Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New Journal of Chemistry

Visible-emitting Cu(I) complexes with N-functionalized benzotriazole-based ligands

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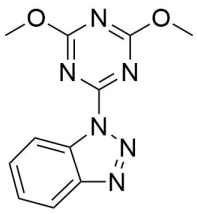
Electronic supporting Information

^{1}H NMR



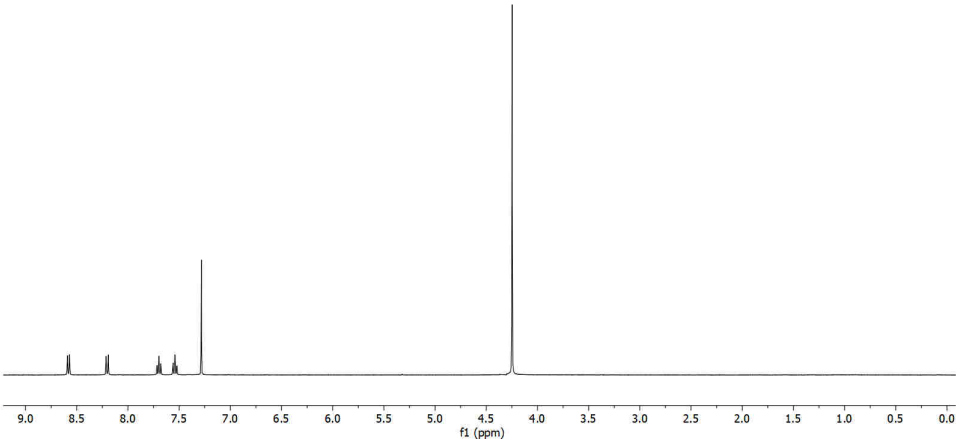


Fig. S1. ^{1}H NMR spectrum of trz^{OMe}-btz ($CDCl_3$, 298 K).

^{13}C {^{1}H} NMR

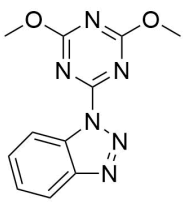


Fig. S2. ^{13}C{^{1}H} NMR spectrum of trz^{OMe}-btz ($CDCl_3$, 298 K). Inset: ^{1}H-^{13}C HSQC ($CDCl_3$, 298 K).

^{1}H NMR

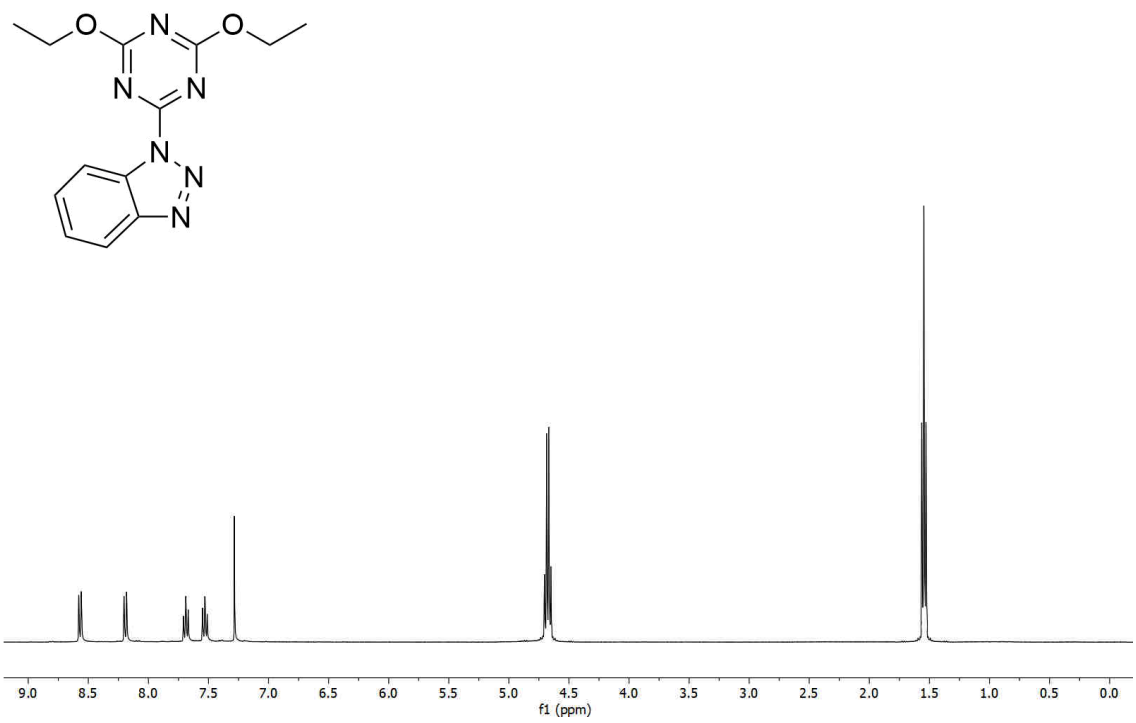


Fig. S3. ^{1}H NMR spectrum of trz^{OEt}-btz ($CDCl_3$, 298 K).

^{13}C {^{1}H} NMR

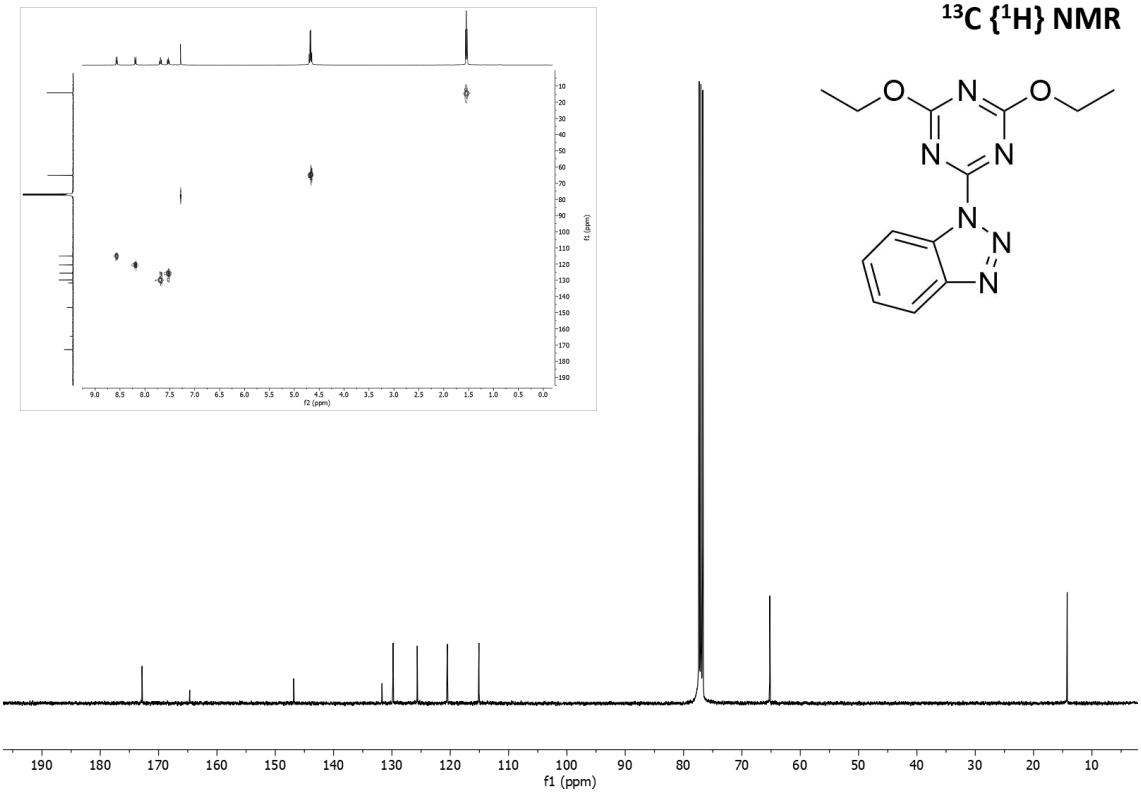


Fig. S4. ^{13}C{^{1}H} NMR spectrum of trz^{OEt}-btz ($CDCl_3$, 298 K). Inset: ^{1}H-^{13}C HSQC ($CDCl_3$, 298 K).

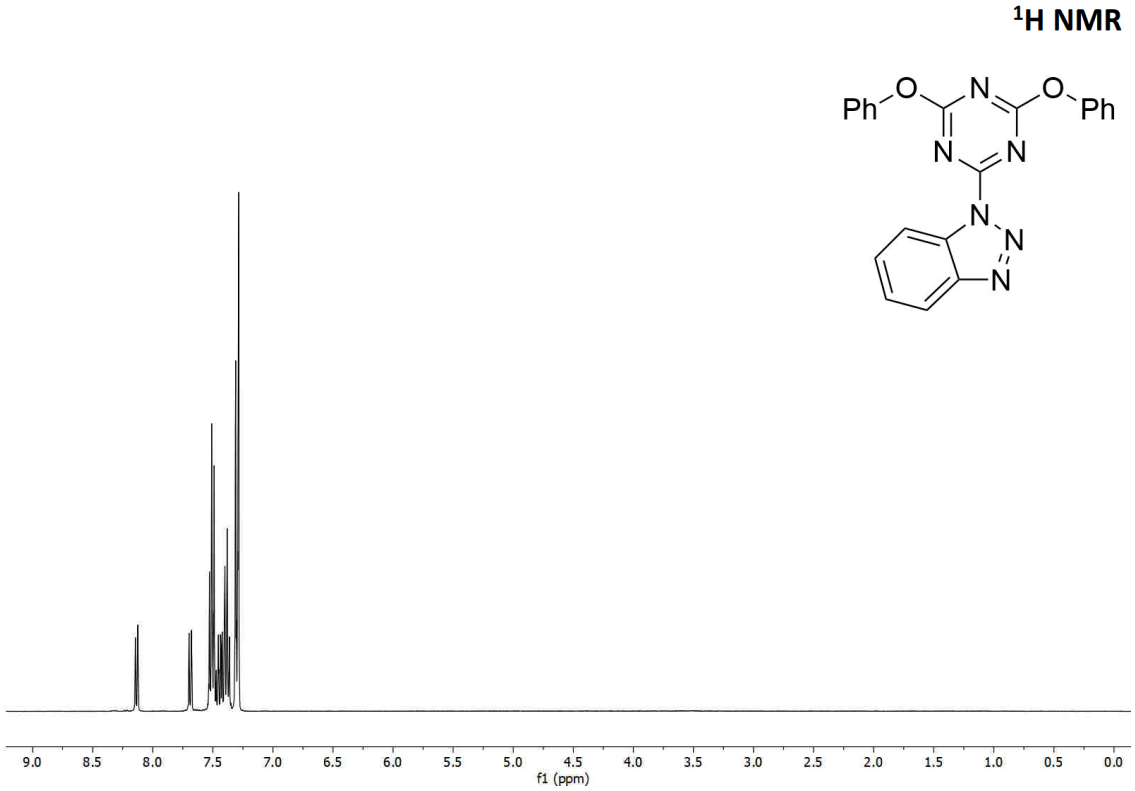


Fig. S5. ^{1}H NMR spectrum of trz^{OPh}-btz ($CDCl_3$, 298 K).

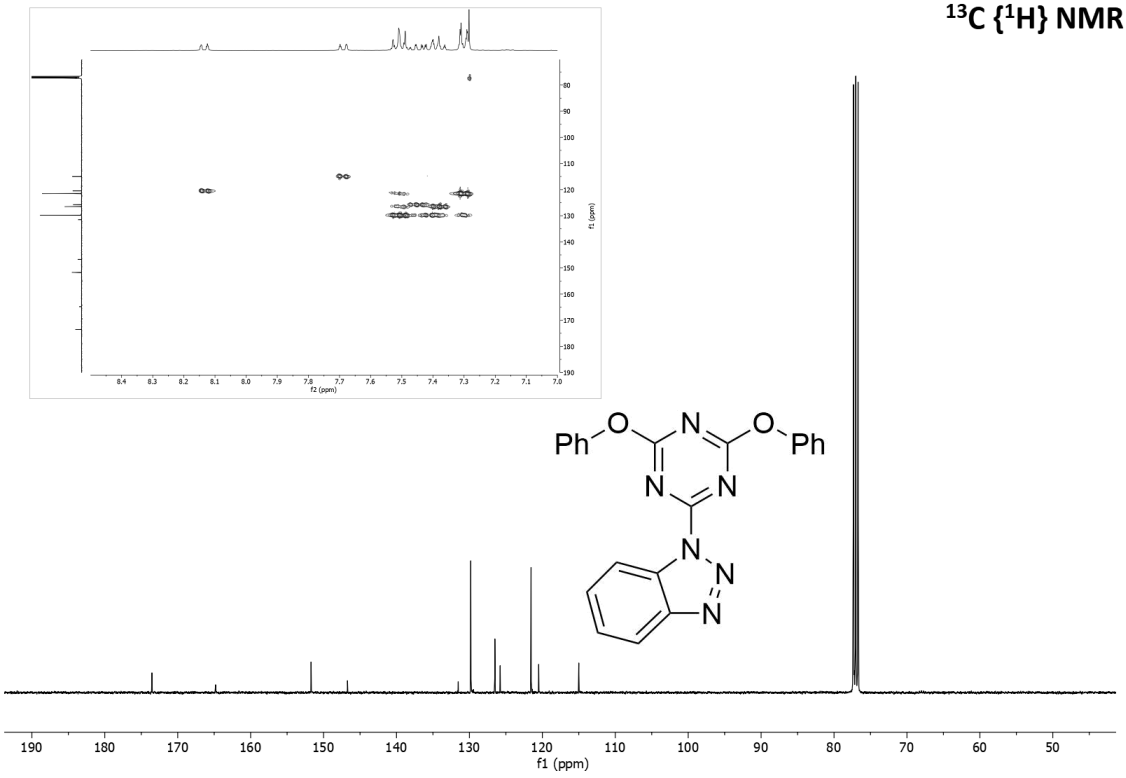


Fig. S6. $^{13}C\{^1H\}$ NMR spectrum of trz^{OPh}-btz ($CDCl_3$, 298 K). Inset: ^1H-^{13}C HSQC ($CDCl_3$, 298 K).

X-Ray structures of trz^{OMe}-btz and trz^{OPh}-btz

The ligand trz^{OMe}-btz crystallizes in the monoclinic $P2_1/c$ group with two equivalent molecules in the asymmetric unit. One of them is shown in Fig. S7a (see Fig. S8 for both the molecules in the asymmetric unit). On the other hand, trz^{OPh}-btz crystallizes in triclinic *P*-1 space group and the molecule found in the asymmetric unit is shown in Fig. 7b. Crystal data and structure refinement are reported in Table S1.

Both molecules of trz^{OMe}-btz are essentially planar, being the root-mean square deviation from the best fitted plane calculated for 15 atoms (methoxy groups excluded) respectively of 0.070 and 0.029 Å, an the O-bonded methyl groups are one in *syn* and the other one in *anti* to the benzotriazole group with respect to the para nitrogen. They also belong to the plane defined by the other atoms, although one of the methyl groups is deviated by 0.27 Å.

The triazinyl-benzotriazole fragment is planar also for trz^{OPh}-btz and the root-mean-square deviation of the atoms in the previously mentioned fragment (trz^{OMe}-btz) is only 0.0062 Å (see also the superimposition reported in Fig. S9). On the other hand, the phenyl rings in trz^{OPh}-btz are situated both in anti and their planes are almost perpendicular to the molecule, the dihedral angles being 75.0(1) and 59.8(1)°.

For what concerns the supramolecular network, in trz^{OMe}-btz the distance between the centroids of a 1,3,5-triazine ring and a benzene ring of a neighbour molecule (sym. op. 1-x, 1-y, 1-z) is only 3.4442(7) Å, allowing a double π,π-stacking interaction (see Fig. S10a). In the asymmetric unit there is another double π,π-stacking interaction, as observable in Fig. S10b, between the 1,2,3-triazole ring of one molecule and the 1,3,5-triazine ring of another molecule. In this case the distances between centroids are slightly longer, 3.9752(7) and 3.9822(7) Å. Despite the steric hindrance of the O-bonded phenyl rings, also trz^{OPh}-btz shows a double π,π-stacking interaction (see Fig. S10c), with a distance of 3.640(3) Å between the 1,3,5-triazine ring and the benzene ring of the benzotriazole. Finally, in both compounds some non-classical hydrogen bonds are observable, as depicted in Fig. S11.

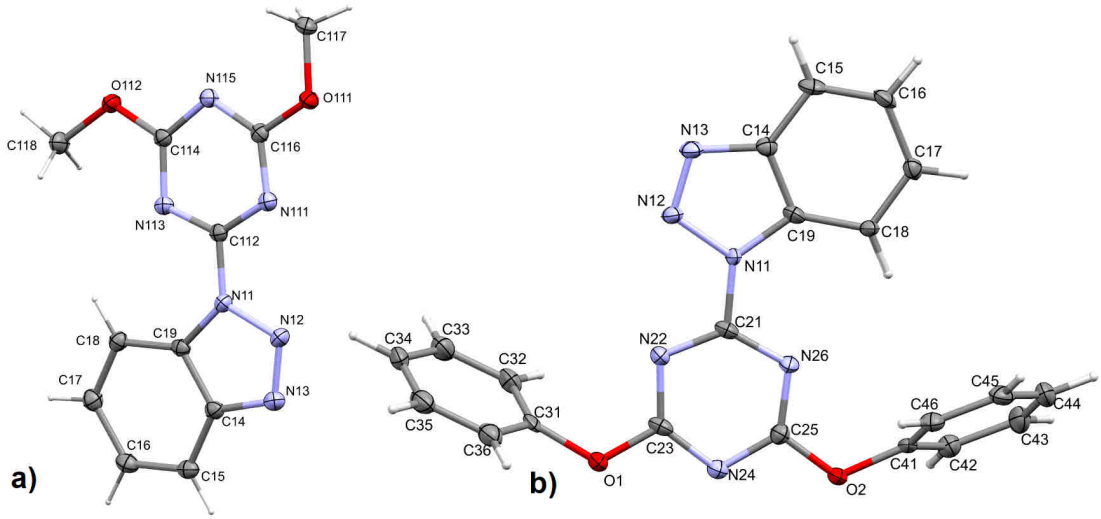


Fig. S7. Ellipsoid representation of one of the molecules found in the asymmetric unit of trz^{OMe}-btz (a) and of trz^{OPh}-btz (b).

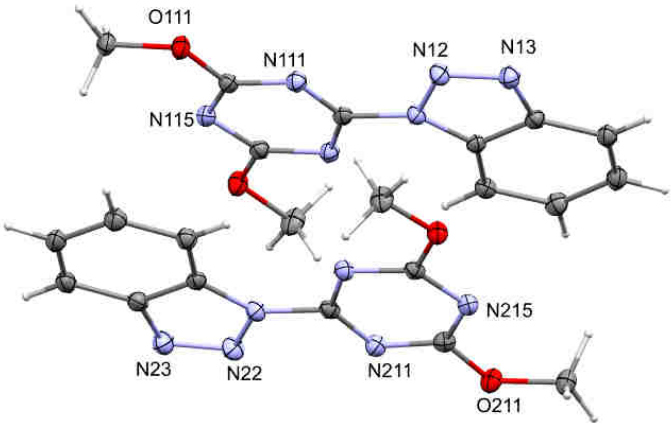


Fig. S8. Asymmetric unit of trz^{OMe}-btz.

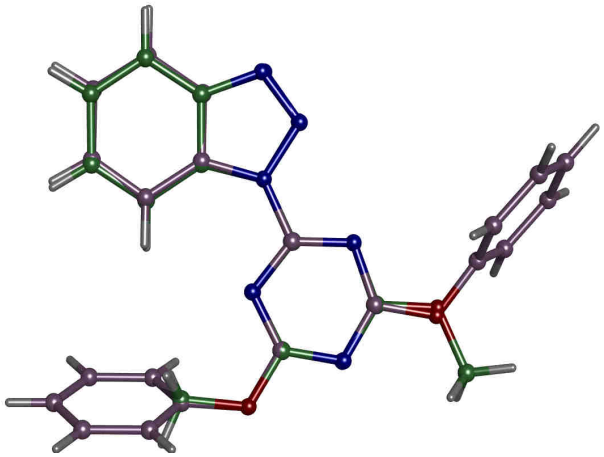


Fig. S9. Superimposition of trz^{OMe}-btz and trz^{OPh}-btz.

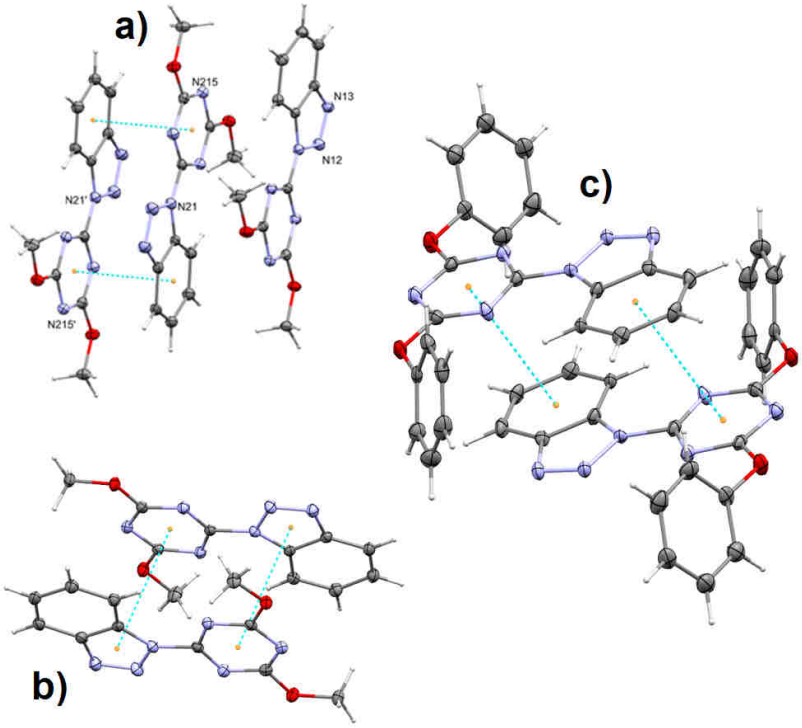


Fig. S10. π,π-stacking interactions.

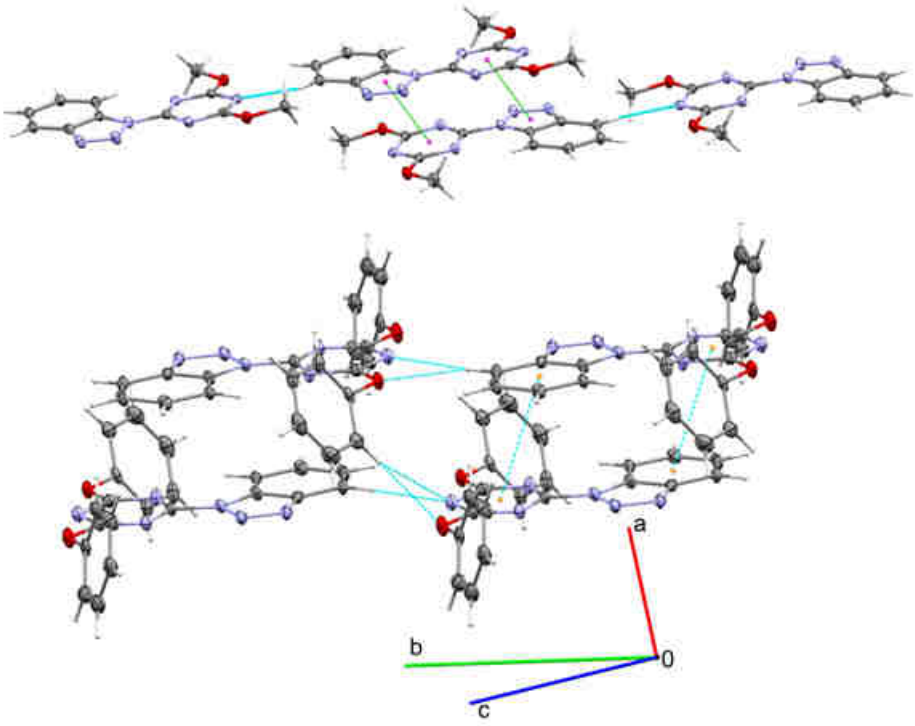


Fig. S11. Hydrogen bonds in trz^{OMe}-btz and trz^{OPh}-btz.

Table S1. Crystal data and structure refinement for ligands trz^{OMe}-btz and trz^{OPh}-btz.

Compound	trz^{OMe}-btz	trz^{OPh}-btz
Empirical formula	C_{11} H_{10} N_6 O_2	C_{21} H_{14} N_6 O_2
Formula weight	258.25	382.38
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions	a = 14.3117(9) Å	a = 6.7497(7) Å
	b = 10.6121(6) Å	b = 10.5961(10) Å
	c = 15.8829(10) Å	c = 12.9511(13) Å
	α = 90°	α = 74.696(4)°
	β = 113.323(2)°	β = 82.773(4)°
	γ = 90°	γ = 81.119(4)°
Volume	2215.1(2) Å^3	879.19(15) Å^3
Z	8	2
Density (calculated)	1.549 Mg/m^3	1.444 Mg/m^3
Absorption coefficient	0.114 mm^{-1}	0.098 mm^{-1}
F(000)	1072	396
Crystal size	0.255 x 0.155 x 0.094 mm	0.139 x 0.054 x 0.014 mm
Theta range for data collection	2.467 to 28.301°	2.009 to 26.462°
Index ranges	$-19 \le h \le 19$	$-8 \le h \le 8$
	$-14 \le k \le 14$	$-13 \le k \le 13$
	$-21 \le l \le 21$	$-16 \le l \le 16$
Reflections collected	55418	3627
Independent reflections	5496 [R_{int} = 0.0388]	3627 [R_{int} = 0.1108]
Reflections observed (>2σ)	4781	3209
Data Completeness	0.998	0.994
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7376 and 0.7145	0.7454 and 0.5587
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5496 / 0 / 349	3627 / 0 / 262
Goodness-of-fit on F^2	1.044	1.190
Final R indices [I>2σ(I)]	R_1 = 0.0348	R_1 = 0.0882
	wR_2 = 0.0935	wR_2 = 0.2144
R indices (all data)	R_1 = 0.0409	R_1 = 0.0997
	wR_2 = 0.0978	wR_2 = 0.2223
Largest diff. peak and hole	0.393 and -0.221 e.Å^{-3}	0.416 and -0.444 e.Å^{-3}

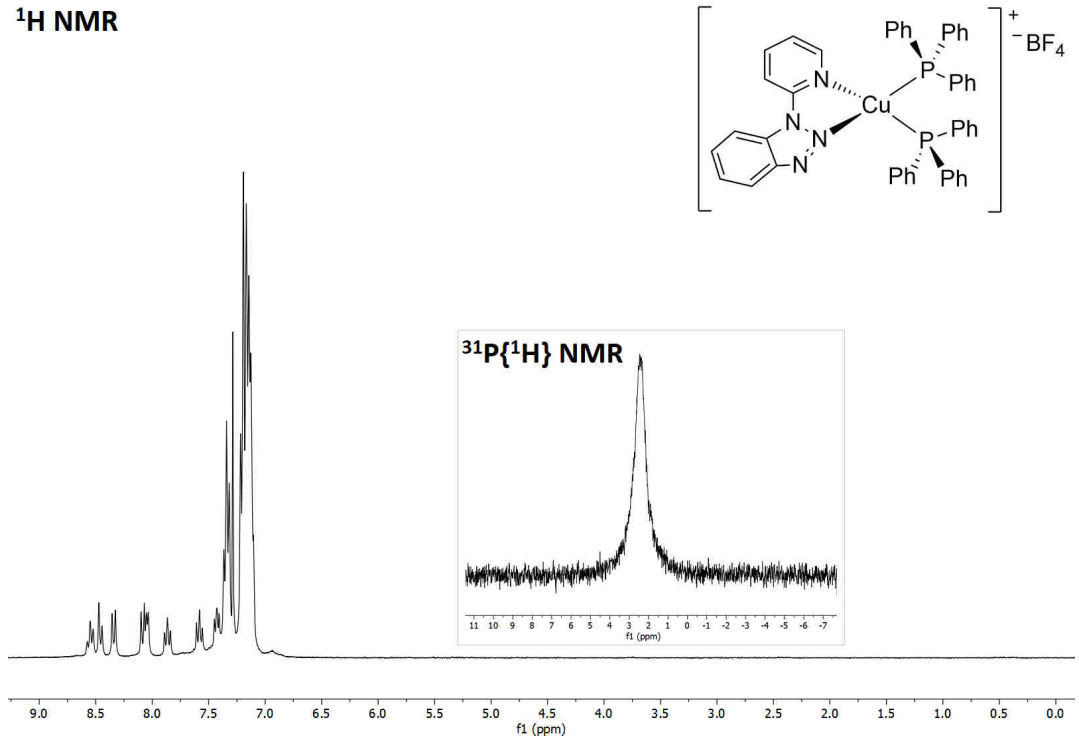


Fig. S12. ^{1}H NMR spectrum of **1a**, [Cu(py-btz)(PPh_3)$_2$][BF_4] ($CDCl_3$, 233 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

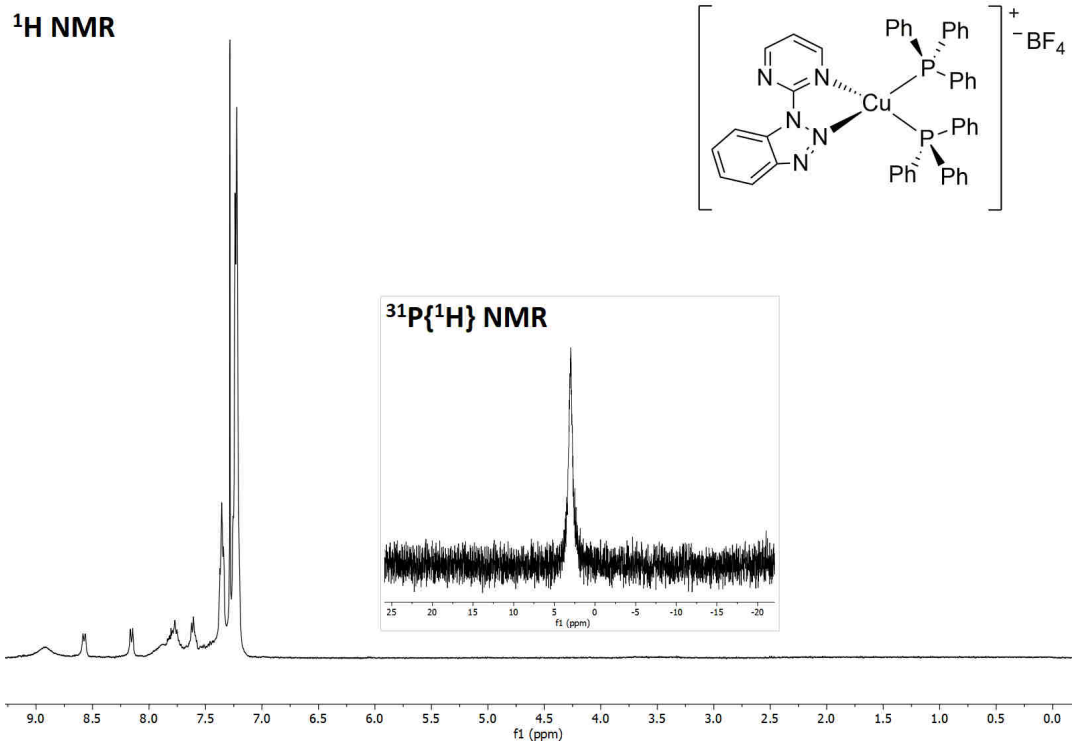


Fig. S13. ^{1}H NMR spectrum of **2a**, [Cu(pym-btz)(PPh_3)$_2$][BF_4] ($CDCl_3$, 298 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

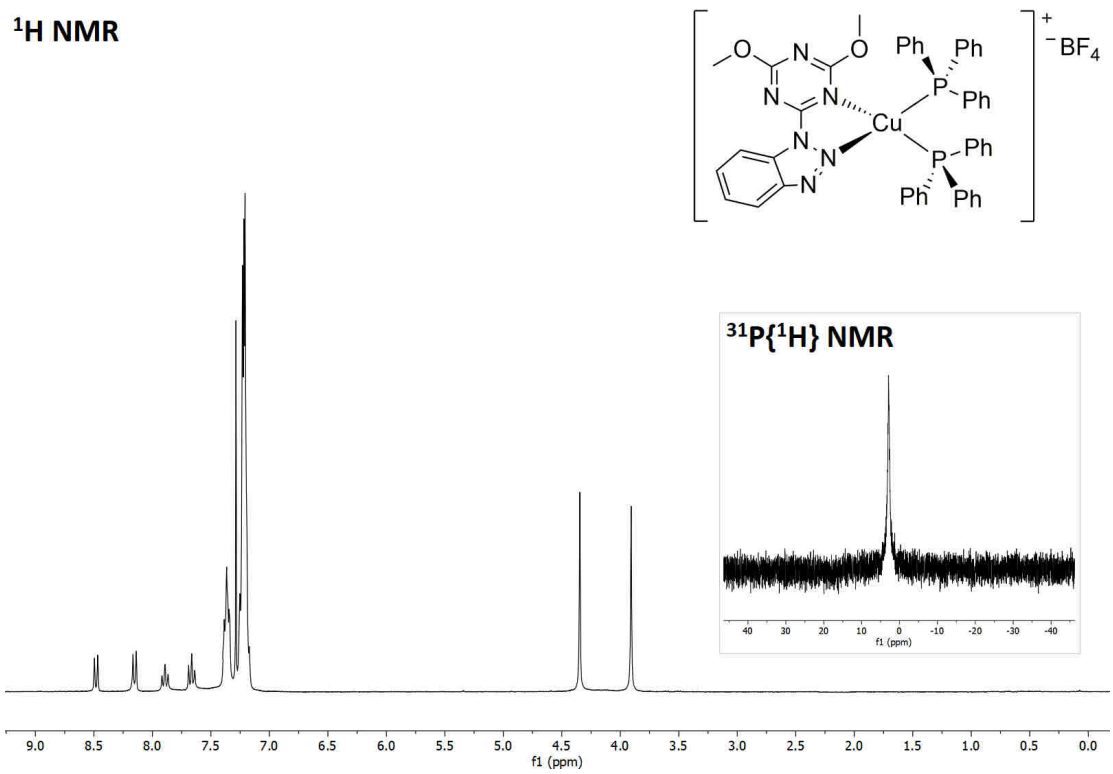


Fig. S14. ^{1}H NMR spectrum of **3a**, [Cu(trz^{OMe}-btz)(PPh$_3$)$_2$][BF$_4$] (CDCl$_3$, 243 K). Inset: ^{31}P{^{1}H} NMR spectrum (CDCl$_3$, 298 K).

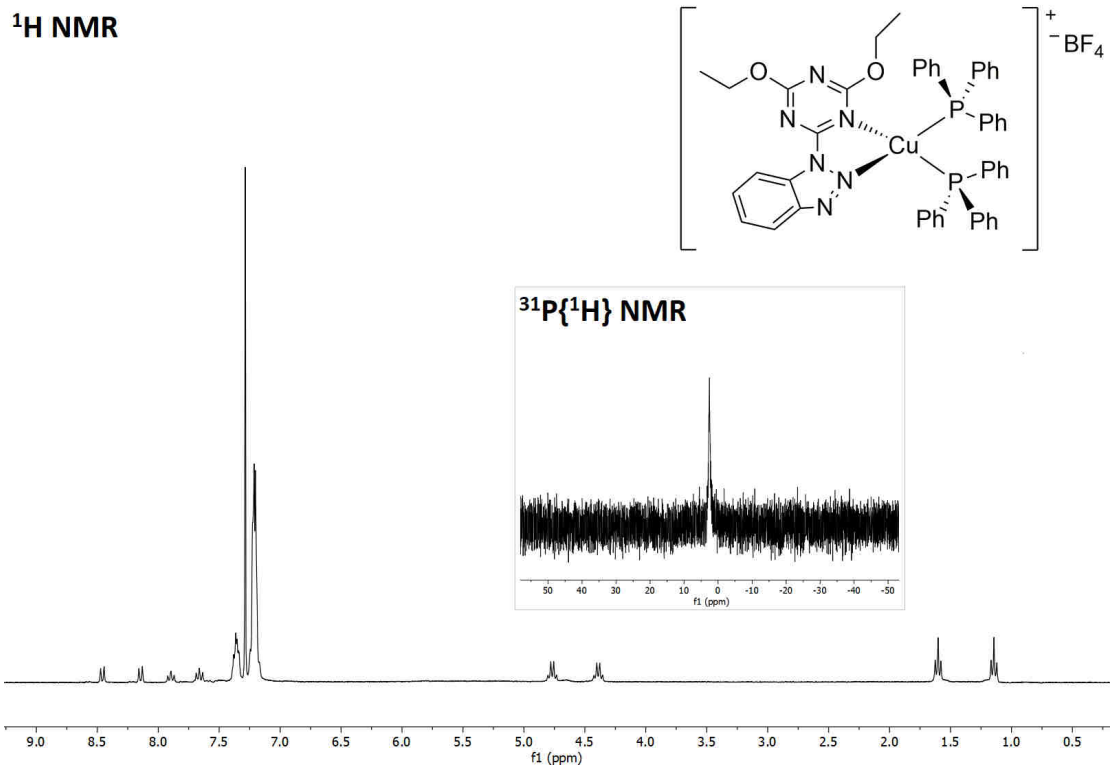


Fig. S15. ^{1}H NMR spectrum of **4a**, [Cu(trz^{OEt}-btz)(PPh$_3$)$_2$][BF$_4$] (CDCl$_3$, 243 K). Inset: ^{31}P{^{1}H} NMR spectrum (CDCl$_3$, 298 K).

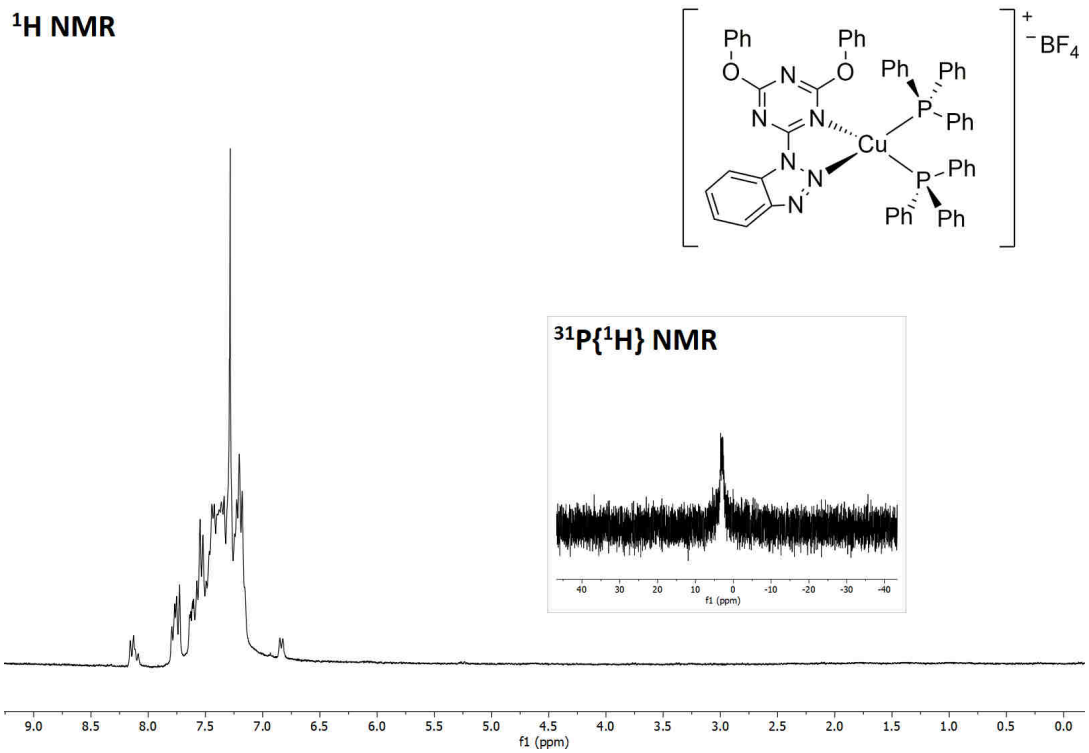


Fig. S16. ^{1}H NMR spectrum of **5a**, [Cu(trz^{OPh}-btz)(PPh$_3$)$_2$][BF$_4$] ($CDCl_3$, 243 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

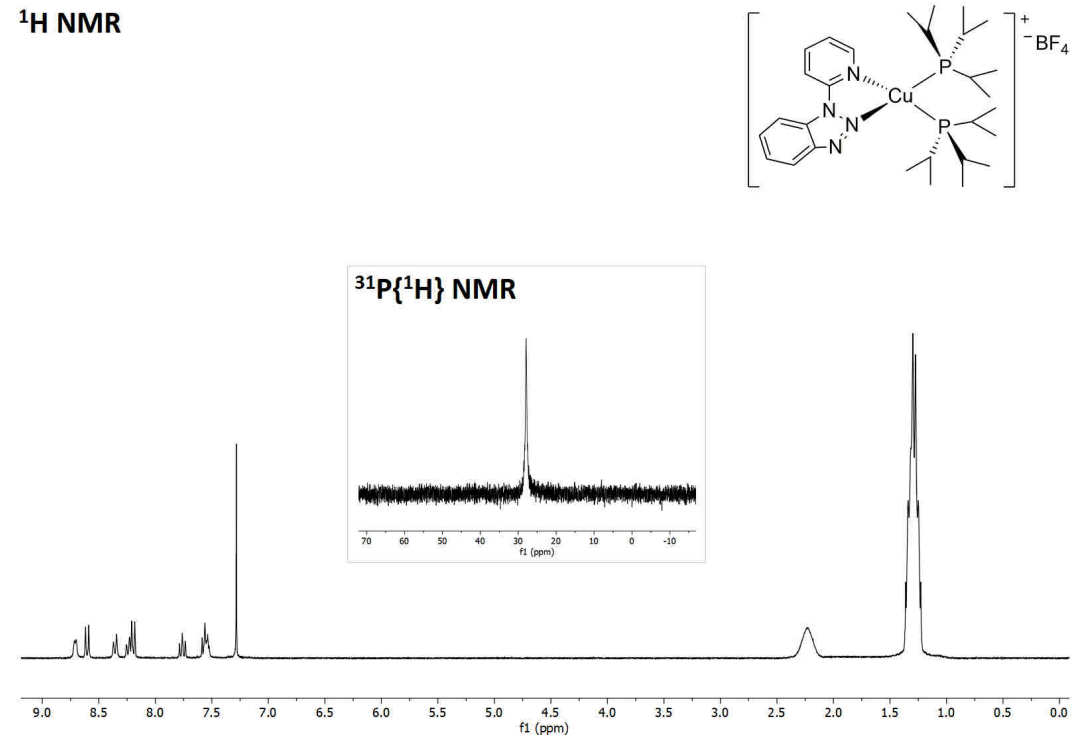


Fig. S17. ^{1}H NMR spectrum of **1b**, [Cu(py-btz)(P^{i}Pr$_3$)$_2$][BF$_4$] ($CDCl_3$, 298 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

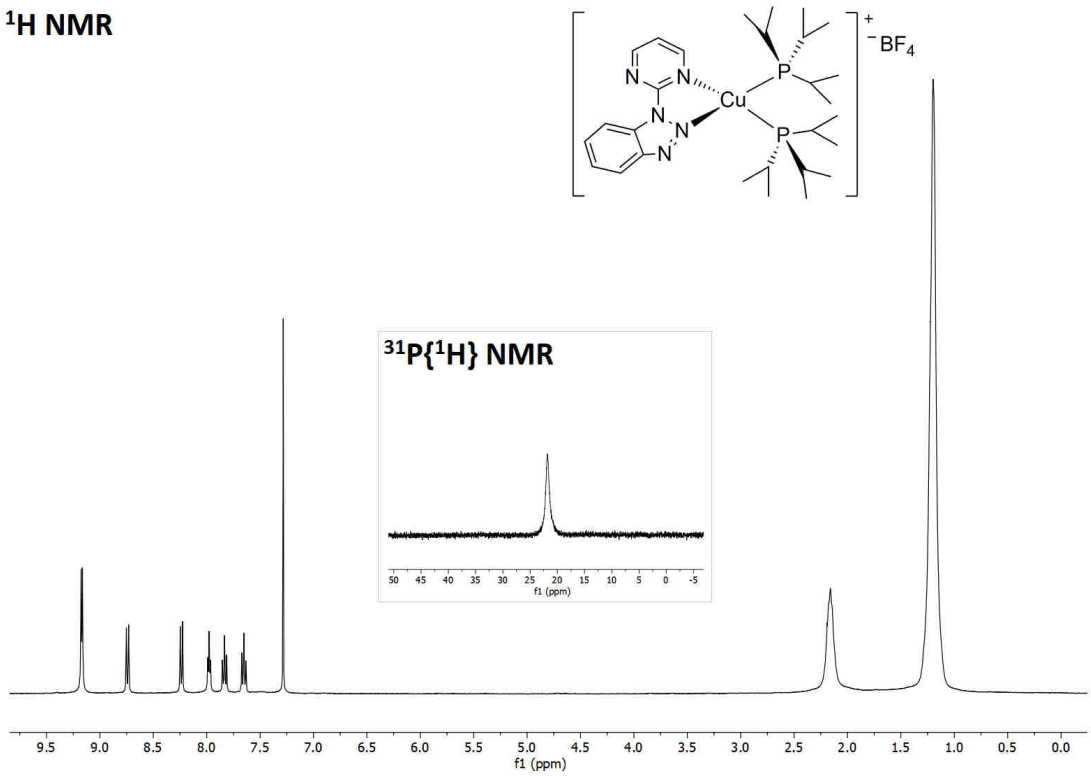


Fig. S18. ^{1}H NMR spectrum of **2b**, [Cu(pym-btz)(P^{i}Pr$_3$)$_2$][BF$_4$] ($CDCl_3$, 298 K). Inset: ^{31}P{^{1}H} NMR spectrum ($CDCl_3$, 298 K).

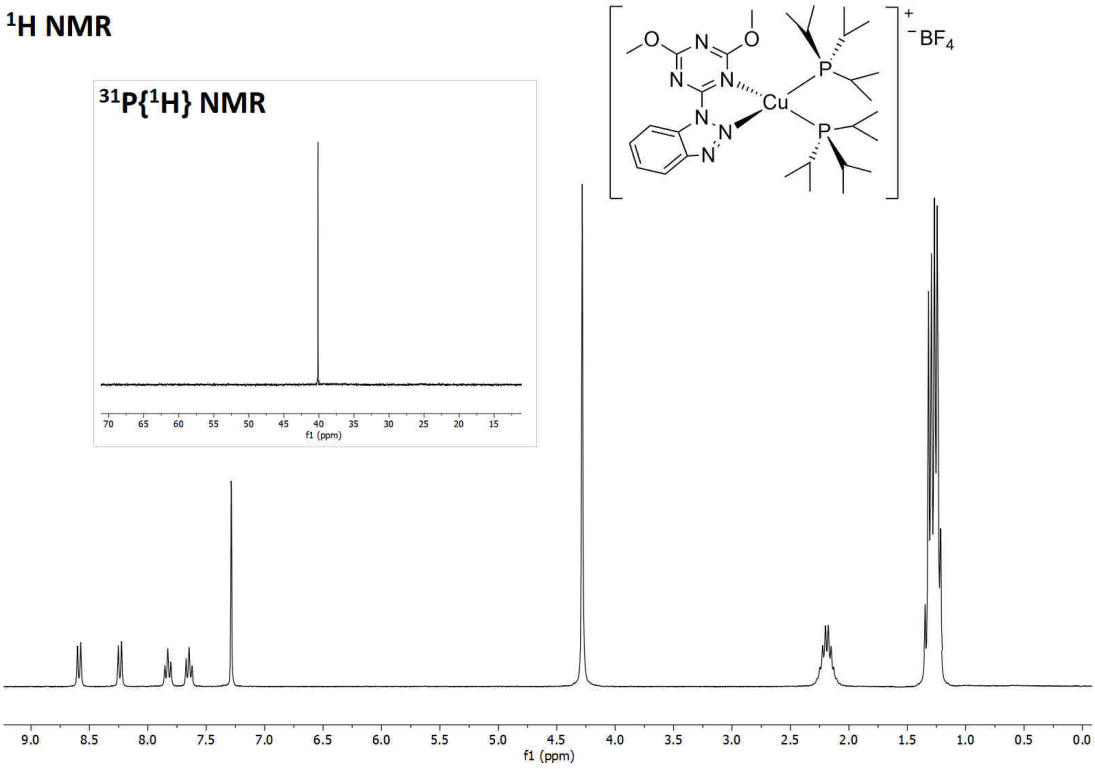


Fig. S19. ^{1}H NMR spectrum of **3b**, [Cu(trz^{OMe}-btz)(P^{i}Pr$_3$)$_2$][BF$_4$] ($CDCl_3$, 298 K). Inset: ^{31}P{^{1}H} NMR spectrum ($CDCl_3$, 298 K).

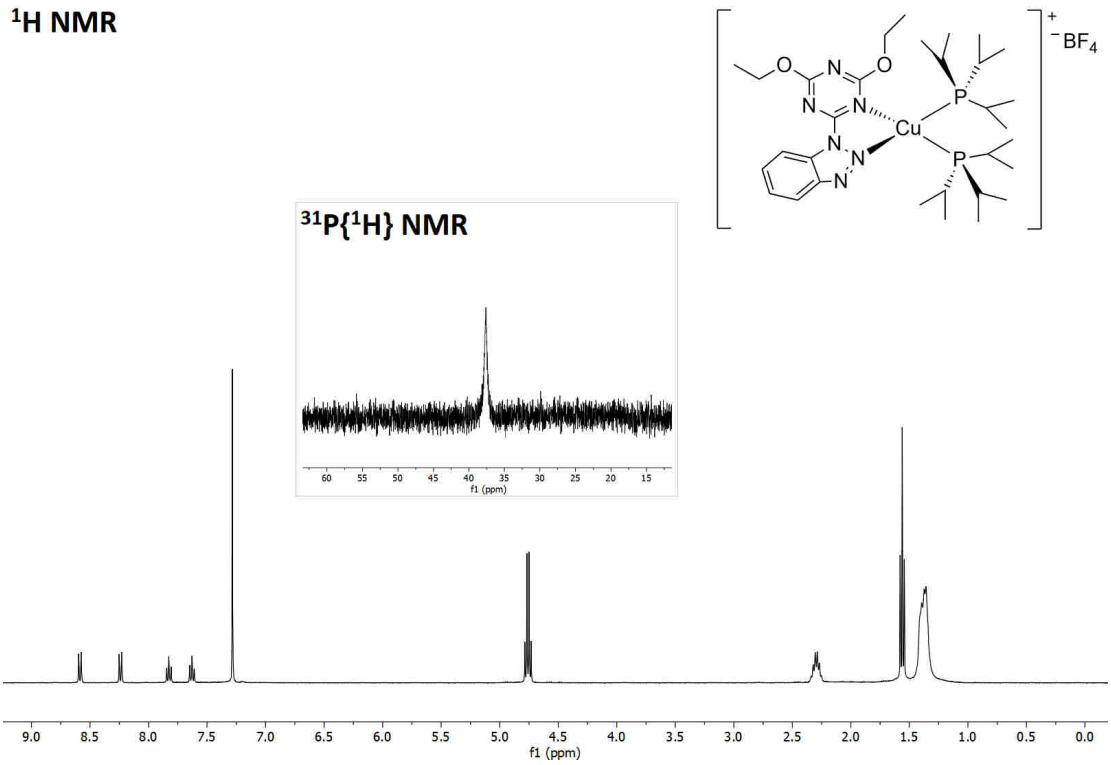


Fig. S20. ^{1}H NMR spectrum of **4b**, [Cu(trz^{OEt}-btz)(P^{i}Pr$_3$)$_2$][BF$_4$] (CDCl$_3$, 298 K). Inset: ^{31}P{^{1}H} NMR spectrum (CDCl$_3$, 298 K).

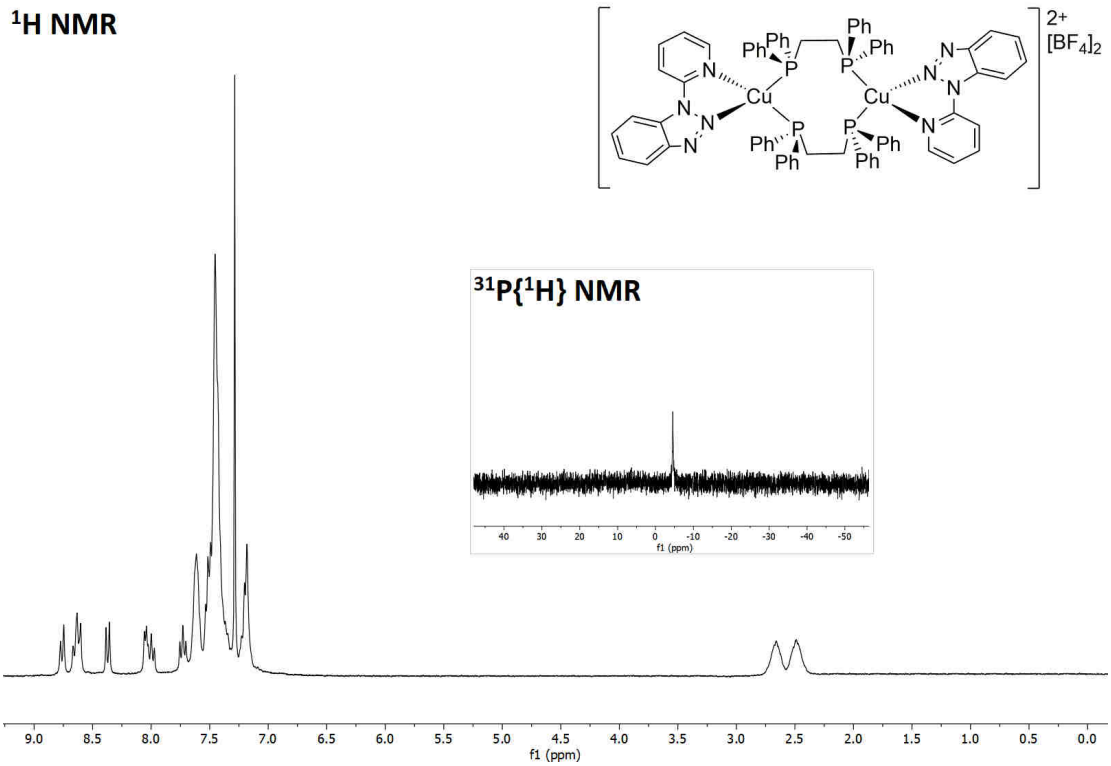


Fig. S21. ^{1}H NMR spectrum of **1c**, [Cu(py-btz)(μ-dppe)]$_2$[BF$_4$]$_2$ (CDCl$_3$, 213 K). Inset: ^{31}P{^{1}H} NMR spectrum (CDCl$_3$, 213 K).

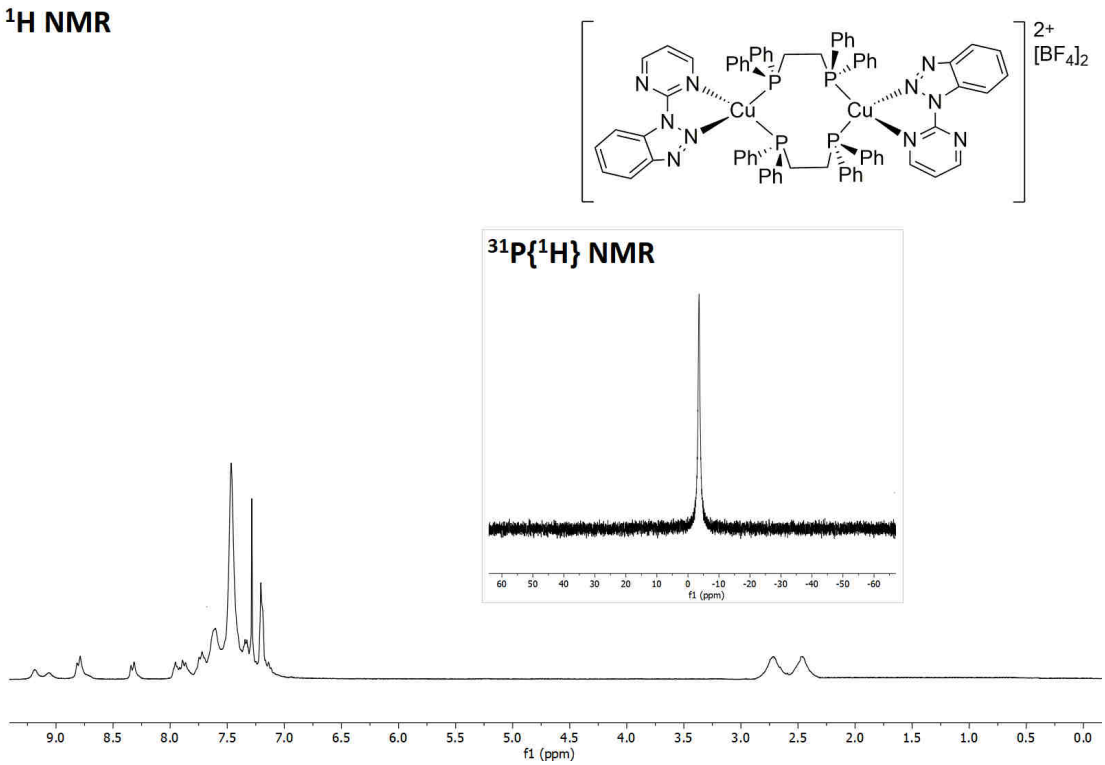


Fig. S22. ^{1}H NMR spectrum of **2c**, $[Cu(pym\text{-}btz)(\mu\text{-}dppe)]_2[BF_4]_2$ ($CDCl_3$, 273 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

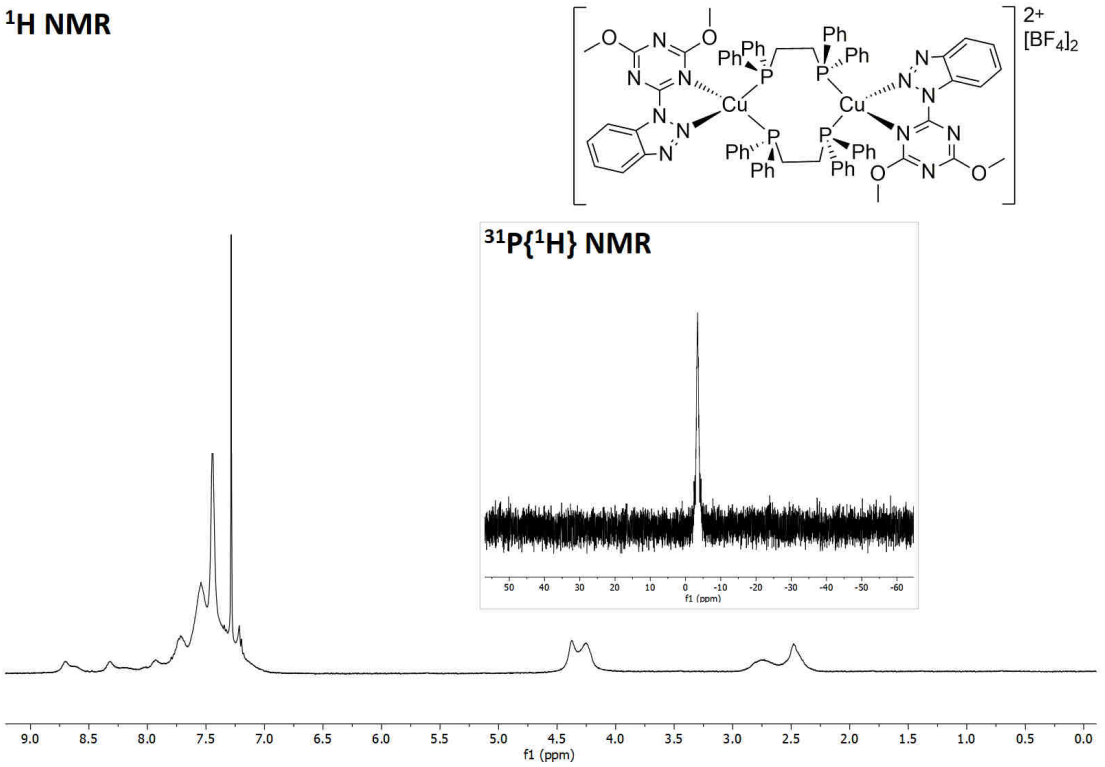


Fig. S23. ^{1}H NMR spectrum of **3c**, $[Cu(trz^{OMe}\text{-}btz)(\mu\text{-}dppe)]_2[BF_4]_2$ ($CDCl_3$, 298 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

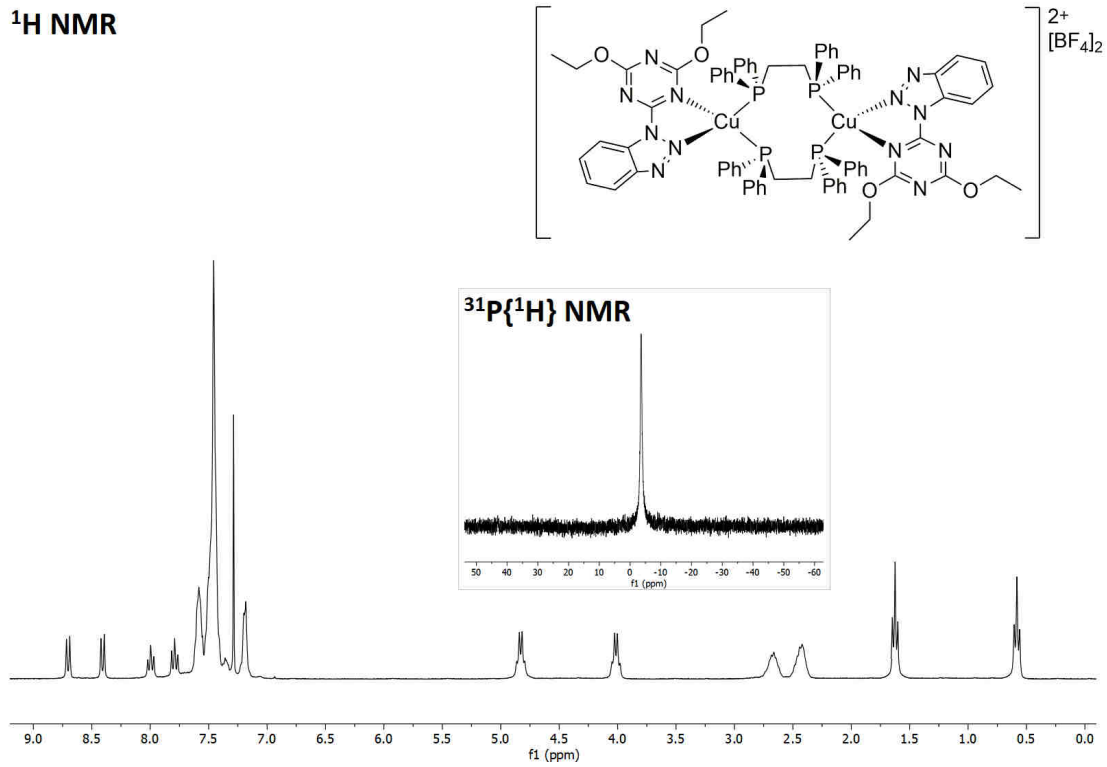


Fig. S24. ^{1}H NMR spectrum of **4c**, [Cu(trz^{OEt}-btz)(μ-dppe)]$_2$[BF$_4$]$_2$ (CDCl$_3$, 233 K). Inset: ^{31}P{^{1}H} NMR spectrum (CDCl$_3$, 298 K).

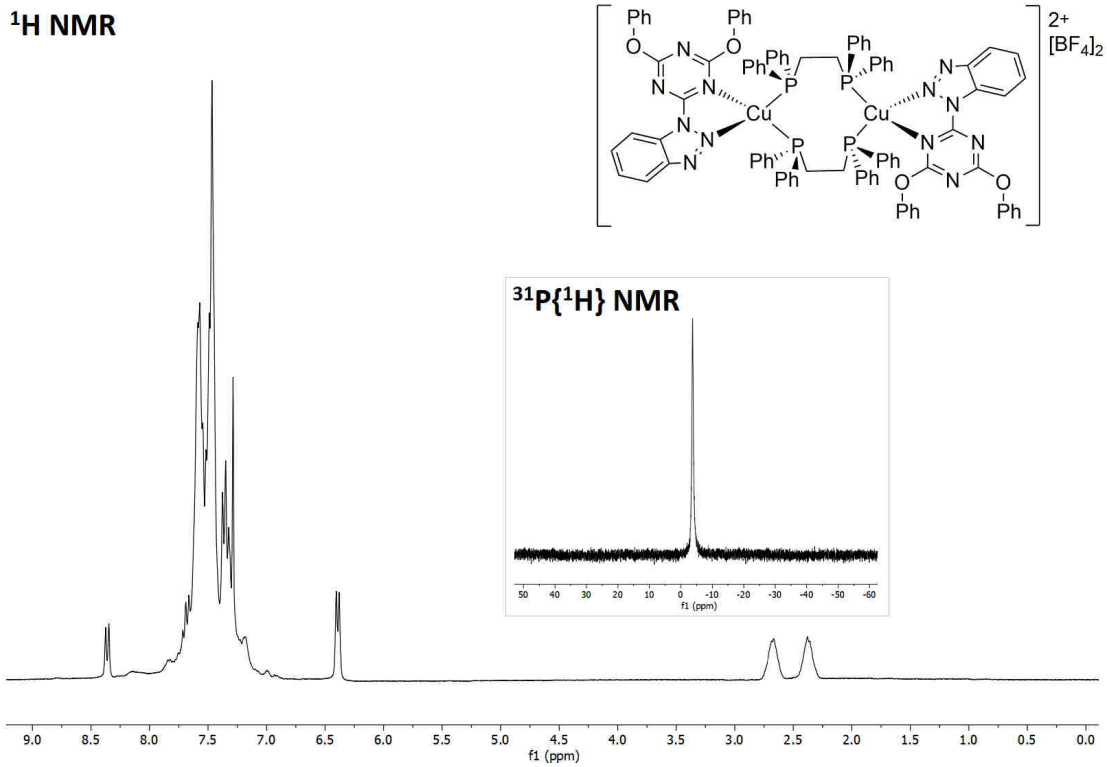


Fig. S25. ^{1}H NMR spectrum of **5c**, [Cu(trz^{OPh}-btz)(μ-dppe)]$_2$[BF$_4$]$_2$ (CDCl$_3$, 213 K). Inset: ^{31}P{^{1}H} NMR spectrum (CDCl$_3$, 298 K).

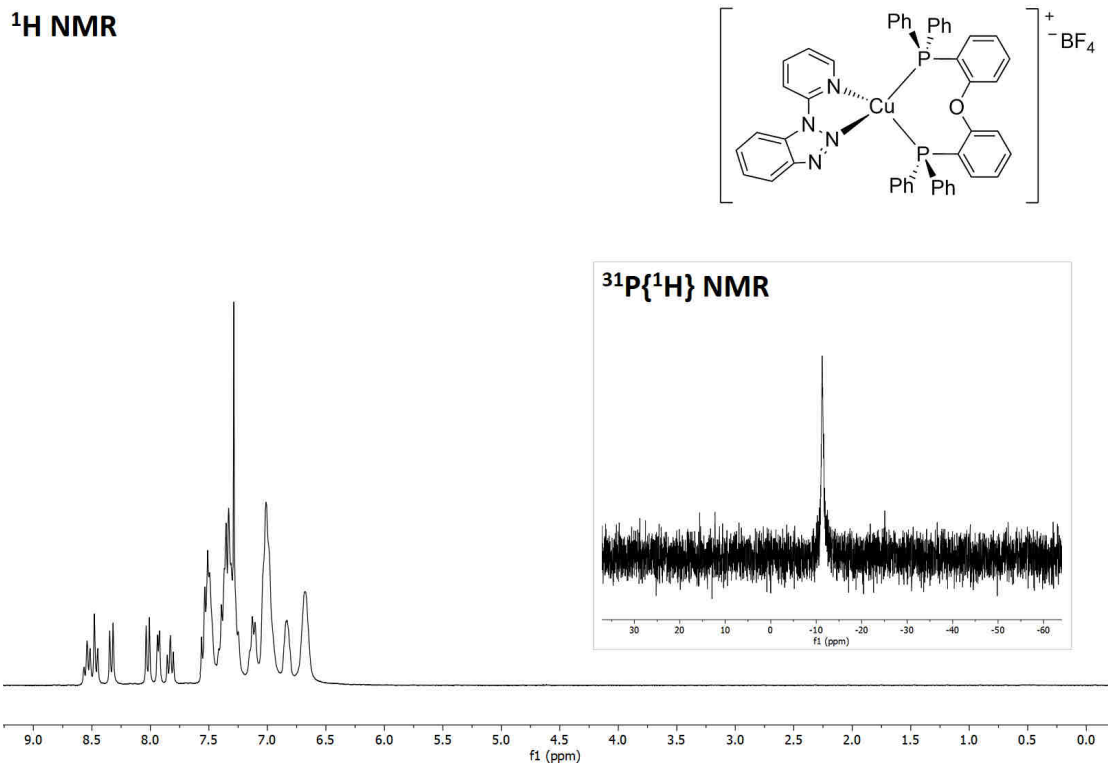


Fig. S26. ^{1}H NMR spectrum of **1d**, [Cu(py-btz)(DPEphos)][BF_4] ($CDCl_3$, 233 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 273 K).

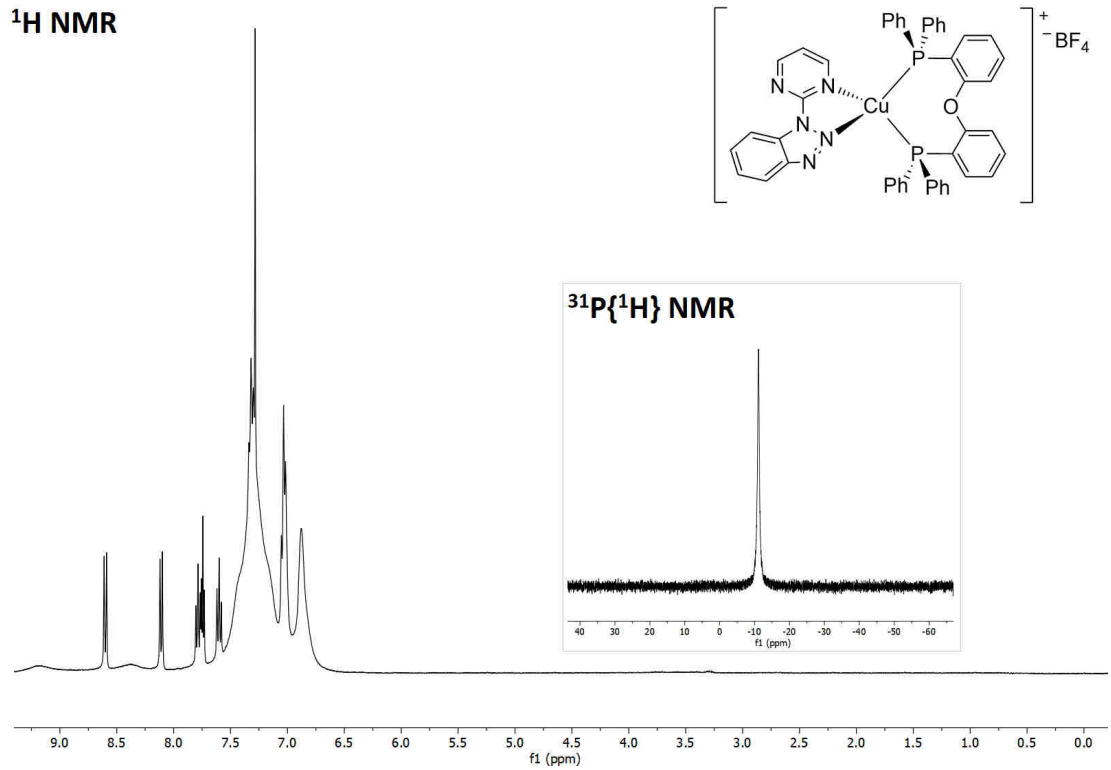


Fig. S27. ^{1}H NMR spectrum of **2d**, [Cu(pym-btz)(DPEphos)][BF_4] ($CDCl_3$, 298 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

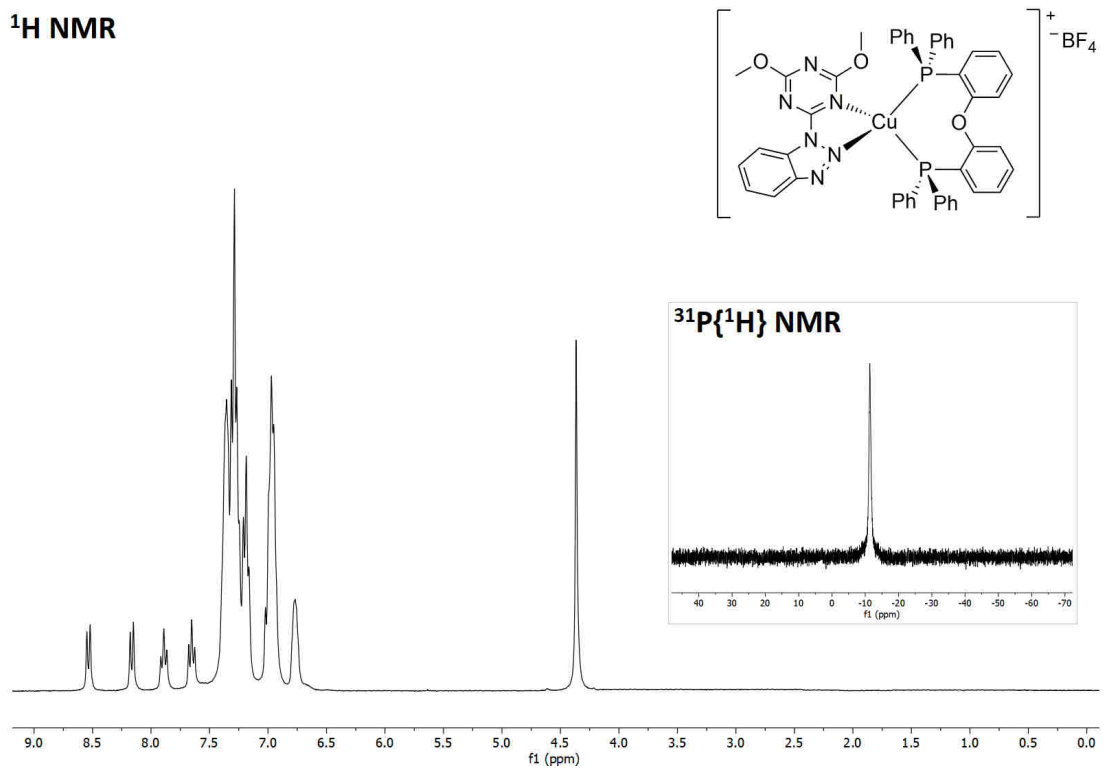


Fig. S28. ^{1}H NMR spectrum of **3d**, [Cu(trz^{OMe}-btz)(DPEphos)][BF_4] ($CDCl_3$, 243 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

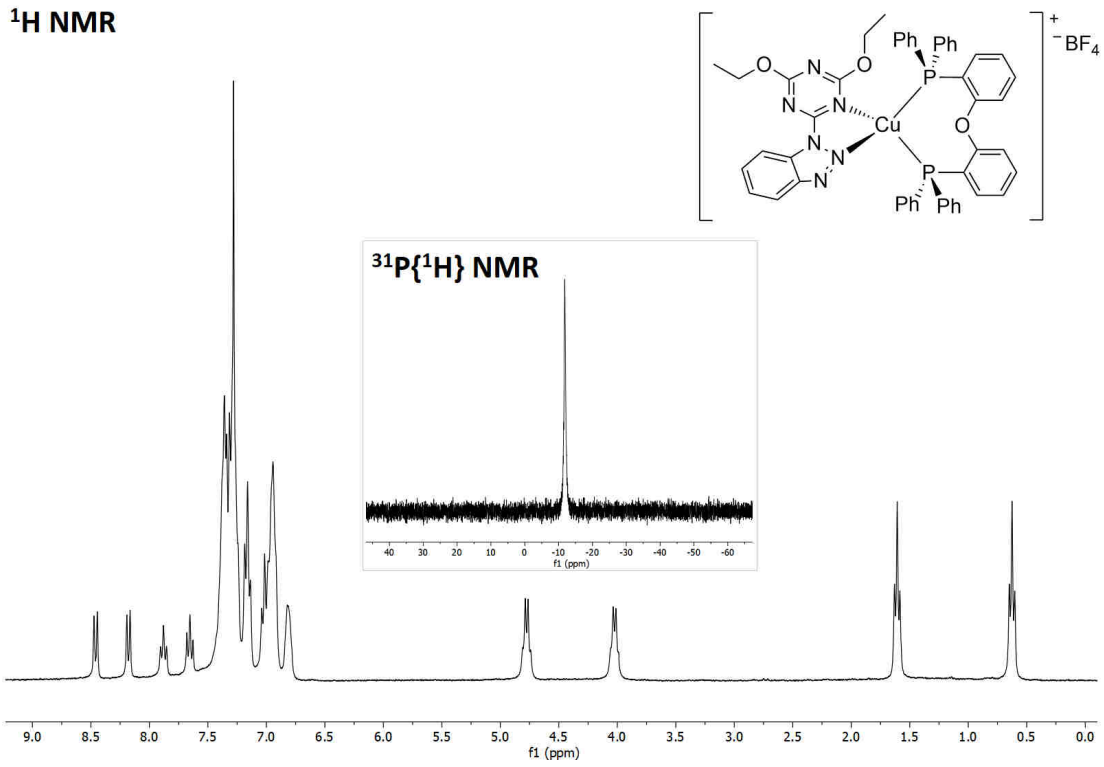


Fig. S29. ^{1}H NMR spectrum of **4d**, [Cu(trz^{OEt}-btz)(DPEphos)][BF_4] ($CDCl_3$, 243 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

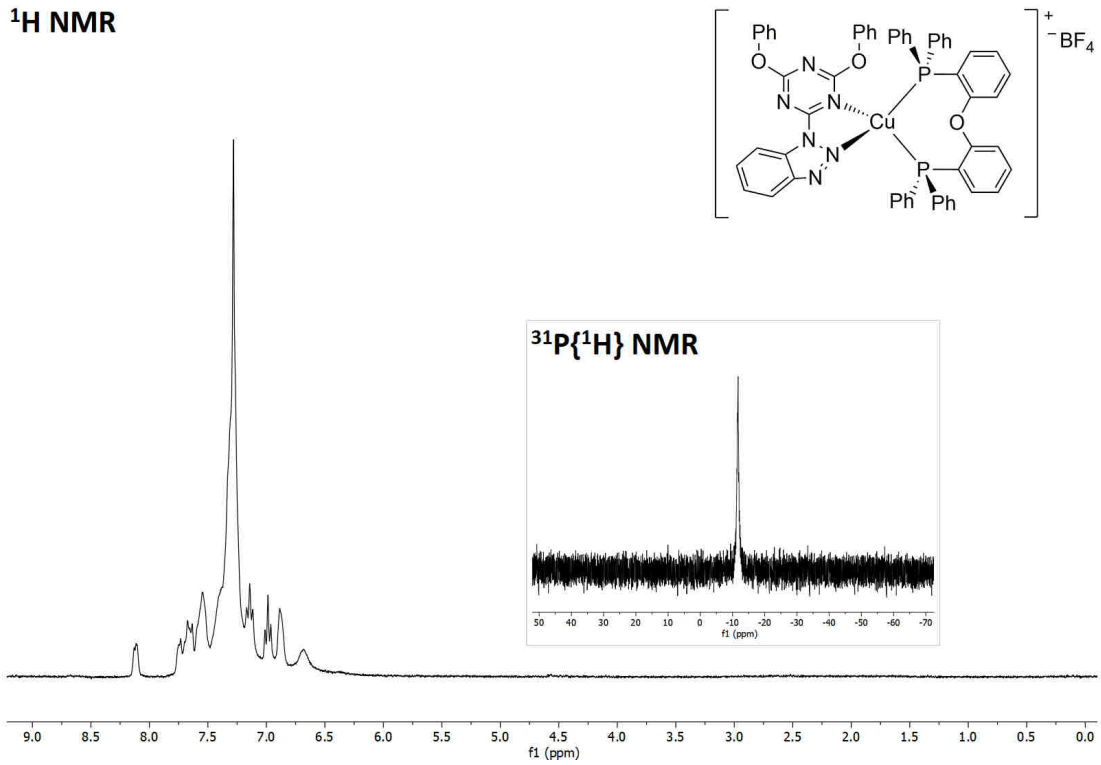


Fig. S30. ^{1}H NMR spectrum of **5d**, [Cu(trz^{OPh}-btz)(DPEphos)][BF_4] ($CDCl_3$, 313 K). Inset: $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K).

Table S2. Crystal data and structure refinement for complexes **1a** and **2a**.

Compound	$[Cu(py\text{-}btz)(PPh_3)_2][BF_4]$	$[Cu(pym\text{-}btz)(PPh_3)_2][BF_4]$
Empirical formula	$C_{47}\ H_{38}\ B\ Cu\ F_4\ N_4\ P_2$	$C_{46}\ H_{37}\ B\ Cu\ F_4\ N_5\ P_2$
Moiety formula	$C_{47}\ H_{38}\ Cu\ N_4\ P_2$, $B\ F_4$	$C_{46}\ H_{37}\ Cu\ N_5\ P_2$, $B\ F_4$
Formula weight	871.10	872.09
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions	a = 12.5593(9) Å	a = 11.5371(7) Å
	b = 13.8159(9) Å	b = 13.8789(7) Å
	c = 14.4530(9) Å	c = 14.6175(8) Å
	α = 73.092(2)°	α = 76.379(2)°
	β = 68.530(2)°	β = 75.218(2)°
	γ = 63.003(2)°	γ = 80.553(2)°
Volume	2055.9(2) $Å^3$	2185.9(2) $Å^3$
Z	2	2
Density (calculated)	1.407 Mg/m^3	1.325 Mg/m^3
Absorption coefficient	0.667 mm^{-1}	0.628 mm^{-1}
F(000)	896	896
Crystal size	0.243 x 0.202 x 0.183 mm	0.214 x 0.076 x 0.034 mm
Theta range for data collection	2.928 to 28.315°	2.510 to 28.311°
Index ranges	$-16 \le h \le 16$	$-15 \le h \le 15$
	$-18 \le k \le 18$	$-18 \le k \le 18$
	$-19 \le l \le 19$	$-19 \le l \le 19$
Reflections collected	92382	134529
Independent reflections	10220 [Rint = 0.0266]	10868 [R_{int} = 0.0478]
Reflections observed (>2σ)	9675	9733
Data Completeness	0.998	0.997
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6946	0.7388 and 0.6985
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10220 / 0 / 532	10868 / 0 / 532
Goodness-of-fit on F2	1.041	1.058
Final R indices [I>2σ(I)]	R_1 = 0.0268	R_1 = 0.0443
	wR_2 = 0.0656	wR_2 = 0.1164
R indices (all data)	R_1 = 0.0287	R_1 = 0.0498
	wR_2 = 0.0667	wR_2 = 0.1199
Largest diff. peak and hole	0.395 and -0.373 e.Å-3	1.397 and -0.864 e.$Å^{-3}$

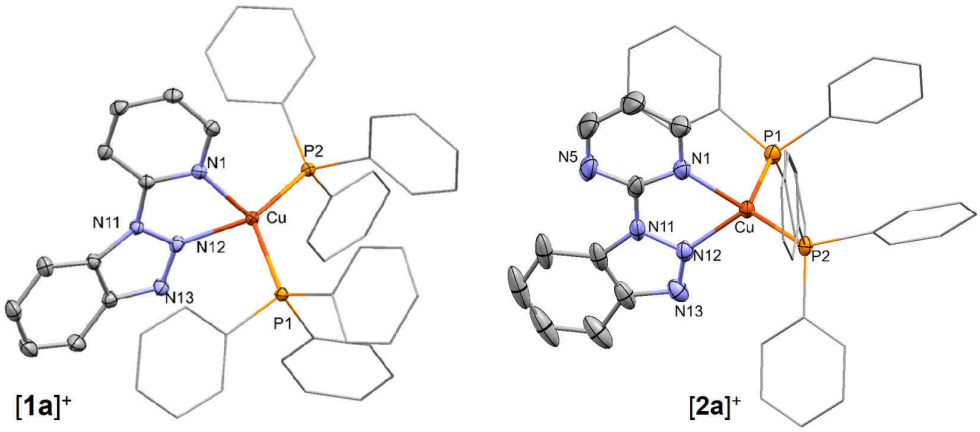


Fig. S31. Ellipsoid plot of the cations [**1a**]$^+$ and [**2a**]$^+$. Hydrogen atoms are omitted for clarity.

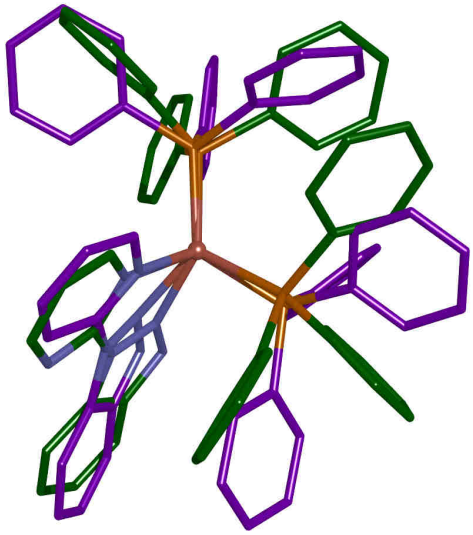


Fig. S32. Best superimposition of the cations [**1a**]$^+$ and [**2a**]$^+$.

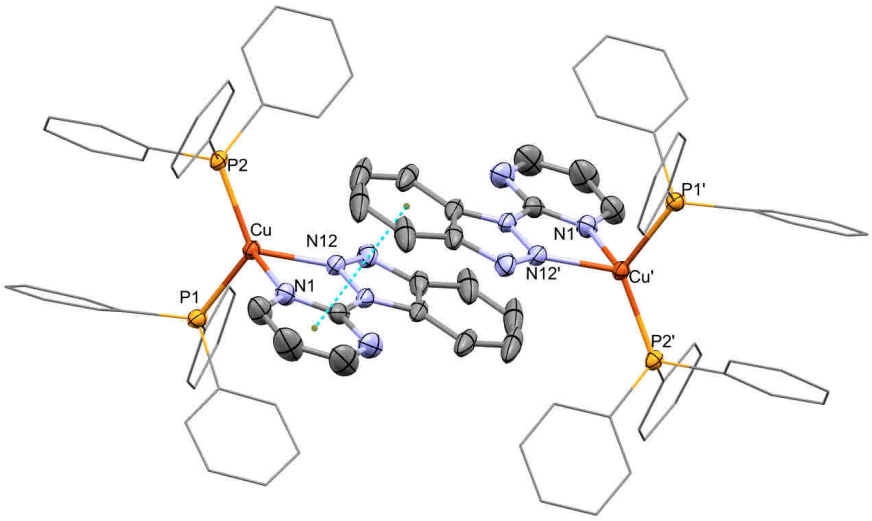


Fig. S33. π,π-staking interaction in complex **2a**.

Table S3. Crystal data and structure refinement for complexes **1d**, **2b** and **2c**.

Compound	[Cu(py-btz)(DPEphos)][BF_4]	[Cu(pym-btz)(P^iPr_3)$_2$][BF_4]	[Cu(pym-btz)(dppe)]$_2$[BF_4]$_2$
Empirical formula	C_{47} H_{36} B Cu F_4 N_4 O P_2	C_{28} H_{49} B Cu F_4 N_5 P_2	C_{72} H_{62} B_2 Cu_2 F_8 N_{10} P_4
Moiety formula	C_{47} H_{36} Cu N_4 O P_2, B F_4	C_{28} H_{49} Cu N_5 P_2, B F_4	C_{72} H_{62} Cu_2 N_{10} P_4, 2(B F_4)
Formula weight	885.09	668.01	1491.89
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*C2/c*	$P2_12_12_1$	*P*-1
Unit cell dimensions	a = 29.5710(14) Å	a = 13.5696(6) Å	a = 12.8974(8) Å
	b = 22.0467(9) Å	b = 15.0666(7) Å	b = 13.1088(8) Å
	c = 25.9445(10) Å	c = 16.2774(8) Å	c = 13.3025(7) Å
	α = 90°	α = 90°	α = 111.144(2)°
	β = 91.716(2)°	β = 90°	β = 99.259(2)°
	γ = 90°	γ = 90°	γ = 109.024(2)°
Volume	16906.8(12) Å^3	3327.9(3) Å^3	1881.56(19) Å^3
Z	16	4	1
Density (calculated)	1.391 Mg/m^3	1.333 Mg/m^3	1.317 Mg/m^3
Absorption coefficient	0.652 mm^{-1}	0.801 mm^{-1}	0.717 mm^{-1}
F(000)	7264	1408	764
Crystal size	0.215 x 0.173 x 0.083 mm	0.173 x 0.135 x 0.109 mm	0.173 x 0.121 x 0.063 mm
Theta range for data collection	1.931 to 28.304°	1.954 to 28.307°	2.042 to 28.328°
Index ranges	-39 ≤ *h* ≤ 39	-18 ≤ *h* ≤ 18	-17 ≤ *h* ≤ 17
	-29 ≤ *k* ≤ 29	-20 ≤ *k* ≤ 20	-17 ≤ *k* ≤ 17
	-34 ≤ *l* ≤ 33	-21 ≤ *l* ≤ 21	-17 ≤ *l* ≤ 17
Reflections collected	234094	45415	86819
Independent reflections	20984 [R_{int} = 0.0567]	8263 [R_{int} = 0.0330]	9358 [R_{int} = 0.0436]
Reflections observed (>2σ)	16754	8088	7986
Data Completeness	0.998	0.999	0.998
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7336 and 0.6915	0.7457 and 0.6651	0.7457 and 0.7013
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	20984 / 0 / 1177	8263 / 0 / 382	9358 / 39 / 465
Goodness-of-fit on F^2	1.021	1.089	1.043
Final R indices [I>2σ(I)]	R_1 = 0.0415	R_1 = 0.0535	R_1 = 0.0858
	wR_2= 0.10208	wR_2 = 0.1396	wR_2 = 0.2467
R indices (all data)	R_1 = 0.0578	R_1 = 0.0543	R_1 = 0.0962
	wR_2 = 0.1120	wR_2 = 0.1402	wR_2 = 0.2572
Largest diff. peak and hole	0.520 and -0.940 e.Å^{-3}	3.158 and -0.743 e.Å^{-3}	4.207 and -2.328 e.Å^{-3}

Table S4. Crystal data and structure refinement for complexes **3b**, **4d** and **5d**.

Compound	[Cu(trz^{OMe}-btz)(P^{i}Pr$_3$)$_2$][BF$_4$]	[Cu(trz^{OEt}-btz)(DPEphos)][BF$_4$]	[Cu(trz^{OPh}-btz)(DPEphos)][BF$_4$]
Empirical formula	C_{29} H_{52} B Cu F_4 N_6 O_2 P_2	C_{49} H_{42} B Cu F_4 N_6 O_3 P_2	C_{61} H_{52} B Cu F_4 N_6 O_4 P_2
Moiety formula	C_{29} H_{52} Cu N_6 O_2 P_2, B F_4	C_{49} H_{42} Cu N_6 O_3 P_2, B F_4	C_{57} H_{42} Cu N_6 O_3 P_2, B F_4, C_4 H_{10} O
Formula weight	729.05	975.17	1145.37
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/c$	*P*-1
Unit cell dimensions	a = 10.1027(6) Å	a = 14.7130(12) Å	a = 11.3664(5) Å
	b = 12.8600(9) Å	b = 23.4115(16) Å	b = 12.6813(6) Å
	c = 13.8962(10) Å	c = 14.0533(12) Å	c = 20.9098(10) Å
	α = 95.446(3)°	α = 90°	α = 96.034(2)°
	β = 100.595(2)°	β = 106.376(3)°	β = 105.307(2)°
	γ = 93.419(2)°	γ = 90°	γ = 106.960(2)°
Volume	1761.1(2) Å^3	4644.3(6) Å^3	2725.9(2) Å^3
Z	2	4	2
Density (calculated)	1.375 Mg/m^3	1.395 Mg/m^3	1.395 Mg/m^3
Absorption coefficient	0.768 mm^{-1}	0.604 mm^{-1}	0.528 mm^{-1}
F(000)	768	2008	1184
Crystal size	0.282 x 0.255 x 0.173 mm	0.273 x 0.156 x 0.087 mm	0.174 x 0.131 x 0.078 mm
Θ range for data collection	2.057 to 28.329°	1.972 to 28.304°	1.970 to 28.302°
Index ranges	-13 ≤ *h* ≤ 13	-19 ≤ *h* ≤ 19	-15 ≤ *h* ≤ 15
	-17 ≤ *k* ≤ 17	-31 ≤ *k* ≤ 31	-16 ≤ *k* ≤ 16
	-18 ≤ *l* ≤ 18	-18 ≤ *l* ≤ 18	-27 ≤ *l* ≤ 27
Reflections collected	109259	139660	168957
Independent reflections	8766 [R_{int} = 0.0418]	11546 [R_{int} = 0.0355]	13508 [R_{int} = 0.0384]
Reflections observed (>2σ)	8168	10628	12432
Data Completeness	0.996	0.999	0.999
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6550	0.7457 and 0.6835	0.7447 and 0.7134
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8766 / 0 / 420	11546 / 1 / 567	13508 / 0 / 714
Goodness-of-fit on F^2	1.017	1.046	1.027
Final *R* indices [*I*>2σ(*I*)]	R_1 = 0.0291	R_1 = 0.1067	R_1 = 0.0298
	wR_2 = 0.0755	wR_2 = 0.2984	wR_2 = 0.0741
R indices (all data)	R_1 = 0.0318	R_1 = 0.1132	R_1 = 0.0333
	wR_2 = 0.0771	wR_2 = 0.3056	wR_2 = 0.0761
Largest diff. peak and hole	0.728 and -0.479 e.Å^{-3}	5.560 and -4.058 e.Å^{-3}	0.354 and -0.417 e.Å^{-3}

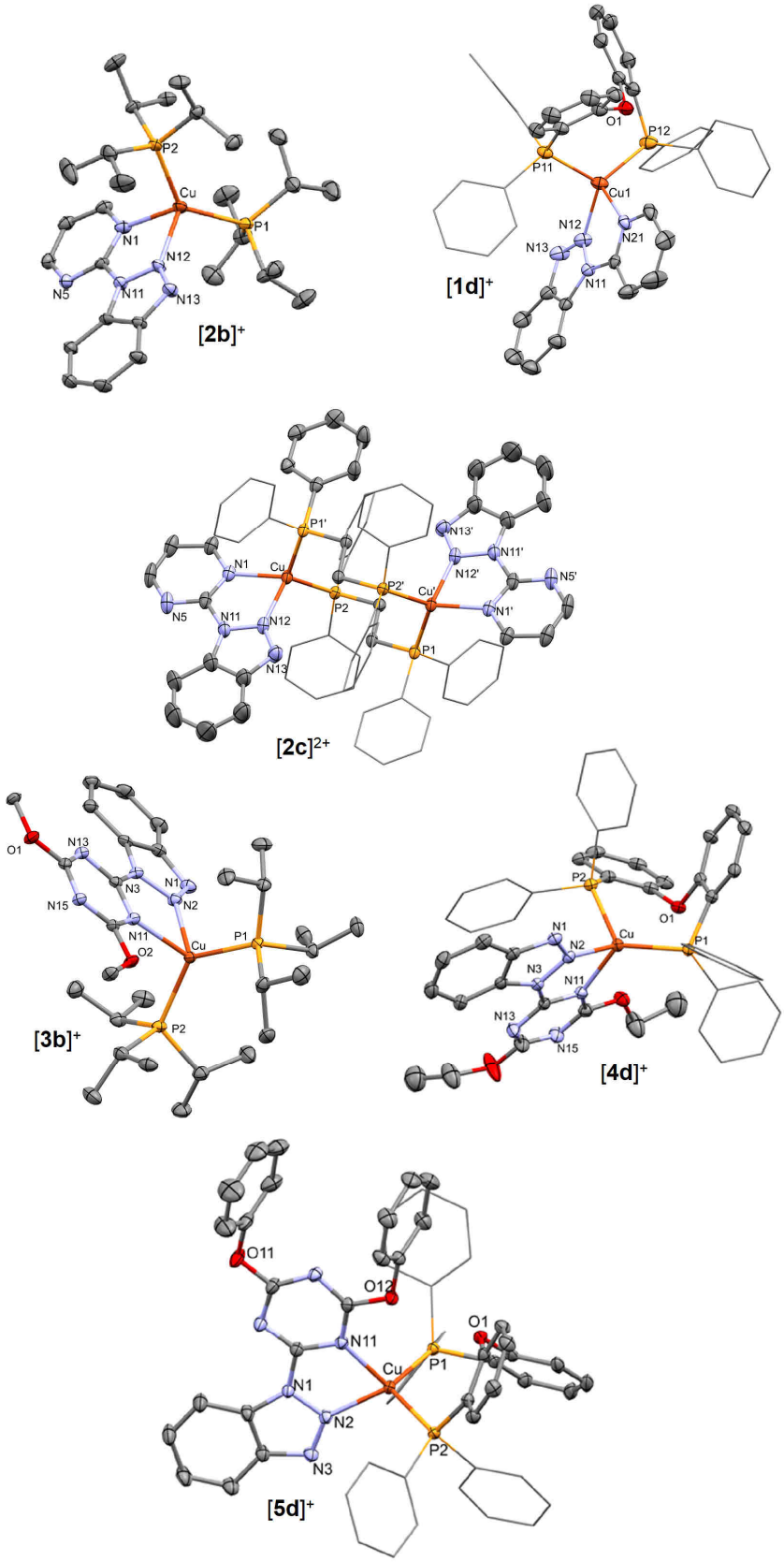


Fig. S34. Ellipsoid plot of the cations [**2b**]$^{+}$, [**1d**]$^{+}$, [**2c**]$^{2+}$, [**3b**]$^{+}$, [**4d**]$^{+}$ and [**5d**]$^{+}$. Hydrogen atoms are omitted for clarity.

Table S5. Selected bond lengths [Å] and angles [°] for the complexes **1a** and **2a**.

	1a	**2a**
Cu-N(1)	2.0670(10)	2.1309(17)
Cu-N(12)	2.1160(11)	2.0710(17)
Cu-P(1)	2.2540(4)	2.2642(6)
Cu-P(2)	2.2279(3)	2.2316(5)
N(1)-Cu-N(12)	78.51(4)	78.03(7)
N(1)-Cu-P(1)	117.03(3)	102.27(5)
N(1)-Cu-P(2)	111.66(3)	119.58(5)
N(12)-Cu-P(1)	101.08(3)	106.68(5)
N(12)-Cu-P(2)	120.82(3)	120.86(5)
P(1)-Cu-P(2)	120.417(13)	120.71(2)

Table S6. Selected bond lengths [Å] and angles [°] for the complexes **1d** (mol. 1 and 2) and **2b**.

	1d (mol. 1)	**1d** (mol. 2)	**2b**
Cu-N(1)	2.0886(17)	2.0526(19)	2.159(4)
Cu-N(12)	2.0532(17)	2.0423(19)	2.156(4)
Cu-P(1)	2.2803(6)	2.1932(5)	2.3001(13)
Cu-P(2)	2.2360(6)	2.280(2)	2.3026(13)
		2.279(3)	
N(1)-Cu-N(12)	78.42(6)	79.23(8)	75.58(14)
N(1)-Cu-P(1)	125.02(5)	130.17(5)	105.91(11)
N(1)-Cu-P(2)	110.46(5)	102.34(8)	113.19(11)
		97.20(11)	
N(12)-Cu-P(1)	110.35(5)	117.67(5)	111.75(11)
N(12)-Cu-P(2)	104.95(5)	98.76(12)	102.84(11)
		108.82(14)	
P(1)-Cu-P(2)	118.21(2)	118.76(5)	132.95(5)
		117.00(7)	

Table S7. Selected bond lengths [Å] and angles [°] for the dimeric **2c** complex.

Cu-N(1)	2.090(3)
Cu-N(12)	2.072(4)
Cu-P(1')	2.2480(11)
Cu-P(2)	2.2435(11)

N(12)-Cu-N(1)	78.10(14)
N(12)-Cu-P(2)	112.48(10)
N(1)-Cu-P(2)	122.57(10)
N(12)-Cu-P(1')	112.58(11)
N(1)-Cu-P(1')	112.51(10)
P(2)-Cu-P(1')	113.54(4)

Symmetry transformations used to generate equivalent atoms: i: 1-x; 1-y, 1-z

Table S8. Selected bond lengths [Å] and angles [°] for the complexes **3b**, **4d** and **5d**.

	3b	**4d**	**5d**
Cu-N(11)	2.1505(11)	2.080(4)	2.0792(10)
Cu-N(2)	2.1672(11)	2.087(4)	2.0814(11)
Cu-P(1)	2.2744(4)	2.2040(12)	2.2555(3)
Cu-P(2)	2.2853(4)	2.2820(12)	2.2482(3)
N(11)-Cu-N(2)	74.70(4)	77.94(15)	77.46(4)
N(11)-Cu-P(1)	108.78(3)	123.45(11)	110.97(3)
N(11)-Cu-P(2)	107.08(3)	99.79(11)	118.95(3)
N(2)-Cu-P(1)	110.96(3)	127.69(10)	120.88(3)
N(2)-Cu-P(2)	110.61(3)	100.72(11)	114.54(3)
P(1)-Cu-P(2)	130.506(14)	118.22(5)	110.717(13)

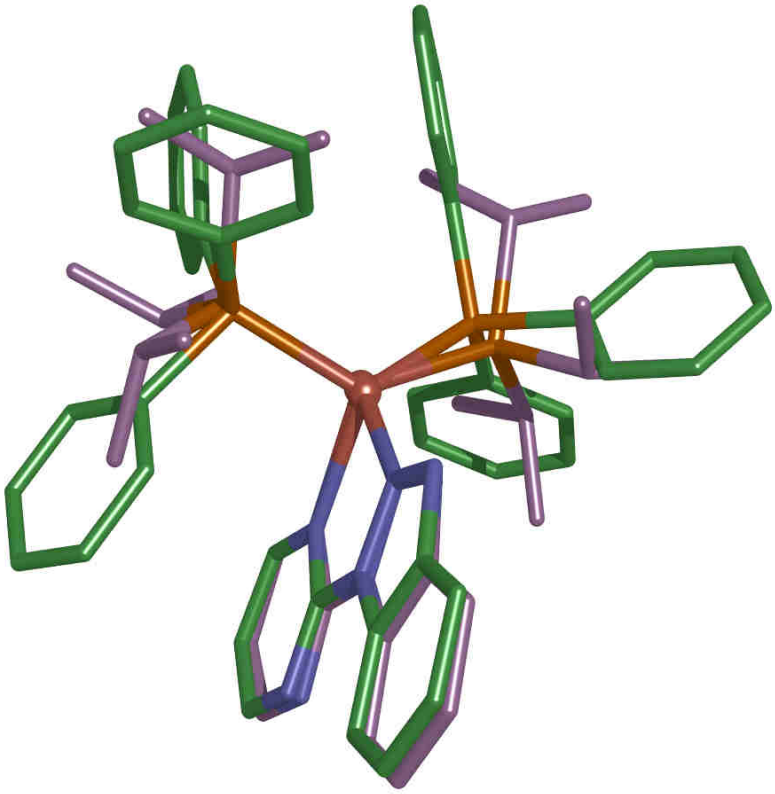


Fig. S35. Best superimposition of complexes **2a** and **2b**.

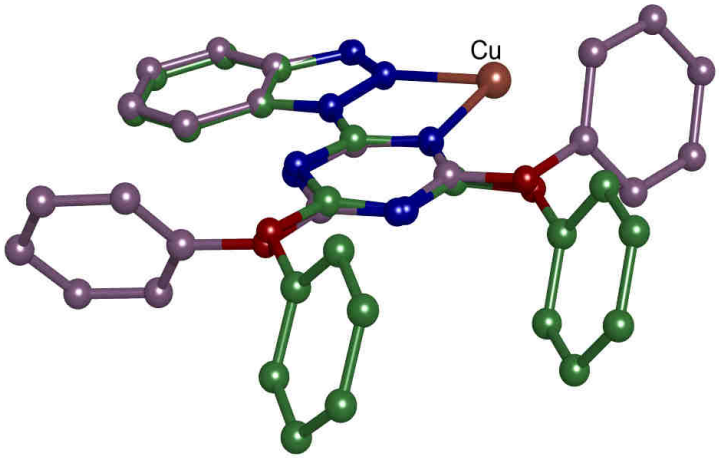


Fig. S36. Superimposition between free and coordinated ligand trz^{OPh}-btz in complex **5d**. Carbon atoms are in violet for the free ligand trz^{OPh}-btz and in green for **5d** (DPEphos and hydrogen atoms were omitted for clarity).

Table S9. S H A P E v2.1 Continuous Shape Measures calculation and other tetrahedral parameters.

Structure [ML_4]	SP-4	T-4	SS-4	vTBPY-4	τ_4[1]	τ'_4[2]
[**1a**]$^+$	25.062	3.573	8.565	3.436	0.84	0.84
[**1d**]$^+$ (Cu1)	28.789	3.438	7.889	2.362	0.83	0.81
[**1d**]$^+$ (Cu2)[(a)]	25.322	3.799	7.071	4.186	0.79	0.75
[**1d**]$^+$ (Cu2)[(b)]	29.700	3.635	7.319	2.916	0.79	0.76
[**2a**]$^+$	29.852	3.329	9.404	3.345	0.84	0.84
[**2b**]$^+$	29.166	4.189	7.319	3.412	0.81	0.75
[**2c**]$^+$	27.067	3.303	8.156	3.195	0.88	0.85
[**3b**]$^+$	31.638	3.918	7.907	2.881	0.84	0.78
[**4d**]$^+$	30.136	3.701	8.086	3.754	0.77	0.76
[**5d**]$^+$	25.478	3.547	8.590	3.923	0.85	0.85

SP-4, Square-planar; **T-4**, Tetrahedron; **SS-4**, Seesaw; **vTBPY-4**, Vacant trigonal bipyramid [C_{3v}]

[(a,b)] There are two disordered phosphorus atoms position.

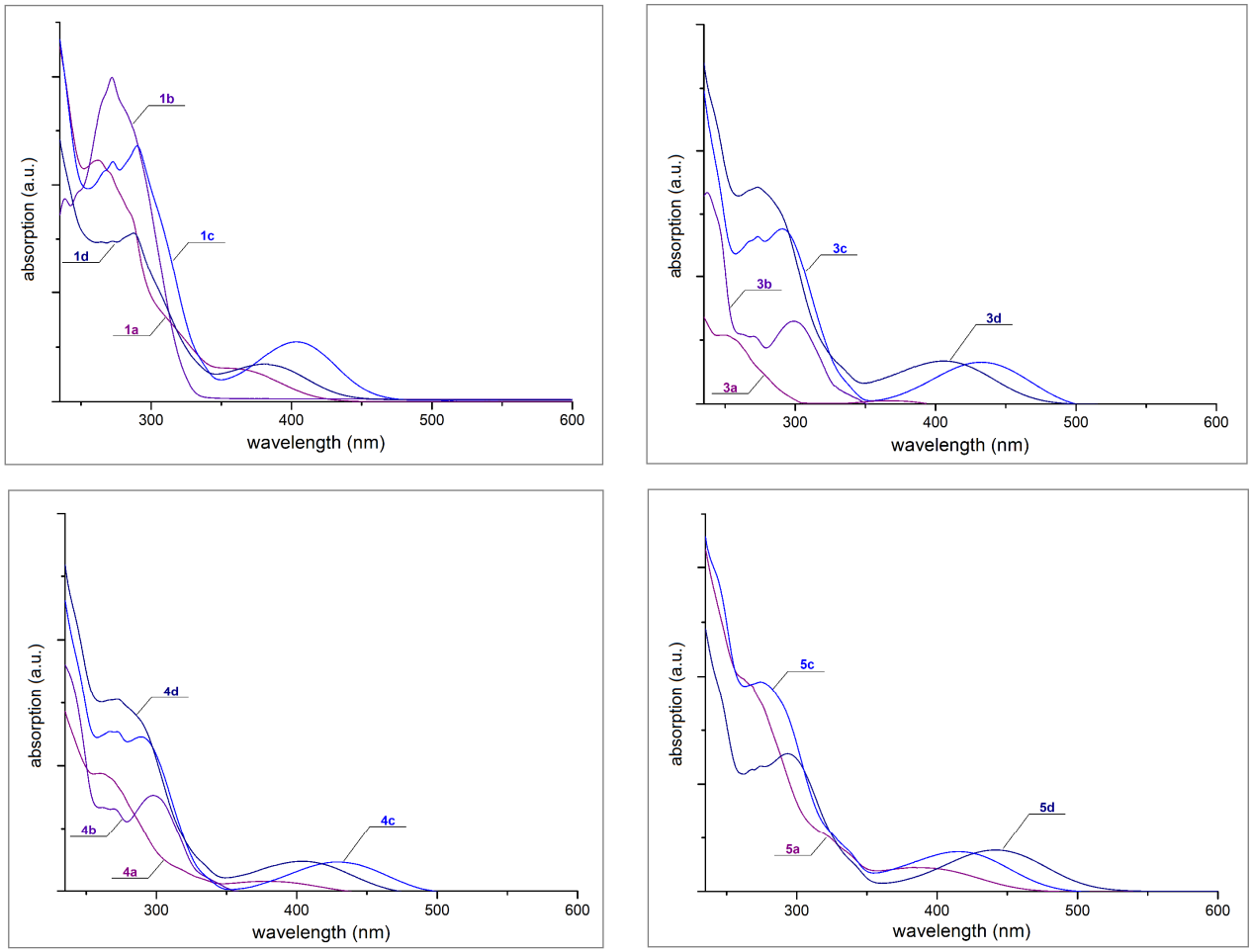


Fig. S37. Absorption spectra of complexes 10^{-5} M in CH_2Cl_2 (**1a**, **3a**, **4a** and **5a**, purple line; **1b**, **3b** and **4b**, violet line; **1c**, **3c**, **4c** and **5c**, navy blue line; **1d**, **3d**, **4d** and **5d**, blue line).