Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Magnetic Coupling Modulation in Meta-Nitroxide-Functionalized Isoalloxazine Magnets with Redox-Active Unit as Efficient Side-Modulator

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## Supporting Information

## Contents

## 1. Relevant Data for Describing the Grounds States for All Designed Diradicals, and Their Magnetic Behaviors

**Table S1.** All estimated energies (in a.u.) of the closed shell (CS) singlet, Broken-symmetry open-shell singlet (BS), and triplet (T) state, corresponding $<S^2>$ values, Magnetic Coupling Constants ($J$/cm$^{-1}$) for all diradicals calculated at **(**U)B3LYP/6-311+G (d, p) level.

| Types | $E_{(CS)}$(au) | $E_{(T)}$(au) ($<S^2>$) | $E_{(BS)}$ (au) ($<S^2>$) | $J$ (cm$^{-1}$) |
|---|---|---|---|---|
| **1a** | -958.8540130 | -958.8635592(2.062) | -958.8608718(1.011) | 561.3 |
| **1b** | -960.1187428 | -960.1215827(2.032) | -960.1269889(0.817) | -976.1 |
| **1c** | -959.2306459 | -959.2201800(2.032) | -959.2319023(0.427) | -1602.9 |
| **1d** | -959.1898011 | -959.2055203(2.103) | -959.2034475(0.903) | 379.1 |
| **1e** | -959.4516180 | -959.4281143(2.079) | -959.4516180(0.000) | - |
| **1b(OH)** | -1035.3645946 | -1035.3677092(2.031) | -1035.3729327(0.824) | -949.8 |
| **1b(NO2)** | -1164.6767663 | -1164.6818318(2.034) | -1164.6859589(0.839) | -757.9 |
| **1b(NH2)** | -1015.4927989 | -1015.4962867(2.032) | -1015.5010931(0.830) | -877.6 |

**Table S2.** The energies (in a.u.) of the broken-symmetry (BS) open-shell singlet and triplet (T) state, corresponding $<S^2>$ values, intramolecular magnetic coupling constants ($J'$/cm$^{-1}$) for all diradicals calculated at the (U)M06-2X/6-311+G(d,p) level.

| Types | $E_{(T)}$(au) ($<S^2>$) | $E_{(BS)}$ (au) ($<S^2>$) | $J'$ (cm$^{-1}$) |
|---|---|---|---|
| **1a** | -958.499891(2.073) | -958.4973545(1.029) | 533.2 |
| **1b** | -959.753139(2.046) | -959.7563254(0.966) | -647.5 |
| **1c** | -958.8483421(2.059) | -958.8568787(0.677) | -1355.7 |
| **1d** | -958.8307407(2.153) | -958.8272419(1.014) | 674.2 |
| **1e** | -959.0439509(2.157) | -959.0726533(0.000) | - |
| **1b(OH)** | -1034.9770312(2.046) | -1034.9800542(0.969) | -616.0 |
| **1b($NO_2$)** | -1164.2384853(2.046) | -1164.2411165(0.972) | -537.7 |
| **1b($NH_2$)** | -1015.1083185(2.046) | -1015.1106948(0.975) | -486.9 |

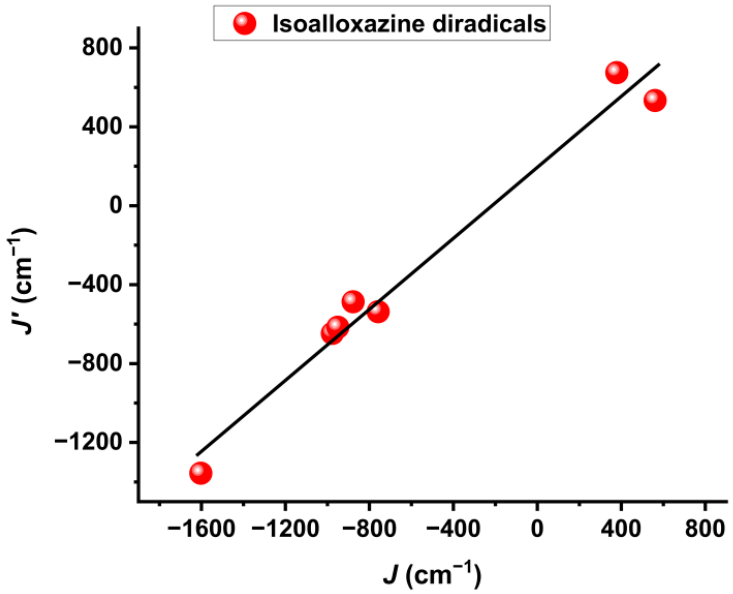



**Figure S1.** A linear correlation between the *J* values of selected all diradicals calculated at the B3LYP/6-311+G(d,p) level and those (*J′* values) calculated at the M06-2X/6-311+G(d,p) level.

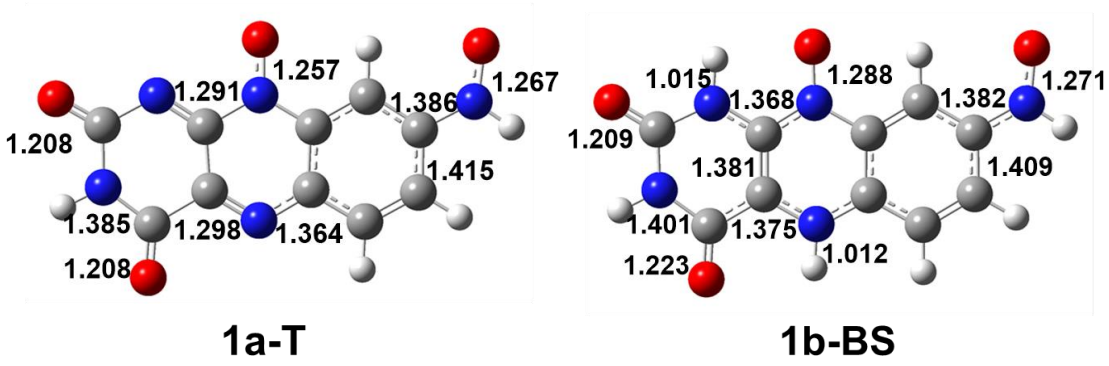
**Table S3**. All calculated energies of open-shell singlet (BS) and triplet (T) states, along with $<S^2>$ values, Magnetic Coupling Constants ($J$/cm$^{-1}$) for all diradicals as well as singlet-triplet energy gaps ($\Delta E_{ST}$) at the (U)B3LYP/6-311+G (d, p) level.

| Types | $E_{(T)}$ ($<S^2>$) (au) | $E_{(BS)}$ ($<S^2>$) (au) | $J$ (cm$^{-1}$) | $\Delta E_{ST}$ (kcal/mol) |
|---|---|---|---|---|
| **1a** | -958.8635592(2.062) | -958.8608718(1.011) | 561.3 | 3.30 |
| **1b** | -960.1215827(2.032) | -960.1269889(0.817) | -976.1 | -5.67 |
| **1c** | -959.2201800(2.032) | -959.2319023(0.427) | -1602.9 | -9.31 |
| **1d** | -959.2055203(2.103) | -959.2034475(0.903) | 379.1 | 2.27 |
| **1b(OH)** | -1035.3677092(2.031) | -1035.3729327(0.824 | -949.8 | -5.51 |
| **1b($NO_2$)** | -1164.6818318(2.034) | -1164.6859589(0.839) | -757.9 | -4.40 |
| **1b($NH_2$)** | -1015.4962867(2.032) | -1015.5010931(0.830) | -877.6 | -5.09 |

**Table S4**. Two SOMO Energies ($E_S$, in au) of the Triplet States, SOMO-SOMO Energy Gaps ($\Delta E_{SS}$, in eV), Calculated at the **(**U)B3LYP/6-311+G (d, p) level

| Types | $^1E_S$ (au) | $^2E_S$ (au) | $\Delta E_{SS}$ (eV) | $\Delta E_{ST}$(kcal/mol) |
|---|---|---|---|---|
| **1a** | –0.27067 | –0.25084 | 0.54 | 3.30 |
| **1b** | –0.23635 | –0.19035 | 1.25 | -5.67 |
| **1c** | –0.43986 | –0.38946 | 1.37 | -9.31 |
| **1d** | –0.41615 | –0.38425 | 0.86 | 2.27 |
| **1b(OH)** | –0.23573 | –0.18813 | 1.29 | -5.51 |
| **1b($NO_2$)** | –0.25381 | –0.21023 | 1.18 | -4.40 |
| **1b($NH_2$)** | –0.23279 | –0.18894 | 1.19 | -5.09 |

## 2. Optimized Molecular Geometries with Corresponding Bond Lengths




**1a-T** **1b-BS**

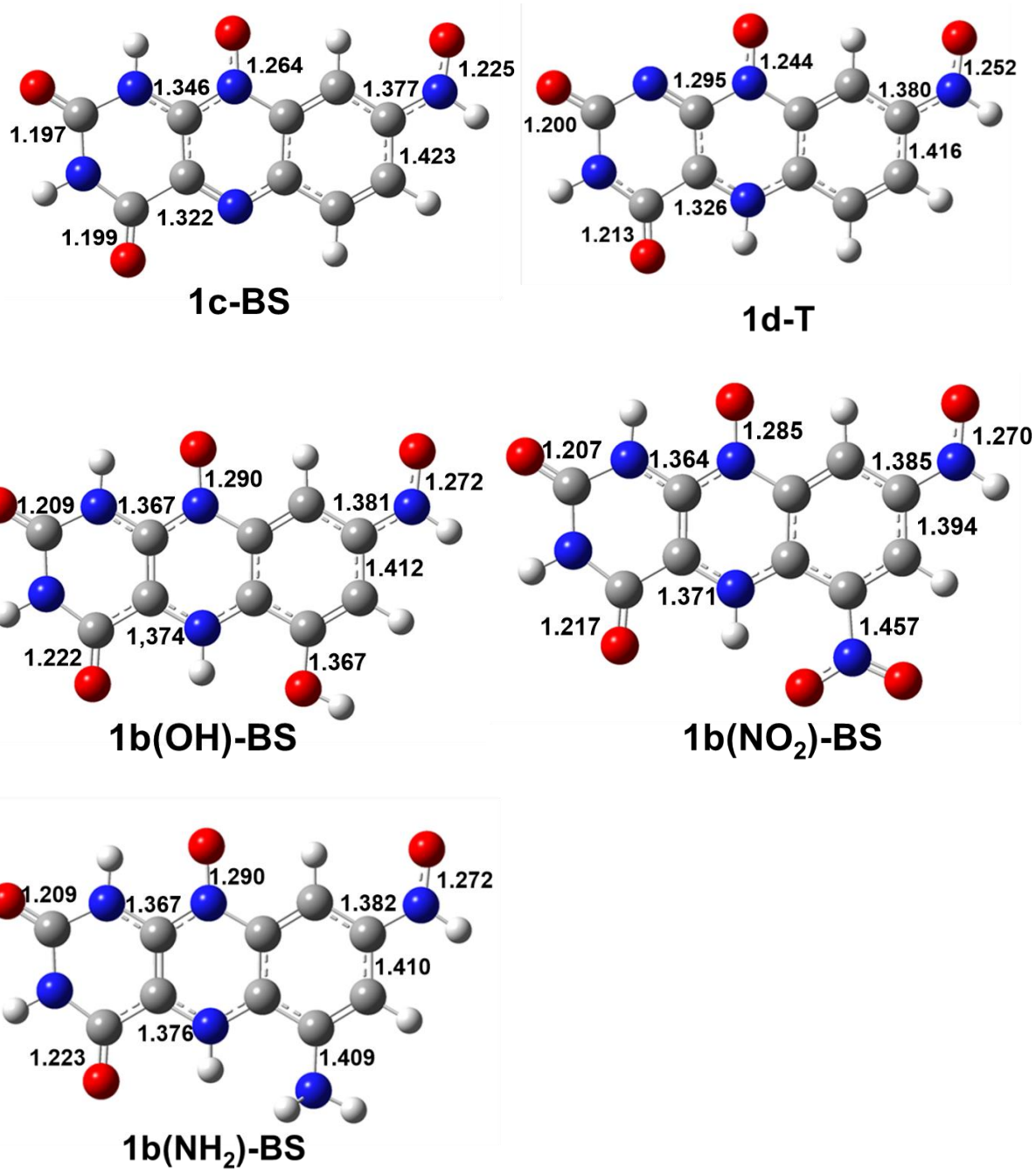
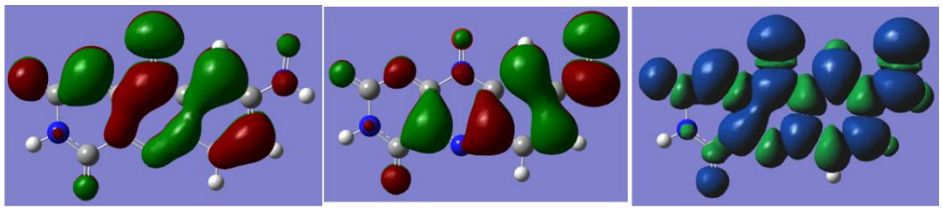
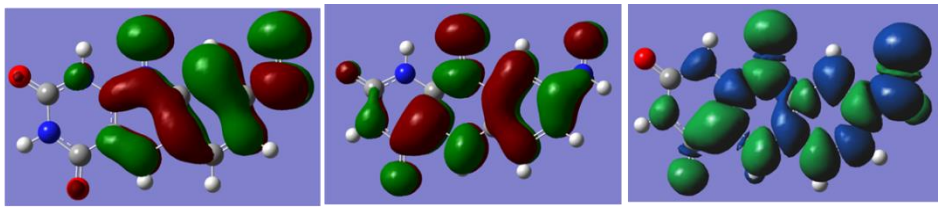



**Figure S2.** The ball-and-stick models for the optimized geometries of all diradicals with the calculated magnetic exchange spin coupling constants ($J$/cm$^{-1}$). White spheres denote H atoms, gray, C atoms, blue, N atoms and red, O atoms.

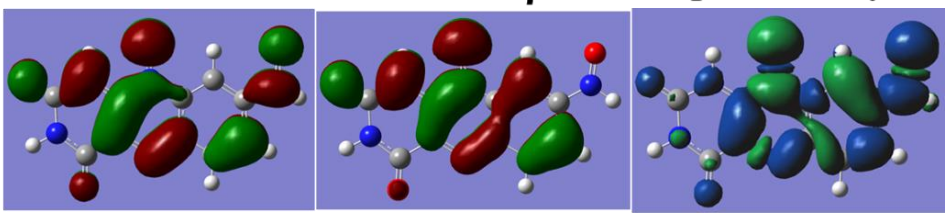
## 3. SOMO Plots and Spin Density Maps for All Diradicals



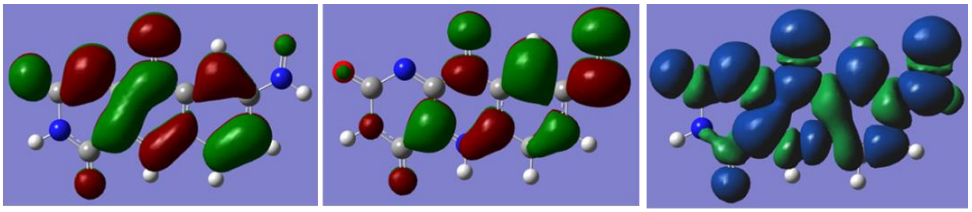
1a SOMO 1 SOMO 2 Spin Density



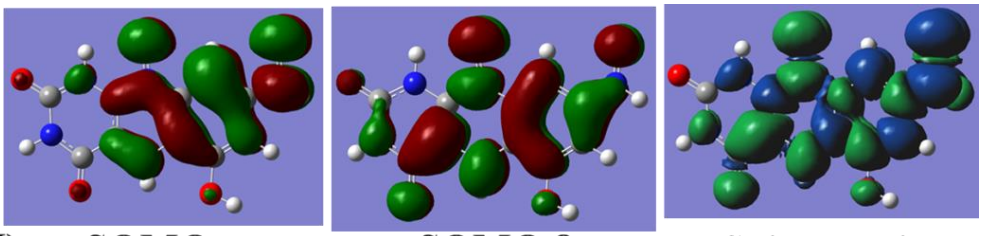
1b SOMO α SOMO β Spin Density



1c SOMO α SOMO β Spin Density



1d SOMO 1 SOMO 2 Spin Density



1b(OH) SOMO α SOMO β Spin Density

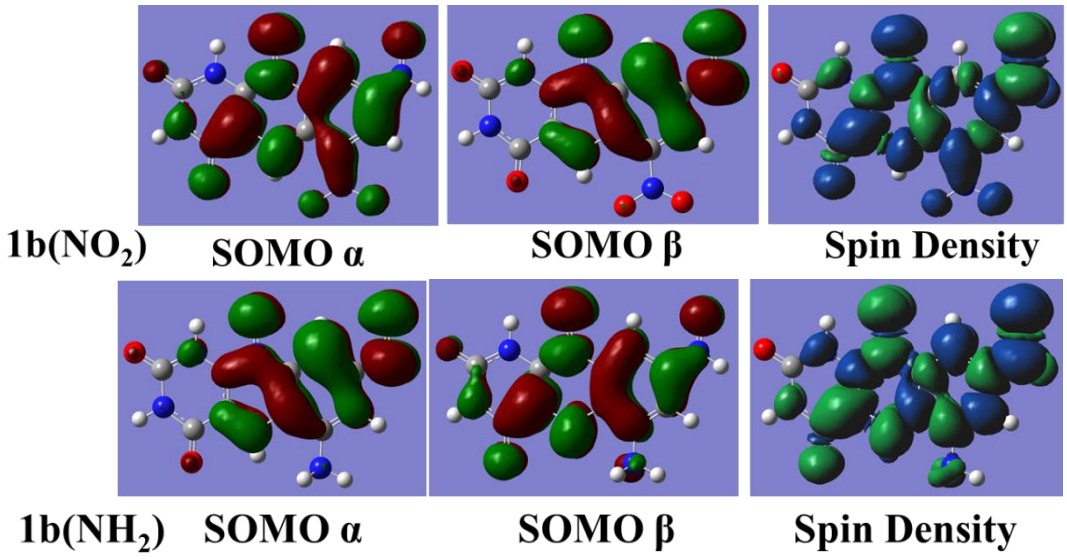
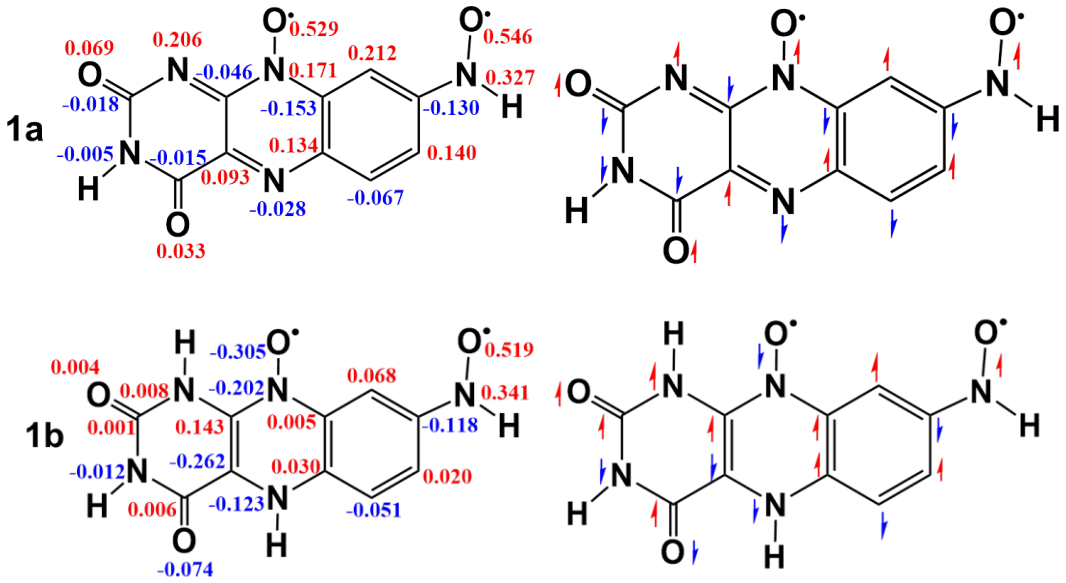
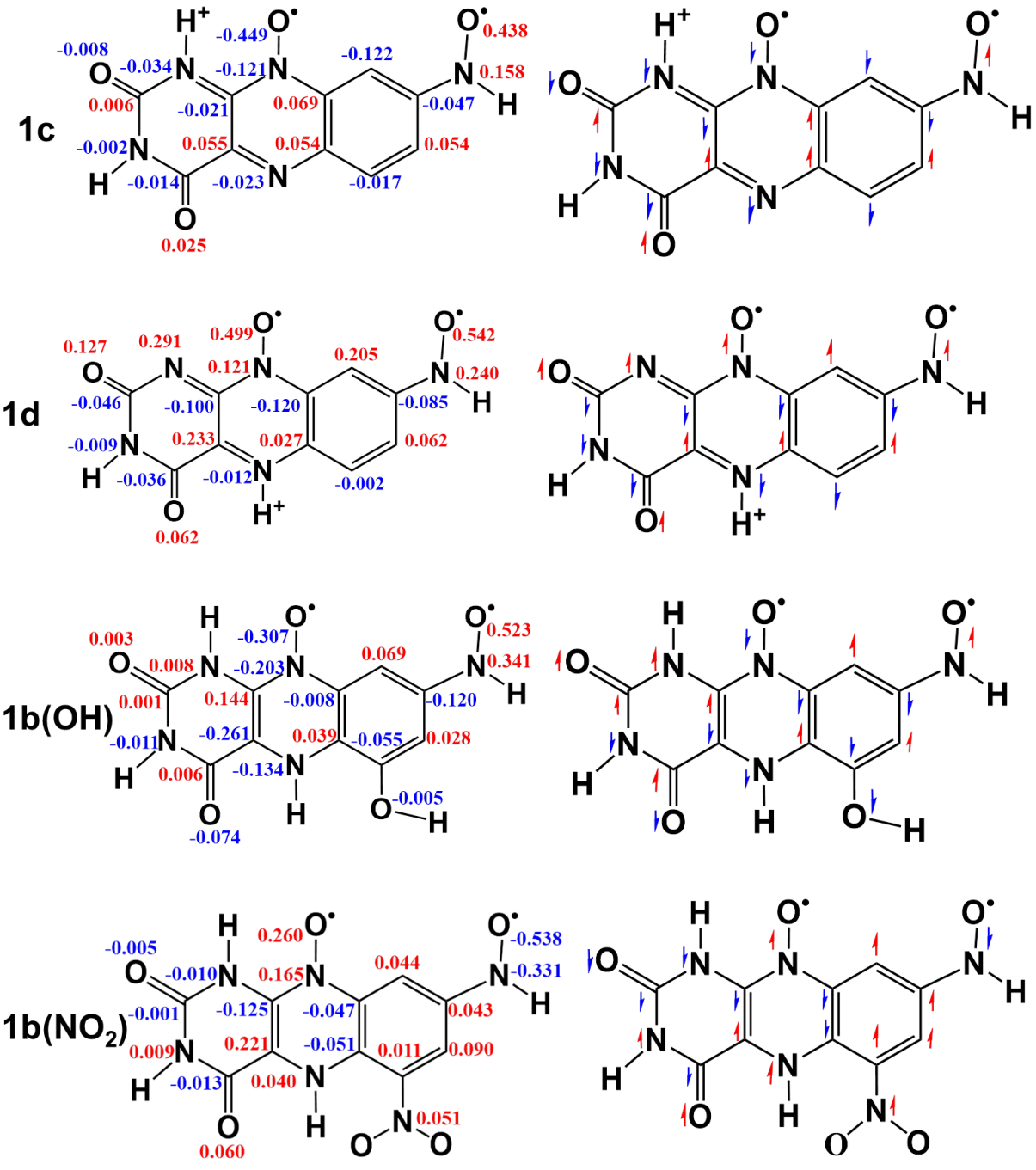



**Figure S3**. The SOMOs (isovalue = 0.02) and spin density maps (isovalue = 0.0004) for the T and BS states of all diradicals at the (U)B3LYP/6-311+G (d, p) level.

## 4. Spin Alternation Plots and Spin Density Distributions




1c
1d
1b(OH)
1b(NO2)

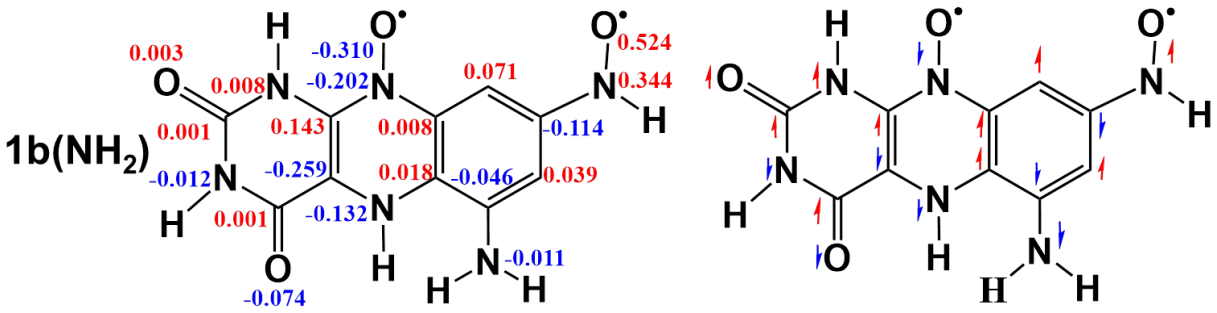



**Figure S4.** Spin density distributions (the left column, numbers) and scheme of spin alternation (the right column, up and down arrows) for all diradicals.