

THE ELECTRONIC STRUCTURE OF THIOXANTHYLIUM SCAFFOLDS

Koki Hirano,^{1,2} Akira Yasuda,¹ Takahiro Sasamori,^{2,†} Kosei Shioji,¹ Kentaro Okuma,¹ and Noriyoshi Nagahora^{*,1}

¹Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma 8-19-1, Jonan-ku, Fukuoka, Fukuoka 814-0180, Japan

²Graduate School of Science, Nagoya City University, Yamanohata 1, Mizuho-cho, Mizuho-ku, Nagoya, Aichi 467-8501, Japan

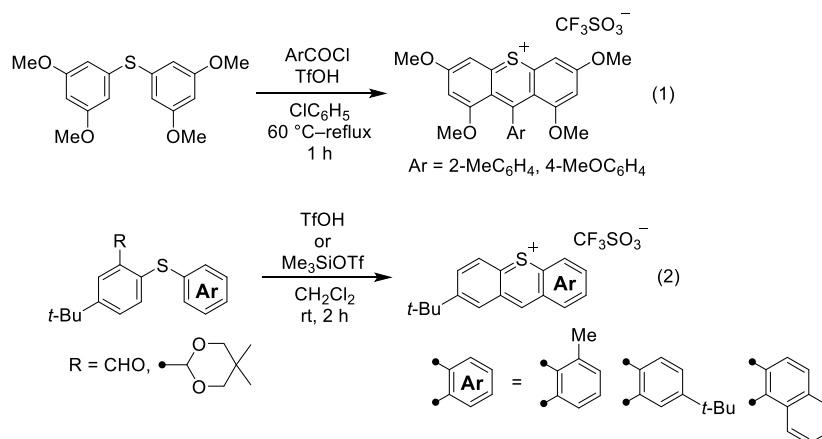
[†]Current address: Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

E-mail: nagahora@fukuoka-u.ac.jp

Abstract – A new series of thioxanthylum trifluoromethanesulfonates has been synthesized via a trifluoromethanesulfonic-acid-induced cyclization of thioether precursors. The electronic structure of these thioxanthylum salts were determined by UV–vis absorption spectroscopy, and theoretically investigated by density functional theory calculations.

INTRODUCTION

Thioxanthylum salts represent a new branch of materials that exhibit fascinating structures as well as optoelectronic and physicochemical properties, which may lead to a multitude of potential applications.¹ Moreover, thiopyrylium salts show promising potential as building blocks in nonlinear optical materials and dye-sensitized solar cells.² Thus, the development of efficient synthetic methods for the thioxanthylum framework and understanding the electronic structures are challenging issues of particular importance in contemporary organic chemistry. Recently, Hoshino and Honda have demonstrated the synthesis of a series of methoxy-substituted thioxanthylum salts by diarylthioethers with acyl chlorides in the presence of a Brønsted acid (equation 1, Scheme 1).³ In 2020, we have reported the novel synthetic methods for the formation of thioxanthylum scaffolds promoted by a Brønsted acid (equation 2, Scheme 1).⁴ Although these synthetic methods for thioxanthylum compounds have been extensively investigated, fundamental research into their photophysical properties has been limited. Herein, we describe the experimental and theoretical examination of electronic structures of their thioxanthylum scaffolds.

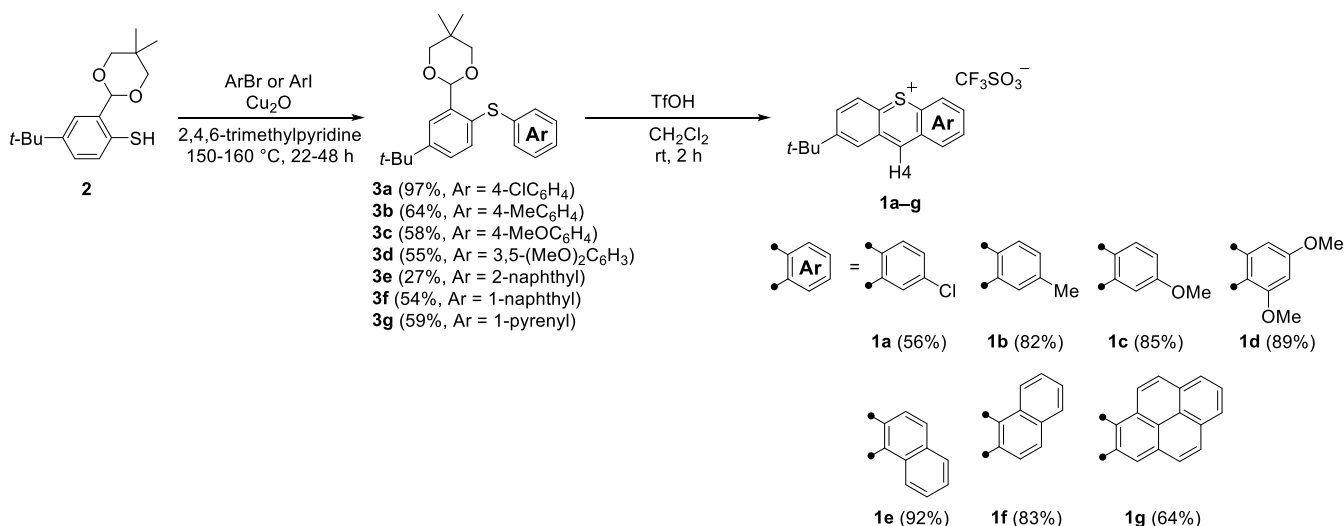


Scheme 1. Recently reported synthetic methods for the formation of thioxanthylum scaffolds

RESULTS AND DISCUSSION

SYNTHESIS OF THIOXANTHYLIUM TRIFLUOROMETHANESULFONATES **1a–1g**

Scheme 2 shows the synthetic procedure that we carried out to synthesize a new series of thioxanthylum trifluoromethanesulfonates (**1a–1g**). This methodology involves a Brønsted-acid-induced intramolecular cyclization of thioethers that bear a formyl group, which has been previously developed by us.⁴ The treatment of benzenethiol **2** with 4-iodochlorobenzene in the presence of copper(I) oxide afforded thioether **3a** in moderate yield. Thioethers **3b–3g**, which serve as precursors for the desired thioxanthylum salts, were prepared via the similar coupling reaction in good yield. The intramolecular cyclization of **3a–3g** with trifluoromethanesulfonic acid at room temperature proceeded to form thioxanthylum trifluoromethanesulfonates **1a–1g**. The resulting suspension was added dropwise to cold ether, which allowed the isolation of analytically pure crystals of **1a–1g** in moderate yield by centrifugation. The molecular structures of **1a–1g** were determined by spectroscopic methods and elemental analysis.



Scheme 2. Synthesis of thioxanthylum trifluoromethanesulfonates **1a–1g**

NMR SPECTROSCOPIC ANALYSIS OF THIOXANTHYLIUM TRIFLUOROMETHANESULFONATES **1a–1g**

The molecular structures of **1a–1g** in CD₃CN were investigated by ¹H and ¹³C NMR spectroscopy. The ¹H NMR spectra of **1a–1g** showed deshielded resonances for all aromatic protons, which suggest the presence of a significant diatropic ring current in the π -scaffold of **1a–1g**. The resonances for **1a–1g** shifted to lowest field can be assigned to the H4 protons (Scheme 1) at 10.15 (**1a**), 10.08 (**1b**), 9.98 (**1c**), 9.92 (**1d**), 10.87 (**1e**), 10.02 (**1f**), and 9.56 (**1g**) ppm. The results can be regarded as a combination of deshielding effects by the ring current and the electron-deficient nature of the thiopyrylium cation subunit. In the ¹³C NMR spectra, all signals for the six-membered thiopyrylium ring were observed in a range of 129–182 ppm, which is comparable to the ¹³C NMR data of previously reported thiopyrylium salts.^{3,4} Moreover, the observed ¹³C NMR chemical shifts are different from those of carbocations such as Ph₂HC⁺ ($\delta = 201$) and Ph₃C⁺ ($\delta = 212$),⁵ suggesting that **1a–1g** do not exhibit the characteristics of a localized carbocation (**B** in Figure 1), but major resonance contributions from a thioxanthylum cation in solution (**A** in Figure 1).

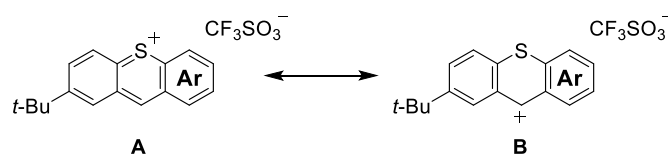


Figure 1. Plausible resonance structures **A** and **B** of thioxanthylum salts

ELECTRONIC STRUCTURES OF THIOXANTHYLIUM TRIFLUOROMETHANESULFONATES **1a–1g**

UV–vis absorption spectra of **1a–1g** were measured in CH₂Cl₂ to examine their electronic structures (Figure 2). The photophysical parameters of the UV–vis absorption spectra are summarized in Table 1. The red-edge absorption bands were observed at 499 (**1a**), 530 (**1b**), 535 (**1c**), 543 (**1d**), 516 (**1e**), 521 (**1f**), 686 (**1g**) nm, which can be assigned to the π – π^* electron transitions of the thioxanthylum chromophore in **1a–1g**. Chloro-substituted **1a** exhibits the most blue-shifted absorption among them. Introduction of methyl/methoxy groups to the thioxanthylum unit in **1b/1c** and **1d** cause a bathochromic shift of the absorption relative to the absorption of **1a**, which indicates perturbation of the electronic structure of the thioxanthylum framework. Naphthalene-fused thioxanthylum salts **1e** and **1f** show similar wavelengths of the red-edge absorption bonds. In the case of **1g**, a broad absorption was observed around 686 nm, which is the lowest energy transition. An expansion of the π -electron system with the pyrene subunit has a profound effect on the electronic structure. Thus, we confirmed that **1a–1g** contain a thioxanthylum chromophore with tunable electronic properties by introducing an electron-donating substituent and/or by expansion of the π -electron system.

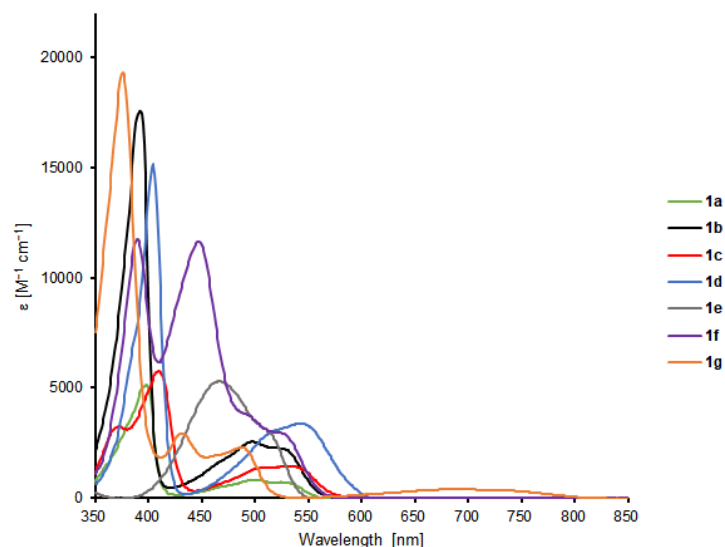


Figure 2. UV-vis absorption spectra of **1a–1g** in CH₂Cl₂ solution (concentration: $1.20\text{--}6.15 \times 10^{-5}$ mol/L) at room temperature

Table 1. Photophysical data of thioxanthylum trifluoromethanesulfonates **1a–1g**

Compound	Absorption	
	λ_{max} [nm]	ϵ [$\text{M}^{-1} \text{cm}^{-1}$]
1a	499	1020
1b	498, 530(sh)	2560, 2180
1c	535	1400
1d	543	3380
1e	466, 516(sh)	5300, 2870
1f	521	2990
1g	686	1300

THEORETICAL INVESTIGATIONS INTO THIOXANTHYLIUM CATIONS **1a'–1g'**

In order to obtain insight into the electronic structures of **1a–1g**, theoretical investigations were carried out on model thioxanthylum cations (**1a'–1g'**), where the counter anions were omitted. These molecules were optimized using density functional theory (DFT) methods implemented using the Gaussian 16 program.⁶ Figure 3 shows the frontier molecular orbitals and their associated energy levels for **1a'–1g'**. The theoretically derived highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for **1a'–1f'** are delocalized exclusively over the π - and π^* -orbitals of the entire molecular framework, respectively. Meanwhile, the HOMO and LUMO of **1g'** are somewhat localized over the pyrene and the thiopyrylium subunits, respectively. Regarding their energy levels, the introduction of methoxy groups into the thioxanthylum framework elevates both the HOMOs and LUMOs. Upon incorporation of the pyrene subunit in the thioxanthylum cation, the HOMO is dramatically destabilized.

Moreover, the assignment of the UV–vis absorption spectra was based on the results of time-dependent (TD) DFT calculations at the B3LYP/6-31G(d) level of theory (Table 2). The experimentally observed red-edge absorption bands of **1a**–**1g** were assigned to the HOMO–LUMO transitions, which are symmetry-allowed π – π^* transitions. In the case of **1g'**, the HOMO–LUMO transitions exhibit a lower oscillator strength and intramolecular charge-transfer character, which is in good agreement with the experimentally observed results for **1g**. It can therefore be concluded that the electronic structures of these new thioxanthylum salts and the characteristic bathochromic shift of the absorption of the π -extended **1g** arise from intramolecular charge-transfer transitions.

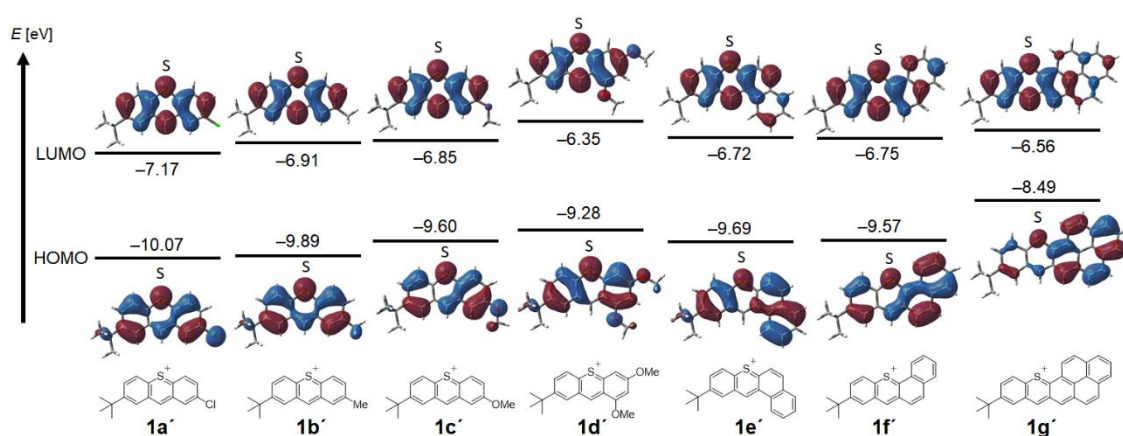


Figure 3. HOMOs and LUMOs (isovalue: 0.02) of thioxanthylum cations **1a'**–**1g'** calculated at the B3LYP/6-31G(d) level of theory

Table 2. Summary of the results obtained from the TD-DFT calculations on **1a'**–**1g'**^a

Molecule	E [eV] ^b	λ [nm] ^c	f^d	Transition
1a'	2.850	486.5	0.0479	HOMO \rightarrow LUMO
1b'	2.533	489.5	0.0488	HOMO \rightarrow LUMO
1c'	2.373	522.6	0.0552	HOMO \rightarrow LUMO
1d'	2.481	499.8	0.1535	HOMO \rightarrow LUMO
1e'	2.579	456.8	0.2177	HOMO \rightarrow LUMO
1f'	2.393	518.2	0.0577	HOMO \rightarrow LUMO
1g'	1.619	765.6	0.0233	HOMO \rightarrow LUMO

^aCalculations were carried out at the TD-PCM(CH₂Cl₂)-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

^bExcitation energy.

^cExcitation wavelength.

^dOscillator strength.

CONCLUSIONS

Herein, we have described a new synthetic method for the transformation of thioether precursors into thioxanthylium salts via a Brønsted-acid-induced intramolecular cyclization. The electronic structures of the resulting thioxanthylium salts were examined by UV-vis absorption spectroscopy and theoretical investigations. The results of this survey can be expected to provide insight into the electronic character of cationic sulfur-heterocycles such as thiopyrylium compounds. The methodology described here can be used to extend the structural diversity and the availability of sulfur-containing building blocks with a thiopyrylium moiety.

EXPERIMENTAL

GENERAL.

All solvents were purified by standard methods. Preparative thin-layer chromatography (PTLC) was performed on Merck silica gel 60 PF254. Column chromatography was performed on silica gel 60N (Kanto Chemical) under an ambient atmosphere. ^1H (400 MHz) and ^{13}C NMR (101 Hz) spectra were recorded in CDCl_3 on a Bruker Avance spectrometer using the residual resonances of CHCl_3 ($\delta_{\text{H}} = 7.26$) and CDCl_3 ($\delta_{\text{C}} = 77.0$) as well as of CD_3CN ($\delta_{\text{H}} = 1.94$; $\delta_{\text{C}} = 1.32$) as the internal standards to reference the ^1H and ^{13}C NMR spectra. ^{19}F NMR spectra (376 MHz) were recorded on a Bruker Avance spectrometer using CFCl_3 ($\delta_{\text{F}} = 0.00$) as an external standard. The assignment of the signals was typically accomplished on the basis of 1D (homodecoupling and DEPT) and 2D (COSY, HMQC, and HMBC) NMR techniques. Unless otherwise stated, all ^{13}C and ^{19}F NMR experiments were performed using broad-band ^1H decoupling. EI and ESI-TOF mass spectral data were obtained on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively. Absorption spectra were recorded on a JASCO V-550 UV/Vis spectrometer. Elemental analyses were carried out on a JM11 CHN analyzer by J-Science Lab. All melting points were determined on a Yanaco micro-melting point apparatus or a Mettler Toledo MP90 melting point system, and are uncorrected.

MATERIALS.

All materials were purchased from common commercial chemical suppliers and used without further purification unless stated otherwise. All reactions were carried out under an inert atmosphere of argon or nitrogen. 4-*tert*-Butyl-2-(5,5-dimethyl-1,3-dioxan-2-yl)benzenethiol (**2**) was prepared according to the reported procedure.⁴

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(4-CHLOROPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE **3a**.

Benzenethiol **2** (1.445 g, 5.15 mmol), 1-chloro-4-iodobenzene (1.490 g, 6.25 mmol), and copper(I) oxide (1.570 g, 11.0 mmol) were dissolved in 2,4,6-trimethylpyridine (15 mL). After being stirred at 150 °C for 24 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/2, v/v) afforded 2-[(5-*tert*-butyl)-2-(4-chlorophenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3a** (1.947 g, 4.98 mmol, 97%) as pale yellow oil. **3a**: ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 2.4 Hz, 1H, ArH), 7.32 (dd, *J* = 2.4, 8.0 Hz, 1H, ArH), 7.26 (d, *J* = 8.0 Hz, 1H, ArH), 7.21 (d, *J* = 8.8 Hz, 2H, ArH), 7.14 (d, *J* = 8.8 Hz, 2H, ArH), 5.82 (s, 1H, CH), 3.72 (d, *J* = 10.4 Hz, 2H, CH₂), 3.62 (d, *J* = 10.4 Hz, 2H, CH₂), 1.33 (s, 9H, CH₃), 1.32 (s, 3H, CH₃), 0.77 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 152.0 (C), 139.4 (C), 136.1 (C), 133.7 (CH), 132.1 (C), 130.7 (CH), 129.1 (CH), 129.0 (C), 127.1 (CH), 123.8 (CH), 99.8 (CH), 77.8 (CH₂), 34.8 (C), 31.2 (CH₃), 30.2 (C), 23.2 (CH₃), 21.8 (CH₃); MS (EI, positive mode): *m/z* 390 ([M]⁺); Anal. Calcd for C₂₂H₂₇ClO₂S: C, 67.59; H, 6.96%; found: C, 67.64; H, 6.86%.

REACTION OF **3a** WITH TfOH.

Trifluoromethanesulfonic acid (0.278 g, 1.85 mmol) was added to a solution of compound **3a** (0.325 g, 0.831 mmol) in CH₂Cl₂ (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-chlorothioxanthylum trifluoromethanesulfonate **1a** (0.261 g, 0.598 mmol, 72%) as red waxy solids. ¹H NMR (400 MHz, CD₃CN) δ 10.15 (s, 1H, ArH), 8.88 (d, *J* = 2.0 Hz, 1H, ArH), 8.81 (d, *J* = 2.0 Hz, 1H, ArH), 8.76 (d, *J* = 9.2 Hz, 1H, ArH), 8.75 (d, *J* = 9.2 Hz, 1H, ArH), 8.62 (dd, *J* = 2.0, 9.2 Hz, 1H, ArH), 8.34 (dd, *J* = 2.0, 9.2 Hz, 1H, ArH), 1.52 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 160.3 (CH), 156.7 (C), 148.7 (C), 147.7 (C), 140.0 (CH), 139.1 (CH), 137.8 (C), 135.7 (CH), 133.2 (CH), 132.2 (C), 131.9 (C), 130.2 (CH), 128.5 (CH), 121.4 (q, *J*_{CF} = 320 Hz, CF₃), 36.6 (C), 30.8 (CH₃); ¹⁹F NMR (376 MHz, CD₃CN) δ -79.4 (s); MS (ESI-TOF, positive mode): *m/z* 287 ([M-OTf]⁺); HRMS (ESI-TOF, positive mode): *m/z* found 287.0655 ([M-TfO]⁺), calcd for C₁₇H₁₆³⁵ClS: 287.0661.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(4-METHYLPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE **3b**.

Benzenethiol **2** (1.517 g, 5.41 mmol), 1-iodo-4-methylbenzene (0.840 g, 4.91 mmol), and copper(I) oxide (1.164 g, 8.13 mmol) were dissolved in 2,4,6-trimethylpyridine (30 mL). After being stirred at 160 °C for

22 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(4-methylphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3b** (1.288 g, 3.48 mmol, 64%) as colorless oil. **3b**: ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 2.4 Hz, 1H, ArH), 7.25 (dd, *J* = 2.4, 8.4 Hz, 1H, ArH), 7.20 (d, *J* = 8.0 Hz, 2H, ArH), 7.15 (d, *J* = 8.4 Hz, 1H, ArH), 7.08 (d, *J* = 8.0 Hz, 2H, ArH), 5.84 (s, 1H, CH), 3.74 (d, *J* = 11.2 Hz, 2H, CH₂), 3.66 (d, *J* = 11.2 Hz, 2H, CH₂), 2.31 (s, 3H, CH₃), 1.32 (s, 3H, CH₃), 1.32 (s, 9H, CH₃), 0.78 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.7 (C), 138.2 (C), 136.7 (C), 132.9 (C), 132.2 (CH), 131.00 (CH), 130.96 (C), 129.8 (CH), 126.8 (CH), 123.3 (CH), 99.8 (CH), 77.7 (CH₂), 34.7 (C), 31.2 (CH₃), 30.2 (C), 23.2 (CH₃), 21.8 (CH₃), 21.0 (CH₃); MS (EI, positive mode): *m/z* 370 ([M]⁺); Anal. Calcd for C₂₃H₃₀O₂S: C, 74.55; H, 8.16%; found: C, 74.21; H, 7.99%.

REACTION OF **3b** WITH TfOH.

Trifluoromethanesulfonic acid (0.157 g, 1.05 mmol) was added to a solution of compound **3b** (0.185 g, 0.500 mmol) in CH₂Cl₂ (8 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-methylthioxanthylum trifluoromethanesulfonate **1b** (0.171 g, 0.410 mmol, 82%) as red solids. **1b**: mp 162–164 °C; ¹H NMR (400 MHz, CD₃CN) δ 10.08 (s, 1H, ArH), 8.77 (d, *J* = 2.0 Hz, 1H, ArH), 8.70 (d, *J* = 9.0 Hz, 1H, ArH), 8.66 (d, *J* = 8.8 Hz, 1H, ArH), 8.62–8.61 (m, 1H, ArH), 8.55 (dd, *J* = 2.0, 9.0 Hz, 1H, ArH), 8.27 (dd, *J* = 2.0, 8.8 Hz, 1H, ArH), 2.75 (s, 3H, CH₃), 1.52 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 160.4 (CH), 155.9 (C), 147.6 (C), 147.4 (C), 143.6 (C), 141.7 (CH), 138.9 (CH), 136.3 (CH), 132.9 (CH), 131.61 (C), 131.59 (C), 128.2 (CH), 128.1 (CH), 122.1 (quart, *J*_{CF} = 322 Hz, CF₃), 36.5 (C), 30.9 (CH₃), 21.7 (CH₃); ¹⁹F NMR (376 MHz, CD₃CN) δ –79.5 (s); MS (ESI-TOF, positive mode): *m/z* 267 ([M–OTf]⁺); Anal. Calcd for C₁₉H₁₉F₃O₃S₂: C, 54.80; H, 4.60%; found: C, 54.59; H, 4.53%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(4-METHOXYPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE **3c**.

Benzenethiol **2** (1.301 g, 4.64 mmol), 1-bromo-4-methoxybenzene (0.955 g, 5.58 mmol), and copper(I) oxide (1.294 g, 9.04 mmol) were dissolved in 2,4,6-trimethylpyridine (20 mL). After being stirred at 150 °C for 24 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane CH₂Cl₂ = 3/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(4-methoxyphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3c** (1.006 g, 2.60 mmol, 58%) as colorless crystals. **3c**: mp 138.0–138.7 °C; ¹H

NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 2.4 Hz, 1H, ArH), 7.32 (d, J = 8.8 Hz, 2H, ArH), 7.22 (dd, J = 2.4, 8.0 Hz, 1H, ArH), 7.01 (d, J = 8.0 Hz, 1H, ArH), 6.85 (d, J = 8.8 Hz, 2H, ArH), 5.83 (s, 1H, CH), 3.79 (s, 3H, OCH₃), 3.76 (d, J = 10.8 Hz, 2H, CH₂), 3.68 (d, J = 10.8 Hz, 2H, CH₂), 1.33 (s, 3H, CH₃), 1.30 (s, 9H, CH₃), 0.80 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.3 (C), 149.9 (C), 136.9 (C), 134.1 (C), 132.6 (C), 130.5 (CH), 126.7 (CH), 126.0 (C), 123.1 (CH), 114.8 (CH), 99.6 (CH), 77.7 (CH₂), 55.3 (CH₃), 34.6 (C), 31.2 (CH₃), 30.3 (C), 23.2 (CH₃), 21.9 (CH₃); MS (EI, positive mode): m/z 386 ([M]⁺); Anal. Calcd for C₂₃H₃₀O₃S: C, 71.47; H, 7.82%; found: C, 71.55; H, 7.98%.

REACTION OF 3c WITH TfOH.

Trifluoromethanesulfonic acid (0.157 g, 1.05 mmol) was added to a solution of compound **3c** (0.193 g, 0.500 mmol) in CH₂Cl₂ (10 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (40 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-methoxythioxanthylum trifluoromethanesulfonate **1c** (0.184 g, 0.425 mmol, 85%) as red waxy solids. **1c**: ¹H NMR (400 MHz, CD₃CN) δ 9.98 (s, 1H, ArH), 8.69 (d, J = 2.0 Hz, 1H, ArH), 8.66 (d, J = 9.0 Hz, 1H, ArH), 8.64 (d, J = 9.2 Hz, 1H, ArH), 8.49 (dd, J = 2.0, 9.0 Hz, 1H, ArH), 8.11 (d, J = 2.7 Hz, 1H, ArH), 8.02 (dd, J = 2.7, 9.2 Hz, 1H, ArH), 4.10 (s, 3H, OCH₃), 1.51 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 162.1 (C), 158.2 (CH), 155.9 (C), 146.7 (C), 144.2 (C), 138.1 (CH), 133.7 (C), 132.5 (CH), 132.1 (CH), 131.7 (C), 129.7 (CH), 128.1 (CH), 121.5 (quart, ¹ J_{CF} = 319 Hz, CF₃), 114.0 (CH), 57.5 (CH), 36.5 (C), 30.8 (CH); ¹⁹F NMR (376 MHz, CD₃CN) δ -79.4 (s); MS (ESI-TOF, positive mode): m/z 283 ([M-OTf]⁺); Anal. Calcd for C₁₉H₁₉F₃O₄S₂: C, 52.77; H, 4.43%; found: C, 52.99; H, 4.67%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(3,5-DIMETHOXYPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3d.

Benzenethiol **2** (0.648 g, 2.31 mmol), 1-bromo-3,5-dimethoxybenzene (0.609 g, 2.81 mmol), and copper(I) oxide (0.678 g, 4.74 mmol) were dissolved in 2,4,6-trimethylpyridine (10 mL). After being stirred at 150 °C for 48 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(3,5-dimethoxyphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3d** (0.526 g, 1.26 mmol, 55%) as colorless oil. **3d**: ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 2.0 Hz, 1H, ArH), 7.32-7.27 (m, 2H, ArH), 6.41 (d, J = 2.0 Hz, 2H, ArH), 6.28 (t, J = 2.4 Hz, 1H, ArH), 5.81 (s, 1H, ArH), 3.74 (d, J = 11.2 Hz, 2H, CH₂), 3.71 (s, 6H, OCH₃), 1.33 (s, 9H, CH₃), 1.32 (s, 3H, CH₃), 0.78 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.0 (C × 2), 151.5 (C), 139.1 (C), 133.4 (CH), 129.2 (C), 126.9 (CH), 123.6 (CH), 107.6 (CH), 99.8 (CH), 99.0

(CH), 77.8 (CH₂), 55.4 (OCH₃), 34.8 (C), 31.2 (CH₃), 30.3 (C), 23.3 (CH₃), 21.9 (CH₃); MS (EI, positive mode): *m/z* 416 ([M]⁺); Anal. Calcd for C₂₄H₃₂O₄S: C, 69.20; H, 7.74%; found: C, 68.98; H, 7.50%.

REACTION OF 3d WITH TfOH.

Trifluoromethanesulfonic acid (0.106 g, 0.706 mmol) was added to a solution of compound **3d** (0.116 g, 0.278 mmol) in CH₂Cl₂ (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-methoxythioxanthylum trifluoromethanesulfonate **1d** (0.116 g, 0.250 mmol, 89%) as red solids. **1d**: mp 246 °C (decomp.); ¹H NMR (400 MHz, CD₃CN) δ 9.92 (s, 1H, ArH), 8.60 (d, *J* = 2.0 Hz, 1H, ArH), 8.33 (d, *J* = 8.8 Hz, 1H, ArH), 8.33 (dd, *J* = 8.8, 2.0 Hz, 1H, ArH), 7.65 (d, *J* = 2.0 Hz, 1H, ArH), 6.94 (d, *J* = 2.0 Hz, 1H, ArH), 4.21 (s, 3H, OCH₃), 4.19 (s, 3H, OCH₃), 1.47 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 173.0 (C), 165.4 (C), 154.6 (C), 152.8 (CH), 152.7 (C), 141.9 (C), 136.9 (CH), 133.8 (CH), 129.1 (C), 127.2 (CH), 122.2 (q, *J* = 321 Hz, CF₃), 121.0 (C), 103.4 (CH), 101.7 (CH), 59.2 (OCH₃), 58.9 (OCH₃), 36.2 (C), 31.1 (CH₃); ¹⁹F NMR (376 MHz, CD₃CN) δ -79.3 (s); MS (ESI-TOF, positive mode): *m/z* 313 ([M-OTf]⁺); Anal. Calcd for C₂₀H₂₁F₃O₅S₂: C, 51.94; H, 4.58%; found: C, 51.99; H, 4.66%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(NAPHTH-2-YLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3e.

Benzenethiol **2** (3.001 g, 10.7 mmol), 2-bromonaphthalene (2.668 g, 12.8 mmol), and copper(I) oxide (3.070 g, 21.4 mmol) were dissolved in 2,4,6-trimethylpyridine (20 mL). After being stirred at 145 °C for 24 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ = 4/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(naphth-2-ylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3e** (1.154 g, 2.84 mmol, 27%) as pale yellow crystals. **3e**: mp 96.8–98.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 2.4 Hz, 1H, ArH), 7.77–7.73 (m, 2H, ArH), 7.46–7.38 (m, 2H, ArH), 7.33–7.27 (m, 1H, ArH), 7.28 (d, *J* = 2.0 Hz, 1H, ArH), 7.24 (d, *J* = 5.6 Hz, 1H, ArH), 5.89 (s, 1H, CH), 3.73 (dd, *J* = 10.8 Hz, 2H, CH₂), 3.64 (dd, *J* = 10.8 Hz, 2H, CH₂), 1.34 (s, 9H, CH₃), 1.32 (s, 3H, CH₃), 0.76 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 151.4 (C), 138.9 (C), 134.4 (C), 133.7 (C), 133.2 (CH), 132.0 (C), 129.8 (C), 128.6 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 126.4 (CH), 125.8 (CH), 123.5 (CH), 99.8 (CH), 77.7 (CH₂), 34.8 (C), 31.2 (CH₃), 30.2 (C), 23.2 (CH₃), 21.8 (CH₃); MS (EI, positive mode): *m/z* 406 ([M]⁺); Anal. Calcd for C₂₆H₃₀O₂S: C, 76.81; H, 7.44%; found: C, 76.95. H, 7.58%.

REACTION OF 3e WITH TfOH.

Trifluoromethanesulfonic acid (0.090 g, 0.60 mmol) was added to a solution of compound **3e** (0.142 g, 0.350 mmol) in CH₂Cl₂ (5 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 10-*tert*-butylbenzo[a]thioxanthen-7-ium trifluoromethanesulfonate **3e** (0.146 g, 0.332 mmol, 92%) as red powder. **3e**: mp 253.1–254.5 °C; ¹H NMR (400 MHz, CD₃CN) δ 10.87 (s, 1H, ArH), 9.21 (d, *J* = 8.4 Hz, 1H, ArH), 8.97 (d, *J* = 2.0 Hz, 1H, ArH), 8.74 (d, *J* = 8.4 Hz, 1H, ArH), 8.71 (d, *J* = 8.0 Hz, 1H, ArH), 8.57 (dd, *J* = 2.4, 9.2 Hz, 1H, ArH), 8.53 (d, *J* = 6.9 Hz, 1H, ArH), 8.35 (d, *J* = 1.3 Hz, 1H, ArH), 8.33 (d, *J* = 1.3 Hz, 1H, ArH), 8.17 (dd, *J* = 7.2, 1.4 Hz, 1H, ArH), 8.05 (dd, *J* = 7.2, 1.4 Hz, 1H, ArH), 1.56 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 181.5 (C), 156.8 (C), 155.2 (C), 152.6 (CH), 143.6 (C), 142.4 (CH), 137.5 (CH), 133.1 (C), 132.8 (C), 132.5 (CH), 132.0 (CH), 131.79 (CH), 131.77 (CH), 130.1 (C), 127.9 (CH), 125.0 (CH), 124.8 (CH), 122.0 (quart, *J*_{CF} = 318 Hz, CF₃SO₃⁻), 36.7 (C), 31.1 (CH); ¹⁹F NMR (376 MHz, CD₃CN) δ -76.4 (s, CF₃SO₃⁻); MS (ESI-TOF, positive mode): *m/z* 303 ([M-OTf]⁺); Anal. Calcd for C₂₂H₁₉F₃O₃S₂: C, 58.40; H, 4.23%; found: C, 58.20. H, 4.15%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(NAPHTH-1-YLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE **3f**.

Benzenethiol **2** (1.678 g, 5.98 mmol), 1-bromonaphthalene (1.489 g, 7.19 mmol), and copper(I) oxide (1.717 g, 12.0 mmol) were dissolved in 2,4,6-trimethylpyridine (12 mL). After being stirred at 150 °C for 48 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(naphth-1-ylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3f** (1.321 g, 3.24 mmol, 54%) as colorless crystals. **3f**: mp 159–161 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.37–8.35 (m, 1H, ArH), 7.86–7.84 (m, 1H, ArH), 7.80 (d, *J* = 2.4 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.53–7.49 (m, 2H, ArH), 7.43 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.36 (dd, *J* = 8.0, 8.0 Hz, 1H, ArH), 7.17 (dd, *J* = 8.4, 2.4 Hz, 1H, ArH), 6.95 (d, *J* = 8.4 Hz, 1H, ArH), 5.91 (s, 1H, CH), 3.75 (d, *J* = 10.8 Hz, 2H, CH₂), 3.65 (d, *J* = 10.8 Hz, 2H, CH₂), 1.34 (s, 3H, CH₃), 1.30 (s, 9H, CH₃), 0.76 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.5 (C), 137.7 (C), 134.0 (C), 132.94 (C), 132.85 (C), 131.4 (CH), 130.7 (CH), 130.6 (C), 128.5 (CH), 128.0 (CH), 126.9 (CH), 126.6 (CH), 126.3 (CH), 125.8 (CH), 125.3 (CH), 123.4 (CH), 99.7 (CH), 77.8 (CH₂), 34.7 (C), 31.2 (CH₃), 30.3 (C), 23.3 (CH₃), 21.8 (CH₃); MS (EI, positive mode): *m/z* 406 ([M]⁺); Anal. Calcd for C₂₆H₃₀O₂S: C, 76.81; H, 7.44%; found: C, 76.48; H, 7.59%.

REACTION OF **3f** WITH TfOH.

Trifluoromethanesulfonic acid (0.090 g, 0.60 mmol) was added to a solution of compound **3f** (0.126 g, 0.310 mmol) in CH₂Cl₂ (6 mL) at room temperature. After the solution was stirred at room temperature for

2 h, the reaction mixture was added dropwise to cold Et₂O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 9-*tert*-butylbenzo[*c*]thioxanthen-12-ium trifluoromethanesulfonate **1f** (0.112 g, 0.248 mmol, 83%) as red powder. **1f**: mp 170 °C (decomp.); ¹H NMR (400 MHz, CD₃CN) δ 10.02 (s, 1H, ArH), 8.98 (d, *J* = 8.4 Hz, 1H, ArH), 8.76 (d, *J* = 2.0 Hz, 1H, ArH), 8.74 (d, *J* = 8.8 Hz, 1H, ArH), 8.56 (dd, *J* = 2.0, 8.8 Hz, 1H, ArH), 8.36 (d, *J* = 8.8 Hz, 1H, ArH), 8.30 (d, *J* = 8.8 Hz, 1H, ArH), 8.20 (d, *J* = 8.0 Hz, 1H, ArH), 8.08–8.12 (m, 1H, ArH), 7.98 (dd, *J* = 8.0, 7.2 Hz, 1H, ArH), 1.55 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 158.8 (CH), 156.9 (C), 154.6 (C), 143.5 (C), 138.1 (CH), 136.3 (CH), 135.7 (C), 133.0 (CH), 132.1 (CH), 131.6 (C), 131.3 (C), 131.1 (CH), 130.9 (CH), 130.4 (CH), 128.8 (C), 128.4 (CH), 126.1 (CH), 122.1 (q, *J* = 321 Hz, CF₃), 36.6 (C), 30.9 (CH₃); ¹⁹F NMR (376 MHz, CD₃CN) δ –79.3 (s); MS (ESI-TOF, positive mode): *m/z* 303 ([M–OTf]⁺); Anal. Calcd for C₂₂H₁₉F₃O₃S₂: C, 58.40; H, 4.23%; found: C, 58.61; H, 4.50%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(PYREN-1-YLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE **3g**.

Benzenethiol **2** (2.987 g, 10.6 mmol), 1-bromopyrene (4.124 g, 12.8 mmol), and copper(I) oxide (3.033 g, 21.2 mmol) were dissolved in 2,4,6-trimethylpyridine (20 mL). After being stirred at 150 °C for 48 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(pyren-1-ylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3g** (2.987 g, 6.21 mmol, 59%) as pale yellow crystals. **3g**: mp 180–181 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.65 (d, *J* = 9.2 Hz, 1H, ArH), 8.19–8.17 (m, 2H, ArH), 8.11 (d, *J* = 9.2 Hz, 1H, ArH), 8.07–7.95 (m, 5H, ArH), 7.83 (d, *J* = 2.4 Hz, 1H, ArH), 7.12 (dd, *J* = 2.4, 8.4 Hz, 1H, ArH), 6.89 (d, *J* = 8.4 Hz, 1H, ArH), 3.78 (d, *J* = 11.5 Hz, CH₂), 3.68 (d, *J* = 10.4 Hz, CH₂), 1.35 (s, 3H, CH₃), 1.29 (s, 9H, CH₃), 0.76 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.2 (C), 137.4 (C), 131.7 (C), 131.4 (C), 131.3 (C), 131.2 (C), 131.1 (CH), 131.0 (C), 130.9 (C), 130.0 (C), 128.2 (CH), 127.7 (CH), 127.3 (CH), 126.9 (CH), 126.2 (CH), 125.4 (CH × 2), 125.3 (C), 125.2 (CH), 124.7 (CH), 124.5 (CH), 123.4 (CH), 99.8 (CH), 77.8 (CH₂), 34.7 (C), 31.2 (CH₃), 30.3 (C), 23.3 (CH₃), 21.8 (CH₃); MS (EI, positive mode): *m/z* 480 ([M]⁺); Anal. Calcd for C₃₂H₃₂O₂S: C, 79.96; H, 6.71%; found: C, 79.78; H, 6.88%.

REACTION OF **3g** WITH TfOH.

Trifluoromethanesulfonic acid (0.106 g, 0.706 mmol) was added to a solution of compound **3e** (0.148 g, 0.307 mmol) in CH₂Cl₂ (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (50 mL). Purification of the resulting suspension using a centrifugal separator afforded 9-*tert*-butylphenaleno[1,9-*bc*]thioxanthen-12-ium

trifluoromethanesulfonate **1g** (0.107 g, 0.203 mmol, 64%) as dark green powder. **1g**: mp 256 °C (decomp.); ¹H NMR (400 MHz, CD₃CN) δ 9.56 (s, 1H, ArH), 8.52–8.49 (m, 2H, ArH), 8.44–8.41 (m, 2H, ArH), 8.34 (d, *J* = 8.8 Hz, 1H, ArH), 8.22 (d, *J* = 8.8 Hz, 1H, ArH), 7.97 (d, *J* = 7.6 Hz, 1H, ArH), 7.88–7.82 (m, 2H, ArH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.69 (dd, *J* = 7.6, 7.6 Hz, 1H, ArH), 1.62 (s, 9H, CH₃); ¹⁹F NMR (376 MHz, CD₃CN) δ -79.3 (s); MS (ESI-TOF, positive mode): *m/z* 377 ([M-OTf]⁺); Anal. Calcd for C₂₈H₂₁F₃O₃S₂: C, 63.87; H, 4.02%; found: C, 63.51; H, 3.90%. Satisfactory ¹³C NMR data of **1g** could not be obtained due to its low solubility in common organic solvents such as CD₃CN, DMSO-*d*₆, DMF-*d*₇, and CD₂Cl₂.

COMPUTATIONAL DETAILS.

All density functional theory (DFT) calculations were performed utilizing the Gaussian 16 package.⁶ The Becke's three-parameter hybrid functional with Lee-Yang-Parr correlation functional (B3LYP)⁷ which was recently reported to demonstrate broader accuracy, were employed with a standard split valence-type basis sets. The geometries of **1a'**–**1e'**, where the counter anions were omitted, were optimized by the 6-31G(d) basis sets. Molecular orbitals and TD-DFT calculations were carried out at the 6-31G(d) levels using the B3LYP density functional models. The bulk solvent effects of dichloromethane might be adequately evaluated by using polarizable continuum model (PCM),⁸ denoted as "PCM(CH₂Cl₂)-".

ACKNOWLEDGEMENTS

This work was partially supported by the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (grants 2018-111 and 2019-119) and a Grant-in-Aid for Scientific Research (C) (JP19K05428) from the Japan Society for the Promotion of Science. The computational work was carried out using computational resources of the Research Institute for Information Technology (Kyushu University).

REFERENCES

1. (a) 'Six-Membered Heteroarenes with One Chalcogen,' ed. by W.-D. Rudolf, Science of Synthesis, Vol. 14, pp. 649–770, Thieme, 2006; (b) A. T. Balaban, 'Aromaticity of Six-Membered Rings with One Heteroatom,' Aromaticity in Heterocyclic Compounds (*Top. Heterocycl. Chem.*), 2009, 19, pp. 204–246.
2. (a) A. Scarpaci, A. Nantalaksakul, J. M. Hales, J. D. Matichak, S. Barlow, M. Rumi, J. W. Perry, and S. R. Marder, *Chem. Mater.*, 2012, **24**, 1606; (b) T. Maeda, S. Nitta, H. Nakao, S. Yagi, and H. Nakazumi, *J. Phys. Chem. C*, 2014, **118**, 16618; (c) S. Barlow, J.-L. Brédas, Y. A. Getmanenko, R. L. Giesecking, J. M. Hales, H. Kim, S. R. Marder, J. W. Perry, C. Risko, and Y. Zhang, *Mater. Horiz.*,

- 2014, **1**, 577; (d) R. L. Giesecking, S. Mukhopadhyay, C. Risko, S. R. Marder, and J.-L. Brédas, *Chem. Mater.*, 2014, **26**, 6439; (e) H. Kearns, S. Sengupta, I. R. Sasselli, L. Bromley III, K. Faulds, T. Tuttle, M. A. Bedics, M. R. Detty, L. Velarde, D. Graham, and W. E. Smith, *Chem. Sci.*, 2016, **7**, 5160; (f) B. Ding, Y. Xiao, H. Zhou, X. Zhang, C. Qu, F. Xu, Z. Deng, Z. Cheng, and X. Hong, *J. Med. Chem.*, 2019, **62**, 2049.
3. K. Tanaka, Y. Tanaka, M. Kishimoto, Y. Hoshino, and K. Honda, *Beilstein J. Org. Chem.*, 2019, **15**, 2105.
 4. N. Nagahora, R. Tanaka, T. Tada, A. Yasuda, Y. Yamada, K. Shioji, and K. Okuma, *Org. Lett.*, 2020, **22**, 6192.
 5. H.-O. Kalinowski, S. Berger, and S. Braun, *Carbon 13 NMR Spectroscopy*, John Wiley and Sons, 1988, pp 409–415.
 6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16*, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.
 7. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
 8. J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.