An eccentric rod-like linear connection of two heterocycles: Synthesis of pyridine trans-tetrafluoro-ω sulfanyl triazoles

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General information

All reactions were performed in oven-dried glassware under positive pressure of nitrogen unless otherwise mentioned. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light. Products were purified by column chromatography carried out on columns packed with silica gel (60N spherical neutral size 63-210 μm). The $^1$H NMR (300 MHz) and $^{19}$F NMR (282 MHz) spectra were recorded for solution in CDCl$_3$ and (CD$_3$)$_2$CO on a Varian Mercury 300. $^{13}$C NMR (125 MHz) spectra for solution in CDCl$_3$ and (CD$_3$)$_2$CO were recorded on a BRUKER 500 UltraShield$^{18}$. Chemical shifts (δ) are expressed in ppm downfield from TMS (δ = 0.00) for $^1$H and C$_6$F$_6$ (δ = −162.2 (CDCl$_3$) or −163.5 ((CD$_3$)$_2$CO)) as an internal standard $^{19}$F NMR. For $^{13}$C NMR, CDCl$_3$ (δ = 77.16) or (CD$_3$)$_2$CO (δ = 29.84) is referred as residual standard. High resolution mass spectrometry was recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020 (ESI-MS and APCI-MS). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Melting points were recorded on a BUCHI M-565. Chemicals were purchased and used without further purification unless otherwise noted. Solvents benzene, toluene, dioxane, DMF and THF were dried and distilled before use.
Table S1. Optimization of reaction conditions.

![Chemical Structures](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Result&lt;sup&gt;b&lt;/sup&gt;</th>
<th>5a isomer A</th>
<th>5a isomer B</th>
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<td>1</td>
<td>3a (2.0 equiv), 4a (1.0 equiv), Cp*Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (10 mol%) in benzene at 80 °C</td>
<td>Traces</td>
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<td>3a (1.0 equiv), 4a (1.0 equiv), Cp*Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (10 mol%) in benzene at 80 °C</td>
<td>9%,&lt;sup&gt;b&lt;/sup&gt; 1:1&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>=</td>
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<td>3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (10 mol%) in benzene at 80 °C</td>
<td>19%,&lt;sup&gt;b&lt;/sup&gt; 1:1&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (10 mol%) in toluene at 80 °C</td>
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<td>3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (10 mol%) in dioxane at 80 °C</td>
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<td>=</td>
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<td>11</td>
<td>3a (1.0 equiv), 4a (3.0 equiv), in toluene at 110 °C</td>
<td>83%,&lt;sup&gt;b&lt;/sup&gt; 2:1&lt;sup&gt;c&lt;/sup&gt;</td>
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<sup>a</sup> Reactions were performed at 0.1 mmol scale at the given conditions for 24 h. <sup>b</sup> Total yield of 5a from <sup>19</sup>F NMR. <sup>c</sup> Ratio of the two regioisomers A and B.
The click reaction was also attempted under more metal catalysed conditions. Reaction 1 was performed under the typical Cu catalysed click reaction condition, but it did not proceed even after 12 h. When the reaction temperature was elevated to 80 °C for 24 h (reaction 2), trace amount of the product could be detected from GCMS. In reaction 3, the product was formed but, no increased selectivity was observed for the regioisomers (A:B = 2:1). Thus, we concluded that, there was no copper assistance in reactions 2 and 3, but they were solely driven by the thermal energy.

We also attempted the reaction under Ir catalysis at room temperature and elevated 50 °C but, could see only traces of 5a isomer A after 24 h (reaction 5 and 6). On the other hand, when we changed the Ru catalyst, the reaction didn’t proceed (reaction 7).

Concluding from these unfavourable results, we opted for the thermally induced click reaction.

**Scheme S1.** Metal catalysed reactions.
Synthesis of the Pyridine-SF₄-alkyne 3, General Procedure 1:

\[
\begin{align*}
\text{X} & \quad \text{Cl} \\
\text{N} & \quad \text{SF}_2 \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{R} & \quad \text{R}
\end{align*}
\]

Prepared according to literature procedure. Pyridine-SF₄-alkene 2 (1.0 equiv) was added to DMSO (0.3 M) in a round-bottom flask at room temperature, followed by Lithium hydroxide monohydrate (10.0 equiv) and allowed to stir at room temperature. The reaction progress was monitored by ¹⁹F NMR, and after the ¹⁹F NMR indicated the complete conversion to product, the reaction mixture was poured onto ice and extracted with Et₂O twice. The organic phase was dried with Na₂SO₄ and concentrated in vacuo to obtain the crude product. The crude product was purified by column chromatography on silica-gel eluting with n-Hexane/AcOEt mixture, to give the product 3a–k.

5-Bromo-2-(tetrafluoro(phenylethynyl)-λ⁶-sulfaneyl)pyridine (3a)

Prepared according to general procedure 1, by stirring 2a (0.8 mmol) at rt for 24 h to obtain 3a as white solid in 90% yield (262 mg). mp: 93–94 °C; HRMS (ESI⁺): m/z calcd for C₁₃H₈BrFSNaS [M+Na⁺]: 387.9395 found: 387.9390. \(^1\)H NMR (300 MHz, CDCl₃): δ = 7.49–7.36 (m, 3H), 7.60 (d, J = 6.6 Hz, 2H), 7.68 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 2.1 Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl₃): δ = 77.61 (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl₃): δ = 74.23 (quint, J = 9.8 Hz), 93.88 (quint, J = 51.2 Hz, 1H), 118.70, 122.81 (quint, J = 3.8 Hz), 123.21, 128.69, 130.56, 132.69, 141.04, 148.58 (quint, J = 2.5 Hz), 167.85 (quint, J = 31.2 Hz). ATR-FTIR (KBr): v = 3115, 3049, 2916, 2222, 1446, 1368, 1092, 1007, 869, 700 cm⁻¹.

5-Chloro-2-(tetrafluoro(phenylethynyl)-λ⁶-sulfaneyl)pyridine (3b)

Prepared according to general procedure 1 by stirring 2b (1.2 mmol) at rt for 24 h to obtain 3b as white solid in 92% yield (354 mg). mp: 133–134 °C; HRMS (ESI⁺): m/z calcd for C₁₃H₇NF₂NaCl [M+Na⁺]: 349.9900 found: 343.9887. \(^1\)H NMR (300 MHz, CDCl₃): δ = 7.36–7.48 (m, 3H), 7.59 (d, J = 6.9 Hz, 2H), 7.73 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 8.50 (d, J = 2.1 Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl₃): δ = 77.70 (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl₃): δ = 74.19 (quint, J = 9.8 Hz), 93.90 (quint, J = 52.3 Hz), 118.67, 122.42 (quint, J = 4.3 Hz), 128.68, 130.55, 132.67, 134.49, 138.10, 146.31, 167.23 (quint, J = 30.6 Hz). ATR-FTIR (KBr): v = 3050, 2221, 1571, 1486, 1448, 1108, 779, 709 cm⁻¹.

5-Nitro-2-(tetrafluoro(phenylethynyl)-λ⁶-sulfaneyl)pyridine (3c)

Prepared according to general procedure 1 by stirring 2c (3.9 mmol) at rt for 24 h to obtain 3c as brown solid in 50% yield (636 mg). mp: 142–143 °C; HRMS (ESI⁺): m/z calcd for C₁₃H₈N₂O₂S [M⁺]: 332.0234 found: 332.0227. \(^1\)H NMR (300 MHz, CDCl₃): δ = 7.38–7.50 (m, 3H), 7.61 (d, J = 6.9 Hz, 2H), 8.00 (d, J = 8.7 Hz, 1H), 8.67 (d, J = 8.7 Hz, 1H), 9.37 (d, J = 2.4 Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl₃): δ = 77.45 (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl₃): δ = 75.16 (quint, J = 9.8 Hz), 93.18 (quint, J = 50.7 Hz), 118.34, 122.44 (quint, J = 3.8 Hz), 128.75, 130.80, 132.71, 133.92, 143.48, 144.98, 171.93 (quint, J = 31.3 Hz). ATR-FTIR (KBr): v = 3060, 2917, 2219, 1604, 1565, 1535, 1488, 1450, 1355, 809, 755, 690 cm⁻¹.
5-Methyl-2-(tetrafluorophenylethynyl)-λ⁶-sulfaneylpiperidine (3d)

Prepared according to general procedure 1 by stirring 2d (3.0 mmol) at rt for 24 h to obtain 3d as light brown solid in 88% yield (799 mg). mp: 102–103 °C; HRMS (EI⁺): m/z calcd for C₁₄H₁₃NF₃NaS [M+Na⁺]: 324.0446 found: 324.0443. ¹H NMR (300 MHz, CDCl₃): δ = 2.40 (s, 3H), 7.34–7.46 (m, 3H), 7.58 (d, J = 6.6 Hz, 2H), 7.65 (s, 2H), 8.34 (s, 1H), ¹³F NMR (282 MHz, CDCl₃): δ = 77.07 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 18.17, 73.55 (quint, J = 10.1 Hz), 94.39 (quint, J = 53.2 Hz), 118.89, 120.81 (quint, J = 5.0 Hz), 128.63, 130.39, 132.62, 136.63, 138.88, 147.57, 167.48 (quint, J = 28.8 Hz). ATR-FTIR (KBr): ν = 3060, 2927, 2217, 1577, 1492, 1461, 1072, 777 cm⁻¹.

2-(tetrafluorophenylethynyl)-λ⁶-sulfaneylpiperidine (3e)

Prepared according to general procedure 1 by stirring 2e (1.0 mmol) at rt for 24 h to obtain 3e as light-yellow solid in 92% yield (264 mg). mp: 78–79 °C; HRMS (EI⁺): m/z calcd for C₁₄H₁₃NF₃NaS [M+Na⁺]: 310.0291. ¹H NMR (300 MHz, CDCl₃): δ = 7.35–7.47 (m, 4H), 7.57–7.60 (m, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.87 (t, J = 7.5 Hz, 1H), 8.55 (dd, J = 4.5 Hz, 1.5 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 76.46 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 73.81 (quint, J = 10.0 Hz), 94.24 (quint, J = 52.5 Hz), 118.79, 121.40–121.47 (m), 126.36, 128.66, 130.47, 132.63, 138.68, 147.65, 169.51 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3060, 2221, 1579, 1490, 1457, 1099, 800, 759 cm⁻¹.

5-Bromo-2-(tetrafluoro(4-nitrophenoxy)ethynyl)-λ⁶-sulfaneylpiperidine (3f)

Prepared according to general procedure 1 by stirring 2f (0.8 mmol) at rt for 24 h to obtain 3f as white solid in 63% yield (206 mg). mp: 209–210 °C; HRMS (EI⁺): m/z calcd for C₁₃H₁₂F₃NO₂SBr [M⁺]: 409.9348 found: 409.9355. ¹H NMR (300 MHz, CDCl₃): δ = 7.67 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.7 Hz, 2H), 8.02 (d, J = 8.7 Hz, 1H), 8.27 (d, J = 8.7 Hz, 2H), 8.62 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 77.08 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 71.48 (quint, J = 10.0 Hz), 97.19 (quint, J = 53.6 Hz), 122.73 (quint, J = 5.0 Hz), 123.54, 123.87, 125.50, 133.66, 141.18, 148.64, 148.75, 167.22 (quint, J = 29.3 Hz). ATR-FTIR (KBr): ν = 3062, 2227, 1594, 1519, 1444, 1346, 1091, 765, 707 cm⁻¹.

5-Bromo-2-(tetrafluoro(4-methoxyphenylethynyl)-λ⁶-sulfaneylpiperidine (3g)

Prepared according to general procedure 1 by stirring 2g (1 mmol) at rt for 24 h to obtain 3g as white solid in 98% yield (387 mg). mp: 163–164 °C; HRMS (EI⁺): m/z calcd for C₁₄H₁₀NO₂F₃NaSBr [M+Na⁺]: 417.9500 found: 417.9501. ¹H NMR (300 MHz, CDCl₃): δ = 3.84 (s, 3H), 6.90 (dt, J = 9.0 Hz, 2.4 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.7 Hz, 1H), 7.99 (dd, J = 8.7 Hz, 0.9 Hz, 1H), 8.60 (d, J = 2.1 Hz 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 77.89 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.52, 74.81 (quint, J = 9.8 Hz), 93.26 (quint, J = 51.3 Hz), 110.40, 114.35, 122.81 (quint, J = 5.0 Hz), 123.11, 134.37, 141.00, 148.53, 161.35, 168.05 (quint, J = 30.6 Hz). ATR-FTIR (KBr): ν = 3046, 2219, 1606, 1511, 1446, 1243, 1093, 1031, 786, 678 cm⁻¹.
5-bromo-2-(((4-butyln phenyl)ethynyl)tetrafluoro-λ⁶-sulfaneyl)pyridine (3h)

Prepared according to general procedure 1 by stirring 2h (1.8 mmol) at rt for 24 h to obtain 3h as white solid in 77% yield (480 mg), mp: 68–69 °C; HRMS (ESI+): m/z calcld for C_{11}H_{12}NF_3NaSBr [M+Na]^+: 367.9708 found: 367.9709. ^1H NMR (300 MHz, CDCl_3): δ = 0.95 (t, J = 7.2 Hz, 3H), 1.41–1.65 (m, 4H), 2.30–2.38 (m, 2H), 7.61 (d, J = 8.7 Hz, 1H), 7.96 (dt, J = 8.7 Hz, 0.9 Hz, 1H), 8.57 (d, J = 3.0 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = 77.61 (s, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 13.64, 17.49, 22.02, 29.50, 76.45 (quint, J = 8.8 Hz), 85.97 (quint, J = 50.0 Hz), 122.76 (quint, J = 3.8 Hz), 123.00, 140.94, 148.46 (t, J = 2.5 Hz), 168.12 (quint, J = 31.3 Hz). ATR-FTIR (KBr): v = 3052, 2960, 2235, 1552, 1448, 1091, 794, 690 cm⁻¹.

5-bromo-2-(tetrafluoro(4-pentyln phenyl)ethynyl)-λ⁶-sulfaneyl)pyridine (3i)

Prepared according to general procedure 1 by stirring 2i (1.2 mmol) at rt for 24 h to obtain 3i as white solid in 83% yield (359 mg), mp: 49–50 °C; HRMS (ESI+): m/z calcld for C_{13}H_{14}NF_3NaSBr [M+Na]^+: 381.9864 found: 381.9859. ^1H NMR (300 MHz, CDCl_3): δ = 0.92 (t, J = 7.2 Hz, 3H), 1.26–1.47 (m, 4H), 1.57–1.67 (m, 2H), 2.29–2.38 (m, 2H), 7.61 (d, J = 8.7 Hz, 1H), 7.96 (dt, J = 8.7 Hz, 1.2 Hz, 1H), 8.57 (d, J = 2.1 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = 77.65 (s, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 14.02, 17.73, 22.20, 27.15, 31.02, 76.48 (quint, J = 9.8 Hz), 85.97 (quint, J = 51.0 Hz), 122.75 (quint, J = 4.4 Hz), 122.99, 140.94, 148.43 (t, J = 2.5 Hz), 168.11 (quint, J = 31.2 Hz). ATR-FTIR (KBr): v = 3052, 2954, 2235, 1567, 1452, 1091, 781, 701 cm⁻¹.

2-fluoro-3-(tetrafluoro(phenylethynyl)-λ³-sulfaneyl)pyridine (3j)

Prepared according to general procedure 1 by stirring 2j (1.2 mmol) at rt for 8 h to obtain 3j as light-yellow solid in 98% yield (334 mg), mp: 85–86 °C; HRMS (ESI+): m/z calcld for C_{10}H_{10}NF_3S [M+H]^+: 306.0376 found: 306.0382. ^1H NMR (300 MHz, CDCl_3): δ = 7.28–7.32 (m, 1H), 7.36–7.49 (m, 3H), 7.58 (d, J = 6.9 Hz, 2H), 8.23 (td, J = 8.1 Hz, 1.8 Hz, 1H), 8.33 (d, J = 4.5 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = −60.29—−59.95 (m, 1F), 91.65 (d, J = 22.6 Hz, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 74.16 (quint, J = 8.8 Hz), 94.32 (quint, J = 51.3 Hz), 118.44, 121.63 (d, J = 5.0 Hz), 128.71, 130.66, 132.64, 139.72 (quint, J = 5.0 Hz), 140.32 (quint, J = 27.5 Hz), 149.92 (d, J = 15.0 Hz), 155.33 (d, J = 24.5 Hz). ATR-FTIR (KBr): v = 3070, 2223, 1583, 1490, 1442, 1276, 1240, 1095, 788, 715 cm⁻¹.

2-fluoro-4-(tetrafluoro(phenylethynyl)-λ³-sulfaneyl)pyridine (3k)

Prepared according to general procedure 1 by stirring 2k (1.9 mmol) at rt for 24 h to obtain 3k as light-yellow solid in 60% yield (350 mg), mp: 93–94 °C; HRMS (ESI+): m/z calcld for C_{13}H_{15}NF_3S [M+H]^+: 306.0376 found: 306.0373. ^1H NMR (300 MHz, CDCl_3): δ = 7.31 (t, J = 2.1 Hz, 1H), 7.37–7.50 (m, 3H), 7.54–7.60 (m, 3H), 8.36 (d, J = 5.4 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = −64.67 (s, 1F), 86.04 (s, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 74.63 (quint, J = 10.0 Hz), 93.73 (quint, J = 51.3 Hz), 107.50–108.00 (m, 118.25–118.37 (m, 128.76, 130.80, 132.68, 148.49 (d, J = 15.0 Hz), 162.72, 164.64, 168.27–169.20 (m). ATR-FTIR (KBr): v = 3029, 2227, 1596, 1575, 1477, 1444, 1228, 1101, 788, 750 cm⁻¹.
Synthesis of benzene-tetrafluoro(phenylethynyl)-λ⁶-sulfane (6)

Alkyne 6b and 6c were prepared according to literature procedure.⁵ Alkyne 6a was synthesized using a modified literature procedure.⁵

(4-bromophenyl)tetrafluoro(phenylethynyl)-λ⁶-sulfane (6a)

Benzene-SF₄-alkene 9a (3.0 mmol) was added to DMSO (0.3 M) in a round-bottom flask at room temperature, followed by Lithium hydroxide monohydrate (10.0 equiv) and allowed to stir at room temperature. The reaction progress was monitored by ¹⁹F NMR, and after the ¹⁹F NMR indicated the complete conversion to product, the reaction mixture was poured onto ice and extracted with Et₂O twice. The organic phase was dried with Na₂SO₄ and concentrated in vacuo to obtain the crude product. The crude product was purified by washing with hexane to obtain 6a as a yellow solid in 30% yield. mp: 69–72 °C; HRMS (ESI⁺): m/z calcd for C₁₄H₈F₄SBr [M–H]⁺: 362.9466 found: 362.9491. ¹H NMR (300 MHz, CDCl₃): δ = 7.38–7.44 (m, 3H), 7.53–7.67 (m, 6H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 88.48 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 73.06 (quint, J = 10.0 Hz), 95.03 (quint, J = 53.6 Hz, 1H), 118.78, 125.05, 127.68 (quint, J = 5.0 Hz), 128.67, 130.44, 131.58, 132.61, 158.17 (quint, J = 23.6 Hz). ATR-FTIR (KBr): v = 3111, 2925, 2225, 1574, 1475, 1070, 752, 683 cm⁻¹.

(Synthesis of the Pyridine/Benzene-SF₄-triazole 5 or 7, General Procedure 2:

An oven dried test tube was charged with alkyne 3 or 6 (0.5 mmol), azide 4 (1.5 mmol) and toluene (2.5 mL) and allowed to stir at 110 °C for 24 h or unless mentioned otherwise. The reaction was allowed to cool to room temperature and the solvent was evaporated in vacuo to give the crude products. The ratio of the two regioisomers was calculated from the crude ¹⁹F NMR. The products were isolated using column chromatography on silica-gel, eluting with n-Hexane/AcOEt mixture, to get pure regioisomers of 5, A and B. The total isolated yield of the reaction was calculated by adding the weight of pure A, B and the inseparable mixture of A, B obtained after column chromatography.
2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl)-5-bromopyridine (5a-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5a-A as white solid. mp: 138–139 °C; HRMS (ESI): m/z calcd for C_{20}H_{13}N_{4}F_{4}NaSb [M+Na]⁺: 521.0035 found: 521.0029. ¹H NMR (300 MHz, CDCl₃): δ = 5.30 (s, 2H), 6.94–6.97 (m, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.20–7.25 (m, 3H), 7.38 (t, J = 6.9 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 8.50 (d, J = 2.1 Hz, 1H), ²⁵F NMR (282 MHz, CDCl₃): δ = 61.31 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 53.06, 122.81, 122.96 (quint, J = 3.8 Hz), 126.27, 127.96, 128.57, 128.60, 128.83, 130.13, 130.24, 133.69–137.03 (m), 134.19, 140.86, 148.28, 159.29 (quint, J = 32.5 Hz), 168.21 (quint, J = 30 Hz). ATR-FTIR (KBr): ν = 3048, 1560, 1496, 1479, 1446, 1361, 1074, 794, 696 cm⁻¹.

2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl)-5-bromopyridine (5a-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure 5b-B as white solid. mp: 155–156 °C; HRMS (ESI): m/z calcd for C_{20}H_{13}N_{4}F_{4}NaSb [M+Na]⁺: 521.0040 found: 521.0040. ¹H NMR (300 MHz, CDCl₃): δ = 5.94 (s, 2H), 7.30–7.35 (m, 5H), 7.39–7.41 (m, 3H), 7.56–7.59 (m, 2H), 7.63 (d, J = 8.1 Hz, 1H), 7.80 (t, J = 7.8 Hz, 1H), 8.48 (d, J = 3.3 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.66 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.77, 122.59–122.69 (m), 123.52, 127.75, 128.02, 128.39, 128.94, 130.21, 131.14, 135.11, 141.13, 144.39, 148.08–148.90 (m), 148.61, 167.38–167.85 (m). ATR-FTIR (KBr): ν = 3062, 1560, 1498, 1446, 1369, 1093, 786, 696 cm⁻¹.

Total isolated yield of 5a is 77% (192 mg).

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl)-5-chloropyridine (5b-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5b-A as white solid. mp: 141–142 °C; HRMS (ESI): m/z calcd for C_{20}H_{13}N_{4}F_{4}NaCl [M+Na]⁺: 477.0540 found: 477.0566. ¹H NMR (300 MHz, CDCl₃): δ = 5.31 (s, 2H), 6.96 (dd, J = 1.5 Hz, 7.2 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.21–7.30 (m, 3H), 7.36–7.42 (m, 2H), 7.45–7.50 (m, 1H), 7.70–7.79 (m, 2H), 8.42 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.39 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 53.10, 122.61 (quint, J = 3.8 Hz), 126.33, 128.00, 128.60, 128.87, 130.16, 130.27, 134.01 (quint, J = 5.0 Hz), 134.13, 134.22, 137.95, 146.07, 159.35 (quint, J = 33.0 Hz), 167.66 (quint, J = 30.0 Hz), ATR-FTIR (KBr): ν = 3066, 3031, 1562, 1482, 1454, 1126, 1108, 777, 700 cm⁻¹.

2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl)-5-chloropyridine (5b-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5b-B as white solid. mp: 140–141 °C; HRMS (ESI): m/z calcd for C_{20}H_{13}N_{4}F_{4}NaCl [M+Na]⁺: 477.0540 found: 477.0536. ¹H NMR (300 MHz, CDCl₃): δ = 5.93 (s, 2H), 7.30–7.37 (m, 5H), 7.40–7.44 (m, 3H), 7.54–7.57 (m, 2H), 7.61 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 8.45 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz,
Total isolated yield of 5b is 86% (195 mg).

2-((1-benzy1-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ6-sulfaneyl)-5-nitropyridine (5c-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure 5c-A as light brown solid. mp: 136–137 °C; HRMS (ESI\(^+\)): m/z calcd for C\(_{26}\)H\(_{30}\)N\(_5\)O\(_2\)F\(_2\)NaS\([\text{M}+\text{Na}^+]\): 488.0780 found: 488.0781. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.32\) (s, 2H), 6.97 (dd, \(J = 7.2\) Hz, 1.5 Hz, 2H), 7.16 (d, \(J = 7.2\) Hz, 2H), 7.22–7.31 (m, 3H), 7.38–7.52 (m, 3H), 7.97 (d, \(J = 9.0\) Hz, 1H), 8.59 (dd, \(J = 9.0\) Hz, 2.4 Hz, 1H), 9.27 (d, \(J = 2.7\) Hz, 1H), 130.08, 130.58, 134.28 (quint, \(J = 3.8\) Hz, 1H) ppm. ATR-FTIR (KBr): \(\nu \) = 3054, 2967, 1567, 1477, 1450, 1124, 1074, 781 cm\(^{-1}\).

2-((1-benzy1-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ6-sulfaneyl)-5-nitropyridine (5c-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure 5c-B as light brown solid. mp: 149–150 °C; HRMS (ESI\(^+\)): m/z calcd for C\(_{26}\)H\(_{30}\)N\(_5\)O\(_2\)F\(_2\)NaS\([\text{M}+\text{Na}^+]\): 488.0780 found: 488.0794. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.93\) (s, 2H), 7.33–7.39 (m, 5H), 7.40–7.45 (m, 3H), 7.54–7.57 (m, 2H), 7.87 (d, \(J = 9.0\) Hz, 1H), 8.60 (dd, \(J = 8.7\) Hz, 2.1 Hz, 1H), 9.30 (d, \(J = 2.4\) Hz, 1H), 131.37, 136.46, 137.72 ppm. ATR-FTIR (KBr): \(\nu \) = 3050, 1606, 1567, 1535, 1482, 1455, 1359, 1076, 779, 763 cm\(^{-1}\).

Total isolated yield of 5c is 92% (214 mg).

2-((1-benzy1-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ6-sulfaneyl)-5-methylpyridine (5d-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure 1d-A as white solid. mp: 130–131 °C; HRMS (ESI\(^+\)): m/z calcd for C\(_{21}\)H\(_{29}\)N\(_5\)O\(_2\)F\(_2\)NaS\([\text{M}+\text{Na}^+]\): 457.1086 found: 457.1109. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.33\) (s, 3H), 5.30 (s, 2H), 6.96 (dd, \(J = 7.8\) Hz, 2.0 Hz, 2H), 7.15 (d, \(J = 7.2\) Hz, 2H), 7.20–7.27 (m, 3H), 7.34–7.47 (m, 3H), 7.56–7.65 (m, 2H), 8.26 (s, 1H), 130.03, 129.33, 132.86–132.92 (m), 133.31, 135.22, 196.37, 158.78 (quint, \(J = 3.2\) Hz) ppm. ATR-FTIR (KBr): \(\nu \) = 3056, 2964, 2933, 1577, 1461, 1376, 1074, 769, 732 cm\(^{-1}\).

Total isolated yield of 5d is 96% (204 mg).
2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁵-sulfaneyl)-5-methylpyridine (5d-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 7/3) to isolate pure 5d-B as white solid. mp: 118–119 °C; HRMS (ESIª): m/z calcd for C₂₁H₁₈N₄F₆NaS [M+Na]⁺: 457.1086 found: 457.1082. ¹H NMR (300 MHz, CDCl₃): δ = 2.37 (s, 3H), 5.94 (s, 2H), 7.34–7.36 (m, 5H), 7.39–7.41 (m, 3H), 7.52–7.62 (m, 4H), 8.30 (s, 1H), 19F NMR (282 MHz, CDCl₃): δ = 67.04 (s, 4F). ¹³C NMR (125 MHz, CDCl₃): δ = 18.17, 55.69, 120.69–120.75 (m), 127.77, 127.95, 128.28, 128.78, 128.81, 130.25, 131.36, 135.27, 136.97, 138.93, 144.21, 147.60, 149.12 (quint, J = 36.3 Hz), 167.13–167.57 (m). ATR-FTIR (KBr): ν = 3033, 2958, 2925, 1573, 1459, 1376, 1076, 781, 725 cm⁻¹.

Total isolated yield of 5d is 60% (130 mg).

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁵-sulfaneyl)pyridine (5e-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5e-A as light brown solid. mp: 141–142 °C; HRMS (ESIª): m/z calcd for C₂₀H₁₆N₄F₆NaS [M+Na]⁺: 443.0929 found: 443.0929. ¹H NMR (300 MHz, CDCl₃): δ = 5.30 (s, 2H), 6.94–6.97 (m, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.20–7.29 (m, 3H), 7.32–7.47 (m, 4H), 7.72–7.81 (m, 2H), 8.45 (d, J = 4.2 Hz, 1H), 19F NMR (282 MHz, CDCl₃): δ = 60.06 (s, 4F). ¹³C NMR (125 MHz, CDCl₃): δ = 52.97, 121.43–121.54 (m), 125.59, 126.35, 127.90, 128.49, 128.50, 128.76, 130.01, 130.22, 133.89 (quint, J = 5.0 Hz), 134.20, 138.47, 147.35, 159.53 (quint, J = 33.8 Hz), 169.84 (quint, J = 28.8 Hz). ATR-FTIR (KBr): ν = 3035, 1577, 1479, 1457, 1361, 1076, 773 cm⁻¹.

2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁵-sulfaneyl)pyridine (5e-B):

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5e-B as light brown solid. mp: 131–132 °C; HRMS (ESIª): m/z calcd for C₂₀H₁₆N₄F₆NaS [M+Na]⁺: 443.0929 found: 443.0921. ¹H NMR (300 MHz, CDCl₃): δ = 5.94 (s, 2H), 7.30–7.35 (m, 5H), 7.39–7.41 (m, 4H), 7.56–7.59 (m, 2H), 7.63 (d, J = 8.1 Hz, 1H), 7.80 (t, J = 7.8 Hz, 1H), 8.49 (d, J = 4.5 Hz, 1H), 19F NMR (282 MHz, CDCl₃): δ = 66.39 (s, 4F). ¹³C NMR (125 MHz, CDCl₃): δ = 55.66, 121.23–121.29 (m), 126.56, 127.70, 127.93, 128.26, 128.75, 128.81, 130.19, 131.26, 135.18, 138.76, 144.23, 147.62, 148.91 (quint, J = 35.0 Hz), 169.26 (quint, J = 27.5 Hz). ATR-FTIR (KBr): ν = 3035, 1581, 1496, 1461, 1361, 1324, 1076, 759 cm⁻¹.

Total isolated yield of 5e is 71% (149 mg).
2-((1-benzyl-5-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl)-5-bromopyridine (5f-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 3/1) to isolate pure 5f-A as white solid. mp: 176–179 °C; HRMS (ESI⁺): m/z calcd for C₂₀H₁₄N₃O₃F₄NaSBr [M+Na]⁺: 565.9885 found: 565.9886. ¹H NMR (300 MHz, CDCl₃): δ = 5.36 (s, 2H), 6.93 (d, J = 6.6 Hz, 2H), 7.23–7.32 (m, 5H), 7.64 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 8.23 (td, J = 8.7 Hz, 2.4 Hz, 2H), 8.52 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.72 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 53.68, 122.85 (quint, J = 5.0 Hz), 123.16, 123.66, 127.75, 129.08, 129.18, 131.63, 131.79 (quint, J = 3.8 Hz), 133.06, 133.68, 141.05, 148.48, 148.90, 159.79 (quint, J = 34.0 Hz), 167.89 (quint, J = 31.0 Hz), ATR-FTIR (KBr): ν = 3056, 1602, 1527, 1448, 1344, 1093, 767, 692 cm⁻¹.

Total isolated yield of 5f is 67% (182 mg).

2-((1-benzyl-4-(4-nitrophenyl)-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl)-5-bromopyridine (5f-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 3/1) to isolate pure 5f-B as white solid. mp: 179–180 °C; HRMS (ESI⁺): m/z calcd for C₂₀H₁₄N₃O₃F₄NaSBr [M+Na]⁺: 565.9885 found: 565.9881. ¹H NMR (300 MHz, CDCl₃): δ = 5.94 (s, 2H), 7.36 (brs, 5H), 7.56 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.1 Hz, 1H), 8.28 (d, J = 8.7 Hz, 2H), 8.57 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.96 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 56.03, 122.48, 123.28, 123.85, 127.85, 128.63, 128.94, 131.34, 134.63, 137.68, 141.31, 142.21, 148.23, 148.77, 148.98 (quint, J = 39.0 Hz), 167.28 (quint, J = 29.0 Hz), ATR-FTIR (KBr): ν = 3056, 1602, 1513, 1450, 1349, 1099, 779, 692 cm⁻¹.

2-((1-benzyl-5-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl)-5-bromopyridine (5g-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5g-A as white solid. mp: 147–148 °C; HRMS (ESI⁺): m/z calcd for C₂₁H₁₄N₄O₄F₄NaSBr [M+Na]⁺: 551.0139 found: 551.0140. ¹H NMR (300 MHz, CDCl₃): δ = 3.83 (s, 3H), 5.82 (s, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.99–7.02 (m, 2H), 7.07 (d, J = 8.7 Hz, 2H), 7.24–7.28 (m, 3H), 7.65 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 8.7 Hz, 1H), 8.52 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.19 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 52.92, 55.42, 114.10, 117.97, 122.79, 122.99 (quint, J = 5.0 Hz), 127.95, 128.58, 128.85, 131.61, 133.96 (t, J = 3.8 Hz), 134.39, 140.86, 148.29, 159.45 (quint, J = 32.4 Hz), 160.86, 168.31 (quint, J = 31.2 Hz), ATR-FTIR (KBr): ν = 3045, 2956, 1562, 1494, 1255, 1091, 1000, 769, 686 cm⁻¹.

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2-[(1-benzyl-4-(4-methoxyphenyl)-1H,1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl]-5-bromopyridine (5g-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5g-B as white solid. mp: 149–150 °C; HRMS (ESI⁺): m/z calcd for C₂₈H₂₂N₆O₆F₆NaSBr [M+Na⁺]: 551.0140 found: 551.0151. ¹H NMR (300 MHz, CDCl₃): δ = 3.83 (s, 3H), 5.91 (s, 2H), 6.94 (d, J = 9.0 Hz, 2H), 7.29–7.34 (m, 5H), 7.48–7.57 (m, 3H), 7.95 (d, J = 9.0 Hz, 1H), 8.55 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.40 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.35, 55.75, 113.48, 122.65, 123.41, 123.47, 127.70, 128.33, 131.81, 131.43, 135.18, 141.12, 144.14, 148.48 (quint, J = 35.0 Hz), 148.58, 160.06, 167.68 (quint, J = 29.5 Hz), ATR-FTIR (KBr): ν = 3064, 2940, 1552, 1486, 1448, 1249, 1095, 1031, 784, 682 cm⁻¹.

Total isolated yield of 5g is 70% (185 mg).

2-[(1-benzyl-5-butyl-1H,1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl]-5-bromopyridine (5h-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5h-A as white solid. mp: 127–128 °C; HRMS (ESI⁺): m/z calcd for C₂₉H₂₄N₆O₆F₆NaSBr [M+Na⁺]: 501.0348 found: 501.0349. ¹H NMR (300 MHz, CDCl₃): δ = 0.84 (t, J = 6.9 Hz, 3H), 1.26–1.35 (m, 4H), 2.76–2.81 (m, 2H), 5.54 (s, 2H), 7.22–7.26 (m, 2H), 7.23–7.36 (m, 3H), 7.78 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H), 8.62 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 59.61 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 13.64, 22.89, 23.42, 30.39, 52.82, 122.91, 123.05 (quint, 5.0 Hz), 127.35, 128.75, 129.19, 134.23–134.29, 141.03, 148.34, 159.00 (quint, J = 32.8 Hz), 168.56 (quint, J = 31.5 Hz). ATR-FTIR (KBr): ν = 3031, 2958, 1563, 1448, 1093, 775, 690 cm⁻¹.

2-[(1-benzyl-4-butyl-1H,1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl]-5-bromopyridine (5h-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5h-B as white solid. mp: 67–68 °C; HRMS (ESI⁺): m/z calcd for C₂₉H₂₄N₆O₆F₆NaSBr [M+Na⁺]: 501.0348 found: 501.0360. ¹H NMR (300 MHz, CDCl₃): δ = 0.95 (t, J = 7.0 Hz, 3H), 1.37–1.50 (m, 2H), 1.74–1.84 (m, 2H), 2.92 (t, J = 7.2 Hz, 2H), 5.82 (s, 2H), 7.22–7.25 (m, 2H), 7.28–7.35 (m, 3H), 7.69 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H), 8.62 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 64.98 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 14.01, 22.76, 26.35, 31.09, 55.16, 122.66 (t, J = 3.8 Hz), 123.51, 127.49, 128.15, 128.71, 135.39, 141.23, 144.96, 148.52 (quint, J = 34.5 Hz), 148.64, 167.97 (quint, J = 29.9 Hz), ATR-FTIR (KBr): ν = 3064, 2960, 1552, 1452, 1091, 769, 694 cm⁻¹.

Total isolated yield of 5h is 68% (163 mg).
2-((1-benzyl-5-pentyl-1H-1,2,3-triazol-4-yl)tetrafluoro-\(\lambda^6\)-sulfaneyl)-5-bromopyridine (5i-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5i-A as white solid. mp: 109–110 °C; HRMS (ESI\(^+\)): \(m/z\) calcd for \(\text{C}_{19}\text{H}_{25}\text{N}_3\text{F}_5\text{NaSBr} [\text{M+Na}]^+\): 515.0504 found: 515.0516. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.83\) (t, \(J = 6.9\) Hz, 3H), 1.19–1.31 (m, 6H), 2.78 (t, \(J = 7.5\) Hz, 2H), 5.54 (s, 2H), 7.22–7.26 (m, 2H), 7.32–7.41 (m, 3H), 7.78 (d, \(J = 8.7\) Hz, 1H), 8.02 (d, \(J = 8.7\) Hz, 1H), 8.62 (d, \(J = 2.1\) Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = 59.57\) (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 13.97\), 22.29, 23.73, 28.15, 31.95, 52.89, 122.95, 123.10 (quint, \(J = 5.0\) Hz), 127.39, 128.83, 129.26, 134.27, 134.29–134.35 (m), 141.07, 148.42, 159.03 (quint, \(J = 32.4\) Hz), 168.61 (quint, \(J = 31.6\) Hz). ATR-FTIR (KBr): \(\nu = 3064, 2935, 1554, 1452, 1093, 765, 692\) cm\(^{-1}\).

2-((1-benzyl-4-pentyl-1H-1,2,3-triazol-5-yl)tetrafluoro-\(\lambda^6\)-sulfaneyl)-5-bromopyridine (5i-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5i-B as white solid. mp: 72–73 °C; HRMS (ESI\(^+\)): \(m/z\) calcd for \(\text{C}_{19}\text{H}_{25}\text{N}_3\text{F}_5\text{NaSBr} [\text{M+Na}]^+\): 515.0504 found: 515.0515. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.90\) (t, \(J = 6.9\) Hz, 3H), 1.30–1.44 (m, 4H), 1.76–1.84 (m, 2H), 2.91 (t, \(J = 7.8\) Hz, 2H), 5.82 (s, 2H), 7.22–7.25 (m, 2H), 7.28–7.35 (m, 3H), 7.68 (d, \(J = 8.7\) Hz, 1H), 8.03 (d, \(J = 9.0\) Hz, 1H), 8.62 (d, \(J = 2.1\) Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = 65.00\) (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 14.14\), 22.58, 26.60, 28.68, 31.84, 55.17, 122.66, 123.51, 127.49, 128.16, 128.71, 135.39, 141.23, 144.99, 148.50 (quint, \(J = 34.4\) Hz), 148.64, 167.98 (quint, \(J = 30.2\) Hz). ATR-FTIR (KBr): \(\nu = 3062, 2933, 1565, 1494, 1450, 1093, 779, 690\) cm\(^{-1}\).

Total isolated yield of 5i is 70% (173 mg).

3-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-\(\lambda^6\)-sulfaneyl)-2-fluoropyridine (5j-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 7/3) to isolate pure 5j-A as white solid. mp: 152–153 °C; HRMS (ESI\(^+\)): \(m/z\) calcd for \(\text{C}_{20}\text{H}_{21}\text{N}_3\text{F}_5\text{NaS} [\text{M+Na}]^+\): 461.0835 found: 461.0837. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.32\) (s, 2H), 6.96 (dd, \(J = 7.8\) Hz, 1.5 Hz, 2H), 7.15 (d, \(J = 7.2\) Hz, 2H), 7.20–7.31 (m, 4H), 7.38–7.43 (m, 2H), 7.46–7.52 (m 1H), 8.17 (td, \(J = 8.1\) Hz, 1.8 Hz, 1H), 8.25 (d, \(J = 4.8\) Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -60.15\) (quintd, \(J = 22.6\) Hz, 8.5 Hz, 1F), 75.11 (d, \(J = 22.6\) Hz, 4F), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 53.11\), 121.47 (d, \(J = 5.0\) Hz), 126.12, 127.96, 128.59, 128.65, 128.87, 130.23 (d, \(J = 3.8\) Hz), 133.92–133.99 (m), 134.14, 139.69–139.81 (m), 140.31–141.42 (m), 149.56 (d, \(J = 15.0\) Hz), 154.30, 156.26, 159.64 (quint, \(J = 31.3\) Hz). ATR-FTIR (KBr): \(\nu = 3031, 2929, 1587, 1573, 1496, 1438, 1280, 1232, 1076, 777, 694\) cm\(^{-1}\).
3-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl)-2-fluoropyridine (5j-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 7/3) to isolate pure 5j-B as white solid. mp: 157–158 °C; HRMS (ESI+): m/z calcd for C₂₀H₁₅N₃F₅NaS [M+Na]⁺: 461.0835 found: 461.0835. ¹H NMR (300 MHz, CDCl₃): δ = 5.92 (s, 2H), 7.23–7.27 (m, 1H), 7.32–7.38 (m, 5H), 7.42–7.45 (m, 3H), 7.53–7.56 (m, 2H), 8.08 (td, J = 8.1 Hz, 1.5 Hz, 1H), 8.31 (d, J = 4.8 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = −60.08 (quint, J = 22.6 Hz, 8.46 Hz, 1F), 81.46 (d, J = 22.6 Hz, 4F). ¹³C NMR (125 MHz, CDCl₃): δ = 55.88, 121.70 (d, J = 5.0 Hz), 127.84, 128.06, 128.50, 128.87, 129.04, 130.17, 130.97, 134.92, 139.51, 140.05–140.68 (m), 144.29, 148.62–149.17 (m), 150.25 (d, J = 15.0 Hz), 155.09 (d, J = 245 Hz). ATR-FTIR (KBr): v = 3035, 2923, 1590, 1438, 1284, 1228, 1093, 813, 730 cm⁻¹.

Total isolated yield of 5j is 95% (208 mg).

4-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl)-2-fluoropyridine (5k-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5k-A as white solid. mp: 131–132 °C; HRMS (ESI+): m/z calcd for C₂₀H₁₅N₃F₅NaS [M+Na]⁺: 461.0835 found: 461.0829. ¹H NMR (300 MHz, CDCl₃): δ = 5.32 (s, 2H), 6.96 (dd, J = 1.2 Hz, 6.9 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 7.24–7.31 (m, 4H), 7.40–7.53 (m, 4H), 8.27 (d, J = 5.7 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 55.19, 107.76 (quintd, J = 42.5 Hz, 5.0 Hz), 118.42 (sextet), 125.05, 128.01, 128.67, 128.72, 128.91, 130.19, 130.34, 133.94–134.01 (m), 134.06, 148.24 (d, J = 13.8 Hz), 159.29 (quint, J = 32.5 Hz), 162.60, 164.52, 169.19 (dquint, J = 27.5 Hz, 7.5 Hz). ATR-FTIR (KBr): v = 3064, 1592, 1475, 1448, 1234, 1105, 786, 701 cm⁻¹.

4-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro-λ⁶-sulfaneyl)-2-fluoropyridine (5k-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5k-B as white solid. mp: 131–132 °C; HRMS (ESI+): m/z calcd for C₂₀H₁₅N₃F₅NaS [M+Na]⁺: 461.0835 found: 461.0822. ¹H NMR (300 MHz, CDCl₃): δ = 5.90 (s, 2H), 7.21–7.22 (m, 1H), 7.31–7.46 (m, 9H), 7.51–7.55 (m, 2H), 8.32 (d, J = 5.7 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = −64.12 (s, 1F), 76.07 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.88, 107.61 (dt, J = 41.3 Hz, 5.0 Hz), 118.00–118.11 (m), 127.58, 128.11, 128.54, 128.93, 129.14, 130.10, 130.82, 134.88, 144.48, 148.57 (quint, J = 33.6 Hz), 148.65 (d, J = 15.0 Hz), 162.66, 164.58, 168.47 (dquint, J = 26.3 Hz, 7.5 Hz). ATR-FTIR (KBr): v = 3035, 1589, 1575, 1473, 1230, 1101, 782, 696 cm⁻¹.

Total isolated yield of 5k is 91% (199 mg).
5-bromo-2-(tetrafluoro(1-(4-nitrobenzyl)-5-phenyl-1H-1,2,3-triazol-4-yl)-λ^6-sulfaneyl)pyridine (SI-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure SI-A as yellow solid. mp: 153–154 °C; HRMS (ESI^'): m/z calcd for C_{20}H_{25}N_5O_4F_6NaSBr [M+Na]^+: 565.9885 found: 565.9889. ^1H NMR (300 MHz, CDCl_3): δ = 5.42 (s, 2H), 7.15 (d, J = 8.7 Hz, 4H), 7.42 (t, J = 7.2 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 8.7 Hz, 2H), 8.53 (d, J = 2.4 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = 61.33 (s, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 52.14, 122.89–123.00 (m), 124.18, 125.91, 128.87, 128.94, 130.08, 130.58, 134.28 (quint, J = 3.8 Hz), 140.97, 141.00, 148.10, 148.43, 159.18–159.71, 167.83–168.31. ATR-FTIR (KBr): ν = 3060, 1604, 1565, 1521, 1481, 1452, 1415, 1348, 1095, 786, 696 cm^{-1}.

5-bromo-2-(tetrafluoro(1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)-λ^6-sulfaneyl)pyridine (SI-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure SI-B as white solid. mp: 186–187 °C; HRMS (ESI^'): m/z calcd for C_{20}H_{21}N_5O_3F_4NaSBr [M+Na]^+: 565.9885 found: 565.9869. ^1H NMR (300 MHz, CDCl_3): δ = 6.03 (s, 2H), 7.41–7.58 (m, 8H), 7.96 (d, J = 8.4 Hz, 1H), 8.24 (dt, J = 8.7 Hz, 1.8 Hz, 2H), 8.55 (d, J = 2.4 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = 67.62 (s, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 54.91, 122.55, 123.75, 124.18, 128.13, 128.41, 129.18, 130.14, 130.69, 141.25, 142.18, 144.75, 147.75, 147.97, 148.69, 167.39 (quint, J = 28.8 Hz). ATR-FTIR (KBr): ν = 3077, 1600, 1517, 1479, 1444, 1417, 1344, 1097, 765, 692 cm^{-1}.

Total isolated yield of SI is 92% (250 mg).

5-bromo-2-(1-(4-bromobenzyl)-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (5m-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5m-A as white solid. mp: 132–133 °C; HRMS (ESI^'): m/z calcd for C_{20}H_{21}N_5O_3F_4NaSBr [M+Na]^+: 598.9140 found: 598.9132. ^1H NMR (300 MHz, CDCl_3): δ = 5.26 (s, 2H), 6.84 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.36–7.51 (m, 5H), 7.65 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 8.51 (d, J = 2.1 Hz, 1H), ^19F NMR (282 MHz, CDCl_3): δ = 61.29 (s, 4F), ^13C NMR (125 MHz, CDCl_3): δ = 52.38, 122.84, 122.86, 122.90–122.97 (m), 126.11, 128.70, 129.70, 130.17, 130.28, 132.01, 133.12, 133.92–134.02 (m), 140.89, 148.30, 159.30 (quint, J = 32.5 Hz), 168.13 (quint, J = 30 Hz). ATR-FTIR (KBr): ν = 3056, 1596, 1558, 1486, 1359, 1095, 782, 698 cm^{-1}.
5-bromo-2-((1-(4-bromobenzyl)-4-phenyl-1H,1,2,3-triazol-5-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (5m-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5m-B as white solid. mp: 150–151 °C; HRMS (ESI^+): m/z calcld for \(\text{C}_{20}\text{H}_{14}\text{BrN}_{3}\text{F}_{4}\text{NaSBr} [M+Na]^+\): 598.9140 found: 598.9147. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.87\) (s, 2H), 7.23 (d, \(J = 8.4\) Hz, 2H), 7.41–7.44 (m, 3H), 7.47–7.52 (m, 2H), 7.53–7.55 (m, 3H), 7.95 (d, \(J = 8.7\) Hz, 1H), 8.56 (d, \(J = 2.4\) Hz, 1H), \(^1^9\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = 67.62\) (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)):\(\delta = 55.15, 122.59, 123.61, 128.05, 129.03, 129.54, 130.18, 130.97, 132.03, 134.08, 141.18, 144.50, 148.90–149.20\) (m), 148.65, 167.30–167.76 (m). ATR-FTIR (KBr): \(\nu = 3048, 1554, 1486, 1446, 1359, 1095, 771, 692\) cm\(^{-1}\).

Total isolated yield of 5m is 63\% (182 mg).

5-bromo-2-(tetrafluoro(1-(3-fluorobenzyl)-5-phenyl-1H,1,2,3-triazol-4-yl)-λ^6-sulfaneyl)pyridine (5n-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure 5n-A as white solid. mp: 134–135 °C; HRMS (ESI^+): m/z calcld for \(\text{C}_{20}\text{H}_{14}\text{BrN}_{3}\text{F}_{4}\text{NaSBr} [M+Na]^+\): 538.9940 found: 538.9933. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.30\) (s, 2H), 6.66 (d, \(J = 9.3\) Hz, 1H), 6.76 (d, \(J = 7.8\) Hz, 1H), 6.99 (td, \(J = 8.4\) Hz, 2.4 Hz, 1H), 7.16 (d, \(J = 7.2\) Hz, 2H), 7.19–7.25 (m, 1H), 7.38–7.52 (m, 3H), 7.66 (d, \(J = 8.7\) Hz, 1H), 7.94 (d, \(J = 8.7\) Hz, 1H), 8.53 (d, \(J = 2.4\) Hz, 1H), \(^1^9\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -112.54\)–\(-112.38\) (m, 1F), 61.29 (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 52.48\) (d, \(J = 1.3\) Hz), 115.11 (d, \(J = 22.5\) Hz), 115.76 (d, \(J = 21.3\) Hz), 122.90, 122.95–123.06 (m), 123.63 (d, \(J = 2.5\) Hz), 126.14, 128.73, 130.19, 130.35, 130.57 (d, \(J = 7.5\) Hz), 134.05–134.15 (m), 136.46 (d, \(J = 7.5\) Hz), 140.91, 148.37, 159.35 (quint, \(J = 32.5\) Hz), 162.83 (d, \(J = 246.3\) Hz), 168.19 (quint, \(J = 31.3\) Hz). ATR-FTIR (KBr): \(\nu = 3077, 1616, 1590, 1556, 1486, 1450, 1361, 1253, 1093, 765, 696\) cm\(^{-1}\).

5-bromo-2-(tetrafluoro(1-(3-fluorobenzyl)-4-phenyl-1H,1,2,3-triazol-5-yl)-λ^6-sulfaneyl)pyridine (5n-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure 5n-B as white solid. mp: 148–149 °C; HRMS (ESI^+): m/z calcld for \(\text{C}_{20}\text{H}_{14}\text{BrN}_{3}\text{F}_{4}\text{NaSBr} [M+Na]^+\): 538.9940 found: 538.9955. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.91\) (s, 2H), 7.04 (d, \(J = 9.3\) Hz, 2H), 7.11 (d, \(J = 7.8\) Hz, 1H), 7.30–7.37 (m, 1H), 7.41–7.44 (m, 3H), 7.53–7.58 (m, 3H), 7.95 (d, \(J = 8.7\) Hz, 1H), 8.56 (d, \(J = 2.1\) Hz, 1H), \(^1^9\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -112.83\)–\(-112.75\) (m, 1F), 67.61 (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 55.14, 114.79\) (d, \(J = 21.3\) Hz), 115.43 (d, \(J = 21.3\) Hz), 122.59–122.65 (m), 123.28 (d, \(J = 2.5\) Hz), 123.60, 128.05, 129.03, 130.19, 130.46 (d, \(J = 8.75\) Hz), 130.97, 137.49 (d, \(J = 7.5\) Hz), 141.18, 144.50, 148.09–149.20 (m), 148.64, 162.99 (d, \(J = 245.0\) Hz), 167.52 (quint, \(J = 28.8\) Hz). ATR-FTIR (KBr): \(\nu = 3052, 1590, 1486, 1448, 1365, 1261, 1097, 798, 692\) cm\(^{-1}\).
Total isolated yield of 5n is 78% (212 mg).

4-((4-((5-bromopyridin-2-yl)tetrafluoro-λ^6-sulfaneyl)-5-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (5o-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (Hexane/AcOEt, 7/3) to isolate pure 5o-A as white solid. mp: 160–161 °C; HRMS (ESI$^+$): m/z calcd for C$_{21}$H$_{14}$N$_2$F$_4$NaSBr [M+Na]$^+$: 545.9987 found: 545.9988. $^1$H NMR (300 MHz, CDCl$_3$): δ = 5.37 (s, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 7.2 Hz, 2H), 7.39–7.44 (m, 2H), 7.47–7.52 (m, 1H), 7.55–7.58 (m, 2H), 7.65 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 8.53 (d, J = 2.1 Hz, 1H), $^{19}$F NMR (282 MHz, CDCl$_3$): δ = 61.33 (s, 4F), $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 52.41, 112.77, 118.25, 122.87–122.97 (m), 125.92, 128.62, 128.86, 130.06, 130.49, 132.73, 134.16–134.26 (m), 139.17, 140.95, 148.38, 159.40 (quint, J = 33.8 Hz), 186.06 (quint, J = 31.25 Hz). ATR-FTIR (KBr): ν = 3064, 2227, 1610, 1565, 1508, 1482, 1450, 1357, 1093, 794, 700 cm$^{-1}$.  

4-((5-((5-bromopyridin-2-yl)tetrafluoro-λ^6-sulfaneyl)-4-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (5o-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (Hexane/AcOEt, 7/3) to isolate pure 5o-B as white solid. mp: 154–155 °C; HRMS (ESI$^+$): m/z calcd for C$_{21}$H$_{14}$N$_2$F$_4$NaSBr [M+Na]$^+$: 545.9987 found: 545.9990. $^1$H NMR (300 MHz, CDCl$_3$): δ = 5.98 (s, 2H), 7.39–7.45 (m, 5H), 7.51–7.57 (m, 3H), 7.66 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 9.0 Hz, 1H), 8.55 (d, J = 2.4 Hz, 1H), $^{19}$F NMR (282 MHz, CDCl$_3$): δ = 67.61 (s, 4F), $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 55.09, 112.40, 118.50, 122.53, 123.70, 128.09, 128.20, 129.13, 130.10, 130.70, 132.71, 140.28, 141.23, 144.64, 148.64, 148.72 (quint, J = 35.0 Hz), 167.37 (quint, J = 28.8 Hz). ATR-FTIR (KBr): ν = 3056, 2229, 1610, 1567, 1506, 1477, 1450, 1359, 1093, 777, 694 cm$^{-1}$.  

Total isolated yield of 5o is 75% (197 mg).

5-bromo-2-(tetrafluoro(1-(4-methoxybenzyl))-5-phenyl-1H-1,2,3-triazol-4-yl)-λ^6-sulfaneyl)pyridine (5p-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5p-A as white solid. mp: 156–157 °C; HRMS (ESI$^+$): m/z calcd for C$_{21}$H$_{12}$NO$_2$F$_4$NaSBr [M+Na]$^+$: 551.0140 found: 551.0162. $^1$H NMR (300 MHz, CDCl$_3$): δ = 3.77 (s, 3H), 5.24 (s, 2H), 6.73–6.78 (m, 2H), 6.87–6.91 (m, 2H), 7.16 (d, J = 6.9 Hz, 2H), 7.38–7.51 (m, 3H), 7.65 (d, J = 8.7 Hz, 1H), 7.92 (dd, J = 8.7 Hz, 1.2 Hz, 1H), 8.52 (d, J = 2.4 Hz, 1H), $^{19}$F NMR (282 MHz, CDCl$_3$): δ = 61.32 (s, 4F), $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 52.66, 55.39, 114.15, 122.82, 122.29 (quint, J = 3.8 Hz), 126.23, 126.43, 128.59, 129.59, 130.13, 130.33, 133.77 (quint, J = 5.0 Hz), 140.86, 148.31, 159.30 (quint, J = 32.5 Hz), 159.78, 168.26 (quint, J = 31.3 Hz). ATR-FTIR (KBr): ν = 3041, 1616, 1589, 1560, 1513, 1446, 1357, 1245, 1089, 1035, 808, 755 cm$^{-1}$.  

S17
5-bromo-2-(tetrafluoro(1-(4-methoxybenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)-λ6-sulfaneyl)pyridine (5p-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5p-B as white solid. mp: 155–156 °C; HRMS (ESI⁻): m/z calcd for C₂₁H₁₇Br₇N₄F₄NaSBr [M+Na]⁻: 551.0140 found: 551.0146. ¹H NMR (300 MHz, CDCl₃): δ = 3.80 (s, 3H), 5.85 (s, 2H), 6.86–6.91 (m, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.39–7.42 (m, 3H), 7.52–7.57 (m, 3H), 7.95 (d, J = 8.7 Hz, 1H), 8.56 (d, J = 2.1 Hz, 1H), ¹³F NMR (282 MHz, CDCl₃): δ = 148.2, 144.4, 1093, 782, 694 (quint, δ = 148.32, 159.30 (quint, J = 28.8 Hz)). ATR-FTIR (KBr): ν = 3066, 1610, 1513, 1454, 1361, 1251, 1097, 1025, 800, 757 cm⁻¹.

Total isolated yield of 5p is 68% (180 mg).

5-bromo-2-(tetrafluoro(1-(3-methylbenzyl)-5-phenyl-1H-1,2,3-triazol-4-yl)-λ6-sulfaneyl)pyridine (5q-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 7/3) to isolate pure 5q-A as white solid. mp: 108–109 °C; HRMS (ESI⁻): m/z calcd for C₂₁H₁₇Br₇N₄F₄NaSBr [M+Na]⁻: 535.0191 found: 535.0189. ¹H NMR (300 MHz, CDCl₃): δ = 2.25 (s, 3H), 5.27 (s, 2H), 6.72–6.76 (m, 2H), 7.06–7.16 (m, 4H), 7.37–7.42 (m, 2H), 7.45–7.50 (m, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.92 (dd, J = 8.7 Hz, 0.9 Hz, 1H), 8.52 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.32 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 21.38, 53.17, 122.83, 122.99 (quint, J = 5.0 Hz), 125.10, 126.37, 128.54, 128.71, 128.88, 129.38, 130.11, 130.33, 133.89–133.96 (m), 134.00, 138.61, 140.87, 148.32, 159.30 (quint, J = 32.5 Hz), 168.26 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3056, 1610, 1554, 1482, 1444, 1093, 782, 694 cm⁻¹.

Total isolated yield of 5q is 67% (172 mg).
5-bromo-2-((1,5-diphenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁶-sulfaneyl)pyridine (5r-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (n-Hexane/AcOEt, 7/3) to get only 5r-A as brown solid in 26% yield (63.4 mg). mp: 177–178 °C; HRMS (ESI⁺): m/z calc. for C_{19}H_{13}NaF_{4}NaSBr [M+Na⁺]: 506.9878 found: 506.9891. ¹H NMR (300 MHz, CDCl₃): δ = 7.28–7.38 (m, 10H), 7.71 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 8.57 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.70 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 122.96, 123.06 (quint, J = 5.0 Hz), 125.51, 126.57, 128.57, 129.34, 129.72, 129.97, 130.57, 134.28, 136.12, 140.96, 148.44, 159.18–159.71 (m), 168.03–168.51 (m). ATR-FTIR (KBr): ν = 3056, 1592, 1565, 1494, 1477, 1446, 1357, 1089, 782, 698 cm⁻¹.

5-bromo-2-(tetrafluoro(1-(4-nitrophenyl)-5-phenyl-1H-1,2,3-triazol-4-yl)-λ⁶-sulfaneyl)pyridine (5s-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (n-Hexane/AcOEt, 4/1) to get only 5s-A as light brown solid in 66% yield (174 mg). mp: 162–163 °C; HRMS (ESI⁺): m/z calc. for C_{19}H_{12}N_2O_2F_4NaSBr [M+Na⁺]: 551.9729 found: 551.9714. ¹H NMR (300 MHz, CDCl₃): δ = 7.35 (d, J = 7.5 Hz, 2H), 7.39–7.52 (m, 5H), 7.70 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 8.22 (dt, J = 9.0 Hz, 2.7 Hz, 2H), 8.56 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.89 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 122.94 (quint, J = 3.8 Hz), 123.11, 124.82, 125.77, 125.82, 129.06, 130.38, 130.60, 134.41 (quint, J = 5.0 Hz), 140.74, 141.03, 147.84, 148.46, 159.80 (quint, J = 33.8 Hz), 167.94 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3056, 1596, 1498, 1444, 1284, 1110, 782, 696 cm⁻¹.

5-bromo-2-(tetrafluoro(1-(4-methoxyphenyl)-5-phenyl-1H-1,2,3-triazol-4-yl)-λ⁶-sulfaneyl)pyridine (5t-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (n-Hexane/AcOEt, 4/1) to get only 5t-A as yellow solid in 72% yield (185 mg). mp: 166–167 °C; HRMS (ESI⁺): m/z calc. for C_{20}H_{13}N_2O_2F_4NaSBr [M+Na⁺]: 536.9984 found: 536.9991. ¹H NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3H), 6.83 (td, J = 9.0 Hz, 2.1 Hz, 2H), 7.18 (td, J = 9.0 Hz, 2.1 Hz, 2H), 7.28–7.39 (m, 5H), 7.70 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 8.56 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.66 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.62, 114.40, 122.90, 123.04 (quint, J = 5.0 Hz), 126.67, 126.87, 128.50, 126.68, 129.00, 130.55, 134.27 (quint, J = 3.8 Hz), 140.93, 148.38, 159.28 (quint, J = 32.5 Hz), 160.30, 168.28 (quint, J = 31.3 Hz). ATR-FTIR (KBr): ν = 3066, 1608, 1513, 1444, 1253, 1091, 773, 694 cm⁻¹.
5-bromo-2-(tetrafluoro-1-hexyl-5-phenyl-1H-1,2,3-triazol-4-yl)-λ⁶-sulfaneyl)pyridine (5u-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5u-A as white solid. mp: 97–98 °C; HRMS (ESI⁺): m/z calcd for C₁₉H₁₃NaF₄NaSBr [M+Na⁺]: 515.0504 found: 515.0505. ¹H NMR (300 MHz, CDCl₃): δ = 0.83 (t, J = 6.6 Hz, 3H), 1.15–1.26 (m, 6H), 1.71–1.80 (m, 2H), 4.09 (t, J = 7.5 Hz, 2H), 7.34–7.37 (m, 2H), 7.47–7.51 (m, 3H), 7.66 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.7 Hz, 1H), 8.52 (d, J = 2.4 Hz, 1H), 159.07 (quint, J = 30 Hz), 168.33 (quint, J = 32 Hz), 140.87, 141.15, 148.09 (m), 122.70, 128.79, 130.15 (d, J = 2.5 Hz), 133.76 (quint, J = 5.0 Hz), 140.88, 148.33, 159.08 (quint, J = 32.5 Hz), 168.33 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3058, 2931, 1556, 1448, 1095, 771, 696 cm⁻¹.

Total isolated yield of 5u is 67% (165 mg).

5-bromo-2-(tetrafluoro-1-hexyl-4-phenyl-1H-1,2,3-triazol-5-yl)-λ⁶-sulfaneyl)pyridine (5u-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5u-B as yellow oil. HRMS (ESI⁺): m/z calcd for C₁₉H₁₃NaF₄NaSBr [M+Na⁺]: 515.0504 found: 515.0511. ¹H NMR (300 MHz, CDCl₃): δ = 0.83 (t, J = 6.6 Hz, 3H), 1.19–1.26 (m, 6H), 1.71–1.78 (m, 2H), 4.09 (t, J = 7.5 Hz, 2H), 7.34–7.37 (m, 2H), 7.46–7.51 (m, 3H), 7.67 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.7 Hz, 1H), 8.52 (d, J = 2.1 Hz, 1H), 19F NMR (282 MHz, CDCl₃): δ = 66.87 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 14.22, 22.75, 26.89, 29.22, 30.52, 31.87, 52.86, 122.65–122.70 (m), 123.48, 127.96, 128.83, 130.20, 131.34, 141.15, 148.09–149.16 (m), 148.58, 167.77 (quint, J = 30.0 Hz). ATR-FTIR (NaCl): ν = 3055, 2927, 1558, 1448, 1093, 777, 690 cm⁻¹.

Total isolated yield of 5u is 67% (165 mg).

5-bromo-2-(tetrafluoro-1-octyl-5-phenyl-1H-1,2,3-triazol-4-yl)-λ⁶-sulfaneyl)pyridine (5v-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5v-A as white solid. HRMS (ESI⁺): m/z calcd for C₂₁H₂₅NaS₄NaSBr [M+Na⁺]: 543.0817 found: 543.0817. ¹H NMR (300 MHz, CDCl₃): δ = 0.86 (t, J = 6.3 Hz, 3H), 1.19–1.26 (m, 10H), 1.76 (t, J = 6.0 Hz, 2H), 4.09 (t, J = 7.2 Hz, 2H), 7.34–7.37 (m, 2H), 7.46–7.51 (m, 3H), 7.67 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 2.4 Hz, 1H); ¹³F NMR (282 MHz, CDCl₃): δ = 61.31 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 14.18, 22.68, 26.39, 28.84, 29.00, 29.97, 31.75, 49.22, 122.80, 123.01 (quint, J = 3.8 Hz), 126.72, 128.78, 130.13, 130.14, 133.75 (quint, J = 3.8 Hz), 140.87, 148.31, 159.07 (quint, J = 32.5 Hz), 168.33 (quint, J = 32.3 Hz). ATR-FTIR (KBr): ν = 3060, 2933, 1563, 1481, 1452, 1361, 1072, 784, 629 cm⁻¹.
5-bromo-2-(tetrafluoro(1-octyl-4-phenyl-1H-1,2,3-triazol-5-yl)-λ⁵-sulfaneyl)pyridine (5v-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5v-B as yellow oil. mp: 90–91 °C; HRMS (ESI): m/z calcd for C₉₁H₇₇Na₄F₆NaBr [M+Na]⁺: 543.0817 found: 543.0809. ¹H NMR (300 MHz, CDCl₃): δ = 0.88 (t, J = 6.6 Hz, 3H), 1.19–1.49 (m, 10H), 2.04–2.17 (m, 2H), 4.68 (t, J = 7.8 Hz, 2H), 7.40–7.43 (m, 3H), 7.52–7.55 (m, 2H), 7.58 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 8.58 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 66.88 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 14.22, 22.75, 26.89, 29.22, 30.52, 31.87, 52.86, 122.65–122.70 (m), 123.48, 127.27, 127.96, 128.83, 130.21, 131.34, 141.15, 144.02, 148.09–149.13 (m), 148.58, 167.77 (quint, J = 30.0 Hz). ATR-FTIR (NaCl): ν = 3062, 2945, 1558, 1448, 1359, 1093, 777, 692 cm⁻¹.

Total isolated yield of 5v is 66% (172 mg).

5-bromo-2-((1-cyclohexyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁵-sulfaneyl)pyridine (5w-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5w-A as white solid. mp: 90–91 °C; HRMS (ESI): m/z calcd for C₉₁H₇₇Na₄F₆NaBr [M+Na]⁺: 513.0348 found: 513.0354. ¹H NMR (300 MHz, CDCl₃): δ = 1.11–1.34 (m, 3H), 1.63–1.72 (m, 1H), 1.83–2.16 (m, 6H), 3.75–3.86 (m, 1H), 7.32–7.35 (m, 2H), 7.48–7.51 (m, 3H), 7.66 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.47 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 24.92, 25.44, 33.23, 59.16, 122.78, 123.05 (quint, J = 3.8 Hz), 126.96, 128.80, 130.11, 130.18, 133.11 (quint, J = 5.0 Hz), 140.85, 148.33, 158.90 (quint, J = 31.3 Hz), 168.44 (quint, J = 31.3 Hz). ATR-FTIR (KBr): ν = 3072, 2940, 1554, 1446, 1355, 1093, 777, 700 cm⁻¹.

5-bromo-2-((1-cyclohexyl-4-phenyl-1H-1,2,3-triazol-5-yl)triazolo-λ⁵-sulfaneyl)pyridine (5w-B)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5w-B as white solid. mp: 116–117 °C; HRMS (ESI): m/z calcd for C₉₁H₇₁Na₄F₆NaBr [M+Na]⁺: 513.0348 found: 513.0346. ¹H NMR (300 MHz, CDCl₃): δ = 1.34–1.47 (m, 3H), 1.72–1.78 (m, 1H), 1.98 (d, J = 12.0 Hz, 2H), 2.13–2.23 (m, 4H), 4.85–4.95 (m, 1H), 7.39–7.42 (m, 2H), 7.50–7.53 (m, 2H), 7.59 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 2.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 66.97 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 25.21, 25.96, 33.82, 62.82, 122.71, 123.45, 127.89, 128.76, 130.33, 131.46, 141.13, 143.32, 148.05 (quint, J = 32.5 Hz), 148.55, 167.91 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3062, 2942, 1565, 1475, 1450, 1371, 1095, 777, 700 cm⁻¹.

Total isolated yield of 5w is 52% (128 mg).
2-((1-((3s,5s,7s)-adamantan-1-yl)-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁵-sulfaneyl)-5-bromopyridine (5x-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (n-Hexane/AcOEt, 4/1) to get pure 5x-A as white solid in 37% yield (100 mg). mp: 170–171 °C; HRMS (ESI⁺): m/z calcld for C₂₉H₂₃N₅NaSBrF₄ [M+Na]⁺: 715.1478 found: 715.1479. ¹H NMR (300 MHz, CDCl₃): δ = 1.53–1.70 (m, 6H), 2.09 (brs, 3H), 2.16 (s, 6H), 7.34–7.49 (m, 5H), 7.61 (d, J = 8.7 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 2.1 Hz, 1H), 19F NMR (282 MHz, CDCl₃): δ = 61.27 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 29.73, 35.68, 42.61, 66.52, 122.65 123.00 (quint, J = 3.8 Hz), 127.82, 128.47, 129.79, 131.50, 133.13–133.18 (m), 140.76, 148.76, 160.68 (quint, J = 30.0 Hz), 168.45 (quint, J = 31.3 Hz). ATR-FTIR (KBr): ν = 3054, 2937, 1552, 1477, 1444, 1093, 779, 698 cm⁻¹.

2-((4-((5-bromopyridin-2-yl)tetrafluoro-λ⁵-sulfaneyl)-5-phenyl-1H-1,2,3-triazol-1-yl)(6-methoxyquinolin-4-yl)methyl)-5-vinylquinuclidine (5y-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 2/3) to isolate pure 5y-A as white solid. mp: 193–194 °C; HRMS (ESI⁺): m/z calcld for C₃₃H₂₄N₇O₂SBr [M+Na]⁺: 715.1478 found: 715.1479. ¹H NMR (300 MHz, (CD₃)₂CO): δ = 0.76 (t, J = 9.9 Hz, 1H), 1.52–1.61 (m, 4H), 2.29 (brs, 1H), 2.73–2.83 (m, 3H), 3.09–3.17 (m, 2H), 3.77 (s, 3H), 4.25 (brs, 1H), 4.97–5.08 (m, 2H), 5.92–6.03 (m, 1H), 6.94 (brs, 2H), 7.40 (dd, J = 9.3 Hz, 2.4 Hz, 3H), 7.60–7.62 (m, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.99 (d, J = 9.3 Hz, 1H), 8.21 (d, J = 8.7 Hz, 1H), 8.56 (d, J = 2.4 Hz, 1H), 8.73 (brs, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.35 (s, 4F), ¹³C NMR (125 MHz, (CD₃)₂CO): δ = 26.19, 28.44, 28.60, 40.52, 42.00, 55.79, 56.27, 100.90, 114.70, 121.98, 122.75, 123.43, 123.75 (quint, J = 5.0 Hz), 127.36, 128.09, 128.68, 129.47, 131.10, 131.51, 131.67, 132.97, 135.30, 139.82, 142.25, 142.97, 145.66, 148.95, 159.08, 159.66 (quint, J = 35.0 Hz), 169.16 (quint, J = 31.3 Hz). ATR-FTIR (KBr): ν = 3062, 2946, 1508, 1475, 1446, 1241, 1091, 777, 696 cm⁻¹.

2-((5-((5-bromopyridin-2-yl)tetrafluoro-λ⁵-sulfaneyl)-4-phenyl-1H-1,2,3-triazol-1-yl)(6-methoxyquinolin-4-yl)methyl)-5-vinylquinuclidine (5y-B)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 2/3) to isolate pure 5y-B as white solid. mp: 172–173 °C; HRMS (ESI⁺): m/z calcld for C₃₃H₂₄N₇O₂SBr [M+Na]⁺: 715.1451. ¹H NMR (300 MHz, CDCl₃): δ = 0.94–1.02 (m, 1H), 1.25–1.38 (m, 1H), 1.60–1.72 (m, 4H), 2.27 (brs, 1H), 2.83–2.96 (m, 2H), 3.12–3.20 (m, 1H), 3.26–3.37 (m, 1H), 4.02 (s, 3H), 4.44–4.54 (m, 1H), 4.98–5.06 (m, 2H), 5.79–5.91 (m, 1H), 7.04 (d, J = 9.9 Hz, 1H), 7.38–7.41 (m, 5H), 7.53–7.61 (m, 2H), 7.88–7.94 (m, 2H), 8.05 (d, J = 9.3 Hz, 1H), 8.51 (d, J = 2.1 Hz, 1H), 8.80 (d, J = 4.5 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.96 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 25.32, 37.75, 28.39, 39.72, 41.38, 55.22, 55.55, 60.58, 61.05, 101.13, 114.80, 120.63, 122.12, 122.56, 123.48, 127.81, 127.87,
Total isolated yield of 5y is 66% (236 mg).

3-(4-((5-bromopyridin-2-yl)tetrafluoro-\(\lambda^6\)-sulfaneyl)-5-phenyl-1H-1,2,3-triazol-1-yl)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (5z-A)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5z-A as white solid. mp: 108–109 °C; HRMS (ESI⁺): m/z calcd for \(\text{C}_{32}\text{H}_{33}\text{N}_{2}\text{ONaSBrF}_{4}\) [M+Na⁺]: 703.1705 found: 703.1700. \(^1\)H NMR (300 MHz, CDCl₃): \(\delta = 0.81\) (s, 3H), 0.86 (s, 3H), 0.95–1.20 (m, 3H), 1.25–1.36 (m, 4H), 1.42–1.59 (m, 4H), 1.65–1.82 (m, 4H), 1.87–2.17 (m, 6H), 2.39–2.48 (m, 1H), 4.31 (s, 1H), 7.30–7.33 (m, 2H), 7.46 (m, 3H), 7.66 (d, \(J = 8.7\) Hz, 1H), 7.93 (d, \(J = 8.54\) (d, \(J = 2.4\) Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl₃): \(\delta = 61.40\) (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl₃): \(\delta = 0.04\), 9.62, 11.93, 18.11, 19.87, 24.35, 26.05, 28.54, 29.58, 31.22 (d, \(J = 6.3\) Hz), 33.09, 33.73, 33.98, 37.17, 45.90, 49.46, 52.00, 52.35, 114.53, 120.77, 121.03 (quint, \(J = 3.8\) Hz), 125.27, 126.78, 128.00, 128.20, 131.38 (quint, \(J = 3.8\) Hz), 138.83, 146.30, 157.03 (quint, \(J = 31.3\) Hz), 166.39 (quint, \(J = 31.3\) Hz). ATR-FTIR (KBr): \(\nu = 3064, 2937, 1735, 1548, 1473, 1446, 1099, 779, 698\) cm⁻¹.

3-(5-((5-bromopyridin-2-yl)tetrafluoro-\(\lambda^6\)-sulfaneyl)-4-phenyl-1H-1,2,3-triazol-1-yl)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (5z-B)

Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 5z-B as white solid. mp: 127–128 °C; HRMS (ESI⁺): m/z calcd for \(\text{C}_{32}\text{H}_{33}\text{N}_{2}\text{ONaSBrF}_{4}\) [M+Na⁺]: 703.1705 found: 703.1696. \(^1\)H NMR (300 MHz, CDCl₃): \(\delta = 0.88\) (s, 3H), 0.90 (s, 3H), 1.05–1.15 (m, 3H), 1.21–1.38 (m, 5H), 1.43–1.60 (m, 2H), 1.72–1.84 (m, 4H), 1.87–1.99 (m, 2H), 2.03–2.23 (m, 5H), 2.40–2.49 (m, 1H), 5.41 (s, 1H), 7.40–7.42 (m, 3H), 7.51–7.56 (m, 3H), 7.96 (d, \(J = 7.2\) Hz, 1H), \(^{19}\)F NMR (282 MHz, CDCl₃): \(\delta = 67.38\) (s, 4F), \(^{13}\)C NMR (125 MHz, CDCl₃): \(\delta = 11.72, 13.99, 20.17, 21.91, 26.79, 28.10, 30.62, 31.65, 33.33, 33.44, 35.21, 35.65, 36.03, 39.05, 47.96, 51.54, 54.06, 56.67, 122.67, 123.43, 127.89, 128.74, 130.29, 131.66, 141.14, 143.40, 148.25–148.78 (m), 148.55, 167.71–168.18 (m). ATR-FTIR (KBr): \(\nu = 3058, 2935, 1737, 1560, 1473, 1448, 1093, 775, 684\) cm⁻¹.

Total isolated yield of 5z is 37% (126 mg).
1-benzyl-4-((4-bromophenyl)tetrafluoro-ω-sulfaneyl)-5-phenyl-1H-1,2,3-triazole (7a-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 7a-A as white solid. mp: 143–145 °C; HRMS (ESI+): m/z calcd for C_{21}H_{16}N_{3}F_{4}NaSBr [M+Na]+: 520.0082 found: 521.0073. 1H NMR (300 MHz, CDCl3): δ = 5.30 (s, 2H), 6.94–6.96 (m, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.20–7.25 (m, 3H), 7.37–7.50 (m, 5H), 7.58 (d, J = 9.0 Hz, 2H), 19F NMR (282 MHz, CDCl3): δ = 71.25 (s, 4F), 13C NMR (125 MHz, CDCl3): δ = 53.08, 126.40, 126.71, 127.77 (quint, J = 3.8 Hz), 127.96, 128.52, 128.59, 128.83, 130.09, 130.25, 131.32, 131.37, 136.60 (quint, J = 3.8 Hz), 134.21, 137.54, 158.63 (quint, J = 25 Hz), 160.46 (quint, J = 33.8 Hz). ATR-FTIR (KBr): ν = 3060, 1574, 1477, 1448, 1325, 1070, 762, 663 cm⁻¹.

Total isolated yield of 7b is 56% (140 mg).

1-benzyl-5-((4-bromophenyl)tetrafluoro-ω-sulfaneyl)-4-phenyl-1H-1,2,3-triazole (7a-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 4/1) to isolate pure 7a-B as white solid. mp: 132–133 °C; HRMS (ESI+): m/z calcd for C_{21}H_{16}N_{3}F_{4}NaSBr [M+Na]+: 520.0082 found: 521.0095. 1H NMR (300 MHz, CDCl3): δ = 5.90 (s, 2H), 7.32–7.43 (m, 8H), 7.47–7.57 (m, 6H), 19F NMR (282 MHz, CDCl3): δ = 55.78, 125.41, 127.52, (t, J = 5 Hz), 127.68, 128.01, 128.38, 128.84, 128.90, 130.19, 131.28, 131.66, 135.21, 144.03, 149.78 (quint, J = 37.5 Hz), 158.02 (quint, J = 23.8 Hz). ATR-FTIR (KBr): ν = 3064, 1573, 1475, 1454, 1329, 1068, 781, 756, 656 cm⁻¹.

1-benzyl-5-phenyl-4-(tetrafluoro(phenyl)-ω-sulfaneyl)-1H-1,2,3-triazole (7b-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 85/15) to isolate pure 7b-A as white solid. mp: 137–138 °C; HRMS (ESI+): m/z calcd for C_{21}H_{16}N_{3}F_{4}NaCl [M+Na]+: 476.0587 found: 476.0589. 1H NMR (300 MHz, CDCl3): δ = 5.30 (s, 2H), 6.94–6.96 (m, 2H), 7.14 (d, J = 7.2 Hz, 2H), 7.21–7.31 (m, 5H), 7.37–7.51 (m, 3H), 7.66 (d, J = 9.0 Hz, 2H), 19F NMR (282 MHz, CDCl3): δ = 72.38 (s, 4F), 13C NMR (125 MHz, CDCl3): δ = 53.08, 126.49, 127.54 (quint, J = 5.0 Hz), 127.98, 128.32, 128.54, 128.61, 128.85, 130.10, 130.27, 133.62 (quint, J = 5.0 Hz), 134.22, 136.34, 158.06 (quint, J = 25.0 Hz), 160.51 (quint, J = 33.8 Hz). ATR-FTIR (KBr): ν = 3037, 1531, 1477, 1454, 1099, 795, 754 cm⁻¹.
1-benzyl-4-phenyl-5-(tetrafluoro(phenyl)-λ⁶-sulfaneyl)-1H-1,2,3-triazole (7b-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 85/15) to isolate pure 7b-B as white solid. mp: 129–132 °C; HRMS (ESI⁺): m/z calcd for C₂₁H₁₅N₃F₄NaS [M+Na⁺]: 476.0587 found: 476.0590. "H NMR (300 MHz, CDCl₃): δ = 5.91 (s, 2H), 7.34–7.43 (m, 8H), 7.53–7.55 (m, 2H), 7.88 (d, J = 9.3 Hz, 2H), 8.23 (d, J = 9.0 Hz, 2H), 133.85 (quint, J = 3.8 Hz), 134.11, 148.31, 159.83 (quint, J = 5.0 Hz), 127.57, 127.63, 128.38, 128.64, 128.91, 130.19, 135.22, 144.02, 149.83 (quint, J = 36.3 Hz), 157.43 (quint, J = 22.5 Hz). ATR-FTIR (KBr): ν = 3035, 1540, 1477, 1455, 1097, 827, 767 cm⁻¹.

1-benzyl-5-phenyl-4-(tetrafluoro(4-nitrophenyl)-λ⁶-sulfaneyl)-1H-1,2,3-triazole (7c-A)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 85/15) to isolate pure 7c-A as white solid. mp: 140–142 °C; HRMS (ESI⁺): m/z calcd for C₂₁H₁₅N₃O₂F₄NaS [M+Na⁺]: 487.0828 found: 487.0820. "H NMR (300 MHz, CDCl₃): δ = 5.32 (s, 2H), 6.97 (d, J = 6.0 Hz, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.26 (d, J = 6.6 Hz, 3H), 7.40–7.54, 7.91 (d, J = 9.0 Hz, 2H), 8.20 (d, J = 8.7 Hz, 2H), 55.78, 127.35 (t, J = 5.0 Hz), 127.68, 128.01, 128.38, 128.64, 128.91, 131.28, 135.22, 144.02, 149.83 (quint, J = 36.3 Hz), 157.43 (quint, J = 22.5 Hz). ATR-FTIR (KBr): ν = 3035, 1540, 1477, 1455, 1097, 827, 767 cm⁻¹.

1-benzyl-4-phenyl-5-(tetrafluoro(4-nitrophenyl)-λ⁶-sulfaneyl)-1H-1,2,3-triazole (7c-B)

Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regiosiomer by column chromatography (n-Hexane/AcOEt, 85/15) to isolate pure 7c-B as white solid. mp: 121–122 °C; HRMS (ESI⁺): m/z calcd for C₂₁H₁₅N₃O₂F₄NaS [M+Na⁺]: 487.0828 found: 487.0832. "H NMR (300 MHz, CDCl₃): δ = 5.91 (s, 2H), 7.34–7.43 (m, 8H), 7.53–7.55 (m, 2H), 7.88 (d, J = 9.3 Hz, 2H), 8.22 (d, J = 9.0 Hz, 2H), 133.85 (quint, J = 3.8 Hz), 134.11, 148.31, 159.83 (quint, J = 32.5 Hz), 163.55 (quint, J = 26.3 Hz), ATR-FTIR (KBr): ν = 3068, 1612, 1529, 1481, 1450, 1089, 757 cm⁻¹.
2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁵-sulfaneyl)-5-(4-phenoxyphenyl)pyridine (8a)

Prepared according to modified literature procedure.⁶ Pd(PPh₃)₄ (3 mg, 3 mol%) was added to a solution of 5a (50 mg, 0.1 mmol) in benzene (0.2 mL), followed by an 2M aqueous solution of Na₂CO₃ (0.1 mL), and the reaction was stirred at room temperature. A solution of (4-phenoxyphenyl)boronic acid (24 mg) in ethanol (0.1 mL) was added and the reaction mixture was heated to 80 °C and refluxed for 22 h. After the designated time, the reaction was allowed to cool to room temperature and water was added. It was extracted with AcOEt and the organic layer was dried over Na₂SO₄. The solvent was concentrated in vacuo to give crude product which was purified by silica gel column chromatography (n-Hexane/AcOEt, 7/3) to give the desired product 6a as white solid in 54% yield (32 mg). mp: 149–150 °C; HRMS (ESI⁺): m/z calc for C₂₀H₁₈NaO₆F₄NaS [M+Na⁺]: 611.1505 found: 611.1502. ¹H NMR (300 MHz, CDCl₃): δ 5.32 (s, 2H), 6.97 (dd, J = 6.9 Hz, 1.5 Hz, 2H), 7.18 (d, J = 6.9 Hz, 2H), 7.22–7.29 (m, 3H), 7.30–7.42 (m, 4H), 7.44–7.50 (m, 3H), 7.57 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.87 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.7 Hz, 1H), 8.75 (d, J = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 60.82 (s, 4F). ¹³C NMR (125 MHz, CDCl₃): δ = 53.11, 112.25, 117.87, 119.87, 121.86 (quint, J = 3.8 Hz), 123.82, 125.43, 125.55, 126.47, 128.02, 128.6 (d, J = 2.5 Hz), 128.87, 130.12, 130.34, 130.83, 133.95–134.01 (m), 134.29, 136.65, 142.66, 145.47, 155.90, 159.65 (quint, J = 30.2 Hz), 168.78 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3064, 1558, 1490, 1461, 1245, 773, 701 cm⁻¹.

5-(benzofuran-3-yl)-2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro-λ⁵-sulfaneyl)pyridine (8b)

Prepared according to modified literature procedure.⁷ In a flame dried schlenk tube in argon atmosphere, 5a (100 mg, 0.2 mmol), PdCl₂(PPh₃)₂ (7 mg, 5 mol%), K₂PO₄ (127 mg, 0.6 mmol), benzofuran-3-ylboronic acid (78 mg, 0.48 mmol) and toluene (2.4 mL) was added. The reaction mixture was evacuated and backfilled with argon and allowed to stir at 100 °C for 48 h. After the designated time, the reaction was allowed to cool to room temperature and diluted with water. It was extracted with CH₂Cl₂ and the organic layer was dried over Na₂SO₄. The solvent was concentrated in vacuo to give crude product which was purified by silica gel column chromatography (n-Hexane/AcOEt, 7/3) to give the desired product 6b as light yellow solid in 46% yield (50 mg). mp: 143–144 °C; HRMS (ESI⁺): m/z calc for C₂₀H₁₈NaO₆F₄Sulfaneyl) [M+Na⁺]: 559.1192 found: 559.1184. ¹H NMR (300 MHz, CDCl₃): δ = 5.33 (s, 2H), 6.98 (dd, J = 6.0 Hz, 3.0 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 7.22–7.29 (m, 3H), 7.30–7.42 (m, 4H), 7.45–7.50 (m, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 9.0 Hz, 1H), 8.75 (d, J = 3.0 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 60.72 (s, 4F). ¹³C NMR (125 MHz, CDCl₃): δ = 53.11, 112.25, 117.87, 119.86, 121.86 (quint, J = 3.8 Hz), 123.82, 125.43, 125.55, 126.47, 128.02, 128.6 (d, J = 2.5 Hz), 128.87, 130.12, 130.34, 130.83, 133.95–134.01 (m), 134.29, 136.65, 142.66, 145.47, 155.90, 159.65 (quint, J = 32.5 Hz), 168.78 (quint, J = 30.0 Hz). ATR-FTIR (KBr): ν = 3127, 3046, 1565, 1477, 1452, 1222, 1095, 777, 701 cm⁻¹.
Reference:


X-ray crystal structure:

Fig. S1: Ortep diagram of 5m isomer A drawn at 50% probability. The hydrogen atoms have been omitted for clarity.

Fig. S2: Ortep diagram of 5m isomer B drawn at 50% probability. The hydrogen atoms have been omitted for clarity.
3b

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