

## Supporting Information

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## 1. Cartesian coordinates, U-DFT/6-31G\* energies, and $\langle S^2 \rangle$ values of the target molecules, 1–6.

Cartesian coordinates of **1** optimized at the U-B3LYP/6-31G\* level.

C	0.000000	0.000000	1.072671
C	0.000000	1.232517	0.336828
C	0.000000	1.216609	-1.046705
C	0.000000	0.000000	-1.747681
C	0.000000	-1.216609	-1.046705
C	0.000000	-1.232517	0.336828
N	0.000000	0.000000	2.400797
H	0.000000	2.164354	0.892961
H	0.000000	2.155064	-1.594614
H	0.000000	0.000000	-2.833691
H	0.000000	-2.155064	-1.594614
H	0.000000	-2.164354	0.892961

E(U-B3LYP/6-31G\*) = -286.307895436 a.u.

$\langle S^2 \rangle = 2.0515$

Cartesian coordinates of **2** optimized at the U-B3LYP/6-31G\* level.

C	-1.420643	0.884946	0.000000
C	-2.403900	-0.157277	0.000000
C	-2.025121	-1.498257	0.000000
C	-0.684274	-1.862063	0.000000
C	0.346272	-0.875193	0.000000
C	1.718119	-1.232366	0.000000
C	2.702383	-0.263493	0.000000
C	2.351047	1.101250	0.000000
C	1.018672	1.479587	0.000000
C	0.000000	0.507979	0.000000
N	-1.796638	2.140948	0.000000
H	-3.449666	0.131456	0.000000
H	-2.792465	-2.267615	0.000000
H	-0.401763	-2.911424	0.000000
H	1.983764	-2.286810	0.000000
H	3.749752	-0.552459	0.000000
H	3.128616	1.859905	0.000000
H	0.742894	2.529627	0.000000

E(U-B3LYP/6-31G\*) = -439.956555080

$\langle S^2 \rangle = 2.0642$

Cartesian coordinates of **3** optimized at the U-B3LYP/6-31G\* level.

C	1.408040	0.753963	0.000000
C	2.210865	-0.420474	0.000000
C	1.543195	-1.711655	0.000000
C	0.183511	-1.784714	0.000000
C	-0.636844	-0.608449	0.000000
C	-2.045834	-0.675256	0.000000
C	-2.811682	0.477614	0.000000
C	-2.189660	1.746628	0.000000
C	-0.814695	1.846078	0.000000
C	0.000000	0.679346	0.000000
H	1.903532	1.720303	0.000000
N	3.530773	-0.343342	0.000000
H	2.160854	-2.603653	0.000000
H	-0.308019	-2.754953	0.000000
H	-2.525467	-1.651174	0.000000
H	-3.895853	0.409024	0.000000
H	-2.800031	2.645321	0.000000
H	-0.331811	2.820044	0.000000

E(U-B3LYP/6-31G\*) = -439.953756540 a.u.

$\langle S^2 \rangle = 2.0613$

Cartesian coordinates of **4** optimized at the U-B3LYP/6-31G\* level.

C	-0.030450	2.671369	0.000000
C	1.220605	3.377385	0.000000
C	2.434654	2.690893	0.000000
C	2.478087	1.303295	0.000000
C	1.277889	0.524563	0.000000
C	1.309247	-0.872754	0.000000
C	0.132383	-1.642566	0.000000
C	0.152048	-3.068353	0.000000
C	-1.018013	-3.787412	0.000000
C	-2.272897	-3.120114	0.000000
C	-2.329965	-1.746779	0.000000
C	-1.139040	-0.967632	0.000000
C	-1.165756	0.443769	0.000000
C	0.000000	1.191678	0.000000
N	-1.152930	3.331938	0.000000
H	1.188996	4.461652	0.000000

H	3.362057	3.257314	0.000000
H	3.432941	0.784683	0.000000
H	2.272041	-1.379851	0.000000
H	1.113563	-3.576295	0.000000
H	-0.990065	-4.873561	0.000000
H	-3.189139	-3.703875	0.000000
H	-3.288077	-1.232907	0.000000
H	-2.124540	0.955220	0.000000

E(U-B3LYP/6-31G\*) = -593.597604415 a.u.

$\langle S^2 \rangle = 2.0802$

Cartesian coordinates of **5** optimized at the U-B3LYP/6-31G\* level.

C	-0.141400	2.538339	0.000000
C	-1.424970	3.158514	0.000000
C	-2.607437	2.296930	0.000000
C	-2.478843	0.947829	0.000000
C	-1.188523	0.301136	0.000000
C	-1.052970	-1.078880	0.000000
C	0.213024	-1.706285	0.000000
C	0.359110	-3.120481	0.000000
C	1.606111	-3.701689	0.000000
C	2.775505	-2.894888	0.000000
C	2.673774	-1.524921	0.000000
C	1.398538	-0.886212	0.000000
C	1.260218	0.512044	0.000000
C	0.000000	1.131498	0.000000
H	0.739648	3.172969	0.000000
N	-1.548672	4.465543	0.000000
H	-3.580463	2.776682	0.000000
H	-3.364539	0.316416	0.000000
H	-1.945680	-1.701342	0.000000
H	-0.536671	-3.736935	0.000000
H	1.702527	-4.783811	0.000000
H	3.752946	-3.369098	0.000000
H	3.566415	-0.904006	0.000000
H	2.153707	1.132711	0.000000

E(U-B3LYP/6-31G\*) = -593.594758551 a.u.

$\langle S^2 \rangle = 2.0834$

Cartesian coordinates of **6** optimized at the U-B3LYP/6-31G\* level.

C	0.000000	2.473539	-1.574398
C	0.000000	3.675855	-0.898296
C	0.000000	3.693978	0.512184
C	0.000000	2.505479	1.225151
C	0.000000	1.267436	0.557886
C	0.000000	0.000000	1.310313
C	0.000000	-1.267436	0.557886
C	0.000000	-2.505479	1.225151
C	0.000000	-3.693978	0.512184
C	0.000000	-3.675855	-0.898296
C	0.000000	-2.473539	-1.574398
C	0.000000	-1.237920	-0.870370
C	0.000000	0.000000	-1.554291
C	0.000000	1.237920	-0.870370
H	0.000000	2.451626	-2.661481
H	0.000000	4.611181	-1.451150
H	0.000000	4.642491	1.041568
H	0.000000	2.514442	2.310675
N	0.000000	0.000000	2.600058
H	0.000000	-2.514442	2.310675
H	0.000000	-4.642491	1.041568
H	0.000000	-4.611181	-1.451150
H	0.000000	-2.451626	-2.661481
H	0.000000	0.000000	-2.641638

E(U-B3LYP/6-31G\*) = -593.603253390 a.u.

$\langle S^2 \rangle = 2.0798$

Cartesian coordinates of **1** optimized at the U-HCTH/407/6-31G\* level.

C	0.000000	0.000000	1.073083
C	0.000000	1.229756	0.336280
C	0.000000	1.214455	-1.046789
C	0.000000	0.000000	-1.747434
C	0.000000	-1.214455	-1.046789
C	0.000000	-1.229756	0.336280
N	0.000000	0.000000	2.401637
H	0.000000	2.163568	0.892070
H	0.000000	2.155001	-1.594195
H	0.000000	0.000000	-2.834987
H	0.000000	-2.155001	-1.594195
H	0.000000	-2.163568	0.892070

$E(\text{U-HCTH}/407/6\text{-}31\text{G}^*) = -286.265750438 \text{ a.u.}$

$\langle S^2 \rangle = 2.0334$

Cartesian coordinates of **2** optimized at the U-HCTH/407/6-31G\* level.

C	-1.416449	0.889807	0.000000
C	-2.399812	-0.148332	0.000000
C	-2.026997	-1.489088	0.000000
C	-0.688111	-1.857528	0.000000
C	0.343012	-0.877370	0.000000
C	1.712842	-1.237477	0.000000
C	2.700745	-0.272658	0.000000
C	2.354170	1.090460	0.000000
C	1.023221	1.473254	0.000000
C	0.000000	0.508374	0.000000
N	-1.796288	2.147310	0.000000
H	-3.446306	0.143411	0.000000
H	-2.798618	-2.256323	0.000000
H	-0.411174	-2.909658	0.000000
H	1.976444	-2.293695	0.000000
H	3.748382	-0.566229	0.000000
H	3.134729	1.848272	0.000000
H	0.754832	2.526399	0.000000

$E(\text{U-HCTH}/407/6\text{-}31\text{G}^*) = -439.887468030 \text{ a.u.}$

$\langle S^2 \rangle = 2.0406$

Cartesian coordinates of **3** optimized at the U-HCTH/407/6-31G\* level.

C	1.405540	0.751329	0.000000
C	2.210534	-0.420189	0.000000
C	1.543980	-1.706695	0.000000
C	0.182418	-1.781169	0.000000
C	-0.637251	-0.610422	0.000000
C	-2.044979	-0.675113	0.000000
C	-2.810529	0.477994	0.000000
C	-2.189489	1.744085	0.000000
C	-0.814250	1.842985	0.000000
C	0.000000	0.678348	0.000000
H	1.901915	1.718655	0.000000
N	3.531748	-0.341686	0.000000
H	2.161302	-2.600721	0.000000
H	-0.305745	-2.754565	0.000000

H	-2.527475	-1.650996	0.000000
H	-3.896212	0.408980	0.000000
H	-2.799612	2.644747	0.000000
H	-0.332258	2.818782	0.000000

E(U-HCTH/407/6-31G\*) = -439.885071301 a.u.  
<S<sup>2</sup>> = 2.0380

Cartesian coordinates of **4** optimized at the U-HCTH/407/6-31G\* level.

C	-0.033640	2.669425	0.000000
C	1.213918	3.373837	0.000000
C	2.427816	2.690900	0.000000
C	2.472884	1.303892	0.000000
C	1.277421	0.527483	0.000000
C	1.308523	-0.871387	0.000000
C	0.135492	-1.643068	0.000000
C	0.155954	-3.065757	0.000000
C	-1.014475	-3.787086	0.000000
C	-2.265779	-3.123141	0.000000
C	-2.324188	-1.748178	0.000000
C	-1.137435	-0.968698	0.000000
C	-1.164153	0.440723	0.000000
C	0.000000	1.193644	0.000000
N	-1.156427	3.336986	0.000000
H	1.181563	4.459620	0.000000
H	3.355641	3.259575	0.000000
H	3.430685	0.788146	0.000000
H	2.273194	-1.376949	0.000000
H	1.117748	-3.575736	0.000000
H	-0.983823	-4.874700	0.000000
H	-3.183663	-3.707182	0.000000
H	-3.285381	-1.237518	0.000000
H	-2.125006	0.950295	0.000000

E(U-HCTH/407/6-31G\*) = -593.581254977 a.u.  
<S<sup>2</sup>> = 2.0436

Cartesian coordinates of **5** optimized at the U-HCTH/407/6-31G\* level.

C	-0.137643	2.534967	0.000000
C	-1.416255	3.161422	0.000000
C	-2.595406	2.305185	0.000000
C	-2.471360	0.952741	0.000000

C	-1.189325	0.304398	0.000000
C	-1.054403	-1.077381	0.000000
C	0.207432	-1.707869	0.000000
C	0.351475	-3.119059	0.000000
C	1.598592	-3.703606	0.000000
C	2.765778	-2.901649	0.000000
C	2.666150	-1.530080	0.000000
C	1.395366	-0.889655	0.000000
C	1.258453	0.506886	0.000000
C	0.000000	1.130964	0.000000
H	0.746133	3.167974	0.000000
N	-1.535013	4.471457	0.000000
H	-3.569345	2.786471	0.000000
H	-3.362765	0.327246	0.000000
H	-1.949588	-1.697883	0.000000
H	-0.544863	-3.736758	0.000000
H	1.691571	-4.787571	0.000000
H	3.744344	-3.377049	0.000000
H	3.562525	-0.912509	0.000000
H	2.153965	1.126294	0.000000

E(U-HCTH/407/6-31G\*) = -593.579641537 a.u.

$\langle S^2 \rangle = 2.0425$

Cartesian coordinates of **6** optimized at the U-HCTH/407/6-31G\* level.

C	0.000000	2.475867	-1.580716
C	0.000000	3.684962	-0.904485
C	0.000000	3.703662	0.511055
C	0.000000	2.511568	1.229071
C	0.000000	1.266583	0.562505
C	0.000000	0.000000	1.312438
C	0.000000	-1.266583	0.562505
C	0.000000	-2.511568	1.229071
C	0.000000	-3.703662	0.511055
C	0.000000	-3.684962	-0.904485
C	0.000000	-2.475867	-1.580716
C	0.000000	-1.238560	-0.871487
C	0.000000	0.000000	-1.557173
C	0.000000	1.238560	-0.871487
H	0.000000	2.454631	-2.670636
H	0.000000	4.622243	-1.460176



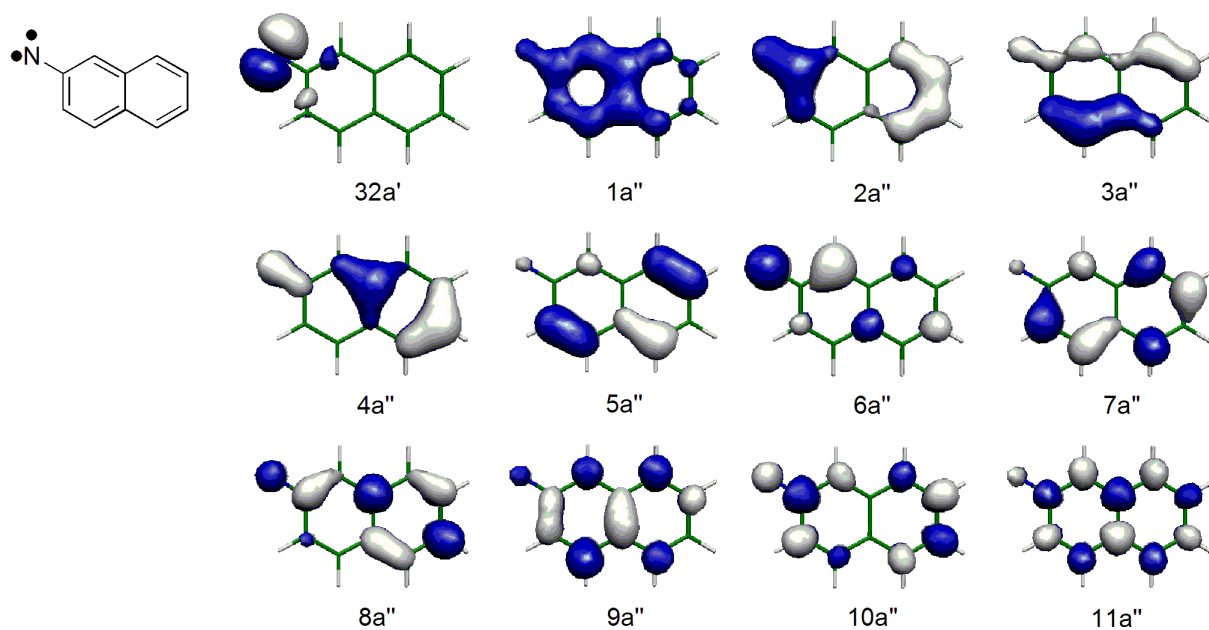
H	0.000000	4.655549	1.041032
H	0.000000	2.528982	2.316996
N	0.000000	0.000000	2.615675
H	0.000000	-2.528982	2.316996
H	0.000000	-4.655549	1.041032
H	0.000000	-4.622243	-1.460176
H	0.000000	-2.454631	-2.670636
H	0.000000	0.000000	-2.647064

$E(\text{U-HCTH}/407/6\text{-}31\text{G}^*) = -593.585590895 \text{ a.u.}$

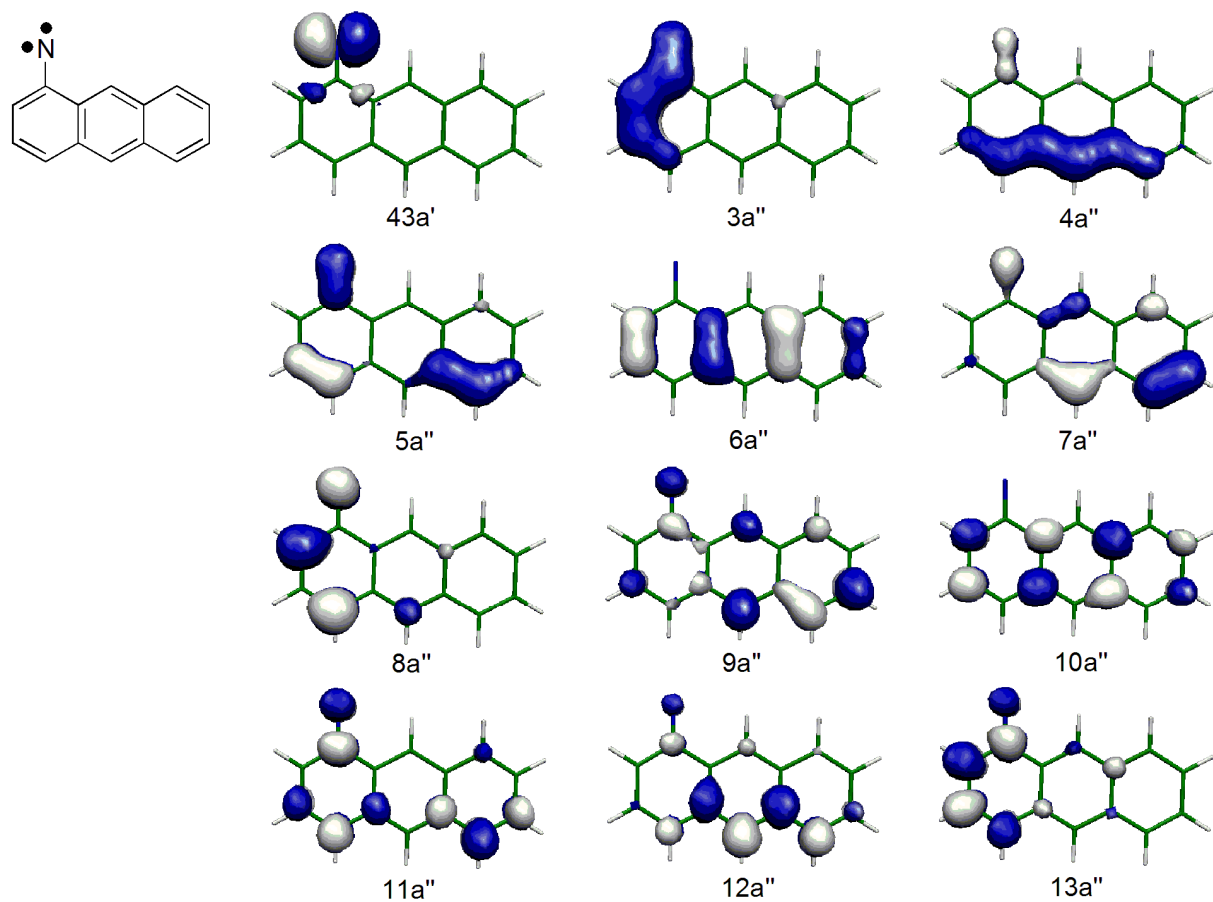
$\langle S^2 \rangle = 2.0515$

## 2. CASSCF active spaces of 3–5.

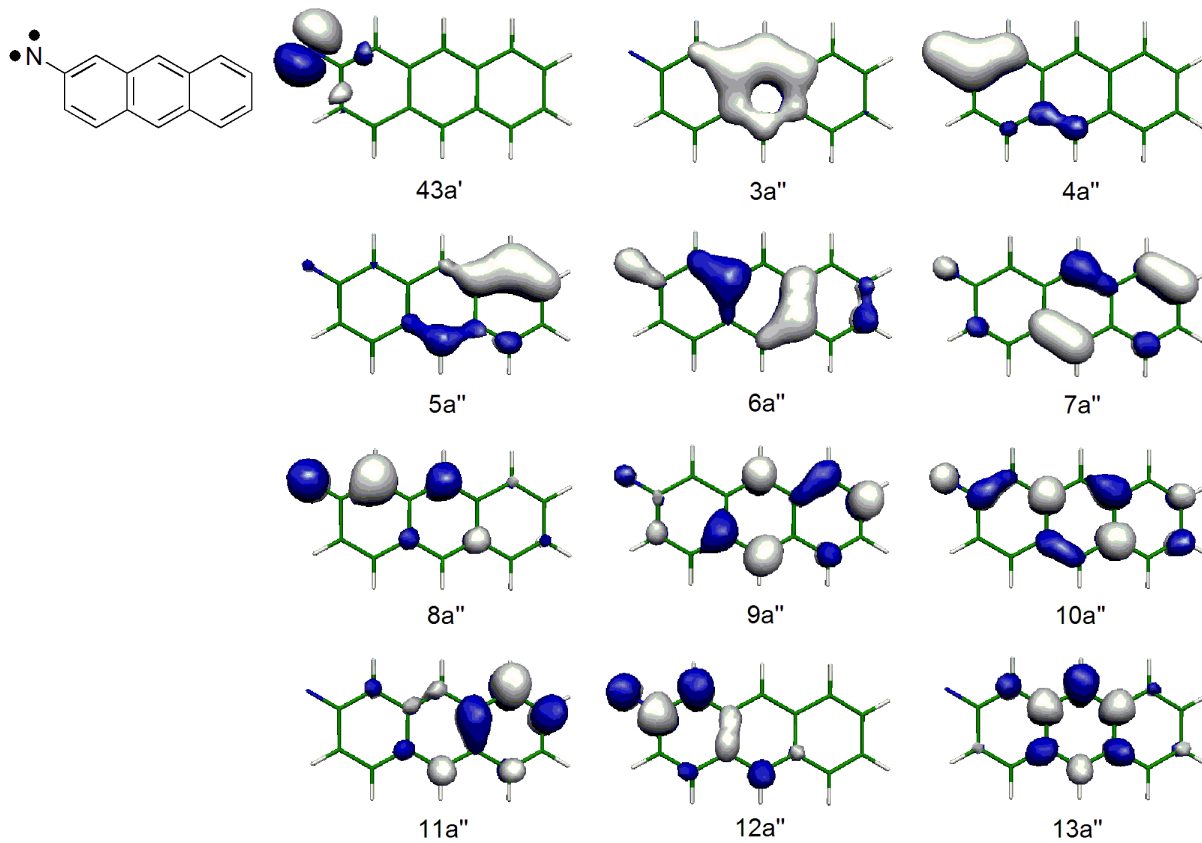
Note that the CASSCF active spaces of the other target molecules, **1**, **2** and **6** are given in the text.



**Figure S1.** CASSCF active orbitals of **3**. The SOMOs are 32a' and 6a''.



**Figure S2.** CASSCF active orbitals of **4**. The SOMOs are 43a' and 8a''.



**Figure S3.** CASSCF active orbitals of **5**. The SOMOs are 43a' and 8a''.

### 3. Selected electronic states of 3–5.

Note that the selected electronic states of the other target molecules, **1**, **2** and **6** are given in the text.

**Table S1.** Selected electronic states of **3**.

State	Main configurations ( $ C  > 0.3$ ) <sup>a</sup>			$\Delta E_{\text{CASSCF}}$ /cm <sup>-1</sup>	$\Delta E_{\text{MRMP2}}$ /cm <sup>-1</sup>	$\langle \Psi_g   H^{SO}   \Psi_e \rangle$ /cm <sup>-1</sup>		$D_{ii}$ /cm <sup>-1 c</sup>	
	$C^b$	$a'$	$a''$			$i = x^d$	$i = y^d$	$i = x^d$	$i = y^d$
1 <sup>3</sup> A''	-0.85	u	22222u00000						
1 <sup>1</sup> A'	0.80	2	22222000000	16067	11709	13.056	0.504	0.0146	0.0000
	-0.30	0	22222200000						
2 <sup>1</sup> A'	0.81	0	22222200000	28545	22488	43.928	2.094	0.0858	0.0002
1 <sup>3</sup> A'	-0.78	2	2222uu00000	36154	31887	7.562	0.618	-0.0018	0.0000
2 <sup>3</sup> A'	0.82	2	2222uu00000	44953	37051	1.759	-0.271	-0.0001	0.0000
3 <sup>3</sup> A'	-0.61	2	2222u0u0000	45779	39480	6.626	0.589	-0.0011	0.0000
	-0.31	2	222u2u00000						
	-0.31	0	2222u2u0000						
4 <sup>1</sup> A'	-0.60	2	2222ud00000	55968	42326	-8.281	-1.305	0.0016	0.0000
5 <sup>3</sup> A'	-0.65	0	22222uu0000	51682	44347	-13.757	-1.281	-0.0043	0.0000
5 <sup>1</sup> A'	-0.42	0	22222ud0000	59707	47995	-7.178	0.366	0.0011	0.0000
	0.34	0	2222u20d000						
6 <sup>1</sup> A'	0.47	2	22u22d00000	56902	48440	-2.216	0.287	0.0001	0.0000
	0.32	2	222u2d00000						
6 <sup>3</sup> A'	-0.34	2	222u20u0000	58888	48738	-3.889	0.437	-0.0003	0.0000
	-0.33	0	22222uu0000						
	-0.30	2	2u222u00000						
7 <sup>3</sup> A'	-0.47	0	2222u2u0000	60555	49884	-4.918	-0.528	-0.0005	0.0000
9 <sup>3</sup> A'	0.35	0	22222u0u000	61168	50431	7.284	0.362	-0.0011	0.0000
	0.32	2	22u22u00000						
10 <sup>3</sup> A'	0.27	0	22222uu0000	63065	52504	1.773	0.845	-0.0001	0.0000
7 <sup>1</sup> A'	0.42	2	2222ud00000	63082	52987	7.720	0.776	0.0011	0.0000
	0.40	2	2u222d00000						
8 <sup>1</sup> A'	0.45	2	2222u0d0000	67677	53776	-7.437	-0.535	0.0010	0.0000
	0.40	2	22220200000						
10 <sup>1</sup> A'	-0.25	2	222u20d0000	70691	57909	2.277	0.548	0.0001	0.0000

<sup>a</sup> The active space consists of 12 orbitals: 32a', and 1a''–11a''. 2, 0, u, and d stand for doubly occupied, unoccupied, spin up ( $\alpha$ ), and spin down ( $\beta$ ), respectively. <sup>b</sup> CAS-CI coefficients.

<sup>c</sup> Zero-field splitting  $D$  values arising from the spin–orbit coupling between the ground and excited states. <sup>d</sup> Molecule is on the  $xy$  plane and an angle between the C–N bond and the  $x$  axis is  $3.7^\circ$  in the standard orientation of Gaussian 03.

**Table S2.** Selected electronic states of **4**.

State	Main configurations ( $ C  > 0.3$ ) <sup>a</sup>			$\Delta E_{\text{CASSCF}}$ /cm <sup>-1</sup>	$\Delta E_{\text{MRMP2}}$ /cm <sup>-1</sup>	$\langle \Psi_g   H^{SO}   \Psi_e \rangle / \text{cm}^{-1}$		$D_{ii} / \text{cm}^{-1 c}$	
	$C^b$	$a'$	$a''$			$i = x^d$	$i = y^d$	$i = x^d$	$i = y^d$
1 <sup>3</sup> A''	0.86	u	22222u00000						
1 <sup>1</sup> A'	-0.83	2	22222000000	17060	11730	-12.394	7.060	0.0131	0.0042
2 <sup>1</sup> A'	-0.83	0	22222200000	30252	24440	-33.315	19.174	0.0454	0.0150
1 <sup>3</sup> A'	-0.83	2	2222uu00000	32299	27603	-8.475	5.602	-0.0026	-0.0011
2 <sup>3</sup> A'	-0.64	2	222u2u00000	46185	34245	-4.181	2.393	-0.0005	-0.0002
	-0.45	2	2222u0u0000						
3 <sup>1</sup> A'	-0.76	2	2222ud00000	48606	34529	-4.904	3.749	0.0007	0.0004
3 <sup>3</sup> A'	-0.55	2	222u2u00000	44174	34983	5.449	-3.418	-0.0008	-0.0003
	-0.46	2	2222u0u0000						
4 <sup>1</sup> A'	-0.71	2	2222ud00000	45982	35005	-7.122	4.318	0.0014	0.0005
	0.31	2	222u2d00000						
4 <sup>3</sup> A'	0.74	0	22222uu0000	48359	39480	-13.859	8.529	-0.0049	-0.0018
5 <sup>3</sup> A'	0.38	2	2222uu00000	55176	41471	4.363	-2.212	-0.0005	-0.0001
	0.34	2	2222u0u0000						
	-0.31	2	222u2u00000						
6 <sup>3</sup> A'	0.57	2	2222u00u000	56503	43377	3.827	-2.486	-0.0003	-0.0001
	-0.32	2	2222uu00000						
6 <sup>1</sup> A'	0.45	2	22220200000	53746	43824	4.198	-2.717	0.0004	0.0002
	0.38	2	2222ud00000						
	0.30	2	2222u0d0000						
7 <sup>1</sup> A'	-0.34	2	2222u00d000	59925	43837	-3.906	1.628	0.0003	0.0001
	0.33	2	222u2d00000						
7 <sup>3</sup> A'	-0.27	2	2222u00u000	59606	46723	4.855	-3.261	-0.0005	-0.0002
8 <sup>1</sup> A'	-0.44	2	22u22d00000	63512	47988	-3.829	3.191	0.0003	0.0002
	-0.32	2	22220ud0000						
9 <sup>3</sup> A'	-0.54	0	2222u2u0000	60820	48305	-4.815	2.983	-0.0005	-0.0002
10 <sup>1</sup> A'	0.44	2	22u22d00000	62713	50592	-4.719	2.845	0.0004	0.0002

<sup>a</sup> The active space consists of 12 orbitals: 43a', and 3a''-13a''. 2, 0, u, and d stand for doubly occupied, unoccupied, spin up ( $\alpha$ ), and spin down ( $\beta$ ), respectively. <sup>b</sup> CAS-CI coefficients.

<sup>c</sup> Zero-field splitting  $D$  values arising from the spin-orbit coupling between the ground and excited states. <sup>d</sup> Molecule is on the  $xy$  plane and an angle between the C-N bond and the  $x$  axis is 146.1° in the standard orientation of Gaussian 03.

**Table S3.** Selected electronic states of **5**.

State	Main configurations ( $ C  > 0.3$ ) <sup>a</sup>			$\Delta E_{\text{CASSCF}}$ /cm <sup>-1</sup>	$\Delta E_{\text{MRMP2}}$ /cm <sup>-1</sup>	$\langle \Psi_g   H^{SO}   \Psi_e \rangle / \text{cm}^{-1}$		$D_{ii} / \text{cm}^{-1c}$	
	$C^b$	$a'$	$a''$			$i = x^d$	$i = y^d$	$i = x^d$	$i = y^d$
1 <sup>3</sup> A''	0.86	u	22222u00000						
1 <sup>1</sup> A'	0.81	2	22222000000	16 823	11 968	1.748	-13.093	0.0003	0.0143
2 <sup>1</sup> A'	-0.81	0	22222200000	29 400	23 125	4.755	-41.992	0.0010	0.0763
1 <sup>3</sup> A'	0.78	2	2222uu00000	33 560	28 499	-0.625	7.921	0.0000	-0.0022
3 <sup>1</sup> A'	0.68	2	2222ud00000	45 347	35 054	-0.148	-2.377	0.0000	0.0002
2 <sup>3</sup> A'	-0.57	2	2222u0u0000	42 855	35 632	-0.632	7.983	0.0000	-0.0018
	-0.41	2	222u2u00000						
3 <sup>3</sup> A'	0.53	0	22222uu0000	48 081	37 769	-0.653	11.236	0.0000	-0.0033
	0.34	2	2222uu00000						
4 <sup>3</sup> A'	-0.45	2	222u2u00000	49 668	38 252	-0.874	7.862	0.0000	-0.0016
	-0.44	2	2222uu00000						
4 <sup>1</sup> A'	0.71	2	2222ud00000	53 178	38 397	0.416	-9.154	0.0000	0.0022
5 <sup>3</sup> A'	0.45	2	2u222u00000	51 424	41 983	0.275	-3.206	0.0000	-0.0002
	-0.35	2	222u20u0000						
	-0.33	2	2222u0u0000						
7 <sup>3</sup> A'	0.44	2	222u20u0000	60 156	46 527	-0.694	6.374	0.0000	-0.0009
	-0.32	2	2222u0u0000						
5 <sup>1</sup> A'	-0.35	0	2222u20d000	60 039	46 909	0.939	-6.084	0.0000	0.0008
	-0.35	0	22222ud0000						
8 <sup>3</sup> A'	0.60	0	2222u2u0000	58 175	48 025	-0.559	10.822	0.0000	-0.0024
	-0.41	0	22222u0u000						
6 <sup>1</sup> A'	-0.35	2	2u222d00000	62 568	48 813	-0.079	4.132	0.0000	0.0003
7 <sup>1</sup> A'	0.52	2	2222u0d0000	65 948	48 910	0.451	-6.192	0.0000	0.0008
8 <sup>1</sup> A'	-0.40	2	22u22d00000	64 598	48 958	0.162	-4.480	0.0000	0.0004
	-0.37	2	222u2d00000						
10 <sup>3</sup> A'	-0.29	2	u2222u00000	63 055	52 164	0.186	-3.188	0.0000	-0.0002

<sup>a</sup> The active space consists of 12 orbitals: 43a', and 3a''–13a''. 2, 0, u, and d stand for doubly occupied, unoccupied, spin up ( $\alpha$ ), and spin down ( $\beta$ ), respectively. <sup>b</sup> CAS-CI coefficients.

<sup>c</sup> Zero-field splitting  $D$  values arising from the spin–orbit coupling between the ground and excited states. <sup>d</sup> Molecule is on the  $xy$  plane and an angle between the C–N bond and the  $x$  axis is 86.0° in the standard orientation of Gaussian 03.

#### 4. CASSCF canonical orbital energies and AO coefficients.

**Table S4.** CASSCF canonical orbital energies of the SOMOs and AO coefficient of the nitrene N atom in the  $\pi$ -SOMO.

Molecule	$E(n\text{-SOMO})/\text{a.u.}$	$E(\pi\text{-SOMO})/\text{a.u.}$	$C(\text{N})(\pi\text{-SOMO})$
1	-0.1511	-0.1342	0.770348
2	-0.1547	-0.1291	0.645878
3	-0.1534	-0.1326	0.709112
4	-0.1537	-0.1260	0.572144
5	-0.1515	-0.1296	0.636053
6	-0.1499	-0.1180	0.465332

**Table S5.** AO coefficient of the HOMO and LUMO of naphthalene and anthracene calculated by the CASSCF/cc-pVDZ level.

Molecule	Atom	$C(\text{HOMO})$	$C(\text{LUMO})$
Naphthalene <sup>a</sup>	C1	0.441026	0.544874
	C2	0.301732	-0.364180
Anthracene <sup>b</sup>	C1	0.330413	-0.376668
	C2	0.271787	0.304607
	C9	0.464889	0.543260

<sup>a</sup> CASSCF(10,10)/cc-pVDZ//B3LYP/6-31G\*. <sup>b</sup> CASSCF(14,14)/cc-pVDZ//B3LYP/6-31G\*

## 5. Exchange-correlation functional dependence of the $D^{SS}$ tensor.

**Table S6.**  $D^{SS}$  values (in units of  $\text{cm}^{-1}$ ) calculated by using the RO-DFT/EPR-II spin density at the U-B3LYP/6-31G\* optimized geometry.

Functional	1	2	3	4	5	6	Mean AD <sup>a</sup>	Maximum AD <sup>b</sup>
<b><math>D(\text{Exptl.}) - D^{SO}</math></b>	<b>+0.8860</b>	<b>+0.7121</b>	<b>+0.8285</b>	<b>+0.5943</b>	<b>+0.6941</b>	<b>+0.4213</b>		
B3LYP	+0.8916	+0.6393	+0.7926	+0.4772	+0.6215	+0.2730	0.0754	0.1483
BLYP	+0.8038	+0.5925	+0.7130	+0.4606	+0.5671	+0.3058	0.1156	0.1337
BHandHLYP	+1.0577	+0.7540	+0.9571	+0.4831	+0.7247	+0.1958	0.1183	0.2255
BPW91	+0.8172	+0.6005	+0.7253	+0.4661	+0.5762	+0.3062	0.1075	0.1282
B3PW91	+0.9084	+0.6512	+0.8090	+0.4844	+0.6339	+0.2730	0.0702	0.1483
BP86	+0.7990	+0.5863	+0.7081	+0.4549	+0.5612	+0.3002	0.1211	0.1394
B3P86	+0.8924	+0.6371	+0.7928	+0.4740	+0.6194	+0.2689	0.0774	0.1524
OLYP	+0.8371	+0.6274	+0.7493	+0.4943	+0.6063	+0.3291	0.0821	0.1000
O3LYP	+0.8844	+0.6531	+0.7925	+0.5038	+0.6371	+0.3089	0.0594	0.1124
PBEPBE	+0.8064	+0.5935	+0.7158	+0.4613	+0.5690	+0.3045	0.1143	0.1330
PBE1PBE	+0.9278	+0.6614	+0.8274	+0.4836	+0.6438	+0.2597	0.0694	0.1616
MPW1PW91	+0.9375	+0.6679	+0.8363	+0.4870	+0.6501	+0.2600	0.0693	0.1613
TPSSTPSS	+0.8581	+0.6291	+0.7633	+0.4840	+0.6042	+0.3095	0.0813	0.1118
BMK	+0.9433	+0.6749	+0.8456	+0.4890	+0.6648	+0.2445	0.0705	0.1768
B1B95	+0.9308	+0.6763	+0.8357	+0.5055	+0.6667	+0.2754	0.0583	0.1459
B97-1	+0.8974	+0.6488	+0.8005	+0.4881	+0.6337	+0.2792	0.0686	0.1421
B97-2	+0.9185	+0.6669	+0.8215	+0.5024	+0.6531	+0.2854	0.0589	0.1359
G96LYP	+0.8136	+0.6008	+0.7228	+0.4680	+0.5764	+0.3102	0.1074	0.1263
B1LYP	+0.9189	+0.6547	+0.8177	+0.4799	+0.6365	+0.2611	0.0722	0.1602
VSXC	+0.8607	+0.6302	+0.7661	+0.4882	+0.6083	+0.3124	0.0784	0.1089
HCTH/93	+0.8588	+0.6442	+0.7696	+0.5087	+0.6245	+0.3378	0.0655	0.0856
HCTH/147	+0.8605	+0.6447	+0.7709	+0.5084	+0.6243	+0.3367	0.0651	0.0859
HCTH/407	+0.8820	+0.6642	+0.7925	+0.5254	+0.6451	+0.3476	0.0466	0.0737
HCTH/407//HCTH/407 <sup>c</sup>	+0.8872	+0.6760	+0.8017	+0.5409	+0.6581	+0.3796	0.0325	0.0534
B3LYP//HCTH/407 <sup>c</sup>	+0.8973	+0.6535	+0.8037	+0.4953	+0.6383	+0.3017	0.0615	0.1196

<sup>a</sup> Mean absolute deviation from the reference  $D(\text{Exptl.}) - D^{SO}$  value, in units of  $\text{cm}^{-1}$ . <sup>b</sup> Maximum absolute deviation from the reference  $D(\text{Exptl.}) - D^{SO}$  value, in units of  $\text{cm}^{-1}$ . <sup>c</sup>  $D^{SS}$  tensor was calculated at the U-HCTH/407/6-31G\* optimized geometry.



**Table S7.**  $D^{SS}$  values (in units of  $\text{cm}^{-1}$ ) calculated by using the U-DFT/EPR-II spin density at the U-B3LYP/6-31G\* optimized geometry.

Functional	1	2	3	4	5	6	Mean AD <sup>a</sup>	Maximum AD <sup>b</sup>
<b><math>D(\text{Exptl.}) - D^{SO}</math></b>	<b>+0.8860</b>	<b>+0.7121</b>	<b>+0.8285</b>	<b>+0.5943</b>	<b>+0.6941</b>	<b>+0.4213</b>		
B3LYP	+1.2693	+1.0846	+1.2021	+0.9745	+1.0975	+0.7802	0.379	0.403
BLYP	+1.0922	+0.9026	+1.0122	+0.7860	+0.8901	+0.6202	0.195	0.206
BHandHLYP	+1.5477	+1.3935	+1.5172	+1.3165	+1.4757	+1.1216	0.706	0.782
BPW91	+1.1253	+0.9324	+1.0453	+0.8156	+0.9228	+0.6437	0.225	0.239
B3PW91	+1.3050	+1.1203	+1.2395	+1.0119	+1.1378	+0.8143	0.415	0.444
BP86	+1.0931	+0.9011	+1.0128	+0.7846	+0.8899	+0.6165	0.194	0.207
B3P86	+1.2780	+1.0914	+1.2111	+0.9819	+1.1073	+0.7852	0.386	0.413
OLYP	+1.1459	+0.9663	+1.0716	+0.8564	+0.9584	+0.6923	0.259	0.271
O3LYP	+1.2430	+1.0647	+1.1749	+0.9575	+1.0700	+0.7767	0.358	0.376
PBEPBE	+1.1032	+0.9117	+1.0233	+0.7952	+0.9008	+0.6262	0.204	0.217
PBE1PBE	+1.3441	+1.1631	+1.2831	+1.0582	+1.1882	+0.8577	0.460	0.494
MPW1PW91	+1.3618	+1.1810	+1.3016	+1.0769	+1.2085	+0.8756	0.478	0.514
TPSSTPSS	+1.2253	+1.0306	+1.1469	+0.9126	+1.0257	+0.7265	0.322	0.339
BMK	+1.3330	+1.1559	+1.2736	+1.0518	+1.1808	+0.8450	0.451	0.487
B1B95	+1.2964	+1.1189	+1.2340	+1.0127	+1.1360	+0.8143	0.413	0.442
B97-1	+1.2799	+1.0977	+1.2136	+0.9893	+1.1108	+0.7952	0.392	0.417
B97-2	+1.3118	+1.1311	+1.2469	+1.0242	+1.1464	+0.8297	0.426	0.452
G96LYP	+1.1080	+0.9195	+1.0290	+0.8041	+0.9086	+0.6374	0.212	0.222
B1LYP	+1.3235	+1.1429	+1.2611	+1.0365	+1.1640	+0.8386	0.438	0.470
VSXC	+1.2632	+1.0726	+1.1881	+0.9610	+1.0729	+0.7804	0.367	0.379
HCTH/93	+1.1993	+1.0169	+1.1248	+0.9071	+1.0120	+0.7385	0.310	0.318
HCTH/147	+1.2140	+1.0309	+1.1395	+0.9212	+1.0266	+0.7515	0.325	0.333
HCTH/407	+1.2395	+1.0587	+1.1665	+0.9504	+1.0559	+0.7799	0.352	0.362

<sup>a</sup> Mean absolute deviation from the reference  $D(\text{Exptl.}) - D^{SO}$  value, in units of  $\text{cm}^{-1}$ . <sup>b</sup> Maximum absolute deviation from the reference  $D(\text{Exptl.}) - D^{SO}$  value, in units of  $\text{cm}^{-1}$ .

**Table S8.** The  $\langle S^2 \rangle$  expectation value of the U-DFT/EPR-II calculations at the U-B3LYP/6-31G\* optimized geometry

Functional	1	2	3	4	5	6
B3LYP	2.0506	2.0624	2.0599	2.0772	2.0805	2.0769
BLYP	2.0212	2.0245	2.0234	2.0285	2.0291	2.0278
BHandHLYP	2.1461	2.1971	2.2025	2.2895	2.3171	2.2759
BPW91	2.0251	2.0291	2.0278	2.0340	2.0348	2.0332
B3PW91	2.0579	2.0716	2.0690	2.0896	2.0938	2.0892
BP86	2.0228	2.0263	2.0251	2.0305	2.0313	2.0297
B3P86	2.0545	2.0671	2.0647	2.0834	2.0874	2.0827
OLYP	2.0251	2.0299	2.0280	2.0354	2.0356	2.0357
O3LYP	2.0403	2.0495	2.0466	2.0605	2.0614	2.0614
PBEPBE	2.0229	2.0266	2.0254	2.0310	2.0318	2.0302
PBE1PBE	2.0698	2.0874	2.0850	2.1116	2.1183	2.1111
MPW1PW91	2.0734	2.0919	2.0897	2.1181	2.1254	2.1175
TPSSTPSS	2.0353	2.0415	2.0396	2.0494	2.0508	2.0482
BMK	2.0603	2.0787	2.0738	2.0994	2.1020	2.1006
B1B95	2.0490	2.0633	2.0591	2.0793	2.0808	2.0807
B97-1	2.0480	2.0598	2.0568	2.0739	2.0762	2.0742
B97-2	2.0516	2.0647	2.0612	2.0803	2.0825	2.0814
G96LYP	2.0225	2.0261	2.0248	2.0305	2.0310	2.0299
B1LYP	2.0641	2.0799	2.0775	2.1011	2.1067	2.1010
VSXC	2.0424	2.0495	2.0477	2.0589	2.0609	2.0587
HCTH/93	2.0291	2.0345	2.0325	2.0410	2.0412	2.0415
HCTH/147	2.0314	2.0371	2.0352	2.0441	2.0447	2.0446
HCTH/407	2.0340	2.0404	2.0381	2.0484	2.0488	2.0492