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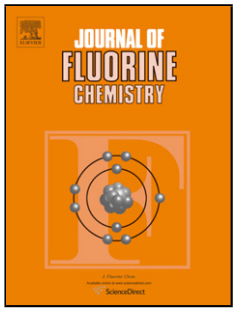

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Shuai Liu[a], Yangen Huang[a], Xiu-Hua Xu[b], Feng-Ling Qing[a,b]*

[a]College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

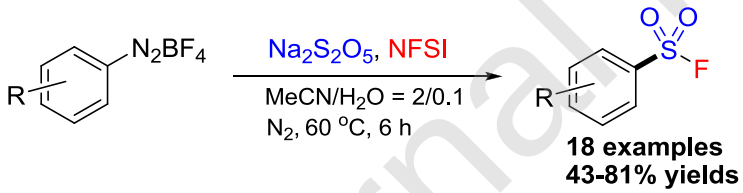
[b]Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Science, 345 Lingling Lu, Shanghai 200032, China

Tel.: 86-21-54925187; Fax: 86-21-64166128; E-mail: flq@mail.sioc.ac.cn

* Corresponding author. Tel.: +86 21 54925187; fax: +86 21 64166128.

E-mail address: flq@mail.sioc.ac.cn (F.-L. Qing).

Graphical Abstract



Highlights

- • Transition-metal-free Sandmeyer-type fluorosulfonylation.
- • An alternative approach to arenesulfonyl fluorides.
- • Three-component reaction.
- • Mild reaction conditions and broad functional group compatibility.

Abstract

A transition-metal-free Sandmeyer-type fluorosulfonylation reaction has been achieved by the three-component reaction of arenediazonium tetrafluoroborates, $Na_2S_2O_5$, and *N*-fluorobenzenesulfonimide (NFSI). The reaction proceeds through a radical tandem process, affording various arenesulfonyl fluorides in moderate to high yields. This protocol not only provides a complement to the previous fluorosulfonylation reactions, but also extends the applications of Sandmeyer reaction.

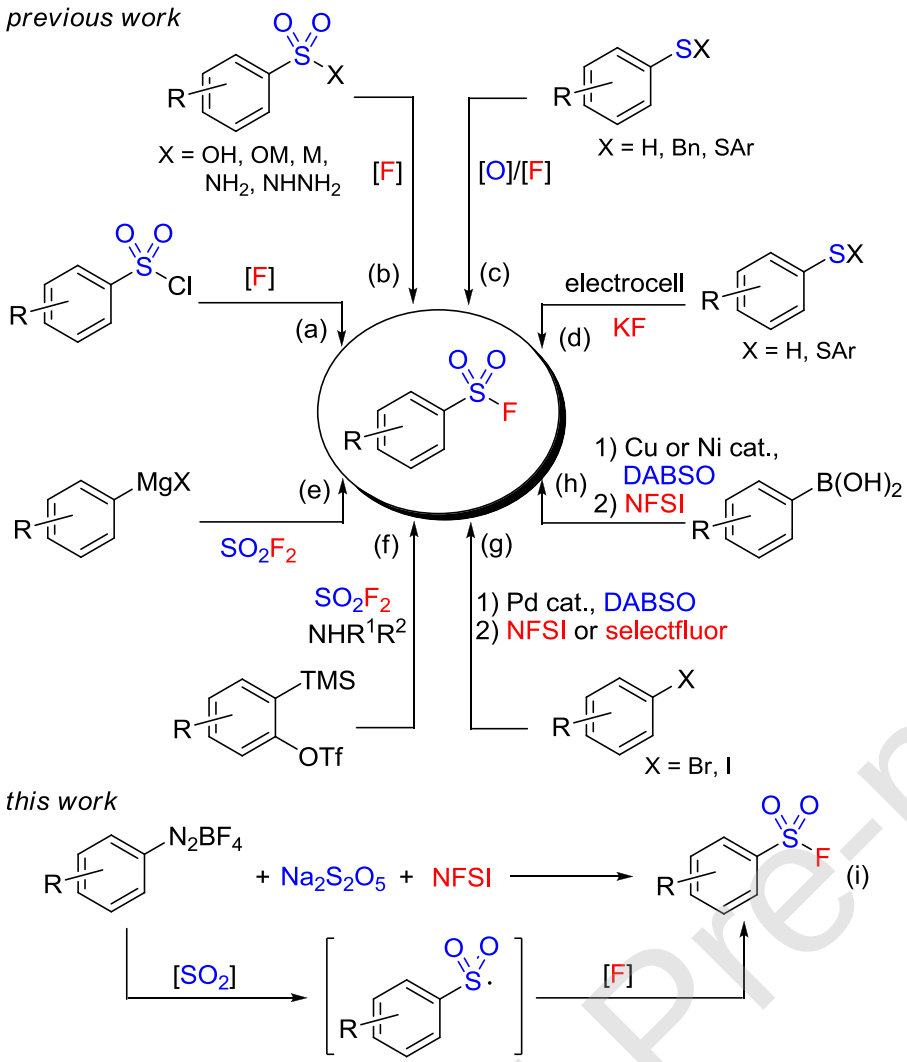
Keywords: Fluorosulfonylation; arenediazonium salts; sulfur dioxide insert; fluorination; transition-metal-free; radical.

1. Introduction

Due to the fortuitous balance between reactivity and stability, arenesulfonyl fluorides have found remarkable utility as intermediates in organic synthesis [1] and covalent probes in chemical biology [2]. Recently, considerable efforts have focused on new applications of sulfonyl fluorides ranging from fluorinating reagents [3] to Sulfur(VI) Fluoride Exchange (SuFEx) click chemistry [4]. Up to now, numerous synthetic approaches to arenesulfonyl fluorides have been reported starting from a myriad of different starting materials. The traditional method involves the nucleophilic fluorination of arenesulfonyl chlorides [5] (Scheme 1a). However, arenesulfonyl chlorides require harsh conditions to synthesize, thus rendering this approach incompatible with many functional groups. To address this issue, alternative fluorination methods have been developed using arenesulfonic acids [6], arenesulfonates [7], arenesulfinates [8], arenesulfonamides [9], or arenesulfonyl hydrazides [10] as the substrates (Scheme 1b). Arenesulfonyl fluorides could also be prepared from the corresponding thiols [11a], thioethers [11b], or disulfides [11c,d] through oxidation and fluorination (Scheme 1c). Very recently, Noël and coworkers developed an oxidant-free electrochemical process to generate arenesulfonyl fluorides from aryl thiols or

disulfides [12] (Scheme 1d). Comparing to the above transformations from sulfur-containing compounds, the direct fluorosulfonylation of easily available aromatic substrates is more attractive. In this context, Sammis and Ball reported the electrophilic fluorosulfonylation of aryl Grignard reagents with sulfuryl fluoride (SO_2F_2) [13] (Scheme 1e). Kim and Kwon also reported the synthesis amino-substituted arenesulfonyl fluorides by the three-component reaction of aryne precursors, secondary amines, and SO_2F_2 [14] (Scheme 1f). In 2017, the groups of Willis and Bagley [15a] as well as Ball [15b] respectively developed the one-pot synthesis of arenesulfonyl fluorides from the corresponding aryl halides, through palladium-catalyzed sulfonylation of aryl halides using DABSO as an SO_2 source followed by *in situ* treatment of the resultant sulfinate with the electrophilic fluorine source NFSI or selectfluor (Scheme 1g). Willis disclosed a similar strategy employing copper- or nickel-catalyzed sulfination and electrophilic fluorination for the conversion of aryl boronic acids to arenesulfonyl fluorides [16] (Scheme 1h). Despite these elegant achievements, the development of new synthetic methods using easily available substrates and simple reagents is still highly desirable.

Scheme 1 Synthetic approaches to arenesulfonyl fluorides



The Sandmeyer reaction is widely used for the preparation of functionalized arenes from aryl diazonium salts, which are easily accessible from commercially available anilines. In organofluorine chemistry, the Sandmeyer-type reactions have proven to be an efficient strategy to introduce F atom [17] and fluorine-containing groups such as CF_3 [18], SCF_3 [19], and OCF_3 [20] into the aromatic rings. In 2015, our group also reported a copper-promoted tunable trifluoromethanesulfonylation and trifluoromethylation of arenediazonium tetrafluoroborates with $NaSO_2CF_3$ [21]. To the best of our knowledge, the Sandmeyer-type fluorosulfonylation had not been reported before we started this work.

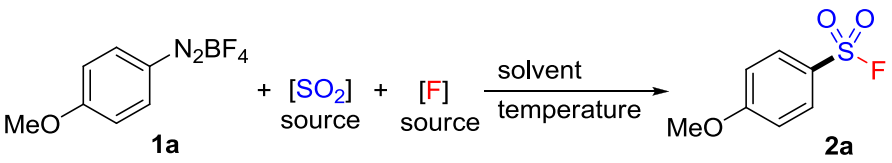
In 2016, Wu and co-workers discovered that the reaction of the SO_2 surrogate of DABCO·$(SO_2)_2$ and aryldiazonium tetrafluoroborates would provide an arenesulfonyl radical, which then underwent further transformations for the synthesis of 3-sulfonated coumarins [22]. Recently, the combination of

arenediazonium salts and a SO_2 surrogate, DABCO·$(SO_2)_2$ [23] or inorganic sulfites [24], have been widely applied in the synthesis of arenesulfonyl-containing compounds. Inspired these achievements, we envisioned that arenesulfonyl fluorides might be constructed starting from aryldiazonium salts, SO_2 surrogates, and F sources via arenesulfonyl radical intermediates. Herein, we disclose a transition-metal-free fluorosulfonylation of arenediazonium tetrafluoroborates with $Na_2S_2O_5$ and NFSI for the preparation of arenesulfonyl fluorides (Scheme 1i). Notably, during the preparation of this manuscript, the analogous fluorosulfonylation of arenediazonium salts have been reported using different SO_2 and F sources [25].

2. Results and Discussion

To test our hypothesis, 4-methoxybenzenediazonium tetrafluoroborate (**1a**) was chosen as the model substrate to optimize fluorosulfonylation reaction conditions (Table 1). To our delight, the reaction of **1a** with $Na_2S_2O_5$ as the SO_2 source and *N*-fluorobenzenesulfonimide (NFSI) as the F source in MeOH at 40 °C afforded the fluorosulfonylated product **2a** in 39% yield (entry 1). The screening of solvents revealed that MeCN was superior, affording **2a** in 54% yield (entries 2 and 3). Slightly higher yields were observed when small amounts of water were added (entries 4 and 5). However, further increasing the amount of water resulted in a decreased yield of **2a** (entry 6). Subsequently, different SO_2 sources including $K_2S_2O_5$ and DABCO·SO_2 were examined, but no better result was obtained (entries 7 and 8). Switching the F source from NFSI to selectfluor led to diminished yield (entry 9), whereas the use of KF as the F source could not deliver the desired product (entry 10). Finally, the reaction temperature was explored, and 60 °C was found to be optimal, furnishing **2a** in 74% yield (entries 11-13). Notably, methoxybenzene was the main by-product of this reaction.

Table 1. Optimization of reaction conditions.[a]

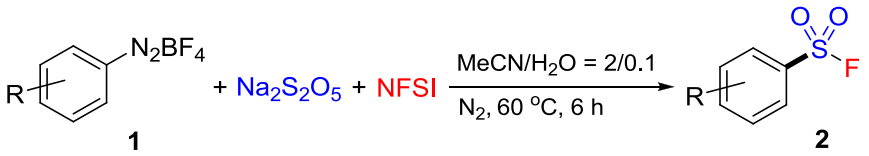


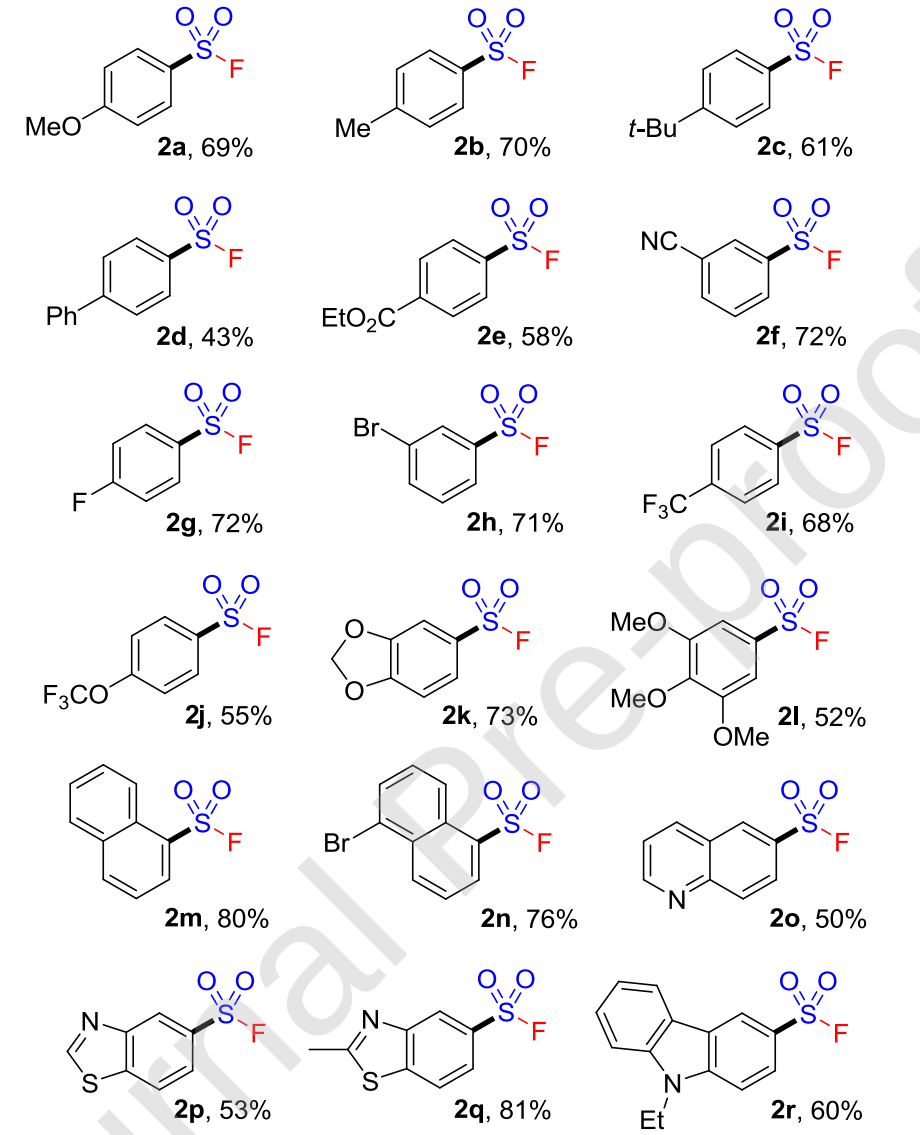
Entry	SO_2 source	F source	Solvent	Temperature	Yield (%)[b]
1	$Na_2S_2O_5$	NFSI	MeOH	40 °C	39
2	$Na_2S_2O_5$	NFSI	DMF	40 °C	trace
3	$Na_2S_2O_5$	NFSI	MeCN	40 °C	54
4	$Na_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.1	40 °C	59
5	$Na_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.02	40 °C	58
6	$Na_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.2	40 °C	47
7	$K_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.1	40 °C	49
8	DABCO·SO_2	NFSI	MeCN/H_2O = 2/0.1	40 °C	23
9	$Na_2S_2O_5$	Selectfluor	MeCN/H_2O = 2/0.1	40 °C	28
10	$Na_2S_2O_5$	KF	MeCN/H_2O = 2/0.1	40 °C	0
11	$Na_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.1	rt	26
12	$Na_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.1	60 °C	74
13	$Na_2S_2O_5$	NFSI	MeCN/H_2O = 2/0.1	80 °C	70

[a]Reaction conditions: **1a** (0.1 mmol), SO_2 Source (0.2 mmol), F Source (0.15 mmol), solvent (2.0 mL), temperature, under N_2, 6 h.
[b]Yields were determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

With the optimized reaction conditions (Table 1, entry 12) in hand, the substrate scope of transition-metal-free fluorosulfonylation of arenediazonium salts was investigated. Arenediazonium salts (**1a-1j**) bearing either electron-donating or electron-withdrawing substituents reacted smoothly to give the corresponding arenesulfonyl fluorides in moderate to high yields. Notably, the fluoro- and bromo-containing substrates (**1g** and **1h**) are suitable substrates for the reaction, enabling further functionalization. Di- and trisubstituted arenediazonium salts **1k** and **1l** were also compatible under the standard reaction conditions. Substrates bearing relatively bulky naphthyl group (**1m** and **1n**) proceeded efficiently to afford the desired products in good yields. Heteroaryl substrates including quinoline (**1o**), benzothiazole (**1p** and **1q**), and carbazole (**1r**) derivatives were smoothly converted to the desired products. However, the reaction of pyridyl diazonium salts resulted in the corresponding products in low yields.

Table 2. Scope of aryldiazonium tetrafluoroborates.[a]

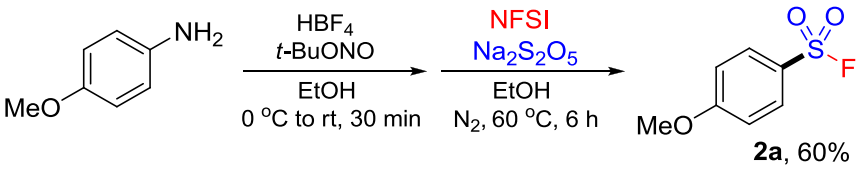




[a]Reaction conditions: **1** (0.2 mmol), $Na_2S_2O_5$ (0.4 mmol), NFSI (0.3 mmol), MeCN/H_2O (4.0/0.2 mL), 60 °C, under N_2, 6 h, isolated yields.

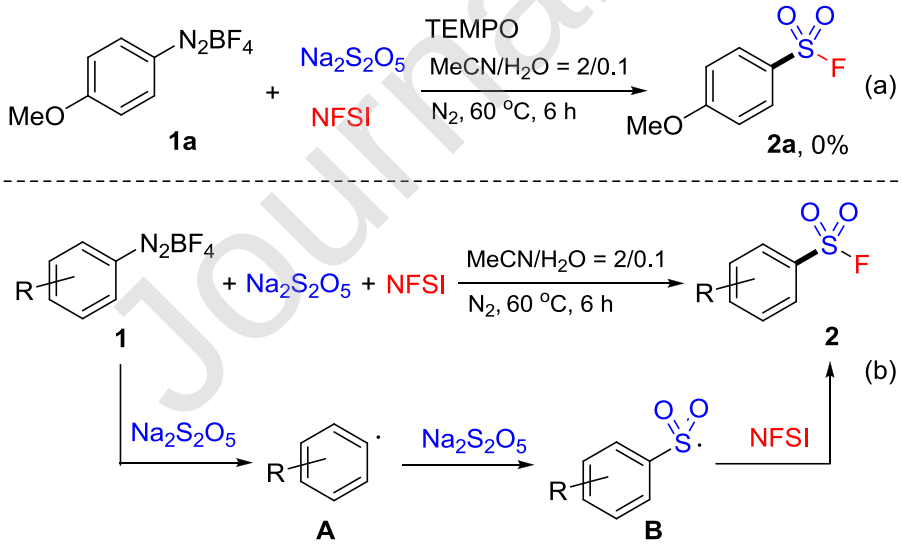
Remarkably, in a representative attempt, 4-methoxyaniline was converted into 4-methoxybenzenesulfonyl fluoride (**2a**) in a one-pot procedure (Scheme 2), albeit in somewhat lower yield than that in the standard protocol (Table 2). Furthermore, when the aliphatic amines were subjected to this one-pot reaction, none of the desired product could be detected.

Scheme 2 One-pot fluorosulfonylation of 4-methoxyaniline



In order to understand the reaction mechanism, a typical radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), was added to the standard reaction of **1a** (Scheme 3a). None of the desired product **2a** was formed, whereas the TEMPO-trapped product could be detected by GC-MS (see the supporting information). These results indicated that a radical process was probably involved in this reaction. On the basis of this result and previous reports [24,25], a plausible reaction mechanism was proposed in Scheme 3b. Initially, aryldiazonium salts **1** undergoes a single electron transfer (SET) reduction to generate aryl radical **A**. Then, aryl radical **A** reacts with SO_2 in $Na_2S_2O_5$, affording the arenesulfonyl radical **B**. Finally, fluorine atom transfer from NFSI to arenesulfonyl radical **B** furnishes the desired arenesulfonyl fluorides **2**. In accordance with the fluorosulfonylation reaction reported by Weng [25b], $Na_2S_2O_5$ probably acts as both of the reductant and SO_2 source in this reaction.

Scheme 3 Mechanistic investigation



3. Conclusion

In conclusion, we have developed an alternative approach to arenesulfonyl fluorides through the three-component reaction of readily available arenediazonium tetrafluoroborates, $Na_2S_2O_5$, and NFSI. Unlike the classic Sandmeyer reaction, this reaction proceeds under copper-free conditions. The mild conditions allow the tolerance of a variety of functional groups and heterocycles. Further extension of the applications of Sandmeyer reaction in the synthesis of other valuable fluorine-containing compounds are currently in progress.

4. Experimental Section

4.1. General information

^{1}H NMR (TMS as the internal standard), ^{13}C NMR, and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a 400 or 600 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 EI were obtained on a GC/MS TOF high resolution mass spectrometer equipped with a liquid chromatography system. All reagents were used as received from commercial sources without further purification or prepared as described in references. Substrates were prepared in accordance with methods described in the reference [26].

4.2. Typical procedure of the preparation for arenediazonium tetrafluoroborates

Method A: In a 100 mL round-bottom flask, the aniline (20 mmol) was dissolved in a mixture of H_2O (10 mL) and HBF_4 (48% aq, 6 mL). After stirring for 15 minutes, the solution of $NaNO_2$ (1.5 g, 1.1 equiv., in 4.0 mL H_2O) was added dropwise at 0 ^oC. The mixture was stirred for another 30 minutes at 0 ^oC. Then, the arenediazonium tetrafluoroborate was removed by filtration and washed successively twice with Et_2O. The crude product was dried in vacuo for 20 minutes and was then directly used without further purification.

Method B: In a 100 mL round-bottom flask, the aniline (20 mmol) was dissolved in a mixture of ethanol (8.0 mL) and HBF_4 (48% aq, 6.0 mL). Subsequently, *tert*-butyl nitrite (4.7 mL, 2.0 equiv.) was added dropwise to the solution at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C, and anhydrous Et_2O was added to precipitate the corresponding arenediazonium tetrafluoroborate. The solid was filtered off and washed twice with Et_2O. The obtained arenediazonium tetrafluoroborate was dried in vacuo for 20 minutes and was then directly used without further purification.

Substrates **1a, 1b, 1c, 1d, 1f, 1h, 1i, 1j, 1l, 1m, 1n,** and **1q** were prepared according to method A. Substrates **1e, 1g, 1k, 1o, 1p,** and **1r** were prepared according to method B.

4.3. General procedures for fluorosulfonylation of aryldiazonium tetrafluoroborates

To a mixture of arenediazonium tetrafluoroborate (0.2 mmol, 1.0 equiv.) and NFSI (94.5 mg, 0.3 mmol, 1.5 equiv.) in MeCN/H_2O (4.0/0.2 mL) was added $Na_2S_2O_5$ (76.0 mg, 0.4 mmol, 2.0 equiv.). The reaction mixture was stirred at 60 ^oC under nitrogen atmosphere for 6 h. After the reaction was complete, brine was added. The resulting mixture was extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography to give the product.

4.3.1. 4-Methoxybenzenesulfonyl fluoride (**2a**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2a** was obtained as a yellow oil (26.2 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 67.29 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 130.9, 124.1 (d, *J* = 24.7 Hz), 114.9, 55.9. The spectroscopic data were consistent with those previously published [15a].

4.3.2. 4-Methylbenzenesulfonyl fluoride (**2b**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 99:1), compound **2b** was obtained as a white solid (24.4 mg, 70%). Mp 41-42 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.29 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 130.3, 130.1 (d, *J* = 24.2 Hz),

128.5, 21.9. The spectroscopic data were consistent with those previously published [15a].

4.3.3. 4-(Tert-butyl)benzenesulfonyl fluoride **(2c)**. After purification by silica gel column chromatography (cyclohexane/EtOAc = 99:1), compound **2c** was obtained as a white solid (26.4 mg, 61%). Mp 64-66 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 1.30 (s, 9H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.21 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 130.0 (d, *J* = 24.2 Hz), 128.4, 126.7, 35.6, 31.0. The spectroscopic data were consistent with those previously published [12].

4.3.4. [1,1'-Biphenyl]-4-sulfonyl fluoride (**2d**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2d** was obtained as a white solid (20.3 mg, 43%). Mp 78-79 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.53 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 138.5, 131.4 (d, *J* = 24.5 Hz), 129.3, 129.2, 129.0, 128.2, 127.5. The spectroscopic data were consistent with those previously published [15a].

4.3.5. Ethyl 4-(fluorosulfonyl)benzoate **(2e)**. After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2e** was obtained as a white solid (27.1 mg, 58%). Mp 36-38 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 65.82 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 136.9, 136.6 (d, *J* = 25.3 Hz), 130.7, 128.5, 62.2, 14.2. The spectroscopic data were consistent with those previously published [15a].

4.3.6. 3-Cyanobenzenesulfonyl fluoride (**2f**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2f** was obtained as an orange solid (26.4 mg, 72%). Mp 48-50 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.12 (m, 2H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.33 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 133.7 (d, *J* = 27.2 Hz), 131.2, 131.0, 129.9, 115.2, 113.7. MS (EI): *m/z* 185 M^+. HRMS (ESI-TOF): *m/z* Calculated for $C_7H_4FNO_2S$ M^+:184.9947; Found: 184.9941.

4.3.7. 4-Fluorobenzenesulfonyl fluoride (**2g**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 99:1), compound **2g** was obtained as a colourless oil (25.6 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.35 (t, *J* = 8.4 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.79 (s, 1F), -99.28 to -99.32 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9 (d, *J* = 259.9 Hz), 131.6 (d, *J* = 10.3 Hz), 129.0 (dd, *J* = 25.7, 3.4 Hz), 117.3 (d, *J* = 23.2 Hz). The spectroscopic data were consistent with those previously published [15a].

4.3.8. 3-Bromobenzenesulfonyl fluoride **(2h)**. After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2h** was obtained as a colorless oil (33.9 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (t, *J* = 1.9 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.26 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 134.7 (d, *J* = 25.5 Hz), 131.3, 131.1, 127.0, 123.6. The spectroscopic data were consistent with those previously published [25b].

4.3.9. 4-(Trifluoromethyl)benzenesulfonyl fluoride (**2i**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 99:1), compound **2i** was obtained as a white solid (30.0 mg, 68%). Mp 44-46 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 65.75 (s, 1F), -63.62 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2 (q, *J* = 33.6 Hz), 136.5 (d, *J* = 25.9 Hz), 129.1, 126.9 (q, *J* = 3.7 Hz), 122.7 (q, *J* = 273.5 Hz). The spectroscopic data were consistent with those previously published [12].

4.3.10. 4-(Trifluoromethoxy)benzenesulfonyl fluoride (**2j**). After purification by silica gel column chromatography (cyclohexane/EtOAc = 20:1), compound **2j** was obtained as a brown oil (26.8 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.57 (s, 1F), -57.71 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 131.1, 130.9, 128.6, 125.4 (t, *J* = 6.2 Hz), 121.2, 120.1 (q, *J* = 260.8 Hz). The spectroscopic data were consistent with those previously published [10].

4.3.11. Benzo[d][1,3]dioxole-5-sulfonyl fluoride **(2k)**. After purification by silica gel column chromatography (cyclohexane/EtOAc = 8:1), compound **2k** was obtained as a white solid (29.8 mg, 73%). Mp 71-72 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.18 (s, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.84 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 148.7, 125.6 (d, *J* = 25.0 Hz), 125.2, 108.8, 108.2, 103.0. The spectroscopic data were consistent with those previously published [15a].

4.3.12. 3,4,5-Trimethoxybenzenesulfonyl fluoride **(2l)**. After purification by silica gel column chromatography (cyclohexane/EtOAc = 50:1), compound **2l** was obtained as a white solid (26.0 mg, 52%). Mp 76-78 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (s, 2H), 3.97 (s, 3H), 3.96 (s, 6H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.65 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 144.1, 126.9 (d, *J* = 24.7 Hz), 105.8, 61.1, 56.6. The spectroscopic data were consistent with those previously published [25b].

4.3.13. Naphthalene-1-sulfonyl fluoride **(2m).** After purification by silica gel column chromatography (cyclohexane/EtOAc = 50:1), compound **2m** was obtained as a colourless oil (33.6 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.84-7.76 (m, 1H), 7.75-7.68 (m, 1H), 7.68-7.59 (m, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 62.58 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 134.1, 131.10, 131.09, 129.5, 129.1, 128.3, 127.8, 124.2, 124.1. The spectroscopic data were consistent with those previously published [15a].

4.3.14. 5-Bromonaphthalene-1-sulfonyl fluoride **(2n).** After purification by silica gel column chromatography (cyclohexane/EtOAc = 8:1), compound **2n** was obtained as a yellow solid (43.9 mg, 76%). Mp 58-62 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.6 Hz, 1H), 8.43 (d, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.1 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 63.18 (s, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.0, 132.6, 132.0, 131.87, 131.86, 129.7, 129.6, 129.54, 125.4, 124.0, 123.9. MS (EI): *m/z* 288 M^+; HRMS (ESI-TOF): *m/z* Calculated for $C_{10}H_6BrFO_2S$ M^+: 287.9256; Found: 287.9250.

4.3.15. Quinoline-6-sulfonyl fluoride **(2o).** After purification by silica gel column chromatography (cyclohexane/EtOAc = 50:1), compound **2o** was obtained as a white solid (21.1 mg, 50%). Mp 80-82 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.65 (d, *J* = 2.1 Hz, 1H), 8.43-8.32 (m, 2H), 8.21 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.66 (dd, *J* = 8.3, 4.2 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 66.41 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.3, 137.6, 132.0, 131.1, 130.7 (d, *J* = 25.5 Hz), 127.2, 126.0, 123.3. The spectroscopic data were consistent with those previously published [25b].

4.3.16. Benzo[d]thiazole-5-sulfonyl fluoride **(2p).** After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2p** was obtained as a white solid (22.9 mg, 53%). Mp 102-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.83 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ 67.38 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 152.9, 141.4, 131.1 (d, *J* = 25.3 Hz), 124.7, 123.9, 123.6. The spectroscopic data were consistent with those previously published [25b].

4.3.17. 2-Methylbenzo[d]thiazole-5-sulfonyl fluoride **(2q).** After purification by silica gel column chromatography (cyclohexane/EtOAc = 10:1), compound **2q** was obtained as a white solid (37.4 mg, 81%). Mp 62-64 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.8 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.97 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.94 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ 67.33 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 153.0, 143.5, 130.6 (d, *J* = 24.9 Hz), 123.2, 123.1, 122.9, 20.5. MS (EI): *m/z* 231 M^+; HRMS (ESI-TOF): *m/z* Calculated for $C_8H_6FNO_2S_2$ M^+: 230.9824; Found: 230.9818.

4.3.18. 9-Ethyl-9H-carbazole-3-sulfonyl fluoride **(2r).** After purification by silica gel column chromatography (cyclohexane/EtOAc = 20:1), compound **2r** was obtained as a brown solid (33.2 mg, 60%). Mp 98-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.58-7.52 (m, 2H), 7.40 (t, *J* = 7.1 Hz, 1H), 4.44 (q, *J* = 6.5 Hz 2H), 1.50 (t, *J* = 6.6 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ 69.22 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.9, 127.7, 125.4, 123.1, 122.3, 122.2, 121.7 (d, *J* = 23.5 Hz), 121.1, 121.0, 109.5, 109.0, 38.1,

13.8. MS (EI): *m/z* 277 M^+; HRMS (EI-TOF): *m/z* Calculated for $C_{14}H_{12}FNO_2S$ $[M+H]^+$: 277.0573; Found: 277.0567.

4.4. One-pot fluorosulfonylation of 4-methoxyaniline

In a 25 mL round-bottom flask, 4-methoxyaniline (61.6 mg, 0.5 mmol) was dissolved in a mixture of ethanol (2.0 mL) and HBF_4 (132 μL, aq. 48%, 1.0 mmol). Subsequently, *tert*-butyl nitrite (135 μL, 1.0 mmol) was added dropwise to the solution at 0 °C. The reaction mixture was stirred for 30 minutes at room temperature, then $Na_2S_2O_5$ (190.1 mg, 1.0 mmol) and NFSI (236.5 mg, 0.75 mmol) were added successively. The reaction mixture was stirred at 60 °C under nitrogen atmosphere for 6 h. After the reaction was complete, brine was added. The resulting mixture was extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (cyclohexane/EtOAc = 10:1) to give **2a** as a yellow oil (57.3 mg, 60%).

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. jfluchem.xxxx.xx.xxx.

References:

[1] (a) X.-H. Xu, K. Matsuzaki, N. Shibata, Chem. Rev. 115 (2015) 731-764;

(b) A. S. Barrow, J. E. Moses, Synlett 27 (2016) 1840-1843;

(c) X. Chen, G.-F. Zha, G. A. L. Bare, J. Leng, S.-M. Wang, H.-L. Qin, Adv. Synth. Catal. 359 (2017) 3254-3260;

(d) P. K. Chinthakindi, P. I. Arvidsson, Eur. J. Org. Chem. (2018) 3648-3666;

(e) P. Mukherjee, C. P. Woroch, L. Cleary, M. Rusznak, R. W. Franzese, M. R. Reese, J. W. Tucker, J. M. Humphrey, S. M. Etuk, S. C. Kwan, C. W. Ende, N. D. Ball, Org. Lett. 20 (2018) 3943-3947;

(f) T. S.-B. Lou, S. W. Bagley, M. C. Willis, Angew. Chem. Int. Ed. 58 (2019) 18859-18863.

[2] (a) A. Narayanan, L. H. Jones, Chem. Sci. 6 (2015) 2650-2659;

(b) P. Martín-Gago, C. A. Olsen, Angew. Chem. Int. Ed. 58 (2019) 957-966;

(c) M. Gehringer, S. A. Laufer, J. Med. Chem. 62 (2019) 5673-5724;

(d) X. Wan, T. Yang, A. Cuesta, X. Pang, T. E. Balius, J. J. Irwin, B. K. Shoichet, J. Taunton, J. Am. Chem. Soc. 142 (2020) 4960-4964.

[3] (a) M. K. Nielsen, C. R. Ugaz, W. Li, A. G. Doyle, J. Am. Chem. Soc. 137 (2015) 9571-9574;

(b) C. J. Smedley, A. S. Barrow, C. Spiteri, M.-C. Giel, P. Sharma, J. E. Moses, Chem. Eur. J. 23 (2017) 9990-9995;

(c) M. K. Nielsen, D. T. Ahneman, O. Riera, A. G. Doyle, J. Am. Chem. Soc. 140 (2018) 5004-5008.

[4] (a) J. Dong, L. Krasnova, M. G. Finn, K. B. Sharpless, Angew. Chem. Int. Ed. 53 (2014) 9430-9448;

(b) T. A. Fattah, A. Saeed, F. Albericio, J. Fluorine Chem. 213 (2018) 87-112;

(c) A. S. Barrow, C. J. Smedley, Q. Zheng, S. Li, J. Dong, J. E. Moses, Chem. Soc. Rev. 48 (2019) 4731-4758.

[5] (a) T. A. Bianchi, L. A. Cate, J. Org. Chem. 42 (1977) 2031-2032;

(b) H. Zhao, F. P. Gabbaï, Org. Lett. 13 (2011) 1444-1446;

(c) J. A. H. Inkster, K. Liu, S. Ait-Mohand, P. Schaffer, B. Guérin, T. J. Ruth, T. Storr, Chem. Eur. J. 18 (2012) 11079-11087;

(d) L. Matesic, N. A. Wyatt, B. H. Fraser, M. P. Roberts, T. Q. Pham, I. Greguric, J. Org. Chem. 78 (2013) 11262-11270.

[6] (a) V. A. Petrov, S. Swearingen, W. Hong, W. C. Petersen, J. Fluorine Chem. 109 (2001) 25-31;

(b) J.-G. Kim, D. O. Jang, Synlett (2010) 3049-3052.

[7] (a) V. Vedovato, E. P. A. Talbot, M. C. Willis, Org. Lett. 20 (2018) 5493-5496;

(b) Y. Jiang, N. S. Alharbi, B. Sun, H.-L. Qin, RSC Adv. 9 (2019) 13863-13867.

[8] (a) R. E. Banks, M. K. Besheesh, S. N. Mohialdin-Khaffaf, I. Sharif, J. Chem. Soc., Perkin Trans. 1 (1996) 2069-2076;

(b) F. Toulgoat, B. R. Langlois, M. Médebielle, J.-Y. Sanchez, J. Org. Chem. 72 (2007) 9046-9052.

[9] (a) B. I. Halperin, M. Krska, E. Levy, C. A. VanderWerf, J. Am. Chem. Soc. 73 (1951) 1857-1858;

(b) M. Pérez-Palau, J. Cornella, Eur. J. Org. Chem. (2020) 2497-2500.

[10] L. Tang, Y. Yang, L. Wen, X. Yang, Z. Wang, Green Chem. 18 (2016) 1224-1228.

[11] (a) S. W. Wright, K. N. Hallstrom, J. Org. Chem. 71 (2006) 1080-1084;

(b) J. W. Tucker, L. Chenard, J. M. Young, ACS Comb. Sci. 17 (2015) 653-657;

(c) M. Kirihara, S. Naito, Y. Ishizuka, H. Hanai, T. Noguchi, Tetrahedron Lett. 52 (2011) 3086-3089;

(d) M. Kirihara, S. Naito, Y. Nishimura, Y. Ishizuka, T. Iwai, H. Takeuchi, T. Ogata, H. Hanai, Y. Kinoshita, M. Kishida, K. Yamazaki, T. Noguchi, S. Yamashoji, Tetrahedron 70 (2014) 2464-2471.

[12] G. Laudadio, A. de A. Bartolomeu, L. M. H. M. Verwijlen, Y. Cao, K. T. de Oliveira, T. Noël, J. Am. Chem. Soc. 141 (2019) 11832-11836.

[13] C. Lee, N. D. Ball, G. M. Sammis, Chem. Commun. 55 (2019) 14753-14756.

[14] J. Kwon, B. M. Kim, Org. Lett. 21 (2019) 428-433.

[15] (a) A. T. Davies, J. M. Curto, S. W. Bagley, M. C. Willis, Chem. Sci. 8 (2017) 1233-1237;

(b) A. L. Tribby, I. Rodríguez, S. Shariffudin, N. D. Ball, J. Org. Chem. 82 (2017) 2294-2299.

[16] (a) Y. Chen, M. C. Willis, Chem. Sci. 8 (2017) 3249-3253;

(b) P. K. T. Lo, Y. Chen, M. C. Willis, ACS Catal. 9 (2019) 10668-10673.

[17] (a) G. Balz, G. Schiemann, Ber. Dtsch. Chem. Ges. B 60 (1927) 1186-1190;

(b) M. Döbele, S. Vanderheiden, N. Jung, S. Bräse, Angew. Chem. Int. Ed. 49 (2010) 5986-5988;

(c) N. H. Park, T. J. Senter, S. L. Buchwald, Angew. Chem. Int. Ed. 55 (2016) 11907-11911;

(d) B. Xing, C. Ni, J. Hu, Angew. Chem. Int. Ed. 57 (2018) 9896-9900.

[18] (a) G. Danoun, B. Bayarmagnai, M. F. Grünberg, L. J. Gooβen, Angew. Chem. Int. Ed. 52 (2013) 7972-7975;

(b) J. J. Dai, C. Fang, B. Xiao, J. Yi, J. Xu, Z. J. Liu, X. Lu, L. Liu, Y. Fu, J. Am. Chem. Soc. 135 (2013) 8436-8439;

(c) X. Wang, Y. Xu, F. Mo, G. Ji, D. Qiu, J. Feng, Y. Ye, S. Zhang, Y. Zhang, J. Wang, J. Am. Chem. Soc. 135 (2013) 10330-10333;

(d) A. Lishchynskyi, G. Berthon, V. V. Grushin, Chem. Commun. 50 (2014) 10237-10240.

[19] (a) D. J. Adams, A. Goddard, J. H. Clark, D. J. Macquarrie, Chem. Commun. (2000) 987-988;

(b) G. Danoun, B. Bayarmagnai, M. F. Gruenberg, L. J. Goossen, Chem. Sci. 5 (2014) 1312-1316;

(c) D. Koziakov, M. Majek, A. J. von Wangelin, Eur. J. Org. Chem. (2017) 6722-6725;

(d) X. Zhao, X. Zheng, M. Tian, Y. Tong, B. Yang, X. Wei, D. Qiu, K. Lu. Org. Chem. Front. 5 (2018) 2636-2640.

[20] (a) S. Yang, M. Chen, P. Tang, Angew. Chem. Int. Ed. 58 (2019) 7840-7844;

(b) Y.-M. Yang, J.-F. Yao, W. Yan, Z. Luo, Z.-Y. Tang, Org. Lett. 21 (2019) 8003-8007.

[21] K. Zhang, X.-H. Xu, F.-L. Qing, J. Org. Chem. 80 (2015) 7658-7665.

[22] D. Zheng, J. Yu, J. Wu, Angew. Chem. Int. Ed. 55 (2016) 11925-11929.

[23] For selected examples, see: (a) K. Zhou, J. Zhang, L. Lai, J. Cheng, J. Sun, J. Wu, Chem. Commun. 54 (2018) 7459-7462;

(b) Y. Wang, L. Deng, Y. Deng, J. Han, J. Org. Chem. 83 (2018) 4674-4680;

(c) H. Xia, Y. An, X. Zeng, J. Wu, Org. Chem. Front. 5 (2018) 366-370;

(d) K. Zhou, M. Chen, L. Yao, J. Wu, Org. Chem. Front. 5 (2018) 371-375;

(e) F. Zhang, D. Zheng, L. Lai, J. Cheng, J. Sun, J. Wu, Org. Lett. 20 (2018) 1167-1170;

(f) G. Li, Z. Gan, K. Kong, X. Dou, D. Yang, Adv. Synth. Catal. 361 (2019) 1808-1814;

(g) T.-H. Zhu, X.-C. Zhang, X.-L. Cui, Z.-Y. Zhang, H. Jiang, S.-S. Sun, L.-L. Zhao, K. Zhao, T.-P. Loh, Adv. Synth. Catal. 361 (2019) 3593-3598;

(h) T.-H. Zhu, X.-C. Zhang, K. Zhao, T.-P. Loh, Org. Chem. Front. 6 (2019) 94-98;

(i) A. M. Nair, S. Kumar, I. Halder, C. M. R. Volla, Org. Biomol. Chem. 17 (2019) 5897-5901;

(j) M. Kumar, R. Ahmed, M. Singh, S. Sharma, T. Thatikonda, P. P. Singh, J. Org. Chem. 85 (2020) 716-725;

(k) B. Ni, B. Zhang, J. Han, B. Peng, Y. Shan, T. Niu, Org. Lett. 22 (2020) 670-674.

[24] For selected examples, see: (a) M. Wang, B.-C. Tang, J.-G. Wang, J.-C. Xiang, A.-Y. Guan, P.-P. Huang, W.-Y. Guo, Y.-D. Wu, A.-X. Wu, Chem. Commun. 54 (2018) 7641-7644;

(b) X. Gong, J. Chen, L. Lai, J. Cheng, J. Sun, J. Wu, Chem. Commun. 54 (2018) 11172-11175;

(c) M. Wang, Q. Fan, X. Jiang, Green Chem. 20 (2018) 5469-5473;

(d) G. You, D. Xi, J. Sun, L. Hao, C. Xia, Org. Biomol. Chem. 17 (2019) 9479-9488;

(e) X. Gong, X. Li, W. Xie, J. Wu, S. Ye, Org. Chem. Front. 6 (2019) 1863-1867;

(f) K. Zhou, J. Zhang, G. Qiu, J. Wu, Org. Lett. 21 (2019) 275-278.

[25] (a) Y. Liu, D. Yu, Y. Guo, J.-C. Xiao, Q.-Y. Chen, C. Liu, Org. Lett. 22 (2020) 2281-2286;

(b) T. Zhong, M.-K. Pang, Z.-D. Chen, B. Zhang, J. Weng, G. Lu, Org. Lett. 22 (2020) 3072-3078;

(c) Q. Lin, Z. Ma, C. Zheng, X.-J. Hu, Y. Guo, Q.-Y. Chen, C. Liu, Chin. J. Chem. 38 (2020) 1107-1110.

[26] C. Lian, G. Yue, J. Mao, D. Liu, Y. Ding, Z. Liu, D. Qiu, X. Zhao, K. Lu, M. Fagnoni, S. Protti, Org. Lett. 21 (2019) 5187-5191.