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Palladium-Catalyzed Mizoroki-Heck-Type Reactions of [Ph₂SR_{fn}][OTf] with Alkenes at Room Temperature

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first Pd-catalyzed Mizoroki-Heck-type The reaction of [Ph2SRfn][OTf] with alkenes is described. The reaction of $[Ph_2SR_{fn}][OTf]$ ($R_{fn} = CF_3$, CH_2CF_3) with alkenes in the presence of 10 mol% Pd[P(t-Bu)₃]₂ and TsOH at room temperature provided the corresponding phenylation products in good to high yields. The bases that benefit the traditional Mizoroki-Heck reactions severely inhibited the transformation with [Ph2SRfn][OTf], whereas acids significantly improved the reaction. This protocol supplies a new class of cross-coupling partners for Mizoroki-Hecktype reaction and gains important insights into the reactivity of phenylsulfonium salts either with or without fluorine-containing alkyl groups as the promising phenylation reagents in organic synthesis.

Fluorine-containing diaryl sulfonium salts are conventional but useful synthetic reagents in the preparation of functional molecules.¹ Such compounds have been extensively studied in fluoroalkylation reactions. For example, trifluoromethyl diaryl sulfonium salts, known as Yagupolskii-Umemoto reagents $([Ar_2SCF_3]X (X = OTf, BF_4))$, were initially exploited as electrophilic ⁺CF₃ transfer sources for a variety of nucleophiles,² and later were confirmed to be available in the reductive trifluoromethylation of alkenes, alkynes, arenes, and others.³ 2,2,2-Trifluoroethyl diphenyl sulfonium salt, a less well-known reagent which was first synthesized by Umemoto and coworkers,⁴ was recently found to be an efficient ylide precursor and trifluoromethylcarbene source for the functionalization of aryl aldehyde, vinyl ketones, and aldimines and olefins, respectively.⁵ Compared to Umemoto and Togni's reagents, trifluoromethyl and 2,2,2-trifluoroethyl diphenyl sulfonium salts have shown a narrow range of applications in organic synthesis. To our knowledge, almost only Cu-mediated, photoredox-catalyzed, and inorganic-reductant-initiated

trifluoromethyaltions with $[Ph_2SCF_3]X$ (X = OTf, BF₄) have been disclosed.³ The reactions in regard to transition-metalmediated transformation of $[Ph_2SCH_2CF_3][OTf]$ are rarely known.⁵



Recently, the Pd-catalyzed arylation of arylboronic acids with $[Ar_2SCF_3][OTf]$ was reported.⁶ When the Umemoto's reagent was treated with arylboronic acid, no arylation product was produced.⁶ This unique reactivity of $[Ar_2SR_{fn}][OTf]$ may hint of new applications of the non-cyclic fluoroalkyl(diaryl)sulfonium salts in an expanded field. On the other hand, the Pd-catalyzed Mizoroki-Heck reaction of aryl halides and pseudo-halides (such as triflates, tosylates, carboxylates, diazoniums, and iodoniums) with alkenes have been well documented. However, examples of the uses of arylsulfoniums, arylphosphoniums, and arylammoniums as cross-coupling partners in the same reaction are very limited despite they having been widely utilized in Suzuki-Miyaura reactions.⁷⁻¹²

Here we found that $[Ph_2SR_{fn}][OTf]$ could be used as cross coupling reagents in Mizoroki-Heck-type reactions with alkenes at room temperature in the presence of Pd-catalysts. The reaction between 1-methoxy-4-vinylbenzene (1a) and trifluoromethyl diphenyl sulfonium triflate (2a) was tested as a model reaction to determine the optimized phenylation conditions (see SI). At the beginning, reaction of 1a with 2a (1.5 equiv) at 80 °C in DMF under a N₂ atmosphere for 24 h in the presence of 10 mol% PdCl₂ gave (E)-1-methoxy-4styrylbenzene (3a) in 30% yield (entry 1, Table 1). Other Pd complexes like Pd₂(dba)₃, Pd(OAc)₂, and Pd(PPh₃)₄ used in the same reaction (at 80 °C) afforded 3a in 30-64% yields (entries 2-4, Table 1). The reaction in the presence of 10 mol% Pd[P(t- Bu_{3}_{2} (at 80 °C) provided **3a** in 76% yield (entry 5, Table 1). Decreasing the reaction temperature from 80 °C to room temperature in the presence of 10 mol% Pd[P(t-Bu)₃]₂, no significant change in the yield of 3a was observed (67% yield)

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(entry 6, Table 1). Nevertheless, if the base such as NaHCO₃, K₂CO₃, K₃PO₄, NaOAc, DBU, or DMAP was added into a mixture of **1a**, **2a**, $Pd[P(t-Bu)_3]_2$, and DMF at 80 °C or room temperature, the Mizoroki-Heck-type reaction was frustrated, affording **3a** in 7-35% or < 1-5% yields (entries 7-10, Table 1). In contrast, the choice of acids can facilitate the reaction. When 1a was treated with 2a in the presence of 10 mol% TsOH and $Pd[P(t-Bu)_3]_2$ at room temperature, **3a** was obtained in 86% yield (entry 11, Table 1). Other sulfonic or carboxylic acids such as CF₃SO₃H, CH₃SO₃H, CH₃CO₂H, and CF₃CO₂H could also provide 3a in good yields (entries 12-15, Table 1). Further studies indicated that 2,2,2-trifluoroethyl diphenyl sulfonium triflate (2b) is a more effective participant than 2a in the functionalization of 1a at room temperature (see SI). Reaction of 1a and 2b without additives in the presence of 10 mol% $Pd[P(t-Bu)_3]_2$ gave higher yield of **3a** than that using **2a** (84%) vs 67%) (entry 16, Table 1). Similarly, the addition of base dramatically suppressed the cross-coupling (6% yield, see SI). When using TsOH instead, the reaction gave 3a in a quantitative yield (entry 17, Table 1).

Table 1. Pd-catalyzed Mizoroki-Heck-type reaction of 2a with $1a^{a}$

MeO 1a	+ C, 5 C, F ₃ OTf (1.5 equiv) 2a	Pd-catalyst (10 mol%) additive (10 mol%) r.t., DMF, 24 h, N ₂	MeO 3a
Entry	Catalyst	Additive	Yield (3a , %) ^b
1 ^c	PdCl ₂	none	30
2 ^{<i>c</i>}	$Pd_2(dba)_3$	none	30
3 ^{<i>c</i>}	Pd(OAc) ₂	none	64
4 ^{<i>c</i>}	$Pd(PPh_3)_4$	none	30
5 ^c	Pd[P(t-Bu) ₃] ₂	none	76
6	Pd[P(t-Bu) ₃] ₂	none	67
7	Pd[P(t-Bu) ₃] ₂	NaHCO ₃	1 (35 [°])
8	Pd[P(t-Bu) ₃] ₂	K ₂ CO ₃	< 1 (7 ^c)
9	Pd[P(t-Bu) ₃] ₂	K ₃ PO ₄	2 (14 ^c)
10	Pd[P(t-Bu) ₃] ₂	DBU	5 (5 ^c)
11	Pd[P(t-Bu) ₃] ₂	TsOH	86 (83)
12	Pd[P(t-Bu) ₃] ₂	CF₃SO₃H	78
13	Pd[P(t-Bu) ₃] ₂	CH₃SO₃H	77
14	Pd[P(t-Bu) ₃] ₂	CH₃CO₂H	82
15	Pd[P(t-Bu) ₃] ₂	CF ₃ CO ₂ H	75
16 ^d	Pd[P(t-Bu) ₃] ₂	none	84
17 ^d	Pd[P(t-Bu) ₃] ₂	TsOH	> 99 (97)

^{*a*} Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), additive (bases: 0.15 mmol; or acids: 0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at 80 °C in a sealed tube under a N₂ atmosphere for 24 h. ^{*b*} The yield was determined by HPLC using (*E*)-1-methoxy-4-styrylbenzene (**3a**, t_R = 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. Otherwise specified, the isolated yield is Page 2 of 4

depicted in the parentheses. ^c The reaction was run at $80^{\circ}C_{Online}$ (0.15 mmol) was used instead of **2a** (0.15 mmol).0.1039/C6CC06089G

In general, bases benefit the Pd-catalyzed Mizoroki-Heck reaction with aryl halides or pseudo-halides by neutralizing the acid formed and allowing for more effective ligand recovery.⁷ However, when $[Ph_2SR_{fn}][OTf]$ ($R_{fn} = CF_3$, CH_2CF_3) were employed as the cross-coupling partners, the reaction was seriously inhibited by the use of bases. This might be attributed to the tendency of decomposition of [Ph₂SR_{fn}][OTf] under the basic conditions,¹³ where the breakage of S-CF₃ [Ph₂SCF₃][OTf] or the defluorination of bond of $[Ph_2SCH_2CF_3][OTf]$ via β -F elimination might happen,⁵ respectively. This assumption was partially supported by the ¹⁹F NMR analysis of the reaction mixtures of [Ph₂SCF₃][OTf] or [Ph₂SCH₂CF₃][OTf], NaHCO₃, and DMF at room temperature, where the cations of [Ph₂SR_{fn}][OTf] were inevitably decayed (see SI).

With the optimized reaction conditions in hand, the scope of the reaction was investigated. To our delight, styrenes with either electron-donating or -withdrawing groups on the phenyl rings were all smoothly converted by 2a or 2b, which gave the cross-coupling products (3b-p) in 21-99% yields (Table 2). The position of the substituents on the phenyl rings has considerable influence on the reaction. Treatment of 1methoxy-2-vinylbenzene (1b) with 2a or 2b at room temperature under N₂ in the presence of TsOH (10 mol%) and Pd[P(t-Bu)₃]₂ (10 mol%) provided **3b** in 70% or 75% yield, while 1-methoxy-3-vinylbenzene (1c) similarly reacting with 2a or 2b afforded 3c in 96% yield. Functional groups such as OAc, F, Cl, Br, CN, NO₂, and CHO were tolerated in the reaction (3k, 3n-p), and even the reaction between 1-iodo-4-vinylbenzene (11) and 2a or 2b could supply 31 in 23% or 21% yield. (Note: Since 1I was completely consumed in the reaction, the breakage of the C-I bond of 1I and/or 3I under the standard reaction conditions might occur which led to side reaction and poor yield of 3I). Moreover, the unconjugated olefin, enolate, and electron-deficient alkenes are also suitable substrates to the reactions. For instance, allyl acetate (1q) or (allyloxy)benzene (1r) reacting with 2b in the presence of TsOH and $Pd[P(t-Bu)_3]_2$ at room temperature for 24 h provided **3q** in 61% or 84% yield. Treatment of vinyl benzoate (1s) with 2b under the standard reaction conditions for 2 days afforded a mixture of E- and Z-isomers of 3s in 92% yield (molar ratio of E / Z = 1 : 0.17). The Pd-catalyzed Mizoroki-Heck reaction of **2b** with ethyl acrylate (1t) and methyl acrylate (1u) at 60 °C for 24 h produced **3t** in 74% yield and **3u** in 60% yield, respectively. The higher reaction temperature benefited the transformation of electron-deficient conjugated alkenes since the reactions at room temperature gave lower yields of the desired products. Besides, acrylonitrile (1v) reacted with 2b to afford 3v in 83% yield with a trace amount of the Z-isomer and the diarylation product (3,3-diphenylacrylonitrile), which was determined by ¹H NMR analysis of the isolated product (see SI). Furthermore, the Suzuki-Miyaura and Mizoroki-Heck crosscouplings of 2a (or 2b) with 1w can be performed in one pot Published on 25 August 2016. Downloaded by Purdue University on 25/08/2016 09:42:05.

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(Scheme 1). Treatment of **1w** with **2a** or **2b** (2 equiv) at room temperature in the presence of 10 mol% $Pd[P(t-Bu)_3]_2$ and equal equivalent of NaHCO₃ for 24 h provided **3w** in 44% or 57% yield, respectively, indicating the feasibility of simultaneous difunctionalization by phenylsulfonium salts.

Table 2 Pd-catalyzed Mizoroki-Heck-type reactions of 2a or 2b with alkenes



In addition, other phenylsulfonium salts either with or without fluorine-containing alkyl groups were tested in the reaction (Table 3). It was surprising that the Pd-catalyzed Mizoroki-Heck cross-coupling of (2,2difluoroethyl)diphenylsulfonium triflate (2c) with 1a under the standard reaction conditions afforded 3a in 8% yield, whereas the reaction of (2-fluoroethyl)diphenylsulfonium triflate (2d) with 1a gave 3a in 79% yield. (Ethyl)diphenylsulfonium triflate (2e), the non-fluorinated version of 2b, reacted with 1a >99% provided 3a in 96% vield (vs vield). (Pentafluoroethyl)diphenylsulfonium triflate (2f), the fully fluorinated version of 2b, however, produced 3a in 1% yield. Treatment of (2,2,3,3,3-pentafluoropropyl)diphenylsulfonium triflate (2g) with 1a supplied 3a in 83% yield. The strong electronegativity of fluorine atoms and/or the tendency of $\beta\mbox{-}F$ elimination might cause these distinct differences, but the rules of the impacts of fluorine content on the reaction still

remain unclear at this stage. Triphenylsulfonium, triflate, ina well-known radical precursor and photoacido generator, 1408an also gave 3a in 59% yield under the standard reaction conditions. (Methyl)diphenylsulfonium triflate (2i), the nonfluorinated version of 2a, reacted with 1a and afforded 3a in 81% vield (vs 86% yield). Treatment of dimethyl(phenyl)sulfonium triflate (2j) with 1a furnished 3a in 13% yield. 1-Phenyl(tetrahydro)thiophenium (2k) that was successfully used as a cross-coupling partner in Suzuki-Miyaura reactions^{8a-d} was treated with **1a** to provide **3a** in 9% yield under the standard reaction conditions. These results suggest that arylsulfonium triflates either with or without S-fluoroalkyl groups can be mildly employed in Pd-catalyzed Mizoroki-Heck cross-coupling and that the reactions with 2a and 2b works better than those with 2c-k under the standard conditions.





standard ($t_R = 8.468 \text{ min}, \lambda_{max} = 302.2 \text{ nm}, \text{ water/methanol} = 20: 80 (v / v), ^ 878% from Pd(OAC)_2 (2 mol %) / imidazolijum / THF / r.t. (Ref 15a); 73% from [Ru(bpy)_{3l2}^+ (1 mol%) / DMSO / 455 nm LED / 20 °C, 2 h (Ref 15b); 15% from Pd(OAC)_2 (1 mol %) / water / r.t. / 16 h (Ref 15c), ^ 89% from Pd(II) / NAHCO_3 / THF / 50 °C / 16 h (Ref 15d), ^ 776% from Et_3N / diatomite-supported Pd (0.1 mol %) / NMP (Ref 15e); 97% from Pd_2(dba)_3 (0.2 mol%) / thiadiazolidine oxide (0.4 mol%) / DMF / DMF / 200 °C / 10 min / microwave. (Ref 15f); 98% from AgOAc / Pd(OAc)_2 / ACCH / 2 h / 110 °C (Ref 15g). ^ 81% (43:57 linear/branched mixture) from Pd_2(dba)_3 (5 mol%) / dppp (10 mol%) / NEt_3 (Ref 15h).$

To compare the efficiency of phenylsulfonium triflates with other commonly used cross-coupling partners in this Heckconversion. the reactions between 1a type and benzenediazonium tetrafluoroborate (21), diphenyliodonium triflate iodobenzene (2n) (2m), or phenyl trifluoromethanesulfonate (20) were explored (Table 3). It was found that 2l reacting with 1a in the presence of TsOH and $Pd[P(t-Bu)_3]_2$ in DMF at room temperature for 24 h gave **3a** in 29% yield (previous complex methods supplied **3a** in 78%,^{15a} 73%,^{15b} or 15%^{15c} yield). Treatment of **2m** with **1a** under the standard reaction conditions furnished **3a** in 97% yield (89% yield in literature^{15d}). The reaction of **2n** or **2o** with **1a** gave trace of 3a (76-98% yield by harsh methods^{15e-h}). Similarly, when 2p was treated with 1a under the standard reaction condition, 1% of 3a was obtained, which had been used as a phenylation reagent at high reaction temperature.9a These

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results imply that phenylsulfonium triflates (**2a**, **2b**, **2d**, **2e**, **2g**, and **2i**) are powerful cross-coupling participants in Pdcatalyzed Mizoroki-Heck reaction with styrene at room temperature.

In conclusion, we have found that $[Ph_2SR_{fn}][OTf]$ ($R_{fn} = CF_3$, CH_2CF_3) can be used as the effective cross-coupling partners in Pd-catalyzed Mizoroki-Heck-type reaction with alkenes. The functionalization of various conjugated and unconjugated alkenes by $[Ph_2SR_{fn}][OTf]$ (**2a**, $R_{fn} = CF_3$ or **2b**, $R_{fn} = CH_2CF_3$) in the presence of 10 mol% Pd[P(*t*-Bu)_3]_2 and TsOH at room temperature provided the corresponding phenylation products in good to high yields. The use of acids significantly improved the reaction. Other phenylsulfonium salts such as **2d**, **2e**, **2g**, **2h**, and **2i** are also available reagents in the reaction. All these salts could be conveniently synthesized by the known means (see ESI). This protocol demonstrates a new class of cross-coupling participants for Heck-type reaction and yields very important insights into the reactivity of phenylsulfonium salts either with or without fluorine-containing alkyl groups.¹⁶

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- 16 The non-symmetric aryl(phenyl) trifluoromethyl sulfonium salts are also applicable to the reaction. The Pd-catalyzed reaction of $[(4-ClC_6H_4)(Ph)SCF_3][OTf]$ (2q) or $[(2,4-(Me)_2C_6H_3)(Ph)SCF_3][OTf]$ (2r) with 1a under the standard conditions gave a mixture of arylation and phenylation products in good yield, respectively (see ESI).

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