Ring Opening of Cyclopropanemonocarboxylates and 1,1-Cyclopropanedicarboxylates Using Samarium(II) Diiodide (SmI_2)–HMPA–THF System[1)]

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The cyclopropane ring in 2-substituted 1,1-cyclopropanedicarboxylates was regioselectively opened by using samarium(II) diiodide (SmI_2) in a hexamethylphosphoric triamide (HMPA)–tetrahydrofuran (THF) (1 : 10) system under mild and neutral conditions to give (2-substituted ethyl)malonates in moderate to good yields. The cyclopropane ring in 2-substituted cyclopropanecarboxylates or 2-substituted 3-(trimethylsilyl)cyclopropanecarboxylates was similarly cleaved regioselectively by using SmI_2 in a HMPA–THF (1 : 1) system to give 4-arylbutyrates or 4-aryl-3-(trimethylsilyl)butyrates in 16—89% yields. The reaction mechanism of these ring-opening reactions is discussed.

Key words samarium diiodide; ring opening; cyclopropanecarboxylate; 1,1-cyclopropanedicarboxylate; (trimethylsilyl)-cyclopropanecarboxylate; cyclopropane ring

Since Kagan and his co-workers first reported the use of samarium diiodide (SmI_2) in synthetic organic chemistry,[2)] many new applications of the reagent have been developed,[3)] including carbon–carbon bond formation, carbon–heteroatom bond cleavage, reduction of functional groups such as carbon–carbon multiple bonds and carbonyl group, deoxygenation of organoheteroatom oxides and so on. Little work has been done on carbon–carbon bond cleavage using SmI_2.[4)] Cyclopropane compounds are of interest due to their reactivity,[5)] but SmI_2 has only been used for the ring opening of cyclopropyl ketones,[4b–d)] except for one report.[4f)] We have been interested in the reactivity of SmI_2,[6a)] especially its use for the cyclopropane ring-opening reaction.[6b,c)] In this paper, we describe the cyclopropane ring-opening of cyclopropanemonocarboxylates (**1** and **2**) and 1,1-cyclopropanedicarboxylates (**3**).

First, we tried the ring opening of 1,1-cyclopropanedicarboxylates (**3**), because **3** would be activated by the two electron withdrawing groups to react with SmI_2. Diethyl 2-(*p*-methylphenyl)-1,1-cyclopropanedicarboxylate (**3a**) was added to a solution of SmI_2 (3.0 eq) in tetrahydrofuran (THF) at room temperature (entry 1 in Table 1). It was found that the cyclopropane ring was cleaved regioselectively at the C1–C2 bond to give diethyl [2-(4-methylphenyl)ethyl]malonate (**6a**), but the yield was only 6% after 10 h and the starting material (**3a**) was recovered in more than 90% yield. This low yield is in contrast to the reported high yields in the case of cyclopropane ring-

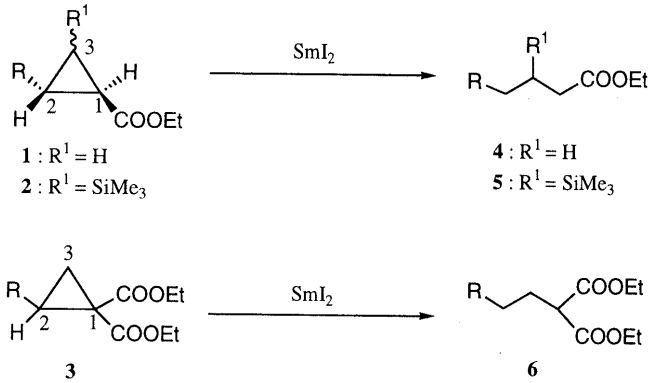
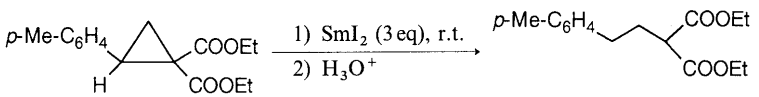


Chart 1

Table 1. Cyclopropane Ring-Opening of **3a**



3a **6a**

Entry	*tert*-BuOH (eq) (Proton source)	HMPA : THF[a)] (v/v)	Reaction time	Yield (%)[b)]
1	None	0 : 5 (0)	10 h	6
2	1	0 : 5 (0)	2 h	8
3	None	1 : 25 (1)	2 h	10
4	None	3 : 25 (3)	2 h	20
5	1	3 : 25 (3)	2 h	22
6	1	1 : 10 (5)	2 h	62
7	2	1 : 10 (5)	< 10 min	88 (80)[c)]

a) Equivalents of HMPA in comparison with **3a** are given in parentheses. *b*) Determined by GLC analysis with an internal standard. *c*) Isolated yield.

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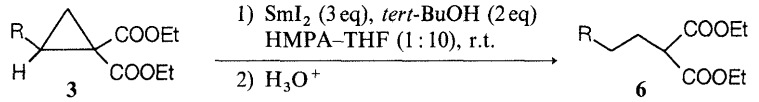
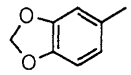
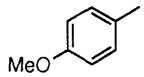
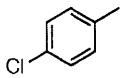
Table 2. Cyclopropane Ring-Opening of **3**



Starting material	R	Product	Isolated yield (%)	Starting material	R	Product	Isolated yield (%)
3b		**6b**	65	**3h**		**6h**	70
3c		**6c**	74	**3i**		**6i**	57
3d		**6d**	97	**3j**	Me_2CH–	**6j**	79
3e		**6e**	70	**3k**	Et_2CH–	**6k**	78
3f		**6f**	88	**3l**	$Me(CH_2)_6$–	**6l**	58
3g		**6g**	74				

opening of cyclopropylketones.[4b,d,7] This may be attributable to the difference of activation ability between the carbonyl group and the alkoxycarbonyl group. Several reaction conditions were examined in order to optimize this reaction and the results are summarized in Table 1.

Additives such as acid, base,[8] or hexamethylphosphoric triamide (HMPA)[9] raised the reducing power of SmI_2 in the SmI_2–THF system. As shown in Table 1 (entries 3—7), addition of HMPA markedly accelerated the cyclopropane ring-opening of **3a**. In entry 7, the best yield of **6a** was obtained by using the HMPA–THF (1 : 10) system in the presence of *tert*-butyl alcohol as a proton source, and the ring was completely opened within 10 min under the conditions used. Recently, Imamoto and his co-workers reported that diethyl 1,1-cyclopropanedicarboxylate was opened with SmI_2 in the presence of tris(dibenzoylmethiodo)iron(III) to give the corresponding diethyl ethylmalonate in high yield, while the product was obtained in only 32% yield by treatment with the SmI_2–HMPA–THF system in the presence of *tert*-butyl alcohol at room temperature.[4f]

Our reaction conditions of entry 7 in Table 1 could be applied to the ring opening of various cyclopropane compounds (**3**), and the results are summarized in Table 2.

The cyclopropanes bearing aromatic, heterocyclic and aliphatic substituents at the 2-position of **3** gave the corresponding **6** as a sole product without formation of any isomer (**7** or **8**) which would be produced by cleavage at the C2–C3 or C1–C3 bond, respectively.

Next, we tried the ring-opening of cyclopropanemonocarboxylates (**1**). A starting material, ethyl *trans*-2-phenylcyclopropanecarboxylate (**1a**), was obtained in low

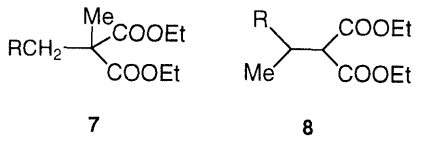


Fig. 1

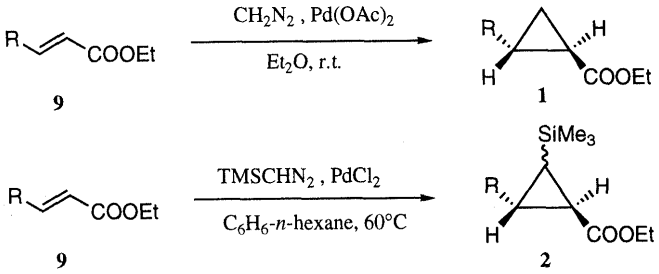


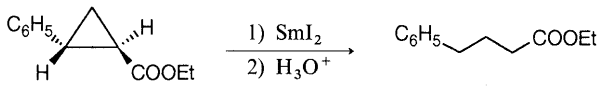
Chart 2

yield (30%) by treatment of ethyl *trans*-3-phenylpropenoate (**9a**) with dimethylsulfoxonium methylide.[10] However, Vorbrüggen's method for the cyclopropanation gave **1a** in 98% yield,[11] when **9a** was treated with an excess of diazomethane in the presence of palladium(II) acetate as a catalyst. Other cyclopropanecarboxylates (**1b—h**) were prepared similarly.

Also, compounds **9** were treated with trimethylsilyldiazomethane in the presence of palladium(II) chloride to give 2-substituted 3-(trimethylsilyl)cyclopropanecarboxylates (**2**) as diastereomeric mixtures in 27—83% yields.[12]

Ethyl 2-phenylcyclopropanecarboxylate (**1a**) was subjected to the same reaction conditions as used for **6** (entry 1 in Table 3). The expected ethyl 4-phenylbutyrate (**4a**)

Table 3. Cyclopropane Ring-Opening of **1a**

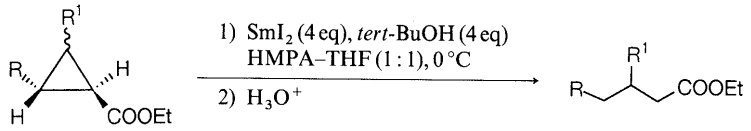


1a **4a**

Entry	SmI_2 (eq)	THF : HMPA[a] (v/v)	*tert*-BuOH (eq)	Temp.	Reaction time (h)	Recovery of **1a**[b] (%)	Yield of **4a**[b] (%)
1	3	10 : 1 (5)	2	r.t.	12	89	11
2	3	5 : 1 (10)	2	r.t.	6	45	19
3	3	5 : 2 (21)	2	r.t.	6	40	44
4	3	5 : 3 (31)	2	r.t.	6	35	65
5	4	5 : 3 (31)	2	r.t.	5	—	59
6	3	1 : 1 (52)	2	0 °C	6	81	19
7	3	1 : 1 (52)	4	0 °C	6	26	40
8	4	1 : 1 (52)	4	0 °C	1	—	74

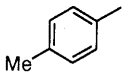
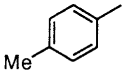
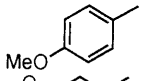
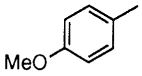
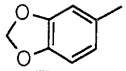
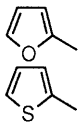
a) Equivarents of HMPA in comparison with **1a** are given in parentheses. *b*) Determined by GLC analysis with an internal standard.

Table 4. Cyclopropane Ring-Opening of **1** and **2**



1: R^1 = H
2: R^1 = $SiMe_3$

4: R^1 = H
5: R^1 = $SiMe_3$

	Product (**4**)		Isolated yield (%)		Product (**5**)		Isolated yield (%)
	R	R^1			R	R^1	
4a		H	70	**5a**		$SiMe_3$	75
4b		H	47	**5b**		$SiMe_3$	80
4c		H	44	**5c**		$SiMe_3$	89
4d		H	87	**5d**		$SiMe_3$	16
4e		H	0[a]	**5e**		$SiMe_3$	54
4f		H	30				
4g	$Me(CH_2)_2$–	H	0[b]				
4h	$Me(CH_2)_6$–	H	0[b]				

a) A complex mixture was obtained. *b*) The starting material was recovered.

was obtained in only 11% yield together with 89% recovery of 1a. The optimal reaction conditions for cyclopropane ring-opening of **1a** were examined, and the results are summarized in Table 3. Increase of HMPA improved the yield of **4a**. In entry 8, the best yield (74%) was obtained and the reaction time was shortened to less than 1 h.

The conditions employed in entry 8 were applied to various cyclopropane compounds (**1** and **2**).

In the cases of 2-aryl compounds (**1a—d, f**) except for **1e**, the expected butyrates (**4a—d, f**) were obtained in moderate to high yields. The failure in the case of **1e** may be attributable to the instability of **1e** itself.[13] However, **1g** and **1h** having an aliphatic group at the 2-position did not react with SmI_2 at all under the same conditions. This difference in reactivity between aliphatic and aromatic substituents may be attributable to differences in the stability of the corresponding intermediate radicals (**10**).

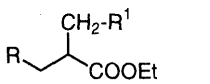
In the series of 2-aryl-3-trimethylsilyl compounds (**2**), the yields of **5** were higher than those of the corresponding **4**. Furthermore, **5d** having a furyl group could be obtained in 16% yield. We presume that the silyl group may participate in the stabilization of the intermediate radical (**10**).[14] The isomers (**14** and **15**) were not obtained in any of our present ring-opening experiments.

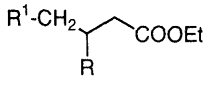
In order to examine the reaction mechanism, **3a** was subjected to similar conditions to those of entry 7 in Table 1 except for use of *tert*-butyl alcohol-*d* (*tert*-BuOD) instead

of *tert*-butyl alcohol, and the γ-deuterated product (**16**) was obtained in 84% chemical yield and 87% deuteration ratio. In the ^{1}H-NMR spectrum of **16**, the signal intensity of the γ-position proton at δ 2.62 was apparently decreased from that of **6a**. A similar deuteration experiment for **1a** gave the α,γ-dideuterated product (**17**) in 63% chemical yield and 95% deuteration ratio. In the ^{1}H-NMR spectrum of **17**, diminution of the signal intensities of the γ-position proton at δ 2.31 and the α-position proton at δ 2.63 compared with those of **4a** was observed.

On the other hand, when the reaction mixture for the cyclopropane ring-opening of **3d** in the presence of one equivalent of *tert*-butyl alcohol was treated with allyl bromide, the α-substituted product (**13a**) was obtained in 94% yield. This α-position trapping reaction was also applied to some cyclopropane compounds (**3a**, **b**, **d**) to give the corresponding alkylmalonates (**13b**—**e**) in moderate yields (Table 5).

The formation of **16** and **17** suggested the generation





14a : R^1 = H **15a** : R^1 = H
14b : R^1 = $SiMe_3$ **15b** : R^1 = $SiMe_3$

Fig. 2

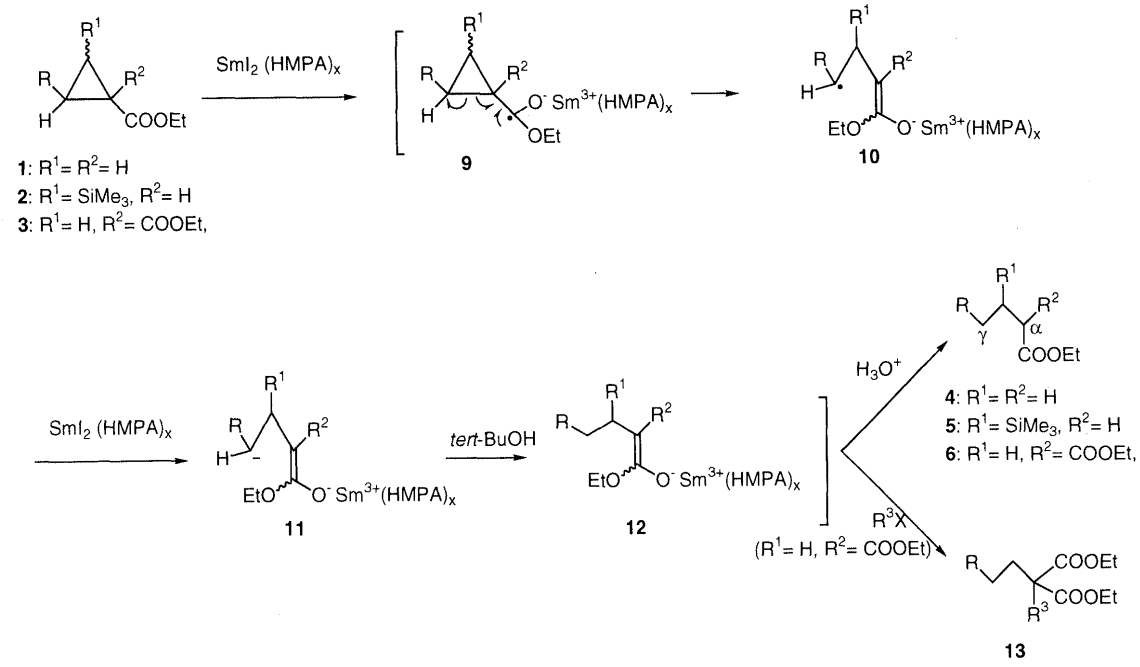
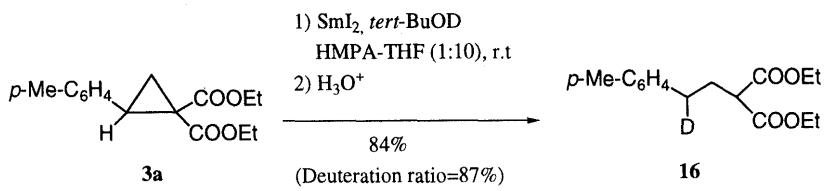


Chart 3



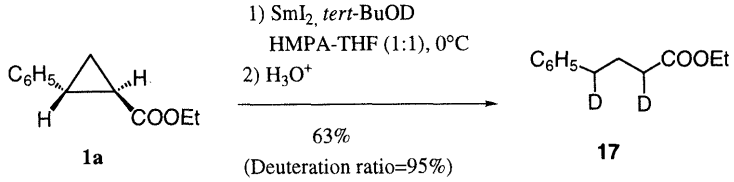


Chart 4

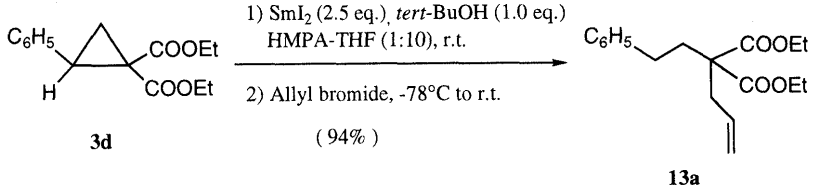
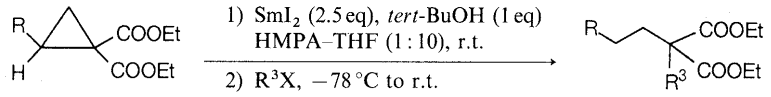
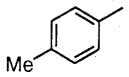
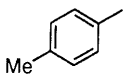
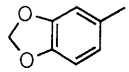
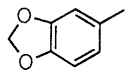
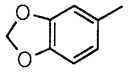
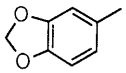


Chart 5

Table 5. α-Position Trapping Reaction after the Cyclopropane Ring-Opening of **3**



3 **13**

Starting material		Product			Isolated yield (%)
	R		R	R^3	
3a		**13b**		$CH_2=CHCH_2$–	48
3b		**13c**		$CH_2=CHCH_2$–	52
3d		**13d**		Me–	40
3b		**13e**		Me–	38

of radical species (**10**) or an anion intermediate (**11**) at the γ-position, and the formation of **13a** suggested the generation of the enolate anion (**12**). On the basis of these results, we propose a possible reaction mechanism, as shown in Chart 3, for the ring opening of **1**, **2**, and **3**.

In conclusion, the cyclopropane ring in the 2-substituted-1,1-cyclopropanedicarboxylates (**3**) was opened regioselectively using SmI_2 in HMPA–THF (1 : 10) to give the corresponding mono- and disubstituted ethylmalonate (**6** and **13**) in moderate to high yields regardless of the kind of 2-substituent. The cyclopropane ring-opening of the 2-arylcyclopropanemonocarboxylates (**1** and **2**) also proceeded regioselectively on treatment with SmI_2 in HMPA–THF (1 : 1) to give the corresponding 4-arylbutyrates (**4** and **5**) in 16—89% yields.

Experimental

Melting points were measured with a Yanaco MP micro-melting point apparatus and are uncorrected. IR spectra were taken with a Shimadzu IR-435 spectrophotometer. ^{1}H-NMR spectra were measured on a JEOL EX-270 (270 MHz) with tetramethylsilane as an internal standard. A Hitachi M-80 spectrometer for low-resolution MS (LRMS) and high-resolution MS (HRMS) and a JEOL JMS-SX 102A QQ spectrometer for FAB-MS were used. All solvents were removed under reduced pressure in the usual work-up procedure. Anhydrous sodium sulfate was used as a drying agent. Silica gel 60 (No. 7734, Merck) for column chromatography and Silica gel 60 PF_{254} (Nacalai Tesque Inc.) for preparative TLC (PTLC) were used. Diethyl 2-substituted 1,1-cyclopropanedicarboxylates (**3**) were prepared by treatment of diethyl substituted methylidenemalonates with dimethylsulfoxonium methylide according to Landor's method.[10]

Cyclopropane Ring-Opening of Diethyl 2-(*p*-Methylphenyl)-1,1-cyclopropanedicarboxylate (3a) Using SmI_2 General Procedure: A solution of 1,2-diiodoethane (422 mg, 1.50 mmol) in THF (2 ml) was added dropwise to a suspension of samarium metal (270 mg, 1.80 mmol) in THF (3 ml) at room temperature under an N_2 atmosphere and the whole was stirred for 1 h. HMPA (0.5 ml) was added dropwise to the blue solution of SmI_2. After 5 min, a solution of **3a** (136 mg, 0.50 mmol) and *tert*-butyl alcohol (0.10 ml, 1.00 mmol) in THF (1 ml) was added dropwise to the SmI_2–HMPA–THF solution at room temperature and the whole was stirred for an additional 10 min. After addition of 3% HCl solution under ice-cooling, the mixture was extracted with diethyl ether. The combined organic layer was washed successively with water, saturated $Na_2S_2O_3$ solution, water, and brine, dried, and evaporated. The residue was chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 15) to give diethyl [2-(*p*-methylphenyl)ethyl]malonate (**6a**, 111 mg, 80%) as a colorless oil.[15]

Compounds **6b**, **c**,[15] **d**,[15] **e**,[15] **h**, **i**, **j**,[16] **k**, and **l**[17] were also prepared in the above-mentioned manner.

Diethyl [2-(3,4-Methylenedioxyphenyl)ethyl]malonate (**6b**): Colorless oil. IR ($CHCl_3$): 1722 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (6H, t, J=7.3 Hz, $-OCH_2C\underline{H}_3$), 2.17 (2H, q, J=7.6 Hz, $ArCH_2C\underline{H}_2$–), 2.58 (2H t, J=7.6 Hz, $ArC\underline{H}_2$–), 3.32 (1H, t, J=7.4 Hz, $-C\underline{H}(COOEt)_2$), 4.20 (4H, q, J=7.3 Hz, $-OC\underline{H}_2CH_3$), 5.91 (2H, s, $-OC\underline{H}_2O$–), 6.60—6.74 (3H, m, Ar-H). LRMS m/z: 308 (M^+). HRMS m/z: 308.1282 (Calcd for $C_{16}H_{20}O_6$: 308.1260).

Diethyl [2-(2-Furyl)ethyl]malonate (**6h**): Colorless oil. IR ($CHCl_3$): 1739 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (6H, t, J=7.1 Hz, $-OCH_2C\underline{H}_3$), 2.24 (2H, q, J=7.4 Hz, $ArCH_2C\underline{H}_2$–), 2.70 (2H, t, J=7.6 Hz, $ArC\underline{H}_2$–), 3.36 (1H, t, J=7.3 Hz, $-C\underline{H}(COOEt)_2$), 4.20 (4H, q, J=6.9 Hz, $-OC\underline{H}_2CH_3$), 6.02 (1H, d, J=3.3 Hz, C^3-H), 6.25—6.30 (1H, m, C^4-H), 7.30 (1H, d, J=2.0 Hz, C^5-H). LRMS m/z: 254 (M^+). HRMS m/z: 254.1142 (Calcd for $C_{13}H_{18}O_5$: 254.1150).

Diethyl [2-(2-Thienyl)ethyl]malonate (**6i**): Colorless oil. IR ($CHCl_3$): 1739 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (6H, t, J=7.1 Hz, $-OCH_2C\underline{H}_3$), 2.27 (2H, q, J=7.4 Hz, $ArCH_2C\underline{H}_2$–), 2.90 (2H, t, J=7.4 Hz, $ArC\underline{H}_2$–), 3.39 (1H, t, J=7.4 Hz, $-C\underline{H}(COOEt)_2$), 4.20 (4H, q, J=7.1 Hz, $-OC\underline{H}_2CH_3$), 6.81—6.82 (1H, m, C^4-H), 6.92 (1H, dd, J=3.5, 5.1 Hz, C^3-H), 7.13 (1H, dd, J=1.3, 5.1 Hz, C^5-H). LRMS m/z: 270 (M^+). HRMS m/z: 270.0918 (Calcd for $C_{13}H_{18}O_4S$: 270.0930).

Diethyl (3-Ethylpentyl)malonate (**6k**): Colorless oil. IR ($CHCl_3$): 1739 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.83 (6H, t, J=7.1 Hz, $(C\underline{H}_3CH_2)_2$-CH–), 1.26 (6H, t, J=7.1 Hz, $-OCH_2C\underline{H}_3$), 1.15—1.50 (8H, m, $(CH_3C\underline{H}_2)_2CHC\underline{H}_2C\underline{H}_2$–), 1.81—1.90 (1H, m, $(CH_3CH_2)_2C\underline{H}$–), 3.27 (1H, t, J=7.4 Hz, $-C\underline{H}(COOEt)_2$), 4.19 (4H, q, J=7.2 Hz, $-OC\underline{H}_2CH_3$). LRMS m/z: 258 (M^+). HRMS m/z: 258.1813 (Calcd for $C_{14}H_{26}O_4$: 258.1831).

In the preparations of **6f** and **6g**,[18] the reactions were carried out in the above-mentioned manner. In work-up, water instead of 3% HCl solution was added carefully to the reaction mixture under ice-cooling and the mixture was filtered with suction. The filtrate was extracted and purified as above.

Diethyl [2-(3-Pyridyl)ethyl]malonate (**6f**): Colorless oil. IR ($CHCl_3$): 1739 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.28 (6H, t, J=7.1 Hz, $-OCH_2C\underline{H}_3$), 2.23 (2H, q, J=7.6 Hz, $ArCH_2C\underline{H}_2$–), 2.68 (2H, t, J=7.9 Hz, $ArC\underline{H}_2$–),

3.35 (1H, t, J=7.4 Hz, –CH(COOEt)$_2$), 4.21 (4H, q, J=7.1 Hz, –OCH$_2$CH$_3$), 7.21—7.25 (1H, m, C^5-H), 7.54 (1H, d, J=7.6 Hz, C^4-H), 8.46 (2H, s, C^2-, C^6-H). LRMS m/z: 265 (M$^+$). HRMS m/z: 265.1337 (Calcd for $C_{14}H_{19}NO_4$: 265.1310).

Cyclopropanation of Ethyl *trans*-3-Phenylpropenoate (9a) with Diazomethane General Procedure: A large excess of diazomethane in diethyl ether (20 ml) was added dropwise to a solution of **9a** (500 mg, 2.90 mmol) and palladium(II) acetate (15 mg) in diethyl ether (10 ml) at room temperature and the whole was stirred for 1 h. After concentration, the residue was chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 3) to give ethyl *trans*-2-phenylcyclopropanecarboxylate (**1a**, 550mg, 98%) as colorless crystals, mp 37.0—38.5 °C,[11,19] after recrystallization from ethyl acetate–*n*-hexane.

Compounds **1b** (96%),[20] **c** (92%),[20] **d**, **e**, **f** (80%),[19] **g** (80%),[10a] and **h** were also prepared in the above-mentioned manner.

Ethyl *trans*-2-(3,4-Methylenedioxyphenyl)cyclopropanecarboxylate (**1d**): 95%. Colorless crystals (from ethyl acetate–*n*-hexane). mp 63.0—64.5 °C. IR (CHCl$_3$): 1714 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.28 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 1.19—1.30 (1H m, ArCHCH$_2$–), 1.50—1.59 (1H m, ArCHCH$_2$–), 1.77—1.84 (1H m, ArCH–), 2.42—2.49 (1H, m, –CHCOOEt), 4.16 (2H, q, J=7.3 Hz, –OCH$_2$CH$_3$), 5.92 (2H, s, –OCH$_2$O–), 6.56—6.62 (2H, m, Ar-H), 6.72(1H, d, J=8.3 Hz, Ar-H). LRMS m/z: 234 (M$^+$). HRMS m/z: 234.0868 (Calcd for $C_{13}H_{14}O_4$: 234.0890).

Ethyl *trans*-2-(2-Furyl)cyclopropanecarboxylate (**1e**) : 75%. Colorless oil. IR (CHCl$_3$): 1716 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.28 (3H, t, J=7.3 Hz, –OCH$_2$CH$_3$), 1.34—1.41 (1H, m, ArCHCH$_2$–), 1.45—1.55 (1H, m, ArCHCH$_2$–), 1.95—2.02 (1H, m, ArCH–), 2.47—2.55 (1H, m, –CHCOOEt), 4.16 (2H, q, J=7.1 Hz, –OCH$_2$CH$_3$), 6.07 (1H, d, J=3.0 Hz, C^3-H), 6.28 (1H, dd, J=2.0, 3.3 Hz, C^4-H), 7.25 (1H, d, J=2.0 Hz, C^5-H). LRMS m/z: 180 (M$^+$). HRMS m/z: 180.0786 (Calcd for $C_{10}H_{12}O_3$: 180.0790).

Ethyl *trans*-2-Heptylcyclopropanecarboxylate (**1h**): 93%. Colorless oil. IR (CHCl$_3$): 1710 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.60—0.70 (1H, m, cyclopropyl CH$_2$), 0.88 (3H, t, J=6.6 Hz, CH$_3$(CH$_2$)$_6$–), 0.82—0.98 (1H, m, cyclopropyl CH$_2$), 1.08—1.24 (1H, m, cyclopropyl CH), 1.26 (3H, t, J=7.3 Hz, –OCH$_2$CH$_3$), 1.20—1.50 (13H, m, CH$_3$(CH$_2$)$_6$–, –CHCOOEt), 4.11 (2H, q, J=7.3 Hz, –OCH$_2$CH$_3$). LRMS m/z: 213 (M$^+$+1).

Cyclopropanation of Ethyl *trans*-2-Phenylpropenoate (9a) with Trimethylsilyldiazomethane General Procedure: A solution of trimethylsilyldiazomethane in *n*-hexane (0.5 M, 3.0 ml, 1.5 mmol) was added dropwise to a solution of **9a** (792 mg, 4.50 mmol) and palladium(II) chloride (5 mol%) in benzene (1 ml) at room temperature and the whole was heated at 60 °C for 1 h. After concentration, the residue was purified by PTLC (ethyl acetate : *n*-hexane = 1 : 5) to give a mixture of *cis*- and *trans*-isomers of ethyl *trans*-2-phenyl-3-(trimethylsilyl)cyclopropanecarboxylate (**2a**; 275 mg, 70%; yield based on trimethylsilyldiazomethane) as a colorless oil.[12]

Compounds **2b—e** were also prepared in the above-mentioned manner.

Ethyl *trans*-2-(*p*-Methylphenyl)-3-(trimethylsilyl)cyclopropanecarboxylate (**2b**): 75%. Colorless oil. IR (CHCl$_3$): 1711 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.12 (9H, s, –Si(CH$_3$)$_3$), 0.60 (1H, dd, J=8.4, 10.1 Hz, –CHSi(CH$_3$)$_3$), 1.27 (3H, t, J=7.3 Hz, –OCH$_2$CH$_3$), 2.03 (1H, dd, J=4.3, 10.2 Hz, ArCH–), 2.31 (3H, s, CH$_3$Ar–), 2.51 (1H, dd, J=4.5, 8.4 Hz, –CHCOOEt), 4.08—4.21 (2H, m, –OCH$_2$CH$_3$), 7.00 (2H, d, J=8.3 Hz, C^2-, C^6-H), 7.07 (2H, d, J=8.2 Hz, C^3-, C^5-H). LRMS m/z: 276 (M$^+$). HRMS m/z: 276.1546 (Calcd for $C_{16}H_{24}O_2Si$: 276.1550).

Ethyl *trans*-2-(*p*-Methoxyphenyl)-3-(trimethylsilyl)cyclopropanecarboxylate (**2c**): 83%. Colorless oil. IR (CHCl$_3$): 1710 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.12 (9H, s, –Si(CH$_3$)$_3$), 0.58 (1H, dd, J=8.6, 9.9 Hz, –CHSi(CH$_3$)$_3$), 1.28 (3H, t, J=7.3 Hz, –OCH$_2$CH$_3$), 1.98 (1H, dd, J=4.5, 10.1 Hz, ArCH–), 2.50 (1H, dd, J=4.3, 8.6 Hz, –CHCOOEt), 3.78 (3H, s, CH$_3$OAr–), 4.08—4.22 (2H, m, –OCH$_2$CH$_3$), 6.82 (2H, d, J=8.9 Hz, C^2-, C^6-H), 7.04 (2H, d, J=8.9 Hz, C^3-, C^5-H). LRMS m/z: 292 (M$^+$). HRMS m/z: 292.1509 (Calcd for $C_{16}H_{24}O_3Si$: 292.1500).

Ethyl *trans*-2-(2-Furyl)-3-(trimethylsilyl)cyclopropanecarboxylate (**2d**): 27%. Colorless oil. IR (CHCl$_3$): 1714 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.11 (9H, s, –Si(CH$_3$)$_3$), 0.73 (1H, dd, J=8.6, 10.2 Hz, –CHSi(CH$_3$)$_3$), 1.28 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 2.14 (1H, dd, J=4.3, 10.2 Hz, ArCH–), 2.53 (1H, dd, J=4.3, 8.6 Hz, –CHCOOEt), 4.07—4.21 (2H, m, –OCH$_2$CH$_3$), 6.03 (1H, d, J=3.0 Hz, C^3-H), 6.27 (1H, dd, J=1.8, 3.1 Hz, C^4-H), 7.24 (1H, d, J=1.8 Hz, C^5-H). LRMS m/z: 252 (M$^+$). HRMS m/z: 252.1200 (Calcd for $C_{13}H_{20}O_3Si$: 252.1180).

Ethyl *trans*-2-(2-Thienyl)-3-(trimethylsilyl)cyclopropanecarboxylate (**2e**): 39%. Colorless oil. IR (CHCl$_3$): 1713 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: –0.14 (9H, s, –Si(CH$_3$)$_3$), 0.83 (1H, dd, J=7.1, 10.7 Hz, –CHSi(CH$_3$)$_3$), 1.30 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 2.10 (1H, dd, J=4.0, 6.9 Hz, ArCH–), 3.10 (1H, dd, J=4.0, 10.6 Hz, –CHCOOEt), 4.18 (H, q, J=7.1 Hz, –OCH$_2$CH$_3$), 6.82—6.89 (2H, m, C^3-, C^4-H), 7.11 (1H, d, J=5.3 Hz, C^5-H). LRMS m/z: 268 (M$^+$). HRMS m/z: 268.0969 (Calcd for $C_{13}H_{20}O_2SSi$: 268.0950).

Cyclopropane Ring-Opening of Ethyl *trans*-2-Phenylcyclopropanecarboxylate (1a) Using SmI_2 General Procedure: The SmI_2 solution [prepared from samarium metal (360 mg, 2.40 mmol) and 1,2-diiodoethane (563 mg, 2.00 mmol) in THF (5 ml) under an N_2 atmosphere] was cooled to 0 °C and HMPA (5.0 ml) was added dropwise. After 5 min, a solution of **1a** (95 mg, 0.50 mmol) and *tert*-butyl alcohol (0.20 ml, 2.00 mmol) in THF (1 ml) was added dropwise to the SmI_2–HMPA–THF solution at 0 °C and the whole was stirred for an additional 1 h. Usual work-up was carried out as above. The residue was chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 5) to give ethyl 4-phenylbutyrate (**4a**, 70 mg, 73%) as a colorless oil.[21,22]

Compounds **4b**, **c**,[22] **d**, **f**,[23] and **5a—e** were prepared similarly.

Ethyl 4-(*p*-Methylphenyl)butyrate (**4b**): Colorless oil. IR (CHCl$_3$): 1723 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.24 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 1.87—1.98 (2H, m, ArCH$_2$CH$_2$–), 2.31 (2H, t, J=7.4 Hz, ArCH$_2$–), 2.31 (3H, s, CH$_3$Ar–), 2.60 (2H, t, J=7.6 Hz, –CH$_2$COOEt), 4.11 (2H, q, J=7.3 Hz, –OCH$_2$CH$_3$), 7.07 (4H, s, Ar-H). LRMS m/z: 206 (M$^+$). HRMS m/z: 206.1278 (Calcd for $C_{13}H_{18}O_2$: 206.1310).

Ethyl 4-(3,4-Methylenedioxyphenyl)butyrate (**4d**): Colorless oil. IR (CHCl$_3$): 1722 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.25 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 1.85—1.96 (2H, m, ArCH$_2$CH$_2$–), 2.30 (2H, t, J=7.6 Hz, ArCH$_2$–), 2.57 (2H, t, J=7.6 Hz, –CH$_2$COOEt), 4.12 (2H, q, J=7.1 Hz, –OCH$_2$CH$_3$), 5.92 (2H, s, –OCH$_2$O–), 6.61—6.74 (3H, m, Ar-H). LRMS m/z: 236 (M$^+$). HRMS m/z: 236.1043 (Calcd for $C_{13}H_{16}O_4$: 236.1050).

Ethyl 4-Phenyl-3-(trimethylsilyl)butyrate (**5a**): Colorless oil. IR (CHCl$_3$): 1719 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.01 (9H, s, –Si(CH$_3$)$_3$), 1.20 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 1.52—1.58 (1H, m, –CHSi(CH$_3$)$_3$), 2.23—2.29 (m, 2H, ArCH$_2$–), 2.50 (1H, dd, J=10.2, 13.9 Hz, –CH$_2$COOEt), 2.82 (1H, dd, J=5.5, 14.2 Hz, –CH$_2$COOEt), 3.97 (2H, q, J=7.2 Hz, –OCH$_2$CH3), 7.18—7.30 (5H, m, Ar-H). LRMS m/z: 264 (M$^+$). HRMS m/z: 264.1545 (Calcd for $C_{15}H_{24}O_2Si$: 264.1550).

Ethyl 4-(*p*-Methylphenyl)-3-(trimethylsilyl)butyrate (**5b**): Colorless oil. IR (CHCl$_3$): 1720 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.07 (9H, s, –Si(CH$_3$)$_3$), 1.13 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 1.35—1.55 (1H, m, –CHSi(CH$_3$)$_3$), 2.05—2.30 (2H, m, ArCH$_2$–), 2.25 (3H, s, CH$_3$Ar–), 2.37 (1H, dd, J=10.2, 13.9 Hz, –CH$_2$COOEt), 2.71 (1H, dd, J=5.5, 14.0 Hz, –CH$_2$COOEt), 3.91 (2H, q, J=7.2 Hz, –OCH$_2$CH$_3$), 7.01 (4H, s, Ar-H). LRMS m/z: 278 (M$^+$). HRMS m/z: 278.1700 (Calcd for $C_{16}H_{26}O_2Si$: 278.1700).

Ethyl 4-(*p*-Methoxyphenyl)-3-(trimethylsilyl)butyrate (**5c**): Colorless oil. IR (CHCl$_3$): 1718 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.20 (9H, s, –Si(CH$_3$)$_3$), 1.40 (3H, t, J=7.3 Hz, –OCH$_2$CH$_3$), 1.62—1.80 (1H, m, –CHSi(CH$_3$)$_3$), 2.38—2.59 (2H, m, ArCH$_2$–), 2.65 (1H, dd, J=10.1, 14.0 Hz, –CH$_2$COOEt), 2.96 (1H, dd, J=5.6, 14.2 Hz, –CH$_2$COOEt), 3.98 (3H, s, CH$_3$OAr–), 4.19 (2H, q, J=7.3 Hz, –CH$_2$CH$_3$), 7.01 (2H, d, J=8.6 Hz, C^2-, C^6-H), 7.31 (2H, d, J=8.6 Hz, C^3-, C^5-H). LRMS m/z: 294 (M$^+$). HRMS m/z: 294.1646 (Calcd for $C_{16}H_{26}O_3Si$: 294.1650).

Ethyl 4-(2-Furyl)-3-(trimethylsilyl)butyrate (**5d**): Colorless oil. IR (CHCl$_3$): 1721 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.14 (9H, s, –Si(CH$_3$)$_3$), 1.38 (3H, t, J=7.1 Hz, –OCH$_2$CH$_3$), 1.58—1.70 (1H, m, –CHSi(CH$_3$)$_3$), 2.39—2.55 (2H, m, ArCH$_2$–), 2.76 (1H, dd, J=8.4, 15.4 Hz, –CH$_2$COOEt), 2.89 (1H, dd, J=5.9, 15.4 Hz, –CH$_2$COOEt), 4.21 (2H, q, J=7.3 Hz, –OCH$_2$CH$_3$), 6.12 (1H, d, J=3.0 Hz, C^3-H), 6.38—6.48 (1H, m, C^4-H), 7.24 (1H, d, J=8.3 Hz, C^5-H). LRMS m/z: 254 (M$^+$). HRMS m/z: 254.1356 (Calcd for $C_{13}H_{22}O_3Si$: 254.1340).

Ethyl 4-(2-Thienyl)-3-(trimethylsilyl)butylate (**5e**): Colorless oil. IR (CHCl$_3$): 1719 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: –0.01 (9H, s, –Si(CH$_3$)$_3$), 1.23 (3H, t, J=7.3 Hz, –OCH$_2$CH$_3$), 1.48—1.59 (1H, m, –CHSi(CH$_3$)$_3$), 2.33 (2H, d, J=6.9 Hz, ArCH$_2$–), 2.79 (1H, dd, J=9.6, 14.9 Hz, –CH$_2$COOEt), 3.00 (1H, dd, J=5.6, 14.2 Hz, –CH$_2$COOEt), 4.05 (2H, q, J=6.9 Hz, –OCH$_2$CH$_3$), 6.80 (1H, d, J=2.6 Hz, C^3-H), 6.89 (1H, dd, J=3.5, 5.1 Hz, C^4-H), 7.12 (1H, dd, J=1.2, 5.1 Hz, C^5-H). LRMS m/z: 270 (M$^+$). HRMS m/z: 270.1131 (Calcd for $C_{13}H_{22}O_2SSi$: 270.1110).

Diethyl [2-Deuterio-2-(*p*-methylphenyl)ethyl]malonate (16) Compound **16** was obtained in a similar manner to that used for the synthesis

of **6a**, starting from **3a** and *tert*-BuOD instead of *tert*-BuOH. Colorless oil. Yield 84% (deuteration ratio = 87%). IR ($CHCl_3$): 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (3H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 1.27 (3H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 2.19 (2H, t, J = 7.6 Hz, $ArCHDC\underline{H}_2-$), 2.31 (3H, s, $C\underline{H}_3Ar-$), 2.54—2.70 (1H, m, $ArC\underline{H}D-$), 3.33 (1H, t, J = 7.4 Hz, $-C\underline{H}(COOEt)_2$), 4.19 (4H, q, J = 7.3 Hz, $-OC\underline{H}_2CH_3$), 7.05 (4H, s, Ar-H). LRMS m/z: 279 (M^+). HRMS m/z: 279.1558 (Calcd for $C_{16}H_{21}DO_4$: 279.1580).

Ethyl 2,4-Dideuterio-4-phenylbutyrate (17) Compound **17** was obtained in a similar manner to that used for the synthesis of **4a** starting from **1a** and *tert*-BuOD instead of *tert*-BuOH. Colorless oil. Yield 63% (deuteration ratio = 95%). IR ($CHCl_3$): 1721 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 1.95 (2H, t, J = 6.9 Hz, $ArCHDC\underline{H}_2-$), 2.23—2.38 (1H, m, $ArC\underline{H}D-$), 2.58—2.73 (1H, m, $-C\underline{H}DCOOEt$), 4.12 (2H, q, J = 6.3 Hz, $-OC\underline{H}_2CH_3$), 7.10—7.39 (5H, m, Ar-H). LRMS m/z: 194 (M^+). HRMS m/z: 194.1265 (Calcd for $C_{12}H_{14}D_2O_2$: 194.1280).

α-Alkylation after Cyclopropane Ring-Opening of Diethyl 2-Phenyl-1,1-cyclopropanedicarboxylate (3d) Using SmI_2 General Procedure: SmI_2 solution [prepared from samarium metal (225 mg, 1.50 mmol) and 1,2-diiodoethane (352 mg, 1.25 mmol) in THF (5 ml) under an N_2 atmosphere] was treated with HMPA (0.5 ml). After 5 min, a solution of **3d** (131 mg, 0.50 mmol) and *tert*-butyl alcohol (0.05 ml, 0.50 mmol) in THF (1 ml) was added dropwise to the SmI_2–HMPA–THF solution at room temperature and the whole was stirred for 1 h. The reaction mixture was cooled to −78 °C, and allyl bromide (0.052 ml, 0.60 mmol) was added. The cooling bath was removed and the whole was stirred for 1 h at the ambient temperature. Usual work-up was carried out as above. The residue was chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 15) to give diethyl 2-allyl-2-(2-phenylethyl)malonate (**13a**, 164 mg, 94%) as a colorless oil. IR ($CHCl_3$): 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (6H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 2.14—2.20 (2H, m, $ArCH_2C\underline{H}_2-$), 2.49—2.56 (2H, m, $ArC\underline{H}_2CH_2-$), 2.74 (2H, d, J = 7.6 Hz, $CH_2=CHC\underline{H}_2-$), 4.20 (4H, q, J = 7.1 Hz, $-OC\underline{H}_2CH_3$), 5.09—5.19 (2H, m, $C\underline{H}_2=CHCH_2-$), 5.61—5.78 (1H, m, $CH_2=C\underline{H}CH_2-$), 7.15—7.30 (5H, m, Ar-H). FAB-MS m/z: 305.1724 (Calcd for $C_{18}H_{24}O_4+H$: 305.1753).

Compounds **13b**, **c**, **d**,[24] and **e** were prepared similarly.

Diethyl 2-Allyl-2-[2-(*p*-methylphenyl)ethyl]malonate (**13b**): Colorless oil. IR ($CHCl_3$): 1722 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (6H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 2.04—2.12 (2H, m, $ArCH_2C\underline{H}_2-$), 2.23 (3H, s, CH_3Ar-), 2.38—2.44 (2H, m, $ArC\underline{H}_2-$), 2.66 (2H, d, J = 7.3 Hz, $CH_2=CHC\underline{H}_2-$), 4.12 (4H, q, J = 7.3 Hz, $-OC\underline{H}_2CH_3$), 5.02—5.10 (2H, m, $C\underline{H}_2=CHCH_2-$), 5.54—5.69 (1H, m, $CH_2=C\underline{H}CH_2-$), 6.90—7.17 (4H, m, Ar-H). LRMS m/z: 318 (M^+). HRMS m/z: 318.1837 (Calcd for $C_{19}H_{26}O_4$: 318.1830).

Diethyl 2-Allyl-2-[2-(3,4-methylenedioxyphenyl)ethyl]malonate (**13c**): Colorless oil. IR ($CHCl_3$): 1721 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (6H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 2.09—2.15 (2H, m, $ArCH_2C\underline{H}_2-$), 2.40—2.50 (2H, m, $ArC\underline{H}_2-$), 2.72 (2H, d, J = 7.3 Hz, $CH_2=CHC\underline{H}_2-$), 4.20 (4H, q, J = 7.1 Hz, $-OC\underline{H}_2CH_3$), 5.10—5.18 (2H, m, $C\underline{H}_2=CHCH_2-$), 5.60—5.80 (1H, m, $CH_2=C\underline{H}CH_2-$), 5.90 (2H, s, $-OCH_2O-$), 6.59—6.72 (3H, m, Ar-H). LRMS m/z: 348 (M^+). HRMS m/z: 348.1577 (Calcd for $C_{19}H_{24}O_6$: 348.1577).

Diethyl 2-Methyl-2-[2-(3,4-methylenedioxyphenyl)ethyl]malonate (**13e**): Colorless oil. IR ($CHCl_3$): 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (6H, t, J = 7.1 Hz, $-OCH_2C\underline{H}_3$), 1.48 (3H, s, CH_3-), 2.08—2.14 (2H, m, $ArCH_2C\underline{H}_2-$), 2.46—2.52 (2H, m, $ArC\underline{H}_2-$), 4.19 (4H, q, J = 7.3 Hz, $-OC\underline{H}_2CH_3$), 5.91 (2H, s, $-OCH_2O-$), 6.61—6.73 (3H, m, Ar-H). LRMS m/z: 322 (M^+). HRMS m/z: 322.1402 (Calcd for $C_{19}H_{22}O_6$: 322.1414).

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