Michael Addition of Methyl 2-(Trimethylsilyl)propenoate with Organomagnesiums or Organolithiums Leading to 1 : 1 and/or 2 : 1 Adducts and Subsequent Peterson Olefination by Condensation with Carbonyl Compounds

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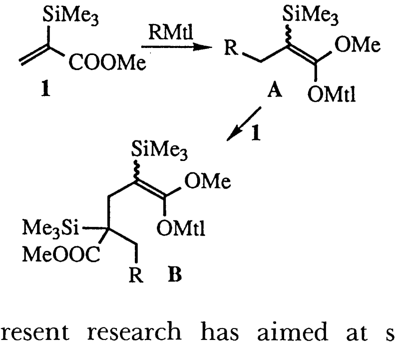
Michael addition of methyl 2-(trimethylsilyl)propenoate with organomagnesiums or organolithiums leads to 1 : 1 and/or 1 : 2 adduct anions which can be utilized in the subsequent step of Peterson olefination with carbonyl compounds. The 1 : 1/1 : 2 ratio depends upon the nature of donor molecules, the reaction conditions such as reaction temperature, polarity of solvent, and rate of addition of the acceptor molecule. Use of acceptors in excess results in the selective formation of 1 : 2 and/or 1 : 3 adducts.

We have briefly reported as a communication letter that methyl 2-(trimethylsilyl)propenoate (**1**) serves as an excellent Michael acceptor in the reactions with Grignard reagents or organolithiums. The resulting adduct anions, stabilized as ester enolates of the α-silylated types, can be effectively applied to the subsequent condensation with a variety of carbonyl compounds. This one-flask reaction, termed a Michael and Peterson sequence, offers an important synthetic route to α-alkylated α,β-unsaturated esters.[1)]

At the stage of Michael addition of 2-silylpropenoate **1**, 1 : 1 Michael adduct anions **A** are not the only products but are accompanied by 1 : 2 adduct anions **B** which consist of one molecule of donor and two molecules of acceptor **1** (Eq. 1).[2)] The product ratio depends upon the nature of Michael donors used. Organolithiums such as 2-lithio-1,3-butadiene and methyl lithio(methylsulfinyl)methyl sulfide exclusively form 1 : 1 adduct anions **A** (Mtl=Li), while 1 : 2 adduct anions **B** (Mtl=MgX) are formed in the reactions with alkyl-[3)] and vinylmagnesium halides. One exception in the reaction cases using Grignard reagents is phenylmagnesium bromide which undergoes Michael addition onto **1** leading to 1 : 1 adduct anion **A** (R=Ph, Mtl=MgBr).



(1)

The present research has aimed at solving the determining factors which influence the formation of 1 : 1 and 1 : 2 Michael adducts, and also at finding out how to control their selective formation. Synthetic applications of the resulting adduct anions by the step of Peterson olefination are described in details.

Results and Discussion

It was previously reported that the reaction of **1** with phenylmagnesium bromide (1.1 equiv) in the presence of copper(I) chloride (0.5 mol%), at −15 °C in dry diethyl ether, gave 80% yield of methyl 2-benzyl-3-phenylpropenoate (**2a**) after quenching the resulting mixture with benzaldehyde.[1)] The propenoate **2a** corresponds to the Peterson olefination product derived from the 1 : 1 Michael adduct anion **A** (R=Ph, Mtl=MgBr). Later we became aware that this reaction was extremely sensitive to the activity of copper(I) chloride catalyst: With a less activated catalyst, not only 1 : 1 adduct **4** but also 1 : 2 adduct **5** was produced after quenching of the reaction mixture with water. In one case, the ratio of **4** : **5**=57 : 20 was provided; reproduction of the above exclusive formation of 1 : 1 adduct anion **A** (R=Ph, Mtl=MgBr), and hence **2a** or **4**, was found to be quite difficult.

Use of phenyllithium instead of phenylmagnesium bromide was expected to solve this problem. As will be discussed below, a nonpolar solvent is desirable for the selective formation of 1 : 1 adduct anions between **1**

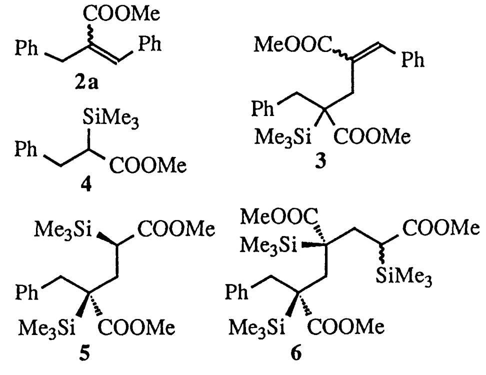


Chart 1.

and the lithium enolates of esters since metal chelation stabilizes the intermediary 1 : 1 ester enolates. However, such chelation must be obstructive for the formation of 1 : 1 adduct anion between **1** and phenyllithium. Accordingly, we carried out the reaction of **1** with phenyllithium (1.1 equiv) in tetrahydrofuran (THF) at −78 °C in the presence of an additive[4] and by means of slow addition (in 2 min) of phenyllithium. The resulting adduct anions were quenched with benzaldehyde. Contrary to our expectation, the condensation product **3** derived from 1 : 2 adduct anion **B** (R=Ph, Mtl=Li) was formed as a major product together with a mixture of two geometrical isomers of **2a** (Entries 1 and 2 of Table 1), while the same reaction in diethyl ether was rather complex.

Relative yield of 1 : 1 adduct **A** was found to be much improved at −30 °C (Entries 3 and 4), and **2a** became the only product when the addition of phenyllithium was quickly completed in a few seconds at −30 °C (Entry 5). This result indicates that the energy barrier for the Michael addition of **1** with phenyllithium is low enough for the reaction to be completed in a few seconds, and accordingly this reaction is kinetically controlled. Finally the optimized conditions were found out under which quick addition of 1.5 equivalent of phenyllithium at −30 °C resulted in 84% of **2a** in the absence of additive (Entry 6).

Under these conditions, a Michael addition and Peterson olefination sequence of 2-silylpropenoate **1**

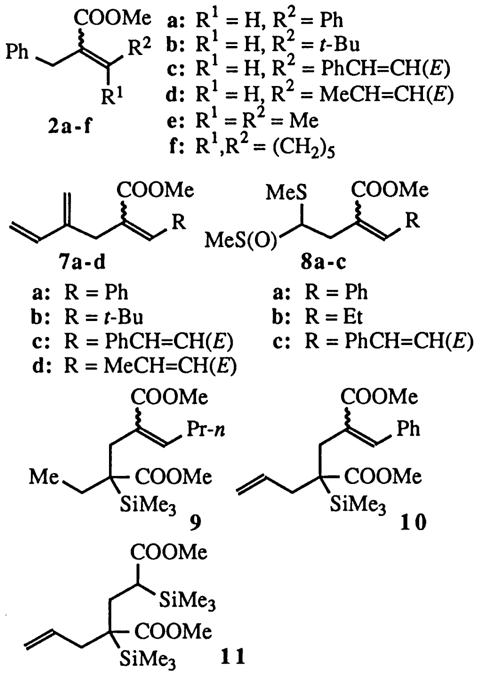


Chart 2.

Table 1. Michael Reactions of Methyl 2-(Trimethylsilyl)propenoate **1**

Entry	Michael donor (Equivalent)	Solvent	Reaction conditions[a)]			Additive[b)]	Quenching reagent	Product (yield/%)[c)]
			Addition	Temp./°C	Time/min			
1	PhLi (1.1)	THF	A	−78	60	HMPA	PhCHO	**2a** (25) **3** (63)
2	PhLi (1.1)	THF	A	−78	60	TMEDA	PhCHO	**2a** (51) **3** (46)
3	PhLi (1.1)	THF	A	−30	60	TMEDA	H_2O	**4** (60)[b)] **5** (15)[d)]
4	PhLi (1.1)	THF	A	−30	60	TMEDA	PhCHO	**2a** (57) **3** (17)
5	PhLi (1.5)	THF	B	−30	20	TMEDA	PhCHO	**2a** (85)
6	PhLi (1.5)	THF	B	−30	20	None	PhCHO	**2a** (84, *E* : *Z*=2 : 3)[e)]
7	PhLi (1.5)	THF	B	−30	20	None	PhCH=CHCHO(*E*)	**2b** (85, *E*: 34%, *Z*: 51%)
8	PhLi (1.5)	THF	B	−30	20	None	MeCH=CHCHO(*E*)	**2c** (78, *E*: 38%, *Z*: 40%)
9	PhLi (1.5)	THF	B	−30	20	None	*t*-BuCHO	**2d** (66, *E* : *Z*=1 : 4)[e,f)]
10	PhLi (1.5)	THF	B	−30	20	None	MeCOMe	**2e** (60)[g)]
11	PhLi (1.5)	THF	B	−30	20	None	Cyclohexanone	**2f** (61)[h)]
12	PhMgBr (1/2)	EtOEt	A	−15	60	None	H_2O	**5** (87)[i)]
13	PhLi (1/3)	THF	A	−78	20 h	None	H_2O	**5** (37)[i)] **6** (47)[i)]
14	C_4H_5Li (1.1)[j)]	EtOEt	B	−78	30	None	PhCHO	**7a** (74, *E* : *Z*=2 : 1)[e)]
15	C_4H_5Li (1.1)[j)]	EtOEt	B	−78	30	None	*t*-BuCHO	**7b** (62, *Z* only)[k)]
16	C_4H_5Li (1.1)[j)]	EtOEt	B	−78	30	None	PhCH=CHCHO(*E*)	**7c** (61, *E*: 15%, *Z*: 46%)
17	C_4H_5Li (1.1)[j)]	EtOEt	B	−78	30	None	MeCH=CHCHO(*E*)	**7d** (57, *E*: 43%, *Z*: 14%)
18	$C_3H_7OS_2Li$ (1.1)[l)]	THF	B	−78	60	None	PhCHO	**8a** (90, *E* only)
19	$C_3H_7OS_2Li$ (1.1)[l)]	THF	B	−78	60	None	EtCHO	**8b** (72, *E* : *Z*=1 : 1)[e)]
20	$C_3H_7OS_2Li$ (1.1)[l)]	THF	B	−78	60	None	PhCH=CHCHO(*E*)	**8c** (71, *E* only)
21	MeMgI (1.1)	EtOEt	B	−15	60	CuCl[m)]	*n*-PrCHO	**9** (73)
22	CH_2=CHMgBr (1.1)	THF	B	−15	60	CuCl[m)]	PhCHO	**10** (84, *E*: 28%, *Z*: 56%)
23	CH_2=CHLi (1.1)	THF	B	−78	90	None	H_2O	**11** (68, single isomer)

a) Reaction conditions for the step of Michael addition. Addition of **1** to the THF solution of phenyllithium took 2 min (Method A) or a few second (Method B). b) Unless otherwise stated, an additive was employed in one equivalent to **1**. c) Yield of isolated products based on **1**. d) Measured by GLC. e) Obtained as an inseparable mixture of two stereoisomers whose ratio was determined by ^{1}H NMR spectrum. f—h) Accompanied by **2a** (f: 14%, g: 10%, h: 6%). i) Yield based on the phenyllithium or phenylmagnesium bromide. j) 2-Lithio-1,3-butadiene. k) Accompanied by 8% of methyl 4-methylene-2-trimethylsilyl-5-hexenoate. m) Lithio(methylsulfinyl)methyl methyl sulfide. n) A catalytic amount (0.5 mol%) of copper(I) chloride was used.

and phenyllithium was examined by using a variety of carbonyl compounds. Aldehydes such as pivalaldehyde, cinnamaldehyde, crotonaldehyde as well as ketones such as acetone and cyclohexanone were all successful to trap the 1 : 1 adduct anion **A** (R=Ph, Mtl=Li) to give **2b—f**, respectively (Entries 7—11).

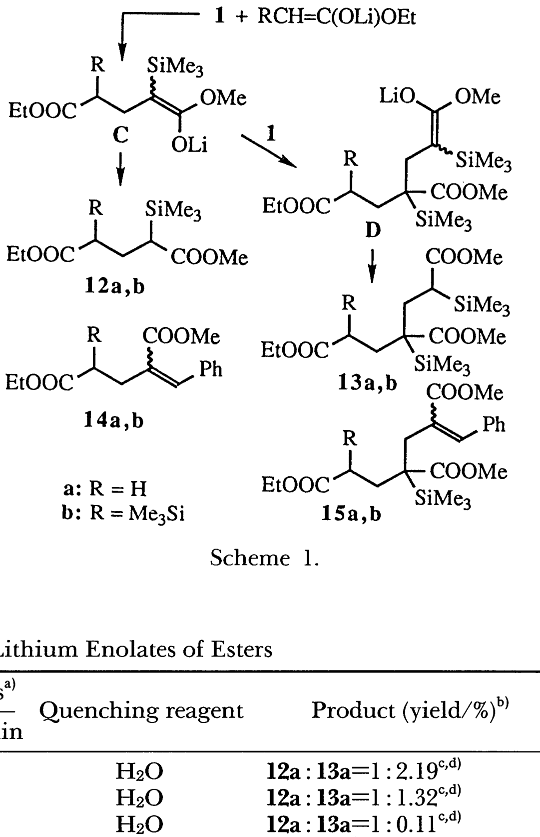
Selective formation of 1 : 2 adduct anions **B** (R=Ph, Mtl=MgBr) was achieved by use of 0.5 equivalent of phenylmagnesium bromide in diethyl ether at −15 °C to give 1 : 2 adduct **5** in 87% yield after water quenching (Entry 12). With 1/3 equivalent of phenyllithium in THF at −78 °C, the expected 1 : 3 adduct **6** was obtained in 47% yield together with 1 : 2 adduct **5** (37%) (Entry 13). The 1 : 2 adduct **5** was a single stereoisomer whose structure was determined as shown in Chart 1 on the basis of the chemical conversion discussed in the following article.[5] The 1 : 3 adduct **6** was a mixture of two diastereomers whose structure was tentatively assigned on the basis of the possible reaction mode for the stereoselective formation of **5**.

It was already reported as a preliminary communication[1] that lithium donors such as 2-lithio-1,3-butadiene and methyl lithio(methylsulfinyl)methyl sulfide also led to the exclusive formation of 1 : 1 adduct anions **A** (Mtl=Li). On the other hand, Grignard reagents such as methylmagnesium iodide and vinylmagnesium bromide exclusively formed 1 : 2 adduct anions **B** (Mtl=MgI or MgBr) even in the presence of copper(I) chloride catalyst.

Both adduct anions **A** and **B** can be utilized for Peterson condensations with aldehydes without trouble to produce α-alkylated α,β-unsaturated esters **7a—d**, **8a—c**, **9**, and **10**. The results are summarized in Table 1 (Entries 14—22). Vinyllithium exceptionally produced 1 : 2 adduct **11** as a single isomer after water quenching, while its stereochemistry is not clear (Entry 23).

The competitive formation of 1 : 2 adduct anions **B** in an equimolar reaction between **1** with phenylmagnesium bromide or phenyllithium indicates an enhanced reactivity of ester enolates toward 2-silylpropenoate **1**. Use of ester enolates as donors in the Michael reactions of 2-silylpropenoate **1** would provide a new entry to 2-silyl- and 2-alkylidenepentanedioates.

The equimolar reaction of **1** with the lithium enolate of ethyl acetate at −78 °C in THF produced 1 : 2 adduct **13a** as major product along with 1 : 1 adduct



Scheme 1.

Table 2. Michael Reactions of **1** with Lithium Enolates of Esters

Entry	Lithium enolate (Equivalent)	Solvent	Reaction conditions[a] Temp./°C	Reaction conditions[a] Time/min	Quenching reagent	Product (yield/%)[b]
1	CH_2=C(OLi)OEt(1)	THF	−78	60	H_2O	**12a** : **13a**=1 : 2.19[c,d]
2	CH_2=C(OLi)OEt(1.5)	THF	−78	60	H_2O	**12a** : **13a**=1 : 1.32[c,d]
3	CH_2=C(OLi)OEt(3)	THF	−78	60	H_2O	**12a** : **13a**=1 : 0.11[c,d]
4	CH_2=C(OLi)OEt(1/2)	THF	−78	60	PhCHO	**15a** (63)[e]
5	CH_2=C(OLi)OEt(1)	EtOEt	−78	60	H_2O	**12a** : **13a**=1 : 0.5[c,d]
6	CH_2=C(OLi)OEt(2)	EtOEt	−78	60	H_2O	**12a** : **13a**=1 : 0.14[d] **12a** (78)[f]
7	CH_2=C(OLi)OEt(3)	EtOEt	−78	60	H_2O	**12a** (84)
8	CH_2=C(OLi)OEt(2)	EtOEt	−78	60	PhCHO	**14a** (88)
9	CH_2=C(OLi)OEt(1.5)	E/T[g]	−78	60	H_2O	**12a** only[d]
10	CH_2=C(OLi)OEt(1)	E/T[g]	−78	60	H_2O	**12a** : **13a**=1 : 0.15[c,d]
11	CH_2=C(OLi)OEt(1.2)	E/T[g]	−78	20	PhCHO	**14a** (81)
12	TMSCH=C(OLi)OEt(1.5)	THF	−78	60	PhCHO	**14b** (37) **15b** (51)
13	TMSCH=C(OLi)OEt(3)	THF	−78	60	PhCHO	**14b** (67) **15b** (26)
14	TMSCH=C(OLi)OEt(1/2)	THF	−78	60	H_2O	**13b** (46)[e]
15	TMSCH=C(OLi)OEt(1/2)	THF	−78	60	PhCHO	**14b** (5)[e] **15b** (74)[e]
16	TMSCH=C(OLi)OEt(2)	EtOEt	−78	60	H_2O	**12b** (92)
17	TMSCH=C(OLi)OEt(2)	EtOEt	−78	60	PhCHO	**14b** (60)

a) Reaction conditions for the step of Michael addition. Addition of a lithium enolate to **1** was completed in a few seconds. b) Yield based on **1**. c) Not separated from each other. d) The ratio was determined by GLC of the crude mixture. e) Yield based on the lithium enolate. f) Only **12a** was isolated by column chromatography. g) Diethyl ether/toluene=5 : 1 v/v.

12a (**12a** : **13a**=1 : 2.19 by GLC) (Scheme 1 and Entry 1 of Table 2). This relatively high reactivity of 1:1 adduct anion **C** (R=H) was quite surprising since the reaction site of **C** is sterically hindered compared with the open carbon of the lithium enolate of ethyl acetate. Only when 3 equivalents of the enolate was employed, formation of 1 : 2 adduct **13a** was practicably suppressed to less than 10% (**12a** : **13a**=1 : 0.11, Entry 3).

Diethyl ether was found to be a solvent which favored the formation of 1 : 1 adduct **12a** more than THF. For example, the reaction of **1** with 2 equivalents of the enolate gave a 1 : 0.14 mixture of **12a** and **13a** (Entry 6), and no trace of **13a** was detected on use of 3 equivalents of the enolate (Entry 7). Even better was toluene in which 1.2—1.5 equivalent of the enolate was enough to suppress the formation of **D** (Entries 9 and 11).[6] Even with only one equivalent of the enolate, a high 1 : 1 product ratio (**12a** : **13a**= 1 : 0.15) resulted (Entry 10, compare with Entry 1).

The Michael additions of 2-silylpropenoate **1** mentioned above belong to a competitive and consecutive second-order reaction on which a kinetic study was previously reported.[7] However, the Michael reaction of **1** with lithium or magnesium donors took place too fast even at −78 °C for the reaction rate to be measured.

Some kinetic informations on this reaction were collected as follows: Each 2/15 molar portion of **1** was added at once to the lithium enolate of ethyl acetate at −78 °C in THF (or diethyl ether). A small part of the reaction mixture was sampled after stirring for 30 min and quenched with water. Amounts of the 1 : 1 adduct **12a** and the 1 : 2 adduct **13a** formed were measured by GLC. The second 2/15 portion of **1** was added and analyzed similarly. This procedure was repeated until total amount of **1** reached 10/15 equivalent. The results are summarized in Table 3.

Table 3. Kinetic Data for the Michael Reaction of **1** with the Lithium Enolate of Ethyl Acetate[a]

Molar equivalent			
1[b]	**12a**[c]	**13a**[c,d]	Remaining CH_2=C(OLi)OEt[e]
In tetrahydrofuran			
0.2	0.19	+	1.31
0.4	0.29	0.05	1.11
0.6	0.37	0.11	0.91
0.8	0.38	0.21	0.70
1.0	0.36	0.32	0.50
In diethyl ether			
0.2	0.19	+	1.31
0.4	0.39	0.01	1.09
0.6	0.57	0.01	0.91
0.8	0.66	0.07	0.70
1.0	0.62	0.17	0.56

a) Each 0.2 portion of **1** was added to the lithium enolate of ethyl acetate (1.5 equivalent to a total amount of **1**) at −78 °C, and reaction was continued for 30 min. b) Total amount of **1** used. c) Based on GLC analysis. d) The number may be duplicated to calculate the yield of **13a** based on **1**. e) Calculated molar equivalent of the remaining lithium enolate.

As clearly shown by Table 3, diethyl ether can be better used than THF in favor for the 1 : 1 adduct **12a**. A satisfactory level of product ratio, higher than 20 : 1 (**12a** : **13a**), could be achieved at the stage of combined yield of 60% in the reaction in diethyl ether. On the other hand, THF may be conveniently used for the formation of 1 : 2 adduct **13a**. Comparison of the results of Tables 2 and 3 shows again that quick addition of acceptor **1** leads to the more favored formation of 1 : 1 adduct **12a**.

Reaction of **1** with 2 equivalents of the lithium enolate of ethyl acetate in diethyl ether at −78 °C and subsequent quenching with benzaldehyde gave 88% of 5-ethyl 1-methyl 2-benzylidenepentanedioate (**14a**) as a sole product (Entry 8 of Table 2), while the reaction of **1** with 0.5 equivalent of the enolate in THF at −78 °C gave 63% of 7-ethyl 1-methyl 2-benzylidene-4-methoxycarbonyl-4-(trimethylsilyl)heptanedioate (**15a**) (Entry 4).

The high reactivity of 1 : 1 adduct anion **C** (R=H) observed above indicates the excellent property of the lithium enolate of ethyl (trimethylsilyl)acetate as a donor molecule, though sterically hindered around the reaction site. Actually this bulky enolate underwent a smooth Michael addition to **1** in diethyl ether at −78 °C; use of 2 equivalents of the enolate gave 5-ethyl methyl 2,4-bis(trimethylsilyl)pentanedioate (**12b**) and ethyl 1-methyl 2-benzylidene-4-(trimethylsilyl)pentanedioate (**14b**) after quenching of the resulting 1 : 1 adduct anion **C** (R=SiMe$_3$) with water and benzaldehyde, respectively (Entries 16 and 17 of Table 2). Similarly, products from the 1 : 2 adduct anion **D** (R=SiMe$_3$), **13b** (46%) and **15b** (74%), were obtained when 0.5 equivalent of the enolate was employed (Entries 14 and 15).

In conclusion, not only 1 : 1 adduct anions but also 1 : 2 adduct anions are formed in Michael addition of methyl 2-(trimethylsilyl)propenoate (**1**) with organomagnesiums or organolithiums depending upon the nature of donor molecules and reaction conditions. Since enhanced reactivity of the 1 : 1 adduct anions **A** as silyl-stabilized ester enolates is clearly responsible for this competitive reaction sequence, predominant formation of 1 : 1 adduct anions **A** can be achieved when the first step of Michael addition is highly accelerated. Use of organolithiums is preferred for this purpose since they are generally more reactive than the corresponding organomagnesiums, but vinyllithium was one exception. Also desired is the quick addition of a donor molecule to **1** at a temperature which is high enough for the reaction to be completed in a short period. In the reactions with lithium enolates of esters, metal chelation would play a critical role. Therefore, stabilization of the 1 : 1 adduct anions **C** by chelation favors the formation of 1 : 1 adduct anions **12**. Use of less polar solvents such as toluene or diethyl ether is the case.

Some more detailed discussion on the solvent effect as well as that on stereochemical feature of the Michael additions to **1** will be made in the following paper of this series.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with JASCO IRA-1 and A-702 spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX-100 (100 MHz for ^{1}H NMR and 25.05 MHz for ^{13}C NMR) and GSX-270 (270 MHz for ^{1}H NMR and 67.94 MHz for ^{13}C NMR) instruments. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra and high-resolution mass spectra (HRMS) were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy unless otherwise stated. Elemental analyses were performed on a Hitachi 026 CHN analyzer. For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vaccuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

General Procedure for the Michael Addition of 1 with Phenyllithium and Subsequent Peterson Olefination Leading to 2a—f. As a typical procedure, the reaction of **1** with phenyllithium and benzaldehyde is described below: A solution of **1**[8] (0.158 g, 1 mmol) in dry THF (1 ml) was added, rapidly (in a few seconds) by the aid of a syringe at −30 °C under dry nitrogen, to the THF solution of phenyllithium (1.6 M in hexane, 0.94 ml, 1.5 mmol in 5 ml of THF; 1 M=1 mol dm^{-3}). The mixture was stirred at −30 °C for 20 min and then benzaldehyde (0.17 g, 1.6 mmol) in THF (1 ml) was added. After stirring was continued at the same temperature for 30 min, the mixture was treated with saturated aqueous ammonium chloride and extracted with diethyl ether (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–diethyl ether (10:1 v/v) to give **2a** (0.212 g, 84%) as a mixture of two geometrical isomers.

Peterson olefinations using other carbonyl compounds were similarly carried out under the reaction conditions listed in Table 1 (Entries 6—11).

Methyl 2-Benzyl-3-phenylpropenoate (2a): Obtained as a 2:3 mixture of (*E*)-**2a** and (*Z*)-**2a** (^{1}H NMR), from which only (*Z*)-**2a** was separated. (*Z*)-**2a**: Colorless liquid; Bp 110—115 °C/21 Pa (bulb-to-bulb); IR (neat) 1720, 1495, 1435, 1220, 740, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.50 (3H, s, COOMe), 3.70 (2H, d, J=1.5 Hz, PhCH$_2$), 6.56 (1H, t, J=1.5 Hz, =CH), and 7.17 (10H, br s, Ph); ^{13}C NMR (CDCl$_3$) δ=41.25 (t, PhCH$_2$), 51.41 (q, COOMe), 126.50, 127.77, 128.06, 128.40, 128.89 (each d, Ph), 133.52 (s), 134.83 (d, =CH), 135.86, 137.90 (each s), and 169.43 (s, COOMe); MS *m*/*z* (rel intensity, %) 252 (M$^+$, 32), 193 (33), 192 (base peak), 191 (53), 165 (29), 115 (94), and 91 (46). Found: C, 80.90; H, 6.46%. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39%. ^{1}H NMR (CDCl$_3$) of (*E*)-**2a**: δ=3.64 (3H, s, COOMe), 3.90 (2H, s, PhCH$_2$), 7.17 (10H, br s, Ph), and 7.85 (1H, s, =CH).

Methyl 2-Benzyl-4,4-dimethyl-2-pentenoate (2b): Two isomers were separated from each other through column chromatography on silica gel with hexane–diethyl ether (15:1 v/v). (*E*)-**2b**: Colorless liquid; IR (neat) 1715, 1285, 1205, 1090, 730, and 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.18 (9H, s, *t*-Bu), 3.58 (3H, s, COOMe), 3.83 (2H, s, PhCH$_2$), 6.94 (1H, s, =CH), and 7.13 (5H, br s, Ph); MS *m*/*z* (rel intensity, %) 232 (M$^+$, 73), 217 (59), 172 (22), 157 (72), 143 (26), 142 (25), 141 (33), 131 (32), 129 (63), 128 (40), 116 (39), 115 (78), 91 (base peak), 78 (22), and 77 (37). Found: C, 77.58; H, 8.57%. Calcd for $C_{13}H_{20}O_2$: C, 77.55; H, 8.68%. (*Z*)-**2b**: Colorless liquid; IR (neat) 1725, 1235, 1200, 1100, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.08 (9H, s, *t*-Bu), 3.48 (2H, s, PhCH$_2$), 3.56 (3H, s, COOMe), 5.47 (1H, =CH), and 7.13 (5H, br s, Ph); MS *m*/*z* (rel intensity, %) 232 (M$^+$, base peak), 217 (70), 201 (23), 157 (26), 129 (23), 115 (35), and 91 (59). HRMS Found: *m*/*z* 232.1474. Calcd for $C_{15}H_{20}O_2$: M, 232.1462.

Methyl 2-Benzyl-5-phenyl-2,4-pentadienoate (2c): Two isomers were separated from each other through silica-gel column chromatography using hexane–dichloromethane (3:1 v/v). (2*E*, 4*E*)-**2c**: Colorless needles (benzene–hexane); mp 81 °C; IR (KBr) 1705, 1620, 1285, 1240, 1080, 750, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.67 (3H, s, COOMe), 3.83 (2H, s, PhCH$_2$), and 6.7—7.6 (13H, m, =CH and Ph); ^{13}C NMR (CDCl$_3$) δ=32.70 (t, PhCH$_2$), 51.80 (q, COOMe), 123.53 (d), 126.06, 127.14, 128.20, 128.35, 128.70, 128.84, 129.91, 136.25 (s), 139.56 (s), 139.76, 140.34 (eacn d, =CH), and 168.12 (s, COOMe); MS *m*/*z* (rel intensity, %) 278 (M$^+$, 42), 219 (23), 218 (23), 141 (24), 116 (33), 92 (22), and 91 (base peak). Found: C, 81.98; H, 6.52%. Calcd for $C_{19}H_{18}O_2$: C, 81.85; H, 6.63%. (2*Z*, 4*E*)-**2c**: Colorless leaflets (hexane); mp 43—44 °C; IR (KBr) 1710, 1225, 1205, 980, 750, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.65 (5H, s, COOMe and PhCH$_2$), 6.48 (1H, $J_{3\text{-}4}$=11.0 Hz, 3-H), 6.62 (1H, d, $J_{5\text{-}4}$=15.5 Hz, 5-H), 7.16 (10H, br s, Ph), and 7.89 (1H, dd, $J_{4\text{-}3}$=11.0 Hz, 4-H); ^{13}C NMR (CDCl$_3$) δ=40.25 (t, PhCH$_2$), 51.31 (q, COOMe), 125.58, 126.16, 127.04, 128.31, 128.40, 128.55, 128.70, 129.57, 136.59 (s), 139.12 (d), 139.31 (s), 141.32 (d), and 167.29 (s, COOMe); MS *m*/*z* (rel intensity, %) 278 (M$^+$, base peak), 219 (34), 218 (29), 187 (29), and 91 (51). Found: C, 81.98; H, 6.52%. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52%.

Methyl 2-Benzyl-2,4-hexadienoate (2d): Two isomers were separated from each other through column chromatography on silica gel with hexane–dichloromethane (2:1 v/v). (2*E*,4*E*)-**2d**: Colorless liquid; IR (neat) 1710, 1640, 1240, 1080, 970, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.87 (3H, dd, J=6.3 and 1.0 Hz, Me), 3.67 (3H, s, COOMe), 3.75 (2H, s, PhCH$_2$), 6.18 (1H, dq, $J_{5\text{-}4}$=15.0 and $J_{5\text{-Me}}$=6.3 Hz, 5-H), 6.48 (1H, ddq, $J_{4\text{-}5}$=15.0, $J_{4\text{-}3}$=11.0 and $J_{4\text{-Me}}$=1.0 Hz, 4-H), 7.0—7.3 (5H, m, Ph), and 7.33 (1H, d, $J_{3\text{-}4}$=11.0 Hz, 3-H); ^{13}C NMR (CDCl$_3$) δ=18.96 (q, Me), 32.41 (t, PhCH$_2$), 51.67 (q, COOMe), 125.93, 127.17 (each d), 127.56 (s, 2-C), 128.16, 128.28, 139.32 (each d), 139.73 (s), 140.08 (d), and 168.38 (s, COOMe); MS *m*/*z* (rel intensity, %) 216 (M$^+$, base peak), 187 (26), 157 (80), 156 (39), 155 (40), 143 (37), 142 (35), 141 (61), 138 (21), 129 (76), 128 (59), 115 (60), 91 (84), and 77 (32). HRMS Found: m/z 216.1150. Calcd for $C_{14}H_{16}O_2$: M, 216.1149. (2Z,4E)-**2d**: Colorless liquid; IR (neat) 1710, 1430, 1220, 980, 745, and 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.82 (3H, dd, J=7.0 and 2.0 Hz, Me), 3.60 (2H, s, PhCH$_2$), 3.68 (3H, s, COOMe), 5.93 (1H, dq, $J_{5\text{-}4}$=15.0 and $J_{5\text{-}\mathrm{Me}}$=7.0 Hz, 5-H), 6.35 (1H, d, $J_{3\text{-}4}$=11.0 Hz, 3-H), 7.08 (1H, ddq, $J_{4\text{-}5}$=15.0, $J_{4\text{-}3}$=11.0, and $J_{4\text{-}\mathrm{Me}}$=2.0 Hz, 4-H), and 7.16 (5H, br s, Ph); ^{13}C NMR (CDCl$_3$) δ=18.55 (q, Me), 40.16 (t, PhCH$_2$), 51.20 (q, COOMe), 126.05 (d), 127.22 (s, 2-C), 128.22, 128.63, 128.81 (each d), 137.67 (s), 139.55, 141.43 (each d), and 167.50 (s, COOMe); MS m/z (rel intensity, %) 216 (M$^+$, 28), 157 (60), 156 (31), 155 (41), 143 (31), 142 (42), 141 (79), 129 (91), 128 (82), 127 (25), 115 (base peak), 91 (92), and 77 (52). HRMS Found: m/z 216.1150. Calcd for $C_{14}H_{16}O_2$: M, 216.1171.

Methyl 2-Benzyl-3-methyl-2-butenoate (2e): Purified by silica-gel column chromatography with hexane–diethyl ether (20 : 1 v/v). Colorless liquid; bp 85—87°C/239 Pa (bulb-to-bulb); IR (neat) 1715, 1285, 1200, 1080, and 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.80, 2.04 (each 3H, s, Me), 3.54 (3H, s, COOMe), 3.66 (2H, s, PhCH$_2$), and 7.10 (5H, br s, Ph); ^{13}C NMR (CDCl$_3$) δ=22.54, 23.13 (each q, Me), 35.40 (t, PhCH$_2$), 51.02 (q, COOMe), 125.81 (d), 126.23 (s), 127.99, 128.70 (each d), 139.85, 145.13 (each s), and 169.20 (s, COOMe); MS m/z (rel intensity, %) 204 (M$^+$, base peak), 173 (40), 172 (45), 145 (50), 144 (88), 129 (20), and 91 (42). HRMS Found: m/z 204.1153. Calcd for $C_{13}H_{16}O_2$: M, 204.1149.

Methyl 2-Cyclohexylidene-3-phenylpropanoate (2f): Purified by silica-gel column chromatography with hexane–dichloromethane (2 : 1 v/v). Colorless liquid; bp 135—137 °C/93 Pa (bulb-to-bulb); IR (neat) 1715, 1450, 1210, 850, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.5—2.6 (10H, m, (CH$_2$)$_5$), 3.60 (3H, s, COOMe), 3.66 (2H, s, PhCH$_2$), and 7.13 (5H, br s, Ph); ^{13}C NMR (CDCl$_3$) δ=26.48, 28.06, 28.36, 31.82, 32.81, 34.93 (each t, CH$_2$), 51.20 (q, COOMe), 123.47 (s), 125.81, 128.05, 128.28 (each d), 139.97, 150.06 (each s), and 170.08 (s, COOMe); MS m/z (rel intensity, %) 244 (M$^+$, base peak), 236 (22), 213 (25), 212 (58), 184 (41), 141 (25), 131 (23), 128 (21), 104 (27), and 91 (55). HRMS Found: m/z 244.1493. Calcd for $C_{16}H_{20}O_2$: C, 244.1462.

Genera Procedure for the Preparation of 3—6. Procedures similar to the above one employed for the preparation of **2a** were applied. In some cases, an additive such as HMPA or TMEDA (each 1 equiv) was used together with phenyllithium, and ice-cold water was used as a quenching agent. Details of the reaction conditions and results are listed in Table 1 (Entries 1—4, 12, 13)

Dimethyl 2-Benzyl-4-benzylidene-2-(trimethylsilyl)pentanedioate (3): Obtained as a 2.9 : 1 inseparable mixture (^{1}H NMR) of two geometrical isomers. Colorless liquid; IR (neat) 1740, 1450, 1260, 860, and 770 cm^{-1}; ^{1}H NMR (CDCl$_3$) E-isomer: δ=0.00 (9H, s, Me$_3$Si), 2.4—3.5 (4H, m, CH$_2$), 3.72, 3.91 (ech 3H, s, COOMe), 7.2—7.6 (10H, m, Ph), and 7.89 (1H, br s, =CH). Z-isomer: δ=0.27 (9H, s, Me$_3$Si), 2.4—3.5 (4H, m, CH$_2$), 3.72, 3.85 (each 3H, s, COOMe), 6.67 (1H, br s, =CH), and 7.2—7.6 (10H, m, Ph); MS (20 eV) m/z (rel intensity, %) 410 (M$^+$, 45), 378 (34), 338 (34), 319 (75), 278 (55), 236 (23), 235 (base peak), 215 (74), 187 (22), 183 (28), 163 (51), and 131 (36). HRMS Found: m/z 410.1907. Calcd for $C_{24}H_{30}O_4Si$: M, 410.1912.

Methyl 3-Phenyl-2-(trimethylsilyl)propanoate (4): Purified by silica-gel column chromatography with hexane–diethyl ether (15 : 1 v/v). Colorless liquid; IR (neat) 1720, 1250, 1145, 845, 750, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.12 (9H, s, Me$_3$Si), 2.35 (1H, dd, J=11.5 and 3.3 Hz, CH), 2.69 (1H, dd, J_{gem}=14.5 and J=3.3 Hz, one of PhCH$_2$), 3.12 (1H, dd, J_{gem}=14.5 and J=11.5 Hz, the other of PhCH$_2$) 3.52 (3H, s, COOMe), and 7.15 (5H, br s, Ph); ^{13}C NMR (CDCl$_3$) δ=2.70 (q, Me$_3$Si), 32.53 (t, PhCH$_2$), 39.57 (d, CH), 50.90 (q, COOMe), 125.93, 128.11, 128.28 (each d), 141.90 (s), and 174.96 (s, COOMe); MS m/z (rel intensity, %) 236 (M$^+$, 26), 131 (30), 104 (59), 91 (26), and 89 (42). Found: C, 65.76; H, 8.50%. Calcd for $C_{13}H_{20}O_2Si$: C, 65.76; H, 8.50%.

Dimethyl 2-Benzyl-2,4-bis(trimethylsilyl)pentanedioate (5): Purified by silica-gel column chromatography with hexane–diethyl ether (20 : 1 v/v). Pale yellow liquid; IR (neat) 1720, 1430, 1250, 1200, and 835 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.00, 0.04 (each 9H, s, Me$_3$Si), 1.9—2.5 (3H, m, 3- and 4-H), 2.96, 3.14 (each 1H, d, J_{gem}=14.5 Hz, PhCH$_2$), 3.48, 3.70 (each 3H, s, COOMe), and 7.1—7.3 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=−2.88, −2.18 (each q, Me$_3$Si), 30.54, 34.59 (each t, CH$_2$), 37.48 (d, 4-C), 44.71 (s, 2-C), 51.00, 51.12 (each q, COOMe), 126.36, 128.18, 130.60 (each d, Ph), 139.71 (s, Ph), 176.48, and 177.01 (each s, COOMe); MS m/z (rel intensity, %) 394 (M$^+$, 5), 145 (21), 117 (15), 91 (17), 89 (25), and 73 (base peak). HRMS Found: m/z, 394.1994. Calcd for $C_{20}H_{34}O_4Si_2$: M, 394.1994.

Methyl 2-Benzyl-4-methoxycarbonyl-2,4,6-tris(trimethylsilyl)heptanedioate (6): Purified by column chromatography on silica gel with hexane–diethyl ether (5 : 1 v/v). Colorless needles (hexane); mp 101—102.5°C; IR (neat) 1730, 1710, 1690, 1245, 1180, and 830 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=−0.12, 0.10, 0.19 (each 9H, s, Me$_3$Si), 1.64 (1H, dd, J_{gem}=14.0 and J=2.7 Hz, one of 3-H), 1.85 (1H, dd, J_{gem}=14.0 and J=3.0 Hz, the other of 3-H), 2.41 (1H, dd, J_{gem}=14.0 and J=8.6 Hz, one of 5-H), 2.52 (1H, dd, J_{gem}=14.0 and J=11.3 Hz, the other of 5-H), 2.58 (1H, d, J_{gem}=14.0 Hz, one of PhCH$_2$), 2.81 (1H, m, 6-H), 3.59, 3.61, 3.65 (each 3H, s, COOMe), 3.65 (1H, d, J_{gem}=14.0 Hz, the other of PhCH$_2$), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=−1.69, −0.36, 0.55 (each Me$_3$Si), 35.20, 35.32, 37.81 (each CH$_2$), 40.92, 41.01, 41.97 (CH and q-C), 50.71, 51.10, 51.24 (each COOMe), 126.32, 127.80, 131.15, 139.48 (each Ph), 175.63, 176.16, and 176.67 (each COOMe). MS m/z (rel intensity, %) 552 (M$^+$, 5), 249 (49), 159 (19), 145 (26), 127 (21), 117 (18), 89 (36), and 73 (base peak). Found: C, 58.44; H, 8.48%. Calcd for $C_{27}H_{48}O_6Si_3$: C, 58.65; H, 8.75%.

General Procedure for the Michael Addition of 1 with 2-Lithio-1,3-butadiene and Subsequent Peterson Olefination Leading to 7a—d. As a typical procedure, the reaction of **1** with 2-lithio-1,3-butadiene and benzaldehyde is described below: Butyllithium (1.6 M, in hexane, 2.1 ml, 3.3 mmol) was added at −78°C under dry nitrogen to 2-(tributylstannyl)-1,3-butadiene (1.132 g, 3.3 mmol) in dry THF (6 ml). After 20 min, **1** (0.474 g, 3 mmol) in THF (1 ml) was added repidly (in a few seconds) by the aid of a syringe, the mixture was stirred at the same temperatre for 30 min, and then benzaldehyde (0.318 g, 3 mmol) in THF (1 ml) was added. After stirring was continued at −78 °C for 30 min, at 0 °C for 15 min, and at room temperture for 15 min, the mixture was treated with saturated aqueous ammonium chloride and extracted with diethyl ether (30 ml×2). The combined extracts were washed with saturated aqueous sodium chloride, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed on silica gel with hexane-diethyl ether (9 : 1 v/v) to give **7a** (0.506 g, 74%) and a mixture of two geometrical isomers.

Peterson olefinations using other carbonyl compounds were simlarly carried out under the reaction conditions listed in Table 1 (Entries 14—17).

Methyl 2-Benzylidene-4-methylene-5-hexenoate (7a): Obtained as an inseparable 3 : 2 mixture of (*E*)-**7a** and (*Z*)-**7a** (GLC). Colorless liquid; IR (neat) 1725, 1210, 1100, 910, 770, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) *E*-isomer: δ=3.34 (2H, s, CH_2), 3.61 (3H, s, COOMe), 4.9—5.4 (4H, m, =CH_2), 6.41 (1H, dd, J_{5-6}=17.5 and 11.0 Hz, 5-H), 6.76 (1H, s, =CHPh), and 7.23 (5H, br s, Ph); *Z*-isomer: δ=3.40 (2H, s, CH_2), 3.78 (3H, s, COOMe), 4.9—5.4 (4H, m, =CH_2), 6.53 (1H, dd, J_{5-6}= 17.5 and 11.0 Hz, 5-H), 7.31 (5H, br s, Ph), and 7.84 (1H, s, =CHPh); MS *m/z* (rel intensity, %) 228 (M^+, 17), 169 (54), 168 (27), 167 (32), 154 (25), 153 (31), 152 (22), 141 (35), 128 (27), 116 (24), 115 (base peak), and 91 (68). Found: C, 78.75; H, 7.16%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

Methyl 2-(2,2-Dimethylpropylidene)-4-methylene-5-hexenoate (7b): Purified by silica-gel column chromatography with hexane-diethyl ether (15 :1 v/v). (*Z*)-**7b** was the only product. Colorless liquid; bp 108—110°C/267 Pa (bulb-to-bulb); IR (neat) 1730, 1240, 1205, and 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (9H, s, *t*-Bu), 3.10 (2H, s, CH_2), 3.68 (3H, s, COOMe), 4.9—5.4 (4H, m, =CH_2), 5.48 (1H, s, =CH), and 6.35 (1H, dd, J_{5-6}=16.0 and 10.0 Hz, 5-H); ^{13}C NMR ($CDCl_3$) δ=29.77 (q, *t*-Bu), 33.23 (s, *t*-Bu), 38.40 (t, CH_2), 51.17 (q, COOMe), 113.98, 118.03 (each t, =CH_2), 128.35 (s), 138.10 (d), 143.07 (s), 144.14 (d), and 170.36 (s, COOMe); MS *m/z* (rel intensity, %) 208 (M^+, 21), 177 (21), 161 (20), 149 (24), 138 (base peak), 133 (52), 123 (20), 119 (25), 108 (39), 106 (46), 95 (33), 93 (57), 91 (67), 81 (27), 79 (67), and 77 (38). HRMS Found: *m/z* 208.1457. Calcd for $C_{13}H_{20}O_2$: M, 208.1462.

Methyl 2-Cinnamylidene-4-methylene-5-hexenoate (7c): Two isomers were separated from each other by column chromatography on silica gel with hexane-diethyl ether (9 : 1 v/v). (*E*)-**7c**: Colorless liquid; IR (neat) 1710, 1620, 1210, 1080, 900, and 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.40 (2H, s, CH_2), 3.73 (3H, s, COOMe), 4.8—5.5 (4H, m, =CH_2), 6.51 (1H, *J*=17.5 and 11.0 Hz, =CH), and 6.8—7.6 (8H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=28.26 (t, CH_2), 51.85 (q, COOMe), 113.30, 116.17 (each t, =CH_2), 123.63, 127.14, 128.45, 128.70 (each d), 136.34 (s), 139.03, 140.15, 140.68 (each d), 143.17 (s), and 168.22 (s, COOMe); MS *m/z* (rel intensity, %) 254 (M^+, 18), 195 (23), 179 (26), 178 (22), 165 (28), 163 (40), 162 (21), 141 (63), 128 (22), 119 (21), 117 (65), 116 (71), 104 (23), and 91 (base peak). HRMS Found: *m/z* 254.1300. Calcd for $C_{17}H_{18}O_2$: M, 254.1306. (*Z*)-**7c**: Colorless liquid; IR (neat) 1710, 1620, 1210, 975, 900, 745, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.28 (2H, s, CH_2), 3.76 (3H, s, COOMe), 4.9—5.3 (4H, m, =CH_2), 6.34 (1H, dd, J_{5-6}=17.5 and 11.0 Hz, =CH), 6.55 (1H, d, *J*=11.5 Hz, =CH), 6.68 (1H, d, *J*=15.5 Hz, =CHPh), 7.2—7.5 (5H, m, Ph), and 7.86 (1H, dd, *J*=15.5 and 11.5 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=35.82 (t, CH_2), 51.61 (q, COOMe), 114.17, 117.83 (each t, =CH_2), 125.77, 127.23 (each d), 127.96 (s), 128.55, 128.70 (each d), 136.84 (s), 138.39, 138.98, 141.22 (each d), 144.05 (s), and 167.77 (s, COOMe); MS *m/z* (rel intensity, %) 254 (M^+, 3), 117 (32), 116 (base peak), 91 (76), and 77 (31). HRMS Found: *m/z* 254.1311. Calcd for $C_{17}H_{18}O_2$: M, 254.1306.

Methyl [(*E*)-2-Butenylidene]-4-methylene-5-hexenoate (7d): Two isomers were separated from each other by column chromatography on silica gel with hexane-diethyl ether (15 : 1 v/v). (*E*)-**7d**: Colorless liquid; IR (neat) 1710, 1640, 1210, and 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.85 (3H, d, *J*=5.0 Hz, Me), 3.25 (2H, s, CH_2), 3.71 (3H, s, COOMe), 4.7—5.4 (4H, m, =CH_2), 6.0—6.2 (2H, m, =CH and =CHMe), 6.46 (1H, dd, J_{5-6}=17.0 and 11.0 Hz, 5-H), and 7.2—7.4 (1H, m, =CH); MS *m/z* (rel intensity, %) 192 (M^+, 79), 137 (22), 133 (73), 131 (22), 119 (21), 117 (58), 116 (26), 105 (86), and 91 (base peak). HRMS Found: *m/z* 192.1145. Calcd for $C_{12}H_{16}O_2$: M, 192.1149. (*Z*)-**7d**: Colorless liquid; IR (neat) 1710, 1640, 1210, 980, and 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.83 (3H, dd, *J*=7.0 and 1.5 Hz, Me), 3.20 (2H, t, CH_2), 3.72 (3H, s, COOMe), 4.9—5.4 (4H, m, =CH_2), 5.92 (1H, dq, *J*=15.0 and 7.0 Hz, =CHMe), 6.32 (1H, d, *J*=11.0 Hz, =CH), 6.38 (1H, dd, J_{5-6}=17.0 and 11.0 Hz, 5-H), and 7.05 (1H, ddq, *J*=15.0, 11.0, and 1.5 Hz, =CH); MS *m/z* (rel intensity, %) 192 (M^+, base peak), 161 (22), 137 (33), 133 (75), 117 (43), 105 (66), and 91 (65). HRMS Found: *m/z* 192.1143. Calcd for $C_{12}H_{16}O_2$: M, 192.1149.

General Procedure for the Michael Addition of 1 with Methyl Lithio(methylsulfinyl)methyl Sulfide and Subsequent Peterson Olefination Leading to 8a—c. As a typical procedure, the reaction of **1** with methyl lithio(methylsulfinyl)methyl sulfide and benzaldehyde is described below: To a solution of methyl (methylsulfinyl)methyl sulfide (0.41 g, 3.3 mmol) in dry THF (6 ml) was added, at −78 °C under dry nitrogen, butyllithium (1.6 M in hexane, 2.1 ml, 3.3 mmol). After 30 min, a solution of **1** (0.747 g, 3 mmol) in THF (1 ml) was added rapidly (in a few seconds) by the aid of a syringe. After 1 h at the same temperature, benzaldehyde (0.318 g, 3 mmol) in THF (1 ml) was added. Stirring was continued at −78°C for 30 min, at 0 °C for 15 min, and at room temperature for 15 min. The resulting mixture was cooled down to 0 °C and poured into saturated aqueous ammonium chloride, extracted with diethyl ether (25 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.805 g, 90%) was almost pure **8a** which was submitted to NMR measurement.

Peterson olefinations using other carbonyl compounds were smilarly carried out under the reaction conditions listed in Table 1 (Entries 18—20).

Methyl 2-[2-Methylsulfinyl-2-(methylthio)ethyl]-3-phenylpropenoate (8a): (*E*)-**8a** was the only product. Colorless liquid; IR (neat) 1700, 1430, 1245, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.10 (3H, s, MeS), 2.56 (3H, s, MeSO), 3.06 (1H, dd, J_{gem}=14.2 and *J*=10.8 Hz, one of CH_2), 3.38 (1H, ddd, J_{gem}=14.2, *J*=4.5, and 1.3 Hz, the other of CH_2), 3.82 (3H, s, COOMe), 3.91 (1H, dd, *J*=10.8 and 4.5 Hz, CH), 7.3—7.5 (5H, m, Ph), and 7.85 (1H, d, *J*=1.3 Hz, =CH); MS *m/z* (rel intensity, %) 235 (M^+−63, 62), 234 (23), 203 (50), 187 (base peak), 175 (77), 160 (30), 155 (31), 143 (51), 142 (25), 129 (33), 128 (79) 127 (22), and 115 (37). On an attempted distillation under vacuum (120 to 130 °C/27 Pa), this compound **8a** changed into methyl (*E*)-2-[2-(methylthio)ethenyl]-3-phenyl-propenoate as a 7 : 4 mixture of two geometrical isomers in 80% yield.[9]

Methyl 2-[2-Methylslfinyl-2-(methylthio)ethyl]-2-pentenoate (8b): Obtained as an inseparable 1 : 1 mixture of (*E*)-**8b** and (*Z*)-**8b** (^{1}H NMR). Purified by silica-gel column chromatography with chloroform. Colorless liquid; IR (neat) 1710, 1430, 1235, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.04, 1.08 (3H, each t, *J*=7.0 Hz, Et), 2.23 (3H, s, MeS), 2.3—3.3 (8H, m, CH_2, CH, Et, and MeSO), 6.13, and 6.93 (1H, each t,

J=8.0 Hz, =CH); MS *m/z* (rel intensity, %) 187 (M^+−63, 52), 155 (88), 127 (base peak), 99 (55), and 79 (52). No analytical data were available due to the absence of parent ion peak.

Methyl 2-[2-Methylsulfinyl-2-(methylthio)ethyl]-5-phenyl-2,4-pentadienoate (8c): (*E*)-**8c** was the only product which was purified by silica-gel column chromatography with chloroform. Colorless needles (benzene-hexane); mp 95—97°C; IR (KBr) 1700, 1435, 1230, 1040, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s, MeS), 2.66 (3H, s, MeSO), 2.86 (1H, dd, J_{gem}=14.5 and J=10.4 Hz, one of CH_2), 2.42 (1H, dd, J=14.5 and J=4.5 Hz, the other of CH_2), 2.68 (1H, dd, J=10.4 and 4.5 Hz, CH), 3.80 (3H, s, COOMe), and 6.8—7.6 (8H, Ph and =CH); MS *m/z* (rel intensity, %) 261 (M^+ −63, 28), 260 (22), 213 (33), 212 (23), 181 (36), 169 (46), 155 (32), 154 (70), 153 (base peak), 152 (58), 141 (43), 128 (27), 115 (40), 91 (71), and 77 (25).

Dimethyl 2-Ethyl-4-butylidene-2-(trimethylsilyl)pentanedioate (9): To the methylmagnesium iodide freshly prepared from Mg (0.08 g, 3.3 mmol) and MeI (0.468 g, 3.3 mmol) in dry diethyl ether (5 ml) was added under dry nitrogen copper(I) chloride (1.5 mg, 0.5 mol%). After stirring at room temperature for 20 min, the mixture was cooled down to −15°C and **1** (0.474 g, 3 mmol) in THF (1 ml) was added rapidly (in a few seconds) by the aid of a syringe. Stirring was continued at the same temperature for 1 h and butanal (0.216 g, 3 mmol) was added. The mixture was stirred at −15°C for 15 min and at room temperature for additional 15 min, poured into saturated aqueous ammonium chloride, and extracted with diethyl ether (25 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane-diethyl ether (9:1 v/v) to give (*Z*)-**9** as a sole product (0.344 g, 73%): Colorless liquid; IR (neat) 1720, 1220, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.09 (9H, s, Me_3Si), 0.89, 0.95 (each 3H, t, J=7.5 Hz, Et and *n*-Pr), 1.2—1.9 (4H, m, *n*-Pr), 2.25 (2H, q, J=7.5 Hz, Et), 2.45, 2.94 (each 1H, d, J_{gem}=14.0 Hz, 3-CH_2), 3.59, 3.68 (each 3H, s, COOMe), and 5.75 (1H, t, J=7.5 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=−2.17 (q, Me_3Si), 11.27, 13.80 (each q, Et and *n*-Pr), 22.66, 24.31, 31.70 36.52 (each t, Et, *n*-Pr, and 3-CH_2), 42.62 (s, 2-C), 50.74, 51.14 (each q, COOMe), 130.22 (s, 4-C), 141.84 (d, =CH), 169.09, and 176.24 (each COOMe); MS *m/z* (rel intensity, %) 314 (M^+, 10), 182 (39), 174 (27), 167 (31), 93 (20), 89 (33), 81 (24), and 73 (base peak). HRMS Found: *m/z* 314.1914. Calcd for $C_{16}H_{30}O_4Si$: M, 314.1912.

Dimethyl 4-Benzylidene-2-(2-propenyl)-2-(trimethylsilyl)-pentanedioate (10): A procedure similar to the above one employed for preparing **9** was applied by using vinylmagnesium bromide (1.5 M in THF, 2.2 ml, 3.3 mmol), copper(I) chloride (1.5 mg, 0.5 mol%), **1** (0.474 g, 3 mmol), benzaldehyde (0.318 g, 3 mmol). The crude product was purified by silica-gel column chromatography with hexane-diethyl ether (9:1 v/v) to give (*E*)-**10** (0.151 g, 28%) and (*Z*)-**10** (0.303 g, 56%). (*E*)-**10**: Colorless liquid; IR (neat) 1720, 1245, 1110, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.05 (9H, s, Me_3Si), 1.86 (1H, dd, J_{gem}=14.5 and J=8.0 Hz, one of CH_2), 2.48 (1H, dd, J_{gem}=14.5 and J=5.5 Hz, the other of CH_2), 2.97, 3.24 (each 1H, d, J_{gem}=13.5 Hz, 3-CH_2), 3.43, 3.75 (each 3H, s, COOMe), 4.7—5.0 (2H, m, =CH_2), 5.5—6.1 (1H, m, =CH), 7.2—7.4 (5H, m, Ph), and 7.65 (1H, s, =CHPh); MS *m/z* (rel intensity, %) 360 (M^+, 13), 185 (17), 115 (17), 102 (24), 89 (30), 81 (27), and 73 (base peak). Found: C, 66.79; H, 7.93%. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83%. (*Z*)-**10**: Colorless liquid; IR (neat) 1720, 1210, 1120, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.13 (9H, s, Me_3Si), 2.3—2.9 (2H, m, CH_2), 2.55, 3.21 (each 1H, d, J_{gem}=13.5 Hz, 3-CH_2), 3.55, 3.61 (each 3H, s, COOMe), 5.03 (1H, br d, J=10.5 Hz, one of =CH_2), 5.06 (1H, br d, J=16.0 Hz, the other of =CH_2), 5.7—6.2 (1H, m, =CH), 6.58 (1H, s, =CHPh), and 7.1 —7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−2.35 (q, Me_3Si), 36.05, 37.57 (each t, CH_2), 41.86 (s, 2-C), 51.02, 51.55 (each q, COOMe), 117.07 (t, =CH_2), 127.81, 128.11 (each d), 131.98 (s), 135.21 (d), 135.86 (s), 136.38 (d), 170.32, and 175.72 (each s, COOMe); MS *m/z* (rel intensity, %) 360 (M^+, 29), 215 (17), 185 (31), 95 (23), 89 (31), 81 (23), and 73 (base peak). Found: C, 66.50; H, 7.83%. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83%.

Dimethyl 2-(2-Propenyl)-2,4-bis(trimethylsilyl)pentanedioate (11): To the THF (6 ml) solution of dibutyldivinyltin (0.474 g, 1.65 mmol) was added at −78°C under dry nitrogen butyllithium (1.6 M in hexane, 2.1 ml, 3.3 mmol). After 20 min, **1** (0.474 g, 3 mmol) was added rapidly (in a few seconds) by the aid of a syringe at −78°C under dry nitrogen. Stirring was continued at the same temperature for 1.5 h, poured into saturated aqueous ammonium chloride, and extracted with diethyl ether (20 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane in order to remove the tin compound and then hexane-diethyl ether (9:1 v/v) to give **10** (0.351 g, 68%) as a single diastereomer. Colorless liquid; IR (neat) 1720, 1435, 1250, 1205, 1155, and 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.09 (9H, s, Me_3Si), 1.8—2.8 (3H, m, CH_2 and CH), 3.54, 3.60 (each 3H, s, COOMe), 4.8—5.1 (2H, m, =CH_2), and 5.6—6.1 (1H, m, =CH); ^{13}C NMR ($CDCl_3$) δ=−2.94, −2.41 (each q, Me_3Si), 29.06 (t, CH_2), 34.99 (d, 4-C), 35.58 (t, CH_2), 44.09 (s, 2-C), 50.96 (q, COOMe), 116.77 (t, =CH_2), 136.56 (d, =CH), 176.07, and 176.30 (each s, COOMe); MS *m/z* (rel intensity, %) 344 (M^+, 4), 199 (14), 186 (18), 95 (34), 89 (27), and 73 (base peak). HRMS Found: *m/z* 344.1806. Calcd for $C_{16}H_{32}O_4Si$: M, 344.1837.

General Procedure for the Preparation of 12a,b and 13a,b. As a typical procedure, the reaction leading to **12a** is described as follows: Freshly prepared LDA (3 mmol) was added at −78°C under nitrogen to a solution of ethyl acetate (0.264 g, 3 mmol) in diethyl ether (5 ml). To this solution was added **1** (0.158 g, 1 mmol) all at once by the aid of a syringe. The mixture was stirred at the same temperature for 1 h, poured into saturated aqueous ammonium chloride, and extracted with diethyl ether (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was purified by vacuum distillation to give **12a** (0.207 g, 84%).

Preparation of **12a**,**b** and **13a**,**b** was performed by a similar procedure under the reaction conditions listed in Table 1 (Entries 1—3, 5—7, 9, 10, 14, 16).

5-Ethyl 1-Methyl 2-(Trimethylsilyl)pentanedioate (12a): Colorless liquid; bp 140—150°C/20 Pa (bulb-to-bulb); IR (neat) 1720, 1430, 1250, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.00 (9H, s, Me_3Si), 1.16 (3H, t, J=7.0 Hz, COOEt), 1.6—1.8 (1H, m, CH_2), 1.9—2.2 (3H, m, CH_2), 2.34 (1H, ddd, J_{gem}=15.5, J=8.4, and 4.8 Hz, 4-H), 3.56 (3H, s, COOMe), and 4.03 (2H, q, J=7.0 Hz, COOEt); ^{13}C NMR ($CDCl_3$) δ=−2.75 (Me_3Si), 14.27 (COOEt), 22.06 (3-C), 34.53 (4-C), 36.86 (2-C), 52.44 (COOMe), 60.27 (COOEt), 173.15, and 175.26 (COO); MS *m/z* (rel intensity, %) 246 (M^+, 6), 215 (17), 201 (36), 160 (37), 159 (base peak), 117 (24), 114 (26), 89 (31), and 73 (76). Found: C, 53.80; H, 9.37%. Calcd for $C_{11}H_{22}O_4Si$: C, 53.63; H, 9.00%.

Ethyl Methyl 2,4-Bis(trimethylsilyl)pentanedioate (12b): Obtained as a single isomer. Colorless liquid; bp 123—125 °C/18 Pa (bulb-to-bulb); IR (neat) 1720, 1250, 1140, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.08 (9H, s, Me_3Si), 1.23 (3H, t, J=7.0 Hz, COOEt), 1.7—2.2 (4H, m, CH_2 and CH), 3.60 (3H, s, COOMe), 4.08, and 4.10 (each q, J=7.0 Hz, COOEt); ^{13}C NMR ($CDCl_3$) δ=−2.64 (q, Me_3Si), 14.56 (q, COOEt), 23.66 (t, 3-C), 38.04, 38.16 (each d, 2- and 4-C), 50.96 (q, COOMe), 59.77 (t, COOEt), 174.78, and 175.31 (each COO); MS m/z (rel intensity, %) 318 (M$^+$, 10), 273 (14), 218 (15), 173 (91), 159 (63), 147 (23), 99 (19), 89 (21), 75 (24), and 73 (base peak). Found: C, 52.54; H, 9.53%. Calcd for $C_{14}H_{30}O_4Si$: C, 52.79; H, 9.40%.

7-Ethyl 1-Methyl 4-Methoxycarbonyl-2,4-bis(trimethylsilyl)-heptanedioate (13a): Obtained as an inseparable 1 : 1 mixture of two diastereomers. Colorless liquid; bp 220°C/20 Pa (bulb-to-bulb); IR (neat) 1710, 1425, 1245, 1150, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.10, −0.02, −0.01 (18H, each s, Me_3Si), 1.12, 1.14 (each 1/2×3H, t, J=7.0 Hz, COOEt), 1.6—2.5 (7H, m, CH_2 and CH), 3.49, 3.50, 3.51, 3.52 (each 1/2×3H, s, COOMe), 4.00, and 4.01 (each 1/2×2H, q, J=7.0 Hz, COOEt); ^{13}C NMR ($CDCl_3$) δ=−2.80, −2.65, −2.25, −2.01 (Me_3Si), 14.48 (COOEt), 26.30, 26.37, 28.89, 29.58, 30.79, 31.57, 34.10, 35.11, 41.97, 43.59 (CH_2, CH, and q-C), 51.30, 51.41 (COOMe), 60.44 (COOEt), 173.60, 173.97, 175.81, 176.20, 176.26, and 176.71 (each COO); MS m/z (rel intensity, %) 404 (M$^+$, 3), 259 (12), 159 (13), 99 (13), 89 (34), 75 (21), and 73 (base peak). HRMS Found: m/z 404.2049. Calcd for $C_{18}H_{36}O_6Si_2$: M, 404.2049.

Ethyl Methyl 4-Methoxycarbonyl-2,4,6-tris(trimethylsilyl)-heptanedioate (13b): Obtained as an inseparable mixture of two diastereomers. Purified by silica-gel column chromatography with hexane–diethyl ether (10 : 1 v/v). Colorless liquid; bp 220 °C/67 Pa (bulb-to-bulb); IR (neat) 1720, 1435, 1250, 1150, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.06, 0.07, 0.08, 0.09, 0.11 (27H, each s, Me_3Si), 1.25 (3H, t, COOEt), 1.7—2.5 (6H, m, CH_2 and CH), 3.54, 3.58, 3.60, 3.64 (6H, each s, COOMe), and 4.0—4.2 (2H, m, COOEt); ^{13}C NMR ($CDCl_3$) δ=−2.91, −2.85, −2.79, −2.75, −2.13, −2.03 (each Me_3Si), 14.37, 14.43 (each COOEt), 28.84, 29.95, 31.69, 34.43, 35.00, 43.96, 44.58 (CH_2, CH, and q-C), 50.68, 50.75, 50.91, 51.09 (each COOMe), 59.72, 59.94 (each COOEt), 175.59, 175.89, 175.98, 176.21, 176.34, and 176.41 (each COO); MS m/z (rel intensity, %) 476 (M$^+$, 6), 225 (14), 173 (18), 159 (16), 117 (15), 89 (19), 75 (34), and 73 (base peak). Found: C, 52.80; H, 9.72%. Calcd for $C_{21}H_{44}O_6Si_3$: C, 52.90; H, 9.50%.

General Procedure for the Preparation of 14a,b and 15a,b. Similar procedures under the reaction conditions shown in Table 1 (Entries 4, 8, 11—14, 17) gave **14a,b** and **15a,b**.

5-Ethyl 1-Methyl 2-Benzylidenepentanedioate (14a): Obtained as an inseparable mixture of (E)-**14a** and (Z)-**14a**. Colorless liquid; bp 140—150 °C/213 Pa (bulb-to-bulb); IR (neat) 1733, 1714, 1252, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) E-isomer: δ=1.22 (3H, t, J=7.0 Hz, COOEt), 2.4—3.0 (4H, m, CH_2), 3.61 (3H, s, COOMe), 4.10 (2H, q, J=7.0 Hz, COOEt), 7.32 (5H, br s, Ph), and 7.72 (1H, s, =CHPh). Z-isomer: δ=1.24 (3H, t, J=7.0 Hz, COOEt), 2.4—3.0 (4H, m, CH_2), 3.80 (3H, s, COOMe), 4.13 (2H, q, J=7.0 Hz, COOEt), 6.72 (1H, s, =CH), and 7.22 (5H, br s, Ph); ^{13}C NMR ($CDCl_3$) δ=14.18, 14.24 (each COOEt), 23.12, 30.67 (each CH_2), 33.40, 33.55 (each CH_2), 51.65, 52.06 (each COOMe), 60.46, 60.52 (each COOEt), 127.93, 128.12, 128.15, 128.64, 128.66, 129.18, 131.20, 132.41, 135.06, 135.26, 135.90, 140.44 (each Ph and =CH), 168.32, 169.53, 172.48, and 172.71 (each COO). MS m/z (rel intensity, %) 262 (M$^+$, 8), 202 (15), 174 (18), 129 (base peak), 128 (30), and 115 (40). Found: C, 68.39; H, 7.12%. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92%.

5-Ethyl 1-Methyl 2-Benzylidene-4-(trimethylsilyl)pentanedioate (14b): Obtained as an inseparable mixture of (E)-**14b** and (Z)-**14b**. Purified by silica-gel column chromatography with hexane–diethyl ether (10:1 v/v). Colorless liquid; bp 150—157 °C/186 Pa (bulb-to-bulb); IR (neat) 1716, 1252, 1155, and 847 cm^{-1}; ^{1}H NMR ($CDCl_3$) E-isomer: δ=0.06 (9H, s, Me_3Si), 1.08 (3H, t, J=7.0 Hz, COOEt), 2.2—3.4 (3H, m, CH_2 and CH), 3.76 (3H, s, COOMe), 3.94 (2H, q, J=7.0 Hz, COOEt), 7.0—7.5 (5H, m, Ph), and 7.62 (1H, s, =CHPh). Z-isomer: δ=0.13 (9H, s, Me_3Si), 1.21 (3H, t, J=7.0 Hz, COOEt), 2.2—3.4 (3H, m, CH_2 and CH), 3.59 (3H, s, COOMe), 4.09 (2H, q, J=7.0 Hz, COOEt), 6.72 (1H, s, =CHPh), and 7.0—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−2.64, −2.54 (each Me_3Si), 14.48, 14.73 (each COOEt), 24.41, 32.49 (each CH_2), 36.86, 37.09 (each CH), 51.73, 52.10 (each COOMe), 59.92, 60.08 (each COOEt), 127.94, 128.13, 128.29, 128.33, 128.50, 128.59, 129.39, 132.96, 133.64, 134.58, 135.83, 136.33, 139.82 (each Ph, =CH, and =C), 168.79, 169.94, 174.39, and 174.75 (each COO); MS m/z (rel intensity, %) 334 (M$^+$, 8), 288 (20), 273 (20), 173 (32), 159 (20), 129 (45), and 75 (24). Found: C, 64.77; H, 7.92%. Calcd for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83%.

7-Ethyl 1-Methyl 2-Benzylidene-4-methoxycarbonyl-4-(trimethylsilyl)heptanedioate (15a): Obtained as an inseparable 1 : 1 mixture of (E)-**15a** and (Z)-**15a** after purification by silica-gel column chromatography with hexane–diethyl ether (2 : 1 v/v). Pale yellow liquid; IR (neat) 1720, 1430, 1245, 1200, and 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.03, 0.14 (each 1/2×9H, s, Me_3Si), 1.20, 1.23 (each 1/2×3H, q, COOEt), 1.4—3.3 (6H, m, CH_2), 3.49, 3.60, 3.64, 3.77 (each 1/2×3H, COOMe), 4.07, 4.08 (each 1/2×2H, COOEt), 6.66 (1/2H, s, =CH(Z)), 7.1—7.4 (5H, m, Ph), and 7.74 (1/2H, s, =CH(E)); ^{13}C NMR ($CDCl_3$) δ=−2.50, −2.37 (each Me_3Si), 14.48, 14.44 (each COOEt), 26.74, 26.91, 30.38, 31.63, 31.80, 38.31, 40.01, 41.79 (each CH_2), 51.24, 51.37, 51.95, 52.26 (each COOMe), 60.37, 60.47 (each COOEt), 128.10, 128.27, 128.46, 128.70, 131.67, 132.47, 135.35, 136.07, 136.15, 141.60 (Ph and =C), 169.05, 170.72, 173.77, 173.91, 175.67, and 176.26 (each COO); MS m/z (rel intensity, %) 420 (M$^+$, 10), 155 (13), 141 (20), 115 (24), 89 (23), and 73 (base peak). Found: C, 62.93; H, 7.92%. Calcd for $C_{22}H_{32}O_6Si$: C, 62.83; H, 7.67%.

7-Ethyl 1-Methyl 2-Benzylidene-4-methoxycarbonyl-4,6-bis(trimethylsilyl)heptanedioate (15b): Obtained as a 1 : 2 mixture of (E)-**15b** and (Z)-**15b** which were separated from each other by column chromatography on silica gel with hexane–diethyl ether (5 : 1 v/v). (E)-**15b**: Colorless liquid; IR (neat) 1720, 1440, 1250, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.08, 0.11 (each 9H, s, Me_3Si), 1.30 (3H, t, J=7.0 Hz, COOEt), 1.70 (1H, d, J_{gem}=14.3 Hz, one of 5-H), 2.18 (1H, dd, J_{gem}=14.3 and J=9.9 Hz, the other of 5-H), 2.30 (1H, d, J=9.9 Hz, 6-H), 3.00, 3.18 (each 1H, d, J_{gem}=14.5 Hz, 3-H), 3.57, 3.84 (each 3H, s, COOMe), 4.14 (2H, q, COOEt), 7.3—7.6 (5H, m, Ph), and 7.75 (1H, s, =CH); ^{13}C NMR ($CDCl_3$) J=−2.58 (Me_3Si), 14.37 (COOEt), 28.87, 29.27 (3- and 5-C), 34.67 (6-C), 42.85 (4-C), 50.70, 51.79 (each COOMe), 59.68

(COOEt), 128.07, 128.48, 129.17, 131.93, 136.02, 140.30 (Ph and =C), 168.99, 175.60, and 176.11 (each COO); MS *m/z* (rel intensity, %) 492 (M^+, 2), 229 (15), 197 (11), 169 (15), 155 (14), 141 (21), 115 (19), 89 (20), 75 (17), and 73 (base peak). HRMS Found: *m/z* 492.2344. Calcd for $C_{25}H_{40}O_6Si_2$: M, 492.2362. (*Z*)-**15b**: Colorless liquid; IR (neat) 1710, 1430, 1210, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08, 0.16 (each 9H, s, Me_3Si), 1.11 (3H, t, J=7.0 Hz, COOEt), 2.1—2.4 (3H, m, CH_2 and CH), 2.79 (2H, br s, 3-H), 3.60, 3.62 (each 3H, s, COOMe), 3.85, 4.01 (each 1H, dq, J_{gem}=10.0 and J=7.0 Hz, COOEt), 6.56 (1H, s, =CH), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−2.59, −2.23 (each Me_3Si), 14.18 (COOEt), 29.96 (5-C), 34.57 (3-C), 37.57 (6-C), 43.92 (4-C), 50.96, 51.76 (each COOMe), 59.87 (COOEt), 127.64, 127.87, 128.16, 133.26, 134.15, 135.98 (Ph and =C), 170.49, 175.72, and 176.01 (each COO); MS *m/z* (rel intensity, %) 492 (M^+, 2), 446 (11), 229 (12), 141 (13), 115 (13), 91 (14), 89 (17), 75 (16), and 73 (base peak). HRMS Found: *m/z* 492.2367. Calcd for $C_{25}H_{40}O_6Si_2$: M, 492.2362.

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