

**Diradicalized Biphenyl Derivative Carbon-Based Materials Molecules: Exploring the
Tuning Effects on the Magnetic Couplings**

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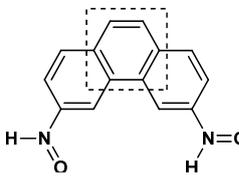
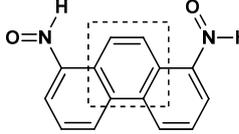
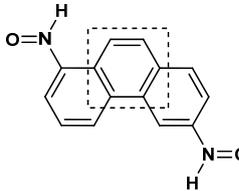
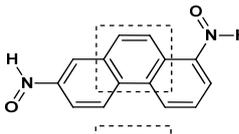
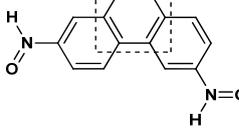
Electronic Supplementary Information

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1. Molecular Structures, Single-Point Energies, Corresponding $\langle S^2 \rangle$ Values, Twist Angle, and Intramolecular Exchange Coupling Constants (J) for the Rest Molecules

Table S1. Molecular Structures and Single-Point Energies in au, Corresponding $\langle S^2 \rangle$ Values, Calculated Intramolecular Exchange Coupling Constants (J , cm^{-1}) and Twist Angle (θ) for the rest molecules at the UB3LYP/6-311++G(d,p) Level.

Molecules	Structures	Energies $\langle S^2 \rangle$		Twist angles	J
		BS	T		
14a		-799.5601444 1.025	-799.5587068 2.022	0	-316.3
14b		-799.5484748 1.041	-799.5469122 2.031	0	-346.1
14c		-799.5552841 1.032	-799.5537313 2.026	0	-342.6
15a		-799.5529805 1.024	-799.5541154 2.050	0	242.6
15b		-799.5593756 1.021	-799.5603589 2.043	0	211.0

2. Linear Correlations between the CASSCF and the UB3LYP Results

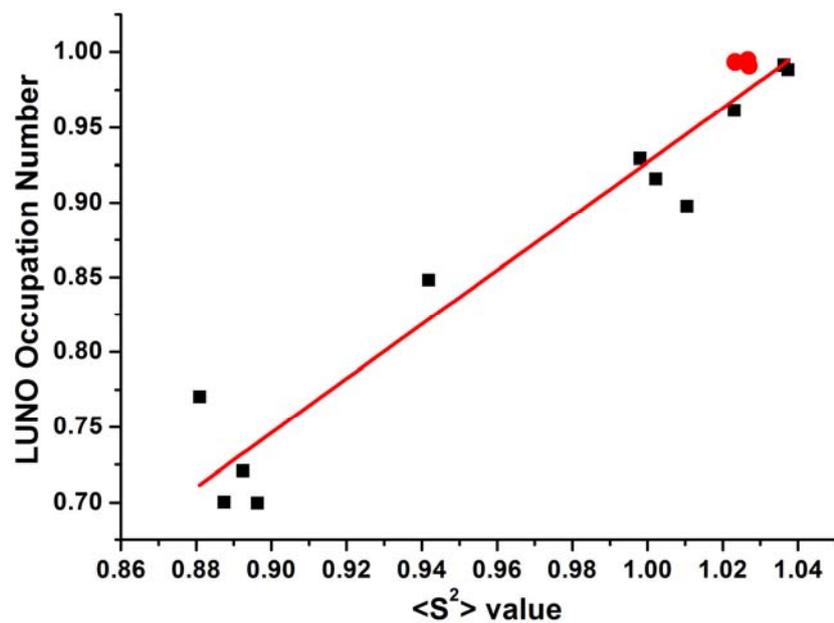


Figure S1. Linear correlations between the CASSCF and the UB3LYP results for the diradical character indexes, where the red dots denote the FM diradical, while the black ones denote the AFM diradical.

3. Singly Occupied Molecular Orbitals and Spin Density Distributions of Some Configurations for Ground State

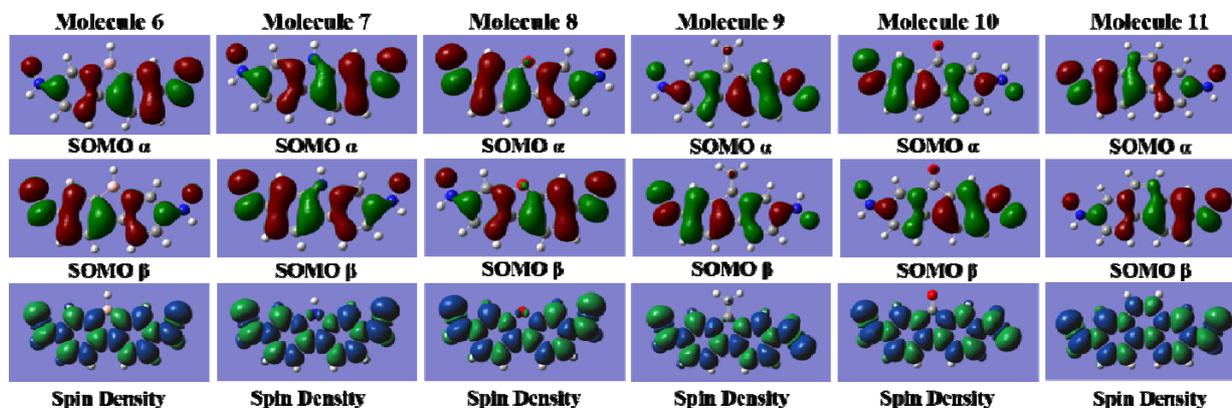


Figure S2. Schematic SOMOs (isovalue = 0.02) of representative BS ground states and T ground states of molecules induced by side-way effect, calculated at the UB3LYP/6-311++G(d,p) level.

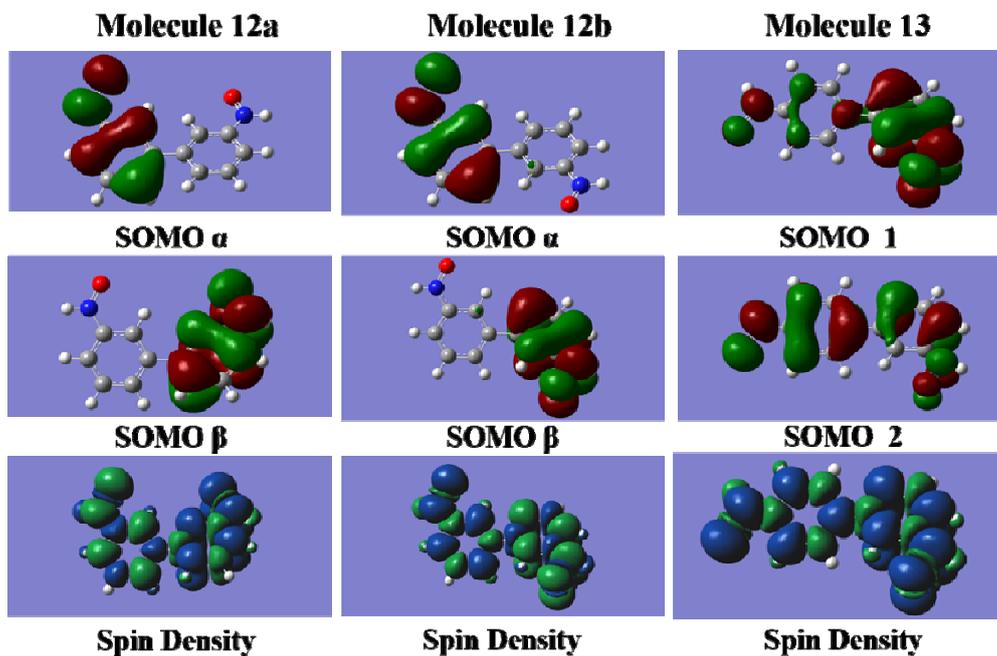


Figure S3. Schematic SOMOs (isovalue = 0.02) of representative BS ground states and T ground states of molecules induced by position effect, calculated at the UB3LYP/6-311++G(d,p) level.

4. The Mismatching of Spin Density Distributions of All Configurations

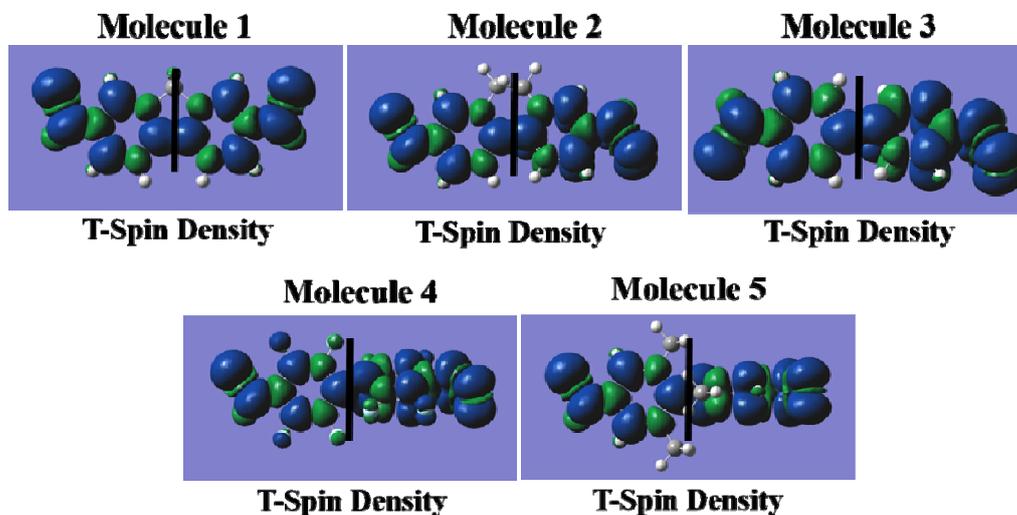


Figure S4. Spin density distributions of the T of molecule 1-5. The blue and green colors correspond to α - and β -spins, respectively. A black solid line represents the mismatching of the spin polarization, calculated at the UB3LYP/6-311++G(d,p) level.

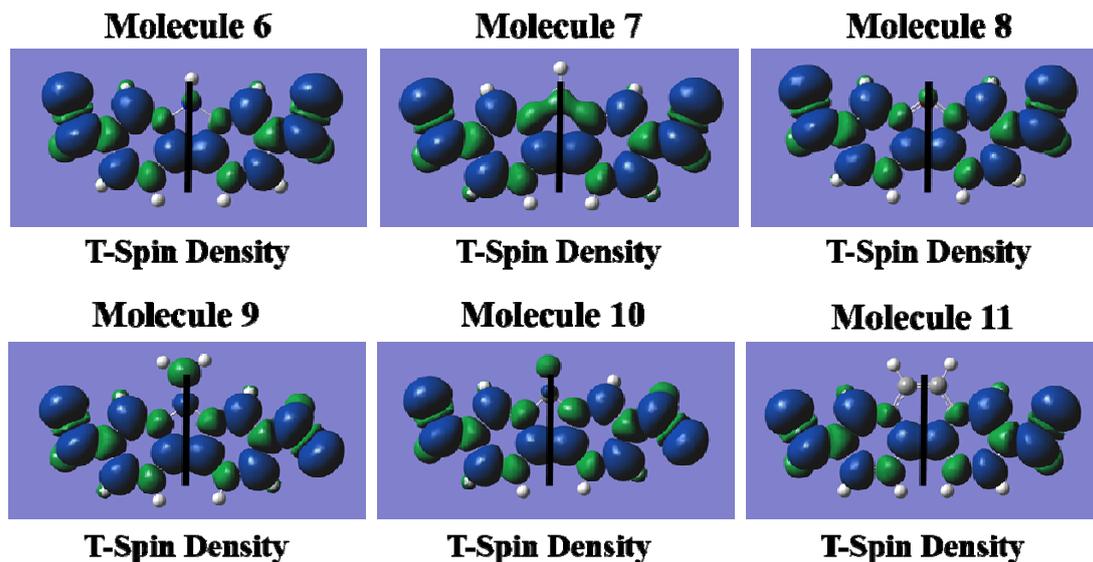


Figure S5. Spin density distributions of the T of molecule 6-11. The blue and green colors correspond to α - and β -spins, respectively. A black solid line represents the mismatching of the spin polarization, calculated at the UB3LYP/6-311++G(d,p) level.

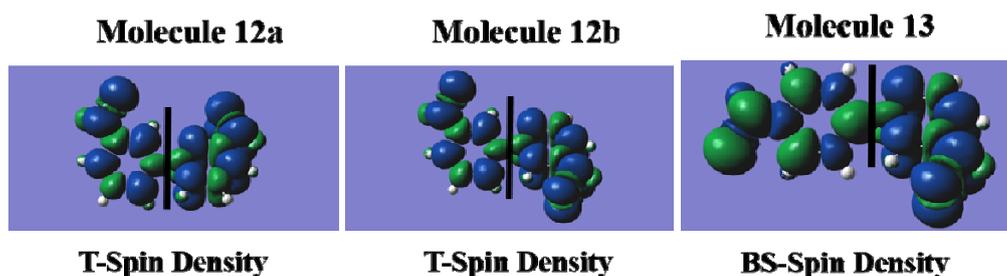


Figure S6. Spin density distributions of the T of molecule **12a**, **12b** and the BS of **13**. The blue and green colors correspond to α - and β -spins, respectively. A black solid line represents the mismatching of the spin polarization, calculated at the UB3LYP/6-311++G(d,p) Level.

5. Energy Levels of Two SOMOs for Triplet States, Their Energy Gaps and Singlet-Triplet Energy Gaps

Table S2. Energy Levels (E_S , au) of Two SOMOs for Triplet States, Their Energy Gaps (ΔE_{SS} , eV) and Singlet-Triplet Energy Gaps (ΔE_{ST} , kcal/mol) Calculated at the UB3LYP/6-311++G(d,p) Level for the Molecules Induced by twisting effect, side-way effect, position effect.

Molecules	1E_S (a.u.)	2E_S (a.u.)	ΔE_{SS} (eV)	ΔE_{ST} (kcal/mol)
1	-0.19030	-0.22372	0.91	8.71
2	-0.19243	-0.22328	0.84	9.81
3	-0.19887	-0.22355	0.67	11.38
4	-0.23805	-0.25161	0.37	18.81
5	-0.20620	-0.20628	0.00	26.69
6	-0.19466	-0.22670	0.87	7.70
7	-0.18929	-0.22361	0.93	8.97
8	-0.19656	-0.22974	0.90	9.30
9	-0.19293	-0.22535	0.88	9.28
10	-0.20405	-0.23478	0.84	10.5
11	-0.19736	-0.22737	0.82	11.95
12a	-0.21001	-0.21158	0.04	29.26
12b	-0.21134	-0.21250	0.03	29.64
13	-0.20732	-0.21499	0.21	29.48
14a	-0.19620	-0.21705	0.57	15.22
14b	-0.19436	-0.21080	0.45	14.06
14c	-0.19562	-0.21720	0.59	14.49

15a	-0.20372	-0.21210	0.23	27.99
15b	-0.20702	-0.21157	0.12	28.59

6. Spin Alternation Rule and Mulliken Atomic Spin Densities for Some Configurations

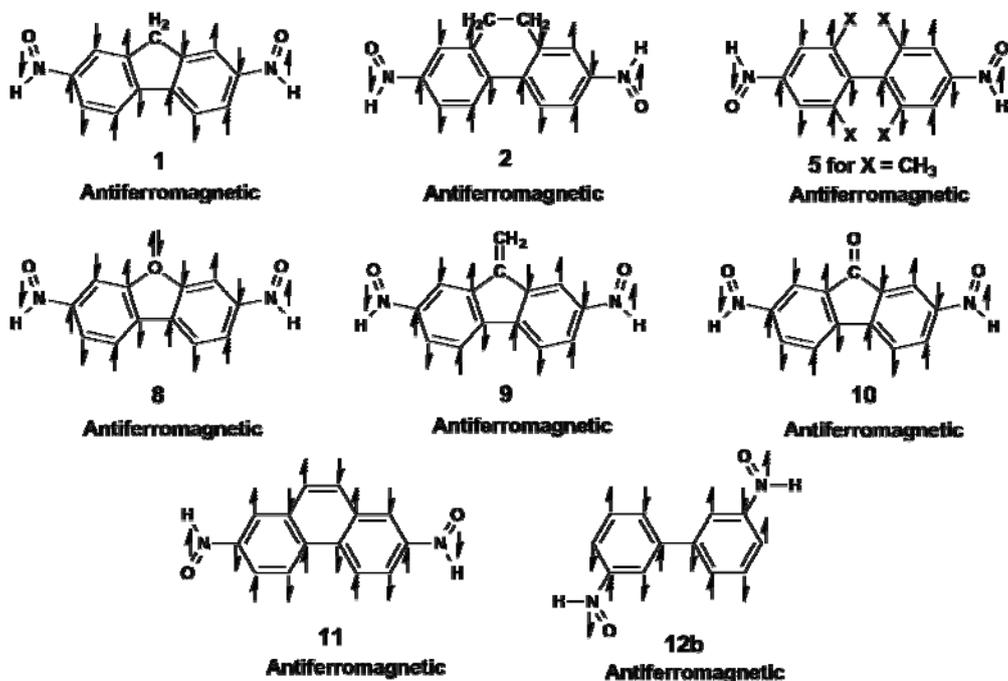


Figure S7. Scheme of spin alternation and the predicted magnetism of the ground states for the rest molecules in terms of the spin alternation rule.

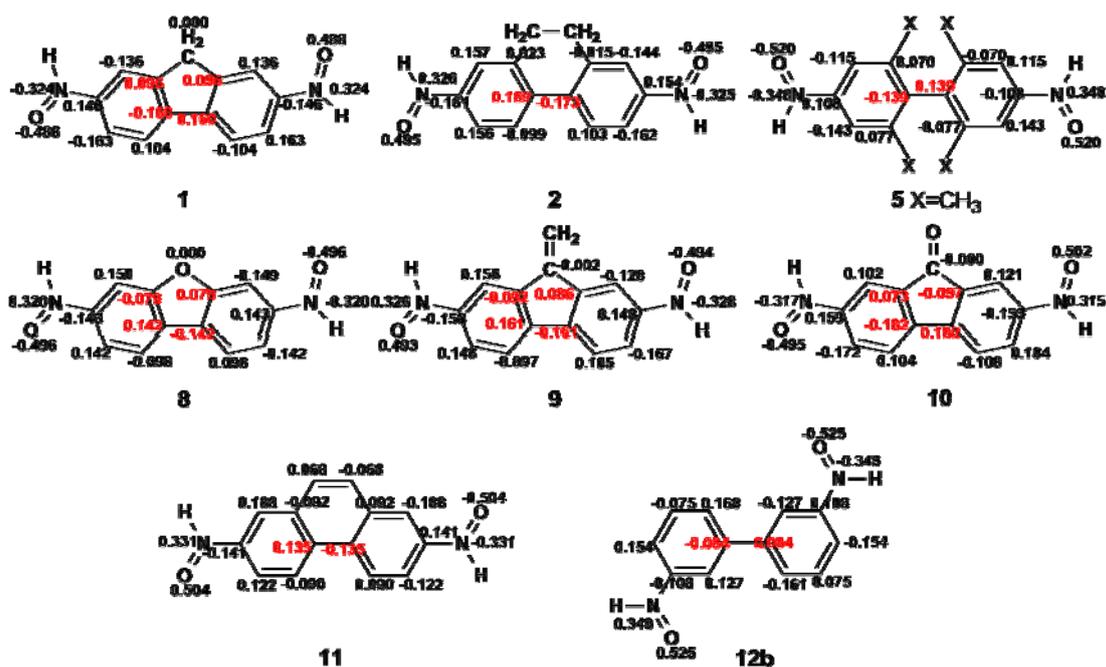


Figure S8. Mulliken atomic spin densities for the ground states of the rest molecules.

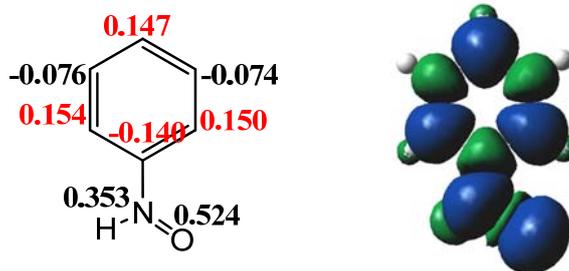


Figure S9. The calculated Mulliken atomic spin densities and the plot of spin density distributions of nitroxide-phenyl radical at the B3LYP/6-311++G(d,p) level. The red numbers denote higher spin densities in the phenyl ring.

7. Simple Analysis of the Side-Way Effects

To further understand the side-way effects, we give a simple analysis here. A question is if the $-\text{CH}=\text{CH}-$ segment can be viewed as a side-way for the spin coupling in molecule **11** because the linking of a $-\text{CH}=\text{CH}-$ to the biphenyl unit at its ortho-sites forms phenanthrene which has a more favorable conjugation than the other couplers modified by other side-way groups. In fact, for this series (Table 2), adding of various side-ways is to fix the main framework (the biphenyl unit) to be coplanar (or at least approximately coplanar), making the spin coupling through the main framework have same or close conditions for examining possible side-way effects. Therefore, the calculated differences in the J values of several systems could be attributed to the side-way effects. Since the main frameworks are coplanar or closely coplanar for all molecules in this series (Table 2), the side-ways with π -orbitals or π -type p orbitals could form extensively conjugated π -orbitals with their main frameworks, except $>\text{CH}_2$ in molecule **1** which can form a super-conjugation using its C-H σ -bond with the framework. For example, each of $>\text{BH}$ and $>\text{NH}$ has an empty or doubly occupied π -type p orbital (lone-pair electron), while each of $>\text{C}=\text{CH}_2$ and $>\text{C}=\text{O}$ has a doubly occupied π -orbital. $>\text{O}$ could be approximately viewed as forming p- π conjugation using its doubly occupied π -type p orbital (lone-pair electron) with the biphenyl framework. Certainly, the $\text{CH}=\text{CH}$ combines with the biphenyl unit, forming a phenanthrene coupler. In short, all these side-way

segments have good condition to form extensive conjugations with the biphenyl unit except $>\text{CH}_2$. More importantly, the two radical groups ($-\text{NOH}$) are linked to the para-sites of the bridging C-C in the biphenyl-derivative units, and the meta-sites of the side-way linkage. In other words, for each diradical in this series, the main coupling pathway is through the two para-sites of the two phenyl-NOH radical moieties with respect to the $-\text{NOH}$ radical groups, while the side-way coupling is realized through the side-way linked to the meta-sites of the two phenyl-NOH radical moieties. It is well-known that for a diradicalized phenylene (HON-phenylene-NOH) the spin coupling (-2022.5 cm^{-1} , antiferromagnetic) of the para-site structure is considerably larger than that (611.3 cm^{-1} , ferromagnetic) of the meta-site structure, as mentioned in the text not only with different magnetisms. All these indicate that the spin-spin coupling through the main framework (the biphenyl unit) is primary and that through the meta-site-linked side-way is secondary. In short, the two ways in **11** have different contributions to the spin coupling.

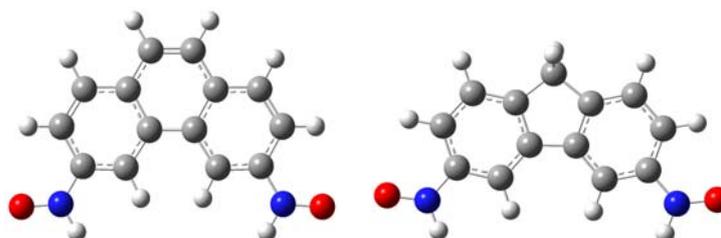


Figure S10. Two diradical molecules derived from **12a** by adding a $-\text{CH}=\text{CH}-$ or $-\text{CH}_2-$ linkage as side-way for coupling.

To distinguish different pathway effects, we also examine two systems derived from molecule **12a** by adding a $-\text{CH}=\text{CH}-$ or a $-\text{CH}_2-$ as additional coupling ways with coplanar structures (Figure S10). The calculated J values are -354.8 cm^{-1} ($-\text{CH}=\text{CH}-$ modified) and -47.0 cm^{-1} ($-\text{CH}_2-$ modified) for them, respectively. These results indicate that for the latter, compared with **12a** ($J = -27.2 \text{ cm}^{-1}$), increase of a $-\text{CH}_2-$ -based way does not considerably improve the spin coupling although the $-\text{CH}_2-$ is linked to the para-sites of the $-\text{NOH}$ groups in the biphenyl unit because the $-\text{CH}_2-$ is also less conductive (similar to the bridging C-C linkage). Undoubtedly, for the former, the considerably large J value (-354.8 cm^{-1}) should be due to the $-\text{CH}=\text{CH}-$ pathway, and thus the $-\text{CH}=\text{CH}-$ -based pathway becomes the primary one

and the bridging C-C pathway is secondary (the coupling through this way is very small, about -27.2 cm^{-1}). But, the primary pathway for the coupling in this molecule (12.62 Å, the N...CH=CH...N distance) is considerably longer than that (9.94 Å, the N...(bridging)C-C(bridging)...N distance) in molecule **11**, and thus the $|J|$ value ($|-354.8|\text{ cm}^{-1}$) is smaller than that ($|-576.0|\text{ cm}^{-1}$) of **11**.

However, an unsolved question is that the J couplings of the systems with conjugating side-ways (all in Table 2 except molecule **1**) are smaller than that of the system without conjugated side-way (molecule **1**), indicating that such conjugated side-ways play an inhibiting role in mediating the spin coupling for those molecules no matter obeying (**6**, **7**, **8**, **11**) or not obeying (**9**, **10**) the spin-alternation rule. The question regarding the side-way effects and the nature needs further study.