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SHORT COMMUNICATION

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Switchable 2,2,2-Trifluoroethylation and *gem*-Difluorovinylation of Organoboronic Acids with 2,2,2-Trifluorodiazoethane

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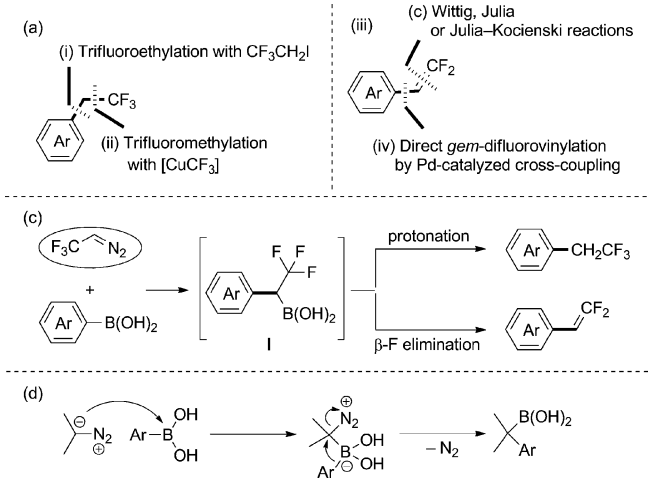
The transition-metal-free 2,2,2-trifluoroethylation and *gem*-difluorovinylation of arylboronic acids were developed. By employing different reaction conditions, these transformations provide both (2,2,2-trifluoroethyl)arenes and *gem*-difluorovinylarenes from arylboronic acids and 2,2,2-trifluorodiazoethane. The operation is simple and scalable with good functional group tolerance.

Introduction

Fluorinated organic molecules have found important applications in various fields including pharmacy and materials.[1] The development of new methods for introducing fluorinated moieties has attracted great attention.[2] In particular, trifluoromethylation has been extensively studied in recent years.[3] In contrast, related 2,2,2-trifluoroethylation remains largely unexplored, regardless of the fact that trifluoromethyl-containing molecules also have various applications.[4] McLoughlin and Thrower in 1969 reported the Cu^0-mediated 2,2,2-trifluoroethylation of iodobenzene with trifluoroethyl iodide (Scheme 1, a, path i).[5] In 2012, the Pd^0-catalyzed 2,2,2-trifluoroethylation of trifluoroethyl iodide with organoboronic acids and esters was developed by Hu[6] and Zou.[7] Trifluoromethylation of benzyl halides represents an alternative approach towards aromatic 2,2,2-trifluoroethylation.[8] For example, trifluoromethylation has been recently achieved via a [$CuCF_3$] species generated from copper powder and the Umemoto regent by Shibata and co-workers (Scheme 1, a, path ii).[8g]

On the other hand, *gem*-difluoroalkenes (CF_2 = CHAr) as another important class of fluorinated organic compounds also have potential applications in various fields.[9–11] However, currently only few methods are available for introducing *gem*-difluorovinyl groups into arenes. Traditional methods for preparing *gem*-difluoroalkenes include the Wittig reaction,[12] the Julia reaction[13] (Scheme 1, b, path iii), and transition-metal-catalyzed cross-coupling reactions (Scheme 1, b, path iv).[14] In general, these methods suffer from some drawbacks, such as substrate scope, tedious transformations, and expensive transition-metal catalysts. Hence, the development of an effective strategy for the *gem*-difluorovinylation of arenes that can largely avoid these drawbacks is highly desirable.



Scheme 1. Methods for the synthesis of trifluoroethylated and difluorovinylated arenes.

Herein, we report a novel method to access both 2,2,2-trifluoroethylated and *gem*-difluorovinylated arenes in a switchable manner from organoboronic acids and 2,2,2-trifluorodiazoethane (Scheme 1, c). This reaction proceeds under transition-metal-free conditions and uses trifluorodiazoethane as the fluorinating agent. The preparation of trifluorodiazoethane was first reported in the 1940s from ammonium salts.[15] However, this reagent did not arouse attention until it was recently used as a valuable CF_3-containing reagent.[16] We previously reported the metal-free reaction of diazo compounds with boronic acids.[17] This type

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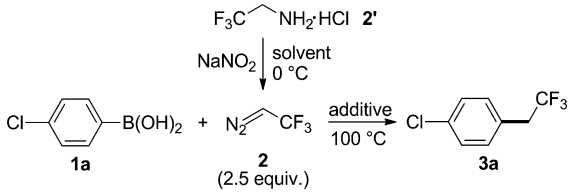
of transformation follows a simple pathway that includes the coordination of the electron-rich diazo carbon atom to the electron-deficient boron center, which is followed by a 1,2-shift of the carbon ligand from boron to carbon to form a C–C bond (Scheme 1, d).[18–20] Thus, if the diazo substrate is CF_3CHN_2, intermediate **I** is expected to be formed, which undergoes subsequent protonation or β-F elimination to achieve 2,2,2-trifluoroethylation or *gem*-difluorovinylation (Scheme 1, c).

Results and Discussion

At first, 2,2,2-trifluorodiazoethane (**2**) was prepared from 2,2,2-trifluoroethylammonium chloride (**2′**) in different solvents according to the method reported Carreira and co-workers.[16e–16i] Then, we investigated the reaction of (*p*-chlorophenyl)boronic acid with CF_3CHN_2 in different solvents. In toluene and 1,2-dichloroethane (DCE), expected 2,2,2-trifluoroethylated product **3a** was formed in 20 and 12% yield, respectively, on the basis of ^{19}F NMR spectroscopy (Table 1, entries 1 and 2). In polar solvents, such as THF, dioxane, MeCN, MeOH, and DMF, product **3a** was not obtained (Table 1, entry 3). To further optimize the reaction, a variety of additives were screened (Table 1, entries 4–8), and KF as a weaker base was identified as an effective additive (Table 1, entry 8). Replacing KF with NH_4F or NH_4Cl further improved the yield (Table 1, entries 9 and 10). Finally, we found that a one-pot reaction directly using **2′** worked well and gave **3a** in 80% yield on the basis of ^{19}F NMR spectroscopy (Table 1, entry 11). Given that the crude product contained a small amount of *gem*-difluoroalkene, which was inseparable from **3a** by silica gel column chromatography, the crude material was treated with KF in DMSO at 100 °C to convert the *gem*-difluoroalkene byproduct into separable compounds. In this way, 2,2,2-trifluoroethylated product **3a** was isolated in 71% yield.

With the optimized conditions, we studied the substrate scope for this direct 2,2,2-trifluoroethylation reaction. As shown in Table 2, a series of arylboronic acids were submitted to the reaction under the optimized conditions. The corresponding (2,2,2-trifluoroethyl)arenes were obtained in moderate to good yields. The reaction proceeded smoothly with arylboronic acids bearing halide substituents and gave corresponding 2,2,2-trifluoroethylated products **3a**–**c**, **3q** **3r**, and **3s**. Notably, even an iodo substituent on the aromatic ring was tolerated in the reaction (see product **3c**), which is beneficial for subsequent transformations. Notably, inter-

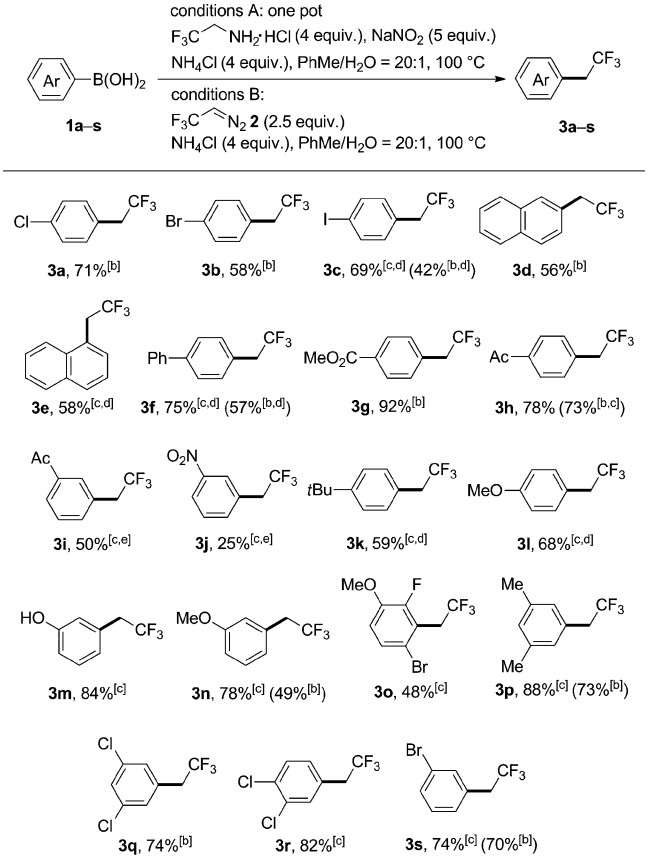
Table 1. Optimization of the reaction conditions.[a]



Entry	Solvent	Additive (4 equiv.)	Yield [%][b]
1	PhMe/H_2O, 20:1	–	20
2	DCE/H_2O, 20:1	–	12
3	PS[c]/H_2O, 20:1	–	–
4	PhMe/H_2O, 20:1	K_2CO_3	–
5	PhMe/H_2O, 20:1	iPr_2NH	45
6	PhMe/H_2O, 20:1	LiO*t*Bu	20
7	PhMe/H_2O, 20:1	CsF	31
8	PhMe/H_2O, 20:1	KF	61
9	PhMe/H_2O, 20:1	NH_4F	72
10	PhMe/H_2O, 20:1	NH_4Cl	75
11[d]	PhMe/H_2O, 20:1	NH_4Cl	80 (71)[e]

[a] If not otherwise noted, the reaction was performed with **1a** (0.22 mmol), **2** (0.55 mmol) in solvent (1 mL). [b] The yield was determined by ^{19}F NMR spectroscopy by using $PhCF_3$ as an internal standard. [c] PS = polar solvents, including THF, dioxane, MeCN, MeOH, and DMF. [d] One-pot reaction with the use of **2′** (0.88 mmol). [e] The yield of the isolated product obtained by treatment of the crude product with KF in DMSO at 100 °C for 10 h is given in parentheses.

Table 2. The scope of the 2,2,2-trifluoroethylation reaction.[a]



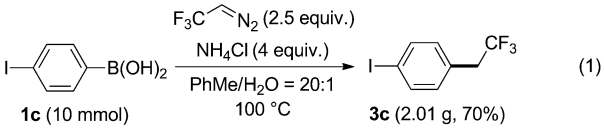
[a] If not otherwise noted, the reaction conditions are as follows: $ArB(OH)_2$ (0.5 mmol), PhMe/H_2O = 20:1 (2.5 mL), 24 h; upon completion of the reaction, the crude product was treated with KF in DMSO (3 mL) at 100 °C. All reported yields refer to yields of the isolated products after column chromatography. [b] One-pot reaction under conditions A. [c] Under conditions B. [d] HCO_2NH_4 was used as an additive instead of NH_4Cl. [e] NH_4SCN was used as an additive instead of NH_4Cl.

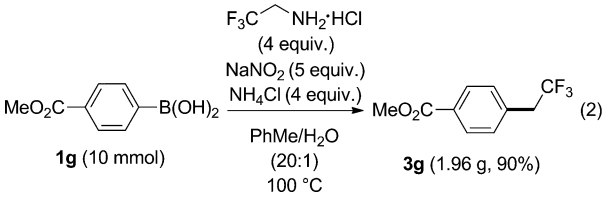
mediate **I** would be oxidized to the alcohol with electron-rich boronic acids under oxidative conditions.

The reaction seemed to be slightly affected by electronic effects. The 2,2,2-trifluoroethylation reaction proceeded smoothly for substrates bearing both electron-withdrawing and -donating substituents. For arylboronic acids bearing electron-withdrawing substituents, such as ester (see **1g**), ketone (see **1h** and **1i**), and nitro groups (see **1j**), the reaction afforded the corresponding trifluoroethylated products; however, the yields varied depending on the substituents. The yields for arylboronic acids bearing electron-donating substituents, such as *tert*-butyl (see **1k**), methoxy (see **1l**), and methyl (see **1p**), showed modest fluctuation. Notably, a free hydroxy group was compatible with the reaction, and desired product **3m** was obtained in good yield.

The yields could be improved by using HCO_2NH_4 as an additive instead of NH_4Cl if arylboronic acids bearing electron-donating substituents in the *para* position of the aromatic ring were used as substrates (see **3k** and **3l**), whereas NH_4SCN as the additive enhanced the yield with arylboronic acids bearing electron-withdrawing groups in the *meta* position (see **3i** and **3j**).

To demonstrate the practical usefulness of this reaction, gram-scale experiments were performed with the arylboronic acids **1c** and **1g**. As shown in Equations (1) and (2), the reaction proceeded smoothly to afford corresponding 2,2,2-trifluoroethylated products **3c** and **3g** in good yields.

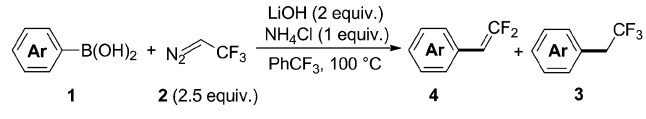


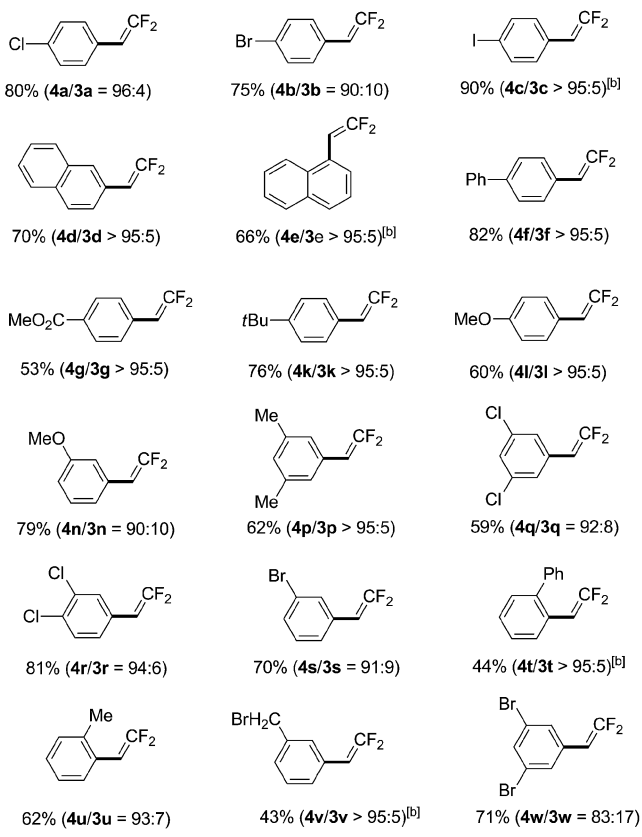


Given that difluoroalkenes were observed as byproducts in this reaction, we next conceived that a useful method for the synthesis of difluoroalkenes may be developed by modulating the reaction conditions to enable fluoride elimination[21] from intermediate **I** (shown in Scheme 1, c) to become the major reaction pathway. Considering that basic conditions can hinder protonation and are thus conducive to the formation of the β-trifluoroethyl carbanion, the addition of base additives was examined. Through extensive screening, LiOH was identified as the base that could afford a satisfactory yield of the desired difluoroalkenes, whereas other bases such as $Mg(OH)_2$, $Ca(OH)_2$, and KOH gave complex mixtures. Notably, this *gem*-difluorovinylation method is not compatible with the one-pot reaction as described for conditions A in Table 2.

Under the optimized reaction conditions for *gem*-difluorovinylation, the scope of arylboronic acids was studied. As shown in Table 3, a series of boronic acids were submitted to the reaction with **2**. The reaction afforded corresponding *gem*-difluoroalkenes **4** in moderate to good yields, along with the formation of a small amount of (2,2,2-trifluoroethyl)arenes as the byproducts. The functional group tolerance is similar to that of the corresponding 2,2,2-trifluoroethylation reaction.

Table 3. *gem*-Difluorovinylation of arylboronic acids with 2,2,2-trifluorodiazoethane.[a]





[a] Reaction conditions: $ArB(OH)_2$ (0.5 mmol), $PhCF_3$ (2.5 mL), 24 h, 100 °C, yields of the isolated products are given, and the ratio was obtained by ^1H NMR spectroscopy. [b] HCO_2K was used instead of (LiOH + NH_4Cl).

Conclusions

In summary, a transition-metal-free method for direct 2,2,2-trifluoroethylation and *gem*-difluorovinylation by the reaction of arylboronic acids with 2,2,2-trifluorodiazoethane has been developed. The transformation is switchable: under weak acidic conditions, 2,2,2-trifluoroethylation proceeds efficiently, whereas under weak basic conditions *gem*-difluorovinylation becomes the major reaction path. Both transformations are performed under mild conditions and various functional groups are tolerated.

Experimental Section

Procedure for 2,2,2-Trifluoroethylation under Conditions A: Arylboronic acid (0.5 mmol), 2,2,2-trifluoroethylamine hydrochloride (2.0 mmol), sodium nitrite (2.5 mmol), and ammonium chloride (2.0 mmol) were added into a Schlenk tube. Toluene (2.5 mL) and water (125 μL) were then added. The mixture was stirred at 100 °C for 24 h. After the mixture had cooled down to room temperature, the solvent was removed under reduced pressure. DMSO (2.5 mL) and potassium fluoride (1.0 mmol) were added to the crude product. Then, the mixture was heated at 100 °C for 10 h. After the solution had cooled down to room temperature, water was added, and the mixture was extracted with DCE. Evaporation of the solvent gave the crude product, which was purified by column chromatography with silica gel to afford product **3**.

Procedure for 2,2,2-Trifluoroethylation under Conditions B: Arylboronic acid (0.5 mmol) and ammonium chloride (2.0 mmol) were added into a Schlenk tube. Toluene (1 mL), 2,2,2-tirfluorodiazoethane (0.88 M in toluene, 1.5 mL), and water (125 μL) were added. The mixture was stirred at 100 °C for 24 h. Then the solution was treated following the same procedure as that described for conditions A.

Procedure for the *gem*-Difluorovinylation: Arylboronic acid (0.5 mmol), ammonium chloride (0.5 mmol), and lithium hydroxide (1.0 mmol) were added into a Schlenk tube. $PhCF_3$ (1 mL) and 2,2,2-tirfluorodiazoethane (0.88 M in $PhCF_3$, 1.5 mL) were then added. Then, the mixture was stirred at 100 °C for 24 h. After the mixture had cooled down to room temperature, the solvent was evaporated to give the crude product, which was purified by column chromatography on silica gel to afford the *gem*-difluorovinylated product.

Supporting Information (see footnote on the first page of this article): Experimental procedures and copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgments

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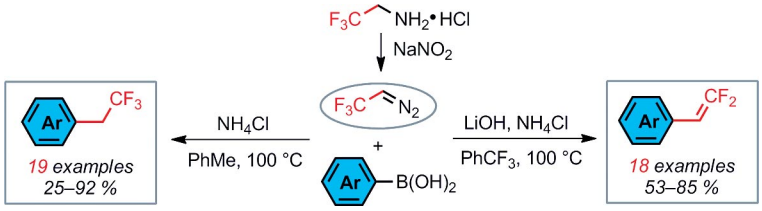
Switchable Transformations



The transition-metal-free 2,2,2-trifluoroethylation and *gem*-difluorovinylation of arylboronic acids are reported. By employing different reaction conditions, these transformations provide both (2,2,2-trifluoroethyl)arenes and *gem*-difluorovinylarenes from arylboronic acids and 2,2,2-trifluorodiazoethane. The operation is simple and scalable with good functional group tolerance.

Keywords: Boron / Fluorine / Diazo compounds / Trifluoroethylation / *gem*-Difluorovinylation

