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A facile and efficient $ZrCl_4$ catalyzed conversion of aldehydes to geminal-diacetates and dipivalates and their cleavage

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Abstract—A novel, mild and efficient method has been developed for the preparation of geminal-diacetates and dipivalates in high yields through a reaction of aldehydes with acetic anhydride or pivalic anhydride using Zirconium (IV) chloride as a catalyst under solvent free conditions. Regeneration of aldehydes from the acylals was also achieved using the same catalyst in CH_3OH.
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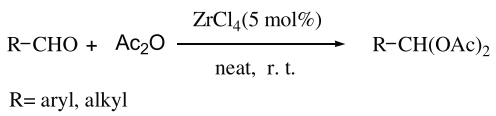
1. Introduction

Selective protection and deprotection of carbonyl group plays an important role in the multistep organic synthesis of complex natural products.[1] geminal-Diacetates (acylals) are one of the useful carbonyl protecting groups due to their stability under neutral and basic media as well as aqueous acids.[2] Moreover, the diacetates of α,β-unsaturated aldehydes serve as important precursors for Diels–Alder reactions[3] and some industrial uses of these compounds also have been reported.[4] Hence, methods for the synthesis and cleavage of acylals have received considerable attention. Usually, they are prepared from aldehydes and acetic anhydride using strong protic acids or Lewis acids. Some of these reagents and catalysts that have been employed include sulfuric acid,[2a] triflic acid,[5] PCl_3,[6] TMSCl-NaI,[7] $ZnCl_2$,[8] I_2,[9] $FeCl_3$,[10] NBS,[11] $Sc(OTf)_3$,[12] $Cu(OTf)_2$,[13] $Bi(OTf)_3{\cdot}xH_2O$,[14] and others.[15] Recently WCl_6,[16] $InCl_3$,[17] CAN,[18] $AlPW_{12}O_{40}$,[19] Amberlyst-15,[20] and $Zn(BF_4)_2$[21] have also reported for this conversion. Although some of these methods present convenient protocols with good to high product yields, it is noteworthy that in all but a few examples, these methods involve strongly acidic or oxidizing conditions, require high temperature or catalyst loading, longer reaction times or expensive and highly toxic catalysts. Hence, a practical and more efficient alternative using an inexpensive and environment friendly reagent is still of interest. Zirconium (IV) chloride ($ZrCl_4$) has gaining prominence in recent times especially as a mild and efficient Lewis acid catalyst and has been used for various organic transformations.[22] It has not been used for the preparation of *gem*-diacetates and dipivalates. Recently we have demonstrated the use of $ZrCl_4$ as a convenient and efficient catalyst for one-pot conversion of *tert*-butyl dimethylsilyl (TBS) and tetrahydropyranyl (THP) ethers to the corresponding acetates.[23] We herein report, a chemoselective and efficient method for the formation of geminal-diacetates by a reaction of an aldehyde and acetic anhydride using $ZrCl_4$ as a catalyst under solvent free conditons at room temperature (Scheme 1).



Scheme 1.

2. Results and discussion

In the first instance, the conversion of 4-phenyl benzaldehyde **1a** to the corresponding diacetate **1b** was carried out with $ZrCl_4$ as catalyst using various solvents like dichloromethane (34%), chloroform (28%) or acetonitrile (88%). However, a high yield of the product (90%) was obtained under solvent free conditions. The scope and generality of the present method was then further demonstrated by converting various aldehyde substrates with different functionalities and protecting groups to their corresponding *gem*-diacetates (Table 1). The versatility of the present methodology is well demonstrated with the fact that both aromatic (entries 1–9 and 13, Table 1) and aliphatic (entries 10–12, Table 1) aldehydes afforded their corresponding diacetates in equally good yields. The acid sensitive substrate furfural **6a** also led to the formation of acylal **6b** in 80% yield without the formation of any side products, normally observed under strongly acidic conditions. The applicability of the present methodology in multistep organic synthesis was also studied by converting the

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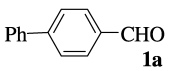
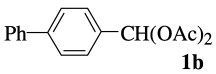
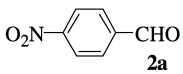
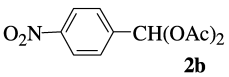
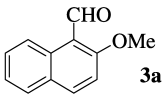
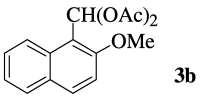
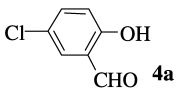
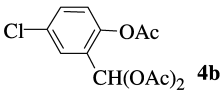
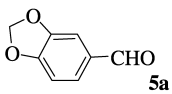
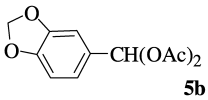
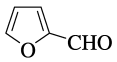
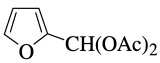
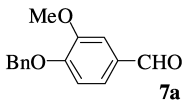
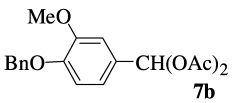
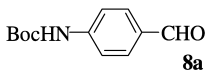
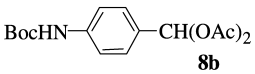
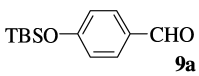
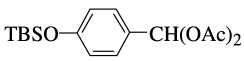
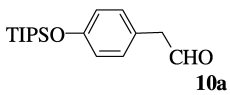
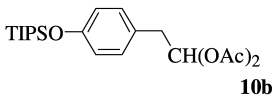
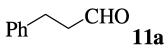
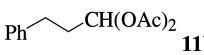
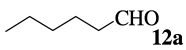
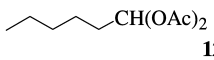
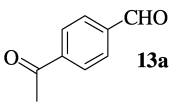
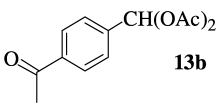
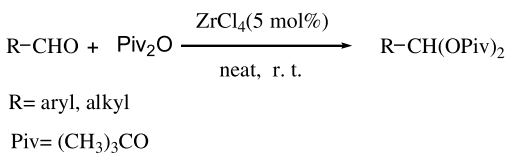
Table 1. Conversion of aldehydes to acylals using $ZrCl_4$

Entry	Substrate (**a**)	Time (min)	Product (**b**)[a]	Yield (%)[b]
1	 **1a**	30	 **1b**	90
2	 **2a**	30	 **2b**	92
3	 **3a**	40	 **3b**	83
4	 **4a**	20	 **4b**	84
5	 **5a**	25	 **5b**	88
6	 **6a**	20	 **6b**	80
7	 **7a**	30	 **7b**	81
8	 **8a**	25	 **8b**	85
9	 **9a**	35	 **9b**	83
10	 **10a**	35	 **10b**	69
11	 **11a**	45	 **11b**	72
12	 **12a**	50	 **12b**	68
13	 **13a**	25	 **13b**	88

[a] All the products were characterized by ^1H NMR, IR and mass spectroscopy.
[b] Isolated yield after purification.

substrates having acid sensitive protecting groups such as benzyl (Bn), *tert*-butyldimethylsilyl (TBS), triisopropyl (TIPS) ethers and *tert*-butyl carbamate (NHBoc) to their corresponding acylals without any effect on them (entries 7–10, Table 1). The chemoselectivity of the present reaction was demonstrated by the conversion of the aldehyde to the diacetate in the presence of a keto group, shown in entry 13.

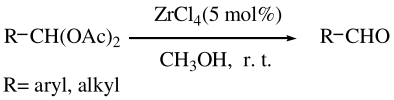
The utility of the present method is further extended by employing it in the formation of *gem*-dipivalates. To the best of our knowledge, there is mention of only one reagent system in the literature employed for the formation of *gem*-dipivalates.[15i] However, long reaction times (25 h) and elevated temperature (60°C) conditions were required. In comparison, *gem*-dipivalates can be prepared by reacting the aldehydes with trimethylacetic anhydride (pivalic anhydride) in the presence of $ZrCl_4$ (5 mol%) under solvent free conditions at ambient temperature (Scheme 2). The reaction times are shorter and yields are comparable to the *gem*-diacetates.



Scheme 2.

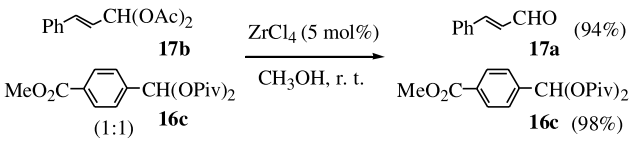
As the present reaction conditions are useful in making both *gem*-diacetates and *gem*-dipivalates, we studied a few more examples in a combinatorial fashion as depicted in Table 2. *gem*-Diacetates and dipivalates are obtained in high yields in the case of aromatic aldehydes having halo or ester functionalities (entry 1–3, Table 2). α,β-Unsaturated aldehyde **17a** also proved amicable to this methodology to produce the corresponding dicarboxylates **17b** and **17c** (entry 4, Table 2).

Further, we have also observed the rapid cleavage of geminal-diacetates with the same catalyst ($ZrCl_4$) in methanol at room temperature (Scheme 3). A few methods are reported in the literature for the conversion of acylals to their corresponding aldehydes. The reagents employed were sulfuric acid,[24] hydrochloric acid,[25] montmorillonite K 10,[26] boron triiodide-*N*,*N*-diethylaniline complex,[27] base-catalyzed cleavage by sodium hydroxide or aqueous potassium carbonate,[28] CAN coated on silica gel,[29] neutral alumina under microwave irradiation,[30] phenoxides[31] and $BiCl_3$.[32] Recently CBr_4[33] and $CeCl_3{\cdot}7H_2O/NaI$[34] were also reported for this conversion. Strong acidic and basic conditions, unsatisfactory yields, high reaction temperatures discourage their usage. The present method however is mild, efficient and can be performed at ambient temperature. Thus all the diacetates **1b** to **17b** were converted to the parent aldehydes in high yields (Table 3) without affecting the sensitive groups such as OMe, OBn, OTBS, OTIPS and NHBoc in shorter reaction times. In the case of entry 4 (Table 3), deprotection led to the formation of 4-chloro-2-formyl phenylacetate **4a′**. It is pertinent to note the fact that, *gem*-dipivalates are unchanged under these reactions conditions.



Scheme 3.

Therefore, we also investigated the possible chemoselective cleavage of *gem*-diacetates in the presence of *gem*-dipivalates. As shown in Scheme 4, where a 1:1 mixture of diacetate **17b** and dipivalate **16c** were subjected for deprotection in the presence of 5 mol% $ZrCl_4$ in methanol at room temperature, after workup the analysis of the crude products consisted of a 1:1 mixture **17a** and **16c**.



Scheme 4.

3. Conclusion

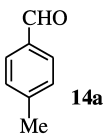
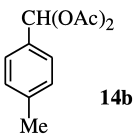
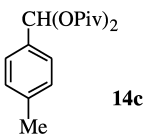
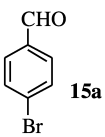
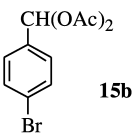
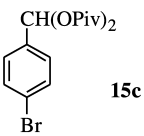
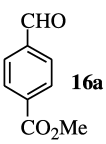
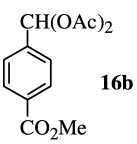
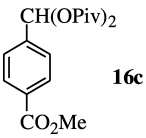
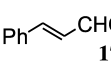
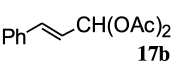
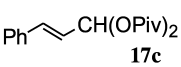
In conclusion, we have developed a simple, mild and chemoselective method for protection of aldehydes to *gem*-diacetates and dipivalates. The chemoselective deprotection of diacetates was achieved with the same catalyst. The method may find a wide application in organic synthesis where aldehydes having acid sensitive protecting groups need to be protected. Shorter reaction times are an noteworthy feature of the reported method.

4. Experimental

4.1. General

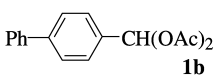
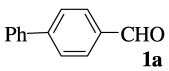
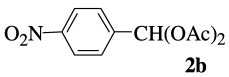
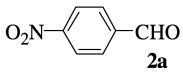
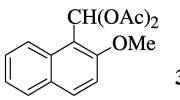
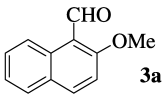
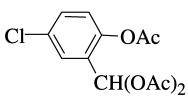
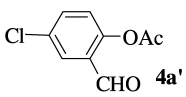
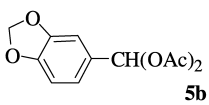
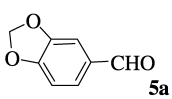
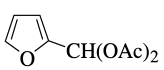
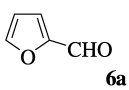
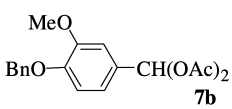
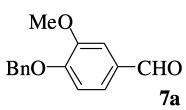
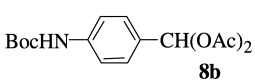
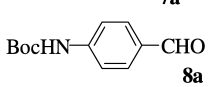
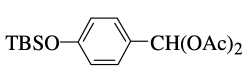
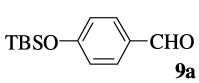
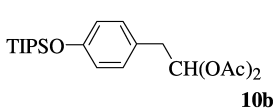
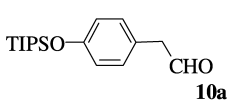
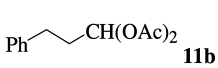
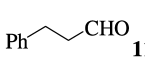
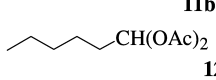
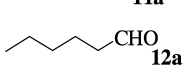
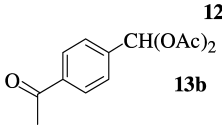
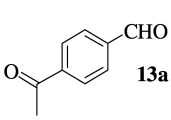
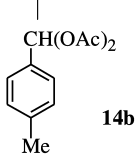
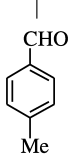
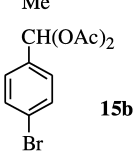
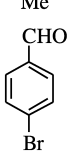
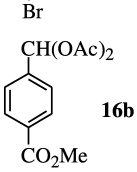
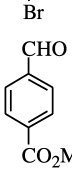
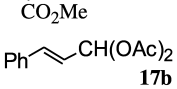
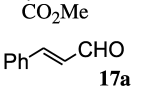
All reagents were purchased from Aldrich or SD Fine Chemicals and were used without further purification. Crude products were purified by column chromatography on silica gel of 60–120 mesh. ^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ at 400 MHz and 100 MHz respectively. Chemical shifts are given in ppm with respect

Table 2. Conversion of aldehydes to *gem*-diacetates and *gem*-dipivalates using $ZrCl_4$

Entry	Substrate (**a**)	Ac_2O		Piv_2O	
		Product (**b**)[a]	Time (min)/yield (%)[b]	Product (**c**)[a]	Time (min)/yield (%)[b]
1	 **14a**	 **14b**	20/93	 **14c**	20/91
2	 **15a**	 **15b**	25/89	 **15c**	30/90
3	 **16a**	 **16b**	15/88	 **16c**	15/89
4	 **17a**	 **17b**	35/82	 **17c**	45/78

[a] All the products were characterized by ^1H NMR, IR and mass spectroscopy.
[b] Isolated yield after purification.

Table 3. Cleavage of acylals using $ZrCl_4$

Entry	Acylal	Time (min)	Aldehyde[a]	Yield (%)[b]
1	 **1b**	3	 **1a**	96
2	 **2b**	5	 **2a**	93
3	 **3b**	5	 **3a**	92
4	 **4b**	8	 **4a'**	90
5	 **5b**	6	 **5a**	89
6	 **6b**	3	 **6a**	85
7	 **7b**	10	 **7a**	92
8	 **8b**	10	 **8a**	86
9	 **9b**	8	 **9a**	94
10	 **10b**	10	 **10a**	80
11	 **11b**	8	 **11a**	86
12	 **12b**	8	 **12a**	81
13	 **13b**	5	 **13a**	93
14	 **14b**	4	 **14a**	95
15	 **15b**	5	 **15a**	94
16	 **16b**	6	 **16a**	89
17	 **17b**	8	 **17a**	83

[a] All the products were characterized by ^1H NMR, IR and mass spectroscopy.
[b] Isolated yield after purification.

to internal TMS, and *J* values are quoted in Hz. IR spectra were obtained neat, and only the most significant absorptions in cm^{-1} are indicated and the molecular ions and/or base peaks in MS are given.

4.2. General procedure for the preparation of *gem*-diacetates and dipivalates

To a stirred solution of aldehyde (1 mmol) in acetic anhydride or pivalic anhydride (3 mmol) was added $ZrCl_4$ (5 mol%) and the reaction mixture stirred at room temperature for the given time. After completion of the reaction (TLC), the mixture was diluted with EtOAc, washed with 10% $NaHCO_3$ solution, brine, dried over Na_2SO_4, evaporated and the crude product purified by column chromatography on silica gel to give the corresponding *gem*-diacetates or dipivalates in excellent yields.

4.2.1. 1,1-Diacetoxy-1-(4-biphenyl)methane (1b). White solid, mp 128–130°C; ^1H NMR ($CDCl_3$): 7.75 (s, 1H), 7.67–7.6 (m, 6H), 7.48–7.46 (m, 3H), 2.17 (s, 6H); ^{13}C NMR ($CDCl_3$): 168.9, 142.8, 140.4, 134.4, 128.9, 127.8, 127.4, 127.2, 127.1, 89.7, 20.9; IR (Neat): 1756, 1233, 1192, 959 cm^{-1}; MS (*m/z*): 284 (M^+). Anal. calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.68; H, 5.68.

4.2.2. 1,1-Diacetoxy-1-(2-methoxy naphthyl)methane (3b). Pale yellow solid, mp 133–135°C; ^1H NMR ($CDCl_3$): 8.66 (s, 1H), 7.88 (d, *J*=9 Hz, 2H), 7.8–7.77 (m, 2H), 7.29–7.26 (m, 2H), 4.01 (s, 3H), 2.09 (s, 6H); ^{13}C NMR ($CDCl_3$): 169.0, 156.0, 132.5, 132.0, 129.7, 128.7, 127.1, 125.5, 124.0, 116.3, 113.0, 86.7, 57.5, 21.2; IR (Neat): 1752, 1206, 1008, 947 cm^{-1}; MS (*m/z*): 288 (M^+). Anal. calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.53; H, 5.42.

4.2.3. 1,1-Diacetoxy-1-[2-(acetyloxy)-5-chloro phenyl] methane (4b). White solid, mp 63–65°C; ^1H NMR ($CDCl_3$): 7.83 (s, 1H), 7.74 (s, 1H), 7.51 (d, *J*=8.6 Hz, 1H), 6.99 (d, *J*=6 Hz, 1H), 2.31 (s, 3H), 2.09 (s, 6H); ^{13}C NMR ($CDCl_3$): 169.7, 169.0, 150.1, 135.2, 130.9, 128.2, 128.1, 124.2, 92.1, 20.9, 20.8; IR (Neat): 1756, 1732, 1237, 923 cm^{-1}; MS (*m/z*): 300 (M^+). Anal. calcd for $C_{13}H_{13}ClO_6$: C, 51.93; H, 4.36. Found: C, 51.89; H, 4.32.

4.2.4. 1,1-Diacetoxy-1-[4-(benzyloxy)-3-methoxyphenyl] methane (7b). Light yellow solid, mp 82–84°C; ^1H NMR ($CDCl_3$): 7.63 (s, 1H), 7.46–7.36 (m, 5H), 7.08–7.07 (m, 2H), 6.92 (s, 1H), 5.19 (s, 2H), 3.94 (s, 3H), 2.14 (s, 6H); ^{13}C NMR ($CDCl_3$): 169.3, 148.4, 146.3, 140.6, 134.1, 128.7, 127.3, 127.2, 120.5, 115.1, 114.4, 92.3, 78.2, 56.9, 20.9; IR (Neat): 1754, 1228, 938, 830 cm^{-1}; MS (*m/z*): 344 (M^+). Anal. calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85. Found: C, 66.24; H, 5.78.

4.2.5. 2-(4-Triisopropylsilyloxy phenyl) ethane-1,1-diyl diacetate (10b). Colourless oil; ^1H NMR ($CDCl_3$): 7.08 (d, *J*=8 Hz, 2H), 6.89 (d, *J*=8 Hz, 2H), 6.7 (t, *J*=6.4 Hz, 1H), 3.2 (d, *J*=6 Hz, 2H), 2.15 (s, 6H), 1.29–1.22 (m, 3H), 1.12 (d, *J*=7.2 Hz, 18H); ^{13}C NMR ($CDCl_3$): 168.9, 153.5, 134.1, 129.6, 120.1, 84.4, 39.9, 21.1, 17.9, 12.6; IR (Neat): 1736, 1218, 1106, 946 cm^{-1}; MS (*m/z*): 394 (M^+). Anal. calcd for $C_{21}H_{34}O_5Si$: C, 63.92; H, 8.69. Found: C, 63.84; H, 8.62.

4.2.6. (4-Methyl phenyl)methylene bis(2,2-dimethyl propanoate (14c). Colourless oil which upon standing at room temperature to give colourless crystals, mp 32–35°C; ^1H NMR ($CDCl_3$): 7.65 (s, 1H), 7.4 (d, *J*=8 Hz, 2H), 7.22 (d, *J*=8 Hz, 2H), 2.4 (s, 3H), 1.24 (s, 18H); ^{13}C NMR ($CDCl_3$): 176.2, 133.9, 133.4, 128.1, 126.3, 88.8, 38.8, 26.8, 21.4; IR (Neat): 2974, 1756, 1282, 1115, 928 cm^{-1}; MS (*m/z*): 306 (M^+). Anal. calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.52; H, 8.57.

4.2.7. (4-Bromo phenyl)methylene bis(2,2-dimethyl propanoate (15c). White solid, mp 63–65°C; ^1H NMR ($CDCl_3$): 7.63 (s, 1H), 7.55 (d, *J*=7.2 Hz, 2H), 7.38 (d, *J*=7.2 Hz, 2H), 1.23 (s, 18H); ^{13}C NMR ($CDCl_3$): 176.2, 134.9, 131.7, 128.1, 123.6, 88.9, 38.8, 26.8; IR (Neat): 2973, 1748, 1281, 1160, 934 cm^{-1}; MS (*m/z*): 370 (M^+). Anal. calcd for $C_{17}H_{23}BrO_4$: C, 55.00; H, 6.24. Found: C, 54.94; H, 6.18.

4.2.8. Methyl 4-[bis(2,2-dimethyl propionyloxy)-methyl]-benzoate (16c). Colourless oil; ^1H NMR ($CDCl_3$): 8.09 (d, *J*=8.1 Hz, 2H), 7.72 (s, 1H), 7.57 (d, *J*=8.1 Hz, 2H), 3.95 (s, 3H), 1.25 (s, 18H); ^{13}C NMR ($CDCl_3$): 176.2, 166.5, 140.4, 131.0, 129.8, 126.4, 88.7, 52.3, 38.8, 26.8; IR (Neat): 2978, 1752, 1723, 1278, 1106 cm^{-1}; MS (*m/z*): 350 (M^+). Anal. calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.08; H, 7.42.

4.2.9. (1*E*)-1-Phenylprop-1-ene-3,3-diyl bis(2,2-dimethyl propanoate (17c). White solid, mp 76–78°C; ^1H NMR ($CDCl_3$): 7.43–7.25 (m, 6H), 6.84 (d, *J*=16 Hz, 1H), 6.23 (dd, *J*=6, 16 Hz, 1H), 1.22 (s, 18H); ^{13}C NMR ($CDCl_3$): 176.2, 135.3, 135.0, 128.6, 127.0, 122.1, 89.6, 38.8, 26.9; IR (Neat): 2967, 1762, 1122, 984 cm^{-1}; MS (*m/z*): 318 (M^+). Anal. calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.63; H, 8.19.

4.2.10. Compounds 2b, 5b and 6b,[5] 8b,[15j] 9b,[15m] 11b,[20] 12b,[17] 13b,[14] 14b and 15b,[5] 16b,[35] and 17b.[15l] ^1H NMR, IR and mass spectral data of these known compounds were identical with the reported data.

4.3. General procedure for the cleavage of acylal

A solution of acylal (1 mmol) and $ZrCl_4$ (5 mol%) in CH_3OH (5 mL) was stirred at room temperature (generally 10–20 min). After complete conversion (TLC), solvent was evaporated in vacuo, extracted with EtOAc, washed with 10% $NaHCO_3$ solution and brine solution. The combined organic layers were dried (Na_2SO_4) and evaporated to give the corresponding aldehydes in good yields.

4.3.1. 4-Chloro-2-formylphenyl acetate (4a′). White crystalline needles, mp 52–54°C; ^1H NMR ($CDCl_3$): 10.08 (s, 1H), 7.87 (s, 1H), 7.61 (d, *J*=8.6 Hz, 1H), 7.18 (d, *J*=8.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$): 187.3, 169.0, 150.1, 135.1, 132.3, 130.4, 129.0, 125.1, 20.8; IR (Neat): 2965, 1712, 1670, 1234, 918 cm^{-1}; MS (*m/z*): 198 (M^+). Anal. calcd for $C_9H_7ClO_3$: C, 54.43; H, 3.55. Found: C, 54.39; H, 3.53.

4.3.2. (4-Triisopropylsilanyloxy phenyl)acetaldehyde (10a). Colourless oil; ^{1}H NMR ($CDCl_3$): 9.73 (d, J=2.3 Hz, 1H), 7.08 (d, J=8.2 Hz, 2H), 6.89 (d, J=8.2 Hz, 2H), 3.62 (s, 2H), 1.29–1.22 (m, 3H), 1.12 (d, J=7 Hz, 18H); ^{13}C NMR ($CDCl_3$): 199.8, 155.4, 131.9, 130.6, 123.9, 120.4, 49.7, 17.9, 12.6; IR (Neat): 2967, 1640, 1238, 1134, 921 cm^{-1}; MS (*m*/*z*): 135 (M^+-157). Anal. calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.65. Found: C, 69.77; H, 9.59.

4.3.3. Compounds 1a to 3a and 5a to 7a,[36] 8a,[37] 9a,[38] and 11a to 17a.[36] ^{1}H NMR, IR and mass spectral data of these known compounds were identical with those of authentic samples.

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