

Supporting Information:

Increased sensitivity in Electron Nuclear Double Resonance spectroscopy with chirped radiofrequency pulses

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1. Generation of chirp RF pulse waveforms

The waveform of the chirp RF pulse for experiments and simulations is calculated according to

$$\nu_2(t) = \nu_{2,\max} \cdot \cos \left(\int_0^t \left(\nu_{\text{RF}} - \frac{\Delta\nu_{\text{chirp}}}{2} + \frac{\Delta\nu_{\text{chirp}}}{t_{\text{chirp}}} \tau d\tau \right) \cdot a(t) \right) \quad (\text{S1})$$

with

$$335 \quad a(t) = \sin \left(\frac{\pi t}{2t_{\text{rise}}} \right) \quad \text{for } t < t_{\text{rise}}, \quad (\text{S2})$$

$$a(t) = \sin \left(\frac{\pi(t_{\text{chirp}} - t)}{2t_{\text{rise}}} \right) \quad \text{for } t > t_{\text{chirp}} - t_{\text{rise}}, \quad (\text{S3})$$

$$a(t) = 1 \quad \text{else.} \quad (\text{S4})$$

Table S1. Definition of parameters for chirp pulses and values used in simulations and experiments. *Amplitudes obtained from nutation experiments on ^{14}N at 23.9 MHz.

Parameter	Symbol	Value used in simulations	Value used in experiments
Center frequency	ν_{RF}	4 - 24 MHz	5 - 95 MHz
Bandwidth	$\Delta\nu_{\text{chirp}}$	0.062 - 8 MHz	0.062 - 8 MHz
Amplitude	$\nu_{2,\max}$	100 & 1000 kHz	140 kHz (500 W) & 62 kHz (100 W)
Pulse length	t_{chirp}	40 μs	10 - 200 μs
Rise/Fall time	t_{rise}	0.2 μs	0.2 μs

2. Supplementary figures

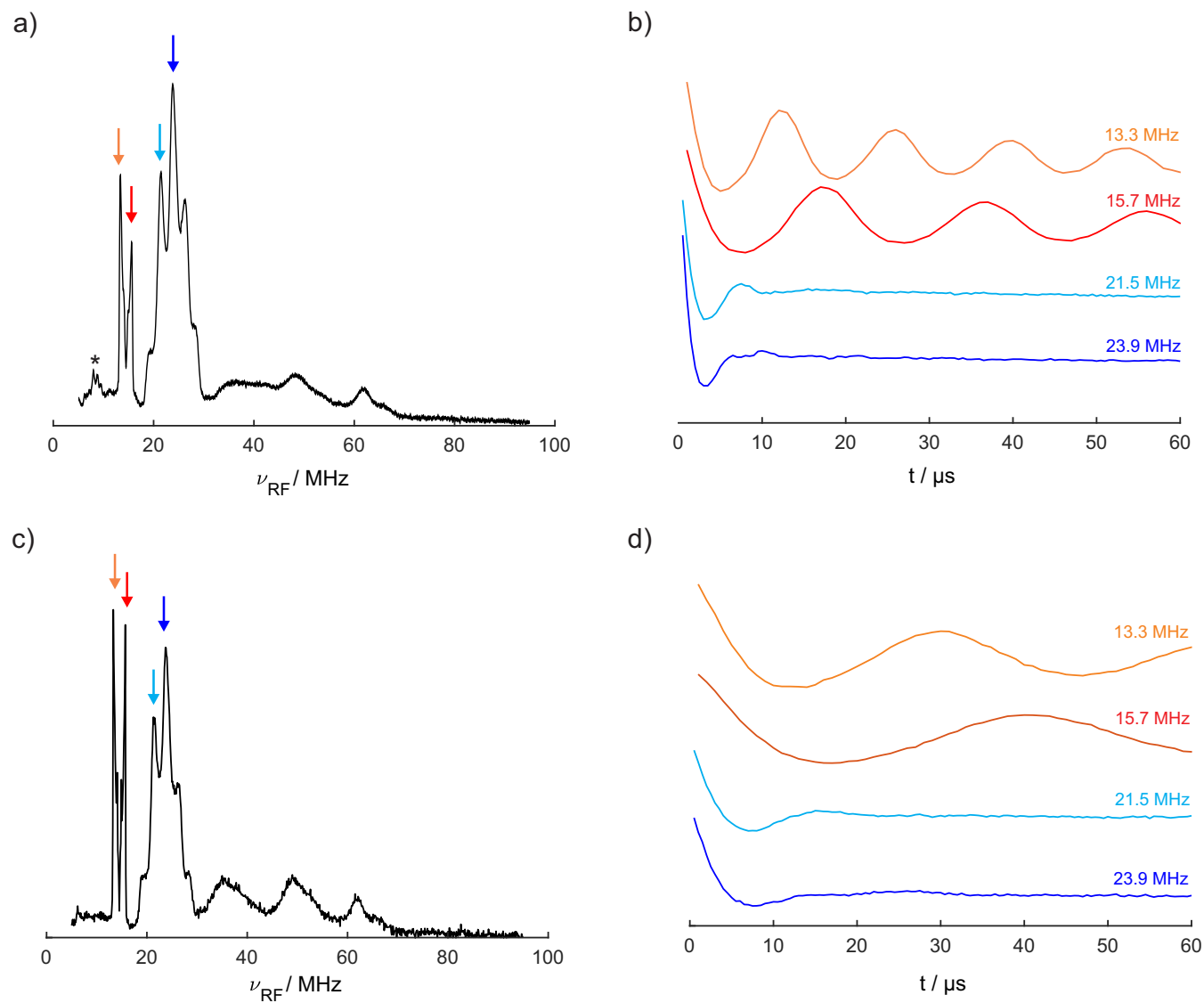


Figure S1. a) Davies ENDOR spectrum of CuTPP with a 500 W single frequency RF pulse of 3.5 μs length; $^{*14}\text{N}$ amplifier overtones. b) Rabi oscillations of four selected positions in the ENDOR spectrum. c) Davies ENDOR spectrum of CuTPP with a 100 W single frequency RF pulse of 18 μs length. d) Rabi oscillations of four selected positions in the ENDOR spectrum.

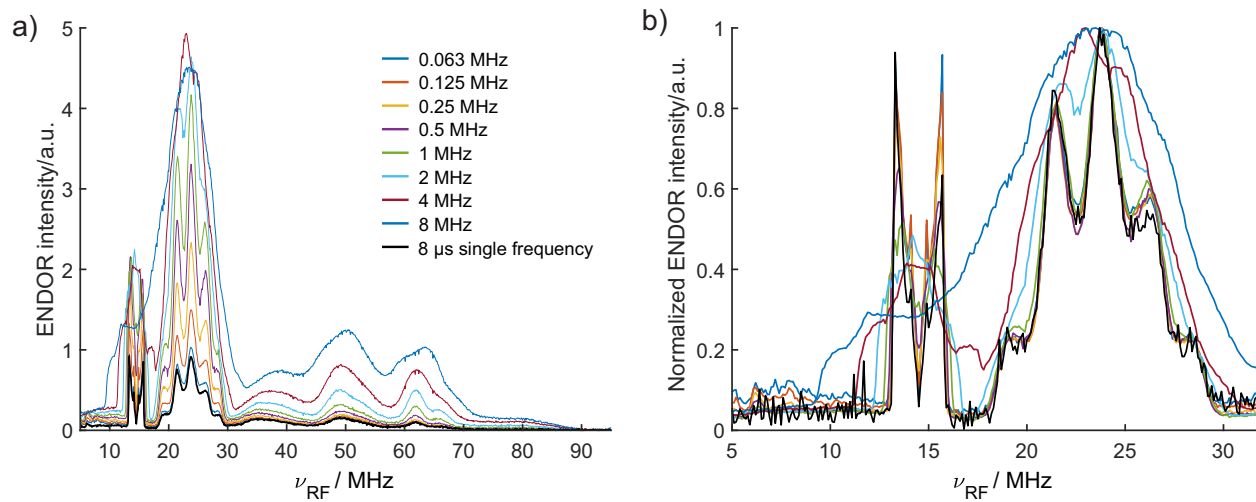


Figure S2. Davies ENDOR spectra of CuTPP with 80 μ s chirped RF pulses of different bandwidths compared to a single frequency (sf) ENDOR spectrum recorded with the same RF power (100 W): a) Absolute ENDOR intensity, b) Normalized ENDOR intensity.

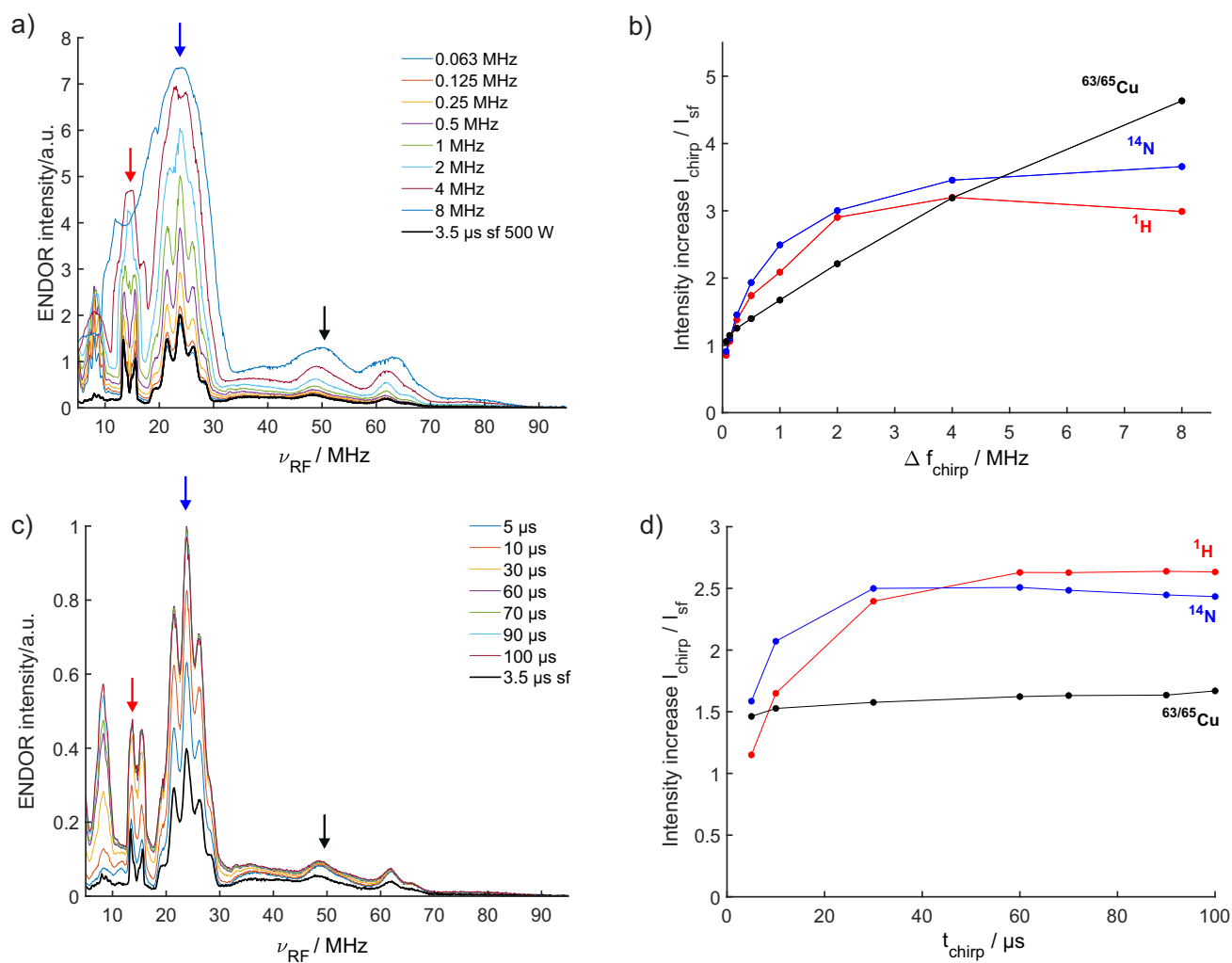


Figure S3. Davies ENDOR spectra of CuTPP with chirped RF pulses of (a) different bandwidths and (c) different pulse lengths compared to a single frequency (sf) ENDOR spectrum recorded with the same RF power of 500 W. b) and d): Relative intensity increase of the largest ^1H , ^{14}N and $^{63,65}\text{Cu}$ peaks in chirp ENDOR spectra compared to the intensities in the single frequency ENDOR spectrum.

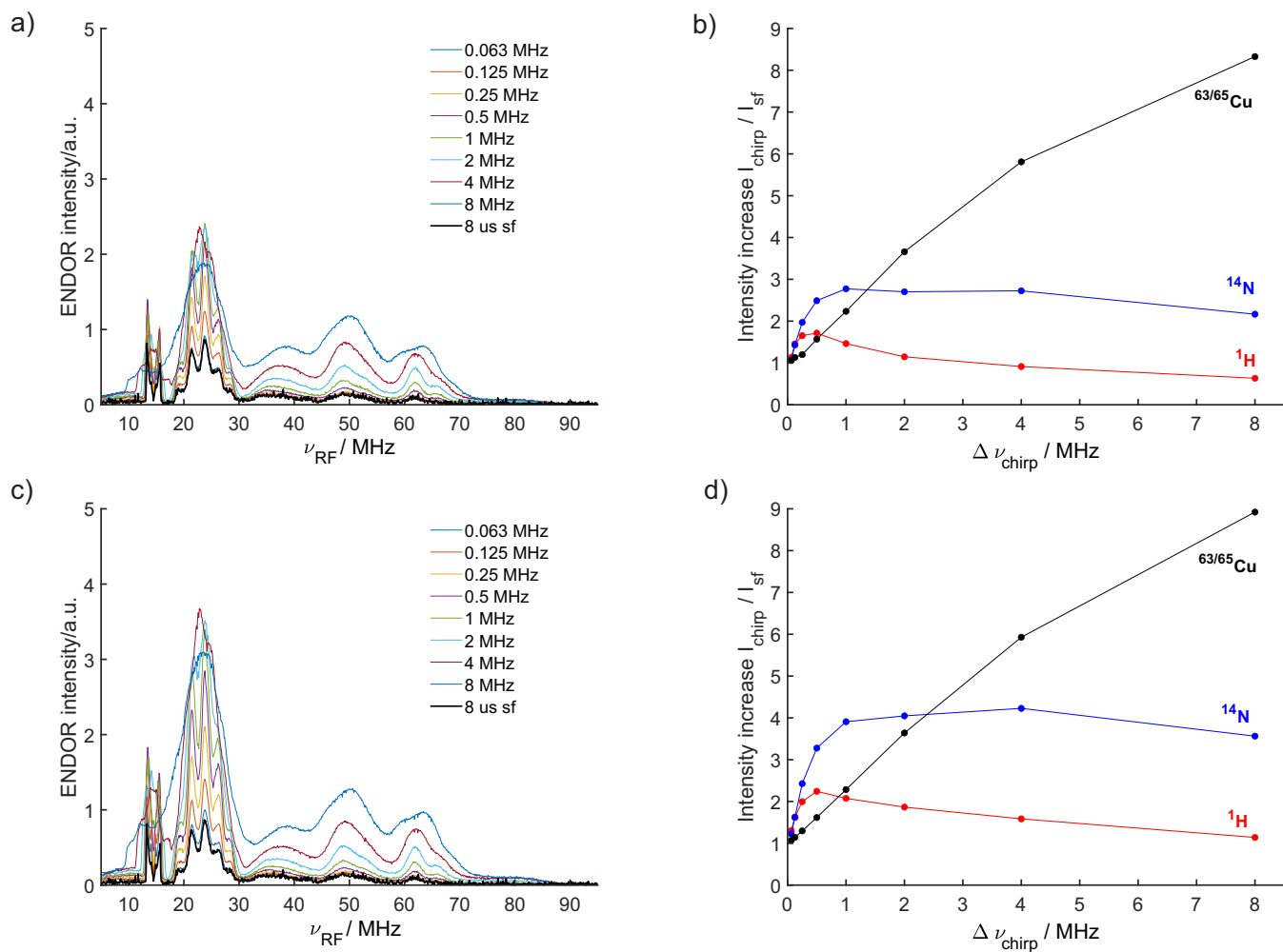


Figure S4. Davies ENDOR spectra of CuTPP with chirped RF pulses of different bandwidths with (a) 20 μ s pulse length and (c) 40 μ s pulse length using an RF power of 100 W. b) and d): Relative intensity increase of the largest ^1H , ^{14}N and $^{63,65}\text{Cu}$ peaks in chirp ENDOR spectra compared to the intensities in single frequency ENDOR spectrum.

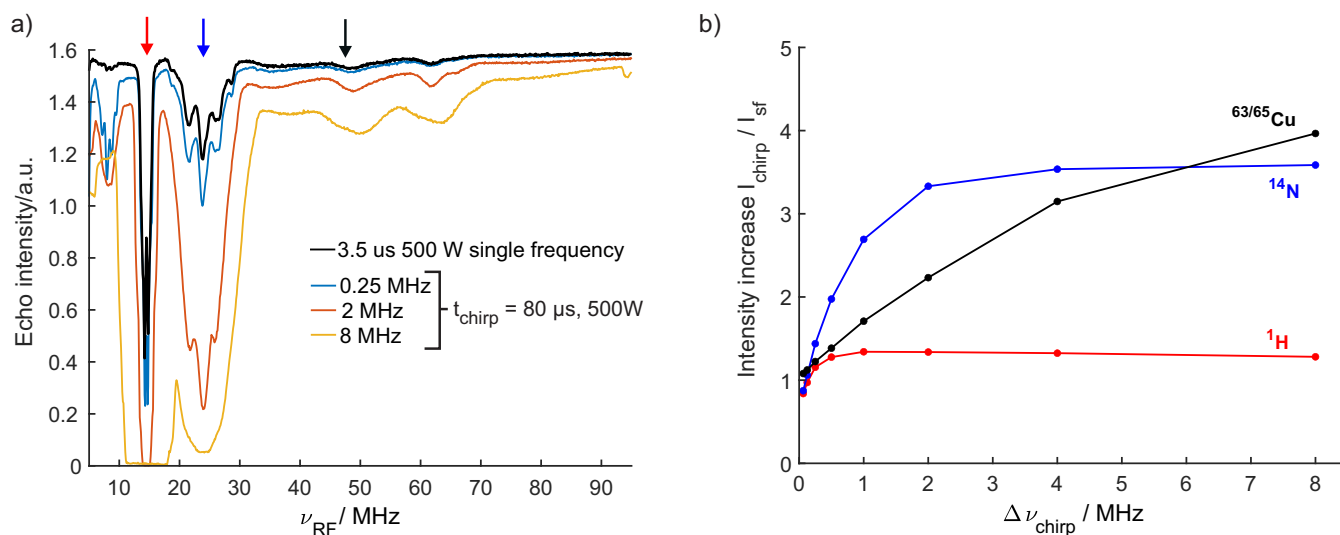


Figure S5. a) Mims ENDOR spectra of CuTPP with 80 μ s chirped RF pulses of different bandwidths compared to a single frequency (sf) ENDOR spectrum recorded with the same RF power (500 W). b) Relative intensity increase of the largest ^1H , ^{14}N and $^{63,65}\text{Cu}$ peaks in chirp ENDOR spectra using different RF-chirp bandwidths compared to the intensities in the single frequency ENDOR spectrum.

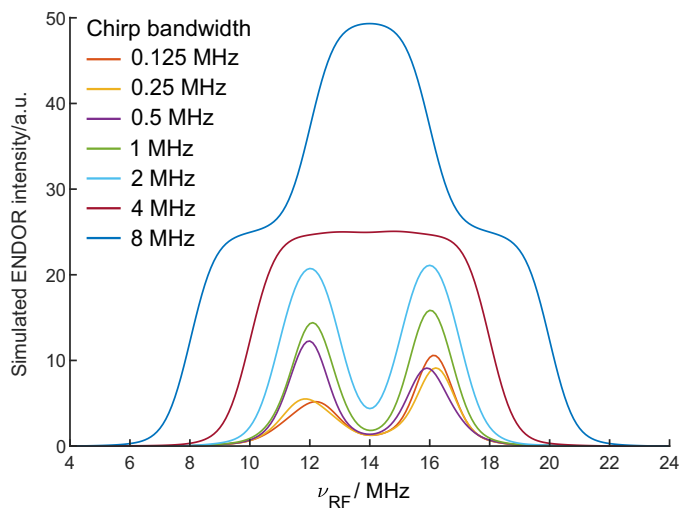


Figure S6. Simulated chirp ENDOR spectra for different chirp bandwidths of an electron-proton 2-spin system with a Gaussian distribution of hyperfine couplings ($\sigma = 0.5$ MHz). The chirp pulse has length of 40 μ s with 200 ns quarter sine wave weighted edges and an RF amplitude of $\nu_{2,max} = 1000$ kHz.

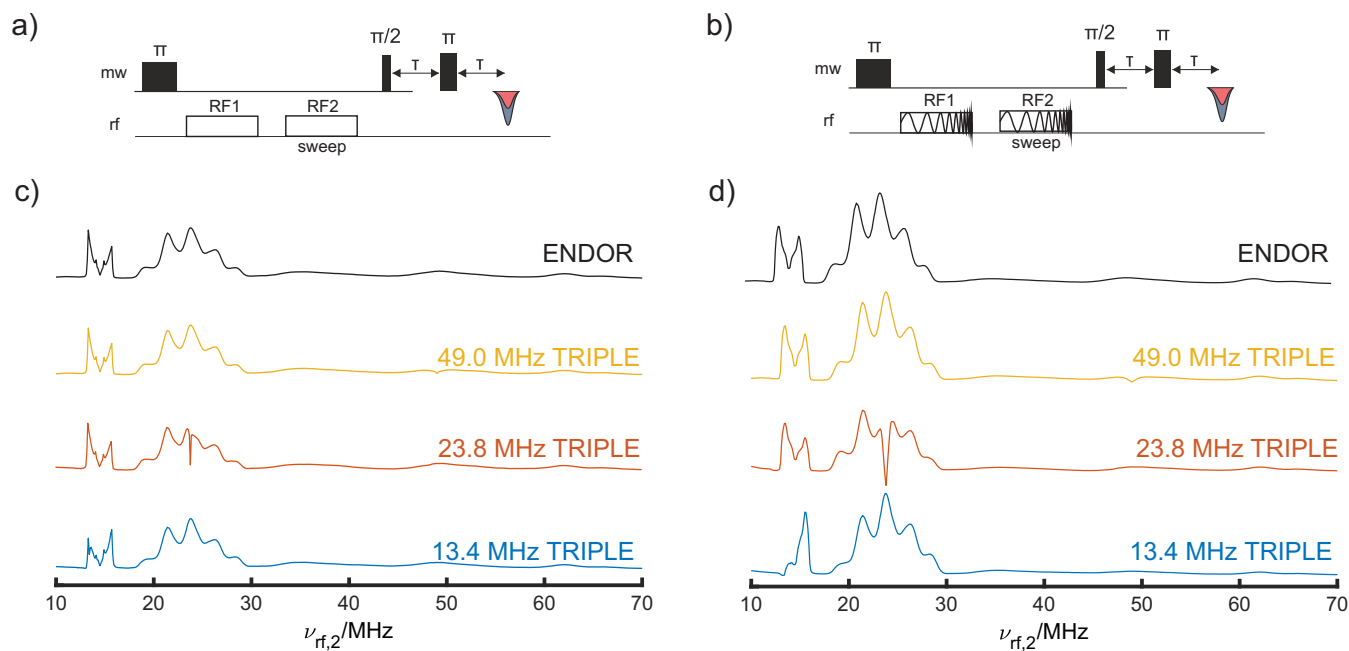


Figure S7. TRIPLÉ pulse sequences with (a) single frequency RF pulses and (b) chirped RF pulses. Selected TRIPLÉ traces and ENDOR spectrum of CuTPP with (c) single frequency RF pulses and (d) chirped RF pulses.