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Cross-Coupling and Carbonylative Cross-Coupling of Organofluorosilanes with Hypervalent Iodonium Tetrafluoroborates

Suk-Ku Kang,* Tokutaro Yamaguchi, Ryung-Kee Hong, Tae-Hyun Kim, and Sung-Jae Pyun

Department of Chemistry, Sung Kyun Kwan University,
Natural Science Campus, Suwon 440-746, Korea

Abstract: The palladium-catalyzed cross-coupling and carbonylative cross-coupling of aryl-, alkenyl-, and alkynylfluorosilanes promoted by fluoride ion with hypervalent aryl-, alkenyliodonium tetrafluoroborates were achieved at room temperature under an atmospheric pressure of carbon monoxide.

Introduction

Recently Hiyama et al.[1] reported the cross-coupling and carbonylative cross-coupling of organosilicon compounds with organic halides promoted by fluoride ion and palladium catalyst as efficient methods for carbon-carbon bond formation. Although these reactions have been successfully utilized for the synthesis of biaryls and unsymmetrical ketones, conditions require high temperature as high as 100 °C. In conection with our programs to utilize hypervalent iodine compounds for palladium-catalyzed C-C bond formation,[2] we wish to report palladium-catalyzed cross-coupling and carbonylative cross-coupling of organofluorosilanes with hypervalent iodonium salts in the presence of KF or TBAF as fluoride source under an atmospheric pressure of carbon monoxide at room temperapure (Eq.1).

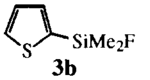
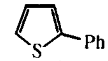
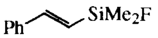
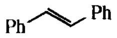
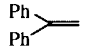
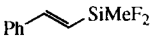
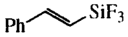
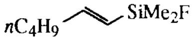
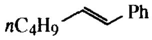
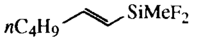
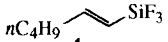
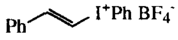
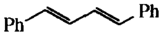
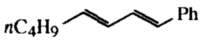
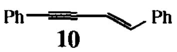
$$R^1SiF_nMe_{3-n} + R^2PhI^+\,BF_4^- \left\{ \begin{array}{l} \xrightarrow{F^-,\ \text{Pd-catalyst}} R^1\text{-}R^2 \\ \xrightarrow[\text{CO (1 atm)}]{F^-,\ \text{Pd-catalyst}} R^1COR^2 \end{array} \right. \qquad (1)$$

Results and Discussion

The results of palladium catalyzed cross-coupling and carbonylative cross-coupling of organofluorosilanes with hypervalent iodonium tetrafluoroborates are summarized in Table 1 and 2. The diphenyliodonium tetrafluoroborate (**1**)[3] was found to couple with phenyl(dimethyl)fluorosilanes (**3a**)[4] in the presence of 2.5 mol

% of $(\eta^3\text{-}C_3H_5PdCl)_2$ as a catalyst and KF (1 equiv) for activation of fluorosilanes in DMF at room temperature for 5 min as optimum conditions to afford biphenyl **6** in 80% yield (entry 1 in Table 1). Under the same conditions, 2-thienyl(dimethyl)fluorosilane (**3b**)[4] was also coupled with diphenyliodonium tetrafluoroborate (**1**) to give 2-phenylthiophene (**6b**) as the sole product (entry 2 in Table 1).

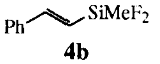
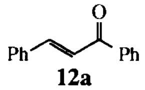
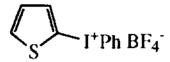
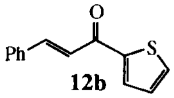
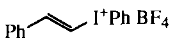
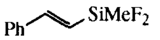
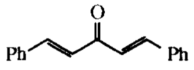
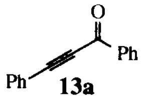
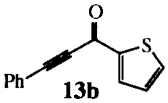
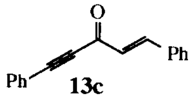
Table 1. Palladium-Catalyzed Cross-Coupling of Organosilanes with Hypervalent Iodine Compounds

Entry	Iodonium Salts	Organo-fluorosilanes	Reaction Conditions[a]	Product	Isolated Yield(%)
1	$Ph_2I^+BF_4^-$ **1**	$PhSiFMe_2$ **3a**	A	Ph−Ph **6a**	80
2	**1**	 **3b**	A	 **6b**	64
3	**1**	 **4a**	B	 +  **7a**(81%) **8**(8%)	89
4	**1**	 **4b**	B	**7a**(91%) **8**(5%)	96
5	**1**	 **4c**	B	**7a**	61
6	**1**	 **4e**	B	 **7b**	84
7	**1**	 **4f**	B	**7b**	87
8	**1**	 **4g**	B	**7b**	57
9	 **2**	**4a**	B	 **7c**	71
10	**2**	**4b**	B	**7c**	77
11	**2**	**4c**	B	**7c**	41
12	**2**	**4f**	B	 **7d**	81
13	**1**	Ph—≡—$SiMe_2F$ **5**	B	Ph—≡—Ph **9**	85
14	**2**	Ph—≡—$SiMe_2F$ **5**	B	 **10**	89

[a] A: $(\eta^3\text{-}C_3H_5PdCl)_2$(2.5 mol %), KF, DMF, rt, 5 min. B: $(\eta^3\text{-}C_3H_5PdCl)_2$(2.5 mol %), TBAF, CH_3CN, rt, 5 min.

The presence of fluorine on the silyl group is indispensable for a smooth coupling and the role of KF on silicon can be explained in terms of stabilization of an anionic silicate intermediate and acceleration of transmetallation step.[5] (*E*)-β-Dimethylfluorosilylstyrene (**4a**)[6] was allowed to react with 2.5 mol % of (η^3-$C_3H_5PdCl)_2$, TBAF (1.1 equiv) as a fluoride source in CH_3CN as solvent at room temperature for 5 min to provide *trans*-stilbene (**7a**) along with 1,1-diphenylethene (**8**) as a minor product resulting from Heck-type reaction (entry 3). (*E*)-β-Difluoromethylsilylstyrene (**4b**)[6] was treated with diphenyliodonium tetrafluoroborate (**1**) under similar conditions to afford the *trans*-stilbene (**7a**) as *ipso*-substitution product in 91% yield (entry 4). It is noteworthy that trifluorosilylstyrene (**4c**)[6] was also participated in the cross-coupling with the iodonium salt **1** to give *trans*-stilbene (**7a**) in 61% yield (entry 5). By similar conditions, (*E*)-1-monofluoro-, difluoro-, and trifluorosilylhexenes **4e-g** were successfully coupled with the iodonium salt **1** to provide the coupled product **7b**[7] in moderate yields (entries 6-8).

Table 2. Palladium-Catalyzed Carbonylative Cross-Coupling of Organofluorosilanes with Hypervalent Iodonium Compounds

Entry	Iodonium Salts	Organo-fluorosilanes	Product	Isolated Yield(%)
1	$Ph_2I^+ BF_4^-$ **1**	 **4b**	 **12a**	65
2	 **11**	 **4b**	 **12b**	78
3	 **2**	 **4b**	 **12c**	72
4	**1**	Ph—≡—$SiMe_2F$ **5**	 **13a**	81
5	**11**	Ph—≡—$SiMe_2F$ **5**	 **13b**	76
6	**2**	Ph—≡—$SiMe_2F$ **5**	 **13c**	78

[a]Reaction Conditions: (η^3-$C_3H_5PdCl)_2$(2.5 mol %), TBAF, DME, CO(1 atm), rt, 5 min.

This method was also applied to the alkenyliodonium salt **2**. When monofluorosilane **4a**[6] was reacted with β-styryl(phenyl)iodonium tetrafluoroborate (**2**) as a iodonium source, only β-styryl group was transfered and the coupled diene **7c** was obtained as the sole product in 71% yield (entry 9). As the reason of such reactivity, it is presumed that the reaction of electrophilic alkenyliodonium salt **2** with catalytic Pd(0) and the redutive elimination of iodobenzene generate an alkenyl palladium tetrafluoroborate, which will be subjected to transmetallation with organofluorosilanes.[8] Similary, for the difluorosilane **4b**[6] and trifluorosilane **4c**[6] the coupled product **7c** was afforded (entries 10 and 11). It is notable that the trifluorosilane **4c** gave the coupled product **7c** in a rather low yield. This coupling was extended to couple vinylsilane **4f** to give **7d**[9] (entry 12). Finally, the alkynylfluorodimethylsilane **5** was smoothly coupled with **1** and **2** to afforded the alkyne **9** and the ynene **10**[10] in 85 and 89% yields, respectively (entries 13 and 14).

We have extended this reaction to carbonylative cross-coupling with iodonium salts. The results of palladium catalyzed carbonylative cross-coupling of organofluorosilanes with iodonium salts are summarized in Table **2**. Although reagents of Sn,[11] B,[12] Al,[13] Hg[14] including Si[15] have been successfully utilized for palladium-catalyzed carbonylative coupling which required high temperature or high CO pressure,[16] it is still needed to carry out the reaction under mild conditions. We have found that alkenyl- and alkynylfluorosilanes activated by tetrabutylammonium fluoride were found to participate in the palladium-catalyzed carbonylative coupling with hypervalent iodonium salts under mild conditions to give unsaturated ketones and ynones. The aryliodonium salts **1** and **11** and alkenyliodonium salt **2** underwent facile carbonylative cross-coupling with β-difluoromethylsilylstyrene (**4b**) under an atmospheric pressure of carbon monoxide and at room temperature to give unsaturated ketones **12a**, **12b**,[17] and **12c**, respectively (entries 1-3). In the case of 2-thienyl(phenyl)iodonium tetrafluoroborate (**11**), 2-thienyl group was transfered (entry 2). Alternatively, for the alkynyl-(dimethyl)fluorosilane **5**,[4] the reaction with **1**, **11**, and **2** provided ynones **13a**,[18] **13b**,[19] and **13c**,[18] respectively in moderate yields (entries 4-6).

In summary, hypervalent aryl-, alkenyl-, and alkynyliodonium salts readily undergo palladium-catalyzed cross-coupling and carbonylative cross-coupling with the organofluorosilanes in the presence of fluoride ion under mild conditions at ambient temperature.

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Experimental

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and all melting points were not corrected. IR spectra were obtained on a Nicolet FT-IR 205 spectrometer. GC-MS spectra were measured on a Hewlett-Packard 5880 GC system. ^1H NMR spectra were obtained on a Bruker 400 (400 MHz) spectrometer. NMR spectra were recorded in ppm (δ) related to tetramethylsilane (δ = 0.00) as an internal standard unless stated otherwise and are reported as follows; chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration.

All reactions involving organometallic reagents were carried out in an inert atmosphere of nitrogen. DME was freshly distilled from sodium benzophenone ketyl, and DMF and CH_3CN from calcium hydride prior to use. Solvents and liquid reagents were transferred using hypodermic syringes. All other reagents and solvents used were reagent grade. Small and medium scale purifications were performed by flash chromatography.

Biphenyl (6a). Method A:

To a stirred solution of diphenyliodonium tetrafluoroborate (**1**) (1.50 g, 4.00 mmol) and (η^3-allylPdCl)$_2$ (36.6 mg, 2.5 mol %) in DMF (10 mL) was added phenyl(dimethyl)fluorosilane (0.66 g, 4.32 mmol) and KF (0.28 g, 4.85 mmol). The reaction mixture was stirred at room temperature for 5 min and extracted with ether (2 X 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, R_f = 0.50) to give **6a** (0.49 g, 80%). TLC, SiO_2, hexanes, R_f= 0.50. m.p. 68.5 - 69.5 °C (lit.[20] 69 - 72 °C). IR (KBr) 3060, 1608, 1475, 831 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35 (m, 2H), 7.45 (m, 4H), 7.61 (m, 4H). MS (EI): m/e (relative intensity) = 154 (100), 152 (29), 77 (6), 76 (18), 63 (9), 51 (8).

***trans,trans*-1, 4-Diphenyl-1, 3-butadiene (7c).** Method B:

To a stirred solution of *(E)*-β-phenylethenyl(phenyl)iodonium tetrafluoroborate (**2**) (1.58 g, 4.00 mmol) and (η^3-allylPdCl)$_2$ (36.6 mg, 2.5 mol %) in CH_3CN(10 mL) was added *(E)*-β-(methyl)difluorosilylstyrene (**4b**) (0.79 g, 4.32 mmol) and TBAF (1.26 g, 4.85 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 min and extracted with ether (2 X 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, R_f = 0.30) to give **7c** (0.65 g, 77%). TLC, SiO_2, hexanes, R_f= 0.30. m.p. 59.5 - 60.5 °C (lit.[21] 60 °C). IR (KBr) 2970, 1482, 1380, 990 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.60 (dd, 2H, *J* = 12, 2.7 Hz), 6.88 (dd, 2H, *J* = 12, 2.7 Hz), 7.17 (m, 2H), 7.27 (m, 4H), 7.37 (m, 4H). MS (EI): m/e (relative intensity) = 206 (99), 205 (34), 190 (31), 128 (41), 91 (100).

1,3-Diphenyl-2-propen-1-one (12a). Method C:

To a stirred solution of diphenyliodonium tetrafluoroborate(**1**) (1.50 g, 4.00 mmol) and (η^3-allylPdCl)$_2$(36.6 mg, 2.5 mol %) in DME (10 mL) under CO atmosphere (1atm) was added (*E*)-β-(methyl)difluorosilylstyrene (**4b**)(0.79 g, 4.32 mmol) and TBAF(1.26 g, 4.85 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 min and extracted with ether (2 X 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes = 1:10, R_f = 0.46) to give **12a** (0.54 g, 65%). TLC, SiO_2, EtOAc/hexanes = 1:10, R_f= 0.46. IR (neat) 3055, 1665, 1606 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42 (m, 3H), 7.51 (m, 2H), 7.54 (d, 1H, *J* = 16 Hz), 7.57 (m, 1H), 7.65 (m, 2H), 7.81 (d, 1H, *J* = 16 Hz), 8.02 (m, 2H). MS (EI): m/e (relative intensity) = 208 (12), 207 (100), 131 (32), 77 (60).

***trans*-Stilbene (7a).**

TLC, SiO_2, hexanes, R_f = 0.45. m.p. 121.5 - 123 °C (lit.[22] 122 - 124 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 7.21 (m, 2H), 7.34 (m, 4H), 7.48 (m, 4H). IR (KBr) 3019, 1597, 1496, 1072, 962, 909, 765, 693, 525 cm^{-1}. MS (EI): m/e (relative intensity) = 180 (88), 179 (100), 178 (72), 165 (45), 89 (32), 76 (24).

(*E*)-1-Phenylhexene (7b).[7] TLC, SiO_2, hexanes, R_f= 0.58. IR (neat) 3015, 1590, 1460, 1374cm^{-1}. ^1H NMR

($CDCl_3$, 400 MHz) δ 0.92 (t, 3H, *J* = 7.2 Hz), 1.36 (m, 4H), 1.63 (m, 2H), 6.20 (dt, 1H, *J* = 16, 6.0 Hz) 6.40 (d, 1H, *J* = 16 Hz), 7.29 (m, 5H). MS (EI): m/e (relative intensity) = 160 (60), 102 (100), 77 (53).

(*E, E*)-1-Phenyl-1, 3-octadiene (7d).[9] TLC, SiO_2, hexanes, R_f = 0.55. IR (neat) 3013, 1570, 1440 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.94 (t, 3H, *J* = 7.0 Hz), 1.38 (m, 4H), 2.10 (m, 2H), 5.82 (dt, 1H, *J* = 16, 5.8 Hz) 6.19 (dd, 1H, *J* = 16, 4.7 Hz), 6.43 (d, 1H, *J* = 15.6 Hz), 6.75 (dd, 1H, *J* = 16, 10 Hz), 7.28 (m, 5H). MS (EI): m/e (relative intensity) = 187 (26), 144 (53), 129 (100), 78 (11).

(*E*)-1, 4-Diphenyl-1-buten-3-yne (10).[10] TLC, SiO_2, hexanes, R_f = 0.45. m.p. 94 - 96 °C (lit.[9] 96 °C). IR (KBr) 3041, 3010, 1605, 1471, 843 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.40 (d, 1H, *J* = 16 Hz), 7.06 (d, 1H, *J* = 16 Hz), 7.31 ~ 7.34 (m, 6H), 7.38 (m, 2H), 7.62 (m, 2H). MS (EI): m/e (relative intensity) = 205 (78), 203 (100), 102 (28).

3-Phenyl-1-(2-thienyl)-2-propen-1-one (12b).[17] TLC, SiO_2, EtOAc/hexanes = 1:10, R_f = 0.41. IR (neat) 3055, 1653, 1600, 1266 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.19 (m, 1H), 7.42 (m, 4H), 7.67 (m, 3H), 7.87 (m, 2H). MS (EI): m/e (relative intensity) = 214 (77), 213 (100), 111 (54), 77 (36).

1,3-Diphenyl-2-propyn-1-one (13a).[18] TLC, SiO_2, EtOAc/hexanes = 1:10, R_f = 0.37. IR (neat) 3058, 1666, 1605 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.41 (m, 2H), 7.45 (m, 1H), 7.50 (m, 2H), 7.63 (m, 1H), 7.69 (m, 2H), 8.22 (m, 2H). MS (EI): m/e (relative intensity) = 206 (96), 177 (100), 128 (96), 77 (14).

3-Phenyl-1-(2-thienyl)-2-propyn-1-one (13b).[19] TLC, SiO_2, EtOAc/hexanes = 1:10, R_f = 0.35. IR (neat) 3055, 2200, 1620 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.20 (m, 1H), 7.42 (m, 2H), 7.48 (m, 1H), 7.67 (m, 2H), 7.73 (m, 1H), 8.01 (m, 1H). MS (EI): m/e (relative intensity) = 213 (11), 212 (83), 184 (100), 129 (97), 77 (11).

1, 5-Diphenyl-1-penten-4-yn-3-one (13c).[18] TLC, SiO_2, EtOAc/hexanes = 1:10, R_f = 0.38. IR (neat) 3056, 2208, 1629, 1606 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.88 (d, 1H, *J* = 16 Hz), 7.32 (m, 3H), 7.46 (m, 5H), 7.65 (m, 2H), 7.92 (d, 1H, *J* = 16Hz). MS (EI): m/e (relative intensity) = 232 (36), 231 (100), 202 (44), 129 (68), 102 (63).

References and Notes

1. Reviews: (a) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845-853. (b) Hatanaka, Y.; Hiyama, T. *Pure Appl. Chem.* **1994**, *66*, 1471-1478.
2. (a) Kang, S-K.; Jung K-Y.; Park, C-H.; Jang, S-B. *Tetrahedron Lett.* **1995**, *36*, 8047-8050. (b) Kang, S-K.; Lee, H-W.; Jang, S-B.; Kim, T-H.; Pyun, S-J. *J. Org. Chem.* **1996**, *61*, 2604-2605. (c) Kang, S-K.; Lee, H-W.; Jang, S-B.; Ho, P-S. *J. Chem. Soc. Chem. Commun.* **1996**, 835-836. (d) Kang, S-K.; Lee, H-W.;

Kim, J-S.; Choi, S-C. *Tetrahedron Lett.* **1996**, *37*, 3723-3726. (e) Kang, S-K.; Lee, H-W.; Jang, S-B.; Ho, P-S. *J. Org. Chem.* **1996**, *61*, 4720-4724.

3. (a) Ochiai, M.; Sumi, K.; Takaoka, Y.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095-4112. (b) The 2-(phenyl)thiopheneiodonium tetrafluoroborate (**11**) was prepared by adaptation of the procedure reported by M. Ochiai.
4. The compounds **3a**, **3b**, and **5** were prepared by a modified procedure reported in the literature, see, Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Tetrahedron* **1992**, *48*, 2113-2126. Preparation of 1-phenyl-2-(dimethylfluorosilyl)acetylene (**5**): To a stirred solution of phenylacetylene (15 mL, 137 mmol) in THF (100 mL) was slowly added butyllithium (2.5 M in hexanes, 60.3 mL, 150 mmol) at -78 °C. The reaction mixture was stirred at room temperature for 10 min. And dichloromethylsilane (28.2 mL, 205 mmol) was added followed by adding copper (II) fluoride trihydrate (9 g, 54.8 mmol). The solvent and other volatiles were evaporated *in vacuo*. The crude product was separated by distillation (b.p. 83-84 °C/9 mmHg) to give **5** (14.1 g, 58%).
5. (a) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490-1494. (b) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793-7794.
6. The compounds **4a**-**4g** were prepared by the hydrosilyation of the corresponding terminal acetylene compounds with appropriate chlorosilanes followed by the reaction with $CuF_2 \cdot 3H_2O$. Hydrosilylation; see, (a) Yoshida, J.; Tamao, K.; Takahashi, M.; Kumada, M. *Tetrahedron Lett.* **1978**, *25*, 2161-2164. (b) Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kumada, M. *Organometallics* **1982**, *1*, 355-368. Fluorination: Tamao, K.; Kakui, T.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983-990. Preparation of (*E*)-β-dimethylfluorosilylstyrene (**4a**): To a stirred solution of chlorodimethylsilane (12.0 g, 117 mmol) and 3 or 4 drops of hexachloroplatinic acid in THF (10 mL) was slowly added phenylacetylene (8.0 g, 78 mmol) at a rate such that a steady reflux was maintained. The reaction mixture was stirred for 4 hours and copper (II) fluoride trihydrate (7.28 g, 46.8 mmol) was added *in situ*. The solvent and other volatiles were evaporated *in vacuo*. The crude product was separated by distillation (b.p. 60-64 °C/0.7 mmHg) to give **4a** (8.43 g, 60%).
7. Marumoto, S.; Kuwajima, I. *Chem. Lett.* **1992**, 1421-1424.
8. (a) Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315-6317. (b) Hinkle, R. J.; Poulter, G. T.; Stang, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 11626-11627. (c) Moriarty, R. M.; Epa, W. R. *Tetrahedron Lett.* **1992**, *33*, 4095-4098.
9. Kim, J-I.; Lee, J.T.; Yeo, K-D. *Bull. Korean Chem. Soc.* **1985**, *6*, 366-369.
10. Thomas S.; Ariel H.; Moris S. E. *J. Am. Chem. Soc.* **1995**, *117*, 6364-6365.
11. (a) Sheffy, F. K.; Godschlax, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833-4840. (b) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417-6422. (c) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1557-1565. (d) Tanaka, M. *Tetrahedron Lett.* **1979**, 2601-2602. (e) Tanaka, M. *Synthesis* **1981**, 47-48. (f) Kikukawa, K.; Idemoto, T.; Katayama, A.; Kondo, K.; Wada, F.; Matsuda, T. *J. Chem. Soc., Perkin Trans. I.* **1987**, 1511-1514.
12. (a) Wakita, Y.; Yasanaga, T.; Akita, M.; Kojima, M. *J. Organomet. Chem.* **1986**, *301*, C17-C20. (b)

Miyaura, N.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1999-2001. (c) Ishiyama, T.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1991**, *32*, 6923-6926. (d) Ishiyama, T.; Kizaki, H.; Miyaura, N.; Suzuki, A. *Tertahedron Lett.* **1993**, *34*, 7595-7598. (e) Ishiyama, T.; Murata, M.; Suzuki, A.; Miyaura, N. *J. Chem. Soc. Chem. Commun.* **1995**, 295-296. (f) Kondo, T.; Tsuji, Y.; Watanabe, Y. *J. Organomet. Chem.* **1988**, *45*, 397-403.

13. (a) Bumagin, N. A.; Ponomaryov, A. B.; Beletskaya, I. P. *Tetrahedron Lett.* **1985**, *26*, 4819-4822. (b) Wakita, Y.; Yasunaga, T.; Kojima, M. *J. Organomet. Chem.* **1985**, *288*, 261-268.
14. Larock, R. C.; Hershberger, S. S. *J. Org. Chem.* **1980**, *45*, 3840-3846.
15. (a) Hatanaka, Y.; Hiyama, T. *Chem. Lett.* **1989**, 2049-2052. (b) Y. Hatanaka, S. Fukusuima, and T. Hiyama, *Chem. Lett.* **1989**, 1971-1974 . (c) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Tetrahedron* **1992**, *48*, 2113-2126.
16. (a) Colguboun, H. M.; Thompson, D. J.; Tiwgg, M. V. *Carbonylation: Direct Synthesis Of Carbonyl Compounds;* Plenum Press: New York, 1991. (b) Tsuji, J. *Palladium Reagents and Catalysts; Innovations in Organic Synthesis* John wiley & Sons Ed: Chichester 1995.
17. Goto, Y.; Hayashi, A.; Kimura, Y.; Nakayama, M.; *J. Cryst. Growth.* **1991**, *108*, 688-698. [*Chem. Abstr. 114*, **1991**, 217435c]
18. Okuro, K.; Furuune, M.; Enna, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *585*, 4716-4721.
19. Elokhina, V. N.; Nakhmanovich, A. S.; Bannikova, O. B.; *Izv. Akad. Nauk. SSSR. Ser. Khim.* **1990**, 2637-2640. [*Chem. Abstr. 114*, **1991**, 122282m]
20. "The Merck Index 11th Edition, M. Windholz, Ed., Merck & Co. Inc., Rahway, N.J., 1989, p 3314, and references cited therein.
21. "The Merck Index 11th Edition, M. Windholz, Ed., Merck & Co. Inc., Rahway, N.J., 1989, p 3320, and references cited therein.
22. "The Merck Index 11th Edition, M. Windholz, Ed., Merck & Co. Inc., Rahway, N.J., 1989, p 8774, and references cited therein.

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