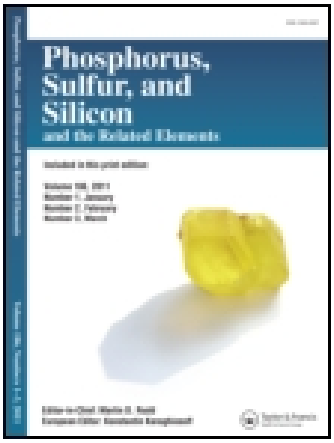

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Convenient Synthesis of 1-(Trimethylsilyl)- and 1-(Trimethylstannyl)vinylphosphonates

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CONVENIENT SYNTHESIS OF 1-(TRIMETHYLSILYL)- AND 1-(TRIMETHYLSTANNYL)VINYLPHOSPHONATES

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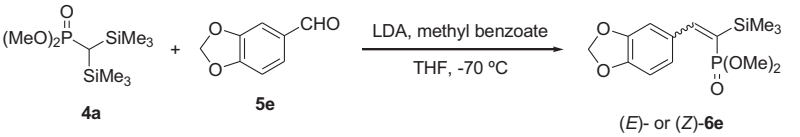
GRAPHICAL ABSTRACT



Abstract *Dimethyl 1,1-bis(trimethylsilyl)methylphosphonate and dimethyl 1-(trimethylsilyl)-1-(trimethylstannyl)methylphosphonate were succeeded to react with aromatic aldehydes in the presence of methyl benzoate as additive to give the corresponding vinylphosphonates in moderate yields.*

Keywords Vinylphosphonates; vinylsilanes; Peterson reaction

INTRODUCTION

Organophosphorus, organosilicon, and organotin compounds are useful intermediates for organic synthesis. Methylphosphonates with two phosphorus functional groups[1] and phosphorus and silicon functional groups[2] are actively used in organic synthesis. However, to the best our knowledge the derivatives with three functional groups are little investigated so far. So, we became interested in the reactivity of multi-functionalized methylphosphonates toward carbonyl compounds. Furthermore, the vinylphosphonates obtained are useful reagents in tandem reactions such as Michael reaction—Horner–Emmons–Woodwards reaction.[3] Here, we report on the convenient synthesis of vinylphosphonates with trimethylsilyl and trimethylstannyl groups at α-position starting from multi-functionalized methylphosphonates with trimethylsilyl and trimethylstannyl groups.

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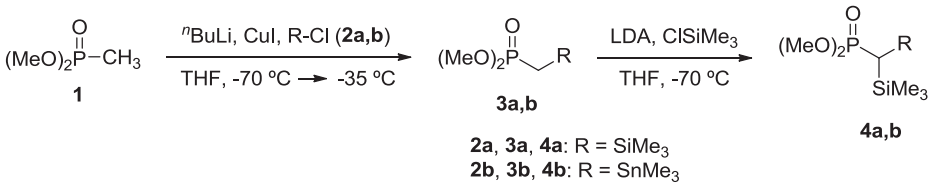
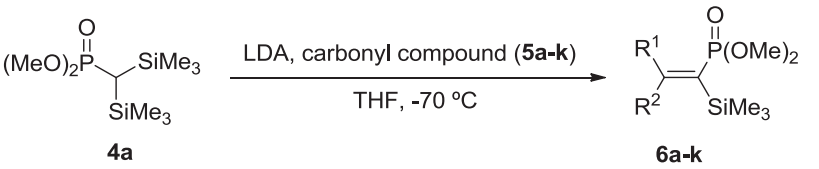
RESULTS AND DISCUSSION

Dimethyl (trimethylsilyl)methylphosphonate (**3a**) and dimethyl (trimethylstannyl)-methylphosphonate (**3b**) were prepared by an established procedure.[2a] Reaction of **3a,b** with chlorotrimethylsilane in the presence of LDA gave dimethyl 1,1-bis(trimethylsilyl)-methylphosphonate (**4a**) and dimethyl 1-(trimethylsilyl)-1-(trimethylstannyl)methylphosphonate (**4b**) in 94% and 28% yield, respectively (Scheme 1).



Scheme 1

The reactions of **4a** with carbonyl compounds **5a-k** in the presence of LDA in THF were carried out to give Peterson olefination products **6a-k** (Equation (1)). The results are summarized in Table 1.



(1)

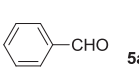
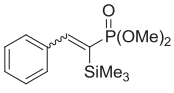
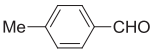
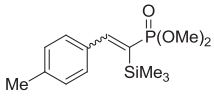
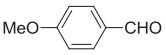
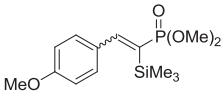
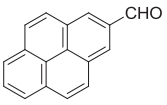
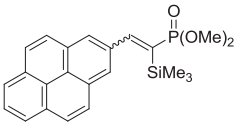
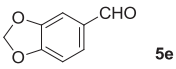
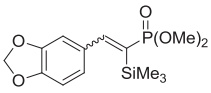
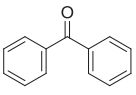
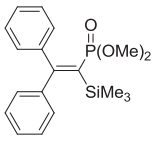
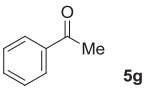
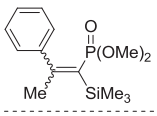
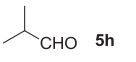
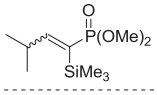
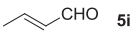
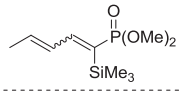
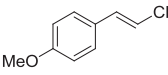
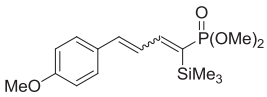
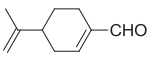
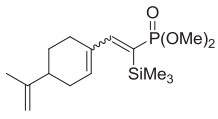
The reaction of **4a** with benzaldehyde **5a** did not give the desired Peterson reaction product **6a**, only **4a** was recovered (entry 1). Similar reaction in the presence of methyl benzoate as an additive gave the mixture of (*E*)-**6a** and (*Z*)-**6a**. Preparative thin layer chromatography (TLC) of these mixture afforded pure (*E*)-**6a** and (*Z*)-**6a** in 28% and 51% yield, respectively (entry 2). Also sodium fluoride as an additive was effective (entry 3).

The structures of (*E*)-**6a** and (*Z*)-**6a** were assigned on the basis of their ^{1}H, ^{13}C, and H,C HETCOR NMR spectra. Thus, the ^{1}H-NMR spectrum of (*E*)-**6a** shows a signal for the olefinic proton at 8.36 (d, $J = 35.4$ Hz), while that of (*Z*)-**6a** shows the respective signal at 7.63 (d, $J = 61.0$ Hz). Minami and co-workers have reported that the olefinic protons of diethyl (*E*)- and (*Z*)-2-(ethylthio)-1-(trimethylsilyl)vinylphosphonates were observed at 8.11 (d, $3JPH = 31.8$ Hz) and 7.35 (d, $^{3}J_{\text{P-H}} = 55.6$ Hz), respectively.[4] Therefore, the larger coupling constant was assigned to the *anti* $^{3}J_{\text{P-H}}$. In order to confirm these assignments, reactions of **4a** with a variety of aromatic aldehydes were carried out (entries 4–8).

The reaction of **4a** with piperonal **5e** gave the mixture of (*E*)-**6e** and (*Z*)-**6e**. The ^{1}H-NMR spectrum of (*E*)-**6e** shows a signal for the olefinic proton at 8.22 (d, $J = 35.2$ Hz), while that of (*Z*)-**6e** shows the respective signal at 7.43 (d, $J = 60.8$ Hz).

Recrystallization of compound (*Z*)-**6e** from ether–hexane gave pure white single crystals, suitable for X-ray diffraction. The X-ray analysis of (*Z*)-**6e** demonstrated that the compound was indeed dimethyl (*Z*)-2-(3,4-methylenedioxyphenyl)-1-(trimethylsilyl)vinylphosphonate (Figure 1).

Table 1 Peterson reaction of **4a** with carbonyl compounds **5a**-**k**.[1)]

entry	carbonyl compound	additive	product (yield, %[2)], *E*/*Z*)
1	 **5a**	—	 **6a** (0)
2		methyl benzoate	**6a** (79, 1/1.7)
3		NaF	**6a** (65, 1/1.2)
4	 **5b**	methyl benzoate	 **6b** (80, 1/1.5)
5		NaF	**6b** (71, 1/1.2)
6	 **5c**	methyl benzoate	 **6c** (67, 1/1.5[3)])
7	 **5d**	methyl benzoate	 **6d** (61, 2/1[3)])
8	 **5e**	methyl benzoate	 **6e** (64, 1/2)
9	 **5f**	methyl benzoate	 **6f** (0)
10		NaF	**6f** (0)
11	 **5g**	methyl benzoate	 **6g** (0)
12		NaF	**6g** (0)
13	 **5h**	methyl benzoate	 **6h** (0)
14		NaF	**6h** (0)
15	 **5i**	methyl benzoate	 **6i** (81, 2.9/1)
16	 **5j**	methyl benzoate	 **6j** (86, 2/1)
17		NaF	**6j** (46, 1.2/1)
18	 **5k**	methyl benzoate	 **6k** (53, 1/1.3)
19		NaF	**6k** (43, 1/1.3)

[1)] All reaction was carried out under Ar atmosphare in THF at -70 ºC for 30 min, and then at room temperature for 12 h.
[2)] Isolated yield. [3)] Determined by ^{1}H NMR.

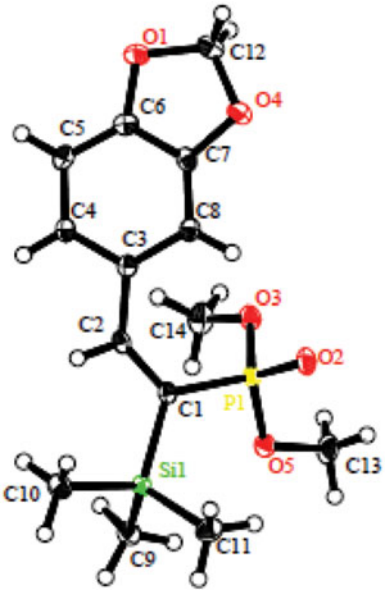
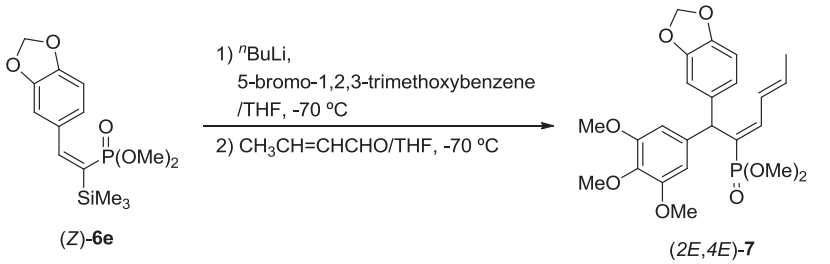


Figure 1 ORTEP diagram of (Z)-**6e.**

In order to determine the limitation of this reaction, a similar reaction of **4a** with aliphatic aldehydes and ketones was carried out. Reaction of **4a** with benzophenone, acetophenone, and isobutyraldehyde did not occur because of steric hindrance and/or more acidic protons (entries 9–14). However, **4a** reacted with α,β-unsaturated aldehydes such as crotonaldehyde, 4-methoxycinnamaldehyde, and pelliraldehyde in the presence of methyl benzoate or sodium fluoride to give **6i-k** in 46%–81% yields (entries 15–19). These results indicate that the additive plays an important role in the activation of the silicon functional group. Methyl benzoate seems to assist the Peterson reaction through a weak interaction between silicon and oxygen. It was found that reaction of **4a** with aromatic aldehydes gave predominantly the *Z*-form of the corresponding vinylphosphonates, while similar reaction with α,β-unsaturated aldehydes afforded mainly the *E*-form vinylphosphonates.

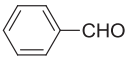
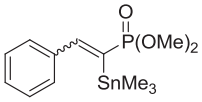
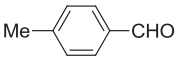
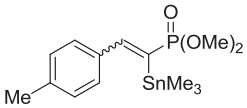
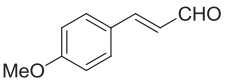
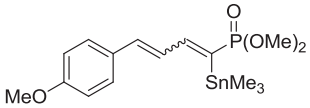
Next, the usage of a second functional group was investigated. Michael addition and subsequent Peterson olefination reaction of **6e** with 3,4,5-trimethoxyphenyllithium and crotonaldehyde afforded the corresponding compound (2*E*,4*E*)-**7** in 34% yield (Equation (2)).[5]



(Z)-**6e** (2*E*,4*E*)-**7** (2)

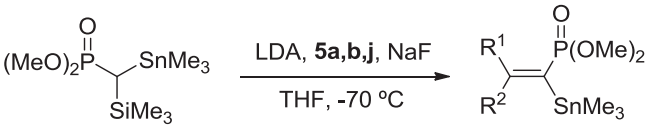
Also the Peterson reaction of 1-(trimethylsilyl)-1-(trimethylstannyl)methyl phosphonate **4b** with aldehydes **5a,b,j** was carried out and gave the corresponding mixture

Table 2 Peterson reaction of **4b** with carbonyl compounds **5a**,**b**,**j**[1)]

entry	carbonyl compound	product (yield, %[2)], *E*/*Z*)
1	 **5a**	 **8a** (42, 2.2/1)
2	 **5b**	 **8b** (55, 1.3/1)
3	 **5j**	 **8j** (68, 1/2)

[1)] All reactions were carried out under Ar atmosphere in THF at -70 ºC for 30 min in the presence of NaF as additive, and then at room temperature for 12 h. [2)] Isolated yield.

of (*E*)- and (*Z*)-1-(trimethylstannyl)vinylphosphonates (*E*)- and (*Z*)-**8a,b,j** in moderate yields (Equation (3)). The results are summarized in Table 2.



4b **8a,b,j** (3)

In this reaction, a similar tendency as in the case of **6a-k** was observed. The reaction of **4b** with aromatic aldehydes afforded mainly (*E*)-1-(trimethylstannyl)vinylphosphonates, while the corresponding reaction with an α,β-unsaturated aldehyde gave predominantly (*Z*)-1-(trimethyl-stannyl)vinylphosphonate.

In conclusion, the multi-functionalized methylphosphonates **4a,b** were useful for the synthesis of 1-(trimethylsilyl)vinylphosphonate and 1-(trimethylstannyl)vinylphosphonate. Reaction of **4a,b** with aromatic aldehydes gave mainly the *anti*-isomers with respect to the olefinic proton and the phosphonyl group. On the other hand, reaction of **4a,b** with α,β-unsaturated aldehydes gave predominantly the respective *syn*-isomers.

EXPERIMENTAL

^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were obtained with a JEOL JNM-EX400 spectrometer in CDCl3 operating at 400 MHz, 100 MHz, 79 MHz, and 160 MHz, respectively, using Me_4Si (^{1}H, ^{13}C, ^{29}Si) and 85% H_3PO_4 (^{31}P) as internal standards. IR spectra were recorded with a Shimadzu FTIR-8100A instrument. X-ray diffraction data were collected with a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Kα radiation (0.71075 Å). Melting points were measured in open capillary tubes and are uncorrected. All reactions were carried out using degassed solvents under an argon atmosphere.

Tetrahydrofuran (THF) was purified by distillation over benzophenone ketyl under an argon atmosphere before use.

Preparation of Dimethyl (Trimethylsilyl)methylphosphonate (3a) and Dimethyl (Trimethylstannyl)methylphosphonate (3b)

A solution of dimethyl methylphosphonate **1** (12.4 g, 100 mmol) in THF (40 mL) was added slowly to *n*-BuLi (1.65 M in hexane, 65.6 mL, 100 mmol) in THF (65 mL) at −70°C under argon atmosphere. After stirring for 15 min at the same temperature copper (I) iodide (20.0 g, 100 mmol) was added to the mixture. The reaction mixture was warmed to −35 °C and was stirred at −35°C for 1 h. A solution of **2a,b** (100 mmol) in THF (30 mL) was added to the mixture at −35°C. The reaction mixture was stirred for 12 h and was quenched by the addition of water (100 mL). The mixture was filtered on celite pad, extracted with diethyl ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue was distilled under reduced pressure to give **3a,b**.

Dimethyl (Trimethylsilyl)methylphosphonate (3a)

Yield: 12.5 g (64%). B.p.: 126–131°C/45 mmHg. ^{1}H NMR ($CDCl_3$): $\delta = 0.09$ (s, 9H, $SiCH_3$), 1.07 (d, $J = 22.0$ Hz, 2H, CH_2), 3.62 (d, $J = 11.2$ Hz, 6H, OCH_3). ^{13}C NMR ($CDCl_3$): $\delta = -0.30$, 13.5 (d, $J = 127.7$ Hz), 52.0 (d, $J = 6.6$ Hz).

Dimethyl (Trimethylstannyl)methylphosphonate (3b)

Yield: 10.7 g (77%). B.p.: 80–85°C/1.0 mmHg. ^{1}H NMR ($CDCl_3$): $\delta = -0.39$ (s, 9H, CH_3), 0.43 (d, $J = 18.2$ Hz, 2H, CH_2), 3.02 (d, $J = 11.0$ Hz, 6H, OCH_3). ^{13}C NMR ($CDCl_3$): $\delta = -8.3$, 4.5 (d, $J = 133.4$ Hz), 51.9 (d, $J = 6.7$ Hz).

Preparation of Dimethyl Bis(trimethylsilyl)methylphosphonate (4a) and Dimethyl (Trimethylsilyl)(trimethylstannyl)methylphosphonate (4b)

To a solution of di*iso*propylamine (15.3 g, 90 mmol) in THF (120 mL) was added *n*-BuLi (1.65 M in hexane, 125 mL, 90 mmol) at −70°C under argon atmosphere. After stirring for 15 min at the same temperature, a solution of **3a,b** (90 mmol) in THF (40 mL) was added to the mixture. After stirring for 15 min at the same temperature chlorotrimethylsilane (14.8 mL, 90 mmol) was added to the mixture. The reaction mixture was warmed to −35°C and stirring was continued at −35°C for 1 h. The reaction mixture was stirred for 12 h at room temperature and was quenched by addition of 2 M hydrochloric acid. The mixture was extracted with diethyl ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue was purified by vacuum distillation or column chromatography on silica gel (chloroform:diethyl ether = 1:1) to give **4a,b**.

Dimethyl Bis(trimethylsilyl)methylphosphonate (4a)

Yield: 22.35 g (93%). B.p.: 84–88°C/0.3 mmHg. ^{1}H NMR ($CDCl_3$): $\delta = 0.14$ (s, 18H, CH_3), 0.65 (d, $J = 25.1$ Hz, 1H, CH), 3.64 (d, $J = 11.0$ Hz, 6H, OCH_3). ^{13}C NMR

($CDCl_3$): $\delta = 1.30, 1.33, 15.8$ (d, $J = 107.0$ Hz), 51.7 (d, $J = 6.6$ Hz). ^{29}Si NMR ($CDCl_3$): $\delta = 0.8$ (d, $J = 6.8$ Hz). ^{31}P NMR ($CDCl_3$): $\delta = 37.5$ (s).

Dimethyl (Trimethylsilyl)(trimethylstannyl)methylphosphonate (4b)

Yield: 2.28 g (18%). ^{1}H NMR ($CDCl_3$): $\delta = 0.15$–0.23 (m, 18H, CH_3), 0.69 (d, $J =$ 25.1 Hz, 1H, CH), 3.69 (d, $J = 11.0$ Hz, 6H, OCH_3). ^{13}C NMR ($CDCl_3$): $\delta = 1.28, 1.31,$ 15.8 (d, $J = 107.8$ Hz, CH), 51.7 (d, $J = 7.5$ Hz, OCH_3).

Reaction of 4a with Carbonyl Compounds 5a-k: General Procedure

To a solution of di*iso*propylamine (0.7 mL, 5.0 mmol) in THF (5 mL) was added *n*-BuLi (1.65 M in hexane, 3 mL, 5.0 mmol) at -70°C under argon atmosphere. After stirring for 15 min at the same temperature, a solution of **4a** (0.54 g, 2.0 mmol) in THF (5 mL) was added to the mixture. After stirring for 15 min at the same temperature, a solution of the respective carbonyl compound **5a-k** (4 mmol) in THF (5 mL) was added to the mixture. After stirring for 15 min at the same temperature, the additive (methyl benzoate (0.41 g, 3.0 mmol) or sodium fluoride (0.10 g, 2.4 mmol)) was added to the mixture in one portion. The reaction mixture was allowed to warm to room temperature and stirring was continued for 12 h. The reaction mixture was quenched by the addition of 2M hydrochloric acid. The mixture was extracted with diethyl ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue was chromatographed on preparative TLC (ethyl acetate:hexane = 2:3) to give compounds **6a-k**. The results are summarized in Table 1.

Dimethyl (*E*)-2-Phenyl-1-(trimethylsilyl)vinylphosphonate (*E*)-6a

Yield 0.16 g (28%). IR (neat): $\nu = 1581, 1244, 1030$ cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta =$ 0.06 (s, 9H, CH_3), 3.78 (d, $J = 11.0$ Hz, 6H, OCH_3), 7.24–7.35 (m, 5H, arom-H), 8.36 (d, $J = 35.4$ Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.7$ (d, $J = 2.5$ Hz), 52.2 (d, $J = 5.8$ Hz), 127.76, 127.78, 127.9, 128.0, 128.4, 131.9 (d, $J = 128.5$ Hz), 138.5 (d, $J =$ 29.9 Hz), 160.5. ^{29}Si NMR ($CDCl_3$): $\delta = -5.9$ (d, $J = 14.2$ Hz).

Dimethyl (*Z*)-2-Phenyl-1-(trimethylsilyl)vinylphosphonate (*Z*)-6a

Yield 0.29 g (51%). IR (neat): $\nu = 1582, 1248, 1030$ cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.29$ (s, 9H, CH3), 3.49 (d, $J = 11.2$ Hz, 6H, OCH_3), 7.32-7.38 (m, 3H, arom-H), 7.62 (d, $J = 6.8$ Hz, 1H, arom-H), 7.63 (d, $J = 61.0$ Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.5$, 51.6 (d, $J = 6.6$ Hz), 127.2, 127.9, 128.8, 128.90, 128.92, 131.4 (d, J = 138.5 Hz), 137.3 (d, $J = 14.1$ Hz), 156.1 (d, $J = 2.5$ Hz). ^{29}Si NMR ($CDCl_3$): $\delta = 1.7$ (d, $J = 15.1$ Hz).

Dimethyl (*E*)-2-(4-Methylphenyl)-1-(trimethylsilyl)vinylphosphonate (*E*)-6b

Yield 0.19 g (32%). IR (neat): $\nu = 1610, 1246, 1030$ cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.08 (s, 9H, CH_3), 2.37 (s, 3H, CH_3), 3.76 (d, $J = 11.0$ Hz, 6H, OCH_3), 7.16 (s, 4H,

arom-H), 8.31 (d, $J = 35.4$ Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.8$ (d, $J = 2.5$ Hz), 21.3, 52.1 (d, $J = 6.6$ Hz), 127.99, 128.00, 128.6, 130.7 (d, $J = 128.5$ Hz), 135.5 (d, $J = 29.9$ Hz), 138.5, 160.7. ^{29}Si NMR ($CDCl_3$): $\delta = -6.2$ (d, $J = 13.7$ Hz).

Dimethyl (*Z*)-2-(4-Methylphenyl)-1-(trimethylsilyl)vinylphosphonate (*Z*)-6b

Yield 0.29 g (49%). IR (neat): $\nu = 1608$, 1246, 1030 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.27$ (s, 9H, CH_3), 2.36 (s, 3H, CH_3), 3.51 (d, $J = 11.2$ Hz, 6H, OCH_3), 7.16 (d, $J = 7.8$ Hz, 2H, arom-H), 7.54 (d, $J = 61.3$ Hz, 1H, olefinic-H), 7.55 (d, $J = 8.1$ Hz, 1H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.5$, 21.4, 51.6 (d, $J = 5.8$ Hz), 128.5, 129.6 (d, $J = 138.5$ Hz), 129.17, 129.19, 134.3 (d, $J = 13.3$ Hz), 139.1, 156.3 (d, $J = 2.5$ Hz). ^{29}Si NMR ($CDCl_3$): $\delta = 1.7$ (d, $J = 15.1$ Hz).

Dimethyl 2-(4-Methoxyphenyl)-1-(trimethylsilyl)vinylphosphonate 6c

Yield 0.42 g (67%). ^{1}H NMR ($CDCl_3$): $\delta = 0.19$ (s, 9H × 2/5, CH_3), 0.26 (s, 9H × 3/5, CH_3), 3.53 (d, $J = 11.2$ Hz, 6H × 3/5, OCH_3), 3.74 (d, $J = 11.0$ Hz, 6H × 2/5, OCH_3), 3.83 (s, 3H × 2/5, OCH_3), 3.83 (s, 3H × 2/5, OCH_3), 6.88–6.90 (m, 4H × 2/5, arom-H), 7.25 (d, $J = 8.5$ Hz, 2H × 3/5, arom-H), 7.49 (d, $J = 61.3$ Hz, 1H × 3/5, olefinic-H), 7.67 (d, $J = 8.8$ Hz, 2H × 3/5, arom-H), 8.27 (d, $J = 35.4$ Hz, 1H × 2/5, olefinic-H).

Dimethyl 2-Pyrenyl-1-(trimethylsilyl)vinylphosphonate 6d

Yield 0.50 g (61%). ^{1}H NMR ($CDCl_3$): $\delta = -0.11$ (s, 9H × 2/3, CH_3), 0.45 (s, 9H × 1/3, CH_3), 3.28 (d, $J = 13.2$ Hz, 6H × 1/3, OCH_3), 3.92 (d, $J = 11.0$ Hz, 6H × 2/3, OCH_3), 7.27–8.32 (m, 9H, arom-H), 8.41 (d, $J = 60.5$ Hz, 1H × 1/3, olefinic-H), 9.05 (d, $J = 34.9$ Hz, 1H × 2/3, olefinic-H).

Dimethyl (*E*)-2-(3,4-methylenedioxyphenyl)-1-(trimethylsilyl) vinylphosphonatet (*E*)-6e

Yield 0.14 g (21%). IR (neat): $\nu = 1568$, 1238, 1030 cm−1. ^{1}H NMR ($CDCl_3$): $\delta = 0.12$ (s, 9H, CH_3), 3.76 (d, $J = 11.0$ Hz, 6H, OCH_3), 5.99 (s, 2H, CH_2), 6.76 (d, $J = 9.5$ Hz, 2H, arom-H), 6.79 (s, 1H, arom-H), 8.22 (d, $J = 35.2$ Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.8$ (d, $J = 2.5$ Hz), 52.1 (d, $J = 5.8$ Hz), 101.2, 107.81, 108.4, 122.5 (d, $J = 1.7$ Hz), 130.2 (d, $J = 129.4$ Hz), 132.2 (d, $J = 29.9$ Hz), 147.3, 147.9, 160.0. ^{29}Si NMR ($CDCl_3$): $\delta = -6.4$ (d, $J = 13.7$ Hz).

Dimethyl (*Z*)-2-(3,4-methylenedioxyphenyl)-1-(trimethylsilyl) vinylphosphonate (*Z*)-6e

Yield 0.28 g (42%). M.p. 85–88°C (from E_t2_O/hexane). IR (KBr): $\nu = 1570$, 1240, 1032 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.41$ (s, 9H, CH_3), 3.56 (d, $J = 11.2$ Hz, 6H, OCH_3), 5.99 (s, 2H, CH_2), 6.80 (d, $J = 8.1$ Hz, 1H, arom-H), 7.15 (dd, $J = 1.7$ Hz, 8.1 Hz, 1H, arom-H), 7.31 (d, $J = 1.7$ Hz, 1H, arom-H), 7.43 (d, $J = 60.8$ Hz, 1H,

olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.4$, 51.6 (d, $J = 5.8$ Hz), 101.2, 107.6, 109.4 (d, $J = 1.7$ Hz), 124.7 (d, $J = 2.5$ Hz), 128.4 (d, $J = 137.7$ Hz), 131.2 (d, $J = 13.3$ Hz), 147.2, 148.3, 155.7 (d, $J = 2.5$ Hz). ^{29}Si NMR ($CDCl_3$): $\delta = 2.0$ (d, $J = 15.1$ Hz). Crystal system: Monoclinic; Space group: $P2_1/n$, a = 6.625(3) Å, b = 7.127(3) Å, c = 34.852(16) Å, $\beta = 91.045(4)^\circ$, V = 1645.3(13) Å^3, Z = 4, R1 = 0.0512, wR = 0.1320.

Dimethyl (*1E,3E*)-1-(Trimethylsilyl)-1,3-pentadienylphosphonate (*1E,3E*)-6i

Yield 0.31 g (62%). IR (neat): $\nu = 1637$, 1250, 1028 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.26$ (s, 9H, CH_3), 1.89 (d, $J = 6.8$ Hz, 3H, CH_3), 3.68 (d, $J = 11.0$ Hz, 6H, OCH_3), 6.17 (sext, $J = 6.8$ Hz, 1H, olefinic-H), 6.24–6.49 (m, 1H, olefinic-H), 7.63 (dd, $J = 11.5$ Hz, 33.7 Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.6$ (d, $J = 2.5$ Hz), 18.8, 51.9 (d, $J = 5.8$ Hz), 125.0 (d, $J = 137.7$ Hz), 130.1 (d, $J = 31.5$ Hz), 141.5, 159.0. ^{29}Si NMR ($CDCl_3$): $\delta = -7.1$ (d, $J = 14.6$ Hz).

Dimethyl (*1Z,3E*)-1-(Trimethylsilyl)-1,3-pentadienylphosphonate (*1Z,3E*)-6i

Yield 0.11 g (22%). IR (neat): 1635, 1248, 1028 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.19$ (s, 9H, CH_3), 1.89 (d, $J = 6.6$ Hz, 3H, CH_3), 3.69 (d, $J = 11.0$ Hz, 6H, OCH_3), 6.10 (sext, $J = 6.8$ Hz, 1H, olefinic-H), 6.94–7.12 (m, 2H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.8$, 18.6, 51.6 (d, $J = 5.8$ Hz), 125.1 (d, $J = 135.2$ Hz), 130.6 (d, $J = 14.1$ Hz), 140.7, 156.9. ^{29}Si NMR ($CDCl_3$): $\delta = -0.3$ (d, $J = 15.6$ Hz).

Dimethyl (*1E,3E*)-4-(4-Methoxyphenyl)-1-(trimethylsilyl)-1,3-butadienylphosphonate (*1E,3E*)-6j

Yield 0.39 g (57%). IR (neat): $\nu = 1601$, 1248, 1028 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.32$ (s, 9H, CH_3), 3.71 (d, $J = 11.0$ Hz, 6H, OCH_3), 3.84 (s, 3H, OCH_3), 6.86 (d, $J = 15.4$ Hz, 1H, olefinic-H), 6.90 (d, $J = 8.8$ Hz, 2H, arom-H), 7.02 (ddd, $J = 2.4$ Hz, 11.5 Hz, 14.9 Hz, 1H, olefinic-H), 7.39 (d, $J = 8.5$ Hz, 2H, arom-H), 7.80 (dd, $J = 11.5$ Hz, 33.0 Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.8$ (d, $J = 2.5$ Hz), 51.9 (d, $J = 5.8$ Hz), 55.3, 114.2, 124.2 (d, $J = 31.5$ Hz), 126.2 (d, $J = 138.5$ Hz), 128.7, 141.8, 158.6, 160.4. ^{29}Si NMR ($CDCl_3$): $\delta = -6.9$ (d, $J = 14.2$ Hz).

Dimethyl (*1Z,3E*)-4-(4-Methoxyphenyl)-1-(trimethylsilyl)-1,3-butadienylphosphonate (*1Z,3E*)-6j

Yield 0.19 g (28%). IR (neat): $\nu = 1603$, 1248, 1030 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.22$ (s, 9H, CH_3), 3.71 (d, $J = 11.2$ Hz, 6H, OCH_3), 3.83 (s, 3H, OCH_3), 6.77 (d, $J = 15.4$ Hz, 1H, olefinic-H), 6.88 (d, $J = 8.5$ Hz, 2H, arom-H), 7.21 (dd, $J = 9.3$ Hz, 59.6 Hz, 1H, olefinic-H), 7.46 (d, $J = 8.8$ Hz, 2H, arom-H), 7.69 (dd, $J = 11.2$ Hz, 14.4 Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.7$, 52.3 (d, $J = 5.8$ Hz), 56.0, 114.7, 125.6 (d, $J =$

17.1 Hz), 127.0 (d, $J = 135.2$ Hz), 129.5, 129.6, 141.8 (d, $J = 2.2$ Hz), 157.4, 160.9. ^{29}Si NMR ($CDCl_3$): $\delta = -0.2$ (d, $J = 15.1$ Hz).

(*Z*)-4-Isopropenyl-1-(2-(dimethylphosphono)-2-(trimethylsilylvinyl)) cyclohexene (*Z*)-6k

Yield 0.16 g (24%). ^{1}H NMR ($CDCl_3$): $\delta = 0.20$ (s, 9H, CH_3), 1.43–1.53 (m, 1H), 1.74 (s, 3H, CH_3), 1.88 (d, $J = 14.2$ Hz, 1H, CH_2), 2.09–2.34 (m, 5H, CH_2 and CH), 3.66 (d, $J = 11.2$ Hz, 6H, OCH_3), 4.73 (d, $J = 8.1$ Hz, 2H, CH_2), 6.16 (s, 1H, olefinic-H), 6.93 (d, $J = 61.5$ Hz, 1H, olefinic-H).

(*E*)-4-Isopropenyl-1-(2-(dimethylphosphono)-2-(trimethylsilylvinyl)) cyclohexene (*E*)-6k

Yield 0.12 g (18%). ^{1}H NMR ($CDCl_3$): $\delta = 0.21$ (s, 9H, CH_3), 1.42–1.53 (m, 1H, CH_2), 1.76 (s, 3H, CH_3), 1.87 (d, $J = 12.5$ H, 1H, CH_2), 2.02–2.33 (m, 5H, CH_2 and CH), 3.72 (d, $J = 11.0$ Hz, 6H, OCH_3), 4.74 (d, $J = 9.3$ Hz, 2H, CH_2), 5.70 (s, 1H, olefinic-H), 7.61 (d, $J = 34.7$ Hz, 1H, olefinic H).

Michael Addition and Peterson Tandem Reaction of 6d

To a solution of 1-bromo-3,4,5-trimethoxybenzene (0.08 g, 0.3 mmol) in THF (3 mL) was added *n*-BuLi (1.65 M in hexane, 0.2 mL, 0.3 mmol) at -70°C under argon atmosphere. After stirring for 15 min at the same temperature a solution of **6e** (0.10 g, 0.3 mmol) in THF (3 mL) was added to the mixture. After being stirring for further 15 min at the same temperature a solution of crotonaldehyde (0.03 g, 0.4 mmol) in THF (2 mL) was added to the mixture. The reaction mixture was warmed to room temperature and stirring was continued for 2 h. The reaction mixture was quenched by the addition of 2 M hydrochloric acid. The mixture was extracted with diethyl ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue was chromatographed on preparative TLC (ethyl acetate:hexane = 2:3) to give 0.05 g of compound **7** (34% yield).

(*2E,4E*)-1-(3,4,5-Trimethoxyphenyl)-1-(3,4-methylenedioxyphenyl)-2-(dimethylphosphono)- hexa-2,4-diene ((*2E,4E*)-7)

^{1}H NMR ($CDCl_3$): $\delta = 1.68$ (d, $J = 6.1$ Hz, 3H, CH_3), 3.51 (d, $J = 11.0$ Hz, 3H, OCH_3), 3.57 (d, $J = 11.0$ Hz, 3H, OCH_3), 3.76 (s, 6H, OCH_3), 3.85 (s, 3H, OCH_3), 5.15 (d, $J = 17.1$ Hz, 1H, CH), 5.93–6.07 (m, 2H, olefinic-H), 5.96 (s, 2H, CH_2), 6.43 (s, 2H, arom-H), 6.60 (dd, $J = 1.0$ Hz, 8.1 Hz, 1H, arom-H), 6.68 (d, $J = 1.7$ Hz, 1H, arom-H), 6.74 (d, $J = 8.1$ Hz, 1H, arom-H), 7.23 (dd, $J = 10.5$ Hz, 24.2 Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 18.8$, 49.6 (d, $J = 10.8$ Hz), 52.1 (d, $J = 5.0$ Hz), 55.9, 60.8, 100.7, 106.1, 107.6, 109.2, 121.8, 126.8 (d, $J = 179.3$ Hz), 127.2 (d, $J = 23.3$ Hz), 135.7 (d, $J = 6.6$ Hz), 136.3, 137.0 (d, $J = 6.6$ Hz), 139.7, 145.7 (d, $J = 4.1$ Hz), 145.9, 147.3, 152.6.

Reaction of 4b With Carbonyl Compounds 5a,b,j

To a solution of di*iso*propylamine (0.7 mL, 5.0 mmol) in THF (5 mL) was added *n*-BuLi (1.65 M in hexane, 3 mL, 5.0 mmol) at −70°C under argon atmosphere. After stirring for 15 min at the same temperature a solution of **4b** (0.72 g, 2.0 mmol) in THF (5 mL) was added to the mixture. After stirring for further 15 min at the same temperature a solution of the respective carbonyl compound **5a**,**b**,**j** (4.0 mmol) in THF (5 mL) was added to the mixture and stirring was continued for 15 min at the same temperature. Sodium fluoride (0.10 g, 2.4 mmol) was added to the mixture one portion. The reaction mixture was warmed to room temperature and stirring was continued for 12 h. The reaction mixture was quenched by the addition of 2 M hydrochloric acid. The mixture was extracted with diethyl ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*, and the residue was chromatographed on preparative TLC (chloroform:diethyl ether = 9:1) to give compounds **8a,b,j**.

Dimethyl (*E*)-2-Phenyl-1-(trimethylstannyl)vinylphosphonate (*E*)-8a

Yield 0.22 g (29%). ^{1}H NMR ($CDCl_3$): $\delta = 0.28$ (s, 9H, CH_3), 3.49 (d, $J = 11.2$ Hz, 6H, OCH_3), 7.30–7.39 (m, 3H, arom-H), 7.58 (d, $J = 61.0$ Hz, 1H, olefinic-H), 7.62 (dd, $J = 1.7$ Hz, 8.1 Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.5$, 51.6 (d, $J = 6.6$ Hz), 127.8, 128.85 (d, $J = 8.3$ Hz), 128.9, 131.3 (d, $J = 137.7$ Hz), 137.3 (d, $J = 13.3$ Hz), 156.2 (d, $J = 2.5$ Hz).

Dimethyl (*Z*)-2-Phenyl-1-(trimethylstannyl)vinylphosphonate (*Z*)-8a

Yield 0.10 g (13%). ^{1}H NMR ($CDCl_3$): $\delta = 0.06$ (s, 9H, CH_3), 3.77 (d, $J = 10.7$ Hz, 6H, OCH_3), 7.23–7.27 (m, 2H, arom-H), 7.32–7.36 (m, 3H, arom-H), 8.35 (d, $J = 35.6$ Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.7$ (d, $J = 2.5$ Hz), 52.2 (d, $J = 6.6$ Hz), 127.8 (d, $J = 1.7$ Hz), 127.9, 128.4, 131.8 (d, $J = 129.4$ Hz), 138.4 (d, $J = 29.9$ Hz), 160.5.

Dimethyl (*E*)-2-(4-Methylphenyl)-1-(trimethylstannyl)vinylphosphonate (*E*)-8b

Yield 0.24 g (31%). ^{1}H NMR ($CDCl_3$): $\delta = 0.27$ (s, 9H, CH_3), 2.35 (s, 3H, CH_3), 3.50 (d, $J = 11.2$ Hz, 6H, OCH_3), 7.16 (d, $J = 7.8$ Hz, 2H, arom-H), 7.54 (d, $J = 61.3$ Hz, 1H, olefinic-H), 7.55 (d, $J = 8.1$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.6$, 21.3, 51.5 (d, $J = 6.6$ Hz), 126.7, 128.4, 128.9 (d, $J = 36.5$ Hz), 129.1, 134.1 (d, $J = 13.3$ Hz), 137.4 (d, $J = 187.4$ Hz), 139.0, 156.3 (d, $J = 2.5$ Hz).

Dimethyl (*Z*)-2-(4-Methylphenyl)-1-(trimethylstannyl)vinylphosphonate (*Z*)-8b

Yield 0.19 g (24%). ^{1}H NMR ($CDCl_3$): $\delta = 0.09$ (s, 9H, CH_3), 2.36 (s, 3H, CH_3), 3.76 (d, $J = 11.0$ Hz, 6H, OCH_3), 7.16 (s, 4H, arom-H), 8.32 (d, $J = 35.4$ Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.8$ (d, $J = 2.5$ Hz), 21.3, 52.1 (d, $J = 5.8$ Hz), 128.0 (d, $J =$

1.7 Hz), 128.5, 130.6 (d, J = 129.4 Hz), 135.4 (d, J = 29.9 Hz), 138.5, 160.7 (d, J = 1.7 Hz).

(*1E,3E*)-4-(4-Methoxyphenyl)-1-(dimethylphosphono)-1-trimethylstannyl-1,3-butadiene (*1E,3E*)-8j

Yield 0.20 g (23%). ^{1}H NMR ($CDCl_3$): $\delta = 0.22$ (s, 9H, CH_3), 3.71 (d, $J = 11.2$ Hz, 6H, OCH_3), 3.83 (s, 3H, OCH_3), 6.77 (d, $J = 15.4$ Hz, 1H, olefinic-H), 6.88 (d, $J = 8.5$ Hz, 2H, arom-H), 7.21 (dd, $J = 11.0$ Hz, 59.6 Hz, olefinic-H), 7.46 (d, $J = 8.5$ Hz, 2H, arom-H), 7.69 (dd, J = 11.0 Hz, 15.4 Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = -0.7$, 51.6 (d, $J = 5.8$ Hz), 55.3, 114.0, 124.9 (d, $J = 14.1$ Hz), 126.2 (d, $J = 136.0$ Hz), 128.8, 128.9, 141.1 (d, $J = 2.5$ Hz), 156.7, 160.2.

(*1Z,3E*)-4-(4-Methoxyphenyl)-1-(dimethylphosphono)-1-trimethylstannyl-1,3-butadiene (*1Z,3E*)-8j

Yield 0.39 g (45%). ^{1}H NMR ($CDCl_3$): $\delta = 0.32$ (s, 9H, CH_3), 3.71 (d, $J = 11.0$ Hz, 6H, OCH_3), 3.84 (s, 3H, OCH_3), 6.86 (d, $J = 15.1$ Hz, 1H, olefinic-H), 6.91 (d, $J = 8.8$ Hz, 2H, arom-H), 7.02 (ddd, $J = 2.7$ Hz, 11.2 Hz, 15.1 Hz, olefinic-H), 7.39 (d, $J = 8.5$ Hz, 2H, arom-H), 7.81 (dd, $J = 11.2$ Hz, 32.7 Hz, 1H, olefinic-H). ^{13}C NMR ($CDCl_3$): $\delta = 0.8$ (d, $J = 2.5$ Hz), 51.9 (d, $J = 5.8$ Hz), 55.3, 114.2, 124.2 (d, $J = 31.5$ Hz), 126.2 (d, $J = 137.7$ Hz), 128.6, 128.7, 141.8, 158.6, 160.3.

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SUPPLEMENTAL MATERIAL

Supplementary data of this article can be accessed on the publisher's website, www.tandfonline.com/gpss

REFERENCES

1. (a) Smith, P. W.; Chamiec, A. J.; Chung, G.; Cobley, K. N.; Duncan, K.; Howes, P. D.; Whittington, A. R.; Wood, M. R. *J. Antibiotics* **1995,** 48, 73-82. (b) Iorga, B.; Eymery, F.; Savignac, P. *Tetrahedron Lett.* **1998,** 39, 4477-4480. (c) Borodkin, V. S.; Ferguson, M. S. J.; Nikolaev, A. V. *Tetrahedron Lett.* **2001,** 42, 5305-5308. (d) Zgani, I.; Menut, C.; Montéro, J. L. *Heteroatom Chem.* **2002,** 13, 654-661. (e) Ronchi, S.; Compostella, F.; Lay, L.; Ronchetti, F.; Toma, L. *Eur. J. Org. Chem.* **2005,** 4459-4463. (f) Watkins, W. J.; Chen, J. M.; Cho, A.; Chong, L.; Collins, N.; Fardis, M.; Huang, W.; Hung, M.; Kirschberg, T.; Lee, W. A.; Liu, X.; Thomas, W.; Xu, J.; Zeynalzadegan, A.; Zhang, J. *Bioorg. Med. Lett.* **2006,** 16, 3479-3483. (g) Bortolini, O.; Mulani, I.; De Nino, A.; Maiuolo, L.; Nardi, M.; Russo, B.; Avnet, S. *Tetrahedron* **2011,** 67, 5635-5641.
2. (a) Savignac, P.; Mathey, F. *Synthesis*, **1982,** 725-726. (b) Kawashima, T.; Ishii, T.; Inamoto, N. *Tetrahedron Lett.* **1983,** 24, 739-742. (c) Aboujaoude, E. E.; Lietje, S.; Collignon, N.; Teulade, M. P.; Savignac, P. *Synthesis* **1986,** 934-937. (d) Savignac, P.; Teulade, M. P.; Collignon, N. *J. Orgnomet. Chem.* **1987,** 323, 135-144. (e) Kawashima, T.; Ishii, T.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1987,** 60, 1831-1837. (f) Umezawa, T.; Seino, T.; Matsuda, F. *Org. Lett.* **2012,** 14, 4206-4209.

3. For a review on synthetic uses of vinylphosphonates, see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992,** 333-349.
4. Kouno, R.; Okauchi, T.; Nakamura, M.; Ichikawa, J.; Minami, T. *J. Org. Chem.* **1998,** 63, 6239-6246.
5. Chang, K.; Ku, B.; Oh, D. Y. *Synth.Commun.* **1989,** 19, 1891-1898.