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Rate-Acceleration in Gold-Nanocluster-Catalyzed Aerobic Oxidative Esterification Using 1,2- and 1,3-Diols and Their Derivatives

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Dedicated to Professor Eiichi Nakamura on the occasion of his 60th birthday

Abstract: Aerobic oxidation of aldehydes to 1,2- and 1,3-diol monoesters was catalyzed by polymer-incarcerated gold nanoclusters under ambient conditions. The esterification proceeded much faster with 1,2- and 1,3-diols and their derivatives rather than with methanol.

Keywords: gold · esterification · heterogeneous catalysis · neighboring-group effects · oxidation

Introduction

Esters are generally prepared from carboxylic acids or activated carboxylic acids, such as acid chlorides or acid anhydrides.[1] Alternatively, several research groups have recently reported the gold-nanocluster-catalyzed[2,3] aerobic oxidative esterification of alcohols or aldehydes.[4] This reaction proceeds under mild conditions, requires molecular oxygen as the only oxidant, and has potential industrial applications as a sustainable chemical process.

The synthesis of glycol monoesters is useful for the intermediates of pheromones of Lepidoptera,[5] cross-linking agents for polyesters or fungicides,[6] miticides,[7] and emulsifiers.[8] Conventionally, they are synthesized by the oxidation of cyclic acetals to avoid the formation of diesters[6,9] or by the addition of carboxylic acids to ethylene oxide.[10] However, these methods involve two steps and require more than stoichiometric amounts of oxidants or employ ethylene oxide, which is difficult to handle in the laboratory. Recently, a one-step direct glycol monoesterification of aldehydes or carboxylic acids was reported.[11] However, to the best of our knowledge, there are no examples of the catalytic glycol monoesterification of aldehydes in which molecular oxygen has been used as an oxidant.

Recently, we disclosed that gold-nanocluster catalysts immobilized on polystyrene-based polymers with cross-linking moieties, that is, polymer-incarcerated gold-nanocluster catalysts (PI-Au),[12] were effective in the direct aerobic oxidation of alcohols in methanol to afford methyl esters under ambient conditions (under atmospheric oxygen conditions and at room temperature).[13] This procedure has advantages in terms of atom and energy efficiency, the E factor, and environmental friendliness, when compared to traditional esterification procedures. However, the rate of esterification reactions catalyzed by gold nanoclusters in other alcohols, such as ethanol, 1-propanol, and benzyl alcohol, is still low.[4g,h]

Herein we report the aerobic oxidative formation of glycol monoesters from aldehydes catalyzed by PI-Au under mild conditions. Results of the comparison of the use of different diols on the reactivity of the esterification reaction, which suggests the existence of effective neighboring group participation between oxygen in diols or its derivatives and gold nanoclusters, are also described.

Results and Discussion

The PI-Au nanoparticles were prepared according to a previously reported procedure (Scheme 1).[12a] We investigated the oxidative esterification of *para*-methylbenzaldehyde using this gold catalyst. When ethanol was used as solvent, the yield of the ethyl ester was 60% (Scheme 2). On the other hand, when *para*-methylbenzaldehyde was treated with ethylene glycol, the reaction proceeded smoothly to

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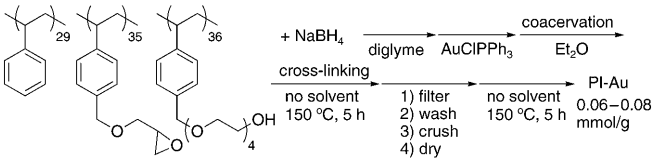
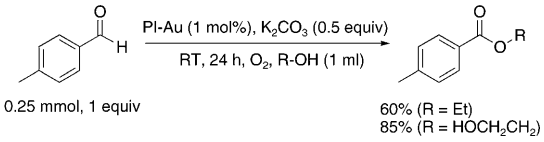


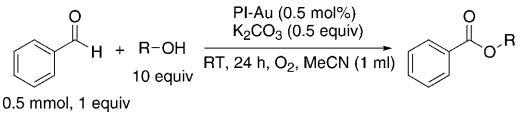
Scheme 1. Preparation of PI-Au nanoclusters.



Scheme 2. Esterification of an aldehyde with ethanol and ethylene glycol.

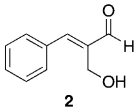
afford the corresponding monoester product in 85% yield (Scheme 2). These results were remarkable because it has been reported that polyols, such as ethylene glycol[4p,14] and glycerol[15] itself, are oxidized in the presence of gold nanoclusters. However, in the esterification reaction, ethylene glycol functioned well as a counterpart in oxidative esterification with an aldehyde. We then examined the esterification of benzaldehyde with 10 equivalents of various diols and their derivatives as counterparts, using this catalyst, in the presence of potassium carbonate under atmospheric oxygen and at room temperature in acetonitrile (Table 1).[16]

Table 1. Monobenzoylation of various diols and alcohols in acetonitrile.



Entry	Alcohol (R–OH)	Conversion [%][a]	Yield [%][b]	PhCOOH [%][b]
1		100	83	16
2[c]		86 (91)[d]	64 (74)[d]	11
3		25	20	2
4		7	4	1
5		14	9	5
6		40	32[e]	5
7		>99 (>99)[d]	65 (78)[d]	13
8		54 (99)[d]	48(78)[d]	6
9		0	0	0
10		85(91)[d]	25 (56)[d,f]	28
11	EtOH	3	1	trace
12	*i*PrOH	no reaction		

[a] Determined by GC analysis. [b] Yield of isolated product. [c] Compound **2** was obtained as a by-product in 3% yield. [d] The yield in parenthesis was obtained under the conditions: 1 mol% PI-Au and 2 mL alcohol instead of acetonitrile as solvent. [e] The ratio of 1-substituted monoester to 2-substituted monoester was 18:14. [f] The ratio of 1-substituted monoester to 2-substituted monoester was 50:6.



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When 10 equivalents of ethylene glycol was used, the corresponding ester was obtained in 83% yield (Table 1, entry 1). The yield decreased as the alkyl chain between the two hydroxy groups increased (Table 1, entries 2–5). These results could be explained by the neighboring-group participation effect, in which the hemiacetal intermediates are stabilized by the two hydroxy groups on the surface of the gold nanoclusters to accelerate the pathway to glycol esterification. In the case of long alkyl chains, it is entropically unfavorable for the two hydroxy groups to coordinate to the gold surface over the alkyl chain. Comparison of the results obtained when using 1,6-hexanediol and 1,2-hexanediol clearly demonstrated the neighboring-group effect where, in the presence of two hydroxy groups at the 1 and 2-positions, the reactivity improved significantly (Table 1, entries 5 versus 6). The neighboring-group effect was observed not only with hydroxy groups but also with ethereal oxygen atoms (Table 1, entries 7 and 8). It is interesting to note that in the case of a sulfur-containing alcohol, no reaction occurred, in spite of the good affinity of sulfur for gold (Table 1, entry 9). When alcohols were used as the solvent instead of acetonitrile, the yields of the corresponding monoesters increased significantly (Table 1, entries 2, 7, 8, and 10). Although stirring of a glycerol solution did not proceed very smoothly, owing to its high viscosity, a mixture of the corresponding monoesters was obtained in moderate yield (Table 1, entry 10). The products shown in Table 1, entries 7 and 8 were difficult to synthesize by conventional methods, that is, by the opening of cyclic acetals.[9] The esterification reactions were dramatically accelerated by the neighboring-group effect when compared to the simple esterification reactions in which ethanol and 2-propanol were used (Table 1, entries 11 and 12, also see below).

Several examples of the aerobic oxidative formation of ethylene glycol monoesters are summarized in Table 2. In the presence of electron-withdrawing groups on the aromatic rings, the reactions proceeded smoothly, but both the desired ester and carboxylic acids were formed. To suppress the formation of carboxylic acids, the reactions were then conducted in the presence of a small amount of a base at lower temperature. We were pleased to see that the yield then improved to about 70% (Table 2, entries 3–4). On the other hand, the presence of electron-donating groups on the aromatic rings decreased the initial hemiacetal formation. In particular, the reaction was rather slow when *para*-methoxybenzaldehyde was used. The desired ester was obtained in 75% yield when ethylene glycol was used as the solvent (Table 2, entry 6). Furthermore, an aliphatic substrate and other aromatic substrates were smoothly converted into the corresponding esters under the standard conditions (Table 2, entries 7–10).

The reaction profiles of the respective oxidative esterifications with methanol, ethanol, and ethylene glycol were compared under the reaction conditions that included PI-Au (1 mol%), K_2CO_3 (0.5 equiv), and the alcohol (10 equiv) in acetonitrile at 30°C (see Figure 1). We had previously observed that the corresponding esters were obtained in good

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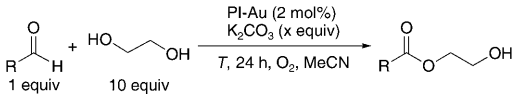
Table 2. Scope of aerobic oxidative formation of ethylene glycol monoesters.



Entry[a]	R	Base [equiv]	T [°C]	Conv. [%][b]	Yield [%][c]	Acid [%][c]
1[d,e]	Ph	0.5	30	>99	83	16
2	4-BrC_6H_4	0.5	30	>99	82	8
3	4-$CF_3C_6H_4$	0.1	0	>99	72	15
4	4-$NO_2C_6H_4$	0.1	0	96	70	10
5	4-MeC_6H_4	0.5	30	92	78	8
6[e,f]	4-$MeOC_6H_4$	0.5	30	94	75	7
7	$PhCH_2CH_2$	0.25	0	96	71	13
8	PhCH=CH	0.25	30	94	73	8
9[e]	2-Napthyl	0.25	0	>99	80	11
10[e]	4-(1,1′-Biphenyl)	0.25	0	83	70	8

[a] 0.25 mmol scale and 0.25 M. [b] Determined by GC analysis. [c] Yield of isolated product. [d] 0.5 M. [e] 0.5 mol% PI-Au was used. [f] Ethylene glycol (1 mL) was used instead of acetonitrile.

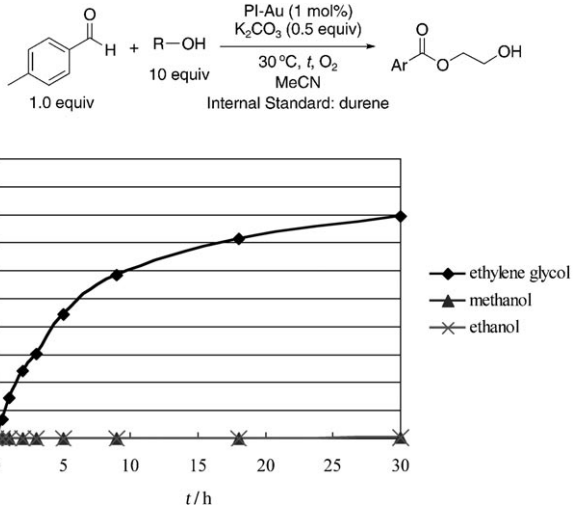
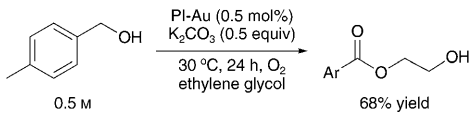


Figure 1. Reaction profiles of oxidative esterification of aldehydes in the presence of 10 equiv ethylene glycol, methanol, and ethanol.

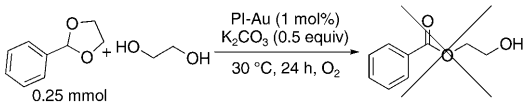
to high yields when methanol or ethanol was used as solvent.[13] In contrast, the methyl ester and ethyl ester hardly formed when 10 equivalents alcohol in acetonitrile was used. On the other hand, the ethylene glycol ester formed readily under the same conditions. These results clearly illustrate the remarkable effect of the neighboring-group participation between gold nanoclusters and the two hydroxy groups in oxidative esterification with ethylene glycol.

The direct aerobic oxidative esterification of glycol from an alcohol was also investigated (Scheme 3). In the presence of 0.5 mol% PI-Au and 0.5 equiv K_2CO_3, *para*-methylbenzyl-



Scheme 3. Glycol esterification from an alcohol.

alcohol was converted into the corresponding ester in 68% yield.[12f] Control experiments, using a cyclic acetal as substrate and ethylene glycol, were also performed. Under both conditions, namely Conditions A, using 10 equivalents ethylene glycol and acetonitrile as solvent, and Conditions B, using 1 mL ethylene glycol, the formation of the corresponding ester was not observed (Scheme 4).



Scheme 4. Control experiments with a cyclic acetal and ethylene glycol. Conditions A: ethylene glycol (2.5 mmol), MeCN (1 mL), starting materials were fully recovered. Conditions B: ethylene glycol (1 mL), starting materials were fully recovered.

On the basis of these results, we have proposed the catalytic cycle shown in Figure 2. Based on the results of the control experiment in which a cyclic acetal was used, the reaction pathway that involved the formation of a cyclic acetal was ruled out. According to Haruta and co-workers and Tsukuda and co-workers, gold nanoclusters immobilized on polymer supports are sufficiently electron rich to activate molecular oxygen, and the subsequent alcohol adsorption on the gold nanoclusters is facilitated by a weak base, such as K_2CO_3 (or even no base).[4e,17,18] In the case of our PI-Au catalysts, a similar mechanism, in which gold nanoclusters adsorb molecular oxygen and possess Lewis acidity (Figure 2, **A**), is assumed.[19] This is because we had already confirmed that PI-Au was sufficiently active in 1) the aerobic oxidation of alcohols and aerobic oxidative methyl esterification with K_2CO_3 at room temperature,[12f,13] and 2) in the aerobic oxidation of alcohols without base at room temperature.[12d]

The remarkable acceleration of the rate of diol esterification has been explained by two main factors, which pertain

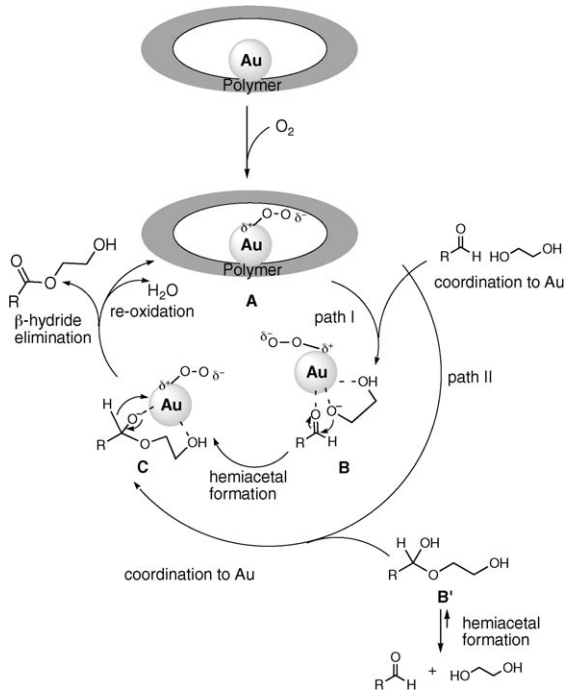


Figure 2. Proposed catalytic cycle.

to the neighboring-group coordination to the gold surface, namely, decreasing the activation energy to form a hemiacetal on the surface of gold nanoclusters, and stabilization of the hemiacetal intermediate by multidentate coordination to the surface of gold nanoclusters.

Although there may be no special stabilization effect in the hemiacetal formation from an aldehyde and ethylene glycol or 2-methoxy ethanol in the liquid phase without gold,[20] a hemiacetal formed from an aldehyde and a diol can be stabilized on the surface of gold nanoclusters by the dual coordination of oxygen atoms to gold (Figure 2, **B**).[21]

In contrast to 1,2- or 1,3-diols, these effects are decreased in diols that have longer alkyl chains between the two hydroxy groups. This decrease is because it is entropically unfavorable for the two hydroxy groups to coordinate to gold. Furthermore, ethereal oxygen atoms may coordinate to gold nanoclusters too. Finally, β-hydride elimination occurs to afford the corresponding ester along with reoxidation of hydrogen to water on the surface of gold nanoclusters, thus completing this catalytic cycle.[22]

Conclusions

We have found that aerobic oxidative esterification of aldehydes or an alcohol with 1,2- and 1,3-diols and its derivatives proceeds smoothly in the presence of PI-Au under ambient conditions. It is of interest to note that esterification proceeded much faster with 1,2- and 1,3-diols and its derivatives than with methanol. The effect of neighboring group participation between the oxygens of diols and its derivatives or hemiacetals and the surface of gold nanoclusters has been discussed. This is the first report of such an effect observed in aerobic oxidation using gold nanoclusters. Further investigations, which include consideration of the mechanism, other possibilities of neighboring group participation, and synthetic applications, are currently underway in our laboratory.

Experimental Section

General

Melting points are uncorrected. JEOL JMN-LA400, 500 or 600 spectrometers were used for NMR spectroscopic measurements. Tetramethylsilane ($\delta=0$) was used as an internal standard for ^{1}H NMR spectroscopy and $CDCl_3$ ($\delta=77.0$) for ^{13}C NMR spectroscopy. ICP analysis was performed on Shimadzu ICPS-7510 equipment. IR spectra were measured on a JASCO FT/IR-610 spectrometer. GC analysis was performed on a Shimadzu GC-2010 apparatus (Column: GL Science, TCWAX, 0.25 mm ID, 0.25 μm, 60.0 m; Gas pressure: 214.2 kPa; Total flow: 90.6 mL min^{-1}; Column flow: 1.86 mL min^{-1}; Velocity: 30.8 cm/sec; Purge flow: 3.0 mL min^{-1}; Sprit ratio: 46.0; Injector: 250 °C, FID: 250 °C; Column program: starting from 50.0 °C, 10 min hold, 10 °C/min to 220 °C, 20 min hold). STEM/EDS images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All STEM specimens were prepared by placing a drop of the solution on carbon-coated copper grids and allowed to dry in air (without staining).

The PI-Au was prepared according to a previously reported procedure.[11a] $AuClPPh_3$ was purchased from Strem Chemical Inc. $NaBH_4$ was purchased from Wako Pure Chemical Company and recrystallized from diglyme by heating according to the literature procedure[1] and stored in a glove box. It is important to manipulate all operations under an argon atmosphere during recrystallization. The activity of the catalysts and its reproducibility were influenced by the purity of $NaBH_4$ in the course of catalyst preparation.

The structures of known compounds were confirmed by comparison with commercially available compounds or data shown in literature.

Typical Procedure for The PI-Au-Catalyzed Aerobic Esterification of Aldehyde in Polyol

(Table 1, entry 2) Benzaldehyde (53.0 mg, 0.5 mmol), K_2CO_3 (34.6 mg, 0.25 mmol), PI-Au (1 mol %), and propane-1,3-diol (2.0 mL) were combined in a round-bottomed flask. After the mixture was stirred for 24 h under an O_2 atmosphere at 30 °C, the catalyst was collected by filtration and washed with dichloromethane using a Kiriyama Rohto funnel. Brine (40 mL) was added and the whole aqueous layer was extracted with ethyl acetate (20~30 mL). The conversion of aldehyde was determined by GC analysis with reference to an internal standard (anisole). The solvent was removed in vacuo and the residue was purified by preparative TLC to afford the mixture of 3-hydroxypropyl benzoate and 2-formyl-3-hydroxyprop-1-enyl benzoate as a by-product (68.7 mg). The ratio of the amounts of the substances was determined by ^{1}H NMR analysis, and then the yield of the ester and the by-product was calculated as 74 % and 3 %, respectively.

3-Hydroxypropyl benzoate:[11c] IR (neat): $\tilde{\nu}=3421$, 3066, 1710, 1456, 1279, 714 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=1.94$ (tt, 2H, $J=6.0$ Hz, 12.0 Hz), 2.02 (t, 1H, $J=5.4$ Hz), 3.71 (dt, 2H, $J=5.4$ Hz, 11.4 Hz), 4.42 (t, 2H, $J=6.0$ Hz), 7.37 (dd, 2H, $J=8.4$ Hz), 7.50 (dd, 1H, $J=7.2$ Hz), 7.97 ppm (d, 2H, $J=6.6$ Hz); ^{13}C NMR: $\delta=31.8$, 59.0, 61.8, 128.3, 129.5, 130.0, 133.0, 166.9 ppm.

2-Formyl-3-hydroxyprop-1-enyl benzoate:[23] ^{1}H NMR ($CDCl_3$): $\delta=4.32$ (s, 2H), 7.42–7.46 (m, 3H), 7.49 (s, 1H), 8.03 (d, 2H, $J=7.2$ Hz), 9.62 ppm (s, 1H).

2-(2-Hydroxyethoxy)ethyl benzoate[11c] **and diethylene glycol**: (Table 1, entry 7) 2-(2-Hydroxyethoxy)ethyl benzoate and diethylene glycol

(81.3 mg, 78%). IR (neat): $\tilde{\nu}$=3439, 3067, 1716, 1454, 1277, 1112, 714 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.48 (br, 1H), 3.60 (t, 2H, J=4.5 Hz), 3.70 (t, 2H, J=4.5 Hz), 3.79 (t, 2H, J=4.5 Hz), 4.44 (t, 2H, J=4.5 Hz), 7.39 (dd, 2H, J=8.4 Hz), 7.51 (dd, 1H, J=7.2 Hz), 8.01 ppm (d, 2H, J=7.2 Hz); ^{13}C NMR: δ=61.7, 64.0, 69.2, 72.3, 128.3, 129.6, 129.9, 133.0, 166.6 ppm.

2-Methoxyethyl benzoate:[24] (Table 1, entry 8) IR (neat): $\tilde{\nu}$=3066, 1722, 1455, 1275, 1110, 712 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.41 (s, 3H), 3.71 (t, 2H, J=5.1 Hz), 4.46 (t, 3H, J=4.5 Hz), 7.41 (dd, 2H, 7.5 Hz), 7.54 (dd, 1H, J=7.8 Hz), 8.05 ppm (d, 2H, J=4.8 Hz); ^{13}C NMR: δ=59.1, 64.0, 70.5, 128.3, 129.7, 130.0, 133.0, 166.6 ppm.

Mixture of 2,3-dihydroxypropyl benzoate and 1,3-dihydroxypropan-2-yl benzoate: (Table 1, entry 10) IR (neat): $\tilde{\nu}$=3439, 3070, 1708, 1455, 1279, 714 cm^{-1} (a mixture of two compounds).

2,3-dihydroxypropyl benzoate:[25] ^1H NMR ($CDCl_3$): δ=2.24 (t, 1H, J=6.3 Hz), 2.69 (d, 1H, J=5.4 Hz), 3.63 (m, 2H), 3.72 (m, 1H), 4.01 (m, 1H), 4.33–4.40 (m, 2H), 7.39 (dd, 2H, J=7.8 Hz), 7.52 (dd, 1H, J=7.5 Hz), 7.98 ppm (d, 2H, J=7.8 Hz); ^{13}C NMR: δ=63.4, 65.6, 70.3, 128.4, 129.5, 129.7, 133.3, 166.9 ppm.

1,3-Dihydroxypropan-2-yl benzoate:[26] ^1H NMR ($CDCl_3$): δ=^1H NMR ($CDCl_3$) δ=3.91 (dd, 4H, J=5.1 Hz), 5.11 (t, 1H, J=4.8 Hz), 7.39 (dd, 2H, J=7.8 Hz), 7.52 (dd, 1H, J=7.5 Hz), 7.98 ppm (d, 2H, J=7.8 Hz); ^{13}C NMR: δ=62.0, 75.6, 128.4, 129.5, 129.7, 133.3, 166.7 ppm.

A typical procedure for aerobic oxidation of aldehyde to ethylene glycol ester in acetonitrile catalyzed by PI-Au[9b,11c]

(Table 1, entry 1) Benzaldehyde (53.0 mg, 0.5 mmol), K_2CO_3 (34.6 mg, 0.25 mmol), PI-Au (0.5 mol%), ethylene glycol (310.4 mg, 5 mmol), and acetonitrile (1 mL) were combined in a round-bottomed flask. After the mixture was stirred for 24 h under O_2 atmosphere at 30°C, the catalyst was collected by filtration and washed with dichloromethane using a Kiriyama Rohto funnel. Aqueous sodium hydroxide solution (1 M, 5 mL) was added and the aqueous layer was extracted with dichloromethane (20~30 mL). The combined organic layers were washed with brine and dried over sodium sulfate. The conversion of the aldehyde was determined by GC analysis with reference to an internal standard (IS=anisole). The solvent was removed in vacuo and the residue was purified by preparative TLC to afford 2-hydroxyethyl benzoate (61.0 mg, 83%). On the other hand, hydrochloric acid (1 M, 10 mL) was added to the aqueous layer and it was extracted with dichloromethane (20~30 mL). The combined organic layers were washed with brine and dried over sodium sulfate and the solvent was removed in vacuo to afford benzoic acid (9.4 mg, 16%). The purity of benzoic acid was determined by NMR analysis (polyol could sometimes be detected by ^1H NMR). IR (neat): $\tilde{\nu}$=3439, 3066, 1712, 1453, 1279, 714 cm^{-1}; ^1H NMR ($CDCl_3$): δ=^1H NMR ($CDCl_3$): δ=2.21 (t, 1H, J=6.0 Hz), 3.94 (dd, 2H, J=5.4, 9.0 Hz), 4.44 (t, 2H, J=4.8 Hz), 7.42 (dd, 2H, J=7.8 Hz), 7.55 (dd, 1H, J=7.5 Hz), 8.04 ppm (d, 2H, J=7.8 Hz); ^{13}C NMR δ=61.2, 66.6, 128.3, 129.6, 129.8, 133.1, 166.9.

4-Hydroxybutyl benzoate:[11c] (Table 1, entry 3) IR (neat): $\tilde{\nu}$=3415, 3065, 1711, 1455, 1278, 714 cm^{-1}; ^1H NMR ($CDCl_3$): δ=1.72 (m, 2H), 1.85 (m, 2H), 3.71 (m, 2H), 4.35 (t, 2H, J=6.3 Hz), 7.42 (dd, 2H, J=8.1 Hz), 7.54 (dd, 1H, J=7.8 Hz), 8.02 ppm (d, 2H, J=8.4 Hz); ^{13}C NMR: δ=25.2, 29.2, 62.4, 64.7, 128.3, 129.5, 130.3, 132.9, 166.6 ppm.

5-Hydroxypentyl benzoate:[27] (Table 1, entry 4) IR (neat): $\tilde{\nu}$=3439, 1708, 1465, 1274, 675 cm^{-1}; ^1H NMR ($CDCl_3$): δ=1.48–1.67 (m, 4H), 1.80 (m, 2H), 3.67 (dt, 2H, J=6.2, 11.4 Hz), 4.32 (t, 2H, J=3.0 Hz), 7.42 (dd, 2H, J=7.4 Hz), 7.52–7.56 (m, 1H), 8.02 ppm (d, 2H, J=5.2 Hz); ^{13}C NMR: δ=22.3, 28.5, 32.3, 62.7, 64.9, 128.3, 129.5, 130.4, 132.9, 166.7 ppm.

6-Hydroxyhexyl benzoate:[27] (Table 1, entry 5) IR (neat): $\tilde{\nu}$=3439, 1709, 1465, 1277, 675 cm^{-1}; ^1H NMR ($CDCl_3$): δ=1.40–1.49 (m, 4H), 1.59 (m, 2H), 1.77 (m, 2H), 3.64 (t, 2H, J=6.3 Hz), 4.32 (t, 2H, J=6.6 Hz), 7.42 (dd, 2H, J=7.8 Hz), 7.53 (dd, 1H, J=7.5 Hz), 8.02 ppm (d, 2H, J=7.2 Hz); ^{13}C NMR: δ=25.4, 25.8, 28.7, 32.6, 62.8, 64.9, 128.3, 129.5, 130.4, 132.8, 166.7 ppm.

Mixture of 2-hydroxyhexyl benzoate and 1-hydroxyhexan-2-yl benzoate: (Table 1, entry 6) IR (neat): 3392, 3069, 1709, 1456, 1279, 714 cm^{-1} (a mixture of two compounds).

2-Hydroxyhexyl benzoate:[28] ^1H NMR ($CDCl_3$): δ=0.90 (t, 3H, J=7.2 Hz), 1.31–1.57 (m, 6H), 2.16 (d, 1H, J=4.8 Hz), 3.97 (m, 1H), 4.21 (dd, 1H, J=6.9, 12.3 Hz), 4.37 (dd, 1H, J=3.0, 5.4 Hz), 7.43 (dd, 2H, J=8.1 Hz), 7.55 (dd, 1H, J=7.5 Hz), 8.04 ppm (d, 2H, J=8.4 Hz); ^{13}C NMR: δ=14.0, 22.6, 27.5, 33.1, 69.2, 70.1, 128.4, 129.6, 129.8, 133.2, 166.7 ppm.

1-Hydroxyhexan-2-yl benzoate:[29] ^1H NMR ($CDCl_3$): δ=0.91 (m, 3H), 1.32–1.76 (m, 6H), 2.09 (br, 1H), 3.97 (m, 1H), 3.75 (dd, 1H, J=6.3, 12.0 Hz), 3.82 (dd, 1H, J=3.0, 12.0 Hz), 5.15 (m, 1H), 7.45 (dd, 2H, J=8.7 Hz), 7.55 (dd, 1H, J=7.5 Hz), 8.03 ppm (d, 2H, J=7.8 Hz); ^{13}C NMR: δ=13.9, 22.5, 27.5, 30.3, 65.0, 76.4, 128.4, 129.7, 130.1, 133.1, 166.9 ppm.

2-Hydroxyethyl benzoate:[9h,11c] (Table 2, entry 1) IR (neat): $\tilde{\nu}$=3439, 3066, 1712, 1453, 1279, 714 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.21 (t, 1H, J=6.0 Hz), 3.94 (dd, 2H, J=5.4, 9.0 Hz), 4.44 (t, 2H, J=4.8 Hz), 7.42 (dd, 2H, J=7.8 Hz), 7.55 (dd, 1H, J=7.5 Hz), 8.04 ppm (d, 2H, J=7.8 Hz); ^{13}C NMR: δ=61.2, 66.6, 128.3, 129.6, 129.8, 133.1, 166.9 ppm.

2-Hydroxyethyl 4-bromobenzoate:[9b] (Table 2, entry 2) IR (neat): $\tilde{\nu}$=3438, 3096, 1717, 1453, 1277, 757 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.14 (t, 1H, J=6.0 Hz), 3.93 (m, 2H), 4.43 (t, 2H, J=4.8 Hz), 7.56 (d, 2H, J=9.0 Hz), 7.88 ppm (d, 2H, J=7.2 Hz); ^{13}C NMR: δ=61.3, 66.8, 128.3, 128.7, 131.2, 131.7, 166.2 ppm.

2-Hydroxyethyl 4-(trifluoromethyl)benzoate: (Table 2, entry 3) IR (neat): 3439, 1724, 1464, 1281 773 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.22 (s, 1H), 3.95 (s, 2H), 4.47 (t, 2H, J=4.8 Hz), 7.67 (d, 2H, J=8.4 Hz), 8.14 ppm (d, 2H, J=9.0 Hz); ^{13}C NMR: δ=61.1, 67.0, 124.5, 125.4, 130.1, 133.1, 134.7, 165.7 ppm; DART-MS: m/z (%) calcd for $C_{10}H_{10}F_3O_3$: 235.05820 [MH^+]; found: 235.05737.

2-Hydroxyethyl 4-nitrobenzoate:[9h] (Table 2, entry 4) m.p. 77–79°C. IR (KBr): $\tilde{\nu}$=3332, 3113, 1726, 1531, 1465, 1356, 1289, 717 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.07 (t, 1H, J=5.7 Hz), 3.98 (t, 2H, J=4.5 Hz), 4.50 (t, 2H, J=4.8 Hz), 8.21 (d, 2H, J=9.0 Hz), 8.26 ppm (d, 2H, J=9.0 Hz); ^{13}C NMR: δ=61.0, 67.3, 123.5, 130.8, 135.2, 150.6, 164.9 ppm.

2-Hydroxyethyl 4-methylbenzoate:[9h] (Table 2, entry 5) IR (neat): $\tilde{\nu}$=3439, 3036, 1709, 1453, 1279, 755 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.28 (t, 1H, J=6.3 Hz), 2.38 (s, 3H), 3.92 (dd, 2H, J=6.3, 9.3 Hz), 4.42 (t, 2H, J=4.5 Hz), 7.21 (d, 2H, J=8.4 Hz), 7.92 ppm (d, 2H, J=7.8 Hz); ^{13}C NMR: δ=21.7, 61.5, 66.5, 127.0, 129.1, 129.7, 143.9, 167.0 ppm.

2-Hydroxyethyl 4-methoxybenzoate:[11d] (Table 2, entry 6) IR (KBr): $\tilde{\nu}$=3452, 3085, 1709, 1462, 1280, 772 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.19 (t, 1H, J=6.0 Hz), 3.84 (s, 3H), 3.92 (dd, 2H, J=5.7, 9.9 Hz), 4.29 (t, 2H, J=4.8 Hz), 6.90 (d, 2H, J=8.4 Hz), 7.99 ppm (d, 2H, J=9.0 Hz); ^{13}C NMR: δ=21.7, 61.5, 66.5, 127.0, 129.1, 129.7, 143.9, 167.0 ppm.

2-Hydroxyethyl 3-phenylpropanoate:[30] (Table 2, entry 7) IR (neat): $\tilde{\nu}$=3440, 3029, 1732, 1454, 749 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.00 (s, 1H), 2.71 (t, 2H, J=7.5 Hz), 3.00 (t, 2H, J=7.5 Hz), 3.78 (dd, 2H, J=5.4, 9.0 Hz) 4.21 (t, 2H, J=4.5 Hz), 7.24 (m, 3H), 7.32 ppm (dd, 2H, J=7.5 Hz); ^{13}C NMR δ=30.9, 35.7, 61.1, 66.0, 126.3, 128.2, 128.5, 140.3, 173.2 ppm.

2-Hydroxyethyl cinnamate:[31] (Table 2, entry 8) IR (neat): $\tilde{\nu}$=3439, 3061, 1708, 1637, 1453, 1278, 768 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.29 (t, 1H, J=5.4 Hz), 3.88 (d, 2H, J=4.2 Hz), 4.33 (t, 2H, J=4.5 Hz), 6.46 (d, 1H, J=15.6 Hz), 7.36 (d, 3H, J=1.8 Hz), 7.50 (dd, 2H, J=3.3 Hz), 7.70 ppm (d, 1H, J=16.8 Hz); ^{13}C NMR: δ=61.3, 66.2, 117.5, 128.1, 128.9, 130.4, 134.2, 145.4, 167.2 ppm.

2-Hydroxyethyl 2-naphthoate:[11c] (Table 2, entry 9) m.p.: 176–179°C; IR (KBr): $\tilde{\nu}$=3452, 3052, 1692, 1466, 1264, 784, 675 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.28 (s, 1H), 3.99 (s, 2H), 4.51 (t, 2H, J=4.8 Hz), 7.51 (dd, 1H, J=7.5 Hz), 7.57 (dd, 1H, J=7.2 Hz), 7.85 (d, 2H, J=7.8 Hz), 7.92 (d, 1H, J=7.2 Hz), 8.04 (dd, 1H, J=1.4, 8.2 Hz), 8.60 ppm (s, 1H); ^{13}C NMR: δ=61.4, 66.8, 125.1, 126.7, 127.0, 127.7, 128.2, 128.3, 129,3 131.2, 132.4, 135.6, 167.1 ppm.

2-Hydroxyethyl [1,1′-biphenyl]-4-carboxylate: (Table 2, entry 10) m.p.: 96–97°C; IR (KBr): $\tilde{\nu}$=3495, 3061, 1697, 1454, 1291, 743, 692 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.26 (s, 1H), 3.96 (s, 2H), 4.47 (t, 2H, J=2.4 Hz), 7.38 (dd, 1H, J=6.5 Hz), 7.39 (dd, 2H, J=12.6 Hz), 7.60 (d, 2H, J=6.8 Hz), 7.64 (d, 2H, J=8.4 Hz), 8.11 ppm (d, 2H, J=8.4 Hz); ^{13}C NMR: δ=61.4, 66.7, 127.0, 127.2, 128.2, 128.5, 128.9, 130.2, 139,9 145.9,

166.8 ppm; DART-MS: *m*/*z* (%) calcd for $C_{15}H_{15}O_3$: 243.10212 [MH^+]; found: 243.10153.

Reaction profiles of aerobic oxidative ethylene glycol monoesterification catalyzed by PI-Au under the conditions using 10 equiv of alcohols in acetonitrile: Ethylene glycol (155.2 mg, 2.5 mmol), K_2CO_3 (17.3 mg, 0.125 mmol) , PI-Au (0.076 mmol g,$^{-1}$ 1 mol %), durene (13.4 mg) as an internal standard, and acetonitrile (1 mL) were combined in a round-bottomed flask, and the mixture was stirred under Ar atmosphere at room temperature for 12 h. After stirring, *para*-methyl benzyaldehyde (30.0 mg, 0.25 mmol) was added and the stirring was re-started under O_2 atmosphere at room temperature. At regular intervals of time, approximately 10 μL of the crude mixture was removed by microsyringe through a septum fitted with the reactor and placed in an NMR tube. In the NMR tube, the reactant was diluted with $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The yield of the corresponding glycol monoester was plotted against the reaction time (Figure 1).

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