Supporting Information for
Elemental Sulfur-Promoted One-Pot Synthesis of
2-(2,2,2-Trifluoroethyl)benzoxazoles and their derivatives
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General information

$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra were recorded using Bruker AVIII 400 spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as the external standard and low field is positive. Coupling constants ($J$) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: $^1$H NMR (chloroform $\delta$ 7.26) and $^{13}$C NMR (chloroform $\delta$ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on Waters GCT-TOF. Reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.
Table 1. The effect of the reaction temperature and time, and the addition of water for the synthesis of 3q

<table>
<thead>
<tr>
<th>Entry</th>
<th>Promoter (equiv)</th>
<th>Base (3.0 equiv)</th>
<th>Additive</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<td>S₈ (8)</td>
<td>NaHCO₃</td>
<td>ADVN/B₂Pin₂</td>
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<td>S₈ (8)</td>
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<td>-</td>
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a Reaction conditions: 1 (0.70 mmol), 2q (0.10 mmol), base (0.30 mmol), solvent (1.0 mL), under N₂ atmosphere; b The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as internal standard; c 1.0 equiv.; d ADVN : B₂Pin₂ : H₂O = 0.9 : 0.7 : 1.0.
Table 2. The effect of relative amounts of elemental sulfur and 2-bromo-3,3,3-trifluoropropene (1) for the cyclization

| Entry | equiv of S₈ | equiv of 1 | Additive | Yield (%)  
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<td>6.0</td>
<td>-</td>
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<td>7.0</td>
<td>-</td>
<td>54</td>
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<td>ADVN/B₂Pin₂&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>7.0</td>
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<tr>
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<td>7.0</td>
<td>ADVN/B₂Pin₂&lt;sup&gt;c&lt;/sup&gt;</td>
<td>79</td>
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<sup>a</sup> Reaction conditions: 1 (0.70 mmol), 2q (0.10 mmol), base (0.30 mmol), solvent (1.0 mL), under N₂ atmosphere;  
<sup>b</sup> The yield was determined by <sup>19</sup>F NMR spectroscopy with PhOCF₃ as internal standard;  
<sup>c</sup> ADVN (0.9 equiv), B₂Pin₂ (0.7 equiv).
Table 3. The reaction of 2q with 1 mediated by other promoters

![Reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Promoter (equiv)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>3q</th>
<th>6q</th>
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<td>1</td>
<td>I&lt;sub&gt;2&lt;/sub&gt; (5)</td>
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<td>2</td>
<td>KI (5)</td>
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<td>3</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>15</td>
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<sup>a</sup> Reaction conditions: 1 (0.70 mmol), 2q (0.10 mmol), base (0.30 mmol), solvent (1.0 mL), under N<sub>2</sub> atmosphere; <sup>b</sup> The yield was determined by <sup>19</sup>F NMR spectroscopy with PhOCF<sub>3</sub> as internal standard.
General procedure of one-pot synthesis of 2-(2,2,2-trifluoroethyl)benzoxazoles, benzothiazoles, and benzoimidazoles

\[
\begin{array}{c}
\text{R} \quad \text{NH}_2 \\
\text{X} = \text{O, S, N}
\end{array} + \begin{array}{c}
\text{Br} \\
\text{CF}_3
\end{array} \xrightarrow{\text{S}_8 (8.0 \text{ equiv}) \\ \text{NaHCO}_3 (3.0 \text{ equiv}) \\ \text{ADVN/B}_2\text{Pin}_2 } \xrightarrow{\text{DMF, 100 °C, 15 h}} \begin{array}{c}
\text{R} \\
\text{X} \\
\text{CF}_3
\end{array}
\]

The 2-aminophenol derivatives (2), \( \alpha \)-aminobenzenethiols, or benzene-1,2-diamines (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (1) (2.10 mmol, 7.0 equiv), \( \text{S}_8 \) (2.40 mmol, 8.0 equiv), \( \text{NaHCO}_3 \) (0.90 mmol, 3.0 equiv), 2,2'-azobis-(2,4-dimethylvaleronitrile) (ADVN) (0.27 mmol, 0.90 equiv), bis(pinacolato)diboron (B\(_2\)Pin\(_2\)) (0.21 mmol, 0.70 equiv), and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 15 h under nitrogen atmosphere. After cooled down to room temperature, the reaction system was quenched with water (10 mL) and ethyl acetate (10 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine (3 × 15 mL), and water (3 × 15 mL), dried over MgSO\(_4\). The solvent was removed by rotary evaporation and the resulting product 3 was purified by column chromatography over silica gel.
### Scalability of the reaction of 2q with 1

The 2-amino-4-chlorophenol (2q) (6.0 mmol, 0.868 g, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (1) (42.0 mmol, 4.2 mL, 7.0 equiv), S₈ (48.0 mmol, 1.74 g, 8.0 equiv), NaHCO₃ (18.0 mmol, 1.50 g, 3.0 equiv), ADVN (5.4 mmol, 1.32 g, 0.90 equiv), B₂Pin₂ (4.2 mmol, 0.96 g, 0.70 equiv), and DMF (40 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 15 h under nitrogen atmosphere. After cooled down to room temperature, the reaction system was quenched with water (150 mL) and ethyl acetate (100 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 × 70 mL). The combined organic layers were washed with saturated brine (3 × 300 mL), and water (3 × 300 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting product 3q (0.51 g, 36% yield) was purified by column chromatography over silica gel.
Mechanistic Study

(a).

\[
\text{Cl-NH}_2 \quad 2q \quad + \quad \text{Br-CF}_3 \quad 1 \quad \xrightarrow{\text{S}_8 \ (8.0 \ \text{equiv}) \ \text{NaHCO}_3 \ (3.0 \ \text{equiv}) \ \text{ADVN/B}_2\text{Pin}_2 \ \text{DMF, 100 °C, 15 h} \ \text{TEMPO (2 equiv)}} \quad \text{Cl} \quad \text{N} \quad \text{CF}_3 \quad 3q, 2\%
\]

The 2-amino-4-chlorophenol (2q) (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (1) (2.10 mmol, 7.0 equiv), S₈ (2.40 mmol, 8.0 equiv), NaHCO₃ (0.90 mmol, 3.0 equiv), ADVN (0.27 mmol, 0.90 equiv), B₂Pin₂ (0.21 mmol, 0.70 equiv), TEMPO (0.60 mmol, 2.0 equiv) and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 15 h under nitrogen atmosphere. The yield was determined by ¹⁹F NMR spectroscopy with PhOCF₃ as internal standard. The yield of the product 3q was calculated to be 2%.

(b).

\[
\text{Cl-NH}_2 \quad 2q \quad + \quad \text{Br-CF}_3 \quad 1 \quad \xrightarrow{\text{NaHCO}_3 \ (3.0 \ \text{equiv}) \ \text{ADVN/B}_2\text{Pin}_2 \ \text{DMF, 100 °C, 15 h}} \quad \text{Cl} \quad \text{NH}_2 \quad 6q, 63\%
\]

The 2-amino-4-chlorophenol (2q) (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (1) (2.10 mmol, 7.0 equiv), NaHCO₃ (0.90 mmol, 3.0 equiv), ADVN (0.27 mmol, 0.90 equiv), B₂Pin₂ (0.21 mmol, 0.70 equiv), and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 15 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (3 × 10 mL), washed with saturated brine (3 × 15 mL), and water (3 × 15 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting product 6q was purified by column chromatography over silica gel.

(c).
The 5-chloro-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)aniline (6q) (0.15 mmol, 1.0 equiv), S₈ (1.20 mmol, 8.0 equiv), NaHCO₃ (0.45 mmol, 3.0 equiv), ADVN (0.14 mmol, 0.90 equiv), B₂Pin₂ (0.11 mmol, 0.70 equiv), and DMF (1.5 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 15 h under nitrogen atmosphere. A ¹⁹F-NMR spectrum was acquired, and no trace of 3q was detectable.

(d).

The 4-bromobenzene-1,2-diamine (0.30 mmol, 1.0 equiv), 2-bromo-3,3,3-trifluoropropene (1) (2.10 mmol, 7.0 equiv), S₈ (2.40 mmol, 8.0 equiv), NaHCO₃ (0.90 mmol, 3.0 equiv), ADVN (0.27 mmol, 0.90 equiv), B₂Pin₂ (0.21 mmol, 0.70 equiv), and DMF (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 15 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (3 × 10 mL), washed with saturated brine (3 × 15 mL), and water (3 × 15 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting product 5c and 7c was purified by column chromatography over silica gel.

(e).
The solution of \( N\)-(2-amino-4-bromophenyl)-3,3,3-trifluoropropanethioamide (7c) (10 mg, 0.030 mmol), in 1.5 mL CDCl\(_3\) was added into a NMR tube. A \(^{19}\text{F}\)-NMR spectrum was acquired. The tube was kept at r.t. for 72 hours, a second \(^{19}\text{F}\)-NMR spectrum was acquired, and the yield of product 5c was determined to be 40%. The solution was analyzed by GC-MS.
Data for compounds

2-(2,2,2-Trifluoroethyl)benzoxazole (3a)

Purification by column chromatography (silica gel, n-pentane) gave final product 3a as a light yellow liquid in 70% yield (42 mg). \( R_f \) (n-pentane) = 0.28. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.79 (d, \( J = 8.4 \) Hz, 1H), 7.59 (d, \( J = 8.2 \) Hz, 1H), 7.46 – 7.36 (m, 2H), 3.85 (q, \( J = 9.8 \) Hz, 2H). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -63.8 (t, \( J = 9.8 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 156.3 (q, \( J = 4.0 \) Hz), 151.1 (s), 140.8 (s), 125.8 (s), 124.8 (s), 123.7 (q, \( J = 278.6 \) Hz), 120.4 (s), 110.8 (s), 34.7 (q, \( J = 32.9 \) Hz). IR (ATR): \( \nu \) 2248, 1617, 1498, 1454, 1261, 1153, 812, 497, 458, 428 cm\(^{-1}\). GC-MS m/z 200 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_7\)NOF\(_3\) [M+H]\(^+\): 202.0474; found: 202.0472.

5-Methyl-2-(2,2,2-trifluoroethyl)benzoxazole (3b)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 25:1) gave final product 3b as a brownish yellow liquid in 65% yield (42 mg). \( R_f \) (n-pentane/ethyl acetate = 25:1) = 0.73. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.56 (s, 1H), 7.45 (d, \( J = 8.4 \) Hz, 1H), 7.22 (d, \( J = 8.2 \) Hz, 1H), 3.82 (q, \( J = 9.8 \) Hz, 2H), 2.50 (s, 3H). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -63.8 (t, \( J = 9.8 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 156.3 (q, \( J = 4.0 \) Hz), 149.4 (s), 141.0 (s), 134.7 (s), 126.9 (s), 123.7 (q, \( J = 277.5 \) Hz), 120.2 (s), 110.2 (s), 34.7 (q, \( J = 32.9 \) Hz), 21.4 (s). IR (ATR): \( \nu \) 2927, 1617, 1578, 1542, 1500, 1484, 1419, 1368, 1334, 1259, 1244, 1147, 1094, 800, 594 cm\(^{-1}\). GC-MS m/z 214 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_{10}\)H\(_9\)F\(_3\)NO [M+H]\(^+\): 216.0631; found: 216.0627.
6-Methyl-2-(2,2,2-trifluoroethyl)benzoxazole (3c)

Purification by column chromatography (silica gel, n-pentane) gave final product 3c as a light yellow liquid in 66% yield (43 mg). $R_f$ (n-pentane) = 0.20. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.1$ Hz, 1H), 7.38 (s, 1H), 7.21 (d, $J = 8.1$ Hz, 1H), 3.81 (q, $J = 9.8$ Hz, 2H), 2.52 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.9 (t, $J = 9.8$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.7 (q, $J = 4.2$ Hz), 151.5 (s), 138.7 (s), 136.3 (s), 126.1 (s), 123.8 (q, $J = 277.6$ Hz), 119.7 (s), 110.9 (s), 34.7 (q, $J = 32.9$ Hz), 21.8 (s). IR (ATR): ν 3252, 2252, 1593, 1498, 1270, 1151, 813, 688, 421 cm$^{-1}$. GC-MS m/z 214 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{10}$H$_9$F$_3$NO [M+H]$^+$: 216.0631; found: 216.0628.

4-Methyl-2-(2,2,2-trifluoroethyl)benzoxazole (3d)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3d as a brown solid in 83% yield (54 mg). M.p. 38.4–40.1 °C. $R_f$ (n-pentane/ethyl acetate = 20:1) = 0.82. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.1$ Hz, 1H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.18 (d, $J = 7.4$ Hz, 1H), 3.84 (q, $J = 9.8$ Hz, 2H), 2.65 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.8 (t, $J = 9.8$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.5 (q, $J = 4.1$ Hz), 151.0 (s), 140.1 (s), 130.9 (s), 125.4 (s), 125.3 (s), 123.8 (q, $J = 277.6$ Hz), 108.1 (s), 34.7 (q, $J = 33.0$ Hz), 16.4 (s). IR (ATR): ν 3328, 2973, 2881, 1379, 1274, 1087, 1046, 880, 807, 609, 474, 421 cm$^{-1}$. GC-MS m/z 214 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{10}$H$_9$F$_3$NO [M+H]$^+$: 216.0631; found: 216.0628.
5-(tert-Butyl)-2-(2,2,2-trifluoroethyl)benzoxazole (3e)

Purification by column chromatography (silica gel, n-pentane) gave final product 3e as a light yellow liquid in 57% yield (44 mg). $R_t$ (n-pentane) = 0.28. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H), 7.55 – 7.42 (m, 2H), 3.83 (q, $J$ = 9.8 Hz, 2H), 1.40 (s, 9H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.9 (t, $J$ = 9.8 Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.4 (q, $J$ = 4.1 Hz), 149.2 (s), 148.5 (s), 140.7 (s), 123.8 (q, $J$ = 277.5 Hz), 123.6 (s), 116.8 (s), 110.0 (s), 35.0 (s), 34.7 (q, $J$ = 32.9 Hz), 31.7 (s). IR (ATR): $\nu$ 2963, 1670, 1579, 1482, 1425, 1365, 1259, 1245, 1146, 1124, 1092, 963, 863, 810, 623 cm$^{-1}$. GC-MS m/z 256 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{13}$H$_{15}$F$_3$NO [M+H]$^+$: 258.1100; found: 258.1096.

5-Phenyl-2-(2,2,2-trifluoroethyl)benzoxazole (3f)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 3f as a light yellow solid in 50% yield (42 mg). M.p. 47.6–49.3 °C. $R_t$ (n-pentane/ethyl acetate = 10:1) = 0.65. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (s, 1H), 7.72 – 7.57 (m, 4H), 7.50 (t, $J$ = 7.2 Hz, 2H), 7.42 (d, $J$ = 7.0 Hz, 1H), 3.87 (q, $J$ = 9.6 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.7 (t, $J$ = 9.6 Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.9 (q, $J$ = 4.3 Hz), 150.7 (s), 141.5 (s), 140.8 (s), 138.9 (s), 128.9 (s), 127.5 (s), 127.4 (s), 125.4 (s), 123.7 (q, $J$ = 277.5 Hz), 118.8 (s), 110.8 (s), 34.7 (q, $J$ = 32.9 Hz). IR (ATR): $\nu$ 2928, 1620, 1577, 1468, 1452, 1420, 1367, 1259, 1201, 1148, 960, 925, 894, 859, 839, 817, 761, 698, 649, 632, 520 cm$^{-1}$. GC-MS m/z 276 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{15}$H$_{11}$F$_3$NO [M+H]$^+$: 278.0787; found: 278.0786.
5-Methoxy-2-(2,2,2-trifluoroethyl)benzoxazole (3g)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 25:1) gave final product 3g as a brown solid in 71% yield (49 mg). M.p. 33.2–34.5 °C. $R_t$ (n-pentane/ethyl acetate = 25:1) = 0.60. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.9$ Hz, 1H), 7.24 (d, $J = 2.2$ Hz, 1H), 7.00 (dd, $J = 8.9$, 2.2 Hz, 1H), 3.87 (s, 3H), 3.81 (q, $J = 9.8$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.8 (t, $J = 9.8$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.5 (s), 157.0 (q, $J = 4.1$ Hz), 145.8 (s), 141.6 (s), 123.7 (q, $J = 277.5$ Hz), 114.6 (s), 111.0 (s), 103.0 (s), 56.0 (s), 34.7 (q, $J = 32.9$ Hz). IR (ATR): ν 2943, 1614, 1577, 1533, 1483, 1439, 1369, 1343, 1260, 1243, 1148, 1093, 1026, 806, 640 cm$^{-1}$. GC-MS m/z 230 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{10}$H$_6$F$_3$NO$_2$ [M+H]$^+$: 232.0580; found: 232.0576.

Methyl 2-(2,2,2-trifluoroethyl)benzoxazole-6-carboxylate (3h)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3h as a light yellow solid in 68% yield (53 mg). M.p. 63.6–65.8 °C. $R_t$ (n-pentane/ethyl acetate = 20:1) = 0.50. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.27 (s, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 3.98 (s, 3H), 3.88 (q, $J = 9.7$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.6 (t, $J = 9.7$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.4 (s), 159.0 (q, $J = 4.1$ Hz), 150.8 (s), 144.5 (s), 128.0 (s), 126.5 (s), 123.5 (q, $J = 277.6$ Hz), 120.1 (s), 112.6 (s), 52.5 (s), 34.8 (q, $J = 33.1$ Hz). IR (ATR): ν 2955, 1718, 1610, 1574, 1497, 1436, 1319, 1284, 1261, 1240, 1220, 1148, 1077, 981, 513, 423 cm$^{-1}$. GC-MS m/z 258 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{11}$H$_6$F$_3$NO$_3$ [M+H]$^+$: 260.0529; found: 260.0524.
1-(2-(2,2,2-Trifluoroethyl)benzoxazol-7-yl)ethanone (3i)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3i as a light yellow solid in 63% yield (47 mg). M.p. 61.7–63.6 °C. 

$R_f$ (n-pentane/ethyl acetate = 20:1) = 0.36. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (t, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.9$ Hz, 1H), 3.94 (q, $J = 9.6$ Hz, 2H), 2.84 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.7 (t, $J = 9.6$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.5 (s), 156.9 (q, $J = 4.1$ Hz), 149.6 (s), 142.1 (s), 126.5 (s), 125.5 (s), 124.9 (s), 123.6 (q, $J = 281.1$ Hz), 122.1 (s), 34.7 (q, $J = 33.2$ Hz), 30.2 (s). IR (ATR): ν 2254, 1618, 1498, 1279, 1155, 814, 543, 504, 478, 443, 421 cm$^{-1}$. GC-MS m/z 242 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{11}$H$_9$F$_3$N$_2$ [M+H]$^+$: 244.0580; found: 244.0576.

2-(2,2,2-Trifluoroethyl)benzoxazole-5-carboxylic acid (3j)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 2:1) gave final product 3j as a light yellow solid in 62% yield (46 mg). M.p. 148.1–150.2 °C. $R_f$ (n-pentane/ethyl acetate = 2:1) = 0.32. $^1$H NMR (400 MHz, CD$_3$OD) δ 8.40 (s, 1H), 8.18 (d, $J = 8.6$ Hz, 1H), 7.75 (d, $J = 8.6$ Hz, 1H), 4.13 (q, $J = 10.1$ Hz, 2H). $^{19}$F NMR (376 MHz, CD$_3$OD) δ -65.4 (t, $J = 10.1$ Hz, 3F). $^{13}$C NMR (101 MHz, CD$_3$OD) δ 167.6 (s), 158.9 (q, $J = 4.5$ Hz), 153.8 (s), 140.7 (s), 128.0 (s), 127.5 (s), 124.1 (q, $J = 276.2$ Hz), 121.6 (s), 110.4 (s), 33.4 (q, $J = 32.8$ Hz). IR (ATR): ν 3371, 2489, 2077, 1691, 1626, 1578, 1439, 1367, 1261, 1237, 1171, 1114, 1086, 967, 900, 836, 774 cm$^{-1}$. GC-MS m/z 244 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{10}$H$_7$F$_3$NO$_3$ [M+H]$^+$: 246.0373; found: 246.0372.
2-(2,2,2-Trifluoroethyl)benzoxazole-6-carboxylic acid (3k)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 5:1) gave final product 3k as a light yellow solid in 58% yield (43 mg). M.p. 145.0–147.0 °C. Rf (n-pentane/ethyl acetate = 5:1) = 0.30. $^1$H NMR (400 MHz, CD$_3$OD) δ 8.28 (s, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.3$ Hz, 1H), 4.14 (q, $J = 10.1$ Hz, 2H). $^{19}$F NMR (376 MHz, CD$_3$OD) δ -65.3 (t, $J = 10.2$ Hz, 3F). $^{13}$C NMR (101 MHz, CD$_3$OD) δ 167.5 (s), 160.1 (q, $J = 4.2$ Hz), 150.7 (s), 144.2 (s), 128.6 (s), 126.3 (s), 124.1 (q, $J = 276.4$ Hz), 119.3 (s), 112.1 (s), 33.5 (q, $J = 32.7$ Hz). IR (ATR): ν 3372, 2924, 2495, 2077, 1679, 1609, 1572, 1435, 1360, 1274, 1238, 1189, 1115, 1044, 1021, 971, 895, 848, 778, 750, 551, 430 cm$^{-1}$. GC-MS m/z 244 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{10}$H$_7$F$_3$NO$_3$ [M+H]$^+$: 246.0373; found: 246.0372.

2-(2,2,2-Trifluoroethyl)benzoxazole-5-carbonitrile (3l)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 3l as a light yellow solid in 72% yield (49 mg). M.p. 51.2–52.8 °C. Rf (n-pentane/ethyl acetate = 10:1) = 0.69. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.77 – 7.61 (m, 2H), 3.89 (q, $J = 9.6$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.6 (t, $J = 9.6$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.7 (q, $J = 4.1$ Hz), 153.3 (s), 141.2 (s), 129.8 (s), 125.2 (s), 123.4 (q, $J = 277.7$ Hz), 118.3 (s), 112.3 (s), 109.1 (s), 34.6 (q, $J = 33.3$ Hz). IR (ATR): ν 3290, 2231, 1626, 1577, 1471, 1417, 1368, 1336, 1258, 1242, 1183, 1095, 963, 861, 818, 741, 618, 527, 487, 430 cm$^{-1}$. GC-MS m/z 225 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{10}$H$_6$F$_3$N$_2$O [M+H]$^+$: 227.0427; found: 227.0425.
5-Nitro-2-(2,2,2-trifluoroethyl)benzoxazole (3m)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3m as a brownish yellow solid in 42% yield (31 mg). M.p. 69.3-70.8 °C. Rf (n-pentane/ethyl acetate = 20:1) = 0.45. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.69 (s, 1H), 8.40 (d, $J = 9.0$ Hz, 1H), 7.72 (d, $J = 8.9$ Hz, 1H), 3.92 (q, $J = 9.6$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.5 (t, $J = 9.6$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.5 (q, $J = 4.1$ Hz), 154.5 (s), 145.6 (s), 141.2 (s), 123.4 (q, $J = 277.9$ Hz), 121.9 (s), 117.0 (s), 111.2 (s), 34.8 (q, $J = 33.4$ Hz). IR (ATR): ν 3110, 1623, 1578, 1533, 1500, 1438, 1348, 1260, 1240, 1149, 1063, 963, 829, 737, 690 cm$^{-1}$. GC-MS m/z 245 (M$^+$. HRMS (ESI) m/z: calcd. for C$_9$H$_6$F$_3$N$_2$O$_3$ [M+H]$^+$: 247.0325; found: 247.0320.

5-Chloro-7-nitro-2-(2,2,2-trifluoroethyl)benzoxazole (3n)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3n as a brownish yellow solid in 38% yield (32 mg). M.p. 68.6–70.0 °C. Rf (n-pentane/ethyl acetate = 20:1) = 0.63. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.26 (s, 1H), 8.10 (s, 1H), 3.98 (q, $J = 9.4$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.5 (t, $J = 9.4$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.0 (q, $J = 4.1$ Hz), 144.9 (s), 142.6 (s), 133.2 (s), 130.7 (s), 127.0 (s), 123.2 (q, $J = 277.7$ Hz), 122.1 (s), 34.6 (q, $J = 33.6$ Hz). IR (ATR): ν 3094, 1612, 1540, 1519, 1452, 1415, 1351, 1327, 1299, 1252, 1206, 1153, 1023, 949, 910, 877, 851, 762, 629, 588 cm$^{-1}$. GC-MS m/z 279 (M$^+$. HRMS (EI) m/z: calcd. for C$_9$H$_6$F$_3$N$_2$O$_3$Cl: 279.9863; found: 279.9868.
5-Fluoro-2-(2,2,2-trifluoroethyl)benzoxazole (3o)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 25:1) gave final product 3o as a light yellow liquid in 78% yield (51 mg). *R*$_f$ (*n*-pentane/ethyl acetate = 25:1) = 0.70. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 9.0 Hz, 1H), 3.84 (q, *J* = 9.7 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.8 (t, *J* = 9.7 Hz, 3F), -117.1 (td, *J* = 8.7, 4.2 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.2 (d, *J* = 241.6 Hz), 158.1 (q, *J* = 4.0 Hz), 147.5 (d, *J* = 1.2 Hz), 141.6 (d, *J* = 13.2 Hz), 123.6 (q, *J* = 277.5 Hz), 113.7 (d, *J* = 26.4 Hz), 111.2 (d, *J* = 10.0 Hz), 106.9 (d, *J* = 25.8 Hz), 34.7 (q, *J* = 33.2 Hz). IR (ATR): ν 3027, 2161, 1578, 1479, 1261, 1244, 1151, 1133, 1095, 857, 807, 635, 607, 536, 434 cm$^{-1}$. GC-MS *m/z* 218 (M$^+$. HRMS (ESI) *m/z*: calcd. for C$_9$H$_6$F$_4$NO [M+H]$^+$: 220.0380; found: 220.0377.

6-Fluoro-2-(2,2,2-trifluoroethyl)benzoxazole (3p)

Purification by column chromatography (silica gel, *n*-pentane/ethyl acetate = 25:1) gave final product 3p as a light yellow liquid in 67% yield (44 mg). *R*$_f$ (*n*-pentane/ethyl acetate = 25:1) = 0.73. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (dd, *J* = 8.7, 4.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 9.1 Hz, 1H), 3.83 (q, *J* = 9.7 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.9 (t, *J* = 9.7 Hz, 3F), -114.0 (td, *J* = 8.7, 5.0 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.0 (d, *J* = 245.4 Hz), 156.9 (q, *J* = 4.1 Hz), 151.1 (d, *J* = 14.7 Hz), 137.1 (d, *J* = 1.6 Hz), 123.6 (q, *J* = 277.6 Hz), 120.8 (d, *J* = 10.2 Hz), 113.0 (d, *J* = 24.8 Hz), 98.9 (d, *J* = 28.3 Hz), 34.6 (q, *J* = 33.1 Hz). IR (ATR): ν 3350, 2963, 1723, 1622, 1578, 1485, 1440, 1369, 1341, 1277, 1258, 1125, 1101, 958, 839, 629 cm$^{-1}$. GC-MS *m/z* 218 (M$^+$. HRMS (ESI) *m/z*: calcd. for C$_9$H$_6$F$_4$NO [M+H]$^+$: 220.0380; found: 220.0377.
5-Chloro-2-(2,2,2-trifluoroethyl)benzoxazole (3q)

Purification by column chromatography (silica gel, n-pentane) gave final product 3q as a brown solid in 85% yield (60 mg). M.p. 32.7–34.1 °C. Rf (n-pentane) = 0.48. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (s, 1H), 7.48 (d, \(J = 8.7\) Hz, 1H), 7.36 (d, \(J = 8.7\) Hz, 1H), 3.83 (q, \(J = 9.7\) Hz, 2H). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.7 (t, \(J = 9.7\) Hz, 3F). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.7 (q, \(J = 4.1\) Hz), 149.7 (s), 141.9 (s), 130.4 (s), 126.2 (s), 123.6 (q, \(J = 277.5\) Hz), 120.4 (s), 111.6 (s), 34.6 (q, \(J = 33.1\) Hz). IR (ATR): \(\nu\) 2958, 1605, 1573, 1453, 1419, 1365, 1331, 1299, 1243, 1145, 1118, 1054, 800, 732, 631, 424 cm\(^{-1}\). GC-MS m/z 234 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_6\)F\(_3\)NOCl [M+H]\(^+\): 236.0085; found: 236.0081.

6-Chloro-2-(2,2,2-trifluoroethyl)benzoxazole (3r)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3r as a light yellow solid in 75% yield (52 mg). M.p. 41.7–42.9 °C. Rf (n-pentane/ethyl acetate = 20:1) = 0.72. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.69 (d, \(J = 8.5\) Hz, 1H), 7.61 (s, 1H), 7.39 (d, \(J = 8.5\) Hz, 1H), 3.83 (q, \(J = 9.7\) Hz, 2H). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.7 (t, \(J = 9.7\) Hz, 3F). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.0 (q, \(J = 3.5\) Hz), 151.3 (s), 139.6 (s), 131.7 (s), 125.7 (s), 123.5 (q, \(J = 275.7\) Hz), 121.0 (s), 111.5 (s), 34.6 (q, \(J = 33.2\) Hz). IR (ATR): \(\nu\) 3352, 2966, 1615, 1578, 1497, 1464, 1429, 1367, 1261, 1243, 1148, 1095, 1053, 928, 814, 688 cm\(^{-1}\). GC-MS m/z 234 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_6\)F\(_3\)NOCl [M+H]\(^+\): 236.0085; found: 236.0081.
5,7-Dichloro-2-(2,2,2-trifluoroethyl)benzoxazole (3s)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3s as a light yellow solid in 52% yield (42 mg). M.p. 103.4–105.1 °C. R\(_f\) (n-pentane/ethyl acetate = 20:1) = 0.68. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68 (s, 1H), 7.45 (s, 1H), 3.87 (q, \(J = 9.5\) Hz, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.6 (t, \(J = 9.5\) Hz, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.1 (q, \(J = 4.1\) Hz), 146.6 (s), 142.6 (s), 130.8 (s), 126.4 (s), 123.4 (q, \(J = 277.8\) Hz), 119.1 (s), 116.8 (s), 34.6 (q, \(J = 33.2\) Hz). IR (ATR): \(\nu\) 2962, 1693, 1591, 1574, 1528, 1459, 1422, 1258, 1153, 1074, 992, 948, 853, 816, 632 cm\(^{-1}\). GC-MS m/z 268 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_5\)F\(_3\)NOCl [M+H]\(^+\): 269.9695; found: 269.9691.

5-Bromo-2-(2,2,2-trifluoroethyl)benzoxazole (3t)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3t as a light yellow solid in 39% yield (33 mg). M.p. 54.2–56.1 °C. R\(_f\) (n-pentane/ethyl acetate = 20:1) = 0.60. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (s, 1H), 7.54 (d, \(J = 8.6\) Hz, 1H), 7.47 (d, \(J = 8.4\) Hz, 1H), 3.84 (q, \(J = 9.6\) Hz, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.7 (t, \(J = 9.6\) Hz, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.5 (q, \(J = 3.9\) Hz), 150.1 (s), 142.4 (s), 129.0 (s), 123.6 (q, \(J = 277.6\) Hz), 123.5 (s), 117.7 (s), 112.1 (s), 34.7 (q, \(J = 33.1\) Hz). IR (ATR): \(\nu\) 2928, 2101, 2062, 2028, 1997, 1964, 1570, 1449, 1421, 1368, 1329, 1259, 1150, 1096, 1044, 961, 921, 890, 866, 840, 803, 683, 631, 588, 465, 426 cm\(^{-1}\). GC-MS m/z 278 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_6\)F\(_3\)NOBr [M+H]\(^+\): 279.9579; found: 279.9583.
Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3u as a light yellow solid in 68% yield (57 mg). M.p. 318.9–320.0 °C. R\textsubscript{f} (n-pentane/ethyl acetate = 20:1) = 0.73. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.73 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 3.88 (q, J = 9.6 Hz, 2H). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ -63.7 (t, J = 9.6 Hz, 3F). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 156.6 (q, J = 3.9 Hz), 149.4 (s), 141.5 (s), 129.0 (s), 126.1 (s), 123.5 (q, J = 277.6 Hz), 119.5 (s), 102.7 (s), 34.6 (q, J = 33.2 Hz). IR (ATR): ν 3328, 2973, 2881, 1593, 1379, 1274, 1087, 1046, 880, 807, 609, 474, 421 cm\textsuperscript{-1}. GC-MS m/z 278 (M\textsuperscript{+}). HRMS (ESI) m/z: calcd. for C\textsubscript{9}H\textsubscript{6}F\textsubscript{3}NOBr [M+H]\textsuperscript{+}: 279.9579; found: 279.9576.

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 3v as a light yellow solid in 36% yield (27 mg). M.p. 116.4–117.3 °C. R\textsubscript{f} (n-pentane/ethyl acetate = 10:1) = 0.77. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.24 (s, 1H), 8.04 (d, J = 7.6 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.65 – 7.46 (m, 2H), 3.90 (q, J = 9.6 Hz, 2H). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ -63.5 (t, J = 9.6 Hz, 3F). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 158.6 (q, J = 3.7 Hz), 149.7 (s), 140.5 (s), 131.9 (s), 131.4 (s), 128.7 (s), 128.0 (s), 126.0 (s), 125.0 (s), 124.0 (q, J = 347.7 Hz), 118.1 (s), 106.8 (s), 34.9 (q, J = 33.0 Hz). IR (ATR): ν 2940, 2288, 2165, 2050, 1982, 1617, 1579, 1505, 1443, 1421, 1367, 1308, 1270, 1257, 1241, 1202, 1162, 1142, 1089, 956, 920, 898, 875, 858, 843, 749, 623, 473 cm\textsuperscript{-1}. GC-MS m/z 250 (M\textsuperscript{+}). HRMS (ESI) m/z: calcd. for C\textsubscript{13}H\textsubscript{9}F\textsubscript{3}NO [M+H]\textsuperscript{+}: 252.0631; found: 252.0631.
6-Methyl-2-(2,2,2-trifluoroethyl)oxazolo[5,4-b]pyridine (3w)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 3w as a light yellow liquid in 39% yield (25 mg). Rf (n-pentane/ethyl acetate = 10:1) = 0.50. 1H NMR (400 MHz, CDCl3) δ 8.25 (s, 1H), 7.90 (s, 1H), 3.85 (q, J = 9.5 Hz, 2H), 2.52 (s, 3H). 19F NMR (376 MHz, CDCl3) δ -63.6 (t, J = 9.5 Hz, 3F). 13C NMR (101 MHz, CDCl3) δ 158.4 (s), 156.9 (q, J = 4.5 Hz), 146.0 (s), 132.4 (s), 131.3 (s), 129.2 (s), 123.5 (q, J = 77.6 Hz), 35.0 (q, J = 33.1 Hz), 18.4 (s). IR (ATR): ν 2931, 2283, 2202, 2160, 2049, 2034, 1996, 1979, 1620, 1570, 1419, 1366, 1264, 1231, 1151, 946, 880, 842, 779, 635, 596, 460, 445 cm⁻¹. GC-MS m/z 215 (M⁺). HRMS (ESI) m/z: calcd. for C9H8F3N2O [M+H]⁺: 217.0583; found: 217.0584.

6-Bromo-2-(2,2,2-trifluoroethyl)oxazolo[5,4-b]pyridine (3x)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 3x as a light yellow solid in 28% yield (23 mg). M.p. 90.7–91.2 °C. Rf (n-pentane/ethyl acetate = 20:1) = 0.50. 1H NMR (400 MHz, CDCl3) δ 8.50 (s, 1H), 8.25 (s, 1H), 3.88 (q, J = 9.8 Hz, 2H). 19F NMR (376 MHz, CDCl3) δ -63.5 (t, J = 9.8 Hz, 3F). 13C NMR (101 MHz, CDCl3) δ 158.6 (q, J = 4.7 Hz), 146.6 (s), 133.9 (s), 131.7 (s), 123.3 (q, J = 77.9 Hz), 116.8 (s), 107.4 (s), 35.0 (q, J = 32.2 Hz). GC-MS m/z 279 (M⁺). HRMS (ESI) m/z: calcd. for C9H5F3N2OBr [M+H]⁺: 280.9532; found: 280.9533.
2,6-Bis(2,2,2-trifluoroethyl)benzo[1,2-d:5,4-d’]bis(oxazole) (3y)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 3y as a light yellow solid in 61% yield (59 mg). M.p. 87.3–88.6 °C. 

$R_f$ (n-pentane/ethyl acetate = 10:1) = 0.42. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 7.77 (s, 1H), 3.88 (q, $J = 9.6$ Hz, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.7 (t, $J = 9.6$ Hz, 6F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.4 (q, $J = 5.1$ Hz), 149.3 (s), 138.7 (s), 123.6 (q, $J = 277.7$ Hz), 111.1 (s), 93.8 (s), 34.8 (q, $J = 33.2$ Hz). IR (ATR): $\nu$ 2926, 1621, 1590, 1431, 1375, 1255, 1106, 877, 837, 673, 627, 529 cm$^{-1}$. GC-MS m/z 323 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{12}$H$_7$F$_6$N$_2$O$_2$ [M+H]$^+$: 325.0406; found: 325.0405.

5,5’-(Perfluoropropane-2,2-diyl)bis(2-(2,2,2-trifluoroethyl)benzoxazole) (3z)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 3z as a light yellow solid in 70% yield (116 mg). M.p. 67.8–69.2 °C. 

$R_f$ (n-pentane/ethyl acetate = 10:1) = 0.73. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (s, 2H), 7.57 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 3.86 (q, $J = 9.6$ Hz, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.6 (s, 6F), -63.7 (t, $J = 9.6$ Hz, 6F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.7 (q, $J = 4.0$ Hz), 151.1 (s), 140.9 (s), 130.5 (s), 128.0 (s), 124.1 (q, $J = 287.4$ Hz), 122.9 (s), 120.8 (q, $J = 277.6$ Hz), 110.7 (s), 65.4 – 64.1 (m), 34.6 (q, $J = 33.2$ Hz). IR (ATR): $\nu$ 2960, 1624, 1580, 1482, 1421, 1368, 1337, 1244, 1203, 1187, 1126, 964, 858, 811, 679, 637, 535, 484, 435 cm$^{-1}$. GC-MS m/z 479 (M$^+$). HRMS (ESI) m/z: calcd. for C$_{21}$H$_{11}$F$_{12}$N$_2$O$_2$ [M+H]$^+$: 551.0623; found: 551.0630.
Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 5:1) gave final product 3aa as a brownish yellow solid in 53% yield (34 mg). M.p. 107.0-108.5 °C. Rf (n-pentane/ethyl acetate = 5:1) = 0.55. \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.59 (d, \(J = 7.1\) Hz, 1H), 7.45 – 7.27 (m, 3H), 4.62 (s, 2H), 3.79 (q, \(J = 10.2\) Hz, 2H). \(^{19}\)F NMR (376 MHz, CD\(_3\)OD) \(\delta\) -65.6 (t, \(J = 10.2\) Hz, 3F). \(^{13}\)C NMR (101 MHz, CD\(_3\)OD) \(\delta\) 192.0 (q, \(J = 3.4\) Hz), 137.4 (s), 136.6 (s), 127.7 (s), 127.5 (s), 127.4 (s), 126.2 (s), 124.2 (q, \(J = 277.4\) Hz), 60.1 (s), 49.5 (q, \(J = 28.6\) Hz). IR (ATR): v 3326, 2483, 2084, 1657, 1493, 1432, 1344, 1255, 1189, 1140, 1043, 754 cm\(^{-1}\). GC-MS m/z 214 (M\(^+\)). HRMS (EI) m/z: calcd. for C\(_{10}\)H\(_9\)F\(_3\)NO [M+H]\(^+\): 216.0631; found: 216.0631.
2-(2,2,2-Trifluoroethyl)benzo[d]thiazole (4a)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 20:1) gave final product 4a as a light yellow liquid in 80% yield (52 mg). $R_f$ (n-pentane/ethyl acetate = 20:1) = 0.44. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 8.1$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 3.99 (q, $J = 10.0$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.5 (t, $J = 10.1$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.3 (q, $J = 3.4$ Hz), 152.7 (s), 135.7 (s), 126.5 (s), 125.9 (s), 124.2 (q, $J = 277.5$ Hz), 123.5 (s), 121.6 (s), 39.1 (q, $J = 31.7$ Hz). IR (ATR): $\nu$ 2930, 1518, 1458, 1434, 1356, 1314, 1285, 1251, 1180, 1141, 1079, 1013, 929, 866, 836, 760, 555, 430 cm$^{-1}$. GC-MS m/z 216 (M$^+$). HRMS (ESI) m/z: calcd. for C$_9$H$_7$F$_3$NS [M+H]$^+$: 218.0246; found: 218.0246.

5-Chloro-2-(2,2,2-trifluoroethyl)benzo[d]thiazole (4b)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 4b as a brownish yellow solid in 85% yield (64 mg). M.p. 75.6–77.0 °C. $R_f$ (n-pentane/ethyl acetate = 10:1) = 0.69. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (s, 1H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.40 (d, $J = 8.6$ Hz, 1H), 3.97 (q, $J = 9.9$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.4 (t, $J = 10.0$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.2 (q, $J = 3.5$ Hz), 153.6 (s), 134.0 (s), 132.6 (s), 126.4 (s), 124.1 (q, $J = 277.6$ Hz), 123.3 (s), 122.3 (s), 39.1 (q, $J = 31.7$ Hz). IR (ATR): $\nu$ 3052, 1595, 1562, 1509, 1435, 1357, 1282, 1250, 1177, 1144, 1069, 941, 838, 806, 688, 613, 581, 560, 542, 433 cm$^{-1}$. GC-MS m/z 250 (M$^+$). HRMS (ESI) m/z: calcd. for C$_9$H$_6$F$_3$NSCI [M+H]$^+$: 251.9856; found: 251.9857.
2,6-Bis(2,2,2-trifluoroethyl)benzo[1,2-d:4,5-d']bis(thiazole) (4c)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 10:1) gave final product 4c as a light yellow solid in 87% yield (93 mg). M.p. 169.6–170.8 °C. \( R_f \) (n-pentane/ethyl acetate = 10:1) = 0.46. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.60 (s, 2H), 4.03 (q, \( J = 9.9 \) Hz, 4H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -64.2 (t, \( J = 9.9 \) Hz, 6F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 160.3 (q, \( J = 3.3 \) Hz), 151.0 (s), 135.1 (s), 124.1 (q, \( J = 277.6 \) Hz), 116.0 (s), 39.4 (q, \( J = 31.9 \) Hz). IR (ATR): \( \nu \) 3070, 2924, 2257, 1597, 1528, 1455, 1420, 1376, 1278, 1249, 1161, 1119, 1086, 1049, 923, 883, 835, 685, 639 cm\(^{-1}\). GC-MS m/z 355 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_{12}\)H\(_7\)F\(_6\)N\(_2\)S\(_2\) [M+H]\(^+\): 356.9949; found: 356.9948.

2-(2,2,2-Trifluoroethyl)-1H-benzo[d]imidazole (5a)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 5:1) gave final product 5a as a brownish yellow solid in 81% yield (49 mg). M.p. 173.9-175.4 °C. \( R_f \) (n-pentane/ethyl acetate = 5:1) = 0.40. \(^1\)H NMR (400 MHz, CD\(_3\)OD) \( \delta \) 7.59 (dd, \( J = 5.9, 3.0 \) Hz, 2H), 7.28 (dd, \( J = 5.9, 3.0 \) Hz, 2H), 3.89 (q, \( J = 10.4 \) Hz, 2H). \(^{19}\)F NMR (376 MHz, CD\(_3\)OD) \( \delta \) -66.1 (t, \( J = 10.4 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, CD\(_3\)OD) \( \delta \) 144.0 (q, \( J = 3.9 \) Hz), 138.2 (s), 124.7 (q, \( J = 276.6 \) Hz), 122.7 (s), 114.6 (s), 33.7 (q, \( J = 31.8 \) Hz). IR (ATR): \( \nu \) 3367, 2914, 2749, 2524, 2227, 1624, 1542, 1513, 1438, 1424, 1294, 1271, 1197, 1178, 1148, 1132, 1104, 1083, 1045, 1006, 980, 805, 744, 616, 434 cm\(^{-1}\). GC-MS m/z 199 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_8\)F\(_3\)N\(_2\) [M+H]\(^+\): 201.0634; found: 201.0609.
Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 5:1) gave final product 5b as a brown solid in 83% yield (53 mg). M.p. 264.2–266.4 °C. Rf (n-pentane/ethyl acetate = 5:1) = 0.60. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.49 (s, 1H), 7.46 (d, \(J = 7.8\) Hz, 1H), 7.24 (t, \(J = 7.6\) Hz, 1H), 7.15 (d, \(J = 7.2\) Hz, 1H), 3.96 (q, \(J = 10.0\) Hz, 2H), 2.62 (s, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -64.0 (t, \(J = 10.0\) Hz, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.7 (q, \(J = 4.2\) Hz), 136.8 (s), 136.6 (s), 125.5 (s), 124.5 (s), 124.2 (q, \(J = 277.4\) Hz), 124.1 (s), 112.3 (s), 34.2 (q, \(J = 32.4\) Hz), 17.0 (s). IR (ATR): \(\nu\) 2923, 2855, 1622, 1537, 1453, 1381, 1351, 1305, 1254, 1148, 1091, 1022, 914, 841, 785, 750, 631, 590, 517 cm\(^{-1}\). GC-MS m/z 213 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_{10}\)H\(_{10}\)F\(_3\)N\(_2\) [M+H]\(^+\): 215.0791; found: 215.0788.

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 5:1) gave final product 5c as a light brown solid in 79% yield (66 mg). M.p. 152.2–153.4 °C. Rf (n-pentane/ethyl acetate = 5:1) = 0.48. \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.03 (s, 1H), 6.96 (d, \(J = 8.2\) Hz, 1H), 6.83 (d, \(J = 8.3\) Hz, 1H), 3.77 (q, \(J = 10.2\) Hz, 2H). \(^{19}\)F NMR (376 MHz, CD\(_3\)OD) \(\delta\) -65.6 (t, \(J = 10.2\) Hz, 3F). \(^{13}\)C NMR (101 MHz, CD\(_3\)OD) \(\delta\) 191.6 (q, \(J = 3.2\) Hz), 144.5 (s), 128.4 (s), 124.2 (q, \(J = 277.2\) Hz), 123.7 (s), 121.6 (s), 119.9 (s), 118.9 (s), 49.3 (q, \(J = 28.7\) Hz). IR (ATR): \(\nu\) 3881, 3703, 3596, 3536, 2685, 2604, 2559, 2396, 2291, 2171, 2109, 2066, 1971, 1929, 1886, 1719, 1055, 970, 922, 894, 726, 590, 555, 494, 454, 429 cm\(^{-1}\). GC-MS m/z 277 (M\(^+\)). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_7\)F\(_3\)N\(_2\)Br [M+H]\(^+\): 278.9739; found: 278.9740.
5-Chloro-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)aniline (6q)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 50:1) gave final product 6q as a brownish yellow liquid in 63% yield (44 mg). $R_f$ (n-pentane) = 0.28. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.84 (d, $J = 8.5$ Hz, 1H), 6.77 (s, 1H), 6.69 (t, $J = 8.1$ Hz, 2H), 5.07 (p, $J = 7.6$ Hz, 1H), 3.93 (br, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.6 (d, $J = 7.9$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.8 (q, $J = 5.3$ Hz), 142.6 (s), 138.6 (s), 130.6 (s), 122.8 (q, $J = 269.3$ Hz), 118.0 (s), 117.5 (s), 115.8 (s), 99.5 (q, $J = 35.3$ Hz). IR (ATR): v 1676, 1619, 1499, 1419, 1265, 1199, 1154, 1123, 1039, 850, 813, 726, 449 cm$^{-1}$. GC-MS m/z 236 (M$^+$). HRMS (ESI) m/z: calcd. for C$_9$H$_8$ClF$_3$NO [M+H$^+$]: 238.0241; found: 238.0236.

N-(2-Amino-4-bromophenyl)-3,3,3-trifluoropropanethioamide (7c)

Purification by column chromatography (silica gel, n-pentane/ethyl acetate = 5:1) gave final product 7c as a light brown solid in 5% yield (5 mg). M.p. 145.0-146.8 °C. $R_f$ (n-pentane/ethyl acetate = 5:1) = 0.40. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 7.10 (d, $J = 8.5$ Hz, 1H), 7.06 – 6.91 (m, 2H), 3.80 (q, 10.1 Hz, 2H), NH$_2$ was not observed. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.8 (t, $J = 10.1$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.8 (q, $J = 3.1$ Hz), 143.1 (s), 128.4 (s), 125.0 (s), 123.2 (q, $J = 46.6$ Hz), 122.3 (s), 122.0 (s), 120.3 (s), 50.9 (q, $J = 28.8$ Hz). IR (ATR): v 3149, 2923, 1697, 1621, 1494, 1401, 1344, 1252, 1144, 896, 806, 756, 682, 624 cm$^{-1}$. GC-MS m/z 311 (M$^+$). HRMS (ESI) m/z: calcd. for C$_9$H$_9$BrF$_3$N$_2$S [M+H$^+$]: 312.9616; found: 312.9615.
Crystal structure analyses

The suitable crystals of 3i (CCDC 1921974) and 7c (CCDC 1922077) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using MoKα radiation (λ = 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

References:

1. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.
ORTEP diagrams

ORTEP diagram of compound 3i. Thermal ellipsoids are drawn at 40% probability.
ORTEP diagram of compound 7c. Thermal ellipsoids are drawn at 40% probability.
Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

$^{19}$F NMR spectrum of 3a in CDCl$_3$

$^1$H NMR spectrum of 3a in CDCl$_3$
$^{13}$C NMR spectrum of 3a in CDCl$_3$ 

$^{19}$F NMR spectrum of 3b in CDCl$_3$
$^1$H NMR spectrum of 3b in CDCl$_3$

$^{13}$C NMR spectrum of 3b in CDCl$_3$
$^{19}$F NMR spectrum of 3c in CDCl$_3$

$^1$H NMR spectrum of 3c in CDCl$_3$
$^{13}$C NMR spectrum of 3c in CDCl$_3$

$^{19}$F NMR spectrum of 3d in CDCl$_3$
$^1$H NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
$^{19}$F NMR spectrum of 3e in CDCl$_3$

$^1$H NMR spectrum of 3e in CDCl$_3$
$^{13}$C NMR spectrum of 3e in CDCl$_3$

$^{19}$F NMR spectrum of 3f in CDCl$_3$
$^1$H NMR spectrum of 3f in CDCl$_3$

$^{13}$C NMR spectrum of 3f in CDCl$_3$
$^{19}$F NMR spectrum of 3g in CDCl$_3$

$^1$H NMR spectrum of 3g in CDCl$_3$
$^{13}$C NMR spectrum of 3g in CDCl$_3$

$^{19}$F NMR spectrum of 3h in CDCl$_3$
$^1$H NMR spectrum of 3h in CDCl$_3$

$^{13}$C NMR spectrum of 3h in CDCl$_3$
$^{19}$F NMR spectrum of 3i in CDCl$_3$

$^1$H NMR spectrum of 3i in CDCl$_3$
$^{13}$C NMR spectrum of 3i in CDCl$_3$

$^{19}$F NMR spectrum of 3j in CD$_3$OD
$^{1}$H NMR spectrum of 3j in CD$_3$OD

$^{13}$C NMR spectrum of 3j in CD$_3$OD
$^{19}$F NMR spectrum of 3k in CD$_3$OD

$^1$H NMR spectrum of 3k in CD$_3$OD
$^{13}$C NMR spectrum of 3k in CD$_3$OD

$^{19}$F NMR spectrum of 3l in CDCl$_3$
$^1$H NMR spectrum of 3I in CDCl$_3$

$^{13}$C NMR spectrum of 3I in CDCl$_3$
$^{19}$F NMR spectrum of 3m in CDCl$_3$

$^1$H NMR spectrum of 3m in CDCl$_3$
$^{13}$C NMR spectrum of $3m$ in CDCl$_3$

$^{19}$F NMR spectrum of $3n$ in CDCl$_3$
$^1$H NMR spectrum of 3n in CDCl$_3$

$^{13}$C NMR spectrum of 3n in CDCl$_3$
$^{19}\text{F NMR spectrum of 3o in CDCl}_3$

$^1\text{H NMR spectrum of 3o in CDCl}_3$
$^{13}$C NMR spectrum of 3o in CDCl$_3$

$^{19}$F NMR spectrum of 3p in CDCl$_3$
$^1$H NMR spectrum of 3p in CDCl$_3$

$^{13}$C NMR spectrum of 3p in CDCl$_3$
$^{19}$F NMR spectrum of 3q in CDCl$_3$

$^1$H NMR spectrum of 3q in CDCl$_3$
$^{13}$C NMR spectrum of 3q in CDCl$_3$

$^{19}$F NMR spectrum of 3r in CDCl$_3$
$^1$H NMR spectrum of 3r in CDCl$_3$

$^{13}$C NMR spectrum of 3r in CDCl$_3$
$^{19}\text{F} \text{ NMR spectrum of } 3\text{s in CDCl}_3$

$^1\text{H} \text{ NMR spectrum of } 3\text{s in CDCl}_3$
$^{13}$C NMR spectrum of 3s in CDCl$_3$

$^{19}$F NMR spectrum of 3t in CDCl$_3$
$^1$H NMR spectrum of 3t in CDCl$_3$

$^{13}$C NMR spectrum of 3t in CDCl$_3$
$^{19}$F NMR spectrum of 3u in CDCl$_3$

$^1$H NMR spectrum of 3u in CDCl$_3$
$^{13}$C NMR spectrum of 3u in CDCl$_3$

$^{19}$F NMR spectrum of 3v in CDCl$_3$
$^1$H NMR spectrum of 3v in CDCl$_3$

$^{13}$C NMR spectrum of 3v in CDCl$_3$
$^{19}$F NMR spectrum of 3w in CDCl$_3$

$^1$H NMR spectrum of 3w in CDCl$_3$
$^{13}$C NMR spectrum of $3w$ in CDCl$_3$

$^{19}$F NMR spectrum of $3x$ in CDCl$_3$
$^1$H NMR spectrum of 3x in CDCl$_3$

$^{13}$C NMR spectrum of 3x in CDCl$_3$
$^{19}$F NMR spectrum of 3y in CDCl$_3$

$^1$H NMR spectrum of 3y in CDCl$_3$
$^{13}$C NMR spectrum of $3y$ in CDCl$_3$

$^{19}$F NMR spectrum of $3z$ in CDCl$_3$
$^1$H NMR spectrum of 3z in CDCl$_3$

$^{13}$C NMR spectrum of 3z in CDCl$_3$
$^{19}$F NMR spectrum of 3aa in CD$_3$OD

$^1$H NMR spectrum of 3aa in CD$_3$OD
$^{13}$C NMR spectrum of 3aa in CD$_3$OD

$^{19}$F NMR spectrum of 4a in CDCl$_3$
$^1$H NMR spectrum of 4a in CDCl$_3$

$^{13}$C NMR spectrum of 4a in CDCl$_3$
$^{19}$F NMR spectrum of 4b in CDCl$_3$

$^1$H NMR spectrum of 4b in CDCl$_3$
$^{13}$C NMR spectrum of $4b$ in CDCl$_3$

$^{19}$F NMR spectrum of $4c$ in CDCl$_3$
$^1$H NMR spectrum of 4c in CDCl$_3$

$^{13}$C NMR spectrum of 4c in CDCl$_3$
$^{19}$F NMR spectrum of 5a in CD$_3$OD

$^1$H NMR spectrum of 5a in CD$_3$OD
$^{13}\text{C NMR spectrum of 5a in CD}_3\text{OD}$

$^{19}\text{F NMR spectrum of 5b in CDCl}_3$
$^1$H NMR spectrum of 5b in CDCl$_3$

$^{13}$C NMR spectrum of 5b in CDCl$_3$
$^{19}\text{F NMR spectrum of } 5\text{c in CD}_3\text{OD}$

$^1\text{H NMR spectrum of } 5\text{c in CD}_3\text{OD}$
$^{13}$C NMR spectrum of $5c$ in CD$_3$OD

$^{19}$F NMR spectrum of $6q$ in CDCl$_3$
$^1$H NMR spectrum of 6q in CDCl$_3$

$^{13}$C NMR spectrum of 6q in CDCl$_3$
$^{19}$F NMR spectrum of 7c in CDCl$_3$

$^1$H NMR spectrum of 7c in CDCl$_3$
$^{13}$C NMR spectrum of 7c in CDCl$_3$