

Tf₂O as a CF₃ Source for the Synthesis of Trifluoromethoxylation Reagent ⁿC₄F₉SO₃CF₃

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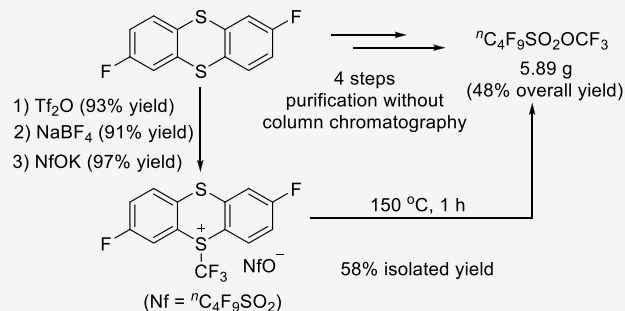
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ABSTRACT: Described herein is the convenient synthesis of an efficient trifluoromethoxylation reagent, ⁿC₄F₉SO₃CF₃, by using cheap and widely available reagents and without the need of any tedious column chromatography purification procedure.



The trifluoromethoxy group (CF₃O) is of particular interest in pharmaceutical chemistry due to its unique properties, such as moderate electronegativity (Hammett constants $\sigma_p = 0.35$, $\sigma_m = 0.38$) and high lipophilicity (Hansch parameter $\pi = 1.04$) effects.¹ The successful development of CF₃O-containing pharmaceuticals, including Delamanid, Riluzole, Sonidegib, and Pretomanid, demonstrates the high value of the CF₃O group, which has driven the chemical community to devote significant research efforts to developing trifluoromethoxylation reagents and trifluoromethoxylation methods.² Many types of trifluoromethoxylation reagents have been developed,³ such as [M⁺ CF₃O⁻],⁴ SO₂-OCF₃,⁵ N-OCF₃,⁶ and C(O)-OCF₃ types.⁷ The SO₂-OCF₃ reagents can release CF₃O⁻ anions in the presence of a nucleophile, such as fluoride anions, which can readily attack the SO₂ moiety to cleave the SO₂-OCF₃ bond. The commonly used SO₂-OCF₃ reagents include ArSO₂-OCF₃,^{5d-k} CF₃SO₂-OCF₃,^{5a-c} and ⁿC₄F₉SO₂OCF₃ (TFNf).^{5l} ArSO₂-OCF₃ has served as a versatile reagent for a wide variety of trifluoromethoxylation reactions.^{5d-k} CF₃SO₂-OCF₃ has a low boiling point (19 °C)⁸ and is highly volatile, which may limit its applications. In sharp contrast, ⁿC₄F₉SO₂OCF₃, developed as a trifluoromethoxylation reagent by Hammond, Umemoto, and co-workers recently,^{5l} has a higher boiling point (87–89 °C) and thus is more convenient for handling. The great synthetic potential of TFNf, demonstrated with the regio- and stereoselectivity, and wide functional group compatibility in trifluoromethoxylation of alkynes,^{5l} may stimulate research efforts to develop cost-effective methods for its preparation.

There have been three reports for the synthesis of ⁿC₄F₉SO₂OCF₃. The first report dates back to 1981, when DesMarteau and Johri developed a two-step procedure starting from ⁿC₄F₉SO₃H (Scheme 1, eq 1).⁹ This process requires the

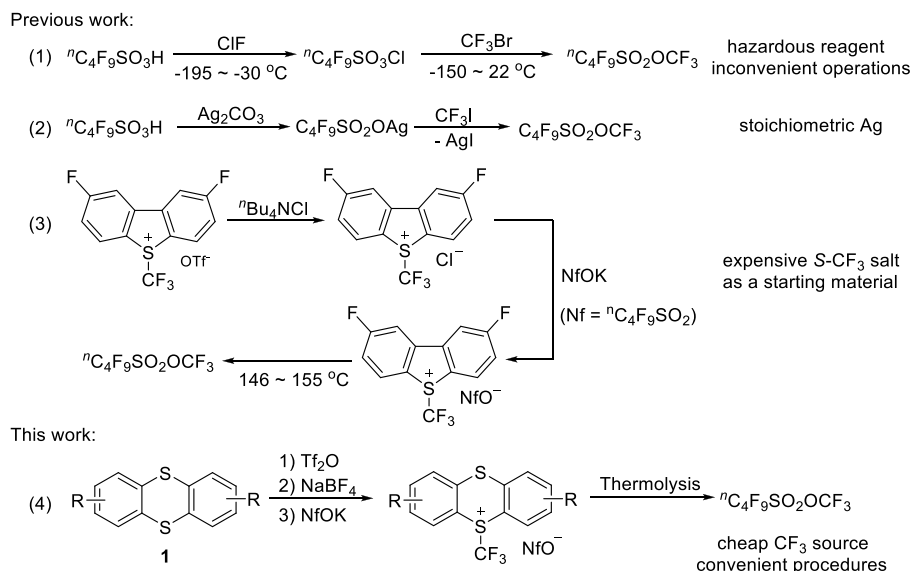
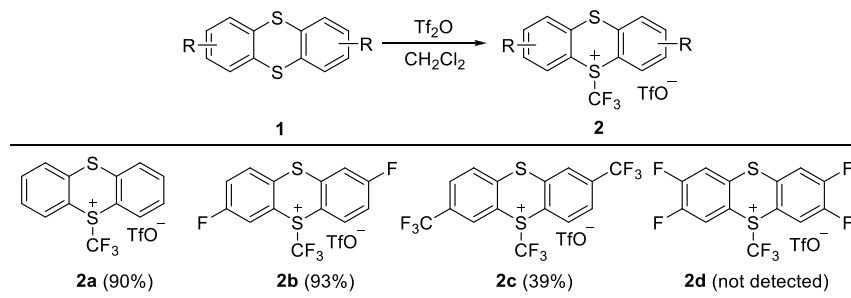
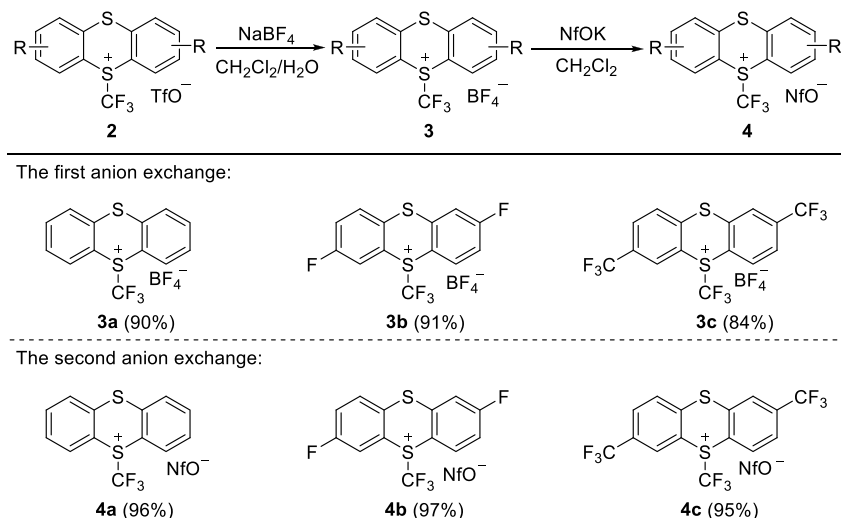
use of a hazardous reagent, ClF, and hazardous Cl₂ would also be produced as a side product. Furthermore, the product of the first step, ⁿC₄F₉SO₃Cl, is quite unstable and would easily decompose at room temperature. The second report necessitates the use of a stoichiometric amount of a silver salt, Ag₂CO₃, and it is quite difficult to isolate ⁿC₄F₉SO₂OCF₃ from the reaction solvent, benzene, due to their similar boiling points (eq 2).¹⁰ The latest method, described by Hammond, Umemoto, and co-workers recently,^{5l} starts from Umemoto's reagent¹¹ to obtain ⁿC₄F₉SO₂OCF₃ via anion exchanges and thermolysis (eq 3). This method features an easy workup procedure, just filtration for the first two steps and distillation for the last step. However, the expensive Umemoto's reagent is required to be used as a starting material, which may restrict the wide applications of ⁿC₄F₉SO₂OCF₃.

Triflic anhydride (Tf₂O) is an abundant and inexpensive industrial raw material. In 2021, Ritter and co-workers developed the synthesis of a S-CF₃ thianthrenium salt by using Tf₂O as a CF₃ source.¹² The thianthrenium salt can act as an efficient electrophilic trifluoromethylation reagent. Based on our previous studies on the electrophilicity of CF₃-containing organic salts,¹³ we speculated that S-CF₃ thianthrenium salts may undergo anion exchanges and thermolysis to provide ⁿC₄F₉SO₂OCF₃ (eq 4). In this process, all reagents and starting materials are widely available, and no tedious purification procedure is required in any step. After isolating

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Scheme 1. Synthesis of ${}^n\text{C}_4\text{F}_9\text{SO}_2\text{OCF}_3$ Table 1. Conversion of Thianthrenes into S-CF₃ Thianthrenium Salts^a^aIsolated yields are shown.Table 2. Two-Step Anion Exchanges^a^aIsolated yields are shown.

the final ${}^n\text{C}_4\text{F}_9\text{SO}_2\text{OCF}_3$ by distillation, thianthrene **1** can be recycled simply by filtration and washing with petroleum ether.

Ritter and co-workers used thianthrene **1a** to synthesize thianthrenium salt **2a**.¹² Besides **1a**, we also examined other thianthrenes containing electron-withdrawing groups (Table

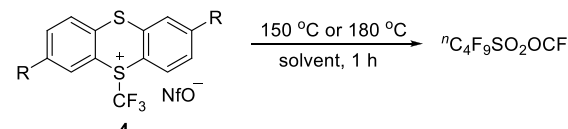
1), since these groups may increase the electrophilicity of thianthrenium salts to facilitate the final thermolysis step. However, electron-withdrawing groups would decrease the efficiency of S-trifluoromethylation. The bi-CF₃-substituted thianthrenium salt was obtained in a low yield (**2c**), and the

tetra-F-substituted substrate cannot be trifluoromethylated at all (**2d**). Fortunately, the *S*-trifluoromethylation of di-F-substituted thianthrene occurred smoothly (**2b**).

The direct anion exchange of TfO⁻ with NfO⁻ cannot occur well because the physicochemical properties of both anions are quite similar. Therefore, a two-step anion exchange was carried out to afford nonafluorobutanesulfonate (nonaflate) salts **4** (Table 2). Both steps proceeded smoothly, and high yields were obtained for each step. The products of each step can be easily isolated by phase separation.

With the nonaflate salts **4** in hand, we then investigate the final thermolysis reactions (Table 3). Salt **4a** can be converted

Table 3. Thermolysis of Nonaflate Salts^a



entry	R	salt 4	yield (%)
1	H	4a	43
2	F	4b	82
3	CF ₃	4c	91

^aReaction conditions: **4** (0.4 mmol) in a reaction solvent (1 mL) at 150 or 180 °C for 1 h. The reaction solvents for the thermolysis of **4a** and **4b** are dibasic esters and 1-chlorooctane, respectively. Thermolysis of **4c** was conducted under neat conditions. ¹⁹F NMR yields are shown.

to give the desired product only in 43% ¹⁹F NMR yield. The presence of electron-withdrawing groups can indeed facilitate the thermolysis reactions (**4b–4c**). The reaction conditions of thermolysis of **4b** were screened (please see the Supporting Information for details), and the highest yield obtained (82%) is shown in entry 2. Although a high yield was obtained in the case of **4c**, the use of **4c** may suffer from a low yield of the first step (**2c**, Table 1). The thermolysis of **4b** gave a lower yield compared with the case of **4c**, but each step starting from thianthrene **1b** can take place smoothly. Therefore, **4b** may be considered as a good precursor of ⁿC₄F₉SO₂OCF₃.

After the optimal conditions of the thermolysis of **4b** was identified, a gram scale reaction was performed (Scheme 2). ⁿC₄F₉SO₂OCF₃ was isolated in 58% yield for the thermolysis step (5.89 g), and the corresponding overall yield was calculated to be 48%. Thianthrene **1b** would be regenerated from **4b** via the thermolysis. After the isolation of ⁿC₄F₉SO₂OCF₃ by distillation, thianthrene **1b** was isolated simply by filtration and washing with petroleum ether (3.9 g, 56%). It is coincidental that the yield of the recovered **1b** is close to the isolated yield of ⁿC₄F₉SO₂OCF₃.

In summary, we have described the development of an efficient route to a versatile trifluoromethoxylation reagent, ⁿC₄F₉SO₂OCF₃. The abundant and inexpensive industrial raw material, Tf₂O, was used as a trifluoromethyl source, only

phase separation or distillation is needed for purification, the starting thianthrene can be recycled simply by filtration and washing, and the synthetic process can be easily scaled up. These attracting features may widen the synthetic applications of reagent ⁿC₄F₉SO₂OCF₃.

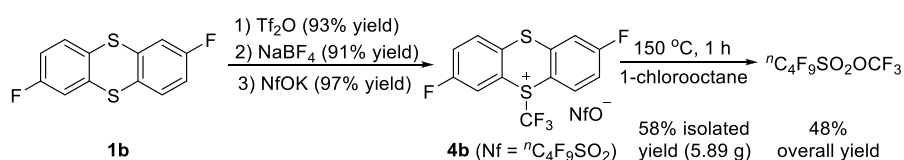
EXPERIMENTAL SECTION

1. General Information. The ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on 400 MHz NMR spectrometers (400 MHz for ¹H, 100 MHz for ¹³C, and 375 MHz for ¹⁹F, respectively). The chemical shifts (δ) for ¹H and ¹³C are given in ppm relative to residual signals of solvents (CHCl₃ at 7.26 ppm for ¹H NMR) while the chemical shifts (δ) for ¹⁹F NMR are given in ppm relative to trichlorofluoromethane (CCl₃F) as standard. Coupling constants (*J*) are reported in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, br = broad. All reactions were monitored by TLC or ¹⁹F NMR. Flash column chromatography was carried out using 300–400 mesh silica gel at medium pressure. Mass spectra were obtained on GC-MS or LC-MS (ESI). High resolution mass spectrometry (HRMS) was performed on a Waters Premier GC-TOF MS instrument with electron impact (EI) ionization mode, or on a Thermo Scientific Q Exactive HF Orbitrap-FTMS instrument with electrospray ionization (ESI) mode. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification.

2. Procedures for the Preparation of 1. 2,7-Difluorothianthrene (1b**).**¹⁴ Into the fuming sulfuric acid (110 mL) in a 1 L round flask was added 4-fluorothiophenol (25 g, 195.0 mmol) slowly at 0 °C. The mixture was stirred at room temperature for 48 h. The mixture was added into 500 mL water slowly. And the mixture was neutralized with solid sodium hydroxide solution at 0 °C. The solution was extracted with ethyl acetate, and the organic phases were combined. The solvent is removed by a vacuum to obtain a solid (16.85 g), which was a mixture of 2,7-difluorothianthrene and 2,7-difluorothianthrene 5,10-dioxide. Into the mixture was added acetic acid (152 mL) and zinc powder (4.5 g), and the resulting mixture was refluxed in an oil bath for 24 h. Then the solid was filtered and washed with ethyl acetate. The organic phases were combined. The acetic acid and ethyl acetate were removed by concentration under a vacuum to afford **1b** as a slightly yellow solid (14.92 g, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.20 (dd, *J* = 8.4, 2.5 Hz, 2H), 6.96 (td, *J* = 8.4, 2.6 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -114.18 (td, *J* = 8.2, 5.4 Hz, 2F). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.4 (d, *J* = 249.5 Hz), 138.1 (d, *J* = 8.61 Hz) 130.1 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 8.7 Hz), 116.0 (d, *J* = 24.1 Hz), 115.1 (d, *J* = 22.5 Hz).

2,7-Bis(trifluoromethyl)thianthrene (1c**).** Into a fuming sulfuric acid (55 mL) in a 1 L round flask was added 4-trifluoromethylphenol (12 g, 67.4 mmol) slowly at 0 °C. The mixture was stirred at room temperature for 48 h. The mixture was poured into 250 mL water slowly. Then the reaction solution is neutralized with solid sodium hydroxide solution at 0 °C. The solution was then extracted with ethyl acetate. The organic phases were combined and the solvent was removed by concentration to give **1c** as a white solid (4.82 g, 41%). mp 70–71 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.69 (s, 6F). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 139.3 (s), 135.5 (s), 130.7 (q, *J* = 32.9 Hz), 129.0 (s), 125.6 (q, *J* = 3.8 Hz) 124.9 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 273.0 Hz). HRMS (EI) (*m/z*)

Scheme 2. Gram-Scale Synthesis of ⁿC₄F₉SO₂OCF₃



calcd for $C_{14}H_6S_2F_6 [M]^+$, 351.9810, found 351.9806. IR ν_{max} (cm^{-1}) = 2925, 1910, 1788, 1596, 1460, 1315, 1255, 1171, 1121, 1072, 896, 829, 732, 714, 629.

2,3,7,8-Tetrafluorothianthrene (1d).¹⁵ Into the mixture of $AlCl_3$ (16.00 g, 120 mmol) and dichloromethane (50 mL) cooled by an ice-salt bath was added 1,2-difluorobenzene (4.66 g, 40 mmol) under a N_2 atmosphere. The mixture was stirred at this temperature for 1 h. $Cl-S-S-Cl$ (11.02 g, 80 mmol) was added and the system was allowed to be warmed to room temperature slowly. Then the reaction mixture was stirred at room temperature for 2 h, and then was refluxed in an oil bath for 20 min. The reaction was quenched by water (about 200 mL). The pH value was adjusted by aqueous HCl (8 M) to 2–3. The crude product was extracted with dichloromethane and the solution was dried with $MgSO_4$. Product **1d** was isolated by flash column chromatography as a solid (0.8 g, 14%). 1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, $J = 8.5$ Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.90 (t, 4F, $J = 8.5$ Hz).

3. General Procedures for the Preparation of 2. Under an ambient atmosphere, a round-bottom flask was charged with thianthrene derivatives **1** (1.0 equiv) and dichloromethane. Subsequently, triflic anhydride (1.1 or 1.3 equiv) was added in one portion at room temperature. The reaction mixture was stirred at room temperature for 22 h (in the cases of **2b** and **2c**, the reaction mixture was refluxed in an oil bath for 48 h). Subsequently, a saturated aqueous $NaHCO_3$ solution was added. The aqueous layer was discarded and the organic layer was concentrated under reduced pressure. The residue was washed with diethyl ether or dichloromethane/petroleum ether and then dried under a vacuum to give products **2**.

S-(Trifluoromethyl)thianthrenium triflate (2a).¹² Thianthrene **1a** (1.082 g, 5.0 mmol) and Tf_2O (1.1 equiv) were used. The crude product was washed with diethyl ether and was obtained as a slightly yellow solid in 90% yield (1.94 g). 1H NMR (400 MHz, $CDCl_3$) δ : 8.46 (d, $J = 7.9$ Hz, 2H), 7.92 (t, $J = 7.5$ Hz, 2H), 7.85 (d, $J = 7.7$ Hz, 2H), 7.72 (t, $J = 7.5$ Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.19 (s, 3F), -78.40 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.0 (s), 136.7 (s), 136.6 (s), 130.3 (s), 129.5 (s), 124.4 (q, $J = 337.7$ Hz), 120.7 (q, $J = 320.7$ Hz), 108.7 (s).

S-(Trifluoromethyl)difluorothianthrenium triflate (2b). 2,7-Difluorothianthrenium (**1b**, 1.770 g, 7.0 mmol) and Tf_2O (1.3 equiv) were used. Crude **2b** was washed with diethyl ether and was obtained as a slightly yellow solid in 93% yield (2.844 g). mp 156–157 °C. 1H NMR (400 MHz, $DMSO-d_6$) δ 8.79–8.68 (m, 2H), 8.28–8.15 (m, 2H), 7.98 (td, $J = 8.5, 2.7$ Hz, 1H), 7.78 (td, $J = 9.0, 2.6$ Hz, 1H). ^{19}F NMR (376 MHz, $DMSO-d_6$) δ -50.95 (s, 3F), -77.84 (s, 3F), -98.47 (td, $J = 8.3, 5.6$ Hz, 1F), -109.56 (td, $J = 7.9, 5.1$ Hz, 1F). $^{13}C\{^1H\}$ NMR (101 MHz, $DMSO-d_6$) δ 166.2 (d, $J = 260.3$ Hz), 161.5 (d, $J = 251.7$ Hz), 139.8 (d, $J = 11.0$ Hz), 138.6 (d, $J = 11.2$ Hz), 131.9 (d, $J = 8.3$ Hz), 130.3 (d, $J = 3.4$ Hz), 124.9 (d, $J = 22.6$ Hz), 124.1 (q, $J = 336.0$ Hz), 123.4 (d, $J = 27.6$ Hz), 121.1 (q, $J = 323.4$ Hz), 118.4 (d, $J = 23.7$ Hz), 117.5 (d, $J = 27.2$ Hz), 113.0 (d, $J = 9.7$ Hz), 106.5 (d, $J = 2.7$ Hz). HRMS (ESI) (m/z) calcd for $C_{13}H_6S_2F_5 [M-TfO]^-$, 320.9826, found 320.9822. IR ν_{max} (cm^{-1}) = 3094, 3067, 1586, 1563, 1459, 1389, 1274, 1223, 1153, 1134, 1066, 1027, 896, 878, 754, 691, 663, 634.

S-(Trifluoromethyl)-bis(trifluoromethyl)thianthrenium triflate (2c). 2,7-Bis(trifluoromethyl)thianthrenium (**1c**, 3.50 g, 9.94 mmol) and Tf_2O (1.3 equiv) were used. Crude **2c** was washed with dichloromethane/petroleum ether (volume ratio was 1:1) and was obtained as a slightly yellow solid in 39% yield (2.22g). mp 181–182 °C. 1H NMR (400 MHz, $DMSO-d_6$) δ 9.15 (s, 1H), 8.82 (d, $J = 8.3$ Hz, 1H), 8.64 (s, 1H), 8.34 (s, 2H), 8.22 (d, $J = 8.2$ Hz, 1H). ^{19}F NMR (376 MHz, $DMSO-d_6$) δ -50.97 (s, 3F), -61.44 (s, 3F), -62.19 (s, 3F), -77.84 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $DMSO-d_6$) δ 138.4 (s), 137.4 (s), 135.4 (q, $J = 33.6$ Hz), 134.7 (s), 133.4 (q, $J = 3.6$ Hz), 132.5 (q, $J = 3.1$ Hz), 130.7 (s), 129.9 (q, $J = 34.1$ Hz), 126.8 (s), 126.7 (s), 123.9 (q, $J = 337.6$ Hz), 123.2 (q, $J = 272.8$ Hz), 123.0 (q, $J = 273.9$ Hz), 121.1 (q, $J = 321.8$ Hz), 118.3 (s), 115.2 (s). HRMS (ESI) (m/z) calcd for $C_{15}H_6S_2F_9 [M-TfO]^-$, 420.9762,

found 420.9757. IR ν_{max} (cm^{-1}) = 3042, 1607, 1394, 1318, 1280, 1238, 1183, 1138, 1072, 1023, 851, 819, 757, 724, 631.

4. General Procedures for the Preparation of 3. Under an ambient atmosphere, into the solution of S-(trifluoromethyl)thianthrenium triflate derivative **2** (1.0 equiv) in dichloromethane was added aqueous $NaBF_4$ solution (8.0 equiv, $c = 0.9$ mol/L). The mixture was stirred for 10 min, and the organic phase was separated and then further mixed with a fresh aqueous $NaBF_4$ solution (8.0 equiv, $c = 0.9$ mol/L). The mixture was stirred for 10 min. The organic phase was isolated and again mixed with a fresh aqueous $NaBF_4$ solution (8.0 equiv, $c = 0.9$ mol/L), and the resulting mixture was stirred for another 10 min. The organic phase is then dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure to give products **3**.

S-(Trifluoromethyl)thianthrenium tetrafluoroborate (3a).¹² The used concentration of S-(trifluoromethyl)thianthrenium triflate (**2a**, 12.00 g, 27.6 mmol) in DCM was 0.15 mol/L. Product **3a** was isolated as a yellow solid in 90% yield (9.26 g). 1H NMR (400 MHz, $DMSO-d_6$) δ 8.59 (d, $J = 7.8$ Hz, 2H), 8.12 (d, $J = 7.8$ Hz, 2H), 8.02 (t, $J = 7.4$ Hz, 2H), 7.85 (t, $J = 7.4$ Hz, 2H). ^{19}F NMR (376 MHz, $DMSO-d_6$) δ -52.69 (s, 3F), [-148.15 (s), -148.20 (s)] (4F). $^{13}C\{^1H\}$ NMR (101 MHz, $DMSO-d_6$) δ 137.0 (s), 136.7 (s), 134.8 (s), 130.3 (s), 129.8 (s), 124.4 (q, $J = 335.6$ Hz), 111.0 (s).

S-(Trifluoromethyl)difluorothianthrenium tetrafluoroborate (3b). The used concentration of S-(trifluoromethyl)-difluorothianthrenium triflate (**2b**, 41.249 g, 94.96 mmol) was 0.4 mol/L. Since the scale was increased, the reaction conditions were slightly different. The concentration of $NaBF_4$ solution was 0.4 mol/L, and the mixture of the **2b** solution and the $NaBF_4$ solution was stirred for 30 min. **3b** was obtained as a slightly brown solid in 91% yield (35.382 g). mp 168–169 °C. 1H NMR (400 MHz, $DMSO-d_6$) δ 8.86–8.66 (m, 2H), 8.32–8.14 (m, 2H), 7.97 (td, $J = 8.7, 2.7$ Hz, 1H), 7.78 (td, $J = 8.5, 2.6$ Hz, 1H). ^{19}F NMR (376 MHz, $DMSO-d_6$) δ -50.94 (s, 3F), -98.44 (td, $J = 7.8, 5.3$ Hz, 1F), -109.53 (td, $J = 7.9, 5.2$ Hz, 1F), [-148.16 (s), -148.21 (s)] (4F). $^{13}C\{^1H\}$ NMR (101 MHz, $DMSO-d_6$) δ 166.2 (d, $J = 260.2$ Hz), 161.5 (d, $J = 251.6$ Hz), 139.9 (d, $J = 11.0$ Hz), 138.5 (d, $J = 11.2$ Hz), 132.0 (d, $J = 8.3$ Hz), 130.3 (d, $J = 3.5$ Hz), 124.9 (d, $J = 22.5$ Hz), 124.1 (q, $J = 336.3$ Hz), 123.5 (d, $J = 27.6$ Hz), 118.4 (d, $J = 23.7$ Hz), 117.5 (d, $J = 27.3$ Hz), 113.1 (d, $J = 9.7$ Hz), 106.6 (d, $J = 2.7$ Hz). HRMS (ESI) (m/z) calcd for $C_{13}H_6S_2F_5 [M-BF_4]^-$, 320.9826, found 320.9822. IR ν_{max} (cm^{-1}) = 3095, 1589, 1460, 1382, 1288, 1267, 1224, 1054, 907, 864, 816, 754, 689, 639.

S-(Trifluoromethyl)-bis(trifluoromethyl)thianthrenium tetrafluoroborate (3c). The used concentration of S-(trifluoromethyl)-bis(trifluoromethyl)thianthrenium triflate (**2c**, 2.00 g, 3.51 mmol) was 0.4 mol/L. **3c** was obtained as a white solid in 84% yield (1.49 g). mp 139–141 °C. 1H NMR (400 MHz, $DMSO-d_6$) δ 9.22 (s, 1H), 8.92 (d, $J = 8.5$ Hz, 1H), 8.68 (s, 1H), 8.44–8.34 (m, 2H), 8.25 (d, $J = 8.5, 1H$). ^{19}F NMR (376 MHz, $DMSO-d_6$) δ -48.53 (s, 3F), -61.42 (s, 3F), -62.16 (s, 3F), [-148.24 (s), -148.29 (s)] (4F). $^{13}C\{^1H\}$ NMR (101 MHz, $DMSO-d_6$) δ 139.8 (s), 138.1 (s), 136.0 (s), 135.9 (q, $J = 33.3$ Hz), 134.1 (q, $J = 3.7$ Hz), 133.1 (q, $J = 3.2$ Hz), 131.3 (s), 130.3 (q, $J = 34.1$ Hz), 127.3 (q, $J = 3.81$ Hz), 127.1 (q, $J = 3.45$ Hz), 123.8 (q, $J = 337.7$ Hz), 123.2 (q, $J = 272.9$ Hz), 123.0 (q, $J = 273.9$ Hz), 116.6 (s), 113.5 (s). HRMS (ESI) (m/z) calcd for $C_{15}H_6S_2F_9 [M-BF_4]^-$, 420.9762, found 420.9758. IR ν_{max} (cm^{-1}) = 3087, 2166, 2071, 1599, 1460, 1391, 1319, 1227, 1187, 1142, 1065, 1024, 896, 837, 755, 723, 633.

5. General Procedures for the Preparation of 4. Under an ambient atmosphere, S-(trifluoromethyl)thianthrenium tetrafluoroborate derivative **3** (1.0 equiv) was dissolved in dichloromethane ($c = 0.15$ or 0.4 mol/L). Into the solution, potassium nonafluorobutanesulfonate (1.2 equiv) was added. Then the reaction mixture was stirred at room temperature for 30 min. The mixture is then filtered, and the solvent was removed under reduced pressure to provide products **4**.

S-(Trifluoromethyl)thianthrenium nonaflate (4a). The used concentration of S-(trifluoromethyl)thianthrenium tetrafluoroborate (**3a**, 1.20 g, 3.2 mmol) was 0.15 mol/L. **4a** was isolated as a slightly

yellow solid in 96% yield (1.81 g). mp 91–92 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, J = 8.1 Hz, 2H), 7.91 (t, J = 7.7 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 7.7 Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -51.33 (s, 3F), -81.03 (tt, J = 10.2, 2.7 Hz, 3F), -114.7 to -114.87 (m, 2F), -121.60 to -121.82 (m, 2F), -126.00 to -126.21 (m, 2F). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 137.0 (s), 136.7 (s), 136.7 (s), 130.3 (s), 129.5 (s), 124.4 (q, J = 336.9 Hz), 117.0–115.2 (m), 114.4–113.2 (m), 111.7–110.0 (m), 109.3–107.4 (m), 108.7 (s). HRMS (ESI) (m/z) calcd for $\text{C}_{13}\text{H}_8\text{S}_2\text{F}_3$ $[\text{M}-\text{NfO}]^+$, 285.0014, found 285.0011. IR ν_{max} (cm^{-1}) = 3079, 3006, 1564, 1454, 1282, 1250, 1194, 1130, 1077, 1053, 1041, 1017, 760, 733, 678, 652, 636, 612.

S-(Trifluoromethyl)difluorothianthrenium nonaflate (4b). The used concentration of S-(trifluoromethyl)difluorothianthrenium tetrafluoroborate (3b, 35.382 g, 86.70 mmol) was 0.4 mol/L. 4b was isolated as a slightly yellow solid in 97% yield (52.089 g). mp 104–105 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.82–8.67 (m, 2H), 8.27–8.14 (m, 2H), 7.96 (td, J = 8.6, 2.4 Hz, 1H), 7.77 (td, J = 8.9, 2.2 Hz, 1H). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -50.38 (s, 3F), -80.98 (tt, J = 9.8, 2.8 Hz, 3F), -94.25 to -94.51 (m, 1F), -105.30 to -105.44 (m, 1F), -114.78 to -115.04 (m, 2F), -121.70 to -121.96 (m, 2F), -125.97 to -126.24 (m, 2F). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO}-d_6$) δ 166.2 (d, J = 260.2 Hz), 161.5 (d, J = 251.5 Hz), 139.9 (d, J = 11.0 Hz), 138.5 (d, J = 11.2 Hz), 132.0 (d, J = 8.3 Hz), 130.3 (d, J = 3.4 Hz), 124.9 (d, J = 22.6 Hz), 124.1 (q, J = 334.9 Hz), 123.5 (d, J = 27.6 Hz), 118.4 (d, J = 23.7 Hz), 117.5 (d, J = 27.3 Hz), 117.3–115.5 (m), 114.5–113.2 (m), 113.1 (d, J = 9.7 Hz), 111.8–110.0 (m), 109.6–107.4 (m), 106.60 (d, J = 2.7 Hz). HRMS (ESI) (m/z) calcd for $\text{C}_{13}\text{H}_6\text{S}_2\text{F}_5$ $[\text{M}-\text{NfO}]^+$, 320.9826, found 320.9823. IR ν_{max} (cm^{-1}) = 3081, 3025, 1592, 1561, 1466, 1388, 1352, 1252, 1215, 1132, 1076, 1054, 841, 825, 803, 755, 697, 654.

S-(Trifluoromethyl)-bis(trifluoromethyl)thianthrenium nonaflate (4c). The used concentration of S-(trifluoromethyl)-bis(trifluoromethyl)thianthrenium tetrafluoroborate (3c, 1.291 g, 2.54 mmol) was 0.4 mol/L. 4c was isolated as a slightly yellow solid in 95% yield (1.740 g). mp 131–132 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.27 (s, 1H), 8.93 (d, J = 8.4 Hz, 1H), 8.68 (s, 1H), 8.43–8.34 (m, 2H), 8.25 (dd, J = 8.5, 1.5 Hz, 1H). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -48.63 (s, 3F), -61.56 (s, 3F), -62.30 (s, 3F), -80.63 (tt, J = 9.9, 2.9 Hz, 3F), -114.85 to -115.06 (m, 2F), -121.33 to -121.70 (m, 2F), -125.72 to -125.97 (m, 2F). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO}-d_6$) δ 139.7 (s), 138.2 (s), 136.0 (s), 135.9 (q, J = 31.1 Hz), 134.1 (d, J = 3.6 Hz), 133.1 (d, J = 3.3 Hz), 131.3 (s), 130.2 (q, J = 34.4 Hz), 127.3 (d, J = 3.8 Hz), 127.0 (d, J = 3.6 Hz), 123.8 (q, J = 336.2 Hz), 123.2 (q, J = 273.0 Hz), 122.9 (q, J = 274.9 Hz), 117.3–115.5 (m), 116.6 (s), 114.5–113.2 (m), 113.5 (s), 111.8–110.0 (m), 109.6–107.4 (m). HRMS (ESI) (m/z) calcd for $\text{C}_{15}\text{H}_6\text{S}_2\text{F}_9$ $[\text{M}-\text{NfO}]^+$, 420.9762, found 420.9758. IR ν_{max} (cm^{-1}) = 3095, 2110, 1589, 1460, 1388, 1288, 1224, 1054, 1023, 907, 864, 816, 754, 689, 639.

6. Thermolysis of S-(Trifluoromethyl)thianthrenium Salts. **Thermolysis of 4a.** The mixture of S-(trifluoromethyl)thianthrenium nonaflate (4a, 0.234 g, 0.4 mmol) and dibasic esters (1 mL) was stirred at 180 °C in an oil bath for 1 h in a sealed tube. 4a was completely converted, as monitored by ^{19}F NMR spectroscopy, and the yield of $^{\text{C}}\text{C}_4\text{F}_9\text{SO}_2\text{OCF}_3$ was determined to be 43% by ^{19}F NMR analysis.

Thermolysis of 4b (0.4 mmol Scale). The mixture of S-(trifluoromethyl)difluorothianthrenium nonaflate (4b, 0.248 g, 0.4 mmol) and 1-chlorooctane (1 mL) in a sealed tube was stirred at 150 °C in an oil bath for 1 h. 4b was completely converted, as monitored by ^{19}F NMR spectroscopy, and the yield of $^{\text{C}}\text{C}_4\text{F}_9\text{SO}_2\text{OCF}_3$ was determined to be 82% by ^{19}F NMR analysis.

Thermolysis of 4b (Gram Scale). The mixture of S-(trifluoromethyl)difluorothianthrenium nonaflate (4b, 17.11 g, 27.58 mmol) and 1-chlorooctane (69 mL) was stirred at 150 °C in an oil bath for 1 h. The reaction was complete, as monitored by ^{19}F NMR spectroscopy. After the system was cooled to room temperature, direct distillation under reduced pressure (40 Pa) with the oil-bath temperature at \sim 70–80 °C gave the desired pure product,

trifluoromethyl nonaflate (5, 5.89 g, 58%), collected in the receiver cooled by liquid nitrogen. After the reaction mixture was cooled to room temperature, a solid was precipitated. After filtration, the solid was washed with petroleum ether to remove 1-chlorooctane and dried under a vacuum to recover 2,7-difluorothianthrenium (1b, 3.90 g, 56%). The structure of recovered 1b was confirmed by ^1H and ^{19}F NMR spectroscopy (please see the last two spectra in Supporting Information; the NMR data consistent with that described above for the synthesis of 1b). NMR data^{SI} of $^{\text{C}}\text{C}_4\text{F}_9\text{SO}_2\text{OCF}_3$: ^{19}F NMR (376 MHz, CDCl_3) δ -49.55 to -50.15 (m, 3F), -78.00 to -78.52 (m, 3F), -105.12 to -105.50 (m, 2F), -118.10 to -118.60 (m, 2F), -123.14 to -123.65 (m, 2F).

Thermolysis of 4c. S-(Trifluoromethyl)thianthrenium nonaflate (4c, 0.288 g, 0.4 mmol) was stirred at 150 °C in an oil bath for 1 h. 4c was completely converted, as monitored by ^{19}F NMR analysis, and the yield of $^{\text{C}}\text{C}_4\text{F}_9\text{SO}_2\text{OCF}_3$ was determined to be 91% by ^{19}F NMR spectroscopy.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.2c03018>.

Supporting spectral data (PDF)

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Notes

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