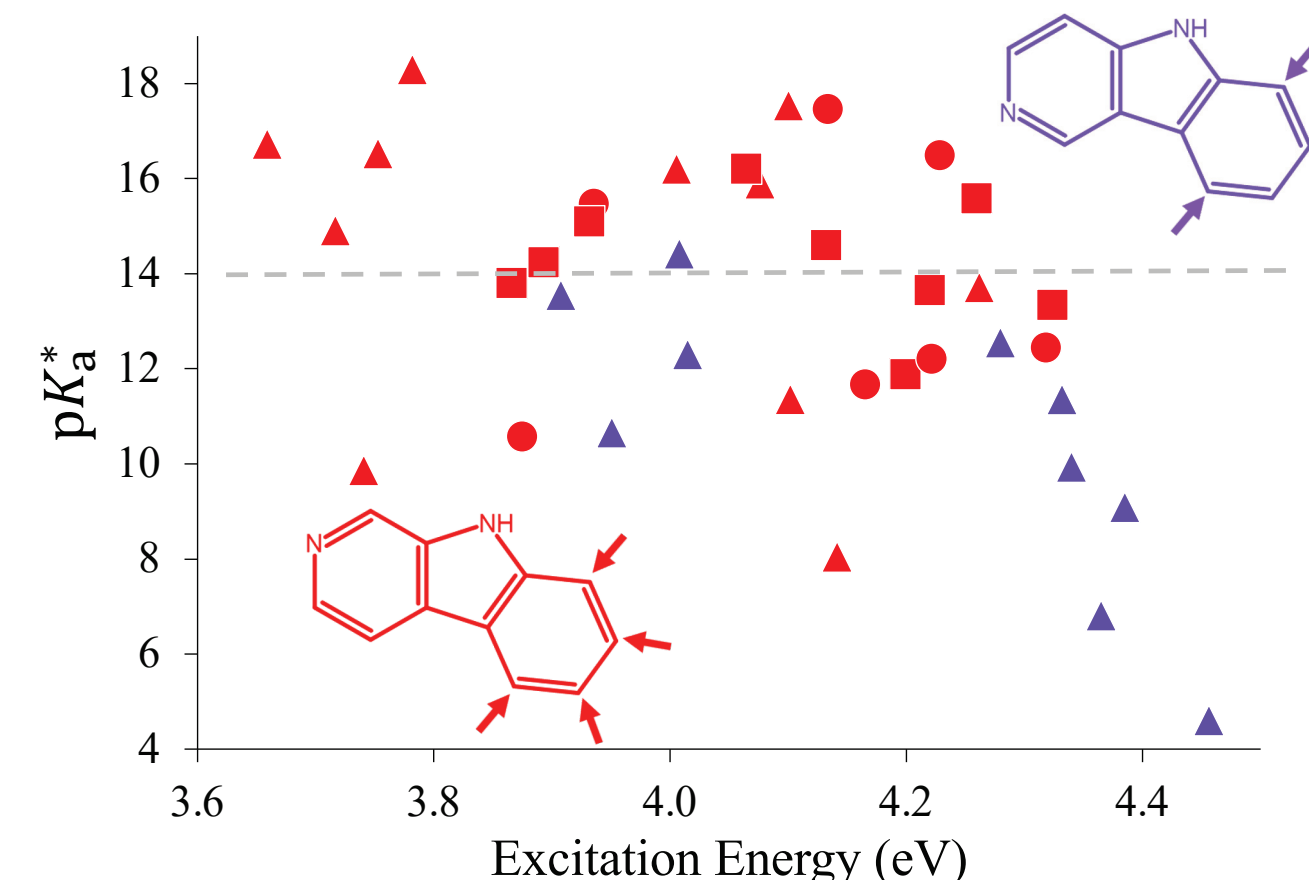
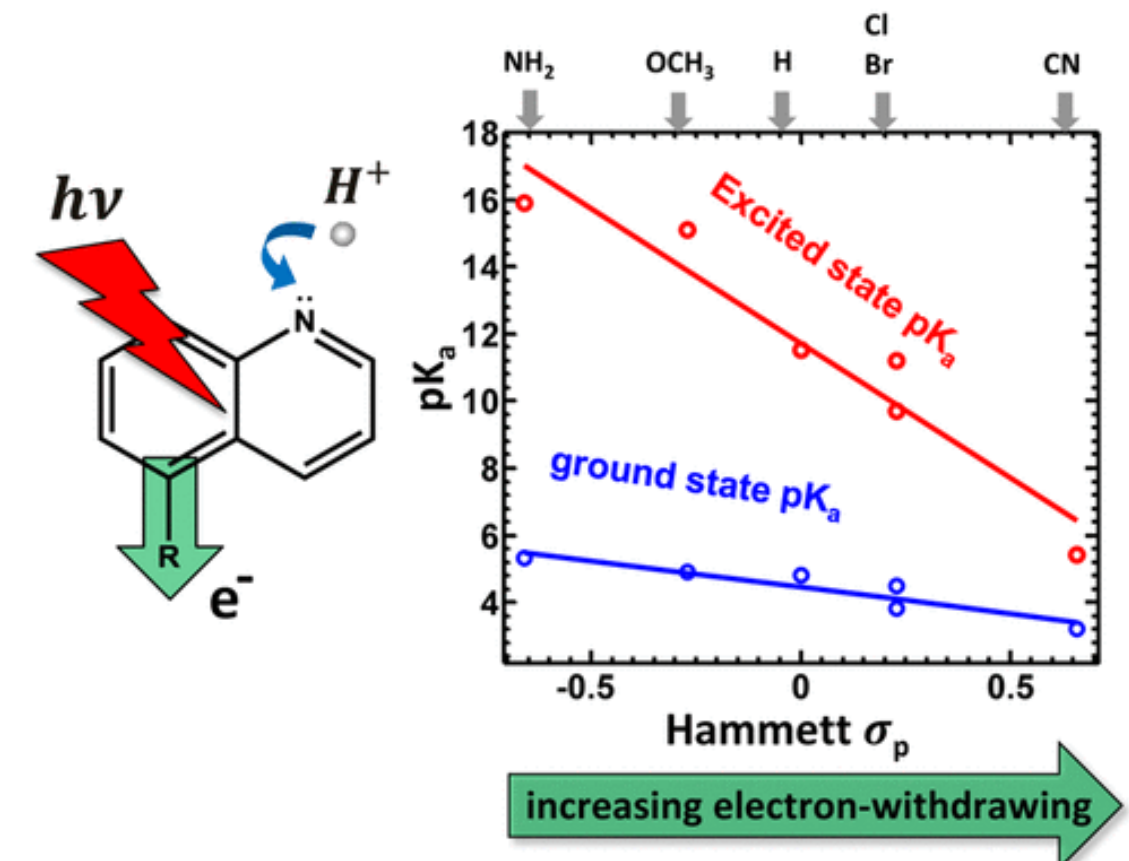
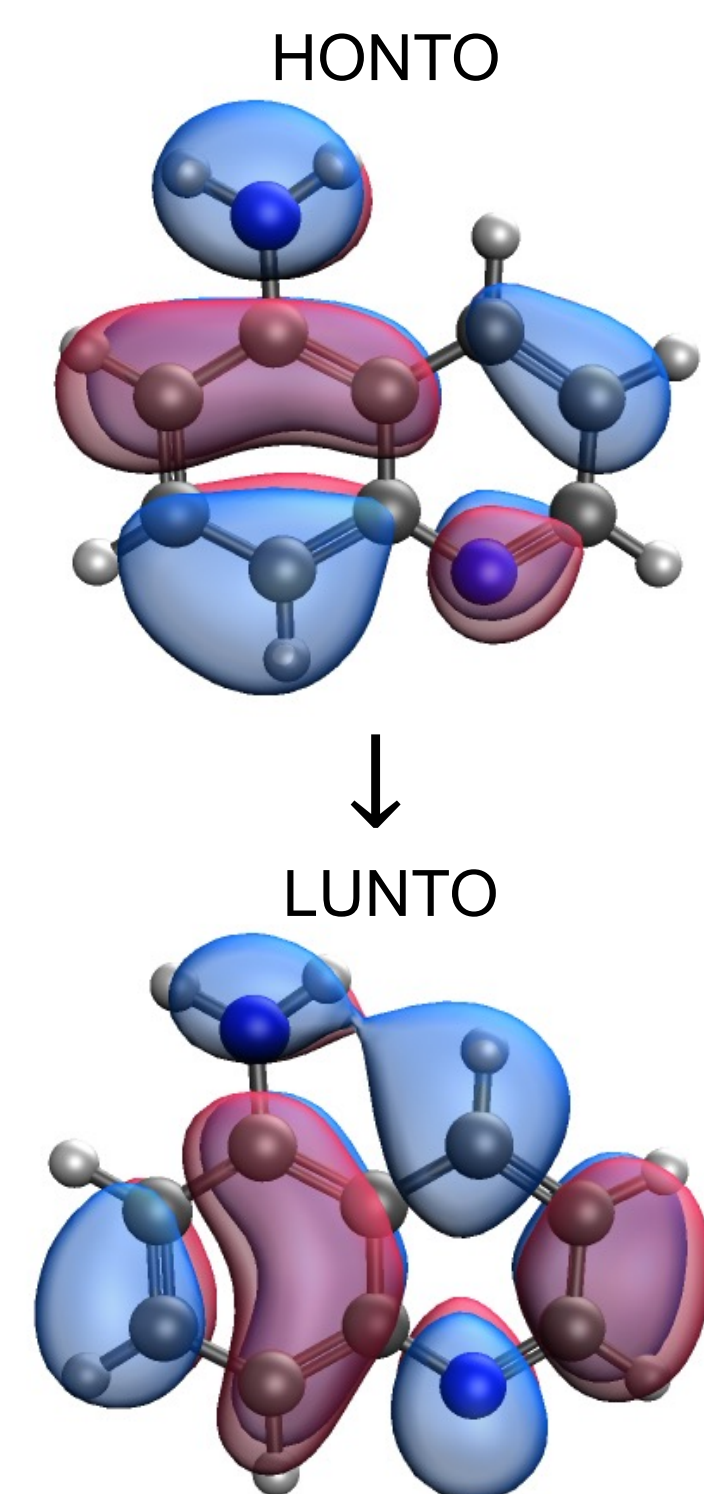
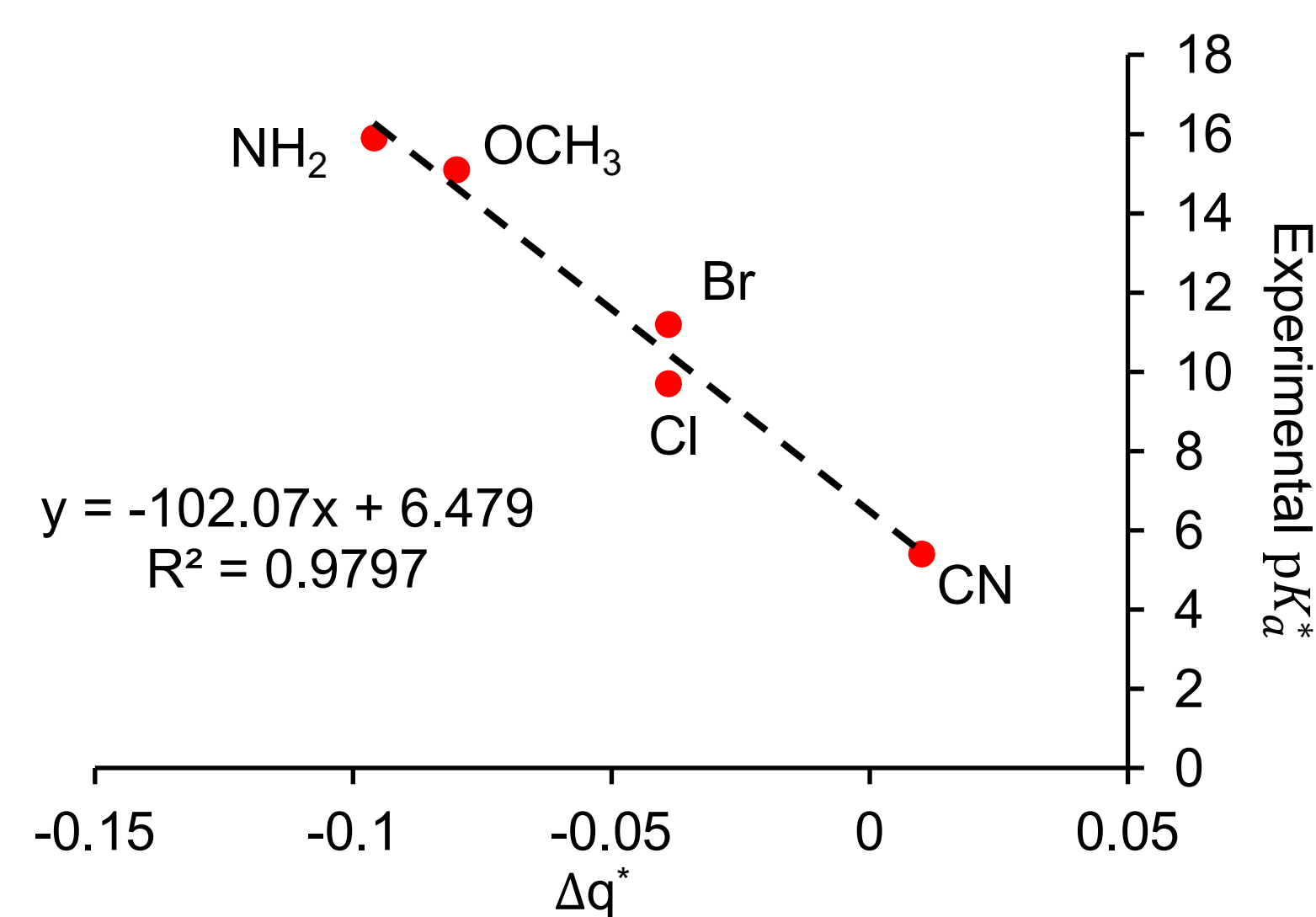


## Introduction

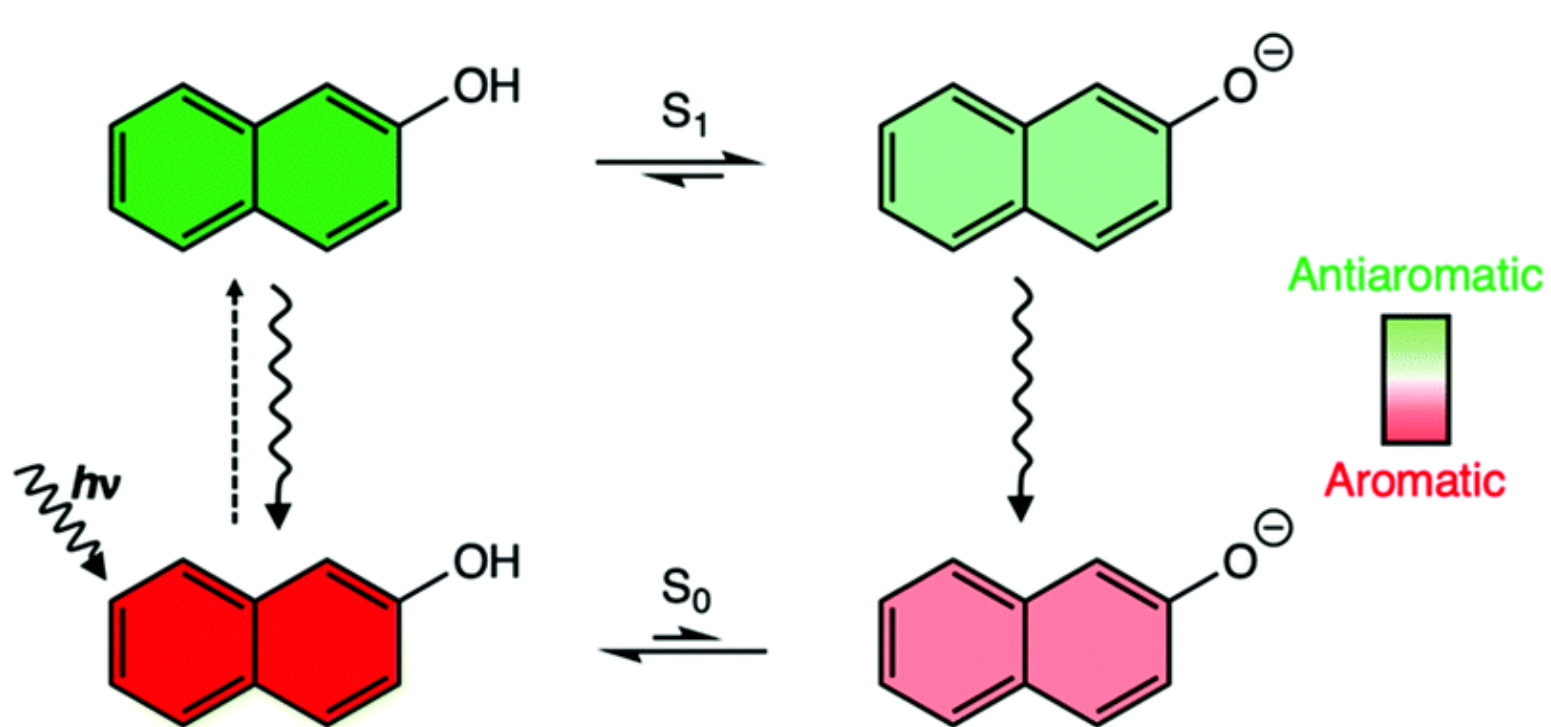
- Photobases are molecules that become more basic after electronic excitation.
- The 5-R-quinolines are representative photobases that have been characterized both experimentally and computationally (below, left).<sup>1,3</sup>
- The Petit lab explored other potential photobases like the  $\beta$ -carbolines and  $\gamma$ -carbolines (below right).<sup>2</sup>



- Both figures show an increase in basicity strength in the excited state (quantified through  $pK_a^*$ ).
- Notably 5-NH<sub>2</sub>-quinoline went from  $pK_a = 5.3$  to  $pK_a^* = 15.9$  (or  $K_b = 1.99 \times 10^{-9}$  to  $K_b^* = 15.9$ ).

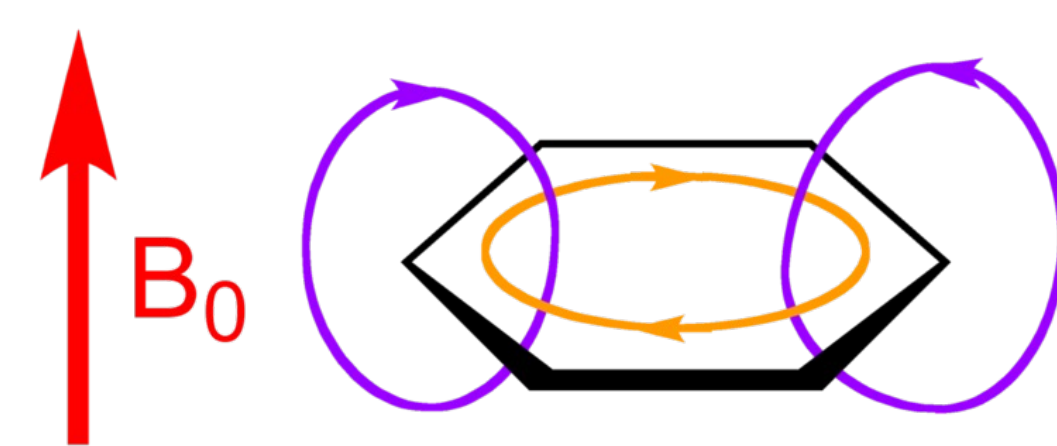


- The thermodynamic driving force for photobasicity was originally thought to reflect intramolecular charge transfer, with the ring nitrogen atom gaining electron density in the transition.<sup>1-3</sup>
- However, the change in electron density in the excited state ( $\Delta q^+$ ) on the ring nitrogen atom is consistently small.



- Judy Wu's group recently explored photoacidity and found a trend involving excited state anti-aromaticity (left).<sup>4</sup>
- The rings are aromatic in the ground state.
- The rings became significantly anti-aromatic after the electronic excitation.
- The thermodynamic driving force for excited state proton transfer attributed to the relief of excited state anti-aromaticity.

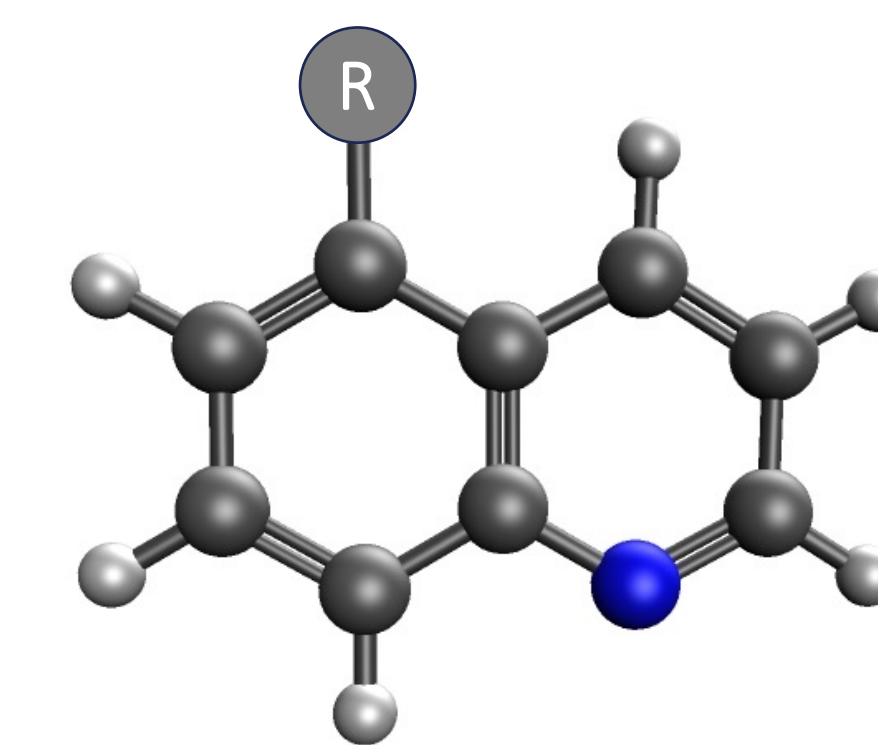
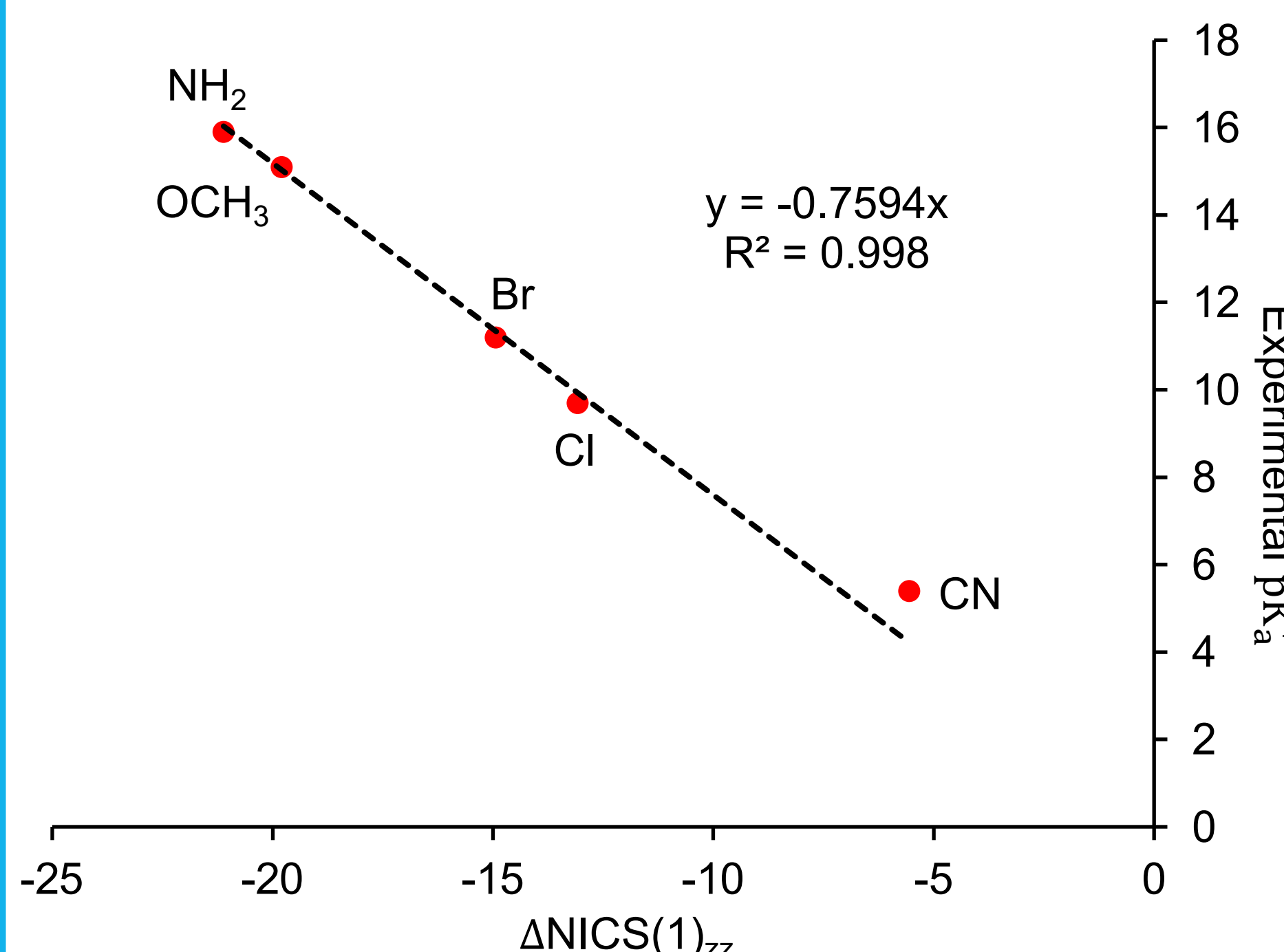
- Aromaticity was calculated using nucleus-independent chemical shifts (NICS) analysis.
- NICS determines the absolute magnetic shielding at the center of a ring by probing with a dummy atom placed 1Å above the ring.
- The magnetic shielding reflects the aromatic ring current, allowing for a quantification of aromaticity/anti-aromaticity.



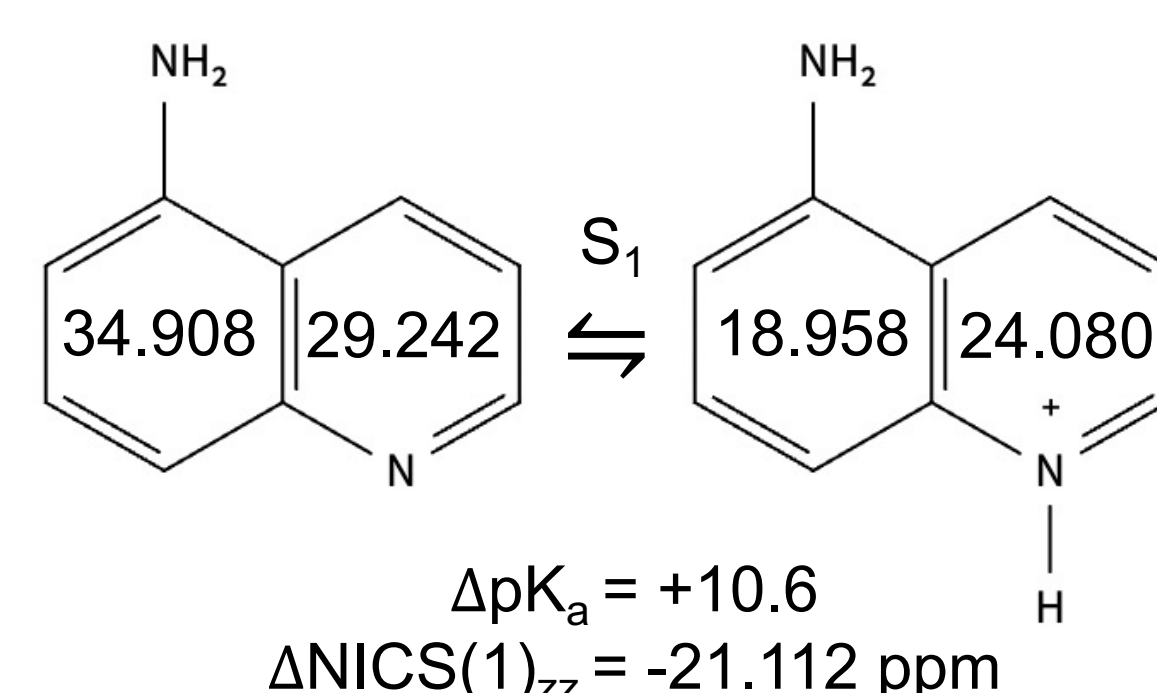
## Objectives

- Is there a relationship between photobasicity and excited state anti-aromaticity?
- Does NICS analysis quantitatively correlate with photobasicity strength?
- How much does the relationship between photobasicity and excited state anti-aromaticity depend on the molecular structure?

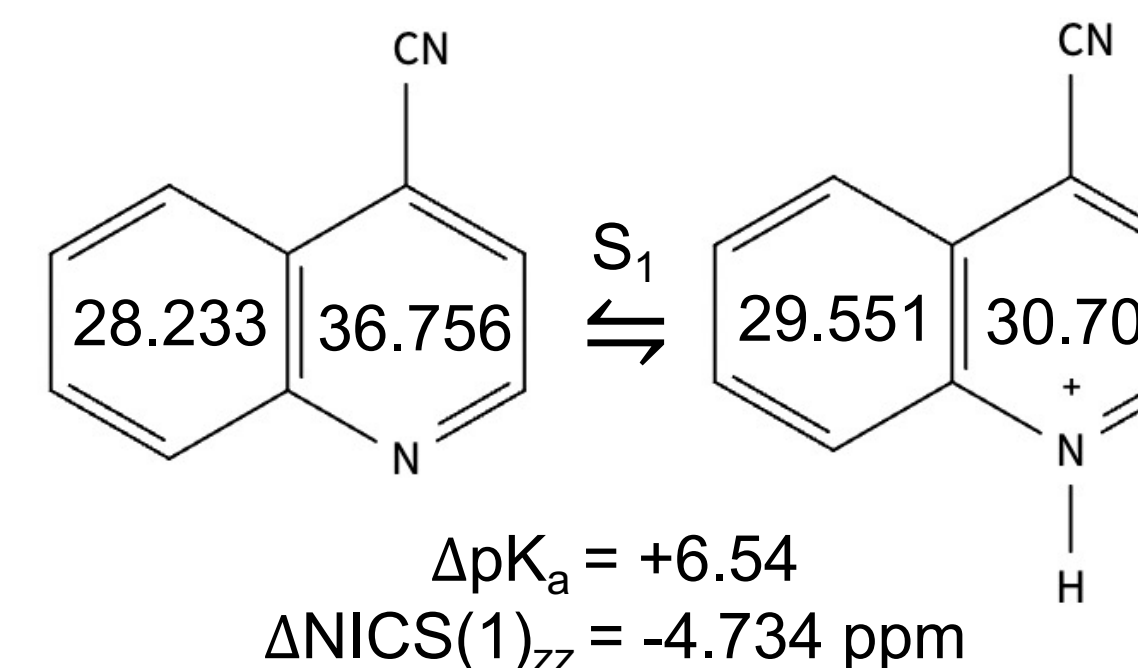
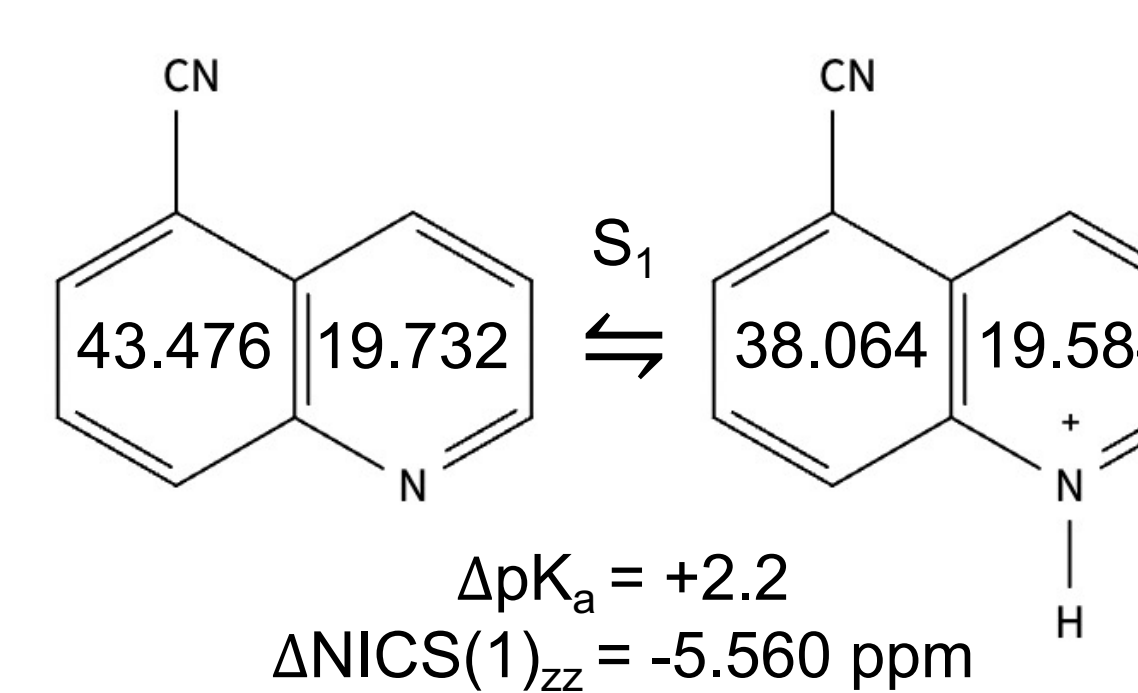
## Results: 5-R Quinolines



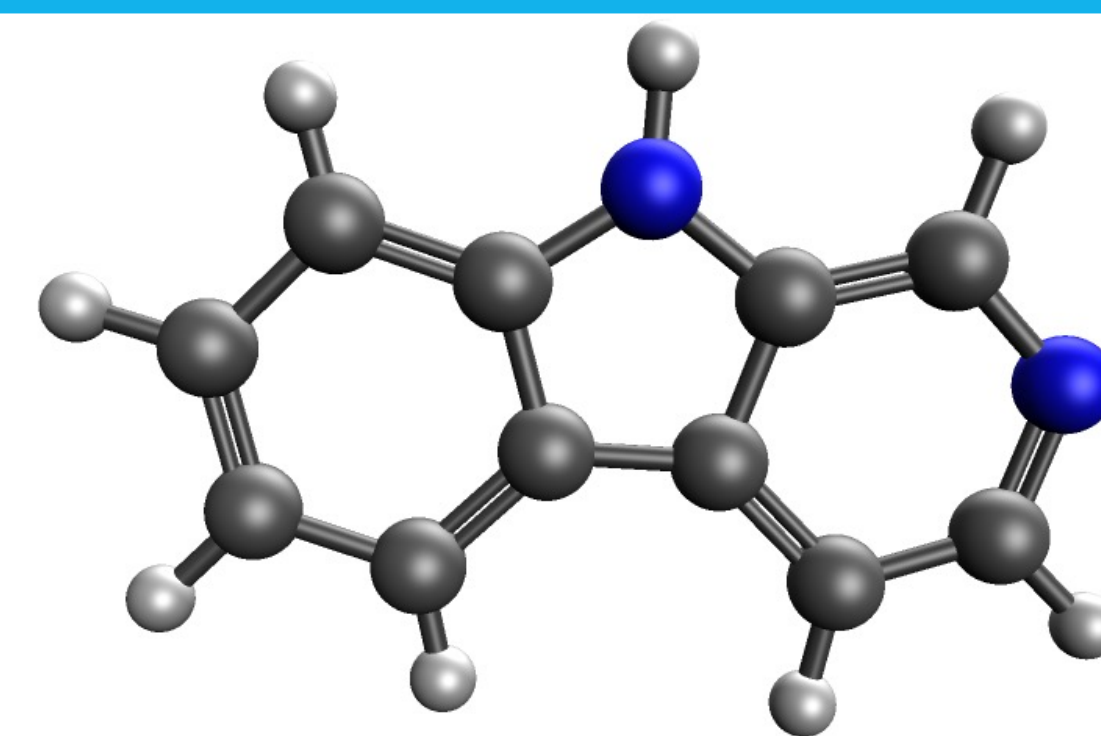
- All 5-R quinolines show a relief in excited state anti-aromaticity after protonation.
- There is a strong correlation between the relief in excited state anti-aromaticity, quantified through  $\Delta NICS(1)_{zz}$ , and the experimental  $pK_a^*$ .



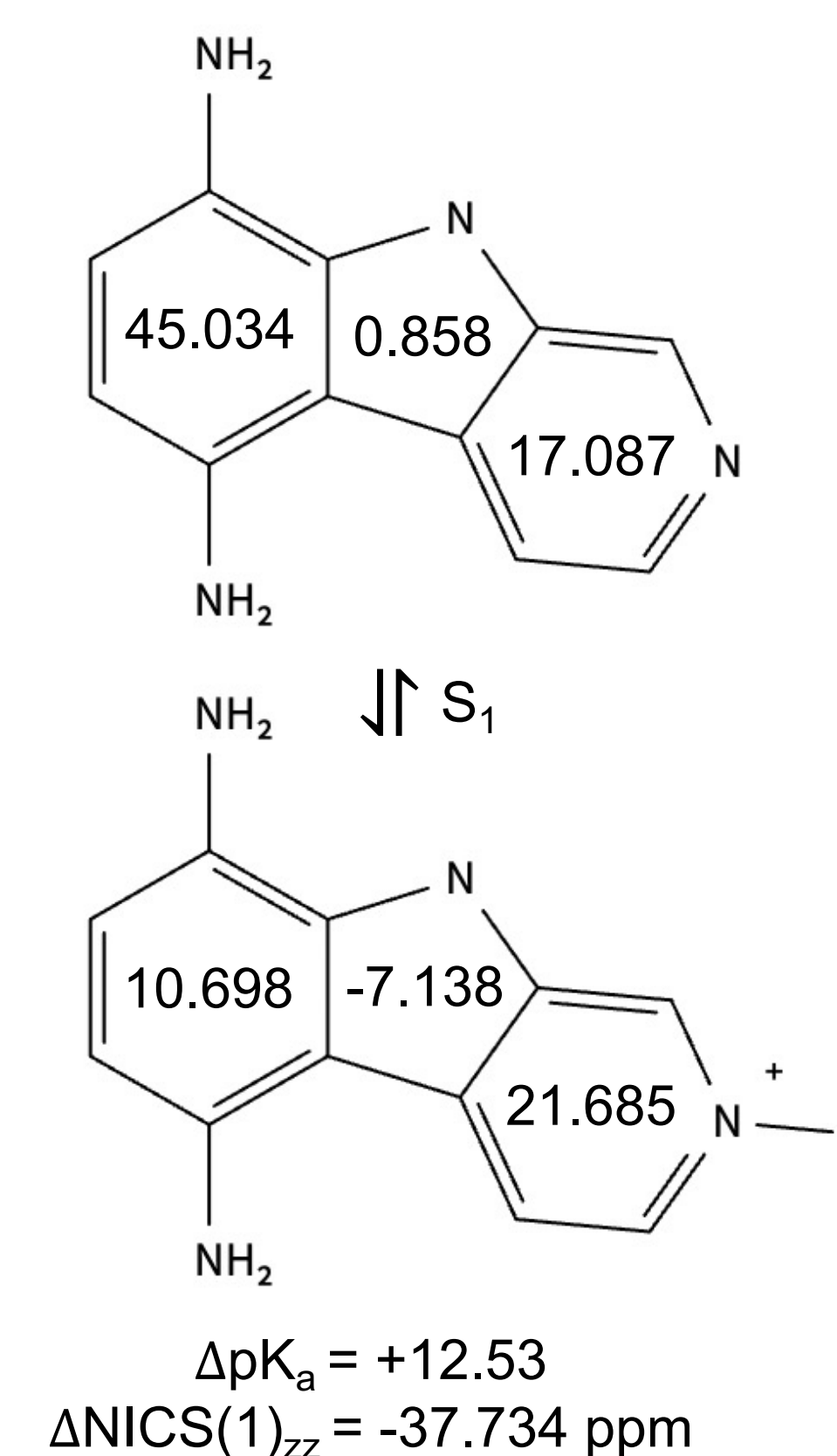
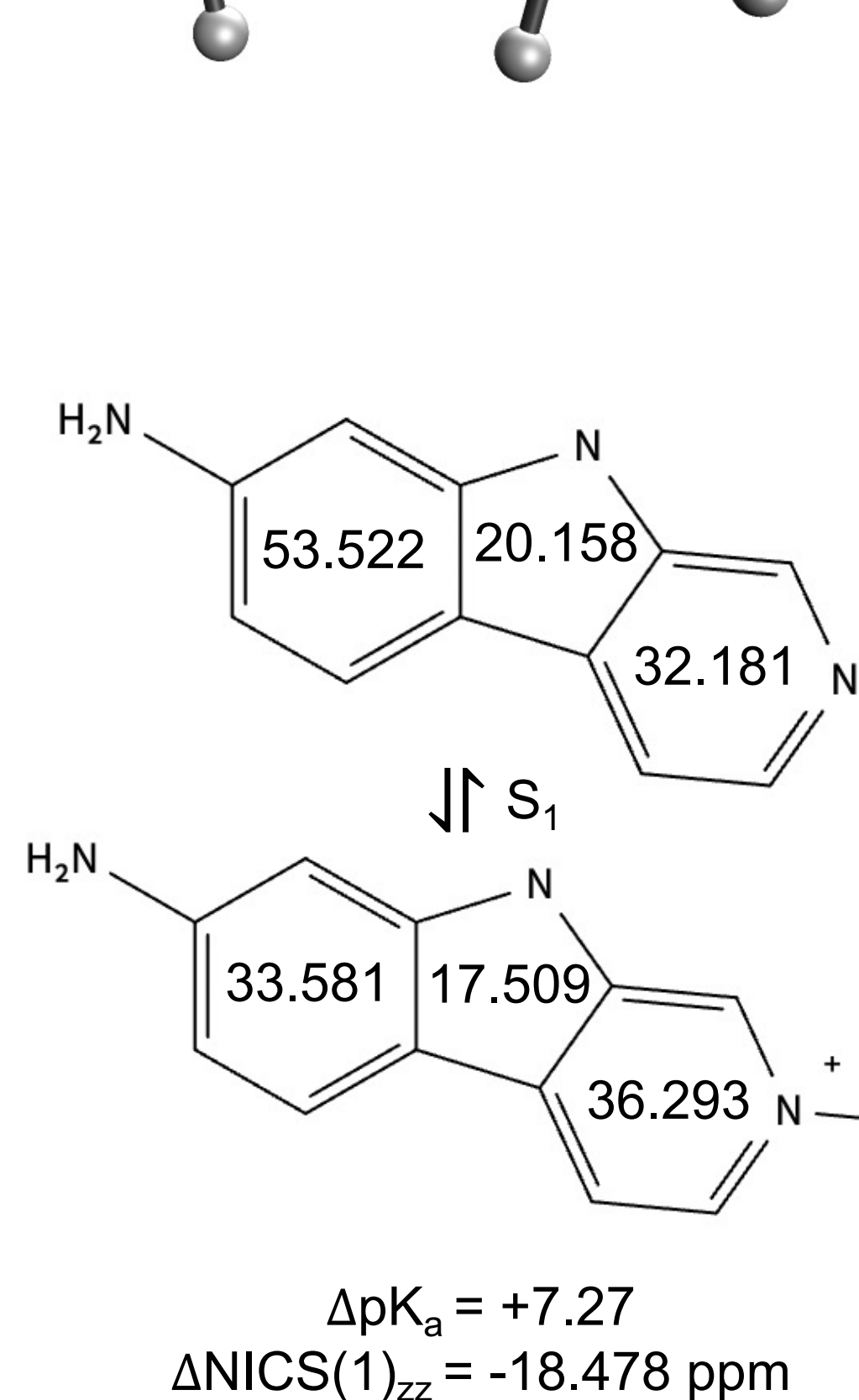
- In S<sub>1</sub>, the NICS(1)<sub>zz</sub> are consistently positive, which indicates anti-aromaticity.
- For all of these photobases, excited state protonation reduces the anti-aromaticity.
- The largest relief of excited state anti-aromaticity occurs at the ring that contains the functional group.
- For the 5-R-quinolines, the anti-aromaticity relief is concentrated in the ring that is **not** protonated.



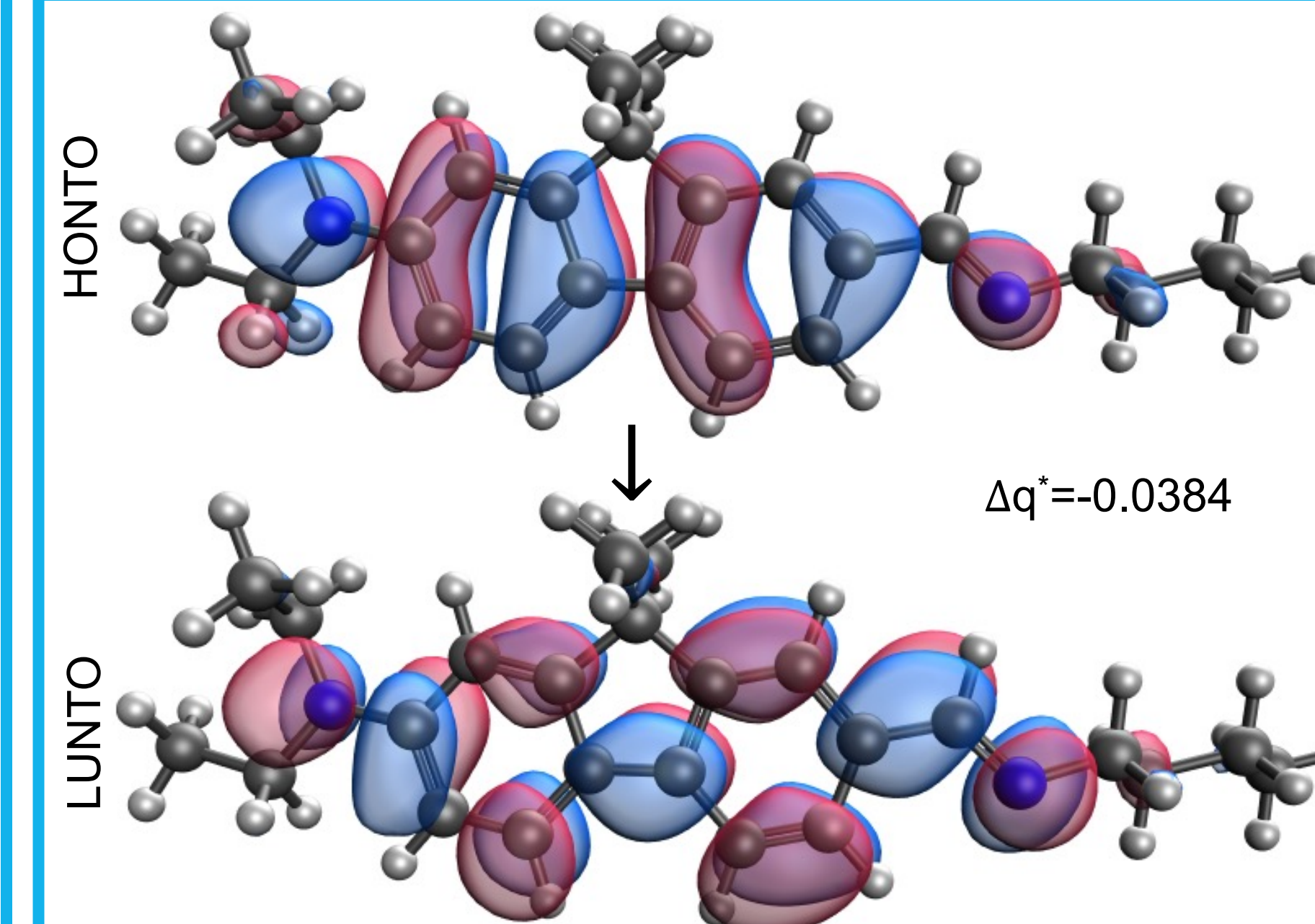
## Results: $\beta$ -Carbolines



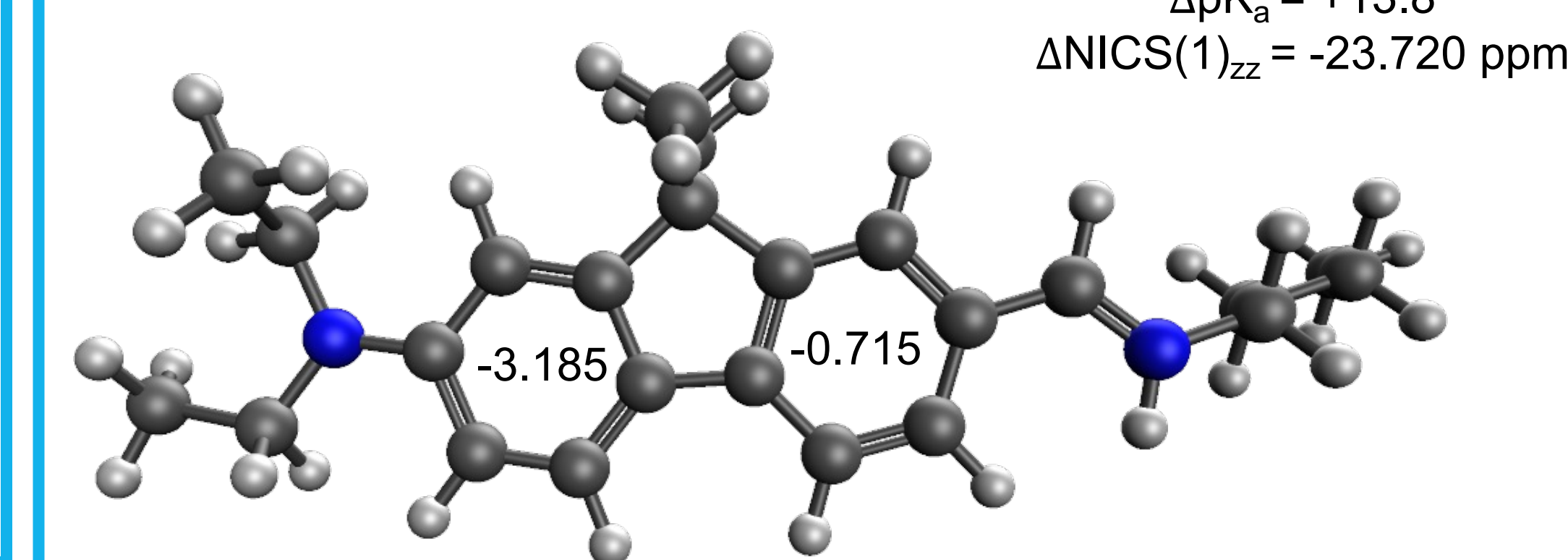
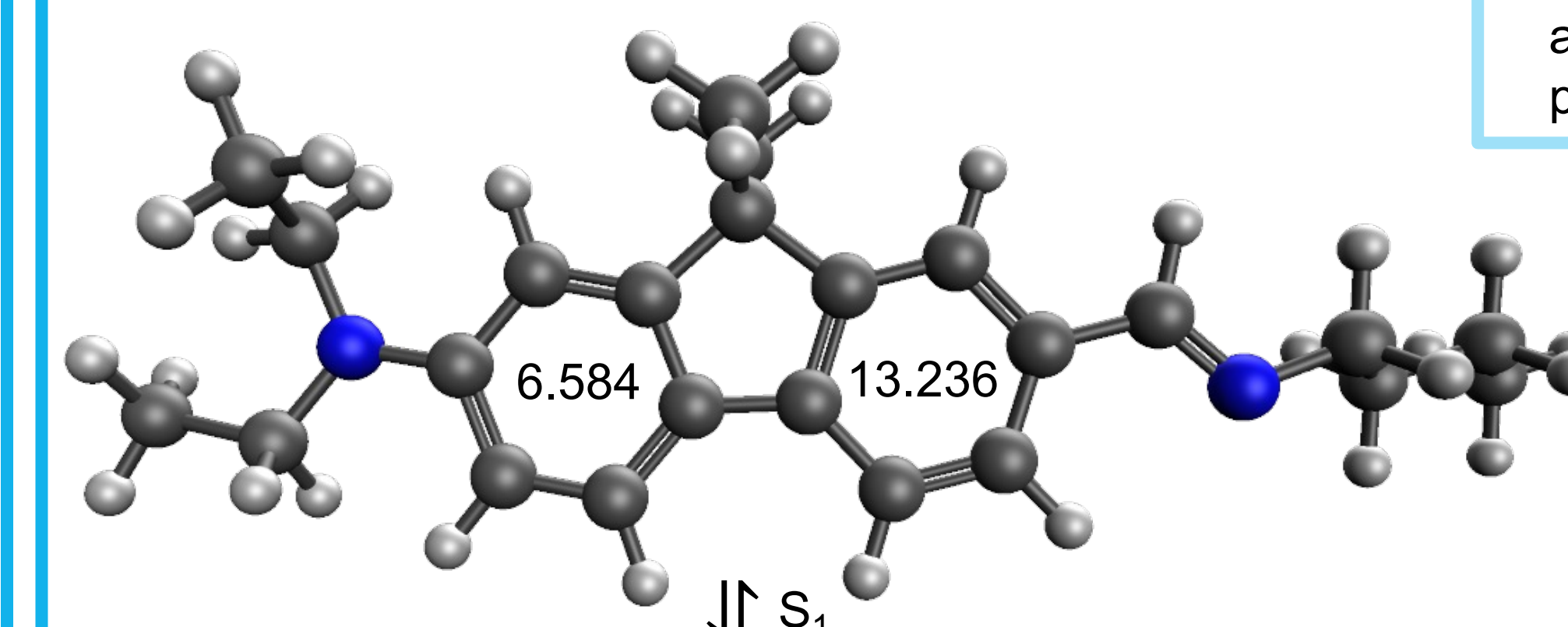
- We are exploring other photobasic N-heterocycles, such as the  $\beta$ -carbolines.
- The  $\beta$ -carbolines are anti-aromatic in the excited state.
- Excited state protonation of these compounds relieves this anti-aromaticity.
- Efforts to develop a quantitative relationship between  $\Delta NICS(1)_{zz}$ , and  $pK_a^*$  are ongoing.



## Results: A Super-Photobase



- This "super" photobase is strong enough to deprotonate EtOH.<sup>5</sup>
- Photobasicity originally ascribed to charge-transfer excited state increasing electron density at imine N.
- $\Delta q^+$  is modest at this N atom.
- Excited state protonation causes a significant relief of excited state anti-aromaticity.
- Photobase goes from anti-aromatic in S<sub>1</sub> to aromatic in S<sub>1</sub> upon protonation.



## Computational Methods

- Geometry optimizations and frequency calculations performed at the  $\omega$ B97X-D/def2-SVPD level of theory with a CPCM solvent model using Q-Chem software.
- All stationary points verified to be true minima using harmonic vibrational analysis
- NICS(1)<sub>zz</sub> were calculated at the TPSS/def2-TZVPPD level of theory with a GIAO treatment of magnetic properties using ORCA software.
- Following literature precedent, The excited state aromaticity/anti-aromaticity was approximated using NICS(1)<sub>zz</sub> values calculated using T<sub>1</sub>.
- For the studied photobases, the electronic characters of the T<sub>1</sub> and S<sub>1</sub> states are similar.

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