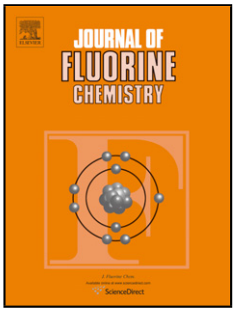

Title: A new version of Umemoto's reagents: A three-step one-pot preparation of 2,3,7,8-tetrafluoro-S-(trifluoromethyl)dibenzothiophenium triflate [1]

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A new version of Umemoto's reagents: A three-step one-pot preparation of 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate [1]

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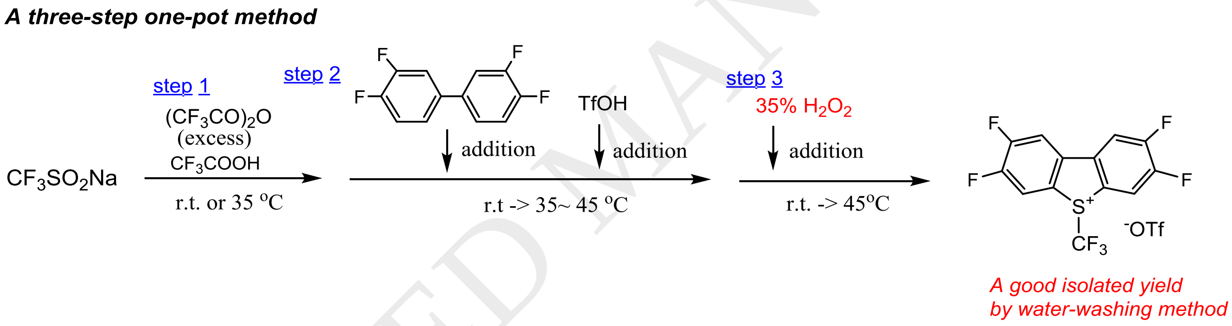
GRAPHICAL ABSTRACT



HIGHLIGHTS

- ・A three-step one-pot method was developed for the practical preparation of powerful electrophilic trifluoromethylating agent, 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **2**.
- ・The one-pot method comprised of (step 1) *in situ* generation of $CF_3S(O)OCOCF_3$, (step 2) its reaction with 3,3',4,4'-tetrafluorobiphenyl in the presence of trifluoromethanesulfonic acid and trifluoroacetic anhydride, and (step 3) treatment with hydrogen peroxide.
- ・The CF_3S by-product formed in step 2 was completely converted to the final product **2** in the step 3.
- ・The powerful reagent **2** was easily isolated in a good yield by simple water-washing method.
- ・The reaction mechanism including the formation of the CF_3S by-product was proposed.

ABSTRACT:

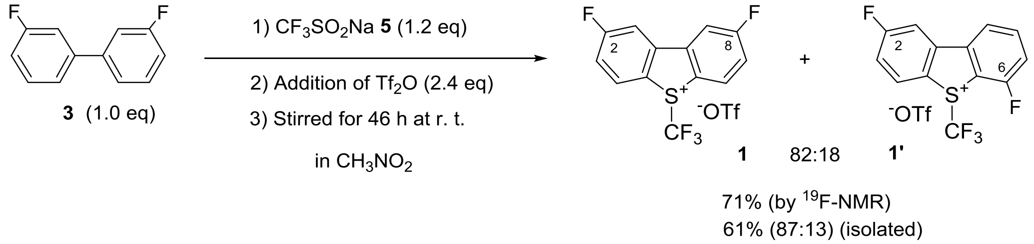
A new one-pot method was developed for the practical preparation of powerful electrophilic trifluoromethylating agent, 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **2**. This method comprised of three steps; (1) *in situ* generation of trifluoromethanesulfinyl trifluoroacetate **7**, (2) treatment of 3,3',4,4'-tetrafluorobiphenyl with **7** in the presence of trifluoromethanesulfonic acid and trifluoroacetic anhydride, and (3) treatment of the resulting mixture with hydrogen peroxide. By means of this effective three-step one-pot method, **2** was prepared in a good isolated yield by simple water-washing method. It is thus expected that easy access to **2** may lead to its wider or new applications to many areas, because tetrafluoro reagent **2** is much more powerful than 2,8-difluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **1**.

KEYWORDS: Umemoto's reagent, 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium salt, a three-step one-pot preparation, tetrafluorobiphenyl, trifluoromethanesulfinate

1. Introduction

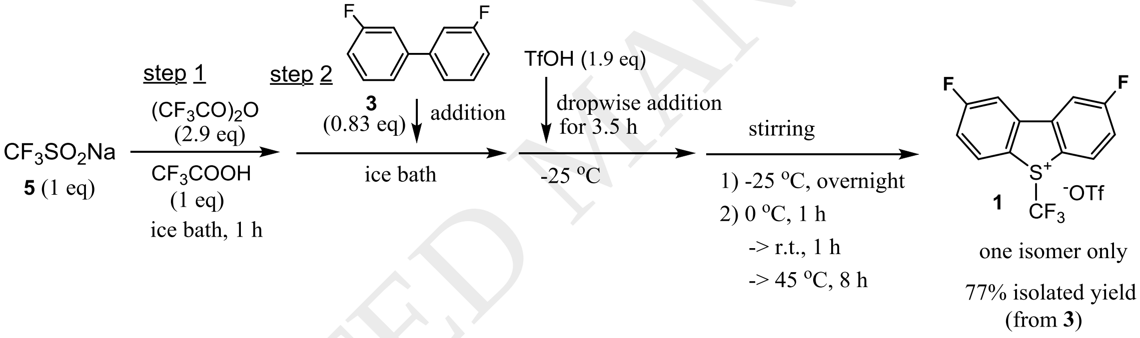
Since it has unique properties such as high stability and lipophilicity [2], the trifluoromethyl group is nowadays a widely attractive functional group, in particular, in pharmaceutical and agrochemical fields [3]. Therefore, how to effectively introduce the trifluoromethyl group into an organic molecule is a very active research target. The development of useful trifluoromethylating agents has been made for a long time to solve the problem [4]. Among them, electrophilic trifluoromethylating agents have occupied an important position in the research and application [5]. We recently developed a new version of Umemoto's reagents, 2,8-difluoro- and 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflates **1** and **2** as practically useful electrophilic trifluoromethylating agents that are powerful, thermally stable, one-pot preparable, and recyclable [5r]. At first, the new reagents **1** and **2** were synthesized from 3,3'-difluoro- and 3,3',4,4'-tetrafluorobiphenyls **3** and **4**, respectively, by modified Magnier's one-pot method [6] using sodium trifluoromethanesulfinate **5** and trifluoromethanesulfonic anhydride (triflic anhydride, Tf_2O) in nitromethane solvent. However, for the case of **3**, this method gave an 82:18 mixture of **1** and isomeric 2,6-difluoro triflate **1'** as shown in Scheme 1.

Scheme 1. Modified Magnier's one-pot treatment of 3,3'-difluorobiphenyl **3**



As an economical and industrially applicable method, we succeeded in the development of a new one-pot method which used cheap trifluoromethanesulfonic acid (triflic acid, TfOH) and trifluoroacetic anhydride in place of expensive triflic anhydride and excluded the use of potentially explosive nitromethane as the solvent [5r]. This two-step one-pot method provided **1** as a sole isomeric product in a good isolated yield (Scheme 2, see [7]) and made it possible to produce 100 kg per batch of **1** in our factory [8].

Scheme 2. A two-step one-pot method for the preparation of **1** using TfOH and $(CF_3CO)_2O$ in place of Tf_2O



However, this method was not useful for the preparation of Umemoto's reagent **2**, because the yield was very low and a significant amount of a by-product was formed.

Reagent **2** with four fluorine atoms on the benzene rings was shown to be much more powerful than **1** with two fluorine atoms [5r]. Because of the higher power of **2** [9], it may be expected that **2** has wider or new applications to many areas. Therefore, an effective and industrially applicable method for the production of **2** is highly desired. In this paper, we report a new three-step one-pot method suitable for the practical production of the powerful tetrafluoro Umemoto's reagent **2**.

2. Results and Discussion

The two-step one-pot method suitable for difluoro Umemoto's reagent **1** was applied to the preparation of more powerful tetrafluoro reagent **2**. However, the reaction temperature for the trifluoromethanesulfinylation of 3,3',4,4'-tetrafluorobiphenyl **4** in step 2 was required to be high (> r.t.) because of lower reactivity of **4** than 3,3'-difluorobiphenyl **3**, the reaction of which smoothly occurred at low temperature (< 0 °C). As a result, a large amount of a by-product was formed as shown in Scheme 3. ^{19}F NMR of the reaction mixture clearly showed a significant amount of the formation of the by-product in addition to **2** (Figure 1). The by-product was tentatively assigned as 3,3',4,4'-tetrafluoro-6-(trifluoromethylthio)biphenyl **6** by the NMR analysis and the reaction progress details discussed below. The ^{19}F NMR (with ^{1}H decoupling) showed a singlet of -42.71 ppm and a set of four doublets with a F-F coupling constant of 22.5 Hz at -132.89, -134.82, -139.03, and -139.50 ppm. The former singlet could easily be assigned as CF_3S fluorine atoms of **6** and the latter four doublets as four different fluorine atoms on the biphenyl ring of **6**. The ratio of **2**/**6** changed depending on the reaction conditions. However, despite all of our efforts, attempts to get rid of the formation of **6** failed.

Scheme 3. Attempt for the preparation of **2** from 3,3',4,4'-tetrafluorobiphenyl **4** by the same method as **1**

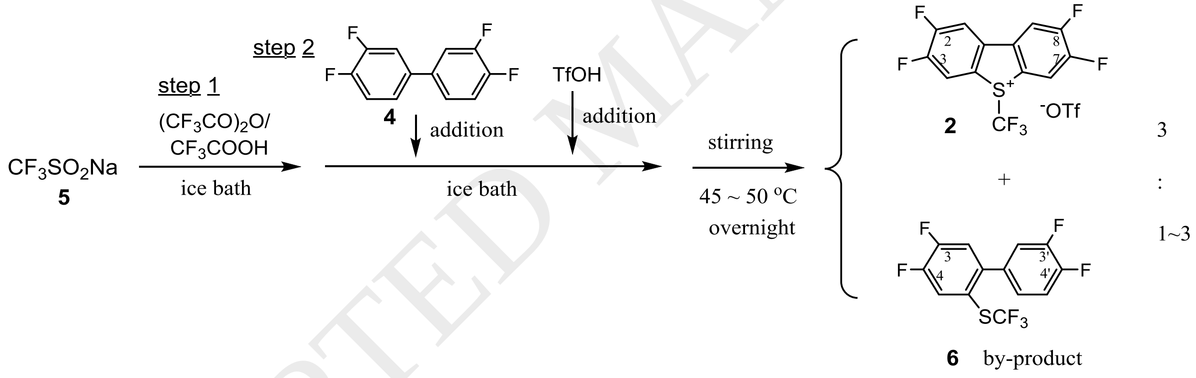
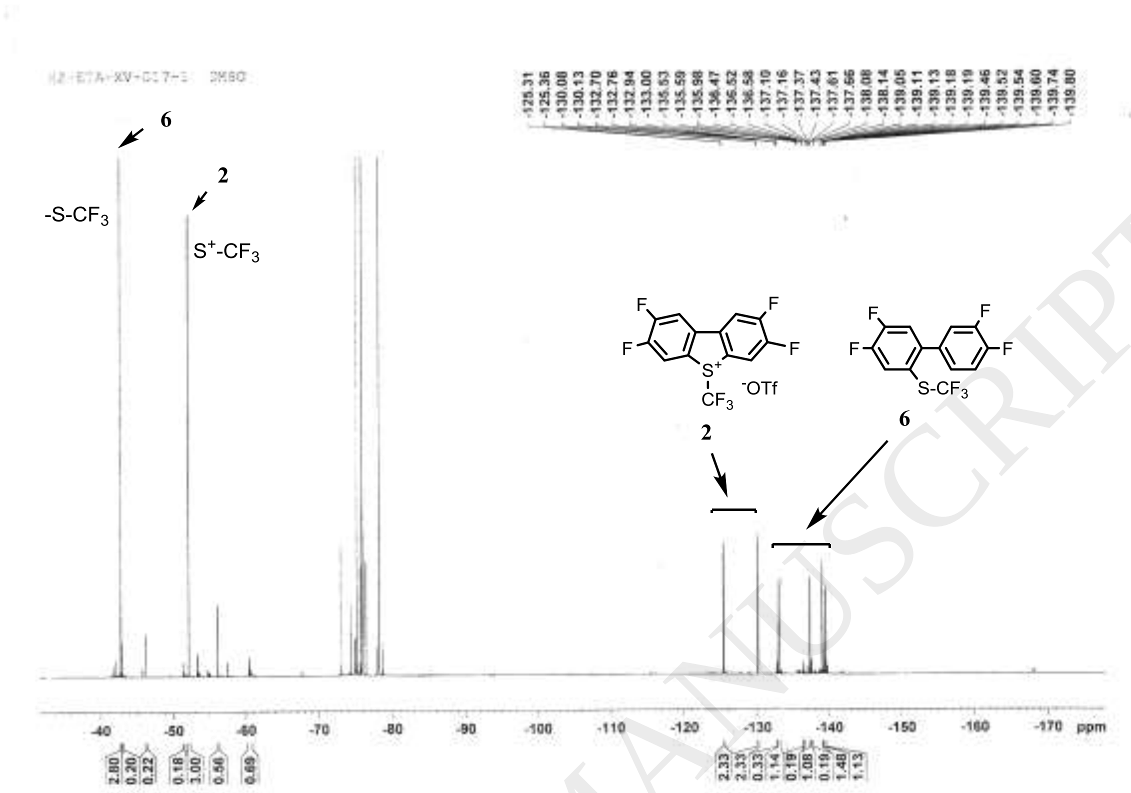
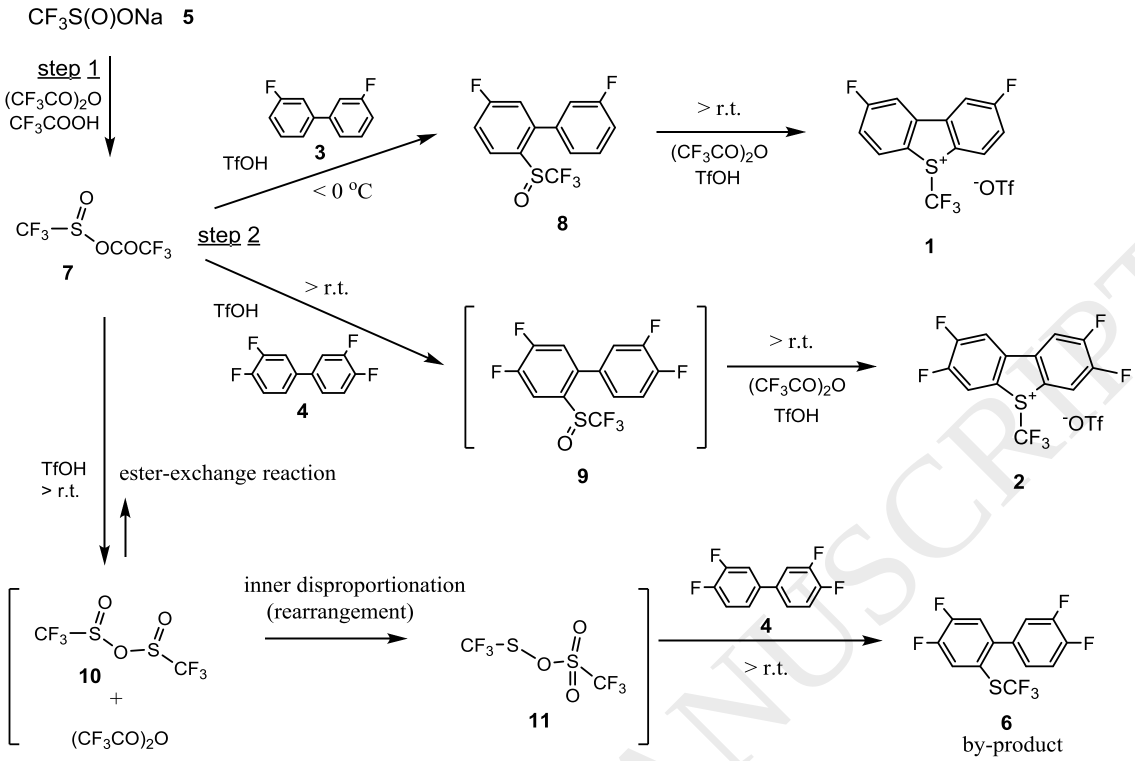


Fig. 1. ^{19}F NMR of the reaction mixture from the reaction of **4** with $CF_3SO_2Na/(CF_3CO)_2O/TfOH$



At this point, it is useful to discuss the difference in reaction between two cases of difluorobiphenyl **3** and tetrafluorobiphenyl **4**. There was nearly no formation of the corresponding by-product in the former case [10], while a large amount of by-product **6** was formed in the latter case. It could be explained clearly by the proposed mechanism as shown in Scheme 4.

Scheme 4. Proposed reaction mechanism for the reactions of **3** and **4** with $CF_3SO_2Na/(CF_3CO)_2O/TfOH$



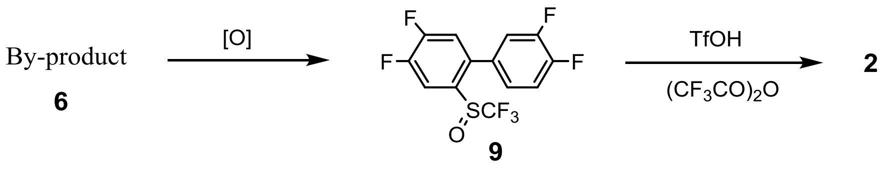
As discussed in our previous paper [5r], intermediate **7** was formed in step 1. In step 2, **7** reacted with **4** at more than room temperature in the presence of TfOH to give **9**, which then underwent cyclization under the reaction conditions to give the final product **2**. However, **7** caused an ester-exchange reaction at more than room temperature to give **10** and trifluoroacetic anhydride, and **10** could undergo inner disproportionation reaction or rearrangement to give **11**, which then reacted with **4** to form the trifluoromethanethiolated by-product **6**. Yi et al. reported similar trifluoromethanethiolation of arenes by the reaction of CF_3SO_2Na with Tf_2O in which **11** was proposed as a reactive species formed by disproportionation of two $CF_3S(O)OTf$ molecules ($2CF_3S(O)OTf$ -> **11** + Tf_2O) [11]. On the other hand, the corresponding by-product was scarcely formed in the case of 3,3'-difluorobiphenyl **3**, because the trifluoromethanesulfinylation of **3** with **7** in step 2 easily occurred at the low temperature (< 0 ºC) to give **8**, which cyclized at more than room temperature to give **1**. Therefore, the strong trifluoromethanethiolating agent **11** could not be generated in the case of **3**.

Scheme 5. Design of the improved method for the preparation of tetrafluoro reagent **2**

$$CF_3SO_2Na \xrightarrow[\substack{(CF_3CO)_2O \\ \text{a large excess amount}}]{\underline{\text{step}}\ \underline{1}} \xrightarrow[\substack{\text{tetrafluorobiphenyl } \mathbf{4} \\ \text{TfOH}}]{\underline{\text{step}}\ \underline{2}} \xrightarrow[\text{oxidant}]{\underline{\text{step}}\ \underline{3}} \text{Umemoto's reagent } \mathbf{2}$$

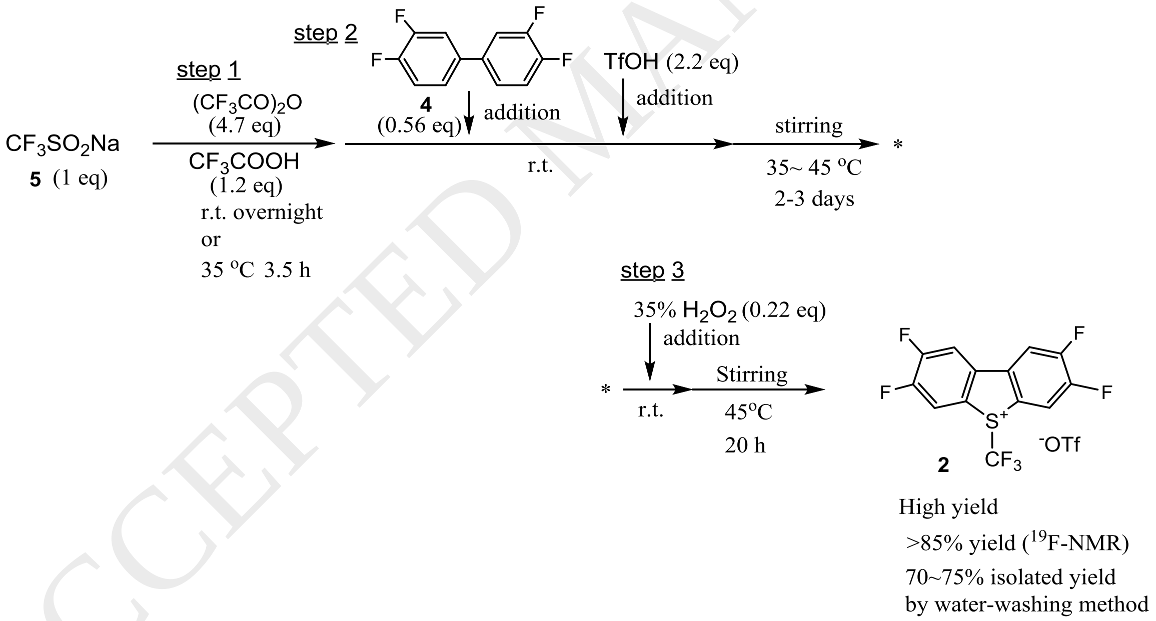
Since we failed in all attempts to get rid of the formation of **6**, we designed to follow the one-pot process with the oxidation step (step 3, Scheme 5). We expected that, in step 3, the by-product **6** could be oxidized to the $CF_3S(O)$-intermediate **9**, which was then cyclized to the final product **2** by action of the existing triflic acid and trifluoroacetic anhydride (Scheme 6).

Scheme 6. Oxidation and cyclization reactions expected in step 3.



As a preliminary examination, we used *m*-chloroperbenzoic acid as an oxidizer and confirmed the conversion of the by-product **6** to the final product **2**. Finally, we chose 35% hydrogen peroxide as the oxidizer that is cheap and does not leave any solid residue from it after the reaction. In step 3, the actual oxidizer would be trifluoroperacetic acid (CF_3COOOH), because H_2O_2 could immediately react with existing $(CF_3CO)_2O$ to form CF_3COOOH.

Scheme 7. A three-step one-pot method for the preparation of powerful Umemoto's reagent **2**



The reaction conditions for each step and the ratios of the reactants were determined by repeated experiments, as shown in Scheme 7. For 1 equiv. of CF_3SO_2Na **5**, $(CF_3CO)_2O$ (4.7 equiv.) and CF_3COOH (1.2 equiv.) in step 1, tetrafluorobiphenyl **4** (0.56 equiv.) and TfOH (2.2 equiv.) in step 2, and aqueous 35% H_2O_2 solution (H_2O_2, 0.22 equiv.) in step 3 were used. The amount (0.56 equiv.) of tetrafluorobiphenyl **4** was chosen so that all of **4** was consumed in these reactions. The amount (0.22 equiv.) of H_2O_2 was chosen as a minimum amount to consume the by-product **6**. By these conditions, the desired product **2** was formed in a high yield and easily isolated in a good yield by the water-washing method as seen in Scheme 7 (*see* Experiment section).

The large amount (4.7 equiv.) of trifluoroacetic anhydride used in step 1 contained not only the amount necessary for the reaction with CF_3SO_2Na in step 1 and for the cyclization in step 2, but also for the reactions with H_2O_2 and H_2O in aqueous 35% H_2O_2 solution, followed by the cyclization reaction giving **2**, in step 3. Trifluoroacetic anhydride also served as a solvent, in particular in step 1. Since all the reactions of Scheme 7 were very sensitive to moisture, they had to be completely dried. Trifluoroacetic anhydride was able to completely get rid of moisture (water) in the reactor by the reaction of $(CF_3CO)_2O + H_2O \rightarrow 2CF_3COOH$, which also served as a solvent. This was a very advantageous point to prepare **2** without special care in highly humid climate areas like east China.

Figures 2 and 3 showed the ^{19}F NMR of the reaction mixture after step 2 and step 3, respectively. For this case, the former NMR showed that a 4:1 mixture of **2** and **6** was formed and a very small amount of the starting material **4** remained intact at this moment. The latter NMR showed that **6** was clearly converted to the final product **2** after the oxidation step 3. Interestingly, it seemed that some of the starting material **4** was converted to **2** in step 3 because **4** was almost completely consumed after step 3. Thus, product **2** was found to be formed in a high yield (89%) by the ^{19}F NMR analysis of the reaction mixture using benzotrifluoride as an internal reference and **2** was easily isolated in a good yield (72%) by the water-washing method (*see* a typical procedure in the experimental section).

Fig. 2. ^{19}F NMR of the reaction mixture after step 2

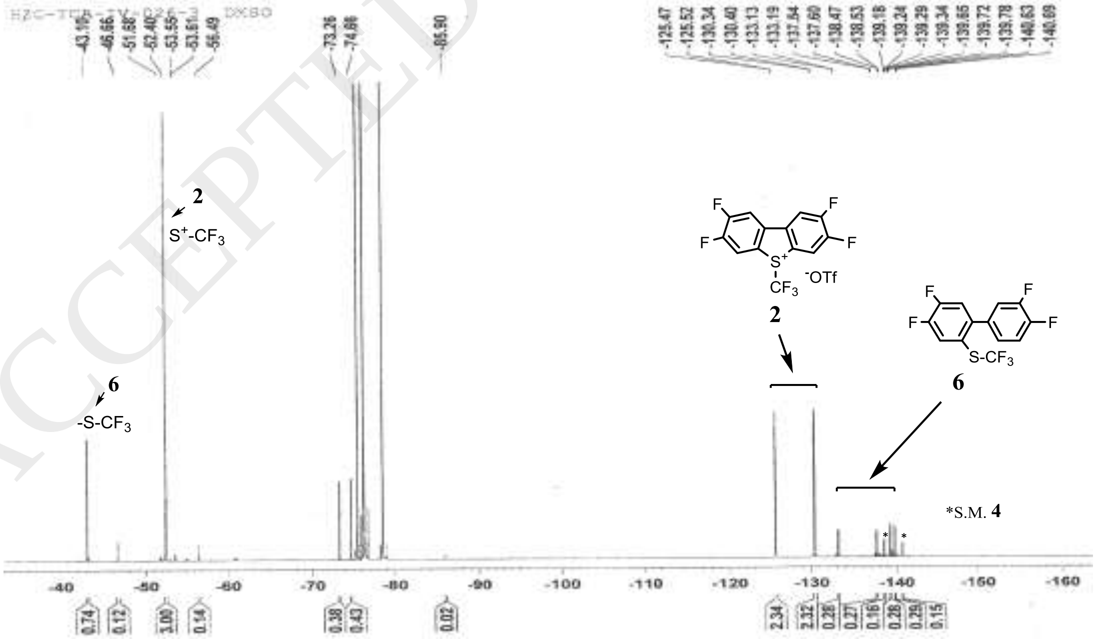
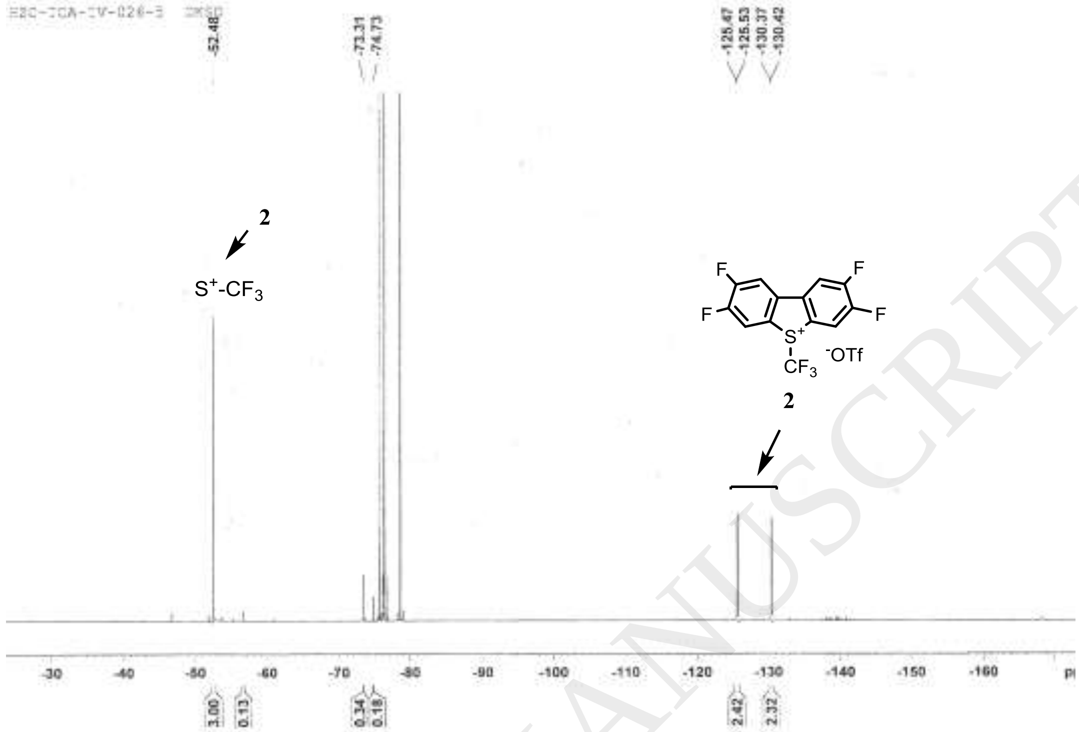


Fig. 3. ^{19}F NMR of the reaction mixture after step 3



4. Conclusion

The problem in the preparation of powerful 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **2** was the significant formation of the by-product **6** due to the low reactivity of 3,3',4,4'-tetrafluorobiphenyl. The practical three-step one-pot method developed here by us clearly dissolved the problem and led to the high yield production of the powerful reagent **2**. Since the tetrafluoro reagent **2** is much more powerful than difluoro reagent **1**, it is thus expected that the easy access to **2** could advance wider or new applications of **2** to many areas.

5. Experimental

General information. ^{19}F and ^{1}H NMR spectra were measured on 400 and 376 MHz spectrometers, respectively. DMSO-d$_6$ was used as a solvent unless otherwise noted and ^{19}F chemical shifts were given as δ in ppm downfield from CFCl$_3$.

Materials. CF_3SO_2Na was dried at 80 °C for several hours by a vacuum pump. Other commercially available compounds, CF_3COOH, $(CF_3CO)_2O$, and TfOH, were used without further purification. 3,3',4,4'-Tetrafluorobiphenyl **4** of high purity was easily prepared in a high yield by the homo-coupling reaction of 3,4-difluoroiodobenzene with copper powder using a small amount of *N*-methylpyrrolidinone [*see* ref. 12]. This method was useful at lab scale. Previously, **4** was prepared by the homo-coupling reaction of 3,4-difluorophenylmagnesium bromide with air, catalyzed by $MnCl_2.2LiCl$ [5r]. However, as the purity of the product was not high, a purification process such as distillation was needed.

A three-step one-pot procedure for the preparation of 2,3,7,8-tetrafluoro-S-(trifluoromethyl)dibenzothiophenium triflate ***2****; a typical procedure.*
(Step 1) In a 250 mL three-necked glassware flask equipped with a dropping funnel, a condenser, a calcium chloride-drying tube, a thermometer, and a magnetic stirrer, were placed 12.5 g (80.1 mmol) of dry sodium trifluoromethanesulfinate **5**. Into the flask, 52 mL (654 mmol) of trifluoroacetic anhydride was dropwise added for 10 min and then 7.4 mL (97 mmol) of trifluoroacetic acid was dropwise added for 10 min with stirring under water bath cooling [13]. The reaction mixture was stirred overnight (19 hr) at room temperature [14]. (Step 2) To the reaction mixture, 10.0 g (44.2 mmol) of 3,3',4,4'-tetrafluorobiphenyl **4** was added by one-portion at room temperature and then 15.5 mL (176 mmol) of triflic acid was dropwise added for 12 min with stirring under water bath cooling. After the reaction mixture was stirred at room temperature for 7 h, the mixture was stirred on an oil bath at 35 ^{o}C for 15 h and then at 45 ^{o}C for 24 h. The mixture was cooled to room temperature. (Step 3) To the reaction mixture, a mixture of 1.72 g of aqueous 35% H_2O_2 solution and 8 mL of CF_3COOH was dropwise added for 30 min with stirring under water bath cooling. After the reaction mixture was stirred at room temperature for 2 h, the reaction mixture was stirred on an oil bath at 45 ^{o}C for 20 h and cooled to room temperature. ^{19}F NMR analysis of the reaction mixture using benzotrifluoride as an internal standard showed that 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **2** was produced in 89% yield based on the starting material **4**. The reaction mixture was evaporated under reduced pressure. To the residue, 25 mL of toluene was added and toluene was evaporated under reduced pressure. This process (addition and evaporation of 25 mL of toluene) was repeated additionally two times. To the residue, 80 mL of water and 80 mL of toluene were added and the mixture was vigorously stirred for 1 h at room temperature and then for 1 h on an ice bath. The resulting precipitates were collected by filtration and washed with cold water (20 mL x 2) and then with toluene (25 mL x 3), giving 15.04 g (72%) of the product **2** after drying. If necessary, further purification could be made by recrystallization from CH_3CN-$^{t}BuOMe$ at room temperature [15]. The spectral data of the product agreed with those of the authentic sample: ^{19}F NMR (with ^{1}H decoupling) δ -51.49 (3F, s, CF_3S), -77.83 (3F, s, CF_3SO_3), -124.90 (2F, d, *J* = 21.5 Hz, 2,8-F), -129.49 ppm (2F, d, *J* = 21.5 Hz, 3,7-F); ^{1}H NMR δ 8.75 (m, 2H), 8.85 ppm (m, 2H).

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[1] Presented in 24th Winter Fluorine Conference held at Clearwater Beach, FL, U.S.A. on January 13-18, 2019, Abstract No. WFC 2.

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[7] In a 1 L glassware flask equipped with a dropping funnel, a condenser, a thermometer, a drying tube ($CaCl_2$), and a magnetic stirrer, were put 120 g (769 mmol) of CF_3SO_2Na, and then 57 mL (745 mmol) of CF_3COOH was added on an ice bath. Trifluoroacetic anhydride (320 ml, 483 g, 2.3 mol) was dropwise added for about 15 min on an ice bath and the resulting mixture was stirred for 1 h on an ice bath. After 121.9 g (640 mmol) of 3,3'-difluorobiphenyl **3** was added, the mixture was cooled to -25 ^oC and 230 g (1.53 mol) of TfOH was dropwise added for 3.5 h so that the temperature of the mixture was kept at -25 ^oC or less. After the addition, the reaction mixture was stirred overnight (17 h) at -25 ^oC and then the mixture was stirred for 1 h on an ice bath, for 1 h at room temperature, and then for 8 h on an oil bath at 45 ^oC. The reaction mixture was evaporated under reduced pressure. The resulting residue was mixed with 300 mL of ethanol and the mixture was evaporated under reduced pressure. Again, the resulting mixture was mixed with 300 mL of ethanol and the mixture was evaporated under reduced pressure. To the resulting residue, 300 mL of toluene and 300 mL of water were added and the mixture was stirred overnight. The resulting precipitates were collected by filtration and washed with water (100 mL x 3) and toluene (100 mL x 3), giving 214.7 g (77%) of 2,8-difluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **1** after drying (6 h at 75 ^oC).

[8] T. Umemoto, 23rd Winter Fluorine Conference held at Clearwater Beach, FL, U.S.A. on January 15-20, 2017, Abstract No. WFC 60.

[9] (a) Mizuta, S.; Verhoog, S.; Wang, X.; Shibata, N.; Gouverneur, V.; Médebielle, M. *J. Fluorine Chem.* **2013**, *155*, 124-131. (b) Li, M.; Xue, X.-S.; Guo, J.; Wang, Y.; Cheng, J.-P. *J. Org. Chem.* **2016**, *81*, 3119-3126.

[10] Three very small singlets at -43.36 ppm (0.03), -43.27 (0.04), and -42.93 (0.01) [the figure in parentheses is a relative intensity to product **1** (1)] were observed in the range in which the peak of SCF_3 might appear. However, they could not be assigned because of very small amount.

[11] Liu, J.; Zhao, X.; Jiang, L.; Yi, W. *Adv. Syn. & Cat.* **2018**, *360*, 4012-4016.

[12] 3,3',4,4'-Tetrafluorobiphenyl **4** was easily prepared by the following method: In a glassware flask, were put 85.7 g (357 mmol) of 3,4-difluoroiodobenzene, 43.2 g (680 mmol) of copper powder, and 86 g of *N*-methylpyrrolidinone (NMP). The mixture was stirred under nitrogen atmosphere on an oil bath at 190 ^oC for 5 h. After cooling to room temperature, the reaction mixture was mixed with 300 mL of *tert*-butyl methyl ether and filtered in order to remove copper and its salt. The filtrate was washed with water (300 mL x 3) and then with saturated aqueous sodium chloride solution (300 mL x 1), and dried with magnesium sulfate and filtered. The filtrate was evaporated and the resulting residue was column-chromatographed using hexane as an eluent to give a white solid (35 g, 87% yield) of product **4**. The spectral data agreed with those of the authentic sample: ^{19}F NMR ($CDCl_3$) (with ^1H decoupling) δ -136.88 (d, *J* = 21 Hz, 2F), -139.64 ppm (d, *J* = 21 Hz, 2F); ^1H NMR ($CDCl_3$) δ 7.25 (m, 4H), 7.34 ppm (m, 2H).

[13] Note: If the stirring is difficult because of solidifying, an additional amount (7.4 mL) of trifluoroacetic acid may be added.

[14] Note: This process (stirring overnight at room temperature) may be replaced by stirring for 3.5 hours at 35 °C.

[15] For the recrystallization, ${}^{t}BuOCH_3$ was added to a solution of **2** in the minimum amount of acetonitrile at room temperature.