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Direct ester condensation from a 1:1 mixture of carboxylic acids and alcohols catalyzed by hafnium(IV) or zirconium(IV) salts

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Abstract—To promote atom efficiency in synthesis and to avoid the generation of environmental waste, the use of stoichiometric amounts of condensing reagents or excess substrates should be avoided. In esterification, excess amounts of either carboxylic acids or alcohols are normally needed. We found that the direct condensation of equimolar amounts of carboxylic acids and alcohols could be achieved using hafnium(IV) or zirconium(IV) salts. These metal salts are highly effective as catalysts for the selective esterification of primary alcohols with carboxylic acids in the presence of secondary alcohols or aromatic alcohols. The present methods can be applied to direct polyesterification and may be suitable for large-scale operations. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Replacing current chemical processes with more environmentally benign alternatives is an increasingly attractive subject.[1] Esterification is one of the most fundamental and important reactions in organic synthesis.[2] Although several methods have been explored and developed,[2] the use of large amounts of condensing reagents and activators should be avoided to promote green chemistry and atom efficiency. The direct condensation of carboxylic acids with alcohols using small amounts of catalysts is the most ideal method, but in most cases, large excess amounts of either carboxylic acids or alcohols are used in this condensation to give esters in high yield.[3] We describe highly efficient and direct ester condensation using equimolar amounts of carboxylic acids and alcohols catalyzed by Hf(IV)[4] or Zr(IV) salts.[5]

2. Results and discussion

2.1. Catalytic activities of metal salts for direct ester condensation

We first investigated the catalytic activities of various metal salts (10 mol%) which promote the model reaction of 4-phenylbutyric acid (1 equiv.) with benzyl alcohol (1 equiv.) in toluene at reflux with the removal of water (calcium hydride in a Soxhlet thimble) for 1.5 h (condition *A* in Table 1). Both $ZrCl_4$[3m,n] and $HfCl_4$ were highly effective catalysts for the present reaction (entries 5, 6, 12, and 13). While $Zr(Oi\text{-}Pr)_4$[3i] and $Hf(Ot\text{-}Bu)_4$ were also effective catalysts (entries 7 and 16), their metal(IV) hydroxides and oxides were inert (entries 9, 10, and 18). Although Ti(IV)[3h,i] and Sn(IV)[3j–l] salts are well known to be good esterification catalysts, their catalytic activities were lower than those of Hf(IV) and Zr(IV) salts (entries 1–4). Various other metal salts and organometallics such as $3,4,5\text{-}F_3C_6H_2B(OH)_2$,[6] BCl_3,[3d,e] $AlCl_3$,[3f] $SiCl_4$,[3g] $ScCl_3$, $Sc(OTf)_3$,[7] $FeCl_3$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $GaCl_3$, $GeCl_4$, $SbCl_5$, $LaCl_3$, and $PbCl_2$ were either less active or inert.

Next, to identify esterification catalysts with a high turnover frequency (TOF), several metal salts, which were suggested by the above screening, were examined again for the same reaction as above under different conditions (reflux for 12 h in the presence of 1 mol% of catalysts; condition *B* in Table 1). As expected, $ZrCl_4\cdot(THF)_2$, $Zr(Oi\text{-}Pr)_4$, $HfCl_4\cdot(THF)_2$, Cp_2HfCl_2, and $Hf(Ot\text{-}Bu)_4$ gave the corresponding esters quantitatively (entries 6, 7, 13, 14, and 16), while Sn(IV) gave only a low yield (entry 1). Cp_2HfCl_2 was gradually decomposed during the esterification (entry 14). Interestingly, Ti(IV) gave better results than other metal halides and metal alkoxides, except Hf(IV) and Zr(IV) (entries 3 and 4).

Green catalysts require not only high catalytic activity and atom efficiency, but also low toxicity, low cost, and ease of handling. Fortunately, Hf(IV) and Zr(IV) compounds generally have low toxicity (LD_{50} [$HfCl_4$, oral, rat]=2400 mg kg^{-1}; LD_{50} [$ZrCl_4$, oral, rat]=1688 mg kg^{-1}), and are not considered particularly poisonous.[8] Commercially available $HfCl_4\cdot(THF)_2$ and $ZrCl_4\cdot(THF)_2$ are hydrolytically

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Keywords: hafnium(IV); zirconium(IV); direct ester condensation; esterification; chemoselective; catalysts; dehydration.

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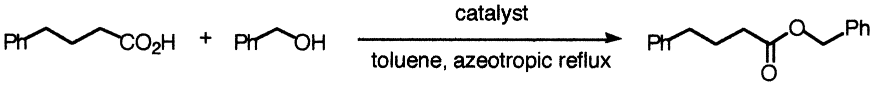
Table 1. Direct esterification of 4-phenylbutyric acid and benzyl alcohol under different conditions



Entry	Catalyst	Yield (%)	
		Condition *A*[a]	Condition *B*[b]
1	$SnCl_4$	34	48
2	$SnBr_4$	12	–
3	$TiCl_4$	28	73
4	$Ti(O\textit{i}\text{-}Pr)_4$	34	82
5	$ZrCl_4$	77	–
6	$ZrCl_4\cdot(THF)_2$	84	99
7	$Zr(O\textit{i}\text{-}Pr)_4$	74	97
8	$ZrOCl_2\cdot 8H_2O$	–	53
9	$Zr(OH)_4$	Trace	–
10	ZrO_2	Trace	–
11	HfF_4	Trace	–
12	$HfCl_4$	83	–
13	$HfCl_4\cdot(THF)_2$	82	>99
14	Cp_2HfCl_2	76	>99
15	Cp^*HfCl_3	51	–
16	$Hf(O\textit{t}\text{-}Bu)_4$	82	>99
17	$HfOCl_2$	35	–
18	HfO_2	Trace	–
19	$Hf(OTf)_4$	Trace[c]	–
20	$Sc(OTf)_3$	Trace[c]	–

The esterification of 4-phenylbutyric acid (1 mmol) and benzyl alcohol (1 mmol) in toluene (5 mL) was carried out in a flask fitted with a pressure-equalized addition funnel (containing a cotton plug and ~1 g of calcium hydride and acting as a Soxhlet extractor) surmounted by a reflux condenser under argon.

[a] For *A*, the reaction mixture was heated under reflux conditions in the presence of 10 mol% of catalyst for 1.5 h.

[b] For *B*, the reaction mixture was heated under reflux conditions in the presence of 1 mol% of catalyst for 12 h.

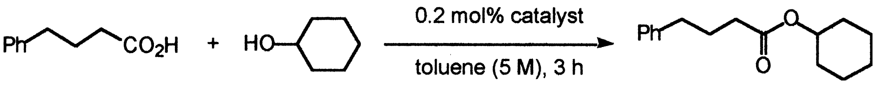
[c] 2- and 4-Benzyltoluenes were obtained quantitatively by dehydrative coupling of benzyl alcohol and toluene.

more stable and less expensive than the corresponding metal(IV) alkoxides. The ability of $HfCl_4$, $ZrCl_4$, and their THF complexes to tolerate water was investigated by comparing their catalytic activities to those upon exposure to air (Table 2). As expected, the coordination of THF to $HfCl_4$ and $ZrCl_4$ effectively showed their hydrolysis. Thus, Hf(IV) was shown to be the most effective metal catalyst for direct esterification.

To optimize the reaction conditions regarding the removal of water and solvents for the esterification of 4-phenylbutyric acid with cyclohexanol in the presence of 0.2 mol% of $HfCl_4\cdot(THF)_2$, the percentage of cyclohexanol condensed with 4-phenylbutyric acid over time was evaluated by ^1H NMR analysis (Fig. 1). We found that heating the reaction mixture in toluene under azeotropic reflux conditions to remove water through a Soxhlet thimble with molecular sieves 4 Å gave the best result. However, heating the reaction mixture without solvents at the same temperature as above was less effective, and the reaction rate was reduced after ~2 h. A similar tendency was observed in control experiments in the absence of any catalysts. These experimental results indicate that not only catalytic activity but also the efficiency of water removal are highly significant for the present esterification system.

To explore the generality and scope of the above Hf(IV)-catalyzed esterification, the reaction was examined with

Table 2. Water tolerability of esterification catalysts



Duration (h) of exposure to air[a]	Conversion (%) to cyclohexyl 4-phenylbutyrate			
	$HfCl_4$	$HfCl_4\cdot(THF)_2$	$ZrCl_4$	$ZrCl_4\cdot(THF)_2$
0	74	71	71	69
40	–	70	65	75
47.5	63	71	49	–
60	31	68	8	–
65	–	67	5	65
96	–	65	5	62
137	–	61	–	48

[a] Catalysts were exposed to air (ca. 50% humidity) at 20°C.

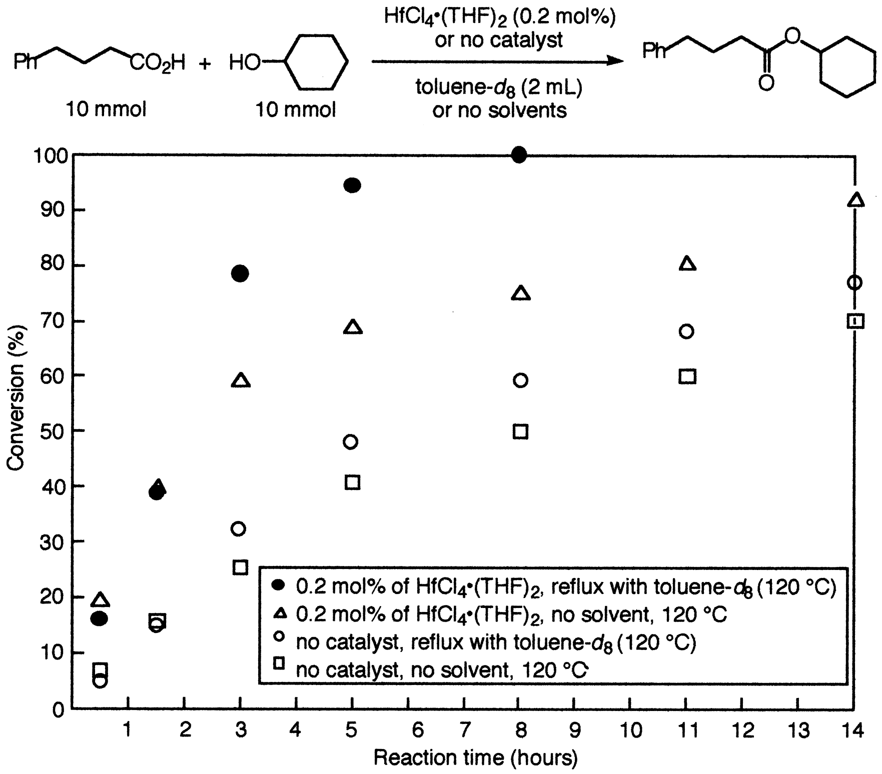
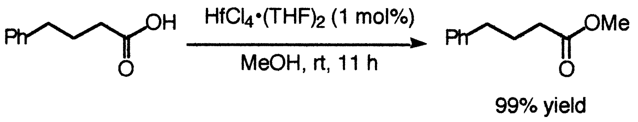


Figure 1. The percentage of cyclohexanol condensed with 4-phenylbutyric acid over time under different conditions was evaluated by ^{1}H NMR, from the integration ratio of the protons of cyclohexanol and the esterification product, cyclohexyl 4-phenylbutyrate.

various structurally diverse carboxylic acids and alcohols (Table 3). Less than 0.2 mol% of $HfCl_4{\cdot}(THF)_2$ was suitable for condensing various carboxylic acids with not only primary alcohols but also sterically hindered secondary alcohols. However, esterification with tertiary alcohols did not proceed (entry 6). Although aromatic substrates such as benzoic acid and phenol were less reactive than aliphatic substrates, their reactions proceeded very well when *o*-xylene or mesitylene was used instead of toluene or the amount of $HfCl_4{\cdot}(THF)_2$ was increased to 1 mol% (entries 7 and 12). $ZrCl_4{\cdot}(THF)_2$ could be used instead of $HfCl_4{\cdot}$ $(THF)_2$ under the same conditions (entries 1 and 2).

Moreover, the $HfCl_4{\cdot}(THF)_2$-catalyzed esterification reaction was examined with various functionalized carboxylic acids and alcohols (Table 4). α,β-Unsaturated alcohols (entries 1 and 2), α,β-unsaturated carboxylic acids (entries 11–17), and acid-sensitive substrates (entries 3–6 and 20) such as a benzylic secondary alcohol, a tetrahydropyranyl (THP) ether, a *tert*-butyldimethylsilyl ether, a nitrile, and tetrahydro-2-furoic acid, could all be used under these conditions. In particular, the resulting α,β-unsaturated esters are industrially important polymer materials. Besides these examples, cyclopropanecarboxylic acid, 4-nitrophenylacetic acid, α-alkoxycarboxylic acids and a perfluorocarboxylic acid could also be used (entries 10, 18, 19, and 21). Notably, direct thioesterifications proceeded quantitatively in the presence of 5 mol% of $HfCl_4{\cdot}(THF)_2$ or $ZrCl_4$ (entries 7–9).[9]

Furthermore, $HfCl_4{\cdot}(THF)_2$ was highly effective for the esterification of carboxylic acids with volatile alcohols such as methanol (Eq. (1)). The reaction proceeded in alcohols at room temperature (rt) without the removal of water.



(1)

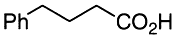
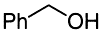
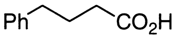
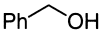
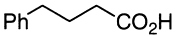
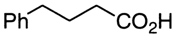
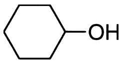
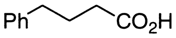
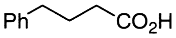
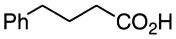
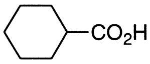
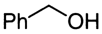
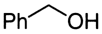
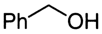
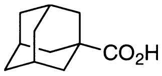
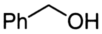
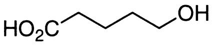
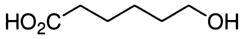
To demonstrate the effectiveness of Hf(IV) salts as esterification catalysts, polyesters were synthesized by polycondensing ω-hydroxy carboxylic acids or equimolar amounts of aliphatic dicarboxylic acids and aliphatic diols in the presence of 0.2 mol% of $HfCl_4{\cdot}(THF)_2$ in *o*-xylene with the removal of water for 1 day.[11] In most cases, polycondensation proceeded quantitatively (Table 5). Although no polycondensation of aromatic dicarboxylic acids and aromatic diols occurred due to the insolubility of aromatic carboxylic acids in *o*-xylene and the lower nucleophilicity of aromatic diols, polycondensation to semiaromatic polyesters proceeded successfully.

2.2. Selective esterification of primary alcohols in the presence of secondary alcohols or aromatic alcohols

Selective esterification of primary alcohols in the presence of secondary alcohols is often required. Several sophisticated and relatively expensive reagents have been developed for this purpose.[12–14] However, the use of large amounts of condensing reagents or activators and the use of highly toxic or hazardous reagents and solvents such as antimony compounds, tin compounds, acyl halides, and dichloromethane should be avoided to promote atom

Table 3. Direct esterification of carboxylic acids with alcohols catalyzed by $HfCl_4\cdot(THF)_2$

$$R^1CO_2H + R^2OH \xrightarrow[\text{toluene, azeotropic reflux}]{HfCl_4\bullet(THF)_2} R^1CO_2R^2$$

Entry	RCO_2H	ROH	$HfCl_4\cdot(THF)_2$ (mol%)[a]	Time (h)	Yield (%)
1[b]			0.1	18	>99
2[b]			$ZrCl_4\cdot(THF)_2$ (0.1)[c]	18	99
3[d]		$EtC(CH_2OH)_3$	0.2	24	>99
4			0.2	5	94 (36)[e]
5		*l*-Menthol	0.2	36	>99
6		Et_3COH	1.0	24	0
7[f]		PhOH	0.2	36	91
8			0.2	7	96
9	Et_2CHCO_2H		0.2	60	98
10	$PhCO_2H$		0.2	15	92
11			0.2	10	92
12[g]	$PhCO_2H$	$3,5\text{-}Me_2C_6H_3OH$	1.0	24	95
13			0.2	10	96[h]
14			0.2	10	94[h]

Unless otherwise noted, the esterification of carboxylic acid (10 mmol) with alcohol (10 mmol) in toluene (2 mL) was carried out in a flask fitted with a pressure-equalized addition funnel (containing a cotton plug and ca. 1.5 g of molecular sieves 4 Å (pellets) and acting as a Soxhlet extractor) surmounted by a reflux condenser under argon.

[a] Values on the basis of hydroxy groups in alcohols are indicated.

[b] Toluene (5 mL) was used.

[c] $ZrCl_4\cdot(THF)_2$ was used instead of $HfCl_4\cdot(THF)_2$.

[d] 4-Phenylbutyric acid (36 mmol) and toluene (4 mL) were used.

[e] Data for the uncatalyzed reaction are indicated.

[f] *o*-Xylene (2 mL) was used.

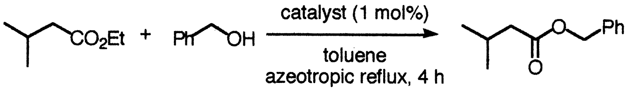
[g] 1,3,5-Mesitylene (2 mL) was used.

[h] Yield of lactones is indicated.

efficiency and reduce the generation of environmental waste. To the best of our knowledge, there are no reported catalytic methods for the selective ester condensation of primary alcohols with carboxylic acids. We describe an extremely simple and environmentally benign procedure for the selective esterification of primary alcohols in the presence of secondary alcohols catalyzed by $HfCl_4\cdot(THF)_2$ or $ZrCl_4\cdot(THF)_2$.[5b]

The substantial difference in reaction rates between primary and secondary alcohols in Hf(IV)-catalyzed esterification prompted us to examine the selective esterification of a primary alcohol in the presence of a secondary alcohol. First, we chose to investigate the selectivity in the esterification of a 1:1 mixture of 1-octanol and cyclohexanol with several carboxylic acids in the presence of 2 mol% of $HfCl_4\cdot(THF)_2$. Some of our results, summarized in Table 6, strongly suggest that the steric hindrance of carboxylic acid plays a crucial role in the chemoselectivity of the reaction. The use of 1-adamantanecarboxylic acid gave the 1-octyl ester in >99% selectivity and quantitative yield (entry 5). A similar chemoselectivity and reactivity were observed using $ZrCl_4\cdot(THF)_2$ (entry 6). Interestingly, $TiCl_4$ was inferior to $HfCl_4$ and $ZrCl_4$ with respect to not only catalytic activity but also chemoselectivity (entry 1 versus entries 2 and 3). The low chemoselectivity observed in the reaction catalyzed by $TiCl_4$ may be ascribed to transesterification.

Actually, Ti(IV) salts are known to be good catalysts for the transesterification of esters with alcohols.[10] Surprisingly, $HfCl_4\cdot(THF)_2$ and $ZrCl_4\cdot(THF)_2$ did not catalyze the transesterification at all (Eq. (2)). These experimental results can be understood by assuming that the active intermediates that are generated in esterification are Hf(IV) carboxylates, Zr(IV) carboxylates, and Ti(IV) alkoxides, respectively. However, their roles are still not clear.



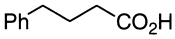
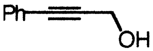
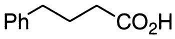
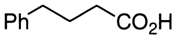
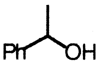
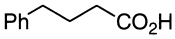
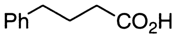
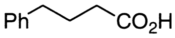
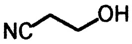
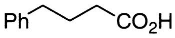
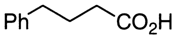
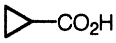
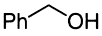
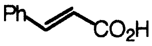
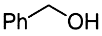
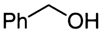
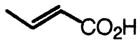
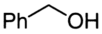
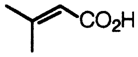
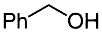
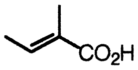
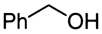
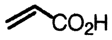
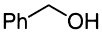
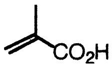
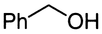
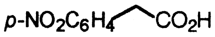
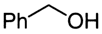
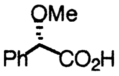
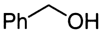
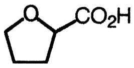
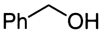
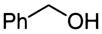
$TiCl_4$: 98% yield
$HfCl_4\bullet(THF)_2$: 0% yield
$ZrCl_4\bullet(THF)_2$: <2% yield

(2)

To explore the generality and scope of the above selective esterification catalyzed by $HfCl_4\cdot(THF)_2$, the esterification was examined with various structurally diverse primary and secondary alcohols. Several features of the results

Table 4. Direct esterification of carboxylic acids with alcohols catalyzed by $HfCl_4{\cdot}(THF)_2$

$$R^1CO_2H \quad + \quad R^2OH \xrightarrow[\text{toluene, azeotropic reflux}]{HfCl_4\bullet(THF)_2} R^1CO_2R^2$$

Entry	RCO_2H	ROH	$HfCl_4{\cdot}(THF)_2$ (mol%)[a]	Time (h)	Yield (%)
1			0.2	6	97
2			0.2	24	92
3			0.2	13	>99
4		$THOP(CH_2)_8OH$	0.2	18	95
5		t-$BuMe_2SiO(CH_2)_8OH$	0.2	24	93
6			0.2	24	94
7[b]			5	24	97(<2)[c]
8[b]		n-$C_{10}H_{21}SH$	5	17	>99
9	n-$C_{11}H_{23}CO_2H$	n-$C_{12}H_{25}SH$	5	24	>99(93)[d]
10			0.2	17	95
11			0.2	10	92
12[e]			1.0	38	>99
13[e]			1.0	38	94
14[e]			1.0	38	>99
15[e]			1.0	45	>99
16[e]			1.0	40	>99
17[e]			1.0	40	99
18			1.0	18	98
19[f]			0.2	13	98
20			0.2	6	>99
21	$C_7F_{15}CO_2H$		0.2	11	82

Unless otherwise noted, the esterification of carboxylic acid (10 mmol) with alcohol (10 mmol) in toluene (2 mL) was carried out in a flask fitted with a pressure-equalized addition funnel (containing a cotton plug and ca. 1.5 g of molecular sieves 4 Å (pellets) and acting as a Soxhlet extractor) surmounted by a reflux condenser under argon.

[a] Values on the basis of hydroxy groups in alcohols are indicated.

[b] 1.2 equiv. of thiol was used.

[c] Data for the uncatalyzed reaction are indicated.

[d] $ZrCl_4$ was used instead of $HfCl_4{\cdot}(THF)_2$.

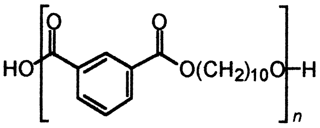
[e] Benzene was used instead of toluene.

[f] Enantiomerically pure carboxylic acid was used. The enantiomeric purity of the ester was 84%.

shown in Table 7 deserve comment: (1) the use of 1-adamantanecarboxylic acid generally gave primary alkyl esters in high selectivity and in high yield (entries 4 and 6), and (2) primary alcohols were esterified in high selectivity with even less bulky 4-phenylbutyric acid in the presence of aromatic alcohols (entries 7 and 8). It has been reported that aromatic alcohols are predominantly acylated in the presence of aliphatic alcohols under basic or nucleophilic conditions.[7] On the other hand, we recently found that aliphatic alcohols were chemoselectively acylated with carboxylic anhydrides in the presence of catalytic amounts of $Sc(OTf)_3$.[7] The present method is a green alternative to the latter reaction.

As a logical extension of this methodology, we further investigated the potential of $HfCl_4{\cdot}(THF)_2$ as a catalyst for the selective esterification of a less-hindered hydroxy group in a series of structurally diverse primary–secondary diols. The results are shown in Table 8. The distance between the two hydroxy groups in the diols strongly affected the reactivity: the reactivity and chemoselectivity for the esterification increased in the order 1,2-, 1,3-, and 1,4-

Table 5. Direct polyesterification catalyzed by $HfCl_4 \cdot (THF)_2$

Polyester	Yield[a] (%)	DP[b]	M_n[b,c] (/10^4)	M_w[c] (/10^4)
$HO[CO(CH_2)_9O]_nH$	95	>200	1.82[>3.40]	3.40
$HO[CO(CH_2)_{11}O]_nH$	97 (88)[d]	>200 (45)[d]	2.77[>3.96] −[(0.89)[d]]	7.24
$HO[CO(CH_2)_2CO_2(CH_2)_6O]_nH$	98	>200	2.24[>4.00]	3.87
$HO[CO(CH_2)_7CO_2(CH_2)_{10}O]_nH$	97	>200	2.69[>6.52]	5.83
	96[e]	>200[e]	−[>6.09][e]	–

Unless otherwise noted, polyesterification was carried out in the presence of 0.2 mol% of $HfCl_4 \cdot (THF)_2$ for 1 day.

[a] Isolated yield.

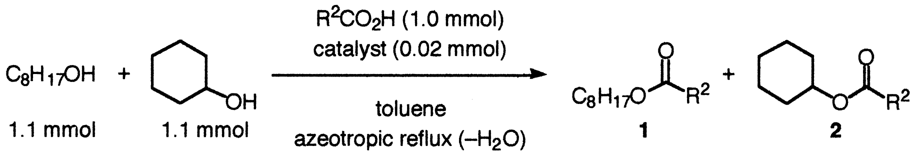
[b] Average degrees of polymerization (DP) and M_n values in brackets were determined by ^{1}H NMR.

[c] Two linear TSK-gel-GMHXL GPC columns were used. The polymers were run at 0.2 wt% in THF at 40°C with a polystyrene standard.

[d] Data in parentheses are for the non-catalyzed thermal polyesterification.

[e] The reaction was carried out in the presence of 1 mol% of $HfCl_4 \cdot (THF)_2$ for 4 days.

Table 6. Selective esterification of octanol in the presence of cyclohexanol



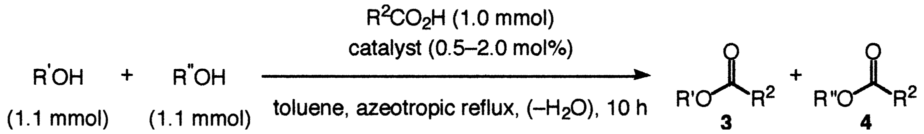
Entry	Catalyst (mmol)	R^2	Time (h)	Yield (%)[a] (**1**+**2**)	Ratio[b] (**1**/**2**)
1	$TiCl_4$ (0.02)	$Ph(CH_2)_3$	10	>99	66:34
2	$ZrCl_4 \cdot (THF)_2$ (0.02)	$Ph(CH_2)_3$	5.5	98	88:12
3	$HfCl_4 \cdot (THF)_2$ (0.01)	$Ph(CH_2)_3$	5.5	99	89:11
4	$HfCl_4 \cdot (THF)_2$ (0.02)	c-C_6H_{11}	10	96	93:7
5	$HfCl_4 \cdot (THF)_2$ (0.02)	1-Adamantyl	11	>99	>99:1
6	$ZrCl_4 \cdot (THF)_2$ (0.02)	1-Adamantyl	11	97	99:1

See Section 4.3.

[a] Esters were purified as a mixture of **1** and **2** by flash column chromatography on silica gel.

[b] Determined by ^{1}H NMR.

Table 7. Selective esterification of primary alcohols in the presence of secondary alcohols or phenols



Entry	R′	R″	R^2	Catalyst (mol%)	Yield (%)[a] (**3**+**4**)	Ratio[b] (**3**/**4**)
1	Bn	PhMeCH	$Ph(CH_2)_3$	$Zr(O\textit{i}\text{-}Pr)_4$ (2)	98	89:11
2	Bn	PhMeCH	$Ph(CH_2)_3$	$HfCl_4 \cdot (THF)_2$ (0.5)	91	94:6
3	Bn	PhMeCH	c-C_6H_{11}	$HfCl_4 \cdot (THF)_2$ (2)	97	96:4
4	Bn	PhMeCH	1-Adamantyl	$HfCl_4 \cdot (THF)_2$ (2)	98	98:2
5	n-C_8H_{17}	2-C_8H_{17}	$Ph(CH_2)_3$	$HfCl_4 \cdot (THF)_2$ (0.5)	>99	96:4
6	n-C_8H_{17}	2-C_8H_{17}	1-Adamantyl	$HfCl_4 \cdot (THF)_2$ (2)	96	>99:1
7	n-C_8H_{17}	p-MeC_6H_4	$Ph(CH_2)_3$	$HfCl_4 \cdot (THF)_2$ (2)	94	99:1
8	c-C_6H_{11}	p-MeC_6H_4	$Ph(CH_2)_3$	$HfCl_4 \cdot (THF)_2$ (2)	84	86:14

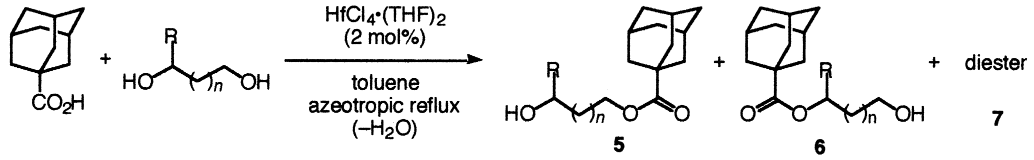
See Section 4.3.

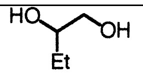
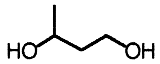
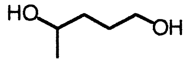
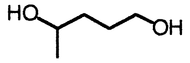
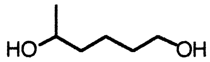
[a] Esters were purified as a mixture of **3** and **4** by flash column chromatography on silica gel.

[b] Determined by ^{1}H NMR.

diol. No esterification product was obtained by heating a 1:1 mixture of 1,2-butanediol and 1-adamantanecarboxylic acid in toluene in the presence of 2 mol% of $HfCl_4 \cdot (THF)_2$. In the reaction of 1,3-butanediol, a 72:28 mixture of primary and secondary monoesters was obtained in 37% yield. In the reaction of 1,4-pentanediol, a 95:4 mixture of primary and secondary monoesters was obtained in 79% yield. The reaction of 1,5-hexanediol gave the primary ester with >99% selectivity and in 94% yield. Production of the corresponding diesters increased in the order 1,5-, 1,4-, and 1,3-diol. These experimental results suggest that an internal acyl transfer between primary and secondary hydroxy

Table 8. Selective esterification of the primary hydroxy group of primary–secondary diols



Entry	Diol	Time (h)	Yield (%)[a] (**5**+**6**)	Ratio[b] (**5**/**6**)	Yield (%) (**7**)
1		11	0	–	0
2		16	37	72:28	<10
3		16	79	95:4	<7
4		16[c]	49[c]	72:28[c]	<23[c]
5		13	94	>99:1	<4

See Section 4.3.

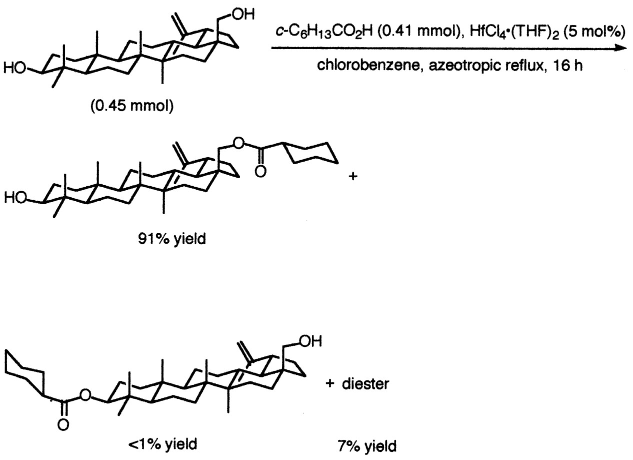
[a] Esters were purified as a mixture of **5** and **6** by flash column chromatography on silica gel.

[b] Determined by ^{1}H NMR.

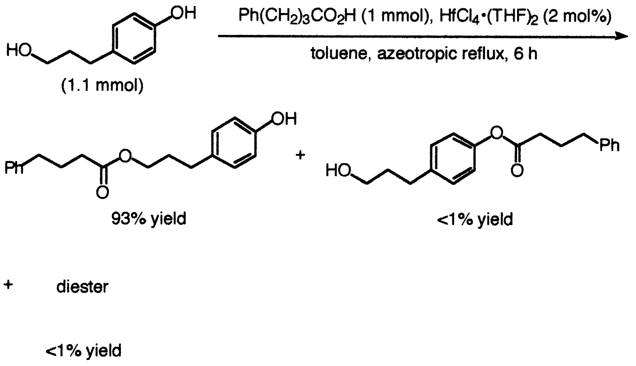
[c] 4-Phenylbutyric acid was used instead of 1-adamantanecarboxylic acid.

groups occurs in the reaction of diols.[15,16] Interestingly, the chemoselectivity in the reaction of 1,4-pentanediol with 4-phenylbutyric acid was much lower than that with 1-adamantanecarboxylic acid, and the diesters were relatively increased. This means that the steric bulkiness of the adamantyl group suppressed internal acyl transfer. In addition, the lower reactivity of diols may be due to tight chelation between diols and Hf(IV).

Furthermore, $HfCl_4·(THF)_2$ was examined for the chemoselective esterification of structurally rigid diols which were unable to chelate with Hf(IV) in a bidentate manner. In the reaction of betulin with cyclohexanecarboxylic acid, the primary monoester was obtained in 91% yield (Eq. (3)). In the reaction of 3-(4-hydroxyphenyl)-1-propanol with 4-phenylbutylic acid, the primary monoester was obtained in 93% yield (Eq. (4)).



(3)



(4)

3. Conclusion

In direct esterification, the catalytic use of inorganic salts is quite practical in view of its simplicity and applicability to large-scale operations. Hf(IV) and Zr(IV) salts are extremely active catalysts for direct esterification and polycondensation to polyesters. Due to the ease of handling, $HfCl_4·(THF)_2$ and $ZrCl_4·(THF)_2$, which are hydrolytically more stable, are recommended as dehydration catalysts. The present method offers considerable advantages in terms of simplicity, high chemoselectivity, high atom efficiency, and low environmental impact.

4. Experimental

4.1. General

Infrared (IR) spectra were recorded on a Shimadzu FT-IR

8100 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-300 spectrometer. Tetramethylsilane was used as an internal standard for ^{1}HNMR (δ 0.00 ppm). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF^{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck 9385. Toluene, xylene, and mesitylene were freshly distilled from calcium hydride. All materials, reagents and catalysts were obtained commercially. Number average molecular weights (M_n) were determined by gel phase chromatography (GPC) on a Waters GPC-224 system equipped with a refractive index detector and two linear TSK-gel-GMHXL GPC columns. The mobile phase, tetrahydrofuran, was used at a flow rate of 1.0 mL/min. Calibration was performed with polystyrene standards. Values of M_n were also determined from the relative area intensities of signals from the polymer end groups to those of the repeat units. The following obtained esters are known compounds: benzyl 4-phenylbutyrate[17] (Tables 1, 3, and 7), cyclohexyl 4-phenylbutyrate[18] (Tables 2 and 7), *l*-menthyl 4-phenylbutyrate[19] (Table 3), phenyl 4-phenylbutyrate[20] (Table 3), benzyl cyclohexanecarboxylate[21] (Tables 3 and 7), benzyl adamantanecarboxylate[22] (Tables 3 and 7), 3,5-dimethylphenyl benzoate[23] (Table 3), cinnamyl 4-phenylbutyrate[24] (Table 4), benzyl cyclopropanecarboxylate[25] (Table 4), benzyl (*E*,*E*)-2,4-hexadienoate[26] (Table 4), benzyl crotonate[27] (Table 4), benzyl 3,3-dimethylacrylate[28] (Table 4), benzyl *p*-nitrophenylacetate[29] (Table 4), benzyl 2-methoxyphenylacetate[30] (Table 4), benzyl tetrahydrofuroate[31] (Table 4), benzyl perfluorooctanoate[32] (Table 4), poly(10-hydroxydecanoic acid)[33] (Table 5), poly(12-hydroxydodecanoic acid)[34] (Table 5), poly(hexamethylene succinate)[35] (Table 5), poly(decamethylene azelate)[36] (Table 5), poly(decamethylene isophthalate)[37] (Table 5), octyl 4-phenylbutyrate[38] (Tables 6 and 7), octyl cyclohexanecarboxylate[39] (Table 6), and octyl adamantanecarboxylate[40] (Table 7). The following obtained esters are commercially available: benzyl benzoate (Table 3), δ-valerolactone (Table 3), ε-caprolactone (Table 3), benzyl cinnamoate (Table 4), benzyl acrylate (Table 4), benzyl methacrylate (Table 4), benzyl tiglate (Table 4), methyl 4-phenylbutyrate (Eq. (1)), and benzyl isovalerate (Eq. (2)).

4.2. General procedure for polycondensation reactions (Table 5)

A flame-dried, 5 mL, single-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a 5 mL pressure-equalized addition funnel (containing a cotton plug and molecular sieves 4 Å (ca. 1.5 g)) surmounted by a reflux condenser was charged with α,ω-hydroxycarboxylic acid (10 mmol) or α,ω-dicarboxylic acid (10.0 mmol) and α,ω-diol (10.0 mmol) as substrates and $HfCl_4{\cdot}(THF)_2$ (0.200 mmol) as a catalyst in *o*-xylene (2 mL). The mixture was brought to reflux with the removal of water. After 1 day, the resulting mixture was cooled to ambient temperature, dissolved with chloroform, and precipitated with acetone or methanol to furnish pure polyester as a white solid in quantitative yield.

4.3. General procedure for the selective esterification of primary alcohols in the presence of secondary alcohols or aromatic alcohols (Tables 6 and 7)

A flame-dried, 5 mL, single-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a 5 mL pressure-equalized addition funnel (containing a cotton plug and calcium hydride (ca. 1 g)) surmounted by a reflux condenser was charged with a primary alcohol (2.2 mmol), a secondary alcohol (2.2 mmol), and a carboxylic acid (2.0 mmol) as substrates and $HfCl_4{\cdot}(THF)_2$ (0.04 mmol) as a catalyst in toluene (4 mL). The mixture was brought to reflux with the removal of water. After 6–12 h, the resulting mixture was cooled to ambient temperature and water (ca. 100 μL) was added. After being stirred for 10 min, the resultant mixture was dried over magnesium sulfate, filtered, and concentrated under vacuum. The crude products were purified by flash column chromatography on silica gel eluted with hexane–ethyl acetate to provide the corresponding primary alkyl ester in quantitative yield.

4.3.1. 1,1,1-Tri(4-phenylbutyroxymethyl)propane (Table 3). IR (film) 3027, 1730, 1497, 1458, 1140, 747, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=7.8 Hz, 3H), 1.46 (q, J=7.8 Hz, 2H), 1.93 (quintet, J=7.8 Hz, 6H), 2.32 (t, J=7.8 Hz, 6H), 2.63 (t, J=7.8 Hz, 6H), 4.01 (s, 6H), 7.17–7.28 (m, 15H). Anal. Calcd for $C_{36}H_{44}O_6$: C, 75.50; H, 7.74. Found: C, 75.56; H, 7.43.

4.3.2. Benzyl 2-ethylbutyrate (Table 3). IR (film) 2965, 1734, 1458, 1173, 1144, 749, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=7.2 Hz, 6H), 1.46–1.73 (m, 4H), 2.22–2.32 (m, 1H), 5.13 (s, 2H), 7.25–7.37 (m, 5H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.64; H, 8.73.

4.3.3. Phenylpropargyl 4-phenylbutyrate (Table 4). IR (film) 1744, 1491, 1138, 756, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94–2.06 (m, 2H), 2.41 (t, J=7.2 Hz, 2H), 2.68 (t, J=7.2 Hz, 2H), 2.90 (s, 2H), 7.19–7.50 (m, 10H). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.96; H, 6.59.

4.3.4. 1-(Phenyl)ethyl 4-phenylbutyrate (Table 4). IR (film) 1730, 1497, 1455, 1375, 1065, 1080, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, J=6.6 Hz, 3H), 1.95 (quintet, J=7.5 Hz, 2H), 2.35 (dd, J=6.9, 8.1 Hz, 2H), 2.62 (t, J=8.1 Hz, 2H), 5.90 (q, J=6.6 Hz, 1H), 7.13–7.36 (m, 10H). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 11.92. Found: C, 80.59; H, 11.90.

4.3.5. 8-(Tetrahydropyranyl-2-oxy)octyl 4-phenylbutyrate (Table 4). IR (film) 2936, 2857, 1736, 1455, 1140, 1032, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26–1.38 (br, 8H), 1.46–1.89 (m, 10H), 1.96 (quintet, J=7.2 Hz, 2H), 2.32 (t, J=7.2 Hz, 2H), 2.65 (t, J=7.2 Hz, 2H), 3.38 (dt, J=9.6, 6.6 Hz, 1H), 3.46–3.54 (m, 1H), 3.73 (dt, J=9.6, 6.6 Hz, 1H), 3.82–3.92 (m, 1H), 4.05 (t, J=6.6 Hz, 2H), 4.55–4.59 (m, 1H), 7.16–7.22 (m, 3H), 7.27–7.32 (m, 2H). Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.37; H, 9.64. Found: C, 74.61; H, 9.55.

4.3.6. 8-*tert*-Butyldimethylsiloxyoctyl 4-phenylbutyrate (Table 4). IR (film) 2930, 2857, 1736, 1500, 1254, 1100, 835 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.00 (s, 6H), 0.85 (s, 9H), 1.15–1.35 (br, 8H), 1.40–1.62 (m, 4H), 1.91 (quintet, J=7.2 Hz, 2H), 2.28 (t, J=7.2 Hz, 2H), 2.61 (t, J=7.5 Hz, 2H), 3.55 (t, J=6.6 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 7.11–7.18 (m, 3H), 7.22–7.27 (m, 2H). Anal. Calcd for $C_{24}H_{42}O_3Si$: C, 70.88; H, 10.41. Found: C, 70.92; H, 10.38.

4.3.7. 2-Cyanoethyl 4-phenylbutyrate (Table 4). IR (film) 1740, 1497, 1455, 1240, 1144, 1042, 749, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.98 (quintet, J=8.7 Hz, 2H), 2.39 (t, J=7.5 Hz, 2H), 2.64–2.71 (m, 4H), 4.26 (t, J=6.3 Hz, 2H), 7.17–7.33 (m, 5H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96. Found: C, 71.92; H, 6.95.

4.3.8. *S*-Benzyl 4-phenylbutanethioate (Table 4). IR (film) 1686, 1497, 1456, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.00 (quintet, J=7.2 Hz, 2H), 2.58 (t, J=7.2 Hz, 2H), 2.65 (t, J=7.2 Hz, 2H), 4.12 (s, 2H), 7.14–7.34 (m, 10H). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.52; H, 6.71. Found: C, 75.58; H, 6.69.

4.3.9. *S*-Decyl 4-phenylbutanethioate (Table 4). IR (film) 2926, 1680, 1497, 994, 745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J=6.0 Hz, 3H), 1.20–1.40 (br, 14H), 1.50–1.65 (m, 2H), 1.99 (quintet, J=7.2 Hz, 2H), 2.57 (t, J=7.2 Hz, 2H), 2.65 (t, J=6.6 Hz, 2H), 2.87 (t, J=6.6 Hz, 2H), 7.15–7.25 (m, 3H), 7.25–7.33 (m, 2H). Anal. Calcd for $C_{20}H_{32}OS$: C, 74.94; H, 10.06. Found: C, 74.93; H, 10.02.

4.3.10. *S*-Dodecyl dodecanoate (Table 4). IR (KBr) 2919, 2849, 1696, 1471, 1464, 963 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, J=6.3 Hz, 6H), 1.25 (br, 34H), 1.50–1.70 (m, 4H), 2.53 (t, J=7.5 Hz, 2H), 2.86 (t, J=7.2 Hz, 2H). Anal. Calcd for $C_{24}H_{48}OS$: C, 74.93; H, 12.58. Found: C, 74.89; H, 12.60.

4.3.11. A 72:28 mixture of 1-adamantanecarboxy-3-hydroxybutane and 3-adamantanecarboxy-1-hydroxybutane (Table 8). IR (film) 3700–3100 (br), 1720, 1455, 1271, 1238, 1078, 783 cm^{-1}; ^{1}H NMR (CDCl$_3$) for 1-adamantanecarboxy-3-hydroxybutane δ 1.20–2.20 (m, 21H), 3.48–3.59 (m, 1H), 3.60–3.67 (m, 1H), 5.10 (ddt, J=3.3, 16.2, 6.3 Hz, 1H); ^{1}H NMR (CDCl$_3$) for 3-adamantanecarboxy-1-hydroxybutane δ 1.20–2.20 (m, 21H), 3.78–3.92 (m, 1H), 4.05–4.12 (m, 1H), 4.33–4.41 (m, 1H). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.44; H, 9.56.

4.3.12. A 95:4 mixture of 1-adamanetanecarboxy-4-hydroxypentane and 4-adamanetanecarboxy-1-hydroxypentane (Table 8). IR (film) 3700–3100 (br), 2907, 1728, 1705, 1456, 1237, 1078 cm^{-1}; ^{1}H NMR (CDCl$_3$) for 1-adamanetanecarboxy-4-hydroxypentane δ 1.20–2.20 (m, 23H), 3.84–2.59 (m, 1H), 3.60–3.67 (m, 1H), 5.10 (ddt, J=3.3, 16.2, 6.3 Hz, 1H); ^{1}H NMR (CDCl$_3$) for 4-adamanetanecarboxy-1-hydroxypentane δ 1.20–2.20 (m, 23H), 3.66 (t, J=6.3 Hz, 2H), 4.88–4.95 (m, 1H). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.48; H, 9.89.

4.3.13. 1-Adamantanecarboxy-5-hydroxyhexane (Table 8). IR (film) 3700–3100 (br), 2907, 1728, 1456, 1238, 1080 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20 (d, J=6.0 Hz, 3H), 1.30–2.20 (m, 22H), 3.73–3.86 (m, 1H), 4.06 (t, J=6.6 Hz, 2H). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.79; H, 10.11.

4.3.14. Betulin cyclohexanecarboxylate (esterification to a primary hydroxy group) (Eq. (3)). IR (CHCl$_3$) 3700–3250 (br), 2941, 1717 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.65–2.00 (m, 53H), 2.24–2.38 (m, 1H), 2.38–2.50 (m, 1H), 3.16–3.20 (m, 1H), 3.83 (d, J=10.8 Hz, 1H), 4.26 (d, J=10.8 Hz, 1H), 4.59 (s, 1H), 4.69 (s, 1H). Anal. Calcd for $C_{37}H_{60}O_3$: C, 80.38; H, 10.94. Found: C, 80.41; H, 10.89.

4.3.15. 3-(*p*-Hydroxyphenyl)propyl 4-phenylbutyrate (Eq. (4)). IR (film) 3600–3100 (br), 1734, 1516 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.86–2.01 (m, 4H), 2.34 (t, J=7.2 Hz, 2H), 2.58–2.68 (m, 4H), 4.08 (t, J=6.6 Hz, 2H), 5.09 (br, 1H), 6.74–6.78 (m, 2H), 7.01–7.06 (m, 2H), 7.17–7.22 (m, 3H), 7.26–7.32 (m, 2H). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.51; H, 7.40.

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