Supporting information for;

S(VI) Lewis Acids: Fluorosulfoxonium Cations

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1. Synthesis of Sulfur Compounds

1.1 General Experimental Procedure

All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (MBraun LABmaster SP dry box and Vacuum Atmospheres glovebox both equipped with a -35 °C freezer). Toluene, pentane, and dichloromethane (DCM) were collected from a Grubbs-type column system manufactured by Innovative Technology. These solvents, along with cyclohexane, were dried over 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating with 1050 W Haier microwave for 5 minutes and cooling under vacuum. The process was repeated until no further moisture was released upon heating. Benzene-d_6 and dichloromethane-d_2, purchased from Cambridge Isotope Laboratories, were degassed and stored over 4 Å molecular sieves in the glovebox for at least 8 h prior to use. Chloroform-d, purchased from Cambridge Isotope Laboratories, was degassed and dried over calcium hydride. Unless otherwise mentioned, reagents were purchased from Sigma Aldrich or TCI America and used without further purification. Dibenzothiophene sulfoxide[1] and $[SiEt_3{\bullet}tol][B(C_6F_5)_4]$[2] were prepared using literature methods. Combustion analyses were performed in-house employing a Flash 2000 from Thermo Instruments CHN Analyzer. Spectra were recorded on a Bruker Avance III 400 MHz, an Agilent DD2 500 MHz, and an Agilent DD2 600 MHz spectrometer and spectra were referenced to residual solvents of CD_2Cl_2 (^1H = 5.32 ppm; ^{13}C = 53.84 ppm), $CDCl_3$ (^1H = 7.26 ppm), or C_6D_6 (^1H = 7.16 ppm), or externally (^{11}B: $(Et_2O)BF_3$ (δ 0.00), ^{19}F: $CFCl_3$ (δ 0.00), ^{31}P: 85% H_3PO_4 (δ 0.00)). Chemical shifts (δ) are reported in ppm and the absolute values of the coupling constants (*J*) are in Hz. In some instances, signal and/or coupling assignment was derived from 2D NMR experiments.

1.2 Synthesis of [Ph(*p*-tol)SOF][B(C_6F_5)$_4$] (1)

Pentafluorosulfanylbenzene (143 mg, 0.7 mmol) in toluene (10 mL) was cooled to -35 °C, then $[SiEt_3{\bullet}tol][B(C_6F_5)_4]$ (619.3 mg, 0.7 mmol) in toluene (10 mL) was added to the former drop-wise. The solution turned red-orange immediately, and was warmed up to room temperature slowly over 3 hours before all volatiles were removed *in vacuo*, leaving a brown residue, which was first washed with pentane (2 x 5 mL) then re-dissolved in DCM and layered with cyclohexane. Letting the solution stand at room temperature for over 24 hours yielded a small crop of colorless crystals, which was confirmed to be the title compound by ^{19}F NMR spectroscopy and single crystal X-ray diffraction analysis. However, as this is only a minor product in a complicated reaction mixture, this species was not fully characterized by ^1H and ^{13}C NMR. **$^{19}F\{^1H\}$ NMR** (376 MHz, C_6D_6, 298 K): δ 33.4 (s, 1F, S-F), -132.0 (m, 8F, *o*-C_6F_5), -162.5 (t, 4F, $^3J_{F\text{-}F}$ = 26.0 Hz, *p*-C_6F_5), -166.5 (m, 8F, *m*-C_6F_5).

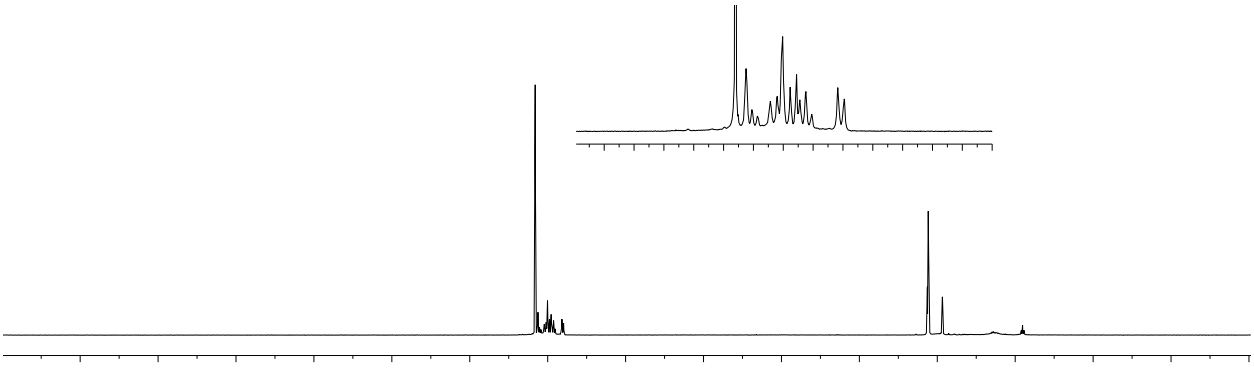


Figure S1. ^{1}H NMR Spectrum of **1**

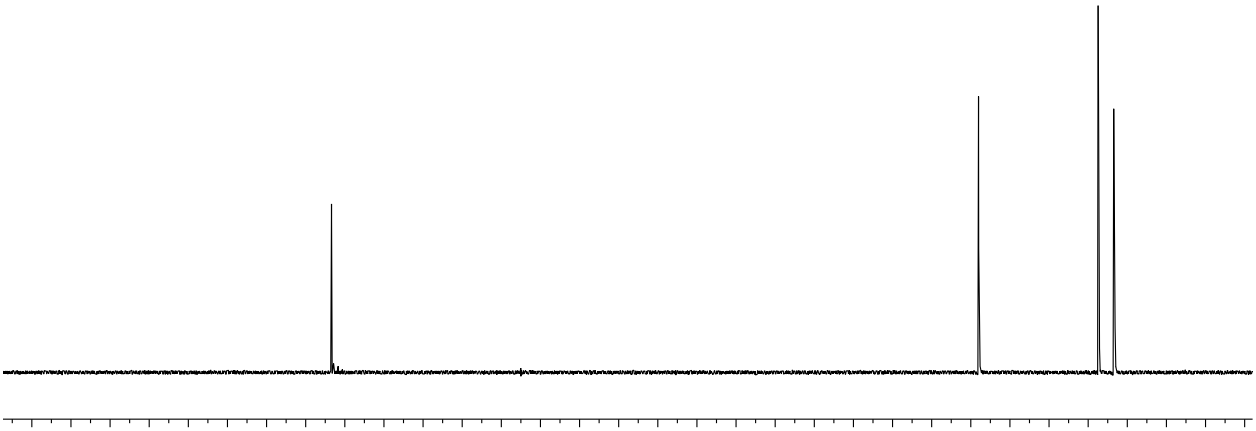
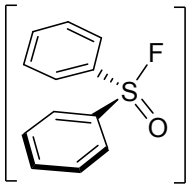


Figure S2. $^{19}F\{^{1}H\}$ NMR Spectrum of **1**

1.3 Preparation of Crystals of $C_{12}H_8SOF_2$ (3)

At room temperature, XeF_2 (15 mg, 0.089 mmol) was added as a solid to a solution of dibenzothiophene sulfoxide (17 mg, 0.085 mmol) and $[NEt_4][Cl]$ (3 mg, 0.02 mmol) in DCM (0.5 mL) in a 1 dram glass scintillation vial. The vial was placed in a 20 mL glass scintillation vial containing pentane (5 mL), which was then sealed to allow for slow pentane vapor diffusion into the DCM solution. Crystals of compound **3** were obtained after 24 hours and were suitable for X-ray crystallography.

1.4 Synthesis of $[Ph_2SOF][B(C_6F_5)_4]$ (4)



At room temperature, XeF_2 (168.3 mg, 0.9942 mmol) in DCM (5 mL) was added dropwise to a solution of diphenylsulfoxide (196.1 mg, 0.9695 mmol) in DCM (5 mL) in a Teflon vial charged with a stir bar. The solution remained clear and colourless and was allowed to stir for 24 hours at room temperature. All volatiles were then removed *in vacuo*, leaving behind a crystalline, colourless solid. The solid was then re-dissolved in toluene (5 mL) and cooled to -35 °C. Freshly prepared $[SiEt_3•tol][B(C_6F_5)_4]$ (840.0 mg, 0.95 mmol) in toluene (5 mL) was added to the above solution dropwise, leading to an immediate change of color of the solution to dark red/brown. The solution was allowed to warm to room temperature over 4 hours and then transferred to a glass scintillation vial. When the stirring was stopped the solution separated into two layers (colourless top layer and red bottom layer), the top layer was decanted using a pipette and the bottom layer was triturated 3 times using pentane to give **4** as a white powder (684.4 mg, 80% yield). Single crystals suitable for X-ray diffraction analysis were grown from a solution of **4** in DCM layered with cyclohexane. **^{1}H NMR** (600 MHz, CD_2Cl_2, 298 K): δ 8.24 (tm, $^3J_{H\text{-}H}$ = 7 Hz, 2H, *p*-Ph), 8.16 (d, $^3J_{H\text{-}H}$ = 8 Hz, 4H, *o*-Ph), 7.98 (tm, $^3J_{H\text{-}H}$ = 8 Hz, 4H, *m*-Ph). **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2, 298 K): δ ([$B(C_6F_5)_4$] peaks not included) 142.4 (s, *p*-Ph), 132.8 (s, *m*-Ph), 129.9 (s, *o*-Ph), 126.1 (d, $^3J_{C\text{-}F}$ = 11 Hz, *i*-Ph). **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2, 298 K): δ 32.2 (s, 1F, S-F), -133.1 (m, 8F, *o*-C_6F_5), -163.6 (t, 4F, $^3J_{F\text{-}F}$ = 19.8 Hz, *p*-C_6F_5), -167.5 (m, 8F, *m*-C_6F_5). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2, 298 K): δ -16.7 (s). Anal. Calc. for $C_{36}H_{10}BF_{21}OS$: C 48.03 %, H 1.12 %. Found: C 48.72%, H 1.47%.

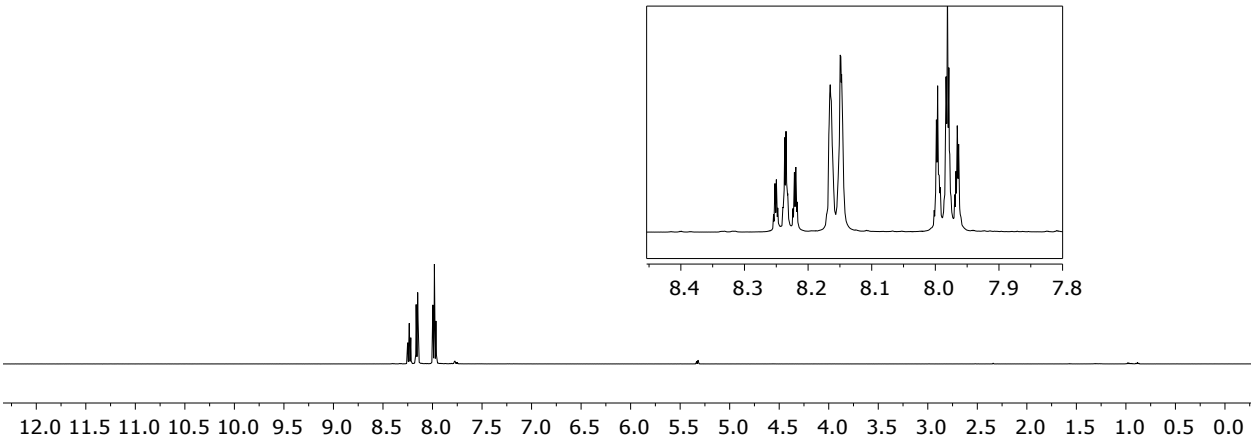


Figure S3. ^{1}H NMR Spectrum of **4**

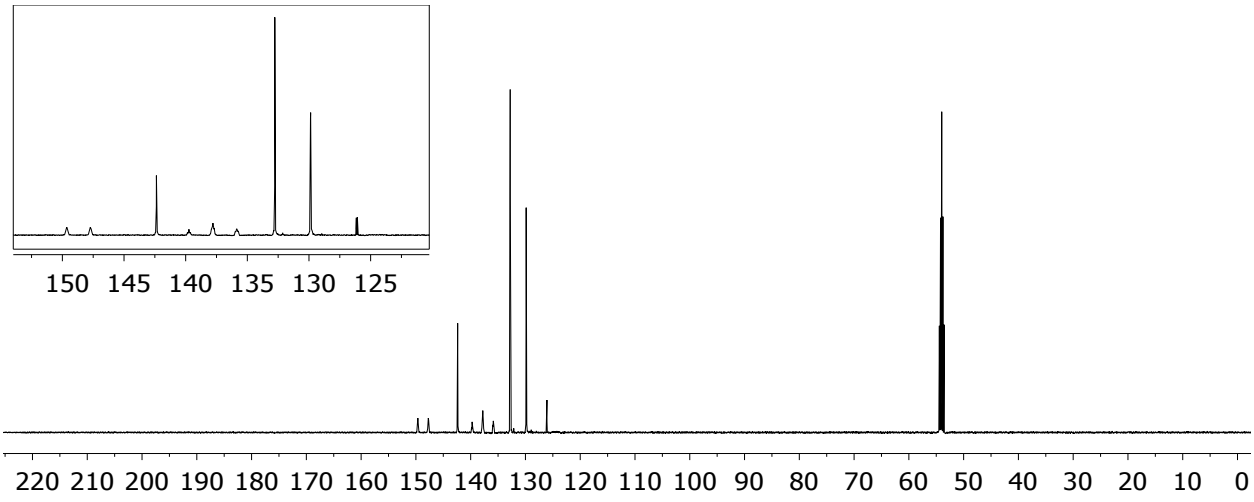


Figure S4. $^{13}C\{^{1}H\}$ NMR Spectrum of **4**

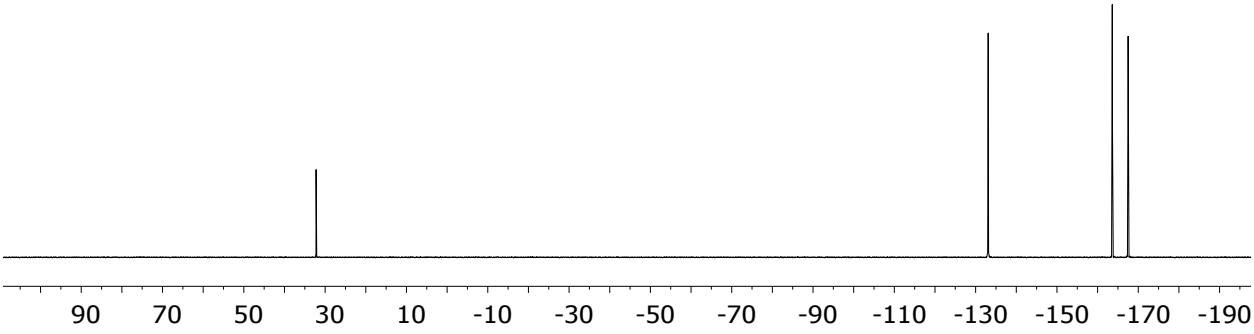


Figure S5. $^{19}F\{^{1}H\}$ NMR Spectrum of **4**

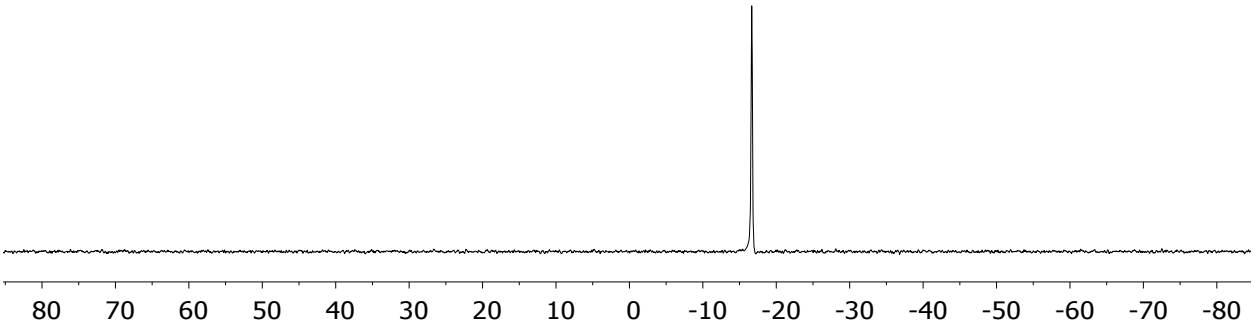
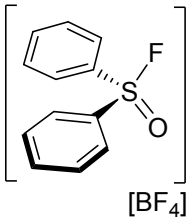


Figure S6. $^{11}B\{^{1}H\}$ NMR Spectrum of **4**

1.5 Synthesis of $[Ph_2SOF][BF_4]$ (5)



At room temperature, XeF_2 (46 mg, 0.27 mmol) in DCM (2 mL) was added dropwise to a solution of diphenylsulfoxide (55 mg, 0.27 mmol) in DCM (2 mL) in a Teflon vial charged with a stir bar. The solution remained clear and colourless and was allowed to stir for 24 hours at room temperature. All volatiles were then removed *in vacuo*, leaving behind a crystalline, colourless solid. The solid was then re-dissolved in toluene (2 mL) and cooled to -35 °C. $BF_3{\cdot}OEt_2$ (33 μL, 0.27 mmol) was added and the solution was stirred for two hours at room temperature. The pale yellow solution was transferred to a glass scintillation vial and the solvent was removed *in vacuo*. The solid was dissolved in DCM (2 mL) and crystals were obtained by slow pentane vapor diffusion in the DCM solution. The crystals were washed with pentane (3 x 2 mL) and dried *in vacuo* to give **5** as a colourless powder (65 mg, 79% yield). **^{1}H NMR** (400 MHz, CD_2Cl_2, 300 K): δ 8.40 (d, $^3J_{H\text{-}H}$ = 8 Hz, 4H, *o*-Ph), 8.19 (tm, $^3J_{H\text{-}H}$ = 8 Hz, 2H, *p*-Ph), 7.98 (tm, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, *m*-Ph). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 298 K): δ 141.9 (s, *p*-Ph), 132.7 (s, *m*-Ph), 130.6 (s, *o*-Ph), 127.0 (d, $^3J_{C\text{-}F}$ = 11 Hz, *i*-Ph). **^{19}F{^{1}H} NMR** (377 MHz, CD_2Cl_2, 300 K): δ 30.9 (s, 1F), -151.7 (s, 4F, BF_4). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2, 300 K): δ -1.0 (s). Anal. Calc. for $C_{36}H_{10}BF_{21}OS$: C 46.79 %, H 3.27 %. Found: C 46.81 %, H 3.34 %.

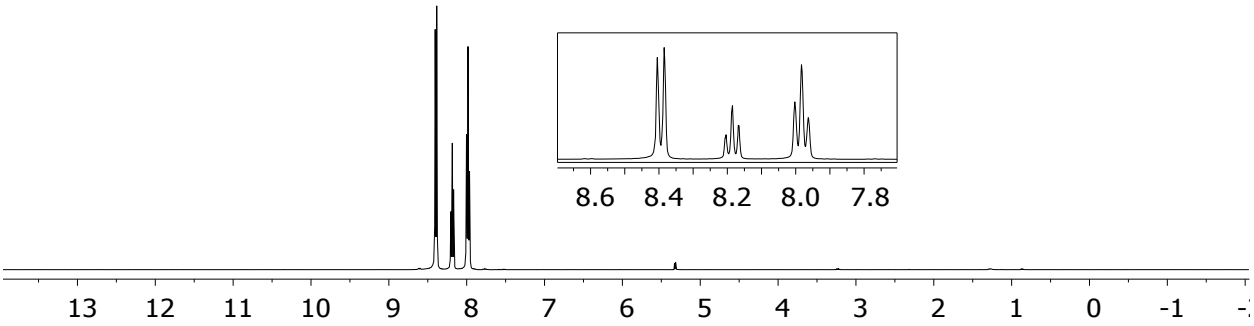


Figure S7. ^{1}H NMR Spectrum of **5**

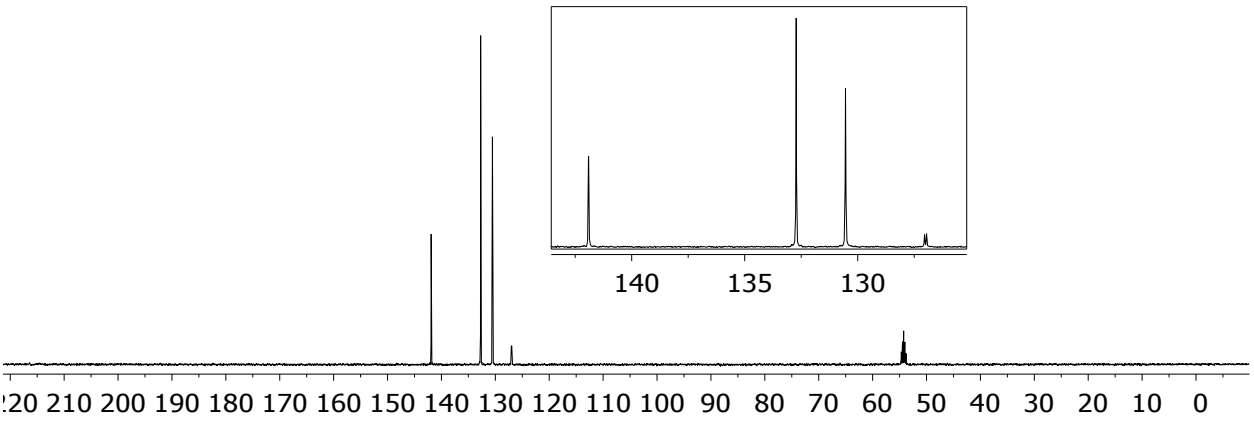


Figure S8. $^{13}C\{^{1}H\}$ NMR Spectrum of **5**

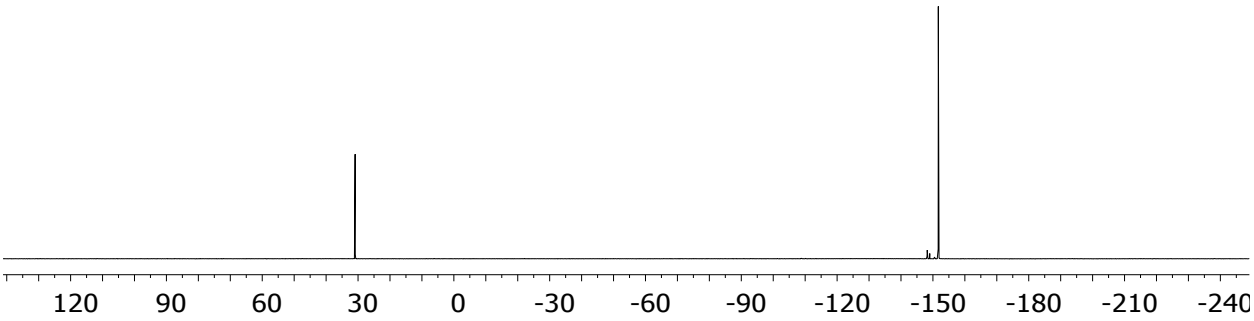


Figure S9. $^{19}F\{^{1}H\}$ NMR Spectrum of **5**

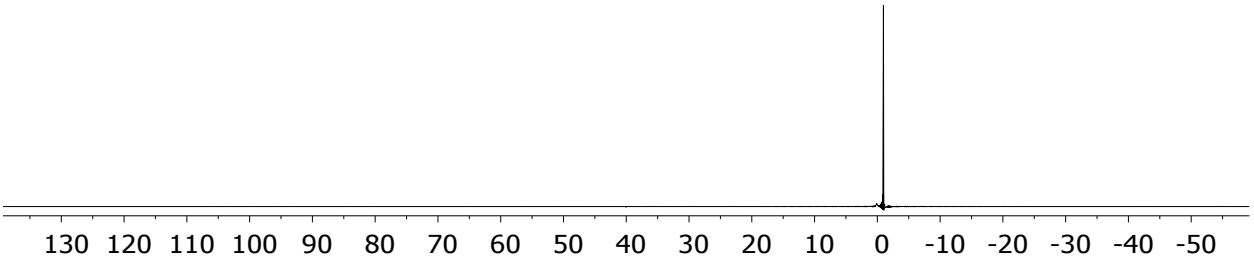
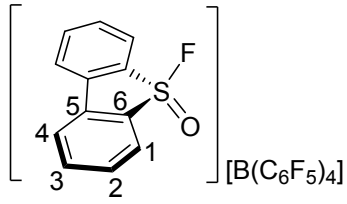


Figure S10. $^{11}B\{^{1}H\}$ NMR Spectrum of **5**

1.6 Synthesis of $[C_{12}H_8SOF][B(C_6F_5)_4]$ (6)



At room temperature, XeF_2 (85 mg, 0.50 mmol) was slowly added as a solid to a solution of dibenzothiophene sulfoxide (98 mg, 0.49 mmol) and $[NEt_4][Cl]$ (10 mg, 0.060 mmol) in DCM (5 mL) while stirring. The solution was stirred for 3 hours and the solvent was removed *in vacuo*. Toluene (5 mL) was added and the suspension was cooled to -35 °C. A -35 °C solution of freshly prepared $[SiEt_3•tol][B(C_6F_5)_4]$ (354 mg, 0.446 mmol) in toluene (5 mL) was slowly added and the resulting yellow solution was stirred for 10 minutes. The solvent was removed *in vacuo* and the crude mixture was recrystallized by layering a concentrated dichloromethane solution of the solid with pentane. The crystals were washed with pentane (3 x 3 mL) and all volatiles were removed *in vacuo* to obtain the product as a yellow powder of a 1:1 mixture of compound **6** and dibenzothiophene sulfone (258 mg, 65% yield). The crystals obtained from the recrystallization were suitable for X-ray crystallography. **^{1}H NMR** (400 MHz, CD_2Cl_2, 300 K): δ (Dibenzothiophene sulfone peaks not included) 8.35 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, H_4), 8.26 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, H_2), 8.14 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, H_1), 7.96 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, H_3). **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2, 298 K): δ ([$B(C_6F_5)_4$] and dibenzothiophene sulfone peaks not included) 144.7 (s, C_2), 135.8 (d, $^4J_{C\text{-}F}$ = Hz, C_5), 134.6 (s, C_3), 128.9 (s, C_4), 126.1 (s, C_1), 122.3 (d, $^3J_{C\text{-}F}$ = 3 Hz, C_6). **^{19}F{^{1}H} NMR** (377 MHz, CD_2Cl_2, 293 K): δ 24.9 (s, 1F, S-F), -133.1 (m, 8F, *o*-C_6F_5), -163.5 (t, 4F, $^3J_{F\text{-}F}$ = 20.3 Hz, *p*-C_6F_5), -167.4 (m, 8F, *m*-C_6F_5). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2, 293 K): δ -16.7 (s). Anal. Calc. for $(C_{36}H_8BF_{21}OS)•(C_{12}H_8O_2S)$: C 51.73 %, H 1.45 %. Found: C 50.18 %, H 1.38 %.

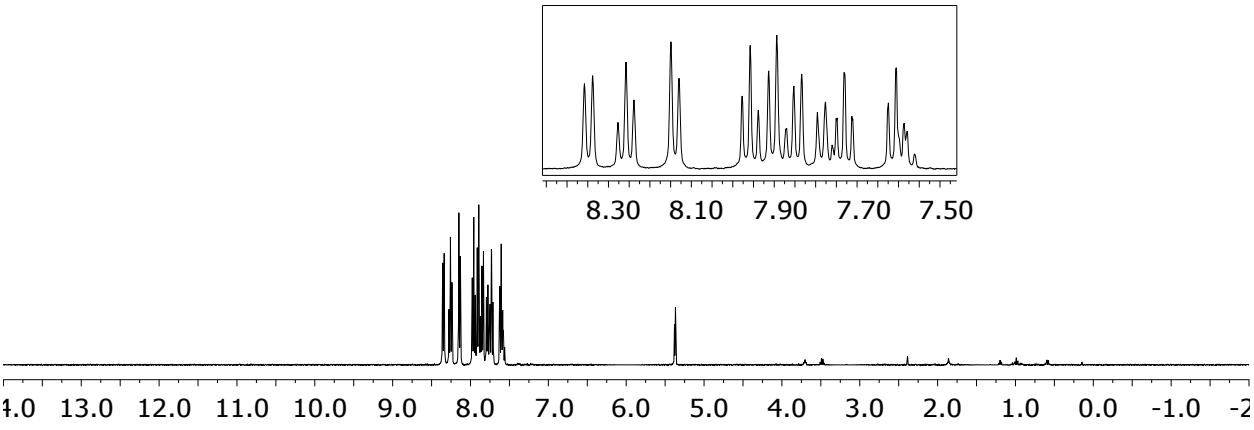


Figure S11. ^{1}H NMR Spectrum of **6**

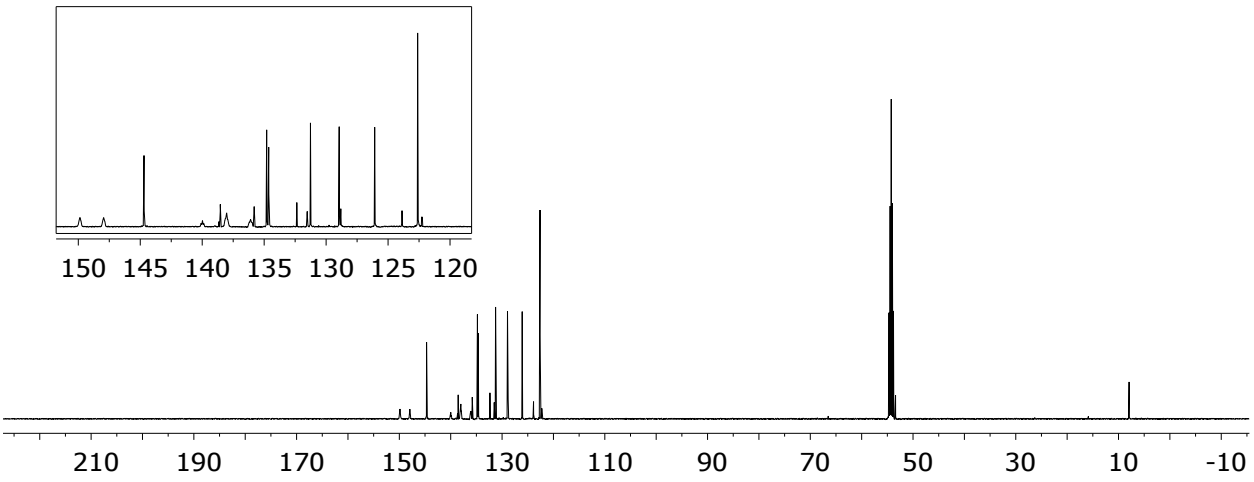


Figure S12. $^{13}C\{^{1}H\}$ NMR Spectrum of **6**

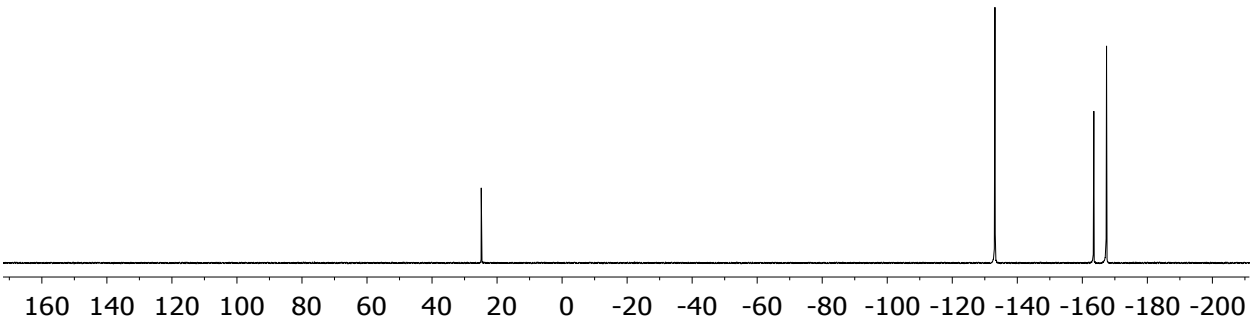


Figure S13. $^{19}F\{^{1}H\}$ NMR Spectrum of **6**

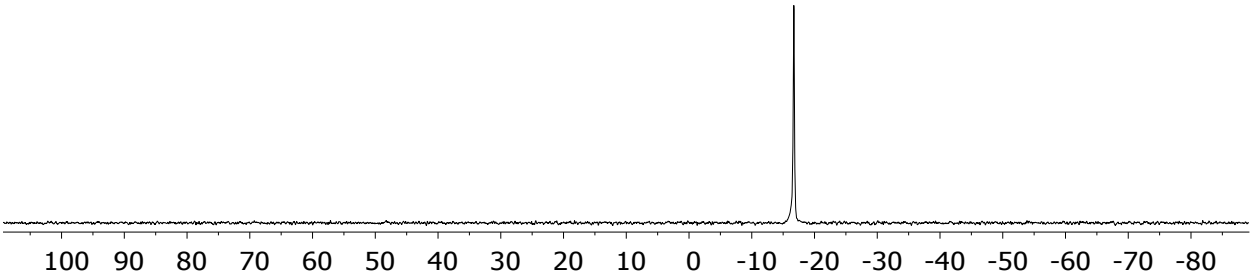
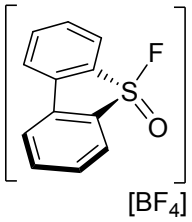


Figure S14. $^{11}B\{^{1}H\}$ NMR Spectrum of **6**

1.7 Synthesis of $[(C_{12}H_8)SOF][BF_4]$ (7)



Dibenzothiophene sulfoxide (60 mg, 0.30 mmol) and $[NEt_4][Cl]$ (7 mg, 0.04 mmol) were dissolved in 1 mL DCM. XeF_2 (54 mg, 0.32 mmol) was slowly added as a solid to the solution while stirring. After stirring for 3 hours, the solution was cooled to -35 °C and $BF_3{\cdot}OEt_2$ (37 µL, 0.30 mmol) was added to form a yellow precipitate. The slurry was stirred for 10 minutes. The solid was filtered, washed with DCM (3 x 1 mL), and dried *in vacuo* to give **7** as a yellow powder (76 mg, 83% yield). A saturated DCM solution of **7** was placed in a -35 °C freezer for 24 hours to obtain crystals suitable for X-ray crystallography. **^{1}H NMR** (400 MHz, CD_2Cl_2, 300 K): δ 8.39 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H), 8.30 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H), 8.26 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H), 7.93 (tm, $^3J_{H\text{-}H}$ = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 298 K): δ 144.7 (s), 134.5 (s), 129.1 (s), 126.7 (s), (2 of the peaks could not be located in the ^{13}C spectrum due to the decreased solubility of **7**). **^{19}F{^{1}H} NMR** (377 MHz, CD_2Cl_2, 298 K): δ 24.6 (s, 1F, S-F), -152.6 (s, 1F, BF_4). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2, 298 K): δ -1.1 (s). Anal. Calc. for $C_{12}H_8BF_5OS$: C 47.09 %, H 2.63 %. Found: C 46.86 %, H 2.55 %.

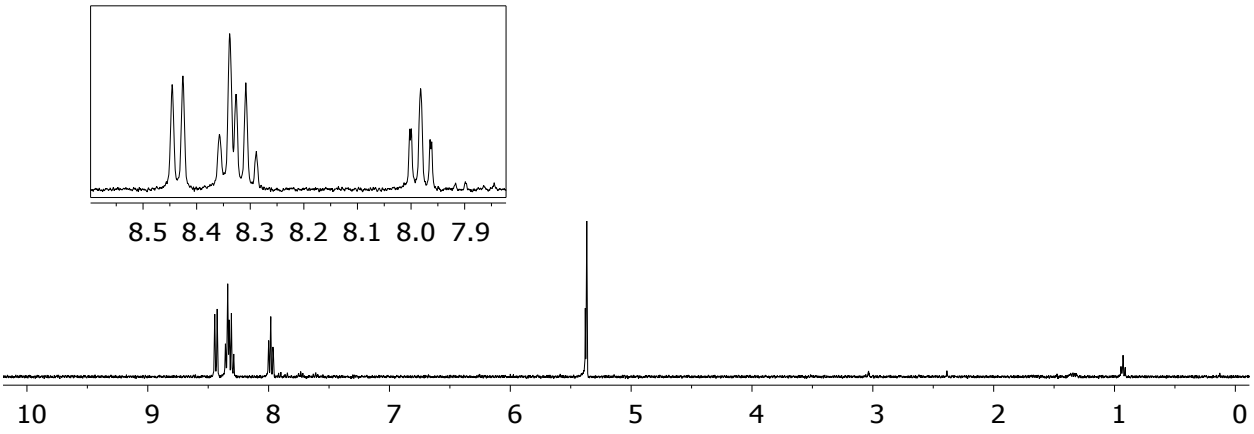


Figure S15. ^{1}H NMR Spectrum of **7**

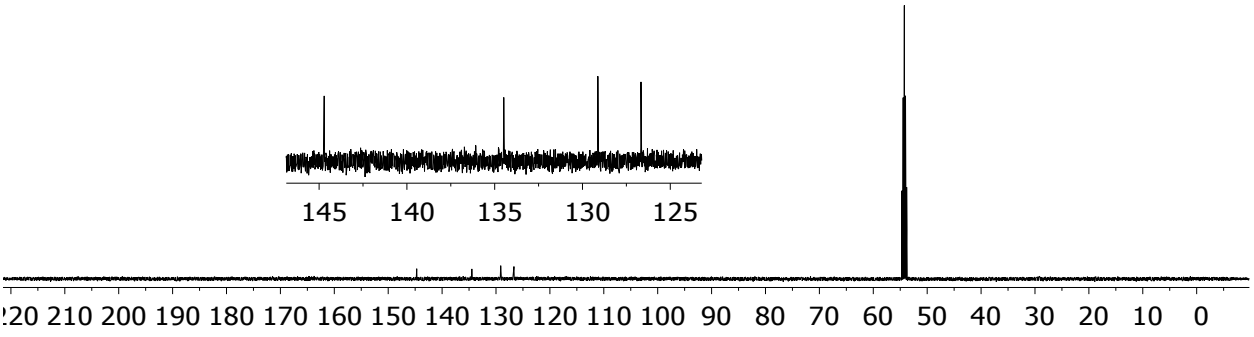


Figure S16. $^{13}C\{^{1}H\}$ NMR Spectrum of **7**

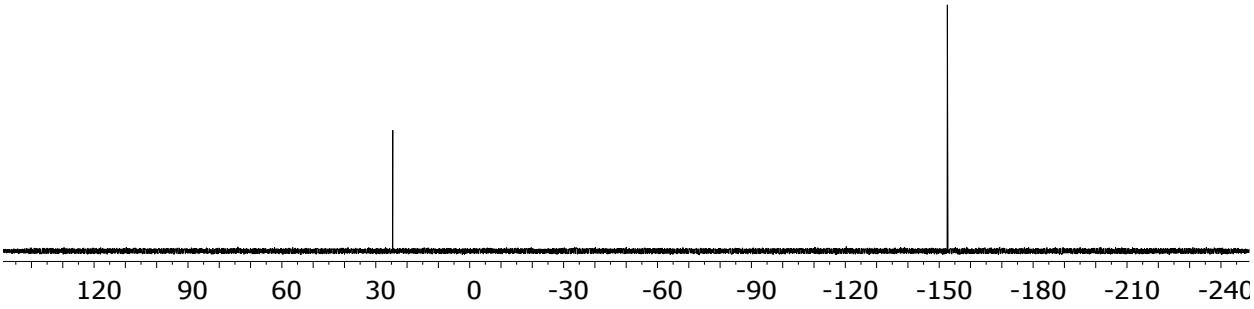


Figure S17. $^{19}F\{^{1}H\}$ NMR Spectrum of **7**

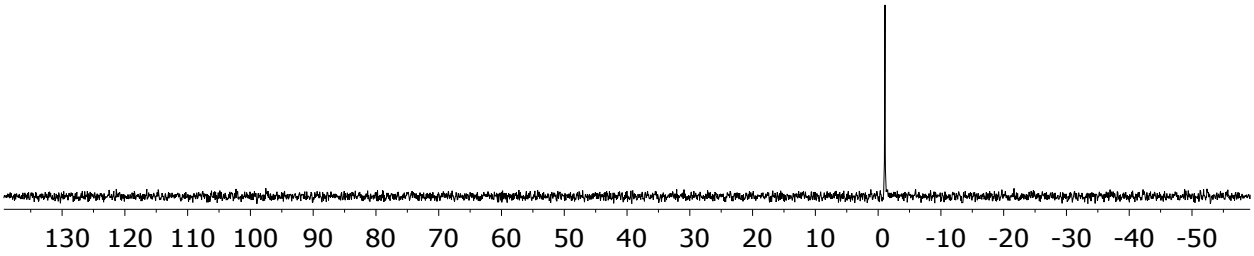


Figure S18. $^{11}B\{^{1}H\}$ NMR Spectrum of **7**

2. Gutmann-Beckett tests

2.1 Reaction of $[Ph_2SOF][B(C_6F_5)_4]$ (4) with Et_3PO

Compound **4** (42.7 mg, 0.047 mmol) and triethylphosphine oxide (2.1 mg, 0.015 mmol) were dissolved in CD_2Cl_2 (1 mL). The reaction mixture was investigated by ^{31}P NMR spectroscopy after one hour at room temperature. **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2, 298 K): δ 84.5 (s).

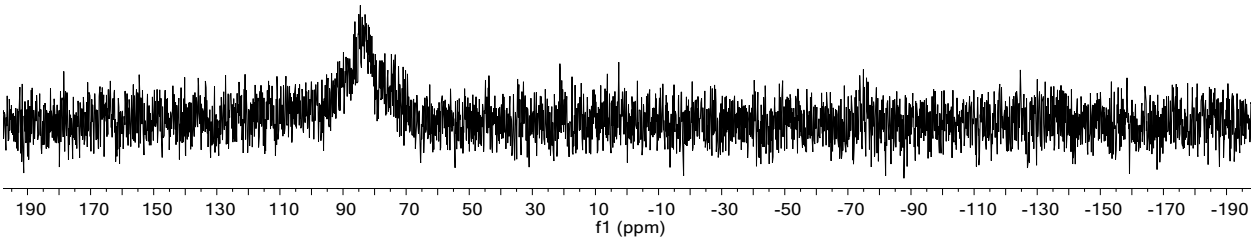


Figure S19. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture in CD_2Cl_2

2.2 Reaction of $[C_{12}H_8SOF][B(C_6F_5)_4]$ (6) with Et_3PO

Compound **6** (12 mg, 0.013 mmol) and triethylphosphine oxide (2 mg, 0.015 mmol) were dissolved in CD_2Cl_2 (1 mL). The formation of dibenzothiophene sulfoxide and $[Et_3PF][B(C_6F_5)_4]$[3] were observed in the ^1H and ^{31}P NMR spectra after one hour at room temperature. ^1H NMR (400 MHz, CD_2Cl_2, 298 K δ 7.83 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H), 7.78 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H), 7.65 (td, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}H}$ = 1 Hz, 2H), 7.54 (td, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}H}$ = 1 Hz, 2H). **$^{31}P\{^1H\}$ NMR** (162 MHz, CH_2Cl_2, 298 K): δ 147.8 (d, $^1J_{P\text{-}F}$ = 973 Hz).

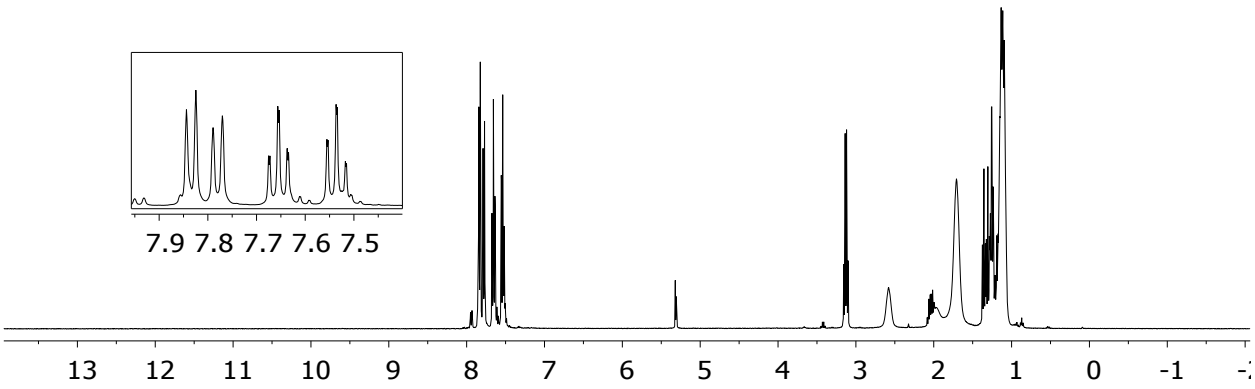


Figure 20. ^1H NMR spectrum of the reaction mixture in CD_2Cl_2

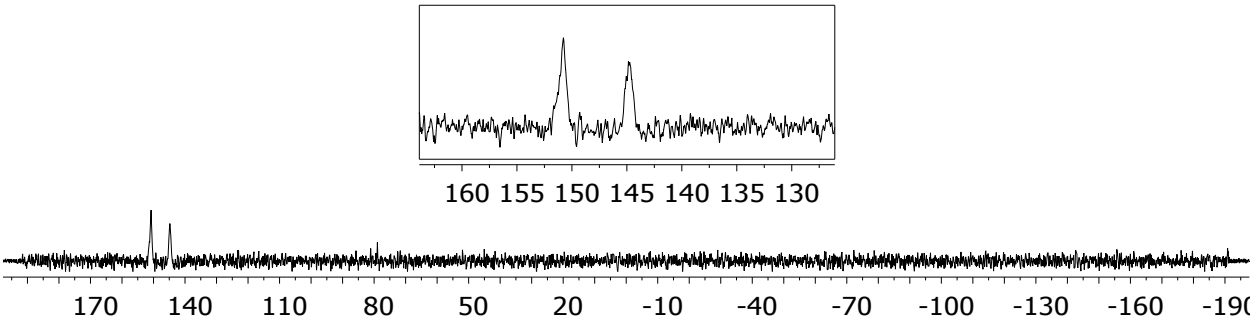
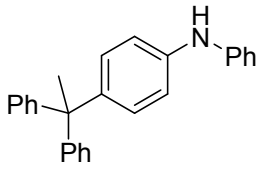


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture in CD_2Cl_2

3. Lewis Acid Catalysis with $[Ph_2SOF][B(C_6F_5)_4]$ (4)

3.1 Hydroarylation of Diphenylamine with 1,1-diphenylethylene



To a solution of catalyst **4** (4.4 mg, 0.0049 mmol, 4 mol %) in $CDCl_3$ (1 mL), diphenylamine (19.0 mg, 0.112 mmol) and 1,1-diphenylethylene (20.4 mg, 0.113 mmol) were added. The solution was transferred to an NMR tube and the reaction was monitored by ^1H NMR. Complete conversion to the desired product was observed after 24 hours. The ^1H resonances match those previously reported.[4]

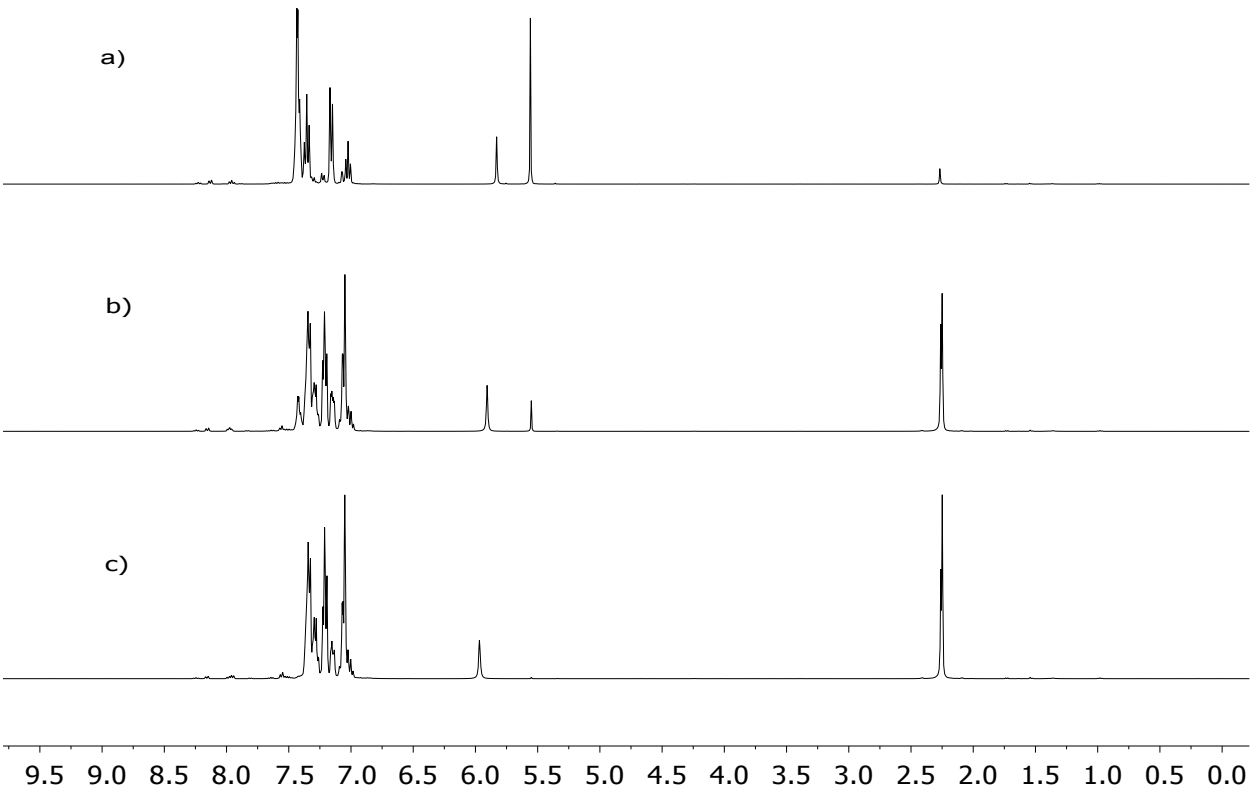
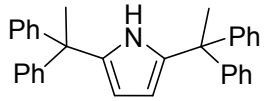


Figure S22. ^1H NMR spectra of the reaction mixture in $CDCl_3$ after a) 1h; b) 12h; c) 24h.

3.2 Hydroarylation of Pyrrole with 1,1-diphenylethylene



To a solution of catalyst **4** (7.1 mg, 0.0079 mmol, 5 mol %) in $CDCl_3$ (1 mL), pyrrole (11.5 mg, 0.171 mmol) and 1,1-diphenylethylene (56.5 mg, 0.314 mmol) were added. The solution was transferred to an NMR tube and the reaction was monitored by ^1H NMR. 91 % conversion to the desired product was observed after 24 hours. The ^1H resonances match those previously reported.[4]

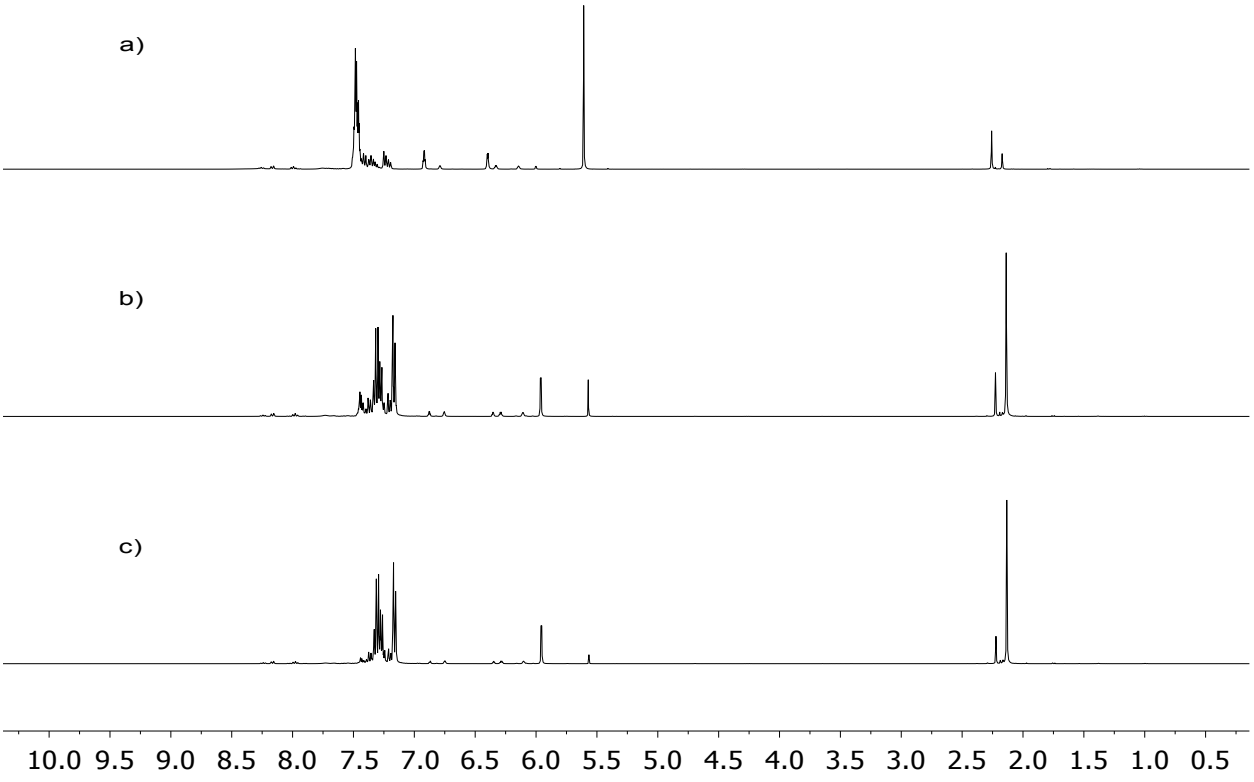
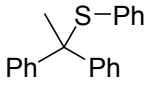


Figure S23. ^1H NMR spectra of the reaction mixture in $CDCl_3$ after a) 1h; b) 12h; c) 24h.

3.3 Hydrothiolation of 1,1-diphenylethylene with Thiophenol



To a solution of catalyst **4** (6 mg, 0.0067 mmol, 5 mol %) in $CDCl_3$ (1 mL), thiophenol (14 mg, 0.13 mmol) and 1,1-diphenylethylene (23 mg, 0.13 mmol) were added. The solution was transferred to an NMR tube and the reaction was monitored by ^1H NMR. After 12 hours, 85 % conversion to the desired product was observed, with no further significant increase in conversion after 24 hours. The ^1H resonances match those previously reported.[4]

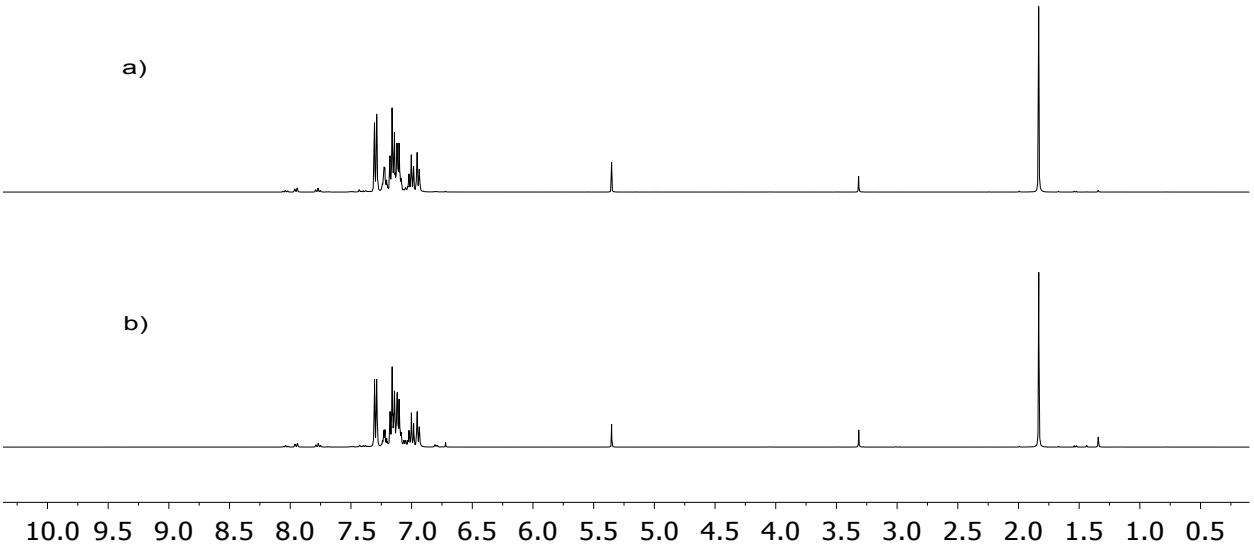


Figure S24. ^1H NMR spectra of the reaction mixture in $CDCl_3$ after a) 1h; b) 12h.

4. X-ray Crystallography

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in an N_2 filled glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS).

Structure Solution and Refinement. The structures were solved by direct methods using XS and subjected to full-matrix least-squares refinement on F^2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined with anisotropically thermal parameters. Carbon bound hydrogen atoms were placed in geometrically calculated positions and refined using an appropriate riding model and coupled isotropic thermal parameters.

Since compound **1** is chiral and there is no chemical reason to believe that it was synthesized with enantioselectivity, the molecular structure was refined as an inversion twin. The possibility of the crystal belonging to a centrosymmetric space group was explored by attempting to solve it in the next most suitable space group (P*nma*), but no reasonable solution could be found this way. Compound **1** was thus solved in P*na*2_1.

In the cases of compounds **4**, **6** and **7**, the possibility of substitutional disorder between the fluorine and the oxygen atoms was considered. Attempts to model potential disorder by splitting the site occupancies of the fluorine and oxygen atoms and allowing the structure to refine freely resulted in non-positive definite thermal parameters for one of the sulfur-fluorine sets in all cases. Even with restraints, the bond lengths and angles within the molecules became inconsistent with each other with large uncertainties. Based on these findings, disorder between the sulfur and fluorine atoms was dismissed.

Table S1. Summary of crystallographic data for compounds **1, 3, 4, 6** and **7**

	1	**3**	**4**	**6**	**7**
empirical formula	$C_{37}H_{12}BF_{21}OS$	$C_{12}H_8F_2OS$	$C_{36}H_{10}BF_{21}OS$	$C_{24}H_8B_{0.50}F_{11}OS$	$C_{12}H_8BF_5OS$
formula weight	914.34	238.24	900.31	558.77	306.05
crystal system	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
space group	$Pna2_1$	$P\bar{1}$	$Pbca$	$C2/c$	$P2_1/n$
a (Å)	14.635(2)	6.924(5)	15.0990(3)	25.433(3)	6.9113(7)
b (Å)	9.785(1)	8.665(6)	18.8792(5)	8.7969(10)	10.7857(9)
c (Å)	23.547(3)	8.772(7)	23.1430(7)	18.856(2)	16.5078(17)
α (deg.)		108.778(18)			
β (deg.)		94.634(17)		97.150(5)	99.049(7)
γ (deg.)		90.550(16)			
vol (Å^3)	3371.9(7)	496.3(6)	6597.1(3)	4186.0(8)	1215.2(2)
Z	4	2	8	8	4
ρ (calcd) (Mg·cm^3)	1.801	1.594	1.813	1.773	1.673
μ (mm^{-1})	0.247	0.327	0.251	0.270	0.320
F(000)	1808	244	3552	2220	616
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
reflections collected	13441	15557	33498	23038	23694
unique reflections	6310	1631	7575	4812	2799
R_{int}	0.0619	0.1685	0.0501	0.0762	0.1017
R1 indices [I>2σ(I)]	0.0463	0.1242	0.0416	0.0593	0.0502
wR2 indices (all data)	0.1153	0.3219	0.1002	0.1422	0.1097
CCDC No.	1500270	1500269	1500271	1500272	1500273

5. Computational Details

All density functional theory (DFT) calculations were performed by employing Turbomole 7.0[5, 6] software. The structures were optimized at the TPSS level of theory,[7] with the BJ-damped variant of the DFT-D3 dispersion correction[8, 9] in conjunction with the def2-TZVP basis set.[10, 11] Harmonic vibrational frequency calculations were conducted at the same level to characterize the nature of the stationary points along the reaction coordinates: no imaginary frequencies were found for the local minima. The thermostatistical contributions to the Gibbs energy in the gas phase were obtained from a modified rigid-rotor-harmonic oscillator approximation[12] at temperatures of 298.15 K and 1 atm pressure. The density-fitting RI-J[13, 14] approach for the Coulomb integrals was used to accelerate the geometry optimization and frequency calculations. Accurate electronic energies were obtained from single point calculations at the PW6B95-D3 level[15] upon the optimized structures, with the same basis set of def2-TZVP. The COSMO-RS (Conductor-like Screening Model for Real Solvents) solvation model[16, 17] was used to compute the solvation Gibbs energies by employing the gas–phase optimized structures, with toluene as the solvent. These calculations were done with the COSMOtherm program.[18] The final Gibbs energies in solution were calculated from the gas-phase single point electronic energies plus the gas-phase thermostatistical contributions, and the COSMO-RS solvation Gibbs energies. The fluoride ion affinities (FIA) were calculated via the following equation:

$$FIA = \Delta G(LA\text{-}F^-) - \Delta G(LA) - \Delta G(F^-)$$

where LA stands for Lewis acid.

Table S2. Calculated fluoride ion affinities (FIAs) of the Lewis acids at the PW6B95-D3/def2-TZVP//TPSS-D3/def2-TZVP level of theory. All values are given in kcal mol^{-1}.

	FIA_g	FIA_{sol}
4	-132.5	-140.0
6	-144.5	-151.8

FIA_g stands for FIA in gas phase and FIA_{sol} stands for FIA in solution (toluene).

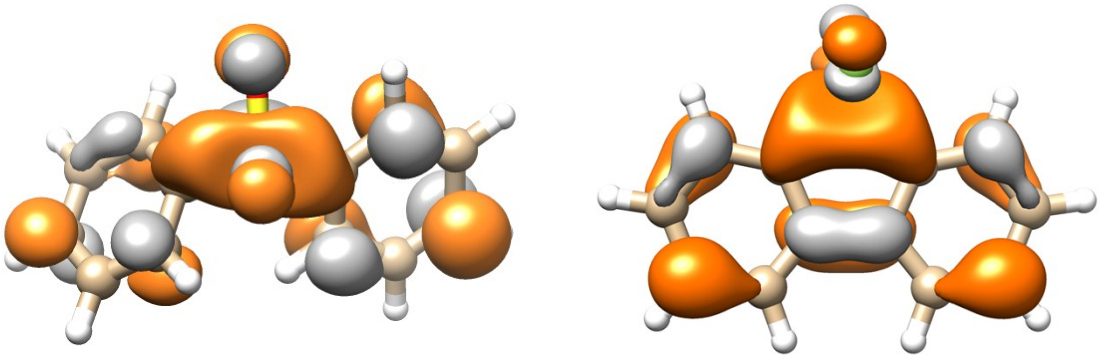


Figure S25. Calculated LUMOs of cations **4** (left) and **6** (right) at a contour surface value of 0.03 a.u. (computational level: TPSS-D3/def2-TZVP).

Cartesian coordinates

The Cartesian coordinates of the optimized structures at the TPSS-D3 level (in Å).

Cation 4

C	0.5069244	-2.2537093	0.7770704
C	0.4732845	-1.4527419	-0.3737484
C	-0.3506421	-1.7304647	-1.4741738
C	-1.1681939	-2.8531803	-1.4040619
C	-1.1555740	-3.6639433	-0.2650475
C	-0.3221095	-3.3696573	0.8170542
S	1.5059987	-0.0530202	-0.3517079
O	2.7415707	-0.2212069	0.3540786
C	0.6519740	1.3971859	0.0859675
C	-0.7331797	1.4882420	-0.1094639
C	-1.3623560	2.6774585	0.2396094
C	-0.6182124	3.7363813	0.7685620
C	0.7615410	3.6202458	0.9612651
C	1.4184432	2.4431890	0.6218851
F	1.7688493	0.1509445	-1.9015295
H	-0.3352511	-1.1057373	-2.3599885
H	-1.8071322	-3.1012353	-2.2450262
H	-1.7958021	-4.5395596	-0.2250987
H	2.4864454	2.3272594	0.7706886
H	1.1719814	-2.0166462	1.6006779
H	-1.3008090	0.6528098	-0.5041927
H	-2.4343848	2.7754457	0.1058319
H	-1.1208568	4.6590735	1.0409739
H	1.3275272	4.4456571	1.3798201
H	-0.3100362	-4.0127902	1.6905542

Cation 6

C	-0.0031876	0.0583426	-3.5157097
C	-1.1013370	-0.0289995	-2.6580588
C	-0.8259855	-0.0536847	-1.2955511
C	0.4680530	0.0158189	-0.7381973
C	1.5410352	0.1025173	-1.6187049
C	1.2943741	0.1193618	-2.9980036
C	0.4680530	0.0158189	0.7381973
C	-0.8259855	-0.0536847	1.2955511
S	-1.9776660	-0.1486258	0.0000000
C	-1.1013370	-0.0289995	2.6580588
C	-0.0031876	0.0583426	3.5157097
C	1.2943741	0.1193618	2.9980036
C	1.5410352	0.1025173	1.6187049
O	-3.1528862	0.6693594	0.0000000
F	-2.4433323	-1.6632973	0.0000000
H	-2.1171780	-0.0732718	-3.0361014
H	-0.1620956	0.0808091	-4.5882788
H	2.1344973	0.1882959	-3.6817622
H	2.5587665	0.1620924	-1.2473811
H	2.5587665	0.1620924	1.2473811
H	2.1344973	0.1882959	3.6817622
H	-0.1620956	0.0808091	4.5882788
H	-2.1171780	-0.0732718	3.0361014

$[C_{12}H_8SOF][BF_4]$ (7)

S	-0.561212	0.997728	0.652068
O	-0.322672	1.664304	1.892938
F	-1.590720	1.751142	-0.272511
F	0.409248	3.137039	-0.297171
F	0.650920	4.571426	1.513621
F	2.497875	3.502894	0.612896
F	1.440227	5.184401	-0.573775
B	1.267096	4.161312	0.342358
C	0.717892	0.304833	-0.353911
C	1.913523	0.895417	-0.743056
H	2.159542	1.913577	-0.454666
C	2.787822	0.104953	-1.496626
H	3.730614	0.533827	-1.819533
C	2.461950	-1.208999	-1.832137
H	3.152143	-1.799351	-2.427425
C	1.269166	-1.792296	-1.391379
H	1.045455	-2.828142	-1.626195
C	0.381699	-1.041373	-0.627912
C	-0.858697	-1.504186	0.014630
C	-1.455237	-2.764089	-0.018486

H	-1.024385	-3.567204	-0.607658
C	-2.617244	-2.984524	0.726869
H	-3.082519	-3.965153	0.703848
C	-3.188312	-1.973797	1.506259
H	-4.084981	-2.174419	2.082999
C	-2.607894	-0.703579	1.549611
H	-3.030865	0.096011	2.148706
C	-1.460435	-0.511753	0.795637

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