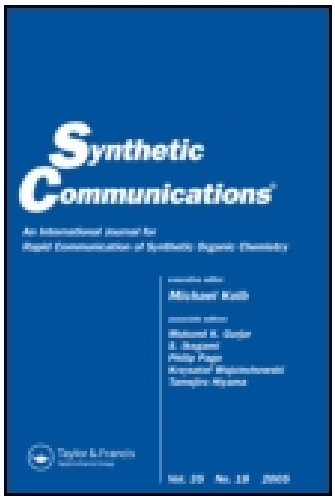

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ULTRASOUND PROMOTED SYNTHESIS OF β-HYDROXYESTERS BY REFORMATSKY REACTION USING INDIUM METAL

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ULTRASOUND PROMOTED SYNTHESIS OF β-HYDROXYESTERS BY REFORMATSKY REACTION USING INDIUM METAL

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This paper is dedicated to Professor In-Sup Han on the occasion of his 65th birthday.

ABSTRACT

Ultrasound promoted Reformatsky reaction by the reaction of aldehydes or ketone with ethyl bromoacetate in the presence of indium metal afforded β-hydroxyesters in good to excellent yields under mild conditions.

The Reformatsky reaction, which is regarded as one of the most fundamental reactions in carbon–carbon bond formations, is the reaction between a carbonyl compound with an α-haloester in the presence of zinc

*Corresponding author.

metal to furnish β-hydroxyesters.[1] The products are one of the most important intermediates in organic synthesis.[2] Recently, several modified Reformatsky reactions using other metals have been described.[3] Also, the scope of the Reformatsky reaction has been extended with special techniques for the activation of the metal (e.g. for removal of the oxide layer, and the preparation of finely dispersed metal).[4] The activation of zinc by treatment with iodine or dibromomethane, or washing with dilute hydrochloric acid prior to use, is only moderately successful in the most known procedures. Much more effective protocol is the use of special alloys – e.g. zinc–copper couple, or the reduction of zinc halides using potassium (the so-called Rieke procedure[5]) or potassium graphite.[4] Although the application of ultrasound has been reported for zinc metal, promoters such as iodine and potassium iodide were needed sometimes to obtain the desired products in good yields.[6] Recently, we reported the indium mediated organic reaction,[7] and in this paper we describe the beneficial effects that ultrasonic irradiation has on the indium mediated Reformatsky reaction.

To find optimum conditions for ultrasound assisted Reformatsky reaction using indium, initially benzaldehyde (entry 4) was reacted with ethyl bromoacetate in the presence of indium in various solvents. Of the several solvents tested, THF gave the best results in terms of conversion and reaction times. The reaction of benzaldehyde with ethyl bromoacetate in the presence of indium in THF afforded ethyl 3-hydroxy-3-phenylpropanoate (**4**) in 97% yield. Sonications were carried out at room temperature in a Fisher Scientific ultrasonic cleaner bath, which delivered a 43 kHz wave, with a fixed electrical power of 435 W. However, the yields were decreased in other solvents under the identical conditions despite longer reaction times. Ultrasound promoted reaction condition was superior to stirring condition. In the absence of sonic waves, the reaction occurs much more slowly (17 h) and the yield of the β-hydroxyester **4** is only 70%. Rate per minute (rpm) for stirring conditions is ca. 900. Ethyl iodoacetate gave the similar results to ethyl bromoacetate.

Table 1 summarizes the experimental results and illustrates the efficiency and scope of the present method.[8] In case of aliphatic aldehydes (entries 1, 2 and 3), the reaction afforded the desired compounds **1**, **2** and **3** in excellent yields. For the aromatic aldehydes, the presence of various substituents, e.g., methyl (entry 5), chloro (entry 6), bromo (entry 7), monomethoxy (entry 8), or dimethoxy (entry 9) on the aromatic ring showed little effects on the efficiency of the reactions. It should be mentioned that 2- or 3-hydroxybenzaldehyde (entries 10 and 11) that contains an acidic hydrogen was reacted with the same efficiency to provide the desired compounds **10** and **11** in 93 and 92% yields, respectively. The protocol developed here was also applied to reactions with ketone. For example, acetophenone (entry 13)

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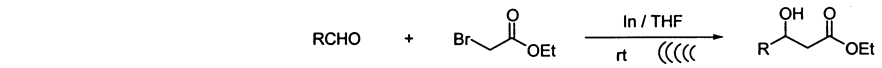
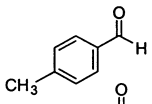
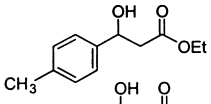
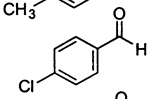
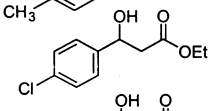
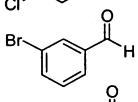
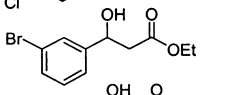
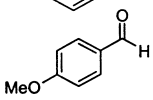
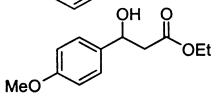
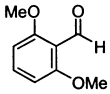
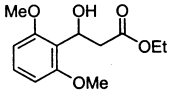
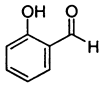
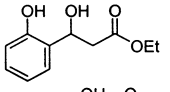
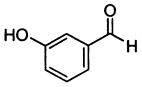
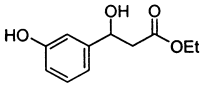
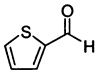
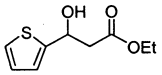
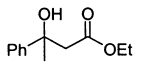
Table 1. Preparation of β-Hydroxyesters by In-mediated Reactions of Carbonyl Compounds with Ethyl Bromoacetate



Entry	Carbonyl Compounds	Time / h	Products		Isolated Yield %[a]
1	$CH_3CH_2CH_2CHO$	3	$CH_3CH_2CH_2CH(OH)CH_2CO_2Et$	**1**	95
2	$(CH_3)_2CHCHO$	2.5	$(CH_3)_2CHCH(OH)CH_2CO_2Et$	**2**	91
3	$c\text{-}C_6H_{11}CHO$	2	$c\text{-}C_6H_{11}CH(OH)CH_2CO_2Et$	**3**	92
4	PhCHO	20	$PhCH(OH)CH_2CO_2Et$	**4**	0[b,c]
		10			0[d,c]
		5			22[d]
		17			70[e,c]
		2			97[f]
		2			97
5		2.5		**5**	92
6		2		**6**	91
7		3		**7**	91
8		2.5		**8**	90
9		2		**9**	90
10		2		**10**	93
11		2.5		**11**	92
12		2.5		**12**	90
13		3		**13**	90

[a]Sonications were carried out at room temperature in a Fisher Scientific ultrasonic cleaner bath, which delivered a 43 kHz wave, with a fixed electrical power of 435 Watts. [b]Solvent: H_2O. [c]The reaction mixture was stirred (rpm:~ 900). [d]solvent: DMF. [e]solvent: THF. [f]Ethyl iodoacetate was used.

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was reacted under the identical conditions to give the β-hydroxyester **13** in 90% yield. However, indium promoted reaction of acetophenone with ethyl bromoacetate gave β-hydroxyester **13** in 40% yield without sonic waves. The sonicated mixture of zinc, ethyl bromoacetate, and acetophenone gave no addition product in the absence of iodine.[6]

In summary, ultrasound mediated Reformatsky reaction using indium afforded β-hydroxyesters in high yields. There are several advantages of the method such as (a) the organoindium compound is prepared and used *in situ*; (b) it has a wide application for elongation of carbon chains; (c) compared to the use of zinc and tin, the reaction with indium did not require any promoter (iodine or potassium iodide); and (d) the organo-indium intermediates do not react with themselves in normal conditions. The present method complements the existing synthetic methods because of mild reaction condition and advantages of indium metal with regard to easy handling, high reactivity and selectivity, low toxicity, and operational simplicity. Further studies are now in progress.

EXPERIMENTAL SECTION

Typical procedure for indium-mediated Reformatsky reaction: Ethyl 3-hydroxy-3-phenylpropanoate (4). To a solution of indium (indium powder (99.99%) purchased from Aldrich Chem Co.; 58.0 mg, 0.5 mmol) in THF (1.0 mL) was added ethyl bromoacetate (125.0 mg, 0.75 mmol), then benzaldehyde (53.0 mg, 0.5 mmol) under nitrogen at room temperature. After sonicating in a Fisher Scientific ultrasonic cleaner bath, which delivered a 43 kHz wave, with a fixed electrical power of 435 W, for 2 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ether (3×25 mL) and the combined organic layers were washed with water (20 mL), brine (20 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel chromatography (hexane : EtOAc = 5:1) leading to ethyl 3-hydroxy-3-phenylpropanoate (94.0 mg, 97%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4–7.25 (5H, m, Ph), 5.14 (1H, q, $J = 4.0$ Hz, H-3), 4.19 (2H, q, $J = 7.20$ Hz, H-2), 3.14 (1H, br s, OH), 2.83–2.64 (2H, m, OCH_2), 1.26 (3H, $J = 7.00$ Hz, OCH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.64 (s, C=O), 142.62 (s, Ph-1), 128.69 (s, Ph-2,6), 127.94 (s, Ph-3,5), 125.81 (s, Ph-4), 70.40 (s, C-OH), 61.02 (s, OCH_2CH_3), 43.41 (s, $OCOCH_2$), 14.23 (s, OCH_2CH_3); IR (film) 3460, 2980, 1720, 1490, 1450, 1395, 1370, 1295, 1260 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{15}O_3$ $[M + H]^+$ 195.1022, found 195.1028.

Ethyl 3-hydroxyhexanoate (1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (2H, q, $J = 7.15$ Hz, OCH_2CH_3), 4.02 (1H, m, H-3), 3.01 (1H, d, $J = 3.69$ Hz,

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OH), 2.49 (1H, dd, $J = 3.32$, 3.16 Hz, H-2), 2.39 (1H, dd, $J = 8.93$, 8.93 Hz, H-2), 1.25–1.53 (4H, m, H-4,5), 1.27 (3H, t, $J = 7.20$ Hz, OCH_2CH_3), 0.93 (3H, t, $J = 6.99$ Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.13 (s, C=O), 67.77 (s, C-OH), 60.67 (s, OCH_2CH_3), 41.38 (s, $OCOCH_2$), 38.68 (s, $CH_2CH_2CH_3$), 18.69 (s, $CH_2CH_2CH_3$), 14.19 (s, $CH_2CH_2CH_3$), 13.97 (s, OCH_2CH_3); IR (film) 3480, 3050, 2960, 1720, 1260 cm^{-1}; HRMS (CI) calcd for $C_8H_{17}O_3$ $[M + H]^+$ 161.1179, found 161.1170.

Ethyl 3-hydroxy-4-methylpentanoate (2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (2H, q, $J = 7.14$ Hz, OCH_2), 3.78 (1H, m, H-3), 3.05 (1H, br s, OH), 2.50 (1H, dd, $J = 2.92$, 2.92 Hz, H-2), 2.40 (1H, dd, $J = 9.53$, 9.53 Hz, H-2), 1.72 (1H, m, H-4), 1.27 (3H, t, $J = 7.15$ Hz, OCH_2CH_3), 0.94 (6H, q, $J = 5.99$ Hz, $CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.86 (s, C=O), 73.09 (s, C-OH), 61.05 (s, OCH_2CH_3), 38.84 (s, $OCOCH_2$), 33.52 (s, $CH(Me)_2$), 18.70 (s, $CH(Me)_2$), 18.10 (s, $CH(Me)_2$), 14.52 (s, OCH_2CH_3); IR (film) 3440, 2975, 1720, 1470, 1370, 1320, 1270 cm^{-1}; HRMS (CI) calcd for $C_8H_{17}O_3$ $[M + H]^+$ 161.1179, found 161.1185.

Ethyl 3-cyclohexyl-3-hydroxypropanoate (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (2H, q, OCH_2CH_3), 3.79–3.75 (1H, m, H-3), 2.84 (1H, br s, OH), 2.51 (1H, dd, $J = 2.80$, 2.86 Hz, H-2), 2.41 (1H, dd, $J = 9.50$, 9.49 Hz, H-2), 1.86 (1H, d, $J = 12.65$ Hz, H-4), 1.76 (2H, m, H-5), 1.66 (2H, d, $J = 12.30$ Hz, H-9), 1.41–1.11 (9H, m, H-6,7,8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.60 (s, C=O), 73.17 (s, C-OH), 61.69 (s, OCH_2CH_3), 44.07 (s, $OCOCH_2$), 39.59 (s, $CHCH_2CH_2CH_2CH_2CH_2$), 29.80 (s, $CHCH_2CH_2CH_2CH_2CH_2$), 29.27 (s, $CHCH_2CH_2CH_2CH_2CH_2$), 27.44 (s, $CHCH_2CH_2CH_2CH_2CH_2$), 27.18 (s, $CHCH_2CH_2CH_2CH_2CH_2$), 27.06 (s, $CHCH_2CH_2CH_2CH_2CH_2$), 15.20 (s, OCH_2CH_3); IR (film) 3500, 3050, 2980, 2920, 2840, 1720, 1450, 1410, 1370, 1260 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{21}O_3$ $[M + H]^+$ 201.1492, found 201.1480.

Ethyl 3-hydroxy-3-(*p*-methylphenyl)propanoate (5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (2H, d, $J = 8.02$ Hz, Ph-2,6), 7.14 (2H, d, $J = 7.95$ Hz, Ph-3,5), 5.08 (1H, q, $J = 4.18$ Hz, H-3), 4.16 (2H, q, $J = 7.13$ Hz, s, OCH_2CH_3), 3.1 (1H, br s, OH), 2.77–2.57 (2H, m, H-2), 2.33 (3H, s, 4-Me-Ph), 1.25 (3H, t, $J = 7.14$ Hz, s, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.80 (s, C=O), 140.04 (s, Ph-1), 137.84 (s, Ph-4), 129.58 (s, Ph-2,6), 126.02 (s, Ph-3,6), 70.57 (s, C-OH), 61.21 (s, OCH_2CH_3), 43.76 (s, $OCOCH_2$), 21.49 (s, 4-Me-Ph), 14.54 (s, OCH_2CH_3); IR (film) 3410, 2960, 2900, 1715, 1510, 1440, 1390, 1365, 1290, 1260 cm^{-1}; HRMS (CI) calcd for $C_{12}H_{17}O_3$ $[M + H]^+$ 209.1179, found 209.1165.

Ethyl 3-(*p*-chlorophenyl)-3-hydroxypropanoate (6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (4H, s, Ph), 5.09 (1H, q, $J = 4.25$ Hz, H-3), 4.17 (2H, q, $J = 7.12$ Hz, s, OCH_2CH_3), 3.22 (1H, br s, OH), 2.68 (2H, m, $OCOCH_2$), 1.25 (3H, t, $J = 7.10$ Hz, s, OCH_2CH_3); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 172.24 (s, C=O), 141.03 (s, Ph-4), 133.45 (s, Ph-3,5), 128.67 (s, Ph-1), 127.09 (s, Ph-2,6), 69.62 (s, C-OH), 61.00 (s, OCH_2CH_3), 43.20 (s, $OCOCH_2$), 14.13 (s, OCH_2CH_3); IR (film) 3400, 2930, 2860, 1695, 1470, 1375, 1350, 1280, 1260, 1240 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{14}Cl_1O_3$ $[M+H]^+$ 229.0633, found 229.0641.

Ethyl 3-(*m*-bromophenyl)-3-hydroxypropanoate (7). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (1H, t, $J=1.62$ Hz, Ph-2), 7.42–7.40 (1H, m, Ph-4), 7.30–7.19 (2H, m, Ph-5,6), 5.08 (1H, m, H-3), 4.18 (2H, q, $J=7.14$ Hz, OCH_2CH_3), 3.41 (1H, d, $J=3.55$ Hz, OH), 2.71 (2H, d, $J=6.84$ Hz, $OCOCH_2$), 1.26 (3H, t, $J=7.17$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.23 (s, C=O), 144.78 (s, Ph-3), 130.84 (s, Ph-4), 130.12 (s, Ph-2), 128.87 (s, Ph-1), 124.28 (s, Ph-5), 122.67 (s, Ph-6), 69.59 (s, C-OH), 61.04 (s, OCH_2CH_3), 43.14 (s, $OCOCH_2$), 14.14 (s, OCH_2CH_3); IR (film) 3500, 3050, 2980, 1720, 1420, 1260 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{14}Br_1O_3$ $[M+H]^+$ 273.0128, found 273.0120.

Ethyl 3-hydroxy-3-(*p*-methoxyphenyl)propanoate (8). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, d, $J=8.09$ Hz, Ph-3,5), 6.89 (2H, d, $J=8.49$ Hz, Ph-2,6), 5.08 (1H, t, $J=4.53$ Hz, H-3), 4.18 (2H, q, $J=7.14$ Hz, OCH_2CH_3), 3.79 (3H, s, OCH_3), 3.20 (1H, br s, OH), 2.78–2.64 (2H, m, H-2), 1.25 (3H, t, $J=7.38$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.44 (s, C=O), 159.20 (s, Ph-4), 134.73 (s, Ph-1), 126.97 (s, Ph-2,6), 113.91 (s, Ph-3,5), 69.97 (s, C-OH), 60.83 (s, OCH_2CH_3), 55.29 (s, OCH_3), 43.33 (s, $OCOCH_2$), 14.16 (s, OCH_2CH_3); IR (film) 3450, 2970, 2830, 1715, 1600, 1500, 1460, 1365, 1295, 1240 cm^{-1}; HRMS (CI) calcd for $C_{12}H_{17}O_4$ $[M+H]^+$ 255.1128, found 255.1120.

Ethyl 3-hydroxy-3-(2,5-dimethoxyphenyl)propanoate (9). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (1H, t, $J=8.34$ Hz, Ph-4), 6.56 (2H, d, $J=8.41$ Hz, Ph-3,5), 5.66 (1H, dd, $J=4.21$, 4.31 Hz, H-3), 4.16 (2H, q, $J=7.14$ Hz, OCH_2CH_3), 3.84 (6H, s, $O(Me)_2$), 3.55 (1H, br s, OH), 2.99 (1H, dd, $J=9.87$, 9.91 Hz, H-2), 2.65 (1H, dd, $J=4.25$, 4.36 Hz, H-2), 1.26 (3H, t, $J=7.1$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.01 (s, C=O), 158.07 (s, Ph-2,6), 129.30 (s, Ph-1), 118.40 (s, Ph-3,5), 104.59 (s, Ph-4), 64.94 (s, C-OH), 60.79 (s, OCH_2CH_3), 56.10 (s, $O(Me)_2$), 42.74 (s, $OCOCH_2$), 14.60 (s, OCH_2CH_3); IR (film) 33525, 2960, 2920, 2820, 1720, 1580, 1460, 1365, 1260 cm^{-1}; HRMS (CI) calcd for $C_{13}H_{19}O_5$ $[M+H]^+$ 255.1234, found 255.1225.

Ethyl 3-hydroxy-3-(*o*-hydroxyphenyl)propanoate (10). ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (1H, m, Ph-3), 6.98 (1H, dd, $J=1.43$, 1.43 Hz, Ph-6), 6.88–6.81 (2H, m, Ph-4,5), 5.27 (1H, dd, $J=3.06$, 3.06 Hz, H-3), 4.21 (2H, q, $J=7.14$ Hz, OCH_2CH_3), 2.95 (1H, dd, $J=10.27$, 10.25 Hz, H-2), 2.72 (1H, dd, $J=3.16$, 3.11 Hz, H-2), 1.28 (3H, t, $J=7.15$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.08 (s, C=O), 155.66 (s,

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Ph-2), 129.32 (s, Ph-1), 126.66 (s, Ph-3), 125.31 (s, Ph-6), 119.97 (s, Ph-4), 117.48 (s, Ph-5), 71.48 (s, C-OH), 61.28 (s, OCH_2CH_3), 40.95 (s, $OCOCH_2$), 14.11 (s, OCH_2CH_3); IR (film) 3370, 2980, 1700, 1610, 1490, 1450, 1370, 1350, 1220 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{15}O_4$ $[M+H]^+$ 211.0972, found 211.0985.

Ethyl 3-hydroxy-3-(*m*-hydroxyphenyl)propanoate (11). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (1H, t, $J=7.8$ Hz, Ph-2), 6.83 (1H, d, $J=7.08$ Hz, Ph-4,6), 6.73 (2H, m, Ph-5), 5.05 (3H, q, $J=4.32$ Hz, H-3, OH), 4.14 (2H, q, $J=7.13$ Hz, OCH_2CH_3), 2.72 (1H, dd, $J=9.02$, 9.02 Hz, H-2), 2.65 (1H, dd, J = 3.95, 3.94 Hz, H-2), 1.23 (3H, t, $J=7.13$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.64 (s, C=O), 156.18 (s, Ph-3), 143.96 (s, Ph-2), 129.81 (s, Ph-1), 117.74 (s, Ph-4), 115.10 (s, Ph-6), 112.77 (s, Ph-5), 70.38 (s, C-OH), 61.15 (s, OCH_2CH_3), 43.18 (s, $OCOCH_2$), 14.07 (s, OCH_2CH_3); IR (film) 3380, 3050, 2980, 1720, 1600, 1450, 1420, 1250 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{15}O_4$ $[M+H]^+$ 211.0972, found 211.0970.

Ethyl 3-hydroxy-3-(2-thienyl)propanoate (12). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.23 (1H, m, S-CH), 6.96–6.94 (2H, m, SCH=CH-CH), 5.36 (1H, m, H-3), 4.58 (2H, q, $J=7.14$ Hz, OCH_2CH_3), 3.55 (1H, d, $J=4.27$ Hz, OH), 2.90–2.79 (1H, m, H-2), 1.26 (3H, t, $J=7.2$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.32 (s, C=O), 146.78 (s, thienyl-2), 127.1 (s, thienyl-5), 125.24 (s, thienyl-3), 124.03 (s, thienyl-4), 66.95 (s, C-OH), 61.39 (s, OCH_2CH_3), 43.61 (s, $OCOCH_2$), 14.53 (s, OCH_2CH_3); HRMS (CI) calcd for $C_9H_{13}O_3S_1$ $[M+H]^+$ 201.0587, found 201.0581.

Ethyl 3-hydroxy-3-phenylbutanoate (13). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, m, Ph-2,6), 7.33 (2H, m, Ph-3,5), 7.25–7.21 (1H, m, Ph-4), 4.39 (1H, s, OH), 4.05 (2H, q, $J=7.13$ Hz, OCH_2CH_3), 2.88 (2H, dd, $J=15.8$, 15.9 Hz, H-2), 1.54 (3H, s, CCH_3), 1.12 (3H, t, $J=7.2$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.72 (s, C=O), 146.83 (s, Ph-1), 128.23 (s, Ph-2,6), 126.84 (s, Ph-3,5), 124.45 (s, Ph-4), 72.74 (s, C-OH), 60.73 (s, OCH_2CH_3), 46.41 (s, $OCOCH_2$), 30.66 (s, CCH_3), 13.98 (s, OCH_2CH_3); IR (film) 3460, 3020, 2960, 2900, 1690, 1480, 1430, 1360, 1320, 1240 cm^{-1}; HRMS (CI) calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 209.1179, found 209.1173.

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8. All new compounds have satisfactory analytical data including ^{1}H, ^{13}C-NMR, MS, and IR spectra. The NMR data were obtained from central instrument facilities in Kangwon National University.

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