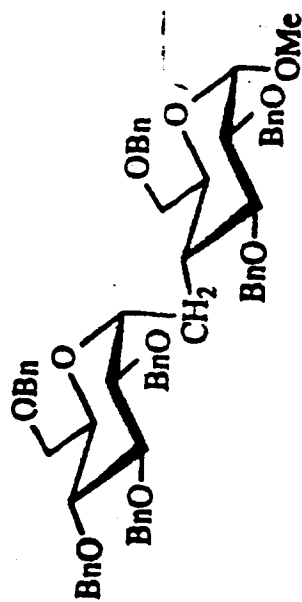




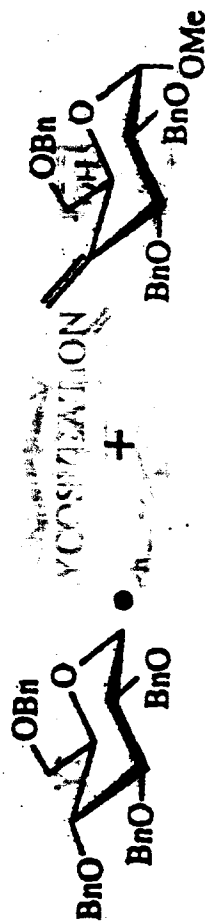
Maltose



C- Maltose



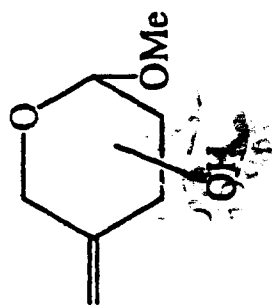
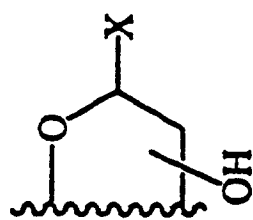
no reaction



Nucleophilic radical

Non-electrophilic alkene

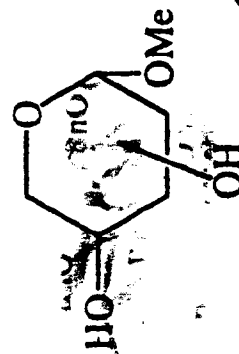
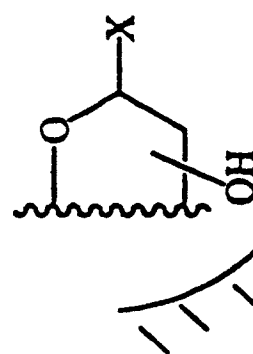
CHEMICAL C-GLYCOSYLATION



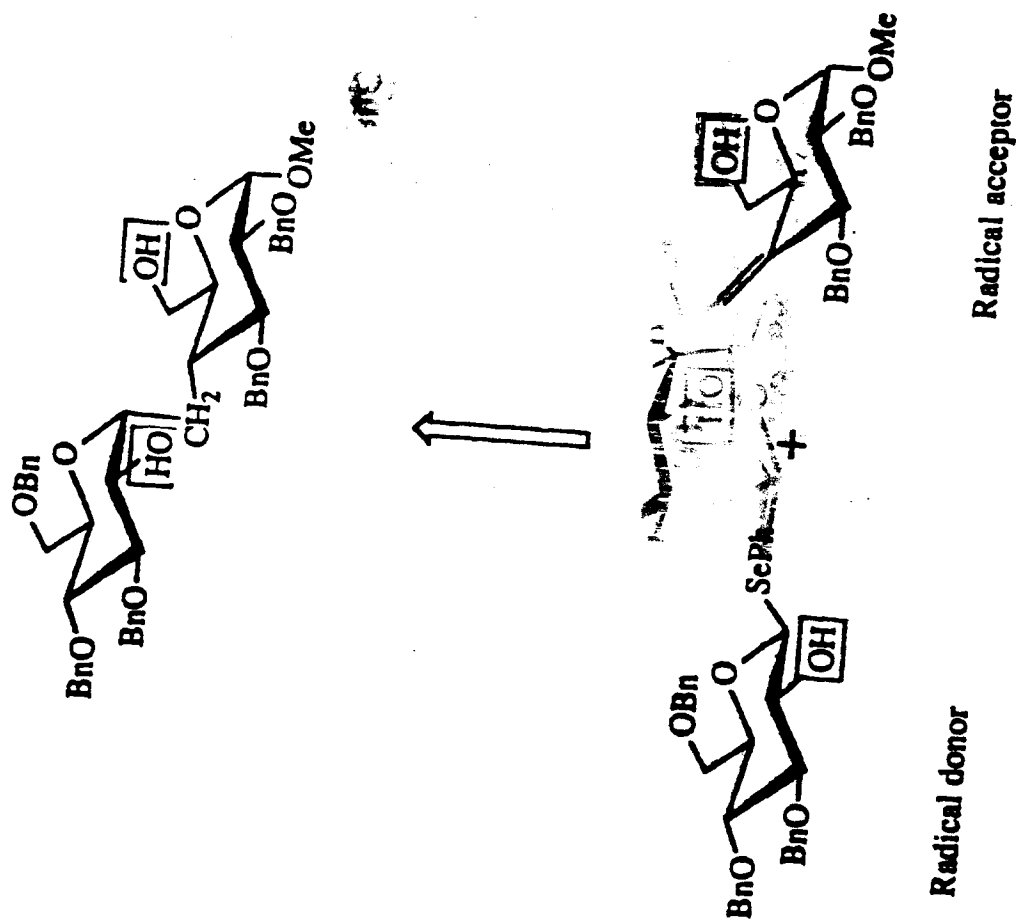
GLYCOSYL DONOR

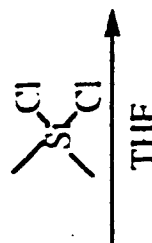
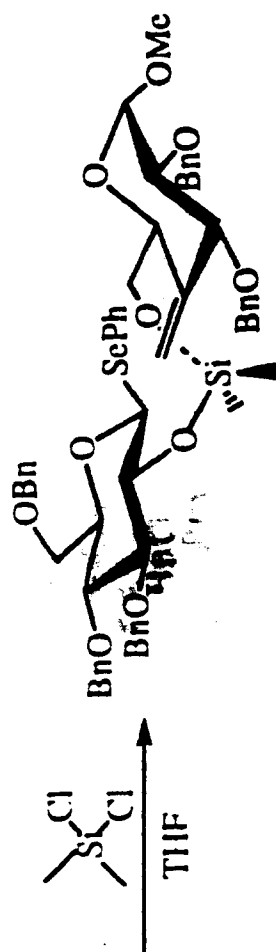
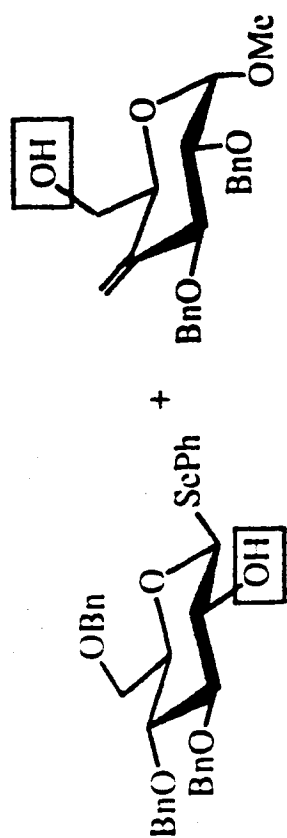
GLYCOSYL ACCEPTOR

ENZYMATIC GLYCOSYLATION



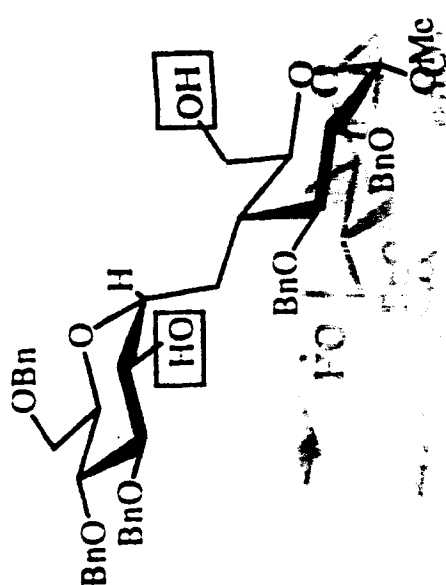
ENZYME





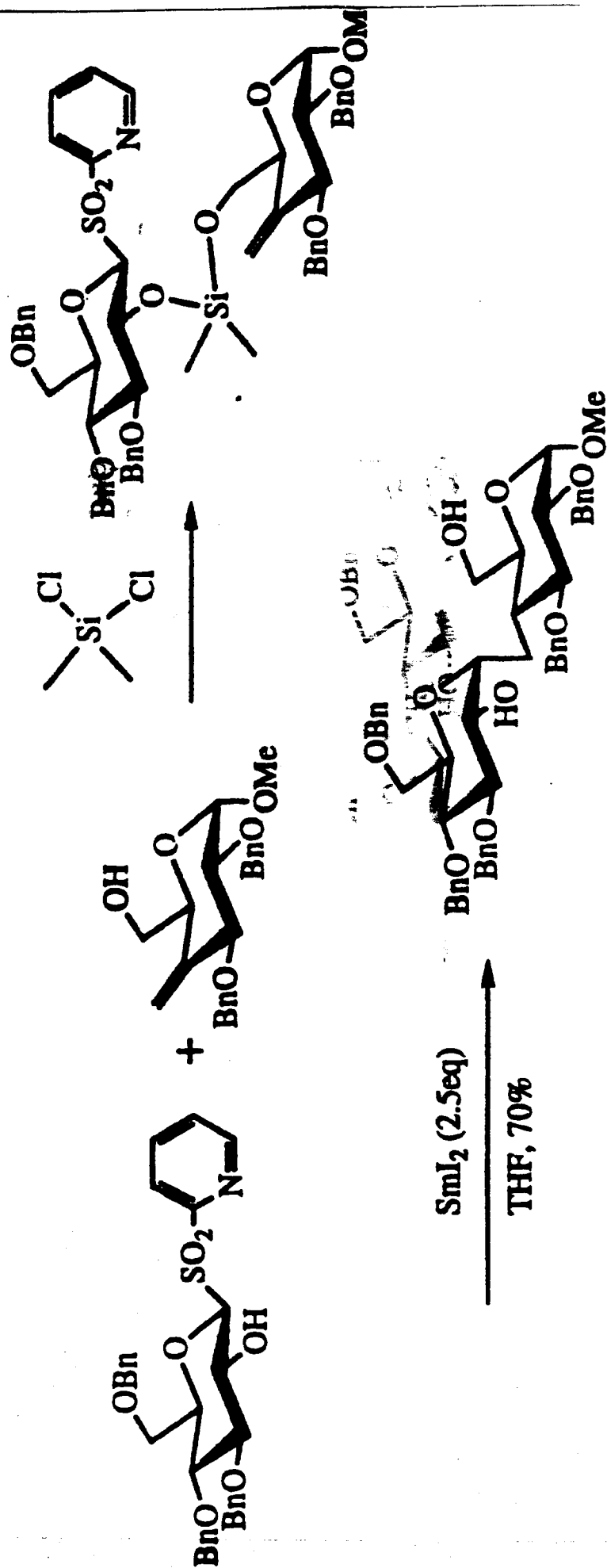
1. Bu_3SnH , AIBN
 2. $\text{HF}\cdot\text{H}_2\text{O}$

40 %



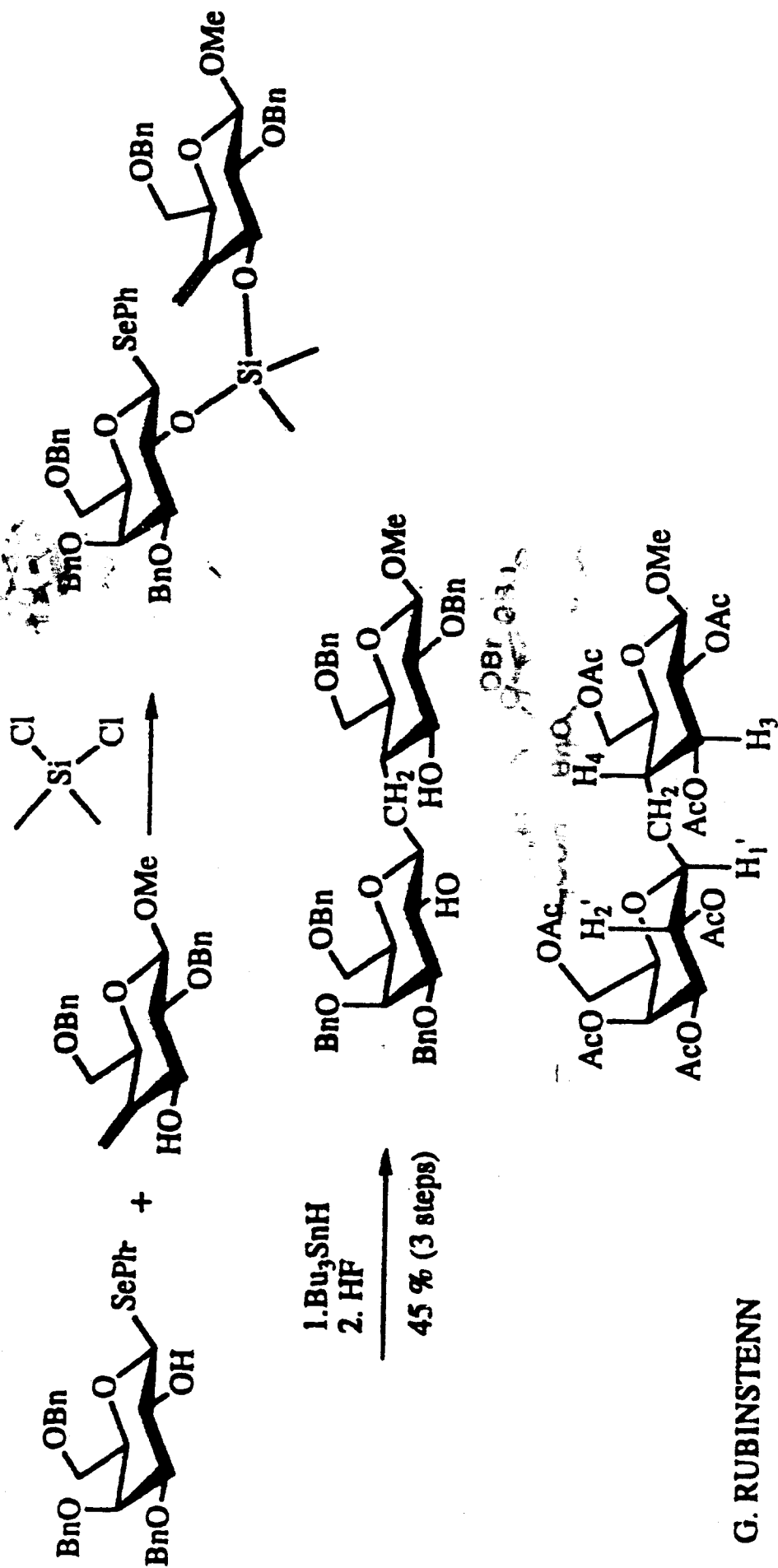
Y.C. XIN

ACR 95

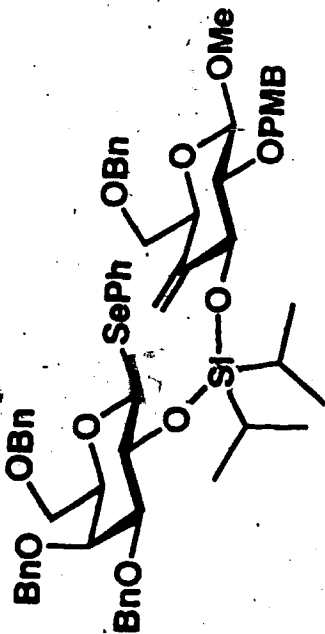
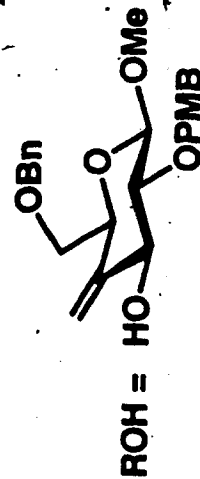
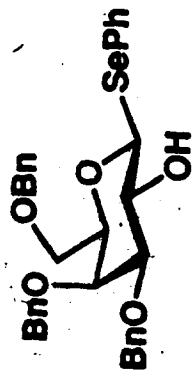


A. CHENEDE, 1995

AN EFFICIENT SYNTHESIS OF C-LACTOSE

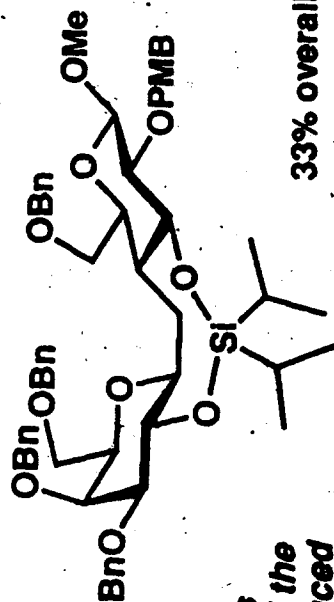


1. BuLi, THF, 0° C
2. Pr_2SiCl_2 , 4 equiv., -78° C to r. t.
3. Concentrate to dryness
4. ROH, DMAP, THF, r. t.



Bu₃SnH, AIBN, Toluene, Δ

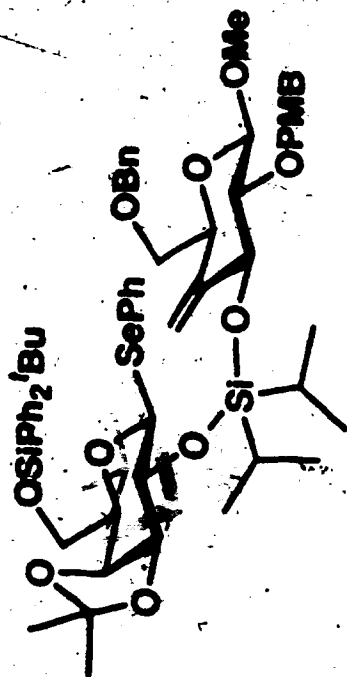
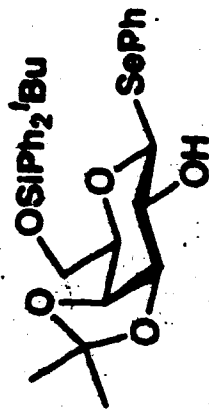
- Tethering yield is 70%
- Cyclisation yield is 69%
- Selectivity is 2.2 / 1



33% overall yield

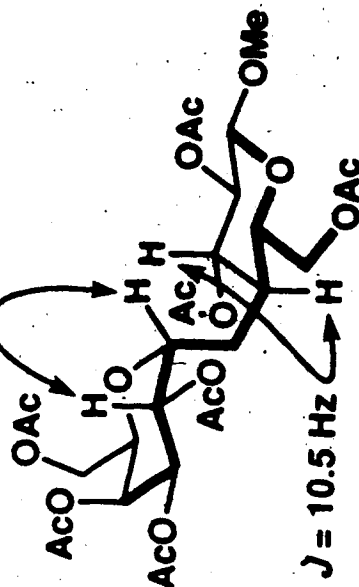
Disopropylsilaketal allows separation and analysis of the tethered cyclised and reduced products

1. BuLi, THF, 0° C
2. Pr_2SiCl_2 , 4 equiv., -78° C to r. t.
3. Concentrate to dryness
4. ROH, DMAP, THF, r. t.



Bu₃SnH, AIBN,
Toluene, Δ

$J = 5 \text{ Hz}$



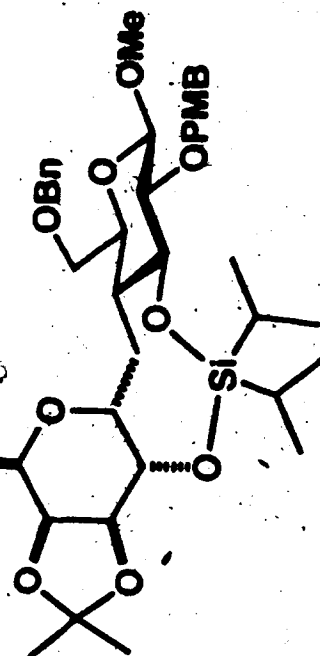
$J = 10.5 \text{ Hz}$

D-Gal- α -(CH₂)-4-D-Glc- β -OMe
[α]_D + 30, c 0.9 (CHCl₃)

OSi^tBuPh₂

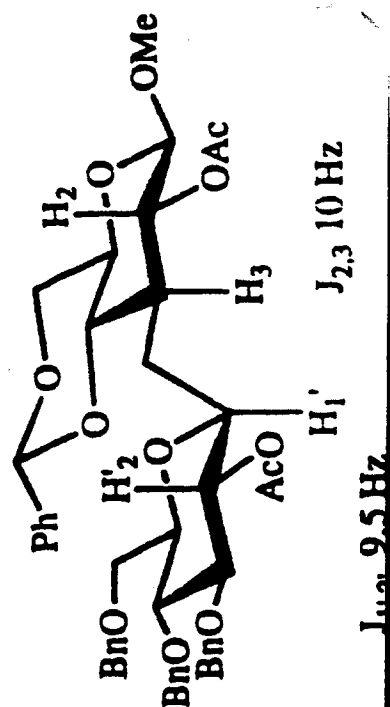
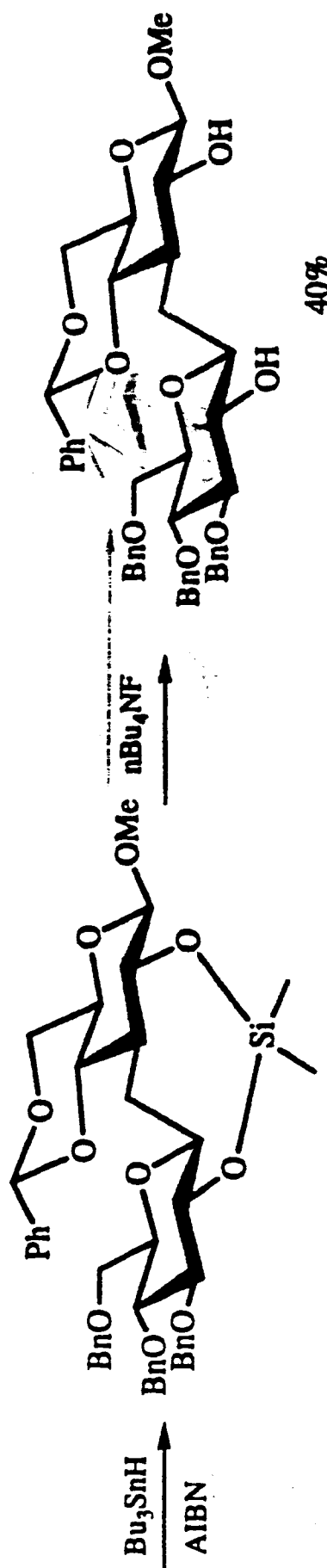
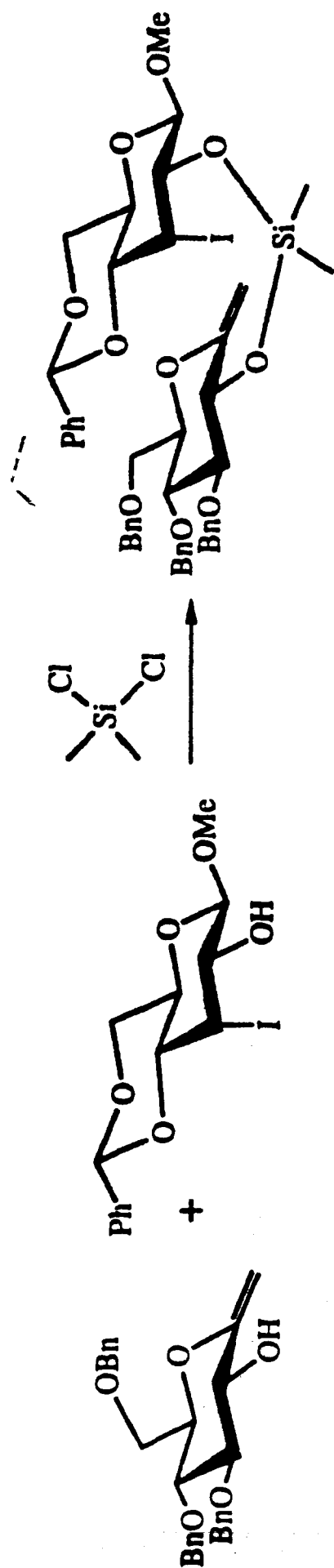
56% overall yield

1. TBAF, THF
2. CF₃COOH
3. H₂, Pd/C
4. Ac₂O, Pyr.



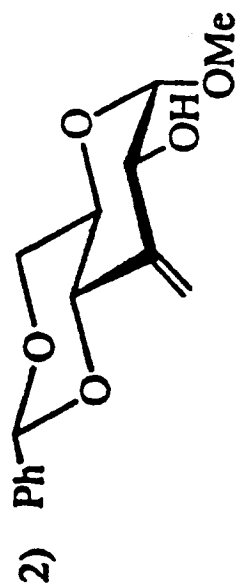
- Tethering yield is 70%
- Cyclisation yield is 80%
- Selectivity is > 20/1

B. LA FERLA and E. UNTERSTELLER

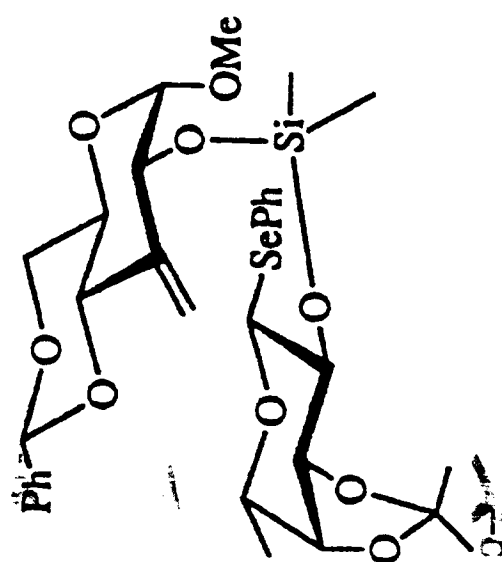
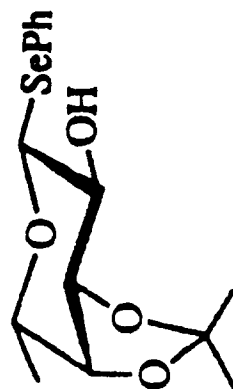


B. Vauzeilles, 1995

1) Me_2SiCl_2 (4.4 eq), BuLi (1.1 eq)
 THF , $-78^\circ\text{C} \rightarrow 20^\circ\text{C}$

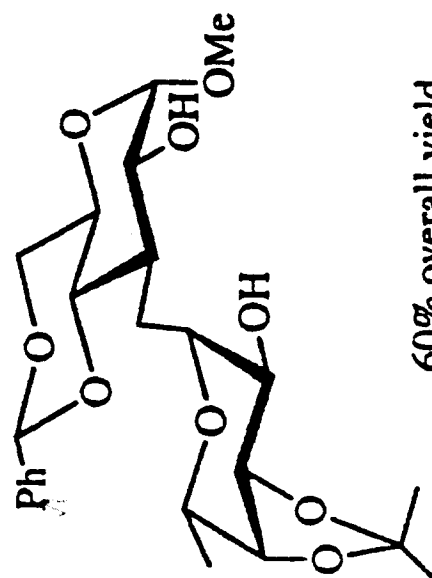


(1 eq), Imidazole (2.5 eq) THF , RT



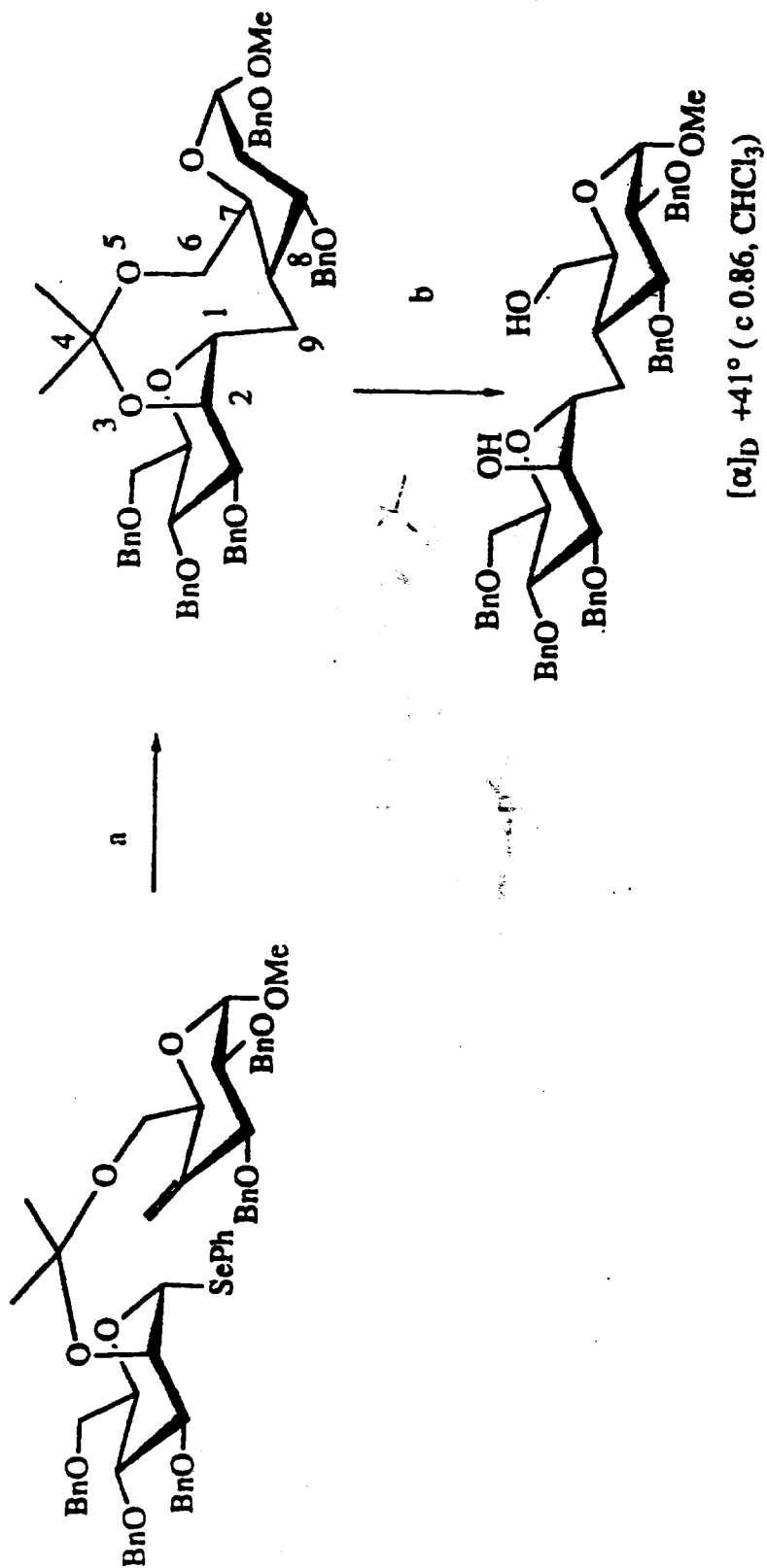
1) Bu_3SnH (2 eq), AIBN (0.3 eq)
 PhMe , 110°C , 17h

2) Bu_4N^+ , F (2eq) THF , RT



60% overall yield

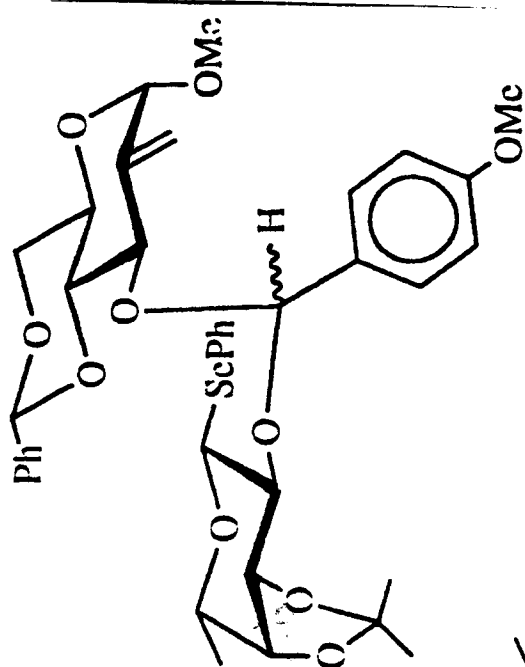
Rubinstenn



B. VAUZEILLES



DDQ, MS 4 Å, CH_2Cl_2
 $0^\circ\text{C} \rightarrow \text{RT}$ (2 h) 80%



2. $\text{Ph}_3\text{CCH}_2\text{OH}$

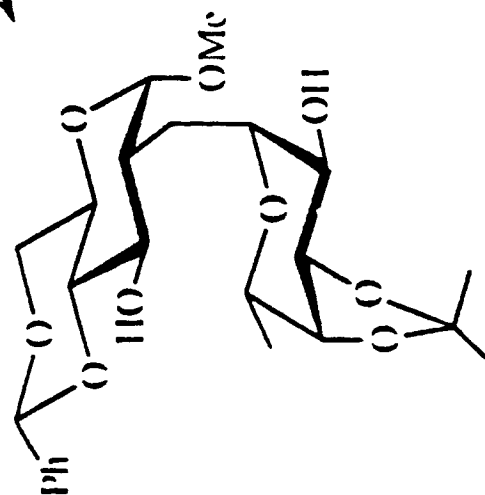
EtO

1) Bu_3SnH , AIBN

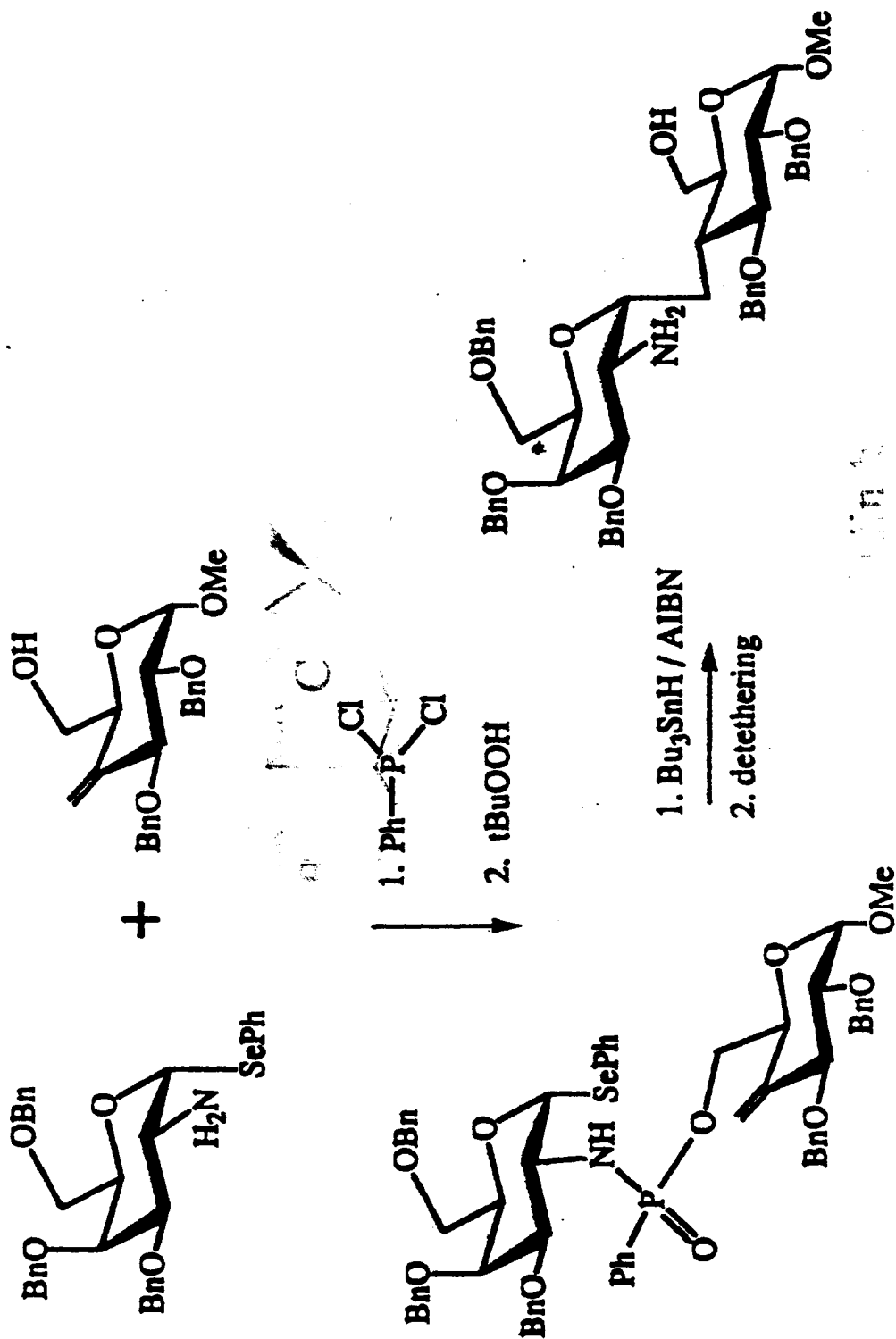
PhMe , 110°C , (syringe pump, 17h)

2) DDQ, $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (20:1) RT 1 h

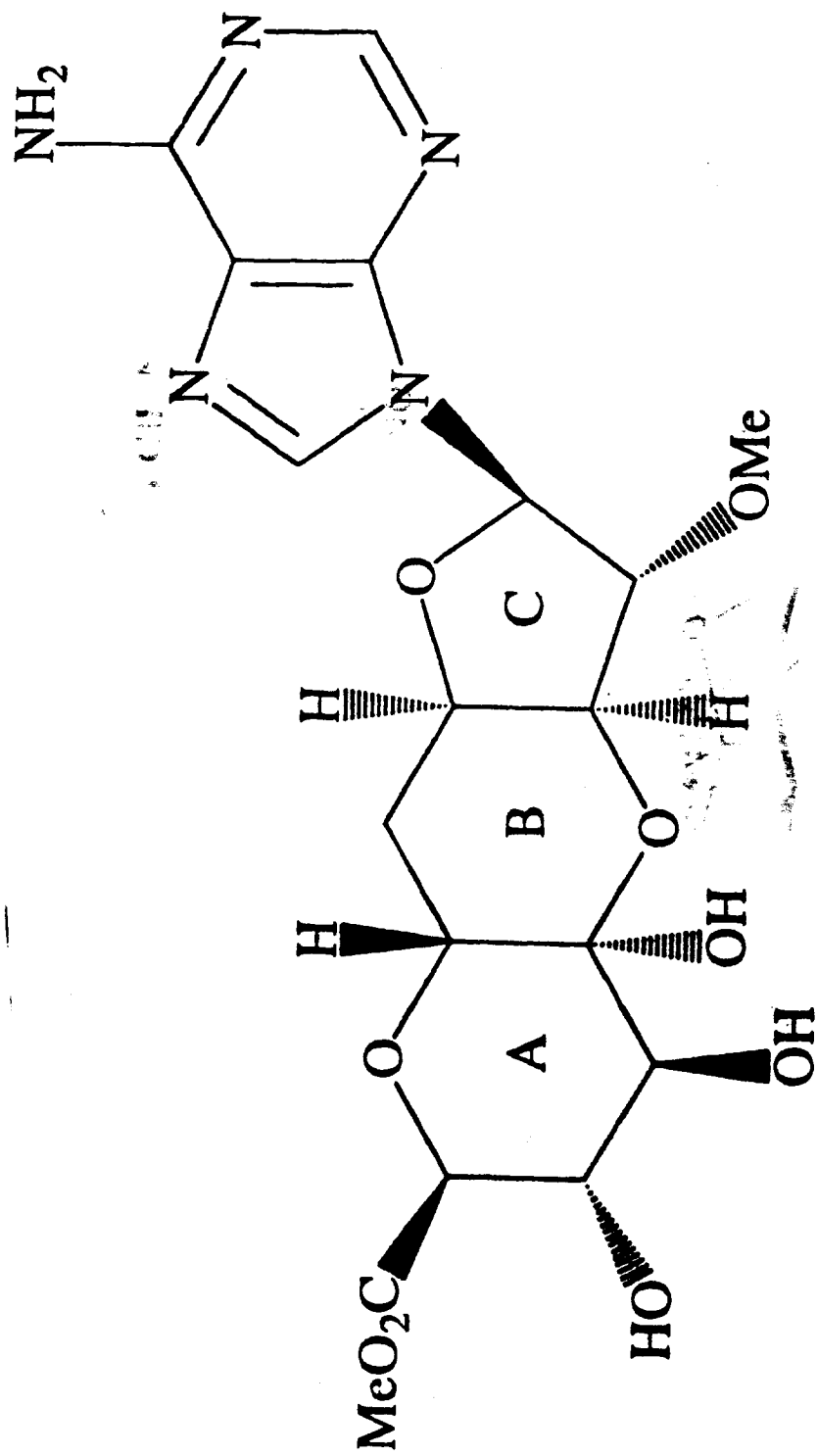
60% overall yield



E. Rekar



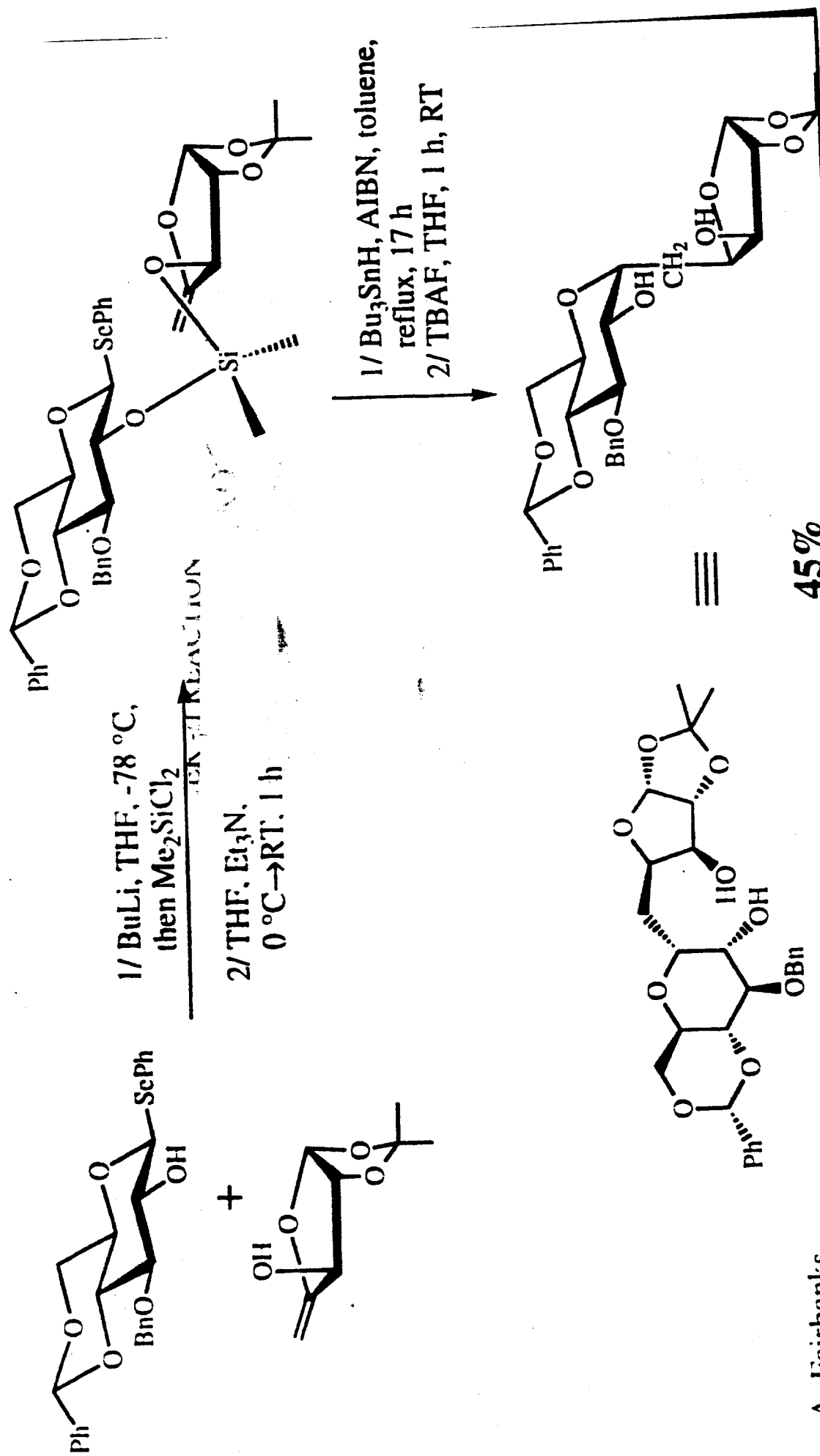
G. Rubinstenn



HERBICIDIN B

One member of the Herbicidin family
(Herbicidins A, B, C, E, F, G and also Aureonuclemycin)

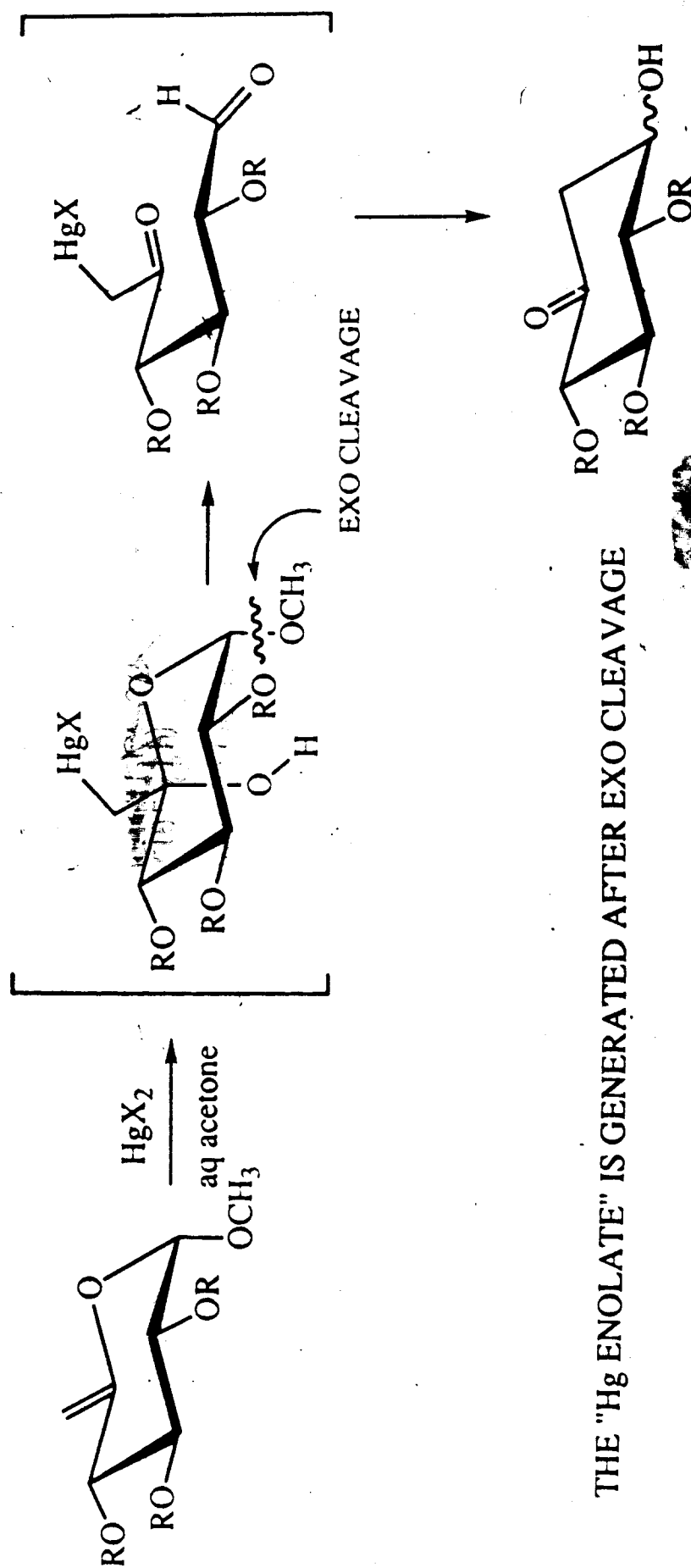
AN EXPEDITIOUS SYNTHESIS OF THE CARBON SKELETON OF HERBICIDIN



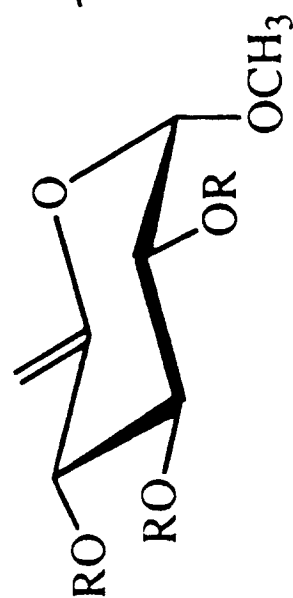
A. Fairbanks

A USEFUL CARBOCYCLIC RING CLOSURE OF HEX-5-ENOPYRANOSIDES :

THE FERRIER -II REACTION

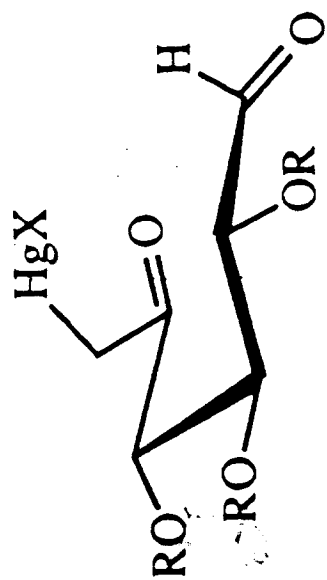


THE "Hg ENOLATE" IS GENERATED AFTER EXO CLEAVAGE

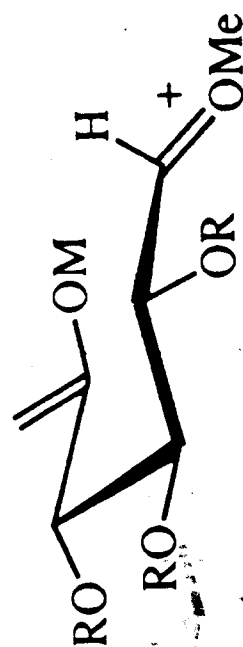


Exo cleavage

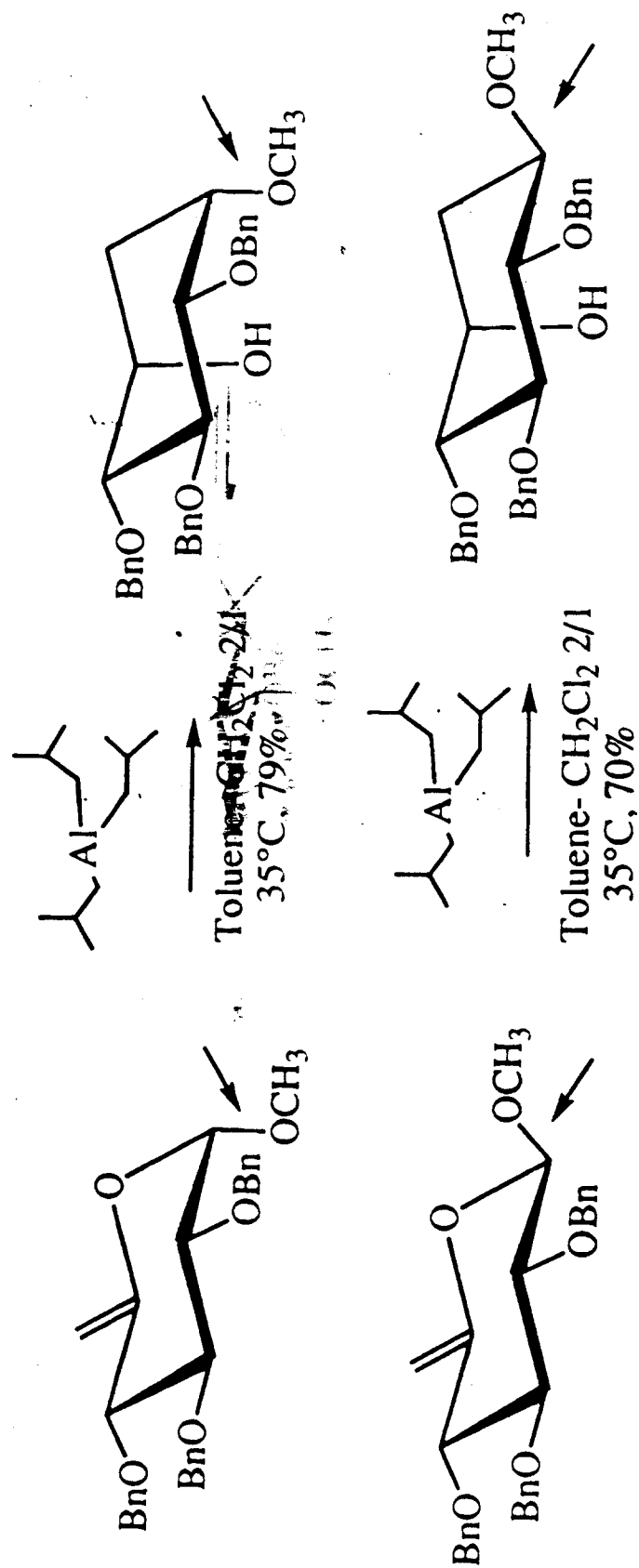
(Ferrier - II)



Endo cleavage ?

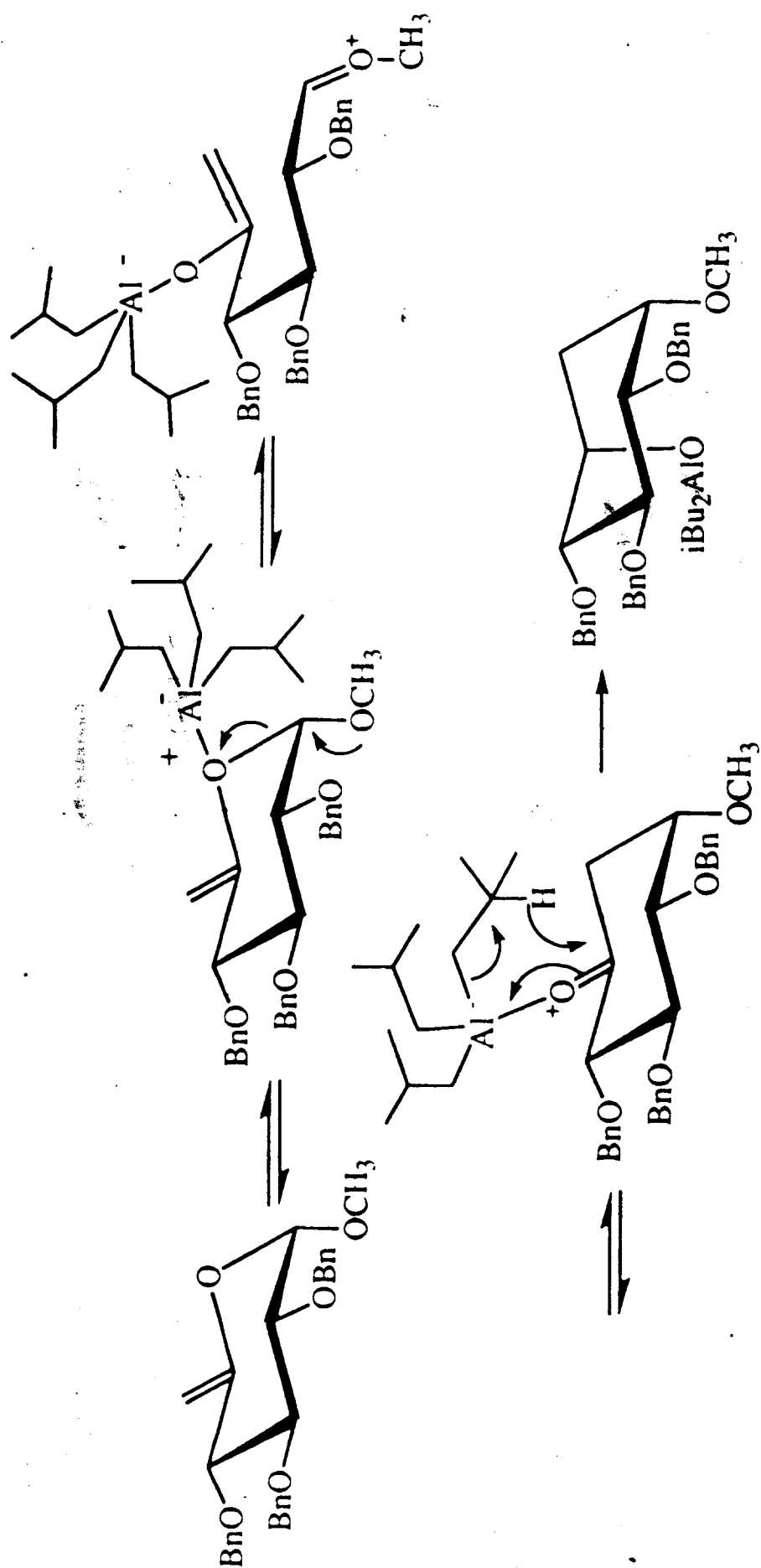


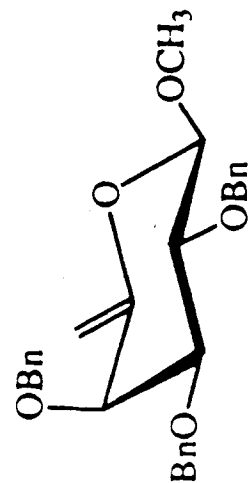
A NOVEL CARBOCYCLIC RING CLOSURE OF HEX-5-ENOPYRANOSIDES



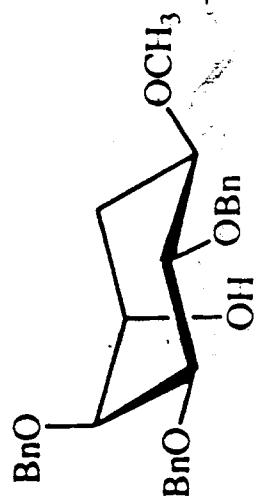
S. K. DAS

THE ANOMERIC CONFIGURATION OF THE STARTING GLUCOSIDE IS RETAINED

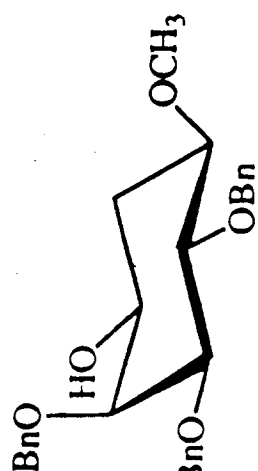




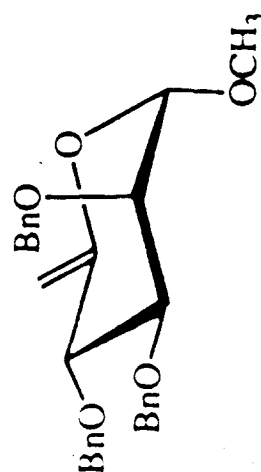
80%



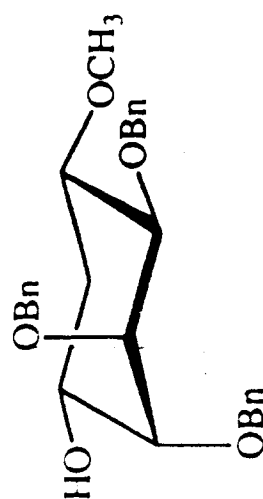
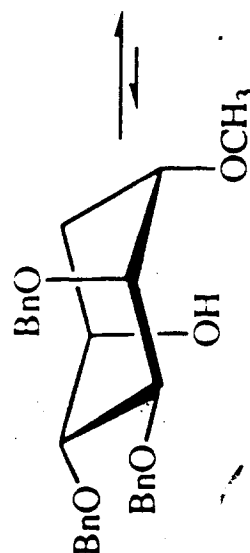
20%



60%



73%



S. K. DAS