Fluorinated Aryl Sulfonimide Tagged (FAST) salts: modular synthesis and structure-property relationships for battery applications

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Theoretical calculations

All calculations were performed employing the Gaussian 09 computational package[1]. Geometries were optimized at the B3LYP/6-31G(d,p)[2,3] level of theory; ground states were verified by the absence of any imaginary frequency. Natural Population Analysis (NPA)[4,5] atomic partial charges were obtained using the optimized geometries at B3LYP/6-31G(d,p). Single point energy calculations were performed at the B3LYP/6-311++G(d,p) level of theory for oxidation energies, nucleophilic substitution free energies, and cation-anion association free energies. The conductor-like polarizable continuum model (CPCM)[6,7] was employed to capture the solvation effects. Electrochemical oxidative stability is estimated by oxidation energy calculations, which is the Gibbs free energy for the electrochemical oxidation reaction $M \rightarrow M^+ + e^-$ in the solution (Dimethyl sulfoxide (DMSO) was selected as the universal solvent in the electrochemical oxidation energy calculations):

$$G_{Ox} = G(M^+) - G(M)$$

The computed electrochemical oxidation energy, G_{Ox}, in eV is converted to the experimentally measured scale versus Li/Li^+ by the subtraction of 1.4 V[8,9]. We computed the free energies of nucleophilic substitution (ΔG_{nuc}) of select carbon sites in ***A-OMe$_3$F$_2$***, ***A-PipOMe$_2$F$_2$***, and ***A-Pip$_2$OMeF$_2$*** by superoxide in implicit DMSO. In the association free energy calculations, the solvation environment is set to the 1,2-dimethoxyethane (DME) solvent, diethylether was selected as the implicit solvent, and the dielectric constant of the implicit solvent was set to 7.2. The likelihood of cation-anion interaction was estimated by the Gibbs free energy of the reaction $M^+ + A^- \rightarrow MA$ (M = Na or Li), which is taken to be the association free energy in the solution:

$$\Delta G_{asso} = G(MA) - G(M^+) - G(A^-)$$

$G(M^+)$ is approximated using the solvation of M^+ in DME, more specifically,

$$G(M^+) = G_{gas}(M^+) + \Delta G_{sol}(M^+) + RT ln(24.46)$$

where $\Delta G_{sol}(M^+)$ is the solvation energy of M^+ in DME, and its value was taken from a computational study[10] where three explicit DME molecules were considered. $G_{gas}(M^+)$ is the gas-phase free energy of M^+ and its value was computed using the same methods/basis sets. The term $RT ln(24.46)$ converts a gas-phase reference state of 1 atm to a liquid-phase reference state of 1 M. We note that the values of $G(M^+)$ obtained using this method are similar to those directly computed using an implicit solvation model.

Electrochemical stability test details

The sulfonimide compounds were vacuum-dried at 75 °C overnight before being transferred into a glove box (H_2O < 0.1 ppm, O_2 < 0.1 ppm, MBraun, USA) without exposure to the atmosphere. The oxidative stability of the sulfonimide compounds was studied in electrochemical cells consisting of a Lithium foil (D = 15 mm, Chemetall, Germany), 90 μL of 0.02 M sulfonimide sample in propylene carbonate (H_2O < 20 ppm by Karl Fischer titration, BASF), one piece of glass fiber separator (D= 18 mm, Whatman®, Grade GF/A), and a 304 stainless steel mesh as current collector (D = 12.7 mm). The assembled electrochemical cells were then transferred to a second glove box (H_2O < 1 ppm, O_2 < 1 %, MBraun, USA) and pressured with dry O_2 (99.994% purity, H_2O < 2 ppm, Airgas, USA) to 30 psi (gauge). In each electrochemical stability test, after holding the cell at open circuit voltage for two hours, a series of potentials were applied sequentially for three hours each: 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2, 4.4, and 4.5 V; the current response was recorded throughout the test. All electrochemical tests were conducted employing a VMP3 potentiostat (BioLogic Science Instruments).

Conductivity measurement details

The impedance measurements were conducted using electrochemical cells consisting of liquid or polymer electrolytes sandwiched between two stainless steel blocking electrodes (D = 15.5 mm). The liquid electrolyte contained one piece of Celgard 2340 separator (thickness = 38 μm, porosity = 0.45) impregnated with 100 μL of 0.1 M sulfonimide sample in 1,2-dimethoxyethane (purchased from Acros, degassed and dried using a glass contour solvent purification system by SG Water USA, LLC), whereas the polymer electrolytes contained 10k PEO-sulfonimide blends ([EO]:[Li+] = 15:1). The conductivity was studied with electrochemical impedance spectroscopy (EIS, VMP3, Bio-Logic Science Instruments) over the frequency range of 1 MHz and 0.1 Hz at a voltage amplitude of 10 mV. The bulk electrolyte conductivity, σ, is estimated from the bulk electrolyte resistance, R, obtained in the EIS measurement according to the equation

$$\sigma = \frac{1}{R}\frac{d}{A}$$

where *d* is the thickness of the electrolyte (i.e., the thickness of the separator for liquid electrolyte, and the thickness of the PEO-sulfonimide sample for polymer electrolyte) and A is the cross-sectional area of tested sample.

^{23}Na NMR measurement of interaction between anion and cations among FAST salts

For A type FAST salts, nitromethane was chosen as the solvent since it has lower value of Gutmann's donor numbers than TFSI anion.[11,12] FAST salts were dissolved in nitromethane to prepare 0.1 M solution and loaded into thin wall NMR tube. The inner reference was a 0.25 M DMSO solution of sodium perchlorate. For measurements, the reference solution was placed in a capillary sealed by PTFE cap and inserted coaxially into the sample NMR tube. The ^{23}Na spectra were collected at Bruker 106 MHz, and the chemical shift of the reference was set to 0 ppm. Since B type and C type salts have low solubility in nitromethane, acetonitrile was chosen as the solvent. The reference and measurement details were the same as in A type salts.

Supplementary figures

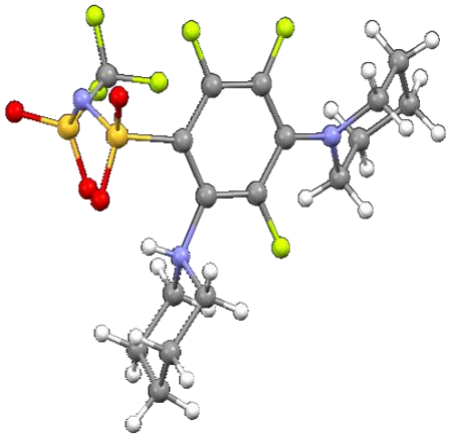


Figure S1. Crystal structures of *A-Pip$_2$F$_3$*●H$^+$.

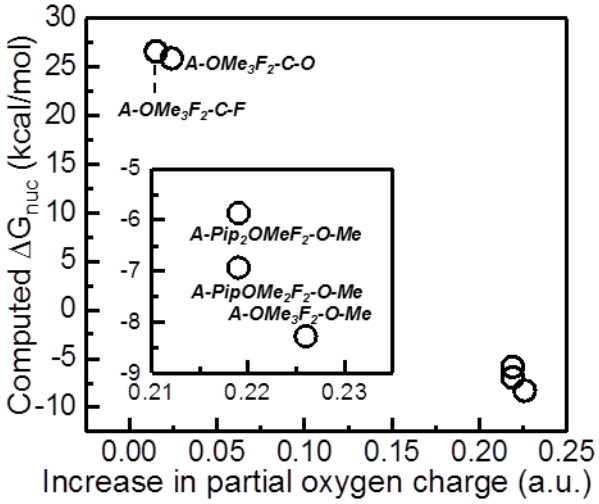


Figure S2. The computed Gibbs free energy for nucleophilic substitution by superoxide, ΔG_{nuc}, at select carbon sites in ***A-OMe$_3$F$_2$***, ***A-PipOMe$_2$F$_2$***, and ***A-Pip$_2$OMeF$_2$*** plotted against the increase in NPA partial charge of the attacking oxygen in superoxide (partial charge of oxygen after the substitution reaction minus its charge before the reaction).

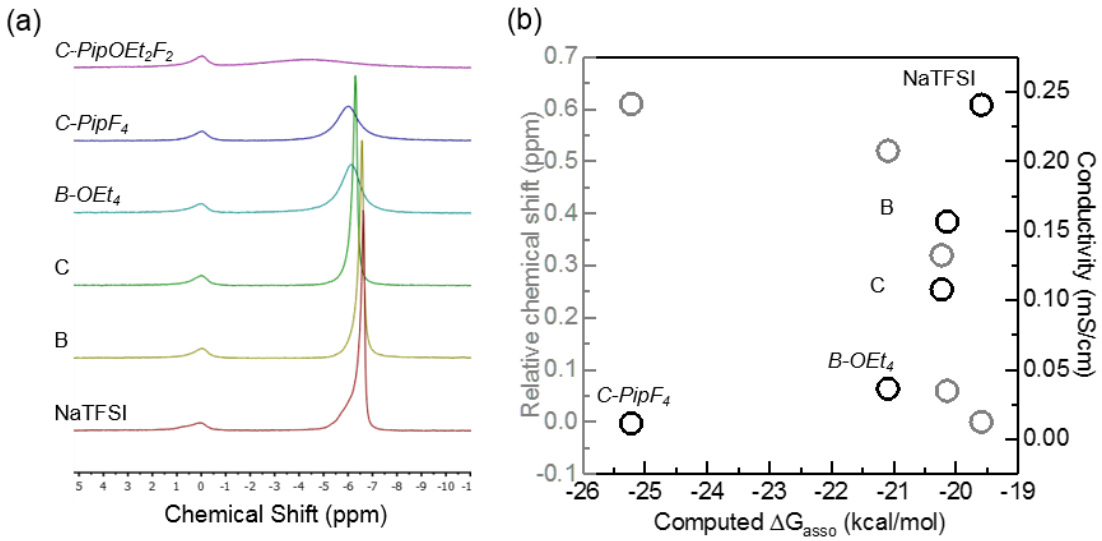


Figure S3. (a) ^{23}Na chemical shifts of representative B type and C type FAST salts (the ^{23}Na signal from the inner standard, $NaClO_4$, is set to 0 ppm). (b) The ^{23}Na NMR chemical shift (relative to **NaTFSI**) and ionic conductivities of 0.1 M 1,2-dimethoxyethane solution at 25 °C versus the computed free energy of anion-Na^+ association, ΔG_{asso}, for representative B type and C type FAST salts in implicit diethylether solvent with dielectric constant set at 7.2.

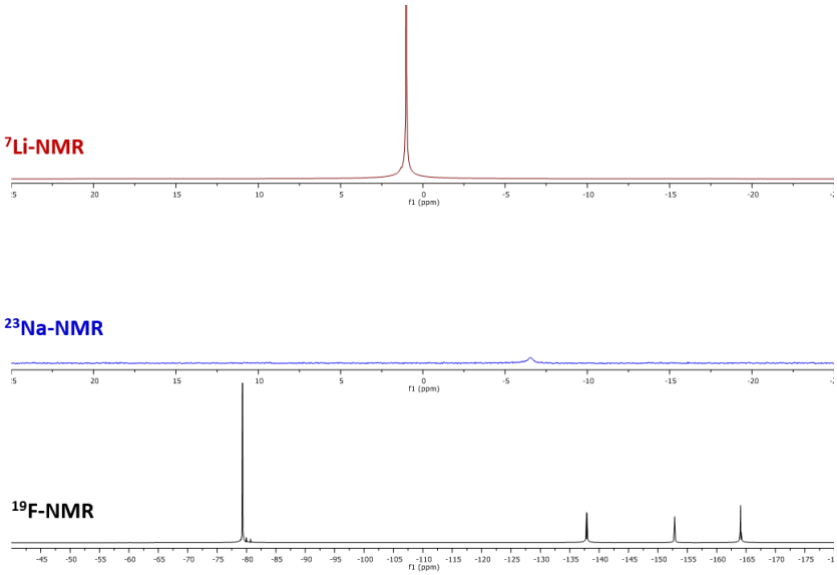


Figure S4 NMR spectrum of **A** after ion exchange with lithium chloride. The very strong ^{7}Li peak and rather weak ^{23}Na peak indicate nearly complete replacement of Na^+ by Li^+.

Table S1. Crystal data

	A-PipOPh$_2$F$_2$	***A-PipOMe$_2$F$_2$***	***A-PipOEt$_2$F$_2$***	***A-Pip$_2$F$_3$●H***
Empirical formula	$C_{24}H_{20}F_5N_2NaO_6S_2$	$C_{14}H_{18}F_5N_2NaO_7S_2$	$C_{16}H_{20}F_5N_2NaO_6S_2$	$C_{17}H_{21}F_6N_3O_4S_2$
a	43.264 Å	7.958 Å	5.399 Å	8.153 Å
b	5.590 Å	28.725 Å	11.412 Å	11.052 Å
c	24.240 Å	8.954 Å	18.037 Å	12.536 Å
α (alpha):	90.00 °	90.00 °	82.42 °	99.43 °
β (beta):	119.48 °	91.06 °	82.10 °	94.08 °
γ (gamma):	90.00 °	90.00 °	86.02 °	110.56 °
Volume:	5103.33 Å^3	2046.48 Å^3	1089.67 Å^3	1033.16 Å^3
Space group:	*C*2/*c*	*P*2$_1$/*n*	*P*-1	*P*-1
Calculated density:	1.600 g/cm^3	1.650 g/cm^3	1.580 g/cm^3	1.638 g/cm^3
Color:	colourless	colourless	colourless	colourless
Z:	8	4	2	2
Temperature:	-173.0 °C	-173.0 °C	-123.0 °C	-173.0 °C
Formula weight:	614.546 g/mole	508.420 g/mole	518.458 g/mole	509.494 g/mole
R(F):	0.0386	0.0741	0.0321	0.0301
$R_w(F^2)$:	0.0969	0.1601	0.0891	0.0836

Table S2. Melting points of representative salts

Samples (sodium salts)	T_m (^{0}C)
A-PipOMe$_2$F$_2$	264 - 265
A-PipOEt$_2$F$_2$	252 - 253
A-PipOiPr$_2$F$_2$	235 - 239
A-PipONeop$_2$F$_2$	216 - 222
A-ONeop$_3$F$_2$	206 - 214

Synthesis part:

2,3,4,5,6-pentafluoro-*N*-[(trifluoromethyl)sulfonyl]benzene sulfonamide (**A**):

To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added trifluoromethane sulfonamide (10.0 mmol), N-methylmorpholine (20.0 mmol), and 50 mL DCM. The mixture was cooled to 0 °C. With stirring, 2,3,4,5,6-pentafluorobenzene sulfonyl chloride (10.5 mmol) in 10 mL DCM was added dropwise via dropping funnel. The solution was further stirred at room temperature for 24 h. After removing DCM solvent under vacuum, the residue was dissolved in 100 mL ethyl acetate, and washed with 1M hydrochloric acid (1x50 mL), water (1x40 mL) and brine solution (2x40 mL). Then organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the product as a white solid (3.28 g, 82%). ^{13}C NMR (126 MHz, acetone-d^6, ppm, δ): 139.53 (dm, *J* = 255.7 Hz), 138.33 (dm, *J* = 257.0 Hz), 132.84 (dm, *J* = 253.2 Hz), 115.14 (q, *J* = 321.7 Hz), 115.27-114.30 (m). ^{19}F NMR (125 MHz, acetone-d^6, ppm, δ): -79.33, -137.86, -152.84, -164.07. MS (*m/z*): Calc. for $C_7NF_8O_4S_2Na$: 400.9. Found $(M-Na)^-$: 377.9.

***A-ONeopF*$_4$ *& A-ONeop*$_2$*F*$_3$:** To a 20 mL vial equipped with a magnetic stirring bar were added dry neopentanol (5.7 mmol), sodium hydride (5.7 mmol) and 5 mL dry DMF under nitrogen. After stirred at room temperature for 0.5 h, the mixture was transferred dropwise to another 40 ml vial which has been charged with **A** (4.0 mmol) and 5 mL DMF first. The solution was quenched by adding 5 ml 1M HCl aqueous solution after further stirred at room temperature for 2 h. Then ethyl acetate (2x50 mL) was added to extract crude product, and washed with water (1x30 mL) and brine solution (2x30 mL). Then organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the products as white foam solids.

***A-ONeopF*$_4$:**(0.79 g, 42%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.05 (s, 2H), 1.06 (s, 9H). ^{13}C NMR (126 MHz, acetone-d$_6$, ppm) δ: 145.44 (dm, *J* = 253.3 Hz), 140.61 (dm, *J* = 245.0 Hz), 141.03-140.32 (m), 120.19 (q, *J* = 320.0 Hz), 118.61-117.32 (m), 84.72, 32.40, 25.31. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -79.23, -139.80, -159.45. MS (*m/z*): Calc. for $C_{12}H_{11}NF_7O_5S_2Na$: 468.99. Found $(M-Na)^-$: 446.0.

***A-ONeop*$_2$*F*$_3$:**(0.77 g, 36%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 3.95 (s, 2H), 3.84 (s, 2H), 1.04 (s, 9H), 1.03 (s, 9H). ^{13}C NMR (126 MHz, acetone-d$_6$, ppm) δ: 146.06 (dm, *J* = 246.9 Hz), 144.65 (dm, *J* = 252.0 Hz), 142.35 (m), 140.37 (dm, *J* = 245.7 Hz), 140.70-140.05 (m), 120.28 (q, *J* = 322.6 Hz), 123.46-122.40 (m), 84.55, 84.13, 32.40, 32.12, 26.06, 25.45. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -78.78, -139.45, -150.64, -160.30. MS (*m/z*): Calc. for $C_{17}H_{22}NF_6O_6S_2Na$: 537.07. Found $(M-Na)^-$: 514.1.

General procedure for ***A-OR$_3$F$_2$***:

A 40 mL vial equipped with a magnetic stirring bar was charged with **A** (1.2 mmol) and 5 mL dry DMF. Then corresponding sodium phenoxide or alkoxide (6.0 mmol) was added under nitrogen. After stirred at room temperature (90 ^{0}C for sodium phenoxide) for 12 h, the solution was quenched by adding 10 ml 1M HCl aqueous solution. Then ethyl acetate (2x30 mL) was added to extract crude product, and washed with water (1x20 mL) and brine solution (2x20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the products as white solids.

A-OPh$_3$F$_2$:(0.62 g, 83%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 7.45-7.30 (m, 4H), 7.17-7.02 (m, 6H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 158.50, 157.14, 146.88 (dd, *J* = 252.9, 3.4 Hz), 138.48 (dd, *J* = 11.6, 4.3 Hz), 135.68 (t, *J* = 13.0 Hz), 131.25, 130.10, 129.40, 123.88, 122.64, 120.77 (q, *J* = 304.0 Hz), 115.90, 115.26. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -77.26, -142.07. MS (*m/z*): Calc. for $C_{25}H_{15}NF_5O_7S_2Na$: 623.01. Found (M-Na)$^-$: 599.9.

A-OMe$_3$F$_2$:(0.29 g, 55%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.02 (s, 3H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 145.90 (dd, *J* = 244.3, 4.7 Hz), 143.02 (dd, *J* = 11.5, 4.2 Hz), 139.92 (t, *J* = 12.9 Hz), 128.17, 120.47 (q, *J* = 324.9 Hz), 62.62, 62.30. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -79.02, -151.70. MS (*m/z*): Calc. for $C_{10}H_9NF_5O_7S_2Na$: 437.28. Found (M-Na)$^-$: 414.2.

A-OEt$_3$F$_2$:(0.40 g, 70%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.29 (q, *J* = 8.0 Hz, 2H), 4.17 (t, *J* = 8.0 Hz, 4H), 1.40-1.30 (t, 9H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 146.34 (dd, *J* = 244.5, 4.6 Hz), 142.00 (dd, *J* = 11.8, 4.3 Hz), 139.23 (t, *J* = 13.6 Hz), 127.55, 120.24 (q, *J* = 322.7 Hz), 71.59, 70.47, 14.87, 14.67. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -78.93, -150.74. MS (*m/z*): Calc. for $C_{13}H_{15}NF_5O_7S_2Na$: 479.36. Found (M-Na)$^-$: 456.0.

A-OiPr$_3$F$_2$:(0.49 g, 78%). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ: 4.67-4.55 (m, 2H), 4.53-4.40 (m, 1H), 1.28 (d, *J* = 8.0 Hz, 6H), 1.21 (d, *J* = 8.0 Hz, 12H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 146.73 (dd, *J* = 242.5, 4.5 Hz), 140.77 (dd, *J* = 11.8, 4.1 Hz), 137.70 (t, *J* = 14.3 Hz), 128.93, 120.37 (q, *J* = 323.2 Hz), 78.19 – 77.31 (m), 77.44, 21.72, 21.41. ^{19}F NMR (376 MHz, DMSO-d$_6$, ppm) δ: -77.31, -146.44. MS (*m/z*): Calc. for $C_{16}H_{21}NF_5O_7S_2Na$: 521.06. Found (M-Na)$^-$: 497.9.

A-ONeop$_3$F$_2$:(0.54 g, 75%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 3.88 (s, 2H), 3.82 (s, 4H), 1.05 (s, 9H), 1.04 (s, 18H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 146.07 (dd, *J* = 244.2, 4.6 Hz), 142.61 (dd, *J* = 11.0, 4.2 Hz), 140.04 (t, *J* = 13.3 Hz), 128.39, 120.47 (q, *J* = 323.6 Hz), 84.33, 84.16, 32.39, 32.13, 26.16,

25.55. ^{19}F NMR (376 MHz, acetone-d_6, ppm) δ: -78.19, -145.87. MS (*m/z*): Calc. for $C_{22}H_{33}NF_5O_7S_2Na$: 605.15. Found $(M\text{-}Na)^-$: 582.1.

***A-PipF*$_4$:** To a 50 mL round-bottomed flask equipped with a magnetic stirring bar were added **A** (5.0 mmol), piperidine (7.5 mmol), triethylamine (10.0 mmol), and 20 mL acetonitrile. The mixture was further stirred at room temperature for 12 h. After removing acetonitrile under vacuum, the residue was dissolved in 30 mL ethyl acetate, and washed with 1M hydrochloric acid (1x20 mL), water (1x20 mL) and brine solution (2x20 mL). Then organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the product as a pale yellow solid (1.86 g, 80%). ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ: 3.33-3.27 (m, 4H), 1.75-1.60 (m, 6H). ^{13}C NMR (101 MHz, acetone-d_6, ppm) δ: 144.54 (dm, *J* = 253.5 Hz), 141.24 (dm, *J* = 243.4 Hz), 133.53 (m), 120.25 (q, *J* = 323.9 Hz), 115.76 (m), 51.81, 26.27, 23.74. ^{19}F NMR (376 MHz, acetone-d_6, ppm) δ: -77.96, -140.13, -151.99. MS (*m/z*): Calc. for $C_{12}H_{10}N_2F_7O_4S_2Na$: 466.0. Found $(M\text{-}Na)^-$: 443.0.

***A-PipOiPrF*$_3$:** To a 40 mL vial equipped with a magnetic stirring bar were added ***A-PipF*$_4$** (1.0 mmol) and 5 mL DMF. Sodium isopropoxide (1.0 mmol) was then added under nitrogen and stirred at room temperature for 2 h. The reaction was quenched by adding 2 mL 1M hydrochloric acid, and diluted with 30 mL ethyl acetate. The organic layer was washed with water (1x20 mL) and brine solution (2x20 mL), dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the product as pale yellow solid (0.26 g, 52%). ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ: 4.75-4.63 (m, 1H), 3.32-3.20 (m, 4H), 1.72-1.57 (m, 6 H), 7.56 (dd, *J* = 6.2, 1.2 Hz, 6 H),. ^{13}C NMR (101 MHz, acetone-d_6, ppm) δ: 147.22 (dm, *J* = 243.41), 145.29 (dm, *J* = 251.49 Hz), 142.67 (dd, *J* = 16.5, 6.5 Hz), 141.07–139.28 (m), 133.80–132.50 (m), 121.57 (d, *J* = 11.4 Hz), 120.35 (q, *J* = 281.8 Hz), 77.97, 51.94, 26.36, 23.86, 21.47. ^{19}F NMR (376 MHz, acetone-d_6, ppm) δ: -78.94, -138.46, -141.21, -153.83. MS (*m/z*): Calc. for $C_{15}H_{17}N_2F_6O_5S_2Na$: 506.0. Found $(M\text{-}Na)^-$: 482.9.

General procedure for ***A-PipOR*$_2$*F*$_2$**:

A 40 mL vial equipped with a magnetic stirring bar was charged with ***A-PipF*$_4$** (1.2 mmol) and 5 mL dry DMF. Then corresponding sodium phenoxide or alkoxide (4.0 mmol) was added under nitrogen. After stirred at room temperature (90 ^{0}C for sodium phenoxide) for 12 h, the solution was quenched by adding 10 ml 1M HCl aqueous solution. Then ethyl acetate (2x30 mL) was added to extract crude product, and washed with water (1x20 mL) and brine solution (2x20 mL). The organic layer was dried over anhydrous

sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the products as white solids.

A-PipOPh$_2$F$_2$ (0.63 g, 85%). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ: 7.35-7.25 (m, 4 H), 7.07-7.00 (m, 2 H), 6.95-6.87 (m, 4 H), 3.15-3.08 (m, 4 H), 1.58-1.50 (m, 6 H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 158.78, 147.40 (dd, *J* = 247.9, 6.7 Hz), 137.79 (dd, *J* = 12.1, 5.7 Hz), 133.71 (t, *J* = 11.7 Hz), 129.15, 126.59, 122.04, 120.51 (q, *J* = 317.2 Hz), 115.80, 51.93, 26.31, 23.80. ^{19}F NMR (376 MHz, DMSO-d$_6$, ppm) δ: -77.24, -137.96. MS (*m/z*): Calc. for $C_{24}H_{20}N_2F_5O_6S_2Na$: 614.06. Found (M-Na)$^-$: 591.1.
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ.

A-PipOMe$_2$F$_2$ (0.40 g, 68%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 3.90 (s, 8H), 3.26-3.20 (m, 4H), 1.73-1.57 (m, 6H). ^{13}C NMR (100 MHz, acetone-d$_6$, ppm) δ: 147.33 (dd, *J* = 250.0, 4.0 Hz), 144.52 (dd, *J* = 13.1, 4.0 Hz), 134.52 (t, *J* = 11.2 Hz), 129.04, 121.24 (q, *J* = 324.5 Hz), 63.44, 57.20, 24.75, 22.17. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -79.56, -144.30. MS (*m/z*): Calc. for $C_{14}H_{16}N_2F_5O_6S_2Na$: 490.03. Found (M-Na)$^-$: 466.9.

A-PipOEt$_2$F$_2$ (0.46 g, 74%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.02 (q, *J* = 8.0 Hz, 4H), 3.11-3.03 (m, 4H), 1.58-1.40 (m, 6H), 1.22 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 147.50 (dd, *J* = 242.9, 6.6 Hz), 141.99 (dd, *J* = 12.6, 4.8 Hz), 133.18 (t, *J* = 12.3 Hz), 126.10, 120.33 (q, *J* = 323.0 Hz), 71.20, 52.04, 26.44, 23.95, 14.76. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -78.70, -143.91. MS (*m/z*): Calc. for $C_{16}H_{20}N_2F_5O_6S_2Na$: 518.06. Found (M-Na)$^-$: 495.0.

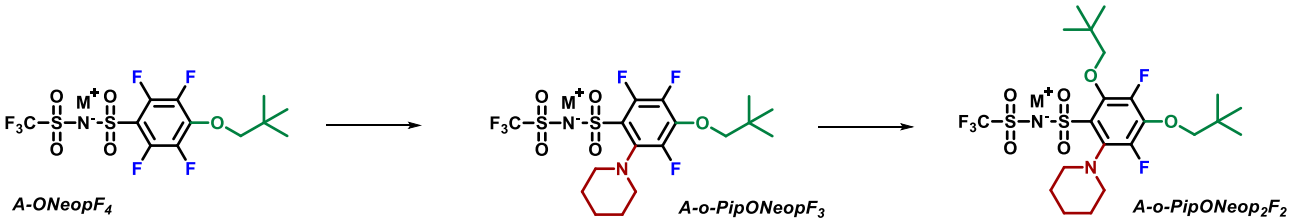
A-PipOiPr$_2$F$_2$:(0.47 g, 72%). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ: 4.62-4.50 (m, 2H), 3.15-3.07 (m, 4H), 1.65-1.50 (m, 6H), 1.20 (d, *J* = 8.0 Hz, 12H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 147.36 (dd, *J* = 241.6, 6.6 Hz), 140.67 (dd, *J* = 12.4, 4.7 Hz), 132.67 (t, *J* = 12.8 Hz), 127.10, 120.36 (q, *J* = 323.1 Hz), 77.48, 52.08, 26.46, 23.97, 21.45. ^{19}F NMR (376 MHz, DMSO-d$_6$, ppm) δ: -77.55, -140.70. MS (*m/z*): Calc. for $C_{18}H_{24}N_2F_5O_6S_2Na$: 546.09. Found (M-Na)$^-$: 522.9.

A-PipONeop$_2$F$_2$:(0.59 g, 81%). ^{1}H NMR (400 MHz, acetonitrile-d$_3$, ppm) δ: 3.77 (s, 4H), 3.24-3.17 (m, 4H), 1.72-1.57 (m, 6H), 1.05 (s, 18H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 147.64 (dd, *J* = 243.1, 6.5 Hz), 142.43 (dd, *J* = 12.0, 4.6 Hz), 133.08 (t, *J* = 12.3 Hz), 127.22, 120.50 (q, *J* = 323.7 Hz), 83.94, 52.10, 32.10, 26.47, 26.19, 23.99. ^{19}F NMR (376 MHz, acetonitrile-d$_3$, ppm) δ: -78.70, -143.30. (LC-MS, *m/z*): Calc. for $C_{22}H_{32}N_2F_5O_6S_2Na$: 602.15. Found (M-Na)$^-$: 579.0.

A-PipOEtOiPrF$_2$: A 40 mL vial equipped with a magnetic stirring bar was charged with ***A-PipOiPrF$_3$*** (0.5 mmol) and 4 mL dry DMF. Then sodium ethoxide (1.5 mmol) was added under nitrogen and stirred at room temperature for 12 h. The reaction was quenched by adding 5 ml 1M HCl aqueous solution. Then ethyl acetate (30 mL) was added to extract crude product, and washed with water (1x20 mL) and brine solution

(2x20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the product as white solids (0.20 g, 77%). ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ: 4.75-4.57 (m, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.25-3.15 (m, 4H), 1.72-1.57 (m, 6H), 1.38 (t, *J* = 7.0 Hz, 3H), 1.28 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d_6, ppm) δ: 148.73 (dd, *J* = 12.9, 6.6 Hz), 146.32 (dd, *J* = 13.9, 6.6 Hz), 142.48 (dd, *J* = 13.4, 3.8 Hz), 140.29 (dd, *J* = 13.7, 3.6 Hz), 132.85 (t, *J* = 12.6 Hz), 126.91, 120.41 (q, *J* = 323.2 Hz), 77.86, 70.86, 52.06, 26.45, 23.96, 21.43, 14.76. ^{19}F NMR (376 MHz, acetone-d_6, ppm) δ: -77.26, -140.26, -142.90. MS (*m/z*): Calc. for $C_{17}H_{22}N_2F_5O_6S_2Na$: 532.07. Found $(M\text{-}Na)^-$: 509.1.

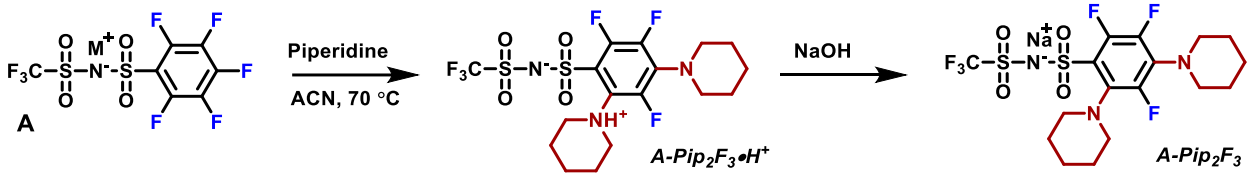
A-o-PipONeop$_2$F$_2$: was synthesized by two more steps:



A 40 mL vial equipped with a magnetic stirring bar was charged with ***A-ONeopF$_4$*** (0.7 mmol), piperidine (2.0 mmol) and 5 mL acetonitrile. The mixture was stirred at 60^{0}C for 12 h under nitrogen. Then 20 mL 1M HCl was added to the reaction. The white precipitate was filtered, washed with saturate sodium carbonate solution (20 mL), water (2x30 mL), and dried in vacuum to afford the product ***A-o-PipONeopF$_3$*** as white solids (0.20 g, 77%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 3.89 (s, 1H), 3.05-2.85 (m, 4H), 1.94 – 1.13 (m, 6H), 0.98 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 151.95 (d, J = 248.7 Hz), 144.97 (dd, J = 253.0, 11.3 Hz), 141.95 (ddd, J = 246.9, 17.6, 5.1 Hz), 139.63 (t, J = 11.3 Hz), 135.92 (d, J = 13.1 Hz), 127.48 (d, J = 6.6 Hz), 120.46 (q, J = 324.9 Hz), 84.53, 52.00, 32.76, 26.08, 25.80, 24.20. ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ: -77.33, -137.57, -140.21, -155.25. MS (*m/z*): Calc. for $C_{17}H_{21}N_2F_6O_5S_2Na$: 534.07. Found $(M\text{-}Na)^-$: 511.1.

To a 20 mL vial equipped with a magnetic stirring bar were added dry neopentanol (1.0 mmol), sodium hydride (1.0 mmol) and 3 mL dry DMF under nitrogen. After stirred at room temperature for 0.5 h, the mixture was transferred dropwise to another 40 ml vial which has been charged with ***A-o-PipONeopF$_3$*** (0.4 mmol) and 3 mL DMF first. The reaction was quenched by adding 20 ml 1M HCl aqueous solution after further stirred at room temperature for 4h. The white precipitate was filtered and washed by water (3x20 mL). The collected solids were dissolved in 30 mL ethyl acetate, washed with 1M NaOH (1x15 mL), water (1x20 mL) and brine solution (2x20 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated and dried in vacuum to afford the product ***A-o-PipONeop$_2$F$_2$*** as white solids (0.20 g, 85%). %).

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 3.72 (s, 2H), 3.67 (s, 2H), 3.05-2.80 (m, 4H), 2.80-2.60 (m, 4H), 2.00-1.50 (m, 6H), 1.40-1.00 (m, 6H), 0.91 (d, *J* = 8.7 Hz, 18H). ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ: 151.43 (dd, *J* = 477.7, 6.1 Hz), 148.98 (dd, *J* = 475.7, 6.1 Hz), 143.05 (dd, *J* = 11.2, 4.1 Hz), 139.55 (t, *J* = 13.8 Hz), 136.12 (dd, *J* = 12.6, 4.1 Hz), 133.04 (d, *J* = 3.4 Hz), 120.66 (q, *J* = 324.7 Hz), 84.20, 51.71, 35.97, 32.37, 32.06, 26.18, 25.66, 25.54, 24.24. ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ: -77.92, -141.28, -147.45. MS (*m/z*): Calc. for $C_{22}H_{32}N_2F_5O_6S_2Na$: 602.15. Found $(M-Na)^-$: 579.1.



A-Pip$_2$F$_3$•H$^+$*:** To a 50 mL round-bottomed flask equipped with a magnetic stirring bar were added **A** (3.0 mmol), piperidine (10 mmol), triethylamine (10.0 mmol), and 20 mL acetonitrile. The mixture was further stirred at 70 ^{0}C for 12 h. After removing acetonitrile under vacuum, the residue was dissolved in 30 mL ethyl acetate, and washed with 1M hydrochloric acid (1x20 mL), water (1x20 mL) and brine solution (2x20 mL). Then organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the product as white solid (1.86 g, 65%), which is the protonated state of ***A-Pip$_2$F$_3$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.69 (s, 1H), 3.90-3.65 (m, 4H), 3.35-3.25 (m, 4H), 2.15-1.95 (m, 5H), 1.75-1.65 (m, 6H), 1.65-1.55 (m, 1H). ^{13}C NMR (101 MHz, CDCl3, ppm) δ: 153.62 (dd, *J* = 244.8, 5.1 Hz), 144.78 (dd, *J* = 250.8, 13.5 Hz), 143.16 (dm, *J* = 245.4 Hz), 135.82 (d, *J* = 15.1 Hz), 133.13 (t, *J* = 11.0 Hz), 125.16, 120.29 (q, *J* = 322.9 Hz), 51.96, 51.75, 26.38, 25.72, 24.18, 23.88 ^{19}F NMR (376 MHz, CDCl3, ppm) δ: -78.42, -129.52, -132.39, -138.54. MS (*m/z*): Calc. for $C_{17}H_{21}N_3F_6O_4S_2$: 466.07. Found $(M-H)^-$: 508.1.

A-Pip$_2$F$_3$: ***A-Pip$_2$F$_3$•H$^+$*** was dissolved in 30 mL ethyl acetate, washed with 1M NaOH (1x15 mL), water (1x20 mL) and brine solution (2x20 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated and dried in vacuum to afford the products as white solids. ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ: 3.26-3.16 (m, 4H), 3.10-2.92 (m, 4H), 1.95-1.77 (m, 2H), 1.75-1.65 (m, 7H), 1.52-1.40 (m, 2H), 1.37-1.20 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ: 151.75 (dd, *J* = 258.6, 15.1 Hz), 150.12 (dm, *J* = 250.5 Hz), 149.36 (dm, *J* = 255.5 Hz), 139.60-139.22 (m), 126.27-125.09 (m), 123.48 (q, *J* = 323.2 Hz), 120.02 (d, *J* = 16.7 Hz), 60.30 (d, *J* = 6.3 Hz), 56.00, 30.18, 28.64, 27.62, 24.95. ^{19}F NMR (376 MHz, acetone-d_6, ppm) δ: -79.23, -133.23, -141.02, -150.07. MS (*m/z*): Calc. for $C_{17}H_{20}N_3F_6O_4S_2Na$: 531.07. Found $(M-H)^-$: 508.1.

General procedure for ***A-Pip$_2$ORF$_2$***:

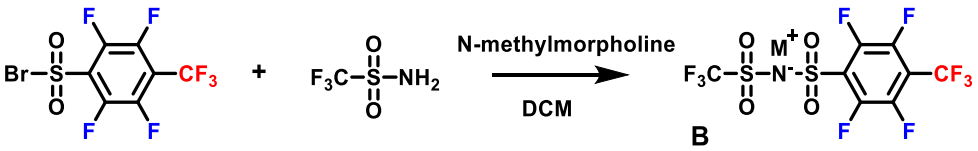
A 40 mL vial equipped with a magnetic stirring bar was charged with ***A-Pip$_2$F$_3$•H$^+$*** (0.7 mmol) and 4 mL dry DMF. Then corresponding sodium alkoxide (2.0 mmol) was added under nitrogen and the mixture was stirred at room temperature for 4h. The reaction was quenched by adding 20 ml 1M HCl aqueous solution. The white precipitate was filtered and washed by water (3x20 mL). The collected solids were dissolved in 30 mL ethyl acetate, washed with 1M NaOH (1x15 mL), water (1x20 mL) and brine solution (2x20 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated and dried in vacuum to afford the products as white solids.

A-Pip$_2$OMeF$_2$ (0.31 g, 81%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 3.89 (s, 3H), 3.25-3.18 (m, 4H), 3.14-2.95 (m, 4H), 2.00-1.85 (m, 2H), 1.75-1.57 (m, 7H), 1.50-1.40 (m, 2H), 1.37-1.23 (m, 1H). ^{13}C NMR (126 MHz, acetone-d$_6$, ppm) δ: 151.81 (dd, *J* = 716.6, 7.0 Hz), 150.83 (dd, *J* = 718.4, 7.0 Hz), 142.57 (dd, *J* = 14.7, 3.8 Hz), 136.09 (dd, *J* = 14.7, 3.8 Hz), 133.43 – 132.41 (m), 130.88 (d, *J* = 4.4 Hz), 120.30 (q, *J* = 322.9 Hz), 62.83, 52.07, 51.70, 26.48, 25.70, 24.26, 23.99. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -79.38, -132.55, -141.28. MS (*m/z*): Calc. for $C_{18}H_{23}N_3F_5O_5S_2Na$: 543.09. Found (M-Na)$^-$: 520.1.

A-Pip$_2$OEtF$_2$ (0.30 g, 78%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.12 (q, *J* = 8.0 Hz, 2H), 3.23-3.15 (m, 4H), 3.14-2.94 (m, 4H), 2.04-1.87 (m, 2H), 1.75-1.57 (m, 7H), 1.50-1.37 (m, 2H), 1.37-1.23 (m, 1H), 1.33 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 151.81 (dd, *J* = 254.4, 7.1 Hz), 147.43 (d, *J* = 7.1 Hz), 145.20-144.75 (m), 134.93 (t, *J* = 12.1 Hz), 122.51(d, *J* = 4.1 Hz), 122.35, 119.70 (q, *J* = 323.2 Hz), 72.20, 55.85, 52.21, 26.40, 24.75, 23.90, 21.33, 15.42. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -78.78, -133.32, -140.70. MS (*m/z*): Calc. for $C_{19}H_{25}N_3F_5O_5S_2Na$: 557.11. Found (M-Na)$^-$: 534.1.

A-Pip$_2$OiPrF$_2$ (0.31 g, 78%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.52-4.40 (m, 1H), 3.24-3.14 (m, 4H), 3.14-2.95 (m, 4H), 2.00-1.85 (m, 2H), 1.75-1.55 (m, 7H), 1.50-1.40 (m, 2H), 1.37-1.23 (m, 1H), 1.28 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (126 MHz, acetone-d$_6$, ppm) δ: 152.85 (dd, *J* = 671.6, 6.3 Hz), 150.92 (dd, *J* = 662.1, 6.3 Hz), 140.02 (dd, *J* = 13.0, 6.3 Hz), 136.06 (dd, *J* = 14.0, 6.3 Hz), 132.58 (t, *J* = 12.5 Hz), 132.04, 120.33 (q, *J* = 323.8 Hz), 78.67, 51.97, 51.56, 26.36, 25.51, 24.12, 23.87, 21.19. ^{19}F NMR (376 MHz, DMSO-d$_6$, ppm) δ: -79.11, -132.63, -137.55. MS (*m/z*): Calc. for $C_{20}H_{27}N_3F_5O_5S_2Na$: 571.12. Found (M-Na)$^-$: 548.1.

A-Pip$_2$ONeopF$_2$ (0.32 g, 77%). ^{1}H NMR (400 MHz, acetonitrile-d$_3$, ppm) δ: 3.77 (s, 2H), 3.28-3.14 (m, 4H), 3.14-2.95 (m, 4H), 2.05-1.87 (m, 2H), 1.80-1.57 (m, 7H), 1.52-1.40 (m, 2H), 1.37-1.23 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, acetonitrile-d$_3$, ppm) δ: 152.93 (dd, *J* = 632.5, 6.1 Hz), 150.98 (dd, *J* = 630.0, 6.1 Hz), 142.87 (dd, *J* = 13.0, 4.1 Hz), 135.94 (dd, *J* = 14.0, 4.3 Hz), 132.90-132.45 (m), 131.94 (d, *J* = 5.0 Hz), 120.69 (q, *J* = 324.7 Hz), 84.23, 52.13, 51.60, 32.10, 26.50, 26.19, 25.74, 24.32, 24.03. ^{19}F NMR (376 MHz, acetonitrile-d$_3$, ppm) δ: -78.31, -133.65, -140.51. (*m/z*): Calc. for $C_{22}H_{31}N_3F_5O_5S_2Na$: 599.15. Found (M-Na)$^-$: 576.1.



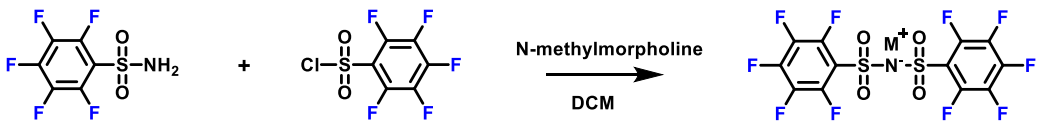
B

B: To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added trifluoromethane sulfonamide (8.0 mmol), N-methylmorpholine (16.0 mmol), and 40 mL DCM. The mixture was cooled to 0 °C. With stirring, 4-trifluoromethyl-2,3,5,6-tetrafluorobenzenesulfonyl bromide[13] (8.2 mmol) in 10 mL DCM was added dropwise via dropping funnel. The solution was further stirred at room temperature for 24 h. After removing DCM solvent under vacuum, the residue was dissolved in 100 mL ethyl acetate, and washed with 1M hydrochloric acid (1x30 mL), water (1x40 mL) and brine solution (2x40 mL). Then organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent to afford the product as a white solid (2.60 g, 72%). ^{13}C NMR (126 MHz, acetone-d^6, ppm, δ): 142.10–139.55 (m), 138.16 (t, *J* = 20.3 Hz), 122.65 (t, *J* = 15.0 Hz), 115.71 (q, *J* = 275.2 Hz), 114.92 (q, *J* = 321.3 Hz), 108.56–103.96 (m). ^{19}F NMR (376 MHz, acetone-d^6, ppm, δ): -57.61, -79.58, -137.16, -141.80. MS (*m/z*): Calc. for $C_8NF_{10}O_4S_2Na$: 450.90. Found (M-Na)$^-$: 427.9.

The synthesis procedure of ***B-OR*$_4$** was similar with ***A-OR*$_3$*F*$_2$**. The product was acquired as white solids by flash chromatography on silica gel with acetone/hexanes (v/v = 1/2) as the eluent.

***B-OEt*$_4$** (58%). ^{1}H NMR (400 MHz, acetone-d$_6$, ppm) δ: 4.19 (q, *J* = 7.0 Hz, 4H), 4.09 (t, *J* = 7.0 Hz, 4H), 1.46-1.32 (m, 12H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 148.03, 147.64, 137.53, 123.18 (q, *J* = 276.1 Hz), 120.80 (q, *J* = 28.2 Hz), 120.33 (q, *J* = 323.8 Hz), 70.21, 69.99, 14.85. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -56.49, -78.67. (*m/z*): Calc. for $C_{16}H_{20}NF_6O_8S_2Na$: 555.04. Found (M-Na)$^-$: 532.0.

***B-OiPr*$_4$** (64%). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ: 4.95-4.70 (m, 4H), 1.45-1.1(m, 24H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 145.94, 145.44, 138.11, 123.35 (q, *J* = 276.1 Hz), 121.20 (q, *J* = 27.2 Hz), 120.37 (q, *J* = 324.2 Hz), 76.02, 74.11, 21.33, 21.29. ^{19}F NMR (376 MHz, DMSO-d$_6$, ppm) δ: -53.74, -78.89. MS (*m/z*): Calc. for $C_{20}H_{28}NF_6O_8S_2Na$: 611.11. Found (M-Na)$^-$: 588.1.



C

C: To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added 2,3,4,5,6-pentafluorobenzene sulfonamide (10.0 mmol), N-methylmorpholine (20.0 mmol), and 60 mL DCM. The

mixture was cooled to 0 °C. With stirring, 2,3,4,5,6-pentafluorobenzene sulfonyl chloride (10.5 mmol) in 15 mL DCM was added dropwise via dropping funnel. The solution was further stirred at room temperature for 24 h. After removing DCM solvent under vacuum, the residue was dissolved in 100 mL ethyl acetate, and washed with 1M HCl (1x30 mL), and brine solution (2x40 mL). Then organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with acetone/hexanes (v/v = 2/3) as the eluent to afford the product as a white solid (2.60 g, 84%). ^{13}C NMR (101 MHz, acetone-d^6, ppm, δ): 144.39 (ddd, *J* = 255.2, 11.7, 5.8 Hz), 142.43 (dm, *J* = 255.4 Hz), 137.38 (dm, *J* = 250.1 Hz), 120.88 (t, *J* = 15.4 Hz). ^{19}F NMR (376 MHz, acetone-d^6, ppm, δ): -137.72, -150.75, -162.13. MS (*m/z*): Calc. for $C_{12}NF_{10}O_4S_2Na$: 498.90. Found $(M\text{-}Na)^-$: 475.9.

***C-PipF*$_4$** (75%): The synthesis procedure was similar with ***A-PipF*$_4$**. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ: 3.25-3.17 (m, 8H), 1.68-1.54 (m, 12H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 144.43 (dm, *J* = 259.1 Hz), 140.99 (dm, *J* = 240.9 Hz), 133.21, 114.80-114.0 (m), 51.86, 26.28, 23.75. ^{19}F NMR (376 MHz, DMSO-d$_6$, ppm) δ: -77.96, -140.13, -151.99. MS (*m/z*): Calc. for $C_{12}H_{10}N_2F_7O_4S_2Na$: 466.0. Found $(M\text{-}Na)^-$: 443.0.

C-PipOEt*$_2$*F*$_2$** (72%): The synthesis procedure was similar with A-PipOEt*$_2$*F*$_2$**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.07 (q, *J* = 6.8 Hz, 1H), 3.23-3.10 (m, 8H), 1.72-1.54 (m, 12H), 1.36 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, acetone-d$_6$, ppm) δ: 146.91 (dm, *J* = 242.4 Hz), 142.86-142.25 (m), 135.80-134.60 (m), 117.90, 71.70, 52.07, 26.53, 24.05, 14.90. ^{19}F NMR (376 MHz, acetone-d$_6$, ppm) δ: -142.00. MS (*m/z*): Calc. for $C_{30}H_{40}N_3F_4O_8S_2Na$: 733.21. Found $(M\text{-}Na)^-$: 710.2.

C-PipOiPr*$_2$*F*$_2$** (68%): The synthesis procedure was similar with A-PipOiPr*$_2$*F*$_2$**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.46-4.32 (m, 4H), 3.15-3.07 (m, 8H), 1.65-1.46 (m, 12H), 1.20 (d, *J* = 6.1 Hz, 24H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 147.23 (dd, *J* = 242.7, 6.2 Hz), 141.68–138.40 (m), 132.82 (t, *J* = 12.7 Hz), 124.77, 78.19, 52.15, 26.60, 24.32, 22.07. ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: -139.86. MS (*m/z*): Calc. for $C_{34}H_{48}N_3F_4O_8S_2Na$: 789.27. Found $(M\text{-}Na)^-$: 766.2.

General Procedure for Chemical Stability Test

A 10 mL microwave vial was charged with 0.040 mmol sulfonamide salts and a stir bar, and transferred into the glove box. Then 0.5 mmol Li_2O_2, 0.5 mmol KO_2, 0.040 mmol 4-Methoxybiphenyl and 0.8 mL DMF were added into the vial. 4-Methoxybiphenyl has been proved to be stable under test condition[14] and is chosen as the inner stand for quantitatively calculation of survived sulfonamide salts via ^{1}H-NMR integration. After the vial was sealed, it was moved out of the glove box and heated in an oil bath at 80 °C

for 3 days. Then, the reaction mixture was cooled down and treated with d^6-DMSO. The mixture was further centrifuged. The liquid layer was analyzed with ^{1}H, ^{19}F-NMR, and LC-MS.

NMR results of chemical stability test

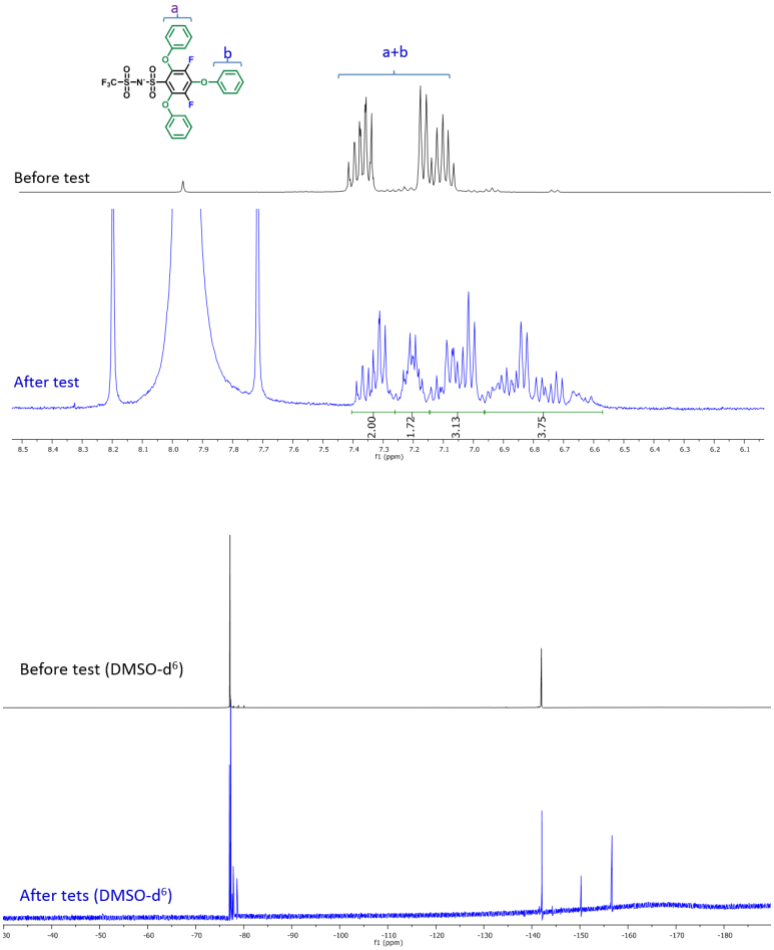


Figure S5. ^{1}H and ^{19}F NMR of ***A-OPh$_3$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

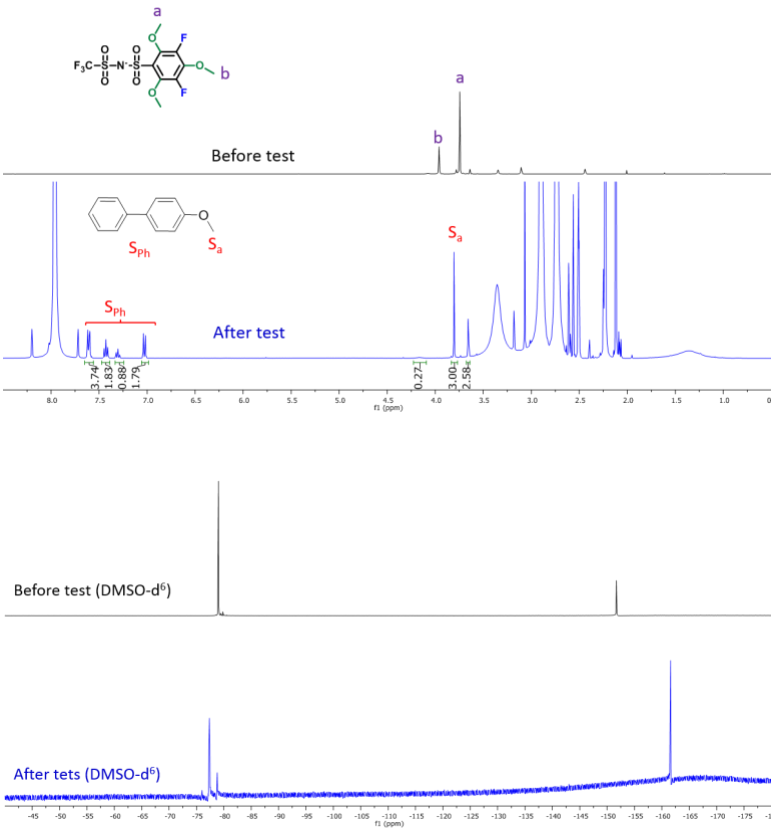


Figure S6. ^{1}H and ^{19}F NMR of ***A-OMe$_3$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

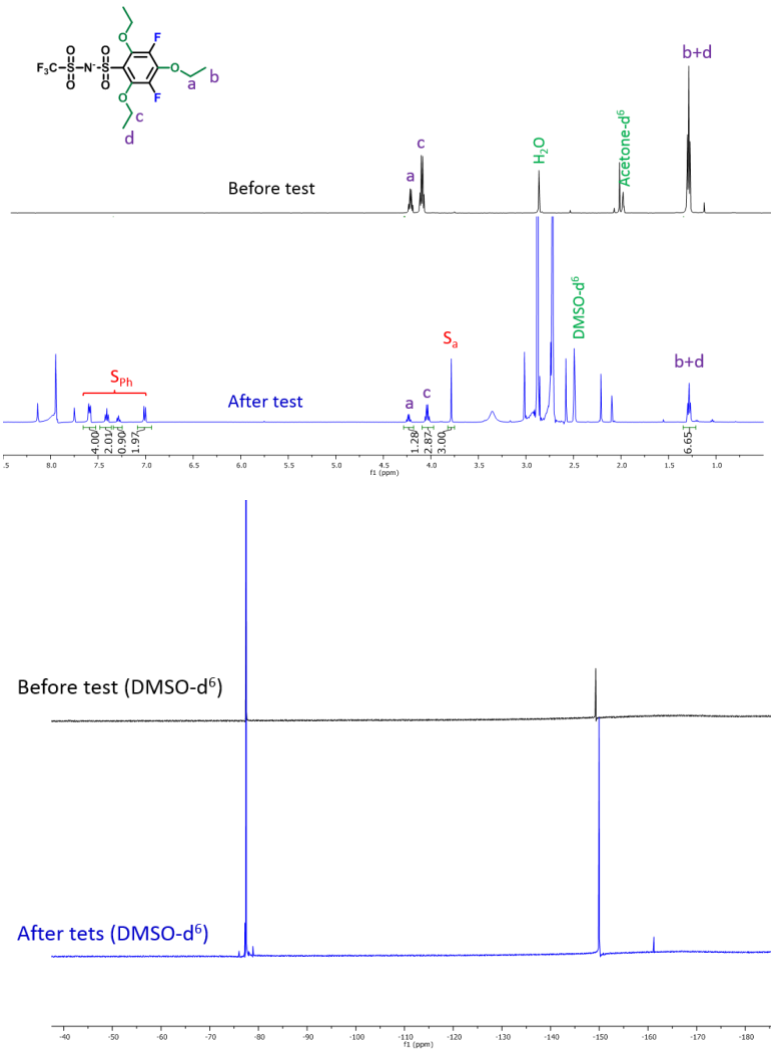


Figure S7. ^{1}H and ^{19}F NMR of ***A-OEt$_3$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

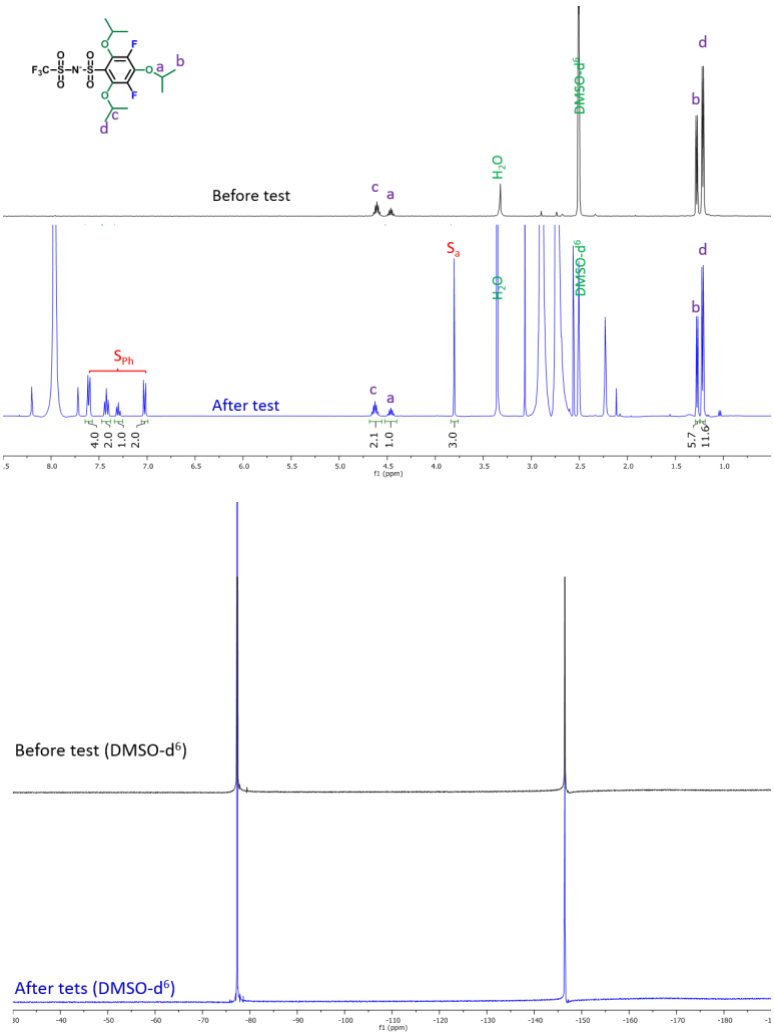


Figure S8. ^{1}H and ^{19}F NMR of ***A-OiPr₃F₂*** before and after stability test in DMF. NMR solvent: d^{6}-DMSO.

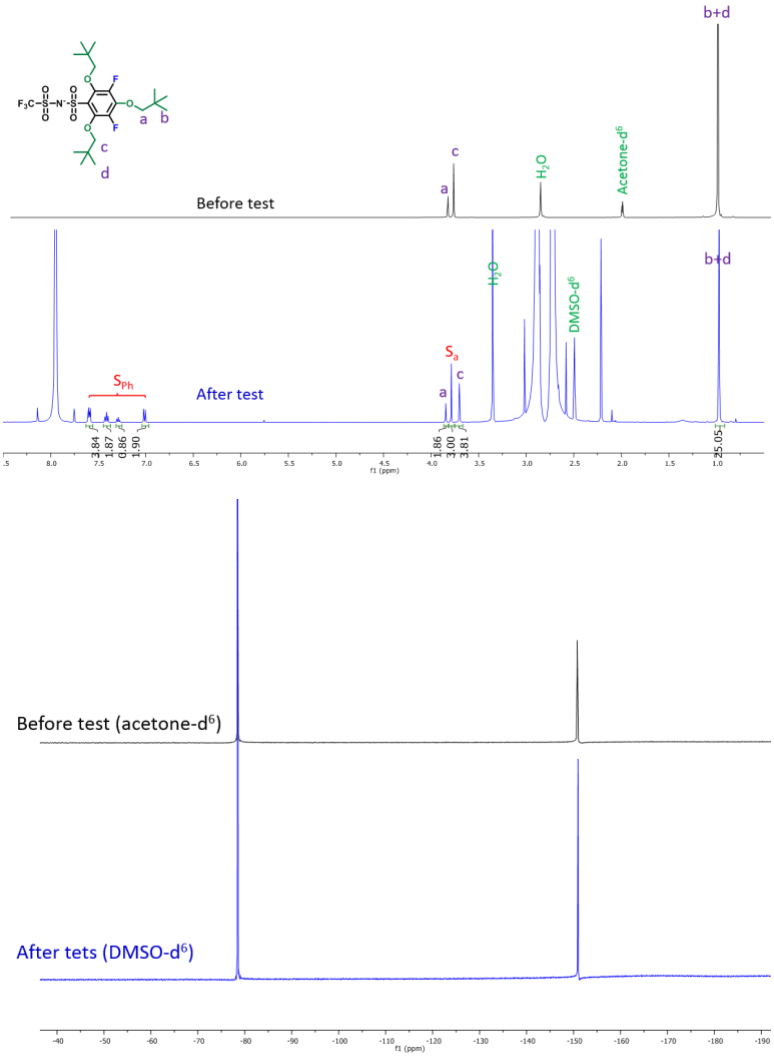


Figure S9. ^{1}H and ^{19}F NMR of ***A-ONeop$_3$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

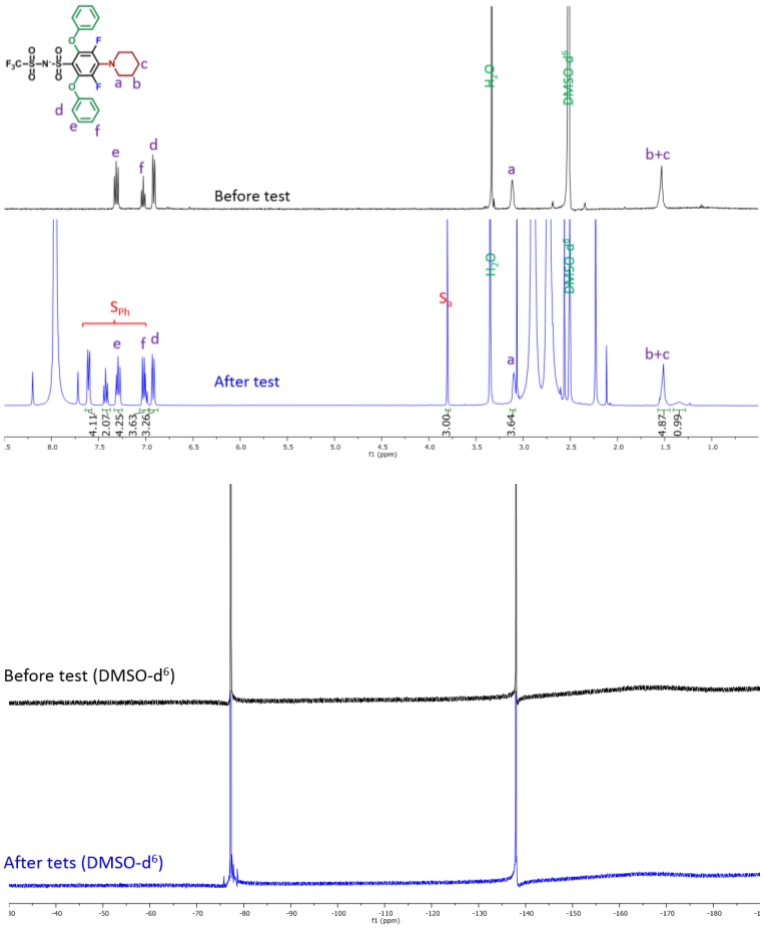


Figure S10. ^{1}H and ^{19}F NMR of ***A-PipOPh$_2$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

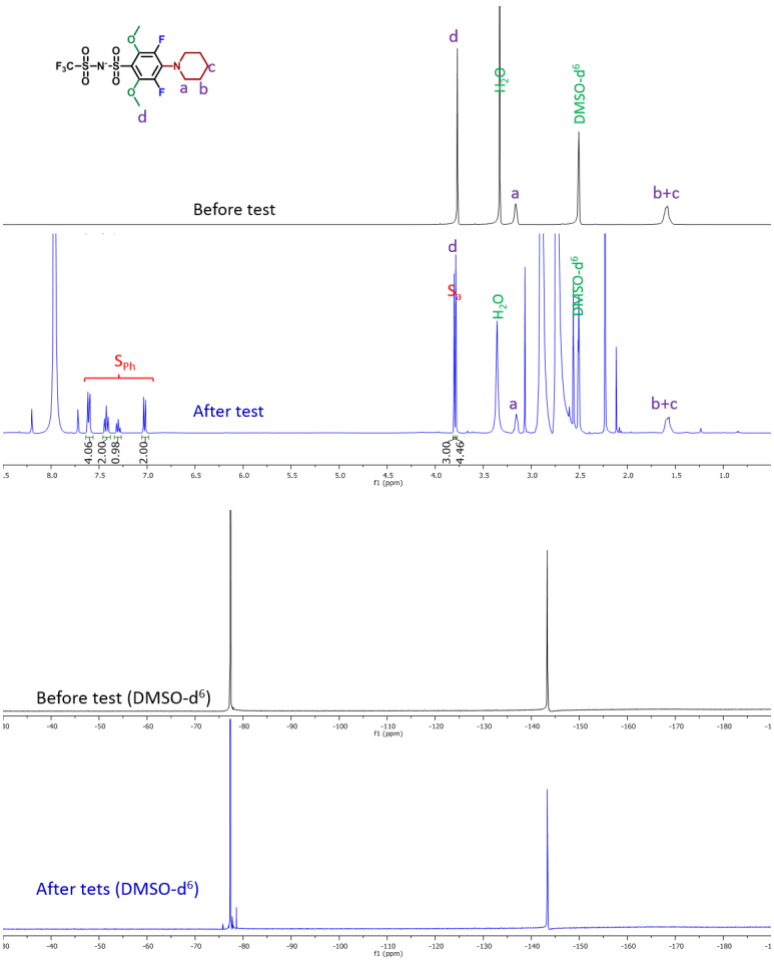


Figure S11. ^{1}H and ^{19}F NMR of ***A-PipOMe$_2$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

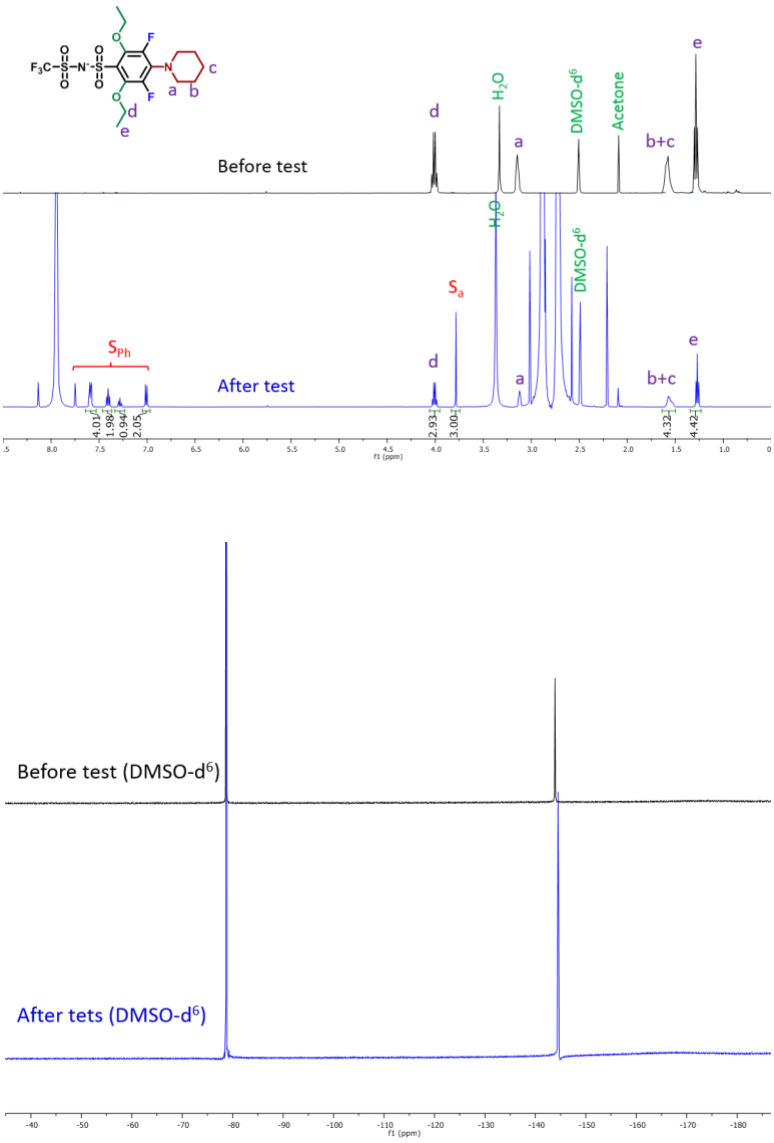


Figure S12. ^{1}H and ^{19}F NMR of ***A-PipOEt₂F₂*** before and after stability test in DMF. NMR solvent: d^{6}-DMSO.

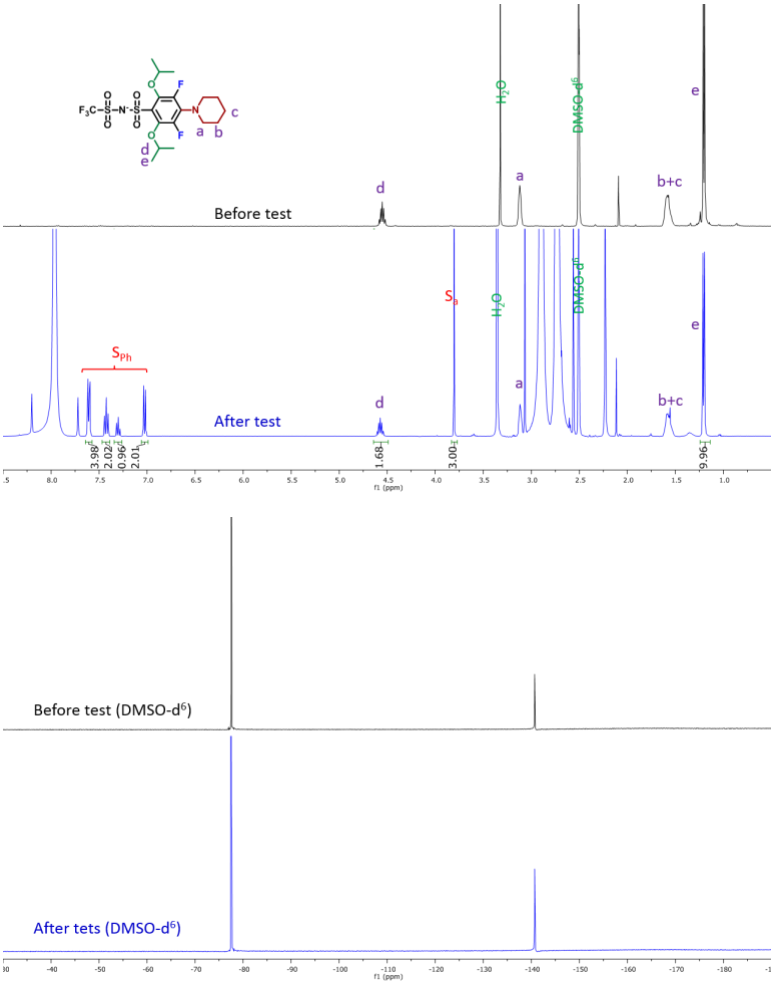


Figure S13. ^{1}H and ^{19}F NMR of ***A-PipOiPr$_2$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

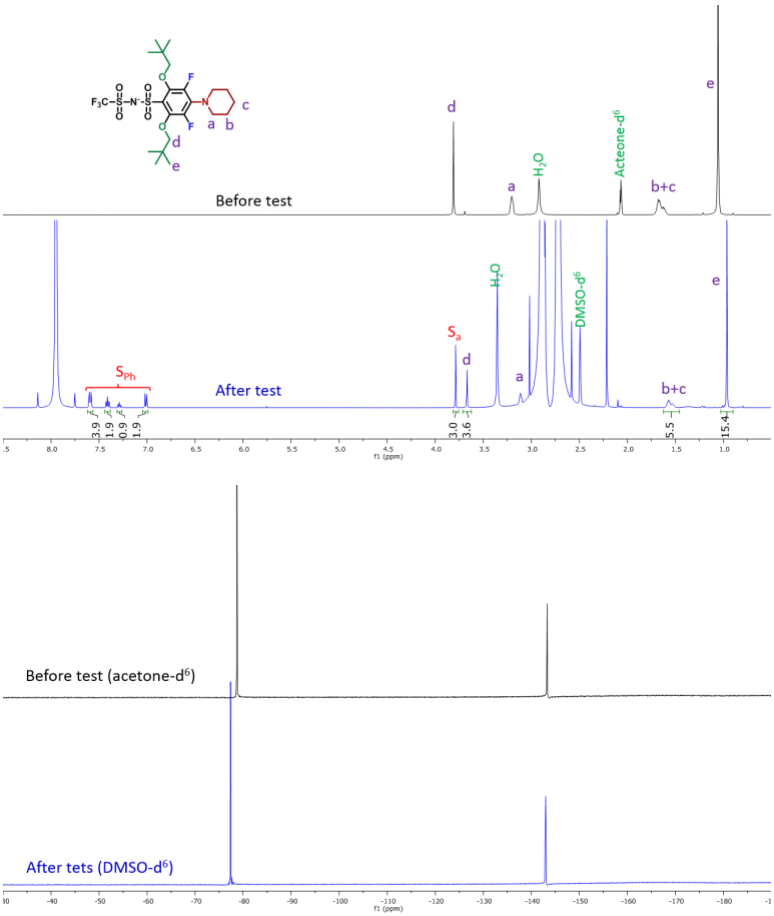


Figure S14. ^{1}H and ^{19}F NMR of ***A-PipONeop$_2$F$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

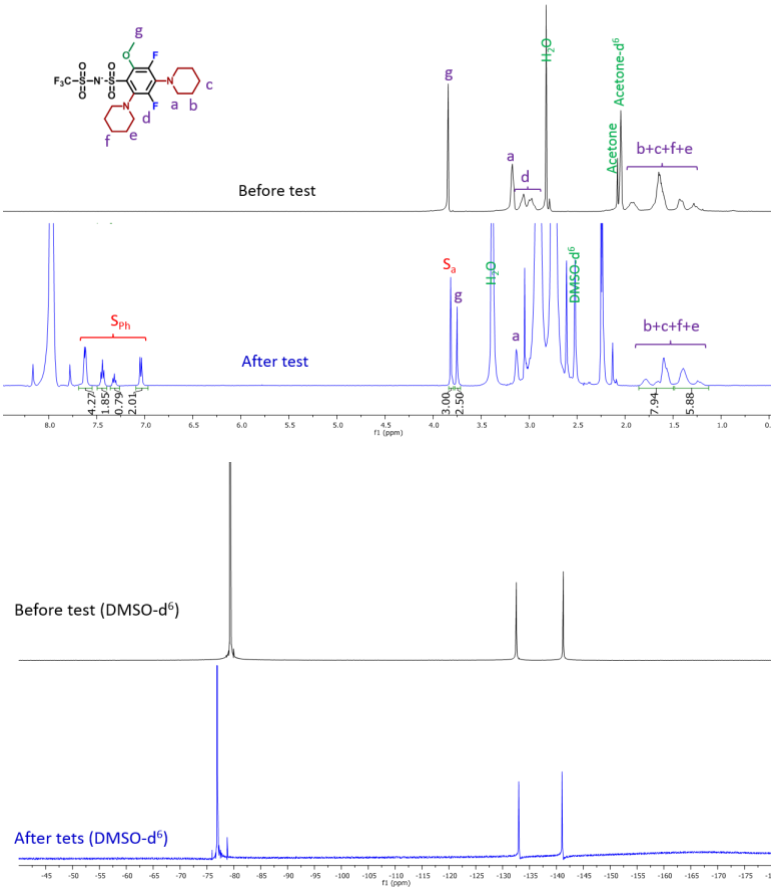


Figure S15. ^{1}H and ^{19}F NMR of ***A-Pip$_2$OMeF$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

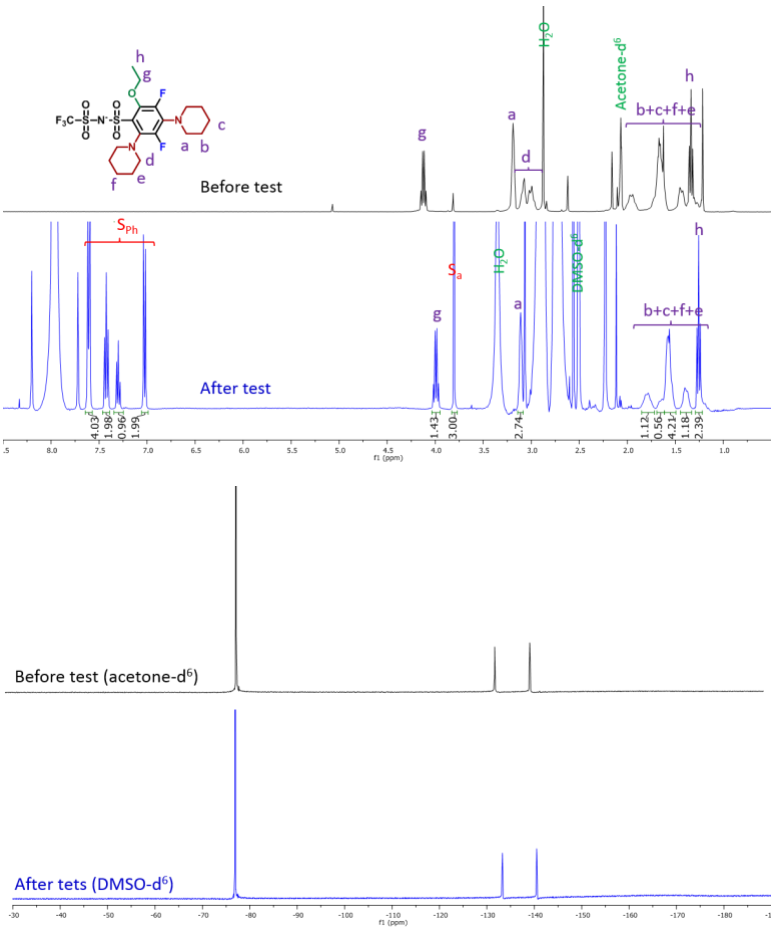


Figure S16. ^{1}H and ^{19}F NMR of ***A-Pip$_2$OEtF$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

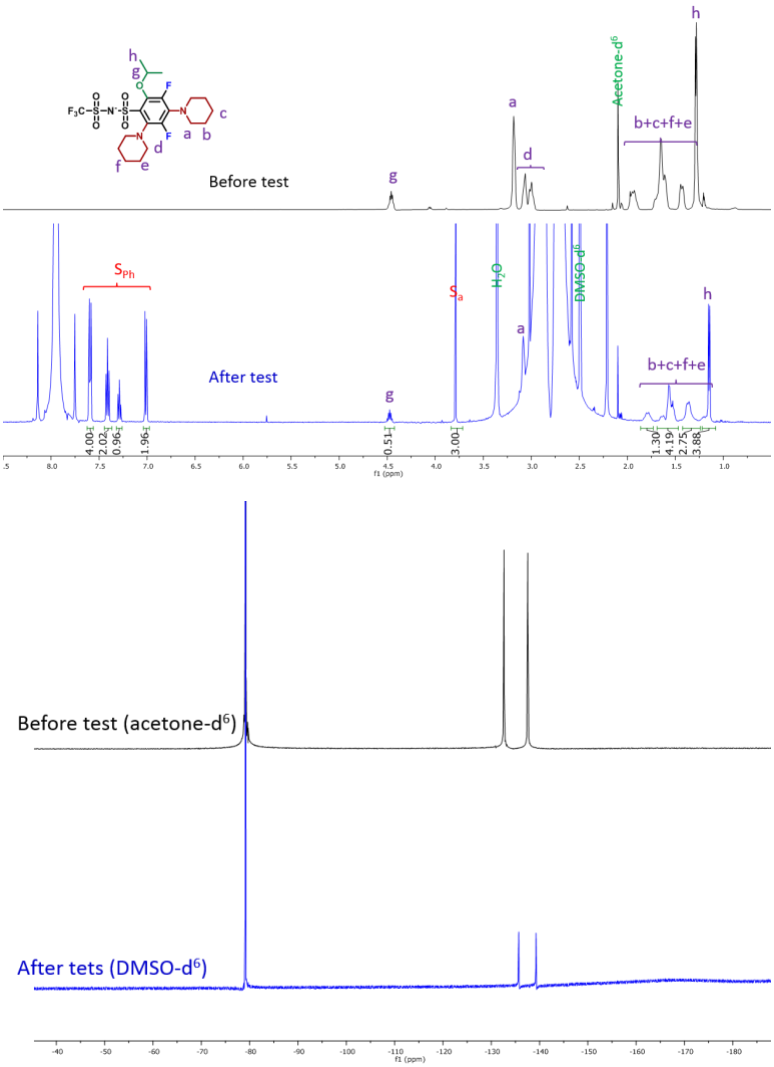


Figure S17. ^{1}H and ^{19}F NMR of ***A-Pip$_2$OiPrF$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

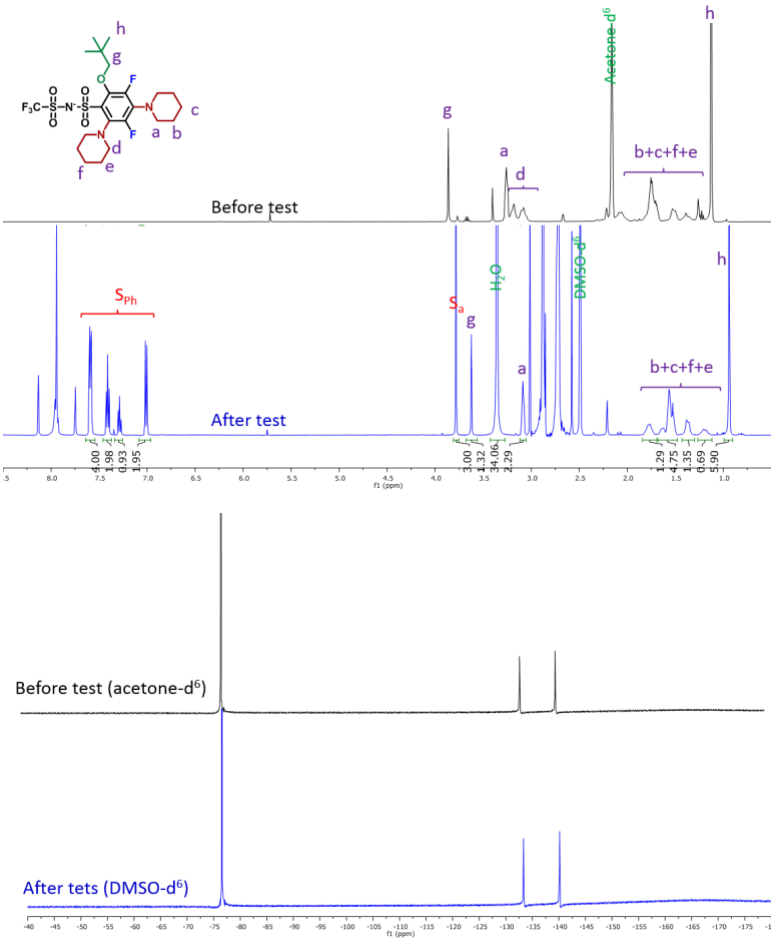


Figure S18. ^{1}H and ^{19}F NMR of ***A-Pip$_2$ONeopF$_2$*** before and after stability test in DMF. NMR solvent: d^6-DMSO.

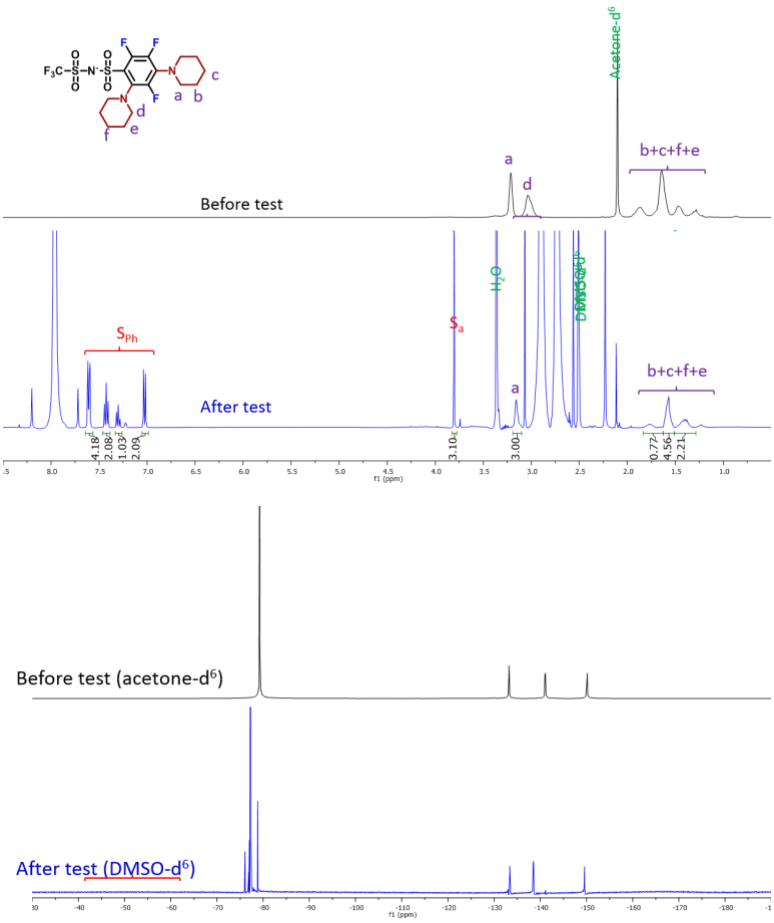


Figure S19. ^{1}H and ^{19}F NMR of ***A-Pip$_2$F$_3$*** before and after stability test in DMF. NMR solvent: d^6-Acetone (before stability test) d^6-DMSO (after stability test).

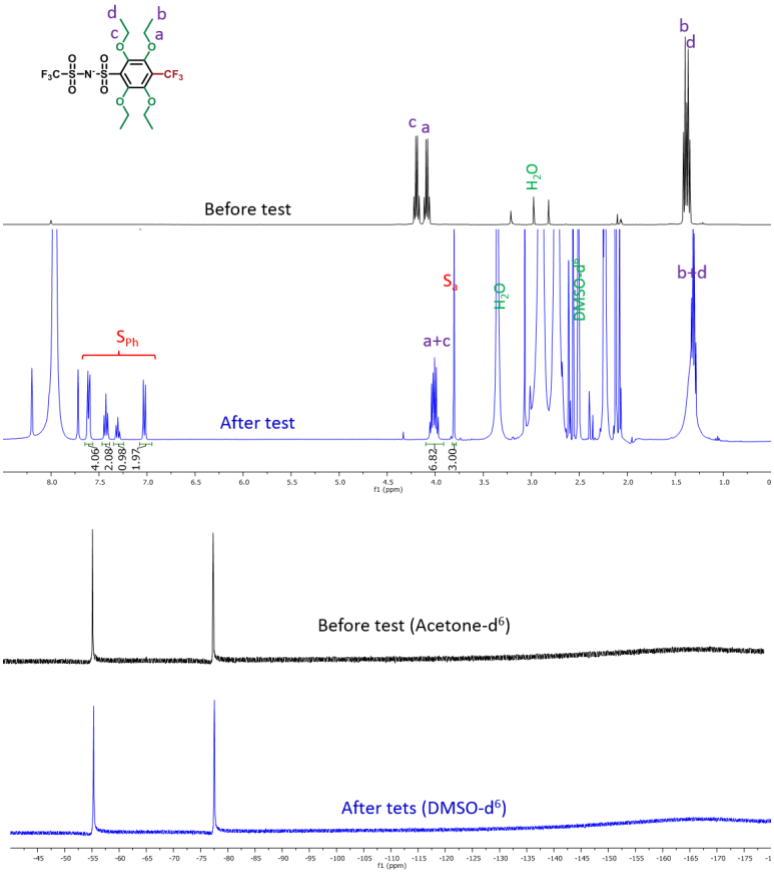


Figure S20. ^{1}H and ^{19}F NMR of ***B-OEt$_4$*** before and after stability test in DMF. NMR solvent: d^6-Acetone (before stability test) d^6-DMSO (after stability test).

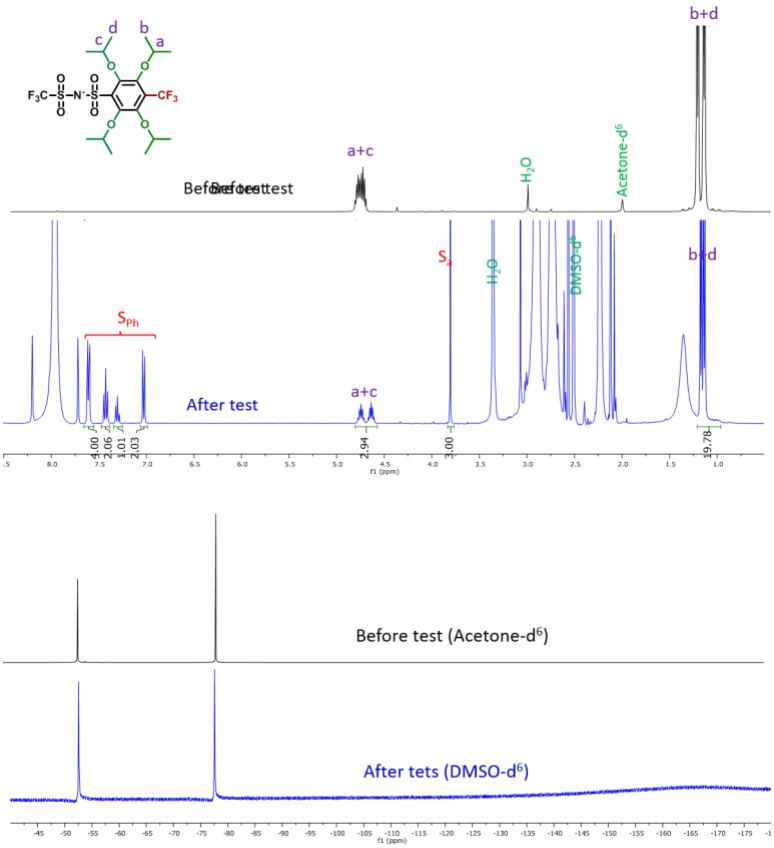


Figure S21. ^{1}H and ^{19}F NMR of ***B-OiPr₄*** before and after stability test in DMF. NMR solvent: d^6-Acetone (before stability test) d^6-DMSO (after stability test).

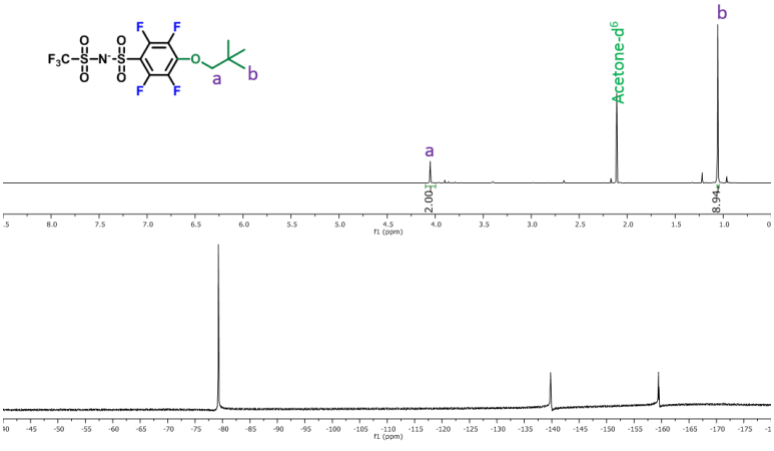


Figure S22. ^{1}H and ^{19}F NMR of ***A-NeopF_4.*** NMR solvent: d^6-Acetone.

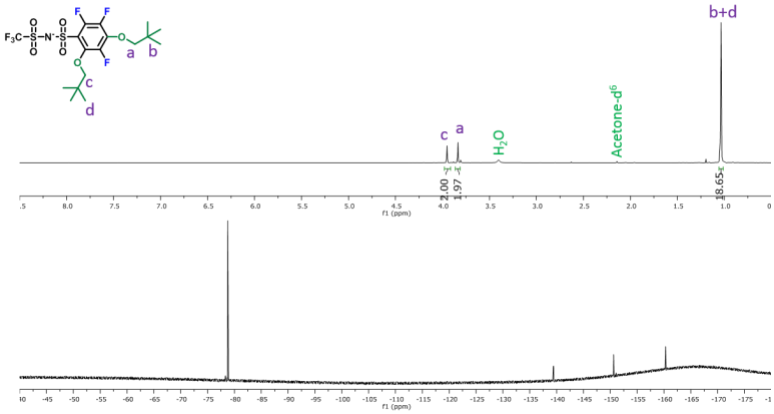


Figure S23. ^{1}H and ^{19}F NMR of ***A-Neop$_2F_3$.*** NMR solvent: d^6-Acetone.

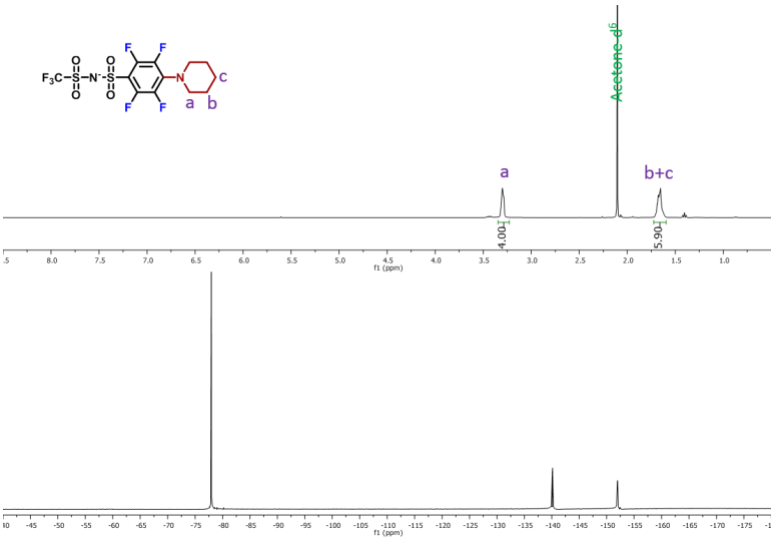


Figure S24. ^{1}H and ^{19}F NMR of ***A-PipF₄***. NMR solvent: d^{6}-Acetone.

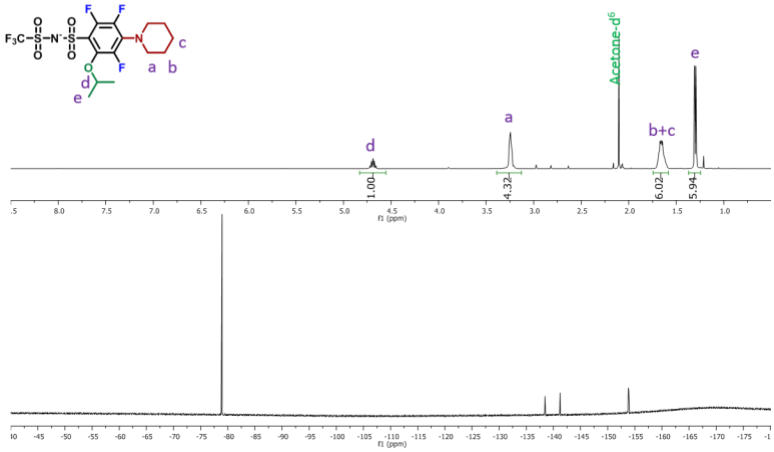


Figure S25. ^{1}H and ^{19}F NMR of ***A-PipOiPrF₃***. NMR solvent: d^{6}-Acetone.

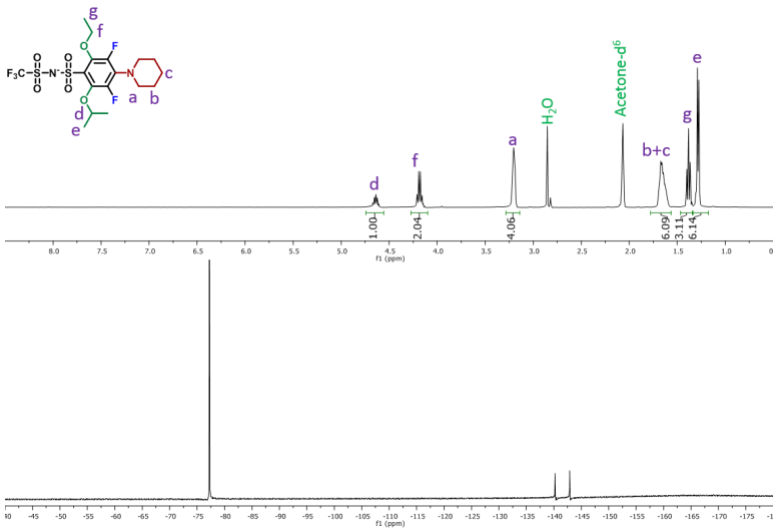


Figure S26. ^{1}H and ^{19}F NMR of ***A-PipOEtOiPrF$_3$***. NMR solvent: d^6-Acetone.

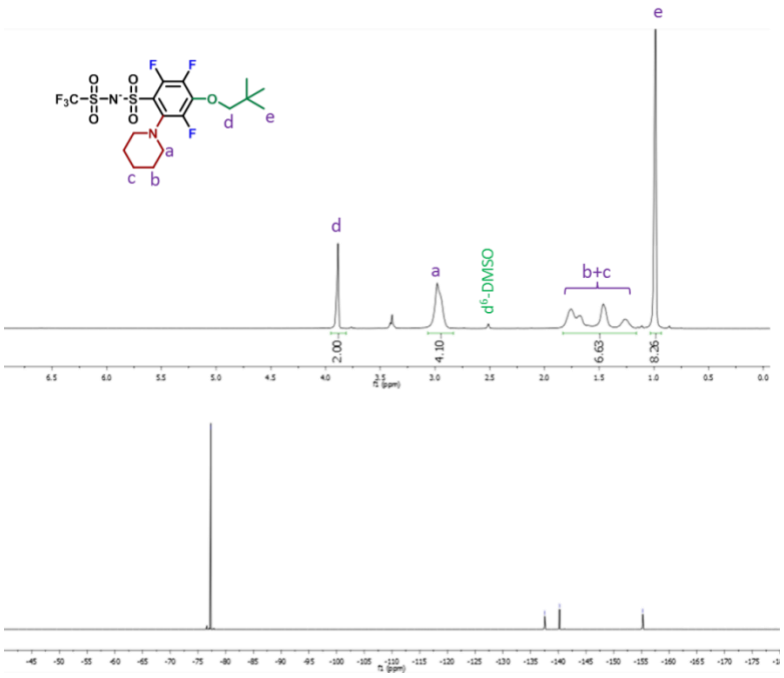


Figure S27. ^{1}H and ^{19}F NMR of ***A-o-PipONeopF$_3$***. NMR solvent: d^6-DMSO.

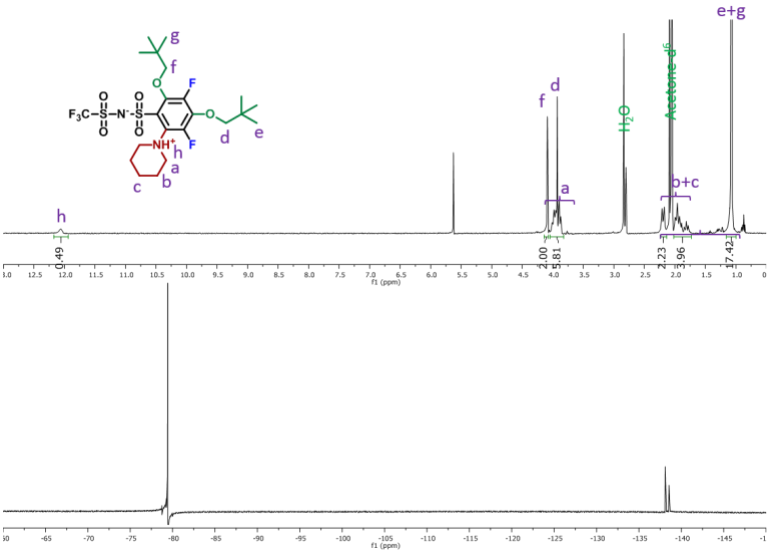


Figure S28. ^{1}H and ^{19}F NMR of ***A-o-PipONeop$_2$F$_2$***●H$^+$. NMR solvent: d^6-Acetone.

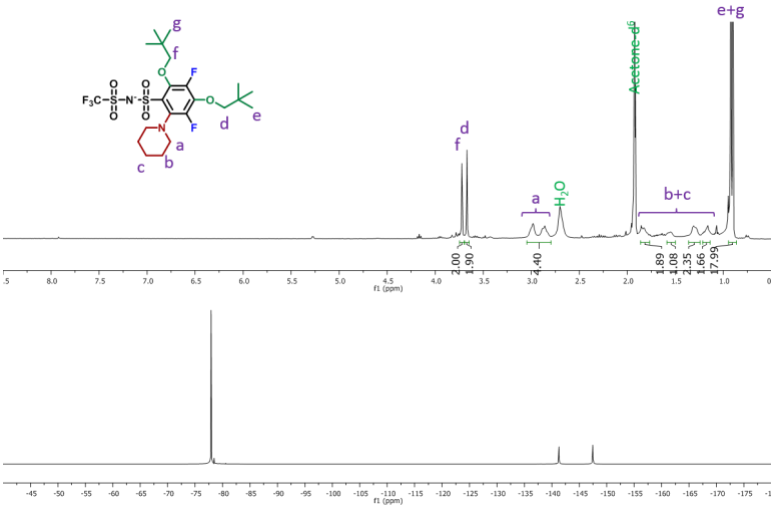


Figure S29. ^{1}H and ^{19}F NMR of ***A-o-PipONeop$_2$F$_2$***. NMR solvent: d^6-Acetone.

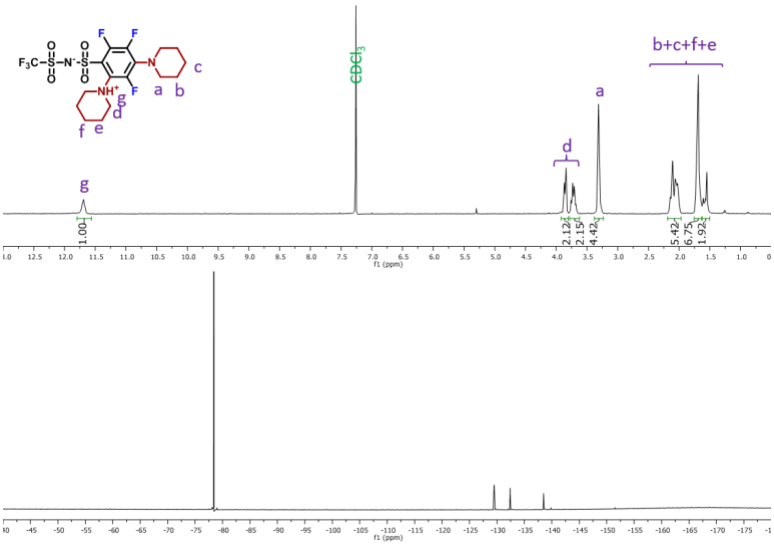


Figure S30. ^{1}H and ^{19}F NMR of ***A-Pip$_2$F$_3$***$\bullet H^+$. NMR solvent: CDCl3.

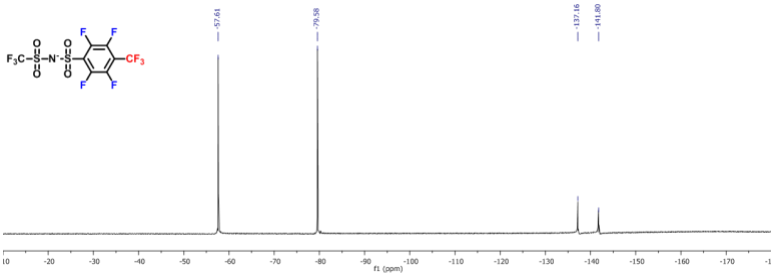


Figure S31. ^{19}F NMR of **B**. NMR solvent: d^6-Acetone.

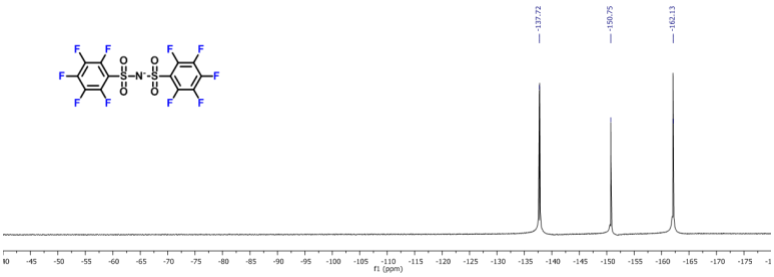


Figure S32. ^{19}F NMR of **C**. NMR solvent: d^6-Acetone.

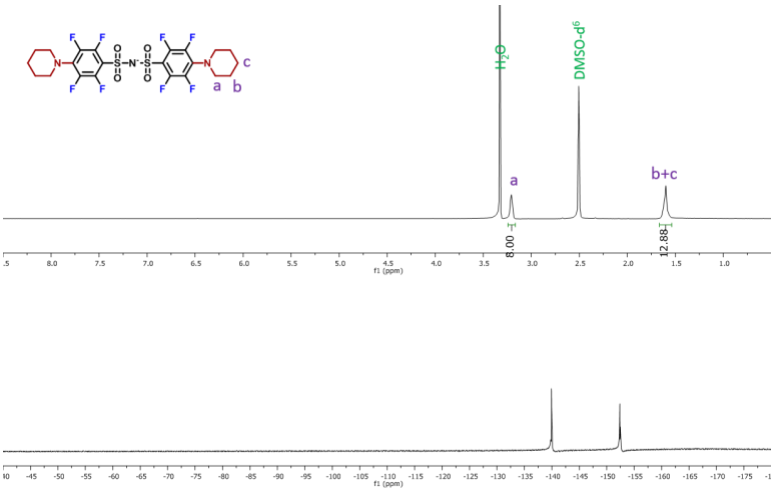


Figure S33. ^{1}H and ^{19}F NMR of ***C-PipF₄***. NMR solvent: d^6-DMSO.

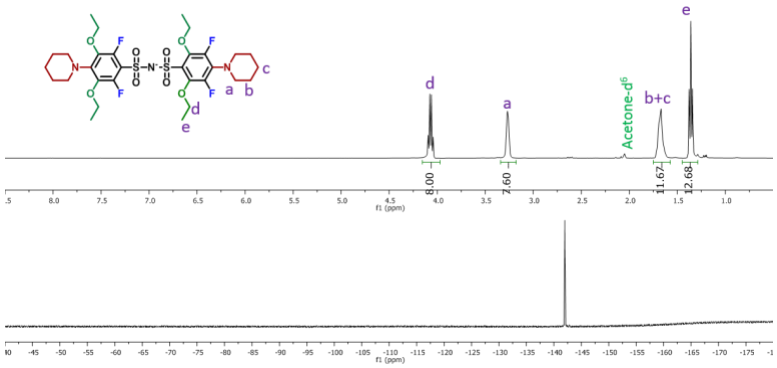


Figure S34. ^{1}H and ^{19}F NMR of ***C-PipOEt$_2$F$_2$***. NMR solvent: d^6-Acetone.

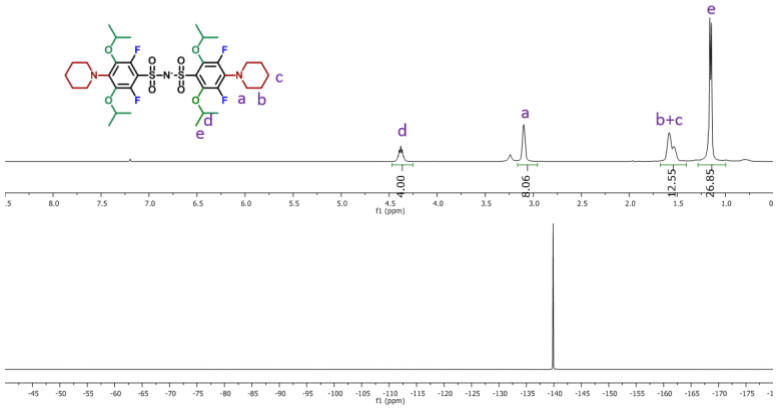


Figure S34. ^{1}H and ^{19}F NMR of ***C-PipOiPr$_2$F$_2$***. NMR solvent: d^6-Acetone.

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