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Electrophilic Aromatic Formylation with Difluoro(phenylsulfanyl)-methane

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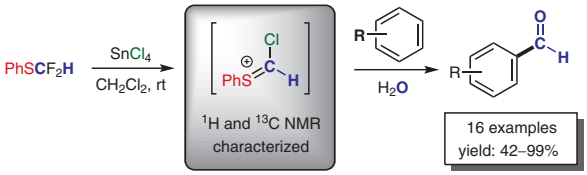

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Abstract Difluoro(phenylsulfanyl)methane ($PhSCF_2H$) was found to undergo a reaction with aromatic compounds mediated by $SnCl_4$, through a thionium intermediate characterized by NMR and TD-DFT analyses, leading to the formation of a mixture of *S*,*S*′-diphenyl dithioacetal and aromatic aldehyde which, after oxidative hydrolysis, provides the aromatic aldehyde in good to excellent yields. The salient feature of the present work is the reaction of activated aromatic compounds containing a deactivating ester functional group, leading to the formylated products in good yields.

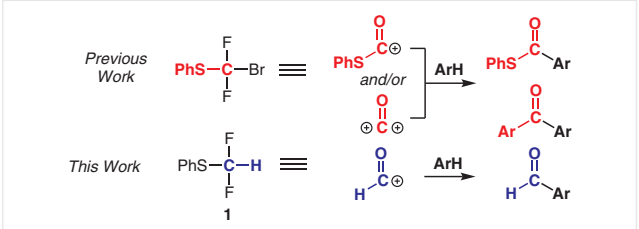
Key words electrophilic formylation, thionium cation, aldehydes, electrophilic addition, carbocations

Research directed at understanding the influence of fluorine atoms on reactive intermediates, including radicals, cations and anions, has long been of interest.[2] In particular, fluorine was demonstrated to exhibit a stabilizing effect, through 2p nonbonded electron-pair back-bonding, to the carbocationic center to which the fluorine atoms are attached.[3] Some α-fluoro carbocations are sufficiently stabilized to allow characterization by means of single-crystal X-ray diffraction.[4] Despite the unique properties, research on α-fluoro carbocations and their synthetic applications in organic synthesis have only been sporadically reported.[5]

The formylation reaction of aromatic compounds is a fundamental reaction in organic chemistry and several methods have been developed for this important synthetic transformation.[6] Generally, introduction of a formyl group onto an aromatic ring is achieved by electrophilic aromatic substitution using various formyl precursors which differ by their reactivity and steric bulkiness; for example, formyl fluoride/BF_3,[7] CO/HCl (Gattermann–Koch formylation),[8] HCN/HCl or $Zn(CN)_2$/HCl (Gattermann reaction),[9] $CHCl_3$/NaOH (Reimer–Tiemann reaction),[10] DMF/$POCl_3$ (Vilsmeier reagent),[11] dichloromethyl methyl ether/Lewis acid (Rieche formylation),[12] hexamethylenetetramine/HOAc or TFA,[13] triformamide/$AlCl_3$,[14] tris(diformylamino)methane/$AlCl_3$,[15] tris(dichloromethyl)amine and oligoformylamine derivatives/super acids.[16] Of these methods, only Rieche formylation works well for both activated aromatic and deactivated compounds.[17]

In continuation of our interest in developing methodologies for the installation of the *gem*-difluoromethylene motif into structurally different organic molecules by using radical, carbanion and cross-coupling methodologies[18] and the synthetic exploitation of the α-fluoro carbocation species generated from the reaction between Lewis acids and *gem*-difluoro compounds,[19] we report herein a novel use of difluoro(phenylsulfanyl)methane (**1**) as an electrophilic formylating agent for activated aromatic compounds, including examples with a deactivating functional group.

Recently, we reported the reactivity of bromodifluoro-(phenylsulfanyl)methane as the synthetic equivalent of the sufanylcarbonyl cation and geminal carbonyl dication, through Lewis acid activation, leading to the Friedel–Crafts alkylation of activated aromatic compounds which, after hydrolysis, yielded thioesters and/or benzophenones.[19a] Inspired by these results, we envisaged difluoro(phenylsulfanyl)methane (**1**) as a synthetic equivalent of a formyl cation (Scheme 1).



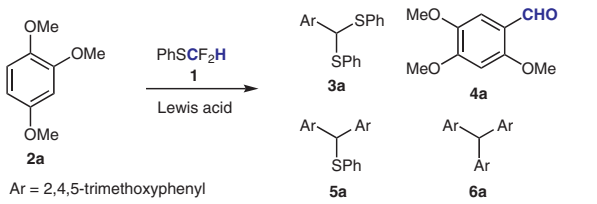
Scheme 1 Synthetic methodology

In an initial attempt and on the basis of our previously reported work,[20] difluoro(phenylsulfanyl)methane ($PhSCF_2H$, **1**)[21] was allowed to react with 1,2,4-trimethoxybenzene (**2a**, 1 equiv) mediated by stannic chloride ($SnCl_4$, 2 equiv based on **1**) in dichloromethane at room temperature for 2 hours under an argon atmosphere. To our delight, three products, *S*,*S*′-diphenyl dithioacetal **3a** (40% yield), aromatic aldehyde **4a** (36% yield) and sulfide **5a** (6% yield), were isolated (Table 1, entry 1). Other Lewis acids, including $AlCl_3$, $TiCl_4$, Ti(O*i*-Pr)$_4$ and TMSOTf, were examined; however, only $SnCl_4$ exhibited superior results (Table 1, entries 2–5). No improvement was observed when $SnCl_4$ was employed in excess amount (5 equiv; Table 1, entry 6) and the reaction failed to proceed at 0 °C (Table 1, entry 7). When the reaction was exposed to oxidative quench employing IBX (1.5 equiv) in DMSO/H_2O (3:1 v/v) at room temperature for 2 hours, before conventional aqueous workup, the aromatic aldehyde **4a** was exclusively isolated in 75% yield after chromatographic purification (Table 1, entry 8).[22]

Analysis of the product mixture (Table 1, entries 1–3, 6) suggested **1** might be a limiting reagent, requiring 2 equivalents for the formation of dithioacetal **3a**. Satisfyingly, when the amount of **1** was increased from 1 to 1.5 equivalents, the desired aldehyde **4a** was isolated in 98% yield after oxidative aqueous workup (Table 1, entry 9). Finally, it is worth mentioning that the use of a catalytic amount (20 mol%) of mild Lewis acids, including Sc(OTf)$_3$, Yb(OTf)$_3$, In(OTf)$_3$ and Bi(OTf)$_3$, proved to be insufficient to promote the reaction in dichloromethane; 1,2,4-trimethoxybenzene was recovered and the difluoro(phenylsulfanyl)methane was consumed, giving diphenyl disulfide and thiophenol as byproducts.

After the optimum reaction conditions were identified (Table 1, entry 9), the synthetic utility of the formylation reaction of benzene and naphthalene derivatives, as well as indole, was evaluated. From the results shown in Table 2, the reactions of benzene derivatives in general gave moderate to excellent yields of the corresponding aldehydes **4**. Activated 1,2,4-trimethoxybenzene and 1,3,5-trimethoxybenzene led to high yields of products **4** (Table 2, entries 1 and 2); however, the reactions of less activated aromatic compounds, namely 1,2,3-trimethoxybenzene and 1,3-dimethoxybenzene, resulted in good yields (Table 2, entries 3 and 4). Low yields were observed when anisole and *N*,*N*-diethylaniline were employed as the substrates (Table 2, entries 5 and 6).

Table 1 Optimization of the Reaction Conditions[a]



Ar = 2,4,5-trimethoxyphenyl

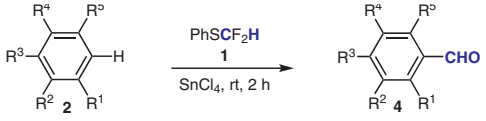
Entry	Lewis acid[b] (equiv)	Yield (%)[c]			
		3a	**4a**	**5a**	**6a**
1	$SnCl_4$ (2)	40	36	6	–
2	$AlCl_3$ (2)	6	7	23	–
3	$TiCl_4$ (2)	25	20	24	3
4	Ti(O*i*-Pr)$_4$ (2)	–	–	–	–
5	TMSOTf (2)	–	–	–	–
6	$SnCl_4$ (5)	42	37	6	–
7[d]	$SnCl_4$ (2)	–	–	–	–
8[e]	$SnCl_4$ (2)	–	75	–	–
9[f]	$SnCl_4$ (2)	–	98	–	–

[a] Reaction conditions: **1** (1 equiv), **2a** (0.5 mmol, 1 equiv), Lewis acid, CH_2Cl_2 (1 mL), stirred, rt, 2 h.
[b] For reactions using $AlCl_3$: **2a** was added to a premixed solution of **1** and $AlCl_3$ at rt; for reactions using $SnCl_4$, $TiCl_4$, Ti(O*i*-Pr)$_4$ or TMSOTf: **1** was added to a solution of the Lewis acid in CH_2Cl_2, followed by **2a**, at rt.
[c] Isolated yields after silica gel column chromatographic purification.
[d] Reaction was carried out at 0 °C.
[e] Reaction was quenched by treatment with a solution of IBX (1.5 equiv) in DMSO/H_2O (3:1 v/v) and the resulting mixture was stirred at rt for 2 h, followed by aqueous workup.
[f] **1** (1.5 equiv) was used, followed by workup identical to that of entry 8.

Under the standard conditions, the reaction of methoxy-substituted naphthalene derivatives also generally worked well (Figure 1). *N*-Methyl-1*H*-indole also gave moderate yields of its corresponding product **4l**. Using 2,3-dimethoxynaphthalene as a starting material resulted in nonselective formylation at both the C1 (**4ma**) and C7 position (**4mb**).

The synthetic utility of our developed method was further demonstrated by employing this protocol for the installation of the formyl group onto activated aromatic compounds containing an electron-withdrawing methyl ester group (Table 3). Under our standard reaction conditions, formylation readily proceeded yielding the corresponding aldehydes **8**, after oxidative quenching, in excellent yields (Table 3, entries 1–3). In comparison, reaction of methyl 3,4,5-trimethoxybenzoate employing the well-known electrophilic formylating reagents dichloro(methoxy)methane[17,23] and the Vilsmeier–Haack reagent (pyrophosphoryl

Table 2 Reaction of Benzene Derivatives Using Difluoro(phenylsulfanyl)methane (**1**) as Formylating Agent[a]



Entry	R^1	R^2	R^3	R^4	R^5	Yield (%) of **4**[b]
1	OMe	H	OMe	OMe	H	**4a**, 98
2	OMe	H	OMe	H	OMe	**4b**, 99
3	OMe	OMe	OMe	H	H	**4c**, 72
4	OMe	H	OMe	H	H	**4d**, 78
5	H	H	OMe	H	H	**4e**, 47
6	H	H	NEt_2	H	H	**4f**, 42

[a] Reaction conditions : A solution of 1 (1.5 equiv) in CH_2Cl_2 (1 mL) was added to a solution of $SnCl_4$ (2 equiv) in CH_2Cl_2 (1 mL) followed by the addition of ArH (1 equiv) iin CH2Cl2 (1 mL) at rt. The reaction was treated with IBX (1.5 equiv) in DMSO/H_2O (3:1 v/v), rt, 2 h, before conventional aqueous workup.
[b] Isolated yields after silica gel column chromatographic purification.

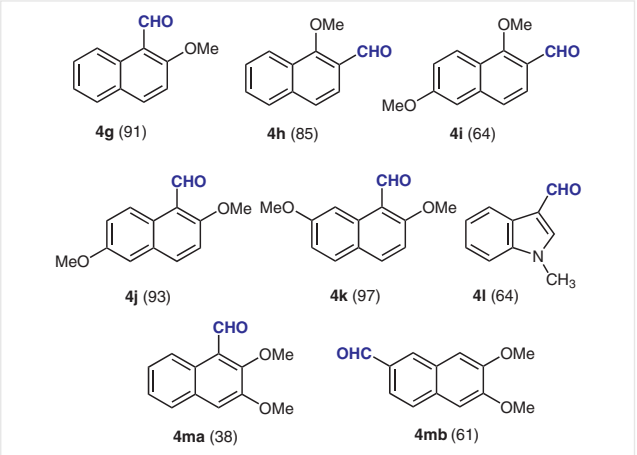
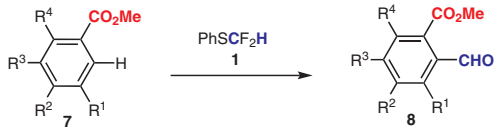


Figure 1 Reaction of naphthalene and indole derivatives using difluoro(phenylsulfanyl)methane (**1**) as formylating agent. *Reagents and conditions*: A solution of **1** (1.5 equiv) in CH_2Cl_2 (1 mL) was added to a solution of $SnCl_4$ (2 equiv) in CH_2Cl_2 (1 mL) followed by the addition of ArH (1 equiv) iin CH_2Cl_2 (1 mL) at rt. The reaction was treated with IBX (1.5 equiv) in DMSO/H_2O (3:1 v/v), rt, 2 h, before conventional aqueous workup. In parentheses: isolated yields after silica gel column chromatographic purification.

chloride/DMF)[24] proved to be less efficient: such reactions required a longer time (16 h) and gave the corresponding aldehyde **8a** in lower yields (Table 3, entries 4 and 5). Unfortunately, under our standard conditions the reaction did not proceed when the number of activating methoxy groups was decreased, for example when employing methyl 4-methoxybenzoate or methyl benzoate as substrate.

On the basis of the experimental results and our prior work, the proposed mechanism for the reaction of difluoro(phenylsulfanyl)methane (**1**) with aromatic compounds,

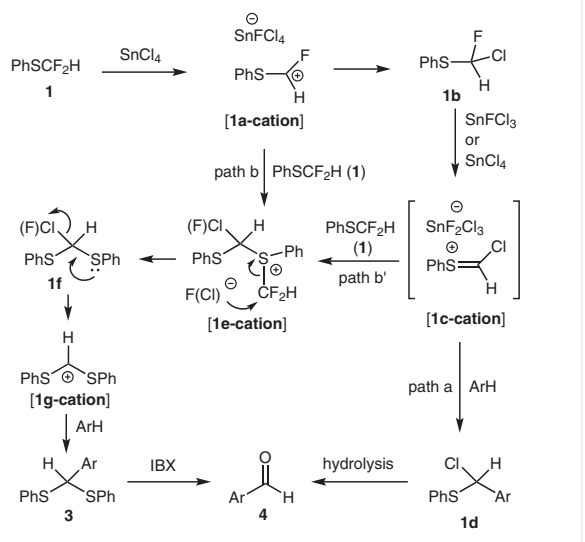
Table 3 Formylation Reaction of Activated Aromatic Compounds Containing a Deactivating Ester Substituent[a]



Entry	R^1	R^2	R^3	R^4	Method	Yield (%) of **8**[b]
1	OMe	OMe	OMe	H	A	**8a**, 95
2	H	OMe	OMe	H	A	**8b**, 85
3	OMe	OMe	OMe	Me	A	**8c**, 88
4	OMe	OMe	OMe	H	B	**8a**, 71
5	OMe	OMe	OMe	H	C	**8a**, 31

[a] Method A: $PhSCF_2H$ (**1**; 1.5 equiv), $SnCl_4$ (2 equiv), CH_2Cl_2, rt, 2 h; then IBX (1.5 equiv) in DMSO/H_2O (3:1 v/v), rt, 2 h, before aqueous workup; Method B: $MeOCHCl_2$ (3 equiv), $TiCl_4$ (0.1 M; 2 equiv), CH_2Cl_2, rt, 16 h; Method C: pyrophosphoryl chloride (1.7 equiv), DMF (1.5 equiv), CH_2Cl_2, rt, 16 h.
[b] Isolated yields after silica gel column chromatographic purification.

leading to the formation of dithioacetals **3** and aldehydes **4**, could be rationalized as shown in Scheme 2. We propose that the mechanism proceeds through a short-lived fluoro(phenylsulfanyl)methylium cation (**1a-cation**) which is immediately trapped by chloride ion from the $SnFCl_4$ anion leading to **1b**.[25] Under excess Lewis acid, **1b** immediately undergoes further fluoride abstraction by either $SnFCl_3$ or $SnCl_4$, resulting in the formation of an α-chloro thionium ion (**1c-cation**) as an active formylating species. Although fluorine is known to stabilize carbocation centers through back-bonding, under the conditions of excess $SnCl_4$ the stronger Sn–F bond (Sn–F 414 vs Sn–Cl 323 kJ/mol) drives the reaction to a single α-chloro thionium ion intermediate.



Scheme 2 Proposed reaction mechanism

Subsequent trapping of **1c-cation** with an aromatic compound yields **1d** which undergoes hydrolysis during aqueous workup, providing the desired aldehyde **4** (path a). The proposed mechanism is analogous to the well-known Vilsmeier–Haack and Rieche formylation reaction mechanisms in which the active formylating species is commonly generated prior to addition of the aromatic compound. The formation of dithioacetals **3** can be rationalized through either path b or path b′. Reagent **1** attacks either the unstable **1a-cation** (path b) or the more stable **1c-cation** (path b′) leading to (difluoromethyl)sulfonium species **1e-cation**. In previous work, we have demonstrated that such a dimerization process is viable, leading to a stable bis(phenylsulfanyl) cation (**1g-cation**).[19b] The resulting **1g-cation** is trapped by the aromatic compound, leading to dithioacetal **3** upon standard aqueous workup; whereas, upon oxidative quench by IBX, dithioacetals **3** undergo oxidative hydrolysis providing the desired aldehydes **4**.[22]

The formation of an α-chloro thionium ion intermediate (**1c-cation**) is analogous to the α-chloro oxonium and iminium ion intermediates proposed in the Rieche and Vilsmeier–Haack reactions, respectively. Based on chemical reactivity and the yields of the products, the proposed **1c-cation** appears to be more reactive as the formylating species. To unequivocally provide mechanistic evidence and insight into the active formylating species, **1c-cation** was generated under anhydrous conditions in the absence of aromatic compound, and was characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. The reaction is remarkably clean, leading to a single species with a characteristic deshielded ^{1}H NMR signal at δ_H 10.18 ppm and ^{13}C NMR signal at δ_C 200.2 ppm. ^{19}F NMR showed a single peak at δ_F –162.19 ppm as a singlet. Splitting was not observed in either the ^{1}H or ^{13}C NMR spectrum, suggesting fluorine is not attached to a carbon or with connectivity to a proton. With limited literature for comparison on ^{19}F NMR shifts of tin(IV) fluoride/chloride complexes, we have tentatively assigned this peak to a $[Sn_nF_{n+1}Cl_{n+2}]^-$ species as the counteranion, which is in the range of similar complexes.[26] To gain further confidence in the structural assignment, DFT calculations [mPW1PW91/6-31+G(d,p) in CH_2Cl_2] were performed on an optimized structure [B3LYP/6-31G(d) in the gas phase] (see the Supporting Information for computational details). Calculated ^{13}C and ^{1}H NMR chemical shifts were in good agreement with experimental values (R^2 = 0.9798 for corrected ^{13}C NMR shifts) (Figure 2).

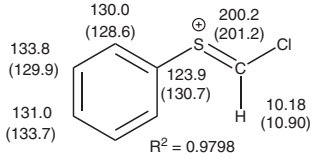


Figure 2 Selected experimental and computational (in parentheses) ^{13}C and ^{1}H NMR chemical shifts for weighted average *E*/*Z* conformers of **1c-cation**

In conclusion, we have described the reactivity of difluoro(phenylsulfanyl)methane (**1**) towards Lewis acids through the formylation reaction of activated aromatic compounds. Our finding is the first report on detailed spectroscopic and theoretical studies for the utilization of difluoro(phenylsulfanyl)methane as a synthetic equivalent to a formyl cation. A room-temperature stable α-chloro thionium ion intermediate has been proposed as the active formylating species and substantiated by means of NMR spectroscopy and TD-DFT NMR calculations for the first time. Our reported procedure offers a quick entry and a viable alternative method to the existing methods available for formylation reactions.

All chemicals were obtained from commercial sources and used without further purification. Anhydrous CH_2Cl_2 was freshly distilled under argon from CaH_2. ^{1}H (500, 400 or 300 MHz) and ^{13}C (125, 100 or 75 MHz) NMR spectra were recorded in $CDCl_3$ solution with either a Bruker Advance-500, Bruker AV-400 or Bruker DPX-300 spectrometer, with TMS or $CHCl_3$ as internal reference; δ values are in parts per million (ppm) and coupling constants (*J*) in hertz (Hz). ^{19}F NMR spectra (376 MHz) were recorded on a Bruker AV-400 spectrometer, with CF_3Cl as internal reference. Mass spectra (HRMS) were recorded using a Bruker micrOTOF spectrometer. All glassware and syringes were oven-dried and kept in a desiccator before use. Radial chromatography on a Chromatotron was performed with Merck silica gel 60 PF_{254} (Art. 7749). Preparative thin-layer chromatography (PTLC) was performed using Merck silica gel 60 PF_{254} (Art. 7747). Analytical TLC was performed with Merck TLC aluminum sheets coated with silica gel 60 PF_{254} (Art. 5554).

Reaction Optimization; General Procedure

In a round-bottomed flask equipped with a stirring bar and rubber septum was placed a Lewis acid in anhydrous CH_2Cl_2 (1 mL). To this solution was added $PhSCF_2H$ (**1**) in anhydrous CH_2Cl_2 (1 mL), followed by a solution of 1,2,4-trimethoxybenzene (**2a**; 0.5 mmol) in anhydrous CH_2Cl_2 (1 mL). The reaction was allowed to proceed for 2 h before it was quenched with a solution of IBX (140 mg, 0.5 mmol) in DMSO/H_2O (4 mL; 3:1 v:v). After 2 h of stirring at rt, the reaction mixture was quenched by addition of a saturated aqueous solution of sodium thiosulfate (10 mL), then basified with a saturated aqueous solution of sodium hydrogen carbonate (10 mL), followed by stirring and extraction with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL) and brine (10 mL), dried (anhydrous $MgSO_4$), filtered and concentrated (aspirator). The residue was purified by PTLC to provide **3a**, **4a**, **5a** and **6a** in various ratios and yields (Table 1).

1-[Bis(phenylsulfanyl)methyl]-2,4,5-trimethoxybenzene (3a)

White solid (Et_2O/hexanes); mp 92.3–92.6 °C; R_f = 0.32 (hexanes/EtOAc, 5:2).

IR (KBr): 3056, 3000, 2945, 2831, 1608, 1582, 1515, 1438, 1237 (Ar–O–C), 1205 (Ar–O–C), 1175 (Ar–O–C), 1033 cm^{-1} (Ar–O–C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 4 H), 7.26–7.19 (m, 6 H), 7.00 (s, 1 H), 6.43 (s, 1 H), 6.05 (s, 1 H), 3.86 (s, 3 H), 3.75 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.2 (C), 149.4 (C), 143.3 (C), 135.0 (2 × C), 132.2 (4 × CH), 128.7 (4 × CH), 127.4 (2 × CH), 119.4 (C), 112.4 (CH), 97.6 (CH), 56.8 (CH_3), 56.4 (CH_3), 56.1 (CH_3), 52.1 (CH).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}O_3S_2Na$: 421.0908; found: 421.0910.

2,4,5-Trimethoxybenzaldehyde (4a)

White solid (96.14 mg, 98%) from EtOAc/hexanes; mp 112.4–112.7 °C; R_f = 0.26 (hexanes/EtOAc, 2:1).

IR (KBr): 2924, 2855, 1660 (C=O), 1607, 1510, 1456, 1291 (Ar–O–C), 1218 (Ar–O–C), 1128 (Ar–O–C), 1026 cm^{-1} (Ar–O–C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.31 (s, 1 H), 7.32 (s, 1 H), 6.50 (s, 1 H), 3.98 (s, 3 H), 3.93 (s, 3 H), 3.88 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.9 (CO), 158.8 (C), 155.7 (C), 143.5 (C), 117.2 (C), 108.9 (CH), 95.9 (CH), 56.2 (CH_3), 56.1 (2 × CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{12}O_4Na$: 219.0633; found: 219.0629.

(Phenylsulfanyl)bis(2,4,5-trimethoxyphenyl)methane (5a)

White solid (EtOAc/hexanes); mp 92.3–92.7 °C; R_f = 0.24 (hexanes/EtOAc, 2:1).

IR (neat): 3037, 2996, 2957, 2931, 1608, 1595, 1505, 1455, 1224 (Ar–O–C), 1203 (Ar–O–C), 1175 (Ar–O–C), 1031 cm^{-1} (Ar–O–C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.09 (m, 7 H), 6.50 (s, 2 H), 6.34 (s, 1 H), 3.86 (s, 6 H), 3.78 (s, 6 H), 3.76 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.1 (2 × C), 148.9 (2 × C), 143.0 (2 × C), 137.3 (C), 129.4 (2 × CH), 128.5 (2 × CH), 125.8 (CH), 121.1 (2 × C), 113.5 (2 × CH), 98.3 (2 × CH), 57.0 (2 × CH_3), 56.6 (2 × CH_3), 56.0 (2 × CH_3), 43.2 (CH).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{28}O_6SNa$: 479.1504; found: 479.1518.

Tris(2,4,5-trimethoxyphenyl)methane (6a)

White solid (EtOAc/hexanes); mp 184.3–185.2 °C; R_f = 0.16 (hexanes/EtOAc, 5:2).

IR (KBr): 2940, 1605, 1521, 1428 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.54 (s, 3 H), 6.41 (s, 3 H), 6.22 (s, 1 H), 3.87 (s, 9 H), 3.66 (s, 9 H), 3.63 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.5 (3 × C), 147.7 (3 × C), 142.5 (3 × C), 124.7 (3 × C), 114.0 (3 × CH), 98.5 (3 × CH), 57.1 (3 × CH_3), 56.6 (3 × CH_3), 55.9 (3 × CH_3), 36.2 (1 × CH).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{34}O_9Na$: 537.2101; found: 537.2182.

^{1}H, ^{13}C and ^{19}F NMR Characterization of Chloro(phenylsulfanyl)methylium Trichlorodifluorostannate(IV) ([1c-cation])

In a screw-cap NMR tube equipped with a septum, a closed capillary tube containing $CDCl_3$, TMS and $CFCl_3$ was inserted. The NMR tube was gently heated under reduced pressure to remove trace moisture, followed by the addition of a 1 M solution of $SnCl_4$ in CH_2Cl_2 (0.4 mL, 0.4 mmol). A solution of $PhSCF_2H$ (**1**; 32 mg, 0.2 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise via syringe. Upon the addition of $PhSCF_2H$, the colorless solution immediately turned a clear light orange color. The reaction is not exothermic, yet small bubbles were observed as the reaction proceeded. After 5 min of gently rotating the NMR tube, a homogeneous clear orange solution was observed and ^{1}H, ^{13}C and ^{19}F NMR data were collected.

^{1}H NMR (400 MHz): δ = 10.18 (s, 1 H), 7.45–7.42 (br s, 5 H).

^{13}C NMR (100 MHz): δ = 200.2 (1 C), 133.8 (2 × CH), 131.0 (1 H), 130.0 (2 × CH), 123.9 (1 C).

^{19}F NMR (376 MHz): δ = –162.19.

Aldehydes 4 and 8; General Procedure

In a round-bottomed flask equipped with a stirring bar and rubber septum was placed a 1 M solution of $SnCl_4$ in anhydrous CH_2Cl_2 (1 mL, 1 mmol). To this solution was added $PhSCF_2H$ (**1**; 240.2 mg, 1.5 mmol) in anhydrous CH_2Cl_2 (1.5 mL), followed by a solution of an aromatic compound (0.5 mmol) in anhydrous CH_2Cl_2 (1 mL). The reaction was allowed to proceed for 2 h before it was quenched with a solution of IBX (140 mg, 0.5 mmol) in DMSO/H_2O (4 mL; 3:1 v:v). After 2 h of stirring at rt, the reaction mixture was quenched by addition of a saturated aqueous solution of sodium thiosulfate (10 mL), then basified with a saturated aqueous solution of sodium hydrogen carbonate (10 mL), followed by stirring and extraction with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL) and brine (10 mL), dried (anhydrous $MgSO_4$), filtered and concentrated (aspirator). The residue was purified by PTLC, radial chromatography or column chromatography to furnish analytically pure product.

2,4,6-Trimethoxybenzaldehyde (4b)

White solid (97.12 mg, 99%) from EtOAc/hexanes; mp 118–120 °C; R_f = 0.23 (hexanes/EtOAc, 5:1).

IR (KBr): 2976, 2949, 2880, 1664 (C=O), 1600, 1475, 1333, 1161, 1127, 1025 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.36 (s, 1 H), 6.09 (s, 2 H), 3.89 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.6 (CO), 166.2 (C), 164.1 (2 × C), 108.9 (C), 90.3 (2 × CH), 56.0 (2 × CH_3), 55.5 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{12}O_4Na$: 219.0633; found: 219.0627.

2,3,4-Trimethoxybenzaldehyde (4c)

White solid (70.63 mg, 72%) from EtOAc/hexanes; mp 38–41 °C; R_f = 0.38 (hexanes/EtOAc, 5:2).

IR (neat): 2944, 2844, 1682 (C=O), 1590, 1291 (Ar–O–C), 1204 (Ar–O–C), 1093 cm^{-1} (Ar–O–C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.25 (s, 1 H), 7.61 (d, *J* = 8.8 Hz, 1 H), 6.77 (d, *J* = 8.8 Hz, 1 H), 4.04 (s, 3 H), 3.95 (s, 3 H), 3.90 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.8 (CO), 159.3 (C), 156.9 (C), 141.6 (C), 124.2 (CH), 123.4 (C), 107.4 (CH), 62.3 (CH_3), 60.9 (CH_3), 56.2 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{12}O_4Na$: 219.0633; found: 219.0635.

2,4-Dimethoxybenzaldehyde (4d)

White solid (64.81 mg, 78%) from EtOAc/hexanes; mp 70.2–72.5 °C; R_f = 0.48 (hexanes/EtOAc, 5:1).

IR (KBr): 2951, 2863, 1660 (C=O), 1605, 1455, 1284 (Ar–O–C), 1217 (Ar–O–C), 1175 (Ar–O–C), 1023 cm^{-1} (Ar–O–C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.29 (s, 1 H), 7.81 (d, *J* = 8.7 Hz, 1 H), 6.55 (dd, *J* = 8.7, 2.2 Hz, 1 H), 6.45 (d, *J* = 2.2 Hz, 1 H), 3.90 (s, 3 H), 3.88 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.3 (CO), 166.2 (C), 163.6 (C), 130.7 (CH), 119.1 (C), 105.8 (CH), 97.9 (CH), 55.6 (2 × CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_9H_{10}O_3Na$: 189.0528; found: 189.0549.

4-Methoxybenzaldehyde (4e)

Colorless liquid (31.99 mg, 47%); R_f = 0.38 (hexanes/EtOAc, 5:1).

IR (neat): 2937, 2841, 1682 (C=O), 1599, 1577, 1160, 1024, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 7.81 (d, J = 8.8 Hz, 2 H), 6.98 (d, J = 8.7 Hz, 2 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7 (CO), 164.5 (C), 131.9 (2 × CH), 129.8 (C), 114.2 (2 × CH), 55.5 (CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_8H_8O_2Na$: 159.0422; found: 159.0464.

4-(Diethylamino)benzaldehyde (4f)

White solid (37.22 mg, 42%) from EtOAc/hexanes; mp 38–41 °C; R_f = 0.33 (hexanes/EtOAc, 5:0.5).

IR (neat): 2974, 2929, 2731, 1667 (C=O), 1595, 1527, 1408, 1274, 1173, 1156 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.71 (s, 1 H), 7.72 (d, J = 9.0 Hz, 2 H), 6.68 (d, J = 9.0 Hz, 2 H), 3.44 (q, J = 7.1 Hz, 4 H), 1.24 (t, J = 9.5 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.9 (CO), 152.2 (C), 124.7 (C), 110.6 (4 × CH), 44.7 (2 × CH_2), 12.5 (2 × CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{11}H_{15}NONa$: 200.1051; found: 200.1053.

2-Methoxy-1-naphthaldehyde (4g)

White solid (84.72 mg, 91%) from EtOAc/hexanes; mp 82–84 °C; R_f = 0.40 (hexanes/EtOAc, 5:1).

IR (neat): 3079, 3011, 2941, 2847, 1682 (C=O), 1574, 1513, 1430, 1251, 1220, 1095, 1060, 816, 765 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.92 (s, 1 H), 9.31 (d, J = 8.8 Hz, 1 H), 8.07 (d, J = 9.2 Hz, 1 H), 7.80 (d, J = 7.9 Hz, 1 H), 7.65 (t, J = 7.7 Hz, 1 H), 7.44 (t, J = 7.5 Hz, 1 H), 7.31 (d, J = 9.2 Hz, 1 H), 4.07 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.9 (CO), 163.9 (C), 137.5 (CH), 131.6 (C), 129.8 (CH), 128.5 (C), 128.2 (CH), 124.9 (CH), 124.7 (CH), 116.7 (C), 112.5 (CH), 56.5 (CH_3).

HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{12}H_{11}O_2$: 187.0759; found: 187.0734.

1-Methoxy-2-naphthaldehyde (4h)

White solid (79.14 mg, 85%) from EtOAc/hexanes; mp 60–63 °C; R_f = 0.38 (hexanes/EtOAc, 5:1).

IR (KBr): 3079, 3011, 2941, 2847, 1682 (C=O), 1574, 1513, 1430, 1251, 1220, 1095, 1060, 816, 765 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.23 (s, 1 H), 9.34 (d, J = 9.5 Hz, 1 H), 8.36 (d, J = 8.5 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.73 (t, J = 7.7 Hz, 1 H), 7.66 (t, J = 7.7 Hz, 1 H), 6.95 (d, J = 8.1 Hz, 1 H), 4.12 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.2 (CO), 160.8 (CO), 139.6 (CH), 131.9 (C), 129.5 (CH), 126.4 (CH), 125.5 (C), 125.0 (C), 124.8 (CH), 122.3 (CH), 102.9 (CH), 55.9 (CH_3).

HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{12}H_{11}O_2$: 187.0759; found: 187.0732.

1,6-Dimethoxy-2-naphthaldehyde (4i)

White solid (69.19 mg, 64%) from EtOAc/hexanes; mp 94–95 °C; R_f = 0.38 (hexanes/EtOAc, 5:1).

IR (Nujol mull): 2924, 2854, 1673 (C=O), 1581, 1455, 1237, 1207, 1055, 803, 650 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.11 (s, 1 H), 8.81 (d, J = 2.4 Hz, 1 H), 8.20 (d, J = 9.2 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.19 (dd, J = 9.2, 2.5 Hz, 1 H), 6.75 (d, J = 8.0 Hz, 1 H), 4.04 (s, 3 H), 3.99 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.4 (CO), 161.0 (C), 160.9 (C), 141.0 (CH), 133.7 (C), 124.0 (C), 123.9 (CH), 120.3 (C), 118.4 (CH), 103.8 (CH), 101.3 (CH), 55.7 (CH_3), 55.3 (CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}O_3Na$: 239.0684; found: 239.0664.

2,6-Dimethoxy-1-naphthaldehyde (4j)

White solid (100.55 mg, 93%) from EtOAc/hexanes; mp 90–91 °C; R_f = 0.45 (hexanes/EtOAc, 5:1).

IR (KBr): 3091, 2969, 2885, 1663 (C=O), 1515, 1372, 1240, 1170, 1061, 844, 817 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.89 (s, 1 H), 9.23 (d, J = 9.4 Hz, 1 H), 7.99 (d, J = 9.2 Hz, 1 H), 7.32 (dd, J = 9.4, 2.8 Hz, 1 H), 7.30 (d, J = 9.2 Hz, 1 H), 7.11 (d, J = 2.8 Hz, 1 H), 4.05 (s, 3 H), 3.93 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.0 (CO), 162.5 (C), 156.6 (C), 136.1 (CH), 129.9 (C), 126.7 (C), 126.6 (CH), 121.9 (CH), 117.1 (C), 113.3 (CH), 106.6 (CH), 56.7 (CH_3), 55.3 (CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}O_3Na$: 239.0684; found: 239.0656.

2,7-Dimethoxy-1-naphthaldehyde (4k)

White solid (104.87 mg, 97%) from EtOAc/hexanes; mp 98–100 °C; R_f = 0.30 (hexanes/EtOAc, 5:1).

IR (neat): 3006, 2966, 2945, 1663 (C=O), 1518, 1249, 1054, 828 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.89 (s, 1 H), 8.84 (d, J = 2.5 Hz, 1 H), 7.98 (d, J = 9.0 Hz, 1 H), 7.66 (d, J = 8.9 Hz, 1 H), 7.11 (d, J = 9.0 Hz, 1 H), 7.06 (dd, J = 9.0, 2.6 Hz, 1 H), 4.04 (s, 3 H), 3.97 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.0 (CO), 164.8 (C), 161.5 (C), 137.3 (CH), 133.5 (C), 129.7 (CH), 124.1 (C), 117.4 (CH), 115.8 (C), 109.5 (CH), 103.5 (CH), 56.4 (CH_3), 55.4 (CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}O_3Na$: 239.0684; found: 239.0638.

1-Methyl-1*H*-indole-3-carbaldehyde (4l)

White solid (50.94 mg, 64%) from EtOAc/hexanes; mp 68–70 °C; R_f = 0.07 (hexanes/EtOAc, 5:1).

IR (neat): 3107, 2806, 1651 (C=O), 1537, 1075, 787, 747 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.98 (s, 1 H), 8.34–8.30 (m, 1 H), 7.66 (s, 1 H), 7.37–7.28 (m, 3 H), 3.86 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.4 (CO), 139.2 (CH), 137.8 (C), 125.2 (C), 124.0 (CH), 122.9 (CH), 122.0 (CH), 118.0 (C), 109.8 (CH), 33.6 (CH_3).

HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{10}H_9NONa$: 182.0582; found: 182.0544.

2,3-Dimethoxy-1-naphthaldehyde (4ma)

White solid (41.08 mg, 38%) from EtOAc/hexanes; mp 153–155 °C; R_f = 0.24 (hexanes/EtOAc, 5:1).

IR (KBr): 3069, 3002, 2972, 2838, 1689 (C=O), 1512, 1487, 1385, 1264, 1239, 1054, 873, 796 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.30 (s, 1 H), 8.82 (s, 1 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 7.85 (d, *J* = 7.0 Hz, 1 H), 7.51 (t, *J* = 7.7 Hz, 1 H), 7.20 (s, 1 H), 4.10 (s, 3 H), 4.04 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.2 (CO), 152.2 (C), 149.8 (C), 135.9 (CH), 133.4 (CH), 130.0 (C), 129.9 (C), 126.7 (C), 123.1 (CH), 106.6 (CH), 104.2 (CH), 56.0 (CH_3), 55.7 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}O_3Na$: 239.0684; found: 239.0619.

6,7-Dimethoxy-2-naphthaldehyde (4mb)

White solid (65.95 mg, 61%) from EtOAc/hexanes; mp 95–96 °C; R_f = 0.16 (hexanes/EtOAc, 5:1).

IR (KBr): 3067, 2996, 2942, 1683 (C=O), 1513, 1488, 1410, 1259, 1161, 1055, 875, 860 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.12 (s, 1 H), 8.23 (d, *J* = 1.0 Hz, 1 H), 7.85 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 1 H), 7.28 (s, 1 H), 7.20 (s, 1 H), 4.07 (s, 3 H), 4.06 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.1 (CO), 152.0 (C), 150.3 (C), 133.0 (C), 132.8 (C), 132.2 (CH), 128.4 (C), 127.2 (CH), 122.0 (CH), 107.6 (CH), 106.4 (CH), 56.1 (CH_3), 56.0 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}O_3Na$: 239.0684; found: 239.0668.

Methyl 2-Formyl-3,4,5-trimethoxybenzoate (8a)

Pale yellow oil (120.76 mg, 95%); R_f = 0.41 (hexanes/EtOAc, 5:2).

IR (neat): 2935, 1758, 1455, 1108, 655 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.30 (s, 1 H), 6.95 (s, 1 H), 3.99 (s, 3 H), 3.95 (s, 3 H), 3.92 (s, 3 H), 3.91 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.2 (CO), 168.3 (CO), 157.1 (C), 155.2 (C), 144.0 (C), 128.6 (C), 123.8 (C), 108.0 (CH), 62.6 (CH_3), 61.2 (CH_3), 56.4 (CH_3), 53.0 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{14}O_6Na$: 277.0688; found: 277.0664. NMR data of **8a** are in agreement with those previously reported.[17]

Methyl 2-Formyl-4,5-dimethoxybenzoate (8b)

White solid (95.29 mg, 85%) from EtOAc/hexanes; mp 100–102 °C; R_f = 0.35 (hexanes/EtOAc, 1:1).

IR (neat): 2926, 1658, 1445, 1206, 1108, 625 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.67 (s, 1 H), 7.53 (s, 1 H), 7.49 (s, 1 H), 4.02 (s, 3 H), 4.01 (s, 3 H), 3.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1 (CO), 166.2 (CO), 155.4 (C), 152.0 (C), 131.3 (C), 126.0 (C), 112.6 (CH), 109.7 (CH), 56.3 (CH_3), 56.2 (CH_3), 52.5 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M$^+$] calcd for $C_{11}H_{12}O_5$: 224.0685; found: 224.0672.

Methyl 2-Formyl-3,4,5-trimethoxy-6-methylbenzoate (8c)

White solid (118.0 mg, 88%) from EtOAc/hexanes; mp 135–137 °C; R_f = 0.36 (hexanes/EtOAc, 3:10).

IR (neat): 3030, 1720, 1713, 1486, 1430, 1311, 1202, 1025, 738 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.26 (s, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 3.94 (s, 3 H), 3.90 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.1 (CO), 169.2 (CO), 157.8 (C), 156.1 (C), 146.3 (C), 130.0 (C), 125.4 (C), 122.4 (C), 62.6 (CH_3), 60.9 (CH_3), 60.7 (CH_3), 52.6 (CH_3), 12.1 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}O_6Na$: 291.0844; found: 291.0729.

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Supporting Information

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