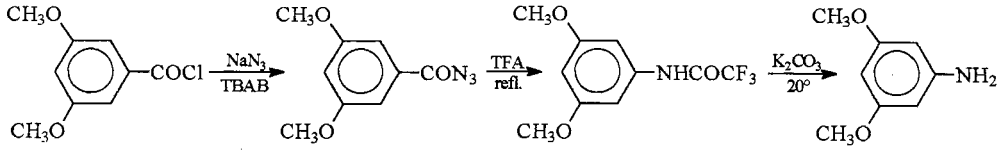
CURTIUS Rearrangement

Degradation of acid hydrazides or acyl azides to amines or amine derivatives (see 1st edition).



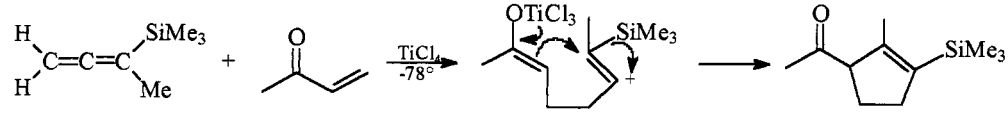
1 2 3 (80%) 4 (94%)

1	Curtius, T.	*Chem. Ber.*	**1890**	*23*	3023
2	Caldwell, W.T.	*J. Am. Chem. Soc.*	**1939**	*61*	3584
3	Newcastle, G.W.	*Synthesis*	**1985**		220
4	Thornton, T.J.	*Synthesis*	**1990**		295
5	Saunders, J.M.	*Chem. Rev.*	**1948**	*43*	205
6	Cohen, L.D.	*Angew. Chem.*	**1961**	*73*	259
7	Smith, P.A.S.	*Org. React.*	**1946**	*3*	337
8	Pfister, J.R.	*Synthesis*	**1983**		39

3,5-Dimethoxyaniline 4.[8] **1** (5.65 g; 28 mmol) in CH_2Cl_2 (50 mL) and TBAB (20 mg) were cooled and treated with NaN_3 (2.5 g; 38.5 mmol) in H_2O (10 mL) with stirring over 2 h at 0°C. After extraction (Et_2O), the extract was added to TFA (2.5 mL; 43 mmol) and refluxed for 40 h to give 5.63 g of **3** (80%), mp 99°C. **3** (4.5 g; 18 mmol), K_2CO_3 (4.2 g; 30 mmol) and water (80 mL) were stirred under N_2 for 20 h at 20°C. Work up and distillation gave 2.6 g of **4** (94%), bp 85-110°C/0.2 torr, mp 48°C.

DANHEISER Annulation

Regiocontrolled synthesis of five membered rings from silylallenes and Michael acceptors in the presence of $TiCl_4$ (see 1st edition).



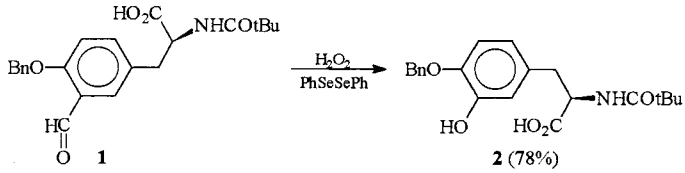
1 2 3 (70%)

1	Danheiser, R.L.	*J. Am. Chem. Soc.*	**1981**	*103*	1604
2	Danheiser, R.L.	*Tetrahedron*	**1983**	*39*	935
3	Danheiser, R.L.	*Org. Synth.*	**1988**	*66*	8

Cyclopentene 3.[1] $TiCl_4$ (0.283 g; 1.5 mmol) was added to **1** (0.126 g; 1 mmol) and **2** (0.07 g; 1 mmol) in CH_2Cl_2 at -78°C. The mixture was stirred for 1 h at -78°C. Work up and chromatography afforded 0.125-0.144 g of **3** (68-75%).

DAKIN Phenol Oxidation

Oxidation of aldo- or keto-phenols to polyphenols by H_2O_2 (a Bayer-Villiger oxidation) (see 1st edition).

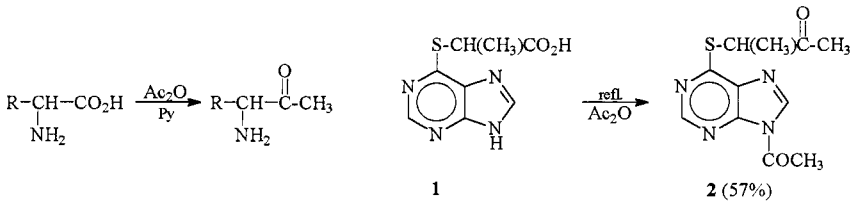


1	Dakin, H.D.	*Am. Chem. J.*	**1909**	*42*	477
2	Baker, J.	*J. Chem. Soc.*	**1953**		1615
3	Criegee, R.	*Liebigs Ann.*	**1948**	*560*	127
4	Seshadri, T.R.	*J. Chem. Soc.*	**1959**		1660
5	Rosenblat, D.H.	*J. Am. Chem. Soc.*	**1953**	*75*	4607
6	Jung, M.E.	*J. Org. Chem.*	**1997**	*62*	1553
7	Lee, J.B.	*Quart. Rev.*	**1969**	*21*	454
8	Varma, R.S.	*Org. Lett.*	**1999**	1	189

Phenol 2.[6] To **1** (96 mg; 0.24 mmol) in CH_2Cl_2 (3 mL) were added $(PhSe)_2$ (3 mg; 0.01 mmol) and 30% H_2O_2 (0.062 mL; 0.614 mmol). After 18 h stirring at 20°C water and EtOAc were added and the organic layer was evaporated. The residue in 3 mL MeOH was treated with NH_3 to give 73 mg of **2** (78%).

DAKIN-WEST Ketone Synthesis

An acylative decarboxylation of α-amino or α-thio acids (see 1st edition).

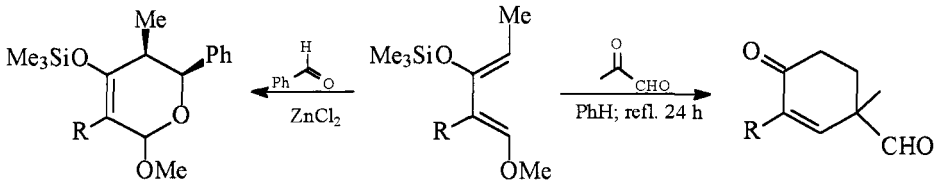


1	Dakin, H.; West, R.	*J. Biol. Chem.*	**1928**	*78*	91
2	Dyer, E.	*J. Org. Chem.*	**1968**	*33*	880
3	Buchanan, G.L.	*Chem. Soc. Rev.*	**1988**	*17*	91
4	Fischer, L.E.	*Org. Prep. Proc. Int.*	**1990**	*22*	467
5	Kawase, M.	*J. Chem. Soc. Chem. Commun.*	**1998**		641

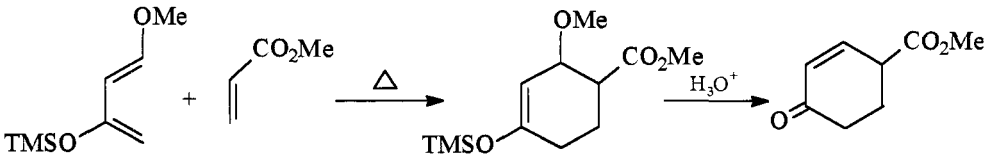
Purine 2.[2] A suspension of acid **1** (1.0 g; 4.4 mmol) in Ac_2O (30 mL) was refluxed for 5 h and stirred overnight at 20°C. The residue on evaporation was triturated with Et_2O, dried (KOH) and extracted (hexane, 9x40 mL) to afford 0.66 g of **2** (57%), mp 98-99°C.

DANISHEFSKY Dienes

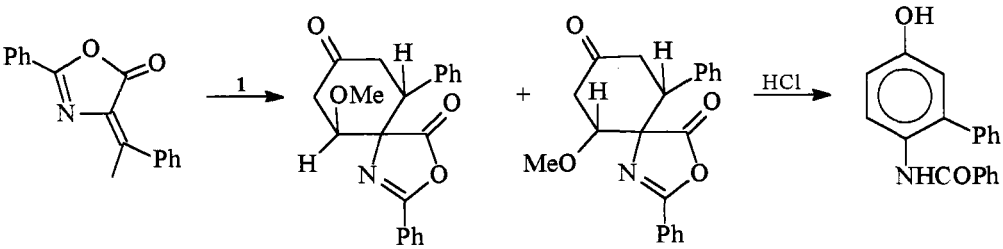
Silyloxydienes in regio- and stereo-controlled Diels-Alder and hetero Diels-Alder reactions (see 1st edition).



1 2 (72%)[1] R: H



(91%)[4]

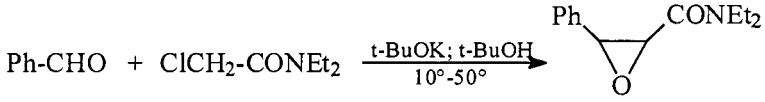


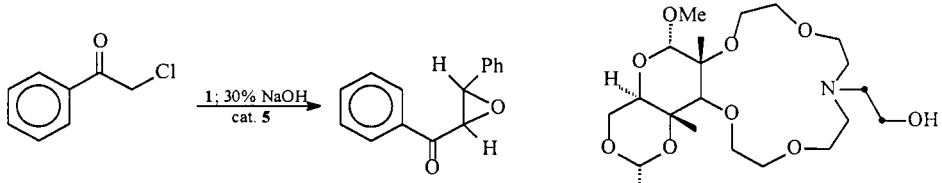
1	Danishefsky, S.	*J. Am. Chem. Soc.*	**1974**	*96*	7807
2	Danishefsky, S.	*J. Am. Chem. Soc.*	**1978**	*100*	6536; 7098
3	Danishefsky, S.	*J. Am. Chem. Soc.*	**1982**	*104*	6457
4	Vorndam, P.E.	*J. Org. Chem.*	**1990**	*55*	3693
5	Nakagawa, N.; Aino, T.	*J. Org. Chem.*	**1992**	*57*	5741
6	Cativiela, C.	*Synthesis*	**1995**		671
7	Danishefsky, S.	*Acc. Chem. Res.*	**1981**	*14*	400

3-Phenyl-4-benzamidophenol 6.[6] Danishefsky diene **1** (468 mg; 4 mmol) was added to oxazolone **3** (474 mg; 2 mmol) in PhH (25 mL) and the mixture was refluxed for 48 h with stirring. After evaporation the cycloadducts **4** and **5** were treated with 0.005N HCl in 20 mL THF (1:4) for 7 h at 20°C. Work up and chromatography (silica gel, hexane:EtOAc 1:1) gave 410 mg of **6** (71%).

DARZENS Epoxide Synthesis

Synthesis of glycidic esters, amides or ketones from an aldehyde or ketone and an α-haloester, amide or ketone (see 1st edition).





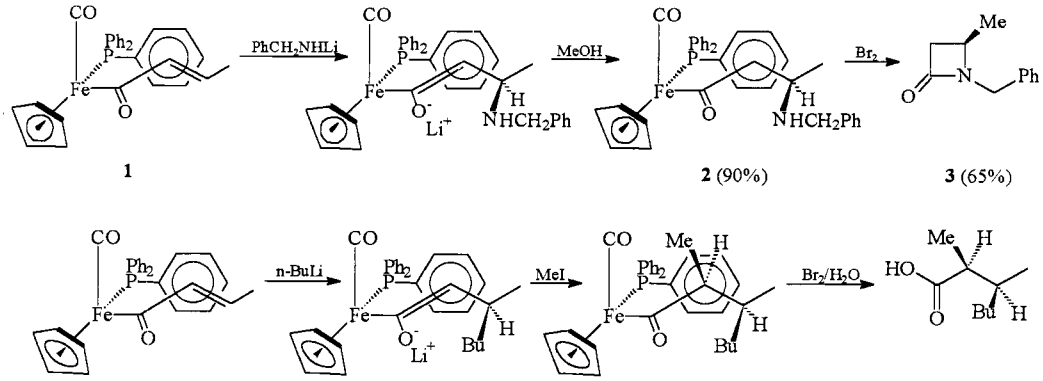
1	Darzens, G.	*C. R.*	**1904**	*139*	1214
2	Tung, T.T.	*J. Org. Chem.*	**1963**	*28*	1514
3	Gladiale, S.	*Synth. Commun.*	**1982**	*12*	355
4	Corey, E.J.	*Tetrahedron Lett.*	**1991**	*32*	2857
5	Pridgen, L.N.	*J. Org. Chem.*	**1993**	*58*	5107
6	Maillard, B.	*J. Org. Chem.*	**1994**	*59*	4765
7	Töke, L.	*Synlett*	**1997**		291
8	Balester, M.	*Chem. Rev.*	**1955**	*55*	283
9	Newman, M.S.	*Org. React.*	**1949**	*5*	414

***cis*- and *trans*-Epoxide 3.**[2] tBuOK (K, 16 g; t-BuOH, 400 mL) was added to a mixture of **1** (42.4 g; 0.4 mol) and **2** (59.8 g; 0.4 mol) under N_2 at 10°C over 90 min. After stirring the solvent was removed at 50°C. Work up gave a viscous oil (87.1 g; 99%) which treated with Et_2O (150 mL) and hexane (300 mL) gave 77 g of **3** (88.4%), mp 43-47°C.

1-Benzoyl-2-phenylethene oxide 6.[7] A toluene solution of phenacyl chloride **4** (0.2 g; 1.3 mmol) was treated with PhCHO **1** (0.2 g; 1.9 mmol) and catalyst **5** (0.1 mmol) in 30% NaOH (0.6 mL). The mixture was stirred for 4 h at 20°C under Ar. Usual work up followed by chromatography (preparative TLC, CH_2Cl_2) gave 262 mg of **6** (90%; 43% ee).

DAVIES Asymmetric synthesis

Iron chiral auxiliary for asymmetric aldol reaction, Michael addition, β-amino acid and β-lactam synthesis.



1 2 (90%) 3 (65%)

1	Davies, S.G.	*Chem. Commun.*	**1982**		1303
2	Davies, S.G.	*Chem. Commun.*	**1985**		607
3	Davies, S.G.	*J. Organometal. Chem.*	**1985**	*296*	C40
4	Davies, S.G.	*Tetrahedron*	**1986**	*42*	175
5	Davies, S.G.	*Tetrahedron*	**1986**	*42*	5123
6	Davies, S.G.	*Aldrichimica Acta*	**1990**	*23*	31

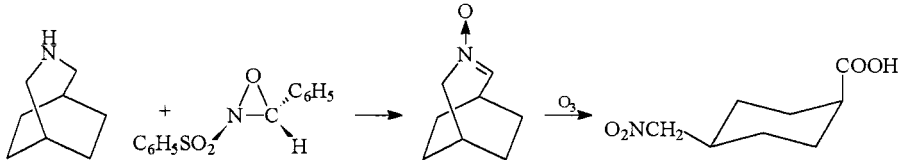
For synthesis of **1** see ref. 3 and 4.

(*RR*/*SS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH(Me)NHCH_2Ph$] 2.[5] n-BuLi (0.4 mL; 0.64 mmol) was added to $PhCH_2NH_2$ (70 mg; 0.66 mmol) in THF (20 mL) at -20°C to give a purple solution. After 1 h stirring at -20°C this was added to **1** (250 mg; 0.52 mmol) in THF (30 mL) at -78°C. MeOH (66.5 mg; 2.08 mmol) was added and the mixture further stirred 1 h at -78°C. After evaporation of the solvent, the residue dissolved in CH_2Cl_2 was filtered through Celite and chromatographed (Alumina I, CH_2Cl_2:EtOAc:MeOH 10:9:1) to afford 690 mg of **2** in 90% single diastereoisomer, $[\alpha]_D^{21}$= +143.0°.

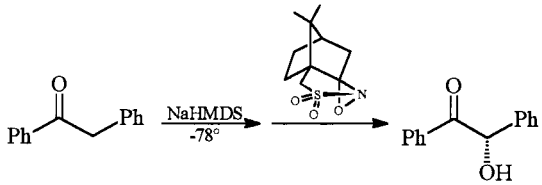
(4*S*)-(-)-4-Methyl-N-benzyl-β-lactam 3. Oxidation of **2** with Br_2 in CH_2Cl_2 at -40°C followed by chromatography on silica gel (Merck 60 H), hexane:Et_2O 2:1 gave the iron complex. Elution with the same solvents 1:2 gave 106 mg of **3** (65%), $[\alpha]_D^{21}$= -38.5° (c 2.1, MeOH).

DAVIS Oxidizing Reagent

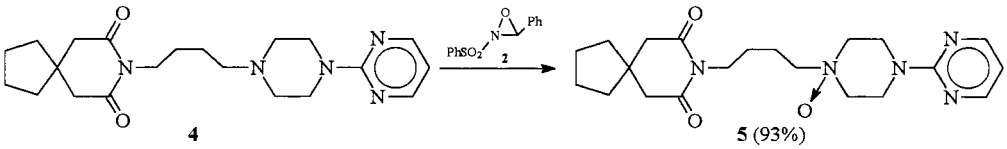
2-Sulfonyloxaziridines as aprotic neutral oxidizing reagents in oxidation of amines, sulfides, selenides and asymmetric oxidation (see 1st edition).



3 (66%)



(85%, (*S*) 93% ee)[6]



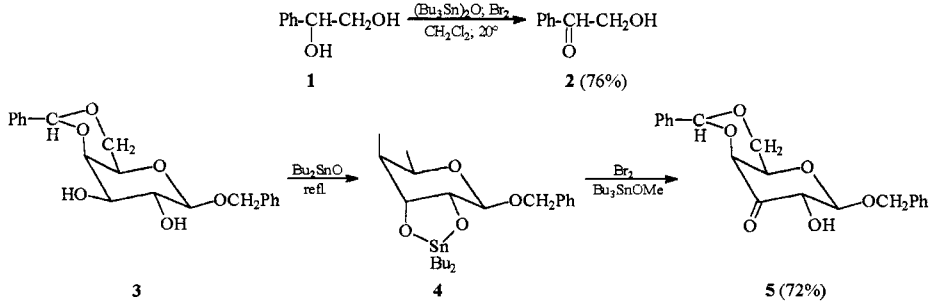
(93%)

1	Davis, F.A.	*J. Org. Chem.*	**1982**	*47*	1174
2	Davis, F.A.	*Tetrahedron Lett.*	**1983**	*24*	1213
3	Davis, F.A.	*J. Org. Chem.*	**1986**	*51*	4083; 4240
4	Zajak, W.W.	*J. Org. Chem.*	**1988**	*53*	5856
5	Davis, F.A.	*J. Org. Chem.*	**1990**	*55*	3715
6	Davis, F.A.	*J. Am. Chem. Soc.*	**1990**	*112*	6679
7	Chen, D.C.	*Org. Prep. Proc. Int.*	**1996**	*28*	115
8	Dimitrenco, G.I.	*J. Am. Chem. Soc.*	**1997**	*119*	1159

***cis*-4-(Nitromethyl)cyclohexanecarboxylic acid 3.**[4] To a solution of 2-(phenylsulfonyl)-3-phenyloxaziridine **2** (0.523 g; 2.0 mmol) in $CHCl_3$ (10 mL) was added 3-azabicyclo[3.2.2]nonane **1** (0.125 g; 1 mmol). The reaction mixture was stirred for 15 min, then the solvent was removed by rotary evaporation and replaced by CH_2Cl_2. This solution was ozonized at -78°C. The CH_2Cl_2 solution was then extracted with saturated $NaHCO_3$ solution. The aqueous layer was neutralized with HCl and then extracted with CH_2Cl_2. The CH_2Cl_2 solution was rotary evaporated and the residue subjected to PLC. The major fraction that was isolated was recrystallized from EtOH to provide 0.123 g of **3** (66%), mp 83-85°C.

DAVID-MUKAIYAMA-UENO Selective Diol Oxidation

Regiospecific oxidation of diols to ketoalcohols by Br_2 via Sn derivatives.

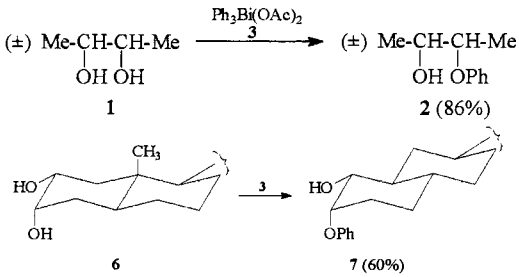


1	Mukaiyama, T.	*Chem. Lett.*	**1975**		145
2	Mukaiyama, T.	*Bull. Soc. Chim. Japan*	**1976**	*49*	1656
3	Ueno, Y.	*Tetrahedron Lett.*	**1976**		4597
4	David, S.	*Nouveau J. Chem.*	**1979**	*3*	63
5	David, S.	*C. R. Acad. Sci. Paris (C)*	**1974**	*278*	1051
6	David, S.	*J. Chem. Soc. Perkin I*	**1979**		1568

Hydroxyacetophenone 2.[3] To **1** (570 mg; 4 mmol) and hexabutyl-distannoxane (2.7 mL; 5.2 mmol) in CH_2Cl_2 was added dropwise Br_2 (0.27 mL; 5.2 mmol) in CH_2Cl_2 (5 mL) under Ar. After 3 h stirring evaporation and crystallization gave 410 mg of **2** (76%), mp 84-86°C.

DAVID-THIEFFRY Monophenylation of Diols

Selective phenylation of one hydroxyl group of glycols by triphenylbismuth diacetate.

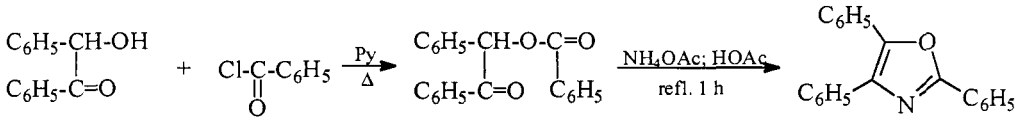


1	David, S.; Thieffry, A.	*Tetrahedron Lett.*	**1981**	*22*	2885
2	David, S.; Thieffry, A.	*Tetrahedron Lett.*	**1981**	*22*	5063
3	David, S.; Thieffry, A.	*J. Org. Chem.*	**1983**	*48*	441

3-Phenoxybutan-2-ol 2.[3] **1** (90 mg; 1 mmol), triphenylbismuth diacetate **3** (558 mg; 1 mmol) in CH_2Cl_2 (5 mL) were refluxed for 4-5 h (TLC). Evaporation and chromatography afforded 142 mg of **2** (86%).

DAVIDSON Oxazole Synthesis

Synthesis of triaryloxazoles from α-hydroxyketones (see 1st edition).

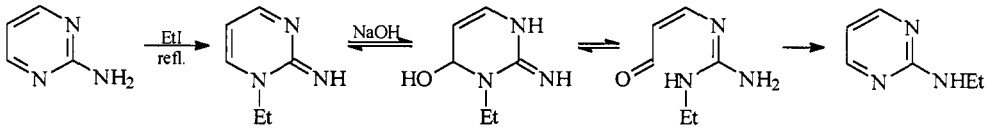


1 **2** **3** (70%) **4** (80%)[1]

1	Davidson, D.	*J. Org. Chem.*	**1937**	*2*	328
2	Cornforth, J.W.	*J. Chem. Soc.*	**1953**		93
3	Theilig, S.	*Chem. Ber.*	**1953**	*86*	96
4	Budevich, M.	*Chem. Ber.*	**1954**	*87*	700
5	Willey, R.H.	*Chem. Rev.*	**1945**		93

DIMROTH Rearrangement

Migration of an alkyl or aryl group from a heterocyclic to an exocyclic N (first descovery by Rathke) (see 1st edition).



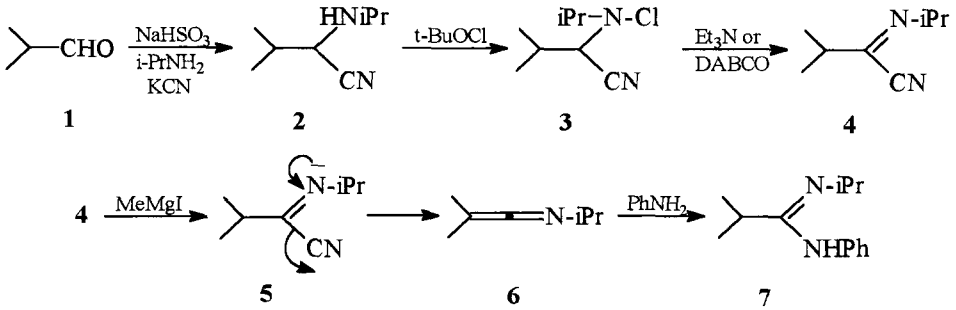
1 **2** (82%) **3** (70%)

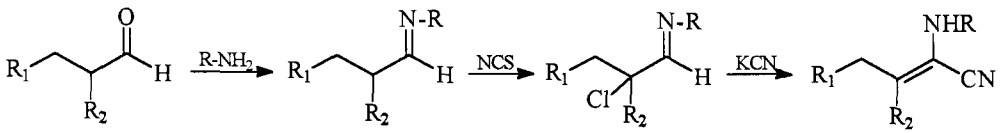
1	Rathke, B.	*Chem. Ber.*	**1888**	*21*	867
2	Dimroth, O.	*Liebigs Ann.*	**1909**	*364*	183
3	Brown, D.J.	*J. Chem. Soc.*	**1963**		1276
4	Brown, D.J.	*Nature*	**1961**	*189*	828
5	Korbonits, D.	*J. Chem. Soc.*	**1986**		2163
6	Katritzky, A.R.	*J. Org. Chem.*	**1992**	*57*	190
7	Saito, T.	*Chem. Pharm. Bull.*	**1993**	*41*	1850
8	Loakes, D.	*J. Chem. Soc. Perkin I*	**1999**	*1*	1333

2-(Ethylamino)pyrimidine 3.[3] **2** (0.25 g; 1 mmol) in 1N NaOH (10 mL) was heated for 15 min on a water bath. The pH was corrected to 5 and all was added to a picric acid solution to afford 0.23 g of picrate **3** (70%), mp 167°C.

DE KIMPE Amidine Synthesis

Conversion of aldehydes to keteneimines (see **6**) and amidines (see **7**) via α-cyano-enamines.





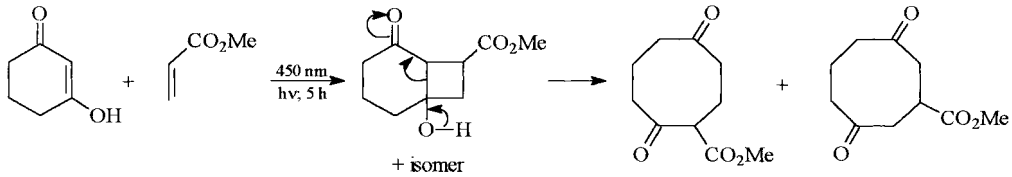
1	De Kimpe, N.	*Tetrahedron*	**1976**	*32*	3063
2	De Kimpe, N.	*Synthesis*	**1978**		895
3	De Kimpe, N.	*J. Org. Chem.*	**1978**	*43*	2670
4	De Kimpe, N.	*Synth. Commun.*	**1979**	*9*	901
5	De Kimpe, N.	*Chem. Ber.*	**1983**	*116*	3846
6	De Kimpe, N.	*Can. J. Chem.*	**1984**	*62*	1812

2-Isopropylimino-3-methylbutanenitrile 4.[2] $NaHSO_3$ (10.9 g; 105 mmol) in water (50 mL) was added with stirring to **1** (7.1 g; 100 mmol). After 2 h at 20°C, KCN (14.3 g; 220 mmol) in water (25 mL) was added and stirring was continued for 5 h. Extraction with Et_2O and vacuum distillation afforded 10 g of **2** (72%), bp 75-76°C/13 torr. To a solution of **2** (10 g; 70 mmol) in PhH (100 mL) at 0°C was added a solution of tBuOCl (8.7 g; 80 mmol) in PhH (15 mL). After 1 h stirring at 0°C Et_3N (8.4 g; 84 mmol) or the same amount of DABCO was added. Stirring was continued 1 h at 20°C and 18 h at 50°C. Usual work up afforded 5.9 g of **4** (61%), bp 47°C/12 torr.

N^1-Phenyl-N^2-isopropyl-2-methylpropanamidine 7.[3] A solution of **4** (6.9 g; 50 mmol) in Et_2O was treated with MeMgI (87.5 mmol) in Et_2O followed by quenching (NH_4Cl) and extraction to give keteneimine **6**. This with $PhNH_2$ (4.5 g; 50 mmol) afforded 6.15 g of amidine **7** (60%).

DE MAYO Photocycloaddition

Photochemical 2+2 cycloaddition (see 1st edition).

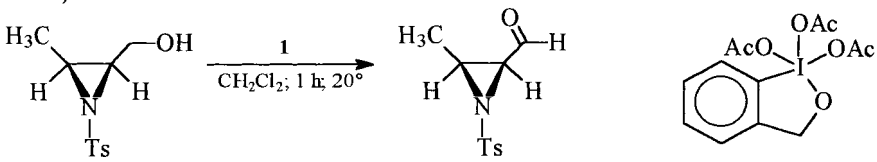


1 **2** **3** (60%) **4**

1	De Mayo, P.	*Proc. Chem. Soc. London*	**1962**		119
2	De May	*Can. J. Chem.*	**1962**	*41*	440
3	De Mayo, P.	*J. Org. Chem.*	**1969**	*34*	794
4	De Mayo, P.	*Acc. Chem. Res.*	**1971**	*4*	41
5	Weedon, A.C.	*The Chemistry of Enols (Wiley)*	**1990**		591

DESS-MARTIN Oxidizing Reagent

Oxidation of alcohols to aldehydes or ketones by means of periodinanes, e.g. **1** (see 1st edition).



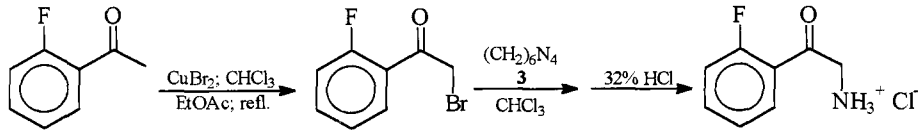
2 **3** (80%) **1**[4]

1	Dess, P.B.; Martin, J.C.	*J. Am. Chem. Soc.*	**1978**	*100*	300
2	Dess, P.B.; Martin, J.C.	*J. Am. Chem. Soc.*	**1979**	*101*	5294
3	Yagupolsky, L.M.	*Synthesis*	**1977**		574
4	Dess, P.B.; Martin, J.C.	*J. Org. Chem.*	**1983**	*48*	4155
5	Robins, J.C.	*J. Org. Chem.*	**1990**	*55*	5186
6	Wipf, P.	*Synlett*	**1997**		1

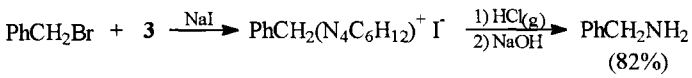
Formylaziridine 3.[6] **2** (1.15 g; 4.76 mmol) in CH_2Cl_2 (24 mL) was added to a suspension of **1**[4] (2.35 g; 5.7 mmol) in CH_2Cl_2 (24 mL). After 1 h stirring at 20°C, usual work up and chromatography (silica gel, 28% EtOAc in hexane) afforded 0.91 g of **3** (80%).

DELEPINE Amine Synthesis

Synthesis of primary amines from alkyl halides with hexamethylenetetramines (see 1st edition).



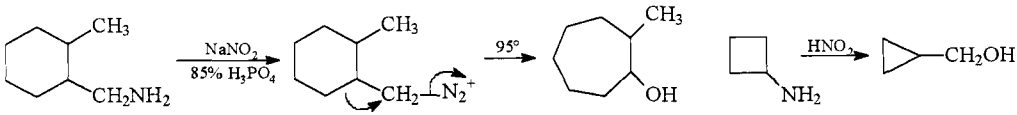
1 2 4 (40%)[3]



1	Delepine, M.	*Bull. Soc. Chim. Fr.*	**1885**	*13*	356
2	Galat, A.	*J. Am. Chem. Soc.*	**1939**	*61*	3585
3	Henry, A.	*J. Org. Chem.*	**1990**	*55*	1796
4	Angyal, S.T.	*Org. Synth.*	Coll. Vol.	*IV*	121

DEMJANOV Rearrangement

Deamination of primary amines to rearranged alcohols (via diazonium compounds) with ring contraction or enlargement for alicyclic amines (see 1st edition).

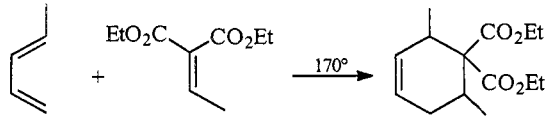


1 2 (78%)

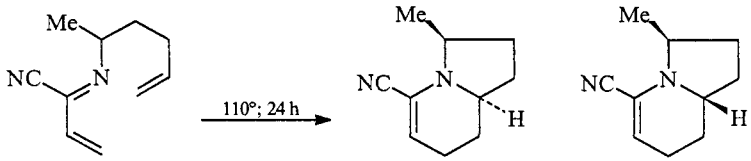
1	Demjanov, N.J.	*J. Russ. Phys. Chem. Soc.*	**1903**	*35*	26
2	Kottany, R.	*J. Org. Chem.*	**1965**	*30*	350
3	Smith, P.A.	*Org. React.*	**1960**	*11*	154

DIELS-ALDER Cyclohexene Synthesis

4+2 Thermal cycloaddition between a diene and an activated alkene or alkyne, sometimes catalyzed by Lewis acids (see 1st edition).



1 **2** **3** (68%)



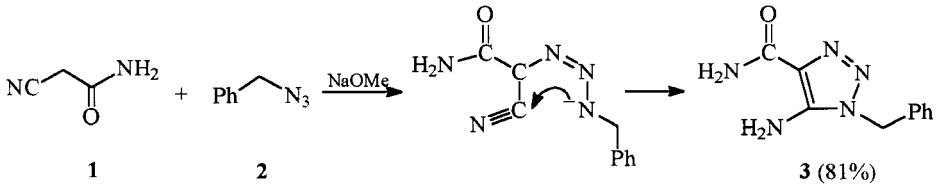
4 **5** 4 : 1 **6** (98%)

1	Diels, O.; Alder, K.	*Liebigs Ann.*	**1928**	*460*	98
2	House, H.O.	*J. Org. Chem.*	**1963**	*28*	27
3	Johnson, C.R.	*J. Org. Chem.*	**1987**	*52*	1493
4	Wenkert, E.	*Chem. Rev.*	**1990**	*22*	131
5	Waldmann, H.	*Tetrahedron Asymm.*	**1991**	*2*	1231
6	Jorgensen, K.A.	*J. Org. Chem.*	**1995**	*60*	6851
7	Fowler, F.W.	*J. Org. Chem.*	**1997**	*62*	2093
8	Oppolzer, W.	*Angew. Chem.*	**1984**	*96*	840
9	Boger, D.L.	*Chem. Rev.*	**1986**	*86*	781
10	Bieker, W.	*Tetrahedron Lett.*	**2001**	42	419

Indolizines 5 and 6.[7] **4** (100 mg; 0.6 mmol) in PhH (4 mL) in a thick-walled glass tube, under Ar was heated (oil bath, 110°C) with stirring for 24 h. The residue obtained after evaporation was chromatography (silica gel, heptane:Et_2O 1:1) afforded **5** and **6** (4:1), 94 mg (94%).

DIMROTH Triazole Synthesis

Synthesis of 1,2,3-triazoles from alkyl or aryl azides and active methylene compounds.

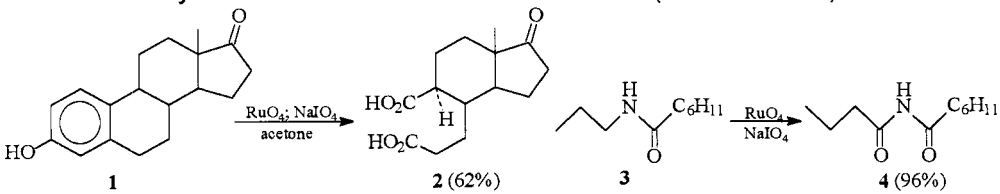


1	Dimroth, O.	*Chem. Ber.*	**1902**	*36*	1029; 4041
2	Hoover, J.R.E.	*J. Am. Chem. Soc.*	**1956**	*78*	5832
3	L'abbé, G.	*Ind. Chim. Belge*	**1971**	*36*	3
4	Olsen, C.E.	*Tetrahedron Lett.*	**1968**		3805
5	Tolman, R.L.	*J. Am. Chem. Soc.*	**1972**	*94*	2530
6	L'abbé, G.	*Angew. Chem. Int. Ed.*	**1975**	*14*	779

Triazole 3.[2] To Na (4.6 g; 0.2 atg) in MeOH (500 mL) were added cyanoacetamide **1** (16.82 g; 0.2 mol) and benzyl azide **2** (26.6 g; 0.2 mol). After 1 h reflux, the mixture was cooled to afford 35 g of **3** (81%), mp 230-232°C.

DJERASSI-RYLANDER Oxidation

RuO_4 in oxidative cleavage of phenols or alkenes, oxidation of aromatics to quinones, oxidation of alkyl amides to imides or of ethers to esters (see 1st edition).

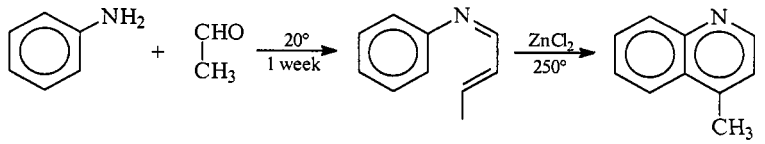


1	Djerassi, C.; Engle, R.R.	*J. Am. Chem. Soc.*	**1953**	*75*	3838
2	Pappo, R.; Becker, A.	*Bull. Res. Council Isr.*	**1956**	*A5*	300
3	Rylander, P.N.	*J. Am. Chem. Soc.*	**1958**	*80*	6682
4	Caputo, J.A.	*Tetrahedron Lett.*	**1962**		2729
5	Caspi, E.	*J. Org. Chem.*	**1969**	*34*	112; 116
6	Tanaka, K.	*Chem. Pharm. Bull.*	**1987**	*35*	364
7	Tamura, O.	*Synlett*	**2000**		1553

Imide 4.[6] **3** (1.04 g; 6 mmol) in EtOAc (20 mL) was added to $RuO_4 \cdot H_2O$ (100 mg) and 10% $NaIO_4$ (30 mL) under vigorous stirring at 20°C (TLC). Extraction with EtOAc, addition of iPrOH, filtration of RuO_2 gave 1.054 g of **4** (96%).

DOEBNER-MILLER Quinoline Synthesis

Quinoline synthesis from anilines and aldehydes (see 1st edition).

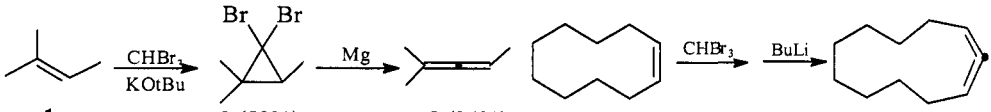


1 2 3 (32%)

1	Doebner, O.; Miller, W.	*Ber.*	**1883**	*16*	2464
2	Leir, C.M.	*J. Org. Chem.*	**1977**	*42*	911
3	Corey, J.E.	*J. Am. Chem. Soc.*	**1981**	*103*	5599
4	Bergstom, F.W.	*Chem. Rev.*	**1944**	*35*	153
5	Johnson, W.S.	*J. Am. Chem. Soc.*	**1944**	*66*	210

DOERING-LA FLAMME Allene Synthesis

Allene synthesis from olefins via gem-dihalocyclopropanes (see 1st edition).



1 2 (50%) 3 (34%)

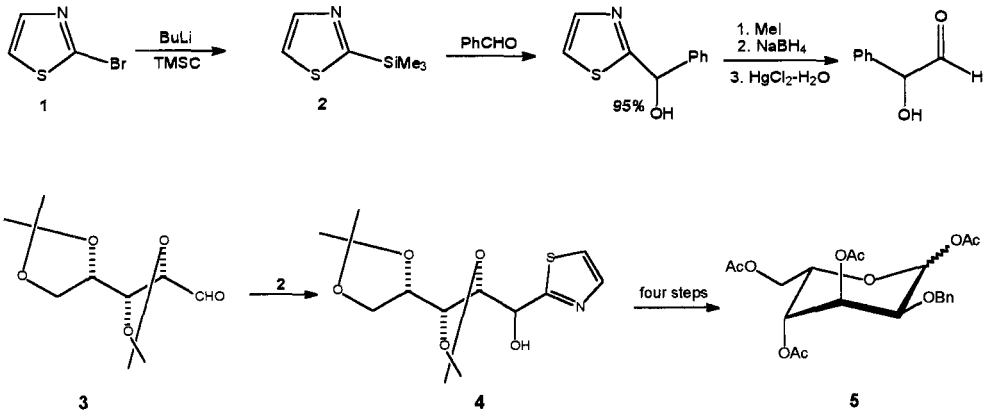
1	Doering, v.W.	*J. Am. Chem. Soc.*	**1954**	*76*	6162
2	La Flamme, P.M.	*Tetrahedron*	**1958**	*2*	75
3	Moore, W.R.	*J. Org. Chem.*	**1962**	*27*	4182
4	Chinoporos, E.	*Chem. Rev.*	**1963**	*63*	235

1,1,3-Trimethyl-2,2-dibromo-cyclopropane 2.[1,2] To a solution of 2-methyl-2-butene **1** (14.0 g; 0.2 mol) in a solution of KOtBu (22.4 g; 0.2 mol) in tBuOH was added under stirring and cooling $CHBr_3$ (50.6 g; 0.2 mol). The mixture was poured into water, extracted with pentane and distilled to give 24.4 g of **2** (50%), bp 63-65°C/15 mm.

2-Methyl-2,3-pentadiene 3.[1,2] **2** (24.4 g; 0.1 mol) in THF (50 mL) was added to Mg turnings (4.86 g; 0.2 atg) in THF. Hydrolysis with water and fractionation afforded 2.75 g of **3** (34%), bp 72.5°C.

DONDONI Homologation

Homologation of aldehydes, ketones, acyl chlorides via 2-(trimethylsilyl) thiazole addition, also two carbon homologation (see 1st edition).

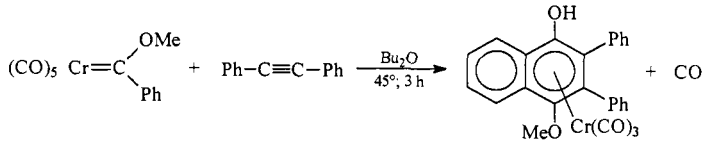


1	Dondoni, A.	*Angew. Chem. Int. Ed.*	**1986**	*25*	835
2	Dondoni, A.	*J. Org. Chem.*	**1989**	*54*	693
2	Dondoni, A.	*J. Org. Chem.*	**1997**	*62*	6261
3	Dondoni, A.	*Synthesis*	**1998**	*1681*	
4	Dondoni, A.	*J. Chem. Soc. Chem. Commun.*	**1999**	*2133*	
5	Vasella, A.	*Helv. Chim. Acta.*	**1998**	*81*	889
6	Nicolaou, A.	*Angew. Chem. Int. Ed.*	**1999**	*38*	3345

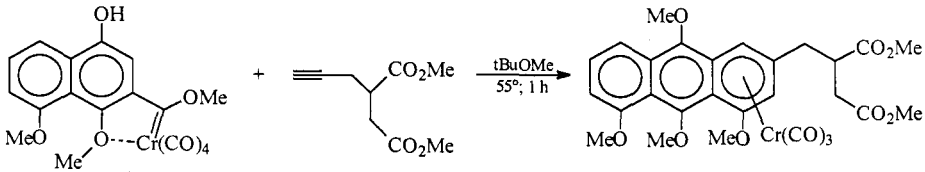
1,3,4,6-Tetra-*O*-acetyl-2-*O*-benzyl-L-gulopyranose (5).[3] To a cooled (-20 °C), stirred solution of crude *aldehydo*-L-xylose diacetonide **3** (3.53 g, ca. 15.3 mmol) in anhydrous CH_2Cl_2 (60 mL) was added 2-(trimethylsilyl) thiazole **2** (3.2 mL,19.9 mmol) during 15 min. The solution was stirred at 0 °C for an additional hour and concentrated. A solution of the residue in anhydrous THF (60 mL) was treated with *n*–$Bu_4NF.3H_2O$ (4.48 g, 15.3 mmol) at room temperature for 30 min and then concentrated. The residue was dissolved in CH_2Cl_2 (300 mL), washed with H_2O (3×50 mL), dried (Na_2SO_4), and concentrated to give the *anti* adduct **4** (4.50 g, 80% from **3**) containing 5% of the *syn* isomer. Crystallization of the crude product from AcOEt-cyclohexane afforded pure **4** (3.42 g, 61% from **3**). The transformation of **4** to **5** was carried out by the following reaction sequence: a) benzylation (BnBr, NaH, DMF); b) aldehyde liberation by cleavage of the thiazole ring (*N*-methylation, reduction, hydrolysis); c) deacetonization (AcOH, H_2O); d) exhaustive acetylation (Ac_2O).

DÖTZ Hydroquinone Synthesis

Hydroquinone synthesis (regiospecific) from alkynes and carbonyl carbene chromium complexes (see 1st edition).



1 2 3 (62%)

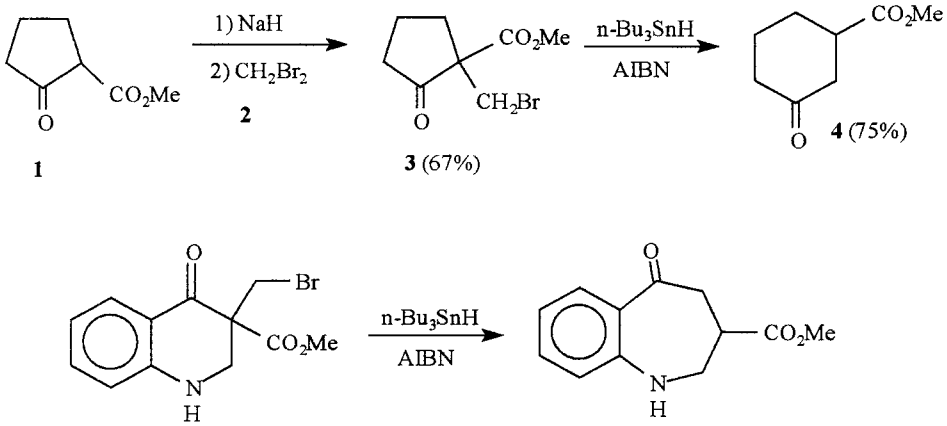


4 5 6 (81%)

1	Dötz, K.H.	*Angew. Chem. Int. Ed.*	**1975**	*14*	644
2	Dötz, K.H.	*Chem. Ber.*	**1988**	*121*	665
3	Hofmann, P.	*Angew. Chem. Int. Ed.*	**1989**	*28*	908
4	Dötz, K.H.	*New J. Chem.*	**1990**	*14*	433
5	Dötz, K.H.	*Synlett*	**1991**		381
6	Schmaltz, H.G.	*Angew. Chem. Int. Ed.*	**1994**	*33*	303

DOWD Ring Expansion

Ring expansion of cyclic ketones mediated by free radicals.



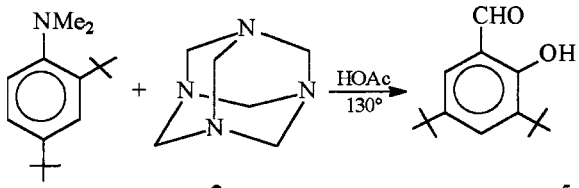
1	Dowd, P.	*J.Am.Chem.Soc.*	1987	*109*	3493
2	Dowd, P.	*Tetrahedron*	1989	*45*	77
3	Dowd, P.	*J.Org.Chem.*	1992	*52*	7163
4	Dowd, P.	*Chem.Rev.*	1993	*93*	2091

Methyl 2-Bromomethylcyclopentanone-2-carboxylate 3.[2] A solution of 2-carbomethoxycyclopentanone **1** (0.43 g, 3 mmol) in THF (2 mL) was added to a suspension of NaH (127 mg, 3.6 mmol) in THF (5mL) containing HMPA (645 mg, 3.6 mmol) at 20°C. After 1 h stirring, was added CH_2Br_2 **2** (2.6 g, 15 mmol). After 10 h reflux, water was added followed by usual work up. Column chromatography (silica gel 8 g, hexane:EtOAc 4:1) gave 435 mg of **3** (67%).

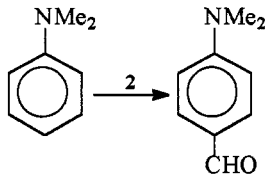
3-Carboxymethoxycyclohexanone 4. To **3** (100 mg, 0.43 mmol) in PhH (80 mL) was added tri-n-butyltin hydride (116 mg, 0.4 mmol) and AIBN (7 mg, 0.04 mmol). Under stirring the mixture was heated to reflux for 24 h. Evaporation of the solvent, extraction with CH_2Cl_2 (30 mL), washing with 10% KF (1 x 10 mL) and column chromatography (silica gel 2 g; hexane:EtOAc 2:1) afforded 49.4 mg of **4** (75%), R_f=0.31 (hexane:EtOAc 2:1).

D U F F Aldehyde Synthesis

Formylation of phenols and anilines with hexamethylenetetramine **2** (see 1st edition).



2 **3** (50%)[5]

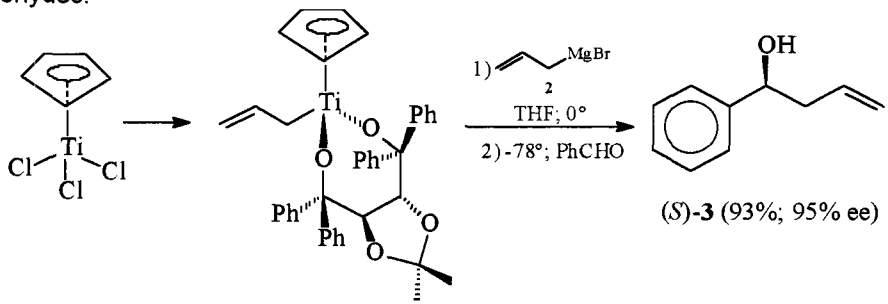


1	Duff, J.C.	*J. Chem. Soc.*	**1932**		1987
2	Duff, J.C.	*J. Chem. Soc.*	**1934**		1305
3	Ogata, Y.	*Tetrahedron*	**1968**	*24*	5001
4	Wada, F.	*Bull. Soc. Chim. Jpn.*	**1980**	*53*	1473
5	Jacobsen, E.N.	*J. Org. Chem.*	**1994**	*59*	1939
6	Ferguson, L.N.	*Chem. Rev.*	**1946**	*38*	230

Aldehyde 3.[5] **1** (125 g; 0.61 mol) and **2** (170 g; 1.21 mol) in HOAc (300 mL) were heated to 130°C with stirring and kept at 130°C (± 5°C) for 2 h.. At 75°C, 33% H_2SO_4 (300 mL) was added and the mixture heated to 105-110°C for 1 h. Work up afforded 56-71 g of **3** (40-50%), mp 53-56°C.

DUTHALER-HAFNER Enantioselective Allylation

Cyclopentadienyldialkoxyallyltitanium complex **1**[4] in enantioselective allylation of aldehydes.



(*R,R*)-**1**

(*S*)-**3** (93%; 95% ee)

1	Duthaler, R.O.	*Helv. Chim. Acta*	**1990**	*73*	353
2	Duthaler, R.O; Hafner, A	*Pure Appl. Chem.*	**1990**	*62*	631
3	Hafner, A; Duthaler, R.O.	Eur. Pat. Appl. Ep. 387,196; *C.A.*, **1991**, *114*, 122718h			
4	Hafner, A.	*J. Am. Chem. Soc.*	**1992**	*114*	2321
5	Duthaler, R.O; Hafner, A.	*Chem. Rev.*	**1992**	*92*	827
6	Duthaler, R.O; Hafner, A.	*Inorg. Chem. Acta*	**1994**	*222*	95

(*1S*)-1-Phenyl-3-buten-1-ol 3.[4] **2** in THF (5.3 mL; 0.8 M 4.25 mmol) was added slowly (10 min) at 0°C under Ar to a solution of (*R,R*)-**1** (3.06 g; 5 mmol) in Et_2O (60 mL). After 1.5 h stirring at 0°C, the mixture was cooled to -78°C and benzaldehyde (403 mg; 3.8 mmol) in Et_2O (5 mL) was added over 5 min. After 3 h stirring at -74°C the mixture was quenched with 45% NH_4F (20 mL) and after separation of 1.68 g of ligand, chromatography on silica gel (CH_2Cl_2:hexane:Et_2O 4:4:1) afforded 521 mg of (*S*)-**3** (93%, 95% ee).