Electronic Supplementary Information

The C-H bond activation in the 1-ethyl-3-methylimidazolium acetate – copper(II) acetate – water – air (dioxygen) systems

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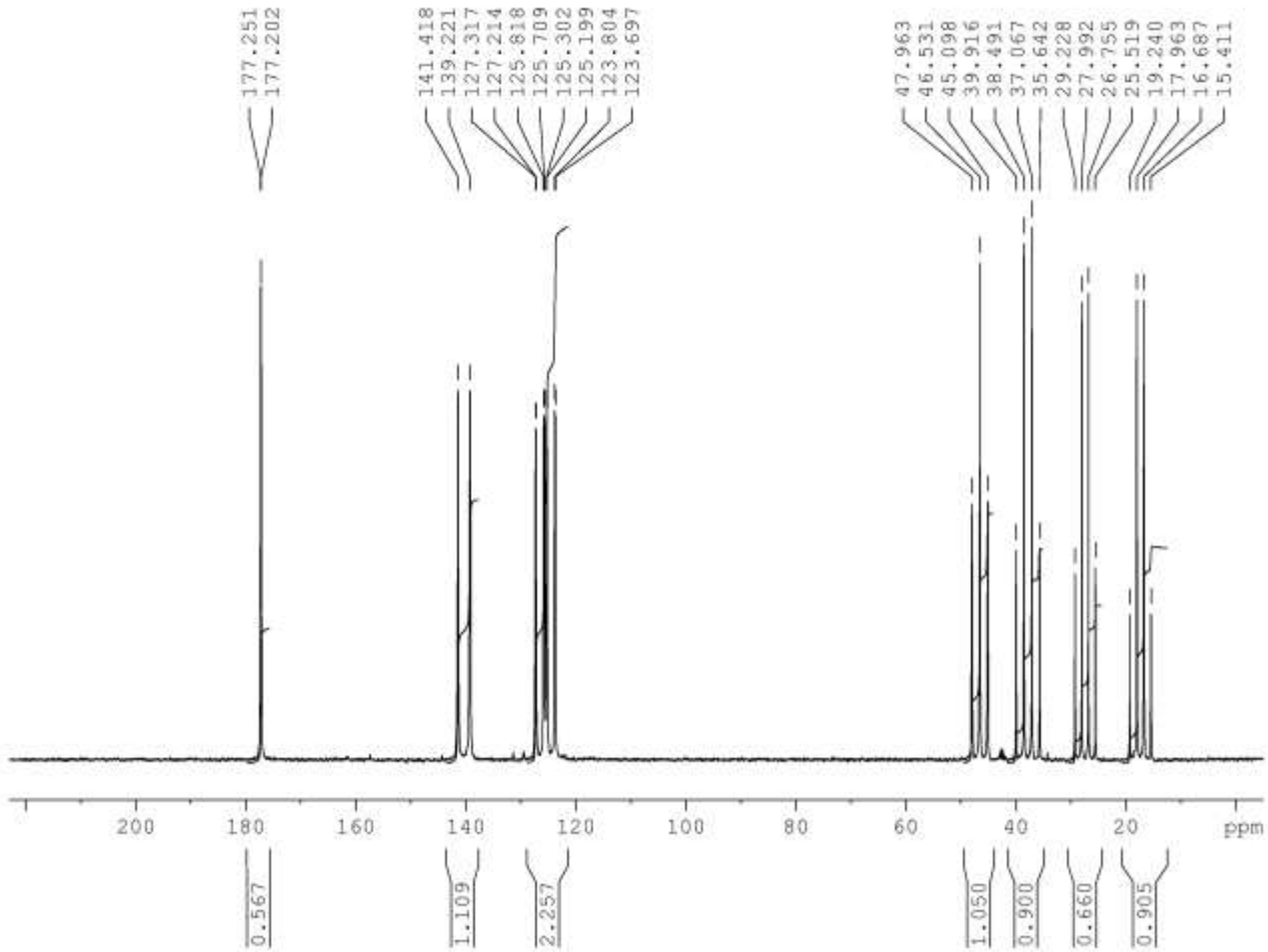

Figure 1S*a* The ^{13}C NMR spectrum of pure IL ([C_2C_1im][AcO]) at 80 °C.

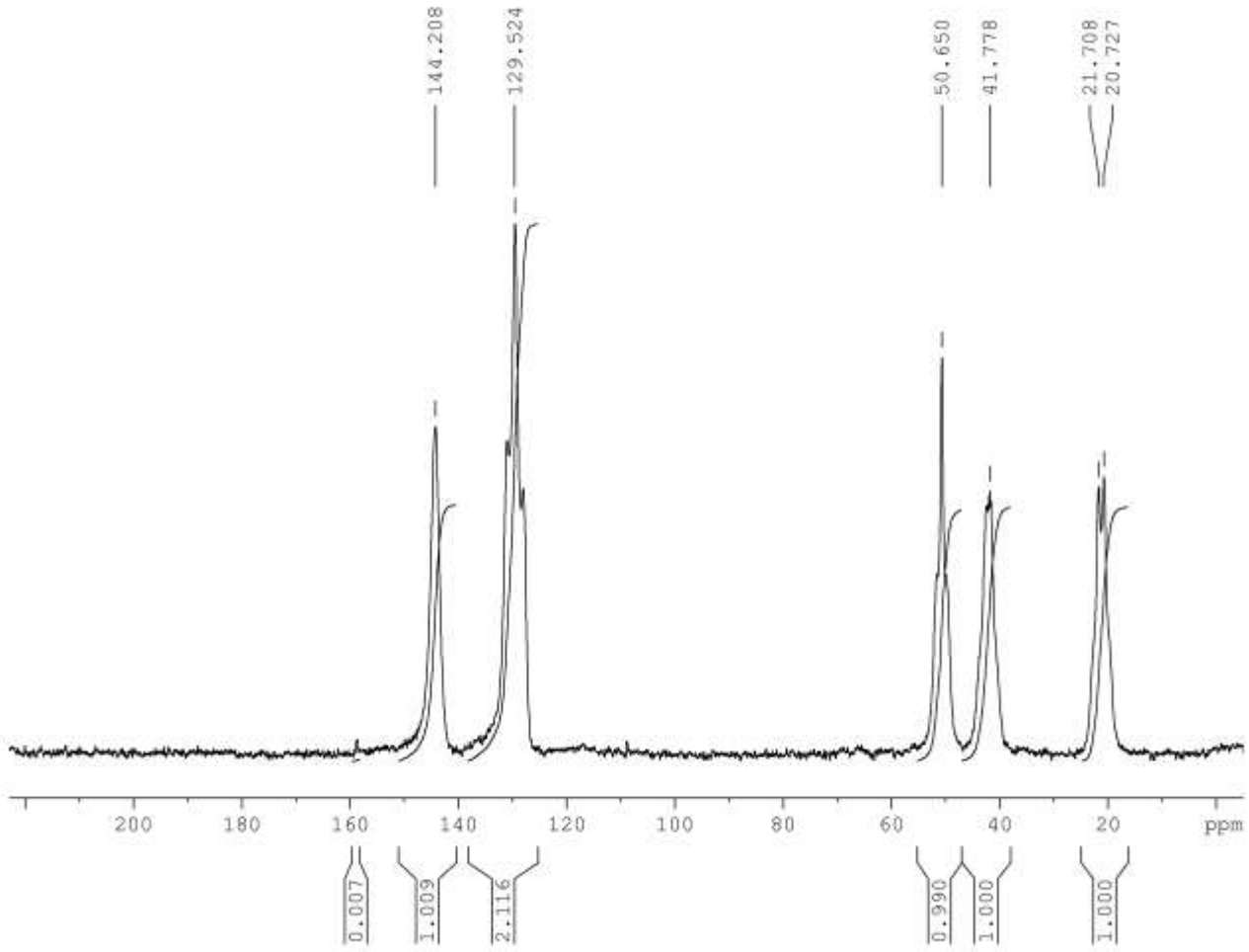

Figure 1S*b* The ^{13}C NMR spectrum of the **A** system after 1 hour heating at 80 °C.

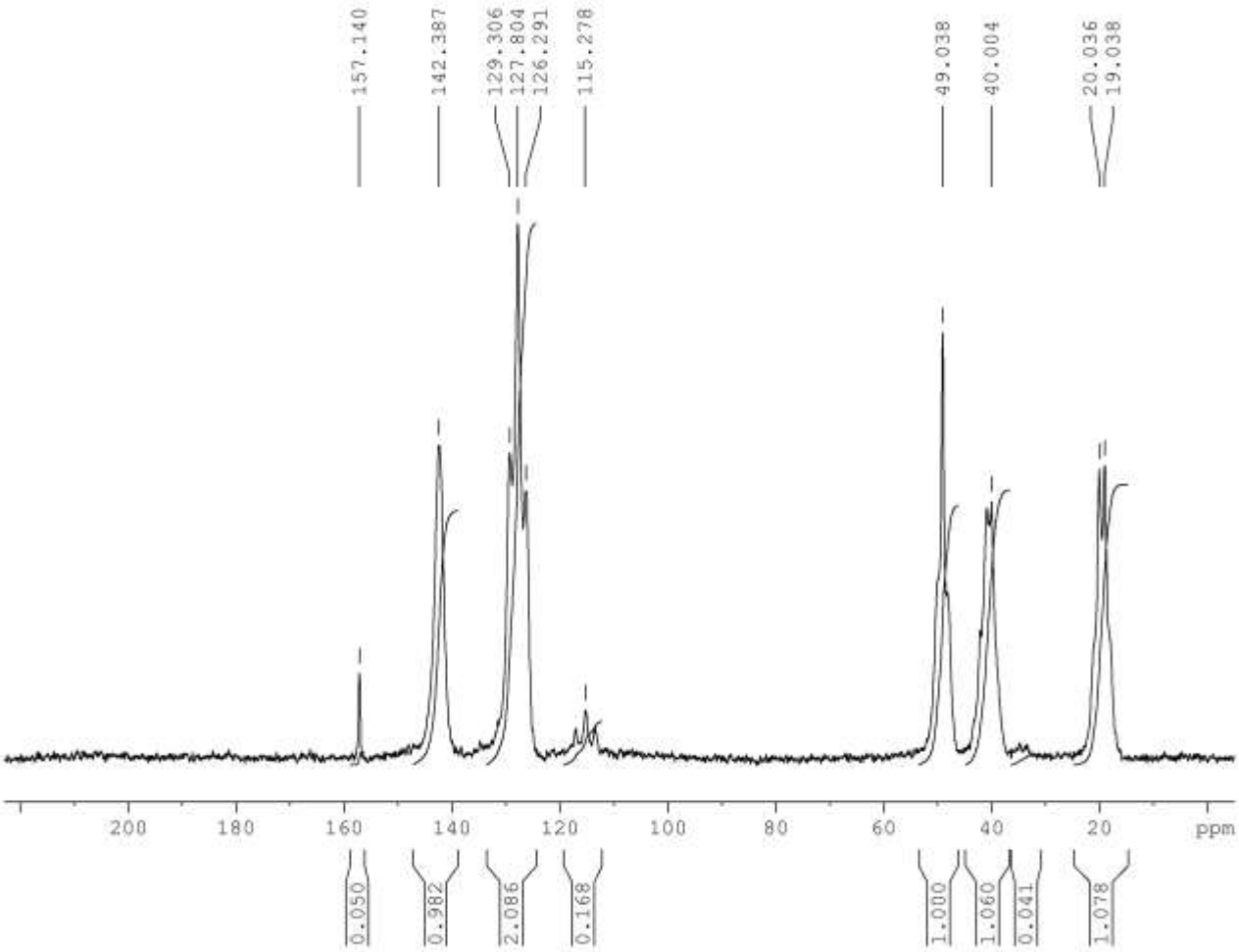

Figure 1S*c* The ^{13}C NMR spectrum of the **D** system after 8 hour heating at 80 °C.

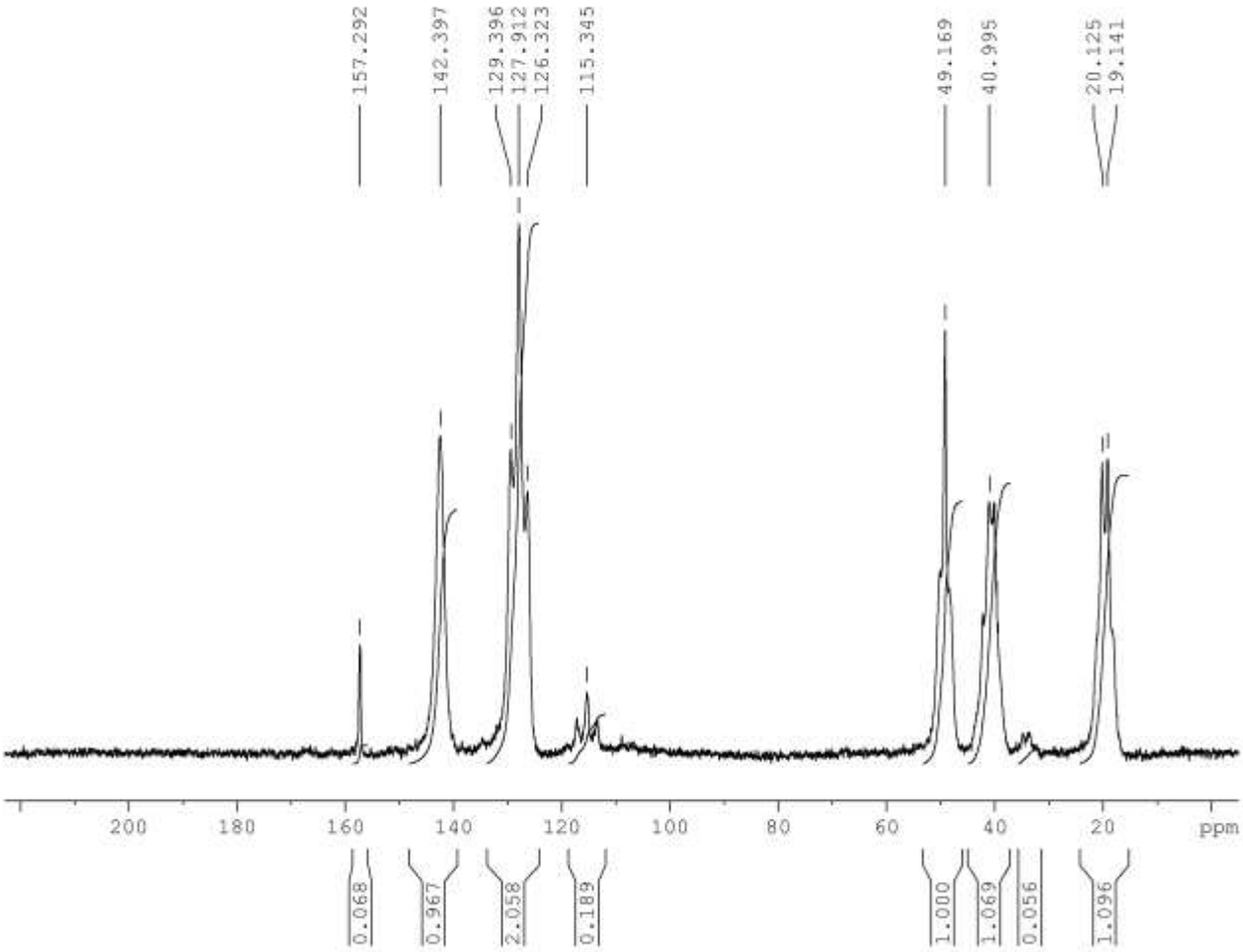

Figure 1S*d* The ^{13}C NMR spectrum of the **D** system after 14 hour heating at 80 °C.

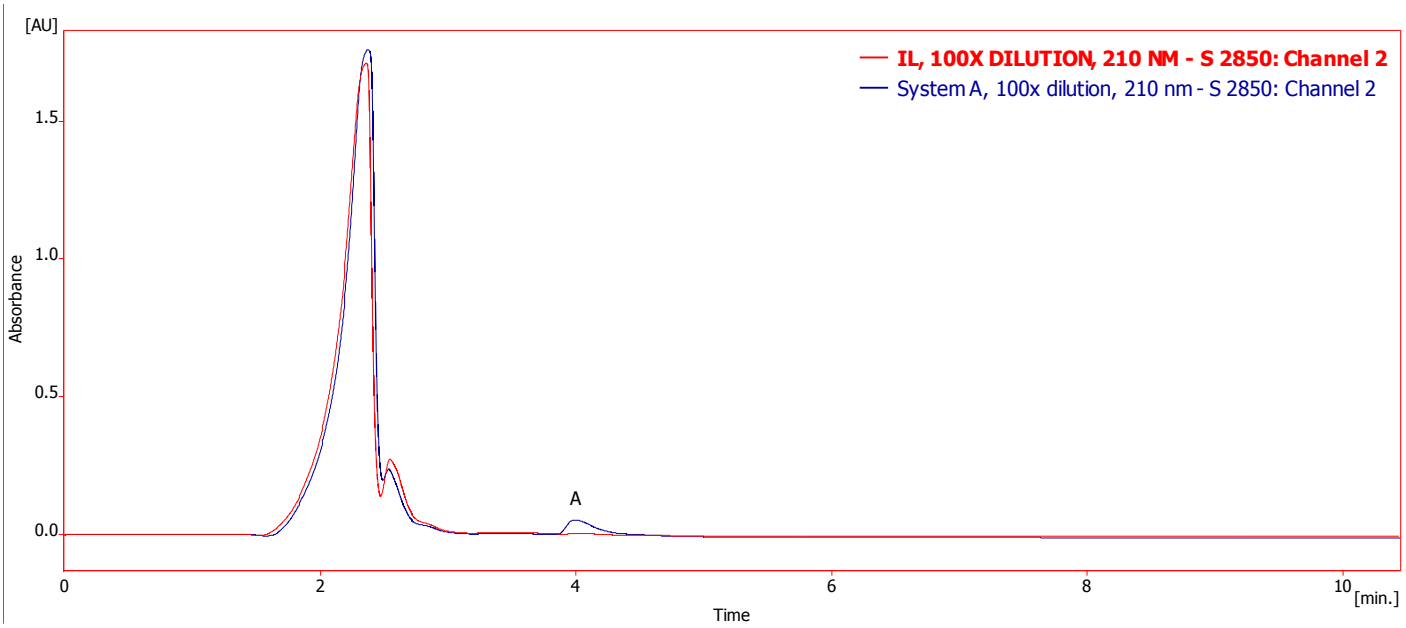

Figure 2S*a* Chromatograms of the IL (red) and system **A** (blue). Mobile phase: 30% acetonitrile/70% double distilled water. Column: Waters Spherisorb ODS-2 column (4.6×250 mm, 5 µm particle size) with pre-column (4.6×10 mm). Separation conditions: 35 °C and 1.0 ml/min flow rate. Detection at 210 nm. Injection volume: 5 µl (after 100-fold dilution of the samples with mobile phase). The A signal corresponds to C_1C_2imO.

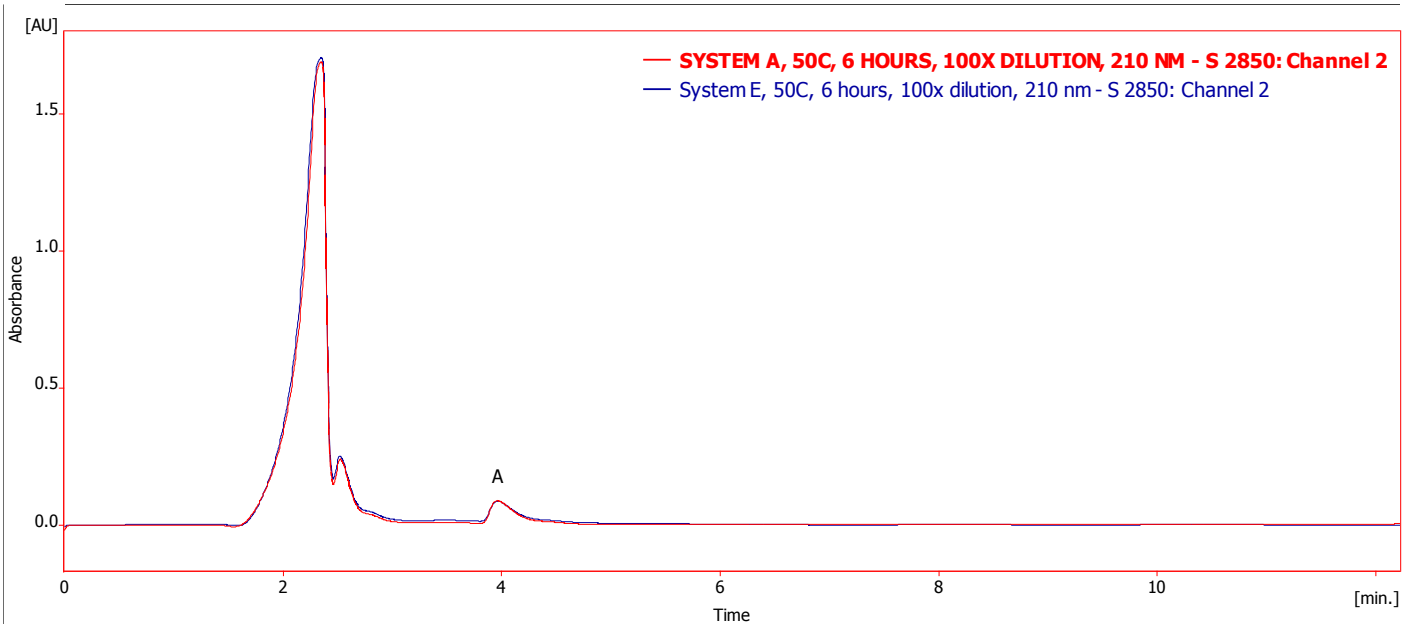

Figure 2S*b* Chromatograms of the **A** (red) and **E** (blue) systems after 6 hour heating at 50 °C. The A signal corresponds to C_1C_2imO. The analysis conditions are the same as in the legend to Fig. 2Sa.

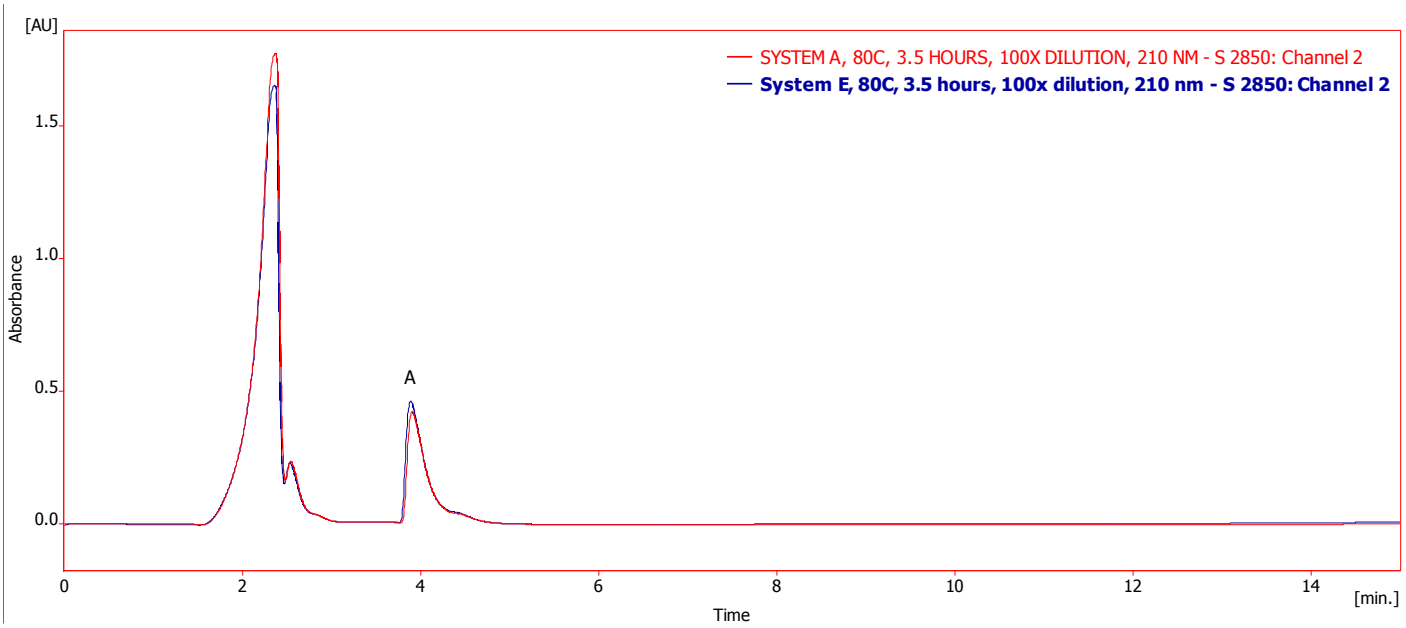

Figure 2S*c* Chromatograms of the **A** (red) and **E** (blue) systems after 3.5 hour heating at 75 °C. The A signal corresponds to C_1C_2imO. The analysis conditions are the same as in the legend to Fig. 2Sa.

Table 1S Selected interatomic distances with standard deviations in parentheses for the **1** crystal

Bond	*d*, Å	Bond	*d*, Å
Cu1-O7	1.931(6)	C18-H18A	0.9900
Cu1-O1	1.961(6)	C18-H18B	0.9900
Cu1-O3	1.964(6)	C20-H20A	0.9800
Cu1-O5	1.976(6)	C20-H20B	0.9800
Cu1-O6	2.783(6)	C20-H20C	0.9800
Cu1-O4	2.727(6)	C12-C13	1.511(12)
O5-C5	1.258(10)	C12-H12A	0.9900
O7-C7	1.278(11)	C12-H12B	0.9900
O1-C1	1.276(11)	C13-H13A	0.9800
O3-C3	1.304(10)	C13-H13B	0.9800
O4-C3	1.238(10)	C13-H13C	0.9800
N1-C9	1.328(10)	C19-H19A	0.9800
N1-C10	1.371(10)	C19-H19B	0.9800
N1-C14	1.464(10)	C19-H19C	0.9800
N3-C15	1.346(10)	C3-C4	1.501(11)
N3-C16	1.366(10)	C4-H4A	0.9800
N3-C20	1.455(11)	C4-H4B	0.9800
N2-C9	1.358(10)	C4-H4C	0.9800
N2-C11	1.371(10)	C1-O2	1.228(10)
N2-C12	1.486(10)	C1-C2	1.523(12)
N4-C15	1.329(11)	C2-H2A	0.9800
N4-C17	1.357(10)	C2-H2B	0.9800
N4-C18	1.484(11)	C2-H2C	0.9800
C9-C15	1.441(11)	O6-C5	1.266(10)
C17-C16	1.324(12)	C5-C6	1.484(13)
C17-H17	0.9500	C6-H6A	0.9800
C16-H16	0.9500	C6-H6B	0.9800
C10-C11	1.353(11)	C6-H6C	0.9800
C10-H10	0.9500	C8-C7	1.508(13)
C14-H14A	0.9800	C8-H8A	0.9800
C14-H14B	0.9800	C8-H8B	0.9800
C14-H14C	0.9800	C8-H8C	0.9800
C11-H11	0.9500	O8-C7	1.251(11)
C18-C19	1.505(14)		

Table 2S Selected angles with standard deviations in parentheses for the **1** crystal

Angle	ω,°
O7-Cu1-O1	89.2(3)
O7-Cu1-O3	91.3(3)
O1-Cu1-O3	179.3(3)
O7-Cu1-O5	172.8(3)
O1-Cu1-O5	87.7(2)
O3-Cu1-O5	91.9(2)
C5-O5-Cu1	110.6(6)
C7-O7-Cu1	129.2(6)
C1-O1-Cu1	115.7(6)
C3-O3-Cu1	108.3(5)

Table 3S Selected interatomic distances with standard deviations in parentheses for the **2** crystal

Bond	*d*, Å	Bond	*d*, Å
Cu1-O3	1.9642(17)	C1-C2	1.511(3)
Cu1-O2	1.9664(17)	C3-O2	1.261(3)
Cu1-O1	1.9670(18)	C3-C4	1.507(3)
Cu1-O4	1.9737(18)	N2-C5	1.370(3)
Cu1-O5	2.1469(16)	N2-C7	1.394(3)
Cu1-Cu1	2.6366(5)	N2-C11	1.449(3)
O4-C3	1.256(3)	N1-C5	1.363(3)
O1-C1	1.260(3)	N1-C6	1.393(3)
O2-C3	1.261(3)	N1-C8	1.457(3)
O3-C1	1.267(3)	C8-C9	1.498(4)
O5-C5	1.251(3)	C6-C7	1.334(4)
C1-O3	1.267(3)		

Table 4S Selected angles with standard deviations in parentheses for the **2** crystal

Angle	ω,°
O3-Cu1-O2	89.27(8)
O3-Cu1-O1	168.30(7)
O2-Cu1-O1	88.58(8)
O3-Cu1-O4	88.52(7)
O2-Cu1-O4	168.27(7)
O1-Cu1-O4	91.26(8)
O3-Cu1-O5	98.59(7)
O2-Cu1-O5	98.18(7)
O1-Cu1-O5	93.10(7)
O4-Cu1-O5	93.55(7)
O3-Cu1-Cu1	86.26(5)
O2-Cu1-Cu1	86.23(5)
O1-Cu1-Cu1	82.13(5)
O4-Cu1-Cu1	82.13(5)
O5-Cu1-Cu1	173.45(5)
C3-O4-Cu1	125.36(16)
C1-O1-Cu1	125.86(15)
C3-O2-Cu1	120.79(15)
C1-O3-Cu1	120.95(15)
C5-O5-Cu1	126.44(16)

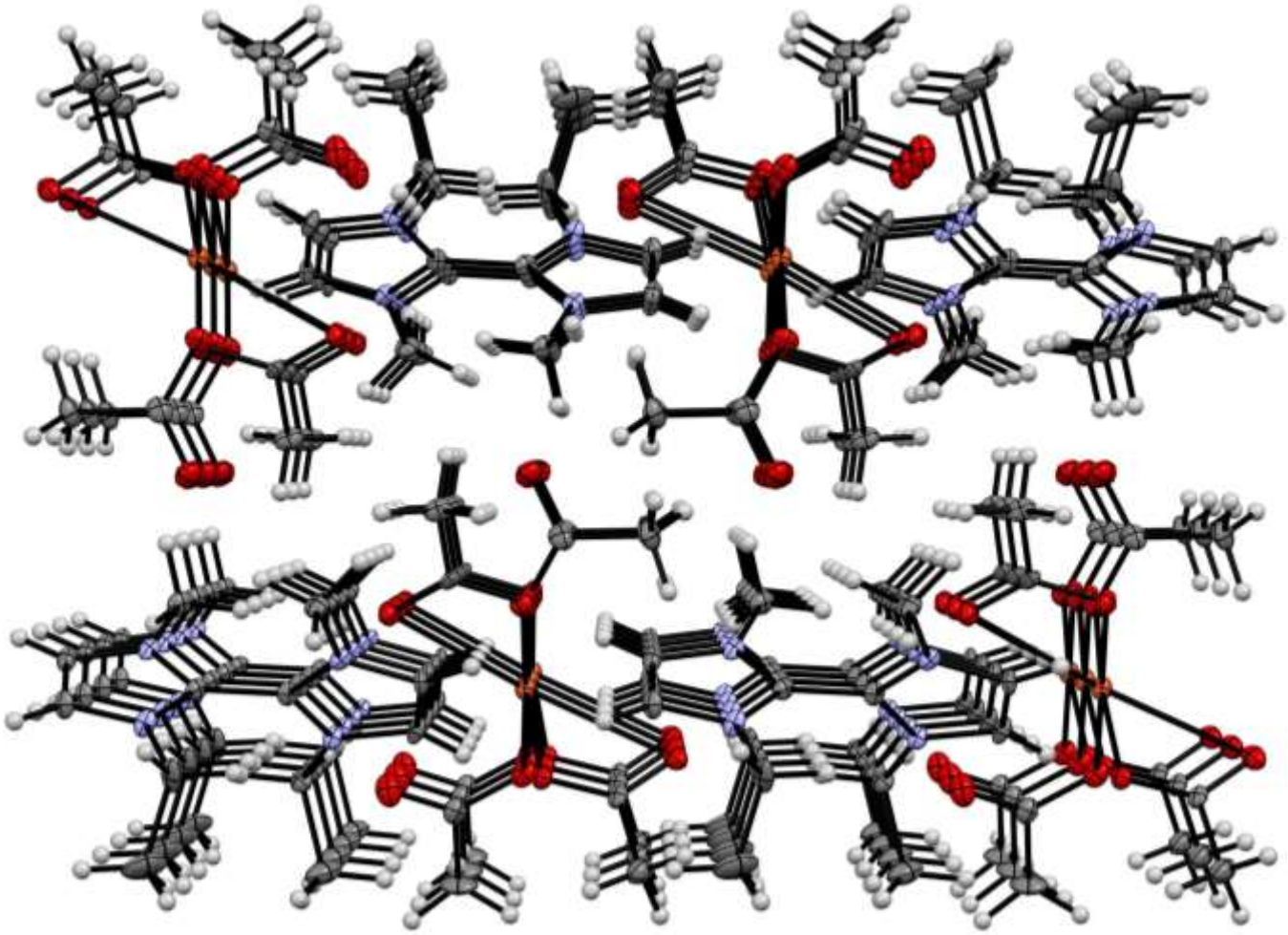

Figure 3S The three-dimensional network of **1** crystal viewed down the *a*-axis direction.

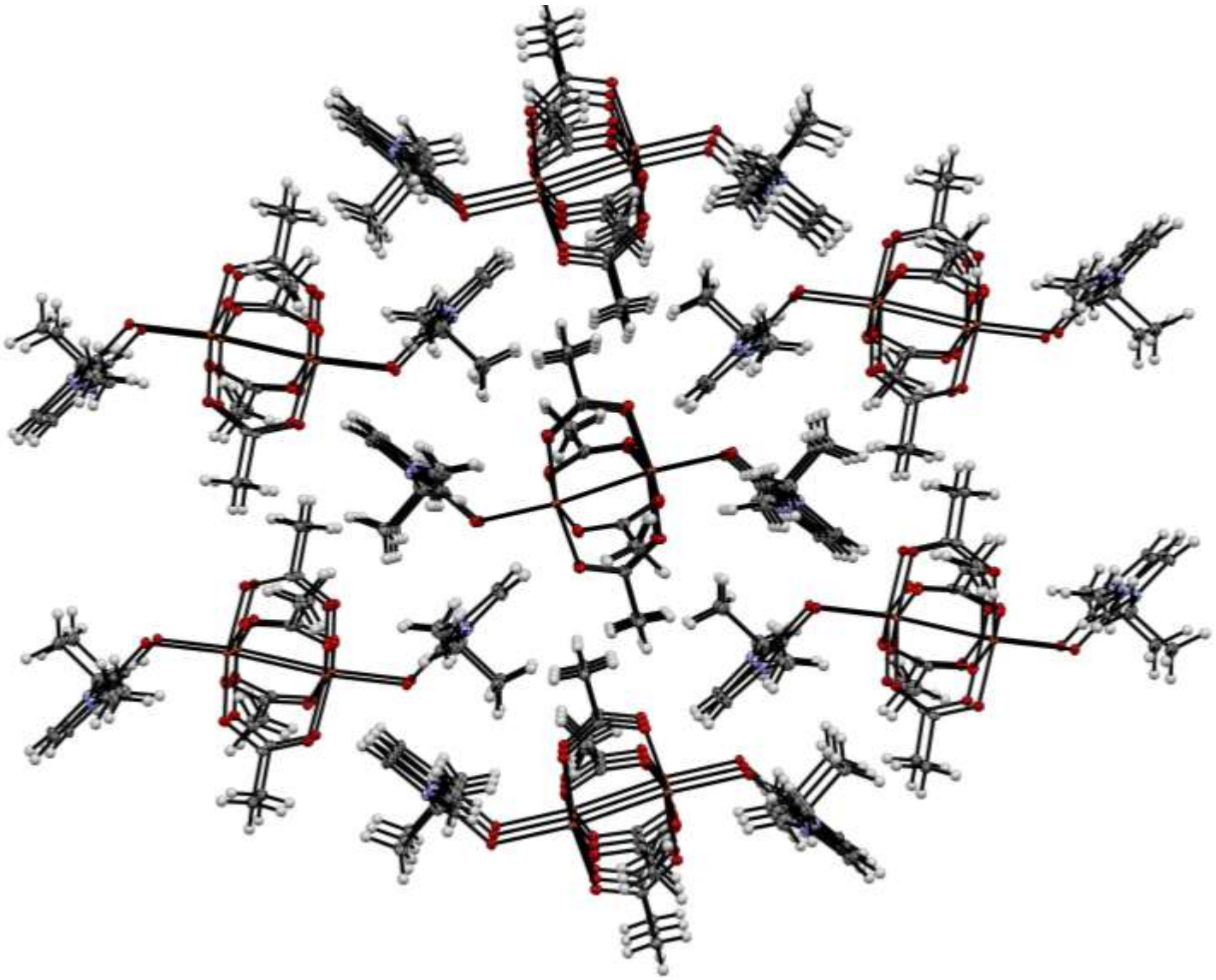

Figure 4S The three-dimensional network of **2** crystal viewed down the *a*-axis direction.

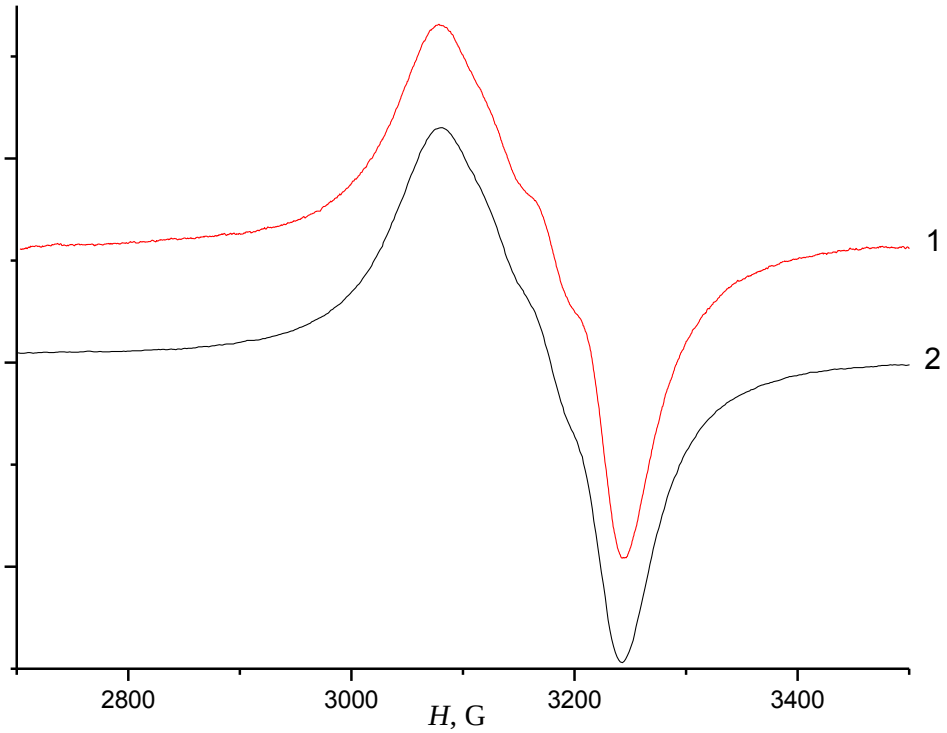

Fig. 5S The experimental EPR spectra (X-band, 20 °C) of aqueous solutions of the crystals **1** (0.06 mole dm^{-3}) and $Cu(AcO)_2 \cdot H_2O$ (0.067 mole dm^{-3}) denoted as 1 and 2 respectively.