ELECTRONIC SUPPLEMENTARY INFORMATION

An MS-CASPT2 Study of the Photodecomposition of *4*-Methoxyphenyl Azide: Role of Internal Conversion and Intersystem Crossing

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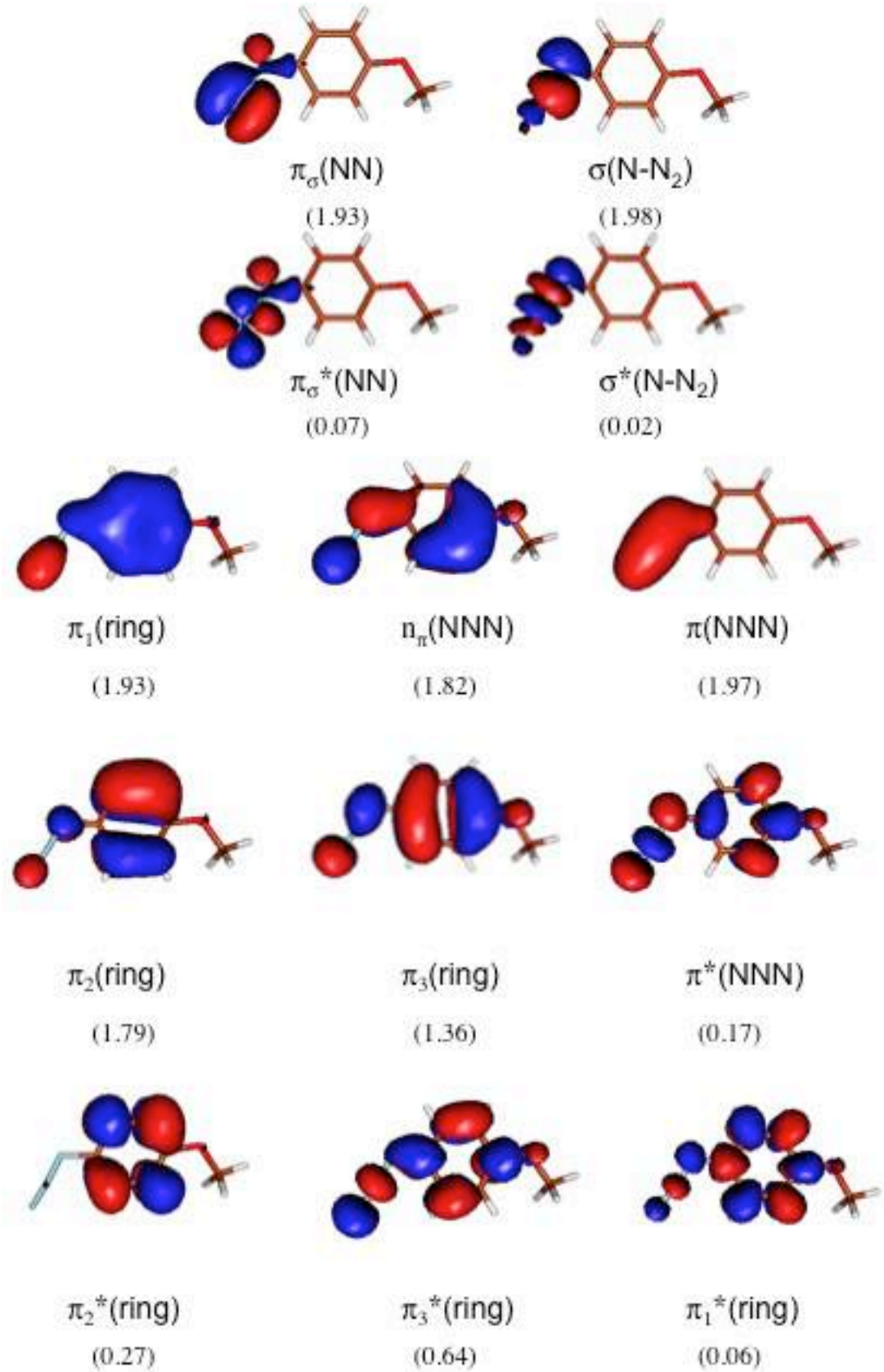

Figure S1. State average active orbitals included in the CAS-SCF wavefunction of 4-methoxyphenyl azide. In parenthesis, mean occupation numbers of the state average orbitals.

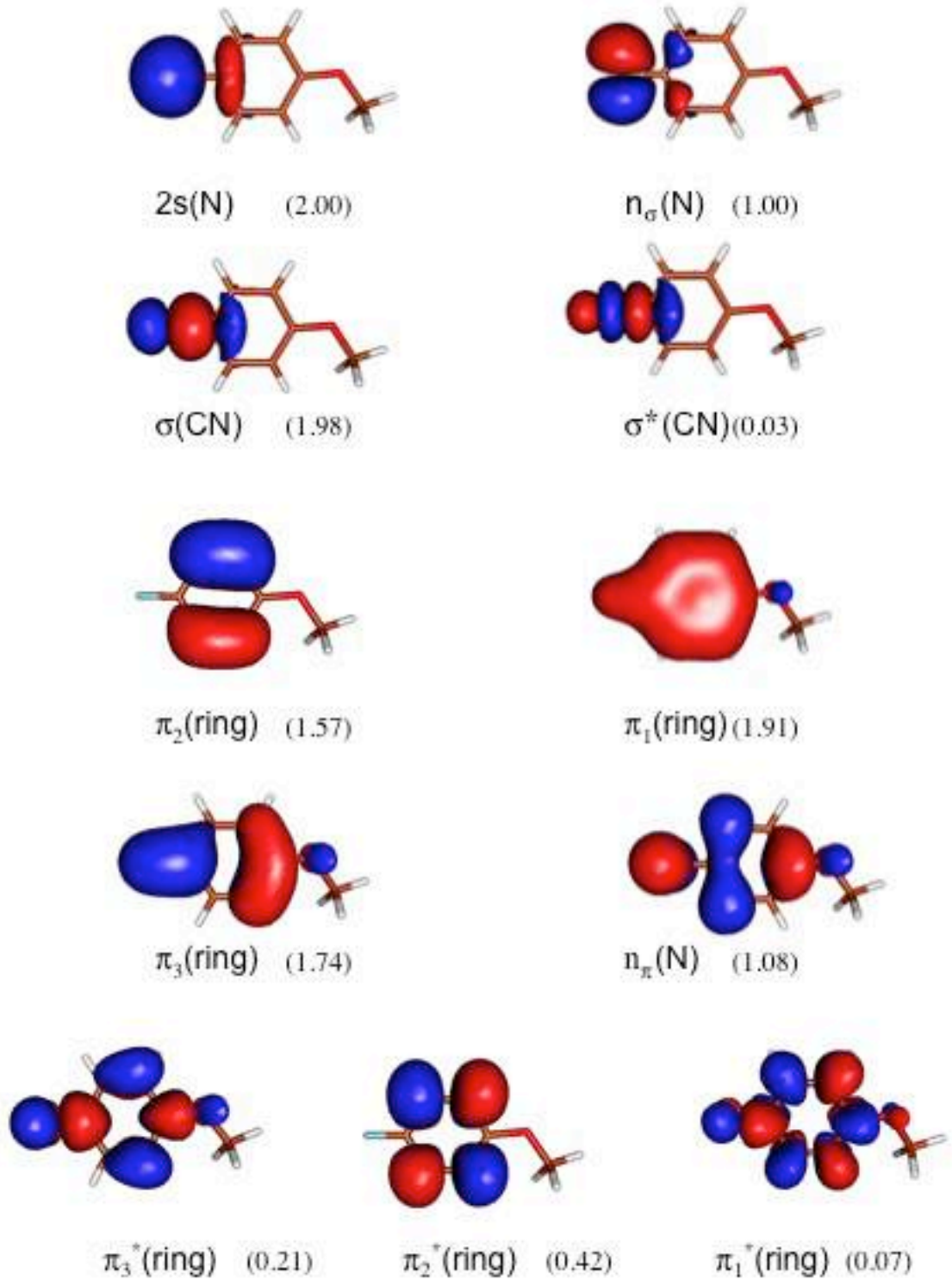

Figure S2. Active orbitals included in the CAS-SCF wavefunction of 4-methoxyphenyl nitrene. In parenthesis, mean occupation numbers of the state average orbitals.

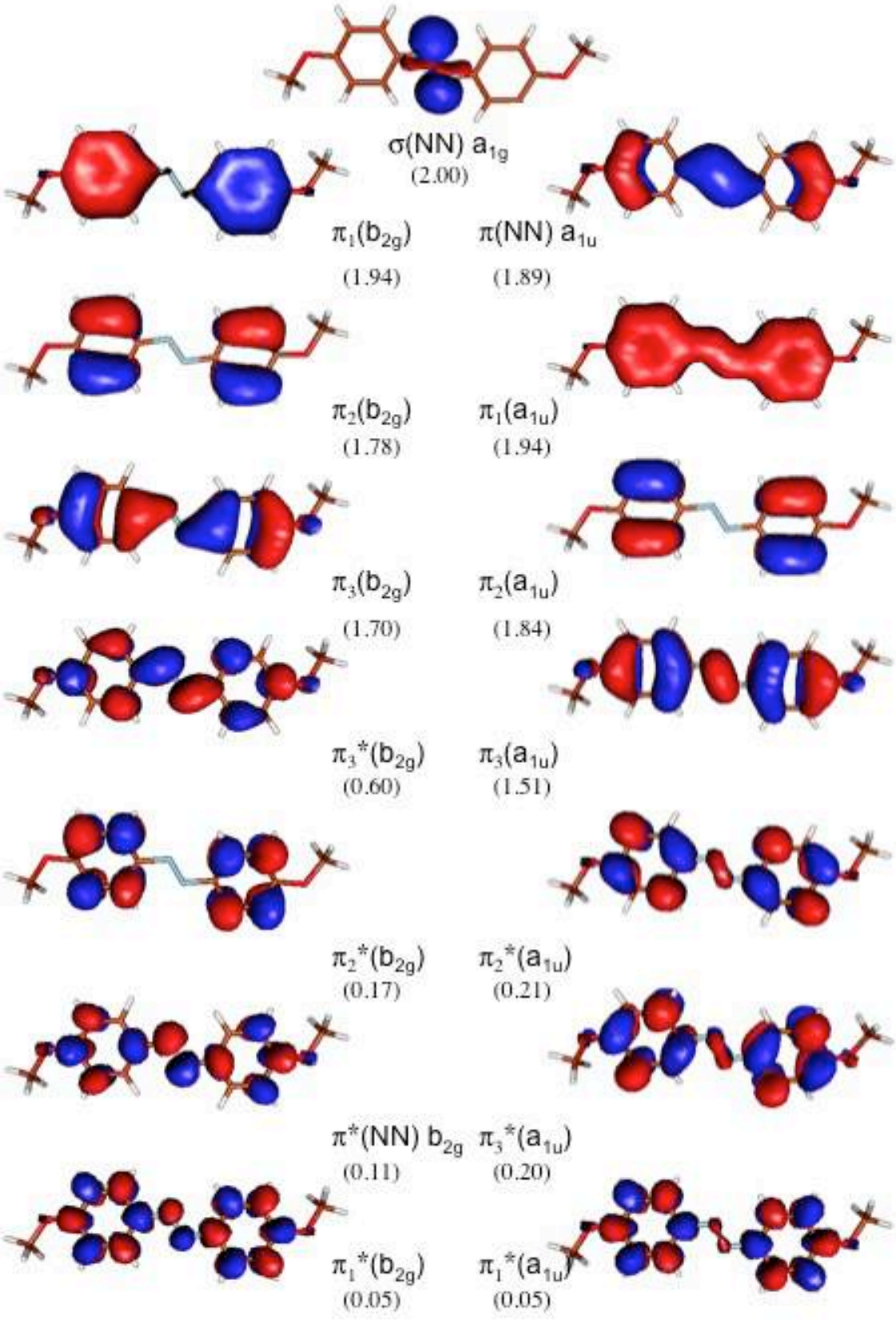

Figure S3. Active orbitals included in the CAS-SCF wavefunction of 4,4'dimethoxyazobenzene. In parenthesis, mean occupation numbers of the state average orbitals.

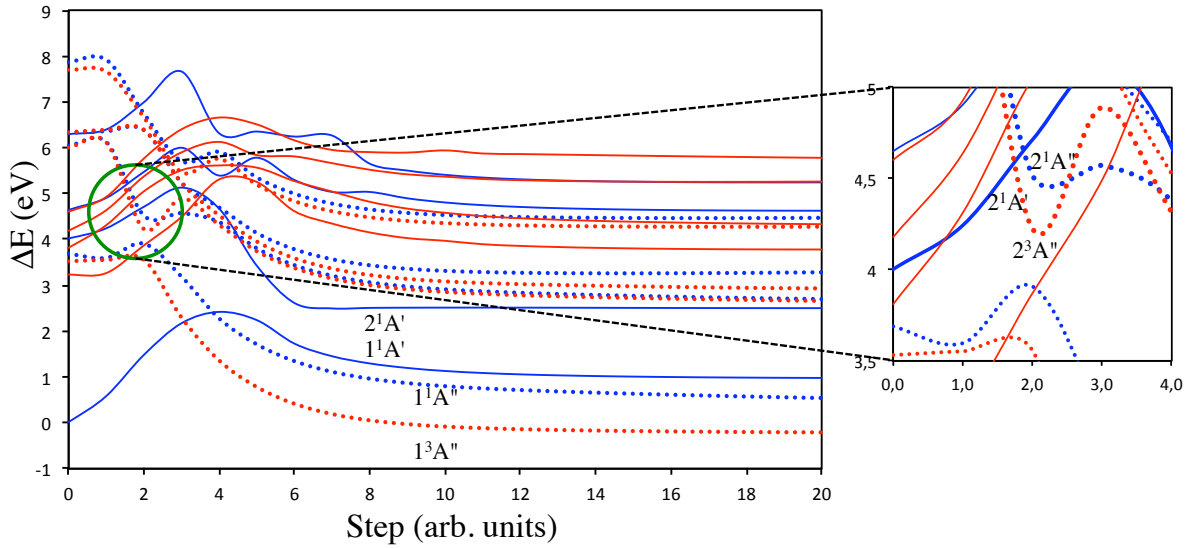

Figure S4. MS-CASPT2/ANO-RCC (C_s symmetry) potential energy curves of the ground and low-lying singlet and triplet excited states of 4-methoxyphenyl azide for dissociation into 4-methoxyphenyl nitrene and N_2. Four state-average CAS-SCF wavefunction in each symmetry block. Blue solid line: singlet A'; red solid line: triplet A'; blue dotted line: singlet A"; red dotted line: triplet A". Inset: expanded view of the 2^1A"/2^1A' and 2^1A'/2^3A" crossings. Final $\boldsymbol{R}$(N-N_2) = 4.7 Å.

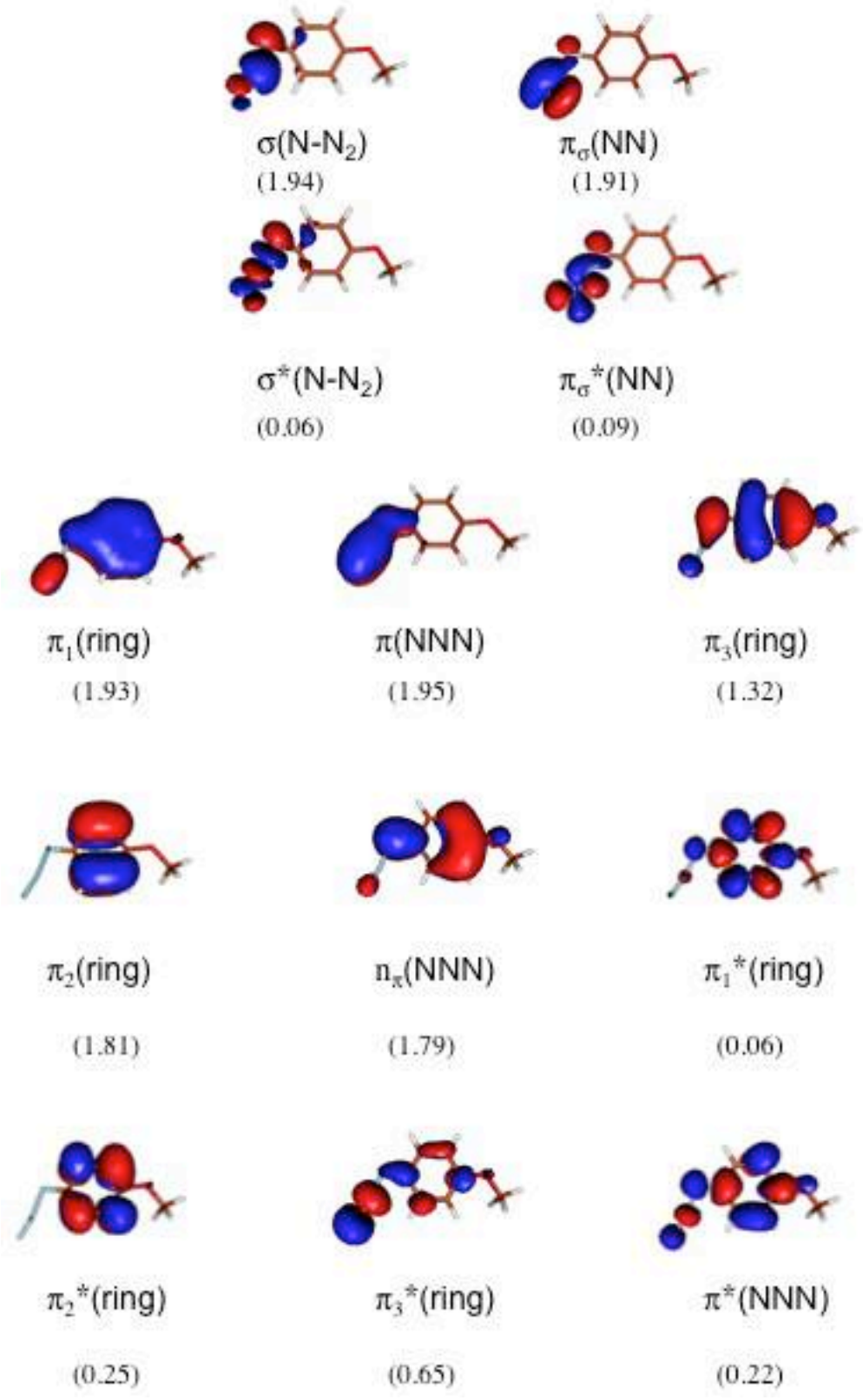

Figure S5. Active orbitals included in the CAS-SCF wavefunction of CI1. In parenthesis, mean occupation numbers of the state averaged orbitals.

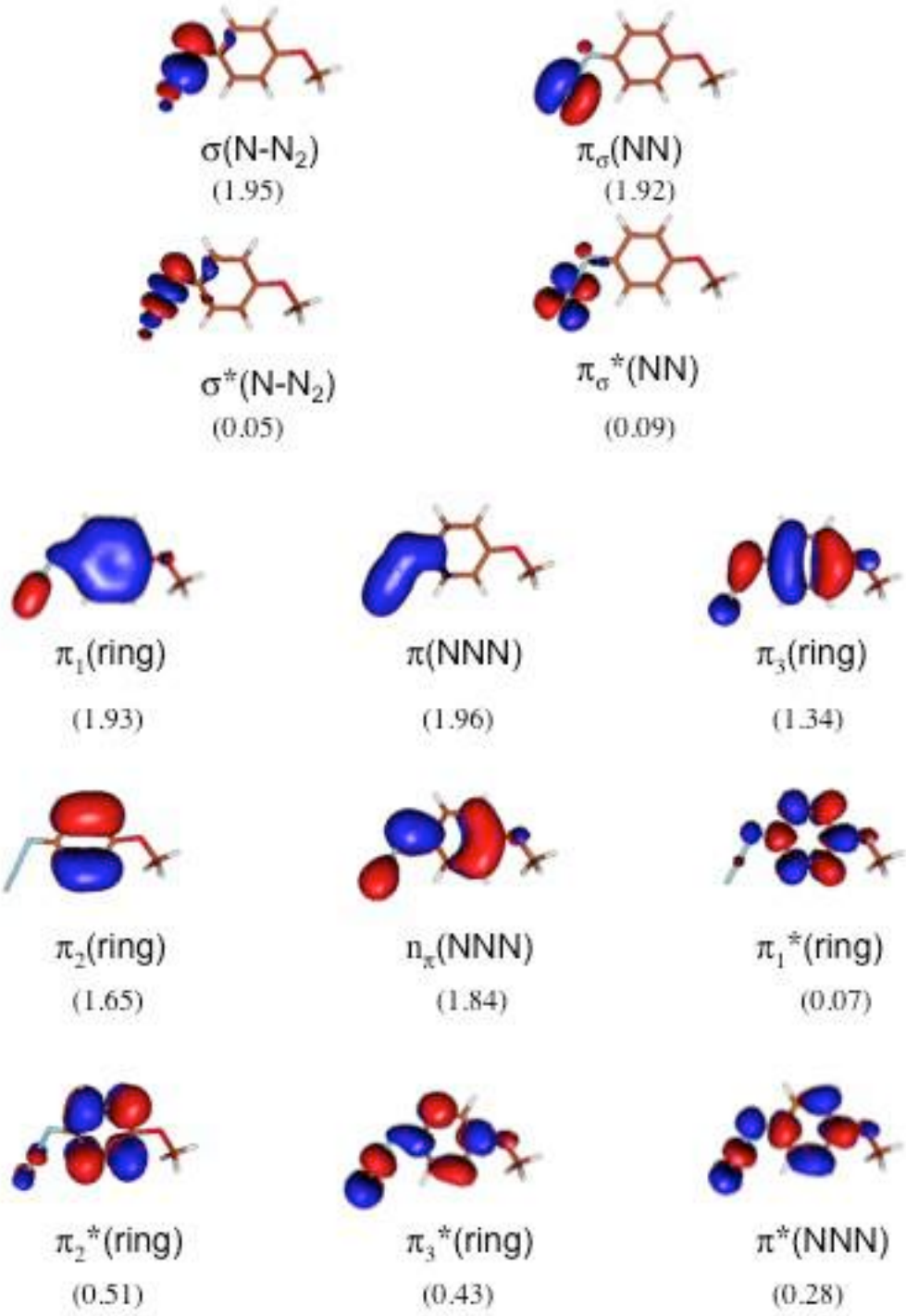

Figure S6. Active orbitals included in the CAS-SCF wavefunction of CI2. In parenthesis, mean occupation numbers of the state average orbitals.

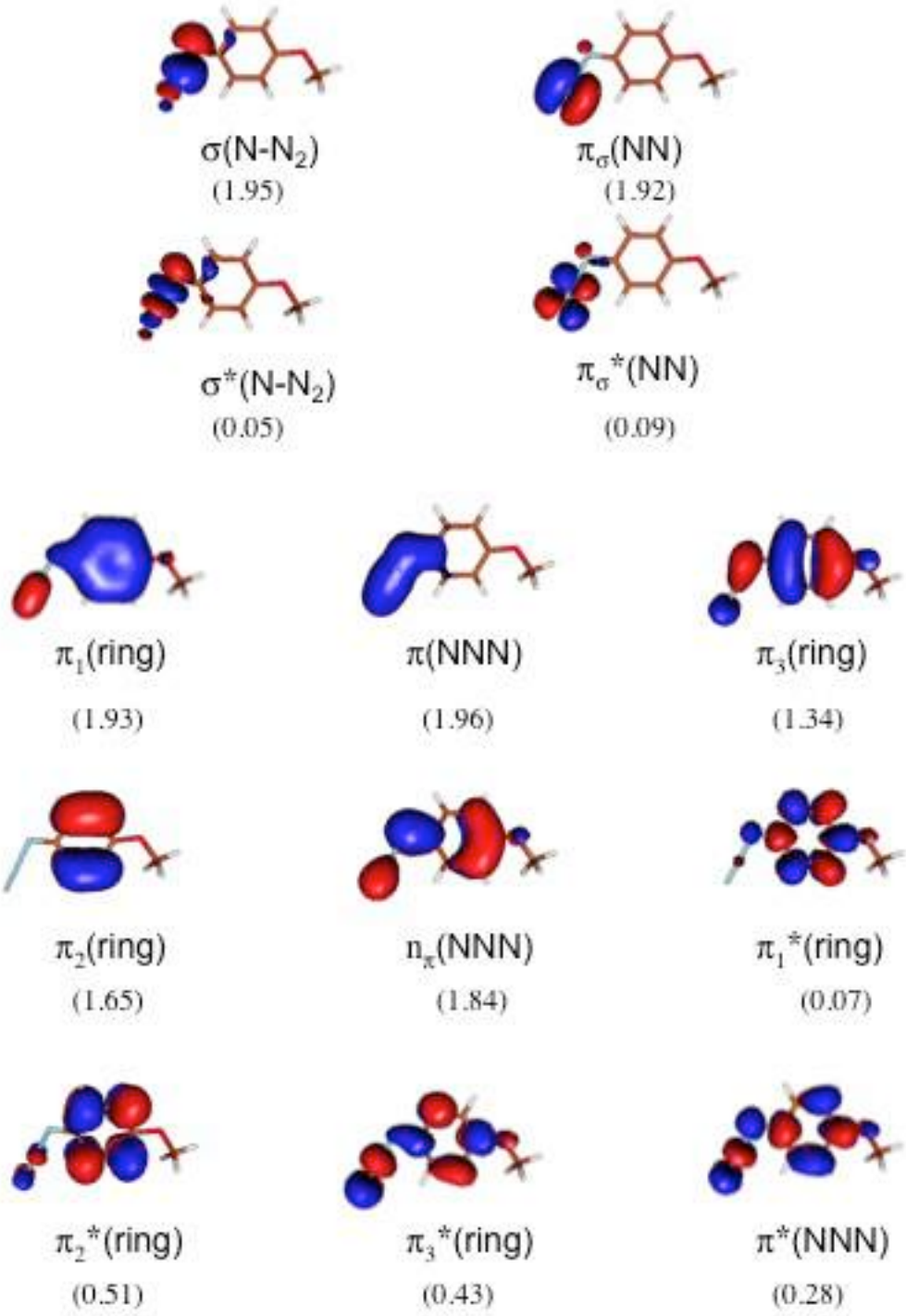

Figure S7. Active orbitals included in the CAS-SCF wavefunction of CI2. In parenthesis, mean occupation numbers of the state averaged orbitals.

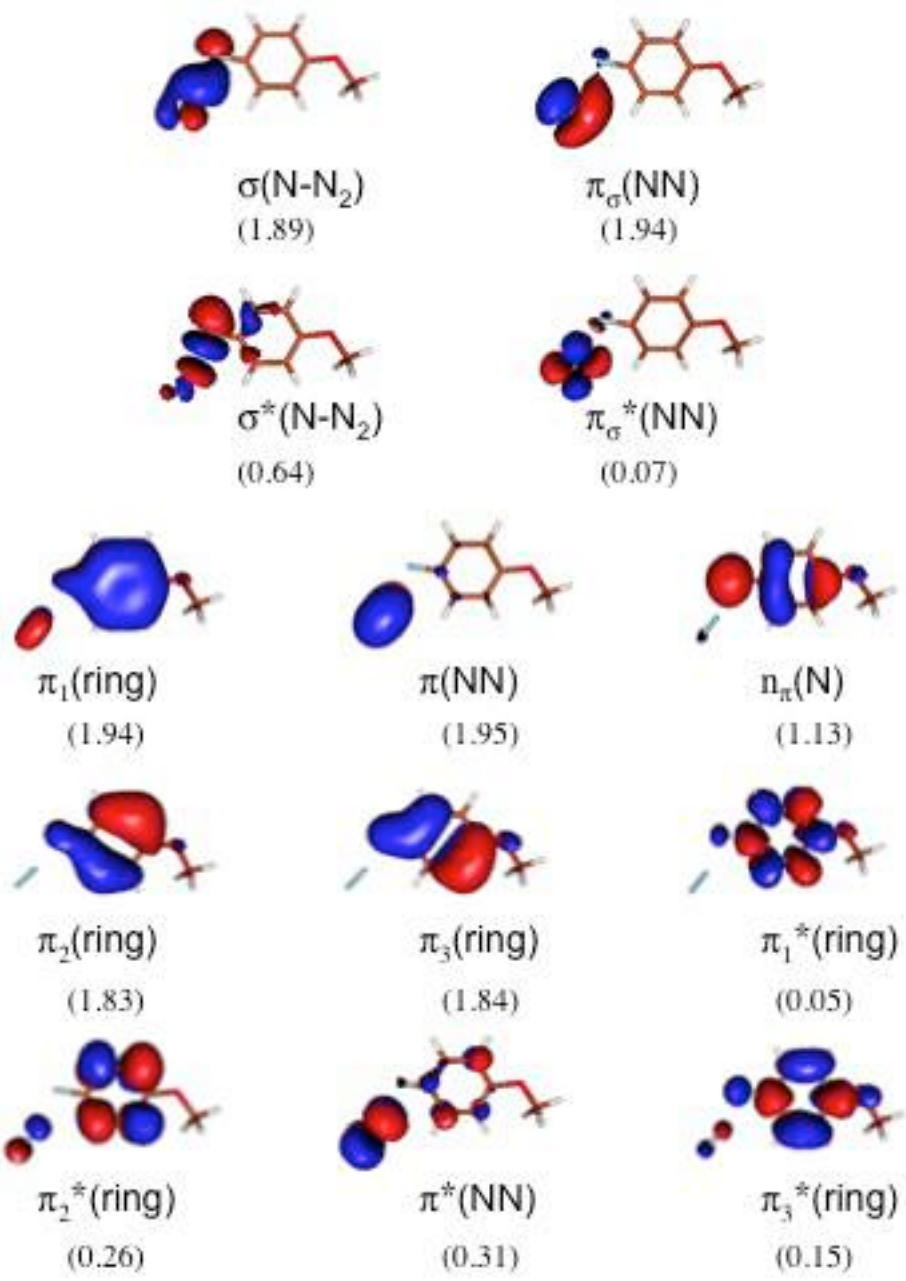

Figure S8. Active orbitals included in the CAS-SCF wavefunction of CI3. In parenthesis, mean occupation numbers of the state average orbitals.

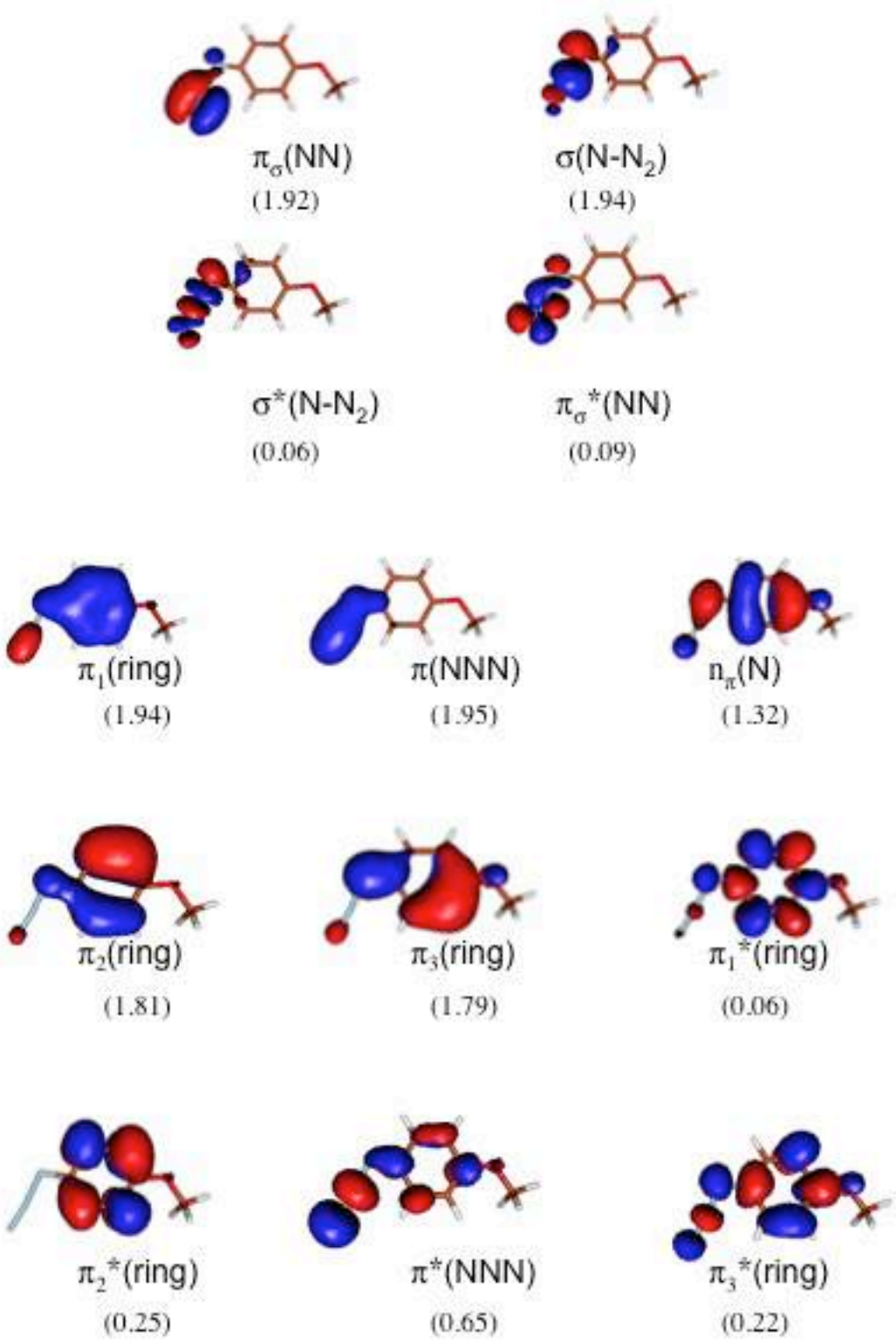

Figure S9. Active orbitals included in the CAS-SCF wavefunction of ISC1. In parenthesis, mean occupation numbers of the state average orbitals.

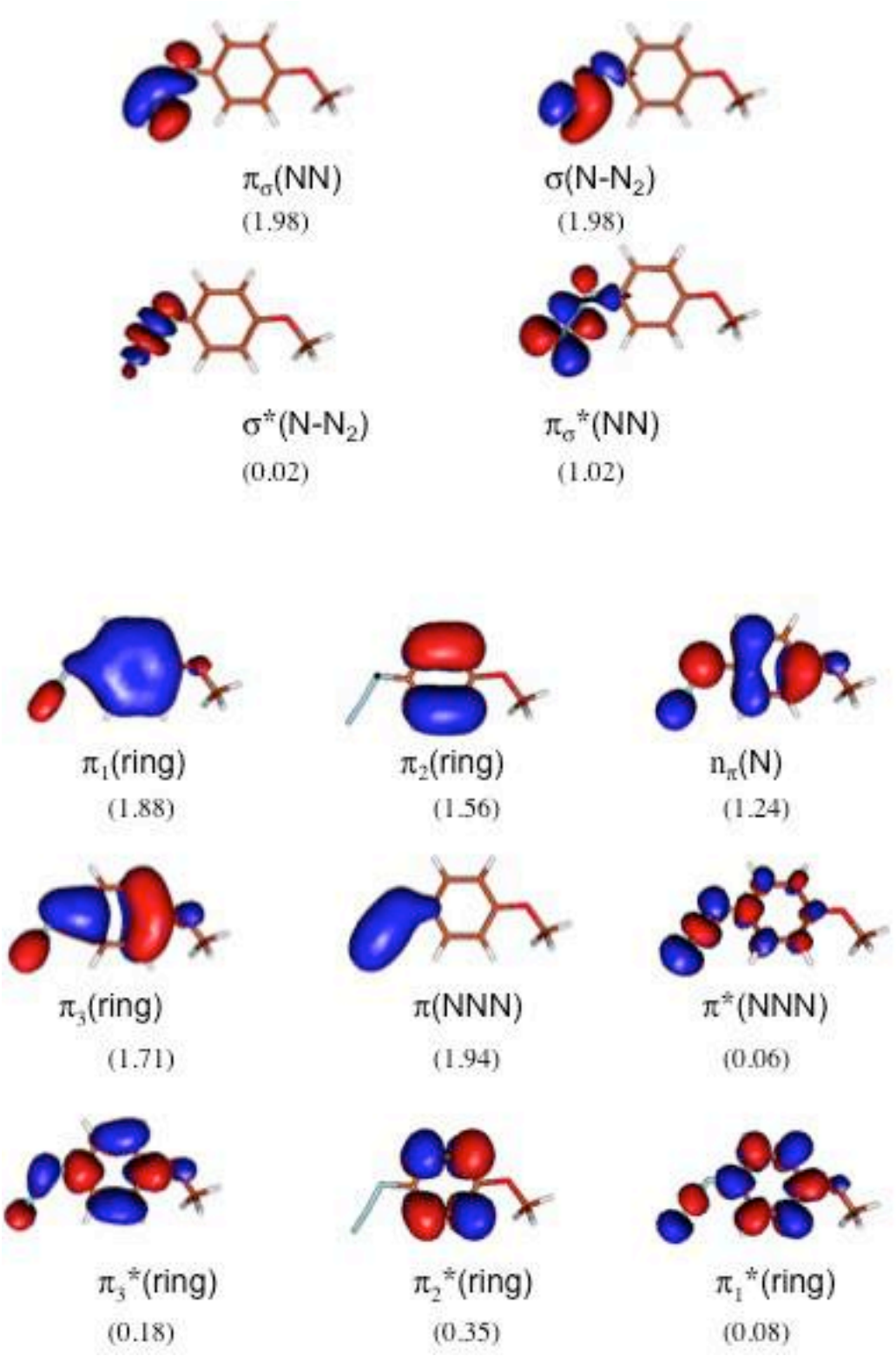

Figure S10. Active orbitals included in the CAS-SCF wavefunction of ISC2. In parenthesis, mean occupation numbers of the state average orbitals.

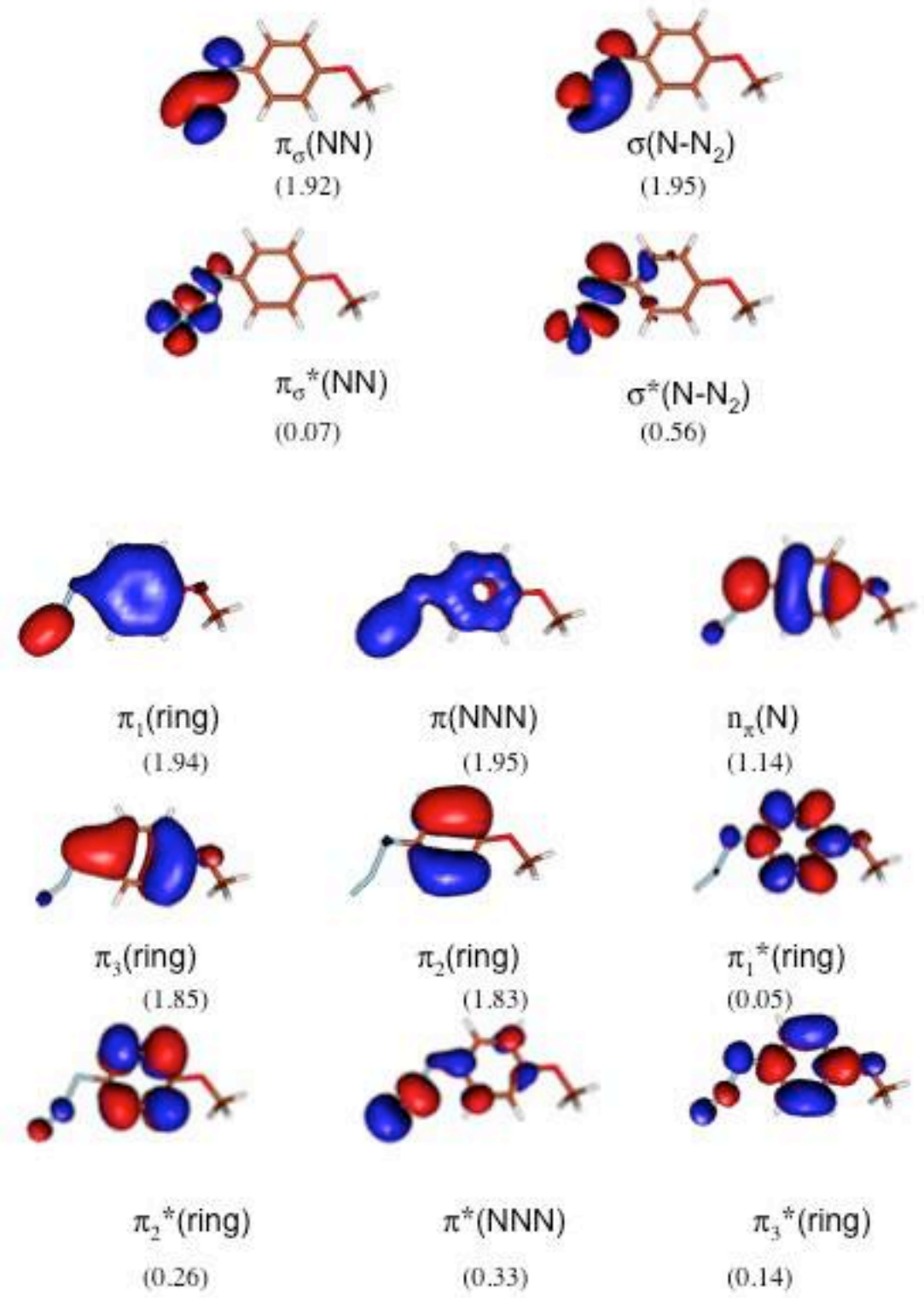

Figure S11. Active orbitals included in the CAS-SCF wavefunction of ISC3. In parenthesis, mean occupation numbers of the state average orbitals.

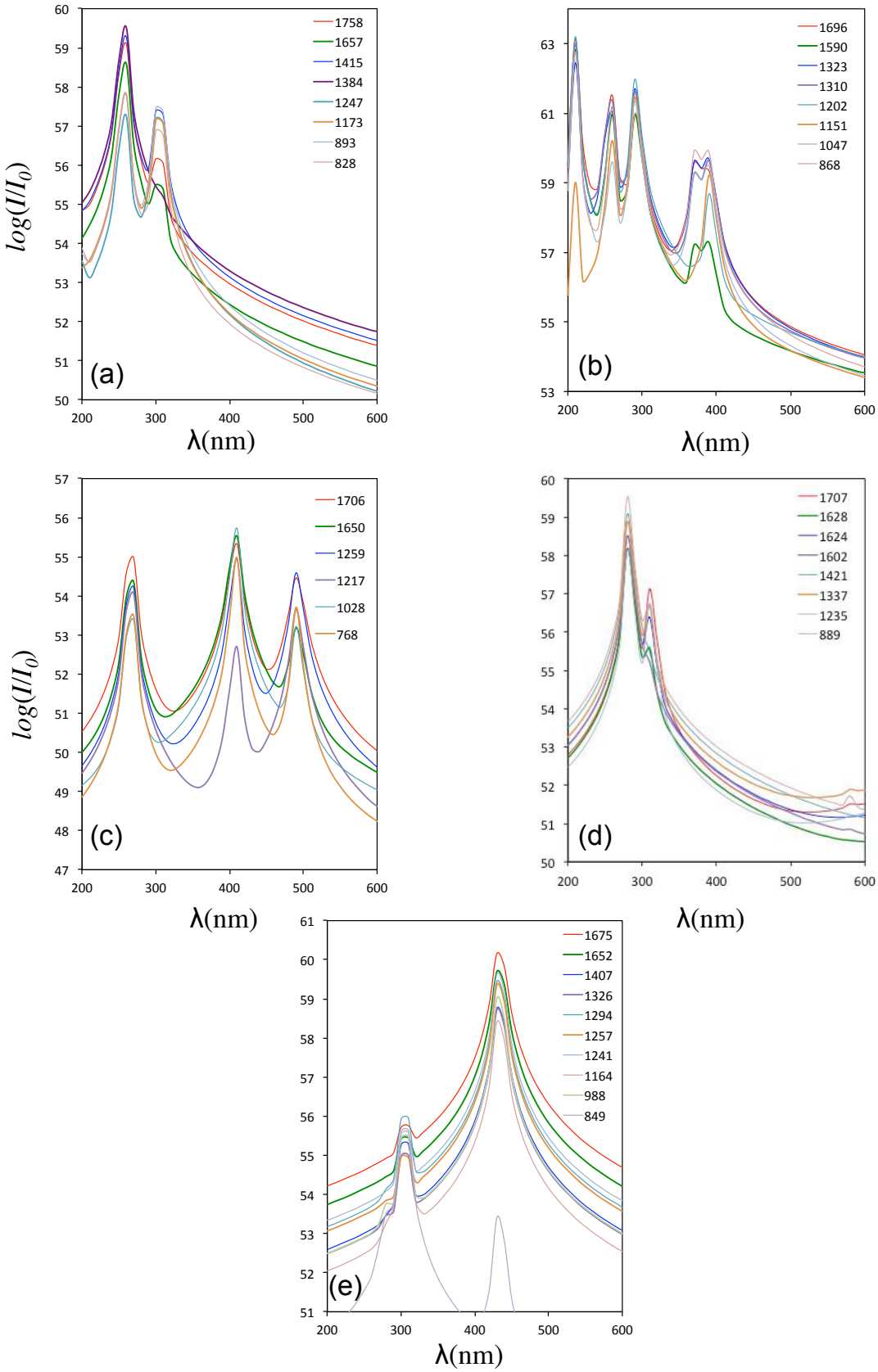

Figure S12. Multi-state Raman excitation profiles of (a) 4-methoxyphenyl azide; (b) triplet 4-methoxyphenyl nitrene; (c) 1^1A" 4-methoxyphenyl nitrene; (d) 1^1A' 4-methoxyphenyl nitrene; (e) 4,4'-dimethoxyazobenzene.

CAS-SCF Cartesian Coordinates in Ångstroms of the Critical Points on the Potential Energy Surfaces of *p*-Methoxyphenyl Azide:

M1 (S_0 Ground State Minimum, $1^1A'$)

N1	2.496888	0.0000000	0.8149510
C2	1.199553	0.0000000	0.2409398
C3	1.152921	0.0000000	-1.1568965
C4	0.013275	0.0000000	0.9544298
C5	-0.059220	0.0000000	-1.8147732
C6	-1.218257	0.0000000	0.2891129
C7	-1.258469	0.0000000	-1.0944310
O8	-2.389936	0.0000000	-1.8340958
C9	-3.630787	0.0000000	-1.1977521
H10	2.072194	0.0000000	-1.7076011
H11	0.014276	0.0000000	2.0272770
H12	-0.101289	0.0000000	-2.8856678
H13	-2.115369	0.0000000	0.8720036
H14	-4.375124	0.0000000	-1.9779406
H15	-3.763854	0.8841296	-0.5839424
H16	-3.763854	-0.8841296	-0.5839424
N17	2.532838	0.0000000	2.0449088
N18	2.658747	0.0000000	3.1652800

M2 (S_2 Excited State Minimum, $2^1A'$)

N1	2.485976	0.000000	0.814358
C2	1.217158	0.000000	0.244241
C3	1.192731	0.000000	-1.180046
C4	0.004198	0.000000	1.004959
C5	-0.062189	0.000000	-1.860509
C6	-1.245474	0.000000	0.321636
C7	-1.263230	0.000000	-1.105009
O8	-2.394033	0.000000	-1.829533
C9	-3.643499	0.000000	-1.203817
H10	2.118182	0.000000	-1.715010
H11	0.022567	0.000000	2.074550
H12	-0.119245	0.000000	-2.927883
H13	-2.151363	0.000000	0.886372
H14	-4.377579	0.000000	-1.993531
H15	-3.782428	0.884491	-0.593575
H16	-3.782428	-0.884491	-0.593575
N17	2.534456	0.000000	2.051281
N18	2.692161	0.000000	3.167318

ISC1 (Intersystem Crossing Minimum, $2^1A'/2^3A''$)

N1	0.109002	0.000000	0.052497
C2	0.012060	0.000000	1.348920
C3	1.284522	0.000000	2.047777
C4	-1.181582	0.000000	2.141092
C5	1.327598	0.000000	3.405038
C6	-1.098002	0.000000	3.529753
C7	0.133753	0.000000	4.176952
O8	0.313413	0.000000	5.507602
C9	-0.794456	0.000000	6.360949
H10	2.181675	0.000000	1.462781
H11	-2.135683	0.000000	1.665000
H12	2.265821	0.000000	3.922913
H13	-2.008950	0.000000	4.091081
H14	-0.404222	0.000000	7.365501
H15	-1.403541	-0.884744	6.217023
N17	-1.379205	0.000000	-0.517833
N18	-2.389649	0.000000	-1.087849

ISC2 (Intersystem Crossing Minimum, $2^1A'/1^3A''$)

N1	-0.046870	0.000000	-0.035160
C2	-0.067425	0.000000	1.370368
C3	1.230934	0.000000	1.981305
C4	-1.262484	0.000000	2.150627
C5	1.327482	0.000000	3.419856
C6	-1.161130	0.000000	3.582635
C7	0.143862	0.000000	4.195100
O8	0.323997	0.000000	5.525975
C9	-0.766944	0.000000	6.399173
H10	2.100348	0.000000	1.360804
H11	-2.229192	0.000000	1.693046
H12	2.274838	0.000000	3.914401
H13	-2.050271	0.000000	4.172201
H14	-0.356085	0.000000	7.396097
H15	-1.379320	-0.884620	6.271566
H16	-1.379320	+0.884620	6.271566
N17	-1.160736	0.000000	-0.590386
N18	-2.107511	0.000000	-1.156899

ISC3 (Intersystem Crossing Minimum, $1^1A'/1^3A''$)

N1	0.044289	0.000000	-0.004226
C2	-0.061996	0.000000	1.392499
C3	1.193011	0.000000	2.033153
C4	-1.201802	0.000000	2.181997
C5	1.281888	0.000000	3.409457
C6	-1.108348	0.000000	3.580825
C7	0.127923	0.000000	4.200130
O8	0.327710	0.000000	5.540643
C9	-0.771167	0.000000	6.396531
H10	2.086664	0.000000	1.439973
H11	-2.177959	0.000000	1.741203
H12	2.239238	0.000000	3.891562
H13	-2.015064	0.000000	4.149162
H14	-0.378956	0.000000	7.401291
H15	-1.385010	-0.883882	6.258838
N17	-1.557602	0.000000	-0.640866
N18	-2.319412	0.000000	-1.427699

CI1 (Conical Intersection, $2^1A''/2^1A'$)

N1	0.116642	-0.000004	0.053027
C2	0.015401	-0.000001	1.352259
C3	1.290426	-0.000000	2.049433
C4	-1.179689	0.000001	2.146523
C5	1.332594	0.000001	3.407092
C6	-1.100892	0.000001	3.533843
C7	0.133552	0.000001	4.178755
O8	0.316580	0.000002	5.511524
C9	-0.794522	-0.000001	6.366161
H10	2.188600	-0.000001	1.461989
H11	-2.135456	0.000001	1.667525
H12	2.270576	0.000003	3.929544
H13	-2.014355	0.000002	4.094879
H14	-0.401895	-0.000003	7.372171
H15	-1.402697	-0.887118	6.221067
H16	-1.402699	0.887116	6.221071
N17	-1.405592	-0.000001	-0.525665
N18	-2.397561	0.000001	-1.134977

CI2 (Conical Intersection, $2^3A''/1^3A''$)

N1	0.089811	-0.000000	0.041534
C2	0.005621	-0.000000	1.368872
C3	1.269017	-0.000000	2.047899
C4	-1.178269	-0.000000	2.158988
C5	1.326696	0.000000	3.415014
C6	-1.100829	-0.000000	3.542028
C7	0.141168	-0.000000	4.182612
O8	0.317123	0.000000	5.515214
C9	-0.795116	0.000000	6.369625
H10	2.163659	-0.000000	1.454914
H11	-2.135389	-0.000000	1.678503
H12	2.268481	0.000000	3.930343
H13	-2.011586	-0.000000	4.107093
H14	-0.401842	0.000000	7.375312
H15	-1.402982	-0.887189	6.225049
H16	-1.402982	0.887189	6.225049
N17	-1.328901	0.000000	-0.586309
N18	-2.389034	0.000000	-1.075055

CI3 (S_1/S_0 Conical Intersection, $1^1A''/1^1A'$)

N1	0.113242	0.000015	-0.013592
C2	-0.042387	0.000009	1.399568
C3	1.209017	0.000003	2.041134
C4	-1.182885	0.000010	2.157863
C5	1.281966	-0.000007	3.420365
C6	-1.105073	0.000006	3.567969
C7	0.119094	-0.000005	4.197188
O8	0.310075	-0.000006	5.543704
C9	-0.801670	-0.000002	6.387192
H10	2.113654	0.000006	1.459881
H11	-2.154019	0.000017	1.703528
H12	2.236427	-0.000015	3.912663
H13	-2.021542	0.000009	4.124500
H14	-0.419725	-0.000001	7.398303
H15	-1.413290	-0.886111	6.240766
H16	-1.413284	0.886111	6.240763
N17	-1.740350	0.000002	-0.759781
N18	-2.598489	-0.000040	-1.436976

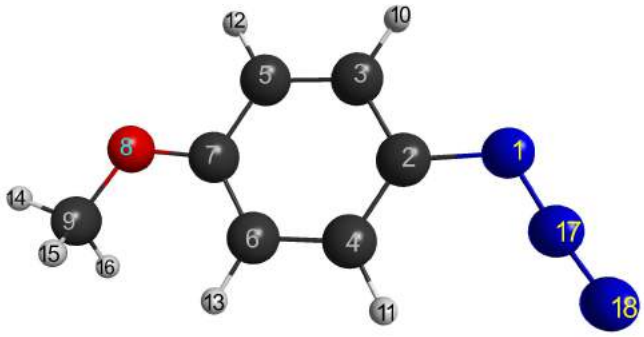

Table S1. CAS-SCF internal coordinates of 4-methoxyphenyl azide.[a]

Coor.	**M1**[b]	**M2**[b]	**CI1**[c]	**CI2**[c]	**CI3**[c]	**ISC1**[b]	**ISC2**[b]	**ISC3**[b]
$R_{1,2}$	1.419	1.391	1.303	1.334	1.422	1.300	1.406	1.401
$R_{3,2}$	1.399	1.424	1.453	1.429	1.406	1.452	1.435	1.409
$R_{4,2}$	1.384	1.432	1.435	1.423	1.370	1.433	1.427	1.387
$R_{5,3}$	1.379	1.428	1.358	1.371	1.381	1.358	1.442	1.379
$R_{6,4}$	1.400	1.424	1.390	1.387	1.412	1.391	1.436	1.402
$R_{7,5}$	1.399	1.419	1.426	1.412	1.398	1.422	1.415	1.399
$R_{8,7}$	1.352	1.343	1.345	1.344	1.360	1.343	1.343	1.355
$R_{9,8}$	1.395	1.397	1.402	1.402	1.396	1.398	1.397	1.393
$R_{10,3}$	1.072	1.069	1.073	1.073	1.075	1.071	1.068	1.073
$R_{11,4}$	1.073	1.070	1.069	1.071	1.072	1.066	1.070	1.071
$R_{12,5}$	1.072	1.069	1.074	1.073	1.074	1.072	1.069	1.072
$R_{13,6}$	1.070	1.068	1.072	1.072	1.072	1.070	1.067	1.070
$R_{14,9}$	1.078	1.078	1.080	1.080	1.081	1.078	1.078	1.079
$R_{15,9}$	1.085	1.084	1.085	1.085	1.087	1.084	1.083	1.085
$R_{16,9}$	1.085	1.084	1.085	1.085	1.087	1.084	1.083	1.085
$R_{17,1}$	1.230	1.238	1.629	1.558	1.998	1.594	1.245	1.724
$R_{18,17}$	1.127	1.127	1.164	1.171	1.093	1.160	1.103	1.095
$A_{3,2,1}$	115.778	115.178	114.214	114.638	110.859	114.500	114.361	112.692
$A_{4,2,1}$	125.108	123.710	128.064	127.256	129.904	127.847	123.979	129.060
$A_{5,3,2}$	120.401	119.451	120.449	120.693	120.171	120.594	119.039	120.738
$A_{6,4,2}$	120.596	119.236	120.357	120.470	120.461	120.126	119.092	120.887
$A_{7,5,4}$	60.508	59.156	59.410	59.593	60.865	59.622	59.331	60.717
$A_{8,7,5}$	115.835	115.180	114.944	115.372	115.671	115.196	115.516	115.941
$A_{9,8,7}$	119.676	120.751	119.747	119.968	119.115	119.916	120.966	119.437
$A_{10,3,2}$	119.014	119.048	118.144	118.293	120.135	118.117	119.285	119.382
$A_{11,4,2}$	120.971	121.110	119.773	119.700	121.309	119.910	121.529	120.989

[a]Intenuclear distance in Ångstrom, valence bond and dihedral angles in degrees.
[b]ANO-RCC (C,N,O[4s3p2d1f]/H[3s2p1d]).
[c]ANO-RCC (C,N,O[3s2p1d]/H[2s1p]).

Table S1. continuation

Coor.	**M1**[b]	**M2**[b]	**CI1**[c]	**CI2**[c]	**CI3**[c]	**ISC1**[b]	**ISC2**[b]	**ISC3**[b]
$A_{12,5,7}$	118.742	119.112	118.118	118.443	118.972	118.217	119.210	118.853
$A_{13,6,7}$	121.349	121.227	120.858	120.930	121.528	120.640	121.311	121.312
$A_{14,9,8}$	106.503	106.308	106.247	106.178	106.494	106.376	106.276	106.591
$A_{15,9,8}$	111.558	111.521	111.264	111.292	111.529	111.359	111.572	111.617
$A_{16,9,8}$	111.558	111.521	111.264	111.292	111.528	111.359	111.572	111.617
$A_{17,1,2}$	115.541	116.440	106.359	110.317	105.643	106.692	115.657	107.323
$A_{18,17,1}$	175.262	174.201	169.255	179.138	163.649	171.540	175.600	155.749
$D_{4,2,1,3}$	180.000	180.000	180.000	-180.000	180.000	180.000	180.000	180.000
$D_{5,3,2,4}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$D_{6,4,2,3}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$D_{7,5,4,2}$	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
$D_{8,7,5,6}$	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
$D_{9,8,7,6}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$D_{10,3,2,5}$	180.000	180.000	180.000	-180.000	180.000	180.000	180.000	180.000
$D_{11,4,2,6}$	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
$D_{12,5,7,3}$	180.000	180.000	180.000	-180.000	180.000	180.000	180.000	180.000
$D_{13,6,7,4}$	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
$D_{14,9,8,7}$	180.000	180.000	180.000	180.000	-180.000	180.000	180.000	180.000
$D_{15,9,8,14}$	-118.770	-118.660	-118.706	-118.661	-118.760	-118.766	-118.599	-118.795
$D_{16,9,8,14}$	118.770	118.660	118.706	118.661	118.760	118.766	118.599	118.795
$D_{17,1,2,3}$	180.000	180.000	180.000	180.000	179.999	180.000	180.000	180.000
$D_{18,17,1,2}$	180.000	180.000	180.000	179.995	-179.993	180.000	180.000	180.000

[a]Intenuclear distance in Ångstrom, valence bond and dihedral angles in degrees.
[b]ANO-RCC (C,N,O[4s3p2d1f]/H[3s2p1d]).
[c]ANO-RCC (C,N,O[3s2p1d]/H[2s1p]).

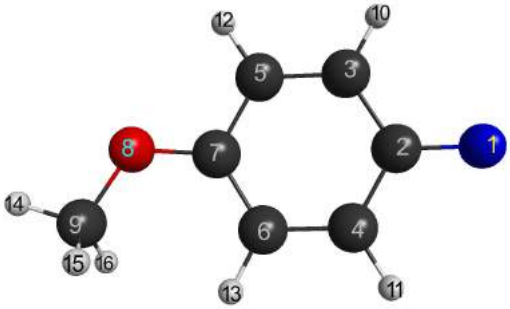

Table S2. CAS-SCF internal coordinates of 4-methoxyphenyl nitrene.[a]

Coor.	$1^3A''$[b]	$1^1A''$[b]	$1^1A'$[b]	$2^1A'$	$2^1A'/2^3A''$	$4^1A/3^1A$
$R_{1,2}$	1.345	1.290	1.346	1.388	1.337	1.330
$R_{3,2}$	1.428	1.469	1.426	1.406	1.421	1.433
$R_{4,2}$	1.419	1.468	1.417	1.393	1.436	1.437
$R_{5,3}$	1.371	1.354	1.370	1.382	1.410	1.419
$R_{6,4}$	1.386	1.368	1.381	1.396	1.410	1.417
$R_{7,5}$	1.409	1.430	1.407	1.396	1.400	1.393
$R_{8,7}$	1.347	1.344	1.330	1.355	1.353	1.354
$R_{9,8}$	1.397	1.398	1.403	1.394	1.394	1.394
$R_{10,3}$	1.072	1.071	1.072	1.072	1.070	1.070
$R_{11,4}$	1.072	1.071	1.072	1.072	1.070	1.070
$R_{12,5}$	1.072	1.072	1.072	1.072	1.071	1.071
$R_{13,6}$	1.070	1.070	1.069	1.070	1.070	1.069
$R_{14,9}$	1.078	1.078	1.077	1.078	1.078	1.078
$R_{15,9}$	1.084	1.084	1.083	1.085	1.085	1.085
$R_{16,9}$	1.084	1.084	1.083	1.085	1.085	1.085
$A_{3,2,1}$	120.818	121.399	121.708	119.600	120.796	121.044
$A_{4,2,1}$	120.835	121.483	120.930	120.788	120.806	120.869
$A_{5,3,2}$	120.207	120.221	121.242	119.581	119.876	119.811
$A_{6,4,2}$	120.709	120.726	121.898	120.002	120.082	120.201
$A_{7,5,4}$	59.627	58.789	59.141	60.672	60.131	60.250
$A_{8,7,5}$	115.431	115.096	115.226	115.898	115.533	115.733
$A_{9,8,7}$	120.016	120.125	120.943	119.562	119.747	119.862
$A_{10,3,2}$	119.023	118.271	117.599	120.287	119.773	119.736
$A_{11,4,2}$	119.023	118.217	117.398	120.358	119.646	119.603
$A_{12,5,7}$	118.274	117.671	118.199	118.789	118.876	118.947
$A_{13,6,7}$	120.925	120.436	120.905	121.251	121.165	121.174
$A_{14,9,8}$	106.394	106.390	106.069	106.543	106.486	106.466

continue

Table S2. Continuation

Coor.	$1^3A''$[b]	$1^1A''$[b]	$1^1A'$[b]	$2^1A'$	$2^1A'/2^3A''$	$4^1A/3^1A$
$A_{15,9,8}$	111.496	111.449	111.229	111.607	111.590	111.627
$A_{16,9,8}$	111.496	111.449	111.229	111.607	111.590	111.627
$D_{4,2,1,3}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{5,3,2,4}$	0.000	0.000	0.000	0.000	0.000	0.000
$D_{6,4,2,3}$	0.000	0.000	0.000	0.000	0.000	0.000
$D_{7,5,4,2}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{8,7,5,6}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{9,8,7,6}$	0.000	0.000	0.000	0.000	0.000	180.000
$D_{10,3,2,5}$	180.000	180.000	180.000	180.000	180.000	0.000
$D_{11,4,2,6}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{12,5,7,3}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{13,6,7,4}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{14,9,8,7}$	180.000	180.000	180.000	180.000	180.000	180.000
$D_{15,9,8,14}$	-118.721	-118.727	-118.683	-118.769	-118.741	-118.707
$D_{16,9,8,14}$	118.721	118.727	118.683	118.769	118.741	118.707

[a]Intenuclear distance in Ångstrom, valence bond and dihedral angles in degrees.
[b]ANO-RCC (C,N,O[4s3p2d1f]/H[3s2p1d]).

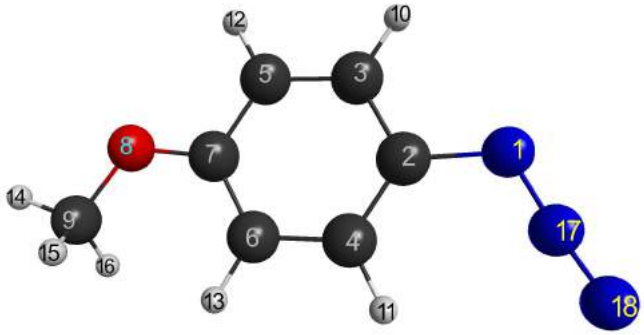

Table S3. Definition of redundant internal coordinates of 4,4′-dimethoxyazobenzene.

N°	*Coor.*	*Connectivity*	*type*
1	r_1	9-14	$\nu(C\text{-}H)_{methyl}$
2	r_2	9-15	$\nu(C\text{-}H)_{methyl}$
3	r_3	9-16	$\nu(C\text{-}H)_{methyl}$
4	r_4	3-10	$\nu(C\text{-}H)_{ring}$
5	r_5	4-11	$\nu(C\text{-}H)_{ring}$
6	r_6	5-12	$\nu(C\text{-}H)_{ring}$
7	r_7	6-13	$\nu(C\text{-}H)_{ring}$
8	r_8	7-8	$\nu(C\text{-}O)$
9	r_9	8-9	$\nu(O\text{-}CH_3)$
10	r_{10}	2-1	$\nu(N\text{-}C_{ring})$
11	r_{11}	1-17	$\nu(N\text{-}N)$
12	r_{12}	17-18	$\nu(N\text{-}N)$
13	R_1	2-3	$\nu(C\text{-}C)$
14	R_2	3-5	$\nu(C\text{-}C)$
15	R_3	5-7	$\nu(C\text{-}C)$
16	R_4	7-6	$\nu(C\text{-}C)$
17	R_5	4-2	$\nu(C\text{-}C)$
18	R_6	6-4	$\nu(C\text{-}C)$
19	β_1	[10-3-2]-[10-3-5]	$\delta(C\text{-}H)_{ring}$
20	β_2	[12-5-7]-[12-5-3]	$\delta(C\text{-}H)_{ring}$
21	β_3	[13-6-7]-[13-6-4]	$\delta(C\text{-}H)_{ring}$
22	β_4	[11-4-2]-[11-4-6]	$\delta(C\text{-}H)_{ring}$
23	β_5	[8-7-5]-[8-7-6]	$\delta(O\text{-}C\text{-}C)$
24	β_6	[1-2-3]-[1-2-4]	$\delta(N\text{-}C\text{-}C)$

Continue

Table S3. Continuation

25	β_7	9-8-7	δ(C-O-C)
26	β_8	2-1-17	δ(C-N-N)
27	β_9	1-17-18	δ(N-N-N)
28	α_1	15-9-16	$\delta(H\text{-}C\text{-}H)_{methyl}$
29	α_2	14-9-16	$\delta(H\text{-}C\text{-}H)_{methyl}$
30	α_3	14-9-15	$\delta(H\text{-}C\text{-}H)_{methyl}$
31	α'_1	14-9-8	$\delta(O\text{-}C\text{-}H)_{methyl}$
32	α'_2	15-9-8	$\delta(O\text{-}C\text{-}H)_{methyl}$
33	α'_3	16-9-8	$\delta(O\text{-}C\text{-}H)_{methyl}$
34	α_4	5-7-6	$\delta(C\text{-}C\text{-}C)_{ring}$
35	α_5	7-6-4	$\delta(C\text{-}C\text{-}C)_{ring}$
36	α_6	6-4-2	$\delta(C\text{-}C\text{-}C)_{ring}$
37	α_7	4-2-3	$\delta(C\text{-}C\text{-}C)_{ring}$
38	α_8	2-3-5	$\delta(C\text{-}C\text{-}C)_{ring}$
39	α_9	3-5-7	$\delta(C\text{-}C\text{-}C)_{ring}$
40	γ_1	13-6-7-4	γ(C-H)
41	γ_2	11-4-6-2	γ(C-H)
42	γ_3	10-3-2-5	γ(C-H)
43	γ_4	12-5-3-7	γ(C-H)
44	γ_5	1-2-4-3	γ(C-N)
45	γ_6	8-7-5-6	γ(O-C)
46	Γ_1	(5,8)-7-6-(4-13)	Γ(CC)
47	Γ_2	(7,13)-6-4-(11-2)	Γ(CC)
48	Γ_3	(6,11)-4-2-(3-1)	Γ(CC)
49	Γ_4	(4,1)-2-3-(5-10)	Γ(CC)
50	Γ_5	(2,10)-3-5-(7-12)	Γ(CC)
51	Γ_6	(3,12)-5-7-(6-8)	Γ(CC)
52	Γ_7	(5,6)-7-8-(9)	Γ(OC)
53	Γ_8	(14,15,16)-9-8-(7)	Γ(CO)
54	Γ_9	(3,4)-1-2-(17)	Γ(CN)
55	Γ_{10}	(2)-1-17-(18)	Γ(NN)

Table S3b. Non-redundant internal coordinates of 4-methoxyphenyl nitrene.

Coordinate	*type*	*Definition*	Wilson
$q_1 \ldots q_3$	$\nu(\text{C-H})_{\text{methyl}}$	$r_1 \ldots r_3$	
$q_4 \ldots q_7$	$\nu(\text{C-H})_{\text{ring}}$	$r_4 \ldots r_7$	
q_8	$\nu(\text{C-O})$	r_8	
q_9	$\nu(\text{O-CH}_3)$	r_9	
q_{10}	$\nu(\text{N-C}_{\text{ring}})$	r_{10}	
q_{11}	$\nu(\text{N-N})$	r_{11}	
q_{12}	$\nu(\text{N-N})$	r_{12}	
q_{13}	$\nu(\text{C-C})$	$6^{-1/2}(R_1+R_2+R_3+R_4+R_5+R_6)$	1
q_{14}	$\nu(\text{C-C})$	$12^{-1/2}(-R_1+2R_2-R_3-R_4+2R_5-R_6)$	8a
q_{15}	$\nu(\text{C-C})$	$2^{-1}(-R_1+R_3-R_4+R_6)$	8b
q_{16}	$\nu(\text{C-C})$	$6^{-1/2}(R_1-R_2+R_3-R_4+R_5-R_6)$	14
q_{17}	$\nu(\text{C-C})$	$2^{-1}(R_1-R_3-R_4+R_6)$	19a
q_{18}	$\nu(\text{C-C})$	$2^{-1/2}(R_2-R_6)$	19b
q_{19}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1+\beta_2+\beta_3+\beta_4)$	9a
q_{20}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1+\beta_2-\beta_3-\beta_4)$	15
q_{21}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1-\beta_2+\beta_3-\beta_4)$	3
q_{22}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1-\beta_2-\beta_3+\beta_4)$	18a
q_{23}	$\delta(\text{O-C-C})$	β_5	
q_{24}	$\delta(\text{N-C-C})$	β_6	
q_{25}	$\delta(\text{C-O-C})$	β_7	
q_{26}	$\delta(\text{C-N-N})$	β_8	
q_{27}	$\delta(\text{N-N-N})$	β_9	
q_{28}	$\delta(\text{C-H})_{\text{methyl}}$	$6^{-1/2}(\alpha_1+\alpha_2+\alpha_3+\alpha'_1-\alpha'_2-\alpha'_3)$	
q_{29}	$\delta(\text{C-H})_{\text{methyl}}$	$6^{-1/2}(2\alpha_1-\alpha_2-\alpha_3)$	
q_{30}	$\delta(\text{C-H})_{\text{methyl}}$	$2^{-1/2}(\alpha_2-\alpha_3)$	
q_{31}	$\delta(\text{C-H})_{\text{methyl}}$	$6^{-1/2}(2\alpha'_1-\alpha'_2-\alpha'_3)$	
q_{32}	$\delta(\text{C-H})_{\text{methyl}}$	$2^{-1/2}(\alpha'_2-\alpha'_3)$	
q_{33}	$\delta(\text{C-C-C})$	$6^{-1/2}(\alpha_4-\alpha_5+\alpha_6-\alpha_7+\alpha_8-\alpha_9)$	12
q_{34}	$\delta(\text{C-C-C})$	$12^{-1/2}(2\alpha_4-\alpha_5-\alpha_6+2\alpha_7-\alpha_8-\alpha_9)$	6a
q_{35}	$\delta(\text{C-C-C})$	$2^{-1}(\alpha_5-\alpha_6+\alpha_8-\alpha_9)$	6b
$q_{36 \ldots 39}$	$\gamma(\text{C-H})$	$\gamma_1 \ldots \gamma_4$	
q_{40}	$\gamma(\text{C-N})$	γ_5	
q_{41}	$\gamma(\text{O-C})$	γ_6	
q_{42}	$\Gamma(\text{CC})$	$6^{-1/2}(\Gamma_1-\Gamma_2+\Gamma_3-\Gamma_4+\Gamma_5-\Gamma_6)$	
q_{43}	$\Gamma(\text{CC})$	$2^{-1}(\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_6)$	

Continue

Table S3b. Continuation

q_{44}	Γ(CC)	$12^{-1/2}(-\Gamma_1+2\Gamma_2-\Gamma_3-\Gamma_4+2\Gamma_5-\Gamma_6)$
q_{45}	Γ(OC)	Γ_7
q_{46}	Γ(CO)	Γ_8
q_{47}	Γ(CN)	Γ_9
q_{48}	Γ(NN)	Γ_{10}

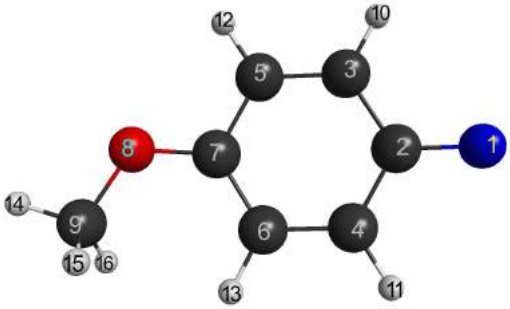

Table S4. Definition of redundant internal coordinates of 4-methoxyphenyl nitrene.

Nº	*Coor.*	*Connectivity*	*type*
1	r_1	9-14	$\nu(C\text{-}H)_{methyl}$
2	r_2	9-15	$\nu(C\text{-}H)_{methyl}$
3	r_3	9-16	$\nu(C\text{-}H)_{methyl}$
4	r_4	3-10	$\nu(C\text{-}H)_{ring}$
5	r_5	4-11	$\nu(C\text{-}H)_{ring}$
6	r_6	5-12	$\nu(C\text{-}H)_{ring}$
7	r_7	6-13	$\nu(C\text{-}H)_{ring}$
8	r_8	7-8	$\nu(C\text{-}O)$
9	r_9	8-9	$\nu(O\text{-}CH_3)$
10	r_{10}	2-1	$\nu(N\text{-}C_{ring})$
11	R_1	2-3	$\nu(C\text{-}C)$
12	R_2	3-5	$\nu(C\text{-}C)$
13	R_3	5-7	$\nu(C\text{-}C)$
14	R_4	7-6	$\nu(C\text{-}C)$
15	R_5	4-2	$\nu(C\text{-}C)$
16	R_6	6-4	$\nu(C\text{-}C)$
17	β_1	[10-3-2]-[10-3-5]	$\delta(C\text{-}H)_{ring}$
18	β_2	[12-5-7]-[12-5-3]	$\delta(C\text{-}H)_{ring}$
19	β_3	[13-6-7]-[13-6-4]	$\delta(C\text{-}H)_{ring}$
20	β_4	[11-4-2]-[11-4-6]	$\delta(C\text{-}H)_{ring}$
21	β_5	[8-7-5]-[8-7-6]	$\delta(O\text{-}C\text{-}C)$
22	β_6	[1-2-3]-[1-2-4]	$\delta(N\text{-}C\text{-}C)$
23	β_7	[9-8-7]	$\delta(C\text{-}O\text{-}C)$

Continue

Table S4. Continuation

24	α_1	[15-9-16]	$\delta(\text{H-C-H})_{\text{methyl}}$
25	α_2	[14-9-16]	$\delta(\text{H-C-H})_{\text{methyl}}$
26	α_3	[14-9-15]	$\delta(\text{H-C-H})_{\text{methyl}}$
27	α'_1	[14-9-8]	$\delta(\text{O-C-H})_{\text{methyl}}$
28	α'_2	[15-9-8]	$\delta(\text{O-C-H})_{\text{methyl}}$
29	α'_3	[16-9-8]	$\delta(\text{O-C-H})_{\text{methyl}}$
30	α_4	[5-7-6]	$\delta(\text{C-C-C})_{\text{ring}}$
31	α_5	[7-6-4]	$\delta(\text{C-C-C})_{\text{ring}}$
32	α_6	[6-4-2]	$\delta(\text{C-C-C})_{\text{ring}}$
33	α_7	[4-2-3]	$\delta(\text{C-C-C})_{\text{ring}}$
34	α_8	[2-3-5]	$\delta(\text{C-C-C})_{\text{ring}}$
35	α_9	[3-5-7]	$\delta(\text{C-C-C})_{\text{ring}}$
36	γ_1	{13-6-7-4}	γ(C-H)
37	γ_2	{11-4-6-2}	γ(C-H)
38	γ_3	{10-3-2-5}	γ(C-H)
39	γ_4	{12-5-3-7}	γ(C-H)
40	γ_5	{1-2-4-3}	γ(C-N)
41	γ_6	{8-7-5-6}	γ(O-C)
42	Γ_1	(5,8)-7-6-(4-13)	Γ(CC)
43	Γ_2	(7,13)-6-4-(11-2)	Γ(CC)
44	Γ_3	(6,11)-4-2-(3-1)	Γ(CC)
45	Γ_4	(4,1)-2-3-(5-10)	Γ(CC)
46	Γ_5	(2,10)-3-5-(7-12)	Γ(CC)
47	Γ_6	(3,12)-5-7-(6-8)	Γ(CC)
48	Γ_7	(5,6)-7-8-(9)	$\Gamma(\text{C-OCH}_3)$
49	Γ_8	(14,15,16)-9-8-(7)	$\Gamma(\text{O-CH}_3)$

Table S4b. Non redundant internal coordinates of 4-methoxyphenyl nitrene.

Coordinate	*Type*	*Definition*	Wilson
$q_1 \ldots q_3$	$\nu(\text{C-H})_{\text{methyl}}$	$r_1 \ldots r_3$	
$q_4 \ldots q_7$	$\nu(\text{C-H})_{\text{ring}}$	$r_4 \ldots r_7$	
q_8	$\nu(\text{C-O})$	r_8	
q_9	$\nu(\text{O-CH}_3)$	r_9	
q_{10}	$\nu(\text{N-C}_{\text{ring}})$	r_{10}	
q_{11}	$\nu(\text{C-C})$	$6^{-1/2}(R_1+R_2+R_3+R_4+R_5+R_6)$	1
q_{12}	$\nu(\text{C-C})$	$12^{-1/2}(-R_1+2R_2-R_3-R_4+2R_5-R_6)$	8a
q_{13}	$\nu(\text{C-C})$	$2^{-1}(-R_1+R_3-R_4+R_6)$	8b
q_{14}	$\nu(\text{C-C})$	$6^{-1/2}(R_1-R_2+R_3-R_4+R_5-R_6)$	14
q_{15}	$\nu(\text{C-C})$	$2^{-1}(R_1-R_3-R_4+R_6)$	19a
q_{16}	$\nu(\text{C-C})$	$2^{-1/2}(R_2-R_5)$	19b
q_{17}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1+\beta_2+\beta_3+\beta_4)$	9a
q_{18}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1+\beta_2-\beta_3-\beta_4)$	15
q_{19}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1-\beta_2+\beta_3-\beta_4)$	3
q_{20}	$\delta(\text{C-H})_{\text{ring}}$	$2^{-1}(\beta_1-\beta_2-\beta_3+\beta_4)$	18a
q_{21}	$\delta(\text{O-C-C})$	β_5	
q_{22}	$\delta(\text{N-C-C})$	β_6	
q_{23}	$\delta(\text{C-O-C})$	β_7	
q_{24}	$\delta(\text{C-H})_{\text{methyl}}$	$6^{-1/2}(\alpha_1+\alpha_2+\alpha_3+\alpha'_1-\alpha'_2-\alpha'_3)$	
q_{25}	$\delta(\text{C-H})_{\text{methyl}}$	$6^{-1/2}(2\alpha_1-\alpha_2-\alpha_3)$	
q_{26}	$\delta(\text{C-H})_{\text{methyl}}$	$2^{-1/2}(\alpha_2-\alpha_3)$	
q_{27}	$\delta(\text{C-H})_{\text{methyl}}$	$6^{-1/2}(2\alpha'_1-\alpha'_2-\alpha'_3)$	
q_{28}	$\delta(\text{C-H})_{\text{methyl}}$	$2^{-1/2}(\alpha'_2-\alpha'_3)$	
q_{29}	$\delta(\text{C-C-C})$	$6^{-1/2}(\alpha_4-\alpha_5+\alpha_6-\alpha_7+\alpha_8-\alpha_9)$	12
q_{30}	$\delta(\text{C-C-C})$	$12^{-1/2}(2\alpha_4-\alpha_5-\alpha_6+2\alpha_7-\alpha_8-\alpha_9)$	6a
q_{31}	$\delta(\text{C-C-C})$	$2^{-1}(\alpha_5-\alpha_6+\alpha_8-\alpha_9)$	6b
$q_{32 \ldots 35}$	$\gamma(\text{C-H})$	$\gamma_1 \ldots \gamma_4$	
q_{36}	$\gamma(\text{C-N})$	γ_5	
q_{37}	$\gamma(\text{O-C})$	γ_6	
q_{38}	$\Gamma(\text{CC})$	$6^{-1/2}(\Gamma_1-\Gamma_2+\Gamma_3-\Gamma_4+\Gamma_5-\Gamma_6)$	
q_{39}	$\Gamma(\text{CC})$	$2^{-1}(\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_6)$	
q_{40}	$\Gamma(\text{CC})$	$12^{-1/2}(-\Gamma_1+2\Gamma_2-\Gamma_3-\Gamma_4+2\Gamma_5-\Gamma_6)$	
q_{41}	$\Gamma(\text{CO})$	Γ_7	
q_{42}	$\Gamma(\text{OCH}_3)$	Γ_8	

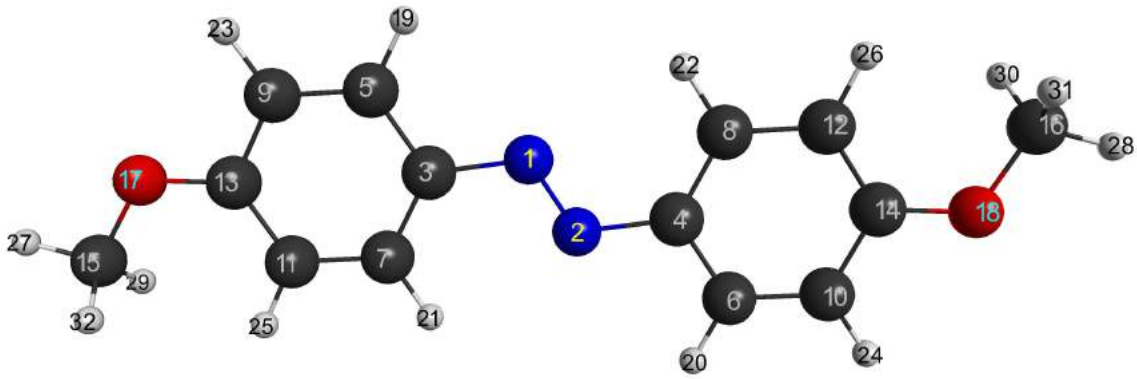

Table S5. Definition of redundant internal coordinates of 4,4′-dimethoxyazobenzene.

N°	*Coor.*	*Connectivity*	*type*
1	r_1	15-27	$\nu(C\text{-}H)_{methyl}$
2	r_2	16 -28	$\nu(C\text{-}H)_{methyl}$
3	r_3	15-29	$\nu(C\text{-}H)_{methyl}$
4	r_4	16-30	$\nu(C\text{-}H)_{ring}$
5	r_5	15-32	$\nu(C\text{-}H)_{ring}$
6	r_6	16-31	$\nu(C\text{-}H)_{ring}$
7	r_7	5-19	$\nu(C\text{-}H)_{ring}$
8	r_8	6-20	$\nu(C\text{-}H)_{ring}$
9	r_9	7-21	$\nu(C\text{-}H)_{ring}$
10	r_{10}	8-22	$\nu(C\text{-}H)_{ring}$
11	r_{11}	9-23	$\nu(C\text{-}H)_{ring}$
12	r_{12}	10-24	$\nu(C\text{-}H)_{ring}$
13	r_{13}	11-25	$\nu(C\text{-}H)_{ring}$
14	r_{14}	12-26	$\nu(C\text{-}H)_{ring}$
15	r_{15}	13-17	$\nu(C\text{-}O)$
16	r_{16}	14-18	$\nu(C\text{-}O)$
17	r_{17}	15-17	$\nu(O\text{-}CH_3)$
18	r_{18}	16-18	$\nu(O\text{-}CH_3)$
19	r_{19}	1-2	$\nu(N\text{-}N)$
20	r_{20}	1-3	$\nu(N\text{-}C_{ring})$
21	r_{21}	2-4	$\nu(N\text{-}C_{ring})$
22	R_1	3-5	$\nu(C\text{-}C)$
23	R_2	5-9	$\nu(C\text{-}C)$
24	R_3	9-13	$\nu(C\text{-}C)$
25	R_4	13-11	$\nu(C\text{-}C)$
26	R_5	11-7	$\nu(C\text{-}C)$
27	R_6	7-3	$\nu(C\text{-}C)$

Continue

Table S5. Continuation

28	R_7	4-6	ν(C-C)
29	R_8	6-10	ν(C-C)
30	R_9	10-14	ν(C-C)
31	R_{10}	14-12	ν(C-C)
32	R_{11}	12-8	ν(C-C)
33	R_{12}	8-4	ν(C-C)
34	β_1	[19-5-3]-[19-5-9]	$\delta(C\text{-}H)_{ring}$
35	β_2	[23-9-13]-[23-9-5]	$\delta(C\text{-}H)_{ring}$
36	β_3	[25-11-13]-[25-11-7]	$\delta(C\text{-}H)_{ring}$
37	β_4	[21-7-3]-[21-7-11]	$\delta(C\text{-}H)_{ring}$
38	β_5	[20-6-4]-[20-6-10]	$\delta(C\text{-}H)_{ring}$
39	β_6	[24-10-14]-[24-10-6]	$\delta(C\text{-}H)_{ring}$
40	β_7	[26-12-14]-[26-12-8]	$\delta(C\text{-}H)_{ring}$
41	β_8	[22-8-4]-[22-8-12]	$\delta(C\text{-}H)_{ring}$
42	β_9	[17-13-9]-[17-13-11]	δ(O-C-C)
43	β_{10}	[18-14-10]-[18-14-12]	δ(O-C-C)
44	β_{11}	[1-3-5]-[1-3-7]	δ(N-C-C)
45	β_{12}	[2-4-6]-[2-4-8]	δ(N-C-C)
46	β_{13}	[3-1-2]	δ(N-N-C)
47	β_{14}	[1-2-4]	δ(N-N-C)
48	β_{15}	[15-17-13]	δ(C-O-C)
49	β_{16}	[16-18-14]	δ(C-O-C)
50	α_1	[27-15-29]	$\delta(H\text{-}C\text{-}H)_{methyl}$
51	α_2	[29-15-32]	$\delta(H\text{-}C\text{-}H)_{methyl}$
52	α_3	[32-15-27]	$\delta(H\text{-}C\text{-}H)_{methyl}$
53	α'_1	[27-15-17]	$\delta(O\text{-}C\text{-}H)_{methyl}$
54	α'_2	[29-15-17]	$\delta(O\text{-}C\text{-}H)_{methyl}$
55	α'_3	[32-15-17]	$\delta(O\text{-}C\text{-}H)_{methyl}$
56	α_4	[28-16-30]	$\delta(H\text{-}C\text{-}H)_{methyl}$
57	α_5	[30-16-31]	$\delta(H\text{-}C\text{-}H)_{methyl}$

Continue

Table S5. Continuation

58	α_6	[31-16-28]	$\delta(\text{H-C-H})_{\text{methyl}}$
59	α'_4	[28-16-18]	$\delta(\text{O-C-H})_{\text{methyl}}$
60	α'_5	[30-16-18]	$\delta(\text{O-C-H})_{\text{methyl}}$
61	α'_6	[31-16-18]	$\delta(\text{O-C-H})_{\text{methyl}}$
62	α_7	[7-3-5]	$\delta(\text{C-C-C})_{\text{ring}}$
63	α_8	[3-5-9]	$\delta(\text{C-C-C})_{\text{ring}}$
64	α_9	[5-9-13]	$\delta(\text{C-C-C})_{\text{ring}}$
65	α_5	[9-13-11]	$\delta(\text{C-C-C})_{\text{ring}}$
66	α_{10}	[13-11-7]	$\delta(\text{C-C-C})_{\text{ring}}$
67	α_{11}	[11-7-3]	$\delta(\text{C-C-C})_{\text{ring}}$
68	α_{12}	[8-4-6]	$\delta(\text{C-C-C})_{\text{ring}}$
69	α_{13}	[4-6-10]	$\delta(\text{C-C-C})_{\text{ring}}$
70	α_{14}	[6-10-14]	$\delta(\text{C-C-C})_{\text{ring}}$
71	α_{15}	[10-14-12]	$\delta(\text{C-C-C})_{\text{ring}}$
72	α_{16}	[14-12-8]	$\delta(\text{C-C-C})_{\text{ring}}$
73	α_{17}	[12-8-4]	$\delta(\text{C-C-C})_{\text{ring}}$
74	γ_1	{19-5-4-9}	$\gamma(\text{C-H})$
75	γ_2	{20-6-4-10}	$\gamma(\text{C-H})$
76	γ_3	{21-7-11-3}	$\gamma(\text{C-H})$
77	γ_4	{22-8-12-4}	$\gamma(\text{C-H})$
78	γ_5	{23-9-13-5}	$\gamma(\text{C-H})$
79	γ_6	{24-10-14-6}	$\gamma(\text{C-H})$
80	γ_7	{25-11-13-7}	$\gamma(\text{C-H})$
81	γ_8	{26-12-14-8}	$\gamma(\text{C-H})$
82	γ_9	{1-3-7-5}	$\gamma(\text{C-N})$
83	γ_{10}	{2-4-8-6}	$\gamma(\text{C-N})$
84	γ_{11}	{17-13-9-11}	$\gamma(\text{O-C})$
85	γ_{12}	{18-14-10-12}	$\gamma(\text{O-C})$
86	Γ_1	(1,7)-3-5-(19,9)	$\Gamma(\text{CC})$
87	Γ_2	(19,3)-5-9-(23,13)	$\Gamma(\text{CC})$
88	Γ_3	(23,5)-9-13-(17,11)	$\Gamma(\text{CC})$
89	Γ_4	(17,9)-13-11-(25,7)	$\Gamma(\text{CC})$
90	Γ_5	(25,13)-11-7-(21,3)	$\Gamma(\text{CC})$
91	Γ_6	(21,11)-7-3-(1,5)	$\Gamma(\text{CC})$

Continue

Table S5. Continuation

92	Γ_7	(2,8)-4-6-(20,10)	Γ(CC)
93	Γ_8	(20,4)-6-10-(24,14)	Γ(CC)
94	Γ_9	(24,6)-10-14-(18,12)	Γ(CC)
95	Γ_{10}	(18,10)-14-12-(26,8)	Γ(CC)
96	Γ_{11}	(26,14)-12-8-(22 ,4)	Γ(CC)
97	Γ_{12}	(22,12)-8-4-(2,6)	Γ(CC)
99	Γ_{13}	(3)-1-2-(4)	Γ(NN)
100	Γ_{14}	(2)-1-3-(7,5)	Γ(CN)
101	Γ_{15}	(1)-2-4-(8,6)	Γ(CN)
102	Γ_{16}	(15)-17-13-(11,9)	Γ(C-OCH_3)
103	Γ_{17}	(16)-18-14-(12,10)	Γ(C-OCH_3)
104	Γ_{18}	(13)-17-15-(27,29,32)	Γ(O-CH_3)
105	Γ_{19}	(14)-18-16-(28,30,31)	Γ(O-CH_3)

Table S5b. Non redundant internal coordinates of 4,4′-dimethoxyazobenzene.

Coordinate	*Type*	*Definition*	Wilson
$q_{1}\ldots q_{6}$	ν(C-H)$_{methyl}$	$r_{1}\ldots r_{6}$	
$q_{7}\ldots q_{14}$	ν(C-H)$_{ring}$	$r_{7}\ldots r_{14}$	
$q_{15,16}$	ν(C-O)	$r_{15,16}$	
$q_{17,18}$	ν(O-CH$_3$)	$r_{17,18}$	
q_{19}	ν(N-N)	r_{19}	
$q_{20,21}$	ν(N-C$_{ring}$)	r_{20}, r_{21}	
$q_{22,23}$	ν(C-C)	$6^{-1/2}(R_{1,7}+R_{2,8}+R_{3,9}+R_{4,10}+R_{5,11}+R_{6,12})$	1
$q_{24,25}$	ν(C-C)	$12^{-1/2}(-R_{1,7}+2R_{2,8}-R_{3,9}-R_{4,10}+2R_{5,11}-R_{6,12})$	8a
$q_{26,27}$	ν(C-C)	$2^{-1}(-R_{1,7}+R_{3,9}-R_{4,10}+R_{6,12})$	8b
$q_{28,29}$	ν(C-C)	$6^{-1/2}(R_{1,7}-R_{2,8}+R_{3,9}-R_{4,10}+R_{5,11}-R_{6,12})$	14
$q_{30,31}$	ν(C-C)	$2^{-1}(R_{1,7}-R_{3,9}-R_{4,10}+R_{6,12})$	19a
$q_{32,33}$	ν(C-C)	$2^{-1/2}(R_{2,8}-R_{5,11})$	19b
$q_{34,35}$	δ(C-H)$_{ring}$	$2^{-1}(\beta_{1,5}+\beta_{2,6}+\beta_{3,7}+\beta_{4,8})$	9a
$q_{36,37}$	δ(C-H)$_{ring}$	$2^{-1}(\beta_{1,5}+\beta_{2,6}-\beta_{3,7}-\beta_{4,8})$	15
$q_{38,39}$	δ(C-H)$_{ring}$	$2^{-1}(\beta_{1,5}-\beta_{2,6}+\beta_{3,7}-\beta_{4,8})$	3
$q_{40,41}$	δ(C-H)$_{ring}$	$2^{-1}(\beta_{1,5}-\beta_{2,6}-\beta_{3,7}+\beta_{4,8})$	18a
$q_{42,43}$	δ(O-C-C)	$\beta_{9,10}$	
$q_{44,45}$	δ(N-C-C)	$\beta_{11,12}$	
$q_{46,47}$	δ(N-N-C)	$\beta_{13,14}$	
$q_{48,49}$	δ(C-O-C)	$\beta_{15,16}$	
$q_{50,51}$	δ(C-H)$_{methyl}$	$6^{-1/2}(\alpha_{1,4}+\alpha_{2,5}+\alpha_{3,6}+\alpha'_{1,4}-\alpha'_{2,5}-\alpha'_{3,6})$	
$q_{52,53}$	δ(C-H)$_{methyl}$	$6^{-1/2}(2\alpha_{1,4}-\alpha_{2,5}-\alpha_{3,6})$	
$q_{54,55}$	δ(C-H)$_{methyl}$	$2^{-1/2}(\alpha_{2,5}-\alpha_{3,6})$	
$q_{56,57}$	δ(C-H)$_{methyl}$	$6^{-1/2}(2\alpha'_{1,4}-\alpha'_{2,5}-\alpha'_{3,6})$	
$q_{58,59}$	δ(C-H)$_{methyl}$	$2^{-1/2}(\alpha'_{2,5}-\alpha'_{3,6})$	
$q_{60,61}$	δ(C-C-C)	$6^{-1/2}(\alpha_{7,13}-\alpha_{8,14}+\alpha_{9,15}-\alpha_{10,16}+\alpha_{11,17}-\alpha_{12,18})$	12
$q_{62,63}$	δ(C-C-C)	$12^{-1/2}(2\alpha_{7,13}-\alpha_{8,14}-\alpha_{9,15}+2\alpha_{10,16}-\alpha_{11,17}-\alpha_{12,18})$	6a
$q_{64,65}$	δ(C-C-C)	$2^{-1}(\alpha_{8,14}-\alpha_{9,15}+\alpha_{11,17}-\alpha_{12,18})$	6b
$q_{66\ldots73}$	γ(C-H)	$\gamma_{1}\ldots\gamma_{8}$	
$q_{74,75}$	γ(C-N)	$\gamma_{9,10}$	
$q_{76,77}$	γ(O-C)	$\gamma_{11,12}$	
$q_{78,79}$	Γ(CC)	$6^{-1/2}(\Gamma_{1,7}-\Gamma_{2,8}+\Gamma_{3,9}-\Gamma_{4,10}+\Gamma_{5,11}-\Gamma_{6,12})$	
$q_{80,81}$	Γ(CC)	$2^{-1}(\Gamma_{1,7}+\Gamma_{3,9}+\Gamma_{4,10}+\Gamma_{6,12})$	
$q_{82,83}$	Γ(CC)	$12^{-1/2}(-\Gamma_{1,7}+2\Gamma_{2,8}-\Gamma_{3,9}-\Gamma_{4,10}+2\Gamma_{5,11}-\Gamma_{6,12})$	
q_{84}	Γ(NN)	Γ_{13}	
$q_{85,86}$	Γ(CN)	$\Gamma_{14,15}$	
$q_{87,88}$	Γ(C-OCH$_3$)	$\Gamma_{16,17}$	
$q_{89,90}$	Γ(O-CH$_3$)	$\Gamma_{18,19}$	

Table S6. Assignment of the CAS-SCF vibrational frequencies of 4-methoxyphenyl azide.[a,b]

N°	*Freq(*cm^{-1}*)*	*PED*[c]	Assignment
1	3364	93 q_7	$\nu(C\text{-}H)_{ring}$
2	3354	52 q_4 + 46 q_6	$\nu(C\text{-}H)_{ring}$
3	3337	47 q_4 + 53 q_6	$\nu(C\text{-}H)_{ring}$
4	3325	94 q_5	$\nu(C\text{-}H)_{ring}$
5	3268	91 q_1	$\nu(C\text{-}H)_{methyl}$
6	3207	50 q_2 + 50 q_3	$\nu(C\text{-}H)_{methyl}$
7	3152	46 q_2 + 46 q_3	$\nu(C\text{-}H)_{methyl}$
8	2191	20 q_{11}+ 79 q_{12}	ν(N-N)
9	1758	36 q_{14}+15 q_{19}+26 q_{34}+18 q_{35}	8a
10	1712	62 q_{15}+ 13 q_{19}	8b
11	1657	35 q_{17}+ 14 q_{18}+ 32 q_{22}	19a+18a
12	1630	89 q_{29}	$\delta(C\text{-}H)_{methyl}$
13	1622	93 q_{30}	$\delta(C\text{-}H)_{methyl}$
14	1606	85 q_{28}	$\delta(C\text{-}H)_{methyl}$
15	1541	49 q_{18}+ 35 q_{20}	19b+15
16	1440	76 q_{21}	3
17	1415	28 q_8+ 12 q_{10}+ 10 q_{13}	ν(C-O)
18	1384	12q_8+ 26q_{10}+22 q_{11}+12q_{22}+10q_{33}	$\nu(N\text{-}C_{ring})$
19	1316	52 q_{31}	$\delta(C\text{-}H)_{methyl}$
20	1282	95 q_{32}	$\delta(C\text{-}H)_{methyl}$
21	1277	21 q_{14}+55q_{19}	9a
22	1247	53 q_{16}+ 14 q_{20}	14
23	1216	27 q_{11}+ 10 q_{17}+ 13 q_{33}	ν(N-N)
24	1173	34 q_{16}+ 45 q_{18}+ 10 q_{20}	19b+15
25	1157	28 q_9+ 12 q_{13}+ 26 q_{16}	$\nu(O\text{-}CH_3)$
26	1090	44 q_{17}+ 20 q_{18}+ 28 q_{33}	12
27	997	34 q_{38}+26 q_{39}+ 26 q_{44}	γ(C-H)
28	953	26 q_{36}+26 q_{37}+21q_{42}+12q_{43}+11q_{44}	γ(C-H)
29	894	22 q_{13}+ 28 q_{34}+ 18 q_{35}	1
30	861	28 q_{38}+ 30 q_{39}+ 23 q_{43}	γ(C-H)
31	832	41 q_{36}+ 37 q_{37}	γ(C-H)
32	828	20 q_{34}+ 16 q_{35}+ 10 q_{26}	6a
33	733	19 q_{40}+ 23 q_{41}+ 40 q_{42}	Γ(CC)
34	688	74 q_{35}	6b
35	674	12 q_{27}+ 34 q_{34}	δ(N-N-N)
36	575	96 q_{48}	Γ(NN)
37	545	23 q_{23}+ 35 q_{25}+ 35 q_{34}	δ(C-O-C)
38	544	37 q_{40}+ 39 q_{41}	γ(C-N)
39	450	10 q_{27}+31 q_{34}+ 41 q_{35}	δ(N-N-N)
40	444	19 q_{43}+ 56 q_{44}	Γ(CC)

Table S6. Continuation**.**

41	381	16 q_{40}+ 10 q_{41}+ 29 q_{42}+ 23 q_{43}	Γ(CC)
42	366	13 q_{24}+ 43 q_{34}+ 22 q_{45}	δ(N-C-C)
43	263	87 q_{46}	Γ(O-CH_3)
44	257	35 q_{23}+ 28 q_{25}+ 12 q_{26}+ 11 q_{27}	δ(O-C-C)
45	165	61 q_{43}	Γ(CC)
46	132	24 q_{24}+ 42 q_{26}+ 20 q_{27}	δ(C-N-N)
47	67	65 q_{45}+ 31 q_{46}	Γ(OC_{ring})
48	53	80 q_{47}	Γ(CN)

[a]According with the potential energy distribution matrix (Refs. 32, 33).
[b]Active space: (12e,11o); ANO-RCC[C,N,O/4*s*3*p*2*d*1*f*||H/3*s*2*p*1*d*].
[c]Potential energy distribution.

Table S7. Assignment of the CAS-SCF vibrational frequencies of triplet 4-methoxyphenyl nitrene.[a,b]

N°	*Freq(*cm^{-1}*)*	*PED*[c]	Assignment
1	3365	85 q_7	$\nu(C\text{-}H)_{ring}$
2	3353	45 q_4 + 53 q_6	$\nu(C\text{-}H)_{ring}$
3	3339	85 q_5	$\nu(C\text{-}H)_{ring}$
4	3335	53 q_4 + 45 q_6	$\nu(C\text{-}H)_{ring}$
5	3273	90 q_1	$\nu(C\text{-}H)_{methyl}$
6	3214	50 q_2 + 50 q_3	$\nu(C\text{-}H)_{methyl}$
7	3156	46 q_2 + 46 q_3	$\nu(C\text{-}H)_{methyl}$
8	1696	28 q_{12}+ 15 q_{19}+ 21 q_{30}+ 13 q_{31}	**8a**
9	1636	46 q_{13}+15 q_{17}+ 12 q_{31}	**8b**
10	1630	86 q_{25}	$\delta(C\text{-}H)_{methyl}$
11	1623	93 q_{26}	$\delta(C\text{-}H)_{methyl}$
12	1611	72 q_{24}	$\delta(C\text{-}H)_{methyl}$
13	1590	16 q_{15}+ 45 q_{18}+ 13 q_{24}	**9b**
14	1516	41 q_{16}+ 30 q_{20}	**19b**
15	1415	35 q_8	$\nu(C\text{-}O)$
16	1393	18 q_{13}+ 44 q_{17}	**9a**
17	1324	21 q_{10}+ 14 q_{19}+ 24 q_{27}	$\nu(N\text{-}C_{ring})$
18	1310	17 q_{10}+ 12 q_{19}+ 35 q_{27}	$\delta(C\text{-}H)_{methyl}$
19	1282	95 q_{28}	$\delta(C\text{-}H)_{methyl}$
20	1228	65 q_{14}	**14**
21	1203	14 q_{10}+ 14 q_{12}+ 18 q_{19} + 14 q_{30}	**3**
22	1176	23 q_{14}+ 53 q_{16}+ 20 q_{20}	**19b**
23	1151	38 q_9+ 13 q_{30}	$\nu(O\text{-}CH_3)$
24	1047	39 q_{15}+ 27 q_{29}	**19a**
25	991	28 q_{34}+ 32 q_{35}	$\gamma(C\text{-}H)$
26	962	31 q_{32}+ 22 q_{33}	$\gamma(C\text{-}H)$
27	868	45 q_{11}+21 q_{30}+ 15 q_{31}	**1**
28	846	32 q_{34}+ 18 q_{35}+ 16 q_{39}	$\gamma(C\text{-}H)$
29	818	24 q_{32}+ 33 q_{33}+ 14 q_{34}+ 15 q_{39}	$\gamma(C\text{-}H)$
30	778	21 q_8+ 21 q_{29}	**12**
31	728	22 q_{36}+ 27 q_{37}+ 29 q_{38}	$\gamma(C\text{-}N)$
32	669	76 q_{31}	**6b**
33	555	24 q_{23}+ 43 q_{30}	**6a** + $\delta(C\text{-}O\text{-}C)$
34	527	33 q_{36}+ 43 q_{37}	$\gamma(O\text{-}C)$
35	445	40 q_{30}+ 47 q_{31}	**6b**
36	427	15 q_{39}+ 55 q_{40}	$\Gamma(CC)$
37	390	53 q_{22}+ 14 q_{23}	$\delta(N\text{-}C\text{-}C)$
38	352	32 q_{38}+ 21 q_{39}	$\Gamma(CC)$
39	257	80 q_{42}	$\Gamma(\ OCH_3)$
40	246	44 q_{21}+ 34 q_{23}	$\delta(O\text{-}C\text{-}C)$
41	151	60 q_{39}+ 20 q_{41}	$\Gamma(CC)$
42	69	66 q_{41}+ 32 q_{42}	$\Gamma(\ CO)$

[a]According with the potential energy distribution matrix (Refs. 32, 33).
[b]Active space: (12e,11o); ANO-RCC[C,N,O/4*s*3*p*2*d*1*f*||H/3*s*2*p*1*d*].
[c]Potential energy distribution.

Table S8. Assignment of the CAS-SCF vibrational frequencies of 1^1A" 4-methoxyphenyl nitrene.[a,b]

N°	*Freq(*cm^{-1}*)*	*PED*[c]	Assignment
1	3365	43 q_5+ 55 q_7	ν(C-H)$_{ring}$
2	3358	72 q_4 + 26 q_7	ν(C-H)$_{ring}$
3	3346	56 q_5 + 26 q_6	ν(C-H)$_{ring}$
4	3337	23 q_4 + 73 q_6	ν(C-H)$_{ring}$
5	3275	90 q_1	ν(C-H)$_{methyl}$
6	3217	50 q_2 + 50 q_3	ν(C-H)$_{methyl}$
7	3158	45 q_2 + 45 q_3	ν(C-H)$_{methyl}$
8	1707	28 q_{12}+ 15 q_{17}+ 25 q_{30}+ 17 q_{31}	**8a**
9	1650	32 q_{10}+17 q_{15}+ 23 q_{20}	ν(N-C$_{ring}$)
10	1630	88 q_{25}	δ(C-H)$_{methyl}$
11	1623	93 q_{26}	δ(C-H)$_{methyl}$
12	1610	18 q_{16}+ 52 q_{24}	δ(C-H)$_{methyl}$
13	1598	28 q_{16}+ 18 q_{24}	**19b**
14	1537	27 q_{10}+ 11 q_{19}+ 26 q_{20}	18a
15	1494	13 q_{16}+ 12 q_{18}+ 44 q_{19}	3
16	1420	39 q_8+ 15 q_{20}+ 10 q_{27}	ν(C-O)
17	1346	24 q_{13}+ 14 q_{14}+ 21 q_{18}+ 24 q_{19}	**8b+3**
18	1322	17 q_{10}+ 12 q_{19}+ 35 q_{27}	δ(C-H)$_{methyl}$
19	1281	95 q_{28}	δ(C-H)$_{methyl}$
20	1259	23 q_{14}+ 32 q_{17}	**9a**
21	1217	45 q_{14}+ 13 q_{16}+ 11 q_{17}	**14**
22	1175	23 q_{14}+ 39 q_{16}+ 39 q_{18}	**19b+15**
23	1153	59 q_9	ν(O-CH$_3$)
24	1029	36 q_{15}+ 51 q_{29}	**12**
25	979	19 q_{34}+ 47 q_{35}+ 23 q_{40}	γ(C-H)
26	952	50 q_{32}+ 12 q_{33}+ 12 q_{38}+ 17 q_{40}	γ(C-H)
27	818	50 q_{11}+12 q_{15}+ 14 q_{30}	**1**
28	800	16 q_{33}+ 41 q_{34}+ 23 q_{36}	γ(C-H)
29	768	18 q_8+ 20 q_{15}+ 17 q_{29}	19a+12
30	744	39 q_{33}+ 13 q_{34}+ 15 q_{35}+ 15 q_{39}	γ(C-H)
31	683	21 q_{32}+ 12 q_{35}+ 22 q_{36}+ 17 q_{38}	γ(C-N)
32	640	20 q_{13}+ 68 q_{31}	**6b**
33	547	12 q_{21}+ 24 q_{23}+ 45 q_{30}	6a + δ(C-O-C)
34	462	31 q_{36}+ 41 q_{37}+ 11 q_{30}	γ(O-C)
35	442	39 q_{30}+ 47 q_{31}	**6a+6b**
36	397	32 q_{22}+ 11 q_{23}+ 34 q_{30}+ 12 q_{31}	δ(N-C-C)
37	364	12 q_{32}+ 12 q_{33}+ 10 q_{35}+ 45 q_{40}	Γ(CC)
38	294	15 q_{37}+ 16 q_{38}+ 13 q_{39}+ 43 q_{42}	Γ(OCH$_3$)
39	244	47 q_{21}+ 33 q_{23}	δ(O-C-C)
40	231	17 q_{37}+ 25 q_{38}+ 16 q_{39}+ 29 q_{42}	Γ(CC)
41	110	14 q_{38}+ 27 q_{39}+ 33 q_{41}	Γ(CC)
42	62	61 q_{41}+ 32 q_{42}	Γ(CO)

[a]According with the potential energy distribution matrix (Refs. 32, 33).
[b]Active space: (12e,11o); ANO-RCC[C,N,O/4*s*3*p*2*d*1*f*||H/3*s*2*p*1*d*].
[c]Potential energy distribution.

Table S9. Assignment of the CAS-SCF vibrational frequencies of 1^1A' 4-methoxyphenyl nitrene.[a,b]

N°	*Freq(*cm^{-1}*)*	*PED*[c]	Assignment
1	3372	24 q_5+ 74 q_7	$\nu(C\text{-}H)_{ring}$
2	3362	71 q_4 + 27 q_6	$\nu(C\text{-}H)_{ring}$
3	3351	75 q_5 + 24 q_7	$\nu(C\text{-}H)_{ring}$
4	3343	28 q_4 + 72 q_6	$\nu(C\text{-}H)_{ring}$
5	3287	89 q_1	$\nu(C\text{-}H)_{methyl}$
6	3236	50 q_2 + 50 q_3	$\nu(C\text{-}H)_{methyl}$
7	3170	45 q_2 + 45 q_3	$\nu(C\text{-}H)_{methyl}$
8	1707	35 q_{12}+ 15 q_{17}+ 22 q_{30}+ 15 q_{31}	**8a**
9	1667	57 q_{13}+14 q_{19}+ 23 q_{20}	**8b**
10	1629	70 q_{25}	$\delta(C\text{-}H)_{methyl}$
11	1625	93 q_{26}	$\delta(C\text{-}H)_{methyl}$
12	1624	21 q_{24}+ 18 q_{25}	$\delta(C\text{-}H)_{methyl}$
13	1602	25 q_{20}+ 57 q_{24}	**18a**
14	1534	47 q_{16}+ 28 q_{18}	**19b**
15	1421	37 q_8+ 13 q_{20}	$\nu(C\text{-}O)$
16	1396	12 q_{13}+ 58 q_{19}	**3**
17	1337	42 q_{10}	$\nu(N\text{-}C_{ring})$
18	1321	25 q_{14}+ 23 q_{27}	$\delta(C\text{-}H)_{methyl}$
19	1287	62 q_{14}+ 19 q_{16}+ 37 q_{17}	**14**
20	1282	95 q_{28}	$\delta(C\text{-}H)_{methyl}$
21	1235	13 q_{10}+ 15 q_{12}+ 37 q_{17}	**9a**
22	1185	38 q_{16}+ 47 q_{18}	**15**
23	1152	72 q_9	$\nu(O\text{-}CH_3)$
24	1078	41 q_{15}+ 14 q_{20}+ 44 q_{29}	**12**
25	1042	49 q_{34}+ 18 q_{35}+ 16 q_{38}	$\gamma(C\text{-}H)$
26	1038	14 q_{32}+ 46 q_{33}+ 22 q_{40}	$\gamma(C\text{-}H)$
27	889	40 q_{11}+26 q_{30}+ 19 q_{31}	**1**
28	889	20 q_{32}+ 30 q_{35}+ 14 q_{37}	$\gamma(C\text{-}H)$
29	846	45 q_{32}+ 14 q_{33}+ 20 q_{35}	$\gamma(C\text{-}H)$
30	802	17 q_8+ 21 q_{15}+ 22 q_{29}+ 12 q_{30}	
31	783	16 q_{36}+ 37 q_{37}+ 27 q_{38}	$\gamma(O\text{-}C)$
32	674	15 q_{13}+ 70 q_{31}	**6b**
33	569	27 q_{21}+ 27 q_{36}+ 48 q_{37}	$\gamma(N\text{-}C)$
34	562	13 q_{21}+ 26 q_{23}+ 42 q_{30}	$\delta(C\text{-}O\text{-}C)$
35	454	36 q_{30}+ 48q_{31}	**6a**
36	427	15 q_{39}+ 61 q_{40}	$\Gamma(CC)$
37	410	43 q_{22}+ 28 q_{30}	$\delta(N\text{-}C\text{-}C)$
38	312	29 q_{38}+ 30 q_{39}+ 18 q_{42}	$\Gamma(CC)$
39	254	44 q_{21}+ 42 q_{23}	$\delta(O\text{-}C\text{-}C)$
40	237	20 q_{38}+ 17 q_{39}+ 49 q_{42}	$\Gamma(OCH_3)$
41	127	20 q_{36}+ 15 q_{38}+ 36 q_{41}	$\Gamma(CC)$
42	80	44 q_{41}+ 18 q_{42}	$\Gamma(\ CO)$

[a]According with the potential energy distribution matrix (Refs. 32, 33).
[b]Active space: (12e,11o); ANO-RCC[C,N,O/4*s*3*p*2*d*1*f*||H/3*s*2*p*1*d*].
[c]Potential energy distribution.

Table S10. Assignment of the CAS-SCF vibrational frequencies of 4,4′-dimethoxyazobenzene.[a,b]

N°	*Freq(*cm^{-1}*)*	*PED*[c]	Assignment
1	3376	40 q_9+ 40 q_{10}	$\nu(C\text{-}H)_{ring}$
2	3376	40 q_9+ 40 q_{10}	$\nu(C\text{-}H)_{ring}$
3	3355	39 q_{13}+ 39 q_{14}	$\nu(C\text{-}H)_{ring}$
4	3355	39 q_{13}+ 39 q_{14}	$\nu(C\text{-}H)_{ring}$
5	3352	21 q_7+ 21 q_8+ 28 q_{11}+ 28 q_{12}	$\nu(C\text{-}H)_{ring}$
6	3352	21 q_7+ 21 q_8+ 28 q_{11}+ 28 q_{12}	$\nu(C\text{-}H)_{ring}$
7	3335	28 q_7+ 28 q_8+ 22 q_{11}+ 22 q_{12}	$\nu(C\text{-}H)_{ring}$
8	3335	28 q_7+ 28 q_8+ 22 q_{11}+ 22 q_{12}	$\nu(C\text{-}H)_{ring}$
9	3269	47 q_1+ 47 q_2	$\nu(C\text{-}H)_{methyl}$
10	3269	47 q_1+ 47 q_2	$\nu(C\text{-}H)_{methyl}$
11	3211	25 q_3+ 25 q_4+ 25 q_5+ 25 q_6	$\nu(C\text{-}H)_{methyl}$
12	3211	25 q_3+ 25 q_4+ 25 q_5+ 25 q_6	$\nu(C\text{-}H)_{methyl}$
13	3154	23 q_3+ 23 q_4+ 23 q_5+ 23 q_6	$\nu(C\text{-}H)_{methyl}$
14	3154	23 q_3+ 23 q_4+ 23 q_5+ 23 q_6	$\nu(C\text{-}H)_{methyl}$
15	1748	26 q_{24}+ 23 q_{25}	8a
16	1746	29 q_{24}+ 29 q_{25}	8a
17	1720	28 q_{26}+ 28 q_{27}	8b
18	1710	34 q_{26}+ 34 q_{27}	8b
19	1675	64 q_{19}	ν(N-N)
20	1659	23 q_{40}+ 23 q_{41} +16 q_{30}+16 q_{31}	18a+19a
21	1652	22 q_{40}+ 22 q_{41} +14 q_{30}+14 q_{31}	18a+19a
22	1630	33 q_{34}+ 33 q_{35}	9a
23	1630	33 q_{34}+ 33 q_{35}	9a
24	1622	35 q_{52}+ 35 q_{53}	$\delta(C\text{-}H)_{methyl}$
25	1622	35 q_{52}+ 35 q_{53}	$\delta(C\text{-}H)_{methyl}$
26	1606	44 q_{50}+ 44 q_{51}	$\delta(C\text{-}H)_{methyl}$
27	1606	43 q_{50}+ 43 q_{51}	$\delta(C\text{-}H)_{methyl}$
28	1536	25 q_{32}+ 25 q_{33}+ 17 q_{36}+ 17 q_{37}	19b
29	1536	24 q_{32}+ 24 q_{33}+ 16 q_{36}+ 16 q_{37}	19b+15
30	1436	38 q_{38}+ 38 q_{39}	3
31	1429	39 q_{38}+ 39 q_{39}	3
32	1406	21 q_{15}+ 21 q_{16}	$\nu(O\text{-}C_{ring})$
33	1402	21 q_{15}+ 21 q_{16}	$\nu(O\text{-}C_{ring})$
34	1338	25 q_{20}+ 25 q_{21}	$\nu(N\text{-}C_{ring})$
35	1326	14 q_{56}+ 14 q_{57}	$\delta(C\text{-}H)_{methyl}$
36	1317	23 q_{56}+ 23 q_{57}	$\delta(C\text{-}H)_{methyl}$
37	1294	12 q_{56}+ 12 q_{57}	$\delta(C\text{-}H)_{methyl}$
38	1282	48 q_{58}+ 48 q_{59}	$\delta(C\text{-}H)_{methyl}$
39	1282	48 q_{58}+ 48 q_{59}	$\delta(C\text{-}H)_{methyl}$
40	1264	14 q_{28}+ 14 q_{29}+ 18 q_{34}+ 18 q_{35}	9a
41	1258	25 q_{34}+ 25 q_{35}	9a
42	1243	24 q_{28}+ 24 q_{29}	14
43	1241	23 q_{28}+ 23 q_{29}	14
44	1173	16 q_{28}+ 16 q_{29}+ 16 q_{32}+ 16 q_{33}	19b
45	1170	18 q_{28}+ 18 q_{29}+ 22 q_{32}+ 22 q_{33}	19b
46	1164	13 q_{17}+ 13 q_{18}+ 18 q_{32}+ 18 q_{33}	$\nu(O\text{-}CH_3)$
47	1164	25 q_{17}+ 25 q_{18}	$\nu(O\text{-}CH_3)$

continue

Table S10. Continuation.

48	1088	21 q_{30}+ 21 q_{31}+ 22 q_{60}+ 22 q_{61}	19a+12
49	1088	21 q_{30}+ 21 q_{31}+ 22 q_{60}+ 22 q_{61}	19a+12
50	1003	11 q_{67}+ 17 q_{82}+ 17 q_{83}	γ(C-H)
51	1003	11 q_{67}+ 17 q_{82}+ 17 q_{83}	γ(C-H)
52	992	13 q_{68}+ 13 q_{60}+ 14 q_{78}+ 14 q_{79}	γ(C-H)
53	989	13 q_{68}+ 13 q_{60}+ 14 q_{78}+ 14 q_{79}	γ(C-H)
54	988	11 q_{22}+ 11 q_{23}+ 20 q_{46}+ 20 q_{47}	δ(N-N-C)
55	891	27 q_{22}+ 27 q_{23}	1
56	876	17 q_{70}+ 15 q_{71}	γ(C-H)
57	869	19 q_{70}+ 17 q_{71}	γ(C-H)
58	849	13 q_{22}+ 13 q_{23}+ 11 q_{62}+ 11 q_{63}	1
59	847	18 q_{72}+ 16 q_{73}+ 21 q_{80}+ 14 q_{81}	γ(C-H)
60	846	18 q_{72}+ 16 q_{73}+ 21 q_{80}+ 14 q_{81}	γ(C-H)
61	800	11 q_{15}+ 11 q_{16}+ 13 q_{60}+ 13 q_{61}	12
62	758	11 q_{76}+ 11 q_{77}+ 15 q_{78}+ 15 q_{79}	γ(O-C)
63	741	12 q_{76}+ 12 q_{77}+ 18 q_{78}+ 18 q_{79}	γ(O-C)
64	695	31 q_{64}+ 31 q_{65}	6b
65	682	38 q_{64}+ 38 q_{65}	6b
66	638	17 q_{62}+ 17 q_{63}	6a
67	588	9q_{44}+ 9q_{45}+ 7 q_{46}+ 9 q_{46}+ 13 q_{64}+ 13 q_{65}	δ(N-C-C)+δ(N-N-C)
68	585	16 q_{74}+ 14 q_{75}+ 17 q_{76}+ 18 q_{77}	γ(C-N)
69	542	18 q_{74}+ 15 q_{75}+ 18 q_{76}+ 18 q_{77}	γ(C-N)
70	531	12 q_{48}+ 12 q_{49}+ 11 q_{62}+ 11 q_{63}	δ(C-O-C)
71	522	15 q_{42}+ 15 q_{43}+ 16 q_{48}+ 16 q_{49}	δ(C-O-C)
72	450	26 q_{82}+ 26 q_{83}	Γ(CC)
73	450	20 q_{80}+ 14 q_{81}+ 15 q_{82}+ 15 q_{83}	Γ(CC)
74	443	19 q_{62}+ 19 q_{63}	6a
75	443	12 q_{78}+ 12 q_{79}	Γ(CC)
76	383	13 q_{74}+ 11 q_{75}+ 13 q_{78}+ 13 q_{79}+ 11 q_{80}	Γ(CC)
77	325	19 q_{44}+ 19 q_{45}+ 17 q_{48}+ 17 q_{49}	δ(N-C-C)
78	274	42 q_{89}+ 42 q_{90}	Γ(O-CH_3)
79	263	49 q_{89}+ 40 q_{90}	Γ(O-CH_3)
80	263	20 q_{42}+ 20 q_{43}+ 20 q_{48}+ 20 q_{49}	δ(O-C-C)
81	249	10 q_{42}+ 10 q_{43}+ 13 q_{62}+ 13 q_{63}	δ(O-C-C)
82	204	11 q_{80}+ 21 q_{84}	Γ(CC)
83	190	13 q_{80}+ 29 q_{85}+ 12 q_{86}	Γ(NN)
84	161	16 q_{44}+ 16 q_{45}	δ(N-C-C)
85	88	24 q_{66}+ 20 q_{85}+ 13 q_{87}+ 13 q_{88}	Γ(CN)
86	77	30 q_{87}+ 30 q_{88}+ 14 q_{89}+ 13 q_{90}	Γ(C-OCH_3)
87	59	13 q_{66}+ 21 q_{87}+ 21 q_{88}+ 12 q_{89}+ 12 q_{90}	Γ(C-OCH_3)
88	58	15 q_{44}+ 15 q_{45}+ 28 q_{46}+ 28 q_{47}	δ(N-N-C)+δ(N-C-C)
89	33	35 q_{66}+ 14 q_{80}+ 10 q_{84}	Γ(CC)
90	20	50 q_{85}+ 20 q_{86}	Γ(CN)

[a]According with the potential energy distribution matrix (Refs. 32, 33).
[b]Active space: (16e,15o); ANO-RCC[C,N,O/4*s*3*p*2*d*1*f*||H/3*s*2*p*1*d*].
[c]Potential energy distribution.

Table S11. Assignment of the calculated Resonance Raman spectrum of singlet 4-methoxyphenyl nitrene and 4-methoxyohenyl azide.[a,b]

CAS-SCF[c]	I_{rel}(320)	I_{rel}(340)	Assignment
1707	100	80	8a
1650	76	100	ν(N-C_{ring})
1259	14	12	9a
1029	23	34	12
CAS-SCF[d]	I_{rel}(320)	I_{rel}(340)	Assignment
1707	100	40	8a
1629	4	11	δ(C-H)$_{methyl}$
1624	19	27	δ(C-H)$_{methyl}$
1602	4	22	18a
1421	11	65	ν(C-O)
1337	28	44	ν(N-C_{ring})
1235	23	11	9a
1152	19	7	ν(O-CH_3)
889	27	100	1
562	44	13	δ(C-O-C)
454	85	34	6a
CAS-SCF[e]	I_{rel}(320)	I_{rel}(340)	Assignment
1758	12	39	8a
1712	6	10	8b
1657	3	11	19a+18a
1415	100	100	ν(C-O)
1384	14	76	ν(N-C_{ring})
1277	15	18	9a
1247	54	33	14
1216	31	24	ν(N-N)
1173	49	31	19b+15
1157	18	12	ν(O-CH_3)
894	87	54	1
828	22	14	6a

[a]According with the potential energy distribution matrix (Refs. 32, 33).

[b]Active space: (12e,11o); ANO-RCC[C,N,O/4*s*3*p*2*d*1*f*||H/3*s*2*p*1*d*]; state average: (4 states A', 4 states A"); IPEA=0.25.

[c]1^1A" 4-methoxyphenyl nitrene. [d]1^1A' 4-methoxyphenyl nitrene.

[e]4-methoxyohenyl azide.

Table S12. Vertical transition energies in eV of triplet 4-methoxyphenyl nitrene (MS-CASPT2), C_s-symmetry.[a]

Transition	VE[b]	*OS*[c]	*Configuration*[d]
1^3A"→2^3A"	3.16	0.20-02	29% $n_\sigma(N)^1\ n_\pi(N)^0\ \pi_2^*(ring)^1$
			36% $n_\sigma(N)^1\ \pi_2(ring)^1\ n_\pi(N)^2$
1^3A"→3^3A"	3.31	0.84-02	43% $n_\sigma(N)^1\ n_\pi(N)^2\ \pi_3\ (ring)^1$
			24% $n_\sigma(N)^1\ \pi_3(ring)^1\ n_\pi(N)^0$
1^3A"→4^3A"	4.80	0.61-03	73% $n_\sigma(N)^1\ \pi_2(ring)^1\ n_\pi(N)^1\ \pi_2^*(ring)^1$
1^3A"→1^3A'	4.22	0.11-04	76% $n_\sigma(N)^2\ n_\pi(N)^1\ \pi_3(ring)^1$
1^3A"→2^3A'	4.24	0.83-02	76% $n_\sigma(N)^1\ \sigma(CN)^1\ n_\pi(N)^2$
1^3A"→3^3A'	4.85	0.19-04	68% $n_\sigma(N)^2\ \pi_2\ (ring)^1\ n_\pi(N)^1$
1^3A"→4^3A'	5.88	0.00	72% $n_\sigma(N)^2\ \pi_2\ (ring)^1\ n_\pi(N)^0\ \pi_2^*(ring)^1$

[a]Four state-average CAS-SCF reference wavefunction: (12e, 11o). ANO-RCC, (C,N)[4s3p2d1f]/(H)[3s2p1d].

[b]Vertical excitation energy in eV.

[c]Oscillator strength, dipole-length formula.

[d]MS-CASPT2 electron configurations. Only contributions greater than 15% are included. Only orbitals with different occupation to the ground state are given.

Table S13. Vertical transition energies in eV of 1^1A" 4-methoxyphenyl nitrene (MS-CASPT2), C_s-symmetry.[a]

Transition	VE[b]	*OS*[c]	*Configuration*[d]
1^1A"→2^1A"	2.52	0.93-03	34% $n_\sigma(N)^1\ n_\pi(N)^0\ \pi_2^*(ring)^1$
			40% $n_\sigma(N)^1\ \pi_2(ring)^1\ n_\pi(N)^0$
1^1A"→3^1A"	3.04	0.30-02	44% $n_\sigma(N)^1\ \pi_3(ring)^1\ n_\pi(N)^2$
			32% $n_\sigma(N)^1\ n_\pi(N)^0\ \pi_2^*(ring)^1$
1^1A"→4^1A"	4.67	0.22-02	25% $n_\sigma(N)^1\ n_\pi(N)^2\ \pi_1(ring)^1$
			28% $n_\sigma(N)^1\ n_\pi(N)^1\ \pi_1(ring)^1\ \pi_2^*(ring)^1$
1^1A"→1^1A'	0.47	0.0	83% $n_\sigma(N)^2\ n_\pi(N)^0$
1^1A"→2^1A'	1.92	0.0	71% $n_\sigma(N)^2\ n_\pi(N)^2$
1^1A"→3^1A'	4.55	0.51-04	53% $n_\sigma(N)^2\ n_\pi(N)^1\ \pi_2(ring)^1$
1^1A"→4^1A'	4.95	0.0	63% $n_\sigma(N)^2\ \pi_3\ (ring)^1\ n_\pi(N)^1$

[a]Four state-average CAS-SCF reference wavefunction: (12e, 11o). ANO-RCC, (C,N)[4s3p2d1f]/(H)[3s2p1d].

[b]Vertical excitation energy in eV.

[c]Oscillator strength, dipole-length formula.

[d]MS-CASPT2 electron configurations. Only contributions greater than 15% are included. Only orbitals with different occupation to the ground state are given.

Table S14. Vertical transition energies in eV of 1^1A' 4-methoxyphenyl nitrene (MS-CASPT2), C_s-symmetry.[a]

Transition	VE[b]	*OS*[c]	*Configuration*[d]
1^1A'→2^1A'	1.42	0.16-01	74% $n_\sigma(N)^0$ $n_\pi(N)^2$
1^1A'→3^1A'	3.97	0.26-01	55% $n_\sigma(N)^2$ $\pi_2(ring)^1$ $n_\pi(N)^1$
1^1A'→4^1A'	4.39	0.3829	60% $n_\sigma(N)^2$ $\pi_3(ring)^1$ $n_\pi(N)^1$
1^1A'→1^1A"	-0.30	0.0	84% $n_\sigma(N)^1$ $n_\pi(N)^1$
1^1A'→2^1A"	2.13	0.24-04	33% $n_\sigma(N)^1$ π_2*$(ring)^1$
			40% $n_\sigma(N)^1$ $\pi_2(ring)^1$ $n_\pi(N)^2$
1^1A'→3^1A"	2.50	0.00	46% $n_\sigma(N)^1$ $n_\pi(N)^1$
			31% $n_\sigma(N)^1$ π_3*$(ring)^1$
1^1A'→4^1A"	3.97	0.0	18% $n_\sigma(N)^2$ $\pi_1(ring)^1$ $n_\pi(N)^2$
			34% $n_\sigma(N)^1$ $\pi_1(ring)^1$ $n_\pi(N)^1$ π_2*$(ring)^1$

[a]Four state-average CAS-SCF reference wavefunction: (12e, 11o). ANO-RCC, (C,N)[4s3p2d1f]/(H)[3s2p1d].

[b]Vertical excitation energy in eV.

[c]Oscillator strength, dipole-length formula.

[d]MS-CASPT2 electron configurations. Only contributions greater than 15% are included. Only orbitals with different occupation to the ground state are given.

Table S15. Vertical transition energies in eV of 4,4′-dimethoxyazobenzene C_{2h} (MS-CASPT2).

Species	VE[a]	*OS*[b]	*Configuration*[c]
$1A_g \rightarrow 2A_g$	4.05	0.0000	24% $\pi_3(b_g)^1\pi^*(NN)^1$
			22% HF
$1A_g \rightarrow 3A_g$	4.76	0.0000	25% $\pi_3(b_g)^1\pi^*(NN)^1$
$1A_g \rightarrow 1B_g$	2.02	0.0000	75% $\sigma(NN)^1\pi^*(NN)^1$
			42% $\sigma(NN)^1\pi_2^*(b_g)^1\pi^*(NN)^2$
$1A_g \rightarrow 2B_g$	4.22	0.0000	
			22% $\sigma(NN)^1\pi_2(b_g)^1$
$1A_g \rightarrow 3B_g$	5.00	0.0000	17% $\sigma(NN)^1\pi_3^*(b_g)^1$
			22% $\sigma(NN)^1\pi_3(a_u)^1\pi^*(NN)^2$
$1A_g \rightarrow 1A_u$	4.10	0.72-03	23% $\sigma(NN)^1\pi_2^*(a_u)^1$
			15% $\sigma(NN)^1\pi_3(a_u)^1\pi^*(NN)^2$
$1A_g \rightarrow 2A_u$	4.49	0.45-03	18% $\sigma(NN)^1\pi_2^*(b_g)^1$
			25% $\sigma(NN)^1\pi^*_2(b_g)^1\pi^*(NN)^1\pi_2(a_u)^1$
$1A_g \rightarrow 3A_u$	5.75	0.0000	22% $\sigma(NN)^1\pi_2(b_g)^1\pi^*(NN)^1\pi_2^*(a_u)^1$
$1A_g \rightarrow 1B_u$	2.83	0.4982	73% $\pi_3(b_g)^1\pi_3(a_u)^1\pi^*(NN)^2$
			26% $\pi_2(a_u)^1\pi^*(NN)^1$
$1A_g \rightarrow 2B_u$	4.04	0.16-01	17% $\pi_3(a_u)^1\pi^*_2(b_g)^1$
$1A_g \rightarrow 3B_u$	6.20	0.21-02	15% $\pi(NN)^1\pi^*(NN)^1$

[a]Vertical excitation energy in eV.

[b]Oscillator strength.

[c]MS-CASPT2 electron configurations. Only contributions greater than 15% are included. Only orbitals with different occupation to the ground state are given.