Electronic Supplementary Information for

Isolation of OH-bridged Ag(I)/Cu(III) and ion-pair Cu(I)/Cu(III) trifluoromethyl complexes with monophosphines

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1. General experimental details

All chemicals and reactants were used as received without further purification. All the reactions were performed in a Schlenk tube under N_2 or O_2 atmosphere which was realized through evacuation/back-fill techniques after three times. For reactions involving AgF, a tinfoil was used to wrap the Schlenk tube to avoid the interference of visible light. 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. Coupling constants are reported in Hertz. 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. FT-IR spectra were recorded on an IRTracer-100 spectrometer.

2. The synthetic procedures, isolation and characterization of complexes 1-4

$(PPh_3)_2CuCl$ (1)

This compound was prepared according to the reported procedure (Vicic, D. A. et al. *Chem. Eur. J.* **2016**, *22*, 858-863). To a solution of CuCl (198 mg, 2.0 mmol) in acetonitrile (10 mL) was added Ph_3P (1049 mg, 4.0 mmol). The reaction mixture was stirred under N_2 atmosphere at room temperature for 12 h. Then the solvent acetonitrile was removed under reduced pressure. The residue was washed by ether and pentane successively to furnish $(PPh_3)_2CuCl$ (946 mg, 76% yield) as a white powder. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (br s, 2H), 7.35 (t, J = 6.8 Hz, 1H), 7.25

(t, J = 7.2 Hz, 2H). HRMS (ESI) m/z calcd for $C_{36}H_{30}CuP_2^+$ (cation part)$^+$ 587.1113, found 587.1111.

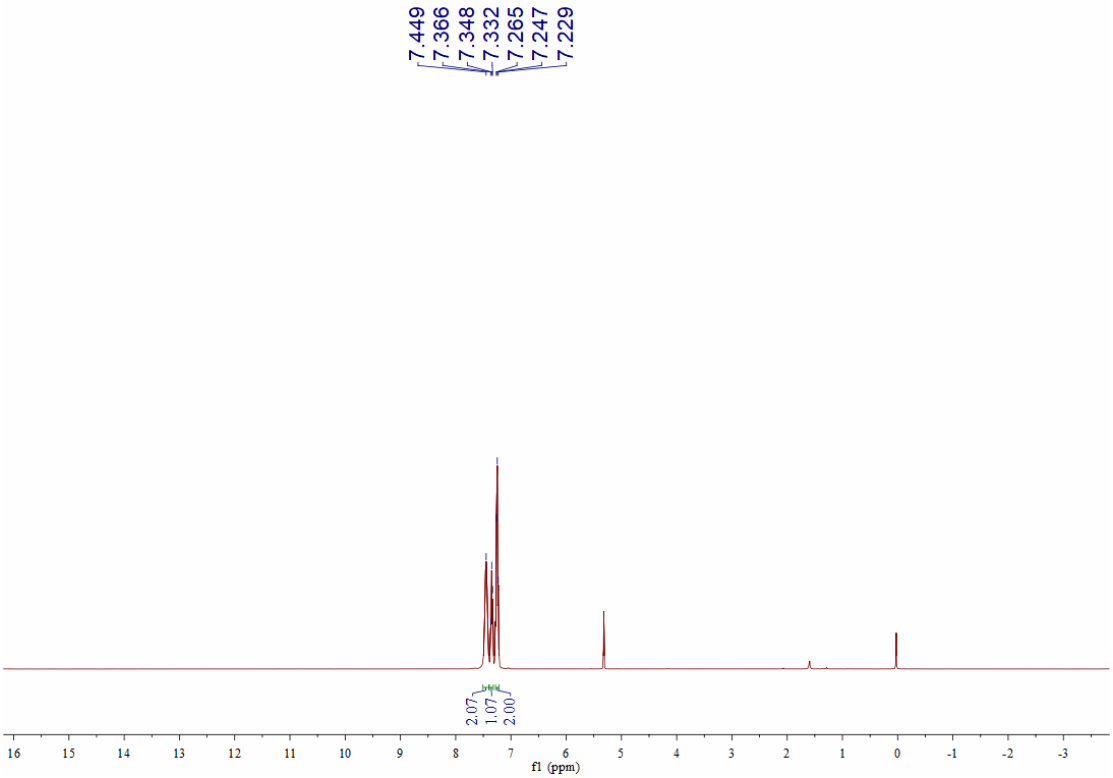


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1** at room temperature.

$[(PPh_3)_2Cu^I]^+[Cu^{III}(CF_3)_4]^-$ (2)

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 $(PPh_3)_2CuCl$ (**1**) (312 mg, 0.5 mmol) and AgF (254 mg, 2.0 mmol) at room temperature. The tube was then evacuated and refilled with dry nitrogen three times. DMF (5 mL) and CF_3SiMe_3 (426 mg, 3 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 (50 mL) three times. Then the organic layer was evaporated to dryness with silica gel. The solid residue was purified by column chromatography (eluent: CH_2Cl_2) to obtain pale-yellow solid of **2** in a yield of 210 mg (90%). Melting point: 165 − 167 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.3 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4 (d, *J* = 15.2 Hz), 131.1 (s), 130.3 (d, *J* = 29.4 Hz), 129.4 (d, *J* = 9.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.2 (s). FT-IR (ν_{max}, cm^{-1}): 3058, 1626, 1480, 1435, 1063, 741, 692, 515. HRMS (ESI) m/z calcd for $C_{36}H_{30}CuP_2^+$ $[(PPh_3)_2Cu^+]$: 587.1113; found: 587.1113. Anal. Calcd for $C_{40}H_{30}Cu_2F_{12}P_2$: C, 51.79; H, 3.26. Found: C, 51.55; H, 3.09. (note that the carbon resonance for CF_3 was not observed in ^{13}C NMR of compound **2** due possibly to dynamic behavior of complex **2** in solution, Cu-C and F-C couplings that lead to broadening and splitting of the carbon resonance. Similarly, the CF_3 carbon resonances are also absent for compounds **3** and **4** described later. For precedents of similar ^{13}C NMR behaviour of Cu(I)-CF_3 and Cu(III)-CF_3 complexes, see: (a) Hartwig et al. *Angew. Chem. Int. Ed.* 2012, **51**, 536. (b) Zhang et al. *Dalton Trans.* 2018, **47**, 4779.)

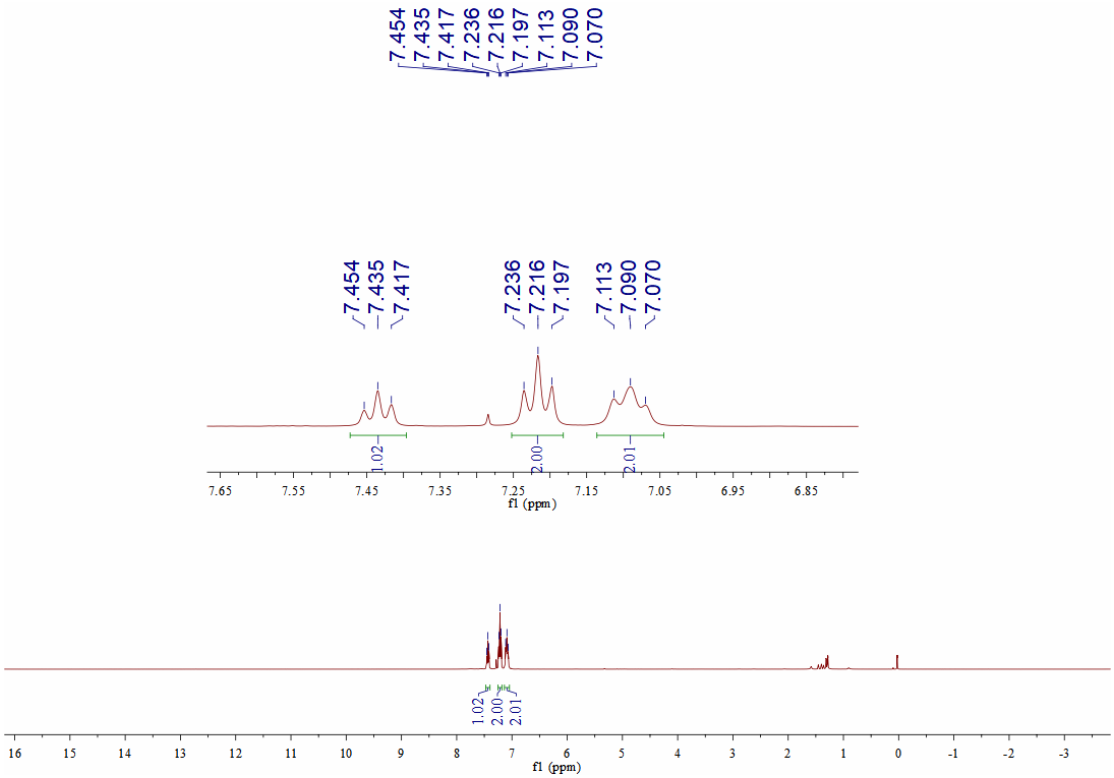


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2** at room temperature.

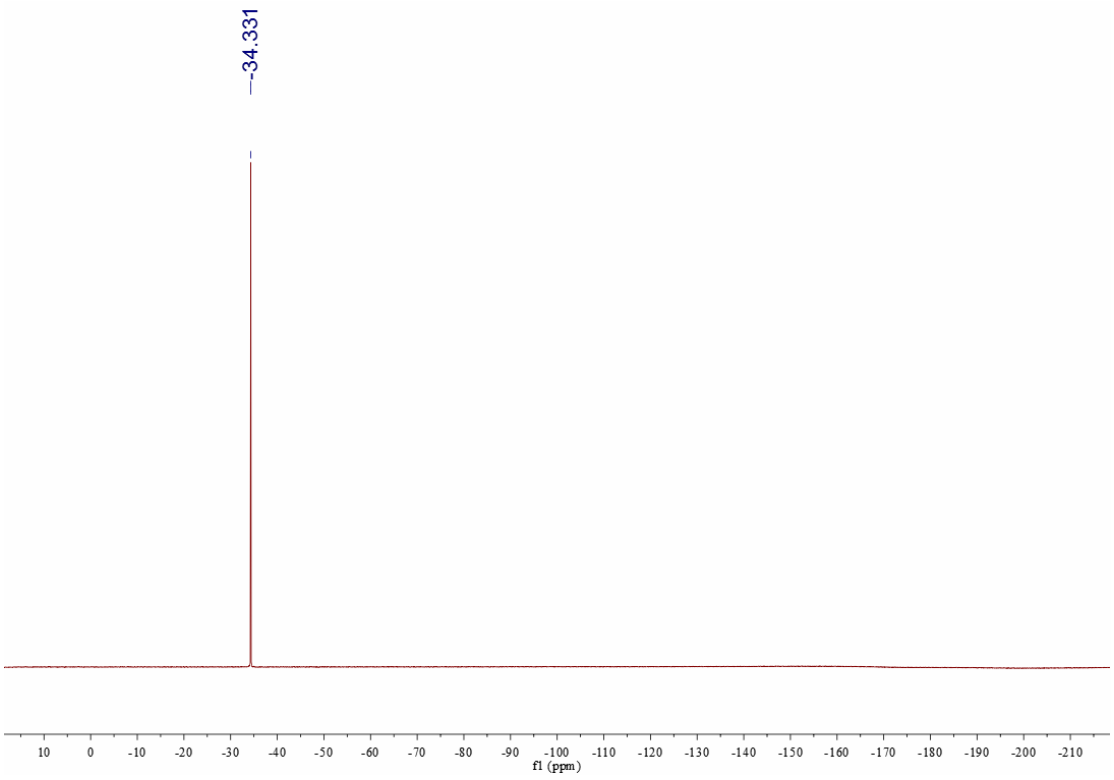


Figure S3. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **2** at room temperature.

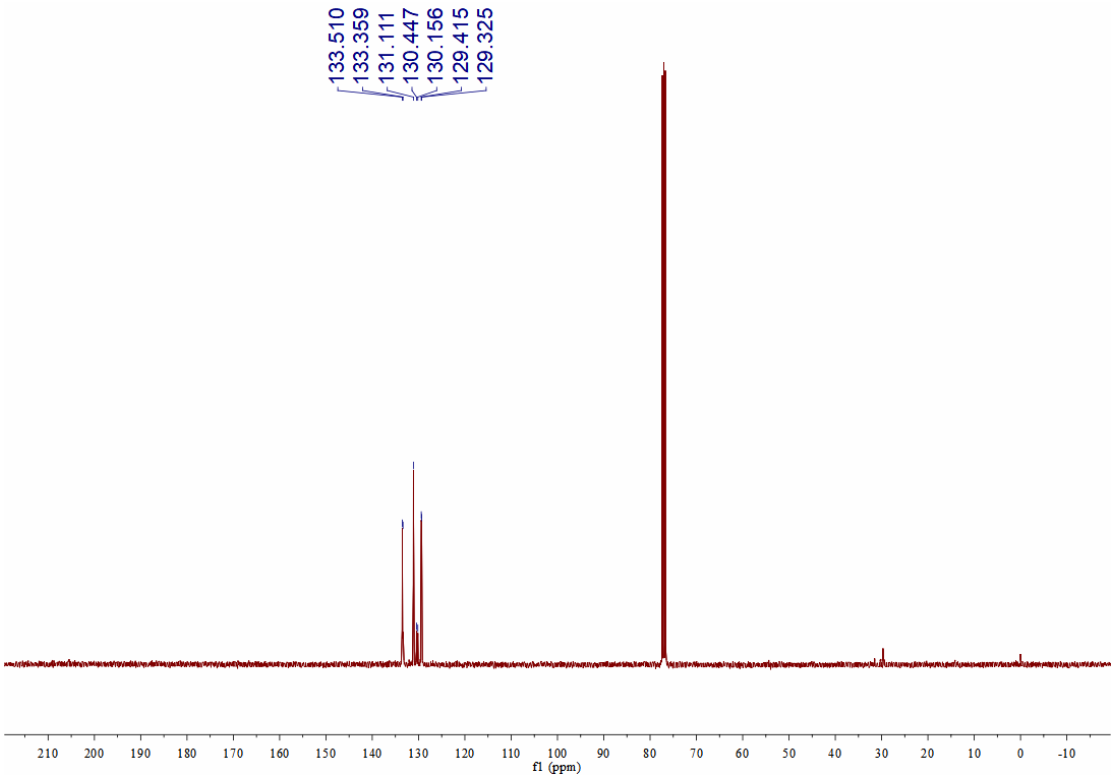


Figure S4. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2** at room temperature.

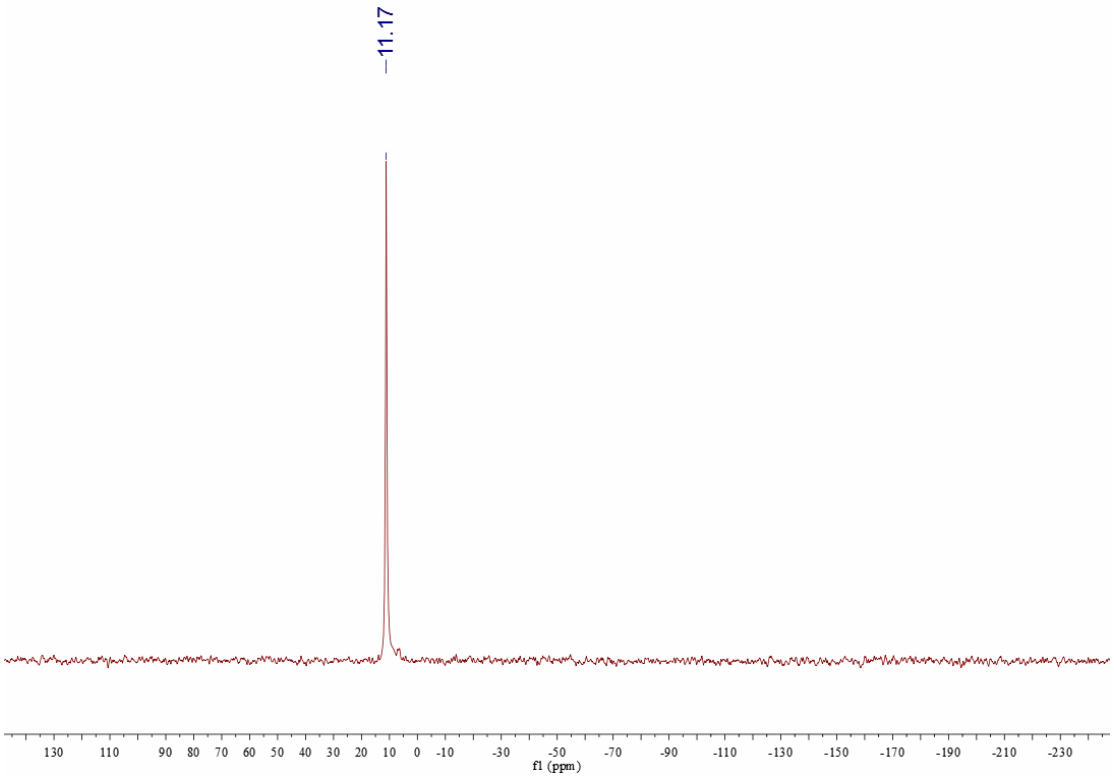


Figure S5. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **2** at room temperature.

(XPhos)Ag(I)(OH)$Cu^{III}(CF_3)_3$ (3)

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), 2-(dicyclohexylphosphino)-2,4,6-triisopropylbiphenyl (XPhos) (238 mg, 0.5 mmol) and AgF (256 mg, 2 mmol) at room temperature. The tube was then evacuated and refilled with dry nitrogen three times. DMF (5 mL) and CF_3SiMe_3 (426 mg, 3 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 (50 mL) three times. Then the organic layer was evaporated to dryness with silica gel. The residue was purified by column chromatography, and the desired product **3** was eluted with mixed petroleum ether/CH_2Cl_2 = 2:1 (v/v) and obtained as yellow solid in a yield of 90 mg (21%). Melting point: 151 − 152 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 1H), 7.57 – 7.47 (m, 2H), 7.25 – 7.22 (m, 1H), 7.14 (s, 2H), 3.05 – 2.91 (m, 1H), 2.29 – 2.22 (m, 2H), 2.07 – 1.95 (m, 4H), 1.90 – 1.62 (m, 9H), 1.37 – 1.18 (m, 22H), 0.95 (d, J = 6.3 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.7 (br, 3F), -39.6 (approximate q, J = 8.3 Hz, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.35 (s), 146.55 (d, J = 20.2 Hz), 146.36 (s), 134.66 (d, J = 9.2 Hz), 132.67 (d, J = 6.9 Hz), 132.20 (d, J = 6.8 Hz), 130.55 (s), 127.87 (d, J = 3.6 Hz), 121.70 (s), 35.39 (d, J = 4.7 Hz), 35.20 (d, J = 4.8 Hz), 33.90 (s), 31.52 (d, J = 7.0 Hz), 30.89 (s), 29.82 (d, J = 2.4 Hz), 27.11 (d, J = 14.1 Hz), 26.70 (d, J = 12.6 Hz),

25.60 (s), 23.95 (s), 23.18 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6 (d, J = 51.0 Hz), 16.1 (d, J = 53.5 Hz). FT-IR (ν_{max}, cm^{-1}) 3645, 2933, 2858, 1602, 1449, 1359, 1299, 1054, 999, 878, 728, 581. HRMS (ESI) m/z calcd for $C_{33}H_{49}PAg^+$ $(XPhosAg)^+$ 583.2617, found 583.2621. Anal. Calcd for $C_{36}H_{50}AgCuF_9OP$: C, 49.58; H, 5.78. Found: C, 49.32; H, 6.07.

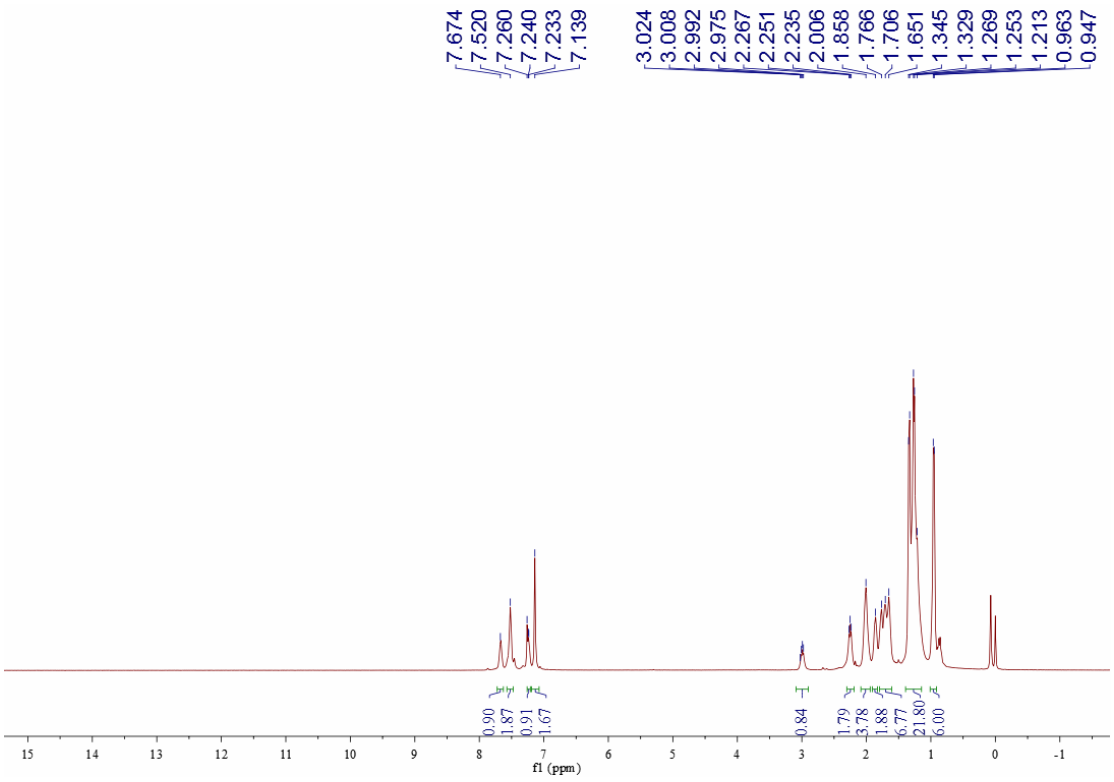


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3** at room temperature.

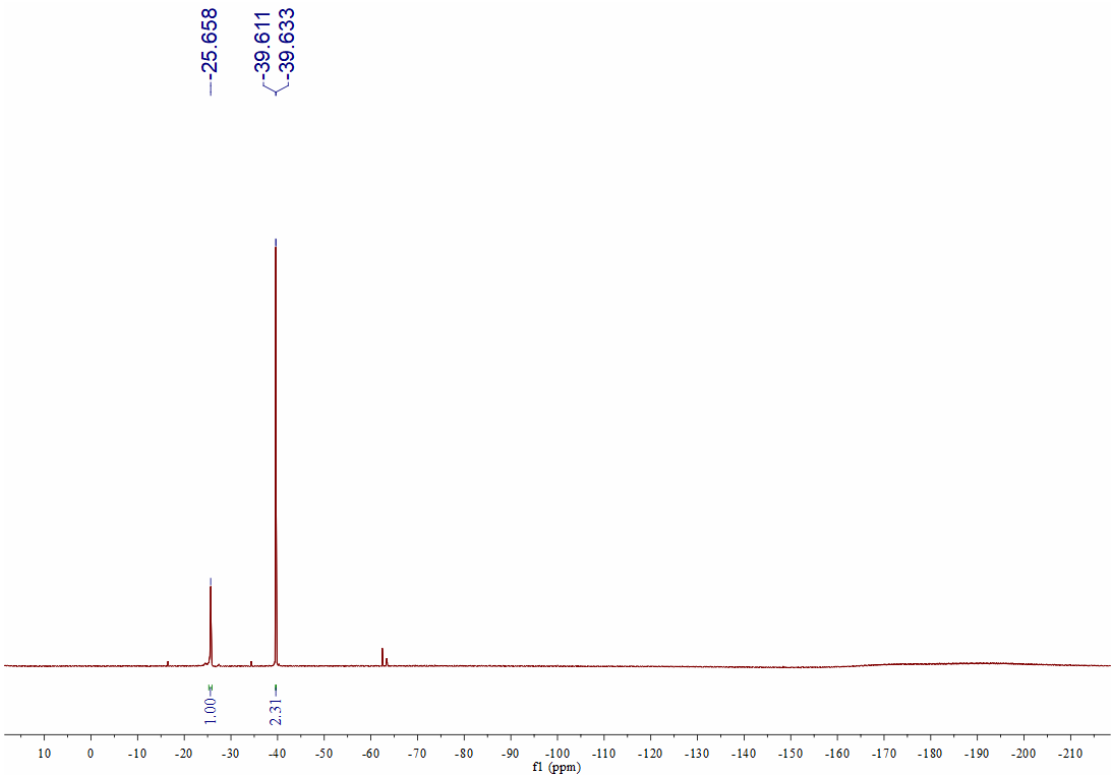


Figure S7. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3** at room temperature.

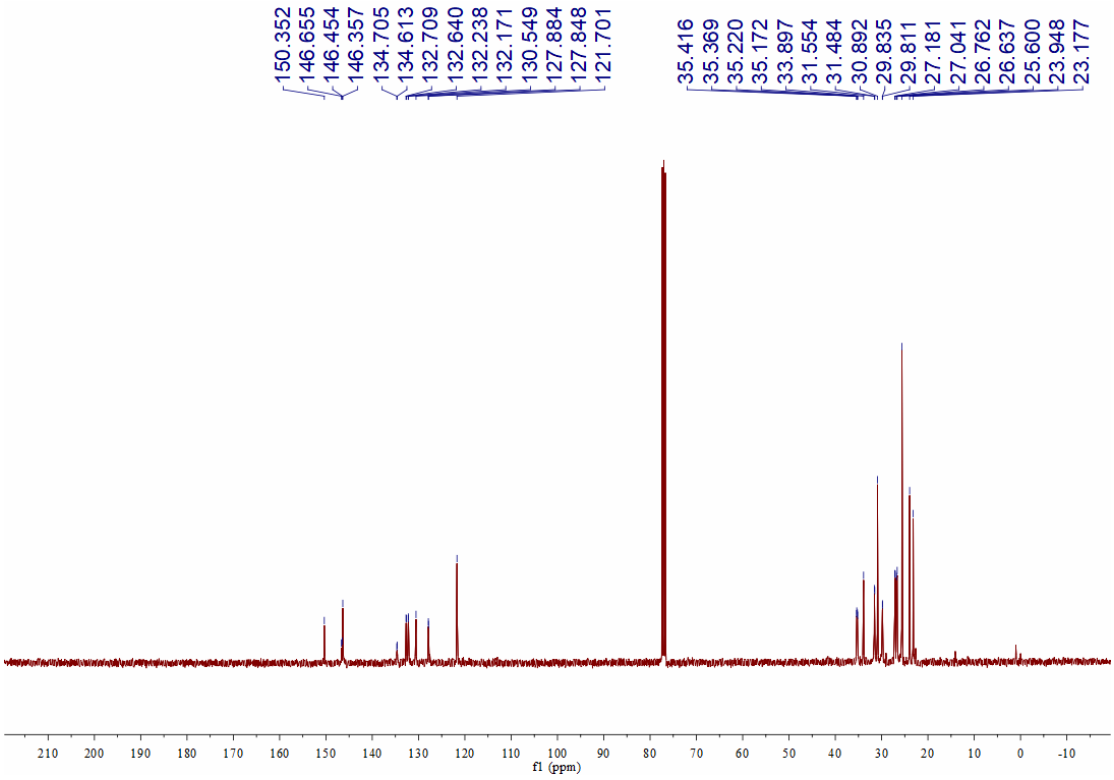


Figure S8. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3** at room temperature.

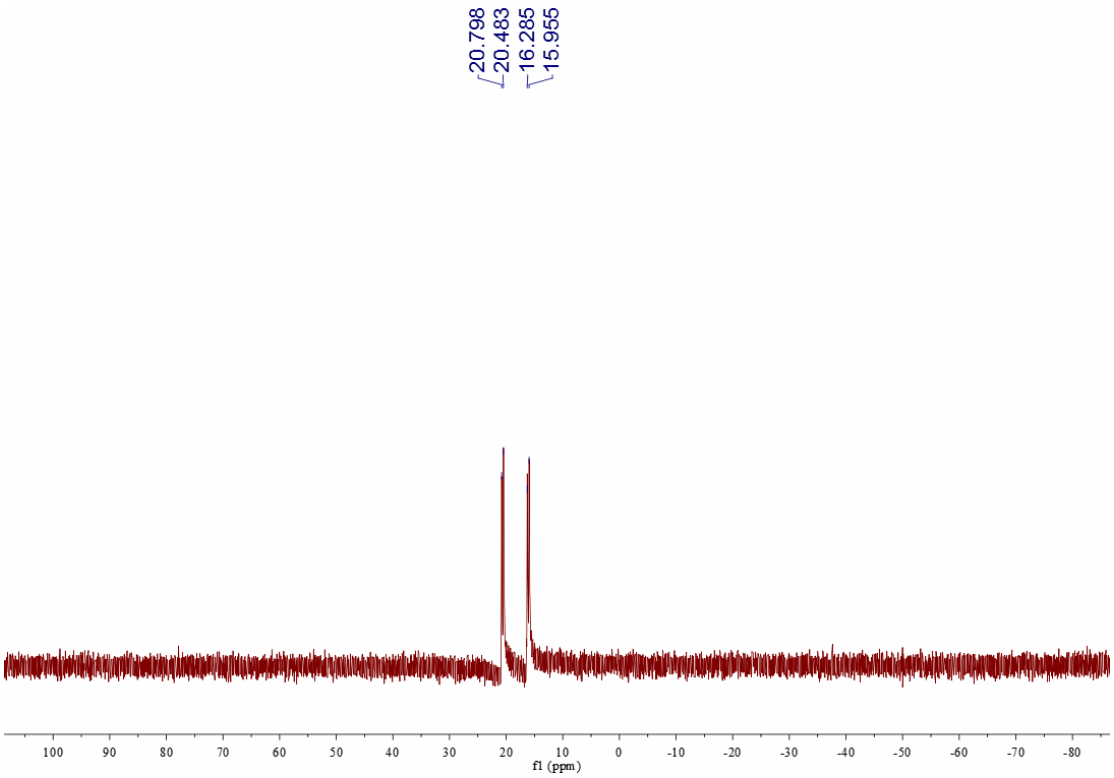


Figure S9. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **3** at room temperature.

$[SPhos_2Cu^{I}]^{+}[Cu^{III}(CF_3)_4]^{-}$ (4)

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), 2-dicyclohexylphosphino-2,6-dimethoxy-1,1-biphenyl (SPhos) (205 mg, 0.5 mmol) and AgF (256 mg, 2 mmol) at room temperature. The tube was was evacuated and refilled with dry nitrogen three times. DMF (5 mL) and CF_3SiMe_3 (426 mg, 3 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 (50 mL) three times. Then the organic layer was evaporated to dryness with silica gel. The residue was purified by column chromatography using CH_2Cl_2 as the eluent to obtain yellow solid of **4** in a yield of 100 mg (33%). Melting point: 52 − 53 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.39 (m, 4H), 7.26 – 7.18 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.16 – 2.03 (m, 2H), 1.88 – 1.66 (m, 10H), 1.42 – 1.08 (m, 10H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.4 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.78 (s), 157.08 (s), 133.59 (d, *J* = 10.8 Hz), 132.62 (d, *J* = 7.1 Hz), 132.49 (d, *J* = 7.2 Hz), 132.05 (s), 131.98 (s), 131.28 (s), 130.73 (s), 130.38 (s), 127.90 – 127.75 (m), 126.89 (d, *J* = 10.8 Hz), 117.97 (s), 104.15 (d, *J* = 24.0 Hz), 60.37 (s), 58.46 (s), 55.85 (s), 55.69 (s), 36.99 (s), 36.37 (s), 34.84 (d, *J* = 4.7 Hz), 34.62 (d, *J* = 4.7 Hz), 31.24 (d, *J* = 7.4 Hz), 29.97 (s), 26.71 (s), 26.58 (s), 26.45 (d, *J* = 3.4 Hz), 26.35 (d, *J* = 1.7 Hz), 26.22 (d, *J* = 2.3 Hz), 25.76 (d, *J* = 6.4 Hz), 21.01 (s), 18.41 (s), 14.18 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.2 (br s), 26.7 (br s), 22.2 (br s). FT-IR (ν_{max}, cm^{-1}) 2930, 2852, 1675, 1588, 1471, 1249, 1065, 779, 732.

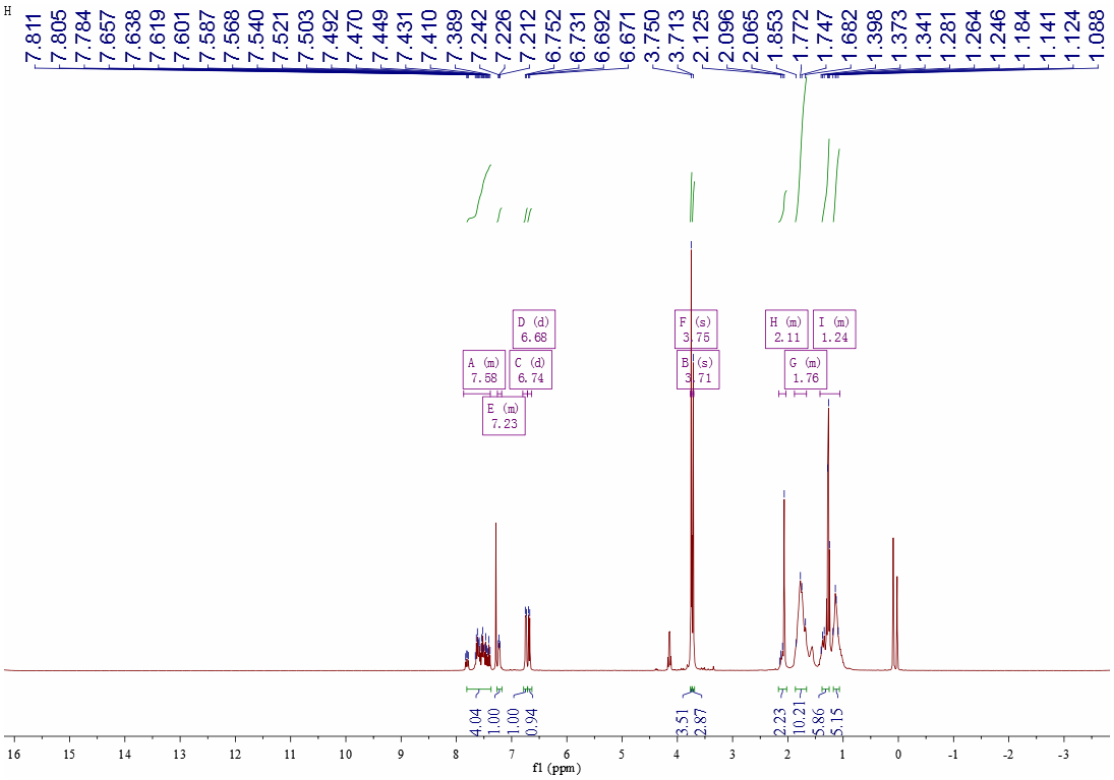


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4** at room temperature.

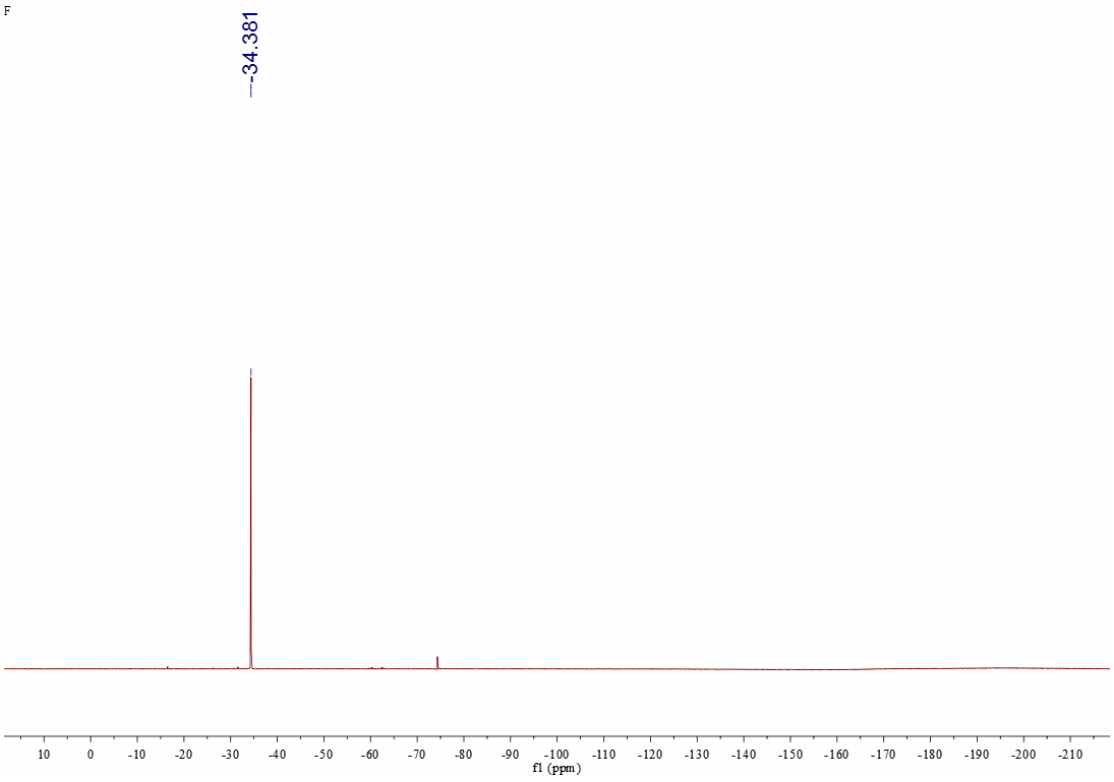


Figure S11. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **4** at room temperature.

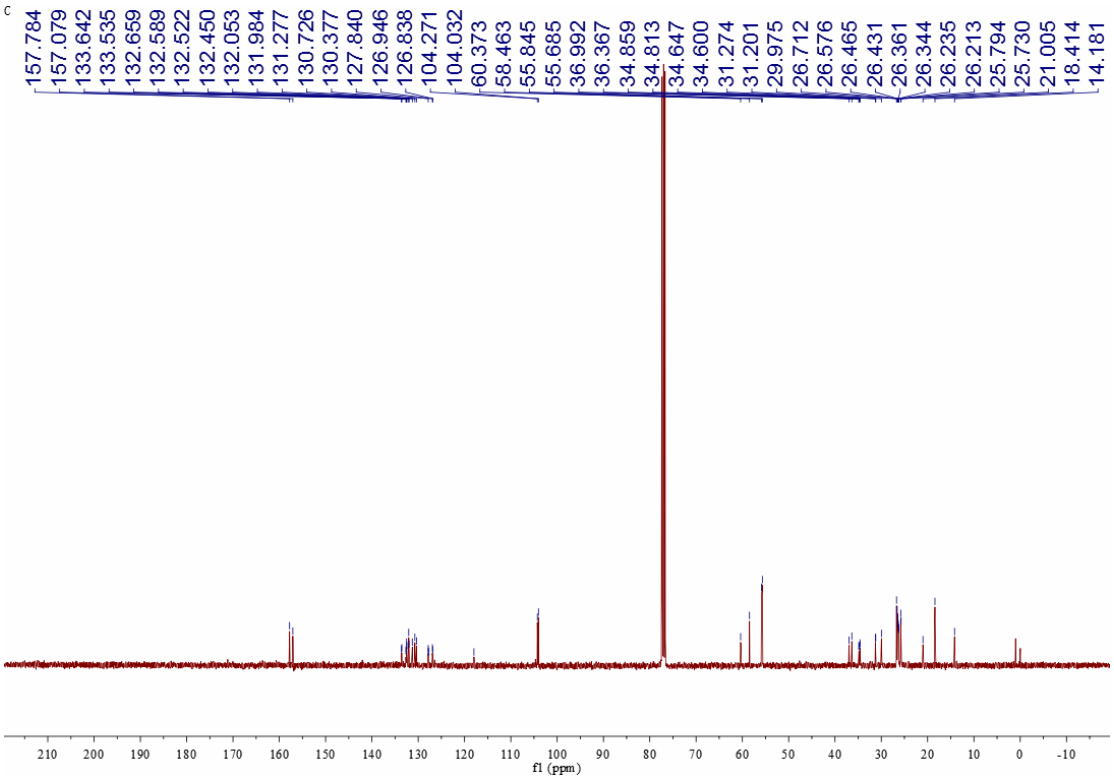


Figure S12. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4** at room temperature.

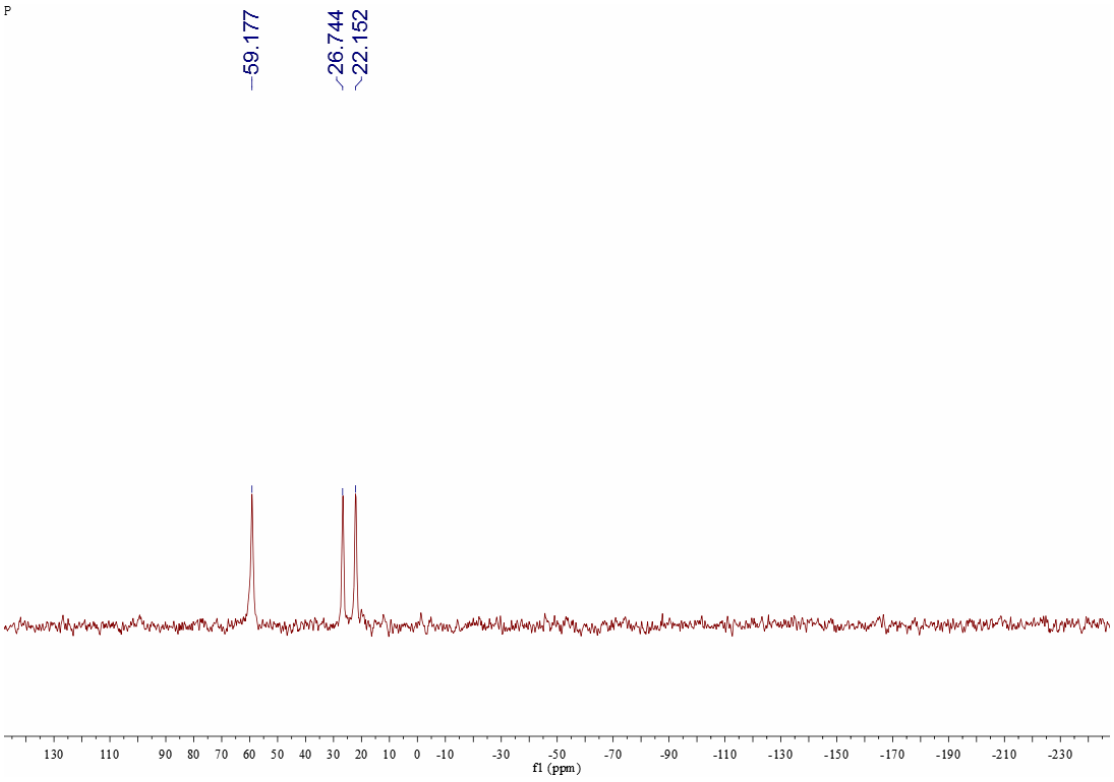


Figure S13. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4** at room temperature.

3. Reactivity studies of trifluoromethylation of aryl boronic acids

3.1 Optimization study of reaction of **3** with **5a**

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added (XPhos)$Ag^{I}(OH)Cu^{III}(CF_3)_3$ (**3**) (44 mg, 0.05 mmol), 4-methoxyphenylboronic acid (**5a**) (15 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 O_2 or N_2. 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 Et_2O. The residue mixture was analyzed by ^{19}F NMR spectroscopy to determine the reaction yield.

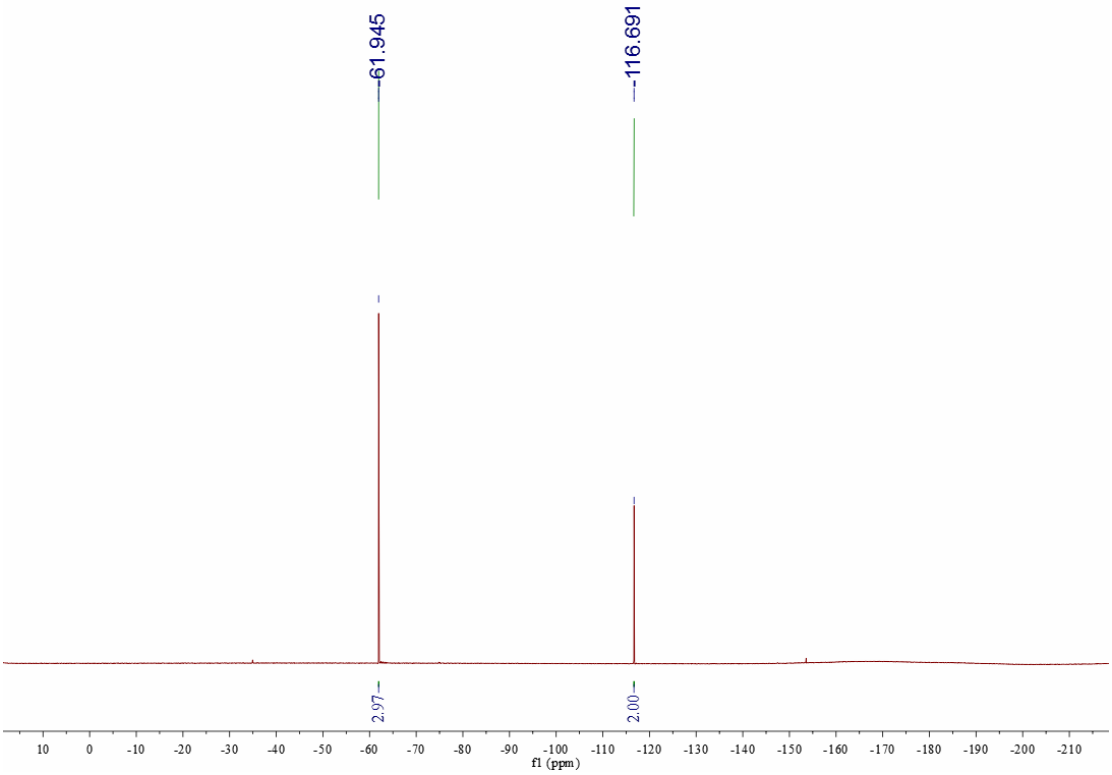


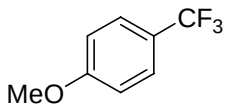
Figure S14. ^{19}F NMR analysis of the crude mixture of reaction of complex **3** with **5a** under the reaction conditions of entry 3 in Table 1.

For example, Figure S14 shows the ^{19}F NMR determination of the reaction solution of entry 3 in Table 1 after workup described above. As can be seen, nearly

quantitative conversion of complex **3** was observed. The new signal at -61.9 ppm corresponds to the formation of trifluoromethylated arene **6a** while the signal at -116.7 ppm is the internal standard 4, 4′-difluorobiphenyl. The trifluoromethylation yield was thus determined to be 99% relative to **5a**.

3.2 General procedure for reaction of **3** with various arylboronic acids

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added $XPhosAg^{I}(OH)Cu^{III}(CF_3)_3$ (**3**) (44 mg, 0.05 mmol), arylboronic acid (**5**, 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 N_2. 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 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. For several products, column chromatography on silica gel was performed to isolate purified products **6** using hexane as the eluent.



1-methoxy-4-(trifluoromethyl)benzene (**6a**; 15 mg, 85%). Colorless oil; ^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). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5 (s, 3F). The spectral data are in accordance with literature report. (see: H. Serizawa, K. Aikawa and K. Mikami, *Chem. Eur. J.,* 2013, **19**, 17692.)

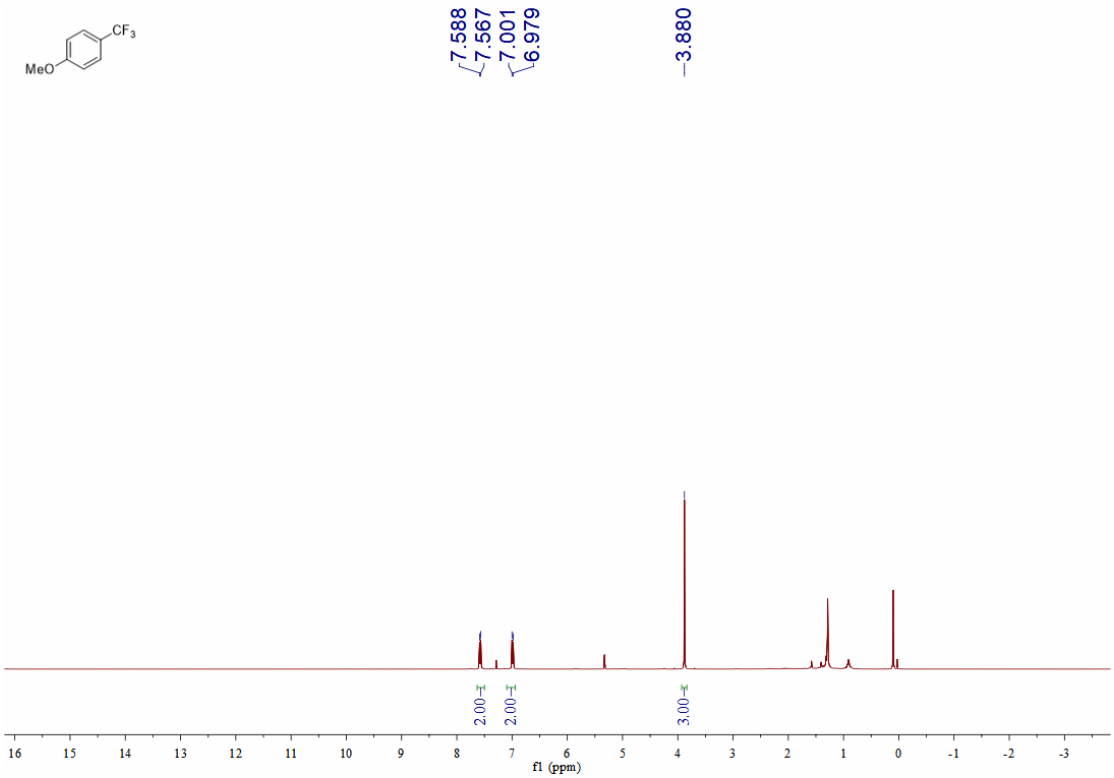


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6a** at room temperature.

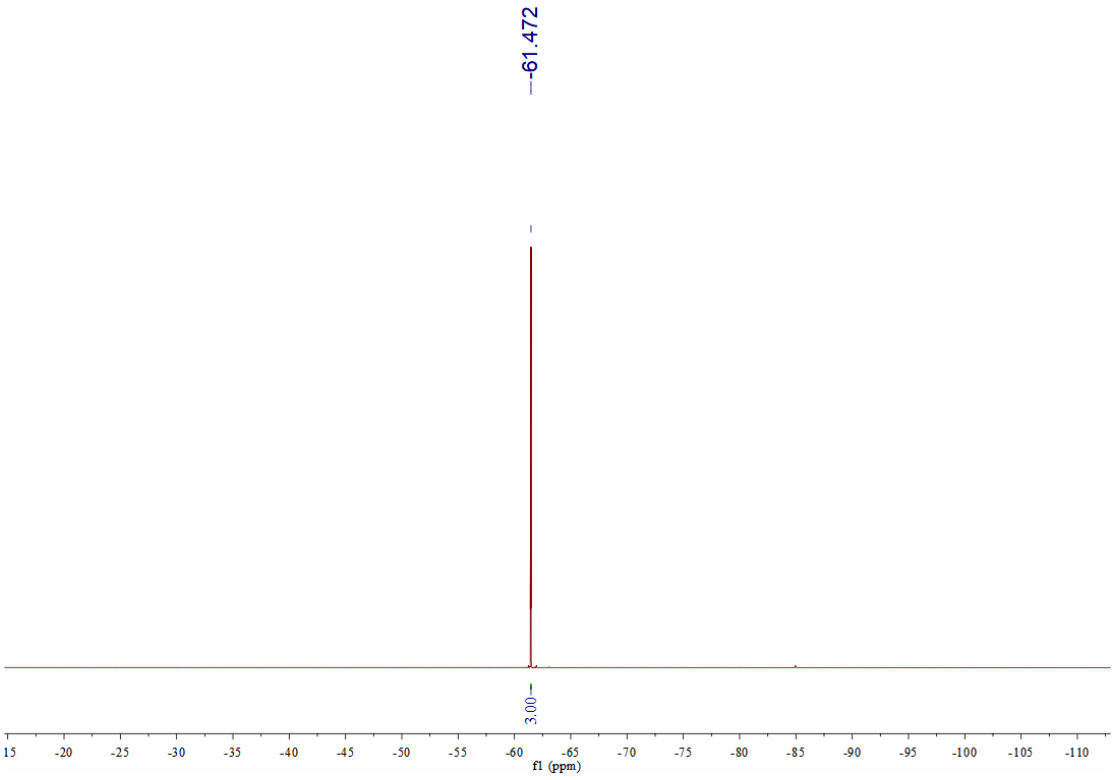
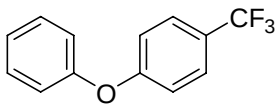


Figure S16. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6a** at room temperature.



1-phenoxy-4-(trifluoromethyl)benzene (**6b**; 15 mg, 63%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.00 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.75 (s, 3F). The spectral data are in accordance with literature report. (see: P. Novak, A. Lishchynskyi and V. V. Grushin, *Angew. Chem. Int. Ed.*, 2012, **51**, 7767.)

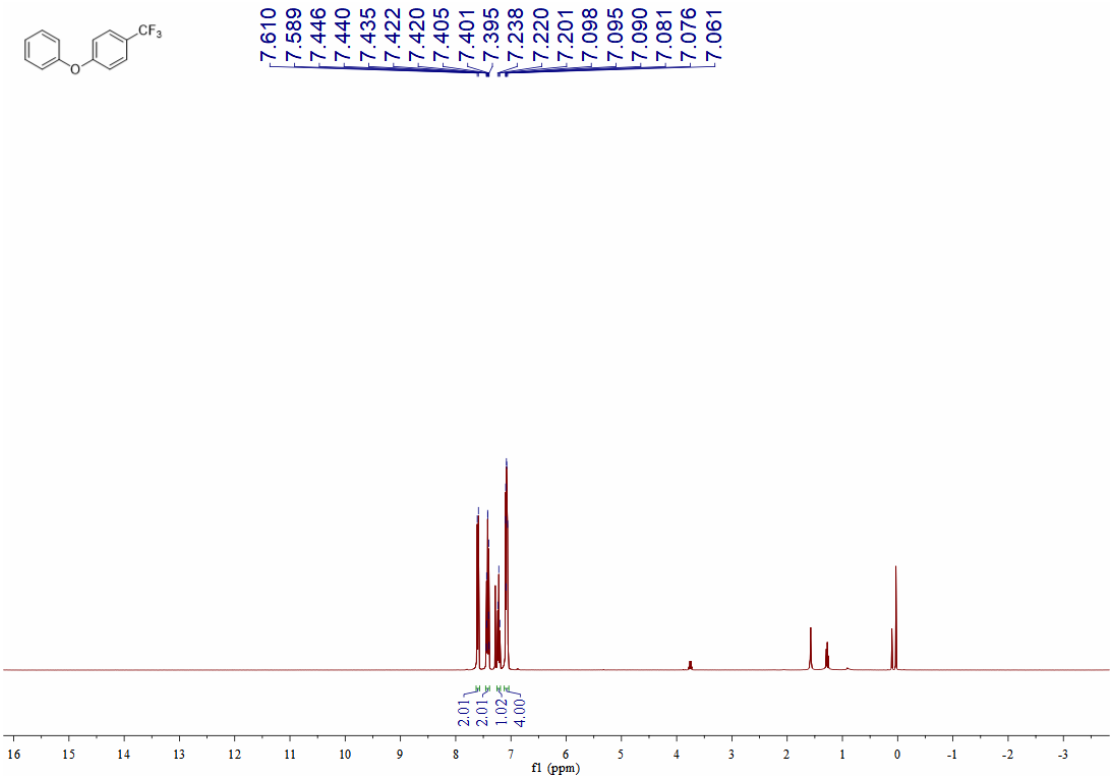


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6b** at room temperature.

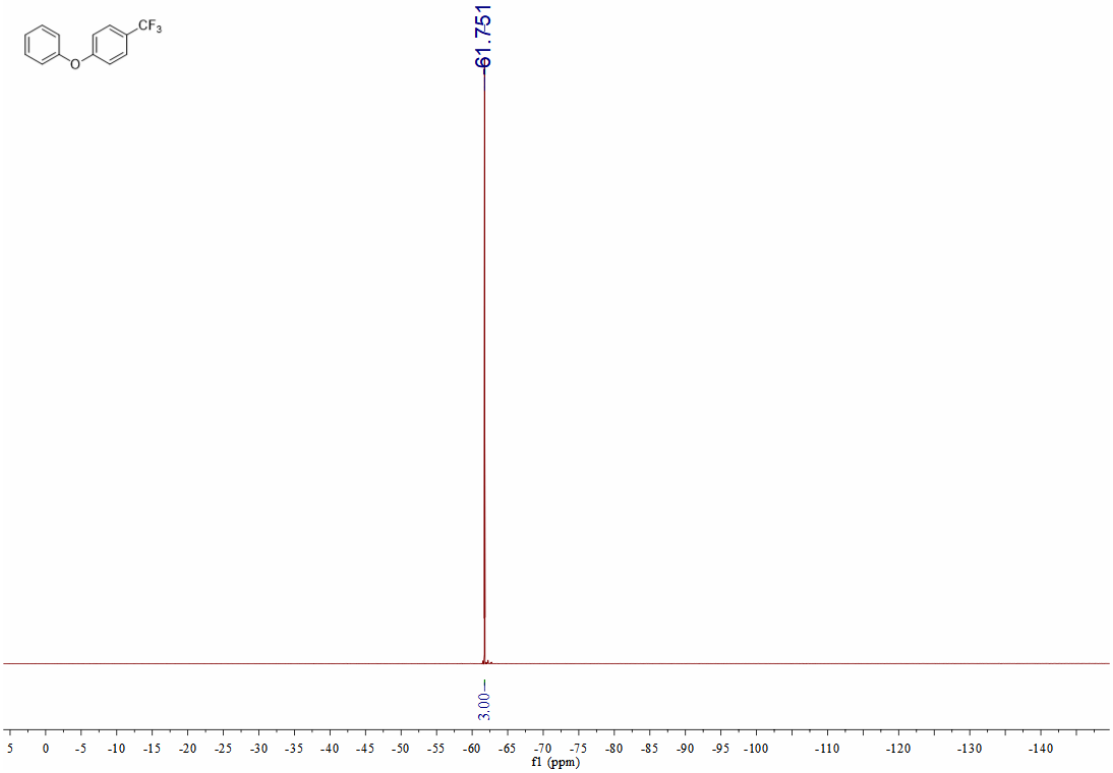
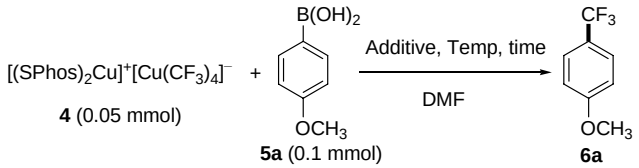


Figure S18. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6b** at room temperature.

3.3 Optimization studies for reactions of **2** and **4** with aryl boronic acids

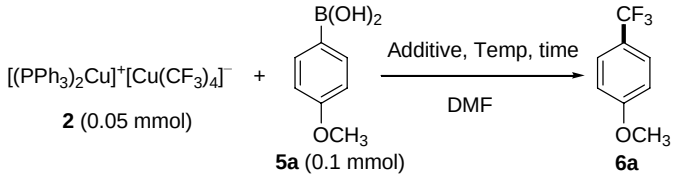
Table S1 Optimization of complex **4** with aryl boronic acid **5a** [a]



Entry	Additive	Solvent	Condition	Temp (℃)	Time (h)	Yield (%)[b]
1	-	DMF	O_2	80	6	6
2	KF	DMF	O_2	80	6	7
3	AgF	DMF	O_2	80	6	13
4	KF	Toluene	O_2	80	6	23
5	KF	DMF	O_2	80	12	2
6	KF	Toluene	O_2	80	12	17
7	KF	Toluene	N_2	80	18	31

[a] Reaction conditions: **4** (0.05 mmol), **5a** (0.1 mmol), additive (0.2 mmol), 4,4′-difluorobiphenyl (0.1 mmol, internal standard), solvent (1 mL). [b] Yields of **6a** determined by ^{19}F NMR spectroscopy based on **5a**.

Table S2 Optimization of complex **2** with aryl boronic acid **5a** [a]



Entry	Additive	Solvent	Condition	Temp (℃)	Time (h)	Yield (%)[b]
1	−	DMF	O_2	100	6	0
2	KF	DMF	O_2	100	6	0
3	K_2CO_3	DMF	O_2	100	6	0
4	Na_2CO_3	DMF	O_2	100	6	0
5	KF	DMF	N_2	100	6	0
6	KF	Toluene	O_2	100	6	17
7	KF	NMP	O_2	100	6	0
8	KF	1,4-dioxane	O_2	100	6	20

[a] Reaction conditions: **2** (0.05 mmol), **5a** (0.1 mmol), additive (0.2 mmol), 4,4′-difluorobiphenyl (0.1 mmol, internal standard), solvent (1 mL). [b] Yields of **6a** determined by ^{19}F NMR spectroscopy based on **5a**.