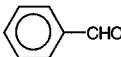
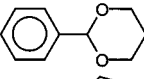
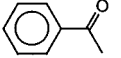
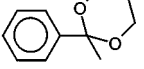
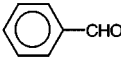
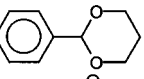
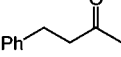
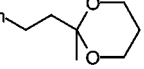
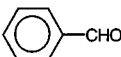
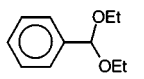
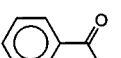
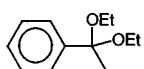
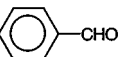
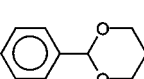
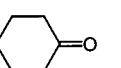
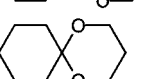
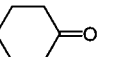
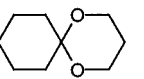
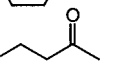
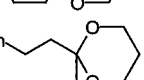
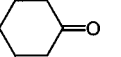
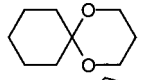
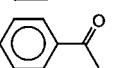
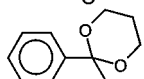


Table 2. Selective Acetalization and *in-situ* Transacetalization with $ZrCl_4$

entry	substrate	subst1/subst2/thiol or diol / $ZrCl_4$	product	time (min)	yield ^{a)} (%)
1		1:1:1.5:0.02 ^{b)}		15	95
				5	5
2		1:1:1.5:0.02 ^{b)}		15	92
				8	8
3		1:1:0:0.01 ^{c)}		7	100
				0	0
4		1:1:1.5:0.02 ^{b)}		10	60
				40	40
5		1:1:1.5:0.02 ^{b)}		10	97
				0	0
6		1:1:1.5:0.02 ^{b)}		10	100
				0	0

a) Yields based on GC and NMR. b) 1 equiv. of $(EtO)_3CH$ was used and the reactions were performed in dry CH_2Cl_2 . c) 1.8 equiv. of $(EtO)_3CH$ was used and the reaction was performed under solvent-free conditions.

carried out efficiently in the presence of $(EtO)_3CH$ (1 eq), 1,3-propanediol (1.5-2 eq) and $ZrCl_4$ (2-3 mol%) in excellent yields (Table 1, **3a-3e**). Aromatic and aliphatic open chain ketones as well as cyclic ketones were also converted to the corresponding 1,3-dioxanes under similar reaction conditions in good to excellent yields (Table 1, **3f-3j**). In order to show the ability of the presented methods for chemoselective acetalization of carbonyl compounds, we have performed several competitive acetalization reactions, whose results are demonstrated in Table 2. Benzaldehyde undergoes acetalization and transacetalization in the presence of acetophenone, benzyl acetone and cyclohexanone respectively (Table 2, entries 1-4). On the other hand, cyclohexanone as a model for cyclic ketones is con-

verted to the corresponding 1,3-dioxane with absolute chemoselectivity in the presence of benzylacetone and acetophenone, respectively (Table 2, entries 5-6).

In conclusion, mild reaction conditions, versatile and good chemoselectivity, easy workup, and high yields of the desired products are worthy to be mentioned as the characteristics of the described methods.

General Procedure for the preparation of diethyl acetals. To a mixture of carbonyl compound **1** (5 mmol) and $(EtO)_3CH$ (10-12.5 mmol), $ZrCl_4$ (0.05-0.1 mmol) was added, and the resulting solution was stirred at room temperature. After completion of the reaction (TLC or GC), a cold aqueous solution of NaOH (10%, 25 mL) was added and the mixture was extracted with CH_2Cl_2 (3×40 mL). The organic extracts were washed with water (2×15 mL) and dried over anhydrous Na_2SO_4 . Evaporation of the solvent under reduced pressure gave almost pure product(s). Further purification was proceeded by vacuum distillation to afford pure diethyl acetals **2** in good to excellent yields (Table 1).

General procedure for the preparation of 1,3-dioxanes via in-situ transacetalization; To a solution of carbonyl compound **1** (5 mmol), 1,3-propanediol (7.5-10 mmol), and $(EtO)_3CH$ (5 mmol) in dry CH_2Cl_2 (15 mL), $ZrCl_4$ (0.05-0.15 mmol) was added and the resulting solution was stirred at room temperature. After completion of the reaction (TLC or GC), the reaction was quenched with a cold aqueous solution of NaOH (10%, 25 mL) and the organic layer was separated and the residue was extracted with CH_2Cl_2 (3×40 mL). The organic extracts were combined together and washed with water (3×35 mL), and dried over anhydrous Na_2SO_4 . Evaporation of the solvent under reduced pressure gave almost pure 1,3-dioxane **3**. Further purification was achieved by vacuum distillation or recrystallization from the appropriate solvent to give pure product(s) in good to excellent yields (Table 1).

Acknowledgement

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References

- a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, **1991**, pp 175-198. b) Kocienski, *Protecting Groups*, eds. D. Enders and B. M. Trost; Thieme: Stuttgart, **1994**.
- a) For a review see: Meskens, A. J. *Synthesis* **1981**, 501. For more recent leading references see: b) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357. c) Shibagaki, M.; Takahashi, K.; Kuno, H.; Matsushita, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1258. d) Ott, J.; Ramos Tombo, G. M.; Schmid, B.; Venanzi, L. M.; Wang, G.; Ward, T. R. *Tetrahedron Lett.* **1989**, *30*, 6151. e) Otera, J.; Mizutani, T.; Nazaki, H. *Organometallics* **1989**, *8*, 2063. f) Ma, S.; Venanzi, L. M. *Synlett* **1993**, 751. g) Wang, W. B.; Shi, L. L.; Huang, Y. Z. *Tetrahedron Lett.* **1990**, *45*, 3315. h) Corla, F.; Venanzi, L. M. *Helv. Chim. Acta* **1993**, *73*, 690. i) Fukuzawa, S.; Tsuchimoto, T.; Hotaka, T.; Hiyama, T. *Synlett* **1995**, 1077

- and references cited therein. j) Tateiwa, J.; Horiuchi, H.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 4039 and references cited therein.
- (3) a) Luche, J. L.; Gemal, A.L. *J. Chem. Soc., Chem. Commun.* **1978**, 976. b) De Graw, J. I.; Goodman, L.; Baker, B. R. *J. Org. Chem.* **1961**, *26*, 1156. c) Taylor, E. C.; Chiang, C. S. *Synthesis* **1977**, 467. d) Thurkauf, A.; Jacobson, A. E.; Rice, K. C. *Synthesis* **1988**, 233. e) Ishihara, K.; Karumi, Y.; Kubota, M.; Yamamoto, H. *Synlett* **1996**, 839.
- (4) a) Fife, T. H.; Jao, L. K. *J. Org. Chem.* **1965**, *39*, 1492. b) Bornstein, J.; Bedell, S. F.; Drummond, P. E.; Kosloski, C. L. *J. Am. Chem. Soc.* **1956**, *78*, 83. c) Patwardhan, S. A.; Dev, S. *Synthesis* **1974**, 348.