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Preparation of Substituted Phenyl Perfluoro-*tert*-butyl Sulfones and Their Use in Nucleophilic Perfluoro-*tert*-butylation Reactions

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Dedicated to the Special Issue in honor of the pioneering contributions of Prof. G. K. Surya Prakash to organic synthetic methodology and fluorine chemistry.

Abstract: A series of perfluoro-*tert*-butyl aryl sulfones are successfully prepared under mild conditions and subsequently employed as reagents for the perfluoro-*tert*-butylation of arynes and benzyl bromides, respectively. It is found that the reactions with benzyl bromides generally showed higher efficiency than those with arynes. The substituents on the phenyl ring of the sulfone reagents have a slightly larger influence on the reactions with arynes than those with benzyl bromides. Notably, increasing the loading of sulfone reagents could attenuate the substituent effect in the reactions with benzyl bromides.

Keywords: aryne · benzyl bromide · perfluoro-*tert*-butylation · sulfone

1. Introduction

Fluorinated organic compounds have attracted considerable attention in the fields of pharmaceuticals,[1] agrochemicals, and functional materials.[2,3] Developing strategies to construct novel fluoroalkyl architectures and efficiently incorporate fluoroalkyl groups into target molecules have emerged as a pivotal research focus in organic synthesis. Featuring nine fluorine atoms exhibiting identical chemical shifts in ^{19}F NMR spectroscopy, the unique structural framework of perfluoro-*tert*-butyl (PF*t*B) group confers outstanding potential across diverse applications including polymers,[4] proteins,[5] amino acids,[6] and peptides,[7] as well as the detection of protein kinases.[8] PF*t*B-containing compounds emerge as promising candidates for ^{19}F-magnetic resonance imaging (MRI), biomarkers and ultra-sensitive ^{19}F-labeled nuclear magnetic resonance (NMR) probes.[9–11] The sterically hindered PF*t*B anion[12] demonstrates significantly different nucleophilicity when compared to smaller perfluoroalkyl counterparts like trifluoromethyl and pentafluoroethyl anions, imparting unique features for incorporating PF*t*B moieties into organic architectures. On the other hand, fluoroalkyl sulfone reagents have been widely used to introduce various fluoroalkyl groups into organic compounds due to their high reactivity.[4,13–24]

Synthetic methodologies have evolved substantially since the pioneering use of perfluoroisobutylene (an extremely toxic gas[25]) as a PF*t*B anion precursor in 1972 (**Scheme 1A**).[26] Subsequent research has progressively expanded the PF*t*B reagent toolbox, achieving successful nucleophilic substitution or radical addition through halogenated derivatives such as PF*t*B bromide and iodide (Scheme 1B,C).[27,28] Our group documented a new method in 2021 with sp^3-carbon perfluoro-*tert*-butylation using 1,1-dibromo-2,2-bis(trifluoromethyl)ethylene (**DBBF**).[10] Building on this foundation, we successfully developed an aryl perfluoro-*tert*-butylation protocol in 2022 by reacting perfluoro-*tert*-butyl phenyl sulfone with arynes (Scheme 1D).[11]

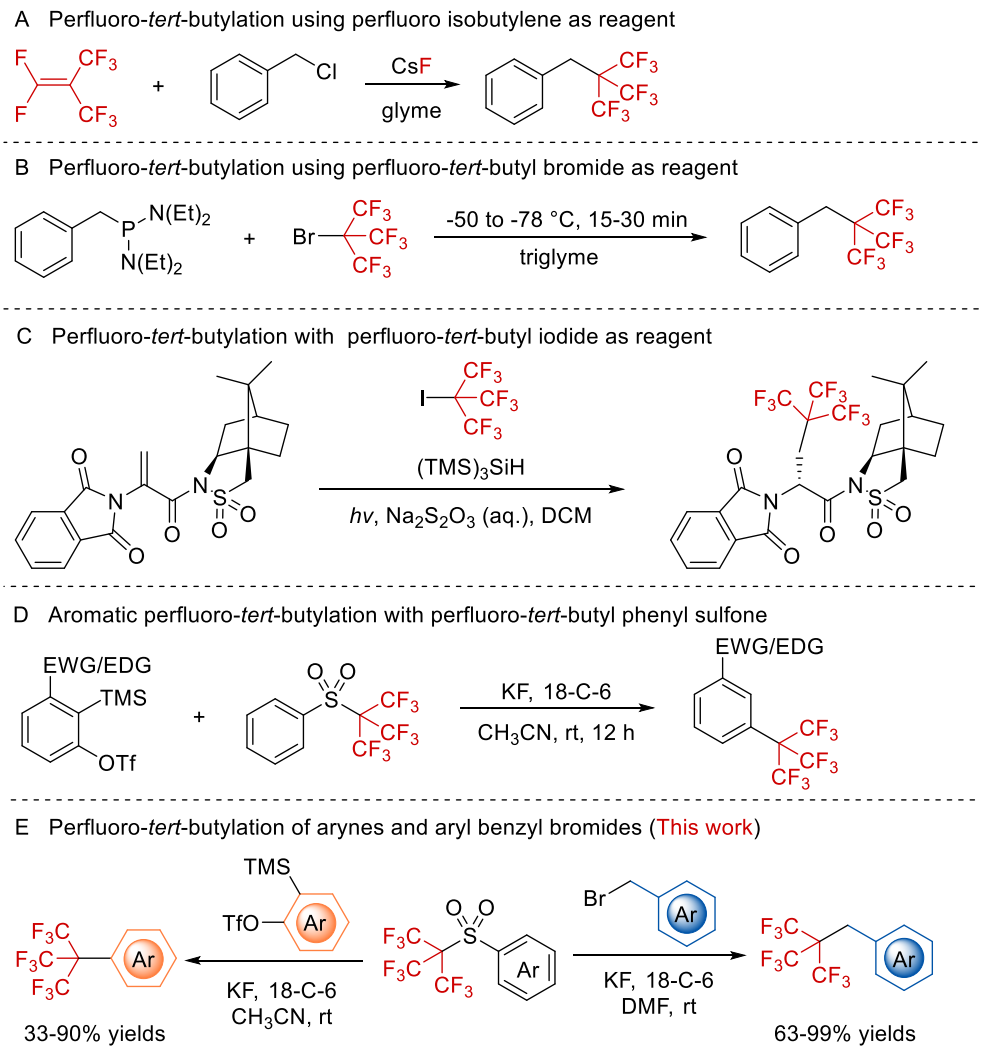
In our earlier study on alcohol deoxyfluorination using 3,3-difluoro-1,2-diarylcyclopropenes (CpFluors), systematic investigation revealed that the electronic characteristics of aryl ring substituents profoundly impacted reaction efficiency.[29] Subsequent exploration of sulfonimidoyl fluoride reagents for deoxyfluorination demonstrated enhanced performance for the *para*-chloro-substituted variant during reagent optimization.[30] Most recently, in the context of copper-catalyzed three-component enantioselective difluoromethylation-alkynylation of alkenes employing difluoromethyl aryl sulfones, comparative evaluation of sulfone substituents (*p*-H, *p*-Cl, *p*-F) revealed a striking superiority of the *para*-chloro-substituted reagent, which afforded substantially

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SCHEME 1. Perfluoro-*tert*-butylation approaches.

improved yields relative to its analogues.[31] This consistent observation of enhanced efficacy with *p*-Cl substituents across distinct reaction systems highlights its potential as a privileged modification for reagent optimization in fluorination chemistry.

Building on these findings, we undertook investigation to elucidate how substituents on the benzene ring of perfluoro-*tert*-butyl aryl sulfone reagents influence their reactivity and selectivity in perfluoro-*tert*-butylation. In this study, we present an analysis of the substituent effect in the sulfone-mediated nucleophilic perfluoro-*tert*-butylation of arynes and benzyl bromides, revealing how the structure–activity relationships influence the reaction outcomes (Scheme 1E).

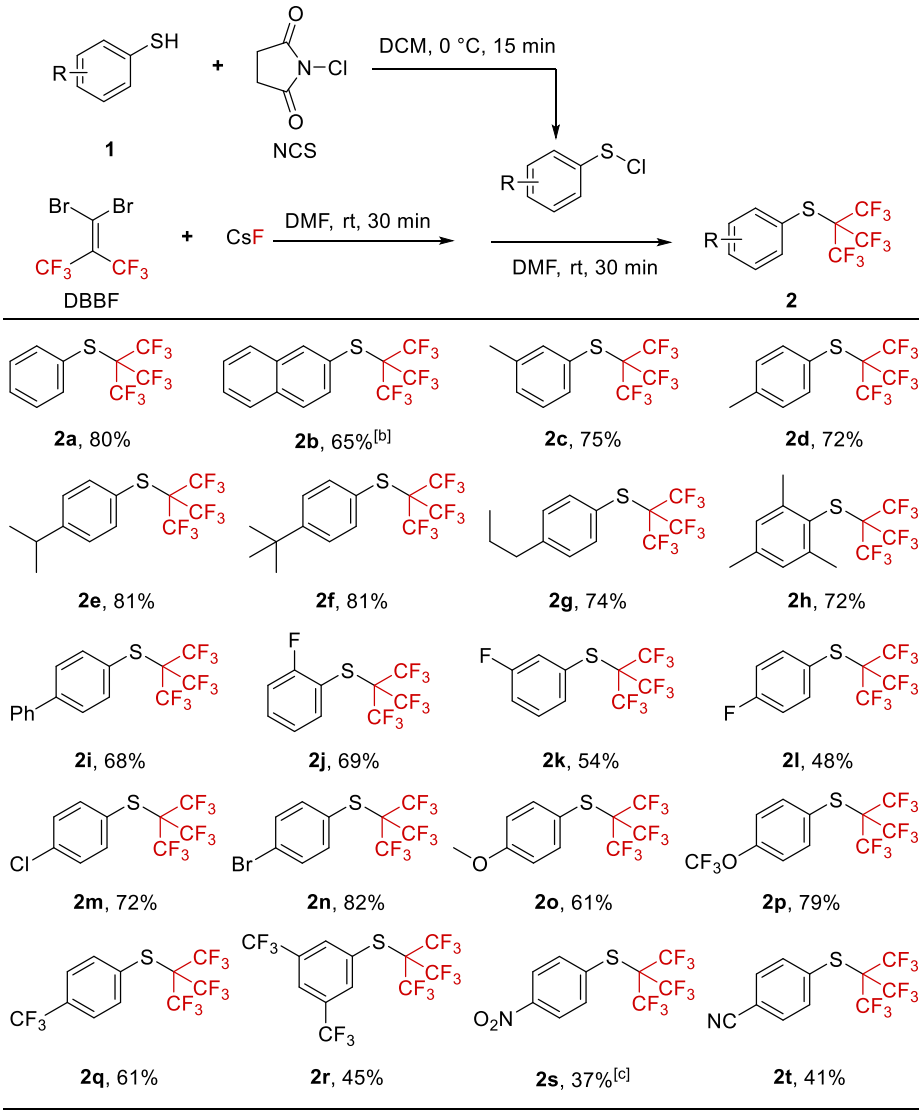
2. Results and Discussion

A modified synthetic approach was developed for perfluoro-*tert*-butyl aryl thioethers (**2a**–**2t**, **Scheme 2**) by replacing chlorine with *N*-chlorosuccinimide (NCS) as the oxidant in sulfenyl chloride generation, significantly enhancing operational safety and practicality compared to previous perfluoro-*tert*-butyl aryl sulfone syntheses.[32] The procedure initiates with NCS-mediated oxidation of thiophenol derivatives to form sulfenyl chloride intermediates, followed by nucleophilic substitution with the in situ-generated $(CF_3)_3C^-$ anion. This anion was prepared through reaction of CsF with DBBF, ultimately yielding the target thioether products as summarized in Scheme 2. Notably, substrates bearing electron-withdrawing substituents (F, NO_2, CF_3, CN) demonstrated substantially reduced yields (**2l**, **2r**, **2s**, **2t**) relative to electron-rich derivatives, underscoring the critical influence of electronic effects on reaction efficiency throughout the substitution process.

Subsequently, the synthesized perfluoro-*tert*-butyl aryl thioethers were subjected to oxidation using "HOF"[33] (generated in situ from F_2/H_2O) under the conditions outlined in (**Scheme 3**). Diminished yields were observed for oxidized products **3h**, and **3j**, a trend attributable to steric hindrance

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SCHEME 2. Syntheses of perfluoro-*tert*-butyl aryl sulfide derivatives.[a] [a]Reaction conditions: **1** (10.0 mmol, 1.0 equiv), NCS (12.5 mmol, 1.25 equiv), DBBF (13.0 mmol, 1.3 equiv), CsF (41.1 mmol, 4.11 equiv), DCM (30 mL), DMF (50 mL). Yields refer to isolated products. [b]NCS (10 mmol, 1.0 equiv) was used. [c]Reaction was performed at 60 °C for 1 h, CCl_4 (30 mL) was used as solvent instead of DCM.

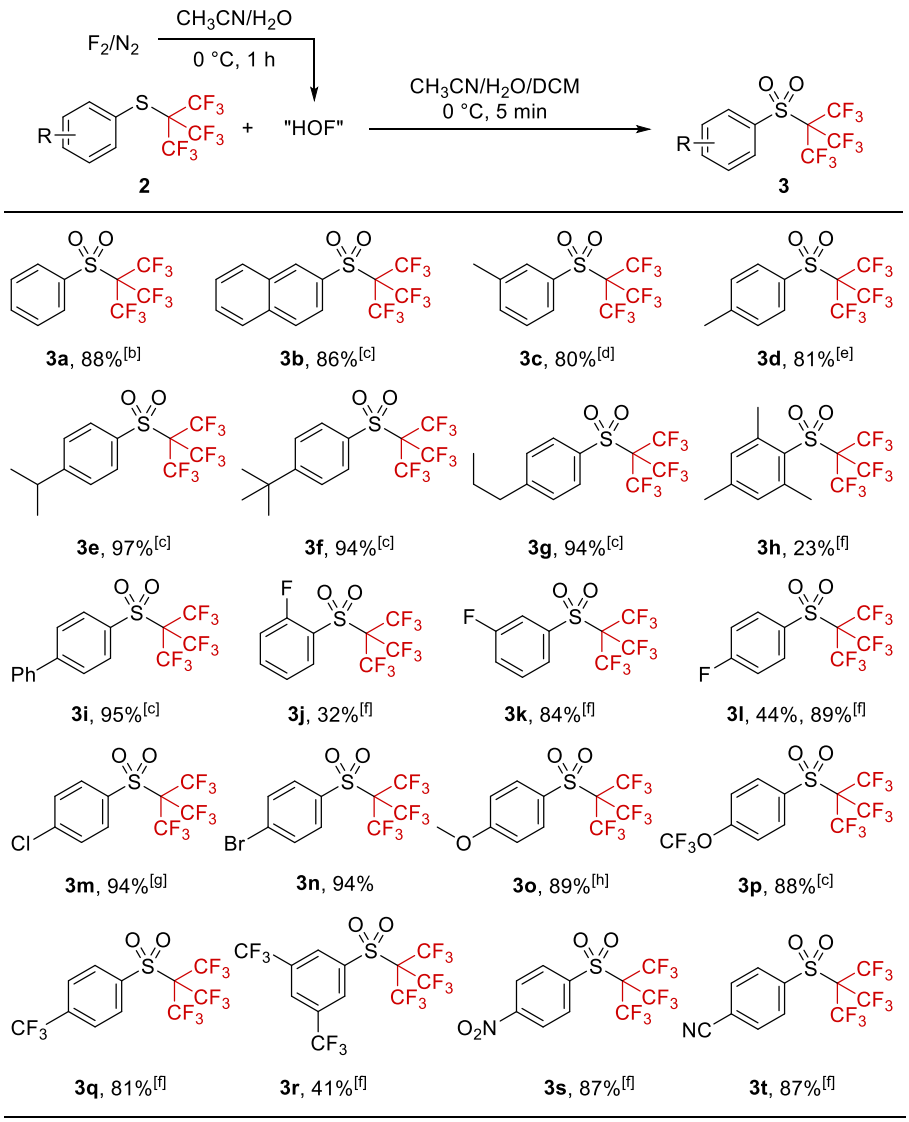
imposed by neighboring substituents, which impeded the conversion of thioethers to the corresponding sulfones. This steric constraint suggests that molecular geometry plays a critical role in determining the accessibility of the sulfur center during oxidation.

With a diverse library of perfluoro-*tert*-butyl aryl sulfones synthesized, benzyne precursor **4a** was selected as a model substrate to evaluate substituent effects on aromatic perfluoro-*tert*-butylation. The reaction protocol mirrored our previously reported conditions, wherein KF served as a dual activator for both the sulfone reagents and **4a**, facilitating the generation of the $(CF_3)_3C^-$ anion and the benzyne intermediate. The addition of 18-C-6 crown ether enhanced the solubility of KF in CH_3CN by coordinating potassium ions. Notably, sulfones bearing strongly electron-withdrawing *para*-substituents (*p*-NO_2, *p*-CN, *p*-Cl; **3s**, **3t**, **3m**) exhibited significantly diminished yields in reactions with **4a** (**Table 1**, entries 16, 17, 11 and **Scheme 4**). In contrast, both electron-donating (e.g., *m*-Me, *p*-Me) and moderately electron-withdrawing groups (*m*-F, *p*-F) on the sulfone reagents demonstrated minimal yield variations under identical conditions (Table 1, entries 3, 4, 9, 10 and Scheme 4), suggesting that substituent electronic properties exert a limited influence on reactivity except in cases of extreme electron deficiency at the *para* position (for details, see Supporting Information).

To investigate the substituent effects of perfluoro-*tert*-butyl aryl sulfones in the reaction with benzyl bromides, kinetic studies were performed using 4-nitrobenzyl bromide (**6a**) as the model substrate under optimized conditions (DMF, KF as co-reagent). As summarized in **Table 2** and Scheme 4, the reactions exhibited moderate to excellent yields (63%–91%). Substrates bearing strong electron-withdrawing group and

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SCHEME 3. Syntheses of perfluoro-*tert*-butyl aryl sulfone derivatives.[a] [a]Reaction conditions: **2** (4.0 mmol), F_2/N_2 (5% F_2, 120–130 mL/min, 1 h), CH_3CN (100 mL), H_2O (10 mL), DCM (5 mL), 0 °C. [b]**2r** (4.0 mmol), F_2/N_2 (10% F_2, 60–70 mL min^{-1}, 1 h). [c]**2** (2.0 mmol), F_2/N_2 (5% F_2, 120–130 mL min^{-1}, 1 h), CH_3CN (100 mL), H_2O (10 mL), 0 °C, after bubbling F_2/N_2 gas to the solution, divided the reaction solution into two equal portions and used one of them. [d]**2d** (2.7 mmol), F_2/N_2 (5% F_2, 80–90 mL min^{-1}, 1 h). [e]**2e** (8.0 mmol), F_2/N_2 (5% F_2, 130–135 mL min^{-1}, 90 min), −10 °C. [f]**2** (2.0 mmol), F_2/N_2 (5% F_2, 120–130 mL min^{-1}, 1 h), CH_3CN (100 mL), H_2O (10 mL), DCM (2.5 mL), 0 °C. Yields refer to isolated products. [g]**2b** (3.64 mmol), F_2/N_2 (5% F_2, 110–120 mL min^{-1}, 1 h). [h]**2i** (2.0 mmol), F_2/N_2 (10% F_2, 60–70 mL min^{-1}, 1 h), CH_3CN (100 mL), H_2O (10 mL), DCM (2.5 mL), after bubbling F_2/N_2 gas to the solution, divided the reaction solution into two equal portions and used one of them.

strong electron-donating group (*p*-NO_2, *p*-MeO) displayed slightly attenuated yields (63%–76%, entries 16, 13). Notably, sulfones with moderate EWGs (e.g., *p*-Cl, *p*-Br) or electron-donating groups (EDGs: *p*-alkyl, *p*-Ph) or strong EWGs (e.g., *p*-CN) demonstrated comparable high efficiencies (79%–91%, entries 2-12, 14, 15) (for details, see Supporting Information), suggesting a threshold electronic effect beyond which substituent polarity minimally impacts reactivity.

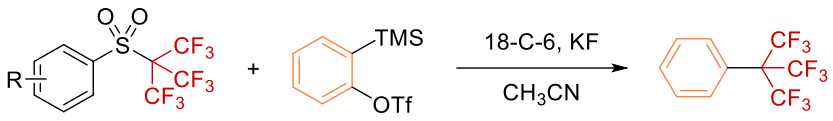
The substituent effect exhibits diminished significance in the reaction between perfluoro-*tert*-butyl sulfones and benzyl bromide compared to their interaction with benzyne. The high reaction yield is largely attributable to the intrinsic stability of benzyl bromide (compared to the less stable benzyne intermediate), which facilitates efficient S_N2 reaction with sulfone-generated $(CF_3)_3C^-$ anion (relatively stable species).

In comparison to the reactions of perfluoro-*tert*-butyl sulfone **3** with benzyne precursor **4a** and benzyl bromide **6a**, the yields obtained using reagent **3i** (R = Ph) were marginally higher (Table 1, entry 8; Table 2, entry 8), whereas the yields with reagent **3s** (R = NO_2) were the lowest (Table 1, entry 16;

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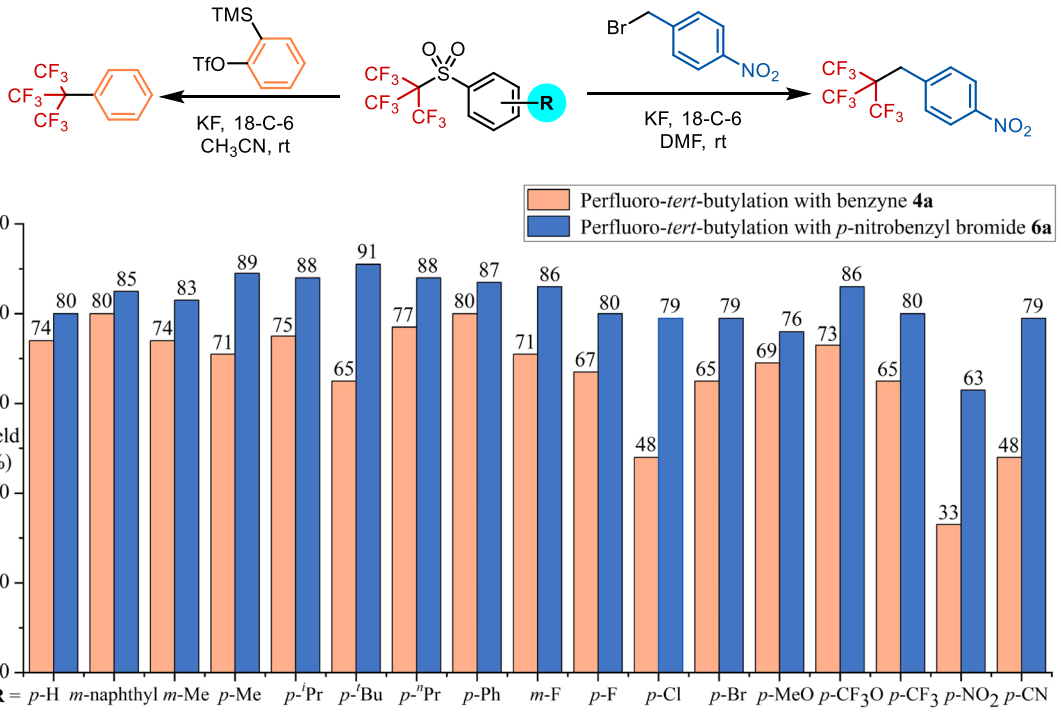
TABLE 1. Perfluoro-*tert*-butylation of benzyne precursor **4a**.



3 **4a** **5a**

Entry[a]	R	Yield (%)[b]
1	*p*-H	74
2	2-naphthyl	80
3	*m*-Me	74
4	*p*-Me	71
5	*p*-*i*Pr	75
6	*p*-*t*Bu	65
7	*p*-*n*Pr	77
8	*p*-Ph	80
9	*m*-F	71
10	*p*-F	67
11	*p*-Cl	48
12	*p*-Br	65
13	*p*-MeO	69
14	*p*-CF_3O	73[c]
15	*p*-CF_3	65
16	*p*-NO_2	33
17	*p*-CN	48

[a]Reaction conditions: **4a** (0.1 mmol, 1.0 equiv), **3** (0.14 mmol, 1.4 equiv), KF (0.24 mmol, 2.4 equiv), 18-C-6 (0.24 mmol, 2.4 equiv), 2 mL of CH_3CN, rt, 12 h. [b]Yields are determined by ^{19}F NMR analysis using $PhOCF_3$ as an internal standard. [c]Yields are determined by ^{19}F NMR analysis using 1-fluoronaphthalene as an internal standard. Note: 18-C-6 denotes 18-crown-6.

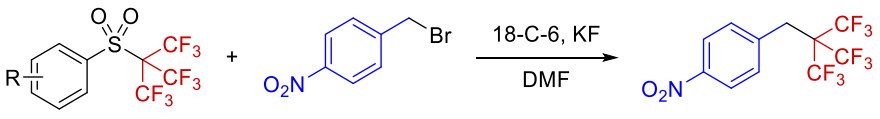


SCHEME 4. Perfluoro-*tert*-butylation with different reagents.

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TABLE 2. Perfluoro-*tert*-butylation of 4-nitrobenzyl bromide **6a**.



3 **6a** **7a**

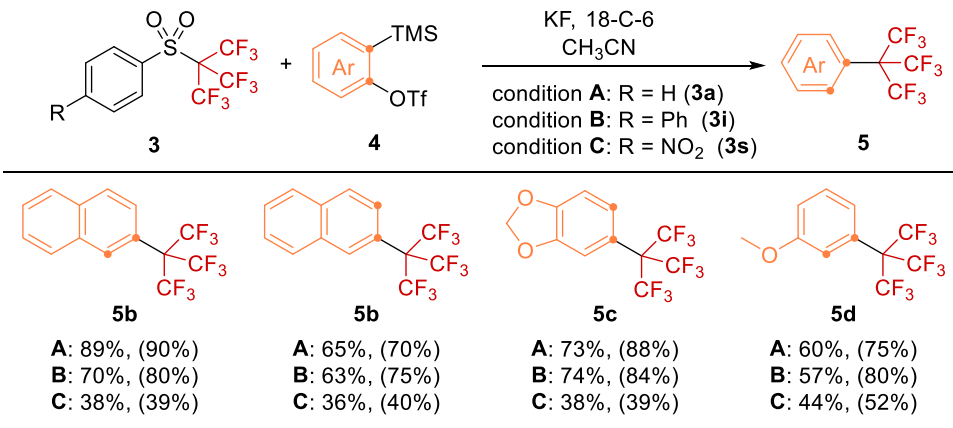
Entry[a]	R	Yield (%)[b]
1	*p*-H	80
2	2-naphthyl	85
3	*m*-Me	83
4	*p*-Me	89
5	*p*-*i*Pr	88
6	*p*-*t*Bu	91
7	*p*-*n*Pr	88
8	*p*-Ph	87
9	*m*-F	86
10	*p*-F	80
11	*p*-Cl	79
12	*p*-Br	79
13	*p*-MeO	76
14	*p*-CF_3O	86[c]
15	*p*-CF_3	80
16	*p*-NO_2	63
17	*p*-CN	79

[a]Reaction conditions: **6a** (0.1 mmol, 1.0 equiv), 3 (0.10 mmol, 1.0 equiv), KF (0.17 mmol, 1.7 equiv), 18-C-6 (0.17 mmol, 1.7 equiv), 2 mL of DMF, rt, 12 h. [b]Yields are determined by ^{19}F NMR using $PhOCF_3$ as an internal standard. [c]Yields are determined by ^{19}F NMR using 1-fluoronaphthalene as an internal standard.

Table 2, entry 16). Consequently, reagents **3a**, **3i**, and **3s** were chosen to investigate the reaction efficiency of perfluoro-*tert*-butylation.

The results shown in **Schemes 5** and **6** suggest that reagents **3a** and **3i** exhibited superior efficacy in the perfluoro-*tert*-butylation of arynes and benzyl bromides, delivering products in good to excellent yields. In contrast, reagent **3s** performed significantly poorer in reactions with aryne compared to **3a** or **3i**, yielding perfluoro-*tert*-butyl compounds in only low to moderate yields.

For benzyl bromide derivatives, increasing the amounts of reagents **3a**, **3i**, and **3s** from 1.0 to 1.4 equiv (Scheme 6) resulted in uniformly high yields across all three reagents, with minimal yield variation. Since the substituents primarily affect



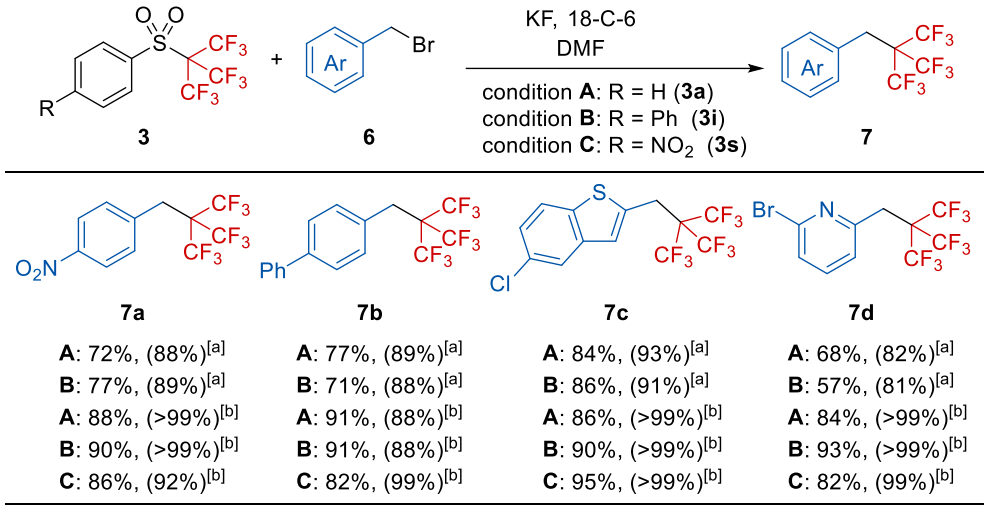
3 **4** **5**

SCHEME 5. Perfluoro-*tert*-butylation of aryne precursors with diverse sulfones.[a] [a]Reaction conditions: **3** (0.28 mmol, 1.4 equiv), **4** (0.20 mmol), KF (0.48 mmol), 18-C-6 (0.48 mmol), CH_3CN (4 mL), rt, 12 h. Yields in parentheses are determined by ^{19}F NMR using $PhOCF_3$ as an internal standard.

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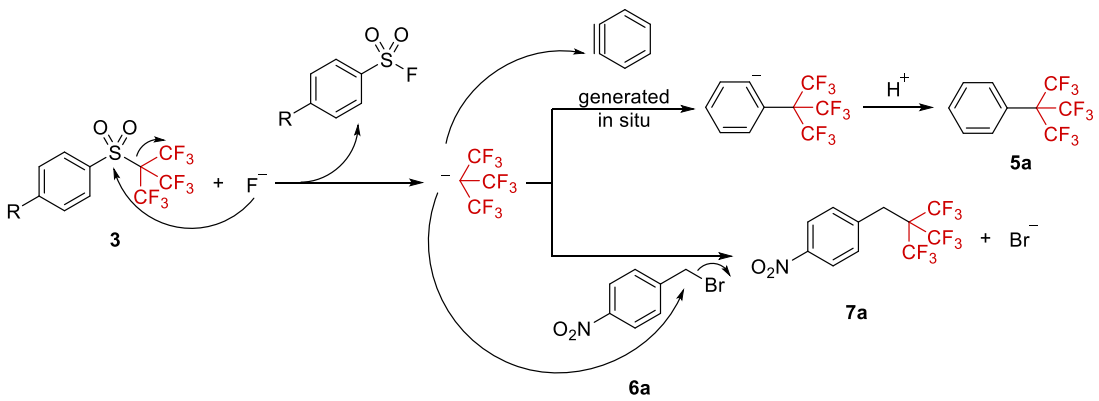
7a	7b	7c	7d
A: 72%, (88%)[a]	**A**: 77%, (89%)[a]	**A**: 84%, (93%)[a]	**A**: 68%, (82%)[a]
B: 77%, (89%)[a]	**B**: 71%, (88%)[a]	**B**: 86%, (91%)[a]	**B**: 57%, (81%)[a]
A: 88%, (>99%)[b]	**A**: 91%, (88%)[b]	**A**: 86%, (>99%)[b]	**A**: 84%, (>99%)[b]
B: 90%, (>99%)[b]	**B**: 91%, (88%)[b]	**B**: 90%, (>99%)[b]	**B**: 93%, (>99%)[b]
C: 86%, (92%)[b]	**C**: 82%, (99%)[b]	**C**: 95%, (>99%)[b]	**C**: 82%, (99%)[b]

SCHEME 6. Perfluoro-*tert*-butylation of benzyl bromides. [a]Reaction conditions: **3** (0.20 mmol), **6** (0.20 mmol), KF (0.34 mmol), 18-C-6 (0.34 mmol), DMF (4 mL), rt, 12 h. Yields in parentheses were determined by ^{19}F NMR using $PhOCF_3$ as an internal standard. [b]Reaction conditions: **3** (0.28 mmol), **6** (0.20 mmol), KF (0.48 mmol), 18-C-6 (0.48 mmol), DMF (4 mL), rt, 24 h. Yields in parentheses were determined by ^{19}F NMR using $PhOCF_3$ as an internal standard.

the generation rate of the $(CF_3)_3C^-$ anion, the above result suggests that the reaction yields do not necessarily reflect the substituent effects of the aryl perfluoro-*tert*-butyl sulfone reagents.

To rationalize the distinct substituent effects observed in the two reactions, we propose a reaction mechanism (**Scheme 7**) based on previous reports.[10,11,29–31] The reaction is initiated by attack of the fluoride anion (F^-) on the sulfur atom, which leads to the release of the $(CF_3)_3C^-$ anion. The substituents on the aryl perfluoro-*tert*-butyl sulfone influence the rate of this release. Subsequently, the $(CF_3)_3C^-$ anion reacts with either in situ generated arynes or benzyl bromides. In the case of arynes, the $(CF_3)_3C^-$ anion is much more stable than benzyne intermediates; therefore, if the rate of benzyne formation does not match the generation rate of the $(CF_3)_3C^-$ anion, the yield will substantially decrease. In contrast, in the case of benzyl bromides, which are stable substrates (unlike arynes), the reaction rate with the $(CF_3)_3C^-$ anion is governed by its S_N2 reactivity, and the release rate of the anion has a lesser impact on the overall outcome. This explains why the substituent effect is not pronounced in either reaction and why the product yields do not necessarily correlate with the substituent effect.

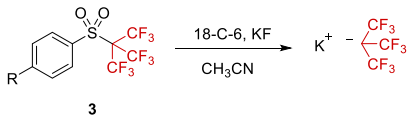
The Hammett constant (σ) is often used to represent the relative electronic effect of different substituents on the aromatic ring.[34] We have listed the σ values of different substituents (as shown in **Figure 1**). It can be seen from Figure 1 that the *p*-H sulfone decomposes the fastest, and the decomposition is almost complete within 5 min. The decomposition rate of the *p*-MeO sulfone is the slowest, and 9% of the sulfone still remains after 100 min (for details, see Supporting Information). For the sulfones with *p*-H, *p*-Me, and *p*-MeO substituents, the decomposition time increases as the σ value decreases. However, when $\sigma > 0$, the decomposition rate for sulfones is not completely consistent with the trend of the σ value. This indicates that the rate-determining step of the reaction may occur after the generation



SCHEME 7. Plausible reaction mechanism.

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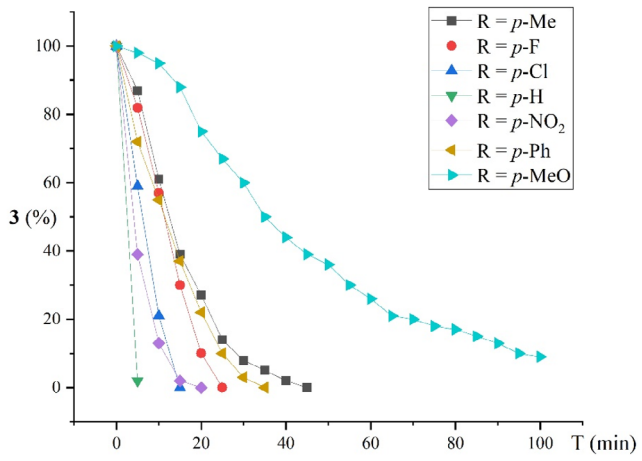


FIGURE 1. Decomposition rate of PF*t*B aryl sulfones.[a] [a]Reaction conditions: **3** (0.14 mmol), KF (0.24 mmol), 18-C-6 (0.24 mmol), 2 mL CH_3CN, 30 μL $PhOCF_3$, rt, N_2. Few solutions were periodically taken from the reaction mixture at 5-minute intervals, quenched with an acetonitrile/water (1/10) solution, and submitted for ^{19}F NMR. Residual was determined by ^{19}F NMR analysis using $PhOCF_3$ as an internal standard.

of PF*t*B anion from sulfone. This result suggests that one can select an appropriate aryl perfluoro-*tert*-butyl sulfone reagent for perfluoro-*tert*-butylation; however, the reaction efficiency does not necessarily correlate with the substituents on the phenyl ring.

3. Conclusions

In summary, we have investigated the substituent effect of perfluoro-*tert*-butyl aryl sulfone reagents in nucleophilic perfluoro-*tert*-butylation of arynes and benzyl bromides, respectively. The results revealed that most substituents on the phenyl rings of sulfone reagents exhibited minimal influence on the reactions with arynes, except for reagents bearing strong electron-withdrawing groups such as nitro and cyano functionalities. When the stoichiometry of sulfone reagent was one equivalent, the reaction yields of the perfluoro-*tert*-butylation reactions with benzyl bromides were comparable to those observed in reactions with aryne precursors. Comparative analysis suggests that the reaction efficiency in nucleophilic perfluoro-*tert*-butylation does not necessarily reflect the substituent effect of the sulfone reagents.

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Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data supporting this research are included and can be found in the Supporting Information of this paper. All data generated or analyzed during this study are included in this published article [and its Supporting Information files].

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