Supporting Information

for

Discovery of practical production processes for arylsulfur pentafluorides and their higher homologues, bis- and tris(sulfur pentafluorides): Beginning of a new era of “super-trifluoromethyl” arene chemistry and its industry

Teruo Umemoto*§, Lloyd M. Garrick§ and Norimichi Saito§

Address: IM&T Research, Inc./Ube America Inc., 6860 N. Broadway, Suite B, Denver, Colorado 80221, U. S. A.

E-mail: Teruo Umemoto* - teroumemoto@comcast.net

*Corresponding author

§ Currently: Ube America Inc.

Experimental details and copies of $^1$H-, $^{19}$F-, and $^{13}$C NMR spectra of new products

Table of Contents

Experimental Section

1. General p. S2

2. Preparation of arylsulfur chlorotetrafluorides (ArSF$_4$Cl) p. S3
   2-1. Preparation of ArSF$_4$Cl from diaryl disulfides p. S3
   2-2. Preparation of ArSF$_4$Cl from aryl thiols (ArSH) p. S7
2-3. Preparation of \( p\text{-}(\text{NO}_2)C_6H_4\text{SF}_4\text{Cl} \) from \( p\text{-}(\text{NO}_2)C_6H_4\text{SCl} \) p. S7

2-4. Preparation of PhSF₄Cl from PhSF₃ p. S8

3. Preparation of aryl bis- and tris(sulfur chlorotetrafluoride), \( \text{Ar(SF}_4\text{Cl)}_n \) \( (n = 2 \) and 3) p. S8

4. Preparation of arylsulfur pentafluorides \( (\text{ArSF}_5) \) from \( \text{ArSF}_4\text{Cl} \) p. S10

4-1. Examination on the reactivity of PhSF₄Cl to different fluorides p. S10

4-2. Preparation of various \( \text{ArSF}_5 \) from \( \text{ArSF}_4\text{Cl} \) with \( \text{ZnF}_2 \) p. S11

4-3. Effect of the atmosphere on the reaction of PhSF₄Cl with \( \text{ZnF}_2 \) p. S11

4-4. Large scale preparation of \( \text{PhSF}_5 \) from \( \text{PhSF}_4\text{Cl} \) with \( \text{ZnF}_2 \) in \( \text{Cl}_2 \) atmosphere p. S13

4-5. Preparation of \( p\text{-ClC}_6H_4\text{SF}_5 \) from \( p\text{-ClIC}_6H_4\text{SF}_4\text{Cl} \) with \( \text{ZnF}_2/\text{ZnCl}_2/\text{AlCl}_3 \) p. S14

5. Preparation of \( \text{ArSF}_5 \) from \( \text{ArSF}_4\text{Cl} \) with anhydrous hydrogen fluoride p. S15

6. Preparation of \( \text{PhSF}_5 \) from \( \text{PhSF}_4\text{Cl} \) with 70% (w/w) HF-pyridine p. S15

7. Preparation of polyfluorinated \( \text{ArSF}_5 \) with \( \text{SbF}_3/\text{SbF}_5(\text{SbCl}_5) \) p. S16

8. Preparation of aryl bis- and tris(sulfur pentafluoride), \( \text{Ar(SF}_5\text{S)}_n \) \( (n = 2,3) \) with \( \text{SbF}_5 \) p. S17

9. DSC measurement of arylsulfur chlorotetrafluorides p. S19

10. Preparation of starting materials \( 1j\text{–}n \) and \( 1r\text{–}u \) p. S21

11. References and Notes p. S27

12. \(^1\text{H}-, \text{^19F}-, \text{and ^13C NMR spectra of new products} \) p. S28

1. General

Chemicals were purchased and used without prior purification unless otherwise noted. Solvents \( \text{CH}_2\text{Cl}_2 \) and \( \text{CH}_3\text{CN} \) were distilled from \( \text{CaH}_2 \) before use. Spray-dried potassium fluoride and dry caesium fluoride were purchased from Sigma-Aldrich and used without further drying. Potassium fluoride (No. 402931) from Sigma-Aldrich was also used after being ground to a powder with a mortar and pestle and being dried at 250 °C for 2 or 3 days with a vacuum pump. Fluorinert® FC-72 (3M Company) (from SynQuest Labs.) was perfluorocarbon having bp 56 °C. Bis(pentafluorophenyl) disulfide (\( 1o \)) was prepared in 92% yield by treating 2,3,4,5,6-pentafluorothiophenol with bromine in acetic acid according to the literature [S1]. Benzene-1,3-dithiol (\( 1p \)) and benzene-1,4-dithiol (\( 1q \)) were
prepared according to the literature procedure except that N-methylpyrrolidinone was used instead of HMPA [S2].

\(^1\)H, \(^1^H\)F and \(^1^C\)C-NMR spectra were recorded on a JEOL at 300.53, 282.78, and 75.57 MHz, respectively. Chemical shifts are reported in ppm with TMS (\(\delta = 0.00\)); \(^19\)F, CFCl\(_3\) (\(\delta =0.00\)).

2. Preparation of arylsulfur chlorotetrafluorides (ArSF\(_4\)Cl)

2-1. Preparation of ArSF\(_4\)Cl from diaryl disulfides

\[
\text{Ar-S-S-Ar} \xrightarrow{\text{Cl}_2, \text{KF}} \text{ArSF}_4\text{Cl}
\]

**General procedure:** A 500 mL round-bottom glassware flask equipped with gas (N\(_2\), Cl\(_2\)) inlet and outlet tubes was charged with a diaryl disulfide (0.15 mol), dry KF (140 g, 2.4 mol, dried at 250 °C for 2 days under vacuum) and 300 mL of dry CH\(_3\)CN. The mixture was heated with stirring under N\(_2\) to almost reflux to dissolve as much KF as possible. Then, the stirred reaction mixture was cooled on an ice/water bath under a flow of N\(_2\) (about 20 mL/min). (Note: When spray-dried KF was used, the preheating to dissolve KF was not conducted.) After N\(_2\) was stopped, chlorine (Cl\(_2\)) was bubbled into a stirred reaction mixture at a rate of about 70 mL/min. The Cl\(_2\) bubbling took about 6.5 h. The total amount of Cl\(_2\) used was about 1.2 mol. After Cl\(_2\) was stopped, the reaction mixture was stirred overnight at room temperature. N\(_2\) was then bubbled through for 2 h to remove an excess of Cl\(_2\). The reaction mixture was then filtered and rinsed with 100 mL of dry hexanes in dry air or nitrogen. About 1 g of dry KF was added to the filtrate. KF may restrain possible decomposition (hydrolysis) of the product. The filtrate was evaporated under vacuum (with a vacuum pump) and the resulting residue was distilled at reduced pressure to give an arylsulfur chlorotetrafluoride. The reaction conditions and results for each ArSF\(_4\)Cl are shown in Table 1 (Text). The physical and spectral data of the products are shown below.

**Phenylsulfur chlorotetrafluorides (2a) [S3]:** trans-Isomer; bp 80 °C /20 mmHg; \(^1\)H NMR (CD\(_3\)CN) 7.79–7.75 (m, 2H), 7.53–7.49 (m, 3H); \(^1^F\)NMR (CD\(_3\)CN) 136.7 (s, SF\(_4\)); \(^1^C\)NMR (CDCl\(_3\)) \(\delta 155.5\) (quintet, \(J = 18\) Hz), 131.7, 128.8, 125.9 (m); IR (neat) 3074, 1487, 1452, 1194, 1097, 809, 740, 687, 638, 544 cm\(^{-1}\).

**p-Methylphenylsulfur chlorotetrafluoride (2b) [S3]:** trans-Isomer; bp 74–75 °C/5 mmHg; \(^1\)H NMR (CD\(_3\)CN) 7.65 (d, 2H), 7.29 (d, 2H), 2.36 (s, 3H, CH\(_3\)); \(^1^F\)NMR (CD\(_3\)CN) 137.66 (s, SF\(_4\)); \(^1^C\)NMR (CDCl\(_3\)) \(\delta 153.1\) (quintet, \(J = 18\) Hz), 142.3, 129.2, 125.7 (m), 21.0; IR (neat) 3040, 2929, 1602, 1504, 1195, 1100, 1087, 805, 699, 566, 545 cm\(^{-1}\). High resolution mass spectrum (HRMS); found 235.986234 (34.9%) (calcd for C\(_7\)H\(_7\)F\(_4\)S\(^{37}\)Cl; 235.986363), found 233.989763 (75.6%) (calcd for C\(_7\)H\(_7\)F\(_4\)S\(^{35}\)Cl; 233.989313).
**p-(tert-Butyl)phenylsulfur chlorotetrafluoride (2c)** [S3]: *trans*-Isomer; bp 98 °C/0.3 mmHg; mp 93 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.32 (s, 9H, C(CH$_3$)$_3$), 7.43 (d, $J$ = 9.2 Hz, 2H), 7.64 (d, $J$ = 9.2 Hz, 2H); $^{19}$F NMR $\delta$ 138.3 (s, SF$_4$); $^{13}$C NMR (CD$_2$CN) 126.1, 125.5 (m), 117.4, 34.8, 30.2. HRMS; found 278.034576 (8.8%) (calcd for C$_{10}$H$_{13}$ClF$_4$S; 278.033313), found 276.037526 (24.7%) (calcd for C$_{10}$H$_{13}$ClF$_4$S; 276.036263). Anal. Calcd for C$_{10}$H$_{13}$ClF$_4$S; C, 43.40%; H, 4.74%. Found; C, 43.69%, H, 4.74%.

**p-Fluorophenylsulfur chlorotetrafluoride (2d)** [S3]: *trans*-Isomer; bp 60 °C/8 mmHg; $^1$H NMR (CD$_2$CN) 7.85–7.78 (m, 2H), 7.25–7.15 (m, 2H); $^{19}$F NMR (CD$_2$CN) 137.6 (s, SF$_4$), −108.3 (s, CF); $^{13}$C NMR (CDCl$_3$) $\delta$ 163.7 (d, $J$ = 254 Hz), 151.2 (m), 128.4 (m), 115.6 (d, $J$ = 23 Hz); IR (neat) 3123, 3084, 1599, 1504, 1412, 1246, 1170, 1091, 814, 707, 566, 550 cm$^{-1}$. HRMS; found 239.961355 (37.4%) (calcd for C$_6$H$_4$F$_3$S$^{37}$Cl; 239.961291), found 237.964201(100%) (calcd for C$_6$H$_4$F$_3$S$^{35}$Cl; 237.964241).

**o-Fluorophenylsulfur chlorotetrafluoride (2e)** [S3]: *trans*-Isomer; bp 96–97 °C/20 mmHg; $^1$H NMR (CD$_2$CN) 7.77–7.72 (m, 1H), 7.60–7.40 (m, 1H), 7.25–7.10 (m, 2H); $^{19}$F NMR (CDCl$_3$) $\delta$ 140.98 (d, $J$ = 24.1 Hz, SF$_4$), −107.69 (m, CF); $^{13}$C NMR (CDCl$_3$) $\delta$ 155.8 (d, $J$ = 260 Hz), 141.4 (m), 133.9 (d, $J$ = 9 Hz), 128.4 (m), 124.0 (d, $J$ = 24 Hz), 117.9 (d, $J$ = 24 Hz). HRMS; found 239.961474 (25.4%) (calcd for C$_6$H$_4$F$_3$S$^{37}$Cl; 239.961291), found 237.964375 (69.8%) (calcd for C$_6$H$_4$F$_3$S$^{35}$Cl; 237.964241).

**p-Chlorophenylsulfur chlorotetrafluoride (2f)** [S3]: *trans*-Isomer; bp 65–66 °C/2 mmHg; $^1$H NMR (CDCl$_3$) $\delta$ 7.38 (d, 2H, $J$ = 9.1 Hz), 7.65 (d, 2H, $J$ = 9.1 Hz); $^{19}$F NMR (CDCl$_3$) 137.4 (s, 4F, SF$_4$); $^{13}$C NMR (CD$_2$CN) $\delta$ 153.4 (quintet, $J$ = 19 Hz), 137.7, 129.0, 127.4 (m); IR (neat) 3107, 1580, 1480, 1401, 1196, 1082, 1014, 810, 763, 671, 621, 545, 493 cm$^{-1}$. HRMS; found 257.927507 (13.3%) (calcd for C$_6$H$_4$F$_3$S$^{37}$Cl$_2$; 257.928790), found 255.930746 (68.9%) (calcd for C$_6$H$_4$F$_3$S$^{35}$Cl$_2$; 255.931740), found 253.933767 (100.0%) (calcd for C$_6$H$_4$F$_3$S$^{35}$Cl$_2$; 253.934690).

**p-Bromophenylsulfur chlorotetrafluoride (2g)** [S3]: *trans*-Isomer; mp 58–59 °C; $^1$H NMR (CD$_3$CN) $\delta$ 7.67 (s, 4H); $^{19}$F NMR (CD$_3$CN) $\delta$ 136.56 (s, SF$_4$); $^{13}$C NMR (CDCl$_3$) $\delta$ 154.2 (m), 131.9, 127.5 (m), 126.2; IR (nujol) 1577, 1396, 1070, 1010, 819, 752, 660, 619, 546 cm$^{-1}$. HRMS; found 301.877066 (16.5%) (calcd for C$_6$H$_4$$^{81}$Br$^{37}$ClF$_4$S; 301.879178), found 299.880655 (76.6%) (calcd for C$_6$H$_4$$^{81}$Br$^{35}$ClF$_4$S; 299.881224 and calcd for C$_6$H$_4$$^{79}$Br$^{37}$ClF$_4$S; 299.882128), found 297.882761 (77.4%) (calcd for C$_6$H$_4$$^{79}$Br$^{35}$ClF$_4$S; 297.884174). Anal. Calcd for C$_6$H$_4$BrClF$_4$S; C, 24.06%; H, 1.35%. Found, C, 24.37%; H, 1.54%.

**m-Bromophenylsulfur chlorotetrafluoride (2h)** [S3]: *trans*-Isomer; bp 57–59 °C/0.8 mmHg; $^1$H NMR (CD$_3$CN) 7.90–7.88 (m, 1H), 7.70–7.50 (m, 2H), 7.40–7.30 (m, 1H); $^{19}$F NMR (CD$_3$CN)
136.74 (s, SF₄); ¹³C NMR (CDCl₃) δ 156.1 (quintet, J = 19 Hz), 134.8, 130.1, 129.1 (m), 124.6 (m), 122.3; IR (neat) 3102, 1578, 1472, 1420, 1124, 1108, 1073, 812, 778, 670, 639, 609 cm⁻¹. HRMS; found 301.878031 (29.1%) (calcd for C₆H₄⁺Br³⁷ClF₄S; 301.879178), found 299.881066 (100%) (calcd for C₆H₄⁺Br³⁵ClF₄S; 299.881224 and calcd for C₆H₄⁺Br³⁷ClF₄S; 299.882128), found 297.883275 (77.4%) (calcd for C₆H₄⁺Br³⁵ClF₃S; 297.884174).

**p-Nitrophenylsulfur chlorotetrafluoride (2i) [S3]:** *trans*-Isomer; mp 130–131 °C; ¹H NMR (CD₂CN) 8.29 (d, J = 7.8 Hz, 2H), 8.02 (d, J = 7.8 Hz, 2H); ¹⁹F NMR (CD₂CN) 134.96 (s, SF₄); ¹³C NMR (CDCl₃) δ 159.3 (m), 149.1, 127.6 (m), 124.1; IR (nujol) 1538, 1354, 1316, 1091, 859, 748, 665, 618, 538 cm⁻¹. HRMS; found 266.956490 (38.4%) (calcd for C₆H₄⁺³⁷ClF₄NO₂S; 266.955791), found 264.959223 (100%) (calcd for C₆H₄⁺³⁵ClF₄NO₂S; 264.958741). Anal. Calcd for C₆H₄ClF₄NO₂S: C, 27.13%; H, 1.52%; N, 5.27%. Found, C, 27.16%; H, 1.74%; N, 4.91%.

**p-({Methanesulfonyl})phenyl chlorotetrafluoride (2j):** *trans*-isomer; mp 159.5–160.3 °C; ¹H NMR (CDCl₃) δ 3.08 (s, CH₃), 7.96 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H); ¹⁹F NMR (CDCl₃) δ 135.55 (s); ¹³C NMR (CDCl₃) δ 159.0 (quintet, J = 20 Hz), 143.5, 128.3, 127.4 (m), 44.4; IR (nujol) 1302, 1149, 1095, 1089, 801, 747, 666, 618, 567, 548, 503 cm⁻¹. Anal. Calcd for C₇H₇ClF₄O₂S₂: C, 28.15%; H, 2.36%. Found: C, 28.19%; H, 2.51%.

**2,6-Difluorophenylsulfur chlorotetrafluoride (2k) [S3]:** The product (bp 120–122 °C/95–100 mmHg) obtained by distillation from Example 8 is a 90:10 mixture of *trans*- and *cis*-isomers of 2,6-difluorophenylsulfur chlorotetrafluoride. The *trans*-isomer was isolated in pure form by crystallization (pentane). *trans*-Isomer; mp. 47.6–48.3 °C; ¹H NMR (CDCl₃) δ 6.97–7.09 (m, 2H, 3,5-H), 7.43–7.55 (m, 1H, 4-H); ¹⁹F NMR (CDCl₃) δ 143.9 (t, J = 26.0 Hz, 4F, SF₄), −104.1 (quintet, J = 26.0 Hz, 2F, 2,6-F); ¹³C NMR (CDCl₃) δ 157.2 (d, J = 262.3 Hz), 133.7 (t, J = 11.6 Hz), 130.6 (m), 113.5 (d, J = 14.6 Hz). HRMS; found 257.950876 (37.6%) (calcd for C₆H₃⁺³⁷ClF₆S; 257.951869), found 255.955740 (100%) (calcd for C₆H₃⁺³⁵ClF₆S; 255.954819). Anal. Calcd for C₆H₃ClF₆S: C, 28.08%, H, 1.18%. Found: C, 28.24%, H, 1.24%. Although the *cis*-isomer of 2,6-difluorophenylsulfur chlorotetrafluoride was not isolated in pure form, the *cis*-isomer was assigned in the following; ¹⁹F NMR (CDCl₃) δ 158.2 (quartet, J = 161.8 Hz, 1F, SF), 121.9 (m, 2F, SF₂), 76.0 (m, 1F, SF). The ¹⁹F NMR assignment of aromatic fluorine atoms of the *cis*-isomer could not be done because of overlapping of the peaks of the *trans*-isomer. IR (mixture of *trans/cis*-isomers) (neat) 1614, 1592, 1296, 1240, 1105, 1015, 843, 789, 686, 642, 545 cm⁻¹.

**2,3,6-Trifluorophenylsulfur chlorotetrafluoride (2l) [S4]:** The product (bp 125–129 °C/95 mmHg) obtained by distillation was a mixture of a 87:13 mixture of *trans*- and *cis*-isomers by NMR analysis. *trans*-Isomer: ¹H NMR (CDCl₃) δ 7.38 (m, 1H), 7.01 (m, 1H); ¹⁹F NMR (CDCl₃) δ 143.19 (t, J
= 27.2 Hz, 4F, SF₄), -109.24 (m, 1F), -127.20 (m, 1F), -137.97 (m, 1F); ¹³C NMR (CDCl₃) δ 152.5 (d, J = 258.7 Hz), 147.5 (ddd, J = 249.3, 14.4, 3.6 Hz), 146.3 (dd, J = 264.4, 17.0 Hz), 131.6 (m), 120.6 (dd, J = 18.1, 10.8 Hz), 112.4 (dm, J = 27.5 Hz). cis-Isomer: ¹⁹F NMR (CDCl₃) δ 155.50 (quartet, J = 160.9 Hz, 1F, SF), 122.12 (m, 2F, SF₂), 76.64 (m, 1F, SF), and aromatic fluorine atoms were not assigned because of overlapping with those of the major trans-isomer; ¹H and ¹³C NMR of the minor cis-isomer was not assigned because of overlapping with those of the major trans-isomer. IR (trans/cis mixture); (neat) 3112, 1620, 1604, 1497, 1523, 1200, 1020, 890, 838, 746, 688, 643, 616, 547 cm⁻¹. Elemental analysis of liquid 2l (trans/cis mixture) failed: Found; C, 27.53%; H, 0.84% (Calcd for C₆H₂ClF₇S: C, 26.24%; H, 0.73%). However, 2l was derived to 3l which provided a satisfactory elemental analysis.

2,4,6-Trifluorophenylsulfur chlorotetrafluoride (2m) [S4]: Purification by recrystallization of the crude product (trans/cis = 96/4) from pentane gave pure trans-isomer: mp 55.8–56.7 °C; ¹H NMR (CDCl₃) δ 6.79 (t, J = 17.5 Hz, m-H); ¹⁹F NMR (CDCl₃) δ 144.07 (t, J = 26.0 Hz, 4F, SF₄), -99.80 (t, J = 26.0 Hz, 2F, o-F), -100.35 (s, 1F, p-F); ¹³C NMR (CDCl₃) δ 164.2 (dt, J = 164.2 Hz, 15.2 Hz, 4-C), 158.2 (dm, J = 260.7 Hz, 2-C), 127.7 (m, 1-C), 102.1 (tm, J = 27.8 Hz, 3-C); IR (nujol) 1607, 1176, 1136, 1092, 1049, 1011, 847, 710, 581, 551 cm⁻¹. Anal. Calcd for C₆H₂ClF₇S: C, 26.24%; H, 0.73%. Found: C, 26.23%; H, 1.01%. cis-Isomer: ¹⁹F NMR (CDCl₃) δ 157.8 (m, 1F, SF₄), 122.3 (m, 2F, SF₄), 77.0 (m, 1F, SF₄), and aromatic fluorine atoms could not be assigned.

2,3,4,6-Tetrafluorophenylsulfur chlorotetrafluoride (2n) [S4]: The product (bp 115–120 °C/120 mmHg) obtained by distillation was a 86:14 mixture of trans- and cis-isomers by ¹⁹F NMR analysis. trans-Isomer of 2n was isolated by crystallization of the mixture on long standing in a freezer. trans-Isomer: mp 38.8–40.0 °C; ¹⁹F NMR (CDCl₃) δ 143.70 (t, J = 26.9 Hz, 4F, SF₄), -106.77 (m, 1F), -124.22 (m, 2F), -160.64 (m, 1F); ¹H NMR (CDCl₃) δ 6.9 (m); ¹³C NMR (CDCl₃) δ 152.5 (m, J = 259.8 Hz), 147.9 (dm, J = 269.0 Hz), 137.5 (dm, J = 253.0 Hz), 128.2 (m), 102.1 (m). cis-Isomer: ¹⁹F NMR (CDCl₃) δ 154.92 (quartet, J = 160.6 Hz, 1F, SF), 122.90 (m, 2F, SF₂), 77.74 (m, 1F, SF), and aromatic fluorine atoms were not assigned because of overlapping with those of the major trans-isomer: ¹H and ¹³C NMR of the minor cis-isomer was not assigned because of overlapping with those of the major trans-isomer. IR (mixture of trans/cis-isomers); (neat) 3094, 1633, 1514, 1450, 1205, 1089, 1061, 837, 703, 666, 559 cm⁻¹. Anal. (for trans-isomer) Calcd for C₆HClF₇S; C, 24.63%; H, 0.34%. Found: C, 24.06%; H, 0.62%.

2,3,4,5,6-Pentafluorophenylsulfur chlorotetrafluoride (2o) [S4]: The product (bp 95–112 °C/100 mmHg) obtained by distillation was a 63:37 mixture of trans and cis isomers of 2,3,4,5,6-pentafluorophenylsulfur chlorotetrafluoride. The isomers were assigned by ¹⁹F NMR. trans-Isomer;
$^{19}$F NMR (CDCl$_3$) $\delta$ 144.10 (t, $J = 26.0$ Hz, 4F, SF$_4$), −132.1 to −133.1 (m, 2F, 2,6-F), −146.6 (m, 1F, 4-F), −158.9 (m, 2F, 3,5-F). cis-Isomer; $^{19}$F NMR (CDCl$_3$) $\delta$ 152.39 (quartet, $J = 158.9$ Hz, 1F, SF), 124.32 (m, 2F, SF$_2$), 79.4 (m, 1F, SF), −132.1 to −133.1 (m, 2F, 2,6-F), −146.6 (m, 1F, 4-F), −158.9 (m, 2F, 3,5-F). $^{13}$C NMR could not be assigned for each of the trans and cis isomers. HRMS of a 63:37 mixture of the trans and cis isomers; found 311.923124 (15.5%) (calcd for C$_6$$_{37}$Cl$_9$S; 311.923604), found 309.926404 (43.1%) (calcd for C$_6$$_{35}$Cl$_9$S; 309.926554). IR (mixture of trans/cis-isomers); (neat) 1644, 1525, 1503, 1110, 1002, 850, 795, 745, 680, 641, 534 cm$^{-1}$.

2-2. Preparation of ArSF$_4$Cl from aryl thiols (ArSH)

Arylsulfur chlorotetrafluorides were also prepared from aryl thiols by the following procedure.

\[ \text{ArSH} \xrightarrow{\text{Cl}_2, \text{CsF}} \text{ArSF}_4\text{Cl} \]

A typical procedure [S3]: Chlorine (Cl$_2$; 10.1 L, 451 mmol) was passed with a flow rate of 37 mL/min into a stirred mixture of 10.1 g (60.2 mmol) of $p$-tert-butylthiophenol and 91.6 g (602 mmol) of dry cesium fluoride in 150 mL of dry acetonitrile at 6–10 °C. The reaction mixture turned yellow and then colorless. After chlorine was passed, the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered and washed with 100 mL of dry acetonitrile in dry air or nitrogen. After complete removal of the solvent in vacuum at room temperature, the obtained solid was mixed with 100 mL of dry hexane and filtered under nitrogen. The filtrate (hexane) was concentrated and $p$-(tert-butyl)phenylsulfur chlorotetrafluoride (2c) (14 g, 84%) was obtained by crystallization. The product was a trans isomer.

The reaction conditions and results for thiophenol are shown in Table 1 (Text).

2-3. Preparation of $p$-(NO$_2$)C$_6$H$_4$SF$_4$Cl from $p$-(NO$_2$)C$_6$H$_4$SCl

$p$-Nitrophenylsulfur chlorotetrafluoride (2i) was also prepared from $p$-nitrophenylsulphenyl chloride by the following procedure [S3].

\[ \text{O}_2\text{N-SCl} \xrightarrow{\text{Cl}_2, \text{KF}} \text{O}_2\text{N-SF}_4\text{Cl} \]

2i

Chlorine (Cl$_2$) was passed with a flow rate of 37 mL/min into a stirred mixture of 5.00 g (26.4 mmol) of $p$-nitrobenzenesulphenyl chloride and 15.3 g (264 mmol) of spray-dried KF in 40 mL of dry
acetonitrile at 5–11 °C. The total amount of chlorine passed was 2.54 L (113 mmol). The reaction mixture was filtered in dry air or nitrogen. After removal of the solvent in vacuum, 4.69 g (76%) of trans-\(p\)-nitrophenylsulfur chlorotetrafluoride \((2i)\) as a solid was obtained.

2-4. Preparation of \(\text{PhSF}_4\text{Cl}\) from \(\text{PhSF}_3\)

Phenylsulfur chlorotetrafluoride \((2a)\) was also prepared from phenylsulfur trifluoride by the following procedure [S3].

\[
\begin{align*}
\text{PhSF}_3 & \xrightarrow{\text{Cl}_2} \text{PhSF}_4\text{Cl} \quad (2a) \\
\text{Cl}_2 & \xrightarrow{\text{KF}} \text{PhSF}_4\text{Cl} \quad (2a)
\end{align*}
\]

Chlorine (\(\text{Cl}_2\)) was passed with a flow rate of 34 mL/min into a stirred mixture of 5.00 g (30.1 mmol) of phenylsulfur trifluoride and 8.74 g (150 mmol) of spray-dried KF in 20 mL of dry acetonitrile at 6–9 °C. Chlorine was passed for 43 min and the total amount of chlorine passed was 1.47 L (65.5 mmol). The reaction mixture was filtered in dry air or nitrogen. After removal of the solvent in vacuum, 5.62 g (84%) of trans-phenylsulfur chlorotetrafluoride was obtained as a colorless liquid.

3. Preparation of aryl bis- and tris(sulfur chlorotetrafluorides), \(\text{Ar(SF}_4\text{Cl)}_n\) \((n = 2 \text{ and } 3)\)

\[
\begin{align*}
\text{Ar(SH)}_n & \xrightarrow{\text{Cl}_2} \text{Ar(SF}_4\text{Cl)}_n \quad n = 2, 3
\end{align*}
\]

A typical procedure [S5]: A 500 mL fluoropolymer (PFA) reactor was set up with a magnetic stirrer, a gas (\(\text{N}_2, \text{Cl}_2\)) inlet tube, and a gas outlet tube protected by a CaCl\(_2\) tube. Gas flow was controlled by a digital controller and measured by a digital integrator. The vessel was charged with dry KF (100 g, 1.72 mol), and set up for reaction under nitrogen flow. Anhydrous acetonitrile (300 mL) was added, followed by 1,3-benzenedithiol (9.78 g, 68.7 mmol). After cooling in the ice bath with stirring under \(\text{N}_2\) flow for 1 hour, \(\text{N}_2\) was stopped and then chlorine gas was introduced below the surface at 60–80 mL/min with vigorous stirring. Over approximately 6 h, a total of 27.1 L (1.21 mol) of \(\text{Cl}_2\) was added. The reaction was then allowed to come to room temperature with stirring. After being stirred for two days at room temperature, the reaction mixture was filtered and washed through with dry acetonitrile (200 mL). The solvent was then removed at room temperature under vacuum, leaving the crude product (23.2 g, crude yield 93%) as a white solid, which was recrystallized from pentane in a freezer to give white crystals of 1,3-bis(chlorotetrafluorosulfanyl)benzene \((2p^+\)) (14.1 g, yield 56%). To obtain a sample for analysis, some of the crystals were further recrystallized. The reaction conditions and results for each of the \(\text{Ar(SF}_4\text{Cl)}_n\) are shown in Table 2 (Text). The physical and spectral data of the products are shown below.
Phenyl-1,3-bis(sulfur chlorotetrafluoride) (2p’) [S5]: mp 82–83.5 °C (in a sealed capillary); 
$^1$H NMR (CDCl$_3$) δ 8.12 (t, $J$ = 2.0 Hz, 1H, 2-H), 7.89 (dd, $J$ = 8.3, 2.0 Hz, 2H, 4.6-H), 7.58 (t, $J$ = 8.3 Hz, 1H, 5-H); $^{19}$F NMR (CDCl$_3$) δ 136.14 (s, SF$_4$); $^{13}$C NMR (CDCl$_3$) δ 155.1 (quintet, $J$ = 20.6 Hz), 129.3, 129.0 (t, $J$ = 4.3 Hz), 124.1 (quintet, $J$ = 4.9 Hz). Anal. Calcd for C$_6$H$_4$Cl$_2$F$_8$S$_2$; C, 19.85%, H, 1.11%. Found, C, 20.30%, H, 1.20%. The NMR showed that product 2p’ obtained is a trans,trans-isomer.

Phenyl-1,4-bis(sulfur chlorotetrafluoride) (2q’) [S5]: mp 200.8–201.6 °C; $^1$H NMR (CDCl$_3$) δ 7.84 (s, 4H); $^{19}$F NMR (CDCl$_3$) δ 135.72 (s, 8F); $^{13}$C NMR (CDCl$_3$) δ 156.9 (quintet, $J$ = 20.2 Hz), 126.7 (m). Anal. Calcd for C$_6$H$_4$Cl$_2$F$_8$S$_2$; C, 19.85%, H, 1.11%. Found, C, 19.71%, H, 1.10%. NMR analysis showed that product 2q’ obtained is a trans,trans-isomer.

5-Bromobenzene-1,3-bis(sulfur chlorotetrafluoride) (2r’) [S5]: The product having all trans-configuration was isolated by recrystallization from chloroform: mp 146.1–148 °C (with decomposition); $^1$H NMR (CDCl$_3$) δ 8.05 (m, 1H), 8.02 (m, 2H); $^{19}$F NMR (CDCl$_3$) δ 135.76 (s); $^{13}$C NMR (CDCl$_3$) δ 155.6 (quintet, $J$ = 21.7 Hz), 132.2 (m), 122.8 (m), 122.3. Anal. Calcd for C$_6$H$_4$BrCl$_2$F$_8$S$_2$; C, 16.30%, H, 0.68%. Found, C, 16.35%, H, 0.72%. The formation of the minor products having cis-configuration at SF$_4$Cl was confirmed by $^{19}$F NMR of the crude product: $^{19}$F NMR (CDCl$_3$) δ 159 (m, 1F), 102 (m, 2F), 69 (m, 1F).

1,4-Difluorophenyl-2,5-bis(sulfur chlorotetrafluoride) (2s’) [S5]: The product was isolated by washing the crude product with a small amount of dichloromethane: mp 161.5–162.9 °C (a 97:3 mixture of trans and cis configuration); $^1$H NMR (CDCl$_3$) (a 97:3 mixture of trans and cis configuration) δ 7.63 (m, 2H); $^{19}$F NMR (CDCl$_3$) (a 97:3 mixture of trans and cis configuration) δ 155.63 (m, cis-SF), 138.52 (m, trans-SF$_4$), 112.95 (m, cis-SF$_2$), 71.37 (m, cis-SF), −109.25 (m, CF); $^{13}$C NMR (CDCl$_3$) (a 97:3 mixture of trans and cis configuration) δ 150.8 (d, $J$ = 263.3 Hz), 143.9 (m), 118.5 (m). Anal. (a 97:3 mixture of trans and cis configuration) Calcd for C$_6$H$_4$Cl$_2$F$_10$S$_2$; C, 18.06%, H, 0.51%. Found, C, 18.01%, H, 0.51%.

2,3,5,6-Tetrafluorophenyl-1,4-bis(sulfur chlorotetrafluoride) (2t’) [S5]: The product was recrystallized from dichloromethane/pentane; mp 135–141 °C (a 78:22 mixture of trans and cis configuration); $^{19}$F NMR (CDCl$_3$) (a 78:22 mixture of trans and cis configuration) δ 148.6–150.4 (m, cis-SF), 142.22 (m, trans-SF$_4$), 122.9–124.2 (m, cis-SF$_2$), 77.7–79.2 (m, cis-SF), −129.2 to −130.3 (m, CF, trans and cis); $^{13}$C NMR (CDCl$_3$) (a 63:37 mixture of trans and cis configuration) δ 143.7–144.7 (m), 140.2–141.2 (m), 134.5 (m). Anal. (a 78:22 mixture of trans and cis configuration) Calcd for C$_6$Cl$_2$F$_2$S$_2$; C, 16.56%, H, 0.00%. Found, C, 16.54%, H, <0.05%.
Phenyl-1,3,5-tris(sulfur chlorotetrafluoride) (2u') [S5]: The product [mp 140–150 °C (sealed capillary)] having all trans-configuration at SF₄Cl was obtained by recrystallization of the mixture twice from pentane, but it was contaminated with a small amount of impurity, presumably compounds having SO₂F and SOF, and further purification failed. The isomer having all trans configuration at SF₄Cl was identified: ¹H NMR (CDCl₃) δ 8.24 (s); ¹⁹F NMR (CDCl₃) δ 135.30 (s); ¹³C NMR (CDCl₃) δ 127.0 (m), 155.0 (quintet, J = 22.9 Hz). The products having cis configuration at SF₄Cl were identified by ¹⁹F NMR: ¹⁹F NMR (CDCl₃) δ 158 (m, 2F of cis-SF₄Cl), 103 (m, 1F of cis-SF₄Cl), 69 (m, 1F of cis-SF₄Cl). We failed to get a pure sample of 2u' which satisfied elemental analysis: Found; C, 15.10%; H, 0.61% (Calcd for C₆H₃Cl₃F₁₂S₃; C, 14.25%; H, 0.60%). However, 2u' was derived to 3u” which provided a satisfactory elemental analysis.

4. Preparation of arylsulfur pentafluorides (ArSF₅) from ArSF₄Cl

4-1. Examination on the reactivity of PhSF₄Cl to different fluorides

\[
\text{PhSF₄Cl (2a) } \xrightarrow{\text{Fluoride}} \text{PhSF₅ (3a)}
\]

Phenylsulfur chlorotetrafluoride (2a) was treated with a different fluoride as shown in Table 3 in the text. For BF₃ (gas) (Runs 1-2), the reaction was carried out in the following way [S3].

Run 1: A steel reactor (25–30 mL) was charged with 1.0 g (4.5 mmol) of trans-2a and cooled in a dry ice-acetone bath. The reactor was then evacuated by a vacuum pump and BF₃ gas was introduced into the reactor until the pressure reached 18 psi. The reaction mixture (reactor) was warmed to room temperature and stood for three days. After that, the reactor was opened and the reaction mixture was analyzed. All of the starting material became a solid residue.

Run 2: A steel reactor (25–30 mL) was charged with 1.42 g (6.4 mmol) of trans-2a and 6.4 mL of dry dichloromethane and cooled to around −100 °C with a liquid N₂ bath. The reactor was evacuated by a vacuum pump and BF₃ gas was introduced into the reactor until the pressure reached 80 psi. The reaction mixture (reactor) was warmed to room temperature and stood for 5 h. In the meantime, additional BF₃ was added until the pressure reached 100 psi. After the reaction, the reactor was opened and the reaction mixture was analyzed. ¹⁹F NMR showed that the yield of 3a was 28%.

For Runs 3–11, the reaction was carried out as shown in the following typical procedure [S3].

*A typical procedure*: In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-2a and 0.26 g (1.4 mmol) of dry SnF₄. The reaction vessel was brought out from the dry box and equipped with a rubber balloon filled with N₂. The mixture was stirred at 80 °C for 2 h. The analysis of the reaction mixture by ¹⁹F-NMR showed that product 3a was produced in 34% yield.
The results with other different fluorides are shown together with reaction conditions in Table 3 in the text.

4-2. Preparation of various ArSF₅ from ArSF₄Cl with ZnF₂

\[
\text{ArSF}_4\text{Cl} \xrightarrow{\text{ZnF}_2 \text{ under a N}_2 \text{ balloon}} \text{ArSF}_5
\]

A typical procedure [S3]: A 100 mL fluoropolymer (TEFLON®-PFA) vessel was charged with PhSF₄Cl (2a) (44 g, 0.2 mol) and dry ZnF₂ (12.3 g, 0.12 mol) in a dry box filled with N₂. The vessel was brought out from the dry box and equipped with a condenser made of fluoropolymer and a balloon filled with N₂. The reaction mixture was slowly heated to 120 °C over a period of one hour. The reaction mixture changed from colorless to yellow, pink, and then eventually green. The reaction mixture was stirred at 120 °C for 20 h. After being cooled to room temperature, about 50 mL of pentane was added to the reaction mixture. The mixture was filtered to remove all insoluble solid to give a yellow solution, which was concentrated. The resulting residue was distilled at reduced pressure to give 30.6 g (75%) of PhSF₅ (3a); bp 70–71 °C/120 mmHg. The reaction conditions and results for other ArSF₄Cl are shown in Table 4 (Text). The physical and spectral data of new compounds are shown below.

\(\text{o-Fluorophenylsulfur pentfluoride (3e)}\) [S3]: bp 75 °C/27 mmHg; \(^1\)H NMR (CDCl₃) δ 7.78–7.73 (m, 1H), 7.55–7.48 (m, 1H), 7.27–7.17 (m, 2H); \(^{19}\)F NMR (CDCl₃) δ 81.77 (quintet, \(J = 150 \text{ Hz, 4F, SF}_4\)), 68.06 (dd, \(J = 150, 26 \text{ Hz, 1F, SF}\), −108.50 (m, 1F, CF); \(^{13}\)C NMR (CDCl₃) δ 156 (d, \(J = 260 \text{ Hz, 140 (m), 134 (m), 129 (m), 124 (m), 118 (d, J = 24 \text{ Hz); IR (neat) 2360, 1596, 1489, 1452, 1276, 1244, 846, 811, 759, 641, 599, 584, 497 cm}^{-1}; \text{GC-Mass } m/z 222 (M^{+}). \text{Anal. Calcd for } C_{6}H_{4}F_{6}S; \text{C, 32.44\%, H, 1.81\%}. \text{Found; C, 32.51\%, H, 1.95\%}.

\(\text{2,6-Difluorophenylsulfur pentfluoride (3k)}\) [S3,4]: mp 40.3–41.1 °C; \(^1\)H NMR (CDCl₃) δ 7.51 (m, 1H), 7.04 (m, 2H); \(^{19}\)F NMR (CDCl₃) 82.32–80.69 (m, 1F, SF), 62.76 (d, 4F, SF₄); \(^{13}\)C NMR (CDCl₃) δ 157 (d, \(J = 262 \text{ Hz), 134 (t, J = 23 Hz), 129 (m), 113 (d, J = 28 Hz); IR (nujol) 1616, 1593, 1568, 1295, 1241, 1222, 1112, 1054, 1010, 876, 843, 790, 756, 720, 684, 608, 588, 554, 542, 516 cm}^{-1}; \text{GC-Mass } m/z 240 (M^{+}). \text{HRMS; found } 239.984509 \text{ (calcd for } C_{6}H_{3}F_{7}S; 239.984370). \text{Anal. Calcd for } C_{6}H_{3}F_{7}S; \text{C, 30.01\%, H, 1.26\%}. \text{Found, C, 30.20\%, H, 1.47\%}.

4-3. Effect of the atmosphere on the reaction of PhSF₄Cl with ZnF₂

Reactions of phenylsulfur chlorotetrafluoride with ZnF₂ were conducted under no flow of N₂ gas (Run 1), a slow flow (Run 2) and a fast flow (Run 3) of N₂ gas, and a flow of Cl₂ gas (Run 4).
The procedure for each of Runs 1–4 is shown below [S3].

[Run 1] In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of \textit{trans}-phenylsulfur chlorotetrafluoride (2a) and 0.28 g (2.7 mmol) of anhydrous ZnF$_2$. The reaction vessel was removed from the dry box and equipped with a rubber balloon filled with N$_2$ gas. The reaction mixture was stirred at 120 °C for 4 h. After being cooled to room temperature, the reaction mixture was analyzed by $^{19}$F NMR. The reaction was completed. The results are shown in Table S-1.

[Run 2] In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (45.4 mmol) of \textit{trans}-2a and 2.8 g (27 mmol) of anhydrous ZnF$_2$. The reaction vessel was removed from the dry box, and equipped with a condenser made of fluoropolymer and connected to a N$_2$ gas flowing device. The reaction mixture was slowly heated to 120 °C with N$_2$ flowing at a rate of 5.4 mL/min. The reaction mixture was stirred at 120 °C with the N$_2$ flowing for 5 h. After being cooled to room temperature, the reaction mixture was analyzed with $^{19}$F NMR. The reaction was not completed. The results are shown in Table S-1.

[Run 3] In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (45.4 mmol) of \textit{trans}-2a and 2.8 g (27 mmol) of anhydrous ZnF$_2$. The reaction vessel was removed from the dry box, and equipped with a condenser made of fluoropolymer and connected to a N$_2$ gas flowing device. The reaction mixture was slowly heated to 120 °C with N$_2$ flowing at the rate of 26.9 mL/min. The reaction mixture was stirred at 120 °C with the N$_2$ flowing for 5 h. After being cooled to room temperature, the reaction mixture was analyzed with $^{19}$F NMR. The reaction was not completed. The results are shown in Table S-1.

[Run 4] In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (45.4 mmol) of \textit{trans}-2a and 2.8 g (27 mmol) of anhydrous ZnF$_2$. The reaction vessel was removed from the dry box, and equipped with a condenser made of fluoropolymer and connected to a Cl$_2$ gas flowing device. The reaction mixture was slowly heated to 120 °C with Cl$_2$ flowing at a rate of 4.6 mL/min. The reaction mixture was stirred at 120 °C with the Cl$_2$ flowing for 1.7 h. After being cooled to room temperature, the reaction mixture was analyzed with $^{19}$F NMR. The reaction was completed. The results are shown in Table S-1.
The results showed that the reaction of 2a with ZnF₂ became slow as the flow rate of N₂ gas increased and that the reaction was fast and its yield was high under the Cl₂ atmosphere.

4-4. Large-scale preparation of PhSF₅ from PhSF₄Cl with ZnF₂ in Cl₂ atmosphere

PhSF₅ (3a) was prepared in a large scale according to the following procedure.

A 1 liter three-neck reactor (made of fluoropolymer FEP) was charged with anhydrous zinc fluoride (ZnF₂; 162.8 g, 1.58 mol) in a dry box filled with N₂. The reactor was taken out of the dry box and set up with a condenser (made of fluoropolymer), a dropping funnel (made of fluoropolymer), a thermometer (protected with a fluoropolymer), a T-shaped gas inlet connector, and a T-shaped gas outlet connector (this gas outlet connector was equipped at the top of the condenser). The gas line (N₂ and Cl₂) was connected to the reactor through the T-shaped inlet connector, and the last one of three ports of the T-shaped inlet connector was directly connected to one of three ports of the T-shaped gas outlet connector. The last one of three ports of the T-shaped gas outlet connector was connected to a solution of an aqueous sodium sulfite solution for neutralization of the discharged Cl₂ gas. All the tubing and connectors were made of fluoropolymer. Phenylsulfur pentafluoride (3a) (180 g, 120 mL) as a solvent was added into the reactor. The reactor was purged with N₂ and then Cl₂ was flowed into the reactor at 200 mL/min flow rate for 10 min. After that, Cl₂ was flowed at 100 mL/min into both the reactor and the gas outlet by opening the line to the gas outlet connector (Note: the reactor was under the pressure of Cl₂ flow of 100 mL/min). The discharged Cl₂ gas was neutralized through the aq. sodium sulfite solution. The reactor was then put in an oil bath and heated to 110 °C (oil bath temperature) under stirring with a magnetic stirrer. trans-Phenylsulfur chlorotetrafluoride (2a) [662 g, 2.85 mol,
purity 95%: Note; impurity (5%) was phenylsulfur trifluoride] was dropwise added to the stirred mixture through the dropping funnel for 72 min. During the addition, the reaction temperature (inside) was mostly 105–101 °C. After the addition, the reaction mixture was stirred for 30 min at 110 °C (oil bath temperature) and then for 3 h at 115 °C (oil bath temperature). After the reaction, the Cl₂ flow was stopped and N₂ flow was started, and the oil bath was removed and the reactor was left at room temperature to cool. ¹⁹F NMR analysis at this moment showed that the reaction was completed. The cooled reaction mixture was filtered with 600 mL of dichloromethane and the filtrate was mixed with 300 mL of a cooled aq. 10% KOH solution. The mixture was stirred for 1 hour and the organic layer was separated, washed with an aq. NaCl solution (300 mL × 2), dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure (30 °C, 100 mmHg) and the resulting residue was distilled under reduced pressure to give 658 g of phenylsulfur pentafluoride (3a), bp 67–71 °C/26–29 mmHg). The real yield was (658 g –180 g =) 478 g (yield 82%). Its purity was >99% (by GC).

4-5. Preparation of p-ClC₆H₄SF₅ from p-ClC₆H₄SF₄Cl with ZnF₂/ZnCl₂/AlCl₃ (100/10/5)

The experimental procedure is shown below.

A 125 mL fluoropolymer reactor with a magnetic stir bar was charged with anhydrous ZnF₂ (10.9 g, 105 mmol), anhydrous ZnCl₂ (1.4 g, 10 mmol), and AlCl₃ (0.7 g, 5 mmol) in a dry box filled with N₂ and then the reactor was taken from the dry box. Dry dichloromethane (5 mL) was added to the reactor and the mixture was stirred for 1 hour under N₂. Dichloromethane was removed by a vacuum pump and then the reactor was equipped with a condenser made of fluoropolymer connected to a T-shaped N₂ gas inlet. The reactor was purged with N₂ and p-chlorophenylsulfur chlorotetrafluoride (2f) [50.8 g, purity 90%, 180 mmol: Note; impurity (10%) was p-chlorophenylsulfur trifluoride] was added by syringe. Heating of the reaction mixture under N₂ to 100 °C (oil bath temperature) was started. It took 15 min for the bath temperature to reach 100 °C. Heating of the reactor at the bath temperature (100 °C) was continued for 20 h. The inside temperature rose to 114 °C (maximum) in 30 min and fell to 100 °C in 60 min. After the reaction, the reaction mixture was cooled to room temperature and filtered with dichloromethane (80 mL). The combined filtrate was poured into a 10% aq. KOH solution (100 mL) cooled in an ice bath and the mixture was stirred for 30 min. The organic layer was separated, washed with aq. NaCl solution two times, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated at 30 °C under 100 mmHg and the resulting residue was distilled under reduced pressure to give 30.3 g (yield 70%) of product p-chlorophenylsulfur pentafluoride (3f); bp 61–64 °C/9.8 mmHg, purity 99.5% by GC.
5. Preparation of ArSF$_5$ from ArSF$_4$Cl with anhydrous hydrogen fluoride

\[
\text{ArSF}_4\text{Cl} \quad \xrightarrow{\text{HF}} \quad \text{ArSF}_5 \\
\quad \quad (\text{KHF}_2)
\]

*Caution! Anhydrous hydrogen fluoride (bp 19 °C) is very toxic. The following experiment should be carried out in an efficient fume hood, and the experimenters should be familiar with the precautions necessary for safe handling of anhydrous hydrogen fluoride (For example, see Safetygram #29 on the Website of Air Products and Chemicals, Inc.).

A typical procedure: While N$_2$ gas was flowed through a 250 mL fluoropolymer (FEP) vessel set with a condenser (made of fluoropolymer), the vessel was cooled in a bath at –20 °C. A coolant (–15 °C) was flowed through the condenser. The vessel cooled to –20 °C was charged with 48 g (2.4 mol) of anhydrous hydrogen fluoride. Into the vessel, 8.6 g (0.11 mol) of potassium hydrogen difluoride (KHF$_2$) was added. While the vessel was warmed to +12 °C, 22.1 g (96.2 mmol) of trans-phenylsulfur chlorotetrafluoride (2a) [purity 96 wt %: Note; impurity (4 wt %) was phenylsulfur trifluoride] was added over 1 hour by a syringe pump. The molar ratio of 2a/hydrogen fluoride/KHF$_2$ was 1/25/1.1. The reaction mixture was then stirred at 15 °C for 18 h. After that, the reaction mixture was warmed to 25 °C and hydrogen fluoride was removed at that temperature under atmospheric pressure. The residue was neutralized with 15% aqueous KOH and extracted with dichloromethane. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated by distilling the solvent at 75 °C under atmospheric pressure. The resulting residue was distilled under reduced pressure (35 mmHg and bath temperature about 106–140 °C) to give 14.4 g (yield 73%) of phenylsulfur pentafluoride (3a). The purity of the product was determined to be 100 % by GC analysis. The product was identified by spectral comparison with an authentic sample.

The reaction conditions and results for the fluorinations with anhydrous hydrogen fluoride are shown in Table 5 (Text).

6. Preparation of PhSF$_5$ from PhSF$_4$Cl with 70 wt % HF-pyridine

Under nitrogen, phenylsulfur chlorotetrafluoride (2a) (32.4 g, 141 mmol) [purity 96 wt %; the impurity (4 wt %) was phenylsulfur trifluoride] was added over 1 hour by syringe pump into a stirred liquid (38.2 mL) of 70 wt % HF-pyridine (available from Sigma-Aldrich) in a fluoropolymer vessel heated in an oil bath at 55 °C. After the addition, the reaction mixture was stirred for an additional 2 h at that temperature (55 °C) and cooled to room temperature. $^{19}$F NMR of the reaction mixture showed that the starting material 2a was consumed. The reaction mixture was slowly poured into a stirred, cooled 25% aq. KOH solution (KOH, 104 g). The resulting alkaline solution was extracted with
dichloromethane and the organic layer was separated, washed with water, 2 M aq. HCl, and water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated at atmospheric pressure and then distilled at reduced pressure to give 18.1 g (63%) of phenylsulfur pentafluoride (3a); bp 62 °C/44 mmHg. Its purity was determined to be 100% by GC.

As another experiment, 32.4 g (141 mmol) (purity 96 wt %) of 2a was mixed with 38.2 mL of 70 wt % HF-pyridine in a fluoropolymer vessel at room temperature under nitrogen, and the stirred mixture was heated at 50 °C (oil bath temperature) for 6 h. The mixture was then cooled to room temperature. The reaction mixture was treated in a similar way as above and 16.4 g (57%) of product 3a was obtained after the distillation.

### 7. Preparation of polyfluorinated ArSF5 with SbF3/SbF5 or SbCl5

\[
(F)_n\text{ArSF}_4\text{Cl} \xrightarrow{\text{SbF}_3/\text{SbF}_5(\text{SbCl}_5)} (F)_n\text{ArSF}_5
\]

A typical procedure [S4]: A 100 mL fluoropolymer (PFA) reactor with a magnetic stir bar was charged with SbF5 (6.59 g, 30.4 mmol), Fluorinart® FC-72 (40 mL), and SbF3 (5.72 g, 32 mmol) in a dry box, and then transferred to a fume hood. Pentafluorophenylsulfur chlorotetrafluoride (2o) (9.41 g, 30.3 mmol) was then added by syringe slowly at room temperature with vigorous stirring. The mixture was stirred at room temperature for 1 hour and quenched with potassium fluoride (powder). The reaction mixture was then filtered and fractional distillation of the filtrate was carried out to give 6.24 g (71%) of pentafluorophenylsulfur pentafluoride (3o).

The reaction conditions and results for products 3l–n are shown in Table 6 (Text). The boiling points and spectral data of products 3l–o and spectral data of a byproduct, 3-chloro-2,4,6-trifluorophenylsulfur pentafluoride (see Text), are shown below. The byproduct was obtained as a mixture with product 3m when 2m was treated with SbF5 alone.

**2,3,6-Trifluorophenylsulfur pentafluoride (3l) [S4]:** bp 154–156 °C; \(^1\)H NMR (CDCl3) \(\delta\) 7.38 (m, 1H), 7.02 (m, 1H); \(^19\)F NMR (CDCl3) \(\delta\) 75.5–77.6 (m, 1F), 72.6–73.6 (m, 4F), −110.0 (m, 1F), −127.8 (m, 1F), −138.0 (m, 1F); \(^13\)C NMR (CDCl3) \(\delta\) 152.7 (d, \(J = 259.4\) Hz), 147.6 (ddd, \(J = 249.3, 14.5, 4.3\) Hz), 146.4 (ddt, \(J = 264.4, 16.6, 2.2\) Hz), 130.3 (m), 120.6 (ddd, \(J = 19.5, 10.8, 1.4\) Hz), 112.3 (dt, \(J = 26.7, 10.1\) Hz); IR (neat) 3115, 1623, 1605, 1500, 1253, 1203, 1134, 1021, 917, 867, 808, 685, 609, 577, 548 cm\(^{-1}\); GC-Mass m/z 258 (M\(^+\)). Anal. Calcd for C\(_6\)H\(_2\)F\(_8\)S: C, 27.92%, H, 0.78%. Found, C, 27.52%, H, 0.81%.

**2,4,6-Trifluorophenylsulfur pentafluoride (3m) [S4]:** bp 138–141 °C; \(^1\)H NMR (CDCl3) \(\delta\) 6.80 (t, \(J = 8.6\) Hz, 3.5-H); \(^19\)F NMR (CDCl3) \(\delta\) 78.7–75.3 (m, SF), 73.8–72.9 (m, SF\(_4\)), −100.6 (m, 4-F),
Ar(SF₄Cl)₂; ¹³C NMR (CDCl₃) δ 164.4 (dt, J = 257.9, 32.5 Hz), 158.4 (dm, J = 260.0 Hz), 126.2 (m), 101.9 (m); IR (neat) 3111, 1640, 1606, 1451, 1178, 1135, 1098, 1048, 1011, 870, 690, 625, 584, 556, 514 cm⁻¹; GC-Mass m/z 258 (M⁺). Anal. Calcd for C₆H₂F₈S; C, 27.92%, H, 0.78%. Found, C, 27.75%, H, 0.84%.

2,3,4,6-Tetrafluorophenylsulfur pentafluoride (3n) [S4]: bp 141–142 °C; ¹H NMR (CDCl₃) δ 6.9–7.0 (m); ¹⁹F NMR (CDCl₃) δ 75.1–77.3 (m, 1F), 73.3–74.3 (m, 4F), −107.5 (m, 1F), −124.1 (m, 1F), −125.0 (m, 1H), −160.6 (m, 1F); ¹³C NMR (CDCl₃) δ 152.7 (dm, J = 259 Hz), 148.0 (dm, J = 265 Hz), 137.6 (dm, J = 253 Hz), 126.8 (m), 102.2 (m); GC-Mass m/z 276 (M⁺). Anal. Calcd for C₆HF₉S; C, 26.10%, H, 0.37%. Found, C, 25.62%, H, 0.44%.

2,3,4,5,6-Pentafluorophenylsulfur pentafluoride (3o) [S3,4]: bp 135–137 °C; ¹⁹F NMR (CDCl₃) δ 74.8 (m, 5F, SF₅), −133.4 (m, 2F, 2,6-F), −146.2 (m, 1F, 4-F), −158.6 (m, 2F, 3,5-F); ¹³C NMR (CDCl₃) δ 143.6 (dm, J = 262 Hz), 137.9 (dm, J = 254 Hz), 126.7 (m); IR (neat) 1643, 1526, 1505, 1305, 1107, 1035, 1002, 874, 786, 685, 611, 574 cm⁻¹; GS-MS m/z 294 (M⁺). HRMS; found 293.956492 (calcd for C₆F₁₀S; 293.956104).

3-Chloro-2,4,6-trifluorophenylsulfur pentafluoride [S3]: ¹H NMR (CDCl₃) δ 6.95 (br.t, J = 9.5 Hz, 5-H); ¹⁹F NMR (CDCl₃) δ 78.7–75.3 (m, SF), 73.8–72.9 (m, SF₄), −101.3 (m, 2 or 6-F), −102.3 (m, 4-F), −102.6 (m, 2 or 6-F); GC-Mass m/z 294, 292 (M⁺).

8. Preparation of aryl bis- and tris(sulfur pentafluorides), Ar(SF₅)n (n = 2, 3) with SbF₅

8-1. Preparation of aryl bis(sulfur pentafluorides)

Ar(SF₄Cl)₂  SbF₅ → Ar(SF₅)₂

A typical procedure: A fluoropolymer (PFA) vessel was set up with a magnetic stirrer, septum, and nitrogen blanket, charged with 35 mL of dry dichloromethane, and cooled in a bath to approximately −25 °C. SbF₅ (1.5 mL, 21.4 mmol) was then added by syringe. After holding for 5–10 min, the clear golden solution was then cooled to −85 °C over 30 min. A solution of 3.92 g (10.8 mmol) of phenyl-1,3-bis(sulfur chlorotetrafluoride) (2p⁺) in 10 mL of dry dichloromethane was then added by syringe. Over 2.5 h the temperature of the stirred solution was allowed to rise to −25 °C, at which time the reaction was carefully quenched by adding KF (total 4 g) in portions. Cooling was removed, 2 g of celite was added to the mixture, and the mixture was stirred while being warmed to room temperature. After suction filtration, solvents were removed by evaporator and the residue was column chromatographed on silica gel (20 g) using pentane as an eluent to give 2.02 g (57%) of phenyl-1,3-
bis(sulfur pentafluoride) (3p") as white crystals. The reaction conditions and results for others are shown in Table 7 (Text). The physical and spectral data of new compounds are shown below.

Phenyl-1,3-bis(sulfur pentafluoride) (3p") [S5]: mp 62.0–62.8 °C (in a sealed capillary); $^1$H NMR (CDCl$_3$) δ 8.16 (t, $J = 2.0$ Hz, 1H, 2-H), 7.93 (dd, $J = 8.2$, 2.0 Hz, 2H, 4.6-H), 7.63 (t, $J = 8.2$ Hz, 1H, 5-H); $^{19}$F NMR (CDCl$_3$) δ 81.88 (quintet, $J = 150.4$ Hz, 2F, 2xSF$_4$), 62.95 (d, $J = 150.4$ Hz, 8F, 2xSF$_4$); $^{13}$C NMR (CDCl$_3$) δ 153.7 (quintet, $J = 19.1$ Hz), 129.5, 129.3 (t, $J = 4.7$ Hz), 124.3 (m); GC-Mass $m/z$ 330 (M$^+$). Anal. Calcd for C$_6$H$_4$F$_{10}$S; C, 21.82%, H, 1.22%. Found, C, 21.79%, H, 1.52%.

Phenyl-1,4-bis(sulfur pentafluoride) (3q") [S5]: mp 108.8–109.7 °C; $^1$H NMR (CDCl$_3$) δ 7.88 (s, 4H); $^{19}$F NMR (CDCl$_3$) δ 81.68 (quintet, $J = 150.3$ Hz, 2F), 62.55 (d, $J = 150.3$ Hz, 8F); $^{13}$C NMR (CDCl$_3$) δ 155.5 (quintet, $J = 19.0$ Hz), 126.9 (m); GC-Mass $m/z$ 330 (M$^+$). Anal. Calcd for C$_6$H$_4$F$_{10}$S; C, 21.82%, H, 1.22%. Found, C, 21.59%, H, 1.23%.

5-Bromophenyl-1,3-bis(sulfur pentafluoride) (3r") [S5]: mp 65.9–66.4 °C (in a sealed capillary); $^1$H NMR δ (CDCl$_3$) 8.05–8.10 (m); $^{19}$F NMR (CDCl$_3$) δ 80.49 (quintet, $J = 151.2$ Hz, 2F), 63.24 (d, $J = 151.2$ Hz, 8F); $^{13}$C NMR (CDCl$_3$) δ 154.2 (quintet, $J = 20.2$ Hz), 132.4 (m), 123.0 (m), 122.5; IR (nujol) 1577, 1140, 867, 729, 662, 599, 574 cm$^{-1}$; GC-Mass $m/z$ 410(M$^+$), 408 (M$^+$). Anal. Calcd for C$_6$H$_3$BrF$_{10}$S; C, 17.62%, H, 0.74%. Found, C, 17.61%, H, 0.73%.

2,5-Difluorophenyl-1,4-bis(sulfur pentafluoride) (3s") [S5]: mp 73.0–74.6 °C; $^1$H NMR (CDCl$_3$) δ 7.67 (m, 2H); $^{19}$F NMR (CDCl$_3$) δ 76.3–78.5 (m, 2F), 67.71 (dd, $J = 152.3$, 24.8 Hz, 8F), $-$109.77 (m, 2F); $^{13}$C NMR (CDCl$_3$) δ 151.1 (d, $J = 262.3$ Hz), 142.8 (m), 118.5 (dm, $J = 26.0$ Hz); GC-Mass $m/z$ 366 (M$^+$). Anal. Calcd for C$_6$H$_2$F$_{12}$S; C, 19.68%, H, 0.55%. Found, C, 19.33%, H, 0.58%.

2,3,5,6-Tetrafluorophenyl-1,4-bis(sulfur pentafluoride) (3t") [S5]: mp 129.2–130.0 °C; $^{19}$F NMR (CDCl$_3$) δ 71.0–74.4 (m, 10F), $-$130.8 (m, 4F); $^{13}$C NMR (CDCl$_3$/FC-72/CF$_2$CICCl$_2$F=−5/2/3 v/v) δ 144.9 (m), 141.3 (m), 133.3 (m); GC-Mass $m/z$ 402 (M$^+$). Anal. Calcd for C$_6$F$_{14}$S; C, 17.92%, H, 0.00%. Found, C, 17.99%, H, <0.05%.

8-2. Preparation of phenyl-1,3,5-tris(sulfur pentafluoride) (3u")

\[
\begin{align*}
1,3,5-\text{Ph(SF}_4\text{Cl)}_3 + \text{SbF}_5 & \rightarrow 1,3,5-\text{Ph(SF}_5)_3 \\
2u' & \rightarrow 3u''
\end{align*}
\]

Procedure: A 500 mL fluoropolymer (PFA) jar (reactor) with septum, magnetic stirrer, nitrogen blanket, and cooling bath was set up and charged with 160 mL of dry dichloromethane. The reactor was cooled to −25 to −30 °C, and 67.5 mL (SbF$_5$, 99 mmol) of a solution of 17.4% (w/w) of SbF$_5$ in FC-72...
was introduced by syringe over 8 min. After holding at this temperature for approximately 7 min, the reaction mixture was cooled to –95 °C over 15 min. A solution of 16.0 g (32 mmol) of phenyl-1,3,5-tris(sulfur chlorotetrafluoride) (2u') in 50 mL of dry dichloromethane was introduced by syringe over 8 min as the temperature rose to –86 °C. The reaction mixture was allowed to warm to +7 °C over 6 h, at which time the reaction was quenched with the addition of KF (10 g) in portions over 20 min. Celite (5 g) was added, and the mixture was suction filtered. Solvents were removed by atmospheric fractional distillation to 70 °C leaving the crude residue as a yellow slush. The crude product was triturated with a minimum volume of ether and filtered to give a solid, which was then dried at room temperature in vacuum to give 8.03 g (55%) of product 3u". The physical and spectral data of 3u" are shown below.

**Phenyl-1,3,5-tris(sulfur pentafluoride) (3u")** [S5]: mp 132.8–133.5 °C (lit. [S6] 126–127 °C); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.31 (s); \(^{19}\)F NMR (CDCl\(_3\)) \(\delta\) 63.31 (dm, \(J = 151.8 \) Hz, 12F), 78.3–80.5 (m, 3F);
\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 153.7 (quintet, \(J = 21.3 \) Hz), 127.3 (m); GC-Mass \(m/z\) 456 (M\(^+\)). Anal. Calcd for \(\text{C}_6\text{H}_3\text{F}_{15}\text{S}_3\): C, 15.79%, H, 0.66%. Found, C, 15.48%, H, 0.62%.

**9. DSC measurement of arylsulfur chlorotetrafluorides**

For DSC analysis, three types of cells were used as shown below.

- Cell 1, a cell made of gold-coated stainless steel
- Cell 2, a cell made of stainless steel
- Cell 3, a cell made of stainless steel with a cap made of gold-coated copper

The analysis using Cells 1 and 2 was conducted by Kayaku Japan Ltd. with Rigaku DSC8230 instrument. We conducted the analysis using Cell 3 with Perkin Elmer Pyris 1. Samples were heated at 5 or 10 °C/min. The results are shown in Table S-2.
Phenylsulfur chlorotetrafluoride (2a), p-methylphenylsulfur chlorotetrafluoride (2b), p-tert-butylphenylsulfur chlorotetrafluoride (2c), p-fluorophenylsulfur chlorotetrafluoride (2d), p-chlorophenylsulfur chlorotetrafluoride (2f), p-bromophenylsulfur chlorotetrafluoride (2g), p-nitrophenylsulfur chlorotetrafluoride (2i), and p-(methanesulfonyl)phenylsulfur chlorotetrafluoride (2j) were used for the measurement. Crystalline 2c, 2g, 2i, and 2j were pure samples obtained by crystallization. Liquid 2a, 2b, 2d, and 2f (obtained by distillation) used were contaminated by the corresponding arylsulfur trifluorides (< ~10%). As the decomposition temperatures of these arylsulfur trifluorides are very high, at more than 270 °C [S7], it may be reasonable that the results obtained for 2a, 2b, 2d, and 2f were not influenced by the impurities, i.e., the arylsulfur trifluorides.

**Table S-2: Results of DSC measurement of Arylsulfur Chlorotetrafluorides.**

| Run | ArSF₄Cl | Decomposition° (– ΔH°) |
|-----|---------|------------------------|
|     |         | Cell 1 | Cell 2 | Cell 3 |
|     |         | Gold (on SS)cd | SSd,e | SS/Gold (on Cu)f |
| 1   | 2a      | 131 °C (347 J/g) | 190 °C (361 J/g) | 147 °C (505 J/g) |
| 2   | 2b      | 139 °C (343 J/g) | 185 °C (497 J/g) | 140 °C (401 J/g) |
| 3   | 2c      | – | – | 129 °C (380 J/g) |
| 4   | 2d      | 139 °C (291 J/g) | 197 °C (189 J/g) | – |
| 5   | 2f      | – | – | 159 °C (336 J/g) |
| 6   | 2g      | – | – | 167 °C (322 J/g) |
| 7   | 2i      | – | – | 187 °C (506 J/g) |
| 8   | 2j      | – | – | 179 °C (236 J/g) |

°Decomposition onset temperture. Exotherm. Gold-coated stainless steel (SS) cell was used. DSC data was measured by Kayaku Japan, Ltd. Samples were heated at 10 °C/min. A stainless steel (SS) cell was used. A cell made of stainless steel (SS) with a cap made of gold-coated copper was used. Samples 2a, 2f, 2i and 2j were heated at 10 °C/min and 2c and 2g were heated at 5 °C/min.
As seen from Table S-2, the decomposition onset temperature by DSC varied depending on the material of the cell. For example, DSC showed that 2a started to decompose at 190 °C in Cell 2 made of stainless steel (SS), but at 131 °C in Cell 1 made of gold-coated SS. It was a surprise that 2a decomposed at a temperature (131 °C), with much less reactive gold, which was much lower than that (190 °C) with reactive SS. This means that 2a reacted with both gold and SS metals of the cells. The observed higher decomposition temperature of SS than gold could probably be a matter of solid surface. The real thermal decomposition temperature of 2a should be higher than at least 190 °C, which was measured with the SS cell, rather than 131 °C measured with the gold-coated SS. This is in accordance with the fact that 2a was stable for 48 h at 150 °C in a Teflon tube that is inactive (see the Text). Thus, it has been concluded that any data (Table S-2) obtained by the DSC measurement did not provide the real thermal decomposition data of arylsulfur chlorotetrafluorides.

10. Preparation of starting materials 1j–n and 1r–u

10.1. Preparation of bis[4-(methanesulfonyl)phenyl] disulfide (1j)

Step 1: A 50 mL single-neck flask with magnetic stirrer and septum was flushed with nitrogen, and charged with sodium tert-butylthiolate (6.95 g, 62 mmol), dry N-methylpyrrolidinone (12 mL), and 4-chlorophenyl methyl sulfone (9.53 g, 50 mmol). The mixture was heated to 50 °C. An exothermic reaction occurred. GC/MS analysis verified complete conversion to the product in 2 h. The reaction mixture was quenched into dilute aq. HCl solution and a mixture of hexane and dichloromethane was added to the mixture. The organic layer was separated and stripped to yield an oil. This residue was then slurried in hexane plus water, and the precipitated solids were filtered and washed through water followed by hexane. The solids were then taken up in dichloromethane and the solution was dried over anhydrous magnesium sulfate, filtered and stripped to yield 10.5 g (93%) of 4-(tert-butylthio)phenyl methyl sulfone as white crystals: 1H NMR (CDCl3) δ 7.86–7.89 (d, 2H), 7.69–7.72 (d, 2H). 3.07 (s, 3H), 1.33 (s, 9H); GC-Mass m/z 244 (M+). Note: 4-(tert-butylthio)phenyl methyl sulfone is poorly soluble in hexane.
Step 2: A 500 mL single-neck flask was flushed with nitrogen, then charged with 4-(tert-butylthio)phenyl methyl sulfone (29.6 g, 0.12 mol) obtained by step 1, followed by dry, deoxygenated toluene (200 mL), and finally aluminium chloride (21.7 g, 0.16 mol). The reaction mixture was stirred at room temperature for 4 h under nitrogen. The reaction was quenched with aq. dilute HCl solution and a small amount of ether. The organic layer was separated and the aq. layer was extracted with hexane. The combined organic layer was washed with water and dried over anhydrous sodium sulfate, and filtered. The solvent of the filtrate was evaporated with a fractional column at elevated temperature (160 °C max) under atmospheric pressure, leaving a biphase oil, which solidified out upon brief freezing and agitation. The oily layer consisting of tert-butylated toluenes was removed by decantation. The solid was slurried in pentane, collected by filtration and dried in vacuum at room temperature, yielding 20.7 g (91%) of 4-(methanesulfonyl)thiophenol [S8] as a fine white powder: $^1$H NMR (CDCl$_3$) $\delta$ 7.77 (dm, $J = 8.6$ Hz, 2H), 7.39 (dm, $J = 8.6$ Hz, 2H), 3.71 (s, 1H), 3.02 (s, 3H); GC-Mass $m/z$ 188 (M$^+$).

Step 3: A flask was charged with 4-(methanesulfonyl)thiophenol (10.5 g, 56 mmol), dichloromethane (40 mL), heptane (70 mL), and acetic acid (30 mL). The flask was placed in an ambient water bath. Bromine (Br$_2$) (1.6 mL, 31.1 mmol) was then added in portions by syringe over a few minutes. Reaction was immediate and exothermic, the bromine color persisted at the end, and a thick precipitate immediately formed. After stirring for 3 h, the solvent was evaporated in vacuum. Ether and hexane were then added to the residue and the precipitate was filtered, washed with pentane, and dried in vacuum to give 10.1 g (97%) of bis[4-(methanesulfonyl)phenyl] disulfide (1j) [S9]: $^1$H NMR (CDCl$_3$) $\delta$ 7.88 (d, $J = 8.5$ Hz, 4H), 7.65 (d, $J = 8.5$ Hz, 4H), 3.04 (s, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 143, 139, 128, 127, 45; IR (nujol) 1579, 1299, 1150, 1089, 1070, 964, 826, 774, 730, 567, 529 cm$^{-1}$.

10-2. Preparation of polyfluorinated diaryl disulfides 1k–n

A typical procedure: A two-liter three-neck flask was set up with magnetic stirring, chiller, N$_2$ flow, thermometer, and condenser. It was charged with 1,3,5-trifluorobenzene (97.8 g, 0.74 mol) and dry THF (800 mL), and cooled to –40 °C under nitrogen. $n$-Butyllithium (1.6 N in hexane) (463 mL, 0.74 mol) was then added in portions by syringe over several hours, with the temperature maintained below –30 °C, after which it was stirred for an additional half hour at –30 °C. Powdered elemental sulfur (23.7 g, 0.74 mol) was then added in portions over 1–2 h, with the temperature maintained below –30 °C. The solution became clear yellow. It was then allowed to room temperature with stirring under
nitrogen overnight. The flask was then transferred to an oil bath and heated under reflux under nitrogen flow to remove 600 mL of the solvent. The reaction was cooled below 0 °C and a solution of K$_3$Fe(CN)$_6$ (244 g, 0.74 mol) in 800 mL of water was then added by addition funnel over 2 h, with the temperature maintained below 5 °C. A thick yellow precipitate formed. Water and ether were then added until two clear phases resulted. The organic phase was separated, washed with dilute brine, dried over anhydrous magnesium sulfate, filtered and stripped to give 108 g of crude product 1m, which was flash vacuum distilled (85–105 °C/0.033 – 0.047 mmHg) to give 90.6 g (overall 75%) of pure 1m. The product was analyzed by TLC, GC/MS, and NMR as pure.

Bis(2,4,6-trifluorophenyl) disulfide (1m)\[S10]\]: 1H NMR (CDCl$_3$) δ 6.67–6.76 (m); 19F NMR (CDCl$_3$) δ −100.32 (s, 4F), −102.31 (s, 2F); GC-Mass m/z 326 (M$^+$).

In the same way as for 1m, bis(2,6-difluorophenyl) disulfide (1k), bis(2,3,6-trifluorophenyl) disulfide (1l), and bis(2,3,4,6-tetrafluorophenyl) disulfide (1n) were prepared from 1,3-difluorobenzene, 1,2,4-trifluorobenzene, and 1,2,3,5-tetrafluorobenzene, in overall 86%, 66%, and 82% yields, respectively.

Bis(2,6-difluorophenyl) disulfide (1k) [S11]: 1H NMR (CDCl$_3$) δ 7.35 (m, 2H), 6.93 (m, 4H); 19F NMR (CDCl$_3$) δ −103.84 (s); GC-Mass m/z 290 (M$^+$).

Bis(2,3,6-trifluorophenyl) disulfide (1l): 1H NMR (CDCl$_3$) δ 7.2 (m, 2H), 6.9 (m, 2H); 19F NMR (CDCl$_3$) δ −109.21 (m, 2F), −126 (dd, 2H), −140 (m, 2H); GC-Mass m/z 326 (M$^+$).

Bis(2,3,4,6-tetrafluorophenyl) disulfide (1n): 1H NMR (CDCl$_3$) δ 6.86 (m); 19F NMR (CDCl$_3$) δ −107.1 (m, 1F), −123.4 (m, 1F), −125.9 (m, 1F), −161.8 (m, 1F); GC-Mass m/z 362 (M$^+$).

10-3. Preparation of aryl dithols 1r–t

10-3-1. Preparation of 5-bromobenzene-1,3-dithiol (1r)

\[
\begin{array}{c}
\text{Br} & \text{F} & \text{Br} \\
\text{F} & \text{F} & \text{S} \\
\end{array} \\
\text{Step 1} \quad \text{t-BuSNa NMP} \\
\begin{array}{c}
\text{Br} & \text{F} & \text{S} \\
\text{S} & \text{S} & \text{Br} \\
\text{Step 2} \quad \text{AlCl$_3$ toluene} \\
\end{array} \\
\text{1r}
\]

\textbf{Step 1}: A 1 liter flask was charged with 1-bromo-3,5-difluorobenzene (67.3 g, 0.349 mol) and dry N-methylpyrrolidinone (300 mL), and sodium tert-butylthiolate (90.5 g, 0.81 mol) was added in portions. The reaction was stirred in the ice bath and warmed to room temperature overnight. The mixture was quenched with dilute aq. HCl, aq. NaCl, hexane, and ether. The phases were separated, and the aqueous layer was extracted again. The combined organic layer was washed once with aq. NaHCO$_3$, ...
dried over Na$_2$SO$_4$, and filtered. Evaporation of solvent from the filtrate gave the crude solid product, 116.8 g. Crystallization from hexane (200 mL) gave 98.6 g (85%) of 1,3-bis(tert-butylthio)-5-bromobenzene as white crystals. GC showed 99+% purity. $^1$H NMR (CDCl$_3$) $\delta$ 7.64 (m, 1H), 7.68 (m, 2H), 1.29 (s, 18H); GC-Mass m/z 334, 332 (M$^+$).

Note: When the reaction was conducted using 1,3,5-tribromobenzene instead of 5-bromo-1,3-difluorobenzene in a way that sodium tert-butylthiolate was added stepwise, the product 1,3-bis(tert-butylthio)-5-bromobenzene was obtained in 72% yield.

Step 2: A 1 liter flask was charged with 1,3-bis(tert-butylthio)-5-bromobenzene (98.5 g, 0.295 mol) and dry deoxygenated toluene (700 mL). AlCl$_3$ (7.02 g, 0.0526 mol) was then quickly added into the mixture keeping a nitrogen blanket. After stirring at room temperature for 65 h, the reaction was quenched and agitated with 1N aq. HCl, aq. NaCl and pentane. The organic layer was separated, washed once with aq. NaCl, dried over MgSO$_4$, and filtered. Evaporation of the solvent from the filtrate under reduced pressure by heating gave a residue, which solidified into a white solid mass (66.9 g) on cooling. The solid was triturated in pentane, filtered, and dried in vacuum to give 57.8 g (88%) of 5-bromobenzene-1,3-dithiol (1r) [S12]. GC showed 99+% purity. $^1$H NMR (CDCl$_3$) $\delta$ 7.08 (m, 1H), 7.19 (m, 2H), 3.46 (s, 2H); GC-Mass m/z 222, 220 (M$^+$).

10-3-2. Preparation of 2,5-difluorobenzene-1,4-dithiol (1s)

$$
\begin{array}{c}
\text{F} & \text{F} \\
\text{F} \searrow \text{S} \nearrow \text{F} \\
\text{F} & \text{F}
\end{array}
\xrightarrow{\text{Step 1}}
\begin{array}{c}
\text{F} & \text{F} \\
\text{S} \searrow \text{S} \nearrow \text{F} \\
\text{F} & \text{F}
\end{array}
\xrightarrow{\text{Step 2}}
\begin{array}{c}
\text{F} & \text{F} \\
\text{S} \searrow \text{S} \nearrow \text{F} \\
\text{F} & \text{F}
\end{array}
$$

1s

Step 1: A 100 mL flask was charged with sodium tert-butylthiolate (35.9 g, 0.32 mol) and dry N-methylpyrrolidinone (160 mL), and the mixture was stirred under nitrogen for a few minutes. 1,2,4,5-Tetrafluorobenzene (23.6 g, 0.16 mol) was then introduced in one portion, slowly, by syringe. After a few minutes a strong exotherm was noted, and the mixture was allowed to come to room temperature under stirring for 1 day. The reaction was quenched and agitated with dilute aq. HCl, aq. NaCl, and hexane plus a small amount of diethyl ether. The organic phase was separated, dried over Na$_2$SO$_4$, filtered and evaporated to give the product as a fine white powder, 40.5 g (87% yield), which was analyzed by GC as 98+% purity. 1,4-Bis(tert-butylthio)-2,5-difluorobenzene [S13]: $^1$H NMR (CDCl$_3$) $\delta$ 7.30 (dt, 2H), 1.33 (s, 18H); $^{19}$F NMR (CDCl$_3$) $\delta$ $-110.42$ (t); $^{13}$C NMR (CDCl$_3$) $\delta$ 160.8 (d), 157.5 (d), 125.7 (dt), 123.0 (dd), 48.2 (s), 31.1 (s); GC-Mass m/z 290 (M$^+$).
Step 2: 1,4-Bis(tert-butylthio)-2,5-difluorobenzene (39.7 g, 0.137 mol) was placed in a flask with 150 mL dry deoxygenated toluene and AlCl₃ (4.1 g, 0.031 mol). The reaction mixture was stirred for 2 days. The reaction was quenched and agitated with dilute aq. HCl, aq. NaCl, and ether. The organic layer was separated, washed with aq. NaCl, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated and distilled. In order to remove tert-butyltoluenes, the distillate was chromatographed with a short column of silica gel with pentane and then dichloromethane as eluents to give 14.6 g (60%) of 2,5-difluorobenzene-1,4-dithiol (1t). An analytical sample was obtained by recrystallization from pentane/dichloromethane; mp 59.9–61.1 °C; ¹H NMR (CDCl₃) δ 7.01 (t, J = 7.4 Hz, 2H), 3.61 (s, 2H); ¹⁹F NMR (CDCl₃) δ −115.40 (t, J = 7.4 Hz); ¹³C NMR (CDCl₃) δ 154.9 (dd, J = 242.8 Hz, 3.6 Hz), 116.5–118.2 (m); IR (nujol) 2572, 2530, 1281, 1181, 873, 777, 559 cm⁻¹; GC-Mass m/z 178 (M⁺). Anal. Calcd for C₆H₄F₂S₂: C, 40.43%, H, 2.26%. Found, C, 40.55%, H, 2.26%.

10-3-3. Preparation of 1,2,4,5-tetrafluorobenzene-1,4-dithiol (1t)

Step 1: A 250 mL flask was charged with hexafluorobenzene (9.38 g, 0.05 mol) and diethyl ether (120 mL). Sodium isopropylthiolate (9.95 g, 0.10 mol) was added and the white slurry was stirred at room temperature for 2 days. A small amount of pentane was added and the reaction quenched with dilute aq. HCl to a pH of 5–6. The separated aqueous phase was extracted twice with diethyl ether, and the combined ether phases washed once with aq. sodium bicarbonate, dried over Na₂SO₄, filtered and evaporated to give a residue (12.7 g), which was dissolved in 20 mL pentane, and the solution was placed in a freezer overnight. The thick crop of resulting crystals was separated by efficient decantation, and then dried at room temperature in vacuum to give 10.7 g (71% yield) of 1,4-bis(isopropylthio)-2,3,5,6-tetrafluorobenzene [S14] as large needles. ¹H NMR (CDCl₃) δ 3.54 (septet, 2H), 1.28 (d, 12H); ¹⁹F NMR (CDCl₃) δ −132.84 (s); ¹³C NMR (CDCl₃) δ 148.9 (m), 145.5 (m), 114.3 (m), 39.1 (s), 23.3 (s); GC-MS m/z 298 (M⁺).

Step 2: A 1 liter flask was charged with 1,4-bis(isopropylthio)-2,3,5,6-tetrafluorobenzene (55.9 g, 0.187 mol) and flushed with nitrogen. Dry, deoxygenated toluene (375 mL) was then added, maintaining nitrogen atmosphere. AlCl₃ (5.0 g, 0.037 mol) was added into the reaction mixture under nitrogen. An immediate red color developed along with a small white crystalline precipitate. The reaction was stirred at room temperature for 3 days. The reaction was quenched with dilute aq. HCl, aq.
NaCl, and ether, and the phases separated. The aqueous layer was extracted once with ether, and the combined organic phases washed once with dilute aq. NaCl, dried over Na$_2$SO$_4$, and filtered. After the removal of most volatiles on a rotovap, the residue solution was subjected to atmospheric distillation, raising the pot to a maximum of 230 °C until no more distillate came over. Upon cooling, crystals of the product appeared from the residue. The crystals were collected by suction filtration, washing through with a little pentane. An additional product was obtained by placing the filtrate in a freezer (−10 °C) overnight. The collected crystalline product was dried at 50 °C in vacuum (~1 mm Hg) for several hours, giving 29.9 g (74% yield) of 2,3,5,6-tetrafluorobenzene-1,4-dithiol (1t) [S15] as an off-white to light yellow crystalline solid: $^1$H NMR (CDCl$_3$) δ 3.67 (s); $^{19}$F NMR (CDCl$_3$) δ −136.83 (s); $^{13}$C NMR (CDCl$_3$) δ 145.1 (m), 141.9 (m), 108.3 (m); GC-MS m/z 214 (M$^+$).

10-4. Preparation of aryl trithiol 1u

Step 1: A 1 liter flask was charged with sodium tert-butylthiolate (81 g, 0.72 mol) and dry N-methylpyrrolidinone (200 mL). While the mixture was stirred, 1,3,5-trichlorobenzene (36.3 g, 0.20 mol) was added. The reaction mixture was then heated to 120 °C and stirred for 17 h at that temperature. The reaction was cooled and the solvent was removed by evaporation under reduced pressure on heating. The residue was dissolved in hexane and the hexane solution was washed with water and dried over magnesium sulfate, and filtered. Evaporation of the solvent from the filtrate gave a residue, which was then recrystallized from hexane to give 43.9 g (64%) of 1,3,5-tris(tert-butylthio)benzene; $^1$H NMR (CDCl$_3$) δ 7.74 (s, 3H), 1.29 (s, 27H); $^{13}$C NMR (CDCl$_3$) δ 146.3, 133.1, 46.6, 31.1; GC-MS m/z 342 (M$^+$).

Step 2: A 500 mL flask was charged with 1,3,5-tris(tert-butylthio)benzene (10.9 g, 31.8 mmol) and dry, deoxygenated toluene (250 mL), and finally AlCl$_3$ (2.81 g, 21 mmol). The reaction mixture was stirred at room temperature for 1 day. The reaction was quenched with dilute aq. HCl and ether, and the phases were seperated. The aqueous layer was extracted with pentane/ether, and the combined organic layer was washed with aq. NaCl, dried over magnesium sulfate, and filtered. Removal of the solvent including byproducts (tert-butylated toluenes) under reduced pressure on heating gave a residue, which solidified into a yellow crystal mass on cooling. The mass was then trituated in pentane and filtered to give 4.67 g (84%) of benzene-1,3,5-tri(thiol) (1u) as fine light yellow needles; mp 60.9–61.8 °C (lit. [S16] 59–60 °C). $^1$H NMR (CDCl$_3$) δ 6.94 (s, 3H), 3.41 (s, 3H); $^{13}$C NMR (CDCl$_3$) δ 133.2, 126.3.
11. References and Notes

S1. Robson, P.; Stacey, M.; Stephens, R.; Tatlow, J. C. J. Chem. Soc. 1960, 4754-4760.
S2. Maiolo, F.; Testaferri, L.; Tiecco, M.; Tingoli, M. J. Org. Chem. 1981, 46, 3070-3073.
S3. Umemoto, T. PCT Int. Appl. WO 2008/118787 A1; U.S. Pat. US 7,592,491; U.S. Pat. US 7,820,864; U.S. Pat. US 7,851,646.
S4. Umemoto, T. U.S. Pat. Appl. Publ. US 2010/0130790 A1.
S5. Umemoto, T. PCT Int. Appl. WO 2010/033930 A1.
S6. Wessel, J.; Hartl, H.; Seppelt, K. Chem. Ber. 1986, 119, 453-463.
S7. Umemoto, T.; Singh, R. P.; Xu, Y.; Saito, N. J. Am. Chem. Soc. 2010, 132, 18199-18205 and Supporting Information.
S8. Yates, J.; Haddock, E. GB Patent No. 1128217 (1968).
S9. Hynd, G.; Ray, N. C.; Finch, H.; Middlemiss, D.; Cramp, M. C.; Blaney, P. M.; Williams, K.; Griffon, Y.; Harrison, T. K.; Crackett, P. US Patent Application No. 2010/0010034.
S10. Sakagami, M.; Mano, S. Jpn Kokai Tokkyo Koho JP 2002-338748.
S11. Nishino, S.; Yoneda, Y.; Oda, H. Jpn Kokai Tokkyo Koho JP 2011-153094.
S12. commercially available from TCI America (B2655).
S13. Wang, Y.; Parkin, S. R.; Gierschner, J.; Watson, M. D. Org. Lett. 2008, 10, 3307-3310.
S14. Crowell, T. R.; Peach, M. E. J. Fluorine Chem. 1982, 21, 469-477.
S15. Mobbs, R. H. Chem. & Ind. (London) 1965, 36, 1562-1563.
S16. Dictionary of Organic Compounds Sixth Ed. Vol. 1, p. 585, Chapman & Hall (London): Commercially available from TCI America (B2656).
12. $^1$H, $^{19}$F, and $^{13}$C-NMR spectra of new products
\begin{align*}
\text{\textsuperscript{1}H NMR} \\
\text{Br--SF}_2\text{Cl} \\
\textit{trans} 2g
\end{align*}

\begin{align*}
\text{\textsuperscript{19}F NMR} \\
\text{Br--SF}_2\text{Cl} \\
\textit{trans} 2g
\end{align*}
$^1$H NMR

CIF$_2$S

$\text{SE}_2$Cl

trans 2p'

$^3$P NMR

CIF$_2$S

$\text{SF}_2$Cl

trans 2p'
$^1$H NMR

Br

$\text{SF}_2\text{Cl}$

trans $2\gamma$

$^1$F NMR

$\text{SF}_2\text{Cl}$

Br

trans $2\gamma$
$\text{CIF}_3\text{S}$

$\text{SF}_4\text{Cl}$

$\text{all trans-conformation}$

$\text{S}^\text{19F NMR}$

$\text{CIF}_3\text{S}$

$\text{SF}_4\text{Cl}$

$\text{all trans-conformation}$
$^{13}C$ NMR

**SFCl**

$\text{ClF}_2S\text{SF}_3^{\text{ClF}}$

trans-configuration

---

$^1H$ NMR

**F**

$\text{SF}_{3}$

3e

---

**Notes:**
- Spectra are provided for both $^{13}C$ and $^1H$ nuclear magnetic resonance (NMR) analysis.
- The structures and assignments indicate the presence of fluorine and sulfur atoms in the molecules.
- The trans-configuration is highlighted for the 2u' mode.

---

**References:**
- JEOL Spectrometer Specifications
- Chemical Shifts Database
3u

F

F

F

F

F

F

SF₃

3v

F

F

F

F

F

F

SF₃

X: parts per Million: 13C

X: parts per Million: 1H
