Proton-Transfer Regulated Magnetic Coupling Characteristics in Blatter-Based

Diradicals

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Supporting Information

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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 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/6-31G (d, p) level.

NO-Bl	$E_{(T)}$/ (au) ($<S^2>$)	$E_{(BS)}$/(au) ($<S^2>$)	J/cm^{-1}
NO-Bl-OH(B)	−1101.8284129(2.019)	−1101.8375330(0.695)	−1510.9
NO-BlH-O(B)	−1101.8134497(2.027)	−1101.8195260(0.814)	−1099.4
NO-Bl-OH(C)	−1101.8287307(2.026)	−1101.8326996(0.505)	−777.5
NO-BlH-O(C)	−1101.8111466(2.026)	−1101.8140490(0.942)	−587.9
NN-Bl	$E_{(T)}$/ (au) ($<S^2>$)	$E_{(BS)}$/(au) ($<S^2>$)	J/cm^{-1}
NN-Bl-OH(B)	−1347.8774827(2.082)	−1347.8748705(1.065)	563.7
NN-BlH-O(B)	−1347.8570165(2.075)	−1347.8553303(1.075)	369.2
NN-Bl-OH(C)	−1347.8773397(2.086)	−1347.8759719(1.072)	296.1
NN-BlH-O(C)	−1347.8593919(2.084)	−1347.8584158(1.073)	211.9
IN-Bl	$E_{(T)}$/ (au) ($<S^2>$)	$E_{(BS)}$/(au) ($<S^2>$)	J/cm^{-1}
IN-Bl-OH(B)	−1272.7085966(2.040)	−1272.7074650(1.025)	244.7
IN-BlH-O(B)	−1272.6881220(2.036)	−1272.6875424(1.030)	126.5
IN-Bl-OH(C)	−1272.7083914(2.040)	−1272.7078886(1.030)	109.2
IN-BlH-O(C)	−1272.6905787(2.038)	−1272.6902038(1.031)	81.7
VER-Bl	$E_{(T)}$/ (au) ($<S^2>$)	$E_{(BS)}$/(au) ($<S^2>$)	J/cm^{-1}
VER-Bl-OH(B)	−1268.8714601(2.052)	−1268.8701887(1.037)	274.9
VER-BlH-O(B)	−1268.8523045(2.050)	−1268.8510676(1.043)	270.9
VER-Bl-OH(C)	−1268.8714188(2.051)	−1268.8707135(1.043)	153.5
VER-BlH-O(C)	−1268.8533438(2.051)	−1268.8527730(1.043)	124.4

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/6-31G(d,p) level.

Types	$E_{(T)}$ ($<S^2>$) (au)	$E_{(BS)}$ ($<S^2>$) (au)	J' (cm^{-1})
NO-Bl-OH(B)	−1101.3799286(2.022)	−1101.3870711(0.875)	−1366.9
NO-BlH-O(B)	−1101.3598321(2.035)	−1101.3650475(0.913)	−1020.2
NO-Bl-OH(C)	−1101.3799494(2.027)	−1101.3827258(0.988)	−586.5
NO-BlH-O(C)	−1101.3571968(2.033)	−1101.3589684(1.013)	−381.0
NN-Bl-OH(B)	−1347.3285495(2.125)	−1347.3245745(1.002)	776.9
NN-BlH-O(B)	−1347.3034188(2.123)	−1347.3015246(1.125)	416.5
NN-Bl-OH(C)	−1347.3271523(2.129)	−1347.3258318(1.114)	285.5
NN-BlH-O(C)	−1347.3040791(2.132)	−1347.3032643(1.121)	176.9
IN-Bl-OH(B)	−1272.1908178(2.040)	−1272.1900430(1.030)	168.3
IN-BlH-O(B)	−1272.1658036(2.043)	−1272.1653656(1.041)	95.90
VER-Bl-OH(B)	−1268.3572773(2.062)	−1268.3554399(1.048)	397.6
VER-BlH-O(B)	−1268.3328822(2.059)	−1268.3316553(1.059)	269.3
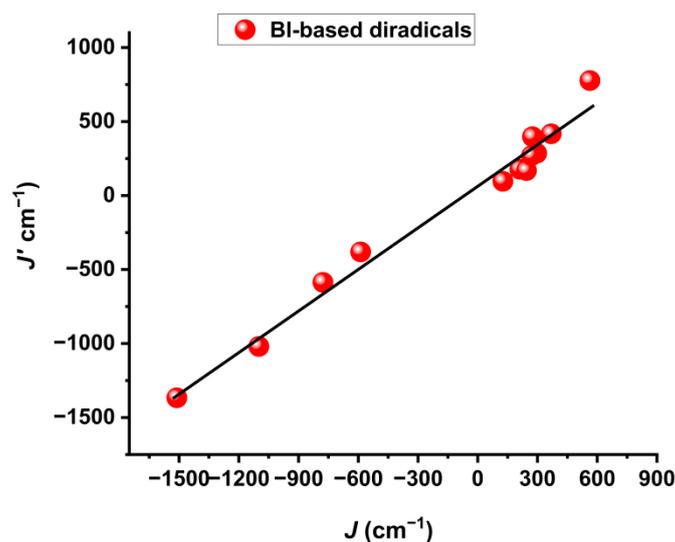
Figure S1. A linear correlation between the J values of selected Blatter diradicals (also presented in Table 1) calculated at the B3LYP/6-31G(d,p) level and those (J' values) calculated at the M06-2X/6-31G(d,p) level.

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 (ΔE_{ST}) at the (U)B3LYP/6-31G (d, p) level.

Types	$E_{(T)}$ ($<S^2>$) (au)	$E_{(BS)}$ ($<S^2>$) (au)	J (cm^{-1})	ΔE_{ST} (kcal/mol)
NN-Bl-OH(B)	−1347.8774827(2.082)	−1347.8748705(1.065)	563.7	3.36
NN-BlH-O(B)	−1347.8570165(2.075)	−1347.8553303(1.075)	369.2	2.19
NN-Bl-OH(C)	−1347.8773397(2.086)	−1347.8759719(1.072)	296.1	1.77
NN-BlH-O(C)	−1347.8593919(2.084)	−1347.8584158(1.073)	211.9	1.26
NO-Bl-OH(B)	−1101.8284129(2.019)	−1101.8375330(0.695)	−1510.9	−8.72
NO-BlH-O(B)	−1101.8134497(2.027)	−1101.8195260(0.814)	−1099.4	−6.37
NO-Bl-OH(C)	−1101.8287307(2.026)	−1101.8326996(0.505)	−777.5	−4.50
NO-BlH-O(C)	−1101.8111466(2.026)	−1101.8140490(0.942)	−587.9	−3.40
IN-Bl-OH(B)	−1272.7085966(2.040)	−1272.7074650(1.025)	244.7	1.42
IN-BlH-O(B)	−1272.6881220(2.036)	−1272.6875424(1.030)	126.5	0.73
IN-Bl-OH(C)	−1272.7083914(2.040)	−1272.7078886(1.030)	109.2	0.64
IN-BlH-O(C)	−1272.6905787(2.038)	−1272.6902038(1.031)	81.7	0.47
VER-Bl-OH(B)	−1268.8714601(2.052)	−1268.8701887(1.037)	274.9	1.61
VER-BlH-O(B)	−1268.8523045(2.050)	−1268.8510676(1.043)	270.9	1.59
VER-Bl-OH(C)	−1268.8714188(2.051)	−1268.8707135(1.043)	153.5	0.90
VER-BlH-O(C)	−1268.8533438(2.051)	−1268.8527730(1.043)	124.4	0.72

Table S4. Two SOMO Energies (E_S, in au) of the Triplet States, SOMO-SOMO Energy Gaps (ΔE_{SS}, in eV), Calculated at the (U) B3LYP/6-31G (d, p) level

Types	^1E_S (au)	^2E_S (au)	ΔE_{SS} (eV)	ΔE_{ST}(kcal/mol)
NO-Bl-OH(B)	−0.20985	−0.16426	1.24	−8.72
NO-BlH-O(B)	−0.20506	−0.17567	0.79	−6.37
NO-Bl-OH(C)	−0.20784	−0.16818	1.07	−4.50
NO-BlH-O(C)	−0.19457	−0.17884	0.42	−3.40
NN-Bl-OH(B)	−0.19433	−0.16991	0.66	3.36
NN-BlH-O(B)	−0.19014	−0.18106	0.42	2.19
NN-Bl-OH(C)	−0.19661	−0.17102	0.70	1.77
NN-BlH-O(C)	−0.19464	−0.18334	0.30	1.26
IN-Bl-OH(B)	−0.20987	−0.16975	1.09	1.42
IN-BlH-O(B)	−0.19242	−0.18221	0.28	0.73
IN-Bl-OH(C)	−0.21231	−0.17102	1.12	0.64
IN-BlH-O(C)	−0.19534	−0.18373	0.32	0.47
VER-Bl-OH(B)	−0.18963	−0.15912	0.83	1.61
VER-BlH-O(B)	−0.17929	−0.17137	0.21	1.59
VER-Bl-OH(C)	−0.19225	−0.16184	0.82	0.90
VER-BlH-O(C)	−0.18556	−0.17436	0.30	0.72

2. Optimized Molecular Geometries for All Diradicals
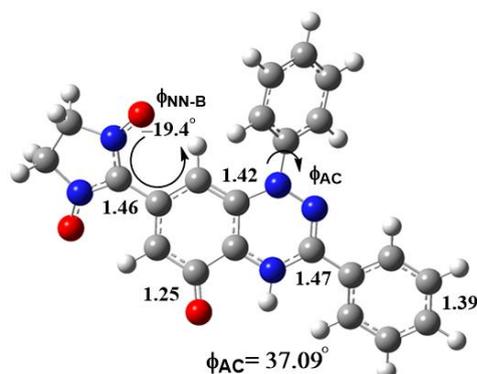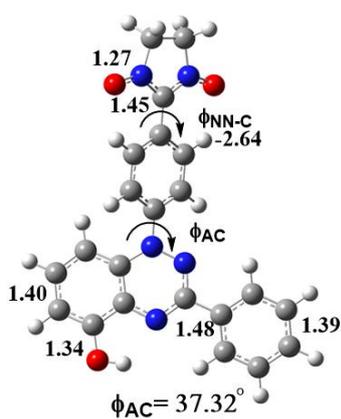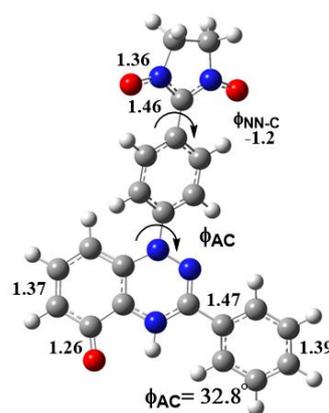
NN-Bl-OH(B)

$J = 563.7$ cm^{-1}

NN-BlH-O(B)

$J = 369.2$ cm^{-1}

NN-Bl-OH(C)

$J = 296.1$ cm^{-1}

NN-BlH-O(C)

$J = 211.9$ cm^{-1}

NO-Bl-OH(B)

$J = -1510.9$ cm^{-1}

NO-BlH-O(B)

$J = -1099.4$ cm^{-1}

NO-Bl-OH(C)

$J = -777.5$ cm^{-1}

NO-BlH-O(C)

$J = -587.9$ cm^{-1}

IN-Bl-OH(B)

$J = 244.7$cm^{-1}

IN-BlH-O(B)
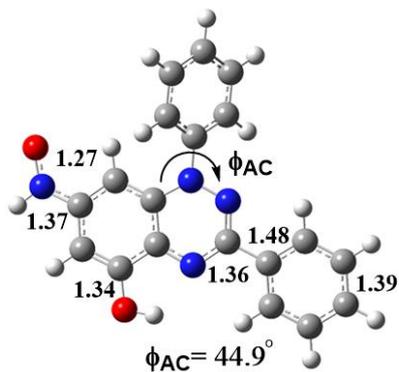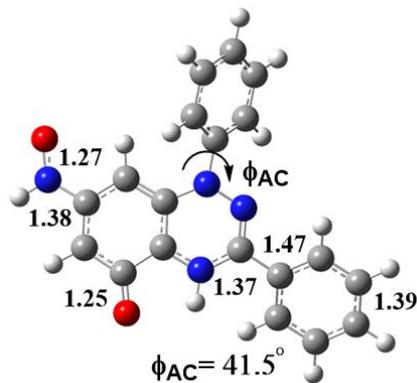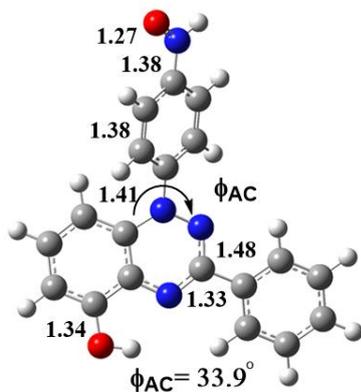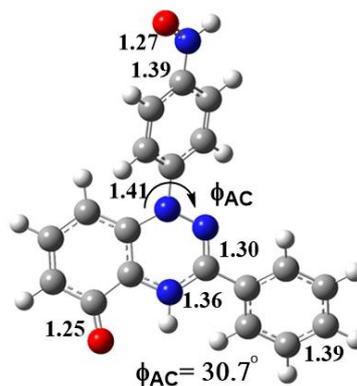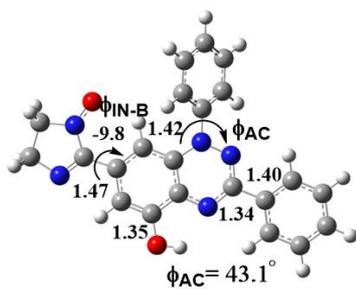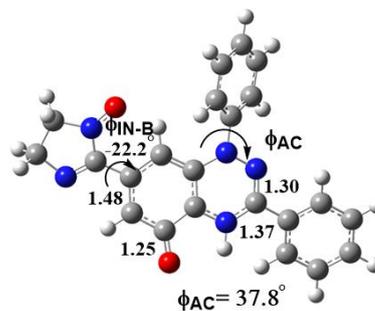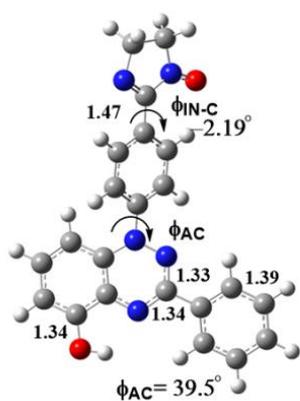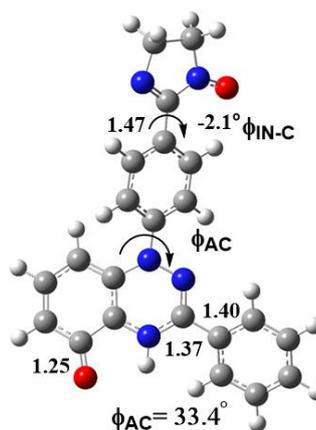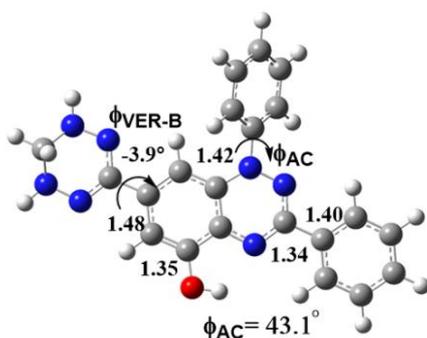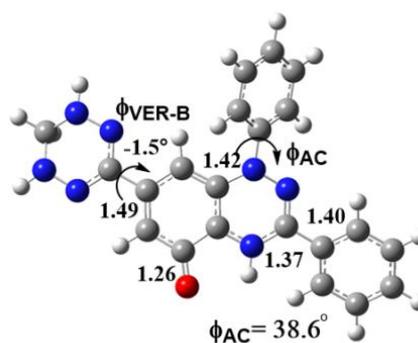
$J = 125.5$cm^{-1}

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. Spin Density Plots of Energetically Favorable and Unfavorable Spin States
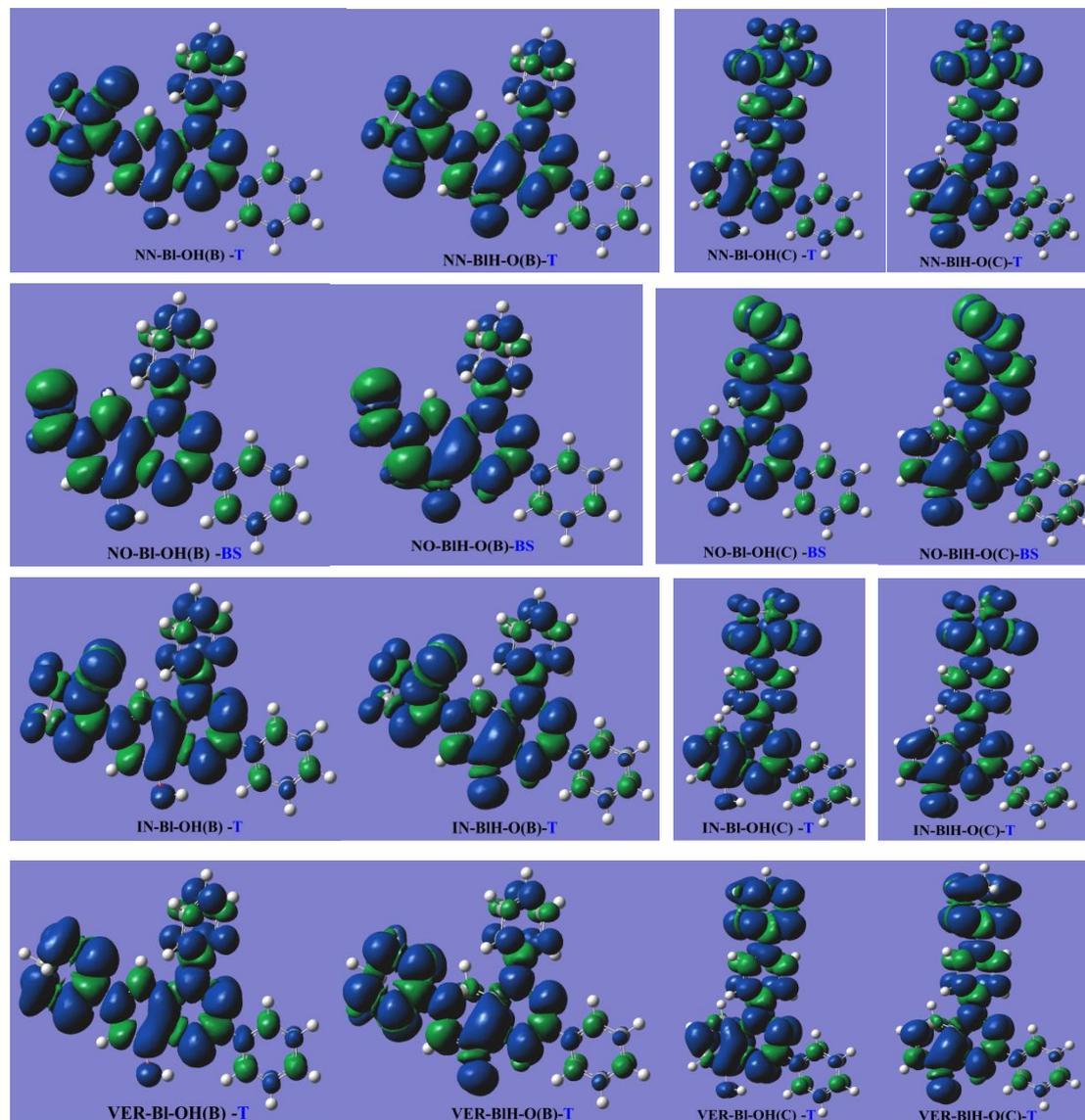
Figure S3. Spin density plots (isovalue = 0.0004) of ground states of all diradicals at the (U)B3LYP/6-31G (d, p) level.
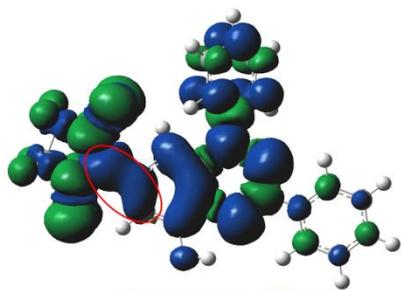
NN-Bl-OH(B) BS state
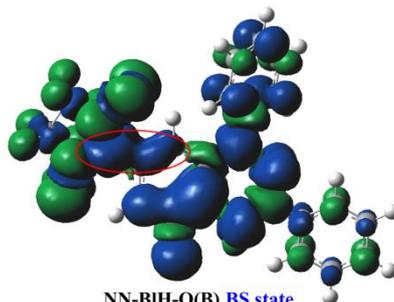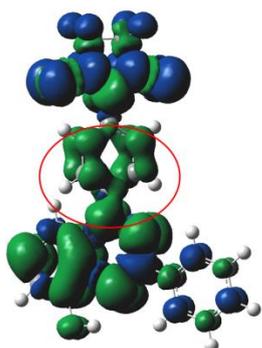
NN-BlH-O(B) BS state

NN-Bl-OH(C) BS state
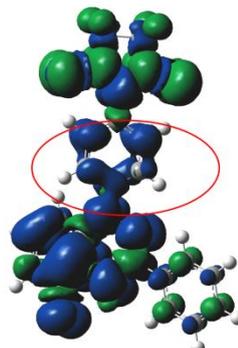
NN-BlH-O(C) BS state
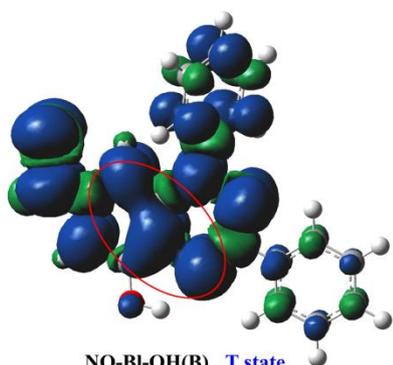
NO-Bl-OH(B) T state
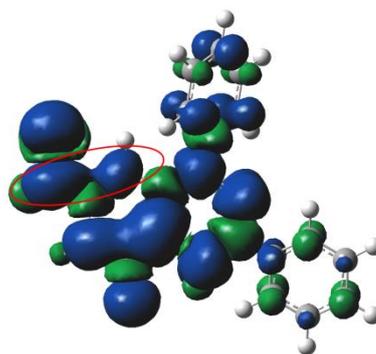
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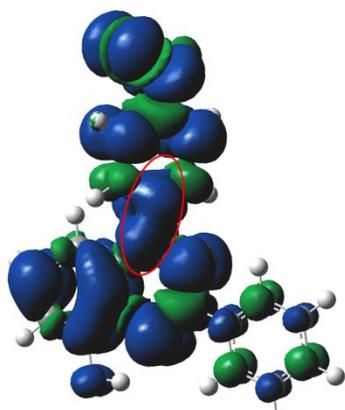
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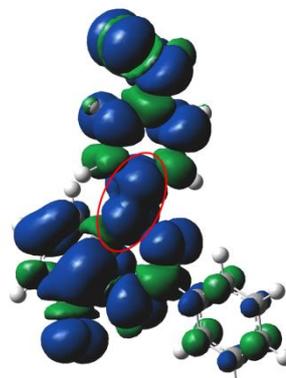
NO-BlH-O(C) T state
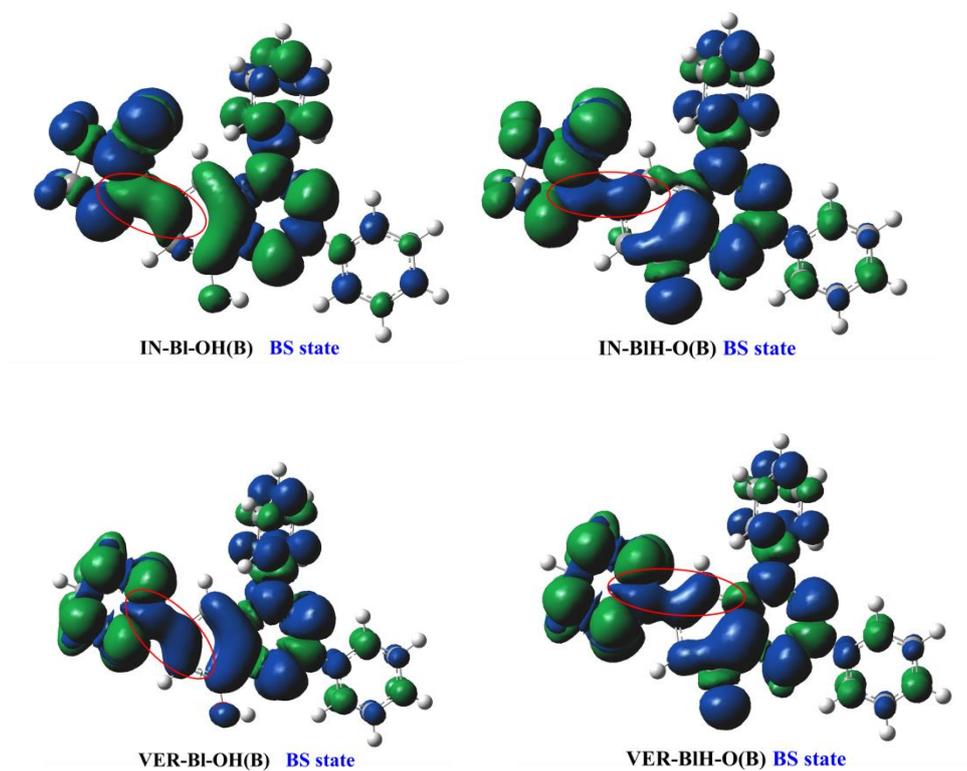
Figure S4. Spin density plots (isovalue = 0.0004) of energetically unfavorable spin states (not the ground states) for all diradicals. The red circles represent the mismatching of the spin polarization.

4. SOMO Plots of Ground States for All Diradicals
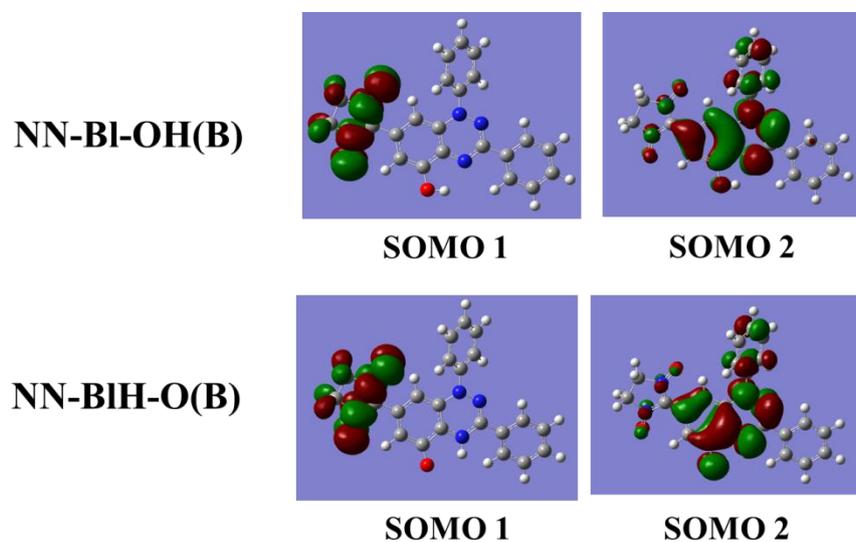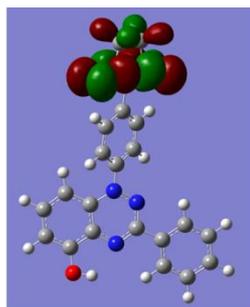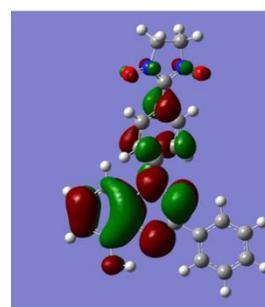
NN-Bl-OH(C)

SOMO 1   SOMO 2

NN-BlH-O(C)
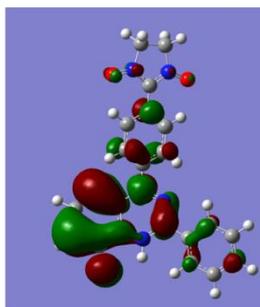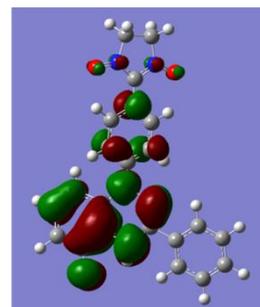
SOMO 1   SOMO 2

NO-Bl-OH(B)
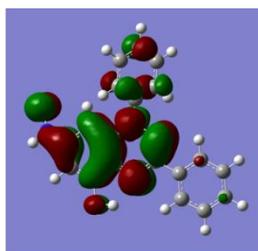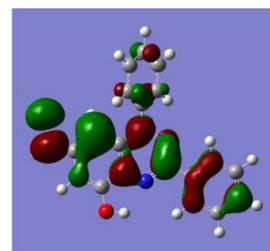
SOMO α   SOMO β

NO-BlH-O(B)

SOMO α   SOMO β

NO-Bl-OH(C)

SOMO α   SOMO β

NO-BlH-O(C)

SOMO α   SOMO β

IN-Bl-OH(B)

SOMO 1   SOMO 2

IN-BlH-O(B)

SOMO 1   SOMO 2

IN-Bl-OH(C)

SOMO 1　　　　SOMO 2

IN-BlH-O(C)

SOMO 1　　　　SOMO 2

VER-Bl-OH(B)
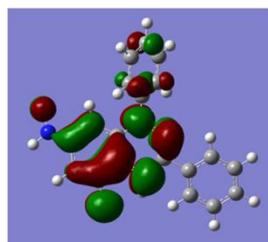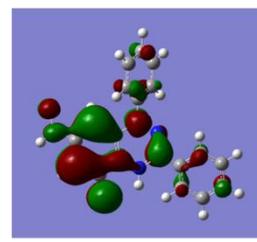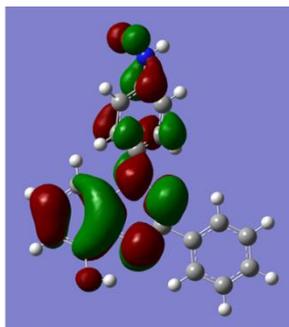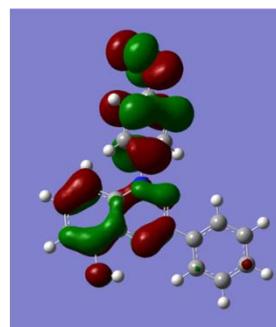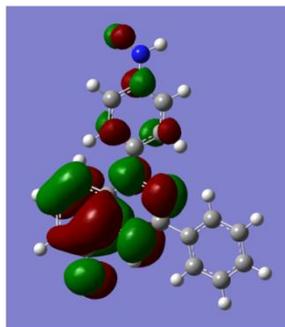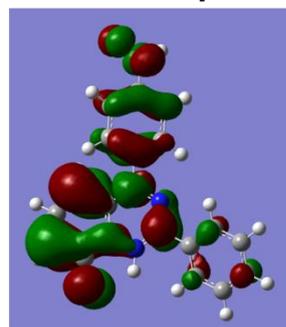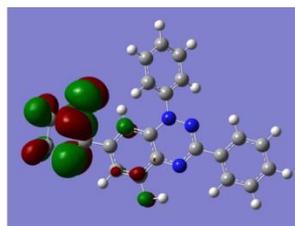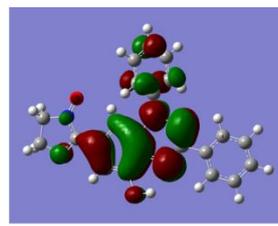
SOMO 1　　　　SOMO 2

VER-BlH-O(B)
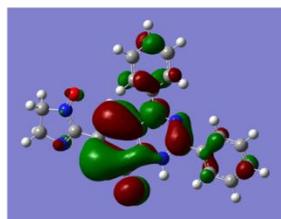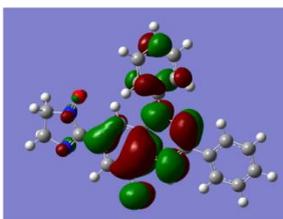
SOMO 1　　　　SOMO 2
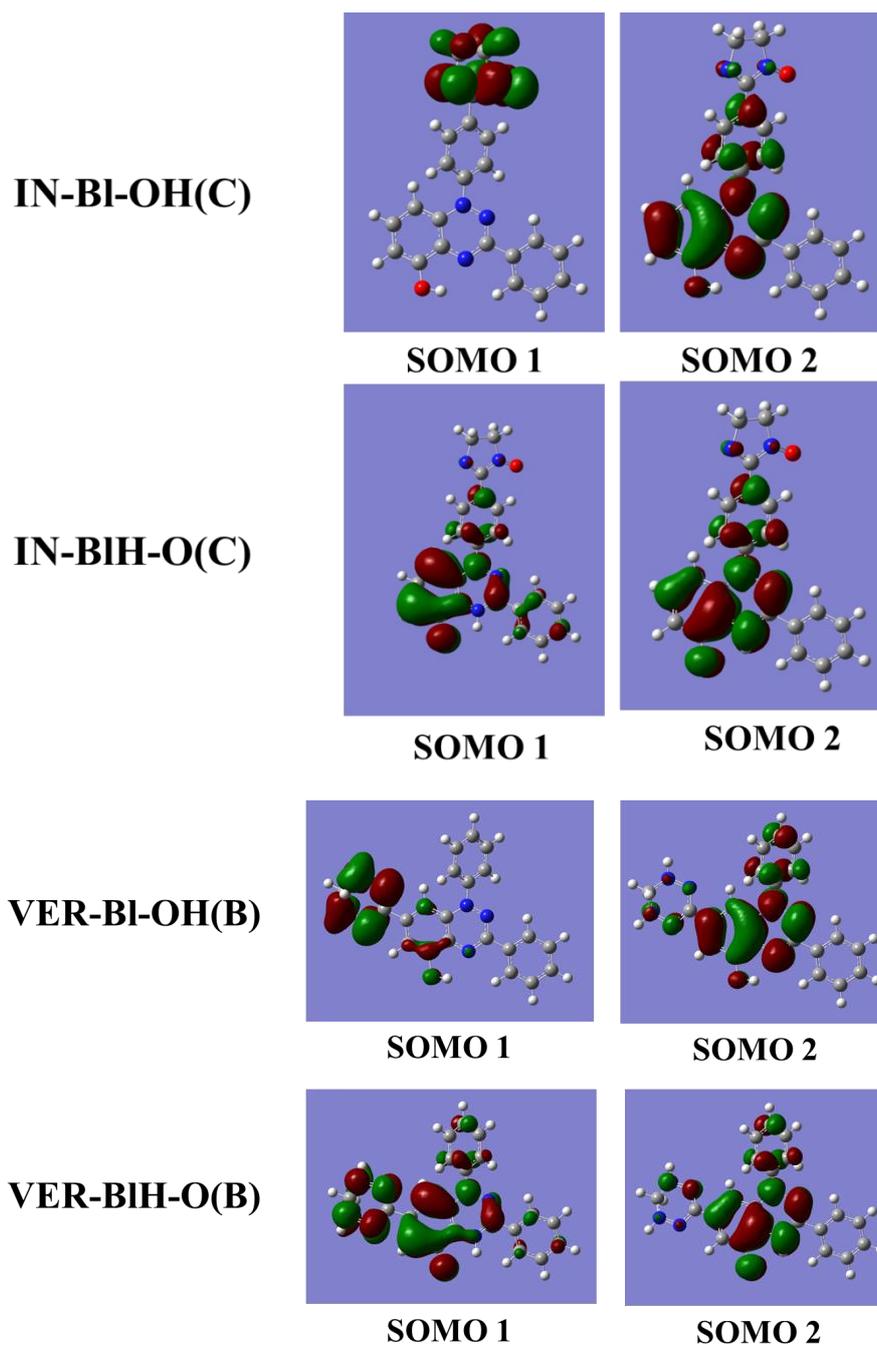
Figure S5. The SOMOs (isovalue = 0.02) for the T and BS states of all diradicals at the (U)B3LYP/6-31G (d, p) level.

5. Spin Alternation Plots and Spin Density Distributions

NN-Bl-OH(B)

NN-BlH-O(B)

NN-Bl-OH(C)

NN-BlH-O(C)

**NO-Bl-OH(B)**

NO-BlH-O(B)

NO-Bl-OH(C)

**NO-BlH-O(C)**
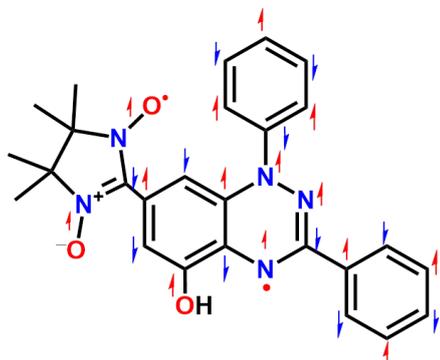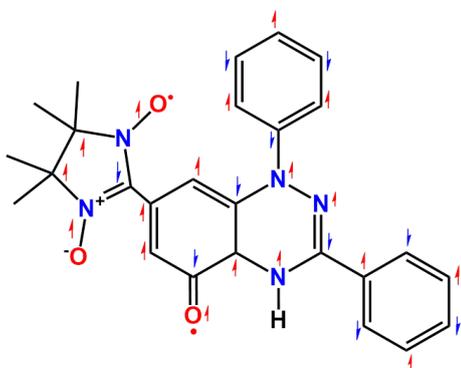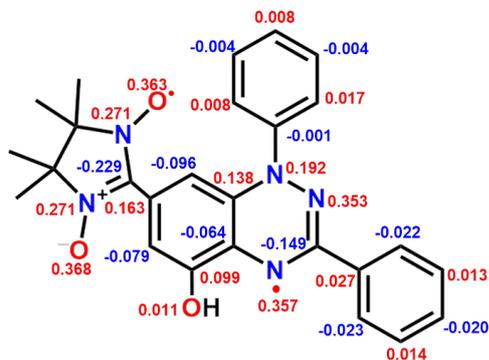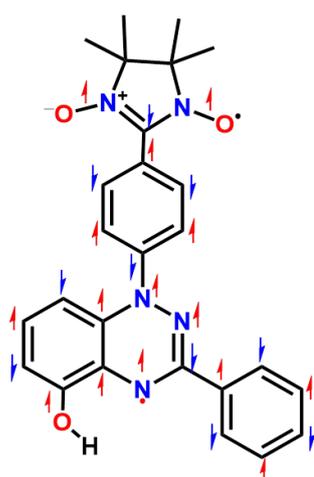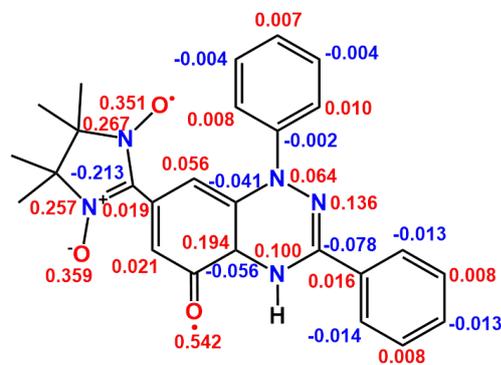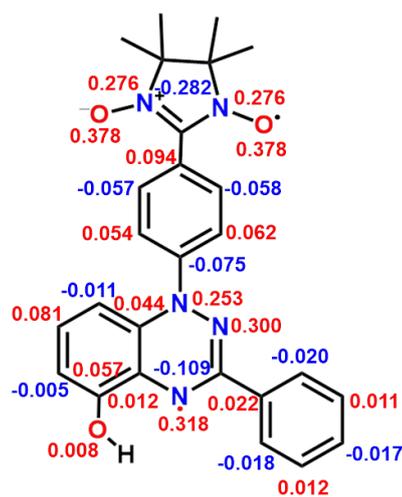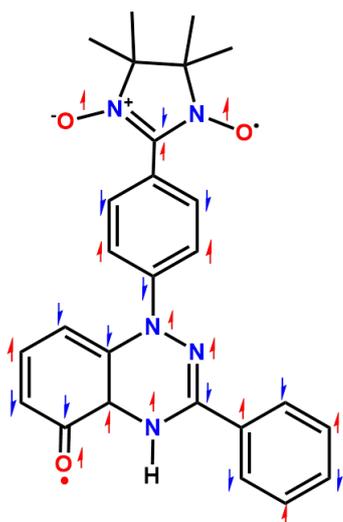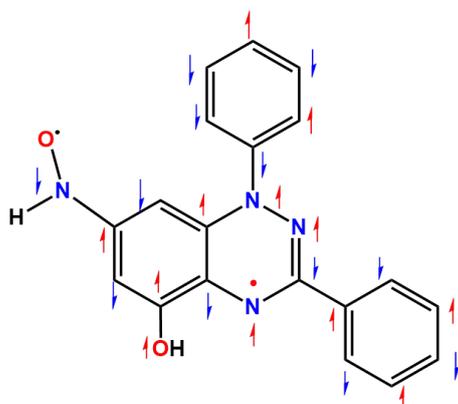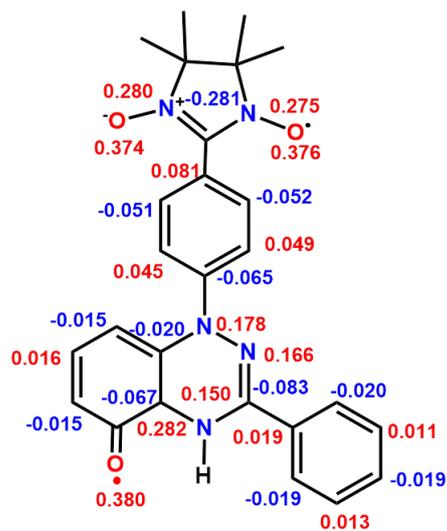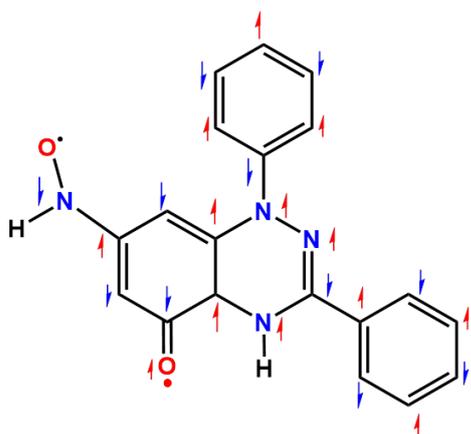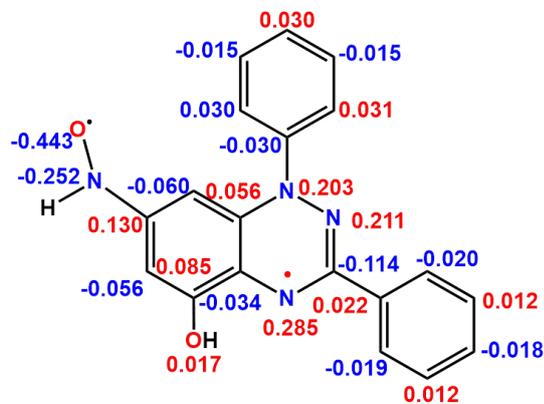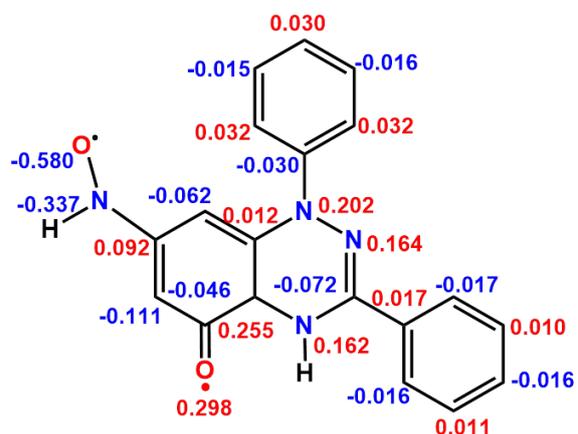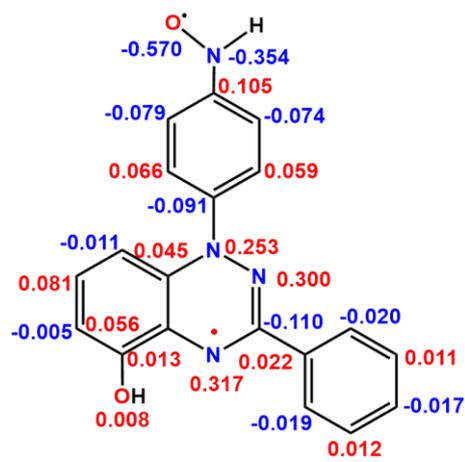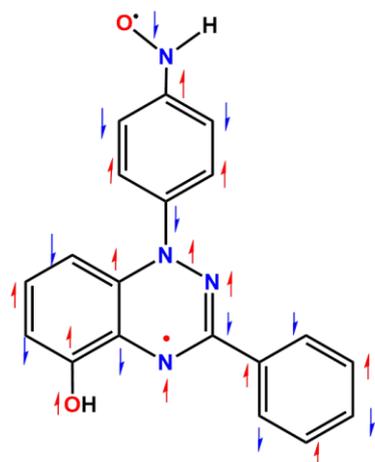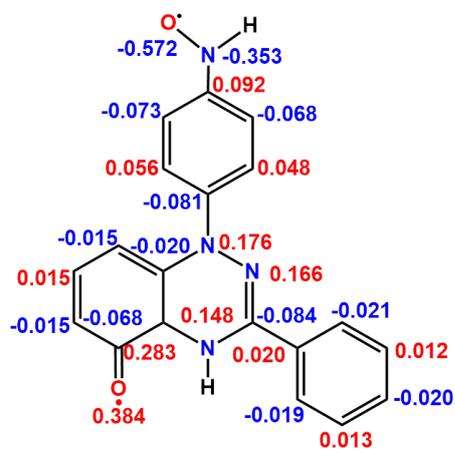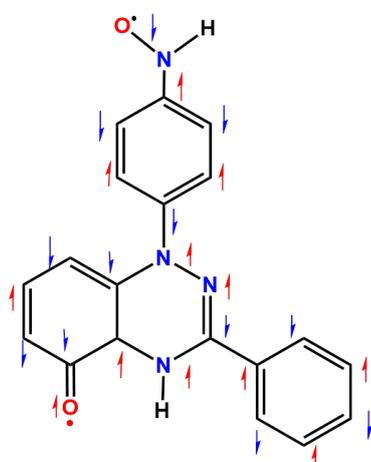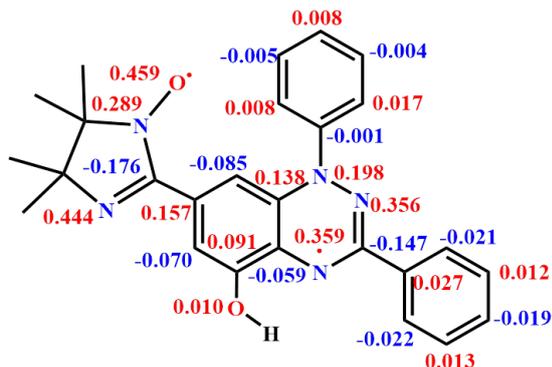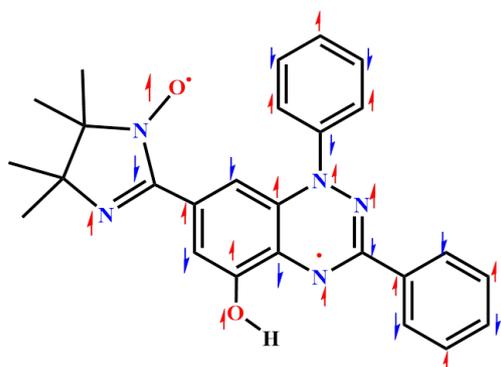
IN-Bl-OH(B)
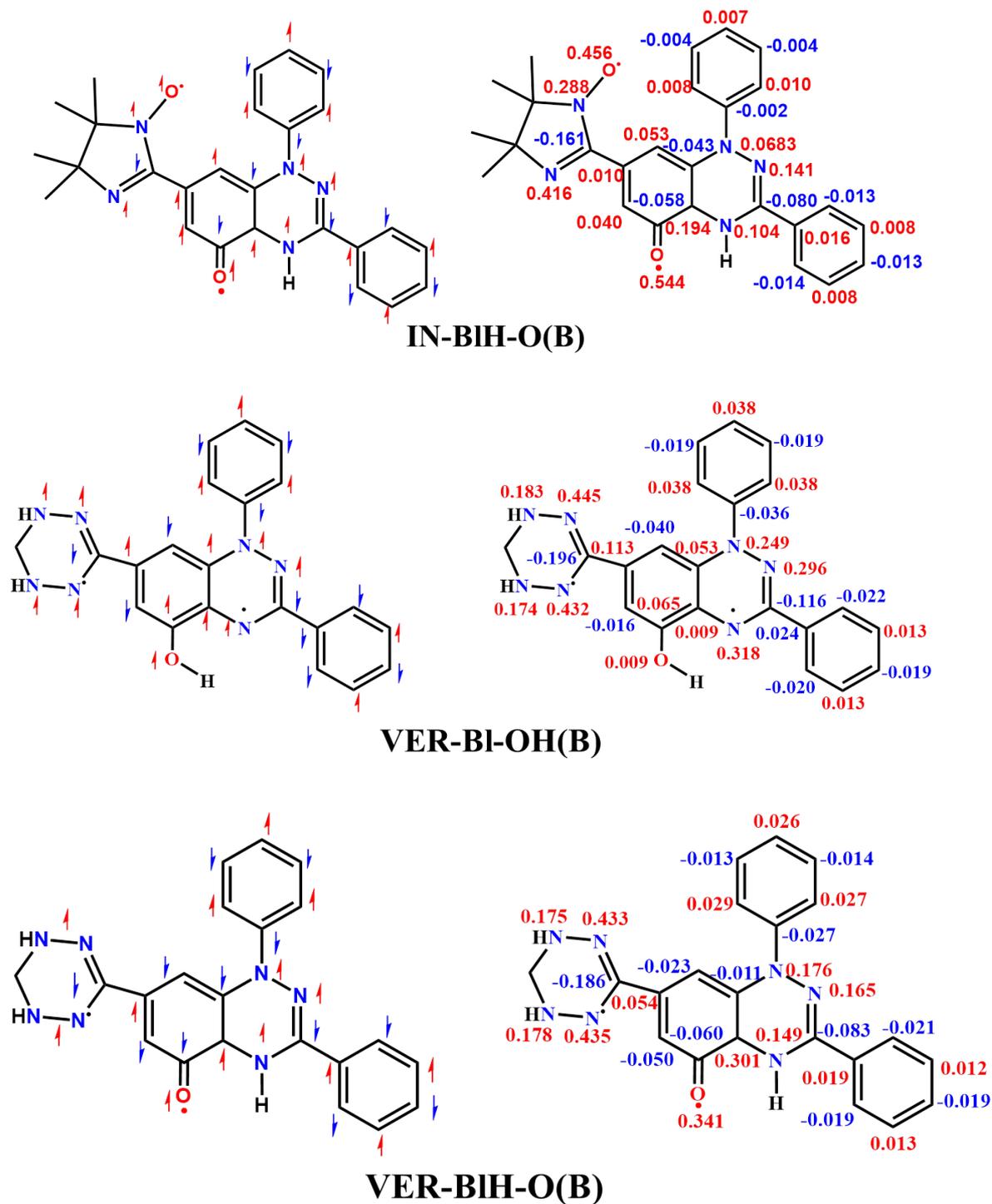
Figure S6. Spin density distributions (the right column, numbers) and scheme of spin alternation (the left column, up and down arrows) for all diradicals.