Electronic Supplementary Information

Exploring Catalytic Activity Modulations: Photoredox Catalysis with Substituted Copper(I)-Dipyridylamine Derivatives

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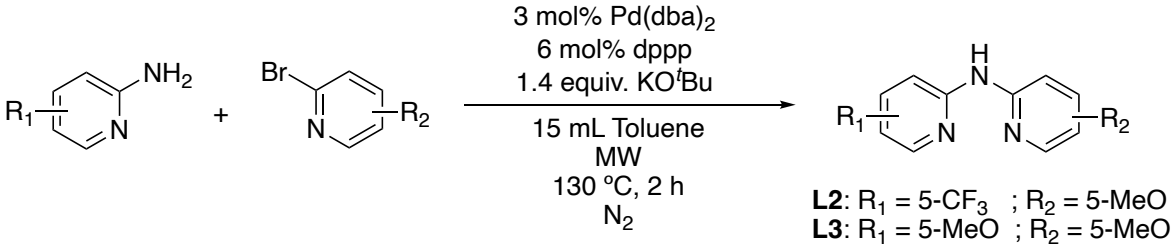
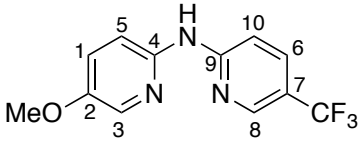
1. SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS.

1.1 General procedure for the synthesis and characterization of substituted 2,2'-dipyridylamines ligands



In a nitrogen-flushed 30 mL microwave glass vessel, 2 mmol of the corresponding aminopyridine, 2 mmol of the bromopyridine, 0.06 mmol of bis(dibenzylideneacetone)-palladium(0), 0.12 mmol of 1,3-bis(diphenylphosphino)propane and 2.8 mmol of KO^{t}Bu were dissolved in 15 mL of anhydrous toluene. The vessel was purged with nitrogen and sealed with a silicone septum. The reaction mixture was stirred at 130 °C in the microwave reactor for 2 h. Then, the solvent was removed under reduced pressure, and the crude product was absorbed into silica gel. The final product was obtained as a solid after flash column chromatography (PE:EA mixture with ratios between 5:2 and 5:3).

5-Methoxy-*N*-(5-(trifluoromethyl)pyridin-2-yl)pyridin-2-amine (**L2**):



Yellow solid, 75 % yield.

MP: 131.4–132.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.47 (s, 1 H, H8), 8.00 (d, *J* = 3.0 Hz, 1 H, H3), 7.74 (dd, *J* = 8.8, 2.4 Hz, 1 H, H6), 7.55 (d, *J* = 9.0 Hz, 1 H, H5), 7.51 (d, *J* = 8.9 Hz, 1 H, H10), 7.27 (dd, *J* = 9.0, 3.0 Hz, 1 H, H1), 3.86 (s, 3 H, OCH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 156.4 (C9), 151.6 (C2), 146.8 (C4), 145.6 (C8), 134.8 (C6), 133.7 (C3), 124.4 (C1), 118.4 (q, J^{C-F} = 33.0 Hz, CF_3), 113.3 (C5), 109.9 (C10), 56.1 (OCH_3).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ/ppm = –61.5.

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3271, 3183, 3075, 2962, 2935, 2839, 1932, 1620, 1408, 1157.

Elemental analysis ($C_{12}H_{10}F_3N_3O$): calc: C 53.54; H 3.74; N 15.61. Found: C 55.29; H 3.65; N 16.25.

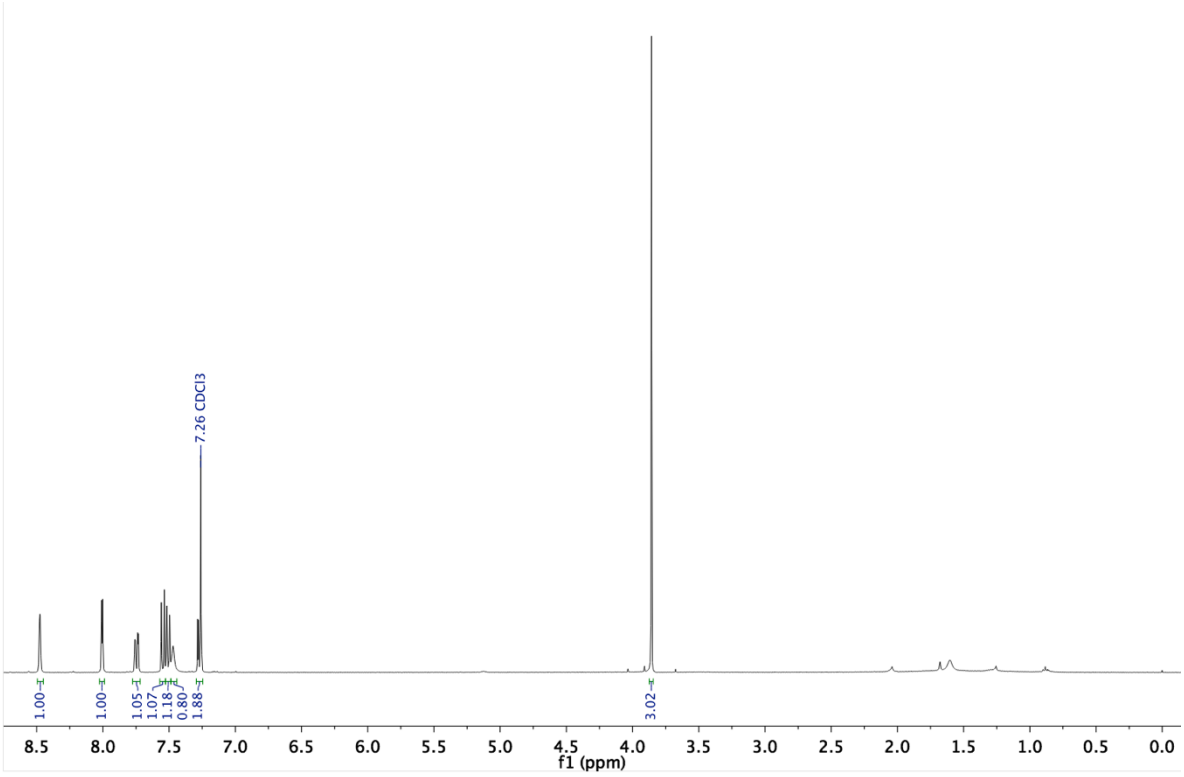


Figure S1. ^1H NMR (400 MHz, $CDCl_3$, 298 K).

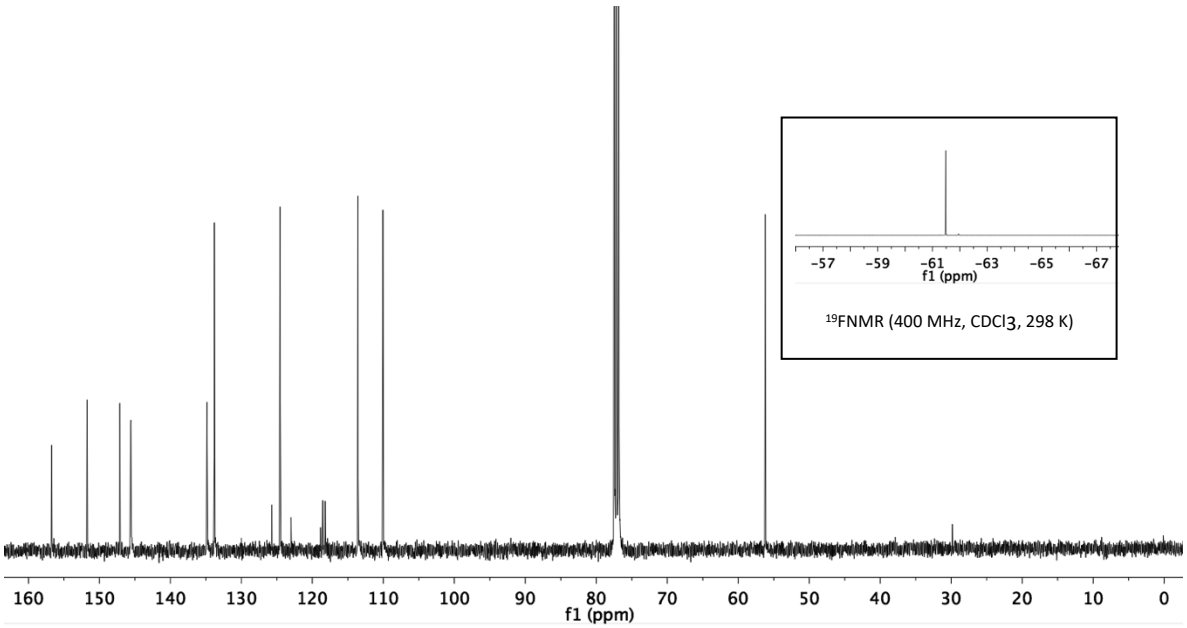
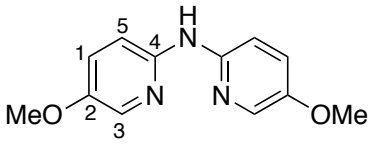


Figure S2. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) and insert of ^{19}F NMR (376 MHz, $CDCl_3$, 298 K).

Bis(5-methoxypyridin-2-yl)amine (**L3**):



White solid. 90 % yield.

MP: 134.5–135.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.33 (d, J = 1.9 Hz, 2 H, H3), 8.24 (d, J = 8.9 Hz, 2 H, H5), 7.29 (dd, J = 8.7, 2.6 Hz, 2 H, H1), 3.90 (s, 6 H, OCH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 155.5 (C2), 149.0 (C4), 136.6 (C3), 121.1 (C1), 120.9 (C5), 55.7 (O*C*H_3).

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3005, 2843, 2511, 1924, 1805, 1589, 1562, 1474, 1288.

Elemental analysis ($C_{12}H_{12}N_3O_2$): calc: C 62.33; H 5.67; N 18.17. Found: C 61.28; H 5.88; N 17.87.

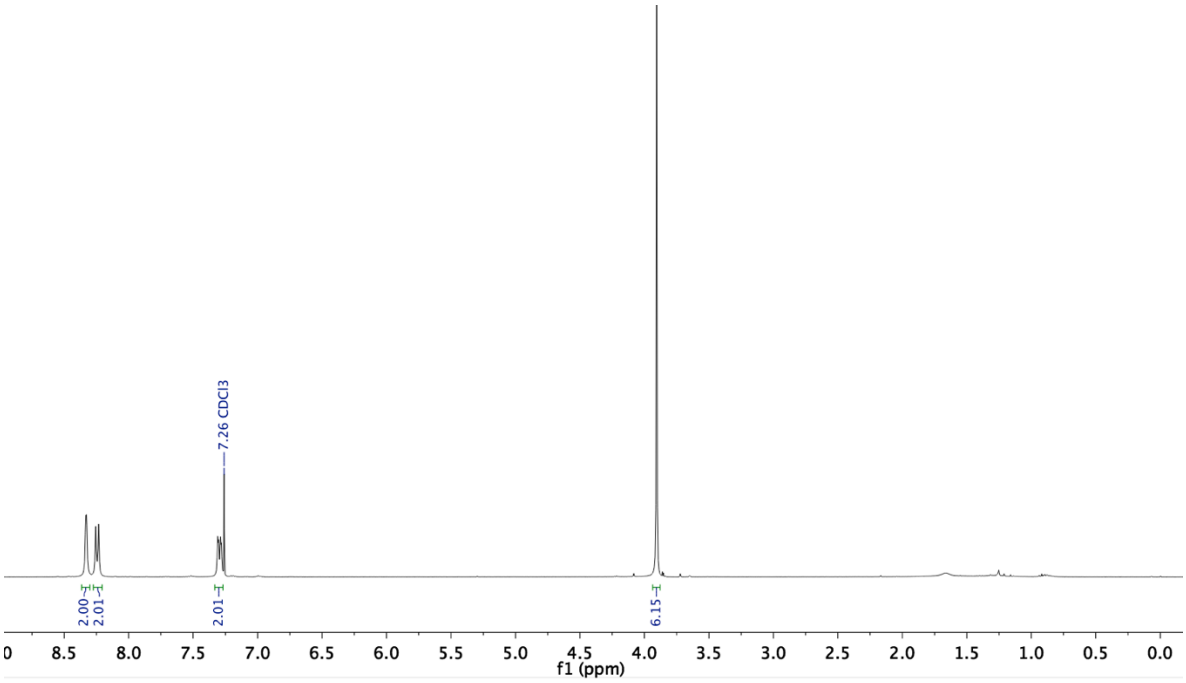


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

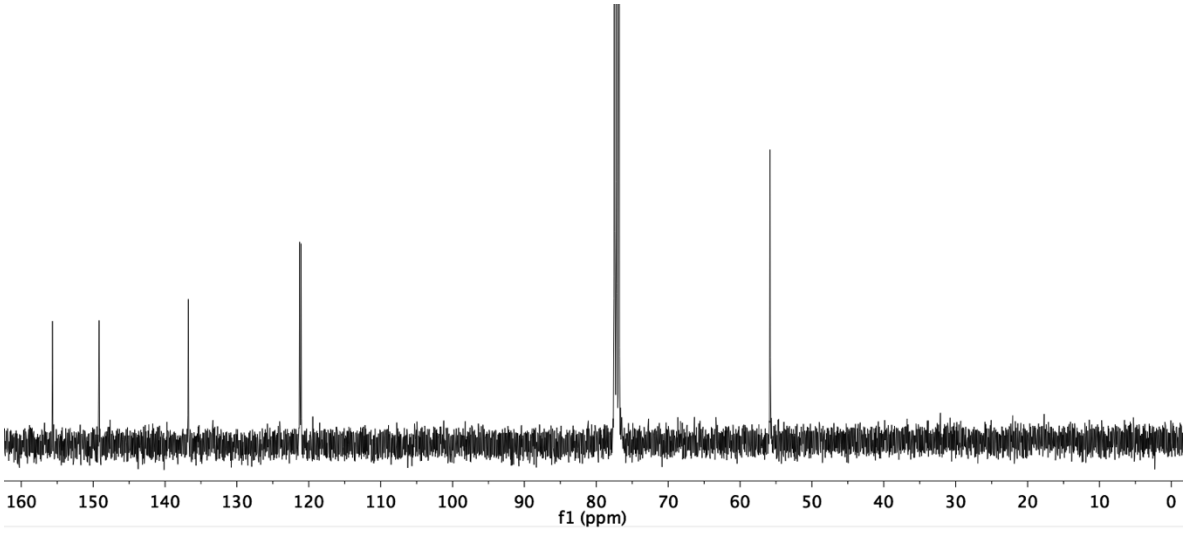
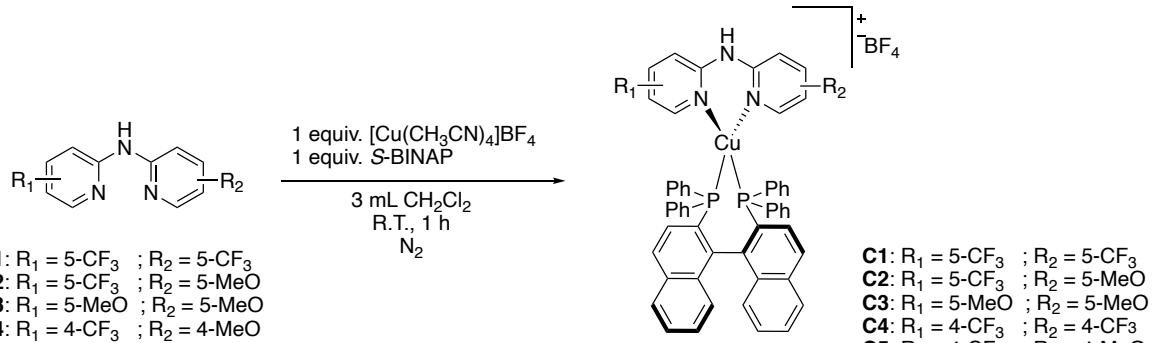


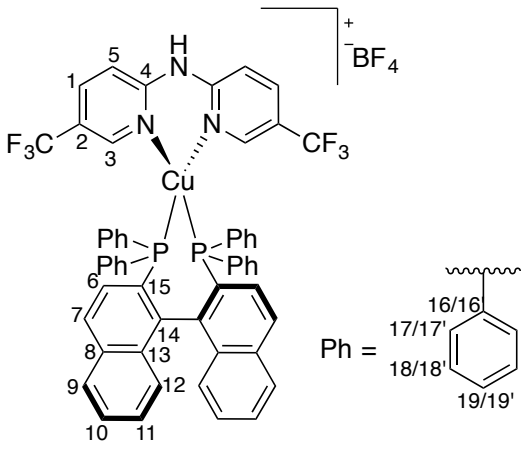
Figure S4. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K)

1.2 General procedure for the synthesis and characterization of the [Cu(*N*,*N*)(*S*-BINAP)]BF_4 complexes.



In a glass vial, 1 mmol of $[Cu(CH_3CN)_4]BF_4$, 1 mmol of *S*-BINAP, and 1 mmol of the corresponding ligand **L1–5** were added. Then, the vial was sealed with a septum and was nitrogen flushed for 5 min. Later, 5 mL of anhydrous dichloromethane was added through a purged syringe, and the reaction mixture was stirred at room temperature for 1 hour under a nitrogen atmosphere. Afterward, the volatiles were removed under reduced pressure, and the crude product was purified by crystallization from a mixture of CH_2Cl_2 and toluene at –20 °C.

[(bis(5-(trifluoromethyl)pyridin-2-yl)amine)((−)2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl)Cu]BF_4 (**C1**).



Yellow solid. 94 % yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 9.64 (s, 1 H, N*H*), 8.12 (s, 2 H, H3), 7.83 (dd, *J* = 8.9 Hz, 1.9 Hz, 2 H, H1), 7.69 (d, *J* = 8.7 Hz, 2 H, H6), 7.62 (d, *J* = 8.3 Hz, 2 H, H12),

7.31–7.51 (m, 16 H, H5, H7, H11, H17', H18', H19'), 7.00 (t, J = 7.7 Hz, 2 H, H10), 6.79–6.85 (m, 8 H, H17, H19), 6.55–6.61 (m, 6 H, H9, H18).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 156.0 (C4), 145.5 (q, $J^{C\text{-}F}$ = 4.6 Hz, C3), 139.6 (t, $J^{C\text{-}P}$ = 9.9 Hz, C13), 136.3 (C1), 134.0 (t, $J^{C\text{-}P}$ = 4.3 Hz, C16'), 133.8 (t, $J^{C\text{-}P}$ = 9.4 Hz, C17'), 133.2 (C8), 132.8 (t, $J^{C\text{-}P}$ = 8.6 Hz, C17), 131.3 (t, $J^{C\text{-}P}$ = 17.5 Hz, C15), 130.7 (t, $J^{C\text{-}P}$ = 13.5 Hz, C14), 130.7 (19'), 129.8 (C19), 129.4 (t, $J^{C\text{-}P}$ = 4.9 Hz, C18'), 129.3 (t, $J^{C\text{-}P}$ = 3.4 Hz, C6), 128.8 (t, $J^{C\text{-}P}$ = 15.7 Hz, C16), 128.0 (C12), 127.7 (t, $J^{C\text{-}P}$ = 5.1 Hz, C18), 126.9 (C11), 126.8 (C9), 126.7 (C10), 126.2 (t, $J^{C\text{-}P}$ = 3.1 Hz, C7), 123.0 (q, $J^{C\text{-}F}$ = 271.1 Hz, CF_3), 121.1 (q, $J^{C\text{-}F}$ = 34.0 Hz, C2), 116.7 (C5).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ/ppm = –0.6 (s, BF_4).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ/ppm = –150.6 (s, BF_4), –62.2 (s, CF_3).

^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ/ppm = –0.6 (s, *S*-BINAP).

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3333, 3225, 3055, 1643, 1581, 1497, 1323, 1173, 745.

Elemental analysis ($C_{56}H_{39}BCuF_{10}N_3P_2$): calc: C 62.27; H 3.64; N 3.89. Found: C 61.31; H 3.78; N 4.10.

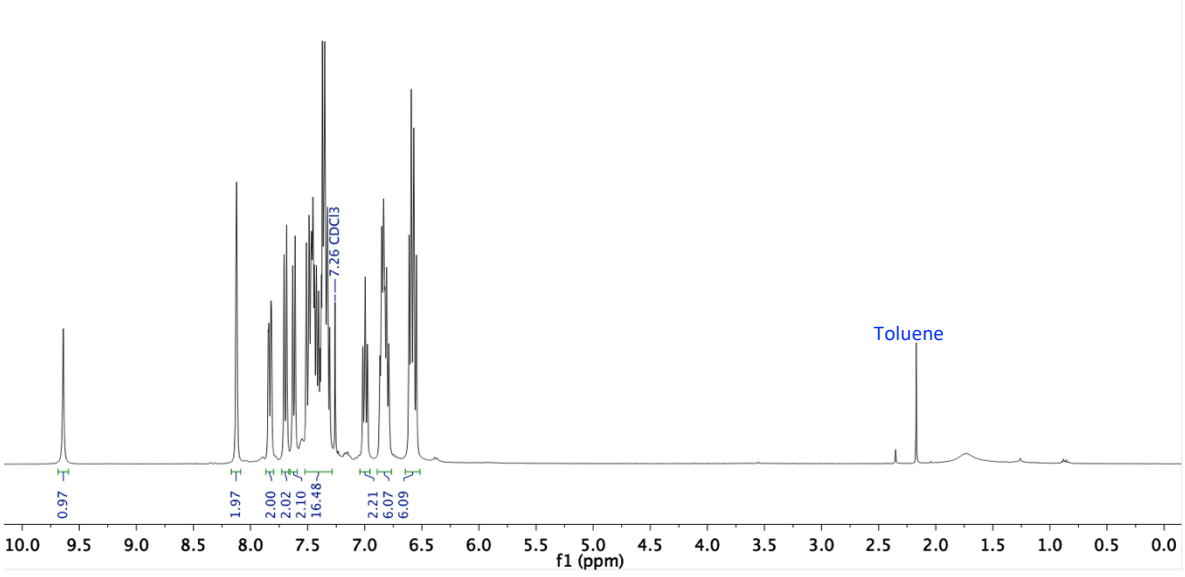


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

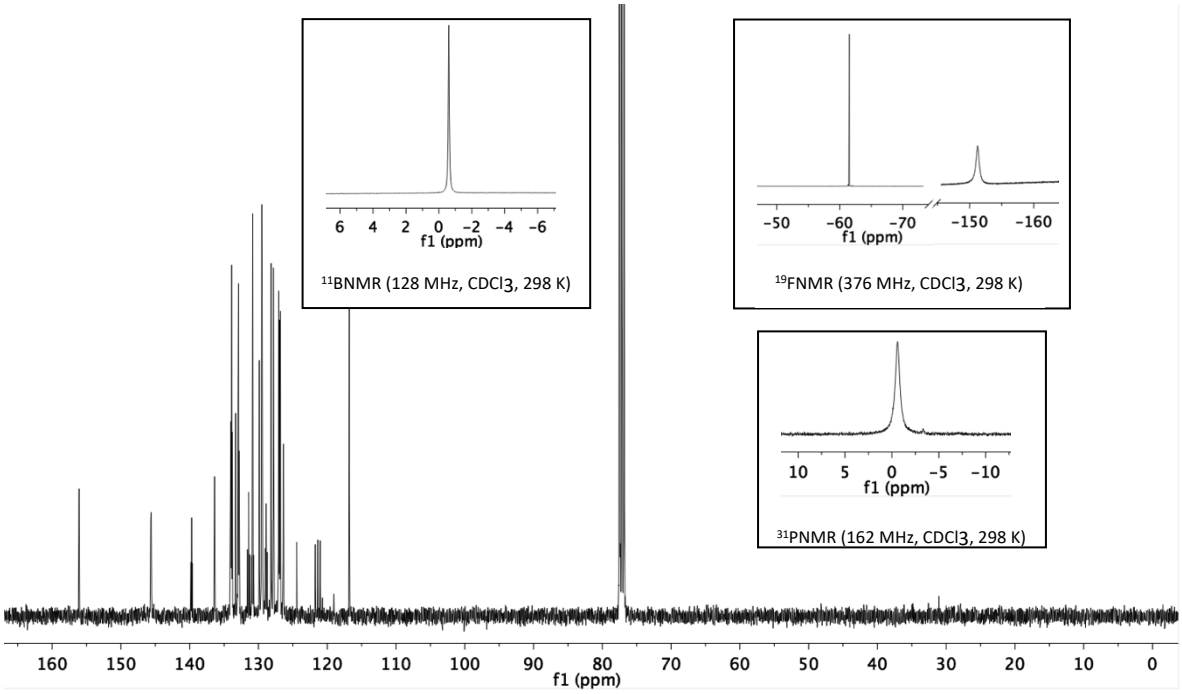


Figure S6. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) and inserts of ^{19}F NMR (376 MHz, $CDCl_3$, 298 K), ^{11}B NMR (128 MHz, $CDCl_3$, 298 K), and ^{31}P NMR (162 MHz, $CDCl_3$, 298 K).

Table S1. Crystal data and structure refinement for **C1**.

Empirical formula	C56 H41 B Cu F10 N3 O P2
Formula weight	1098.21
Temperature	99.99(10) K
Wavelength	1.54184 A
Crystal system, space group	Tetragonal, P 41 21 2
Unit cell dimensions	a = 21.2079(2) A; alpha = 90 deg. b = 21.2079(2) A; beta = 90 deg. c = 11.48610(10) A; gamma = 90 deg.
Volume	5166.16(11) A^3
Z, Calculated density	4, 1.412 Mg/m^3
Absorption coefficient	1.869 mm^-1
F(000)	2240
Crystal size	0.28 x 0.19 x 0.14 mm
Theta range for data collection	2.947 to 77.262 deg.
Limiting indices	-26<=h<=26 -26<=k<=25 -14<=l<=14
Reflections collected / unique	61139 / 5425 [R(int) = 0.0674]
Completeness to theta = 67.684	99.9 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.663

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5425 / 127 / 397
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0733
R indices (all data)	R1 = 0.0340, wR2 = 0.0769
Absolute structure parameter	-0.018(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.239 and -0.417 e.A^-3

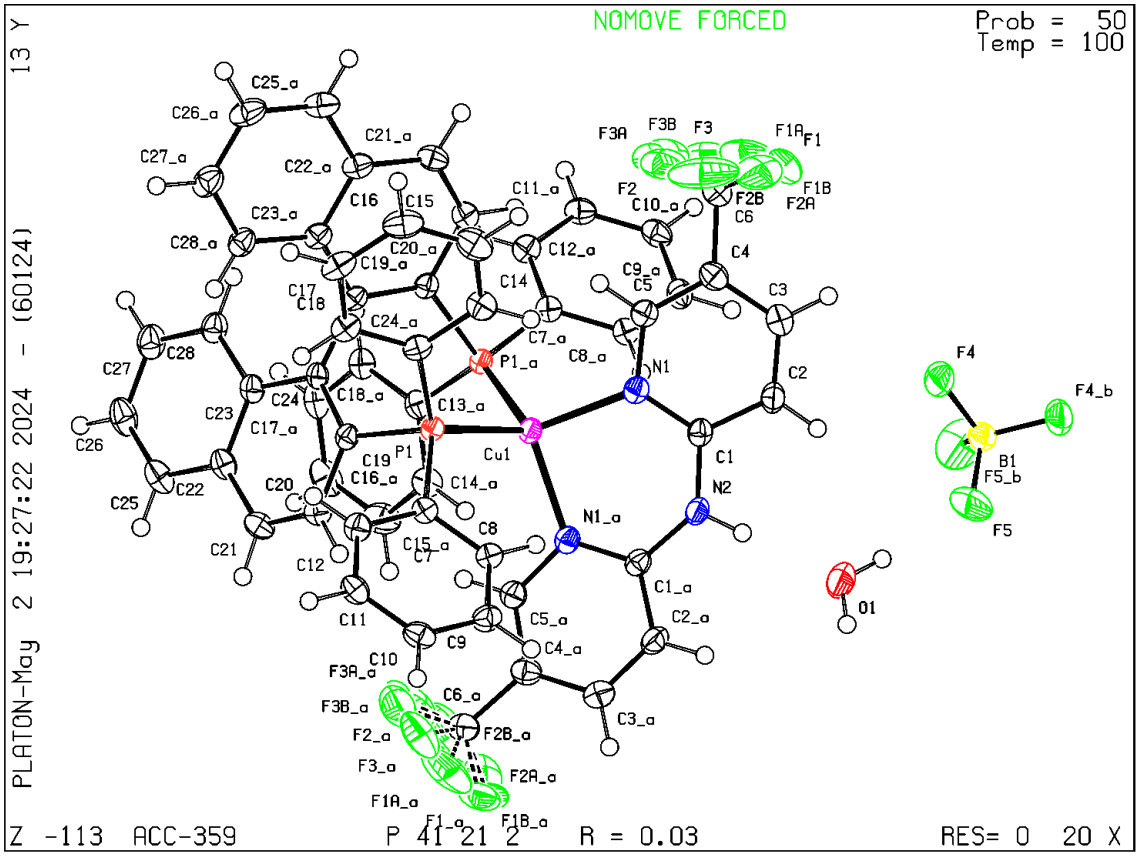
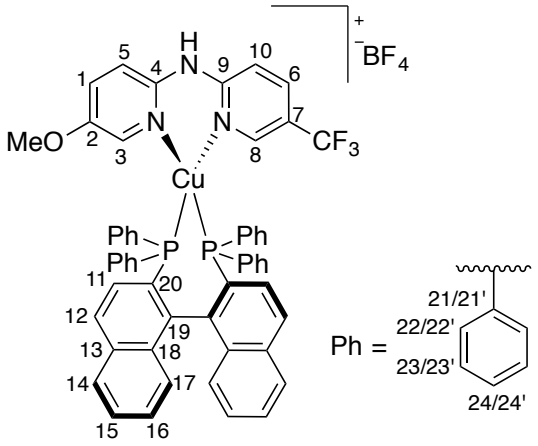


Figure S7. Molecular structure of **C1** obtained by XRD.

[(5-Methoxy-*N*-(5-(trifluoromethyl)pyridin-2-yl)pyridin-2-amine)((−)2,2′-Bis(diphenyl-phosphino)-1,1′-binaphthyl)Cu]BF_4 (**C2**).



Yellow solid. 92 % yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 9.06 (s, 1 H, N*H*), 7.95 (s, 1 H, H8), 7.19–7.62 (m, 27 H, H1, H3, H5, H6, H10, H11, H12, H16, H17, H22', H23', H24'), 6.64–6.92 (m, 8 H, H15, H22, H24), 6.46–6.53 (m, 6 H, H14, H23), 3.44 (s, 3 H, OCH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 152.0 (C2), 157.0 (C9), 147.8 (C4), 145.4 (C8), 139.5 (t, $J^{C\text{-}P}$ = 9.6 Hz, C18), 135.5 (C6), 134.1 (t, $J^{C\text{-}P}$ = 9.3 Hz, C22'), 133.9 (t, $J^{C\text{-}P}$ = 3.9 Hz, C13), 132.8 (t, $J^{C\text{-}P}$ = 8.4 Hz, C3, C22), 131.7 (t, $J^{C\text{-}P}$ = 17.4 Hz, C20), 130.7 (C24'), 129.5 (C24), 129.3 (t, $J^{C\text{-}P}$ = 4.9 Hz, C23'), 129.2 (C1), 129.1 (C11), 127.8, 128.0 (C17), 127.6 (t, $J^{C\text{-}P}$ = 4.9 Hz, C23), 127.0 (C14), 126.8 (C16), 126.6 (C15), 126.5 (C12), 123.4 (q, $J^{C\text{-}F}$ = 271.2 Hz, *C*F_3), 119.4 (q, $J^{C\text{-}F}$ = 34.0 Hz, C7), 117.7 (C5), 115.8 (C10), 56.1 (O*C*H_3).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ/ppm = –0.6 (s, *B*F_4).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ/ppm = –151.2 (s, B*F*$_4$), –62.0 (s, C*F*$_3$).

^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ/ppm = –0.9 (s, *S*-BINAP).

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3337, 3225, 3055, 1635, 1582, 1493, 1331, 1261, 995.

Elemental analysis ($C_{56}H_{42}BCuF_7N_3OP_2$): calc: C 64.53; H 4.06; N 4.03. Found: C 64.17; H 3.62; N 4.48.

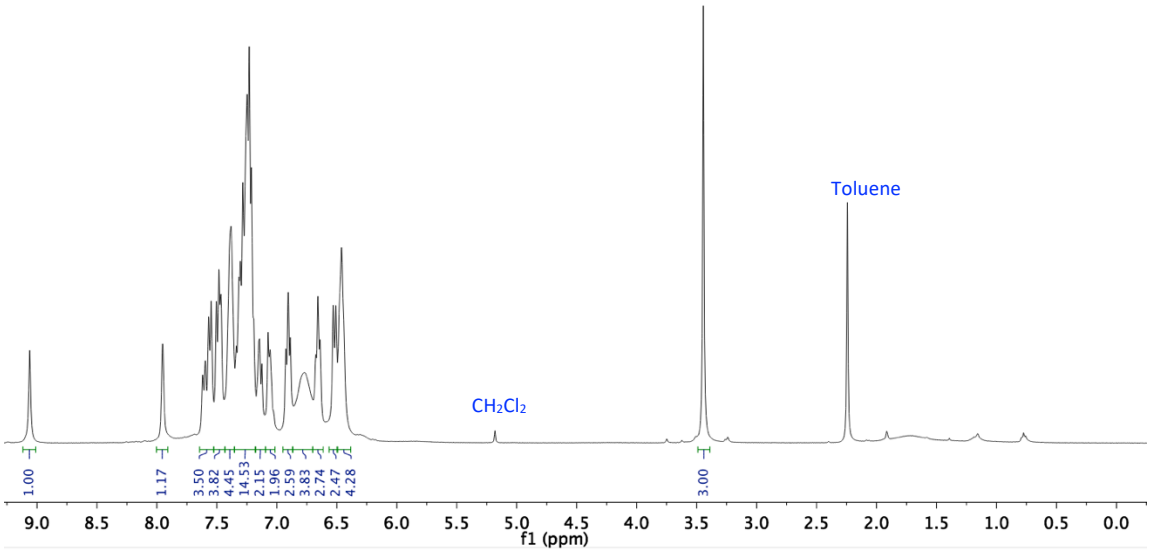


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

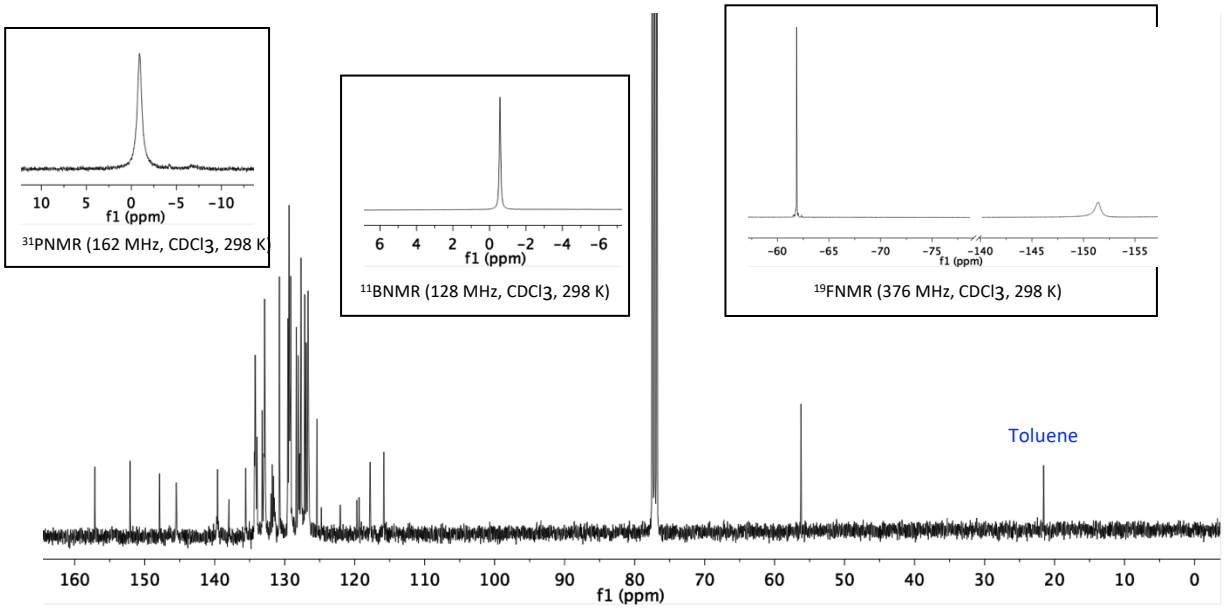
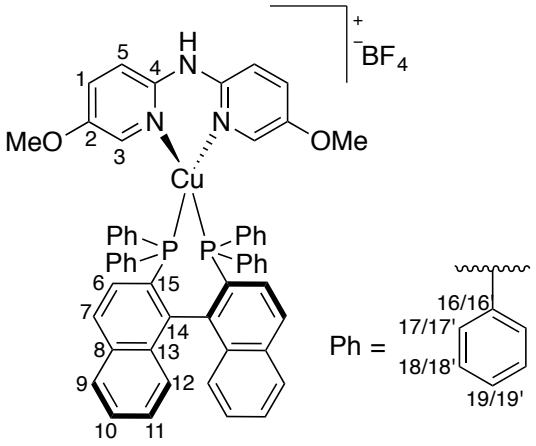


Figure S9. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) and inserts of ^{19}F NMR (376 MHz, $CDCl_3$, 298 K), ^{11}B NMR (128 MHz, $CDCl_3$, 298 K), and ^{31}P NMR (162 MHz, $CDCl_3$, 298 K).

[(bis(5-methoxypyridin-2-yl)amine)((−)2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl)Cu]BF_4 (**C3**).



Yellow solid. 98 % yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.48 (d, *J* = 8.7 Hz, 2 H, H5), 7.87 (s, 2 H, H3), 7.58–7.65 (m, 6 H, H1, H6, H12), 7.29–7.35 (m, 4 H, H11, H19'), 7.17–7.23 (m, 10 H, H7, H17', H18'), 7.06–7.13 (m, 2 H, H10), 6.96 (q, *J* = 6.0 Hz, 4 H, H17), 6.75–6.81 (m, 4 H, H9, H19), 6.58 (t, *J* = 7.3 Hz, 4 H, H18), 3.75 (s, 6 H, OCH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 156.9 (C2), 145.0 (C4), 139.4 (t, $J^{C\text{-}P}$ = 9.3 Hz, C13), 137.7 (C3), 134.1 (t, $J^{C\text{-}P}$ = 9.5 Hz, C17'), 133.8 (t, $J^{C\text{-}P}$ = 3.9 Hz, C8), 133.2 (not assigned), 132.8 (t, $J^{C\text{-}P}$ = 8.7 Hz, C16), 132.1 (t, $J^{C\text{-}P}$ = 18.1 Hz, C17), 131.2 (t, $J^{C\text{-}P}$ = 13.1 Hz), 130.7 (C19'), 129.5 (C19), 129.2 (t, $J^{C\text{-}P}$ = 5.0 Hz, C18'), 129.0 (q, $J^{C\text{-}P}$ = 3.4 Hz, C6), 128.1 (C12), 127.5 (t, $J^{C\text{-}P}$ = 5.5 Hz, C18), 127.3 (t, $J^{C\text{-}P}$ = 6.5 Hz, C9), 127.0 (C11), 126.7 (C10), 123.5 (C5), 123.3 (C1), 56.2 (O*C*H_3).

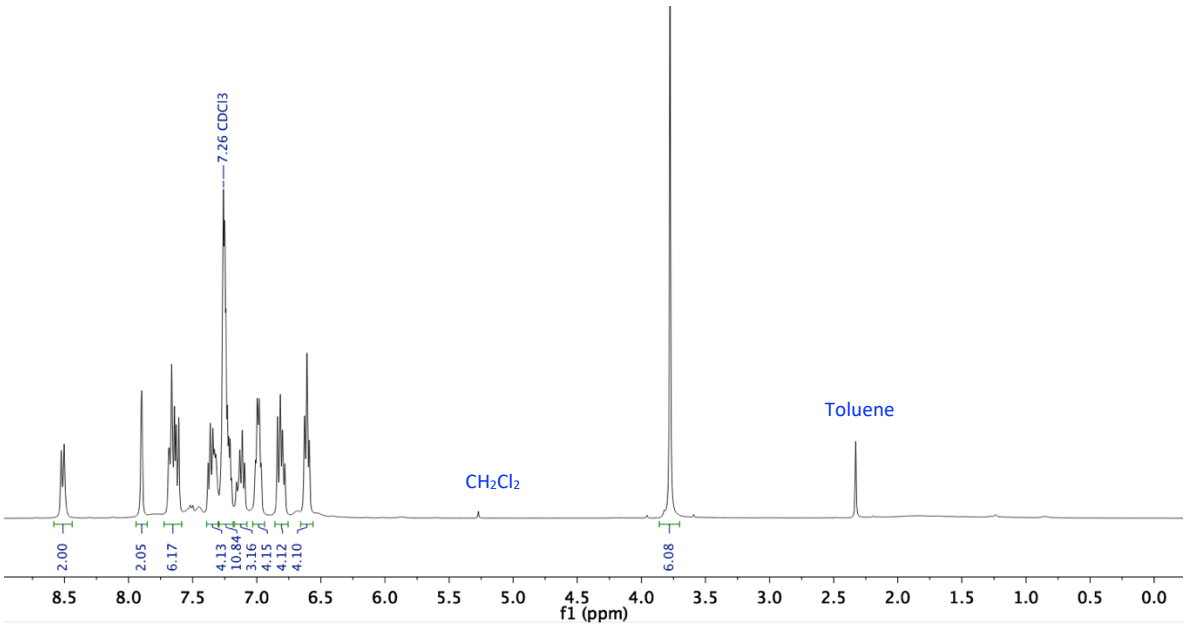
^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ/ppm = –0.6 (s, *B*F_4).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ/ppm = –153.7 (s, B*F*$_4$).

^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ/ppm = 1.1 (s, *S*-BINAP).

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055, 2936, 2839, 1601, 1578, 1481, 1292, 1234, 1057.

Elemental analysis ($C_{56}H_{45}BCuF_4N_3O_2P_2$): calc: C 66.97; H 4.52; N 4.18. Found: C 66.39; H 2.94; N 4.41.



199

200 **Figure S10**. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

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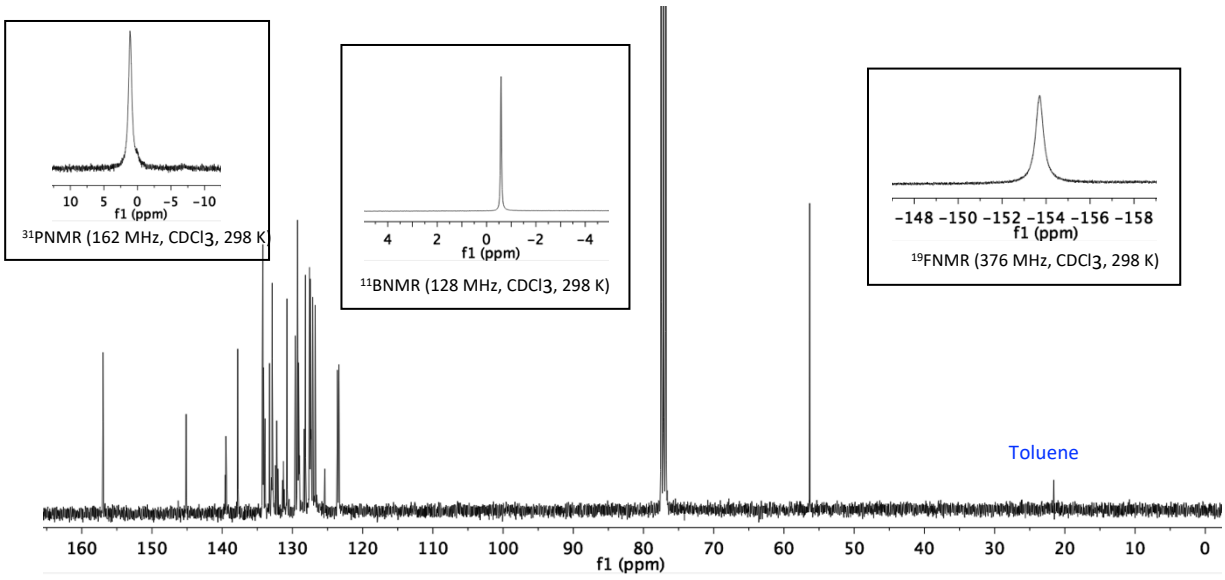
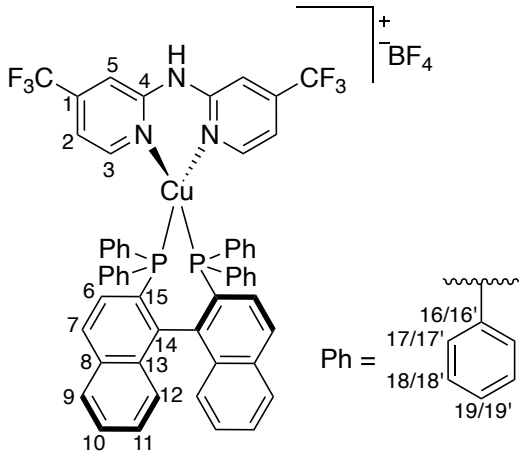


202

203 **Figure S11**. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) and inserts of ^{19}F NMR (376 MHz,
204 $CDCl_3$, 298 K), ^{11}B NMR (128 MHz, $CDCl_3$, 298 K), and ^{31}P NMR (162 MHz, $CDCl_3$,
205 298 K).

206

[(bis(4-(trifluoromethyl)pyridin-2-yl)amine)((−)2,2′-Bis(diphenylphos-phino)-1,1′-binaph-thyl)Cu]BF_4 (**C4**).



Yellow solid. 92 % yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm 9.27 (s, 1H, NH), 7.86 (d, J = 5.5 Hz, 2H, H3), 7.58 (d, J = 8.6 Hz, 2H, H7), 7.49 (m, 4H, H5,H9), 7.37–7.29 (m, 8H, H6, H17), 7.25–7.13 (m, 6H, H10), 6.92 (d, J = 5.5 Hz, 2H, H2), 6.83 (t, J = 7.6 Hz, 2H, H11), 6.73–6.59 (m, 6H, H18), 6.47 (t, J = 7.4 Hz, 4H, H19), 6.35 (d, J = 8.6 Hz, 2H, H12).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 155.0 (C4), 148.8 (C3), 141.6 (q, $J^{C\text{-}F}$ = 34.7 Hz, C1), 139.8 (t, $J^{C\text{-}P}$ = 10.1 Hz, C14), 134.0 (t, $J^{C\text{-}P}$ = 9.1 Hz, C18), 133.2 (C13), 133.0 (t, $J^{C\text{-}P}$ = 8.5 Hz, C18'), 131.4 (t, $J^{C\text{-}P}$ = 17.4 Hz, C16), 131.0 (t, $J^{C\text{-}P}$ = 13.4 Hz, C15), 130.8 (C6), 129.9 (C7), 129.5 (t, $J^{C\text{-}P}$ = 4.9 Hz, C19), 129.2 (t, $J^{C\text{-}P}$ = 3.3 Hz, C17), 128.9 (t, $J^{C\text{-}P}$ = 15.5 Hz, C16'), 128.0 (C9), 127.9 (t, $J^{C\text{-}P}$ = 5.2 Hz, C19'), 127.1 (C12), 126.9 (C10), 126.8 (C11), 126.3 (t, $J^{C\text{-}P}$ = 3.4 Hz, C17'), 122.0 (q, $J^{C\text{-}F}$ = 273.9 Hz, CF$_3$), 113.7 (d, $J^{C\text{-}F}$ = 3.2 Hz, C2), 113.1 (d, $J^{C\text{-}F}$ = 4.2 Hz, C5).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ/ppm = –0.67 (s, BF$_4$).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ/ppm = –150.48 (s, BF_4), –65,35 (s, CF_3)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ/ppm = –0.43 (s, *S*-BINAP).

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3337, 3057, 1637, 1538, 1472, 1401, 1347, 1308, 1181, 1138, 1092, 816, 741, 671.

Elemental analysis ($C_{56}H_{39}BCuF_{10}N_3P_2$): calc: C 62.27; H 3.64; N 3.89. Found: C 61.52; H 3.85; N 3.93.

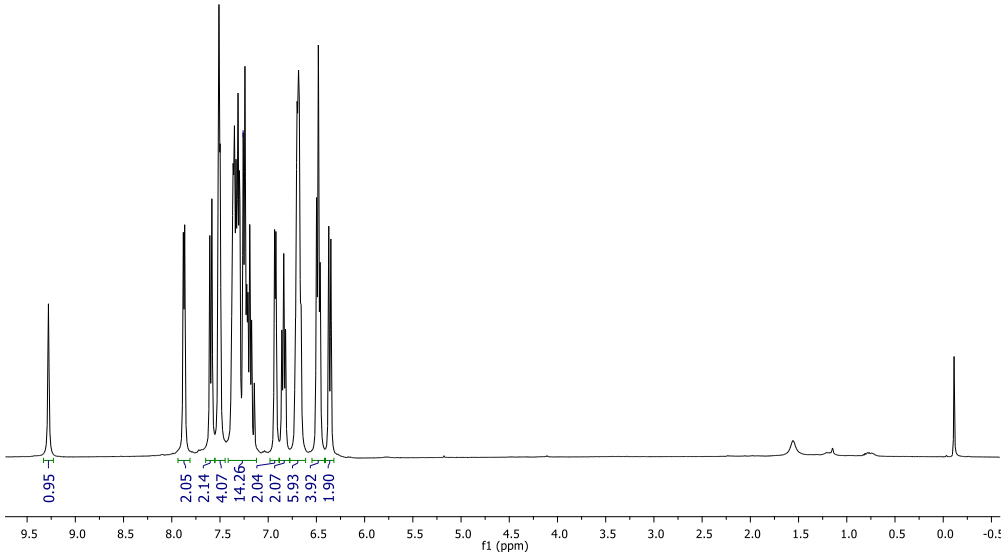


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

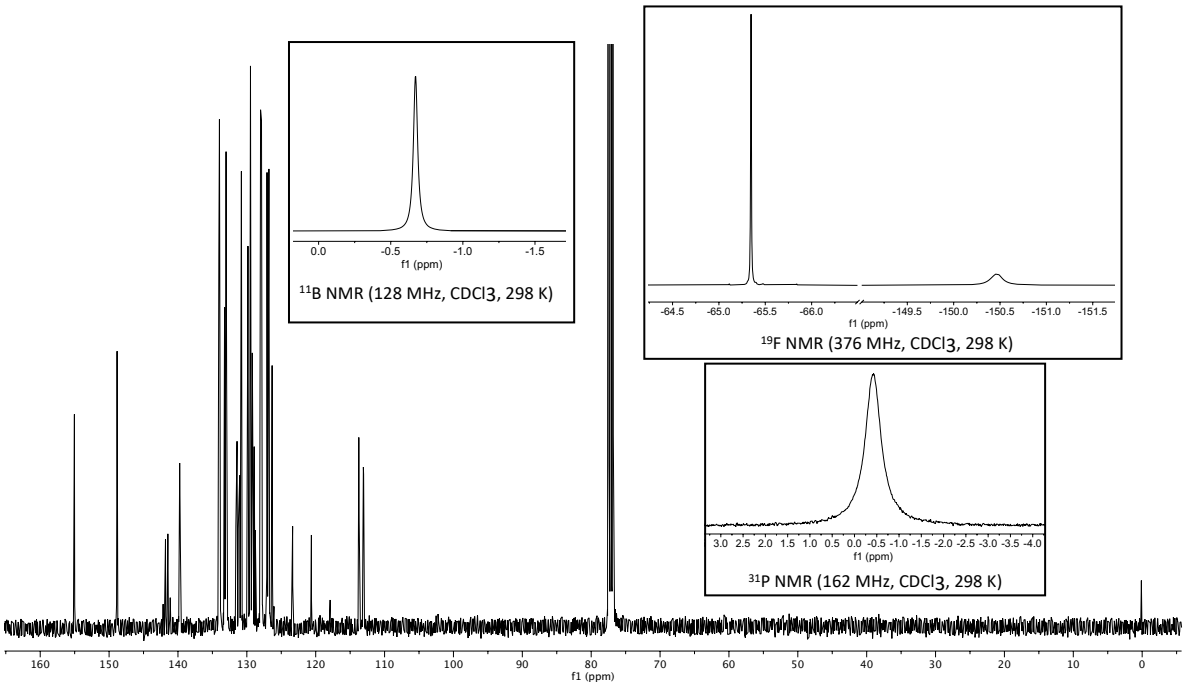


Figure S13. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) and inserts of ^{19}F NMR (376 MHz, $CDCl_3$, 298 K), ^{11}B NMR (128 MHz, $CDCl_3$, 29 K), and ^{31}P NMR (162 MHz, $CDCl_3$, 298 K).

Table S2. Crystal data and structure refinement for **C4**.

Empirical formula	C57 H41 B Cl2 Cu F10 N3 P2
Formula weight	1165.12
Temperature	100 K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 12.3842 (1) A; alpha = 90 deg. b = 19.9197(2) A; beta = 90 deg. c = 21.0692(2) A; gamma = 90 deg.
Volume	5197.55(8) A^3
Z, Calculated density	4, 1.489 Mg/m^3
Absorption coefficient	2.801 mm^-1
F(000)	2368
Crystal size	0.41 x 0.33 x 0.24 mm
Theta range for data collection	3.053 to 76.854 deg.
Limiting indices	-13<=h<=15, -25<=k<=25, -26<=l<=26
Reflections collected / unique	60749 / 10811 [R(int) = 0.0641]
Completeness to theta = 67.684	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.348
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10811 / 14 / 698
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0877
R indices (all data)	R1 = 0.0348, wR2 = 0.0879
Absolute structure parameter	-0.020(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.544 and -0.567 e.A^-3

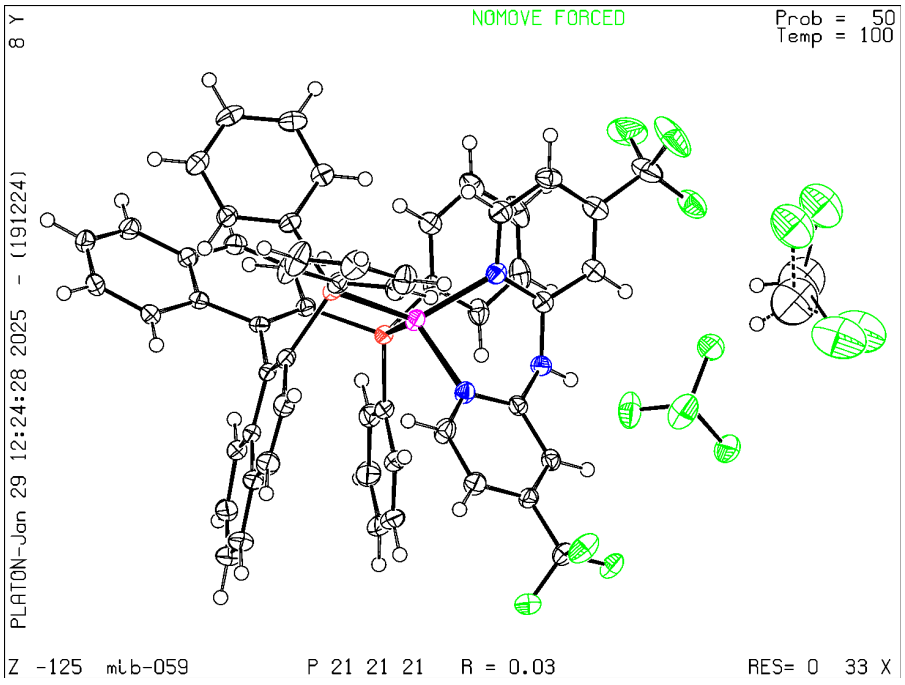
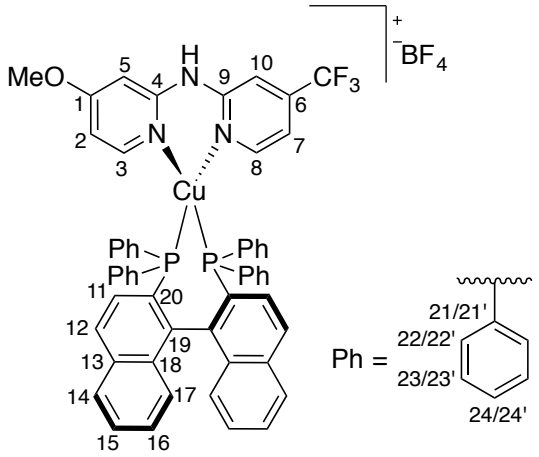


Figure S14. Molecular structure of **C4** obtained by XRD.

[(4-Methoxy-*N*-(4-(trifluoromethyl)pyridin-2-yl)pyridin-2-amine)((−)2,2′-Bis(diphenyl-phosphino)-1,1′-binaphthyl)Cu]BF_4 (**C5**).



Yellow solid. 89 % yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 9.00 (s, 1 H, N*H*), 7.95 (d, *J* = 5.6 Hz, 1 H, H8), 7.66–7.68 (m, 3 H, H3, H11), 7.60(d, *J* = 8.2 Hz, 2 H, H17), 7.28–7.49 (m, 15 H, H10, H12, H16, H22', H23', H24'), 6.92–6.98 (m, 4 H, H5, H7, H15), 6.85 (dd, *J* = 11.3, 6.1 Hz, 4 H, H22), 6.76 (t, ^3J = 7.3 Hz, 2 H, H24), 6.53–6.59 (m, 6 H, H14, H23), 6.45 (dd, *J* = 6.4, 1.5 Hz, 1 H, H2), 3.91 (s, 3 H, OCH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ/ppm = 168.3 (C1), 156.0 (C4), 155.6 (C9), 148.8 (C8), 148.3 (C3), 141.1 (q, $J^{C\text{-}F}$ = 34.6 Hz, C6), 139.6 (t, $J^{C\text{-}P}$ = 9.8 Hz, C18), 134.0 (t, $J^{C\text{-}P}$ = 4.0 Hz, C13), 134.2 (C22'), 133.1 (not assigned), 133.0 (t, $J^{C\text{-}P}$ = 8.4 Hz, C22), 131.9 (t, $J^{C\text{-}P}$ = 16.9 Hz, C20), 131.8 (t, $J^{C\text{-}P}$ = 13.7 Hz, C19), 130.6 (C24'), 129.5 (t, $J^{C\text{-}P}$ = 8.7 Hz, C21), 129.5 (C24), 129.3 (t, $J^{C\text{-}P}$ = 4.8 Hz, C23'), 129.0 (t, $J^{C\text{-}P}$ = 2.5 Hz, C11), 128.0 (C17), 127.7 (t, $J^{C\text{-}P}$ = 5.1 Hz, C23), 127.1 (C14), 126.9 (C16), 126.6 (C12, C15), 122.1 (q, $J^{C\text{-}F}$ = 272.2 Hz, 1 C, *C*F_3), 112.5 (C7, C10), 109.2 (C2), 98.5 (C5), 56.5 (O*C*H_3).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ/ppm = –0.6 (s, *B*F_4).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ/ppm = –150.8 (s, B*F*$_4$), –65.3 (s, C*F*$_3$).

^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ/ppm = –1.0 (s, *S*-BINAP).

FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3333, 3217, 3055, 1635, 1535, 1497, 1350, 1269, 887.

Elemental analysis ($C_{56}H_{42}BCuF_7N_3OP_2$): calc: C 64.53; H 4.06; N 4.03. Found: C 63.22; H 4.08; N 4.18.

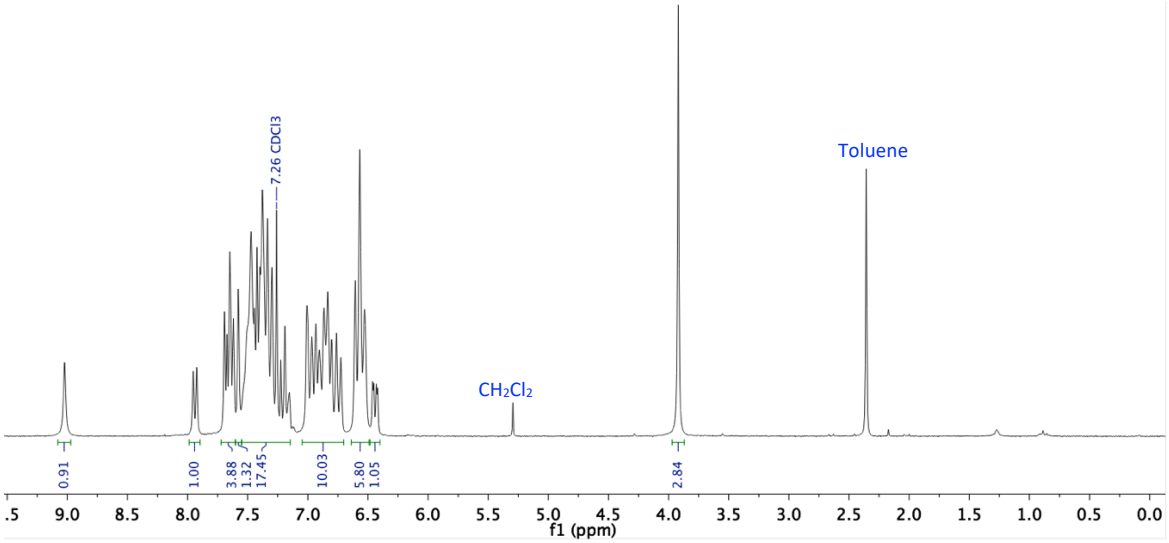


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

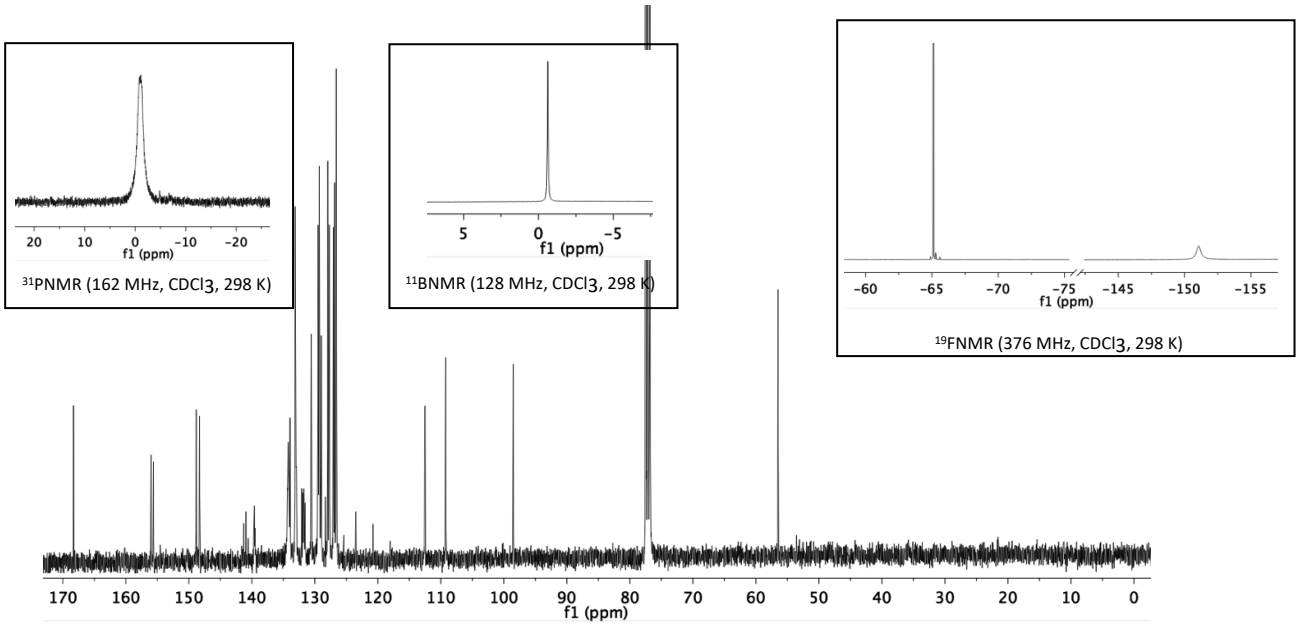


Figure S16. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) and inserts of ^{19}F NMR (376 MHz, $CDCl_3$, 298 K), ^{11}B NMR (128 MHz, $CDCl_3$, 298 K), and ^{31}P NMR (162 MHz, $CDCl_3$, 298 K).

Table S3. Crystal data and structure refinement for **C5**.

Empirical formula	C56.75 H43.50 B Cl1.50 Cu F7 N3 O P2
Formula weight	1105.91
Temperature	99.94(13) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 12.1556(3) A; alpha = 90 deg. b = 19.4730(6) A; beta = 90 deg. c = 21.5417(6) A; gamma = 90 deg.
Volume	5099.0(2) A^3
Z, Calculated density	4, 1.446 Mg/m^3
Absorption coefficient	0.645 mm^-1
F(000)	2270
Crystal size	0.32 x 0.09 x 0.08 mm
Theta range for data collection	2.295 to 29.468 deg.
Limiting indices	-16<=h<=16, -26<=k<=26 -29<=l<=28
Reflections collected / unique	67425 / 12956 [R(int) = 0.0530]
Completeness to theta = 67.684	99.8 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.702
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12956 / 799 / 852
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0789
R indices (all data)	R1 = 0.0623, wR2 = 0.0715
Absolute structure parameter	-0.014(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.332 and -0.308 e.A^-3

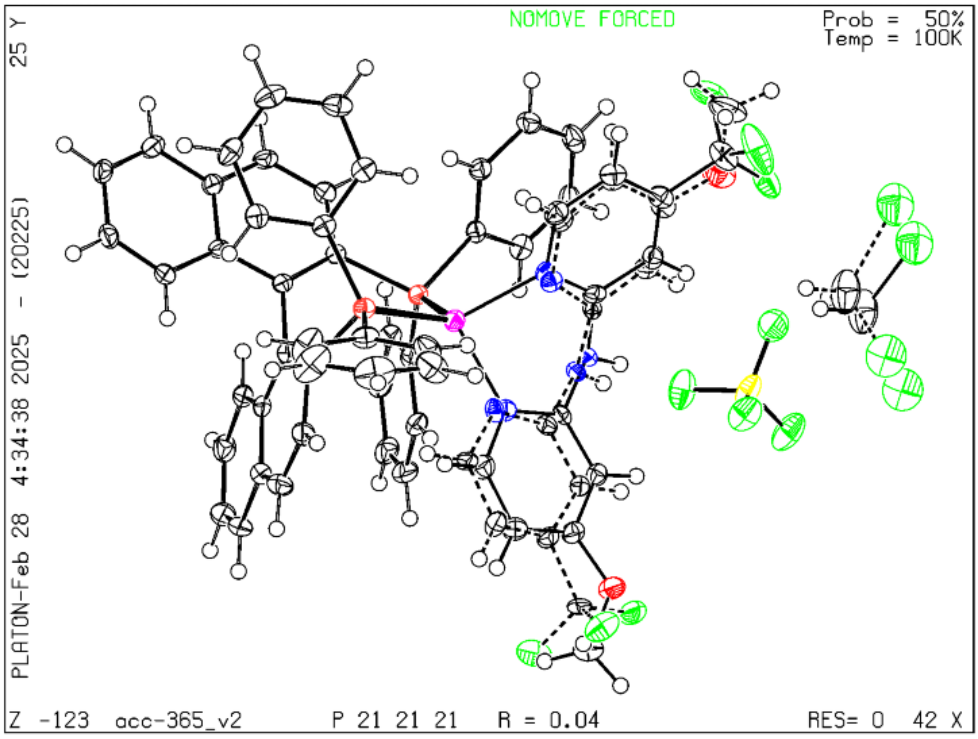


Figure S17. Molecular structure of **C5** obtained by XRD.

2. ELECTROCHEMICAL CHARACTERIZATION

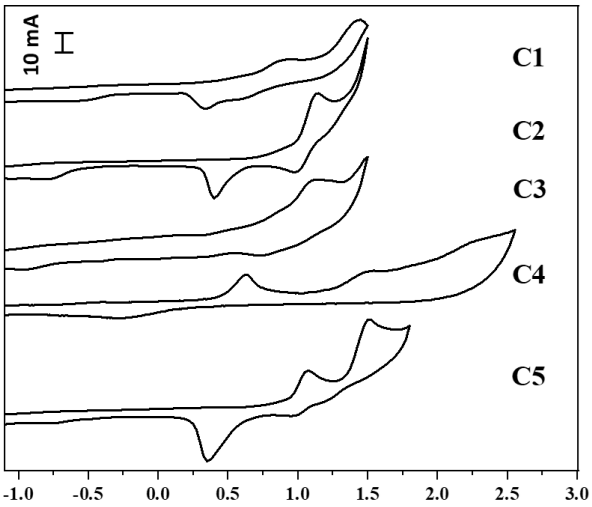
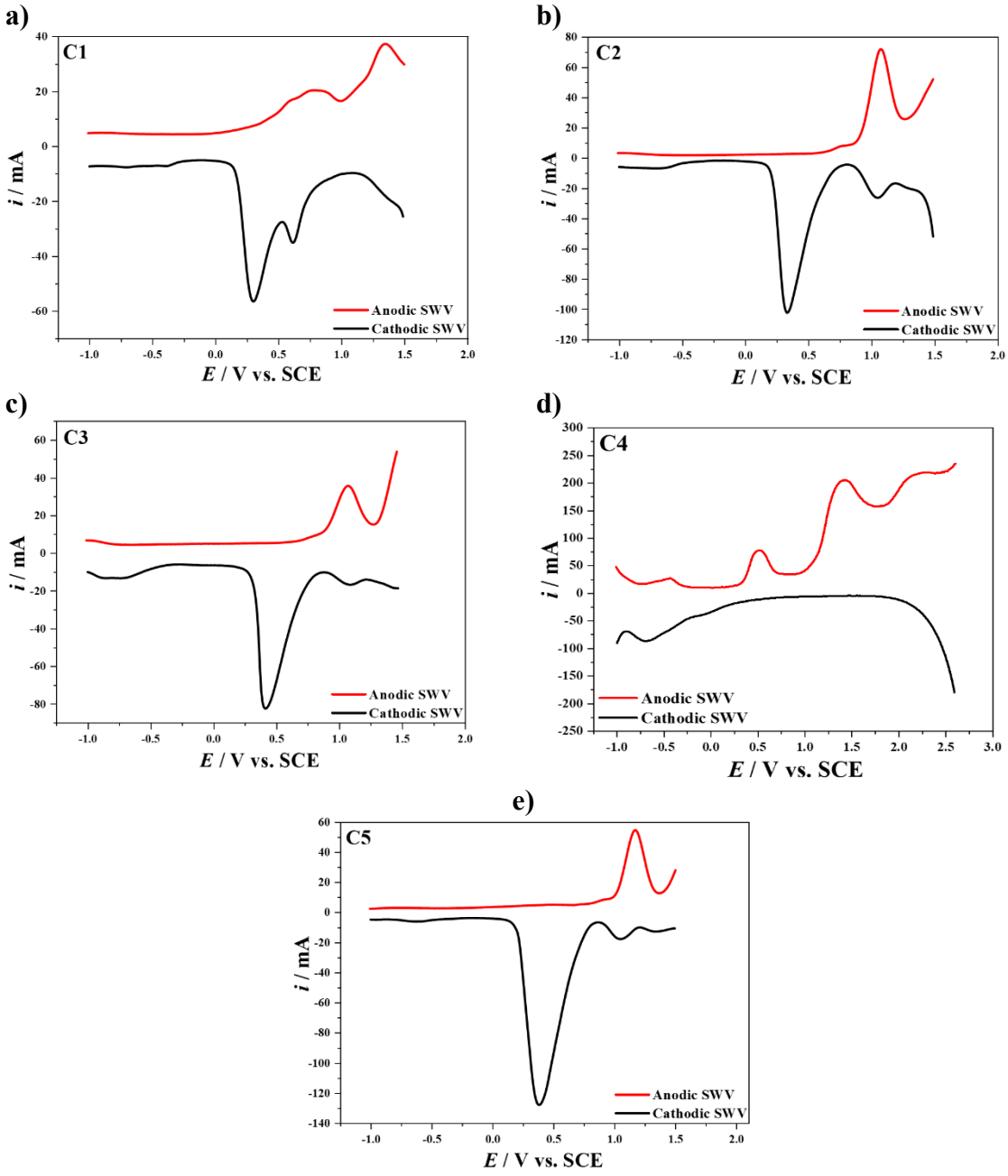


Figure S18. Cyclic voltammetry profiles of different complexes (**C1–5**) at 100 mV s^{-1} using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (CH_2Cl_2) under N_2 saturated atmosphere.



282

283 **Figure S19.** Square wave voltammetry (SWV) for (a) **C1** [R_1: 5-CF_3 // R_2: 5-CF_3],
284 (b) **C2** [R_1: 5-CF_3 // R_2: 5-MeO], (c) **C3** [R_1: 5-MeO // R_2: 5-MeO], (d) **C4** [R_1: 4-CF_3 //
285 R_2: 4- CF_3], (e) **C5** [R_1: 4-CF_3 // R_2: 4-MeO], using 0.1 M $TBAPF_6$ in CH_2Cl_2, under N_2
286 saturated atmosphere.

287
288

3. PHOTOPHYSICAL AND PHOTOCATALYTIC STUDY

3.1 Luminescence studies

Table S4. Summary of luminescence data of complexes **C1–5** in the solid state.

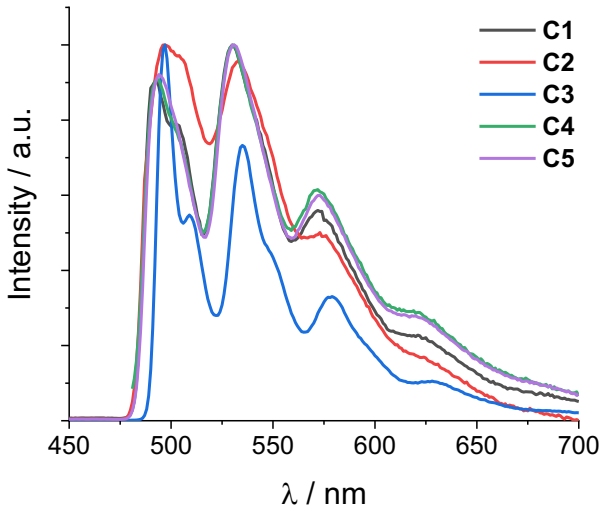
	77 K	**PMMA**
Complex	**λ / nm**	**λ / nm**
C1	492, 503, 530, 572, 621	508, 541
C2	496, 504, 534, 573, 623	512, 541
C3	497, 509, 535, 579, 628	569
C4	493, 530, 571, 620	518, 548
C5	494, 530, 573, 620	517, 547

Table S5. Summary of luminescence properties of complexes **C1–5** in CH_2Cl_2.

Complex	**λ / nm**	**Φ / %**	**τ / μs**	k_R (s^{-1})	k_{NR} (s^{-1})
C1	503	0.40 [a]	10.7	$3.7\cdot10^2$	$9.3\cdot10^4$
C2	557	0.20 [b]	17.0	$1.2\cdot10^2$	$5.9\cdot10^4$
C3	652	0.02 [b]	0.14	$1.4\cdot10^3$	$7.1\cdot10^6$
C4	499	0.30 [a]	0.17	$1.8\cdot10^4$	$5.9\cdot10^6$
C5	501	0.10 [a]	0.37	$2.7\cdot10^3$	$2.0\cdot10^6$
[Cu(dpa)(*S*-BINAP)]PF_6 [c]	567	0.09	20.8	$4.3\cdot10^1$	$4.8\cdot10^4$

[a] Estimated using either fluorescein in 0.1 M NaOH aqueous solution (Φ = 94 %) or $[Ir(ppy)_3]$ in 2-MeTHF (Φ = 96 %) as a standard; [b] estimated using $[Ru(bpy)_3]^{2+}$ in air-equilibrated H_2O as a standard (Φ = 2.8 %); [b] see ref 40 of the main article.

a)



b)

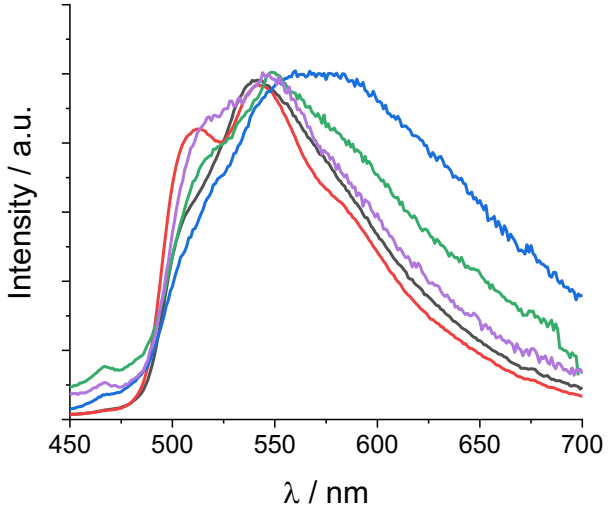


Figure S20. Luminescence spectra of complexes **C1–5** in a) a 2-MeTHF glassy matrix at 77 K and b) PMMA solid-state matrix.

3.2 Photocatalytic study

3.2.1 Light source

All photochemical reactions were performed using a Kessil® PR160L LED lamp as an irradiation source. The wavelength of the light was 440 nm with 399 mW/cm^2 (measured from 1 cm distance)

3.2.2 General procedure for photocatalytic reactions.

Inside a glovebox filled with nitrogen as an atmosphere, a 4.0 mL flame-dried glass vial with a magnetic stirring bar was charged with the corresponding reactant (0.5 mmol, *p* - toluenesulfonyl chloride or bromonitromethane), copper catalyst (1 mol%), styrene (0.5 mmol), and 3 mL of anhydrous solvent. The vial was sealed with a rubber septum, removed from the glovebox, and installed in a rack surrounded by four LED lamps (see Figure S21). The irradiation system has powerful fans to keep the reaction at the desired temperature. The reaction mixture was magnetically stirred at 20 °C for 24 h. Then, the volatiles were removed, and the crude was dried. To this, (1.3.5-trimethoxybenzene) was added as an internal standard and then dissolved in $CDCl_3$, for product determination using NMR.[1]

Figure S21. Irradiation setup for the reactions studied.

[1] Pauli, G.F.; Chen, S-.N.; Simmler, C.; Lankin, D.C.; Gödecke, T.; Jaki, B.U.; Friesen, J.B.; McAlpine, J.B.; Napolitano, J.G. *J. Med. Chem.* **2014**, *57*, 9220−9231.

3.2.3 Excited-state reduction potentials (Rehm-Weller equation).

The excited-state potentials for **C1–5** ($E_{1/2}(C^*)$) were estimated via Rehm-Weller equation (Equation 1) using the ground-state electrochemical potential for the Cu^{2+}/Cu^{+} couple ($E_{1/2}(C)$) obtained by cyclic voltammetry experiments and the zero-zero spectroscopic energy of the excited state ($E_{0\text{-}0}$), calculated, on first approximation, from the maximum of the emission spectrum at room temperature.

$$E_{1/2}(C^*) = E_{1/2}(C) - E_{0-0} \qquad \text{Equation 1}$$

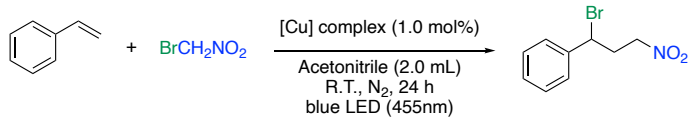
Table S6. Summary of optoelectronic properties of **C1–5** in CH_2Cl_2 solution and comparison with other copper(I) photocatalysts.[a]

Complex	λ_{emi}(nm)	τ (μs)	$E_{1/2}$ (V)	$E_{1/2}^*$ (V)
C1	503	10.7	1.32	–1.15
C2	557	17.0	1.10	–1.13
C3	652	0.14	1.07	–0.83
C4	499	0.17	1.49	–1.00
C5	501	0.37	1.24	–1.24
[Cu(dpa)(*S*-BINAP)]PF_6	567	20.8	0.55	–1.64
[Cu(dap)$_2$]Cl[2]	670	0.27	0.62	–1.43

[2] Hernandez-Perez, A.C.; Collins, S.K. *Acc Chem Res.* **2016**, 49, *8*, 1557-1565.

3.2.4 Bromonitromethylation of styrene using two different solvents

Table S7. Bromonitromethylation reaction of styrene using **C1–5**.[a]



Entry	Catalyst	Yield % [b] CH_2Cl_2	Yield % [b] CH_3CN
1	without	n.r.	n.r.
3	[Cu(dpa)(S-BINAP)]BF_4	19	52
4	**C1**	44	68
5	**C2**	38	66
6	**C3**	83	83
7	**C4**	29	64
8	**C5**	24	46

[a] Styren0.5 mmol, 1.0 equiv.), $BrCH_2NO_2$ (0.5 mmol, 1.0 equiv.), catalyst (1 mol%) in the selected solvent (dry, degassed, 2 mL); Irradiation at 440 nm (LED) under N_2 atmosphere for 24 h at R.T. [b] ^1H NMR Yield was determined using 1,3,5-trimethoxybenzene as an internal standard.