

Supplementary Information

Table S1 Selected IR data (cm^{-1}) for the secondary amines **3a-k** recorded as KBr discs

amine	$\nu(\text{N-H}) \text{ cm}^{-1}$ stretching	$\nu(\text{N-H}) \text{ cm}^{-1}$ bending	$\nu(\text{O-H}) \text{ cm}^{-1}$	$\nu(\text{C-H}) \text{ cm}^{-1}$	$\nu(\text{C-N}) \text{ cm}^{-1}$	lactone $\nu(\text{C=O}) \text{ cm}^{-1}$	phenolic $\nu(\text{C-O}) \text{ cm}^{-1}$
3a	3346	1529	-na-	2922	1086	1663	1226
3b	3375	1479	3220	-na-	1075	1649	1281
3c*	-	-	-	-	-	-	-
3d	3331	1529	-na-	3006	1069	1686	1268
3e	3351	1528	-na-	2981	1051	1700	1268
3f*	-	-	-	-	-	-	-
3g	3367	1464	3267	3104	1065	1681	1269
3h	3401	1460	3261	3099	1008	1682	1228
3i	3382	1444	3272	3083	1006	1678	1292
3j	3364	1521	3198	-na-	1075	1663	1285
3k	3483	1518	-na-	3102	1066	1698	1286

*compounds not isolated, -na- = not assigned

Table S2 Characteristic $^1\text{H-NMR}$ signals (ppm), peak multiplicity and coupling constants J (Hz) for the secondary amines **3a-3k** recorded in $\text{d}_6\text{-DMSO}$

amine	H3 (vinyl)	H5	H6	H11 (CH ₃)	H12 (-NH-)	H13 (-CH ₂ -)	H15 (OH)	R ₁	R ₂	R ₃
3a	5.88, s	7.41, d, $J=8.8$	6.63, dd, $J=8.7, J=2.2$	2.28, s	7.05, t	4.25, d, $J=5.9$	9.59, s	6.83, d, $J=8.1$	7.07, t, $J=7.0$	6.73, t, $J=7.5$
3b	5.87, s	7.40, d, $J=8.8$	m	2.27, s	7.00, t	4.25, d, $J=5.9$	9.26, s	8.44, s(-OH)	m	m
3c*	-	-	-	-	-	-	-	-	-	-
3d	5.83, s	7.40, d, $J=8.8$	6.62, dd, $J=8.6, J=1.9$	2.28, s	7.04, t	4.27, d, $J=5.9$	8.76, s	3.79, s, (-OCH ₃)	6.84, dd, $J=7.7, J=2.4$	6.79, t, $J=7.5$
3e	5.87, s	7.40, d, $J=8.6$	m	2.28, s	7.04, t	4.28, d, $J=5.9$	8.56, s	4.05, q, (-OCH ₂) 1.34, t, (-	m	m
3f*	-	-	-	-	-	-	-	CH ₃)	-	-
3g	5.94, s	7.46, d, $J=8.6$	6.63, dd, $J=8.8, J=2.2$	2.30, s	7.17, t	4.35, d, $J=5.9$	9.85, s	-	7.41, d, $J=2.6$	-Cl
3h	5.91, s	7.44, d, $J=8.6$	6.62, dd, $J=8.6, J=2.2$	2.24, s	7.12, t	4.35, d, $J=6.2$	9.65, s	-Cl	7.60, d, $J=2.6$	-Br
3i	5.94, s	7.42, d, $J=7.1$	6.62, dd, $J=8.8, J=2.0$	2.29, s	7.07, t	4.32, d, $J=5.5$	9.51, s	-Br	7.88, s	-I
3j	5.93, s	7.44, d, $J=8.8$	6.67, dd, $J=8.8, J=2.2$	2.30, s	7.27, t	4.35, d, $J=5.7$	11.45, s	-I	8.06, dd, $J=7.3, J=3.0$	-NO ₂
3k	5.92, s	7.45, d, $J=8.8$	6.65, dd, $J=8.7, J=2.2$	2.35, s	7.28, t	4.37, d, $J=5.9$	10.69, s	7.03, d, $J=8.4$ 3.95, s, (-OCH ₃)	7.70, $J=2.6$	-NO ₂

(s = singlet, d = doublet, t = triplet, dd = double-doublet, m – multiplet)

* not isolated

Table S3 Characteristic ^{13}C -NMR signals (ppm), peak multiplicity and coupling constants J (Hz) for the secondary amines **3a-3k** recorded in d_6 -DMSO

amine	C2 (lactone)	C3 (vinyl)	C4	C5	C6	C7	C8	C9	C10	C11 (methyl)	C13 (amine)	C14	C15 (phenol)	C16	C17	C18	C19
3a	157.3	102.6	155.9	121.1	110.2	147.7	91.8	150.8	119.9	13.2	35.7	123.6	150.3	148.9	114.1	123.1	121.1
3b	155.9	102.6	na*	121.1	104.0	140.2	97.8	150.8	109.3	13.2	36.2	138.4	148.9	147.7	105.6	120.8	114.0
3c	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3d	160.7	107.5	153.8	125.9	110.3	147.4	96.5	155.5	108.8	18.0	40.7	125.2	144.0	153.7	110.6	118.7	120.2
3e	160.6	107.4	153.6	125.8	110.3	144.2	96.5	152.4	108.7	17.9	40.7	125.2	155.5	146.4	120.2	118.7	111.7
3f	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3g	160.6	107.9	153.7	126.2	123.3	155.5	96.6	149.6	109.3	18.0	41.1	130.2	151.9	110.2	127.3	121.8	126.4
3h	160.8	111.6	153.9	126.4	110.5	151.3	97.1	152.1	109.5	18.2	41.6	130.1	155.7	108.2	133.1	112.7	130.9
3i	160.6	108.0	153.7	126.1	110.3	151.9	96.9	155.5	109.3	18.0	41.6	129.5	154.1	90.3	144.1	83.8	136.5
3j	161.7	107.9	153.7	126.2	111.3	152.0	96.6	155.5	109.2	18.0	40.3	139.6	160.6	115.3	124.6	126.4	123.9
3k	160.6	107.9	153.7	126.2	111.1	151.9	96.6	151.0	109.2	18.0	40.3	125.8	147.1	155.5	105.6	139.2	116.5

* na - not assigned (assignment impossible due to high levels of noises)

Table S4 Crystal data and structure refinement for the Schiff base **1e**

Empirical formula	C ₁₉ H ₁₇ NO ₄
Formula weight	323.36
Temperature	85 (2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 11.8125(13) Å α = 90° b = 11.1729(13) Å β = 103.765(6) ° c = 11.8630(13) Å γ = 90°
Volume	1520.7(3) Å ³
Z	4
Density (calculated)	1.412 Mg/m ³
Absorption coefficient	0.100 mm ⁻¹
Crystal size	0.48 x 0.26 x 0.24 mm ³
Index ranges	-14 ≤ h ≤ 14 -14 ≤ k ≤ 13 -14 ≤ l ≤ 14
Theta range for data collection	2.19 to 26.47°
Reflections collected	29052
Independent reflections	3139 [R(int) = 0.0272]
Completeness to theta = 26.42°	99.8 %
Max. and min. transmission	0.9765 and 0.9537
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3139 / 0 / 220
Goodness-of-fit on F ²	1.033
Final R indices [I > 2σ(I)]	R1 = 0.0327, wR2 = 0.0899
R indices (all data)	R1 = 0.0340, wR2 = 0.0915
Largest diff. peak and hole	0.317 and -0.230 e.Å ⁻³

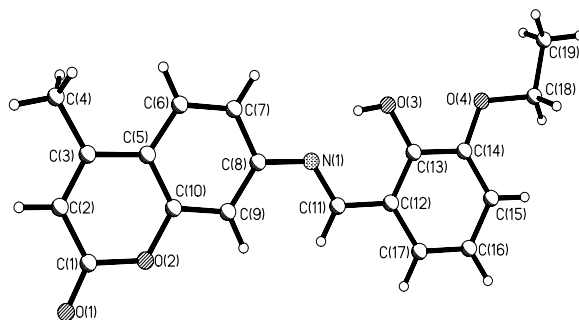


Fig. S1. Structure showing X-ray crystallography atom labelling of Schiff base **1e**

The structure of **1e** was very similar to that previously reported for **1a**. [1]. A single unit cell of each structure contains four molecules. Whilst the Schiff base molecules themselves are not planar the coumarin moieties and the phenolic rings of diagonally located molecules are co-planar. There is also a centre of symmetry in the middle of the cell. Both crystal structures exhibit 4-fold rotational symmetry around all three axes. The location of the imine bond between the coumarin and phenolic ring systems allows for *cis* or *trans* conformations and both structures reveal that the respective ring systems are *trans* to each other. In addition both crystal structures revealed the presence of an intermolecular hydrogen bond between the imine nitrogen and the phenolic hydrogen of the salicylaldehyde-derived moiety. The crystal structure of **1a** has been previously reported by Aazam et al. and our results concurred with their structure

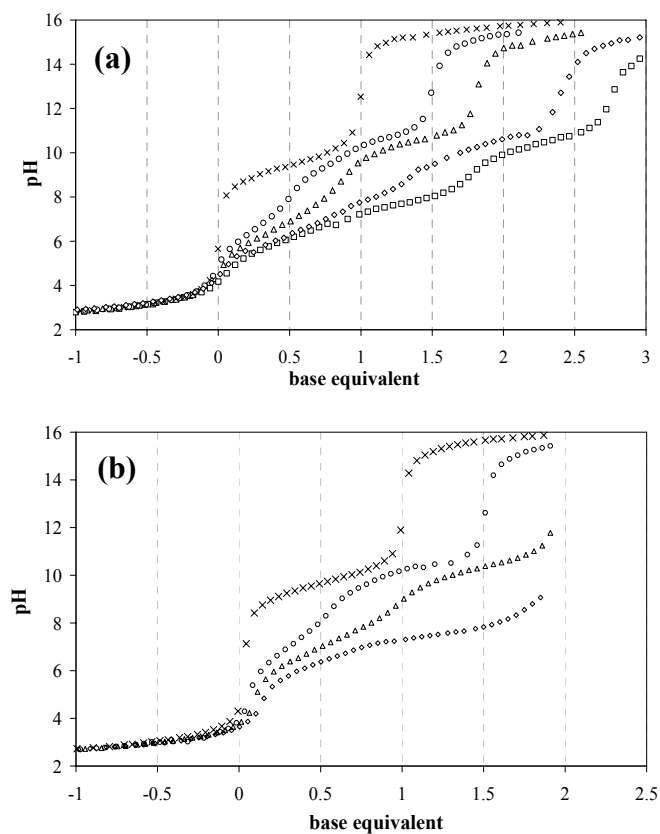


Fig. S2. The pH-potentiometric titration curves in 80 %(w/w) DMSO/water at various metal to ligand ratios for (a) the Cu(II) – **1e** system (x: **1e**; O: 1:3.4; Δ: 1:2; ◇: 1: 1.4; □: 1:1.1) and (b) the Cu(II) - salicylaldehyde system (x: ligand; O: 1:4; Δ: 1:2.2; ◇: 1: 1). The ligand concentration was 1.0 mM; I = 0.1 M (KCl); $t=25.0$ °C; base equivalent = $[V_{\text{KOH}} \times c_{\text{KOH}} - n_{\text{added}}(\text{HCl})]/n(\text{ligand})$; negative base equivalent values mean acid excess.

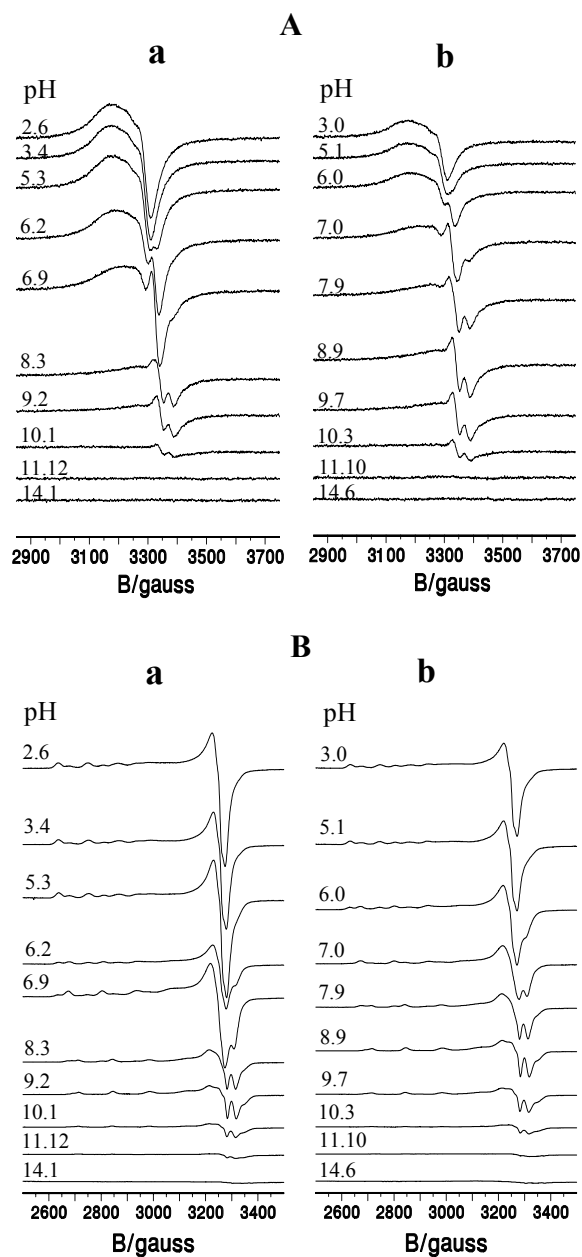


Fig. S3. ESR spectra for the Cu(II) – 1a equilibrium system A) in liquid solution at 298 K and B) in frozen solution at 77 K; a) $T_{Cu}=1\text{mM}$, $T_L=1\text{mM}$; b) $T_{Cu}=0.5\text{mM}$, $T_L=1\text{mM}$.

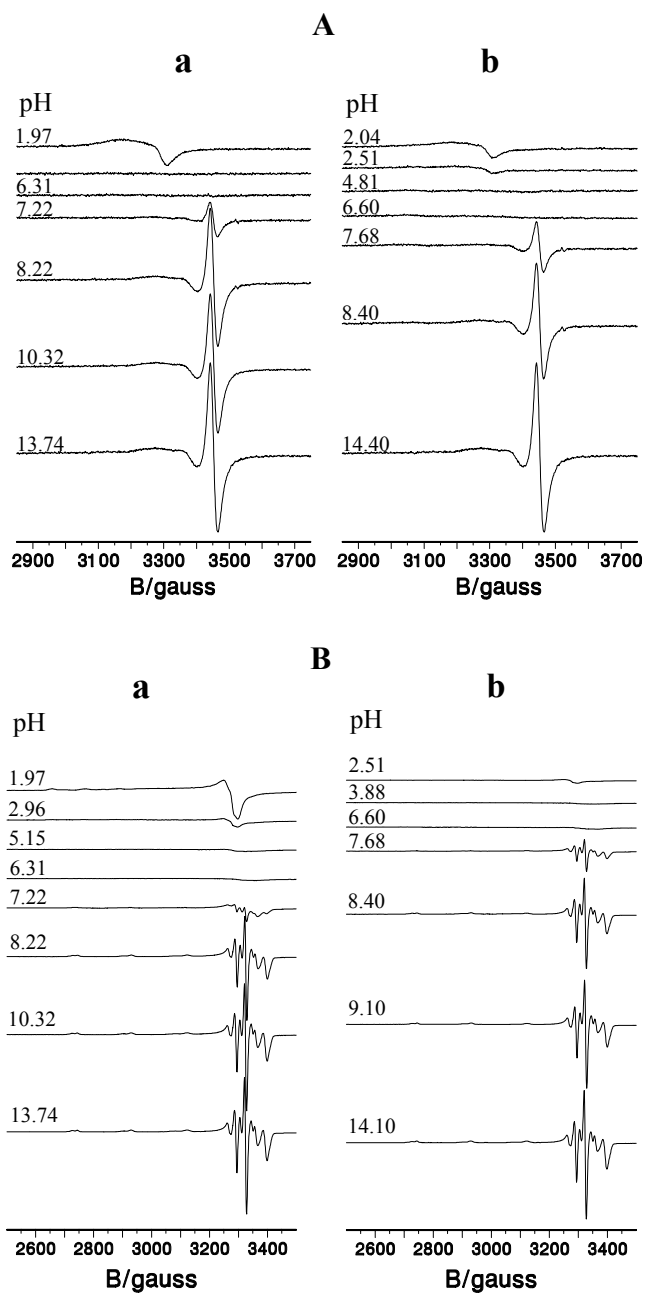


Fig. S4. ESR spectra for the Cu(II) – 1b equilibrium system A) in liquid solution at 298 K and B) in frozen solution at 77 K; a) $T_{Cu}=1\text{ mM}$, $T_L=1\text{ mM}$; b) $T_{Cu}=0.5\text{ mM}$, $T_L=1\text{ mM}$.

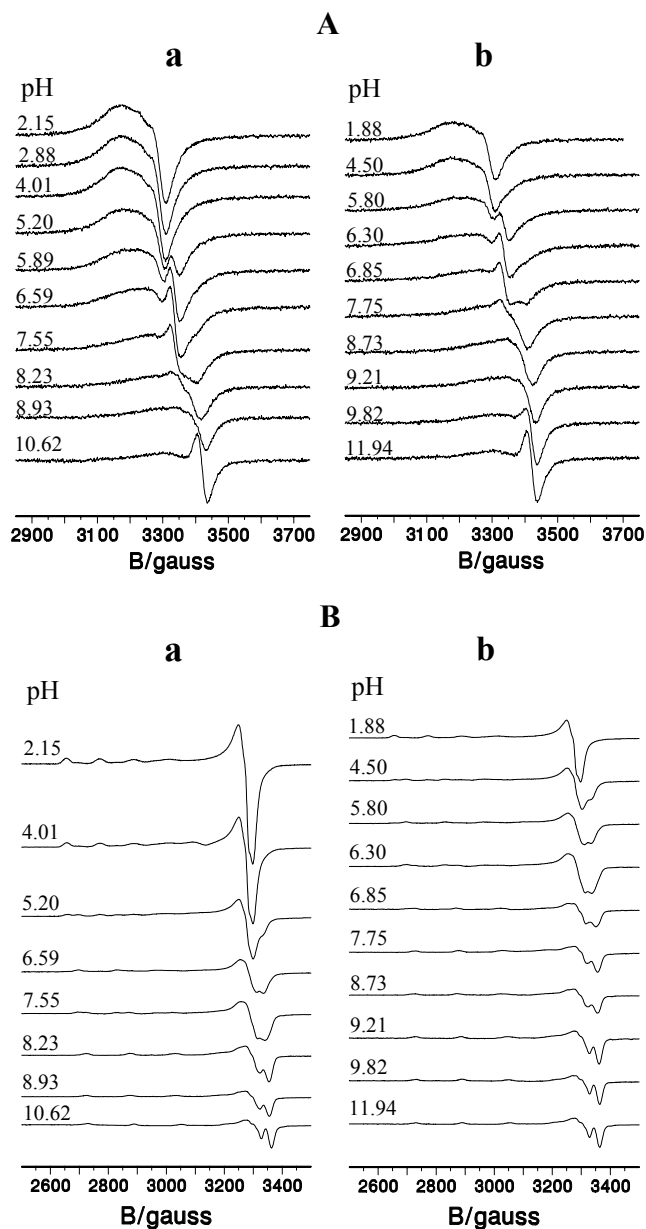


Fig. S5. ESR spectra for the Cu(II) – 1c equilibrium system in liquid solution A) at 298 K and B) in frozen solution at 77 K; a) $T_{\text{Cu}}=1\text{mM}$, $T_{\text{L}}=1\text{mM}$; b) $T_{\text{Cu}}=0.5\text{mM}$, $T_{\text{L}}=1\text{mM}$.

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1. E.S Aazam, A. Fawazy, P.B. Hitchcock, *Acta Cryst.*, 2006, **E62**, o4285-o4287