

Supporting Information

**Demonstration of a Common Indole-based Aromatic Core in
Natural and Synthetic Eumelanins by Solid-State NMR**

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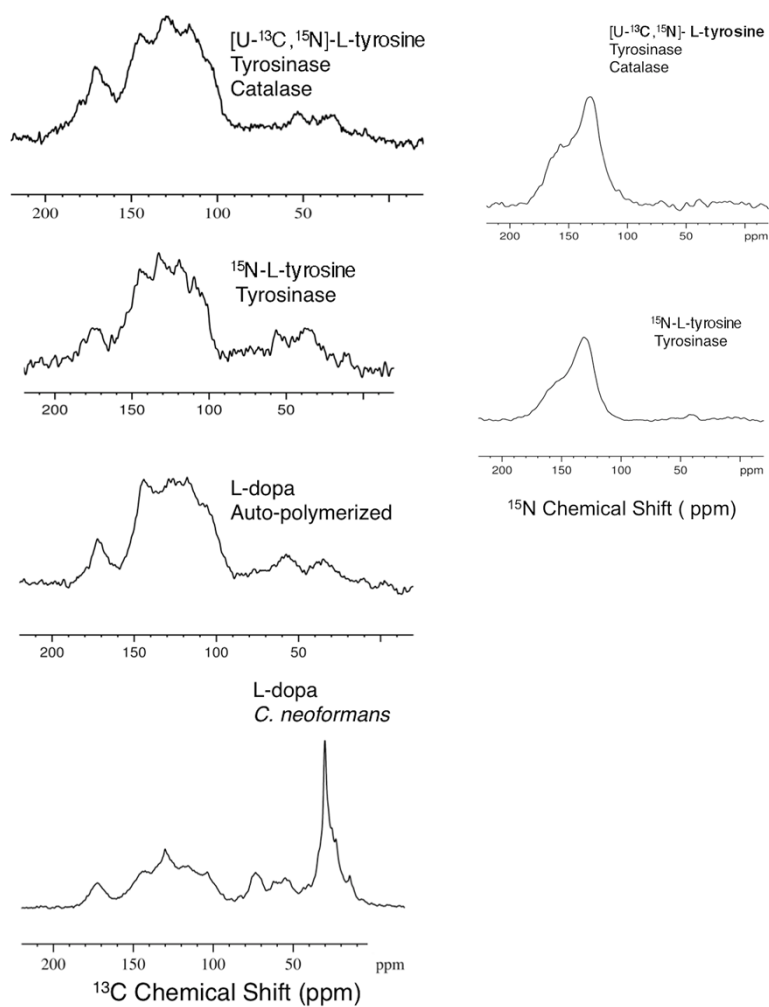


Figure S1. *Left:* Solid-state CPMAS ^{13}C NMR spectra of melanins produced from amino acid and catecholamine precursors, obtained at a ^1H operating frequency of 600 MHz and spinning rate of 15 kHz. From top to bottom (including number of transients): synthetic L-tyrosine melanin (tyrosinase with catalase, 1400; tyrosinase without catalase, 4096), L-dopa melanin (cell-free reaction, 4096); with *Cryptococcus neoformans* (CN), 21,000). *Right:* CPMAS ^{15}N NMR spectra of melanins produced from amino acid precursors, obtained at ^1H operating frequencies of 600 MHz and 750 MHz, spinning rate of 15 kHz. Top: synthetic L-tyrosine (tyrosinase with catalase, 4096). Bottom: tyrosinase without catalase, 512.

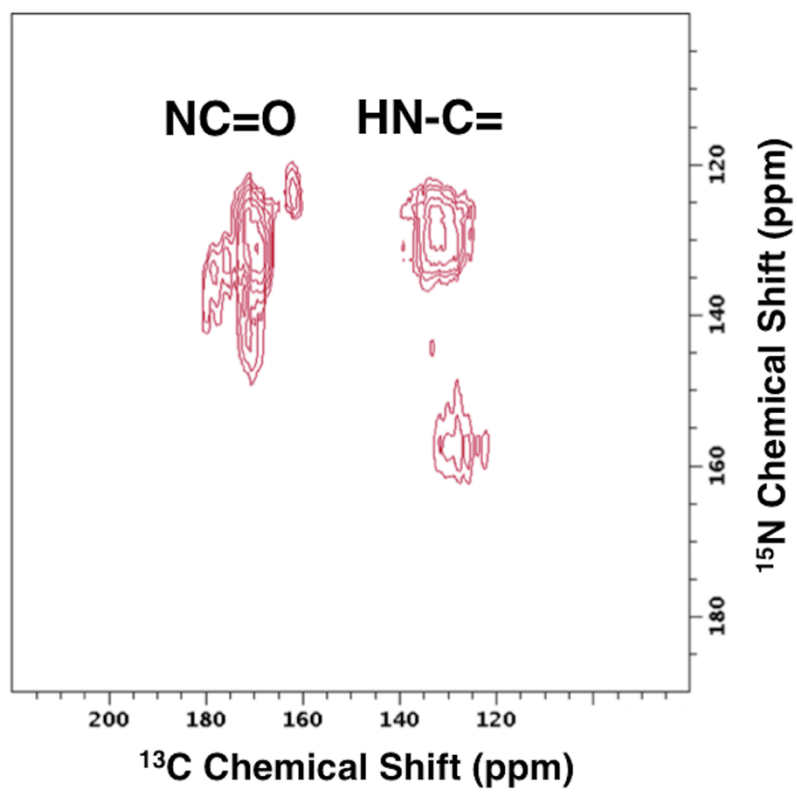


Figure S2. Two-dimensional ^{13}C - ^{15}N Proton Assisted Insensitive Nuclei Cross Polarization (PAIN-CP) NMR contour diagram of synthetic $[\text{U-}^{13}\text{C},^{15}\text{N}]$ -L-tyrosine melanin, obtained at a ^1H operating frequency of 900 MHz and spinning rate of 20 kHz.

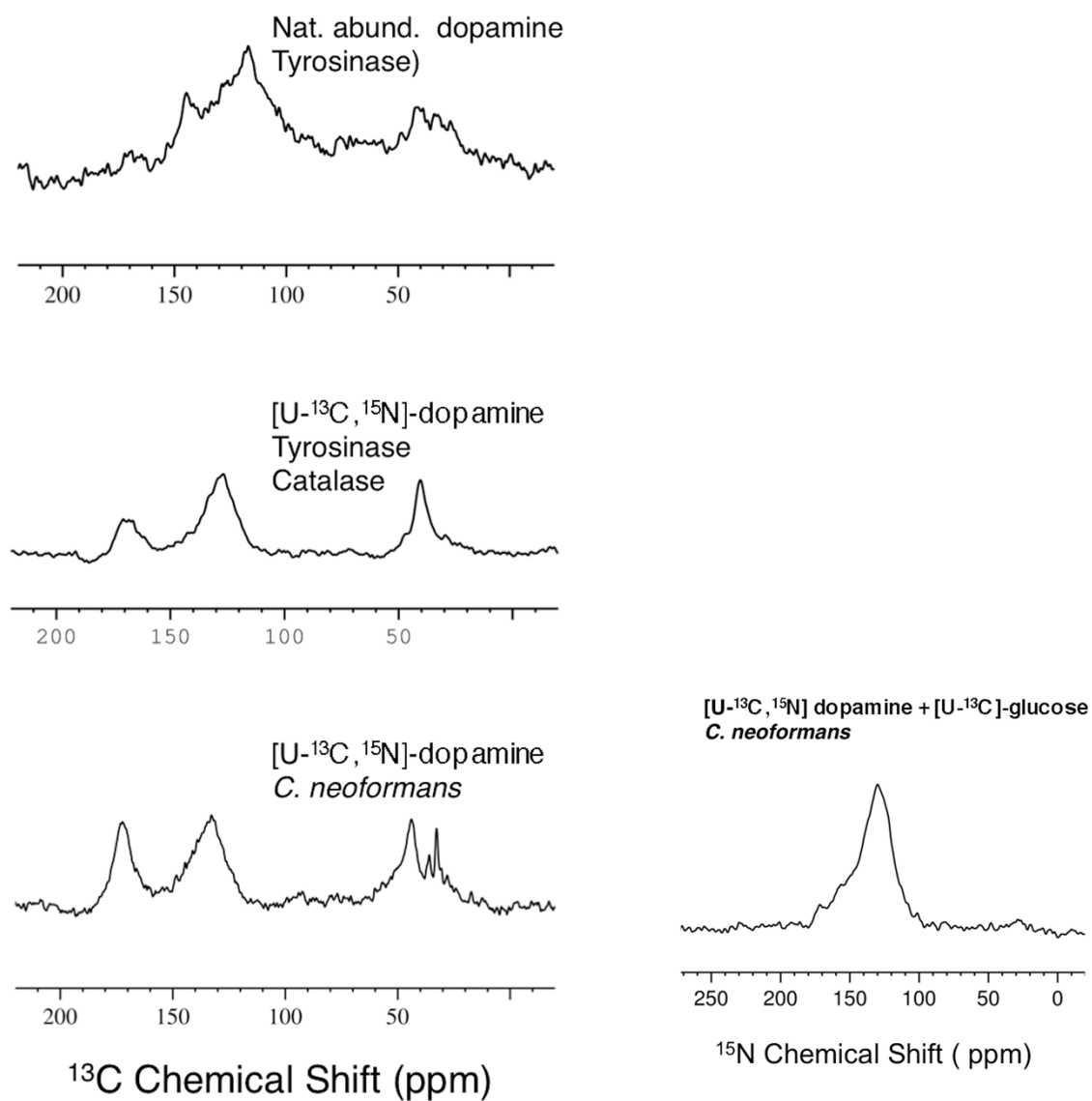


Figure S3. Left: Solid-state CPMAS ¹³C NMR spectra of dopamine melanins produced in cell-free and fungal systems, obtained with a spinning rate of 15 kHz at two resonance frequencies. From top to bottom (including number of transients): tyrosinase-catalyzed synthesis without catalase (4096, 5 mg sample) and with catalase (~12000, ~2 mg sample) (600 MHz ¹H); *Cryptococcus neoformans* (CN) biosynthesis (1024, (750 MHz ¹H). Right: One-dimensional solid-state CPMAS ¹⁵N NMR spectrum of CN dopamine melanin (10000, ~5mg) obtained at ¹H operating frequency of 750 MHz and a spinning rate of 15 kHz.