Supporting Information

Convenient Synthesis of Pentafluoroethyl Thioethers via Catalytic Sandmeyer Reaction with a Stable Fluoroalkylthiolation Reagent

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General Methods

The reactions were performed in oven-dried glassware containing a Teflon-coated stirrer bar and septum under a nitrogen atmosphere. Acetonitrile were dried by refluxing over CaH₂ and subsequent fractionally distillation. All reactions were monitored by GC and the yields were determined by ¹⁹F NMR using trifluoroethanol as internal standard. GC analyses were carried out using a HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. Column chromatography was performed using a Combi Flash Companion-Chromatography-System (Isco-Systems) and Grace Reveleris packed flash columns (12 g). NMR spectra were obtained on a Bruker AMX 400 system using chloroform-d₅, acetonitrile-d₃ or methanol-d₄ as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 101 MHz and 375 MHz, respectively. Mass spectral data were acquired on a Varian Saturn 2100 T.

All commercially available starting materials were used without further purification. Me₄NSC₂F₅ was commercially available by CF Plus Chemicals s. r. o.
Synthesis of Starting Materials

Synthesis of arene diazoniun tetrafluoroborates

In a 50 mL round-bottom flask, the aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF₄ (50%, 2.5 mL, 20 mmol) and tert-butyl nitrite (2.7 mL, 20 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3 × 10 mL). The arenediazonium tetrafluoroborate was dried in vacuo (10⁻³ mbar) for 10 minutes and was then directly used without further purification.
Synthesis of pentafluoroethyl thioethers from arenediazonium salts

**Standard procedure:** An oven-dried 20 mL crimp-cap vessel with stirrer bar was charged with Cu (6.4 mg, 0.10 mmol), Me₄NSC₂F₅ (338 mg, 1.50 mmol) and MeCN (2 mL). Then, the arenediazonium salt (1.00 mmol) in MeCN (2 mL) was added dropwise and the reaction mixture was stirred for 15 h at room temperature. The resulting mixture was diluted with diethyl ether (20 mL). The organic solution was washed with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over MgSO₄, filtered and concentrated (700 mbar, 40 °C). The residue was purified by flash chromatography (SiO₂, cyclohexane / ethyl acetate gradient), yielding the aryl pentafluoroethyl thioethers. The yields of particularly volatile compounds were determined by ¹⁹F NMR, and their identity by mass spectroscopy.

**Synthesis of 1-methoxy-4-[(pentafluoroethyl)thio]benzene (2a).** Compound 2a was prepared following the standard procedure, starting from 4-methoxybenzenediazonium tetrafluoroborate (222 mg, 1.00 mmol). After purification, 2a was isolated as colorless oil (253 mg, 0.98 mmol, 98%). ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, 3J = 8.8 Hz, 2H), 6.94 (d, 3J = 8.8 Hz, 2H), 3.85 ppm (s, 3H); ¹⁹F NMR (375 MHz, CDCl₃): δ = –82.5 (t, J = 4.1 Hz, 3F), –92.8 ppm (q, J = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 162.0, 139.0 (2C), 115.0 (2C), 113.1 (t, 3J(C,F) = 2.7 Hz), 120.0 (qt, ¹J(C,F) = 287.0 Hz, ²J(C,F) = 40.3 Hz), 118.8 (tq, ¹J(C,F) = 286.1 Hz, ²J(C,F) = 37.0 Hz), 55.4 ppm; IR (neat): ν = 2934, 2842, 1593, 1495, 1293, 1252, 1205, 1102, 1087, 1030, 956, 828, 749 cm⁻¹; MS (ion trap, El, 70 eV): m/z (%) = 258 [M⁺] (73), 139 (100), 123 (11), 96 (14); HRMS (EI-TOF) calcd. for C₉H₅F₅OS: 258.0138; found: 258.0143.

**Synthesis of 1-methyl-3-[(pentafluoroethyl)thio]benzene (2b).** Compound 2b was prepared following the standard procedure, starting from 3-methylbenzenediazonium tetrafluoroborate (206 mg, 1.00 mmol). After purification, 2b was isolated as colorless oil (225 mg, 0.93 mmol, 93%). ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.47 (m, 2H), 7.33-7.32 (m, 2H), 2.41 ppm (s, 3H); ¹⁹F NMR (375 MHz, CDCl₃): δ = –82.5 (t, J = 4.1 Hz, 3F), –91.0 ppm (q, J = 3.8 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 139.5, 137.7, 134.2, 131.8, 129.2, 122.4 (t, 3J(C,F) = 2.7 Hz), 120.2 (qt, ¹J(C,F) = 288.4 Hz, ²J(C,F) = 40.0 Hz), 118.8 (tq, ¹J(C,F) = 286.8 Hz, ²J(C,F) = 36.8 Hz), 21.1 ppm; IR (neat): ν = 3053, 2929, 1595, 1477, 1330, 1203, 1095, 957, 780, 750, 691 cm⁻¹; MS
(Ion trap, El, 70 eV): m/z (%) = 242 [M'] (100), 173 (12), 123 (67), 91 (14); HRMS (El-TOF) calcd. for C_{9}H_{7}F_{5}S: 242.0189; found: 242.0183.

Synthesis of 4-((pentafluoroethyl)thio)-1,1'-biphenyl [CAS No.: 933673-37-1] (2c). Compound 2c was prepared following the standard procedure, starting from [1,1'-biphenyl]-4-diazonium tetrafluoroborate (268 mg, 1.00 mmol). After purification, 2c was isolated as colorless solid (289 mg, 0.95 mmol, 95%). m.p.: 60-61°C; ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.78 (m, 2H), 7.70-7.66 (m, 4H), 7.56-7.45 ppm (m, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 144.1, 139.6, 137.6, 129.0 (2C), 128.2 (2C), 128.1 (2C), 127.2 (2C), 121.4, 120.5 (qt, ¹J(C,F) = 288.4 Hz, ²J(C,F) = 39.9 Hz), 118.9 ppm (tq, ¹J(C,F) = 287.0 Hz, ²J(C,F) = 37.1 Hz); IR (neat): v= 3033, 1478, 1333, 1200, 1100, 960, 836, 760, 688 cm⁻¹; MS (Ion trap, El, 70 eV): m/z (%) = 304 [M'] (100), 190 (19), 188 (59), 185 (85), 152 (44); HRMS (El-TOF) calcd. for C_{14}H_{9}F_{5}S: 304.0345; found: 304.0368.

Synthesis of 1-phenoxy-4-((pentafluoroethyl)thio)benzene (2d). Compound 2d was prepared following the standard procedure, starting from 4-phenoxybenzenediazonium tetrafluoroborate (284 mg, 1.00 mmol). After purification, 2d was isolated as colorless oil (311 mg, 0.97 mmol, 97%). ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, ³J = 8.8 Hz, 2H), 7.42 (t, ³J = 8.0 Hz, 2H), 7.22 (t, ³J = 7.5 Hz, 1H), 7.09 (d, ³J = 8.5 Hz, 2H), 7.01 ppm (d, ³J = 8.8 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = -82.4 (t, ³J = 3.8 Hz, 3F), -92.5 ppm (q, ³J = 4.1 Hz, 2F); ¹⁹F NMR (375 MHz, CDCl₃): δ = -288.8 Hz, ³J(C,F) = 40.4 Hz), 115.5 ppm (t, ³J(C,F) = 3.2 Hz); IR (neat): v= 3043, 1582, 1485, 1331, 1242, 1200, 1085, 957, 869, 833, 749, 691 cm⁻¹; MS (Ion trap, El, 70 eV): m/z (%) = 320 [M'] (94), 201 (100), 129 (16), 77 (23); HRMS (El-TOF) calcd. for C_{14}H_{9}F_{5}OS: 320.0294; found: 320.0279.

Synthesis of 1-bromo-4-((pentafluoroethyl)thio)benzene [CAS No.: 782491-17-2] (2e). Compound 2e was prepared following the standard procedure, starting from 4-bromobenzenediazonium tetrafluoroborate (271 mg, 1.00 mmol). After purification, 2e was isolated as colorless oil (239 mg, 0.78 mmol, 78%). ¹H NMR (400 MHz, CDCl₃): δ = 7.58-7.51 ppm (m, 4H); ¹³C NMR (375 MHz, CDCl₃): δ = -82.7 (t, S6)
was isolated as colorless oil (acetylbenzenediazonium (2h)).

**Synthesis of 1-fluoro-4-[(pentafluoroethyl)thio]-benzene [CAS No.: 75220-65-4] (2f).**[^1] Compound 2f was prepared following the standard procedure, starting from 4-fluorodiazonium tetrafluoroborate (105 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36.0 µL, 0.50 mmol) was added to the reaction mixture and the pentafluoroethylthiolated product 2f was formed in 61% yield as determined by $^1$F NMR spectroscopic analysis and confirmed by GC-MS analytics. $^1$F NMR (375 MHz, CDCl$_3$): $\delta = -85.7$ (t, $J = 3.6$ Hz, 3F), $-92.1$ ppm (q, $J = 4.1$ Hz, 2F); MS (ion trap, EI, 70 eV): m/z (%) = 245.9 [$M^+$] (100), 177.0 (9), 127.0 (92), 83.0 (44), 75.0 (9), 68.9 (23), 57.0 (15).

**Synthesis of 1-chloro-4-[(pentafluoroethyl)thio]-benzene [CAS No.: 782491-17-2] (2g).** Compound 2g was prepared following the standard procedure, starting from 4-chlorobenzenediazonium tetrafluoroborate (226 mg, 1.00 mmol). After purification, 2g was isolated as colorless oil (181 mg, 0.69 mmol, 69%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.59$ (d, $^3J = 8.5$ Hz, 2H), 7.41 ppm (d, $^3J = 8.8$ Hz, 2H); $^1$F NMR (375 MHz, CDCl$_3$): $\delta = -82.5$ (t, $J = 3.8$ Hz, 3F), $-92.0$ ppm (q, $J = 4.1$ Hz, 2F); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 138.4$ (2C), 138.0, 129.8 (2C), 121.2 (t, $^3J(C,F) = 3.2$ Hz), 120.2 (qt, $^1J(C,F) = 288.8$ Hz, $^2J(C,F) = 40.3$ Hz), 119.1 ppm (qt, $^1J(C,F) = 287.0$ Hz, $^2J(C,F) = 36.3$ Hz); IR (neat): $\nu = 3045, 2925, 2855, 1575, 1478, 1331, 1204, 1088, 957, 822, 749$ cm$^{-1}$; MS (ion trap, EI, 70 eV): m/z (%) = 261 [$M^+$] (100), 145 (31), 143 (82), 108 (32); HRMS (EI-TOF) calcd. for C$_9$H$_4$F$_5$S$^{35}$ClS: 261.9642; found: 261.9633.

**Synthesis of 4-[(pentafluoroethyl)thio]acetophenone [CAS No.: 1328939-62-3] (2h).** Compound 2h was prepared following the standard procedure, starting from 4-acetylbenzenediazonium tetrafluoroborate (234 mg, 1.00 mmol). After purification, 2h was isolated as colorless oil (264 mg, 0.98 mmol, 98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.99$ (d, $^3J = 7.0$ Hz, 2H), 7.76 (d, $^3J = 7.0$ Hz, 2H), 2.64 ppm (s, 3H); $^1$F NMR...
(375 MHz, CDCl₃): δ = -82.5 (t, J = 4.1 Hz, 3F), -91.2 ppm (q, J = 3.8 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 197.0, 138.7, 136.9 (2C), 128.9 (2C), 128.4 (t, ³J(C,F) = 2.7 Hz), 120.3 (qt, ¹J(C,F) = 289.7 Hz, ²J(C,F) = 40.8 Hz), 118.6 (tq, ¹J(C,F) = 286.5 Hz, ²J(C,F) = 36.4 Hz), 26.7 ppm; IR (neat): ν= 3015, 2971, 1690, 1365, 1207, 1104, 954, 827, 750 cm⁻¹; MS (ion trap, EI, 70 eV): m/z (%) = 270 [M⁺] (39), 255 (100), 136 (9); HRMS (EI-TOF) calcd. for C₁₀H₇F₅O₅S: 270.0138; found: 270.0132.

**Synthesis of 4-[(pentafluoroethyl)thio]benzophenone (2i).** Compound 2i was prepared following the standard procedure, starting from 4-benzylophenediazonium tetrafluoroborate (296 mg, 1.00 mmol). After purification, 2i was isolated as colorless solid (309 mg, 0.99 mmol, 99%). m.p.: 56-57°C; ¹H NMR (400 MHz, CDCl₃): δ = 7.88-7.77 (m, 6H), 7.64 (t, ³J = 7.5 Hz, 1H), 7.52 ppm (t, ³J = 7.5 Hz, 2H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.4 (t, J = 3.8 Hz, 3F), -91.1 ppm (q, J = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 195.6, 139.7, 136.7, 136.7, 133.0, 130.6, 130.1, 128.5, 127.4 (t, ³J(C,F) = 2.7 Hz), 120.0 (qt, ¹J(C,F) = 289.7 Hz, ²J(C,F) = 41.0 Hz), 118.6 ppm (tq, ¹J(C,F) = 286.6 Hz, ²J(C,F) = 36.8 Hz); IR (neat): ν= 2929, 1650, 1592, 1448, 1304, 1199, 1103, 961, 850, 791, 730, 694 cm⁻¹; MS (ion trap, EI, 70 eV): m/z (%) = 332 [M⁺] (100), 254 (28), 108 (6); HRMS (EI-TOF) calcd. for C₁₅H₉F₅OS: 332.0296; found: 332.0288.

**Synthesis of methyl-4-[(pentafluoroethyl)thio]benzoate (2j).** Compound 2j was prepared following the standard procedure, starting from 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (250 mg, 1.00 mmol). After purification, 2j was isolated as colorless oil (269 mg, 0.94 mmol, 94%). ¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, ³J = 8.2 Hz, 2H), 7.73 (d, ³J = 8.0 Hz, 2H), 3.95 ppm (s, 3H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.5 (t, J = 3.8 Hz, 3F), -91.2 ppm (q, J = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 168.0, 136.7 (2C), 132.5, 130.3 (2C), 128.2 (t, ³J(C,F) = 2.7 Hz), 120.0 (qt, ¹J(C,F) = 289.7 Hz, ²J(C,F) = 40.9 Hz), 118.6 (tq, ¹J(C,F) = 286.6 Hz, ²J(C,F) = 36.3 Hz), 52.5 ppm; IR (neat): ν= 2925, 1713, 1438, 1282, 1214, 1106, 961, 764 cm⁻¹; MS (ion trap, EI, 70 eV): m/z (%) = 286 [M⁺] (56), 154 (100), 135 (17), 108 (15); HRMS (EI-TOF) calcd. for C₁₀H₇F₅O₂S: 286.0087; found: 286.0105.
Synthesis of $N,N$-dimethyl-$4$-[(pentafluoroethyl)thio]benzenamine (2k). Compound 2k was prepared following the standard procedure, starting from 4-(dimethylamino)benzenediazonium tetrafluoroborate (235 mg, 1.00 mmol). After purification, 2k was isolated as colorless oil (247 mg, 0.91 mmol, 91%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52$-$7.50$ (m, 2H), 6.72-6.69 (m, 2H), 3.04 ppm (s, 6H); $^{19}$F NMR (375 MHz, CDCl$_3$): $\delta = -82.4$ (t, $J = 4.1$ Hz, 3F), $-93.5$ ppm (q, $J = 4.1$ Hz, 2F); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 151.1$, 138.6 (2C), 120.3 (qt, $^1$J(C,F) = 287.9 Hz, $^2$J(C,F) = 39.9 Hz), 120.0 (tq, $^1$J(C,F) = 286.1 Hz, $^2$J(C,F) = 37.2 Hz), 112.2 (2C), 106.3 (t, $^3$J(C,F) = 2.7 Hz), 39.9 (2C) ppm; IR (neat): $\nu$ = 2986, 1593, 1509, 1446, 1365, 1329, 1193, 1086, 955, 810, 749 cm$^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = 271 [$M^+$] (19), 257 (38), 152 (49), 138 (100), 109 (26), 104 (20), 82 (29), 62 (40); HRMS (EI-TOF) calcd. for C$_{10}$H$_{10}$F$_5$NS: 271.0454; found: 271.0450.

Synthesis of $N$-[4-[(pentafluoroethyl)thio]phenyl]acetamide (2l). Compound 2l was prepared following the standard procedure, starting from 4-(acetylamino)benzenediazonium tetrafluoroborate (249 mg, 1.00 mmol). After purification, 2l was isolated as slightly yellow solid (234 mg, 0.82 mmol, 82%), m.p.: 137-138°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.60$ (s, 4H), 2.21 ppm (s, 3H); $^{19}$F NMR (375 MHz, CDCl$_3$): $\delta = -82.4$ (t, $J = 4.1$ Hz, 3F), $-92.3$ ppm (q, $J = 4.1$ Hz, 2F); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 172.1$, 143.4, 139.3 (2C), 121.6 (2C), 121.5 (qt, $^1$J(C,F) = 286.8 Hz, $^2$J(C,F) = 40.1 Hz), 120.4 (tq, $^1$J(C,F) = 285.9 Hz, $^2$J(C,F) = 37.1 Hz), 117.3 (t, $^3$J(C,F) = 2.9 Hz), 24.1 ppm; IR (neat): $\nu$ = 3456, 3018, 2975, 1738, 1368, 1229, 1217 cm$^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = 285 [$M^+$] (40), 243 (35), 124 (100); HRMS (EI-TOF) calcd. for C$_{10}$H$_{10}$F$_5$OS: 285.0247; found: 285.0254.

Synthesis of 4-[(pentafluoroethyl)thio]nitrobenzene (2m). Compound 2m was prepared following the standard procedure, starting from 4-nitrobenzenediazonium tetrafluoroborate (237 mg, 1.00 mmol). After purification, 2m was isolated as slightly yellow oil (262 mg, 0.96 mmol, 96%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.29$ (d, $^3$J = 8.8 Hz, 2H), 7.86 ppm (d, $^3$J = 8.8 Hz, 2H); $^{19}$F NMR (375 MHz, CDCl$_3$): $\delta = -82.5$ (t, $J = 3.8$ Hz, 3F), $-90.8$ ppm (q, $J = 3.8$ Hz, 2F); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 149.4$, 137.5 (2C), 130.8 (t, $^3$J(C,F) = 2.7 Hz), 124.2 (2C), 120.0 (qt, $^1$J(C,F) = 290.5 Hz, $^2$J(C,F) = 41.1 Hz), 118.4 ppm (tq, $^1$J(C,F) = 286.5 Hz,
3.6 Hz); IR (neat): ν= 3459, 3003, 2971, 1602, 1524, 1347, 1207, 1103, 956, 851, 750, 729, 685 cm⁻¹; MS (ion trap, EI, 70 eV): m/z (%) = 272 [M⁺] (56), 243 (98), 206 (12), 124 (100), 108 (30), 96 (12), 80 (21); HRMS (EI-TOF) calcd. for C₈H₄NF₅O₂S: 272.9883; found: 272.9897.

**Synthesis of 4-[(pentafluoroethyl)thio]benzonitrile (2n).** Compound 2n was prepared following the standard procedure, starting from 4-cyanobenzenediazonium tetrafluoroborate (217 mg, 1.00 mmol). After purification, 2n was isolated as colorless solid (208 mg, 0.82 mmol, 82%). m.p.: 45-46°C; ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (d, 3J = 8.3 Hz, 2H), 7.73 ppm (d, 3J = 8.8 Hz, 2H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.5 (t, J = 3.4 Hz, 3F), -91.0 ppm (q, J = 3.8 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 137.2 (2C), 132.8 (2C), 128.9 (t, 3JC,F = 2.7 Hz), 120.0 (qt, 1JC,F = 290.6 Hz, 2JC,F = 40.9 Hz), 118.4 (tq, 1JC,F = 287.0 Hz, 2JC,F = 36.3 Hz), 117.5, 115.0 ppm; IR (neat): ν= 3073, 3039, 2232, 1487, 1318, 1202, 1092, 959, 851, 830, 749 cm⁻¹; MS (ion trap, EI, 70 eV): m/z (%) = 253 [M⁺] (100), 184 (69), 134 (94), 102 (13), 90 (16); HRMS (EI-TOF) calcd. for C₉H₄NF₅S: 252.9985; found: 252.9991.

**Synthesis of 3-[(pentafluoroethyl)thio]quinoline (2o).** Compound 2o was prepared following the standard procedure, starting from quinoline-3-diazonium tetrafluoroborate (243 mg, 1.00 mmol). After purification, 2o was isolated as colorless solid (249 mg, 0.89 mmol, 89%). m.p.: 35-36°C; ¹H NMR (400 MHz, CDCl₃): δ = 9.00 (s, 1H), 8.49 (s, 1H), 8.14 (d, 3J = 8.5 Hz, 1H), 7.84-7.79 (m, 2H), 8.19 ppm (t, 3J = 7.5 Hz, 1H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.5 (t, J = 4.1 Hz, 3F), -91.4 ppm (q, J = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 154.9, 148.4, 145.5, 131.7, 129.5, 128.0, 127.7, 119.6, 120.3 (qt, 1JC,F = 289.6 Hz, 2JC,F = 40.6 Hz), 118.6 (tq, 1JC,F = 286.1 Hz, 2JC,F = 36.3 Hz), 116.7 ppm (t, 3JC,F = 2.9 Hz); IR (neat): ν= 3031, 1972, 1617, 1565, 1489, 1321, 1199, 1090, 948, 786, 748 cm⁻¹; MS (ion trap, EI, 70 eV): m/z (%) = 279 [M⁺] (87), 160 (100), 116 (14), 89 (31); HRMS (EI-TOF) calcd. for C₁₁H₆NF₅S: 279.0141; found: 279.0145.

**Synthesis of 6-[(pentafluoroethyl)thio]quinoline (2p).** Compound 2p was prepared following the standard procedure, starting from quinoline-6-diazonium tetrafluoroborate (243 mg, 1.00 mmol). After purification, 2p was isolated as colorless oil (229 mg, 0.82 mmol, 82%). ¹H NMR (400 MHz, CDCl₃): δ = 9.01 (dd, 3J = 4.3,
1.8 Hz, 1H), 8.19 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 8.8 Hz, 1H), 7.89 (dd, J = 8.8, 1.8 Hz, 1H), 7.48 ppm (dd, J = 8.5, 4.3 Hz, 1H); \(^{19}\)F NMR (375 MHz, CDCl\(_3\)): \(\delta = -82.4\) (t, J = 3.8 Hz, 3F), -91.5 ppm (q, J = 4.1 Hz, 2F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 152.4, 148.7, 137.7, 136.2, 136.1, 130.8, 128.3, 122.1, 121.1\) (t, J(C,F) = 2.9 Hz), 120.2 (qt, J(C,F) = 289.0 Hz, \(J(C,F) = 40.6\) Hz), 118.6 ppm (tq, J(C,F) = 286.8 Hz, \(J(C,F) = 36.7\) Hz); IR (neat): v = 3037, 1591, 1488, 1331, 1202, 1095, 835, 794, 749, 660 cm\(^{-1}\); MS (ion trap, EI, 70 eV): m/z (%) = 279 \([M^+]\) (88), 160 (100), 116 (23); HRMS (EI-TOF) calcd. for C\(_{11}\)H\(_6\)NF\(_S\): 279.0141; found: 279.0130.

Synthesis of 8-[{pentfluoroethyl}thio]quinoline (2q). Compound 2q was prepared following the standard procedure, starting from quinoline-8-diazonium tetrafluoroborate (243 mg, 1.00 mmol). After purification, 2q was isolated as colorless oil (198 mg, 0.71 mmol, 71%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.07\) (dd, J = 4.3, 1.8 Hz, 1H), 8.21 (dd, J = 8.3, 1.5 Hz, 1H), 8.15 (d, J = 7.3 Hz, 1H), 7.94 (dd, J = 8.0, 1.3 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.50 ppm (dd, J = 8.3, 4.3 Hz, 1H); \(^{19}\)F NMR (375 MHz, CDCl\(_3\)): \(\delta = -82.6\) (t, J = 4.1 Hz, 3F), -91.0 ppm (q, J = 4.1 Hz, 2F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 151.2, 147.9, 137.5, 136.5, 130.9, 130.0, 126.4, 124.3, 122.0, 120.3\) (qt, J(C,F) = 290.3 Hz, \(J(C,F) = 40.6\) Hz), 118.7 ppm (tq, J(C,F) = 286.6 Hz, \(J(C,F) = 36.8\) Hz); IR (neat): v = 3065, 1596, 1493, 1328, 1204, 1093, 950, 826, 787, 750, 660 cm\(^{-1}\); MS (ion trap, EI, 70 eV): m/z (%) = 279 \([M^+]\) (80), 160 (100), 116 (15); HRMS (EI-TOF) calcd. for C\(_{11}\)H\(_6\)NF\(_S\): 279.0141; found: 279.0134.

Synthesis of 9-ethyl-3-{[pentfluoroethyl]thio]-9H-carbazole (2r). Compound 2r was prepared following the standard procedure, starting from 9-ethyl-9H-carbazol-3-diazonium tetrafluoroborate (309 mg, 1.00 mmol). After purification, 2r was isolated as colorless solid (249 mg, 0.72 mmol, 72%). m.p.: 64-65°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.40\) (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.73 (dd, J = 8.5, 1.8 Hz, 1H), 7.55 (dt, J = 7.7, 1.1 Hz, 1H), 7.44 (t, J = 8.8 Hz, 2H), 7.32 (t, J = 7.8 Hz, 1H), 4.38 (q, J = 7.3 Hz, 2H), 1.47 ppm (t, J = 7.3 Hz, 3H); \(^{19}\)F NMR (375 MHz, CDCl\(_3\)): \(\delta = -82.2\) (t, J = 4.1 Hz, 3F), -92.7 ppm (q, J = 3.6 Hz, 2F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 141.1, 140.3, 134.3, 130.2, 126.6, 123.9, 122.2, 120.7, 120.2\) (qt, J(C,F) = 287.9 Hz, \(J(C,F) = 40.0\) Hz), 119.8, 118.8 (tq, J(C,F) = 287.0 Hz,
\( J(C,F) = 37.2 \text{ Hz}, \) 110.7 (t, \( J(C,F) = 3.1 \text{ Hz} \)), 109.2, 108.9, 37.7, 13.8 ppm; IR (neat): \( \nu = 3055, 2975, 1588, 1474, 1330, 1200, 1074, 958, 884, 798, 742, 654 \text{ cm}^{-1} \); MS (Ion trap, EI, 70 eV): m/z (%) = 345 \([M^+]\) (54), 330 (12), 226 (100), 211 (27), 197 (14), 167 (16); HRMS (EI-TOF) calcd. for \( C_{16}H_{12}NF_5S \): 345.0611; found: 345.0616.

**Synthesis of methyl-3-[(pentfluoroethyl]thio]thiophene-2-carboxylate (2s).** Compound 2s was prepared following the standard procedure, starting from 2-(methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate (256 mg, 1.00 mmol). After purification, 2s was isolated as colorless oil (286 mg, 0.98 mmol, 98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.59 \text{ (d, } J = 5.3 \text{ Hz, 1H)}, 7.30 \text{ (d, } J = 5.3 \text{ Hz, 1H)}, 3.92 \text{ ppm (s, 3H)} \); \(^{19}\)F NMR (375 MHz, CDCl\(_3\)): \( \delta = -82.8 \text{ (t, } J = 4.1 \text{ Hz, 3F)}, -91.2 \text{ ppm (q, } J = 4.1 \text{ Hz, 2F)} \); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta = 161.3, 132.6, 132.2 \text{ (t, } J(C,F) = 2.7 \text{ Hz), 131.0, 126.6 \text{ (t, } J(C,F) = 1.8 \text{ Hz)}, 120.3 \text{ (qt, } J(C,F) = 291.9 \text{ Hz), 118.1 \text{ (tq, } J(C,F) = 287.0 \text{ Hz)}, 117.9 \text{ (qt, } J(C,F) = 41.3 \text{ Hz)}, 111.8 \text{ ppm (tq, } J(C,F) = 35.8 \text{ Hz)} \); IR (neat): \( \nu = 2955, 1709, 1502, 1439, 1266, 1204, 1075, 958, 893, 793, 768, 750 \text{ cm}^{-1} \); MS (Ion trap, EI, 70 eV): m/z (%) = 291 \([M^+]\) (95), 261 (52), 172 (100), 142 (43), 114 (20); HRMS (EI-TOF) calcd. for \( C_8H_5F_5O_2S_2 \): 291.9651; found: 291.9675.
Spectroscopic data