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Copper-Promoted Trifluoromethanesulfonylation and Trifluoromethylation of Arenediazonium Tetrafluoroborates with $NaSO_2CF_3$

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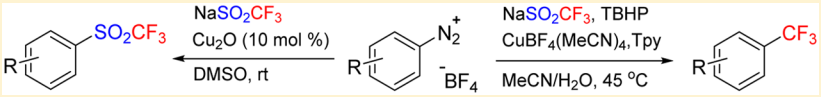
Supporting Information



ABSTRACT: A tunable chemoselective trifluoromethanesulfonylation and trifluoromethylation of arenediazonium tetrafluoroborates with Langlois' reagent ($NaSO_2CF_3$) was developed. The Cu_2O-catalyzed reaction in DMSO gave aryl trifluoromethanesulfones as the major products. On the other hand, the trifluoromethylated arenes were produced in the presence of oxidant *tert*-butyl hydroperoxide, $CuBF_4(MeCN)_4$, and 2,2′;6′,2″-terpyridine (tpy). Both of these transformations proceed under mild conditions and tolerate functional groups.

INTRODUCTION

Incorporation of fluorine-containing groups into aromatic compounds is extremely important in pharmaceutical and agrochemical industries, because fluorine-containing groups could impart unique chemical and physical properties to aromatic compounds including improved metabolic stability, higher lipophilicity, and better bioavailability.[1] Consequently, the preparation of fluorinated aromatic compounds has attached continuous interest in organic synthesis. Recently, tremendous new synthetic methods have been developed, mainly involving transition-metal-catalyzed/mediated fluorination/fluoroalkylation reactions.[2] The Sandmeyer reaction is widely used for the preparation of functionalized arenes from aryl diazonium salts, which are easily accessible from commercially available anilines.[3] The transformation of anilines to aryl fluorides, named the Balz−Schiemann reaction,[4] is a typical example (Scheme 1a). Very recently, the Sandmeyer-type reactions have proven to be an efficient strategy to introduce fluorine-containing groups, including trifluoromethyl (CF_3),[5] trifluoromethylthio (SCF_3),[6] difluoromethyl (CF_2H),[7] difluoromethylthio (SCF_2H),[8] and perfluoroalkyl (R_F),[9] into the aromatic rings (Scheme 1b). Inspired by these advances, we wondered if aryl trifluoromethanesulfones ($ArSO_2CF_3$) could be prepared from aryl diazonium salts.

Aryl trifluoromethanesulfones are important structural motifs frequently found in bioactive compounds,[10] chiral catalysts,[11] and functional materials[12] taking advantage of the unique properties of the trifluoromethanesulfonyl group (SO_2CF_3).[13] For more than half a century, various methods have been developed for the preparation of these compounds.[2w,14] Among them, the electrophilic and nucleophilic trifluoromethanesulfonylation (triflylation) of aromatic substrates provided the most direct approaches to aryl trifluoromethanesulfones. However, the electrophilic triflylation suffered from the narrow substrate scope and low reaction yields.[15] Recently, Avdeenko,[16a] Shekhar,[16b] and Singh[16c] reported the nucleophilic triflylation of several types of substrates with Langlois' reagent ($NaSO_2CF_3$) (Scheme 1c). However, these substrates were not easily available. Herein, we disclose the efficient synthesis of aryl trifluoromethanesulfones from the Sandmeyer-type triflylation of easily available aryl diazonium tetrafluoroborates with $NaSO_2CF_3$ (Scheme 1d). This protocol boasts high levels of reactivity and site selectivity.

It was noteworthy that at the beginning $NaSO_2CF_3$ was developed by Langlois as a trifluoromethylating reagent.[17] In the presence of an oxidant such as *tert*-butyl hydroperoxide (TBHP), the CF_3 radical was generated from $NaSO_2CF_3$ and then reacted with electron-rich arenes and alkenes.[18] Because of the electrophilic nature of the CF_3 radical, the trifluoromethylation of electron-poor arenes with $NaSO_2CF_3$ has been less explored. In continuation of our recent research interest in trifluoromethylation,[19] we also want to report here the copper-mediated Sandmeyer-type trifluoromethylation of both electron-rich and electron-deficient aryl diazonium derivatives with $NaSO_2CF_3$ in the presence of TBHP (Scheme 1e). Although the Sandmeyer trifluoromethylation has been independently reported by Fu,[5a] Wang,[5b] and Gooßen[5c] in 2013 (Scheme 1f), they employed either costly Umemoto's reagent or *in situ* generated moisture-sensitive [$AgCF_3$] and [$CuCF_3$] as trifluoromethyl sources.

RESULTS AND DISCUSSION

We initially investigated the reaction of 4-(ethoxycarbonyl)-benzenediazonium tetrafluoroborate **1a** and $NaSO_2CF_3$ in MeCN

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Scheme 1. Preparation of Fluorinated Aromatic Compounds

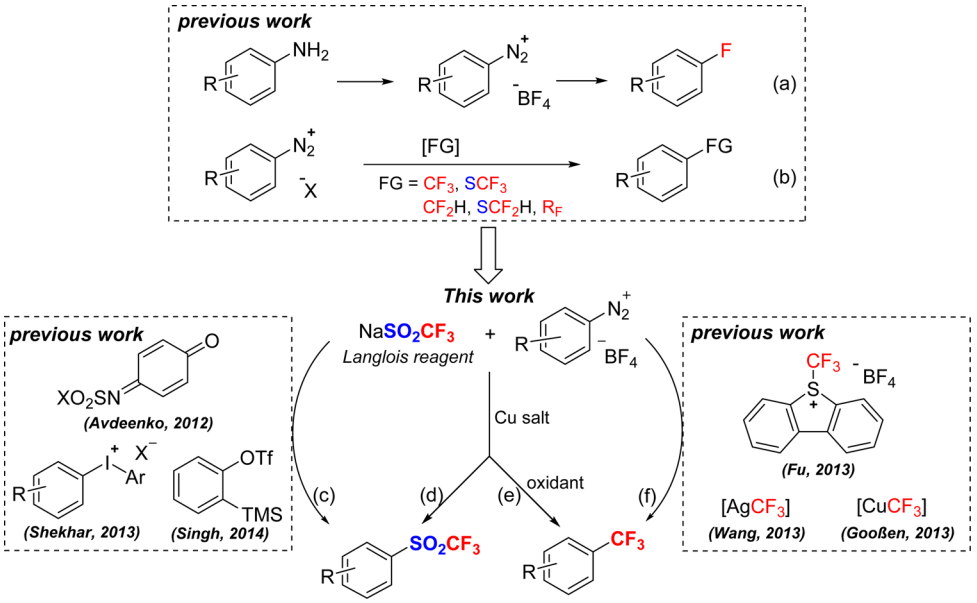
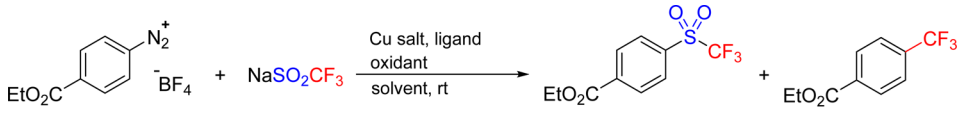


Table 1. Optimization of Reaction Conditions[a]



entry	Cu salt	ligand	oxidant	solvent	additive	yield (**2a**/**3a**, %)[b]
1	–	–	–	MeCN	–	3/0
2	Cu_2O	–	–	MeCN	–	20/23
3	Cu_2O	–	–	DMF	–	14/0
4	Cu_2O	–	–	DMSO	–	54/0
5	CuTC	–	–	DMSO	–	45/0
6	CuCN	–	–	DMSO	–	33/0
7	$Cu(OAc)_2$	–	–	DMSO	–	33/0
8[c]	Cu_2O	–	–	DMSO	–	53/0
9[c,d]	Cu_2O	–	–	DMSO	–	62/0
10	Cu_2O	–	TBHP	MeCN	–	0/11
11	CuTc	–	TBHP	MeCN	–	0/10
12	$CuBF_4(MeCN)_4$	–	TBHP	MeCN	–	0/15
13	$Cu(OAc)_2$	–	TBHP	MeCN	–	0/trace
14	$CuBF_4(MeCN)_4$	Py	TBHP	MeCN	–	0/9
15	$CuBF_4(MeCN)_4$	Bipy	TBHP	MeCN	–	0/5
16	$CuBF_4(MeCN)_4$	Phen	TBHP	MeCN	–	0/4
17	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	–	0/24
18[d]	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	–	0/35
19[d,e]	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	–	0/47
20[d,e]	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	TEA	0/14
21[d,e]	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	$NaHCO_3$	0/53
22[d,e,f]	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	$NaHCO_3$	0/59
23[d,e,f,g]	$CuBF_4(MeCN)_4$	Tpy	TBHP	MeCN	$NaHCO_3$	0/65

[a]Reaction conditions: **1a** (0.1 mmol), $NaSO_2CF_3$ (0.15 mmol), metal salt (0.1 mol), solvent (2.0 mL), room temperature, under N_2, overnight. [b]Yield determined by ^{19}F NMR spectroscopy using trifluoromethoxybenzene as an internal standard. [c]10 mol % Cu_2O was used. [d]3.0 equiv of $NaSO_2CF_3$ was used. [e]2.0 equiv of $CuBF_4(MeCN)_4$ and 2.0 equiv of ligand were added. [f]H_2O (0.1 mL) was added. [g]The reaction temperature was 45 °C.

under a N_2 atmosphere at room temperature. The trifluoromethanesulfonylated (triflylated) product **2a** was formed in only 3% yield (Table 1, entry 1). A patent also disclosed that the reaction of **1a** with KSO_2CF_3 in MeCN gave **2a** in low yield.[20] Inspired by Shekhar's triflylation method,[16b] the addition of Cu_2O to the reaction mixture afforded **2a** in 20% yield along

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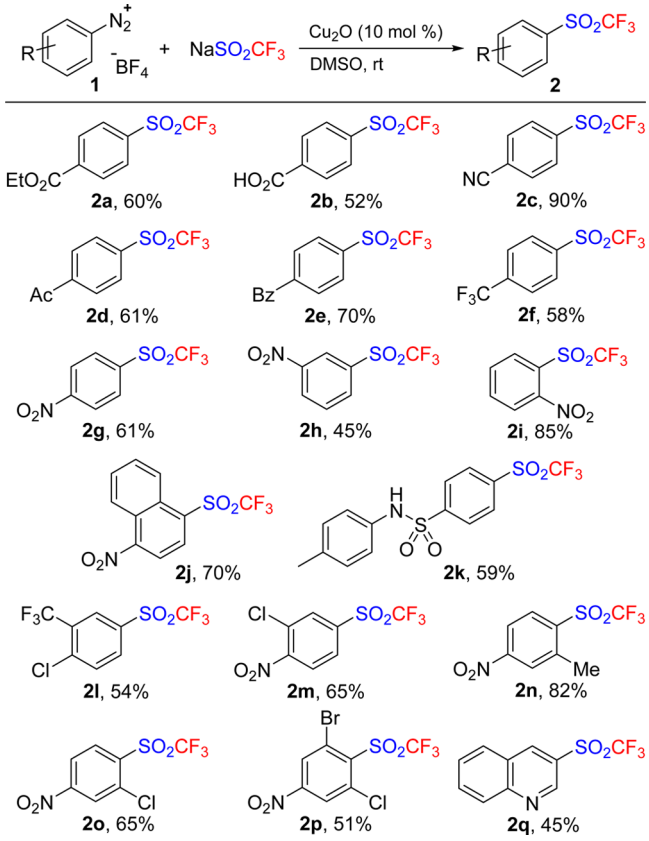
with the trifluoromethylated product **3a** in 23% yield (entry 2). With these initial results in hand, we continued to optimize the reaction conditions for selective formation of **2a** and **3a**. A slightly lower yield of **2a** was observed in DMF, while the yield sharply increased to 54% in DMSO (entries 3 and 4). Compound **3a** was not detected in DMF or DMSO. Other copper salts, including CuTC, CuCN, and $Cu(OAc)_2$, were then screened (entries 5−7). However, none of them gave better results. To our delight, the yield of **2a** (54%) in the presence of the catalytic amount of Cu_2O (10 mol %) was similar to that of the stoichiometric amount of Cu_2O (entry 8). Finally, the yield of **2a** was improved to 62% when 3.0 equiv of $NaSO_2CF_3$ were used (entry 9).

After obtaining the optimal reaction conditions for trifluoromethanesulfonylation, we then focused on the exploration of trifluoromethylation. It is well-known that $NaSO_2CF_3$ easily reacts with TBHP to generate the CF_3 radical. Thus, TBHP was added to the reaction mixture to accelerate the decomposition of $NaSO_2CF_3$. As we expected, the formation of **2a** was totally inhibited, but the trifluoromethylated compound **3a** was formed in low yield (entry 10). Among the different copper salts evaluated, $CuBF_4(MeCN)_4$ proved to be more efficient than Cu_2O, CuTC, and $Cu(OAc)_2$ (entries 11−13). Notably, the coordination of the ligand to copper is important to trifluoromethylation. Neither the monodentate ligand pyridine (py) nor the bidentate ligands 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) were effective (entries 14−16). To our delight, the tridentate ligand 2,2′;6′,2″-terpyridine (tpy) had a beneficial effect on the reactivity, producing **3a** in 24% yield (entry 17). Increasing the amount of $NaSO_2CF_3$, $CuBF_4(MeCN)_4$, and tpy improved the yield of **3a** to 47% (entries 18 and 19). A poor yield (14%) of **3a** was obtained when triethylamine (TEA) was added (entry 20). In contrast, a slightly higher yield was gained when $NaHCO_3$ was used as the additive (entry 21). The yield of **3a** was further improved to 59% using a small amount of water (0.1 mL) as the cosolvent (entry 22). Finally, the screening of reaction temperature revealed that compound **3a** was formed in the highest yield (65%) when the reaction was conducted at 45 °C (entry 23).

With the optimized reaction conditions established, we first explored the substrate scope of copper-catalyzed trifluoromethanesulfonylation of arenediazonium tetrafluoroborates (Scheme 2). In general, the arenediazonium salts **1** bearing electron-withdrawing groups reacted efficiently to afford the corresponding triflylated products **2** in moderate to excellent yields. However, the electron-donating group-bearing substrates led to much lower yields, probably due to the lack of the nucleophilicity of these arenediazonium salts. The substituents, such as ester, carboxylic acid, nitrile, ketone, sulfonamide, and nitro groups, at different positions of the aromatic ring were all well tolerated (**2a**−**2k**). Di- and trisubstituted arenediazonium salts **1l**−**1p** were also compatible under the standard reaction conditions. It was noteworthy that quinoline derivative **1q** proceeded smoothly to give heteroaryl trifluoromethanesulfone **2q** in 45% yield.

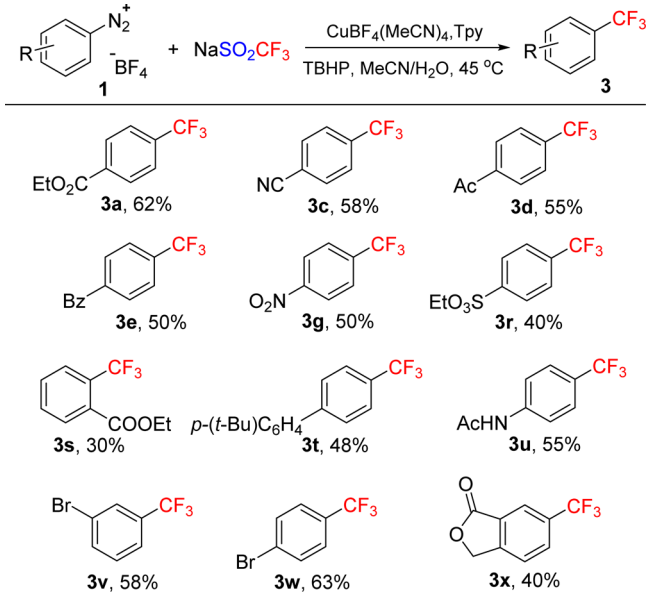
Then, the substrate scope of copper-mediated trifluoromethylation of arenediazonium tetrafluoroborates was also investigated. As shown in Scheme 3, a range of arenediazonium tetrafluoroborates **1** were subjected to the reaction conditions, producing the trifluoromethylated arenes **3** in acceptable yields. The mild reaction conditions allowed the tolerance of electron-withdrawing groups such as ester (**3a** and **3s**), nitrile (**3c**), ketones (**3d** and **3e**), the nitro group (**3g**), and sulfonate (**3r**) as well as electron-donating groups including the aryl group

Scheme 2. Substrate Scope of Copper-Catalyzed Trifluoromethanesulfonylation of Arenediazonium Tetrafluoroborates[a]



[a]Reaction conditions: **1** (0.2 mmol), $NaSO_2CF_3$ (0.6 mmol), Cu_2O (0.02 mmol), DMSO (2.0 mL), room temperature, under N_2, overnight. Yields are those of the isolated products.

Scheme 3. Substrate scope of copper-mediated trifluoromethylation of arenediazonium tetrafluorobroates[a]



[a]Reaction conditions: **1** (0.2 mmol), $NaSO_2CF_3$ (0.6 mmol), $CuBF_4(MeCN)_4$ (0.4 mmol), Tpy (0.4 mmol), $MeCN/H_2O$ (2.0 mL/0.1 mL), 45 °C, under N_2, overnight. Yields are those of the isolated products.

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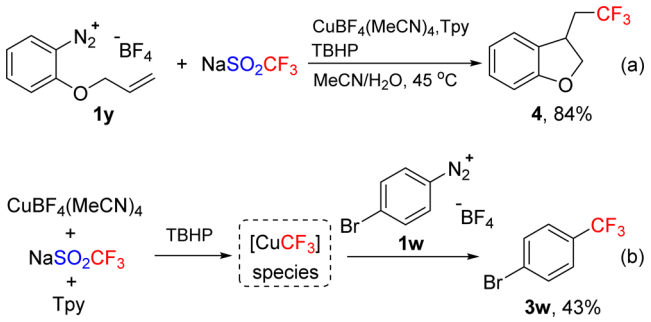
(**3t**) and amine (**3u**). Notably, the bromo-containing substrates (**1v** and **1w**) are also suitable substrates for the reaction, enabling further functionalization.

A preliminary mechanistic investigation was carried out to understand the trifluoromethylation of arenediazonium tetrafluoroborates using $NaSO_2CF_3$ as the trifluoromethyl source. Under the standard conditions, a radical clock substrate **1y** was transformed into cyclized product **4** in 84% yield (Scheme 4a).

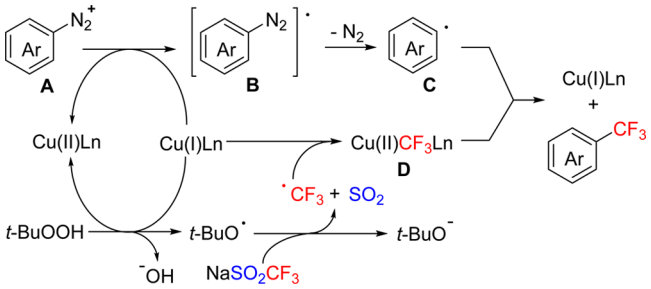
Scheme 4. Mechanistic Experiments



This result revealed that the radical process was involved in this transformation. Furthermore, the trifluoromethylation reaction was monitored by ^{19}F NMR spectroscopy (see the Supporting Information). When TBHP was added to the mixture of $CuBF_4(MeCN)_4$, $NaSO_2CF_3$, and Tpy in MeCN, $NaSO_2CF_3$ was totally converted into $CuCF_3$ species. Then treatment of $CuCF_3$ species with arenediazonium tetrafluoroborate **1w** gave trifluoromethylated product **3w** in 43% yield (Scheme 4b).

On the basis of the above experimental results, a plausible mechanism of this Sandmeyer trifluoromethylation was shown in Scheme 5. The Cu(I) species transferred a single electron to

Scheme 5. Proposed Mechanism



diazonium salt **A** to give diazo radical **B**, which released nitrogen gas with the formation of an aryl radical **C**. On the other hand, *t*-BuOOH was transformed into the *t*-BuO radical in the presence of Cu(I) species. Then the reaction of the *t*-BuO radical with $NaSO_2CF_3$ gave the CF_3 radical, which reacted with Cu(I) species to afford the corresponding Cu(II) species **D**. Finally, the aryl radical **C** abstracted the CF_3 group from intermediate **D** to give trifluoromethylated arenes and the Cu(I) species.[5c,6b,7,8] As the reaction of $NaSO_2CF_3$ and *t*-BuOOH in the presence of a Cu salt released the CF_3 radical rapidly,[19f,i] the excess amounts of $CuBF_4(MeCN)_4$ and tpy were required to stabilize the CF_3 radical in this reaction process.

CONCLUSION

We have developed a tunable copper-promoted trifluoromethanesulfonylation and trifluoromethylation of arenediazonium tetrafluoroborates with Langlois' reagent by the appropriate choice of the reaction conditions. The triflylation strategy is an important complement to the previously reported triflylation methods, while the employment of stable and inexpensive $NaSO_2CF_3$ as the CF_3 source is a valuable extension of the Sandmeyer trifluoromethylation. A variety of functional groups are well tolerated in these transformations. Thus, these protocols provide an alternative approach for the preparation of both aryl trifluoromethanesulfones and trifluoromethylated arenes. Work is ongoing to develop conditions for triflylation of electron-rich arenediazonium salts and to reduce the amounts of Cu salt and ligand in Sandmeyer trifluoromethylation reactions.

EXPERIMENTAL SECTION

General Experimental Methods. ^1H NMR (TMS as the internal standard), ^{19}F NMR ($CFCl_3$ as the outside standard and low field is positive), and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS data using ESI were obtained on an ESI-FTMS mass spectrometer; HRMS data using EI were obtained on a GC-TOF mass spectrometer. The diazonium salts were prepared from the corresponding anilines following the procedures below and were directly used. Sodium trifluoromethanesulfinate ($NaSO_2CF_3$, 95%) was purchased from TCI and used without further purification. All other starting materials were purchased from commercial sources and used as received. Unless otherwise noted, all reagents were obtained commercially and used without further purification. **2a**,[16b] **2b**,[21] **2c**,[14f] **2d**,[22] **2e**,[23] **2f**,[16b] **2g**,[16b] **2h**,[14f] **2i**,[24] **3a**,[5b] **3c**,[5c] **3d**,[25] **3e**,[5a] **3g**,[26] **3r**,[5b] **3s**,[5b] **3t**,[27] **3u**,[5c] **3v**,[28] **3w**,[5b] and **3x**[5b] are all known compounds.

General Procedure for the Synthesis of Arenediazonium Tetrafluoroborates. *Procedure A.*[5c] In a 50 mL round-bottom flask, the aniline (10.0 mmol) was dissolved in a mixture of absolute ethanol (3.0 mL) and an aqueous solution of HBF_4 (40%, 3.1 mL, 20.0 mmol). *tert*-Butyl nitrite (2.7 mL, 20 mmol) was added dropwise by a syringe to the solution at 0 °C. The reaction was stirred at room temperature for 1 h, and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. Then the mixture was filtered off and washed with diethyl ether (3 × 10 mL). The arenediazonium tetrafluoroborate was dried in vacuo for 30 min and used without further purification.

Procedure B.[5a] To a 50 mL round-bottom flask containing HCl (6 mL) and H_2O (6 mL) was added aniline (25.0 mmol). Aniline hydrochloride crystals were formed at 0−5 °C, and then sodium nitrite (1.79 g, 26.0 mmol) in H_2O (4 mL) was added dropwise, followed by addition of sodium tetrafluoroborate (3.95 g, 36.0 mmol) in H_2O (8 mL). The reaction mixture was allowed to stir for another 10 min at 5 °C. The arenediazonium salt solid was filtered off and then washed with 5% sodium tetrafluoroborate (3 × 10 mL), followed by methanol (2 × 15 mL). The crude product was purified by recrystallization with acetone and cold diethyl ether. The obtained arenediazonium tetrafluoroborate was dried in vacuo for 30 min and used without further purification.

General Procedure for Trifluoromethanesulfonylation of Arenediazonium Tetrafluoroborate. A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with arenediazonium tetrafluoroborate (0.2 mmol, 1.0 equiv), Cu_2O (2.8 mg, 0.02 mmol, 0.1 equiv), and $NaSO_2CF_3$ (99.2 mg, 0.6 mmol, 3.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then DMSO (2.0 mL) was added by a syringe. The mixture was stirred at room temperature overnight. Then the reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (15 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified by silica gel column chromatography to provide the desired product.

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*Ethyl 4-(Trifluoromethylsulfonyl)benzoate (**2a**).* Compound **2a** was prepared following the general procedure, starting from 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (52.8 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (10/1) as the eluent, compound **2a** was obtained as a white solid (34.5 mg, 60%), mp 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.32 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.3 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.4, 137.8, 134.9, 130.8, 130.8, 119.7 (q, J_{C-F} = 323.8 Hz), 62.2, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −78.09 (s, 3F). MS (EI): m/z 282 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_{10}H_9F_3O_4S$ 282.0174; Found: 282.0173.

*4-(Trifluoromethylsulfonyl)benzoic Acid (**2b**).* Compound **2b** was prepared following the general procedure, starting from 4-carboxybenzenediazonium tetrafluoroborate (47.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using dichloromethane/methanol (20/1) as the eluent, compound **2b** was obtained as a white solid (27.1 mg, 52%), mp 250−255 °C. ^{1}H NMR (400 MHz, CD_3OD) δ ppm 8.39−8.27 (m, 2H), 8.18 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ ppm 165.8, 138.6, 134.5, 130.8, 130.8, 119.8 (q, J_{C-F} = 325.2 Hz). ^{19}F NMR (376 MHz, CD_3OD) δ ppm −77.95 (s, 3F). IR (ATR): ν_{max} 3101, 2853, 1697, 1370, 1287, 1204, 1218, 1141, 721, 623, 579 cm^{-1}. MS (EI): m/z 254 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_8H_5F_3O_4S$ 253.9861; Found: 253.9855.

*4-(Trifluoromethylsulfonyl)benzonitrile (**2c**).* Compound **2c** was prepared following the general procedure, starting from 4-cyanobenzenediazonium tetrafluoroborate (43.4 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2c** was obtained as a white solid (42.3 mg, 90%), mp 90−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.19 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 135.5, 133.5, 131.4, 120.4, 119.5 (q, J_{C-F} = 323.9 Hz), 116.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.68 (s, 3F). MS (EI): m/z 235 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_8H_4F_3NO_2S$ 234.9915; Found: 234.9911.

*1-(4-(Trifluoromethylsulfonyl)phenyl)ethan-1-one (**2d**).* Compound **2d** was prepared following the general procedure, starting from 4-acetylbenzenediazonium tetrafluoroborate (46.8 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (10/1) as the eluent, compound **2d** was obtained as a white solid (30.8 mg, 61%), mp 54−56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.27−7.95 (m, 4H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 196.3, 143.0, 134.9, 131.2, 129.4, 119.6 (q, J_{C-F} = 324.00 Hz), 26.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −78.05 (s, 3F). MS (EI): m/z 252 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_9H_7F_3O_3S$ 252.0068; Found: 252.0070.

*Phenyl(4-(trifluoromethylsulfonyl)phenyl)methanone (**2e**).* Compound **2e** was prepared following the general procedure, starting from 4-benzoylbenzenediazonium tetrafluoroborate (59.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (10/1) as the eluent, compound **2e** was obtained as a white solid (44.0 mg, 70%), mp 92−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.18 (d, J = 8.2 Hz, 2H), 8.07−7.97 (m, 2H), 7.90−7.75 (m, 2H), 7.71−7.63 (m, 1H), 7.54 (t, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 194.6, 144.8, 135.9, 134.2, 133.8, 130.9, 130.7, 130.2, 128.8, 119.7 (q, J_{C-F} = 324.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.99 (s, 3F). MS (EI): m/z 314 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_{14}H_9F_3O_3S$ 314.0224; Found: 314.0229.

*1-(Trifluoromethyl)-4-(trifluoromethylsulfonyl)benzene (**2f**).* Compound **2f** was prepared following the general procedure, starting from 4-(trifluoromethyl)benzenediazonium tetrafluoroborate (52.0 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2f** was obtained as a white solid (33.1 mg, 58%), mp 38−40 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.21 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 138.0 (q, J = 33.7 Hz), 135.1, 131.5, 127.0 (q, J = 3.7 Hz), 122.7 (q, J_{C-F} = 273.5 Hz), 119.62 (q, J_{C-F} = 326.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.62 (s, 3F), −77.95 (s, 3F). MS (EI): m/z 278 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_8H_4F_6O_2S$ 277.9836; Found: 277.9831.

*1-Nitro-4-(trifluoromethylsulfonyl)benzene (**2g**).* Compound **2g** was prepared following the general procedure, starting from 4-nitrobenzenediazonium tetrafluoroborate (47.4 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2g** was obtained as a white solid (31.2 mg, 61%), mp 85−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.52 (d, J = 8.7 Hz, 2H), 8.28 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.5, 137.0, 132.4, 125.0, 119.5 (q, J_{C-F} = 326.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.57 (s, 3F). MS (EI): m/z 255 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_7H_4F_3NO_4S$ 254.9813; Found: 254.9812.

*1-Nitro-3-(trifluoromethylsulfonyl)benzene (**2h**).* Compound **2h** was prepared following the general procedure, starting from 3-nitrobenzenediazonium tetrafluoroborate (47.4 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2h** was obtained as a yellow oil (23.2 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.89 (t, J = 2.0 Hz, 1H), 8.71 (dd, J = 8.3, 1.9 Hz, 1H), 8.45−8.32 (m, 1H), 7.96 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 148.7, 136.0, 133.7, 131.6, 131.0, 125.9, 119.5 (q, J_{C-F} = 325.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.57 (s, 3F). MS (EI): m/z 255 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_7H_4F_3NO_4S$: 254.9813; Found: 254.9817.

*1-Nitro-2-(trifluoromethylsulfonyl)benzene (**2i**).* Compound **2i** was prepared following the general procedure, starting from 2-nitrobenzenediazonium tetrafluoroborate (47.4 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2i** was obtained as a yellow oil (43.6 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.25−8.21 (m, 1H), 7.92−7.97 (m, 1H), 7.92−7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.0, 137.8, 134.1, 132.9, 126.0 (q, J_{C-F} = 2.2 Hz), 125.4, 119.8 (q, J_{C-F} = 327.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −73.39 (s, 3F). MS (EI): m/z 255 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_7H_4F_3NO_4S$: 254.9813; Found: 254.9819.

*1-Nitro-4-(trifluoromethylsulfonyl)naphthalene (**2j**).* Compound **2j** was prepared following the general procedure, starting from 4-nitronaphthalene-1-diazonium tetrafluoroborate (57.4 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2j** was obtained as a yellow solid (42.7 mg, 45%), mp 75−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.00−8.84 (m, 1H), 8.58 (d, J = 8.1 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.3, 133.9, 131.6, 131.0, 130.5, 125.4, 124.9 (q, J_{C-F} = 1.5 Hz), 123.6, 120.1, 120.0 (q, J_{C-F} = 325.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.03 (s, 3F). IR (ATR): ν_{max} 3098, 2927, 1534, 1364, 1209, 1108, 855, 804, 768, 621, 561 cm^{-1}. MS (EI): m/z 305 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_{11}H_6F_3NO_4S$: 304.9970; Found: 304.9962.

*N-(p-Tolyl)-4-(trifluoromethylsulfonyl)benzenesulfonamide (**2k**).* Compound **2k** was prepared following the general procedure, starting from 4-(*N*-(*p*-tolyl)sulfamoyl)benzenediazonium tetrafluoroborate (72.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (5/1) as the eluent, compound **2k** was obtained as a white solid (44.8 mg, 59%), mp 131−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.11 (d, J = 8.2 Hz, 2H), 8.00−7.97 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.64 (s, 1H). 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.8, 137.0, 135.4, 132.3, 131.5, 130.3, 128.6, 123.3, 119.6 (q, J_{C-F} = 325.8 Hz), 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.78 (s, 3F). IR (ATR): ν_{max} 3273, 3096, 1512, 1382, 1214, 1167, 1078, 927, 824, 635, 520 cm^{-1}. MS (EI): m/z 379 [M^+]. HRMS (EI-TOF): m/z [M^+] Calcd for $C_{14}H_{12}F_3NO_4S_2$: 379.0160; Found: 379.0164.

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*1-Chloro-2-(trifluoromethyl)-4-(trifluoromethylsulfonyl)benzene (**2l**).* Compound **2l** was prepared following the general procedure, starting from 4-chloro-3-(trifluoromethyl)benzenediazonium tetrafluoroborate (58.9 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2l** was obtained as a white solid (33.8 mg, 54%), mp 36−38 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.34 (s, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.2, 134.7, 133.5, 130.8 (q, J_{C-F} = 32.9 Hz). 130.0 (q, J_{C-F} = 5.4 Hz), 121.5 (q, J_{C-F} = 274.2 Hz), 119.5 (q, J_{C-F} = 325.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.36 (s, 3F), −77.78 (s, 3F). IR (ATR): ν_{max} 3096, 1595, 1468, 1378, 1311, 1145, 1081, 837, 643, 580, 494 cm^{-1}. MS (EI): m/z 312 [M$^+$]. HRMS (EI-TOF): m/z [M$^+$] Calcd for $C_8H_3ClF_6O_2S$: 311.9446; Found: 311.9444.

*2-Chloro-1-nitro-4-((trifluoromethyl)sulfonyl)benzene (**2m**).* Compound **2m** was prepared following the general procedure, starting from 3-chloro-4-nitrobenzenediazonium tetrafluoroborate (54.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2m** was obtained as a white solid (37.8 mg, 65%), mp 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.25 (d, J = 1.8 Hz, 1H), 8.11 (dd, J = 8.5, 1.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.8, 135.8, 134.2, 130.1, 129.0, 126.5, 119.4 (q, J_{C-F} = 326.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.24 (s, 3F). IR (ATR): ν_{max} 3100, 3015, 1544, 1373, 1212, 1079, 169, 632, 491 cm^{-1}. MS (EI): m/z 289 [M$^+$]. HRMS (EI-TOF): m/z [M$^+$] Calcd for $C_7H_3ClF_3NO_4S$: 288.9423; Found: 288.9426.

*2-Methyl-4-nitro-1-(trifluoromethylsulfonyl)benzene (**2n**).* Compound **2n** was prepared following the general procedure, starting from 2-methyl- 4-nitrobenzenediazonium tetrafluoroborate (50.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2n** was obtained as a white solid (44.4 mg, 82%), mp 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.32−8.26 (m, 3H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.0, 144.7, 135.4, 135.0, 128.0, 121.9, 119.8 (q, J_{C-F} = 326.4 Hz), 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −77.50 (s, 3F). IR (ATR): ν_{max} 3105, 3034, 1538, 1360, 1202, 1133, 1044, 901, 802, 697, 626, 581, 530 cm^{-1}. MS (EI): m/z 269 [M$^+$]. HRMS (EI-TOF): m/z [M$^+$] Calcd for $C_8H_6F_3NO_4S$: 268.9970; Found: 268.9973.

*2-Chloro-4-nitro-1-(trifluoromethylsulfonyl)benzene (**2o**).* Compound **2o** was prepared following the general procedure, starting from 2-chloro-4-nitrobenzenediazonium tetrafluoroborate (54.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2o** was obtained as a light yellow oil (37.9 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.49 (d, J = 2.1 Hz, 1H), 8.43 (d, J = 8.7 Hz, 1H), 8.37 (dd, J = 8.8, 2.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.2, 137.8, 136.1, 135.5, 127.9, 122.4, 119.6 (q, J_{C-F} = 326.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −75.28(s, 3F). IR (ATR): ν_{max} 3103, 1538, 1385, 1356, 1214, 1129, 898, 773, 683, 621, 577, 349 cm^{-1}. MS (EI): m/z 289 [M$^+$]. HRMS (EI-TOF): m/z [M$^+$] Calcd for $C_7H_3ClF_3NO_4S$: 288.9423; Found:, 288.9428.

*1-Bromo-3-chloro-5-nitro-2-(trifluoromethylsulfonyl)benzene (**2p**).* Compound **2p** was prepared following the general procedure, starting from 2-bromo-6-chloro-4-nitrobenzenediazonium tetrafluoroborate (70.1 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **2p** was obtained as a white solid (38.3 mg, 51%), mp 72−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.61 (d, J = 2.3 Hz, 1H), 8.42 (d, J = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.0, 141.3, 135.1, 130.5, 128.3, 127.3, 119.6 (q, J_{C-F} = 328.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −74.77 (s, 3F). IR (ATR): ν_{max} 3088, 2921, 1538, 1395, 1344, 1223, 1130, 1101, 779, 739, 624, 579, 464 cm^{-1}. MS (EI): m/z 369 [M$^+$]. HRMS (EI-TOF): m/z [M$^+$] Calcd for $C_7H_2BrClF_3NO_4S$: 366.8529; Found: 366.8531.

*3-(Trifluoromethylsulfonyl)quinoline (**2q**).* Compound **2q** was prepared following the general procedure, starting from quinoline-3-diazonium tetrafluoroborate (48.6 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (5/1) as the eluent, compound **2q** was obtained as a white solid (24.3 mg, 45%), mp 67−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.33 (d, J = 2.3 Hz, 1H), 8.94 (d, J = 2.3 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.05−8.01 (m, 1H), 7.83−7.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.9, 147.5, 142.0, 134.8, 130.0, 129.7, 129.2, 126.1, 124.5, 119.7 (q, J_{C-F} = 325.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −78.16 (s, 3F). IR (ATR): ν_{max} 3072, 2924, 1608, 1364, 1203, 1125, 1062, 838, 671, 576, 515 cm^{-1}. MS (EI): m/z 261 [M$^+$]. HRMS (EI-TOF): m/z [M$^+$] Calcd for $C_{10}H_6F_3NO_2S$: 261.0071; Found: 261.0068.

General Procedure for Trifluoromethylation of Arenediazonium Tetrafluoroborate with $NaSO_2CF_3$. A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with $CuBF_4(MeCN)_4$ (125.8 mg, 0.4 mmol, 2.0 equiv), Tpy (93.3 mg, 0.4 mmol, 2.0 equiv), $NaHCO_3$ (33.6 mg, 0.4 mmol, 2.0 equiv), and $NaSO_2CF_3$ (98.5 mg, 0.6 mmol, 3.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with N_2 three times. Then MeCN (1.0 mL) and deionized water (0.1 mL) were added. The red brown mixture was stirred at 23 °C for 5 min. Then TBHP (70 wt %, 138.7 mg, 1.0 mmol, 5.0 equiv) was added dropwise by a microsyringe. The reaction mixture was heated to 45 °C. A solution of arenediazonium tetrafluoroborate (0.2 mmol, 1.0 equiv) in MeCN (1.0 mL) was added dropwise by a syringe over 15 min. Then the reaction mixture was stirred at 45 °C overnight. Afterward, a saturated ammonium chloride aqueous solution was added. The resulting mixture was filtered by Celite, followed by elution with diethyl ether. The water phase was extracted with diethyl ether (2 × 15 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified by silica gel column chromatography to provide the desired product.

*Ethyl 4-(Trifluoromethyl)benzoate (**3a**).* Compound **3a** was prepared following the general procedure, starting from 4-(ethoxycarbonyl)-benzenediazonium tetrafluoroborate (52.8 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **3a** was obtained as a light yellow oil (27.2 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) 8.15 (d, J = 8.1 Hz), 7.69 (d, J = 8.1 Hz), 4.41 (q, J = 7.0 Hz), 1.41 (t, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.4, 134.3 (q, J_{C-F} = 32.7 Hz), 133.7, 129.9, 125.3 (d, J_{C-F} = 3.7 Hz), 123.7 (q, J_{C-F} = 272.7 Hz), 61.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.18 (s, 3F).

*4-(Trifluoromethyl)benzonitrile (**3c**).* Compound **3c** was prepared following the general procedure, starting from 4-cyanobenzenediazonium tetrafluoroborate (43.8 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-pentane as the eluent, compound **3c** was obtained as a white solid (19.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.81 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 134.6 (d, J_{C-F} = 33.3 Hz), 132.7, 126.2 (q, J_{C-F} = 3.7 Hz), 123.1 (q, J_{C-F} = 273.0 Hz), 117.4, 116.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.58 (s, 3F).

*1-(4-(Trifluoromethyl)phenyl)ethan-1-one (**3d**).* Compound **3d** was prepared following the general procedure, starting from 4-acetyl-benzenediazonium tetrafluoroborate (46.8 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **3d** was obtained as a colorless oil (20.8 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.13−7.99 (m, 2H), 7.81−7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 196.9, 139.7, 134.5 (q, J_{C-F} = 32.4 Hz), 128.6, 125.7 (q, J_{C-F} = 3.8 Hz), 123.1 (q, J_{C-F} = 272.8 Hz), 26.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.58 (s, 3F).

*Phenyl(4-(trifluoromethyl)phenyl)methanone (**3e**).* Compound **3e** was prepared following the general procedure, starting from 4-benzoylbenzenediazonium tetrafluoroborate (59.2 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent,

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compound **3e** was obtained as a white solid (25.3 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.90 (d, J = 8.0 Hz, 2H), 7.83−7.79 (m, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.67−7.61 (m, 1H), 7.54−7.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 197.0, 140.8, 136.8, 133.8 (q, J_{C-F} = 32.7 Hz), 133.1, 130.1, 130.0, 128.5, 125.4 (q, J_{C-F} = 3.8 Hz), 123.7 (q, J_{C-F} = 274.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.05 (s, 3F).

*1-Nitro-4-(trifluoromethyl)benzene (**3g**).* Compound **3g** was prepared following the general procedure, starting from 4-nitrobenzenediazonium tetrafluoroborate (47.4 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (50/1) as the eluent, compound **3g** was obtained as a colorless oil (19.0 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.36 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.0, 136.1 (q, J_{C-F} = 33.1 Hz), 126.8 (q, J_{C-F} = 3.8 Hz), 124.1, 123.0 (q, J_{C-F} = 272.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.24 (s, 3F).

*Ethyl 4-(Trifluoromethyl)benzenesulfonate (**3r**).* Compound **3r** was prepared following the general procedure, starting from 4-(ethoxysulfonyl)-benzenediazonium tetrafluoroborate (60.0 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **3r** was obtained as a colorless oil (20.4 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.08−8.01 (m, 2H), 7.83 (d, J = 8.2 Hz, 2H), 4.28−4.11 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 140.0, 135.4 (q, J_{C-F} = 33.3 Hz), 128.4, 126.4 (q, J_{C-F} = 3.6 Hz), 123.1 (q, J_{C-F} = 273.2 Hz), 67.7, 14.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −63.33 (s, 3F).

*Ethyl 2-(Trifluoromethyl)benzoate (**3s**).* Compound **3s** was prepared following the general procedure, starting from 2-(ethoxycarbonyl)-benzenediazonium tetrafluoroborate (52.8 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **3s** was obtained as a light yellow oil (14.4 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.89−7.69 (m, 2H), 7.67−7.49 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.9, 131.7, 131.6 (q, J_{C-F} = 1.7 Hz), 131.0, 130.1, 128.7 (q, J_{C-F} = 32.5 Hz), 126.6 (q, J_{C-F} = 5.0 Hz), 123.4 (q, J_{C-F} = 273.3 Hz) 62.0, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −59.41 (s, 3F).

*4-(tert-Butyl)-4′-(trifluoromethyl)-1,1′-biphenyl (**3t**).* Compound **3t** was prepared following the general procedure, starting from 4′-(*tert*-butyl)-[1,1′-biphenyl]-4-diazonium tetrafluoroborate (64.8 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent, compound **3t** was obtained as a white solid (27.2 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (s, 4H), 7.60−7.45 (m, 4H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.4, 144.6, 136.8, 129.0 (q, J_{C-F} = 32.3 Hz), 127.2, 126.9, 126.0, 125.6 (q, J_{C-F} = 4.1 Hz), 123.0, 34.6, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −62.37 (s, 3F).

*N-(4-(Trifluoromethyl)phenyl)acetamide (**3u**).* Compound **3u** was prepared following the general procedure, starting from 4-acetamido-benzenediazonium tetrafluoroborate (49.8 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (5/1) as the eluent, compound **3u** was obtained as a white solid (20.3 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H), 7.49 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.3, 140.6, 126.3 (q, J_{C-F} = 3.4 Hz), 124.0 (q, J_{C-F} = 271.77 Hz), 119.7, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −62.22 (s, 3F).

*1-Bromo-3-(trifluoromethyl)benzene (**3v**).* Compound **3v** was prepared following the general procedure, starting from 3-bromo-benzenediazonium tetrafluoroborate (54.2 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-pentane as the eluent, compound **3v** was obtained as a colorless oil (25.8 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.79 (d, J = 2.4 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 135.0, 132.5 (q, J_{C-F} = 33.0 Hz), 130.4, 128.5 (q, J_{C-F} = 3.8 Hz), 123.6 (q, J_{C-F} = 3.4 Hz), 123.2 (q, J_{C-F} = 272.7 Hz), 122.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −62.98 (s, 3F).

*1-Bromo-4-(trifluoromethyl)benzene (**3w**).* Compound **3w** was prepared following the general procedure, starting from 4-bromo-benzenediazonium tetrafluoroborate (54.2 mg, 0.2 mmol) prepared by **procedure B**. After purification by silica gel column chromatography using *n*-pentane as the eluent, compound **3w** was obtained as a colorless oil (28.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 132.1, 129.6 (q, J_{C-F} = 33.0 Hz), 126.9 (q, J_{C-F} = 3.7 Hz), 126.4 (q, J_{C-F} = 1.3 Hz), 123.9 (q, J_{C-F} = 272.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −62.85 (s, 3F).

*6-(Trifluoromethyl)isobenzofuran-1(3H)-one (**3x**).* Compound **3x** was prepared following the general procedure, starting from 3-oxo-1,3-dihydroisobenzofuran-5-diazonium tetrafluoroborate (49.6 mg, 0.2 mmol) prepared by **procedure A**. After purification by silica gel column chromatography using *n*-hexane/ethyl acetate (10/1) as the eluent, compound **3x** was obtained as a white solid (17.3 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.27−8.13 (m, 1H), 8.06−7.89 (m, 1H), 7.66 (dt, J = 8.0, 0.8 Hz, 1H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.5, 149.7, 132.1 (q, J_{C-F} = 33.2 Hz), 130.9 (q, J_{C-F} = 3.3 Hz), 126.7, 123.1 (q, J_{C-F} = 3.7 Hz), 123.4 (q, J_{C-F} = 272.7 Hz), 123.2, 70.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −62.55 (s, 3F).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{19}F, and ^{13}C NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01295.

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Notes

The authors declare no competing financial interest.

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