

# Silica supported perchloric acid ( $\text{HClO}_4\text{-SiO}_2$ ): A highly efficient and reusable catalyst for geminal diacylation of aldehydes under solvent-free conditions

Abu T. Khan\*, Lokman H. Choudhury, Subrata Ghosh

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

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## Abstract

Perchloric acid immobilized on silica gel has been found to be an efficient and expedient catalyst for geminal diacylation of aldehydes. A wide variety of aromatic and aliphatic aldehydes can be easily transformed into the corresponding acylals using 0.5 mol%  $\text{HClO}_4\text{-SiO}_2$  within 2–10 min under solvent-free conditions at room temperature. The notable advantages of this protocol are: the reaction requires less reaction time and only stoichiometric amount of acetic anhydride being used, is highly economic and the catalyst is recyclable.

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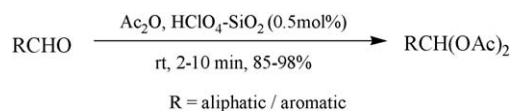
**Keywords:** Acetic anhydride; *gem*-Diacylation; Aldehydes; Silica supported perchloric acid; Catalytic synthetic protocol

## 1. Introduction

The protection of aldehydes as acetal or oxathioacetal or dithioacetal or acylal is a common practice for manipulation of other functional groups during multi-step synthesis. Sometimes the protection of aldehydic compounds as acylal is usually preferred due to ease of preparation and their stability towards basic and neutral conditions [1]. In addition, the preparation of 1,1-diacetates from the corresponding aldehydes can be achieved very easily in the presence of ketones. Moreover, they also serve as valuable precursors for asymmetric allylic alkylation [2a] and natural product synthesis [2b] as well as for the synthesis of 1-acetoxydienes for Diels–Alder reactions [3]. The preparation of acylal is usually performed from the reaction of an aldehyde with acetic anhydride in the presence of protonic acids, e.g. sulfuric acid [4] or methanesulfonic acid/phosphoric acid [5] or by employing a Lewis acid, which acts as a catalyst. Over the years, a large number of methods have been developed for the preparation of 1,1-diacetates from the corresponding aldehydes by employing various new reagents such as  $\text{LiOTf}$  [6], ceric ammonium nitrate [7],  $\text{InCl}_3$  [8],  $\text{H}_2\text{NSO}_3\text{H}$

[9],  $\text{LiBF}_4$  [10], NBS [11],  $\text{I}_2$  [12],  $\text{TMSCl-NaI}$  [13],  $\text{FeCl}_3$  [14],  $\text{CoCl}_2$  [15],  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  [16], Wells–Dawson acid ( $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$ ) [17] and tetrabutylammonium tribromide (TBATB) [18]. Some metal triflates, e.g.  $\text{Cu}(\text{OTf})_2$  [19],  $\text{Sc}(\text{OTf})_3$  [20] and  $\text{Bi}(\text{OTf})_3$  [21] have also been utilized as catalysts for the preparation of 1,1-diacetate derivatives from the corresponding aldehydes. Very recently, we have demonstrated the applicability of acetonilytriphenylphosphonium bromide (ATPB) [22] and bromodimethylsulfonium bromide (BDMS) [23] for acetylation of alcohols, phenols, amines and thiols and for 1,1-diacylation of aldehydes. Unfortunately, many of these methods have drawbacks such as harsh reaction conditions, requirement of excess amount of acetic anhydride, tedious work-up procedure and involvement of expensive and moisture sensitive catalyst. Some new methods are also known in the literature by involving heterogeneous catalysts, for examples, aluminum dodecatungstophosphate ( $\text{AlPW}_{12}\text{O}_{40}$ ) [24] and zirconium sulfophenyl phosphonate [ $\text{Zr}(\text{CH}_3\text{PO}_3)_{1.2} (\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{0.8}$ ] [25]. Though these methods are quite efficient, some of them encountered difficulties, e.g. difficulty in preparing an acylal from furfural [24] and longer reaction times particularly for aliphatic and  $\alpha,\beta$ -unsaturated aldehydes [25]. Therefore, a new methodology by using an inexpensive and mild catalyst, which might overcome these drawbacks in the preparation of acylals from the corresponding aldehydes, is still required.

\* Corresponding author. Tel.: +91 3612582305; fax: +91 3612690762.  
E-mail address: [atk@iitg.ernet.in](mailto:atk@iitg.ernet.in) (A.T. Khan).



Scheme 1.

In recent years, silica supported reagents are gaining considerable attention because of higher activity of the catalyst due to the larger surface area and better selectivity. In addition, silica supported reagents have high mechanical and thermal stabilities, easiness in handling, low toxicity, non-corrosiveity, easy separation of the catalyst after completing the reaction and reusability of the catalyst, which make it promising for both academic and industrial applications. From our recent result [26] as well as from the other results [27,28], we realized that perchloric acid adsorbed on silica gel has higher catalytic activity than most of the moisture sensitive and highly costly metal triflates. As a part of our ongoing research project to develop new synthetic methodologies particularly in protection and deprotection chemistry [29], we perceived that silica supported perchloric acid (HClO<sub>4</sub>-SiO<sub>2</sub>) might be a useful, effective, versatile and reusable catalyst for chemoselective protection of aldehydes as acylals. So far, silica supported perchloric acid (HClO<sub>4</sub>-SiO<sub>2</sub>) has been utilized mainly as catalyst for acetylation of phenols, thiols, alcohols and amines [27], peracetylation of carbohydrates [30], acetalization followed by acetylation [31] and Ferrier rearrangement of glucals [28]. Very recently, we have demonstrated that the same solid supported catalyst can be used for thia-Michael addition reactions [32]. Herein, we report silica supported perchloric acid as a highly efficient catalyst for *gem*-diacylation of aldehydes under solvent-free conditions as shown in Scheme 1.

## 2. Result and discussion

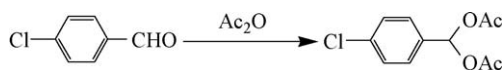
We initially prepared the catalyst silica supported perchloric acid by following the literature procedure [27]. To prove the better catalytic activity of this supported reagent over the aqueous perchloric acid, we have carried out a model study with 4-chlorobenzaldehyde and acetic anhydride using various catalytic conditions as shown in Table 1 (Scheme 2).

Table 1  
The results of the reaction of 4-chlorobenzaldehyde with acetic anhydride in different catalytic conditions at room temperature

Entry	Catalyst	Time	Yield <sup>a,b</sup> (%)
I	No catalyst	12 h	0
II	SiO <sub>2</sub> (10 mg/mmol)	12 h	43
III	Aqueous HClO <sub>4</sub> (0.5 mol%)	20 min	93
IV	HClO <sub>4</sub> -SiO <sub>2</sub> (10 mg/mmol, 0.5 mol%)	2 min	98

<sup>a</sup> Isolated yields.

<sup>b</sup> All the reactions were carried out in 5-mmol scale with two equivalents of acetic anhydride under solvent-free conditions.



Scheme 2.

Table 1 clearly demonstrates that silica supported perchloric acid is an effective catalyst in terms of reaction time and yield obtained. Then, we attempted the reaction of 1-heptanal with two equivalent of acetic anhydride in the presence of catalytic amount of HClO<sub>4</sub>-SiO<sub>2</sub> at room temperature. The reaction was complete within 5 min and the pure acylal was obtained in 86% yield by just passing through a small silica gel column. Similarly, 1-decanal and crotyl aldehyde (entries 1b and 1c) provided the corresponding acylals under similar reaction conditions. It is noteworthy to mention that 1d undergoes *gem*-diacylation within shorter time than the reported method [14] with good yields by keeping intact the acid sensitive protecting group *tert*-butyldiphenylsilyl ether and the corresponding product 2d is a valuable key ingredient for the synthesis of a potent antifungal agent spingofungin F [2]. In a similar manner phenacyl aldehyde (1e) was also converted to the corresponding *gem*-diacetates using the same catalyst within a short while. Interestingly, we did not observe any cyclotrimerization for aliphatic aldehyde (entries 1a–1e). Likewise, a wide variety of aromatic aldehydes containing both electron-donating and electron-withdrawing substituents underwent *gem*-diacylation within a very short reaction time, which is summarized in Table 2. It is important to point out that the formation of acylals from the aldehydes containing electron-donating groups such as methoxy and hydroxyl groups result in failure by some of the reported procedures [16] whereas by using this protocol it can be easily achieved (entries 1m–q) without any difficulty in good yields.

Likewise, various aldehydes containing other protecting groups such as TBS, allyl and benzoyl (entries 1r–t) were smoothly converted to the desired acylals with the protecting groups kept intact in good yields. Moreover, acid sensitive aldehyde (entry 1v) and dialdehydes (entries 1w and 1x) can also be transformed to the required diacylals without any difficulty. Furthermore, polycyclic aromatic aldehydes (entries 1y and 1z) also provided the desired acylals in very good yields.

Interestingly, the aldehyde functionality of the keto aldehydes (entries 1a' and 1b') can be chemoselectively transformed into the corresponding acylals in good yields under identical conditions. Remarkably, it is also possible to carry out the same transformation in a 50-mmol scale or even more without any difficulty. For checking the reusability of the catalyst, we have performed the reaction in the following way. The reaction of 4-nitrobenzaldehyde with acetic anhydride was carried out using 0.5 mol% HClO<sub>4</sub>-SiO<sub>2</sub> in a 50 mmol scale; after completion of the reaction the catalyst was filtered off and washed with dry ether and finally it was dried under vacuum for 30 min, which was reused for the next cycle. The recovered catalyst was reused for two more consecutive runs for acylation of 4-nitrobenzaldehyde (entry 1j) with acetic anhydride, providing the desired acylal in 89% and 87% yield within 10 min.

The generality and the scope of the reagent can be easily reflected from the comparison of the data in Table 3. The superiority of silica supported perchloric acid over the metal triflates and some of the recently reported heterogeneous catalyst can be easily visualized at a glance by comparing the results of some substrates. Here, we have chosen some model substrates and

Table 2  
Formation of acylals from the corresponding aldehydes catalyzed by  $\text{HClO}_4\text{-SiO}_2$

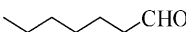
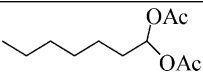
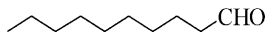
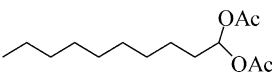
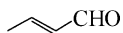
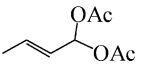
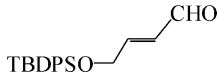
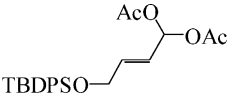
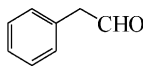
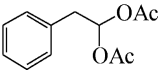
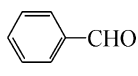
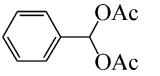
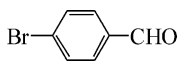
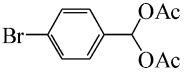
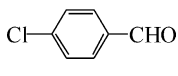
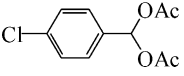
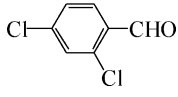
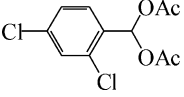
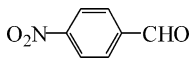
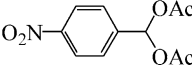
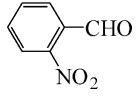
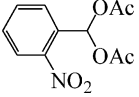
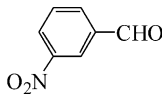
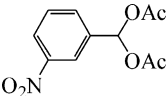
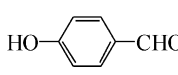
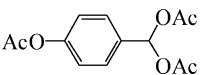
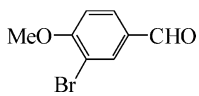
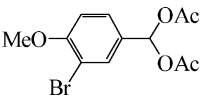
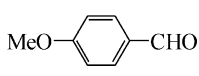
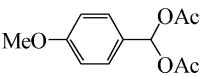
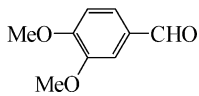
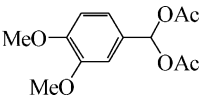
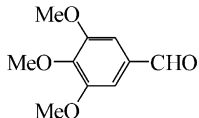
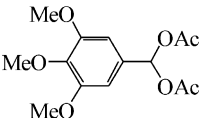
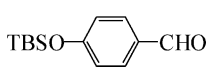
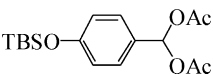
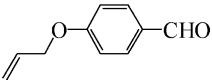
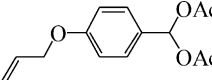
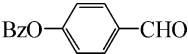
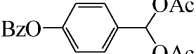
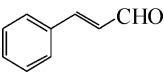
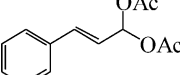
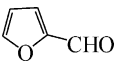
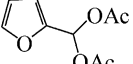


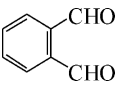
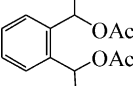
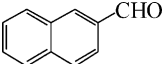
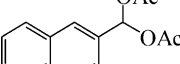
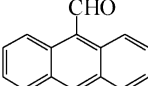
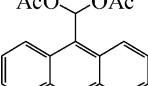
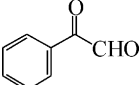
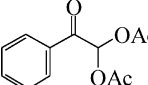
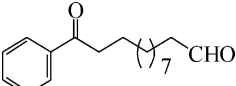
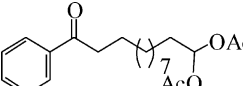
Entry	Substrate (1)	Time (min)	Product (2)	Yield <sup>a</sup> (%)	Mp (°C)
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b		5		91	Gummy liquid
c		2		83 [12]	Gummy liquid
d		10		95	Gummy liquid
e		5		85 [23]	Gummy liquid
f		2		97 [14]	45 [lit.44–45]
g		2		96 [22]	84 [lit. 84]
h		2		98 [12]	80 [lit. 80]
i		5		95	100–102
j		5		96 [12]	125 [lit.125]
k		5		93 [22]	85–86 [lit. 85–86]
l		5		96 [14]	65 [lit. 64–66]
m		5		82 [15a]	57 [lit. 58]
n		5		94	81–83
o		5		91 [12]	66 [lit.67–68]
p		5		93 [22]	64 [lit. 63–64]
q		5		96	114–116
r		3		87 [6]	57–59

Table 2 (Continued)

Entry	Substrate (1)	Time (min)	Product (2)	Yield <sup>a</sup> (%)	Mp (°C)
s		5		93	40–41
t		5		91 [6]	98–99
u		5		98 [14]	84 [lit. 84–85]
v		2		90 [14]	54 [lit. 55]
w		5		90	174–175
x		5		95	137–139
y		5		94 [15b]	101 [lit.101–02]
z		5		96 [15b]	197 [lit.197–98]
a'		10		93 [10b]	50–51
b'		10		94	39–40

<sup>a</sup> Isolated yields, melting point and the reference for spectroscopic data.

the comparison is made with respect of yields, reaction time and mol% of the catalyst used. It is worthy to mention that cinnamaldehyde and 4-nitrobenzaldehyde provide the desired acylal within 5 min with much better yield than other reported methods. Again, the present protocol is much more effective for the substrate furfural in terms of reaction timing as well as yield, which is usually difficult to be diacylated by the reported procedures [24].

As a whole, we have revealed that silica supported perchloric acid is a highly effective, cheap and reusable catalyst for *gem*-diacylation of aldehydes.

### 3. Experimental

IR spectra were recorded in KBr or neat condition on a Nicolet Impact 410 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian 400 MHz and Bruker 200 MHz spectrophotometers in CDCl<sub>3</sub> using TMS as internal reference.

Elemental analyses were carried out in a Perkin-Elmer 2400 automatic carbon, hydrogen, nitrogen and sulfur analyzer.

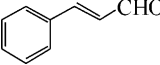
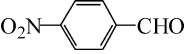
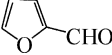
#### 3.1. Preparation of silica supported perchloric acid (HClO<sub>4</sub>-SiO<sub>2</sub>) [27]

HClO<sub>4</sub> (1.8 gm, 12.5 mmol, as a 70% aq solution) was added to a suspension of SiO<sub>2</sub> (230–400 mesh, 23.7 g) in Et<sub>2</sub>O (70.0 mL). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to furnish HClO<sub>4</sub>-SiO<sub>2</sub> (0.5 mmol/g) as a free flowing powder (50 mg = 0.025 mmol of HClO<sub>4</sub>).

#### 3.2. Typical procedure for the preparation of acylals from 4-nitrobenzaldehyde

To a mixture of 4-nitrobenzaldehyde (5 mmol, 0.750 g) and freshly distilled acetic anhydride (10 mmol, 0.92 mL), the

Table 3  
Comparison of HClO<sub>4</sub>-SiO<sub>2</sub> with other catalysts for *gem*-diacylation of aldehydes

Substrate	Catalyst	Catalyst (mol%)	Reaction time	Yields <sup>a</sup> (%)
	NBS	20	48 h	80 [11]
	Bi(OTf) <sub>3</sub>	0.1	15 min	70 [21]
	TBATB	10	5.2 h	87 [18]
	AIPW <sub>12</sub> O <sub>40</sub>	0.1	5 min	92 [24]
	Cu(OTf) <sub>2</sub>	2.5	3 h	76 [19]
	H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ·24 H <sub>2</sub> O	1.0	30 min	98 [17]
	HClO <sub>4</sub> -SiO <sub>2</sub>	0.5	5 min	98
	NBS	10	8 h	98 [11]
	TBATB	10	22 h	78 [18]
	AIPW <sub>12</sub> O <sub>40</sub>	0.1	45 min	89 [24]
	H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ·24 H <sub>2</sub> O	1.0	30 min	92 [17]
	HClO <sub>4</sub> -SiO <sub>2</sub>	0.5	5 min	96
	NBS	10	24 h	81 [11]
	TBATB	10	7 h	80 [18]
	AIPW <sub>12</sub> O <sub>40</sub>	0.1	30 min	0 [24]
	H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ·24 H <sub>2</sub> O	1	30 min	88 [17]
	HClO <sub>4</sub> -SiO <sub>2</sub>	0.5	2 min	90

<sup>a</sup> Reference for earlier methods.

catalyst HClO<sub>4</sub>-SiO<sub>2</sub> (50 mg, 0.025 mmol) was added and the mixture was stirred at room temperature. When the reaction was complete as judged by TLC, diethyl ether (2 × 25 mL) was added into it. The ether layer was separated, washed with saturated solution of NaHCO<sub>3</sub> (5 mL), water (2 × 10 mL) and finally dried over anhydrous MgSO<sub>4</sub>. After removal of ether, the residue was obtained as almost pure acylal, which was recrystallized from hexane. The desired product was obtained as yellowish crystalline solid (1.22 g) in 96% yield.

### 3.2.1. 1,1-Diacetate of 1-decanal (2c)

IR (Neat): 2930, 2858, 1767, 1470, 1370, 1250, 1209 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.88 (t, *J* = 6.8 Hz, 3H, CH<sub>3</sub>), 1.26 (bs, 14H, CH<sub>2</sub>), 1.72–1.76 (m, 2H, CH<sub>2</sub>), 2.07 (s, 6H, -COCH<sub>3</sub>), 6.75 (t, 1H, *J* = 5.6 Hz, CH(OAc)<sub>2</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 14.2, 20.9 (2C), 22.7, 23.5, 29.2, 29.3, 29.4, 29.5, 31.9, 33.2, 90.5, 168.8 (2C) ppm. Anal. Calcd for C<sub>14</sub>H<sub>26</sub>O<sub>4</sub> (258.36): C, 65.09; H, 14.14%. Found: C, 64.89; H, 14.06%.

### 3.2.2. 1,1-Diacetate of 4-*tert*-butyldiphenylsilyloxy but-2-ene-1-al (2d)

IR (Neat): 3073, 2970, 2940, 2863, 1762, 1434, 1372, 1244, 1208, 1121, 1009, 707 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.07 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 2.10 (s, 6H, 2 × -COCH<sub>3</sub>), 4.23 (bs, 2H, -OCH<sub>2</sub>), 5.91 (ddt, 1H, *J* = 2.0 Hz, *J* = 6.4 Hz, *J* = 15.6 Hz, =CH), 6.06 (dt, 1H, *J* = 2.8 Hz, *J* = 15.6 Hz, =CH), 7.17 (d, 1H, *J* = 6.4 Hz, -CH(OAc)<sub>2</sub>), 7.34–7.41 (m, 6H, ArH), 7.63 (dd, 4H, *J* = 1.2 Hz, *J* = 7.6 Hz, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 19.4, 21.0 (2C), 26.9 (3C), 62.8, 89.2, 122.0, 127.6 (4C), 129.6 (2C), 133.0, 135.3 (4C), 135.8 (2C), 168.5 (2C) ppm. Anal.

Calcd for C<sub>24</sub>H<sub>30</sub>O<sub>5</sub>Si (426.58): C, 67.58; H, 7.09%. Found: C, 67.38; H, 7.01%.

### 3.2.3. 1,1-Diacetate of 2,4-dichlorobenzaldehyde (2i)

IR (KBr): 3088, 3022, 2945, 1757, 1434, 1378, 1235, 1199, 1081 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.14 (s, 6H, 2 × -COCH<sub>3</sub>), 7.31 (d, *J* = 7.6 Hz, 1H, ArH), 7.43 (s, 1H, ArH), 7.50 (d, *J* = 7.9 Hz, 1H, ArH), 7.91 (s, 1H, CH(OAc)<sub>2</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 20.7 (2C), 87.7, 127.4, 128.8, 129.9, 132.0, 133.9, 136.3, 168.3 (2C) ppm. Anal. Calcd for C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> (277.10): C, 47.68; H, 3.64%. Found: C, 47.49; H, 3.59%.

### 3.2.4. 1,1-Diacetate of 3-bromo-4-methoxybenzaldehyde (2n)

IR (KBr): 3077, 3015, 2967, 1762, 1605, 1505, 1360, 1258, 936 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 2.12 (s, 6H, 2 × -COCH<sub>3</sub>), 3.91 (s, 3H, OCH<sub>3</sub>), 6.89 (d, *J* = 8.5 Hz, 1H, ArH), 7.42 (dd, *J* = 8.5 Hz, *J* = 2.2 Hz, 1H, ArH), 7.57 (s, 1H, CH(OAc)<sub>2</sub>) 7.71 (d, *J* = 2.2 Hz, 1H, ArH) ppm. Anal. Calcd for C<sub>12</sub>H<sub>13</sub>BrO<sub>5</sub> (317.13): C, 45.45; H, 4.13%. Found: C, 45.21; H, 4.06%.

### 3.2.5. 1,1-Diacetate of 3,4,5-trimethoxybenzaldehyde (2q)

IR (KBr): 3017, 2976, 2950, 2848, 1757, 1603, 1506, 1470, 1424, 1368, 1209, 1076 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.14 (s, 6H, 2 × -COCH<sub>3</sub>), 3.85 (s, 3H, -OCH<sub>3</sub>), 3.89 (s, 6H, 2 × -OCH<sub>3</sub>), 6.75 (s, 2H, ArH), 7.59 (s, 1H, CH(OAc)<sub>2</sub>). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>7</sub> (298.29): C, 56.37; H, 6.08%. Found: C, 56.09; H, 6.01%.

### 3.2.6. 1,1-Diacetate of 4-allyloxybenzaldehyde (2s)

IR (KBr): 3104, 2986, 2950, 1757, 1615, 1527, 1429, 1373, 1245, 1209, 1066, 1004, 922 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.11 (s, 6H, COCH<sub>3</sub>), 4.54 (d, *J*=4.9 Hz, 2H, OCH<sub>2</sub>), 5.29 (d, *J*=10.2 Hz, 1H), 5.41 (d, *J*=17.3 Hz, 1H), 5.98–6.10 (m, 1H), 6.92 (d, *J*=8.6 Hz, 2H, ArH), 7.44 (d, *J*=8.6 Hz, 2H, ArH), 7.61 (s, 1H, CH(OAc)<sub>2</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 20.9 (2C), 68.9, 89.8, 114.8 (2C), 117.9, 127.9, 128.2 (2C), 132.9, 158.5, 168.8 (2C) ppm. Anal. Calcd for C<sub>14</sub>H<sub>16</sub>O<sub>5</sub> (264.28): C, 63.63; H, 6.10%. Found: C, 63.45; H, 6.05%.

### 3.2.7. 1,1-Diacetate of terephthaldehyde (2w)

IR (KBr): 3119, 3032, 2940, 1752, 1603, 1434, 1378, 1250, 1076, 963, 861 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.13 (s, 12H, 4 × -COCH<sub>3</sub>), 7.57 (s, 4H, ArH), 7.68 (s, 2H, CH(OAc)<sub>2</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) 20.8 (2C), 89.3 (2C), 127.1 (4C), 137.0 (2C), 168.7 (2C) ppm. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>8</sub> (338.31): C, 56.80; H, 5.36%. Found: C, 56.69; H, 5.28%.

### 3.2.8. 1,1-Diacetate of phthaldehyde (2x)

IR (KBr): 3086, 2953, 1766, 1605, 1434, 1377, 1258, 1116 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.11 (s, 12H, 4 × -COCH<sub>3</sub>), 7.46–7.49 (m, 2H, ArH), 7.61–7.63 (m, 2H, ArH), 8.00 (s, 2H, 2 × -CH(OAc)<sub>2</sub>) ppm. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>8</sub> (338.31): C, 56.80; H, 5.36%. Found: C, 56.64; H, 5.26%.

### 3.2.9. 1,1-Diacetate of ketoaldehyde (2b')

IR (KBr): 2919, 2858, 1752, 1680, 1455, 1378, 1271, 1209, 1112, 1020, 979 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.21–1.27 (m, 16H, -CH<sub>2</sub>), 1.64–1.69 (m, 2H, -CH<sub>2</sub>), 2.00 (s, 6H, -COCH<sub>3</sub>), 2.89 (t, *J*=7.6 Hz, 2H, -CH<sub>2</sub>), 6.70 (t, *J*=5.6 Hz, 1H, CH(OAc)<sub>2</sub>), 7.39 (dd, *J*=8.0 Hz, *J*=1.4 Hz, 2H, ArH), 7.46 (dd, *J*=7.3 Hz, *J*=1.4 Hz, 1H, ArH), 7.89 (dd, *J*=1.2 Hz, *J*=8.2 Hz, 2H, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 20.83 (2C), 23.36, 24.35, 29.13, 29.36 (2C), 29.40 (3C), 33.15, 38.60, 90.55, 128.03 (2C), 128.53 (2C), 132.85, 137.08, 169.05 (2C), 200.60 ppm. Anal. Calcd for C<sub>22</sub>H<sub>32</sub>O<sub>5</sub> (376.49): C, 70.19; H, 8.57%. Found: C, 70.01; H, 8.49%.

## 4. Conclusion

In conclusion we have developed a rapid and mild synthetic protocol for *gem*-diacylation of aromatic and aliphatic aldehydes under solvent-free conditions. Interestingly aliphatic aldehydes did not show any other side reactions such as cyclotrimerization under the experimental conditions. The notable advantages of this protocol are very good yields, short reaction times, tolerance for a wide variety of other protecting groups. Furthermore due to the simplicity of the procedure and involvement of cheap and reusable catalyst, we believe this protocol will be a new addition in the field of modern organic synthesis.

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