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Powerful, Thermally Stable, One-Pot-Preparable, and Recyclable Electrophilic Trifluoromethylating Agents: 2,8-Difluoro- and 2,3,7,8-Tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium Salts

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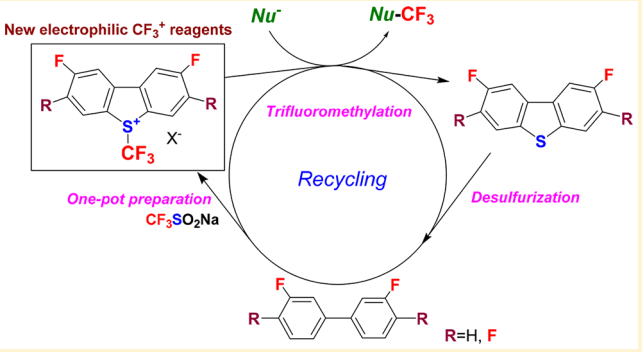
Supporting Information

ABSTRACT: Although many electrophilic trifluoromethylating agents have been reported to date, practically useful reagents have yet to be developed. *S*-(Trifluoromethyl)dibenzothiophenium salts, known as Umemoto's reagents, have two significant drawbacks that have hampered their practical application: (1) synthesis involving many steps and (2) the formation of large amounts of dibenzothiophene as waste after trifluoromethylation. Our idea to substitute fluorine at specific positions on the dibenzothiophenium rings has resulted in massive improvements in the synthesis, properties, reactivity, and applications of these compounds. On the basis of this idea, 2,8-difluoro- and 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflates and other salts were developed as powerful, thermally stable, one-pot-preparable, and recyclable reagents for the trifluoromethylation of various types of nucleophilic substrates, such as carbanions, (hetero)aromatics, alkenes, alkynes, thiols, sulfinates, and phosphines. This one-pot and recycled production tremendously decreases the chemical and environmental costs of this process. Because of their higher reactivity and thermal stability, these new reagents may have wider applications than Umemoto's reagents. Therefore, these new versions of Umemoto's reagents could be widely used as the first practically useful electrophilic trifluoromethylating agents for the production of many types of trifluoromethyl-containing compounds in academic and industrial applications.



1. INTRODUCTION

Since a fluorine atom has unique properties such as the highest electronegativity, strong C−F bonding, and the smallest size after a hydrogen atom,[1] fluorinated organic compounds have attracted much interest from chemists, particularly for developing new and effective medicines, agrochemicals, and functional materials such as liquid crystals.[1,2] Among the fluorinated compounds, much attention has recently been paid to trifluoromethylated compounds because the trifluoromethyl (CF_3) group has additional unique properties such as high lipophilicity and stability.[1,2] The introduction of a trifluoromethyl group into certain organic compounds can often result in a positive and significant change in the chemical, biochemical, and physical properties of the original compound. Therefore, the trifluoromethylation of organic compounds has been a frequent target of recent synthetic organic chemistry efforts.[3]

There are three fundamental trifluoromethylation methodologies:[4] nucleophilic, free radical, and electrophilic. Among them, the electrophilic method presents a great challenge, and its development has lagged far behind the others because the generation of the trifluoromethyl cation (CF_3^+) species is extremely difficult owing to very electronegative fluorine atoms. This electrophilic method is completely different from the electrophilic methylation in hydrocarbon chemistry, which is easily accomplished as follows: $CH_3X + Nu^- \rightarrow CH_3Nu + X^-$ (X = Br or I). CF_3X does not undergo electrophilic trifluoromethylation because its polarization is opposite as $CF_3^{\delta-}-X^{\delta+}$ due to the higher electronegativity of the CF_3 group (3.45) compared to that of Br or I.[5,6] Even trifluoromethyl triflate cannot undergo electrophilic trifluoromethylation because a nucleophile will attack the sulfur atom instead of the CF_3 carbon.[7] Many attempts have been made to overcome this difficulty, and thus, many types of electrophilic trifluoromethylating agents have been reported to date (Figure 1).[8]

Previously, Yagupolskii and the author (T.U.) attempted to synthesize (trifluoromethyl)aryliodonium compounds from CF_3I but failed.[9] Afterward, the author and co-workers tried to synthesize a CF_3-diazonium compound as a source of "CF_3^+". However, they instead isolated *N*-(trifluoromethyl)-*N*-

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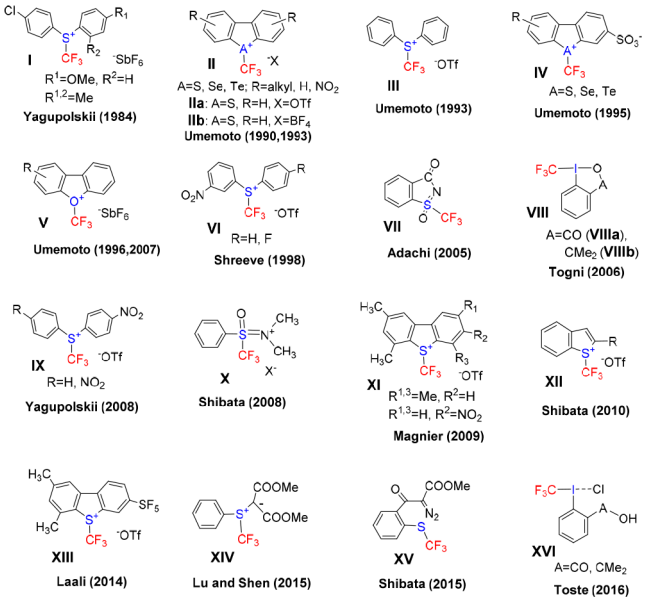


Figure 1. Various electrophilic trifluoromethylating agents.

nitroso-benzene- and -trifluoromethane-sulfonamide (TNS-B and -Tf), which acted as new sources of CF_3 radicals.[10,11] Yagupolskii synthesized *S*-(trifluoromethyl)diarylsulfonium salts **I** and reported the reaction of **I** with sodium 4-nitrophenylthiolate, giving 4-nitrophenyl trifluoromethyl sulfide in 65% yield.[12] However, the reactivity of the salts **I** was so low that **I** did not react with a reactive aromatic compound, *N*,*N*-dimethylaniline, even at elevated temperature.[12]

In the 1990s, the author and coworkers published reactive *S*-, *Se*-, and *Te*-(trifluoromethyl)dibenzo-thiophenium, -selenophenium, and -tellurophenium salts **II** as power-variable electrophilic trifluoromethylating agents.[4,13a] The heterocyclic salt structure **II** had more trifluoromethylation power than the nonheterocyclic salt structure **III**. The electron-withdrawing effect of the heteroatom and the ring substituent of the salts **II** increased the power (reactivity) in the order of Te < Se < S and alkyl < H < NO_2. The variable power enabled the first trifluoromethylation of a wide range of *C*-, *S*-, and *P*-nucleophiles. The zwitterionic reagents **IV** were also developed.[13b] Afterward, these authors succeeded in the in situ synthesis of *O*-(trifluoromethyl)dibenzofuranium salts **V** as a real CF_3^+ reagent, which enabled the first trifluoromethylation of *O*- and *N*-nucleophiles.[4,14] However, salts **V** decomposed at ≥−60 °C.

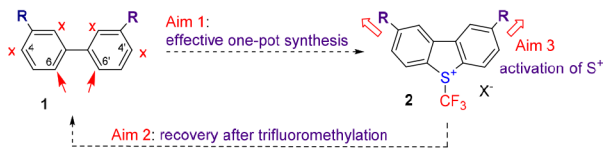
Since then, many other reagents have been reported. Schreeve developed another set of power-variable electrophilic reagent, electron-withdrawing group-substituted *S*-(trifluoromethyl)diarylsulfonium salts **VI**.[15] Adachi reported *S*-(trifluoromethyl)benzoisothiazolone **VII**.[16] Long after the attempt by Yagupolskii and Umemoto, Togni succeeded in synthesizing stabilized cyclic CF_3-iodine(III) reagents, **VIIIa** and **b**, using Me_3SiCF_3.[17] Yagupolskii synthesized differently substituted *S*-(trifluoromethyl)diarylsulfonium salts **IX**.[18] Shibata developed *S*-(trifluoromethyl)sulfoximinium salts **X**[19] and another type of *S*-(trifluoromethyl)benzothiophenium salt **XII**.[20] Magnier synthesized multimethylated *S*-(trifluoromethyl)dibenzothiophenium salts **XI** through a one-pot preparative method.[21] Similarly, Laali prepared an SF_5 analogue **XIII**.[22] Lu and Shen and Shibata reported an *S*-(trifluoromethyl)phenylsulfonium ylide **XIV**[23] and 2-diazo-3-(trifluoromethylthiophenyl)oxopropanoate **XV**,[24] respectively. Recently, Toste reported the first isolation and reactivity determination of (trifluoromethyl)iodonium salts **XVI** (**VIIIa**·HCl and **VIIIb**·HCl), which were prepared from the reaction of **VIIIa** and **VIIIb** with HCl gas.[25,26] However, all of these reagents have significant drawbacks, such as high cost, low reactivity, instability, or explosiveness.

Among the reagents listed above, **IIa** and **IIb**, known as Umemoto's reagents,[3e] and **VIIIa** and **VIIIb**, known as Togni's reagents,[3f] have become the most popular, and many new types of trifluoromethylations of organic compounds have been developed using these reagents by many other synthetic chemists.[3e,f,27,28] We thought that Umemoto's reagents may potentially have higher applicability than Togni's reagents because Umemoto's reagents have high thermal stability and high oxidation potential.[29] Togni's reagents reportedly have an explosive nature.[30] Safety is essential in practice, and a high oxidation potential may be key for the broad application of electrophilic trifluoromethylation.[29]

However, Umemoto's reagents have two significant drawbacks: (1) many reaction steps are required for their preparation and (2) large amounts of dibenzothiophene are formed as waste after trifluoromethylation. The reported practical preparative method consists of nine steps, starting from inexpensive 2-hydroxybiphenyl.[13c] Dibenzothiophene could not be converted to Umemoto's reagents.

In 2006, Magnier et al. reported a one-pot preparation method for *S*-(trifluoromethyl)diarylsulfonium triflates from an arene, CF_3SO_2K, and triflic anhydride.[21a] These authors applied this method for the preparation of Umemoto's reagent **IIa** using biphenyl as the arene,[21b] but the yield was very low (12%). Later, this report inspired us to achieve three aims to develop practically useful Umemoto's reagents: (aim 1) a one-pot, high-yield synthesis; (aim 2) recovery from the waste; and (aim 3) a higher reactivity than the original Umemoto's reagents (Scheme 1).

Scheme 1. Concept for Developing Useful CF_3 Reagents



These reagents could be developed if the R substituent could (i) cause strong *p*-activation (*o*-deactivation), (ii) survive under the reducing conditions of desulfurization, and (iii) possess strong electronegativity. We believed that R must be a fluorine atom alone because it produces an abnormal *p*-activation effect[31] and strong C−F bonding and has the highest electronegativity. As a result, we successfully developed new, one-pot-preparable, and recyclable 2,8-di- and 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium salts with high power and thermal stability as the first practically useful electrophilic trifluoromethylating agents. Here, we report the synthesis, properties, reactivity, and recycling of these fluorinated *S*-(trifluoromethyl)dibenzothiophenium salts.[32]

2. RESULTS AND DISCUSSION

2.1. One-Pot Synthesis of *S*-(Trifluoromethyl)dibenzothiophenium Triflates. 3,3′-Difluorobiphenyl **3** (1 equiv) was

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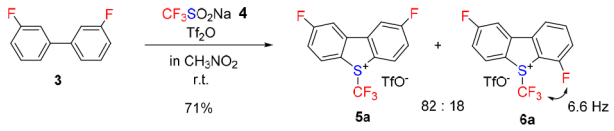
treated with sodium trifluoromethanesulfinate **4** (CF_3SO_2Na) (1.2 equiv) and triflic anhydride (Tf_2O) (2.4 equiv) in dry nitromethane (CH_3NO_2) at room temperature for 46 h to give a mixture of 2,8- and 2,6-difluoro-*S*-(trifluoromethyl)-dibenzothiophenium triflates, **5a** and **6a**, in 71% yield (92% conversion of **3**) (Scheme 2). The ratio of **5a**/**6a** was 82/18.

Scheme 2. Reaction of 3 with 4/Tf_2O

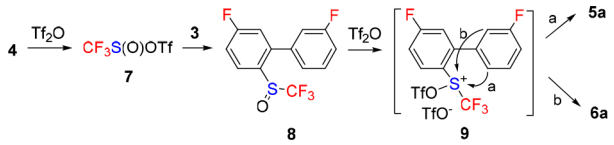


The isolation of the salt products was another key issue, for which we found a simple and effective method. The reaction residue was washed with water and an organic solvent such as dichloromethane or toluene, and the resulting precipitates were then filtered to give the products.

The pure isomer **5a** was obtained by recrystallization of the mixture and identified by spectral and elemental analyses. The minor isomer **6a** was separated by column chromatography on silica gel and identified. The structural identification was clear because the CF_3 signal of **5a** appeared as a singlet, whereas that of **6a** was a doublet with a coupling constant of 6.6 Hz due to coupling with the neighboring fluorine atom at the 6 position.

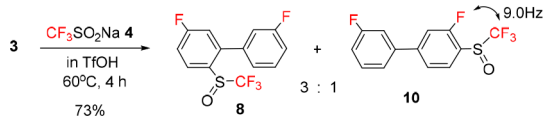
The one-pot synthesis can be explained by the consecutive reactions shown in Scheme 3. Trifluoromethanesulfinyl triflate

Scheme 3. Proposed Mechanism for the Formation of Isomers 5a and 6a



7 resulting from the reaction of **4** with Tf_2O reacted with **3** to form intermediate **8**, which then reacted with existing Tf_2O to give **5a** and **6a** through **9**. The ^{19}F NMR spectrum of the intermediate reaction mixture showed a singlet at −73.2 ppm that corresponded to **8**, which was synthesized and identified using a different method (Scheme 4).

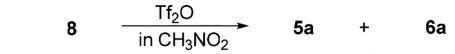
Scheme 4. Preparation of Intermediate 8



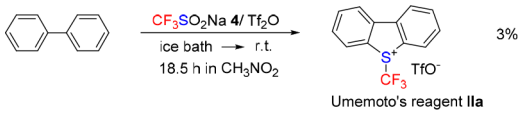
The identification of isomers **8** and **10** was clear because the CF_3 peak of **8** was a singlet, while that of **10** appeared as a doublet with a coupling constant of 9.0 Hz due to the neighboring 3-fluorine atom. Compound **8** was demonstrated to cyclize with Tf_2O to give a similar mixture of **5a** and **6a** (Scheme 5).

As mentioned above, Magnier et al. reported that the one-pot method gave only a 12% yield of Umemoto's reagent **IIa**.[21b] Since their method did not use any solvent, we attempted the one-pot approach using our method with CH_3NO_2 as a solvent (Scheme 6). The reaction was very complex, and the ^{19}F NMR

Scheme 5. Reaction of 8 with Tf_2O



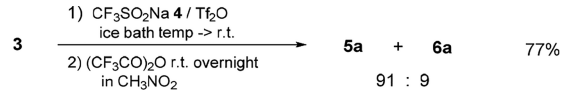
Scheme 6. One-Pot Preparation of Umemoto's Reagent IIa



spectra of the resulting reaction mixture showed that **IIa** was formed in only 3% yield. This clearly demonstrated the great *p*-activation effect of the fluorine atoms at the 3,3′-positions.

As shown in Scheme 7, the one-pot reaction of **3** (1 equiv) was improved by using **4** (1.4 equiv)/Tf_2O (1.55 equiv)/

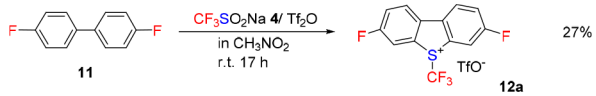
Scheme 7. Reaction of 3 with 4/Tf_2O/$(CF_3CO)_2O$



$(CF_3CO_2)_2O$ (1.2 equiv), in which the proportion of expensive Tf_2O was decreased to 1.55 equiv by adding inexpensive $(CF_3CO)_2O$. Using this method, the conversion of **3** was 100%, and the product yield increased to 77% (isolated yield after the water-washing method).

4,4′-Difluorobiphenyl **11** was treated with **4** (3 equiv)/Tf_2O (3.6 equiv) in CH_3NO_2 at room temperature for 17 h. The reaction was complex, and the ^{19}F NMR spectrum of the reaction mixture showed that product **12a** had formed in 27% yield. The isolated yield after column chromatography on silica gel was 12% (Scheme 8). The modified reaction of **11** with **4**

Scheme 8. Reaction of 11 with 4/Tf_2O



(1.3 equiv)/Tf_2O (1.4 equiv)/$(CF_3CO)_2O$ (1.2 equiv) in CH_3NO_2 at an increased scale (74.7 mmol of **11**), followed by solvent evaporation and then water washing, resulted in only 8% isolated yield of **12a**.

Interestingly, when the reaction of **11** with **4** (3 equiv) and Tf_2O (3.6 equiv) was carried out in sulfolane as the solvent, the ^{19}F NMR spectrum of the reaction mixture showed that **12a** had formed in 72% yield. The isolated yield after column chromatography was 49%. The high yield obtained with sulfolane might have been due to its higher polarity compared to CH_3NO_2. However, we excluded sulfolane as a solvent for practical production because its very high boiling point made separating the product from the solvent extremely difficult.

3,3′,4,4′-Tetrafluorobiphenyl **13** was similarly treated with **4**/Tf_2O in CH_3NO_2 to give 2,3,7,8-tetrafluoro-*S*-(trifluoromethyl)dibenzothiophenium triflate **14a** in 68% yield (Scheme 9). Product **14a** was easily isolated using the water-washing method.

The reaction of 3,3′,5,5′-tetrafluorobiphenyl with **4**, Tf_2O, and $(CF_3CO)_2O$ in CH_3NO_2 was attempted. ^{19}F NMR of the reaction mixture after 1 day showed that the reaction was complex and a considerable amount of the starting biphenyl

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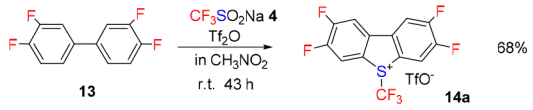
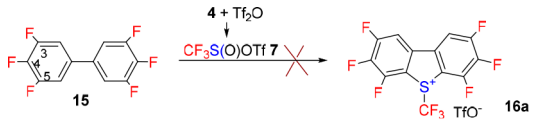
Scheme 9. Synthesis of 14a



compound was left unreacted. In the NMR spectrum, we could not detect a signal for the CF_3 group of the expected product, which might appear as a triplet due to coupling with the fluorine atoms at the 4- and 6-positions. The NMR essentially did not change over 3 days. Therefore, further attempts at this reaction were not made.

When 3,3′,4,4′,5,5′-hexafluorobiphenyl **15** was treated similarly to tetrafluorobiphenyl **13** separately in a solvent of CH_3NO_2 and sulfolane, the reaction did not occur (Scheme 10). Therefore, each of the benzene rings of **15** could no longer

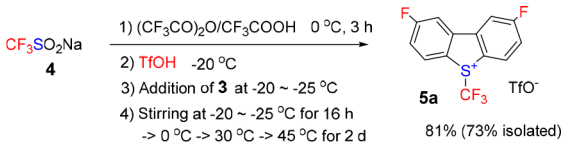
Scheme 10. Attempt To Synthesize 16a



react with **7** because the deactivation by the δ-electron-withdrawing effect of the two fluorine atoms at the 4- and 5-positions exceeded the *p*-activation by the π-electron-donating effect of the fluorine atom at the 3-position.

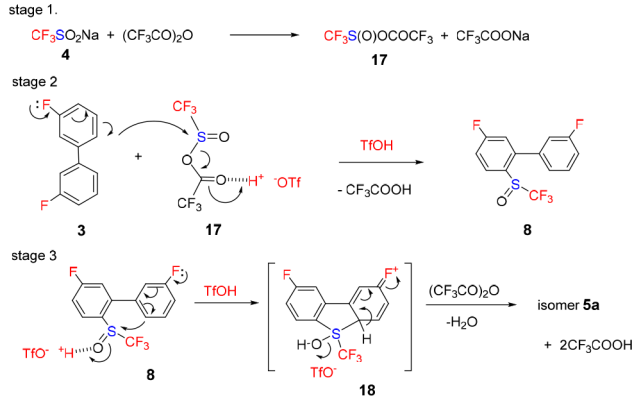
2.2. Exclusive Preparation of Isomer 5a. We found that Tf_2O could be replaced with triflic acid (TfOH) in the one-pot synthesis of **5a**. This method provided significant merits: the exclusive formation of isomer **5a** and no need for expensive Tf_2O. In addition, CH_3NO_2 was not necessary as a solvent. Thus, **4** (1 equiv) was treated with $(CF_3CO)_2O$ (2.2 equiv) in the presence of CF_3COOH (1 equiv) at 0 °C, and then TfOH (2 equiv) and 3,3′-difluorobiphenyl **3** (1 equiv) were added at −20 to −25 °C. The reaction mixture was stirred at the temperature for 16 h and then warmed stepwise to 45 °C for 2 days (Scheme 11). ^{19}F NMR analysis showed that only isomer **5a** was formed in 81% yield. The salt **5a** was obtained in 73% isolated yield after the water-washing method.

Scheme 11. Exclusive Preparation of Isomer 5a



The reaction mechanism of the new method could be explained as shown in Scheme 12. In stage 1, **4** reacted with $(CF_3CO_2)O$ to generate trifluoromethanesulfinyl trifluoroacetate **17**, which then reacted with **3** via activation by the strong acid TfOH to give **8** (stage 2). In stage 3, **8** underwent intramolecular cyclization with TfOH in the presence of $(CF_3CO_2)_2O$ to give the final product **5a**. The ^{19}F NMR spectrum (in DMSO-d_6) of the reaction mixture at stage 1 contained a singlet peak at −77.9 ppm, which might correspond to a characteristic peak of the CF_3S group (−77.6 ppm) of **17** reported in the literature.[33] The reactive $CF_3S(O)^+$ species resulting directly from **4** under the strong acidic conditions with TfOH may have reacted with **3** to form **8**. The exclusive

Scheme 12. Proposed Mechanism for the Exclusive Formation of 5a

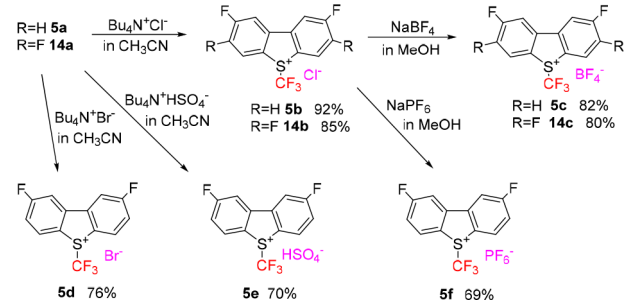


formation of **5a** could have been caused by the mild reaction conditions with TfOH/$(CF_3CO)_2O$ via **18** for the cyclization. In contrast, the Tf_2O method via **9** was so severe that isomer **5a** was accompanied by the less thermally stable isomer **6a**, as shown in Schemes 3 and 5.

A large-scale production of **5a** was successfully conducted by this new economical one-pot process using a 20 L glassware reactor, applying the small-scale conditions to a large-scale production. Crystalline product **5a** (6.5 kg) was obtained in 71% isolated yield from 4.0 kg of starting material **3**.

2.3. Counteranion Replacement Reactions. When triflate **5a** was treated with tetrabutylammonium chloride, bromide, and hydrogensulfate in acetonitrile at room temperature, immediate reactions occurred to produce the chloride **5b**, bromide **5d**, and hydrogensulfate **5e** as precipitates in good to high yields (Scheme 13). Similarly, triflate **14a** was converted to chloride **14b** in high yield. Triflate **5a** was recovered in 93% yield by treating chloride **5b** with TfOH in water at 40−45 °C.

Scheme 13. Counteranion Replacement Reactions



Borates **5c** and **14c** and phosphate **5f** were prepared in good yields from the corresponding chloride **5b** or **14b** by treating with $NaBF_4$ or $NaPF_6$ in methanol. The direct conversion of triflate **5a** to borate **5c** did not proceed well.

2.4. Thermal Stability. The thermal stability of the *S*-(trifluoromethyl)dibenzothiophenium salts was determined from TGA/DSC measurements. The results are shown in Table 1.

The thermal stability of the salts was affected by the position of the fluorine substituents. While Umemoto's reagent **IIa** had a decomposition point of 153 °C, 2,8-difluoro triflate **5a** had a very high decomposition point of 204 °C. The decomposition point of 3,7-difluoro triflate **12a** was 164 °C. Thus, the fluorine

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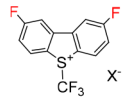
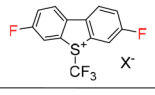
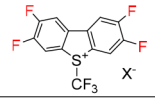
Table 1. Thermal Data for *S*-(Trifluoromethyl)dibenzothiophenium Salts Based on TGA/DSC Measurements

S-CF_3-Dibenzothiophenium salts structure	X^-	Decompostion point (onset) °C	Heat exchange △H (J/g)
	TfO^- (**5a**)	204	-36 (endo)
	Cl^- (**5b**)	232	+183 (exo)
	BF_4^- (**5c**)	185 (1st) 190 (2nd)	+40 (exo) -25 (endo)
	Br^- (**5d**)	182	+113 (exo)
	HSO_4^- (**5e**)	155	+79 (exo)
	PF_6^- (**5f**)	186	-33 (endo)
	TfO^- (**6a**)	135 (1st) 140 (2nd)	-72 (endo) +89 (exo)
	TfO^- (**12a**)	164	+15 (exo)
	TfO^- (**14a**)	171	+28 (exo)
	Cl^- (**14b**)	217	+200 (exo)
	BF_4^- (**14c**)	152	+33 (exo)
Umemoto's reagent **IIa**[1]		153	-67 (endo)
Togni's reagent **VIIIa**[2]		149	+502 (exo)
Togni's reagent **VIIIb**[2]		135	+790 (exo)

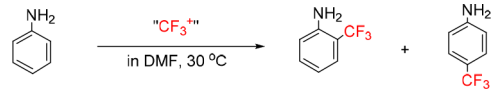
[1]Umemoto's reagent **IIa** from Sigma-Aldrich was used for the measurement. [2]The data cited are from ref 30a. The data were obtained by DSC measurements.

atom at the 2(8)-position exerts a strong stabilizing effect and that at the 3(7)-position exerts a moderate stabilizing effect. In contrast, 2,6-difluoro triflate **6a** had a low decomposition point of 135 °C, indicating that the fluorine at the 4(6)-position has a strong destabilizing effect. 2,3,7,8-Tetrafluoro triflate **14a** had a higher decomposition temperature of 171 °C compared to Umemoto's reagent **IIa** (153 °C) due to the stabilizing effect of the fluorine atoms at the 2(8)- and 3(7)-positions, in spite of its high reactivity mentioned below. The heat exchange of **5a** and **6a** was endothermic at 36 and 72 J/g, whereas that of **12a** and **14a** was slightly exothermic at 15 and 28 J/g, respectively. The stability of the salts was affected by the type of counteranion. Among them, chlorides **5b** and **14b** produced unexpectedly high decomposition points of 232 and 217 °C, respectively.

As a reference, the reported data for Togni's reagents **VIIIa** and **VIIIb** are shown in Table 1. Togni's reagents were considered to be explosive in nature, as they decomposed at low temperatures and generated much exothermic heat upon decomposition.[30]

2.5. Relative Reactivity. The relative reactivity of the fluorinated *S*-(trifluoromethyl)dibenzothiophenium salts **5a**, **6a**, and **14a** and Umemoto's reagent **IIa** was examined through the reaction with aniline at 30 °C in DMF, which produced *o*- and *p*-(trifluoromethyl)anilines, as shown in Table 2. The reaction was traced by ^{19}F NMR at various time intervals. At 3 h, ~7% of unsubstituted **IIa** had reacted with aniline, whereas 30% of the 2,8-diF isomer **5a**, 64% of 2,6-diF **6a**, and 78% of 2,3,7,8-tetraF **14a** had reacted with aniline. Thus, the reaction power increased in the order of **IIa** < **5a** < **6a** < **14a**, confirming that the fluorinated salts are more powerful than Umemoto's reagent **IIa** because of the electron-withdrawing effect of the fluorine atoms.

Table 2. Reactivity of *S*-(Trifluoromethyl)dibenzothiophenium Triflates



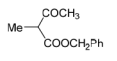
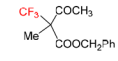
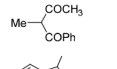
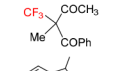
Run	"CF_3^+"	Reaction time	Reaction conversion	Yield 2-CF_3-aniline	Yield 4-CF_3-aniline
1	**IIa**	1 h	~3%	2%	1%
		3 h	~7%	5%	2%
		20 h	22%	15%	7%
2	**5a**	1 h	14%	7%	3%
		3 h	30%	14%	6%
3	**6a**	1 h	49%	28%	14%
		3 h	64%	37%	17%
4	**14a**	1 h	59%	37%	19%
		3 h	78%	44% (56%*)	23% (29%*)

*These yields were calculated on the basis of the consumed CF_3^+ reagent.

Isomer **5a** has much higher thermal stability than **IIa** despite its higher reactivity. Compound **6a** is more powerful than **5a**, but **6a** has low thermal stability (Table 1). Compound **14a** is very powerful. Nevertheless, **14a** is more stable than Umemoto's reagent **IIa**. Thus, the fluorine atoms at the 2(8)- and 3(7)-positions have favorable effects on both the reactivity and stability of the salt. On the other hand, the fluorine atom at the 4(6)-position has a favorable effect on the reactivity but an unfavorable effect on the stability.

2.6. Trifluoromethylation of Substrates. Various substrates were trifluoromethylated by the *S*-(trifluoromethyl)-dibenzothiophenium salts as shown in Table 3. As seen in runs

Table 3. Trifluoromethylation of Subststes with *S*-(Trifluoromethyl)dibenzothiophenium Salts

Run	Substrate	"CF_3^+"	reaction conditions[a]	Product	Yield (%)[b]
1		**5a**	NaH, DMF, -50 °C, 1 h -> rt, 0.5 h		88
2		**5a**	tBuOK, DMF, -50 °C, 1 h -> rt, 0.5 h		86
3		**5b**	NaH, DMF, -50 °C, 1 h -> rt, 0.5 h		78
4		**5c**	NaH, DMF, -50 °C, 1 h -> rt, 0.5 h		84
5		**14a**	NaH, DMF, -50 °C , 1 h-> rt, 0.5 h		68
6		**IIa**	NaH, DMF, -50 °C, 1 h -> rt, 0.5 h		84
7		**5a**	tBuOK, DMF, -50 °C, 1 h -> rt, 0.5 h		78[c]
8		**14a**	tBuOK, DMF, -50 °C, 1 h -> rt, 0.5 h		88[c]
9		**IIa**	tBuOK, DMF, -50 °C, 1 h -> rt, 0.5 h		67[c]
10		**14a**	*N*-methylmorpholine, DMF, rt, 6 h		69
11	$PhCH=CH_2$	**5a**	Ru(II)[d], LED, acetone/H_2O, rt, 2.5h	$PhCH(OH)CH_2CF_3$	84
12		**5b**	Ru(II)[d], LED, acetone/H_2O, rt, 2.5h		81[c]
13	$TsO(CH_2)_2C\equiv CH$	**5a**	CuCl/*s*-collidine, DMAC, 30 °C, 24 h	$TsO(CH_2)_2C\equiv CCF_3$	65
14	1,4-FC_6H_4I	**5a**	Cu, DMF, rt -> 80 °C, 16 h	1,4-$FC_6H_4CF_3$[e]	83
15	2-Br-pyridine	**5a**	Cu, DMF, 0°C -> 80 °C, 3 h	2-CF_3-pyridine	99
16	1,4-$(BrCH_2)C_6H_4CO_2Me$	**5a**	Cu, DMF, rt -> 80 °C, 22 h	1,4-$(CF_3CH_2)C_6H_4CO_2Me$	77
17	1,4-BrC_6H_4SH	**5a**	Et_3N, DMF, rt, 1 h	1,4-$BrC_6H_4SCF_3$	67
18	$PhSO_2Na$	**5a**	DMSO, rt, 1 h	$PhSO_2CF_3$	70
19	Ph_2PH	**5a**	pyridine, DMF, rt, 6 h	Ph_2P-CF_3	74

[a]See the Experimental Section for details. [b]Yields were determined by ^{19}F NMR. [c]The reaction was carried out twice. The avarage yield of two runs is shown. [d]Tris(2,2′-bipyridine)ruthenium hexafluorophosphate was used as a catalyst (0.5 mol %). [e]1,4-$FC_6H_4CF_2CF_3$ was formed in 2.5% yield.

1−4, a metal salt of a keto ester was trifluoromethylated with the diF OTf salt **5a**, diF Cl salt **5b**, and diF BF_4 salt **5c** in 88−78% yields, which were comparative to the yield obtained with Umemoto's reagent **IIa** (84%, run 6). The tetraF OTf salt **14a** gave a slightly lower yield (68%, run 5).

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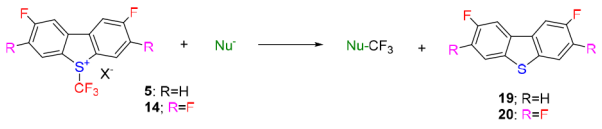
As observed in runs 7−9, a diketone salt was trifluoromethylated by **5a**, **14a**, and **IIa** in 78, 88, and 67% yield, respectively. In this case, the more powerful **14a** afforded the higher yield, and the less powerful **IIa** gave the lower yield. A cyclic keto ester, methyl 1-indanone-2-carboxylate, was trifluoromethylated by **5a**, **5b**, **5c**, **14a**, and **IIb** in 85, 91, 100, 61, and 88% yield, respectively, under Cahard's conditions,[34] in which a catalytic amount of Bu_4NI was used in the presence of K_2CO_3 in DMF. We attempted the trifluoromethylation of the potassium salt of a malonate ester, $MeCH(COOEt)COOCH_2Ph$, but since the ^{19}F NMR of the reaction mixture indicated a low yield (≤25%), we did not proceed further.

In run 10, under the conditions involving *N*-methylmorpholine reported by Cheng et al.[27d] for Umemoto's reagent **IIb**, 3-methylindole readily reacted with tetraF **14a** to produce the 2-CF_3 product in good yield. With the diF isomer **5a**, the trifluoromethylation of the indole was slow. Runs 11 and 12 are examples of a visible-light reaction with a Ru(II) photocatalyst, which was first reported by Akita et al. with Umemoto's reagent **IIb**.[29b] Thus, styrene was treated with **5a** and **5b** in acetone/water at room temperature in the presence of $[Ru(bpy)_3](PF_6)_2$ (0.5 mol %) under irradiation by an LED, giving an addition product in 84 and 81% yield, respectively. Using 5 mol % of the Ru catalyst and **5b**, the yield was 94%. An acetylene compound was treated with **5a** in the same way as that reported by Luo et al.,[35] giving a CF_3 acetylide product in good yield (run 13). Referring to a report by Xiao et al.,[36] an aryl iodide was treated at 60 °C for 16 h with reactive "CF_3Cu" species resulting from the reaction of **5a** and Cu powder, providing an Ar−CF_3 product in high yield (run 14). This reaction was accompanied by the formation of a trace amount of an Ar-C_2F_5 (2.5%). In run 15, 2-bromopyridine was treated with **5a**/Cu in a similar manner as in run 14 to give 2-(trifluoromethyl)-pyridine in very high yield. In this case, there was no formation of 2-C_2F_5-pyridine. In run 16, a benzyl bromide was treated with **5a** similar to that reported by Shibata et al.,[37] generating a CF_3 product in good yield. As observed in runs 17−19, **5a** reacted with arenethiol, arylsulfinate, and diarylphosphine compounds to give the corresponding CF_3 products in good yields. As described above, the fluorinated *S*-(trifluoromethyl)-dibenzothiophenium salts reacted with a wide range of substrates to give the corresponding CF_3 products in satisfactory yields. However, the *S*-CF_3 salts **5a** and **14a** were readily hydrolyzed by alkaline at 0 °C to produce the corresponding *S*-oxides in 84 and 90% yield, respectively (see the Experimental Section).

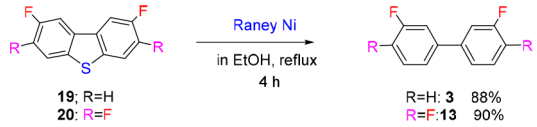
2.7. Desulfurization of Fluorinated Dibenzothiophenes. When the *S*-(trifluoromethyl)dibenzothiophenium salts **5** and **14** were used as trifluoromethylating agents, fluorinated dibenzothiophenes **19** and **20** were formed in quantitative or high yields in addition to the CF_3 products (Scheme 14).

Scheme 14. Trifluoromethylation with *S*-(Trifluoromethyl)dibenzothiophenium Salts



Dibenzothiophenes **19** and **20** were treated with Raney Ni in ethanol, giving fluorinated biphenyls **3** and **13** in high yields, respectively, as shown in Scheme 15.

Scheme 15. Desulfurization of Fluorinated Dibenzothiophenes



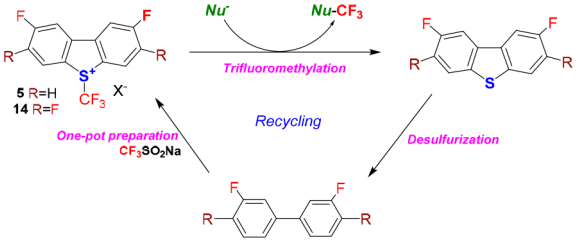
Biphenyls **3** and **13** are the starting materials for the production of the trifluoromethylating agents. Thus, the fluorinated *S*-(trifluoromethyl)dibenzothiophenium salts could be reproduced from the dibenzothiophenes obtained after trifluoromethylation.

3. CONCLUSION

Fluorine atoms at the 3- and 3′-positions of biphenyl led to a very effective one-pot preparation of 2,8-difluoro-*S*-(trifluoromethyl)dibenzothiophenium salts **5** via abnormal *p*-activation. 3,3′,4,4′-Tetrafluorobiphenyl also successfully produced salts **14**. In addition, the fluorine atom substitution made these salts more powerful and unexpectedly more thermally stable than Umemoto's reagents. Furthermore, the fluorinated dibenzothiophenes resulting from the trifluoromethylation were desulfurized to generate the starting fluorobiphenyls in high yields, as a result of the strong C−F bonding.

As shown in Scheme 16, the CF_3 reagents can be recycled. The one-pot process and recycling dramatically reduce the

Scheme 16. Recycling of Fluoro *S*-(Trifluoromethyl)dibenzothiophenium Salts



chemical and environmental cost of the production of these compounds. Thus, the new, powerful, and thermally stable reagents **5** and **14** could be used as the first practically useful electrophilic trifluoromethylating agents for the production of a wide range of CF_3-containing compounds in academic and industrial applications.

4. EXPERIMENTAL SECTION

General Methods. ^1H, ^{19}F, and ^{13}C NMR spectra were measured on a 400, 376, and 100 MHz spectrometers, respectively. DMSO-d_6 was used as a solvent unless otherwise noted. ^{19}F chemical shifts were given as δ in ppm downfield from $CFCl_3$. High-resolution mass spectra (HRMS) (ESI method) were obtained by Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. TGA/DSC were measured by Mettler Toledo/STAR° System: The sample holder was made of aluminum and the temperature was from 30 to 300 °C with 10 °C/min.

Materials. CF_3SO_2Na was used after drying at 80 °C by a vacuum pump for several hours. Other commercially available compounds, Tf_2O, TfOH, CF_3COOH, $(CF_3CO)_2O$, 3-fluorobromobenzene, 3,4-difluorobromobenzene, 3,5-difluorobromobenzene, 3,4,5-trifluorobro-

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mobenzene, and 4,4′-difluorobiphenyl, were used without further purification. 3,3′-Difluorobiphenyl,[38] 3,3′,4,4′-tetrafluorobiphenyl,[39] and 3,3′,4,4′,5,5′-hexafluorobiphenyl[40] were prepared as shown in refs 41−43. 3,3′,5,5′-Tetrafluorobiphenyl[44] was prepared in the same way as for 3,3′,4,4′-tetrafluorobiphenyl.

Synthesis of 2,8- and 2,6-Difluoro-*S*-(trifluoromethyl)-dibenzothiophenium Triflates 5a and 6a. *Use of CF_3SO_2Na and Tf_2O.* To a stirred mixture of 14.0 g (90 mmol) of CF_3SO_2Na and 100 mL of dry CH_3NO_2 under N_2 atmosphere was added 14.2 g (74.4 mmol) of **3** at room temperature (rt). After the mixture was stirred for 40 min at rt, 50.6 g (179.4 mmol) of Tf_2O was added for 10 min under cooling on a water bath, and the mixture was stirred at rt for 46 h. ^{19}F NMR analysis of the mixture using benzotrifluoride ($C_6H_5CF_3$) as an internal standard showed that a 82:18 mixture of **5a** and **6a** was produced in 71% yield and 8% of **3** remained unreacted. The total yield of **5a** and **6a** based on the consumed **3** was 77%. After the mixture was evaporated to dryness under reduced pressure, 30 mL of CH_2Cl_2 was added to the residue, and the mixture was again evaporated to dryness under reduced pressure. To the residue were added 100 mL of water and 125 mL of CH_2Cl_2, and the mixture was stirred for 45 min. The resulting precipitates were collected by filtration, giving 20.1 g of a 87:13 mixture of **5a** and **6a** as a solid. The isolated yield was 61% (66% based on the consumed **3**). Compound **5a** was obtained as pure crystals by recrystallization from a mixture of CH_3CN and Et_2O: decomposition starting point 204 °C (by TGA/DSC); ^{19}F NMR {^1H} δ −53.25 (3F, s, CF_3), −77.78 (3F, s, SO_2CF_3), −101.81 (2F, s, 2,8-F); ^1H NMR δ 8.76 (2H, dd, J = 9.0, 4.8 Hz, 4,6-H), 8.56 (2H, dd, J = 8.8, 2.8 Hz, 1,9-H), 7.84 (2H, dt, J = 2.8, 9.0 Hz, 3,7-H); ^{13}C NMR δ 166.9 (d, J = 261.6 Hz), 143.8 (dd, J = 11.6, 2.5 Hz), 132.9 (d, J = 10.1 Hz), 123.4 (q, J = 332.3 Hz, CF_3) (q = quartet), 123.0 (d, J = 2.0 Hz), 121.1 (q, J = 321.9 Hz, CF_3), 120.1 (d, J = 24.1 Hz), 113.7 (d, J = 27.2 Hz); IR (KBr) 3112, 3057, 1593, 1584, 1583, 1263, 1237, 1178, 1157, 1090, 1029, 903, 838, 757, 636, 571, 517, 492, 465 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ (M − OSO_2CF_3)$^+$ 289.0110, found 289.0129. Anal. Calcd for $C_{14}H_6F_8O_3S_2$: C, 38.36; H, 1.38. Found: C, 38.45; H. 1.67. Compound **6a** was isolated in the following way. The organic layer of the filtrate, which was obtained when the CH_2Cl_2/water mixture was filtered to collect the precipitates of **5a** and **6a**, was separated and concentrated, and the residue was column chromatographed on silica gel using a 10:1 mixture of CH_2Cl_2 and MeOH as an eluent to give pure **6a** as a solid: decomposition starting point 135 °C (by TGA/DSC) (recrystallized from CH_3CN−Et_2O); ^{19}F NMR {^1H} δ −52.45 (3F, d, J = 6.6 Hz, CF_3), −77.78 (s, CF_3SO_2), −100.76 (1F, s, 2-F), −108.23 (1F, q, J = 6.6 Hz, 6-F); ^1H NMR δ 8.77 (1H, dd, J = 4.6, 8.9 Hz, 4-H), 8.67 (1H, dd, J = 2.6, 8.9 Hz, 1-H), 8.47 (1H, d, J = 8.4 Hz, 9-H), 8.26 (1H, dt, J = 5.2, 8.4 Hz, 8-H), 7.95 (1H, t, J = 8.4 Hz, 7-H), 7.88 (1H, dt, J = 2.6, 8.9 Hz, 3-H); ^{13}C NMR δ 167.3 (d, J = 255.9 Hz, 2-C), 159.5 (d, J = 257.5 Hz, 6-C), 144.1 (dd, J = 11.2, 1.9 Hz), 143.0 (d, J = 2.5 Hz), 140.2 (d, J = 8.3 Hz), 133.2 (d, J = 10.8 Hz), 123.5 (q, J = 333.1 Hz, CF_3), 122.5 (d, J = 2.8 Hz), 121.1 (q, J = 322.2 Hz, SO_2CF_3), 120.8 (d, J = 2.1 Hz), 120.6 (d, J = 24.8 Hz), 119.7 (d, J = 18.0 Hz), 114.5 (d, J = 26.8 Hz), 113.3 (d, J = 17.1 Hz); IR (KBr) 3059, 1603, 1583, 1490, 1474, 1447, 1267, 1224, 1169, 1155, 1103, 1075, 1027, 904, 838, 815, 804, 758, 733, 665, 634, 573, 516, 495, 454, 435, 404 cm^{-1}. Anal. Calcd for $C_{14}H_6F_8O_3S_2$: C, 38.36; H, 1.38. Found: C, 38.28; H, 1.45.

Use of CF_3SO_2Na, Tf_2O, and $(CF_3CO)_2O$. To a stirred mixture of 32.9 g (211 mmol) of CF_3SO_2Na and 100 mL of dry CH_3NO_2 under N_2 atmosphere was added 28.3 g (149 mmol) of **3** at rt After that, 65.1 g (231 mmol) of Tf_2O was dropwise added for 40 min under cooling on an ice bath, and the mixture was stirred for additional 2 h on an ice bath. The mixture was stirred at rt for 3 h, and 37.8 g (180 mmol) of $(CF_3CO)_2O$ was added. After being stirred for 17 h at rt, the mixture was evaporated to dryness under reduced pressure. Then 130 mL of toluene was added to the residue, and the mixture was again evaporated to dryness under reduced pressure. To the residue were added 130 mL of water and 130 mL of toluene, and the mixture was stirred for 20 min. The resulting precipitates were collected by filtration, giving 50.4 g (77%) of a 91:9 mixture of **5a** and **6a**.

Exclusive Preparation of Isomer 5a. In a dried 0.5 L four-necked flask equipped with a condenser, a thermometer, a drying tube, and a magnetic stirrer were added 88.7 g (422 mmol) of $(CF_3CO)_2O$ and 21.8 g (191 mmol) of CF_3COOH. The flask was a jacketed 0.5 L glassware flask connected to a cool and hot liquid circulator for the temperature control. After the reaction mixture was cooled to −6 °C, 30.0 g (192 mmol) of dry CF_3SO_2Na was added portion by portion to the stirred mixture in a period of 7 min under N_2 atmosphere. The temperature of the mixture was 1 °C at the time when the addition was completed. The mixture was stirred for 3 h at 0 °C and then cooled to −20 °C. After that, 59.0 g (393 mmol) of TfOH was dropwise added for 44 min at −20 °C, and the mixture was stirred for additional 30 min at −20 °C. Then 36.5 g (192 mmol) of **3** (liquid) was dropwise added for 75 min at −20 to −25 °C, and the mixture was stirred for 16 h at −20 to −25 °C and warmed to 0 °C. The reaction mixture was homogeneous. ^{19}F NMR analysis of the mixture at this point showed that a large amount of intermediate **8**, a very small amount of its isomer **10**, and a trace amount of product **5a** were formed. After that, the mixture was stirred for 8.5 h at 0 °C, for 24 h at 30 °C, and then for 15 h at 45 °C. ^{19}F NMR analysis of the mixture using $C_6H_5CF_3$ as an internal standard showed that isomer **5a** alone was produced in 81% yield. The mixture was evaporated to dryness under the reduced pressure at 45 °C (bath temperature). To the residue was added 150 mL of EtOH, and then the mixture was evaporated to dryness under reduced pressure. Again, 150 mL of EtOH was added, and then the mixture was evaporated up to dryness. After that, 250 mL of toluene and 250 mL of water were added to the residue, and the mixture was stirred at rt overnight. The resulting precipitates were filtered and washed with water (50 mL × 2) and then with toluene (100 mL × 3) to give 61.0 g (73%) of **5a** after drying. The spectral data agreed with those of the authentic sample.

Synthesis of 3,7-Difluoro-*S*-(trifluoromethyl)dibenzothiophenium Triflate 12a. To a stirred mixture of 2.81 g (18.0 mmol) of CF_3SO_2Na and 20 mL of dry CH_3NO_2 under Ar atmosphere was slowly added 6.08 g (21.6 mmol) of Tf_2O at rt. After the mixture was stirred for 3 h, a solution of 1.14 g (6.0 mmol) of **11** in 5 mL of dry CH_3NO_2 was added slowly, and the resulting mixture was stirred at rt overnight (∼17 h). ^{19}F NMR analysis of the mixture using $C_6H_5CF_3$ as an internal standard showed that **12a** was produced in 27% yield. The mixture was evaporated to dryness under reduced pressure, and 20 mL of water and 20 mL of CH_2Cl_2 were added to the residue (no solid appeared). The organic layer was separated and concentrated, and the residue was column chromatographed on silica gel using CH_2Cl_2/MeOH (95/5) as an eluent, giving 0.32 g (12% yield) of **12a** as a solid: decomposition starting point 164 °C (by TGA/DSC) (recrystallized from CH_3CN−Et_2O); ^{19}F NMR {^1H} δ −52.10 (3F, s, CF_3S), −77.78 (3F, s, CF_3SO_2), −107.03 (2F, s, 3,7-F); ^1H NMR δ 8.59−8.62 (4H, m. 1,4,6,9-H), 8.01 (2H, dt, J = 2.4, 8.8 Hz, 2,8-H); ^{13}C NMR δ 162.7 (d, J = 252.0 Hz), 137.5 (s), 128.5 (d, J = 11.6 Hz), 127.1 (d, J = 9.3 Hz), 123.8 (d, J = 23.0 Hz), 123.4 (q, J = 333.3 Hz, CF_3), 121.2 (q, J = 322.5 Hz, SO_2CF_3), 117.8 (d, J = 29.1 Hz); IR (KBr) 3096, 1595, 1467, 1269, 1232, 1215, 1069, 1034, 873, 841, 758, 694, 575, 516, 459 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ (M − OSO_2CF_3)$^+$ 289.0110, found 289.0116. Anal. Calcd for $C_{14}H_6F_8O_3S_2$: C, 38.36; H, 1.38. Found: C, 38.40; H, 1.43.

Synthesis of 2,3,7,8-Tetrafluoro-*S*-(trifluoromethyl)-dibenzothiophenium Triflate 14a. To a stirred mixture of 14.1 g (90.4 mmol) of CF_3SO_2Na in 70 mL of dry CH_3NO_2 cooled on an ice bath was added 30.4 g (108 mmol) of Tf_2O for 8 min under N_2 atmosphere. After addition, the mixture was stirred for 6 h at rt. A solution of 6.8 g (30.1 mmol) of **13** in 30 mL of dry CH_3NO_2 was added, and the mixture was stirred for 43 h at rt. ^{19}F NMR of the mixture using $C_6H_5CF_3$ as an internal standard showed that **14a** was produced in 68% yield. The mixture was evaporated to dryness under the reduced pressure. Then 100 mL of water and 125 mL of CH_2Cl_2 were added, and the mixture was stirred for 80 min. The resulting precipitates were collected by filtration, giving 8.3 g (58% yield) of **14a** as a solid. The analytically pure product was obtained by recrystallization from CH_3CN−Et_2O. **14a**: mp 147−149 °C; decomposition starting point 171 °C (by TGA/DSC); ^{19}F NMR

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{^{1}H} δ −51.48 (3F, s, CF_3S), −77.82 (3F, s, CF_3SO_2), −124.89 (2F, d, J = 21.5 Hz, 2,8-F), −129.47 (2F, d, J = 21.5 Hz, 3,7-F); ^{1}H NMR δ 8.81 (2H, dd, J = 8.8, 7.2 Hz, 4,6-H), 8.72 (2H, dd, J = 10.2, 7.0 Hz, 1,9-H); ^{13}C NMR δ 155.0 (dd, J = 257.4, 13.2 Hz), 151.0 (dd, J = 255.7, 14.2 Hz), 138.4 (d, J = 10.5 Hz), 123.5 (d, J = 7.5 Hz), 123.2 (q, J = 333.7 Hz, CF_3), 121.1 (q, J = 322.5 Hz, SO_2CF_3), 120.1 (d, J = 24.2 Hz), 115.2 (d, J = 22.0 Hz); IR (KBr) 3102, 3038, 1608, 1493, 1438, 1277, 1256, 1242, 1224, 1172, 1073, 1029, 1001, 882, 784, 756, 639, 573, 521, 455 cm^{-1}: HRMS (ESI) m/z calcd for $C_{13}H_4F_7S$ (M − OSO_2CF_3)$^+$ 324.9922, found 324.9926. Anal. Calcd for $C_{14}H_4F_{10}O_3S_2$: C, 35.45; H, 0.85. Found: C, 35.65; H, 0.88.

Synthesis of Intermediate 8. In a 100 mL flask, were put 3.9 g (25 mmol) of CF_3SO_2Na and 13.2 mL (150 mmol) of TfOH under N_2 atmosphere. After the mixture was stirred for 5 min, 4.75 g (25 mmol) of **3** was added, and the mixture was heated to 60 °C. After being stirred at 60 °C for 4 h, the mixture was cooled to rt, mixed with 20 mL of water, neutralized with 35 mL of aq satd Na_2CO_3 solution, and then extracted with ethyl acetate. The organic layer was dried with $MgSO_4$ and filtered. The filtrate was evaporated to dryness, and the residue was purified by column chromatography on silica gel to give 5.59 g (73%) of a yellow oil, which was a 3:1 mixture of **8** and its isomer **10**. Each of these isomers was isolated in pure form by careful column chromatography on silica gel and identified. 3,3′-Difluoro-6-(trifluoromethanesulfinyl)biphenyl **8**: oil; ^{19}F NMR {^{1}H} ($CDCl_3$) δ −72.91 (3F, s, CF_3), −104.06 (1F, s, 3 or 3′-F), −111.42 (1F, 3 or 3′-F); ^{1}H NMR ($CDCl_3$) δ 7.05−7.08 (1H, m), 7.12−7.20 (3H, m), 7.37−7.48 (2H, m), 8.22 (1H, m); ^{13}C NMR ($CDCl_3$) δ 116.2 (d, J = 21.1 Hz), 116.5 (d, J = 23.1 Hz), 116.8 (d, J = 22.1 Hz), 118.3 (d, J = 23.1 Hz), 125.0 (q, J = 335.5 Hz, CF_3), 125.2 (d, J = 3.0 Hz), 129.5 (d, J = 10.6 Hz), 130.3 (s, 6-C), 130.6 (d, J = 8.0 Hz), 137.9 (d, J = 8.0 Hz), 144.6 (d, J = 8.0 Hz), 162.7 (d, J = 248.5 Hz, 3 or 3′-C), 165.5 (d, J = 256.5 Hz, 3 or 3′-C); IR (nujol) 2959, 2926, 2857, 1578, 1468, 1138, 1090, 872, 829, 789 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_7F_5OS$ (M + H)$^+$ 307.0211, found 307.0225. 3,3′-Difluoro-4-(trifluoromethanesulfinyl)biphenyl **10**: oil; ^{19}F NMR {^{1}H} ($CDCl_3$) δ −74.29 (3F, d, J = 9.0 Hz, CF_3), −111.75 (1F, s, 3′-F), −112.36 (1F, q, J = 9.0 Hz, 3-F); ^{1}H NMR ($CDCl_3$) δ 7.16 (1H, td, J = 8.4, 2.0 Hz), 7.31 (1H, dm, J = 10.0 Hz), 7.37−7.53 (3H, m), 7.65 (1H, dd, J = 8.6, 1.4 Hz), 8.04 (1H, t, J = 7.4 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 114.4 (d, J = 23.1 Hz), 115.1 (d, J = 21.1 Hz), 116.2 (d, J = 21.1 Hz), 122.6 (d, J = 16.1 Hz), 123.1 (d, J = 2.0 Hz), 124.3 (d, J = 16.1 Hz), 125.0 (q, J = 355.7 Hz, CF_3), 123.0 (s), 131.0 (s), 140.4 (m), 147.9 (m), 160.0 (d, J = 252.5 Hz), 163.4 (d, J = 247.5 Hz); HRMS (ESI) m/z calcd for $C_{13}H_7F_5OS$ (M + H)$^+$ 307.0211, found 307.0208.

Cyclization of Intermediate 8 to 5a and 6a. A 3.5:1 mixture of **8** and its isomer **10** was used as a starting material, which included 2.98 g (9.72 mmol) of **8**. To the stirred mixture of **8** and **10** in 12.5 mL of dry CH_2Cl_2 cooled at 0−5 °C on an ice−water bath was dropwise added 3.53 g (12.5 mmol) of Tf_2O under N_2 atmosphere. After being stirred at rt overnight, the reaction mixture was evaporated to dryness. The residue was mixed with 10 mL of toluene and 10 mL of water, and the mixture was stirred for 30 min. The precipitates were collected by filtration and washed with 10 mL of toluene and then with 20 mL of ethyl acetate, giving 3.45 g (81%) of a 91:9 mixture of **5a** and **6a**. These products were identified by spectral analysis.

One-Pot Preparation of Umemoto's Reagent IIa. To a stirred mixture of 2.81 g (18 mmol) of CF_3SO_2Na and 15 mL of dry CH_3NO_2 at rt under N_2 atmosphere was added 6.08 g (21.6 mmol) of Tf_2O. After the mixture was stirred for 3 h at rt, a solution of 0.93 g (6.0 mmol) of biphenyl in 5 mL of dry CH_3NO_2 was added, and the mixture was stirred for 60 h at rt. ^{19}F NMR analysis of the mixture using $C_6H_5CF_3$ as a standard showed that **IIa** was produced in 3% yield.

Counteranion Replacement Reaction. Synthesis of 5b, 5d, 5e, and 14b Having Cl, Br, or HSO_4 as a Counteranion. *General Procedure.* A solution of 9 mmol of tetrabutylammonium salt ($Bu_4N^+X^-$) in 10 mL of CH_3CN was added to a stirred solution of 9 mmol of **5a** or **14a** in 120 mL of CH_3CN at rt. After the mixture was stirred overnight at rt, the resulting precipitates (product) were collected by filtration. The pure sample for analysis was obtained by recrystallization.

2,8-Difluoro-S-(trifluoromethyl)dibenzothiophenium Chloride ***5b.*** According to the general procedure, the reaction was carried out by using $Bu_4N^+Cl^-$. Compound **5b** obtained by filtration of the reaction mixture was an adduct with $(CH_3CN)_{0.45}$ per molecule by ^{1}H NMR analysis. The yield was 92%. The pure (CH_3CN-free) product was obtained by recrystallization from MeOH−Et_2O. **5b**: solid; decomposition starting point 230 °C (by TGA/DSC); ^{19}F NMR {^{1}H} δ −53.51 (3F, s, CF_3), −102.80 (2F, s, 2,8-F); ^{1}H NMR δ 7.81 (2H, dt, J = 2.6, 8.8 Hz, 3,7-H), 8.55 (2H, dd, J = 8.8, 2.6 Hz, 1,9-H), 8.78 (2H, dd, J = 8.8, 4.8 Hz, 4,6-H); ^{13}C NMR δ 113.5 (d, J = 26.6 Hz), 119.7 (d, J = 24.7 Hz), 123.3 (q, J = 334.9 Hz, CF_3), 124.9 (d, J = 2.3 Hz), 132.4 (d, J = 10.5 Hz), 114.7 (dd, J = 11.1, 2.3 Hz), 166.6 (d, J = 253.8 Hz); IR (KBr) 3010, 2985, 1590, 1581, 1475, 1434, 1220, 1206, 1179, 1124, 1113, 1079, 1042, 940, 912, 828, 749, 569, 491, 445, 410 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ (M-Cl)$^+$ 289.0110, found 289.0115. Anal. Calcd for $C_{13}H_6F_5ClS$: C, 48.09; H, 1.86. Found: C, 48.03; H, 1.92.

2,8-Difluoro-S-(trifluoromethyl)dibenzothiophenium Bromide ***5d.*** According to the general procedure, the reaction was carried out by using $Bu_4N^+Br^-$. The yield was 76%. The product obtained by filtration was recrystallized from MeOH, giving its methanol adduct as $C_{13}H_6BrS\cdot 1/2(CH_3OH)$. **5d**: solid; decomposition starting point 182 °C (by TGA/DSC); ^{19}F NMR {^{1}H} δ −53.17 (3F, s, CF_3), −102.42 (2F, s, 2,8-F); ^{1}H NMR δ 8.82 (2H, dd, J = 4.6, 8.8 Hz, 4,6-H), 8.57 (2H, dd, J = 2.8, 8.8 Hz, 1,9-H), 7.81 (2H, dt, J = 2.8, 8.8 Hz, 3,7-H), 4.0 (br, OH), 3.17 (1.4H, s, CH_3OH); ^{13}C NMR δ 166.7 (d, J = 254.5 Hz), 143.7 (dd, J = 2.0, 11.1 Hz), 132.6 (d, J = 10.1 Hz), 127.6 (s), 122.6 (q, J = 334.3 Hz, CF_3), 119.9 (d, J = 24.1 Hz), 113.6 (d, J = 27.2 Hz), 48.9 (s, CH_3OH); IR (KBr) 3443, 3019, 2990, 1583, 1475, 1438, 1300, 1217, 1178, 1124, 1081, 1041, 945, 902, 829, 750, 721, 568, 491, 441, 411 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ (M − Br)$^+$ 289.0110, found 289.0113. Anal. Calcd for $C_{13}H_6BrF_5S\cdot{}^1/_2CH_3OH$: C, 42.10; H, 2.09. Found: C, 41.90; H, 1.94.

2,8-Difluoro-S-(trifluoromethyl)dibenzothiophenium Hydrogensulfate ***5e.*** According to the general procedure, the reaction was carried out by using $Bu_4N^+HSO_4^-$. Compound **5e** was obtained by filtration of the reaction mixture. The yield was 70%. The solid was recrystallized from MeOH−Et_2O to obtain a sample for analysis, which was assigned as monohydrate by the elemental analysis. **5e**: solid; decomposition starting point 155 °C (by TGA/DSC); ^{19}F NMR {^{1}H} δ −53.27 (3F, s, CF_3), −101.81 (2F, s, 2,8-F); ^{1}H NMR δ 8.76 (2H, dd, J = 4.8, 9.0 Hz, 4,6-H), 8.56 (2H, dd, J = 2.4, 9.0 Hz, 1,9-H), 7.83 (2H, dt, J = 2.4, 8.8 Hz, 3,7-H); ^{13}C NMR δ 166.9 (d, J = 254.7 Hz, 2,8-C), 143.8 (dd, J = 11.2, 2.3 Hz, 10,11-C), 132.9 (d, J = 10.6 Hz, 4,6-C), 123.4 (q, J = 332.0 Hz, CF_3), 123.0 (d, J = 2.4 Hz, 12,13-C), 120.1 (d, J = 24.7 Hz, 1,9- or 3,8-C), 113.7 (d, J = 26.6 Hz, 1,9- or 3,8-C); IR (KBr) 2983, 1592, 1581, 1507, 1477, 1436, 1213, 1177, 1123, 1082, 1040, 943, 884, 827, 584, 567, 490, 441 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ (M − HSO_4)$^+$ 289.0110, found 289.0109. Anal. Calcd for $C_{13}H_7F_5O_4S_2\cdot H_2O$: C, 38.62; H, 2.24. Found: C, 38.79; H, 2.53.

2,3,7,8-Tetrafluoro-S-(trifluoromethyl)dibenzothiophenium Chloride ***14b.*** According to the general procedure, the reaction was carried out using $Bu_4N^+Cl^-$. Product **14b** were obtained by filtration of the reaction mixture. The yield was 85%. The pure sample was obtained by recrystallization from MeOH/*tert*-BuOMe. **14b**: solid; decomposition starting point 217 °C (by TGA/DSC): ^{19}F NMR {^{1}H} δ −51.84 (3F, s, CF_3), −126.26 (2F, d, J = 21.3 Hz), −130.44 (2F, d, J = 21.3 Hz); ^{1}H NMR δ 9.02 (2H, dd, J = 9.2, 7.2 Hz), 8.76 (2H, dd, J = 10.4, 7.2 Hz); ^{13}C NMR δ 114.9 (d, J = 22.0 Hz, 1 or 4-C), 119.5 (d, J = 24.2 Hz, 1 or 4-C), 123.1 (q, J = 338.0 Hz, CF_3), 126.7 (d, J = 7.6 Hz), 138.2 (d, J = 10.2 Hz), 150.6 (dd, J = 254.5, 14.2 Hz, 2 or 3-C), 154.4 (dd, J = 256.2, 13.3 Hz, 2 or 3-C); IR (KBr) 3042, 2988, 1607, 1522, 1489, 1435, 1418, 1273, 1234, 1215, 1076, 999, 918, 895, 783, 750, 625, 571, 523, 455 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_4F_7S$ (M − Cl)$^+$ 324.9922, found 324.9921. Anal. Calcd for $C_{13}H_4ClF_7S$: C, 43.29; H, 1.12. Found: C, 43.24; H, 1.14.

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Synthesis of 5c, 5f, and 14c Having BF_4 or PF_6 as a Counteranion. *General Procedure.* To a stirred solution of 0.101 g (0.920 mmol) of $NaBF_4$ in 5 mL of MeOH heated at 40 °C was added 0.30 g (0.875 mmol) of **5b** [$(CH_3CN)_{0.45}$ adduct]. After it became a homogeneous solution, the mixture was cooled to rt, and 15 mL of CH_3CN was added slowly. The resulting white precipitate (NaCl) was removed by filtration, and the filtrate was evaporated to dryness under reduce pressure. After 15 mL of CH_3CN was added, the insoluble solid (NaCl) was removed by filtration. The filtrate was evaporated to dryness under reduced pressure, and the resulting crystalline solid was recrystallized from CH_3CN–Et_2O to give 0.27 g (82%) of 2,8-difluoro-*S*-(trifluoromethyl)dibenzothiophenium tetrafluoroborate **5c** as white solid. **5c**: decomposition starting point 185 °C (by TGA/DSC); ^{19}F NMR {^1H} δ −53.24 (3F, s, CF_3), −101.80 (2F, s, 2,8-F), −148.24 (4F, s, BF_4); ^1H NMR δ 7.82 (2H, dt, J = 2.6, 8.9 Hz, 3,7-H), 8.55 (2H, J = 8.8, 2.6 Hz, 1,9-H), 8.75 (2H, J = 8.8, 4.8 Hz, 4,6-H); ^{13}C NMR δ 113.7 (d, J = 26.6 Hz), 120.1 (d, J = 24.6 Hz), 123.0 (q, J = 332.2 Hz, CF_3), 132.9 (d, J = 10.7 Hz), 143.8 (dd, J = 11.0, 2.3 Hz), 116.9 (d, J = 254.7 Hz); IR (KBr) 3101, 2984, 1591, 1479, 1437, 1300, 1252, 1223, 1182, 1082, 943, 881, 829, 756, 573, 522, 490, 456, 441, 429, 409 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ $(M - BF_4)^+$ 289.0110, found 289.0110. Anal. Calcd for $C_{13}H_6F_9SB$: C, 41.52; H, 1.61. Found: C, 41.78; H, 1.64.

2,8-Difluoro-S-(trifluoromethyl)dibenzothiophenium Hexafluorophosphate ***5f.*** $NaPF_6$ was used instead of $NaBF_4$. The product was recrystallized from CH_3CN–Et_2O. The yield was 69%. **5f**: solid; decomposition starting point 186 °C (by TGA/DSC); ^{19}F NMR {^1H} δ −53.23 (3F, s, CF_3), −70.13 (6F, d, J = 711.2 Hz, PF_6), −101.80 (2F, s, 2,8-F); ^1H NMR δ 8.76 (2H, dd, J = 4.6, 8.9 Hz, 4,6-H), 8.56 (2H, dd, J = 2.7, 8.9 Hz, 1,9-H), 7.83 (2H, dt, J = 2.7, 8.9 Hz, 3,7-H); ^{13}C NMR δ 166.9 (d, J = 254.7 Hz, 2,8-C), 143.7 (dd, J = 11.1, 2.0 Hz, 10,11-C), 132.9 (d, J = 10.6 Hz, 4,6-C), 123.4 (q, J = 331.4 Hz, CF_3), 123.0 (d, J = 2.2 Hz, 12,13-C), 120.1 (d, J = 24.6 Hz, 1,9- or 3,8-C), 113.7 (d, J = 26.2 Hz, 1,9- or 3,8-C); IR (KBr) 3101, 1596, 1481, 1440, 1413, 1302, 1260, 1233, 1178, 1128, 1067, 1043, 944, 894, 845, 822, 756, 742, 571, 558, 491, 454, 431, 409 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_6F_5S$ $(M - PF_6)^+$ 289.0110, found 289.0106.

2,3,7,8-Tetrafluoro-S-(trifluoromethyl)dibenzothiophenium tetrafluoroborate ***14c.*** Chloride **14b** was used instead of **5b**. The yield of **14c** was 80%. The pure compound for analysis was obtained by recrystallization from CH_3CN/*tert*-BuOMe. **14c**: solid; decomposition starting point 152 °C (by TGA/DSC): ^{19}F NMR {^1H} δ −51.50 (3F, s), −124.92 (2F, d, J = 21.5 Hz), −129.45 (2F, d, J = 21.5 Hz), −148.21 (4F, s); ^1H NMR δ 8.86 (2H, dd, J = 8.6, 7.4 Hz), 8.75 (2H, dd, J = 10.0, 7.2 Hz); ^{13}C NMR δ 115.2 (d, J = 22.1 Hz, 1 or 4-C), 120.0 (d, J = 24.1 Hz, 1 or 4-C), 123.2 (q, J = 333.7 Hz, CF_3), 123.7 (d, J = 7.6 Hz), 138.4 (d, J = 10.5 Hz), 151.0 (dd, J = 255.6, 14.2 Hz, 2 or 3-C), 154.9 (dd, J = 257.3, 13.1 Hz, 2 or 3-C); IR (KBr) 3063, 1609, 1489, 1437, 1420, 1279, 1246, 1179, 1040, 1001, 899, 783, 756, 625, 571, 523, 457 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_4F_7S$ $(M - BF_4)^+$ 324.9922, found 324.9925.

Conversion of Chloride ***5b*** *to Triflate* ***5a.*** In a flask were added 10 g (29.2 mmol) of **5b** [$(CH_3CN)_{0.45}$ adduct] and 100 mL of water. After the mixture was stirred at 40 °C until all **5b** was dissolved, 4.8 g (32 mmol) of TfOH was dropwise added for 20 min. During the addition, the temperature rose to 47 °C. After the addition, the mixture was stirred at 40–45 °C for 30 min and cooled to rt. The resulting white precipitate (**5a**) was filtered and washed with water (5 mL) and then with toluene (3 mL × 3) to give 11.93 g (93%) of **5a** after drying. The spectral data agreed with those of the authentic sample.

Trifluoromethylation of Substrates with *S*-(Trifluoromethyl)-dibenzothiophenium Salts. The fluorinated *S*-(trifluoromethyl)-dibenzothiophenium salts reacted with various types of substrates to produce the corresponding trifluoromethyl compounds and fluoro dibenzothiophenes **19** and **20** (see Scheme 14). The dibenzothiophenes were formed in quantitative or high yields. They were isolated from the reaction mixture by the standard post-treatment including column chromatography on silica gel. 2,8-Difluorodibenzothiophene **19**: mp 148.4–149.3 °C; ^{19}F NMR {^1H} ($CDCl_3$) δ −117.81 (s); ^1H NMR ($CDCl_3$) δ 7.24 (2H, dt, J = 8.8, 2.4 Hz, 3,7-H), 7.75 (2H, dd, J = 9.2, 2.4 Hz, 1,9-H), 7.78 (2H, dd, J = 8.8, 4.8 Hz, 4,6-H); ^{13}C NMR ($CDCl_3$) δ 108.0 (d, J = 23.4 Hz, 1 or 3-C), 115.6 (d, J = 24.5 Hz, 1 or 3-C), 124.0 (d, J = 9.0 Hz, 4 or 6-C), 135.8 (d, J = 1.8 Hz, 4 or 6-C), 136.3 (dd, J = 8.9, 3.8 Hz, C–S), 160.9 (d, J = 242.9 Hz, C-2); GC–MS m/z 220 (M^+); HRMS (EI) m/z calcd for $C_{12}H_6F_2S$ (M^+) 220.0158, found 220.0156. 2,3,7,8-Tetrafluorodibenzothiophene **20**: mp 145.0–146.4 °C; ^{19}F NMR {^1H} ($CDCl_3$) δ −136.41 (2F, d, J = 20.7 Hz, 3,7- or 2,8-F), −139.69 (2F, d, J = 20.7 Hz, 2,8- or 3,7-F); ^1H NMR ($CDCl_3$) δ 7.61 (2H, dd, J = 9.6, 6.8 Hz, 4,6- or 1,9-H), 7.77 (2H, dd, J = 10.0, 7.2 Hz, 1,9- or 4,6-H); ^{13}C NMR ($CDCl_3$) δ 109.4 (d, J = 19.4 Hz), 111.0 (d, J = 21.2 Hz), 130.7 (m), 135.1 (d, J = 7.8 Hz), 149.4 (dd, J = 247.0, 14.2 Hz), 150.1 (dd, J = 250.7, 14.7 Hz); IR (KBr) 3076, 1577, 1490, 1439, 1263, 1151, 1059, 907, 861, 831, 774, 666, 625, 572, 520, 438 cm^{-1}; GC–MS m/z 256 (M^+); HRMS (EI) m/z calcd for $C_{12}H_4F_4S$ (M^+) 255.9970, found 255.9973.

Trifluoromethylation of Aniline. Under N_2 atmosphere, a mixture of 1 mmol of a CF_3 reagent, 2 mmol of aniline, and 1 mmol of 4-chlorobenzotrifluoride (p-$ClC_6H_4CF_3$) in 2 mL of *N,N*-dimethylformamide (DMF) was stirred at 30 °C for the period as shown in Table 2. Salts **IIa**, **5a**, **6a**, and **14a** were used as the CF_3 reagent. Each of the reactions was traced by ^{19}F NMR at time intervals. The results are shown in Table 2. A half amount (1 mmol) of aniline used acted as a base for the reaction because this reaction generated 1 mmol of TfOH. The yields of 2- and 4-(trifluoromethyl)anilines were based on the half amount of aniline used, unless otherwise noted. p-$ClC_6H_4CF_3$ was an internal standard for ^{19}F NMR analysis. The products were identified by spectral comparison with authentic samples.

Trifluoromethylation of Salts of Diketone and Keto Ester. Under N_2 atmosphere, 1.1 mmol of KO^{t}Bu or NaH in oil was added to a stirred solution of 1.0 mmol of benzyl 2-methylacetoacetate or 3-methyl-1-phenylbutan-1,3-dione in 5 mL of dry DMF cooled in an ice bath. The resulting mixture was stirred at 0 °C for 20 min and then cooled to −50 °C. After being stirred at −50 °C for 15 min, 1.2 mmol of a CF_3 reagent was added. The mixture was stirred at −50 °C for 1 h and then at rt for 0.5 h. The mixture was analyzed by ^{19}F NMR using p-$ClC_6H_4CF_3$ as an internal standard. The results are shown in Table 3. The product was isolated by the standard post-treatment and identified. Benzyl 2-methyl-2-(trifluoromethyl)acetoacetate: pale yellow oil; ^{19}F NMR {^1H} ($CDCl_3$) δ −68.39 (s, CF_3); ^1H NMR ($CDCl_3$) δ 7.38–7.35 (m, 5H, Ph), 5.26 (s, 2H, -CH_2Ph), 2.29 (s, 3H, CH_3CO), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.9 (s), 166.1 (q, J = 2.0 Hz), 134.5 (s), 128.78 (s), 128.75 (s), 128.3 (s), 124.0 (q, J = 282.7 Hz, CF_3), 68.2 (s), 64.4 (q, J = 25.2 Hz), 27.3 (q, J = 2.0 Hz), 15.5 (q, J = 2.0 Hz); HRMS (ESI) m/z calcd for $C_{13}H_{13}F_3KO_3$ [M + K]$^+$, 313.0448, found 313.0459. 2-Methyl-1-phenyl-2-(trifluoromethyl)butan-1,3-dione: pale yellow oil; ^{19}F NMR {^1H} ($CDCl_3$) δ −67.25 (s, CF_3); ^1H NMR ($CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 2.29 (s, 3H), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 200.1 (s), 191.9 (s), 134.9 (s), 133.9 (s), 129.1 (s), 128.9 (s), 124.4 (q, J = 284.4 Hz, CF_3), 69.2 (q, J = 22.8 Hz), 28.7 (q, J = 2.0 Hz), 16.8 (q, J = 2.3 Hz); HRMS (ESI) m/z calcd for $C_{12}H_{11}F_3NaO_3$ [M + Na]$^+$ 267.0603, found 267.0620.

Trifluoromethylation of Methyl 1-Indanone-2-Carboxylate under Cahard's Conditions. To a stirred mixture of 0.5 mmol of methyl 1-indanone-2-carboxylate, 1.5 mmol of K_2CO_3, and 0.025 mmol of $Bu_4N^+I^-$ in 5 mL of dry DMF at rt under N_2 atmosphere was added 0.75 mmol of a CF_3 reagent. The mixture was stirred for 1 h at rt and analyzed by ^{19}F NMR using p-$ClC_6H_4CF_3$ as an internal standard. The results are described in the text. The product, methyl 1-indanone-2-(trifluoromethyl)-2-carboxylate, was isolated and identified by spectral comparison with the reported data.[34]

Trifluoromethylation of an Indole. To a stirred solution of 0.5 mmol of 3-methylindole and 0.75 mmol of *N*-methylmorpholine in 2 mL of dry DMF at rt under N_2 atmosphere was added 0.6 mmol of **14a**. The mixture was stirred for 6 h at rt and analyzed by ^{19}F NMR using p-$ClC_6H_4CF_3$ as an internal standard. 3-Methyl-2-(trifluoromethyl)indole was produced in 69% yield. The product was isolated by post-treatment and identified by spectral comparison with the reported data.[27d]

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Trifluoromethylation of Styrene with Visible-Light Irradiation. In a 50 mL Schlenk tube were added 2.5 mmol of styrene, 3.0 mmol of **5a** or **5b**, 10.7 mg (0.0125 mmol, 0.5 mol %) of $Ru(bpy)_3(PF_6)_2$, 2.5 mL of water, and 20 mL of acetone. The mixture was degassed with nitrogen gas by three freeze−pump−thaw cycles. The Schlenk tube was placed at a distance of less than 1 cm from 4 W LED lamp (white) and irradiated for 2.5 h. ^{19}F NMR analysis of the mixture using *p*-$ClC_6H_4CF_3$ as an internal standard showed that the product was formed in 84% and 81% yield by **5a** and **5b**, respectively. The product was isolated by column chromatography and identified by spectral comparison with the reported data.[29b]

Trifluoromethylation of an Alkyne. Under Ar atmosphere, 0.2 mmol of dry copper(I) chloride, 2 mmol of *s*-collidine, 1.2 mmol of **5a** (including 3% of its isomer **6a**), 1 mmol of 4-(*p*-toluenesulfonyloxy)-1-butyne, and then 5 mL of *N,N*-dimethylacetamide were added in a flask. The mixture was stirred for 24 h at 30 °C. ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard showed that 5-(*p*-tolylsulfonyloxy)-1,1,1-trifluoro-2-pentyne was produced in 65% yield. The product was isolated by post-treatment and identified by spectral comparison with the reported data.[35]

Trifluoromethylation of 4-Fluoroiodobenzene. Cu power (6 mmol) was added to a stirred solution of 444 mg (2 mmol) of 4-fluoroiodobenzene and 1.75 g (4 mmol) of **5a** in 6 mL of dry DMF under N_2 atmosphere. After being stirred at rt for 1 h, the mixture was heated up to 60 °C and stirred at that temperature for 16 h. After cooling, the mixture was analyzed by ^{19}F NMR using *p*-$ClC_6H_4CF_3$ as an internal standard. The conversion was 100%. 4-Fluorobenzotrifluoride was produced in 82% yield, and 1,4-fluoro(pentafluoroethyl)-benzene was formed in 2.5% yield. The products were identified by spectral analysis.

Trifluoromethylation of 2-Bromopyridine. In a 10 mL Schlenk flask were added 876 mg (2 mmol) of **5a** and 192 mg (3 mmol) of Cu powder under N_2 atmosphere. The flask was cooled on an ice bath, and then 158 mg (1 mmol) of 2-bromopyridine and 5 mL of dry DMF were added. The mixture was stirred at 0 °C for 1 h and then heated at 80 °C for 3 h. ^{19}F NMR analysis of the mixture using *p*-$ClC_6H_4CF_3$ as an internal standard showed that 2-(trifluoromethyl)pyridine was produced in 99% yield. The product was identified by spectral comparison with an authentic sample.

Trifluoromethylation of a Benzyl Bromide. In a flask were added 4.58 g (10.0 mmol) of **5a**, 950 mg (14.9 mmol) of Cu powder, and 10 mL of dry DMF under N_2 atmosphere. After the mixture was stirred for 4 h at rt, 1.15 g (5.02 mmol) of methyl 4-(bromomethyl)benzoate was added, and the mixture was stirred at 60 °C overnight (18 h). ^{19}F NMR analysis of the mixture using $C_6H_5CF_3$ as an internal standard showed that methyl 4-(2′,2′,2′-trifluoroethyl)benzoate was produced in 77% yield. The product was isolated by post-treatment and identified by spectral comparison with the reported data.[37]

Trifluoromethylation of a Thiol. To a stirred solution of 1.0 mmol of 4-bromobenzenethiol in 4 mL of DMF were added 1.0 mmol of Et_3N and 1.0 mmol of **5a** at rt under N_2 atmosphere. The mixture was stirred at rt for 1 h and analyzed by ^{19}F NMR using *p*-$ClC_6H_4CF_3$ as an internal standard. 4-Bromophenyl trifluoromethyl sulfide was produced in 67% yield. The product was isolated and identified by spectral analysis.

Trifluoromethylation of Sodium Benzenesulfinate. To a stirred solution of 1.0 mmol of sodium benzenesulfinate and 1.0 mmol of *p*-$ClC_6H_4CF_3$ in 5 mL of dimethyl sulfoxide was added 1.0 mmol of **5a** at rt under N_2 atmosphere. The mixture was stirred at rt for 1 h. ^{19}F NMR analysis of the mixture using *p*-$ClC_6H_4CF_3$ as an internal standard showed that phenyl trifluoromethyl sulfone was produced in 70% yield. The product was isolated by post-treatment and identified by spectral analysis.

Trifluoromethylation of Diphenylphosphine. To a stirred solution of 0.5 mmol of diphenylphosphine and 0.6 mmol of pyridine in 2 mL of DMF was added 0.6 mmol of **5a** under N_2 atmosphere. The mixture was stirred at rt for 6 h. ^{19}F NMR analysis of the mixture using *p*-$ClC_6H_4CF_3$ as an internal standard showed that (trifluoromethyl)-diphenylphosphine was produced in 74% yield. The product was isolated by post-treatment and identified by spectral comparison with the reported data.[45]

Hydrolysis of *S*-CF_3 Salts. Salt **5a** or **14a** (1 mmol) was added to a stirred aq NaOH solution (1 N, 5 mL) cooled in an ice bath, and the reaction mixture was stirred for 1 h on the ice bath. The resulting white precipitates were collected by filtration, washed with water, and dried. The NMR showed the products to be pure. The yields were 84% and 90% for *S*-oxides **21** and **22**, respectively. 2,8-Difluorodibenzothiophene *S*-oxide **21**: mp 206.5−207.5 °C; ^1H NMR δ 8.18 (dd, J = 8.4, 4.8 Hz), 8.12 (dd, J = 9.2, 2.0 Hz), 7.47 (dt, J = 8.6, 2.1 Hz); ^{19}F NMR {^1H} δ −106.72 (s, 3F); ^{13}C NMR δ 111.1 (d, J = 25.2 Hz), 117.7 (d, J = 24.1 Hz), 130.4 (d, J = 10.1 Hz), 139.1 (dd, J = 10.1, 3.0 Hz), 142.2 (dd, J = 2.0 Hz), 165.5 (d, J = 250.5 Hz); HRMS (ESI) m/z calcd for $C_{12}H_7F_2OS$ $(M + H)^+$ 237.0180, found 237.0181. 2,3,7,8-Tetrafluorodibenzothiophene *S*-oxide **22**: mp 230−232 °C; ^1H NMR δ 8.42 (dd, J = 8.8, 7.6 Hz), 8.33 (dd, J = 10.6, 7.0 Hz); ^{19}F NMR {^1H} δ −130.72 (d, J = 20.7 Hz, 2F), −134.68 (d, J = 20.7 Hz, 2F); ^{13}C NMR δ 112.8 (d, J = 21.1 Hz), 117.9 (d, J = 21.1 Hz), 133.4 (br.s), 142.4 (br.s), 150.7 (dd, J = 252.5, 14.1 Hz), 153.2 (dd, J = 251.5, 13.1 Hz); HRMS (ESI) m/z calcd for $C_{12}H_5F_4OS$ $(M + H)^+$ 272.9992, found 272.9996.

Desulfurization of Fluorinated Dibenzothiophenes. *Desulfurization of 2,8-Difluorodibenzothiophene **19**.* A mixture of 0.10 g (0.45 mmol) of **19**, 0.8 mL (in EtOH) of Raney Ni, and 20 mL of EtOH was heated under reflux for 4 h. Raney Ni (in water) (A-4F00 or A-7F63 purchased from Johnson Matthey, U.S.A.) was washed with water several times by decantation, and then the water layer was replaced with the EtOH layer by washing with EtOH several times by decantation before use. ^{19}F NMR analysis of the reaction mixture using an internal standard showed that 3,3′-difluorobiphenyl **3** was produced in 88% yield. The product was isolated and identified.

*Desulfurization of 2,3,7,8-Tetrafluorodibenzothiophene **20**.* A mixture of 128 mg (0.5 mmol) of **20**, 1.2 mL (in EtOH) of Raney Ni, and 20 mL of EtOH was treated in the same way as for **19**. The yield of 3,3′,4,4′-tetrafluorobiphenyl **13** was 90%, which was determined by ^{19}F NMR analysis of the reaction mixture. The product was isolated and identified.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00669.

^{19}F, ^1H, and ^{13}C NMR spectra of new compounds and TGA/DSC charts of *S*-CF_3 salts (PDF)

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Notes

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(41) 3,3′-Difluorobiphenyl **3** was prepared by application of a known method (ref 38b): In a 0.5 L four-necked flask equipped with a dropping funnel, a condenser, a thermometer, and a magnetic stirrer were added 3.75 g (154 mmol) of Mg and 200 mL of dry THF. In the dropping funnel was added 24.5 g (140 mmol) of 3-fluorobromobenzene. The reactor was purged with N_2 gas. A small amount of 3-fluorobromobenzene in the dropping funnel and a trace of iodine (I_2) were added to the flask, and the Grignard reaction was started. Then,

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3-fluorobromobenzene in the dropping funnel was dropwise added to the flask under stirring so that the temperature was maintained at 40−50 °C. After addition, the mixture was stirred for 3 h. In another four-necked flask equipped with a dropping funnel, a condenser, a thermometer, and a magnetic stirrer were added 8.3 g (83.8 mmol) of 1,2-dichloroethane, 0.7 g (4.3 mmol) of $FeCl_3$, and 84 mL of dry THF under N_2 atmosphere. The Grignard reaction solution was transferred to the dropping funnel and added dropwise to the stirred mixture of 1,2-dichloroethane and $FeCl_3$ in THF for 1.5 h at room temperature (rt). The temperature of the mixture was 49 °C just after the addition was completed. The mixture was stirred at rt for an additional 2 h. ^{19}F NMR analysis of the mixture using C_6H_5F as a standard showed that **3** was produced in 96% yield. The mixture was acidified (pH ∼2) with dilute hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated, and the residue was distilled under reduced pressure to give **3**, 10.4 g (78%) (bp 84−86 °C/1.7 mmHg).

(42) 3,3′,4,4′-Tetrafluorobiphenyl **13** was prepared by application of a known method (ref 39b): In a 1 L three-necked flask equipped with a dropping funnel, a condenser, a thermometer, and a magnetic stirrer were added 18.6 g (765 mmol) of Mg, 6.0 g (31 mmol) of 3,4-difluorobromobenzene, and 700 mL of dry THF. In the dropping funnel was added 129.5 g (671 mmol) of 3,4-difluorobromobenzene. After the Grignard reaction was started by adding a trace of 1,2-dibromoethane, 3,4-difluorobromobenzene was added dropwise via the dropping funnel, and the mixture was stirred for additional 4.5 h. The Grignard reaction was conducted in a N_2 atmosphere. The reaction solution was then transferred to another 1 L three-necked flask containing 70 mL of 0.5 M (mol/L) $MnCl_2$·2LiCl in dry THF under N_2 atmosphere, which was equipped with a thermometer, a condenser, a gas inlet of a fluoropolymer tube (o.d. 1/8 in., i.d. 1/16 in.), a gas outlet, and a magnetic stirrer. The reaction mixture was cooled to about −20 °C under stirring, and then a gaseous mixture of 21.5% O_2/78.5% N_2 (v/v) was flown into the stirred mixture through the fluoropolymer tube at a rate of 200 mL/min so that the temperature of the reaction mixture did not exceed −10 °C. The gaseous mixture was stopped after 2 h, and the reaction mixture was stirred at rt overnight. ^{19}F NMR analysis of the mixture using C_6H_5F as a standard showed that **13** was produced in 66% yield. The reaction mixture was then acidified with aq dilute HCl and extracted with ethyl acetate. The organic layer was washed with water and filtered, and the filtrate was evaporated up to dryness. The residue was distilled under reduced pressure twice (bath temperature 150 °C/2.3 mmHg), giving 48.9 g (62%) of **13**.

(43) 3,3′,4,4′,5,5′-Hexafluorobiphenyl **15** was prepared as follows: In a 0.5 L four-necked flask were added 36.5 g (372 mmol) of KOAc, 7.95 g (10 wt %) of $Pd(OAc)_2$, 31.8 g (125 mmol) of bis(pinacolato) diboron, and 200 mL of DMSO. After the reactor was purged with N_2 gas, 79.5 g (377 mmol) of 3,4,5-trifluorobromobenzene was added, and the reaction mixture was stirred at 80 °C for 16 h. After cooling, the mixture was poured into 350 mL of water and extracted with ethyl acetate. The organic layer was dried on 50 g of Na_2SO_4 and filtered. The filtrate was mixed with active carbon, and the mixture was stirred at 80 °C for 45 min. After filtration through Celite, the filtrate was concentrated and triturated in 2-propanol to give **15**, 13 g (40% yield based on bis(pinacolato)diboron).

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