 Bull. Chem. Soc. Jpn., 75, 2497–2502 (2002)

Palladium-Catalyzed Carbonylative Coupling of Tributyl(1-fluorovinyl)stannane with Aryl Halides and Aryl Triflates

Takeshi Hanamoto,* Kumiko Handa, and Tomonori Mido

Department of Chemistry and Applied Chemistry, Saga University, Honjyo-machi 1, Saga 840-8502

(Received May 14, 2002)

We have found that tributyl(1-fluorovinyl)stannane (**2**) could be readily prepared from the reaction of (1-fluorovinyl)methyldiphenylsilane[1] (**1**) and bis(tributyltin) oxide in the presence of a catalytic amount of CsF in DMF in good yields. The palladium-catalyzed carbonylative cross-coupling reaction of **2** with aryl iodides bearing various functional groups smoothly proceeded giving the corresponding aryl 1-fluorovinyl ketones in good yields under an atmospheric pressure of carbon monoxide. A similar carbonylative cross-coupling reaction of **2** with aryl triflates was also accomplished in the presence of tetrabutylammonium iodide (Bu_4NI) as an additive.

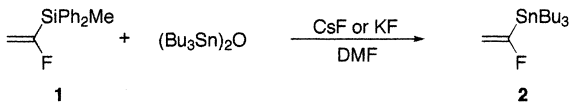
α,β-Unsaturated ketones are widely employed as dienophiles in the Diels–Alder reaction or as Michael acceptors in organic synthesis. The corresponding fluorinated α,β-unsaturated ketones are also considered to be promising reagents for the preparation of complex fluorinated compounds.[2] However, the use of α-fluorinated α,β-unsaturated ketones seems to be limited. One of the reasons is considered to be the difficulty of their general preparation.[3] Recently, we reported the efficient cross-coupling reaction of **1** with aryl iodides.[4] As a part of these investigations, we became interested in the carbonylative cross-coupling reaction.[5] Although the carbonylative cross-coupling reaction proceeded giving the desired products, the reaction was sluggish and the yield was not satisfactory.[6] We then focused on the reactivity of **2** for the carbonylative cross-coupling reaction.[7] While the same ketones can be prepared by the palladium-catalyzed reaction of acid chlorides, the utility of this route should be limited by the availability of the corresponding carboxylic acids. In this article, we report the preparation of aryl 1-fluorovinyl ketones via the Pd-catalyzed carbonylative coupling of **2** with aryl iodides and aryl triflates under an atmospheric pressure of carbon monoxide.[8]

Results and Discussion

Preparation of Tributyl(1-fluorovinyl)stannane. Although **2** is a known compound, we did not find the literature procedure easy to replicate.[3a] Therefore, prior to the examination of the carbonylative coupling, we needed a convenient method for the synthesis of **2**.[8a,9] Burton and co-workers have already found the direct transformation of several fluorinated vinyl silanes to the corresponding stannanes.[10] This prompted us to apply their method to the preparation of **2**. According to their method, we first examined the reaction of **1** and tributyltin chloride under various conditions, however, no target stannane was produced. Ultimately, we obtained **2** by the reaction of **1** with *bis(tributyltin) oxide* in the presence of a catalytic amount of CsF in DMF at room temperature in 76% yield (Table 1, entry 3). Ultrasonic irradiation dramatically accelerated the reaction rate (entries 3, 4, and 5), and the reaction was completed within 10 min. Although spray-dried KF as a fluoride source is also effective for the reaction, it requires a higher reaction temperature and longer reaction time (entries 1 and 2).

Carbonylative Coupling of 2 with Aryl Iodides. We

Table 1. Preparation of Tributyl(1-fluorovinyl)stannane

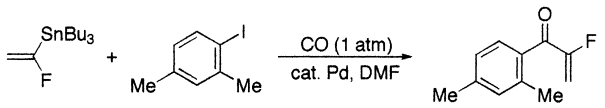


1 **2**

Entry	$(Bu_3Sn)_2O$	MF	Temp	u.s.	Time	Yield
	equiv	0.1 equiv	°C	min[a)]	h	%[b)]
1	0.6	KF	100	10	3.5	70
2	0.6	KF	80	10	7.5	71
3	0.6	CsF	rt	10	0	76
4	0.6	CsF	rt	0	1	71
5	0.5	CsF	rt	10	0	69
6	1.0	CsF	rt	10	72	68

a) Ultrasound. b) Isolated yield.

Table 2. Reaction of **2** with 1-Iodo-2,4-dimethylbenzene under Various Conditions



2 **3a**

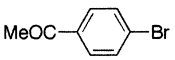
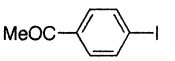
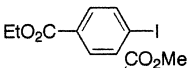
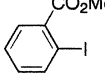
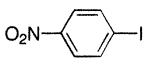
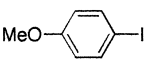
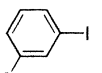
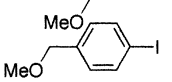
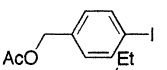
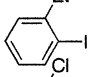
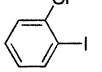
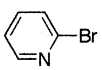
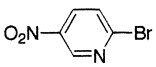
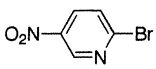
Entry	Pd (2.5 mol%)	Temp/°C	Time/h	Yield/%[a]
1	$Pd[PPh_3]_4$	50	72	trace
2	$Pd[PPh_3]_4$	80	2	99
3	$Pd[PPh_3]_4$	100	3	85
4	$PdCl_2[PPh_3]_2$	80	3.5	93
5	$Pd(OAc)_2$	80	72	71

a) Isolated yield.

first examined the reaction of **2** and 1-iodo-2,4-dimethylbenzene under an atmospheric pressure of carbon monoxide in DMF to establish the optimum conditions. These results are shown in Table 2. Under the optimum conditions (entry 2), the reaction cleanly proceeded giving the corresponding aryl 1-fluorovinyl ketone (**3a**) in quantitative yield. The forced conditions resulted in the decreased yield to some extent (entry 3). The catalytic activity of several palladium complexes roughly decreased in the order $Pd[PPh_3]_4 > PdCl_2[PPh_3]_2 >> Pd(OAc)_2$ (entries 2, 4, and 5). These carbonylative coupling reactions required the temperature of 80 °C, and no reaction took place at 50 °C (entries 1 and 2).

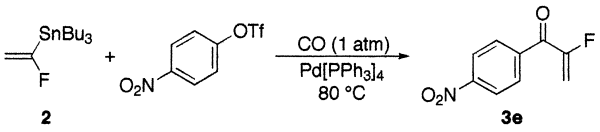
Representative results of the carbonylative cross-coupling reaction of the 2-, 3-, and 4-substituted aryl halides are depicted in Table 3. As expected, the reaction is quite general for the

Table 3. Carbonylative Cross-Coupling Reaction of **2** with Various Aryl Halides[a]

Entry	Ar-X	Temp / °C	Time / h	Product	Yield[b] / %
1		100	24	**3b**	23
2		80	2	**3b**	81
3		80	2.5	**3c**	72
4		80	3	**3d**	86
5		80	3	**3e**	64
6		80	2.5	**3f**	86
7		100	3	**3g**	71
8		100	0.5	**3h**	86
9		100	0.5	**3i**	77
10		80	2	**3j**	99
11		80	3.5	**3k**	72
12		120	70	—	0[c]
13		80	18	**4a**	0[d,e]
14[f]		80	14	**4a**	0[d,g]

a) Unless otherwise noted, the reactions were carried out under the following conditions: tributyl(1-fluorovinyl)stannane (1.2 equiv) with aryl halides (1.0 equiv) in the presence of $Pd[PPh_3]_4$ (2.5 mol%) in DMF. b) Isolated yield. c) No reaction. d) No CO insertion reaction occurred. Instead, the corresponding cross-coupling product was obtained (see text). e) 66% yield. f) Tributyl(1-fluorovinyl)stannane (1.0 equiv) with aryl halides (1.2 equiv) in the presence of $Pd[PPh_3]_4$ (2.5 mol%) in DMI. g) 78% yield.

Table 4. Reaction of **2** with 4-Nitrophenyl Triflate under Various Conditions



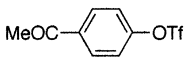
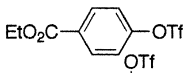
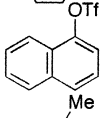
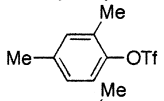
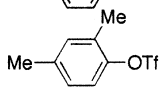
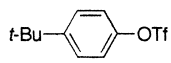
Entry	Additive/equiv	Solvent	Time/h	Yield/%[a]
1	None	DMF	3.5	0
2	LiCl (3.0)	DMF	3	trace
3	LiCl (3.0)	NMP[b]	1	0
4	Bu_4NI (1.2)	DMF	5	57
5	Bu_4NI (2.5)	DMF	5	75

a) Isolated yield. b) 1-Methyl-2-pyrrolidone.

substrate bearing not only an electron-withdrawing group (ketone, ester, nitro, and halogen) but also an electron-donating one (alkyl and ether) on the aromatic ring. The functional group compatibility of this process as illustrated in these examples is noteworthy. Even the aryl bromide could be employed; however, it was less effective compared to the corresponding aryl iodide (entries 1 and 2). The heteroaromatic bromide did not afford the corresponding ketone under the forced reaction conditions along with the decomposition of **2** (entry 12). Interestingly, when we employed another heteroaromatic bromide bearing an electron-withdrawing group as the reaction partner, no carbonylation occurred and the simple cross-coupling product was obtained in good yields (entries 13 and 14).

Carbonylative Coupling of 2 with Aryl Triflates. In light of the above successful carbonylative reaction using aryl halides, we envisaged that the carbonylative coupling with an aryl triflate would also be accessible. Since aryl triflates are readily accessible from the corresponding phenols, the reaction using triflates would expand the scope of our reaction.[11] The reaction was first examined using 4-nitrophenyl triflate under conditions similar to those employed for the carbonylative coupling of aryl halides. However, the treatment of **2** with the triflate in the presence of 2.5 mol% of $Pd[PPh_3]_4$ in DMF resulted in no reaction along with the recovery of **2** and the triflate (Table 4, entry 1). The addition of an inorganic salt like lithium chloride was less effective for the carbonylative coupling reaction (entries 2 and 3).[12] However, the addition of tetrabutylammonium iodide (Bu_4NI) was very effective for the reaction, and the reaction in the presence of 2.5 molar amounts of Bu_4NI to the triflate proceeded smoothly to afford the corresponding aryl 1-fluorovinyl ketone in good yield.[12d] Although we have no evidence about the real role of Bu_4NI, we confirmed that no transformation of the triflate into the corresponding aryl iodide occurred during the reaction on the basis of GC-MS analysis. The added Bu_4NI should be essential in order to assure the formation of the reactive aryliodopalladium(II) species. Representative results of the carbonylative cross-coupling reaction of a variety of aryl triflates in the presence of Bu_4NI are shown in Table 5. When we compared it with the reactions with aryl iodides, we found that the carbonylative coupling reaction with the triflate has the following features; (1) The addition of Bu_4NI is essential for a successful reaction. (2) An electron-donating group on the aromatic ring retarded the reaction. In order to overcome the second limitation, we employed the catalyst system containing the combination of $Pd[dba]_2$ and $AsPh_3$ as a more reactive catalyst system[13] instead of $Pd[PPh_3]_4$; however, no carbonylative product was observed, while **2** and the triflate were recovered.

Table 5. Carbonylative Cross-Coupling Reaction of **2** with Vrious Aryl Triflates[a]

Entry	Ar-OTf	Time/h	Product	Yield/%[b]
1		5	**3b**	75
2		2.5	**3c**	81
3		4	**3m**	88
4		96	—	0
5[c]		72	—	0
6		96	—	trace

a) Unless otherwise noted, the reactions were carried out under the following conditions: tributyl(1-fluorovinyl)stannane (1.2 equiv) with aryl triflates (1.0 equiv) in the presence of $Pd[PPh_3]_4$ (2.5 mol%) and $^nBu_4NI$ (2.5 equiv) in DMF at 80 °C. b) Isolated yield. c) $Pd[dba]_2$ + $AsPh_3$ was used instead of $Pd[PPh_3]_4$.

Conclusion

We have demonstrated the synthetic utility of **2**. This compound is easily prepared from **1** with bis(tributyltin) oxide in one step. The carbonylative coupling reaction of **2** with various aryl halides worked well to give the corresponding aryl 1-fluorovinyl ketones in good yields. The generality of the reaction was shown to be high with regard to the aryl iodide functionality and the substituted pattern. Although the carbonylative coupling with aryl triflates proceeded in the presence of Bu_4NI, these reactions require electron-withdrawing groups on the aromatic rings. Further studies on its synthetic utility are now in progress in our laboratory.

Experimental

General. Melting points were measured with a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Infrared (IR) spectra were recorded on a Perkin Elmer SPECTRUM 2000. ^1H NMR and ^{19}F NMR spectra were measured on a JEOL JNM-AL300. Chemical shifts were given by δ relative to that of an internal Me_4Si (TMS) for ^1H NMR spectra and benzylidyne trifluoride ($CF_3C_6H_5$) for ^{19}F NMR spectra. GC-MS spectra were obtained with a JEOL JMS-AMII15. HRMS spectra were obtained with a JEOL JMS-HX100A at the institute for fundamental research of organic chemistry (IFOC), Kyushu University. Elemental analyses were accomplished at the service center for the

elementary analysis of organic compounds, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on a silica gel plate (Merck , Kieselgel 60 F254, 20 × 20 cm, 0.25 mm). DMF, DMI, and NMP were used as a reaction solvent after distillation from CaH_2.

Tributyl(1-fluorovinyl)stannane (2). To a solution of **1**[14] (844.5 mg, 3.48 mmol) in DMF (15 mL) were added bis(tributyltin) oxide (1.1 mL, 2.16 mmol) and a catalytic amount of CsF (53.0 mg 0.35 mmol) at room temperature under a flow of argon. The whole mixture was irradiated with ultrasonic waves for 10 min. The resulting mixture was quenched with water, extracted with hexane–ether (3:1), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (hexane as an eluent) to give the desired product **2** as a colorless oil (889.5 mg, 76%): IR (neat) 2959, 2929, 2873, 2855, 1608, 1465, 1129, 904, and 856 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (9H, t, J = 7.3 Hz), 0.97–1.05 (6H, m), 1.25–1.40 (6H, m), 1.50–1.65 (6H, m), 4.55 (1H, m, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}F}$ = 67.7 Hz, $J_{H\text{-}Sn}$ = 15.0 Hz), 5.31 (1H, m, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}F}$ = 38.4 Hz, $J_{H\text{-}Sn}$ = 66.8, 71.0 Hz); ^{19}F NMR($CDCl_3$, 283 MHz) δ −86.15 (m, dd (84%), J = 38.3, 67.6 Hz, $J_{F\text{-}^{117}Sn}$ = 228 (7.6%), $J_{F\text{-}^{119}Sn}$ = 234 (8.6%) Hz); GC MS *m/z* 279 (4.9), 277 (3.9), 177 (100); Anal. Calcd for $C_{14}H_{29}FSn$: C, 50.18; H, 8.72%. Found: C, 50.29; H, 8.70%.

Palladium-Catalyzed Carbonylative Coupling Reaction: General Procedure (Table 2 and 3). 1-(2,4-Dimethylphenyl)-2-fluoro-2-propen-1-one (3a) (Table 2, Entry 2). To a solution of **2** (46.2 mg, 0.138 mmol) in DMF (3 mL) were added 1-iodo-2,4-dimethylbenzene (16 μL, 0.112 mmol) and a catalytic amount of $Pd[PPh_3]_4$ (4.5 mg, 2.5 mol%). After argon was replaced with carbon monoxide (balloon), the mixture was heated at 80 °C for 2 h. After the usual workup, column chromatography (silica gel, hexane–ether = 20:1) of the residue afforded 19.7 mg of 1-(2,4-dimethylphenyl)-2-fluoro-2-propen-1-one (**3a**) as a colorless oil (99% yield).

1-(2,4-Dimethylphenyl)-2-fluoro-2-propen-1-one (3a). A colorless oil; yield 99%; IR (neat) 2926, 1678, 1613, 1450, 1370, 1324, 1203, 1131, 970, 907, 827, and 778 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.37 (3H, s), 2.38 (3H, s), 5.39 (1H, dd, J = 44.4, 3.4 Hz), 5.53 (1H, dd, J = 14.2, 3.4 Hz), 7.05 (1H, d, J = 7.8 Hz), 7.09 (1H, s), 7.35 (1H, d, J = 7.8 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −114.03 (1F, ddd, J = 44.3, 13.8, 1.1 Hz); GC MS *m/z* 179 (9, M^+ + 1), 178 (86, M^+), 177 (43), 133 (74), 129 (41), 115 (29), 105 (100), 103 (36), 79 (48), 78 (25), 77 (74), 51 (25); Anal. Calcd for $C_{11}H_{11}FO$: C, 74.14; H, 6.22%. Found: C, 74.06; H, 6.18%.

1-(4-Acetylphenyl)-2-fluoro-2-propen-1-one (3b). A pale yellow oil; yield 81%; IR (neat) 3051, 2926, 1689, 1683, 1641, 1565, 1501, 1427, 1407, 1359, 1285, 1199, 1150, 1076, 1018, 989, 959, 936, 854, 774, 713, and 687 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.66 (3H, s), 5.55 (1H, dd, J = 15.8, 3.7 Hz), 5.64 (1H, dd, J = 43.9, 3.5 Hz), 7.94 (2H, dm, J = 8.3 Hz), 8.05 (2H, dm, J = 8.3 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −112.76 (1F, ddm, J = 43.8, 16.3 Hz); GC MS *m/z* 193 (9, M^+ + 1), 192 (4, M^+), 177 (100), 147 (10), 101 (48), 91 (11), 76 (16), 75 (11); HRMS *m/z* calcd for $C_{11}H_9FO_2$ (M): 192.0587, found: M^+, 192.0575. Further purification for elementary analysis resulted in the decomposition of the product.

1-(4-Ethoxycarbonylphenyl)-2-fluoro-2-propen-1-one (3c). A colorless oil; yield 72%; IR (neat) 3051, 2926, 1689, 1683, 1641, 1565, 1501, 1427, 1407, 1359, 1285, 1199, 1150, 1076, 1018, 989, 959, 936, 854, 774, 713, and 687 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.42 (3H, t, J = 7.2 Hz), 4.42 (2H, q, J = 7.2 Hz), 5.55 (1H, dd, J = 17.1, 3.7 Hz), 5.61 (1H, dd, J = 42.6, 3.5 Hz), 7.91 (2H, dm, J = 8.3 Hz), 8.15 (2H, dm, J = 8.3 Hz); ^{19}F NMR($CDCl_3$, 283 MHz) δ −112.71 (1F, ddm, J = 42.8, 16.5 Hz); GC MS *m/z* 222 (3, M^+), 177 (100), 176 (23), 149 (43), 101 (33), 76 (26); HRMS *m/z* calcd for $C_{12}H_{11}FO_3$ (M): 222.0692, found: M^+, 222.0658. Further purification for elementary analysis resulted in the decomposition of the product.

2-Fluoro-1-(2-methoxycarbonylphenyl)-2-propen-1-one (3d). A colorless oil; yield 86%; IR (neat) 2956, 2361, 1722, 1694, 1645, 1598, 1577, 1488, 1437, 1365, 1288, 1198, 1139, 1089, 1043, 988, 971, 937, 830, 761, 729, 701, and 670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.88 (3H, s), 5.29 (1H, dd, J = 43.7, 3.7 Hz), 5.36 (1H, dd, J = 13.9, 3.7 Hz), 7.42 (1H, dd, J = 7.3, 1.5 Hz), 7.58 (1H, dt, J = 1.5, 7.3 Hz), 7.65 (1H, dt, J = 1.5, 7.3 Hz), 8.03 (1H, dd, J = 7.3, 1.5 Hz); ^{19}F NMR($CDCl_3$, 283 MHz) δ −115.96 (1F, ddm, J = 43.6, 14.2 Hz); GC MS *m/z* 208 (1, M^+), 177 (24), 163 (100), 162 (22), 151 (37), 104 (26), 101 (29), 92 (29), 77 (64), 76 (39), 75 (27), 50 (35); HRMS *m/z* calcd for $C_{11}H_9FO_3$ (M): 208.0536, found: M^+, 208.0544. Further purification for elementary analysis resulted in the decomposition of the product.

2-Fluoro-1-(4-nitrophenyl)-2-propen-1-one (3e). A white solid; yield 64%; mp 45.8–46.4 °C; IR (KBr) 3110, 3055, 2924, 1844, 1682, 1602, 1532, 1409, 1352, 1296, 1195, 1114, 1012, 976, 935, 868, 853, 789, 750, 723, 684, and 668 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.58 (1H, dd, J = 13.2, 3.7 Hz), 5.68 (1H, dd, J = 43.1, 3.7 Hz), 8.02 (2H, dt, J = 7.0, 2.0 Hz), 8.34 (2H, dt, J = 9.2, 2.0 Hz); ^{19}F NMR($CDCl_3$, 283 MHz) δ −112.91 (1F, dd, J = 44.6, 1.5 Hz); GC MS *m/z* 195 (1, M^+), 150 (100), 149 (44), 104 (68), 101 (43), 92 (52), 76 (64), 75 (45), 74 (22), 73 (31), 50 (47); Anal. Calcd for $C_9H_6FNO_3$: C, 56.39; H, 3.10; N, 7.18%. Found: C, 56.44; H, 3.44; N, 6.99%.

2-Fluoro-1-(4-methoxyphenyl)-2-propen-1-one (3f). A colorless oil; yield 86%; IR (neat) 2937, 2843, 1667, 1629, 1602, 1572, 1510, 1463, 1423, 1361, 1313, 1287, 1263, 1206, 1170, 1115, 1030, 986, 968, 934, 846, and 776 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.89 (3H, s), 5.41 (1H, dd, J = 15.4, 2.8 Hz), 5.54 (1H, dd, J = 45.9, 2.8 Hz), 6.96 (2H, dm, J = 8.6 Hz), 7.92 (2H, dm, J = 8.3 Hz); ^{19}F NMR($CDCl_3$, 283 MHz) δ −110.76 (1F, ddm, J = 45.8, 15.5 Hz); GC MS *m/z* 181 (2, M^+ + 1), 180 (31, M^+), 135 (100), 134 (17), 107 (17), 92 (32), 77 (40), 64 (13), 63 (12); HRMS *m/z* calcd for $C_{10}H_9FO_2$ (M): 180.0587, found: M^+, 180.0584. Further purification for elementary analysis resulted in the decomposition of the product.

2-Fluoro-1-(3-methoxyphenyl)-2-propen-1-one (3g). A colorless oil; yield 71%; IR (neat) 2940, 2839, 1675, 1636, 1598, 1582, 1487, 1465, 1431, 1363, 1327, 1290, 1254, 1192, 1168, 1047, 1008, 996, 939, 897, 832, 802, 763, and 687 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.86 (3H, s), 5.51 (1H, dd, J = 16.0, 3.3 Hz), 5.57 (1H, dd, J = 44.4, 3.3 Hz), 7.14 (1H, ddd, J = 8.1, 2.8, 1.1 Hz), 7.36–7.47 (3H, m); ^{19}F NMR($CDCl_3$, 283 MHz) δ −112.10 (1F, ddm, J = 44.2, 15.8 Hz); GC MS *m/z* 181 (3, M^+ + 1), 180 (58, M^+), 152 (25), 137 (38), 135 (85), 107 (91), 92 (65), 77 (100), 64 (31); HRMS *m/z* calcd for $C_{10}H_9FO_2$ (M): 180.0587, found: M^+, 180.0586. Further purification for elementary analysis resulted in the decomposition of the product.

2-Fluoro-1-(4-methoxymethylphenyl)-2-propen-1-one (3h). A colorless oil; yield 86%; IR (neat) 2929, 2360, 1672, 1635, 1610, 1415, 1375, 1284, 1198, 1105, 969, 936, 849, and 767 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.43 (3H, s), 4.53 (2H, s), 5.47 (1H, dd, J = 6.4, 3.1 Hz), 5.57 (1H, dd, J = 36.3, 3.3 Hz), 7.44 (2H, d, J = 7.9 Hz), 7.86 (2H, d, J = 7.7 Hz); ^{19}F NMR

($CDCl_3$, 283 MHz) δ −112.01 (1F, ddt, J = 45.1, 15.7, 1.5 Hz); GC MS m/z 194 (24, M^+), 149 (24), 134 (37), 133 (33), 121 (43), 91 (32), 90 (35), 89 (100), 77 (29), 73 (33); HRMS m/z calcd for $C_{11}H_{11}FO_2$ (M): 194.0743, found: M^+, 194.0777. Further purification for elementary analysis resulted in the decomposition of the product.

2-Fluoro-1-(4-acethoxymethylphenyl)-2-propen-1-one (3i). A colorless oil; yield 77%; IR (neat) 2938, 1745, 1675, 1635, 1611, 1417, 1380, 1321, 1284, 1229, 1200, 1179, 1045, 988, 970, 936, 845, and 769 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.14 (3H, s), 5.18 (2H, s), 5.50 (1H, dd, J = 15.6, 3.4 Hz), 5.58 (1H, dd, J = 44.4, 3.4 Hz), 7.46 (2H, d, J = 7.8 Hz), 7.88 (2H, d, J = 7.9 Hz); ^{19}F NMR($CDCl_3$, 283 MHz) δ −112.17 (1F, ddt, J = 44.8, 15.3, 1.6 Hz); GC MS m/z 222 (5, M^+), 180 (59), 135 (22), 133 (34), 107 (100), 90 (29), 89 (71), 73 (30); HRMS m/z calcd for $C_{12}H_{11}FO_3$ (M): 222.0692, found: M^+, 222.0698. Further purification for elementary analysis resulted in the decomposition of the product.

1-(2-Ethylphenyl)-2-fluoro-2-propen-1-one (3j). A colorless oil; yield 99%; IR (neat) 2938, 1745, 1675, 1635, 1611, 1417, 1380, 1321, 1284, 1229, 1200, 1179, 1045, 988, 970, 936, 845, and 769 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21 (3H, t, J = 7.3 Hz), 2.71 (2H, q, J = 7.3 Hz), 5.37 (1H, dd, J = 44.0, 3.4 Hz), 5.58 (1H, dd, J = 13.7, 3.4 Hz), 7.21–7.46 (4H, m); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −114.97 (1F, ddm, J = 44.0, 13.6 Hz); GC MS m/z 178 (13, M^+), 163 (44), 143 (24), 133 (33), 132 (33), 131 (22), 129 (26), 115 (100), 105 (22), 103 (25), 79 (20), 77 (38), 51 (16); HRMS m/z calcd for $C_{11}H_{11}FO$ (M): 178.0794, found: M^+, 178.0829. Further purification for elementary analysis resulted in the decomposition of the product.

1-(2-Chlorophenyl)-2-fluoro-2-propen-1-one (3k). A colorless oil; yield 72%; IR (neat) 2361, 1698, 1642, 1592, 1435, 1300, 1202, 1065, 969, 937, and 747 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.43 (1H, dd, J = 43.0, 3.4 Hz), 5.59 (1H, dd, J = 13.2, 3.4 Hz), 7.34–7.46 (4H, m); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −116.72 (1F, ddm, J = 42.9, 13.1 Hz); GC MS m/z 184 (9, M^+), 183 (26), 141 (22), 139 (79), 138 (100), 111 (41), 75 (47), 74 (23); HRMS m/z calcd for C_9H_6ClFO (M): 184.0091, found: M^+, 184.0056. Further purification for elementary analysis resulted in the decomposition of the product.

2-(1-Fluorovinyl)-5-nitropyridine (4a). A white solid; yield 78%; mp 68.3–69.8 °C; IR (KBr) 3141, 1652, 1593, 1525, 1475, 1349, 1276, 1132, 1105, 1018, 926, 899, 859, 780, 767, and 718 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.25 (1H, dd, J = 16.0, 3.1 Hz), 5.98 (1H, dd, J = 48.1, 3.1 Hz), 7.73 (1H, d, J = 8.6 Hz), 8.55 (1H, dd, J = 8.6, 2.4 Hz), 9.40 (1H, d, J = 1.7 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −117.24 (1F, ddd, J = 48.3, 15.9, 1.1 Hz); GC MS m/z 169 (7, M^+ + 1), 168 (100, M^+), 167 (20), 122 (55), 102 (25), 95 (76), 75 (69), 51 (26), 50 (20); Anal. Calcd for $C_7H_5FN_2O_2$: C, 50.01; H, 3.00; N, 16.66%. Found: C, 50.09; H, 3.01, N, 16.63%.

Palladium-Catalyzed Carbonylative Coupling Reaction: General Procedure (Table 4 and 5). 2-Fluoro-1-(1-naphthyl)-2-propen-1-one (3m) (Table 5, Entry 3). To a solution of **2** (92.7 mg, 0.28 mmol) in DMF (3.5 mL) were added 1-naphthyl triflate (56.6 mg, 0.21 mmol), Bu_4NI (189.0 mg, 0.51 mmol), and a catalytic amount of $Pd[PPh_3]_4$ (4.9 mg, 2.5 mol%). After argon was replaced with carbon monoxide (balloon), the mixture was heated at 80 °C for 4 h. After the usual workup, column chromatography (silica gel, hexane–ether = 20:1) of the residue afforded 35.9 mg of 2-fluoro-1-(1-naphthyl)-2-propen-1-one (**3m**) as a colorless oil (88% yield).

2-Fluoro-1-(1-naphthyl)-2-propen-1-one (3m). IR (neat) 1673, 1636, 1509, 1371, 1318, 1289, 1226, 1172, 1087, 1063, 931, 803, and 780 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.48 (1H, dd, J = 44.0, 3.5 Hz), 5.63 (1H, dd, J = 13.9, 3.5 Hz), 7.49–7.62 (3H, m), 7.72 (1H, d, J =7.2 Hz), 7.85–7.94 (1H, m), 8.02 (1H, d, J = 8.3 Hz), 8.12–8.20 (1H, m); ^{19}F NMR($CDCl_3$, 283 MHz) δ −113.98 (1F, dd, J = 43.6, 13.8 Hz); GC MS m/z 201 (0.9, M^+ + 1), 200 (50, M^+), 199 (39), 171 (24), 155 (34), 127 (100), 126 (27); HRMS m/z calcd for $C_{13}H_9FO$ (M): 200.0637, found: M^+, 200.0643. Further purification for elementary analysis resulted in the decomposition of the product.

We thank Chemetall Japan Co., Ltd. for a gift of CsF, F-Tech Co., Ltd for a gift of 1,1-difluoroethylene for the preparation of **1** and Kawaken Fine Chemicals Co., Ltd for a gift of DMI.

References

1 We are sorry for the incorrect name of this silane in our previous paper.[4,14]

2 M. Hudlicky and A. E. Pavlath, "Chemistry of Organic Fluorine Compounds II," ACS Monograph 187, Washington, DC (1995).

3 a) D. P. Matthews, P. P. Waid, J. S. Sabol, and J. R. McCarthy, *Tetrahedron Lett.*, **35**, 5177 (1994). b) T. Satoh, N. Itoh, K. Onda, Y. Kitoh, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **65**, 2800 (1992). c) Y. Bessiere, N. H. S. Dang, and M. Schlosser, *Helv. Chim. Acta*, **60**, 1739 (1977).

4 T. Hanamoto, T. Kobayashi, and M. Kondo, *Synlett*, **2001**, 281.

5 W. F. Goure, M. E. Wright, P. D. Davis, S. S. Labadie, and J. K. Stille, *J. Am. Chem. Soc.*, **106**, 6417 (1984).

6 We obtained the corresponding carbonlylative product, 1-(4-acetylphenyl)-2-fluoro-2-propen-1-one, in 11% yield by the reaction of **1** with 4′-iodoacetophenone under carbon monoxide at atmospheric pressure.

7 a) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986). b) J. K. Stille, *Pure Appl. Chem.*, **57**, 1771 (1985). c) T. G. Crisp, W. J. Scott, and J. K. Stille, *J. Am. Chem. Soc.*, **106**, 7500 (1984).

8 To the best of our knowledge, McCarthy's group has reported only one reaction of (*E*)-1-fluoro-2-phenyl-1-tributylstanylethene and iodobenzene in the presence of Pd/Cu(I) under CO atmosphere. However, they obtained a mixture of the corresponding direct coupling product and the carbonylative product with a ratio of 2:3. a) C. Chen, K. Wilcoxen, K. Kim, and J. R. McCarthy, *Tetrahedron Lett.*, **38**, 7677 (1997). b) C. Chen, K. Wilcoxen, Y. Zhu, K. Kim, and J. R. McCarthy, *J. Org. Chem.*, **64**, 3476 (1999).

9 Although the related β-substituted (fluorovinyl)stannanes were prepared from the corresponding β-substituted fluorovinyl sulfones, the attempt of the preparation of **2** was unsuccessful. J. R. McCarthy, E. W. Huber, T. Le, F. M. Laskovics, and D. P. Matthews, *Tetrahedron*, **52**, 45 (1996).

10 L. Xue, L. Lu, S. D. Pedersen, Q. Liu, R. M. Narske, and D. J. Burton, *J. Org. Chem.*, **62**, 1064 (1997).

11 P. J. Stang, M. Hanack, and L. R. Subramanian, *Synthesis*, **1982**, 85.

12 a) H. B. Kwon, B. H. McKee, and J. K. Stille, *J. Org. Chem.*, **55**, 3114 (1990). b) A. M. Echavarren and J. K. Stille, *J. Am. Chem. Soc.*, **110**, 1557 (1988). c) E. A. Echavarren and J. K.

Stille, *J. Am. Chem. Soc.*, **109**, 5478 (1987). d) W. J. Scott and J. K. Stille, *J. Am. Chem. Soc.*, **108**, 3033 (1986).
13 V. Farina and B. Krishnan, *J. Am. Chem. Soc.*, **113**, 9585 (1991).
14 T. Hanamoto, S. Harada, K. Shindo, and M. Kondo, *Chem. Commun.*, **1999**, 2397.