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Silver-Mediated Decarboxylative Fluorodiiodination of Alkynoic Acids: Synthesis of Regio- and Stereoselective Fluoroalkenes

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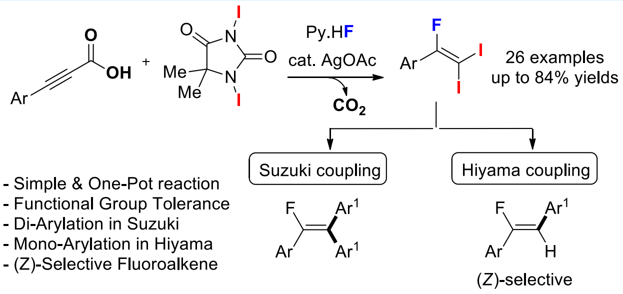
Supporting Information

ABSTRACT: A variety of arylalkynoic acids reacted with 1,3-diiodo-5,5-dimethylhydantoin and HF·pyridine in the presence of AgOAc to provide the corresponding 1-fluoro-2,2-diiodovinylarenes in good yields and high regioselectivity. In addition, Pd-catalyzed cross-coupling reaction of 1-fluoro-2,2-diiodovinylarenes afforded diaryl coupling products in the Suzuki reaction and monoaryl coupling products with high stereoselectivity in the Hiyama reaction. It was found that C−F-activated borylation of fluoroalkenes using Pd catalyst afforded the vinylboranes with good yields.

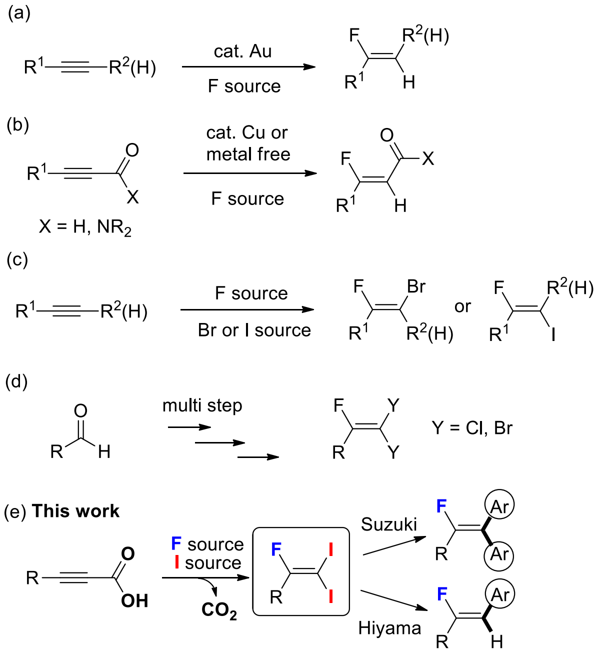


Many biological and medicinal products, as well as important functional materials, contain the fluorine functionality.[1] Substitution of hydrogen with fluorine in organic materials can dramatically change the reactivity and the chemical, physical, and biological properties of the corresponding compounds.[2] As a consequence, fluorinated compounds have recently gained considerable attention in various fields, and the number of methodologies introducing the fluorine functionality into organic compounds has increased drastically over the last few decades.[3]

Fluoroalkene, one of the numerous fluorine-containing compounds, is an important structural motif found in many bioactive compounds and is a useful building block.[4] A variety of synthetic methods for fluoroalkenes have been reported in the literature, and hydrofluorination of alkynes is one such straightforward method (Scheme 1a).[5] Sadighi first reported hydrofluorination of alkynes using Au catalyst to furnish fluoroalkenes in good yields. A number of Au-catalyzed hydrofluorination reactions of alkynes have been developed by several groups. In addition, it was reported that alkynes having a carbonyl group could be converted into the corresponding fluoroalkenes under metal-free or copper catalysis conditions (Scheme 1b).[6]

Moreover, fluoroalkene derivatives 1,2-bromofluoro- and 1,2-fluoroiodoalkenes have received considerable attention as useful fluorinated building blocks because these vinyl bromides and iodides can be further transformed into versatile molecules via cross-coupling reactions (Scheme 1c). Jiang demonstrated that 1,2-bromofluoroalkenes could be synthesized by the reaction of terminal alkynes with NBS/AgF.[7] Synthesis of 1,2-fluoroiodoalkenes was accomplished by the fluoroiodination of alkynes employing HF-based reagents along with the iodine reagents such as I_2, Tol-IF_2, IF_5, PhIO, and 1,3-diiodo-5,5-dimethylhydantoin (DIH).[8] In contrast, much less attention has been paid toward *gem*-dihalo-substituted fluoroalkenes, although in theory, they are highly likely to be employed as coupling partners in the cross-coupling reactions for the preparation of mono- and disubstituted fluoroalkenes. It has been reported that the preparation of *gem*-dibromo- and *gem*-dichlorofluoroalkenes from aldehydes requires a multistep process (Scheme 1d).[9] Therefore, simple and one-step synthetic methods are required.

Scheme 1. Synthesis of Fluoroalkenes



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Given our interest in the decarboxylation of alkynoic carboxylic acids for the synthesis of halogenated compounds, we recently reported the first general synthesis of 2,2,2-trichloroacetophenone, 2,2,2-tribromoacetone, and 1,2,2-tribromoalkene via decarboxylative halogenation of alkynoic acids.[10] We found that water works as a nucleophile and adds to the alkyne in the presence of the halogen source. From these studies, we envisioned that 1-fluoro-2,2-diiodovinyl arenes could be obtained via the decarboxylation of alkynoic acid if a fluorine reagent worked as a nucleophile in the presence of the iodine source.

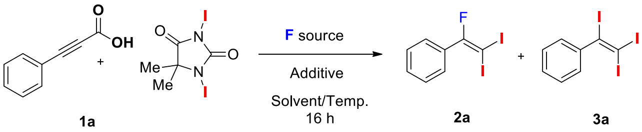
Moreover, we paid attention to developing the selective mono- and diaryl coupling reactions with 1-fluoro-2,2-diiodovinylarenes because they can further be readily transformed into a variety of molecules bearing a fluoroalkene group. Although many synthetic methods for fluoroalkenes have been developed,[11] preparation of (*Z*)-fluoroalkenes is much less explored.[12] Herein, we report the synthesis of 1-fluoro-2,2-diiodovinyl arenes from alkynoic acids and demonstrate their applications in the selective aryl cross-coupling reactions.

To find optimal conditions, phenyl propiolic acid was chosen as a standard substrate and reacted with 1,3-diiodo-5,5-dimethylhydantoin (DIH) and different fluorine reagents. The results are summarized in Table 1

It was found that 1-fluoro-2,2-diiodovinylbenzene **2a** was formed in 18% yield when Py·HF was treated with **1a** and DIH at room temperature (entry 1). When either KF, CsF, or $Et_3N\cdot 3HF$ was employed as a fluoride source, triiodoalkene **3a** was formed without the formation of **2a** (entries 2–4). When the amount of Py·HF was increased to 15 equiv, the yield of **2a** increased to 51%; however, byproduct **3a** was still formed (entry 5). The reactions in other solvents such as CH_2Cl_2, THF, toluene, and acetone did not give satisfactory results (entries 6–9). Increasing the reaction temperature to 40 °C afforded 62% yield of **2a** with a small amount of **3a**. In addition, iodoethynylbenzene was formed with 12% yield (entry 10). Addition of AgI to the reaction mixture did not enhance the yield of **2a**; however, the reaction with Ag_2O provided a 69% yield of **2a** (entry 12). Finally, when the reaction was conducted with a catalytic amount of AgOAc (20 mol %), **2a** was formed selectively in 82% yield without the formation of **3a**. Moreover, no iodoethynylbenzene was found (entry 13). Product **2a** was successfully isolated in 81% yield. Increasing the amount of Py·HF did not improve the yield of **2a** (entry 14). The reaction at 80 °C did not give a satisfactory result (entry 15). The identification of structure **2a** was confirmed by 2D HSQC (see the Supporting Information).[13]

Under these optimal conditions, we evaluated this transformation with a number of arylalkynoic acids (Scheme 2).

Table 1. Optimal Conditions for the Synthesis of 1-Fluoro-2,2-diiodovinylbenzene[a]



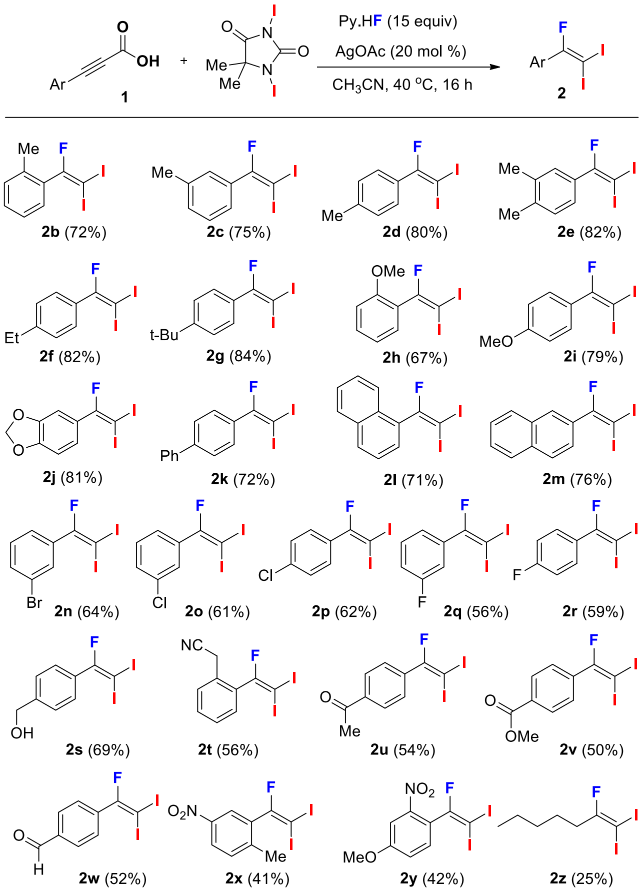
entry	F source (equiv)	solvent	temp (°C)	additive (20 mol %)	yield[b] (%)	
					2a	3a
1	Py·HF (5)	CH_3CN	25		18	8
2	KF (5)	CH_3CN	25		0	20
3	CsF (5)	CH_3CN	25		0	24
4	$Et_3N\cdot 3HF$	CH_3CN	25		0	2
5	Py·HF (15)	CH_3CN	25		51	6
6	Py·HF (15)	CH_2Cl_2	25		17	26
7	Py·HF (15)	THF	25		3	55
8	Py·HF (15)	toluene	25		2	22
9	Py·HF (15)	acetone	25		8	2
10	Py·HF (15)	CH_3CN	40		62	3
11	Py·HF (15)	CH_3CN	40	AgI	41	14
12	Py·HF (15)	CH_3CN	40	Ag_2O	69	8
13	Py.HF (15)	CH_3CN	40	AgOAc	82 (81)[c]	0
14	Py.HF (20)	CH_3CN	40	AgOAc	82	0
15	Py.HF (15)	CH_3CN	80	AgOAc	73	5

[a]Reaction conditions: **1a** (1.0 mmol), DIH (1.1 mmol), and F source were reacted in solvent (4.0 mL) for 16 h. [b]Determined by ^1H NMR and gas chromatography with an internal standard. [c]Isolated yield.

Methyl-substituted arylpropiolic acids afforded the corresponding products **2b**, **2c**, **2d**, and **2e** in good yields. 4-Ethyl- and 4-*tert*-butyl-substituted phenyl propiolic acid gave **2f** and **2g** in 82% and 84% yields, respectively. Arylpropiolic acids having 2-methoxy-, 4-methoxy-, and 3,4-dioxane groups produced the corresponding 1-fluoro-2,2-diiodovinylarenes **2h**, **2i**, and **2j**, respectively, in good yields. 1,1′-Biphenyl-4-yl-, 1-naphthyl-, and 2-naphthylpropiolic acids were transformed into **2k**, **2l**, and **2m** in 72%, 71%, and 76% yields, respectively. Bromo-, chloro-, and fluoro-substituted phenylpropiolic acids provided the desired products **2n**, **2o**, **2p**, **2q**, and **2r** in yields ranging between 56 and 64%. Alcohol, nitrile, ketone, ester, and aldehyde groups exhibited good tolerance in the formation of **2s**, **2t**, **2u**, **2v**, and **2w**, respectively. Arylpropiolic acid bearing a nitro group furnished **2x** and **2y** in a slightly lower yield. Although the alkyl-substituted propiolic acids such as octynoic acid afforded desired product **2z**, we failed to isolate it in pure form as it could not be separated from the byproduct (1,1,2-triiodoheptene) by column chromatography. From these results, it could be generalized that (i) the steric hindrance of substituents on the aryl ring of alkynoic acids did not affect this transformation, and the arylalkynoic acids bearing substituents at the *ortho*, *meta*, and *para* positions worked well, and (ii) the electronic properties of different substituents on the aryl ring influenced the yields of the products, with the electron-donating groups increasing the efficiency of the reaction, and resulting in product in excellent yield, and the electron-withdrawing groups decreasing the efficiency of the reaction to a certain extent. The broad tolerance toward the functional groups such as halogen, alcohol, nitrile, ketone, ester, aldehyde, and nitro offered a great opportunity to further functionalize the corresponding products.

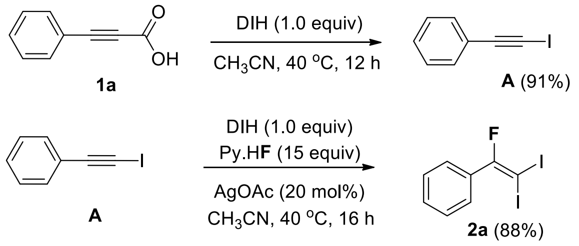
Afterward, to study the reaction pathway, control experiments were carried out (Scheme 3). When phenylpropiolic acid was reacted with DIH in the absence of Py·HF, iodoethynylbenzene (**A**) was formed in 91% yield. We found that (1-fluoro-2,2-diiodovinyl)benzene (**2a**) was formed in

Scheme 2. Synthesis of 1-Fluoro-2,2-diiodovinylarenes[a]



[a]Reaction conditions: **1** (2.0 mmol), DIH (2.2 mmol), Py.HF (30.0 mmol), and AgOAc (0.4 mmol) were reacted in CH_3CN at 40 °C for 16 h. Isolated yields in parentheses. Compound **2z** was obtained with 1,1,2-triiodohept-1-ene.

Scheme 3. Control Experiments

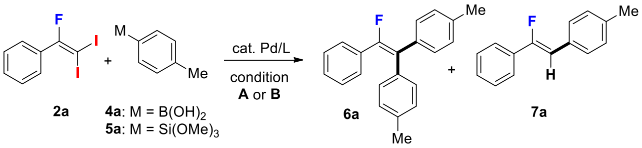


88% yield when iodoethynylbenzene was treated under the standard conditions. From these results, it was elucidated that alkynyl iodide was an intermediate in this transformation. We suggest that alkynyl iodide reacts with DIH to provide a iodonium bridged ion which is opened by the fluoride ion.

We further studied the application of 1-fluoro-2,2-diiodovinylarenes as coupling partners in the Pd-catalyzed cross-coupling reactions. We found that the 2,2-diiodovinyl group showed different reactivities in the Suzuki and Hiyama cross-coupling reactions. The results are summarized in Table 2 (see the Supporting Information for details).

When 2.5 equiv of *p*-tolylboronic acid was treated with **2a** under conditions A, diaryl coupling product **6a** was formed in 91% yield (entry 1). However, when trimethoxy-*p*-tolylsilane was allowed to react under conditions B, no diaryl coupled product was found and only deiodo monoaryl coupling product **7a** was formed in 73% yield (entry 2). It was found that only (*Z*)-**7a** was formed in the reaction mixture. The Suzuki coupling of **2a** and **4a** afforded **6a** as the major product even when 1.1 equiv of **4a** was employed, and the reaction was conducted under conditions B (entries 3 and 4). When **2a** was allowed to react with 1.1 equiv of **5a**, only **7a** was formed in 5% yield (entry 5). In addition, neither **6a** nor **7a** was formed when the Hiyama coupling was carried out under conditions A (entry 6). When 5.0 equiv of **5a** was used, only **7a** was formed with 72% yield (entry 7).

Table 2. Pd-Catalyzed Mono- and Diaryl Coupling Reactions of 2a

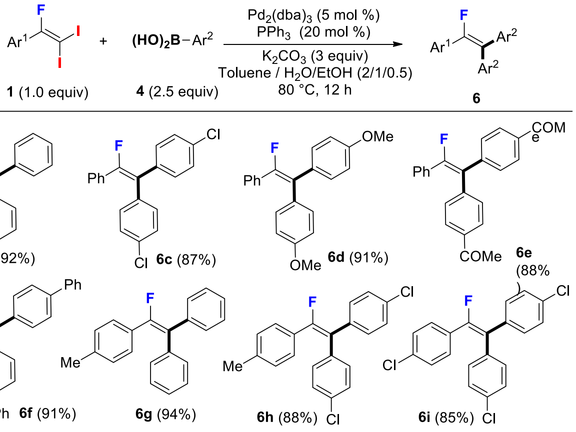


entry	Ar-M	1a/Ar-M (equiv)	conditions[a]	yield[b] (%) 6a	yield[b] (%) 7a
1	**4a**	1.0/2.5	A	91	0
2	**5a**	1.0/2.5	B	0	73
3	**4a**	1.0/1.1	A	34	9
4	**4a**	1.0/2.5	B	40	0
5	**5a**	1.0/1.1	B	0	5
6	**5a**	1.0/2.5	A	0	0
7	**5a**	1.0/5.0	B	0	72

[a]Conditions: (A) 5 mol % of $Pd_2(dba)_3$, 20 mol % of PPh_3, and K_2CO_3 (3.0 equiv) were employed in toluene/H_2O/EtOH at 80 °C for 12 h; (B) 10 mol % of $Pd(OAc)_2$, 20 mol % of DABCO, and TBAF (3.0 equiv) were employed in dioxane at 80 °C for 12 h. [b]Isolated yield.

We evaluated the Suzuki coupling reactions of 1-fluoro-2,2-diiodovinylarenes and arylboronic acids under conditions A. As shown in Scheme 4, **2a** reacted with substituted arylboronic acids to furnish diaryl coupling product **6** in good yields. In addition, 1-fluoro-2,2-diiodovinylarenes, having substituents

Scheme 4. Suzuki Coupling Reactions of 1-Fluoro-2,2-diiodovinylarenes[a]



[a]Reaction conditions: **1** (1.5 mmol), **4** (3.75 mmol), $Pd_2(dba)_3$ (0.075 mmol), PPh_3 (0.3 mmol), and K_2CO_3 (4.5 mmol) were reacted in toluene/H_2O/EtOH at 80 °C for 12 h.

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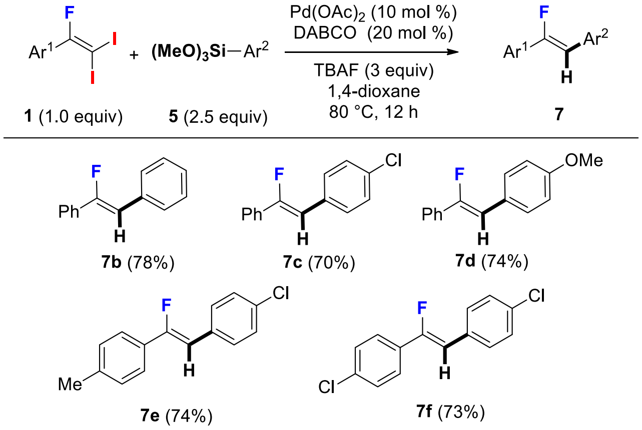
such as methyl and chloride, also afforded diaryl coupling products **6g**, **6h**, and **6i** in good yields.

The Hiyama coupling reactions were also tested with 1-fluoro-2,2-diiodovinylarenes and aryl siloxanes under conditions B. As expected, all of the tested arylsiloxanes exclusively afforded the monoaryl coupling products in good yields. It was noteworthy that only (*Z*)-fluoroethene derivatives were observed in the formation of monoaryl coupling product **7** (Scheme 5). The reaction mechanism of the coupling reactions with 1-fluoro-2,2-diiodovinylarenes is not clear at this time.[14]

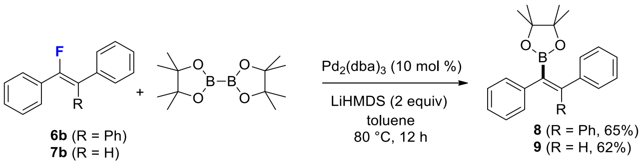
Scheme 5. Hiyama Coupling Reactions of 1-Fluoro-2,2-diiodovinylarenes[a]



[a]Reaction conditions: **1** (1.5 mmol), **5** (3.75 mmol), $Pd(OAc)_2$ (0.15 mmol), DABCO (0.3 mmol), and TBAF (4.5 mmol) were reacted in 1,4-dioxane at 80 °C for 12 h.

We found that C−F bond of fluoroalkenes **6b** and **7b** can be activated by palladium to react with bis(pinacolato)diboron (B_2Pin_2) to furnish the corresponding vinylboranes with good yields (Scheme 6).[15]

Scheme 6. C−F-Activated Borylation of 6b and 7b



In summary, we have developed a simple and efficient method for the synthesis of 1-fluoro-2,2-diiodovinylarenes via the decarboxylation of alkynoic acids. 1-Fluoro-2,2-diiodovinylarenes were obtained in high yields when alkynoic acids were reacted with DIH in the presence of Py·HF. The reaction showed high regioselectivity in the decarboxylative halogenation and good tolerance toward functional groups such as bromide, chloride, alcohol, nitrile, ketone, ester, aldehyde, and nitro. Furthermore, 1-fluoro-2,2-diiodovinylarenes were employed as coupling partners in the Suzuki and Hiyama coupling reactions. In the Suzuki coupling, 1-fluoro-2,2-diiodovinylarenes coupled with aryl boronic acids to furnish the corresponding diaryl coupling products. However, in the Hiyama coupling, (*Z*)-fluoroethenes, which are deiodo monoaryl coupling products, were predominately formed by the reaction between 1-fluoro-2,2-diiodovinylarenes and arylsiloxanes. It was found that 1-fluoro-2,2-diiodovinylarenes resulted in good yields of the cross-coupling products in both Suzuki and Hiyama coupling reactions. We also demonstrated that C−F bond activation of fluoroalkenes for the synthesis of vinylboranes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00597.

Experimental procedures and spectral data for the products (PDF)

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Notes

The authors declare no competing financial interest.

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