Reductive esterification of aromatic aldehydes using Zn/Ac$_2$O/imidazole or Zn/Yb(OTf)$_3$/(RCO)$_2$O system

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Abstract—Benzaldehydes are reduced by metallic zinc in the presence of Ac$_2$O and imidazole, giving the corresponding benzyl acetates in good yields. Reductive esterification of aromatic aldehydes is also carried out via *gem*-diacetoxy compounds. Carbonyl compounds are readily converted to the *gem*-diacyloxy compounds in excellent yields on treatment with 2 molar amounts of acid anhydride and 10 mol% of Yb(OTf)$_3$ in MeCN at room temperature. Thus-formed diacyloxy compounds derived from aromatic aldehydes are reduced in situ by metallic zinc to afford the corresponding esters.
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1. Introduction

Reductive activation of carbonyl group by one-, two-, or four-electron reduction process has been widely applied to organic synthesis.[1] Controlling the reduction conditions such as the choice of reducing metals and additives enables a highly chemo-/stereo-selective reaction. For example, combination of one-electron reductant such as a low-valent vanadium or titanium and metallic zinc as a co-reductant in the presence of a silylating reagent realizes a catalytic system for reductive coupling reaction of carbonyl compounds including McMurry coupling[2] and pinacol coupling.[3–5] Our system consisting of cat. Cp$_2$VCl$_2$/R$_3$SiCl/Zn shows excellent diastereoselectivity in the pinacol coupling reaction of aliphatic aldehydes and aromatic aldimines, giving the corresponding vicinal *dl*-diols and *meso*-diamines, respectively.

Metallic zinc is widely utilized as a relatively mild reducing reagent and addition of an activator such as acids or Lewis acids is required to enhance the reactivity. Reductive deoxygenation of carbonyl groups, well-known as the Clemmensen reduction,[6] requires four-electron reduction and a proton source, which is performed by zinc (usually amalgamated) and strong acids (e.g. HCl). Although several intermediates including zinc carbenoids[7] have been postulated,[8] it is very difficult to apply these intermediates to other transformations, partly due to the multiple reaction pathways and the severe reaction conditions. In addition, an

alcohol or its derivatives are not considered to be involved as an intermediate of the Clemmensen reduction.[9] Therefore, metallic zinc has not been utilized frequently in two-electron reduction such as transformation of carbonyl groups to the corresponding alcohols. Most of the reported procedures for Zn-promoted reduction to alcohols or reductive esterification of carbonyl compounds are performed under acidic conditions (Scheme 1).[10,11]
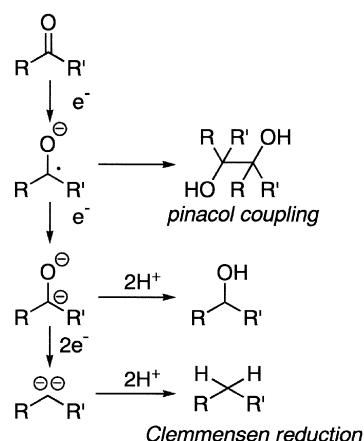
Scheme 1. Reductive activation of carbonyl compounds.

We are interested in the utility of metallic zinc in the reduction reaction, especially under mild, non-amalgamated, and neutral conditions. Addition of an appropriate activator such as metal salts realizes the unique reactivity. For example, a combination of Zn/ZnI$_2$ was demonstrated to promote the novel 2:1 coupling of an acrylic acid ester and an aromatic aldehyde to give the corresponding

α-aroyladipate.[12] Recently, we also reported that acylating reagents such as Ac_2O assist the vanadium-catalyzed pinacol coupling reaction as well as chlorosilanes in the presence of metallic zinc as a co-reductant.[13] Since Ac_2O is considered both to activate zinc and to trap the anionic intermediates as well as silylating reagents,[4] zinc reduction with acid anhydride in an aprotic solvent is expected to develop the reductive esterification of carbonyl group under relatively neutral conditions. In this paper we wish to present two routes to the reductive esterification using $Zn/(RCO)_2O$. One of them involves $Zn/Ac_2O/imidazole$ reduction system, which enables one-pot aldehyde-selective reductive acetylation. Another method is based on the $Yb(OTf)_3$-catalyzed diacyloxylation of carbonyl compounds, which is further reduced with zinc to yield the reductive esterification products (Scheme 2).
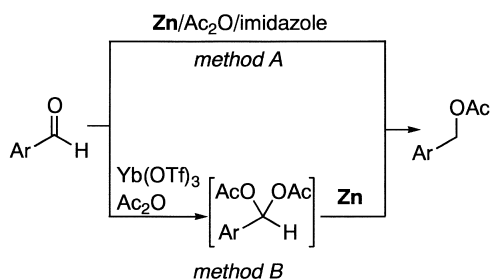
Scheme 2. Reductive esterification of aromatic aldehyde.

2. Results and discussion

2.1. Zn/Ac₂O/imidazole reduction system

Previous reports from our laboratory demonstrated that the vanadium-catalyzed pinacol coupling of benzaldehyde **1a** proceeds in the presence of Zn and Ac_2O, in which benzyl acetate **2a** is also detected as a by-product (Table 1, entry 1).[13] Pinacol coupling product **3a** seems to be formed via one-electron reduction process, while **2a** might be produced by two-electron reduction. In order to screen the effect of additives on the reaction pathway, 2 molar amounts of imidazole were added to the reaction mixture of benzaldehyde, 3 mol% of Cp_2VCl_2, Zn (200 mol%), and Ac_2O (200 mol%) in DME, giving **2a** and **3a** in 59 and 30%

yields, respectively (entry 2). Imidazole is considered to work as a mild proton source in the reaction. In fact, deuterium was introduced at the benzylic position when deuterized imidazole was employed. In order to prevent the one-electron reduction process, the reduction was conducted without vanadium catalyst. As expected, pinacol coupling did not proceed, but **2a** was obtained as a sole product in the absence of the vanadium catalyst. When the reaction was performed in DME, the yield of **2a** was increased to 97% (entry 3). The reaction also occurred in apolar solvents such as toluene even at room temperature despite the slightly lower yield (entries 4 and 5).

Table 2 summarizes the results of the reaction using aromatic aldehydes (ketone) in DME. The reaction was found to be influenced by the electronic effect. Aromatic aldehydes bearing a weak electron-donating or withdrawing group such as *p*-isopropyl (**1b**) or *p*-chloro (**1d**) group underwent the smooth reductive esterification as well as benzaldehyde (entries 1, 2 and 4). The stronger electron-donating substituent such as *p*-methoxy group (**1e**) diminished the yield. On the other hand, pinacol coupling pathway preferentially proceeded in the reaction of *p*-cyanobenzaldehyde (**1c**) as shown in entry 3. This may be due to the stabilization of the radical anion intermediate by the electron-withdrawing effect of cyano group. These results indicate an electron transfer process. On the contrary, aliphatic aldehydes such as hydrocinnamaldehyde (**1i**) did not effectively undergo the reduction under the similar reaction conditions (entry 6). No reaction took place in the case of acetophenone (**1j**, entry 7).

Table 2. Reduction of aromatic aldehyde or ketone using $Zn/Ac_2O/imidazole$ system

$$ArCHO\ (PhCOMe)\ \mathbf{1} \xrightarrow[\text{DME, 80 °C, 24 h}]{\substack{\text{200 mol\% Zn}\\ \text{200 mol\% } Ac_2O \\ \text{200 mol\% imidazole}}} \mathbf{2} + \mathbf{3}$$

| Entry	1	Yields (%)	
		2	**3**
1	PhCHO (**1a**)	97 (**2a**)	0
2	*p*-Cl−C₆H₄CHO (**1b**)	84 (**2b**)	0
3	*p*-NC−C₆H₄CHO (**1c**)	19 (**2c**)	76 (**3c**)
4	*p*-Pr^i−C₆H₄CHO (**1d**)	66 (**2d**)	0
5	*p*-MeO−C₆H₄CHO (**1e**)	45 (**2e**)	0
6	PhCH₂CH₂CHO (**1i**)	5 (**2i**)	0
7[a]	PhCOMe (**1j**)	0	0

[a] The reaction time is 42 h and 71% of **1i** was recovered.

As described above, aldehyde-selective reductive esterification was carried out under mild and neutral conditions using $Zn/Ac_2O/imidazole$ system. Since most of functional groups are tolerant under these conditions, the reduction system is likely to be applied to the highly chemoselective transformation.

### 2.2. Zn/Yb(OTf)₃/(RCO)₂O reduction system

In the protic acid conditions such as HCl or AcOH, a possible reaction intermediate in the zinc reduction of carbonyl group is postulated as the corresponding

Table 1. Formation of benzyl acetate (**2a**) by $Zn/Ac_2O/imidazole$ system

Entry	Additives (mol%)		Conditions[a]		Yields (%)	
	Cp₂VCl₂	Imidazole	Solvent	Temperature (°C)	**2a**	**3a**
1[b]	3	None	DME	80	5	83
2	3	200	DME	80	59	30
3	None	200	DME	80	97	0
4	None	200	Toluene	80	76	0
5	None	200	Toluene	20	66	0

[a] Reaction time is 24 h.
[b] Ref. 13.

gem-dichloro or diacetoxy compound (Scheme 3).[8c] Efficient reductive esterification might be expected if the diacetoxy compound is generated under mild conditions, followed by two-electron reduction with zinc.
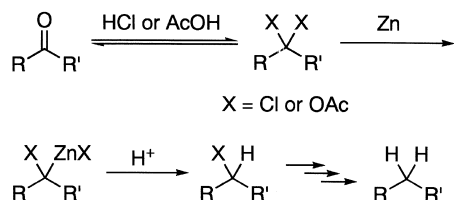
Scheme 3. A possible reduction pathway via *gem*-dichloro or diacetoxy compounds.[8c]

Table 3. Lewis acid catalyzed diacyloxylation of benzaldehyde
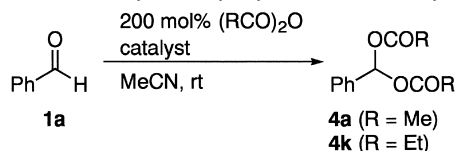
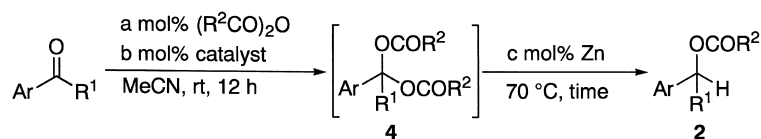| Entry	R	Catalyst (mol%)	Time (h)	Yield (%)
1	Me	Me_3SiCl/NaI (20)	8	76
2	Et	Me_3SiCl/NaI (20)	8	65
3	Et	Me_3SiOTf (20)	19	50
4	Et	$BF_3 \cdot Et_2O$ (20)	19	60
5	Et	$Sm(OTf)_3$ (20)	8	80
6	Et	$Sc(OTf)_3$ (20)	8	>99
7	Et	$Yb(OTf)_3$ (10)	8	>99
8	Me	$Yb(OTf)_3$ (10)	8	>99

It has been reported that the conversion of the carbonyl compounds into the diacetoxy compounds by the reaction with Ac_2O is catalyzed by strong acid such as H_2SO_4[14a] or H_3PO_4,[14b] or Lewis acid such as $ZnCl_2$,[15a] $FeCl_3$,[15b]

PCl_3,[15c] $Bi(OTf)_3$,[15d] $Zn(BF_4)_2$,[15e] or $LiOTf$.[15f] Since most of the reported procedures do not realize effective and quantitative conversion under mild conditions, new catalytic system for the diacyloxylation should be monitored. Some representative results of the reaction of PhCHO with Ac_2O or $(EtCO)_2O$ are listed in Table 3.

Recently, a catalytic amount of Me_3SiI, generated in situ from Me_3SiCl and NaI in MeCN, was reported to promote the diacetoxylation of aryl aldehyde in a good yield.[16] We first applied this procedure to the reaction of benzaldehyde with Ac_2O or $(EtCO)_2O$. Me_3SiI conditions were proved to be applied to both acid anhydrides as listed in entries 1 and 2 although that the yields were not satisfactory. Therefore, more suitable Lewis acid catalyst was chosen. Several Lewis acids were screened in the reaction of benzaldehyde with $(EtCO)_2O$, resulting in the less yields than those of the Me_3SiI-catalyzed reaction. By the analogy of Me_3SiI, Me_3SiOTf was used, but the yield was lowered (entry 3). Standard Lewis acid such as $BF_3 \cdot Et_2O$ (entry 4) also showed the moderate activity. Rare earth metal triflates have been utilized as a Lewis acid catalyst as exemplified by the $Sc(OTf)_3$-catalyzed diacetoxylation of benzaldehyde in $MeNO_2$ solution.[17] We also found that rare earth metal triflates are efficient catalysts. Especially, with use of $Sc(OTf)_3$ or $Yb(OTf)_3$, **4** was obtained quantitatively in MeCN solution (entries 6 and 7). The catalytic diacetoxylation also proceeded quantitatively with 10 mol% of $Yb(OTf)_3$ (entry 8).

Next, one-pot reductive esterification via diacyloxy intermediate **4** was attempted. After confirmation of the conversion to **4** by TLC and ^1H NMR, zinc powder, which was purified according to the literature[18] and non-amalgamated, was added to the reaction mixture and the mixture was heated for the listed time.[19] Table 4 lists both yields of **4**, which were estimated by ^1H NMR, and **2**, which

**Table 4**. One-pot reductive esterification using $Zn/Yb(OTf)_3/(RCO)_2O$ system

Entry	Ar	R^1	R^2	Catalyst	Conditions			Time (h)	Yields (%)	
					a	b	c		4	2
1	Ph	H (**1a**)	Et	Me_3SiCl/NaI	200	20	200	24	64 (**4k**)	34 (**2k**)
2	Ph	H (**1a**)	Et	$Sm(OTf)_3$	200	20	200	24	80 (**4k**)	67 (**2k**)
3	Ph	H (**1a**)	Et	$Sc(OTf)_3$	200	20	200	24	>99 (**4k**)	61 (**2k**)
4	Ph	H (**1a**)	Et	$Yb(OTf)_3$	200	10	200	24	>99 (**4k**)	88 (**2k**)
5	Ph	H (**1a**)	Me	$Yb(OTf)_3$	200	10	200	24	>99 (**4a**)	97 (**2a**)
6	Ph	H (**1a**)	*i*-Pr	$Yb(OTf)_3$	200	10	200	24	91 (**4l**)	66 (**2l**)
7	Ph	H (**1a**)	*t*-Bu	$Yb(OTf)_3$	200	10	200	24	81 (**4m**)	53 (**2m**)
8	Ph	H (**1a**)	Ph	$Yb(OTf)_3$	200	10	200	24	80 (**4n**)	61 (**2n**)
9	*p*-ClC$_6$H$_4$	H (**1b**)	Me	$Yb(OTf)_3$	200	10	200	70	>99 (**4b**)	89 (**2b**)
10	*p*-NCC$_6$H$_4$	H (**1c**)	Me	$Yb(OTf)_3$	200	10	800	192	>99 (**4c**)	62 (**2c**)
11	*p*-MeOC$_6$H$_4$	H (**1e**)	Me	$Yb(OTf)_3$	700	10	400	120	>99 (**4e**)	Complex mixture
12	*o*-MeC$_6$H$_4$	H (**1f**)	Me	$Yb(OTf)_3$	200	10	200	120	>99 (**4f**)	77 (**2f**)
13	2,4,6-C$_6$H$_2$	H (**1g**)	Me	$Yb(OTf)_3$	200	10	200	70	>99 (**4g**)	18 (**2g**)
14	PhCH=CH	H (**1h**)	Me	$Yb(OTf)_3$	500	100	200	32	95 (**4h**)	5 (**2h**)
15	PhCH$_2$CH$_2$	H (**1i**)	Me	$Yb(OTf)_3$	200	10	400	32	90 (**4i**)	Complex mixture
16[a]	Ph	Me (**1j**)	Me	$Yb(OTf)_3$	200	20	400	48	>99 (**4j**)	No reaction

[a] **4j** was generated after heating at 70°C.

was total isolated yield based on the corresponding carbonyl compound **1**.

Effect of Lewis acid was monitored using Zn/Lewis acid/(EtCO)$_2$O system. As shown in entries 1–4, lanthanoid triflates gave the better results, but the accommodation of the metals to the reduction process was different, as compared with that of the diacyloxylation process. Sm(OTf)$_3$, which was less effective in the diacyloxylation than Sc(OTf)$_3$, gave the better yield for the one-pot reductive esterification. Finally, Yb(OTf)$_3$ was found to be the more suitable catalyst for both processes (entry 4). The above phenomena strongly suggest that Lewis acid catalyst also affects the Zn-induced reduction process. Indeed, when Zn-reduction was operated from the isolated compound **4a** in the absence of Yb(OTf)$_3$ catalyst, no reduction took place with almost quantitative recovery of **4a** (Scheme 4).
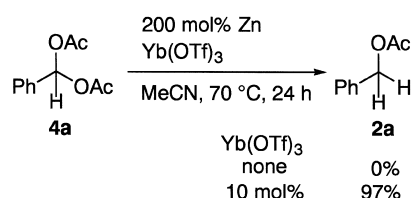
Scheme 4.

Various kind of acid anhydrides were employed in the reaction with benzaldehyde under the one-pot Zn/Yb(OTf)$_3$ conditions (entries 4–8). Although the diacyloxylation did not proceed quantitatively in the reaction with bulky acid anhydride, **4** and **2** were produced in moderate to excellent yields. Substituent effect of the aryl aldehydes was examined using Ac$_2$O as an acylating reagent (entries 5, and 9–13) and in every case, diacetylated compounds **4** were obtained quantitatively. With these results, we concluded that the diacyloxylation does not depend on either electronic or steric nature of aldehydes but was influenced by the structure of acid anhydrides. In contrast, the reduction step was strongly dependent both on electronic and steric effects. Aldehydes bearing electron-withdrawing group such as *p*-Cl (entry 9) or *p*-CN (entry 10) underwent the reductive esterification in 89 and 62% yields, respectively. On the other hand, aldehydes bearing electron-donating group such as *p*-OMe (entry 11) reacted with Zn to give the complex mixture without the formation of the expected ester. Such inclination of the electronic effect resembles that observed in the Zn/Ac$_2$O/imidazole system as shown in Table 2. Only the difference lies in the reactivity of *p*-cyanobenzaldehyde: no pinacol-type product **3c** was detected in the Zn/Yb(OTf)$_3$/Ac$_2$O system, indicating that a radical intermediate is unlikely to be stable under the above conditions. As for the steric effect, *o*-tolylaldehyde (entry 12) was reduced to **2f** in 77% yield, while mesitylaldehyde (entry 13) was restrictive to be reduced (18% yield). Yb-catalyzed diacetoxylation was also employed in the reaction of cinnamaldehyde (**1h**), hydrocinnamaldehyde (**1i**), and acetophenone (**1j**) in 95, 90, and >99% yield, respectively. On the contrary, these aldehydes/ketone did not effectively undergo the reductive esterification. As shown in entry 14, reduction of **4h** with Zn occurred, but **2h** was produced in very low yield (5%) with complex mixture. Addition of zinc powder into the mixture of **4i** and

Yb(OTf)$_3$ did not give the ester **2i** with 82% recovery of **4i** (entry 15). No reaction was observed with **4j** as shown in entry 16.

The above-mentioned results suggest that the reduction process would proceed via the direct contact and insertion of metallic zinc to the C–OAc bond of **4** and Lewis acid such as Yb(OTf)$_3$ would assist the insertion process by weakening the C–O bond. However, electron transfer mechanism, including direct or fast successive two-electron transfer mechanism, cannot be excluded.

3. Conclusion

We have demonstrated two types of reductive esterification of aromatic aldehydes, Zn/Ac$_2$O/imidazole and Zn/Yb(OTf)$_3$/(RCO)$_2$O systems. Features of each reaction are as follows:

1. Zn/Ac$_2$O/imidazole operates direct conversion to the esters under nearly neutral conditions. Electron transfer mechanism may be proposed.
2. Zn/Yb(OTf)$_3$/(RCO)$_2$O system enables the two-step transformation via the corresponding diacyloxy compounds. Yb(OTf)$_3$ catalyst does not only accelerate the diacyloxylation step, but also act as an activator for the Zn-induced reduction. Judging from the electronic and steric susceptibility, the reduction process is likely to proceed by the direct contact of Zn to the acyloxy compound.
3. Yb(OTf)$_3$ is also found to be an excellent catalyst for the transformation of the carbonyl compounds to the corresponding diacyloxy compounds. Although the reactivity is slightly dependent on the structure of acid anhydrides, the reaction has large versatility to widen the scope and utility of the starting aldehydes and ketones.

4. Experimental

4.1. General

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer. CDCl$_3$ was used as a solvent, and residual chloroform (^{1}H=7.24 ppm; ^{13}C=77.0 ppm) or Me$_4$Si was used as an internal standard. Infrared spectra were recorded on Perkin–Elmer Model 1600 Series FT-IR. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using either electron impact (EI) or chemical ionization (CI) modes. Elemental analyses were carried out at the Analytical Center, Graduate School of Engineering, Osaka University. Column chromatography was conducted on silica gel (Wakogel C-200). DME and toluene were freshly distilled from CaH$_2$ prior to use. MeCN was distilled from P$_2$O$_5$, then from CaH$_2$, and dried over Molecular Sieves 4A. Zinc powder was purified according to the literature without amalgamation.[18] There was no significant difference of reactivity of the following reactions depending on the commercial resources. Other organic compounds such as

arylaldehydes, acid anhydrides, and imidazole were purchased and purified according to the standard methods.[20]

4.2. General procedure for Zn/Ac₂O/imidazole reduction system

To a mixture of zinc powder (131 mg, 2 mmol) and imidazole (136 mg, 2 mmol) in DME (4 mL) was added acetic anhydride (204 mg, 2 mmol) at room temperature under argon. The reaction mixture was heated to 80°C, and then aldehyde **1** (1 mmol) was added. After stirring for 24 h at 80°C, the reaction was quenched with ether (10 mL) and HCl aq (1 M, 10 mL). After the filtration through Celite, the organic layer was separated and the aqueous phase was extracted with Et₂O (10 mL×2). The combined organic layer was washed with water (10 mL×3), then brine (10 mL), dried over MgSO₄, and concentrated in vacuo. The crude product was purified by silica-gel column chromatography, giving the benzyl acetate derivative **2**.

4.3. General procedure for Yb(OTf)₃-catalyzed diacyloxylation of carbonyl compounds

To a MeCN (1 mL) solution of **1** (1 mmol) were added acid anhydride (2 mmol) and Yb(OTf)₃ (62 mg, 0.1 mmol). The mixture was stirred at room temperature under argon. When the reaction was completed (monitoring by TLC and ¹H NMR), excess water was added. The product was extracted with CH₂Cl₂. The organic layer was washed with saturated solution of NaHCO₃ followed by water, dried over NaSO₄, and concentrated in vacuo. Distillation or flash chromatography, if necessary, gave the diacyloxylated compound **4**.

4.3.1. Diacetoxyphenylmethane (4a): [581-55-5]; 1-chloro-4-diacetoxymethylbenzene (4b): [13086-93-6]; 4-diacetoxymethylbenzonitrile (4c): [36735-42-9]; 1-diacetoxymethyl-4-methoxybenzene (4e): [14202-31-4]; 2-diacetoxymethyltoluene (4f): [31675-37-3]; 1-diacetoxymethyl-2,4,6-trimethylbenzene (4g). ¹H NMR δ=2.10 (s, 6H), 2.27 (s, 3H), 2.52 (s, 6H), 6.87 (s, 2H), 8.024 (s, 1H); ¹³C NMR 20.34, 21.34, 21.44, 88.89, 128.79, 130.10, 138.01, 139.73, 169.02 ppm; IR (neat) 3020, 2925, 2872, 2736, 1760, 1612, 1035, 852 cm⁻¹. Found: C, 67.23; H, 7.20%. Calcd for C₁₄H₁₈O₄: C, 67.18; H, 7.25%. HRMS found: m/z 250.1214. Calcd for C₁₄H₁₈O₄: 250.1205.

4.3.2. 3,3-Diacetoxy-1-phenyl-1-propene (4h): [37973-54-9]; 1,1-diacetoxy-3-phenylpropane (4i): [85337-09-3]; 1,1-diacetoxy-1-phenylethane (4j): [28153-24-4]. ¹H NMR δ=2.21 (s, 6H), 2.60 (s, 3H), 7.45–7.62 (m, 3H), 7.95 (d, 2H, J=7.2 Hz); ¹³C NMR 20.83, 22.26, 26.70, 128.20, 128.45, 133.01, 177.02 ppm.

4.3.3. Phenyl-bis-propanoyloxymethane (4k): [55696-47-4]; bis(2-methylpropanoyloxy)phenylmethane (4l). ¹H NMR δ=1.15–1.23 (m, 12H), 2.58–2.65 (m, 2H), 7.37–7.41 (m, 3H), 7.47–7.51 (m, 2H), 7.68 (s, 1H); ¹³C NMR 18.55, 18.75, 33.88, 89.47, 126.51, 128.54, 129.53, 135.80, 174.89 ppm; IR (neat) 3050, 2976, 2895, 2780, 1757, 1690, 1092, 697 cm⁻¹. Found: C, 67.92; H, 7.53%. Calcd for C₁₅H₂₀O₄: C, 68.16; H, 7.63%. HRMS found: m/z 264.1360. Calcd for C₁₅H₂₀O₄: 264.1361.

4.3.4. Bis(2,2-dimethylpropanoyloxy)phenylmethane (4m). ¹H NMR δ=1.23 (s, 18H), 7.31–7.41 (m, 3H), 7.42–7.48 (m, 2H), 7.67 (s, 1H); ¹³C NMR 26.85, 38.80, 89.44, 126.40, 128.50, 129.39, 135.94, 176.31 ppm; IR (neat) 3070, 2975, 2890, 2845, 2800, 1750, 1145, 1109, 697 cm⁻¹. HRMS found: m/z 292.1680. Calcd for C₁₇H₂₄O₄: 292.1674.

4.3.5. Bis(benzoyloxy)phenylmethane (4n) [1459-18-3]. ¹H NMR δ=7.42–7.74 (m, 11H), 8.09–8.14 (m, 4H), 8.23 (s, 1H); ¹³C NMR 90.58, 126.66, 128.34, 128.60, 128.99, 129.69, 129.94, 133.48, 135.58, 164.29; IR (neat) 3050, 3020, 1732, 1601, 1451, 1277, 1059, 707 cm⁻¹.

4.4. General procedure for Zn/Yb(OTf)₃/(RCO)₂O reduction system

To a MeCN (1 mL) solution of **1** (1 mmol) were added acid anhydride (2 mmol) and Yb(OTf)₃ (62 mg, 0.1 mmol). The mixture was stirred at room temperature under argon. When the reaction was completed (monitoring by TLC and ¹H NMR), zinc powder (2 mmol) was added and the reaction was refluxed. After stirring for the appropriate time listed in Table 4, the reaction was quenched with ether (10 mL) and HCl aq (1 M, 10 mL). After the filtration through Celite, the organic layer was separated. The aqueous phase was extracted with Et₂O (10 mL×2). The combined organic layer was washed with water (10 mL×3), then brine (10 mL), dried over MgSO₄, and concentrated in vacuo. The crude product was purified by thin layer chromatography, giving the ester derivative **2**. All of the products are known compounds, and their spectral data are in good agreement with those of authentic samples.

Benzyl acetate (2a): [140-11-4]; 4-chlorobenzyl acetate (2b): [5046-33-7]; 4-acetoxymethylbenzonitrile (2c): [21388-95-4]; 4-isopropylbenzyl acetate (2d): [59230-57-6]; 1-acetoxymethyl-4-methoxybenzene (2e): [104-21-2]; 2-methylbenzyl acetate (2f): [17373-93-2]; 2,4,6-trimethylbenzyl acetate (2g): [63548-92-5]; *trans*-**cinnamyl acetate (2h): [21040-45-9]; benzyl propionate (2k): [122-63-4]; benzyl isobutylate (2l): [103-28-6]; benzyl pivalate (2m): [2094-69-1]; benzyl benzoate (2n): [120-51-4].**

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19. It is important to ascertain the formation of the diacyloxy compound. When all the reagent, Yb(OTf)$_3$, Zn, and Ac$_2$O is treated with PhCHO at once, reductive esterification does not proceed effectively.
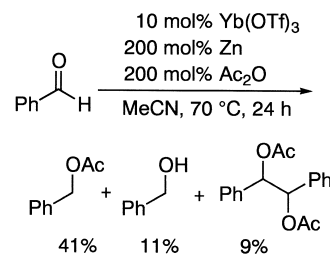
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