Electronic Supplementary Information for

Ligand-Dependent Formation of Ion-Pair Cu^{I}/Cu^{III} Trifluoromethyl Complexes Containing Bisphosphines

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1. General experimental details

All chemicals were purchased commercially. CH_2Cl_2, toluene and DMF solvents were simply dried over Na_2SO_4 before use to extrude adventitious water. 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/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. Coupling constants are reported in Hertz. Elemental analyses were performed by the Analytic Laboratory of Jiangnan University.

2. The synthetic procedures, isolation and characterization of complexes 3-5

$[(DPPE)_2Cu]^+[Cu(CF_3)_4]^-$ (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 (190 mg, 1 mmol), DPPE (398 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 (3 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 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 to dryness with silica gel. The crude mixture was purified by flash silica gel column chromatography under air with petroleum ether (PE)/ethylacetate (EA) (v/v = 10:1) as eluent to extrude residual DPPE. Then the silica gel column was washed with CH_2Cl_2 to obtain crude $[(DPPE)_2Cu]^+[Cu(CF_3)_4]^-$ (**3**). The crude product **3** was recrystallized using CH_2Cl_2 followed by hexane. The white crystals of $[(DPPE)_2Cu]^+[Cu(CF_3)_4]^-$ (**3**) were separated by decantation, washed with hexane (2 x 10 mL), and dried under vacuum. The yield of **3** was 391 mg (65%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.43 – 7.34 (m, 4H), 7.30 – 7.18 (m, 16H), 2.47 (t, J = 6.9 Hz, 4H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ: -34.7 (s). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 4.7 (br s).

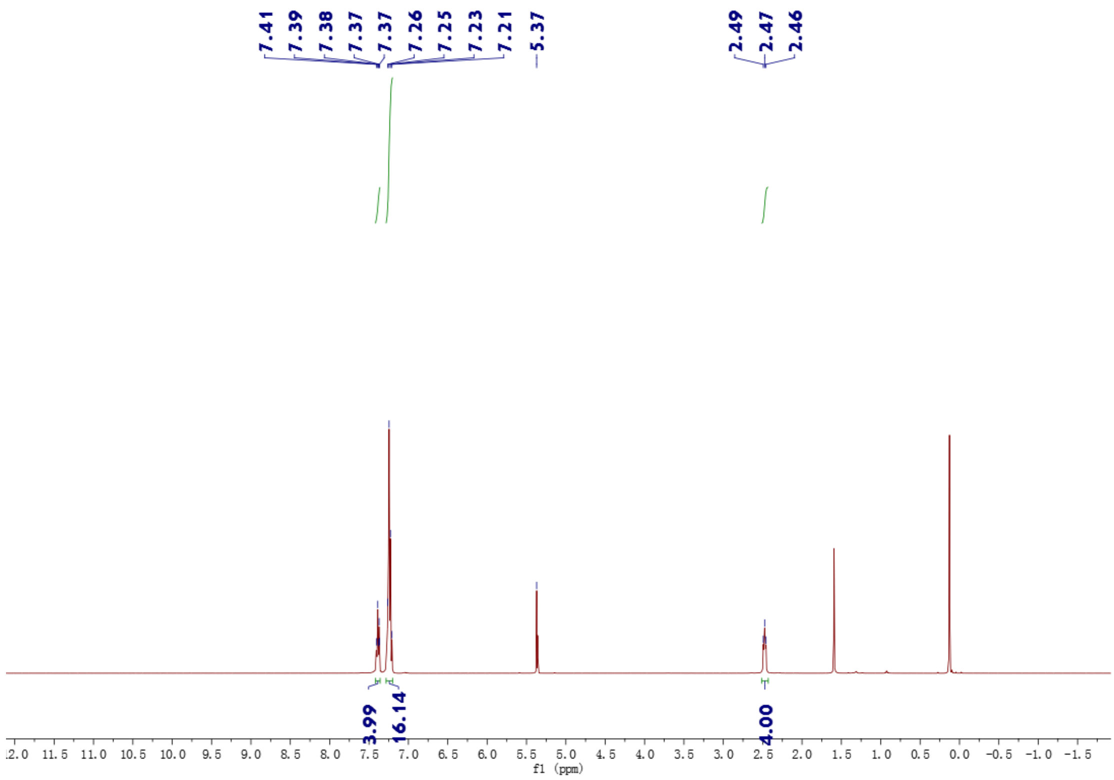


Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2) of complex **3**. Peak at 5.37 ppm is resonance of residual CH_2Cl_2 solvent. The peak at 1.59 ppm is resonance of residual water.

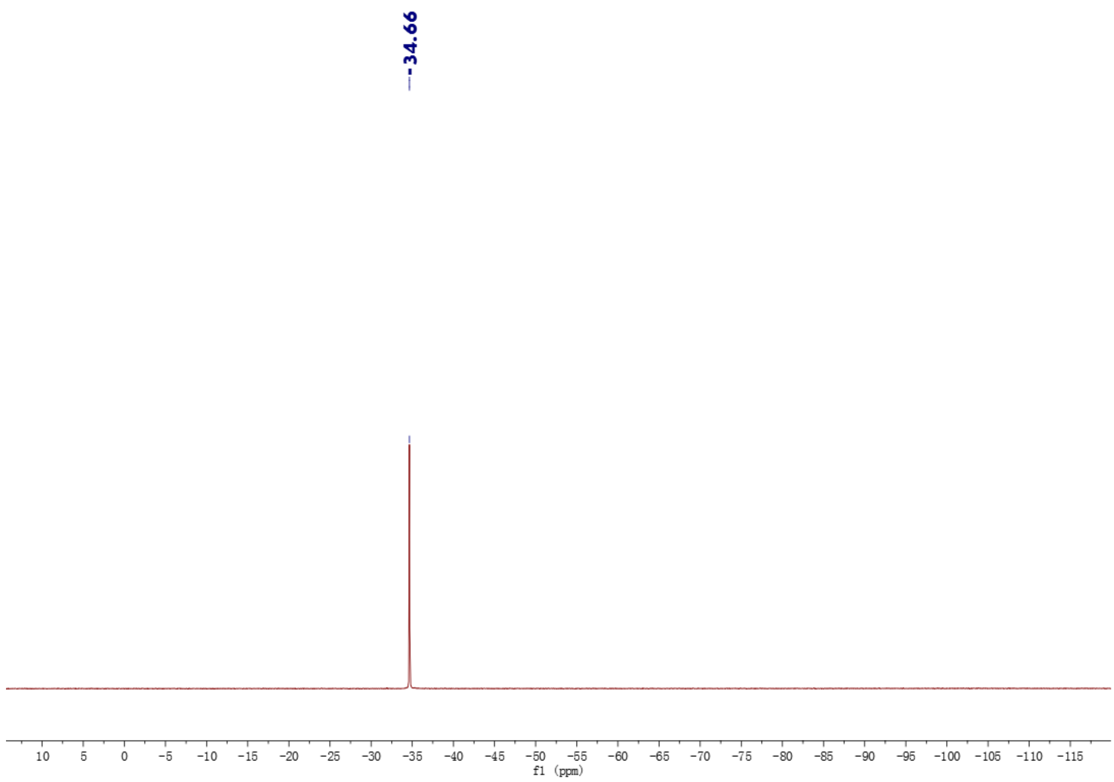


Figure S2. [19]F NMR (376 MHz, CD_2Cl_2) of complex **3**.

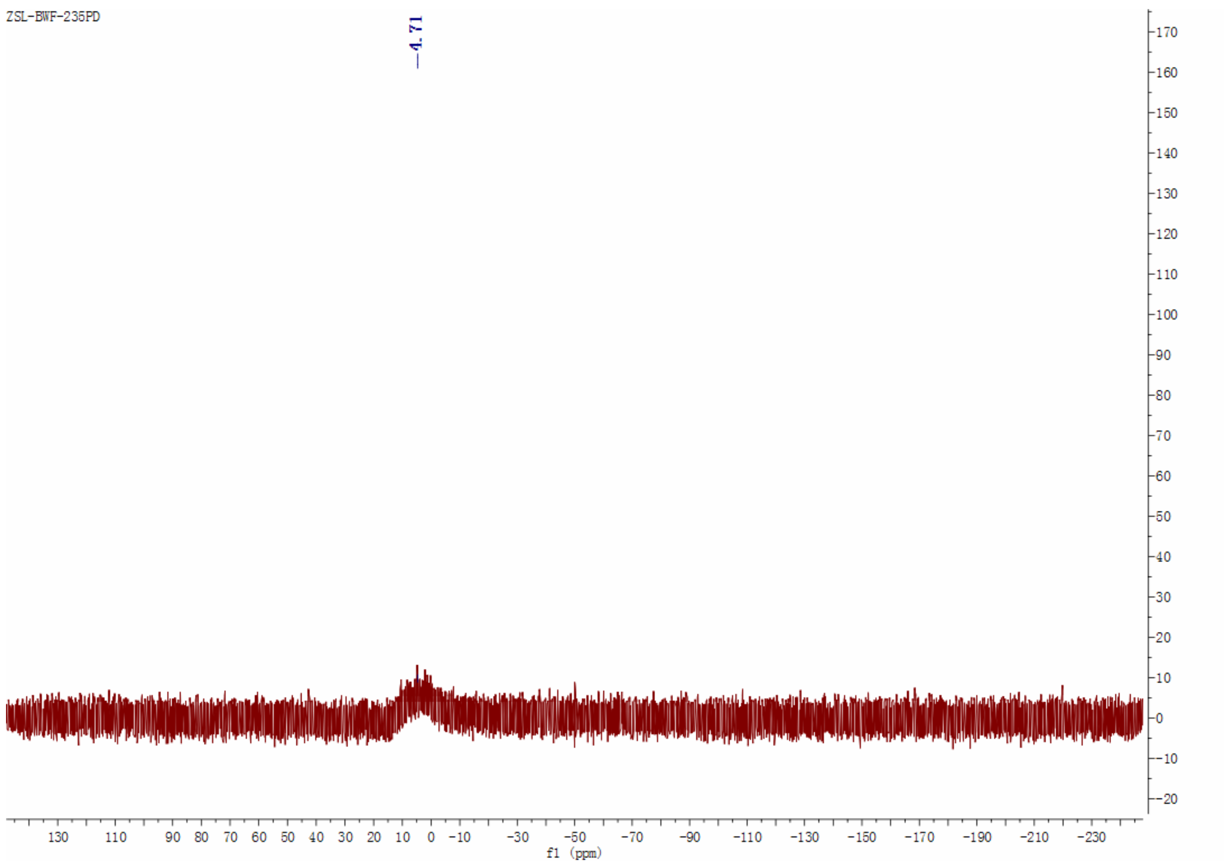


Figure S3. [31]P NMR (162 MHz, CD_2Cl_2) of complex **3**.

$[(BINAP)_2Cu]^+[Cu(CF_3)_4]^-$ (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 (190 mg, 1 mmol), BINAP (622 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 (3 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 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 to dryness with silica gel. The crude mixture was purified by flash silica gel column chromatography under air with petroleum ether (PE)/ethylacetate (EA) (v/v = 10:1) as eluent to extrude residual BINAP. Then the silica gel column was washed with CH_2Cl_2 to give crude $[(BINAP)_2Cu]^+[Cu(CF_3)_4]^-$ **(4)**. The crude product **4** was recrystallized using CH_2Cl_2 followed by hexane. The pale yellow crystals of $[(BINAP)_2Cu]^+[Cu(CF_3)_4]^-$ (**4**) were separated by decantation, washed with hexane (2 x 10 mL), and dried under vacuum. The yield of **4** was 765 mg (93%). ^1H NMR (400 MHz, CD_2Cl_2) δ: 8.00 (d, *J* = 6.5 Hz, 8H), 7.73 (d, *J* = 8.7 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 8H), 7.53-7.40 (m, 12H), 7.43 (t, *J* = 7.5 Hz, 4H), 7.22 (t, *J* = 7.3 Hz, 4H), 7.13 (d, *J* = 5.2 Hz, 8H), 7.02 (d, *J* = 8.6 Hz, 4H), 6.52 (t, *J* = 7.4 Hz, 4H), 6.07 (t, *J* = 7.6 Hz, 8H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ: -34.7 (s). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 15.9 (d, *J*

= 17.4 Hz), 14.4 (d, *J* = 17.4 Hz). ---caused by *R* and *S*-isomers of racemic BINAP used in our study.

(Both ^{1}H and ^{31}P NMR spectra show a minor impurity containing BINAP (the ratio is *ca* 1:10 to the major product). ^{31}P NMR (162 MHz, CD_2Cl_2) for the minor product: δ 10.84 (d, *J* = 17.4 Hz), 9.34 (d, *J* = 17.6 Hz).)

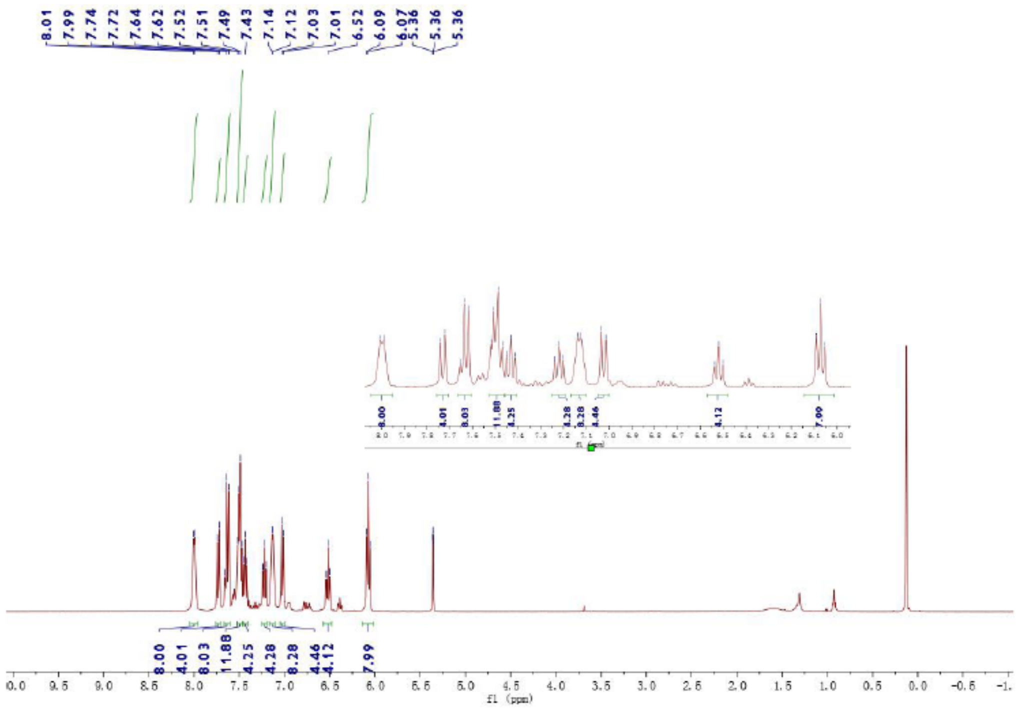


Figure S4. ^{1}H NMR (400 MHz, CD_2Cl_2) of complex **4**. A minor impurity was observed in a ratio of *ca* 1:10 to the desired product **4**.

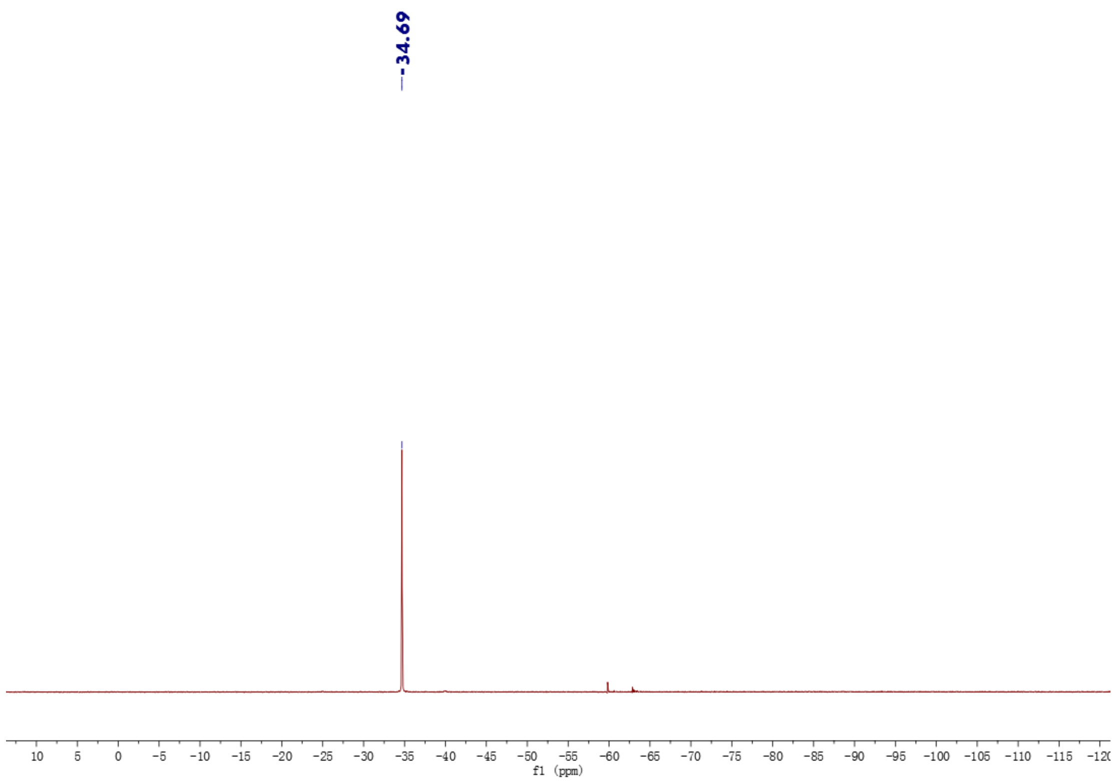


Figure S5. [19]F NMR (376 MHz, CD_2Cl_2) of complex **4**.

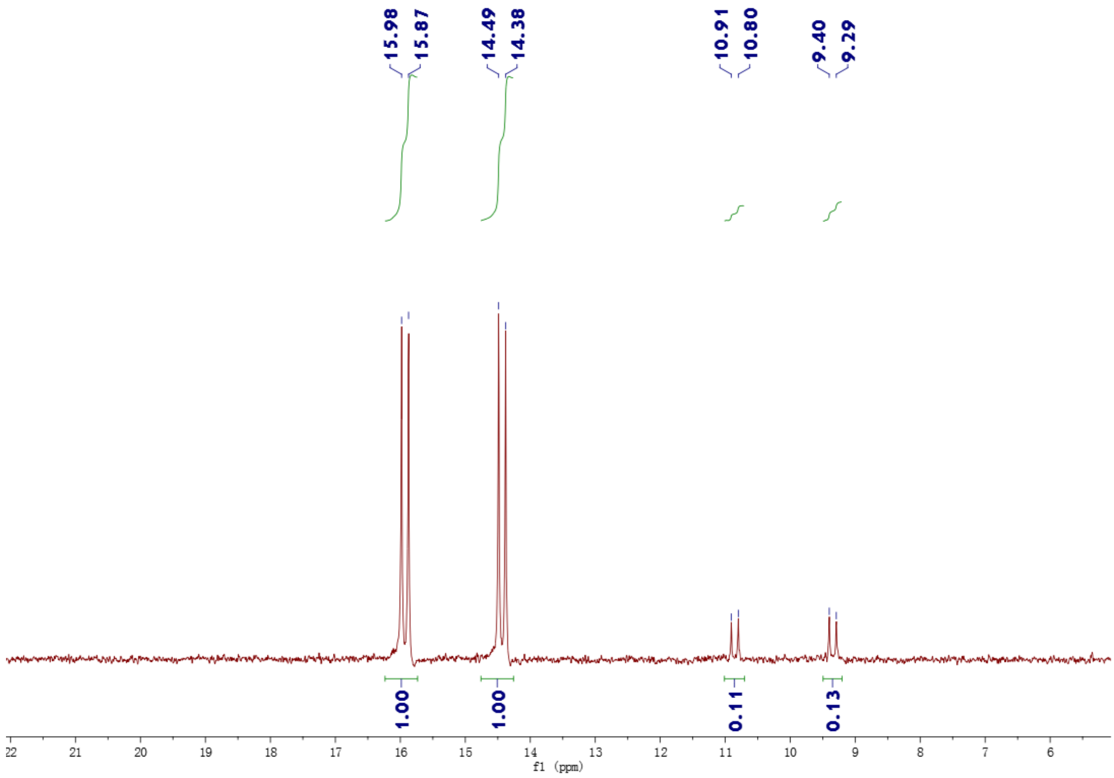


Figure S6. [31]P NMR (162 MHz, CD_2Cl_2) of complex **4**. A minor impurity was observed in a ratio of *ca* 1:10 to the desired **4**.

$[(XantPhos)_2Cu]^+[Cu(CF_3)_4]^-$ (5)

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 (190 mg, 1 mmol), XantPhos (578 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 (3 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 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 to dryness with silica gel. The crude mixture was purified by flash silica gel column chromatography under air with petroleum ether (PE)/ethylacetate (EA) (v/v = 10:1) as eluent to extrude residual Xantphos. Then the silica gel column was washed with CH_2Cl_2 to give crude $[(XantPhos)_2Cu]^+[Cu(CF_3)_4]^-$ (**5**). The crude product **5** was recrystallized using CH_2Cl_2 followed by hexane. The white crystals of $[(XantPhos)_2Cu]^+[Cu(CF_3)_4]^-$ (**5**) were separated by decantation, washed with hexane (2 × 10 mL), and dried under vacuum. The yield of **5** was 705 mg (90%). ^1H NMR (400 MHz, CD_2Cl_2) δ: 7.58 (d, *J* =7.5 Hz, 4H), 7.28 (s, 8H), 7.11 (t, *J* = 7.6 Hz, 4H), 6.93 (s, 32H), 6.75 (d, *J* = 6.1 Hz, 4H), 1.54 (s, 12H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ: -34.7 (s). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: -8.2 (d, *J* = 18.1 Hz), -9.7 (d, *J* = 18.0

Hz).----caused by the endo/exo plane of Xantphos ligand which distinguishes the four P atoms into two categories.

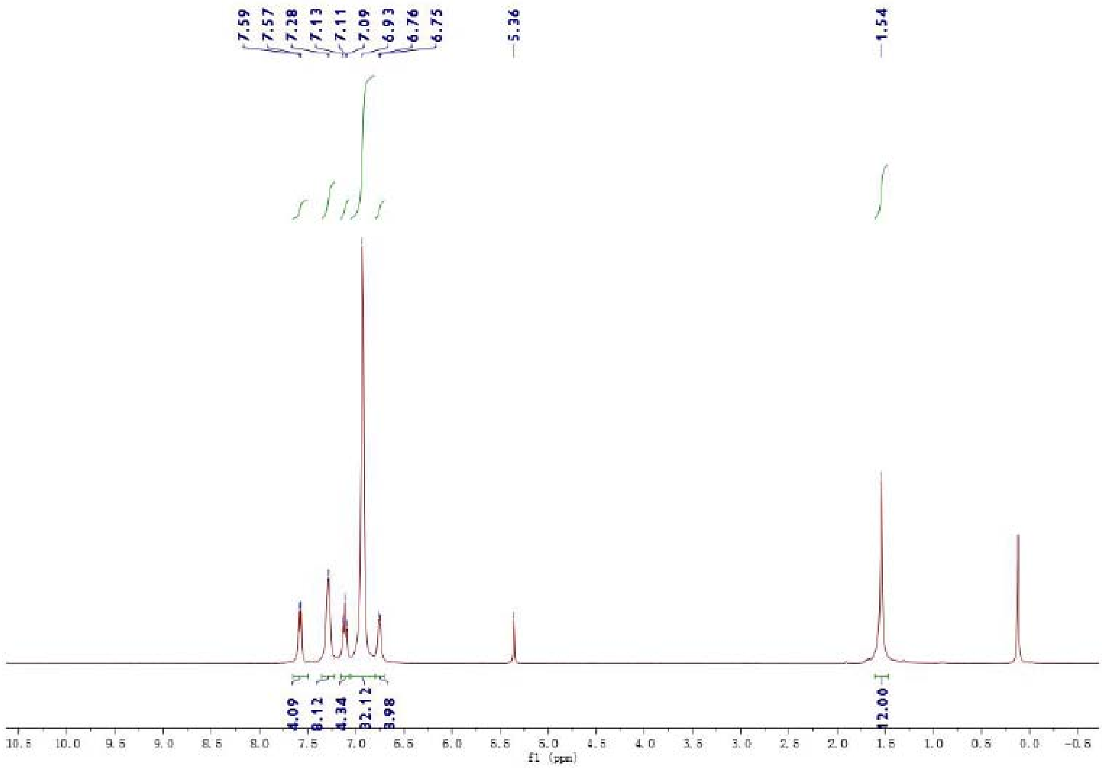


Figure S7. ^{1}H NMR (400 MHz, CD_2Cl_2) of complex **5**.

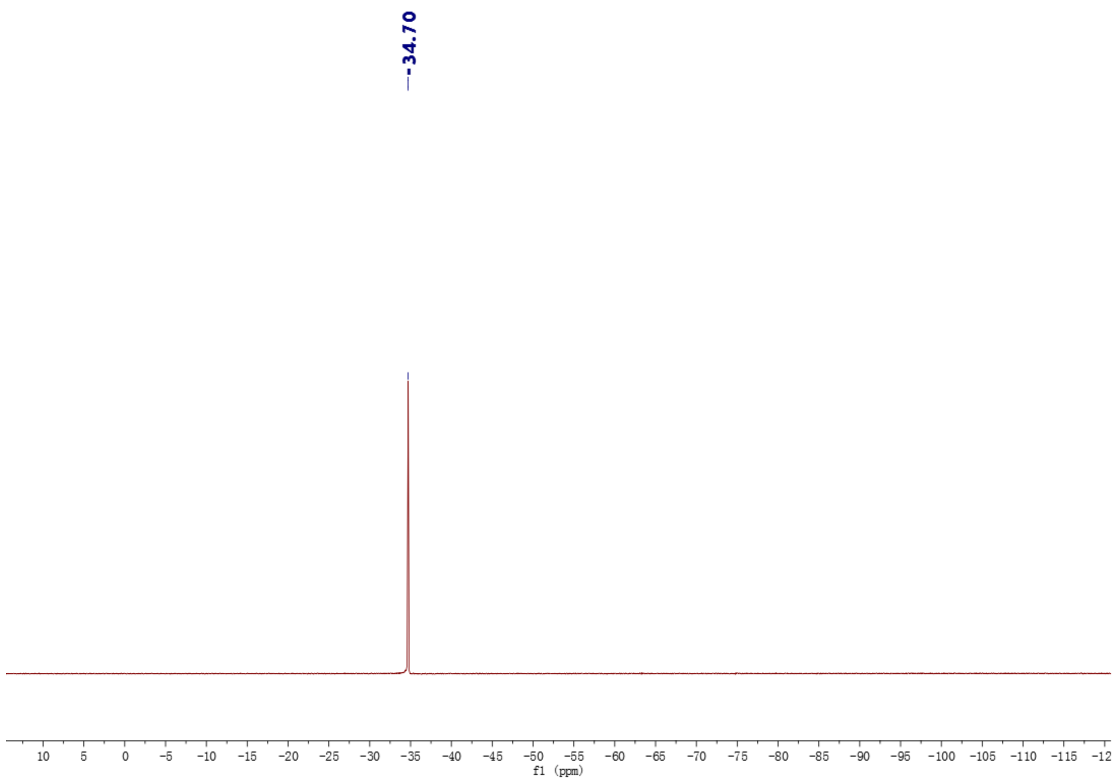


Figure S8. ^{19}F NMR (376 MHz, CD_2Cl_2) of complex **5**.

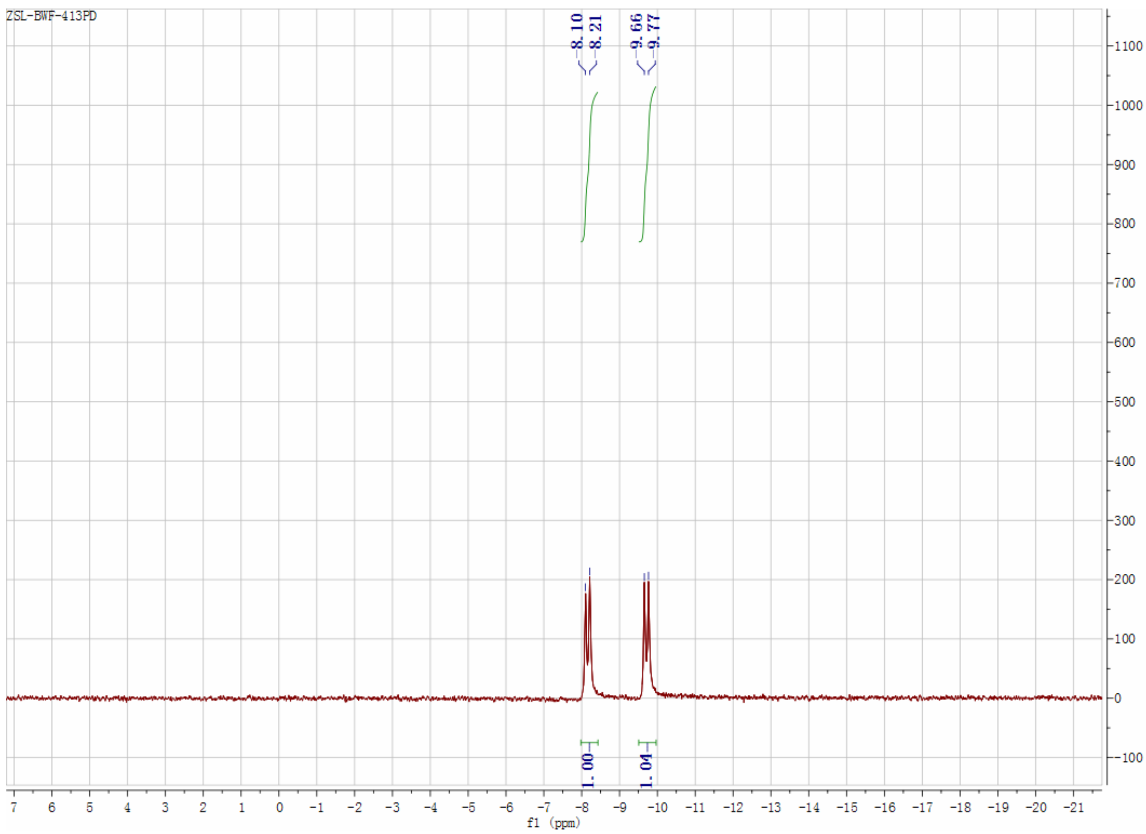


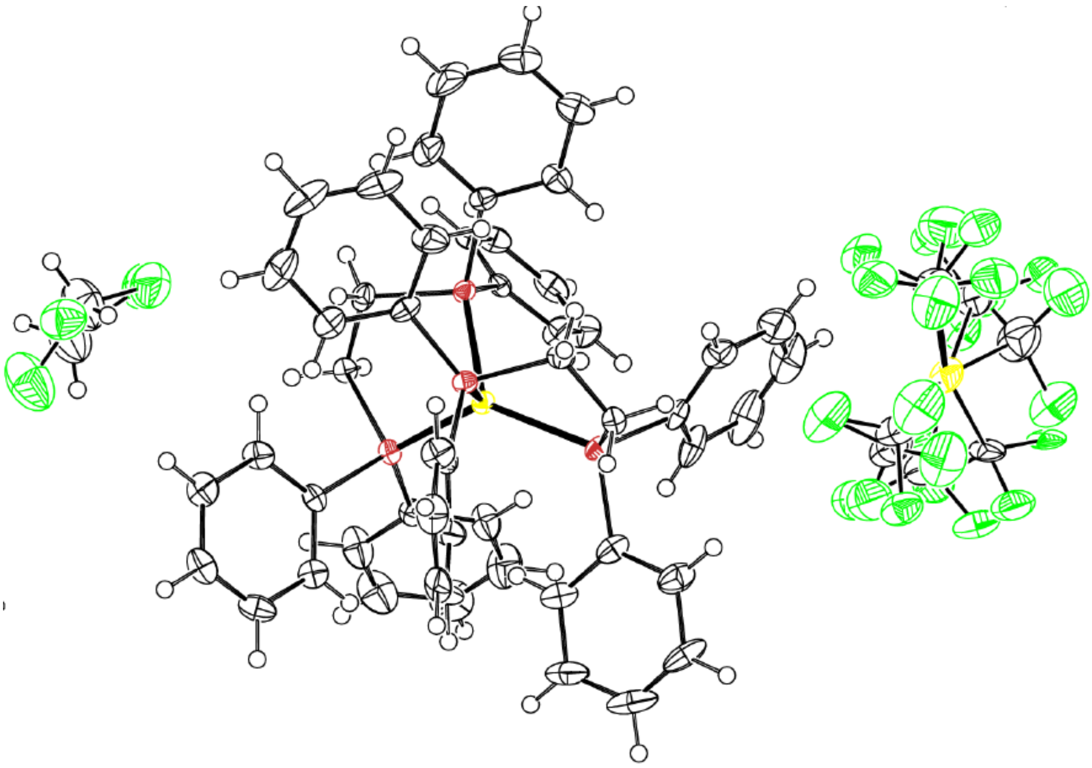
Figure S9. ^{31}P NMR (162 MHz, CD_2Cl_2) of complex **5**.

The conversion of **$[(BINAP)_2Cu]^+[Cu(CF_3)_4]^-$** (**4**) *to* **$(phen)Cu(CF_3)_3$ (1)** *in the presence of excess additional phen ligand*

Into a 25-mL Schlenk tube equipped with a stir bar were added $[(BINAP)_2Cu]^+[Cu(CF_3)_4]^-$ (**4**) (247 mg, 0.15 mmol) and phen (81 mg, 0.45 mmol). The air in the Schlenk was evacuated and refilled with dry nitrogen three times. Then, AcOH (2 mL) was added by syringe. The resulting mixture was stirred at 90 ^oC for 2h under nitrogen. Then, the mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). The resulting mixture was separated by filtration and washed with water (3 x 5 mL). The combined organic layers were evaporated to dryness with silica gel. The crude mixture was purified by flash silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 2:1) as eluent to give $(phen)Cu(CF_3)_3$ (**1**) (40 mg, 60%).

3. Crystallographic study

Crystals of complex **3** suitable for X-ray crystallographic analyses were grown by dissolving **3** in a mixed solvent of CH_2Cl_2/hexane and then stored in the refrigerator for 2-3 days. CCDC 1441928 contains the detailed information about the crystallographic study and crystal structure of complex **3**. The following sections show some key information.



Crystal data

$C_{52}H_{48}CuP_4 \cdot C_4CuF_{12} \cdot CH_2Cl_2$	Complex **3**
M_r = 1284.83	D_x = 1.519 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: ?	Mo *K*α radiation, λ = 0.71073 Å
a = 14.5621 (10) Å	Cell parameters from 9771 reflections
b = 15.2407 (11) Å	θ = 2.7–27.3°

c = 25.3334 (16) Å	μ = 1.04 mm^{-1}
β = 92.568 (2)°	T = 273 K
V = 5616.8 (7) $Å^3$	Block, colourless
Z = 4	0.40 × 0.20 × 0.20 mm
F(000) = 2608	

Data collection

Bruker APEX-II CCD diffractometer	12912 independent reflections
Radiation source: fine-focus sealed tube	10591 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.051
Detector resolution: ? pixels mm^{-1}	θ_{max} = 27.6°, θ_{min} = 2.2°
φ and ω scans	h = −18 18
Absorption correction: multi-scan Jacobson, R. (1998) Private communication	k = −19 19
T_{min} = 0.680, T_{max} = 0.818	l = −32 25
62209 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: ?
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.109	H-atom parameters constrained
$wR(F^2)$ = 0.239	$w = 1/[\sigma^2(F_o^2) + 74.0416P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.28	$(\Delta/\sigma)_{max}$ = 0.001
12912 reflections	$\Delta\rho_{max}$ = 0.93 e $Å^{-3}$
835 parameters	$\Delta\rho_{min}$ = −0.84 e $Å^{-3}$
336 restraints	Extinction correction: none

? constraints	Extinction coefficient: ?
Primary atom site location: ?	

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	1.22181 (6)	0.19520 (5)	0.22912 (3)	0.01657 (19)	
Cu2	0.74637 (8)	0.25058 (8)	0.03468 (4)	0.0390 (3)	
P1	1.36491 (12)	0.13794 (12)	0.23329 (7)	0.0175 (4)	
P2	1.17386 (12)	0.07957 (12)	0.27836 (7)	0.0169 (4)	
P3	1.13827 (13)	0.25108 (12)	0.15961 (7)	0.0198 (4)	
P4	1.19328 (12)	0.31999 (11)	0.27543 (7)	0.0178 (4)	
F1	0.6025 (9)	0.1177 (8)	0.0198 (4)	0.048 (3)	0.5
F1A	0.5789 (10)	0.1834 (11)	0.0117 (6)	0.074 (4)	0.5
F2	0.6855 (12)	0.0879 (11)	0.0279 (6)	0.059 (3)	0.5
F2A	0.7361 (10)	0.0620 (8)	0.0158 (5)	0.052 (3)	0.5
F3	0.6846 (8)	0.0961 (8)	0.0903 (4)	0.054 (3)	0.5
F3A	0.6904 (13)	0.1585 (10)	−0.0521 (6)	0.066 (4)	0.5
F4	0.9357 (9)	0.2575 (10)	0.0078 (5)	0.068 (3)	0.5
F4A	0.7229 (9)	0.1719 (10)	−0.0662 (4)	0.046 (3)	0.5
F5	0.8464 (12)	0.1356 (9)	−0.0254 (6)	0.057 (4)	0.5
F5A	0.7818 (11)	0.2910 (11)	−0.0638 (5)	0.064 (3)	0.5
F6	0.8394 (10)	0.2623 (8)	−0.0632 (4)	0.046 (3)	0.5
F6A	0.8647 (11)	0.1749 (14)	−0.0359 (6)	0.071 (4)	0.5
F7	0.8641 (9)	0.4045 (8)	0.0107 (4)	0.046 (3)	0.5
F7A	0.9038 (12)	0.3331 (12)	0.0166 (6)	0.077 (4)	0.5
F8	0.8684 (6)	0.3621 (4)	0.0911 (3)	0.0723 (19)	
F9	0.7569 (11)	0.4323 (9)	0.0673 (6)	0.077 (4)	0.5
F9A	0.7800 (13)	0.4187 (10)	0.0228 (7)	0.087 (4)	0.5

F10	0.7259 (9)	0.2521 (9)	0.1461 (4)	0.053 (3)	0.5
F10A	0.7204 (9)	0.3095 (11)	0.1366 (5)	0.063 (3)	0.5
F11	0.6690 (11)	0.3659 (9)	0.1060 (5)	0.071 (3)	0.5
F11A	0.6017 (9)	0.3303 (10)	0.0846 (5)	0.067 (3)	0.5
F12	0.5928 (9)	0.2460 (11)	0.1032 (5)	0.062 (3)	0.5
F12A	0.6353 (12)	0.1968 (11)	0.1094 (7)	0.087 (4)	0.5
C1	1.4075 (5)	0.0809 (5)	0.1759 (3)	0.0231 (15)	
C2	1.3481 (6)	0.0688 (6)	0.1325 (3)	0.0346 (19)	
H2	1.2887	0.0909	0.1326	0.043*	
C3	1.3777 (7)	0.0235 (7)	0.0889 (4)	0.050 (3)	
H3	1.3369	0.0140	0.0594	0.059*	
C4	1.4636 (7)	−0.0076 (7)	0.0878 (4)	0.049 (3)	
H4	1.4833	−0.0366	0.0583	0.058*	
C5	1.5245 (7)	0.0041 (7)	0.1306 (4)	0.050 (3)	
H5	1.5833	−0.0183	0.1296	0.058*	
C6	1.4962 (6)	0.0487 (6)	0.1751 (4)	0.041 (2)	
H6	1.5372	0.0568	0.2040	0.051*	
C7	1.4585 (5)	0.2086 (4)	0.2575 (3)	0.0197 (14)	
C8	1.5129 (5)	0.2524 (5)	0.2231 (3)	0.0256 (16)	
H8	1.5046	0.2430	0.1871	0.031*	
C9	1.5810 (6)	0.3108 (5)	0.2422 (3)	0.0320 (18)	
H9	1.6169	0.3397	0.2186	0.039*	
C10	1.5951 (5)	0.3248 (5)	0.2957 (3)	0.0303 (18)	
H10	1.6411	0.3629	0.3080	0.037*	
C11	1.5406 (6)	0.2818 (5)	0.3307 (3)	0.0325 (18)	
H11	1.5487	0.2920	0.3665	0.041*	
C12	1.4725 (5)	0.2234 (5)	0.3118 (3)	0.0271 (16)	
H12	1.4366	0.1941	0.3357	0.032*	

C13	1.3601 (5)	0.0484 (4)	0.2833 (3)	0.0198 (14)	
H13A	1.3536	−0.0078	0.2651	0.026*	
H13B	1.4172	0.0470	0.3044	0.026*	
C14	1.2788 (5)	0.0609 (5)	0.3197 (3)	0.0232 (15)	
H14A	1.2904	0.1113	0.3425	0.029*	
H14B	1.2716	0.0097	0.3414	0.029*	
C15	1.0791 (5)	0.0791 (5)	0.3228 (3)	0.0202 (14)	
C16	1.0904 (7)	0.0760 (8)	0.3771 (3)	0.050 (3)	
H16	1.1494	0.0742	0.3929	0.063*	
C17	1.0145 (8)	0.0753 (10)	0.4080 (4)	0.065 (4)	
H17	1.0224	0.0728	0.4446	0.081*	
C18	0.9279 (6)	0.0779 (6)	0.3854 (4)	0.041 (2)	
H18	0.8775	0.0767	0.4067	0.049*	
C19	0.9152 (6)	0.0842 (6)	0.3317 (4)	0.038 (2)	
H19	0.8560	0.0881	0.3165	0.045*	
C20	0.9911 (5)	0.0842 (5)	0.3001 (3)	0.0278 (17)	
H20	0.9824	0.0871	0.2635	0.035*	
C21	1.1594 (4)	−0.0247 (4)	0.2434 (3)	0.0171 (13)	
C22	1.1683 (5)	−0.1065 (5)	0.2686 (3)	0.0230 (15)	
H22	1.1781	−0.1090	0.3051	0.027*	
C23	1.1631 (5)	−0.1823 (5)	0.2401 (3)	0.0280 (17)	
H23	1.1698	−0.2359	0.2573	0.035*	
C24	1.1473 (5)	−0.1805 (5)	0.1857 (4)	0.0316 (18)	
H24	1.1449	−0.2322	0.1665	0.039*	
C25	1.1355 (6)	−0.1015 (6)	0.1603 (3)	0.0351 (19)	
H25	1.1247	−0.0997	0.1241	0.043*	
C26	1.1419 (6)	−0.0242 (5)	0.1894 (3)	0.0290 (17)	
H26	1.1335	0.0293	0.1722	0.037*	

C27	1.0501 (5)	0.1829 (5)	0.1268 (3)	0.0237 (15)	
C28	0.9600 (6)	0.1810 (5)	0.1413 (3)	0.0333 (19)	
H28	0.9412	0.2196	0.1669	0.044*	
C29	0.8965 (8)	0.1233 (7)	0.1182 (4)	0.052 (3)	
H29	0.8353	0.1250	0.1265	0.062*	
C30	0.9259 (9)	0.0625 (6)	0.0818 (4)	0.057 (3)	
H30	0.8849	0.0209	0.0677	0.072*	
C31	1.0156 (9)	0.0621 (7)	0.0672 (4)	0.058 (3)	
H31	1.0352	0.0220	0.0424	0.072*	
C32	1.0758 (7)	0.1236 (6)	0.0890 (3)	0.042 (2)	
H32	1.1355	0.1250	0.0778	0.051*	
C33	1.1966 (6)	0.3008 (5)	0.1043 (3)	0.0287 (17)	
C34	1.1485 (6)	0.3527 (6)	0.0678 (4)	0.038 (2)	
H34	1.0855	0.3606	0.0696	0.047*	
C35	1.1955 (8)	0.3921 (7)	0.0273 (4)	0.051 (3)	
H35	1.1637	0.4278	0.0032	0.059*	
C36	1.2867 (8)	0.3805 (7)	0.0232 (4)	0.053 (3)	
H36	1.3171	0.4073	−0.0041	0.066*	
C37	1.3369 (7)	0.3276 (7)	0.0598 (4)	0.045 (2)	
H37	1.3998	0.3189	0.0576	0.056*	
C38	1.2892 (6)	0.2880 (5)	0.1003 (3)	0.0327 (18)	
H38	1.3209	0.2529	0.1248	0.040*	
C39	1.0776 (5)	0.3459 (5)	0.1873 (3)	0.0247 (16)	
H39A	1.1078	0.3994	0.1768	0.031*	
H39B	1.0151	0.3471	0.1725	0.031*	
C40	1.0763 (5)	0.3416 (5)	0.2486 (3)	0.0232 (15)	
H40A	1.0355	0.2953	0.2591	0.029*	
H40B	1.0545	0.3968	0.2622	0.029*	

C41	1.2530 (5)	0.4208 (5)	0.2589 (3)	0.0189 (14)	
C42	1.3098 (5)	0.4215 (6)	0.2166 (3)	0.0304 (17)	
H42	1.3236	0.3696	0.1998	0.039*	
C43	1.3460 (6)	0.4994 (7)	0.1992 (4)	0.039 (2)	
H43	1.3834	0.4991	0.1704	0.047*	
C44	1.3280 (6)	0.5773 (6)	0.2244 (4)	0.038 (2)	
H44	1.3513	0.6302	0.2124	0.048*	
C45	1.2746 (6)	0.5759 (6)	0.2677 (4)	0.039 (2)	
H45	1.2640	0.6276	0.2858	0.049*	
C46	1.2363 (6)	0.4991 (5)	0.2844 (3)	0.0329 (18)	
H46	1.1987	0.4996	0.3132	0.041*	
C47	1.1884 (5)	0.3220 (5)	0.3466 (3)	0.0226 (15)	
C48	1.2707 (6)	0.3269 (8)	0.3760 (3)	0.045 (2)	
H48	1.3251	0.3321	0.3584	0.057*	
C49	1.2734 (9)	0.3247 (9)	0.4301 (4)	0.065 (3)	
H49	1.3293	0.3296	0.4492	0.083*	
C50	1.1916 (9)	0.3162 (7)	0.4565 (4)	0.054 (3)	
H50	1.1926	0.3146	0.4930	0.066*	
C51	1.1121 (8)	0.3101 (7)	0.4286 (4)	0.051 (3)	
H51	1.0582	0.3008	0.4460	0.064*	
C52	1.1077 (6)	0.3147 (6)	0.3733 (3)	0.038 (2)	
H52	1.0514	0.3138	0.3549	0.047*	
C53A	0.6839 (16)	0.1335 (13)	0.0415 (8)	0.044 (3)	0.5
C53	0.6685 (18)	0.1589 (16)	0.0021 (10)	0.067 (4)	0.5
C54	0.8448 (15)	0.2295 (15)	−0.0134 (8)	0.055 (3)	0.5
C54A	0.7782 (13)	0.2155 (14)	−0.0354 (6)	0.043 (3)	0.5
C55	0.8131 (17)	0.3603 (13)	0.0497 (9)	0.049 (4)	0.5
C55A	0.838 (2)	0.3417 (18)	0.0385 (11)	0.066 (4)	0.5

C56A	0.6786 (8)	0.2774 (8)	0.0971 (4)	0.054 (2)	
Cl1_1	1.488 (2)	0.025 (4)	0.424 (3)	0.071 (6)	0.5
Cl2_1	1.5535 (4)	0.1858 (4)	0.4758 (2)	0.0599 (14)	0.5
C1_1	1.5848 (13)	0.0889 (12)	0.4428 (11)	0.073 (5)	0.5
H1A_1	1.6176	0.1042	0.4116	0.088*	0.5
H1B_1	1.6259	0.0546	0.4659	0.088*	0.5
Cl1_2	1.6532 (5)	0.1179 (6)	0.4419 (3)	0.093 (3)	0.5
Cl2_2	1.477 (2)	0.037 (4)	0.423 (3)	0.071 (6)	0.5
C1_2	1.5381 (9)	0.1171 (18)	0.4607 (10)	0.073 (5)	0.5
H1A_2	1.5105	0.1743	0.4545	0.088*	0.5
H1B_2	1.5356	0.1035	0.4980	0.088*	0.5

Geometric parameters (Å, °)

Cu1—P1	2.2573 (19)	C16—C17	1.382 (13)
Cu1—P2	2.2862 (19)	C17—H17	0.930 (10)
Cu1—P3	2.2616 (19)	C17—C18	1.362 (15)
Cu1—P4	2.283 (2)	C18—H18	0.930 (8)
Cu2—C53A	2.014 (17)	C18—C19	1.369 (13)
Cu2—C53	1.958 (18)	C19—H19	0.930 (9)
Cu2—C54	1.949 (17)	C19—C20	1.394 (11)
Cu2—C54A	1.931 (14)	C20—H20	0.931 (8)
Cu2—C55	1.962 (16)	C21—C22	1.403 (10)
Cu2—C55A	1.922 (17)	C21—C26	1.382 (10)
Cu2—C56A	1.945 (10)	C22—H22	0.930 (7)
P1—C1	1.825 (8)	C22—C23	1.363 (11)
P1—C7	1.821 (7)	C23—H23	0.928 (8)
P1—C13	1.865 (7)	C23—C24	1.388 (12)

P2—C14	1.835 (7)	C24—H24	0.925 (8)
P2—C15	1.819 (7)	C24—C25	1.372 (12)
P2—C21	1.827 (7)	C25—H25	0.925 (8)
P3—C27	1.822 (8)	C25—C26	1.390 (11)
P3—C33	1.834 (8)	C26—H26	0.929 (8)
P3—C39	1.848 (8)	C27—C28	1.378 (11)
P4—C40	1.835 (8)	C27—C32	1.382 (11)
P4—C41	1.823 (7)	C28—H28	0.926 (9)
P4—C47	1.807 (7)	C28—C29	1.386 (12)
F1—C53A	1.31 (2)	C29—H29	0.926 (11)
F1A—C53	1.39 (3)	C29—C30	1.388 (16)
F2—C53	1.28 (3)	C30—H30	0.931 (10)
F2A—C53A	1.49 (3)	C30—C31	1.373 (17)
F3—C53A	1.36 (2)	C31—H31	0.931 (10)
F3A—C53	1.42 (3)	C31—C32	1.381 (14)
F4—C54	1.47 (3)	C32—H32	0.926 (10)
F4A—C54A	1.28 (2)	C33—C34	1.383 (11)
F5—C54	1.46 (3)	C33—C38	1.372 (12)
F5A—C54A	1.36 (3)	C34—H34	0.929 (9)
F6—C54	1.36 (2)	C34—C35	1.394 (13)
F6A—C54A	1.40 (3)	C35—H35	0.926 (9)
F7—C55	1.43 (2)	C35—C36	1.347 (16)
F7A—C55A	1.14 (3)	C36—H36	0.933 (9)
F8—C55	1.29 (3)	C36—C37	1.408 (15)
F8—C55A	1.42 (3)	C37—H37	0.930 (10)
F9—C55	1.45 (3)	C37—C38	1.400 (11)
F9A—C55A	1.49 (4)	C38—H38	0.928 (9)
F10—C56A	1.445 (16)	C39—H39A	0.970 (8)

F10A—C56A	1.248 (15)	C39—H39B	0.969 (7)
F11—C56A	1.377 (17)	C39—C40	1.553 (10)
F11A—C56A	1.404 (17)	C40—H40A	0.968 (7)
F12—C56A	1.353 (16)	C40—H40B	0.968 (8)
F12A—C56A	1.421 (18)	C41—C42	1.382 (10)
C1—C2	1.379 (11)	C41—C46	1.385 (11)
C1—C6	1.384 (11)	C42—H42	0.925 (8)
C2—H2	0.928 (8)	C42—C43	1.380 (12)
C2—C3	1.389 (12)	C43—H43	0.930 (9)
C3—H3	0.945 (9)	C43—C44	1.378 (14)
C3—C4	1.339 (14)	C44—H44	0.931 (8)
C4—H4	0.925 (9)	C44—C45	1.374 (14)
C4—C5	1.381 (14)	C45—H45	0.928 (9)
C5—H5	0.923 (9)	C45—C46	1.371 (12)
C5—C6	1.395 (12)	C46—H46	0.932 (9)
C6—H6	0.932 (9)	C47—C48	1.384 (12)
C7—C8	1.376 (10)	C47—C52	1.386 (11)
C7—C12	1.400 (11)	C48—H48	0.930 (9)
C8—H8	0.927 (7)	C48—C49	1.370 (13)
C8—C9	1.402 (11)	C49—H49	0.931 (11)
C9—H9	0.923 (8)	C49—C50	1.399 (16)
C9—C10	1.380 (12)	C50—H50	0.925 (9)
C10—H10	0.930 (7)	C50—C51	1.332 (16)
C10—C11	1.380 (12)	C51—H51	0.927 (10)
C11—H11	0.923 (8)	C51—C52	1.403 (13)
C11—C12	1.400 (10)	C52—H52	0.924 (9)
C12—H12	0.931 (8)	Cl1_1—C1_1	1.761 (10)
C13—H13A	0.975 (7)	Cl2_1—C1_1	1.766 (10)

C13—H13B	0.969 (7)	C1_1—H1A_1	0.9700
C13—C14	1.544 (11)	C1_1—H1B_1	0.9700
C14—H14A	0.972 (7)	Cl1_2—C1_2	1.763 (10)
C14—H14B	0.963 (7)	Cl2_2—C1_2	1.765 (10)
C15—C16	1.380 (11)	C1_2—H1A_2	0.9700
C15—C20	1.382 (10)	C1_2—H1B_2	0.9700
C16—H16	0.931 (9)		

P1—Cu1—P2	88.88 (7)	C29—C30—H30	119.9 (14)
P1—Cu1—P3	130.19 (8)	C31—C30—C29	120.5 (9)
P1—Cu1—P4	119.14 (7)	C31—C30—H30	119.7 (12)
P3—Cu1—P2	123.25 (7)	C30—C31—H31	120.6 (12)
P3—Cu1—P4	89.00 (7)	C30—C31—C32	119.0 (9)
P4—Cu1—P2	107.15 (7)	C32—C31—H31	120.4 (14)
C53—Cu2—C55	164.1 (11)	C27—C32—H32	118.9 (9)
C54—Cu2—C53	92.7 (11)	C31—C32—C27	122.3 (10)
C54—Cu2—C55	83.7 (10)	C31—C32—H32	118.8 (10)
C54A—Cu2—C53A	87.8 (8)	C34—C33—P3	120.7 (7)
C54A—Cu2—C56A	163.3 (6)	C38—C33—P3	119.3 (6)
C55A—Cu2—C53A	161.8 (12)	C38—C33—C34	120.0 (8)
C55A—Cu2—C54A	93.0 (10)	C33—C34—H34	120.8 (9)
C55A—Cu2—C56A	100.5 (10)	C33—C34—C35	119.3 (9)
C56A—Cu2—C53A	82.5 (7)	C35—C34—H34	120.0 (9)
C56A—Cu2—C53	100.8 (9)	C34—C35—H35	119.3 (11)
C56A—Cu2—C54	163.2 (8)	C36—C35—C34	121.1 (9)
C56A—Cu2—C55	85.9 (7)	C36—C35—H35	119.5 (10)
C1—P1—Cu1	119.5 (2)	C35—C36—H36	120.1 (12)
C1—P1—C13	102.5 (3)	C35—C36—C37	120.6 (8)
C7—P1—Cu1	117.5 (2)	C37—C36—H36	119.3 (12)

C7—P1—C1	105.9 (3)	C36—C37—H37	121.7 (9)
C7—P1—C13	104.7 (3)	C38—C37—C36	117.9 (9)
C13—P1—Cu1	104.6 (2)	C38—C37—H37	120.3 (10)
C14—P2—Cu1	99.4 (2)	C33—C38—C37	121.0 (8)
C15—P2—Cu1	126.8 (2)	C33—C38—H38	119.5 (8)
C15—P2—C14	106.4 (3)	C37—C38—H38	119.4 (9)
C15—P2—C21	102.8 (3)	P3—C39—H39A	108.8 (6)
C21—P2—Cu1	116.0 (2)	P3—C39—H39B	109.0 (6)
C21—P2—C14	102.5 (3)	H39A—C39—H39B	107.8 (7)
C27—P3—Cu1	118.9 (2)	C40—C39—P3	112.0 (5)
C27—P3—C33	103.2 (4)	C40—C39—H39A	109.6 (7)
C27—P3—C39	106.2 (3)	C40—C39—H39B	109.6 (7)
C33—P3—Cu1	119.9 (3)	P4—C40—H40A	109.8 (6)
C33—P3—C39	102.3 (4)	P4—C40—H40B	109.7 (6)
C39—P3—Cu1	104.4 (2)	C39—C40—P4	109.0 (5)
C40—P4—Cu1	98.4 (2)	C39—C40—H40A	109.9 (6)
C41—P4—Cu1	119.0 (2)	C39—C40—H40B	109.8 (7)
C41—P4—C40	102.0 (3)	H40A—C40—H40B	108.6 (7)
C47—P4—Cu1	122.9 (2)	C42—C41—P4	119.5 (6)
C47—P4—C40	106.8 (3)	C42—C41—C46	118.6 (7)
C47—P4—C41	104.8 (3)	C46—C41—P4	121.6 (6)
C2—C1—P1	118.4 (6)	C41—C42—H42	120.0 (8)
C2—C1—C6	119.5 (7)	C43—C42—C41	120.3 (8)
C6—C1—P1	122.1 (6)	C43—C42—H42	119.7 (8)
C1—C2—H2	120.1 (8)	C42—C43—H43	119.4 (10)
C1—C2—C3	119.7 (8)	C44—C43—C42	120.7 (8)
C3—C2—H2	120.3 (8)	C44—C43—H43	119.9 (9)
C2—C3—H3	120.0 (10)	C43—C44—H44	121.0 (10)

C4—C3—C2	121.1 (9)	C45—C44—C43	118.8 (8)
C4—C3—H3	119.0 (10)	C45—C44—H44	120.1 (10)
C3—C4—H4	120.6 (11)	C44—C45—H45	119.6 (9)
C3—C4—C5	120.4 (8)	C46—C45—C44	120.8 (8)
C5—C4—H4	119.0 (10)	C46—C45—H45	119.6 (10)
C4—C5—H5	119.7 (9)	C41—C46—H46	119.6 (8)
C4—C5—C6	119.7 (9)	C45—C46—C41	120.7 (8)
C6—C5—H5	120.6 (10)	C45—C46—H46	119.8 (9)
C1—C6—C5	119.7 (8)	C48—C47—P4	117.8 (6)
C1—C6—H6	120.4 (9)	C48—C47—C52	118.3 (7)
C5—C6—H6	119.9 (9)	C52—C47—P4	123.8 (6)
C8—C7—P1	121.1 (6)	C47—C48—H48	118.8 (8)
C8—C7—C12	118.7 (7)	C49—C48—C47	121.6 (9)
C12—C7—P1	120.0 (5)	C49—C48—H48	119.6 (10)
C7—C8—H8	119.7 (8)	C48—C49—H49	120.3 (12)
C7—C8—C9	120.6 (7)	C48—C49—C50	119.5 (10)
C9—C8—H8	119.7 (8)	C50—C49—H49	120.2 (10)
C8—C9—H9	119.5 (8)	C49—C50—H50	120.3 (12)
C10—C9—C8	120.5 (7)	C51—C50—C49	119.5 (9)
C10—C9—H9	119.9 (8)	C51—C50—H50	120.2 (12)
C9—C10—H10	119.9 (9)	C50—C51—H51	119.6 (10)
C9—C10—C11	119.5 (7)	C50—C51—C52	121.7 (9)
C11—C10—H10	120.6 (9)	C52—C51—H51	118.7 (11)
C10—C11—H11	119.9 (8)	C47—C52—C51	119.3 (9)
C10—C11—C12	120.1 (7)	C47—C52—H52	120.5 (8)
C12—C11—H11	119.9 (8)	C51—C52—H52	120.1 (9)
C7—C12—H12	119.9 (7)	F1—C53A—Cu2	122.1 (16)
C11—C12—C7	120.5 (7)	F1—C53A—F2A	98.7 (15)

C11—C12—H12	119.6 (8)	F1—C53A—F3	106.0 (15)
P1—C13—H13A	109.1 (5)	F2A—C53A—Cu2	111.6 (12)
P1—C13—H13B	109.4 (5)	F3—C53A—Cu2	117.7 (12)
H13A—C13—H13B	107.7 (6)	F3—C53A—F2A	96.1 (16)
C14—C13—P1	111.6 (5)	F1A—C53—Cu2	105.4 (15)
C14—C13—H13A	109.3 (6)	F1A—C53—F3A	115 (2)
C14—C13—H13B	109.6 (6)	F2—C53—Cu2	107.0 (15)
P2—C14—H14A	109.6 (6)	F2—C53—F1A	107 (2)
P2—C14—H14B	110.0 (5)	F2—C53—F3A	116 (2)
C13—C14—P2	108.6 (5)	F3A—C53—Cu2	105.1 (14)
C13—C14—H14A	109.6 (6)	F4—C54—Cu2	113.5 (14)
C13—C14—H14B	110.3 (7)	F5—C54—Cu2	108.1 (13)
H14A—C14—H14B	108.8 (7)	F5—C54—F4	109.8 (17)
C16—C15—P2	123.9 (6)	F6—C54—Cu2	120.4 (15)
C16—C15—C20	118.9 (7)	F6—C54—F4	104.3 (15)
C20—C15—P2	117.2 (6)	F6—C54—F5	99.6 (16)
C15—C16—H16	119.7 (9)	F4A—C54A—Cu2	122.2 (11)
C15—C16—C17	120.1 (9)	F4A—C54A—F5A	99.0 (15)
C17—C16—H16	120.2 (9)	F4A—C54A—F6A	107.7 (16)
C16—C17—H17	119.9 (11)	F5A—C54A—Cu2	105.6 (13)
C18—C17—C16	120.8 (9)	F5A—C54A—F6A	108.3 (15)
C18—C17—H17	119.3 (10)	F6A—C54A—Cu2	112.6 (12)
C17—C18—H18	119.8 (10)	F7—C55—Cu2	122.4 (13)
C17—C18—C19	120.0 (8)	F7—C55—F9	100.0 (16)
C19—C18—H18	120.1 (10)	F8—C55—Cu2	117.4 (16)
C18—C19—H19	119.9 (9)	F8—C55—F7	103.0 (14)
C18—C19—C20	119.7 (8)	F8—C55—F9	94.2 (14)
C20—C19—H19	120.4 (9)	F9—C55—Cu2	115.0 (14)

C15—C20—C19	120.4 (8)	F7A—C55A—Cu2	119 (2)
C15—C20—H20	119.9 (7)	F7A—C55A—F8	104 (2)
C19—C20—H20	119.7 (8)	F7A—C55A—F9A	116 (2)
C22—C21—P2	123.1 (5)	F8—C55A—Cu2	113.2 (15)
C26—C21—P2	119.1 (5)	F8—C55A—F9A	103 (2)
C26—C21—C22	117.7 (7)	F9A—C55A—Cu2	100.1 (16)
C21—C22—H22	119.6 (7)	F10—C56A—Cu2	113.8 (8)
C23—C22—C21	120.7 (7)	F10A—C56A—Cu2	119.2 (10)
C23—C22—H22	119.6 (8)	F10A—C56A—F11A	108.1 (12)
C22—C23—H23	119.7 (8)	F10A—C56A—F12A	111.6 (13)
C22—C23—C24	120.8 (7)	F11—C56A—Cu2	113.5 (9)
C24—C23—H23	119.5 (8)	F11—C56A—F10	99.7 (10)
C23—C24—H24	120.4 (9)	F11A—C56A—Cu2	111.5 (8)
C25—C24—C23	119.6 (7)	F11A—C56A—F12A	100.8 (11)
C25—C24—H24	120.0 (9)	F12—C56A—Cu2	121.5 (8)
C24—C25—H25	120.2 (8)	F12—C56A—F10	102.4 (10)
C24—C25—C26	119.5 (7)	F12—C56A—F11	103.1 (12)
C26—C25—H25	120.3 (9)	F12A—C56A—Cu2	104.1 (9)
C21—C26—C25	121.6 (7)	Cl1_1—C1_1—Cl2_1	111.5 (14)
C21—C26—H26	118.9 (8)	Cl1_1—C1_1—H1A_1	109.3
C25—C26—H26	119.5 (8)	Cl1_1—C1_1—H1B_1	109.3
C28—C27—P3	123.4 (6)	Cl2_1—C1_1—H1A_1	109.3
C28—C27—C32	117.4 (8)	Cl2_1—C1_1—H1B_1	109.3
C32—C27—P3	118.8 (6)	H1A_1—C1_1—H1B_1	108.0
C27—C28—H28	119.1 (8)	Cl1_2—C1_2—Cl2_2	108.6 (14)
C27—C28—C29	121.8 (9)	Cl1_2—C1_2—H1A_2	110.0
C29—C28—H28	119.1 (9)	Cl1_2—C1_2—H1B_2	110.0
C28—C29—H29	121.1 (11)	Cl2_2—C1_2—H1A_2	110.0

C28—C29—C30	119.0 (10)	Cl2_2—C1_2—H1B_2	110.0
C30—C29—H29	119.9 (11)	H1A_2—C1_2—H1B_2	108.4

Cu1—P1—C1—C2	−4.6 (8)	C14—P2—C21—C26	−132.2 (6)
Cu1—P1—C1—C6	176.4 (7)	C15—P2—C14—C13	172.6 (4)
Cu1—P1—C7—C8	−97.5 (6)	C15—P2—C21—C22	−64.8 (6)
Cu1—P1—C7—C12	78.4 (6)	C15—P2—C21—C26	117.6 (6)
Cu1—P1—C13—C14	−20.4 (5)	C15—C16—C17—C18	0 (2)
Cu1—P2—C14—C13	−54.4 (5)	C16—C15—C20—C19	−1.5 (13)
Cu1—P2—C15—C16	−108.5 (8)	C16—C17—C18—C19	−2.2 (19)
Cu1—P2—C15—C20	69.9 (7)	C17—C18—C19—C20	2.8 (15)
Cu1—P2—C21—C22	152.7 (5)	C18—C19—C20—C15	−0.9 (13)
Cu1—P2—C21—C26	−25.0 (7)	C20—C15—C16—C17	2.0 (16)
Cu1—P3—C27—C28	90.3 (7)	C21—P2—C14—C13	65.0 (5)
Cu1—P3—C27—C32	−83.1 (7)	C21—P2—C15—C16	114.5 (8)
Cu1—P3—C33—C34	−165.0 (6)	C21—P2—C15—C20	−67.0 (6)
Cu1—P3—C33—C38	13.2 (8)	C21—C22—C23—C24	−1.1 (11)
Cu1—P3—C39—C40	−17.7 (5)	C22—C21—C26—C25	−1.5 (12)
Cu1—P4—C40—C39	−55.0 (5)	C22—C23—C24—C25	−1.0 (12)
Cu1—P4—C41—C42	4.2 (7)	C23—C24—C25—C26	1.7 (13)
Cu1—P4—C41—C46	177.8 (5)	C24—C25—C26—C21	−0.4 (13)
Cu1—P4—C47—C48	81.9 (8)	C26—C21—C22—C23	2.3 (11)
Cu1—P4—C47—C52	−94.8 (7)	C27—P3—C33—C34	59.9 (8)
P1—C1—C2—C3	−178.2 (8)	C27—P3—C33—C38	−121.9 (7)
P1—C1—C6—C5	178.7 (8)	C27—P3—C39—C40	108.8 (5)
P1—C7—C8—C9	176.1 (6)	C27—C28—C29—C30	3.8 (14)
P1—C7—C12—C11	−176.1 (6)	C28—C27—C32—C31	−2.2 (13)
P1—C13—C14—P2	50.3 (6)	C28—C29—C30—C31	−2.7 (16)
P2—C15—C16—C17	−179.6 (10)	C29—C30—C31—C32	−0.6 (16)

P2—C15—C20—C19	−180.0 (6)	C30—C31—C32—C27	3.2 (15)
P2—C21—C22—C23	−175.4 (6)	C32—C27—C28—C29	−1.3 (12)
P2—C21—C26—C25	176.3 (7)	C33—P3—C27—C28	−134.0 (7)
P3—C27—C28—C29	−174.8 (7)	C33—P3—C27—C32	52.5 (7)
P3—C27—C32—C31	171.6 (7)	C33—P3—C39—C40	−143.3 (5)
P3—C33—C34—C35	177.7 (8)	C33—C34—C35—C36	−0.1 (16)
P3—C33—C38—C37	−177.5 (7)	C34—C33—C38—C37	0.7 (13)
P3—C39—C40—P4	49.2 (6)	C34—C35—C36—C37	0.3 (17)
P4—C41—C42—C43	171.5 (7)	C35—C36—C37—C38	−0.1 (16)
P4—C41—C46—C45	−173.2 (7)	C36—C37—C38—C33	−0.4 (14)
P4—C47—C48—C49	−177.0 (10)	C38—C33—C34—C35	−0.4 (14)
P4—C47—C52—C51	175.0 (7)	C39—P3—C27—C28	−26.8 (7)
C1—P1—C7—C8	39.0 (7)	C39—P3—C27—C32	159.8 (6)
C1—P1—C7—C12	−145.0 (6)	C39—P3—C33—C34	−50.2 (8)
C1—P1—C13—C14	−145.8 (5)	C39—P3—C33—C38	127.9 (7)
C1—C2—C3—C4	−1.0 (16)	C40—P4—C41—C42	−102.6 (6)
C2—C1—C6—C5	−0.2 (14)	C40—P4—C41—C46	71.1 (7)
C2—C3—C4—C5	0.6 (18)	C40—P4—C47—C48	−165.9 (7)
C3—C4—C5—C6	0.0 (18)	C40—P4—C47—C52	17.4 (8)
C4—C5—C6—C1	−0.2 (17)	C41—P4—C40—C39	67.1 (6)
C6—C1—C2—C3	0.8 (14)	C41—P4—C47—C48	−58.2 (8)
C7—P1—C1—C2	−140.2 (7)	C41—P4—C47—C52	125.1 (7)
C7—P1—C1—C6	40.9 (8)	C41—C42—C43—C44	1.5 (13)
C7—P1—C13—C14	103.8 (5)	C42—C41—C46—C45	0.6 (12)
C7—C8—C9—C10	0.4 (12)	C42—C43—C44—C45	1.2 (13)
C8—C7—C12—C11	0.0 (11)	C43—C44—C45—C46	−3.0 (13)
C8—C9—C10—C11	−0.9 (13)	C44—C45—C46—C41	2.1 (14)
C9—C10—C11—C12	0.9 (13)	C46—C41—C42—C43	−2.4 (12)

C10—C11—C12—C7	−0.5 (13)	C47—P4—C40—C39	176.8 (5)
C12—C7—C8—C9	0.0 (11)	C47—P4—C41—C42	146.2 (6)
C13—P1—C1—C2	110.3 (7)	C47—P4—C41—C46	−40.2 (7)
C13—P1—C1—C6	−68.6 (8)	C47—C48—C49—C50	1 (2)
C13—P1—C7—C8	147.0 (6)	C48—C47—C52—C51	−1.7 (14)
C13—P1—C7—C12	−37.1 (7)	C48—C49—C50—C51	0 (2)
C14—P2—C15—C16	7.2 (9)	C49—C50—C51—C52	−2.1 (18)
C14—P2—C15—C20	−174.4 (6)	C50—C51—C52—C47	2.8 (16)
C14—P2—C21—C22	45.5 (6)	C52—C47—C48—C49	−0.1 (16)

References:

[S1] Data collection with APEX2. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.

[S2] Cell refinement and data reduction with Bruker SAINT. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.

[S3] Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

[S4] Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

4. Reactivity studies of 3-5 with arylboronic acids

4.1 Optimization of reaction of **3** with 4-methoxyphenylboronic acid

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added $[(DPPE)_2Cu]^+[Cu(CF_3)_4]^-$ (**3**) (120 mg, 0.1 mmol), 4-methoxyphenylboronic acid (**6a**) (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.

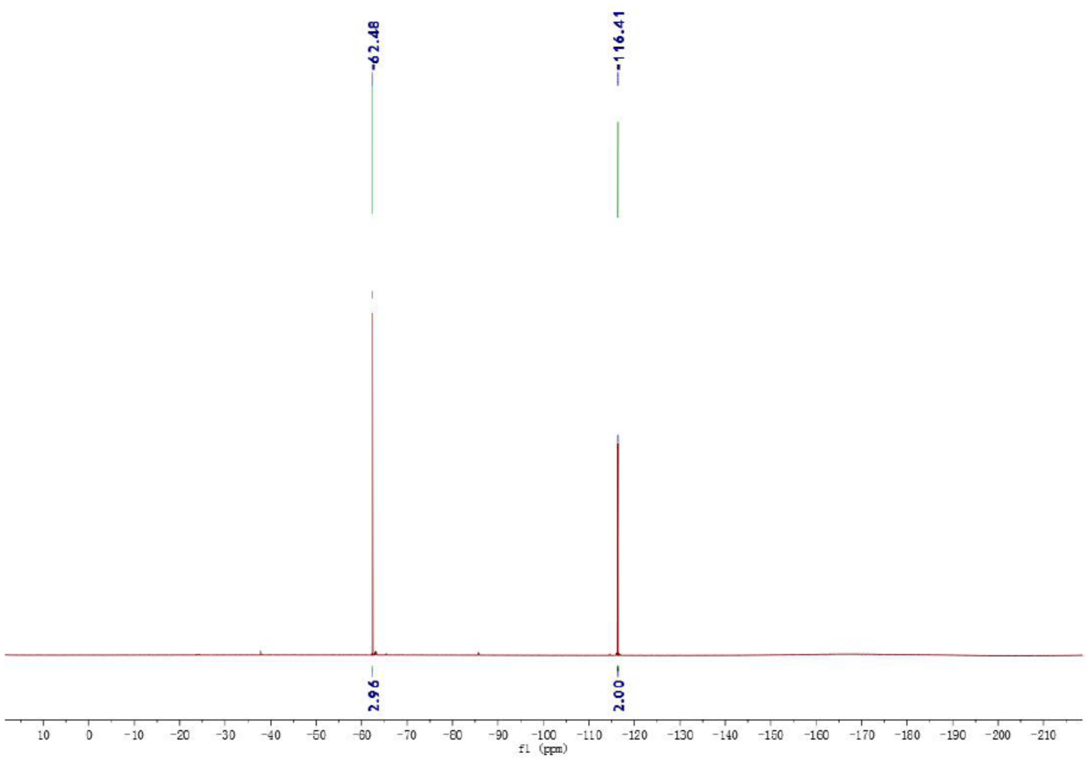


Figure S10. ^{19}F NMR determination of the reaction mixture of reaction of complex 3 with 6a under the reaction conditions of entry 7 in Table 1.

For example, Figure S10 shows the ^{19}F NMR determination of the reaction solution of entry 7 in Table 1 after workup described above. As can be seen, quantitative conversion of complex **3** was observed. The new signal at -62.5 ppm corresponds to the formation of trifluoromethylated arene **7a** while the signal at -116.4 ppm is the internal standard 4, 4′-difluorobiphenyl. The trifluoromethylation yield was thus determined to be 99% relative to **6a**.

4.2 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 $[(DPPE)_2Cu]^+[Cu(CF_3)_4]^-$ (**3**) (120 mg, 0.1 mmol), arylboronic acid (0.2 mmol), **KF** (0.2 mmol), 4 Å MS and 4, 4′-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The Schlenk tube was evacuated and refilled with dry oxygen. Dry **toluene** (1 mL) was then added by syringe. The contents in the tube were vigorously stirred and heated in an oil bath at 80°C for 18 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.

4.3 General procedure for reaction of **4** with various arylboronic acids

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added $[(BINAP)_2Cu]^+[Cu(CF_3)_4]^-$ (**4**) (165 mg, 0.1 mmol), arylboronic acid (0.2 mmol), **AgF** (0.2 mmol)**,** 4 Å MS and 4, 4′-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The Schlenk tube was evacuated and refilled with dry oxygen. Dry **toluene** (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 18 hours. The mixture was allowed to cool to room temperature, diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et_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.

4.4 General procedure for reaction of **5** with various arylboronic acids

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added $[(XantPhos)_2Cu]^+[Cu(CF_3)_4]^-$ (**5**) (156 mg, 0.1 mmol), arylboronic acid (0.2 mmol), **AgF** or **KF** (0.2 mmol), 4 Å MS and 4, 4′-difluorobiphenyl (internal standard; 38 mg, 0.2 mmol). The Schlenk tube was evacuated and refilled with dry oxygen. Dry **toluene** (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 18 hours. The mixture was allowed to cool to room temperature, diluted with ether and filtered through a pad of Celite. The Celite pad was washed with Et_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.