Supporting Information

Reference 28: Gaussian 03 (Revision B.03), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 2003.

TABLE S1: Total energies and total spin angular momentum for the singlet and quintet states, and the Ni-NNN-Ni dihedral angles (τ) dependence for $J_{ab}^{(3)}$ [a] of 1-LT and 2-HT at the UPBE0/LANL2DZ level.

From 1-LT

τ	Ni-N-N	E_{BS}	E_{QS}	$<S^2>_{BS}$	$<S^2>_{QS}$	$J_{ab}^{(3)}$
4.34	120.73	-1913.083597	-1913.081751	2.007413	6.015154	-101.10
-0.22	120.79	-1913.083544	-1913.081812	2.008336	6.0153	-94.88
-5.33	120.79	-1913.08359	-1913.081839	2.008231	6.015562	-95.93
-10.42[b]	120.66	-1913.083856	-1913.082215	2.008833	6.016166	-89.87
-15.46	120.41	-1913.083013	-1913.081548	2.0094	6.016514	-80.24
-17.95	120.23	-1913.082806	-1913.081584	2.009919	6.016738	-66.90
-20.42	120.03	-1913.08258	-1913.081443	2.010048	6.017012	-62.23
-25.29[b]	119.53	-1913.082675	-1913.081532	2.01103	6.0174	-62.58
-27.67[b]	119.23	-1913.082381	-1913.081331	2.011453	6.017596	-57.50
-30.02[b]	118.91	-1913.082054	-1913.081097	2.011879	6.017778	-52.44
-34.63[b]	118.19	-1913.081295	-1913.080517	2.012716	6.018095	-42.61
-35.76[b]	117.99	-1913.081081	-1913.080347	2.012919	6.018163	-40.24
-35.98	117.95	-1913.080329	-1913.079727	2.011444	6.01855	-32.98
-36.43	117.87	-1913.080029	-1913.079634	2.011801	6.018589	-21.63
-43.38	116.44	-1913.078602	-1913.078258	2.013857	6.0192	-18.89
-48.52	115.17	-1913.077718	-1913.077422	2.014973	6.018575	-16.25

From 2-HT

τ	Ni-N-N	E_{BS}	E_{QS}	$<S^2>_{BS}$	$<S^2>_{QS}$	$J_{ab}^{(3)}$
-49.81	115.73	-1912.861823	-1912.861542	2.011418	6.018373	-15.37
-46.64	116.71	-1912.861697	-1912.86134	2.009733	6.018132	-19.51
-45.69[b]	116.97	-1912.862668	-1912.861856	2.01184	6.017068	-44.48
-36.93[b]	119.20	-1912.862088	-1912.860873	2.00989	6.016383	-66.54
-34.63	119.71	-1912.86124	-1912.859993	2.010066	6.017103	-68.29
-29.93	120.64	-1912.860582	-1912.85914	2.005327	6.016597	-78.89
-25.07[b]	121.46	-1912.860498	-1912.858796	2.007548	6.015329	-93.21
-20.09[b]	122.17	-1912.859657	-1912.857802	2.006804	6.014969	-101.56
-15.01[b]	122.76	-1912.858727	-1912.856762	2.006244	6.014713	-107.60
-9.84 [b]	123.21	-1912.857727	-1912.855702	2.005904	6.014598	-110.83
-4.61[b]	123.53	-1912.856671	-1912.854644	2.005805	6.014643	-110.97
0.64[b]	123.72	-1912.855573	-1912.8536	2.005955	6.014848	-108.01
5.90[b]	123.76	-1912.854439	-1912.852572	2.00634	6.015188	-102.22

a. Total energies are in a.u., J_{ab} are shown in cm^{-1}. $J_{ab}^{(1)}$, $J_{ab}^{(2)}$ and $J_{ab}^{(3)}$ correspond to eq 2, 3 and 4, respectively.

b. The STABLE=OPT option is used for the BS calculation. (Sometimes the BS calculation is automatically converged to the spin restricted solution. In such cases, it should be detected by an application of the STABLE = OPT option to test the stability of the restricted DFT solution.)