Supplementary Information

Structure of Bis(trifluoromethyl)cuprate and Its Role in Trifluoromethylation Reactions

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General Considerations. All manipulations were performed using standard Schlenk and high-vacuum techniques[1] or in a nitrogen-filled dry box, unless otherwise noted. Solvents were distilled from Na/benzophenone or CaH_2. All reagents were used as received from commercial vendors unless otherwise noted. Celite was dried at 200 °C under vacuum for two days prior to use. ^{1}H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent peaks. ^{19}F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz and were referenced to $CFCl_3$ set to zero. A Rigaku SCXMini diffractometer was used for X-ray structure determinations.

Preparation of (SIMes)Cu–O*t*Bu: A suspension of [(SIMes)CuCl][2,3] (811 mg, 2 mmol) and *t*-BuOK (224 mg, 2 mmol) in 20 ml THF was stirred 2h at room temperature and then filtered through a pad of Celite. The Celite was washed two times with 5 ml of THF. The filtrate was evaporated on a high vacuum line and the resulting white residue was washed with pentane and filtered. Yield 89 %. ^{1}H NMR (25 ˚C, C_6D_6): δ 1.31 (s, 9H), 2.10 (s, 6H), 2.12 (s, 12H), 2.96 (s, 4H), 6.71 (s, 4H).

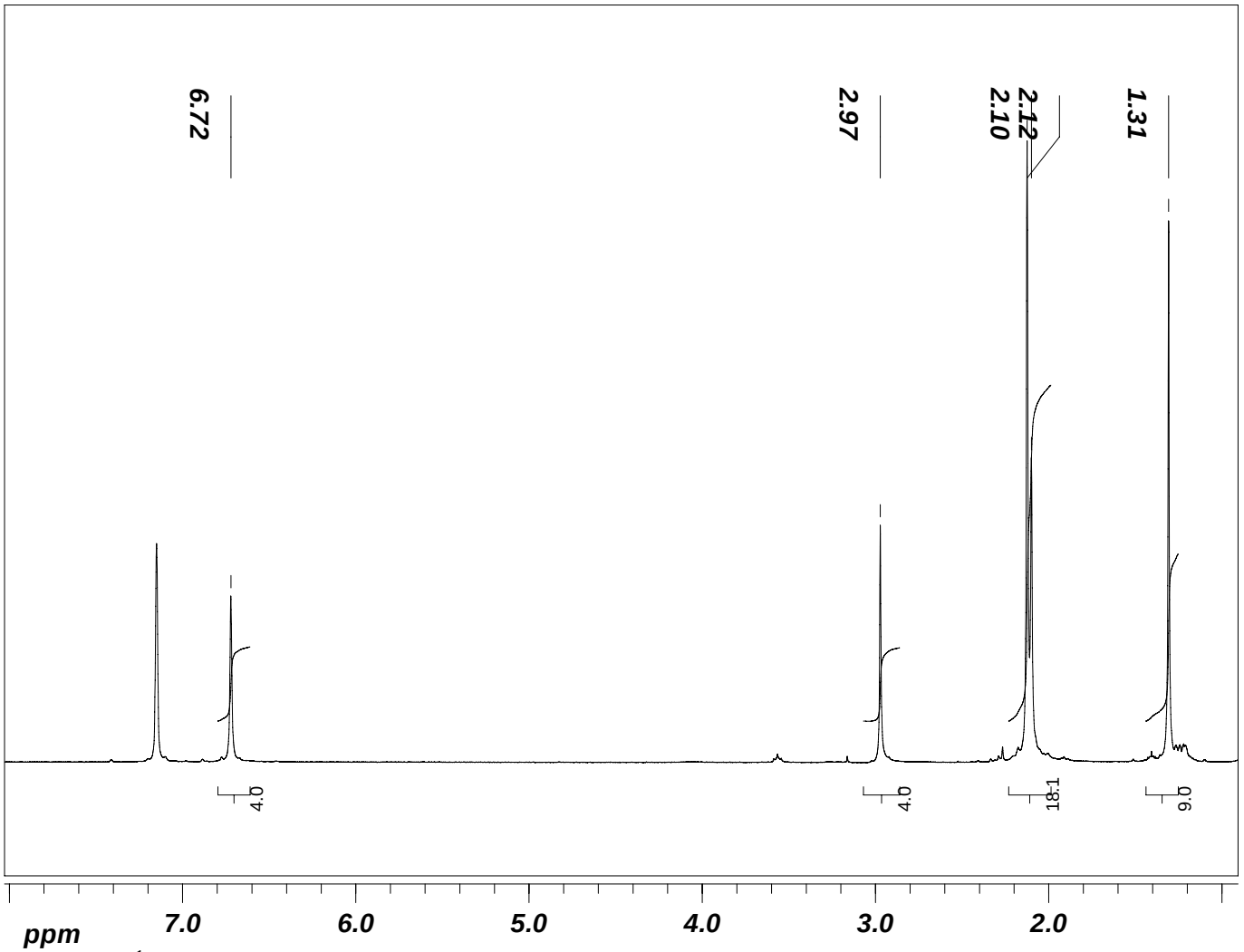


Figure S1: ^{1}H NMR spectrum of (SIMes)Cu-O*t*Bu in C_6D_6.

Preparation of $[(SIMes)_2Cu][Cu(CF_3)_2]$ (2): A solution of (SIMes)Cu–O*t*Bu (390 mg, 0.882 mmol) and $CF_3Si(CH_3)_3$ (0.260 ml, 1.76 mmol) in 15 ml THF was stirred at room temperature. The conversion was monitored by ^{19}F NMR spectroscopy, and after 21 h the volatiles were evaporated using a high vacuum line. The white residue was filtered and washed four times with 5 ml toluene and pentane. Yield of $[(SIMes)_2Cu][Cu(CF_3)_2]$ was 67 %. ^{1}H NMR (25 ˚C, CD_2Cl_2): δ 1.83 (s, 12H), 2.38 (s, 6H), 3.80 (s, 4H), 6.89 (s, 4H). ^{19}F NMR (25 ˚C, CD_2Cl_2): δ -31.33 (s, 3F). ^{1}H NMR (THF-d_8): 1.88 (s, 12H), 2.38 (s, 6H), 3.88 (s, 4H), 6.93 (s, 4H). ^{19}F NMR (25 ˚C, CD_2Cl_2): δ -31.54 (s, 3F).

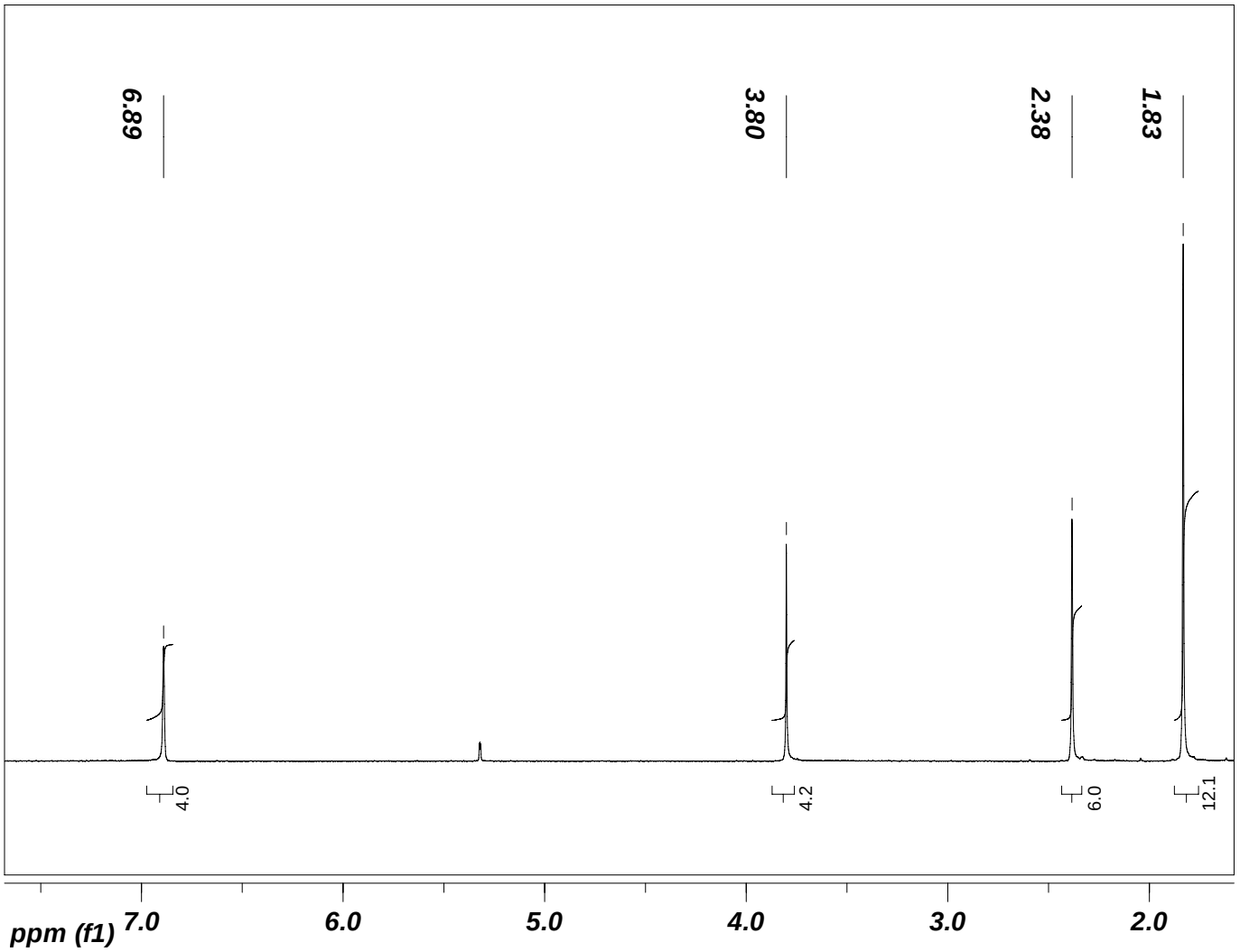


Figure S2: ^{1}H NMR spectrum of $[(SIMes)_2Cu][(CF_3)_2Cu]$ (**2**) in CD_2Cl_2.

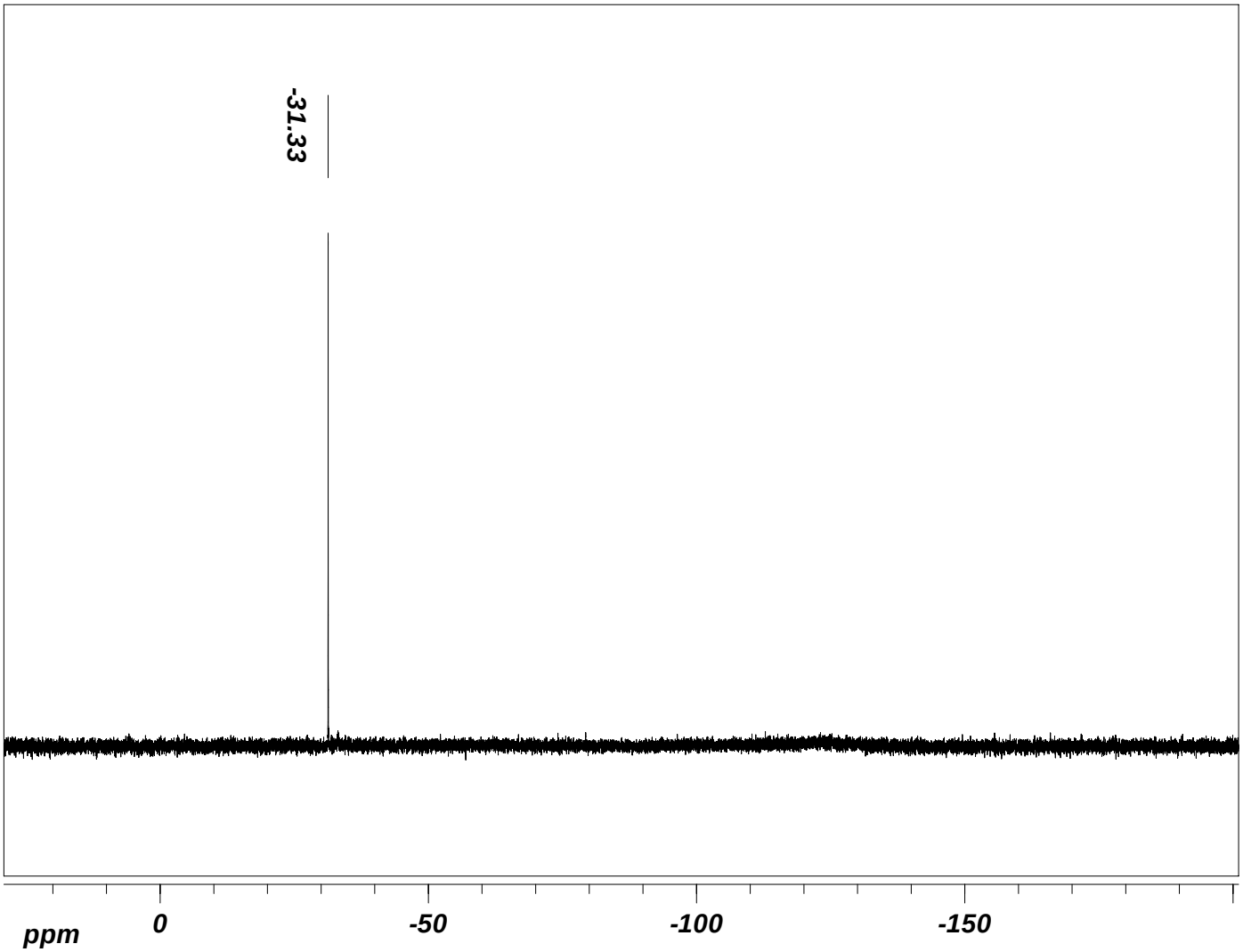


Figure S3: ^{19}F NMR spectrum of $[(SIMes)_2Cu][(CF_3)_2Cu]$ (**2**) in CD_2Cl_2.

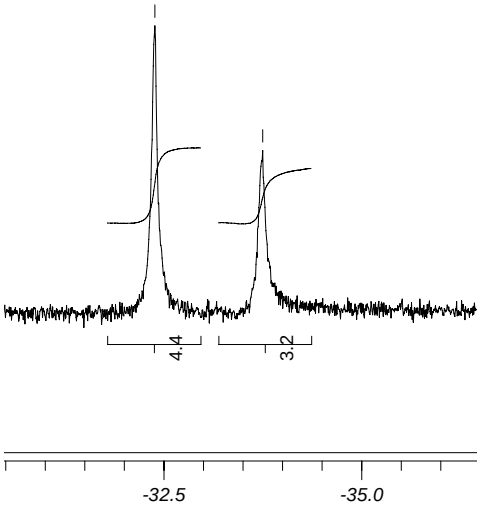
NMR spectrum of [(SIMes)CuCF$_3$] present in solutions of 2: ^1H NMR (THF-d_8): 2.29 (s, 6H), 2.35 (s, 12H), 4.01 (s, 4H), 6.99 (s, 4H). ^{19}F NMR (THF-d_8): δ -32.97 (s, 3F).

Experimental Procedure For Reactions in Table 1: An NMR tube was sealed with (SI*i*Pr)$CuCF_3$ (16.7 mg, 0.058 mmol) or $[(SIMes)_2Cu][Cu(CF_3)_2]$ (26 mg, 0.029 mmol), internal standard (10 μl, 0.07957 mmol) in 1 ml of corresponding aryl halide and kept at the appropriate temperature. Yields were determined by ^{19}F NMR relative to 1,3-dimethyl-2-fluorobenzene as an internal standard. Yields based on copper as the limiting reagent.

Experimental Procedures For Reactions in Table 2:
$[(SIMes)_2Cu][Cu(CF_3)_2]$ (99 mg, 0.1125 mmol) was dissolved in a mixture of 7.5 ml benzene, 1.5 ml DMI and internal standard (50 μl, 0.3979 mmol) . Then 1 ml aliquots (0.0125 mmol) were taken for each reaction and 0.125 mmol, 5 equiv. (for each trifluoromethyl group) of corresponding aryl

halide was added. Reaction mixtures were placed in sealed NMR tubes and kept at 50^{o}C in an oil bath. Yields were determined by ^{19}F NMR relative to 1,3-dimethyl-2-fluorobenzene as an internal standard. Yields based on copper as the limiting reagent.

Figure S4: ^{19}F NMR spectrum of the reaction mixture of cuprate **2** (0.029 M) dissolved in phenyl iodide after one hour. The [cuprate]/[neutral species] was determined to be 1.3.



X-Ray Data.

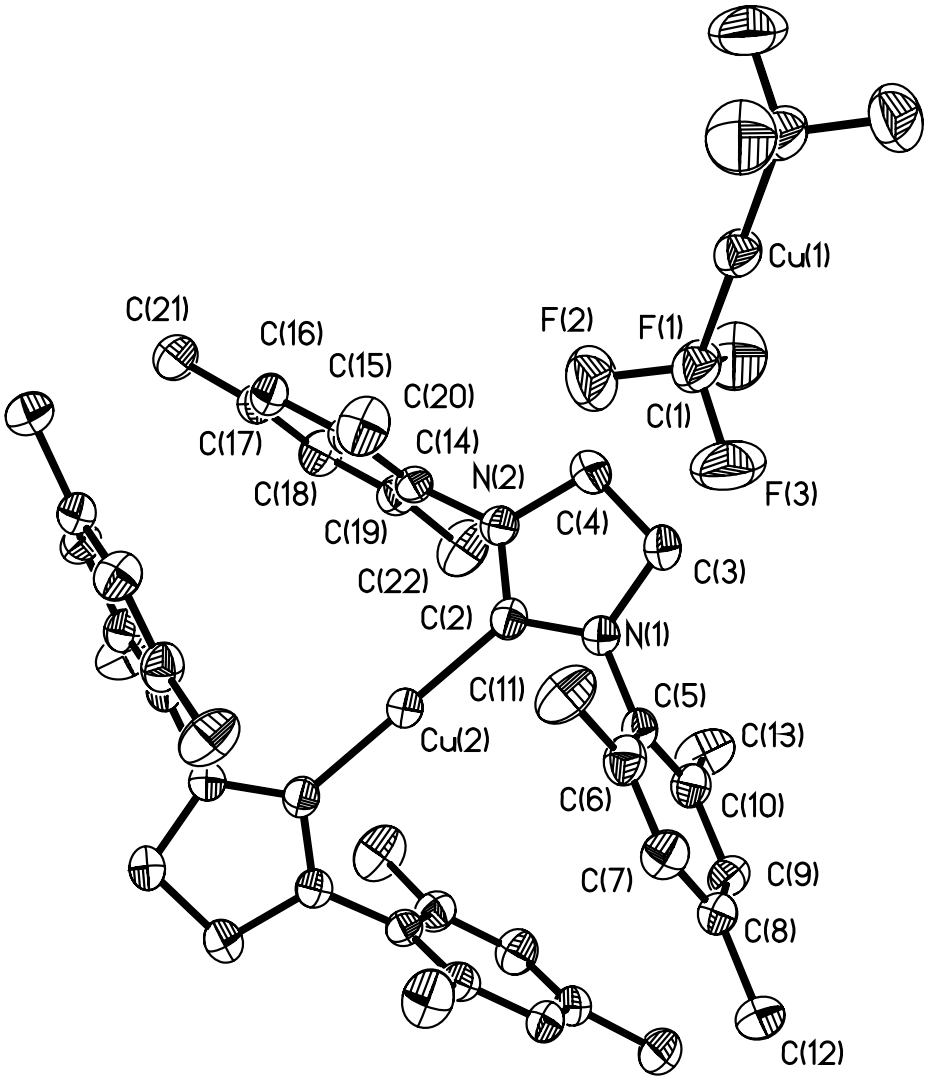


Figure S5. ORTEP diagram of **2**. Ellipsoids shown at the 40 % level. Hydrogens are omitted for clarity. Half the molecule is generated by symmetry.

Table S1. Crystal data and structure refinement for Compound 2.

Identification code	Compound 2
Empirical formula	C44 H52 Cu2 F6 N4
Formula weight	877.98
Temperature	173(2) K
Wavelength	0.71075 A
Crystal system, space group	monoclinic, P2/c
Unit cell dimensions	a = 12.23(2) A alpha = 90 deg. b = 8.460(15) A beta = 101.43(2) deg. c = 23.49(4) A gamma = 90 deg.
Volume	2382(7) A^3
Z, Calculated density	2, 1.224 Mg/m^3
Absorption coefficient	0.947 mm^-1
F(000)	912
Crystal size	0.40 x 0.26 x 0.20 mm
Theta range for data collection	1.70 to 31.89 deg.
Limiting indices	-17<=h<=17, -11<=k<=11, -33<=l<=33
Reflections collected / unique	25014 / 7588 [R(int) = 0.1119]
Completeness to theta = 31.89	92.5 %
Max. and min. transmission	0.8331 and 0.7031
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7588 / 0 / 262
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0946, wR2 = 0.2139
R indices (all data)	R1 = 0.2065, wR2 = 0.2684
Largest diff. peak and hole	0.892 and -0.645 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Compound 2.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	5000	10000	0	53(1)
Cu(2)	10000	4054(1)	2500	40(1)
F(1)	5957(4)	6872(5)	97(2)	96(1)
F(2)	6252(3)	8120(5)	942(2)	95(1)
F(3)	7231(3)	8743(6)	277(2)	107(2)
N(1)	9131(3)	4376(5)	1217(2)	46(1)
N(2)	7825(3)	3666(5)	1706(2)	45(1)
C(1)	6134(5)	8433(8)	339(3)	67(2)
C(2)	8937(4)	4040(6)	1757(2)	41(1)
C(3)	8093(4)	4305(8)	739(2)	59(2)
C(4)	7187(5)	3678(8)	1083(2)	62(2)
C(5)	10218(4)	4951(6)	1094(2)	44(1)
C(6)	10525(5)	6579(6)	1204(2)	52(1)
C(7)	11566(4)	7099(6)	1078(2)	53(1)
C(8)	12293(4)	6074(6)	849(2)	47(1)
C(9)	11957(4)	4451(6)	741(2)	47(1)
C(10)	10916(4)	3871(6)	860(2)	45(1)
C(11)	9755(6)	7742(7)	1455(3)	72(2)
C(12)	13430(4)	6656(8)	724(2)	62(2)
C(13)	10593(5)	2110(7)	738(3)	72(2)
C(14)	7320(4)	3102(6)	2192(2)	39(1)
C(15)	6763(4)	4204(6)	2501(2)	45(1)
C(16)	6242(4)	3591(6)	2959(2)	48(1)
C(17)	6298(4)	1969(6)	3113(2)	47(1)
C(18)	6882(4)	919(6)	2806(2)	54(1)
C(19)	7415(4)	1446(6)	2353(2)	49(1)
C(20)	6704(6)	5983(7)	2350(3)	70(2)
C(21)	5693(5)	1357(8)	3597(3)	70(2)
C(22)	8069(6)	258(7)	2031(3)	75(2)

Table S3. Bond lengths [A] and angles [deg] for Compound 2.

Cu(1)-C(1)#1	1.970(6)
Cu(1)-C(1)	1.970(6)
Cu(2)-C(2)	1.959(5)
Cu(2)-C(2)#2	1.959(5)
F(1)-C(1)	1.437(8)
F(2)-C(1)	1.419(7)
F(3)-C(1)	1.403(7)
N(1)-C(2)	1.365(6)
N(1)-C(5)	1.497(6)
N(1)-C(3)	1.520(7)
N(2)-C(2)	1.379(6)
N(2)-C(14)	1.480(6)
N(2)-C(4)	1.516(6)
C(3)-C(4)	1.586(7)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(10)	1.433(7)
C(5)-C(6)	1.438(8)
C(6)-C(7)	1.431(7)
C(6)-C(11)	1.557(7)
C(7)-C(8)	1.422(7)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.441(7)
C(8)-C(12)	1.558(7)
C(9)-C(10)	1.442(7)
C(9)-H(9A)	0.9500
C(10)-C(13)	1.553(8)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.433(7)
C(14)-C(19)	1.449(7)
C(15)-C(16)	1.451(7)
C(15)-C(20)	1.544(8)
C(16)-C(17)	1.418(8)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.422(7)
C(17)-C(21)	1.562(7)
C(18)-C(19)	1.426(7)
C(18)-H(18A)	0.9500
C(19)-C(22)	1.569(8)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800

C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

C(1)#1-Cu(1)-C(1)	180.0(3)
C(2)-Cu(2)-C(2)#2	179.3(3)
C(2)-N(1)-C(5)	124.9(4)
C(2)-N(1)-C(3)	113.8(4)
C(5)-N(1)-C(3)	120.9(4)
C(2)-N(2)-C(14)	124.3(4)
C(2)-N(2)-C(4)	113.1(4)
C(14)-N(2)-C(4)	122.2(4)
F(3)-C(1)-F(2)	103.2(5)
F(3)-C(1)-F(1)	101.7(5)
F(2)-C(1)-F(1)	101.6(5)
F(3)-C(1)-Cu(1)	116.3(4)
F(2)-C(1)-Cu(1)	117.0(4)
F(1)-C(1)-Cu(1)	114.8(4)
N(1)-C(2)-N(2)	108.5(4)
N(1)-C(2)-Cu(2)	128.3(4)
N(2)-C(2)-Cu(2)	123.2(3)
N(1)-C(3)-C(4)	101.7(4)
N(1)-C(3)-H(3A)	111.4
C(4)-C(3)-H(3A)	111.4
N(1)-C(3)-H(3B)	111.4
C(4)-C(3)-H(3B)	111.4
H(3A)-C(3)-H(3B)	109.3
N(2)-C(4)-C(3)	102.5(4)
N(2)-C(4)-H(4A)	111.3
C(3)-C(4)-H(4A)	111.3
N(2)-C(4)-H(4B)	111.3
C(3)-C(4)-H(4B)	111.3
H(4A)-C(4)-H(4B)	109.2
C(10)-C(5)-C(6)	121.7(5)
C(10)-C(5)-N(1)	119.2(4)
C(6)-C(5)-N(1)	119.1(4)
C(7)-C(6)-C(5)	118.0(5)
C(7)-C(6)-C(11)	120.9(5)
C(5)-C(6)-C(11)	121.1(5)
C(8)-C(7)-C(6)	122.6(5)
C(8)-C(7)-H(7A)	118.7
C(6)-C(7)-H(7A)	118.7
C(7)-C(8)-C(9)	118.0(4)
C(7)-C(8)-C(12)	121.8(5)
C(9)-C(8)-C(12)	120.1(5)
C(8)-C(9)-C(10)	121.5(5)
C(8)-C(9)-H(9A)	119.3
C(10)-C(9)-H(9A)	119.3
C(5)-C(10)-C(9)	118.3(5)
C(5)-C(10)-C(13)	122.2(5)
C(9)-C(10)-C(13)	119.6(5)
C(6)-C(11)-H(11A)	109.5
C(6)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(6)-C(11)-H(11C)	109.5

H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	121.3(4)
C(15)-C(14)-N(2)	119.5(4)
C(19)-C(14)-N(2)	119.2(4)
C(14)-C(15)-C(16)	117.7(5)
C(14)-C(15)-C(20)	121.6(4)
C(16)-C(15)-C(20)	120.7(5)
C(17)-C(16)-C(15)	122.0(4)
C(17)-C(16)-H(16A)	119.0
C(15)-C(16)-H(16A)	119.0
C(16)-C(17)-C(18)	118.6(4)
C(16)-C(17)-C(21)	120.1(5)
C(18)-C(17)-C(21)	121.3(5)
C(17)-C(18)-C(19)	122.3(5)
C(17)-C(18)-H(18A)	118.9
C(19)-C(18)-H(18A)	118.9
C(18)-C(19)-C(14)	118.1(4)
C(18)-C(19)-C(22)	120.8(5)
C(14)-C(19)-C(22)	121.1(5)
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(17)-C(21)-H(21A)	109.5
C(17)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(17)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z #2 -x+2,y,-z+1/2

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for Compound 2. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	52(1)	58(1)	51(1)	4(1)	16(1)	14(1)
Cu(2)	42(1)	44(1)	35(1)	0	10(1)	0
F(1)	116(3)	74(3)	99(3)	5(2)	26(2)	36(2)
F(2)	104(3)	120(4)	59(2)	20(2)	13(2)	38(3)
F(3)	56(2)	134(4)	132(4)	39(3)	25(2)	28(2)
N(1)	40(2)	61(3)	37(2)	3(2)	9(2)	5(2)
N(2)	40(2)	56(3)	40(2)	9(2)	9(2)	-1(2)
C(1)	66(4)	81(4)	59(4)	12(3)	23(3)	25(3)
C(2)	46(3)	42(3)	37(2)	3(2)	12(2)	5(2)
C(3)	53(3)	87(4)	36(3)	10(3)	10(2)	6(3)
C(4)	50(3)	91(5)	42(3)	8(3)	4(2)	-3(3)
C(5)	45(3)	53(3)	33(2)	7(2)	8(2)	4(2)
C(6)	62(3)	49(3)	47(3)	-2(2)	16(2)	8(3)
C(7)	59(3)	44(3)	59(3)	-6(2)	17(2)	-10(3)
C(8)	44(3)	58(3)	40(2)	5(2)	10(2)	-5(2)
C(9)	44(3)	52(3)	49(3)	2(2)	17(2)	1(2)
C(10)	51(3)	42(3)	43(3)	2(2)	12(2)	1(2)
C(11)	79(4)	50(3)	98(5)	-5(3)	45(4)	12(3)
C(12)	48(3)	79(4)	61(3)	3(3)	15(2)	-14(3)
C(13)	66(4)	49(4)	108(5)	-1(3)	35(4)	0(3)
C(14)	36(2)	45(3)	38(2)	2(2)	9(2)	-7(2)
C(15)	40(3)	48(3)	46(3)	0(2)	5(2)	1(2)
C(16)	48(3)	58(3)	40(3)	-2(2)	13(2)	6(2)
C(17)	45(3)	57(3)	41(3)	9(2)	9(2)	1(2)
C(18)	62(3)	45(3)	56(3)	8(2)	17(2)	-3(3)
C(19)	49(3)	50(3)	51(3)	-3(2)	14(2)	2(2)
C(20)	90(5)	51(4)	74(4)	5(3)	28(3)	11(3)
C(21)	59(4)	98(5)	58(3)	10(3)	20(3)	-13(3)
C(22)	96(5)	48(4)	90(5)	-9(3)	39(4)	4(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Compound 2.

	x	y	z	U(eq)
H(3A)	8191	3565	427	70
H(3B)	7893	5363	570	70
H(4A)	6537	4397	1035	74
H(4B)	6929	2604	953	74
H(7A)	11779	8171	1151	64
H(9A)	12432	3748	588	56
H(11A)	8993	7665	1228	108
H(11B)	10029	8825	1435	108
H(11C)	9757	7468	1861	108
H(12A)	13306	7571	463	93
H(12B)	13779	5804	540	93
H(12C)	13922	6960	1090	93
H(13A)	10297	1679	1064	108
H(13B)	11254	1507	692	108
H(13C)	10023	2032	382	108
H(16A)	5852	4298	3161	58
H(18A)	6917	-170	2906	64
H(20A)	7462	6403	2387	106
H(20B)	6319	6545	2617	106
H(20C)	6296	6128	1950	106
H(21A)	5430	2259	3794	106
H(21B)	6214	728	3879	106
H(21C)	5056	700	3421	106
H(22A)	7971	-819	2166	113
H(22B)	8864	530	2114	113
H(22C)	7781	322	1611	113

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