Electronic Supplementary Information for

Isolation and Characterization of Copper(III) Trifluoromethyl Complexes and Reactivity Studies of Aerobic Trifluoromethylation of Arylboronic Acids

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1. General experimental details

All reactants and solvents were purchased commercially except complex **1**. CH_2Cl_2 and DMF solvents were simply dried over Na_2SO_4 before use. Other 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/backfill techniques 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 Bruker Avance III HD 400 MHz spectrometer. 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.

2. Procedures for the synthesis and characterization of complexes 1-5

$(PPh_3)_3CuBr$

In an Erlenmeyer flask, methanol (150 mL) was heated to boiling and triphenyl phosphine (9.98 g, 38.1 mmol) was added slowly to the stirring methanol. After complete dissolution, $CuBr_2$ (2.24 g, 10.0 mmol) was slowly added in small portions. Upon addition of copper bromide, a white precipitate was formed. After all of $CuBr_2$ added, the mixture was stirred for 30 min and then cooled down to room temperature. The precipitate was filtered and washed with ethanol and ether, and dried in vacuum to give $(PPh_3)_3CuBr$ as a white powder in a yield of 7.876 g (85%).

(phen)Cu(PPh_3)Br (1)

In an Erlenmeyer flask, $(PPh_3)_3CuBr$ (4.65 g, 5 mmol) was dissolved in 50 mL of chloroform at room temperature. 1,10-phenanthroline (900 mg, 5 mmol) was then added to the reaction mixture. The colorless solution immediately turned orange. The contents of the flask were allowed to stir at room temperature for 30 min and the solvent was removed in vacuo. The resulting orange solid was dissolved in 80 mL of dichloromethane and layered with 200 mL of ether. The precipitate was collected on the Buchner funnel, washed with 100mL of ether and dried in vacuum to give (phen)Cu(PPh_3)Br (**1**) as an orange solid in a yield of 2.573 g (88%).

[(phen)$Cu^I(PPh_3)_2]^+[Cu^{III}(CF_3)_4]^-$ (2) and (phen)$Cu^{III}(CF_3)_3$ (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) was added phenCu(PPh_3)Br (586 mg, 1 mmol,) and AgF (381 mg, 3 mmol) at room temperature. The air in the Schlenk tube was evacuated and backfilled with dry nitrogen three times. CH_2Cl_2 (10 mL) was then added by syringe and the contents were vigorously stirred for 30 minutes. $TMSCF_3$ (426 mg, 3 mmol) was then slowly added by syringe. The resulting mixture was further stirred for 18 hours at room temperature under nitrogen. The crude mixture was separated by filtration and washed with CH_2Cl_2 (10 mL).The combined filtrate and the washings were evaporated to dryness. The solid residue was treated with CH_2Cl_2 (10 mL) and evaporated with silica gel. The crude mixture was purified by flash silica gel column chromatography under air with petroleum ether (PE) /ethylacetate (EA) (v/v = 2:1) as eluent to give phenCu(CF_3)$_3$ (**3**) as yellow solid in a yield of 140 mg (31%). Then the flash silica gel column chromatography was washed with CH_2Cl_2. The washings were reduced in volume on a rotary evaporator to give yellow solid. The solid residue was treated with CH_2Cl_2 (3 mL) followed by hexane (6 mL) and stored in refrigerator. Yellow crystals were separated by filtration, washed with hexane (4 x 1 mL), and dried under vacuum. Complex **2** was thus obtained as yellow solid in a yield of 164 mg (30%). Complexes **2** and **3** were stable under air for at least two weeks.

[(phen)$Cu^I(PPh_3)_2]^+[Cu^{III}(CF_3)_4]^-$ (2): ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.74 (d, J = 4.4 Hz, 2H), 8.50 (d, J = 8.0 Hz, 2H), 8.03 (s, 2H), 7.75 (dd, J = 7.9, 4.7 Hz, 2H), 7.38 (t, J = 7.6 Hz, 6H), 7.21 (t, J = 7.6 Hz, 12H), 7.14 (d, J = 7.2 Hz, 12H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ: -34.6 (s). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 3.0 (br). Anal. Calc. for $C_{52}H_{38}F_{12}N_2P_2Cu_2$: C, 56.37, H, 3.46, N, 2.53; Found: C, 56.77, H, 3.69, N, 2.73.

(phen)$Cu^{III}(CF_3)_3$ (**3**): ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.47 (dd, J = 4.8, 1.3 Hz, 2H), 8.67 (dd, J = 8.2, 1.4 Hz, 2H), 8.10 (s, 2H), 8.05 (dd, J = 8.2, 4.8 Hz, 2H). ^{19}F NMR (376 MHz, CD_2Cl_2): δ -24.4 (septet, J = 9.6 Hz), -37.4 (quartet, J = 9.6 Hz). Anal.

Calc. for $C_{15}H_8Cu_1F_9N_2$: C, 39.97, H, 1.79, N, 6.21; Found: C, 40.36, H, 2.00, N, 6.33.

An alternative synthesis of (phen)$Cu^{III}(CF_3)_3$ (3) and (bpy)$Cu^{III}(CF_3)_3$ (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) was added CuI (190 mg, 1 mmol), phen (180 mg, 1 mmol) or bpy (156 mg, 1 mmol) and AgF (508 mg, 4 mmol) at room temperature. The tube was then sealed with Teflon. The air in the tube was evacuated and backfilled with dry nitrogen three times. DMF (3 mL) was added by syringe and the contents were vigorously stirred for 30 minutes. CF_3SiMe_3 (852 mg, 6 mmol) was subsequently slowly added into the tube by syringe. The resulting mixture was further stirred for 18 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 (5 mL). The combined filtrate and the washings were washed with water (5 mL) three times. Then the organic layer was evaporated with silica gel. The crude mixture was purified by flash column chromatography on silica gel to give (phen)$Cu(CF_3)_3$ (**3**) (eluent: PE/EA (v/v = 2:1)) as yellow solids in a yield of 283 mg (63 %) or (bpy)$Cu(CF_3)_3$ (**4**) (eluent: CH_2Cl_2) as yellow solids in a yield of 303 mg (71 %).

(bpy)$Cu(CF_3)_3$ (4): ^{1}H NMR (400 MHz, d^6-DMSO) δ: 9.25 (d, *J* = 5.0 Hz, 2H), 8.81 (d, *J* = 8.1 Hz, 2H), 8.39 (td, *J* = 7.9, 1.4 Hz, 2H), 7.92 (dd, *J* = 6.8, 5.5 Hz, 2H). ^{19}F NMR (376 MHz, d^6-DMSO) δ: -24.0 (sept, *J* = 9.2 Hz), -36.1 (q, *J* = 9.2 Hz).

$[(Ph_3P)_3Ag_2Br_2]$ (5)

Into a 25-mL Schlenk tube equipped with a stir bar and wrapped with tinfoil was added phenCu(PPh_3)Br (586 mg, 1 mmol,) and AgF (381 mg, 3 mmol) at room temperature. The air in the Schlenk was evacuated and backfilled with dry nitrogen three times. CH_2Cl_2 (10 mL) was then added into the tube by syringe. The resulting mixture was stirred at room temperature for 18 h under nitrogen. The resulting mixture was separated by filtration and washed with CH_2Cl_2 (5 mL).The combined filtrate and the washings were evaporated to dryness. The solid residue was treated with CH_2Cl_2 (5 mL) followed by hexane (15 mL). The pale yellow crystals were separated by filtration, washed with hexane (4 x 5 mL), and dried under vacuum. Crystals of complex **[$(Ph_3P)_3Ag_2Br_2$] (5)** suitable for X-ray diffraction analysis were then obtained by dissolving the solid in CH_2Cl_2/hexane mixed solvent and stored in refrigerator for several days. ^{31}P NMR (162 MHz, $CDCl_3$): δ 5.8 (s).

3. NMR Spectra for the key complexes 2-4

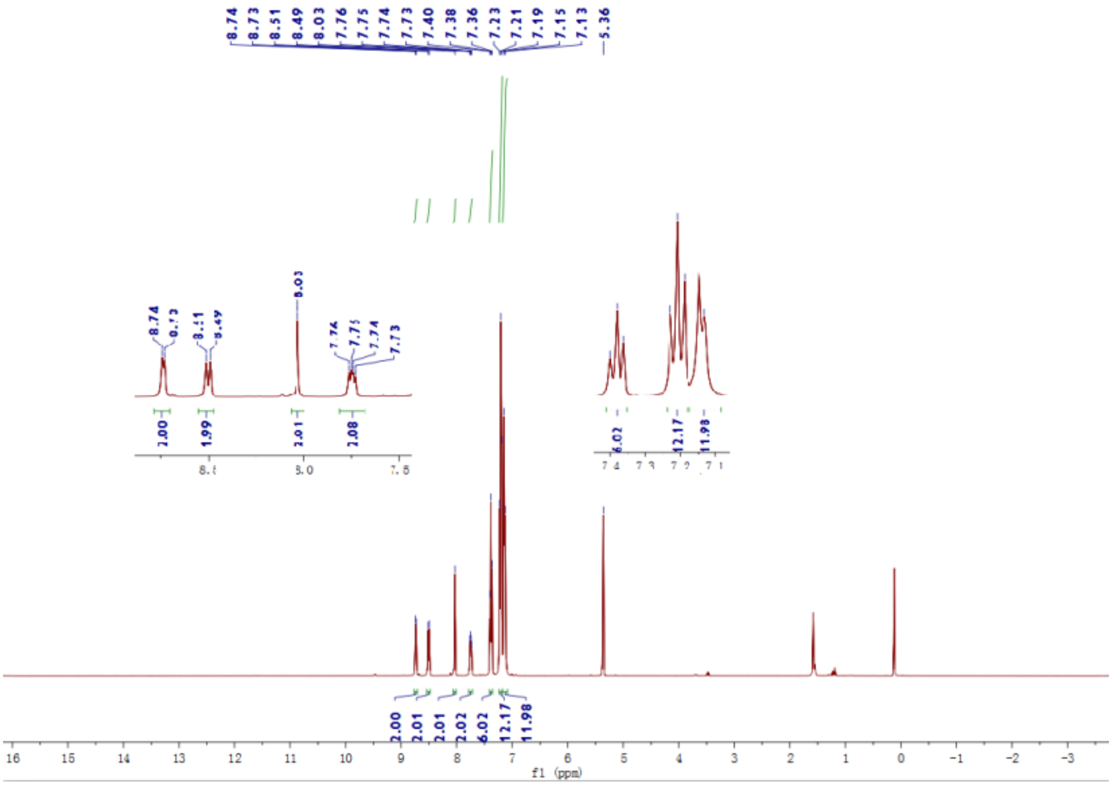


Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2) of complex **2** (The two insets show the fine splitting of phen and PPh_3 respectively).

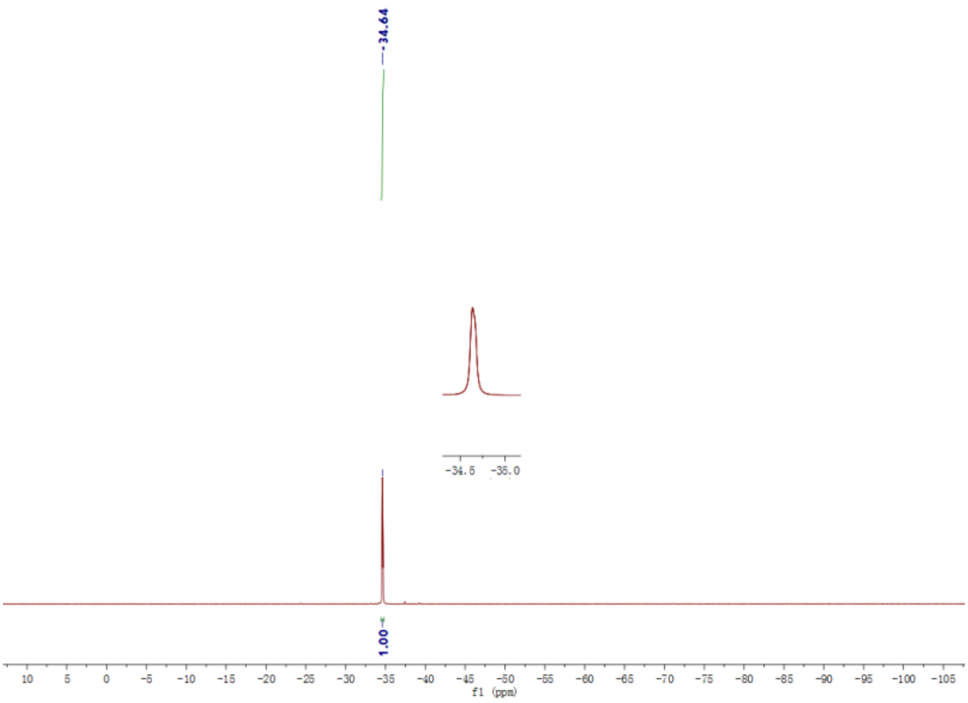


Figure S2. ^{19}F NMR (376 MHz, CD_2Cl_2) of complex **2.**

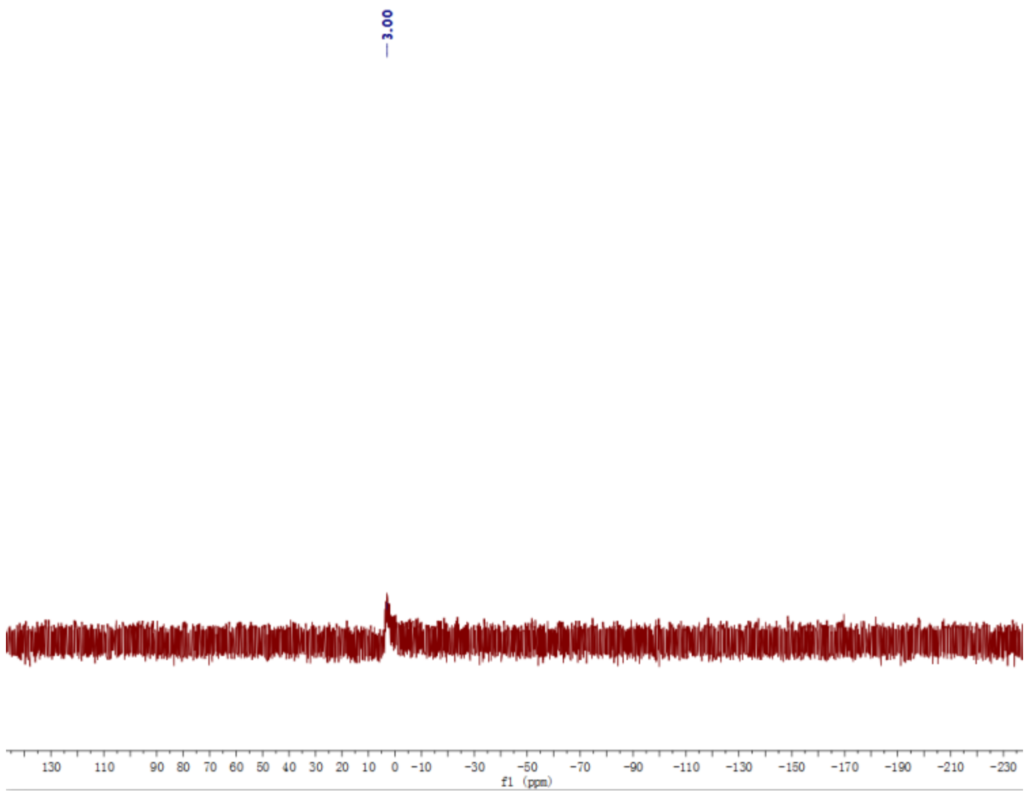


Figure S3. [31]P NMR (162 MHz, CD_2Cl_2) of complex **2.**

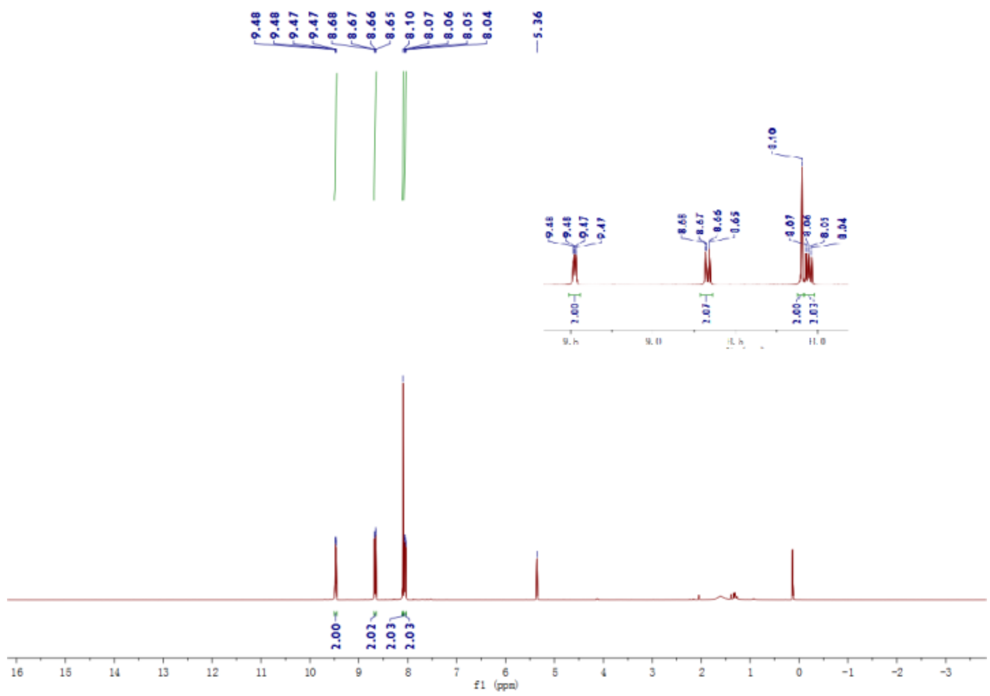


Figure S4. [1]H NMR (400 MHz, CD_2Cl_2) of complex **3** (the inset shows fine splitting of phen).

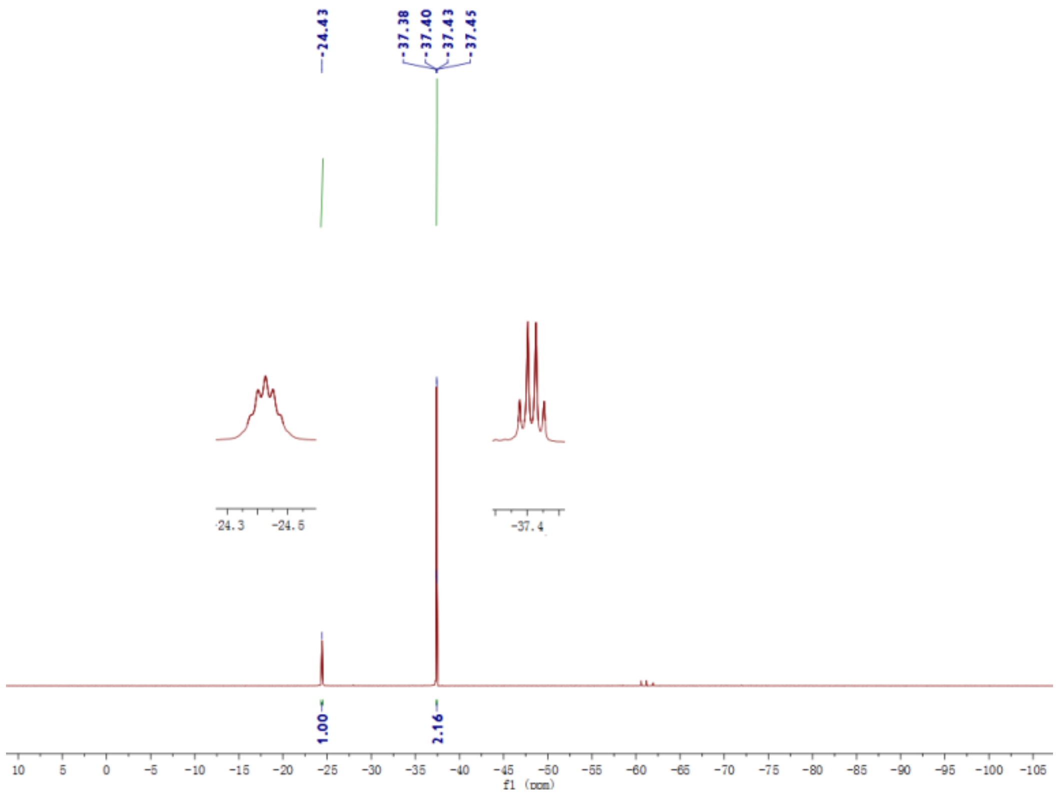


Figure S5. ^{19}F NMR (376 MHz, CD_2Cl_2) of complex **3** (the two insets show fine splitting of the two signals).

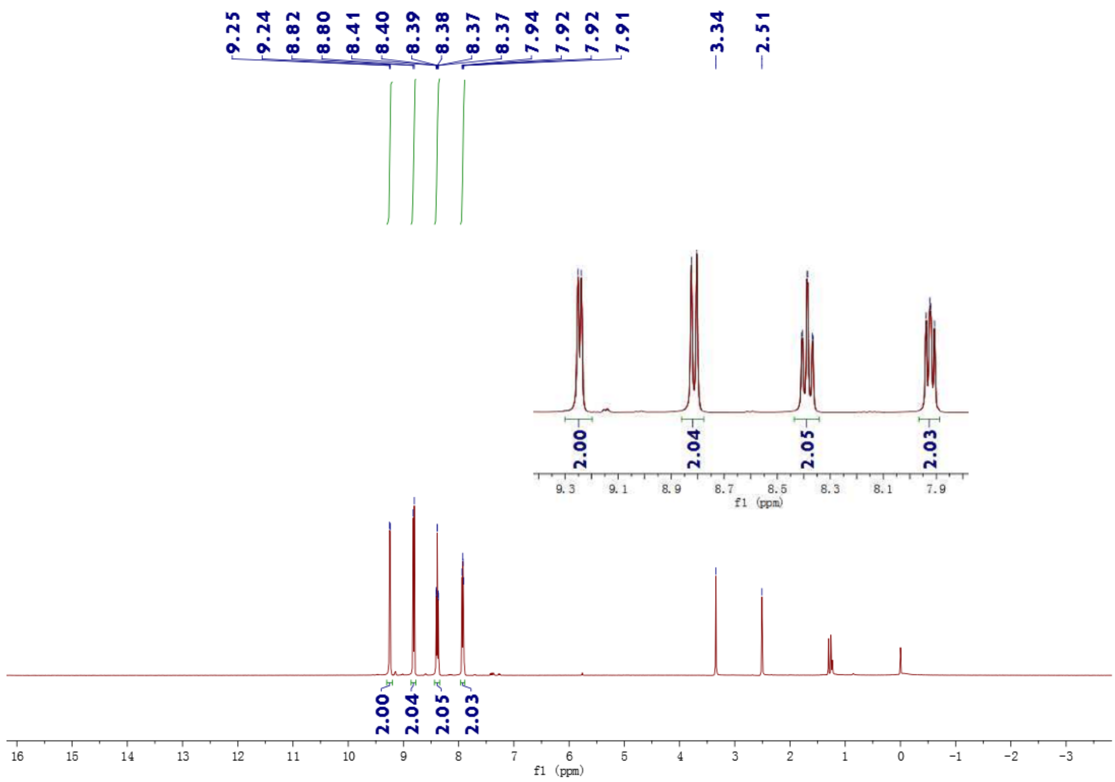


Figure S6. ^{1}H NMR (400 MHz, d^{6}-DMSO) of complex **4** (the inset shows fine splitting of bpy). Signals at 2.51 and 3.34 ppm are resonances of residual DMSO.

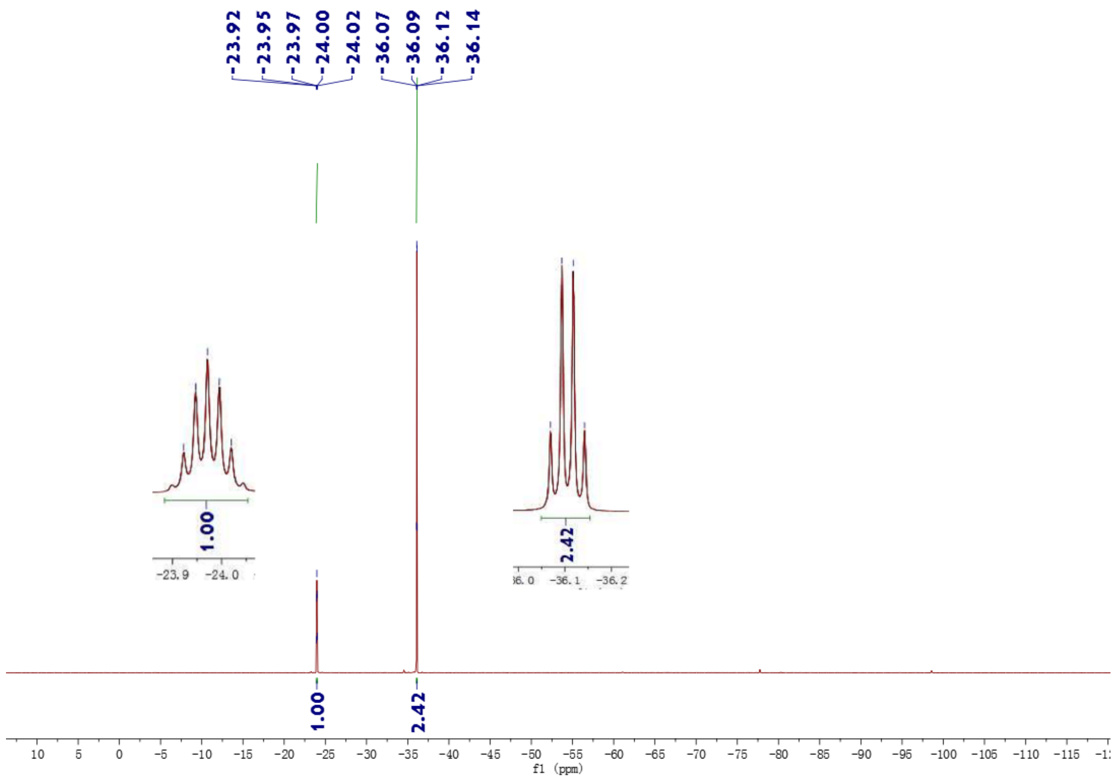


Figure S7. ^{19}F NMR (376 MHz, d^{6}-DMSO) of complex **4** (the two insets show fine splitting of the two signals).

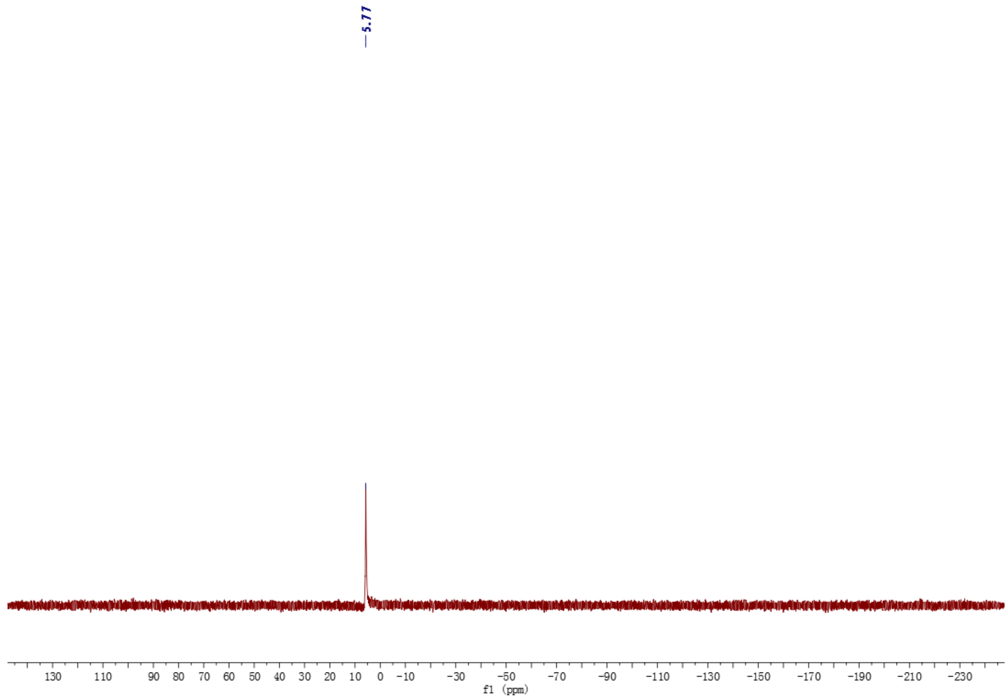
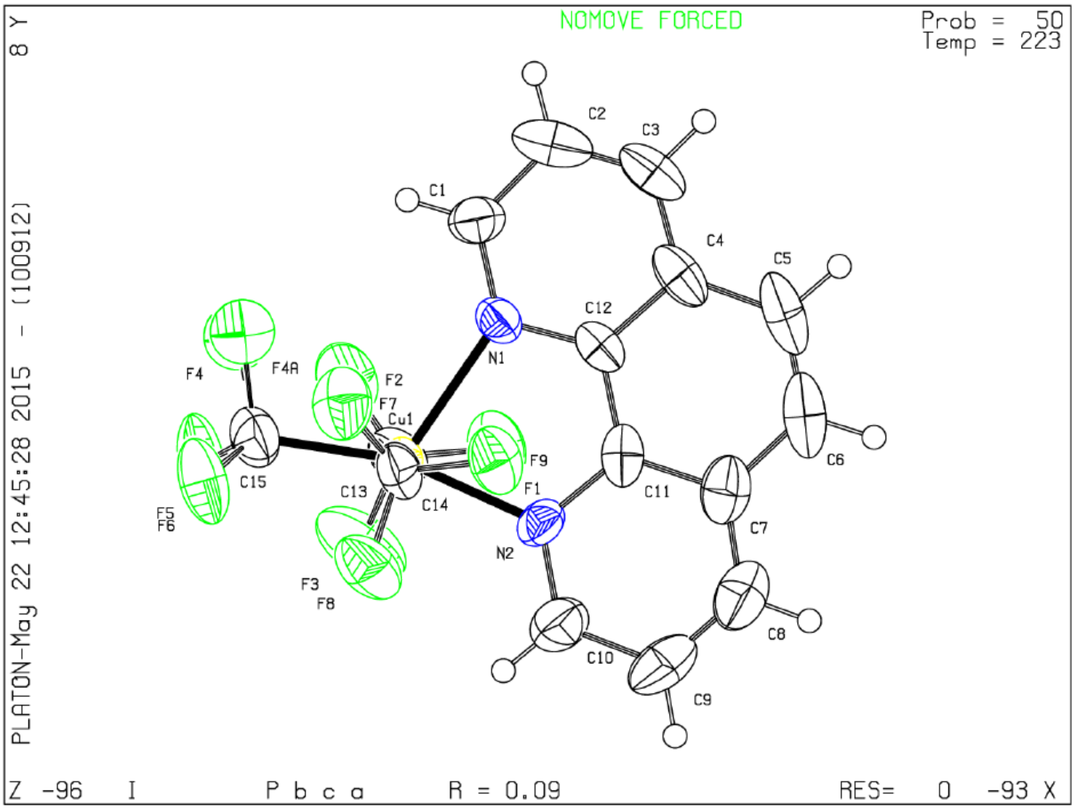


Figure S8. ^{31}P NMR (162 MHz, $CDCl_3$) of complex **5**.

4. Crystallographic study

Crystals of complexes **2**, **3** and **5** suitable for X-ray crystallographic analyses were grown by dissolving **2**, **3** or **5** in a mixed solvent of CH_2Cl_2/hexane and then stored in the refrigerator for 2-3 days. CCDCs 1402421, 1402422 and 1402423 contain the detailed information about the crystallographic study and crystal structures of complexes **3**, **2** and **5**. The following sections show some key information.

(1) Complex **3**:



*Crystal data for complex **3***

$C_{15}H_8CuF_9N_2$	
M_r = 450.77	D_x = 1.819 Mg m^{-3}
Orthorhombic, *Pbca*	Melting point: ? K
Hall symbol: -P 2ac 2ab	Mo *Kα* radiation, λ = 0.71073 Å
a = 11.1138 (9) Å	Cell parameters from 1382 reflections
b = 16.303 (2) Å	θ = 3.2–23.5°
c = 18.1646 (17) Å	μ = 1.42 mm^{-1}

V = 3291.3 (6) Å^3	T = 223 K
Z = 8	Plate, yellow
F(000) = 1776	0.35 × 0.30 × 0.20 mm

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.73286 (8)	0.12077 (5)	0.33566 (5)	0.0379 (4)	
F1	0.7020 (5)	−0.0256 (3)	0.4113 (3)	0.0676 (15)	
F2	0.7995 (6)	−0.0434 (3)	0.3113 (3)	0.0801 (18)	
F3	0.6091 (6)	−0.0255 (4)	0.3074 (4)	0.102 (2)	
F4	0.8932 (11)	0.0862 (8)	0.2300 (6)	0.080 (4)*	0.50
F4A	0.9064 (11)	0.1255 (8)	0.2318 (7)	0.073 (4)*	0.50
F5	0.7406 (7)	0.0456 (4)	0.1965 (3)	0.097 (2)	
F6	0.7472 (6)	0.1743 (4)	0.1895 (3)	0.0789 (18)	
F7	0.8391 (5)	0.2704 (3)	0.2891 (3)	0.0709 (15)	
F8	0.6447 (5)	0.2734 (3)	0.2945 (3)	0.0724 (15)	
F9	0.7531 (4)	0.2792 (3)	0.3928 (3)	0.0597 (14)	
N1	0.8818 (6)	0.1163 (4)	0.4152 (3)	0.0410 (15)	
N2	0.6432 (5)	0.1364 (4)	0.4280 (3)	0.0425 (16)	
C1	0.9997 (7)	0.1047 (5)	0.4082 (5)	0.052 (2)	
H1	1.0315	0.0972	0.3608	0.062*	
C2	1.0786 (9)	0.1032 (5)	0.4681 (7)	0.068 (3)	
H2	1.1620	0.0979	0.4609	0.081*	
C3	1.0325 (9)	0.1095 (5)	0.5362 (6)	0.063 (3)	
H3	1.0839	0.1056	0.5771	0.076*	
C4	0.9097 (9)	0.1215 (5)	0.5472 (5)	0.053 (2)	
C5	0.8528 (13)	0.1305 (6)	0.6176 (5)	0.076 (3)	

H5	0.9002	0.1294	0.6605	0.091*	
C6	0.7329 (12)	0.1404 (6)	0.6237 (6)	0.077 (3)	
H6	0.6985	0.1449	0.6708	0.092*	
C7	0.6576 (9)	0.1442 (5)	0.5614 (5)	0.058 (2)	
C8	0.5343 (10)	0.1579 (6)	0.5634 (6)	0.072 (3)	
H8	0.4971	0.1656	0.6093	0.087*	
C9	0.4651 (8)	0.1605 (6)	0.5019 (6)	0.071 (3)	
H9	0.3816	0.1692	0.5047	0.085*	
C10	0.5241 (8)	0.1495 (6)	0.4324 (5)	0.064 (2)	
H10	0.4784	0.1515	0.3889	0.077*	
C11	0.7102 (8)	0.1349 (4)	0.4915 (4)	0.046 (2)	
C12	0.8381 (7)	0.1240 (4)	0.4846 (4)	0.0416 (18)	
C13	0.7114 (8)	0.0015 (5)	0.3392 (5)	0.055 (2)	
C14	0.7457 (8)	0.2398 (6)	0.3260 (4)	0.049 (2)	
C15	0.7781 (9)	0.1099 (6)	0.2331 (5)	0.061 (3)	

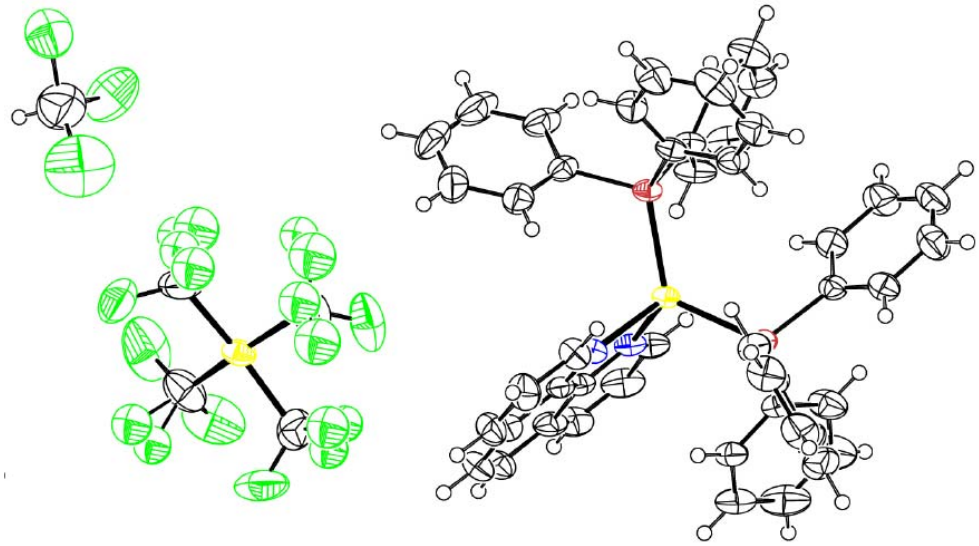
Geometric parameters (Å, °)

Cu1—C15	1.939 (10)	C1—H1	0.9400
Cu1—C14	1.953 (9)	C2—C3	1.342 (14)
Cu1—C13	1.960 (9)	C2—H2	0.9400
Cu1—N2	1.968 (6)	C3—C4	1.393 (14)
Cu1—N1	2.198 (6)	C3—H3	0.9400
F1—C13	1.386 (9)	C4—C12	1.389 (11)
F2—C13	1.324 (10)	C4—C5	1.435 (15)
F3—C13	1.349 (10)	C5—C6	1.346 (15)
F4—C15	1.337 (15)	C5—H5	0.9400
F4A—C15	1.449 (16)	C6—C7	1.410 (14)
F5—C15	1.310 (11)	C6—H6	0.9400

F6—C15	1.358 (10)	C7—C8	1.389 (14)
F7—C14	1.333 (9)	C7—C11	1.405 (12)
F8—C14	1.374 (9)	C8—C9	1.357 (14)
F9—C14	1.376 (9)	C8—H8	0.9400
N1—C1	1.330 (10)	C9—C10	1.433 (12)
N1—C12	1.357 (10)	C9—H9	0.9400
N2—C10	1.343 (10)	C10—H10	0.9400
N2—C11	1.373 (10)	C11—C12	1.438 (12)
C1—C2	1.397 (12)		
C15—Cu1—C14	89.2 (4)	C9—C8—C7	122.9 (9)
C15—Cu1—C13	88.4 (4)	C9—C8—H8	118.6
C14—Cu1—C13	175.7 (3)	C7—C8—H8	118.6
C15—Cu1—N2	164.3 (4)	C8—C9—C10	117.5 (8)
C14—Cu1—N2	89.1 (3)	C8—C9—H9	121.2
C13—Cu1—N2	92.2 (3)	C10—C9—H9	121.2
C15—Cu1—N1	115.7 (4)	N2—C10—C9	121.5 (8)
C14—Cu1—N1	92.1 (3)	N2—C10—H10	119.3
C13—Cu1—N1	92.1 (3)	C9—C10—H10	119.3
N2—Cu1—N1	79.9 (3)	N2—C11—C7	122.1 (8)
C1—N1—C12	117.0 (7)	N2—C11—C12	117.7 (6)
C1—N1—Cu1	133.2 (6)	C7—C11—C12	120.2 (8)
C12—N1—Cu1	109.7 (5)	N1—C12—C4	123.6 (8)
C10—N2—C11	119.2 (7)	N1—C12—C11	116.5 (6)
C10—N2—Cu1	124.7 (6)	C4—C12—C11	119.9 (8)
C11—N2—Cu1	116.1 (5)	F2—C13—F3	106.2 (7)
N1—C1—C2	123.2 (9)	F2—C13—F1	104.0 (7)
N1—C1—H1	118.4	F3—C13—F1	103.8 (7)
C2—C1—H1	118.4	F2—C13—Cu1	116.5 (6)

C3—C2—C1	118.5 (9)	F3—C13—Cu1	114.3 (6)
C3—C2—H2	120.8	F1—C13—Cu1	110.9 (5)
C1—C2—H2	120.8	F7—C14—F8	106.1 (7)
C2—C3—C4	121.1 (8)	F7—C14—F9	102.8 (7)
C2—C3—H3	119.5	F8—C14—F9	103.3 (6)
C4—C3—H3	119.5	F7—C14—Cu1	118.3 (6)
C12—C4—C3	116.6 (9)	F8—C14—Cu1	112.0 (6)
C12—C4—C5	118.3 (9)	F9—C14—Cu1	112.9 (5)
C3—C4—C5	125.0 (9)	F5—C15—F4	93.0 (9)
C6—C5—C4	121.4 (9)	F5—C15—F6	104.0 (8)
C6—C5—H5	119.3	F4—C15—F6	116.2 (10)
C4—C5—H5	119.3	F5—C15—F4A	116.5 (10)
C5—C6—C7	121.8 (10)	F4—C15—F4A	27.0 (7)
C5—C6—H6	119.1	F6—C15—F4A	95.9 (8)
C7—C6—H6	119.1	F5—C15—Cu1	118.6 (7)
C8—C7—C11	116.8 (9)	F4—C15—Cu1	108.3 (8)
C8—C7—C6	124.9 (10)	F6—C15—Cu1	115.1 (7)
C11—C7—C6	118.3 (10)	F4A—C15—Cu1	104.8 (7)

(2) Complex **2**



Some disorders of the fluorine atoms were observed in the crystal structure of complex **2**.

Crystal data for complex ***2***

$C_{52}H_{38}Cu_2F_{12}N_2P_2$•$CHCl_3$	
M_r = 1227.23	D_x = 1.580 Mg m^{-3}
Monoclinic, *P*2$_1$/*n*	Melting point: ? K
Hall symbol: -P 2yn	Mo *K*α radiation, λ = 0.71073 Å
a = 14.4553 (12) Å	Cell parameters from 9023 reflections
b = 19.5245 (15) Å	θ = 2.5–29.7°
c = 18.3344 (15) Å	μ = 1.13 mm^{-1}
β = 94.601 (2)°	*T* = 273 K
V = 5157.9 (7) Å^3	Block, yellow
Z = 4	0.20 × 0.15 × 0.10 mm
F(000) = 2472	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters

(Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.62946 (4)	0.56005 (3)	0.29358 (3)	0.0274 (2)	
Cu2	0.88867 (5)	0.38884 (4)	0.71689 (4)	0.0400 (2)	
P1	0.58315 (9)	0.53579 (7)	0.17614 (7)	0.0289 (3)	
P2	0.68626 (9)	0.66245 (7)	0.33057 (7)	0.0283 (3)	
N1	0.7014 (3)	0.4784 (2)	0.3440 (2)	0.0303 (9)	
N2	0.5250 (3)	0.5194 (2)	0.3545 (3)	0.0319 (9)	
C1	0.4759 (4)	0.4865 (3)	0.1728 (3)	0.0347 (11)	
C2	0.4766 (4)	0.4262 (3)	0.2137 (3)	0.0401 (13)	
H2	0.5319	0.4106	0.2374	0.048*	
C3	0.3954 (5)	0.3893 (3)	0.2191 (4)	0.0518 (17)	
H3	0.3961	0.3498	0.2474	0.062*	
C4	0.3153 (5)	0.4110 (4)	0.1833 (6)	0.069 (2)	
H4	0.2614	0.3854	0.1862	0.082*	
C5	0.3123 (5)	0.4707 (4)	0.1424 (6)	0.077 (3)	
H5	0.2565	0.4858	0.1191	0.093*	
C6	0.3945 (4)	0.5085 (4)	0.1364 (5)	0.0543 (17)	
H6	0.3936	0.5480	0.1080	0.065*	
C7	0.6609 (4)	0.4843 (3)	0.1255 (3)	0.0324 (11)	
C8	0.6298 (5)	0.4320 (3)	0.0777 (4)	0.0459 (14)	
H8	0.5671	0.4206	0.0728	0.055*	
C9	0.6922 (6)	0.3970 (4)	0.0375 (4)	0.0555 (17)	
H9	0.6709	0.3621	0.0060	0.067*	
C10	0.7849 (5)	0.4133 (4)	0.0439 (4)	0.0545 (17)	
H10	0.8260	0.3905	0.0158	0.065*	
C11	0.8170 (5)	0.4646 (4)	0.0928 (4)	0.0518 (16)	
H11	0.8800	0.4750	0.0982	0.062*	

C12	0.7560 (4)	0.4998 (3)	0.1332 (4)	0.0417 (13)	
H12	0.7779	0.5338	0.1655	0.050*	
C13	0.5566 (4)	0.6092 (3)	0.1155 (3)	0.0336 (11)	
C14	0.5106 (5)	0.6642 (3)	0.1445 (4)	0.0463 (14)	
H14	0.4934	0.6619	0.1922	0.056*	
C15	0.4902 (5)	0.7225 (4)	0.1028 (5)	0.0584 (18)	
H15	0.4570	0.7582	0.1218	0.070*	
C16	0.5196 (5)	0.7273 (4)	0.0325 (4)	0.0552 (18)	
H16	0.5080	0.7668	0.0048	0.066*	
C17	0.5658 (5)	0.6730 (4)	0.0047 (4)	0.0553 (17)	
H17	0.5850	0.6757	−0.0424	0.066*	
C18	0.5844 (4)	0.6143 (3)	0.0458 (3)	0.0413 (13)	
H18	0.6160	0.5781	0.0260	0.050*	
C19	0.7841 (4)	0.6950 (3)	0.2840 (3)	0.0317 (11)	
C20	0.7769 (4)	0.6944 (3)	0.2086 (3)	0.0403 (13)	
H20	0.7240	0.6765	0.1833	0.048*	
C21	0.8480 (5)	0.7205 (4)	0.1698 (4)	0.0532 (17)	
H21	0.8418	0.7204	0.1190	0.064*	
C22	0.9272 (5)	0.7464 (4)	0.2060 (5)	0.0583 (19)	
H22	0.9746	0.7637	0.1800	0.070*	
C23	0.9356 (5)	0.7465 (4)	0.2818 (5)	0.0578 (19)	
H23	0.9894	0.7631	0.3068	0.069*	
C24	0.8635 (4)	0.7216 (3)	0.3208 (4)	0.0459 (15)	
H24	0.8689	0.7229	0.3717	0.055*	
C25	0.6026 (4)	0.7328 (3)	0.3194 (3)	0.0340 (11)	
C26	0.5107 (4)	0.7189 (3)	0.3312 (4)	0.0457 (15)	
H26	0.4947	0.6756	0.3473	0.055*	
C27	0.4430 (5)	0.7679 (4)	0.3196 (5)	0.0590 (19)	

H27	0.3817	0.7575	0.3272	0.071*	
C28	0.4655 (5)	0.8327 (4)	0.2968 (4)	0.0542 (17)	
H28	0.4199	0.8659	0.2879	0.065*	
C29	0.5572 (5)	0.8471 (3)	0.2873 (4)	0.0557 (17)	
H29	0.5734	0.8909	0.2731	0.067*	
C30	0.6247 (4)	0.7985 (3)	0.2984 (4)	0.0437 (14)	
H30	0.6860	0.8096	0.2918	0.052*	
C31	0.7286 (4)	0.6656 (3)	0.4267 (3)	0.0347 (12)	
C32	0.7911 (4)	0.6158 (3)	0.4533 (4)	0.0452 (14)	
H32	0.8101	0.5822	0.4218	0.054*	
C33	0.8254 (6)	0.6151 (4)	0.5261 (4)	0.063 (2)	
H33	0.8683	0.5821	0.5430	0.075*	
C34	0.7955 (7)	0.6640 (5)	0.5732 (4)	0.074 (3)	
H34	0.8161	0.6628	0.6225	0.089*	
C35	0.7355 (7)	0.7144 (5)	0.5473 (5)	0.073 (3)	
H35	0.7170	0.7480	0.5791	0.088*	
C36	0.7020 (5)	0.7158 (4)	0.4744 (4)	0.0513 (16)	
H36	0.6616	0.7505	0.4573	0.062*	
C37	0.7891 (4)	0.4587 (3)	0.3391 (3)	0.0402 (13)	
H37	0.8255	0.4834	0.3087	0.048*	
C38	0.8285 (5)	0.4031 (4)	0.3773 (4)	0.0516 (16)	
H38	0.8899	0.3909	0.3725	0.062*	
C39	0.7751 (5)	0.3662 (3)	0.4224 (4)	0.0490 (15)	
H39	0.8004	0.3289	0.4485	0.059*	
C40	0.6837 (5)	0.3849 (3)	0.4288 (3)	0.0397 (13)	
C41	0.6233 (6)	0.3482 (3)	0.4730 (4)	0.0530 (17)	
H41	0.6459	0.3107	0.5002	0.064*	
C42	0.5342 (5)	0.3674 (3)	0.4757 (4)	0.0518 (16)	

H42	0.4960	0.3419	0.5039	0.062*	
C43	0.4965 (4)	0.4256 (3)	0.4366 (3)	0.0409 (13)	
C44	0.4040 (5)	0.4466 (4)	0.4374 (4)	0.0513 (17)	
H44	0.3636	0.4231	0.4654	0.062*	
C45	0.3742 (4)	0.5011 (3)	0.3974 (4)	0.0513 (17)	
H45	0.3127	0.5153	0.3974	0.062*	
C46	0.4353 (4)	0.5363 (3)	0.3561 (4)	0.0405 (13)	
H46	0.4129	0.5734	0.3282	0.049*	
C47	0.5545 (4)	0.4639 (3)	0.3936 (3)	0.0307 (11)	
C48	0.6491 (4)	0.4425 (2)	0.3889 (3)	0.0300 (11)	
C49	0.8224 (6)	0.3259 (5)	0.6459 (5)	0.071 (2)	
C50	0.9308 (7)	0.4407 (6)	0.6340 (7)	0.091 (3)	
C51	0.9683 (7)	0.4402 (4)	0.7835 (7)	0.086 (3)	
C52	0.8212 (7)	0.3498 (5)	0.7918 (5)	0.074 (2)	
C53	0.9105 (11)	0.6208 (7)	0.9993 (9)	0.119 (5)	
H53	0.9046	0.6033	1.0488	0.143*	
Cl1	0.9982 (2)	0.68306 (18)	1.00929 (18)	0.0999 (9)	
Cl2	0.8040 (2)	0.6587 (2)	0.9735 (2)	0.1203 (12)	
Cl3	0.9323 (4)	0.5563 (3)	0.9528 (4)	0.173 (2)	
F1	0.8095 (4)	0.2626 (2)	0.6736 (4)	0.101 (2)	
F4	0.8653 (5)	0.4465 (4)	0.5773 (3)	0.109 (2)	
F9	0.9953 (6)	0.4077 (3)	0.8474 (4)	0.115 (3)	
F10	0.8158 (7)	0.3893 (4)	0.8525 (4)	0.132 (3)	
F12	0.7316 (4)	0.3379 (4)	0.7754 (5)	0.113 (2)	
F2	0.7479 (7)	0.3521 (5)	0.6101 (6)	0.059 (2)*	0.50
F3	0.8896 (9)	0.3232 (6)	0.5865 (6)	0.079 (3)*	0.50
F5	0.9440 (7)	0.5154 (5)	0.6616 (6)	0.066 (2)*	0.50
F6	1.0157 (8)	0.4328 (6)	0.6201 (6)	0.076 (3)*	0.50

F7	0.9229 (7)	0.4985 (5)	0.8164 (6)	0.069 (2)*	0.50
F8	1.0450 (8)	0.4633 (6)	0.7713 (6)	0.072 (3)*	0.50
F11	0.8449 (7)	0.2824 (5)	0.8077 (6)	0.064 (2)*	0.50
F2A	0.7275 (7)	0.3435 (5)	0.6368 (6)	0.064 (2)*	0.50
F3A	0.8545 (8)	0.3053 (6)	0.5896 (6)	0.067 (3)*	0.50
F5A	0.9653 (10)	0.4925 (8)	0.6330 (8)	0.098 (4)*	0.50
F6A	0.9945 (9)	0.3966 (7)	0.5930 (7)	0.095 (3)*	0.50
F7A	0.9554 (9)	0.5035 (7)	0.7850 (8)	0.092 (3)*	0.50
F8A	1.0651 (9)	0.4438 (6)	0.7440 (7)	0.080 (3)*	0.50
F11A	0.8713 (8)	0.2969 (6)	0.8308 (7)	0.073 (3)*	0.50

Geometric parameters (Å, °)

Cu1—N1	2.079 (4)	C26—C27	1.374 (10)
Cu1—N2	2.104 (4)	C26—H26	0.9300
Cu1—P2	2.2455 (14)	C27—C28	1.379 (11)
Cu1—P1	2.2534 (15)	C27—H27	0.9300
Cu2—C51	1.896 (9)	C28—C29	1.379 (10)
Cu2—C52	1.905 (8)	C28—H28	0.9300
Cu2—C50	1.962 (10)	C29—C30	1.364 (9)
Cu2—C49	1.980 (9)	C29—H29	0.9300
P1—C7	1.817 (6)	C30—H30	0.9300
P1—C1	1.822 (5)	C31—C36	1.389 (8)
P1—C13	1.835 (6)	C31—C32	1.389 (9)
P2—C31	1.819 (6)	C32—C33	1.385 (10)
P2—C19	1.825 (5)	C32—H32	0.9300
P2—C25	1.831 (6)	C33—C34	1.380 (14)
N1—C37	1.335 (7)	C33—H33	0.9300

N1—C48	1.358 (7)	C34—C35	1.371 (14)
N2—C46	1.340 (7)	C34—H34	0.9300
N2—C47	1.350 (7)	C35—C36	1.385 (12)
C1—C6	1.374 (9)	C35—H35	0.9300
C1—C2	1.396 (8)	C36—H36	0.9300
C2—C3	1.387 (9)	C37—C38	1.390 (9)
C2—H2	0.9300	C37—H37	0.9300
C3—C4	1.353 (11)	C38—C39	1.379 (10)
C3—H3	0.9300	C38—H38	0.9300
C4—C5	1.385 (13)	C39—C40	1.385 (10)
C4—H4	0.9300	C39—H39	0.9300
C5—C6	1.411 (10)	C40—C48	1.410 (8)
C5—H5	0.9300	C40—C41	1.431 (9)
C6—H6	0.9300	C41—C42	1.346 (11)
C7—C8	1.396 (8)	C41—H41	0.9300
C7—C12	1.403 (8)	C42—C43	1.428 (10)
C8—C9	1.389 (10)	C42—H42	0.9300
C8—H8	0.9300	C43—C44	1.400 (10)
C9—C10	1.374 (11)	C43—C47	1.411 (8)
C9—H9	0.9300	C44—C45	1.343 (11)
C10—C11	1.399 (11)	C44—H44	0.9300
C10—H10	0.9300	C45—C46	1.391 (9)
C11—C12	1.379 (9)	C45—H45	0.9300
C11—H11	0.9300	C46—H46	0.9300
C12—H12	0.9300	C47—C48	1.438 (8)
C13—C18	1.375 (9)	C49—F3A	1.234 (14)
C13—C14	1.390 (8)	C49—F2	1.318 (12)
C14—C15	1.390 (10)	C49—F1	1.356 (11)

C14—H14	0.9300	C49—F2A	1.410 (13)
C15—C16	1.392 (12)	C49—F3	1.518 (16)
C15—H15	0.9300	C50—F5A	1.129 (16)
C16—C17	1.373 (11)	C50—F6	1.284 (14)
C16—H16	0.9300	C50—F4	1.354 (13)
C17—C18	1.386 (9)	C50—F6A	1.505 (18)
C17—H17	0.9300	C50—F5	1.550 (17)
C18—H18	0.9300	C51—F8	1.234 (15)
C19—C20	1.379 (8)	C51—F7A	1.250 (15)
C19—C24	1.385 (8)	C51—F9	1.362 (12)
C20—C21	1.392 (9)	C51—F7	1.467 (15)
C20—H20	0.9300	C51—F8A	1.627 (18)
C21—C22	1.372 (11)	C52—F12	1.326 (12)
C21—H21	0.9300	C52—F10	1.362 (12)
C22—C23	1.384 (12)	C52—F11	1.386 (13)
C22—H22	0.9300	C52—F11A	1.422 (14)
C23—C24	1.397 (9)	C53—Cl3	1.567 (15)
C23—H23	0.9300	C53—Cl2	1.739 (14)
C24—H24	0.9300	C53—Cl1	1.755 (15)
C25—C30	1.384 (8)	C53—H53	0.9800
C25—C26	1.390 (8)		

N1—Cu1—N2	80.22 (18)	C29—C30—H30	119.7
N1—Cu1—P2	112.98 (13)	C25—C30—H30	119.7
N2—Cu1—P2	115.85 (12)	C36—C31—C32	118.6 (6)
N1—Cu1—P1	111.31 (13)	C36—C31—P2	123.0 (5)
N2—Cu1—P1	104.88 (13)	C32—C31—P2	118.4 (4)
P2—Cu1—P1	123.31 (6)	C33—C32—C31	121.2 (7)
C51—Cu2—C52	93.8 (5)	C33—C32—H32	119.4

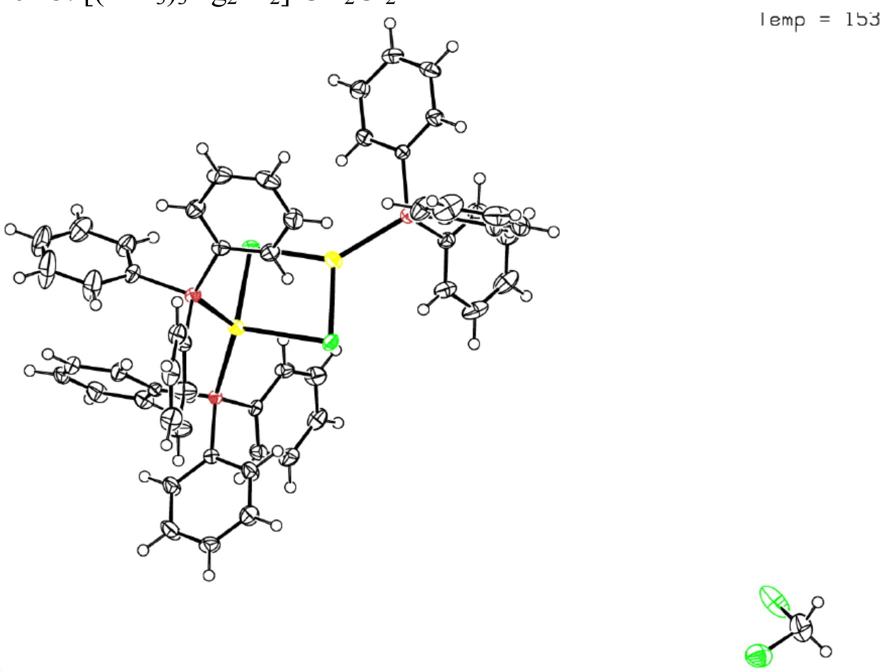
C51—Cu2—C50	90.9 (5)	C31—C32—H32	119.4
C52—Cu2—C50	166.5 (4)	C34—C33—C32	119.3 (8)
C51—Cu2—C49	171.1 (4)	C34—C33—H33	120.3
C52—Cu2—C49	88.7 (4)	C32—C33—H33	120.3
C50—Cu2—C49	88.6 (5)	C35—C34—C33	120.1 (7)
C7—P1—C1	104.5 (3)	C35—C34—H34	119.9
C7—P1—C13	103.3 (3)	C33—C34—H34	119.9
C1—P1—C13	104.8 (3)	C34—C35—C36	120.7 (8)
C7—P1—Cu1	117.14 (18)	C34—C35—H35	119.6
C1—P1—Cu1	109.27 (19)	C36—C35—H35	119.6
C13—P1—Cu1	116.51 (18)	C35—C36—C31	120.0 (8)
C31—P2—C19	103.2 (2)	C35—C36—H36	120.0
C31—P2—C25	104.5 (3)	C31—C36—H36	120.0
C19—P2—C25	102.5 (2)	N1—C37—C38	123.0 (6)
C31—P2—Cu1	114.15 (18)	N1—C37—H37	118.5
C19—P2—Cu1	116.57 (18)	C38—C37—H37	118.5
C25—P2—Cu1	114.32 (18)	C39—C38—C37	119.0 (6)
C37—N1—C48	118.1 (5)	C39—C38—H38	120.5
C37—N1—Cu1	129.4 (4)	C37—C38—H38	120.5
C48—N1—Cu1	112.5 (3)	C38—C39—C40	119.8 (6)
C46—N2—C47	116.8 (5)	C38—C39—H39	120.1
C46—N2—Cu1	131.0 (4)	C40—C39—H39	120.1
C47—N2—Cu1	112.0 (3)	C39—C40—C48	117.9 (6)
C6—C1—C2	119.6 (5)	C39—C40—C41	123.0 (6)
C6—C1—P1	123.0 (5)	C48—C40—C41	119.1 (6)
C2—C1—P1	117.2 (4)	C42—C41—C40	120.6 (6)
C3—C2—C1	120.4 (6)	C42—C41—H41	119.7
C3—C2—H2	119.8	C40—C41—H41	119.7

C1—C2—H2	119.8	C41—C42—C43	122.1 (6)
C4—C3—C2	120.0 (7)	C41—C42—H42	119.0
C4—C3—H3	120.0	C43—C42—H42	119.0
C2—C3—H3	120.0	C44—C43—C47	117.4 (6)
C3—C4—C5	120.9 (6)	C44—C43—C42	123.7 (6)
C3—C4—H4	119.5	C47—C43—C42	118.9 (6)
C5—C4—H4	119.5	C45—C44—C43	119.5 (6)
C4—C5—C6	119.5 (7)	C45—C44—H44	120.3
C4—C5—H5	120.2	C43—C44—H44	120.3
C6—C5—H5	120.2	C44—C45—C46	119.9 (6)
C1—C6—C5	119.5 (7)	C44—C45—H45	120.1
C1—C6—H6	120.3	C46—C45—H45	120.1
C5—C6—H6	120.3	N2—C46—C45	123.3 (6)
C8—C7—C12	118.9 (5)	N2—C46—H46	118.3
C8—C7—P1	122.9 (4)	C45—C46—H46	118.3
C12—C7—P1	118.1 (4)	N2—C47—C43	123.1 (5)
C9—C8—C7	120.2 (6)	N2—C47—C48	117.6 (5)
C9—C8—H8	119.9	C43—C47—C48	119.2 (5)
C7—C8—H8	119.9	N1—C48—C40	122.3 (5)
C10—C9—C8	120.8 (6)	N1—C48—C47	117.6 (5)
C10—C9—H9	119.6	C40—C48—C47	120.0 (5)
C8—C9—H9	119.6	F3A—C49—F2	93.2 (9)
C9—C10—C11	119.4 (6)	F3A—C49—F1	95.0 (9)
C9—C10—H10	120.3	F2—C49—F1	114.1 (9)
C11—C10—H10	120.3	F3A—C49—F2A	114.1 (9)
C12—C11—C10	120.5 (6)	F2—C49—F2A	25.8 (5)
C12—C11—H11	119.8	F1—C49—F2A	96.0 (8)
C10—C11—H11	119.8	F3A—C49—F3	23.3 (7)

C11—C12—C7	120.2 (6)	F2—C49—F3	101.5 (9)
C11—C12—H12	119.9	F1—C49—F3	110.6 (8)
C7—C12—H12	119.9	F2A—C49—F3	126.5 (9)
C18—C13—C14	118.9 (5)	F3A—C49—Cu2	123.9 (9)
C18—C13—P1	123.9 (4)	F2—C49—Cu2	114.8 (7)
C14—C13—P1	117.1 (5)	F1—C49—Cu2	113.2 (6)
C15—C14—C13	120.6 (6)	F2A—C49—Cu2	110.0 (7)
C15—C14—H14	119.7	F3—C49—Cu2	100.9 (7)
C13—C14—H14	119.7	F5A—C50—F6	70.9 (10)
C14—C15—C16	119.9 (7)	F5A—C50—F4	101.2 (11)
C14—C15—H15	120.1	F6—C50—F4	118.5 (11)
C16—C15—H15	120.1	F5A—C50—F6A	102.4 (12)
C17—C16—C15	119.0 (6)	F6—C50—F6A	36.7 (7)
C17—C16—H16	120.5	F4—C50—F6A	94.7 (10)
C15—C16—H16	120.5	F5A—C50—F5	28.2 (9)
C16—C17—C18	121.1 (7)	F6—C50—F5	94.7 (9)
C16—C17—H17	119.5	F4—C50—F5	103.4 (8)
C18—C17—H17	119.5	F6A—C50—F5	129.5 (9)
C13—C18—C17	120.5 (6)	F5A—C50—Cu2	129.8 (13)
C13—C18—H18	119.8	F6—C50—Cu2	117.0 (8)
C17—C18—H18	119.8	F4—C50—Cu2	113.4 (7)
C20—C19—C24	119.0 (5)	F6A—C50—Cu2	109.4 (8)
C20—C19—P2	117.8 (4)	F5—C50—Cu2	105.7 (8)
C24—C19—P2	123.1 (4)	F8—C51—F7A	77.3 (10)
C19—C20—C21	120.6 (6)	F8—C51—F9	97.3 (9)
C19—C20—H20	119.7	F7A—C51—F9	118.3 (11)
C21—C20—H20	119.7	F8—C51—F7	103.3 (9)
C22—C21—C20	120.6 (7)	F7A—C51—F7	32.0 (7)

C22—C21—H21	119.7	F9—C51—F7	96.5 (10)
C20—C21—H21	119.7	F8—C51—F8A	24.0 (7)
C21—C22—C23	119.2 (6)	F7A—C51—F8A	95.9 (11)
C21—C22—H22	120.4	F9—C51—F8A	101.8 (8)
C23—C22—H22	120.4	F7—C51—F8A	125.3 (9)
C22—C23—C24	120.3 (6)	F8—C51—Cu2	125.7 (11)
C22—C23—H23	119.9	F7A—C51—Cu2	117.0 (9)
C24—C23—H23	119.9	F9—C51—Cu2	115.1 (6)
C19—C24—C23	120.3 (6)	F7—C51—Cu2	114.0 (7)
C19—C24—H24	119.9	F8A—C51—Cu2	103.6 (8)
C23—C24—H24	119.9	F12—C52—F10	99.5 (8)
C30—C25—C26	118.0 (5)	F12—C52—F11	95.8 (8)
C30—C25—P2	124.2 (4)	F10—C52—F11	113.3 (8)
C26—C25—P2	117.8 (4)	F12—C52—F11A	115.8 (9)
C27—C26—C25	121.1 (6)	F10—C52—F11A	93.4 (8)
C27—C26—H26	119.4	F11—C52—F11A	25.4 (6)
C25—C26—H26	119.4	F12—C52—Cu2	117.0 (7)
C26—C27—C28	120.2 (6)	F10—C52—Cu2	115.4 (7)
C26—C27—H27	119.9	F11—C52—Cu2	113.5 (7)
C28—C27—H27	119.9	F11A—C52—Cu2	112.6 (7)
C27—C28—C29	118.6 (6)	Cl3—C53—Cl2	114.0 (9)
C27—C28—H28	120.7	Cl3—C53—Cl1	116.0 (11)
C29—C28—H28	120.7	Cl2—C53—Cl1	110.5 (7)
C30—C29—C28	121.5 (6)	Cl3—C53—H53	105.1
C30—C29—H29	119.3	Cl2—C53—H53	105.1
C28—C29—H29	119.3	Cl1—C53—H53	105.1
C29—C30—C25	120.5 (6)		

(3) Complex **5**: $[(PPh_3)_3Ag_2Br_2]\cdot CH_2Cl_2$



Crystal data

$C_{55}H_{47}Ag_2Br_2Cl_2P_3$	complex 4 with a CH2Cl2 solvent molecule
M_r = 1247.30	D_x = 1.604 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: -P 2ybc	Mo *Kα* radiation, λ = 0.71073 Å
a = 16.3137 (7) Å	Cell parameters from 9685 reflections
b = 18.3199 (9) Å	θ = 2.5–28.2°
c = 18.5850 (9) Å	μ = 2.54 mm^{-1}
β = 111.592 (1)°	*T* = 153 K
V = 5164.6 (4) Å^3	Block, colourless
Z = 4	0.44 × 0.40 × 0.30 mm
F(000) = 2480	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$

Ag1	0.672935 (10)	0.925727 (9)	0.805631 (9)	0.01888 (4)
Ag2	0.839837 (11)	0.912236 (10)	0.744962 (10)	0.02504 (5)
Br1	0.755855 (15)	0.802587 (12)	0.779016 (13)	0.02246 (5)
Br2	0.753992 (14)	1.031434 (12)	0.744515 (14)	0.02270 (5)
Cl1	0.77902 (5)	0.01349 (4)	0.54962 (5)	0.04968 (19)
Cl2	0.80528 (5)	0.11328 (6)	0.43857 (6)	0.0698 (3)
P1	0.51851 (3)	0.91432 (3)	0.71880 (3)	0.01450 (11)
P2	0.73216 (4)	0.94584 (3)	0.94520 (3)	0.01727 (11)
P3	0.96462 (4)	0.88804 (3)	0.71008 (3)	0.01871 (12)
C1	0.50120 (14)	0.90296 (11)	0.61694 (12)	0.0164 (4)
C2	0.56932 (15)	0.92298 (12)	0.59311 (13)	0.0226 (5)
H2	0.6229	0.9412	0.6298	0.027*
C3	0.55944 (17)	0.91648 (14)	0.51613 (14)	0.0308 (6)
H3	0.6068	0.9294	0.5005	0.037*
C4	0.48124 (17)	0.89140 (13)	0.46199 (14)	0.0295 (6)
H4	0.4742	0.8883	0.4090	0.035*
C5	0.41368 (16)	0.87097 (13)	0.48515 (14)	0.0283 (5)
H5	0.3600	0.8532	0.4481	0.034*
C6	0.42332 (15)	0.87607 (13)	0.56222 (13)	0.0244 (5)
H6	0.3766	0.8612	0.5778	0.029*
C7	0.45797 (14)	0.99637 (11)	0.72449 (13)	0.0178 (4)
C8	0.39856 (15)	1.03133 (13)	0.66069 (15)	0.0264 (5)
H8	0.3869	1.0124	0.6103	0.032*
C9	0.35584 (17)	1.09422 (14)	0.67028 (17)	0.0343 (6)
H9	0.3159	1.1186	0.6262	0.041*
C10	0.37108 (16)	1.12135 (13)	0.74324 (18)	0.0340 (6)
H10	0.3412	1.1640	0.7493	0.041*
C11	0.42969 (17)	1.08669 (13)	0.80747 (17)	0.0333 (6)

H11	0.4399	1.1051	0.8578	0.040*
C12	0.47345 (16)	1.02500 (13)	0.79802 (14)	0.0265 (5)
H12	0.5147	1.0017	0.8422	0.032*
C13	0.45269 (13)	0.84103 (11)	0.73743 (12)	0.0164 (4)
C14	0.48590 (16)	0.77034 (13)	0.74539 (15)	0.0291 (5)
H14	0.5414	0.7615	0.7413	0.035*
C15	0.43905 (17)	0.71285 (13)	0.75923 (16)	0.0334 (6)
H15	0.4621	0.6647	0.7635	0.040*
C16	0.35952 (16)	0.72453 (13)	0.76683 (15)	0.0295 (5)
H16	0.3276	0.6849	0.7767	0.035*
C17	0.32666 (17)	0.79435 (14)	0.75998 (19)	0.0403 (7)
H17	0.2719	0.8030	0.7655	0.048*
C18	0.37268 (16)	0.85230 (13)	0.74506 (16)	0.0318 (6)
H18	0.3489	0.9002	0.7401	0.038*
C19	0.68865 (14)	0.87720 (12)	0.99227 (13)	0.0198 (5)
C20	0.60999 (17)	0.84316 (14)	0.94906 (15)	0.0331 (6)
H20	0.5805	0.8561	0.8963	0.040*
C21	0.5741 (2)	0.79066 (16)	0.98206 (18)	0.0453 (7)
H21	0.5199	0.7680	0.9520	0.054*
C22	0.6165 (2)	0.77119 (15)	1.05805 (17)	0.0414 (7)
H22	0.5916	0.7352	1.0808	0.050*
C23	0.69494 (19)	0.80390 (14)	1.10113 (15)	0.0347 (6)
H23	0.7246	0.7901	1.1536	0.042*
C24	0.73134 (17)	0.85690 (13)	1.06869 (14)	0.0278 (5)
H24	0.7856	0.8793	1.0990	0.033*
C25	0.85068 (14)	0.93931 (12)	0.99768 (12)	0.0199 (5)
C26	0.89399 (15)	0.88231 (13)	0.97767 (14)	0.0262 (5)
H26	0.8623	0.8507	0.9362	0.031*

C27	0.98355 (16)	0.87119 (15)	1.01792 (15)	0.0337 (6)
H27	1.0126	0.8313	1.0048	0.040*
C28	1.03038 (16)	0.91813 (15)	1.07701 (14)	0.0339 (6)
H28	1.0918	0.9111	1.1041	0.041*
C29	0.98759 (17)	0.97505 (16)	1.09625 (14)	0.0362 (6)
H29	1.0199	1.0074	1.1367	0.043*
C30	0.89776 (16)	0.98607 (14)	1.05734 (14)	0.0294 (5)
H30	0.8688	1.0254	1.0715	0.035*
C31	0.69968 (15)	1.03275 (12)	0.97436 (13)	0.0230 (5)
C32	0.6678 (2)	1.03934 (16)	1.03316 (18)	0.0508 (8)
H32	0.6639	0.9976	1.0620	0.061*
C33	0.6413 (3)	1.10682 (19)	1.0501 (2)	0.0748 (13)
H33	0.6188	1.1110	1.0904	0.090*
C34	0.6473 (2)	1.16778 (17)	1.0094 (2)	0.0591 (9)
H34	0.6300	1.2141	1.0221	0.071*
C35	0.6782 (2)	1.16171 (15)	0.95101 (18)	0.0455 (7)
H35	0.6818	1.2038	0.9224	0.055*
C36	0.70432 (18)	1.09454 (13)	0.93301 (16)	0.0337 (6)
H36	0.7256	1.0907	0.8920	0.040*
C37	0.92970 (14)	0.86194 (12)	0.60896 (13)	0.0218 (5)
C38	0.85169 (16)	0.82279 (13)	0.57658 (15)	0.0305 (6)
H38	0.8176	0.8115	0.6070	0.037*
C39	0.82346 (18)	0.80024 (14)	0.50016 (16)	0.0384 (7)
H39	0.7705	0.7730	0.4786	0.046*
C40	0.8715 (2)	0.81704 (15)	0.45558 (16)	0.0406 (7)
H40	0.8517	0.8018	0.4031	0.049*
C41	0.9487 (2)	0.85602 (17)	0.48707 (16)	0.0447 (7)
H41	0.9821	0.8676	0.4561	0.054*

C42	0.97789 (17)	0.87838 (15)	0.56348 (15)	0.0346 (6)
H42	1.0313	0.9051	0.5848	0.041*
C43	1.03520 (14)	0.81345 (12)	0.76208 (14)	0.0230 (5)
C44	1.06567 (16)	0.75935 (14)	0.72631 (16)	0.0318 (6)
H44	1.0489	0.7597	0.6716	0.038*
C45	1.12050 (18)	0.70456 (15)	0.76967 (19)	0.0408 (7)
H45	1.1406	0.6673	0.7447	0.049*
C46	1.14551 (18)	0.70429 (15)	0.8484 (2)	0.0468 (8)
H46	1.1840	0.6673	0.8780	0.056*
C47	1.1153 (2)	0.75738 (17)	0.88496 (19)	0.0522 (9)
H47	1.1327	0.7568	0.9397	0.063*
C48	1.05948 (19)	0.81149 (15)	0.84194 (15)	0.0380 (6)
H48	1.0377	0.8475	0.8672	0.046*
C49	1.04025 (14)	0.96375 (12)	0.72028 (12)	0.0186 (4)
C50	1.00609 (15)	1.03419 (12)	0.70952 (13)	0.0231 (5)
H50	0.9451	1.0416	0.6989	0.028*
C51	1.06014 (16)	1.09348 (13)	0.71415 (15)	0.0285 (5)
H51	1.0362	1.1414	0.7064	0.034*
C52	1.14885 (16)	1.08309 (13)	0.72997 (14)	0.0290 (5)
H52	1.1858	1.1239	0.7324	0.035*
C53	1.18394 (16)	1.01391 (14)	0.74220 (16)	0.0339 (6)
H53	1.2452	1.0070	0.7539	0.041*
C54	1.13015 (15)	0.95430 (14)	0.73758 (15)	0.0293 (5)
H54	1.1547	0.9066	0.7463	0.035*
C55	0.8296 (2)	0.0270 (2)	0.4828 (2)	0.0661 (10)
H55A	0.8096	−0.0113	0.4424	0.079*
H55B	0.8942	0.0221	0.5093	0.079*

Geometric parameters (Å, °)

Ag1—P2	2.4399 (6)	C23—C24	1.387 (3)
Ag1—P1	2.4500 (6)	C23—H23	0.9500
Ag1—Br1	2.7670 (3)	C24—H24	0.9500
Ag1—Br2	2.8097 (3)	C25—C26	1.386 (3)
Ag1—Ag2	3.3174 (3)	C25—C30	1.388 (3)
Ag2—P3	2.3942 (6)	C26—C27	1.390 (3)
Ag2—Br2	2.5925 (3)	C26—H26	0.9500
Ag2—Br1	2.6364 (3)	C27—C28	1.383 (4)
Cl1—C55	1.743 (4)	C27—H27	0.9500
Cl2—C55	1.759 (4)	C28—C29	1.373 (4)
P1—C1	1.820 (2)	C28—H28	0.9500
P1—C7	1.823 (2)	C29—C30	1.390 (4)
P1—C13	1.830 (2)	C29—H29	0.9500
P2—C19	1.818 (2)	C30—H30	0.9500
P2—C25	1.821 (2)	C31—C32	1.378 (4)
P2—C31	1.822 (2)	C31—C36	1.386 (3)
P3—C37	1.816 (2)	C32—C33	1.384 (4)
P3—C43	1.819 (2)	C32—H32	0.9500
P3—C49	1.819 (2)	C33—C34	1.372 (5)
C1—C2	1.388 (3)	C33—H33	0.9500
C1—C6	1.393 (3)	C34—C35	1.359 (4)
C2—C3	1.384 (3)	C34—H34	0.9500
C2—H2	0.9500	C35—C36	1.383 (4)
C3—C4	1.381 (3)	C35—H35	0.9500
C3—H3	0.9500	C36—H36	0.9500
C4—C5	1.374 (4)	C37—C42	1.383 (3)
C4—H4	0.9500	C37—C38	1.390 (3)

C5—C6	1.385 (3)	C38—C39	1.385 (4)
C5—H5	0.9500	C38—H38	0.9500
C6—H6	0.9500	C39—C40	1.369 (4)
C7—C8	1.382 (3)	C39—H39	0.9500
C7—C12	1.397 (3)	C40—C41	1.376 (4)
C8—C9	1.392 (3)	C40—H40	0.9500
C8—H8	0.9500	C41—C42	1.383 (4)
C9—C10	1.378 (4)	C41—H41	0.9500
C9—H9	0.9500	C42—H42	0.9500
C10—C11	1.379 (4)	C43—C44	1.384 (3)
C10—H10	0.9500	C43—C48	1.389 (4)
C11—C12	1.382 (3)	C44—C45	1.388 (4)
C11—H11	0.9500	C44—H44	0.9500
C12—H12	0.9500	C45—C46	1.366 (4)
C13—C18	1.379 (3)	C45—H45	0.9500
C13—C14	1.391 (3)	C46—C47	1.378 (5)
C14—C15	1.380 (3)	C46—H46	0.9500
C14—H14	0.9500	C47—C48	1.384 (4)
C15—C16	1.373 (3)	C47—H47	0.9500
C15—H15	0.9500	C48—H48	0.9500
C16—C17	1.374 (4)	C49—C50	1.390 (3)
C16—H16	0.9500	C49—C54	1.392 (3)
C17—C18	1.386 (3)	C50—C51	1.382 (3)
C17—H17	0.9500	C50—H50	0.9500
C18—H18	0.9500	C51—C52	1.380 (3)
C19—C24	1.383 (3)	C51—H51	0.9500
C19—C20	1.386 (3)	C52—C53	1.375 (4)
C20—C21	1.381 (4)	C52—H52	0.9500

C20—H20	0.9500	C53—C54	1.384 (3)
C21—C22	1.371 (4)	C53—H53	0.9500
C21—H21	0.9500	C54—H54	0.9500
C22—C23	1.373 (4)	C55—H55A	0.9900
C22—H22	0.9500	C55—H55B	0.9900
P2—Ag1—P1	128.464 (19)	C22—C23—C24	120.6 (2)
P2—Ag1—Br1	106.548 (15)	C22—C23—H23	119.7
P1—Ag1—Br1	105.342 (15)	C24—C23—H23	119.7
P2—Ag1—Br2	105.340 (15)	C19—C24—C23	120.0 (2)
P1—Ag1—Br2	108.382 (15)	C19—C24—H24	120.0
Br1—Ag1—Br2	98.968 (9)	C23—C24—H24	120.0
P2—Ag1—Ag2	108.613 (15)	C26—C25—C30	119.5 (2)
P1—Ag1—Ag2	122.916 (14)	C26—C25—P2	116.83 (17)
Br1—Ag1—Ag2	50.365 (6)	C30—C25—P2	123.62 (18)
Br2—Ag1—Ag2	49.210 (6)	C25—C26—C27	120.3 (2)
P3—Ag2—Br2	131.852 (17)	C25—C26—H26	119.8
P3—Ag2—Br1	119.516 (16)	C27—C26—H26	119.8
Br2—Ag2—Br1	108.344 (9)	C28—C27—C26	120.0 (2)
P3—Ag2—Ag1	172.659 (16)	C28—C27—H27	120.0
Br2—Ag2—Ag1	55.137 (6)	C26—C27—H27	120.0
Br1—Ag2—Ag1	53.926 (7)	C29—C28—C27	119.6 (2)
Ag2—Br1—Ag1	75.709 (8)	C29—C28—H28	120.2
Ag2—Br2—Ag1	75.652 (8)	C27—C28—H28	120.2
C1—P1—C7	105.94 (10)	C28—C29—C30	121.0 (2)
C1—P1—C13	103.62 (10)	C28—C29—H29	119.5
C7—P1—C13	103.05 (10)	C30—C29—H29	119.5
C1—P1—Ag1	115.03 (7)	C25—C30—C29	119.6 (2)
C7—P1—Ag1	109.83 (7)	C25—C30—H30	120.2

C13—P1—Ag1	118.08 (7)	C29—C30—H30	120.2
C19—P2—C25	102.84 (10)	C32—C31—C36	118.8 (2)
C19—P2—C31	104.68 (10)	C32—C31—P2	123.3 (2)
C25—P2—C31	105.41 (11)	C36—C31—P2	117.88 (18)
C19—P2—Ag1	109.57 (8)	C31—C32—C33	120.0 (3)
C25—P2—Ag1	119.11 (7)	C31—C32—H32	120.0
C31—P2—Ag1	113.79 (8)	C33—C32—H32	120.0
C37—P3—C43	104.37 (11)	C34—C33—C32	120.7 (3)
C37—P3—C49	104.54 (10)	C34—C33—H33	119.7
C43—P3—C49	104.18 (10)	C32—C33—H33	119.7
C37—P3—Ag2	110.78 (7)	C35—C34—C33	119.7 (3)
C43—P3—Ag2	115.49 (8)	C35—C34—H34	120.1
C49—P3—Ag2	116.25 (7)	C33—C34—H34	120.1
C2—C1—C6	118.9 (2)	C34—C35—C36	120.3 (3)
C2—C1—P1	117.74 (16)	C34—C35—H35	119.9
C6—C1—P1	123.40 (17)	C36—C35—H35	119.9
C3—C2—C1	120.3 (2)	C35—C36—C31	120.5 (3)
C3—C2—H2	119.9	C35—C36—H36	119.7
C1—C2—H2	119.9	C31—C36—H36	119.7
C4—C3—C2	120.4 (2)	C42—C37—C38	118.9 (2)
C4—C3—H3	119.8	C42—C37—P3	122.88 (18)
C2—C3—H3	119.8	C38—C37—P3	118.20 (19)
C5—C4—C3	119.7 (2)	C39—C38—C37	120.3 (3)
C5—C4—H4	120.2	C39—C38—H38	119.9
C3—C4—H4	120.2	C37—C38—H38	119.9
C4—C5—C6	120.4 (2)	C40—C39—C38	120.3 (2)
C4—C5—H5	119.8	C40—C39—H39	119.8
C6—C5—H5	119.8	C38—C39—H39	119.8

C5—C6—C1	120.3 (2)	C39—C40—C41	119.8 (3)
C5—C6—H6	119.8	C39—C40—H40	120.1
C1—C6—H6	119.8	C41—C40—H40	120.1
C8—C7—C12	118.9 (2)	C40—C41—C42	120.4 (3)
C8—C7—P1	123.80 (18)	C40—C41—H41	119.8
C12—C7—P1	117.35 (17)	C42—C41—H41	119.8
C7—C8—C9	120.0 (2)	C37—C42—C41	120.3 (2)
C7—C8—H8	120.0	C37—C42—H42	119.9
C9—C8—H8	120.0	C41—C42—H42	119.9
C10—C9—C8	120.5 (2)	C44—C43—C48	118.9 (2)
C10—C9—H9	119.8	C44—C43—P3	123.51 (19)
C8—C9—H9	119.8	C48—C43—P3	117.58 (18)
C9—C10—C11	120.1 (2)	C43—C44—C45	120.5 (3)
C9—C10—H10	119.9	C43—C44—H44	119.7
C11—C10—H10	119.9	C45—C44—H44	119.7
C10—C11—C12	119.5 (2)	C46—C45—C44	119.9 (3)
C10—C11—H11	120.2	C46—C45—H45	120.0
C12—C11—H11	120.2	C44—C45—H45	120.0
C11—C12—C7	121.0 (2)	C45—C46—C47	120.4 (3)
C11—C12—H12	119.5	C45—C46—H46	119.8
C7—C12—H12	119.5	C47—C46—H46	119.8
C18—C13—C14	118.3 (2)	C46—C47—C48	120.0 (3)
C18—C13—P1	123.57 (17)	C46—C47—H47	120.0
C14—C13—P1	118.08 (16)	C48—C47—H47	120.0
C15—C14—C13	120.7 (2)	C47—C48—C43	120.3 (3)
C15—C14—H14	119.7	C47—C48—H48	119.9
C13—C14—H14	119.7	C43—C48—H48	119.9
C16—C15—C14	120.6 (2)	C50—C49—C54	118.8 (2)

C16—C15—H15	119.7	C50—C49—P3	118.17 (16)
C14—C15—H15	119.7	C54—C49—P3	123.07 (17)
C15—C16—C17	119.1 (2)	C51—C50—C49	120.5 (2)
C15—C16—H16	120.4	C51—C50—H50	119.7
C17—C16—H16	120.4	C49—C50—H50	119.7
C16—C17—C18	120.7 (2)	C52—C51—C50	120.0 (2)
C16—C17—H17	119.7	C52—C51—H51	120.0
C18—C17—H17	119.7	C50—C51—H51	120.0
C13—C18—C17	120.6 (2)	C53—C52—C51	120.2 (2)
C13—C18—H18	119.7	C53—C52—H52	119.9
C17—C18—H18	119.7	C51—C52—H52	119.9
C24—C19—C20	118.9 (2)	C52—C53—C54	120.1 (2)
C24—C19—P2	122.81 (18)	C52—C53—H53	120.0
C20—C19—P2	118.32 (17)	C54—C53—H53	120.0
C21—C20—C19	120.6 (2)	C53—C54—C49	120.4 (2)
C21—C20—H20	119.7	C53—C54—H54	119.8
C19—C20—H20	119.7	C49—C54—H54	119.8
C22—C21—C20	120.2 (3)	Cl1—C55—Cl2	112.08 (18)
C22—C21—H21	119.9	Cl1—C55—H55A	109.2
C20—C21—H21	119.9	Cl2—C55—H55A	109.2
C21—C22—C23	119.7 (2)	Cl1—C55—H55B	109.2
C21—C22—H22	120.2	Cl2—C55—H55B	109.2
C23—C22—H22	120.2	H55A—C55—H55B	107.9
P2—Ag1—Ag2—P3	68.57 (13)	C14—C15—C16—C17	0.4 (4)
P1—Ag1—Ag2—P3	−110.52 (13)	C15—C16—C17—C18	0.4 (4)
Br1—Ag1—Ag2—P3	−27.82 (12)	C14—C13—C18—C17	−0.3 (4)
Br2—Ag1—Ag2—P3	163.05 (13)	P1—C13—C18—C17	−179.3 (2)
P2—Ag1—Ag2—Br2	−94.479 (17)	C16—C17—C18—C13	−0.5 (5)

P1—Ag1—Ag2—Br2	86.423 (18)	C25—P2—C19—C24	28.2 (2)
Br1—Ag1—Ag2—Br2	169.131 (11)	C31—P2—C19—C24	−81.8 (2)
P2—Ag1—Ag2—Br1	96.390 (16)	Ag1—P2—C19—C24	155.81 (17)
P1—Ag1—Ag2—Br1	−82.708 (18)	C25—P2—C19—C20	−150.80 (19)
Br2—Ag1—Ag2—Br1	−169.131 (11)	C31—P2—C19—C20	99.2 (2)
P3—Ag2—Br1—Ag1	176.072 (18)	Ag1—P2—C19—C20	−23.2 (2)
Br2—Ag2—Br1—Ag1	−9.381 (9)	C24—C19—C20—C21	1.0 (4)
P2—Ag1—Br1—Ag2	−100.733 (16)	P2—C19—C20—C21	−180.0 (2)
P1—Ag1—Br1—Ag2	120.294 (15)	C19—C20—C21—C22	−0.5 (5)
Br2—Ag1—Br1—Ag2	8.310 (8)	C20—C21—C22—C23	−0.3 (5)
P3—Ag2—Br2—Ag1	−177.13 (2)	C21—C22—C23—C24	0.6 (4)
Br1—Ag2—Br2—Ag1	9.240 (9)	C20—C19—C24—C23	−0.7 (3)
P2—Ag1—Br2—Ag2	101.562 (16)	P2—C19—C24—C23	−179.67 (18)
P1—Ag1—Br2—Ag2	−118.008 (15)	C22—C23—C24—C19	−0.1 (4)
Br1—Ag1—Br2—Ag2	−8.454 (8)	C19—P2—C25—C26	79.11 (19)
P2—Ag1—P1—C1	177.76 (8)	C31—P2—C25—C26	−171.47 (18)
Br1—Ag1—P1—C1	−55.72 (8)	Ag1—P2—C25—C26	−42.2 (2)
Br2—Ag1—P1—C1	49.44 (8)	C19—P2—C25—C30	−98.4 (2)
Ag2—Ag1—P1—C1	−3.33 (8)	C31—P2—C25—C30	11.0 (2)
P2—Ag1—P1—C7	58.38 (8)	Ag1—P2—C25—C30	140.24 (18)
Br1—Ag1—P1—C7	−175.10 (7)	C30—C25—C26—C27	1.2 (4)
Br2—Ag1—P1—C7	−69.94 (8)	P2—C25—C26—C27	−176.43 (19)
Ag2—Ag1—P1—C7	−122.71 (7)	C25—C26—C27—C28	−1.6 (4)
P2—Ag1—P1—C13	−59.30 (8)	C26—C27—C28—C29	0.9 (4)
Br1—Ag1—P1—C13	67.22 (8)	C27—C28—C29—C30	0.2 (4)
Br2—Ag1—P1—C13	172.38 (8)	C26—C25—C30—C29	−0.1 (4)
Ag2—Ag1—P1—C13	119.61 (8)	P2—C25—C30—C29	177.35 (19)
P1—Ag1—P2—C19	53.46 (8)	C28—C29—C30—C25	−0.6 (4)

Br1—Ag1—P2—C19	−72.59 (8)	C19—P2—C31—C32	13.0 (3)
Br2—Ag1—P2—C19	−177.08 (8)	C25—P2—C31—C32	−95.1 (3)
Ag2—Ag1—P2—C19	−125.57 (8)	Ag1—P2—C31—C32	132.6 (2)
P1—Ag1—P2—C25	171.36 (8)	C19—P2—C31—C36	−164.4 (2)
Br1—Ag1—P2—C25	45.31 (9)	C25—P2—C31—C36	87.5 (2)
Br2—Ag1—P2—C25	−59.17 (9)	Ag1—P2—C31—C36	−44.8 (2)
Ag2—Ag1—P2—C25	−7.67 (9)	C36—C31—C32—C33	−0.2 (5)
P1—Ag1—P2—C31	−63.33 (9)	P2—C31—C32—C33	−177.6 (3)
Br1—Ag1—P2—C31	170.62 (8)	C31—C32—C33—C34	−0.7 (6)
Br2—Ag1—P2—C31	66.13 (9)	C32—C33—C34—C35	1.1 (7)
Ag2—Ag1—P2—C31	117.64 (9)	C33—C34—C35—C36	−0.7 (6)
Br2—Ag2—P3—C37	−91.51 (8)	C34—C35—C36—C31	−0.2 (5)
Br1—Ag2—P3—C37	81.53 (8)	C32—C31—C36—C35	0.6 (4)
Ag1—Ag2—P3—C37	107.21 (14)	P2—C31—C36—C35	178.1 (2)
Br2—Ag2—P3—C43	150.12 (8)	C43—P3—C37—C42	−87.4 (2)
Br1—Ag2—P3—C43	−36.83 (9)	C49—P3—C37—C42	21.8 (2)
Ag1—Ag2—P3—C43	−11.15 (17)	Ag2—P3—C37—C42	147.7 (2)
Br2—Ag2—P3—C49	27.59 (9)	C43—P3—C37—C38	91.7 (2)
Br1—Ag2—P3—C49	−159.36 (8)	C49—P3—C37—C38	−159.20 (18)
Ag1—Ag2—P3—C49	−133.68 (13)	Ag2—P3—C37—C38	−33.3 (2)
C7—P1—C1—C2	102.71 (18)	C42—C37—C38—C39	0.5 (4)
C13—P1—C1—C2	−149.18 (17)	P3—C37—C38—C39	−178.52 (19)
Ag1—P1—C1—C2	−18.81 (19)	C37—C38—C39—C40	−0.8 (4)
C7—P1—C1—C6	−76.6 (2)	C38—C39—C40—C41	0.5 (4)
C13—P1—C1—C6	31.5 (2)	C39—C40—C41—C42	0.0 (5)
Ag1—P1—C1—C6	161.84 (16)	C38—C37—C42—C41	−0.1 (4)
C6—C1—C2—C3	0.3 (3)	P3—C37—C42—C41	179.0 (2)
P1—C1—C2—C3	−179.11 (19)	C40—C41—C42—C37	−0.2 (5)

C1—C2—C3—C4	1.3 (4)	C37—P3—C43—C44	11.5 (2)
C2—C3—C4—C5	−1.7 (4)	C49—P3—C43—C44	−97.9 (2)
C3—C4—C5—C6	0.6 (4)	Ag2—P3—C43—C44	133.35 (19)
C4—C5—C6—C1	0.9 (4)	C37—P3—C43—C48	−168.7 (2)
C2—C1—C6—C5	−1.3 (3)	C49—P3—C43—C48	81.9 (2)
P1—C1—C6—C5	178.00 (18)	Ag2—P3—C43—C48	−46.8 (2)
C1—P1—C7—C8	11.3 (2)	C48—C43—C44—C45	−0.8 (4)
C13—P1—C7—C8	−97.2 (2)	P3—C43—C44—C45	179.01 (19)
Ag1—P1—C7—C8	136.12 (18)	C43—C44—C45—C46	−0.7 (4)
C1—P1—C7—C12	−168.51 (17)	C44—C45—C46—C47	1.2 (4)
C13—P1—C7—C12	82.96 (19)	C45—C46—C47—C48	−0.2 (5)
Ag1—P1—C7—C12	−43.71 (19)	C46—C47—C48—C43	−1.3 (5)
C12—C7—C8—C9	0.5 (3)	C44—C43—C48—C47	1.8 (4)
P1—C7—C8—C9	−179.35 (18)	P3—C43—C48—C47	−178.0 (2)
C7—C8—C9—C10	−1.2 (4)	C37—P3—C49—C50	91.38 (19)
C8—C9—C10—C11	0.7 (4)	C43—P3—C49—C50	−159.35 (18)
C9—C10—C11—C12	0.5 (4)	Ag2—P3—C49—C50	−31.1 (2)
C10—C11—C12—C7	−1.2 (4)	C37—P3—C49—C54	−88.0 (2)
C8—C7—C12—C11	0.7 (3)	C43—P3—C49—C54	21.3 (2)
P1—C7—C12—C11	−179.43 (19)	Ag2—P3—C49—C54	149.53 (18)
C1—P1—C13—C18	−104.5 (2)	C54—C49—C50—C51	1.5 (3)
C7—P1—C13—C18	5.7 (2)	P3—C49—C50—C51	−177.93 (18)
Ag1—P1—C13—C18	126.93 (19)	C49—C50—C51—C52	−0.3 (4)
C1—P1—C13—C14	76.4 (2)	C50—C51—C52—C53	−0.9 (4)
C7—P1—C13—C14	−173.33 (19)	C51—C52—C53—C54	1.0 (4)
Ag1—P1—C13—C14	−52.1 (2)	C52—C53—C54—C49	0.2 (4)
C18—C13—C14—C15	1.1 (4)	C50—C49—C54—C53	−1.4 (4)
P1—C13—C14—C15	−179.8 (2)	P3—C49—C54—C53	178.0 (2)

C13—C14—C15—C16	−1.2 (4)		

5. ^{19}F NMR monitoring of the reaction course

^{19}F NMR monitoring of the reaction of $TMSCF_3$ (3 equiv) with phenCu(PPh_3)Br (1 mmol), AgF (3 equiv) in the presence of 4,4'-difluorobiphenyl (0.5 equiv) as internal standard in CH_2Cl_2 at room temperature. Figures S9, S10 and S11 show the ^{19}F signals for the reaction after 4, 8, and 18 hours respectively.

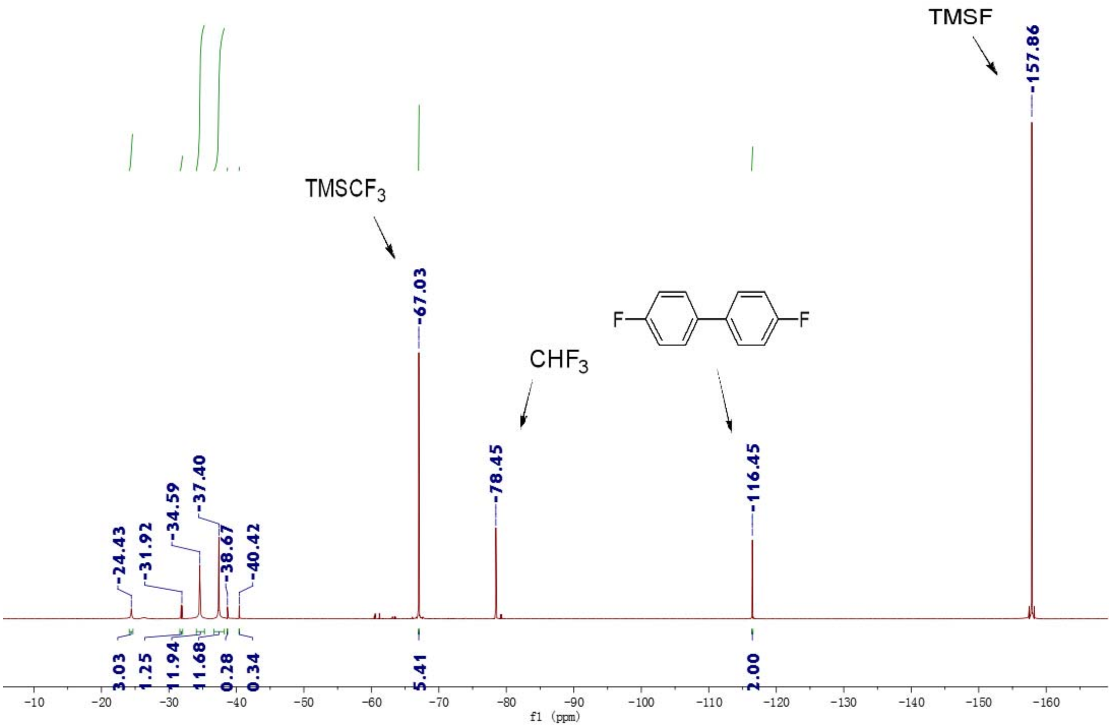


Figure S9. ^{19}F NMR monitoring of the reaction solution after 4 hours.

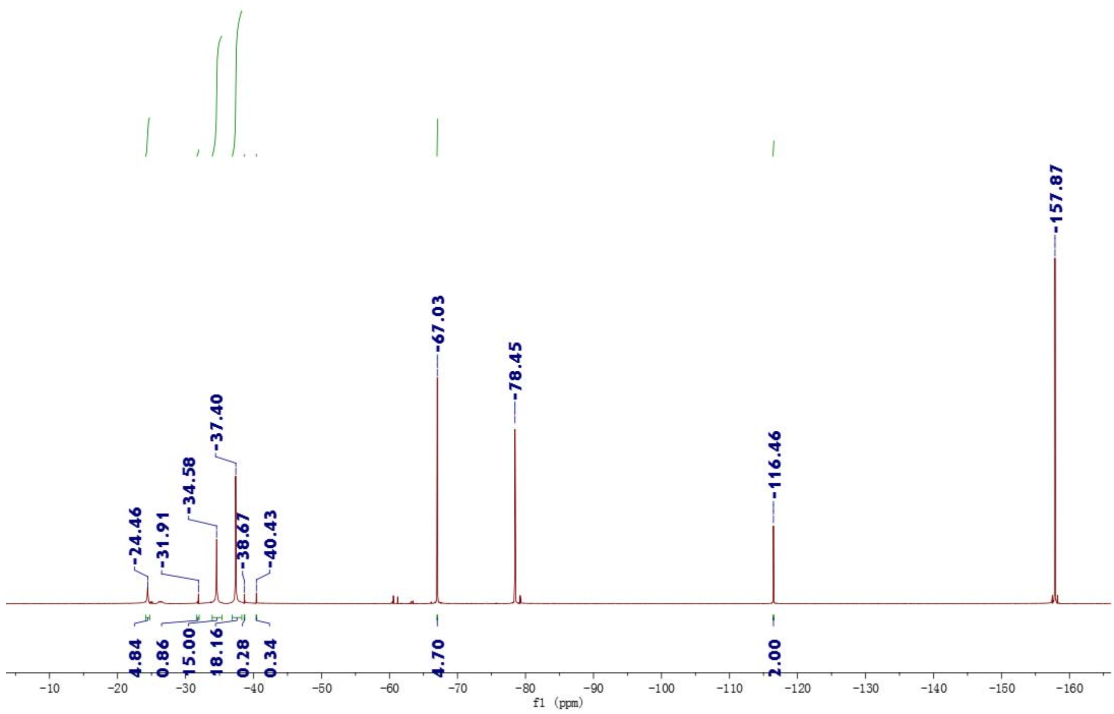


Figure S10. ^{19}F NMR monitoring of the reaction solution after 8 hours.

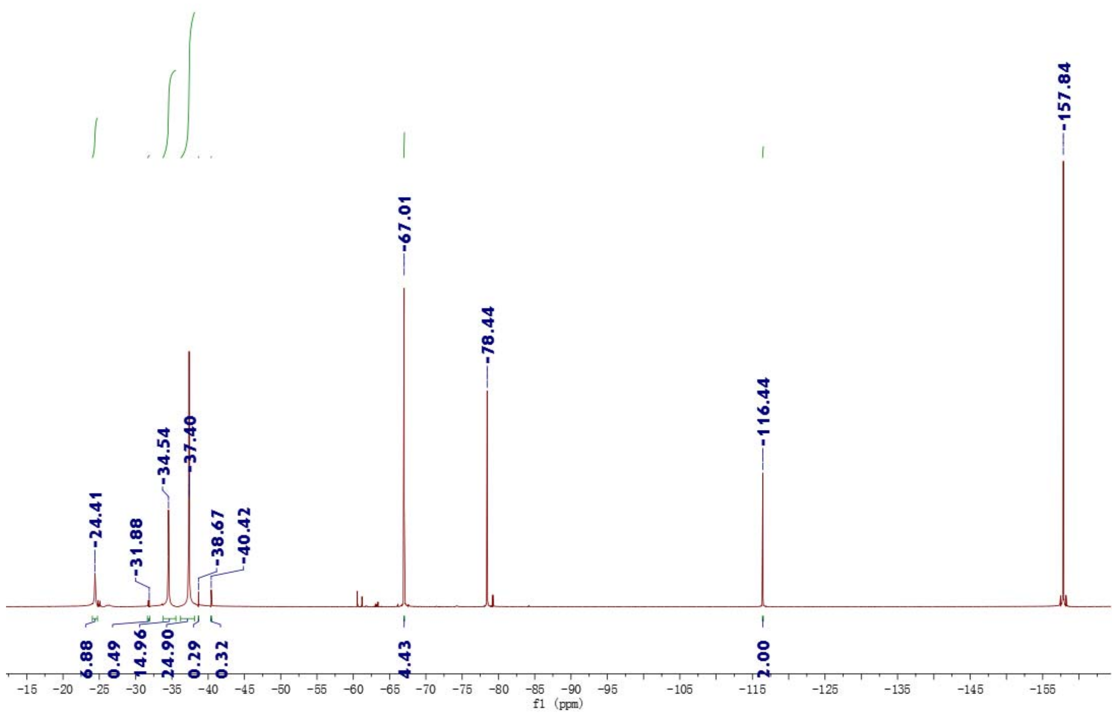
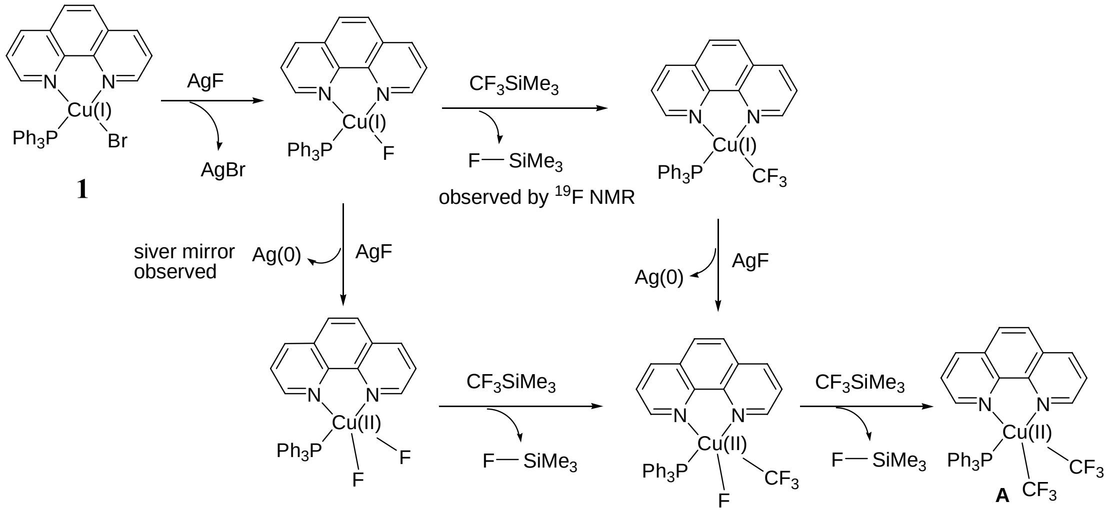


Figure S11. ^{19}F NMR monitoring of the reaction solution after 18 hours.

6. Reaction mechanism relevant

Scheme S1. The formation of intermediate **A**



Scheme S1 shows possible mechanisms for the formation of Cu(II) trifluoromethyl intermediate **A**.

Reaction Procedure for the conversion of 2 to 3 in the presence of additional phen ligand*:* Into a 25-mL Schlenk tube equipped with a stir bar were added $[phenCu(pph_3)_2]^+[Cu(CF_3)_4]^-$ (**2**) (166 mg, 0.15mmol) and phen (54 mg, 0.30 mmol). The air in the Schlenk was evacuated and backfilled with dry nitrogen three times. Then, AcOH (1 mL) was added by syringe. The resulting mixture was stirred at 90 ^{o}C for 2h under nitrogen. Then, the mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (5 mL). The resulting mixture was separated by filtration and washed with brine (2 x 5 mL). The combined organic layers were evaporated with silica gel. The crude mixture was purified by flash silica gel column chromatography with PE/EA (v/v = 2:1) as eluent to give $phenCu(CF_3)_3$ (**3**) (31 mg, 45%).

7. Reactivity studies of 2 and 3 with boronic acids

7.1 Optimization of conditions for reaction of **3** with **6a** (Table 1):

Into a 25-mL Schlenk tube equipped with a stir bar were added (phen)Cu(CF_3)$_3$ (**3**) (45 mg, 0.1 mmol), (4-methoxyphenyl)boronic acid (**6a**) (30 mg, 0.2 mmol), additive (0.2 mmol), 4,4'-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The air in the Schlenk tube was evacuated and backfilled 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 where necessary). The mixture was allowed to cool to room temperature and diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et_2O.The combined filtrate and the washings were concentrated to extrude ether, and the residue mixture was analyzed by ^{19}F NMR spectroscopy to determine the reaction yield (Table 1). Figure S12 shows the quantitative trifluoromethylation of **6a** at RT in 3 hours (entry 10 in Table 1). Figures S13 and S14 are ^{1}H and ^{19}F NMR spectra of the isolated product **7a**.

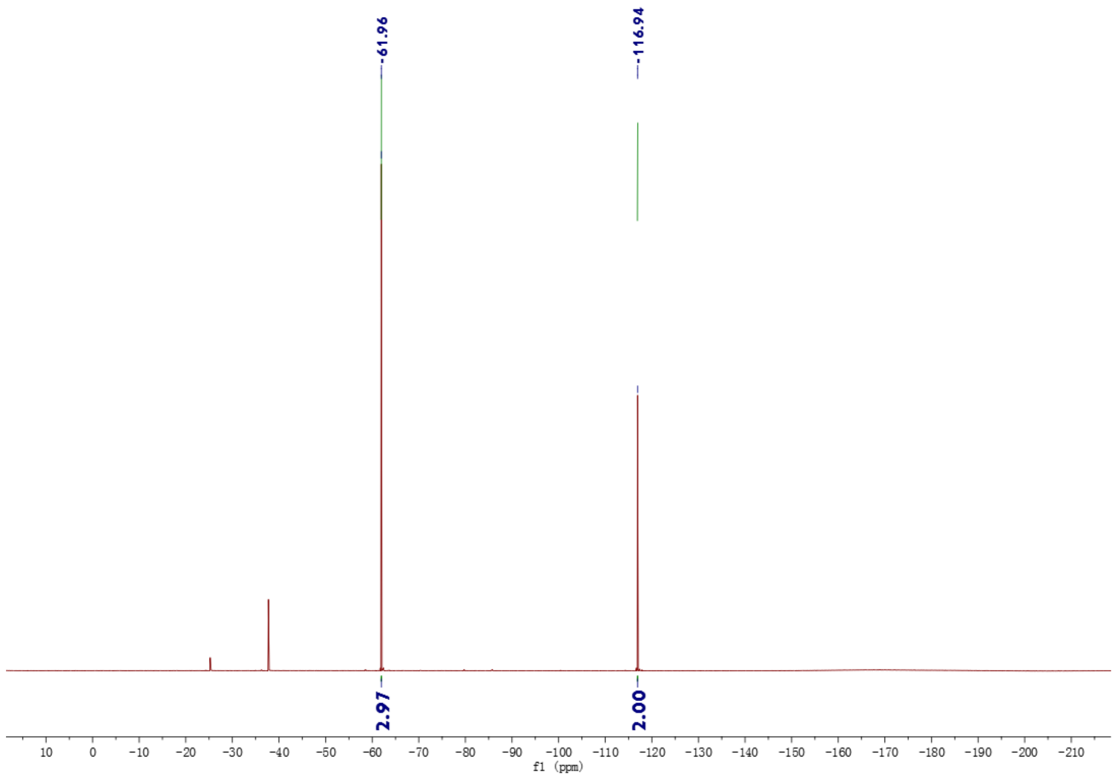


Figure S12. ^{19}F NMR spectrum of reaction solution of **3** with **6a** (entry 10 in Table 1).

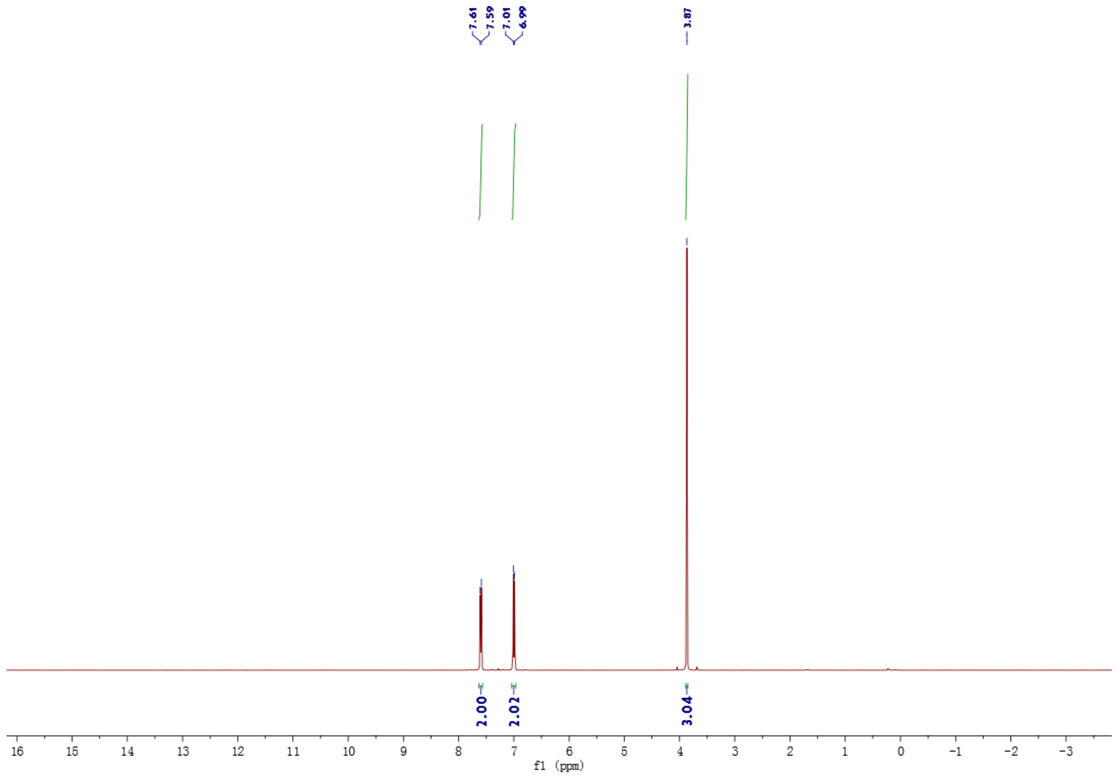


Figure S13. [1]H NMR of 4-methoxybenzotrifluoride (**7a**).

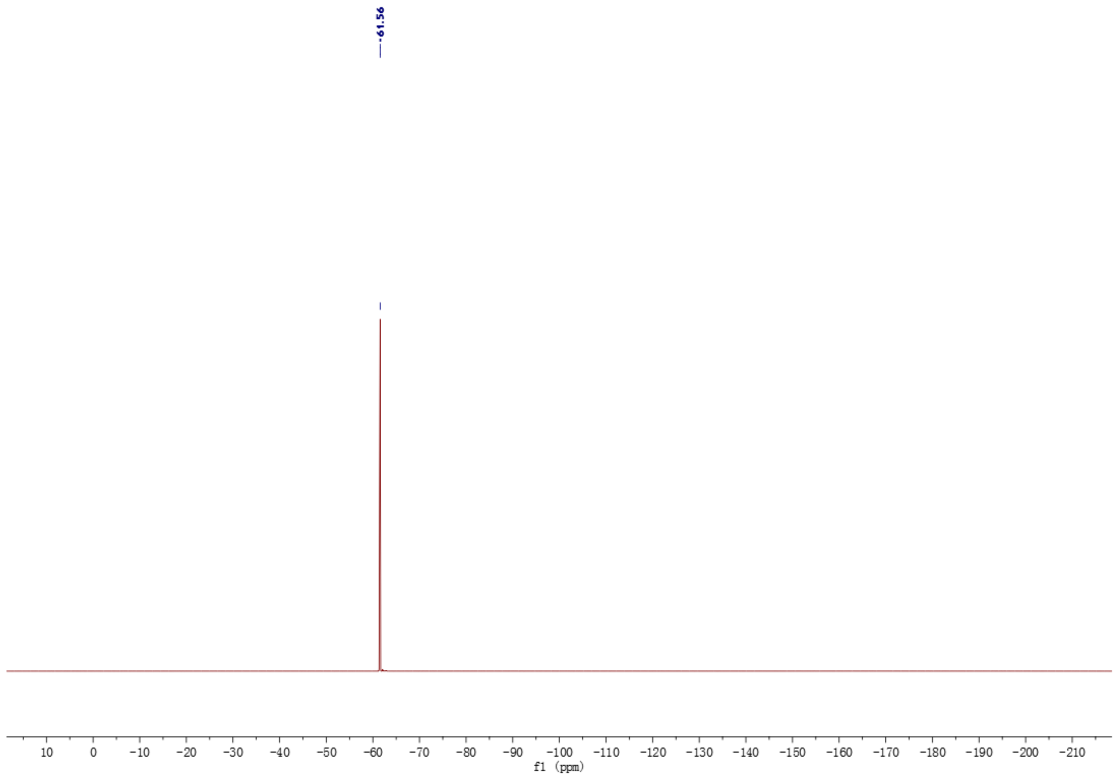


Figure S14. [19]F NMR spectrum of 4-methoxybenzotrifluoride (**7a**).

7.2 General procedures for reaction of **3** with various boronic acids (Table 2):

Condition A: Into a 25-mL Schlenk tube equipped with a stir bar were added (phen)Cu(CF_3)$_3$ (**3**) (45 mg, 0.1 mmol), boronic acid (**6**) (0.2 mmol), **KF** (0.2 mmol), 4,4'-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The air in the Schlenk tube was evacuated and backfilled with dry oxygen. Dry DMF (1 mL) was then added by syringe. The contents in the tube were vigorously stirred **at room temperature** for 3 hours. The mixture was then diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et_2O.The combined filtrate and the washings were concentrated to extrude ether, and the residue mixture was analyzed by ^{19}F NMR spectroscopy to determine the reaction yields (Table 2).

Condition B: Into a 25-mL Schlenk tube equipped with a stir bar were added (phen)Cu(CF_3)$_3$ (**3**) (45 mg, 0.1 mmol), boronic acid (**6**) (0.2 mmol), **AgF (0.2 mmol), 4 Å MS**, 4,4'-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The air in the Schlenk tube was evacuated and backfilled 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 to **50℃** for 3 hours. The mixture was allowed to cool to room temperature and diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et_2O. The combined filtrate and the washings were concentrated to extrude ether, and the residue mixture was analyzed by ^{19}F NMR spectroscopy to determine the reaction yields (Table 2, marked with [c]).

For another example, Figure S15 shows the ^{19}F NMR spectrum for the reaction mixture of **3** with *p*-biphenylboronic acid (**6b**), which determines a reaction yield of 92% for the formation of **7b**. Figures S16 and S17 are the ^{1}H and ^{19}F NMR spectra for isolated **7b**.

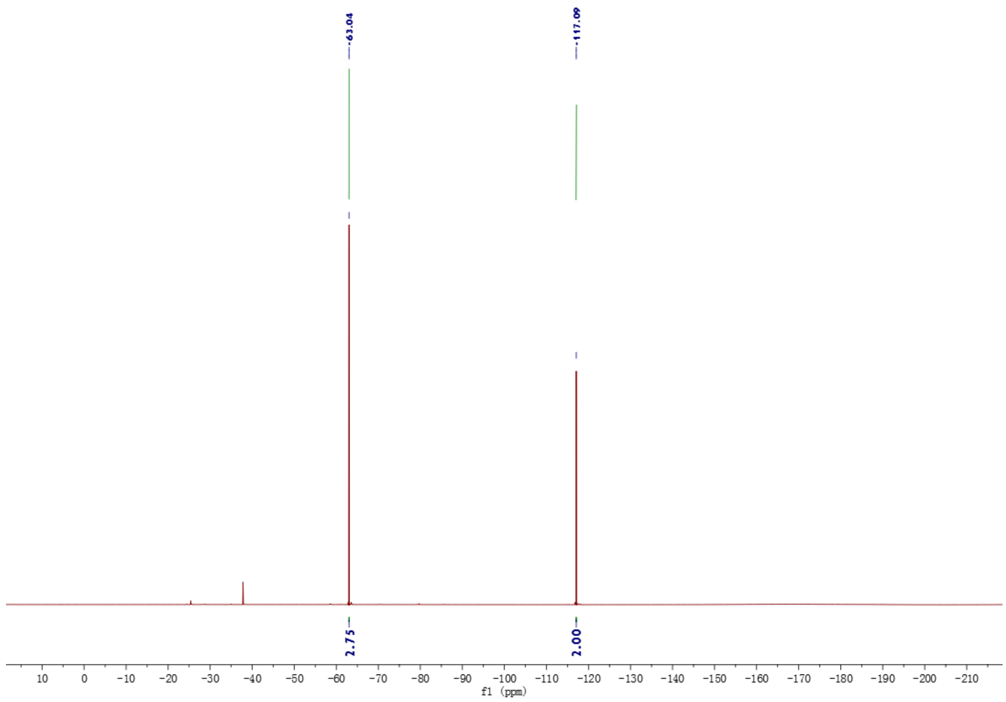


Figure S15. ^{19}F NMR spectrum of reaction solution of **3** with **6b**.

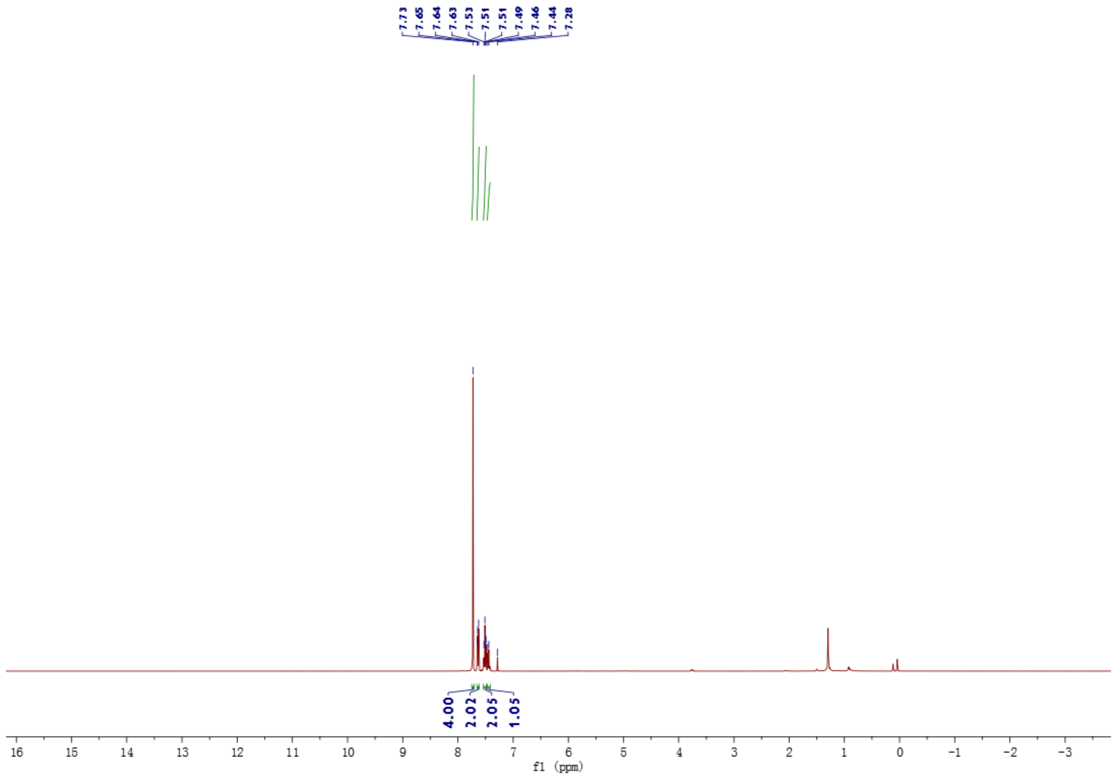


Figure S16. ^{1}H NMR of 4-phenylbenzotrifluoride (**7b**).

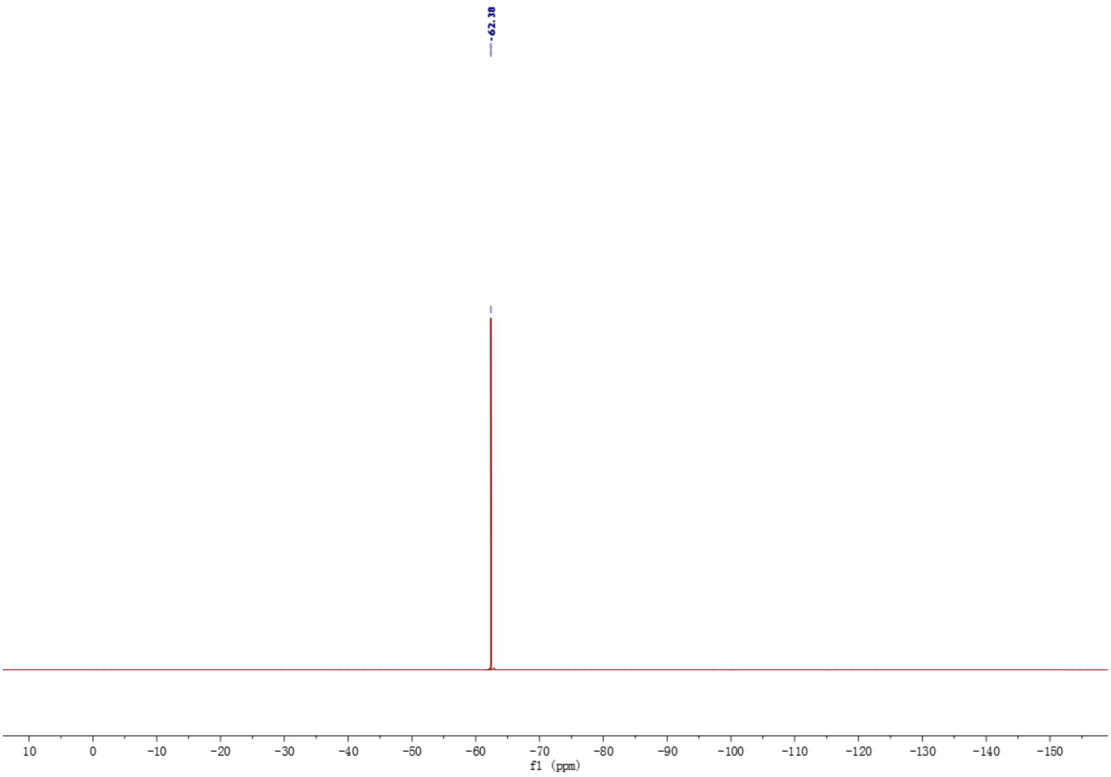
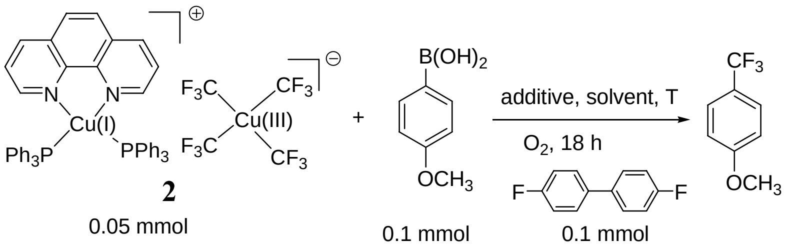


Figure S17. ^{19}F NMR of 4-phenylbenzotrifluoride (**7b)**.

7.3 Reaction of **2** with boronic acids:

Table S1. Summary of reaction of **2** with **6a**



Entry	Additive	Solvent	T (℃)	Yield (%)
1	—	DMF	80	trace
2	KF	DMF	80	trace
3	AgF	DMF	80	6
4	K_3PO_4	DMF	80	0
5	KI	DMF	80	15
6	KI	Toluene	80	16
7	AgF	Toluene	80	0
8	KF	Toluene	80	0
9	Cs_2CO_3	Toluene	80	10
10	NaO*t*Bu	Toluene	80	7
11	KF	Toluene	80	0
12	KF	CH_3CN	50	0
13	KF	DMSO	80	trace

Procedure of reaction of **2** with **6a**: Into a 25-mL Schlenk tube equipped with a stir bar were added $[phenCu(pph_3)_2]^+[Cu(CF_3)_4]^-$ (**2**) (55 mg, 0.05 mmol), (4-methoxyphenyl)boronic acid (**6a**) (15 mg, 0.10 mmol), additive (0.10 mmol), and 4,4'-difluorobiphenyl (internal standard; 19 mg, 0.10 mmol). The air in the Schlenk was evacuated and backfilled with dry oxygen. Dry solvent (1 mL) was then added by syringe. The contents in Schlenk tube were vigorously stirred and heated in an oil bath for 18h under specified temperature. The mixture was allowed to cool to room temperature and diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et_2O.The combined filtrate and the washings were concentrated to extrude ether, the residue mixture was analyzed by ^{19}F NMR spectroscopy to determine the reaction yield. Figure S18 shows the ^{19}F NMR spectrum for the reaction of **2** with **6a** under reaction conditions of entry 5, Table S1.

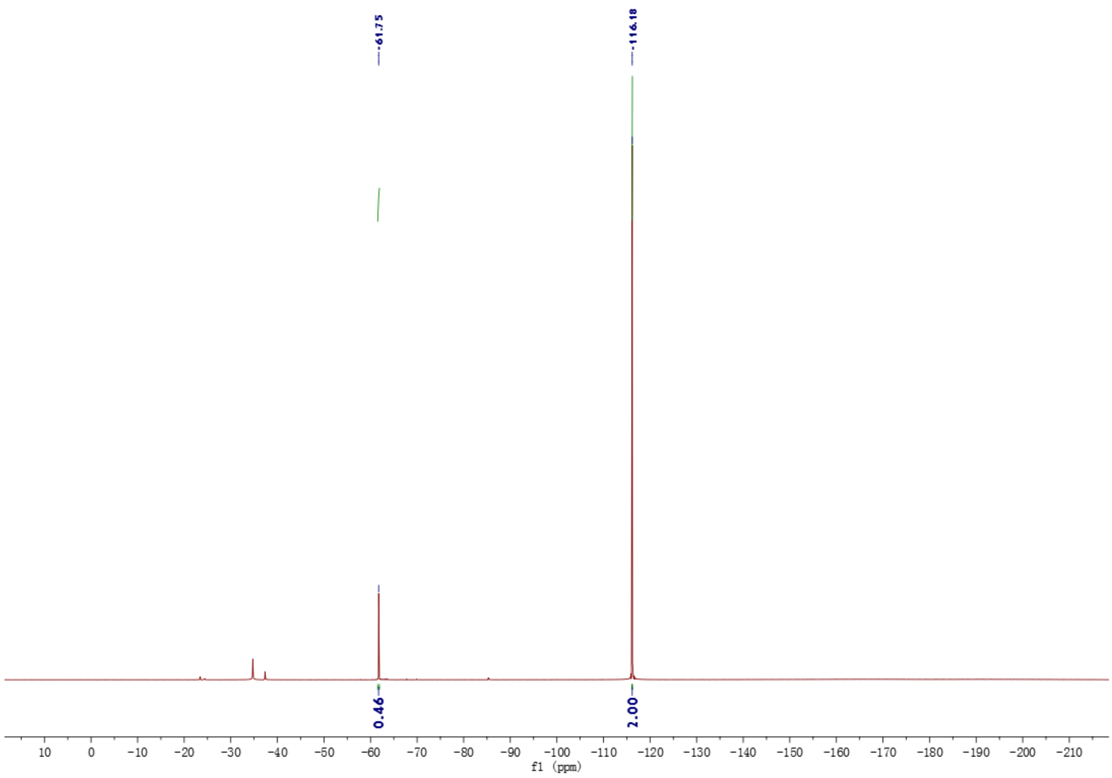


Figure 18. ^{19}F NMR spectrum for the reaction of **2** with **6a** (entry 5, Table S1).