Electronic Supporting Information

SF$_5$-pyridylaryl-$\lambda^1$-iodonium salts and their utility as electrophilic reagents to access SF$_5$-pyridine derivatives in the late-stage of synthesis

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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 and KMnO₄ in water/heat. Products were purified by preparative thin-layer plates (PLC) carried out on 2.0 mm Merck silica gel (60-F254) or Column chromatography. Column chromatography was carried out on columns packed with silica gel (60N spherical neutral size 63-210 μm). The ¹H NMR (300 MHz) and ¹⁹F NMR (282 MHz) spectra were recorded for solution in CDCl₃ and (CD₃)₂CO on a Varian Mercury 300. ¹³C NMR (125 MHz) spectra for solution in CDCl₃ and (CD₃)₂CO were recorded on a BRUKER 500 UltraShield. Chemical shifts (δ) are expressed in ppm downfield from TMS (δ = 0.00) and C₆F₆ (δ = -162.2 (CDCl₃) or -163.5 ((CD₃)₂CO)) as an internal standard for ¹H and ¹⁹F NMR respectively. For ¹³C NMR, CDCl₃ (δ = 77.16) or (CD₃)₂CO (δ = 29.84) is referred as residual standard. High resolution mass spectrometry was recorded on a Waters Synapt G2 HDMS (ESI-MS). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Melting point were recorded on a BUCHI M-565.

Chemicals were purchased and used without further purification unless otherwise noted. Solvents CH₃CN, CH₂Cl₂, toluene, DMF and NMP were dried and distilled before use.

Scheme S1: Synthesis of the SF₅-pyridines from commercial reagents:

![Scheme S1](image)

Table S1: Optimization of Temperature for Reagent 1b with amides 11a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate 11</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>rl</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
<td>5</td>
<td>68</td>
<td></td>
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<tr>
<td>3</td>
<td>H</td>
<td>rl</td>
<td>24</td>
<td>7</td>
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<td>4</td>
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<td>50</td>
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</tr>
<tr>
<td>5</td>
<td>H</td>
<td>rl</td>
<td>19</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
<td>5</td>
<td>30</td>
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<tr>
<td>7</td>
<td>55</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aReaction conditions: 11 (0.10 mmol), reagent 1b (0.15 mmol), NaH (0.15 mmol), Toluene, Temperature, Time. bIsolated yield
Synthesis of starting material for 6a:

4-(4-(benzyloxy)phenoxy)-2,6-dimethoxypyrimidine (13I):

It was prepared following a literature condition. In a flame dried round bottomed flask, Cs₂CO₃ (652mg, 2 mmol) was added to 4-chloro-2,6-dimethoxypyrimidine (350 mg, 2mmol) in DMF (15 mL) and the mixture was stirred at rt for 10 minutes. 4-(benzyloxy)pheno (400 mg, 2mmol) was added to the reaction mixture and the reaction vessel was transferred to a preheated oil bath at 85 °C and stirred at that temperature for 4 hours. The reaction was quenched with water and extracted with ethyl acetate 3 times. The combined organic phase was washed with brine and then dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give the crude product which was purified under column chromatography on silica gel (n-hexane/EtOAc, 4/1) to give the desired product 13I as a white solid (576.7 mg) in 85% yield.

m.p.: (110.8 °C); HRMS (ESI) calcd. for C₂₆H₂₅N₄O₆Na [(M+Na)⁺]: 585.1361 found 585.1363; ¹H NMR (CDCl₃, 300 MHz): δ = 7.45-7.34 (m, 5H), 7.05 (d, J = 9 Hz, 2H), 6.98 (d, J = 9 Hz, 2H), 5.63 (s, 1H), 5.06 (s, 2H), 3.92 (s, 3H), 3.93 (s, 3H); ¹³C NMR (CDCl₃, 126 MHz): δ = 153.56, 151.58, 141.58, 139.79, 139.79, 137.12, 125.59, 122.66, 122.66, 118.47, 118.47, 115.88, 115.88, 111.88, 111.88, 110.34, 110.34, 100.00. ATR-FTIR (KBr): ν = 3616, 3017, 2947, 2553, 2001, 1815, 1540, 1296, 1118, 933 cm⁻¹.

4-[(2,6-dimethoxypyrimidin-4-yloxy)phenol (13I):

It was prepared from modified procedure from the literature. In a dry round bottomed flask NiCl₂·6H₂O (535 mg, 2.25 mmol) was added to solution of 13I (507 mg, 1.5 mmol) in methanol/ethyl acetate (1:1, 5 mL) and it was stirred at rt till a homogenous solution was formed. The reaction mixture was cooled to 0 °C and NaBH₄ (170 mg, 4.5 mmol) was added in portions. The reaction was stirred at 0 °C for 30 minutes and then warmed to rt. It was then transferred to a preheated oil bath at 65 °C and allowed to stir at that temperature for 5 days. The reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The organic phase was washed with water and then dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give the crude product which was purified under column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 13I as a white solid (153 mg) in 41% yield.

m.p.: (120.5 °C); HRMS (ESI) calcd. for C₂₅H₂₄N₄O₅Na [(M+Na)⁺]: 527.1568 found 527.1569; ¹H NMR (CDCl₃, 300 MHz): δ = 6.98 (d, J = 9 Hz, 2H), 6.83 (d, J = 9 Hz, 2H), 5.65 (s, 1H), 5.40 (s, 2H), 5.93 (s, 3H), 3.94 (s, 3H); ¹³C NMR (CDCl₃, 126 MHz): δ = 153.56, 151.58, 141.58, 139.79, 139.79, 137.12, 125.59, 122.66, 122.66, 118.47, 118.47, 115.88, 115.88, 110.34, 110.34, 100.00. ATR-FTIR (KBr): ν = 3616, 3112, 2950, 2890, 1815, 1540, 1296, 1118, 933 cm⁻¹.

Synthesis of disulfide:

1,2-bis(6-bromopyridin-2-yl)disulfane (i):

Prepared according to literature procedure. In a 500 ml round bottom flask, under Ar atmosphere, a mixture of 2,6-dibromopyridine (18.95 g, 80.0 mmol) and THF (114 ml) at 0 °C was stirred for 30 min. At 0 °C, isopropylmagnesium chloride lithium chloride (PrMgCl·LiCl) complex solution (70.2 ml, 80.0 mmol) was added slowly to the reaction mixture and was stirred at room temperature for 2 h. After cooling to -78 °C, a solution of sulfur (2.57 g, 80.0 mmol) in toluene (258 ml) was added to the mixture and was stirred at room temperature for 1 h. The reaction mixture was then transferred to another round bottom flask containing a mixture of aqueous solution of NaOH (3.84 g in 155 mL of H₂O) and K₂[Fe(CN)]₆ (31.6 g in 20 mL of H₂O) and was stirred at room temperature for 12 h. The reaction mixture was extracted by CH₂Cl₂, and the combined organic phase was washed withaq. NH₄Cl (200 ml X 2) and brine and then dried over MgSO₄. The solvent was removed in vacuo to give a crude product which was purified by column chromatography on silica gel (n-hexane/EtOAc, 4/1) to give the target product as a yellow solid (17 mg) in 56% yield.

m.p.: (96.8 °C); HRMS (ESI) calcd. for C₁₃H₁₂N₄S₂Br₂ [(M+Na)⁺]: 398.8237 found 398.8237; ¹H NMR (CDCl₃, 300 MHz): δ = 7.3 (d, J = 7.1 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 126 MHz): δ = 118.47, 125.59, 139.54, 141.58, 159.79. ATR-FTIR (KBr): ν = 3102, 3030, 2924, 1543, 1409, 1143, 1131, 1106, 784, 760 cm⁻¹.
A dry 500 ml flask was charged with 2-hydroxy-5-bromopyridine (5.0 g; 28.7 mmol), Lawesson’s reagent (10.9 g; 27 mmol) and toluene (250 mL). The reaction mixture was then stirred at reflux for 48 h. After cooling it was transferred into the separatory funnel which contained a solution of NaOH (25 g) in water (250 mL). The resulting reaction mixture was stirred at room temperature for 2 h. After cooling, it was extracted with CH$_2$Cl$_2$ (2×50 mL) and the organic extracts were discarded. The aqueous phase was washed with brine (100 mL) and dried with MgSO$_4$. The crude residue that was obtained after filtration and CH$_2$Cl$_2$ evaporation was further coevaporated in vacuo with toluene (2×100 mL) to remove residual AcOH and to give pure 5-bromopyridine-2-thiol as a yellow solid (4.95 g; 88%). In a 250 mL flask containing the obtained 5-bromopyridine-2-thiol (4.9 g; 39 mmol) was added a solution of NaOH (1.8 g; 45 mmol) in water (100 mL) was added to it. The resulting reaction mixture was stirred for 14 h, and the formed precipitate was filtered, thoroughly washed with water and dried, first in air then in vacuo to give 4.02 g (83%) of pure 1,2-bis(5-bromopyridin-2-yl)disulfane as a beige solid. The $^1$H NMR spectrum matched the one reported by Dolbier et al.$^3$

A dry 250 mL flask was charged with 2-chloro-3-bromopyridine (5.00 g; 38 mmol), thiourea (2.9 g; 38 mmol) and anhydrous ethanol (50 mL). The reaction mixture was then stirred at reflux for 48 h. After cooling, the solvent was evaporated in vacuo. To the obtained residue, a solution of NaOH (3.6 g; 90 mmol) in water (75 mL) was added, and the mixture was stirred at reflux for 2 h. After cooling, it was extracted with CH$_2$Cl$_2$ (2×50 mL), and the organic extracts were discarded. The aqueous phase was transferred into 250 mL flask, and a solution of K$_2$[Fe(CN)$_6$] (14.8 g; 45 mmol) in water (75 mL) was added to it. The resulting reaction mixture was stirred for 14 h, and the formed precipitate was filtered, thoroughly washed with water and dried, first in air then in vacuo to give 1.34 g (18%) of pure 1,2-bis(3-bromopyridin-2-yl)disulfane as a brown solid. The $^1$H NMR spectrum matched the one reported by Dolbier et al.$^3$

Prepared according to literature procedure.$^3$ In a 500 mL round bottom flask, under Ar atmosphere, a mixture of 2-bromo-4-fluoropyridine (4 g, 22.7 mmol) and THF (58 ml) at 0 °C was stirred for 30 min. At 0 °C, isopropylmagnesium chloride lithium PrMgCl.LiCl) complex solution (23.1 mL, 25.0 mmol) was added slowly to the reaction mixture and was stirred at room temperature for 30 minutes and then a solution of K$_2$[Fe(CN)$_6$] (14.82 g; 45 mmol) in water (100 mL) was added to it. The resulting reaction mixture was stirred for 14 h, and the formed precipitate was filtered, thoroughly washed with water and dried, first in air then in vacuo to give 4.02 g (83%) of pure 1,2-bis(5-bromopyridin-2-yl)disulfane as a beige solid. The $^1$H NMR spectrum matched the one reported by Dolbier et al.$^3$
free edge was immersed into the solvent and chlorine gas was bubbled through it as the bottle was being cooled by ice bath. The chlorine gas was bubbled for approximately 10 minutes. The septum was removed and the disulfide was added in one portion (1.89 g, 5 mmol) and then sealed with the closure. The FEP bottle was placed inside an ice bath and the reaction mixture was stirred for 2 h and then at room temperature for 20-72 h. The reaction mixture was transferred to another FEP bottle using a PP/ETFE suction filter (Flom Cat. # 8800) under nitrogen environment and the solvent was evaporated in vacuo to give crude 2-pyridylsulfur chlorotetrafluorides.

(The purity of crude 2-pyridylsulfur chlorotetrafluorides was usually in the range of 80-95% according to 1H, 19F NMR data.)

6-bromo-2-pyridylsulfur chlorotetrafluoride (8a‘):

\[
\begin{array}{c}
\text{Br} \\
\text{N} \\
\text{SF}_4\text{Cl}
\end{array}
\]

Prepared according to the general procedure from 1,2-bis(6-bromopyridin-2-yl)disulfane (i) by stirring at rt for 48 h and obtained the crude product as white solid in 90% yield (2.75 g).

1H NMR (CDCl₃, 300 MHz) \(\delta = 8.63\) (d, \(J = 1.9\) Hz, 1H), 8.04 (d, \(J = 8.8\) Hz, 1H), 7.65 (d, \(J = 8.7\) Hz, 1H); 19F NMR (CDCl₃, 282 MHz) \(\delta = 124.77\) (s, 4F).

5-bromo-2-pyridylsulfur chlorotetrafluoride (8b’):

\[
\begin{array}{c}
\text{Br} \\
\text{N} \\
\text{SF}_4\text{Cl}
\end{array}
\]

Prepared according to the general procedure from 1,2-bis(5-bromopyridin-2-yl)disulfane (ii) by stirring at rt for 20 h and obtained the crude product as white solid in 94% yield (2.85 g). The 19F NMR spectrum matched the one reported by Dolbier et al.

19F NMR (CDCl₃, 282 MHz) \(\delta = 124.82\) (s, 4F).

3-bromo-2-pyridylsulfur chlorotetrafluoride (8c’):

\[
\begin{array}{c}
\text{Br} \\
\text{N} \\
\text{SF}_4\text{Cl}
\end{array}
\]

Prepared according to the general procedure from 1,2-bis(3-bromopyridin-2-yl)disulfane (iii) (1.25g, 3.3 mmol) by stirring at rt for 72 h and obtained the crude product as an oil in 75% yield (1.5 g) which was a crude mixture of the required product and the SF₃ derivative. The 19F NMR spectrum matched the one reported by Dolbier et al.

19F NMR (CDCl₃, 282 MHz) \(\delta = 124.87\) (s, 4F).

4-fluoro-2-pyridylsulfur chlorotetrafluoride (8d’):

\[
\begin{array}{c}
\text{F} \\
\text{N} \\
\text{SF}_4\text{Cl}
\end{array}
\]

Prepared according to the general procedure from 1,2-bis(6-bromopyridin-2-yl)disulfane (iv) by stirring at rt for 48 h and obtained the crude product as white solid in 48% yield (1.4 g).

1H NMR (CDCl₃, 300 MHz) \(\delta = 7.25\)–7.30 (m, 1H), 7.51 (d, \(J = 9\) Hz, 1H), 8.58 (t, \(J = 6\) Hz, 1H); 19F NMR (CDCl₃, 282 MHz) \(\delta = 96.42\) (s, 1F), 123.80 (s, 4F).

Synthesis of 2-pyridylsulfur pentafluorides 8:

The 2-pyridylsulfur pentafluorides were prepared according to the literature procedure. The crude 2-pyridylsulfur chlorotetrafluorides was transferred into FEP bottles (Nalgene®) in the glove box and their exact amount was measured. Solid AgF (2 equiv) was then added in one portion and the bottle was sealed with closure. It was taken out of the glove box, covered with tin foil, placed in a preheated oil bath at 60-70 °C and then left for 16-72 h. The content of the vial was washed out into a beaker first with CH₂Cl₂ (30 mL) and then with water (30 mL), the contents of the beaker stirred for 1h and then filtered from solids. The organic phase was separated and the aqueous phase extracted with CH₂Cl₂ (20 X 3 mL). The
combined CH$_2$Cl$_2$ extracts were dried with Na$_2$SO$_4$. The residue obtained after filtration and evaporation of solvent in vacuo was purified by column chromatography, eluting with pentane/CH$_2$Cl$_2$ to give title 2-pyridylsulfur pentafluorides.

6-bromo-2-pyridylsulfur pentafluoride (8a):

![Structure of 6-bromo-2-pyridylsulfur pentafluoride](image)

Prepared according to the general procedure from 6-bromo-2-pyridylsulfur chlorotetrafluoride 8a’ (2.75 g, 9.15 mmol) and AgF (2.32 g, 18.3 mmol), by stirring at 60 °C for 40 h. It was isolated by column chromatography on silica gel (pentane/CH$_2$Cl$_2$ : 9:1) to give 6-bromo-2-pyridylsulfur pentafluoride as a white solid in 69% yield (1.95 g).

m.p.: 65.3 °C; HRMS (El) calcd. for C$_8$H$_7$F$_5$SBr ([M]$^+$): 282.9090 found 282.9109; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.70–7.83 (m, 3H); $^{31}$F NMR (CDCl$_3$, 282 MHz) δ = 52.42 (d, J = 146.64 Hz, 4F), 76.45 (quintet, J = 152.28 Hz, 1F); $^{13}$C NMR (CDCl$_3$, 126 MHz) δ = 120.34 (quintet, J = 5 Hz), 131.83, 139.91, 140.64, 164.50–164.88 (m). ATR-FTIR (KBr): ν = 3118, 3096, 3051, 2011, 1567, 1553, 1426, 1126, 811, 739 cm$^{-1}$.

5-bromo-2-pyridylsulfur pentafluoride (8b):

![Structure of 5-bromo-2-pyridylsulfur pentafluoride](image)

Prepared according to the general procedure from 5-bromo-2-pyridylsulfur chlorotetrafluoride 8b’ (2.85 g, 9.5 mmol) and AgF (2.4 g, 19 mmol), by stirring at 60 °C for 20 h. It was isolated by column chromatography on silica gel (pentane/CH$_2$Cl$_2$ : 9:1) to give 5-bromo-2-pyridylsulfur pentafluoride as a white solid in 70% yield (1.98 g). The $^1$H NMR and $^{19}$F NMR spectrum matched the one reported by Dolbier et al.$^5$

$^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.66 (d, J = 9 Hz, 1H), 8.05 (d, J = 9 Hz, 1H), 8.65 (s, 1H); $^{19}$F NMR (CDCl$_3$, 282 MHz) δ = 52.68 (d, J = 149.45 Hz, 4F), 77.12 (quintet, J = 149.46 Hz, 1F).

3-bromo-2-pyridylsulfur pentafluoride (8c)

![Structure of 3-bromo-2-pyridylsulfur pentafluoride](image)

Prepared according to the general procedure from 3-bromo-2-pyridylsulfur chlorotetrafluoride 8c’ (1.5 g, 4.8 mmol) and AgF (1.2 g, 9.6 mmol), by stirring at 70 °C for 72 h. It was isolated by column chromatography on silica gel (pentane/CH$_2$Cl$_2$ : 4:1) to give 3-bromo-2-pyridylsulfur pentafluoride as a white solid in 20% yield (275.8 mg). The $^1$H NMR and $^{19}$F NMR spectrum matched the one reported by Dolbier et al.$^5$

$^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.37 (q, J = 3 Hz, 1H), 8.18 (d, J = 9 Hz, 1H), 8.56 (d, J = 3 Hz, 1H); $^{19}$F NMR (CDCl$_3$, 282 MHz) δ = 53.97 (d, J = 152.28 Hz, 4F), 76.55 (quintet, J = 152.28, 1F).

4-fluoro-2-pyridylsulfur pentafluoride (8d):

![Structure of 4-fluoro-2-pyridylsulfur pentafluoride](image)

Prepared according to the general procedure from 4-fluoro-2-pyridylsulfur chlorotetrafluoride (1.4 g, 5.8 mmol) and AgF (1.5 g, 11.6 mmol), by stirring at 80 °C for 72 h. After workup, CH$_2$Cl$_2$ was removed by distillation and crude was purified by column chromatography on silica gel (pentane/CH$_2$Cl$_2$ : 5:5). The solvent was removed by distillation to give 4-fluoro-2-pyridylsulfur pentafluoride as a volatile liquid. The solvent could not be removed completely fearing loss of the compound and it was used as such for the next step.

HRMS (El) calcd. for C$_8$H$_7$F$_3$SBr ([M]$^+$): 222.9890 found 222.9882; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.25–7.30 (m, 1H), 7.52 (dd, J = 3 Hz, 6 Hz, 1H), 8.58–8.63 (m, 1H); $^{19}$F NMR (CDCl$_3$, 282 MHz) δ = -96.94 (q, J = 8.46 Hz, 1F), 51.91 (d, J = 149.46 Hz, 4F), 76.57 (quintet, J = 149.46 Hz, 1F); $^{13}$C NMR (CDCl$_3$, 126 MHz) δ = 100.34–110.64 (m), 115.12 (d, J = 15 Hz), 150.37–150.46 (m), 166.77–167.22 (m), 168.27, 170.39.
Synthesis of 4-aminopyridylsulfur pentafluoride (8e):

\[
\begin{align*}
\text{NH}_2 & \quad \text{SF}_5 \\
& \quad \text{N}
\end{align*}
\]

8d (1.6 g including CHCl₃) and excess of NH₂ (6 ml, 28% aqueous solution) was placed in the tight-cap vial. The reaction mixture was stirred for 72 h at 120 °C. After cooling, the mixture was diluted with water and extracted with ether (3×20 mL). Combined organic layer was dried over anhydrous Na₂SO₄, filtered, and solvent was evaporated under reduced pressure to give practically pure 4-aminopyridylsulfur pentafluoride 8e as a brown solid (566 mg) in 44% yield with respect to 4-fluoro-2-pyridylsulfur chlorotetrafluoride 10d.

\[
\begin{align*}
\text{m.p.: 93.4 °C; HRMS (EI) calcd. for C}_7\text{H}_5\text{N}_2\text{SF}_5 & \quad & \text{C}_7\text{H}_5\text{N}_2\text{SF}_5; \text{found} & \quad & \text{C}_7\text{H}_5\text{N}_2\text{SF}_5 \\
\end{align*}
\]

Synthesis of 4-amino-2-pyridylsulfur pentafluorides 7:

**General method A:** Iodo-2-pyridylsulfur pentafluorides 7a–c were prepared from the corresponding Bromo-2-pyridylsulfur pentafluorides 8a–c by aromatic Finkelstein reaction (Scheme S2). Although the resulting aryl iodides contained traces of the aryl bromide starting material due to the difficulties in separation, these products were used in next step without further purification.

To a flame dried Schlenk-tube, Cul (10 mol%), NaI (2.0 eq.) and Bromo-2-pyridylsulfur pentafluorides (1.0 eq.) were added and evaporated and backfilled with argon. n-Pentyl alcohol and N₂N'-dimethylethlenediamine (20 mol%) were then added and the mixture was stirred at room temperature for 5 min then at 130 °C for 48 - 96 h. The resulting suspension was cooled to room temperature, diluted with aqueous NH₄ solution (28 wt%) and H₂O, extracted with CH₂Cl₂ for three times. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/CH₂Cl₂) to give the desired product.

**General method B:** Iodo-2-pyridylsulfur pentafluoride 7d was prepared from 4-amino-2-pyridylsulfur pentafluoride by sandmayer reaction.

To a cooled (0 °C) solution of amino-2-pyridylsulfur pentafluoride (1.0 eq.) in 50% aqueous tetrafluoroboric acid (1 mL/mmol) was added aqueous NaN₃O₂ solution (1.1 eq.) dropwise. The resultant slurry was stirred at 0 °C for 30 min. The reaction mixture was then quickly transferred portion-wise to a stirring saturated solution of KI (1.6 eq.) in water. The resultant brown slurry was allowed to stir at room temperature for 30 min and then extracted with Et₂O (3 x 15 mL). The combined organic layer was washed with Na₂SO₄ (20 mL), NaHCO₃ (20 mL) and brine. It was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (n-hexane/EtOAc) to give the desired product.

6-iodo-2-pyridylsulfur pentafluoride (7a):

Following the General method A, Cul (123.7 mg, 0.65 mmol), NaI (1.92 g, 13 mmol), 6-bromo-2-pyridylsulfur pentafluorides 8a (1.85 g, 6.5 mmol) and N₂N'-dimethylethlenediamine (139 µL, 1.3 mmol) were used in n-Pentyl alcohol (6.5 mL) at 130
°C for 48 h. The crude product was purified by column chromatography on silica gel (pentane/CH₂Cl₂ 9/1) to give the desired product (1.55 g, 72% yield) as white solid.

m.p.: 50.3 °C; HRMS (EI) calcd. for C₅H₃NF₅SI [(M)+]: 330.8951 found 330.8965; ¹H NMR (CDCl₃, 300 MHz) δ = 7.55 (t, J = 6 Hz, 1H), 7.73 (d, J = 6 Hz, 1H), 7.93 (d, J = 6 Hz, 1H); ¹F NMR (CDCl₃, 282 MHz) δ = 52.27 (d, J = 152.28 Hz, 4F), 76.67 (quintet, J = 149.46 Hz, 1F); ¹³C NMR (CDCl₃, 126 MHz) δ = 114.37, 120.62 (quintet, J = 3.78 Hz), 138.48, 139.68, 164.80 (quintet, J = 23.94 Hz). ATR-FTIR (KBr): ν = 3108, 3086, 3042, 2005, 1565, 1420, 1109, 798, 723, 665 cm⁻¹.

5-iodo-2-pyridylsulfur pentafluoride (7b):

Following the General method A, CuI (110.5 mg, 0.58 mmol), NaI (1.72 g, 11.6 mmol), 5-bromo-2-pyridylsulfur pentafluorides 8b (1.65 g, 5.8 mmol) and N,N’-dimethylethylenediamine (124 μL, 1.16 mmol) were used in n-Pentyl alcohol (6.0 mL) at 130 °C for 72 h. The crude product was purified by column chromatography on silica gel (pentane/CH₂Cl₂ 9/1) to give the desired product (1.82 g, 95% yield) as light yellow oil.

HRMS (EI) calcd. for C₅H₃NF₅SI [(M)+]: 330.8954 found 330.8974; ¹H NMR (CDCl₃, 300 MHz) δ = 7.54 (d, J = 9 Hz, 1H), 8.24 (d, J = 6 Hz, 1H), 8.80 (d, J = 2.1 Hz, 1H); ¹F NMR (CDCl₃, 282 MHz) δ = 52.38 (d, J = 149.46 Hz, 4F), 77.07, (quintet, J = 152.28 Hz, 1F); ¹³C NMR (CDCl₃, 126 MHz) δ = 97.03, 123.01 (quintet, J = 3.78 Hz), 147.06, 154.30, 164.82 (quintet, J = 23.94 Hz). ATR-FTIR (NaCl): ν = 3186, 3044, 2926, 1557, 1445, 1002, 844, 662, 600 cm⁻¹.

3-iodo-2-pyridylsulfur pentafluoride (7c):

Following the General method A, CuI (23.4 mg, 0.123 mmol), NaI (364 mg, 2.46 mmol), 3-bromo-2-pyridylsulfur pentafluorides 8c (350 mg, 1.23 mmol) and N,N’-dimethylethylenediamine (25.6 μL, 0.246 mmol) were used in n-Pentyl alcohol (2 mL) at 130 °C for 96 h. Only a minor portion was converted to the iodide (as determined from GC MS). Isolation by column chromatography on silica gel (pentane/CH₂Cl₂ 9/1) provided with an inseparable mixture of the starting material 8c (from ¹⁹F NMR). This mixture of compounds was used for the next step without any further purification.

¹⁹F NMR (CDCl₃, 282 MHz) δ = 53.38 (d, 4F), 77.25 (quintet, 1F).
4-iodo-2-pyridylsulfur pentafluoride (7d):

Following the General method B, 4-amino-2-pyridylsulfur pentafluoride (550 mg, 2.5 mmol), tetrafluoroboric acid (2 mL), NaNO₂ (190 mg, 2.75 mmol in 1.5 mL H₂O) and KI (664 mg, 4 mmol in 6 mL H₂O) were used at 0 °C—rt for 1 h. The crude product was purified by column chromatography on silica gel (n-hexane/EtOAc, 9/1) to give the desired product (633 mg, 76% yield) as white solid.

m.p.: 77.8 °C; HRMS (EI) calcd. for C₁₃H₁₇F₁₅N₂S: 330.8951 found 330.8973; ¹H NMR (CDCl₃, 300 MHz) δ = 7.88 (d, J = 3 Hz, 1H), 8.12 (s, 1H), 8.27 (d, J = 6 Hz, 1H); ¹³F NMR (CDCl₃, 282 MHz) δ = 52.26 (d, J = 149.46 Hz, 4F), 76.83 (quintet, J = 152.28 Hz, 1F); ¹³C NMR (CDCl₃, 126 MHz) δ = 106.60, 130.53 (quintet, J = 5Hz), 136.24, 148.47, 165.38 (quintet, J = 22.5 Hz). ATR-FTIR (NaCl): ν = 3119, 3051, 2466, 1558, 1457, 1376, 1140, 1086, 823, 655 cm⁻¹.

**Synthesis of pyridine aryliodonium salts 1:**

Pyridine aryliodonium salts 1 were prepared by modified procedure as given in the literature.⁷

Following the general procedure, mCPBA (assume 70-77 wt%, 1.5 eq.) was dried in vacuo at room temperature for 1 h before addition of iodo-2-pyridylsulfur pentafluoride 2 (1.0 eq.) and CH₂Cl₂ (6.0 mL/mmol ArI) in a round bottomed flask. The solution was cooled to 0 °C followed by dropwise addition of TFOH (4.0 eq.), resulting mixture was stirred at room temperature for 2 h. It was then cooled to 0 °C and mesitylene (1.1 eq.) was added dropwise. The mixture was warmed to room temperature and stirred for 18 h. The solvent was then removed under reduced pressure. The resulting crude product was precipitated by the addition of Et₂O and storing at -20 °C for several hours. The precipitate was filtered and dried in vacuo to give 1 as white to brown solid.

**Mesityl(2-(pentafluoro-α-sulfanyl)pyridyl)-6-iodonium trifluoromethanesulfonate 1a:**

Following the general procedure, mCPBA (assume 70 wt%, 1.85 g, 7.5 mmol), 6-iodo-2-pyridylsulfur pentafluoride 7a (1.8 g, 5.0 mmol), TFOH (2.3 mL, 20 mmol) and mesitylene (0.76 mL, 5.5 mmol) were used in CH₂Cl₂ (30 mL) at room temperature for 18 h to give 1a (1.8 g, 61% yield) as white solid.

m.p.: 117.9 °C; HRMS (ESI) calcd. for C₂₅H₂₀F₁₄N₂O₃S: 449.9812 found 449.9807; ¹H NMR (CDCl₃, 300 MHz) δ = 7.88 (d, J = 9 Hz, 1H), 8.03 (t, J = 6 Hz, 1H), 8.55 (d, J = 9 Hz, 1H); ¹³F NMR (CDCl₃, 282 MHz) δ = -78.95 (s, 3F), 52.66 (d, J = 152.28 Hz, 4F), 74.78 (quintet, J = 152.28 Hz, 1F); ¹³C NMR (CDCl₃, 126 MHz) δ = 21.31, 27.13, 121.99, 124.10, 130.06, 130.66, 134.70, 143.06 (d, J = 12.6 Hz), 144.73, 164.86–165.26 (m). ATR-FTIR (KBr): ν = 3024, 2928, 1550, 1420, 1407, 1260, 1177, 1098, 1035, 799 cm⁻¹.

**Mesityl(2-(pentafluoro-α-sulfanyl)pyridyl)-5-iodonium trifluoromethanesulfonate 1b:**

Following the general procedure, mCPBA (assume 77 wt%, 1.8 g, 8.1 mmol), 5-iodo-2-pyridylsulfur pentafluoride 7b (1.8 g, 5.4 mmol), TFOH (2.5 mL, 21.7 mmol) and mesitylene (0.80 mL, 5.94 mmol) were used in CH₂Cl₂ (30 mL) at room temperature for 18 h to give 1b (1.97 g, 61% yield) as white solid.

m.p.: 175.1 °C; HRMS (ESI) calcd. for C₂₅H₂₀F₁₄N₂O₃S: 449.9812 found 449.9825; ¹H NMR ((CD₃)₂CO, 300 MHz) δ = 2.38 (s, 3H), 2.76 (s, 6H), 7.33 (s, 2H), 8.15 (d, J = 9 Hz, 1H), 8.82 (d, J = 9 Hz, 1H), 9.15 (s, 1H); ¹³F NMR ((CD₃)₂CO, 282 MHz) δ = -
77.89 (s, 3F), 53.28 (d, $J = 146.64$ Hz, 4F), 77.34 (quintet, $J = 146.64$ Hz, 1F); $^{13}$C NMR ((CD$_3$)$_2$CO, 126 MHz) $\delta = 20.01$, 26.19, 114.43, 121.01, 124.61-124.77 (m), 130.36, 142.76, 144.87, 145.23, 151.37, 165.56-166.31. ATR-FTIR (KBr): $\nu = 3060, 2992, 1451, 1275, 1231, 1170, 1029, 995, 879, 844$ cm$^{-1}$.

**Mesityl(2-(pentafluoro-$\lambda^6$-sulfaneyl)pyridyl)-3-iodonium trifluoromethanesulfonate 1c:**

Following the general procedure, mCPBA (assume 70 wt%, 347.6 mg, 1.41 mmol), 3-iodo-2-pyridylsulfur pentafluoride 7c (310 mg, 0.94 mmol), TfOH (0.4 mL, 3.76 mmol) and mesitylene (0.14 mL, 1.034 mmol) were used in CH$_2$Cl$_2$ (6 mL) at room temperature for 18 h to give 1c (40 mg, 5% yield in overall two steps starting from the 3-bromo-2-pyridylsulfur pentafluoride 8c) as brown solid. m.p.: 129.4 °C; HRMS (ESI) calcd. for C$_{14}$H$_{14}$NF$_5$SI [(M-OTf)$^+$]:449.9812 found 449.9812; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta = 2.44$ (s, 3H), 2.60 (s, 6H), 7.25 (s, 2H), 7.52 (t, $J = 6$ Hz, 2H), 8.71 (s, 1H); $^{19}$F NMR (CDCl$_3$, 282 MHz) $\delta = -78.98$ (s, 3F), 53.63 (d, $J = 149.46$ Hz, 4F), 75.86 (quintet, $J = 152.28$ Hz, 1F); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta = 21.45, 27.25, 104.29, 121.61, 130.44, 131.36, 142.09, 143.41, 146.87, 149.66, 163.16-163.58$ (m). ATR-FTIR (KBr): $\nu = 3061, 2925, 1550, 1456, 1394, 1283, 1241, 1172, 1025, 848$ cm$^{-1}$.

**Mesityl(2-(pentafluoro-$\lambda^6$-sulfaneyl)pyridyl)-4-iodonium trifluoromethanesulfonate 1d:**

Following the general procedure, mCPBA (assume 70 wt%, 554 mg, 2.25 mmol), 4-iodo-2-pyridylsulfur pentafluoride (496 mg, 1.5 mmol), TfOH (0.68 mL, 6.0 mmol) and mesitylene (0.23 mL, 1.65 mmol) were used in CH$_2$Cl$_2$ (9 mL) at room temperature for 18 h to give 1d (500 mg, 56% yield) as beige solid. m.p.: 156.9 °C; HRMS (ESI) calcd. for C$_{14}$H$_{14}$NF$_5$SI [(M-OTf)$^+$]:449.9812 found 449.9808; $^1$H NMR ((CD$_3$)$_2$CO, 300 MHz) $\delta = 2.41$ (s, 3H), 2.72 (s, 6H), 7.37 (s, 2H), 8.01 (d, $J = 6$ Hz, 1H), 8.65 (s, 1H), 8.71 (d, $J = 3$ Hz, 1H); $^{19}$F NMR ((CD$_3$)$_2$CO, 282 MHz) $\delta = -76.78$ (s, 3F), 54.61 (d, $J = 152.28$ Hz, 4F), 78.62 (quintet, $J = 152.28$ Hz, 1F); $^{13}$C NMR ((CD$_3$)$_2$CO, 126 MHz) $\delta = 20.07, 26.12, 120.46, 124.19, 125.57$ (quintet, $J = 3.75$ Hz), 130.46, 130.72, 143.07, 145.30, 150.92, 164.78-165.53, 209.11. ATR-FTIR (KBr): $\nu = 3038, 2972, 2250, 1700, 1551, 1538, 1166, 1024, 827, 712$ cm$^{-1}$.

**SF$_5$-heteroarylation of $\beta$-ketoesters:**

The $\beta$-ketoesters were prepared according to the literature procedure.$^8$

![Diagram of SF$_5$-heteroarylation of $\beta$-ketoesters](image)

A flame dried test tube was charged with the $\beta$-ketoester 9 (0.1 mmol), NaH (60% suspension in oil, 0.12 mmol) in DMF (10 mL/mmole $\beta$-ketoester) and stirred for 10 min at room temperature. The reagent 1 (0.11 mmol) was then added to the mixture in one portion at room temperature. After completion of the reaction, H$_2$O was slowly added to the reaction mixture and extracted with Et$_2$O three times. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give (2-pyridyl-SF$_5$)-$\beta$-ketoester 2.
Methyl 1-oxo-2-(6-(pentafluoro-λ⁵-sulfaneyl)pyridin-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (2aa):

Following general procedure β-ketoester 9a, (19 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1a (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 2aa as white solid (30 mg) in 76% yield.

\[ \text{M. p.: 124.7 °C; HRMS (EI) calcd. for C}_{15}\text{H}_{19}\text{NO}_{2}\text{F}_5\text{S} ([M]+):} 393.0458 \text{ found 393.0464; } ^1\text{H NMR (CDCl}_3\text{, 300 MHz)} \delta = 3.22 (d, J = 18 Hz, 1H), 3.71 (s, 3H), 4.58 (d, J = 18 Hz, 1H), 7.31 (d, J = 6 Hz, 1H), 7.45 (t, J = 9 Hz, 1H), 7.52 (d, J = 9 Hz, 2H), 7.70 (t, J = 9 Hz, 1H), 7.86 (t, J = 9 Hz, 2H); \text{^19F} \text{ NMR (CDCl}_3\text{, 282 MHz)} \delta = 62.70 (d, J = 155.1 Hz, 4F), 76.74 (quintet, J = 155.1 Hz, 1F); ^13C \text{ NMR (CDCl}_3\text{, 126 MHz)} \delta = 37.77, 53.77, 64.31, 123.56, 125.35, 126.41, 126.83, 127.05, 128.26, 134.61, 136.80, 153.68, 157.03-157.35 (m), 166.72, 198.52. ATR-FTIR (KBr): ν = 2958, 1709, 1392, 1271, 1247, 1214, 1159, 910, 877, 853 cm⁻¹.

Methyl 1-oxo-2-(6-(pentafluoro-λ⁵-sulfaneyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate (2ba):

Following general procedure β-ketoester 9a, (19 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1b (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 2ba as white solid (20 mg) in 51% yield.

\[ \text{M. p.: 150.4 °C; HRMS (ESI) calcld. for C}_{15}\text{H}_{19}\text{NO}_{2}\text{F}_5\text{S} [(M+Na)^+]:} 416.0356 \text{ found 416.0353; } ^1\text{H NMR (CDCl}_3\text{, 300 MHz)} \delta = 3.63 (d, J = 18 Hz, 1H), 3.76 (s, 3H), 4.27 (d, J = 18 Hz, 1H), 7.48 (t, J = 6 Hz, 1H), 7.55 (d, J = 6 Hz, 1H), 7.69–7.67 (m, 2H) 7.85 (d, J = 9 Hz, 1H), 8.16 (d, J = 9 Hz, 1H), 8.63 (d, J = 6 Hz, 1H); \text{^19F} \text{ NMR (CDCl}_3\text{, 282 MHz)} \delta = 52.14 (d, J = 149.46 Hz, 4F), 77.70 (quintet, J = 149.46 Hz, 1F); ^13C \text{ NMR (CDCl}_3\text{, 126 MHz)} \delta = 39.72, 53.97, 63.00, 121.15 (t, J = 3.78 Hz), 125.65, 126.47, 128.74, 134.31, 136.55, 137.60, 138.45, 147.47, 151.77, 164.55 (t, J = 22.68 Hz), 169.78, 198.60. ATR-FTIR (KBr): ν = 2961, 1724, 1468, 1434, 1285, 1228, 1208, 1177, 846, 761 cm⁻¹.

Methyl 1-oxo-2-(6-(pentafluoro-λ⁵-sulfaneyl)pyridin-4-yl)-2,3-dihydro-1H-indene-2-carboxylate (2da):

Following general procedure β-ketoester 2a, (19 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1d (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 6/4) to give the desired product 2da as yellow oil (30.3 mg) in 77% yield.

\[ \text{HRMS (ESI) calcld. for C}_{15}\text{H}_{19}\text{NO}_{2}\text{F}_5\text{S} [(M+H]^+):} 394.0536 \text{ found 394.0539; } ^1\text{H NMR (CDCl}_3\text{, 300 MHz)} \delta = 3.59 (d, J = 18 Hz, 1H), 3.76 (s, 3H), 4.24 (d, J = 18 Hz, 1H), 7.49 (t, J = 9 Hz, 1H), 7.56 (d, J = 6 Hz, 1H), 7.66–7.75 (m, 2H) 7.85–7.90 (m, 2H), 8.57 (d, J = 6 Hz, 1H); \text{^19F} \text{ NMR (CDCl}_3\text{, 282 MHz)} \delta = 52.06 (d, J = 149.46 Hz, 4F), 77.78 (quintet, J = 149.46 Hz, 1F); ^13C \text{ NMR (CDCl}_3\text{, 126 MHz)} \delta = 39.67, 54.02, 64.41, 120.70 (t, J = 3.75 Hz), 125.69, 126.19, 126.46, 128.76, 134.32, 136.39, 148.32, 150.17, 151.65, 166.03 (quintet, J = 22.5 Hz), 169.31, 197.98. ATR-FTIR (KBr): ν = 3421, 2957, 2847, 1744, 1594, 1217, 1039, 844 cm⁻¹.

Ethyl 1-oxo-2-(6-(pentafluoro-λ⁵-sulfaneyl)pyridin-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (2ab):

[Diagram of the molecule]
Following general procedure β-ketoester 9b, (20 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1a (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2ab as yellow solid (28.5 mg) in 70% yield.
m.p.: 89.0 °C HRMS (EI) calcd. for C_{12}H_{14}NO_{3}F_{3}S ([M]+): 407.0615 found 407.0611; ^{1}H NMR (CDCl_{3}, 300 MHz) δ = 1.15 (t, J = 9 Hz, 3H), 3.22 (d, J = 18 Hz, 1H), 4.03–4.43 (m, 1H), 4.24–4.34 (m, 1H), 1.58 (d, J = 18 Hz, 1H), 1.30 (d, J = 9 Hz, 1H), 1.75 (t, J = 9 Hz, 1H), 7.50–7.54 (m, 2H), 7.67–7.72 (m, 1H), 7.83–7.88 (m, 2H); ^{13}C NMR (CDCl_{3}, 282 MHz) δ = 13.93, 37.74, 62.81, 64.41, 123.46, 125.29, 126.32, 126.81, 127.04, 128.20, 134.67, 136.73, 153.70, 153.82, 166.12, 198.70. IR (KBr): v = 3118, 1736, 1393, 1288, 1272, 1242, 1208, 909, 833, 785 cm^{-1}.

Ethyl 1-oxo-2-(6-(pentafluoro-λ^5-sulfanenyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate (2bb):

Following general procedure β-ketoester 9b, (20 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1b (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2bb as white solid (23.6 mg) in 58% yield.
m.p.: 80.1 °C; HRMS (ESI) calcd. for C_{12}H_{14}F_{3}N_{2}O_{4}S ([M]+): 430.0512 found 430.0515; ^{1}H NMR (CDCl_{3}, 300 MHz) δ = 1.21 (t, J = 9 Hz, 3H), 3.63 (d, J = 18 Hz, 1H), 4.19–4.26 (m, 3H), 7.48 (t, J = 6 Hz, 1H), 7.56 (d, J = 6 Hz, 1H), 7.69–7.76 (m, 2H), 7.86 (d, J = 6 Hz, 1H), 8.16 (d, J = 9 Hz, 1H), 8.64 (s, 1H); ^{19}F NMR (CDCl_{3}, 282 MHz) δ = 52.12 (d, J = 152.28 Hz, 4F), 77.74 (quintet, J = 152.28 Hz, 1F); ^{13}C NMR (CDCl_{3}, 126 MHz) δ = 13.93, 37.74, 62.81, 64.41, 123.46, 125.29, 126.32, 126.81, 127.04, 128.20, 134.67, 136.73, 153.75, 153.82, 166.12, 198.70. IR (KBr): v = 3118, 1736, 1393, 1288, 1272, 1242, 1208, 909, 833, 785 cm^{-1}.

Tert-butyl 1-oxo-2-(6-(pentafluoro-λ^5-sulfanenyl)pyridin-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (2ac):

Following general procedure β-ketoester 9c, (23 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1a (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2ac as white solid (26.1 mg) in 60% yield.
m.p.: 146.3 °C; The compound was unstable for both ESI and EI conditions while analysing HRMS. Hence, it was characterized by ^{1}H, ^{19}F and ^{13}C NMR for purity. ^{1}H NMR (CDCl_{3}, 300 MHz) δ = 1.34 (s, 9H), 3.20 (d, J = 18 Hz, 1H), 4.51 (d, J = 18 Hz, 1H), 7.27 (t, J = 9 Hz, 1H), 7.43 (t, J = 9 Hz, 1H), 7.49–7.53 (m, 2H), 7.65–7.70 (m, 1H), 7.81–7.87 (m, 2H); ^{19}F NMR (CDCl_{3}, 282 MHz) δ = 62.79 (d, J = 155.1 Hz, 4F), 77.11 (quintet, J = 152.28 Hz, 1F); ^{13}C NMR (CDCl_{3}, 126 MHz) δ = 27.56, 37.62, 65.10, 83.05, 123.13, 125.17, 125.97, 126.72, 126.85, 128.05, 134.86, 136.55, 153.87, 154.28, 157.07 (t, J = 18.9 Hz), 164.93, 199.11. ATR-FTIR (KBr): v = 2971, 1715, 1466, 1370, 1288, 1224, 1187, 1006, 759, 747 cm^{-1}.

Tert-butyl 1-oxo-2-(6-(pentafluoro-λ^5-sulfanenyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate (2bc):

Following general procedure β-ketoester 9c, (23 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1b (66 mg, 0.11mmol) in DMF (1 mL) were used at room temperature for 12 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2bc as yellow oil (31.3 mg) in 72% yield.
HRMS (ESI) calcd. for C_{25}H_{21}NO_{3}F_{3}S ([M]+): 548.0825 found 548.0825; ^{1}H NMR (CDCl_{3}, 300 MHz) δ = 1.38 (s, 9H), 3.61 (d, J = 18 Hz, 1H), 4.15 (d, J = 18 Hz, 1H), 7.46 (t, J = 9 Hz, 1F), 7.54 (d, J = 9 Hz, 1H), 7.71 (q, J = 9 Hz, 2H), 7.84 (d, J = 9 Hz, 1H),
8.18 (d, J = 9 Hz, 1H), 8.65 (s, 1H); \(^{19}F\) NMR (CDCl\(_3\), 282 MHz) \(\delta = 52.14\) (d, \(J = 149.46\) Hz, 4F). 77.86 (quintet, \(J = 152.28\) Hz, 1F); \(^{13}C\) NMR (CDCl\(_3\), 126 MHz) \(\delta = 27.78, 39.49, 63.91, 84.05, 120.93\) (t, \(J = 7.56\) Hz), 125.43, 126.35, 128.55, 134.55, 136.23, 137.88, 138.53, 147.48, 151.80, 164.39 (t, \(J = 23.94\) Hz), 168.15, 198.99. ATR-FTIR (NaCl): \(\nu = 2980, 1715, 1606, 1592, 1466, 1395, 1371, 1252, 1148, 847\) cm\(^{-1}\).

**Methyl 6-methyl-1-oxo-2-(6-pentafluoro-α-sulfanyl)pyridin-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (2ad):**

![Image of 2ad structure]

Following general procedure β-ketoester 9d, (20 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1a (66 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2ad as white solid (16 mg) in 40% yield.

m.p.: 150.2 °C; HRMS (EI) calcd. for C\(_{27}\)H\(_{23}\)NO\(_2\)F\(_3\): 407.0615 found 407.0627; \(^1H\) NMR (CDCl\(_3\), 300 MHz) \(\delta = 2.43\) (s, 3H), 3.16 (d, \(J = 18\) Hz, 1H), 3.70 (s, 3H), 4.52 (d, \(J = 18\) Hz, 1H), 7.29 (d, \(J = 9\) Hz, 1H), 7.39 (d, \(J = 9\) Hz, 1H), 7.51 (d, \(J = 6\) Hz, 2H), 7.66 (s, 1H), 7.84 (dd, \(J = 9\) Hz, 3 Hz, 1H); \(^{19}F\) NMR (CDCl\(_3\), 282 MHz) \(\delta = 62.68\) (d, \(J = 155.1\) Hz, 4F), 76.77 (quintet, \(J = 155.1\) Hz, 1F); \(^{13}C\) NMR (CDCl\(_3\), 126 MHz) \(\delta = 21.22, 37.44, 53.73, 64.64, 123.50, 125.12, 126.36, 126.49, 127.01, 134.79, 138.16, 138.38, 151.15, 153.85, 157.18, 166.80, 198.56. ATR-FTIR (KBr): \(\nu = 2955, 1746, 1718, 1391, 1291, 1234, 886, 855, 835, 819\) cm\(^{-1}\).

**Methyl 6-methyl-1-oxo-2-(6-pentafluoro-α-sulfanyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate (2bd):**

![Image of 2bd structure]

Following general procedure β-ketoester 9d, (20 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1b (66 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2bd as white solid (21.3 mg) in 56% yield.

m.p.: 112.9 °C; HRMS (ESI) calcd. for C\(_{27}\)H\(_{23}\)NO\(_2\)F\(_3\)Na\([\text{M}+\text{Na}]\)^+: 430.0512 found 430.0517; \(^1H\) NMR (CDCl\(_3\), 300 MHz) \(\delta = 2.43\) (s, 3H), 3.57 (d, \(J = 18\) Hz, 1H), 3.75 (s, 3H), 4.17 (d, \(J = 15\) Hz, 1H), 7.43 (d, \(J = 6\) Hz, 1H), 7.52 (d, \(J = 6\) Hz, 1H), 7.65 (s, 1H), 7.73 (d, \(J = 9\) Hz, 1H), 8.14 (d, \(J = 9\) Hz, 1H), 8.62 (s, 1H); \(^{19}F\) NMR (CDCl\(_3\), 282 MHz) \(\delta = 52.15\) (d, \(J = 149.46\) Hz, 4F), 77.76 (quintet, \(J = 152.28\) Hz, 1F); \(^{13}C\) NMR (CDCl\(_3\), 126 MHz) \(\delta = 21.24, 39.45, 53.90, 63.33, 121.11\) (t, \(J = 3.78\) Hz), 125.46, 126.12, 134.47, 137.74, 137.84, 138.44, 138.90, 147.48, 149.19, 164.49 (t, \(J = 23.94\) Hz), 169.92, 198.65. ATR-FTIR (KBr): \(\nu = 2954, 1714, 1498, 1468, 1430, 1234, 1156, 836, 770, 597\) cm\(^{-1}\).

**Methyl 5,6-dimethoxy-1-oxo-2-(6-pentafluoro-α-sulfanyl)pyridin-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (2ae):**

![Image of 2ae structure]

Following general procedure β-ketoester 9e, (25 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1a (66 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 8/2) to give the desired product 2ae as white solid (41.6 mg) in 92% yield.

m.p.: 163.7 °C; HRMS (ESI) calcd. for C\(_{32}\)H\(_{25}\)NO\(_3\)F\(_2\)Na\([\text{M}+\text{Na}]\)^+: 476.0576 found 476.0577; \(^1H\) NMR (CDCl\(_3\), 300 MHz) \(\delta = 3.75-3.82\) (m, 4H), 3.90 (s, 3H), 4.01 (s, 3H), 4.47 (d, \(J = 18\) Hz, 1H), 7.00 (s, 1H), 7.16 (s, 1H), 7.67 (d, \(J = 6\) Hz, 1H), 7.94 (t, \(J = 6\) Hz, 1H), 8.10 (d, \(J = 9\) Hz, 1H); \(^{19}F\) NMR (CDCl\(_3\), 282 MHz) \(\delta = 52.26\) (d, \(J = 149.46\) Hz, 4F), 77.98 (quintet, \(J = 149.46\) Hz, 1F); \(^{13}C\) NMR (CDCl\(_3\), 126 MHz) \(\delta = 36.19, 53.50, 56.24, 56.55, 67.39, 105.24, 107.34, 120.37\) (t, \(J = 5.04\) Hz), 126.67, 127.80, 139.04, 149.71, 150.04, 154.65, 156.77, 163.96 (t, \(J = 22.68\) Hz), 170.69, 197.50. ATR-FTIR (KBr): \(\nu = 2945, 1726, 1682, 1590, 1507, 1439, 1278, 1260, 1237, 1127, 850, 610\) cm\(^{-1}\).
Methyl 5,6-dimethoxy-1-oxo-2-(6-pentafluoro-λ⁶-sulfaneyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate (2be):

Following general procedure β-ketoester 9e, (25 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent 1b (66 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 2be as white solid (30.3 mg) in 67% yield.

m.p.: 165.4 °C; HRMS (ESI) calcd. for C₄₃H₃₄NO₂F₃NaS [(M+Na)⁺]: 746.0566; ¹H NMR (CDCl₃, 300 MHz) δ = 3.49 (d, J = 18 Hz, 1H), 3.76 (s, 3H), 3.93 (s, 3H), 4.01 (s, 3H), 4.14 (d, J = 15 Hz, 1H), 6.94 (s, 1H), 7.23 (s, 1H), 7.73 (d, J = 9 Hz, 1H), 8.14 (J = 9 Hz, 1H), 8.60 (d, J = 3 Hz, 1H); ¹⁹F NMR (CDCl₃, 282 MHz) δ = 52.15, (d, J = 149.46 Hz, 4F), 77.81 (quintet, J = 149.46 Hz, 1F); ¹³C NMR (CDCl₃, 126 MHz) δ = 53.89, 56.37, 56.64, 63.35, 105.41, 107.11, 121.11 (t, J = 3.78 Hz), 127.02, 138.20, 138.39, 147.51, 147.66, 150.46, 157.08, 164.43 (t, J = 23.94 Hz), 170.05, 196.95. ATR-FTIR (KBr): ν = 2959, 1732, 1700, 1594, 1505, 1468, 1316, 1284, 1120, 874, 833, 769 cm⁻¹.

SF₅-heteroarylation of pyroles:

The heteroarylation of pyroles were performed according to literature procedure.⁹

A reflux tube equipped with a magnetic stir bar was charged with reagent 1a or 1b (1.0 eq.), NaOH (1.5 eq.), pyrrole 10 (0.5 mL/mmol), and the reaction vessel was placed in an 80 °C oil bath. After stirring at this temperature for 10 h, the mixture was distilled in vacuo to recover the redundant pyrrole. The residue was cooled to room temperature, diluted with ethyl acetate, and washed with brine (15 mL) and water (15 mL), and then the organic layer was dried over Na₂SO₄. After being concentrated in vacuo, the crude product was purified by column chromatography on silica gel (n-hexane/EtOAc).

5-(1H-pyrrol-2-yl)-2-(pentafluoro-λ⁶-sulfaneyl)pyridine (3ba):

Following general procedure reagent 1b (60 mg, 0.1 mmol), NaOH (6 mg, 0.15 mmol) in pyrrole 10a (0.5 mL) were used at 80 °C for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 4/1) to give the desired product 3ba as white solid (18 mg) in 66% yield.

m.p.: 158.3 °C; HRMS (ESI) calcd. for C₃₃H₂₄N₂N₂F₁₂S [(M⁺): 721.0328 found 721.0320; ¹H NMR (CDCl₃, 300 MHz) δ = 6.375 (q, J = 3 Hz, 1H), 6.71 (s, 1H), 7.005 (d, J = 3 Hz, 1H), 7.72 (d, J = 9 Hz, 1H), 7.89 (d, J = 9 Hz, 1H), 8.65 (s, 1H), 8.66 (s, 1H); ¹⁹F NMR (CDCl₃, 282 MHz) δ = 52.49 (d, J = 149.46 Hz, 4F), 78.76 (quintet, J = 149.46 Hz, 1F); ¹³C NMR (CDCl₃, 126 MHz) δ = 109.74, 111.34, 121.75 (quintet, J = 3.78 Hz), 121.90, 126.84, 131.85, 132.56, 142.57, 162.75 (t, J = 23.94 Hz). ATR-FTIR (KBr): ν = 3253, 2956, 1594, 1479, 1456, 114, 1120, 870, 780, 680 cm⁻¹.

2-(3,5-dimethyl-1H-pyrrol-2-yl)-6-(pentafluoro-λ⁶-sulfaneyl)pyridine (3ab):

Following general procedure reagent 1a (60 mg, 0.1 mmol), NaOH (6 mg, 0.15 mmol) in pyrrole 10b (0.5 mL) were used at 80 °C for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 4/1) to give the desired product 3ab as light yellow solid (29 mg) in 97% yield.

S13
m.p.: 66.9 °C; HRMS (ESI) calcd. for C_{16}H_{22}F_{5}S [[(M)^+]: 285.0485 found 285.0492; 1H NMR (CDCl$_3$, 300 MHz) $\delta$ = 2.31 (s, 3H), 2.35 (s, 3H), 5.80 (s, 1H), 7.33 (d, $J$ = 6 Hz, 1H), 7.52 (d, $J$ = 9 Hz, 1H), 7.77 (t, $J$ = 9 Hz, 1H), 9.04 (brs, 1H); 19F NMR (CDCl$_3$, 282 MHz) $\delta$ = 51.03 (d, $J$ = 149.46 Hz, 4F), 78.77 (quintet, $J$ = 149.46 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) $\delta$ = 37.74, 108.04, 112.34, 116.54 (quintet, $J$ = 3.78 Hz), 122.91, 128.30, 129.61, 138.61, 151.10, 163.96 (t, $J$ = 21.42 Hz). ATR-FTIR (KBr): $\nu$ = 3453, 2924, 1604, 1508, 1464, 850, 820, 790, 760, 720 cm$^{-1}$.

2-(1-methyl-1H-pyrrol-2-yl)-6-(pentafluoro-λ$^5$-sulfenyl)pyridine (3ac):

Following general procedure reagent 1a (60 mg, 0.1 mmol), NaOH (6 mg, 0.15 mmol) in pyrrole 10c (0.5 mL) were used at 80 °C for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 4/1) to give the desired product 3ac as white solid (12.6 mg) in 44% yield.

m.p.: 56.6 °C; HRMS (ESI) calcd. for C$_{16}$H$_{22}$N$_{2}$O$_{2}$S [[(M)$^+$/Na$^+$]: 361.0410 found 361.0414; 1H NMR (CDCl$_3$, 300 MHz) $\delta$ = 4.03 (s, 3H), 6.19 (s, 1H), 6.76 (d, $J$ = 12 Hz, 2H), 7.43 (d, $J$ = 9 Hz, 1H), 7.68 (d, $J$ = 9 Hz, 1H), 7.80 (t, $J$ = 9 Hz, 1H); 19F NMR (CDCl$_3$, 282 MHz) $\delta$ = 51.21 (d, $J$ = 149.46 Hz, 4F), 78.53 (quintet, $J$ = 149.46 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) $\delta$ = 37.74, 108.04, 112.34, 116.54 (quintet, $J$ = 3.78 Hz), 122.91, 128.30, 129.61, 138.61, 151.10, 163.96 (t, $J$ = 21.42 Hz). ATR-FTIR (KBr): $\nu$ = 3111, 2958, 1595, 1542, 1486, 1451, 1181, 1090, 910, 855, 733, 680, 611 cm$^{-1}$.

**SF$_5$-heteroarylation of secondary amides:**

The heteroarylation of secondary amides were performed according to literature procedure.$^{10}$

The secondary amide 11 (1.0 eq.), reagent 1a or 1b (1.5 eq.) and NaH (60%, 1.5 eq.) were added to a flame dried schlenk tube. The tube was evacuated and backfilled with nitrogen three times. The stirring was started and anhydrous toluene (2 mL/mmol) was added. The solution was stirred at rt~65 °C for 4–10 h. The crude reaction mixture was then transferred to a round flask using ethyl acetate. The solvent was evaporated and then the crude reaction mixture was purified using column chromatography on silica gel or preparative thin-layer plates (PLC) to yield the product 4.

$N$-phenyl-$N$-{6-(pentafluoro-λ$^5$-sulfenyl)pyridin-2-yl}acetamide (4aa):

Prepared according to general procedure using amide 11a (14 mg, 0.1 mmol), reagent 1a (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at rt for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 4aa as yellow solid (14 mg) in 43% yield.

m.p.: 108.2 °C; HRMS (ESI) calcd. for C$_{16}$H$_{22}$N$_{2}$OF$_{2}$Na$^+$ [[(M+Na)$^+$]: 361.0401 found 361.0414; 1H NMR (CDCl$_3$, 300 MHz) $\delta$ = 2.17 (s, 3H), 7.27 (d, $J$ = 9 Hz, 2H), 7.37–7.49 (m, 4H), 7.79–7.90 (m, 2H); 19F NMR (CDCl$_3$, 282 MHz) $\delta$ = 51.63 (d, $J$ = 152.28 Hz, 4F), 77.47 (quintet, $J$ = 149.46 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) $\delta$ = 25.14, 117.53 (quintet, $J$ = 3.78 Hz), 122.36, 128.53, 129.15, 129.75, 140.07, 141.09, 153.00, 163.00 (t, $J$ = 22.68 Hz), 171.62. ATR-FTIR (NaCl): $\nu$ = 3067, 1694, 1589, 1441, 1371, 1295, 848, 738, 698, 595 cm$^{-1}$.
**N-phenyl-N-(6-pentafluoro-λ⁶-sulfaneyl)pyridin-3-ylacetamide (4ba):**

![Chemical Structure](attachment:structure.png)

Prepared according to general procedure using amide 11a (14 mg, 0.1 mmol), reagent 1b (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at 55 °C for 4 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 4ba as yellow solid (15 mg) in 44% yield.

m.p.: 129.8 °C; HRMS (ESI) calcd. for C₁₃H₁₂F₆N₄O₆SNa [(M+Na)⁺]: 396.0723 found 396.0730; ¹H NMR (CDCl₃, 300 MHz) δ = 2.09 (s, 3H), 7.26–7.31 (m, 2H), 7.44–7.56 (m, 3H), 7.69 (d, J = 9 Hz, 1H), 7.64 (d, J = 9 Hz, 1H), 8.395 (d, J = 3 Hz, 1H); ¹³C NMR (CDCl₃, 282 MHz) δ = 52.63 (d, J = 149.46 Hz, 4F), 78.20 (quintet, J = 149.46 Hz, 1F); ¹⁹F NMR (CDCl₃, 282 MHz) δ = 24.34, 121.41, 128.87, 129.31, 130.72, 134.00, 141.29, 143.97, 170.98. ATR-FTIR (KBr): ν = 3210, 3071, 1440, 1380, 1299, 1255, 1190, 1151, 792, 709 cm⁻¹.

**N-phenyl-N-(6-pentafluoro-λ⁶-sulfaneyl)pyridin-2-ylisobutyramide (4ab):**

![Chemical Structure](attachment:structure.png)

Prepared according to general procedure using amide 11b (16 mg, 0.1 mmol), reagent 1a (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at rt for 7.5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 4/1) to give the desired product 4ab as colourless oil (30 mg) in 82% yield.

HRMS (ESI) calcd. for C₁₃H₁₂F₆N₄O₆SNa [(M+Na)⁺]: 396.0723 found 396.0730; ¹H NMR (CDCl₃, 300 MHz) δ = 1.16 (d, J = 6 Hz, 6H), 2.78 (quintet, J = 9 Hz, 1H), 7.27 (d, J = 6 Hz, 2H), 7.38–7.48 (m, 4H), 7.77–7.86 (m, 2H); ¹³C NMR (CDCl₃, 282 MHz) δ = 51.65 (d, J = 149.46 Hz, 4F), 77.55 (quintet, J = 149.46 Hz, 1F); ¹⁹F NMR (CDCl₃, 282 MHz) δ = 19.71, 33.33, 117.48 (quintet, J = 8.46 Hz), 122.80, 128.37, 129.22, 129.64, 139.90, 140.88, 153.29, 163.07 (t, J = 53.58 Hz), 178.91. ATR-FTIR (NaCl): ν = 2978, 2936, 2876, 1683, 1588, 1442, 1252, 851, 801, 597 cm⁻¹.

**N-phenyl-N-(6-pentafluoro-λ⁶-sulfaneyl)pyridin-3-ylisobutyramide (4bb):**

![Chemical Structure](attachment:structure.png)

Prepared according to general procedure using amide 11b (16.3 mg, 0.1 mmol), reagent 1b (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at 65 °C for 5 h. Isolated by using preparative thin-layer plates (PLC) (n-hexane/EtOAc, 4/1) to give the desired product 4bb as yellow oil (23 mg) in 63% yield.

HRMS (ESI) calcd. for C₁₃H₁₂F₆N₄O₆SNa [(M+Na)⁺]: 396.0723 found 396.0719; ¹H NMR (CDCl₃, 300 MHz) δ = 1.0410 (t, J = 3 Hz, 6H), 2.61 – 2.74 (m, 1H), 7.26–7.30 (m, 2H), 7.43–7.54 (m, 3H), 7.68 (d, J = 9 Hz, 1H), 7.90 (d, J = 9 Hz, 1H), 8.32 (d, J = 2.7 Hz, 1H); ¹³C NMR (CDCl₃, 282 MHz) δ = 52.63 (d, J = 152.28 Hz, 4F), 78.26 (quintet, J = 149.46 Hz, 1F); ¹⁹F NMR (CDCl₃, 282 MHz) δ = 19.65, 32.53, 121.29 (t, J = 3.78 Hz), 128.91, 129.16, 130.66, 134.36, 140.96, 142.04, 144.24, 161.08 (t, J = 21.42 Hz), 178.20. ATR-FTIR (NaCl): ν = 2979, 2935, 2876, 1682, 1595, 1492, 1386, 1299, 1242, 858, 702, 598 cm⁻¹.
\(N\)-(4-nitrophenyl)-\(N\)-(6-pentafluoro-\(\lambda^6\)-sulfaneyl)pyridin-2-yl)acetamide (4ac):

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N} \\
\text{SF}_5
\end{array}
\]

Prepared according to general procedure using amide 11c (18 mg, 0.1 mmol), reagent 1a (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at rt for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 4ac as yellow solid (37.5 mg) in 98% yield.

m.p.: 108.2 °C; HRMS (ESI) calcd. for C\(_{13}\)H\(_9\)N\(_2\)O\(_3\)F\(_5\)Na\(_5\) [[M+Na]\(^+\)]: 406.0261 found 406.0258; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 2.21\) (s, 3H), 7.45 (d, \(J = 9\) Hz, 2H), 7.59 (d, \(J = 9\) Hz, 1H), 7.74 (d, \(J = 6\) Hz, 1H), 7.96 (t, \(J = 9\) Hz, 1H), 8.32 (d, \(J = 9\) Hz, 2H); \(^{19}\)F NMR (CDCl\(_3\), 282 MHz) \(\delta = 51.86\) (d, \(J = 149.46\) Hz, 4F), 76.92 (quintet, \(J = 149.46\) Hz, 1F); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta = 25.12, 118.61\) (t, \(J = 3.78\) Hz), 122.71, 125.06, 129.61, 140.85, 146.73, 147.07, 152.40, 163.22 (t, \(J = 23.94\) Hz), 171.62.

\(N\)-(4-nitrophenyl)-\(N\)-(6-pentafluoro-\(\lambda^3\)-sulfaneyl)pyridin-3-yl)acetamide (4bc):

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N} \\
\text{SF}_5
\end{array}
\]

Prepared according to general procedure using amide 11c (18 mg, 0.1 mmol), reagent 1b (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at 55 °C for 5.5 h. Isolated by using preparative thin-layer plates (PLC) (n-hexane/EtOAc, 7/3) to give the desired product 4bc as yellow oil (22 mg) in 50% yield.

HRMS (ESI) calcd. for C\(_{11}\)H\(_7\)N\(_2\)O\(_2\)F\(_5\)S ([M\(^{+}\)][M+Na]\(^{+}\)]: 384.0441 found 384.0438; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 2.21\) (s, 3H), 7.45 (d, \(J = 9\) Hz, 2H), 7.59 (d, \(J = 9\) Hz, 1H), 7.74 (d, \(J = 6\) Hz, 1H), 7.96 (t, \(J = 9\) Hz, 1H), 8.32 (d, \(J = 9\) Hz, 2H); \(^{19}\)F NMR (CDCl\(_3\), 282 MHz) \(\delta = 51.88\) (d, \(J = 152.28\) Hz, 4F), 76.94 (quintet, \(J = 149.46\) Hz, 1F); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta = 42.18, 122.17, 125.68, 128.94, 131.04, 141.07, 146.91, 169.76\). IR (NaCl): \(\nu = 2357, 1652, 1507, 1456, 1260, 900, 820, 513\) cm\(^{-1}\).

\(N\)-phenyl-\(N\)-(6-pentafluoro-\(\lambda^3\)-sulfaneyl)pyridin-2-yl)benzamide (4ad):

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N} \\
\text{SF}_5
\end{array}
\]

Prepared according to general procedure using amide 11d (20 mg, 0.1 mmol), reagent 1a (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at rt for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 4ad as white solid (28 mg) in 70% yield.

m.p.: 119.5 °C; HRMS (ESI) calcd. for C\(_{12}\)H\(_{10}\)N\(_2\)O\(_4\)F\(_5\)Na\(_6\) [[M+Na]\(^{+}\)]: 423.0566 found 423.0556; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 7.18-7.38\) (m, 8H), 7.44-7.50 (m, 4H), 7.85 (t, \(J = 6\) Hz, 1H); \(^{19}\)F NMR (CDCl\(_3\), 282 MHz) \(\delta = 51.74\) (d, \(J = 160.74\) Hz, 4F), 77.18 (quintet, \(J = 149.46\) Hz, 1F); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta = 117.77\) (t, \(J = 3.78\) Hz), 122.82, 127.64, 128.18, 128.37, 129.56, 130.84, 135.77, 140.07, 141.80, 154.50, 163.28 (t, \(J = 23.94\) Hz), 171.62. ATR-FTIR (KBr): \(\nu = 3102, 3074, 1682, 1655, 1586, 1445, 1306, 1269, 867, 835\) cm\(^{-1}\).
N-(4-methoxyphenyl)-N-(6-pentafluoro-λ₆-sulfaneyl)pyridin-2-yl]benzamide (4ae):

Prepared according to general procedure using amide 11e (23 mg, 0.1 mmol), reagent 1a (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at rt for 10 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 4ae as yellow solid (22.3 mg) in 52% yield.

m.p.: 121.5 °C; HRMS (ESI) calcd. for C₁₉H₁₅N₂O₂F₅NaS [(M+Na)+]: 454.0750 found 453.0672;

1H NMR (CDCl₃, 300 MHz) δ = 3.80 (s, 3H), 6.86 (d, J = 9 Hz, 2H), 7.12 (d, J = 9 Hz, 2H), 7.22–7.32 (m, 4H), 7.44–7.50 (m, 4H), 7.84 (t, J = 6 Hz, 1H);

19F NMR (CDCl₃, 282 MHz) δ = 51.72 (d, J = 149.46 Hz, 4F), 77.26 (quintet, J = 149.46 Hz, 1F);

13C NMR (CDCl₃, 126 MHz) δ = 54.57, 113.79, 116.57 (t, J = 3.78 Hz), 121.57, 127.17, 127.88, 128.63, 129.69, 133.47, 134.93, 138.98, 153.63, 157.86, 162.24 (t, J = 23.94 Hz), 170.71. ATR-FTIR (KBr): ν = 2962, 1410, 1377, 1311, 1266, 1140, 1106, 1004, 953, 781 cm⁻¹.

N-(4-methoxyphenyl)-N-(6-pentafluoro-λ₆-sulfanyle)pyridin-3-yl]benzamide (4be):

Prepared according to general procedure using amide 11e (23 mg, 0.1 mmol), reagent 1b (90 mg, 0.15 mmol), NaH (60%, 6.1 mg, 0.15 mmol) in toluene (2 mL) at 55 °C for 5.5 h. Isolated by column chromatography on silica gel (n-hexane/EtOAc, 7/3) to give the desired product 4be as yellow oil (11.8 mg) in 30% yield.

HRMS (ESI) calcd. for C₁₉H₁₄N₂O₂F₅NaS [(M+Na)+]: 453.0672 found 453.0672;

1H NMR (CDCl₃, 300 MHz) δ = 3.78 (s, 3H), 6.83 (d, J = 9 Hz, 2H), 7.01 (d, J = 9 Hz, 2H), 7.23–7.37 (m, 3H), 7.44 (d, J = 6 Hz, 2H), 7.69–7.78 (m, 2H), 8.385 (d, J = 3 Hz, 1H);

19F NMR (CDCl₃, 282 MHz) δ = 52.72 (d, J = 149.46 Hz, 4F), 78.24 (quintet, J = 152.28 Hz, 1F);

13C NMR (CDCl₃, 126 MHz) δ = 55.57, 114.79, 117.57 (t, J = 3.78 Hz), 122.57, 128.17, 128.88, 129.63, 130.69, 134.47, 135.93, 139.98, 154.63, 158.86, 163.24 (t, J = 23.94 Hz), 171.72. ATR-FTIR (NaCl): ν = 3063, 2936, 2841, 1681, 1578, 1506, 1470, 1278, 1031, 874 cm⁻¹.

SF₅-heteroarylation of amines:

The heteroarylation of amines were performed according to literature procedure.¹¹

To a flame dried test tube, Cu (0) powder (10 mol %), NMP (2.0 mL/mmol aniline) and aniline 12 (1.0 eq.) were added and the resulting mixture was stirred at room temperature for 10 min under nitrogen. To the mixture, reagent 1a or 1b (1.1 eq.) was added in one portion and the mixture was then stirred at 80 °C. After completion of the reaction, the mixture was cooled to room temperature, filtered through a pad of silica and the residue was rinsed with Et₂O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give the desired product 5.
**N-phenyl-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine (Saa):**

![Chemical structure of N-phenyl-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine](image)

Prepared according to the general procedure using aniline 12a (18.2 μL, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent 1a (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 5 h. Isolated by column chromatography (n-hexane/EtOAc, 7/3) to give the desired product Saa as green solid (44 mg) in 74% yield.

m.p.: 58.0 °C; HRMS (ESI) calcd. for C_{18}H_{12}F_{16}N_{2}S: 397.0485 found 397.0485; 1H NMR (CDCl$_3$, 300 MHz) δ = 6.68 (brs, 1H), 6.92 (d, J = 9 Hz, 1H), 7.12 (d, J = 6 Hz, 2H), 7.36–7.38 (m, 4H), 7.64 (t, J = 9 Hz, 1H); 19F NMR (CDCl$_3$, 282 MHz) δ = 51.40 (d, J = 149.46 Hz, 4F), 79.01 (quintet, J = 149.46 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) δ = 111.05, 111.27 (quintet, J = 3.78 Hz), 120.70, 124.01, 129.60, 139.29, 154.38, 164.14 (t, J = 22.68 Hz). ATR-FTIR (KBr): ν = 3116, 3086, 1697, 1586, 1523, 1434, 1296, 883, 807, 741 cm$^{-1}$.

**N-(4-bromophenyl)-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine (Sab):**

![Chemical structure of N-(4-bromophenyl)-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine](image)

Prepared according to the general procedure using aniline 12b (34 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent 1a (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 4 h. Isolated by column chromatography (n-hexane/EtOAc, 7/3) to give the desired product Sab as white solid (42 mg) in 56% yield.

m.p.: 127.6 °C; HRMS (ESI) calcd. for C$_{18}$H$_{11}$F$_{16}$N$_{2}$S$_{2}$Br$_{2}$ : 437.9590 found 374.9592; 1H NMR (CDCl$_3$, 300 MHz) δ = 6.63 (brs, 1H), 6.87 (d, J = 9 Hz, 1H), 7.15 (d, J = 9 Hz, 1H), 7.35 (d, J = 9 Hz, 2H), 7.46 (d, J = 9 Hz, 2H), 7.67 (t, J = 9 Hz, 1H); 19F NMR (CDCl$_3$, 282 MHz) δ = 51.43 (d, J = 149.46 Hz, 4F), 78.75 (quintet, J = 152.28 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) δ = 111.74 (quintet, J = 3.78 Hz), 116.05, 121.63, 123.45, 138.49, 139.87, 153.66, 163.95 (t, J = 21.42 Hz). ATR-FTIR (KBr): ν = 3454, 1611, 1517, 1491, 1473, 845, 825, 810, 795, 781 cm$^{-1}$.

**N-(3,5-dimethoxyphenyl)-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine (Sac):**

![Chemical structure of N-(3,5-dimethoxyphenyl)-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine](image)

Prepared according to the general procedure using aniline 12c (30 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent 1a (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 4 h. Isolated by column chromatography (n-hexane/EtOAc, 3/2) to give the desired product Sac as white solid (40 mg) in 56% yield.

m.p.: 90.9 °C; HRMS (ESI) calcd. for C$_{18}$H$_{15}$F$_{16}$N$_{2}$S$_{2}$: 375.0696 found 375.0699; 1H NMR (CDCl$_3$, 300 MHz) δ = 3.80 (s, 6H), 6.23 (t, J = 3 Hz, 1H), 6.65 (brs, 1H), 6.73 (d, J = 2.1 Hz, 2H), 6.91 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 8.1 Hz, 1H); 19F NMR (CDCl$_3$, 282 MHz) δ = 51.42 (d, J = 149.46 Hz, 4F), 79.00 (quintet, J = 146.64 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) δ = 55.51, 95.95, 97.96, 111.42 (t, J = 3.78 Hz), 112.24, 139.67, 141.27, 153.86, 161.49, 163.91 (t, J = 22.68 Hz). ATR-FTIR (KBr): ν = 3359, 3000, 2968, 2918, 2848, 1621, 1593, 1484, 1457, 1208, 1148, 1062, 855, 835, 787 cm$^{-1}$.

**N-(2-bromophenyl)-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine (Sbd):**

![Chemical structure of N-(2-bromophenyl)-6-(pentafluoro-λ^5-sulfaneyl)pyridin-2-amine](image)

Prepared according to the general procedure using aniline 12d (34.4 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent 1b (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 5 h. Isolated by column chromatography (n-hexane/EtOAc, 9/1) to give the desired product Sbd as white solid (21.3 mg) in 57% yield.

m.p.: 72.8 °C; HRMS (ESI) calcd. for C$_{18}$H$_{15}$F$_{16}$N$_{2}$S: 374.9590 found 374.9590; 1H NMR (CDCl$_3$, 300 MHz) δ = 6.26 (brs, 1H), 6.95–7.01 (m, 1H), 7.26–7.40 (m, 2H), 7.48 (d, J = 6 Hz, 1H), 7.64 (t, J = 9 Hz, 2H), 8.27 (d, J = 6 Hz, 1H); 19F NMR (CDCl$_3$, 282 MHz) δ = 51.39 (d, J = 149.46 Hz, 4F), 79.35 (quintet, J = 149.46 Hz, 1F); 13C NMR (CDCl$_3$, 126 MHz) δ = 115.92, 119.89, 122.23 (quintet, J = 5.04 Hz), 123.74, 125.03, 128.64, 130.80, 136.24 (t, J = 1.26 Hz), 138.11, 141.95, 198.06 (quintet, J = 22.68 Hz). ATR-FTIR (KBr): ν = 3394, 1586, 1576, 1507, 1461, 1323, 1121, 1026, 760, 741 cm$^{-1}$.
SF₂-heteroarylation of phenols, alcohols and thiol:

The heteroarylation of phenols, alcohols and thiol were performed according to literature procedure.\textsuperscript{7a}

![Chemical structure](image)

To a suspension of \( \text{BuOK} \) (1.2 eq.) in THF (0.3 mL/mmol), was added the phenol/alcohol/thiol 13 (1.0 eq.) at 0 °C and the reaction mixture was stirred at this temperature for 10 minutes. The reagent 1a or 1b (1.2 eq.) was added in one portion and the reaction was stirred in a preheated oil bath at 40 °C till completion. The reaction was quenched by water at 0 °C. The organic phase was separated and the aqueous phase was extracted with dichloromethane (10 mL). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and the solvent was concentrated under reduced pressure. The crude product was isolated by column chromatography over silica gel (n-hexane/EtOAc) to give the desired product 6.

2-(4-iodophenoxy)-6-(pentafluoro-λ⁶-sulfanyle)pyridine (6aa):

Prepared according to the general procedure using \( \text{BuOK} \) (13.5 mg, 0.12 mmol), phenol 13a (22 mg, 0.1 mmol) and reagent 1a (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 4 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6aa as a white solid (39.2 mg) in 92% yield.

m.p.: 46.3 °C; HRMS (EI) calcld. for C₁₅H₁₅N₃F₃S ([M]+): 364.9995 found 364.9998; \(^1\)H NMR (CDCl₃, 300 MHz) \( \delta = 6.98 \) (d, \( J = 9 \) Hz, 2H), 7.07 (d, \( J = 9 \) Hz, 1H), 7.45 (d, \( J = 9 \) Hz, 2H), 7.70 (t, \( J = 9 \) Hz, 1H); \(^{19}\)F NMR (CDCl₃, 282 MHz) \( \delta = 52.22 \) (d, \( J = 152.28 \) Hz, 4F), 77.53 (quintet, \( J = 149.46 \) Hz, 1F); \(^{13}\)C NMR (CDCl₃, 126 MHz) \( \delta = 89.02, 114.79, 115.80 \) (quintet, \( J = 3.78 \) Hz), 123.20, 138.75, 141.75, 153.12, 160.75, 162.81 (quintet, \( J = 22.68 \) Hz). ATR-FTIR (KBr): \( \nu = 3519, 3164, 2953, 1381, 1260, 1244, 1146, 1110, 1060, 922, 778 \) cm\(^{-1}\).

2-(2-nitrophenoxy)-6-(pentafluoro-λ⁶-sulfanyle)pyridine (6ab):

Prepared according to the general procedure using \( \text{BuOK} \) (13.5 mg, 0.12 mmol), phenol 13b (14 mg, 0.1 mmol) and reagent 1a (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 5 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6ab as a white solid (28.4 mg) in 83% yield.

m.p.: 76.6 °C; HRMS (ESI) calcld. for C₁₅H₁₅F₅N₃S ([M]+): 364.9995 found 364.9998; \(^1\)H NMR (CDCl₃, 300 MHz) \( \delta = 7.25 \) (d, \( J = 6 \) Hz, 1H), 7.37–7.47 (m, 3H), 7.66–7.72 (m, 1H), 7.95 (t, \( J = 9 \) Hz, 1H); \(^{19}\)F NMR (CDCl₃, 282 MHz) \( \delta = 52.29 \) (d, \( J = 149.46 \) Hz, 4F), 77.23 (quintet, \( J = 149.46 \) Hz, 1F); \(^{13}\)C NMR (CDCl₃, 126 MHz) \( \delta = 114.85, 116.15 \) (quintet, \( J = 3.78 \) Hz), 125.26, 125.93, 126.35, 134.84, 142.02, 142.39, 145.93, 160.20, 162.47 (quintet, \( J = 22.68 \) Hz). ATR-FTIR (KBr): \( \nu = 3442, 3110, 2865, 1979, 1713, 1594, 1446, 1349, 1264, 809 \) cm\(^{-1}\).

2-(4-methoxyphenoxy)-6-(pentafluoro-λ⁶-sulfanyle)pyridine (6ac):

Prepared according to the general procedure using \( \text{BuOK} \) (13.5 mg, 0.12 mmol), phenol 13c (9.4 mg, 0.1 mmol) and reagent 1a (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 4.5 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6ac as a colorless oil (20.8 mg) in 82% yield.

HRMS (ESI) calcld. for C₁₅H₁₅F₅N₃S ([M]+): 364.9995 found 364.9998; \(^1\)H NMR (CDCl₃, 300 MHz) \( \delta = 3.83 \) (s, 3H), 6.91–6.99 (m, 3H), 7.11 (d, \( J = 9 \) Hz, 2H), 7.40 (d, \( J = 9 \) Hz, 1H); \(^{19}\)F NMR (CDCl₃, 282 MHz) \( \delta = 52.11 \) (d, \( J = 149.46 \) Hz, 4F), 77.81 (quintet, \( J = 149.46 \) Hz, 1F); \(^{13}\)C NMR (CDCl₃, 126 MHz) \( \delta = 55.72, 113.85, 114.83, 115.11 \) (quintet, \( J = 3.78 \) Hz),
Prepared according to the general procedure using BuOK (13.5 mg, 0.12 mmol), phenol 11d (12 mg, 0.1 mmol) and reagent 1a (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 3 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6ad as a yellow solid (20 mg) in 62% yield.

5-phenoxy-2-(pentafluoro-λ^6-sulfaneyl)pyridine (6be):

Prepared according to the general procedure using BuOK (13.5 mg, 0.12 mmol), phenol 13e (9.4 mg, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 4 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6be as a colourless oil (20.8 mg) in 70% yield.

5-(3-methoxyphenoxy)-2-(pentafluoro-λ^6-sulfaneyl)pyridine (6bf):

Prepared according to the general procedure using BuOK (13.5 mg, 0.12 mmol), phenol 13f (11 μL, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 3 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6bf as a yellow solid (11.4 mg) in 31% yield.

2-(benzylxyloxy)-6-(pentafluoro-λ^6-sulfaneyl)pyridine (6ag):

Prepared according to the general procedure using BuOK (13.5 mg, 0.12 mmol), alcohol 13g (10 μL, 0.1 mmol) and reagent 1a (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 3 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9/1) to give the desired product 6ag as white solid (22.5 mg) in 72% yield.
5-(benzyloxy)-2-(pentafluoro-λ⁵-sulfaneyl)pyridine (6bg):

Prepared according to the general procedure using 'BuOK (13.5 mg, 0.12 mmol), alcohol 13g (10 μL, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 3 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9:1) to give the desired product 6bg as white solid (22 mg) in 70% yield.

Prepared according to the general procedure using 'BuOK (13.5 mg, 0.12 mmol), alcohol 13h (16 mg, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 3 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9:1) to give the desired product 6bh as white solid (14.6 mg) in 40% yield.

Prepared according to the general procedure using 'BuOK (13.5 mg, 0.12 mmol), alcohol 13i (21 mg, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 3 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 9:1) to give the desired product 6bi as yellow solid (15 mg) in 36% yield.

3-{2-[(6-pentafluoro-λ⁵-sulfaneyl)pyridin-3-yl]oxy}ethyl-1H-indole (6bj):

ATR-FTIR (KBr): ν = 3645, 3045, 2966, 2311, 1573, 1462, 1291, 1242, 837, 822 cm⁻¹.
Prepared according to the general procedure using 3BuOK (13.5 mg, 0.12 mmol), alcohol 13j (16 mg, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 5 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 4/1) to give the desired product 6bj as white oil (20 mg) in 56% yield.

HRMS (ESI) calcd. for C₁₂H₁₄N₂O₂S₂ ([M]+): 365.0747 found 365.0754; ¹H NMR (CDCl₃, 300 MHz) δ = 3.28 (t, J = 6 Hz, 2H), 4.29 (t, J = 6 Hz, 2H), 7.08 (s, 1H), 7.12–7.19 (m, 1H), 7.22–7.25 (m, 1H), 7.35 (d, J = 9 Hz, 1H), 7.61 (d, J = 3 Hz, 1H), 7.64 (s, 1H), 8.12 (bs, 1H), 8.16 (d, J = 2.7 Hz); ¹³C NMR (CDCl₃, 282 MHz) δ = 53.68 (d, J = 149.46 Hz, 4F), 79.82 (quintet, J = 146.64 Hz, 1F); 1F NMR (CDCl₃, 126 MHz) δ = 25.28, 69.36, 111.50, 118.68, 119.72, 122.31–122.40 (m), 122.49, 122.57, 127.36, 135.39, 136.31, 157.01, 157.94 (quintet, J = 23.75 Hz). ATR-FTIR (NaCl): ν = 3687, 3414, 3298, 3058, 2928, 1577, 1459, 1249, 862, 743 cm⁻¹.

(89,95,135,145)-13-methyl-3-((6-pentafluoro-L⁶-sulfaneyl)pyridin-3-yl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (6bk):

Prepared according to the general procedure using 3BuOK (13.5 mg, 0.12 mmol), phenol 13k (27 mg, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 80 °C for 5 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 4/1) to give the desired product 6bk as white solid (33 mg) in 70% yield.

m.p.: 158.0 – 164.3 °C; HRMS (ESI) calcd. for C₁₆H₁₆N₂O₂S₂ ([M]+): 496.1346 found 496.1345; ¹H NMR (CDCl₃, 300 MHz) δ = 0.94 (s, 3H), 1.15–1.65 (m, 6H), 1.98–2.11 (m, 3H), 2.17–2.22 (m, 1H), 2.32 (s, 1H), 2.41–2.57 (m, 2H), 2.915 (d, J = 3 Hz, 2H), 6.83 (s, 1H), 6.87 (d, J = 6 Hz, 1H), 7.34 (d, J = 6 Hz, 2H), 7.67 (d, J = 9 Hz, 1H), 8.26 (s, 1H); ¹³C NMR (CDCl₃, 282 MHz) δ = 53.39 (d, J = 149.46 Hz, 4F), 79.09 (quintet, J = 149.46 Hz, 1F); 1F NMR (CDCl₃, 126 MHz) δ = 13.96, 21.71, 25.94, 26.40, 29.99, 31.65, 35.96, 38.16, 44.24, 48.06, 50.51, 117.41, 120.16, 122.43–122.52 (m), 125.45, 127.48, 137.40, 137.73, 139.34, 152.51, 156.77, 159.07 (quintet, J = 23.94 Hz). ATR-FTIR (KBr): ν = 3649, 2933, 2881, 2372, 2311, 1736, 1492, 1462, 1288, 1246, 846, 823 cm⁻¹.

2,4-dimethoxy-6-4-((6-pentafluoro-L⁶-sulfaneyl)pyridin-2-yl)oxy)phenoxy)pyrimidine (6al):

Prepared according to the general procedure using 3BuOK (67.3 mg, 0.6 mmol), phenol 13l (124 mg, 0.5 mmol) and reagent 1b (360 mg, 0.6 mmol) in THF (45 mL) at 65 °C for 5 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 3/2) to give the desired product 6al as white solid (226 mg) in 70% yield.

m.p.: 40.5 °C; HRMS (EI) calcd. for C₁₂H₁₄N₂O₂S₂ ([M]+): 451.0625 found 451.0622; ¹H NMR (CDCl₃, 300 MHz) δ = 3.36 (s, 3H), 3.90 (s, 3H), 5.78 (s, 1H), 7.09–7.13 (m, 3H), 7.18–7.23 (m, 2H), 7.26–7.28 (m, 1H), 7.67 (dd, J = 9 Hz, 3 Hz, 1H); ¹³C NMR (CDCl₃, 282 MHz) δ = 63.37 (d, J = 155.1 Hz, 4F), 76.56 (quintet, J = 152.28 Hz, 1F); 1F NMR (CDCl₃, 126 MHz) δ = 54.44, 55.02, 84.61, 115.57, 119.93, 121.59, 123.48, 123.63, 150.10, 151.16, 157.95 (quintet, J = 18.9 Hz), 159.65, 165.19, 172.12, 173.60. ATR-FTIR (KBr): ν = 3699, 3150, 1725, 1581, 1476, 1450, 984, 845, 803 cm⁻¹.

5-((4-bromophenyl)thio)-2-(pentafluoro-L⁶-sulfaneyl)pyridine (6bm):

Prepared according to the general procedure using 3BuOK (13.5 mg, 0.12 mmol), thiol 13m (27 mg, 0.1 mmol) and reagent 1b (72 mg, 0.12 mmol) in THF (0.3 mL) at 40 °C for 5 h. Isolated using column chromatography over silica gel (n-hexane/EtOAc, 3/2) to give the desired product 6bm as pale yellow solid (23 mg) in 74% yield.

m.p.: 63.3 °C; HRMS (EI) calcd. for C₁₂H₁₄N₂O₂S₂Br ([M]+): 390.9123 found 390.9128; ¹H NMR (CDCl₃, 300 MHz) δ = 7.36–7.40 (m, 2H), 7.55–7.59 (m, 4H), 8.31 (s, 1H); ¹³C NMR (CDCl₃, 282 MHz) δ = 52.61 (d, J = 152.28 Hz, 1F), 78.03 (quintet, J = 146.64 Hz, 1F); 1F NMR (CDCl₃, 126 MHz) δ = 121.56–121.68, 124.33, 129.60, 133.47, 135.63, 137.17, 139.70, 146.21, 162.84–163.57. ATR-FTIR (KBr): ν = 2963, 1558, 1471, 1452, 1354, 1261, 1085, 1008, 811, 745, 598 cm⁻¹.
Reference:
