Interactions of an asymmetric amine with a non-C_2 symmetric Cu-salen complex: An EPR/ ENDOR and HYSCORE Investigation

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Electronic Supplementary Information

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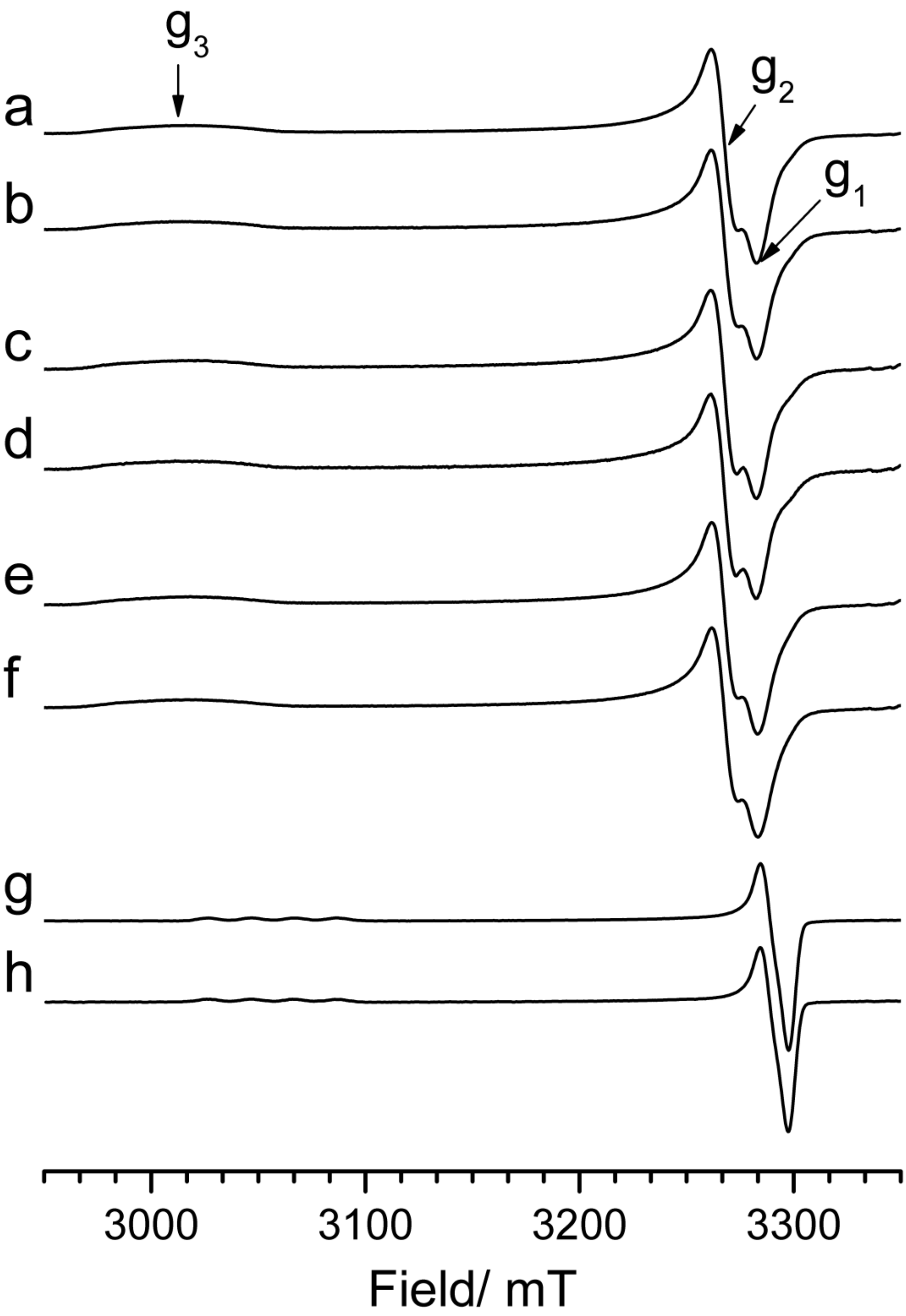

Figure S1: W-band CW-EPR spectra (recorded at 100K) of (a) *R*,*R′*-[Cu(**3**)] in *rac*-MBA (b) *S*,*S′*-[Cu(**3**)] in *rac*-MBA (c) *R*,*R′*-[Cu(**3**)] in *R*-MBA (d) *S*,*S′*-[Cu(**3**)] in *S*-MBA (e) *R*,*R′*-[Cu(**3**)] in *S*-MBA (f) *S*,*S′*-[Cu(**3**)] in *R*-MBA (g) *R*,*R′*-[Cu(**3**)] in dichloromethane/ toluene and (h) *S*,*S′*-[Cu(**3**)] in dichloromethane/ toluene.

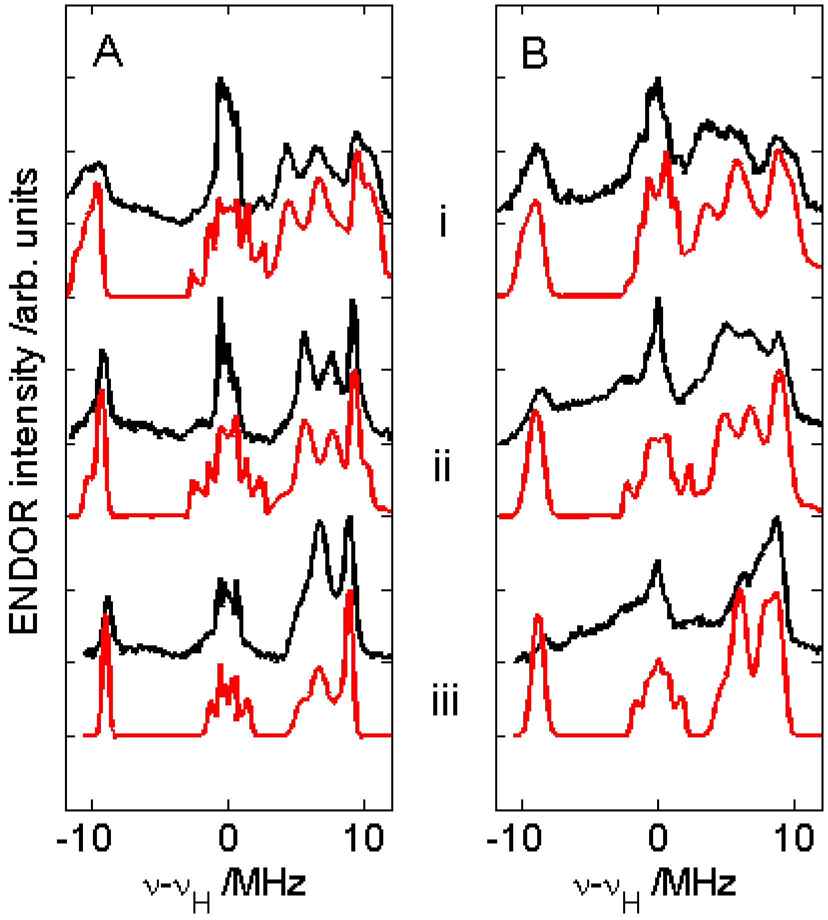

Figure S2 Experimental (black) and simulated (red) pulsed Davies ^{1}H ENDOR of [Cu(**3**)] in (A) CD_2Cl_2:d^8-toluene and (B) *rac*-MBA recorded at the field positions corresponding to (i) $g_{2,3}$ (ii) g_{iso} and (iii) g_1. The simulations were done assuming the parameters from Tables 1-3 (main text).

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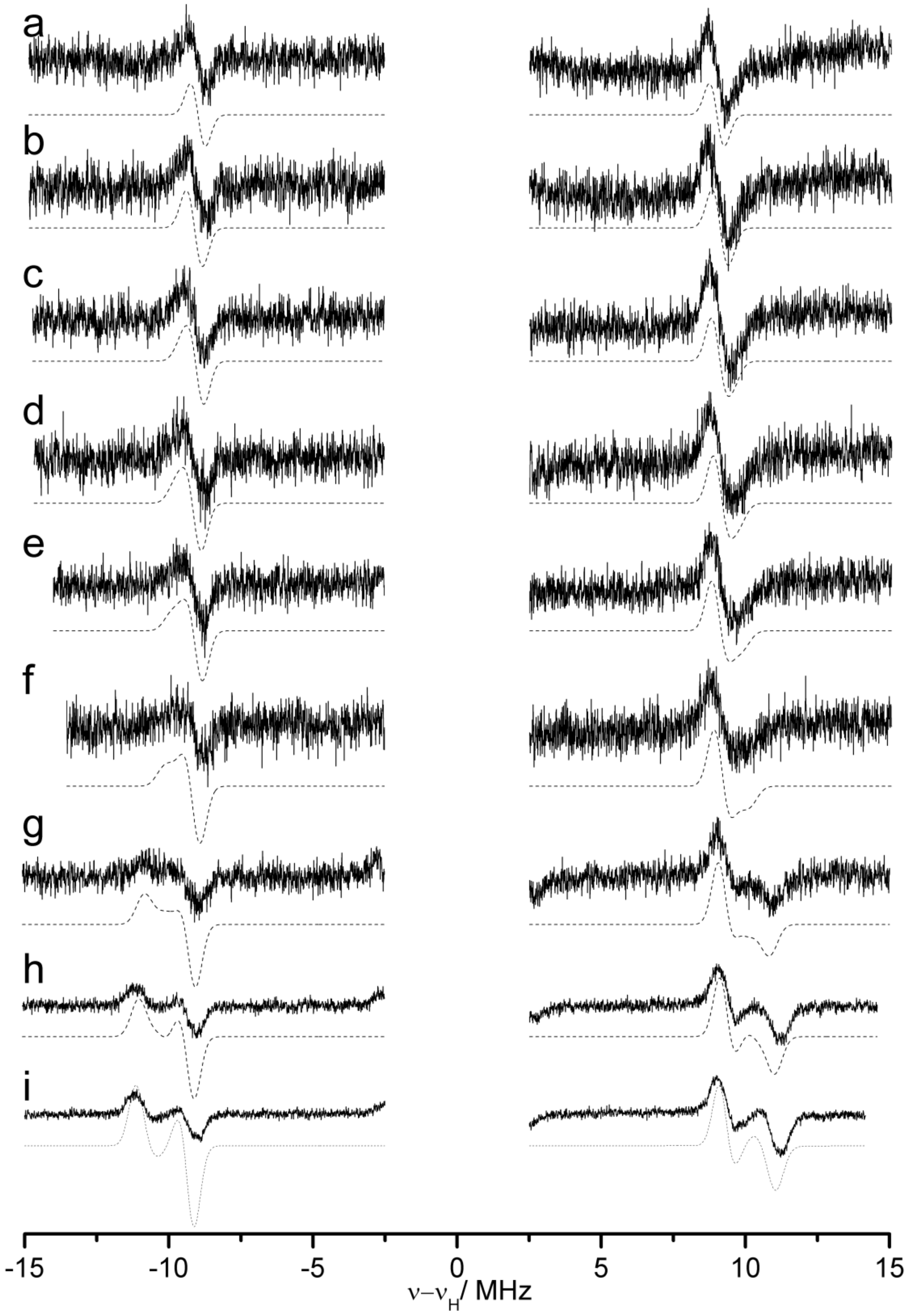


Figure S3a Q-band CW- ^{1}H-ENDOR spectra of [Cu(**3**)] dissolved in **dichloromethane/ toluene,** of the ligand imine protons recorded at the field positions (a) 1086.7, (b) 1098.7, (c) 1107.8, (d) 1119.3, (e) 1128.3, (f) 1138.6, (g) 1176.2, (h) 1186.3 and (i) 1194.3 mT.

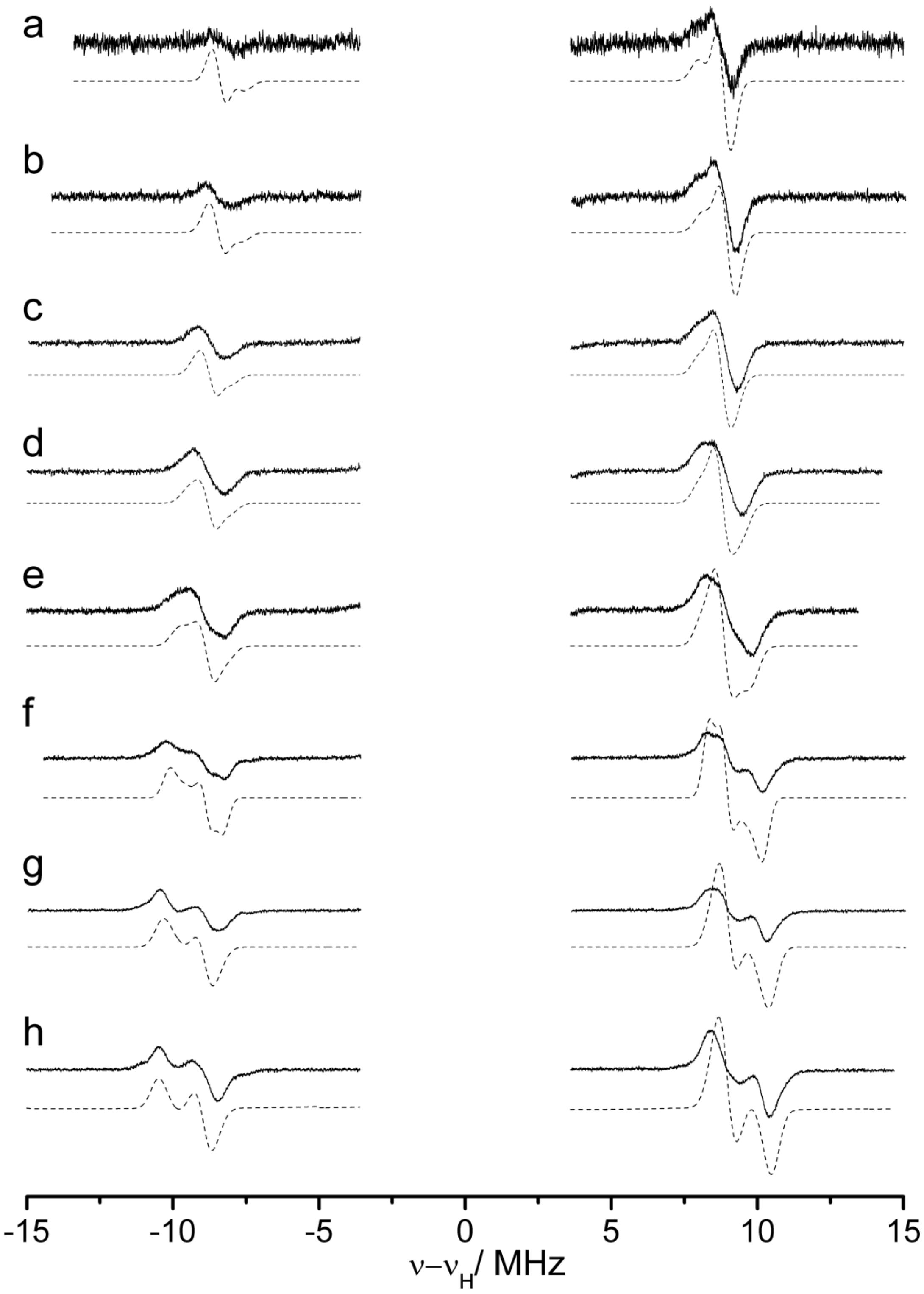


Figure S3b: Q-band CW- ^{1}H-ENDOR spectra of [Cu(**3**)] dissolved in **MBA,** highlighting the ligand imine protons recorded at the field position (a) 1066.4, (b) 1084.5, (c) 1102.9, (d) 1120.9, (e) 1140.2, (f) 1160.8, (g) 1173.4 and (h) 1182.4 mT.

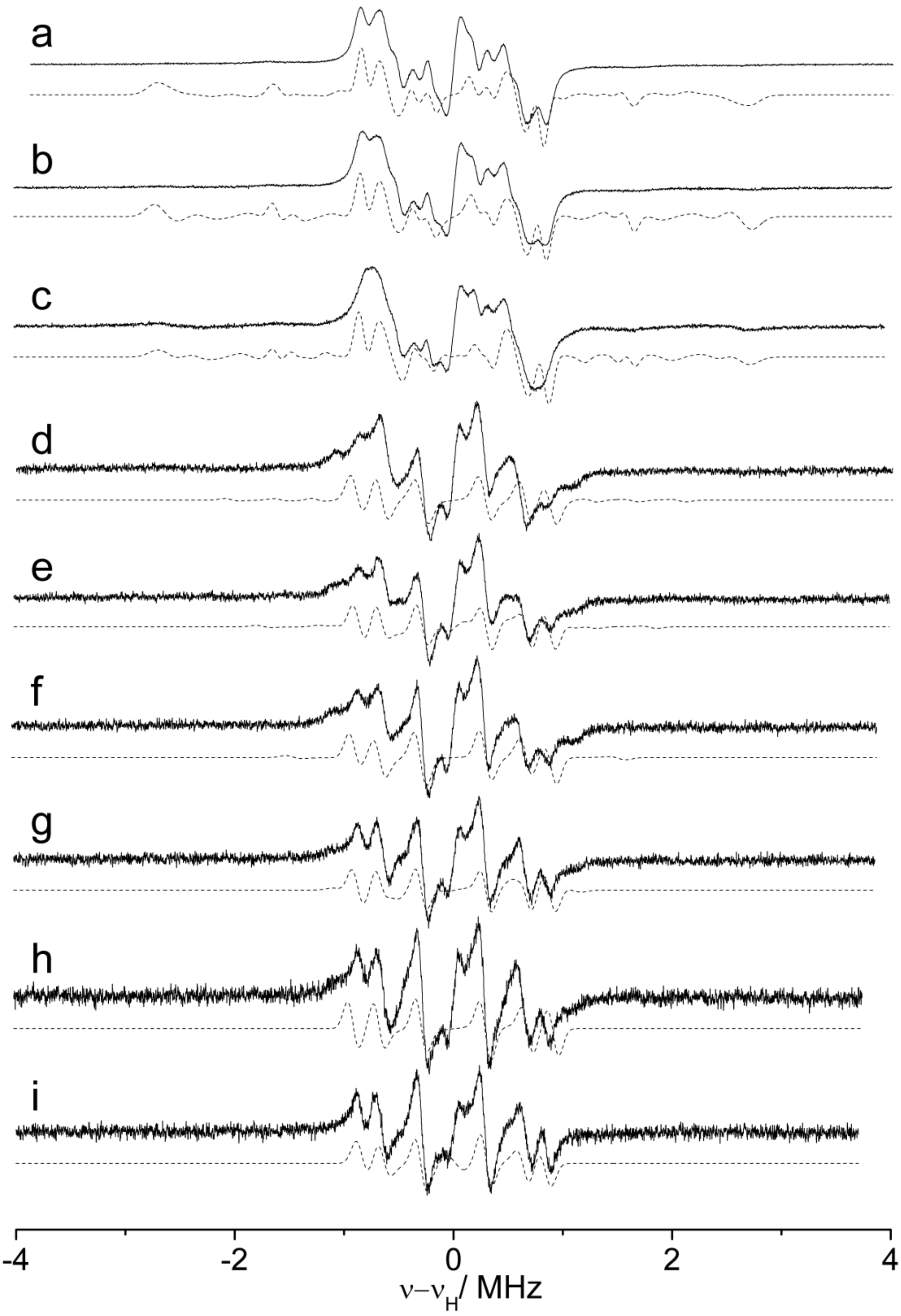


Figure S4: Q-band CW- ^{1}H-ENDOR spectra of [Cu(**3**)] dissolved in dichloromethane/ toluene recorded at the field position (a) 1194.2, (b) 1186.3, (c) 1176.2, (d) 1138.6, (e) 1128.3, (f) 1119.2, (g) 1107.8, (h) 1098.7 and (i) 1087.3 mT. The line-widths of the largest couplings have been left un-broadened.

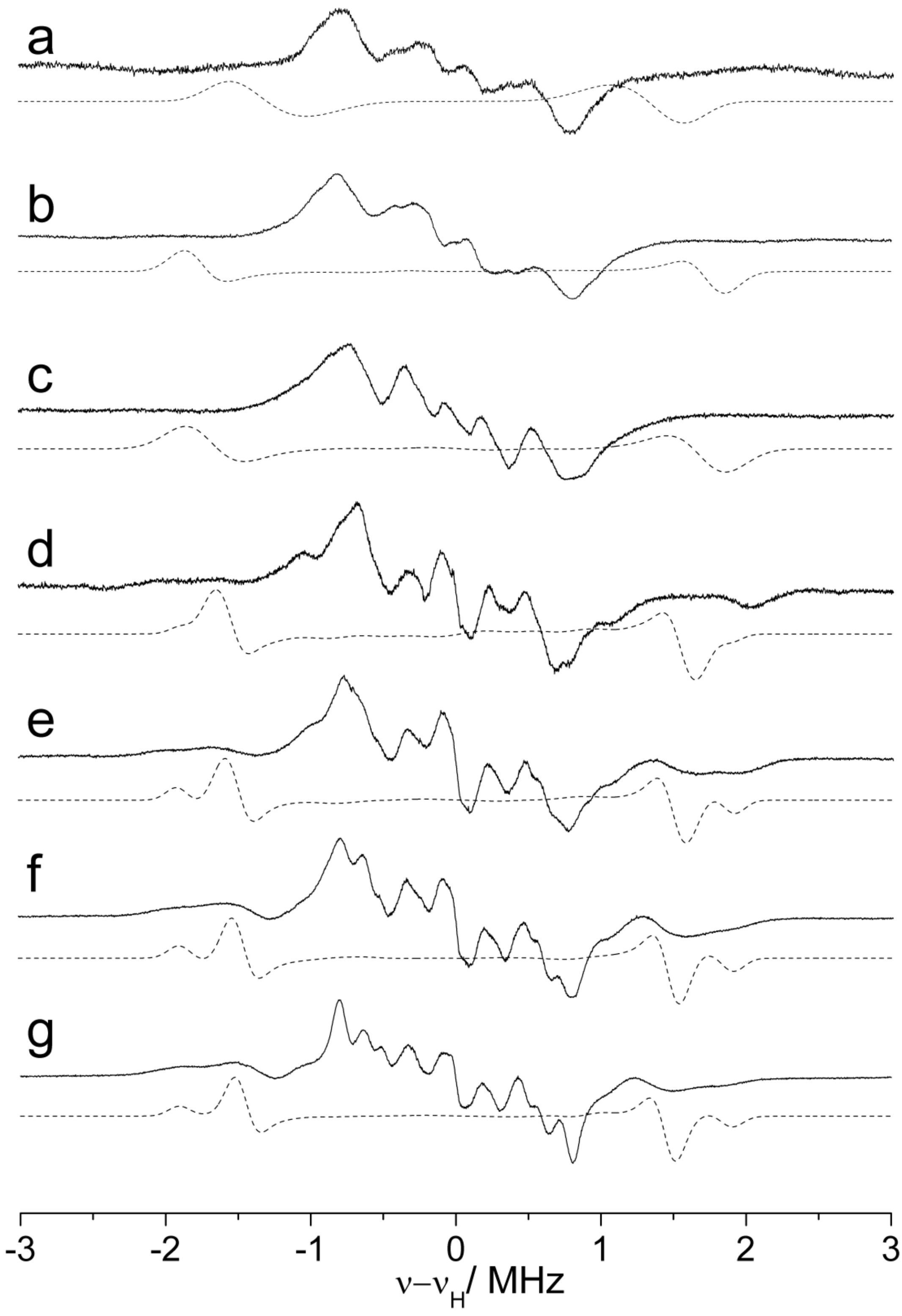


Figure S5: Q-band CW- ^{1}H-ENDOR spectra of [Cu(**3**)] dissolved in MBA highlighting the amine –NH_2 protons recorded at the field position (a) 1065.0, (b) 1092.4, (c) 1118.5, (d) 1160.7, (e) 1173.3, (f) 1182.5, and (g) 1190.4 mT. Only couplings arising from the –NH_2 protons have been included in these simulations (ligand methine and tert-butyl peaks are displayed in Fig S4).

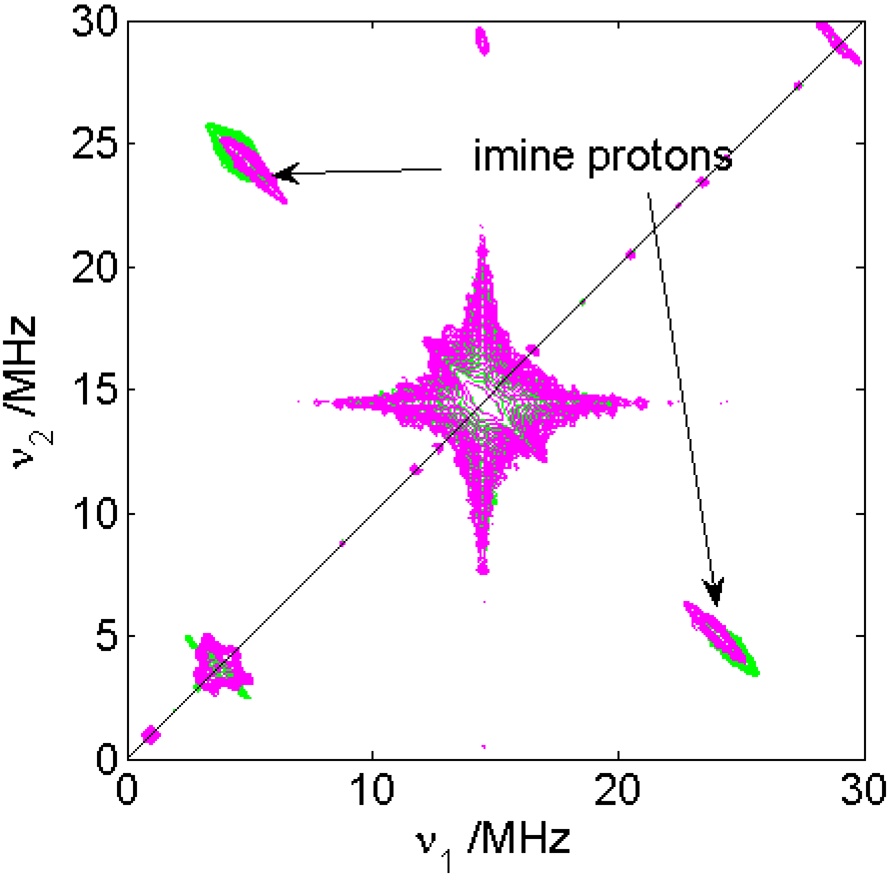


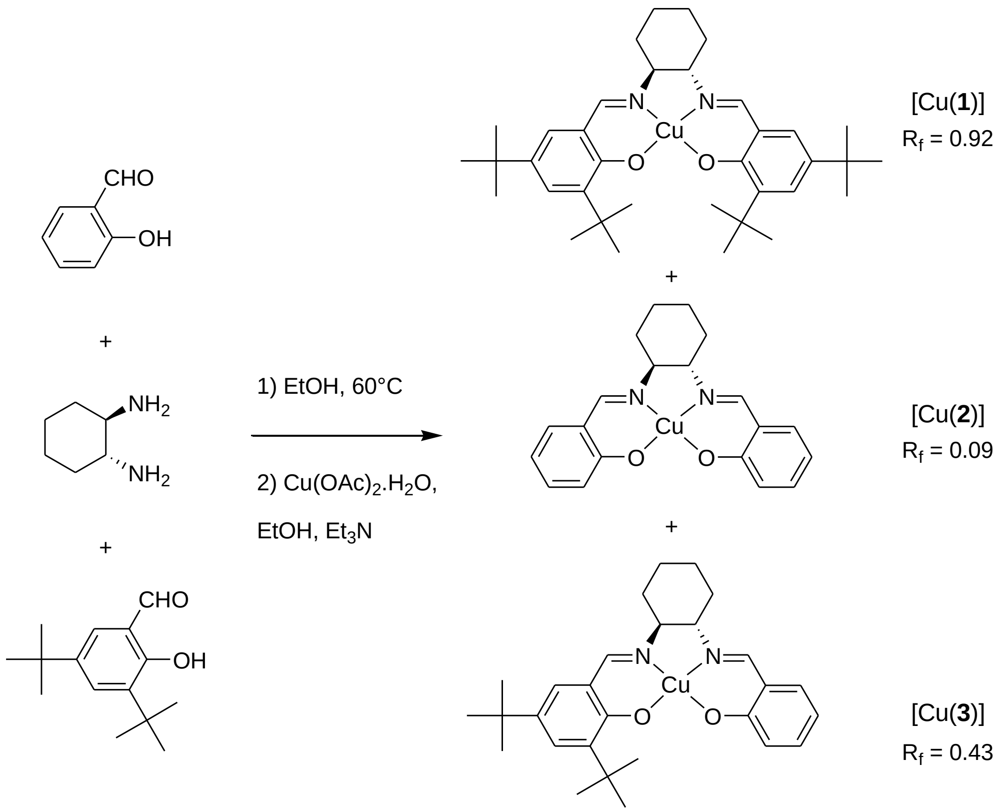
Figure S6 Comparison between the HYSCORE spectra of *S*,*S′*-[Cu(**3**)] in dichloromethane (green) and in *R*-MBA (magenta). The HYSCORE spectra are taken at an observer position agreeing with $g=g_{1,2}$ (B_0=340 mT) with τ=96, 176 ns.
We notice here a smaller ^{1}H hyperfine coupling of the imine protons for the bound [Cu(**3**)]-MBA complex (see analogy with ENDOR data in Fig 3 of main text).

Synthetic details for preparation of [Cu(3)]

***rac*-[Cu(3)]**, *rac-N*-(3,5-Di-tert-butylsalicylidene)-*N'* -salicylidene-1,2-cyclohexane-diamino-copper (II).

All materials were purchased from Sigma – Aldrich or Alfa Aesar and used as received. To a mixture of 3,5-di-*tert*-butylsalicylaldehyde (2.34 g, 10 mmol) and salicylaldehyde (1.22 g, 10 mmol) in warm ethanol (200ml) was added racemic *trans*-1,2-diaminocyclohexane (0.114 g, 10 mmol) one portion. The reaction mixture was allowed to cool overnight to afford a clear yellow homogeneous solution. Copper (II) acetate monohydrate (2.4 g, 12 mmol) was added and the solution stirred vigorously for one hour. Triethylamine (1g) was added and stirring was continued for a further 10 minutes. The resulting brown/purple precipitate was filtered, washed with methanol (50 ml) and air dried. TLC analysis (dichloromethane eluent) indicated the presence of three complexes: one purple (R_f = 0.09) and two green materials (R_f = 0.43, 0.92). These were separated by dry flash column chromatography (silica, 5 x 7 cm) using 1:1 hexane-dichloromethane and subsequently dichloromethane as eluent (fraction size, 50 ml). The yields, based upon 1,2-diaminocyclohexane, obtained of chromatographically homogenous materials were 12% ([Cu(**1**)]), 17 % ([Cu(**2**)] and 14% of the desired complex [Cu(**3**)].

***R,R*-[Cu(3)]** and ***S,S*-[Cu(3)]** were prepared by a similar method from *R,R*- and *S,S*-1,2-diaminocyclohexane respectively. These materials had essentially identical analytical properties to those of the racemic material.



Scheme S1. Synthesis of [Cu(**3**)]