Supplementary Information

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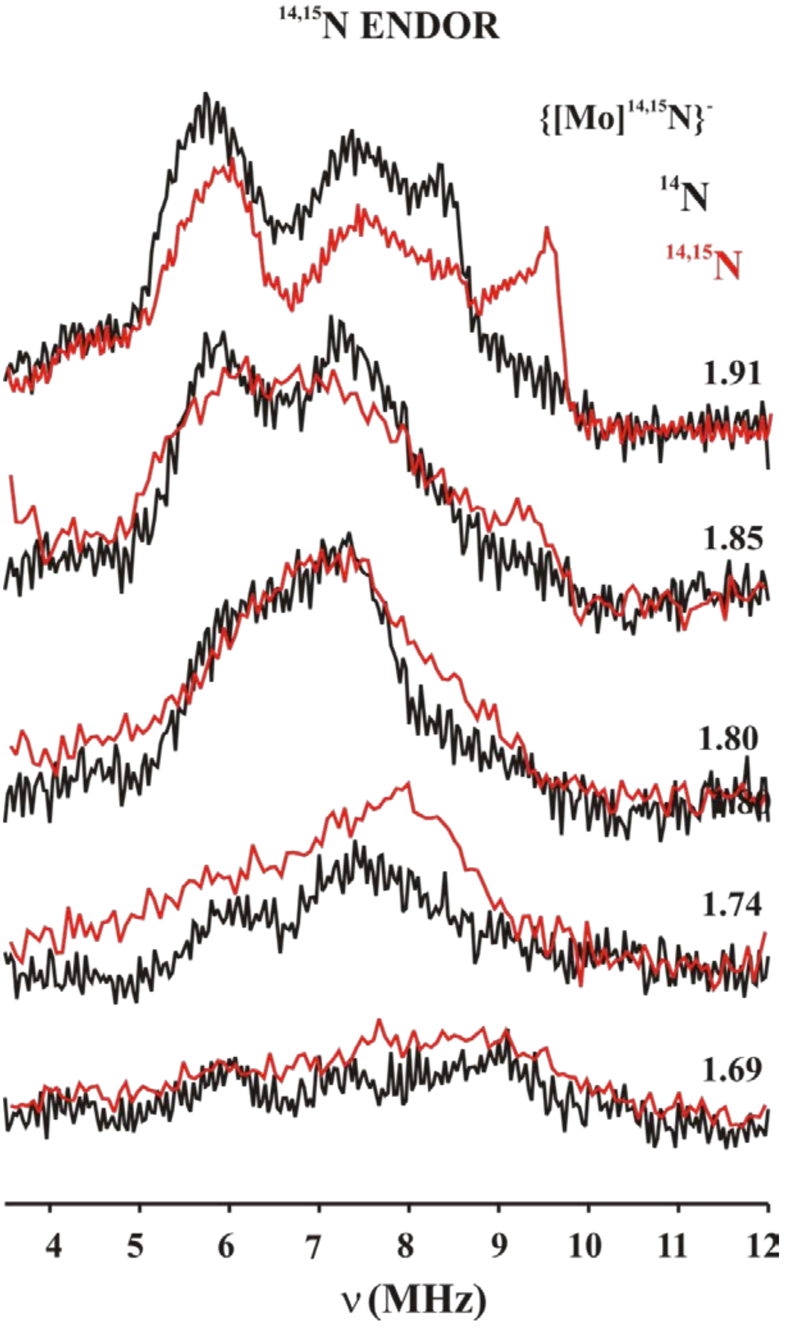

Figure SI 1. Orientation selective Davies ^{14,15}N ENDOR spectra of {[**Mo**]^{14}N}$^{-}$(black), and 50% ^{15}N labeled {[**Mo**]^{14,15}N}$^{-}$(red) recorded across the EPR envelope. microwave frequency, 34.881-34.965 GHz; π = 200 ns; τ = 700 ns; t_{rf} = 30 μs; repetition time, 50 ms; RF frequency randomly hopped.

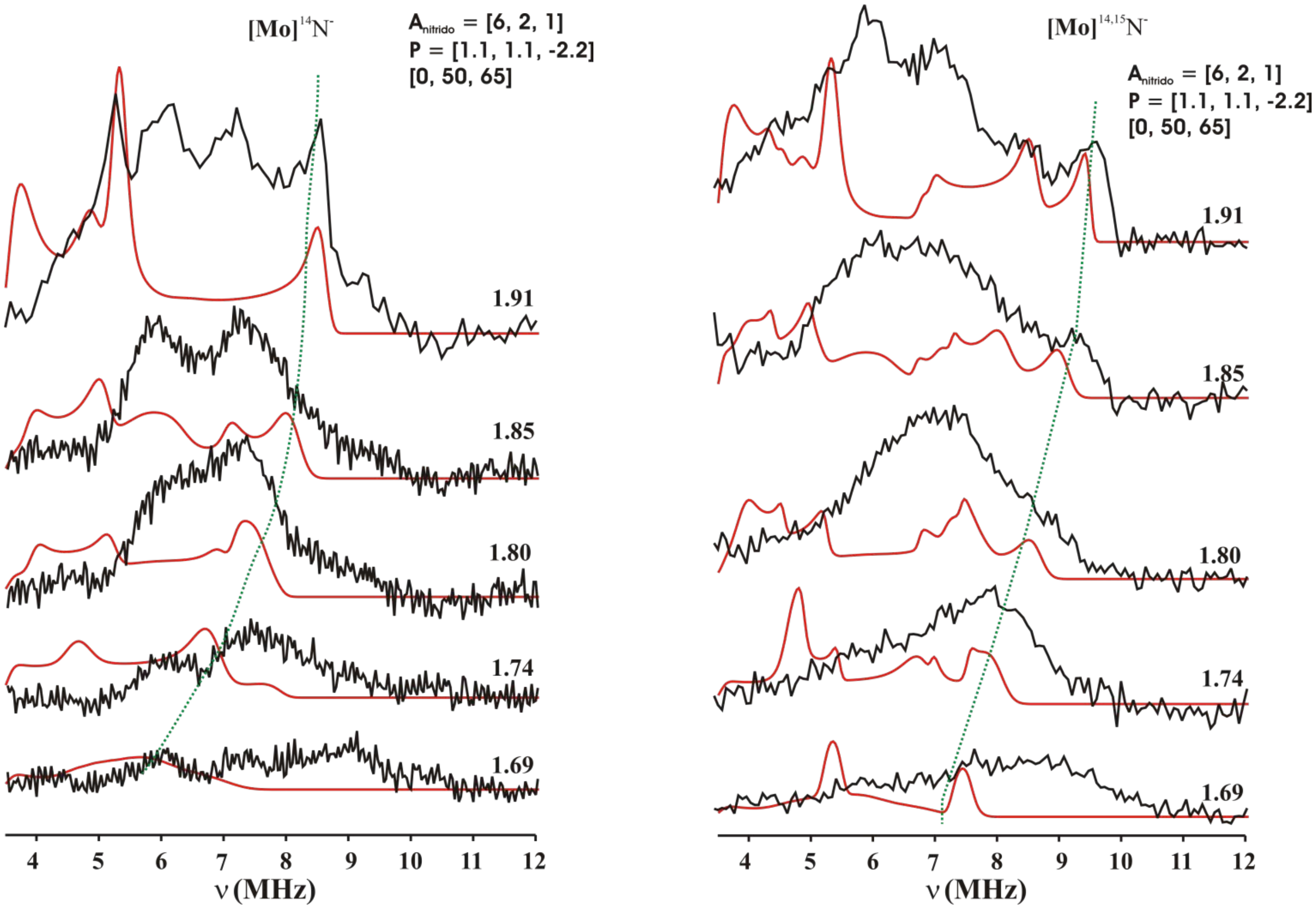

Figure SI 2. Simulated (in red) orientation selective Davies ^{14}N ENDOR spectra of {[**Mo**]^{14}N}$^-$ (left) and 50% ^{15}N labeled {[**Mo**]^{14,15}N}$^-$ (right). The simulated ENDOR spectra considered only Nitride nitrogen with parameters from the DFT calculations. For parameters see text and figure.

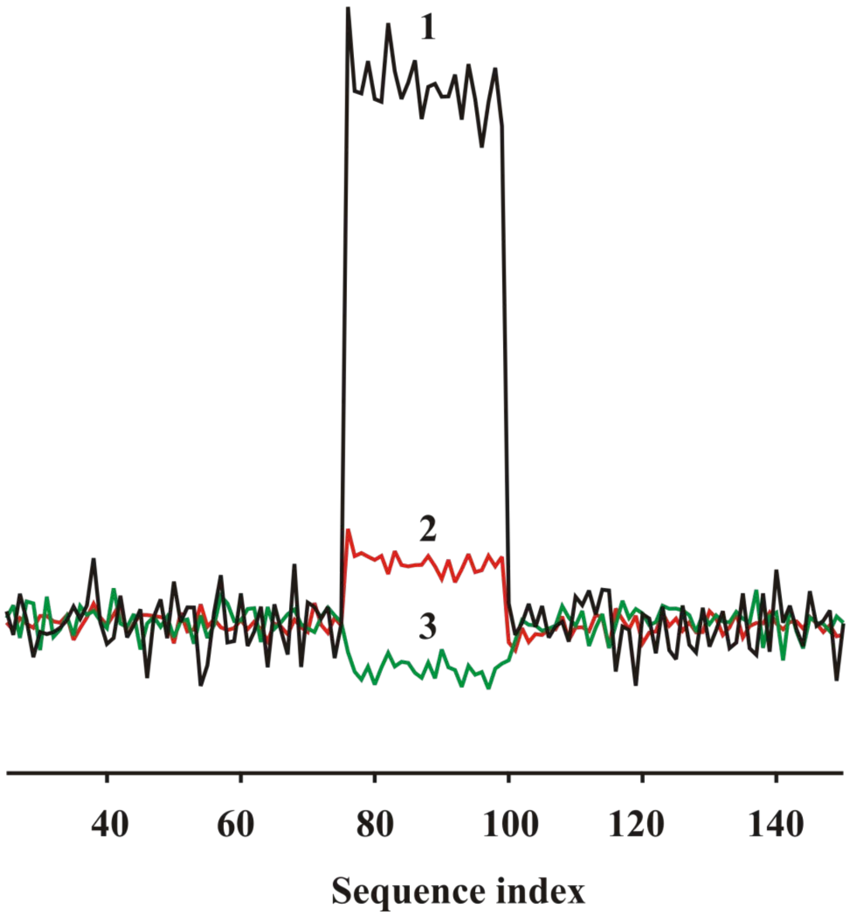

Figure SI 3. Variable Mixing Time (VMT) PESTRE spectra recorded at ν_+ peak of the ^{15}N nitride. The mixing time is increased in the order of 1(5 us),2 (1 ms), 3 (5 ms). Other conditions same as fig. 9.

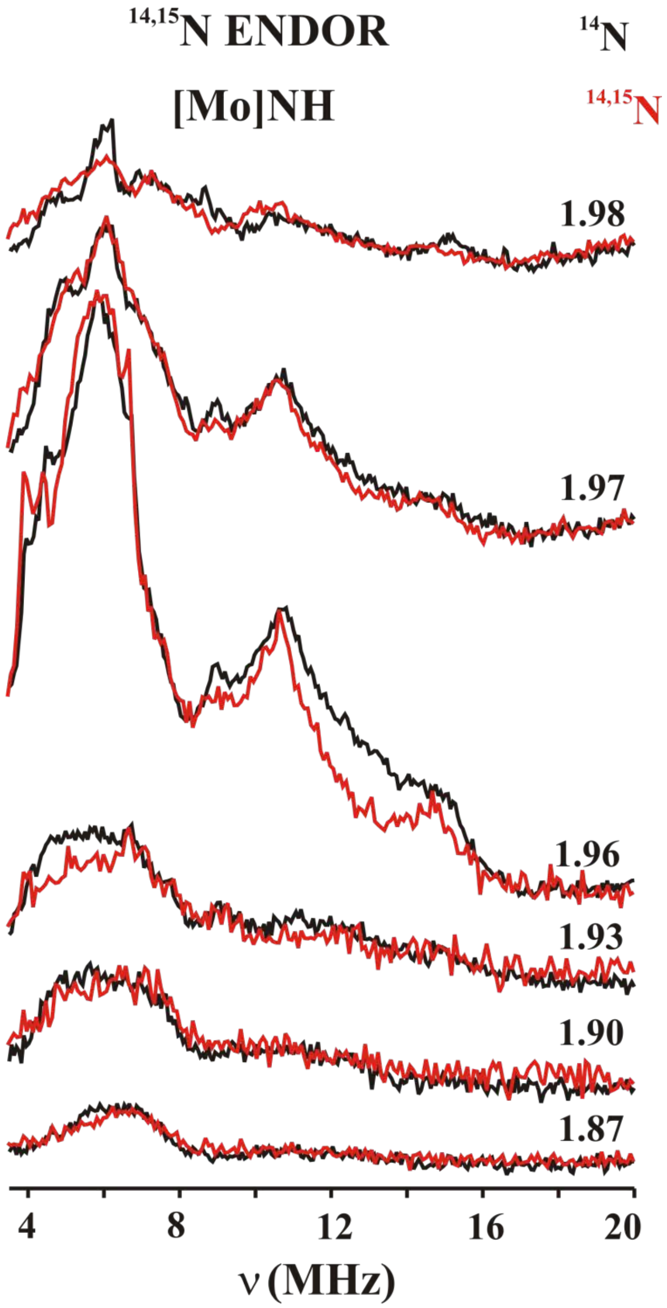

Figure SI 4. Davies ^{14,15}N ENDOR of [**Mo**]^{14}NH (black), and 50% ^{15}N labeled [**Mo**]^{14,15}NH (red) recorded across the EPR envelope. Conditions as in fig 9.

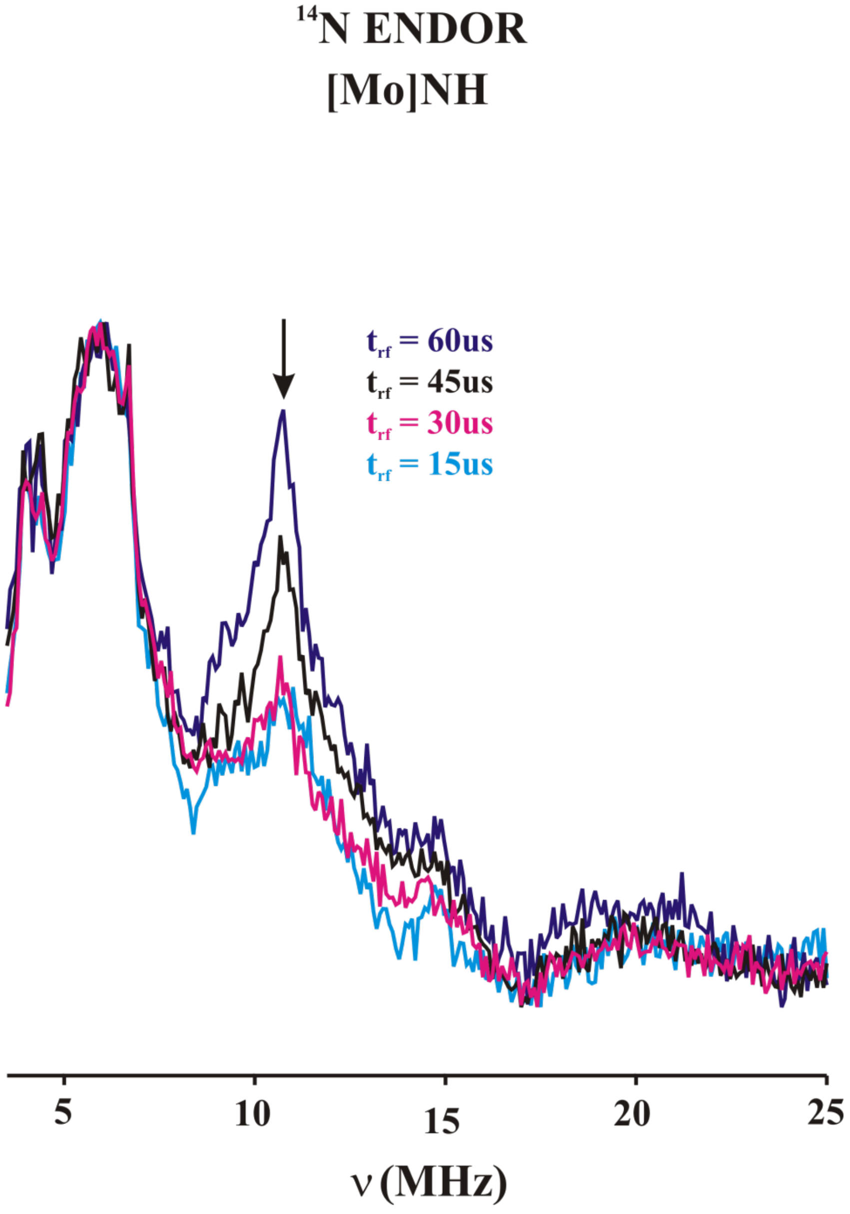

Figure SI 5. Davies ^{14,15}N ENDOR of [**Mo**]^{14}NH recorded at various length scale of the RF pulse t_{rf}. The arrow shows the double quantum peak of a ^{14}N nitrogen with A~3 MHz. conditions as in fig. 9b.

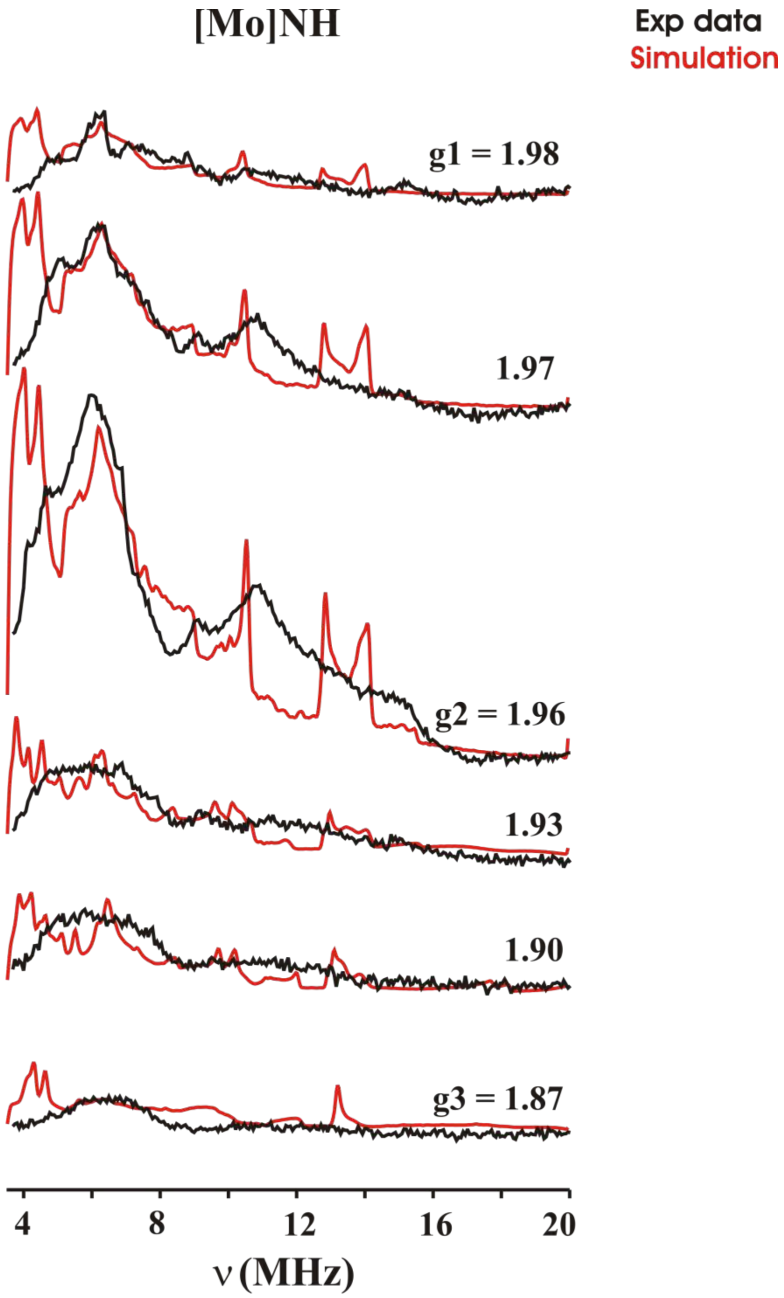

Figure SI 6. Davies ^{14}N ENDOR of [**Mo**]^{14}NH recorded across the EPR envelope. ^{14}N simulations that include the imido and the three amido nitrogens using calculated parameters, are in red (see text for parameter values). In these simulations, the intensity for $\nu \lesssim 8$ MHz is dominated by the -^{14}NH; the intensity (including all peaks) at higher frequencies is associated with the ^{14}N of the TPP ligand.

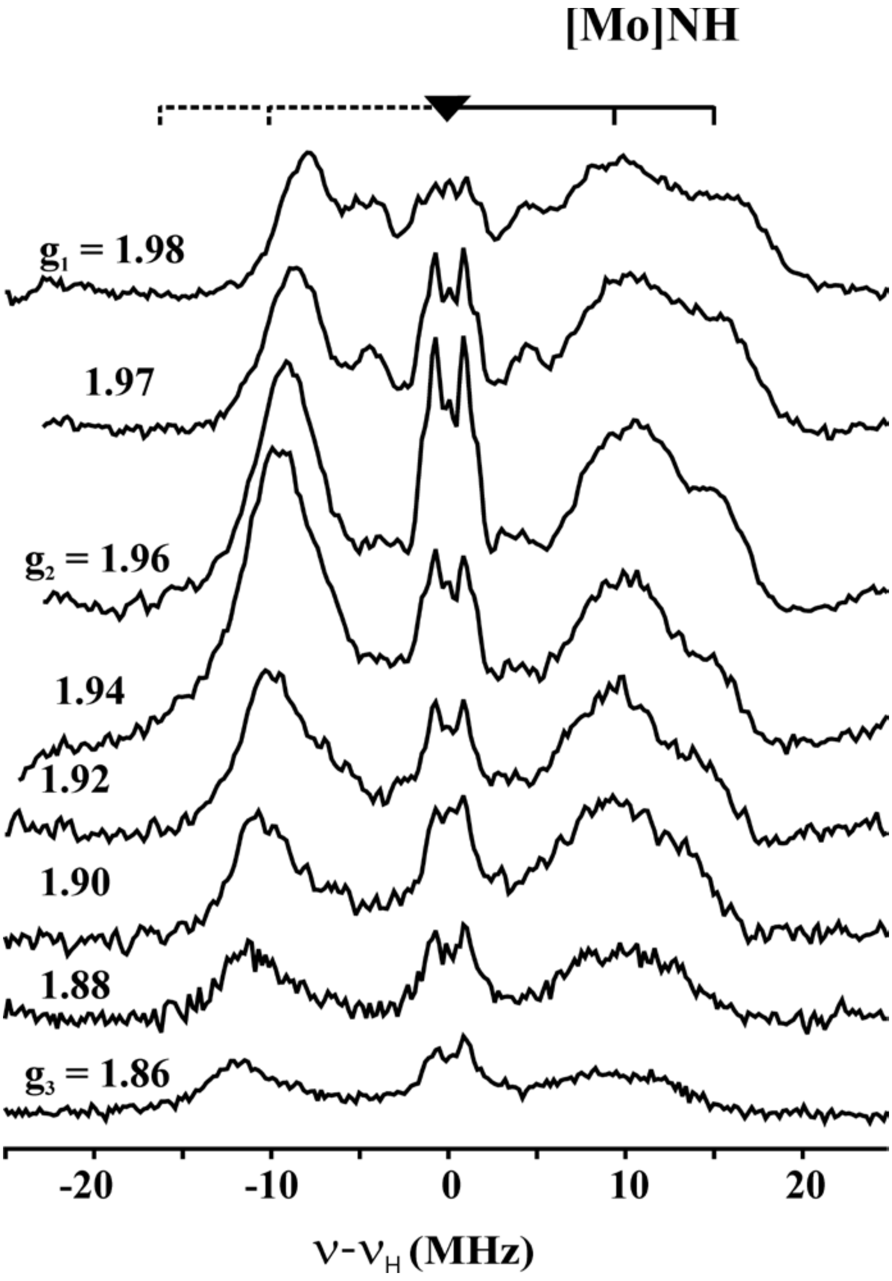

Figure SI 7. Orientation selective Davies ^{1}H ENDOR spectra of [**Mo**]NH recorded at the selected fields across the EPR envelope. The ‘goalposts’ on the g_1 spectrum show the tentative assignment to ^{1}H signls from two N^{1}H conformers. Estimated hyperfine couplings: $A_1(1)$ ~ 20 MHz; $A_1(2)$ ~ 30 MHz; we further estimate, $A_3(1)$ ~ 16 MHz; $A_3(2)$ ~ 22 MHz. Conditions: microwave frequency, 34.881-34.965 GHz; π = 120 ns; τ = 700 ns; t_{rf} = 60 μs; repetition time, 50 ms; RF frequency randomly hopped.

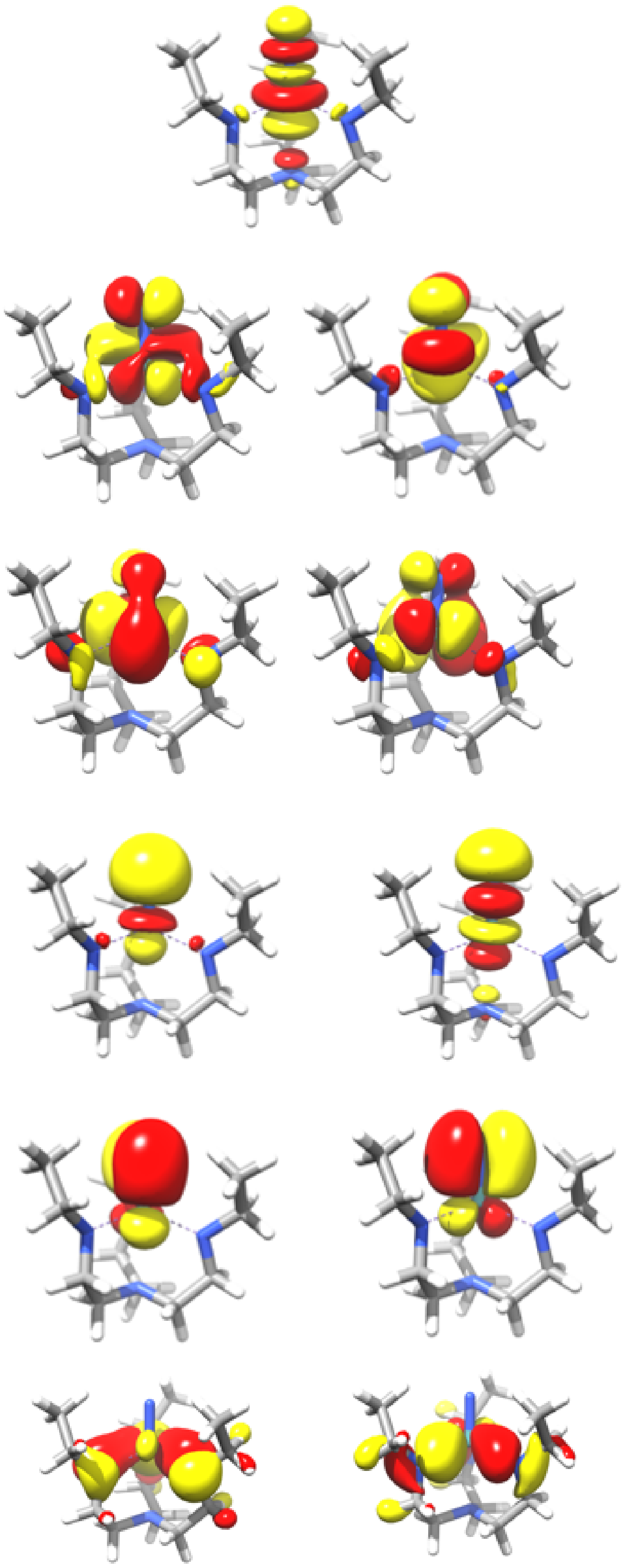

Figure SI 8. Active orbitals of {[**Mo**]N}$^-$ in CASSCF(13,11) and NEVPT2(13,11) calculations.

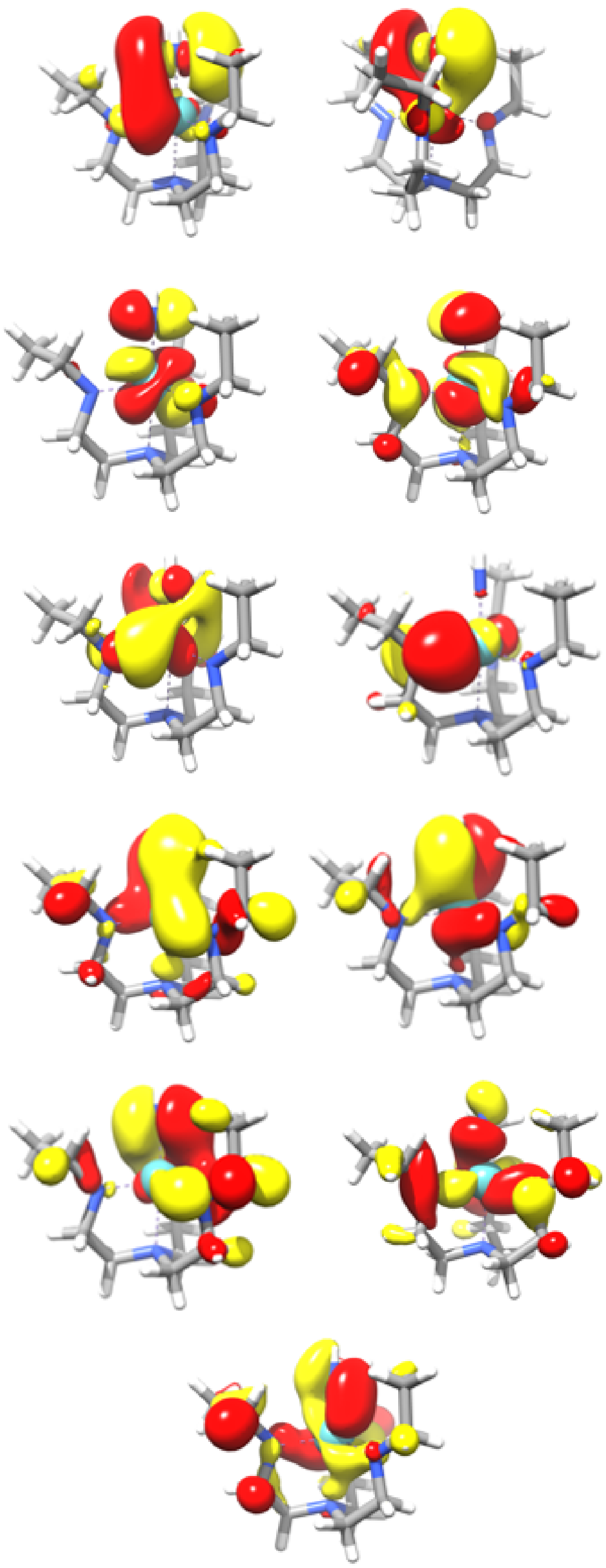

Figure SI 9. Active orbitals of [**Mo**]NH in CASSCF(13,11) and NEVPT2(13,11) calculations.

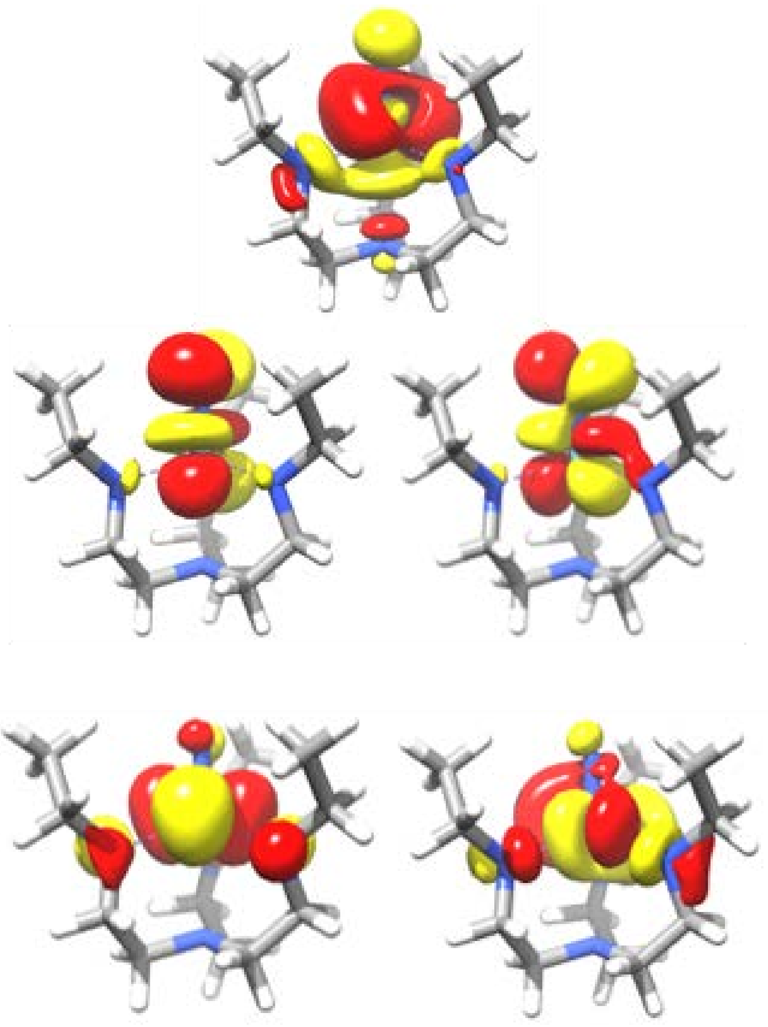

Figure SI 10. Active orbitals of {[**Mo**]N}$^-$ in CASSCF(1,5) and DDCI2(1,5) calculations.

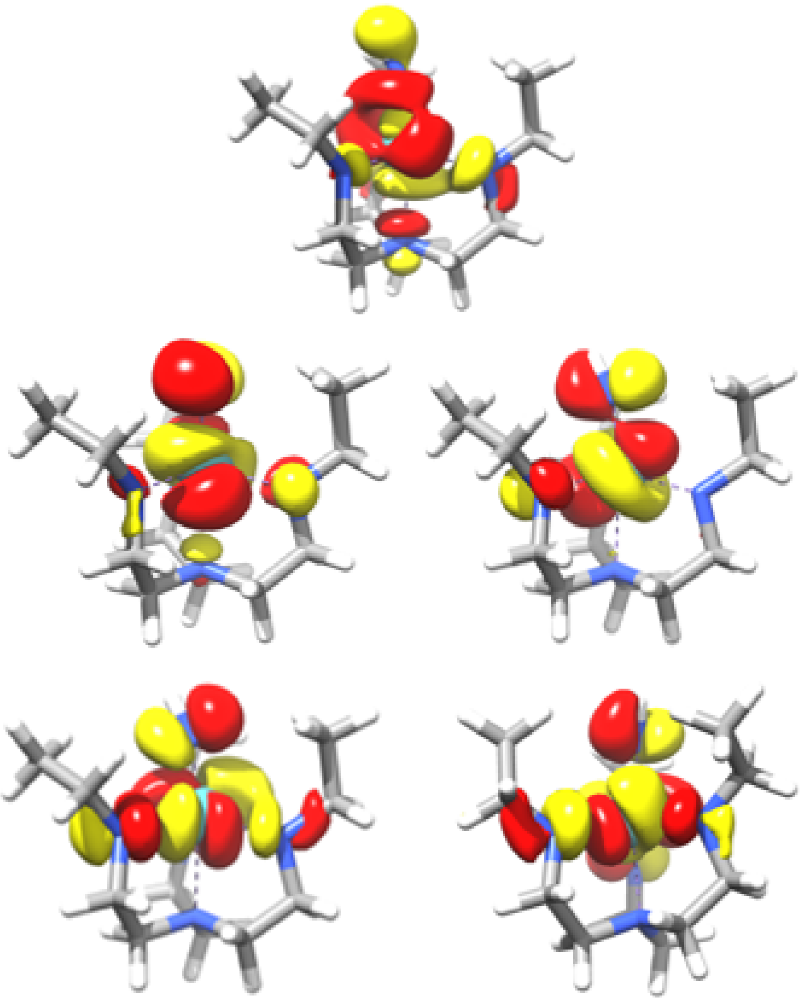

Figure SI 11. Active orbitals of [**Mo**]NH in CASSCF(1,5) and DDCI2(1,5) calculations.

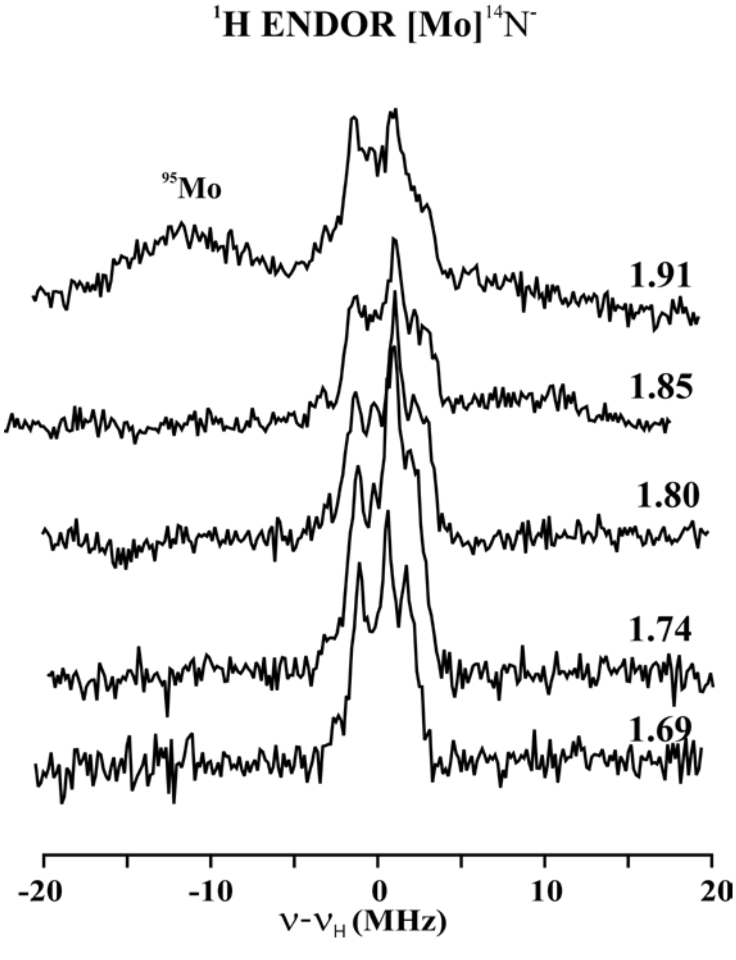

Figure SI 12. Orientation selective Davies ^{1}H ENDOR spectra of [**Mo**]NH recorded at the selected fields across the EPR envelope. Conditions: microwave frequency, 34.881-34.965 GHz; π = 120 ns; τ = 700 ns; t_{rf} = 60 μs; repetition time, 50 ms; RF frequency randomly hopped.

Townes-Dailey Quadrupole Analysis

The quadrupole parameter can be discussed in terms of the Townes-Dailey model, in which the quadrupole parameter for Mo-bound nitride is simply determined by the charge densities in the nitride 2p orbital, being proportional to the difference between the charge density in the nitride 2pσ orbital along the Mo-N bond (denoted N_3) and the average of the densities in the two orthogonal 2pπ orbitals (N_1, N_2):

$$|e^2qQ/e^2qQ_0| = |N_3 - (N_1 + N_2)/2| \approx 0.4$$

where, e^2qQ_0 = -(8-10) MHz, for a single electron in a 2p orbital. For clarity, let us discuss the nitride as bonding to Mo solely through its three 2p orbitals, 2pσ, with occupancy, *b*, and two 2p π orbitals, occupancy *a* for each. In this limiting case, $|e^2qQ/e^2qQ_0| = |b-a| = 0.4$, namely there is a large differential electron donation to Mo of ~ 0.4 electrons between σ and π bonds. Although it intuitively seem likely that σ donation is more effective than π donation, and thus that (b-a) < 0, the sign of (b-a) actually is not obvious from simple inspection. The interaction between the filled 2pσ of nitride and empty $4d_{z2}$ of Mo is much greater than that between the two filled 2pπ and empty $4d_{zy/yz}$, but so is the difference between the p and d atomic orbital energies in trigonally symmetric $\{[\mathbf{Mo}]^{14}N\}^-$. The alternative assumption of s-p hybridization on nitride yields analogous conclusions about electron donation to those presented here.

Overall, the results of this simplified treatment qualitatively parallel those of the DFT computations, although overestimating the difference between the σ and π donation.