Supporting Information for

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

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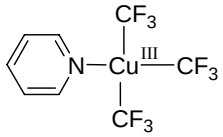
1. General experimental details

All chemicals were purchased commercially and used directly as received without further purification. CH_2Cl_2 and DMF solvents were simply dried over Na_2SO_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)$Cu^{III}(CF_3)_3$ (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_3SiMe_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_2. After completion of the reaction, the crude mixture was diluted with CH_2Cl_2 (10 mL), separated by filtration and washed with CH_2Cl_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%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.4 Hz, 2H), 8.08 (t, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 6.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -23.62 (br s), -37.13 (br s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 140.6, 126.2. IR (KBr, cm^{-1}): 3055 (w), 3026 (w), 1657, 1614, 1454, 1270, 1223, 1148, 757, 694. Anal. Calcd. for $C_8H_5CuF_9N$: 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_3 was not observed in ^{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 ^{13}C NMR observation of Cu-CF_3 complex, see: Hartwig et al. *Angew. Chem. Int. Ed.*, 2012, **51**, 536.)

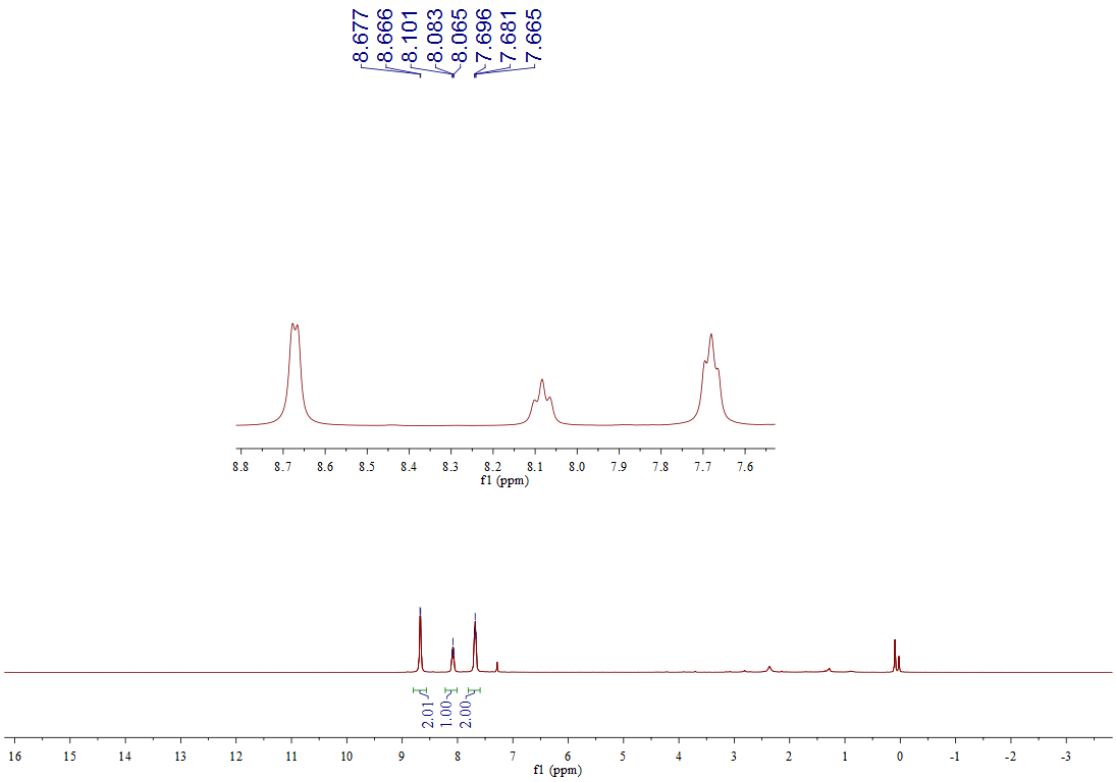


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6** at room temperature. As can bee seen, the resonances are broadened greatly due to dynamic ligand exchange.

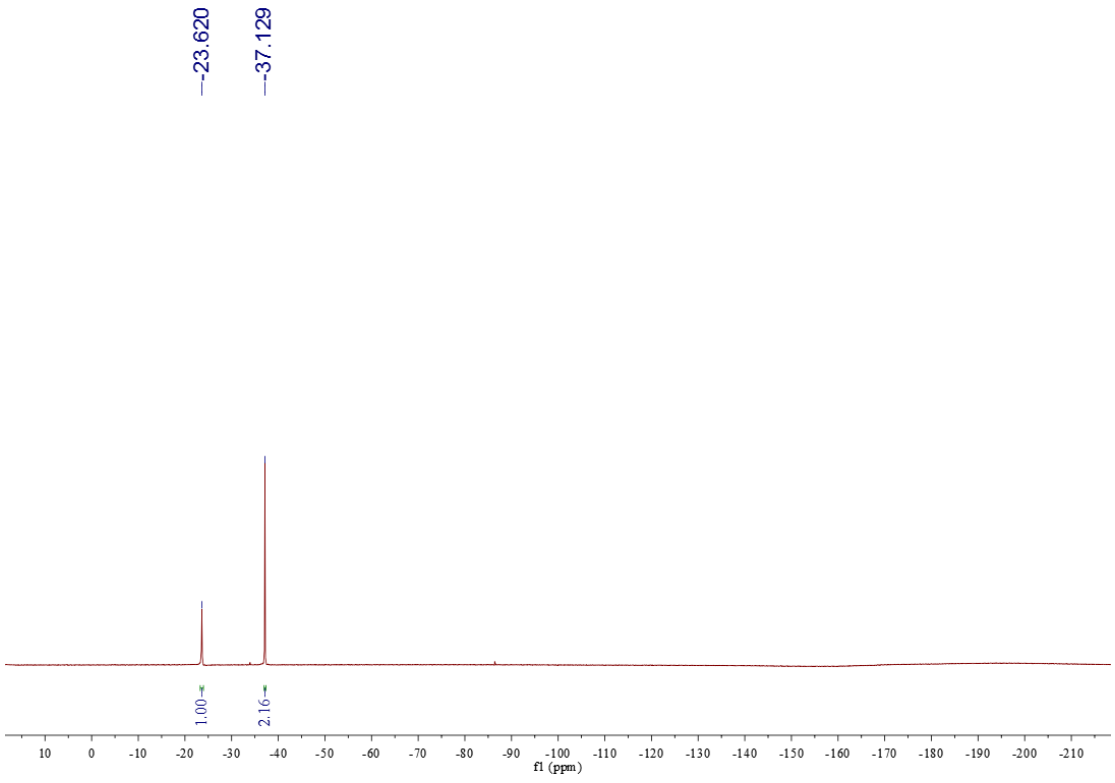


Figure S2. ^{19}F NMR (376 MHz, $CDCl_3$) of complex **6** at room temperature.

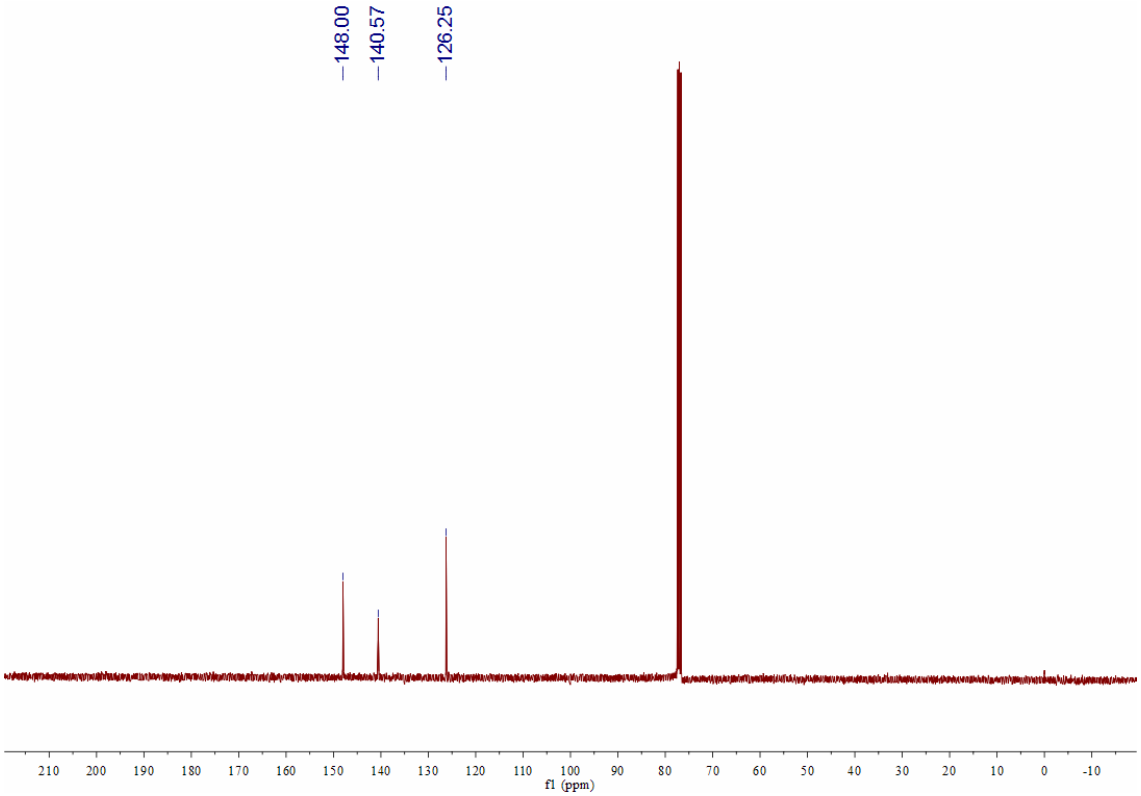


Figure S3. ^{13}C NMR (101 MHz, $CDCl_3$) of complex **6** at room temperature.

Low-temperature ^{19}F NMR spectra of complex 6

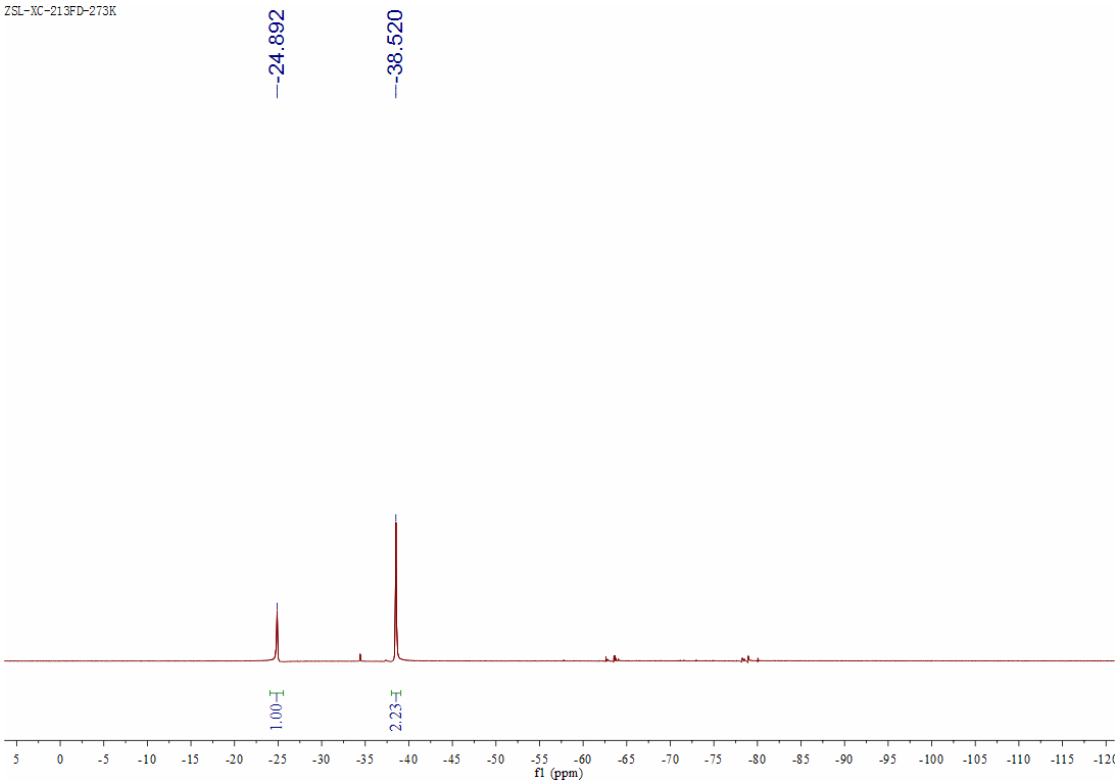


Figure S4. ^{19}F NMR (376 MHz, $CDCl_3$, 273K) of complex **6**.

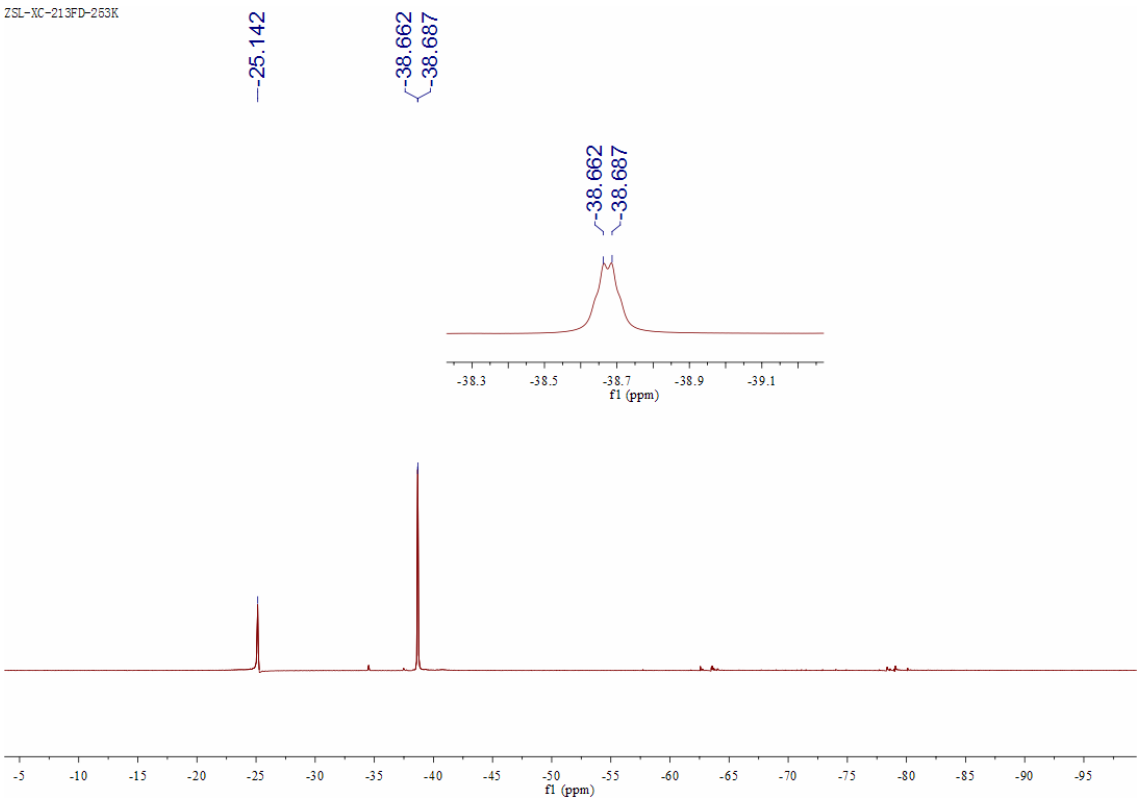


Figure S5. ^{19}F NMR (376 MHz, $CDCl_3$, 253K) of complex **6**. The inset shows fine splitting of the signal at ca 38.7 ppm.

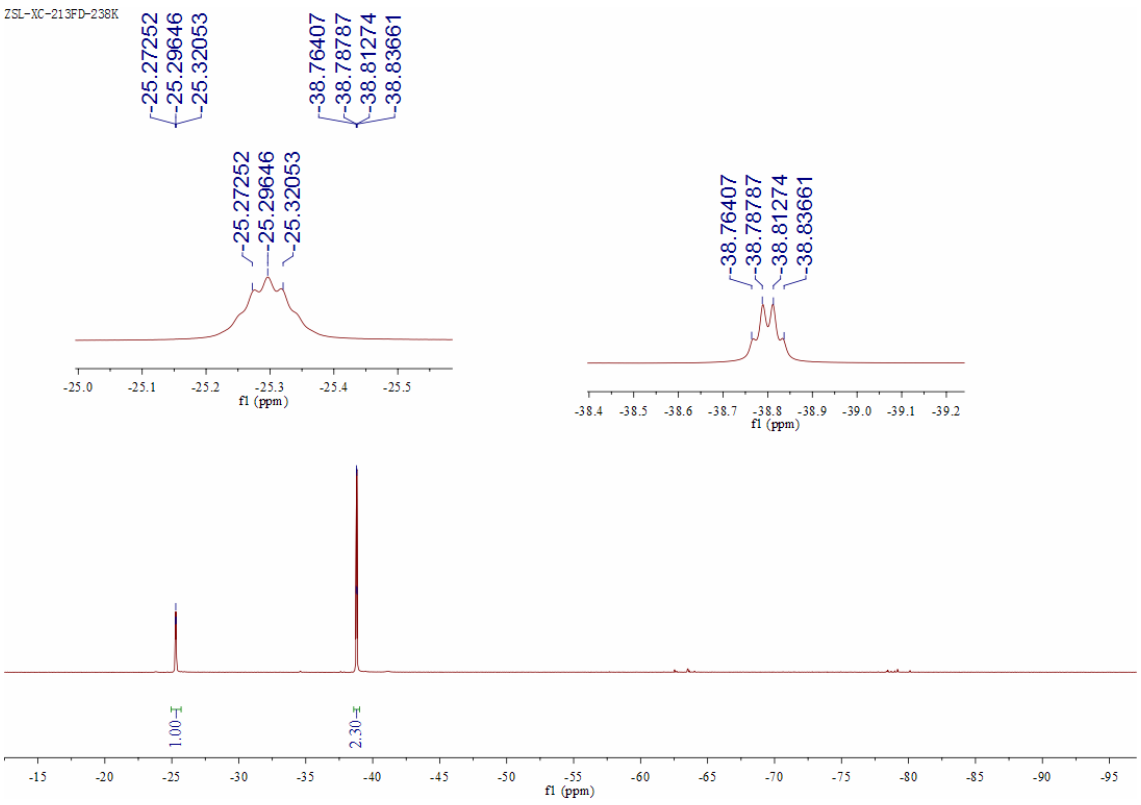
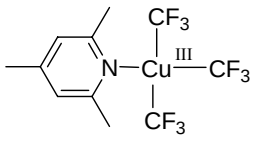


Figure S6. ^{19}F NMR (376 MHz, $CDCl_3$, 238K) of complex **6**. The two insets show fine splitting of both signals.

(2,4,6-trimethylpyridine)$Cu^{III}(CF_3)_3$ (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_3SiMe_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_2Cl_2 (10 mL), separated by filtration and washed with CH_2Cl_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).

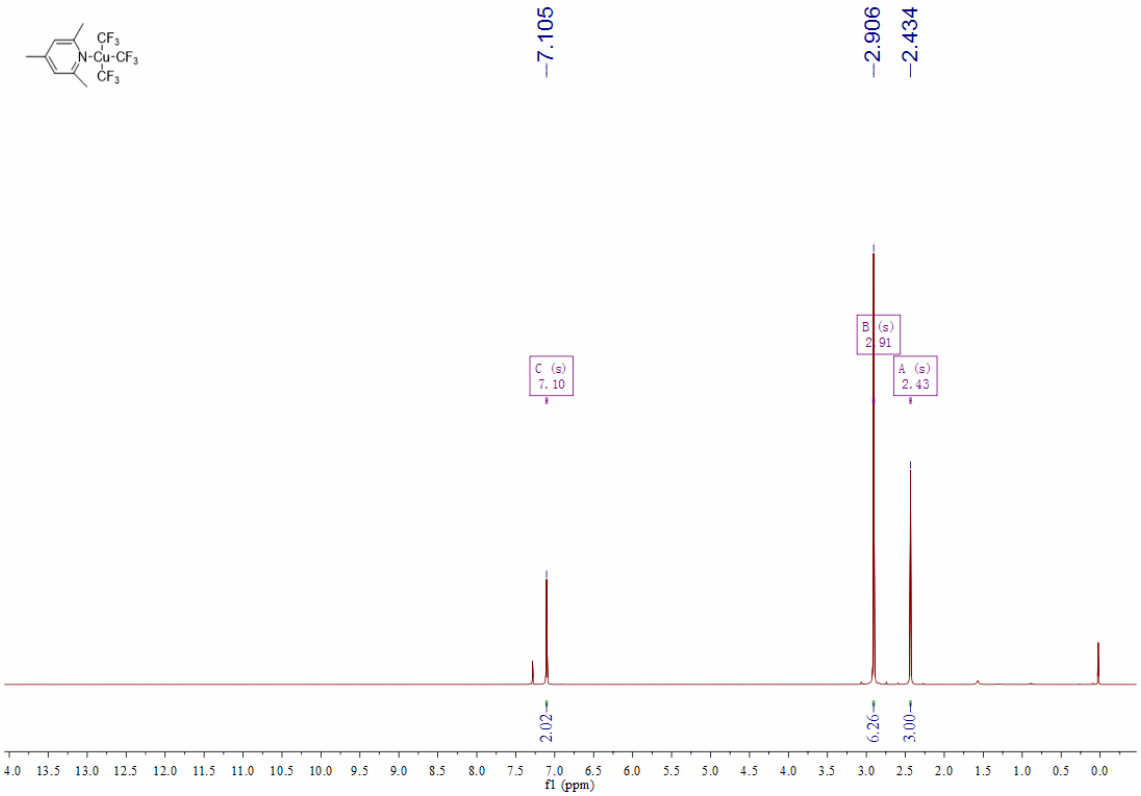


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of complex **7** at room temperature.

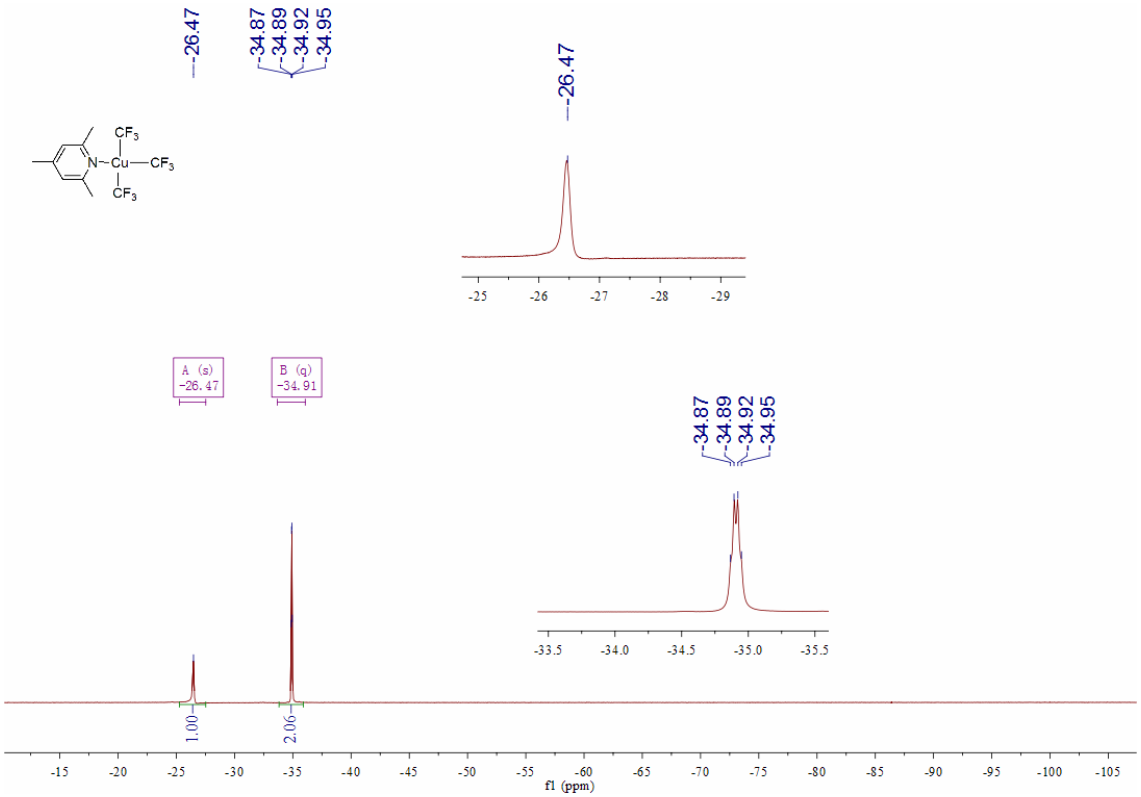


Figure S8. ^{19}F NMR (376 MHz, $CDCl_3$) of complex **7**.

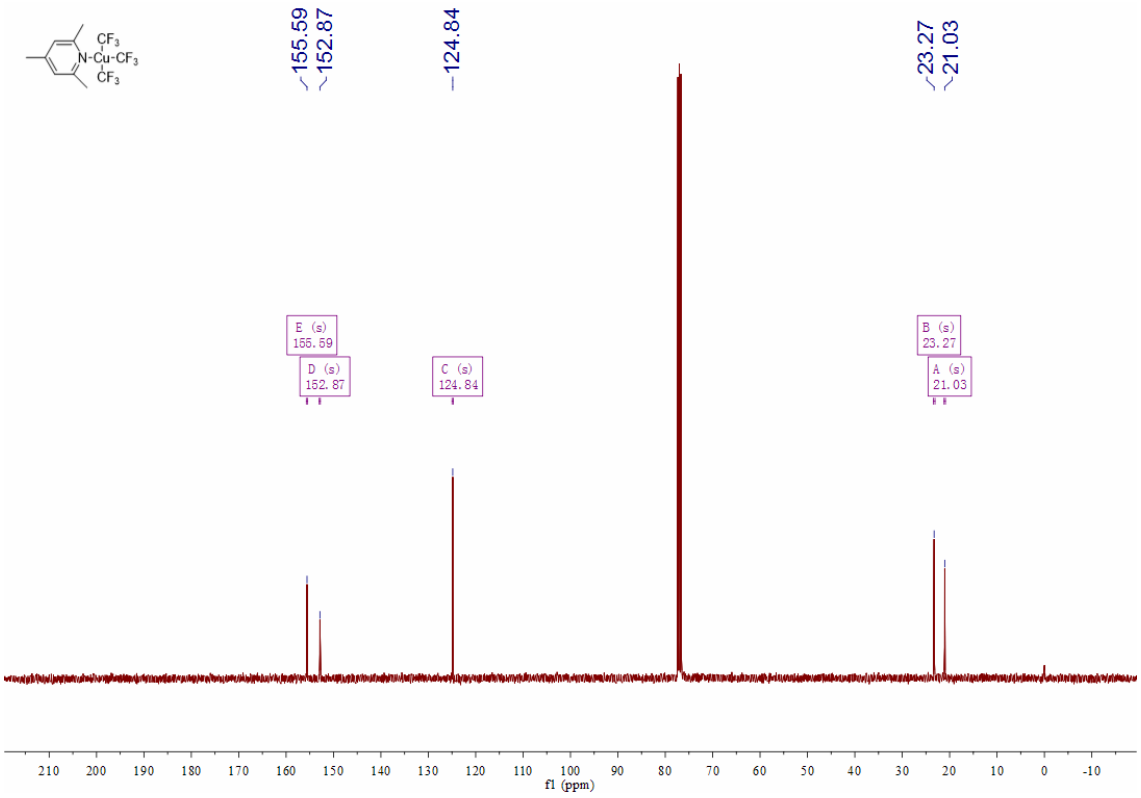


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) of complex **7** at room temperature.

Selective preparation of $[(L)_2Cu^{I}]^{+}[Cu^{III}(CF_3)_4]^{-}$ (8) in CH_3CN

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. CH_3CN (4 mL) and a mixture of CF_3SiMe_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_3CN (10 mL), separated by filtration and washed with CH_3CN (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%). ^{1}H NMR (400 MHz, CD_3CN-d^3) δ 7.11 (s, 2H), 2.61 (s, 6H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, CD_3CN-d^3) δ -34.83 (s). ^{13}C NMR (101 MHz, CD_3CN-d^3) δ 156.17 (s), 152.69 (s), 122.88 (s), 23.31 (s), 20.22 (s). HRMS (ESI) m/z calcd for $C_{16}H_{22}CuN_2^{+}$ (the cation part L_2Cu^{+} of **8**) $(M)^{+}$ 305.10735, found 305.10742.

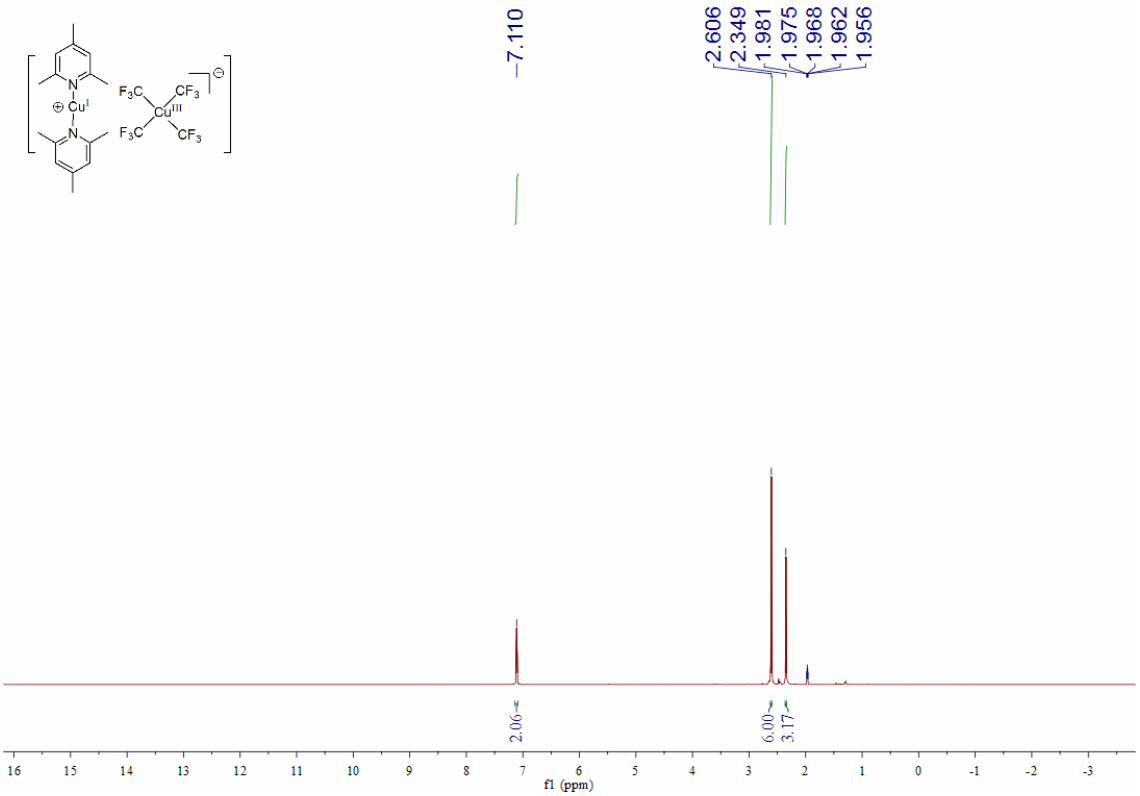


Figure S10. ^{1}H NMR (400 MHz, CD_3CN-d^3) of complex **8**. A quintet appearing at ca 1.96 ppm is the resonance of residual CH_3CN.

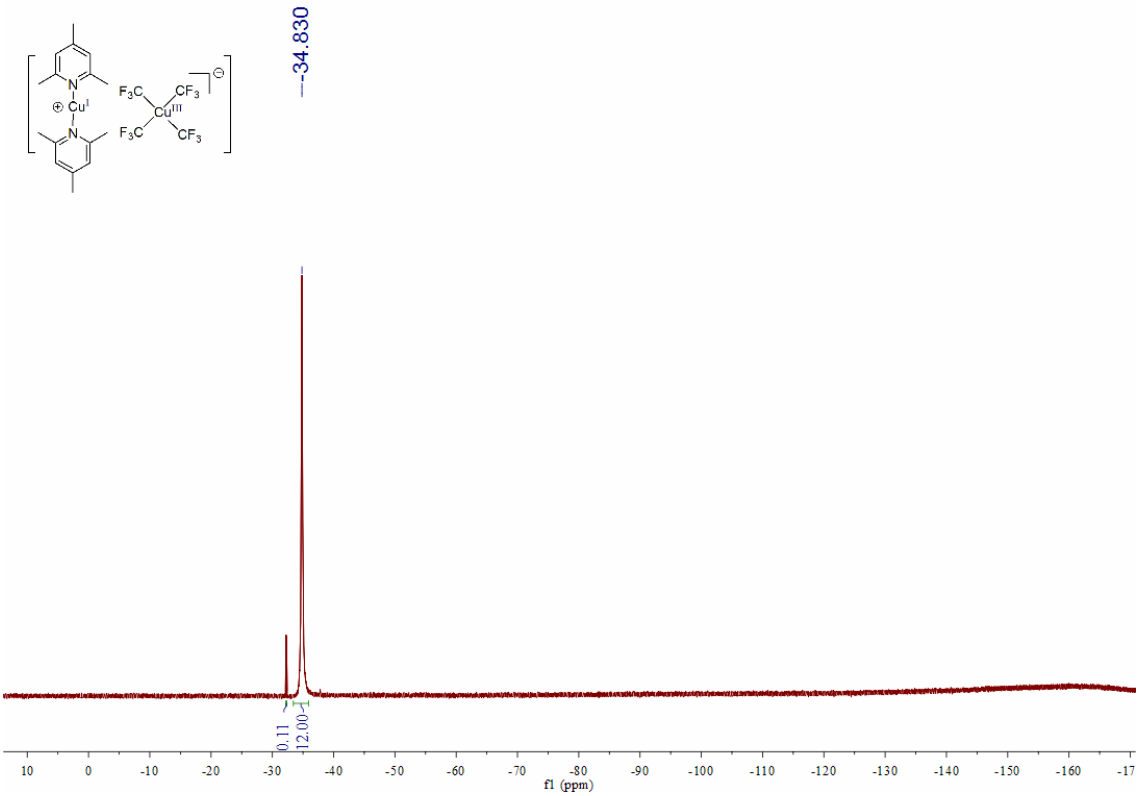


Figure S11. ^{19}F NMR (376 MHz, CD_3CN-d^3) of complex **8**. A very minor (less than 1%) amount of impurity was observed at *ca* -32 ppm.

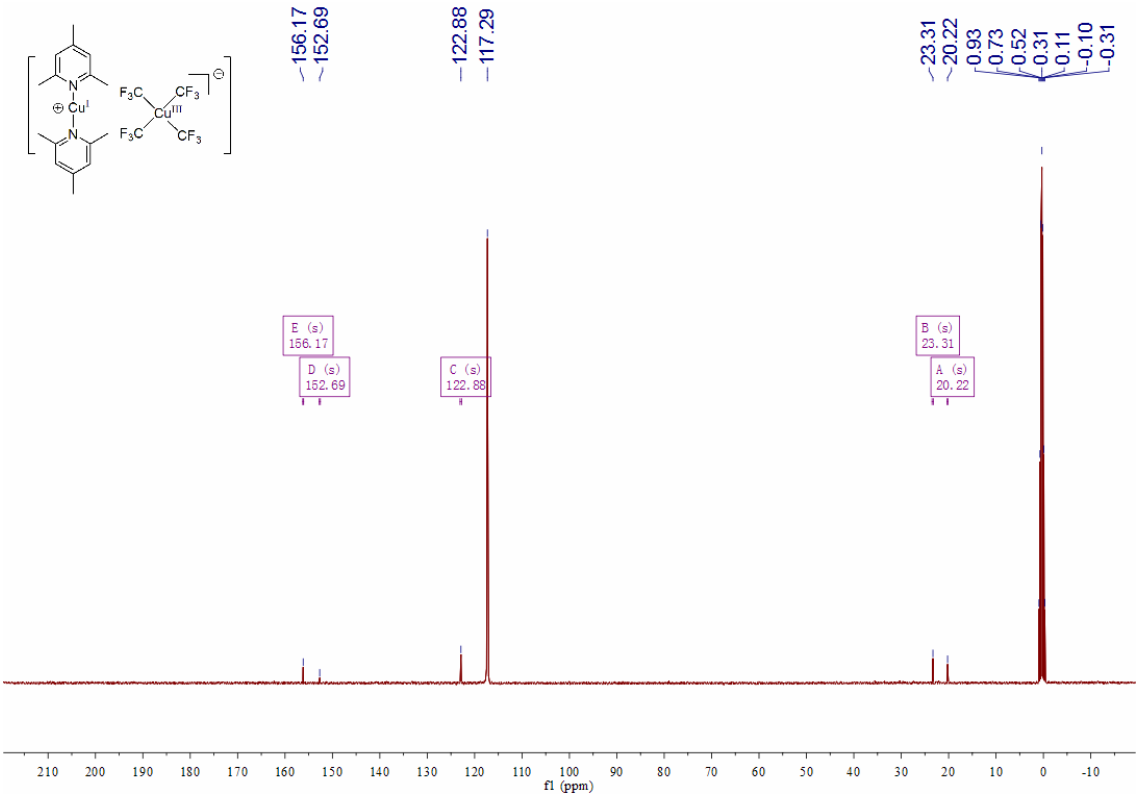
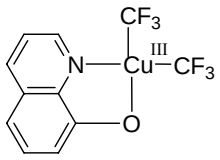


Figure S12. ^{13}C NMR (101 MHz, CD_3CN-d^3) of complex **8**. Peaks at ca 117 (singlet) and 0.3 (septet) ppm are resonances of residual CH_3CN.

(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 ^oC.



^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 5.2, 1.0 Hz, 1H), 8.48 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.61 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -26.74 (br s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 147.6, 143.2, 141.3, 131.3, 130.3, 121.8, 115.2, 114.2. MS (ES+): 208.0 (M-2CF_3), 100%; 146.1 (8-hydroxyquinoline), 28%. Anal. Cacld for $C_{11}H_6CuF_6NO$: 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 $C_{11}H_7CuF_6NO^+$ $(M+H)^+$ 345.97224, found 345.97202.

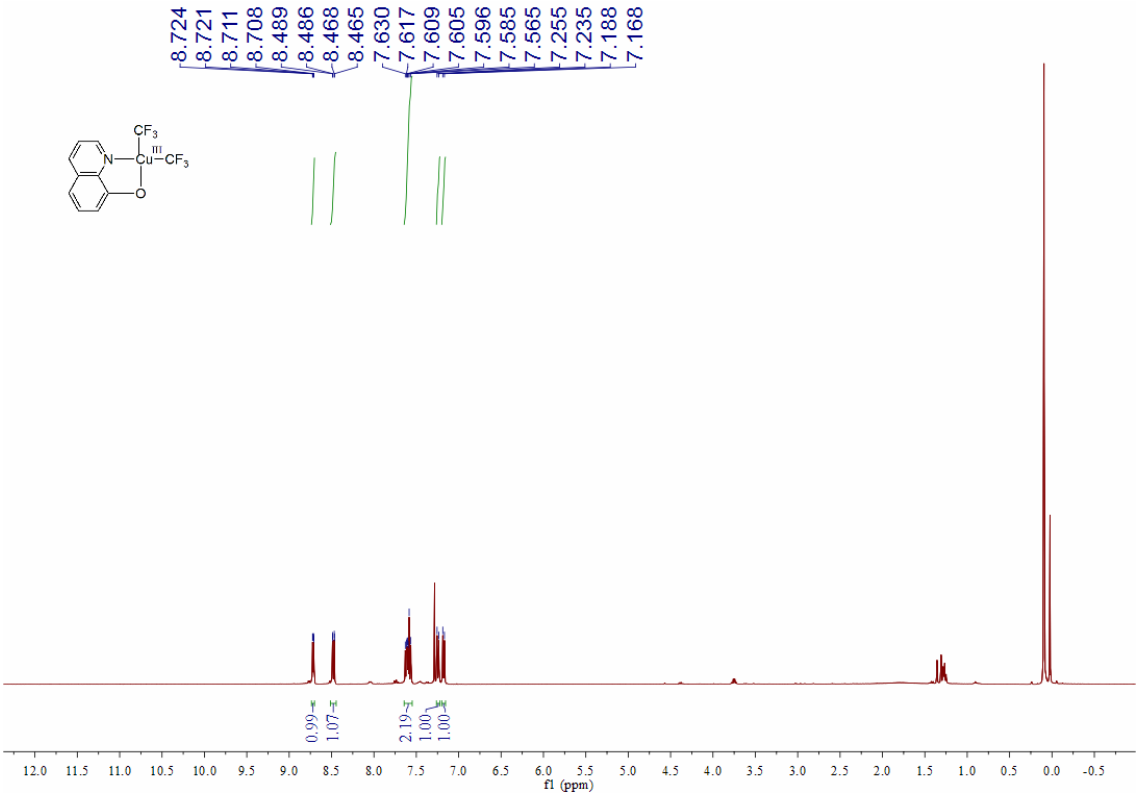


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of complex **9** at room temperature.

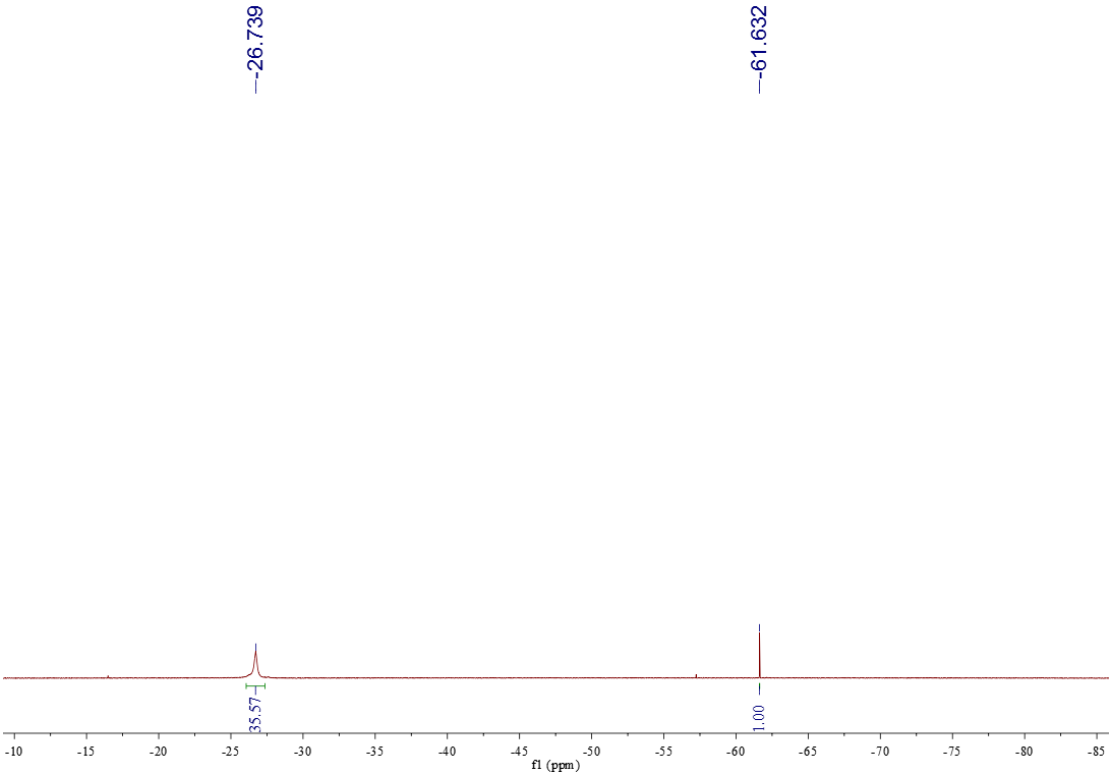


Figure S14. ^{19}F NMR (376 MHz, $CDCl_3$) of complex **9**. The peak at -61.6 ppm is assigned to be very minor C-H trifluoromethylation byproduct at room temperature.

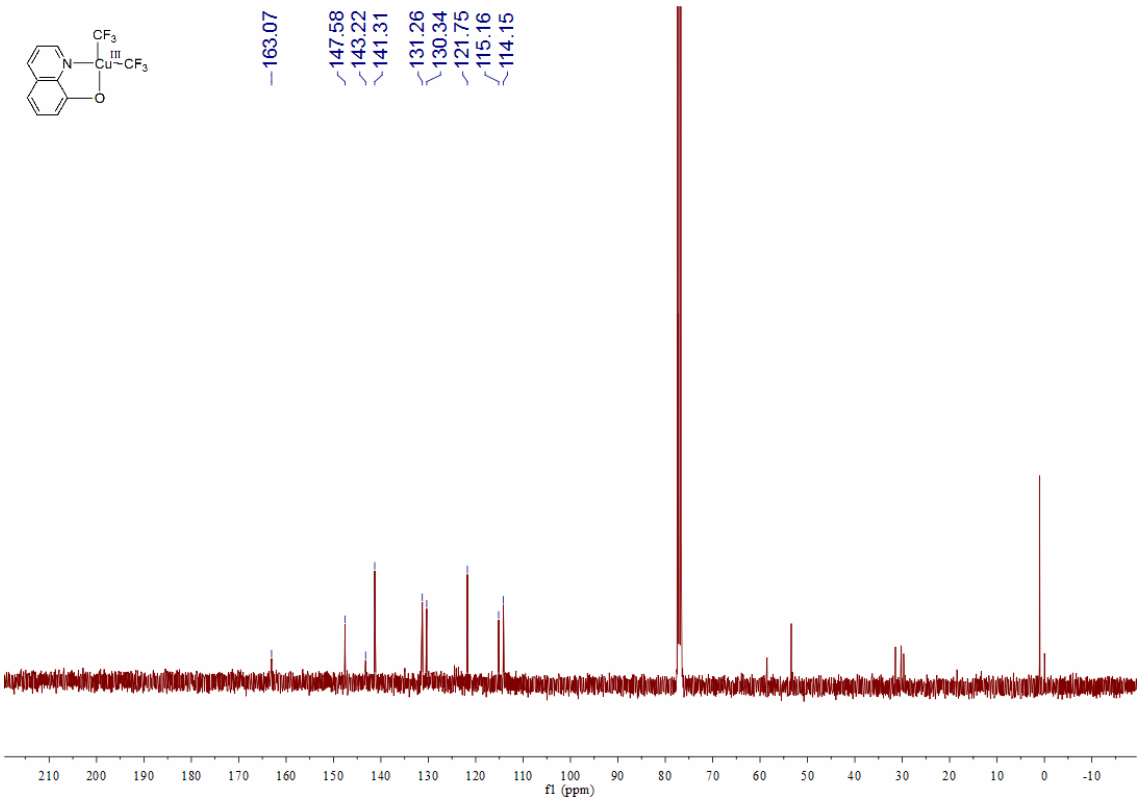
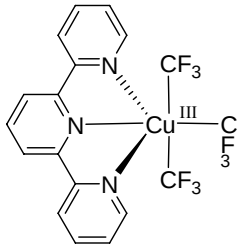


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) of complex **9** at room temperature.

(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%).



^{1}H NMR (400 MHz, DMSO-d^6) δ 9.08 (d, J = 4.4 Hz, 2H), 8.85 (d, J = 8.0 Hz, 2H), 8.74 (d, J = 8.1 Hz, 2H), 8.52 (t, J = 7.9 Hz, 1H), 8.28 (td, J = 7.9, 1.5 Hz, 2H), 7.87 (dd, J = 7.3, 5.0 Hz, 2H). ^{19}F NMR (376 MHz, DMSO-d^6) δ -25.20 (septet, J = 9.8 Hz), -34.57 (q, J = 9.8 Hz). ^{13}C NMR (101 MHz, DMSO-d^6) δ 151.61 (s), 149.40 (s), 148.80 (m), 142.36 (s), 139.76 (s), 127.03 (s), 124.51 (s), 123.22 (s). HRMS (ESI) m/z calcd for $C_{15}H_{11}CuN_3^+$ $(M\text{-}3CF_3)^+$ 296.02435, found 296.02426.

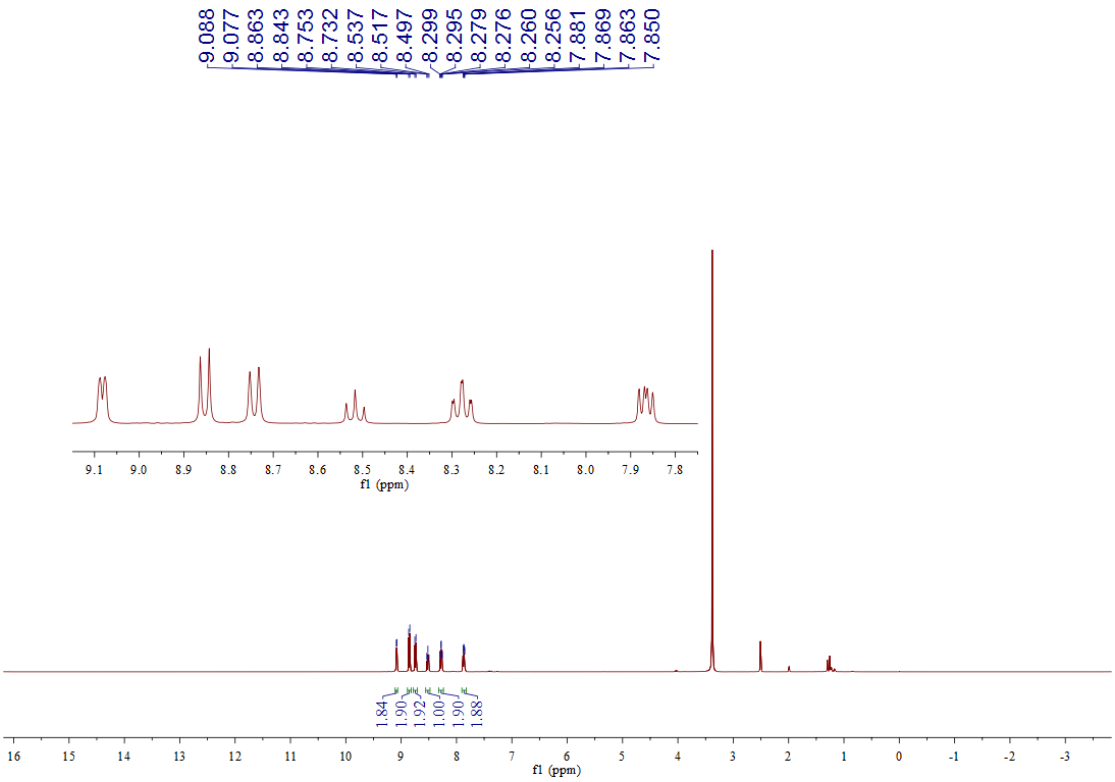


Figure S16. ^{1}H NMR (400 MHz, DMSO-d^{6}) of complex **10**.

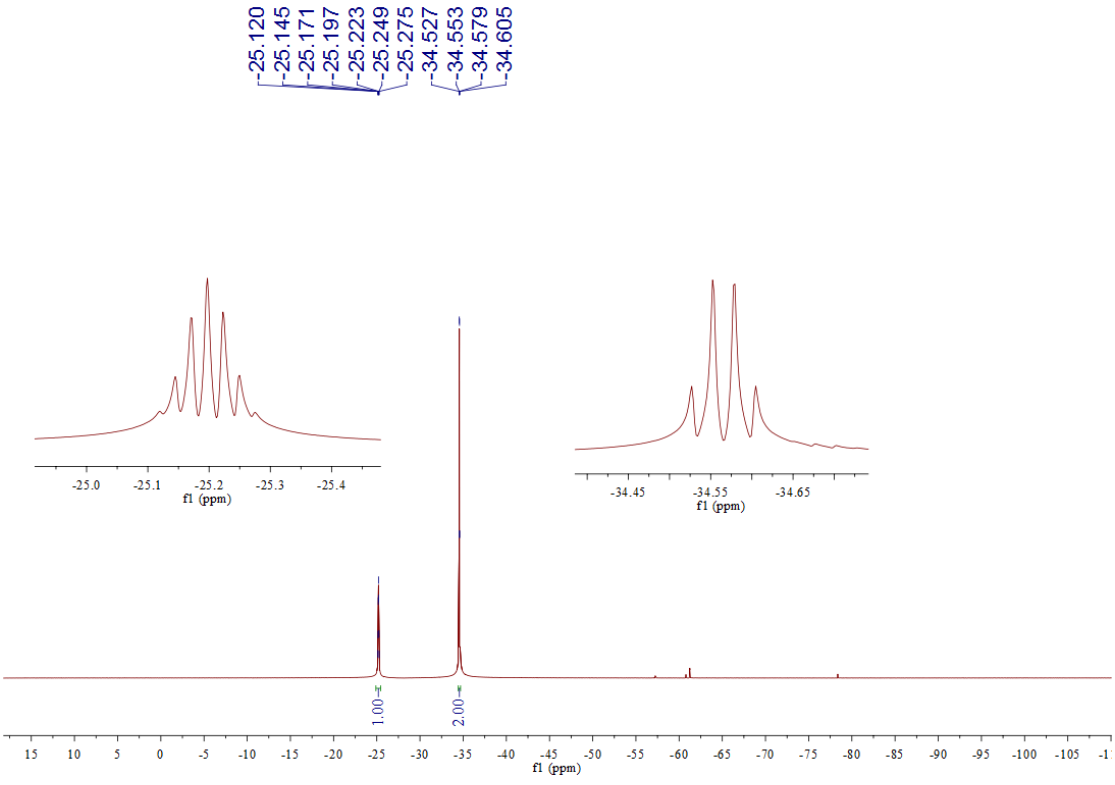


Figure S17. ^{19}F NMR (376 MHz, DMSO-d^{6}) of complex **10**.

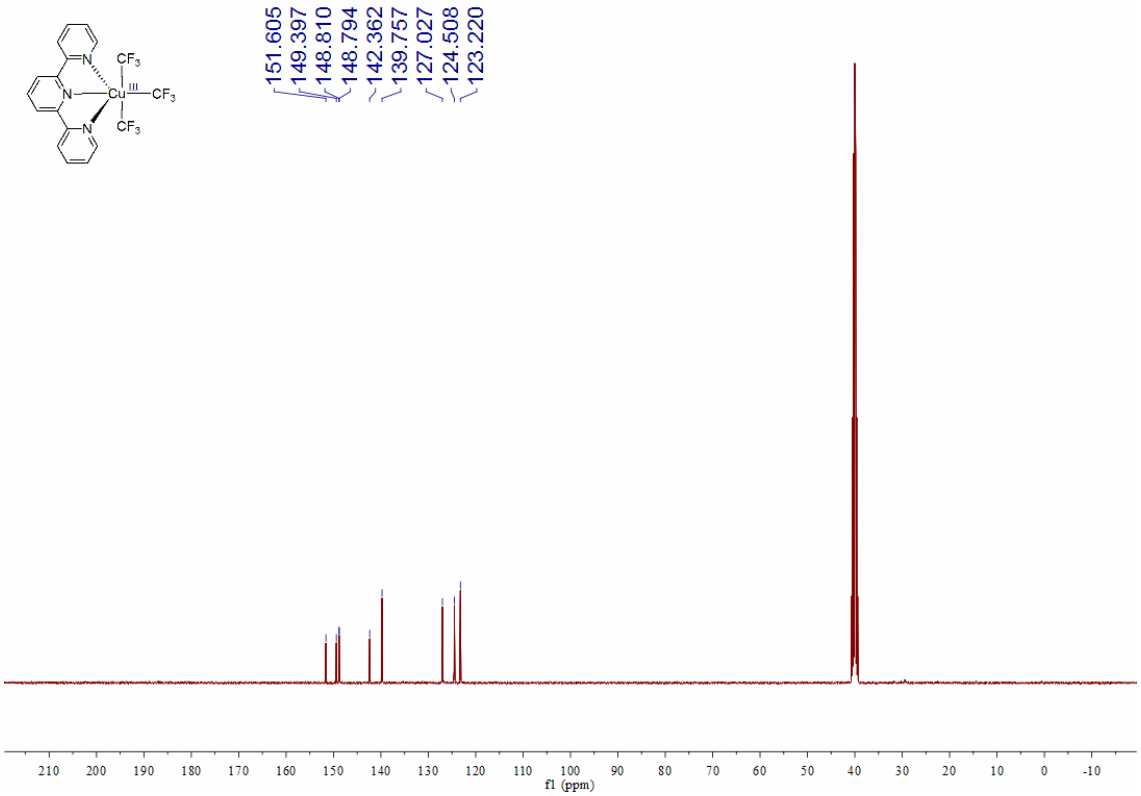


Figure S18. ^{13}C NMR (101 MHz, DMSO-d^6) of complex **10**.

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_2Cl_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***

$C_{11}H_{12}CuF_9N_2O$	complex 6•DMF
M_r = 422.77	D_x = 1.725 Mg m^{-3}
Orthorhombic, *Pnma*	Melting point: ? K
Hall symbol: ?	Mo *K*α radiation, λ = 0.71073 Å
a = 19.9959 (11) Å	Cell parameters from 3878 reflections
b = 8.1241 (5) Å	θ = 3.1–26.3°
c = 10.0188 (6) Å	μ = 1.44 mm^{-1}
V = 1627.54 (17) Å^3	*T* = 273 K
Z = 4	Block, yellow
F(000) = 840	0.30 × 0.25 × 0.20 mm

*Crystal data for **7***

$C_{11}H_{11}CuF_9N$	Complex 7
M_r = 391.75	D_x = 1.779 Mg m^{-3}
Orthorhombic, *Cmcm*	Melting point: ? K
Hall symbol: ?	Mo *K*α radiation, λ = 0.71073 Å
a = 8.4272 (4) Å	Cell parameters from 2912 reflections
b = 19.4683 (9) Å	θ = 4.0–27.1°
c = 8.9136 (4) Å	μ = 1.59 mm^{-1}

V = 1462.39 (12) Å^3	T = 273 K
Z = 4	Block, colorless
F(000) = 776	0.30 × 0.23 × 0.21 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_2O and filtered through a pad of Celite. The Celite pad was washed with Et_2O. 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.

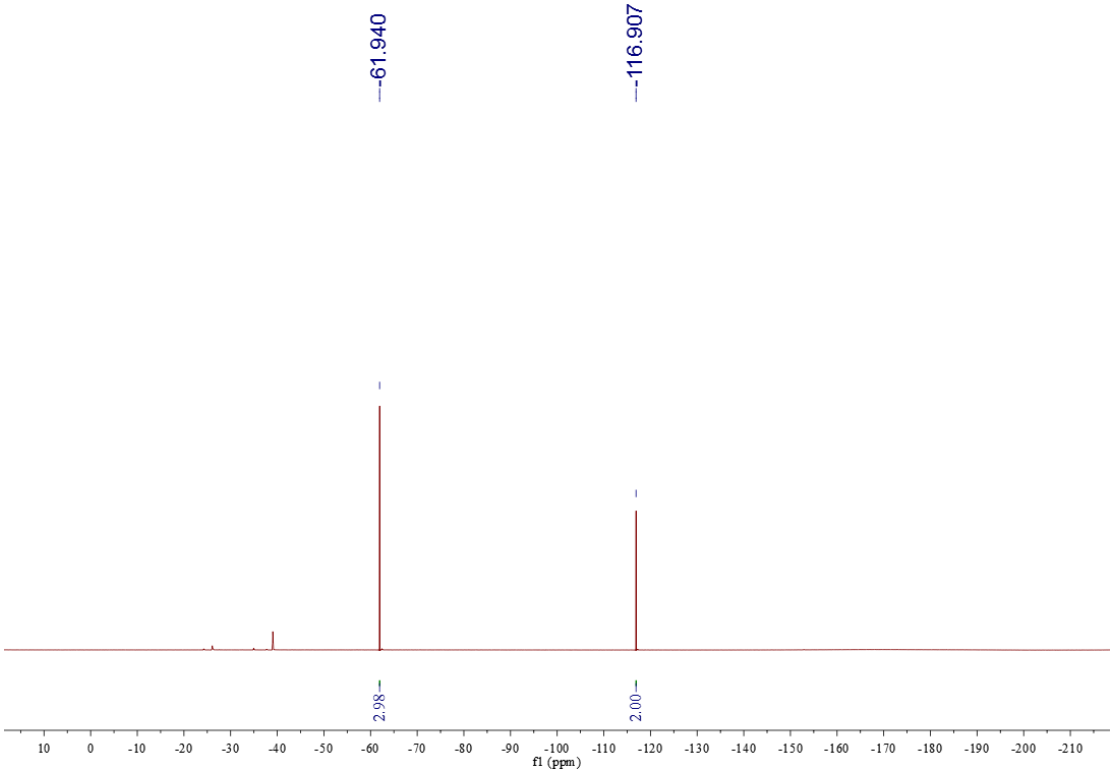


Figure S19. ^{19}F NMR determination of the reaction mixture of reaction of complex **6** with **11a** under the reaction conditions of entry 2 in Table 1.

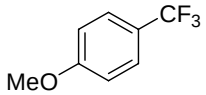
For example, Figure S19 shows the ^{19}F NMR determination of the reaction solution of entry 2 in Table 1 after workup described above. As can be seen, nearly

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 $PyCu(CF_3)_3$ (**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 ^oC for 6 hours. The mixture was allowed to cool to room temperature, diluted with Et_2O and filtered through a pad of Celite. The Celite pad was washed with Et_2O. 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.



12a (14 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.47 (s). ^{13}C NMR (101 MHz, $CDCl_3$) 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).

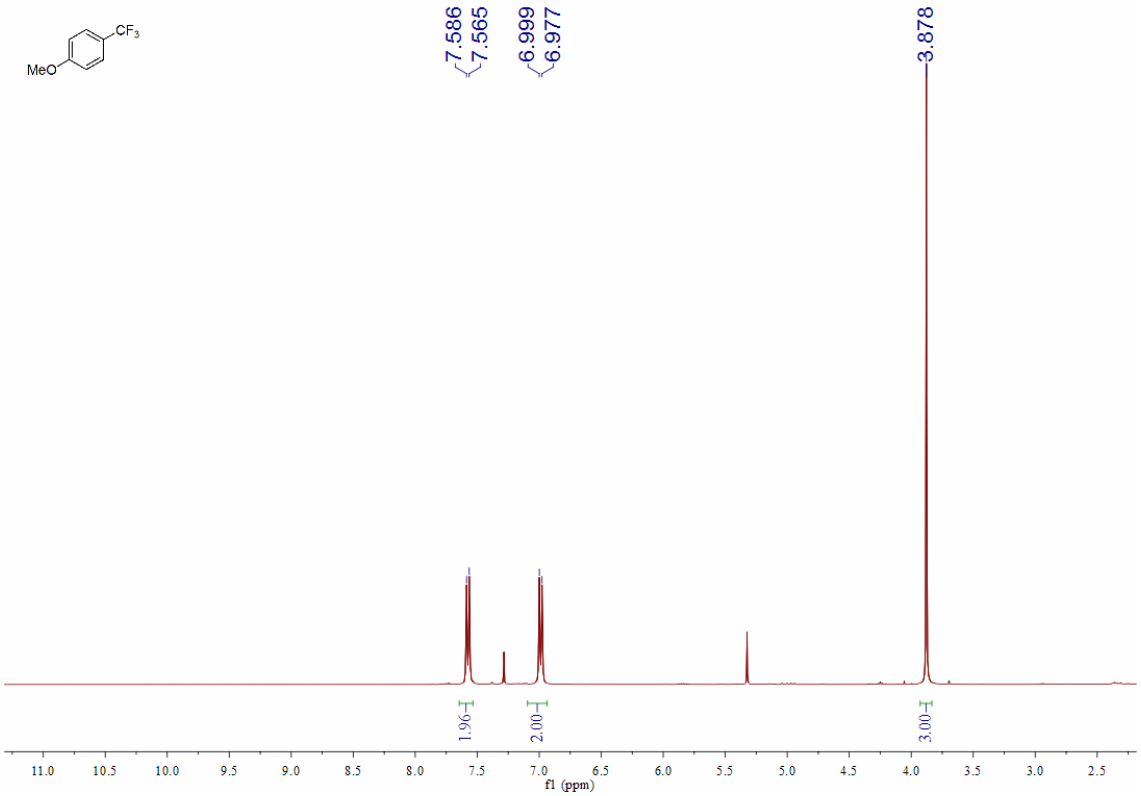


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of **12a**.

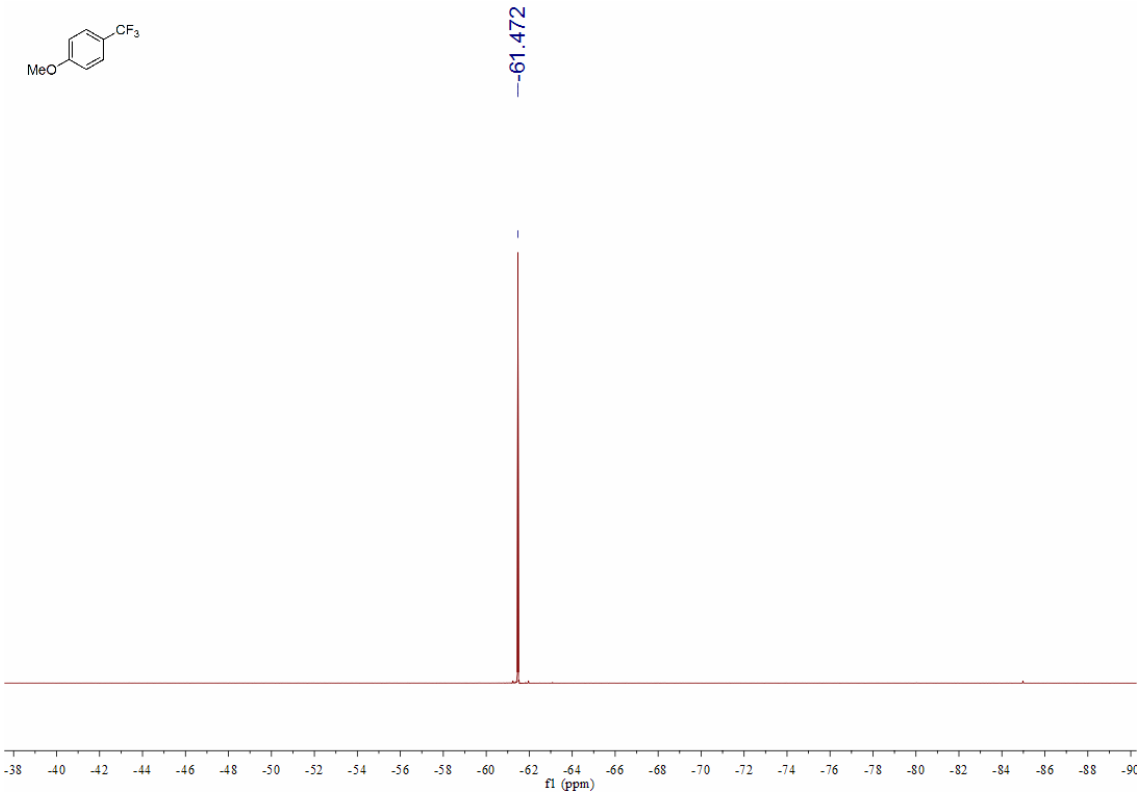


Figure S21. ^{19}F NMR (376 MHz, $CDCl_3$) of **12a**.

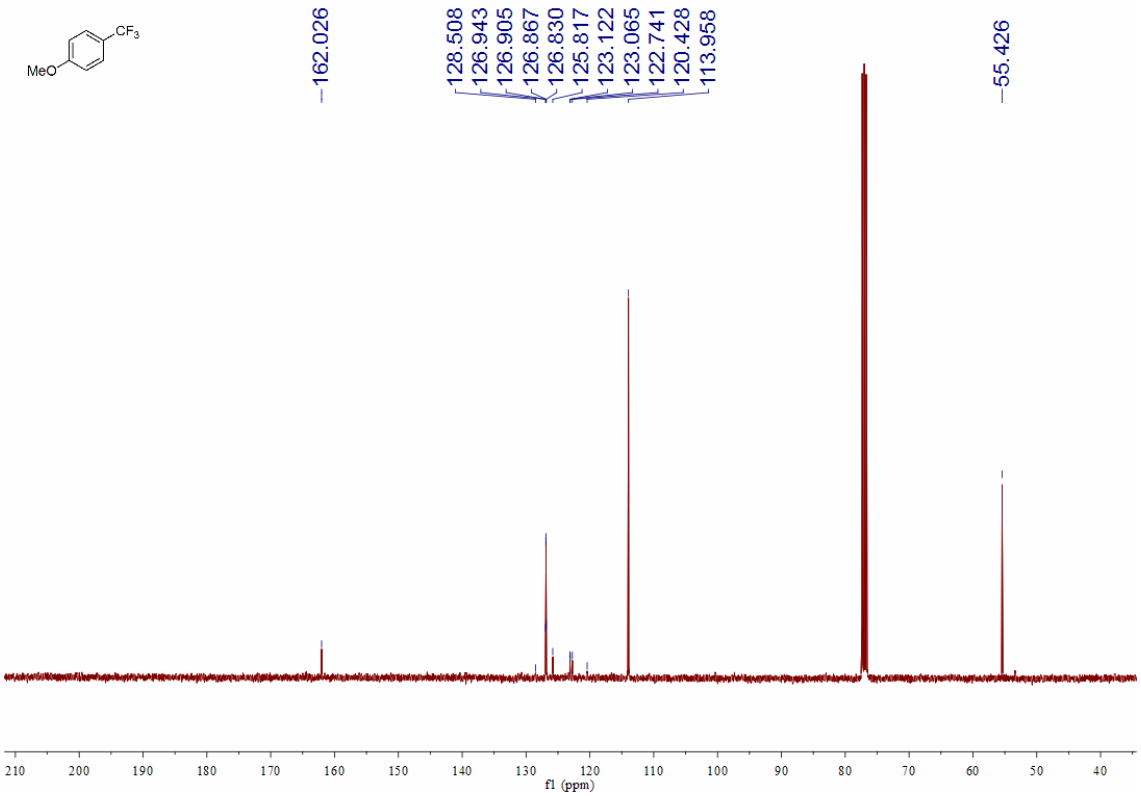
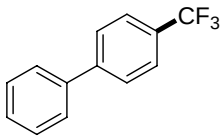


Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$) of **12a**.



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).

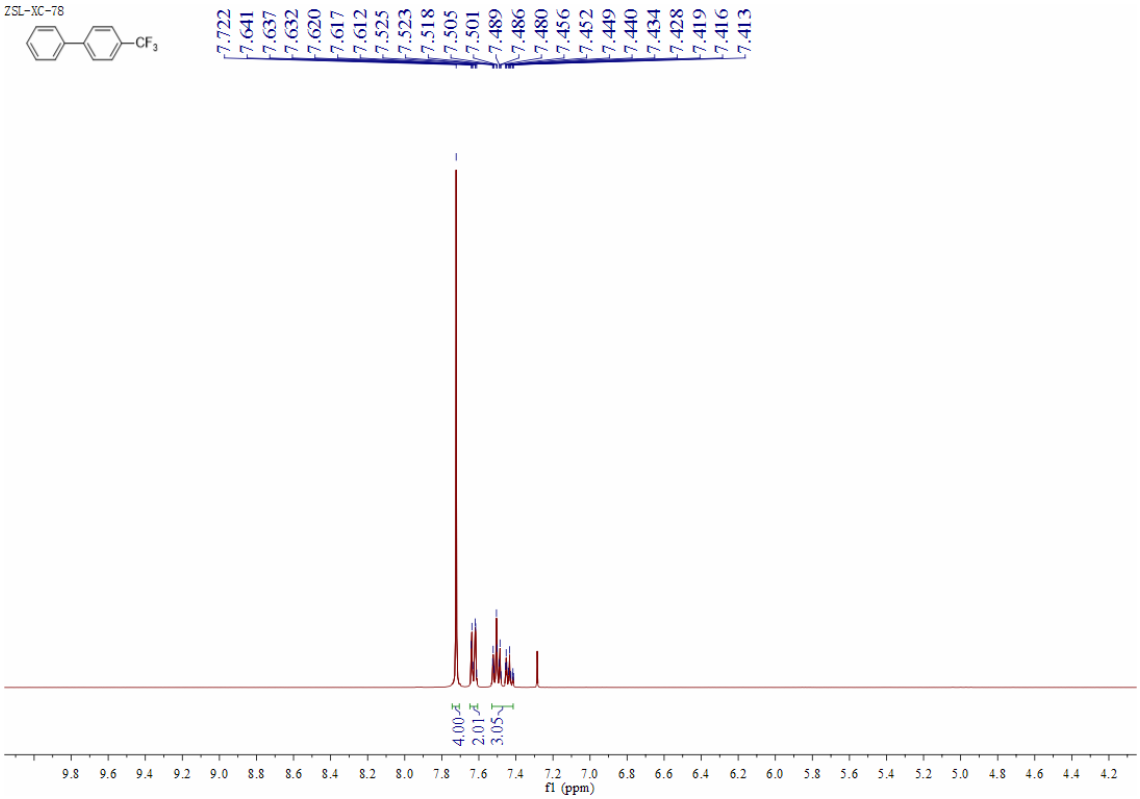


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of **12b**.

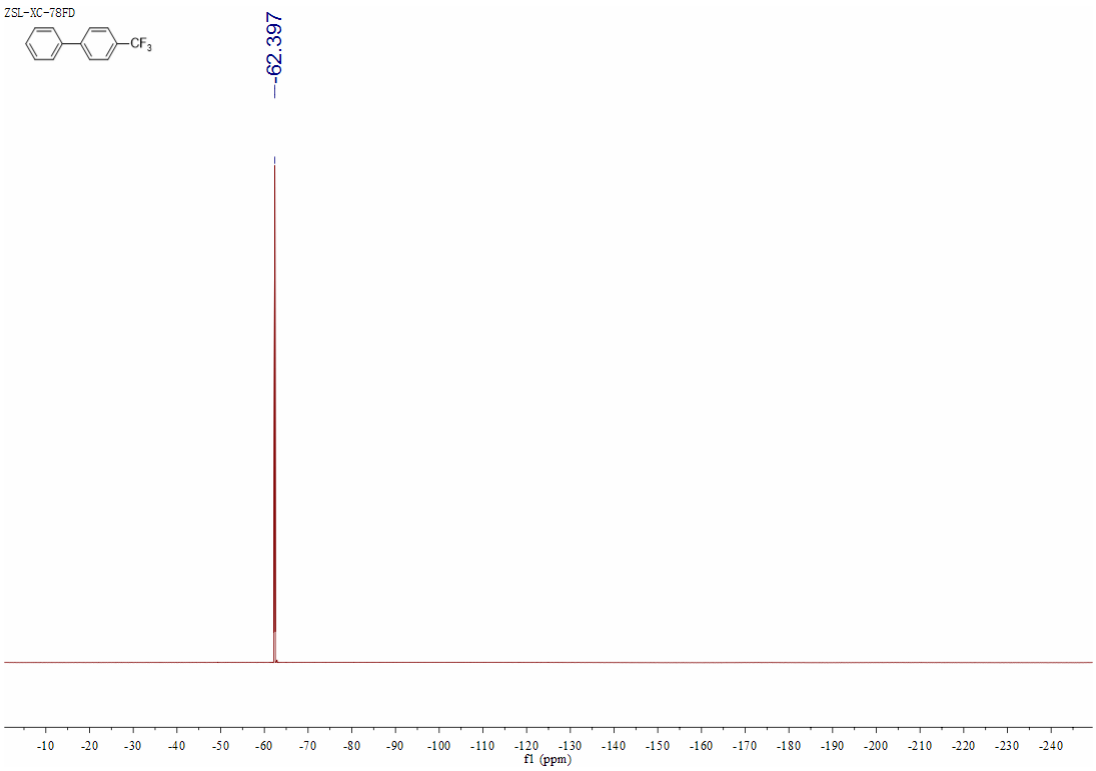
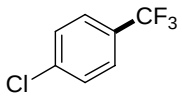


Figure S24. ^{19}F NMR (376 MHz, $CDCl_3$) of **12b**.



12c (22 mg, 61%). ^{1}H NMR (400 MHz, CDCl3) 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).

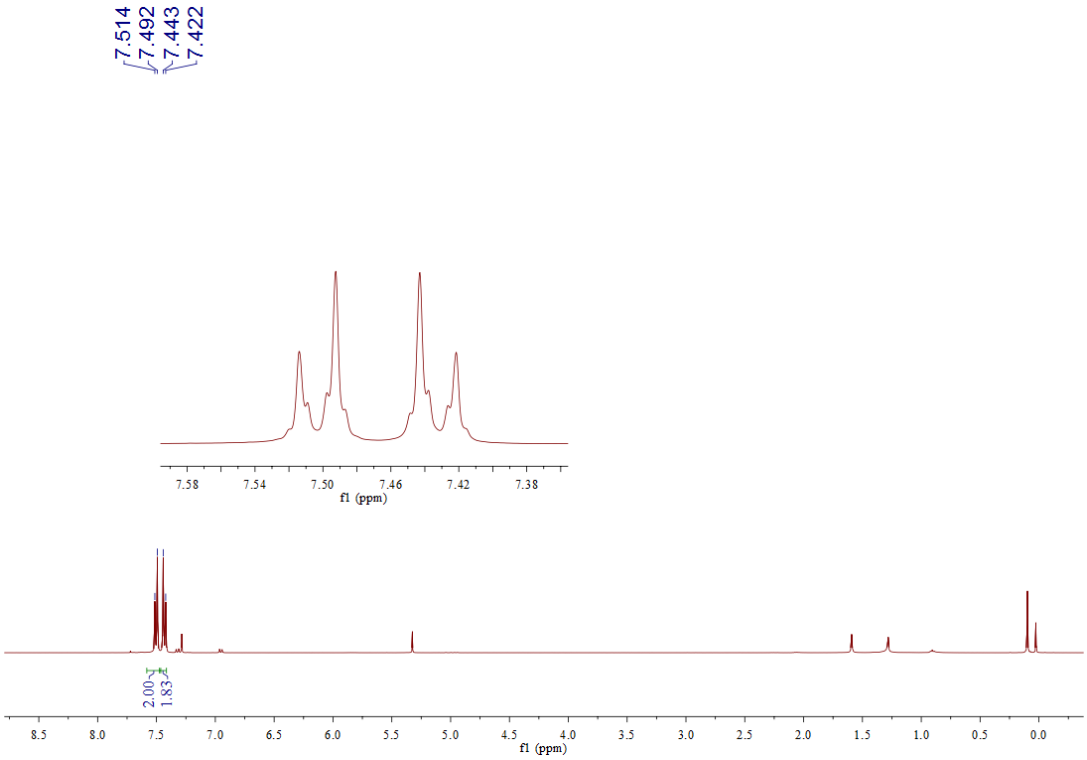


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of **12c**.

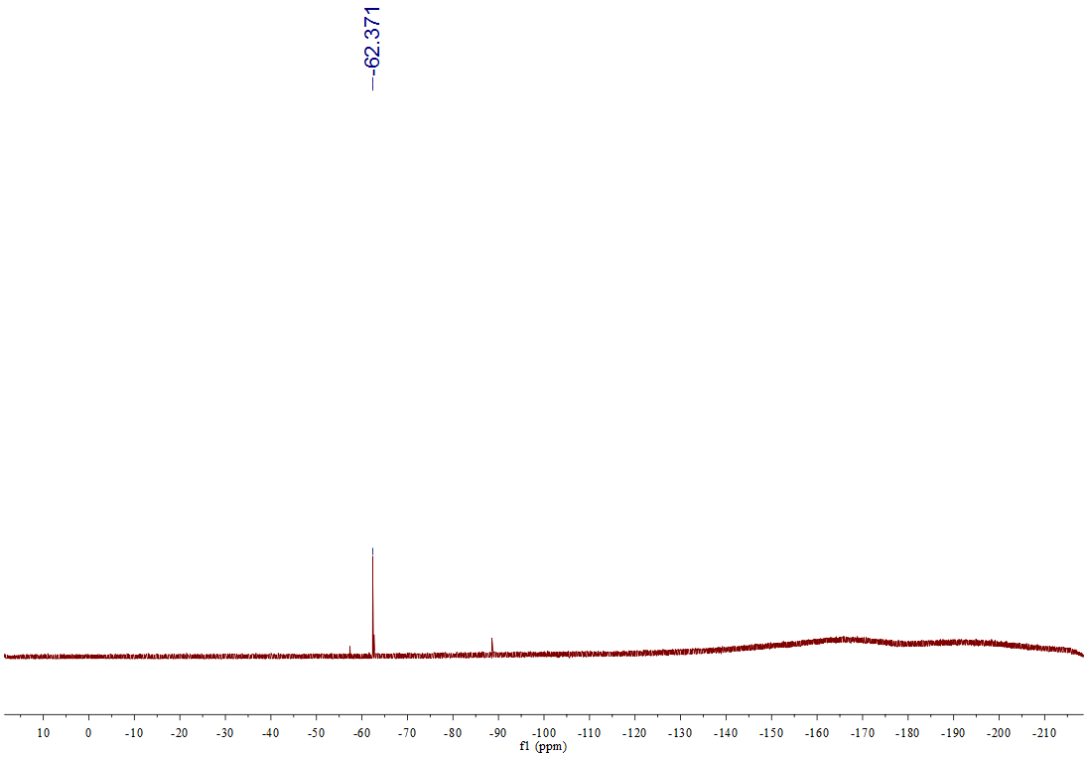
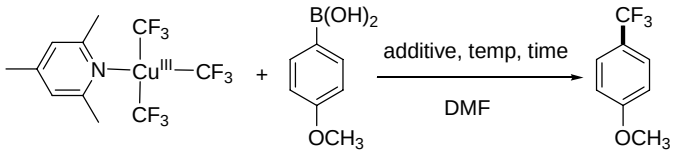


Figure S26. ^{19}F NMR (376 MHz, $CDCl_3$) of **12c**.

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_2O and filtered through a pad of Celite. The Celite pad was washed with Et_2O. 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 [a]



7 (0.1 mmol) **11a** (0.2 mmol) **12a**

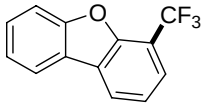
entry	additive	temp (^{o}C)	time (h)	yield (%) [b]
1	—	80	6	72
2	—	80	6	67 [c]
3	—	80	6	99 [d]
4	KF	80	6	99
5	KF	80	6	99 [e]

[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^{o}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 Et2O. 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, CDCl3) δ 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, CDCl3) δ -61.05 (s).

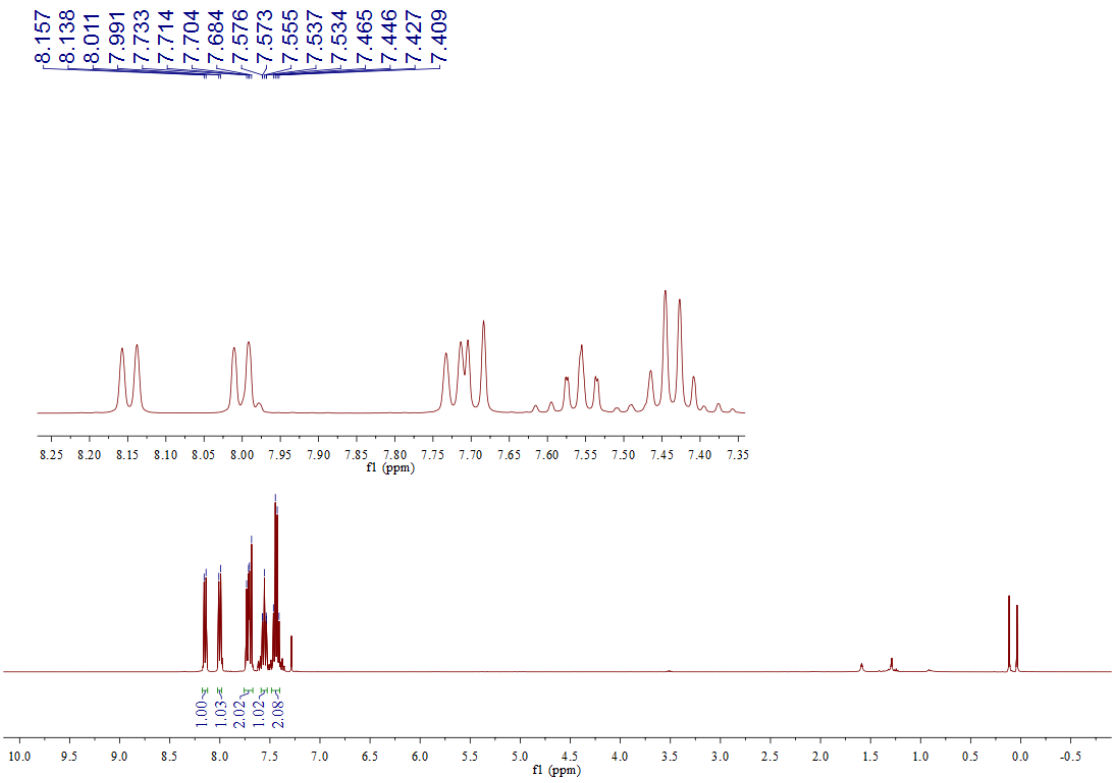


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of **12q**.

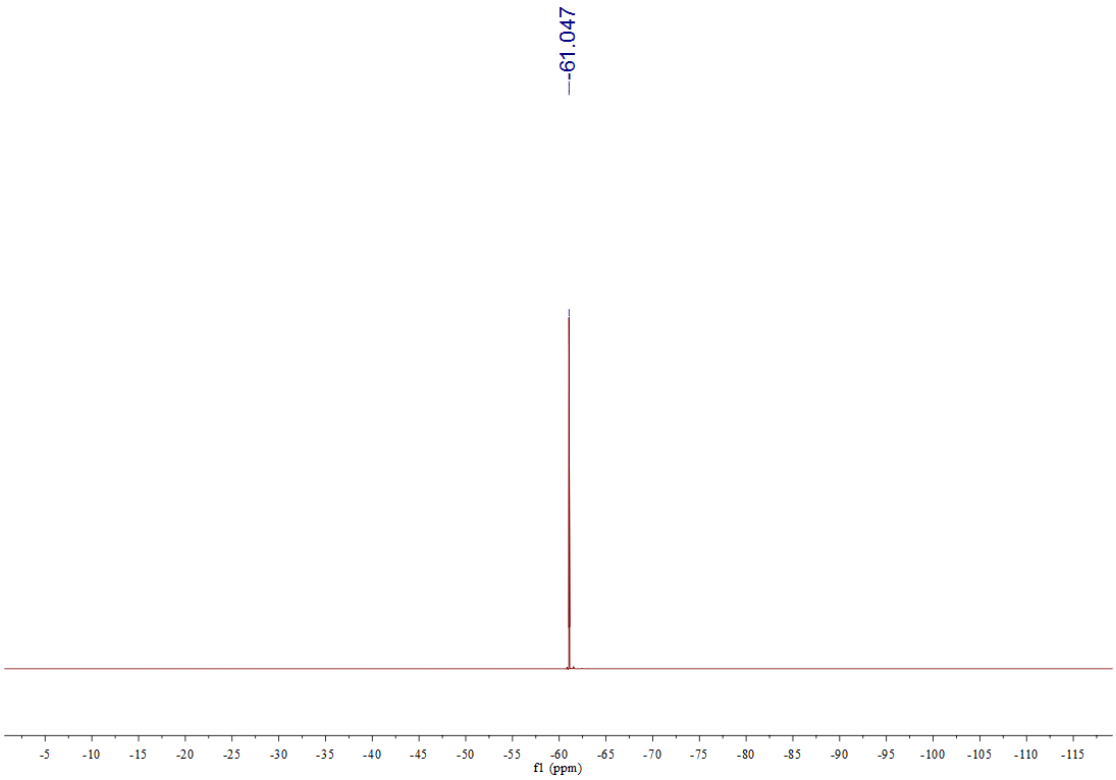
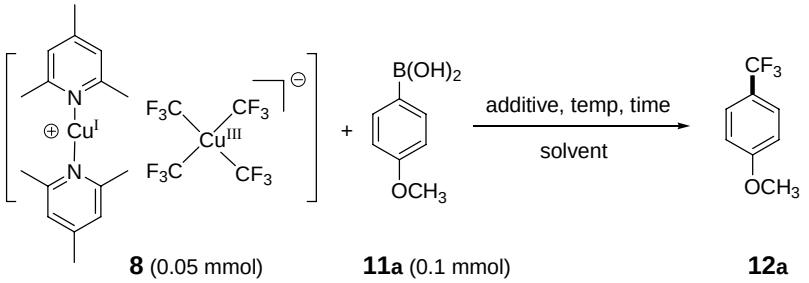


Figure S28. ^{19}F NMR (376 MHz, $CDCl_3$) of **12q**.

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_2O and filtered through a pad of Celite. The Celite pad was washed with Et_2O. 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 [a]



8 (0.05 mmol) **11a** (0.1 mmol) **12a**

entry	*additive*	*solvent*	*temp (°C)*	*time (h)*	*yield (%)* [b]
1	—	DMF	80	6	31 (in air)
2	—	DMF	100	6	23 (in air)
3	—	DMF	100	6	27 (in air)
4	KF	DMF	100	6	24
5	KF	DMF	80	18	25
6	KF	Toluene	80	18	15

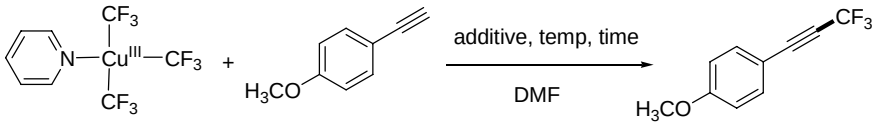
[a] Reaction conditions: **8** (0.05 mmol), **11a** (0.1 mmol), additive (0.1 mmol), 4,4′-difluorobiphenyl (0.1 mmol, internal standard), DMF (1 mL), under dry oxygen atmosphere. [b] Yields determined by ^{19}F NMR spectroscopy based on **11a**.

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 $PyCu(CF_3)_3$ (**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 CH_2Cl_2 and filtered through a pad of Celite. The Celite pad was washed with CH_2Cl_2. 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 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 [a]



6 (0.1 mmol) **13a** (0.1 mmol) **14a**

Entry	Additive	T (^oC)	Time (h)	Yield (%) [b]
1	—	100	1	10
2	CsF	100	1	92 [c]
3	CsF	100	1	53
4	KF	100	0.5	47
5	KF	100	1	87
6	KF	100	8	77
7	KF	100	8	99 [d]
8	KF	100	1	59 (in O2)
9	AgF	100	8	72
10	NaO*t*Bu	100	1	99
11	NaO*t*Bu	100	12	99
12	CH_3ONa	100	8	50
13	NH_4F	100	8	Trace [e]
14	NaF	100	8	30 [f]
15	C_2H_5ONa	100	8	Cplx.mix. [g]

[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 N_2 atmosphere. [b] Yields determined by ^{19}F

NMR spectroscopy based on **13a**. [c] CsF (0.5 mmol). [d] KF (0.5 mmol). [e] NH_4F (0.5 mmol). [f] NaF (0.5 mmol). [g] C_2H_5ONa (0.5 mmol).

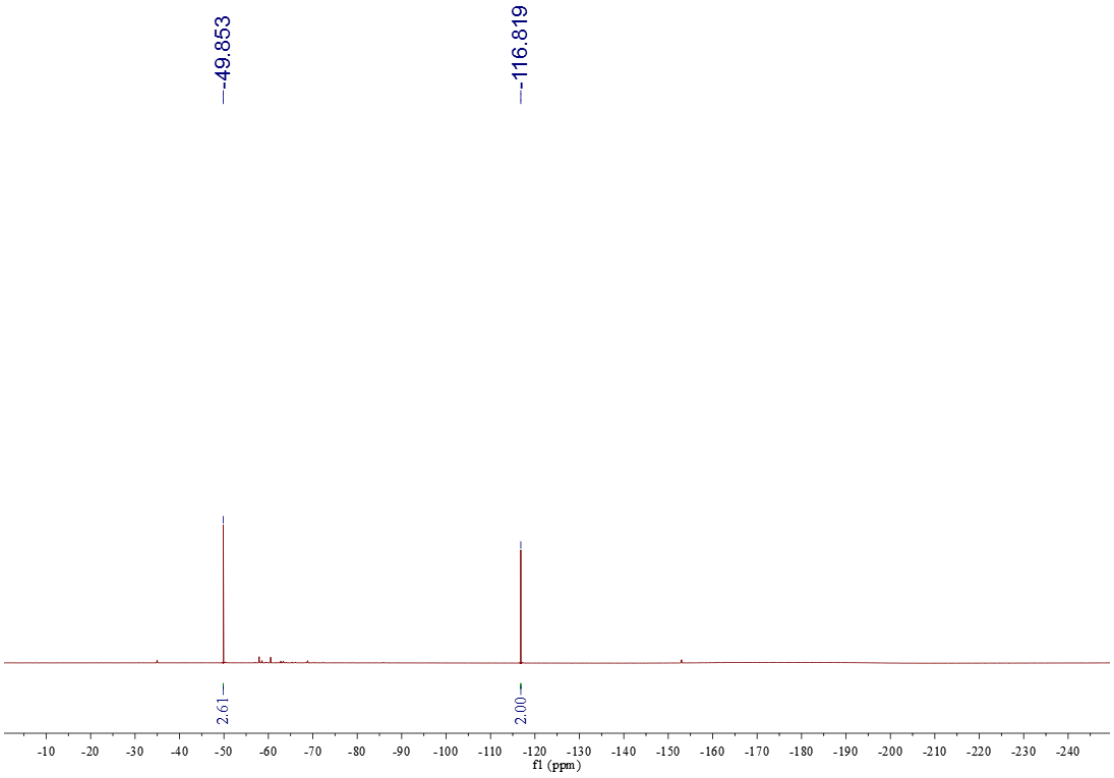
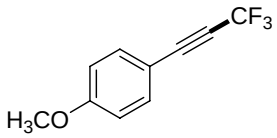


Figure S29. ^{19}F NMR determination of the reaction mixture of reaction of **6** with **13a**.

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 $PyCu(CF_3)_3$ (**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 ^oC 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 CH_2Cl_2. 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 **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, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -49.40 (s). ^{13}C NMR (101 MHz, $CDCl_3$) 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).

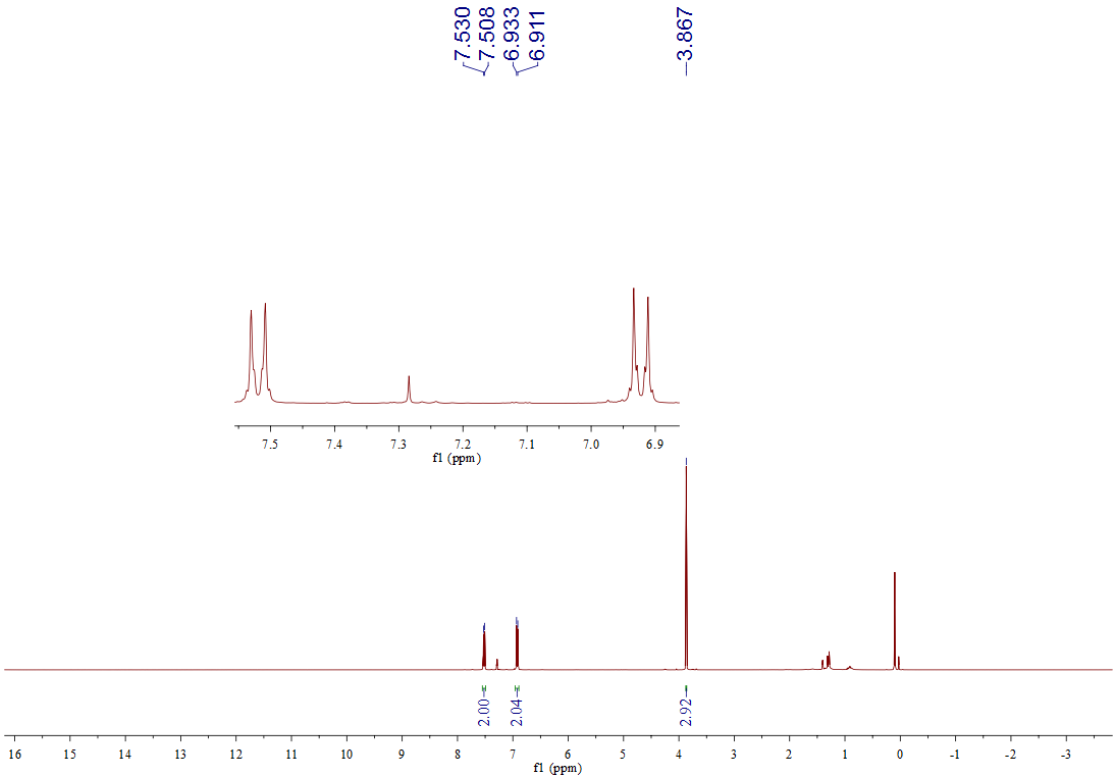


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of **14a**.

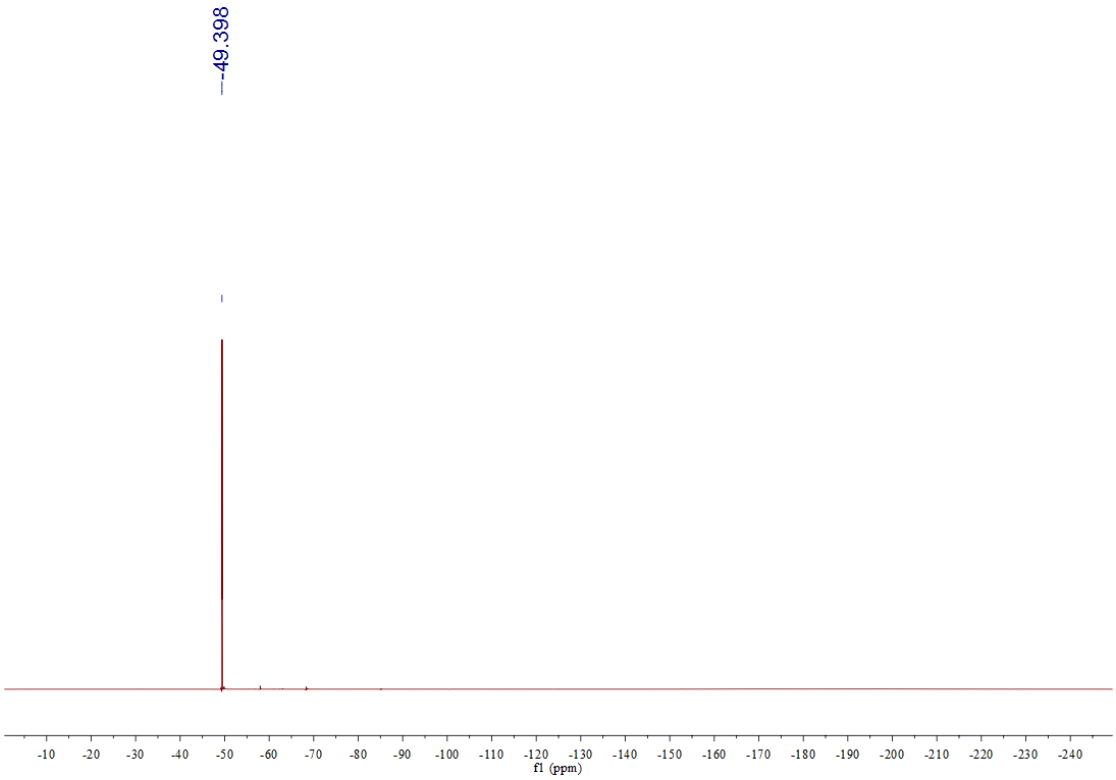


Figure S31. ^{19}F NMR (376 MHz, $CDCl_3$) of **14a**.

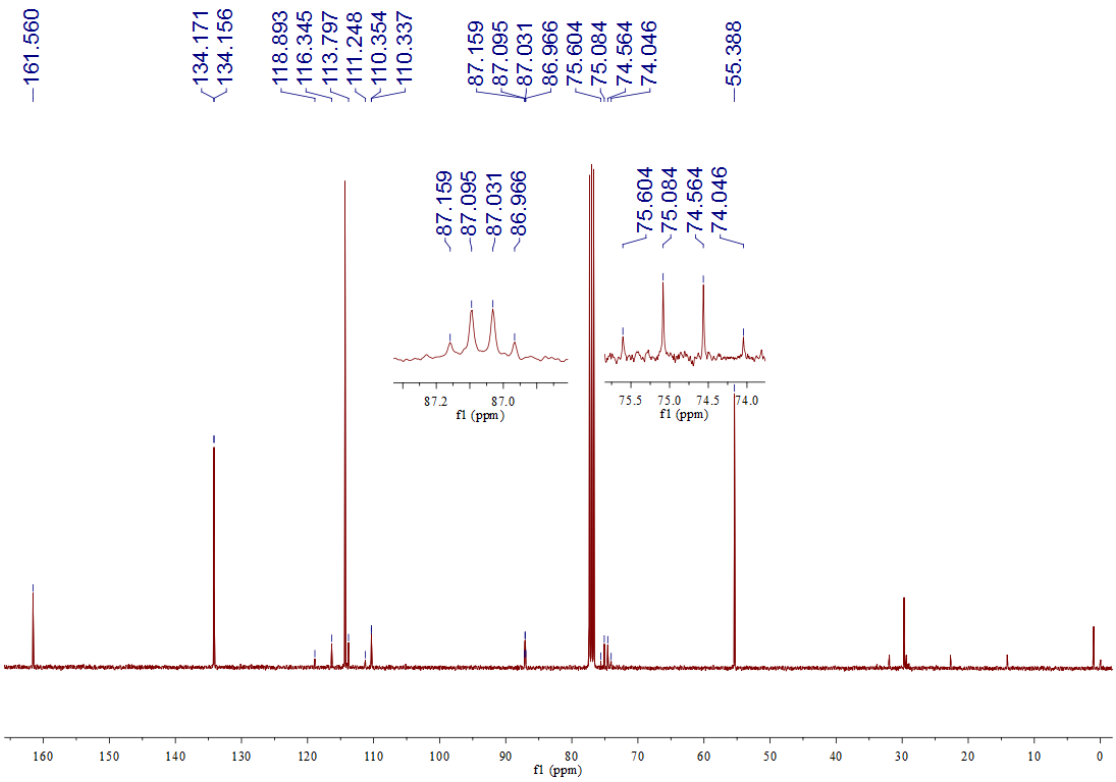
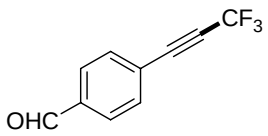


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) of **14a**.



1**4b** (13 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ -50.31 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 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).

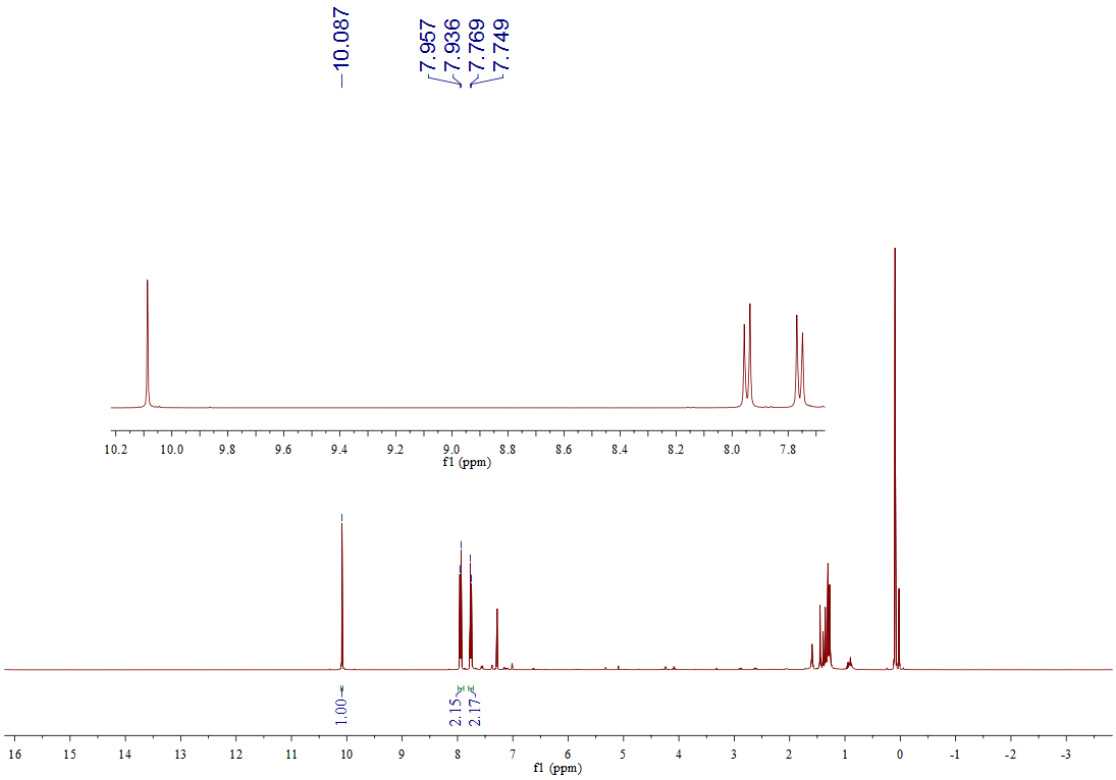


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of **14b**.

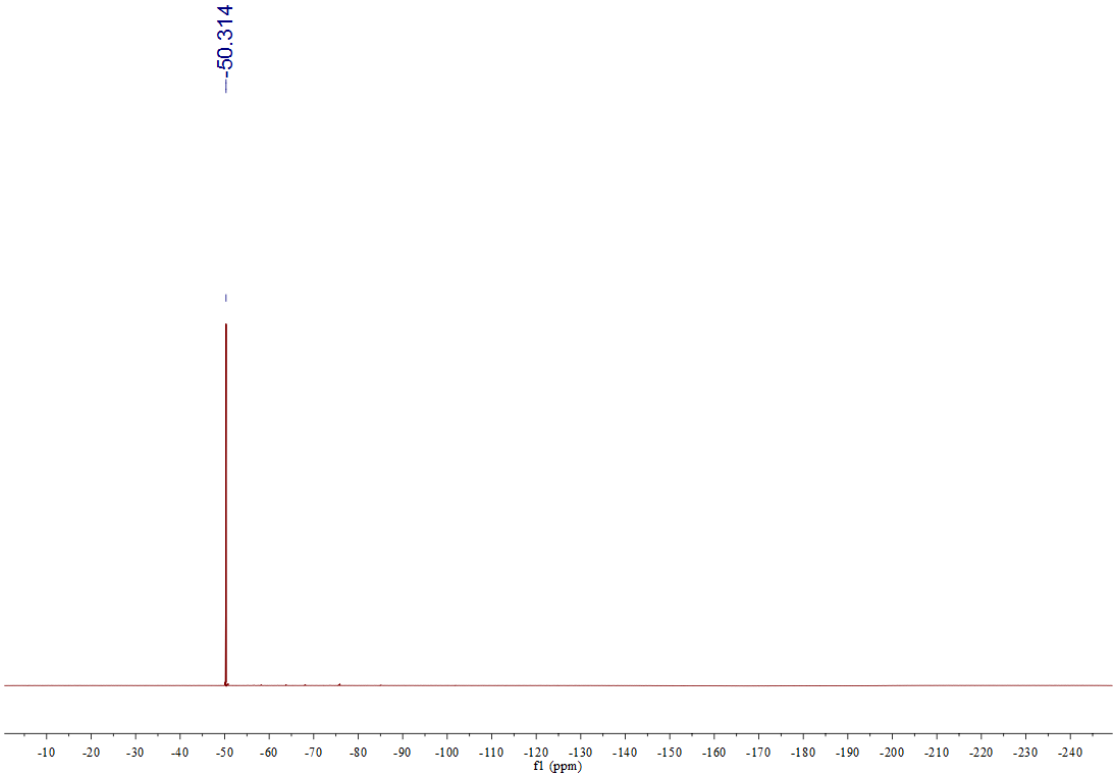


Figure S34. ^{19}F NMR (376 MHz, $CDCl_3$) of **14b**.

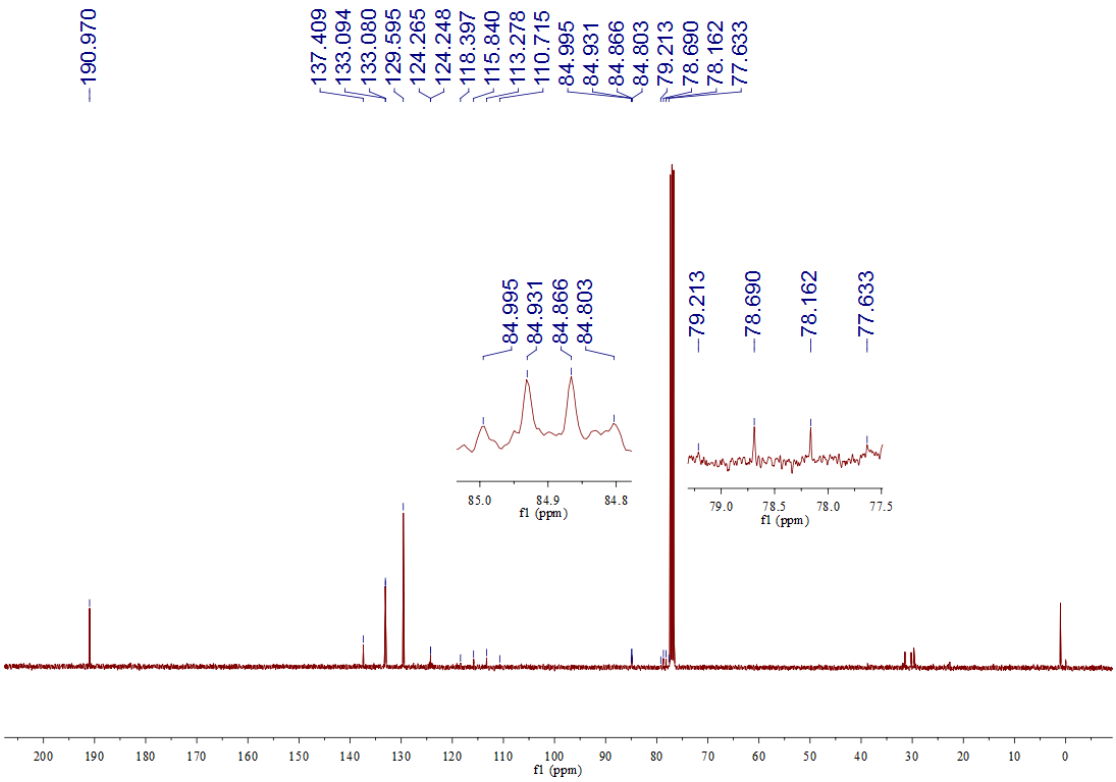
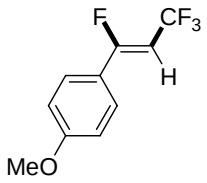


Figure S35. ^{13}C NMR (101 MHz, $CDCl_3$) of **14b**.

6. *syn*-Fluoro- and -oxy-trifluoromethylation of arylacetylenes

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added $PyCu(CF_3)_3$ (**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 ^oC 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 CH_2Cl_2. 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**.



15a (12 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$) 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, $CDCl_3$) δ -56.62 (d, *J* = 16.4 Hz, 3F), -102.23 (q, *J* = 16.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) 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).

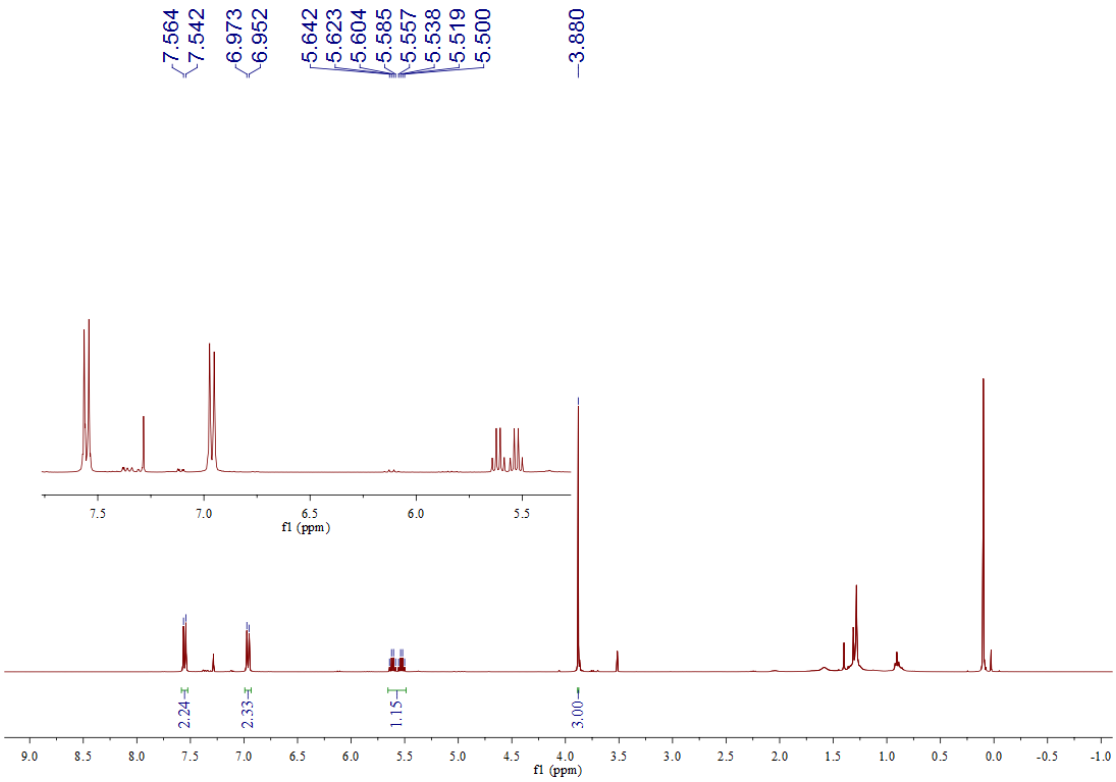


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of **15a**.

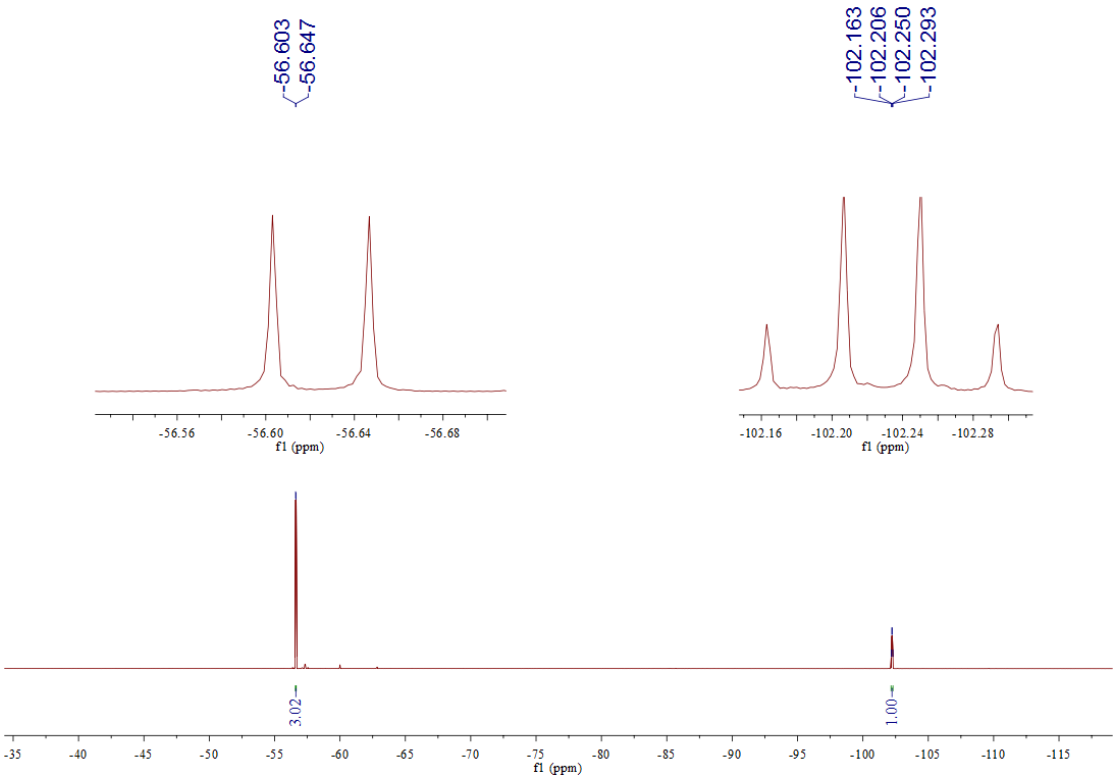


Figure S37. ^{19}F NMR (376 MHz, $CDCl_3$) of **15a**.

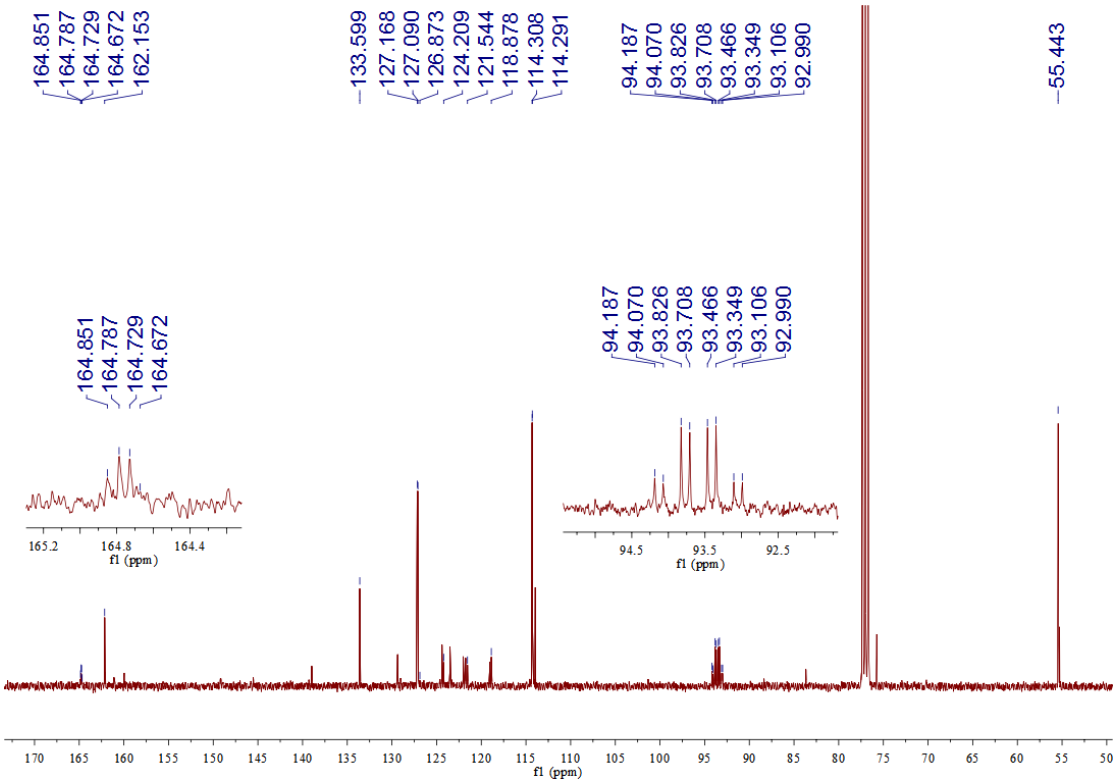
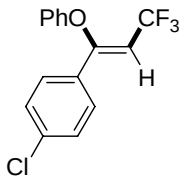


Figure S38. ^{13}C NMR (101 MHz, $CDCl_3$) of **15a**.



16a (18 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ -57.83 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 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).

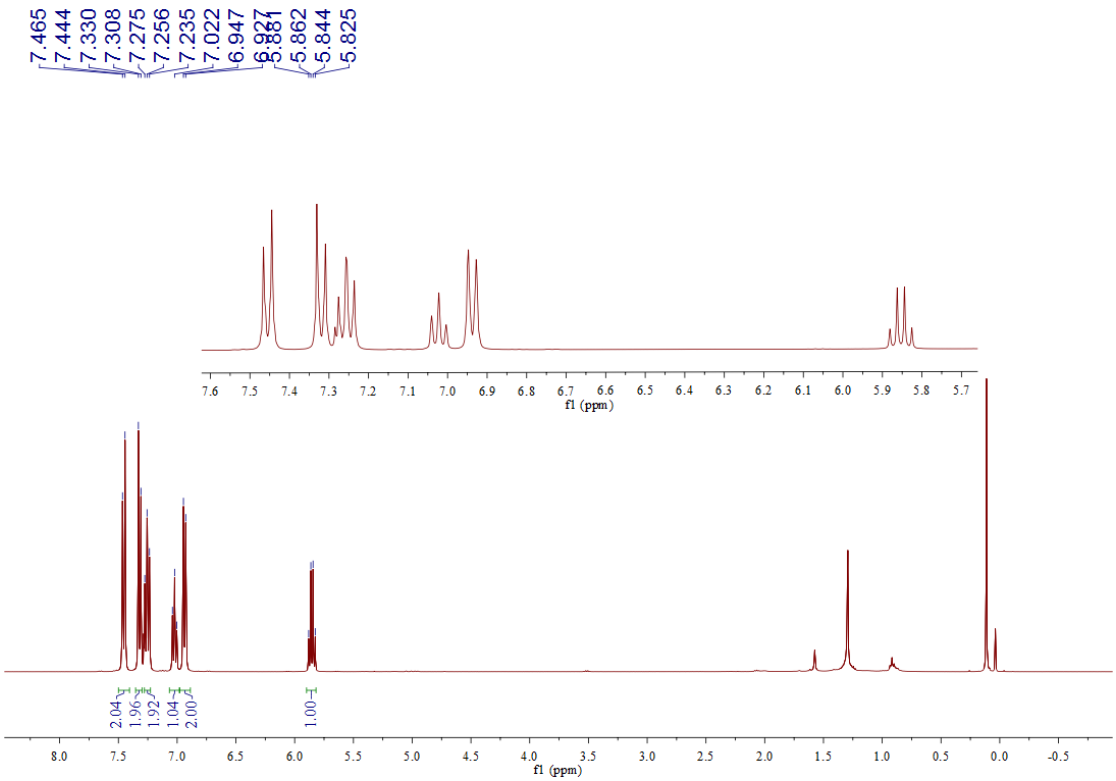


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of **16a**.

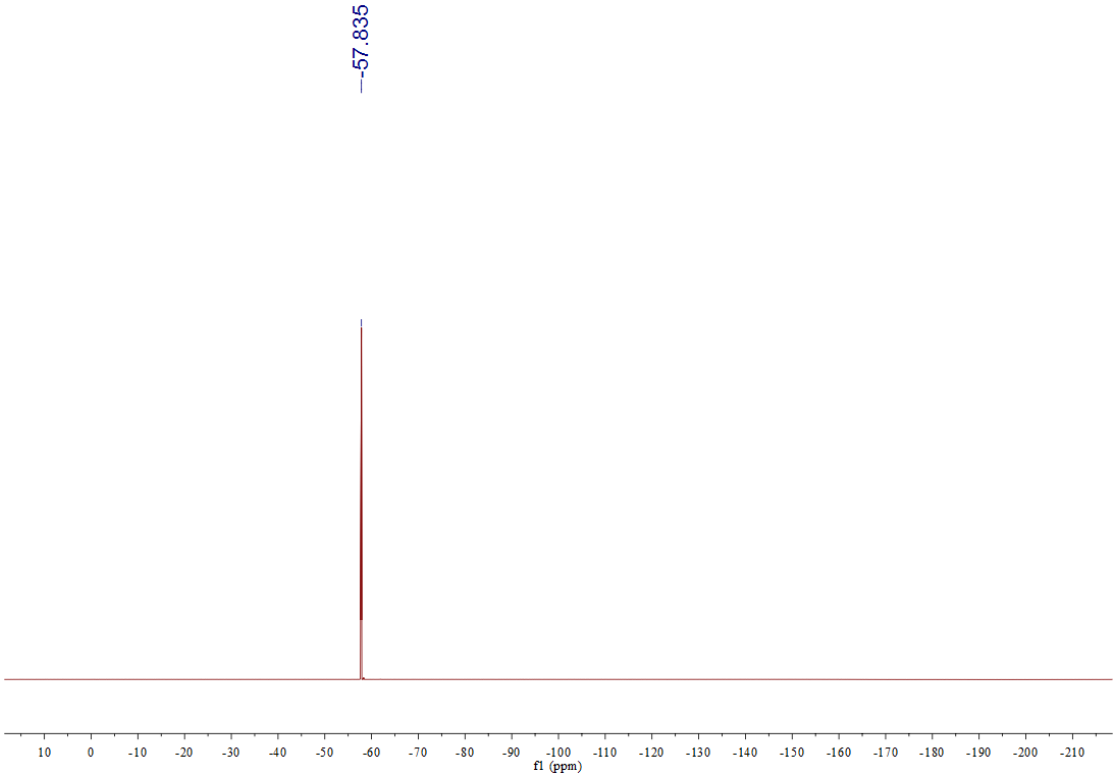


Figure S40. ^{19}F NMR (376 MHz, $CDCl_3$) of **16a**.

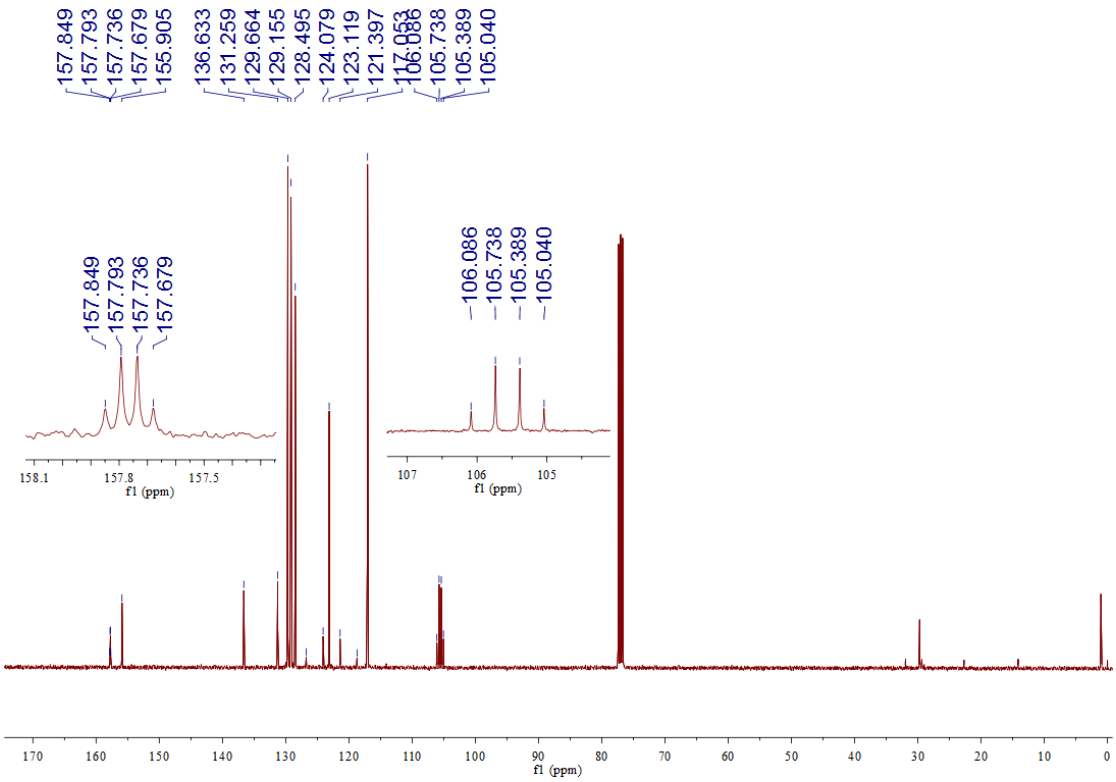


Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$) of **16a**.