Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Conjugated Coupler Curvature Enhances Magnetic Spin Coupling in π-Diradicals

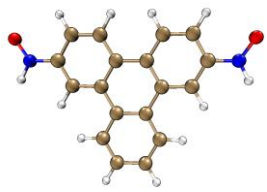
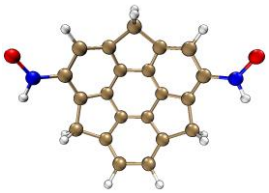
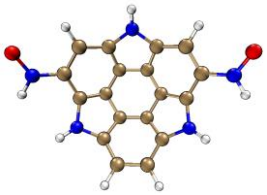
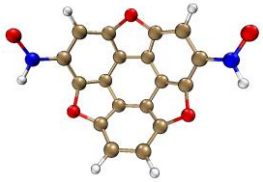
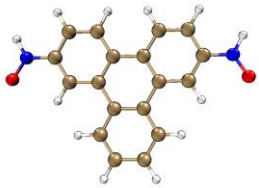
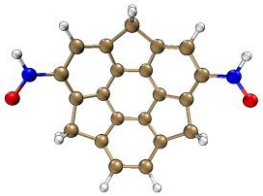
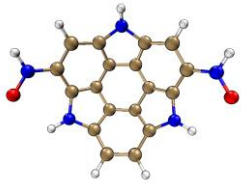
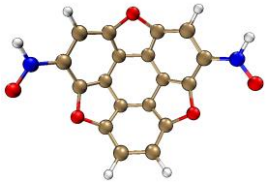
Shaofen Yu, Yamin Song, Yuxiang Bu, Xinyu Song*

School of Chemistry and Chemical Engineering, *Shandong University, Jinan 250100, People's Republic of China*

Supporting Information

1. **The structures of all diradicals.**
2. **E_{BS}, E_T, $<S^2>$ values, and *J* values of a calculated at the (U)M06-2X/6-311G (d, p) and (U)WB97XD/6-311++G (d, p) levels.**
3. **The geometry character of diradicals.**
4. **The ground state spin density distribution (isovalue =0.001) of the diradicals.**
5. **The SOMO (α, β) (isovalue =0.02)**
6. **AV1245 value of benzene ring in diradicals.**
7. **Orbital energy of the diradicals in the CS state.**

1. The structures of all diradicals.

1a	2a	3a	4a
			
1b	**2b**	**3b**	**4b**
			

2. E_{BS}, E_T, $<S^2>$ values, and *J* values of a calculated at the (U)M06-2X/6-311G (d, p) and (U)WB97XD/6-311++G (d, p) levels

		E_{BS}/a.u.	$<S^2>$	E_T/a.u.	$<S^2>$	*J*/cm^{-1}
(U)M06-2X/6-311G (d, p)	**1a**	-952.8326374	1.024	-952.8310671	2.017	-346.8
	2a	-1067.0745126	1.027	-1067.0726244	2.021	-417.2
	3a	-1115.1869189	1.030	-1115.1846028	2.022	-512.2
	4a	-1174.7420384	1.032	-1174.7397592	2.024	-504.2
(U)WB97XD/6-311++G (d, p)	**1a**	-952.8981916	1.051	-952.8962026	2.026	-448.1
	2a	-1067.1442895	1.064	-1067.1417695	2.032	-571.3
	3a	-1115.2454184	1.066	-1115.2422373	2.032	-722.7
	4a	-1174.7880138	1.071	-1174.7850553	2.037	-672.7

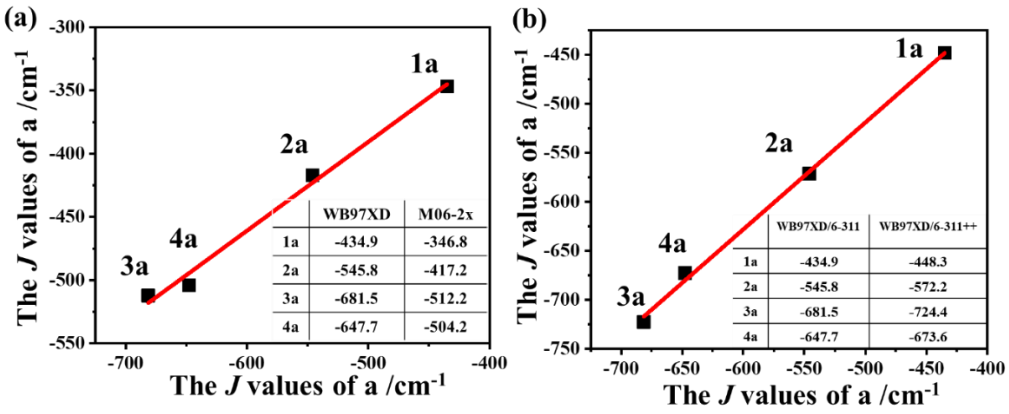


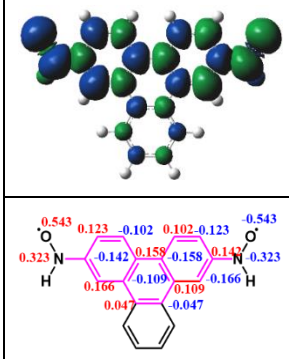
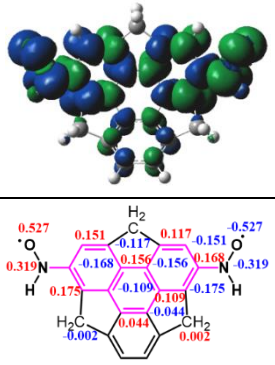
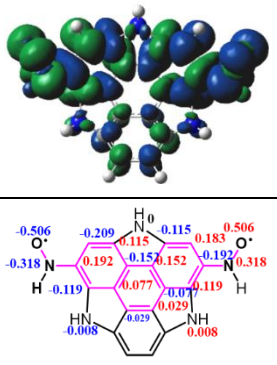
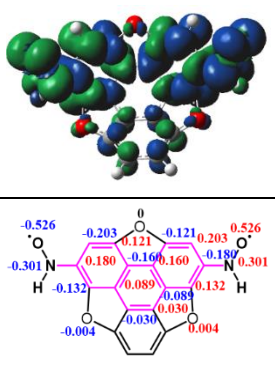
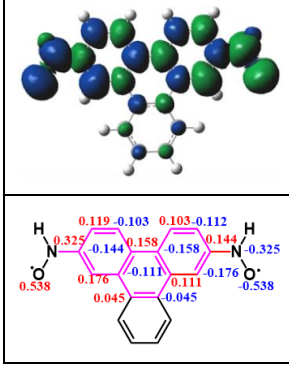
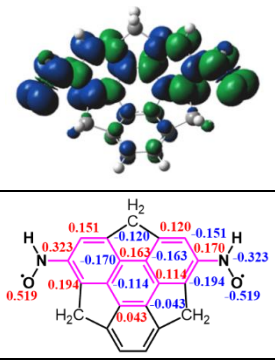
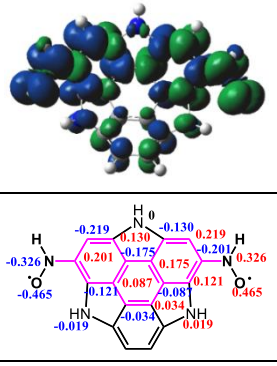
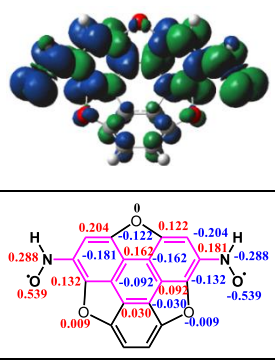
Figure S1. **(a)** A linear correlation between the *J* values of **a** at the (U)WB97XD/6-311G (d, p) and (U)M06-2X/6-311G (d, p) levels. **(b)** A linear correlation between the *J* values of **a** at

the (U)WB97XD/6-311G (d, p) and (U)WB97XD/6-311++G (d, p) levels.

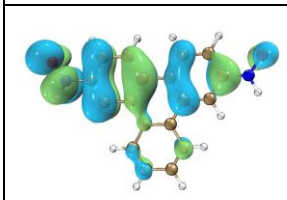
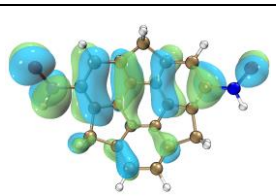
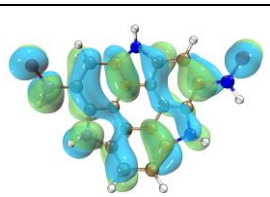
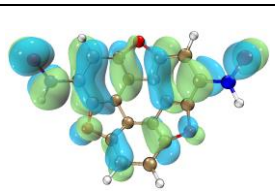
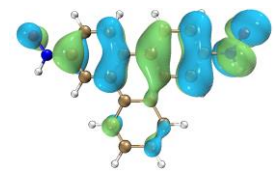
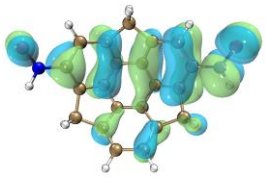
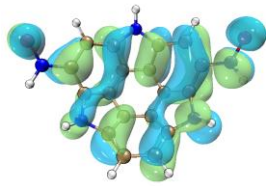
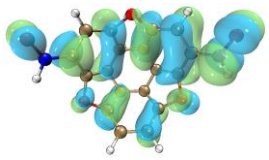
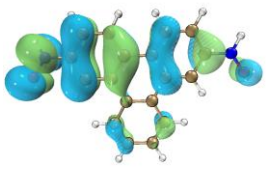
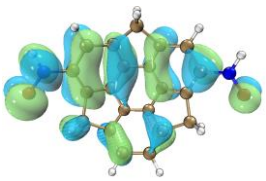
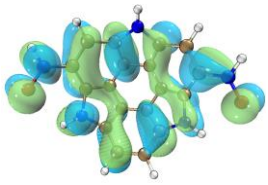
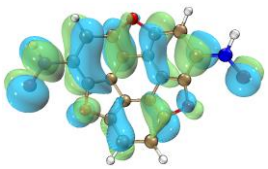
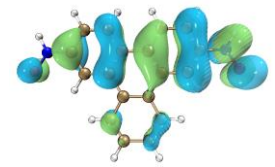
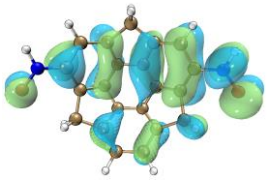
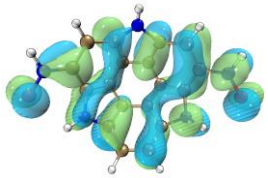
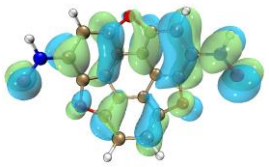
3. The geometry character of diradicals

Molecules	θ/°	$\cos^2\theta$	$d_{(C\text{-}N)}$/ Å	$d_{(N\cdots N)}$/ Å	$d_{(C\text{-}X)}$/ Å	Dihedral angle/°
1a	0	1.000	1.392	9.847	——	0
1b	0	1.000	1.392	9.848	——	0
2a	29.2	0.762	1.390	8.880	1.544	5.13
2b	29.3	0.761	1.387	8.890	1.545	-5.13
3a	34.2	0.684	1.387	8.724	1.407	1.42
3b	35.3	0.666	1.375	8.557	1.413	-1.43
4a	37.9	0.623	1.383	8.338	1.391	7.77
4b	39.1	0.602	1.380	8.447	1.392	-7.75

4. The ground state spin density distribution (isovalue =0.001) of the diradicals.

1a	2a	3a	4a
			
1b	**2b**	**3b**	**4b**
			

5. SOMO (α, β) (isovalue =0.02)

1a	2a	3a	4a
			
			
1b	**2b**	**3b**	**4b**
			
			

6. AV1245 value of benzene ring in diradicals.

Molecules	left	right	below	middle
1a	8.9661482	8.9674485	12.0505648	1.7509438
1b	8.9572431	8.9577971	12.0563530	1.6936870
2a	7.5985271	7.6002653	10.8370851	1.3433154
2b	7.3921811	7.3931996	10.7798020	1.3312120
3a	5.3100775	5.3079867	8.1179833	1.1205044
3b	4.1822512	4.1822403	7.1744050	1.2905020
4a	6.0958194	6.0963494	9.2114945	0.7984385
4b	6.01761431	6.0170917	8.8828115	0.8126150
2a'	8.0989954	8.1008082	11.3386427	1.6983248
3a'	7.9783487	7.9782810	11.3756971	1.4826711
4a'	7.49998761	7.5005885	11.0312446	1.5147055

7. Orbital energy of the diradicals in the CS state.

Molecules	$E_{(HOMO)}$/a.u.	$E_{(LUMO)}$/a.u.	Energy Gap/eV
1a	-0.22684	-0.07278	4.192
2a	-0.22656	-0.06542	4.385
3a	-0.22837	-0.05310	4.769
4a	-0.24577	-0.07430	4.666