Electronic Supplementary Material (ESI) for Dalton Transactions

Ligand Spheres in asymmetric hetero Diels-Alder reactions catalyzed by Cu(II) box complexes: Experiment and Modeling

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Supplementary Information

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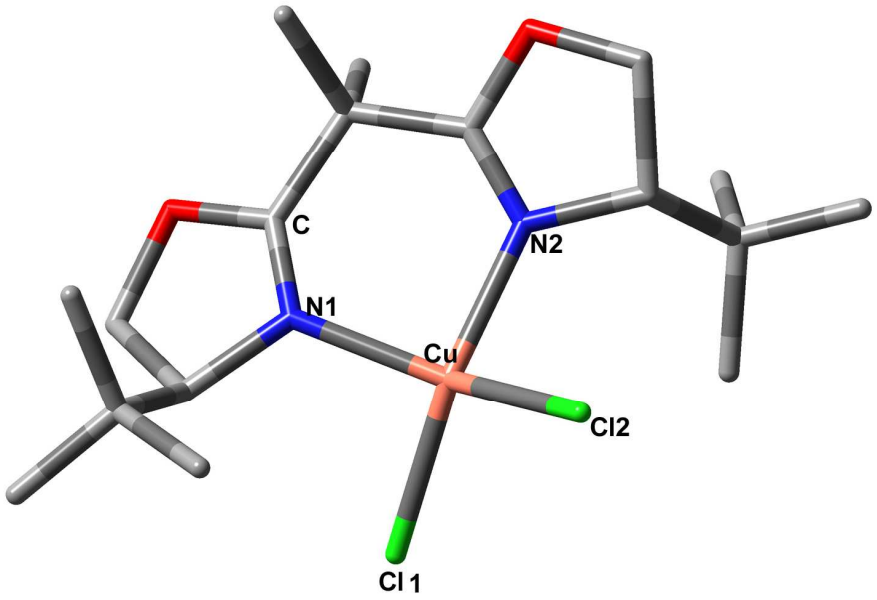

	X-ray (Ref 35)	B3LYP/TZVP
Cu-N1	198	200
Cu-Cl1	223	224
N1-Cu-N2	90.5	90.9
Cl1-Cu-Cl2	99.8	98.9
C-N1-Cu-Cl2	108.9	109.8

Figure/Table S1: Experimental and calculated geometry of CuboxCl_2. Hydrogen atoms are omitted for clarity. Distances are given in pm, angles in °.

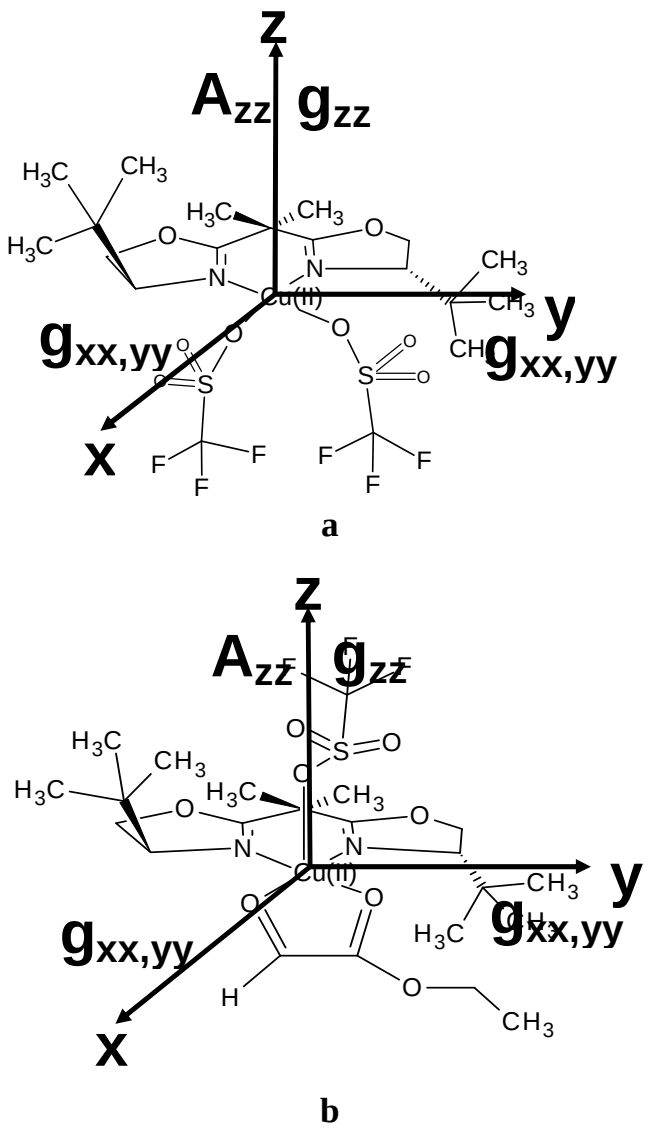

Figure S2. Tensor diagram showing the orientation of the principal axes frames with respect to the (a) distorted square planar complex structure for Stage **1** (**S1**) - $Cu(OTf)_2$/*tert*-butylbox and (b) distorted square pyramidal complex structure for Stage **2** (**S2**) - $Cu(OTf)_2$/*tert*-butylbox + ethyl glyoxylate and Stage **3** (**S3**) - $Cu(OTf)_2$/*tert*-butylbox + ethyl glyoxylate + 1,3-cyclohexadiene (1,3-cyclohexadiene is not included in the picture since it is not directly coordinated to the Cu(II) center)

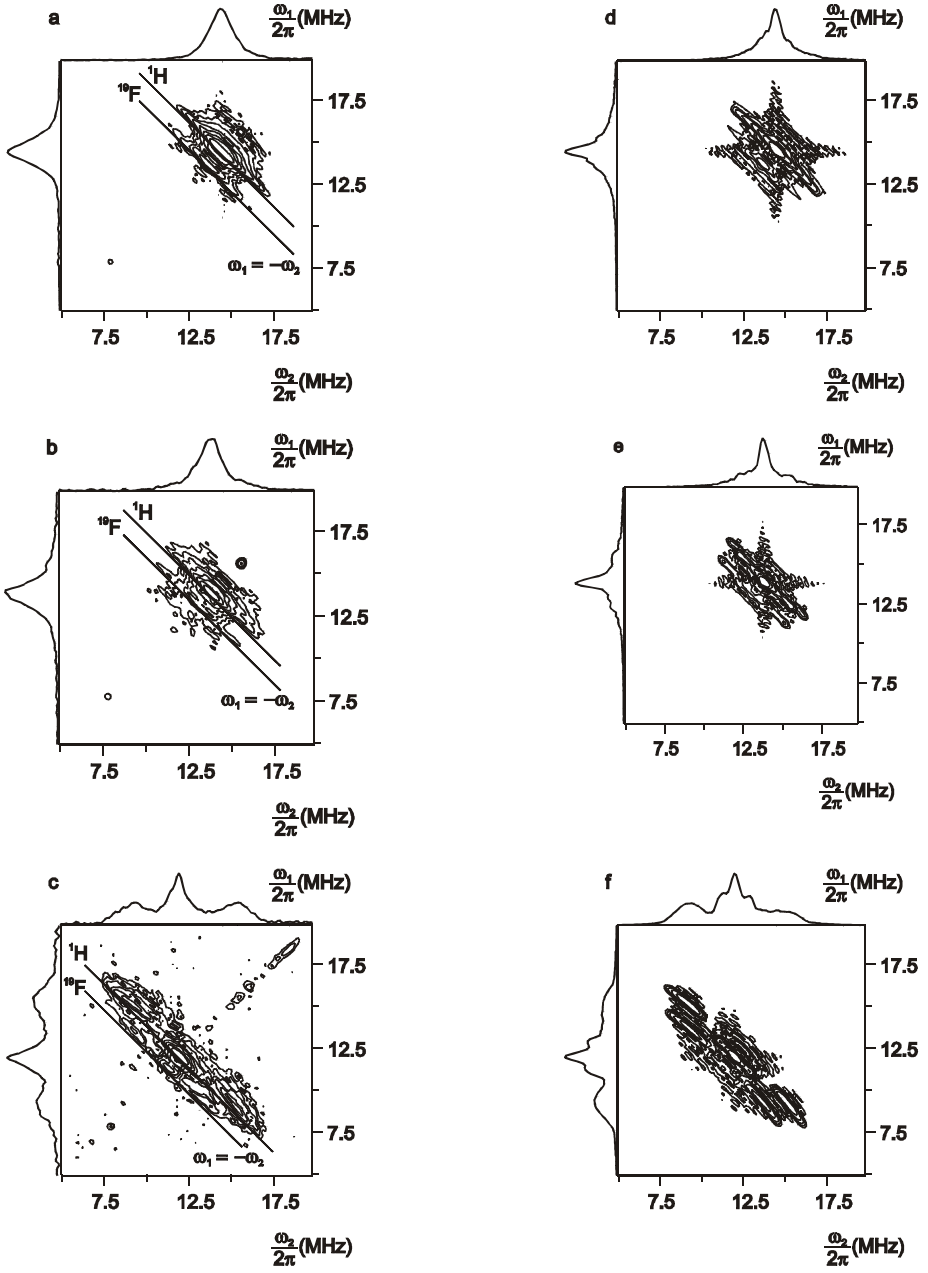

Figure S3. Added X- band HYSCORE spectra of stage **1** (**S1**) - $Cu(OTf)_2$/tert-butylbox, measured at 4 K, (a) 339.5 mT, τ = 104 + 160 + 32 ns (b) 325.5 mT, τ = 104 + 160 + 32 ns (c) 281.5 mT, τ = 160 + 40 ns at 4 K, (a, b, c – Experimental) and (d, e, f – Simulated)

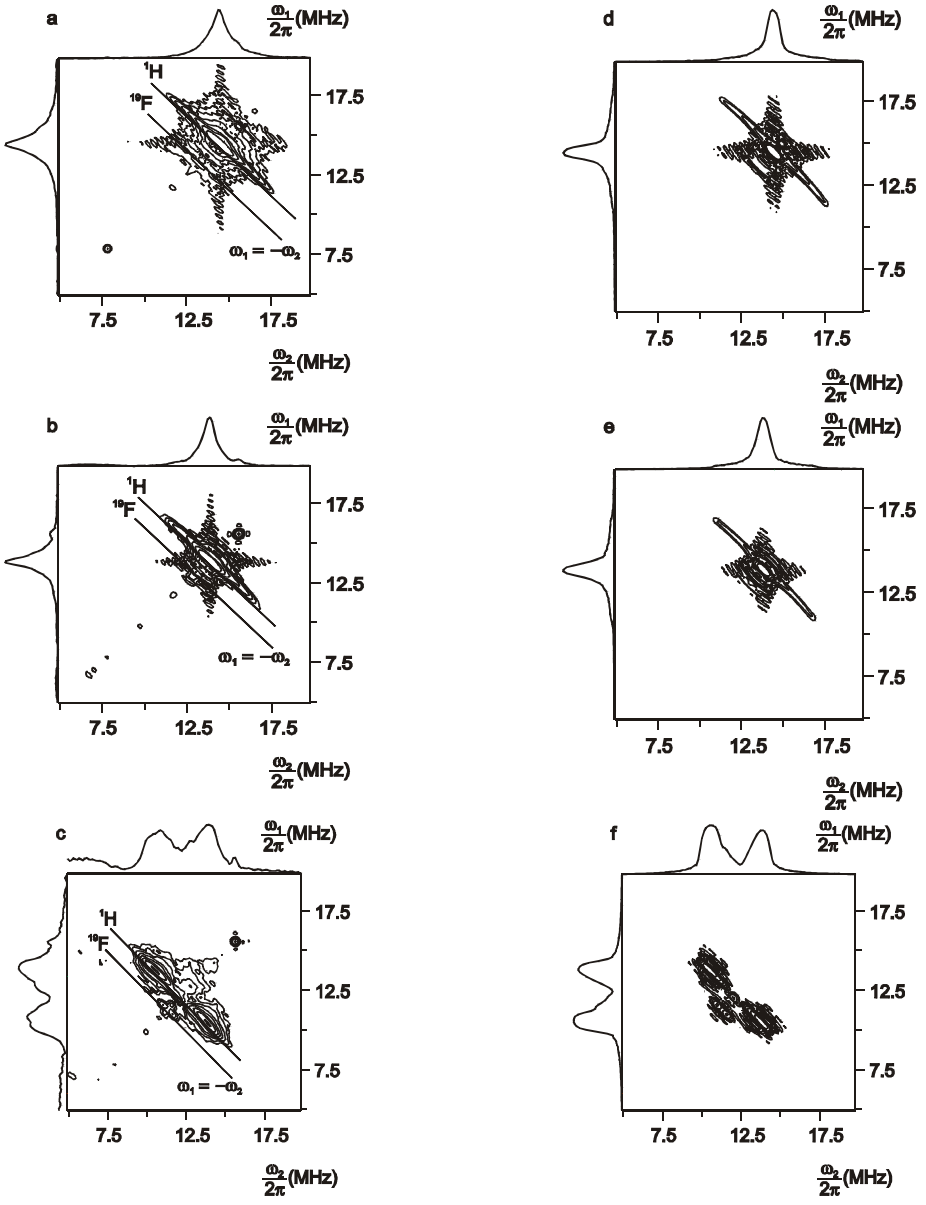

Figure S4. X- band HYSCORE spectra of stage **3** (**S3**) - $Cu(OTf)_2$/tert-butylbox + ethyl glyoxylate + 1,3-cyclohexadiene (a) 339.5 mT, τ = 104 + 160 + 32 ns (b) 325.5 mT, τ = 104 + 160 + 32 ns (c) 281.5 mT, τ = 160 ns at 4 K, (a, b, c – Experimental) and (d, e, f – Simulated)

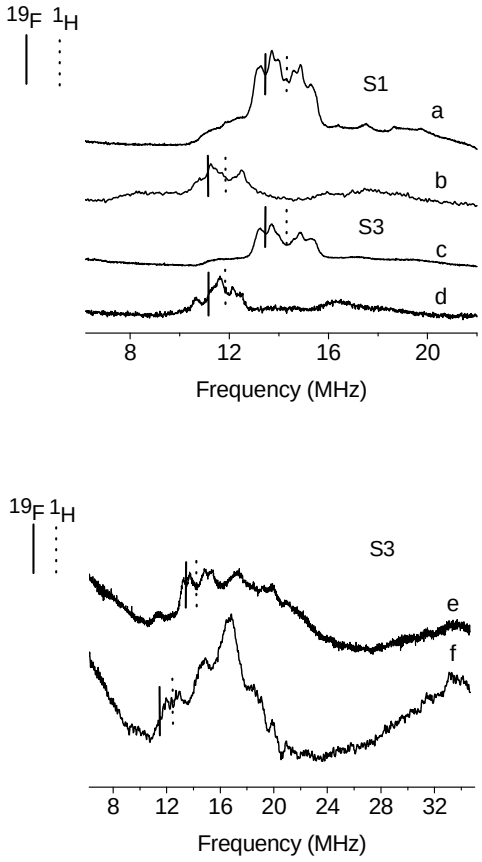

Figure S5. X- band Experimental Davies ENDOR spectra of **S1** – $Cu(OTf)_2$/tert-butylbox (a – 335.4 mT and b – 278.5 mT), and S 3 - $Cu(OTf)_2$/tert-butylbox + ethyl glyoxylate + 1,3-cyclohexadiene (c – 335.4, d – 278.5 mT), measured at 4 K with long microwave pulses of $t_{\pi/2}$ = 96 and t_{π} = 192 ns, and (e – 335.4 mT) and (f – 290 mT) of **S3** measured with short microwave pulses $t_{\pi/2}$ = 16 and t_{π} = 32 ns

This hf contrast selective ENDOR experiments for **S3** prove unambiguously the presence of broad ^{14}N ENDOR signals in the range 16 MHz – 24 MHz (spectrum in Fig. S5 /e/ recorded at 335.4 mT) and 16 MHz – 20 MHz (Fig. S5 /f/ recorded at 290.0 mT). The data provide a rough estimate of $A_{\parallel}^{N} \approx 48$ MHz and $A_{\perp}^{N} \approx 32$ MHz for the ^{14}N hfc parameters in sample III. Note that the largest ^{14}N hfc is observed in the ENDOR spectrum taken at 335.4 mT (Fig. S5 /e/). Therefore, the $A_{\parallel}^{N}$ principal axis of the ^{14}N hfc tensor lies within the *x-y* plane of the Cu(II) g tensor. In the same way we may likewise assign the broad baseline signals ranging from 17 MHz to 20 MHz in the ENDOR spectra of sample I (Fig. S5 /a and b/) to ^{14}N signals yielding hfc estimates of $A_{\parallel}^{N} \approx 40$ MHz and $A_{\perp}^{N} \approx 34$ MHz for the respective hfc parameters.

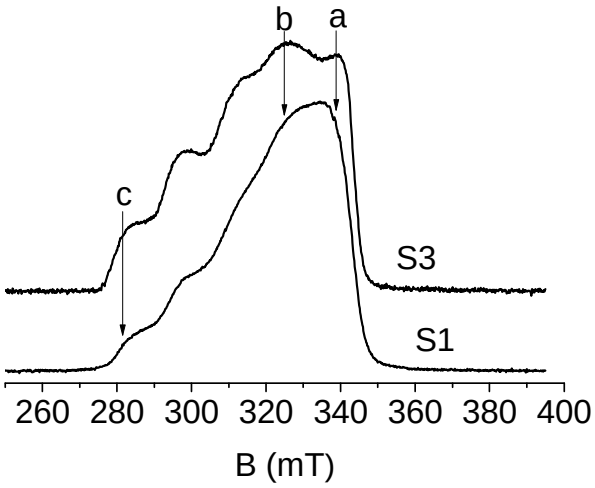

Figure S6. X- band two pulse field-swept ESE spectra measured with short pulses $\pi/2$ = 16 ns and π = 32 ns, and the pulse delay of τ = 800 ns at 4 K, of **S1** - $Cu(OTf)_2$/*tert*-butylbox and **S3** - $Cu(OTf)_2$/*tert*-butylbox + ethyl glyoxylate **(1)** + 1,3 - cyclohexadiene **(2)**, the arrows with a, b and c represents the fields 339.5 mT, 325.5 mT and 281.5 mT respectively, at which the HYSCORE spectra were measured.

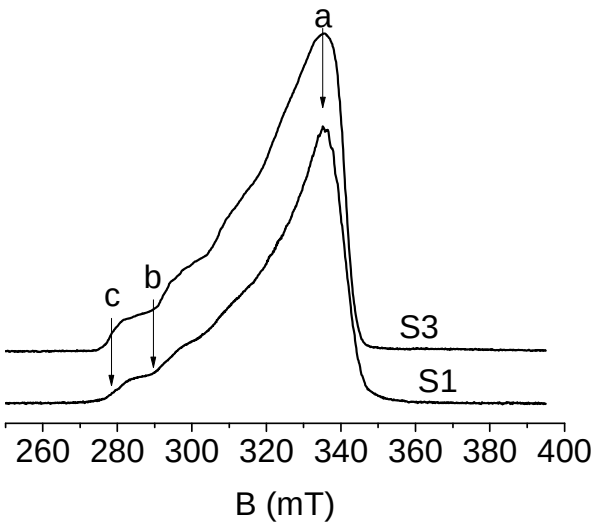

Figure S7. X- band two pulse field-swept ESE spectra measured with the selective microwave pulses of $t_{\pi/2}$ = 96 ns and t_{π} = 192 ns, and with the pulse delay of τ = 1200 ns, at 4 K, of S1 - Cu(OTf)$_2$/*tert*-butylbox and Stage **3** (**S3**) - Cu(OTf)$_2$/*tert*-butylbox + ethyl glyoxylate **(1)** + 1,3 - cyclohexadiene **(2),** the arrows with a, b and c represents the fields 335.4 mT, 290 mT and 278.5 mT respectively, at which the ENDOR spectra were measured

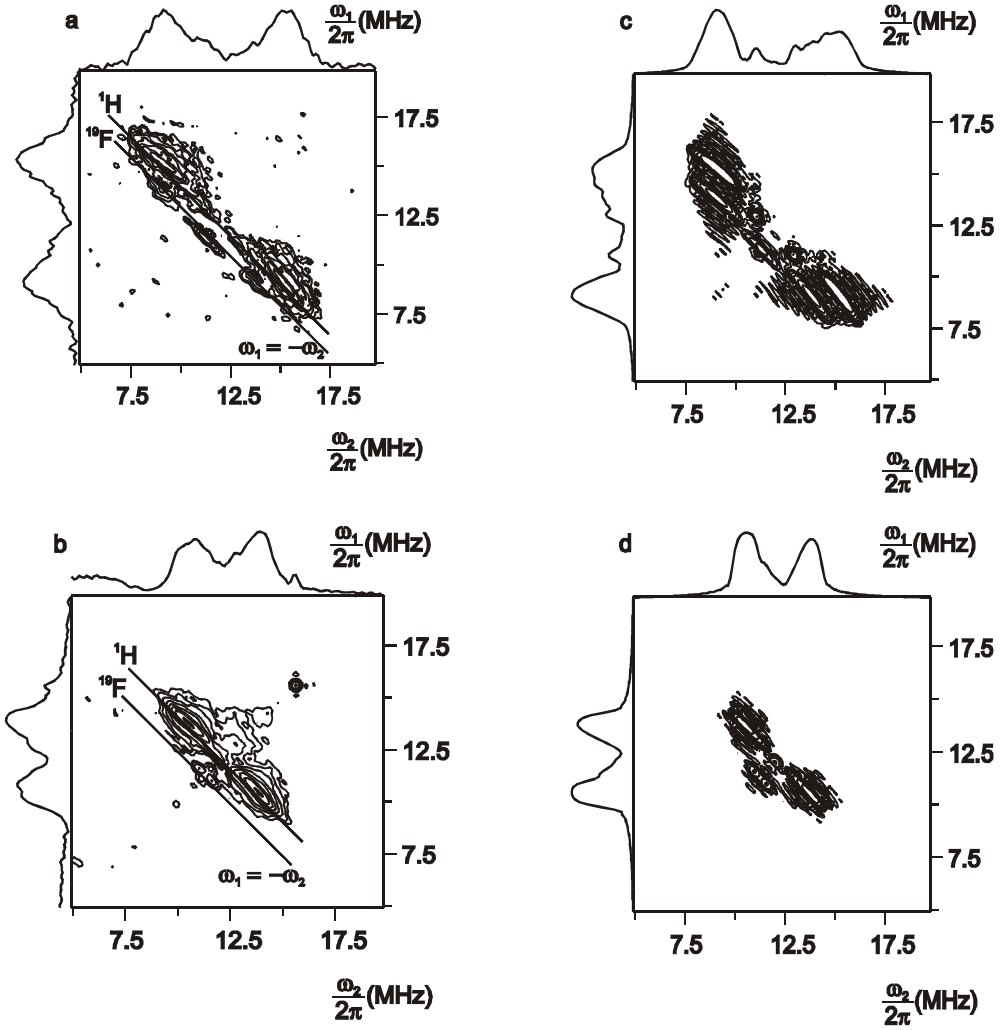

Figure S8. X- band HYSCORE spectra of **S1** - Cu(OTf)$_2$/*tert*-butylbox (a – Experimental, c – Simulated) and S3 - Cu(OTf)$_2$/*tert*-butylbox + Ethyl glyoxylate + 1,3 - Cyclohexadiene (b – Experimental, d – Simulated), measured at the g_{zz} Cu(II) EPR spectral position 281.5 mT at 4 K, with τ = 160 ns

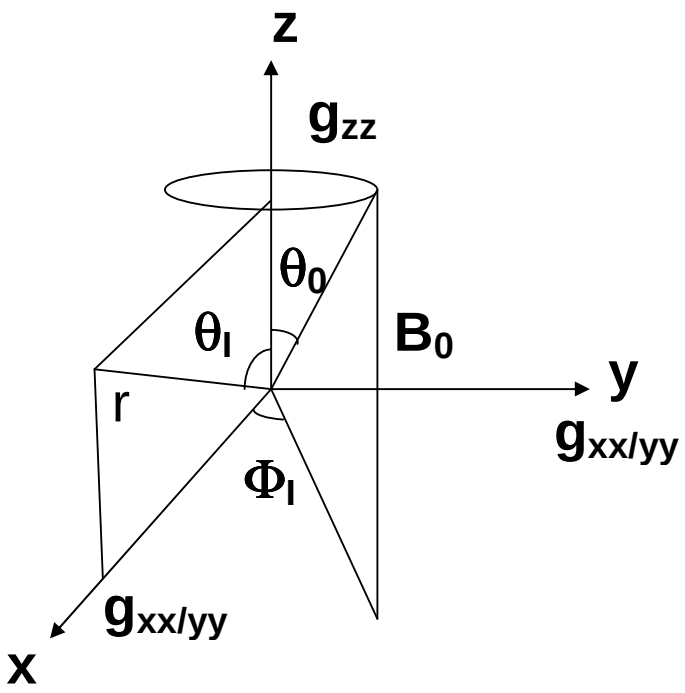

Figure S9. Vector diagram showing the relationship between the external field B_0 and the vector **r** joining the electron spin and the nucleus (^{1}H or ^{19}F) which lies in the *xz* plane. **r** is at an angle of θ_I to the z axis. The *xyz* coordinate frame corresponds to the **g** tensor frame. θ_0 is the angle between the external magnetic field B_0 and the g_{zz} axis. Φ_I is the azimuthal angle from *z* between the *zx* plane and the zB_0 plane.

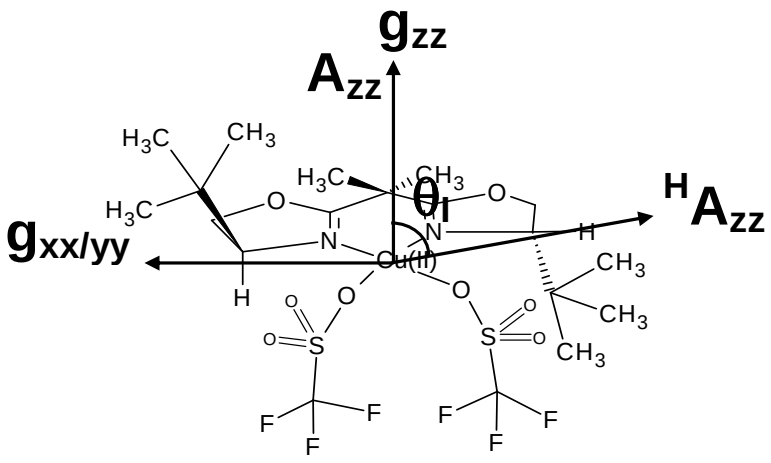

Figure S10. Schematic drawing of the Cu(OTf)$_2$/*tert*-butylbox complex **(S1)** together with the vector diagram showing the relationship between the **g** tensor frame and the *z* axis of the proton hf tensor. The z axis of the proton hyperfine tensor is shown to be perpendicular to the g_{zz} axis. The $g_{xx/yy}$ and g_{zz} axes of the Cu(II) **g** tensor frame are respectively parallel and perpendicular to the complex plane containing Cu(II) ion, the two equatorially coordinated imine nitrogen atoms from the oxazoline rings of the *tert*-butylbox ligand, and the two equatorially coordinated oxygen atoms from the triflate (-O-SO_2-CF_3) (which are slightly tilted about 26°from the Cu(II) plane).

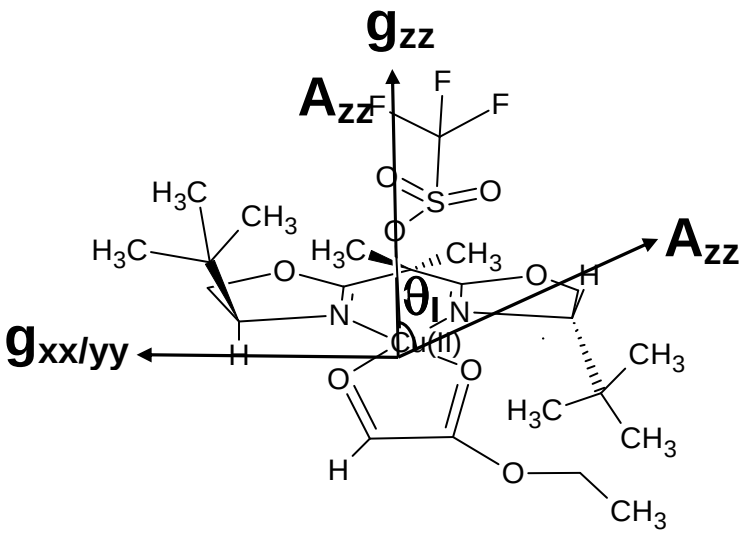

Figure S11. Schematic drawing of the Cu(OTf)$_2$/*tert*-butylbox + ethyl glyoxylate complex (**S2**) together with a vector diagram showing the relationship between the **g** tensor frame and the *z* axis of the proton hf tensor. The z axis of the proton hyperfine tensor is shown to be at an angle of 51° from the g_{zz} axis. The $g_{xx/yy}$ and g_{zz} axis of the Cu(II) **g** tensor frame are respectively parallel and perpendicular to the complex plane containing Cu(II) ion, two equatorially coordinated imine nitrogen atoms from the oxazoline rings of the *tert*-butylbox ligand and the two equatorially coordinated oxygen atoms from the dienophile (which are slightly tilted about 26° from the Cu(II) plane). Here the –OTf ligans is axially coordinated to the Cu(II), through the sulphonic oxygen atom and is perpendicular to the complex plane containing Cu(II), and parallel to g_{zz} axis.

	$g_{\perp}$		g_{II}	
	Exp	Calc	Exp	Calc
S1	2.077	2.067	2.303	2.208
S2	2.068	2.063	2.304	2.195
S3	2.080	2.072	2.323	2.198

Table S12. Comparison of calculated and experimental g-factors for **S1**, **S2** and **S3** structures.

	$A_{\perp}$				A_{II}				A_{iso}			
	LP1	**LP2**	**LP3/S2**	sim	**LP1**	**LP2**	**LP3/S2**	sim	**LP1**	**LP2**	**LP3/S2**	sim
Cu	91.4	20.0	52.8	38.0	-411.2	-498.5	-536.6	424.0	-	-	-	-
N	25.6	33.0	35.7	35.0	35.1	44.7	48.6	35.0	28.6	37.1	40.3	35.0
H	-1.10	-0.48	-1.42	-1.46	-1.30	0.83	4.66	6.82	0.06	-0.04	0.50	1.3
F	1.58	0.07	-0.59	-0.73	-5.08	3.81	1.19	1.46	-2.61	1.11	0.00	0.00

Table S13. Comparison of calculated and experimental/simulated HFC couplings of Cu, N, relevant F and H nuclei for **LP1**, **LP2** and **LP3** structures.