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A New Method for the Synthesis of Carboxylic Esters and Lactones with Di-2-thienyl Carbonate (2-DTC) by the Promotion of DMAP and Iodine

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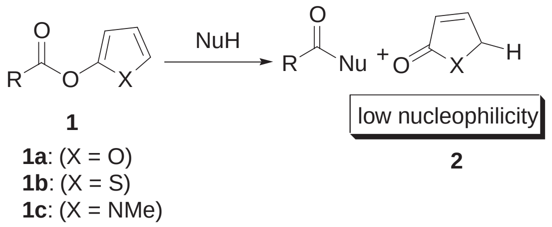
The esterification of carboxylic acids with alcohols by using di-2-thienyl carbonate (2-DTC) in the presence of a catalytic amount of 4-(dimethylamino)pyridine (DMAP) proceeded smoothly to afford the corresponding esters in good-to-high yields along with 2(5*H*)-thiophenone. This esterification was accelerated by the addition of an equimolar amount of iodine to afford the esters in higher yields within a shorter reaction time. Further, cyclization of ω-hydroxycarboxylic acids with an equimolar amount of 2-DTC in the presence of a catalytic amount of DMAP, followed by the addition of 1–4 equimolar amounts of iodine, afforded the corresponding lactones in good-to-high yields under mild conditions. This method was successfully employed in the synthesis of *erythro*-aleuritic acid lactone.

The preparation of carboxylic esters from nearly equimolar amounts of carboxylic acids and alcohols is one of the most important and fundamental methods in synthetic organic chemistry. Therefore, several useful methods for those esterifications have been developed,[1–11] and are widely employed in the synthesis of natural or unnatural molecules that have carboxylic ester moieties. Since the development of useful coupling reagents is still an important topic, to design and prepare active esters that possess a new efficient leaving group is an important problem in synthetic chemistry. Thus, carboxylic acid ester **1**, derived from a five-membered hetero lactone **2**, such as 2(5*H*)-thiophenone **2b**, was chosen because it would behave as a useful reagent that reacts effectively accompanied by the transformation of 2-oxyheteroaryl moieties of **1** to more stable lactone **2**, which is inert and no longer involved in further reactions (Scheme 1). Next, the synthetic strategy for the preparation of active ester **1** from carboxylic acid was planned; namely, the desired active ester **1** is derived from the corresponding carbonate **3** formed by the reaction of a carboxylic acid with a coupling reagent, such as **4** (Scheme 2).

In this communication, we would like to report on di-2-thienyl carbonate (2-DTC), a new and effective coupling reagent, for the esterification of carboxylic acids with alcohols, and also the lactonization of ω-hydroxycarboxylic acids in the presence of a catalytic amount of DMAP and 1–4 equimolar amounts of iodine under mild conditions.

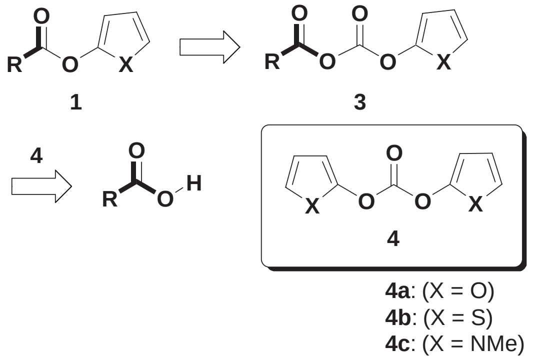


Scheme 1. Esterification by using new active esters.

Results and Discussion

Esterification of Carboxylic Acids with Alcohols by Using Di-2-thienyl Carbonate (2-DTC) via 2-Thienyl Active Esters. In the first place, the reaction of various 2-heteroaryl benzoates **5** with alcohols was tried in the presence of DMAP to examine the reactivity of various active carboxylic esters (Table 1). The desired esters were formed most effectively in the case when 2-furyl benzoate **5a** was used (Entries 1 and 2). The corresponding esters were obtained in good yields upon a treatment of 2-thienyl benzoate **5b** with alcohols for a long time (Entries 3 and 4) while reactions of 2-(1-methylpyrroryl) benzoate **5c** with alcohols proceeded sluggishly and afforded the desired esters in lower yields (Entries 5 and 6).

Next, syntheses of the corresponding coupling reagents **4** were examined to use in the preparations of 2-furanyl ester **1a** (X = O) and 2-thienyl ester **1b** (X = S). The reaction was carried out by using commercially available γ-crotonolactone or 2(5*H*)-thiophenone and triphosgene in the presence of various bases, such as NEt_3 and i-Pr_2NEt in CH_3CN (Table 2). Di-2-thienyl carbonate (2-DTC) **4b** was prepared in good yield



Scheme 2. Preparation of **1** from carboxylic acid by using new coupling reagents **4**.

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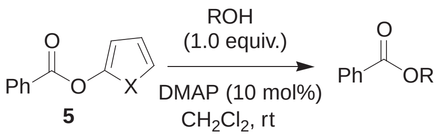
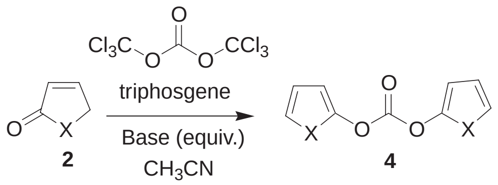
Table 1. Esterification of Various Active Esters **5a**–**c** Prepared from Benzoic Acid with Alcohols in the Presence of DMAP



Entry	**5**	X	ROH	Time/h	Yield ( )[a)]/%
1	**5a**	O	BnOH	1	80
2	**5a**	O	PhOH	1.5	90
3	**5b**	S	BnOH	48	72 (6)
4	**5b**	S	PhOH	24	85 (15)
5	**5c**	NMe	BnOH	48	39 (46)
6	**5c**	NMe	PhOH	24	44 (56)

a) Yield of active esters **5**.

Table 2. Synthesis of Di-2-thienyl Carbonate (2-DTC) from 2(5*H*)-Thiophenone



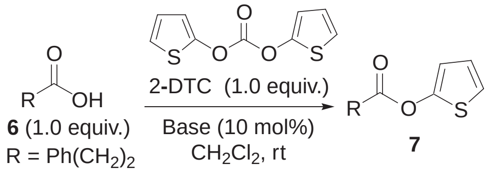
Entry	Base/equiv	**4b** (X = S)		**4a** (X = O)	
		Time /h	Yield /%	Time /h	Yield /%
1	TEA (1.05)	6	29	24	N.D.
2	Pyridine (1.05)	6	N.D.	24	N.D.
3	DBU (1.05)	6	trace	24	N.D.
4	*i*-Pr_2NEt_2 (1.0)	4	73	24	N.D.
5	2,6-di-*t*Bu-Pyridine (1.05)	4	N.D.		
6	Proton sponge[a)] (1.05)	4	N.D.		

a) 1,8-Bis(dimethylamino)naphthalene.

upon a treatment of 2(5*H*)-thiophenone with triphosgene in the presence of *i*-Pr_2NEt (Entry 4); however, the desired di-2-furyl carbonate **4a** was not prepared in the case when γ-crotonolactone was used. It is noted that di-2-thienyl carbonate (2-DTC) **4b** is a stable crystalline compound, and can be stored under argon at room temperature for over one month without any decomposition.

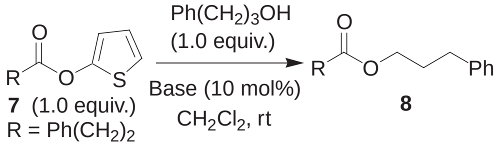
Then, the preparation of 2-thienyl 3-phenylpropionate **7** by using 3-phenylpropionic acid and 2-DTC in the presence of various bases was examined (Table 3). The reaction completed immediately to afford thienyl ester **7** in high yield along with the evolution of carbon dioxide when DMAP was used as a base (Entry 2). On the other hand, the reaction did not proceed effectively in the cases of using other bases, such as NEt_3 or pyridine (Entries 3–6).

Table 3. Synthesis of 2-Thienyl 3-Phenylpropionate



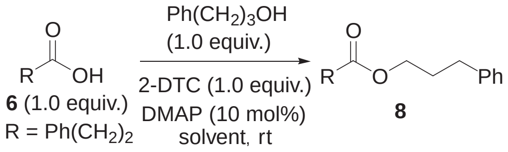
Entry	Base	Time/h	Yield/%
1	none	5	N.D.
2	DMAP	10 (min)	quant.
3	TEA	10	83
4	DBU	4	77
5	Pyridine	32	64
6	TMEDA	4	93

Table 4. Synthesis of 3-Phenylpropyl 3-Phenylpropionate



Entry	Base	Time/h	Yield/%
1	none	22	N.D.
2	DMAP	4	93
3	TEA	22	23
4	DBU	6	76
5	Pyridine	22	N.D.
6	TMEDA	22	16

Table 5. Effect of Solvent



Entry	Solvent	Time/h	Yield/%
1	CH_2Cl_2	6	94
2	Et_2O	9	92
3	THF	24	87
4	CH_3CN	9	84
5	Toluene	24	89
6	DMF	48	38

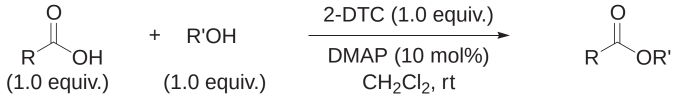
Alcohol was added to mixture of RCO_2H and 2-DTC, DMAP in solvent at 10 min latter.

Next, the effect of bases on the synthesis of the ester from thus-formed thienyl ester **7** and 3-phenyl-1-propanol was studied (Table 4). The corresponding ester **8** was not detected when the acylation of 3-phenyl-1-propanol with **7** was tried in the absence of bases (Entry 1). On the other hand, this reaction proceeded most smoothly when DMAP was used (Entry 2). These results indicate that a catalytic amount of DMAP worked as a useful activator, and the acylpyridinium salts are considered to be key intermediates in the above two steps.

The esterification of 3-phenylpropionic acid with 3-phenyl-1-propanol was then tried by using 2-DTC. The reaction proceeded smoothly in the presence of a catalytic amount of DMAP in CH_2Cl_2 to afford the corresponding ester in high yield.[12] The desired ester was similarly afforded in other solvents, such as Et_2O, CH_3CN, and toluene (Table 5).

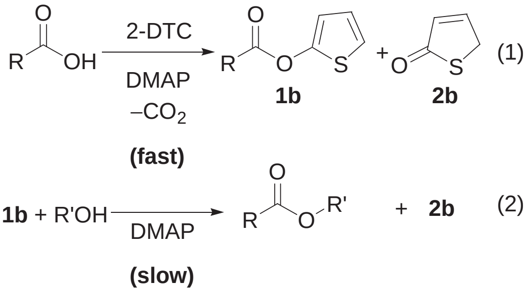
The experimental results obtained by using various carboxylic acids and alcohols are listed in Table 6. The condensation

Table 6. Esterification of Various Carboxylic Acids and Alcohols by Using 2-DTC

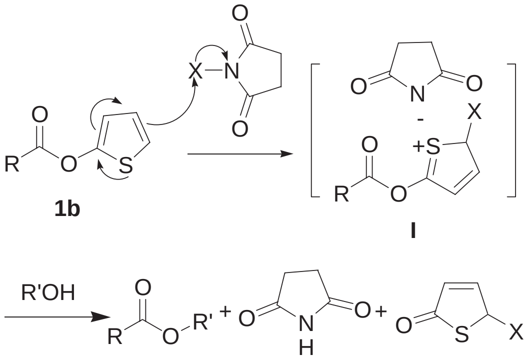


Entry	RCO_2H	$R'OH$	RCO_2R'	Time/h	Yield/%
1	$PhCH_2CH_2CO_2H$	$Ph(CH_2)_3OH$	**8**	6	94
2	$PhCH_2CH_2CO_2H$	BnOH	**9**	4	96
3	$PhCH_2CH_2CO_2H$	$Ph(CH_2)_2CHCH_3OH$	**10**	8	82[a)]
4	$PhCH_2CH_2CO_2H$	$c\text{-}C_6H_{11}OH$	**11**	11	81[a)]
5	$PhCH_2CH_2CO_2H$	PhOH	**12**	2	95
6	$c\text{-}C_6H_{11}CO_2H$	$Ph(CH_2)_3OH$	**13**	11	87
7	$PhMeCHCO_2H$	$Ph(CH_2)_3OH$	**14**	4	95[a)]
8	$PhMeCHCO_2H$	$c\text{-}C_6H_{11}OH$	**15**	8	92[a)]
9	Ph_2CHCO_2H	$Ph(CH_2)_3OH$	**16**	11	95[a)]
10	Ph_2CHCO_2H	$Ph(CH_2)_2CHCH_3OH$	**17**	22	86[a)]
11	$3\text{-}PyCH_2CH_2CO_2H$	$Ph(CH_2)_3OH$	**18**	6	84
12	$PhCH_2CH_2CO_2H$	$THPO(CH_2)_5OH$	**19**	9	93
13	$PhCH(OTBS)CH_2CO_2H$	$Ph(CH_2)_3OH$	**20**	21	85
14	$(E)\text{-}PhCH{=}CHCO_2H$	$Ph(CH_2)_3OH$	**21**	22	37
15	$PhCO_2H$	$Ph(CH_2)_3OH$	**22**	22	33
16	Me_3CCO_2H	$Ph(CH_2)_3OH$	**23**	22	N.D.

a) 1.2 equiv of alcohol was used.



Scheme 3. Esterification of carboxylic acids with alcohols using 2-DTC in the presence of DMAP.



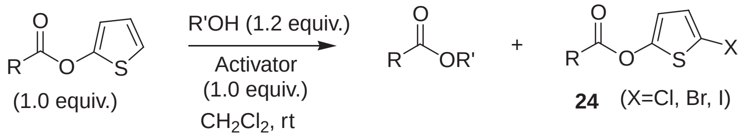
Scheme 4. Acylation of 2-thienyl ester **1b** with alcohol using halogenating reagents.

of 3-phenylpropionic acid with various alcohols afforded the corresponding esters in good-to-high yields (Entries 1–5). The corresponding esters were also obtained in good yields when α,α-disubstituted carboxylic acids and secondary alcohols were used (Entries 8 and 10). In the case when substrates possessing a basic part or acid-sensitive moieties in the same molecule were used, esters were also obtained in good-to-high yields (Entries 11–13). On the other hand, this method had some disadvantages because it needed a relatively long reaction time, and failed to work well when cinnamic acid, aromatic acid, or hindered carboxylic acid, such as pivalic acid, were used (Entries 14–16). Therefore, it was desired to develop a more effective method of 2-DTC-mediated esterification applicable to a variety of carboxylic acids.

This reaction is considered to proceed via a two-step procedure: i.e., i) the reaction of carboxylic acid with 2-DTC that formed thienyl ester **1b** and ii) the formation of an ester from thus-formed **1b** and various alcohols (Scheme 3). Since it was the second step that controlled the reaction rate, it was assumed that acceleration of the acylation step of alcohol with thienyl ester **1b** was essential. Then, the halogenation of thienyl ester **1b** was studied first because 2-oxythiophene moiety of the thienyl ester **1b** was thought to behave as a nucleophile in the coexistence of oxidants, such as halogenating reagents. Since thienyl ester **1b** was halogenated readily by using suitable halogenating reagents, such as *N*-haloimides, to form an active intermediate **I**, the reaction was expected to proceed smoothly under mild conditions to afford esters (Scheme 4). Based on this consideration, the esterification of thienyl esters with alcohols by using several halogenating reagents was studied next.

Then, the reaction of 2-thienyl 3-phenylpropionate **7** ($R = Ph(CH_2)_2$) with 3-phenyl-1-propanol was tried by using various halogenating reagents (Table 7). When *N*-haloimides, such as *N*-bromosuccinimide, *N*-iodosuccinimide, *N*-chlorosuccinimide, and *N*-bromophthalimide, were used (Entries 3–6), the desired esters were always obtained in low yields, and mostly 5-halogenated 2-thienyl 3-phenylpropionate **24** was afforded. In the case of using copper(I) iodide, the desired ester was not detected, although it was thought that the affinity of copper to sulfur would promote this reaction (Entry 7). On the other

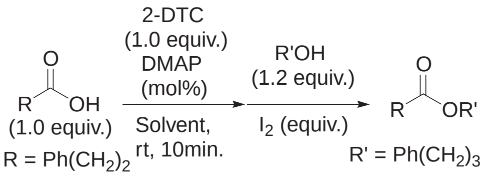
Table 7. Effect of Halogenating Reagents



Entry	R	R′	Activator	Time/h	Yield/%	
					Ester	**24**
1	$PhCH_2CH_2$	$Ph(CH_2)_3$	none	22	N.D.	N.D.
2	$PhCH_2CH_2$	$Ph(CH_2)_3$	DMAP[a)]	4	93	N.D.
3	$PhCH_2CH_2$	$Ph(CH_2)_3$	NBS	2	23[c)]	59
4	$PhCH_2CH_2$	$Ph(CH_2)_3$	NIS	48	40[c)]	35
5	$PhCH_2CH_2$	$Ph(CH_2)_3$	NCS	48	22[c)]	39
6	$PhCH_2CH_2$	$Ph(CH_2)_3$	NBP[b)]	4	36	52
7[d)]	$PhCH_2CH_2$	$Ph(CH_2)_3$	CuI	22	N.D.	N.D.
8	$PhCH_2CH_2$	$Ph(CH_2)_3$	I_2	1	83	N.D.
9	$PhCH_2CH_2$	$Ph(CH_2)_3$	Br_2	2	94	N.D.
10	Ph	Bn	I_2	2.5	76	N.D.
11	Ph	Bn	Br_2	3	28	36

a) 10 mol% of DMAP was used. b) *N*-bromophthalimide. c) 1.0 equiv of alcohol was used. d) CH_3CN was used as a solvent.

Table 8. Esterification of 3-Phenylpropionic Acid with 3-Phenyl-1-propanol in the Presence of DMAP and Iodine



Entry	DMAP /mol%	I_2/equiv	Solvent	Time/h	Yield/%
1	10	none	CH_2Cl_2	6	94
2	10	I_2 (1.1)	Et_2O	2	94
3	10	I_2 (1.1)	THF	2	71
4	10	I_2 (1.1)	Toluene	1	82
5	10	I_2 (1.1)	CH_2Cl_2	0.5	91
6	10	I_2 (1.1)	CH_3CN	0.5	91
7	5	I_2 (1.05)	CH_2Cl_2	1.5	92[a)]
8	5	I_2 (1.05)	CH_3CN	0.5	94

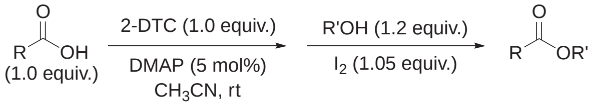
a) Reaction time for the formation of 2-thienyl ester, active ester, became longer (1 h).

hand, the desired ester was obtained in good-to-high yields when iodine or bromine was used as an activator (Entries 8 and 9). Then, the esterification of 2-thienyl benzoate **5b** (R = Ph) with benzyl alcohol was further examined by using iodine or bromine as an activator, and the corresponding ester was obtained in a good yield when iodine was used (Entry 10). In the case of using bromine, however, the yield was low and 5-bromo-2-thienyl benzoate was formed as a main product (Entry 11). These results clearly indicated that iodine is effective for promoting of the present esterification.

The esterification of carboxylic acids with alcohols was then tried by using 2-DTC (Table 8). The reaction proceeded rapidly when an equimolar amount of iodine was added in the presence of a catalytic amount of DMAP in CH_2Cl_2 or CH_3CN, and the corresponding esters were obtained in high yields (Entries 5 and 6). Further, it is noteworthy that even when the amount of DMAP was reduced to 1/2, the formation of thienyl ester **1b** of the first step proceeded smoothly in CH_3CN while the reaction of forming **1b** proceeded more sluggishly in CH_2Cl_2 (Entries 7 and 8).

The results of esterifications using various carboxylic acids and alcohols by the above-mentioned method of using only a catalytic amount of DMAP (method A)[12] or a method of the combined use of a catalytic amount of DMAP and an equimolar amount of iodine (method B)[13] are listed in Table 9. The esterification of 3-phenylpropionic acid with various alcohols proceeded smoothly to afford the corresponding esters in good-to-high yields when nearly equimolar amounts of primary or secondary alcohols were used (method B, Entries 1–4). Also, esters were obtained in good-to-high yields in the case when α,α-disubstituted carboxylic acids were used (method B, Entries 5–7). A hindered carboxylic acid, such as pivalic acid, also afforded the desired esters rapidly in good-to-high yields, whereas the corresponding ester was not afforded at all in the absence of iodine (method A, Entry 8). It is interesting to note that these reactions completed rapidly in the presence of iodine i.e. 30 min–1 h (method B, Entries 1–9). On the other hand, it took a much longer time i.e. 2–48 h in the absence of iodine (method A, Entries 1–8). Similarly, the corresponding esters were also obtained rapidly in good-to-high yields when *trans*-cinnamic acid as well as crotonic acid and aromatic acids were used (method B, Entries 14–17, 20, and 21), whereas these acids gave the corresponding esters in low yields when the reactions were carried out under the conditions of method A (Entries 14–16, 20, and 21). It is noteworthy that the corresponding esters were obtained in good-to-high yields when substrates containing active olefinic moieties, such as *trans*-hexenoic acid or *trans*-styrylacetic acid, were used in the presence of iodine (method B, Entries 18 and 19). However, it needed a relatively long reaction time, and failed to work well when aliphatic acids having an aryl group on the α-position of carbonyl or aromatic acids having elec-

Table 9. Esterification of Various Carboxylic Acids with Alcohols Using 2-DTC Promoted by DMAP and Iodine (Methods A and B)



Entry	RCO_2H	R′OH	RCO_2R'	Method B		Method A	
				Time/h	Yield/%	Time/h	Yield/%
1	$PhCH_2CH_2COOH$	$Ph(CH_2)_3OH$	**8**	0.5	94	6	94[a)]
2	$PhCH_2CH_2COOH$	$Ph(CH_2)_2CH(OH)CH_3$	**10**	0.5	90	8	82
3	$PhCH_2CH_2COOH$	$c\text{-}C_6H_{11}OH$	**11**	1	88	11	81
4	$PhCH_2CH_2COOH$	PhOH	**12**	0.5	84	2	95[a)]
5	$c\text{-}C_6H_{11}COOH$	$Ph(CH_2)_3OH$	**13**	0.5	91	11	87[a)]
6	$c\text{-}C_6H_{11}COOH$	$Ph(CH_2)_2CH(OH)CH_3$	**25**	0.5	93[b)]	48	69
7	$c\text{-}C_6H_{11}COOH$	$c\text{-}C_6H_{11}OH$	**26**	0.5	89	42	86
8	Me_3CCOOH	$Ph(CH_2)_3OH$	**23**	0.5	91	22	N.D.
9	Me_3CCOOH	$Ph(CH_2)_2CH(OH)CH_3$	**27**	0.5	81		
10	PhMeCHCOOH	$Ph(CH_2)_3OH$	**14**	2	93[b)]	4	95
11	PhMeCHCOOH	$c\text{-}C_6H_{11}OH$	**15**	2	81[c)]	8	92
12	$Ph_2CHCOOH$	$Ph(CH_2)_3OH$	**16**	6	51[c)]	11	95
13	$Ph_2CHCOOH$	$Ph(CH_2)_2CH(OH)CH_3$	**17**	6	52[c)]	22	86
14	(*E*)-PhCH=CHCOOH	$Ph(CH_2)_3OH$	**21**	0.5	88	22	37
15	(*E*)-PhCH=CHCOOH	$Ph(CH_2)_2CH(OH)CH_3$	**28**	0.5	83	22	22
16	(*E*)-$CH_3CH=CHCOOH$	$Ph(CH_2)_3OH$	**29**	0.5	84	22	<8
17	(*E*)-$CH_3CH=CHCOOH$	$Ph(CH_2)_2CH(OH)CH_3$	**30**	0.5	82		
18	(*E*)-$PhCH=CHCH_2COOH$	$Ph(CH_2)_3OH$	**31**	2	85[d)]		
19	(*E*)-$EtCH=CHCH_2COOH$	$Ph(CH_2)_3OH$	**32**	1	80[d)]		
20	PhCOOH	$Ph(CH_2)_3OH$	**22**	6	89	22	33[a)]
21	*p*-MeOPhCOOH	$Ph(CH_2)_3OH$	**33**	0.5	87	22	3[a)]
22	*p*-ClPhCOOH	PhOH	**34**	4	68	14	94
23	*p*-$CF_3PhCOOH$	PhOH	**35**	24	32	12	91
24	*p*-$NO_2PhCOOH$	PhOH	**36**	24	25	14	90

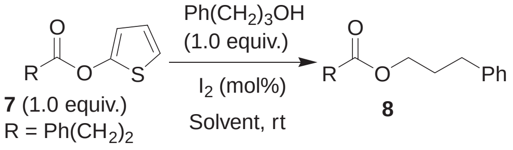
Method A: To a mixture of carboxylic acids (1.0 equiv) and 2-DTC (1.0 equiv) in CH_2Cl_2 was added DMAP (10 mol %). After stirring for 10 minutes at room temperature, alcohols (1.2 equiv) was added and the mixture was stirred at room temperature. Method B: To a mixture of carboxylic acids (1.0 equiv) and 2-DTC (1.0 equiv) in CH_3CN was added DMAP (5 mol %). After stirring for 10 minutes at room temperature, alcohols (1.2 equiv) was added and then iodine (1.05 equiv) was added. The reaction mixture was stirred at room temperature. a) 1.0 equiv of alcohol was used. b) Reactions were performed by using 10 mol % of DMAP, and 1.1 equiv of iodine, and CH_2Cl_2 as a solvent. c) Reactions were performed by using 10 mol % of DMAP, and 1.5 equiv of iodine, and CH_2Cl_2 as a solvent. d) Toluene was used as a solvent.

tron-withdrawing groups were used (method B, Entries 10–13 and 22–24). On the other hand, these acids gave the corresponding esters in high yields under the conditions of method A (Entries 10–13 and 22–24). These results indicate that the desired esters were obtained in high yields by a suitable choice of one of these two methods (method A and B) according to the nature of the substrates.

In order to improve the utility of 2-DTC mediated esterification, the above reaction was tried by using catalytic amounts of DMAP and iodine. Then, the acylation of 3-phenyl-1-propanol with 2-thienyl ester **7** in the presence of a catalytic amount of iodine was examined (Table 10). The reaction proceeded effectively to afford the corresponding ester in high yield when 10 mol % of iodine was used in CH_3CN (Entry 6), whereas the reaction was very slow in CH_2Cl_2 (Entry 2). The above results indicate that a catalytic amount of iodine worked effectively in the second step that afforded esters.

Next, the esterification of various carboxylic acids with alcohols was tried by using 2-DTC in the presence of a catalytic amount of DMAP and iodine in CH_3CN (Table 11). The reaction proceeded smoothly to afford the corresponding esters in good-to-high yields, except when cyclohexanol or pivalic acid was used (Entries 4 and 7).

Table 10. Esterification of 2-Thienyl 3-Phenylpropionate in the Presence of a Catalytic Amount of Iodine

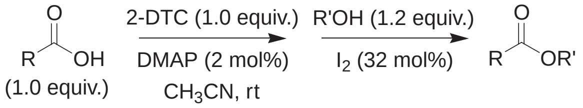


7 (1.0 equiv.)
R = $Ph(CH_2)_2$

8

Entry	I_2/mol %	Solvent	Time/h	Yield/%
1	100	CH_2Cl_2	2.5	83
2	20	CH_2Cl_2	24	71
3	100	CH_3CN	0.5	93
4	30	CH_3CN	0.5	87
5	20	CH_3CN	0.5	95
6	10	CH_3CN	1	90

Table 11. Esterification of Various Carboxylic Acids and Alcohols in the Presence of Catalytic Amounts of DMAP and Iodine



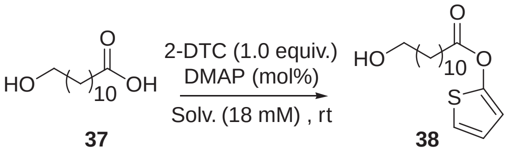
Entry	RCO_2H	$R'OH$	Time/h	Yield/%
1	$PhCH_2CH_2COOH$	$Ph(CH_2)_3OH$	2	90
2	$PhCH_2CH_2COOH$	BnOH	0.5	91
3	$PhCH_2CH_2COOH$	$Ph(CH_2)_2CH(OH)CH_3$	2	80
4	$PhCH_2CH_2COOH$	c-$C_6H_{11}COOH$	3.5	58[a)]
5	c-$C_6H_{11}COOH$	$Ph(CH_2)_3OH$	0.5	84
6	c-$C_6H_{11}COOH$	$Ph(CH_2)_2CH(OH)CH_3$	0.5	81
7	Me_3CCOOH	$Ph(CH_2)_3OH$	2	57[b)]
8	$PhCH{=}CHCOOH$	$Ph(CH_2)_3OH$	0.5	81
9	$CH_3CH{=}CHCOOH$	$Ph(CH_2)_3OH$	1.5	74
10	p-MeOPhCOOH	$Ph(CH_2)_3OH$	2	86

a) 2 mol % of DMAP and 52 mol % of iodine were used. b) 5 mol % of DMAP and 35 mol % of iodine were used.

Lactonization of ω-Hydroxycarboxylic Acids by Using Di-2-thienyl Carbonate (2-DTC) via 2-Thienyl Active Esters. Natural products having a macrolide structure are important therapeutic agents in clinical medicine because of their antibiotic, antitumoral, and other various helpful biochemical activities. Accordingly, to prepare macrolactones from ω-hydroxycarboxylic acids is also a major concern in synthetic organic chemistry. Several useful methods have therefore been reported: namely, the use of *N*,*N*-dicyclohexylcarbodiimide (DCC),[1] 2,4,6-trichlorobenzoyl chloride,[2] 2,2′-dipyridyl disulfide/Ph_3P,[3] 1-methyl-2-chloropyridinium iodide/Et_3N,[4] diethyl azodicarboxylate (DEAD)/Ph_3P,[5] 2-methyl-6-nitrobenzoic anhydride (MNBA),[8] 4-(trifluoromethyl)benzoic anhydride,[9] 4-nitrobenzoic anhydride/$Sc(OTf)_3$,[10] etc.

In the previous section, a new esterification method between nearly equimolar amounts of carboxylic acids and alcohols by using 2-DTC in the presence of a catalytic amount of DMAP is described. In addition, it was found that this esterification was accelerated by further addition of an equimolar amount of iodine, which improved the reaction time and yield. This result prompted us to study the 2-DTC-mediated macrolactonization of ω-hydroxycarboxylic acids in the coexistence of iodine.[14] In the first place, the synthesis of 2-thienyl 12-hydroxydodecanoate **38**, an active ester intermediate, was examined by treating 12-hydroxydodecanoic acid **37** with 2-DTC in the presence of a catalytic amount of DMAP (Table 12). The formation of **38** was considerably influenced by solvents, and was obtained most effectively when the reaction was carried out in CH_3CN (Entry 5), and also when the amount of DMAP was reduced to 5 mol % (Entry 6). It is interesting to note that the corresponding lactone was not detected when it was allowed to react under more concentrated conditions (35 mM) for 9 h (Entry 7). This indicates that the lactonization is not accelerated by DMAP alone; therefore, it needed to use the second activator so as to form a lactone efficiently.

Table 12. Synthesis of 2-Thienyl 12-Hydroxy Dodecanoate **38** Using 12-Hydroxydodecanoic Acid **37** and 2-DTC in the Presence of DMAP



Entry	Solvent	DMAP/mol %	Time/min	Yield/%
1	CH_2Cl_2	10	60	81
2	Toluene	10	90	73
3	THF	10	120	59
4	Et_2O	10	120	49
5	CH_3CN	10	15	97
6	CH_3CN	5	15	95
7	CH_3CN	5	9 h	96[a)]

a) Concentration 35 mM.

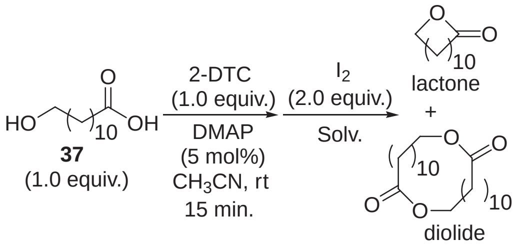
Next, the lactonization of 12-hydroxydodecanoic acid which uses 2-DTC in the presence of DMAP and iodine, was examined (Table 13). Acetonitrile then turned out to be the most suitable solvent for the preparation of thienyl ester **38**, as described above. However, the corresponding lactone was obtained in low yield when a solution of 12-hydroxydodecanoic acid, 2-DTC, and DMAP in CH_3CN was diluted to 2 mM by further addition of CH_3CN and iodine at room temperature (Entry 1).

Thus, thienyl ester **38** was successfully prepared in CH_3CN, and the effect of the further addition of other solvents to the above solution in the lactonization step under diluted condition was examined next. After screening several solvents, it was show that the desired lactone was obtained in 47% yield in a 2 mM solution by further addition of toluene (Entry 6).

It is also noted that the corresponding lactone was not detected when the above reaction was carried out in the presence of DMAP (2.05 equiv) instead of iodine (Entry 7). This result indicates that iodine works quite effectively in this lactonization step.

With these results in mind, the amounts of iodine and solvents were further examined in order to optimize the reaction conditions (Table 14). Finally, it was found that the desired 12-dodecanolide was obtained in 77% yield in the case when the

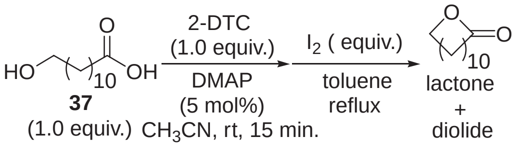
Table 13. Lactonization of 12-Hydroxydodecanoic Acid **37** by Using 2-DTC Promoted by DMAP and Iodine



Entry	Solvent (2 mM)[a)]	Time/h	Yield[b)]/%	
			Lactone	Diolide
1	CH_3CN	24	28	8.6
2	CH_3NO_2	24	25	3
3[c)]	Et_2O	8	N.D.	N.D.
4[c)]	THF	8	N.D.	trace
5[c)]	CH_2Cl_2	8	<26	11
6[c)]	toluene	8	47	22
7[c),d)]	toluene	8	N.D.	N.D.

A solution of **37** with 2-DTC in CH_3CN (10 mL) was added DMAP and diluted with solvent (78 mL), followed by addition of iodine at room temperature. a) Values in parentheses was the concentration without consideration of a change of total volume owing to mix plural solvents. b) Isolated yield. c) reflux. d) Reaction was carried by using 2 equivalents of DMAP instead of iodine.

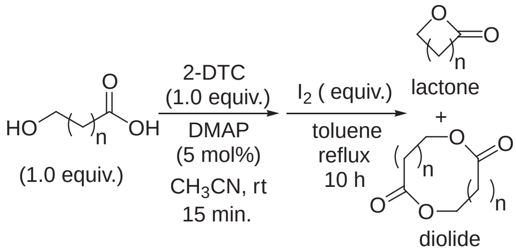
Table 14. Lactonization of 12-Hydroxydodecanoic Acid **37** by Using 2-DTC Promoted by DMAP and Iodine in CH_3CN–Toluene



Entry	I_2 /equiv	Conc. /mM[a)]	Time/h	Yield[b)]/%	
				Lactone	Diolide
1	0.5	2	20	40	21
2	1	2	8	50	19
3	2	2	8	47	19
4	1	1	8	57	16
5	2	1	8	67	15
6	4	1	8	77	14

A solution of **37** with 2-DTC in CH_3CN (10 mL) was added DMAP and diluted with toluene (2 mM; 78 mL, 1 mM; 166 mL), followed by addition of iodine at room temperature. a) The concentration without consideration of a change of total volume owing to mix plural solvents. b) Isolated yield.

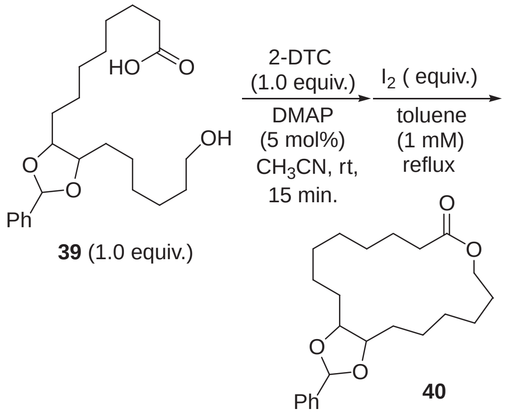
Table 15. Lactonization of Various *ω*-Hydroxy Carboxylic Acids by Using 2-DTC Promoted by DMAP and Iodine



Entry	n	I_2/equiv	Yield[a)]/% (ring size)	
			Lactone	Diolide
1	9	4	58 (12)	18
2	10	4	77 (13)	14
3	11	4	85 (14)	<8
4	12	4	87 (15)	<11
5	13	2	90 (16)	<6
6	14	2	92 (17)	<7

a) Isolated yield.

Table 16. Lactonization of the Protected *erythro*-Aleuritic Acid by Using 2-DTC Promoted by DMAP and Iodine



Entry	I_2 /equiv	Time/h	Yield[a)]/%	
			40	Diolide
1	2	3	85	5
2	1	4	85	<9
3	0.2	20	65	9

A solution of **39** with 2-DTC in CH_3CN (10 mL) was added DMAP and diluted with toluene (166 mL), followed by addition of iodine at room temperature. a) Isolated yield.

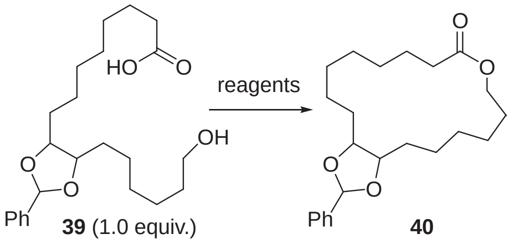
reaction was carried out in a 1 mM solution of toluene in the presence of 4 equimolar amounts of iodine (Entry 6).[12]

The results concerning the lactonization of various *ω*-hydroxycarboxylic acids are listed in Table 15. The corresponding macrolactones were obtained in good-to-high yields along with a small amount of diolide under the reaction conditions mentioned above. The desired product was also obtained in 58% yield when 11-hydroxyundecanoic acid was used (Entry 1). Fourteen to seventeen-membered ring macrolactones were obtained in high yields when the cyclization was carried out using the corresponding *ω*-hydroxycarboxylic acids (Entries 3–6).

Further, the application of this 2-DTC mediated lactonization method to the synthesis of functionalized macrocyclic molecule was tried; that is, the lactonization of seco acid **39** derived from *erythro*-aleuritic acid by using 2-DTC in the presence of DMAP and iodine was examined (Table 16). It is interesting to note that the reaction proceeded smoothly within 3 h under the above reaction conditions to afford the desired lactone **40** in high yield without damaging the acid-sensitive benzylidene protective group (Entry 1). The lactone **40** was also obtained in 85% and 65% yields, respectively, when an equimolar amount of iodine (Entry 2) or a catalytic amount of iodine (20 mol %) was used (Entry 3).

The reported results[8] concerning the synthesis of lactone **40** by using a mixed anhydride, namely, well-known Yamaguchi and the MNBA methods, are listed in Table 17 to compare with that obtained by the present new 2-DTC method.[12] It is noteworthy that the 2-DTC method gave the desired lactone **40** in high yield within a shorter time without employing a slow addition procedure (Entry 1), whereas the above-mentioned mixed anhydride methods needed a long reaction time under the slow addition conditions (Entries 2 and 3).

Table 17. Lactonization of the Protected *erythro*-Aleuritic Acid by Using Other Useful Reagents



39 (1.0 equiv.) **40**

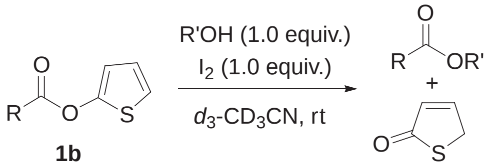
Entry	Reagents /equiv	Time/h	Yield/%	
			40	Diolide
1[a)]	2-DTC (1.0 equiv) /DMAP (5 mol %) /I_2 (2.0 equiv)	3	85	5
2[b)]	2,4,6-Trichlorobenzoyl chloride (1.0 equiv) /Et_3N (1.1 equiv) /DMAP (6.0 equiv)	9	70	9
3[c)]	MNBA (1.2 equiv) /DMAP (2.4 equiv)	16	90	2

a) A solution of **39** (0.177 mmol) with 2-DTC in CH_3CN (10 mL) was added DMAP and diluted with toluene (166 mL), followed by addition of iodine at room temperature and then stirred at reflux temperature. b) A solution of MA derived from **39** (0.360 mmol) and 2,4,6-trichlorobenzoyl chloride in toluene (36 mL) was slowly added to solution of DMAP in toluene (180 mL) at reflux temperature. c) A solution of **39** (0.380 mmol) in CH_2Cl_2 (84.6 mL) was slowly added to solution of reagents in CH_2Cl_2 (135.8 mL) at rt.

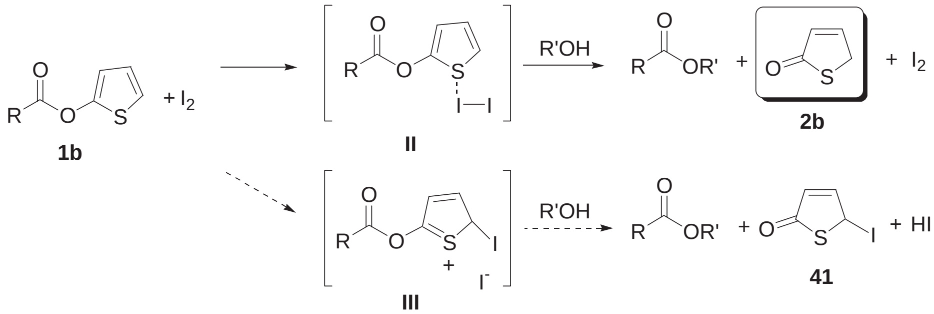
Mechanism for the Esterification of Carboxylic Acids with Alcohols by Using 2-DTC Promoted by DMAP and Iodine. The above procedure consists of two reactions. Step 1; thienyl ester **1b** was formed immediately by treating carboxylic acid with 2-DTC in the presence of DMAP (5 mol %) in CH_3CN. However, no product was formed when an equimolar amount of iodine was used instead of DMAP under the above conditions. Step 2; the corresponding ester was obtained by the acylation of alcohol with isolated thienyl ester **1b** in the presence of 10 mol % of DMAP within 4 h. It is noted that the above reaction proceeded faster (<1 h) in the presence of 10 mol % of iodine to afford the ester in higher yield. These results are explained by considering that a catalytic amount of DMAP behaved effectively in the first step and iodine worked efficiently in the second step.

In order to study the mechanism of this reaction, several 2-thienyl esters were treated with alcohols in the presence of an equimolar amount of iodine in d_3-CD_3CN (Scheme 5). The reaction sequence was followed by measuring ^1H NMR of the reaction mixture to observe the formation of the corresponding esters along with 2(5*H*)-thiophenone **2b**, but not the assumed 5-iodo-2(5*H*)-thiophenone **41**. This is explained by considering an initial formation of the active intermediate **II** instead of the expected active intermediate **III**, and **II** reacts with alcohols to afford the desired esters along with 2(5*H*)-thiophenone (Scheme 6).

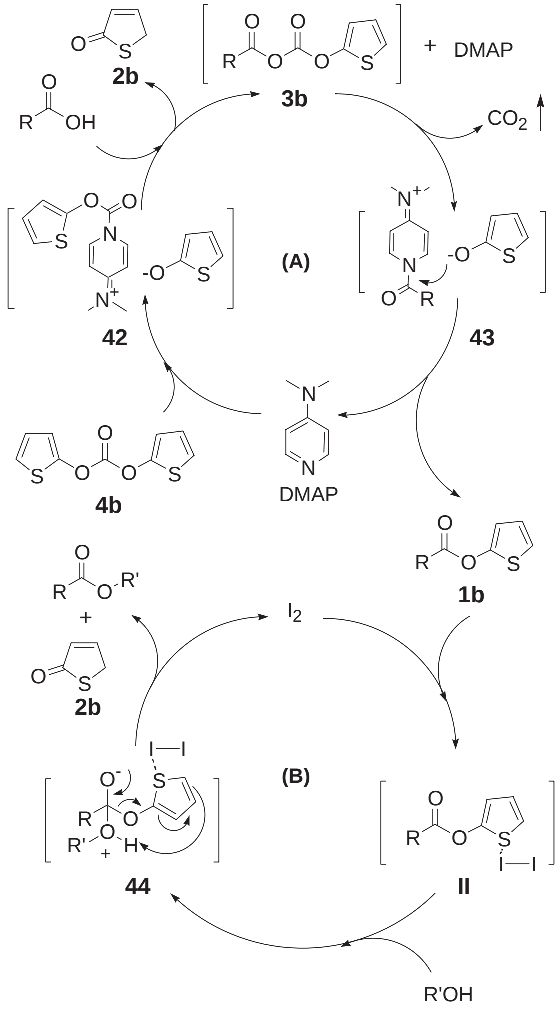
The detailed mechanism concerning the esterification of carboxylic acids with alcohols by using 2-DTC in the presence of DMAP and iodine is shown in Scheme 7. The reaction of 2-DTC **4b** with DMAP formed acylpyridinium salt **42**, which reacted with carboxylic acid to give 2-thienyl carbonate **3b** and 2(5*H*)-thiophenone **2b**. This carbonate **3b** reacted with DMAP to afford the acylpyridinium salt **43** along with the evolution of carbon dioxide. The salt was then converted to 2-thienyl active ester intermediate **1b** along with the regeneration of DMAP (cycle A). The thus-formed **1b** was activated by iodine to generate an intermediate **II**, which in turn reacted with alcohol to afford intermediate **44**. The subsequent capture of a proton from alcohol by the 2-thienyl part of **44** afforded the desired ester along with **2b**, and iodine was regenerated (cycle B).



Scheme 5. NMR study of the reaction of 2-thienyl ester with alcohol in the presence of iodine in d_3-CD_3CN.



Scheme 6. The active intermediate **II** derived from 2-thienyl ester **1b** and iodine.



Scheme 7. The reaction mechanism of esterification of carboxylic acid with alcohol using 2-DTC promoted by DMAP and iodine.

Conclusion

It is noted that an effective method for the synthesis of various esters was developed by using nearly equimolar amounts of free carboxylic acids including aromatic or hindered ones, alcohols, and 2-DTC in the presence of a catalytic amount of DMAP and an equimolar amount of iodine. Further, a simple and effective method for the synthesis of various macrolactones by using equimolar amounts of ω-hydroxycarboxylic acids and 2-DTC in the presence of a catalytic amount of DMAP (5 mol %) and 1–4 equimolar amounts of iodine according to an ordinary addition procedure was successfully established under mild conditions. The utility of this 2-DTC mediated lactonization method was demonstrated by the synthesis of *erythro*-aleuritic acid lactone having an acid-sensitive benzylidene protective group.

Experimental

General. All melting points were determined on a Yanagimoto micro melting-point apparatus (Yanaco MP-S3) and were not corrected. Infrared (IR) spectra were recorded on a JASCO FT-IR 620 spectrometer, or a Horiba FT 710 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. The splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on an EX270L (68 MHz) spectrometer with complete proton decoupling. The chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$; $\delta = 77.0$ ppm, C$_6$D$_6$; $\delta = 128.0$ ppm). Mass spectra (MS) were recorded on a JEOL JMS-SX102A, or SSQ7000 thermoelectron. High-resolution mass spectra (HRMS) were recorded on a Q-Tof ultima global micromass. Analytical TLC was performed on Merck preparative TLC plates (silica gel 60 GF254, 0.25 mm). Column chromatography was carried out on Merck silica gel 60 (0.063–0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica-gel Wakogel B-5F. Reactions in anhydrous dichloromethane, acetonitrile, or toluene were carried out under an argon atmosphere in dried glassware. Dichloromethane was distilled from diphosphorus pentaoxide, then calcium hydride, and dried over MS 4A. Acetonitrile and toluene were purchased from Kanto Chemical as dehydrated solvents and dried over MS 4A. 4-(Dimethylamino)pyridine (DMAP) was purchased from Tokyo Kasei Kogyo and used without further purification. Iodine was purchased from Wako Pure Chemical Industries or Aldrich Chemical and used without further purification. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Kokusan Chemical, Wako Pure Chemical Industries, or Aldrich Chemical. Some carboxylic acids, alcohols, and ω-hydroxycarboxylic acids were used after purification by distillation or recrystallizaion. Other carboxylic acids,[8] alcohols,[8] and ω-hydroxycarboxylic acids ($n = 11$, 12)[10] were prepared following literature procedures.

Di-2-thienyl Carbonate (2-DTC) (4b). Di-2-thienyl carbonate was synthesized from 2(5*H*)-thiophenone. 2(5*H*)-Thiophenone was purchased from Aldrich Chemical. After a mixture of 2(5*H*)-thiophenone (100 mg, 1.0 mmol) and *i*-Pr$_2$NEt (0.174 mL, 1.0 mmol) in CH$_3$CN (3 mL) had been stirred for 10 minutes at room temperature under an argon atmosphere, triphosgene (49.6 mg, 0.167 mmol) in CH$_3$CN (1 mL) was added at -50 °C, and the reaction mixture was stirred for 2 h at -50 °C. After evaporation of the solvent, the residue was dissolved in ether and filtered. After evaporation of the solvent, the residue was separated by short silica-gel column chromatography (eluent: hexane/AcOEt = 12/1) and recrystallized from 2-propanol to afford 2-DTC (82.4 mg, 73%) as a colorless solid. The thus-prepared 2-DTC was stable crystalline and showed no sign of decomposition when kept standing under argon at room temperature for over one month. White powder. mp 53–54 °C. IR (KBr, cm^{-1}) 1766. ^{1}H NMR (270 MHz, C$_6$D$_6$) δ 6.47 (dd, $J = 3.2$, 1.8 Hz, 2H), 6.35 (dd, $J = 6.0$, 3.2 Hz, 2H), 6.29 (dd, $J = 6.0$, 1.8 Hz, 2H). ^{13}C NMR (68 MHz, C$_6$D$_6$) δ 152.6, 150.2, 123.8, 118.5, 114.5. HRMS (EI$^+$) calcd for C$_9$H$_6$O$_3$S$_2$ [M]$^+$ 225.9758, found m/z 225.9784.

2-Thienyl 3-Phenylpropionate (7). Pale yellow oil. IR (neat, cm^{-1}) 1758. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.34–7.19 (m, 5H), 6.87 (dd, $J = 5.8$, 1.9 Hz, 1H), 6.81 (dd, $J = 5.8$, 3.9 Hz, 1H), 6.65 (dd, $J = 3.9$, 1.9 Hz, 1H), 3.06 (t, $J = 7.4$ Hz, 2H), 2.91–2.83 (m, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 169.3, 152.0, 140.0, 128.5, 128.2, 126.4, 123.2, 117.9, 113.2, 35.7, 30.7. HRMS (EI$^+$) calcd for C$_{13}$H$_{12}$O$_2$S [M]$^+$ 232.0558, found m/z 232.0573.

Typical Experimental Procedure for the Synthesis of Carboxylic Esters by Using 2-DTC in the Presence of a Catalytic Amount of DMAP (Method A). To a mixture of 3-phenylpropionic acid (26.5 mg, 0.176 mmol) and 2-DTC (40.0 mg, 0.176 mmol) in CH$_2$Cl$_2$ (0.2 mL) was added DMAP (2.2 mg, 0.0176 mmol). After stirring for 10 minutes at room temperature, 3-phenyl-1-propanol (24.1 mg, 0.176 mmol) was added, and the mixture was stirred for 6 h at room temperature. After evaporation of the solvent, the crude product was purified by preparative thin-layer chromatography to afford the corresponding ester (44.6 mg, 94%).

Typical Experimental Procedure for the Synthesis of Carboxylic Esters by Using 2-DTC Promoted by a Catalytic Amount of DMAP and an Equimolar Amount of Iodine (Method B). To a mixture of 3-phenylpropionic acid (26.5 mg, 0.176 mmol) and 2-DTC (40.0 mg, 0.176 mmol) in CH$_3$CN (0.2 mL) was added DMAP (1.08 mg, 0.0088 mmol). After stirring for 10 minutes at room temperature, 3-phenyl-1-propanol (28.8 mg, 0.211 mmol) and then iodine (47 mg, 0.185 mmol) were added. The reaction mixture was stirred for 30 minutes at room temperature, and then 10% aqueous sodium thiosulfate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin-layer chromatography to afford the corresponding ester (44.3 mg, 94%).

3-Phenylpropyl 3-Phenylpropionate[8] (8). Colorless oil. IR (neat, cm^{-1}) 1734. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32–7.11 (m, 10H), 4.08 (t, $J = 6.5$ Hz, 2H), 2.95 (t, $J = 7.7$ Hz, 2H), 2.68 (t, $J = 7.7$ Hz, 4H), 1.94 (tt, $J = 7.7$, 6.5 Hz, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.7, 141.0, 140.4, 128.4, 128.3, 128.3, 128.2, 126.1, 125.9, 63.8, 35.9, 32.2, 31.0, 30.2.

Benzyl 3-Phenylpropionate[8] (9). Colorless oil. IR (neat, cm^{-1}) 1736. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.39–7.17 (m, 10H), 5.11 (s, 2H), 2.97 (t, $J = 7.8$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.5, 140.2, 135.7, 128.4, 128.4, 128.2, 128.2, 128.1, 126.1, 66.3, 36.0, 31.0.

1-Methyl-3-phenylpropyl 3-Phenylpropionate[8] (10). Colorless oil. IR (neat, cm^{-1}) 1731. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.31–7.11 (m, 10H), 4.86 (tq, $J = 9.5$, 6.3 Hz, 1H), 2.95 (t, $J = 7.8$ Hz, 2H), 2.66–2.48 (m, 2H), 2.60 (t, $J = 7.8$ Hz, 2H), 1.96–1.70 (m, 2H), 1.21 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.3, 141.4, 140.4, 128.3, 128.3, 128.2, 128.2, 126.1, 125.8, 70.5, 37.6, 36.2, 31.8, 31.1, 20.1.

Cyclohexyl 3-Phenylpropionate[8] (11). Colorless oil. IR (neat, cm^{-1}) 1731. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.34–7.16 (m, 5H, Ph), 4.81–4.70 (m, 1H), 2.95 (t, $J = 7.8$ Hz, 2H), 2.61 (t, $J = 7.8$ Hz, 4H), 1.84–1.21 (m, 10H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.2, 140.5, 128.3, 128.2, 126.1, 72.6, 36.3, 31.7, 31.1, 25.4, 23.8.

Phenyl 3-Phenylpropionate[15] (12). Colorless oil. IR (neat, cm^{-1}) 1759. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.39–6.97 (m, 10H), 3.08 (t, $J = 7.4$ Hz, 2H), 2.88 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 171.2, 150.4, 140.0, 129.3, 128.5, 128.3, 126.3, 125.7, 121.4, 36.0, 31.0.

3-Phenylpropyl Cyclohexanecarboxylate[8] (13). Colorless oil. IR (neat, cm^{-1}) 1732. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32–7.16 (m, 5H), 4.08 (t, $J = 6.6$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 2.35–2.24 (m, 1H), 2.00–1.88 (m, 4H), 1.78–1.63 (m, 2H), 1.52–1.12 (m, 6H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 176.0, 141.1, 128.3, 128.3, 125.8, 63.4, 43.3, 32.2, 30.3, 29.1, 25.8, 25.5.

3-Phenylpropyl 2-Phenylpropionate (14). Colorless oil. IR (neat, cm^{-1}) 1733. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.36–7.13 (m, 8H), 7.06–7.03 (m, 2H), 4.06 (t, $J = 6.3$ Hz, 2H), 3.72 (q, $J = 7.2$ Hz, 1H), 2.54 (t, $J = 7.7$ Hz, 2H), 1.88 (tt, $J = 7.7$, 6.3 Hz, 2H), 1.51 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 174.4, 141.1, 140.6, 128.6, 128.3, 128.3, 127.5, 127.1, 125.9, 63.8, 45.5, 31.9, 30.1, 18.3. HRMS (EI$^+$) calcd for C$_{18}$H$_{20}$O$_2$ [M]$^+$ 268.1463, found m/z 268.1507.

Cyclohexyl 2-Phenylpropionate (15). Colorless oil. IR (neat, cm^{-1}) 1730. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.33–7.18 (m, 5H), 4.75 (m, 1H), 3.68 (q, $J = 7.0$ Hz, 1H), 1.85–1.20 (m, 10H), 1.49 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 173.9, 140.8, 128.1, 127.2, 126.9, 72.6, 45.8, 31.4, 31.2, 28.6, 25.3, 23.5, 23.4, 18.4. HRMS (EI$^+$) calcd for C$_{15}$H$_{20}$O$_2$ [M]$^+$ 232.1463, found m/z 232.1502.

3-Phenylpropyl Diphenylacetate (16). Colorless oil. IR (neat, cm^{-1}) 1735. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.36–7.02 (m, 15H), 5.03 (s, 1H), 4.15 (t, $J = 6.5$ Hz, 2H), 2.57 (t, $J = 7.7$ Hz, 2H), 1.98–1.86 (m, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.4, 141.0, 138.7, 128.6, 128.6, 128.6, 128.4, 127.2, 125.9, 64.3, 57.2, 31.9, 30.1. HRMS (EI$^+$) calcd for C$_{23}$H$_{22}$O$_2$ [M]$^+$ 330.1620, found m/z 330.1605.

1-Methyl-3-phenylpropyl Diphenylacetate (17). White crystal. mp 59–60 °C. IR (KBr, cm^{-1}) 1720. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.34–7.01 (m, 15H), 5.05–4.92 (m, 1H), 5.00 (s, 1H), 2.56–2.40 (m, 2H), 1.95–1.68 (m, 2H), 1.24 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.0, 141.5, 141.5, 138.8, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 127.2, 127.2, 125.9, 71.3, 57.4, 37.6, 31.5, 19.9. HRMS (EI$^+$) calcd for C$_{24}$H$_{22}$O$_2$ [M]$^+$ 344.1776, found m/z 344.1816.

3-Phenylpropyl 3-(3-Pyridyl)propionate (18). Pale orange oil. IR (neat, cm^{-1}) 1734. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.49–8.45 (m, 2H), 7.56–7.52 (m, 1H), 7.31–7.14 (m, 6H), 4.09 (t, $J = 6.6$ Hz, 2H), 2.95 (t, $J = 7.6$ Hz, 2H), 2.64 (t, $J = 7.6$ Hz, 4H), 1.94 (tt, $J = 7.6$, 6.6 Hz, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.1, 149.5, 147.5, 140.9, 135.9, 135.8, 128.3, 128.2, 125.9, 123.3, 64.0, 35.3, 32.2, 30.1, 28.1. HRMS (EI$^+$) calcd for C$_{17}$H$_{19}$NO$_2$ [M]$^+$ 269.1416, found m/z 269.1395.

5-(Tetrahydropyranyloxy)pentyl 3-Phenylpropionate[8] (19). Colorless oil. IR (neat, cm^{-1}) 1735. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32–7.16 (m, 5H), 4.58–4.56 (m, 1H), 4.07 (t, $J = 6.6$ Hz, 2H), 3.91–3.85 (m, 1H), 3.78–3.68 (m, 1H), 3.54–3.46 (m, 1H), 3.42–3.32 (m, 1H), 2.95 (t, $J = 7.8$ Hz, 2H), 2.66–2.58 (m, 2H), 1.83–1.32 (m, 12H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.8, 140.4, 128.3, 128.1, 126.1, 98.8, 67.3, 64.5, 62.3, 35.9, 31.0, 30.8, 29.4, 28.5, 25.5, 22.8, 19.7.

3-Phenylpropyl 3-(*t*-Butyldimethylsiloxy)-3-phenylpropionate[8] (20). Colorless oil. IR (neat, cm^{-1}) 1737. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32–7.12 (m, 10H), 5.13 (dd, $J = 9.2$, 4.3 Hz, 1H), 4.12–4.02 (m, 2H), 2.78–2.61 (m, 2H), 2.54 (dd, $J = 14.9$, 4.3 Hz, 2H), 1.98–1.87 (m, 2H), 0.82 (s, 9H), 0.00 (s, 3H), −0.19 (s, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 171.0, 143.9, 141.1, 128.3, 128.3, 128.2, 127.4, 125.9, 125.7, 72.2, 63.9, 46.4, 32.2, 30.2, 25.7, 18.1, −4.6, −5.1.

3-Phenylpropyl (*E*)-3-Phenyl-2-propenoate[8] (21). Colorless oil. IR (neat, cm^{-1}) 1712. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.68 (d, $J = 16.1$ Hz, 1H), 7.59–7.51 (m, 2H), 7.41–7.15 (m, 8H), 6.45 (d, $J = 16.1$ Hz, 1H), 4.23 (t, $J = 6.5$ Hz, 2H), 2.75 (t, $J = 7.7$ Hz, 2H), 2.04 (tt, $J = 7.7$, 6.5 Hz, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 166.9, 144.6, 141.1, 134.3, 130.2, 128.8, 128.3, 128.3, 128, 125.9, 118, 63.9, 32.3, 30.4.

3-Phenylpropyl Benzoate[8] (22). Colorless oil. IR (neat, cm^{-1}) 1718. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.85–7.81 (m, 2H), 7.54–7.05 (m, 8H), 4.34 (t, $J = 6.5$ Hz, 2H), 2.77 (t, $J = 7.7$ Hz, 2H), 2.16–2.06 (m, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 166.4, 141.0, 132.8, 130.2, 129.4, 128.3, 128.3, 128.2, 125.9, 64.2, 32.3, 30.3.

3-Phenylpropyl 2,2-Dimethylpropionate[8] **(23).** Colorless oil. IR (neat, cm^{-1}) 1729. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32–7.14 (m, 5H), 4.07 (t, $J = 6.3$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 1.96 (tt, $J = 7.7$, 6.3 Hz, 2H), 1.21 (s, 9H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 178.4, 141.1, 128.3, 128.3, 125.9, 63.5, 38.8, 32.2, 30.3, 27.3.

1-Methyl-3-phenylpropyl Cyclohexanecarboxylate[8] **(25).** Colorless oil. IR (neat, cm^{-1}) 1729. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.31–7.13 (m, 5H), 4.99–4.87 (m, 1H), 2.73–2.53 (m, 2H), 2.32–2.21 (m, 1H), 1.97–1.18 (m, 12H), 1.23 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 175.5, 141.5, 128.3, 128.2, 125.8, 69.8, 43.5, 37.8, 31.9, 29.2, 29.0, 25.8, 25.6, 25.5, 20.1.

Cyclohexyl Cyclohexanecarboxylate[8] **(26).** Colorless oil. IR (neat, cm^{-1}) 1729. ^{1}H NMR (270 MHz, CDCl$_3$) δ 4.81–4.68 (m, 1H), 2.31–2.20 (m, 1H), 1.91–1.19 (m, 20H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 175.3, 71.8, 43.4, 31.6, 29.1, 25.8, 25.5, 25.5, 23.7.

1-Methyl-3-phenylpropyl 2,2-Dimethylpropionate[8] **(27).** Colorless oil. IR (neat, cm^{-1}) 1725. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.35–7.15 (m, 5H), 4.97–4.85 (m, 1H), 2.75–2.52 (m, 2H), 2.00–1.71 (m, 2H), 1.24 (d, $J = 7.3$ Hz, 3H), 1.21 (s, 9H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 177.9, 141.5, 128.3, 128.2, 125.8, 70.0, 38.8, 37.8, 31.9, 27.3, 20.0.

1-Methyl-3-phenylpropyl (*E*)-3-Phenyl-2-propenoate[8] **(28).** Colorless oil. IR (neat, cm^{-1}) 1710. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.67 (d, $J = 16.1$ Hz, 1H), 7.53–7.51 (m, 2H), 7.39–7.15 (m, 8H), 6.43 (d, $J = 16.1$ Hz, 1H), 5.14–5.02 (m, 1H), 2.80–2.63 (m, 2H), 2.04–1.80 (m, 1H), 1.96–1.81 (m, 1H), 1.33 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 166.5, 144.3, 141.4, 134.3, 130.1, 128.8, 128.3, 128.2, 128.0, 125.8, 118.5, 70.6, 37.8, 31.9, 20.2.

3-Phenylpropyl (*E*)-Crotonate[8] **(29).** Colorless oil. IR (neat, cm^{-1}) 1719. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.31–7.16 (m, 5H), 6.97 (dq, $J = 15.4$, 7.0 Hz, 1H), 5.84 (dq, $J = 15.4$, 1.8 Hz, 1H), 4.14 (t, $J = 6.5$ Hz, 2H), 2.70 (t, $J = 7.7$ Hz, 2H), 2.03–1.90 (m, 2H), 1.88 (dd, $J = 7.0$, 1.8 Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 166.4, 144.5, 141.1, 128.3, 128.3, 125.8, 122.5, 63.5, 32.2, 30.3, 18.1.

1-Methyl-3-phenylpropyl (*E*)-Crotonate[8] **(30).** Colorless oil. IR (neat, cm^{-1}) 1717. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.30–7.15 (m, 5H), 6.96 (dq, $J = 15.4$, 7.0 Hz, 1H), 5.84 (dq, $J = 15.4$, 1.8 Hz, 1H), 5.05–4.93 (m, 1H), 2.75–2.55 (m, 2H), 2.06–1.75 (m, 2H), 1.88 (dd, $J = 7.0$, 1.8 Hz, 3H), 1.27 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 166.0, 144.1, 141.5, 128.3, 128.2, 125.7, 123.0, 70.1, 37.8, 31.8, 20.2, 18.0.

3-Phenylpropyl 4-Phenyl-3-butenoate (31). Colorless oil. IR (neat, cm^{-1}) 1735. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.42–7.10 (m, 10H), 6.50 (d, $J = 16.2$ Hz, 1H), 6.30 (dt, $J = 16.2$, 6.8 Hz, 1H), 4.16 (t, $J = 6.2$ Hz, 2H), 3.24 (d, $J = 6.8$ Hz, 2H), 2.70 (t, $J = 7.7$ Hz, 2H), 2.05–1.91 (m, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 171.6, 141.1, 136.8, 133.4, 128.5, 128.4, 128.4, 127.5, 126.3, 126.0, 121.7, 64.1, 38.4, 32.1, 30.1. HRMS (FAB^{+}) calcd for $C_{19}H_{21}O_2$ $[M+H]^{+}$ 281.1542, found m/z 281.1519.

3-Phenylpropyl 3-Hexenoate (32). Colorless oil. IR (neat, cm^{-1}) 1737. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32–7.15 (m, 5H), 5.63 (dt, $J = 16.1$, 6.3 Hz, 1H), 5.53 (dt, $J = 16.1$, 6.1 Hz, 1H), 4.10 (t, $J = 6.6$ Hz, 2H), 3.03 (d, $J = 6.3$ Hz, 2H), 2.69 (t, $J = 7.3$ Hz, 2H), 2.11–1.91 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 172.3, 141.2, 136.3, 128.4, 128.4, 126.0, 120.6, 63.8, 38.1, 32.1, 30.2, 25.5, 13.4. HRMS (FAB^{+}) calcd for $C_{15}H_{20}AgO_2$ $[M+Ag]^{+}$ 339.0514, found m/z 339.0524.

3-Phenylpropyl 4-Methoxybenzoate[15] **(33).** Colorless oil. IR (neat, cm^{-1}) 1712. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.98 (d, $J = 8.9$ Hz, 2H), 7.32–7.15 (m, 5H), 6.92 (d, $J = 8.9$ Hz, 2H), 4.31 (t, $J = 6.2$ Hz, 2H), 3.85 (s, 3H), 2.78 (t, $J = 7.3$ Hz, 2H), 2.15–2.05 (m, 2H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 166.2, 163.1, 141.1, 131.4, 128.3, 128.3, 125.9, 122.7, 113.5, 64.0, 55.4, 32.4, 30.4.

Phenyl 4-Chlorobenzoate[16] **(34).** White crystal. mp 102–103 °C. IR (KBr, cm^{-1}) 1733. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.16–8.12 (m, 2H), 7.50–7.40 (m, 4H), 7.35–7.20 (m, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 164.2, 150.6, 140.0, 131.4, 129.4, 128.8, 127.9, 125.9, 121.5.

Phenyl 4-(Trifluoromethyl)benzoate[16] **(35).** White crystal. mp 89–90 °C. IR (KBr, cm^{-1}) 1735. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.32 (d, $J = 8.1$ Hz, 2H), 7.77 (d, $J = 8.1$ Hz, 2H), 7.47–7.41 (m, 2H), 7.32–7.18 (m, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 163.8, 150.5, 134.9 (q, ^{2}J (^{13}C,^{19}F) = 32.95 Hz), 132.7 (d, ^{4}J (^{13}C,^{19}F) = 1.15 Hz), 130.4, 129.5, 126.1, 125.5 (q, ^{3}J (^{13}C,^{19}F) = 3.86 Hz), 123.7 (q, ^{1}J (^{13}C,^{19}F) = 273.5 Hz), 121.4.

Phenyl 4-Nitrobenzoate[16] **(36).** White crystal. mp 127–128 °C. IR (KBr, cm^{-1}) 1742. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.41–8.33 (m, 4H), 7.50–7.40 (m, 2H), 7.35–7.20 (m, 3H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 163.2, 150.7, 150.3, 134.8, 131.2, 130.0, 126.3, 123.6, 121.3.

Typical Experimental Procedure for the Synthesis of Lactones by Using 2-DTC. To a mixture of 12-hydroxydodecanoic acid (38.1 mg, 0.176 mmol) and 2-DTC (40.0 mg, 0.176 mmol) in CH$_3$CN (10 mL) was added DMAP (1.08 mg, 0.0088 mmol). After stirring for 15 minutes at room temperature, the resultant solution was diluted by the addition of 166 mL of toluene and treated with iodine (179 mg, 0.707 mmol). The reaction mixture was stirred for 10 h at the reflux temperature of toluene and then cooled to room temperature. Then, 10% aqueous sodium thiosulfate was added and CH$_3$CN and toluene were evaporated. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin-layer chromatography to afford the corresponding lactone (26.8 mg, 77%).

2-Thienyl 12-Hydroxydodecanoate (38). White crystal. mp 69–70 °C. IR (KBr, cm^{-1}) 3367, 1749. ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.88 (dd, $J = 5.8$, 1.6 Hz, 1H), 6.82 (dd, $J = 5.8$, 3.8 Hz, 1H), 6.68 (dd, $J = 3.8$, 1.6 Hz, 1H), 3.63 (t, $J = 6.6$ Hz, 2H), 2.55 (t, $J = 7.5$ Hz, 2H), 1.79–1.67 (m, 2H), 1.67–1.51 (m, 2H), 1.45–1.20 (m, 14H). ^{13}C NMR (68 MHz, CDCl$_3$) δ 170.4, 152.0, 123.2, 117.9, 113.1, 63.1, 34.0, 32.8, 29.5, 29.5, 29.4, 29.4, 29.2, 29.0, 25.7, 24.7. HRMS (FAB^{+}) calcd for $C_{16}H_{27}O_3S$ $[M+H]^{+}$ 299.1681, found m/z 299.1685.

Undecan-11-olide[10] **(12-Membered Ring Lactone).** Colorless oil. IR (neat, cm^{-1}) 1735. ^{1}H NMR (270 MHz, CDCl$_3$) δ 4.20 (t, $J = 5.2$ Hz, 2H), 2.40–2.33 (m, 2H), 1.80–1.60 (m, 4H), 1.60–1.47 (m, 2H), 1.47–1.23 (m, 10H). MS (EI^{+}) m/z 184 $[M]^{+}$.

Dodecan-12-olide[8] **(13-Membered Ring Lactone).** Colorless oil. IR (neat, cm^{-1}) 1734. ^{1}H NMR (270 MHz, CDCl$_3$) δ 4.15 (t, $J = 5.3$ Hz, 2H), 2.38–2.33 (m, 2H), 1.73–1.60 (m, 4H), 1.48–1.25 (m, 14H). MS (EI^{+}) m/z 198 $[M]^{+}$.

Tridecan-13-olide[8] **(14-Membered Ring Lactone).** Colorless oil. IR (neat, cm^{-1}) 1735. ^{1}H NMR (270 MHz, CDCl$_3$) δ 4.15 (t, $J = 5.4$ Hz, 2H), 2.40–2.35 (m, 2H), 1.72–1.59 (m, 4H), 1.50–1.21 (m, 16H). MS (EI^{+}) m/z 212 $[M]^{+}$.

Tetradecan-14-olide[8] **(15-Membered Ring Lactone).** Colorless oil. IR (neat, cm^{-1}) 1736. ^{1}H NMR (270 MHz, CDCl$_3$) δ 4.14 (t, $J = 5.3$ Hz, 2H), 2.37–2.32 (m, 2H), 1.74–1.58 (m, 4H), 1.45–1.20 (m, 18H). MS (EI^{+}) m/z 226 $[M]^{+}$.

Pentadecan-15-olide[8] (16-Membered Ring Lactone). Colorless oil. IR (neat, cm^{-1}) 1737. ^1H NMR (270 MHz, $CDCl_3$) δ 4.13 (t, $J = 5.5$ Hz, 2H), 2.33 (t, $J = 6.8$ Hz, 2H), 1.72–1.58 (m, 4H), 1.44–1.24 (m, 20H). MS (FAB^+) m/z 241 $[M + H]^+$.

Hexadecan-16-olide[8] (17-Membered Ring Lactone). Colorless oil. IR (neat, cm^{-1}) 1737. ^1H NMR (270 MHz, $CDCl_3$) δ 4.12 (t, $J = 5.6$ Hz, 2H), 2.32 (t, $J = 6.6$ Hz, 2H), 1.72–1.58 (m, 4H), 1.43–1.20 (m, 22H). MS (FAB^+) m/z 255 $[M + H]^+$.

***erythro*-9,10-Benzylidenedioxyhexadecan-16-olide[8] (40).** White crystal. mp 56–57 °C. IR (KBr, cm^{-1}) 1732. ^1H NMR (270 MHz, $CDCl_3$) δ 7.75–7.66 (m, 2H), 7.28–7.10 (m, 3H), 6.03 (1H, s), 4.08–4.02 (m, 2H), 3.88–3.71 (m, 2H), 2.19 (t, $J = 7.0$ Hz, 2H), 1.94–1.01 (m, 22H). MS (ESI^+) m/z 397 $[M + Na]^+$.

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