

New Tetrazole-based Cu(I) Homo- and Heteroleptic Complexes with Various Diphosphine Ligands: Synthesis, Characterization and Study of their Redox and Photophysical Properties

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SUPPORTING INFORMATION

Selected ESI-MS spectra

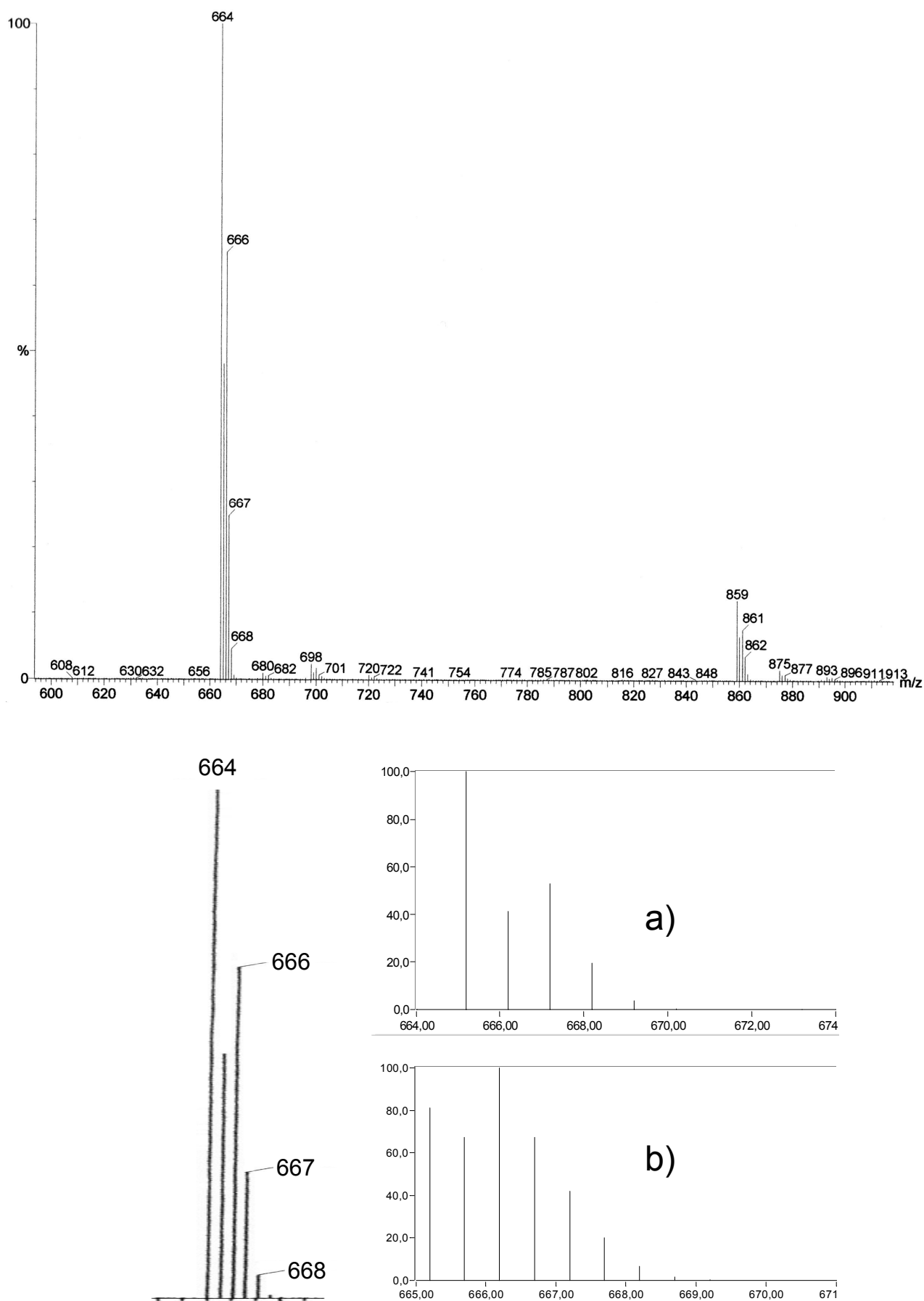


Fig. S1. $[\text{Cu}_n(\text{N}^{\wedge}\text{N})_n(\text{dppe})_n]^{n+}$ ($n = 1, 2$): (top) ESI-MS spectrum (positive ions region) and (down) comparison of the experimental isotopic pattern distribution (left) with those simulated for $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{dppe})]^+$ (a) and $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppe})_2]^{2+}$ (b), respectively.

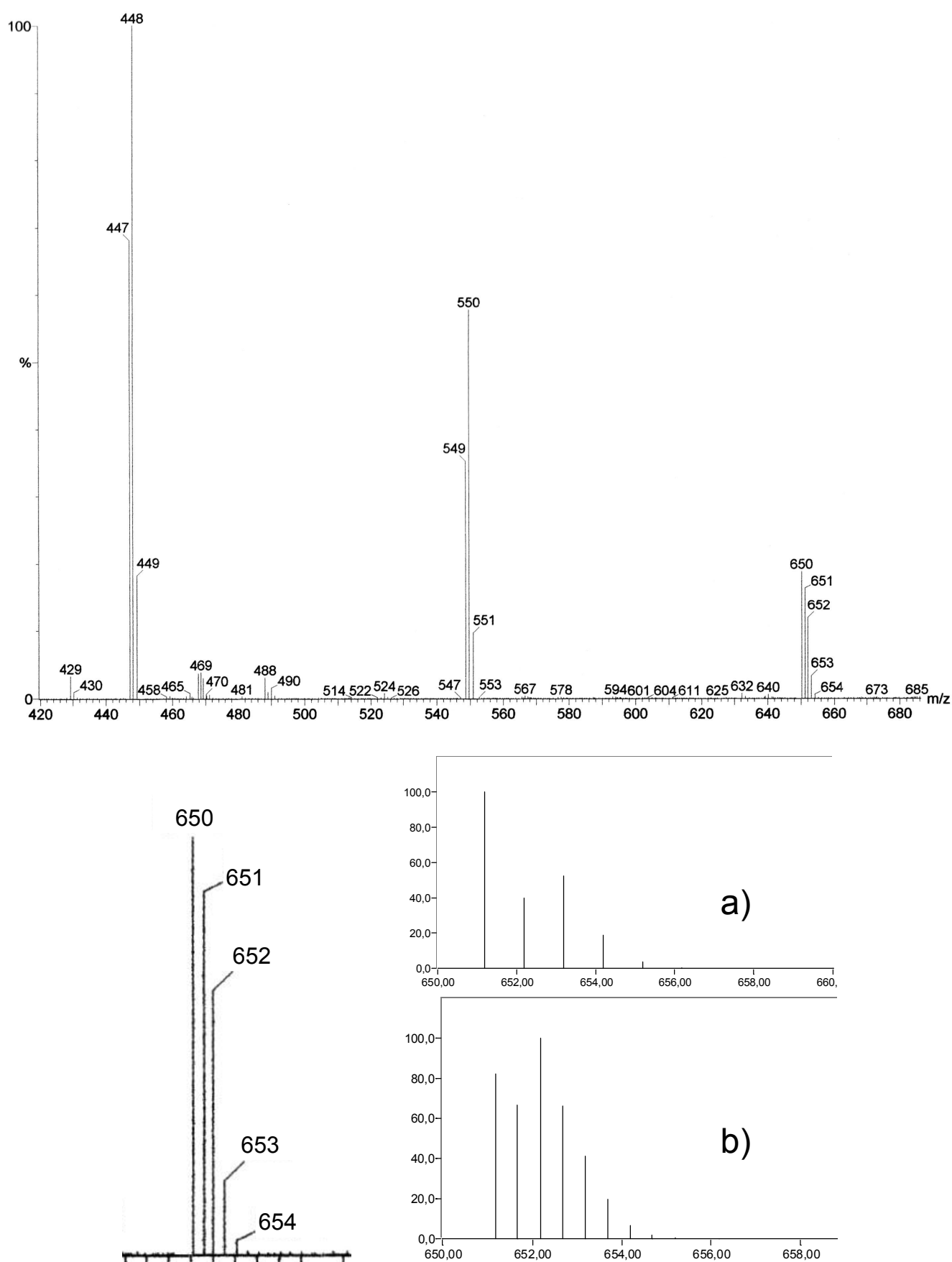


Fig. S2. (top) ESI-MS spectrum (positive ions) of $[\text{Cu}_n(\text{N}^{\wedge}\text{N})_n(\text{dppm})_n]^{n+}$ ($n = 1,2$) and (down) comparison of the experimental isotopic pattern distribution (left) with those simulated for $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{dppm})]^+$ (a) and $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppm})_2]^{2+}$ (b), respectively.

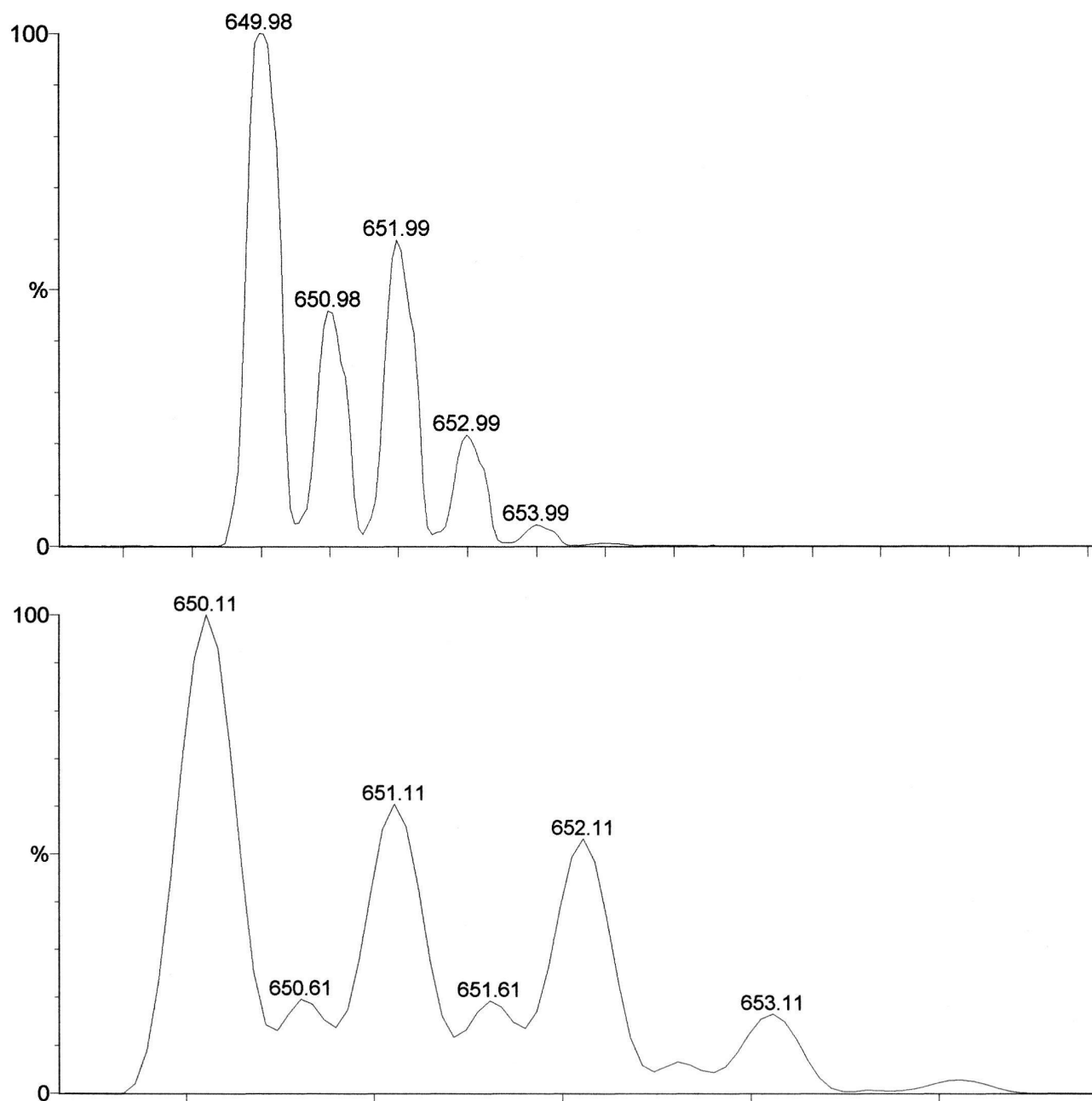


Fig. S3. High Resolution ESI-MS spectra (positive ions) of $[\text{Cu}_n(\text{N}^{\wedge}\text{N})_n(\text{dppm})_n]^{n+}$ ($n = 1, 2$) showing the gradual appearance (bottom) of the peaks spaced by $1/2 m/z$ units that are due to the dinuclear dimeric species $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppm})_2]^{2+}$.

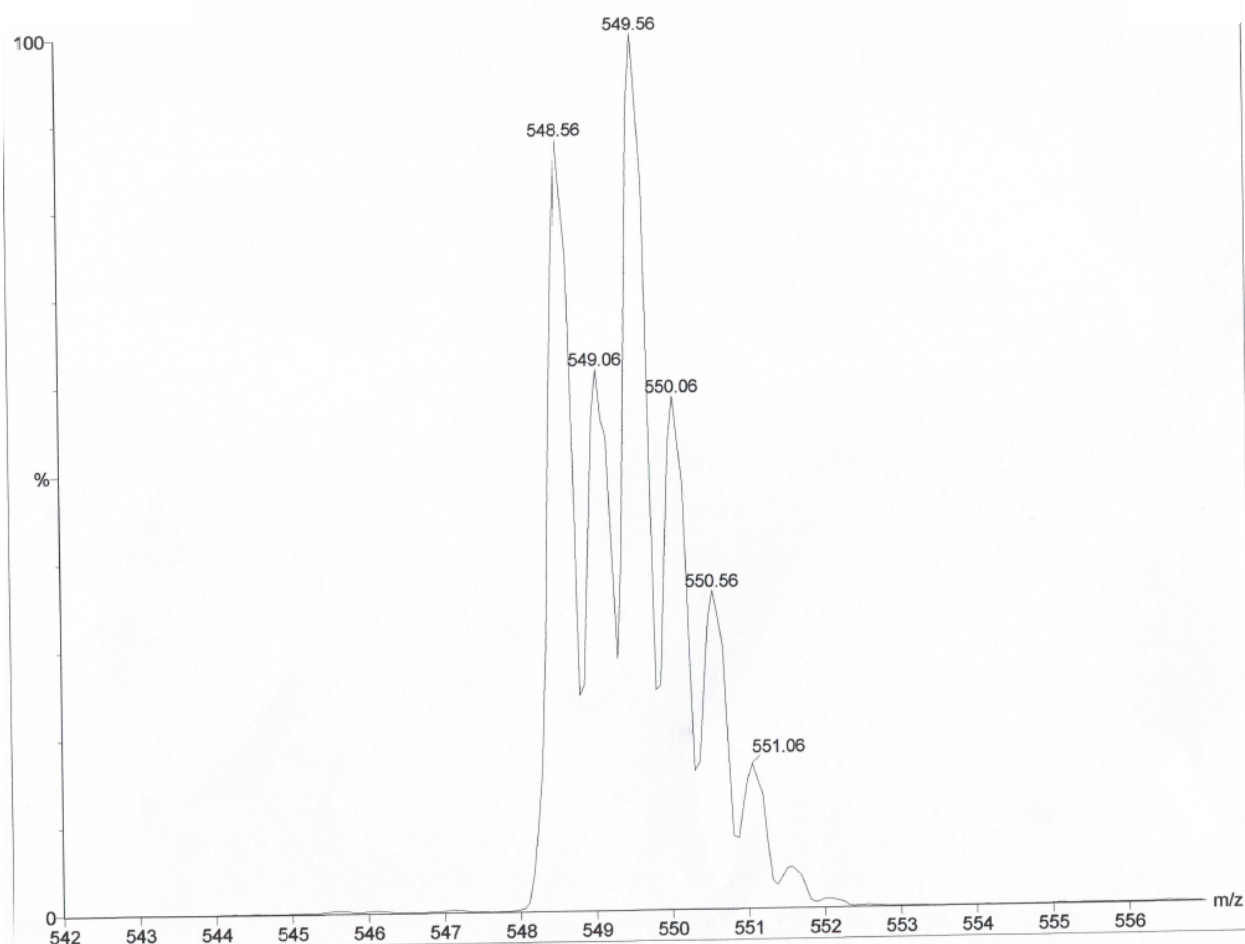


Fig. S4. High Resolution ESI-MS spectra (positive ions) of $[\text{Cu}_n(\text{N}^{\wedge}\text{N})_n(\text{dppm})_n]^{n+}$ ($n = 1,2$) showing the isotopic distribution pattern, with peaks spaced by $1/2 m/z$ units, of the signal centered at 550 m/z , that is due to bis-cationic dimer $[\text{Cu}_2(\text{N}^{\wedge}\text{N})(\text{dppm})_2]^{2+}$.

NMR (^1H , ^{13}C , ^{31}P) spectra

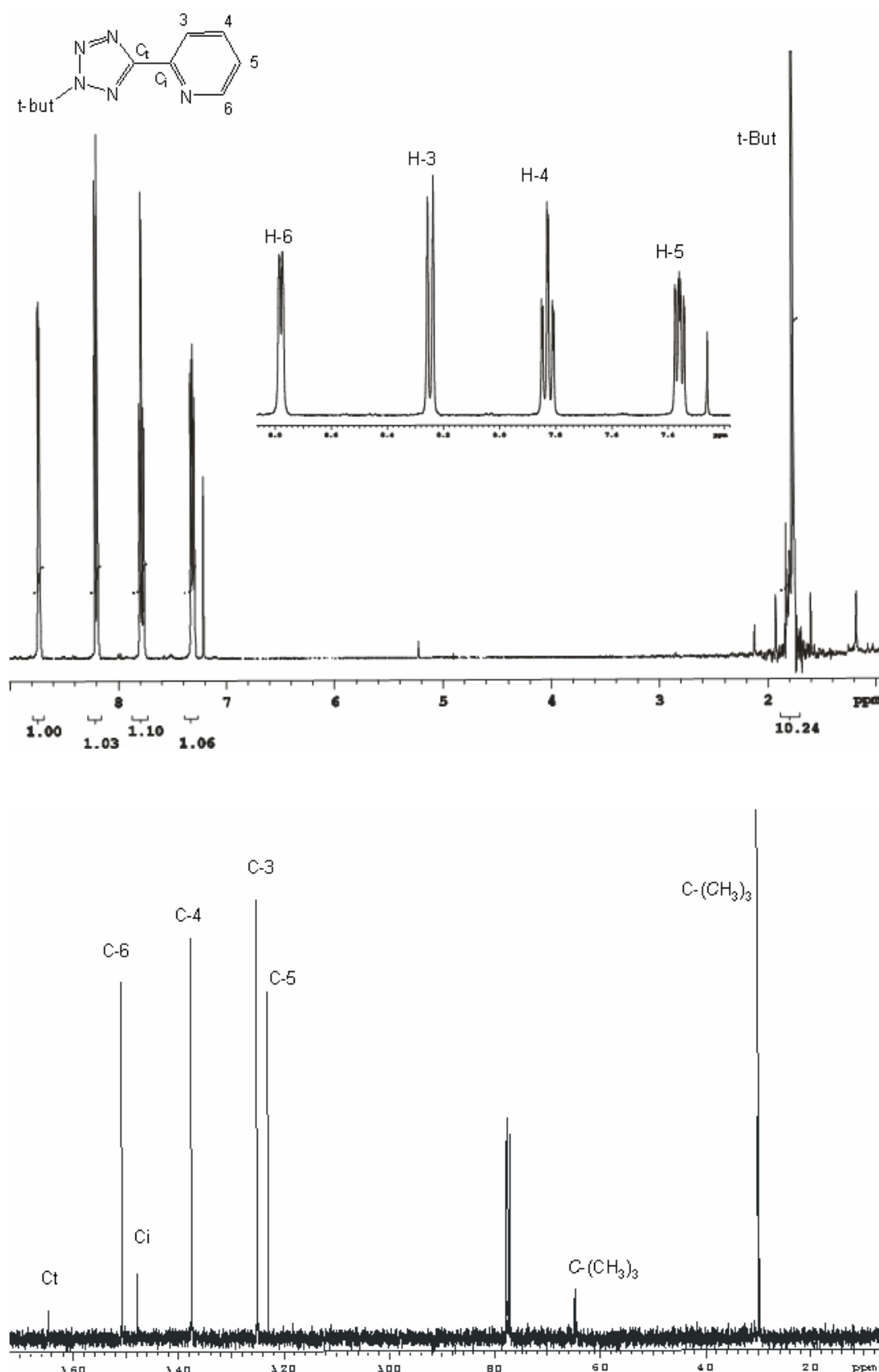


Fig. S5. ¹H (CDCl₃, 400 MHz, r.t., top) and ¹³C (CDCl₃, 101 MHz, r.t., bottom) NMR spectra of the free ligand N^N

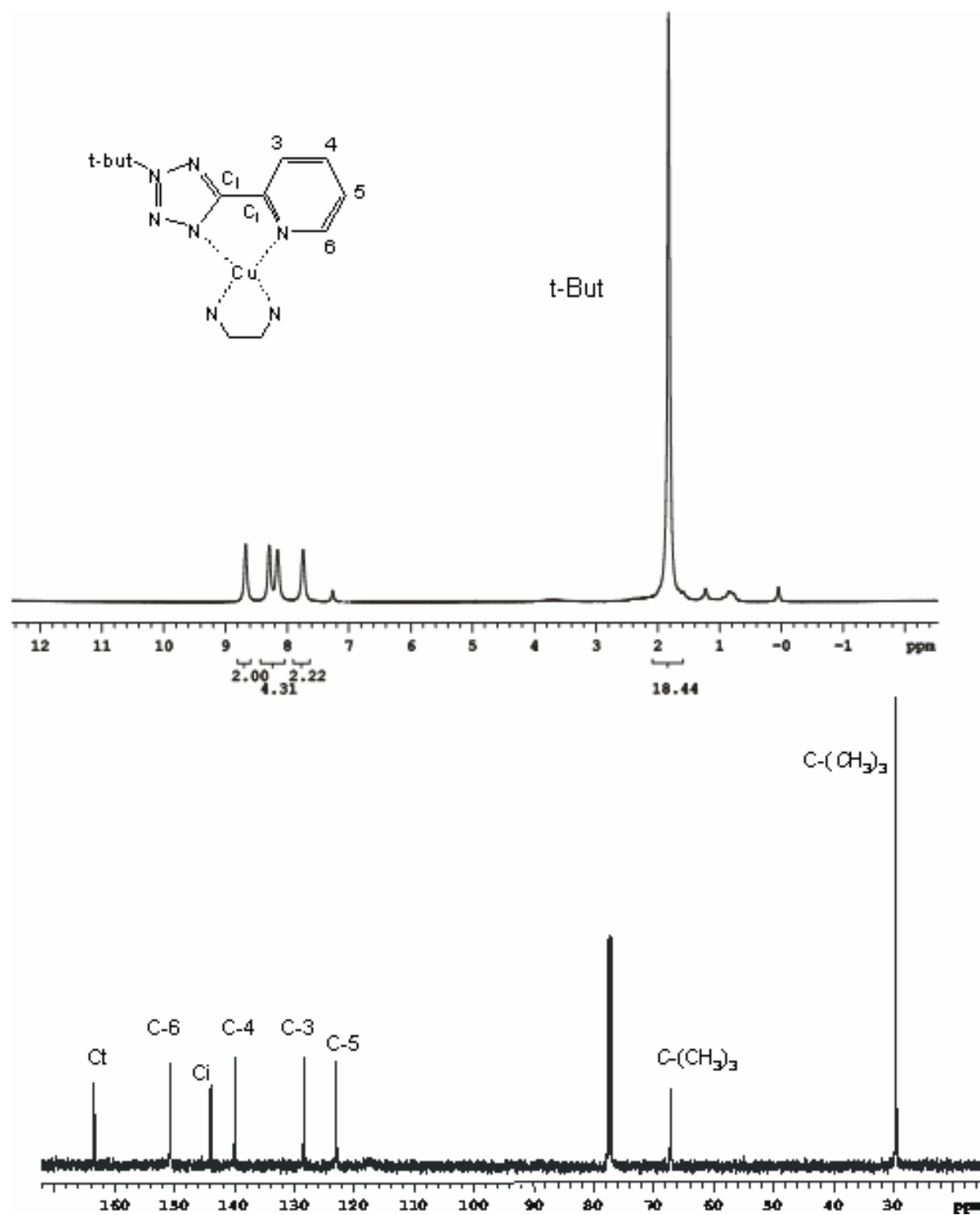


Fig. S6. ^1H NMR (CDCl_3 , 400 MHz, r.t., top) and ^{13}C NMR (CDCl_3 , 101 MHz, r.t., bottom) spectra of the homoleptic complex $[\text{Cu}(\text{N}^{\wedge}\text{N})_2][\text{BF}_4]$.

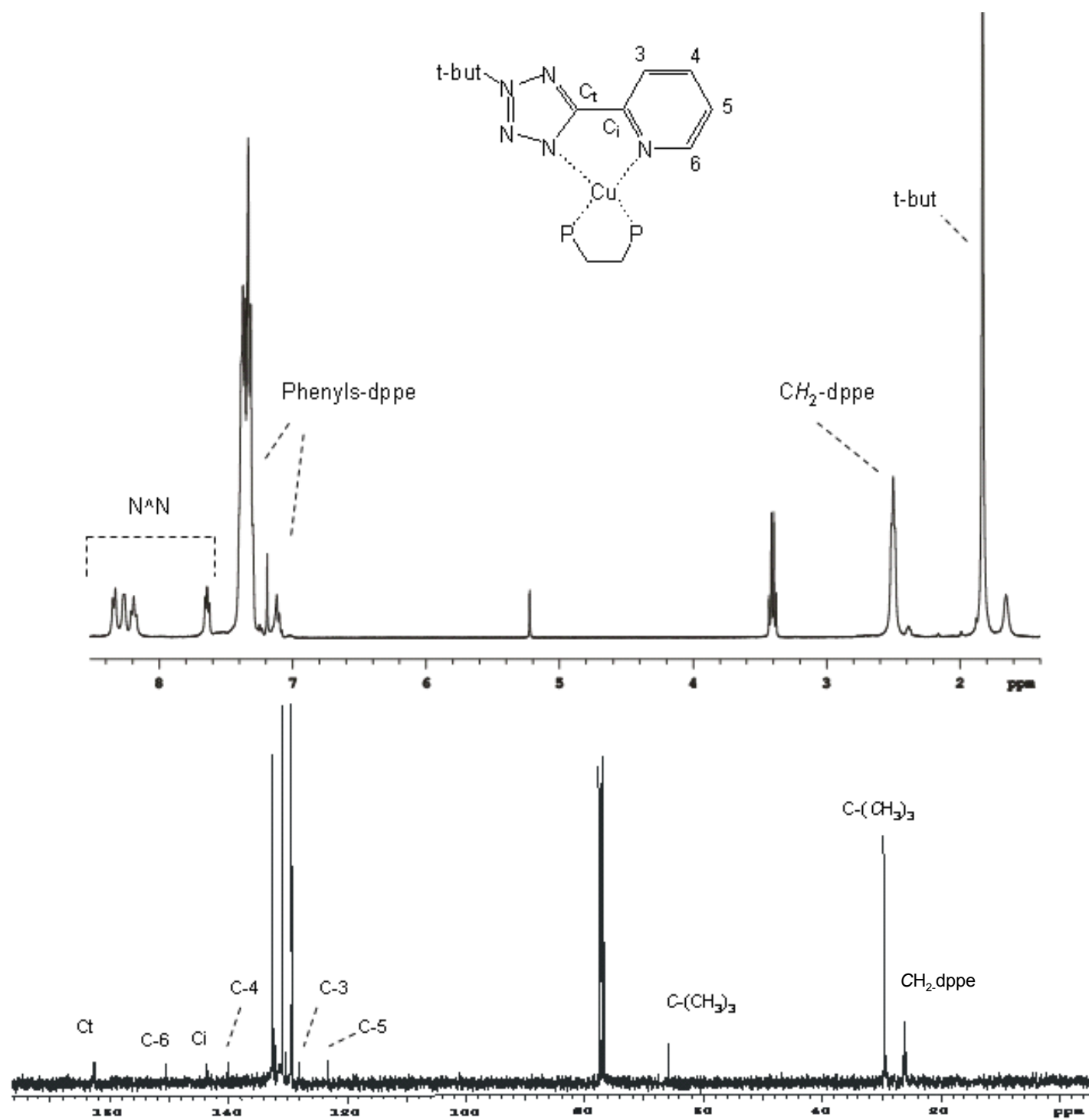


Fig. S7. ¹H NMR (CDCl₃, 400 MHz, r.t., top) and ¹³C NMR (CDCl₃, 101 MHz, r.t., bottom) spectra of the heteroleptic species considered as [Cu₂(N^N)₂(dppe)₂][BF₄]₂.

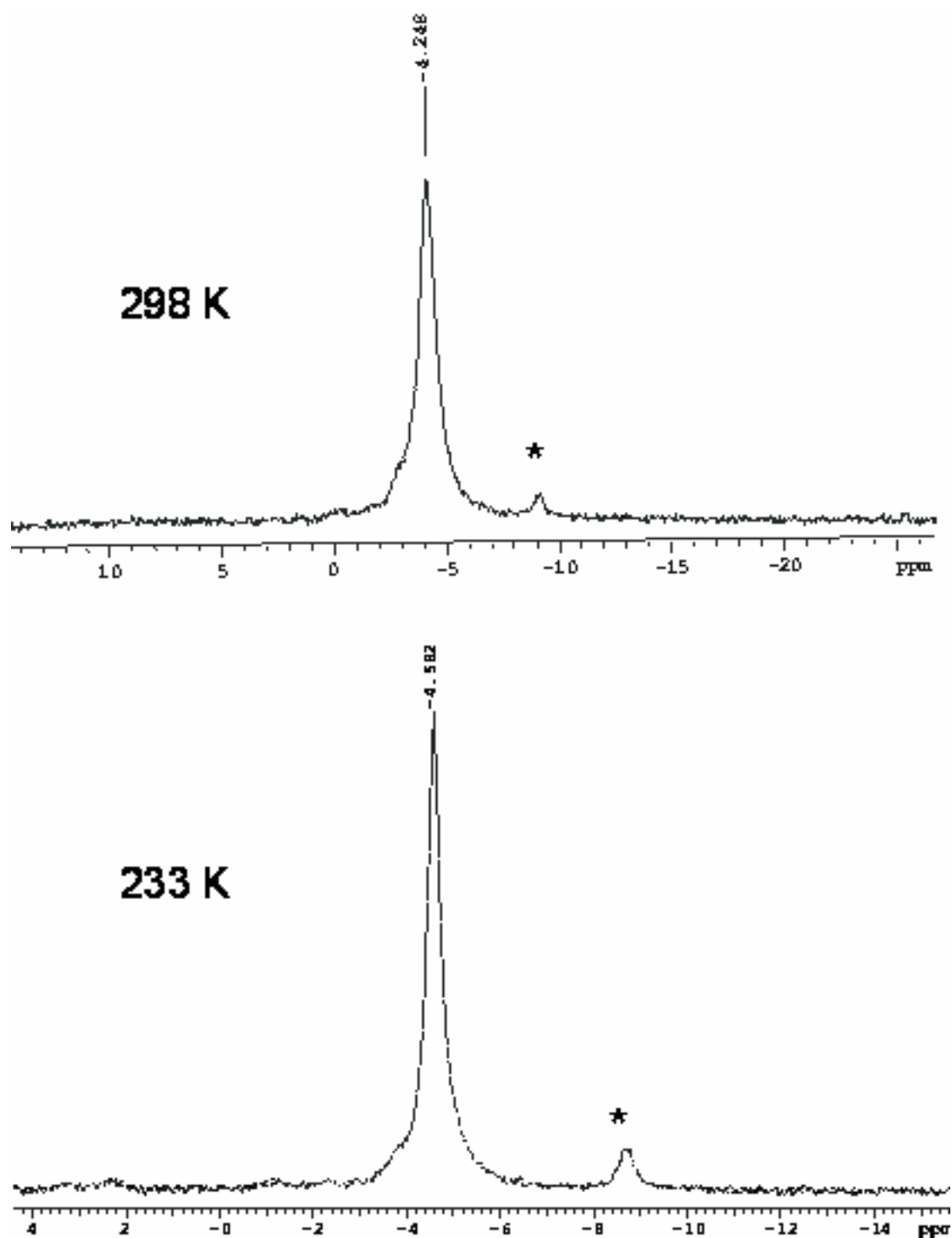


Fig. S8. VT ^{31}P NMR (CDCl_3 , 162 MHz) spectra of the heteroleptic species considered as $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppe})_2][\text{BF}_4]_2$ recorded at 298 K (top) and 233 K (bottom). The signal marked with an asterisk is relative to small amounts of $[\text{Cu}(\text{dppe})_2][\text{BF}_4]$

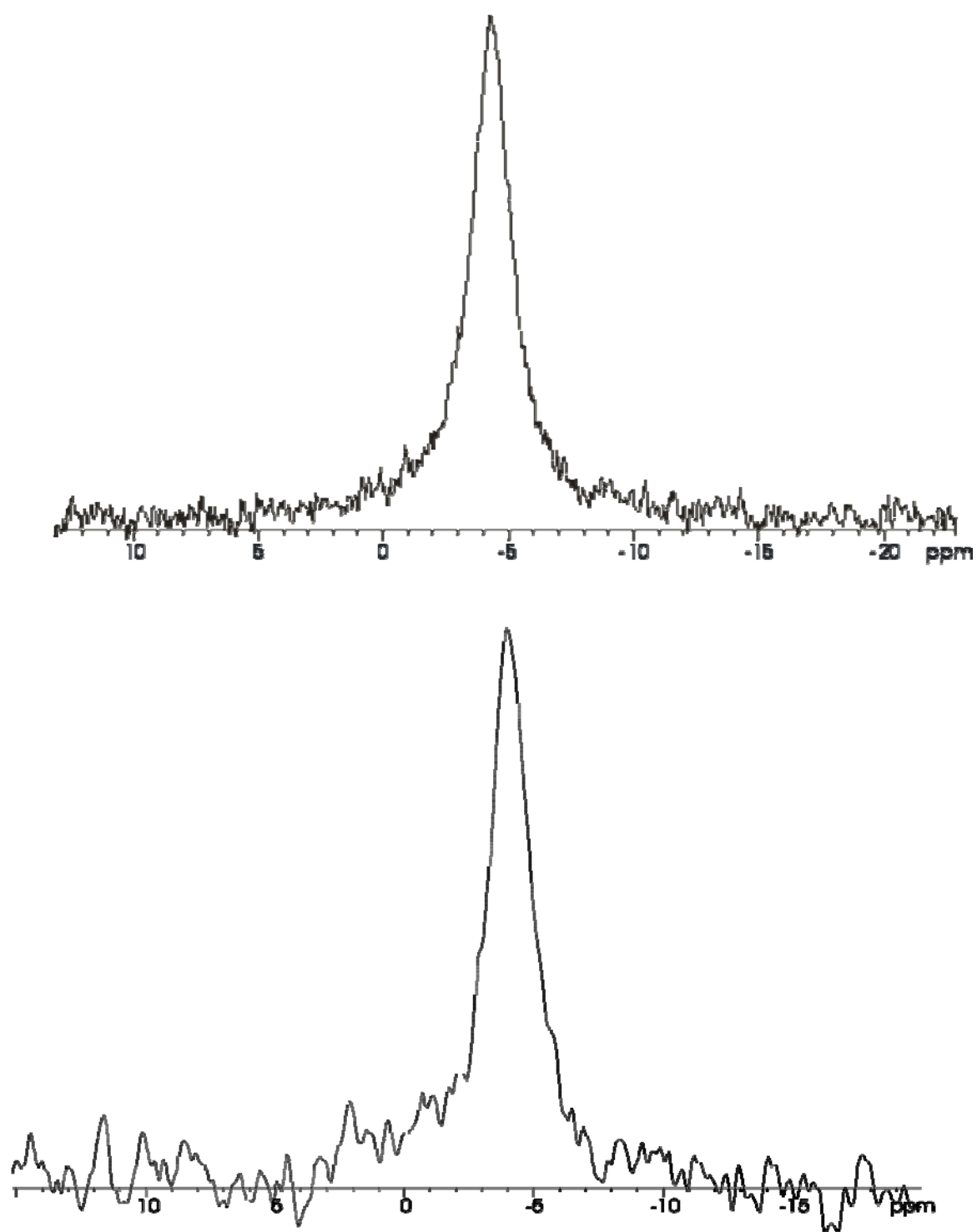


Fig. S9. Stacking plot of ^{31}P NMR spectra (CDCl_3 as the solvent, room temperature) of the complex considered as $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppe})_2][\text{BF}_4]_2$ at different concentrations: $2.0 \times 10^{-2} \text{ M}$ (top) and $2.0 \times 10^{-4} \text{ M}$ (bottom).

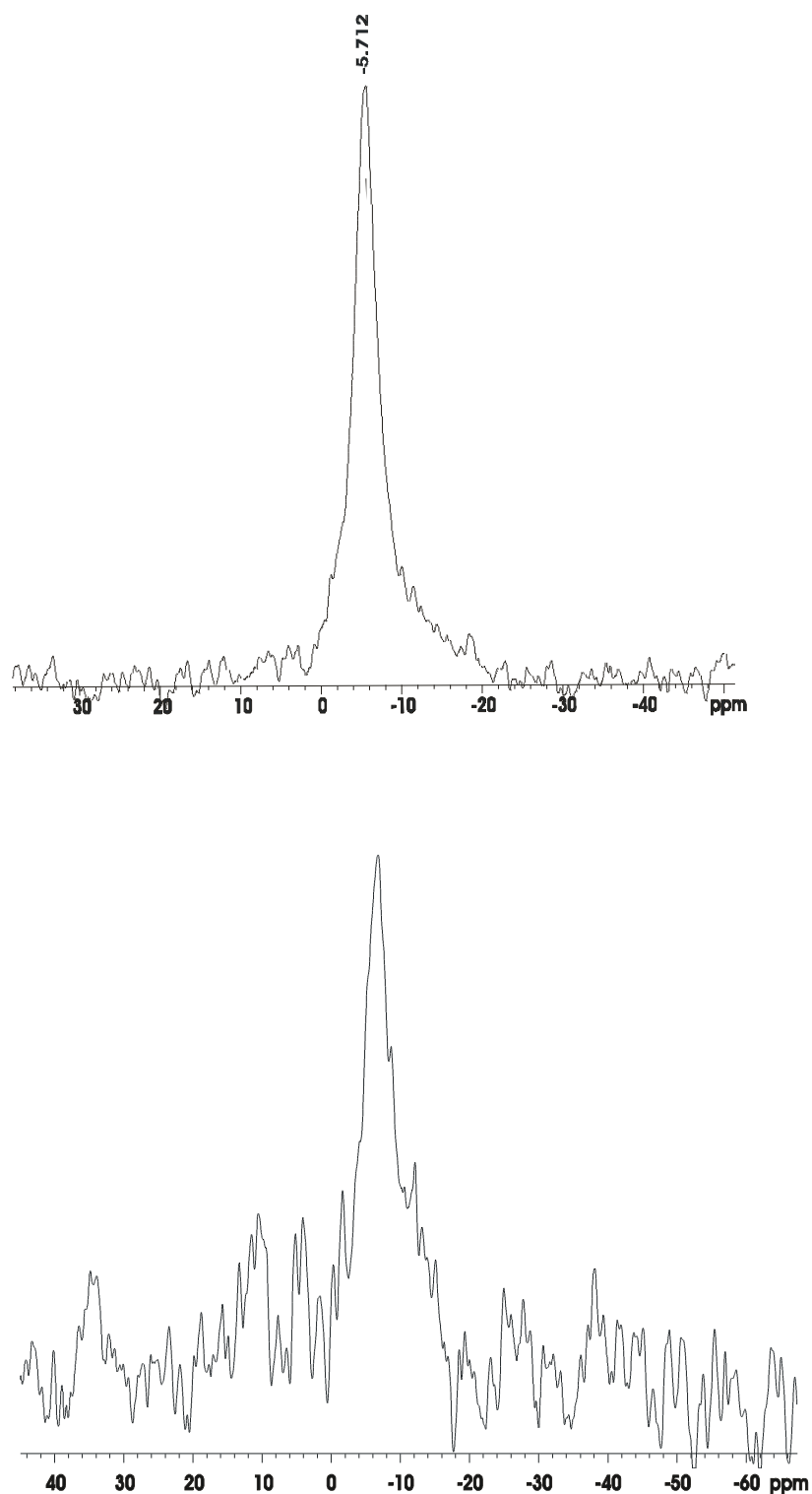


Fig. S10. Stacking plot of ^{31}P NMR spectra (162 MHz, CD_3CN as the solvent, room temperature) of the samples obtained by dissolving solid $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppe})_2][\text{BF}_4]_2$ in CD_3CN . The spectra refer to samples at different concentrations: 2.0×10^{-2} M (top) and 2.0×10^{-4} M (bottom).

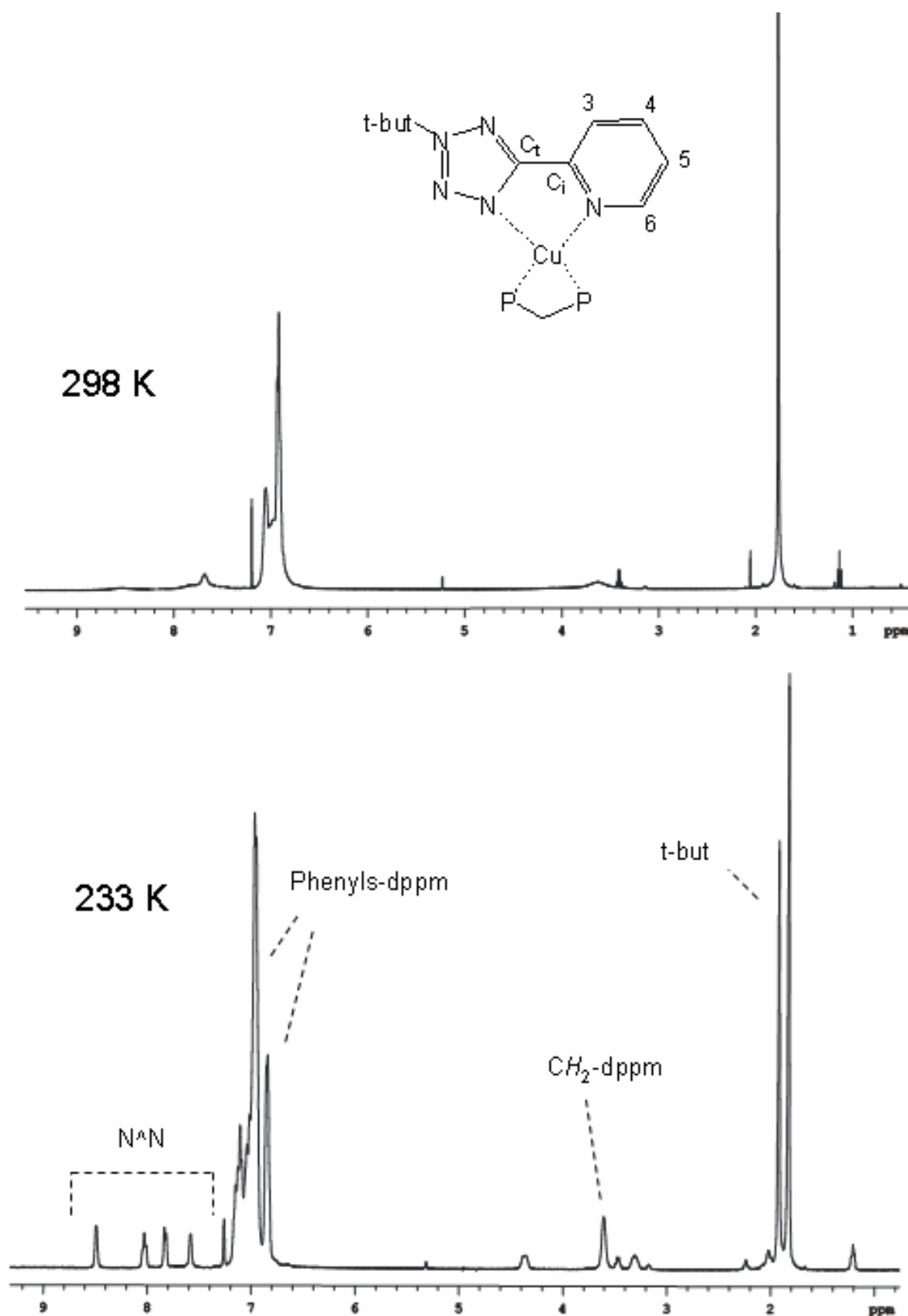


Fig. S11. VT ¹H NMR (CDCl₃, 400 MHz) spectra of the heteroleptic species considered as a mixture of [Cu₂(N[^]N)₂(dppm)₂][BF₄]₂ and [Cu(N[^]N)(dppm)][BF₄] recorded at 298 K (top) and 233 K (bottom).

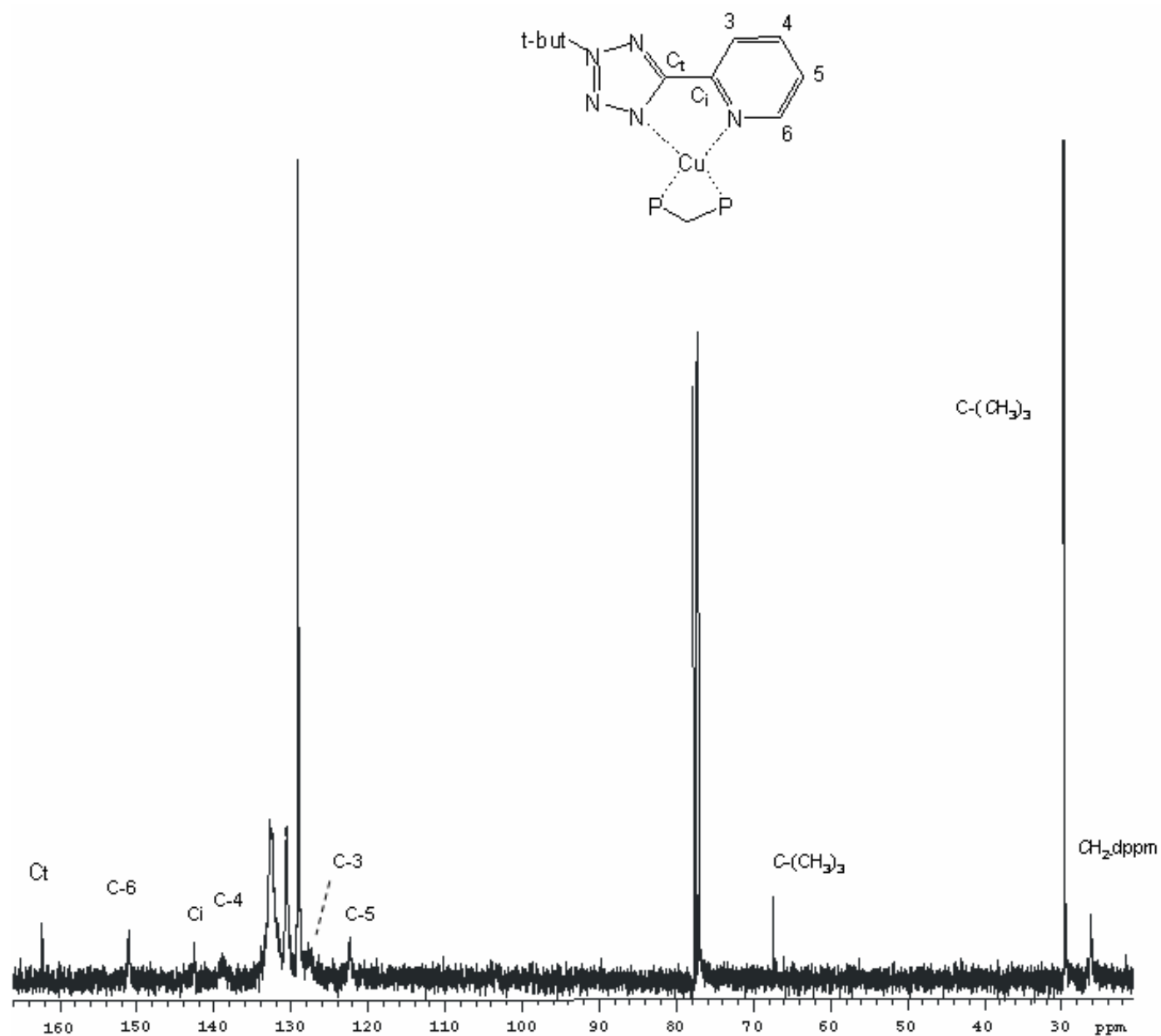


Fig. S12. ^{13}C NMR (CDCl₃, 101 MHz, r.t.) spectrum of the heteroleptic species considered as a mixture of $[\text{Cu}_2(\text{N}^{\wedge}\text{N})_2(\text{dppm})_2][\text{BF}_4]_2$ and $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{dppm})][\text{BF}_4]$.

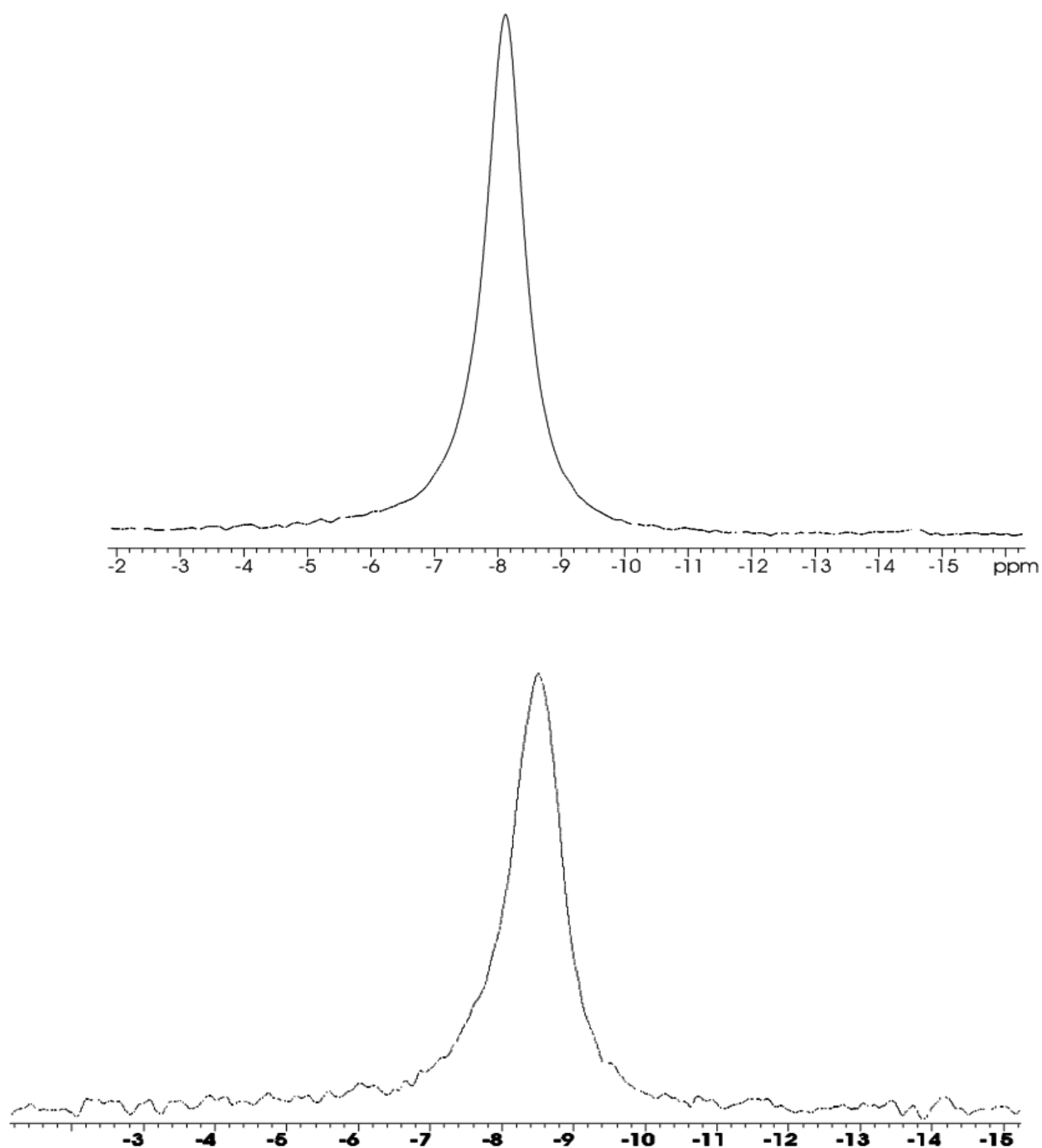


Fig. S13. Stacking plot of ^{31}P NMR spectra (CD_3CN as the solvent, room temperature) of the complex considered as the mixture of monomeric ($n=1$) and dimeric ($n=2$) $[\text{Cu}_n(\text{N}^{\wedge}\text{N})_n(\text{dppm})_n][\text{BF}_4]_n$ at different concentrations: $2.0 \times 10^{-2} \text{ M}$ (top) and $2.0 \times 10^{-4} \text{ M}$ (bottom).

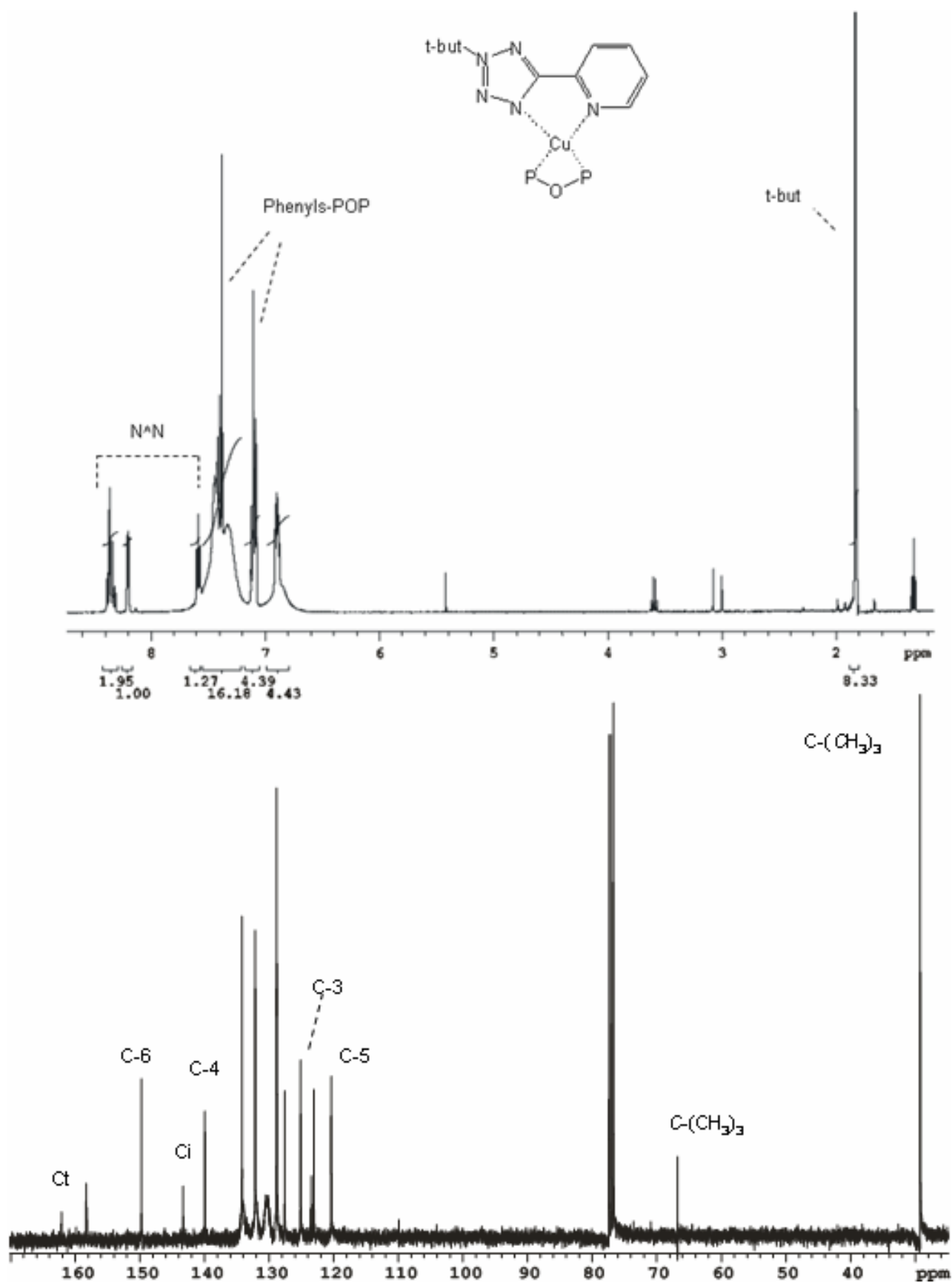


Fig. S14. ^1H NMR (CDCl₃, 400 MHz, r.t., top) and ^{13}C NMR (CDCl₃, 101 MHz, r.t., bottom) spectra of the heteroleptic species considered as $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{POP})][\text{BF}_4]$.

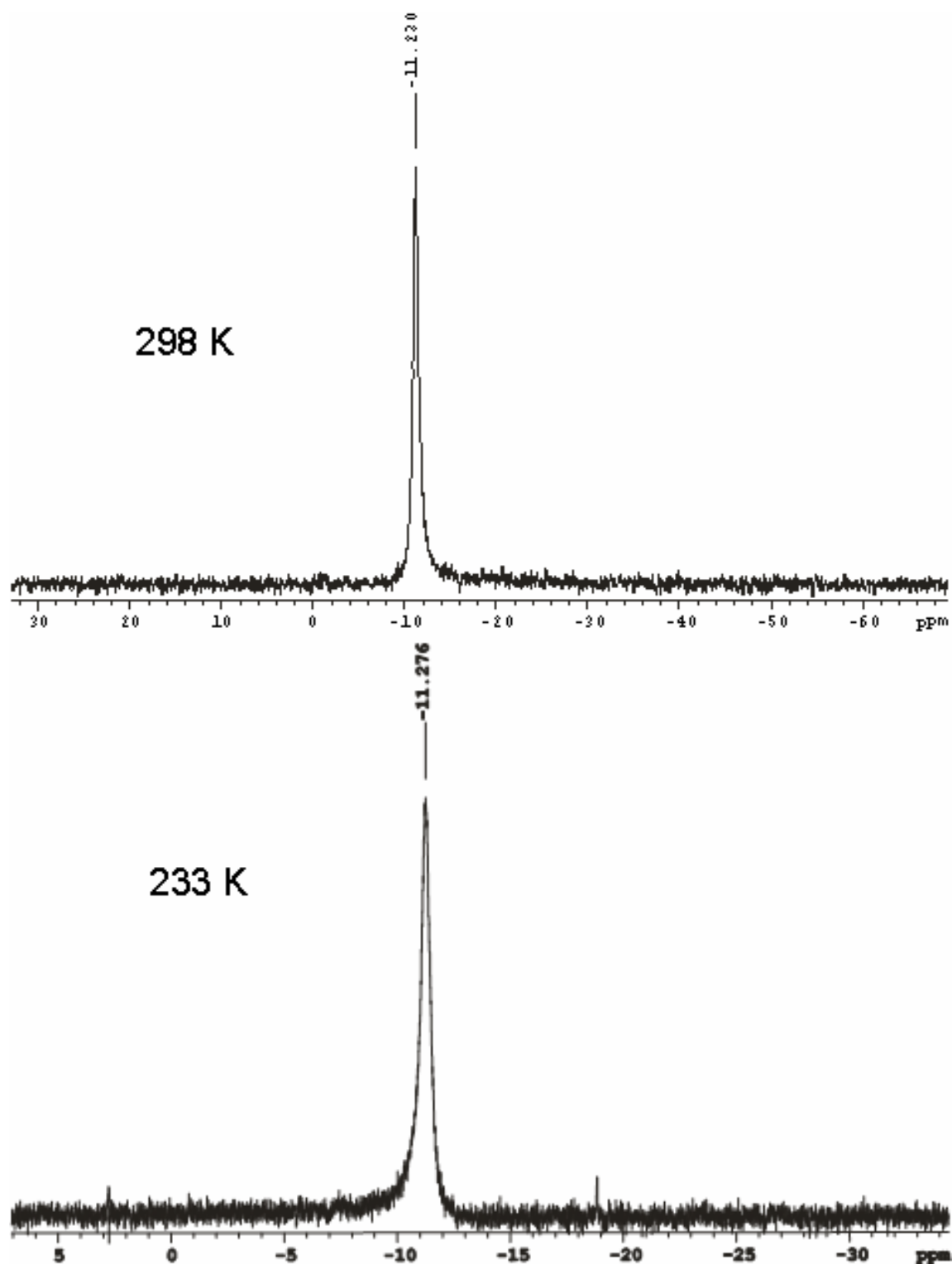


Fig. S15. VT ^{31}P NMR (CDCl_3 , 162 MHz) spectra of the heteroleptic species considered as $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{POP})][\text{BF}_4]$ recorded at 298 K (top) and 233 K (bottom).