Supporting Information

1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried Schlenk tubes. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Dry solvents (<50 ppm H₂O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere and were transferred under argon.

Commercially available chemicals were obtained from ABCR, Acros Organics, Aldrich Chemical Co., Alfa Aesar, Combi-Blocks, Fluorochem and TCI Europe and used as received unless otherwise stated. Compound 6j was prepared according to a procedure by Doucet et al.[1]

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques. Solvents used for flash column chromatography were distilled before use.

¹H-, ¹³C- and ¹⁹F-NMR spectra were recorded on a Bruker AV 300, Bruker AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts (δ) for ¹H- and ¹³C-NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ¹H- and ¹³C-NMR spectra and the chemical shifts converted to the TMS scale (CDCl₃: δH = 7.26 ppm, δC = 77.2 ppm; CD₂Cl₂: δH = 5.32 ppm, δC = 53.8 ppm; (CD₃)₂CO: δH = 2.05 ppm, δC = 29.8 ppm). ¹⁹F-NMR spectra are not calibrated and δ (ppm) is given relative to CCl₃F. Coupling constants (J) are quoted in Hz. To describe the multiplicities of the signals, the following abbreviations were used: s: singlet, bs: broad signal, d: doublet, t: triplet, q: quartet, hept: heptet, m: multiplet; dm: doublet of multiplets, qm: quartet of multiplets.

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (νmax) of recorded IR-signals are quoted in cm⁻¹.
Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTof. High resolution APCI mass spectra were recorded on a Thermo-Fisher Scientific Orbitrap LTQ XL.

GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with Agilent 5975C VL MSD or 5975 inert Mass Selective Detector (EI) on an HP-5MS column (0.25 mm x 30 m, Film: 0.25 µm). The measurement begins with injection at temperature T0 (50 °C), which is held for 3 min. The column is then heated to temperature T1 (280 °C, ramp = 40 °C), which is held for 3 min.

Melting points were determined on a Stuart Scientific Melting Point Apparatus SMP3.
2. Optimization of reaction conditions

An oven-dried screw-cap tube was filled with furan 6a (21.2 mg, 0.1 mmol, 1.0 eq), catalyst (0.01 mmol, 10 mol%) and SCF₃-reagent (0.13 mmol, 1.3 eq). The given solvent (0.5 mL) was added and the reaction mixture was stirred for 16 h at 90 °C. The reaction was analyzed by GC-FID with mesitylene as internal standard.

Table 1: Catalyst optimization.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield</th>
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<tr>
<td>LiCl</td>
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<tr>
<td>NaCl</td>
<td>95%</td>
</tr>
<tr>
<td>NaBr</td>
<td>0%</td>
</tr>
<tr>
<td>NaBF₄</td>
<td>0%</td>
</tr>
<tr>
<td>KCl</td>
<td>64%</td>
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<tr>
<td>no catalyst</td>
<td>0%</td>
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Table 2: Solvent optimization.

<table>
<thead>
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<th>Solvent</th>
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<tbody>
<tr>
<td>DMF</td>
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<tr>
<td>DMSO</td>
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</tr>
<tr>
<td>toluene</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN</td>
<td>0%</td>
</tr>
<tr>
<td>THF</td>
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<tr>
<td>DCE</td>
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Table 3: Reagent optimization.

<table>
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<th>Equivalents</th>
<th>Yield</th>
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</thead>
<tbody>
<tr>
<td>1.3 eq 2</td>
<td>95%</td>
</tr>
<tr>
<td>1.3 eq 1</td>
<td>0%</td>
</tr>
<tr>
<td>1.5 eq 2</td>
<td>99%</td>
</tr>
</tbody>
</table>
3. Synthesis of starting materials

General procedure A: Synthesis of 3-aryl furans

According to a procedure by Tofi et al.,[2] a solution of furan-3-boronic acid (135 mg, 1.2 mmol, 1.2 eq) in methanol (0.6 mL) was added to a solution of aryl halide (1.0 mmol, 1.0 eq), Pd(PPh₃)₄ (46 mg, 0.04 mmol, 4 mol%) and sodium carbonate (233 mg, 2.2 mmol, 2.2 eq) in a toluene/water-mixture (2:1, 3.3 mL). The reaction mixture was stirred for 16 h at 80 °C. The reaction mixture was diluted with dichloromethane (10 mL) and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layer was washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography.

3-(4-(Trifluoromethyl)phenyl)furan

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 1-bromo-4-(trifluoromethyl)benzene (140 μL, 1.0 mmol, 1.0 eq). The desired product (107 mg, 0.50 mmol, 50%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

\[ R_f = 0.23 \text{ (n-pentane).} \]

\[ ^1H-NMR \ (300 \text{ MHz, CDCl}_3): \delta = 7.83 - 7.77 \text{ (m, 1H), 7.68 - 7.55 \text{ (m, 4H), 7.53 - 7.50 \text{ (m, 1H), 6.76 - 6.70 \text{ (m, 1H).}} \]

\[ ^13C-NMR \ (75 \text{ MHz, CDCl}_3): \delta = 144.3, 139.5, 136.2, 129.1 \text{ (q, } J = 31.7 \text{ Hz), 126.1, 125.9 \text{ (q, } J = 3.8 \text{ Hz), 125.5, 124.3 \text{ (q, } J = 272.3 \text{ Hz), 108.8.} \]

\[ ^19F-NMR \ (272 \text{ MHz, CDCl}_3): \delta = -62.5. \]

3-(4-Nitrophenyl)furan

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol, 1.0 eq). The desired product (100 mg, 0.53 mmol, 53%) was obtained as a white solid after flash column chromatography eluting with 3% EtOAc in n-pentane.

\[ R_f = 0.34 \text{ (5% EtOAc in n-pentane).} \]
$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 8.29 – 8.20$ (m, 2H), 7.89 – 7.83 (m, 1H), 7.65 – 7.58 (m, 2H), 7.57 – 7.50 (m, 1H), 6.79 – 6.72 (m, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 146.7$, 144.7, 140.4, 139.2, 126.3, 125.0, 124.4, 108.6.

**Ethyl 4-(furan-3-yl)benzoate**

![COOEt](furan-benzoate.png)

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and ethyl 4-bromobenzoate (160 μL, 1.0 mmol, 1.0 eq). The desired product (110 mg, 0.51 mmol, 51%) was obtained as a white solid after flash column chromatography eluting with 3% EtOAc in $n$-pentane.

$R_f = 0.35$ (5% EtOAc in $n$-pentane).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 8.09 – 8.02$ (m, 2H), 7.83 – 7.81 (m, 1H), 7.58 – 7.48 (m, 3H), 6.76 – 6.73 (m, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 166.5$, 144.2, 139.6, 137.0, 130.3, 129.0, 125.8, 125.6, 108.8, 61.1, 14.5.

**3-(4-Chlorophenyl)furan**

![Cl](furan-chlorophenyl.png)

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 1-bromo-4-chlorobenzene (192 mg, 1.0 mmol, 1.0 eq). The desired product (53 mg, 0.30 mmol, 30%) was obtained as a white solid after flash column chromatography eluting with 3% EtOAc in $n$-pentane.

$R_f = 0.29$ (3% EtOAc in $n$-pentane).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.73 – 7.70$ (m, 1H), 7.48 (d, $J = 1.8$ Hz, 1H), 7.45 – 7.30 (m, 4H), 6.67 (d, $J = 1.8$ Hz, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta = 144.0$, 138.7, 132.8, 131.1, 129.1, 127.2, 125.6, 108.8.
3-Phenylfuran

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and bromobenzene (106 μL, 1.0 mmol, 1.0 eq). The desired product (70 mg, 0.49 mmol, 49%) was obtained as a white solid after flash column chromatography eluting with 3% EtOAc in n-pentane.

\[ R_f = 0.26 \text{ (3\% EtOAc in n-pentane)}. \]

\(^1\)H-NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 7.79 – 7.74 \text{ (m, 1H)}, 7.55 – 7.49 \text{ (m, 3H)}, 7.45 – 7.36 \text{ (m, 2H)}, 7.34 – 7.26 \text{ (m, 1H)}, 6.73 \text{ (d, } J = 1.9 \text{ Hz, 1H)}. \)

\(^{13}\)C-NMR (101 MHz, CDCl\textsubscript{3}): \( \delta = 143.8, 138.6, 132.6, 128.9, 127.1, 126.6, 126.0, 109.0. \)

3-(4-Methoxyphenyl)furan

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 1-bromo-4-methoxybenzene (126 μL, 1.0 mmol, 1.0 eq). The desired product (103 mg, 0.59 mmol, 59%) was obtained as a white solid after flash column chromatography eluting with 3% EtOAc in n-pentane.

\[ R_f = 0.15 \text{ (3\% EtOAc in n-pentane)}. \]

\(^1\)H-NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 7.69 – 7.66 \text{ (m, 1H)}, 7.49 – 7.46 \text{ (m, 1H)}, 7.46 – 7.40 \text{ (m, 2H)}, 6.96 – 6.91 \text{ (m, 2H)}, 6.69 – 6.65 \text{ (m, 1H)}, 3.84 \text{ (s, 3H)}. \)

\(^{13}\)C-NMR (101 MHz, CDCl\textsubscript{3}): \( \delta = 158.9, 143.6, 137.8, 127.1, 126.2, 125.2, 114.4, 109.0, 55.4. \)

3-(3-(Trifluoromethyl)phenyl)furan

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 1-bromo-3-(trifluoromethyl)benzene (140 μL, 1.0 mmol, 1.0 eq). The desired product (104 mg, 0.49 mmol, 49%) was obtained as a colorless oil after flash column chromatography eluting with n-pentane.

\[ R_f = 0.30 \text{ (n-pentane)}. \]
1H-NMR (300 MHz, CDCl₃): \( \delta = 7.82 - 7.78 \) (m, 1H), 7.76 - 7.70 (m, 1H), 7.69 - 7.63 (m, 1H), 7.56 - 7.48 (m, 3H), 7.38 - 7.29 (m, 2H), 6.73 (dd, \( J = 1.9, 1.0 \) Hz, 1H).

13C-NMR (75 MHz, CDCl₃): \( \delta = 144.2, 139.2, 129.4, 129.2 \) (q, \( J = 1.5 \) Hz), 128.7, 125.5, 124.2 (q, \( J = 272.3 \) Hz), 123.7 (q, \( J = 3.8 \) Hz), 122.7 (q, \( J = 3.9 \) Hz), 108.8.

19F-NMR (272 MHz, CDCl₃): \( \delta = -62.8 \).

\( \nu_{\text{max}} \) (neat)/ cm\(^{-1}\): 1439, 1339, 1273, 1165, 1107, 1061, 1018, 999, 899, 872, 783, 721, 694, 598.

m/z (APCI): Found (M\(^+\)), 212.0443. C\(_{11}\)H\(_7\)OF\(_3\)\(^+\) requires \( M \), 212.0444.

2-(3-(Furan-3-yl)phenyl)-1,3-dioxolane

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 2-(3-bromophenyl)-1,3-dioxolane (161 \( \mu \)L, 1.0 mmol, 1.0 eq). The desired product (93 mg, 0.43 mmol, 43%) was obtained as a colorless oil after flash column chromatography eluting with 10% EtOAc in \( n \)-pentane.

\( R_f = 0.17 \) (10% EtOAc in \( n \)-pentane).

1H-NMR (300 MHz, CDCl₃): \( \delta = 7.78 - 7.75 \) (m, 1H), 7.64 - 7.59 (m, 1H), 7.50 - 7.46 (m, 2H), 7.42 - 7.37 (m, 2H), 6.75 - 6.70 (m, 1H), 5.85 (s, 1H), 4.20 - 4.02 (m, 5H).

13C-NMR (75 MHz, CDCl₃): \( \delta = 143.8, 138.8, 138.6, 132.7, 129.0, 126.8, 126.3, 125.2, 124.0, 109.0, 103.7, 65.4. \)

\( \nu_{\text{max}} \) (neat)/ cm\(^{-1}\): 1701, 1161, 1096, 1080, 1018, 988, 949, 872, 783, 687, 648, 598.

m/z (ESI): Found (M+Na\(^+\)), 239.0673. C\(_{13}\)H\(_{12}\)O\(_3\)Na\(^+\) requires \( M \), 239.0679.

3-(3,5-Dimethylphenyl)furan

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 1-bromo-3,5-dimethylbenzene (136 \( \mu \)L, 1.0 mmol, 1.0 eq). The desired product (130 mg, 0.75 mmol, 75%) was obtained as a colorless oil after flash column chromatography eluting with \( n \)-pentane.

\( R_f = 0.51 \) (\( n \)-pentane).
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.82 – 7.76$ (m, 1H), 7.53 (t, $J = 1.8$ Hz, 1H), 7.44 – 7.39 (m, 1H), 7.23 – 7.17 (m, 2H), 7.02 – 6.96 (m, 1H), 6.76 (dd, $J = 1.9$, 0.9 Hz, 1H), 2.44 – 2.40 (m, 6H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta = 143.6$, 138.5, 138.4, 132.4, 128.8, 126.7, 123.9, 109.1, 21.4.

2-(Furan-3-yl)pyridine

The desired product was synthesized according to the general procedure starting from furan-3-boronic acid and 2-bromopyridine (96 $\mu$L, 1.0 mmol, 1.0 eq). The desired product (58 mg, 0.40 mmol, 40%) was obtained as a colorless oil after flash column chromatography eluting with 10% EtOAc in $n$-pentane.

$R_f = 0.26$ (10% EtOAc in $n$-pentane).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 8.62 – 8.53$ (m, 1H), 8.06 – 8.00 (m, 1H), 7.67 (td, $J = 7.7$, 1.9 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.18 – 7.10 (m, 1H), 6.89 (dd, $J = 1.9$, 0.9 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 151.9$, 149.7, 144.0, 141.3, 136.7, 127.1, 121.9, 120.2, 108.7.

General procedure B: Synthesis of 2-aryl furans

According to a procedure by Oxford et al.,[3] furan-2-boronic acid (168 mg, 1.5 mmol, 1.5 eq), aryl halide (1.0 mmol, 1.0 eq), Pd(PPh$_3$)$_4$ (116 mg, 0.1 mmol, 10 mol%) and cesium carbonate (350 mg, 1.1 mmol, 1.1 eq) were suspended in a toluene/MeOH-mixture (4:1, 10 mL). The reaction mixture was stirred for 16 h at 100 °C. The reaction mixture was diluted with EtOAc (8 mL) and the organic layer was extracted was washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography.

2-Phenylfuran

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and phenylbromide (105 $\mu$L, 1.0 mmol, 1.0 eq). The desired product (r mg, 0.50 mmol,
50\%) was obtained as a yellowish oil after flash column chromatography eluting with n-pentane.

\[ R_f = 0.28 \text{ (n-pentane)}. \]

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.73 - 7.63 \) (m, 2H), 7.48 (dd, \( J = 1.8, 0.8 \text{ Hz, 1H} \)), 7.44 - 7.35 (m, 2H), 7.31 - 7.22 (m, 1H), 6.66 (dd, \( J = 3.4, 0.8 \text{ Hz, 1H} \)), 6.48 (dd, \( J = 3.4, 1.8 \text{ Hz, 1H} \)).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 154.1, 142.2, 131.0, 128.8, 127.5, 123.9, 111.8, 105.1. \)

**2-(4-Fluorophenyl)furan**

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 1-bromo-4-fluorobenzene (110 \( \mu \text{L, 1.0 mmol, 1.0 eq} \)). The desired product (125 mg, 0.77 mmol, 77\%) was obtained as clear crystals after flash column chromatography eluting with n-pentane.

\[ R_f = 0.35 \text{ (n-pentane)}. \]

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.72 - 7.58 \) (m, 2H), 7.46 (dd, \( J = 1.9, 0.8 \text{ Hz, 1H} \)), 7.13 - 7.02 (m, 2H), 6.59 (dd, \( J = 3.4, 0.8 \text{ Hz, 1H} \)), 6.47 (dd, \( J = 3.4, 1.8 \text{ Hz, 1H} \)).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 162.2 \) (d, \( J = 246.8 \text{ Hz} \)), 153.3, 142.2 (d, \( J = 1.0 \text{ Hz} \)), 127.4 (d, \( J = 3.2 \text{ Hz} \)), 125.7 (d, \( J = 8.0 \text{ Hz} \)), 115.8 (d, \( J = 22.0 \text{ Hz} \)), 111.8, 104.8 (d, \( J = 1.4 \text{ Hz} \)).

\(^{19}\)F-NMR (282 MHz, CDCl\(_3\)): \( \delta = -114.4. \)

**2-(4-Bromophenyl)furan**

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 1,4-dibromobenzene (235.9 mg, 1.0 mmol, 1.0 eq). The desired product (64 mg, 0.29 mmol, 29\%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

\[ R_f = 0.30 \text{ (n-pentane)}. \]
$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.60 - 7.42$ (m, 5H), 6.65 (dd, $J = 3.4$, 0.7 Hz, 1H), 6.48 (dd, $J = 3.4$, 1.8 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 153.1$, 142.5, 131.9, 129.9, 125.4, 121.2, 111.9, 105.7.

2-(4-(Trifluoromethyl)phenyl)furan

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 1-iodobenzotrifluoride (147 µL, 1.0 mmol, 1.0 eq). The desired product (199 mg, 0.94 mmol, 94%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

$R_f = 0.47$ (n-pentane).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.77$ (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 1.7$ Hz, 1H), 6.77 (d, $J = 3.4$ Hz, 1H), 6.51 (dd, $J = 3.4$, 1.8 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 152.7$, 143.2, 134.1, 125.8 (q, $J = 3.8$ Hz), 124.3 (q, $J = 271.9$ Hz), 123.9, 112.1, 107.1.

$^{19}$F-NMR (282 MHz, CDCl$_3$): $\delta = -62.5$.

4-(Furan-2-yl)benzonitrile

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 4-bromobenzonitrile (182 mg, 1.0 mmol, 1.0 eq). The desired product (157 mg, 0.92 mmol, 92%) was obtained as a brownish solid after flash column chromatography eluting with 3% EtOAc in n-pentane.

$R_f = 0.24$ (3% EtOAc in n-pentane).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.80 - 7.70$ (m, 2H), 7.70 - 7.61 (m, 2H), 7.54 (dd, $J = 1.8$, 0.7 Hz, 1H), 6.81 (dd, $J = 3.4$, 0.7 Hz, 1H), 6.53 (dd, $J = 3.4$, 1.8 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 152.1$, 143.8, 134.8, 132.7, 124.1, 119.1, 112.4, 110.4, 108.3.
1-(4-(Furan-2-yl)phenyl)pyrrolidine

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 1-(4-iodophenylpyrrolidine) (273 mg, 1.0 mmol, 1.0 eq). The product (150 mg) was obtained as a white solid after flash column chromatography eluting with 3% EtOAc in n-pentane.

$$R_f = 0.47\ (n\text{-pentane}).$$

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.62 - 7.52$ (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 1H), 6.70 — 6.62 (m, 1H) 6.44 (d, $J = 1.4$ Hz, 2H), 3.47 – 3.24 (m, 4H), 2.13 – 1.96 (m, 4H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 140.8, 134.0, 133.7, 128.8, 128.7, 128.6, 125.3, 111.6, 25.5.$

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 1613, 1516, 1481, 1431, 1377, 1188, 1161, 995, 961, 818, 787, 718, 694, 667.

Melting point: 129 – 130 °C.

m/z (ESI): Found (M+H$^+$), 214.1226. C$_{14}$H$_{15}$NOH$^+$ requires $M$, 214.1226.

Note: The isolated product contained 20% of an inseparable side product.

Methyl 3-(furan-2-yl)benzoate

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and ethyl 3-bromobenzoate (166 µL, 1.0 mmol, 1.0 eq). The desired product (180 mg, 0.89 mmol, 89%) was obtained as a colorless oil after flash column chromatography eluting with 5% EtOAc in n-pentane.

$$R_f = 0.51\ (10\%\ EtOAc\ in\ n\text{-pentane}).$$

$^1$H-NMR (300 MHz, CDCl$_3$): 8.28 – 8.24 (m, 1H), 7.88 – 7.81 (m, 1H), 7.80 – 7.73 (m, 1H), 7.42 – 7.32 (m, 2H), 6.65 (dd, $J = 3.4, 0.8$ Hz, 1H), 6.40 (dd, $J = 3.4, 1.8$ Hz, 1H), 3.85 (s, 3H).
\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 166.9, 153.0, 142.5, 142.5, 128.8, 128.2, 127.9, 124.9, 111.9, 106.0, 105.9, 52.2\).

2-(3-Methoxyphenyl)furan

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 3-bromoanisol (126 \(\mu\)L, 1.0 mmol, 1.0 eq). The desired product (170 mg, 0.97 mmol, 97%) was obtained as a clear liquid after flash column chromatography eluting with 5% EtOAc in \(n\)-pentane.

\(R_f = 0.50\) (5% EtOAc in \(n\)-pentane).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.47\) (dd, \(J = 1.8, 0.8\) Hz, 1H), 7.36 – 7.16 (m, 3H), 6.82 (dt, \(J = 7.2, 2.4\) Hz, 1H), 6.65 (dd, \(J = 3.3, 0.8\) Hz, 1H), 6.47 (dd, \(J = 3.4, 1.8\) Hz, 1H), 3.86 (s, 3H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 160.0, 142.2, 132.3, 129.9, 116.5, 113.3, 111.8, 110.1, 109.2, 105.4, 55.4\).

2-(\(\alpha\)-Tolyl)furan

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 2-bromotoluene (120 \(\mu\)L, 1.0 mmol, 1.0 eq). The desired product (71 mg, 0.45 mmol, 45%) was obtained as a clear liquid after flash column chromatography eluting with \(n\)-pentane.

\(R_f = 0.57\) (\(n\)-pentane).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.78 – 7.71\) (m, 1H), 7.56 (dd, \(J = 1.8, 0.8\) Hz, 1H), 7.36 – 7.21 (m, 3H), 6.64 – 6.51 (m, 2H), 2.55 (s, 3H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 153.7, 141.8, 134.7, 131.3, 130.4, 127.6, 127.2, 126.1, 111.4, 108.6, 22.0\).

2-(3,5-Dimethylphenyl)furan

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 2-bromo-m-xylene (136 \(\mu\)L, 1.0 mmol, 1.0 eq). The desired product (177 mg, 1.00 mmol, 100%) was obtained as a yellow oil-like solid after flash
column chromatography eluting with n-pentane.

\[ R_f = 0.40 \text{ (n-pentane).} \]

\(^1\)H-NMR (300 MHz, CDCl\textsubscript{3}): \[ \delta = 7.45 \text{ (d, } J = 1.7 \text{ Hz, 1H), 7.31 \text{ (s, 2H), 6.91 \text{ (s, 1H),}} \]
\[ 6.61 \text{ (d, } J = 3.4 \text{ Hz, 1H), 6.46 \text{ (dd, } J = 3.3, 1.8 \text{ Hz, 1H), 2.35 \text{ (s, 6H).}} \]

\(^{13}\)C-NMR (75 MHz, CDCl\textsubscript{3}): \[ \delta = 154.4, 141.9, 138.3, 130.9, 129.3, 121.8, 111.7, 104.9, 21.5. \]

\( \nu_{\text{max}} \) (neat)/ cm\textsuperscript{-1}: 1462, 1439, 1377, 1207, 1153, 1030, 999, 903, 810, 768, 733, 687, 598, 567.

m/z (APCI): Found (M+Ag\textsuperscript{+}), 278.9934. C\textsubscript{12}H\textsubscript{12}OAg\textsuperscript{+} requires \( M \), 278.9934.

2-(Naphthalen-2-yl)furan

The desired product was synthesized according to the general procedure starting from furan-2-boronic acid and 2-bromonaphthalene (207 mg, 1.0 mmol, 1.0 eq). The desired product (190 mg, 0.98 mmol, 98%) was obtained as a white solid after flash column chromatography eluting with 5% EtOAc in n-pentane.

\[ R_f = 0.56 \text{ (5\% EtOAc in n-pentane).} \]

\(^1\)H-NMR (400 MHz, CDCl\textsubscript{3}): \[ \delta = 8.06 \text{ (d, } J = 1.6 \text{ Hz, 1H), 7.77 – 7.62 \text{ (m, 3H), 7.42 – 7.30 \text{ (m, 3H),}} \]
\[ 7.27 – 7.19 \text{ (m, 1H), 6.64 \text{ (d, } J = 3.3 \text{ Hz, 1H), 6.39 \text{ (dd, } J = 3.4, 1.8 \text{ Hz, 1H).}} \]

\(^{13}\)C-NMR (101 MHz, CDCl\textsubscript{3}): \[ \delta = 154.1, 142.4, 133.6, 132.7, 128.5, 128.2, 127.8, 126.5, 126.0, 122.4, 122.2, 111.9, 105.7. \]

2-(Furan-2-yl)pyridine

The desired product was synthesized according to the general procedure B starting from furan-2-boronic acid and 2-bromopyridine (96 µL, 1.0 mmol, 1.0 eq). The desired product (68 mg, 0.47 mmol, 47%) was obtained as a yellow oil after flash column chromatography eluting with 15% EtOAc in n-pentane.

\[ R_f = 0.31 \text{ (15\% EtOAc in n-pentane).} \]
\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.64 - 8.51\) (m, 1H), 7.75 - 7.65 (m, 2H), 7.52 (dd, \(J = 1.8, 0.8\) Hz, 1H), 7.16 - 7.10 (m, 1H), 7.05 (dd, \(J = 3.4, 0.8\) Hz, 1H), 6.52 (dd, \(J = 3.4, 1.8\) Hz, 1H).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta = 153.7, 149.7, 149.5, 143.4, 136.7, 122.0, 118.7, 112.2, 108.7\).

**2,3-Diphenylfuran**

According to a procedure by Akai et al.,\(^4\) AuPPh\(_3\)Cl (0.5 mg, 0.01 mmol, 0.1 mol%) and AgNTf\(_2\) (0.5 mg, 0.01 mmol, 0.1 mol%) were added to a solution of 1,2-diphenylbut-3-yne-1,2-di ool (240 mg, 1.0 mmol, 1.0 eq) in toluene (2.5 ml). The reaction was stirred for 16 h at room temperature. Saturated NH\(_4\)Cl-solution (5 mL) was added and the aqueous layer was extracted with Et\(_2\)O (3 x 10 ml). The combined organic layers were washed with brine (30 mL), dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The desired product (65 mg, 0.3 mmol, 30%) was obtained as a colorless oil after flash column chromatography eluting with 5% EtOAc in \(n\)-pentane. 

\(R_f = 0.76\) (5% EtOAc in \(n\)-pentane).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.59 - 7.51\) (m, 3H), 7.48 - 7.43 (m, 2H), 7.39 (tt, \(J = 6.3, 1.1\) Hz, 2H), 7.36 - 7.26 (m, 4H), 6.59 (d, \(J = 1.9\) Hz, 1H).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta = 148.7, 141.7, 134.5, 131.3, 128.8, 128.8, 128.5, 127.7, 127.3, 126.4, 122.4, 114.1\).

**5-(Furan-3-yl)-1-methyl-1\(^H\)-indole**

The desired product was synthesized according to the general procedure A starting from furan-3-boronic acid (270 mg, 2.4 mmol, 1.2 eq) and 5-bromo-1-methyl-1\(^H\)-indole (420 µL, 2.0 mmol, 1.0 eq). The desired product (250 mg, 1.27 mmol, 63%) was obtained as a white solid after flash column chromatography eluting with 25% EtOAc in \(n\)-pentane.

\(R_f = 0.36\) (25% EtOAc in \(n\)-pentane).
$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.80 - 7.73$ (m, 2H), 7.54 – 7.47 (m, 1H), 7.44 – 7.38 (m, 1H), 7.37 – 7.31 (m, 1H), 7.07 (d, $J = 3.1$ Hz, 1H), 6.81 – 6.77 (m, 1H), 6.52 (dd, $J = 3.1$, 0.9 Hz, 1H), 3.81 (s, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 143.4$, 137.7, 136.2, 129.5, 129.0, 127.6, 123.8, 120.3, 118.1, 109.6, 109.5, 101.1, 33.0.
4. Synthesis of products

Unless otherwise noted, an oven-dried screw-cap tube was filled with heterocycle (if solid, 0.2 mmol, 1.0 eq), sodium chloride (1.2 mg, 0.02 mmol, 10 mol%) and SCF$_3$-reagent 2 (85 mg, 0.3 mmol, 1.5 eq). Heterocycle (if liquid, 0.2 mmol, 1.0 eq.) and DMF (1.0 mL) were added and the reaction mixture was stirred for 16 h at 90 °C. After the reaction mixture was cooled down to room temperature, it was poured into water (30 mL) and the aqueous phase was extracted with Et$_2$O (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure (500 mbar). The crude product was purified by flash column chromatography.

3-(4-(Trifluoromethyl)phenyl)-2-((trifluoromethyl)thio)furan (7a)

The desired product 7a was synthesized according to the general procedure starting from 3-(4-(trifluoromethyl)phenyl)furan (42 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7a (56 mg, 0.18 mmol, 90%) was obtained as a colorless oil after flash column chromatography eluting with n-pentane.

$R_f$: 0.34 (n-pentane).

$^1$H-NMR (300 MHz, Acetone-$d_6$): $\delta$ = 8.08 (d, $J = 2.1$ Hz, 1H), 7.98 – 7.92 (m, 2H), 7.88 – 7.81 (m, 2H), 7.10 (d, $J = 2.0$ Hz, 1H).

$^{13}$C-NMR (75 MHz, Acetone-$d_6$): $\delta$ = 150.3, 137.1, 136.1, 130.6 (q, $J = 32.5$ Hz), 129.7, 129.2 (q, $J = 312.0$ Hz), 126.5 (q, $J = 3.9$ Hz), 125.2 (q, $J = 271.3$ Hz), 114.2.

$^{19}$F-NMR (282 MHz, Acetone-$d_6$): $\delta$ = -63.2, -44.0.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 1705, 1620, 1474, 1416, 1323, 1250, 1126, 1088, 1065, 1018, 953, 891, 841, 768.

m/z (APCI): Found (M$^+$), 312.0033. C$_{12}$H$_6$OSF$_6^+$ requires $M$, 312.0038.

3-(4-Nitrophenyl)-2-((trifluoromethyl)thio)furan (7b)

The desired product 7b was synthesized according to the general procedure starting from 3-(4-nitrophényl)furan (38 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7b (35 mg, 0.12 mmol, 61%) was obtained as a white solid after flash column chromatography eluting with 10% Et$_2$O in n-pentane.

$R_f$: 0.18 (10% Et$_2$O in n-pentane).
H-NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 7.81 - 7.75$ (m, 2H), $7.08 - 7.02$ (m, 2H), 6.89 (d, $J = 2.0$ Hz, 1H), 5.93 (d, $J = 2.0$ Hz, 1H).

\(^{13}\)C-NMR (75 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 148.3$, 147.7, 137.0, 135.4, 128.6, 128.6 (q, $J = 312.9$ Hz), 123.8, 112.8.

\(^{19}\)F-NMR (282 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = -42.6$.

$\nu_{\text{max}}$ (neat)/ cm\(^{-1}\): 2280, 1605, 1520, 1501, 1343, 1134, 1092, 1061, 953, 891, 853, 814, 752.

Melting point: 85 – 86 °C.

m/z (APCI): Found (M+H\textsuperscript{+}), 290.0088. C\textsubscript{11}H\textsubscript{6}NO\textsubscript{3}SF\textsubscript{3}H\textsuperscript{+} requires $M$, 290.0093.

**Ethyl 4-(2-((trifluoromethyl)thio)furan-3-yl)benzoate (7c)**

The desired product 7c was synthesized according to the general procedure starting from ethyl 4-(furan-3-yl) benzoate (43 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7c (55 mg, 0.17 mmol, 87%) was obtained as a colorless oil after flash column chromatography eluting with 10% Et\textsubscript{2}O in $n$-pentane.

$R_f$: 0.25 (10% Et\textsubscript{2}O in $n$-pentane).

H-NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 8.17 - 8.12$ (m, 2H), $7.42 - 7.36$ (m, 2H), 6.94 (d, $J = 2.0$ Hz, 1H), 6.07 (d, $J = 2.0$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 1.04 (t, $J = 7.1$ Hz, 3H).

\(^{13}\)C-NMR (75 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 165.9$, 148.2, 136.7, 135.7, 130.9, 130.3, 128.9 (q, $J = 313.0$ Hz), 128.3, 126.8, 113.1, 61.1, 14.3.

\(^{19}\)F-NMR (282 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = -42.7$.

$\nu_{\text{max}}$ (neat)/ cm\(^{-1}\): 1809, 1782, 1709, 1613, 1474, 1416, 1370, 1273, 1130, 1088, 1061, 1022, 949, 891, 856, 756.

m/z (ESI): Found (M+Na\textsuperscript{+}), 339.0282. C\textsubscript{14}H\textsubscript{11}O\textsubscript{3}SF\textsubscript{3}Na\textsuperscript{+} requires $M$, 339.0273.

**3-(4-Chlorophenyl)-2-((trifluoromethyl)thio)furan (7d)**

The desired product 7d was synthesized according to the general procedure starting from 3-(4-chlorophenyl)furan (36 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7d (45 mg, 0.16 mmol, 79%) was obtained as a colorless oil after flash column chromatography eluting with $n$-pentane.

$R_f$: 0.42 ($n$-pentane).
\(^1\)H-NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 7.75\) (d, \(J = 2.0\) Hz, 1H), 7.62 – 7.55 (m, 2H), 7.46 – 7.40 (m, 2H), 6.77 (d, \(J = 2.0\) Hz, 1H).
\(^{13}\)C-NMR (75 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 148.7, 136.6, 134.6, 130.2, 129.8, 129.2, 128.6\) (q, \(J = 312.8\) Hz), 113.4.
\(^{19}\)F-NMR (282 MHz, CD\(_2\)Cl\(_2\)): \(\delta = -43.2\).

\(\nu\)\(_{\text{max}}\) (neat)/ cm\(^{-1}\): 2361, 1778, 1505, 1493, 1408, 1130, 1088, 1057, 1038, 1015, 949, 891, 868, 829, 756.

m/z (APCI): Found (M\(^+\)), 277.9769. C\(_{11}\)H\(_6\)OC\(_3\)SF\(_3\) requires \(M\), 277.9774.

3-Phenyl-2-((trifluoromethyl)thio)furan (7e)

The desired product 7e was synthesized according to the general procedure starting from 3-phenylfuran (29 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7e (39 mg, 0.16 mmol, 80%) was obtained as a colorless oil after flash column chromatography eluting with \(n\)-pentane.

\(R_f\) : 0.33 (\(n\)-pentane).
\(^1\)H-NMR (300 MHz, Acetone-\(d_6\)): \(\delta = 8.02\) (d, \(J = 2.0\) Hz, 1H), 7.73 – 7.68 (m, 2H), 7.53 – 7.41 (m, 3H), 7.01 (d, \(J = 2.1\) Hz, 1H).
\(^{13}\)C-NMR (75 MHz, Acetone-\(d_6\)): \(\delta = 149.9, 132.0, 129.6, 129.5, 129.3\) (q, \(J = 311.6\) Hz), 129.3, 128.9, 128.2, 114.2.
\(^{19}\)F-NMR (282 MHz, Acetone-\(d_6\)): \(\delta = -44.1\).

\(\nu\)\(_{\text{max}}\) (neat)/ cm\(^{-1}\): 1802, 1782, 1505, 1439, 1370, 1126, 1107, 1088, 1057, 1030, 949, 914, 891, 864, 752.

m/z (APCI): Found (M\(^+\)), 244.0157. C\(_{11}\)H\(_7\)OSF\(_3\) requires \(M\), 244.0164.

3-(4-Methoxyphenyl)-2-((trifluoromethyl)thio)furan (7f)

The desired product 7f was synthesized according to the general procedure starting from 3-(4-methoxyphenyl)furan (35 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7f (45 mg, 0.16 mmol, 82%) was obtained as a colorless oil after flash column chromatography eluting with 2% Et\(_2\)O in \(n\)-pentane.

\(R_f\) : 0.37 (2% Et\(_2\)O in \(n\)-pentane).
\(^1\)H-NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 7.71\) (d, \(J = 2.0\) Hz, 1H), 7.62 – 7.56 (m, 2H), 7.01 – 6.95 (m, 2H), 6.76 (d, \(J = 2.0\) Hz, 1H), 3.84 (s, 3H).
$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 160.2, 148.4, 137.5, 133.1, 129.6, 128.7$ (q, $J = 312.9$ Hz), 123.9, 114.4, 113.4, 55.7.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -43.5$.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 1613, 1516, 1458, 1366, 1281, 1250, 1126, 1103, 1084, 1034, 949, 891, 829.

m/z (APCI): Found (M$^+$), 274.0264. C$_{12}$H$_9$O$_2$S$_3^+$ requires M, 274.0270.

3-(3-Trifluoromethyl)phenyl)-2-((trifluoromethyl)thio)furan (7g)

The desired product 7g was synthesized according to the general procedure starting from 3-(3-(trifluoromethyl)phenyl)furan (42 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7g (46 mg, 0.15 mmol, 74%) was obtained as a colorless oil after flash column chromatography eluting with n-pentane.

$R_f$: 0.53 (n-pentane).

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.90 - 7.82$ (m, 2H), 7.78 (d, $J = 2.0$ Hz, 1H), 7.69 - 7.56 (m, 2H), 6.82 (d, $J = 2.0$ Hz, 1H).

$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 148.9, 136.5, 132.6, 131.9, 131.2$ (q, $J = 32.3$ Hz), 129.7, 128.5 (q, $J = 312.8$ Hz), 125.4 (q, $J = 3.8$ Hz), 125.2 (q, $J = 3.9$ Hz), 124.5 (q, $J = 272.3$ Hz), 113.4.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -63.1, -43.2$.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 2361, 1782, 1501, 1331, 1261, 1096, 1057, 1042, 957, 891, 868, 806.

m/z (APCI): Found (M$^+$), 312.0033. C$_{12}$H$_6$OSF$_3^+$ requires M, 312.0038.

2-(3-(2-((Trifluoromethyl)thio)furan-3-yl)phenyl)-1,3-dioxolane (7h)

The desired product 7h was synthesized according to the general procedure starting from 2-(3-(furan-3-yl)phenyl)-1,3-dioxolane (43 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7h (45 mg, 0.14 mmol, 71%) was obtained as a colorless oil after flash column chromatography eluting with 30% Et$_2$O in n-pentane.

$R_f$: 0.20 (30% Et$_2$O in n-pentane).

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.75$ (d, $J = 2.0$ Hz, 1H), 7.73 - 7.69 (m, 1H), 7.67 - 7.62 (m, 1H), 7.52 - 7.43 (m, 2H), 6.81 (d, $J = 2.0$ Hz, 1H), 5.83 (s, 1H), 4.17 - 3.99 (m, 4H).
$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 148.5, 139.3, 137.5, 131.7, 129.1, 129.0, 128.6$ (q, $J = 312.8$ Hz), 126.9, 126.7, 113.6, 103.8, 65.8.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -43.2$.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 2361, 2330, 1497, 1389, 1362, 1207, 1126, 1111, 1088, 1030, 968, 941, 891, 799.

m/z (APCI): Found (M+H$^+$), 317.0447. C$_{14}$H$_{11}$O$_3$SF$_3$H$^+$ requires $M$, 317.0454.

3-(3,5-Dimethylphenyl)-2-((trifluoromethyl)thio)furan (7i)

The desired product 7i was synthesized according to the general procedure starting from 3-(3,5-dimethylphenyl)furan (34 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7i (46 mg, 0.17 mmol, 84%) was obtained as a yellow oil after flash column chromatography eluting with n-pentane.

$R_f$: 0.46 (n-pentane).

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.72$ (d, $J = 2.0$ Hz, 1H), 7.25 – 7.19 (m, 2H), 7.06 – 7.01 (m, 1H), 6.75 (d, $J = 2.0$ Hz, 1H), 2.36 (s, 6H).

$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 148.3, 138.6, 138.0, 133.1, 131.4, 130.3, 128.7$ (q, $J = 312.8$ Hz), 126.3, 113.7, 21.4.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -43.3$.

m/z (APCI): Found (M$^+$), 272.0471. C$_{13}$H$_{11}$OSF$_3$H$^+$ requires $M$, 272.0477.

3-(o-Tolyl)-2-((trifluoromethyl)thio)furan (7j)

The desired product 7j was synthesized according to the general procedure starting from 3-(o-tolyl)furan (32 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7j (42 mg, 0.16 mmol, 81%) was obtained as a colorless oil after flash column chromatography eluting with n-pentane.

$R_f$: 0.24 (n-pentane).

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.75$ (d, $J = 2.0$ Hz, 1H), 7.34 – 7.16 (m, 4H), 6.63 (d, $J = 2.0$ Hz, 1H), 2.21 (s, 3H).

$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 148.0, 138.4, 137.1, 131.7, 130.6, 130.5, 128.9, 128.6$ (q, $J = 312.7$ Hz), 126.0, 115.2, 20.2.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -43.4$. 
2-(2-((Trifluoromethyl)thio)furan-3-yl)pyridine (7k)

The desired product 7k was synthesized according to the general procedure starting from 2-(furan-3-yl)pyridine (29 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 7k (40 mg, 0.16 mmol, 82%) was obtained as a colorless oil after flash column chromatography eluting with 30% Et2O in n-pentane.

\( R_f : 0.18 \) (30% Et2O in n-pentane).

\(^1\text{H-NMR} (300 \text{ MHz, CD}_2\text{Cl}_2)\): \( \delta = 8.68 - 8.64 \) (m, 1H), 7.97 - 7.92 (m, 1H), 7.81 - 7.73 (m, 2H), 7.30 - 7.24 (m, 1H), 7.12 (d, \( J = 2.0 \text{ Hz} \), 1H).

\(^{13}\text{C-NMR} (75 \text{ MHz, CD}_2\text{Cl}_2)\): \( \delta = 150.4, 150.1, 148.3, 136.8, 133.1, 128.7 \) (q, \( J = 312.8 \text{ Hz} \)), 123.2, 122.5, 120.3, 113.4.

\(^{19}\text{F-NMR} (282 \text{ MHz, CD}_2\text{Cl}_2)\): \( \delta = -42.8 \).

\( \nu_{\text{max}} \) (neat)/ cm\(^{-1}\): 2361, 2330, 1593, 1493, 1458, 1427, 1373, 1126, 1088, 1049, 995, 961, 891.

m/z (APCI): Found (M+), 258.0320. \( \text{C}_{12}\text{H}_9\text{OSF}_3^+ \) requires \( M, 258.0321 \).

2-(4-(Trifluoromethyl)phenyl)-5-((trifluoromethyl)thio)furan (9a)

The desired product 9a was synthesized according to the general procedure starting from 2-(4-(trifluoromethyl)phenyl)furan (42 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9a (60 mg, 0.19 mmol, 95%) was obtained as a clear oil after flash column chromatography eluting with \( n \)-pentane.

\( R_f : 0.37 \) (\( n \)-pentane).

\(^1\text{H-NMR} (300 \text{ MHz, CD}_2\text{Cl}_2)\): \( \delta = 7.87 - 7.82 \) (m, \( J = 7.7, 1.7, 0.9 \text{ Hz} \), 2H), 7.73 - 7.66 (m, 2H), 7.06 (d, \( J = 3.5 \text{ Hz} \), 1H), 6.91 (d, \( J = 3.5 \text{ Hz} \), 1H).

\(^{13}\text{C-NMR} (75 \text{ MHz, CD}_2\text{Cl}_2)\): \( \delta = 158.5, 135.5, 133.2, 130.5 \) (q, \( J = 32.6 \text{ Hz} \)), 128.4 (q, \( J = 312.1 \text{ Hz} \)), 126.3 (q, \( J = 3.8 \text{ Hz} \)), 126.2, 124.9, 109.6.

\(^{19}\text{F-NMR} (282 \text{ MHz, CD}_2\text{Cl}_2)\): \( \delta = -44.1, -63.1 \).

\( \nu_{\text{max}} \) (neat)/ cm\(^{-1}\): 2361, 2330, 1620, 1420, 1323, 1273, 1142, 1099, 1069, 1049, 1014, 941, 922, 841, 795, 772.

m/z (APCI): Found (M+), 246.0188. \( \text{C}_{10}\text{H}_6\text{NOSF}_3\text{H}^+ \) requires \( M, 246.0195 \).
4-(5-((Trifluoromethyl)thio)furan-2-yl)benzonitrile (9b)

The desired product 9b was synthesized according to the general procedure starting from 2-(4-cyanophenyl)furan (34 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9b (53 mg, 0.20 mmol, 100%) was obtained as a clear oil after flash column chromatography eluting with 10% EtOAc in n-pentane.

R_f: 0.22 (10% EtOAc in n-pentane).

^1H-NMR (300 MHz, CD_2Cl_2): δ = 7.83 – 7.78 (m, 2H), 7.74 – 7.68 (m, 2H), 7.06 (d, J = 3.5 Hz, 1H), 6.93 (d, J = 3.5 Hz, 1H).

^13C-NMR (75 MHz, CD_2Cl_2): δ = 157.9, 133.6, 133.1, 128.4 (q, J = 311.9 Hz), 126.4, 126.4, 125.0, 118.9, 112.3, 110.4.

^19F-NMR (282 MHz, CD_2Cl_2): δ = -43.9.

^ν_(max) (neat)/ cm^-1: 2226, 1609, 1551, 1508, 1474, 1142, 1099, 1053, 1022, 941, 841, 806, 795.

m/z (APCI): Found (M^+), 269.0111, C_{12}H_6NOSF_3 requires M, 269.0117.

2-(4-Bromophenyl)-5-((trifluoromethyl)thio)furan (9c)

The desired product 9c was synthesized according to the general procedure starting from 2-(4-bromophenyl)furan (45 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9c (57 mg, 0.18 mmol, 90%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

R_f: 0.29 (n-pentane).

^1H-NMR (300 MHz, CD_2Cl_2): δ = 7.64 – 7.52 (m, 4H), 7.03 (d, J = 3.5 Hz, 1H), 6.80 (d, J = 3.5 Hz, 1H).

^13C-NMR (75 MHz, CD_2Cl_2): δ = 159.1, 134.5, 132.4, 132.4 (q, J = 311.3 Hz), 128.9, 126.4, 126.3, 123.1, 108.3.

^19F-NMR (282 MHz, CD_2Cl_2): δ = -44.3.

^ν_(max) (neat)/ cm^-1: 3649, 1508, 1466, 1404, 1184, 1130, 1088, 1072, 1049, 1007, 937, 918, 872, 826, 791.

Melting point: 63 – 64 °C.

m/z (APCI): Found (M^+), 321.9264, C_{11}H_6OSBrF_3 requires M, 321.9269.
2-(4-Fluorophenyl)-5-((trifluoromethyl)thio)furan (9d)

The desired product 9d was synthesized according to the general procedure starting from 2-(4-fluorophenyl)furan (32 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9d (52 mg, 0.20 mmol, 100%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

\[ R_f : 0.31 \ (n\text{-pentane}). \]

\[ ^1H\text{-NMR (300 MHz, CD}_2\text{Cl}_2): \delta = 7.75 - 7.64 \ (m, 2H), 7.19 - 7.08 \ (m, 2H), 7.01 \ (d, J = 3.4 \ Hz, 1H), 6.73 \ (d, J = 3.5 \ Hz, 1H). \]

\[ ^13C\text{-NMR (75 MHz, CD}_2\text{Cl}_2): \delta = 165.0, 160.5 \ (d, J = 181.2 \ Hz), 128.4 \ (q, J = 311.8 \ Hz), 126.8 \ (d, J = 8.7 \ Hz), 126.5, 116.4 \ (d, J = 16.9 \ Hz), 107.7 \ (d, J = 1.1 \ Hz). \]

\[ ^19F\text{-NMR (282 MHz, CD}_2\text{Cl}_2): \delta = -44.4, -112.6. \]

\[ \nu_{\text{max}} \ (\text{neat})/ \ \text{cm}^{-1}: 1717, 1609, 1516, 1474, 1238, 1169, 1134, 1084, 1049, 1018, 937, 837, 799, 752. \]

Melting point: 49 - 50 °C.

m/z (APCI): Found (M⁺), 262.0064. C₁₁H₆OSF₄ requires \( M, 262.0070. \)

2-Phenyl-5-((trifluoromethyl)thio)furan (9e)

The desired product 9e was synthesized according to the general procedure starting from 2-phenylfuran (29 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9e (27 mg, 0.11 mmol, 55%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

\[ R_f : 0.37 \ (n\text{-pentane}). \]

\[ ^1H\text{-NMR (300 MHz, CD}_2\text{Cl}_2): \delta = 7.88 - 7.63 \ (m, 2H), 7.56 - 7.26 \ (m, 3H), 7.03 \ (d, J = 3.5 \ Hz, 1H), 6.79 \ (d, J = 3.4 \ Hz, 1H). \]

\[ ^13C\text{-NMR (75 MHz, CD}_2\text{Cl}_2): \delta = 160.2, 130.0, 129.3, 129.2, 128.5 \ (q, J = 311.5 \ Hz), 126.4, 126.4, 124.7, 107.8. \]

\[ ^19F\text{-NMR (282 MHz, CD}_2\text{Cl}_2): \delta = -44.4. \]

\[ \nu_{\text{max}} \ (\text{neat})/ \ \text{cm}^{-1}: 2967, 2924, 1589, 1508, 1458, 1261, 1138, 1099, 1057, 1018, 937, 918, 883, 799, 760. \]

Melting point: 45 – 46 °C.

m/z (APCI): Found (M⁺), 244.0158. C₁₁H₇OSF₃ requires \( M, 244.0164. \)
1-(4-(5-((Trifluoromethyl)thio)furan-2-yl)phenyl)pyrrolidine (9f)

The desired product 9f was synthesized according to the general procedure starting from 1-(4-(furan-2-yl)phenyl)pyrrolidine (43 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9f (15 mg, 0.05 mmol, 25%) was obtained as a clear oil after flash column chromatography eluting with Et₂O.

\[ R_f : 0.67 \text{ (Et}_2\text{O)} \].

\[ ^1\text{H-NMR (300 MHz, CD}_2\text{Cl}_2) : \delta = 7.59 - 7.53 \text{ (m, 2H)}, 6.97 \text{ (d, } J = 3.5 \text{ Hz, 1H)}, 6.63 - 6.55 \text{ (m, 2H)}, 6.53 \text{ (d, } J = 3.5 \text{ Hz, 1H)}, 3.37 - 3.28 \text{ (m, 4H)}, 2.05 - 1.99 \text{ (m, 4H)} \].

\[ ^{13}\text{C-NMR (75 MHz, CD}_2\text{Cl}_2) : \delta = 161.8, 148.7, 128.4 \text{ (q, } J = 312.4 \text{ Hz)}, 126.8, 126.0, 117.2, 111.9, 104.3, 47.9, 25.8 \].

\[ ^{19}\text{F-NMR (282 MHz, CD}_2\text{Cl}_2) : \delta = -45.0 \].

\[ \nu_{\text{max}} \text{ (neat)/ cm}^{-1} : 2369, 1613, 1524, 1458, 1385, 1134, 1096, 1053, 1015, 961, 937, 914, 864, 818, 783 \].

\[ m/z \text{ (APCI): Found (M}^+\text{), 313.0738, C}_{15}\text{H}_{14}\text{NOSF}_3 \text{ requires } M, 313.0743. \]

**Note:** The starting material contained 20% of an inseparable impurity.

Methyl 3-(5-((Trifluoromethyl)thio)furan-2-yl)benzoate (9g)

The desired product 9g was synthesized according to the general procedure starting from methyl 3-(furan-2-yl)benzoate (40 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9g (33 mg, 0.11 mmol, 53%) was obtained as a clear oil after flash column chromatography eluting with 10% Et₂O in n-pentane.

\[ R_f : 0.57 \text{ (20% Et}_2\text{O in n-pentane)} \].

\[ ^1\text{H-NMR (300 MHz, CD}_2\text{Cl}_2) : \delta = 8.38 - 8.33 \text{ (m, 1H)}, 8.04 - 7.96 \text{ (m, 1H)}, 7.94 - 7.89 \text{ (m, 1H)}, 7.57 - 7.49 \text{ (m, 1H)}, 7.05 \text{ (d, } J = 3.5 \text{ Hz, 1H)}, 6.88 \text{ (d, } J = 3.5 \text{ Hz, 1H)}, 3.93 \text{ (s, 3H)} \].

\[ ^{13}\text{C-NMR (75 MHz, CD}_2\text{Cl}_2) : \delta = 166.7, 159.1, 131.5, 130.3, 129.9, 129.5, 128.8, 128.4 \text{ (q, } J = 311.9 \text{ Hz)}, 126.4, 125.6, 108.7, 52.6 \].

\[ ^{19}\text{F-NMR (282 MHz, CD}_2\text{Cl}_2) : \delta = -44.2 \].

\[ \nu_{\text{max}} \text{ (neat)/ cm}^{-1} : 1724, 1717, 1439, 1319, 1285, 1238, 1134, 1099, 1061, 1022, 988, 941, 910, 802, 752. \]
m/z (ESI): Found (M+Na\(^+\)), 325.0121, C\(_{13}\)H\(_9\)O\(_3\)SF\(_3\)Na requires \(M\), 325.0117.

2-(3-Methoxyphenyl)-5-((trifluoromethyl)thio)furan (9h)

The desired product 9h was synthesized according to the general procedure starting from 2-(3-methoxyphenyl)furan (35 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9h (55 mg, 0.2 mmol, 100%) was obtained as a red oil after flash column chromatography eluting with Et\(_2\)O.

\(R_f\) : 0.63 (Et\(_2\)O).

\(^1\)H-NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 7.40 - 7.19\) (m, 3H), 7.02 (d, \(J = 3.5\) Hz, 1H), 6.95 – 6.85 (m, 1H), 6.78 (d, \(J = 3.5\) Hz, 1H), 3.85 (s, 3H).

\(^{13}\)C-NMR (75 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 160.6, 160.2, 134.2, 131.4, 130.5, 128.6\) (q, \(J = 311.8\) Hz), 126.6 (q, \(J = 1.0\) Hz), 117.4, 115.0, 110.3, 108.3, 55.9.

\(^{19}\)F-NMR (282 MHz, CD\(_2\)Cl\(_2\)): \(\delta = -44.4\).

\(\nu_{\text{max}}\) (neat)/ cm\(^{-1}\): 3021, 2963, 2943, 2916, 2843, 1605, 1570, 1481, 1416, 1316, 1288, 1277, 1215, 1157, 1126, 1103, 1042, 1018, 995, 937, 833, 795, 775.

m/z (APCI): Found (M+H\(^+\)), 275.0346, C\(_{12}\)H\(_9\)O\(_2\)SF\(_3\)H\(^+\) requires \(M\), 275.0348.

2-(3,5-Dimethylphenyl)-5-((trifluoromethyl)thio)furan (9i)

The desired product 9i was synthesized according to the general procedure starting from 2-(3,5-dimethylphenyl)furan (34 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9i (39 mg, 0.14 mmol, 70%) was obtained as a clear oil after flash column chromatography eluting with n-pentane.

\(R_f\) : 0.50 (n-pentane).

\(^1\)H-NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 7.35\) (d, \(J = 1.5\) Hz, 2H), 7.01 (d, \(J = 3.3\) Hz, 2H), 6.75 (d, \(J = 3.4\) Hz, 1H), 2.36 (s, 6H).

\(^{13}\)C-NMR (75 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 139.0, 133.1, 131.0, 129.7, 128.4\) (q, \(J = 312.1\) Hz), 126.4, 122.5, 110.4, 107.6, 21.4.

\(^{19}\)F-NMR (282 MHz, CD\(_2\)Cl\(_2\)): \(\delta = -44.5\).

\(\nu_{\text{max}}\) (neat)/ cm\(^{-1}\): 2357, 1636, 1551, 1508, 1489, 1474, 1458, 1057, 995, 937, 833, 795, 775.

m/z (APCI): Found (M+H\(^+\)), 273.0553, C\(_{13}\)H\(_{11}\)OSF\(_3\)H\(^+\) requires \(M\), 273.0556.
2-(o-Tolyl)-5-((trifluoromethyl)thio)furan (9j)

The desired product 9j was synthesized according to the general procedure starting from 2-(o-tolyl)furan (32 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9j (27 mg, 0.10 mmol, 50%) was obtained as a clear oil after flash column chromatography eluting with n-pentane.

$R_f$: 0.30 (n-pentane).

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.71 – 7.61$ (m, 1H), 7.28 (d, $J = 2.8$ Hz, 3H), 7.04 (d, $J = 3.5$ Hz, 1H), 6.67 (d, $J = 3.4$ Hz, 1H), 2.50 (s, 3H).

$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 160.3$, 135.9, 131.7, 129.4, 129.2, 128.5 (q, $J = 311.7$ Hz), 127.9, 126.5, 125.9, 111.2, 21.9.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -44.4$.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 2959, 2928, 1458, 1142, 1096, 1018, 941, 918, 864, 795.

m/z (APCI): Found (M$^+$), 258.0319, C$_{12}$H$_9$OSF$_3$ requires $M$, 258.0321.

2-(Naphthalen-2-yl)-5-((trifluoromethyl)thio)furan (9k)

The desired product 9k was synthesized according to the general procedure starting from 2-(naphthalen-2-yl)furan (39 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9k (50 mg, 0.17 mmol, 84%) was obtained as a white solid after flash column chromatography eluting with n-pentane.

$R_f$: 0.21 (n-pentane).

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 8.26 – 8.20$ (m, 1H), 7.95 – 7.77 (m, 4H), 7.57 – 7.48 (m, 2H), 7.08 (d, $J = 3.5$ Hz, 1H), 6.90 (d, $J = 3.5$ Hz, 1H).

$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 160.2$, 133.7, 129.0, 128.7, 128.4 (q, $J = 311.9$ Hz), 128.1, 127.2, 127.2, 127.1, 126.5, 123.7, 122.4, 108.4.

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): $\delta = -44.3$.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 1574, 1489, 1265, 1165, 1130, 1100, 1053, 1018, 957, 937, 895, 864, 833, 795.

Melting point: 97 – 98 °C.

m/z (APCI): Found (M+H$^+$), 295.0393. C$_{15}$H$_9$OSF$_3$H$^+$ requires $M$, 295.0399.
2-(5-((Trifluoromethyl)thio)furan-2-yl)pyridine (9l)

The desired product 9l was synthesized according to the general procedure starting from 2-(furan-2-yl)pyridine (29 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9l (40 mg, 0.16 mmol, 82%) was obtained as a white solid after flash column chromatography eluting with 30% Et₂O in n-pentane.

\( R_f : 0.34 \) (30% Et₂O in n-pentane).

\(^1\)H-NMR (300 MHz, CD₂Cl₂): \( \delta = 8.62 - 8.58 \) (m, 1H), 7.80 - 7.75 (m, 2H), 7.28 - 7.22 (m, 1H), 7.15 (d, \( J = 3.5 \) Hz, 1H), 7.07 (d, \( J = 3.5 \) Hz, 1H).

\(^{13}\)C-NMR (75 MHz, CD₂Cl₂): \( \delta = 159.7, 150.2, 148.5, 137.2, 128.4 \) (q, \( J = 311.8 \) Hz), 126.4, 123.6, 119.5, 110.8.

\(^{19}\)F-NMR (282 MHz, CD₂Cl₂): \( \delta = -42.2 \).

\( \nu_{\text{max}} \) (neat)/ cm\(^{-1}\): 1601, 1578, 1559, 1497, 1466, 1424, 1269, 1196, 1153, 1138, 1092, 1065, 1045, 988, 937, 922, 849, 775.

Melting point: 55 – 56 °C.

m/z (APCI): Found (M+Na\(^+\)), 268.0012. C\(_{10}\)H\(_6\)NOSF\(_3\)Na\(^+\) requires \( M \), 268.0014.

2,3-Diphenyl-5-((trifluoromethyl)thio)furan (9m)

The desired product 9m was synthesized according to the general procedure starting from 2,3-diphenylfuran (44 mg, 0.20 mmol, 1.0 eq) and reagent 2. The desired product 9m (33 mg, 0.10 mmol, 52%) was obtained as a colorless oil after flash column chromatography eluting with n-pentane.

\( R_f : 0.33 \) (n-pentane).

\(^1\)H-NMR (300 MHz, CD₂Cl₂): \( \delta = 7.57 - 7.52 \) (m, 2H), 7.40 - 7.31 (m, 8H), 7.09 (s, 1H).

\(^{13}\)C-NMR (75 MHz, CD₂Cl₂): \( \delta = 154.9, 133.1, 130.3, 129.2, 129.0, 128.9, 128.3 \) (q, \( J = 311.9 \) Hz), 128.2, 127.8, 127.1, 125.1.

\(^{19}\)F-NMR (282 MHz, CD₂Cl₂): \( \delta = -44.0 \).

\( \nu_{\text{max}} \) (neat)/ cm\(^{-1}\): 1605, 1501, 1474, 1443, 1389, 1227, 1138, 1115, 1092, 1072, 1022, 953, 914, 841, 760.

m/z (APCI): Found (M\(^+\)), 320.0475. C\(_{17}\)H\(_{11}\)OSF\(_3\) requires \( M \), 320.0477.
2-Butyl-5-((trifluoromethyl)thio)furan (9n)

The desired product 9n was synthesized according to the general procedure starting from 2-butylfuran (28 μL, 0.20 mmol, 1.0 eq) and reagent 2. The yield of the desired product 9n was determined by $^{19}$F NMR spectroscopic analysis with (trifluoromethoxy)benzene as internal standard.

$^{19}$F-NMR (CDCl$_3$, 282 MHz): $\delta = -45.3$.

MS (EI): Found (M$^+$), 224.0. C$_9$H$_{11}$OSF$_3^+$ requires M, 224.0.

2,3-Dimethyl-5-((trifluoromethyl)thio)furan (9o)

The desired product 9o was synthesized according to the general procedure starting from 2,3-dimethylfuran (21 μL, 0.20 mmol, 1.0 eq) and reagent 2. The yield of the desired product 9o was determined by $^{19}$F NMR spectroscopic analysis with (trifluoromethoxy)benzene as internal standard.

$^{19}$F-NMR (CDCl$_3$, 282 MHz): $\delta = -45.3$.

MS (EI): Found (M$^+$), 196.0. C$_7$H$_7$OSF$_3^+$ requires M, 196.0.

1-Methyl-3-((trifluoromethyl)thio)-5-(2-((trifluoromethyl)thio)furan-3-yl)-1H-indole (11b)

1) An oven-dried screw-cap tube was filled with 5-(furan-3-yl)-1-methyl-1H-indole (43 mg, 0.20 mmol, 1.0 eq), sodium chloride (1.2 mg, 0.02 mmol, 10 mol%) and SCF$_3$-reagent 1 (54 mg, 0.22 mmol, 1.1 eq). DMF (1.0 mL) was added and the reaction mixture was stirred for 24 h at 90 °C. SCF$_3$-reagent 2 (85 mg, 0.30 mmol, 1.5 eq) was added and the reaction mixture was stirred for additional 16 h at 90 °C.

2) The desired product 11b was synthesized according to the general procedure starting from 5-(furan-3-yl)-1-methyl-1H-indole (43 mg, 0.20 mmol, 1.0 eq) and reagent 2 (142 mg, 0.50 mmol, 2.5 eq).

After the reaction mixture was cooled down to room temperature, it was poured into water (30 mL) and the aqueous phase was extracted with Et$_2$O (3 x 30 mL). The
combined organic phases were washed with brine (50 mL), dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure (500 mbar). The crude product was purified by flash column chromatography eluting with 50% Et$_2$O in $n$-pentane. The desired product 11b (1) 60 mg, 0.15 mmol, 76%; 2) 56 mg, 0.14 mmol, 70%) was obtained as a colorless oil.

$R_f$: 0.37 (50% Et$_2$O in $n$-pentane).

$^{1}$H-NMR (300 MHz, Acetone-$d_6$): $\delta$ = 8.09 – 8.05 (m, 1H), 8.02 (d, $J = 2.0$ Hz, 1H), 7.85 – 7.84 (m, 1H), 7.65 (d, $J = 1.2$ Hz, 2H), 7.06 (d, $J = 2.0$ Hz, 1H), 3.98 (s, 3H).

$^{13}$C-NMR (75 MHz, Acetone-$d_6$): $\delta$ = 149.7, 139.9, 138.2, 135.0, 133.5, 130.4 (q, $J = 309.2$ Hz), 129.4 (q, $J = 312.1$ Hz), 125.2, 124.0, 123.7, 119.3, 114.5, 111.8, 33.6.

$^{19}$F-NMR (282 MHz, Acetone-$d_6$): $\delta$ = -44.2, -46.0.

$\nu_{\text{max}}$ (neat)/ cm$^{-1}$: 2361, 1701, 1512, 1366, 1339, 1246, 1123, 1088, 957, 891, 795.

m/z (APCI): Found (M$^+$), 397.0019. C$_{15}$H$_9$NOS$_2$F$_6$$^+$ requires $M$, 397.0024.
5. Unsuccessful Starting Materials

Unless otherwise noted, an oven-dried screw-cap tube was filled with heterocycle (if solid, 0.2 mmol, 1.0 eq), sodium chloride (1.2 mg, 0.02 mmol, 10 mol%) and SCF$_3$-reagent 2 (85 mg, 0.3 mmol, 1.5 eq). DMF (1.0 mL) was added and the reaction mixture was stirred for 16 h at 90 °C. After the reaction mixture was cooled down to room temperature, the reaction mixture was checked by GC-MS.

<table>
<thead>
<tr>
<th>Remaining starting material</th>
<th>0%</th>
<th>&lt;5%</th>
<th>&gt;95%</th>
<th>&gt;95%</th>
<th>&gt;95%</th>
<th>&gt;95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structures]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. Radical Trapping Experiments

Reactions were performed according to the general procedure on a 0.1 mmol scale with 0.05 mmol additive. Yields determined by $^{19}$F NMR spectroscopic analysis with 1-(trifluoromethoxy)benzene as internal standard. Reactions were analyzed by GC-MS and ESI-MS to determine possible radical coupling products.

Table 4. Radical trapping experiments.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Yield</th>
<th>Coupling products</th>
</tr>
</thead>
<tbody>
<tr>
<td>no additive</td>
<td>100%</td>
<td>-</td>
</tr>
<tr>
<td>hydroquinone</td>
<td>58%</td>
<td>no coupling products detected</td>
</tr>
<tr>
<td>BHT</td>
<td>99%</td>
<td>no coupling products detected</td>
</tr>
<tr>
<td>TEMPO</td>
<td>18%</td>
<td>no coupling products detected</td>
</tr>
<tr>
<td>galvinoxyl</td>
<td>33%</td>
<td>no coupling products detected</td>
</tr>
</tbody>
</table>

Previous results that phenolic compounds (hydroquinone) and free radicals (TEMPO, galvinoxyl) could lead to decomposition of reagent 2 and the fact that no radical coupling products could be observed by mass spectrometry indicate that the reaction mechanism is not likely to be radical in nature. The observation that BHT does not lead to diminished yields can be explained by steric shielding of the phenol moiety by the tert-butyl substituents.
7. Robustness Screen

A simplified robustness screen as reported within our group\textsuperscript{[5]} has been undertaken to evaluate the tolerance of this reaction to the given functionalities and chemical motifs, as well as the stability of these ‘additives’ to the reaction conditions. This procedure requires the undertaking of a standard reaction in the presence of one molar equivalent of a given additive (functional group or heterocycle). After the predetermined reaction time the yield of the product and the starting material remaining is determined by \textsuperscript{19}F-NMR-analysis and the additive remaining is determined by GC analysis.

Reactions are run in parallel on a small scale to minimize experimental time and consumption of material. The calibration of the additives and the product of the reaction was undertaken using the single point calibration technique for gas chromatography (GC) analysis as previously reported. The robustness screen was undertaken using two ‘standard’ batches of additives as previously reported. 2-Butylfuran was excluded because it represents a possible product.

Sample procedure: 1) In a flame dried Schlenk flask under argon was prepared a stock solution of substrate 6c (216 mg, 1.0 mmol, 1.0 eq) and SCF\textsubscript{3}-reagent 2 (425 mg, 1.5 mmol, 1.5 eq) in DMF (5.0 mL).

2) NaCl (0.6 mg, 0.01 mmol, 10 mol\%) and the distributed stock solution (0.5 mL, ~0.1 mmol/reaction) were added to the reaction vessels, followed by the addition of the given additive (0.1 mmol).

3) The reactions were heated for 16 h at 90 °C prior to cooling, the addition of mesitylene (15 μL, 0.11 mmol, 1.1 eq) and 1-(trifluoromethoxy)benzene (15 μL, 0.11 mmol, 1.1 eq) and analysis by GC and \textsuperscript{19}F-NMR.

Note: Change in volume of stock solution due to addition of starting materials was not accounted for, hence a control reaction (no additive) was undertaken to determine the maximum yield of reaction. N-methylimidazole and dodecylamine should be filtered through celite and not silica when preparing samples for GC analysis.
Table 5. Table shows the effect of a given additive on the standard reaction. The yield of 7c and the additive remaining after reaction is given. Color-coding should help the ready assessment of the data: green (above 66%), yellow (34-66%), red (below 34%).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Yield of 7c %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Additive remaining %&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>Yield of 7c %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Additive remaining %&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>x</td>
<td>26</td>
</tr>
<tr>
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</table>
8. Literature

9. NMR spectra

*Note:* Due to volatility of the products, traces of solvent are left in some cases.
Note: Compound 11b contains slight impurities of coeluted phthalimide.