A New and Efficient Esterification Reaction via Mixed Anhydrides by the Promotion of a Catalytic Amount of Lewis Acid

Mitsutomo MIYASHITA, Isamu SHIINA,* So MIYOSHI, and Teruaki MUKAIYAMA*
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
(Received December 21, 1992)

In the presence of a catalytic amount of Lewis acid, various carboxylic esters or *S*-phenyl carbothioates are prepared in excellent yields by the respective reactions of equimolar amounts of silyl carboxylates and alkyl silyl ethers or phenyl silyl sulfides with 4-trifluoromethylbenzoic anhydride.

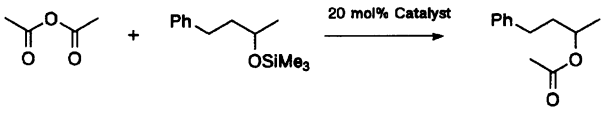
While numerous esterification reactions between carboxylic acids and alcohols using protic acids or bases have been reported, a few methods were known for the effective preparation of esters from equimolar amounts of carboxylic acids and alcohols under mild conditions.[1] For example, 1-alkyl-2-halopyridinium salts which were developed in our laboratory have been demonstrated as useful reagents for the preparation of carboxylic esters in the coexistence of tertiary amines.[2] Furthermore, a convenient method for the chemoselective preparation of esters and lactones via mixed anhydrides in the presence of triethylamine and 4-dimethylaminopyridine was developed by using 2,4,6-trichlorobenzoyl chloride as a bulky acid moiety of the intermediary mixed anhydride.[3]

In this paper, we would like to describe fully the results of our investigations on the effective method for the preparation of carboxylic esters from equimolar amounts of silyl carboxylates and alkyl silyl ethers by using an active Lewis acid catalyst preliminarily reported in the previous communication,[4] and also further developments of the above reactions applied to preparations of *S*-phenyl carbothioates and phenyl carboxylates.

Results and Discussion

Reaction of Anhydrides with Alkyl Silyl Ethers. Recently, $FeCl_3$-catalyzed acylation reactions of alkyl silyl ethers with large excess of acetic anhydride,[1f] and $CoCl_2$-catalyzed acylation reactions of alcohols with 2 mol of acetic anhydride were reported.[1k] On the other hand, in the course of our studies on the exploration of new catalytic synthetic reactions using active Lewis acids,[5] it was postulated that the acid catalyzed alcoholysis of an anhydride with an alkyl silyl ether would proceed to form the corresponding ester. Actually, the reaction between 1-methyl-3-phenylpropyl trimethylsilyl ether and acetic anhydride smoothly proceeded in the presence of an active Lewis acid generated in situ from $TiCl_4$ and $AgClO_4$ to give the corresponding ester in 90% yield (Table 1, Entry 3). In Table 2, the results of above mentioned reaction by using several anhydrides are shown. It is noteworthy that a pivaloyl ester, derived from a bulky carboxylic acid, was also obtained in high yield by the present reaction.

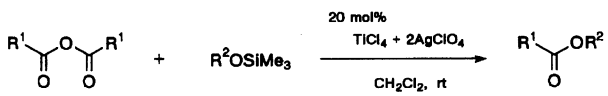
Table 1. Esterification with Carboxylic Anhydride



1

Entry	Catalyst	Temp/°C	Solvent	Yield/%
1	$TiCl_4$	r.t.	CH_2Cl_2	37
2	$AgClO_4$	r.t.	CH_2Cl_2	8
3	$TiCl_4$+$AgClO_4$	r.t.	CH_2Cl_2	90
4	$TiCl_4$+$AgClO_4$	0	CH_2Cl_2	74
5	$TiCl_4$+$AgClO_4$	−23	CH_2Cl_2	17
6	$TiCl_4$+$AgClO_4$	r.t.	Toluene	84
7	$TiCl_4$+$AgClO_4$	r.t.	CH_3CN	82
8	$TiCl_4$+$AgClO_4$	r.t.	THF	43

Table 2. Synthesis of Carboxylic Ester

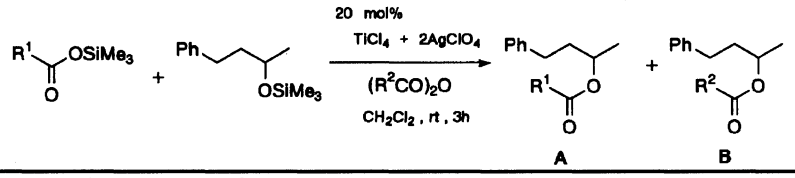


Entry	R^1	R^2	R^1COOR^2	Yield/%
1	Me	$Ph(CH_2)_2CHCH_3$	**1**	86
2	^{t}Bu	$Ph(CH_2)_2CHCH_3$	**2**	82
3	Ph	$Ph(CH_2)_2CHCH_3$	**3**	85
4	Me	Ph	**4**	62

Esterification Reaction via Mixed Anhydrides. Based on the above results that the desired esters are formed from equimolar amounts of alkyl silyl ethers and carboxylic anhydrides, we planned to develop an efficient preparative method of esters from equimolar amounts of both carboxylic acids and alcohols. It was indicated that the following successive reactions would lead to the formation of carboxylic esters starting from silyl carboxylates and alkyl silyl ethers via the active intermediary mixed anhydrides; that is, (1) the initial formation of the mixed anhydride, and (2) the alcoholysis of the initially formed anhydride with alkyl silyl ether (Chart 1).

The effect of the kind of anhydride on the yields of the two possible ester, **A** and **B** is listed in Table 3. When bulky acid moiety such as pivaloyl anhydride was employed in this reaction, the results were not satisfactory

Table 3. Effect of Anhydride



Entry	R^1	R^2	Ester **A**	Yield/%	Ester **B**	Yield/%
1	Me	Ph	**1**	90	**3**	1
2	Me	(*E*)-CH_3CH=CH–	**1**	67	**5**	16
3	Me	^{t}Bu	**1**	30	**2**	47
4	Me	CF_3	**1**	39	**6**	23
5	^{i}Pr	Ph	**7**	83	**3**	1.5
6	^{t}Bu	Ph	**2**	89	**3**	4

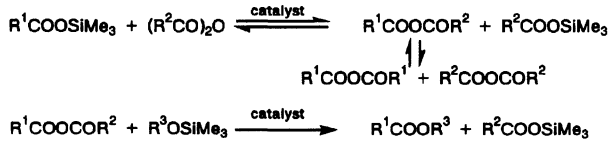


Chart 1.

(Entry 3), but the use of benzoic anhydride gave good result with high chemoselectivity (Entry 1). In Entries 5 and 6, trimethylsilyl 2-methylpropionate and trimethylsilyl 2,2-dimethylpropionate were used as carboxylic components in this mixed anhydride method by using benzoic anhydride, and the corresponding esters were obtained in high yields.

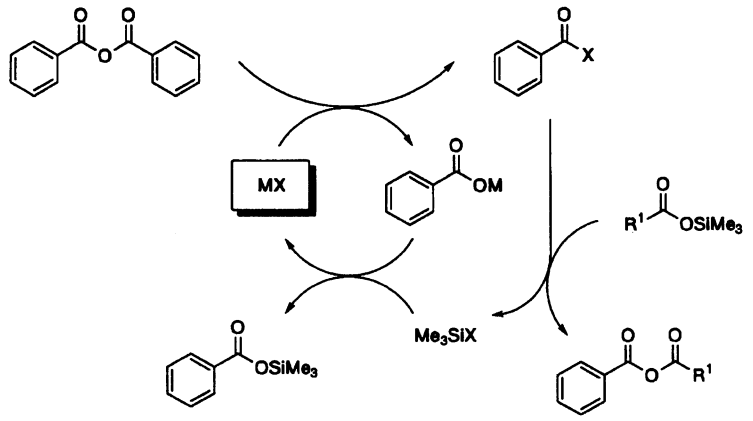
In this reaction, the mixed anhydride formed in situ from silyl carboxylate and benzoic anhydride is assumed to be an important intermediate. Actually, when trimethylsilyl acetate was treated with benzoic anhydride in the presence of a catalytic amount of active Lewis acid generated in situ from $TiCl_4$ and $AgClO_4$, a facile formation of the mixed anhydride along with two homo anhydrides was suggested by ^{1}H NMR experiment. Of the above three anhydrides, the following experiments would support the hypothesis that the mixed anhydride is a key intermediate of the present reaction; that is, 1-methyl-3-phenylpropyl trimethylsilyl ether smoothly reacted with trimethylsilyl acetate and benzoic anhydride in the presence of the above active acidic species in dichloromethane at −23 °C for 3 h to form the corresponding ester in 58% yield, while the 1-methyl-3-phenylpropyl trimethylsilyl ether reacted with acetic anhydride under the same condition to give the desired ester in 17% yield (See Table 1, Entry 5). A small peak of acetylium ion derived from trimethylsilyl acetate (δ=2.65) also observed in the above ^{1}H NMR experiment supports the following catalytic cycles of this reaction (Scheme 1). The mixed anhydride is generated in the first cycle and the desired ester is successively afforded in the second cycle.

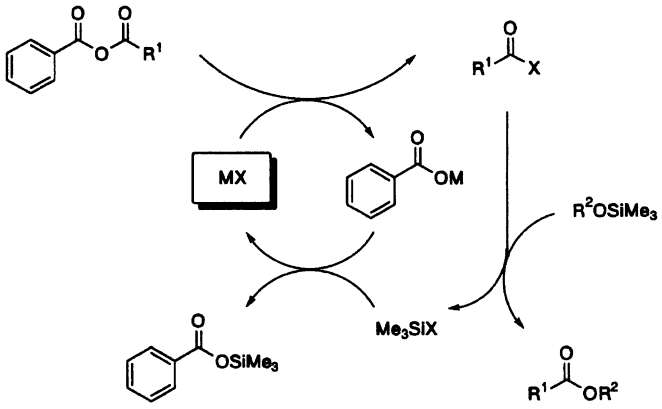
Then our effort was focused on achieving chemoselectivity of the second step. In order to find a suitable acid moiety in the mixed anhydride, the effect of substitutes in aromatic ring of benzoic anhydrides was examined (See Table 4). It was found that the anhydride having an electron withdrawing group such as trifluoromethyl group at para-position gave good selectivity (Entry 6). Furthermore, several Lewis acids were examined by taking the reaction of trimethylsilyl 3-methylbutyrate and 1-methyl-3-phenylpropyl trimethylsilyl ether as a model (see Table 5). It was shown there that the active Lewis acid generated in situ from $TiCl_4$ and AgOTf (Tf=trifluoromethanesulfonyl), or $Sn(OTf)_2$ gave good results. In the cases of using Sn(IV) and Sb(V) for central metal of Lewis acids, the reaction rates were slow and a small amount of 1-methyl-3-phenylpropyl 4-trifluoromethylbenzoate was isolated as a by-product.

Several examples of the present esterification reaction are demonstrated in Table 6. In every case, the reactions proceed smoothly at room temperature in dichloromethane to give the corresponding esters in excellent yields from nearly equimolar amounts of silyl derivatives of carboxylic acids and alcohols. It is noteworthy to point out that the use of only 1 mol% of $Sn(OTf)_2$ gave the desired ester **8** in high yield.

This method was successfully applied to esterification reaction between various trimethylsilyl carboxylates and alkyl *t*-butyldimethylsilyl ethers affording the desired esters in high yields (Table 7). It is noted that *t*-butyldimethylsilyl ethers were easily converted to acyl protected derivatives by the treatment of corresponding silyl carboxylates under mild conditions.[1f,1h]

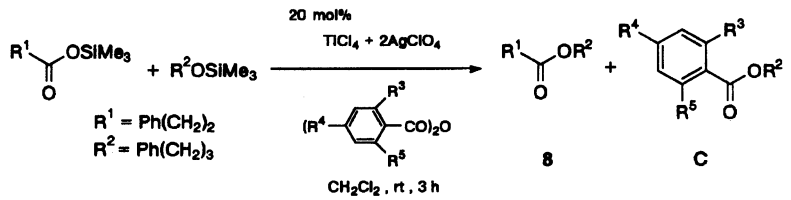
Preparation of *S*-Phenyl Carbothioates via Mixed Anhydrides. In recent years, a considerable attention has been paid to the preparation of activated derivatives of carboxylic acids such as thiol esters because of their high reactivities toward various nucleophiles, and a wide availability was shown in organic synthesis.[6] Therefore, it was desired to develop a facile and efficient method which are applicable to the preparation of various carboxylic acids derivatives under mild conditions.[7] In this section, a useful method for the preparation of *S*-phenyl carbothioates from nearly equimolar amounts of silyl carboxylates and





Scheme 1.

Table 4. Effect of Substituents in Aromatic Ring of Benzoic Anhydride



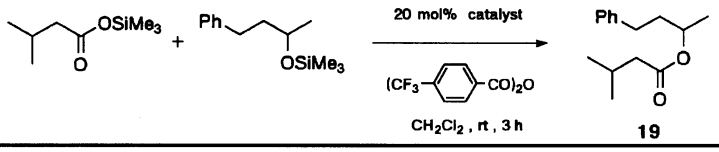
Entry	R^3	R^4	R^5	Yield/%	Ratio of 8/C[a)]	Ester C
1	H	H	H	98	94/ 6	**9**
2	Cl	H	H	89	93/ 7	**10**
3	Cl	H	Cl	68	78/22	**11**
4	H	Cl	H	60	97/ 3	**12**
5	H	F	H	93	98/ 2	**13**
6	H	CF_3	H	91	>200/ 1	**14**
7	H	MeO	H	95	38/62	**15**
8	MeO	H	H	91	4/96	**16**
9	Me	H	H	90	36/64	**17**
10	Me	H	Me	97	3/97	**18**

a) Determined by ^{1}H NMR.

substituted or unsubstituted phenyl silyl sulfide by using a titanium(IV) salt catalyst is described.

First, 10 mol% of $Sn(OTf)_2$, which gave good results in the previous esterification reaction, was used

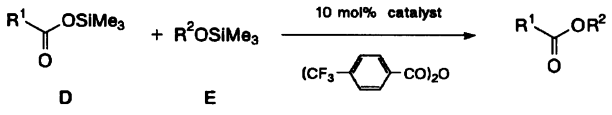
Table 5. Effect of Lewis Acid



Entry	Catalyst	Yield/%	Entry	Catalyst	Yield/%
1	$TiCl_4$	42 (1.9)[a)]	8	$AlCl_3$+2AgOTf	89
2	$TiCl_4$+2$AgClO_4$	84	9	$GaCl_3$+2AgOTf	83
3	$TiCl_4$+2AgOTf	94	10	$InCl_3$+2AgOTf	91
4	$ZrCl_4$+2AgOTf	84	11	$FeCl_3$+2AgOTf	81
5	$HfCl_4$+2AgOTf	86	12	$SnCl_2$+2$AgClO_4$	83
6	$SnCl_4$+2AgOTf	68 (2.1)[a)]	13	$Sn(OTf)_2$	95
7	$SbCl_5$+2AgOTf	39 (0.8)[a)]	14	$TrClO_4$	80

a) Yields of 1-methyl-3-phenylpropyl 4-trifluoromethylbenzoate (**20**).

Table 6. Esterification by the Promotion of a Catalytic Amount of Lewis Acid[a)]

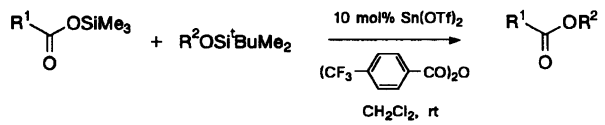


R^1	R^2	R^1COOR^2	Yield/%[b)]		
			Cat. A[c)]	Cat. A[d)]	Cat. B[d)]
Me	$Ph(CH_2)_3$	**21**	90	96	96
^{i}Pr	$Ph(CH_2)_3$	**22**	90	99	99
^{i}Bu	$Ph(CH_2)_3$	**23**	93	99	99
^{t}Bu	$Ph(CH_2)_3$	**24**	91[e)]	97[e)]	97
$Ph(CH_2)_2$	$Ph(CH_2)_3$	**8**	92[f)]	98	95
Me	$Ph(CH_2)_2CHCH_3$	**1**	91	95	95
^{i}Pr	$Ph(CH_2)_2CHCH_3$	**7**	91	99	99
^{i}Bu	$Ph(CH_2)_2CHCH_3$	**19**	96	99	99
^{t}Bu	$Ph(CH_2)_2CHCH_3$	**2**	89	99	93
$Ph(CH_2)_2$	$Ph(CH_2)_2CHCH_3$	**25**	94	98	97

a) Cat A: 10 mol% of $Sn(OTf)_2$; Cat B: 10 mol% of $TiCl_4$ and 20 mol% of AgOTf. b) The yields were determined by isolation. c) **D**/**E**=1.0. d) **D**/**E**=1.1. e) 3-Phenylpropyl 4-trifluoromethylbenzoate **14** (0.9%) was also formed. f) When 1 mol% of $Sn(OTf)_2$ was used, yield of **8** was 92%.

as a catalyst for the reaction of trimethylsilyl 2,2-dimethylpropionate and phenyl trimethylsilyl sulfide. It was found that both *S*-phenyl 2,2-dimethylpropanethioate (**28**) and *S*-phenyl 4-trifluoromethylbenzenecarbothioate (**29**) were obtained together, which indicates an unsatisfactory chemoselectivity (see Table 8, Entry 1). Then, in order to improve the chemoselectivity, several catalysts were examined by taking the reaction of trimethylsilyl 2,2-dimethylpropionate and phenyl trimethylsilyl sulfide as a model. It was found that the chemoselectivity was improved when the titanium(IV) salt, generated in situ from 1 mol of $TiCl_4$ and 2 mol of AgOTf, was used as a catalyst (Entry 6). This result was different from that obtained by using $TiCl_2(OTf)_2$ separately prepared from $TiCl_4$ and trifluoromethanesulfonic acid (Entry 3).[8)] Since 2 mol of AgCl was formed (quantitatively) by mixing 1 mol of $TiCl_4$ and 2 mol of AgOTf in dichloromethane, the difference in the chemoselectivities might depend on AgCl coexisted. This was further supported by the experiment with the addition of 20 mol% of AgCl to the suspension of 10 mol% of isolated $TiCl_2(OTf)_2$ in the present reaction, which led to the improvement in the chemoselectivity

Table 7. Reaction with Alkyl *t*-Butyldimethylsilyl Ether



Entry	R^1	R^2	R^1COOR^2	Yield/%
1	$Ph(CH_2)_2$	$Ph(CH_2)_3$	**8**	88
2	*c*-C_6H_{11}	$Ph(CH_2)_3$	**26**	79
3	^{t}Bu	$Ph(CH_2)_3$	**24**	88
4	$Ph(CH_2)_2$	$Ph(CH_2)_2CHCH_3$	**25**	90
5	*c*-C_6H_{11}	$Ph(CH_2)_2CHCH_3$	**27**	86
6	^{t}Bu	$Ph(CH_2)_2CHCH_3$	**2**	91

(Entry 4).

Next, the titanium(IV) salts were further examined by taking the reaction of trimethylsilyl acetate and 4-methoxyphenyl trimethylsilyl sulfide as a model. It was shown that the chemoselectivity was improved by using the titanium(IV) salt generated from 10 mol% of $TiCl_4$ and 30 mol% of AgOTf compared with that obtained when the titanium(IV) salt formed from 10 mol% of $TiCl_4$ and 20 mol% of AgOTf was used (Table 9, Entries 6 and 7). Since 2 mol of AgCl was formed even when 1 mol of $TiCl_4$ was treated with more than 2 mol of AgOTf in dichloromethane, this result might also be explained by considering the effect of silver salts such as AgCl and AgOTf. Expectantly, when 20 mol% of AgOTf was added to the suspension of 10 mol% of $Sn(OTf)_2$ in dichloromethane, the chemoselectivity of the reaction was improved (Entry 2). Furthermore, experimental results by changing the molar ratio of $TiCl_4$ to AgOTf proved our above mentioned hypothesis (Entries 3, 6—8).

Thus, several carboxylic acids including pivalic acid are successfully employed in the present procedure to form the corresponding *S*-phenyl carbothioates in high yields with perfect chemoselectivity (Table 10). In every case, the reaction proceeds smoothly at room temperature in dichloromethane to give the corresponding *S*-phenyl carbothioates in excellent yields starting from nearly equimolar amounts of silyl carboxylate and phenyl silyl sulfides.

Preparation of Phenyl Carboxylates via Mixed Anhydrides. While it is generally difficult to synthesize phenyl carboxylates efficiently by the promotion of protic acids, when 10 mol% of $Sn(OTf)_2$ was used in the reaction of trimethylsilyl 2-methylpropionate and phenyl trimethylsilyl ether with 4-trifluoromethylbenzoic anhydride, the corresponding phenyl carboxylate and phenyl 4-trifluoromethylbenzoate were obtained in 68% and 0.7% yield, respectively. It was also made clear that the chemoselectivity was improved when the titanium(IV) salt generated in situ from 1 mol of $TiCl_4$ and 2 mol of AgOTf was used as a catalyst. It is noted that several substituted and unsubstituted phenyl carboxylates were obtained in high to excellent yields with perfect chemoselectivity from nearly equimolar amounts of trimethylsilyl carboxylates and the corresponding substituted and unsubstituted phenyl silyl ethers by using a catalytic amount of titanium(IV) salt as shown in Table 11.

Preparation of Alkyl Crotonate and Alkyl 3-Methyl-2-butenoate via Mixed Anhydrides. Esterification reaction of crotonic acid or 3-methyl-2-butenoic acid is a base sensitive reaction leading to the rearrangement of olefinic double bond to form the ester **74** or **76** even under weakly basic condition (Chart 2).[9] For example, the esterification reaction of crotonic acid and 3-phenyl-1-propanol by using 1-ethyl-2-fluoropyridinium tetrafluoroborate and triethylamine, a mixture of the desired ester and rearrangement product was obtained (76%, **73**/**74**=4/1). The same result was also observed in the case of 3-methyl-2-butenoic acid (50%, **75**/**76**=1/2). Therefore, the esterification reaction between equimolar amounts of crotonic acid and alcohol has been generally carried out using DCC or thionyl chloride.

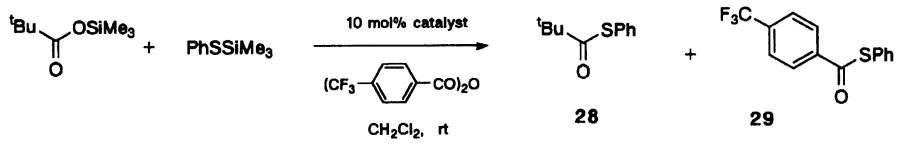
It is also noted that the present method was successfully applied to the synthesis of alkyl crotonate and alkyl 3-methyl-2-butenoate from equimolar amounts of silyl carboxylates and alkyl silyl ethers under mild condition. When 20 mol% of $Sn(OTf)_2$ was employed in the present experiment, no rearranged product was isolated at all and the desired ester was obtained in 94 or 91% yield, respectively. These examples show mildness in reaction conditions of the present esterification reaction.

Preparation of Alkyl (*Z*)-2-Methyl-2-butenoate (Angelate) and Alkyl (*E*)-2-Methyl-2-butenoate (Tiglate) via Mixed Anhydrides. Though alkyl angelate and alkyl tiglate such as homogynolide-A and homogynolide-B which possess antifeedant effect exist in nature,[10] an efficient method to construct the alkyl angelate has not yet been developed (Chart 3). In order to synthesize alkyl angelate, the corresponding alcohol has commonly been treated with (*Z*)-2-methyl-2-butenoyl chloride, but the desired alkyl angelate is obtained in only poor yield, often accompanied with the corresponding alkyl tiglate. Similar results were reported concerning the reaction of (*Z*)-2-methyl-2-butenoic acid using DCC. Recently, Greene et al. developed the effective method for the preparation of alkyl angelate by using of 2,4,6-trichlorobenzoyl chloride under neutral condition.[11] However, in the above procedure, using 2 mol of mixed anhydride derived from (*Z*)-2-methyl-2-butenoic acid and 2,4,6-trichlorobenzoyl chloride was necessary to complete the reaction. Therefore, exploration of an efficient method to obtain alkyl angelate is still strongly desired.

First, the preparation of a trimethylsilyl angelate by using trimethylsilyl chloride and pyridine was tried and the desired silyl derivative was isolated without accompanying isomerization of double bond. Next, the esterification reaction between trimethylsilyl angelate and (−)-menthyl trimethylsilyl ether was tried by the standard procedure and the corresponding ester (**77**) was obtained in high yield without accompanying isomerization. Since the optical purity of this ester was kept safely, esterification reactions between trimethylsilyl angelate and several alkyl silyl ethers were examined (See Table 12). In all cases, the reactions proceeded smoothly to afford the desired products in high to excellent yields without accompanying isomerization.

It is concluded that the esterification reaction via mixed anhydride by the promotion of a catalytic amount of Lewis acid provides an efficient methods for the preparation of various derivatives of carboxyl-

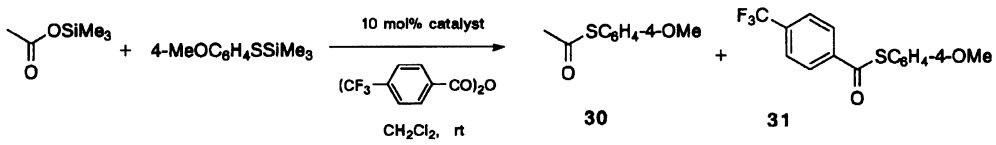
Table 8. Effect of Catalyst



Entry	Catalyst	Yield/%	Ratio fo **28**/**29**[a)]
1	10 mol% $Sn(OTf)_2$	92	84/16
2	10 mol% $Sn(OTf)_2$+20 mol% AgOTf	78	96/ 4
3	10 mol% $TiCl_2(OTf)_2$[b)]	88	99/ 1
4	10 mol% $TiCl_2(OTf)_2$+20 mol% AgCl	93	>200/ 1
5	10 mol% $TiCl_4$+10 mol% AgOTf	83	99/ 1
6	10 mol% $TiCl_4$+20 mol% AgOTf	89	>200/ 1
7	10 mol% $TiCl_4$+30 mol% AgOTf	88	>200/ 1
8	10 mol% $TiCl_4$+40 mol% AgOTf	86	>200/ 1

a) Determined by ^{1}H NMR. b) Prepared according to the procedure reported by Ref. 8.

Table 9. Effect of Catalyst



Entry	Catalyst	Yield/%	Ratio fo **30**/**31**[a)]
1	10 mol% $Sn(OTf)_2$	93	73/27
2	10 mol% $Sn(OTf)_2$+20 mol% AgOTf	81	91/ 9
3	10 mol% $TiCl_2(OTf)_2$[b)]	93	99/ 1
4	10 mol% $TiCl_2(OTf)_2$+20 mol% AgCl	92	99/ 1
5	10 mol% $TiCl_4$+10 mol% AgOTf	91	94/ 6
6	10 mol% $TiCl_4$+20 mol% AgOTf	94	99/ 1
7	10 mol% $TiCl_4$+30 mol% AgOTf	95	>200/ 1
8	10 mol% $TiCl_4$+40 mol% AgOTf	93	>200/ 1

a) Determined by ^{1}H NMR. b) Prepared according to the procedure reported by Ref. 8.

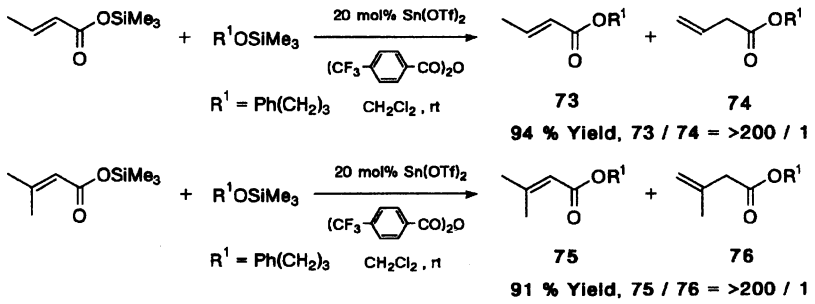


Chart 2.

ic acids. Furthermore, esterification reactions, which have not been able to perform under basic or acidic conditions so far, were successfully achieved, because the present reaction could proceed under extremely mild condition.

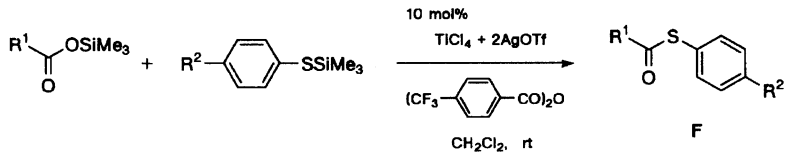
Experimental

All melting points were uncorrected. Optical rotations were recorded on a JASCO DIP-370 digital polarimeter. IR spectra were recorded on a Horiba FT-300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-1200 or JEOL JNR-EX270L spectrometer, and tetramethylsilane (TMS) served as internal standard. Column chromatography was performed on Silica gel 60 (Merck) or Wakogel B5F. All reactions were carried out under argon atmosphere in dried glassware.

Dichloromethane was distilled from P_2O_5, then CaH_2, and dried over MS4A.

Alkyl trimethylsilyl ethers were prepared from the corre-

Table 10. Synthesis of *S*-Phenyl Carbothioate



Entry	R^1	R^2	*S*-Phenyl carbothioate **F**	Yield/%[a]
1	Me	H	**32**	84
2	^{i}Pr	H	**33**	94
3	^{i}Bu	H	**34**	99
4	^{t}Bu	H	**28**	89
5	$Ph(CH_2)_2$	H	**35**	99
6	Me	MeO	**30**	95[b]
7	^{i}Pr	MeO	**36**	96[b]
8	^{i}Bu	MeO	**37**	98
9	^{t}Bu	MeO	**38**	94
10	$Ph(CH_2)_2$	MeO	**39**	95
11	Me	Cl	**40**	93
12	^{i}Pr	Cl	**41**	94
13	^{i}Bu	Cl	**42**	94
14	^{t}Bu	Cl	**43**	97
15	$Ph(CH_2)_2$	Cl	**44**	96

a) Isolated yield. b) Ten mol% of $TiCl_4$ and 30 mol% of AgOTf were used as a catalyst.

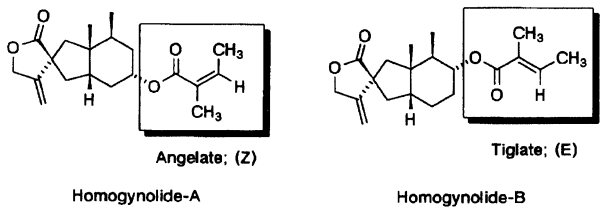


Chart 3.

sponding alcohols by the treatment with trimethylsilyl chloride and triethylamine in dichloromethane, and were purified by distillation. Trimethylsilyl acetate was purchased from Aldrich. Other trimethylsilyl carboxylates were prepared from the corresponding carboxylic acids by the treatment with trimethylsilyl chloride and pyridine in dichloromethane, and were purified by distillation. 4-Trifluoromethylbenzoic acid and 4-trifluoromethylbenzoyl chloride were purchased from Tokyo Kasei Co., Ltd. and were used without further purification.

Preparation of 4-Trifluoromethylbenzoic Anhydride. To the mixture of 4-trifluoromethylbenzoic acid (13.69 g, 72 mmol) and 4-trifluoromethylbenzoyl chloride (15.02 g, 72 mmol) in dichloromethane (144 ml), pyridine (6.11 ml, 75.6 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 21 h at r.t., and then quenched with cold water (50 ml). After usual work up, the crude product was purified by recrystallization from dichloromethane to afford 4-trifluoromethylbenzoic anhydride (23.2 g, 89% yield). Mp 132—133 °C; IR (KBr) 1732, 1795 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.80 (4H, d, J=9 Hz), 8.26 (4H, d, J=9 Hz). Found: C, 53.09; H, 2.04%. Calcd for $C_{16}H_8F_6O_3$: C, 53.05; H, 2.23%.

Typical Experimental Procedure for the Catalytic Esterification Reaction. A typical experimental procedure is described for the reaction of trimethylsilyl 2-methylpropionate and 3-phenylpropyl trimethylsilyl ether in the presence of a catalytic amount of tin(II) triflate; to the suspension of $Sn(OTf)_2$ (0.02 mmol) in dichloromethane (2.0 ml), the mixture of 4-trifluoromethylbenzoic anhydride (0.22 mmol) and trimethylsilyl 2-methylpropionate (0.22 mmol) in dichloromethane (1.0 ml) and the solution of 3-phenylpropyl trimethylsilyl ether (0.2 mmol) in dichloromethane (0.5 ml) were successively added. The reaction mixture was stirred for 3 h at r.t., and then quenched with aq sat. $NaHCO_3$. After usual work up, the crude product was purified by preparative TLC on silica gel to afford 3-phenylpropyl 2-methylpropionate (99% yield) with an excellent chemoselectivity (>200/1).

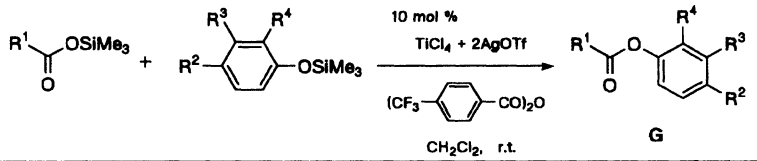
1-Methyl-3-phenylpropyl Acetate (1). IR (neat) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.24 (3H, d, J=6.3 Hz, 1.73—2.00 (2H, m), 2.02 (3H, s), 2.55—2.73 (2H, m), 4.93 (1H, m), 7.15—7.30 (5H, m). Found: C, 74.77; H, 8.20%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

1-Methyl-3-phenylpropyl 2,2-Dimethylpropionate (2). IR (neat) 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (9H, s), 1.25 (3H, d, J=6.3 Hz), 1.73—2.00 (2H, m), 2.54—2.74 (2H, m), 4.91 (1H, m), 7.15—7.31 (5H, m). Found: C, 76.70; H, 9.52%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.

1-Methyl-3-phenylpropyl Benzoate (3). IR (neat) 1716 cm^{-1}; ^1H NMR (CCl_4) δ=1.44 (3H, d, J=6 Hz), 1.74—2.23 (2H, m), 2.55—2.90 (2H, m), 5.15 (1H, m), 7.05—7.54 (8H, m), 7.98 (2H, dd, J=8, 2 Hz). Found: C, 80.47; H, 7.22%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

1-Methyl-3-phenylpropyl (*E*)-2-Butenoate (5). IR (neat) 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (3H, d, J=6.2 Hz), 1.95—2.04 (2H, m), 1.88 (3H, dd, J=7.0, 1.7 Hz), 2.55—2.73 (2H, m), 4.89—5.02 (1H, m), 5.84 (1H, dd, J=15.5, 1.7 Hz), 6.96 (1H, dq, J=15.5, 7.0 Hz). Found: C, 77.10; H, 8.41%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

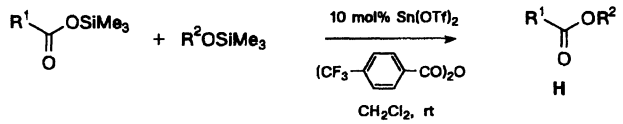
Table 11. Synthesis of Phenol Ester



Entry	R^1	R^2	R^3	R^4	Phenol ester **G**	Yield/%[a)]
1	^{i}Pr	H	H	H	**45**	77
2	^{i}Bu	H	H	H	**46**	89
3	^{t}Bu	H	H	H	**47**	82
4	$Ph(CH_2)_2$	H	H	H	**48**	99
5	^{i}Pr	H	H	Cl	**49**	90
6	^{i}Bu	H	H	Cl	**50**	93
7	^{t}Bu	H	H	Cl	**51**	90
8	$Ph(CH_2)_2$	H	H	Cl	**52**	95
9	^{i}Pr	H	MeO	H	**53**	83
10	^{i}Bu	H	MeO	H	**54**	76
11	^{t}Bu	H	MeO	H	**55**	88
12	$Ph(CH_2)_2$	H	MeO	H	**56**	94
13	^{i}Pr	H	Me	H	**57**	80
14	^{i}Bu	H	Me	H	**58**	79
15	^{t}Bu	H	Me	H	**59**	86
16	$Ph(CH_2)_2$	H	Me	H	**60**	93
17	^{i}Pr	MeO	H	H	**61**	95
18	^{i}Bu	MeO	H	H	**62**	94
19	^{t}Bu	MeO	H	H	**63**	93
20	$Ph(CH_2)_2$	MeO	H	H	**64**	91
21	^{i}Pr	Cl	H	H	**65**	93
22	^{i}Bu	Cl	H	H	**66**	95
23	^{t}Bu	Cl	H	H	**67**	92
24	$Ph(CH_2)_2$	Cl	H	H	**68**	94
25	^{i}Pr	NO_2	H	H	**69**	86
26	^{i}Bu	NO_2	H	H	**70**	79
27	^{t}Bu	NO_2	H	H	**71**	88
28	$Ph(CH_2)_2$	NO_2	H	H	**72**	80

a) Isolated yield.

Table 12. Synthesis of Alkyl Angelate and Tiglate



Entry	R^1	R^2	Ester **H**	Yield/%[a)]
1	(*Z*)-$CH_3CH{=}C(CH_3)$–	(−)-Menthyl	**77**	96
2	(*E*)-$CH_3CH{=}C(CH_3)$–	(−)-Menthyl	**78**	90
3	(*Z*)-$CH_3CH{=}C(CH_3)$–	(+)-5α-Cholestan-3β-yl	**79**	92
4	(*E*)-$CH_3CH{=}C(CH_3)$–	(+)-5α-Cholestan-3β-yl	**80**	93
5	(*Z*)-$CH_3CH{=}C(CH_3)$–	Ph	**81**	95
6	(*E*)-$CH_3CH{=}C(CH_3)$–	Ph	**82**	93

a) Isolated yield.

1-Methyl-3-phenylpropyl Trifluoroacetate (6). IR (neat) 1782 cm^{-1}; ^1H NMR (CCl_4) δ=1.35 (3H, d, J=6 Hz), 1.65—2.25 (2H, m), 2.45—2.90 (2H, m), 4.75—5.25 (1H, m), 7.10 (5H, m). Found: C, 58.67; H, 5.59%. Calcd for $C_{12}H_{13}F_3O_2$: C, 58.54; H, 5.32%.

1-Methyl-3-phenylpropyl 2-Methylpropionate (7). IR (neat) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (6H, d, J=6.9 Hz), 1.26 (3H, d, J=6.3 Hz), 1.73—2.00 (2H, m), 2.45—2.74 (3H, m), 4.94 (1H, m), 7.15—7.31 (5H, m). Found: C, 76.58; H, 9.41%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

3-Phenylpropyl 3-Phenylpropionate[12] (8). IR (neat) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.91 (2H, m), 2.62

(4H, m), 2.95 (2H, t, J=7.8 Hz), 4.08 (2H, t, J=6.6 Hz), 7.13—7.31 (10H, m). Found: C, 80.35; H, 7.77%. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

3-Phenylpropyl Benzoate (9). IR (neat) 1718 cm^{-1}; ^1H NMR (CCl_4) δ=2.23 (2H, m), 2.77 (2H, t, J=8 Hz), 4.27 (2H, t, J=6 Hz), 7.05—7.54 (8H, m), 7.85—8.10 (2H, m). Found: C, 79.69; H, 6.97%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

3-Phenylpropyl 2-Chlorobenzoate (10). IR (neat) 1730 cm^{-1}; ^1H NMR (CCl_4) δ=2.05 (2H, m), 2.75 (2H, t, J=8 Hz), 4.30 (2H, t, J=6 Hz), 7.00—7.50 (8H, m), 7.55—7.90 (1H, m). Found: C, 69.92; H, 5.61%. Calcd for $C_{16}H_{15}ClO_2$: C, 69.95; H, 5.50%.

3-Phenylpropyl 2,6-Dichlorobenzoate (11). IR (neat) 1736 cm^{-1}; ^1H NMR (CCl_4) δ=2.05 (2H, m), 2.75 (2H, t, J=8 Hz), 4.35 (2H, t, J=6 Hz), 6.85—7.50 (8H, m). Found: C, 62.35; H, 4.59%. Calcd for $C_{16}H_{14}Cl_2O_2$: C, 62.15; H, 4.56%.

3-Phenylpropyl 4-Chlorobenzoate (12). IR (neat) 1718 cm^{-1}; ^1H NMR (CCl_4) δ=1.65—2.07 (4H, m), 2.57—2.73 (2H, m), 7.12—7.44 (7H, m), 7.72—7.74 (2H, m). Found: C, 70.07; H, 5.41%. Calcd for $C_{16}H_{15}ClO_2$: C, 69.95; H, 5.50%.

3-Phenylpropyl 4-Fluorobenzoate (13). IR (neat) 1718 cm^{-1}; ^1H NMR (CCl_4) δ=2.03 (2H, m), 2.77 (2H, t, J=7 Hz), 4.27 (2H, t, J=6 Hz), 6.80—7.26 (7H, m), 7.80—8.16 (2H, m). Found: C, 74.25; H, 5.70%. Calcd for $C_{16}H_{15}FO_2$: C, 74.40; H, 5.85%.

3-Phenylpropyl 4-Trifluoromethylbenzoate (14). IR (neat) 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08—2.18 (2H, m), 2.79 (2H, t, J=7.3 Hz), 4.38 (2H, t, J=6.6 Hz), 7.17—7.33 (5H, m), 7.70 (2H, d, J=8.3 Hz), 8.12 (2H, d, J=8.3 Hz). Found: C, 66.48; H, 4.96%. Calcd for $C_{17}H_{15}F_3O_2$: C, 66.23; H, 4.90%.

3-Phenylpropyl 4-Methoxybenzoate (15). IR (neat) 1712 cm^{-1}; ^1H NMR (CCl_4) δ=2.00 (2H, m), 2.70 (2H, t, J=8 Hz), 3.75 (3H, s), 4.25 (2H, t, J=6 Hz), 6.75 (2H, d, J=9 Hz), 7.15 (5H, s), 7.95 (2H, d, J=9 Hz). Found: C, 75.53; H, 6.84%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

3-Phenylpropyl 2-Methoxybenzoate (16). IR (neat) 1726 cm^{-1}; ^1H NMR (CCl_4) δ=2.00 (2H, m), 2.75 (2H, t, J=8 Hz), 3.80 (3H, s), 4.20 (2H, t, J=6 Hz), 6.70—7.80 (9H, m). Found: C, 75.75; H, 6.73%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

3-Phenylpropyl 2-Methylbenzoate (17). IR (neat) 1716 cm^{-1}; ^1H NMR (CCl_4) δ=2.00 (2H, m), 2.55 (3H, s), 2.75 (2H, t, J=8 Hz), 4.25 (2H, t, J=6 Hz), 6.90—7.55 (8H, m), 7.70—8.00 (1H, m). Found: C, 80.37; H, 7.27%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

3-Phenylpropyl 2,6-Dimethylbenzoate (18). IR (neat) 1726 cm^{-1}; ^1H NMR (CCl_4) δ=2.00 (2H, m), 2.25 (6H, s), 2.70 (2H, t, J=8 Hz), 4.25 (2H, t, J=6 Hz), 6.75—7.30 (8H, m). Found: C, 80.35; H, 7.59%. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

1-Methyl-3-phenylpropyl 3-Methylbutyrate (19). IR (neat) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (6H, d, J=6.3 Hz), 1.25 (3H, d, J=6.3 Hz), 1.73—2.00 (2H, m), 2.06—2.19 (3H, m), 2.54—2.74 (2H, m), 4.96 (1H, m), 7.15—7.31 (5H, m). Found: C, 76.85; H, 9.17%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.

1-Methyl-3-phenylpropyl 4-Trifluoromethylbenzoate (20). IR (neat) 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (3H, d, J=6.3 Hz), 1.90—2.19 (2H, m), 2.65—2.82 (2H, m), 5.22 (1H, m), 7.15—7.30 (5H, m), 7.69 (2H, d, J=8.6 Hz), 8.13 (2H, d, J=8.6 Hz). Found: C, 66.99; H, 5.51%. Calcd for $C_{18}H_{17}F_3O_2$: C, 67.07; H, 5.32%.

3-Phenylpropyl Acetate[13] (21). IR (neat) 1739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.91—2.01 (2H, m), 2.05 (3H, s), 2.69 (2H, t, J=7.6 Hz), 4.09 (2H, t, J=6.3 Hz), 7.17—7.32 (5H, m). Found: C, 74.25; H, 7.94%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

3-Phenylpropyl 2-Methylpropionate (22). IR (neat) 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (6H, d, J=7.3 Hz), 1.91—2.01 (2H, m), 2.55 (1H, m), 2.69 (2H, t, J=7.6 Hz), 4.09 (2H, t, J=6.3 Hz), 7.17—7.32 (5H, m). Found: C, 75.86; H, 8.86%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%.

3-Phenylpropyl 3-Methylbutyrate (23). IR (neat) 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (6H, d, J=6.6 Hz), 1.90—2.01 (2H, m), 2.03—2.21 (3H, m), 2.69 (2H, t, J=7.6 Hz), 4.09 (2H, t, J=6.6 Hz), 7.16—7.31 (5H, m). Found: C, 76.07; H, 9.16%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

3-Phenylpropyl 2,2-Dimethylpropionate (24). IR (neat) 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (9H, s), 1.97—2.03 (2H, m), 2.74 (2H, t, J=7.6 Hz), 4.12 (2H, t, J=6.3 Hz), 7.21—7.34 (5H, m). Found: C, 76.06; H, 9.21%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

1- Methyl- 3- phenylpropyl 3- Phenylpropionate (25). IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (3H, d, J=6.3 Hz), 1.72—1.96 (2H, m), 2.51—2.69 (4H, m), 2.95 (2H, t, J=7.6 Hz), 4.94 (1H, m), 7.11—7.31 (10H, m). Found: C, 80.74; H, 7.99%. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85%.

3-Phenylpropyl Cyclohexanecarboxylate (26). IR (neat) 1732 cm^{-1}; ^1H NMR (CCl_4) δ=1.05—2.40 (13H, m), 2.65 (2H, t, J=8 Hz), 4.00 (2H, t, J=6 Hz), 7.15 (5H, s). Found: C, 77.89; H, 8.90%. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%.

1-Methyl-3-phenylpropyl Cyclohexanecarboxylate (27). IR (neat) 1728 cm^{-1}; ^1H NMR (CCl_4) δ=1.15 (3H, d, J=6 Hz), 1.25—2.25 (13H, m), 2.25—2.80 (2H, m), 4.85 (1H, m), 7.15 (5H, s). Found: C, 78.18; H, 9.07%. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%.

Typical Experimental Procedure for the Synthesis of Activated Derivatives of Carboxylic Acids. A typical experimental procedure is described for the reaction of trimethylsilyl 3-methylbutyrate and phenyl trimethylsilyl sulfide in the presence of a catalytic amount of titanium(IV) chloride–silver triflate ($TiCl_4$–AgOTf); to a suspension of AgOTf (0.034 mmol) and $TiCl_4$ (0.017 mmol) in dichloromethane (2.0 ml), a solution of 4-trifluoromethylbenzoic anhydride (0.19 mmol) and trimethylsilyl 3-methylbutyrate (0.19 mmol) in dichloromethane (1.0 ml) and a solution of phenyl trimethylsilyl sulfide (0.17 mmol) in dichloromethane (1.0 ml) were successively added. The reaction mixture was stirred for 6 h at r.t., and then quenched with aq sat. $NaHCO_3$. After usual work up, the crude product was purified by preparative TLC on silica gel to afford *S*-phenyl 3-methylbutanethioate (99% yield) with an excellent chemoselectivity (>200/1).

***S*-Phenyl 2,2-Dimethylpropanethioate[14] (28).** IR (neat) 1697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (9H, s), 7.39 (5H, s).

***S*- Phenyl 4- Trifluoromethylbenzenecarbothioate**

(29). Mp 114—115 °C, IR (KBr) 1674 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.47—7.55 (5H, m), 7.76 (2H, d, J=8.9 Hz), 8.14 (2H, d, J=8.9 Hz). Found: C, 59.55; H, 3.13; F, 20.02; S, 11.20%. Calcd for $C_{14}H_9F_3OS$: C, 59.56; H, 3.22; F, 20.19; S, 11.36%.

***S*-4-Methoxyphenyl Ethanethioate[15] (30).** IR (neat) 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.39 (3H, s), 3.82 (3H, s), 6.94 (2H, d, J=8.9 Hz), 7.32 (2H, d, J=8.9 Hz).

***S*-4-Methoxyphenyl 4-Trifluoromethylbenzenecarbothioate (31).** Mp 84—85 °C; IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.86 (3H, s), 7.01 (2H, d, J=8.9 Hz), 7.42 (2H, d, J=8.9 Hz), 7.75 (2H, d, J=8.6 Hz), 8.12 (2H, d, J=8.6 Hz). Found: m/z 312.0409. Calcd for $C_{15}H_{11}F_3O_2S$: M, 312.0432.

***S*-Phenyl Ethanethioate[16] (32).** IR (neat) 1709 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.42 (3H, s), 7.41 (5H, s).

***S*-Phenyl 2-Methylpropanethioate[16] (33).** IR (neat) 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (6H, d, J=6.9 Hz), 2.86 (1H, m), 7.40 (5H, s).

***S*-Phenyl 3-Methylbutanethioate[17] (34).** IR (neat) 1709 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.01 (6H, d, J=6.6 Hz), 2.22 (1H, m), 2.54 (2H, d, J=6.9 Hz), 7.41 (5H, m).

***S*-Phenyl 3-Phenylpropanethioate[18] (35).** Mp 45 °C; IR (KBr) 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.92—3.05 (4H, m), 7.19—7.33 (5H, m), 7.39 (5H, s).

***S*-4-Methoxyphenyl 2-Methylpropanethioate (36).** IR (neat) 1699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (6H, d, J=6.9 Hz), 2.85 (1H, m), 3.82 (3H, s), 6.93 (2H, d, J=8.6 Hz), 7.31 (2H, d, J=8.6 Hz). Found: C, 62.88; H, 6.71; S, 15.01%. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.72; S, 15.24%.

***S*-4-Methoxyphenyl 3-Methylbutanethioate (37).** IR (neat) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (6H, d, J=6.6 Hz), 2.20 (1H, m), 2.51 (2H, d, J=7.3 Hz), 3.82 (3H, s), 6.94 (2H, d, J=8.9 Hz), 7.31 (2H, d, J=8.9 Hz). Found: C, 64.22; H, 7.17; S, 14.17%. Calcd for $C_{12}H_{16}O_2S$: C, 64.24; H, 7.20; S, 14.29%.

***S*-4-Methoxyphenyl 2,2-Dimethylpropanethioate[19] (38).** IR (neat) 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (9H, s), 3.81 (3H, s), 6.93 (2H, d, J=8.9 Hz), 7.29 (2H, d, J=8.9 Hz).

***S*-4-Methoxyphenyl 3-Phenylpropanethioate (39).** Mp 52—53 °C; IR (KBr) 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.89—3.04 (4H, m), 3.80 (3H, s), 6.92 (2H, d, J=8.9 Hz), 7.18—7.32 (7H, m). Found: C, 70.24; H, 5.85; S, 11.66%. Calcd for $C_{16}H_{16}O_2S$: C, 70.55; H, 5.93; S, 11.77%.

***S*-4-Chlorophenyl Ethanethioate[15] (40).** IR (neat) 1712 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.42 (3H, s), 7.29—7.45 (4H, m).

***S*-4-Chlorophenyl 2-Methylpropanethioate[20] (41).** IR (neat) 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (6H, d, J=6.9 Hz), 2.85 (1H, m), 7.26—7.42 (4H, m).

***S*-4-Chlorophenyl 3-Methylbutanethioate (42).** IR (neat) 1712 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (6H, d, J=6.6 Hz), 2.21 (1H, m), 2.54 (2H, d, J=6.9 Hz), 7.26—7.42 (4H, m). Found: C, 57.83; H, 5.71; Cl, 15.24; S, 13.92%. Calcd for $C_{11}H_{13}ClOS$: C, 57.75; H, 5.74; Cl, 15.50; S, 14.02%.

***S*-4-Chlorophenyl 2,2-Dimethylpropanethioate[19] (43).** IR (neat) 1697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (9H, s), 7.25—7.42 (4H, m).

***S*-4-Chlorophenyl 3-Phenylpropanethioate (44).** Mp 58—59 °C; IR (KBr) 1709 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.92—3.05 (4H, m), 7.18—7.39 (9H, m). Found: C, 64.92; H, 4.63; Cl, 12.82; S, 11.56%. Calcd for $C_{15}H_{13}ClOS$: C, 65.09; H, 4.74; Cl, 12.81; S, 11.58%.

Phenyl 2-Methylpropionate[21] (45). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (6H, d, J=6.9 Hz), 2.80 (1H, m), 7.07 (2H, d, J=7.6 Hz), 7.21 (1H, t, J=7.6 Hz), 7.37 (2H, t, J=7.6 Hz).

Phenyl 3-Methylbutyrate (46). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06 (6H, d, J=6.6 Hz), 2.25 (1H, m), 2.43 (2H, d, J=7.3 Hz), 7.07 (2H, d, J=7.6 Hz), 7.22 (1H, t, J=7.6 Hz), 7.37 (2H, t, J=7.6 Hz). Found: C, 74.24; H, 7.86%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

Phenyl 2,2-Dimethylpropionate[22] (47). IR (neat) 1749 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.36 (9H, s), 7.05 (2H, d, J=7.6 Hz), 7.21 (1H, t, J=7.6 Hz), 7.37 (2H, t, J=7.6 Hz).

Phenyl 3-Phenylpropionate[23] (48). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.88 (2H, t, J=7.9 Hz), 3.08 (2H, t, J=7.9 Hz), 7.00 (2H, d, J=7.3 Hz), 7.17—7.39 (8H, m).

2-Chlorophenyl 2-Methylpropionate (49). IR (neat) 1765 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.36 (6H, d, J=6.9 Hz), 2.87 (1H, m), 7.10—7.31 (3H, m), 7.43 (1H, dd, J=7.9, 1.7 Hz). Found: C, 60.29; H, 5.64%. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58%.

2-Chlorophenyl 3-Methylbutyrate (50). IR (neat) 1768 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (6H, d, J=6.6 Hz), 2.28 (1H, m), 2.50 (2H, d, J=7.3 Hz), 7.10—7.31 (3H, m), 7.43 (1H, dd, J=7.9, 1.7 Hz). Found: C, 62.38; H, 6.26%. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16%.

2-Chlorophenyl 2,2-Dimethylpropionate (51). IR (neat) 1761 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (9H, s), 7.08—7.31 (3H, m), 7.43 (1H, dd, J=7.9, 1.7 Hz). Found: C, 62.13; H, 6.31%. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16%.

2-Chlorophenyl 3-Phenylpropionate[24] (52). IR (neat) 1766 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.95 (2H, t, J=7.9 Hz), 3.11 (2H, t, J=7.9 Hz), 7.05 (1H, dd, J=7.6, 1.7 Hz), 7.15—7.36 (7H, m), 7.43 (1H, dd, J=7.9, 1.7 Hz).

3-Methoxyphenyl 2-Methylpropionate (53). IR (neat) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (6H, d, J=6.9 Hz), 2.76 (1H, m), 3.77 (3H, s), 6.60 (1H, t, J=2.3 Hz), 6.64 (1H, dd, J=7.9, 2.3 Hz), 6.74 (1H, dd, J=7.9, 2.3 Hz), 7.24 (1H, t, J=7.9 Hz). Found: C, 67.92; H, 7.27%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

3-Methoxyphenyl 3-Methylbutyrate (54). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06 (6H, d, J=6.6 Hz), 2.24 (1H, m), 2.43 (2H, d, J=7.3 Hz), 3.80 (3H, s), 6.63 (1H, t, J=2.3 Hz), 6.68 (1H, dd, J=9.2, 2.3 Hz), 6.78 (1H, dd, J=9.2, 2.3 Hz), 7.27 (1H, t, J=9.2 Hz). Found: C, 68.99; H, 7.71%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

3-Methoxyphenyl 2,2-Dimethylpropionate (55). IR (neat) 1751 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (9H, s), 3.80 (3H, s), 6.61 (1H, t, J=2.3 Hz), 6.65 (1H, dd, J=9.2, 2.3 Hz), 6.77 (1H, dd, J=9.2, 2.3 Hz), 7.26 (1H, t, J=9.2 Hz). Found: C, 68.99; H, 7.54%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

3-Methoxyphenyl 3-Phenylpropionate[24] (56). IR (neat) 1761 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.87 (2H, t, J=7.9 Hz), 3.07 (2H, t, J=7.9 Hz), 3.77 (3H, s), 6.54 (1H, t, J=2.3 Hz), 6.61 (1H, dd, J=8.2, 2.3 Hz), 6.76 (1H, dd, J=8.2, 2.3 Hz), 7.20—7.35 (6H, m).

3-Methylphenyl 2-Methylpropionate (57). IR (neat) 1757 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (6H, d, J=7.3

Hz), 2.33 (3H, s), 2.76 (1H, m), 6.84 (1H, d, J=7.6 Hz), 6.85 (1H, s), 7.00 (1H, d, J=7.6 Hz), 7.23 (1H, t, J=7.6 Hz). Found: C, 74.14; H, 8.03%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

3-Methylphenyl 3-Methylbutyrate (58). IR (neat) 1757 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06 (6H, d, J=6.6 Hz), 2.24 (1H, m), 2.36 (3H, s), 2.42 (2H, d, J=7.3 Hz), 6.87 (1H, d, J=7.3 Hz), 6.88 (1H, s), 7.03 (1H, d, J=7.3 Hz), 7.25 (1H, t, J=7.3 Hz). Found: C, 75.25; H, 8.47%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

3-Methylphenyl 2,2-Dimethylpropionate (59). IR (neat) 1751 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (9H, s), 2.35 (3H, s), 6.85 (1H, d, J=7.6 Hz), 6.87 (1H, s), 7.02 (1H, d, J=7.6 Hz), 7.25 (1H, t, J=7.6 Hz). Found: C, 74.72; H, 8.31%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

3-Methylphenyl 3-Phenylpropionate[24] (60). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.34 (3H, s), 2.87 (2H, t, J=8.3 Hz), 3.07 (2H, t, J=8.3 Hz), 6.81 (1H, d, J=7.9 Hz), 6.82 (1H, s), 7.03 (1H, d, J=7.9 Hz), 7.20—7.35 (6H, m).

4-Methoxyphenyl 2-Methylpropionate[21] (61). IR (neat) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (6H, d, J=6.9 Hz), 2.78 (1H, m), 3.79 (3H, s), 6.88 (2H, d, J=9.2 Hz), 6.98 (2H, d, J=9.2 Hz).

4-Methoxyphenyl 3-Methylbutyrate (62). IR (neat) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05 (6H, d, J=6.6 Hz), 2.24 (1H, m), 2.42 (2H, d, J=7.3 Hz), 3.79 (3H, s), 6.88 (2H, d, J=9.2 Hz), 6.98 (2H, d, J=9.2 Hz). Found: C, 69.25; H, 7.82%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

4-Methoxyphenyl 2,2-Dimethylpropionate[22] (63). IR (neat) 1751 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.34 (9H, s), 3.79 (3H, s), 6.88 (2H, d, J=9.2 Hz), 6.96 (2H, d, J=9.2 Hz).

4-Methoxyphenyl 3-Phenylpropionate[23] (64). IR (neat) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.86 (2H, t, J=7.9 Hz), 3.07 (2H, t, J=7.9 Hz), 3.78 (3H, s), 6.86 (2H, d, J=9.2 Hz), 6.92 (2H, d, J=9.2 Hz), 7.23—7.35 (5H, m).

4-Chlorophenyl 2-Methylpropionate (65). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (6H, d, J=6.9 Hz), 2.79 (1H, m), 7.01 (2H, d, J=8.9 Hz), 7.33 (2H, d, J=8.9 Hz). Found: C, 60.38; H, 5.72%. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58%.

4-Chlorophenyl 3-Methylbutyrate (66). IR (neat) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05 (6H, d, J=6.6 Hz), 2.23 (1H, m), 2.43 (2H, d, J=7.3 Hz), 7.02 (2H, d, J=8.9 Hz), 7.33 (2H, d, J=8.9 Hz). Found: C, 62.17; H, 6.21%. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16%.

4-Chlorophenyl 2,2-Dimethylpropionate (67). IR (neat) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (9H, s), 7.00 (2H, d, J=8.9 Hz), 7.33 (2H, d, J=8.9 Hz). Found: C, 62.20; H, 6.32%. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16%.

4-Chlorophenyl 3-Phenylpropionate[23] (68). IR (neat) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.87 (2H, d, J=7.9 Hz), 3.06 (2H, d, J=7.9 Hz), 6.94 (2H, d, J=8.6 Hz), 7.20—7.35 (7H, m).

4-Nitrophenyl 2-Methylpropionate[25] (69). IR (neat) 1765 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.34 (6H, d, J=6.9 Hz), 2.85 (1H, m), 7.28 (2H, d, J=9.2 Hz), 8.27 (2H, d, J=9.2 Hz).

4-Nitrophenyl 3-Methylbutyrate[26] (70). IR (neat) 1765 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.07 (6H, d, J=6.6 Hz), 2.25 (1H, m), 2.48 (2H, d, J=7.3 Hz), 7.28 (2H, d, J=9.2 Hz), 8.27 (2H, d, J=9.2 Hz).

4-Nitrophenyl 2,2-Dimethylpropionate[22] (71). Mp 95—96 °C; IR (KBr) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.38 (9H, s), 7.25 (2H, d, J=9.2 Hz), 8.27 (2H, d, J=9.2 Hz).

4-Nitrophenyl 3-Phenylpropionate[23] (72). Mp 98—99 °C; IR (KBr) 1747 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.94 (2H, t, J=6.9 Hz), 3.09 (2H, t, J=6.9 Hz), 7.16—7.37 (7H, m), 8.25 (2H, d, J=9.2 Hz).

Typical Experimental Procedure for the Synthesis of α,β-Unsaturated Esters. The same procedure as typical experimental procedure for the catalytic esterification reaction except using phosphate buffer (pH=7) as a reagent for quenching.

3-Phenylpropyl (*E*)-2-Butenoate (73). IR (neat) 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.87 (3H, dd, J=6.9, 1.7 Hz), 1.99 (2H, tt, J=7.6, 6.6 Hz), 2.70 (2H, t, J=7.6 Hz), 4.14 (2H, t, J=6.6 Hz), 5.85 (1H, dq, J=15.0, 1.7 Hz), 6.96 (1H, dq, J=15.0, 6.9 Hz), 7.15—7.31 (5H, m). Found: C, 76.21; H, 8.00%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

3-Phenylpropyl 3-Methyl-2-butenoate (75). IR (neat) 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.88 (3H, d, J=1.0 Hz), 1.95 (2H, tt, J=7.9, 6.6 Hz), 2.17 (3H, d, J=1.0 Hz), 2.69 (2H, t, J=7.9 Hz), 4.10 (2H, t, J=6.6 Hz), 5.69 (1H, q, J=1.3 Hz), 7.14—7.30 (5H, m). Found: C, 76.86; H, 8.37%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

(−)-Menthyl (*Z*)-2-Methyl-2-butenoate[11] (77). $[\alpha]_D^{24}$ −86.3° (*c* 1.23, $CHCl_3$); IR (neat) 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.77 (3H, d, J=6.9 Hz), 0.89 (3H, d, J=7.3 Hz), 0.92 (3H, d, J=6.6 Hz), 0.95—2.10 (9H, m), 1.88 (3H, dq, J=1.6, 1.3 Hz), 1.96 (3H, dq, J=7.3, 1.3 Hz), 4.77 (1H, td, J=10.9, 4.3 Hz), 6.00 (1H, qq, J=7.3, 1.6 Hz).

(−)-Menthyl (*E*)-2-Methyl-2-butenoate (78). $[\alpha]_D^{25}$ −85.3° (*c* 1.22, $CHCl_3$); IR (neat) 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.74—2.20 (9H, m), 0.76 (3H, d, J=6.9 Hz), 0.89 (6H, d, J=6.9 Hz), 1.78 (3H, d, J=6.9 Hz), 1.82 (4H, d, J=1.3 Hz), 4.73 (3H, td, J=10.9, 4.3 Hz), 6.83 (1H, qq, J=6.9, 1.3 Hz). Found: C, 75.43; H, 10.71%. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99%.

(+)-5α-Cholestan-3β-yl (*Z*)-2-Methyl-2-butenoate (79). Mp 73—74 °C; $[\alpha]_D^{27}$ +14.86° (*c* 1.00, $CHCl_3$); IR (KBr) 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.60—2.00 (30H, m), 0.65 (3H, s), 0.84 (3H, s), 0.86 (6H, d, J=6.6 Hz), 0.90 (3H, d, J=6.6 Hz), 1.87 (3H, s), 1.95 (3H, d, J=7.25 Hz), 4.77 (1H, tt, J=11.4, 5.0 Hz), 6.00 (q, 1H, J=7.3 Hz); ^{13}C NMR ($CDCl_3$) δ=12.06, 12.26, 15.69, 18.65, 20.61, 21.19, 22.55, 22.82, 23.83, 24.21, 27.64, 28.00, 28.23, 28.63, 32.01, 34.20, 35.47, 35.80, 36.16, 36.79, 39.50, 39.97, 42.57, 42.57, 44.71, 54.20, 56.25, 56.41, 73.51, 128.54, 136.46, 167.89. Found: C, 81.80; H, 11.63%. Calcd for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56%.

(+)-5α-Cholestan-3β-yl (*E*)-2-Methyl-2-butenoate (80). Mp 109—110 °C; $[\alpha]_D^{26}$ +17.95° (*c* 1.03, $CHCl_3$); IR (KBr) 1714 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.60—2.05 (30H, m), 0.65 (3H, s), 0.83 (3H, s), 0.86 (6H, d, J=6.6 Hz), 0.90 (3H, d, J=6.6 Hz), 1.77 (3H, d, J=6.9 Hz), 1.81 (3H, s), 4.74 (1H, tt, J=11.2, 4.8 Hz), 6.82 (1H, q, J=6.9 Hz); ^{13}C NMR ($CDCl_3$) δ=12.04, 12.24, 12.24, 14.27, 18.64, 21.19, 22.54, 22.81, 23.81, 24.19, 27.53, 27.98, 28.23, 28.61, 32.00, 34.11, 35.46, 35.78, 36.14, 36.77, 39.48, 39.97, 42.55, 42.55, 44.64, 54.20, 56.23, 56.39, 73.59, 129.13, 136.44, 167.69. Found: C, 81.84; H, 11.65%. Calcd for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56%.

Phenyl (*Z*)-2-Methyl-2-butenoate (81). IR (neat)

1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.05 (3H, d, J=1.0 Hz), 2.08 (3H, d, J=7.3 Hz), 6.25 (1H, qq, J=7.3, 1.0 Hz), 7.10—7.14 (2H, m), 7.19—7.25 (1H, m), 7.36—7.42 (2H, m). Found: C, 74.76; H, 6.76%. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%.

Phenyl (*E*)-2-Methyl-2-butenoate (82). IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.87 (3H, d, J=7.3 Hz), 1.95 (3H, s), 7.07—7.15 (3H, m), 7.18—7.24 (1H, m), 7.34—7.41 (2H, m). Found: C, 74.76; H, 6.80%. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%.

We would like to thank Mr. Hideji Saito (Kyorin Pharmaceutical Co., Ltd.) for the elemental analysis.

References

1) a) E. Haslam, *Tetrahedron*, **36**, 2409 (1980); Acidic condition: b) $(CF_3CO)_2O$: R. C. Parish and L. M. Stock, *J. Org. Chem.*, **30**, 927 (1965); c) BF_3·Et_2O: J. L. Marshall, K. C. Erickson, and T. K. Folsom, *Tetrahedron Lett.*, **1970**, 4011; d) H_3BO_3: W. W. Lowrance, Jr., *Tetrahedron Lett.*, **1971**, 3453; e) $AlCl_3$; E. C. Blossey, L. M. Turner, and D. C. Neckers, *Tetrahedron Lett.*, **1973**, 1823; f) $FeCl_3$: B. Ganem and V. R. Small, Jr., *J. Org. Chem.*, **39**, 3728 (1974); S. J. Danishefsky and N. Mantlo, *J. Am. Chem. Soc.*, **110**, 8129 (1988); g) Me_3SiCl, Me_2SiCl_2, $MeSiCl_3$, $SiCl_4$: R. Nakao, K. Oka, and T. Fukumoto, *Bull. Chem. Soc. Jpn.*, **54**, 1267 (1981); h) $ZnCl_2$: S. Kim and W. J. Lee, *Synth. Commun.*, **16**, 659 (1986); i) R_2SnCl_2: A. K. Kumar and T. K. Chattopadhyay, *Tetrahedron Lett.*, **28**, 3713 (1987); j) $(^nBu_2XSnOSn^nBu_2Y)_2$: J. Otera, N. Dan-oh, and H. Nozaki, *J. Org. Chem.*, **56**, 5307 (1991); k) $CoCl_2$: J. Iqbal and R. R. Srivastava, *J. Org. Chem.*, **57**, 2001 (1992).

2) K. Saigo, M. Usui, K. Kikuchi, E. Shimada, and T. Mukaiyama, *Bull Chem. Soc. Jpn.*, **50**, 1863 (1977).

3) J. Inanaga, K. Hirata, H. Saeki, T. Katsuki, and M. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **52**, 1989 (1979).

4) T. Mukaiyama, I. Shiina, and M. Miyashita, *Chem. Lett.*, **1992**, 625; T. Mukaiyama, M. Miyashita, and I. Shiina, *Chem. Lett.*, **1992**, 1747.

5) a) Stereoselective glycosylations: T. Mukaiyama, M. Katsurada, and T. Takashima, *Chem. Lett.*, **1991**, 985; T. Mukaiyama and K. Matsubara, *Chem. Lett.*, **1992**, 1755; T. Mukaiyama, M. Katsurada, and Y. Iida, *Chem. Lett.*, **1992**, 2105; b) Catalytic Friedel-Crafts acylation reactions: T. Mukaiyama, T. Ohno, T. Nishimura, S. Suda, and S. Kobayashi, *Chem. Lett.*, **1991**, 1059; T. Mukaiyama and K. Suzuki, *Chem. Lett.*, **1992**, 1751; c) Catalytic Beckmann rearrangement: T. Mukaiyama and T. Harada, *Chem. Lett.*, **1991**, 1653; d) Catalytic Pinacol rearrangement: T. Harada and T. Mukaiyama, *Chem. Lett.*, **1992**, 81; e) Catalytic esterification reaction: I. Shiina and T. Mukaiyama, *Chem. Lett.*, **1992**, 2319.

6) S. Masamune, G. S. Bates, and J. W. Corcoran, *Angew. Chem., Int. Ed. Engl.*, **16**, 585 (1977).

7) Basic condition: a) Y. Watanabe, S. Shoda, and T. Mukaiyama, *Chem. Lett.*, **1976**, 741; b) Y. Kawanami, Y. Dainobu, J. Inanaga, T. Katsuki, and M. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 943 (1981); Acidic condition: c) $AlCl_3$: T. Mukaiyama, T. Takeda, and K. Atsumi, *Chem. Lett.*, **1974**, 187; d) ZnI_2: J. Y. Gauthier, F. Bourdon, and R. N. Young, *Tetrahedron Lett.*, **27**, 15 (1986); e) $CoCl_2$: S. Ahmad and J. Iqbal, *Tetrahedrom Lett.*, **27**, 3791 (1986).

8) M. Schmeißer, P. Sartori, and B. Lippsmeier, *Chem. Ber.*, **103**, 868 (1970); Y. Tanabe, *Bull. Chem. Soc. Jpn.*, **62**, 1917 (1989).

9) S. Shoda and T. Mukaiyama, *Chem. Lett.*, **1980**, 391; S. Shoda, Ph. D. Thesis, The University of Tokyo, Tokyo, Japan, 1980.

10) Homogynolide-A: a) B. Hartmann, A. M. Kanazawa, J.-P. Deprés, and A. E. Greene, *Tetrahedron Lett.*, **32**, 767 (1991); Homogynolide-B: b) F. Coelho, J.-P. Deprés, T. J. Brocksom, and A. E. Greene, *Tetrahedron Lett.*, **30**, 565 (1989).

11) B. Hartmann, A. M. Kanazawa, J.-P. Deprés, and A. E. Greene, *Tetrahedron Lett.*, **32**, 5077 (1991).

12) J. Blum and B. Zinger, *J. Org. Chem.*, **43**, 2961 (1978).

13) A. Alexakis, D. Jachiet, and J. F. Normant, *Tetrahedron*, **42**, 5607 (1986).

14) H.-J. Gais, *Angew. Chem.*, **89**, 251 (1977).

15) D. L. Foerst and J. R. Grunwell, *J. Org. Chem.*, **42**, 3307 (1977).

16) S. Oae, T. Aida, and N. Furukawa, *Chem. Pharm. Bull.*, **23**, 3011 (1975).

17) S. Hackett and T. Livinghouse, *Tetrahedron Lett.*, **25**, 3539 (1984).

18) E. Vedejs, H. Mastalerz, G. P. Meier, and D. W. Powell, *J. Org. Chem.*, **46**, 5253 (1981).

19) M. Tada, T. Uetake, and M. Matsumoto, *J. Chem. Soc., Chem. Commun.*, **1990**, 1408.

20) R. H. Ryubrandt and F. E. Dutton, *J. Org. Chem.*, **40**, 3079 (1975).

21) M. I. Amer, B. L. Booth, G. F. M. Noori, and M. F. J. R. P. Proenca, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1075.

22) K. B. Sloan and S. A. M. Koch, *J. Org. Chem.*, **48**, 3777 (1983).

23) S. Takahashi and L. A. Cohen, *J. Org. Chem.*, **35**, 1505 (1970).

24) L. A. Cohen and S. Takahashi, *J. Am. Chem. Soc.*, **95**, 443 (1973).

25) S. Kim, J. I. Lee, and Y. C. Kim, *J. Org. Chem.*, **50**, 560 (1985).

26) J. B. Milstien and T. H. Fife, *J. Am. Chem. Soc.*, **90**, 2164 (1968).