Supporting Information for

Diverse copper(III) trifluoromethyl complexes with mono-, bi- and tridentate ligands and their versatile reactivity

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1. General experimental details

All chemicals were purchased commercially and used directly as received without further purification. CH$_2$Cl$_2$ and DMF solvents were simply dried over Na$_2$SO$_4$ before use to extrude adventitious water. All the reactions were performed in a Schlenk tube under N$_2$ or O$_2$ which was realized through evacuation/back-fill techniques, or under air atmosphere without the need of evacuation operation. For reactions involving AgF, a tinfoil was used to wrap the Schlenk tube to avoid the interference of visible light. Reaction progress was monitored by TLC analysis with stains visualized under UV irradiation, and $^{19}$F NMR analysis of the crude mixture after some necessary preliminary workup as detailed later in the corresponding sections. NMR yields were determined using $^{19}$F NMR analysis of the crude mixture with 4,4'-difluorobiphenyl as the internal standard (ca 117.0 ppm). Column chromatography on silica gel was used to obtain purified products. NMR spectra were recorded on a 400 MHz spectrometer and processed with MestReNova program. Chemical shifts are reported in ppm and referenced to residual solvent peaks or TMS. NMR signals are reported as follows to delineate possible splittings: s, singlet; bs, broad; d, doublet; t, triplet; q, quartet; and m, multiplet. Coupling constants are reported in Hertz where present. All the $^{13}$C and $^{19}$F NMR spectra were obtained with proton decoupling. Elemental analyses were performed by the Analytic Laboratory of Jiangnan University. High resolution mass spectra (HRMS) were determined on Thermo Scientific LTQ Orbitrap XL with ESI ionization technique.
2. Synthetic procedures, isolation and characterization of complexes 6-10

(Py)Cu\textsuperscript{III}(CF\textsubscript{3})\textsubscript{3} (6)

Into a 25-mL Schlenk tube equipped with a stir bar and wrapped with tinfoil (to avoid possible interference of visible light with AgF) were added CuI (95 mg, 0.5 mmol) and AgF (254 mg, 2 mmol) at room temperature. The tube was then sealed, evacuated and refilled with dry nitrogen three times. DMF (4 mL) and a mixture of CF\textsubscript{3}SiMe\textsubscript{3} (426 mg, 3 mmol) and pyridine (40 mg, 0.5 mmol) were sequentially added to the reaction solution by syringe. The contents in the tube were stirred at room temperature for 21 h under N\textsubscript{2}. After completion of the reaction, the crude mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2} (10 mL), separated by filtration and washed with CH\textsubscript{2}Cl\textsubscript{2} (5 mL). The combined filtrate and the washings were washed with water (5 mL) three times. Then the organic layer was evaporated to dryness with silica gel. The solid residual was purified by column chromatography (eluent: petroleum ether (PE) / dichloromethane (DCM) = 4: 1 (v/v)) to obtain yellow solids of 6 in a yield of 100 mg (57%).

\[
\begin{array}{c}
\text{CF}_3 \\
\text{N} \text{Cu}^{\text{III}} \text{CF}_3 \\
\text{CF}_3
\end{array}
\]

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.67 (d, \(J = 4.4\) Hz, 2H), 8.08 (t, \(J = 7.2\) Hz, 1H), 7.68 (t, \(J = 6.2\) Hz, 2H). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta\) -23.62 (br s), -37.13 (br s). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 148.0, 140.6, 126.2. IR (KBr, cm\textsuperscript{-1}): 3055 (w), 3026 (w), 1657, 1614, 1454, 1270, 1223, 1148, 757, 694. Anal. Calcd. for C\textsubscript{8}H\textsubscript{5}CuF\textsubscript{9}N: C, 27.48; H, 1.44; N, 4.01. Found: C, 26.96; H, 1.79; N, 4.51. (note that the carbon resonance for CF\textsubscript{3} was not observed in \textsuperscript{13}C NMR due possibly to dynamic behavior of complex 6 in solution (as discussed in the main text), Cu-C and F-C couplings that lead to broadening and splitting of the carbon resonance. For similar \textsuperscript{13}C NMR observation of Cu-CF\textsubscript{3} complex, see: Hartwig et al. \textit{Angew. Chem. Int. Ed.}, 2012, 51, 536.)
Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 6 at room temperature. As can be seen, the resonances are broadened greatly due to dynamic ligand exchange.

Figure S2. $^{19}$F NMR (376 MHz, CDCl$_3$) of complex 6 at room temperature.
Figure S3. $^{13}$C NMR (101 MHz, CDCl$_3$) of complex 6 at room temperature.
Low-temperature $^{19}$F NMR spectra of complex 6

Figure S4. $^{19}$F NMR (376 MHz, CDCl$_3$, 273K) of complex 6.
Figure S5. $^{19}$F NMR (376 MHz, CDCl$_3$, 253K) of complex 6. The inset shows fine splitting of the signal at ca 38.7 ppm.

Figure S6. $^{19}$F NMR (376 MHz, CDCl$_3$, 238K) of complex 6. The two insets show fine splitting of both signals.
(2,4,6-trimethylpyridine)Cu$^{	ext{III}}$(CF$_3$)$_3$ (7)

Into a 25-mL Schlenk tube equipped with a stir bar and wrapped with tinfoil (to avoid possible interference of visible light with AgF) were added CuI (95 mg, 0.5 mmol) and AgF (254 mg, 2 mmol) at room temperature. The tube was then sealed, evacuated and refilled with dry nitrogen three times. DMF (4 mL) and a mixture of CF$_3$SiMe$_3$ (426 mg, 3 mmol) and 2,4,6-trimethylpyridine (61 mg, 0.5 mmol) were sequentially added to the reaction solution by syringe. The contents in the tube were stirred at room temperature for 21 h under N$_2$. After completion of the reaction, the crude mixture was diluted with CH$_2$Cl$_2$ (10 mL), separated by filtration and washed with CH$_2$Cl$_2$ (5 mL). The combined filtrate and the washings were washed with water (5 mL) three times. Then the organic layer was evaporated to dryness with silica gel. The solid residual was purified by silica gel column chromatography (eluent: petroleum ether (PE) / dichloromethane (DCM) = 6: 1 (v/v)) to obtain white solids of 7 in a yield of 59 mg (30%). Afterwards, the silica gel column was eluted with dichloromethane to get the ion-pair complex 8 as yellow solids in a yield of 58 mg, 36%.

7: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.10 (s, 2H), 2.91 (s, 6H), 2.43 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -26.47 (br s), -34.91 (q, $J$ = 10.2 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.59 (s), 152.87 (s), 124.84 (s), 23.27 (s), 21.03 (s).
Figure S7. $^1$H NMR (400 MHz, CDCl$_3$) of complex 7 at room temperature.

Figure S8. $^{19}$F NMR (376 MHz, CDCl$_3$) of complex 7.
Figure S9. $^{13}$C NMR (101 MHz, CDCl$_3$) of complex 7 at room temperature.
Selective preparation of [(L)₂Cu⁺][Cu III(CF₃)₄]⁻ (8) in CH₃CN

Into a 25-mL Schlenk tube equipped with a stir bar and wrapped with tinfoil (to avoid possible interference of visible light with AgF) were added CuI (95 mg, 0.5 mmol) and AgF (254 mg, 2 mmol) at room temperature. The tube was then sealed. The air in the tube was evacuated and refilled with dry nitrogen three times. CH₃CN (4 mL) and a mixture of CF₃SiMe₃ (426 mg, 3 mmol) and 2, 4, 6-trimethylpyridine (61 mg, 0.5 mmol) were sequentially added to the reaction solution by syringe. The contents in the tube were stirred at room temperature for 21 h under N₂. After completion of the reaction, the crude mixture was diluted with CH₃CN (10 mL), separated by filtration and washed with CH₃CN (5 mL). The combined filtrate and the washings were evaporated to dryness with silica gel. The solid residual was purified by column chromatography on silica gel (eluent: DCM) to obtain yellow solid of 8 in a yield of 73 mg (45%). ¹H NMR (400 MHz, CD₃CN-d₃) δ 7.11 (s, 2H), 2.61 (s, 6H), 2.35 (s, 3H). ¹⁹F NMR (376 MHz, CD₃CN-d₃) δ -34.83 (s). ¹³C NMR (101 MHz, CD₃CN-d₃) δ 156.17 (s), 152.69 (s), 122.88 (s), 23.31 (s), 20.22 (s). HRMS (ESI) m/z calcd for C₁₆H₂₂CuN₂⁺ (the cation part L₂Cu⁺ of 8) (M)⁺ 305.10735, found 305.10742.
Figure S10. $^1$H NMR (400 MHz, CD$_3$CN-$d^3$) of complex 8. A quintet appearing at ca 1.96 ppm is the resonance of residual CH$_3$CN.
Figure S11. $^{19}$F NMR (376 MHz, CD$_3$CN-$d^3$) of complex 8. A very minor (less than 1%) amount of impurity was observed at ca -32 ppm.

Figure S12. $^{13}$C NMR (101 MHz, CD$_3$CN-$d^3$) of complex 8. Peaks at ca 117 (singlet) and 0.3 (septet) ppm are resonances of residual CH$_3$CN.
(quinol-8-yloxide)Cu^{III}(CF_3)_2 (9)

Into a 50-mL Schlenk tube equipped with a stir bar and wrapped with tinfoil (to avoid possible interference of visible light with AgF) were added CuI (190 mg, 1 mmol), 8-Hydroxyquinoline (145 mg, 1 mmol) and AgF (508 mg, 4 mmol) at room temperature. The tube was then sealed. The air in the tube was evacuated and refilled with dry nitrogen three times. DMF (10 mL) was then added by syringe and the contents were vigorously stirred for 30 minutes. CF_3SiMe_3 (852 mg, 6 mmol) was then slowly added by syringe. The resulting mixture was further stirred for 21 hours at room temperature under nitrogen. The crude mixture was diluted with CH_2Cl_2 (10 mL), separated by filtration and washed with CH_2Cl_2 (10 mL). The combined filtrate and the washings were washed with water (10 mL) three times. Then the organic layer was evaporated to dryness with silica gel. The dried solid was purified by 200 to 300 mesh silica gel column chromatography, and the product was separated and purified by using mixed petroleum ether/ethyl acetate = 5:1 (v/v) as the eluent to obtain gray-black solid of 9 in a yield of 102 mg (30%). Melting point: 264-265 °C.

\[
\text{CF}_3\quad \text{O} \quad \begin{array}{c}
\text{Cu}^{\text{III}}
\end{array} \quad \text{CF}_3
\]

\(^1\text{H} \text{NMR (400 MHz, CDCl}_3) \delta 8.72 (\text{dd, } J = 5.2, 1.0 \text{ Hz, } 1\text{H}), 8.48 (\text{dd, } J = 8.2, 1.1 \text{ Hz, } 1\text{H}), 7.61 (\text{dd, } J = 8.2, 5.2 \text{ Hz, } 1\text{H}), 7.58 (\text{t, } J = 8.0 \text{ Hz, } 1\text{H}), 7.24 (\text{d, } J = 8.0 \text{ Hz, } 1\text{H}), 7.18 (\text{d, } J = 7.8 \text{ Hz, } 1\text{H}). \]

\(^{19}\text{F} \text{NMR (376 MHz, CDCl}_3) \delta -26.74 (\text{br s}). \]

\(^{13}\text{C} \text{NMR (101 MHz, CDCl}_3) \delta 163.1, 147.6, 143.2, 141.3, 131.3, 130.3, 121.8, 115.2, 114.2. \]

\text{MS (ES+): 208.0 (M-2CF}_3\text{), 100%; 146.1 (8-hydroxyquinoline), 28\%}. \]

\text{Anal. Cacld for C}_{11}\text{H}_{6}\text{CuF}_{6}\text{NO: C, 38.22; H, 1.75; N, 4.05. Found: C, 39.0; H, 2.20; N, 4.20. HRMS (ESI) m/z calcd for C}_{11}\text{H}_{7}\text{CuF}_{6}\text{NO}^+ (M+H)^+ 345.97224, found 345.97202.} \]
Figure S13. $^1$H NMR (400 MHz, CDCl$_3$) of complex 9 at room temperature.

Figure S14. $^{19}$F NMR (376 MHz, CDCl$_3$) of complex 9. The peak at -61.6 ppm is assigned to be very minor C-H trifluoromethylation byproduct at room temperature.
Figure S15. $^{13}$C NMR (101 MHz, CDCl$_3$) of complex 9 at room temperature.
(terpyridine)Cu^{III}(CF_3)_3 (10)

Into a 25-mL Schlenk tube equipped with a stir bar and wrapped with tinfoil (to avoid possible interference of visible light with AgF) were added CuI (57 mg, 0.3 mmol), 2,6-bis(2-pyridyl)pyridine (70 mg, 0.3 mmol) and AgF (152 mg, 1.2 mmol) at room temperature. The tube was then sealed. The air in the tube was evacuated and refilled with dry nitrogen three times. CH_2Cl_2 (5 mL) was then added by syringe and the contents were vigorously stirred for 30 minutes. CF_3SiMe_3 (256 mg, 1.8 mmol) was then slowly added by syringe. The resulting mixture was further stirred for 21 hours at ice-water under nitrogen. The crude mixture was diluted with CH_2Cl_2 (10 mL), separated by filtration and washed with CH_2Cl_2 (10 mL). Then the volatiles was evaporated to dryness with silica gel. The dried solid was purified by 200 to 300 mesh silica gel column chromatography, and the product was separated and purified by using mixed petroleum ether/ethyl acetate = 1:1 (v/v) as eluent to obtain brownish yellow solid of 10 in a yield of 53 mg (35%).

\[
\begin{align*}
\text{Cu}^{\text{III}} & \quad \text{CF}_3 \\
\text{N} & \quad \text{CF}_3 \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[^1\text{H} \text{NMR} \ (400 \text{ MHz, DMSO-}d_6) \ \delta \ 9.08 \ (d, \ J = 4.4 \text{ Hz, 2H}), \ 8.85 \ (d, \ J = 8.0 \text{ Hz, 2H}), \ 8.74 \ (d, \ J = 8.1 \text{ Hz, 2H}), \ 8.52 \ (t, \ J = 7.9 \text{ Hz, 1H}), \ 8.28 \ (td, \ J = 7.9, 1.5 \text{ Hz, 2H}), \ 7.87 \ (dd, \ J = 7.3, 5.0 \text{ Hz, 2H}). \ \[^{19}\text{F} \text{NMR} \ (376 \text{ MHz, DMSO-}d_6) \ \delta \ -25.20 \ (\text{septet, } J = 9.8 \text{ Hz}), \ -34.57 \ (\text{q, } J = 9.8 \text{ Hz}). \ \[^{13}\text{C} \text{NMR} \ (101 \text{ MHz, DMSO-}d_6) \ \delta \ 151.61 \ (\text{s}), \ 149.40 \ (\text{s}), \ 148.80 \ (\text{m}), \ 142.36 \ (\text{s}), \ 139.76 \ (\text{s}), \ 127.03 \ (\text{s}), \ 124.51 \ (\text{s}), \ 123.22 \ (\text{s}). \ \text{HRMS (ESI) m/z caled for C}_{15}\text{H}_{11}\text{CuN}_3^{+} (\text{M-3CF}_3)^{+} 296.02435, \ \text{found 296.02426}.\]

Figure S16. $^1$H NMR (400 MHz, DMSO-$d_6$) of complex 10.

Figure S17. $^{19}$F NMR (376 MHz, DMSO-$d_6$) of complex 10.
Figure S18. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of complex 10.
3. X-ray crystallographic study

Crystals of 6 and 7 suitable for X-ray crystallographic diffraction analysis were grown from slow evaporation of mixed solvent of 6 or 7 in CH$_2$Cl$_2$/DMF/hexane under low temperature in the refrigerator for several days. CCDC 1810661-1810662 contain the detailed crystallographic data for the determination of 6 and 7. Some key crystallographic parameters regarding 6 and 7 are presented below.

**Crystal data for 6•DMF**

<table>
<thead>
<tr>
<th>C$<em>{11}$H$</em>{12}$CuF$_9$N$_2$O</th>
<th>complex 6•DMF</th>
</tr>
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<tbody>
<tr>
<td>$M_r = 422.77$</td>
<td>$D_\chi = 1.725$ Mg m$^{-3}$</td>
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<td>Orthorhombic, Pnma</td>
<td>Melting point: ? K</td>
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<tr>
<td>Hall symbol: ?</td>
<td>Mo Kα radiation, $\lambda = 0.71073$ Å</td>
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<tr>
<td>$a = 19.9959$ (11) Å</td>
<td>Cell parameters from 3878 reflections</td>
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<tr>
<td>$b = 8.1241$ (5) Å</td>
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<td>$c = 10.0188$ (6) Å</td>
<td>$\mu = 1.44$ mm$^{-1}$</td>
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<tr>
<td>$V = 1627.54$ (17) Å$^3$</td>
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<tr>
<td>$Z = 4$</td>
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<tr>
<td>$F(000) = 840$</td>
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</tr>
</tbody>
</table>

**Crystal data for 7**

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</tr>
</thead>
<tbody>
<tr>
<td>$M_r = 391.75$</td>
<td>$D_\chi = 1.779$ Mg m$^{-3}$</td>
</tr>
<tr>
<td>Orthorhombic, Cmcm</td>
<td>Melting point: ? K</td>
</tr>
<tr>
<td>Hall symbol: ?</td>
<td>Mo Kα radiation, $\lambda = 0.71073$ Å</td>
</tr>
<tr>
<td>$a = 8.4272$ (4) Å</td>
<td>Cell parameters from 2912 reflections</td>
</tr>
<tr>
<td>$b = 19.4683$ (9) Å</td>
<td>$\theta = 4.0$–27.1°</td>
</tr>
<tr>
<td>$c = 8.9136$ (4) Å</td>
<td>$\mu = 1.59$ mm$^{-1}$</td>
</tr>
</tbody>
</table>
$V = 1462.39 \pm 12 \, \text{Å}^3$

$T = 273 \, \text{K}$

$Z = 4$

Block, colorless

$F(000) = 776$

$0.30 \times 0.23 \times 0.21 \, \text{mm}$
4. Reactivity studies of 6-10 with arylboronic acids

4.1 Optimization study of reaction of 6 with 11a

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added (Py)Cu(CF$_3$)$_3$ (6) (35 mg, 0.1 mmol), 4-methoxyphenylboronic acid (11a) (30 mg, 0.2 mmol), additive (0.2 mmol) and 4,4′-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The Schlenk tube was evacuated and refilled with dry oxygen. Dry solvent (1 mL) was then added by syringe. The contents in the tube were vigorously stirred for specified time at specified temperature (heated in an oil bath). The mixture was allowed to cool to room temperature, diluted with Et$_2$O and filtered through a pad of Celite. The Celite pad was washed with Et$_2$O. The combined filtrate was washed with brine, and then concentrated to extrude ether. The residue mixture was analyzed by $^{19}$F NMR spectroscopy to determine the reaction yield.

![Figure S19. $^{19}$F NMR determination of the reaction mixture of reaction of complex 6 with 11a under the reaction conditions of entry 2 in Table 1.](image)

For example, Figure S19 shows the $^{19}$F NMR determination of the reaction solution of entry 2 in Table 1 after workup described above. As can be seen, nearly
quantitative conversion of complex 6 was observed. The new signal at -61.9 ppm corresponds to the formation of trifluoromethylated arene 12a while the signal at -116.9 ppm is the internal standard 4, 4'-difluorobiphenyl. The trifluoromethylation yield was thus determined to be 99% relative to 11a.

4.2 General procedure for reaction of 6 with various arylboronic acids

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added PyCu(CF₃)₃ (6) (35 mg, 0.1 mmol), arylboronic acid (11, 0.2 mmol), KF (0.2 mmol), and 4, 4'-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The Schlenk tube was evacuated and refilled with dry oxygen. Dry DMF (1 mL) was then added by syringe. The contents in the tube were vigorously stirred and heated in an oil bath at 50 °C for 6 hours. The mixture was allowed to cool to room temperature, diluted with Et₂O and filtered through a pad of Celite. The Celite pad was washed with Et₂O. The combined filtrates were concentrated to extrude ether, and the residue mixture was analyzed by ¹⁹F NMR spectroscopy to determine the reaction yields.

The following sections show some of the purified products 12 after column chromatography on silica gel.

12a (14 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -61.47 (s). ¹³C NMR (101 MHz, CDCl₃) δ 162.03 (s), 126.89 (q, J = 3.8 Hz), 124.5 (q, J = 271.1 Hz), 122.90 (q, J = 32.7 Hz), 113.96 (s), 55.43 (s).
Figure S20. $^1$H NMR (400 MHz, CDCl$_3$) of 12a.

Figure S21. $^{19}$F NMR (376 MHz, CDCl$_3$) of 12a.
Figure S22. $^{13}$C NMR (101 MHz, CDCl$_3$) of 12a.

**12b** (35 mg, 81%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (s, 4H), 7.64-7.61 (m, 2H), 7.54–74.0 (m, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.40 (s).
Figure S23. $^1$H NMR (400 MHz, CDCl$_3$) of 12b.

Figure S24. $^{19}$F NMR (376 MHz, CDCl$_3$) of 12b.
**12c** (22 mg, 61%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, $J$ = 8.6 Hz, 2H), 7.43 (d, $J$ = 8.6 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.37 (s).

Figure S25. $^1$H NMR (400 MHz, CDCl$_3$) of 12c.
Figure S26. $^{19}$F NMR (376 MHz, CDCl$_3$) of 12c.

4.3 Optimization study of reaction of 7 with 11a

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added 7 (39 mg, 0.1 mmol), 4-methoxyphenylboronic acid (11a) (30 mg, 0.2 mmol), additive (0.2 mmol) and 4,4′-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). Dry solvent (1 mL) was then added by syringe. The contents in the tube were vigorously stirred for specified time at specified temperature (heated in an oil bath). The mixture was allowed to cool to room temperature, diluted with Et$_2$O and filtered through a pad of Celite. The Celite pad was washed with Et$_2$O. The combined filtrate was washed with brine, and then concentrated to extrude ether. The residue mixture was analyzed by $^{19}$F NMR spectroscopy to determine the reaction yield. Table S1 summarizes the results of screening of additives, and the effects of temperature and time.
Table S1. Reactivity study of complex 7 with arylboronic acids

![Image of reactivity study](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>yield (%) $^b$</th>
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<td>—</td>
<td>80</td>
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<td>72</td>
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<td>99 $^d$</td>
</tr>
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<td>80</td>
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<tr>
<td>5</td>
<td>KF</td>
<td>80</td>
<td>6</td>
<td>99 $^e$</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 7 (0.1 mmol), 11a (0.2 mmol), additive (0.2 mmol), 4,4'-difluorobiphenyl (0.2 mmol, internal standard), DMF (1 mL), under air atmosphere.

$^b$ Yields determined by $^{19}$F NMR spectroscopy based on 11a.

$^c$ N$_2$ atmosphere.

$^d$ O$_2$ atmosphere.

$^e$ O$_2$ atmosphere.

4.4 General procedure for reaction of 7 with various arylboronic acids

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added 7 (39 mg, 0.1 mmol), arylboronic acid (11, 0.2 mmol), KF (0.2 mmol), and 4, 4'-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). Dry DMF (1 mL) was then added by syringe. The contents in the tube were vigorously stirred and heated in an oil bath at 80°C for 6 hours. The mixture was allowed to cool to room temperature, diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et$_2$O. The combined filtrates were concentrated to extrude ether, and the residue mixture was analyzed by $^{19}$F NMR spectroscopy to determine the reaction yields.

The following sections show some of the purified products 12 after column chromatography on silica gel.
12q (40 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J$ = 7.7 Hz, 1H), 8.00 (d, $J$ = 7.6 Hz, 1H), 7.71 (dd, $J$ = 11.7, 8.0 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.44 (q, $J$ = 7.5 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -61.05 (s).

Figure S27. $^1$H NMR (400 MHz, CDCl$_3$) of 12q.
Figure S28. $^{19}$F NMR (376 MHz, CDCl$_3$) of 12q.

4.5 Optimization study of reaction of 8 with 11a

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added 7 (32 mg, 0.05 mmol), 4-methoxyphenylboronic acid (11a) (15 mg, 0.1 mmol), additive (0.1 mmol) and 4,4′-difluorobiphenyl (internal standard; 19 mg, 0.1 mmol). The Schlenk tube was evacuated and refilled with dry oxygen. Dry solvent (1 mL) was then added by syringe. The contents in the tube were vigorously stirred for specified time at specified temperature (heated in an oil bath). The mixture was allowed to cool to room temperature, diluted with Et$_2$O and filtered through a pad of Celite. The Celite pad was washed with Et$_2$O. The combined filtrate was washed with brine, and then concentrated to extrude ether. The residue mixture was analyzed by $^{19}$F NMR spectroscopy to determine the reaction yield. Table S2 summarizes the results of screening of additives, and the effects of temperature, time and solvent.
Table S2. Reactivity study of complex 8 with arylboronic acids.

![Chemical structure of complex 8 and reaction scheme involving arylboronic acids.]

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>yield (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>DMF</td>
<td>80</td>
<td>6</td>
<td>31 (in air)</td>
</tr>
<tr>
<td>2</td>
<td>—</td>
<td>DMF</td>
<td>100</td>
<td>6</td>
<td>23 (in air)</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>DMF</td>
<td>100</td>
<td>6</td>
<td>27 (in air)</td>
</tr>
<tr>
<td>4</td>
<td>KF</td>
<td>DMF</td>
<td>100</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>KF</td>
<td>DMF</td>
<td>80</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>KF</td>
<td>Toluene</td>
<td>80</td>
<td>18</td>
<td>15</td>
</tr>
</tbody>
</table>

Reactions conditions: 8 (0.05 mmol), 11a (0.1 mmol), additive (0.1 mmol), 4,4'-difluorobiphenyl (0.1 mmol, internal standard), DMF (1 mL), under dry oxygen atmosphere. b Yields determined by \(^{19}\)F NMR spectroscopy based on 11a.
5. C-H trifluoromethylation of terminal alkynes

5.1 Optimization study of reaction of 6 with 13a

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added PyCu(CF₃)₃ (6) (35 mg, 0.1 mmol), 4-methoxyphenylacetylene (13a) (14 mg, 0.1 mmol), additive (0.2 mmol) and 4, 4'-difluorobiphenyl (internal standard; 19 mg, 0.1 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry solvent (1 mL) was then added by syringe. The contents in the tube were vigorously stirred for specified time at specified temperature (heated in an oil bath). The mixture was allowed to cool to room temperature, diluted with CH₂Cl₂ and filtered through a pad of Celite. The Celite pad was washed with CH₂Cl₂. The combined filtrate was washed with brine, and then concentrated to extrude ether. The residue mixture was analyzed by ¹⁹F NMR spectroscopy to determine the reaction yield. Table S3 summarizes the results of screening of various additive, the effects of temperature, time and etc.

Table S3. Reactivity study of complex 6 with terminal alkynes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>100</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>CsF</td>
<td>100</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>CsF</td>
<td>100</td>
<td>1</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>KF</td>
<td>100</td>
<td>0.5</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>KF</td>
<td>100</td>
<td>1</td>
<td>87</td>
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<tr>
<td>6</td>
<td>KF</td>
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<td>77</td>
</tr>
<tr>
<td>7</td>
<td>KF</td>
<td>100</td>
<td>8</td>
<td>99</td>
</tr>
<tr>
<td>8</td>
<td>KF</td>
<td>100</td>
<td>1</td>
<td>59 (in O₂)</td>
</tr>
<tr>
<td>9</td>
<td>AgF</td>
<td>100</td>
<td>8</td>
<td>72</td>
</tr>
<tr>
<td>10</td>
<td>NaO₂Bu</td>
<td>100</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>11</td>
<td>NaO₂Bu</td>
<td>100</td>
<td>12</td>
<td>99</td>
</tr>
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<td>12</td>
<td>CH₃ONa</td>
<td>100</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>NH₄F</td>
<td>100</td>
<td>8</td>
<td>Trace</td>
</tr>
<tr>
<td>14</td>
<td>NaF</td>
<td>100</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>15</td>
<td>C₂H₅ONa</td>
<td>100</td>
<td>8</td>
<td>Cplx.mix.</td>
</tr>
</tbody>
</table>

a Reaction conditions: 6 (0.1 mmol), 13a (0.1 mmol), additive (0.2 mmol), 4,4'-difluorobiphenyl (0.2 mmol, internal standard), DMF (1 mL), under dry N₂ atmosphere. b Yields determined by ¹⁹F NMR.
NMR spectroscopy based on 13a.  

Figure S29. $^{19}$F NMR determination of the reaction mixture of reaction of 6 with 13a.

For example, Figure S29 shows the $^{19}$F NMR determination of the reaction solution of entry 5 in Table S3 after workup as described above. As can be seen, nearly quantitative conversion of complex 6 was observed. The new signal at -49.9 ppm corresponds to the formation of trifluoromethylated alkyne 14a while the signal at -116.8 ppm is the internal standard 4, 4′-difluorobiphenyl. The trifluoromethylation yield was thus determined to be 87% relative to 13a.
5.2 General procedure for C-H trifluoromethylation of terminal alkynes by 6

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added PyCu(CF₃)₃ (6) (35 mg, 0.1 mmol), alkyne (13, 0.1 mmol), KF (0.2 mmol), and 4, 4'-difluorobiphenyl (internal standard; 19 mg, 0.1 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry DMF (1 mL) was then added by syringe. The contents in the tube were vigorously stirred and heated in an oil bath at 100 °C for 1 hour. The mixture was allowed to cool to room temperature, diluted with ether and filtered through a pad of Celite. The Celite pad was washed with CH₂Cl₂. The combined filtrates were concentrated to extrude ether, and the residue mixture was analyzed by ¹⁹F NMR spectroscopy to determine the reaction yields of 14. The following sections show some of the purified products 14 after column chromatography on silica gel eluted with pentane.

14a (12 mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -49.40 (s). ¹³C NMR (101 MHz, CDCl₃) δ 161.56 (s), 134.16 (q, J = 1.5 Hz), 115.07 (q, J = 256.4 Hz), 114.33 (s), 110.35 (q, J = 1.7 Hz), 87.06 (q, J = 6.5 Hz), 74.82 (q, J = 52.3 Hz), 55.39 (s).
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$) of 14a.

Figure S31. $^{19}$F NMR (376 MHz, CDCl$_3$) of 14a.
Figure S32. $^{13}$C NMR (101 MHz, CDCl$_3$) of 14a.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.97 (s), 137.41 (s), 133.09 (q, $J = 1.4$ Hz), 129.60 (s), 124.26 (q, $J = 1.7$ Hz), 114.56 (q, $J = 257.8$ Hz), 84.90 (q, $J = 6.5$ Hz), 78.43 (q, $J = 53.1$ Hz).

14b (13 mg, 64%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.09 (s, 1H), 7.95 (d, $J = 8.3$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -50.31 (s).
Figure S33. $^1$H NMR (400 MHz, CDCl$_3$) of 14b.

Figure S34. $^{19}$F NMR (376 MHz, CDCl$_3$) of 14b.
Figure S35. $^{13}$C NMR (101 MHz, CDCl$_3$) of 14b.
6. *syn*-Fluoro- and -oxy-trifluoromethylation of arylacetylenes

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added PyCu(CF₃)₃ (6) (35 mg, 0.1 mmol), alkyne (13, 0.1 mmol), CsF (0.5 mmol) or NaOPh (0.2 mmol), and 4, 4′-difluorobiphenyl (internal standard; 19 mg, 0.1 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry DMF (2 mL) was then added by syringe. The contents in the tube were vigorously stirred and heated in an oil bath at 100 °C for 8 h (for CsF) or 6 h (for NaOPh). The mixture was allowed to cool to room temperature, diluted with ether and filtered through a pad of Celite. The Celite pad was washed with CH₂Cl₂. The combined filtrates were concentrated to extrude ether, and the residue mixture was analyzed by ^{19}F NMR spectroscopy to determine the reaction yields of 15 or 16.

![Chemical Structure](image)

15a (12 mg, 55%). ^{1}H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 5.57 (dq, J = 33.9, 7.5 Hz, 1H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, CDCl₃) δ -56.62 (d, J = 16.4 Hz, 3F), -102.23 (q, J = 16.3 Hz, 1F). ^{13}C NMR (101 MHz, CDCl₃) δ 163.40 (dq, J = 269.1, 5.8 Hz), 162.15 (s), 127.13 (d, J = 7.8 Hz), 122.88 (q, J = 269.1 Hz), 121.89 (d, J = 26.4 Hz), 114.30 (d, J = 1.7 Hz), 93.59 (qd, J = 36.2, 11.7 Hz), 55.44 (s).
Figure S36. $^1$H NMR (400 MHz, CDCl$_3$) of 15a.

Figure S37. $^{19}$F NMR (376 MHz, CDCl$_3$) of 15a.
Figure S38. $^{13}$C NMR (101 MHz, CDCl$_3$) of 15a.

16a (18 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 8.6$ Hz, 2H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.26 (t, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.94 (d, $J = 7.8$ Hz, 2H), 5.85 (q, $J = 7.4$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.83 (s). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.76 (q, $J = 5.7$ Hz), 155.90 (s), 136.63 (s), 131.26 (s), 129.66 (s), 129.16 (s), 128.49 (s), 123.12 (s), 122.74 (q, $J = 269.8$ Hz), 117.05 (s), 105.56 (q, $J = 35.1$ Hz).
Figure S39. $^1$H NMR (400 MHz, CDCl$_3$) of $^{16a}$.

Figure S40. $^{19}$F NMR (376 MHz, CDCl$_3$) of $^{16a}$. 
Figure S41. $^{13}$C NMR (101 MHz, CDCl$_3$) of 16a.