

Electronic Supplementary Information

An eccentric rod-like linear connection of two heterocycles: Synthesis of pyridine *trans*-tetrafluoro- λ^6 -sulfanyl triazoles

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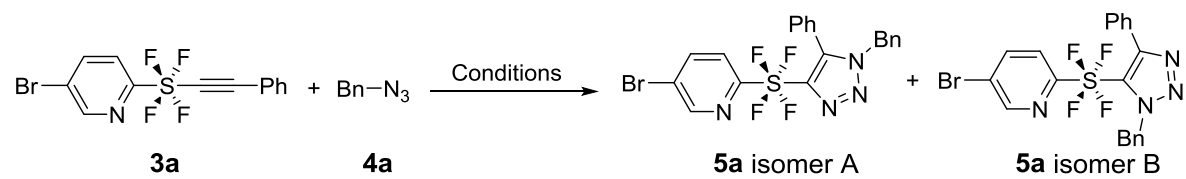
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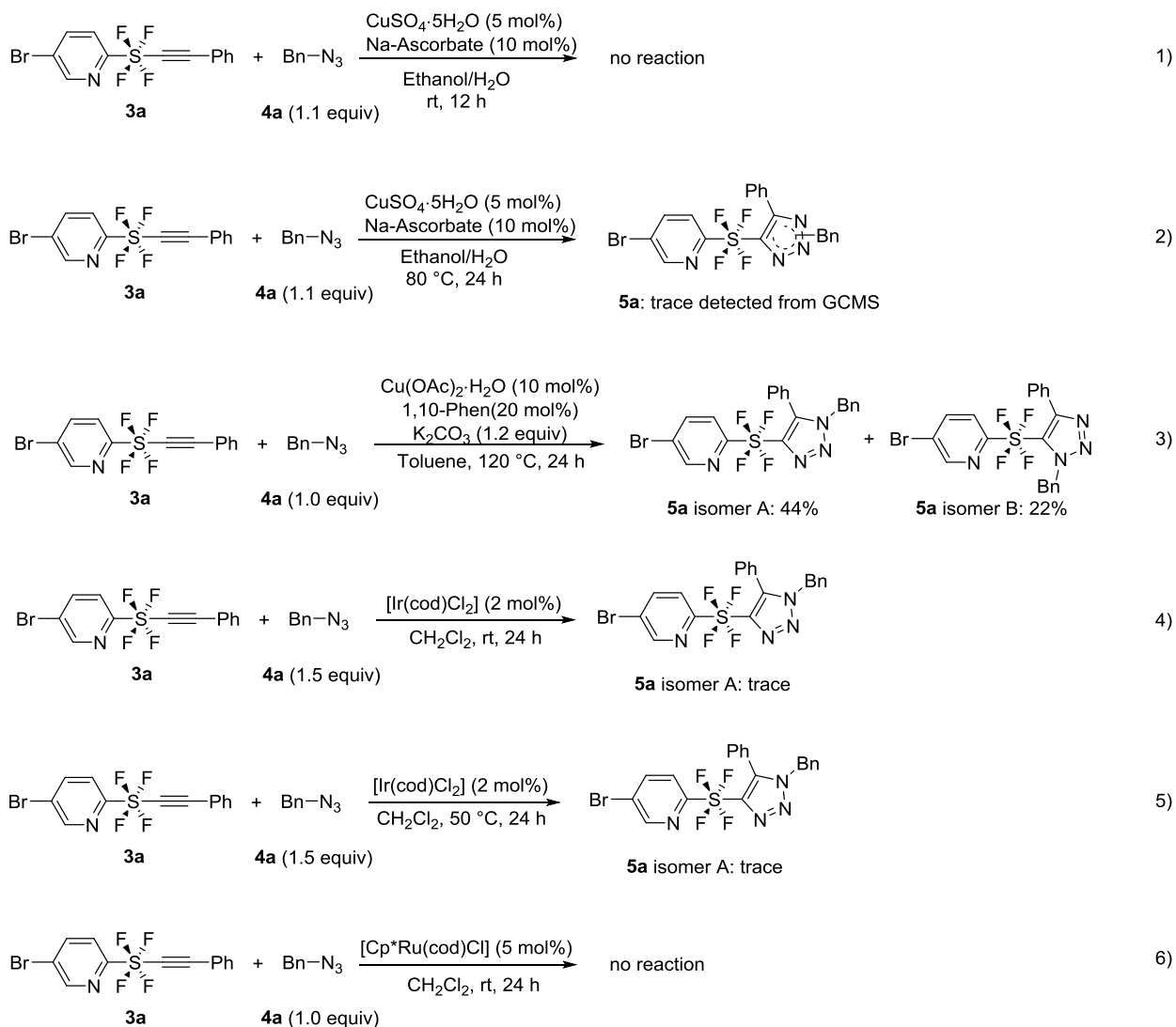
General information

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 through 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 ^1H NMR (300 MHz) and ^{19}F NMR (282 MHz) spectra were recorded for solution in CDCl_3 and $(\text{CD}_3)_2\text{CO}$ on a Varian Mercury 300. ^{13}C NMR (125 MHz) spectra for solution in CDCl_3 and $(\text{CD}_3)_2\text{CO}$ were recorded on a BRUKER 500 UltraShield^{TR}. Chemical shifts (δ) are expressed in ppm downfield from TMS ($\delta = 0.00$) for ^1H and C_6F_6 [$\delta = -162.2$ (CDCl_3) or -163.5 ($(\text{CD}_3)_2\text{CO}$)] as an internal standard ^{19}F NMR. For ^{13}C NMR, CDCl_3 ($\delta = 77.16$) or $(\text{CD}_3)_2\text{CO}$ ($\delta = 29.84$) 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.

Entry	Conditions ^a	Result
1	3a (2.0 equiv), 4a (1.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in benzene at 80 °C	Traces
2	3a (1.0 equiv), 4a (1.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in benzene at 80 °C	9%, ^b 1:1 ^c
3	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in benzene at 80 °C	19%, ^b 1:1 ^c
4	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in toluene at 80 °C	24%, ^b 1.5:1 ^c
5	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in dioxane at 80 °C	23%, ^b 1.5:1 ^c
6	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in DMF at 80 °C	17%, ^b 1.4:1 ^c
7	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in THF at 80 °C	19%, ^b 1.7:1 ^c
8	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (10 mol%) in toluene at 110 °C	32%, ^b 1.5:1 ^c
9	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (20 mol%) in toluene at 110 °C	10%, ^b 1.5:1 ^c
10	3a (1.0 equiv), 4a (3.0 equiv), Cp*Ru(PPh ₃) ₂ Cl ₂ (5 mol%) in toluene at 110 °C	56%, ^b 1.5:1 ^c
11	3a (1.0 equiv), 4a (3.0 equiv), in toluene at 110 °C	83%, ^b 2:1 ^c

^a Reactions were performed at 0.1 mmol scale at the given conditions for 24 h. ^b Total yield of **5a** from ¹⁹F NMR. ^c Ratio of the two regioisomers A and B.



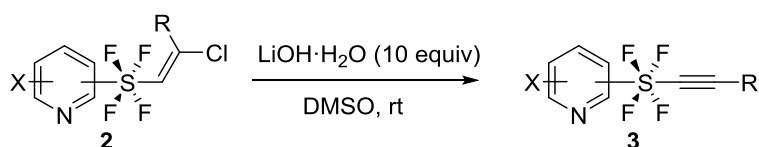
Scheme S1. Metal catalysed reactions.

The click reaction was also attempted under more metal catalysed conditions. Reaction 1 was performed under the typical Cu catalysed click reaction condition,¹ 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 3,² 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 catalysis³ 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,⁴ the reaction didn't proceed (reaction 7).

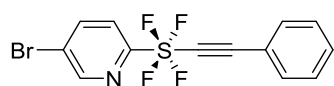
Concluding from these unfavourable results, we opted for the thermally induced click reaction.

Synthesis of the Pyridine-SF₄-alkyne **3**, General Procedure 1:



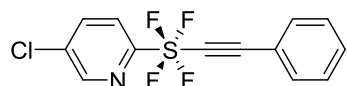
Prepared according to literature procedure.¹ Pyridine-SF₄-alkene **2** (1.0 equiv) was added to DMSO (0.3 M) in a round-bottom flask at room temperature, followed by Lithium hydroxide monohydrate (10.0 equiv) and allowed to stir at room temperature. The reaction progress was monitored by ¹⁹F NMR, and 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**)



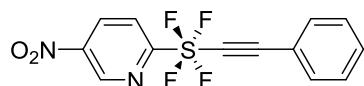
Prepared according to general procedure 1, by stirring **2a** (0.8 mmol) at rt for 24 h to obtain **3a** as white solid in 90% yield (262 mg). mp: 93–94 °C; HRMS (ESI⁺): *m/z* calcd for C₁₃H₈BrF₄NNaS [M+Na]⁺: 387.9395 found: 387.9390. ¹H NMR (300 MHz, CDCl₃): δ = 7.49–7.36 (m, 3H), 7.60 (d, *J* = 6.6 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 77.61 (s, 4F), ¹³C 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): ν = 3115, 3049, 2916, 2222, 1446, 1368, 1092, 1007, 869, 700 cm⁻¹.

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



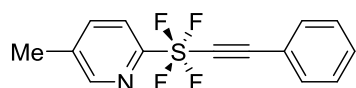
Prepared according to general procedure 1 by stirring **2b** (1.2 mmol) at rt for 24 h to obtain **3b** as white solid in 92% yield (354 mg). mp: 133–134 °C; HRMS (ESI⁺): *m/z* calcd for C₁₃H₈NF₄NaS [M+Na]⁺: 343.9900 found: 343.9887. ¹H NMR (300 MHz, CDCl₃): δ = 7.36–7.48 (m, 3H), 7.59 (d, *J* = 6.9 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 77.70 (s, 4F), ¹³C 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): ν = 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 (EI⁺): *m/z* calcd for C₁₃H₈N₂O₂F₄S [M]⁺: 332.0243 found: 332.0227. ¹H 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 77.45 (s, 4F), ¹³C 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): ν = 3060, 2917, 2219, 1604, 1565, 1535, 1488, 1450, 1355, 809, 755, 690 cm⁻¹.

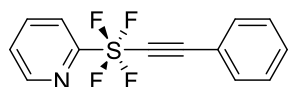
5-Methyl-2-(tetrafluoro(phenylethynyl)- λ^6 -sulfaneyl)pyridine (**3d**)



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 (ESI⁺): *m/z* calcd for C₁₄H₁₁NF₄NaS [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), ¹⁹F 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.

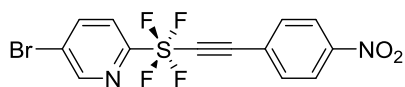
2-(tetrafluoro(phenylethynyl)- λ^6 -sulfaneyl)pyridine (**3e**)



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 (ESI⁺): *m/z* calcd for C₁₃H₉NF₄NaS [M+Na]⁺: 310.0290 found:

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.

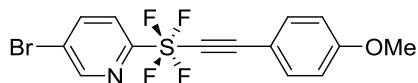
5-Bromo-2-(tetrafluoro((4-nitrophenyl)ethynyl)- λ^6 -sulfaneyl)pyridine (**3f**)



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 C₁₃H₇N₂O₂F₄SBr

[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.

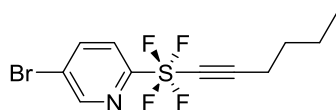
5-Bromo-2-(tetrafluoro((4-methoxyphenyl)ethynyl)- λ^6 -sulfaneyl)pyridine (**3g**)



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 (ESI⁺): *m/z* calcd for

C₁₄H₁₀NOF₄NaSBr [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.

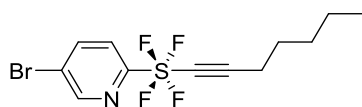
5-bromo-2-(((4-butylphenyl)ethynyl)tetrafluoro- λ^6 -sulfaneyl)pyridine (3h)



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* calcd for C₁₁H₁₂NF₄NaSBr [M+Na]⁺: 367.9708

found: 367.9709. ¹H NMR (300 MHz, CDCl₃): 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, CDCl₃): δ = 77.61 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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): ν = 3052, 2960, 2235, 1552, 1448, 1091, 794, 690 cm⁻¹.

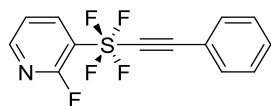
5-bromo-2-(tetrafluoro((4-pentylphenyl)ethynyl)- λ^6 -sulfaneyl)pyridine (3i)



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* calcd for C₁₂H₁₄NF₄NaSBr [M+Na]⁺:

381.9864 found: 381.9859. ¹H NMR (300 MHz, CDCl₃): 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, CDCl₃): δ = 77.65 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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): ν = 3052, 2954, 2235, 1567, 1452, 1091, 781, 701 cm⁻¹.

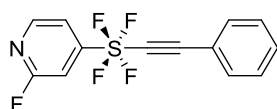
2-fluoro-3-(tetrafluoro(phenylethynyl)- λ^6 -sulfaneyl)pyridine (3j)



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* calcd for C₁₃H₉NF₅S [M+H]⁺: 306.0376 found: 306.0382. ¹H

NMR (300 MHz, CDCl₃): 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, CDCl₃): δ = -60.29–-59.95 (m, 1F), 91.65 (d, *J* = 22.6 Hz, 4F), ¹³C NMR (125 MHz, CDCl₃): 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): ν = 3070, 2223, 1583, 1490, 1442, 1276, 1240, 1095, 788, 715 cm⁻¹.

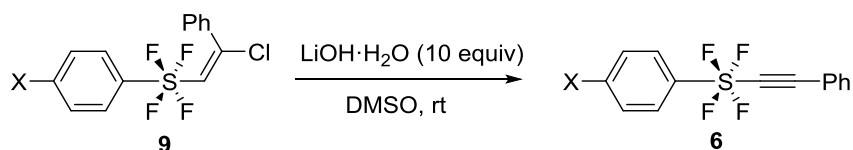
2-fluoro-4-(tetrafluoro(phenylethynyl)- λ^6 -sulfaneyl)pyridine (3k)



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* calcd for C₁₃H₉NF₅S [M+H]⁺: 306.0376 found: 306.0373. ¹H

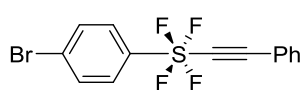
NMR (300 MHz, CDCl₃): δ = 7.31 (t, *J* = 2.1 Hz, 1H), 7.37–7.50 (m, 3H), 7.54–7.60 (m, 3H), 8.36 (d, *J* = 5.4 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = -64.67 (s, 1F), 86.04 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 74.63 (quint, *J* = 10.0 Hz), 93.73 (quint, *J* = 51.3 Hz), 107.50–108.00 (m), 118.25–118.37 (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): ν = 3029, 2227, 1596, 1575, 1477, 1444, 1228, 1101, 788, 750 cm⁻¹.

Synthesis of benzene-tetrafluoro(phenylethynyl)- λ^6 -sulfane (6)



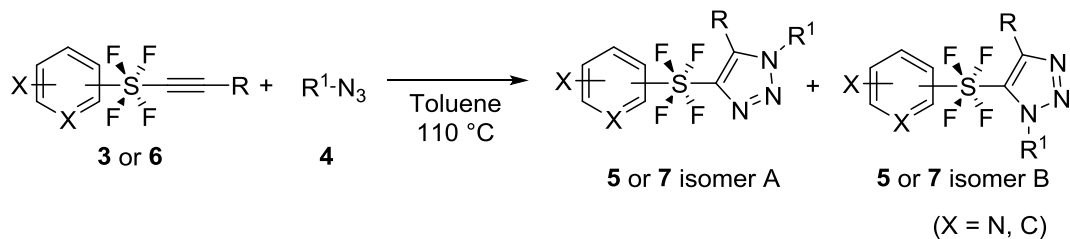
Alkyne **6b** and **6c** were prepared according to literature procedure.⁵ Alkyne **6a** was synthesized using a modified literature procedure.⁵

(4-bromophenyl)tetrafluoro(phenylethynyl)- λ^6 -sulfane (6a)



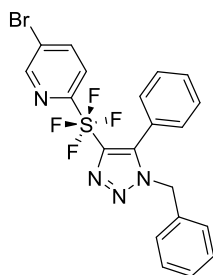
Benzene-SF₄-alkene **9a** (3.0 mmol) was added to DMSO (0.3 M) in a round-bottom flask at room temperature, followed by Lithium hydroxide monohydrate (10.0 equiv) and allowed to stir at room temperature. The reaction progress was monitored by ¹⁹F NMR, and after the ¹⁹F NMR indicated the complete conversion 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): ν = 3111, 2925, 2225, 1574, 1475, 1070, 752, 683 cm⁻¹.

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



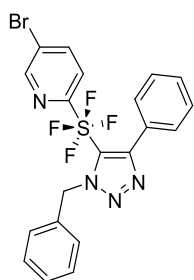
An oven dried test tube was charged with alkyne **3** or **6** (0.5 mmol), azide **4** (1.5 mmol) and toluene (2.5 mL) and allowed to stir at 110 °C for 24 h or unless mentioned otherwise. The reaction was allowed to cool to room temperature and the solvent was evaporated *in vacuo* to give the crude 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- λ^6 -sulfaneyl)-5-bromopyridine (5a-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, 4/1) to isolate pure **5a-A** as white solid. mp: 138–139 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₄NaSBr [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), ¹⁹F 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.

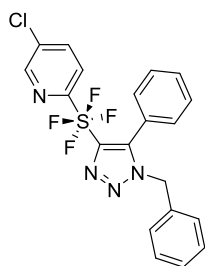
2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5a-B)



Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure **5b-B** as white solid. mp: 155–156 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₄NaSBr [M+Na]⁺: 521.0035 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, 128.84, 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.

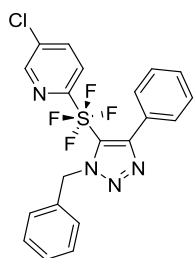
Total isolated yield of **5a** is 77% (192 mg).

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-chloropyridine (5b-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 **5b-A** as white solid. mp: 141–142 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₄NaSCL [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, 128.64, 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- λ^6 -sulfaneyl)-5-chloropyridine (5b-B)

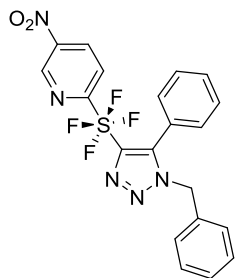


Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 7/3) to isolate pure **5b-B** as white solid. mp: 140–141 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₄NaSCL [M+Na]⁺: 477.0540 found: 477.0536. ¹H NMR (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,

CDCl₃): δ = 67.78 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.75, 122.25–122.31 (m), 127.72, 128.00, 128.37, 128.82, 128.92, 130.20, 131.15, 134.79, 135.11, 138.18, 144.36, 146.32, 148.64 (quint, J = 35.0 Hz), 166.98 (quint, J = 29.0 Hz), ATR-FTIR (KBr): ν = 3054, 2967, 1567, 1477, 1450, 1124, 1074, 781 cm⁻¹.

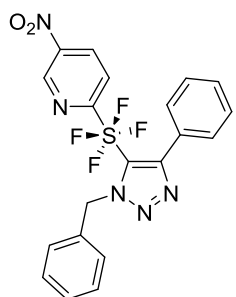
Total isolated yield of **5b** is 86% (195 mg).

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-nitropyridine (**5c-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, 4/1) to isolate pure **5c-A** as light brown solid. mp: 136–137 °C; HRMS (ESI⁺): m/z calcd for C₂₀H₁₅N₅O₂F₄NaS [M+Na]⁺: 488.0780 found: 488.0781. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.23 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 52.14, 122.89–122.96 (m), 123.01, 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 (m), 167.83–168.31 (m). ATR-FTIR (KBr): ν = 3050, 1606, 1567, 1535, 1482, 1455, 1359, 1076, 779, 763 cm⁻¹.

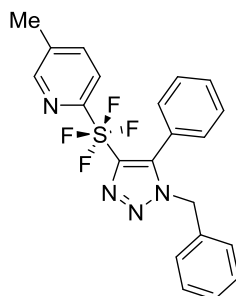
2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-nitropyridine (**5c-B**)



Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure **5c-B** as light brown solid. mp: 149–150 °C; HRMS (ESI⁺): m/z calcd for C₂₀H₁₅N₅O₂F₄NaS [M+Na]⁺: 488.0780 found: 488.0794. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.49 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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, 147.97, 148.48–149.04 (m), 148.69, 167.16–167.61 (m). ATR-FTIR (KBr): ν = 3035, 1602, 1569, 1533, 1494, 1473, 1448, 1357, 1074, 806, 763 cm⁻¹.

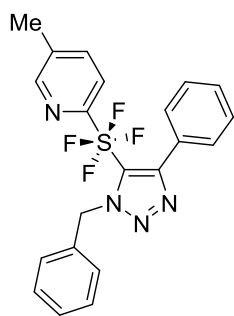
Total isolated yield of **5c** is 92% (214 mg).

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-methylpyridine (**5d-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 **5d-A** as white solid. mp: 130–131 °C; HRMS (ESI⁺): m/z calcd for C₂₁H₁₈N₄F₄NaS [M+Na]⁺: 457.1086 found: 457.1109. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 60.62 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 17.10, 52.05, 119.93–120.03 (m), 125.52, 126.98, 127.54, 127.57, 127.83, 129.03, 129.33, 132.86–132.92 (m), 133.31, 135.22, 137.72, 146.37, 158.78 (quint, J = 32.5 Hz), 166.95 (quint, J = 28.8 Hz). ATR-FTIR (KBr): ν = 3056, 2964, 2933, 1577, 1461, 1376, 1074, 769, 732 cm⁻¹.

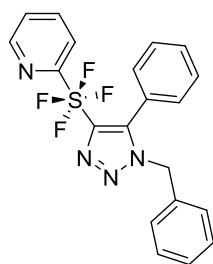
2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-methylpyridine (5d-B)



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 **5d-B** as white solid. mp: 118–119 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈N₄F₄NaS [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.

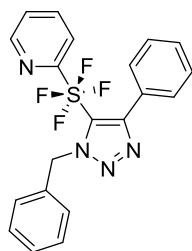
Total isolated yield of **5d** is 60% (130 mg).

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)pyridine (5e-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 **5e-A** as light brown solid. mp: 141–142 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₆N₄F₄NaS [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.

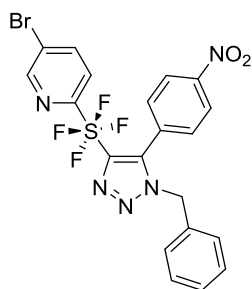
2-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)pyridine (5e-B):



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 **5e-B** as light brown solid. mp: 131–132 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₆N₄F₄NaS [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.

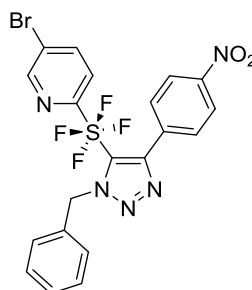
Total isolated yield of **5e** is 71% (149 mg).

2-((1-benzyl-5-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5f-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, 3/1) to isolate pure **5f-A** as white solid. mp: 176–179 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₅O₂F₄NaSBr [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.

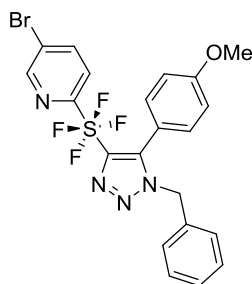
2-((1-benzyl-4-(4-nitrophenyl)-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5f-B)



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, 3/1) to isolate pure **5f-B** as white solid. mp: 179–180 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₅O₂F₄NaSBr [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* = 8.7 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.

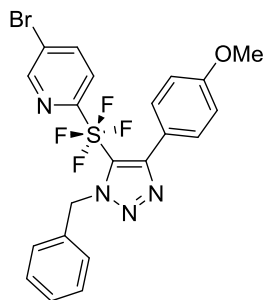
Total isolated yield of **5f** is 67% (182 mg).

2-((1-benzyl-5-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5g-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 **5g-A** as white solid. mp: 147–148 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇N₄O₂F₄NaSBr [M+Na]⁺: 551.0140 found: 551.0139. 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.

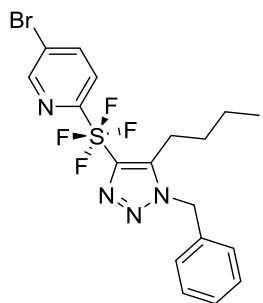
2-((1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5g-B)



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 **5g-B** as white solid. mp: 149–150 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇N₄OF₄NaSBr [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, 128.81, 131.43, 135.18, 141.12, 144.14, 148.46 (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.

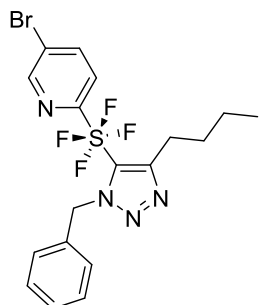
Total isolated yield of **5g** is 70% (185 mg).

2-((1-benzyl-5-butyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5h-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, 4/1) to isolate pure **5h-A** as white solid. mp: 127–128 °C; HRMS (ESI⁺): *m/z* calcd for C₁₈H₁₉N₄F₄NaSBr [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.

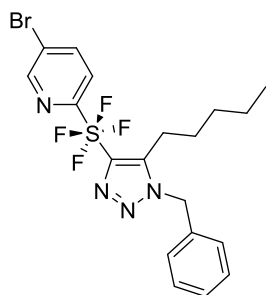
2-((1-benzyl-4-butyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5h-B)



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, 4/1) to isolate pure **5h-B** as white solid. mp: 67–68 °C; HRMS (ESI⁺): *m/z* calcd for C₁₈H₁₉N₄F₄NaSBr [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.

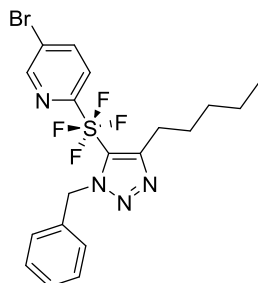
Total isolated yield of **5h** is 68% (163 mg).

2-((1-benzyl-5-pentyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5i-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, 4/1) to isolate pure **5i-A** as white solid. mp: 109–110 °C; HRMS (ESI⁺): *m/z* calcd for C₁₉H₂₁N₄F₄NaSBr [M+Na]⁺: 515.0504 found: 515.0516. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 59.57 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 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): ν = 3064, 2935, 1554, 1452, 1093, 765, 692 cm⁻¹.

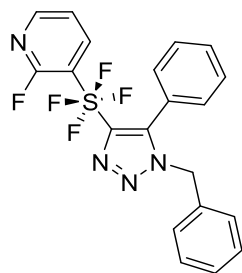
2-((1-benzyl-4-pentyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5i-B)



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, 4/1) to isolate pure **5i-B** as white solid. mp: 72–73 °C; HRMS (ESI⁺): *m/z* calcd for C₁₉H₂₁N₄F₄NaSBr [M+Na]⁺: 515.0504 found: 515.0515. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 65.00 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 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): ν = 3062, 2933, 1565, 1494, 1450, 1093, 779, 690 cm⁻¹.

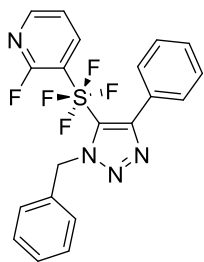
Total isolated yield of **5i** is 70% (173 mg).

3-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-2-fluoropyridine (5j-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 **5j-A** as white solid. mp: 152–153 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₅NaS [M+Na]⁺: 461.0835 found: 461.0837. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = -60.15 (quintd, *J* = 22.6 Hz, 8.5 Hz, 1F), 75.11 (d, *J* = 22.6 Hz, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 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): ν = 3031, 2929, 1587, 1573, 1496, 1438, 1280, 1232, 1076, 777, 694 cm⁻¹.

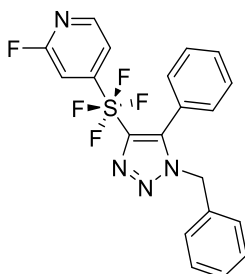
3-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-2-fluoropyridine (5j-B)



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 **5j-B** as white solid. mp: 157–158 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₅NaS [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 (quintd, *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): ν = 3035, 2923, 1590, 1438, 1284, 1228, 1093, 813, 730 cm⁻¹.

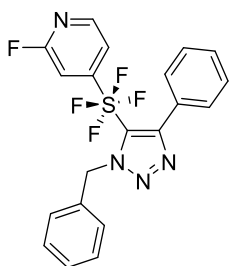
Total isolated yield of **5j** is 95% (208 mg).

4-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-2-fluoropyridine (5k-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, 4/1) to isolate pure **5k-A** as white solid. mp: 131–132 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₅NaS [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 = -65.11 (s, 1F), 69.64 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 53.19, 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 (dq, *J* = 27.5 Hz, 7.5 Hz). ATR-FTIR (KBr): ν = 3064, 1592, 1475, 1448, 1234, 1105, 786, 701 cm⁻¹.

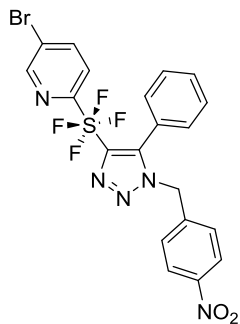
4-((1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)-2-fluoropyridine (5k-B)



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, 4/1) to isolate pure **5k-B** as white solid. mp: 131–132 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄F₅NaS [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 (dq, *J* = 26.3 Hz, 7.5 Hz). ATR-FTIR (KBr): ν = 3035, 1589, 1575, 1473, 1230, 1101, 782, 696 cm⁻¹.

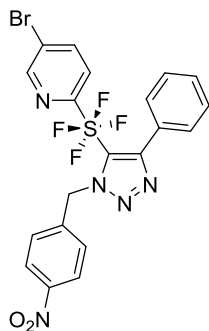
Total isolated yield of **5k** is 91% (199 mg).

5-bromo-2-(tetrafluoro(1-(4-nitrobenzyl)-5-phenyl-1H-1,2,3-triazol-4-yl)- λ^6 -sulfaneyl)pyridine (5I-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 **5I-A** as yellow solid. mp: 153–154 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₅O₂F₄NaSBr [M+Na]⁺: 565.9885 found: 565.9889. ¹H NMR (300 MHz, CDCl₃): 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, CDCl₃): δ = 61.33 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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.

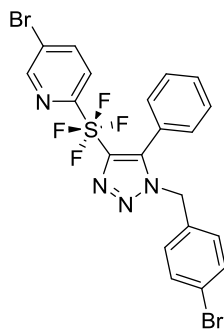
5-bromo-2-(tetrafluoro(1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)- λ^6 -sulfaneyl)pyridine (5I-B)



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 **5I-B** as white solid. mp: 186–187 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₅O₂F₄NaSBr [M+Na]⁺: 565.9885 found: 565.9869. ¹H NMR (300 MHz, CDCl₃): 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, CDCl₃): δ = 67.62 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 54.91, 122.55, 123.75, 1242.18, 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.

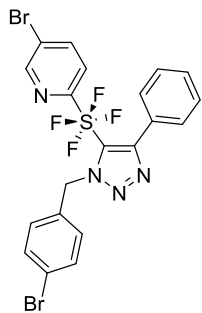
Total isolated yield of **5I** is 92% (250 mg).

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 regioisomer 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 C₂₀H₁₄N₄F₄NaSBr₂ [M+Na]⁺: 598.9140 found: 598.9132. ¹H NMR (300 MHz, CDCl₃): 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, CDCl₃): δ = 61.29 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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.

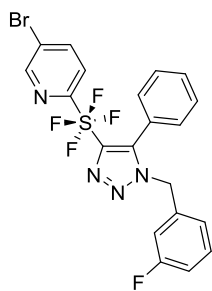
5-bromo-2-((1-(4-bromobenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)pyridine (5m-B)



Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 7/3) to isolate pure **5m-B** as white solid. mp: 150–151 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₄F₄NaSBr₂ [M+Na]⁺: 598.9140 found: 598.9147. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.62 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.15, 122.59, 123.61, 128.05, 129.03, 129.54, 130.18, 130.97, 132.03, 134.08, 141.18, 144.50, 148.28–148.84 (m), 148.65, 167.30–167.76 (m). ATR-FTIR (KBr): ν = 3048, 1554, 1486, 1446, 1359, 1095, 771, 692 cm⁻¹.

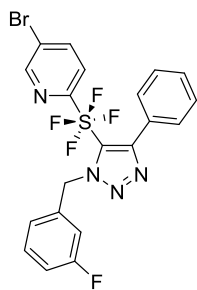
Total isolated yield of **5m** is 63% (182 mg).

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 regioisomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure **5n-A** as white solid. mp: 134–135 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₄F₅NaSBr [M+Na]⁺: 538.9940 found: 538.9933. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = -112.47–-112.38 (m, 1F), 61.29 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 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): ν = 3077, 1616, 1590, 1556, 1486, 1450, 1361, 1253, 1093, 765, 696 cm⁻¹.

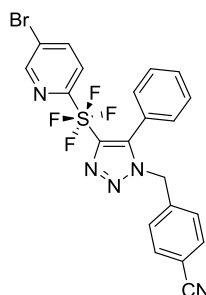
5-bromo-2-(tetrafluoro(1-(3-fluorobenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)- λ^6 -sulfaneyl)pyridine (5n-B)



Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (Hexane/AcOEt, 4/1) to isolate pure **5n-B** as white solid. mp: 148–149 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₄N₄F₅NaSBr [M+Na]⁺: 538.9940 found: 538.9955. ¹H NMR (300 MHz, CDCl₃): δ = 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = -112.83–-112.75 (m, 1F), 67.61 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 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): ν = 3052, 1590, 1486, 1448, 1365, 1261, 1097, 798, 692 cm⁻¹.

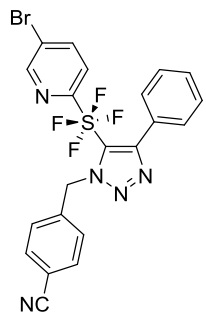
Total isolated yield of **5n** is 78% (212 mg).

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 C₂₁H₁₄N₅F₄NaSBr [M+Na]⁺: 545.9987 found: 545.9988. ¹H NMR (300 MHz, CDCl₃): 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.33 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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.

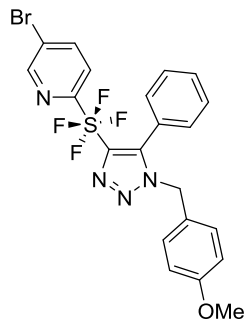
4-((5-((5-bromopyridin-2-yl)tetrafluoro- λ^6 -sulfaneyl)-4-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (**5o-B**)



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 C₂₁H₁₄N₅F₄NaSBr [M+Na]⁺: 545.9987 found: 545.9990. ¹H NMR (300 MHz, CDCl₃): 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.61 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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.

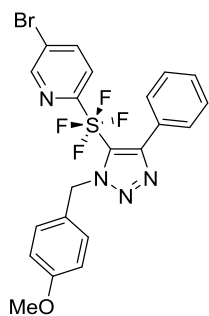
Total isolated yield of **5o** is 75% (197 mg).

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 C₂₁H₁₇N₄OF₄NaSBr [M+Na]⁺: 551.0140 found: 551.0162. ¹H NMR (300 MHz, CDCl₃): 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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.32 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): 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.

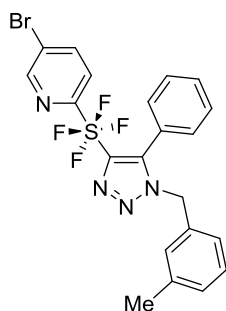
5-bromo-2-(tetrafluoro(1-(4-methoxybenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)- λ^6 -sulfaneyl)pyridine (5p-B)



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-B** as white solid. mp: 155–156 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇N₄O₄NaSBr [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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.76 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.40, 114.15, 122.65, 123.49, 127.02, 127.98, 128.88, 129.59, 130.20, 131.20, 141.13, 144.28, 148.10–148.38 (m), 148.59, 159.69, 167.66 (quint, *J* = 28.8 Hz). ATR-FTIR (KBr): ν = 3066, 1610, 1513, 1454, 1361, 1251, 1097, 1025, 800, 757 cm⁻¹.

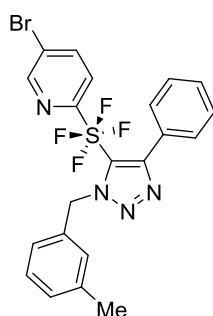
Total isolated yield of **5p** is 68% (180 mg).

5-bromo-2-(tetrafluoro(1-(3-methylbenzyl)-5-phenyl-1H-1,2,3-triazol-4-yl)- λ^6 -sulfaneyl)pyridine (5q-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 **5q-A** as white solid. mp: 108–109 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇N₄F₄NaSBr [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.

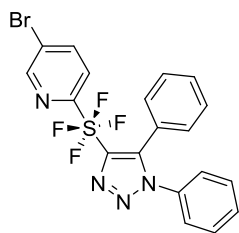
5-bromo-2-(tetrafluoro(1-(3-methylbenzyl)-4-phenyl-1H-1,2,3-triazol-5-yl)- λ^6 -sulfaneyl)pyridine (5q-B)



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 **5q-B** as white solid. mp: 104–105 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇N₄F₄NaSBr [M+Na]⁺: 535.0191 found: 535.0203. ¹H NMR (300 MHz, CDCl₃): δ = 2.34 (s, 3H), 5.88 (s, 2H), 7.11–7.16 (m, 3H), 7.21–7.28 (m, 1H), 7.39–7.41 (m, 3H), 7.52–7.57 (m, 3H), 7.92 (d, *J* = 8.7 Hz, 1H), 8.54 (d, *J* = 2.1 Hz, 1H), ¹⁹F NMR (282 MHz, CDCl₃): δ = 67.69 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 21.54, 55.71, 122.60–122.65 (m), 123.47, 124.80, 127.97, 128.37, 128.67, 128.89, 129.14, 130.19, 131.15, 134.97, 138.53, 141.11, 144.29, 148.03–148.86 (m), 148.54, 167.59 (quint, *J* = 30.0 Hz). ATR-FTIR (KBr): ν = 3048, 1606, 1562, 1479, 1446, 1091, 786, 690 cm⁻¹.

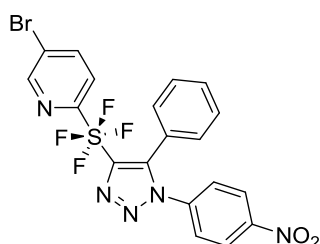
Total isolated yield of **5q** is 67% (172 mg).

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



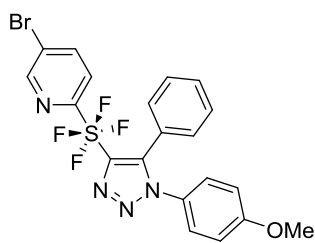
Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (*n*-Hexane/AcOEt, 7/3) to get only **5r-A** as brown solid in 26% yield (63.4 mg). mp: 177–178 °C; HRMS (ESI⁺): *m/z* calcd for C₁₉H₁₃N₄F₄NaSBr [M+Na]⁺: 506.9878 found: 506.9891. ¹H NMR (300 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)- λ^6 -sulfaneyl)pyridine (5s-A)



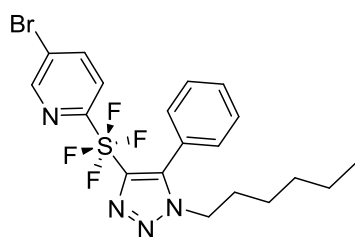
Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (*n*-Hexane/AcOEt, 4/1) to get only **5s-A** as light brown solid in 66% yield (174 mg). mp: 162–163 °C; HRMS (ESI⁺): *m/z* calcd for C₁₉H₁₂N₅O₂F₄NaSBr [M+Na]⁺: 551.9729 found: 551.9714. ¹H 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)- λ^6 -sulfaneyl)pyridine (5t-A)



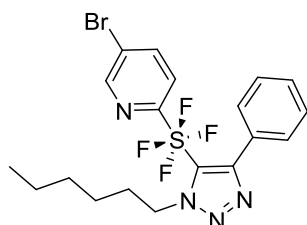
Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (*n*-Hexane/AcOEt, 4/1) to get only **5t-A** as yellow solid in 72% yield (185 mg). mp: 166–167 °C; HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₅N₄OF₄NaSBr [M+Na]⁺: 536.9984 found: 536.9991. ¹H NMR (300 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, 129.84, 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)- λ^6 -sulfaneyl)pyridine (5u-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, 4/1) to isolate pure **5u-A** as white solid. mp: 97–98 °C; HRMS (ESI⁺): *m/z* calcd for C₁₉H₂₁N₄F₄NaSBr [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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 61.30 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 14.01, 22.41, 26.10, 29.96, 31.04, 31.08, 49.23, 122.82, 123.01 (quint, *J* = 5.0 Hz), 126.72, 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.

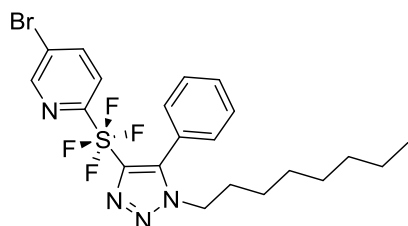
5-bromo-2-(tetrafluoro(1-hexyl-4-phenyl-1H-1,2,3-triazol-5-yl)- λ^6 -sulfaneyl)pyridine (5u-B)



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, 4/1) to isolate pure **5u-B** as yellow oil. HRMS (ESI⁺): *m/z* calcd for C₁₉H₂₁N₄F₄NaSBr [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.

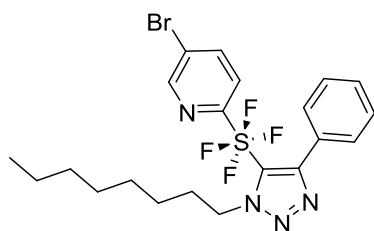
Total isolated yield of **5u** is 67% (165 mg).

5-bromo-2-(tetrafluoro(1-octyl-5-phenyl-1H-1,2,3-triazol-4-yl)- λ^6 -sulfaneyl)pyridine (5v-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, 4/1) to isolate pure **5v-A** as white solid. HRMS (ESI⁺): *m/z* calcd for C₂₁H₂₅N₄F₄NaSBr [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); ¹⁹F 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.

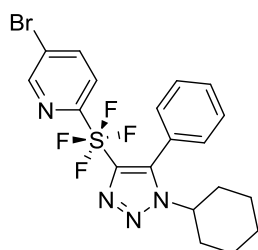
5-bromo-2-(tetrafluoro(1-octyl-4-phenyl-1H-1,2,3-triazol-5-yl)- λ^6 -sulfaneyl)pyridine (**5v-B**)



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, 4/1) to isolate pure **5v-B** as yellow oil. mp: 90–91 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₂₅N₄F₄NaSBr [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.

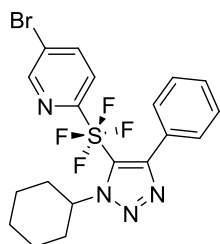
Total isolated yield of **5v** is 66% (172 mg).

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



Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regioisomer 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 C₁₉H₁₉N₄F₄NaSBr [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.

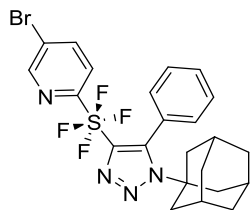
5-bromo-2-((1-cyclohexyl-4-phenyl-1H-1,2,3-triazol-5-yl)tetrafluoro- λ^6 -sulfaneyl)pyridine (**5w-B**)



Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regioisomer 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 C₁₉H₁₉N₄F₄NaSBr [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, 3H), 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.

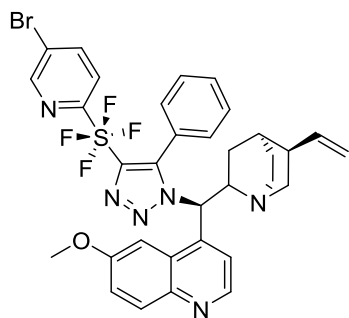
Total isolated yield of **5w** is 52% (128 mg).

2-((1-((3s,5s,7s)-adamantan-1-yl)-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -sulfaneyl)-5-bromopyridine (5x-A)



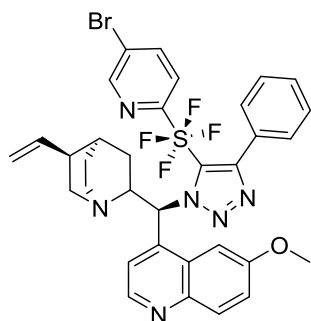
Prepared according to general procedure 2, by stirring at 110 °C for 48 h and isolated by column chromatography (*n*-Hexane/AcOEt, 4/1) to get pure **5x-A** as white solid in 37% yield (100 mg). mp: 170–171 °C; HRMS (ESI⁺): *m/z* calcd for C₂₃H₂₃N₄NaSBrF₄ [M+Na]⁺: 565.0661 found: 565.0669. ¹H NMR (300 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- λ^6 -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 regioisomer by column chromatography (*n*-Hexane/AcOEt, 2/3) to isolate pure **5y-A** as white solid. mp: 193–194 °C; HRMS (ESI⁺): *m/z* calcd for C₃₃H₃₂N₆OF₄SBr [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, 1027, 777, 696 cm⁻¹.

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

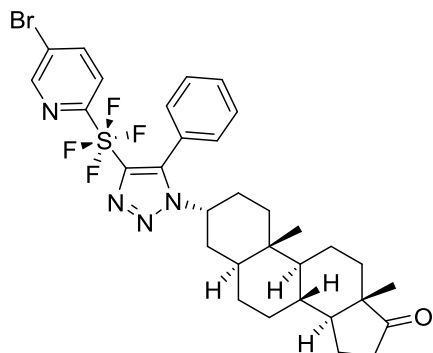


Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 2/3) to isolate pure **5y-B** as white solid. mp: 172–173 °C; HRMS (ESI⁺): *m/z* calcd for C₃₃H₃₂N₆OSBrF₄ [M+Na]⁺: 715.1478 found: 715.1451. ¹H NMR (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,

128.82, 130.41, 131.28, 132.16, 141.11, 141.21, 141.76, 143.95, 144.83, 148.18, 148.42, 149.20–149.73 (m), 158.11, 167.42–167.89 (m). ATR-FTIR (KBr): $\nu = 3060, 2938, 1508, 1475, 1446, 1241, 1093, 1031, 775, 700 \text{ cm}^{-1}$.

Total isolated yield of **5y** is 66% (236 mg).

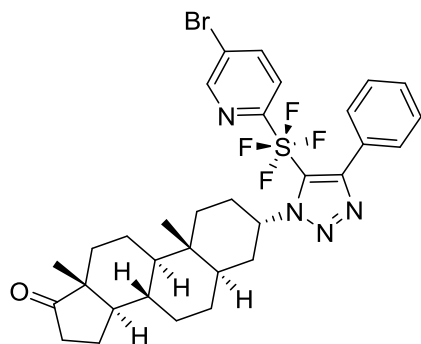
3-(4-((5-bromopyridin-2-yl)tetrafluoro- λ^6 -sulfaneyl)-5-phenyl-1H-1,2,3-triazol-1-yl)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (5z-A**)**



Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regioisomer 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 $\text{C}_{32}\text{H}_{37}\text{N}_4\text{ONaSBrF}_4$ $[\text{M}+\text{Na}]^+$: 703.1705 found: 703.1700. ¹H NMR (300 MHz, CDCl_3): $\delta = 0.81$ (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, $J =$

8.7 Hz, 1H), 8.54 (d, $J = 2.4$ Hz, 1H), ¹⁹F NMR (282 MHz, CDCl_3): $\delta = 61.40$ (s, 4F), ¹³C NMR (125 MHz, CDCl_3): $\delta = 0.04, 9.62, 11.93, 18.11, 19.87, 24.35, 26.05, 28.54, 29.58, 31.22$ (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): $\nu = 3064, 2937, 1735, 1548, 1473, 1446, 1099, 779, 698 \text{ cm}^{-1}$.

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

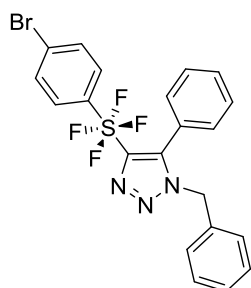


Prepared according to general procedure 2, by stirring at 110 °C for 48 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 4/1) to isolate pure **5z-B** as white solid. mp: 127–128 °C; HRMS (ESI⁺): m/z calcd for $\text{C}_{32}\text{H}_{37}\text{N}_4\text{ONaSBrF}_4$ $[\text{M}+\text{Na}]^+$: 703.1705 found: 703.1696. ¹H NMR (300 MHz, CDCl_3): $\delta = 0.88$ (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),

8.57 (d, $J = 2.1$ Hz, 1H), ¹⁹F NMR (282 MHz, CDCl_3): $\delta = 67.38$ (s, 4F), ¹³C NMR (125 MHz, CDCl_3): $\delta = 11.72, 13.99, 20.17, 21.91, 26.79, 28.10, 30.62, 31.65, 33.33, 33.44, 35.21, 35.65, 36.03, 39.05, 47.96, 51.54, 54.06, 56.67, 122.67, 123.43, 127.89, 128.74, 130.29, 131.66, 141.14, 143.40, 148.25–148.78$ (m), 148.55, 167.71–168.18 (m). ATR-FTIR (KBr): $\nu = 3058, 2935, 1737, 1560, 1473, 1448, 1093, 775, 684 \text{ cm}^{-1}$.

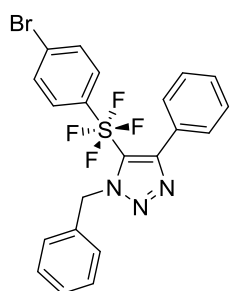
Total isolated yield of **5z** is 37% (126 mg).

1-benzyl-4-((4-bromophenyl)tetrafluoro- λ^6 -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 regioisomer 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 C₂₁H₁₆N₃F₄NaSBr [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 = 53.06, 124.61, 126.45, 127.72 (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.

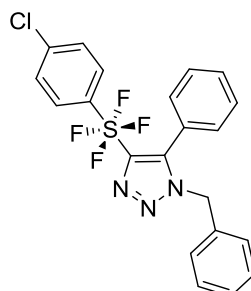
1-benzyl-5-((4-bromophenyl)tetrafluoro- λ^6 -sulfaneyl)-4-phenyl-1H-1,2,3-triazole (**7a-B**)



Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer 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 C₂₁H₁₆N₃F₄NaSBr [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 = 77.90 (s, 4F), ¹³C NMR (125 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.

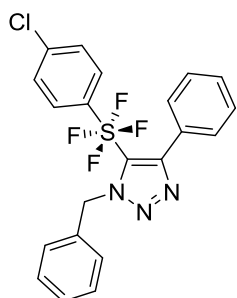
Total isolated yield of **7b** is 56% (140 mg).

1-benzyl-5-phenyl-4-(tetrafluoro(phenyl)- λ^6 -sulfaneyl)-1H-1,2,3-triazole (**7b-A**)



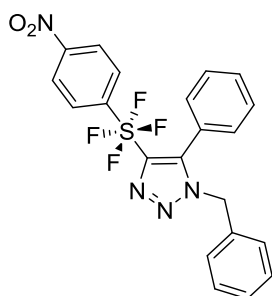
Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 85/15) to isolate pure **7b-A** as white solid. mp: 137–138 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₆N₃F₄NaS [M+Na]⁺: 476.0587 found: 476.0589. ¹H NMR (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)- λ^6 -sulfaneyl)-1H-1,2,3-triazole (7b-B)



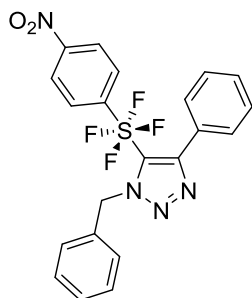
Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 85/15) to isolate pure **7b-B** as white solid. mp: 129–132 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₆N₃F₄NaCl [M+Na]⁺: 476.0587 found: 476.0590. ¹H NMR (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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 78.04 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 55.78, 127.35 (t, *J* = 5.0 Hz), 127.68, 128.01, 128.38, 128.64, 128.84, 128.91, 130.19, 131.28, 135.22, 137.14, 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)- λ^6 -sulfaneyl)-1H-1,2,3-triazole (7c-A)



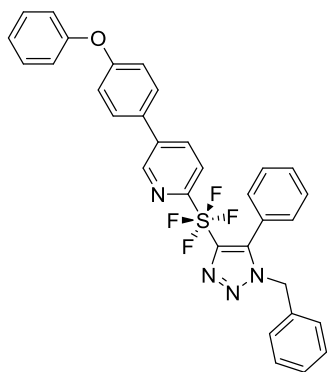
Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 85/15) to isolate pure **7c-A** as white solid. mp: 140–142 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₆N₄O₂F₄NaS [M+Na]⁺: 487.0828 found: 487.0820. ¹H NMR (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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 71.01 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 53.17, 123.66, 126.23, 127.63 (quint, *J* = 5.0 Hz), 128.01, 128.64, 128.69, 128.90, 130.23, 130.27, 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.

1-benzyl-4-phenyl-5-(tetrafluoro(4-nitrophenyl)- λ^6 -sulfaneyl)-1H-1,2,3-triazole (7c-B)



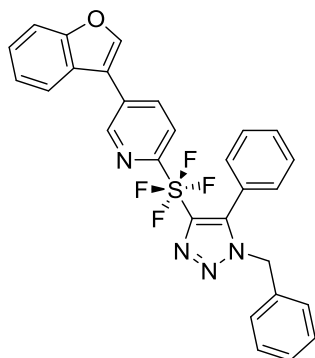
Prepared according to general procedure 2, by stirring at 110 °C for 24 h and separated from its regioisomer by column chromatography (*n*-Hexane/AcOEt, 85/15) to isolate pure **7c-B** as white solid. mp: 121–122 °C; HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₆N₄O₂F₄NaS [M+Na]⁺: 487.0828 found: 487.0832. ¹H NMR (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), ¹⁹F NMR (282 MHz, CDCl₃): δ = 77.52 (s, 4F), ¹³C NMR (125 MHz, CDCl₃): δ = 58.83, 123.89, 127.45 (t, *J* = 5.0 Hz), 127.57, 128.05, 128.45, 128.87, 129.03, 130.11, 130.98, 134.99, 144.26, 148.63, 149.12 (quint, *J* = 35.0 Hz), 162.77 (quint, *J* = 23.8 Hz). ATR-FTIR (KBr): ν = 3064, 1610, 1535, 1479, 1448, 1079, 767 cm⁻¹.

2-((1-benzyl-5-phenyl-1H-1,2,3-triazol-4-yl)tetrafluoro- λ^6 -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* calcd for C₃₂H₂₄N₄OF₄NaS [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* = 32.5 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- λ^6 -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%), K₃PO₄ (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* calcd for C₂₈H₂₀N₄OF₄NaS [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, 128.60, 128.63, 128.87, 130.12, 130.34, 130.83, 134.01 (quint, *J* = 3.8 Hz), 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.

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X-ray crystal structure:

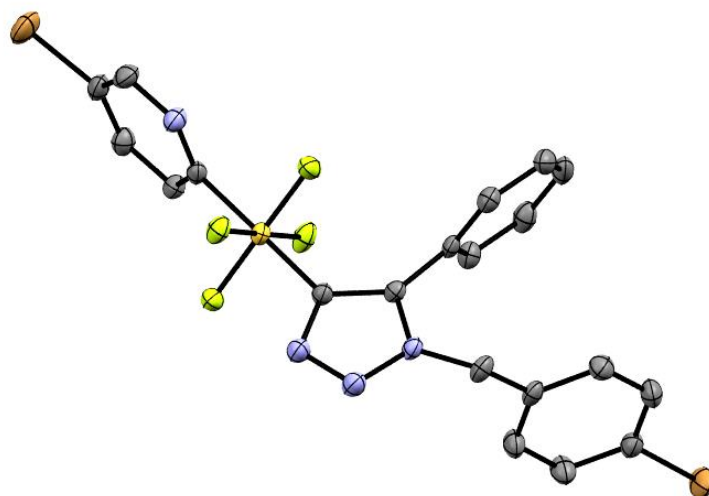


Fig. S1: Ortep diagram of **5m** isomer A drawn at 50% probability. The hydrogen atoms have been omitted for clarity.

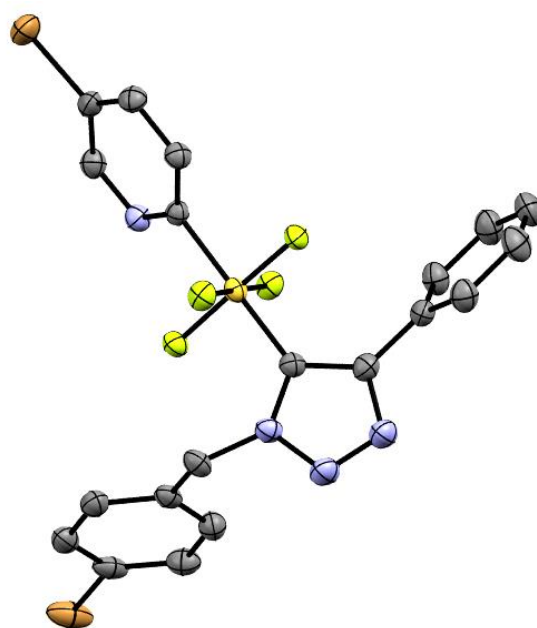


Fig. S2: Ortep diagram of **5m** isomer B drawn at 50% probability. The hydrogen atoms have been omitted for clarity.

