SUPPORTING INFORMATION

^{1}H, ^{13}C, ^{19}F NMR spectra were recorded in $CDCl_3$ (except in CD_2Cl_2 for compounds **1aac**, **1aad**, **1aae**) at 300, 75, and 282 MHz, respectively. Chemical shifts are given in ppm relative to TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F) as internal references. Coupling constants are given in Hertz.

Typical procedure: Synthesis of **1aab to 1aai, 1abi**

A flame-dried double-necked vessel was successively charged, under nitrogen, with diisopropylethylamine (14 mL, 80 mmol) and anhydrous dichloromethane (80 mL). The resulting mixture was cooled to -20°C before addition of diethylaminosulfurtrifluoride (5.5 mL, 44 mmol), followed by the addition of trimethylsilyltrifluoromethane (5.9 mL, 40 mmol) or trimethylsilylpentafluoroethane (7.7 mL, 40 mmol) in 20 min interval. After 1 hour under stirring at -20°C, the amine (1eq.) bearing an electron withdrawing group is added at 0°C (in its liquid form, solid form, or in 0,5 M solution from ethylacetate or dichloromethane). The reaction medium is then cooled to room temperature and kept under stirring for further 4 hours. After this period, the reaction medium was washed with 6% aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was simply washed with pentane or purified by chromatography over silica gel in presence of 0.5% of Et_3N to afford the corresponding sulfinamidines.

N,N-diethyl-1,1,1-trifluoro-N'-(4-nitrophenyl)methane sulfinimidamide (**1aab**): Orange solid. mp: 40-41°C. ^{1}H NMR: δ= 7.97 (m, 2H), 6.78 (m, 2H), 3.31 (q, ^{3}J(H,H)= 7.3, 4H), 1.11 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 123.8 (q, ^{4}J(C,F)= 1.1), 140.9, 125.7, 123.8 (q, ^{1}J(C,F)= 329), 119.7, 41.0, 13.8. ^{19}F NMR: δ= -70.85. Elemental analysis calcd (%) for $C_{11}H_{14}F_3N_3O_2S$: C 42.71, H 4.56, N 13.59, S 10.37. Found: C 42.82, H 4.63, N 13.87, S 10.14.

N,N-diethyl-1,1,1-trifluoro-N'-(3-nitrophenyl)methane sulfinimidamide (**1aac**): Brown oil. ^{1}H NMR: δ= 7.72-7.68 (massif, 2H), 7.36 (m, 1H), 7.24 (m, 1H), 3.43 (q, ^{3}J(H,H)= 7.2, 4H), 1.24 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 153.6 (q, ^{4}J(C,F)= 1.3), 149.5, 129.9, 127.1, 123.8 (q, ^{1}J(C,F)= 329), 114.9, 114.5, 40.6, 13.8. ^{19}F NMR: δ= -71.13. (not enough stable to obtain elemental analysis).

N,N-diehyl-1,1,1-trifluoro-N'-(2-nitrophenyl)methanesulfinimidamide (**1aad**): Brown oil. ^{1}H NMR: δ= 7.61 (m, 1H), 7.38 (m, 1H), 6.98-6.92 (massif, 2H), 3.41 (q, ^{3}J(H,H)= 7.1, 4H), 1.23 (t, ^{3}J(H,H)= 7.1, 6H). ^{13}C NMR: δ= 145.6 (q, ^{4}J(C,F)= 1.1), 136.6, 132.8, 124.7, 123.8 (q, ^{1}J(C,F)= 329), 121.4, 120.0, 41.1, 13.8. ^{19}F NMR: δ= -71.39. (not enough stable to obtain elemental analysis).

N,N-diethyl-1,1,1-trifluoro-N'-[2-(trifluoromethyl)phenyl]methanesulfinimidamide (**1aae**): Colorless oil. ^{1}H NMR: δ= 7.56 (m, 1H), 7.41 (m, 1H), 6.99–6.90 (massif, 2H), 3.42 (m, 4H), 1.24 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 151.0 (q, ^{4}J(C,F)= 1.1), 132.9 (q, ^{4}J(C,F)= 1.1), 127.2 (q, ^{3}J(C,F)= 5.5), 125.0 (q, ^{1}J(C,F)= 273), 123.9 (q, ^{1}J(C,F)= 329), 123.6 (q, ^{2}J(C,F)= 29), 119.7, 119.6, 40.8, 13.8. ^{19}F NMR: δ= -62.79, -68.68. (not enough stable to obtain elemental analysis).

N-[(diethylamino)(trifluoromethyl)-λ^{4}-sulfanylidene]-4-methylbenzenesulfonamide (**1aaf**): Yellow oil. ^{1}H NMR: δ= 7.77 (m, 2H), 7.25 (m, 2H), 3.36 (dq, ^{2}J(H,H)= 14.2, ^{3}J(H,H)= 7.2, 2H), 3.27 (dq, ^{2}J(H,H)= 14.2 ^{3}J(H,H)= 7.2, 2H), 2.39 (s, 3H), 1.17 (t, ^{3}J(H,H)= 7.2, 2H). ^{13}C NMR: δ= 142.9, 140.8, 129.7, 126.5, 123.5 (q, ^{1}J(C,F)= 328), 46.4, 21.7, 16.5. ^{19}F NMR: δ= -69.25. Elemental analysis calcd (%) for $C_{12}H_{17}F_3N_2O_2S_2$: C 42.09, H 5.00, N 8.18, S 18.73. Found: C 41.91, H 4.82, N 8.11, S 18.70.

N-[(diethylamino)(trifluoromethyl)-λ^4-sulfanylidene]-1,1,1-trifluoromethanesulfonamide (**1aag**): Colorless oil. ^{1}H NMR: δ= 3.49 (dq, ^2J(H,H)= 14.5, ^3J(H,H)= 7.2, 2H), 3.40 (dq, ^2J(H,H)= 14.5, ^3J(H,H)= 7.2, 2H), 1.25 (t, ^3J(H,H)= 7.2, 2H). ^{13}C NMR: δ= 123.3 (q, ^1J(C,F)= 328), 120.2 (q, ^1J(C,F)= 321), 43.8, 13.4. ^{19}F NMR: δ= -69.47 and -79.04. Elemental analysis calcd (%) for $C_6H_{10}F_2N_2O_2S_2$: C 22.50, H 3.15, N 8.75, S 20.02. Found: C 22.81, H 3.05, N 8.64, S 19.61.

Benzyl[diethylamino(trifluoromethyl)-λ^4-sulfanylidene]carbamate (**1aah**): Yellow oil. ^{1}H NMR: δ= 7.40–7.24 (massif, 5H), 5.18 (d, AB system, ^2J(H,H)= 12.3), 5.13 (d, AB system, ^2J(H,H)= 12.3), 3.35 (m, 4H), 1.20 (t, ^3J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 164.6 (q, ^4J(C,F)= 1.5), 137.0, 128.7, 128.6, 128.3, 123.8 (q, ^1J(C,F)= 325), 68.5, 13.8. ^{19}F NMR: δ= -69.19. Elemental analysis calcd (%) for $C_{13}H_{17}F_3N_2O_2S$: C 48.44, H 5.32, N 8.69, O 9.93, S 9.95. Found: C 48.56 H 5.45 N 8.42.

N-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}-N',N'-diethyl-1,1,1-trifluoromethanesulfinimidamide (**1aai**): Brown solid. mp: 93-94°C. ^{1}H NMR: δ= 7.69 (s, 2H), 5.96 (s, 1H), 3.32 (q, ^3J(H,H)= 7.2, 4H), 1.18 (q, ^3J(H,H)= 7.2, 6H. ^{13}C NMR: δ= 153.2 (q, ^4J(C,F)= 1.6), 137.7 (q, ^5J(C,F)= 1.1), 136.8, 136,5, 133.6 (q, ^2J(C,F)= 34), 127.3, 125.82 (q, ^3J(C,F)= 3.4), 125.80 (q, ^3J(C,F)= 3.4), 123.3 (q, ^1J(C,F)= 329), 122.6 (q, ^1J(C,F)= 273), 114.5, 93.9, 41.1, 13.9. ^{19}F NMR: δ= -63,66 and -70,62. Elemental analysis calcd (%) for $C_{16}H_{13}Cl_2F_6N_5S$: C 39.04, H 2.66, Cl 14.40, N 14.23, S 6.51. Found: C 38.77, H 2.59, Cl 14.13, N 13.80 S 6.71.

N-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}-N',N'-diethyl-1,1,2,2,2-pentafluoroethane sulfinimidamide (**1abi**): Brown solid. mp: 113-114°C. ^{1}H NMR: δ= 7.69 (m, 2H), 5.90 (s, 1H), 3.40 (m, 4H), 1.23 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 152.6 (q, ^{4}J(C,F)= 3.3), 137.6, 137.1, 136,6, 133.8 (q, ^{2}J(C,F)= 34), 127.3, 125.71 (q, ^{3}J(C,F)= 3.4), 125.70 (q, ^{3}J(C,F)= 3.4), 122.6 (q, ^{1}J(C,F)= 273), 115.9 (tq, ^{1}J(C,F)= 287, ^{2}J(C,F)= 34), 113.5 (qt, ^{1}J(C,F)= 284, ^{2}J(C,F)= 34), 114.4, 94.0, 40.8, 14.0. ^{19}F NMR: δ= -63.63, -79.35, -108.87 (d, ^{2}J(F,F)= 233), -120.66 (d, ^{2}J(F,F)= 233). Elemental analysis calcd (%) for $C_{17}H_{13}Cl_2F_8N_5S$: C 37.65, H 2.42, N 12.91. Found: C 37.51, H 2.63, N 13.19.

Typical procedure: Synthesis of **1baf, 1bai, 1baj**

A flame-dried double-necked vessel was successively charged, under nitrogen, with diisopropylethylamine (7 mL, 40 mmol) and anhydrous dichloromethane (80 mL). The resulting mixture was cooled to -20°C before addition of morpholinosulfurtrifluoride (5 mL, 40 mmol), followed by the addition of trimethylsilyltrifluoromethane (5.9 mL, 40 mmol) in 20 min interval. After 1 hour under stirring at -20°C, the amine (1eq.) is added at 0°C (in its liquid form, solid form, or in 0,5 M solution from ethylacetate or dichloromethane). The reaction medium is then cooled to room temperature and kept under stirring for further 4 hours. After this period, the reaction medium was washed with 6% aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was simply washed with pentane or purified by chromatography over silica gel in presence of 0.5% of Et_3N to afford the corresponding sulfinamidines.

4-methyl-N-[morpholin-4-yl(trifluoromethyl)-λ^{4}-sulfanylidene] benzenesulfonamide (**1baf**): White solid. mp: 113-114°C. ^{1}H NMR: δ= 7.79 (m, 2H), 7.28 (m, 2H), 3.71 (ddd, ^{2}J(H,H)= 11.7, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.4, 2H), 3.61 (ddd, ^{2}J(H,H)= 11.7, ^{3}J(H,H)= 6.3,

^{3}J(H,H)= 3.1, 2H), 3.43 (ddd, ^{2}J(H,H)= 12.4, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.3, 2H), 3.24 (ddd, ^{2}J(H,H)= 12.4, ^{3}J(H,H)= 6.4, ^{3}J(H,H)= 3.1, 2H), 2.41 (s, 3H). ^{13}C NMR: δ= 143.3, 140.6, 129.9, 126.7, 123.9 (q, ^{1}J(C,F)= 330), 66.7, 46.7, 21.9. ^{19}F NMR: δ= -66.93. Elemental analysis calcd (%) for $C_{12}H_{15}F_3N_2O_3S_2$: C 40.44, H 4.24, N 7.86, S 17.99. Found C 40.48, H 4.13, N 7.83, S 17.99.

1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-{[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene]amino}-1H-pyrazole-3-carbonitrile (**1bai**): White solid. mp: 129-130°C. ^{1}H NMR: δ= 7.70 (s, 2H), 6.07 (s, 1H), 3.80-3.65 (massif, 4H), 3.41 (m, 2H), 3.19 (m, 2H). ^{13}C NMR: δ= 152.5 (q, ^{4}J(C,F)= 1.6), 137.4 (q, ^{5}J(C,F)= 1.1), 136.8, 136.4, 133.8 (q, ^{2}J(C,F)= 34), 127.4, 125.9 (q, ^{3}J(C,F)= 3.8), 125.9 (q, ^{3}J(C,F)= 3.8), 123.7 (q, ^{1}J(C,F)= 331), 122.6 (q, ^{1}J(C,F)= 274), 114.3, 94.0, 67.1, 45.4. ^{19}F NMR: δ= -63,58 and -67,88. Elemental analysis calcd (%) for $C_{16}H_{11}Cl_2F_6N_5OS$: C 37.96, H 2.19, Cl 14.01, N 13.83, O 3.16, S 6.33. Found: C 38.09, H 2.17, Cl 14.22, N 13.73, S 6.48.

1-(4-{[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene]amino}phenyl)ethanone (**1baj**): White solid. mp: 61-62°C. ^{1}H NMR: δ= 7.81-7.76 (massif, 2H), 6.94-6.90 (massif, 2H), 3.75 (ddd, ^{2}J(H,H)= 11.5, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.3, 2H), 3.67 (ddd, ^{2}J(H,H)= 11.5, ^{3}J(H,H)= 6.3, ^{3}J(H,H)= 3.3), 3.44 (ddd, ^{2}J(H,H)= 12.3, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.3, 2H), 3.25 (ddd, ^{2}J(H,H)= 12.3, ^{3}J(H,H)= 6.3, ^{3}J(H,H)= 3,3, 2H), 2.4 (s, 3H). ^{13}C NMR: δ= 197.1, 156.6 (q, ^{4}J(C,F)= 1.1), 130.5, 130.4, 124.1 (q, ^{1}J(C,F)= 331), 120.4, 67.2, 45.1, 26.6. ^{19}F NMR: δ= -68.06. Elemental analysis calcd (%) for $C_{13}H_{15}F_3N_2O_2S$: C 48.74, H 4.72, N 8.75. Found: C 48.99, H 4.96, N 8.49.

Typical procedure: Synthesis of **5aa, 5ak, 5al, 5am, 5an, 5ap, 5aq, 5ar, 5ba, 5bp, 5br**

A flame-dried double-necked vessel was successively charged, under nitrogen, with diisopropylethylamine (7 mL, 40 mmol) and anhydrous dichloromethane (80 mL). The resulting mixture was cooled to -20°C before addition of diethylaminosulfurtrifluoride (5.5 mL, 44 mmol), followed by the addition of trimethylsilyltrifluoromethane (5.9 mL, 40 mmol) or trimethylsilylpentafluoroethane (7.7 mL, 40 mmol) in 20 min interval.. After 1 hour under stirring at -20°C, the amine (1eq.) bearing an electron withdrawing group is added at 0°C (in its liquid form, solid form, or in 0,5 M solution from ethylacetate or dichloromethane). The reaction medium is then cooled to room temperature and kept under stirring overnight. After this period, the reaction medium was washed with distilled water. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was purified by chromatography over silica gel to afford the corresponding sulfanylamides.

N-[(trifluoromethyl)thio]aniline (**5aa**): Yellow oil. ^{1}H NMR: δ= 7.35 (m, 2H), 7.15 (m, 2H), 7.06 (m, 1H), 5.09 (NH). ^{13}C NMR: δ= 145.5, 129.8 (q, ^1J(C,F)= 315), 129.7, 122.3, 115,6. ^{19}F NMR: δ= -53.33. Elemental analysis calcd (%) for $C_7H_6F_3NS$: C 43.52, H 3.13, N 7.25 S 16.60. Found: C 43.55, H 3.08, N 7.36, S 16.24.

4-methyl-N-[(trifluoromethyl)thio]aniline (**5ak**): Orange oil. ^{1}H NMR: δ= 7.10 (d, ^3J(H,H)= 8.3, 2H), 6.99 (d, ^3J(H,H)= 8.3, 2H), 4.99 (NH), 2.31 (s, 3H). ^{13}C NMR: δ= 143.1, 131.7, 130.2, 129.9 (q, ^1J(C,F)= 317), 115.5, 20.9. ^{19}F NMR: δ= -53.40. Elemental analysis calcd (%) for $C_8H_8F_3NS$: C 46.37, H 3.89, N 6.76. Found: C 46.56, H 4.01, N 6.65.

4-methoxy-N-[(trifluoromethyl)thio]aniline (**5al**): Orange oil. ^{1}H NMR: δ= 7.02 (m, 2H), 6.85 (m, 2H) ; 4.97 (NH), 3.78 (s, 3H). ^{13}C NMR: δ= 155.4, 139.1, 129.9 (q, ^{1}J(C,F)= 318), 117.0, 115.0 56.0. ^{19}F NMR: δ= -53.45. Elemental analysis calcd (%) for $C_8H_8F_3NOS$: C 43.05, H 3.61, N 6.27. Found: C 42.98, H 3.70, N 6.03.

4-chloro-*N*-[(trifluoromethyl)thio]aniline (**5am**): Yellow oil. ^{1}H NMR: δ= 7.26 (d, ^{3}J(H,H)= 9.0, 2H), 7.04 (d, ^{3}J(H,H)= 9.0, 2H), 5.14 (NH). ^{13}C NMR: δ= 144.1, 129.7 (q, ^{1}J(C,F)= 317), 129.6, 127.2, 116.8. ^{19}F NMR: δ= -53.25. Elemental analysis calcd (%) for $C_7H_5ClF_3NS$: C 36.93, H 2.21, N 6.15. Found: C 36.78, H 2.07, N 6.38.

4-fluoro-N-[(trifluoromethyl)thio]aniline (**5an**): Yellow oil. ^{1}H NMR: δ= 7.00–6.94 (massif, 4H), 5.03 (NH). ^{13}C NMR: δ= 158.7 (d, ^{1}J(C,F)= 240), 141.6 (d, ^{4}J(C,F)= 2.2), 129.8 (q, ^{1}J(C,F)= 318), 116.8 (d, ^{3}J(C,F)= 8.8) , 116.2 (d, ^{2}J(C,F)=23). ^{19}F NMR: δ= -53,38, -122,93 (tt, ^{3}J(H,F)= 8.5, ^{4}J(H,F)= 4.2). Elemental analysis calcd (%) for $C_7H_5F_4NS$: C 39.81, H 2.39, N 6.63. Found: C 39.55, H 2.51, N 6.52.

1-phenyl-N-[(trifluoromethyl)thio]methanamine (**5ap**): Colorless oil. ^{1}H NMR: δ= 7.36–7.40 (massif, 5H), 4,26 (d, ^{3}J(H,H)= 5.4, 2H), 3.17 (NH). ^{13}C NMR: δ= 138.7, 131.0 (q, ^{1}J(C,F)= 318), 129.1, 128.6, 128.3, 58.1. ^{19}F NMR: δ= -52.45. Elemental analysis calcd (%) for $C_8H_8F_3NS$: C 46.37, H 3.89, N 6.76. Found: C 46.25, H 3.94, N 6.62.

1-phenyl-N-[(trifluoromethyl)thio]ethanamine (**5aq**): Colorless oil. ^{1}H NMR: δ= 7.33–7.35 (massif, 5H), 4.28 (m, 1H), 3.31 (NH), 1.53 (d, ^{3}J(H,H)= 6.6, 3H). ^{13}C NMR: δ= 143.8, 130.8 (q, ^{1}J(C,F)= 317), 129.1, 128.3, 127.1, 61.0, 22.9. ^{19}F NMR: δ= -52.30. Elemental analysis calcd (%) for $C_9H_{10}F_3NS$: C 48.86, H 4.56, N 6.33. Found: C 49.02, H 4.77, N 6.41.

N,N-diethyl-N'-[(trifluoromethyl)thio]pentane-1,4-diamine (**5ar**): Colorless oil. ^{1}H NMR: δ= 3.48 (NH), 3.05 (m, 1H), 2.51 (q, ^{3}J(H,H)= 7.1, 4H), 2.40 (t, ^{3}J(H,H)= 7.0, 2H), 1.53–1.41 (massif, 4H), 1.14 (d, ^{3}J(H,H)= 6.4, 3H), 1.01 (t, ^{3}J(H,H)= 7.1, 6H). ^{13}C NMR: δ= 130.7 (q, ^{1}J(C,F)= 317), 57.1, 53.3, 47.0, 35.7, 23.9, 20.8, 11.8. ^{19}F NMR: δ= -53.35. Elemental analysis calcd (%) for $C_{10}H_{21}F_3N_2S$: C 46.49, H 8.19, N 10.84. Found: C 46.40, H 8.04, N 11.01.

N-[(pentafluoroethyl)thio]aniline (**5ba**): Colorless oil. ^{1}H NMR: δ= 7.28 (m, 2H), 7.08 (m, 2H), 6.97 (m, 1H), 4.97 (NH). ^{13}C NMR: δ= 145.6, 129.8, 122.4, 120.0 (tq, ^{1}J(C,F)= 292, ^{2}J(C,F)= 39), 119.2 (qt, ^{1}J(C,F)= 286, ^{2}J(C,F)= 37), 115.6. ^{19}F NMR: δ= -83.09 (t, ^{3}J(F,F)= 2.87), -103.45 (t, ^{3}J(F,F)= 2.87). Elemental analysis calcd (%) for $C_8H_6F_5NS$: C 39.51, H 2.49, N 5.76.Found: C 39.39, H 2.35, N 5.92.

N-[(pentafluoroethyl)thio]-1-phenylmethanamine (**5bp**): Colorless oil. ^{1}H NMR: δ= 7.28–7.36 (massif, 5H), 4.24 (d, ^{3}J(H,H)= 5.3, 2H), 3.06 (NH). ^{13}C NMR: δ= 138.6, 129.1, 128.5, 128.4, 121.0 (tq, ^{1}J(C,F)= 291, ^{2}J(C,F)= 38), 119.3 (qt, ^{1}J(C,F)= 286, ^{2}J(C,F)= 38), 58.5. ^{19}F NMR: δ= -83,19 (t, ^{3}J(F,F)= 2.77) and -102.93 (s, ^{3}J(F,F)= 2.77). Elemental analysis calcd (%) for $C_9H_8F_5NS$: C 42.02, H 3.13, N 5.45. Found: C 41.70, H 2.98, N 5.67.

N,N-diethyl-N'-[(pentafluoroethyl)thio]pentane-1,4-diamine (**5br**): Colorless oil. ^{1}H NMR: δ= 3.34 (NH), 3.05 (m, 1H), 2.60 (q, ^{3}J(H,H)= 7.2, 4H), 2.49 (t, ^{3}J(H,H)= 6.4, 2H), 1.55–1.44 (massif, 4H), 1.16 (d, ^{3}J(H,H)= 6.4, 3H), 1.07 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 121.1 (tq, ^{1}J(C,F)= 289, ^{2}J(C,F)= 38), 119.0 (qt, ^{1}J(C,F)= 286, ^{2}J(C,F)= 38), 57.5, 53.1, 47.0, 35.5, 23.3, 20.9, 11.4. ^{19}F NMR: δ= -83.05 (t, ^{3}J(F,F)= 3.4), -103.15 (m). Elemental analysis calcd (%) for $C_{11}H_{21}F_5N_2S$: C 42.85, H 6.86, N 9.08. Found: C 42.64, H 6.52, N 9.33.

Typical procedure: Synthesis of **5ca**

To a cooled solution of diisopropylethylamine (175 µL, 1 mmol) and anhydrous dichloromethane (2 mL) at -20°C, is added under nitrogen, diethylaminosulfurtrifluoride (135 µL, 1.1 mmol), followed by the addition of (Difluorophenylsulfanylmethyl)trimethylsilane (232 mg, 1 mmol) in 20 min interval. After 1 hour under stirring at -20°C, aniline (91 µL, 1mmol) is added in its liquid form. The reaction medium is then cooled to room temperature and kept under stirring overnight. After this period, the reaction medium was washed with distilled water. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was purified by chromatography over silica gel to afford the corresponding sulfanylamide **5cb**.

N-{[difluoro(phenylthio)methyl]thio}aniline (**5ca**): Colorless oil. ^{1}H NMR: δ= 7.69 (m, 2H), 7.55–7.42 (massif, 3H), 7.24 (m, 2H), 7.00–6.92 (massif, 3H), 5.23 (NH). ^{13}C NMR: δ= 146.3, 136.9 (t, ^{4}J(C,F)= 1.1), 134.2 (t, ^{1}J(C,F)= 319), 130.8, 129.7, 129.6, 127.3 (t, ^{3}J(C,F)= 1.6), 121.7, 115.4. ^{19}F NMR: δ= -59,37. Elemental analysis calcd (%) for $C_{13}H_{11}F_2NS_2$: C 55.10, H 3.91, N 4.94. Found: C 55.18, H 4.03, N 4.81.

Typical procedure: Synthesis of **5dp**

To a cooled solution of diisopropylethylamine (175 µL, 1 mmol) and anhydrous dichloromethane (2 mL) at -20°C, is added under nitrogen, diethylaminosulfurtrifluoride (135 µL, 1,1 mmol), followed by the addition of 2-(Difluorotrimethylsilanylmethyl)benzooxazole (241 mg in 2 mL of CH_2Cl_2) in 20 min interval. After 1 hour under stirring at -20°C, benzylamine (110 µL, 1 mmol) is added in its liquid form. The reaction medium is then cooled to room temperature and kept under stirring for 4 hours. After this period, the reaction medium was washed with distilled water. The organic phase was dried over Na_2SO_4 and

evaporated in vacuo. The crude residue was washed with cooled pentane to afford the corresponding sulfanylamide **5dp**.

N-{[1,3-benzoxazol-2-yl(difluoro)methyl]thio}-1-phenylmethanamine (**5dp**): White solid. mp: 46-47°C. ^{1}H NMR: δ= 7.86 (m, 1H), 7.64 (m, 1H), 7.53-7.44 (massif, 2H), 7.40-7.26 (massif, 5H), 4.28 (d, ^{3}J(H,H)= 4.9, 2H), 3.27 (NH). ^{13}C NMR: δ= 156.9 (t, ^{2}J(C,F)= 33), 151.0, 140.5, 139.0, 128.9, 128.6, 128.2, 127.5, 125.9, 123,4 (t, ^{1}J(C,F)= 279), 121.9, 111.9, 58.35. ^{19}F NMR: δ= -84.41. Elemental analysis calcd (%) for $C_{15}H_{12}F_2N_2OS$: C 58.81, H 3.95, N 9.14, S 10.47. Found: C 59.11, H 4.21, N 8.95, S 10.06.

Typical procedure: Synthesis of **5ab, 5aj, 5ao**

In a solution of pure sulfinamidine (or a mixture of sulfanylamide/sulfinamidine) in dichloromethane (2 mL/mmol) is added 1.2 eq. of trifluoroacetic acid per mmol of sulfinamidine. The resulting mixture is then kept under stirring for 1 hour at room temperature. After this period, the reaction medium is washed with distilled water. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The corresponding sulfanylamide is directly obtained pure after work up.

4-nitro-N-[(trifluoromethyl)thio]aniline (**5ab**): Brown solid. mp: 88-89°C. ^{1}H NMR: δ= 8.22 (m, 2H), 7.20 (m, 2H), 5.64 (NH). ^{13}C NMR: δ= 151.9, 142.4, 129.4 (q, ^{1}J(C,F)= 317), 126.1, 115.3. ^{19}F NMR: δ= -52.71. Elemental analysis calcd (%) for $C_7H_5F_3N_2O_2S$: C 35.30, H 2.12, N 11.76. Found: C 35.41, H 2.21, N 11.63.

1-(4-{[(trifluoromethyl)thio]amino}phenyl)ethanone (**5aj**): Beige solid. mp: 90-91°C. ^{1}H NMR: δ= 7.91 (d, ^{3}J(H,H)= 8.7, 2H), 7.16 (d, ^{3}J(H,H)= 8.7, 2H), 6.11 (NH), 2.56 (s, 3H). ^{13}C NMR: δ= 197.6, 150.3, 131.4, 130.8, 129.6 (q, ^{1}J(C,F)= 317), 115.1, 26.7. ^{19}F NMR: δ= -52.93. Elemental analysis calcd (%) for $C_9H_8F_3NOS$: C 45.95, H 3.43, N 5.95. Found: C 46.19, H 3.61, N 5.78.

4-(trifluoromethyl)-N-[(trifluoromethyl)thio]aniline (**5ao**): Yellow oil. ^{1}H NMR: δ= 7.54 (d, ^{3}J(H,H)= 8.5, 2H), 7.16 (d, ^{3}J(H,H)= 8.5, 2H), 5.35 (NH). ^{13}C NMR: δ= 148.4 (q, ^{5}J(C,F)= 1.1), 129.6 (q, ^{1}J(C,F)= 317), 127.1 (q, ^{3}J(C,F)= 3.7), 124.7 (q, ^{1}J(C,F)= 271), 124.5 (q, ^{2}J(C,F)= 32.7), 115.3. ^{19}F NMR: δ= -53.14 and -63.24. Elemental analysis calcd (%) for $C_8H_5F_6NS$: C 36.79, H 1.93, N 5.36,. Found: C 37.01, H 2.07, N 5.74.

Typical procedure: Synthesis of **5af, 5ah**

In a solution of sulfinamidine (1 mmol of **1aaf** or **1aah**) in dichloromethane (2 mL) is added (26 μL, 3.5 mmol) of trifluoroacetic acid. The resulting mixture is then stirred at 50°C for 24h. After this period, the reaction medium is washed with distilled water. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The corresponding sulfanylamide is directly obtained pure after work up.

4-methyl-N-[(trifluoromethyl)thio]benzenesulfonamide (**5af**): White solid. mp: 85-86°C. ^{1}H NMR: δ= 7.81 (d, ^{3}J(H,H)= 8.1, 2H), 7.35 (d, ^{3}J(H,H)= 8.1, 2H), 6.75 (NH), 2.45. ^{13}C NMR: δ= 145.6, 135.4, 130.3, 128.4 (q, ^{1}J(C,F)= 314), 128.2, 22.0. ^{19}F NMR: δ= -51.86. Elemental analysis calcd (%) for $C_8H_8F_3NO_2S_2$: C 35.42, H 2.97, N 5.16, S 23.64. Found: C 35.61, H 3.36, N 5.16, S 23.23.

Benzyloxytrifluorométhanesulfacarbamide (**5ah**): Orange solid. mp: 73-74°C. ^{1}H NMR: δ= 7.43-7.39 (massif, 5H), 6.15 (NH), 5.42 (s, 2H). ^{13}C NMR: δ= 156.4, 135.3, 129.1, 129.09 (q, ^{1}J(C,F)= 314), 129.08, 128.8, 69.7. ^{19}F NMR: δ= -53.31. Elemental analysis calcd (%) for $C_9H_8F_3NO_2S$: C 43.03, H 3.21, N 5.58, S 12.76. Found: C 43.25, H 3.10, N 5.74, S 12.62.