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Perfluoroalkanesulfonylation of Alkynyl(phenyl)iodonium Tosylates by the Weakly Nucleophilic Sodium Perfluoroalkanesulfinates

Jia-Bin Han,[a] Lian Yang,[a] Xing Chen,[a] Gao-Feng Zha,[a] and Cheng-Pan Zhang[a,*]

[a] School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, 205 Luoshi Road, Wuhan 430070, People's Republic of China
E-mail: cpzhang@whut.edu.cn or zhangchengpan1982@hotmail.com

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Abstract: An additive- and transition metal-free perfluoroalkanesulfonylation of alkynyl(phenyl)iodonium tosylates with sodium perfluoroalkanesulfinates ($R_{fn}SO_2Na$) is described. The poorly nucleophilic $R_{fn}SO_2Na$ reacted with alkynyl(phenyl)iodonium salts in dichloromethane at room temperature under a nitrogen atmosphere for 5–60 minutes to afford a variety of acetylenic triflones and alkynyl perfluoroalkyl sulfones in good to quantitative yields. The position of substituents on the phenyl rings of the arylethynyl moiety in the iodonium salts had a big influence on the reaction. The formation of five-membered cyclic vinyl sulfones suggested that the reaction proceeds *via* an alkylidene carbene intermediate. Furthermore, successful scaling-up of the reaction demonstrates the practicality of the new method. Advantages of the method include short reaction times, mild conditions, and the easy access to perfluoroalkanesulfonylation reagents ($R_{fn}SO_2Na$).

Keywords: alkynes; fluorine; iodonium salts; perfluoroalkanesulfonylation; substituent effects; transition metal-free conditions

Fluorine has a small atomic size and the highest electronegativity among all elements (Pauling scale), and it forms the strongest C–X single bonds with carbon atoms.[1] The introduction of fluorine and fluorine-containing groups into organic molecules can desirably modulate their physical, chemical, and biological properties.[2] Fluorination has been widely used in the synthesis of potent pharmaceuticals, agrochemicals, and functional materials.[2,3] Among the prevalent fluorine-containing moieties, the perfluoroalkanesulfonyl ($R_{fn}SO_2$) group has become one of the most important functionalities in the construction of new organic scaffolds due to its strong electron-withdrawing ability and high lipophilicity.[1,4] The combination of $R_{fn}SO_2$ segments with alkynes has resulted in alkynyl perfluoroalkyl sulfones which have been confirmed as highly reactive building blocks.[4] Acetylenic triflones are useful building blocks for the preparation of vinyl triflones,[5] and they are reliable reagents for the radical alkynylation of Csp^3–H bonds.[6] They can also undergo [4+2] or [3+2] cycloaddition with dienes or 1,3-dipoles to furnish a variety of CF_3SO_2-substituted heterocycles.[7] In view of their wide applications, the development of an effective method to prepare alkynyl perfluoroalkyl sulfones is of broad interest.

To the best of our knowledge, the known synthetic methods to prepare acetylenic triflones require *n*-BuLi or Na as the base and Tf_2O as the trifluomethanesulfonylation reagent. Such methods suffer from disadvantages such as a narrow range of substrates, harsh reaction conditions, and the use of toxic and expensive agents.[5–8] Because of the lack of variety of perfluoroalkanesulfonylation reagents [$R_{fn}SO_2X$ (X = F, Cl) or $(R_{fn}SO_2)_2O$], the production of diversified alkynyl perfluoroalkyl sulfones from terminal alkynes is severely limited.

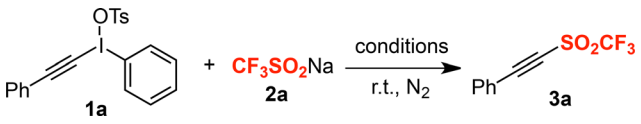
Perfluoroalkanesulfinates ($R_{fn}SO_2M$) including Langois' reagent (CF_3SO_2Na), derived from $R_{fn}X$ (X = I, Br) by a sulfinatodehalogenation reaction and others,[3j] have been exploited as versatile perfluoroalkylation and perfluoroalkylthiolation reagents in the last several years (especially CF_3SO_2Na as trifluoromethylation and trifluoromethylthiolation reagents).[9] They can also be used as perfluoroalkanesulfonylation reagents.[10,11] Trifluoromethanesulfonylation of sp^3 carbon electrophiles by CF_3SO_2Na provided the corresponding triflated products, the utility of which was fully demonstrated in organic synthesis.[10a–c] Owing to the strong electronegativity of the CF_3 group,[3j] CF_3SO_2Na reacts slowly with electrophiles, leading to

a limited substrate scope in reactions involving nucleophilic CF_3SO_2Na components.[10] Transition metal-catalyzed trifluoromethanesulfonylation of sp^2 carbon electrophiles by CF_3SO_2Na could be accomplished to build C(sp^2)–SO_2CF_3 bonds.[11] However, in these reactions only diaryliodonium salts, arenediazonium tetrafluoroborates, and aryl triflates have been investigated.[11] Compared to perfluoroalkylation and perfluoroalkylthiolation, the perfluoroalkanesulfonylation with $R_{fn}SO_2Na$ is much less studied, and the construction of C(sp)–SO_2R_{fn} bonds by $R_{fn}SO_2Na$ is rarely reported.[12] Given the great interest in alkynyl perfluoroalkyl sulfones, we were motivated to develop a convenient synthetic method to these compounds with the easily accessed and bench-stable $R_{fn}SO_2Na$ salts.

On the other hand, hypervalent alkynyl(aryl)iodonium salts are very versatile reagents capable of reacting with a variety of nucleophiles.[13,14] Reactions between alkynyl(aryl)iodonium salts and the non-fluorinated alkyl or aryl sulfinates have supplied a large number of alkynyl sulfones and/or cyclic vinyl sulfones.[15] Although 1-alkynyl-λ^3-bromanes can undergo a tandem reaction with trifluoromethanesulfinate,[12a] the interaction between alkynyl(phenyl)iodonium salts and CF_3SO_2Na was unknown. Alkynyl(phenyl)iodonium salts are less electrophilic than 1-alkynyl-λ^3-bromanes,[12] and sodium perfluoroalkanesulfinates bearing long-chain perfluoroalkyl groups have much poorer nucleophilicity than the non-fluorinated analogues (even poorer than CF_3SO_2Na).[3j,10] Nevertheless, it is notable that all these reagents can be conveniently synthesized.[3j,12,13] Hence, we wondered whether the reaction of $R_{fn}SO_2Na$ with alkynyl(phenyl)iodonium salts could expediently form the useful alkynyl triflones.

To our delight, the reaction of phenylethynyl(phenyl)iodonium tosylate (**1a**) with an equal equivalent of CF_3SO_2Na in CH_2Cl_2 at room temperature under a nitrogen atmosphere for 2 h provided **3a** in 70% yield (entry 1, Table 1). By varying the molar ratio of CF_3SO_2Na from 1.0 to 1.5 or 2.0 equivalents and a reaction time of 6 h, **3a** was obtained in 87% or 91% yield, respectively (entries 2 and 3, Table 1). Further increments of CF_3SO_2Na to 3.0 or 4.0 equivalents did not improve the trifluoromethanesulfonylation (entries 4 and 5, Table 1). Furthermore, reaction of **1a** with CF_3SO_2Na (2 equiv.) in CH_2Cl_2 at room temperature for 0.5 h also afforded **3a** in 91% yield, suggesting that the trifluoromethanesulfonylation is completed in 30 min (entry 6, Table 1). Taking phenylethynyl(phenyl)iodonium trifluoroacetate instead of **1a** in the same reaction for 2 h provided **3a** only in 57% yield (entry 7, Table 1), despite the former being more stable than the latter (**1a**).[15c] Moreover, the choice of solvent had a big influence on the reaction. Reactions of **1a** with CF_3SO_2Na (2 equiv.) in $CHCl_3$ and toluene for 0.5 h afforded **3a** in 45% and 35% yield, respectively (entries 8 and 9, Table 1). Nonetheless, when using CH_3CN, THF, DMF, and acetone as solvents, there was no **3a** obtained (entries 10–13, Table 1). These results implied that CH_2Cl_2 is a suitable solvent for the reaction. In addition, the reaction of CF_3SO_2Na with 1-phenylethynyl-1,2-benziodoxol-3(1*H*)-one (EBX, the commonly used alkynylation reagent) instead of **1a** failed to afford **3a** (entry 14, Table 1). EBX had successfully been used for the alkynylation of the non-fluorinated sulfinates.[13,15] This lack of reactivity is believed to stem from the poor nucleophilicity of sodium trifluoromethanesulfinate.

Table 1. Trifluoromethanesulfonylation of **1a** by CF_3SO_2Na.[a]

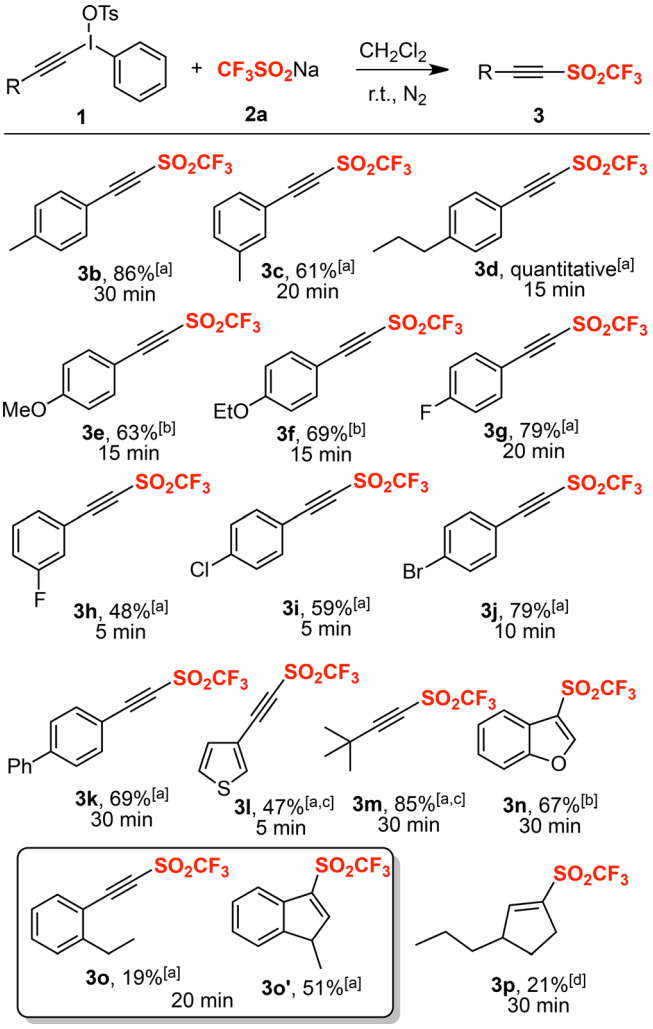


Entry	**1a**:**2a**[b]	Conditions	Yield (**3a** [%])[c]
1	1:1	CH_2Cl_2, 2 h	70
2	1:1.5	CH_2Cl_2, 6 h	87
3	1:2	CH_2Cl_2, 6 h	91
4	1:3	CH_2Cl_2, 6 h	86
5	1:4	CH_2Cl_2, 6 h	67
6	**1:2**	**CH_2Cl_2, 0.5 h**	**91**
7[d]	1:2	CH_2Cl_2, 2 h	57
8	1:2	$CHCl_3$, 0.5 h	45
9	1:2	toluene, 0.5 h	35
10	1:2	CH_3CN, 0.5 h	0
11	1:2	THF, 0.5 h	0
12	1:2	DMF, 0.5 h	0
13	1:2	acetone, 0.5 h	0
14[e]	1:2	CH_2Cl_2, 4 h	0

[a] *Reaction conditions:* **1a** (0.1 mmol), CF_3SO_2Na (0.1, 0.15, 0.2, 0.3, or 0.4 mmol), solvent (1 mL), room temperature, N_2.
[b] Molar ratio.
[c] Yields were determined by HPLC using [(trifluoromethanesulfonyl)ethynyl]benzene (**3a**) as the external standard [t_R = 6.922 min, λ_{max} = 260.6 nm, CH_3CN/H_2O = 65:35 (v/v)].
[d] Phenyl(phenylethynyl)iodonium trifluoroacetate was used instead of **1a**.
[e] 1-Phenylethynyl-1,2-benziodoxol-3(1*H*)-one (EBX) was used instead of **1a**.

With the optimized reaction conditions in hand, the scope of the reaction was investigated. Arylethynyl(phenyl)iodonium tosylates like **1b–l** reacted smoothly with CF_3SO_2Na in CH_2Cl_2 at room temperature under N_2 to give the corresponding acetylenic triflones (**3b–l**) in moderate to quantitative yields (Table 2). Treatment of (3,3-dimethylbutynyl)(phenyl)iodonium tosylate (**1m**) with CF_3SO_2Na afforded 3,3-dimethyl-1-(trifluoromethanesulfonyl)butyne (**3m**) in 85% yield (determined by ^{19}F NMR). TLC technique was employed

Table 2. Transition metal- and additive-free trifluoromethanesulfonylation of **1b–p** by CF_3SO_2Na.



[a] *Reaction conditions:* **1** (0.2 mmol), CF_3SO_2Na (0.4 mmol), CH_2Cl_2 (2 mL), room temperature, N_2. Isolated yield.

[b] *Reaction conditions:* **1** (0.3 mmol), CF_3SO_2Na (0.2 mmol), CH_2Cl_2 (2 mL), room temperature, N_2. Isolated yield.

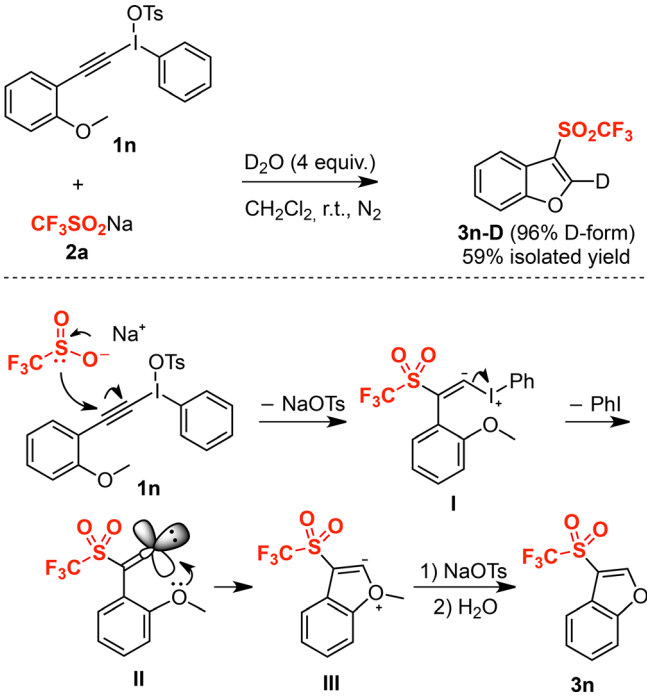
[c] Yield was determined by ^{19}F NMR using $C_6H_5CF_3$ as an internal standard.

[d] *Reaction conditions:* 1-octyne (6.0 mmol), Koser's reagent (2.0 mmol), CH_2Cl_2 (10 mL), reflux, 4 h, then CF_3SO_2Na (4.0 mmol), room temperature, 30 min. Isolated yield.

to monitor the progress of the reaction. Once the iodonium salt was completely consumed, the product was isolated from the reaction mixture by flash column chromatography. The position of the substituents on the phenyl rings of arylethynyl iodonium salts had a significant impact on the reaction. It was found that iodoniums bearing *meta*-substitution on the arylethynyl groups gave lower yields of the desired products than those with *para*-substitution (e.g., **3b** *vs.* **3c**, **3g** *vs.* **3h**). [(4-Methoxyphenyl)ethynyl](phenyl)iodonium tosylate (**1e**) reacted with CF_3SO_2Na under the standard conditions for 15 min to provide 1-methoxy-4-[(trifluoromethanesulfonyl)ethynyl]benzene (**3e**) in 63% yield, whereas the reaction of [(2-methoxyphenyl)ethynyl](phenyl)iodonium tosylate (**1n**) with CF_3SO_2Na afforded 3-(trifluoromethanesulfonyl)benzofuran (**3n**) in 67% yield. Additionally, treatment of [(2-ethylphenyl)ethynyl](phenyl)iodonium tosylate (**1o**) with CF_3SO_2Na under the standard reaction conditions gave a mixture of 1-methyl-3-(trifluoromethanesulfonyl)-1*H*-indene (**3o′,** 51% yield) and 1-ethyl-2-[(trifluoromethanesulfonyl)ethynyl]benzene (**3o**, 19% yield). These findings indicated that an alkylidene carbene intermediates might be formed in the reaction, which underwent 1,2-rearrangement to yield acetylenic triflones (e.g., **3a–m** and **3o**) or was inserted into an appropriate C–H bond to form five-membered cyclic vinyl sulfones (e.g. **3o′**).[12,14–16] Also, alkynyl(phenyl)iodoniums bearing stronger *para*-electron-withdrawing groups such as CO_2Me and $COCH_3$ on the arylethynyl moieties could also give the desired trifluoromethanesulfonylation products, which were unstable and rapidly decomposed during the work-up.

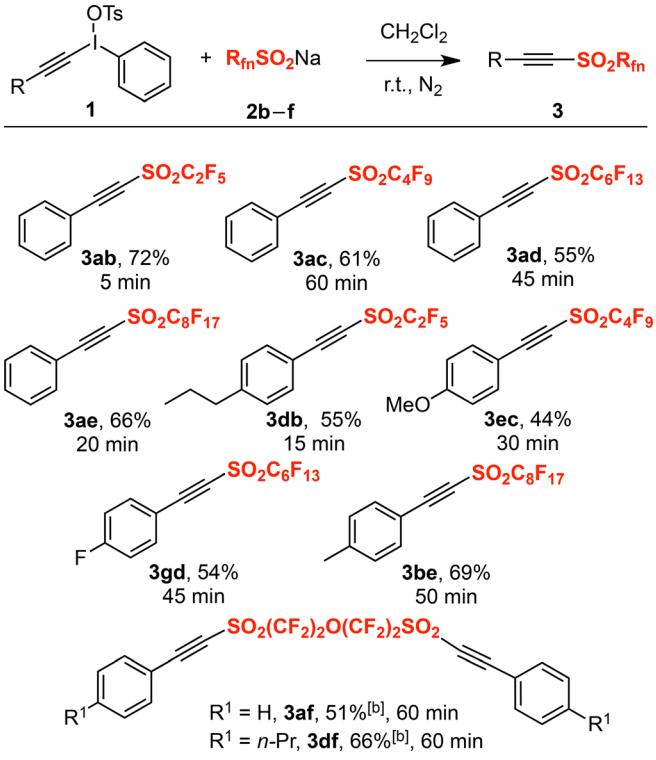
Although the insertion of an alkylidene carbene into the C–H bond of an adjacent alkyl group to form five-membered rings is well documented,[12,14–16] the reaction between an alkylidene carbene and the *ortho*-OCH_3 group on the phenyl ring has never been reported. Here we report a new method to access 3-trifluoromethanesulfonylbenzofuran. A proposed reaction mechanism is suggested (Scheme 1), which involves the formation of alkylidene carbene (**II**), the bonding of **II** with an oxygen atom of an *ortho*-OCH_3 group, the demethylation of **III** by nucleophilic attack of tosylate anion, and the protonation by residual moisture in CH_2Cl_2.[16,17] These assumptions are supported in part by the isolation of methyl 4-methylbenzenesulfonate from the reaction mixture and by the formation of 2-deuterated-3-(trifluoromethanesulfonyl)benzofuran (**3n**-D) when 4 equiv. of D_2O were used at the beginning of the reaction (see the Supporting Information). Nevertheless, the exact details of the mechanism are still unclear.

Sodium perfluoroalkanesulfinates with long-chain perfluoroalkyl groups that have stronger electronegativity than CF_3 group[3j] were also suitable reagents in the reaction. Sulfinates like $C_2F_5SO_2Na$ (**2b**), $C_4F_9SO_2Na$ (**2c**), $C_6F_{13}SO_2Na$ (**2d**), and $C_8F_{17}SO_2Na$ (**2e**) reacted with alkynyl(phenyl)iodonium salts in CH_2Cl_2 at room temperature under a nitrogen atmosphere to afford **3ab–ae**, **3db**, **3ec**, **3gd**, and **3be** in 44–72% yields (Table 3). Notably, if disodium 2,2′-oxybis(1,1,2,2-tetrafluoroethanesulfinate) (**2f**) was treated with **1a** and **1d** under the standard reaction conditions for 60 min, **3af** and **3df** were formed in 51% and 66% yield, respectively. It should be men-



Scheme 1. A proposed reaction mechanism for the formation of **3n**.

Table 3. Transition metal- and additive-free perfluoroalkanesulfonylation of alkynyl(phenyl)iodonium tosylates by $R_{fn}SO_2Na$.[a]

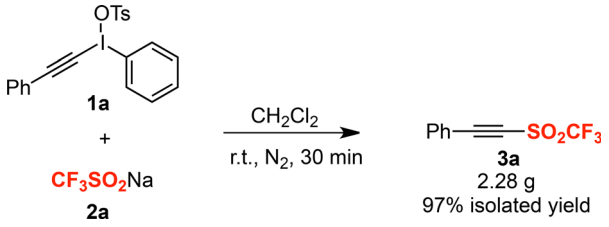


[a] *Reaction conditions:* **1** (0.2 mmol), $R_{fn}SO_2Na$ (0.4 mmol), CH_2Cl_2 (2 mL), room temperature, N_2. Isolated yield.

[b] *Reaction conditions:* **1** (0.3 mmol), $NaO_2SR_{fn}SO_2Na$ (0.1 mmol), CH_2Cl_2 (2 mL), room temperature, N_2.

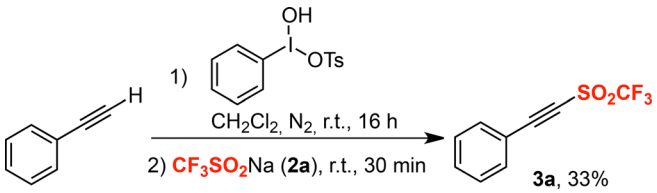
tioned again that alkynyl perfluoroalkyl sulfones (e.g., **3af** and **3df**) are difficult to synthesize by the known means due to the lack of appropriate electrophilic $R_{fn}SO_2X$ or $(R_{fn}SO_2)_2O$ reagents.[8] This transition metal-free reaction does not require $R_{fn}SO_2X$ or $(R_{fn}SO_2)_2O$ and proceeds very rapidly, thus allowing for a simple, efficient, and reliable access to these compounds.

Furthermore, a 10 mmol scale reaction of **1a** with CF_3SO_2Na was performed to test the practicality of the method. The reaction at room temperature under standard conditions for 30 min provided **3a** in 97% yield (2.28 g), indicating that alkynyl perfluoroalkyl sulfones could be prepared in a large scale by our method (Scheme 2). In addition, the one-pot reaction



Scheme 2. Scaled-up synthesis of **3a** from **1a** and **2a**.

was explored. Treatment of ethynylbenzene with Koser's reagent in CH_2Cl_2 at room temperature for 16 h without purification followed by addition of **2a** provided **3a** in 33% isolated yield (Scheme 3). A similar one-pot reaction was also performed for 1-octyne, which gave **3p** in 21% yield (Table 2). These results demonstrate the feasibility of a one-pot synthesis of acetylenic triflones from the corresponding arylacetylenes, albeit at the cost of lower product yields being obtained.



Scheme 3. One-pot synthesis of **3a** from ethynylbenzene and **2a**.

In conclusion, we have developed a fast, convenient, and transition metal-free method for the preparation of acetylenic triflones that are valuable building blocks in organic sythesis. Alkynyl perfluoroalkyl sulfones bearing long perfluoroalkyl chains that are difficult to synthesize by the known approaches are also favorably prepared under our reaction conditions. Since sodium perfluoroalkanesulfinates can be

easily derived from the commercially available perfluoroalkyl iodides by a sulfinatodehalogenation reaction, the accessibility of perfluoroalkanesulfonylation reagents is no longer problematic. Moreover, the scaled-up reaction and the one-pot synthesis have demonstrated the practicality of the new method. This protocol features short reaction times (5–60 min), mild reaction conditions, the easy preparation of perfluoroalkanesulfinates, and provides an efficient way to numerous alkynyl perfluoroalkyl sulfones without the use of additives.

Experimental Section

Typical Procedure for the Synthesis of 3b

In a nitrogen-filled glovebox, a reaction tube was charged with phenyl(*p*-tolylethynyl)iodonium tosylate (**1b**, 98.1 mg, 0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol), and CH_2Cl_2 (2 mL) with vigorous stirring. The mixture was reacted at room temperature for 30 minutes, concentrated to dryness, and purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 20:1 (v/v) as eluents to give **3b** as a yellow solid; yield: 42.5 mg (0.17 mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.58$ (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 2.44 (s, 3H); ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -79.7$ (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta =$ 144.8, 133.8, 129.9, 119.0 (q, $J = 323.9$ Hz), 112.6, 101.8, 77.2, 22.0.

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