

Cross-Coupling Reactions of (1-Fluorovinyl)methyldiphenylsilane¹ with Aryl Halides and Aryl Triflates

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The cesium fluoride (CsF)-assisted cross-coupling reaction of (1-fluorovinyl)methyldiphenylsilane (**1**) with aryl halides and aryl triflates was examined. The reaction with aryl iodides smoothly proceeded to afford the corresponding (1-fluorovinyl)arenes in the presence of a catalytic amount of CuI and Pd(PPh₃)₄ in aprotic polar solvents such as DMF, DMI, DMA, and NMP in good yields. A variety of functional groups (nitro, ester, ketone, and ether) on the aromatic rings can be tolerated under these mild conditions. Aryl iodides are superior to aryl bromides as the coupling reaction partner. The cross-coupling reaction of **1** with aryl triflates instead of aryl halides was also accomplished in the presence of tetrabutylammonium iodide (*n*-Bu₄NI) as the additive under similar conditions.

Introduction

Monofluorinated olefins have recently received much attention for the design of an amide bond isostere² and the design of several mechanism-based enzyme inhibitors.³ This is because the introduction of fluorine into bioactive organic molecules often results in their increased activity, stability, and lipophilicity.⁴ Therefore, the development of new methods to introduce monofluorinated olefins into organic molecules remains a significant task. Although much progress has also been made in the cross-coupling reaction of fluorinated olefins,^{3a,5} very few involve the facile introduction of an unsubstituted 1-fluorovinyl group into organic molecules. To the best of our knowledge, only two groups have accomplished this type of reaction. McCarthy et al. reported the successful cross-coupling reactions of tributyl(1-fluorovinyl)stannane with aryl halides or sulfonates; however, the preparation of tributyl(1-fluorovinyl)stan-

nane requires five steps from commercially available reagents.^{5g} On the other hand, Martin et al. reported only one example of the atypical Heck reaction of 1,1-difluoroethylene with 5-iodo-*N*-tosylindole in moderate yield.⁶ We have been interested in new methodologies for the incorporation of the monofluorovinyl moiety⁷ and have initially demonstrated the cross-coupling reactions of (1-fluorovinyl)methyldiphenylsilane (**1**) and aryl halides.^{7d} In this paper, we report a full experimental procedure to the one-step preparation of (1-fluorovinyl)methyldiphenylsilane (**1**) and a detailed study on the cross-coupling reaction of **1** with aryl halides and aryl triflates.

Results and Discussion

Cross-Coupling Reaction of (1-Fluorovinyl)methyldiphenylsilane (1**) with Aryl Iodides.** We have previously reported the palladium-catalyzed cross-coupling reaction of **1** with aryl iodides.^{7d} To obtain the optimum conditions for the cross-coupling reaction, we reexamined the coupling reaction of **1** with 4'-iodoacetophenone (**2**) under various conditions (solvent, catalyst, concentration, the ratio of stoichiometry, and the addition order of reagents). The selected results are shown in Table 1. These data revealed the following features. (1) All the aprotic polar solvents employed are effective for the reaction (entries 2–5). The longer reac-

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(1) Please note the change to the correct nomenclature for silane **1** from that cited in our previous papers.^{7d,f}

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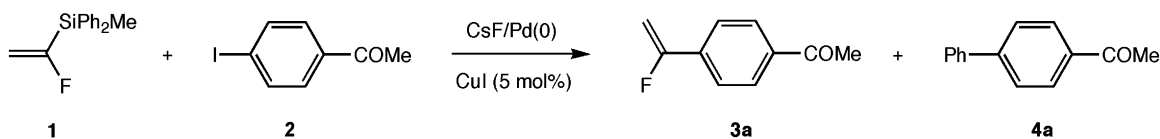
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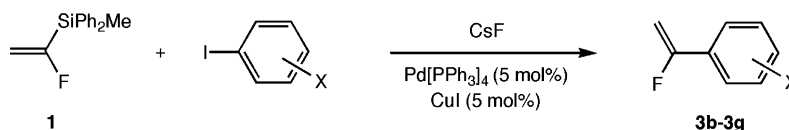
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TABLE 1. Optimization of the Cross-Coupling Reaction of 1 with 2^a

| entry | 1 (equiv) | CsF (equiv) | Pd (5 mol %) | solvent | time/h | yield ^b /% | ratio ^c |
|----------------|-----------|-------------|---|----------------------|--------|-----------------------|--------------------|
| 1 | 1.5 | 3.7 | Pd(PPh ₃) ₄ | DMI-THF ^d | 2 | (92) ^{e,f} | 100:0 |
| 2 | 1.5 | 2.3 | Pd(PPh ₃) ₄ | DMI | 3.5 | quant (91) | 100:0 |
| 3 | 1.5 | 2.3 | Pd(PPh ₃) ₄ | DMF | 2 | 98 | 100:0 |
| 4 | 1.5 | 2.3 | Pd(PPh ₃) ₄ | NMP | 2 | 97 | 100:0 |
| 5 | 1.5 | 2.3 | Pd(PPh ₃) ₄ | DMA | 2 | 98 | 100:0 |
| 6 | 1.5 | 2.3 | Pd(dba) ₂ /TFP | DMI | 3 | 94 | 99:1 |
| 7 | 1.5 | 2.3 | Pd(dba) ₂ /AsPh ₃ | DMF | 3 | 87 | 98:2 |
| 8 ^g | 1.2 | 1.5 | Pd(PPh ₃) ₄ | DMI | 40 | 60 | 100:0 |
| 9 | 1.2 | 1.5 | Pd(PPh ₃) ₄ | DMI | 44 | 70 | 100:0 |
| 10 | 1.2 | 1.8 | Pd(PPh ₃) ₄ | DMI | 28 | 74 | 100:0 |
| 11 | 1.5 | 1.8 | Pd(PPh ₃) ₄ | DMI | 116 | 95 | 100:0 |
| 12 | 1.5 | 1.8 | Pd(PPh ₃) ₄ | DMF | 3 | 85 | 100:0 |

^a All reactions were conducted with 4'-iodoacetophenone (**2**) (1.0 equiv) in the presence of CuI (5 mol %) at room temperature in the solvent (0.073–0.10 M). ^b GC yield. ^c Target molecule (**3a**)/byproduct (**4a**). ^d DMI-THF = 9:1. ^e Isolated yield in parentheses. ^f Our previous data. See ref 7d. ^g The concentration was 0.20 M.

TABLE 2. Cross-Coupling Reaction of 1 with Various Aryl Iodides^a

| entry | Ar-1 | 1 (equiv) | CsF (equiv) | solvent | product | time/h | yield ^b /% | ratio ^c |
|------------------|-----------------------|-----------|-------------|---------|-----------|--------|-----------------------|--------------------|
| 1 | 4-NO ₂ | 1.5 | 2.3 | DMF | 3b | 2.5 | 86 | 100:0 |
| 2 | 4-CO ₂ Et | 1.5 | 2.3 | DMF | 3c | 2 | 91 | >99:1 |
| 3 ^d | 4-CH ₂ OMe | 2.5 | 3.0 | DMF | 3d | 10 | 72 | 100:0 |
| 4 | 4-CH ₂ OAc | 1.5 | 2.3 | DMF | 3e | 2 | 84 | 100:0 |
| 5 ^d | 3-OMe | 2.5 | 3.0 | DMI | 3f | 16 | 67 | 100:0 |
| 6 ^{d,e} | 2-CO ₂ Me | 2.5 | 3.0 | DMI | 3g | 10 | 90 | 97:3 |

^a All reactions were conducted with **1** with aryl iodides (1.0 equiv) in the presence of CuI (5 mol %), Pd(PPh₃)₄ (5 mol %), and CsF (2.3 equiv) at room temperature unless otherwise noted. ^b Isolated yield. ^c Target molecule/byproduct. ^d The reaction was conducted with 2.5 equiv of **1** and 3.0 equiv of CsF. ^e At 42–45 °C.

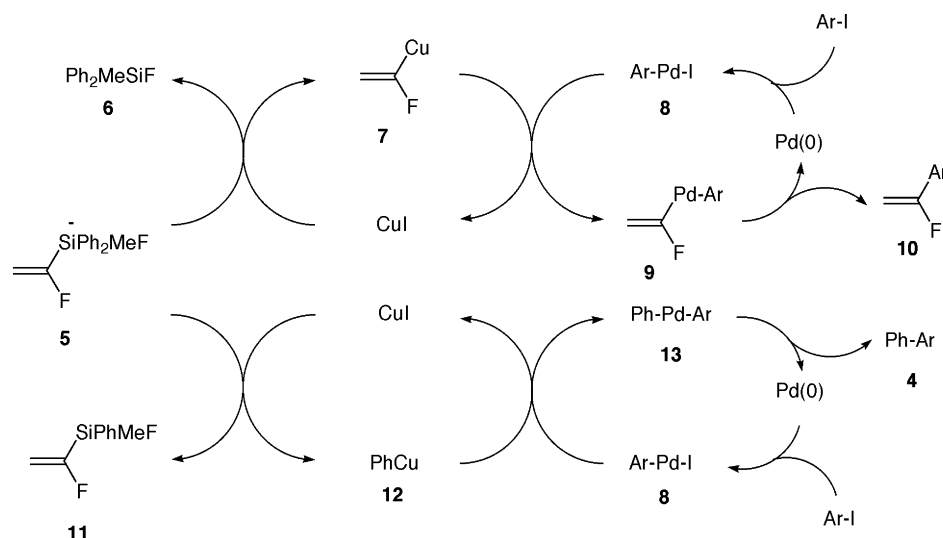
tion time being required in DMI appeared to be due to the lower solubility of CsF in DMI. (2) Among the palladium catalysts employed, the ordinary palladium(0) complex, Pd(PPh₃)₄, was the most effective with respect to selectivity. On the other hand, slightly less effective are the recently reported high-performance catalyst systems of Pd(dba)₂/TFP and Pd(dba)₂/AsPh₃ (entries 6 and 7).⁸ (3) The yield slightly improved under the higher dilution conditions (0.2 M) in DMI without any loss of selectivity (entries 8 vs 9). (4) The decrease in the amount of **1** to **2** up to 1.2 equiv caused the incomplete consumption of **2** (entries 2 vs 10). After considerable experimentation, we determined that the optimized amount of **1** to **2** was 1.5 equiv for the complete consumption of **2**. On the other hand, any decrease in the amount of CsF to **2** (1.8 equiv) required a much longer reaction time in DMI (entry 11). The use of DMF is effective for the shorter reaction time albeit a slightly decreased yield (entry 12). (5) The last addition of CsF to the reaction mixture including all other reagents suppressed the unnecessary consumption of **1**. Based on these considerations, we determined entry 2 as the optimum condition for this coupling reaction.

The generality of the cross-coupling reaction of aryl iodides with **1** was studied using the optimum conditions. These results are summarized in Table 2. Notable is that the reaction is slightly influenced by the substituents and substitution patterns on the aromatic ring of the coupling partner. Although we needed a minor modification of original optimum conditions in some cases, the successful reactions proceeded and afforded the corresponding (1-fluorovinyl)arenes with excellent stereoselectivity and in good to high yields. In general, aryl iodides bearing an electron-withdrawing group (entries 1 and 2) were viable. On the other hand, an electron-rich aryl iodide required longer reaction time due to the efficiency of the oxidative addition of the palladium catalyst to the carbon-iodide bond (entry 5). The functional group compatibility of this process as illustrated in these examples is noteworthy.

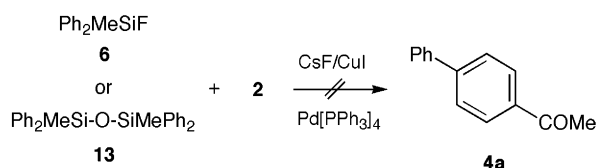
We have already proposed a plausible mechanism for this coupling reaction and suggested the formation of the (1-fluorovinyl)copper species (**7**) as an intermediate via a transmetalation of the 1-fluorovinyl group from the silicate (**5**) to copper iodide. Subsequent reductive elimination of the resulting diorganopalladium species (**9**) afforded the coupled product (**10**) (Scheme 1, upper catalytic cycle).^{7d,9} In a similar manner, we proposed the

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SCHEME 1



SCHEME 2



plausible mechanism for the formation of the byproduct (**4**) (Scheme 1, lower catalytic cycle). However, when this reaction was monitored with time, we noticed that **4** had begun to be generated after the complete consumption of **1** and the incomplete consumption of **2**. On the basis of this observation, we anticipated that the corresponding phenyl copper (**12**) could be formed not from **5** but by the combination of methylphenylfluorosilane (**6**) and CsF or that of 1,1,3,3-tetraphenyldimethyldisiloxane (**13**) and CsF (Scheme 2). The former (**6**) was produced after the transmetalation of **5** to CuI and the latter (**13**) might be produced after the hydrolysis of **5** by a trace amount of water. To confirm these possibilities, we independently prepared both **9** and **13**. Although we then examined their cross-coupling reaction with **2** under similar conditions, neither **9** nor **13** afforded the desired coupling product at all. Therefore, we are unable to explain the formation of **4** at this time.

Cross-Coupling Reaction of (1-Fluorovinyl)methyldiphenylsilane (1) with Aryl Bromides. In light of the above successful cross-coupling reaction with aryl iodides, we postulated that the cross-coupling reaction with aryl bromides would also be accessible. Since aryl bromides are more readily commercially available compared to aryl iodides, the reaction with aryl bromides would expand the scope of our reaction. Initial attempts at the cross-coupling of **1** with 4'-bromoacetophenone (**14**) under similar conditions afforded the expected cross-coupling product (**3a**) with low selectivity (Table 3, entry 1). As expected, the aryl bromide (**14**) as the coupling

partner was less effective than the corresponding aryl iodide. The increase in the amount of CuI to **14** (up to 10 mol %) improved both the yield and the selectivity to some extent (entry 2). We observed the complete consumption of **1** and the incomplete consumption of **14** through these two reactions. When the amount of **1** to **14** was increased to 2.5 equiv, the reaction proceeded with perfect selectivity in comparable yield (entry 3). The comparable yield was attributed to the reflection of the slow oxidative addition rate of **14** to Pd(PPh₃)₄. To accelerate the oxidative addition rate, a new catalyst system, Pd(dba)₂/[(*t*-Bu)₃PH]·BF₄,¹⁰ was used in our reaction system. However, no notable improvement was observed (entries 4–6).

The next attempt at the cross-coupling of **1** with 2-bromo-5-nitropyridine (**15**) as the heteroaromatic coupling partner under similar conditions gave the desired coupling product (**3h**) with perfect selectivity in modest yield (Scheme 3).

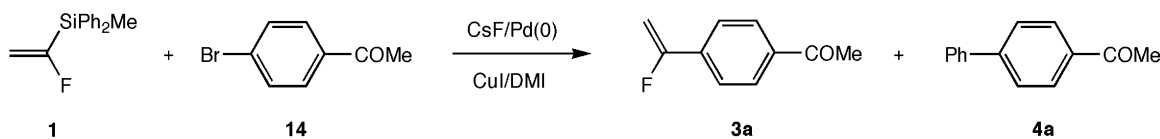
Cross-Coupling Reaction of (1-Fluorovinyl)methyldiphenylsilane (1) with Aryl Triflates. Since aryl triflates are easily accessible from the corresponding phenols, the reaction using triflates would also expand the scope of our reaction.¹¹ The reaction was first examined using 4'-acetylphenyl triflate (**16**) under the conditions similar to those employed for the coupling of aryl iodides.¹² These results are summarized in Table 4 and revealed the following features: (1) The use of LiCl completely retarded the reaction, probably due to the formation of LiF and CsCl (entry 1). (2) The addition of *n*-Bu₄NI instead of LiCl exclusively afforded the expected coupling product (entries 2–7). The yields depended on the amount of added *n*-Bu₄NI. The addition of *n*-Bu₄NI in the range from 0.5 equiv to 1.0 equiv to **16** essentially afforded the same yield. (3) The coupling reaction was

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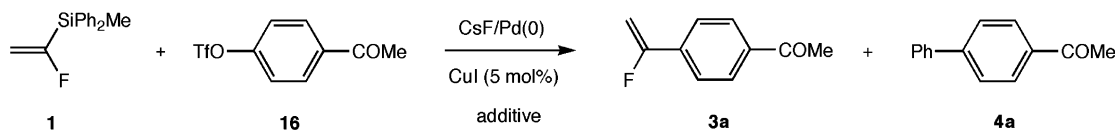
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TABLE 3. Optimization of the Cross-Coupling Reaction of 1 with 14^a

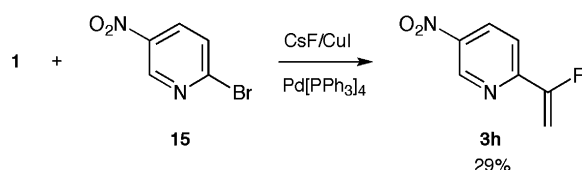
| entry | 1 (equiv) | CuI (mol %) | CsF (equiv) | Pd (5 mol %) | T/°C | time/h | yield ^b /% | ratio ^c |
|----------------|-----------|-------------|-------------|---|------|--------|-----------------------|--------------------|
| 1 | 1.5 | 5 | 2.6 | Pd(PPh ₃) ₄ | rt | 68 | 43 | 63:37 |
| 2 | 1.2 | 10 | 1.6 | Pd(PPh ₃) ₄ | rt | 63 | 62 | 84:16 |
| 3 | 2.5 | 5 | 3.0 | Pd(PPh ₃) ₄ | rt | 18 | 46 | 100:0 |
| 4 ^d | 2.5 | 5 | 3.8 | Pd(dba) ₂ /[(<i>t</i> -Bu) ₃ PH]·BF ₄ | 30 | 52 | 27 | 100:0 |
| 5 | 2.5 | 5 | 2.8 | Pd(dba) ₂ /[(<i>t</i> -Bu) ₃ PH]·BF ₄ | 42 | 18 | 20 | 96:4 |
| 6 | 2.5 | 5 | 3.0 | Pd(dba) ₂ /[(<i>t</i> -Bu) ₃ PH]·BF ₄ | 50 | 3 | 46 | 86:14 |

^a All reactions were conducted with 4'-bromoacetophenone (**14**) (1.0 equiv) in DMI. ^b GC yield. ^c Target molecule (**3a**)/byproduct (**4a**). ^d The reaction was conducted in DMF.

TABLE 4. Optimization of the Cross-Coupling Reaction of 1 with 16^a

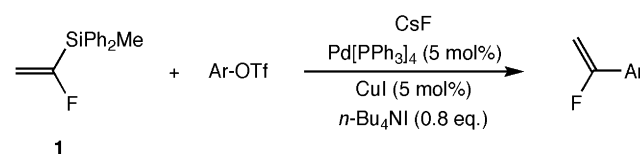
| entry | additive (equiv) | Pd (5 mol %) | solvent | time/h | yield ^b /% | ratio ^c |
|----------------|------------------------------------|------------------------------------|---------|--------|-----------------------|--------------------|
| 1 | LiCl (3.0) | Pd(PPh ₃) ₄ | DMI | 15 | 0 | |
| 2 | <i>n</i> -Bu ₄ NI (3.0) | Pd(PPh ₃) ₄ | DMI | 39 | 21 | 100:0 |
| 3 | <i>n</i> -Bu ₄ NI (3.0) | Pd(PPh ₃) ₄ | DMF | 16 | 53 | 100:0 |
| 4 | <i>n</i> -Bu ₄ NI (1.0) | Pd(PPh ₃) ₄ | DMF | 15 | 43 | 100:0 |
| 5 | <i>n</i> -Bu ₄ NI (0.8) | Pd(PPh ₃) ₄ | DMF | 13 | 78 (74) ^d | 100:0 |
| 6 | <i>n</i> -Bu ₄ NI (0.5) | Pd(PPh ₃) ₄ | DMF | 19 | 73 | 100:0 |
| 7 | <i>n</i> -Bu ₄ NI (0.1) | Pd(PPh ₃) ₄ | DMF | 19 | 34 | 100:0 |
| 8 | none | Pd(PPh ₃) ₄ | DMF | 47 | 19 | 100:0 |
| 9 ^e | none | Pd(PPh ₃) ₄ | DMF | 21 | 15 | 29:71 |
| 10 | <i>n</i> -Bu ₄ NI (3.0) | Pd(dba) ₂ /dppf | DMF | 15 | 15 | 75:25 |
| 11 | KI (0.8) | Pd(PPh ₃) ₄ | DMF | 55 | 52 | 100:0 |
| 12 | NaI (0.8) | Pd(PPh ₃) ₄ | DMF | 12 | 0 | |
| 13 | Me ₃ S(O)I (0.8) | Pd(PPh ₃) ₄ | DMF | 42 | 2 | 100:0 |

^a All reactions were conducted with **1** (1.5 equiv.) and 4-(trifluoromethoxy)acetophenone (**16**) (1.0 equiv) in the presence of CuI (5 mol %) and CsF (2.3 equiv) at room temperature. ^b GC yield. ^c Target molecule (**3a**)/byproduct (**4a**). ^d Isolated yield in parentheses. ^e CuI (20 mol %) was used.

SCHEME 3

accelerated in DMF (entries 2 vs 3). (4) Despite the absence of *n*-Bu₄NI, the coupling reaction proceeded giving the desired product in low yield (entries 8 and 9). These findings suggested that CuI plays the second role for supplying the iodide ion source. (5) Pd(PPh₃)₄ is a more efficient catalyst than Pd(dba)₂/dppf (entry 10).^{12c} (6) Although KI as the iodide source can be effective for the coupling, it required a longer reaction time (entry 11). Other iodide sources such as NaI and trimethyloxosulfonium iodide were not effective for these reactions (entries 12 and 13).

Representative results of the cross-coupling reaction of a variety of aryl triflates under the optimum conditions are shown in Table 5. All the reactions afforded the desired product with perfect selectivity. With regard to the yield, the triflate bearing an electron-withdrawing

TABLE 5. Cross-Coupling Reaction of 1 with Various Triflates^a

| entry | Ar-OTf | product | time/h | yield ^b /% | ratio ^c |
|----------------|--|-----------|--------|-----------------------|--------------------|
| 1 | 4-CO ₂ Et-C ₆ H ₄ | 3c | 5 | 66 | 100:0 |
| 2 ^d | 3-OMe-C ₆ H ₄ | 3f | 18 | 53 | 100:0 |
| 3 ^d | 1-naphthyl | 3i | 28 | 53 | 100:0 |

^a All reactions were conducted with **1** (1.5 equiv) and triflate (1.0 equiv) in the presence of CuI (5 mol %), Pd(PPh₃)₄ (5 mol %), *n*-Bu₄NI (0.8 equiv), and CsF (2.3 equiv) at room temperature unless otherwise noted. ^b Isolated yield. ^c Target molecule/byproduct. ^d The reaction was conducted with **1** (2.5 equiv) and CsF (3.0 equiv) at 30 °C.

group on the aromatic ring produced high yields when compared to the other triflates.

Although we have no evidence for the actual role of *n*-Bu₄NI, we confirmed that no transformation of the triflate into the corresponding aryl iodide occurred during the reaction on the basis of a GC–MS analysis. The

added *n*-Bu₄NI should be essential in order to ensure the formation of the reactive aryl iodopalladium(II) species.¹²

Conclusion

We have developed a facile synthesis of (1-fluorovinyl)-arenes through the fluoride ion-assisted cross-coupling reaction of the readily available reagent (1-fluorovinyl)-methylidiphenylsilane (**1**) with aryl halides and aryl triflates using the Pd(0)/Cu(I) system. The generality of the reaction was illustrated with aryl iodides, aryl bromides and aryl triflates. These reactions are proposed to proceed via transmetalation of the 1-fluorovinyl group from silicate (**5**) to copper(I) followed by a second transmetalation with palladium(0). These coupling reactions will be useful for the synthesis of a wide variety of new monofluoroolefins.

Experimental Section

General Methods. Melting points are uncorrected. Infrared (IR) spectra are reported in cm⁻¹. ¹H, ¹⁹F, and ¹³C NMR spectra were measured in CDCl₃ solutions. Chemical shifts were given by δ relative to that of an internal Me₄Si (TMS) for ¹H NMR and ¹³C NMR spectra and benzyldiylne trifluoride (CF₃C₆H₅) for ¹⁹F NMR spectra. DMI (1,3-dimethyl-2-imidazolidinone), DMF, DMA, and NMP (1-methyl-2-pyrrolidinone) were used after distillation from CaH₂.

(1-Fluorovinyl)methylidiphenylsilane (**1**) was prepared according to our method.^{7f} The elaborate workup made an improvement over the previous yield.

A 100 mL two-neck flask equipped with a magnetic stir bar, a stopcock, and a three-way stopcock was charged with cut lithium wire (0.40 g, 57.6 mmol) and 40 mL of THF under argon. To the stirred mixture was added chlorodiphenylmethylsilane (4.0 mL, 19.0 mmol) dropwise via syringe at room temperature. After the flask was immersed in an ultrasonic cleaner bath, the solution was irradiated with ultrasonic wave for 30 min at the temperatures not exceeding 40 °C and a black-green color gradually developed. After removal of the ultrasonic cleaner bath, the solution was stirred for an additional 2 h. The solution was cooled to -78 °C, and then argon was replaced with 1,1-difluoroethylene (balloon). The mixture was stirred at -78 °C for 30 min and gradually warmed to room temperature. After removal of remaining lithium wire by decantation, sodium sulfate decahydrate (Na₂SO₄·10H₂O) was carefully added to the resulting solution. After the mixture was dried over sodium sulfate and filtered through a short silica gel column (ether as an eluent), the combined ethereal solution was concentrated in vacuo. The resulting oily residue was purified by chromatography on silica gel (hexane as an eluent) to give the desired product (**1**) as a colorless oil (3.96 g, 86%): IR (neat) 1620 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.72 (3H, s), 4.86 (1H, dd, *J* = 61.5, 3.4 Hz), 5.48 (1H, dd, *J* = 32.7, 3.4 Hz), 7.34–7.66 (10H, m); ¹³C NMR (CDCl₃) δ -5.0 (d, *J* = 1.2 Hz), 109.2 (d, *J* = 1.2 Hz), 128.1, 130.0, 132.2 (d, *J* = 1.9 Hz), 134.9, 172.9 (d, *J* = 282.1 Hz); ¹⁹F NMR (CDCl₃) δ -103.93 (dd, *J* = 61.4, 32.9 Hz); GC-MS *m/z* 242 (0.7, M⁺), 201 (100). Anal. Calcd for C₁₅H₁₃FSi: C, 74.34; H, 6.24. Found: C, 74.43; H, 6.25.

Typical Procedure for 1-Fluorovinyl Arenes from Aryl Iodides (Table 1, Entry 2). Anhydrous CsF (61.4 mg, 0.40 mmol) was added to a solution of **1** (62.1 mg, 0.26 mmol), **2** (42.4 mg, 0.17 mmol), CuI (1.6 mg, 5 mol %), and Pd(PPh₃)₄ (10.9 mg, 5 mol %) in DMI (2 mL), and the mixture was stirred at room temperature. After being stirred for 3.5 h, the resulting mixture was quenched with water and extracted with hexane/ether = 3/1. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel

chromatography (hexane/ethyl acetate = 20/1) and afforded 25.8 mg of **3a** in 91% yield.

Typical Procedure for 1-Fluorovinyl Arenes from Aryl triflates (Table 4, Entry 5). Anhydrous CsF (108.7 mg, 0.72 mmol) was added to a solution of **1** (111.5 mg, 0.46 mmol), **16** (83.4 mg, 0.31 mmol), *n*-Bu₄NI (91.9 mg, 0.25 mmol), CuI (3.0 mg, 5 mol %), and Pd(PPh₃)₄ (18.3 mg, 5 mol %) in DMF (4 mL), and the mixture was stirred at room temperature. After being stirred for 13 h, the resulting mixture was quenched with water and extracted with hexane/ether = 3/1. The organic layer was dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 20/1) and afforded 37.6 mg of **3a** in 74% yield.

4'-(1-Fluorovinyl)acetophenone (3a): white solid; yield 91%; mp 56.2–57.8 °C; IR (KBr) 1679, 1651, 1610, 830 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 2.62 (3H, s), 5.00 (1H, dd, *J* = 17.6, 3.9 Hz), 5.16 (1H, dd, *J* = 48.8, 3.9 Hz), 7.65 (2H, d, *J* = 8.3 Hz), 7.97 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 26.5, 91.9 (d, *J* = 21.8 Hz), 124.5 (d, *J* = 6.9 Hz), 128.4 (d, *J* = 2.5 Hz), 135.9 (d, *J* = 29.3 Hz), 137.3, 161.8 (d, *J* = 250.4 Hz), 197.1; ¹⁹F NMR (CDCl₃, 283 MHz) δ -109.49 (dd, *J* = 49.1, 18.0 Hz); GC-MS *m/z* 164 (26, M⁺), 149 (100). Anal. Calcd for C₁₀H₉FO: C, 73.16; H, 5.53. Found: C, 73.11; H, 5.62.

4'-(1-Fluorovinyl)nitrobenzene (3b): pale yellow solid; yield 86%; mp 62.7–63.4 °C; IR (KBr) 1651, 1346, 854 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 5.11 (1H, dd, *J* = 17.6, 3.9 Hz), 5.27 (1H, dd, *J* = 48.6, 3.9 Hz), 7.72 (2H, d, *J* = 8.3 Hz), 8.25 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 93.7 (d, *J* = 21.8 Hz), 123.8 (d, *J* = 2.5 Hz), 125.3 (d, *J* = 6.9 Hz), 137.7 (d, *J* = 29.9 Hz), 148.1, 160.8 (d, *J* = 251.0 Hz); ¹⁹F NMR (CDCl₃, 283 MHz) δ -109.29 (dd, *J* = 48.0, 17.2 Hz); GC-MS *m/z* 167 (32, M⁺), 101 (100). Anal. Calcd for C₈H₆FNO₂: C, 57.49; H, 3.62; N, 8.38. Found: C, 57.64; H, 3.67; N, 8.30.

Ethyl 4'-(1-fluorovinyl)benzoate (3c): colorless oil; yield 91%; IR (neat) 1714, 1651, 866 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 1.40 (3H, t, *J* = 7.3 Hz), 4.39 (2H, q, *J* = 7.3 Hz), 4.98 (1H, dd, *J* = 17.8, 3.4 Hz), 5.17 (1H, dd, *J* = 49.1, 3.4 Hz), 7.62 (2H, d, *J* = 8.3 Hz), 8.05 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 14.2, 61.1, 91.7 (d, *J* = 22.4 Hz), 124.3 (d, *J* = 6.9 Hz), 129.6 (d, *J* = 1.9 Hz), 131.1, 135.8 (d, *J* = 29.3 Hz), 162.0 (d, *J* = 251.0 Hz), 165.9 (d, *J* = 1.2 Hz); ¹⁹F NMR (CDCl₃, 283 MHz) δ -109.40 (dd, *J* = 49.1, 18.0 Hz); GC-MS *m/z* 194 (6, M⁺), 149 (100). Anal. Calcd for C₁₁H₁₁FO₂: C, 68.03; H, 5.71. Found: C, 68.06; H, 5.69.

4'-(1-Fluorovinyl)(methoxymethyl)benzene (3d): colorless oil; yield 72%; IR (neat) 1651, 1103, 822 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 3.40 (3H, s), 4.48 (2H, s), 4.84 (1H, dd, *J* = 18.1, 3.4 Hz), 5.03 (1H, dd, *J* = 49.8, 3.4 Hz), 7.34 (2H, d, *J* = 8.3 Hz), 7.54 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 58.1, 74.1, 89.4 (d, *J* = 23.0 Hz), 124.6 (d, *J* = 7.5 Hz), 127.6 (d, *J* = 2.5 Hz), 131.2 (d, *J* = 29.3 Hz), 139.5, 162.7 (d, *J* = 249.7 Hz); ¹⁹F NMR (CDCl₃, 283 MHz) δ -109.10 (dd, *J* = 49.6, 17.7 Hz); GC-MS *m/z* 166 (29, M⁺), 135 (100). Anal. Calcd for C₁₀H₁₁FO: C, 72.27; H, 6.67. Found: C, 72.45; H, 6.83.

4'-(1-Fluorovinyl)(acetoxymethyl)benzene (3e): colorless oil; yield 84%; IR (neat) 1744, 1652, 838 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 2.11 (3H, s), 4.88 (1H, dd, *J* = 18.1, 3.4 Hz), 5.05 (1H, dd, *J* = 49.8, 3.4 Hz), 5.11 (2H, s), 7.36 (2H, d, *J* = 8.3 Hz), 7.55 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 20.8, 65.6, 89.8 (d, *J* = 22.4 Hz), 124.7 (d, *J* = 7.9 Hz), 128.1 (d, *J* = 1.9 Hz), 131.8 (d, *J* = 29.3 Hz), 137.1, 162.4 (d, *J* = 249.7 Hz), 170.7; ¹⁹F NMR (CDCl₃, 283 MHz) δ -109.24 (dd, *J* = 49.6, 18.4 Hz); GC-MS *m/z* 194 (8, M⁺), 133 (100). Anal. Calcd for C₁₁H₁₁FO: C, 68.03; H, 5.71. Found: C, 68.07; H, 5.76.

3'-(1-Fluorovinyl)anisole (3f): colorless oil, which generally turned dark yellow on standing under an argon atmosphere; yield 67%; IR (neat) 1653, 1233, 1049, 782, 688 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 3.83 (3H, s), 4.85 (1H, dd, *J* = 17.6, 3.4 Hz), 5.03 (1H, dd, *J* = 49.3, 3.4 Hz), 6.89–73.5 (4H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 55.2, 89.8 (d, *J* = 22.4 Hz), 110.0 (d, *J* = 7.5 Hz), 115.1, 117.1 (d, *J* = 7.5 Hz), 129.5 (d, *J*

= 1.9 Hz), 133.4 (d, $J = 29.3$ Hz), 160.0, 162.7 (d, $J = 250.4$ Hz); ^{19}F NMR (CDCl_3 , 283 MHz) δ -108.53 (dd, $J = 49.5, 18.0$ Hz); GC-MS m/z 153 (4, $\text{M}^+ + 1$), 152 (100, M^+); HRMS (EI) m/z calcd for $\text{C}_9\text{H}_9\text{FO}$ 152.0670, found 152.0654.

Methyl 2'-(1-fluorovinyl)benzoate (3g): pale yellow oil; yield 90%; IR (neat) 1732, 1662, 772 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 3.91 (3H, s), 4.80 (1H, dd, $J = 47.4, 3.4$ Hz), 4.96 (1H, dd, $J = 16.1, 3.4$ Hz), 7.43–7.54 (3H, m), 7.79 (1H, d, $J = 6.4$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 52.3, 93.0 (d, $J = 21.2$ Hz), 129.5 (d, $J = 1.2$ Hz), 129.6, 129.7 (d, $J = 4.3$ Hz), 130.1 (d, $J = 1.2$ Hz), 131.3, 132.6 (d, $J = 27.4$ Hz), 163.4 (d, $J = 254.7$ Hz), 167.8; ^{19}F NMR (CDCl_3 , 283 MHz) δ -91.42 (dd, $J = 47.5, 16.2$ Hz); GC-MS m/z 180 (14, M^+), 129 (100). Anal. Calcd for $\text{C}_{10}\text{H}_9\text{FO}_2$: C, 66.66; H, 5.03. Found: C, 66.77; H, 5.16.

2-(1-Fluorovinyl)-5-nitropyridine (3h): white solid; yield 29%; mp 68.3–69.8 $^\circ\text{C}$; IR (KBr) 3141, 1652, 1593, 1475, 1276, 1018, 859, 767 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, $J = 8.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 97.2 (d, $J = 17.4$ Hz), 118.5 (d, $J = 4.4$ Hz), 132.3, 143.7, 145.0 (d, $J = 3.7$ Hz), 154.6 (d, $J = 37.3$ Hz), 160.2 (d, $J = 249.7$ Hz); ^{19}F NMR

(CDCl_3 , 283 MHz) δ -117.24 (ddd, $J = 48.3, 15.9, 1.1$ Hz); GC-MS m/z 169 (7, $\text{M}^+ + 1$), 168 (100, M^+). Anal. Calcd for $\text{C}_7\text{H}_5\text{FN}_2\text{O}_2$: C, 50.01; H, 3.00; N, 16.66. Found: C, 50.09; H, 3.01; N, 16.62.

1-(1-Fluorovinyl)naphthalene (3i): colorless oil; yield 53%; IR (neat) 3049, 1660, 857, 803, 776 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.89 (1H, dd, $J = 48.3, 2.9$ Hz), 5.16 (1H, dd, $J = 16.1, 2.9$ Hz), 7.43–7.63 (4H, m), 7.86–7.91 (2H, m), 8.18–8.22 (1H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ 94.9 (d, $J = 23.0$ Hz), 124.9, 125.6 (d, $J = 4.4$ Hz), 126.1, 126.8, 127.3 (d, $J = 4.4$ Hz), 128.4, 130.2 (d, $J = 1.2$ Hz), 130.5 (d, $J = 26.2$ Hz), 133.5, 164.0 (d, $J = 254.7$ Hz); ^{19}F NMR (CDCl_3 , 283 MHz) δ -89.09 (ddq, $J = 48.1, 16.2, 1.2$ Hz); GC-MS m/z 173 (7, $\text{M}^+ + 1$), 172 (76, M^+), 171 (100). Anal. Calcd for $\text{C}_{12}\text{H}_9\text{F}$: C, 83.70; H, 5.27. Found: C, 83.69; H, 5.36.

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