Silylcupration of 1-Alkynylphosphine Oxides: Stereo- and Regioselective Synthesis of β-Silyl Substituted Vinylphosphine Oxides

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Abstract: β-Silyl substituted vinylphosphine oxides were prepared stereo- and regioselectively by the silylcupration of 1-alkynylphosphine oxides followed by hydrolysis or by reacting with other electrophiles.

Key words: silylcupration, 1-alkynylphosphine oxide, β-silyl substituted vinylphosphine oxides

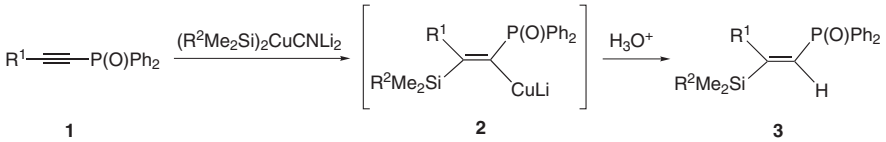
Stereoselective synthesis of substituted alkenes has always been an interesting topic in organic synthesis, in which the organometalation of acetylenes is one of the most efficient routes to stereo-defined alkenes.[1] Among the organometalation reagents, organocopper reagents have received an especially great deal of attention regarding *cis*-conjugate addition reactions with acetylenic compounds.[2] In the case of functionalized acetylenes, most reactions with organocopper reagents also undergo a facile *cis*-addition.[3]

Our group has prepared several kinds of functionalized vinyl compounds by hydrozirconation,[4a] hydrotelluration,[4b] carbomagnesiation,[5] carbocupration,[6] and selenomagnesiation[7] of various functionalized acetylenes, to afford stereo-defined polysubstituted alkenes.

Unsaturated phosphorus compounds containing various functional groups have been widely studied due to their synthetic and biological usefulness.[8] On the other hand, functionalized vinylphosphine oxides are useful synthetic intermediates for nucleophilic addition[9] and cycloaddition reactions.[10] And some derivatives of vinylphosphine oxides can be used as biologically active compounds.[11] In the past years the organosilylcupration of acetylenes has provided efficient procedures for introducing organosilyl group to organic molecules,[12] giving rise to a wide range of silicon synthons of great potential.[13] Moreover, the intermediate cuprates resulting from *syn*-addition of the silylcuprate to acetylene react with a great variety of electrophiles to give vinylsilanes.[12,13] We report herein a synthetic route for the preparation of β-silyl substituted vinylphosphine oxides, which are versatile synthetic reagents serving as not only vinylphosphine oxides but also as vinylsilanes, by the Michael addition of organosilylcopper(I) reagents to 1-alkynylphosphine oxides[14].

Preliminary experiments involved the treatment of 1-alkynylphosphine oxides[15] with organosilylcopper(I) reagents, prepared in situ from CuCN and 2 equivalents of organosilyllithium,[16] followed by hydrolysis with saturated ammonium chloride solution (Scheme 1). The results are summarized in Table 1.

As indicated in Table 1, the Michael addition proceeded smoothly and was complete within 30 minutes with organosilylcuprates at –78 °C in THF. However, probably due to steric hindrance of the bulky group, a low yield was observed along with recovery of starting material for entry 3. In all cases, organosilylcopper(I) reagents attacked β-position of 1-alkynylphosphine oxides exclusively. The regioselectivity can be rationalized in terms of carbanion stabilization by the phosphine oxides. A *cis*-addition was found when 1-alkynylphosphine oxides reacted with organosilylcopper(I) reagents. The *cis*-stereoselectivity in these reactions and the *E* configuration of **3a** and **3b** were confirmed by NOE experiments, which showed the correlation between the vinylic proton and the protons of trimethylsilyl or phenyldimethylsilyl group, while there is no correlation between the vinylic proton and the methylene group.



Scheme 1

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Table 1 Reaction of Organosilylcopper(I) Reagents with 1-Alkynylphosphine Oxides ($E^+ = H^+$)

Entry	R^1	R^2	Product[a]	Yield (%)[b]
1	$EtOCH_2$	Me	**3a**	82
2	$EtOCH_2$	Ph	**3b**	78
3	Ph	Me	**3c**	22[c]
4	*n*-C_4H_9	Me	**3d**	80
5	*n*-C_4H_9	Ph	**3e**	76
6	$MeOCH_2$	Ph	**3f**	89
7	$MeOCH_2$	Me	**3g**	81

[a] Other isomers were not detected in NMR studies.
[b] Isolated yield based on **1.**
[c] The starting material was recovered to an extent of 67%.

The dimetalated intermediates **2** are important intermediates because they can react with a series of electrophiles to give the polysubstituted vinylphosphine oxides with retention of configuration (Scheme 2). We have thus further investigated the reactions of intermediate **2** with several electrophiles. Results were summarized in Table 2.

Table 2 Reaction of Organosilylcopper(I) Reagents with 1-Alkynylphosphine Oxides (Electrophile = E^+)

Entry	R^1	R^2	E^+	Product	Yield (%)[a]
1	$EtOCH_2$	Me	I	**4a**	79
2	*n*-C_4H_9	Me	I	**4b**	75
3	$MeOCH_2$	Me	I	**4c**	80
4	Ph	Me	I	**4d**	24
5	$EtOCH_2$	Me	Br	**4e**	68
6	*n*-C_4H_9	Ph	Cl	**4f**	82
7	*n*-C_4H_9	Me	SePh	**4g**	69
8	*n*-C_4H_9	Me	TePh	**4h**	78
9	*n*-C_4H_9	Me		**4i**	76
10	$MeOCH_2$	Ph		**4j**	75
11	$MeOCH_2$	Me	Ph_2ICl	**4k**	62

[a] Isolated yield based on **1**.

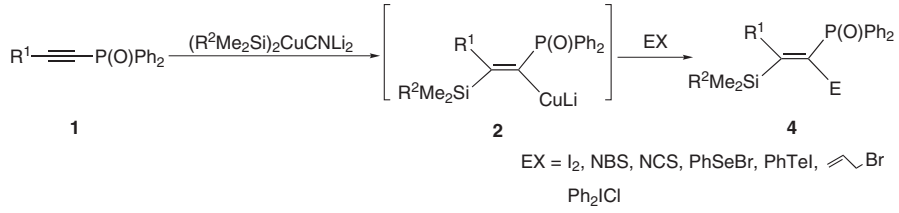
1-Halovinylphosphine oxides **4a–f** were obtained smoothly by treating **2** with iodine (or NBS, NCS). When electrophiles such as phenylselenyl bromide and phenyltelluryl iodide were added, 1-phenylchalcogenovinylphosphine oxides **4g** and **4h** were formed.[17] Allylation products of **4i** and **4j** were also generated with allyl bromide in good yields. Even the arylation product **4k** was produced by the reaction with diphenyliodonium chloride in good yield (Table 2, entry 11), but with acetylenylphenyliodonium tosylate we did not obtain the corresponding product. The intermediate cuprate **2** did not react with carbonyl compounds. Attempts to trap this vinylcopper(I) intermediates with benzaldehyde, acetyl chloride and benzoyl chloride led only to compound **3**. At the same time, no anticipated products were obtained from the reactions of other electrophiles such as methyl iodide, methyloxirane or α,β-unsaturated ketones. This is probably due to the coordination between the phosphine oxide function and copper,[18] which could also partially explain why only some activated electrophilic reagents react with intermediate **2**.

The stereochemistry of the reaction was unequivocally established by NOESY spectra of compound **4i** and **4j**. The NOESY spectra of compounds **4i** and **4j** show that there is a strong correlation between the allylic protons of the allyl group and the protons of trimethylsilyl or phenyldimethylsilyl group, while no correlation was found between the allylic protons of the allyl group and R^1 group.

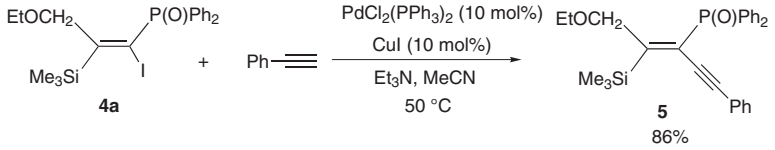
1-Halovinylphosphine oxide **4a–f** are very useful intermediates, for example, the Sonogashira cross-coupling reaction of α-iodovinylphosphine oxide **4a** with phenylacetylene in the presence of catalytic amount of Pd/Cu(I) provided a novel kind of enyne compound **5** containing phosphorus and silyl functional groups (Scheme 3).

Besides the coupling reaction, the carbomethoxylation of haloalkene **4c** also proceeded smoothly and introduced a CO_2Me group into the molecule, which cannot be generated directly by the reaction of intermediate **2** with methyl chloroformate (Scheme 4).

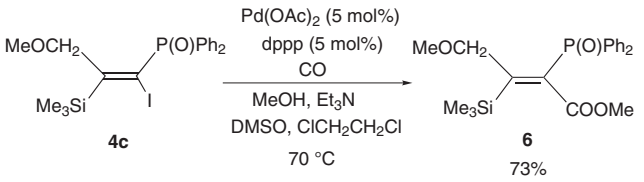
In conclusion, *cis*-silylcupration of 1-alkynylphosphine oxides and further reaction with electrophiles provide an efficient, regio- and stereoselective method for the synthesis of synthetically useful β-silyl substituted vinylphosphine oxides in a one-pot process. The reactions of intermediate **2** with other electrophiles to synthesize various substituted β-silyl substituted vinylphosphine oxides



Scheme 2



Scheme 3



Scheme 4

and the applications of these products are now carried out in our laboratory.

All ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance 400 (400 MHz) spectrometer with TMS as the internal standard. ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance 400 (100 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. IR spectra were run on a Bruker vector 22 spectrometer. EIMS were determined with a HP5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument.

Vinylphosphine Oxides 3a–g; General Procedure

CuCN (1 mmol, 90 mg) was introduced into a stirred solution of organosilyllithium[16] (2 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min, the temperature was lowered to –78 °C, and a solution of the appropriate 1-alkynylphosphine oxide **1** (1 mmol) in THF (3 mL) was added slowly. The reaction mixture was allowed to warm at –20 °C during several hours, followed by hydrolysis with sat. aq NH_4Cl (5 mL), and then extraction with Et_2O (3 × 15 mL). The combined Et_2O layers were dried ($MgSO_4$). After filtration and removal of the solvent in vacuo, the crude product was purified with flash chromatography (hexane–EtOAc, 2:1).

3a

Oil.

IR (film): 1437, 1245, 1193, 1113, 839 cm^{-1}.

^{1}H NMR: δ = 7.64 (m, 4 H), 7.37 (m, 6 H), 6.35 (d, *J* = 31.2 Hz, 1 H), 4.53 (d, *J* = 17.3 Hz, 2 H), 3.25 (q, *J* = 6.8 Hz, 2 H), 1.00 (t, *J* = 6.8 Hz, 3 H), 0.13 (s, 6 H), 0.01 (s, 3 H).

^{13}C NMR: δ = 171.62 (d, *J* = 6.4 Hz), 134.97 (d, *J* = 101.0 Hz), 131.54, 130.86 (d, *J* = 2.0 Hz), 128.67 (d, *J* = 4.0 Hz), 128.55 (d, *J* = 4.0 Hz), 71.97 (d, *J* = 12.0 Hz), 66.21 (d, *J* = 11.0 Hz), 15.03 (d, *J* = 2.2 Hz), –0.96, –1.73.

MS (EI): *m*/*z* (%) = 73 (80), 84 (100), 201 (53), 358 (6, [M$^+$]).

Anal. Calcd for $C_{20}H_{27}O_2PSi$: C, 67.01; H, 7.59. Found: C, 67.13; H, 7.46.

3b

Oil.

IR (film): 1437, 1249, 1193, 1115, 819 cm^{-1}.

^{1}H NMR: δ = 7.63 (m, 4 H), 7.52 (m, 2 H), 7.36 (m, 6 H), 7.30 (m, 3 H), 6.39 (d, *J* = 29.6 Hz, 1 H), 4.61 (d, *J* = 15.6 Hz, 2 H), 3.19 (q, *J* = 7.2 Hz, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 0.46 (s, 6 H).

^{13}C NMR: δ = 169.72 (d, *J* = 6.2 Hz), 137.69, 135.14 (d, *J* = 102.0 Hz), 134.50, 131.98 (d, *J* = 3.0 Hz), 131.40 (d, *J* = 88.2 Hz), 131.26 (d, *J* = 9.9 Hz), 129.60, 129.03 (d, *J* = 12.2 Hz), 128.13, 71.79 (d, *J* = 12.2 Hz), 66.52, 15.32, –1.96.

MS (EI): *m*/*z* (%) = 135 (75), 201 (14), 313 (100), 421 (27, [M$^+$ + 1]).

Anal. Calcd for $C_{25}H_{29}O_2PSi$: C, 71.40; H, 6.95. Found: C, 71.50; H, 6.83.

3c

Oil.

IR (film): 1486, 1437, 1243, 1200, 1117, 847 cm^{-1}.

^{1}H NMR: δ = 7.75 (m, 4 H), 7.45 (m, 6 H), 7.31 (m, 2 H), 7.24 (m, 1 H), 7.08 (m, 2 H), 6.74 (d, *J* = 30.0 Hz), 0.22 (s, 9 H).

^{13}C NMR: δ = 170.96 (d, *J* = 7.6 Hz), 148.38 (d, *J* = 22.9 Hz), 136.71 (d, *J* = 90.8 Hz), 135.70 (d, *J* = 100.6 Hz), 131.89 (d, *J* = 2.5 Hz), 131.53 (d, *J* = 9.4 Hz), 129.02 (d, *J* = 11.9 Hz), 128.44, 126.96, 126.30 (d, *J* = 1.4 Hz), –1.46.

MS (EI): *m*/*z* (%) = 43 (100), 73 (77), 201 (11), 377 (5, [M$^+$ + 1]).

Anal. Calcd for $C_{23}H_{25}OPSi$: C, 73.37; H, 6.69. Found: C, 73.51; H, 6.53.

3d

Oil.

IR (film): 1436, 1248, 1193, 1115, 835 cm^{-1}.

^{1}H NMR: δ = 7.72 (m, 4 H), 7.43 (m, 6 H), 6.42 (d, *J* = 30.0 Hz, 1 H), 2.62 (t, *J* = 6.4 Hz, 2 H), 1.19 (m, 4 H), 0.74 (t, *J* = 7.1 Hz, 3 H), 0.19 (s, 3 H), 0.07 (s, 6 H).

^{13}C NMR: δ = 174.05 (d, *J* = 6.0 Hz), 135.80 (d, *J* = 100.0 Hz), 131.31 (d, *J* = 2.8 Hz), 130.96 (d, *J* = 9.0 Hz), 129.86 (d, *J* = 91.0 Hz), 128.45 (d, *J* = 2.0 Hz), 34.74 (d, *J* = 12.0 Hz), 31.95 (d, *J* = 2.0 Hz), 23.12 (d, *J* = 6.0 Hz), 13.78, –1.22, –1.91.

MS (EI): *m*/*z* (%) = 73 (100), 201 (34), 283 (9), 311 (74), 357 (4, [M$^+$ + 1]).

Anal. Calcd for $C_{21}H_{29}OPSi$: C, 70.75; H, 8.20. Found: C, 70.62; H, 8.34.

3e

Oil.

IR (film): 1588, 1483, 1248, 1194, 1112, 830 cm^{-1}.

^{1}H NMR: δ = 7.69 (m, 4 H), 7.48 (m, 2 H), 7.39 (m, 6 H), 7.31 (m, 3 H), 6.48 (d, *J* = 30.4 Hz, 1 H), 2.64 (t, *J* = 6.6 Hz, 2 H), 1.11 (m, 4 H), 0.64 (t, *J* = 6.8 Hz, 3 H), 0.42 (s, 6 H).

^{13}C NMR: δ = 172.07 (d, *J* = 5.8 Hz), 137.23, 135.89 (d, *J* = 100.0 Hz), 134.36, 132.18, 131.79 (d, *J* = 2.0 Hz), 131.30 (d, *J* = 11.0 Hz), 129.84, 128.97 (d, *J* = 11.5 Hz), 128.34, 34.35 (d, *J* = 12.1 Hz), 32.11 (d, *J* = 1.5 Hz), 23.33, 14.06, –2.32.

MS (EI): *m*/*z* (%) = 135 (60), 201 (33), 283 (4), 311 (100), 419 (6, [M$^+$ + 1]).

Anal. Calcd for $C_{26}H_{31}OPSi$: C, 74.60; H, 7.46. Found: C, 74.49; H, 7.60.

3f
Oil.

IR (film): 1434, 1248, 1192, 1113, 831 cm^{-1}.

^1H NMR: δ = 7.64 (m, 4 H), 7.53 (m, 2 H), 7.44 (m, 6 H), 7.34 (m, 3 H), 6.42 (d, *J* = 29.6 Hz, 1 H), 4.57 (s, 2 H), 3.06 (s, 3 H), 0.47 (s, 6 H).

^{13}C NMR: δ = 168.87 (d, *J* = 5.8 Hz), 137.04, 134.65 (d, *J* = 102.0 Hz), 134.05, 131.56 (d, *J* = 2.0 Hz), 131.45, 130.76 (d, *J* = 10.0 Hz), 129.22, 128.62 (d, *J* = 12.2 Hz), 127.75, 73.24 (d, *J* = 11.9 Hz), 58.27, –2.47.

MS (EI): *m*/*z* (%) = 135 (63), 201 (21), 313 (100), 391 (14), 407 (2, $[M^+ + 1]$).

Anal. Calcd for $C_{24}H_{27}O_2PSi$: C, 70.91; H, 6.69. Found: C, 70.79; H, 6.80.

3g
Oil.

IR (film): 1437, 1246, 1192, 1114, 845 cm^{-1}.

^1H NMR: δ = 7.75 (m, 4 H), 7.50 (m, 6 H), 6.47 (d, *J* = 30.0 Hz, 1 H), 4.62 (s, 2 H), 3.20 (s, 3 H), 0.21 (s, 9 H).

^{13}C NMR: δ = 170.73 (d, *J* = 6.7 Hz), 134.22 (d, *J* = 101.1 Hz), 131.49 (d, *J* = 2.7 Hz), 130.78 (d, *J* = 9.2 Hz), 129.52 (d, *J* = 85.7 Hz), 128.54 (d, *J* = 11.8 Hz), 73.39 (d, *J* = 12.8 Hz), 58.26, –1.17.

MS (EI): *m*/*z* (%) = 73 (22), 201 (10), 313 (30), 329 (100), 344 (28, $[M^+]$).

Anal. Calcd for $C_{19}H_{25}O_2PSi$: C, 66.25; H, 7.32. Found: C, 66.41; H, 7.20.

Vinylphosphine Oxides 4a–k; General Procedure

CuCN (90 mg, 1 mmol) was introduced into a stirred solution of organosilyllithium (2 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min, the mixture was cooled to –78 °C, and a solution of appropriate 1-alkynylphosphine oxide (1 mmol) in THF (3 mL) was added slowly and the reaction mixture was allowed to warm to –20 °C during several hours. The mixture was cooled to –78 °C again and the respective electrophile {in the cases of **4a**, **4b**, **4c** and **4d**, I_2 (508 mg, 2 mmol) in THF (3 mL); in the cases of **4e** and **4f**, NBS and NCS (356 mg and 267 mg, respectively, 2 mmol); in the case of **4g**, phenylselenyl bromide (472 mg, 2 mmol) in THF (3 mL); in the case of **4h,** phenyltelluryl iodine [2 mmol: prepared by reaction of diphenyl ditelluride (408 mg, 1 mmol) with iodine (254 mg, 2 mmol) in THF (3 mL) for 1 h at r.t.]; in the cases of **4i** and **4j**, allyl bromide (242 mg, 2 mmol) in THF (3 mL)} was added dropwise [in the case of **4k**, diphenyliodonium chloride (640 mg, 2 mmol) was added directly]. The reaction mixture was allowed to warm to r.t. and quenched with aq NH_4Cl (5 mL), then extracted with Et_2O (3 × 15 mL), and dried ($MgSO_4$). After filtration and removal of the solvent in vacuo, the crude product was purified with flash chromatography (hexane–EtOAc, 1:1).

4a
Oil.

IR (film): 1437, 1245, 1192, 1115, 839 cm^{-1}.

^1H NMR: δ = 7.77 (m, 4 H), 7.51 (m, 2 H), 7.43 (m, 4 H), 4.42 (d, *J* = 27.2 Hz, 2 H), 3.05 (q, *J* = 6.8 Hz, 2 H), 0.93 (t, *J* = 6.8 Hz, 3 H), 0.35 (s, 6 H), 0.18 (s, 3 H).

^{13}C NMR: δ = 173.15, 133.44 (d, *J* = 101.0 Hz), 132.46 (d, *J* = 9.4 Hz), 132.11 (d, *J* = 2.3 Hz), 128.39 (d, *J* = 4.2 Hz), 128.27 (d, *J* = 3.2 Hz), 72.45 (d, *J* = 10.5 Hz), 65.59 (d, *J* = 24.0 Hz), 15.07 (d, *J* = 5.6 Hz), –0.55, –0.83.

MS (EI): *m*/*z* (%) = 73 (100), 201 (16), 357 (9), 485 (2, $[M^+ + 1]$).

Anal. Calcd for $C_{20}H_{26}IO_2PSi$: C, 49.59; H, 5.41. Found: C, 49.67; H, 5.26.

4b
Oil.

IR (film): 1437, 1246, 1193, 1116, 836 cm^{-1}.

^1H NMR: δ = 7.75 (m, 4 H), 7.43 (m, 6 H), 2.77 (s, 2 H), 1.15 (m, 4 H), 0.70 (t, *J* = 7.2 Hz, 3 H), 0.29 (s, 6 H), 0.14 (s, 3 H).

^{13}C NMR: δ = 176.13 (d, *J* = 10.0 Hz), 133.92 (d, *J* = 105.7 Hz), 133.86 (d, *J* = 102.0 Hz), 132.44 (d, *J* = 4.0 Hz), 132.34 (d, *J* = 4.0 Hz), 131.91, 128.36 (d, *J* = 12.0 Hz), 39.03 (d, *J* = 9.0 Hz), 32.16, 22.74, 13.80, –0.37, –0.48.

MS (EI): *m*/*z* (%) = 73 (100), 201 (40), 355 (23), 483 (3, $[M^+ + 1]$).

Anal. Calcd for $C_{21}H_{28}IO_2PSi$: C, 52.28; H, 5.85. Found: C, 52.20; H, 5.96.

4c
Oil.

IR (film): 1437, 1244, 1190, 1098, 835 cm^{-1}.

^1H NMR: δ = 7.76 (m, 4 H), 7.52 (m, 2 H), 7.44 (m, 4 H), 4.42 (s, 2 H), 2.94 (s, 3 H), 0.35 (s, 9 H). ^{13}C NMR: δ = 170.78, 132.57 (d, *J* = 107.1 Hz), 132.19 (d, *J* = 9.4 Hz), 131.94 (d, *J* = 2.9 Hz), 128.18 (d, *J* = 12.0 Hz), 107.76 (d, *J* = 75.7 Hz), 73.84 (d, *J* = 10.8 Hz), 57.32, –0.19.

MS (EI): *m*/*z* (%) = 73 (37), 201 (18), 327 (42), 343 (3), 439 (11), 455 (100), 471 (3, $[M^+ + 1]$).

Anal. Calcd for $C_{19}H_{24}IO_2PSi$: C, 48.52; H, 5.14. Found: C, 48.41; H, 5.29.

4d
Oil.

IR (film): 1484, 1246, 1196, 1115, 839 cm^{-1}.

^1H NMR: δ = 7.56 (m, 4 H), 7.38 (m, 2 H), 7.27 (m, 4 H), 6.85 (m, 3 H), 6.56 (m, 2 H), 0.26 (s, 5 H), 0.18 (s, 4 H).

^{13}C NMR: δ = 173.91, 143.45 (d, *J* = 9.2 Hz), 133.46 (d, *J* = 107.0 Hz), 132.33 (d, *J* = 9.0 Hz), 131.79, 131.76 (d, *J* = 3.1 Hz), 128.55 (d, *J* = 11.0 Hz), 127.90 (d, *J* = 3.0 Hz), 126.58, 126.43 (d, *J* = 13.2 Hz), –0.49.

MS (EI): *m*/*z* (%) = 73 (85), 178 (100), 201 (55), 375 (93), 503 (2, $[M^+ + 1]$).

Anal. Calcd for $C_{23}H_{24}IOPSi$: C, 54.99; H, 4.82. Found: C, 54.86; H, 4.96.

4e
Oil.

IR (film): 1437, 1245, 1196, 1094, 838 cm^{-1}.

^1H NMR: δ = 7.79 (m, 4 H), 7.53 (m, 2 H), 7.45 (m, 4 H), 4.61 (d, *J* = 18.0 Hz, 2 H), 3.20 (q, *J* = 7.2 Hz, 2 H), 0.99 (t, *J* = 7.2 Hz, 3 H), 0.32 (s, 6 H), 0.12 (s, 3 H).

^{13}C NMR: δ = 165.59, 132.70 (d, *J* = 108.0 Hz), 132.37 (d, *J* = 10.0 Hz), 132.15 (d, *J* = 2.0 Hz), 131.32 (d, *J* = 10.0 Hz), 128.44 (d, *J* = 4.0 Hz), 70.33 (d, *J* = 15.0 Hz), 65.63 (d, *J* = 25.0 Hz), 15.17 (d, *J* = 5.0 Hz), –1.25, –1.90.

MS (EI): *m*/*z* (%) = 73 (100), 201 (29), 357 (5), 438 (2, $[M^+ + 1]$).

Anal. Calcd for $C_{20}H_{26}BrO_2PSi$: C, 54.92; H, 5.99. Found: C, 54.80; H, 6.08.

4f
Oil.

IR (film): 1434, 1251, 1198, 1114, 817 cm^{-1}.

^{1}H NMR: δ = 7.77 (m, 4 H), 7.54 (m, 4 H), 7.44 (m, 4 H), 7.35 (m, 3 H), 2.92 (t, *J* = 7.6 Hz, 2 H), 1.33 (m, 2 H), 1.20 (m, 2 H), 0.75 (t, *J* = 7.6 Hz, 3 H), 0.57 (s, 6 H).

^{13}C NMR: δ = 163.82 (d, *J* = 5.0 Hz), 137.82, 134.37, 133.02 (d, *J* = 107.0 Hz), 132.56, 132.47, 132.42 (d, *J* = 3.0 Hz), 129.63, 128.80 (d, *J* = 13.0 Hz), 128.18 (d, *J* = 2.0 Hz), 37.02, 33.96 (d, *J* = 7.0 Hz), 23.20, 14.09, –1.15.

MS (EI): *m*/*z* (%) = 135 (67), 201 (38), 317 (3), 345 (100), 417 (8), 453 (3, [M$^+$ + 1]).

Anal. Calcd for $C_{26}H_{30}ClOPSi$: C, 68.93; H, 6.67.Found: C, 68.80; H, 6.81.

4g
Oil.

IR (film): 1437, 1246, 1189, 1112, 841 cm^{-1}.

^{1}H NMR: δ = 7.59 (m, 4 H), 7.23 (m, 2 H), 7.12 (m, 4 H), 6.94 (m, 3 H), 6.80 (m, 2 H), 2.87 (t, *J* = 7.6 Hz, 2 H), 1.18 (m, 4 H), 0.73 (t, *J* = 7.5 Hz, 3 H), 0.25 (s, 7 H), 0.12 (s, 2 H).

^{13}C NMR: δ = 184.16 (d, *J* = 2.0 Hz), 134.48, 133.45 (d, *J* = 21.6 Hz), 132.08 (d, *J* = 9.0 Hz), 131.06 (d, *J* = 3.0 Hz), 130.97 (d, *J* = 102.0 Hz), 129.16, 128.58 (d, *J* = 11.0 Hz), 127.53 (d, *J* = 12.0 Hz), 125.87, 38.23 (d, *J* = 9.0 Hz), 31.82, 23.14, 13.78, –1.32, –1.86.

MS (EI): *m*/*z* (%) = 73 (100), 201 (21), 355 (51), 512 (5, [M$^+$ + 1]).

Anal. Calcd for $C_{27}H_{33}OPSeSi$: C, 63.39; H, 6.50. Found: C, 63.29; H, 6.61.

4h
Oil.

IR (film): 1436, 1203, 1117, 835 cm^{-1}.

^{1}H NMR: δ = 7.60 (m, 4 H), 7.29 (m, 2 H), 7.15 (m, 4 H), 7.05 (m, 3 H), 6.98 (m, 2 H), 2.91 (t, *J* = 6.8 Hz, 2 H), 1.16 (m, 4 H), 0.71 (t, *J* = 6.8 Hz, 3 H), 0.17 (s, 6 H), 0.09 (s, 3 H).

^{13}C NMR: δ = 178.31 (d, *J* = 3.2 Hz), 136.82 (d, *J* = 7.0 Hz), 134.60 (d, *J* = 104.0 Hz), 131.36 (d, *J* = 8.9 Hz), 130.70 (d, *J* = 2.0 Hz), 129.23 (d, *J* = 11.0 Hz), 127.62, 127.46, 126.50 (d, *J* = 10.5 Hz), 124.21, 39.32 (d, *J* = 13.0 Hz), 34.61, 22.85, 14.02, –1.41, –2.09.

MS (EI): *m*/*z* (%) = 73 (100), 201 (24), 355 (16), 561 (2, [M$^+$ + 1]).

Anal. Calcd for $C_{27}H_{33}OPSiTe$: C, 57.89; H, 5.94. Found: C, 57.98; H, 5.80.

4i
Oil.

IR (film): 1437, 1251, 1186, 1109, 838 cm^{-1}.

^{1}H NMR: δ = 7.54 (m, 4 H), 7.23 (m, 6 H), 5.27 (m, 1 H), 4.67 (d, *J* = 10.8 Hz, 1 H), 4.56 (d, *J* = 10.8 Hz, 1 H), 2.91 (t, *J* = 7.8 Hz, 2 H), 2.35 (m, 2 H), 0.95 (m, 4 H), 0.54 (t, *J* = 7.6 Hz, 3 H), 0.13 (s, 6 H), 0.03 (s, 3 H).

^{13}C NMR: δ = 164.66 (d, *J* = 18.0 Hz), 139.89 (d, *J* = 83.2 Hz), 135.55 (d, *J* = 5.0 Hz), 135.30 (d, *J* = 96.7 Hz), 131.89 (d, *J* = 9.0 Hz), 131.11 (d, *J* = 4.0 Hz), 128.02 (d, *J* = 12.0 Hz), 117.32 (d, *J* = 9.0 Hz), 40.38 (d, *J* = 17.0 Hz), 38.82 (d, *J* = 16.8 Hz), 31.98 (d, *J* = 11.0 Hz), 22.95, 13.70, –1.23, –1.62.

MS (EI): *m*/*z* (%) = 73 (100), 201 (12), 323 (14), 397 (16, [M$^+$ + 1]).

Anal. Calcd for $C_{24}H_{33}OPSi$: C, 72.69; H, 8.39. Found: C, 72.81; H, 8.27.

4j
Oil.

IR (film): 1437, 1248, 1180, 1110, 817, 727 cm^{-1}.

^{1}H NMR: δ = 7.56 (m, 6 H), 7.37 (m, 2 H), 7.30 (m, 7 H), 5.11 (m, 1 H), 4.63 (d, *J* = 10.4 Hz, 1 H), 4.40 (d, *J* = 17.2 Hz, 1 H), 4.27 (s, 2 H), 2.83 (d, *J* = 4.4 Hz, 2 H), 2.77 (s, 3 H), 0.42 (s, 6 H).

^{13}C NMR: δ = 157.62, 145.19 (d, *J* = 80.0 Hz), 138.92, 134.40, 134.19 (d, *J* = 98.6 Hz), 133.90, 133.43, 131.95 (d, *J* = 10.0 Hz), 131.38 (d, *J* = 3.0 Hz), 128.98, 128.00 (d, *J* = 11.0 Hz), 117.44, 73.30 (d, *J* = 15.0 Hz), 57.69, 38.95 (d, *J* = 18.0 Hz), –0.81.

MS (EI): *m*/*z* (%) = 135 (100), 201 (63), 353 (89), 447 (2, [M$^+$ + 1]).

Anal. Calcd for $C_{27}H_{31}O_2PSi$: C, 72.61; H, 7.00. Found: C, 72.74; H, 6.88.

4k
Oil.

IR (film): 1437, 1256, 1196, 1112, 836 cm^{-1}.

^{1}H NMR: δ = 7.82 (m, 4 H), 7.53 (m, 6 H), 7.39 (m, 5 H), 4.23 (s, 2 H), 3.24 (s, 3 H), 0.26 (s, 9 H).

^{13}C NMR: δ = 168.26, 133.11 (d, *J* = 102.2 Hz), 131.34 (d, *J* = 4.6 Hz), 130.86, 130.47 (d, *J* = 11.2 Hz), 130.05, 129.78 (d, *J* = 12.2 Hz), 129.44 (d, *J* = 20.2 Hz), 129.09 (d, *J* = 7.6 Hz), 122.38 (d, *J* = 13.3 Hz), 70.45 (d, *J* = 11.6 Hz), 57.59, –1.09.

MS (EI): *m*/*z* (%) = 73 (31), 201 (43), 405 (100), 421 (2, [M$^+$ + 1]).

Anal. Calcd for $C_{25}H_{29}O_2PSi$: C, 71.40; H, 6.95. Found: C, 71.29; H, 7.01.

Sonogashira Cross-Coupling Reaction; (*E*)-3-Ethoxy-1-(2-phenylethynyl)-2-(trimethylsilyl)prop-1-enyl(diphenyl)phosphine Oxide (5)

A mixture of the α-iodovinylphosphine oxide **4a** (484 mg, 1 mmol), phenylacetylene (204 mg, 2 mmol, 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (70 mg, 10 mol%), CuI (20 mg, 10 mol%), and Et_3N (0.14 mL, 1 mmol, 1.0 equiv) in MeCN (5 mL) was stirred at 50 °C for about 8 h. After the completion of the reaction, the mixture was washed with NH_4Cl, and filtered through a Celite pad. The organic layer was extracted with EtOAc, and dried ($MgSO_4$). The solvent was evaporated and the residue purified by TLC or flash chromatography to afford the product **5** as a pale yellow oil; yield: 392 mg (86%).

IR (film): 2191, 1438, 1245, 1189, 1116, 845 cm^{-1}.

^{1}H NMR: δ = 7.80 (m, 4 H), 7.54 (m, 2 H), 7.45 (m, 4 H), 7.19 (m, 3 H), 6.82 (m, 2 H), 4.64 (d, *J* = 2.0 Hz, 2 H), 3.14 (q, *J* = 6.8 Hz, 2 H), 0.95 (t, *J* = 6.8 Hz, 3 H), 0.35 (s, 9 H).

^{13}C NMR: δ = 171.89, 133.83 (d, *J* = 103.0 Hz), 131.93 (d, *J* = 9.0 Hz), 131.72 (d, *J* = 2.0 Hz), 130.96 (d, *J* = 2.0 Hz), 129.00, 128.60, 128.33, 128.21, 122.65 (d, *J* = 3.0 Hz), 89.94, 89.77, 70.20 (d, *J* = 10.0 Hz), 65.63, 15.04, –0.59.

MS: *m*/*z* (%) = 73 (100), 201 (32), 257 (2), 385 (2), 429 (63), 458 (7, [M$^+$]).

Anal. Calcd for $C_{28}H_{31}O_2PSi$: C, 73.33; H, 6.81. Found: C, 73.20; H, 6.96.

Carbomethoxylation Reaction; Methyl (*E*)-2-(Diphenylphosphoryl)-4-methoxy-3-(trimethylsilyl)but-2-enoate (6)

A mixture of **4c** (470 mg, 1 mmol), $Pd(OAc)_2$ (12 mg, 5 mol%), 1,3-bis(dipheny1phosphino) propane (dppp, 21 mg, 5 mol%), Et_3N (0.28 mL, 2 mmol), methanol (2 mL), 1,2-dichloroethane (2 mL), and DMSO (5 mL) was heated at 70 °C under an atmosphere of CO for 6 h. The cooled reaction mixture was then diluted with $CHCl_3$, washed with H_2O, 10% aq HCl, 10% aq $NaHCO_3$, and brine, and dried ($MgSO_4$). The solvent was evaporated and the residue purified by TLC or flash chromatography to afford the product **6** as an oil; yield: 294 mg (73%).

IR (film): 1720, 1437, 1219, 1192, 1098, 843 cm^{-1}.

^{1}H NMR: δ = 7.74 (m, 4 H), 7.53 (m, 6 H), 4.36 (s, 2 H), 3.87 (s, 3 H), 3.18 (s, 3 H), 0.24 (s, 9 H).

^{13}C NMR: δ = 170.3, 164.67, 142.65 (d, *J* = 118.4 Hz), 131.83, 131.33 (d, *J* = 3.1 Hz), 130.15 (d, *J* = 5.7 Hz), 129.49 (d, *J* = 4.9 Hz), 68.36 (d, *J* = 11.3 Hz), 57.59, 52.23 (d, *J* = 2.6 Hz), –0.96.

MS: *m*/*z* (%) = 73 (31), 201 (32), 371 (56), 387 (100), 402 (7, [M$^+$]).

Anal. Calcd for $C_{21}H_{27}O_4PSi$: C, 62.67; H, 6.76. Found: C, 62.53; H, 6.96.

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