Supporting Information

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1. Relevant Data of Describing Ground States for All Designed Diradicals, Their Diradical Character and Magnetic Behaviors

Table S1. (U)B3LYP/6-311++G(d,p) level estimated energies (in a.u.) of the closed-shell (CS) singlet, broken-symmetry (BS) open-shell singlet and triplet (T) state, corresponding $<S^2>$ values, intramolecular magnetic coupling constants (J, in cm^{-1}) as well as S-T energy gaps (ΔE_{ST}, kcal/mol) for all studied nitroxide-based diradicals

Species	$E_{(CS)}$	$E_{(BS)}$ ($<S^2>$)	$E_{(T)}$ ($<S^2>$)	J	ΔE_{ST}
1a	-641.4380263	-641.4634223(1.034)	-641.4630648(2.082)	-74.8	-0.44
1b	-642.6473530	-642.6867238(1.005)	-642.6893172(2.036)	551.6	3.21
2a	-795.1248350	-795.1560298(1.035)	-795.1557353(2.054)	-63.4	-0.37
2b	-796.3303225	-796.3700529(1.014)	-796.3720239(2.050)	417.2	2.44
3a	-948.8084098	-948.8452382(1.026)	-948.8450641(2.034)	-37.9	-0.22
3b	-950.0009064	-950.0400077(1.022)	-950.0419894(2.087)	408.0	2.43
4a	-1102.4838078	-1102.5234243(1.031)	-1102.5233129(2.036)	-24.3	-0.14
4b	-1103.6719639	-1103.7118323(1.038)	-1103.7142024(2.157)	464.5	2.86
5a	-1256.1593704	-1256.2012445(1.036)	-1256.2011761(2.038)	-15.0	-0.09
5b	-1257.3416378	-1257.3807977(1.055)	-1257.3840817(2.304)	576.6	3.79
6a	-1409.8314648	-1409.8740725(1.050)	-1409.8740212(2.051)	-11.2	-0.07
6b	-1411.0054185	-1411.0494578(1.146)	-1411.0540885(2.517)	740.7	5.33
1c	-524.2320891	-524.2848499(1.009)	-524.2877531(2.033)	621.7	3.61
1d	-525.4602392	-525.4651502(0.768)	-525.4578212(2.036)	-1267.5	-7.37
2c	-677.9224919	-677.9653040(1.014)	-677.9670894(2.042)	380.9	2.22
2d	-679.1392148	-679.1531832(0.974)	-679.1503393(2.032)	-589.4	-3.43
3c	-831.5986800	-831.6375954(1.023)	-831.6392154(2.069)	339.6	2.01

3d	-832.8271046	-832.8500366(1.015)	-832.8486393(2.028)	-302.5	-1.75
4c	-985.2703056	-985.3081681(1.036)	-985.3100701(2.125)	383.0	2.32
4d	-985.5017878	-986.5314217(1.027)	-986.5305793(2.029)	-184.4	-1.07
5c	-1138.9406872	-1138.9770855(1.059)	-1138.9796257(2.236)	473.3	3.02
5d	-1140.1774835	-1140.2125906(1.033)	-1140.2121423(2.031)	-98.5	-0.57
6c	-1292.6097857	-1292.6453885(1.096)	-1292.6491806(2.434)	621.6	4.32
6d	-1293.8491436	-1293.8867316(1.045)	-1293.8864305(2.039)	-66.4	-0.39

Table S2. (U)M06-2X/6-311++G(d,p) level estimated 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, in cm^{-1}) for all studied nitroxide-based diradicals

Species	$E_{(BS)}$ ($<S^2>$)	$E_{(T)}$ ($<S^2>$)	J
1a	-641.2044049(1.065)	-641.2043554(2.089)	-10.6
1b	-642.4329108(1.010)	-642.4348843(2.034)	422.6
2a	-794.8393614(1.048)	-794.8393233(2.057)	-8.5
2b	-796.0555291(1.019)	-796.0569467(2.046)	302.7
3a	-948.4710141(1.030)	-948.4709925(2.034)	-4.7
3b	-949.6639157(1.026)	-949.6652353(2.073)	276.4
4a	-1102.0882483(1.032)	-1102.0882310(2.034)	-3.8
4b	-1103.2734185(1.039)	-1103.2748595(2.123)	291.5
5a	-1255.7050989(1.034)	-1255.7050882(2.035)	-2.3
5b	-1256.8795817(1.052)	-1256.8815429(2.246)	360.2
6a	-1409.3160678(1.042)	-1409.3160602(2.043)	-1.7
6b	-1410.4853052(1.090)	-1410.4883008(2.483)	471.6
1c	-524.0739089(1.012)	-524.0763106(2.034)	515.3
1d	-525.2441507(0.994)	-525.2406114(2.039)	-742.7
2c	-677.6928119(1.018)	-677.6941157(2.039)	280.0
2d	-678.8748725(1.033)	-678.8736934(2.034)	-258.3
3c	-831.3019635(1.027)	-831.3030659(2.060)	234.0
3d	-832.5121497(1.033)	-832.5116849(2.029)	-102.3
4c	-984.9101606(1.039)	-984.9113111(2.097)	238.5
4d	-986.1328909(1.033)	-986.1325996(2.029)	-64.1
5c	-1138.5159686(1.056)	-1138.5174119(2.176)	282.6
5d	-1139.7535376(1.033)	-1139.7533716(2.030)	-36.5
6c	-1292.1212049(1.080)	-1292.1233559(2.352)	370.8

6d	-1293.3659531(1.040)	-1293.3658228(2.036)	-28.7

Table S3. (U)B3LYP/6-311++G(d,p) level estimated 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, in cm^{-1}) for four couples of bis(tert-butyl)-nitroxide-based diradicals

Species	$E_{(BS)}$ ($<S^2>$)	$E_{(T)}$ ($<S^2>$)	J
2a′	-1109.7289295(1.023)	-1109.7285674(2.041)	-78.0
2b′	-1110.9444029(1.014)	-1110.9449151(2.025)	111.1
3a′	-1263.4271834(1.022)	-1263.4269754(2.030)	-45.2
3b′	-1264.6185796(1.021)	-1264.6201755(2.074)	332.3
2c′	-992.5502641(1.012)	-992.5516567(2.036)	298.2
2d′	-993.7322030(0.990)	-993.7301652(2.028)	-430.5
3c′	-1146.2180983(1.019)	-1146.2194055(2.059)	275.6
3d′	-1147.4265221(1.019)	-1147.4255500(2.024)	-212.1

2. HOMO and LUMO Energy Levels and HOMO-LUMO Gaps of Couplers for Ferromagnetic Diradicals

Table S4. The HOMO and LUMO energy levels (in a.u.) as well as HOMO-LUMO energy gaps (in eV) of the couplers for **1b**, **2b**, **3b**, **4b**, **5b**, **6b**, **1c**, **2c**, **3c**, **4c**, **5c** and **6c**

Species	HOMO	LUMO	HOMO-LUMO gap
1b	-0.21624	-0.02532	5.19
2b	-0.20364	-0.04993	4.18

3b	-0.18824	-0.07304	3.13
4b	-0.17981	-0.08907	2.47
5b	-0.17194	-0.09962	1.97
6b	-0.16691	-0.10785	1.61
1c	-0.26357	-0.06933	5.29
2c	-0.25900	-0.08638	4.70
3c	-0.23666	-0.10346	3.62
4c	-0.21393	-0.11366	2.73
5c	-0.20275	-0.12250	2.18
6c	-0.19179	-0.12798	1.74

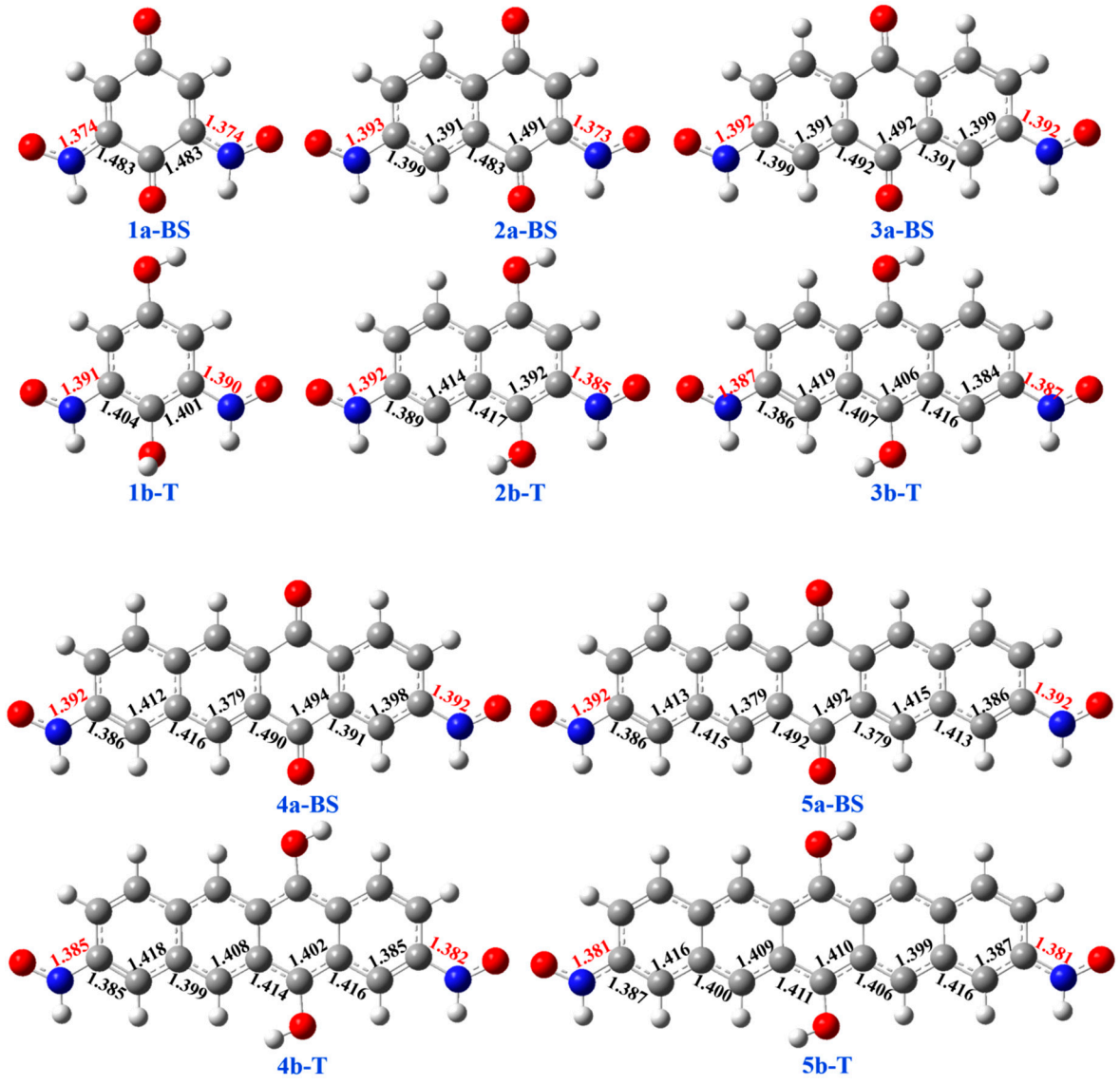
3. SOMO Energies, SOMO-SOMO Energy Gaps of Triplet States and S-T Energy Gaps of All Diradicals

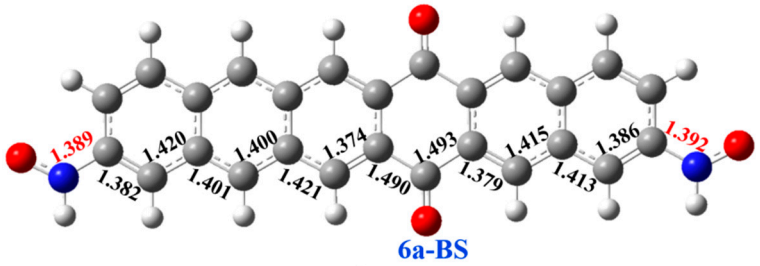
Table S5. The SOMO energies (a.u.) of the triplet states, SOMO-SOMO energy gaps (ΔE_{SS} in eV) and singlet-triplet energy gaps (ΔE_{ST} in kcal/mol) of **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **1c**, **1d**, **2c**, **2d**, **3c**, **3d**, **4c**, **4d**, **5c**, **5d**, **6c** and **6d**

Species	^1E_S	^2E_S	ΔE_{SS}	ΔE_{ST}
1a	-0.26895	-0.25176	0.47	-0.44
1b	-0.22440	-0.22309	0.04	3.21
2a	-0.25497	-0.23599	0.52	-0.37
2b	-0.21725	-0.20529	0.33	2.44
3a	-0.23748	-0.22857	0.24	-0.22
3b	-0.21282	-0.19715	0.43	2.43
4a	-0.23136	-0.22176	0.26	-0.14
4b	-0.20879	-0.19062	0.49	2.86
5a	-0.22320	-0.21825	0.13	-0.09
5b	-0.20630	-0.18635	0.54	3.79
6a	-0.21973	-0.21214	0.21	-0.07
6b	-0.20370	-0.18369	0.54	5.33
1c	-0.25389	-0.24039	0.37	3.61
1d	-0.22052	-0.18064	1.09	-7.37
2c	-0.23978	-0.22624	0.37	2.22
2d	-0.21425	-0.17891	0.96	-3.43
3c	-0.22591	-0.21998	0.16	2.01
3d	-0.20933	-0.17656	0.89	-1.75
4c	-0.20749	-0.19857	0.24	2.32
4d	-0.20479	-0.17773	0.74	-1.07

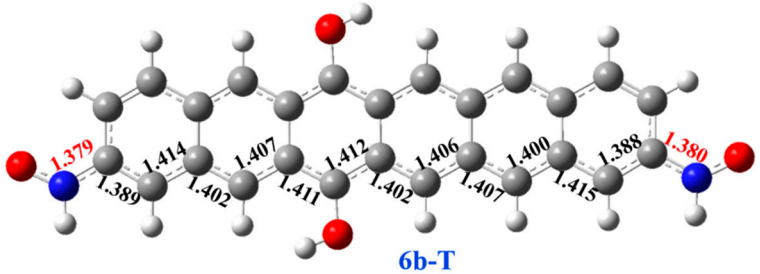
5c	-0.21143	-0.21064	0.02	3.02
5d	-0.20318	-0.18038	0.62	-0.57
6c	-0.20983	-0.20463	0.14	4.32
6d	-0.19871	-0.18186	0.46	-0.39

4. Optimized Molecular Geometries for Ground States of All Diradicals

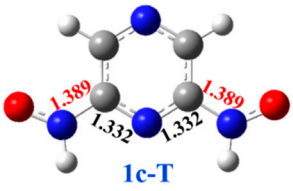




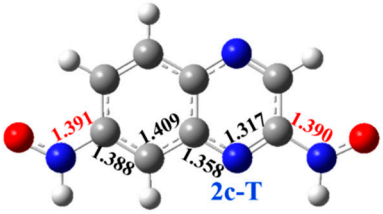
6a-BS



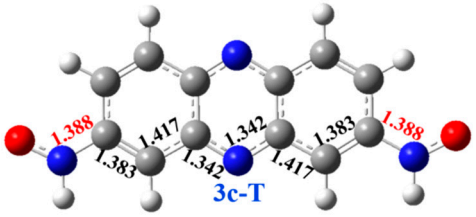
6b-T



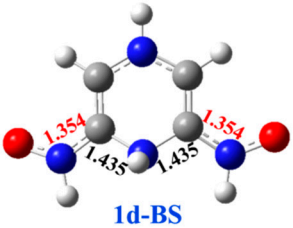
1c-T



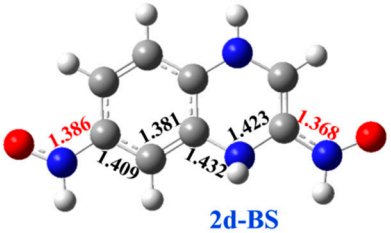
2c-T



3c-T



1d-BS



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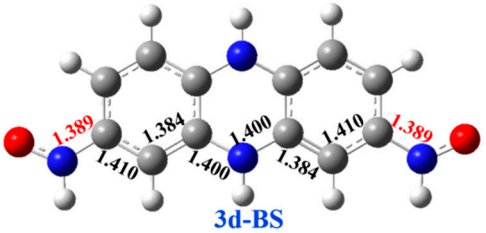

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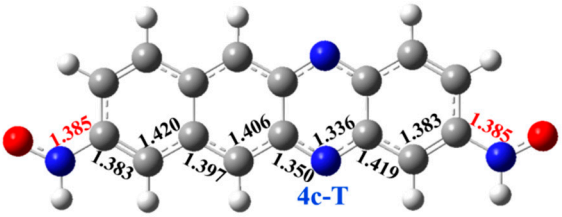
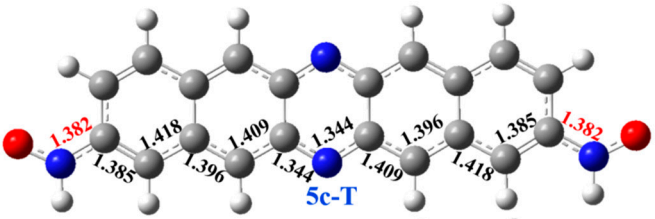
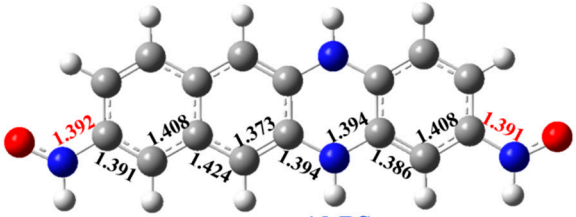


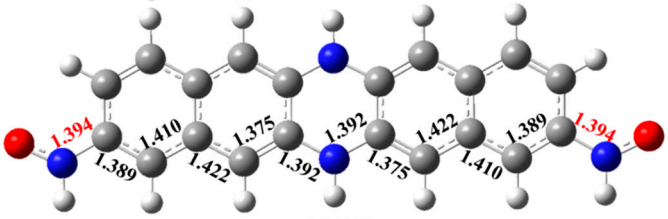
4c-T



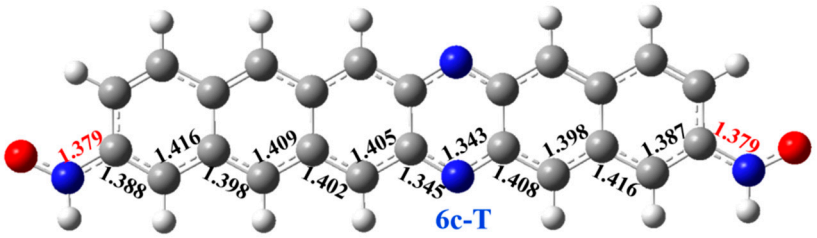
5c-T



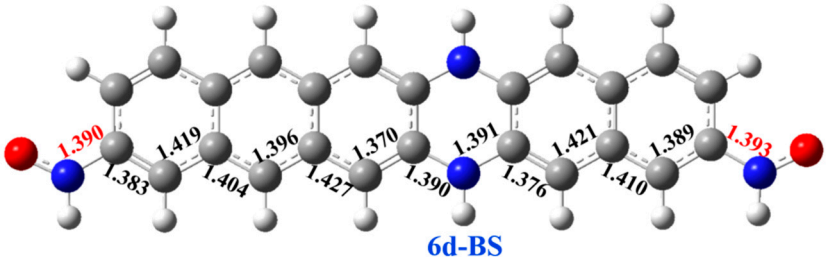
4d-BS



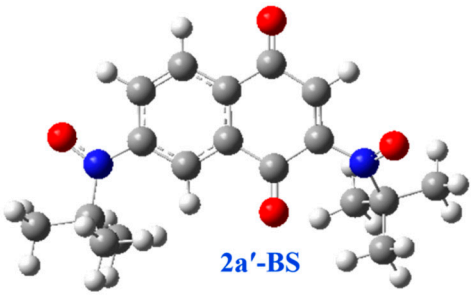
5d-BS



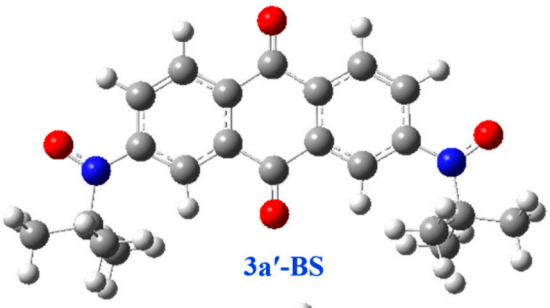
6c-T



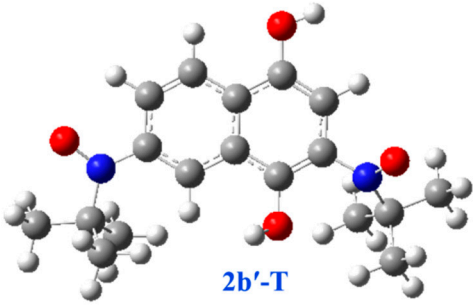
6d-BS



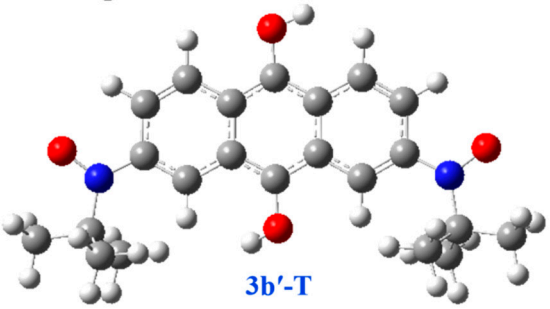
2a′-BS



3a′-BS



2b′-T



3b′-T

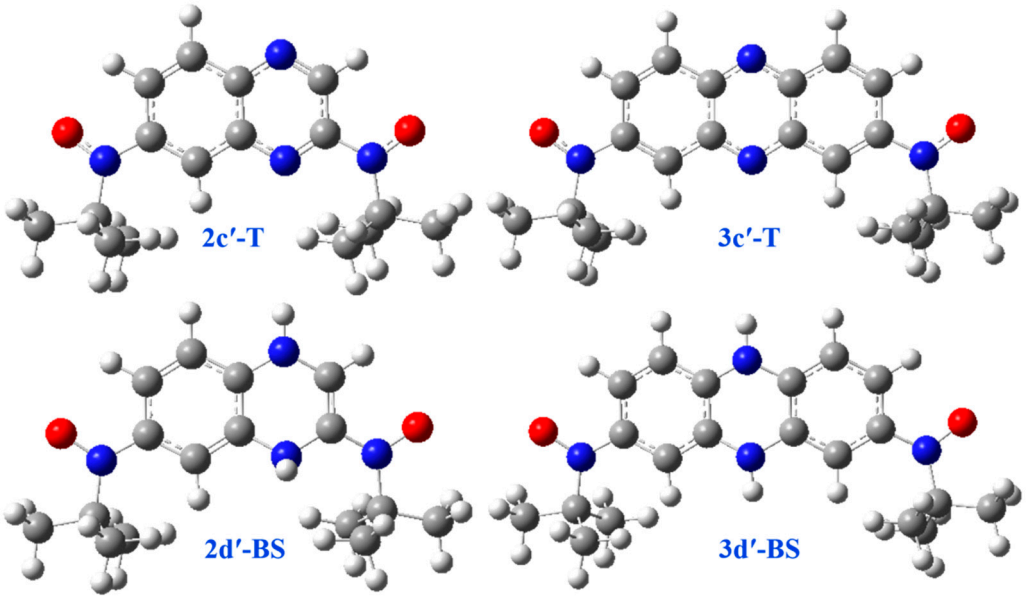
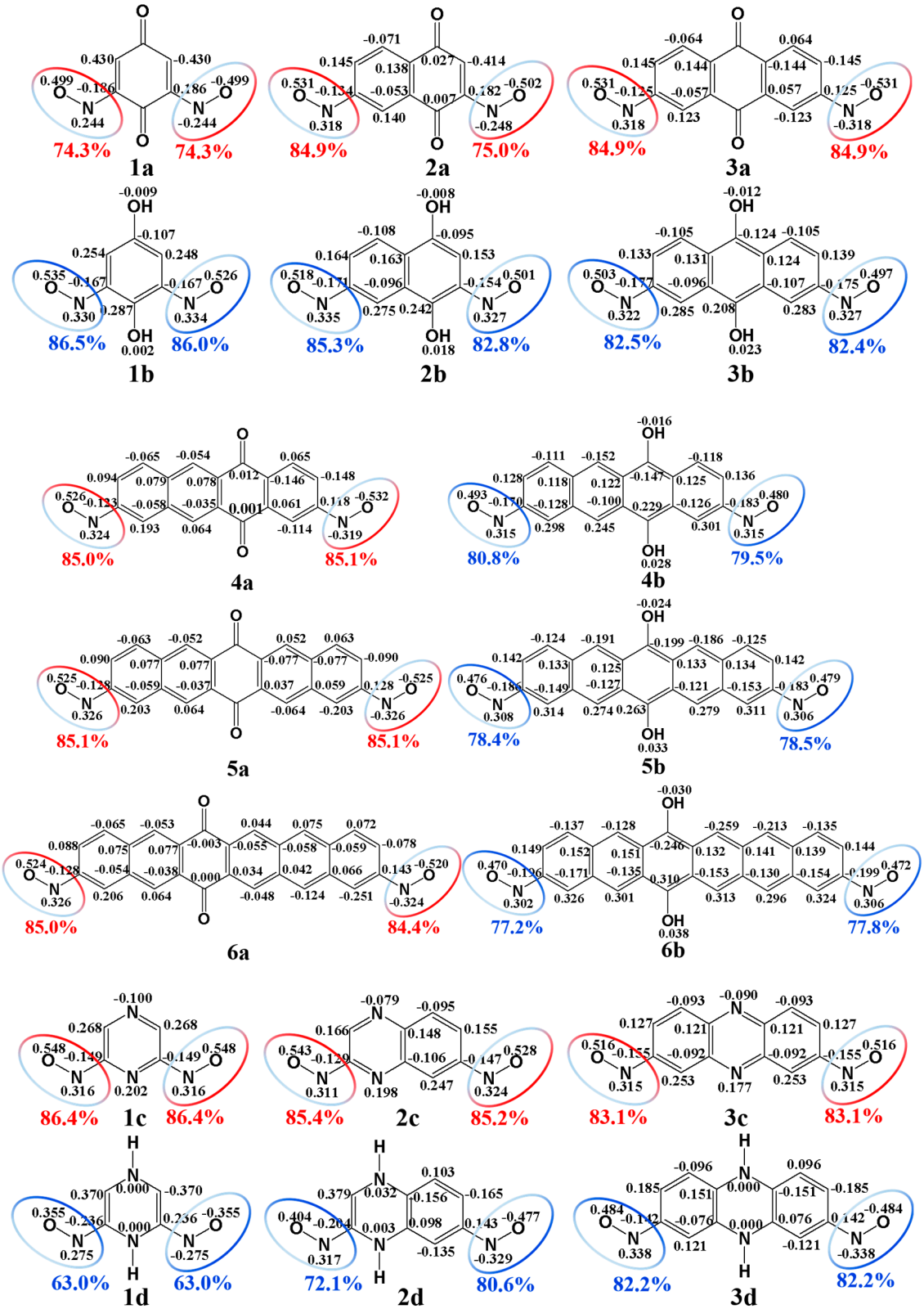


Figure S1. Optimized geometries for the ground states of all diraidcals at the (U)B3LYP/6-311++G (d,p) level, including the bond lengths of the adjacent atoms between two spin centers of the nitroxide-based diradicals. Their linking bond lengths between the coupler and two spin centers are marked in red.

5. Distributions of Mulliken Atomic Spin Density of All Diradicals


1a
74.3%
74.3%
2a
84.9%
75.0%
3a
84.9%
84.9%
1b
86.5%
86.0%
2b
85.3%
82.8%
3b
82.5%
82.4%
4a
85.0%
85.1%
4b
80.8%
79.5%
5a
85.1%
85.1%
5b
78.4%
78.5%
6a
85.0%
84.4%
6b
77.2%
77.8%
1c
86.4%
86.4%
2c
85.4%
85.2%
3c
83.1%
83.1%
1d
63.0%
63.0%
2d
72.1%
80.6%
3d
82.2%
82.2%

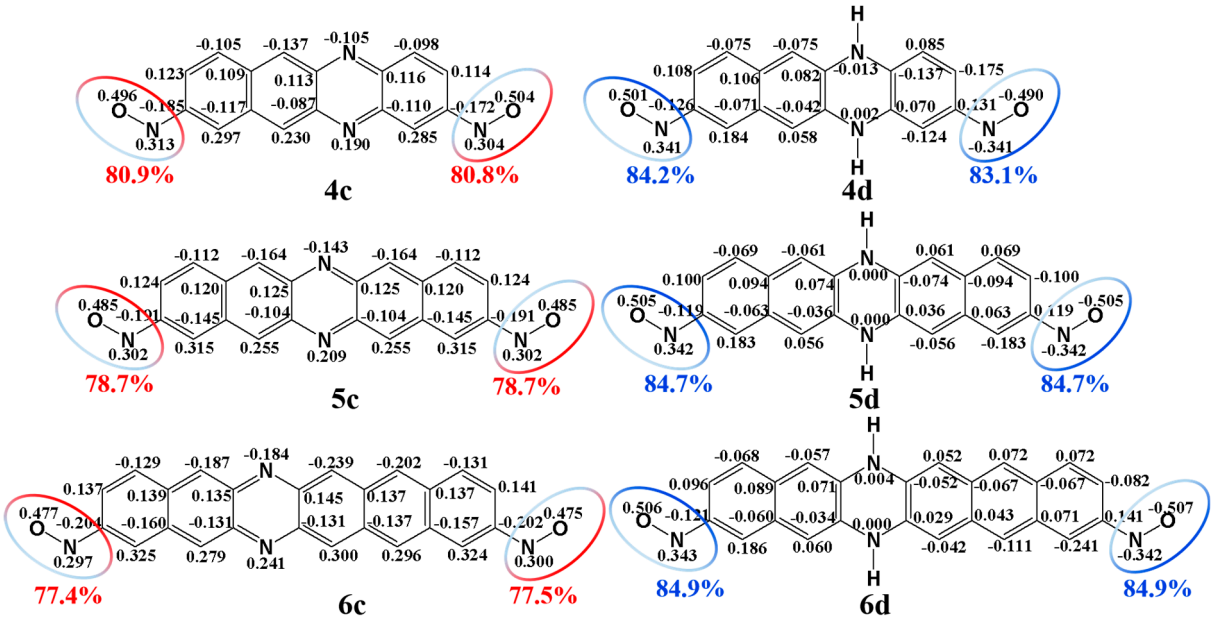
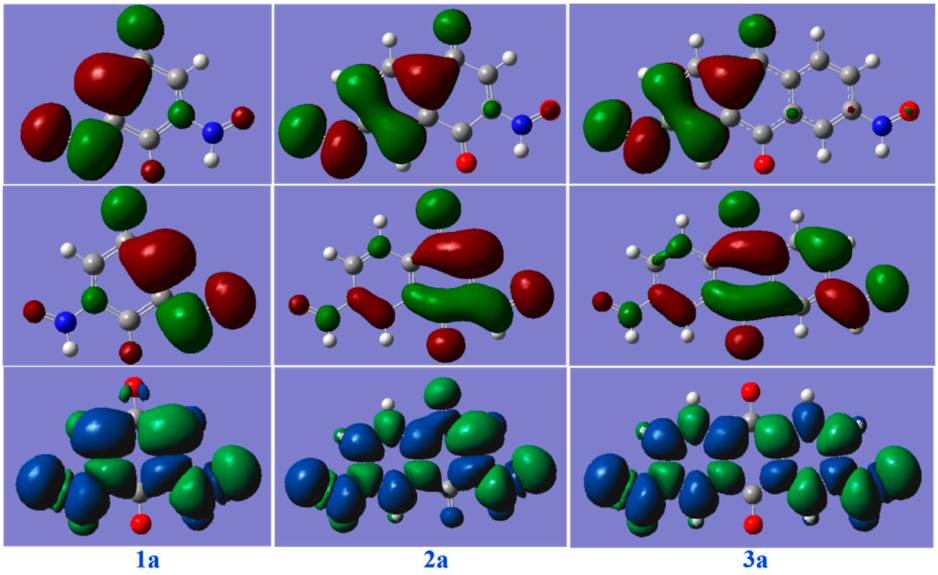
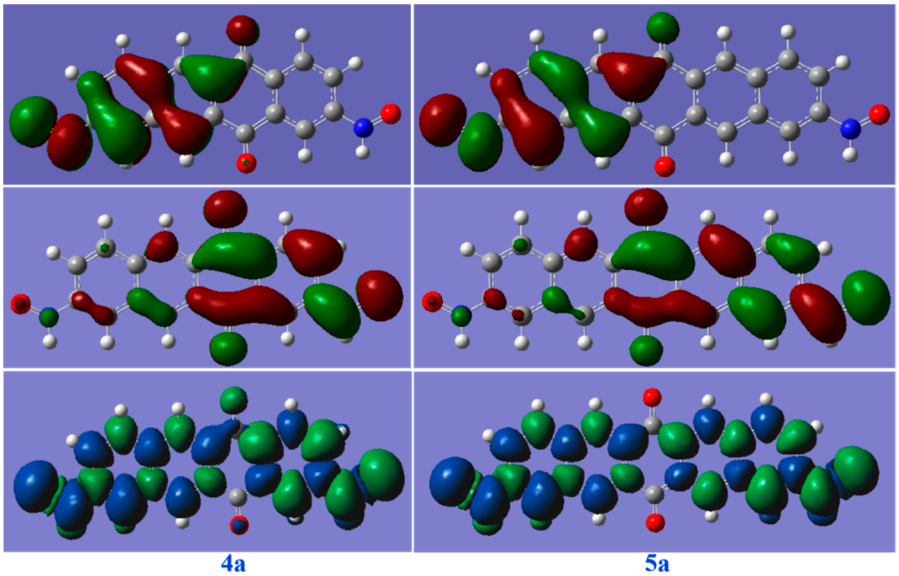


Figure S2. Comparison of spin polarization and the Mulliken atomic spin density distributions of all diradicals before and after dihydrogenation.

6. SOMO Plots and Spin Density Maps for All Diradicals





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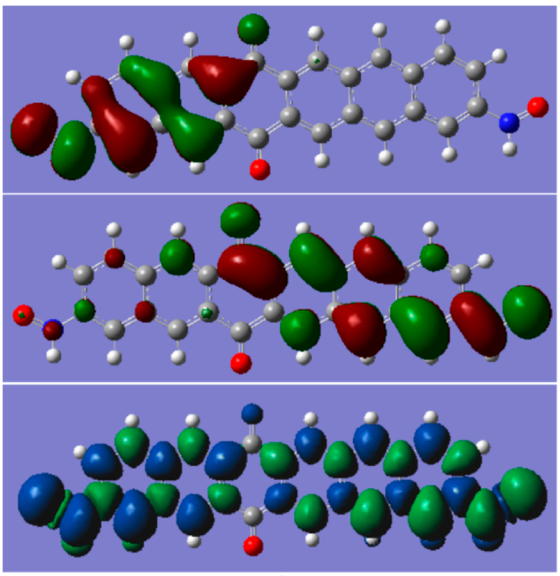

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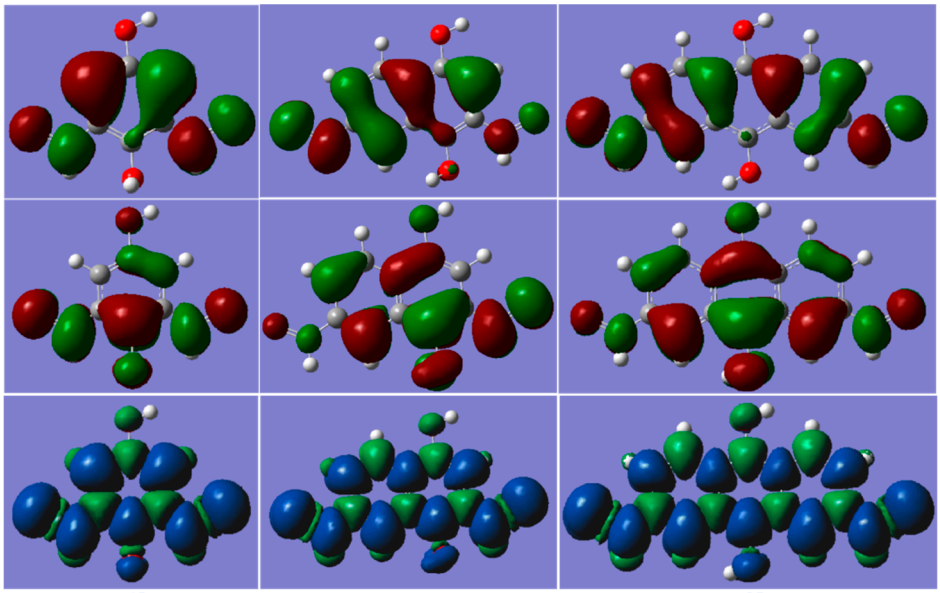
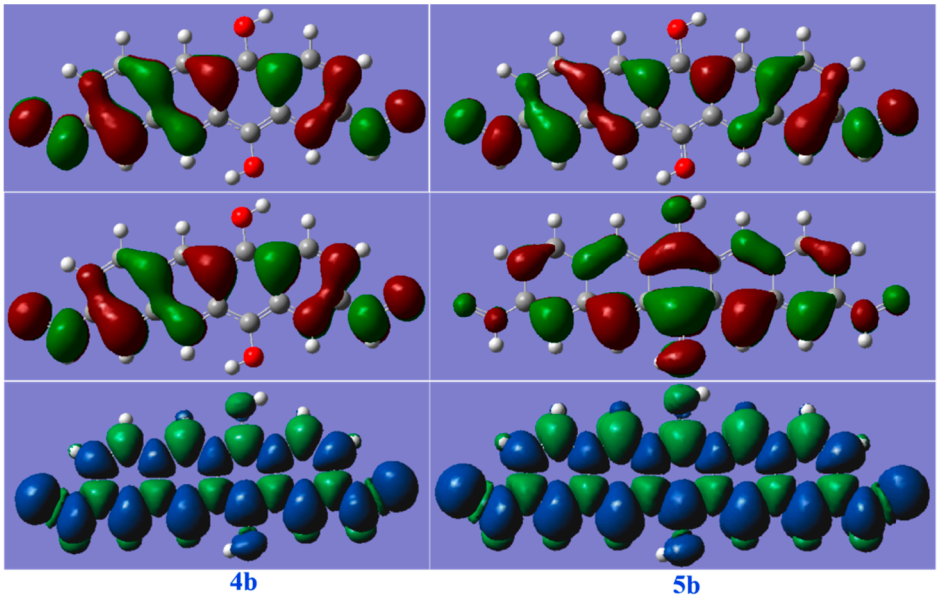
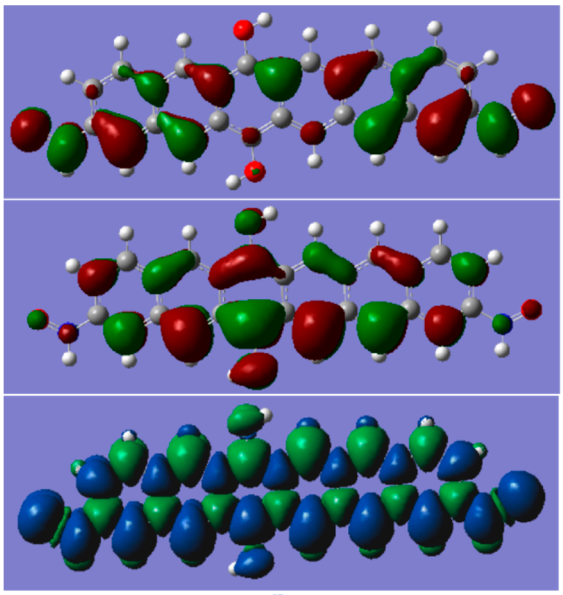


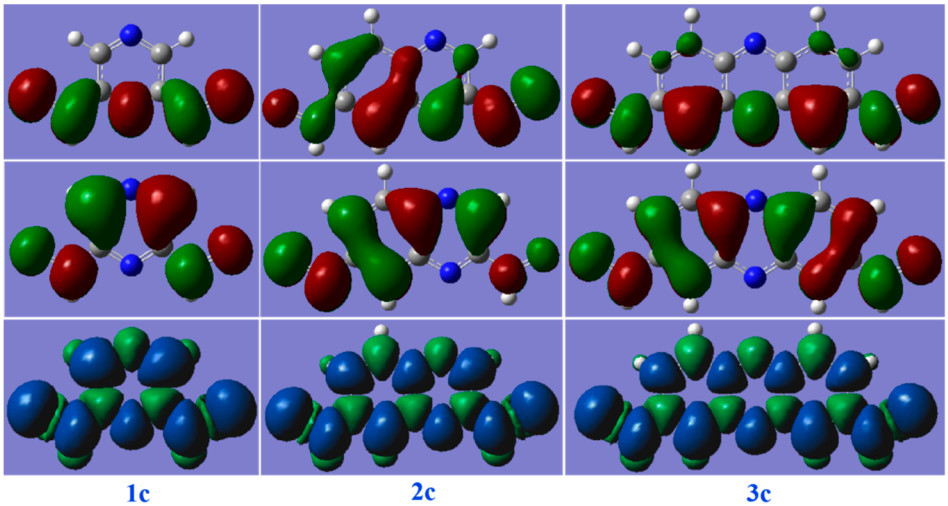
1b 2b 3b



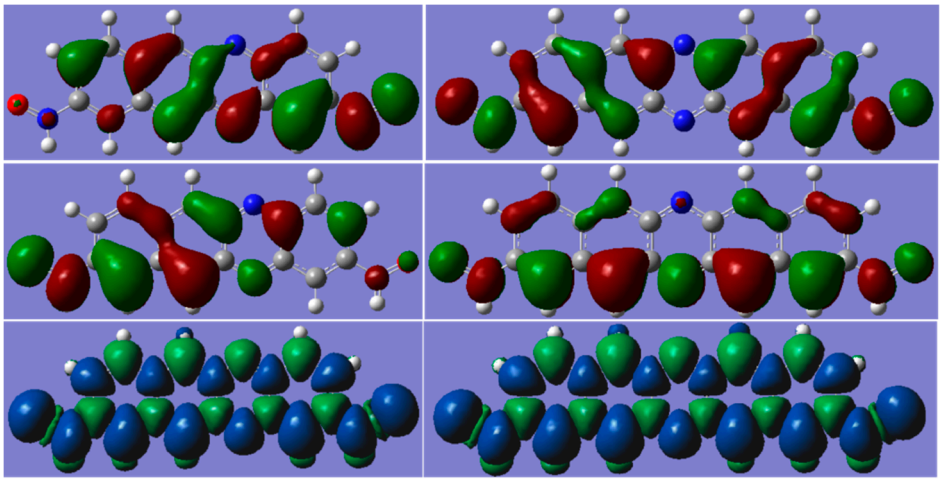
4b 5b



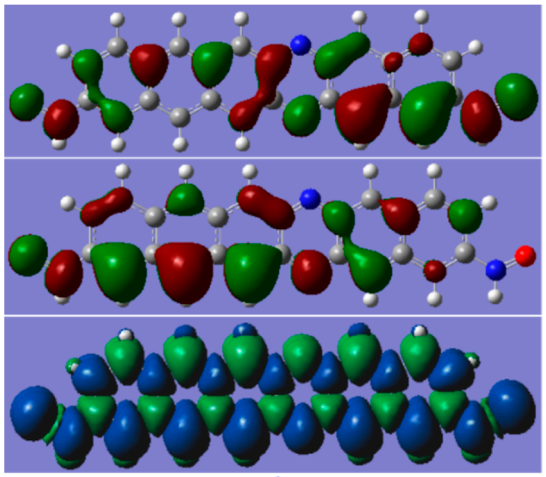
6b



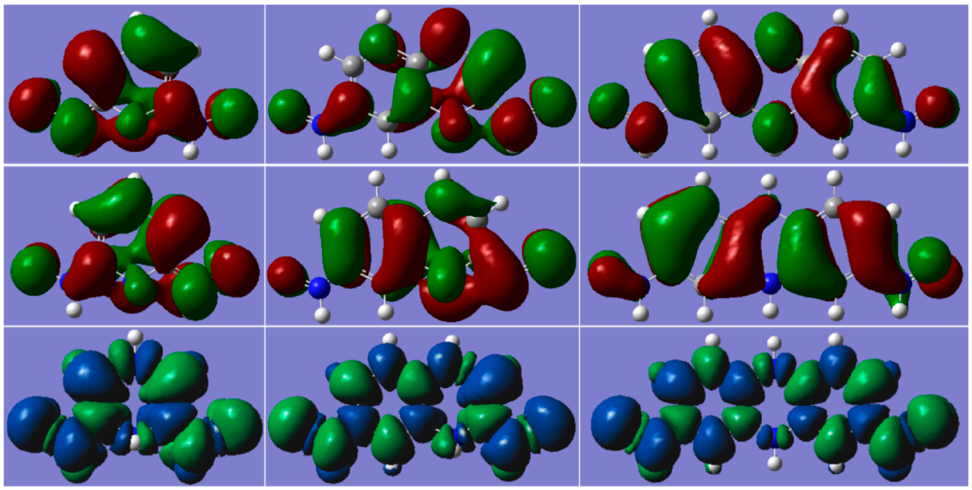
1c 2c 3c



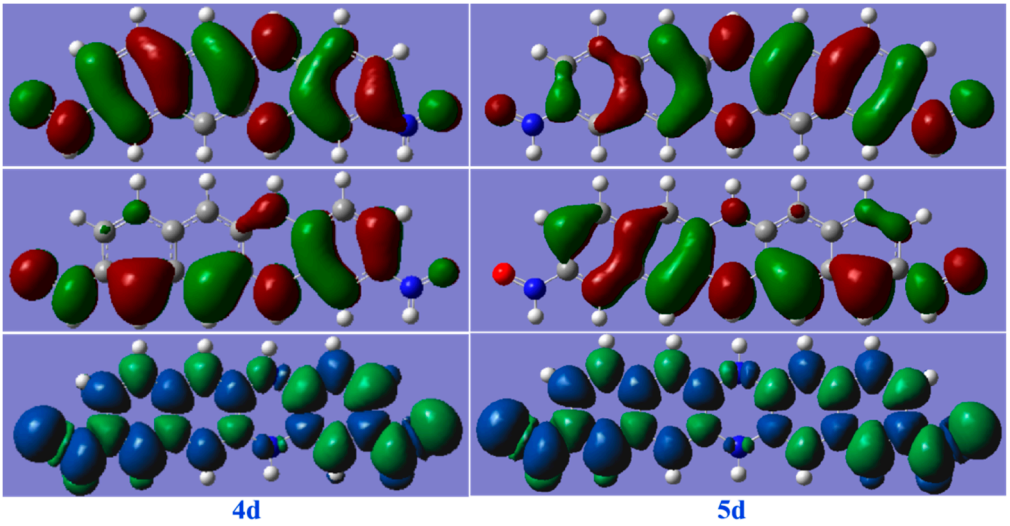
4c 5c



6c



1d 2d 3d



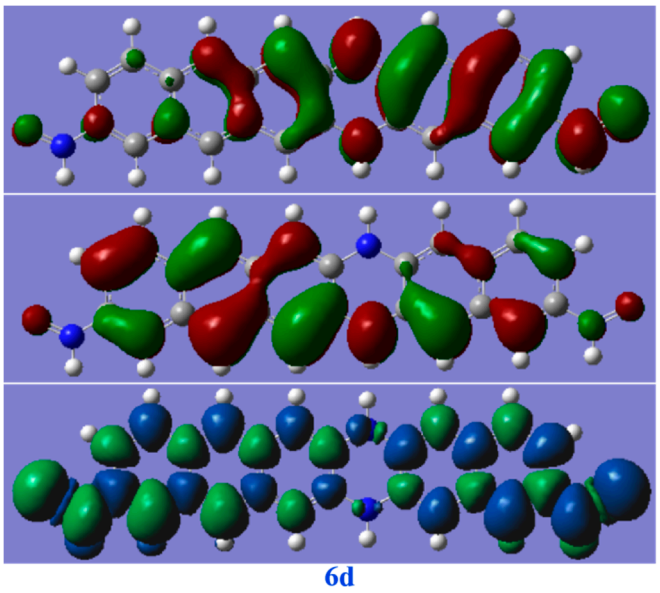
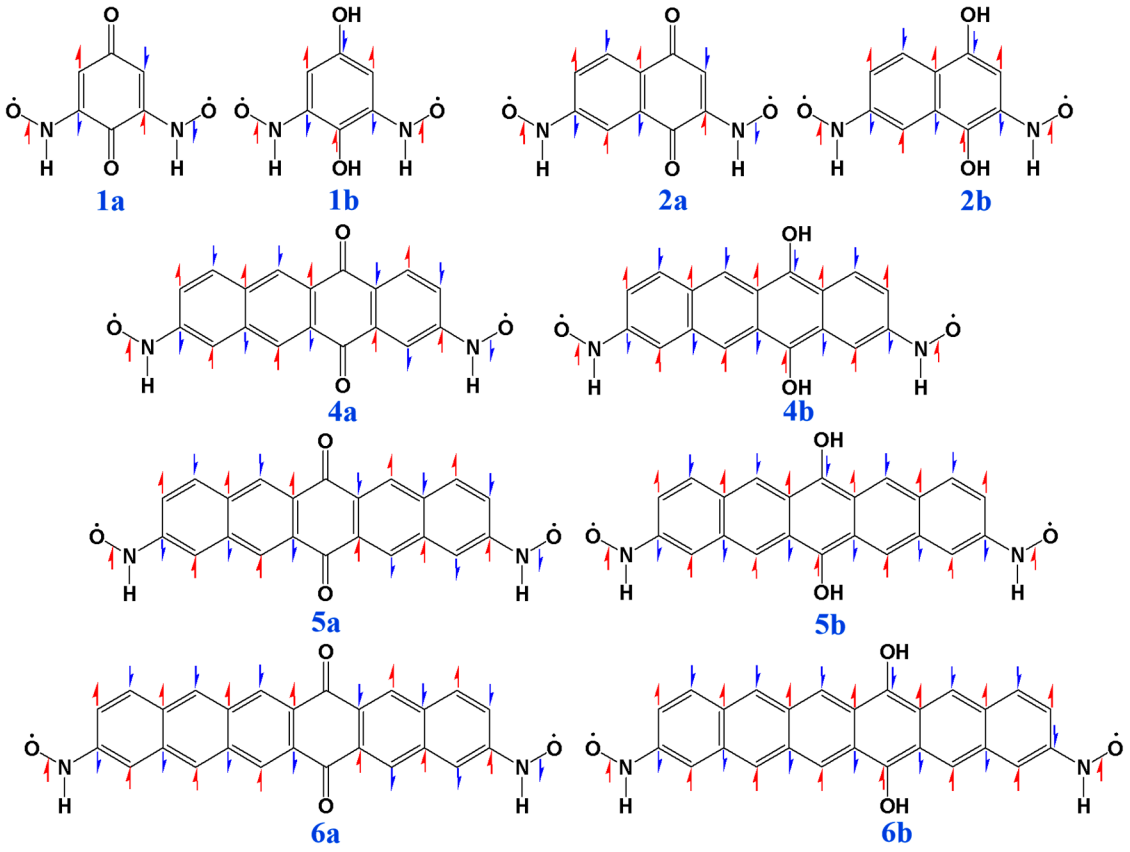


Figure S3. SOMOs (isovalue = 0.02) and spin density map (isovalue = 0.0004) of the ground states for the diradicals **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **1b**, **2b**, **3b**, **4b**, **5b**, **6b**, **1c**, **2c**, **3c**, **4c**, **5c**, **6c**, **1d**, **2d**, **3d**, **4d**, **5d** and **6d**.

7. Spin Alteration Plots for for Ten Couples of Diradicals



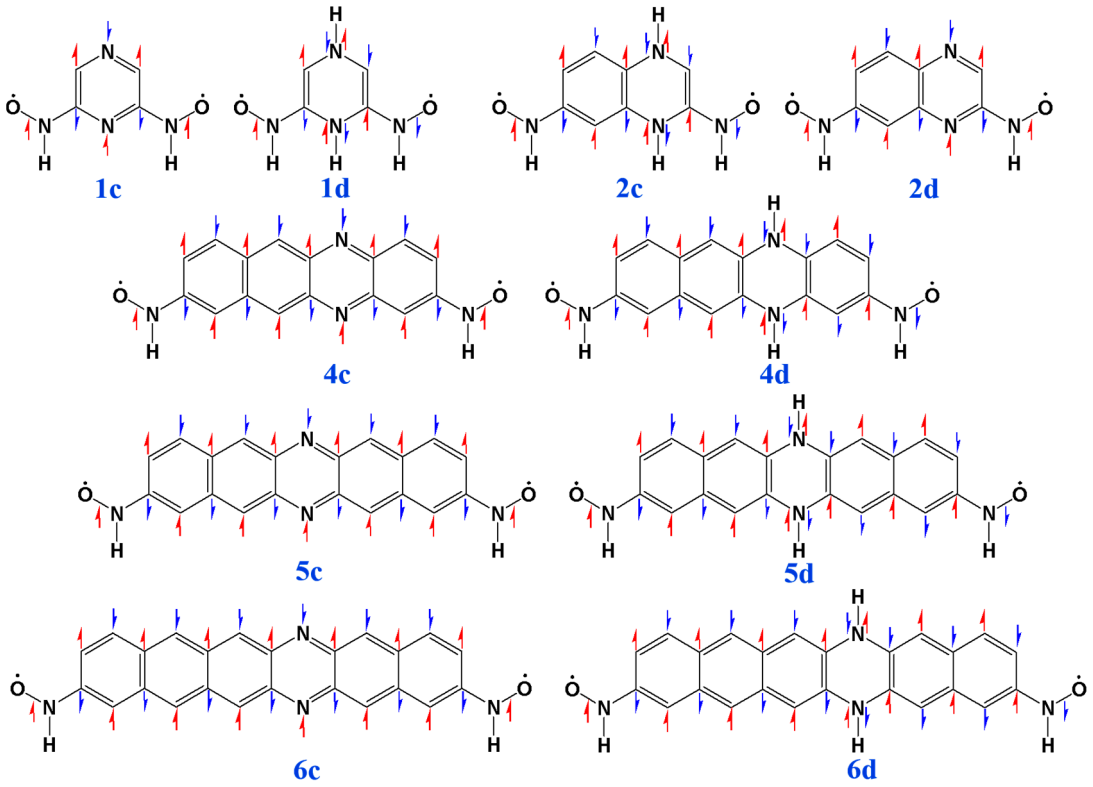


Figure S4. Scheme of spin alteration rule for ten couples of diradicals, including **1a** ↔ **1b**, **2a** ↔ **2b**, **4a** ↔ **4b**, **5a** ↔ **5b**, **6a** ↔ **6b**, **1c** ↔ **1d**, **2c** ↔ **2d**, **4c** ↔ **4d**, **5c** ↔ **5d** and **6c** ↔ **6d**.