Highly Selective Synthesis of *Z*-Unsaturated Esters by Using New Horner−Emmons Reagents, Ethyl (Diarylphosphono)acetates

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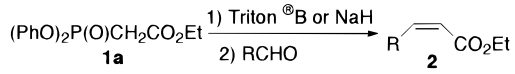
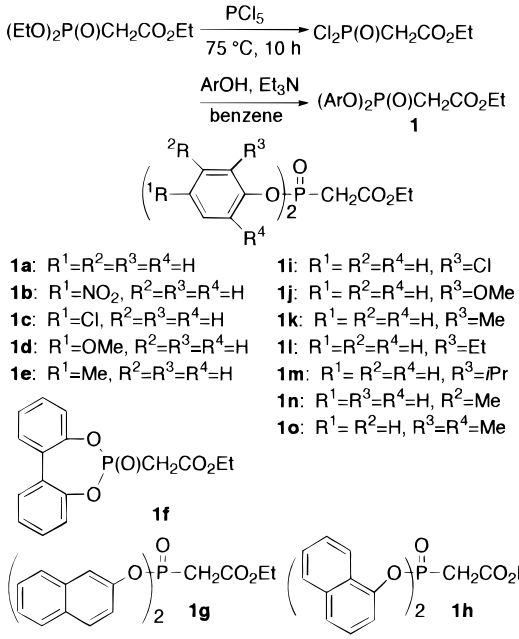
New Horner−Emmons reagents, ethyl (diarylphosphono)acetates **1**, were prepared from triethyl phosphonoacetate, PCl_5, and the corresponding phenols. The reaction of **1** with several kinds of aldehydes in the presence of Triton B or NaH in THF solvent revealed that these reagents are useful for the synthesis of *Z*-unsaturated esters. Among the reagents examined, ethyl(di-*o*-tolylphosphono)-, [bis(*o*-ethylphenyl)phosphono]-, and [bis(*o*-isopropylphenyl)phosphono]acetates (**1k**−**m**) were found to be the most effective, giving *Z*-unsaturated esters with 93−99% selectivity.

The Horner−Emmons modification of the Wittig reaction is a widely used method for the preparation of unsaturated esters. The phosphonate anions are strongly nucleophilic and react readily with carbonyl compounds under mild conditions to form an olefin and a water-soluble phosphate ester in good yields. However, in general, this reaction preferentially gives more stable *E*-disubstituted olefins. In order to prepare *Z*-olefins, several attempts have been made by the choice of cation, temperature, solvent, and phosphonate reagents, but they were with a limited success.[2,3] Some other reports on the preferential formation of *Z*-olefins involve the five-membered cyclic phosphonate,[4] five-membered cyclic phosphonamide,[5] and bis(trifluoroethyl)phosphonate.[6] Among them, Still's method using methyl [bis(trifluoroethyl)phosphono]acetate in the presence of KHMDS/18-crown-6 in THF has been shown to be the most selective and versatile. Although this method has attained widespread recognition in synthesis,[7,8] the use of 5 equiv of expensive and hygroscopic 18-crown-6 is a considerable drawback. We therefore felt the need of developing a more practical way to make *Z*-unsaturated esters. Recently, we have reported the preparation of ethyl (diphenylphosphono)acetate (**1a**) and the reaction of **1a** with some aldehydes in the presence of an inexpensive base, Triton B or NaH in THF, to give *Z*-unsaturated esters in 89−93% selectivity (Scheme 1).[9] Furthermore, when Still's conditions (KHMDS/18-crown-6) were applied to this reaction, selectivity for *Z*-isomers was increased up to 99%. Although **1a** is as *Z*-selective as Still's reagent, it still leaves some room for improvement. In this paper we report full details of our study on the Horner−Emmons reaction with ethyl (diphenylphosphono)acetate (**1a**) and also with the new reagents, ethyl (diarylphosphono)acetates **1b**−**o**.

Scheme 1



Scheme 2



Results and Discussion

Horner−Emmons Reaction of Ethyl (Diphenylphosphono)acetate. Ethyl (diphenylphosphono)acetate (**1a**) was readily prepared from commercially available triethyl phosphonoacetate, PCl_5, and phenol via ethyl (dichlorophosphono)acetate in 60% overall yield (Scheme 2).

Horner−Emmons reaction of **1a** was first carried out with benzaldehyde. The results are summarized in Table 1. When **1a** was treated with benzyltrimethylammonium hydroxide (40% in MeOH) (Triton B) followed by the reaction with benzaldehyde in tetrahydrofuran (THF) at

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Table 1. Horner−Emmons Reaction of 1a with Benzaldehyde

entry	base	solvent	conditions	yield (%)	**2a** (*Z*/*E* ratio)
1	Triton B	THF (3)[a]	−78 °C, 30 min	96	91:9
2	Triton B	THF (20)	−78 °C, 30 min	98	93:7
3	Triton B[b]	THF (20)	−78 °C, 1 h	71 (24)[c]	91:9
4	Triton B	ether (20)	0 °C, 1 h	67	29:71
5	Triton B	DME (20)	−78 °C, 20 min→−50 °C	63 (34)	79:21
6	Triton B	toluene (20)	−78 °C, 1 h	46 (7)	66:34
7	BuLi	THF (3)	−78 °C, 30 min	60 (34)	67:33
8	LDA	THF (5)	−78 °C, 1 h	85 (12)	80:20
9	NaH	THF (5)	−78 °C, 30 min→−35 °C	100	85:15
10	*t*-BuOK	THF (3)	−78 °C, 30 min	94	86:14
11	*t*-BuOK	THF (20)	−78 °C, 2.5 h→−50 °C	98	91:9
12	*t*-BuOK	DME (20)	−78 °C, 40 min	59 (41)	89:11
13	KHMDS	THF (20)	−78 °C, 1 h	93	92:8
14	KHMDS	THF (20)[d]	−78 °C, 1 h	98	99:1

[a] The number in parentheses is the quantity of solvent (mL/**1**, mmol). [b] Methanol of Triton B was removed by aspirator. [c] The number in parentheses is the recovered yield of **1** (%). [d] 5 equiv of 18-crown-6 was added.

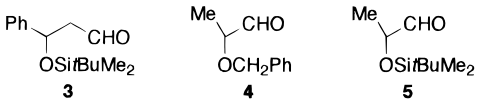
Table 2. Horner−Emmons Reaction of 1a with Several Types of Aldehydes in THF Solvent

entry	R	base	THF[a]	conditions[b]	yield (%)	**2** (*Z*/*E* ratio)
1	Ph	Triton B	20	−78 °C, 30 min	98	93:7
2	PrCH=CH[t]	Triton B	20	−78 → −35 °C	97	89:11
3	*n*-C_7H_{15}	Triton B	20	−78 → −25 °C	99	90:10
4	*n*-C_7H_{15}	NaH	20	−78 → 0 °C	99	90:10
5	*n*-C_7H_{15}	NaH	5	−78 → −10 °C	100	90:10
6	*n*-C_7H_{15}	KHMDS[c]	20	−78 → 0 °C	68 (19)[d]	92:8
7	BuCHEt	Triton B	20	−78 → −20 °C	100	89:11
8	BuCHEt	NaH	5	−78 → −10 °C	90	93:7
9	BuCHEt	NaH	5	−78 → −10 °C[e]	100	94:6
10	cyclohexyl	NaH	5	−78 → −25 °C	97	90:10
11	cyclohexyl	NaH	5	−78 → −20 °C[e]	98	91:9
12	**3**	NaH	5	−78 → −10 °C	100[f]	92:8
13	**4**	NaH	5	−78 → −10 °C	91[f]	94:6
14	**5**	NaH	5	−78 → −10 °C	78[f,g]	97:3

[a] mL/**1a**, mmol. [b] Base was added at −78 °C unless otherwise stated. The reaction mixture was warmed over 1−2 h except for entry 1. [c] 5 equiv of 18-crown-6 was added. [d] The number in parentheses is the recovered yield of **1** (%). [e] NaH was added at 0 °C. [f] The aldehyde was prepared by DIBAL reduction of the corresponding ethyl ester. The yield was calculated from the starting ester. [g] This rather low yield is mainly due to the moderate yield of the reduction.

−78 °C, 91% *Z*-selectivity was obtained (entry 1). Dilution of the reaction medium favored the formation of the *Z*-isomer achieving 93% *Z*-selectivity in 98% chemical yield (entry 2). Low solubility of **1a** in ether and toluene prevented the use of these solvents. Among the solvents examined, THF turned out to be the best choice with respect to both the *Z*-selectivity and the chemical yield (entries 4−6). The effect of bases on the *Z*/*E* ratio was next studied (entries 7−13). Moderate to good *Z*-selectivity (67−85%) was obtained with BuLi, LDA, or NaH, while better results were observed with potassium bases, *t*-BuOK and potassium hexamethyldisilazide (KHMDS) (91−92% *Z*-selectivity). Furthermore, when Still's conditions (KHMDS/18-crown-6) were applied to this reaction, an extremely high *Z*-selectivity (99:1) was attained in 98% chemical yield (entry 14). These results show that the reagent **1a** is as effective as or better than Still's reagent for the synthesis of ethyl (*Z*)-cinnamate.

Next, we examined the reaction with other aldehydes in THF (Table 2). The reaction with an α,*β*-unsaturated aldehyde or aliphatic aldehydes in the presence of Triton B gave 89−90% *Z*-selectivity with almost quantitative yields irrespective of the aldehyde structure (entries 2, 3, 7). The *Z*-selectivity with octyl aldehyde is not changed by the use of NaH instead of Triton B, and the same 90% *Z*-selectivity was obtained over the range of two concentrations (entries 4, 5). Still's conditions (KHMDS/18-crown-6) again gave a slightly improved selectivity (92%), which is identical with the result from Still's reagent. In the case of α-branched aldehydes, the selectivity was improved to 90−94% by the use of NaH (entries 8−11). In entries 9 and 11, **1a** was treated with NaH at 0 °C for 10 min, and then the mixture was cooled to −78 °C. Slightly improved selectivities were obtained compared with the results when NaH was added at −78 °C (entries 8, 10). It should be noted that **1a** is much more selective than Still's reagent in the reaction with cyclohexanecarboxaldehyde (91% vs 80% *Z*-selectivity). Furthermore, we also performed the reaction of **1a** with aldehydes **3**−**5**, containing an oxygen functionality at the α or *β* position. The latter compounds were prepared from the corresponding ethyl esters and used without purification. The highest selectivity (97%) was attained by the reaction with *O*-(*tert*-butyldimethylsilyl)lactaldehyde (**5**). These results suggest that the oxygen functionality does not affect the *Z*/*E* ratio but that the steric hindrance at the α position favors *Z*-isomers.



3 **4** **5**

The *Z*/*E* ratios of all the Horner−Emmons products **2** were determined by integrating the vinyl proton signals in the 500 MHz ^{1}H NMR spectra. In general, the vinyl protons of a *Z*-isomer exhibit signals that are upfield compared to those of a corresponding *E*-isomer. All the *E*-isomers were also separately prepared from triethyl phosphonoacetate with more than 90% selectivity. The signal assignments were confirmed by nuclear Overhouser effect (NOE) experiments.

Table 3. Horner−Emmons Reaction of 1b−o with Benzaldehyde[a]

entry	**1**	conditions	yield (%)	**2** (*Z*/*E* ratio)
1	**1b**	−78 °C, 1 h	trace	70:30
2	**1c**	−78 °C, 2 h	100	92:8
3	**1d**	−78 °C, 1.5 h	95	89:11
4	**1e**	−78 °C, 1 h	96	93:7
5	**1f**	−78 °C, 1 h	95	87:13
6	**1g**	−78 °C, 1.5 h	97	92:8
7	**1h**	−78 °C, 1 h	89	95:5
8	**1i**	−78 °C, 3 h	98	96:4
9	**1j**	−78 °C, 1.5 h	96	92:8
10	**1k**	−78 °C, 1.5 h	100	96:4
11	**1l**	−78 °C, 1.5 h	100	97:3
12	**1m**	−78 °C, 2 h	100	97:3
13	**1n**	−78 °C, 1.5 h	99	93:7
14	**1o**	−78 °C, 2 h	92	78:22

[a] The reaction was perfomed in THF (20 mL/**1**, mmol) by using Triton B (1.2 equiv).

Horner−Emmons Reaction of Ethyl (Diarylphosphono)acetates (1b−o). The above high-*Z*-selective effect of the phenyl group prompted us to investigate substituted phenyl groups. In order to make highly *Z*-selective new reagents, some phenols were treated in the same manner as **1a** to give **1b−o** (∼60% yields) (Scheme 2).

The Horner−Emmons reaction of these new reagents (**1b−o**) with benzaldehyde was carried out in THF using Triton B at −78 °C. The results are summarized in Table 3. Ethyl [bis(*p*-nitrophenyl)phosphono]acetate (**1b**) is unstable to moisture and gradually decomposes to *p*-nitrophenol during purification. The reaction of **1b** with benzaldehyde was slow, and only a trace amount of ethyl cinnamate (*Z*:*E* = 70:30) was obtained along with a large amount of *p*-nitrophenol (entry 1). Bis(*p*-chlorophenyl), bis(*p*-methoxyphenyl), and di-*p*-tolyl reagents **1c−e** reacted smoothly with benzaldehyde to give ethyl cinnamate in nearly quantitative yields. However, little substituent effect was observed (entries 2−4). That is, both *p*-chloro- and *p*-methyl-substituted reagents **1c**,**e** showed about the same *E*/*Z*-selectivity as **1a**, and the *p*-methoxy-substituted reagent **1d** was slightly less selective; indicating no electronic effect of a substituent on the selectivity. A few years ago, Fuji *et al.* reported an asymmetric Horner−Emmons reaction of a chiral methyl (binaphthylphosphono)acetate, which reacted with a *meso* α-dicarbonyl compound to give a *Z*-product in high enantiomeric purity.[10] This report prompted us to prepare biphenyl, di-2-naphthyl, and di-1-naphthyl reagents **1f−h**. Only ethyl (di-1-naphthylphosphono)acetate (**1h**) gave a better result (95% *Z*-selectivity) than **1a** (entry 7). These results suggested that an *ortho*-substituent might be effective for enhancing *Z*-selectivity. We therefore prepared bis(*o*-chlorophenyl), bis(*o*-methoxyphenyl), di-*o*-tolyl, bis(*o*-ethylphenyl), bis(*o*-isopropylphenyl), di-*m*-tolyl, and bis(*o*-dimethylphenyl) reagents **1i−o** and reacted them with benzaldehyde to give ethyl *Z*-cinnamate in 96%, 92%, 97%, 97%, 97%, 93%, and 84% selectivity, respectively. Again, *o*-chloro-, *o*-methyl-, *o*-ethyl-, and *o*-isopropyl-substituted reagents **1i**,**1k−m** showed no difference in the selectivity (96−97%). Obviously, the *o*-dimethyl reagent **1o** is less selective than the other reagents, probably because of the steric hindrance around the phosphorus atom. Since the chlorophenyl reagent **1i** (also **1c**) is rather unstable and gradually decomposes upon storage at room temperature,[11] *o*-tolyl, *o*-ethylphenyl, and *o*-isopropylphenyl reagents **1k−m** are the reagents of choice.

Table 4. Horner−Emmons Reaction of 1c−o with 2-Ethylhexanal

entry	**1**	conditions[a]	yield (%)	**2** (*Z*/*E* ratio)
1	**1c**	−78 → 0 °C	81	93:7
2	**1d**	−78 → 0 °C	97	92:8
3	**1e**	−78 → 0 °C	91	93:7
4	**1f**	−78 → 0 °C	93	82:18
5	**1g**	−78 → 0 °C	100	93:7
6	**1h**	−78 → 0 °C	95	94:6
7	**1i**	−78 → 0 °C	88	95:5
8	**1j**	−78 → 0 °C	96	92:8
9	**1k**	−78 → 0 °C	96	96:4
10	**1l**	−78 → 0 °C	91	97:3
11	**1m**	−78 → −10 °C	98	96:4
12	**1n**	−78 → 0 °C	90	94:6
13	**1o**	−78 → 0 °C	82 (9)[b]	84:16

[a] NaH (1.4 equiv) was added at 0 °C in THF (5 mL/**1**, mmol). After adding aldehyde at −78 °C, the mixture was warmed over 1−2 h. [b] The yield was not optimized, and the number in parentheses is the recovered yield of **1** (%).

Next, the reaction of the new reagents **1c−o** with 2-ethylhexanal as a representative aliphatic aldehyde was examined by using NaH in THF (Table 4). There are some similar tendencies to the reaction with benzaldehyde. That is, both the reagents containing electron-withdrawing (Cl) and electron-donating (Me) substituents showed about the same *Z*-selectivity, while those with a highly electron-donating group (OMe) were slightly less selective. Here also, the reagents having *ortho*-substituents gave better selectivity than those having *meta*- or *para*-substituents. These results once again confirm that **1k−m**, exibiting 96−97% *Z*-selectivity, are the reagents of choice.

In order to determine the versatility of the reagents **1k−m**, we further examined the reaction of these reagents with several other aldehydes. The results are summarized in Table 5. The use of **1k** in the reaction with *trans*-2-hexenal improved *Z*-selectivity from 89% attained by the use of **1a** to 93% (entry 3). The reaction of **1k** with an α,β-unsaturated aldehyde or aliphatic aldehydes in the presence of Triton B was not sensitive to the structure of aldehydes, giving a uniform 92−93% *Z*-selectivity (entries 3, 6, 8, 10). In the reaction of **1k** with octyl aldehyde using NaH as a base, 94% *Z*-selectivity was obtained. In the case of α- or β-branched aldehydes, higher selectivities (95−99%) have been attained (entries 7, 9, 11−13). The *o*-ethyl and *o*-isopropyl reagents **1l**,**m** showed almost the same selectivities (93−99%) as the *o*-methyl reagent **1k** (entries 14−26). These results clearly show that the new *Z*-selective Horner−Emmons reagents **1k−m** are applicable to a diverse range of aldehydes for the synthesis of *Z*-unsaturated esters with high stereoselectivities.

Discussion

It is generally accepted that the stereoselectivity in Horner−Emmons reactions is a result of both kinetic and thermodynamic control upon the reversible formation of the *erythro* and *threo* adducts and their decomposition to olefins (Scheme 3).[8] That is, the stereochemistry is determined by a combination of the stereoselectivity in

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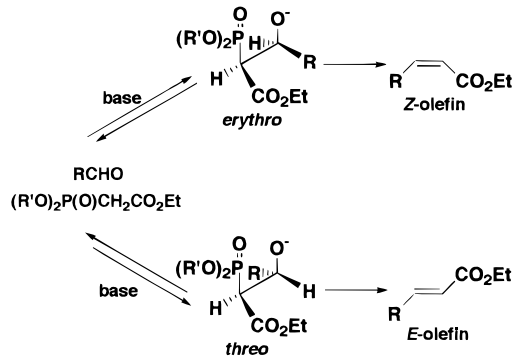
(11) The reagents **1i**,**c** can be stored under an argon atmosphere in a refrigerator for more than 1 month without any decomposition.

Table 5. Horner−Emmons Reaction of 1k−m with Several Types of Aldehydes in THF Solvent

entry	1	R	base	THF[a]	conditions[b]	yield (%)	2 (*Z*/*E* ratio)
1	**1k**	Ph	Triton B	20	−78 °C, 1.5 h	100	96:4
2	**1k**	Ph	*t*-BuOK	20	−78 °C, 2.5 h	99	95:5
3	**1k**	PrCH=CH[t]	Triton B	5	−78 → −10 °C	100	93:7
4	**1k**	*n*-C_7H_{15}	NaH	5	−78 → −20 °C	97	94:6
5	**1k**	*n*-C_7H_{15}	NaH	20	−78 → −20 °C	94	94:6
6	**1k**	*n*-C_7H_{15}	Triton B	20	−78 → 0 °C	96	93:7
7	**1k**	BuCHEt	NaH	5	−78 → 0 °C	96	96:4
8	**1k**	BuCHEt	Triton B	20	−78 → 0 °C	97	92:8
9	**1k**	cyclohexyl	NaH	5	−78 → −20 °C	100	95:5
10	**1k**	cyclohexyl	Triton B	20	−78 → 0 °C	95	92:8
11	**1k**	**3**	NaH	5	−78 → −20 °C	100[c]	95:5
12	**1k**	**4**	NaH	5	−78 → 0 °C	87[c]	98:2
13	**1k**	**5**	NaH	5	−78 → 0 °C	74[c,d]	99:1
14	**1l**	Ph	Triton B	20	−78 °C, 1.5 h	100	97:3
15	**1l**	PrCH=CH[t]	Triton B	5	−78 → −10 °C	98	93:7
16	**1l**	*n*-C_7H_{15}	NaH	5	−78 → −10 °C	100	93:7
17	**1l**	BuCHEt	NaH	5	−78 → 0 °C	91	97:3
18	**1m**	Ph	Triton B	20	−78 °C, 2 h	100	97:3
20	**1m**	PrCH=CH[t]	Triton B	5	−78 → −10 °C	98	93:7
21	**1m**	*n*-C_7H_{15}	NaH	5	−78 → −20 °C	95	93:7
22	**1m**	BuCHEt	NaH	5	−78 → −10 °C	98	96:4
23	**1m**	cyclohexyl	NaH	5	−78 → −10 °C	97	95:5
24	**1m**	**3**	NaH	5	−78 → −20 °C	92	95:5
25	**1m**	**4**	NaH	5	−78 → 0 °C	85	98:2
26	**1m**	**5**	NaH	5	−78 → 0 °C	70	99:1

[a] mL/**1a**, mmol. [b] The reaction was warmed over 1−2 h except for entry 1. [c] The aldehyde was prepared from DIBAL reduction of the corresponding ethyl ester. The yield was calculated from the starting ester. [d] This rather low yield is mainly due to the moderate yield of the reduction.

Scheme 3



the initial carbon−carbon bond-forming step and reversibility of the intermediate adducts. The predominant formation of the *E*-olefins in the case of (dialkylphosphono)acetate reagents can be explained by the formation of thermodynamically more stable *threo* adducts. On the other hand, the *Z*-stereoselectivities of the (diarylphosphono)acetate reagents **1** can be interpreted by the predominant formation of the *erythro* adducts which irreversibly collapse to the *Z*-olefins. Due to the electron-withdrawing character of the aryloxy group (pK_a(PhOH) = 10.0 vs pK_a(CF_3CH_2OH) = 12.4 vs pK_a(CH_3CH_2OH) = 16), the electrophilicity of the phosphorus of the intermediate adducts derived from the reagents **1** is enhanced. Increased reactivity of the intermediate adducts to olefins would result in lower rates of decomposition to the starting materials; consequently formation of considerable amounts of *Z*-olefins could be expected. One possible explanation for the substituent effects of the aryl group is enhanced kinetic selectivity for the *erythro* adducts due to the steric hindrance rather than the electronic effects. Since at this time there are insufficient data to discuss the details of the reaction transition state, we are pursuing a computational study using ab initio molecular orbital theory for the evaluation of the transition states. These results will be reported elsewhere.

In summary, the methods described above provide simple, economical, and highly selective routes to a wide range of *Z*-unsaturated esters in almost quantitative yields. Our new reagents, namely, ethyl (diarylphosphono)acetates of type **1**, will undoubtedly prove to be of considerable utility in synthesis. In order to expand the scope and utility, these new *Z*-selective Horner−Emmons reagents are presently under active investigation in this laboratory.

Experimental Section

Tetrahydrofuran (THF) was distilled from sodium/benzophenone just before use. All reactions were conducted under an argon atmosphere. Column chromatography was performed on silica gel (Wakogel C-300). In general, an analytical sample was obtained by bulb-to-bulb distillation, and the boiling points refer to the external air bath temperature. Melting points were determined in open capillaries and are uncorrected. The ^{1}H NMR spectra were recorded in $CDCl_3$ at 500 MHz unless otherwise stated, and the chemical shifts are expressed in ppm relative to internal tetramethylsilane.

Ethyl (Diphenylphosphono)acetate (1a). PCl_5 (15.6 g, 75 mmol) was added to triethyl phosphonoacetate (5.95 mL, 30 mmol) at 0 °C. When the exothermic reaction was completed, the mixture was heated at 75 °C for 10 h. Distillation removed $P(O)Cl_3$ and excess PCl_5 and yielded the dichloride (5.96 g, 3 mmHg/105−110 °C), which was dissolved in benzene (30 mL) and treated with a solution of PhOH (5.65 g, 60 mmol) in benzene (10 mL) and Et_3N (10.1 mL, 73 mmol) at 0 °C. After stirring for 1 h at 25 °C, the mixture was filtered. The filtrate was diluted with AcOEt (30 mL), washed successively with 1 N NaOH (20 mL × 3), saturated NH_4Cl, and brine, dried ($MgSO_4$), and concentrated to give a pale yellow residue. Column chromatography (silica gel/hexane−AcOEt (8:1)) provided **1a** (5.80 g, yield 60%) as a colorless oil: ^{1}H NMR δ 1.28 (3H, t, J = 7 Hz), 3.26 (2H, d, J = 22 Hz), 4.23 (2H, q, J = 7 Hz), 7.18−7.25 (6H, m), 7.32−7.36 (4H, m); MS m/e 320 (M^+), 199; bp 220 °C/3 mmHg. Anal. Calcd for $C_{16}H_{17}PO_5$: C, 60.00; H, 5.35; P, 9.67. Found: C, 59.78; H, 5.21; P, 9.40.

Instead of distillation of the dichloride, just removal of the volatiles under vacuum (3 mmHg/100 °C) gave the same results, and this simple method was applied for the preparation of **1b**−**o**.

Ethyl [bis(*p*-chlorophenyl)phosphono]acetate (1c): colorless oil (yield 62%); ^{1}H NMR δ 1.28 (3H, t, J = 7 Hz), 3.26 (2H, d, J = 22 Hz), 4.23 (2H, q, J = 7 Hz), 7.14−7.24 (4H, m), 7.26−7.37 (4H, m); MS m/e 388, 390 (M^+), 233, 235; bp 270 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{16}H_{15}Cl_2PO_5$: C, 49.38; H, 3.89; Cl, 18.22; P, 7.96. Found: C, 49.35; H, 3.78; Cl, 18.21; P, 8.01.

Ethyl [bis(*p*-methoxyphenyl)phosphono]acetate (1d): colorless oil (yield 54%); ^{1}H NMR δ 1.28 (3H, t, J = 7 Hz), 3.22 (2H, d, J = 22 Hz), 3.77 (6H, s), 4.23 (2H, q, J = 7 Hz), 6.82−6.89 (4H, m), 7.12−7.18 (4H, m); MS m/e 380 (M^+), 334, 229; bp 280 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{18}H_{21}PO_7$: C, 56.84; H, 5.57; P, 8.14. Found: C, 57.11; H, 5.56; P, 8.13.

Ethyl (di-*p*-tolylphosphono)acetate (1e): colorless oil (yield 63%); ^{1}H NMR δ 1.28 (3H, t, J = 7 Hz), 2.31 (6H, s), 3.22 (2H, d, J = 22 Hz), 4.23 (2H, q, J = 7 Hz), 7.11 (8H, s); MS m/e 348 (M^+), 241, 213; bp 250 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{18}H_{21}PO_5$: C, 62.07; H, 6.08; P, 8.89. Found: C, 61.90; H, 6.01; P, 8.90.

Ethyl (biphenylphosphono)acetate (1f): colorless needles (yield 24%); mp 81−82 °C (recrystallized from hexane−CH_2Cl_2); ^{1}H NMR δ 1.27 (3H, t, J = 7 Hz), 3.23 (2H, d, J = 21 Hz), 4.20 (2H, q, J = 7 Hz), 7.33−7.40 (4H, m), 7.44−7.48 (2H, m), 7.51−7.55 (2H, m); MS m/e 318 (M^+). Anal. Calcd for $C_{16}H_{15}PO_5$: C, 60.38; H, 4.75. Found: C, 60.28; H, 4.67.

Ethyl (di-2-naphthylphosphono)acetate (1g): colorless viscous oil (yield 64%); ^{1}H NMR δ 1.25 (3H, t, J = 7 Hz), 3.35 (2H, d, J = 22 Hz), 4.23 (2H, q, J = 7 Hz), 7.38−7.47 (6H, m), 7.71−7.81 (8H, m); MS m/e 420 (M^+), 249; HRMS calcd for $C_{24}H_{21}PO_5$ 420.1125, found 420.1128.

Ethyl (di-1-naphthylphosphono)acetate (1h): colorless viscous oil (yield 57%); ^{1}H NMR δ 1.19 (3H, t, J = 7 Hz), 3.49 (2H, d, J = 22 Hz), 4.20 (2H, q, J = 7 Hz), 7.35−7.38 (2H, m), 7.46−7.56 (6H, m), 7.66−7.68 (2H, m), 7.81−7.85 (2H, m), 8.10−8.14 (2H, m); MS m/e 420 (M^+), 249; HRMS calcd for $C_{24}H_{21}PO_5$ 420.1125, found 420.1129.

Ethyl [bis(*o*-chlorophenyl)phosphono]acetate (1i): colorless oil (yield 46%); ^{1}H NMR δ 1.24 (3H, t, J = 7 Hz), 3.46 (2H, d, J = 22 Hz), 4.21 (2H, q, J = 7 Hz), 7.12−7.18 (2H, m), 7.20−7.25 (2H, m), 7.40−7.44 (4H, m); MS m/e 388, 390 (M^+), 233, 235; bp 260 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{16}H_{15}Cl_2PO_5$: C, 49.38; H, 3.89; Cl, 18.22; P, 7.96. Found: C, 49.45; H, 3.75; Cl, 18.33; P, 7.78.

Ethyl [bis(*o*-methoxyphenyl)phosphono]acetate (1j): colorless oil (yield 57%); ^{1}H NMR δ 1.26 (3H, t, J = 7 Hz), 3.42 (2H, d, J = 22 Hz), 3.83 (6H, s), 4.22 (2H, q, J = 7 Hz), 6.85−6.90 (2H, m), 6.93−4.96 (2H, m), 7.11−7.15 (2H, m), 7.21−7.25 (2H, m); MS m/e 381 (($M + H)^+$), 257, 211; bp 280 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{18}H_{21}PO_7$: C, 56.84; H, 5.57; P, 8.14. Found: C, 56.87; H, 5.30; P, 7.88.

Ethyl (di-*o*-tolylphosphono)acetate (1k): colorless oil (yield 61%); ^{1}H NMR δ 1.26 (3H, t, J = 7 Hz), 2.25 (6H, s), 3.33 (2H, d, J = 22 Hz), 4.22 (2H, q, J = 7 Hz), 7.05−7.16 (4H, m), 7.18−7.20 (2H, m), 7.27−7.30 (2H, m); MS m/e 348 (M^+), 241, 213; bp 240 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{18}H_{21}PO_5$: C, 62.07; H, 6.08; P, 8.89. Found: C, 61.90; H, 5.93; P, 8.81.

Ethyl [bis(*o*-ethylphenyl)phosphono]acetate (1l): colorless oil (yield 53%); ^{1}H NMR δ 1.16 (6H, t, J = 7.5 Hz), 1.26 (3H, t, J = 7 Hz), 2.64 (4H, q, J = 7.5 Hz), 3.33 (2H, d, J = 22 Hz), 4.22 (2H, q, J = 7 Hz), 7.10−7.16 (4H, m), 7.19−7.24 (2H, m), 7.32−7.35 (2H, m); MS m/e 377 (($M + H)^+$), 227; bp 250 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{20}H_{25}PO_5$: C, 63.82; H, 6.69; P, 8.23. Found: C, 63.70; H, 6.61; P, 8.00.

Ethyl [bis(*o*-isopropylphenyl)phosphono]acetate (1m): colorless oil (yield 55%); ^{1}H NMR δ 1.15 (6H, d, J = 7 Hz), 1.18 (6H, d, J = 7 Hz), 1.26 (3H, t, J = 7 Hz), 3.26 (2H, septet, J = 7 Hz), 3.34 (2H, d, J = 22 Hz), 4.22 (2H, q, J = 7 Hz), 7.08−7.16 (4H, m), 7.24−7.30 (2H, m), 7.31−7.38 (2H, m); MS m/e 405 (($M + H)^+$), 241; bp 250 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{22}H_{29}PO_5$: C, 65.33; H, 7.23; P, 7.66. Found: C, 65.30; H, 7.15; P, 7.56.

Ethyl (di-*m*-tolylphosphono)acetate (1n): colorless oil (yield 55%). ^{1}H NMR δ 1.28 (3H, t, J = 7 Hz), 2.33 (6H, s), 3.24 (2H, d, J = 22 Hz), 4.23 (2H, q, J = 7 Hz), 6.99−7.06 (6H, m), 7.19−7.24 (2H, m). MS m/e 348 (M^+), 213. bp 230 °C/3 mmHg (bulb-to-bulb). Anal. Calcd for $C_{18}H_{21}PO_5$: C, 62.07; H, 6.08; P, 8.89. Found: C, 62.21; H, 5.78; P, 8.67.

Ethyl [bis(*o*-dimethylphenyl)phosphono]acetate (1o): colorless needles (yield 57%). mp 83−84 °C (recrystallized from hexane-CH_2Cl_2). ^{1}H NMR δ 1.27 (3H, t, J = 7 Hz), 2.27 (12H, s), 3.37 (2H, d, J = 22 Hz), 4.22 (2H, q, J = 7 Hz), 6.96−7.04 (6H, m). MS m/e 376 (M^+), 255, 227. Anal. Calcd for $C_{20}H_{25}PO_5$: C, 63.82; H, 6.69. Found: C, 63.57; H, 6.60.

Horner−Emmons Reaction with Benzaldehyde: Procedure 1. A solution of **1** (0.50 mmol) in THF (10 mL) was treated with Triton B (0.27 mL, 0.60 mmol) at −78 °C for 15 min. Benzaldehyde (0.054 mL, 0.53 mmol) was then added, and the resulting mixture was stirred at −78 °C. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with AcOEt (10 mL × 3). The combined extracts were washed with water (15 mL × 2) followed by brine, dried ($MgSO_4$), and concentrated. After determining the *Z*/*E* ratio of the crude mixture by 500 MHz ^{1}H NMR, ethyl cinnamate was isolated by flash chromatography as a colorless oil. The *Z*/*E* ratio did not change by flash chromatography.

Ethyl (*Z*)-cinnamate:[12] ^{1}H NMR δ 1.24 (3H, t, J = 7 Hz), 4.17 (2H, q, J = 7 Hz), 5.95 (1H, d, J = 12 Hz), 6.94 (1H, d, J = 12 Hz), 7.29−7.39 (3H, m), 7.56−7.59 (2H, m); GCMS m/e 176 (M^+), 131.

Ethyl (*E*)-cinnamate:[12,13] ^{1}H NMR δ 1.34 (3H, t, J = 7 Hz), 4.27 (2H, q, J = 7 Hz), 6.44 (1H, d, J = 16 Hz), 7.33−7.43 (3H, m), 7.51−7.53 (2H, m), 7.69 (1H, d, J = 16 Hz); GCMS m/e 176 (M^+), 131.

Preparation of the *E*-Isomer: Procedure 2. To a solution of triethyl phosphonoacetate (0.205 mL, 1.00 mmol) in THF (3 mL) was added BuLi in hexane (0.75 mL, 1.20 mmol) at 0 °C. After 10 min, the mixture was treated with benzaldehyde (0.112 mL, 1.10 mmol) for 30 min and the reaction quenched in the same way as in procedure 1 (*E*:*Z* = 99.7:0.3) (yield 99%).

Horner−Emmons Reaction with 2(*E*)-Hexenal. A solution of **1** (0.50 mmol) in THF (2 mL) was treated with Triton B (0.27 mL, 0.60 mmol) at −78 °C for 15 min. 2(*E*)-Hexenal (0.066 mL, 0.55 mmol) in THF (0.5 mL) was then added, and the resulting mixture was gradually warmed to the indicated temperature over 1−2 h. The following reaction procedure was the same as procedure 1. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*),4(*E*)-octadienoate: ^{1}H NMR δ 0.93 (3H, t, J = 7 Hz), 1.30 (3H, t, J = 7 Hz), 1.47 (2H, sex, J = 7 Hz), 2.18 (2H, q, J = 7 Hz), 4.18 (2H, q, J = 7 Hz), 5.56 (1H, d, J = 11 Hz), 6.06 (1H, dt, J = 15, 7 Hz), 6.55 (1H, t, J = 11 Hz), 7.37 (1H, dd, J = 15, 11 Hz); GCMS m/e 168 (M^+); HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1150.

Ethyl 2(*E*),4(*E*)-octadienoate: ^{1}H NMR δ 0.92 (3H, t, J = 7 Hz), 1.29 (3H, t, J = 7 Hz), 1.46 (2H, sex, J = 7 Hz), 2.15 (2H, q, J = 7 Hz), 4.20 (2H, q, J = 7 Hz), 5.78 (1H, d, J = 15 Hz), 6.08−6.20 (2H, m), 7.26 (1H, dd, J = 15, 11 Hz); GCMS m/e 168 (M^+); HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1149.

The *E*-isomer was prepared by procedure 2 using DME[2e] (2 mL) instead of THF (*E*:*Z* = 97:3) (yield 93%).

Horner−Emmons Reaction with Octanal: Procedure 3. To a solution of **1** (0.50 mmol) in THF (2 mL) was added NaH (0.028 g, 0.70 mmol) at 0 °C; 15 min later, octanal (0.086 mL, 0.55 mmol) in THF (0.5 mL) was added, and the resulting mixture was gradually warmed to the indicated temperature over 1−2 h. The following reaction procedure was the same as procedure 1. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*)-decenoate: ^{1}H NMR δ 0.88 (3H, t, J = 7 Hz), 1.26−1.38 (11H, m), 1.40−1.47 (2H, m), 2.64 (2H, dq, J = 2, 7 Hz), 4.17 (2H, q, J = 7 Hz), 5.75 (1H, dt, J = 12, 2 Hz), 6.21 (1H, dt, J = 12, 7 Hz); GCMS m/e 198 (M^+), 153; HRMS calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1620.

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Ethyl 2(*E*)-decenoate: ^{1}H NMR δ 0.88 (3H, t, J = 7 Hz), 1.25−1.35 (11H, m), 1.39−1.48 (2H, m), 2.19 (2H, dq, J = 2, 7 Hz), 4.18 (2H, q, J = 7 Hz), 5.81 (1H, dt, J = 16, 2 Hz), 6.97 (1H, dt, J = 16, 7 Hz); MS m/e 198 (M^+), 153; HRMS calcd for $C_{12}H_{23}O_2$ ($(M + H)^+$) 199.1698, found 199.1692.

The *E*-isomer was prepared by procedure 2 using DME (2 mL) instead of THF (*E*:*Z* = 98:2) (yield 100%).

Horner−Emmons Reaction with 2-Ethylhexanal. The reaction was performed by procedure 3. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*)-4-ethyloctenate: ^{1}H NMR δ 0.86 (3H, t, J = 7 Hz), 0.87 (3H, t, J = 7 Hz), 1.18−1.52 (11H, m), 3.31−3.39 (1H, m), 4.16 (2H, q, J = 7 Hz), 5.79 (1H, d, J = 12 Hz), 5.89 (1H, dd, J = 10, 12 Hz); GCMS m/e 198 (M^+), 153; HRMS calcd for $C_{12}H_{22}O_2$ 198.1619, found 198.1603.

Ethyl 2(*E*)-4-ethyloctenate: ^{1}H NMR δ 0.85 (3H, t, J = 7 Hz), 0.88 (3H, t, J = 7 Hz), 1.17−1.54 (11H, m), 2.00−2.07 (1H, m), 4.19 (2H, q, J = 7 Hz), 5.77 (1H, d, J = 16 Hz), 6.73 (1H, dd, J = 10, 16 Hz); MS m/e 198 (M^+), 153; HRMS calcd for $C_{12}H_{22}O_2$ 198.1619, found 198.1614.

The *E*-isomer was prepared by procedure 2 using DME (2 mL) instead of THF (*E*:*Z* = 98:2) (yield 96%).

Horner−Emmons Reaction with Cyclohexanecarboxaldehyde. The reaction was performed by procedure 3. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*)-3-cyclohexylpropenoate: ^{1}H NMR δ 1.04−1.39 (8H, m), 1.65−1.75 (5H, m), 3.29 (1H, brq, J = 11 Hz), 4.16 (2H, q, J = 7 Hz), 5.65 (1H, dd, J = 1, 12 Hz), 6.02 (1H, dd, J = 10, 12 Hz); GCMS m/e 182 (M^+), 137; HRMS calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1308.

Ethyl 2(*E*)-3-cyclohexylpropenoate: ^{1}H NMR δ 1.08−1.37 (8H, m), 1.66−1.80 (5H, m), 2.07−2.17 (1H, m), 4.18 (2H, q, J = 7 Hz), 5.76 (1H, dd, J = 1, 16 Hz), 6.91 (1H, dd, J = 7, 16 Hz); GCMS m/e 182 (M^+); HRMS calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1309.

The *E*-isomer was prepared by procedure 2 using DME (2 mL) instead of THF (*E*:*Z* = 98:2) (yield 91%).

Horner−Emmons Reaction with 3-Phenyl-3-[(*tert*-butyldimethylsilyl)oxy]propionaldehyde 3: Procedure 4. To a solution of ethyl 3-phenyl-3-[(*tert*-butyldimethylsilyl)oxy]-propionate (0.0926 g, 0.30 mmol) in toluene (1.5 mmol) was added DIBAL-H in toluene (0.44 mL, 0.33 mmol) at −78 °C. After 1 h, water was added, and the mixture was extracted with AcOEt (10 mL × 3). The combined extracts were washed with water (15 mL × 2) and brine, dried ($MgSO_4$), and concentrated. The crude aldehyde was submitted to the Horner−Emmons reaction by procedure 3. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*)-5-phenyl-5-[(*tert*-butyldimethylsilyl)oxy]-pentenoate: ^{1}H NMR δ −0.13 (3H, s), 0.03 (3H, s), 0.89 (9H, s), 1.27 (3H, t, J = 7 Hz), 3.01 (1H, ddt, J = 2, 15, 7 Hz), 3.08 (1H, dddd, J = 2, 5, 7, 15 Hz), 4.14 (2H, q, J = 7 Hz), 4.83 (1H, dd, J = 5, 7 Hz), 5.81 (1H, dt, J = 12, 2 Hz), 6.29 (1H, dt, J = 12, 7 Hz), 7.20−7.35 (5H, m); MS m/e 277 ($(M - t\text{-Bu})^+$). Anal. Calcd for $C_{19}H_{30}O_3Si$: C, 68.22; H, 9.04. Found: C, 68.47; H, 8.81.

Ethyl 2(*E*)-5-phenyl-5-[(*tert*-butyldimethylsilyl)oxy]-pentenoate: ^{1}H NMR δ −0.14 (3H, s), 0.02 (3H, s), 0.88 (9H, s), 1.27 (3H, t, J = 7 Hz), 2.51 (1H, dddd, J = 1, 5, 8, 14 Hz), 2.56 (1H, ddt, J = 1, 14, 8 Hz), 4.175 (1H, dq, J = 11, 7 Hz), 4.178 (1H, dq, J = 11, 7 Hz), 4.75 (1H, dd, J = 5, 8 Hz), 5.81 (1H, dt, J = 16, 1 Hz), 6.96 (1H, dt, J = 8, 16 Hz), 7.22−7.33 (5H, m); MS m/e 334 (M^+), 277. Anal. Calcd for $C_{19}H_{30}O_3Si$: C, 68.22; H, 9.04. Found: C, 68.29; H, 8.85.

The *E*-isomer was prepared by procedure 2 using DME (3 mL) instead of THF (*E*:*Z* = 93:7) (yield 94%).

Horner−Emmons Reaction with *O*-Benzyllactaldehyde (4). *O*-Benzyllactaldehyde was prepared from ethyl *O*-benzyllactate by procedure 4. Horner−Emmons reaction was performed by procedure 3. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*)-4-(benzyloxy)pentenoate:[14] ^{1}H NMR δ 1.28 (3H, t, J = 7 Hz), 1.33 (3H, d, J = 6 Hz), 4.16 (2H, q, J = 7 Hz), 4.44 (1H, d, J = 12 Hz), 4.52 (1H, d, J = 12 Hz), 5.16 (1H, ddq, J = 1, 8, 6 Hz), 5.85 (1H, dd, J = 1, 12 Hz), 6.23 (1H, dd, J = 8, 12 Hz), 7.24−7.37 (5H, m); ^{1}H NMR (CCl_4)[15] δ 1.269 (3H, t, J = 7 Hz), 1.274 (3H, d, J = 6 Hz), 4.11 (2H, q, J = 7 Hz), 4.39 (1H, d, J = 12 Hz), 4.44 (1H, d, J = 12 Hz), 5.09 (1H, ddq, J = 1, 8, 6 Hz), 5.74 (1H, dd, J = 1, 12 Hz), 6.15 (1H, dd, J = 8, 12 Hz), 7.14−7.25 (5H, m); MS m/e 205 ($(M - Et)^+$).

Ethyl 2(*E*)-4-(benzyloxy)pentenoate:[14,16,17] ^{1}H NMR δ 1.31 (3H, t, J = 7 Hz), 1.33 (3H, d, J = 6 Hz), 4.12 (1H, dquint, J = 1, 6 Hz), 4.22 (2H, q, J = 7 Hz), 4.44 (1H, d, J = 12 Hz), 4.57 (1H, d, J = 12 Hz), 6.02 (1H, dd, J = 1, 16 Hz), 6.89 (1H, dd, J = 6, 16 Hz), 7.25−7.38 (5H, m); MS m/e 189 ($(M - OEt)^+$), 143 ($(M - CH_2Ph)^+$).

The *E*-isomer was prepared by procedure 2 using DME (3 mL) instead of THF (*E*:*Z* = 90:10) (yield 80%).

Horner−Emmons Reaction with *O*-(*tert*-Butyldimethylsilyl)lactaldehyde (5). *O*-(*tert*-Butyldimethylsilyl)lactaldehyde was prepared from ethyl *O*-(*tert*-butyldimethylsilyl)-lactate by procedure 4. Horner−Emmons reaction was performed by procedure 3. For characterization, the isomers were separated by pTLC.

Ethyl 2(*Z*)-4-[(*tert*-butyldimethylsilyl)oxy]pentenoate:[14] ^{1}H NMR δ 0.035 (3H, s), 0.053 (3H, s), 0.88 (9H, s), 1.25 (3H, d, J = 6 Hz), 1.29 (3H, t, J = 7 Hz), 4.170 (1H, dq, J = 11, 7 Hz), 4.172 (1H, dq, J = 11, 7 Hz), 5.44 (1H, ddq, J = 1, 8, 6 Hz), 5.65 (1H, dd, J = 1, 12 Hz), 6.20 (1H, dd, J = 8, 12 Hz); MS m/e 201 ($(M - t\text{-Bu})^+$).

Ethyl 2(*E*)-4-[(*tert*-butyldimethylsilyl)oxy]pentenoate:[14,16] ^{1}H NMR δ 0.065 (3H, s), 0.070 (3H, s), 0.91 (9H, s), 1.26 (3H, d, J = 6 Hz), 1.30 (3H, t, J = 7 Hz), 4.191 (1H, dq, J = 11, 7 Hz), 4.201 (1H, dq, J = 11, 7 Hz), 4.46 (1H, ddq, J = 2, 4, 6 Hz), 5.99 (1H, dd, J = 2, 16 Hz), 6.93 (1H, dd, J = 4, 16 Hz); MS m/e 213 ($(M - OEt)^+$), 201 ($(M - t\text{-Bu})^+$).

The *E*-isomer was prepared by procedure 2 using DME (3 mL) instead of THF (*E*:*Z* = 98:2) (yield 73%).

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Supporting Information Available: ^{1}H NMR spectra of compounds **1g**,**h** and **2** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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