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# A convenient and efficient $H_2SO_4$-promoted regioselective monobromination of phenol derivatives using *N*-bromosuccinimide

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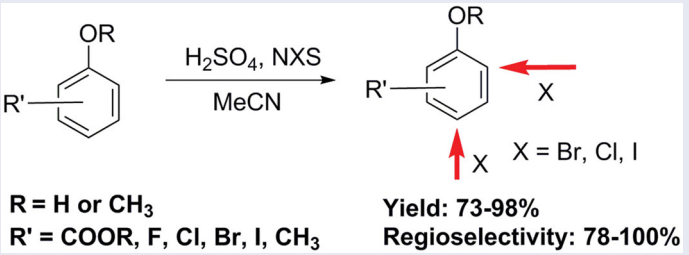
**ABSTRACT**

A convenient, rapid $H_2SO_4$-promoted regioselective monobromination reaction with *N*-bromosuccinimide was developed. The desired *para*-monobrominated or *ortho*-monobrominated products of phenol derivatives were obtained in good to excellent yields with high selectivity. Regioselective chlorination and iodination were also achieved in the presence of $H_2SO_4$ using *N*-chlorosuccinimide and *N*-iodosuccinimide, respectively.

**GRAPHICAL ABSTRACT**

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**KEYWORDS**
*N*-Bromosuccinimide; phenol analogs; regioselective monobromination; salicylic acid derivatives; sulfuric acid

## Introduction

Brominated aromatic compounds are valuable precursors for synthesizing many natural products and bioactive compounds. The bromine atom provides a critical reactive site for the formation of carbon–carbon and carbon–heteroatom bonds in metal-catalyzed cross-coupling reactions, such as Suzuki, Sonogashira, or Buchwald couplings. The classic approach to obtaining bromoaromatic compounds is electrophilic aromatic bromination with bromine or other bromonium ion sources. However, achieving

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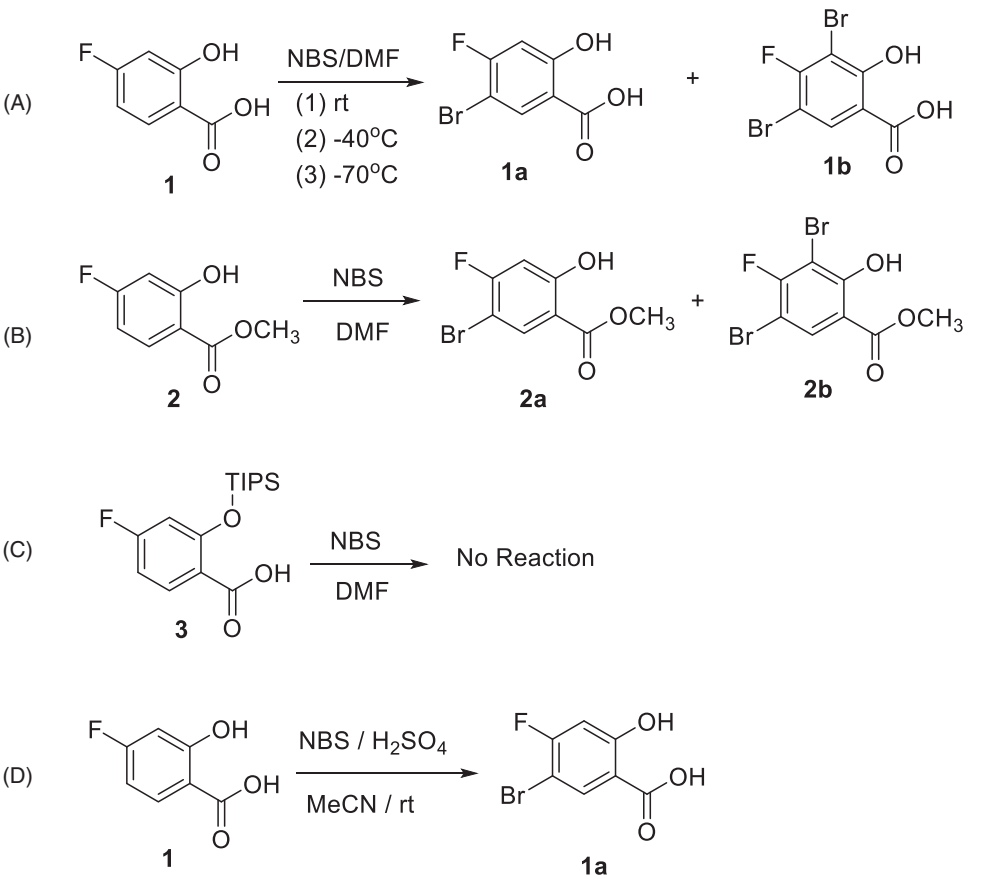
monobromination and regioselectivity can be challenging, especially for highly activated aromatic substrates, such as phenol and its derivatives.

Many selective monobromination reagents have been reported, including pyridinium tribromide,[1–3] tetrabutylammonium tribromide,[4] tetrapropylammonium nonabromide,[5] 1-butyl-3-methylimidazolium tribromide,[6] $\{[K.18\text{-Crown-}6]Br_3\}_n$,[7] dioxane dibromide,[8] hexamethylenetetramine-bromine complex,[9] a DABCO-derived bromine complex,[10] *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonylamide,[11] ammonium bromide and oxone,[12] and a $ZrBr_4$/diazene mixture.[13] However, these reagents are expensive or difficult to use.

*N*-Bromosuccinimide (NBS) is a readily available, cheap reagent that provides a precise stoichiometric amount of the bromonium ion and allows easy reaction handling because the by-product, succinimide, is soluble in water. Several selective monobromination methods using NBS have been developed. Typical examples are NBS/$HBF_4{\cdot}Et_2O$,[14] NBS/silica gel,[15,16] NBS/HZSM-5,[17] NBS/NaOH,[18] NBS/*p*-toluenesulfonic acid,[19] NBS/$NH_4OAc$,[20] NBS/Amberlyst-15,[21] NBS/thioamide,[22] NBS/ionic liquid,[23] NBS/$CF_3COOH/H_2SO_4$,[24] NBS/UV irradiation,[25] and solvent-controlled regioselective bromination using NBS.[26] However, these methods still use reagents that are expensive, not commercially available, or corrosive acids, and the scope of substrates in some reactions is restricted. Thus, the development of a selective monobromination method using cheap, commercially available and environmentally friendly reagents is still required.

5-Bromo-4-fluoro-2-hydroxybenzoic acid (**1a**) has become an important starting material for us to construct a small molecule library for biological screening. However, **1a** is not readily available on a large scale and is expensive as well. This prompted us to develop a facile method to synthesize 5-bromo-4-fluoro-2-hydroxybenzoic acid. According to a literature method,[27] we prepared **1a** from 4-fluoro-2-hydroxybenzoic acid (**1**) in DMF using NBS (Scheme 1A). However, in contrast to the literature, a nearly equal mixture of **1a** and dibrominated product **1b** was obtained, and the mixture was difficult to be separated. The amount of **1b** could not be decreased, even at the reaction temperatures of −40 and −70 °C. The dibrominated compound **2b** was the major product when methyl 4-fluoro-2-hydroxybenzoate (**2**) was used as the starting material in DMF (Scheme 1B). To decrease the amount of dibrominated product, we increased the steric hindrance at the *ortho* hydroxyl group in **3**, but the bromination reaction did not occur (Scheme 1C).

The combination of NBS/$H_2SO_4$ had been used for the monobromination of highly deactivated aromatic compounds under harsh reaction condition (conc. $H_2SO_4$ as a solvent, 60 °C).[28] Thomas Oberhauser also reported the synthesis of 3-bromo-4-hydroxybenzonitrile using $H_2SO_4$ and NBS in $CH_3CN$, however, the selectivity was only 71% and the reaction time was long up to 24 h.[14] Based on these results, we tried to use NBS and $H_2SO_4$ in $CH_3CN$ to prepare **1a**. To our delight, the desired monobrominated product was obtained in excellent yield (Scheme 1D). In consideration of the limited research of NBS and $H_2SO_4$ as the regioselective monobromination reagents, in the present work, we further investigate the application of the combination of NBS/$H_2SO_4$ in the regioselective monobromination of salicylic acid derivatives and other phenol analogs.



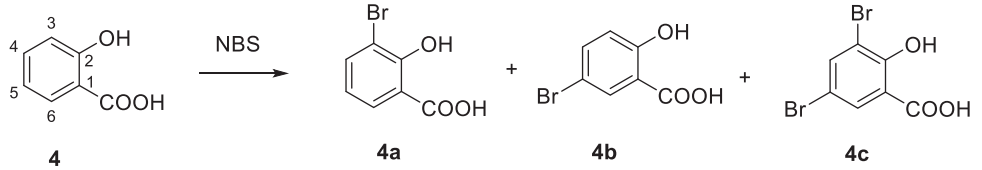

**Scheme 1.** Synthesis of 5-bromo-4-fluoro-2-hydroxybenzoic acid (**1a**).

## Results and discussion

The bromination reaction was optimized with salicylic acid (**4**). Bromination of salicylic acid with NBS in $CH_3CN$ without $H_2SO_4$ gave a mixture of the starting material, the *ortho*-monobrominated product (**4a**), the desired *para*-monobrominated product (**4b**), and the corresponding dibromo product (**4c**) (Table 1, entry 1). When 1 equiv. of $H_2SO_4$ was added to the reaction, the desired *para*-monobrominated product was afforded with 92.6% selectivity, and the reaction time was only 0.5 h (Table 1, entry 2). Lowering the number of equivalents of $H_2SO_4$ did not increase the selectivity and yield of the desired product, and the reaction time was long (Table 1, entries 3 and 4). Regioselective monobromination also occurred in $CH_2Cl_2$ and ethyl acetate, although compared with the reaction in $CH_3CN$, the selectivity and yield were decreased in $CH_2Cl_2$ (Table 1, entry 5), and the reaction time was up to 22.5 h in ethyl acetate (Table 1, entry 6). Consequently, 1 equiv. of $H_2SO_4$ and $CH_3CN$ was identified as the optimal reaction conditions.

With the optimized reaction conditions in hand, we explored the scope of the monobromination reaction (Table 2). The control reactions for every substrate were carried out to verify the effectiveness of our approach. In the absence of $H_2SO_4$, the selectivity and yield of the regioselective monobrominated products were low (Table 2, entries 2a

**Table 1.** Optimization of the reaction conditions for the bromination reaction.[a]




| | | | | | Product ratio (%)[b] | | | |
|---|---|---|---|---|---|---|---|---|
| Entry | Acid | Solvent | Temp. | Time (h) | SM (**4**) | 3 (**4a**) | 5 (**4b**) | 3,5 (**4c**) |
| 1 | – | $CH_3CN$ | rt | 16 | 15.8 | 4.4 | 63.3 | 16.5 |
| 2 | $H_2SO_4$ (1.05eqv) | $CH_3CN$ | rt | 0.5 | 0 | 3.7 | 92.6 | 3.7 |
| 3 | $H_2SO_4$ (0.5eqv) | $CH_3CN$ | rt | 1 | 4.2 | 4.2 | 84.0 | 7.6 |
| 4 | $H_2SO_4$ (0.2eqv) | $CH_3CN$ | rt | 3 | 8.0 | 4.0 | 80.0 | 8.0 |
| 5 | $H_2SO_4$ (1.05eqv) | $CH_2Cl_2$ | rt | 0.5 | 0 | 5.2 | 87.0 | 7.8 |
| 6 | $H_2SO_4$ (1.05eqv) | EtOAc | rt | 22.5 | 0 | 3.6 | 90.9 | 5.5 |

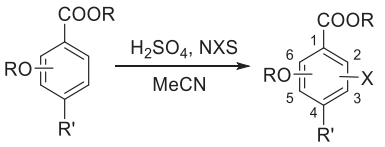
[a]Reaction conditions: salicylic acid (**4**):NBS = 1:1.05.
[b]Products characterized by $^1$H NMR, SM refers to the substrate, the numbers in the product composition denote the positions of bromination.

and 4a–6a), except for compounds **1** and **6** (Table 2, entries 1a and 3a). However, with these substrates, the reaction times were longer than for the reaction with $H_2SO_4$. The results demonstrated that $H_2SO_4$ was vital for promoting the bromination reaction. With $H_2SO_4$, the bromination of compounds **1** and **5–9** afforded high *para*-selective yields of brominated products (Table 2, entries 1b–6b). For compounds **5–7**, the monobrominated products **5a**, **6a**, and **7a** were obtained in the yields of 97%, 94%, and 98%, respectively, and with 100% selectivity (Table 2, entries 2b–4b). $H_2SO_4$-promoted regioselective monobromination was suitable for 3-methoxybenzoic acid (**10**), providing the *para* product (**10a**) in 91% yield and quantitative selectivity (Table 2, entry 7b). Gram-scale synthesis of 5-bromo-4-fluoro-2-hydroxybenzoic acid (**1a**) was performed to demonstrate the practical application of this method, which afforded 14.2 g **1a** in an excellent yield (95%) with straightforward manipulation (see Supporting Information).

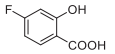
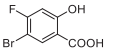
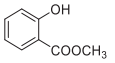
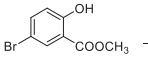
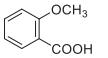
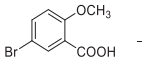
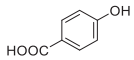
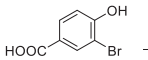
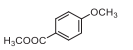
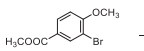
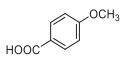
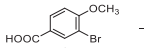
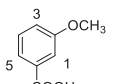
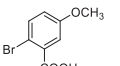
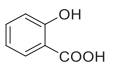
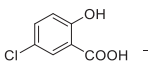
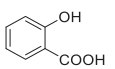
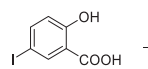
With the bromination data in hand, we extended our work to investigate the effect of $H_2SO_4$ on chlorination and iodination using *N*-chlorosuccinimide (NCS) or *N*-iodosuccinimide (NIS), respectively, and salicylic acid (**4**) as a template substrate (Table 2). Compared with the control reactions, the chlorination and iodination of compound **4** afforded regioselective monochlorination product **4d** and monoiodination product **4e** in the yields of 92 and 82%, respectively, with good selectivity (Table 2, entries 8b and 9b). The results demonstrated that $H_2SO_4$ also increases the speed and selectivity of chlorination and iodination.

The combination of $H_2SO_4$ and NBS in $CH_3CN$ was applied to the bromination of other phenol derivatives (Table 3). Bromination of phenol gave good yield and high regioselectivity for the *para* product (**11a**) after only 2 h of stirring (Table 3, entry 1b). Various *ortho*-substituted phenol analogs containing electron-donating or -withdrawing groups were investigated. Bromination of **13–17** afforded high *para*-selective yields of brominated products, although bromination of **12** did not. Compared with the reactions without $H_2SO_4$, the reaction times were only 2 or 3 h in the presence of $H_2SO_4$. For *para*-substituted phenol analogs (**18** and **19**), bromination with NBS in acetonitrile with

**Table 2.** Substrate scope for phenol derivatives (salicylic acid analogs).[a]




R = H or $CH_3$, R' = F or H  X = Br, Cl, I

| Entry[b] | Compds | Time (h) | Product ratio (%)[c] SM | 3 | 5 | 3,5 | Product | Yield (%)[d] |
|---|---|---|---|---|---|---|---|---|
| 1a |  1 | 24 | 9.9 | - | 90.1 | - |  1a | |
| 1b | | 1 | 7.4 | - | 92.6 | - | | 85 |
| 2a |  5 | 30 | 20.1 | 3.9 | 42.7 | 33.3 |  5a | |
| 2b | | 2 | - | - | 100 | - | | 97 |
| 3a |  6 | 24 | 0.3 | - | 99.4 | 0.3 |  6a | |
| 3b | | 3 | - | - | 100 | - | | 94 |
| 4a |  7 | 48 | 15 | 12.5 | - | 72.5 |  7a | |
| 4b | | 4 | - | 100 | - | - | | 98 |
| 5a |  8 | 48 | 95.9 | 4.1 | - | - |  8a | |
| 5b | | 48 | 14.5 | 77.5 | - | 8.0 | | 76 |
| 6a |  9 | 48 | 35.9 | 44.0 | - | 20.1 |  9a | |
| 6b | | 48 | 8.3 | 91.7 | - | - | | 82 |
| 7a |  10 | 48 | 15.2 | 4.8 | 80.0 | - |  10a | |
| 7b | | 0.5 | - | - | 100 | - | | 91 |
| 8a |  4 | 48 | 23.5 | 23.0 | 53.5 | - |  4d | |
| 8b | | 2.5 | - | 5.3 | 94.7 | - | | 92 |
| 9a |  4 | 48 | - | 10.6 | 59.2 | 30.2 |  4e | |
| 9b | | 1.5 | - | 11.0 | 84.8 | 4.2 | | 82 |

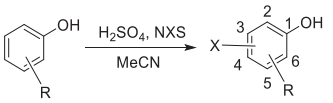
[a]Reaction conditions: $H_2SO_4$ (285 $\mu$L, 1.05 equiv.) was added to $CH_3CN$ (10 mL) containing the substrate (5 mmol) at room temperature, and after 5 min, NBS, NCS, or NIS (1.05 equiv.) was added to the mixture. The reaction was monitored using TLC until completion or extended to 48 h. The product was isolated by chromatography.

[b]Entry a: without $H_2SO_4$, entry b: with $H_2SO_4$ (1.05 equiv.).

[c]Products characterized by $^1$H NMR, SM refers to the substrate, the numbers in the product composition denote the positions of bromination.

[d]Isolated yield.

**Table 3.** Scope of the bromination reaction.[a]



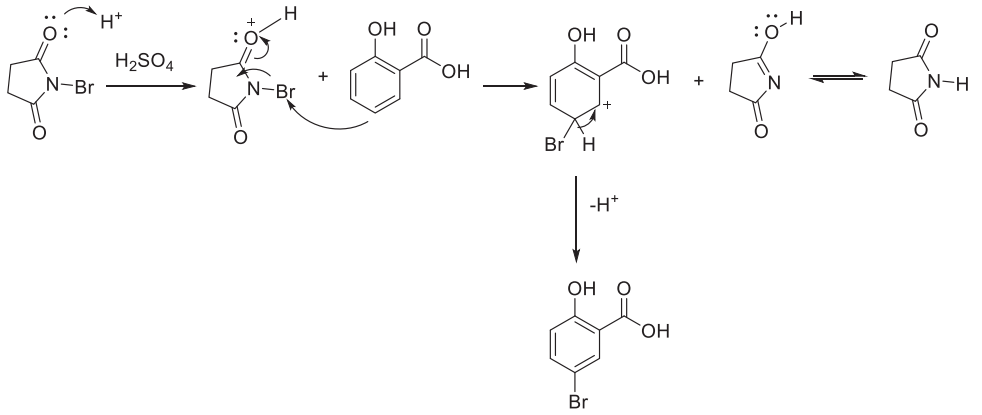

| Entry[b] | Compds | Time (h) | Product ratio (%)[c] SM | 2 | 4 | 6 | 2,4 | 2,6 | 4,6 | 2,4,6 | Product | Yield (%)[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1a |  **11** | 56 | 10.4 | 4.4 | 41.3 | - | 18.4 | 1.4 | - | 24.1 |  **11a** | - |
| 1b | | 2 | - | 2.8 | 94.1 | - | 3.1 | - | - | - | | 79 |
| 2a |  **12** | 24 | 36.2 | - | 38.9 | 1.9 | - | - | 23.0 | - |  **12a** | - |
| 2b | | 24 | 26.5 | - | 55.2 | 3.3 | - | - | 15.0 | - | | - |
| 3a |  **13** | 24 | 15.1 | - | 37.7 | 9.4 | - | - | 37.8 | - |  **13a** | - |
| 3b | | 2 | - | - | 97.1 | 2.9 | - | - | - | - | | 80 |
| 4a |  **14** | 24 | 31.5 | - | 23.1 | 6.9 | - | - | 38.5 | - |  **14a** | - |
| 4b | | 3 | - | - | 91.7 | 5.5 | | - | 2.8 | - | | 80 |
| 5a |  **15** | 6 | 31.6 | - | 21.9 | 5.5 | - | - | 41.0 | - |  **15a** | - |
| 5b | | 2 | 5.3 | - | 88.5 | 6.2 | - | - | - | - | | 73 |
| 6a |  **16** | 7 | 26.8 | - | 46.9 | 8.0 | - | - | 18.3 | - |  **16a** | - |
| 6b | | 2 | - | - | 88.5 | 6.2 | - | - | 5.3 | - | | 80 |
| 7a |  **17** | 2 | 4.8 | - | 80.6 | 8.1 | - | - | 6.5 | - |  **17a** | - |
| 7b | | 2 | - | - | 93.5 | 3.7 | - | - | 2.8 | - | | 77 |
| 8a |  **18** | 9 | 34.1 | 19.8 | - | - | - | 46.1 | - | - |  **18a** | - |
| 8b | | 2 | - | 100 | - | - | - | - | - | - | | 92 |
| 9a |  **19** | 24 | 7.0 | 87.0 | - | - | - | 6.0 | - | - |  **19a** | - |
| 9b | | 6 | 7.4 | 92.6 | - | - | - | - | - | - | | 78 |
| 10a |  **20** | 48 | 34.7 | 61.5 | - | 3.8 | - | - | - | - |  **20a** | - |
| 10b | | 2 | - | 98.0 | - | 2.0 | - | - | - | - | | 95 |
| 11a |  **15** | 48 | 11.1 | - | 79.4 | 9.5 | - | - | - | - |  **18a** | - |
| 11b | | 3 | - | - | 87.1 | 8.6 | - | - | 4.3 | - | | 86 |
| 12a |  **15** | 48 | 21.4 | - | 46.0 | 0.9 | - | - | 31.7 | - |  **15b** | - |
| 12b | | 1 | 1.0 | - | 97.1 | 1.0 | - | - | 0.9 | - | | 89 |

[a]Reaction conditions: $H_2SO_4$ (285 $\mu$L, 1.05 equiv.) was added to $CH_3CN$ (10 mL) containing the substrate (5 mmol) at room temperature, and after 5 min, NBS, NCS, or NIS (1.05 equiv.) was added to the mixture. The reaction was monitored using TLC until completion. The product was isolated by chromatography.

[b]Entry a: without $H_2SO_4$, entry b: with $H_2SO_4$ (1.05 equiv.).

[c]Products characterized by $^1$H NMR or GC-MS (**11a**), SM refers to the substrate, the numbers in the product composition denote the positions of bromination.

[d]Isolated yield.




**Scheme 2.** The proposed pathway of sulfuric acid-promoted regioselective monobromination.

$H_2SO_4$ gave excellent yields and selectivity of the desired products (Table 3, entries 8b and 9b). The effectiveness of the monobromination reaction was demonstrated further in the reaction of chromen (**20**), which furnished the *ortho* product (**20a**) in 95% yield and 98% selectivity (Table 3, entry 10b).

The effect of $H_2SO_4$ on chlorination and iodination of phenol derivatives was examined using 2-bromo-phenol (**15**) as a template substrate (Table 3). Compared with the control reactions, the chlorination and iodination of compound **15** afforded regioselective monochlorination product **18a** and monoiodination product **15b** in yields of 86% and 89% with 87.1% and 97.1% selectivity, respectively (Table 3, entries 11b and 12b). The selectivity and yield were better than the results in the literatures,[19,29] and we found that the chlorination could be achieved without $H_2SO_4$ after sufficient reaction time. The results showed that $H_2SO_4$ increases the speed and selectivity of chlorination and iodination of other phenol derivatives.

To gain further insight into the NBS-$H_2SO_4$ method, $^{13}C$ NMR measurements were performed. Immediately after the addition of equal equivalent of concentrated $H_2SO_4$ to NBS in $CD_3CN$, the carbonyl and methylene signals showed changes (see Supporting Information). The carbonyl signal (175.36 ppm) was split into two signals (178.42 and 181.64 ppm), and the methylene signal (29.21 ppm) was split into two signals (29.40 and 29.24 ppm). The results showed that NBS was protonated by $H_2SO_4$ to form an NBS–$H_2SO_4$ complex via hydrogen bonding, and the N–Br bond was polarized. The polarized Br attacked the position activated by the OH group to form the desired product (Scheme 2). The bromination was accelerated by the formation of the NBS–$H_2SO_4$ complex and polarized N–Br bond.

## Conclusion

An efficient, convenient aromatic monobromination method was developed for brominating phenol derivatives, especially salicylic acid analogs. Rapid, regioselective monobromination was accomplished using NBS as a safe bromine source in the presence of $H_2SO_4$, and good to excellent selectivity and yield were obtained. Furthermore, the reaction is also applicable to chlorination and iodination using NCS and NIS, respectively.

The mild reaction conditions, rapid conversion, straightforward manipulation, and excellent selectivity are notable advantages of the method and make it potentially suitable for large-scale aromatic halogenation.

## Experimental

### General information

All the substrates and reagents were purchased from commercial suppliers and were used without further purification. $^{1}$H NMR or $^{13}$C NMR spectra were recorded on Varian 400 MHz or 500 MHz spectrometer using $CDCl_3$, DMSO-$d_6$ or acetone-$d_6$ as solvents and tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were recorded using a Thermo Exactive Orbitrap plus mass spectrometer (ESI).

### Representative procedure for the preparation of compound 1a

To a solution of 4-fluoro-2-hydroxybenzoic acid (780.6 mg, 5 mmol) in MeCN (10 mL) was added con. $H_2SO_4$ (285 µL, 1.05 equiv.) at room temperature, the mixture was stirred for 5 min. Then, NBS (934.4 mg, 1.05 equiv.) was added to the mixture. The reaction was monitored using TLC analysis. The mixture was evaporated to dryness and MeCN (1 mL) was added to the flask. The mixture was stirred for 10 min and filtered. The filter cake was washed by water and dried to obtain the product as a white solid; yield: 85% (0.99 g). $^{1}$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 8.01 (d, $J = 8.0$ Hz, 1 H), 7.05 (d, $J = 10.0$ Hz, 1 H).[27]

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 169.9, 162.1 (d, $J_{C\text{-}F} = 13.1$ Hz), 161.9 (d, $J_{C\text{-}F} = 249.8$ Hz), 134.5 (d, $J_{C\text{-}F} = 3.2$ Hz), 112.0, 105.5 (d, $J_{C\text{-}F} = 24.9$ Hz), 97.1 (d, $J_{C\text{-}F} = 22.0$ Hz).

### Representative procedure for the preparation of compound 11a

To a solution of phenol (470.6 mg, 5 mmol) in MeCN (10 mL) was added con. $H_2SO_4$ (285 µL, 1.05 equiv.) at room temperature, the mixture was stirred for 5 min. Then, NBS (934.4 mg, 1.05 equiv.) was added to the mixture. The reaction was monitored using TLC analysis. The mixture was evaporated to dryness. $H_2O$ (15 mL) was added to the residue and extracted with $CH_2Cl_2$ ($3 \times 15$ mL). The combined organic layers were washed with water and brine, dried over $Na_2SO_4$, and concentrated under reduced pressure to afford the crude product. The major product was isolated using silica gel chromatography to obtain the product as light yellow liquid; yield: 79% (0.69 g). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.31 (dd, $J = 8.8$ Hz, 2 H), 6.71 (dd, $J = 8.8$ Hz, 2 H), 5.67 (brs, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 154.7, 132.5, 117.2, 112.9.[22]

All synthesized compounds were characterized using $^{1}$H NMR and $^{13}$C NMR spectra which can be found in Supporting Information. The products reported herein are known compounds (except **20a**) which spectroscopic data are in agreement with the public literatures.

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