

Electronic Supplementary Information to the paper:

Selective, catalytic aerobic oxidation of alcohols using CuBr₂ and bifunctional triazine-based ligands containing both a bipyridine and a TEMPO group

Zhengliang Lu,^a Tim Ladrak,^a Olivier Roubeau,^b John van der Toorn,^a Simon J. Teat,^c Chiara Massera,^d Patrick Gamez^{a,*} and Jan Reedijk^{a,*}

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^a Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P. O. Box 9502, 2300 RA Leiden, The Netherlands

^b Université Bordeaux 1, CNRS-CRPP, 115, avenue du Dr. Schweitzer, 33600 Pessac, France

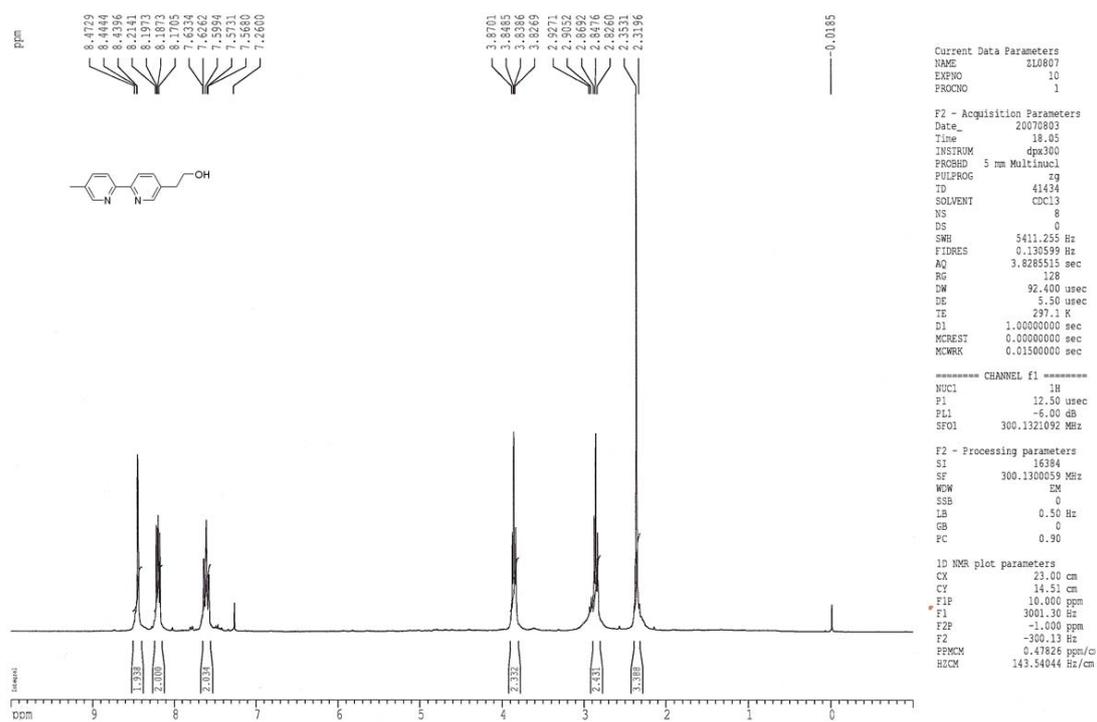
^c ALS, Berkeley Lab, 1 Cyclotron Rd, MS2-400, Berkeley, CA 94720, USA

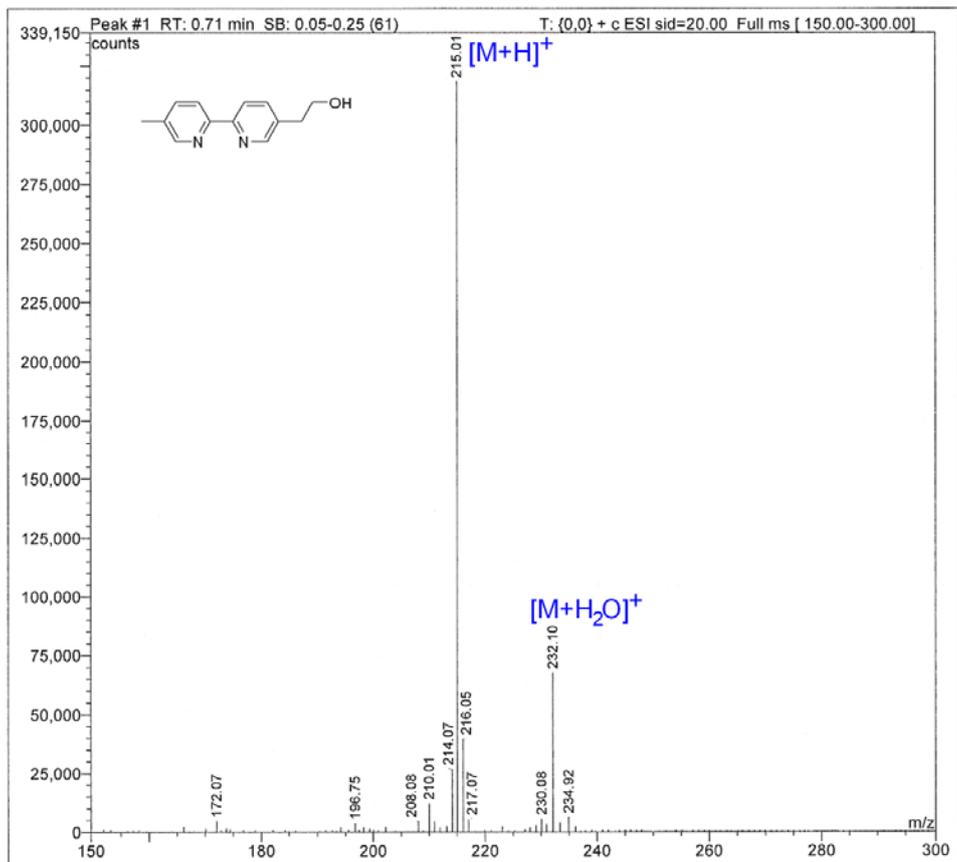
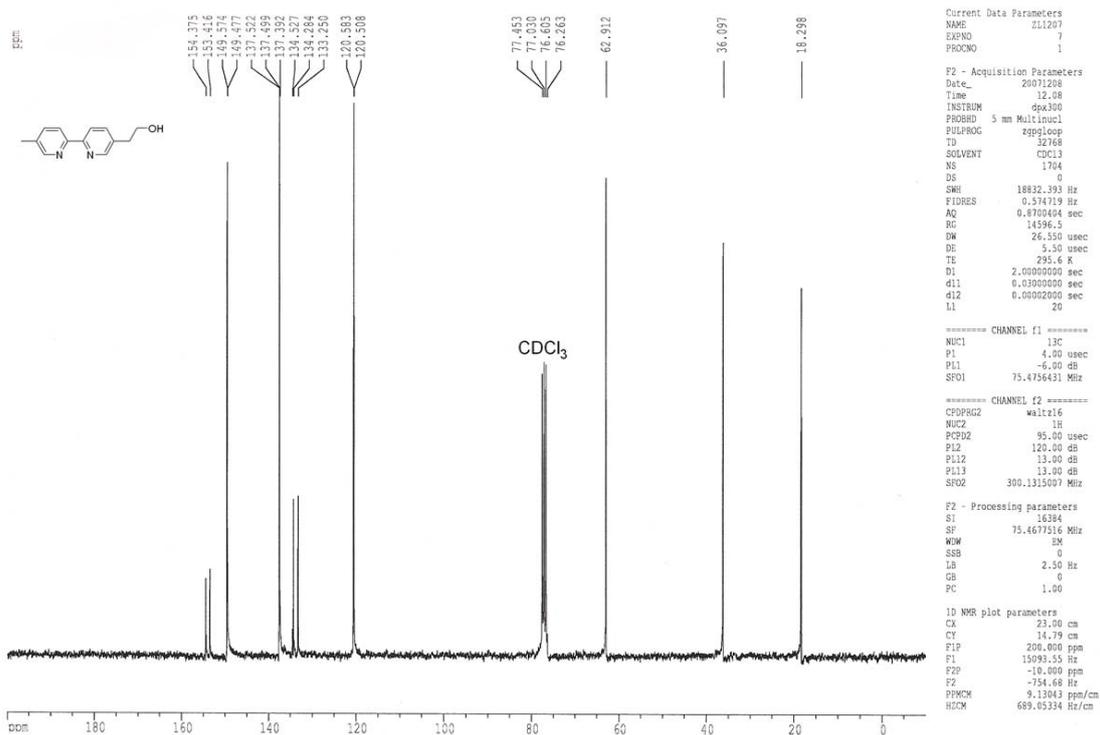
^d Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Viale G. Usberti 17/A, 43100 Parma, Italy

Table S1. Oxidation of selected alcohols to corresponding aldehydes and ketones carried out at 50 °C with the copper/**4-bpyT**/base system.

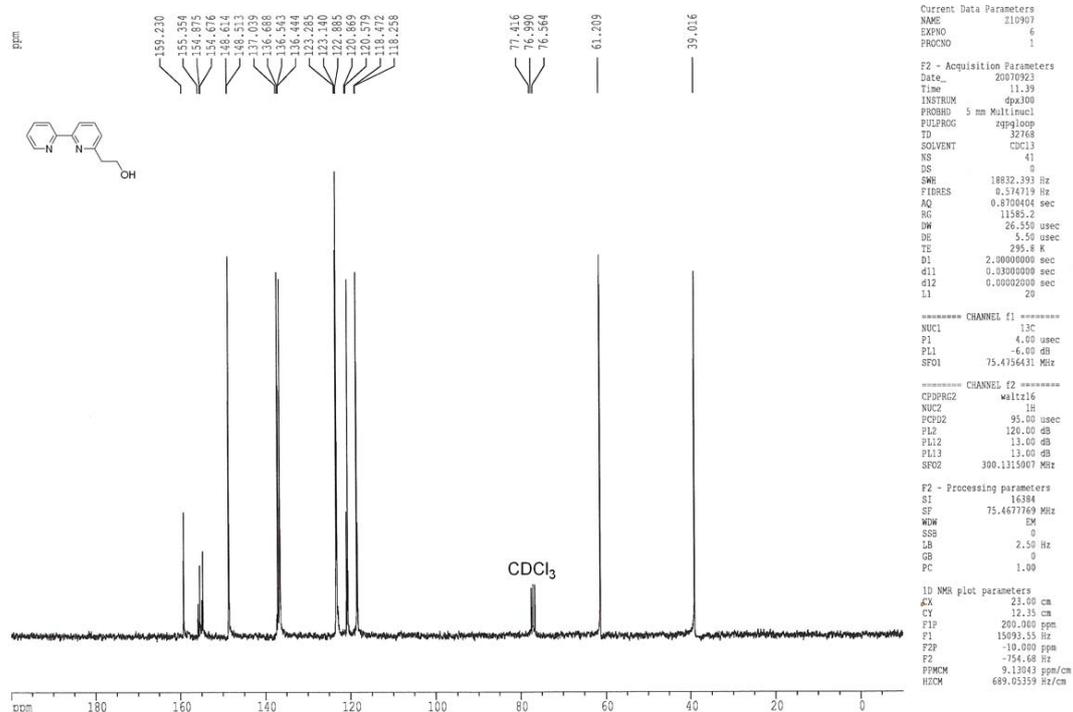
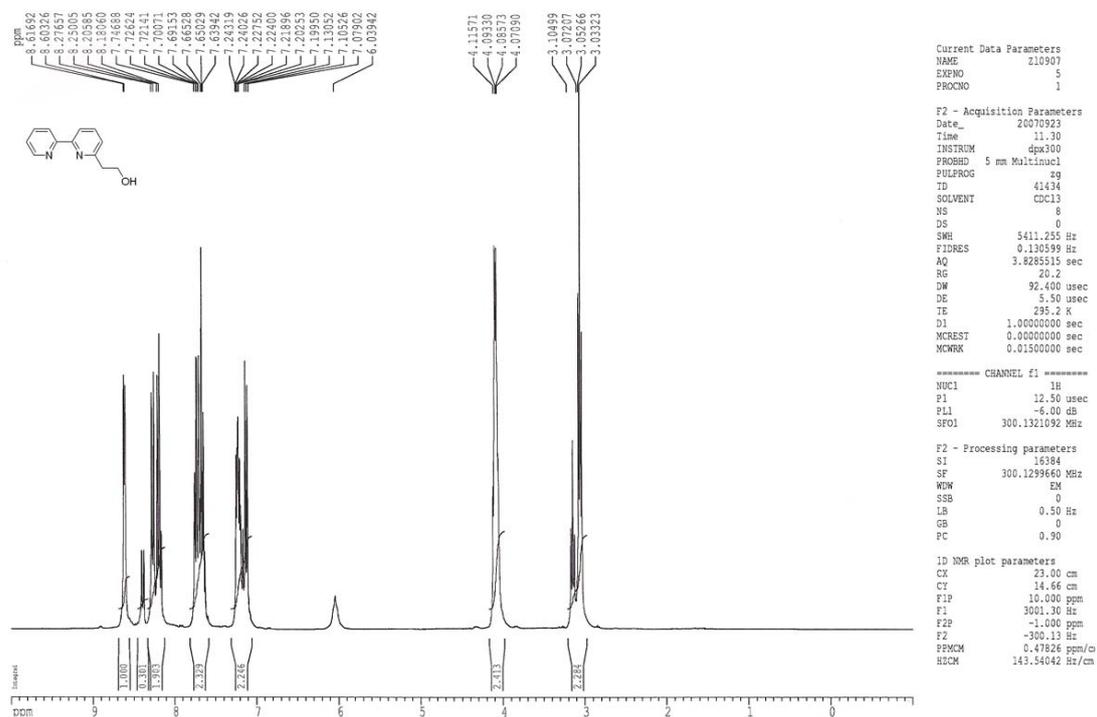
Entry	Substrate	Time [h]	Conversion [%] ^a
1	Benzyl alcohol	1.5	33
		10	91
		24	100
2	1-Phenylethanol	1.5	30
		7	88
		9	97
3	1-Octanol	3	26
		24	57

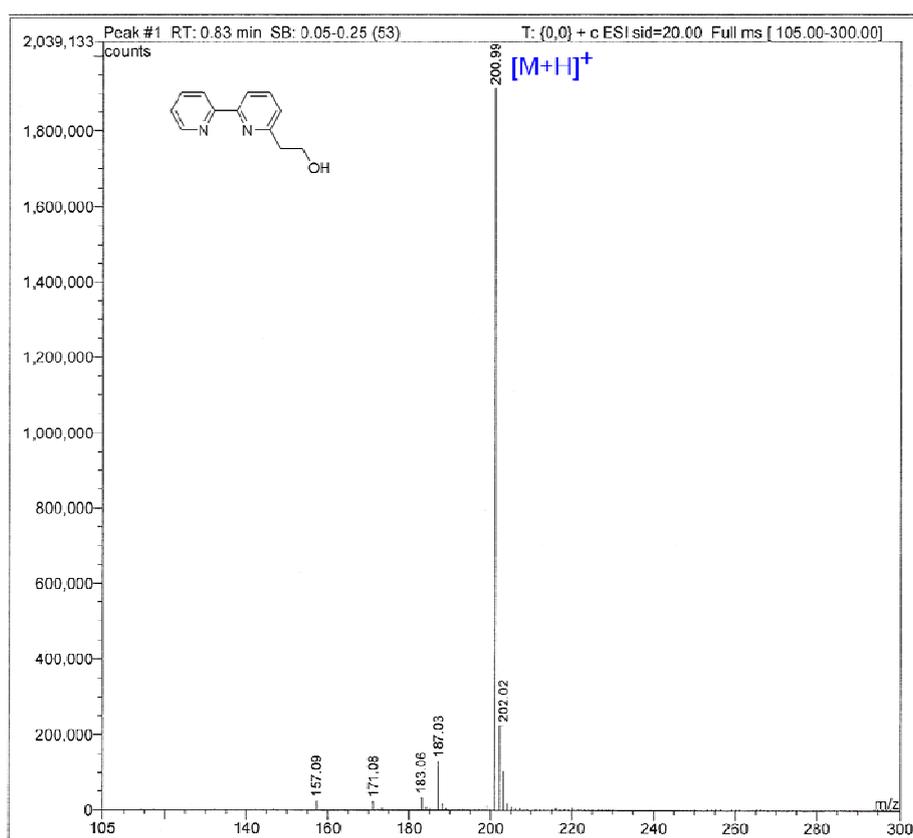
¹H, ¹³C and mass spectra for **3b**



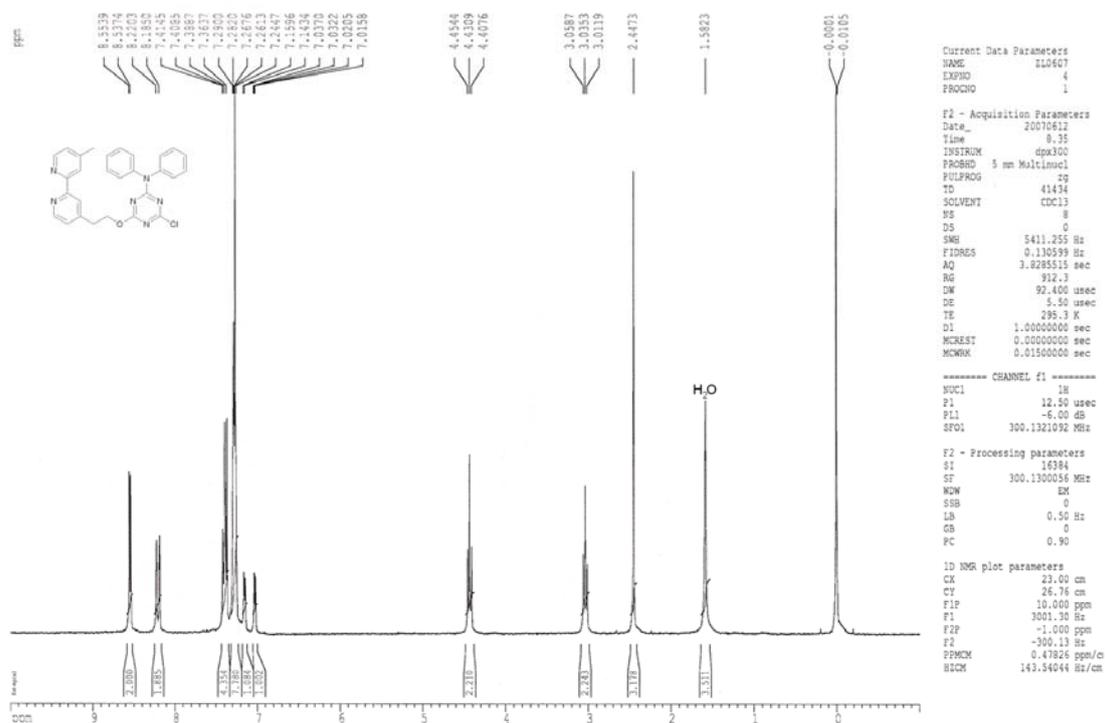


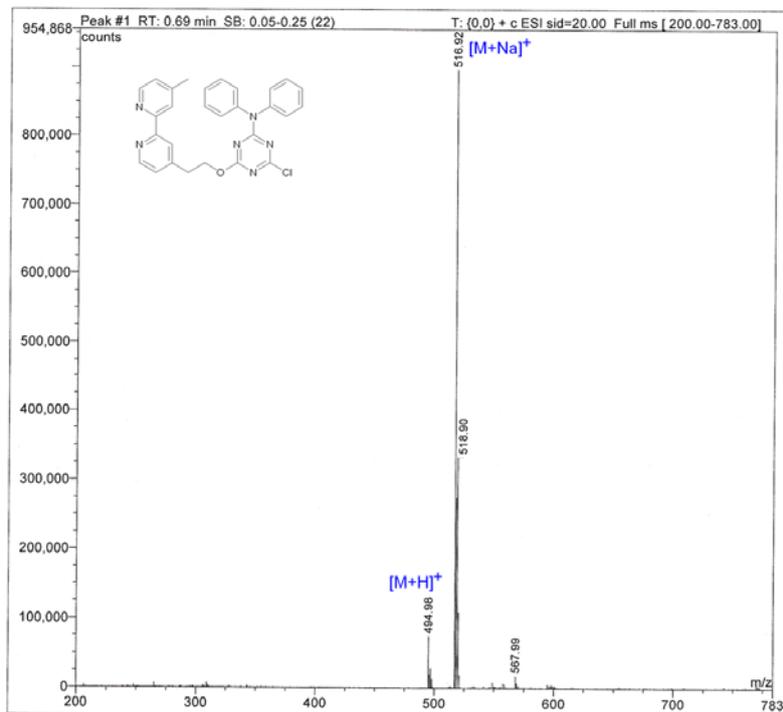
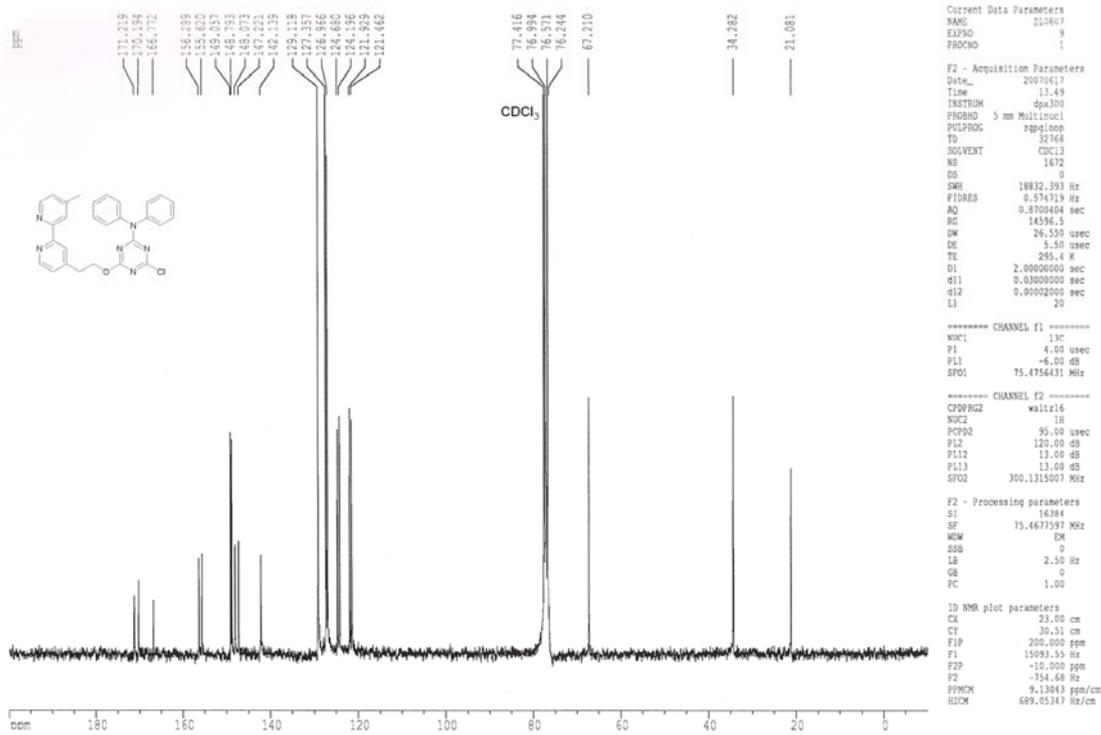
¹H, ¹³C and mass spectra for 3c



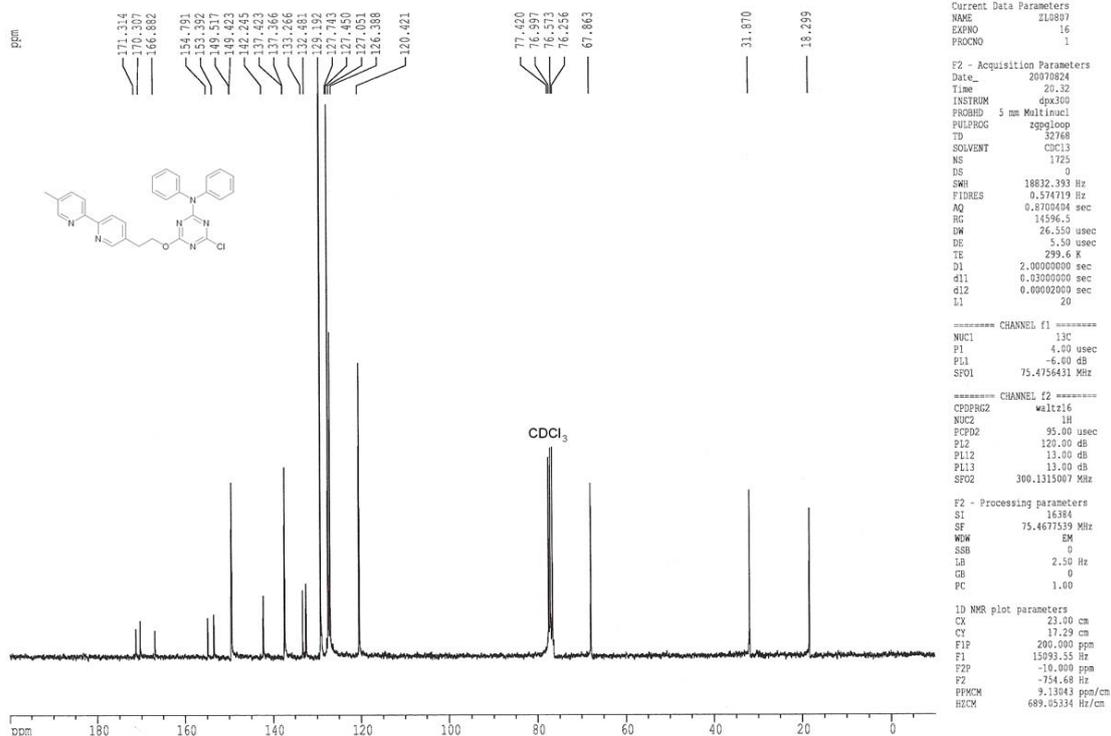
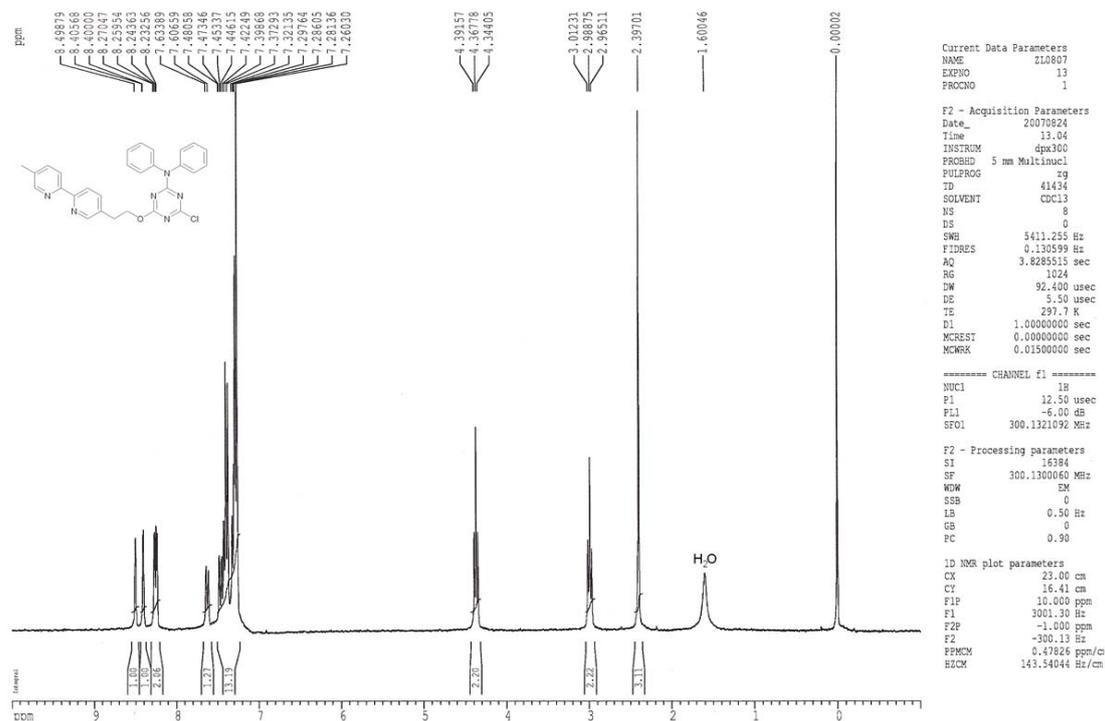


¹H, ¹³C and mass spectra for 5a





¹H, ¹³C and mass spectra for 5b



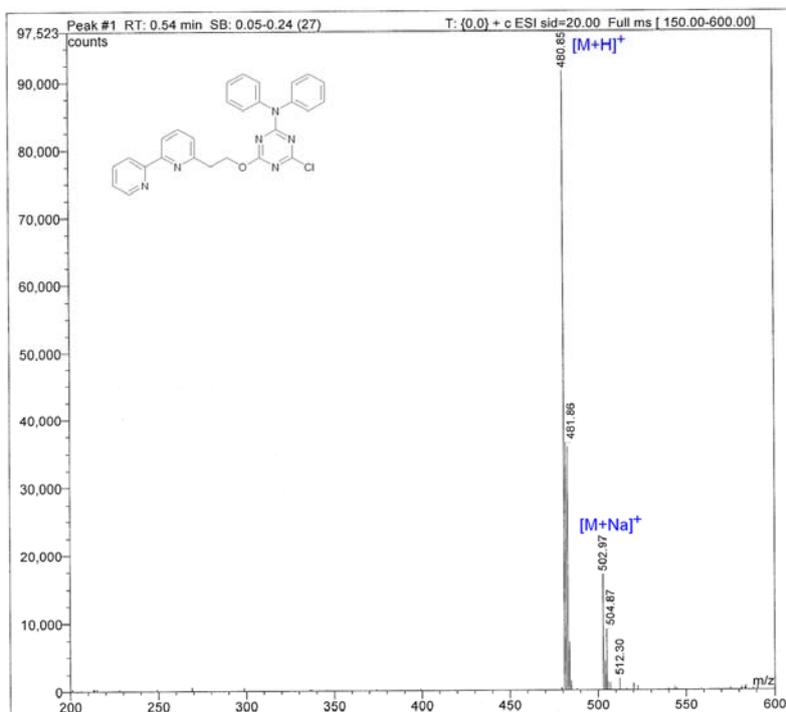
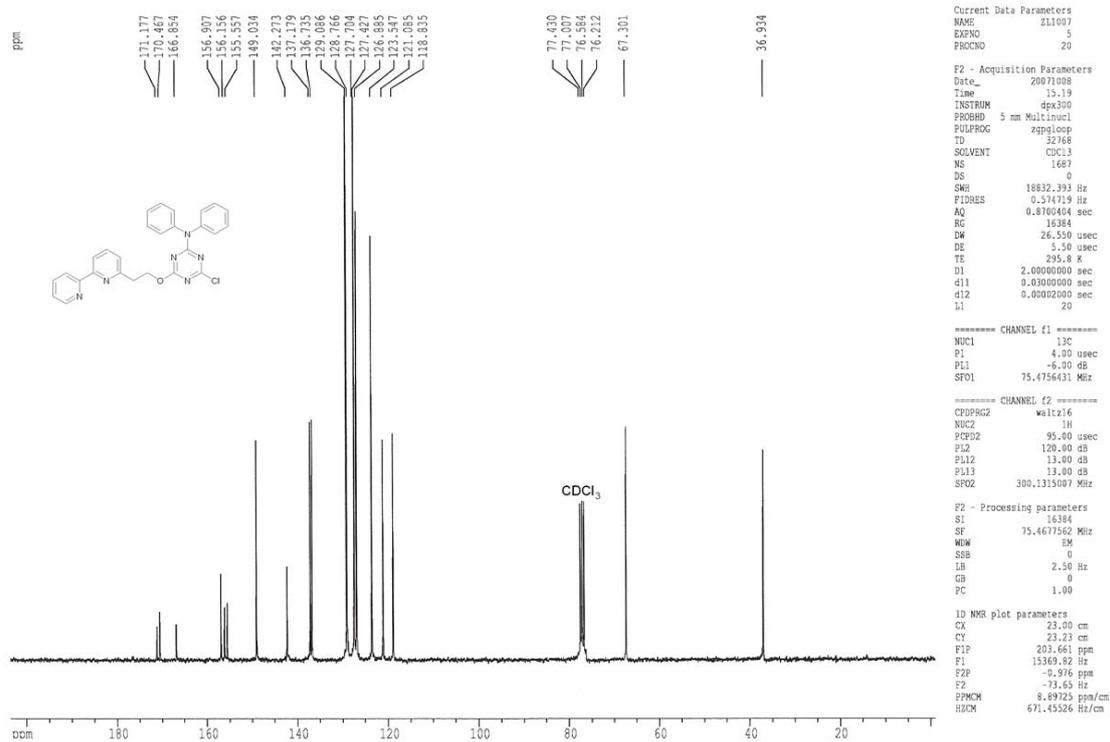


Table S2. Crystal data and structure and refinement data for **5a** and **5b**.

Compound	5a	5b
formula	C ₂₈ H ₂₃ ClN ₆ O	C ₂₈ H ₂₃ ClN ₆ O
Fw (g mol ⁻¹)	494.97	494.97
cryst size (mm ³)	0.13 × 0.10 × 0.09	0.18 × 0.15 × 0.10
cryst color	colorless	colorless
Temperature (K)	293(2)	293(2)
cryst syst, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	triclinic, <i>P</i> -1
<i>a</i> (Å)	8.335(1)	9.807(1)
<i>b</i> (Å)	9.607(1)	10.877(1)
<i>c</i> (Å)	31.311(3)	12.740(1)
α (deg)	-	75.296(2)
β (deg)	-	78.660(2)
γ (deg)	-	70.606(2)
volume (Å ³)	2507.0(4)	1230.5(2)
<i>Z</i>	4	2
calcd density (g cm ⁻³)	1.311	1.336
F(000)	1032	516
abs coeff (mm ⁻¹)	0.186	0.189
θ for data collection (deg)	1.30–29.52	1.67–29.04
rflns collected (<i>R</i> _{int})	31276 (0.0469)	15197 (0.276)
Data / params	6449 / 329	6001 / 407
goodness of fit on F ²	1.007	1.010
R1 (wR2) [<i>I</i> > 2 σ (<i>I</i>)]	0.0518 (0.1139)	0.0469 (0.1291)
R1 (wR2) (all data)	0.0984 (0.1260)	0.0743 (0.1460)
largest diff. peak and hole (<i>e</i> Å ³)	0.279 and -0.171	0.261 and -0.352

Figure S1. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **5a**.

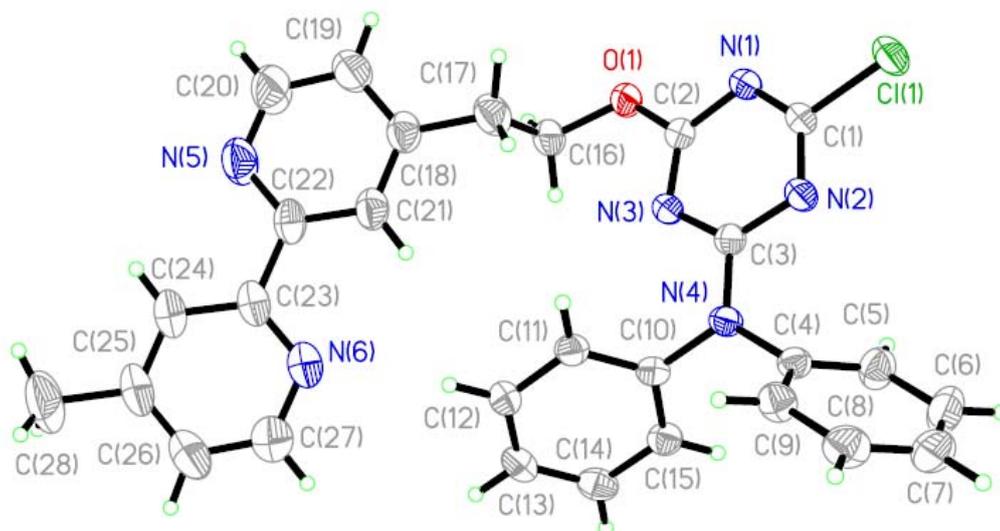
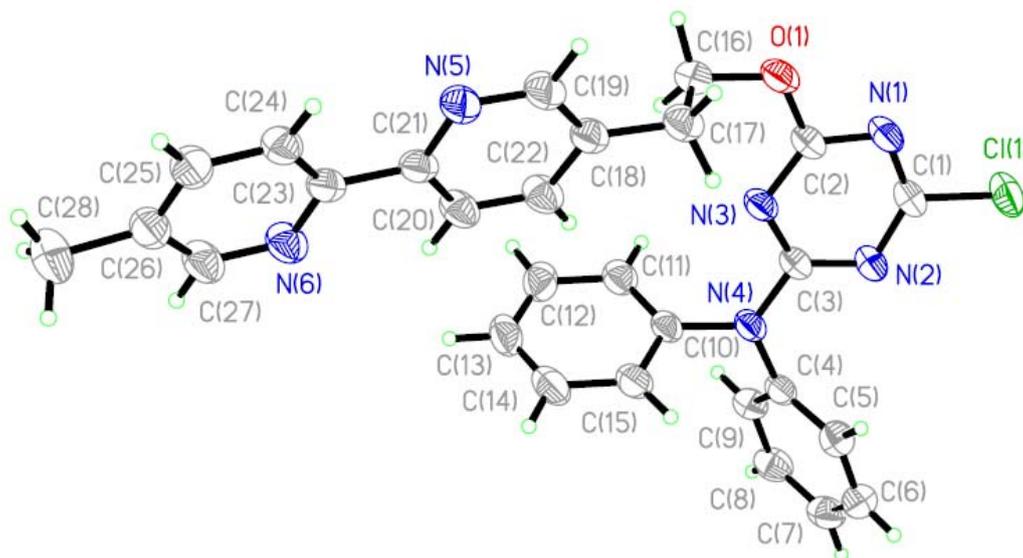
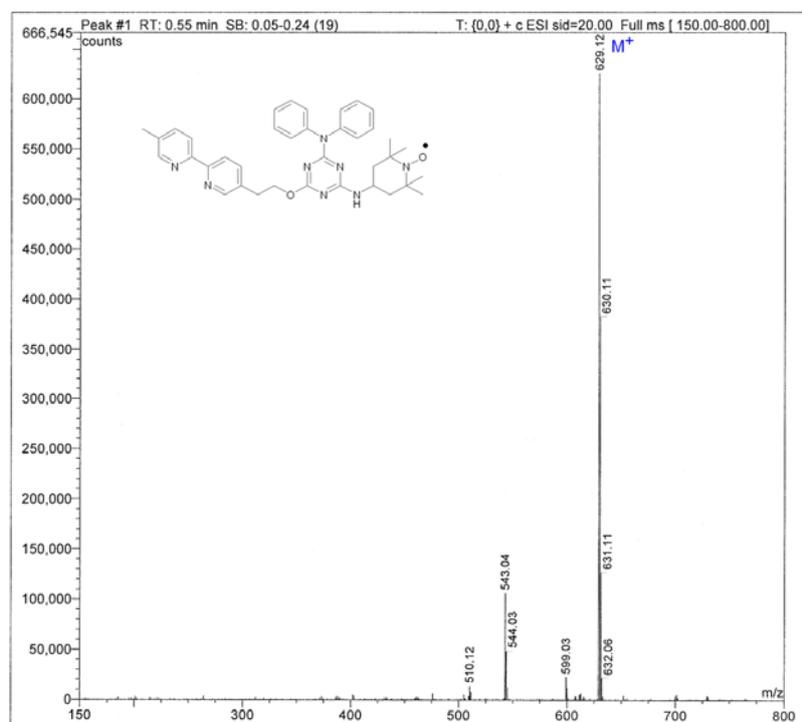
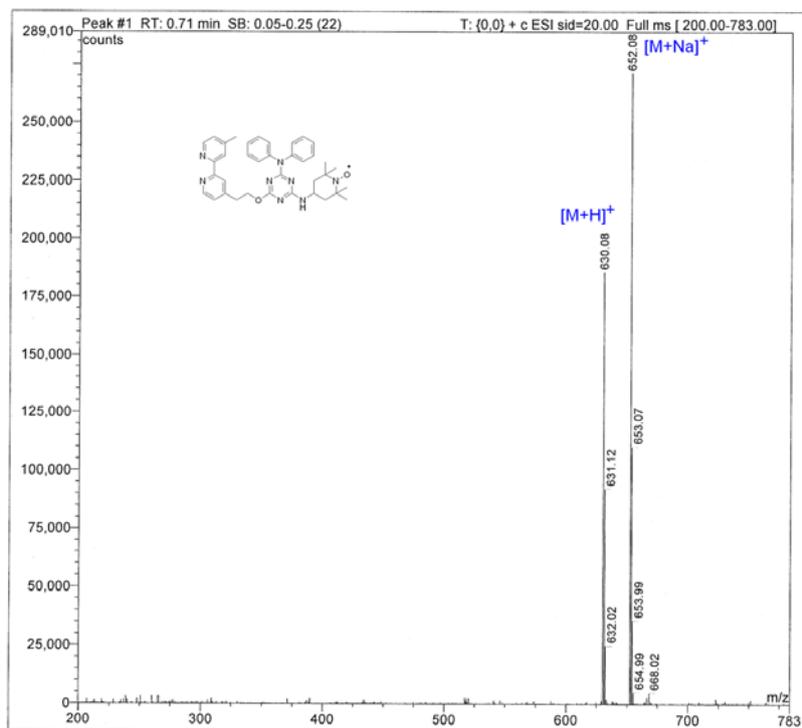


Figure S2. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **5b**.



Mass spectra for 4-bpyT, 5-bpyT and 6-bpyT



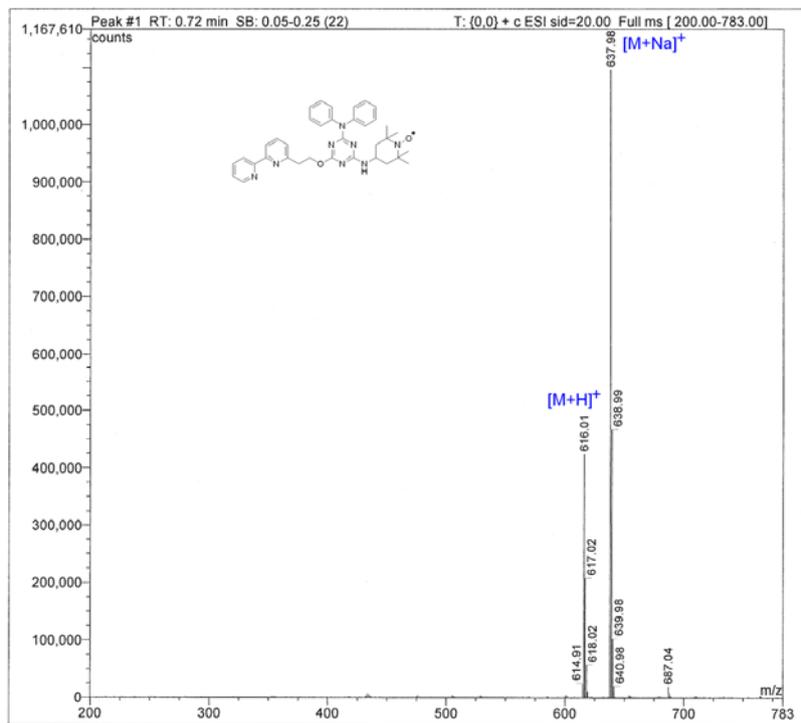


Table S3. Crystal data and structure and refinement data for **4-bpyT** and **6-bpyT**

Compound	4-bpyT	6-bpyT
formula	C ₃₇ H ₄₁ N ₈ O ₂	C ₃₆ H _{39.25} N ₈ O _{2.13}
Fw (g mol ⁻¹)	629.78	618.00
cryst size (mm ³)	0.15 × 0.13 × 0.08	0.35 × 0.30 × 0.20
cryst color	pink	orange
Temperature (K)	293(2)	150(2)
cryst syst, space group	Triclinic, <i>P</i> -1	Triclinic, <i>P</i> -1
<i>a</i> (Å)	10.880(2)	12.079(1)
<i>b</i> (Å)	11.557(2)	17.585(2)
<i>c</i> (Å)	15.819(2)	17.697(2)
<i>α</i> (deg)	97.708(2)	63.904(2)
<i>β</i> (deg)	108.723(2)	78.702(2)
<i>γ</i> (deg)	110.203(2)	89.122(2)
volume (Å ³)	1699.5(4)	3299.6(6)
<i>Z</i>	2	4
calcd density (g cm ⁻³)	1.231	1.244
F(000)	670	1313
abs coeff (mm ⁻¹)	0.079	0.096
<i>θ</i> for data collection (deg)	1.95–29.64	2.55–33.60
rflns collected (<i>R</i> _{int})	21470 (0.0452)	47124 (0.0622)
Data / params	8568 / 534	19590 / 910
goodness of fit on F ²	1.030	1.068
R1 (wR2) [<i>I</i> > 2σ(<i>I</i>)]	0.0540 (0.0972)	0.0693(0.2029)
R1 (wR2) (all data)	0.1569 (0.1201)	0.0838(0.2203)
largest diff. peak and hole (<i>e</i> Å ³)	0.150 and -0.242	0.630 and -0.445

Figure S3. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **4-bpyT**. Hydrogen atoms are omitted for clarity.

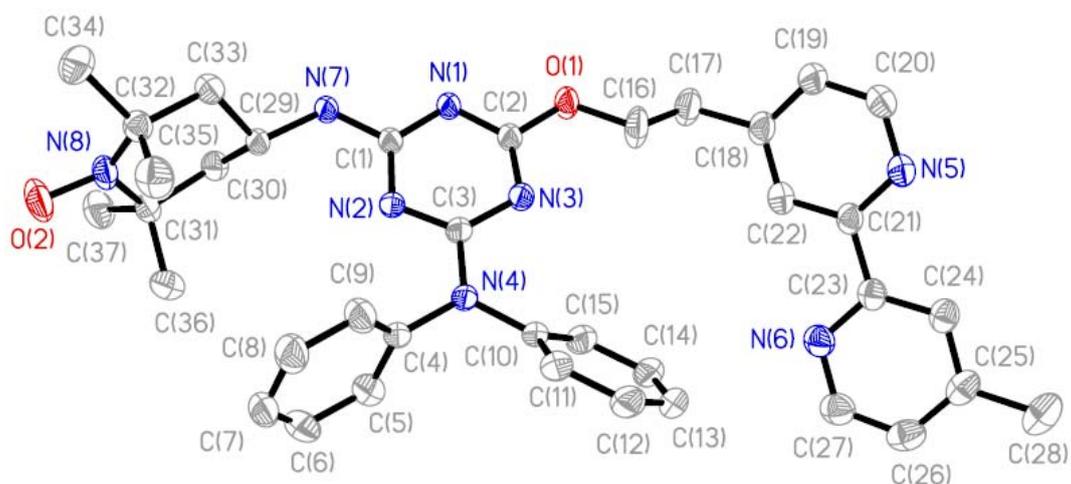


Figure S4. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **6-bpyT**. Hydrogen atoms and water molecule are omitted for clarity.

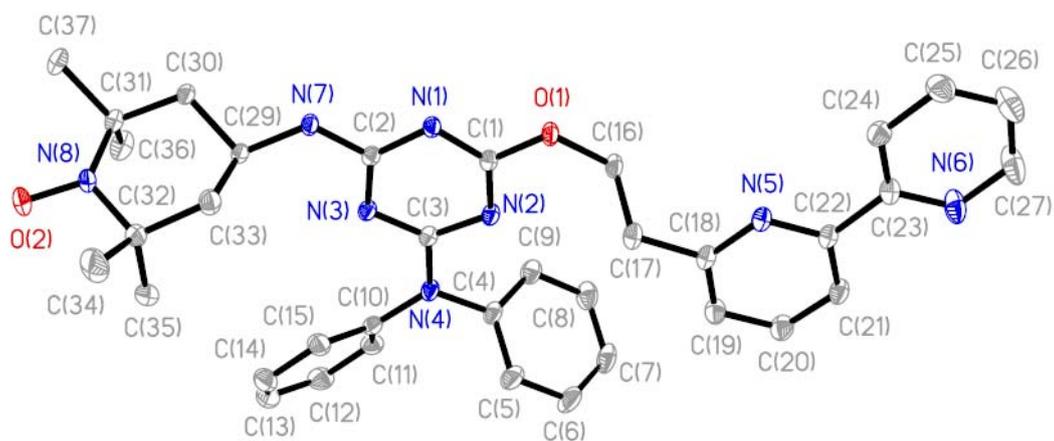


Figure S5. Mass spectrum of compound **6** dissolved in acetonitrile.

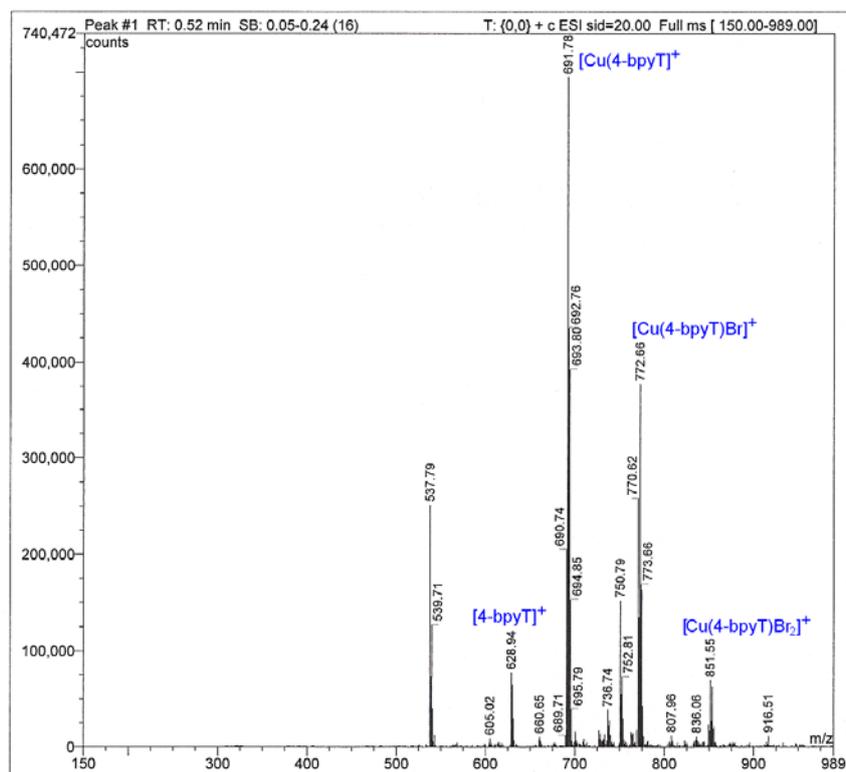


Figure S6. Mass spectrum of compound **7** dissolved in acetonitrile.

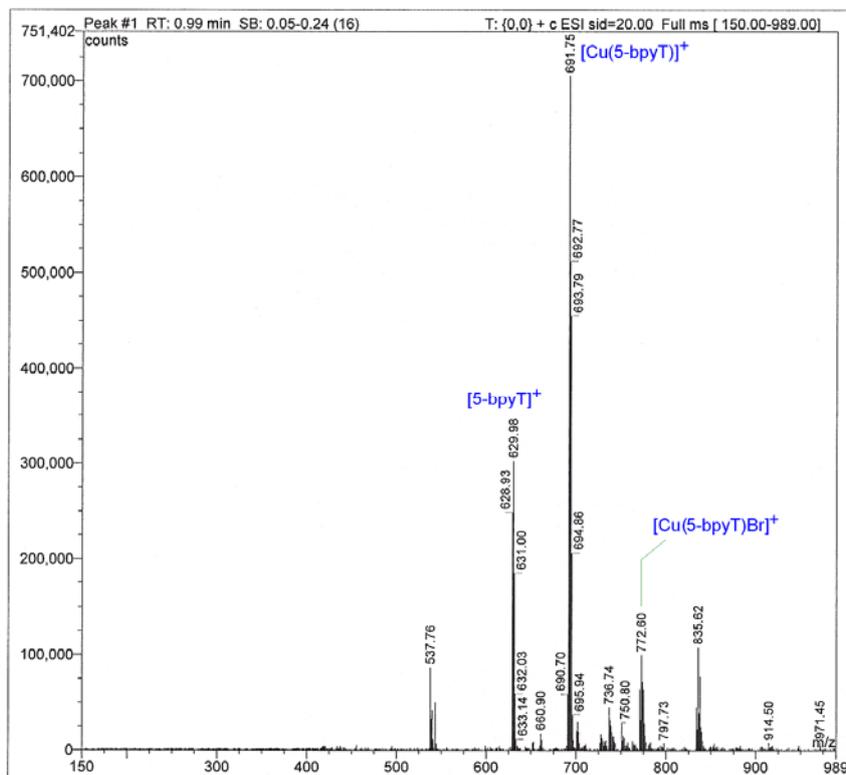
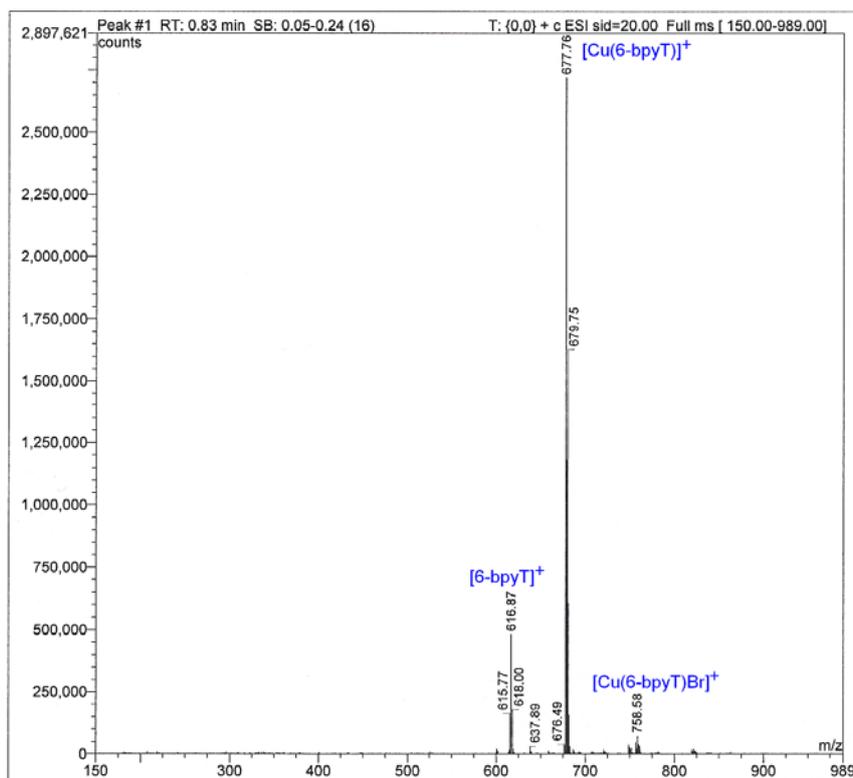


Figure S7. Mass spectrum of compound **8** dissolved in acetonitrile.



Structural determination

The molecular structure of compounds **5a**, **5b**, **4-bpyT**, **6-bpyT**, **6**, **7** and **8** were determined by single-crystal X-ray diffraction methods. Crystallographic data and refinement details for **5a**, **5b**, **4-bpyT** and **6-bpyT** are given in Tables S2 and S3.

X-ray crystallographic data for **5a**, **5b** and **4-bpyT** were collected on a Bruker AXS Smart 1000 single-crystal diffractometer (MoK α radiation) equipped with a CCD area detector. The data reductions were performed using the SAINT and SADABS programs (SAINT, Software Users Guide, Version 6.0; Bruker Analytical X-ray Systems. In Software Users Guide, Version 6.0; Bruker Analytical X-ray Systems, Madison, WI, 1999. Sheldrick, G. M., SADABS v2.03: Area-Detector Absorption Correction. University of Göttingen, Germany, 1999.) The structures were solved by Direct Methods using the SIR97 program (Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119) and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program (Sheldrick, G. M., SHELXL-97. Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997).

All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were found in the difference Fourier map with the exception of the H atoms of compound **5a** and of the methyl groups in compounds **5b** and **4-bpyT**, which were included in the refinement at idealized geometries (C–H 0.95 Å) and refined “riding” on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_o^2 + (0.0598P)^2]$, $w = 1/[\sigma^2 F_o^2 + (0.0860P)^2]$ and $w = 1/[\sigma^2 F_o^2 + (0.0409P)^2]$ (where $P = (F_o^2 + 2F_c^2)/3$) for **5a**, **5b** and **4-bpyT** respectively.

X-ray crystallographic data for **6-bpyT**, **6**, **7** and **8** were collected on station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, from synchrotron radiation at 0.7749 Å, from a silicon 111 monochromator, using either a Bruker Apex II CCD diffractometer (**6-bpyT**, **6** and **8**) or a Bruker Platinum 200 CCD diffractometer (**7**). The structures were solved with SIR97 (**6-bpyT**) (Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119) or SHELXS (**6**, **7** and **8**) (G. M. Sheldrick, (2001) *SHELXS*: Bruker AXS, Madison, Wisconsin, USA) and refined over F^2 with SHELXTL (G. M. Sheldrick, (2001) *SHELXTL*: Bruker AXS, Madison, Wisconsin, USA). In the case of **6-bpyT**, a fraction of one molecule (from the triazine ring to the first pyridine ring) was disordered over two positions, disorder that was modeled with displacement parameters restraints, the minor part of the disorder being refined isotropically. The rest of the non-hydrogens were refined anisotropically. Hydrogens were placed geometrically and refined with a riding model except the N–H hydrogens that were found in the difference map and were allowed to refine freely. For compound **6**, all atoms were refined anisotropically except for one disordered acetonitrile molecule. Displacement parameter restraints were used in modelling the ligand, while the disordered acetonitrile was modelled using geometrical and displacement parameter restraints. Hydrogens were constrained geometrically and refined using a riding model, except the N–H hydrogen that was allowed to refine freely. For compound **7**, all non-hydrogens were refined anisotropically, while hydrogens were placed geometrically and refined with a riding model. No single-crystals of compound **8** could be found; therefore, for this compound the data were collected on a non-merohedral twin. The two orientation matrices were determined using CELL_NOW

(G. M. Sheldrick, CELL_NOW, v. 2007/3 Bruker AXS, Madison, Wisconsin, USA). TWINABS (G. M. Sheldrick, TWINABS v. 2007/3 Bruker AXS, Madison, Wisconsin, USA) produced the merged files for the structure solution and refinement. The reported $R(\text{int})$ is that from merging in TWINABS 4.68% for all data 37239 observations. All non-hydrogens were refined anisotropically. Hydrogens were placed geometrically, constrained and refined using a riding model, except the N–H hydrogen that was found in the difference map and refined freely.

Visible spectroscopic studies on the Cu systems

For these investigations, 0.01 mmol of the ligand was dissolved in 3 mL of acetonitrile. 0.01 mmol of CuBr_2 was subsequently added and the visible spectrum of the resulting complex solution was recorded on a Varian Cary 50 UV/Vis spectrophotometer in the 400-1100 nm range. Next, 0.01 mmol of base was added to the previous mixture and the ensuing solution was measured.