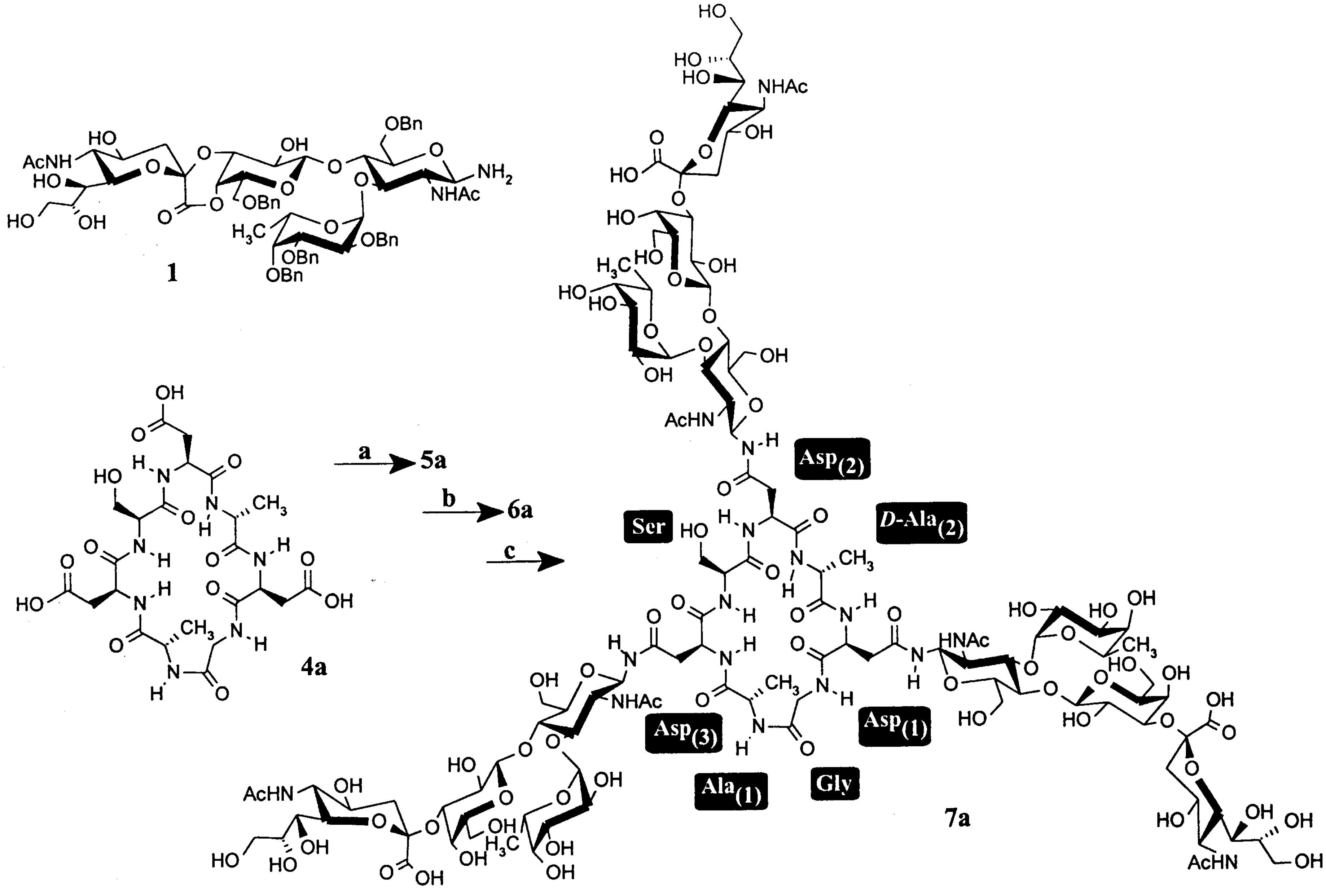
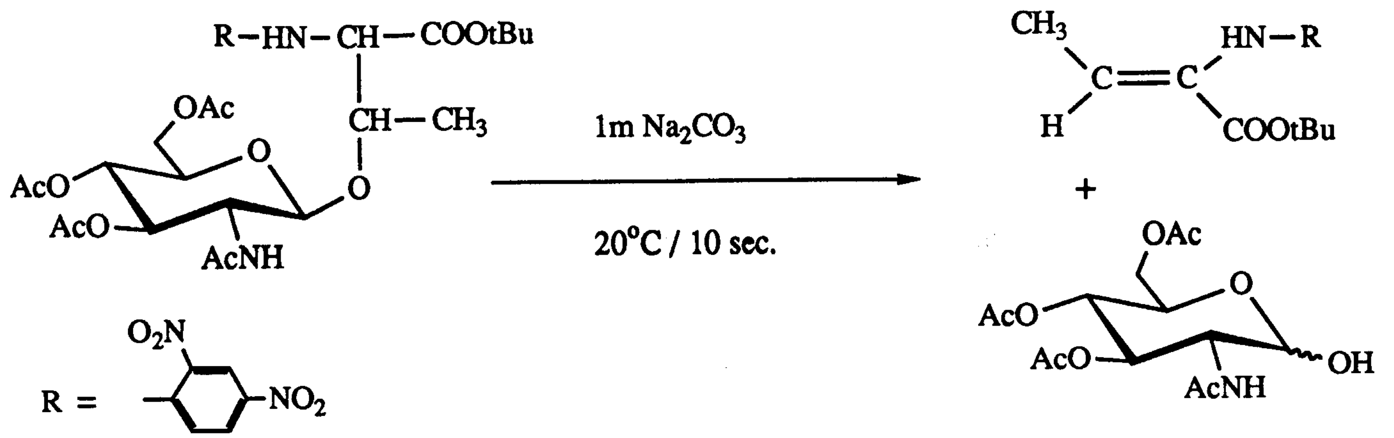
1

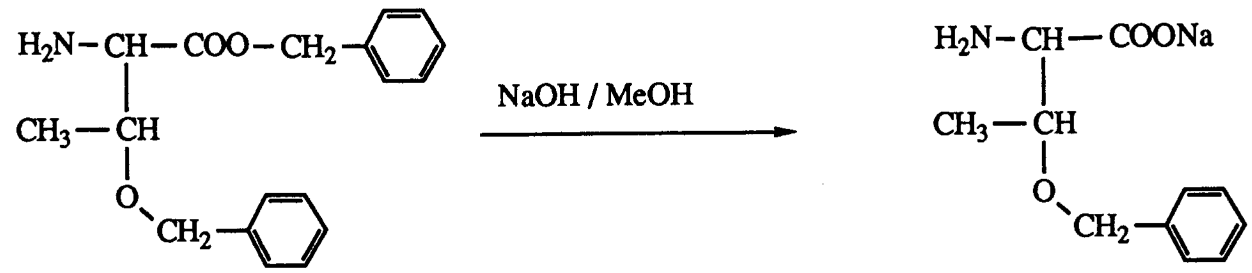


β-Elimination of the Carbohydrate Part from O-Glycosyl Serine and Threonine Derivatives



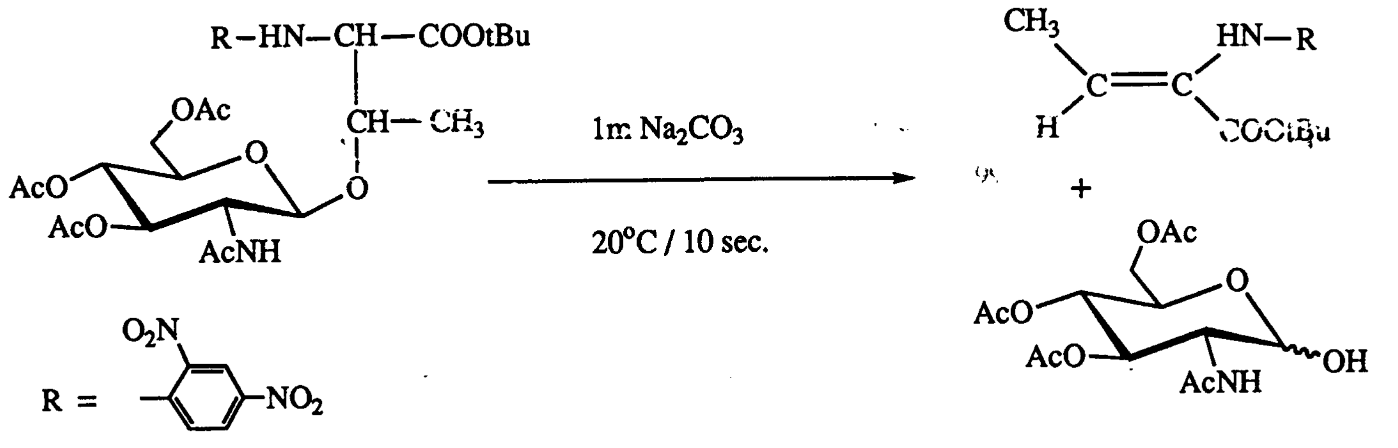
J. R. Vercellotti et al. 1967 R. Kuhn et al. 1938

Contrast: Experiences from peptide chemistry



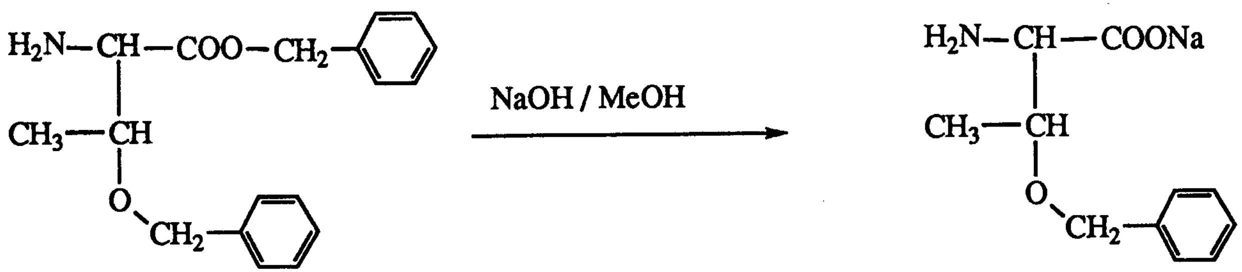
T. Mizoguchi et al. 1968

β-Elimination of the Carbohydrate Part from O-Glycosyl Serine and Threonine Derivatives



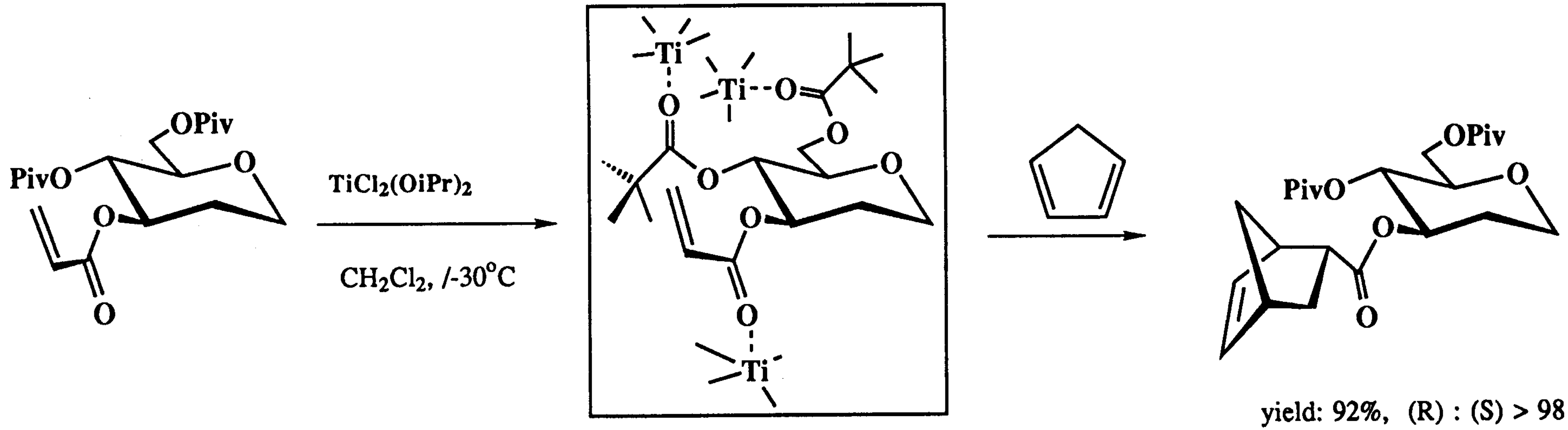
J. R. Vercellotti et al. 1967 R. Kuhn et al. 1938

Contrast: Experiences from peptide chemistry



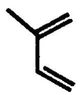
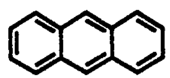
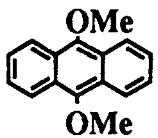
T. Mizoguchi et al. 1968

Stereoselective Diels-Alder Synthesis Using Dihydro-glucal as the Chiral Template



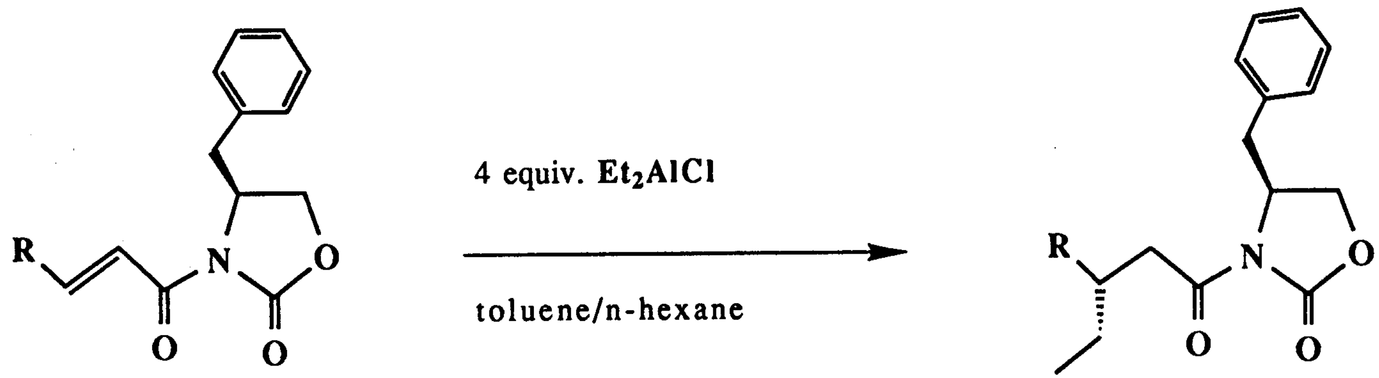
yield: 92%, (R) : (S) > 98 : 2

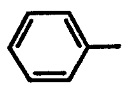
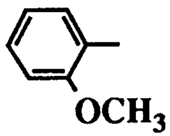
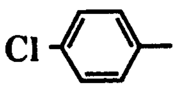
with $TiCl_4$ at -78°C: yield: 66%, (R) : (S) =80 : 20

Diene	Catalyst	Temp.(°C)	Time	Yield (%)	(R) : (S) (Ratio of Diastereomers)
	$TiCl_3(OiPr)$	0	48 h	94	95 : 5
	$TiCl_3(OiPr)$	0	6 h	90	92 : 8
	$TiCl_4$	0	4 h	87	> 99 : 1
	$TiCl_4$	0	3 h	91	> 99 : 1

Wolfgang Stähle 1990

Diastereoselective Synthesis of β-Branched Carboxylic Acid Derivatives via Diethyl Aluminium Chloride Addition to α,β-Unsaturated Acyl Oxazolidones Derived from Phenylalaninol (Evans´ Auxiliary)

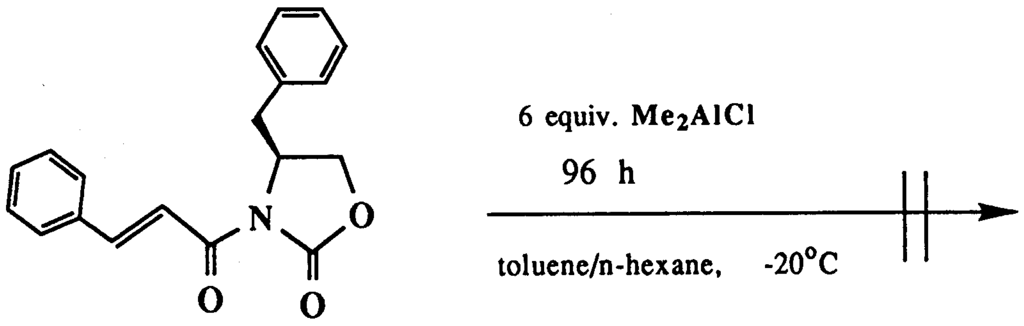


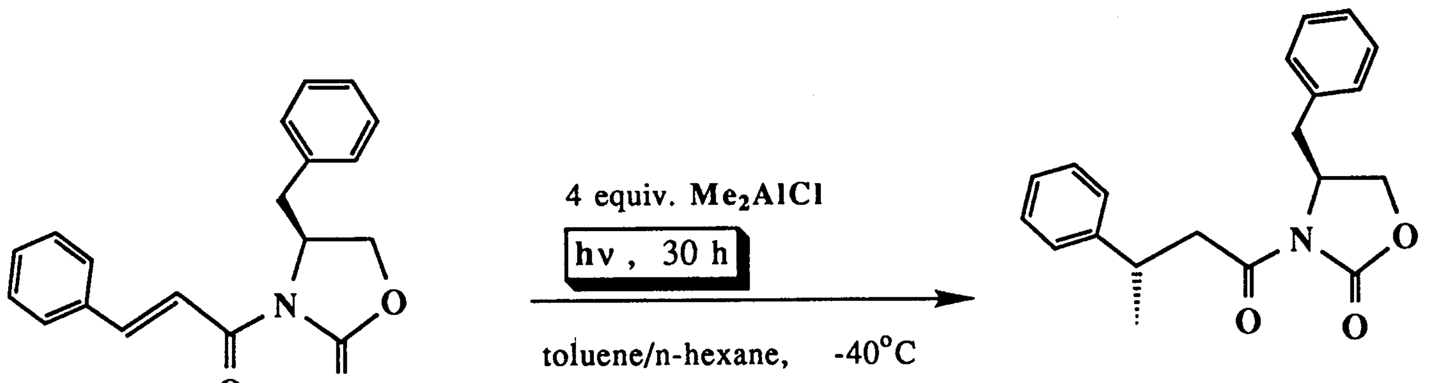
R	Temp. (°C)	Time	Yield (%)	ratio of diastereomers
CH_3 -	- 78	50 min	88	85 : 15
CH_3-CH_2-CH_2 -	- 78	270 min	95	78 : 22
$(CH_3)_3C$ -	+10	4 d	48 (70% turn.)	72 : 28
	- 78	40 min	98	89 : 11 (S) : (R)
	- 78	22 h	82	86 : 14
	- 78	160 min	78	91 : 9

Karola Rück 1990

6

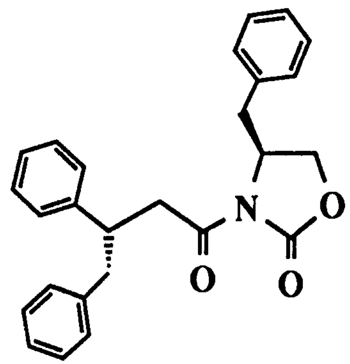
Diastereoselective Methyltransfer from Dimethyl Aluminium Chloride to α,β-Unsaturated Acyl Oxazolidones Derived from Phenylalaninol (Evans´ Auxiliary) - A Radical Process





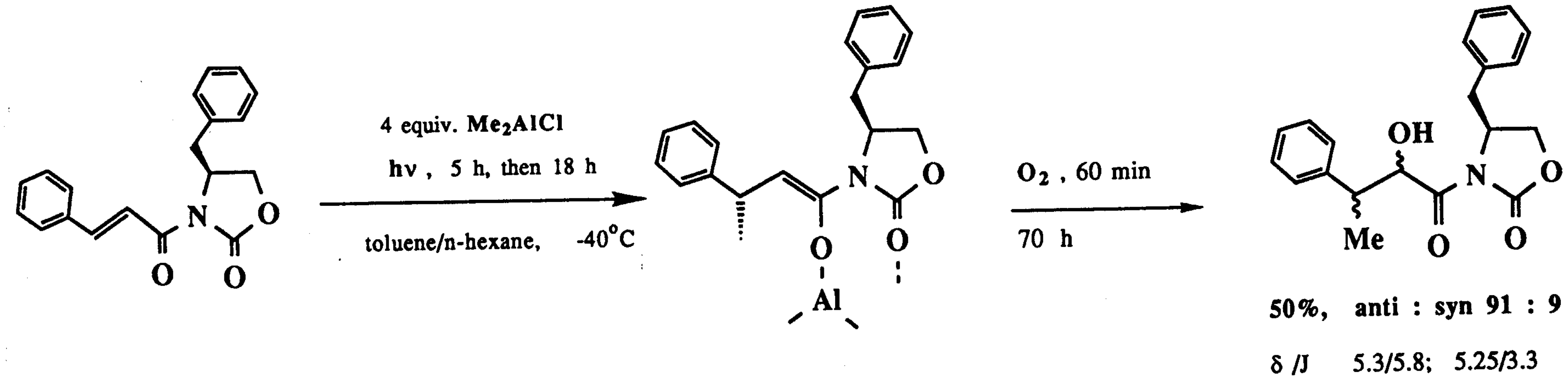
56 - 63% , (S) : (R) 92 : 8

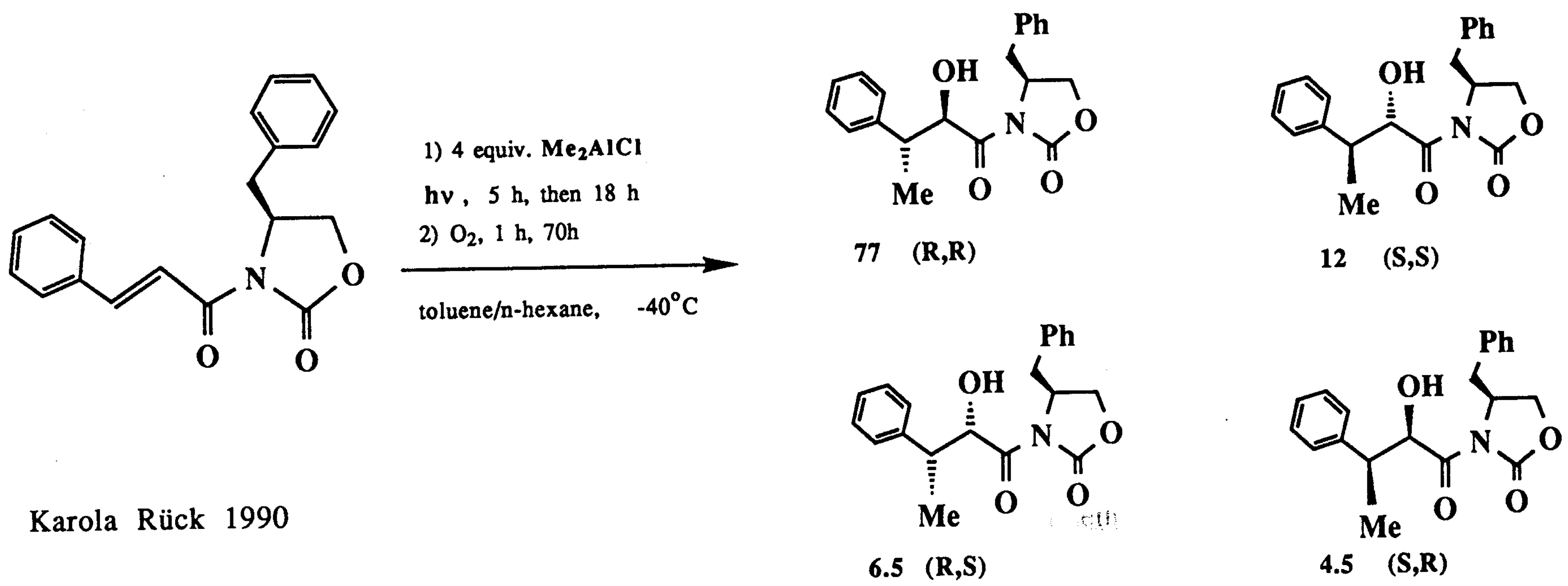
15%



Karola Rück 1990

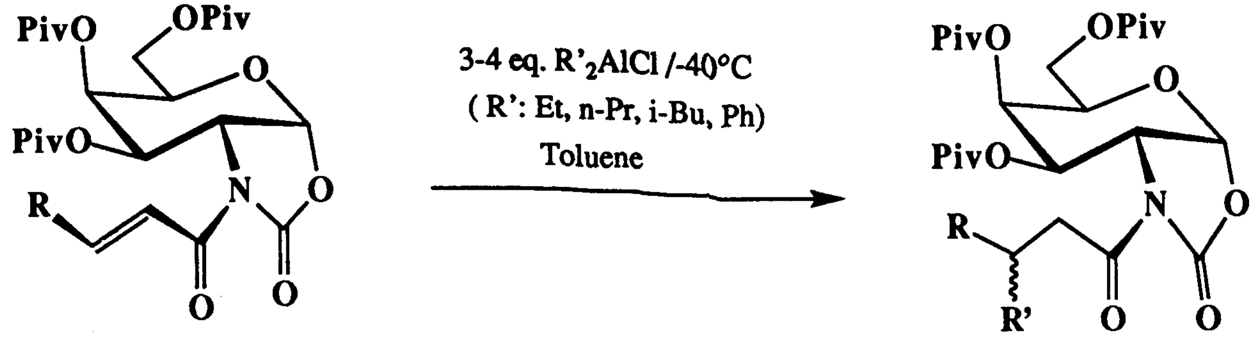
Diastereoselection in a Cascade Consisting of Methyl Transfer from Dimethyl Aluminium Chloride to α,β-Unsaturated Acyl Oxazolidones and Subsequent Aluminum Enolat Oxidation to give β-Branched α-Hydroxy Acids

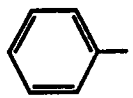
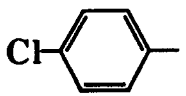




Karola Rück 1990

Diastereoselective 1,4-Addition of Alkylaluminum Chlorides to Corbohydrate Derived Acyl Oxazolidinones

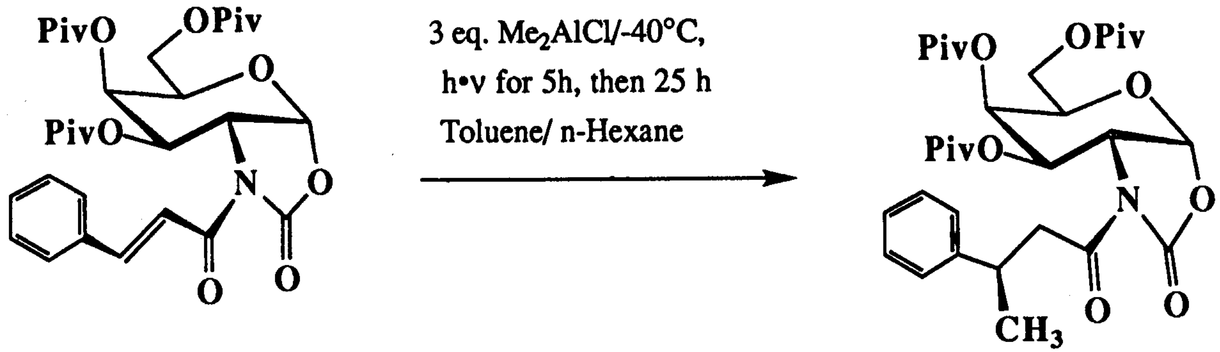


R	R'_2AlCl	Reaction Time	Yield	Ratio of Diastereomers
	Et_2AlCl	28 h	55 %	96 : 4
	iBu_2AlCl/Me_2AlCl	24 h	78 %	> 99 : 1
	$n\text{-}Pr_2AlCl$	5 h	74 %	97.5 : 2.5
	Et_2AlCl	54 h	62 %	91 : 9
CH_3	Et_2AlCl	40 h	70 %	90 : 10
	iBu_2AlCl/Me_2AlCl	24 h	75 %	> 99 : 1
	$n\text{-}Pr_2AlCl$	6 h	50/38 %	95 : 5
	Ph_2AlCl	20 h	62 %	2.5 : 97.5

Karola Rück 1991

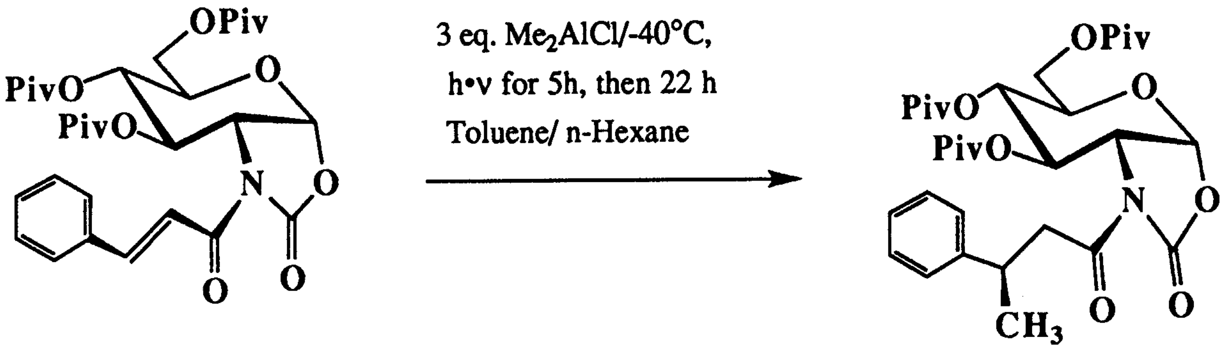
H. Kunz, K. Rück, SYNLETT 1992,343

Diastereoselective Photoinduced 1,4-Addition of Dimethylaluminum Chloride to α,β-Unsaturated Acyl Oxazolidinones Derived from Carbohydrates



Yield: 82 %

Ratio of Diastereomers: > 98 : 2



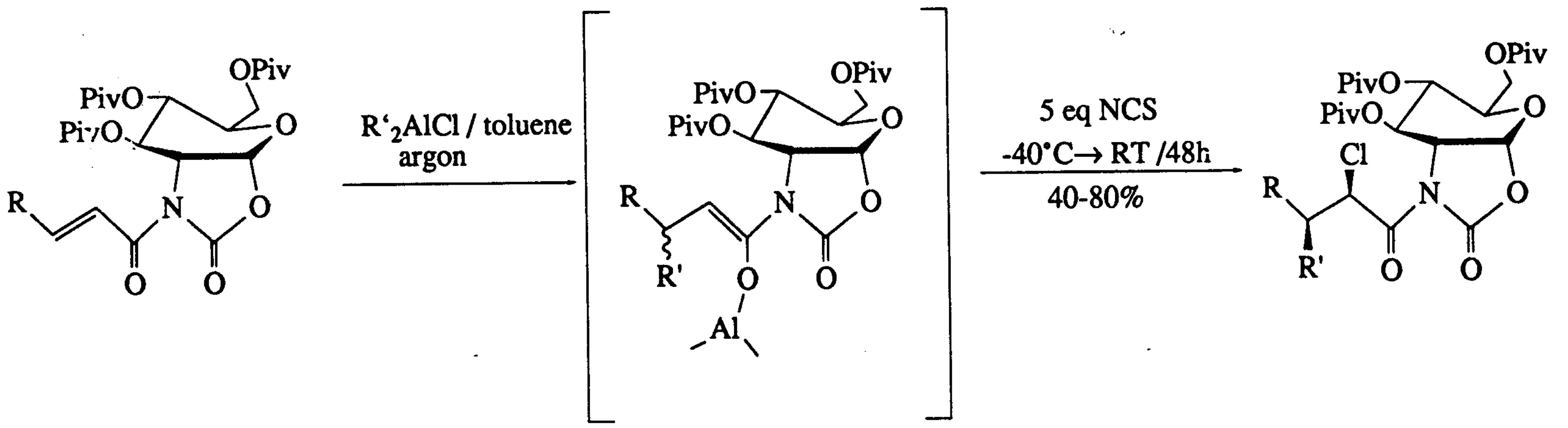
Yield: 76 %

Ratio of Diastereomers: 94 : 6

Karola Rück 1991

Cascade of Stereoselective 1,4 Addition and α-Halogenation of Unsaturated N-Acyl Oxazolidinones Derived from Glucosamine

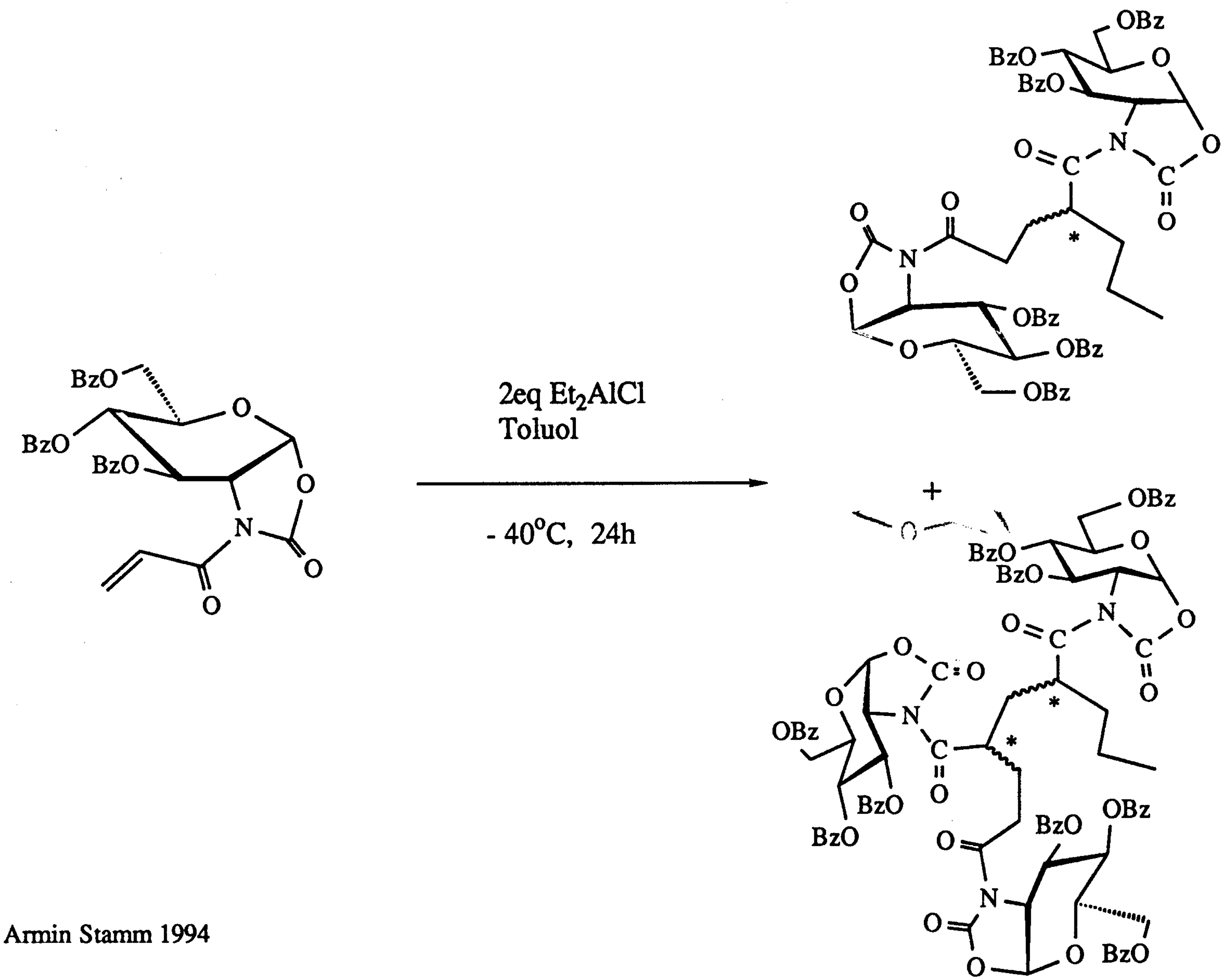
β-Alkyl-α-chlorocarboxylic Acid Derivatives



R	R'_2AlCl	Reaction Temp./ Time	Yield	Diastereomeric Ratio
Phenyl	3 eq Et_2AlCl	a.) -40°C/ 24h b.) 5 eq NCS/ 48h	64%	91.8 : 7.1 : 1.1 : 0 (2R,3S) (2R,3R)
Phenyl	1 eq Me_2AlCl 4 eq iBu_2AlCl	a.) -40°C/ 32h b.) 5 eq NCS/ 36h	48%	91.1 : 6.3 : 2.6 : 0
Methyl	3 eq Et_2AlCl	a.) -40°C/ 30h b.) 5 eq NCS/ 48h	77%	80 : 20 : 0 : 0 (2R,3R) (2R,3S)

Karola Rück 1993

Stereocontrolled Oligomerisation of Acrylic Acid Derivatives



Single Diastereomer

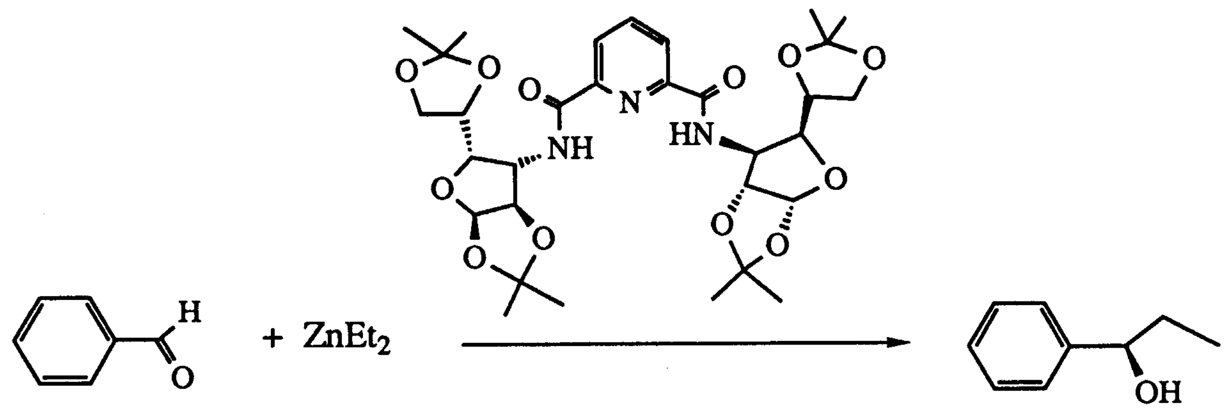
45%

Single Diastereomer

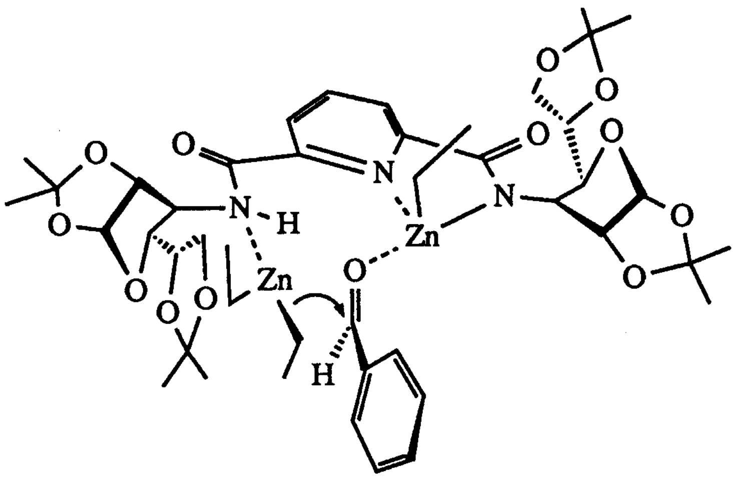
25%

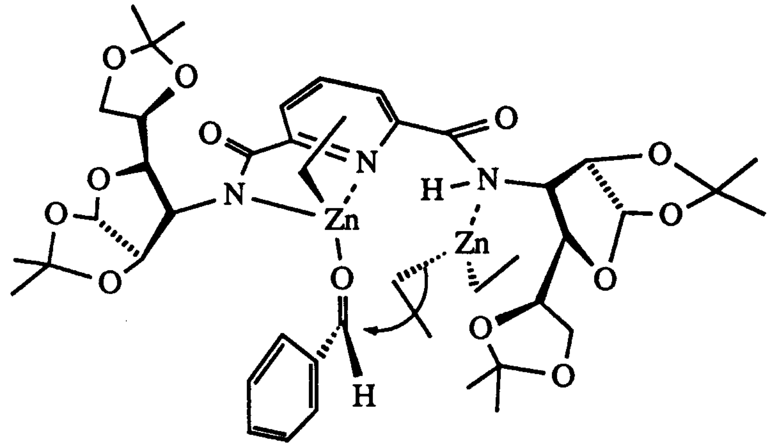
Armin Stamm 1994

Enantioselective Addition of Diethyl Zinc to Aldehydes Using Carbohydrate-Derived Catalysts



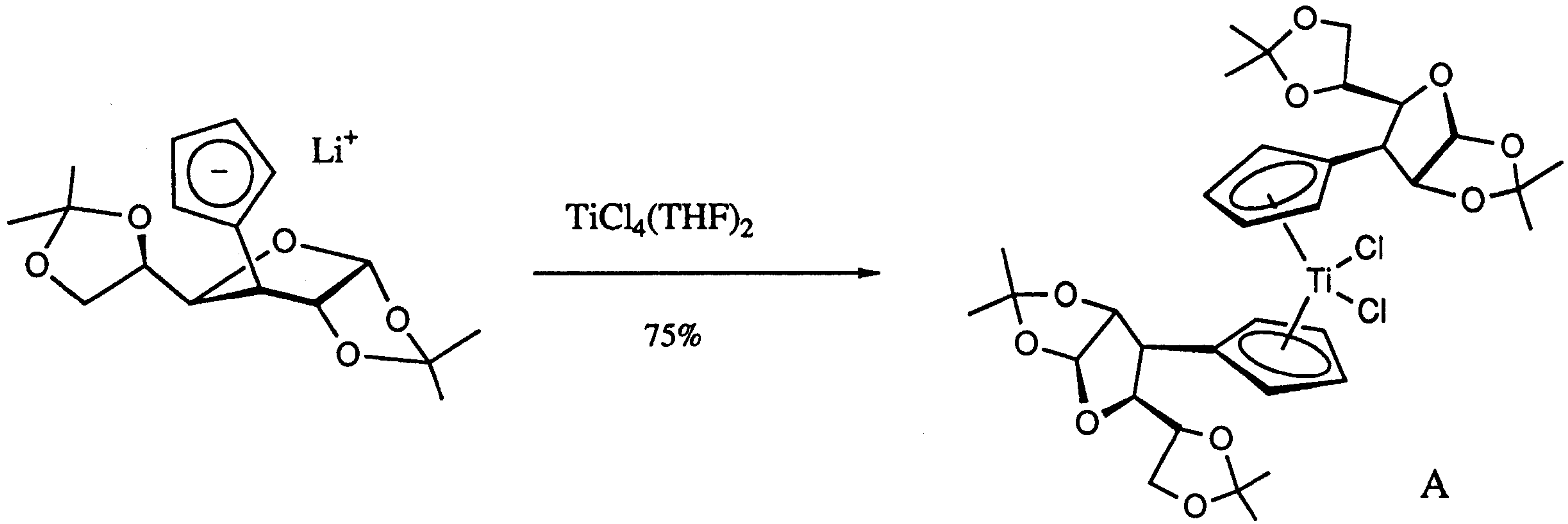
70 - 90%   (R) : (S) up to 93 : 7





Michael Puhl 1994

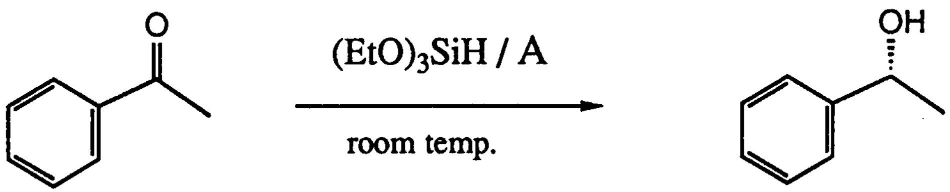
Carbohydrate-substituted Metallocenes Molecules with Interesting Properties



A

A^1 (red) $[\alpha]_D$ +538° ⟶ A^2 (brick-red) $[\alpha]_D$ +893°

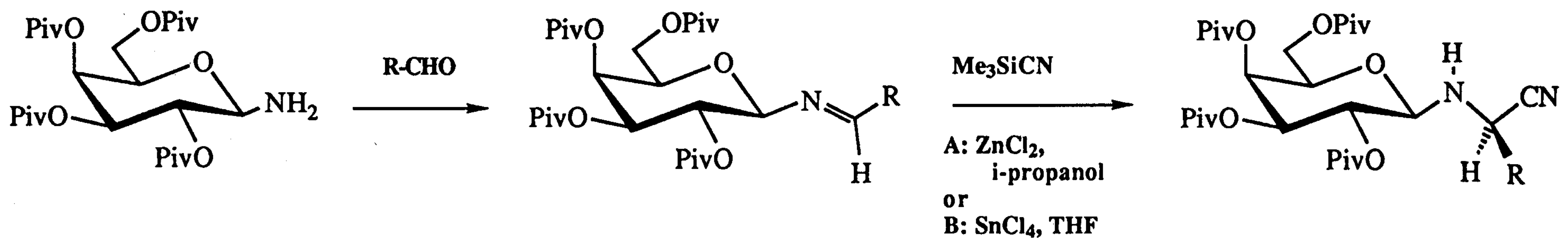
$CHCl_3$ solution $[\alpha]_D$ +330°

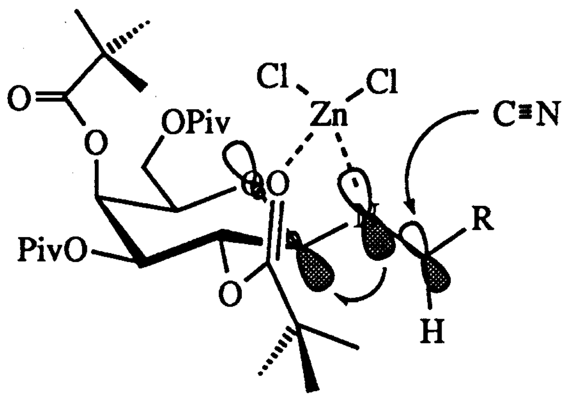


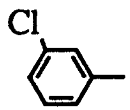
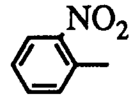
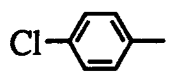
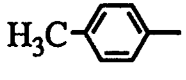
quantitative (R) : (S) 64 : 36

Michael Puhl 1993

Diastereoselective Strecker Synthesis on Carbohydrate Amine Templates

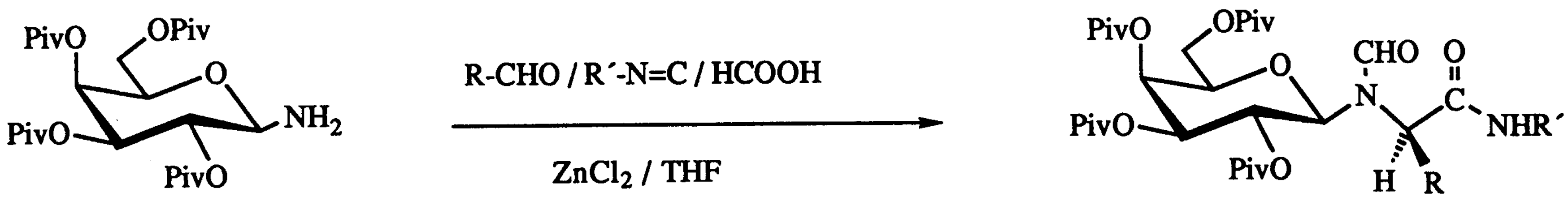


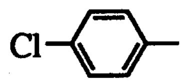
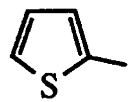
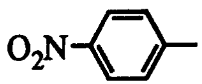


R	method	yield (%)	ratio of diastereomers (R) : (S)	pure (R)
	A	95	7 : 1	78%
	A	90	>50 : 1	91%
	B	95	11 : 1	84%
	B	95	12 : 1	87%
$(CH_3)_3C-$	B	93	13 : 1	86%

Wilfried Sager 1986

Diastereoselective Ugi-Reaction on Carbohydrate Matrices

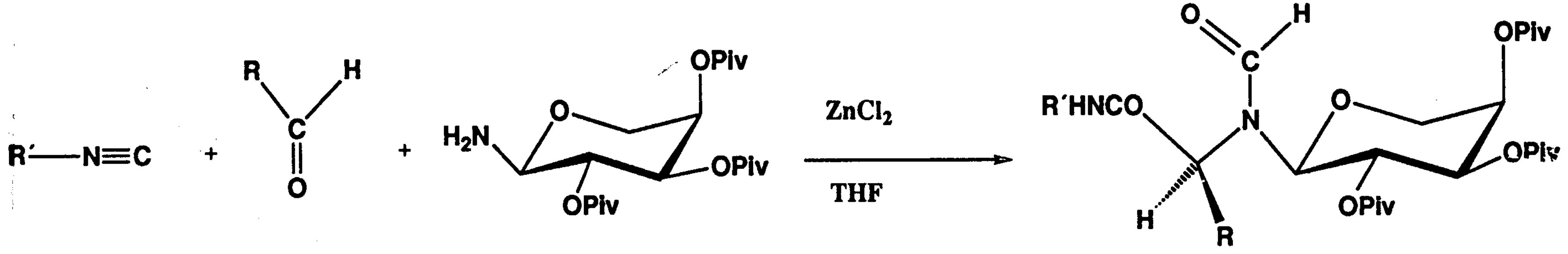


R	R´	T (°C)	(2R) : (2S)	rein (2R) Ausb. (%)
$(CH_3)_3C$—	$(CH_3)_3C$—	-78	>100 : 1	80
$C_6H_5-CH_2$–	$(CH_3)_3C$—	- 78	19 : 1	80
	$(CH_3)_3C$—	- 25	30 : 1	92
	$(CH_3)_3C$—	- 25	22 : 1	93
	$(CH_3)_3C$—	0	16 : 1	91

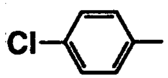
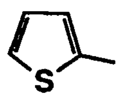
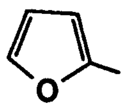
Waldemar Pfrengle 1987

H. Kunz, W. Pfrengle, J. Am. Chem. Soc. 110 (1988), 651; Tetrahedron 44(1988),5487.

Diastereoselective Ugi-Synthese von S-Aminosäure-Derivaten an D-Arabinosylamin als Matrix



(S)

R	R´	T (°C)	(2R) : (2S)	rein (2S) Ausb. (%)
$(CH_3)_3C$—	$(CH_3)_3C$—	-25	1 : 25	85
$C_6H_5-CH_2$—	$(CH_3)_3C$—	-78	1 : 29	87
	$(CH_3)_3C$—	-25	1 : 30	91
	$(CH_3)_3C$—	-25	1 : 23	85
	$(CH_3)_3C$—	-25	1 : 22	88

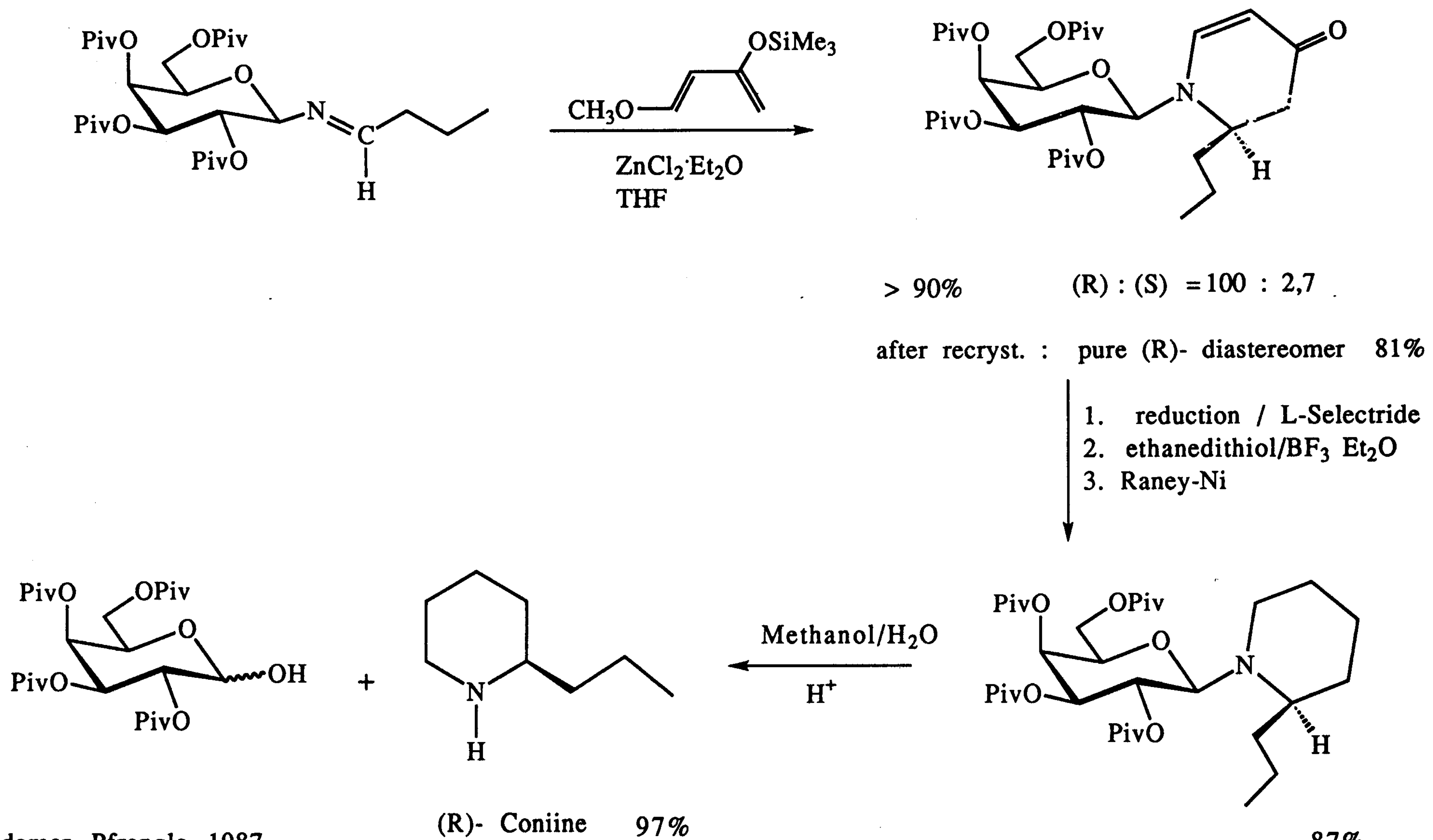
W.Pfrengle

1987

17

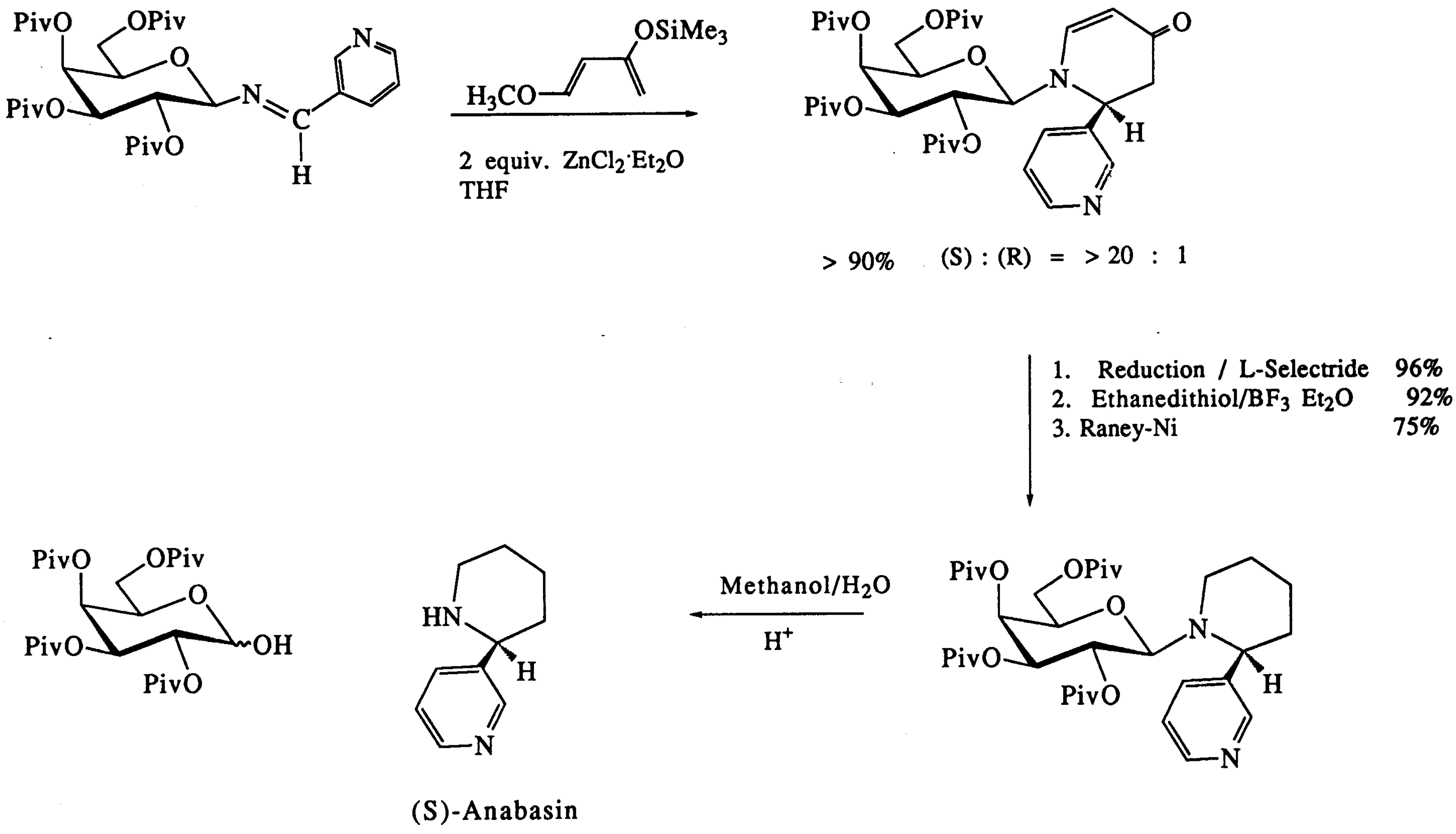
Stereoselective Synthesis of Alkaloids Using the D-Galactosylamine as the Chiral Template:

Stereoselective Synthesis of Coniine



Waldemar Pfrengle 1987

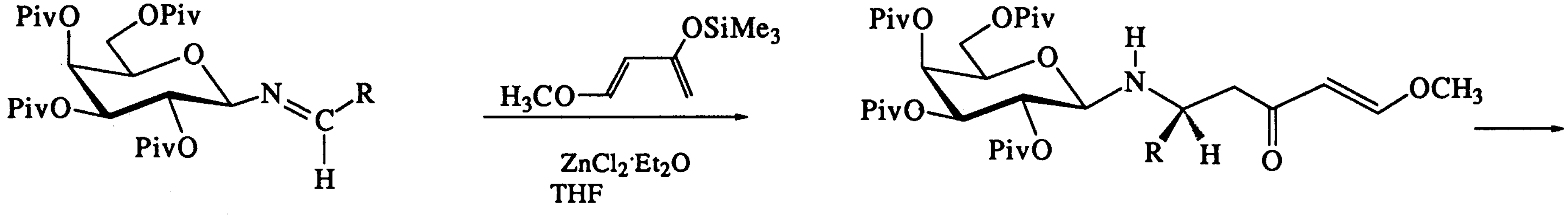
Diastereoselective Synthesis of the Alkaloid (S)-Anabasin on a Carbohydrate Template



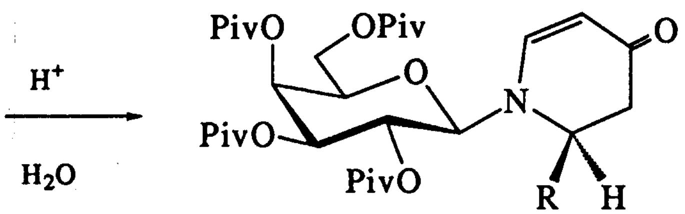
> 90%

Waldemar Pfrengle 1988

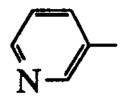
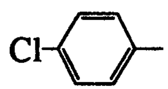
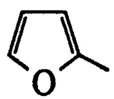
Diastereoselective Tandem-Mannich-Michael-Reaction on N-Galactosyl Imines



A



B

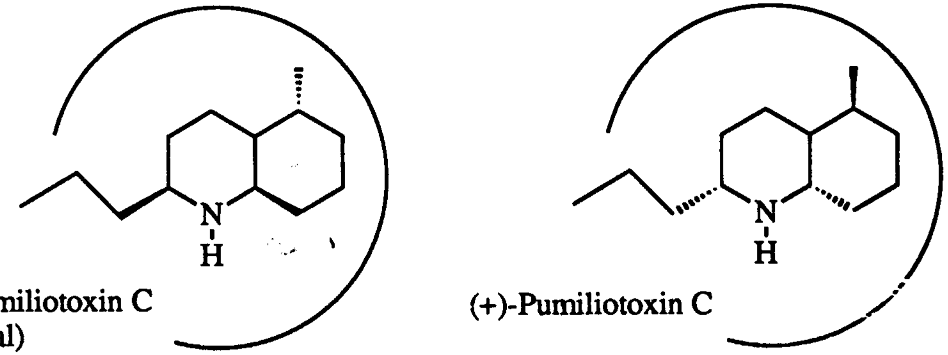
R	Yield (%) A	Yield (%) B	Ratio of Diastereomers B	Pure Isomer (%)
CH_3-CH_2-CH_2 -	-	90	40 : 1 (R) : (S)	81
	57	92	>20 : 1 (S) : (R)	86
	68	>97	50 : 1 (S) : (R)	94
	35	96	20 :1 (S) : (R)	88

Waldemar Pfrengle 1988

Markus Weymann 1996

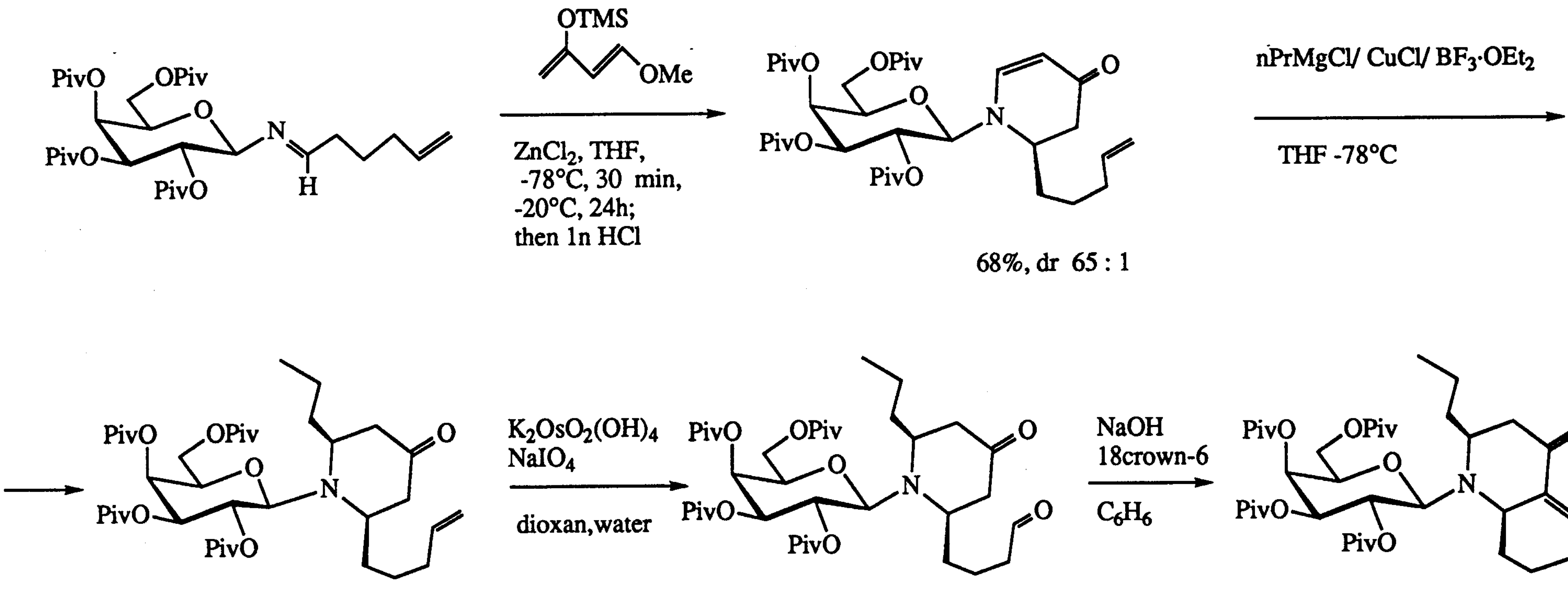
Towards the Stereoselective Synthesis of Pumiliotoxin C

Markus Weymann 1995



(-)-Pumiliotoxin C (natural)

(+)-Pumiliotoxin C



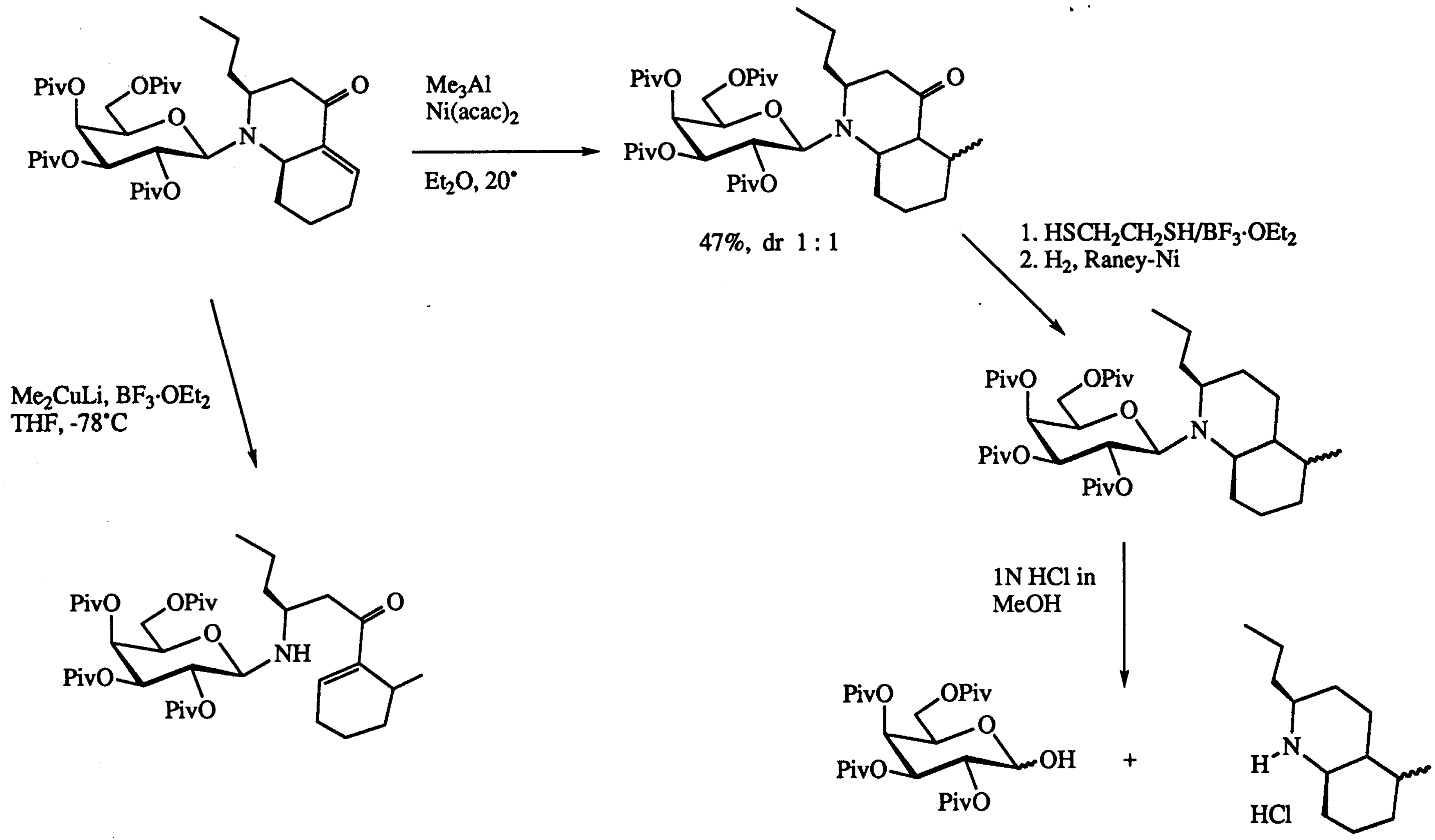
68%, dr 65 : 1

81% dr »10 : 1

75%

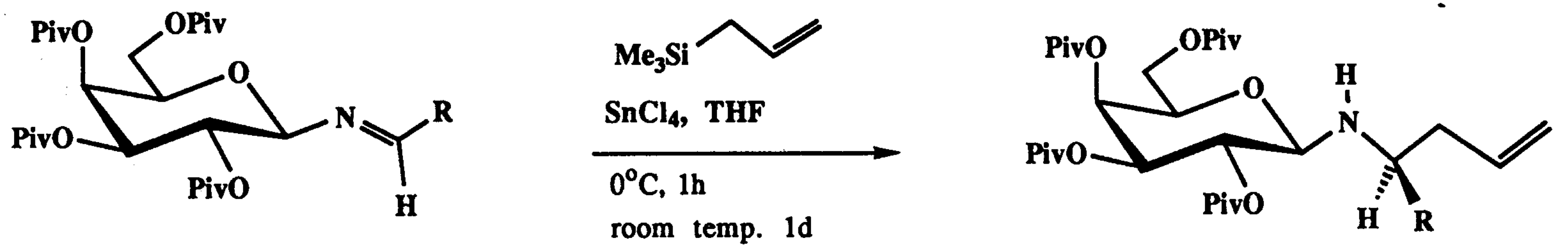
79%

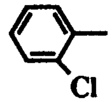
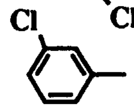
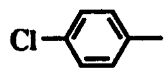
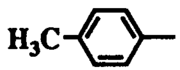
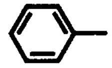
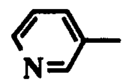
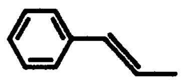
Introduction of Methyl at C-5: An Unexpected Problem



Markus Weymann 1994

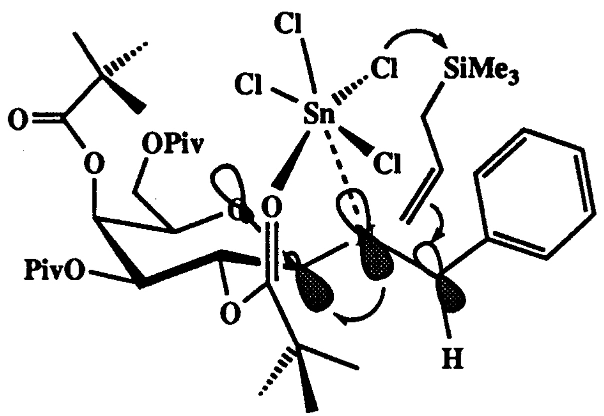
Diastereoselective Synthesis of Chiral Homoallyl Amines on Carbohydrate Amine Templates



R	yield (%)	ratio of diastereomers (S) : (R)
	82	27 : 1
	47	7 : 1
	49	22 : 1
	55	22 : 1
	65	14 : 1
	28	11 : 1
	76	15 : 1

Using  -78°C

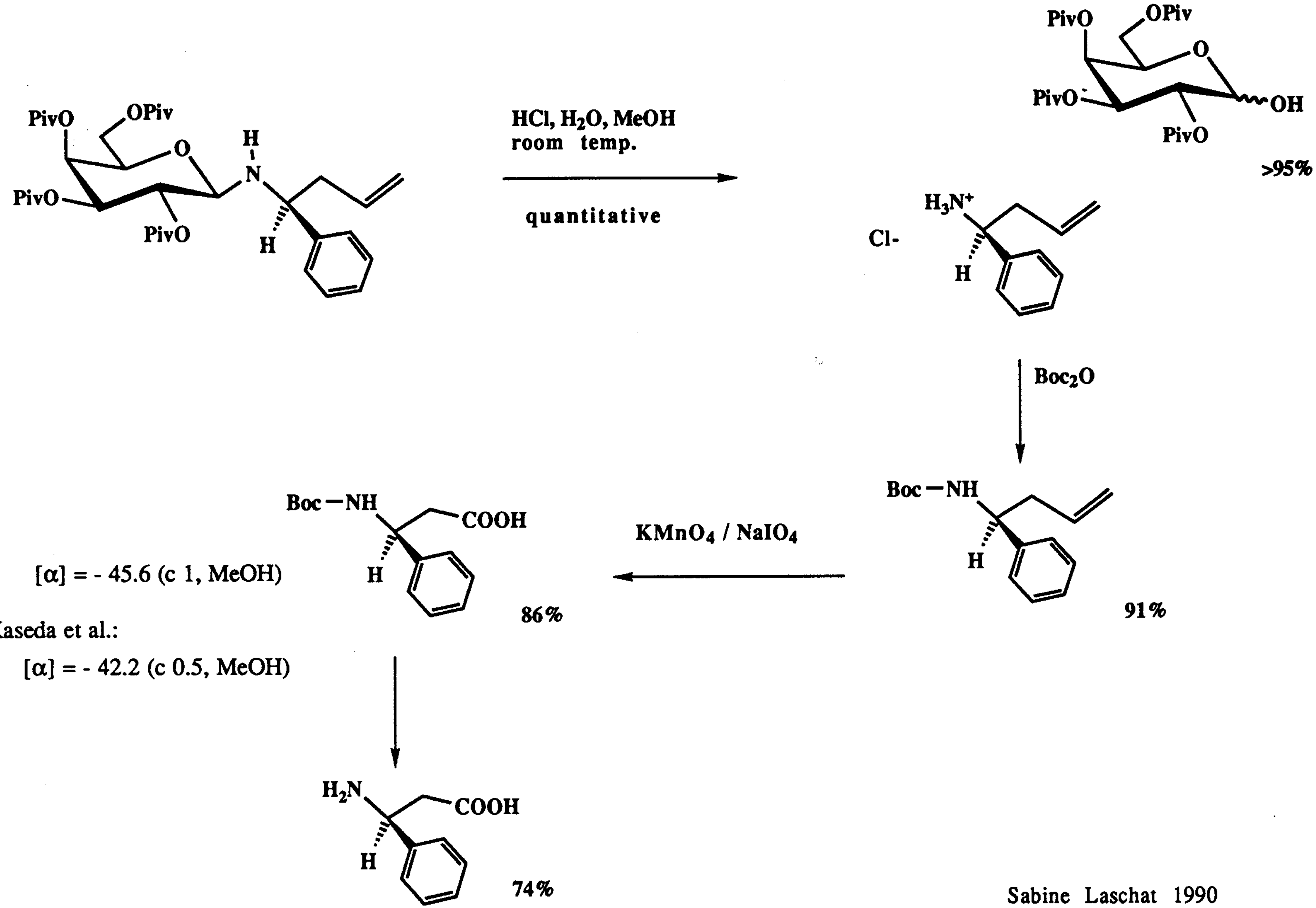
R	yield (%)	ratio of diastereomers (S) : (R)
CH_3-CH_2-CH_2 –	32	>25 : 1



Sabine Laschat 1990

S. Laschat, H. Kunz, Synlett 1990,51;
J. Org. Chem. 56 (1991), 5883.

Release of the Homoallyl Amine from the Carbohydrate Template



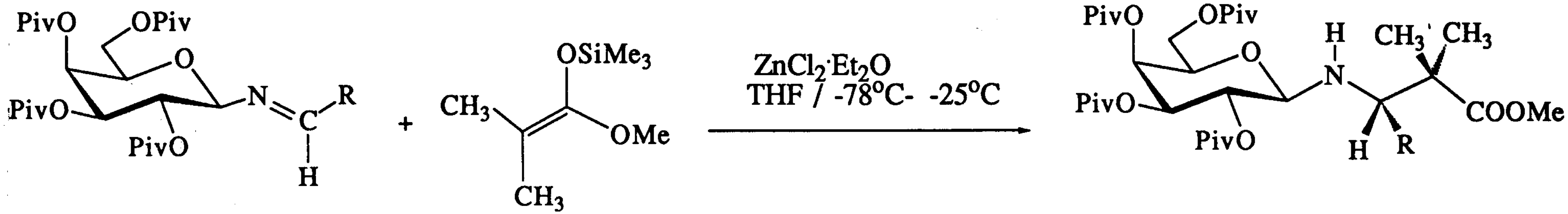
[α] = - 45.6 (c 1, MeOH)

T. Kaseda et al.:

[α] = - 42.2 (c 0.5, MeOH)

Sabine Laschat 1990

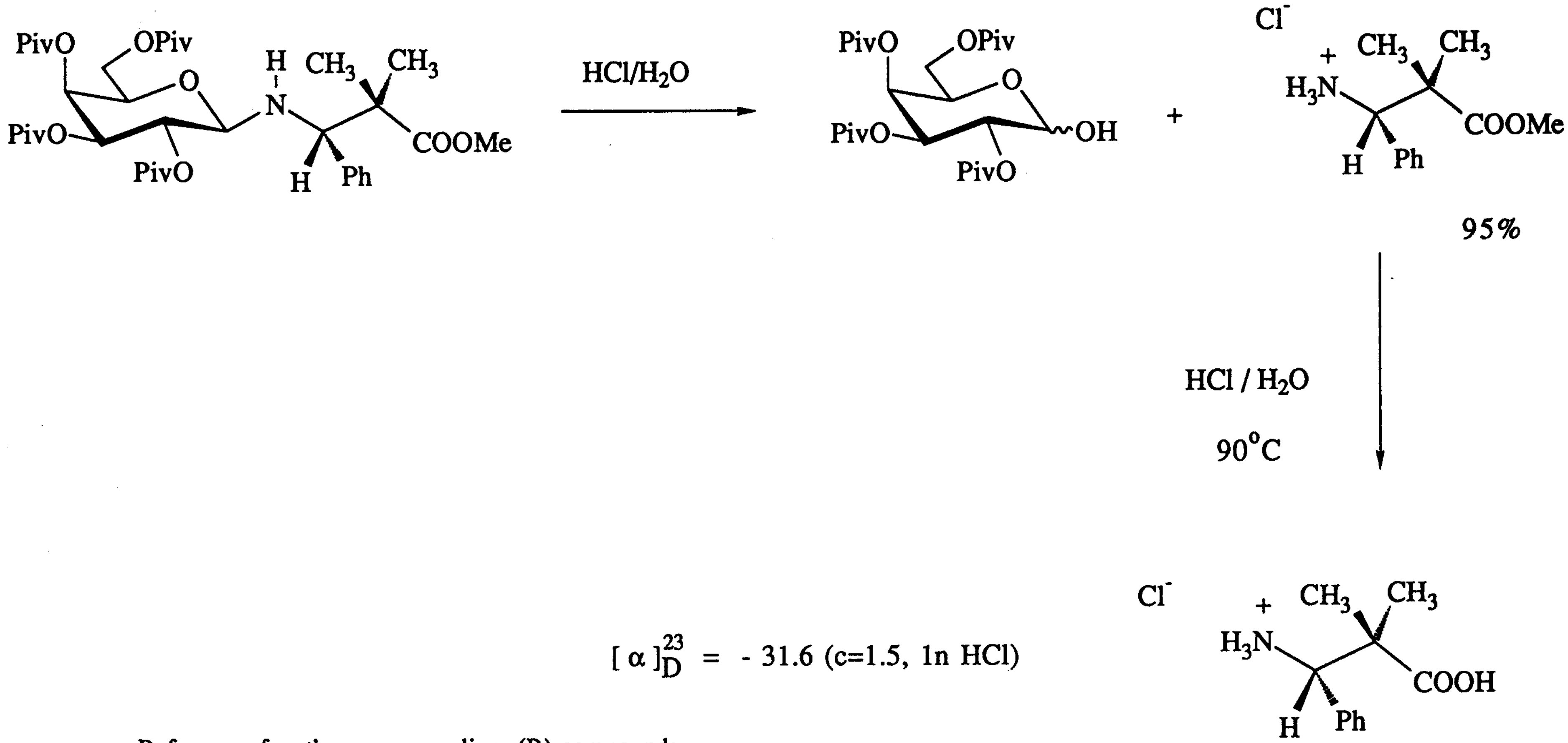
Diastereoselective Synthesis of β-Amino Acids on Galactosylamine as the Chiral Template



R	Yield (%)	Ratio of Diastereomers (S) : (R)
Phenyl	89	147 : 1
" (+30°C)	95	105 : 1
4-Cl-Ph	92	68 : 1
3-Cl-Ph	89	210 : 1
4-F-Ph	88	146 : 1
4-Me-Ph	90	75 : 1
2-Naphthyl (+20°C)	89	12 : 1

Dirk Schanzenbach 1989

Hydrolysis and Structural Assignement of N-Galactosyl β-Amino Acid Derivatives

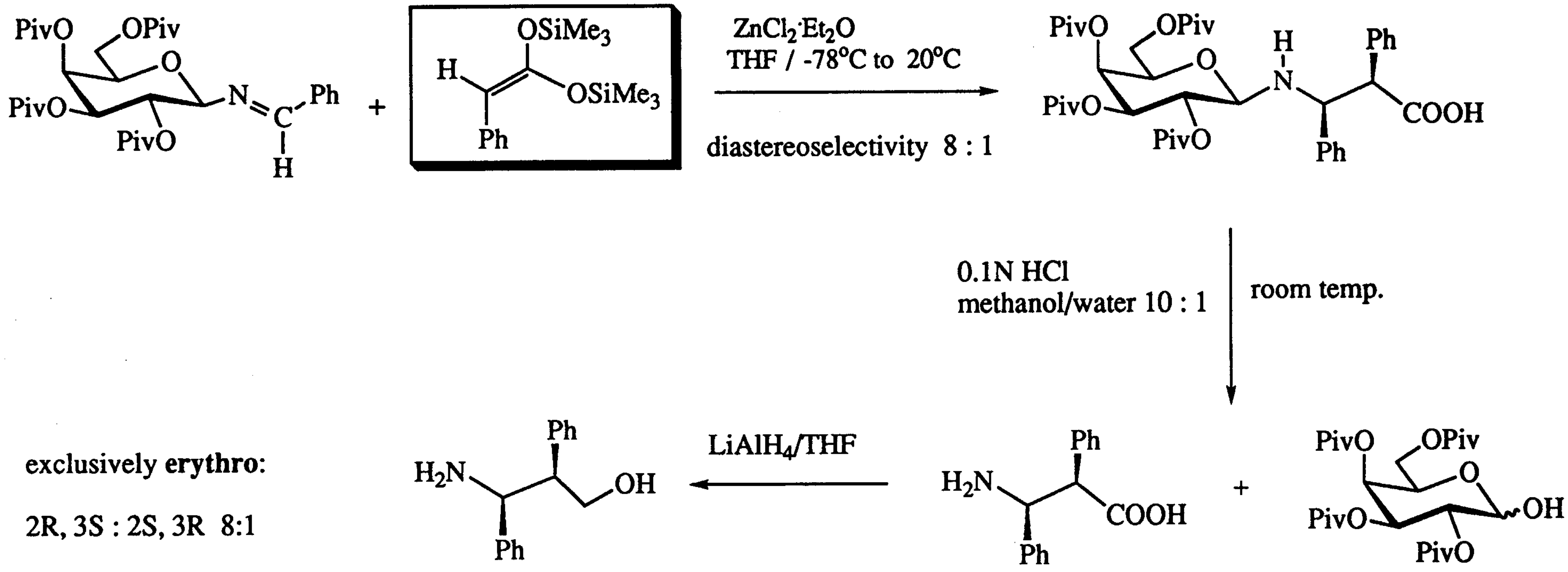


$[\alpha]_D^{23}$ = - 31.6 (c=1.5, 1n HCl)

Reference for the corresponding (R)-compound:
Furukawa et al., Heterocycles 6 (1977), 1323 : $[\alpha]^{25}_D$= + 30.6 (c=1.5, 1n HCl)

Control of Diastereoselectivity of Mannich Reactions by Choice of the Nucleophile

Silyl Ketene Acetal as the C-Nucleophile



exclusively **erythro**:

2R, 3S : 2S, 3R 8:1

Andreas Burgard 1995