Electronic Supporting Information

for

Synthesis of new hybrid 1,4-thiazinyl-1,2,3-dithiazolyl radicals via Smiles rearrangement

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1. General Methods, Synthetic Procedures, and Instrument Details

1a. General Methods

All reactions were performed under an atmosphere of dry argon. Solvents used were at least reagent grade. Acetonitrile (MeCN), dichloromethane (DCM), and dichloroethane (DCE) were dried over P_2O_5 and/or CaH_2. Propionitrile (EtCN) was purified by standard procedures and distilled from P_2O_5 and CaH_2 prior to use. The reagent 2-aminothiophenol was purchased from Sigma-Aldrich, while regents 2-amino-5-chlorothiophenol,[1] 3-aminopyrazinethiol,[2] 2-aminoquinoxalinethiol,[3] 2-amino-5,6-dichloropyrazinethiol,[4a,b,d] 2-amino-5-chloropyrazinethiol,[4c,d] 2,6-difluoro-*N*-methylpyridinium trifluoromethanesulfonate,[5] and 2-amino-6-fluoro-*N*-methylpyridinium trifluoromethanesulfonate[4] were prepared and purified according to literature methods.

1b. Synthetic Procedures

Preparation of 3$^+$[OTf]. A mixture of one equivalent of the appropriate 2-aminobenzenethiol/3-aminopyrazinethiol/2-aminoquinoxalinethiol and one equivalent of 2-amino-6-fluoro-*N*-methylpyridinium trifluoromethanesulfonate in 25 – 75 ml of MeCN was stirred at room temperature (RT) with an excess of anhydrous Na_2CO_3 for 5 h. The yellow-orange solution was filtered, the insoluble precipitate washed with 2 x 20 ml of MeCN, and the volatiles removed by flash distillation to afford a yellow-orange solid. Recrystallization afforded the intermediate thioethers **3**$^+$[OTf] as spectroscopically pure crystalline solids in essentially quantitative yields.

3a$^+$[OTf]. Recrystallization from isopropyl alcohol (*i*-PrOH) afforded pale cream needles. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S1): 7.54 (t, 1H), 7.40 (dd, 1H), 7.36 (dd, 1H), 6.90 (dd, 1H), 6.84 (dd, 2H) 6.81 (br, s, 2H), 6.20 (d, 1H), 4.93 (br, s, 2H), 3.81 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 157.2, 153.1, 151.4, 142.2, 138.5, 134.5, 119.4, 117.0, 111.7, 110.1, 107.4, 37.9 (N-CH_3). IR (ATR, cm^{-1}): 3465 m, 3356 s, 3226 s, 3108 w, 1642 sh, s, 1620 s, 1590 m, 1570 s, 1505 m, 1485 m, 1447 s, 1410 w, 1371 w, 1327 w, 1280 s, 1245 vs, 1222 m, 1158 vs, 1089 w, 1055 vw, 1027 s, 946 w, 900 w, 870 w, 838 w, 787 m, 759 m, 719 w, 636 vs, 595 vw, 574 m, 516 s, 467 m, 413 w. High resolution +ESI-MS (MeCN) m/z [M]$^+$ for $C_{12}H_{14}N_3S$, found (calcd.): 232.0906 (232.0903).

3b$^+$[OTf]. Recrystallization from DCE afforded clear colorless plates. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S2): 7.54 (t, 1H), 7.41 (d, 1H), 7.34 (dd, 1H), 6.90 (d, 1H), 6.83 (dd, 1H), 6.79 (br, s, 2H), 6.22 (dd, 1H), 4.92 (br, s, 2H), 3.79 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 157.6, 135.5, 151.9, 142.6, 138.9, 134.9, 119.8, 117.4, 112.1, 111.0, 107.8, 38.3 (N-CH_3). IR (ATR, cm^{-1}): 3482 m, 3402 w, 3364 s, 3293 w, 3230 vs, 3111 w, 1668 m, 1621 m, 1573 s, 1514 m, 1480 m, 1445 m, 1399 w, 1374 w, 1294 s, 1276 m, 1244 vs, 1222 m, 1147 vs, 1053 m, 1028 s, 902 w, 886 w, 867 m, 816 m, 786 m, 755w, 724 m, 636 vs, 573 w, 558 w, 544 w, 513 s, 464 w, 424 w. Elemental analysis for $C_{13}H_{13}ClF_3N_3O_3S_2$, found (calcd.): C 37.66 (37.55), H 3.02 (3.15), N 10.09 (10.11).

3c$^+$[OTf]·MeCN. Recrystallization from MeCN afforded yellow needles. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S3): 8.03 (d, 1H), 7.81 (d, 1H), 7.68 (dd, 1H), 7.07 (dd, 1H), 6.96 (s, br, 2H), 6.85 (dd, 1H), 5.53 (s, br, 2H), 3.78 (s, 3H), 1.96 (s, 3H; MeCN). ^{13}C-NMR (CD_3CN, δ ppm): 156.5, 154.5, 144.7, 143.2, 141.4, 134.5, 131.8, 118.3, 113.9, 37.7 (N-CH_3). IR (ATR, cm^{-1}): 3443 m, 3379 m, 3343 s, 3311 m, 3212 s, 3167 s, 3096 vw, 3061 vw, 3000 vw, 2946 vw, 2250 w, 1666 s, 1640 s, 1621 m, 1561 s, 1512 s, 1471 m, 1445 m, 1416 m, 1384 m, 1326 vw, 1272 s, 1246 s, 1224 s, 1195 s, 1156 vs, 1105 m, 1079 m, 1054 m, 1022 vs, 922 vw, 903 vw, 859

m, 794 m, 759 w, 727 w, 627 w, 578 vs, 550 s, 512 s, 483 s, 438 vs. Elemental analysis for $C_{13}H_{15}F_3N_6O_3S_2$, found (calcd.): C 36.48 (36.79), H 3.39 (3.56), N 19.57 (19.80).

3d$^+$[OTf]. Recrystallization from MeCN at -20 °C afforded bright yellow needles. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S4): 8.07 (s, 1H), 7.71 (t, 1H), 7.81 (d, 1H), 7.05 (s, br 1H), 6.95 (d, 1H), 5.67 (s, br, 2H), 3.79 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 157.7, 154.6, 144.6, 143.4, 142.4, 136.6, 131.0, 124.1, 119.8, 115.4, 38.8 (N-CH_3). IR (ATR, cm^{-1}): 3444 w, 3373 w, 3344 m, 3314 w, 3209 s, 3165 s,br, 2252 w, 1660 m, 1639 m, 1622 w, 1560 s, 1509 s, 1474 w, 1446 w, 1416 w, 1378 w, 1327 vw, 1265 vs, 1247 vs, 1191 s, 1164 vs, 1105 m, 1075 w, 1049 m, 1023 vs, 920 vw, 901 vw, 855 m, 790 m, 757 w, 725 vw, 628 vs, 576 s, 513 s, 487 m, 438 vs. High resolution +ESI-MS (MeCN) m/z [M]$^+$ for $C_{10}H_{11}ClN_5S$, found (calcd.): 268.0428 (268.0418).

3e$^+$[OTf]. Recrystallization from MeCN afforded dark orange blocks. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S5): 7.70 (t, 1H), 7.08 (d, 1H), 7.03 (s, br, 2H), 6.93 (d, 1H), 5.90 (s, br, 2H), 3.79 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 157.8, 154.2, 146.4, 144.8, 142.6, 133.5, 129.0, 119.6, 115.5, 39.0 (N-CH_3). IR (ATR, cm^{-1}): 3078 w, 3020 w, 1591 m, 1537 s, 1489 s, 1439 m, 1406 m, 1380 m, 1365 s, 1333 m, 1267 s, 1241 vs, 1224 vs, 1195 vs, 1174 vs, 1151 vs, 1082 m, 102 vs, 943 w, 918 w, 898 m, 877 w, 829 s, 789 m, 759 s, 741 m, 717 w, 694 w, 673 m, 627 vs, 584 s, 571 s, 540 m, 514 vs, 471 w, 455 s, 412 w. Elemental analysis for $C_{11}H_{10}Cl_2F_3N_5O_3S_2$, found (calcd.): C 29.06 (29.21), H 2.27 (2.23), N 15.77 (15.49).

3f$^+$[OTf]. Recrystallization from MeCN afforded yellow needles. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S6):[a] 7.59 (m, 1H), 7.41 (d, 3H), 7.36 (dd, 1H), 7.33 (m, 1H), 7.28 (dd, 1H), 7.11 (s, br, 2H), 5.70 (s, br, 2H), 3.82 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 157.9, 150.6, 142.6, 141.8, 138.7, 131.0, 128.6, 126.9, 126.4, 124.4, 116.5, 110.1, 108.2, 39.2 (N-CH_3). IR (ATR, cm^{-1}): 3465 w, 3348 m, 3301 w, 3181 s, br, 1667 m, 1629 , 1606 w, 1568 m, 1548 m, 1517 m, 1492 w, 1473 w, 1441 m, 1427 m, 1374 w, 1283 s, 1247 vs, 1158 s, 1143 vs, 1130 m, 1077 w, 1049 m, 1029 s, 940 w, 913 w, 894 w, 824 w, 809 m, 755 s, 728 m, 636 vs, 607 m, 593 w, 557 w, 513 m, 488 w, 480 w, 472 w, 438 m. Elemental analysis for $C_{15}H_{14}F_3N_5O_3S_2$, found (calcd.): C 40.82 (41.57), H 3.22 (3.26), N 16.28 (16.16).

Preparation of 4c$^+$[OTf]. Method A. A solution of **3c**$^+$[OTf]·MeCN (1.009 g, 2.378 mmol) in 45 ml of dry MeCN was gently refluxed for 8 days. The mixture was cooled to room temperature, filtered, and the solvent flash distilled to afford **4c**$^+$[OTf] as an orange-brown solid. Recrystallization from a MeCN afforded pure **4c**$^+$[OTf] as pale orange needles. Yield 50 % (0.456 g, 1.189 mmol). **Method B.** A solution of **3c**$^+$[OTf]·MeCN (0.681 g, 1.605 mmol) in 100 ml of MeCN was heated in a sealed vessel at 110 °C for 40 h. The solution was concentrated to dryness under reduced pressure and the solid was triturated with 55 ml of 1:5 mixture of MeCN in DCM, collected by filtration, washed with 2 x 20 ml of DCM, and dried in air to afford **4c**$^+$[OTf] as a reddish-orange solid. Yield 79 % (0.489 g, 1.276 mmol).

4c$^+$[OTf]. ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S7): 9.60 (s, 1H), 7.85 (t, 1H), 7.53 (dd, 1H), 7.47 (d, 1H), 7.20 (dd, 1H), 6.84 (dd, 1H), 6.66 (s, 2H), 3.68 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 164.9, 154.9, 153.0, 143.7, 142.9, 128.0, 121.7, 108.6, 106.4, 35.0 (N-CH_3). IR (ATR, cm^{-1}): 3354 m, 3306 w, 3229 vs, 3133 m, 3092 m, 3003 w, 1666 s, 1635 m, 1605 m, 1585 s, 1536 vs, 1510 vs, 1482 vs, 1461 s, 1421 m, 1385 m, 1332 m, 1240 vs, 1223 vs, 1163 vs, 1145 vs, 1098 s, 1060 s, 1025 vs, 971 m, 939 m, 888 m, 867 m, 788 vs, 762 m, 725 w,

[a] Recrystallization of **3f**$^+$[OTf] to afford an analytically pure sample was difficult due to the facile nature of the Smiles rearrangement. Hence, small quantities (< 10 %) of **4f**$^+$[OTf] were observed in the ^{1}H-NMR spectrum of **3f**$^+$[OTf] (see Fig. S6).

633 vs, 615 s, 571 vs, 556 m, 543 m, 514 s, 489 m, 456 w, 435 w, 426 w. Elemental analysis for $C_{11}H_{12}F_3N_5O_3S_2$, found (calcd.): C 34.18 (34.46), H 3.07 (3.16), N 18.61 (18.27).

Preparation of 4f[OTf]. A solution of crude **3f**$^+$[OTf] (0.389 g, 0.898 mmol) in 25 mL of dry MeCN was gently refluxed for 6 h. The mixture was cooled to room temperature, filtered, and the solvent flash distilled to afford **4f**$^+$[OTf] as an orange solid. Recrystallization from MeCN afforded pure **4f**$^+$[OTf] as orange irregular plates. Yield 80 % (0.308 g, 0.711 mmol).

4f$^+$**[OTf].** ^{1}H-NMR (CD_3CN, δ ppm, see Fig. S8): 9.77 (s, 1H), 7.91 (t, 1H), 7.74 (d, 1H), 7.65 (d, 1H), 7.49 (m, 3H), 6.90 (d, 1H), 6.70 (s, br, 2H), 3.73 (s, 3H). ^{13}C-NMR (CD_3CN, δ ppm): 170.0, 161.8, 156.1, 149.9, 144.7, 144.1, 135.5, 130.3, 128.9, 127.8, 116.5, 110.0, 108.1, 36.3 (N-CH_3). IR (ATR, cm^{-1}): 3353 vs, 3218 vs, 3120 m, 3054 m, 2996 m, 2944 m, 1667 m, 1636 m, 1611 vw, 1592 m, 1556 s, 1510 s, 1440 m, 1415 w, 1392 w, 1366 m, 1244 vs, 1225 s, 1082 vs, 1030 m, 956 s, 896 vs, 863 w, 817 m, 792 m, 778 w, 761 m, 744 m, 723 w, 670 m, 635 vs, 610 m, 594 m, 574 m, 557 w, 515 m, 477 w, 432 m. Elemental analysis for $C_{15}H_{14}F_3N_5O_3S_2$, found (calcd.): C 40.87 (41.57), H 3.19 (3.26), N 16.21 (16.06).

Preparation of 5a$^+$**[OTf].** To a solution of **3a**$^+$[OTf] (1.754 g, 4.600 mmol) in 40 ml of MeCN was added neat S_2Cl_2 (2.2 ml g, 27.600 mmol) dropwise and the mixture was gently refluxed for 16 h to afford a dark blue-black solution that was cooled to RT. A solution of *N*-benzyltriethylammonium chloride (1.840 g, 8.078 mmol) in 25 ml of MeCN was added with rapid stirring and the mixture was refluxed for 30 min and hot filtered to afford a blue-black solid that was washed with MeCN, 1:3 mixture of CS_2 in DCM, DCM, and dried in *vacuo*. To a suspension of crude **5a**$^+$[Cl] in 50 ml MeCN was added neat TMSOTf (1.0 ml, 5.525 mmol) and the mixture was refluxed for 2 h, hot filtered, and the volatiles were removed by flash distillation to afford a tacky black solid. The solid was triturated with 1:1 mixture of CS_2 in EtOAc, filtered, and the solid washed with DCM and dried in *vacuo* to afford a dark purple solid. Recrystallization from glacial acetic acid afforded a waxy blue-black solid, putatively **5a**$^+$[OTf]. Yield 2 % (0.042 g, 0.096 mmol).

5a$^+$**[OTf].** Low resolution +ESI-MS (MeCN): m/z 290 $[M]^+$, 324 $[M\text{-}Cl]^+$, 358 $[M\text{-}2Cl]^+$, and 392 $[M\text{-}3Cl]^+$.

Preparation of 5b$^+$**[OTf].** To a solution of **3b**$^+$[OTf] (0.974 g, 2.342 mmol) in 40 ml of MeCN was added neat S_2Cl_2 (1.857 g, 13.754 mmol) dropwise and the mixture was stirred at RT for 30 min before gently refluxing for 16 h to afford a dark blue solution. A solution of *N*-benzyltriethylammonium chloride (0.720 g, 3.189 mmol) in 10 ml of MeCN was added dropwise and the mixture was refluxed for 30 min and hot filtered to afford a blue-black solid that was washed with MeCN, hot DCE, DCM, and dried in *vacuo*. To a suspension of crude **5b**$^+$[Cl] in 50 ml of MeCN was added neat TMSOTf (0.651 g, 2.929 mmol) and the mixture refluxed for 90 min, hot filtered, and the volatiles removed by flash distillation to afford a violet powder. Repeated recrystallization from MeCN and EtCN afforded solid **5b**$^+$[OTf]. Yield 43 % (0.484 g, 1.021 mmol).

5b$^+$**[OTf].** IR (ATR, cm^{-1}): 3031 w, 2935 w, 1613 m, 1576 m, 1538 m, 1480 vs, 1439 vs, 1417 vs, 1380 s, 1322 w, 1307 m, 1247 vs, 1215 m, 1171 s, 1131 s, 1096 vs, 1012 vs, 937 s, 880 w, 856 s, 840 s, 815 vs, 789 s, 741 s, 717 s, 701 vs, 680 m, 663 m, 629 m, 578 w, 550 m, 532 s, 511 w, 485 w, 475 w, 459 m, 443 m, 416 m. Elemental analysis for $C_{13}H_7ClF_3N_3O_3S_4$, found (calcd.): C 32.49 (32.95), H 1.63 (1.49), N 8.87 (9.05). Low resolution +ESI-MS (MeCN): m/z 324 $[M]^+$.

Preparation of 5d$^+$**[OTf].** To a solution of **3d**$^+$[OTf] (0.331 g, 0.662 mmol) in 25 ml of MeCN was added neat S_2Cl_2 (0.761 g, 5.636 mmol) dropwise and the mixture was stirred at RT for 30 min before gently

refluxing for 24 h to afford a dark blue solution. A solution of *N*-benzyltriethylammonium chloride (0.278 g, 1.220 mmol) in 5 ml of MeCN was added dropwise and the mixture was refluxed for 30 min to afford a dark purple solution that was filtered and the solid washed with MeCN, hot DCE, DCM, and dried in *vacuo*. To a suspension of crude **5d**$^+$[Cl] in 25 ml of MeCN was added neat TMSOTf (0.184 g, 0.829 mmol) and the mixture refluxed for 60 min, hot filtered, and the volatiles removed by flash distillation to afford a dark blue-black powder. Repeated recrystallization from MeCN at -20 ^{o}C afforded dark blue microcrystalline solid **5d**$^+$[OTf]. Yield 48 % (0.139 g, 0.292 mmol).

5d$^+$[OTf]. IR (ATR, cm^{-1}): 3073 w, 3021 w, 1590 m, 1536 s, 1489 S, 1438 m, 1406 m, 1382 m, 1333 w, 1268 vs, 1240 vs, 1224 vs, 1196 vs, 1173 vs, 1152 vs, 1081 m, 1022 vs, 943 m, 918 m, 897 m, 879 m, 830 s, 791 m, 759 s, 741 m, 718 m, 694 w, 673 m, 628 vs, 584 m, 572 s, 514 vs, 469 m, 452 s. High resolution +ESI-MS (MeCN) m/z [M]$^+$ for $C_{10}H_5ClN_5S_3$, found (calcd.): 325.9403 (325.939).

Preparation of 5e$^+$[OTf]. Method A. To a solution of **3e**$^+$[OTf] (0.181 g, 0.040 mmol) was added neat S_2Cl_2 (0.506 g, 3.751 mmol) dropwise to give a deep-green mixture that was gently refluxed for 16 h. The mixture was cooled to RT and a solution of *N*-benzyltriethylammonium chloride (0.238 g, 1.045 mmol) in 10 ml of MeCN was added dropwise to afford a black precipitate which was collected by filtration, washed twice with MeCN, hot DCE, 1:5 mixture of CS_2 in DCM, DCM, and dried in *vacuo*. To a suspension of crude **5e**$^+$[Cl] in 20 ml of MeCN neat TMSOTf (0.147 g, 0.066 mmol) was added and the mixture was gently refluxed for 1 h. The mixture was filtered and the volatiles removed by flash distillation to afford a black solid. The solid was washed with hot DCE, DCM, and then dried in *vacuo*. Recrystallization from MeCN afforded **5e**$^+$[OTf] as purple crystalline solid. Yield 78 % (0.134 g, 0.026 mmol). **Method B.** To a solution of **4c'**$^+$[OTf] (0.384 g, 1.001 mmol) in 35 ml of MeCN was added 0.65 ml of neat S_2Cl_2 dropwise over 2 min to give a deep orange-red mixture which was stirred for 30 min at RT, then gently refluxed for 16 h. The mixture was allowed to cool to RT, filtered, and the solid washed with 2 x 10 ml of MeCN. The volatiles were removed from the soluble fraction to afford a black solid. The solid was washed with hot DCE, 1:5 mixture of CS_2 in DCM, DCM, and dried in *vacuo*. The crude material was repeatedly recrystallized from MeCN to afford pure **5e**$^+$[OTf] as purple crystalline blocks.

5e$^+$[OTf]. IR (ATR, cm^{-1}): 3083 w, 1532 m, 1488 s, 1401 w, 1357 s, 1323 m, 1274 s, 1246 vs, 1156 vs, 1116 vs, 1024 s, 983 s, 934 m, 898 m, 875 m, 835 m, 760 s, 734 s, 694 w, 666 w, 631 s, 570 m, 526 w, 511 m, 487 w, 473 w, 454 m, 424 w. Low resolution +ESI-MS (MeCN): m/z 360 [M]$^+$. Elemental analysis for $C_{11}H_4Cl_2F_3N_5O_3S_4$, found (calcd.): C 25.73 (25.89), H 1.15 (0.79), N 13.98 (13.89).

Preparation of 5b$^\bullet$. The reduction of a solution of **5b**$^+$[OTf] (0.048 g, 0.101 mmol) in 20 ml of degassed MeCN (four freeze-pump-thaw cycles) with a similarly degassed solution of octamethylferrocene (Me_8Fc; 0.046 g, 0.154 mmol) in 15 ml of MeCN. The crystals were obtained by slow diffusion of the solution of **5b**$^+$[OTf] through a medium porosity sintered glass frit into the Me_8Fc solution using an H-cell apparatus (see Fig. S9), affording **5b$^\bullet$** as crystalline blocks. The crystals were washed repeatedly with MeCN and dried under a stream of argon. Yield 81 % (0.027 g, 0.083 mmol).

5b$^\bullet$. IR (ATR, cm^{-1}): 3058 w, 2961 w, 1584 m, 1545 m, 1488 vs, 1408 vs, 1361 vs, 1320 s, 1268 s, 1237 vs, 1220 vs, 1157 vs, 1132 vs, 1102 vs, 1064 s, 1023 vs, 938 m, 874 s, 842 m, 822 m, 799 s, 749 m, 733 m, 717 w, 688 m, 633 vs, 572 s, 536 w, 515 m, 495 s, 456 s. Elemental analysis for $C_{12}H_7ClN_3S_3$, found (expected): C 43.36 (44.37), H 2.30 (2.17), N 13.01 (12.94).

Preparation of 5e$^{\bullet}$. Crystals were grown as described above for **5b$^{\bullet}$** using **5d**$^{+}$[OTf] (0.043 g, 0.084 mmol) and Me_8Fc (0.038 g, 0.126 mmol). The procedure afforded **5e$^{\bullet}$** as very thin crystalline needles. The crystals were washed repeatedly with MeCN and dried under a stream of argon. Yield 70 % (0.021 g, 0.058 mmol).

5e$^{\bullet}$. IR (ATR, cm^{-1}): 1535 m, 1490 s, 1466 m, 1442 s, 1400 vs, 1324 m, 1305 s, 1284 s, 1224 s, 1180 vs, 1165 s, 1146 vs, 1110 vs, 1025 s, 977 m, 964 m, 922 m, 865 s, 820 m, 783 w, 759 w, 750 m, 726 s, 716 s, 678 w, 668 w, 654 m, 621 w, 591 w, 565 m, 509 s, 465 vs, 425 m. Elemental analysis for $C_{10}H_4Cl_2N_5S_3$, found (expected): C 32.72 (33.25), H 1.48 (1.12), N 19.57 (19.39).

1c. Instrument Details

All FT-IR spectra were recorded on a Bruker Alpha Platinum single reflection diamond ATR module using 24 scans at 4 cm^{-1} resolution in an Argon filled glove box as neat solid samples. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 MHz and/or Bruker Avance III 300 MHz spectrometers and referenced internally to the residual solvent peak. X-band EPR spectra were recorded on a Magnettech MS-200 Miniscope high resolution X-band spectrometer equipped with a XL Microwave frequency counter (Model 3200). EPR spectra were simulated with the program EasySpin.[6] Positive ion electrospray ionization mass spectra (+ESI-MS) were recorded on a Micromass LCT mass spectrometer instrument using internal calibration. Elemental analyses for C, H, and N were performed in house using an Elementar Vario EL III elemental analyzer.

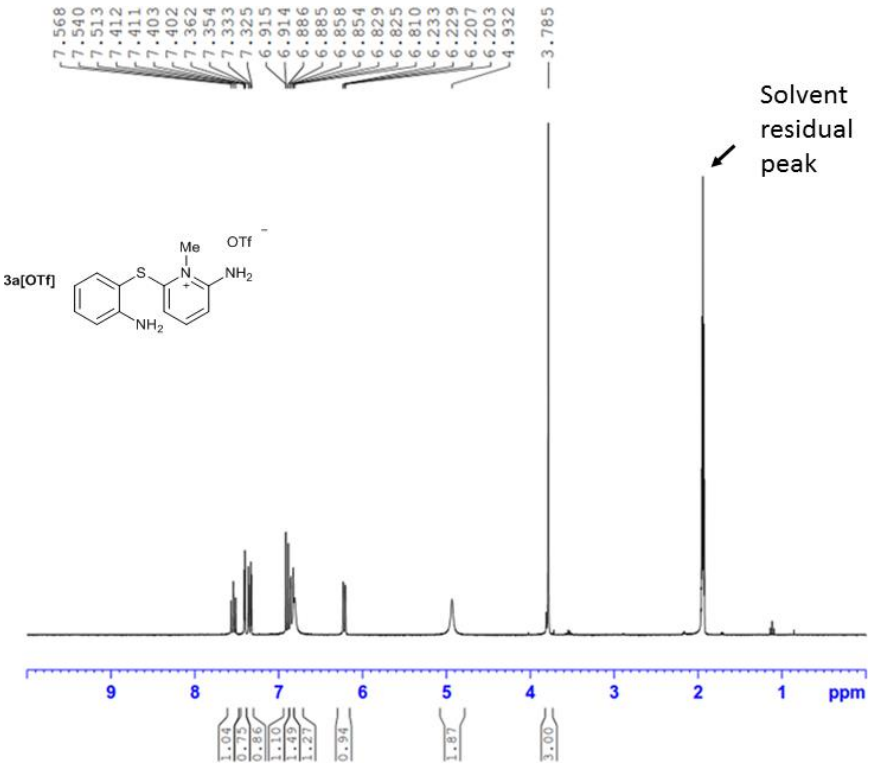

Fig. S1 ^{1}H-NMR of **3a**$^{+}$[OTf] in CD_3CN.

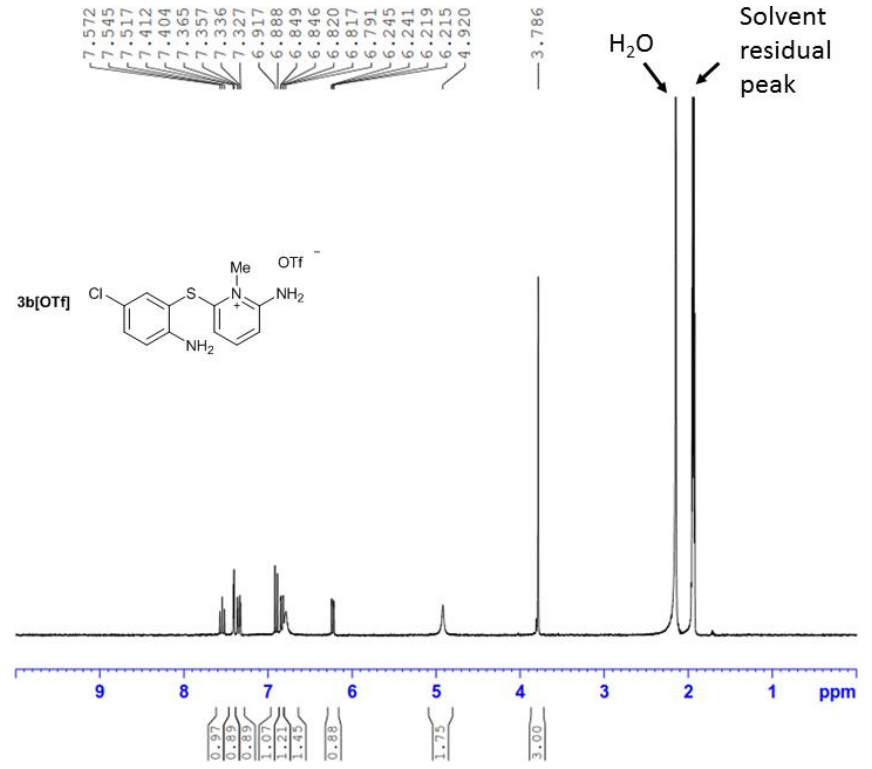

Fig. S2 ^{1}H-NMR of **3b**$^{+}$[OTf] in CD_3CN.

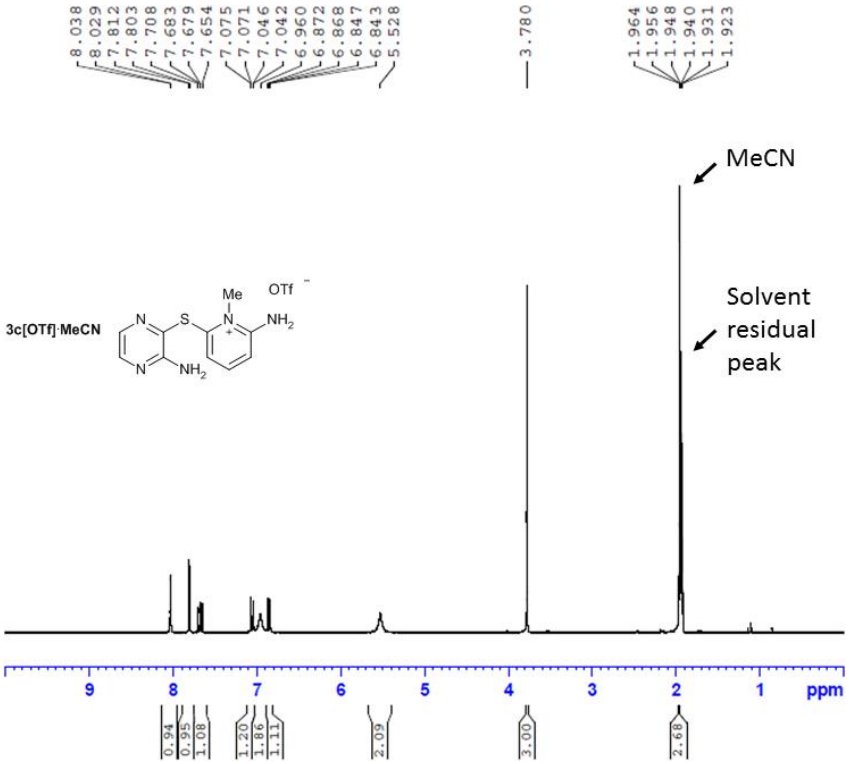

Fig. S3. ^{1}H-NMR of **3c**$^{+}$[OTf]·MeCN in CD_3CN.

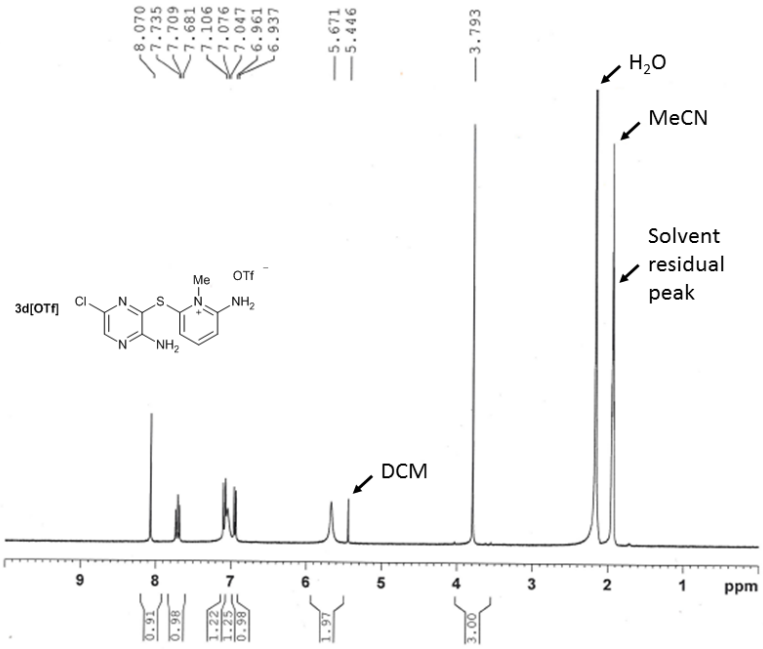

Fig. S4. ^{1}H-NMR of **3d**$^{+}$[OTf] in CD_3CN.

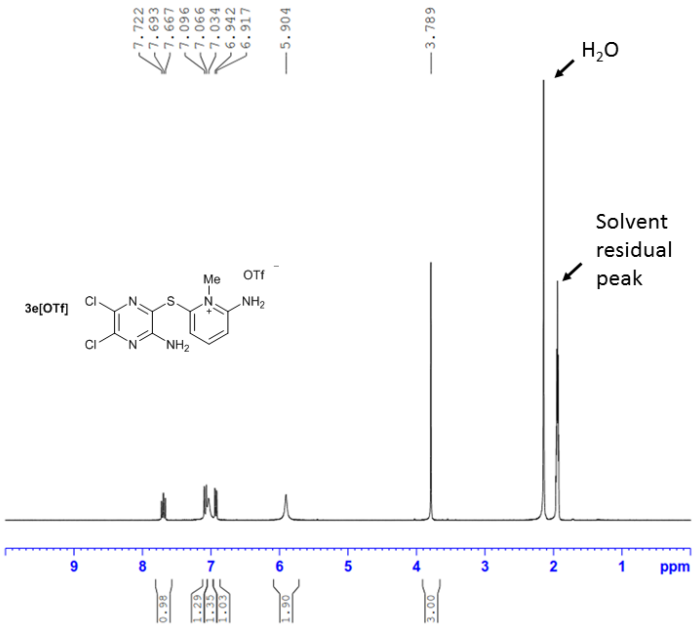

Fig. S5. ^{1}H-NMR of **3e**$^{+}$[OTf] in CD_3CN.

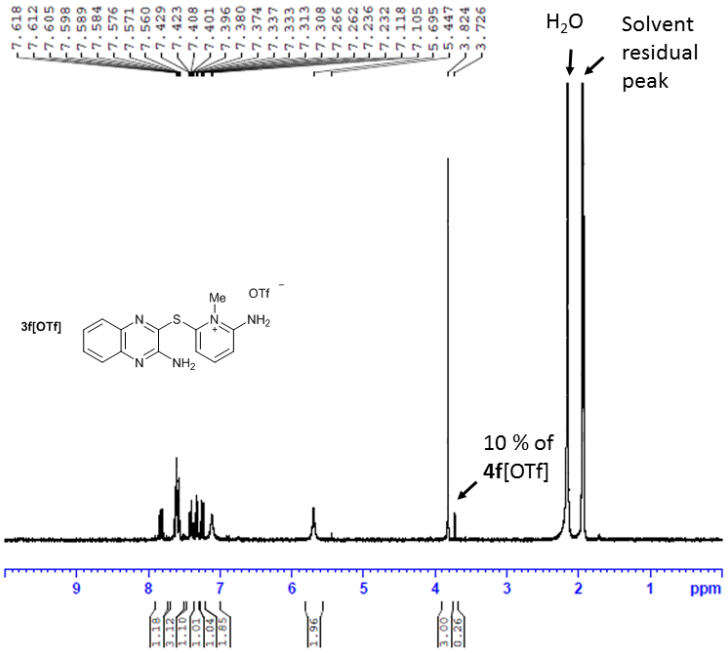

Fig. S6 ^{1}H-NMR of **3f**$^{+}$[OTf] in CD_3CN.

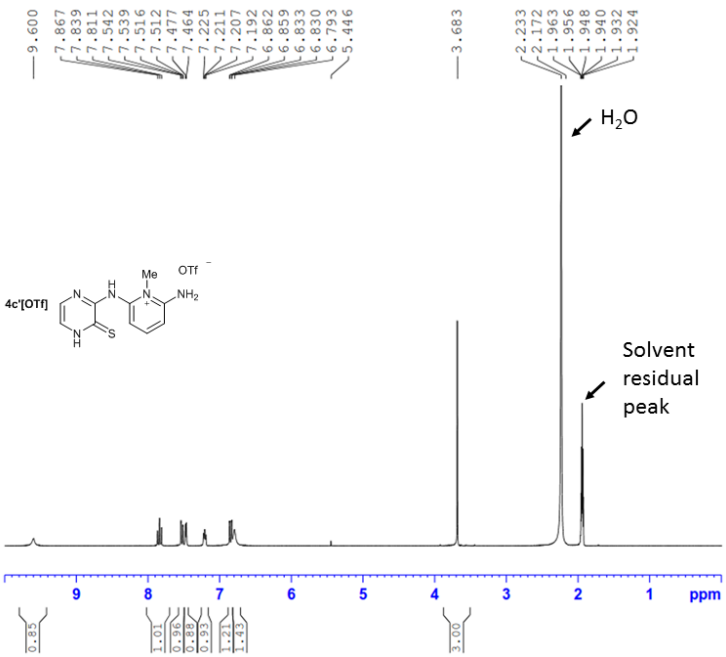

Fig. S7 ^{1}H-NMR of **4c'**$^{+}$[OTf] in CD_3CN.

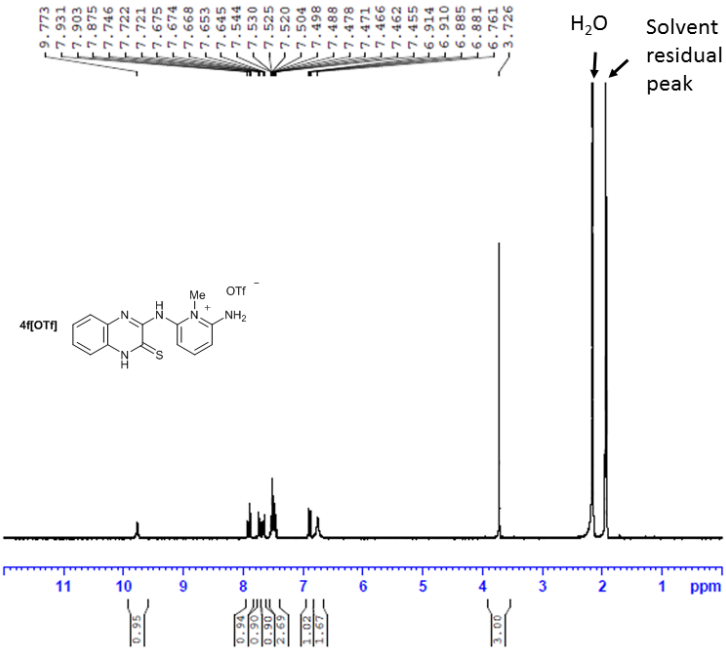

Fig. S8 ^{1}H-NMR of **4f**$^{+}$[OTf] in CD_3CN.

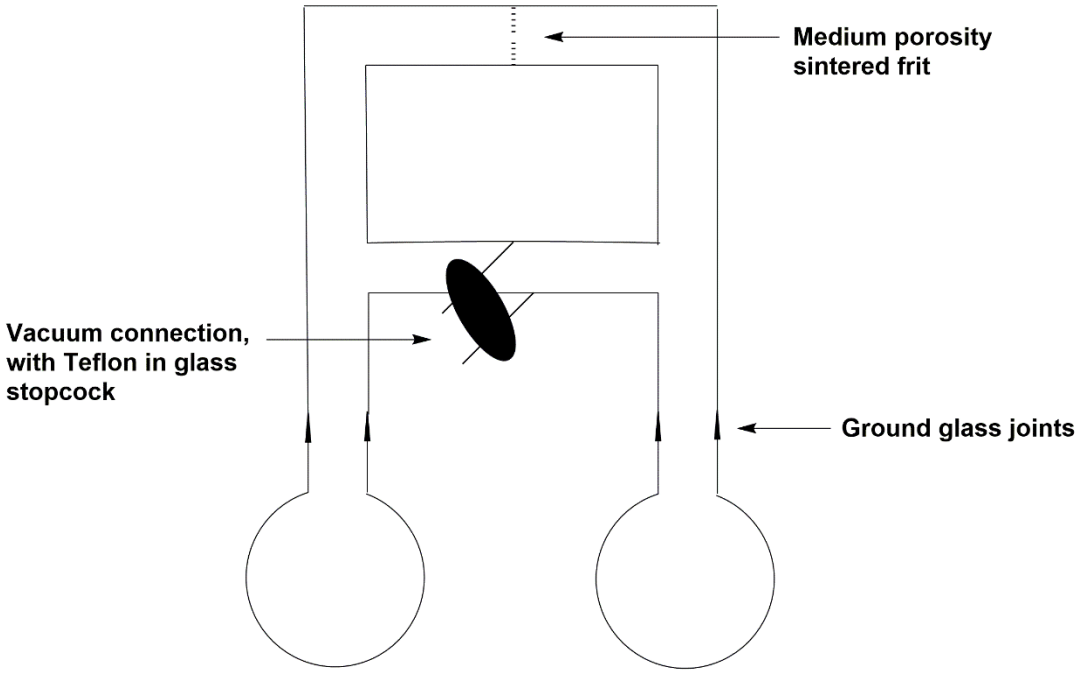

Fig. S9 H-cell apparatus.

2. X-ray Crystallography

All crystal data were collected on an Agilent SuperNova diffractometer equipped with multilayer optics monochromated dual source (Cu and Mo) Atlas detector, using CuKα (1.54184 Å) or MoKα (0.71073 Å) radiation. Data acquisitions, reductions, and analytical face-index based absorption corrections were made using CrysAlis^{PRO}.[7] The structures were solved using ShelXS[8] program and refined on F^2 by full-matrix least-squares techniques with the ShelXL[8] program in the Olex^2 (v.1.2) program package.[9] All C-H hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 (sp^2 group) and 1.5 (sp^3 group) larger than that of the host atom. All N-H hydrogen atoms were located from the difference Fourier map and refined as riding atoms using isotropic displacement parameters 1.2 times the host atom but without positional restrictions.

Table S1. Crystallographic data for compounds **3c**$^+$[OTf]·MeCN, **3f**$^+$[OTf], **4c**$^+$[OTf],and **4f**$^+$[OTf].

Identification code	**3c**$^+$[OTf]·MeCN	**3f**$^+$[OTf]	**4c**$^+$[OTf]	**4f**$^+$[OTf]
Empirical formula	$C_{13}H_{15}F_3N_6O_3S_2$	$C_{15}H_{14}F_3N_5O_3S_2$	$C_{11}H_{12}F_3N_5O_3S_2$	$C_{15}H_{14}F_3N_5O_3S_2$
Formula weight [g mol^{-1}]	424.43	433.43	383.38	433.43
Temperature [K]	120.00(10)	120.00(10)	123.00(10)	120.00(10)
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	*P*-1	*P*-1	$P2_1/c$	*P*-1
a [Å]	6.2134(4)	6.1521(15)	10.0148(4)	6.1376(2)
b [Å]	10.3216(7)	11.658(2)	20.0201(6)	11.7508(5)
c [Å]	14.0396(9)	13.584(2)	8.2625(3)	13.2119(6)
α [°]	86.713(6)	69.289(16)	90	107.777(4)
β [°]	78.198(6)	79.357(16)	110.096(5)	96.045(3)
γ [°]	89.864(6)	85.084(18)	90	90.188(3)
Volume [Å^3]	879.87(11)	895.4(3)	1555.74(11)	901.69(7)
Z	2	2	4	2
ρ_{calc} [g cm^{-3}]	1.602	1.608	1.637	1.596
μ [mm^{-1}]	0.362	0.356	3.653	0.354
F(000)	436.0	444.0	784.0	444.0
Crystal size [mm^3]	0.2595 × 0.2133 × 0.0385	0.158 × 0.117 × 0.073	0.162 × 0.086 × 0.072	0.161 × 0.078 × 0.039
Radiation	MoK*α* (*λ* = 0.71073)	MoK*α* (*λ* = 0.71073)	CuK*α* (*λ* = 1.54184)	MoK*α* (*λ* = 0.71073)
2Θ range for data collection [°]	5.938 to 51.994	5.738 to 51.986	8.834 to 139.996	6.416 to 53.988
Index ranges	$-7 \le h \le 5$ $-12 \le k \le 12$ $-17 \le l \le 14$	$-7 \le h \le 7$ $-13 \le k \le 14$ $-16 \le l \le 16$	$-11 \le h \le 12$ $-24 \le k \le 14$ $-10 \le l \le 9$	$-7 \le h \le 6$ $-15 \le k \le 12$ $-16 \le l \le 15$
Reflections collected	5350	5516	5404	6674
Independent reflections	3444 [R_{int} = 0.0241, R_{sigma} = 0.0469]	3497 [R_{int} = 0.0358, R_{sigma} = 0.0817]	2927 [R_{int} = 0.0173, R_{sigma} = 0.0252]	3867 [R_{int} = 0.0263, R_{sigma} = 0.0548]
Data/restraints/parameters	3444/0/258	3497/37/298	2927/0/230	3867/0/2705
Goodness-of-fit on F^2	1.043	1.092	1.026	1.059
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0366, wR_2 = 0.0897	R_1 = 0.0622, wR_2 = 0.1343	R_1 = 0.0435, wR_2 = 0.1108	R_1 = 0.0434, wR_2 = 0.0936
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.0951	R_1 = 0.0954, wR_2 = 0.1555	R_1 = 0.0492, wR_2 = 0.1155	R_1 = 0.0637, wR_2 = 0.1033
Largest diff. peak/hole [e Å^{-3}]	0.39/−0.47	0.40/−0.44	0.55/−0.41	0.49/−0.40

Table S2. Crystallographic data for compounds **5b**$^{+}$[OTf], **5e**$^{+}$[OTf], and **5b**$^{\bullet}$.

Identification code	**5b**$^{+}$[OTf]	**5e**$^{+}$[OTf]	**5b**$^{\bullet}$
Empirical formula	$C_{13}H_7ClF_3N_3O_3S_4$	$C_{11}H_4Cl_2F_3N_5O_3S_4$	$C_{12}H_7ClN_3S_3$
Formula weight [g mol^{-1}]	473.91	510.33	324.84
Temperature [K]	120.01(10)	293.97(10)	123.01(10)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$
a [Å]	7.4918(4)	8.1151(9)	10.9966(3)
b [Å]	21.1396(9)	8.6552(10)	21.7939(5)
c [Å]	11.7057(10)	12.6232(11)	10.4376(3)
α [°]	90	84.653(8)	90
β [°]	94.745(7)	75.348(9)	99.356(3)
γ [°]	90	87.368(9)	90
Volume [Å^3]	1847.5(2)	853.83(16)	2468.19(11)
Z	4	2	8
ρ_{calc} [g cm^{-3}]	1.704	1.985	1.748
μ [mm^{-1}]	6.542	0.928	7.375
F(000)	952.0	508.0	1320.0
Crystal size [mm^3]	0.212 × 0.062 × 0.061	0.203 × 0.096 × 0.058	0.124 × 0.071 × 0.053
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection [°]	12.574 to 135.978	6.02 to 51.998	8.114 to 137.986
Index ranges	$-7 \le h \le 9$ $-25 \le k \le 18$ $-14 \le l \le 13$	$-9 \le h \le 9$ $-10 \le k \le 10$ $-15 \le l \le 15$	$-13 \le h \le 13$ $-26 \le k \le 16$ $-8 \le l \le 12$
Reflections collected	5601	5803	7946
Independent reflections	3312 [R_{int} = 0.0277, R_{sigma} = 0.0391]	3335 [R_{int} = 0.0242, R_{sigma} = 0.0440]	4567 [R_{int} = 0.0264, R_{sigma} = 0.0376]
Data/restraints/parameters	3312/0/245	3335/0/254	4567/0/345
Goodness-of-fit on F^2	1.195	1.040	1.024
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0989, wR_2 = 0.2731	R_1 = 0.0421, wR_2 = 0.1077	R_1 = 0.0382, wR_2 = 0.0947
Final R indexes [all data]	R_1 = 0.1117, wR_2 = 0.2889	R_1 = 0.0509, wR_2 = 0.1146	R_1 = 0.0448, wR_2 = 0.0994
Largest diff. peak/hole [e Å^{-3}]	1.69/−0.46	0.56/−0.74	1.03/−0.40

Table S3. Bond lengths (Å) for the cations in **5b**$^{+}$[OTf] and **5e**$^{+}$[OTf].

5b^{+}[OTf]		**5e**$^{+}$[OTf]	
S1 – S2	2.051(2)	S1 – S2	2.0366(12)
S1 – N1	1.628(5)	S1 – N1	1.613(3)
S2 – C2	1.693(6)	S2 – C2	1.687(3)
S3 – C4	1.712(6)	S3 – C4	1.729(3)
S3 – C5	1.746(5)	S3 – C5	1.743(3)
N1 – C1	1.311(8)	N1 – C1	1.312(4)
N2 – C10	1.384(8)	N2 – C8	1.371(4)
N2 – C11	1.300(8)	N2 – C9	1.307(4)
N3 – C1	1.368(8)	N3 – C1	1.375(4)
N3 – C11	1.385(8)	N3 – C9	1.382(4)
N3 – C12	1.480(7)	N3 – C10	1.480(4)
C1 – C2	1.444(8)	C1 – C2	1.429(4)
C2 – C3	1.391(9)	C2 – C3	1.403(4)
C3 – C4	1.372(8)	C3 – C4	1.365(4)
C4 – C11	1.459(8)	C4 – C9	1.460(4)
C5 – C10	1.408(8)	C5 – C8	1.401(4)
C7 – C8	1.396(9)	C6 – C7	1.402(5)
C5 – C6	1.388(9)	C5 – N5	1.332(4)
C6 - C7	1.376(9)	C6 – N5	1.324(4)
C8 – C9	1.359(10)	C7 – N4	1.308(4)
C9 – C10	1.391(8)	C8 – N4	1.341(4)
Cl1 – C7	1.735(6)	Cl1 – C6	1.711(3)
		Cl2 – C7	1.720(3)

Table S4. Bond angles (°) for the cations in **5b**$^{+}$[OTf] and **5e**$^{+}$[OTf].

5b^{+}[OTf]		**5e**$^{+}$[OTf]	
N1 - S1 - S2	98.71(19)	N1 - S1 - S2	98.65(11)
C2 - S2 - S1	92.7(2)	C2 - S2 - S1	92.77(12)
C4 - S3 - C5	103.0(3)	C4 - S3 - C5	102.04(15)
C1 - N1 - S1	115.2(4)	C1 - N1 - S1	115.4(2)
C11 - N2 – C10	123.1(5)	C9 - N2 - C8	121.8(3)
C1 - N3 – C11	121.7(5)	C1 - N3 - C9	122.1(3)
C1 - N3 - C12	120.2(5)	C1 - N3 - C10	118.8(3)
C11 - N3 - C12	118.1(5)	C9 - N3 - C10	119.1(3)
N1 –C1 – N3	121.0(5)	C7 - N4 - C8	117.9(3)
N1 – C1 – C2	119.3(5)	C6 - N5 - C5	116.9(3)
N3 - C1 – C2	119.7(5)	N1 - C1 - N3	121.1(3)
C1 – C2 - S2	114.1(5)	N1 - C1 - C2	119.0(3)
C3 – C2 - S2	125.6(5)	N3 - C1 - C2	119.8(3)
C3 - C2 – C1	120.3(5)	C1 - C2 - S2	114.1(2)
C4 – C3 – C2	119.0(5)	C3 - C2 - S2	125.9(2)
C3 – C4 – S3	117.4(4)	C3 - C2 - C1	120.0(3)
C3 – C4 – C11	121.6(5)	C4 - C3 - C2	118.8(3)
C3 - C4 - S3	121.0(5)	C3 - C4 - S3	117.5(2)
C3 - C4 – C11	117.0(4)	C3 - C4 - C9	122.3(3)
C11 - C4 - S3	120.9(5)	C9 - C4 - S3	120.2(2)
C6 - C5 - S3	122.1(5)	N5 - C5 - S3	114.2(2)
C10 - C5 – S3	119.3(5)	N5 - C5 - C8	123.3(3)
C7 - C6 - C5	119.7(5)	C8 - C5 - S3	122.5(3)
C6 - C7 - C11	119.7(5)	N5 - C6 - Cl1	117.4(3)
C6 - C7- C8	120.4(6)	N5 - C6 - C7	120.0(3)
C8 - C7 - C11	120.0(5)	C7 - C6 - Cl1	122.6(3)
C9 - C8 - C7	120.1(6)	N4 - C7 - Cl2	116.6(3)
C8 - C9 - C10	121.4(6)	N4 - C7 - C6	123.0(3)
N2 - C10 - C5	124.5(5)	C6 - C7 - Cl2	120.4(3)
N2 - C10 - C4	117.6(5)	N2 - C8 - C5	125.4(3)
C9 - C10 - C5	117.9(6)	N4 - C8 - N2	115.8(3)
N2 - C11 - N3	116.0(5)	N4 - C8 - C5	118.8(3)
N2 - C11 - C4	126.3(5)	N2 - C9 - N3	116.0(3)
N3 - C11 - C4	117.7(5)	N2 - C9 - C4	127.1(3)
		N3 - C9 - C4	116.8(3)

3. Cyclic Voltammetry

Cyclic voltammetry was performed with a Gamry Instruments Reference 600 potentiostat. Degassed solutions of **5b**$^{+}$[OTf] and **5e**$^{+}$[OTf] containing 0.1 M *n*-Bu_4NPF_6 were used. The potentials were measured in a single compartment cell under an argon atmosphere using Pt electrodes and a scan rate of 150 mV s^{-1}, and referenced to Fc^{+}/Fc couple (0.38 V *vs.* SCE). The $E_{pa} - E_{pc}$ separations of the samples were within 10 % of that of the Fc^{+}/Fc redox couple.[10]

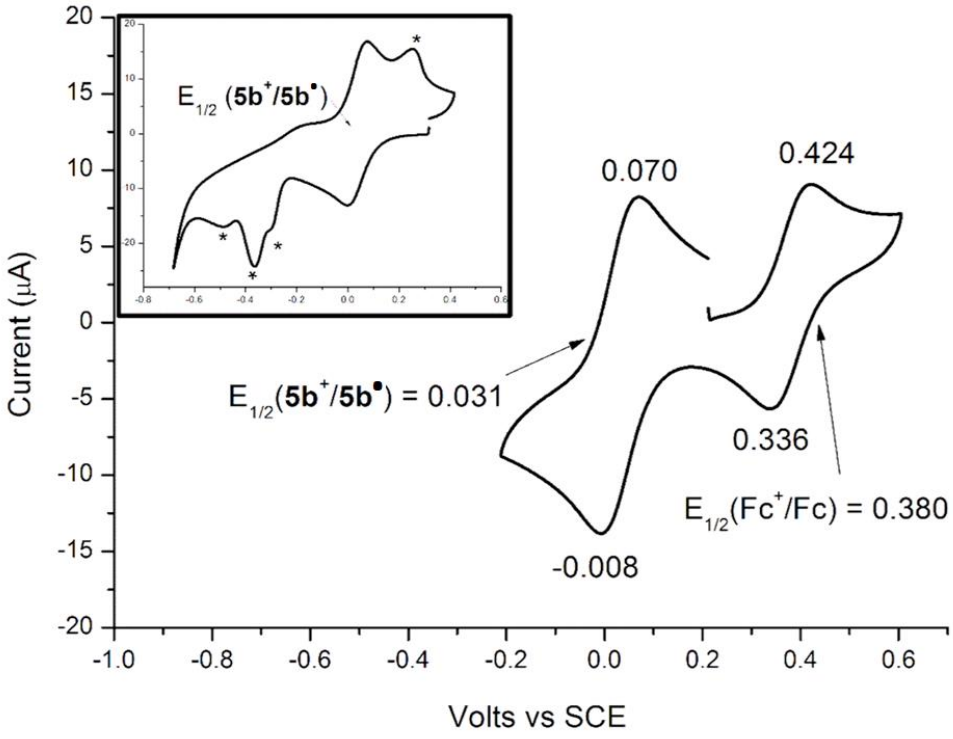

Fig. S10 Cyclic voltammogram of **5b**$^{+}$[OTf]. The inset shows a full sweep illustrating the irreversible 0/−1 redox process (the resulting cathodic and anodic processes are denoted by asterisks).

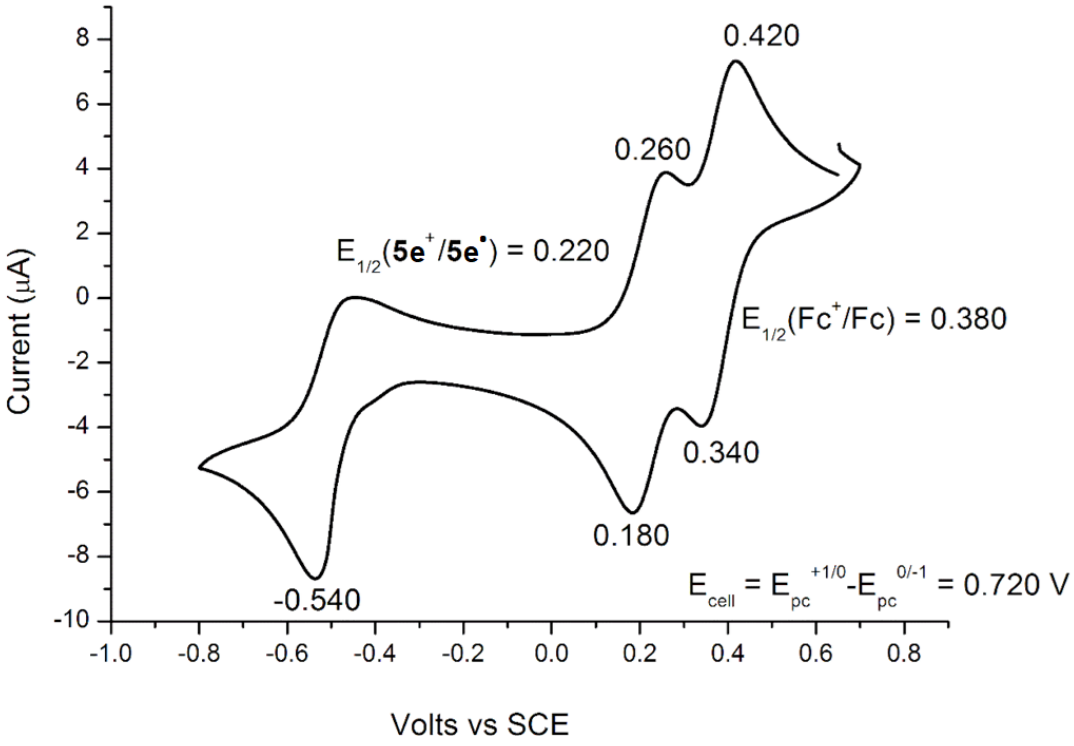

Fig. S11 Cyclic voltammogram of **5e**$^{+}$[OTf].

4. Computational Mehods

All geometry optimizations and frequency calculations were performed with the Gaussian 09 program.[11] Density functional theory was used in conjunction with the PBE1PBE hybrid exchange-correlation functional [12] and def2-TZVP basis sets. [13] In mechanistic calculations, the integral equation formalism variant of the polarizable continuum model (IEF-PCM) was used to model the bulk effects of the solvent (MeCN).[14] Vibrational analyses were carried out for all optimized structures to ensure that the stationary points correspond to either first order transition states or to true minima on the potential energy surface. Atomic spin densities of radicals **5b**$^{\bullet}$, **5e**$^{\bullet}$, and **5f**$^{\bullet}$ were calculated with the natural population analysis as implemented in the NBO code in Gaussian09.[15]

Table S5. Calculated spin densities and hyperfine couplings [mT] of **5b**$^{\bullet}$ and **5e**$^{\bullet}$.

5b$^{\bullet}$			**5e**$^{\bullet}$		
Atom	**Spin density**	**Hyperfine coupling**	**Atom**	**Spin density**	**Hyperfine coupling**
N1	0.190	0.330	N1	0.206	0.356
N2	0.137	0.198	N2	0.109	0.154
N3	−0.022	−0.051	N3	−0.016	−0.038
			N4	0.026	0.028
			N5	0.002	−0.017
S1	0.140	0.268	S1	0.163	0.313
S2	0.160	0.363	S2	0.167	0.389
S3	0.129	0.298	S3	0.110	0.251
C1	−0.080	−0.734	C1	−0.086	−0.751
C2	0.237	1.013	C2	0.218	0.925
C3	−0.150	−0.965	C3	−0.138	−0.889
C4	0.260	1.079	C4	0.243	0.993
C5	0.021	0.047	C5	0.005	0.002
C6	−0.008	−0.096	C6	0.035	0.095
C7	0.025	0.091	C7	0.005	−0.074
C8	−0.004	−0.070	C8	−0.024	−0.239
C9	0.027	0.058	C9	−0.035	−0.530
C10	−0.014	−0.261	C10	0.000	0.005
C11	−0.051	−0.621			
C12	0.001	0.013			
H3	0.005	0.366	H3	0.004	0.333
H6	0.000	0.013			
H8	0.000	0.007			
H9	−0.001	−0.073			
H12A	−0.000	−0.002	H10A	−0.000	−0.000
H12B	−0.001	−0.068	H10B	−0.001	−0.046
H12C	−0.001	−0.068	H10C	−0.001	−0.046
Cl1	0.003	0.010	Cl1	0.005	0.016
			Cl2	0.001	−0.002

Table S6. Calculated Gibbs energies (kJ·mol^{-1}) for the SR reaction of **3a**–**e**$^{+}$.

x	**3x**$^{+}$	**TS1**	**Int1**	**TS2**	**4X**$^{+}$	**TS3**	**4X'**$^{+}$
a	0	162	4	10	4		
b	0	162	6	9	0		
c	0	168	2	13	−7	96	−43
d	0	166	3	11	−7	111	−20
e	0	180	5	14	−4	119	−11

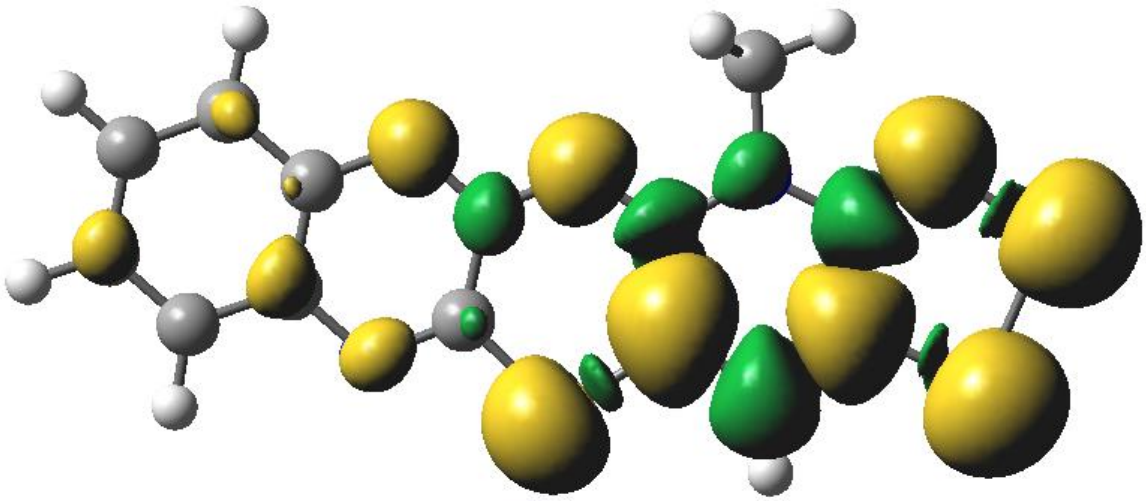

Fig. S12 Isosurface plot of the spin density (± 0.001) of **5f**$^{\bullet}$.

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