

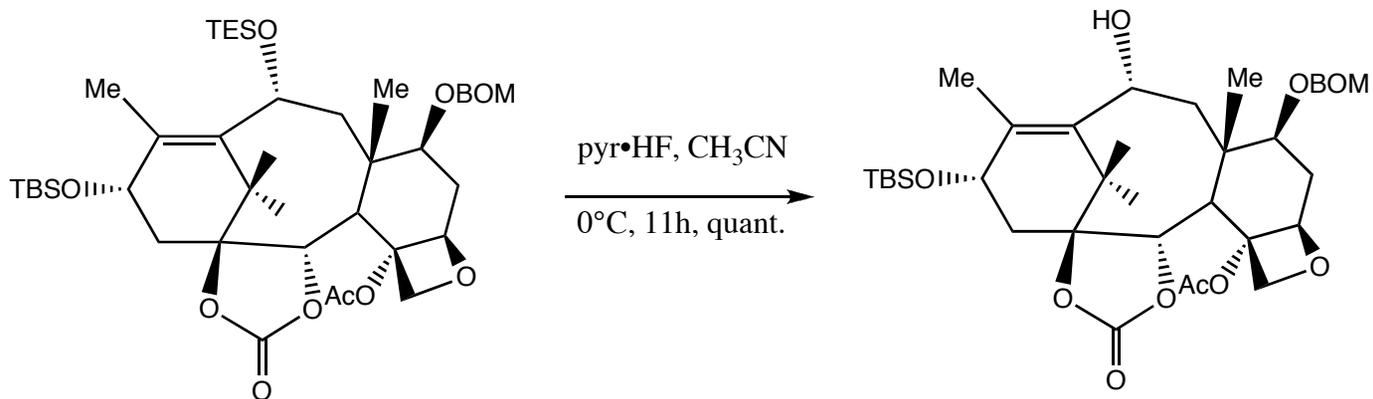
JACS, 111, 1989, 7530.

- a. **1**: $R_1 = \text{OMe}$, $R_2 = \text{Ac}$, $R_3 = (\text{tBu})(\text{Me})_2\text{Si}$, $R_4 = 4\text{-MeOPhCH}_2$, $R_5 = \text{Bz}$, $R_6 = \text{Me}$, $R_7 = \text{acetonide}$, $R_8 = (\text{Me})_3\text{SiCH}_2\text{CH}_2\text{OCO}$
2: $R_1 = \text{OH}$, $R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = \text{H}$

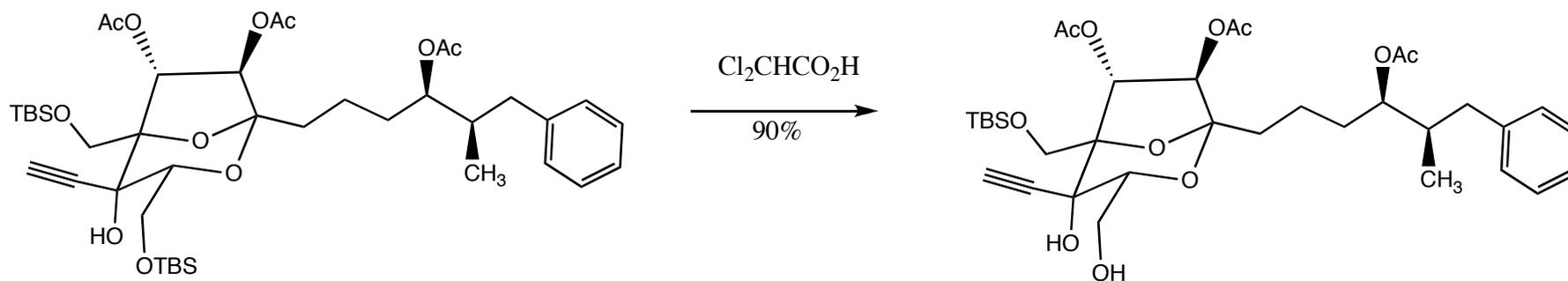
Deprotection of 42 protecting groups:

- a. (1) DDQ/*t*-BuOH- CH_2Cl_2 -phosphate buffer (pH 7.0) r.t., 4.5h, followed by acetylation (Ac_2O -DMAP/pyridine, rt)
 (2) HClO_4 (1.18N)-THF (1:12) 25°C, 8 days. (3) 0.08 N LiOH/ H_2O -MeOH-THF (1:2:8) 25°C, 20h. (4) (*n*-Bu) $_4$ NF in THF, 22°C, 18 h and then in THF-DMF (1:1), 22°C, 72h. (5) AcOH- H_2O (1:350), 22°C, 36 hours. **35% overall yield.**

Selective Deprotection: Often conditions must be determined empirically:



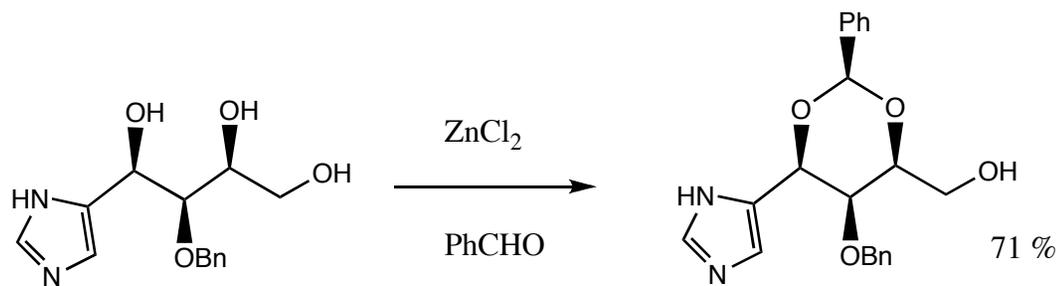
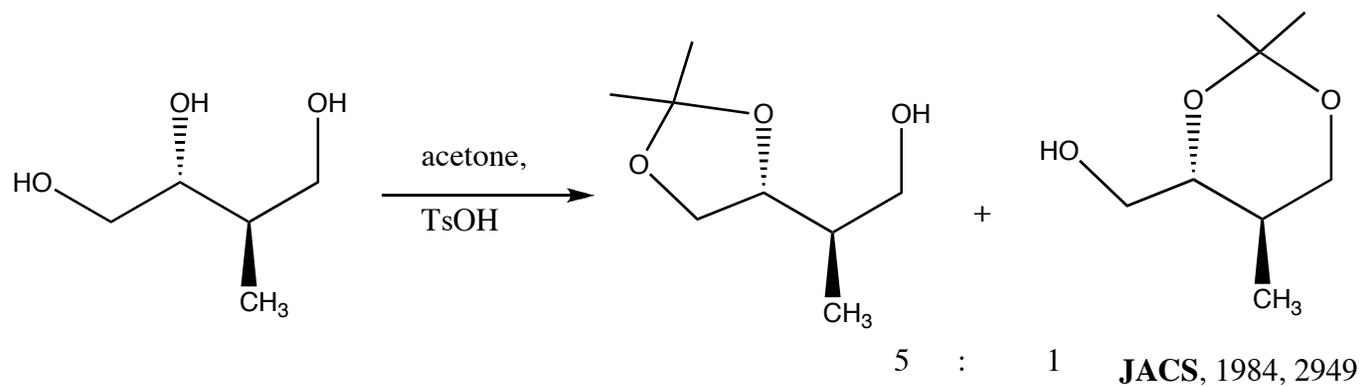
Holton **JACS**, *116*, **1994**, 1599.



Carreira, **JACS**, *117*, **1995**, 8106.

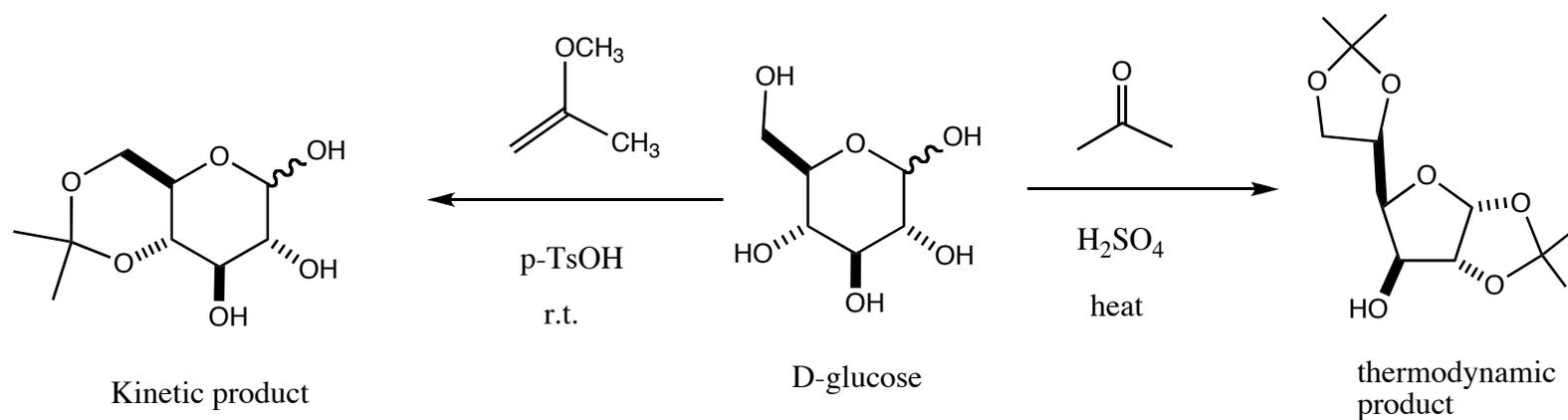
Review: **Synthesis**, 1996, 1065.

Acetonide formation with 1,2 diols occurs in preference to 1,3-diols; benzylidene acetals display reversed selectivity



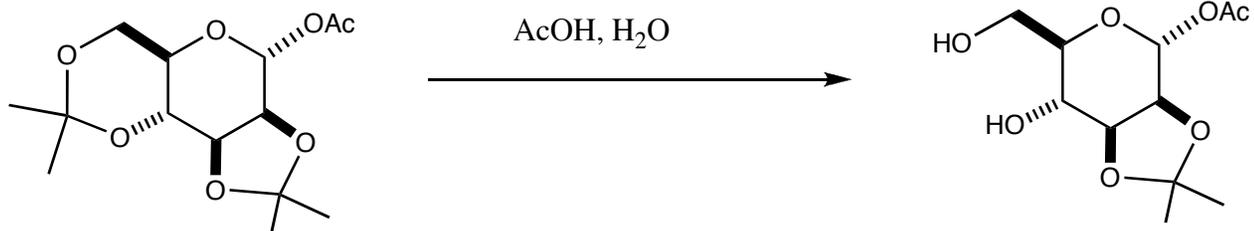
Helv. Chim. Acta. **1995**, 1837.

Selective Protection

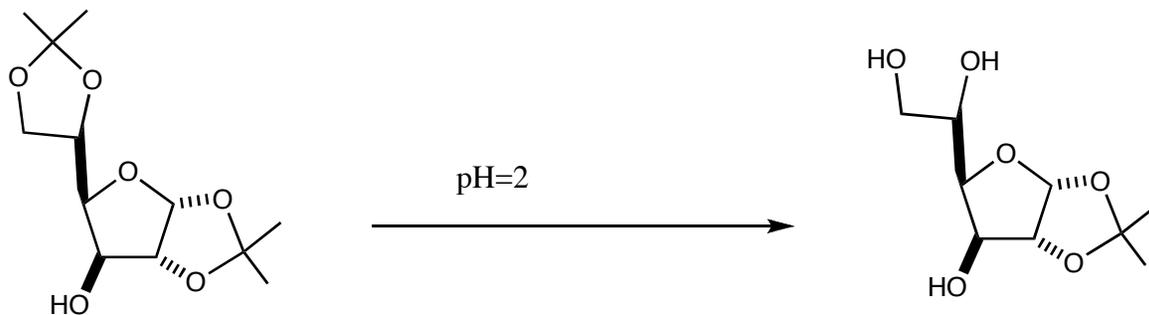


Carb. Res. **1974**, 87.

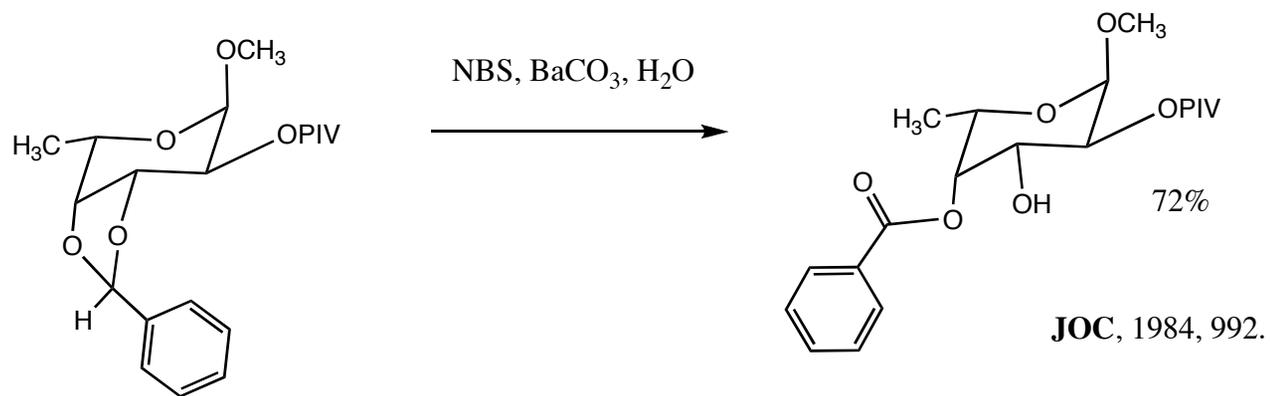
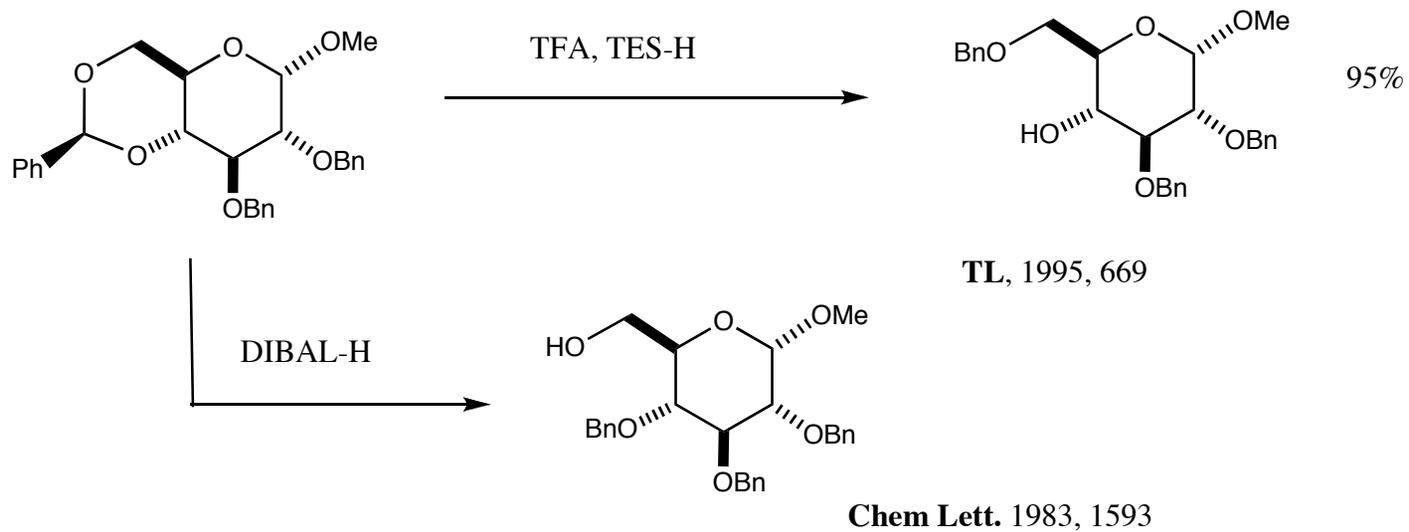
Selective Deprotections



Carb. Res **1978**, 181



Methods Carbohydrate Chem., **1963**, 318.



Key References for Protecting Groups

General : Green, W.T.; Wuts, P.G.M *Protective Groups in Organic Synthesis*, **1991**.

ROH:

1. Silyl groups

a. *JACS*, **1972**, 94, 6190. b. *TL*, **1981**, 22, 3455. c. *ACIEE* **2000**, 39, 2536.

2. Esters

a. *ACIEE*, **1978**, 17, 522. b. *TL*, **1986**, 27, 1255. c. *Tetrahedron*, **1985**, 41, 643.

3. Carbonates

a. *TL*, **1978**, 19, 1375. b. *JCS Chem. Commun.* **1982**, 672. c. *TL*, **1988**, 29, 2227. d. *Synlett*, **1993**, 680.

d. *TL*, **1981**, 22, 969. E. *JACS*, **1939**, 61, 3328.

4. Acetals

a. *JOC*, **1977**, 42, 3772. b. *TL*, **1985**, 51, 635. c. *JOC*, **1986**, 51, 635. c. *JACS*, **1975**, 97, 6260.

d. *Tetrahedron* **1987**, 43, 4395. e. *TL*, **1987**, 28, 5125. f. *TL*, **1976**, 809. g. *TL*, **1980**, 21, 3343. h. *JOC*, **1977**, 44, 1438

5. Ethers

a. *JOC*, **1973**, 38, 3224. b. *Tet*, **1998**, 54, 2967. c. *TL*, **1979**, 19, 95. D. *Carb. Res.* **1978**, 60, 206. e. *TL*, **1976**, 17, 3535.

f. *TL*, **1988**, 29, 2459. g. *Tet*, **1986**, 42, 3021.

Key References for Protecting Groups

Phenols

a. *JOC*, **1977**, 42, 3761. b. *JOC*, **1986**, 51, 11.

1,2-diols and 1,3 diols

a. *Carb. Res.* **1977**, 58, 337. b. *JACS*, **1984**, 206, 2949. c. *TL*, **1990**, 31, 717. d. *Methods Carb. Chem.* **1963**, 2, 318. e. *Carb. Res.* **1974**, 35, 87. f. *J. Het. Chem.* **1966**, 3, 485.
e. *Carb. Res.* **1975**, 45, 181. f. *TL*, **1996**, 37, 8643. g. *Methods Carb. Chem.* **1978**, 45, 181.
h. *TL*, **1995**, 5, 669. i. *Chem. Lett.* **1983**, 1593. j. *JOC*, **1969**, 34, 1035, 1045, and 1053.
k. *JOC*, **1984**, 49, 992. l. *JOC*, **1989**, 54, 17.

Carbonyls

a. *TL*, **1993**, 34, 995. b. *TL*, **1975**, 499. c. *JOC*, **1986**, 51, 773. d. *TL*, **1980**, 21, 1357.
e. *TL*, **1971**, 871. f. *TL*, **1989**, 30, 15. g. *TL*, **1989**, 30, 287.

Carboxyl groups

a. *TL*, **1984**, 25, 2557. b. *TL*, **1977**, 3529. c. *TL*, **1993**, 34, 975. d. *JOC*, **1982**, 47, 1962.
e. *JACS*, **1977**, 99, 2353. f. *Tet.* **1998**, 54, 2967. g. *JOC*, **1997**, 62, 8932. h. *Org. React.* **1953**, 7, 263.
i. *Synthesis*, **1991**, 294.

Key References for Protecting Groups

Amines

- a. *JACS*, **1987**, 109, 442. B. *Synthesis*, **1976**, 457. c. *J. Chem. Soc., Chem. Commun.* **1979**, 514.
d. *JACS*, **1997**, 49, 2325. e. *JOC*, **1996**, 61, 2413. f. *JOC*, **1987**, 52, 4984. g. *TL*, **1992**, 33, 477.
h. *Chem Ber.* **1932**, 65, 1192. i. *JOC*, **1988**, 53, 3108.

Alkynes

- a. *JACS*, **1991**, 113, 694. b. *JACS*, **1995**, 117, 8106. c. *Helv.Chim. Acta.* **1995**, 78, 732.