Supporting Information

Copper-Mediated Trifluoromethylation of Aryl-, Heteroaryl-, and Vinyltrifluoroborates with Langlois' Reagent

By
Srinivas Reddy Dubbaka*, Manohar Salla, Raghu Bolisetti, and Shashidhar Nizalapur

Department of Medicinal Chemistry, Albany Molecular Research Singapore Research Centre, Pte. Ltd., 61 Science Park Road, #05-01, Galen, Science Park II, Singapore-117525

TABLE OF CONTENTS
I. General information ............................................................................................................. S2
II. Reagents’ commercial source information table .............................................................. S2
III. Base, solvent, copper salts and radical initiators screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate with NaSO₂CF₃. S3 – S6
IV. General procedures for the synthesis of Aryl-CF₃ compounds .................................... S7 – S7
V. Spectral data of Aryl-CF₃ compounds ........................................................................... S7 – S14
VI. General procedure for the synthesis of potassium alkenyltrifluoroborates ............... S14
VII. Spectral data of alkenyltrifluoroborates ..................................................................... S14 – S15
VIII. General procedure for the synthesis of alkenyl-CF₃ compounds ............................. S16
IX. Spectral data of alkenyl-CF₃ compounds ..................................................................... S16 – S19
X. References ....................................................................................................................... S20
XI. ¹H-NMR, ¹⁹F NMR, ¹³C NMR and GC-MS spectra ....................................................... S21 - S129
EXPERIMENTAL

General information: $^1$H NMR Spectra, $^{19}$F NMR and $^{13}$C NMR were recorded on Bruker 400 MHz or 300 MHz in the solvents indicated; chemical shifts are reported in units (ppm) by assigning CDCl$_3$ resonance in the $^1$H spectrum as 7.26 ppm and CDCl$_3$ resonance in the $^{13}$C spectrum as 77.0 ppm. $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as internal standard and are measured proton decoupled. All coupling constants ($J$ values) were reported in Hertz (Hz). GC-MS spectra were measured on Shimadzu. Column chromatography was performed on silica gel 200-300 mesh on Combiflash. If not specially mentioned, all the solvents and reagents were used as purchased and without further purification.

Reagents’ commercial sources: Reactants (boronic acids or trifluoroborates) were purchased from Combi-Blocks, Tokyo chemical industry (TCI) Japan, Frontier Scientific and Aldrich and used without purification. Commercial sources for other relevant reagents are shown below.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Commercial source</th>
<th>CAS no</th>
<th>Product no</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (I) chloride</td>
<td>Aldrich</td>
<td>7758-89-6</td>
<td>61168</td>
</tr>
<tr>
<td>NaSO$_2$CF$_3$ (Langlois Reagent)</td>
<td>Tokyo chemical industry (TCI)</td>
<td>2926-29-6</td>
<td>T2033</td>
</tr>
<tr>
<td>tert-Butyl Hydroperoxide (TBHP) (70% in Water)</td>
<td>Tokyo chemical industry (TCI)</td>
<td>75-91-2</td>
<td>B3153</td>
</tr>
</tbody>
</table>
Experimental Details:

Base and solvent screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (PhBF₃K, 1a) with NaSO₂CF₃/TBHP.

\[
\text{PhBF}_3\text{K} + \text{CuI} + \text{NaSO}_2\text{CF}_3/\text{TBHP} \rightarrow \text{PhCF}_3
\]

A mixture of the PhBF₃K (27.6 mg, 0.15 mmol, 1.0 equiv), CuI (28.6 mg, 0.15 mmol, 1.0 equiv), NaSO₂CF₃ (70.2 mg, 0.45 mmol, 3.0 equiv), Base (0.15 mmol, 3.0 equiv) in CH₂Cl₂ (0.7 mL), and H₂O (0.5 mL) was cooled to 0 °C, and TBHP (70% solution in water) (104 µL, 5.0 equiv, 0.75 mmol) was added under vigorous stirring. Stirring was continued for overnight at room temperature. To this, 4-fluorobenzonitrile (0.15 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃. The yields of 2a as a function of bases and solvents are listed in **Table S1**.

**Table S1.** Base and solvent screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (1a) with NaSO₂CF₃/TBHP.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bases</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et₃N</td>
<td>traces</td>
</tr>
<tr>
<td>2</td>
<td>Na₂CO₃</td>
<td>15</td>
</tr>
<tr>
<td>3c</td>
<td>Cs₂CO₃</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>NaHCO₃</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>NaOAc</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>K₃PO₄</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>NaHCO₃</td>
<td>5 a</td>
</tr>
<tr>
<td>8</td>
<td>NaHCO₃/MeOH (0.7 mL)</td>
<td>51</td>
</tr>
<tr>
<td>9</td>
<td>NaHCO₃/1,4-Dioxane (0.7 mL)</td>
<td>45</td>
</tr>
<tr>
<td>10</td>
<td>NaHCO₃/1,2-dimethoxyethane (0.7 mL)</td>
<td>45</td>
</tr>
</tbody>
</table>

a reaction carried out without H₂O and TBHP (5.5 M in decane)
Copper salt screen for Cu-Mediated for Trifluoromethylation of PhBF$_3$K (1a) with NaSO$_2$CF$_3$/TBHP.

\[
\begin{align*}
\text{Ph--BF$_3$K} & \xrightarrow{[\text{Cu}]} \text{NaSO$_2$CF$_3$/TBHP} \\
1a & \xrightarrow{\text{NaHCO}_3} \text{CH$_2$Cl$_2$/H$_2$O/MeOH} \xrightarrow{} \text{Ph--CF$_3$} \Rightarrow 2a
\end{align*}
\]

A mixture of the PhBF$_3$K (27.6 mg, 0.15 mmol, 1.0 equiv), Cu salt (0.15 mmol, 1.0 equiv), NaSO$_2$CF$_3$ (70.2 mg, 0.45 mmol, 3.0 equiv), NaHCO$_3$ (12.6 mg, 0.15 mmol, 3.0 equiv) in CH$_2$Cl$_2$ (0.7 mL), MeOH (0.7 mL), and H$_2$O (0.5 mL) was cooled to 0 °C, and TBHP (70% solution in water) (104 µL, 5.0 equiv, 0.75 mmol) was added under vigorous stirring. Stirring was continued for overnight at room temperature. To this, 4-fluorobenzonitrile (0.15 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the $^{19}$F NMR measurement in CDCl$_3$. The yields of 2a as a function of copper salts are listed in Table S2.
Table S2. Copper salt screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (1a) with NaSO$_2$CF$_3$/TBHP.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu Salts</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(I) acetate</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Cu(II) acetate</td>
<td>traces</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OCOCF$_3$)</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OCOCF$_3$)$_2$</td>
<td>20</td>
</tr>
<tr>
<td>5$^a$</td>
<td>Cu(OSO$_2$CF$_3$)</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Cu(OSO$_2$CF$_3$)$_2$</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>(CH$_3$CN)$_4$CuPF$_6$</td>
<td>traces</td>
</tr>
<tr>
<td>8</td>
<td>CuBr</td>
<td>10</td>
</tr>
<tr>
<td>9$^b$</td>
<td>CuTc</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>CuCl</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>CuCl/1,10-Phen</td>
<td>(8)$^c$(15)$^d$</td>
</tr>
<tr>
<td>12</td>
<td>catalytic</td>
<td>(8)$^e$</td>
</tr>
</tbody>
</table>

$^a$Used as benzene complex. $^d$Copper(I)-thiophene-2-carboxylate; $^c$20% CuCl; $^b$20% CuCl and 20% 1,10-phenanthroline. $^e$1a (1.0 equiv., 0.15 mmol), Cu(OAc)$_2$ (0.2 equiv.), imidazole (0.2 equiv.), 2,4,6-collidine (2.0 equiv.), NH$_4$Cl (2.5 equiv.), NaSO$_2$CF$_3$ (7.0 equiv.), TBHP (70% in H$_2$O, 16.0 equiv.), CH$_2$Cl$_2$/H$_2$O, air, rt, 15 h.
Radical initiators screen for Cu-Mediated for Trifluoromethylation of PhBF₃K (1a) with NaSO₂CF₃.

A mixture of the PhBF₃K (27.6 mg, 0.15 mmol, 1.0 equiv), CuCl (14.8 mg, 0.15 mmol, 1.0 equiv), NaSO₂CF₃ (70.2 mg, 0.45 mmol, 3.0 equiv), NaHCO₃ (12.6 mg, 0.15 mmol, 3.0 equiv) in CH₂Cl₂ (0.7 mL), MeOH (0.7 mL), and H₂O (0.5 mL) was cooled to 0 °C, and radical initiators (5.0 equiv, 0.75 mmol) was added under vigorous stirring. Stirring was continued for overnight at room temperature. To this, 4-fluorobenzonitrile (0.15 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃. The yields of 2a as a function of radical initiators are listed in Table S3.

Table S3. Radical initiators screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (1a) with NaSO₂CF₃.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Radical initiators</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O₂</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>NaOCl</td>
<td>traces</td>
</tr>
<tr>
<td>3</td>
<td>O₂</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>DDQ</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Phl(OAc)₂</td>
<td>traces</td>
</tr>
<tr>
<td>6</td>
<td>BzOOBz</td>
<td>20</td>
</tr>
</tbody>
</table>
General procedure for the Synthesis of Aryl-CF$_3$ compounds: (Table 2).

A mixture of the trifluoroborate (0.25 mmol, 1.0 equiv), CuCl (24.8 mg, 0.25 mmol, 1.0 equiv), Na$_2$SO$_2$CF$_3$ (117 mg, 0.75 mmol, 3.0 equiv), NaHCO$_3$ (21.0 mg, 0.25 mmol, 3.0 equiv) in CH$_2$Cl$_2$ (1.5 mL), MeOH (1.5 mL), and H$_2$O (1.2 mL) was cooled to 0 ºC, and TBHP (70% solution in water) (172 µL, 5.0 equiv, 1.25 mmol, (86 µL, 2.5 equiv, 0.625 mmol for 2i, and 138 µL, 4.0 equiv, 1.0 mmol for 2j)) was added under vigorous stirring. Stirring was continued for 6 –12 h at room temperature.

For the compounds reported as isolated yields (2b, 2n, and 2r), the organic phase was separated, the aqueous phase was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, the solvent was removed at 1 atm and the residue was purified by column chromatography on Combiflash with hexanes to afford the desired compounds.

The volatile products were not isolated and their yields were determined only by $^{19}$F NMR of the reaction mixture. For the compounds reported with $^{19}$F NMR yields, 4-fluorobenzonitrile (0.25 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the $^{19}$F NMR measurement in CDCl$_3$.

Spectral data of Aryl-CF$_3$ compounds (Table 2):

1-(Trifluoromethyl)benzene (2a):

![Structure of 1-(Trifluoromethyl)benzene (2a)]

The yield (80%) of 2a was determined by $^{19}$F NMR. The $^{19}$F NMR spectral data for 2a matched that of an authentic sample (Aldrich, s, $-62.3$ ppm).

$^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ –62.75 (s, 3F); GC–MS $m/z$, 146 (M$^+$).

1-(Trifluoromethyl)naphthalene (2b):$^1$
Compound 2b was isolated in 60% yield (49 mg) and 82% yield was determined by $^{19}$F NMR.

$^{1}$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.18 (d, $J = 8.6$ Hz, 1H), 8.0 (d, $J = 8.2$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H); 7.86 (d, $J = 7.3$ Hz, 1H), 7.55-7.65 (m, 2H), 7.50 (t, $J = 7.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 133.9 (s, 1C), 132.7 (s, 1C), 129.0 (s, 1C), 128.7 (s, 1C), 127.6 (s, 1C), 127.4 (q, $J = 269.8$ Hz, 1C), 126.6 (s, 1C), 124.6 (q, $J = 6.2$ Hz, 1C), 124.2 (J = 2.2 Hz, 1C), 124.1 (s, 1C), 123.3 (s, 1C).

$^{19}$F NMR (CDCl$_3$, 282 M Hz): $\delta$ –60.43 (s, 3F); GC–MS m/z, 196 (M$^+$).

2-(Trifluoromethyl)naphthalene (2c):$^2$

The yield (59%) of 2c was determined by $^{19}$F NMR.

$^{19}$F NMR (CDCl$_3$, 282 M Hz): $\delta$ –62.86 (s, 3F); GC–MS m/z, 196 (M$^+$).

1-Methoxy-4-(trifluoromethyl)benzene (2d):$^3$

The yield (74%) of 2d was determined by $^{19}$F NMR.

$^{19}$F NMR (CDCl$_3$, 282 M Hz): $\delta$ –62.20 (s, 3F); GC–MS m/z, 176 (M$^+$).
1-Methyl-4-(trifluoromethyl)benzene (2e): The yield (79%) of 2e was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –62.98 (s, 3F); GC–MS m/z, 160 (M$^+$).

1-(Tert-Butyl)-4-(trifluoromethyl)benzene (2f): The yield (77%) of 2f was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –62.98 (s, 3F); GC–MS m/z, 202 (M$^+$).

1-Methoxy-3-(trifluoromethyl)benzene (2g): Compound 2g was isolated in 56% yield (25.0 mg) and 60% yield was determined by $^{19}$F NMR. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.39 (d, $J = 8.0$ Hz, 1H), 7.21 (dt, $J = 7.6$ Hz, $J = 0.9$ Hz, 1H), 7.12 (br.s, 1H); 7.07 (dd, $J = 8.0$ Hz, $J = 0.9$ Hz, 1H); $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –63.34 (s, 3F); GC–MS m/z, 176 (M$^+$).
1-Methyl-3-(trifluoromethyl)benzene (2h): \textsuperscript{3,4}

![Chemical Structure](image)

The yield (51\%) of 2h was determined by \textsuperscript{19}F NMR. \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz): δ –63.25 (s, 3 F); GC–MS \textit{m/z}, 160 (M\textsuperscript{+}).

4-(trifluoromethyl)benzonitrile (2i):\textsuperscript{5}

![Chemical Structure](image)

The yield (40\%) of 2i was determined by \textsuperscript{19}F NMR. \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz): δ –64.17 (s, 3 F); GC–MS \textit{m/z}, 171 (M\textsuperscript{+}).

Methyl 4-(trifluoromethyl)benzoate (2j):\textsuperscript{5}

![Chemical Structure](image)

The yield (41\%) of 2j was determined by \textsuperscript{19}F NMR. \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz): δ –63.79 (s, 3 F); GC–MS \textit{m/z}, 204 (M\textsuperscript{+}).

1,4-Bis(trifluoromethyl)benzene (2k):\textsuperscript{5}
Traces product of 2k was determined by GC-MS.

**1-Chloro-4-(trifluoromethyl)benzene (2l):**

![Structure of 2l]

The yield (45%) of 2l was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –63.18 (s, 3F); GC–MS $m/z$, 180 (M$^+$).

**1-Bromo-4-(trifluoromethyl)benzene (2m):**

![Structure of 2m]

The yield (57%) of 2m was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –63.48 (s, 3F); GC–MS $m/z$, 224 (M$^+$).

**1-Methoxy-2-(trifluoromethyl)benzene (2n):**

![Structure of 2n]

Compound 2n was isolated in 65% yield (29 mg) and 89% yield was determined by $^{19}$F NMR. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.56 (d, 1H, $J = 7.8$ Hz), 7.49 (t, 1H, $J = 7.8$ Hz), 7.05-6.95 (m, 3H), 3.90 (s, 3H); $^{13}$CNMR (CDCl$_3$, 100 MHz): $\delta$ 157.5 (s, 1C), $\delta$
133.2 (s, 1C), 127.1 (q, J = 5.2 Hz, 1C), 123.5 (q, J = 277.1 Hz, 1C), 120.0 (s, 1C), 118.7 (q, J = 30.1 Hz, 1C), 111.9 (s, 1C), 55.9 (s, 1C); $^{19}$F NMR (CDCl$_3$, 282 MHz): δ –63.05 (s, 3F); GC–MS m/z, 176 (M$^+$).

1-Methyl-2-(trifluoromethyl)benzene (2o):$^5$

![Diagram of 2o]

The yield (55%) of 2o was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 M Hz): δ –63.21 (s, 3 F); GC–MS m/z, 160 (M$^+$).

2-Methoxy-3-(trifluoromethyl)pyridine (2p):$^2$

![Diagram of 2p]

The yield (85%) of 2p was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 M Hz): δ –64.47 (s, 3F); GC–MS m/z, 177 (M$^+$).

Tert-Butyl-2-(trifluoromethyl)-1H-indole-1-carboxylate (2q):$^2$

![Diagram of 2q]

Compound 2r was isolated in 53% yield (37.8 mg) and 55% yield was determined by $^{19}$F NMR. $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.29 (dd, J = 8.4 Hz, J = 0.8 Hz 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.45 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.29 (td, J = 7.1 Hz, J = 1.1 Hz, 1H); 7.14 (br.s), 1.67 (s, 3H); $^{19}$F NMR (CDCl$_3$, 376 M Hz): δ –58.29 (s, 3F); GC–MS m/z, 185 (M–Boc).
2-(Trifluoromethyl)benzofuran (2r):²

![Image of 2-(Trifluoromethyl)benzofuran (2r)]

Compound 2r was isolated in 75% yield (34.8 mg) and 91% yield was determined by $^{19}$F NMR.

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.66 (d, $J = 8.05$ Hz, 1H), 7.56 (dq, $J = 8.4$ Hz, $J = 0.9$ Hz, 1H), 7.44 (td, $J = 8.4$ Hz, $J = 1.2$ Hz, 1H); 7.32 (td, $J = 8.4$ Hz, $J = 0.9$ Hz 1H), 7.17-7.13 (m, 1H); $^{13}$CNMR (CDCl$_3$, 100 MHz): $\delta$ 155.2 (s,1C), $\delta$ 143.5 (q, $J = 48.5$ Hz, 1C), 126.9 (s,1C), 126.9 (s,1C), 126.0 (s,1C), 124.2 (s,1C), 122.5 (s,1C), 119.4 (q, $J = 268.2$ Hz, 1C), 112.1 (s,1C), 108.1 (q, $J = 2.9$ Hz, 1C).

$^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ −66.09 (s, 3 F); GC–MS $m/z$, 186 (M$^+$).

2-(Trifluoromethyl)benzo[b]thiophene (2s):²

![Image of 2-(Trifluoromethyl)benzo[b]thiophene (2s)]

Compound 2r was isolated in 52% yield (26.2 mg) and 54% yield was determined by $^{19}$F NMR.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.89-7.85 (m, 2H), 7.70 (s, 1H), 7.47-7.43 (m, 2H).

$^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ −57.04 (s, 3 F); GC–MS $m/z$, 202 (M$^+$).

1-Methyl-3-(trifluoromethyl)benzene (2h) from 2h-Bpin:³⁴
The yield (28%) of 2h was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –63.27 (s, 3 F); GC–MS m/z, 160 (M$^+$).

2-Chloro-5-(trifluoromethyl)pyrimidine (2t) from 1t-Bpin: $^{3,4}$

The yield (30%) of 2t was determined by $^{19}$F NMR. $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –62.80 (s, 3 F); GC–MS m/z, 182 (M$^+$).

**General Procedure for the Synthesis of Potassium Alkenyltrifluoroborats:**

Synthesis of compounds 3a-d (Scheme 2).

To a solution of the boronic acid (1.4 mmol, 1.0 equiv) in MeOH (1.0 mL) was added 4.5 m aq. KHF$_2$ (933 µL, 4.2 mmol, 3.0 equiv) at 0 °C, the resulting mixture was stirred at the same temperature for 1 h. Solvent was removed by distillation; residue was dissolved in hot acetone (20 mL) and filtered. The filtrate was concentrated and dissolved in minimum amount of acetone, precipitated by adding MTBE. The precipitate was collected by filtration to get products as white solids.$^6$

**Cyclohex-1-en-1-yltrifluoroborate (4a).** The title compound was isolated as a colourless solid in 84% yield (220 mg). The physical data matched with the literature data.$^6$

$^1$H NMR (CD$_3$OD, 300 MHz): $\delta$ ppm 5.75 (s, 1H), 2.0-3.39 (m, 4H), 1.57-1.52 (m,
$^{13}$C NMR (CD$_3$OD, 100 MHz): $\delta$ ppm 126.5 (q, $J = 3.5$ Hz, 1C), 126.22 (s, 1C), 27.52 (s, 1C), 27.09 (s, 1C), 24.61 (s, 1C), 24.41 (s, 1C); $^{19}$F NMR (CD$_3$OD, 282 MHz): $\delta$ ppm –147.9.

**Potassium trans-styryltrifluoroborate (4b).** The title compound was isolated as a colourless solid in 81% yield (240 mg). The physical data matched with the literature data. \(^6\)

$^1$H NMR (CD$_3$OD, 300 MHz): $\delta$ ppm 7.46–7.34 (m, 5H), 6.67 (d, $J = 18.0$ Hz, 1H), 6.27-6.19 (m, 1H); $^{19}$F NMR (CD$_3$OD, 282 MHz): $\delta$ ppm –143.5.

**Potassium 4-methoxy trans-styryltrifluoroborate (4c).** The title compound was obtained as a colorless solid in 73% yield (245 mg). physical data matched with the literature data. \(^6\)

$^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ ppm 7.22 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.4$ Hz, 2H), 6.39 (d, $J = 18.0$ Hz, 1H), 6.01-5.92 (m, 1H); $^{19}$F NMR (DMSO-$d_6$, 282 MHz): $\delta$ ppm –138.0.

**Potassium 4-chloro trans-styryltrifluoroborate (4d).** The title compound was obtained as a colorless solid in 62% yield (215 mg). physical data matched with the literature data. \(^6\)

$^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ ppm 7.34–7.25 (m, 4H), 6.44 (d, $J = 18.3$ Hz, 1H), 6.21-5.93 (m, 1H); $^{19}$F NMR (DMSO-$d_6$, 282 MHz): $\delta$ ppm –138.53.
**General procedure for the Synthesis of Alkenyl-CF$_3$ compounds:** Synthesis of compounds 5a to 5d (Scheme 2).

A mixture of boronic acids or trifluoroborates (0.25 mmol, 1.0 equiv), CuCl (24.8 mg, 0.25 mmol, 1.0 equiv), NaSO$_2$CF$_3$ (117 mg, 0.75 mmol, 3.0 equiv), NaHCO$_3$ (21.0 mg, 0.25 mmol, 3.0 equiv) in CH$_2$Cl$_2$ (1.5 mL), MeOH (1.5 mL), and H$_2$O (1.2 mL) was cooled to 0 °C, and TBHP (70% solution in water) (172 µL, 5.0 equiv, 1.25 mmol) was added under vigorous stirring. Stirring was continued for 6–12 h at room temperature.

For the compounds reported as isolated yields, the organic phase was separated, the aqueous phase was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, the solvent was removed at 1 atm and the residue was purified by column chromatography on Combiflash with hexanes to afford the desired compounds.

The volatile products were not isolated and their yields were determined only by $^{19}$F NMR of the reaction mixture. For the compounds reported with $^{19}$F NMR yields, 4-fluorobenzonitrile (0.25 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the $^{19}$F NMR measurement in CDCl$_3$.

**1-(Trifluoromethyl)cyclohex-1-ene (5a)$^7$ from 3a:**

![Chemical structure](image)

According to the general procedure; compound 5a was formed in 64% yield by $^{19}$F NMR.

$^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –70.30 (s, 3F); GC–MS m/z, 150 (M$^+$).

**1-(Trifluoromethyl)cyclohex-1-ene (5a)$^7$ from 4a:**
According to the general procedure; compound 5a was formed in 60% yield by $^{19}$F NMR.
$^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –70.30 (s, 3F); GC–MS m/z, 150 (M$^+$).

(E)-(3,3,3-Trifluoro-1-en-1-yl)benzene (5b) from 3b:

According to the general procedure compound 5b was obtained in 80% (35 mg) yield and 92% yield was determined by $^{19}$F NMR. A ratio of E/Z = 25:1 was determined by $^1$H NMR

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.46-7.42 (m, 2H, mixed signal of $E$ and $Z$ isomers), 7.40-7.34 (m, 3H, mixed signal of $E$ and $Z$ isomers), 7.14 (dq, $J$ = 16.2, 2.2 Hz, 1H, $E$-isomer), 6.91 (d, $J$ = 12.7 Hz, $Z$-isomer), 6.19 (dq, $J$ = 16.4, 7.3 Hz, 1H, $E$-isomer), 5.76 (d, $J$ = 12.7, 9.2 Hz, $Z$-isomer); $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –64.05 (s, 3F, $E$-isomer); GC–MS m/z, 172 (M$^+$).

(E)-(3,3,3-Trifluoro-1-en-1-yl)benzene (5b) from 4b:

According to the general procedure; compound 5b was formed in 98% yield by $^{19}$F NMR. A ratio of E/Z = 20:1 was determined by $^1$H NMR.

$^{19}$F NMR (CDCl$_3$, 282 MHz). $\delta$ –64.03 (s, 3F, $E$-isomer); GC–MS m/z, 172 (M$^+$).
(E)-1-methoxy-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5c)$^9$ from 3c:

According to the general procedure compound 5c was isolated in 85% yield (43mg) and 93% yield was determined by $^{19}$F NMR. A ratio of E/Z = 16:1 was determined by $^1$H NMR

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.39 (d, $J$ = 8.8 Hz, 2H, mixed signals of E and Z isomers), 7.08 (dq, $J$ = 16.2, 2.3 Hz, 1H, E-isomer), 6.90 (d, $J$ = 8.8 Hz, 2H, mixed signals of E and Z isomers), 6.81 (d, $J$ = 12.8 Hz, Z-isomer), 6.05 (dq, $J$ = 16.2, 6.6 Hz, 1H, E-isomer), 5.62 (dq, $J$ = 12.8, 9.4 Hz, Z-isomer), 3.82 (s, 3H, mixed signals of E and Z isomers); $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –63.49 (s, 3 F, E-isomer); GC–MS m/z, 202 (M$^+$).

(E)-1-chloro-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5d)$^9$ from 3d:

According to the general procedure; compound 5c was formed in 94% yield by $^{19}$F NMR. A ratio of E/Z = 13:1 was determined by $^1$H NMR.

$^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –63.36 (s, 3F, E-isomer); GC–MS m/z, 202 (M$^+$).
(32mg) and 86% yield was determined by $^{19}$F NMR. A ratio of E/Z = 12:1 was determined by $^1$H NMR.

$^1$H NMR (DMSO $d_6$, 300 MHz): $\delta$ 7.37–7.32 (m, 4H, mixed signals of E and Z isomers), 7.09 (dq, $J$ = 16.2, 2.2 Hz, 1H, E-isomer), 6.86 (d, $J$ = 12.4 Hz, E-isomer), 6.17 (dq, $J$ = 16.2, 6.6 Hz, 1H, E-isomer), 5.78 (dq, $J$ = 12.4, 9.0 Hz, Z-isomer); $^{19}$F NMR (CDCl$_3$, 282 M Hz): $\delta$ –64.08 (s, 3F, E-isomer); GC–MS m/z, 206 ($M^+$).

(E)-1-chloro-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5d)$^9$ from 4d:

According to the general procedure compound 5d was formed in 74% yield by $^{19}$F NMR. A ratio of E/Z = 3:1 was determined by $^1$H NMR.

$^{19}$F NMR (CDCl$_3$, 282 M Hz): $\delta$ –63.98 (s, 3F, E-isomer); GC–MS m/z, 206 ($M^+$).
References

$^{19}$F NMR of 4-fluorobenzonitrile (internal standard) in CDCl$_3$
GC-MS of crude 2a
\[ ^{19}\text{F NMR yield of compound 2a} \times \frac{2.48}{1\times3} \times 100\% = 82\% \] in CDCl$_3$
GC-MS of crude 2b
$^1$H NMR of compound 2b
$^{13}$C NMR of compound 2b
$^{19}\text{F} \text{ NMR of isolated 2b in CDCl}_3$
GC-MS of crude 2c
$^{19}$F NMR of crude 2c in CDCl$_3$
$^{19}$F NMR yield of compound 2c (1.72/(1×3)×100% = 57%) in CDCl$_3$
GC-MS of crude 2d
$^{19}$F NMR of crude 2d in CDCl$_3$
$^{19}$F NMR yield of compound 2d (2.22/(1×3)×100% = 74%) in CDCl$_3$
GC-MS of crude 2e
$^{19}\text{F NMR of crude 2e in CDCl}_3$
$^{19}\text{F} \text{ NMR yield of compound 2e (2.36/(1×3)×100\% = 79\% ) in CDCl}_3$
GC-MS of crude 2f
$^{19}$F NMR of crude 2f in CDCl$_3$
$^{19}$F NMR yield of compound 2f ($2.31/(1\times3)\times100\% = 77\%$) in CDCl$_3$
GC-MS of crude 2g
$^{19}$F NMR of crude 2g in CDCl$_3$
$^{19}$F NMR yield of compound 2g ($\frac{1.78}{(1 \times 3)} \times 100\% = 60\%$) in CDCl$_3$
$^1$H NMR of compound 2g
$^{19}$F NMR of isolated 2g in CDCl$_3$
GC-MS of crude 2h
$^{19}$F NMR of crude 2h in CDCl$_3$
$^{19}$F NMR yield of compound 2h ($1.53/(1\times3)\times100\% = 51\%$) in CDCl$_3$
GC-MS of crude 2i
$^{19}$F NMR of crude 2i in CDCl$_3$
$^{19}$F NMR yield of compound 2i (1.21/(1\(\times\)3)\(\times\)100\% = 40\%) in CDCl$_3$
GC-MS of crude 2j
$^{19}$F NMR of crude 2j in CDCl$_3$
$^{19}$F NMR yield of compound 2j \((1.24/(1\times3)\times100\% = 41\%)\) in CDCl$_3$
GC-MS of crude 2l
$^{19}$F NMR of crude 2l in CDCl$_3$
$^{19}$F NMR yield of compound 2l (1.24/(1×3)×100% = 41%) in CDCl$_3$
GC-MS of crude 2m
$^{19}$F NMR of crude 2m in CDCl$_3$
$^{19}$F NMR yield of compound 2m ($\frac{1.70}{1\times3} \times 100\% = 57\%$) in CDCl$_3$
GC-MS of crude 2n
$^{19}$F NMR of crude 2n in CDCl$_3$
$^{19}$F NMR yield of compound 2n (2.68/(1×3)×100% = 89%) in CDCl$_3$
$^1$H NMR of 2n in CDCl$_3$
$^{13}$C NMR of 2n in CDCl$_3$
$^{19}$F NMR of isolated 2n in CDCl$_3$
GC-MS of crude 2o
$^{19}$F NMR of crude 2o in CDCl$_3$
$^{19}$F NMR yield of compound 2o \((1.66/(1\times3)\times100\% = 55\%)\) in CDCl$_3$. 

![Diagram showing NMR signal at -62.208 and -103.198 ppm.](image)
GC-MS of crude 2p
$^{19}$F NMR of crude 2p in CDCl$_3$
$^{19}$F NMR yield of compound 2p \( \frac{2.54}{(1 \times 3)} \times 100\% = 85\% \) in CDCl$_3$
GC-MS of crude 2q
$^{19}$F NMR of crude 2q in CDCl$_3$
$^{19}$F NMR yield of compound 2q (1.67/(1×3)×100% = 55%) in CDCl$_3$
$^1$H NMR of compound 2q
$^{19}$F NMR of isolated 2q in CDCl$_3$
GC-MS of crude 2r
$^{19}$F NMR of crude 2r in CDCl$_3$
$^{19}F$ NMR yield of compound 2r \( \frac{2.75}{(1 \times 3)} \times 100\% = 91\% \) in CDCl$_3$. 

Figure: Spectra showing the $^{19}F$ NMR yield of compound 2r in CDCl$_3$. 

Chemical Structure: Compound 2r.
$^1$H NMR of 2r in CDCl$_3$
$^{13}$C NMR of 2$r$ in CDCl$_3$
$^{19}$F NMR of isolated 2r in CDCl$_3$
GC-MS of crude 2s
$^{19}$F NMR of crude 2s in CDCl$_3$
$^{19}$F NMR yield of compound 2s (1.62/(1×3)×100% = 54%) in CDCl$_3$
$^1$H NMR of compound 2s
$^{19}$F NMR of isolated 2s in CDCl$_3$
GC-MS of crude 2h
$^{19}$F NMR of crude 2h in CDCl$_3$
$^{19}\text{F} \text{ NMR yield of compound 2h (0.84/(1x3)×100\% = 28\%) in CDCl}_3$
GC-MS of crude 2t
$^{19}F$ NMR of crude 2t in CDCl$_3$
$^{19}$F NMR yield of compound 2t (0.91/(1×3)×100% = 30%) in CDCl$_3$
$^1$H NMR of 4a in CD$_3$OD
$^{19}$F NMR of 4a in CD$_3$OD
$^{13}\text{C}$ NMR of 4a in CD$_3$OD
$^1$H NMR of 4b in CD$_3$OD
$^{13}$F NMR of 4b in CD$_3$OD
$^1$H NMR of 4c in DMSO-$d_6$
$^{19}$F NMR of 4c in DMSO-$d_6$
$^1$H NMR of 4d in DMSO-$d_6$
$^{19}\text{F NMR of 4d in DMSO-}d_6$
GC-MS of crude 5a
$^{19}$F NMR yield of compound 5a (1.93/(1×3)×100% = 64%) in CDCl$_3$
GC-MS of crude 5a
$^{19}$F NMR of crude 5a in CDCl$_3$
$^{19}$F NMR yield of compound 2h $(1.82/(1\times3)\times100\% = 60\%)$ in CDCl$_3$
GC-MS of crude 5b
$^{19}$F NMR of crude 5b in CDCl$_3$
$^{19}$F NMR yield of compound 5b ($2.77/(1\times3)\times100\% = 92\%$) in CDCl$_3$
$^1$H NMR of 5b in CDCl$_3$
$^{19}$F NMR of isolated 5b in CDCl$_3$
GC-MS of crude 5b
$^{19}$F NMR of crude 5b in CDCl$_3$
$^{19}$F NMR yield of compound 5b ($2.95/(1\times3)\times100\% = 98\%$) in CDCl$_3$
GC-MS of crude 5c
$^{19}$F NMR yield of compound 5c (2.81/(1×3)×100% = 93%) in CDCl$_3$
$^1$H NMR of 5c in CDCl$_3$
$^{19}$F NMR of isolated 5c in CDCl$_3$
GC-MS of crude 5c
$^{19}$F NMR of crude 5c in CDCl$_3$
$^{19}$F NMR yield of compound 5c ($2.82/(1 \times 3) \times 100\% = 94\%$) in CDCl$_3$.
$^{19}$F NMR yield of compound 5d \((2.58/(1\times3)\times100\% = 86\%)\) in CDCl$_3$
\( ^1\text{H NMR of 5c in CDCl}_3 \)
$^{19}$F NMR of isolated 5d in CDCl$_3$
GC-MS of crude 5d
$^{19}$F NMR of crude 5d in CDCl$_3$
$^{19}$F NMR yield of compound 5d ($2.22/(1\times3)\times100\% = 74\%$) in CDCl$_3$