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*Supporting Information*

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**Investigating the Nonradiative Decay Pathway  
in the Excited State of Silepin Derivatives:  
A Study with Second-Order Multireference  
Perturbation Wavefunction Theory**

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## Estimation of the angle between two benzene rings of noPh

The angles between two benzene rings in **noPh** was estimated at  $\mathbf{R}^{\text{DFT}}(\text{FC})$  and  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  by fitting of coefficients in equation of planes. An equation of a plane is given by,

$$y = az + bx + c, \quad (1)$$

where  $x, y$ , and  $z$  are cartesian coordinates, and  $a, b$ , and  $c$  are the coefficients to be fitted, respectively. A function  $F$  to be minimized for fitting was defined as,

$$F = \sum_{i=1}^6 (az_i + bx_i + c - y_i)^2, \quad (2)$$

where  $x_i, y_i, z_i$  are the cartesian coordinates of the carbon atoms in the benzene ring. The coefficients  $a$ ,  $b$ , and  $c$  were determined so as to minimize the function  $F$ ; the resultant RMSDs in prediction of  $y$  was 0.009 and 0.016 Å for  $\mathbf{R}^{\text{DFT}}(\text{FC})$  and  $\mathbf{R}^{\text{DFT}}(\text{Flu})$ , respectively. In a similar procedure, fittings for  $x$  and  $z$  were carried out; the resultant RMSDs of  $x$  and  $z$  were 0.040 and 0.019 Å for  $\mathbf{R}^{\text{DFT}}(\text{FC})$ , and 0.080 and 0.084 Å for  $\mathbf{R}^{\text{DFT}}(\text{Flu})$ , respectively. We decided to employ the results of fittings for  $y$  because their RMSDs were the smallest of the three fittings.

Because one of the normal vectors,  $\mathbf{n}$ , of the plane expressed as equation (1) is given by  $\mathbf{n} = (b, -1, a)$ , the angle between the planes fitted for the benzene rings in left and right side of **noPh** was estimated by,

$$\cos^{-1} \left( \frac{|b_l b_r + 1 + a_l a_r|}{\sqrt{b_l^2 + 1 + a_l^2} \sqrt{b_r^2 + 1 + a_r^2}} \right), \quad (3)$$

where the subscripts  $l$  and  $r$  stand for the benzene ring on left and right side of **noPh**, respectively. The angles between two benzene rings of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{FC})$  and  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  were estimated as  $50^\circ$  and  $22^\circ$ , respectively. Finally, subtraction of these values from  $180^\circ$  resulted in  $130^\circ$  and  $158^\circ$ , as written in the manuscript.

## Geometries of *p*-Ph and *m*-Ph at the (TD-)DFT level calculations

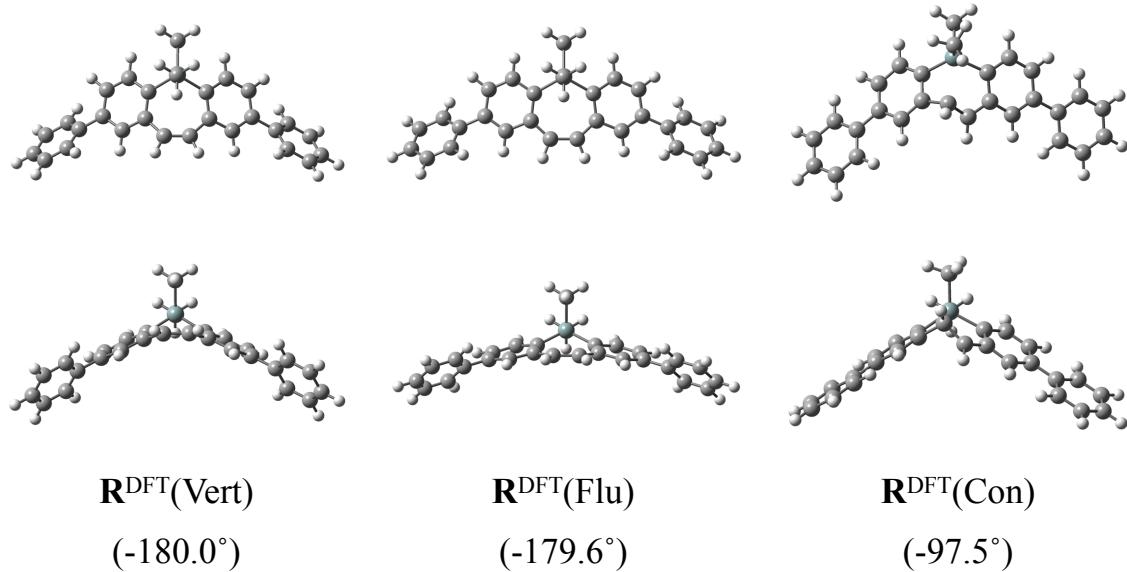


Figure S1: Optimized geometries of *p*-Ph at the (TD-)DFT level calculations.  $\mathbf{R}^{\text{DFT}}(\text{Vert})$ ,  $\mathbf{R}^{\text{DFT}}(\text{Flu})$ , and  $\mathbf{R}^{\text{DFT}}(\text{Con})$  represent the geometries optimized for the ground state, fluorescent state and MECI point, respectively. The images show the top (first line) and side (second line) view of each geometry. The dihedral angle of C4-C3-C1-C2 defined in Figure 3 is shown in parenthesis.

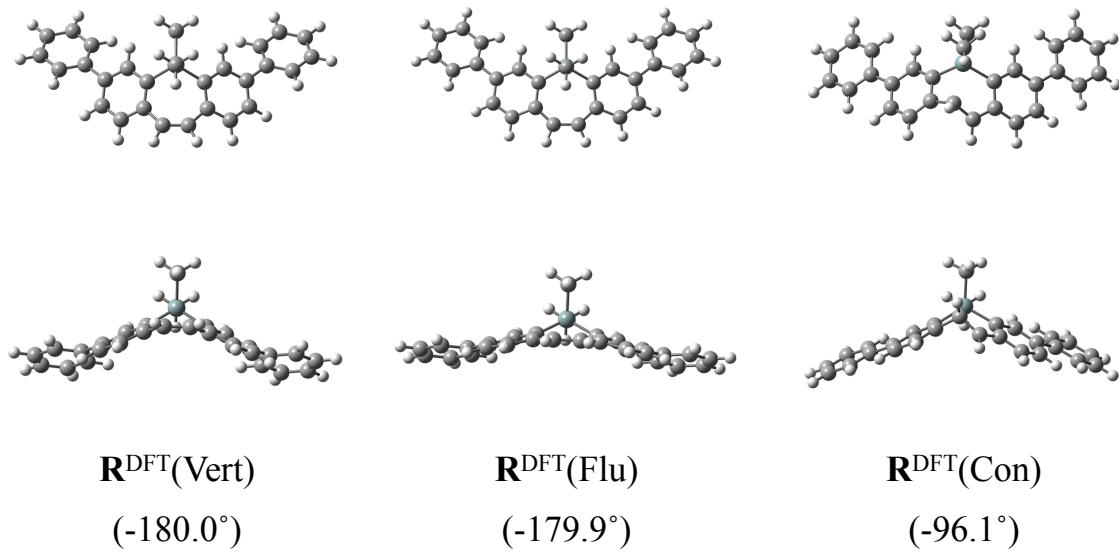


Figure S2: Optimized geometries of *m*-Ph at the (TD-)DFT level calculations.  $\mathbf{R}^{\text{DFT}}(\text{Vert})$ ,  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  and  $\mathbf{R}^{\text{DFT}}(\text{Con})$  represent the geometries optimized for the ground state, fluorescent state and MECI point, respectively. The images show the top (first line) and side (second line) view of each geometry. The dihedral angle of C4-C3-C1-C2 defined in Figure 3 is shown in parenthesis.

## Comparison of the geometries of noPh at the TD-DFT and XMS-CASPT2 level calculations

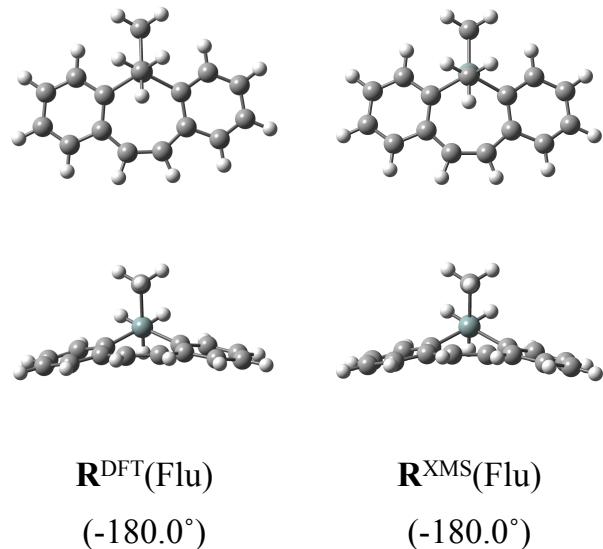


Figure S3: Comparison of the  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  and  $\mathbf{R}^{\text{XMS}}(\text{Flu})$  of **noPh**. The images show the top (first line) and side (second line) view of each geometry. The dihedral angle of C3-C2-C4-C1 in Figure 3 is shown in parenthesis.

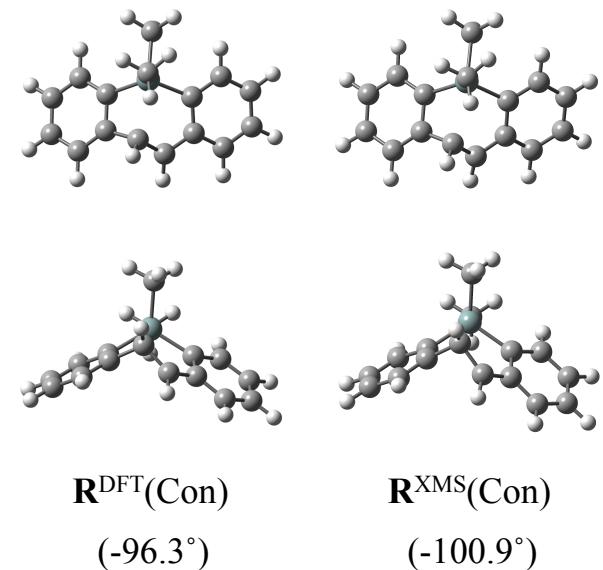


Figure S4: Comparison of the  $\mathbf{R}^{\text{DFT}}(\text{Con})$  and  $\mathbf{R}^{\text{XMS}}(\text{Con})$  of **noPh**. The images show the top (first line) and side (second line) view of each geometry. The dihedral C3-C2-C4-C1 in Figure 3 is shown in parenthesis.

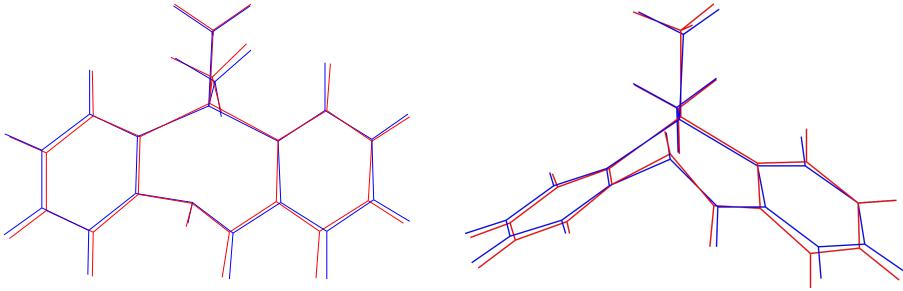


Figure S5: Superposition of the  $\mathbf{R}^{\text{DFT}}(\text{Con})$  (blue) and  $\mathbf{R}^{\text{XMS}}(\text{Con})$  (red) of **noPh**. The images show the top (left) and side (right) view of the superposed geometry. RMSD between the two mass-weighted cartesian coordinates was computed to be 0.176 Å.

Figure S5 indicates that the DFT/TD-DFT and XMS-CASPT2 level geometry optimizations gave CI geometries with slight differences. The similarity of two geometries is also supported by the internal coordinates shown in Table S1–S3.

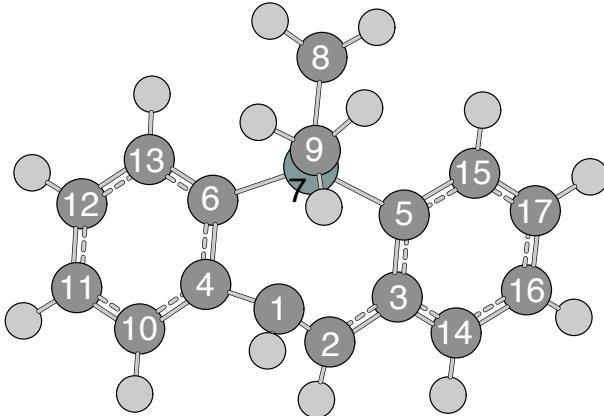


Figure S6: Atom labeling of **noPh**. Label of hydrogen atoms are omitted.

**Table S1: Comparison of bond lengths in  $\mathbf{R}^{\text{DFT}}(\text{Con})$  and  $\mathbf{R}^{\text{XMS}}(\text{Con})$  (Å)**

Bond	DFT	XMS	Bond	DFT	XMS
C1–C2	1.439	1.460	C1–C4	1.520	1.516
C2–C3	1.412	1.420	C3–C5	1.425	1.431
C3–C14	1.418	1.420	C4–C6	1.401	1.420
C4–C10	1.394	1.394	C5–Si7	1.946	1.939
C5–C15	1.396	1.400	C6–Si7	1.913	1.911
C6–C13	1.396	1.406	Si7–C8	1.923	1.925
Si7–C9	1.893	1.895	C10–C11	1.396	1.409
C11–C12	1.396	1.407	C12–C13	1.396	1.401
C14–C16	1.377	1.396	C15–C17	1.393	1.407
C16–C17	1.403	1.397			

**Table S2: Comparison of angles in  $\mathbf{R}^{\text{DFT}}(\text{Con})$  and  $\mathbf{R}^{\text{XMS}}(\text{Con})$  ( $^\circ$ )**

Angle	DFT	XMS	Angle	DFT	XMS
C1–C2–C3	119.4	120.1	C1–C4–C6	106.0	107.1
C1–C4–C10	132.3	131.4	C2–C1–C4	109.6	99.7
C2–C3–C5	116.2	116.9	C2–C3–C14	121.7	121.3
C3–C5–Si7	117.8	117.7	C3–C5–C15	116.5	116.9
C3–C14–C16	119.5	119.2	C4–C6–Si7	104.1	105.7
C4–C6–C13	119.5	119.4	C4–C10–C11	118.1	118.5
C5–C3–C14	122.0	121.8	C5–Si7–C6	115.0	110.8
C5–Si7–C8	98.9	99.4	C5–Si7–C9	115.5	118.2
C5–C15–C17	121.3	121.0	C6–C4–C10	121.6	121.5
C6–Si7–C8	101.4	101.9	C6–Si7–C9	120.9	121.0
C6–C13–C12	119.4	119.2	Si7–C5–C15	125.6	125.0
Si7–C6–C13	136.3	134.6	C8–Si7–C9	99.1	100.6
C10–C11–C12	120.6	120.4	C11–C12–C13	120.6	120.9
C14–C16–C17	119.0	119.4	C15–C17–C16	121.6	121.4

**Table S3: Comparison of angles in  $\mathbf{R}^{\text{DFT}}(\text{Con})$  and  $\mathbf{R}^{\text{XMS}}(\text{Con})$  ( $^\circ$ )**

Dihedral	DFT	XMS	Dihedral	DFT	XMS
C1–C2–C3–C5	-12.0	-9.9	C1–C2–C3–C14	169.9	168.3
C1–C4–C6–Si7	-1.6	-0.5	C1–C4–C6–C13	-178.3	-174.7
C1–C4–C10–C11	177.8	175.3	C2–C1–C4–C6	-100.4	-98.2
C2–C1–C4–C10	81.0	82.5	C2–C3–C5–C7	-4.3	-13.0
C2–C3–C5–C15	179.9	173.7	C2–C3–C14–C16	-178.1	-171.9
C3–C2–C1–C4	106.5	105.0	C3–C5–Si7–C6	-46.5	-39.0
C3–C5–Si7–C8	-153.6	-145.7	C3–C5–Si7–C9	101.8	106.9
C3–C5–C15–C17	-1.0	0.4	C3–C14–C16–C17	-2.7	-3.6
C4–C6–Si7–C5	66.6	67.2	C4–C6–Si7–C8	172.2	172.1
C4–C6–Si7–C9	-79.8	-77.7	C4–C6–C13–C12	-0.1	-3.1
C4–C10–C11–C12	0.5	1.7	C5–C3–C14–C16	3.9	6.2
C5–Si7–C6–C13	-117.4	-120.0	C5–C15–C17–C16	2.2	2.1
C6–C4–C10–C11	-0.7	-4.0	C6–Si7–C5–C15	128.9	133.8
C6–C13–C12–C11	-0.1	1.0	Si7–C5–C3–C14	173.7	168.8
Si7–C5–C15–C17	-176.4	-172.5	Si7–C6–C4–C10	177.2	178.9
Si7–C6–C13–C12	-175.5	-175.3	C8–Si7–C5–C15	21.8	27.1
C8–Si7–C6–C13	-11.9	-15.0	C9–Si7–C5–C15	-82.8	-80.3
C9–Si7–C6–C13	96.1	95.2	C10–C4–C6–C13	0.5	4.7
C10–C11–C12–C13	-0.1	-0.2	C14–C3–C5–C15	-2.0	-4.5
C14–C16–C17–C15	-0.3	-0.4			

## Contribution of the DMRG-CASSCF eigenstates to the DMRG-XMS-CASPT2 S<sub>1</sub> state of noPh

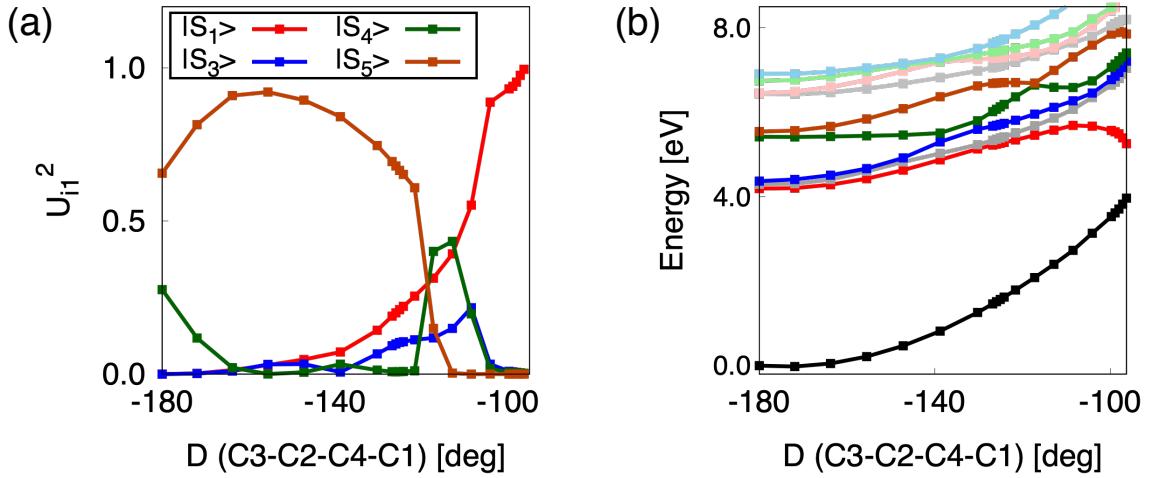


Figure S7: (a) Contribution of the DMRG-CASSCF eigenstates to the S<sub>1</sub> state in the DMRG-XMS-CASPT2 calculations and (b) energies of the DMRG-CASSCF eigenstates along with the LIIC linking  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  and  $\mathbf{R}^{\text{DFT}}(\text{Con})$ . In (a), contributions of the DMRG-CASSCF eigenstates which show more than 10 % contribution to the S<sub>1</sub> state at least at one geometry are shown. Contribution to the S<sub>1</sub> state was estimated by the square of the elements in the XMS-CASPT2 rotation matrix at each geometry. In (b), 10 lowest singlet eigenstates are shown.

In the region where the dihedral C4-C3-C1-C2 is smaller than 120°, the DMRG-CASSCF S<sub>5</sub> eigenstate shows the largest contribution to the DMRG-XMS-CASPT2 S<sub>1</sub> state. This region contains both of the  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  and  $\mathbf{R}^{\text{DFT}}(\text{TS})$ , and there DMRG-CASSCF S<sub>5</sub> eigenstate is continuous. In the region where the dihedral C4-C3-C1-C2 is larger than that at the  $\mathbf{R}^{\text{DFT}}(\text{TS})$ , the contribution of the DMRG-CASSCF S<sub>5</sub> eigenstate drastically decreased; instead, the contribution of the DMRG-CASSCF S<sub>4</sub> state becomes large. This may come from the change in the ordering of S<sub>4</sub> and S<sub>5</sub> states as shown in Figure S7b. Finally, in the area between  $\mathbf{R}^{\text{DFT}}(\text{D104})$  and  $\mathbf{R}^{\text{DFT}}(\text{CI})$ , the DMRG-CASSCF S<sub>1</sub> eigenstate shows the largest contribution to the DMRG-XMS-CASPT2 S<sub>1</sub> state. As Figure S7a shows, the character of the DMRG-XMS-CASPT2 S<sub>1</sub> state gradually changes from open-shell character to closed-shell character.

## Natural orbitals of noPh in the DMRG-CASSCF calculations

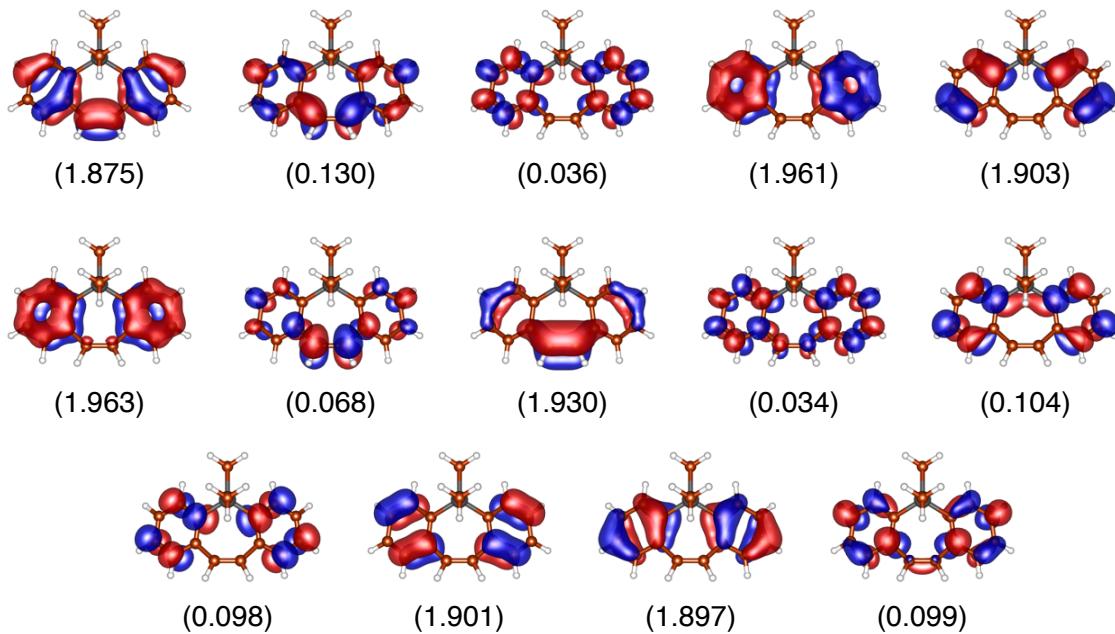


Figure S8: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_0$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{FC})$ . The occupation numbers are shown in parentheses.

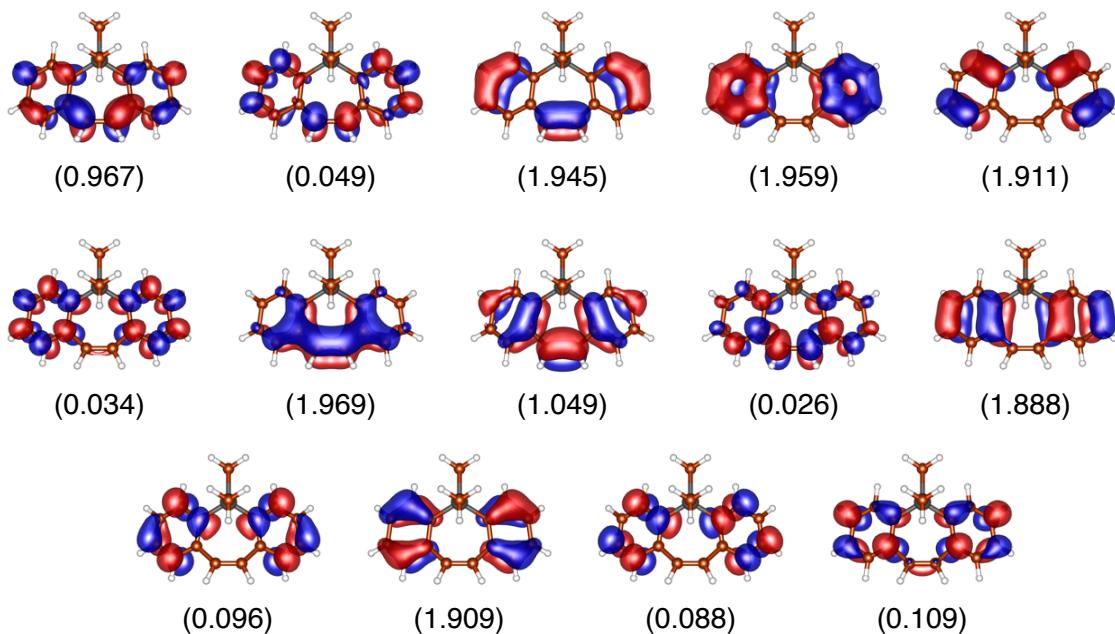


Figure S9: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_4$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{FC})$ . The occupation numbers are shown in parentheses. This eigenstate showed the largest contribution to the DMRG-XMS-CASPT2 level  $S_1$  state.

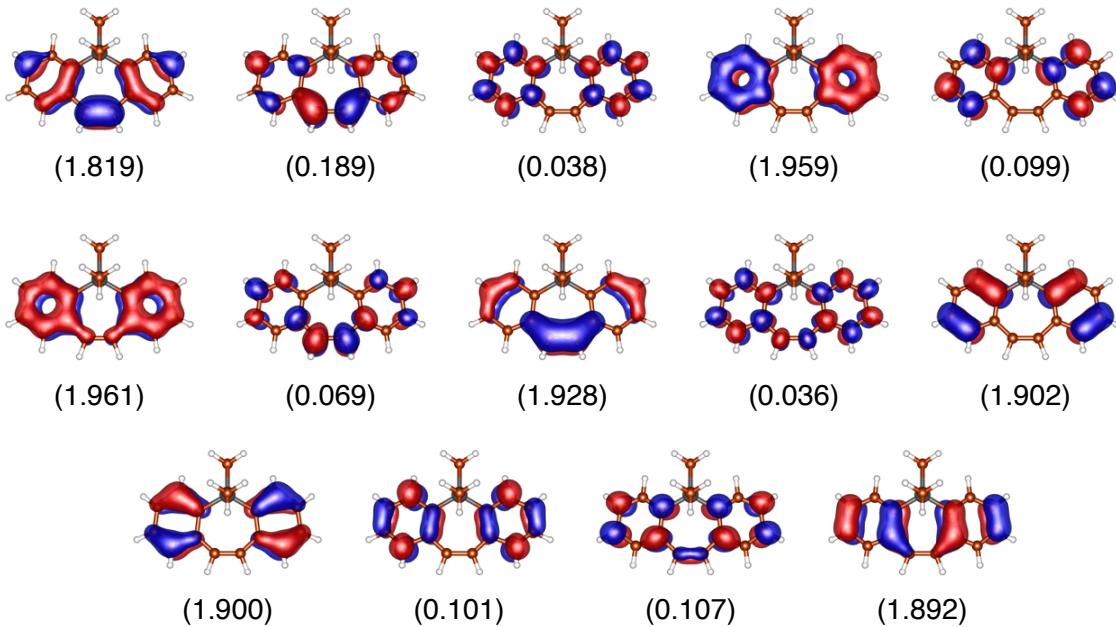


Figure S10: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_0$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{Flu})$ . The occupation numbers are shown in parentheses.

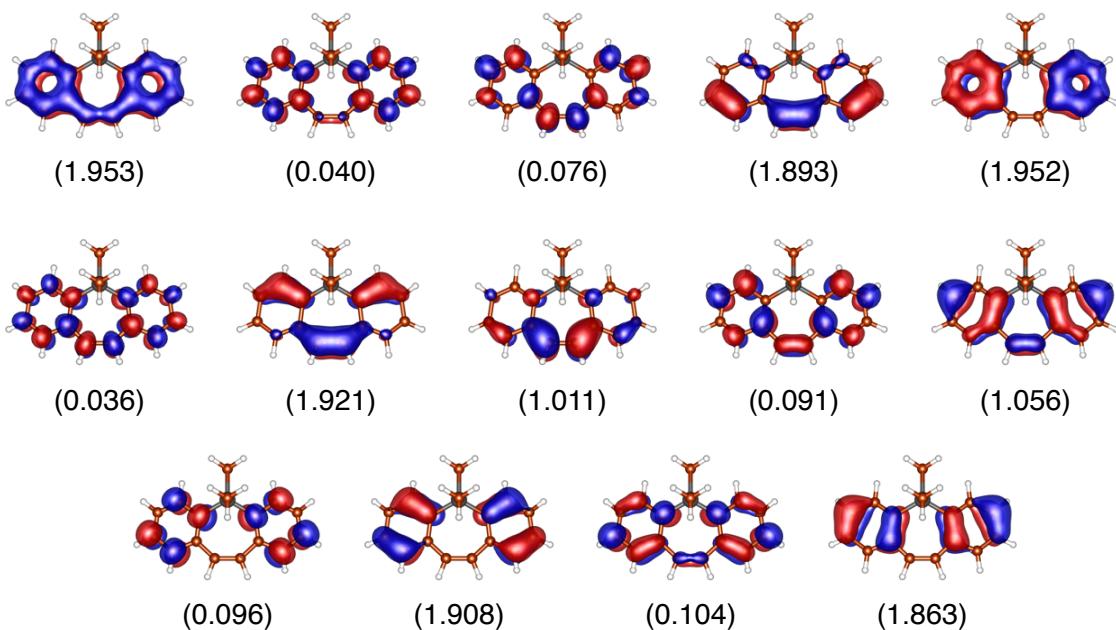


Figure S11: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_5$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{Flu})$ . The occupation numbers are shown in parentheses.

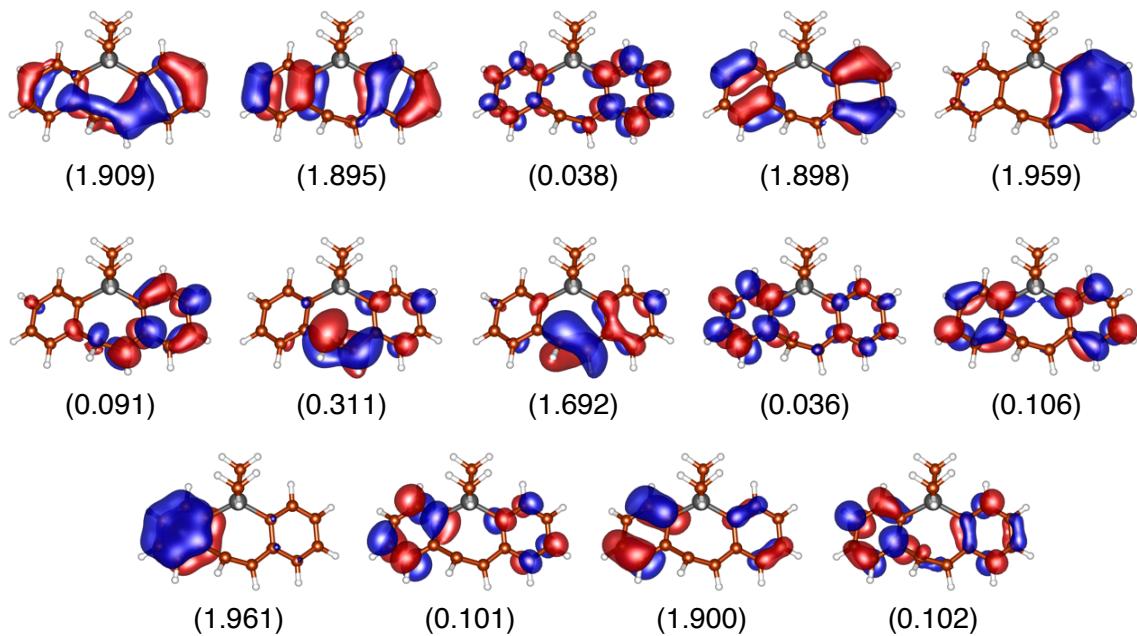


Figure S12: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_0$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{TS})$ . The occupation numbers are shown in parentheses.

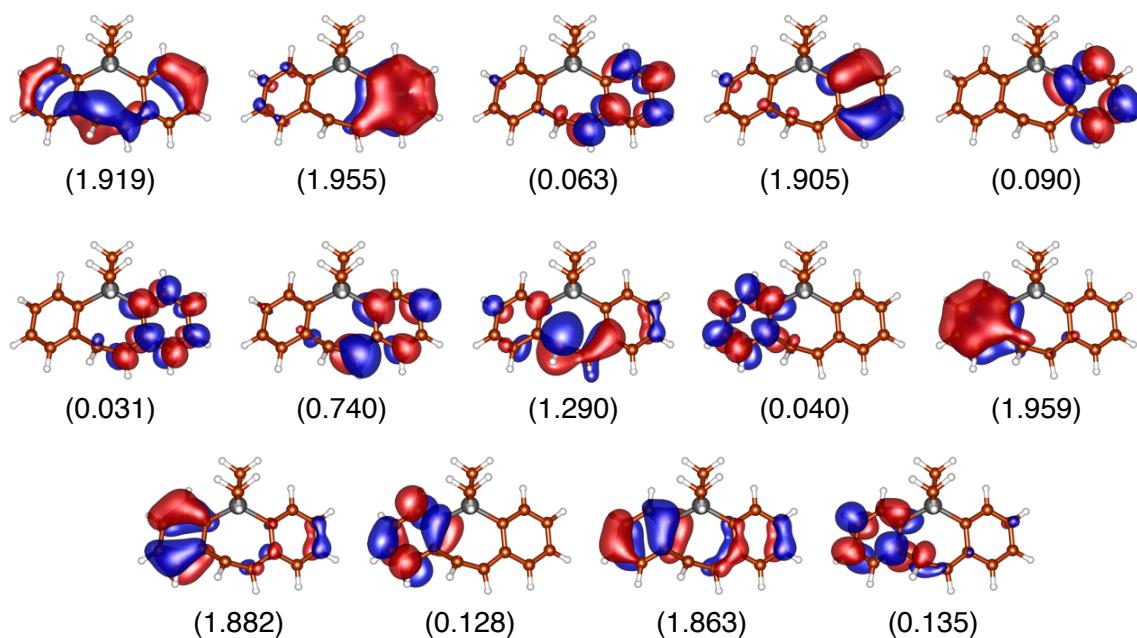


Figure S13: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_5$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{TS})$ . The occupation numbers are shown in parentheses.

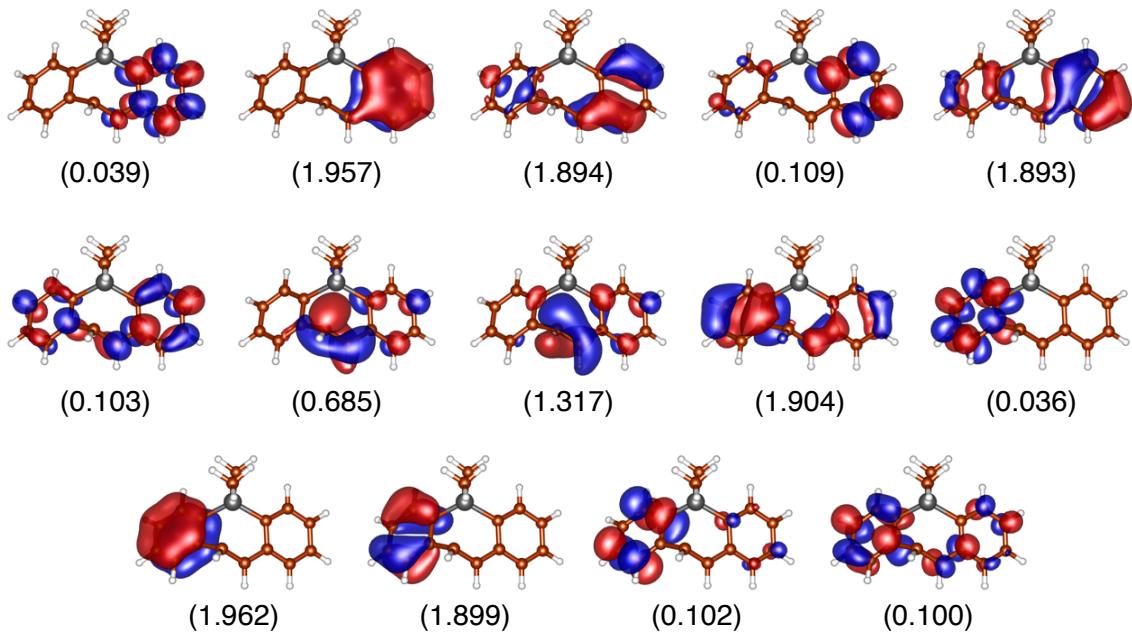


Figure S14: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_0$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{D104})$ . The occupation numbers are shown in parentheses.

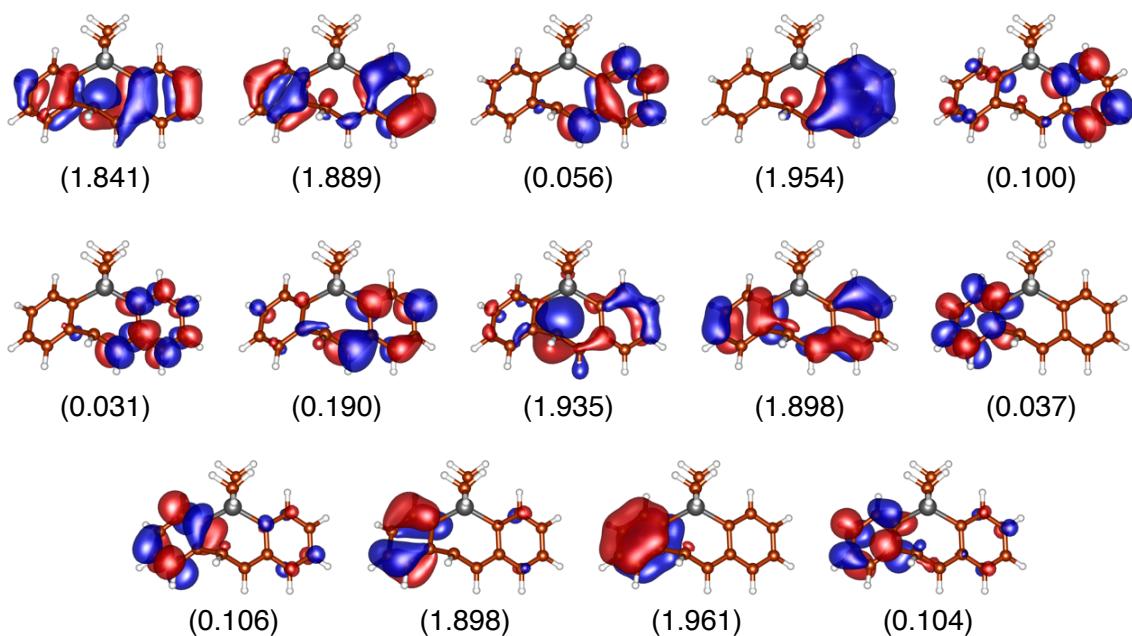


Figure S15: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_1$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{D104})$ . The occupation numbers are shown in parentheses.

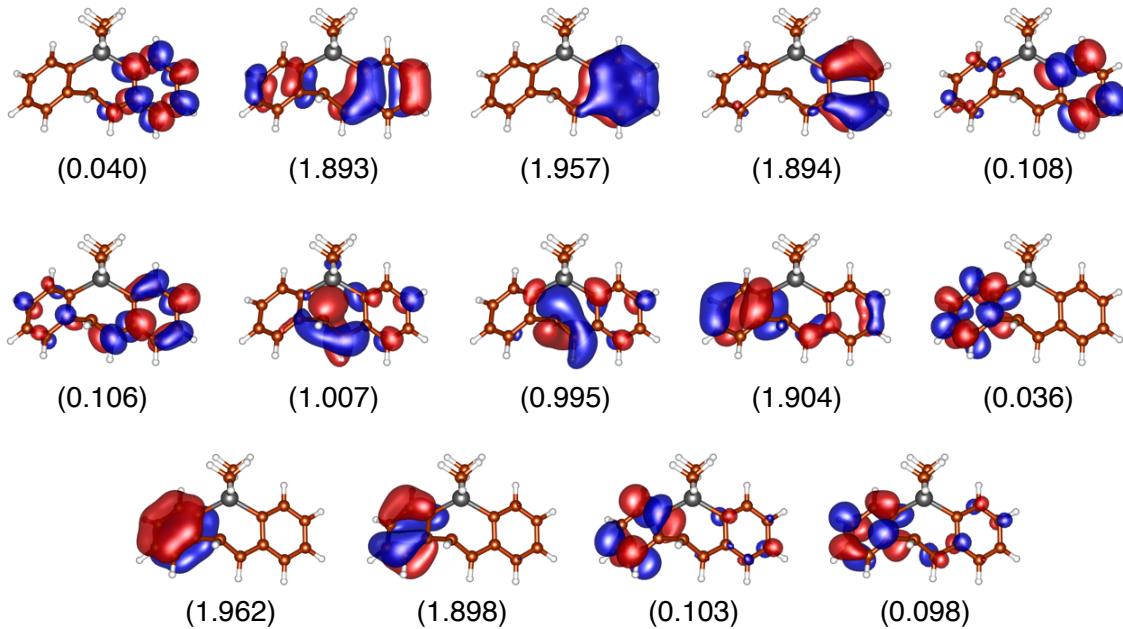


Figure S16: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_0$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{Con})$ . The occupation numbers are shown in parentheses.

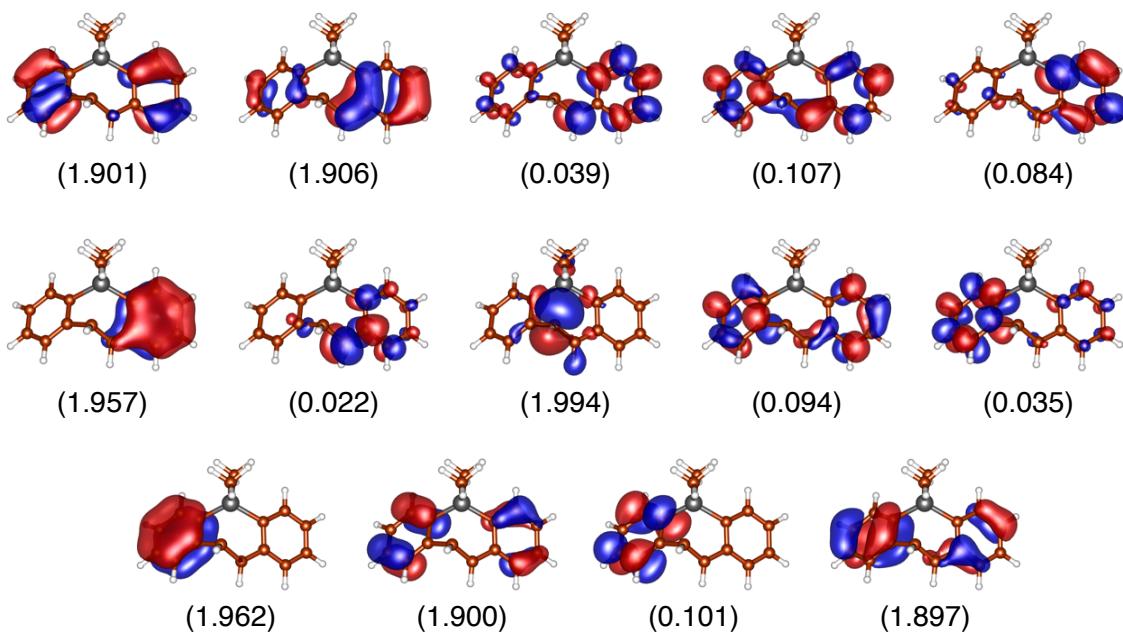


Figure S17: DMRG-CASSCF natural orbitals and their occupation numbers for the  $S_1$  state of **noPh** at the  $\mathbf{R}^{\text{DFT}}(\text{Con})$ . The occupation numbers are shown in parentheses.

Active spaces of noPh at the XMS-CASPT2 calculations using BAGEL

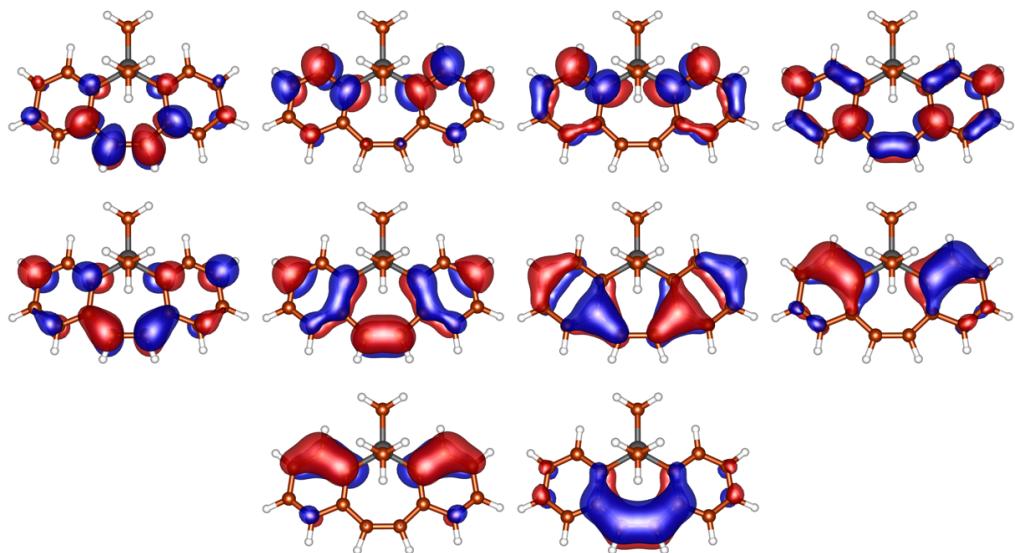


Figure S18: Active space at the XMS-CASPT2 calculation of **noPh** at the  $\mathbf{R}^{\text{XMS}}(\text{Flu})$

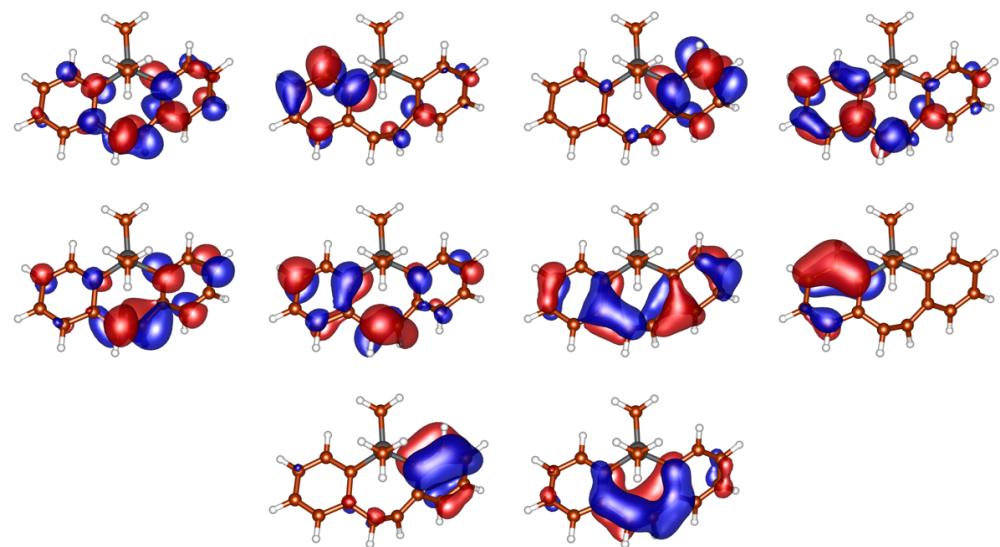


Figure S19: Active space at the XMS-CASPT2 calculation of **noPh** at the  $\mathbf{R}^{\text{XMS}}(\text{TS})$

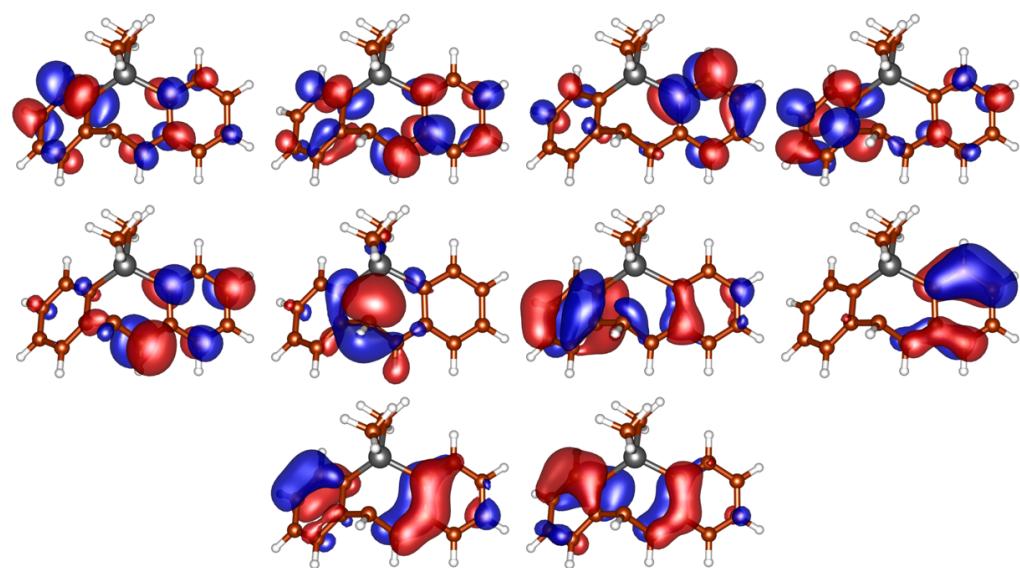


Figure S20: Active space at the XMS-CASPT2 calculation of **noPh** at the  $\mathbf{R}^{\text{XMS}}(\text{Con})$

## Choice of dihedral to plot PEC of noPh

In the manuscript, we plotted the energies with respect to the dihedral C3-C2-C4-C1. This is because the new  $S_0$  state PEC was somewhat smoothly connected at the  $\mathbf{R}^{\text{XMS}}(\text{TS})$ . The plot with respect to dihedral H2-C2-C1-H1, which corresponds to the twist at central C-C bond, is shown here. Since the new PEC is far from smooth at the  $\mathbf{R}^{\text{XMS}}(\text{TS})$ , we concluded that this dihedral was inappropriate for reaction coordinate. Note that the dihedral H2-C2-C1-H1 at the  $\mathbf{R}^{\text{XMS}}(\text{TS})$  was  $9.8^\circ$  smaller than that at the  $\mathbf{R}^{\text{DFT}}(\text{TS})$ .

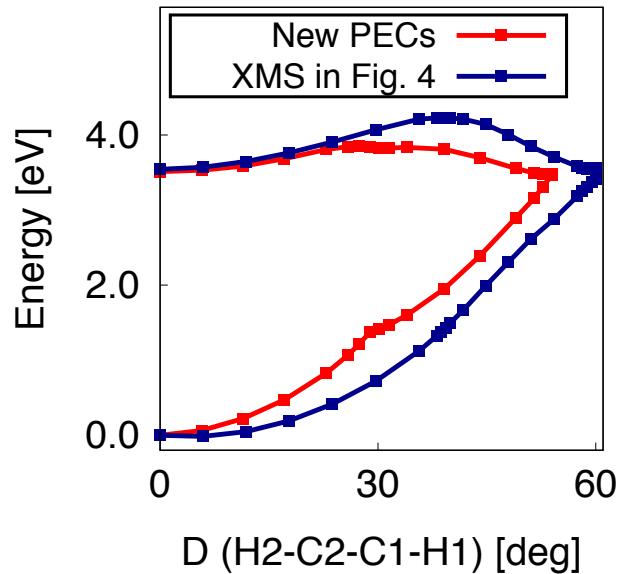


Figure S21: Computed PECs of the  $S_0$  and  $S_1$  state of **noPh**. The blue lines were plotted using the same data as those used for XMS in Figure 4. The red lines were computed along the same coordinate as red line in Figure 8. The energies of blue and red lines are given by the difference from that of the  $S_0$  state at the  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  and at the  $\mathbf{R}^{\text{XMS}}(\text{Flu})$ , respectively.

## Cartesian coordinates obtained by (TD-)DFT calculations

**Table S4: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{FC})$  of noPh (Å)**

	x	y	z
C	-1.9489999460	0.8046772970	-0.6738660390
C	-1.9489986846	0.8046768643	0.6738650676
C	-1.0761603532	0.1577841324	1.6697895923
C	-1.0761609502	0.1577844446	-1.6697897968
C	0.3100451089	-0.0603518179	1.5072915388
C	0.3100440522	-0.0603534167	-1.5072898203
H	-2.8093531549	1.3077190740	-1.1274264239
H	-2.8093521253	1.3077181215	1.1274268832
SI	1.2229349819	0.5794466795	0.0000004968
C	2.9861554484	-0.0542817504	-0.0000002485
H	3.5297767240	0.3110187348	-0.8856203761
H	3.5297783504	0.3110208783	0.8856179472
H	3.0373361235	-1.1541822121	0.0000009659
C	1.2557963649	2.4530562484	-0.0000014868
H	1.7824168812	2.8295562866	-0.8916465749
H	0.2417614076	2.8783880101	-0.0000029129
H	1.7824158142	2.8295590609	0.8916430104
C	-1.6974907957	-0.2489679235	-2.8620312597
H	-2.7650027894	-0.0575240297	-2.9931554580
C	-0.9908069032	-0.9021152815	-3.8615786298
H	-1.5011789316	-1.2171526972	-4.7736786596
C	0.3688524224	-1.1490927611	-3.6939610493
H	0.9379728588	-1.6597454839	-4.4729681407
C	1.0015024053	-0.7236346108	-2.5308821076
H	2.0726043276	-0.9061100564	-2.4221927701
C	-1.6974908296	-0.2489700815	2.8620300050
H	-2.7650032509	-0.0575276033	2.9931527346
C	1.0015036678	-0.7236324552	2.5308839854
H	2.0726059784	-0.9061071046	2.4221966309
C	-0.9908071544	-0.9021168830	3.8615777776
H	-1.5011800354	-1.2171558395	4.7736767987
C	0.3688527786	-1.1490924303	3.6939618341
H	0.9379719991	-1.6597446808	4.4729701412

**Table S5:** Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  of noPh (Å)

	x	y	z
C	-2.0689293906	0.3361880394	-0.7078974840
C	-2.0689281299	0.3361871256	0.7078965413
C	-1.1354729261	0.0436020674	1.7260214823
C	-1.1354731246	0.0436035220	-1.7260218411
C	0.2912779236	-0.1586633493	1.5594923922
C	0.2912773789	-0.1586638822	-1.5594916515
H	-3.0680008489	0.5421159376	-1.1038196855
H	-3.0680001977	0.5421122040	1.1038201062
SI	1.1926302639	0.3224813707	0.0000005608
C	2.9320437242	-0.3761296673	0.0000000090
H	3.4918455501	-0.0334585711	-0.8840399537
H	3.4918465767	-0.0334577275	0.8840389683
H	2.9347430536	-1.4771947539	0.0000005726
C	1.2783026711	2.2121853222	-0.0000016488
H	1.8058942780	2.5769620286	-0.8952284584
H	0.2638260225	2.6385523466	-0.0000023929
H	1.8058943182	2.5769647388	0.8952240023
C	-1.6755940883	-0.0779716832	-3.0528052447
H	-2.7419810498	0.1141077305	-3.1919841290
C	-0.9043503740	-0.4490603459	-4.1232812731
H	-1.3546617801	-0.5498472864	-5.1125252237
C	0.4705263355	-0.7044617834	-3.9413575267
H	1.0878501614	-1.0249976790	-4.7825095843
C	1.0369088216	-0.5332666950	-2.6825588211
H	2.1106602145	-0.7019183014	-2.5745218825
C	-1.6755943310	-0.0779747104	3.0528045813
H	-2.7419817095	0.1141030343	3.1919824774
C	1.0369099571	-0.5332633248	2.6825601242
H	2.1106617881	-0.7019130870	2.5745246770
C	-0.9043506155	-0.4490623585	4.1232809317
H	-1.3546627915	-0.5498504865	5.1125244613
C	0.4705269221	-0.7044605862	3.9413584869
H	1.0878498291	-1.0249952121	4.7825116952

**Table S6: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{Con})$  of noPh (Å)**

	x	y	z
C	-0.5198162669	-0.9127552170	1.3391186074
C	0.4644493713	-1.7518086625	0.7090739620
C	1.6194368191	-1.1649136841	0.1475049044
C	-1.7451661427	-0.8069737694	0.4464880498
C	1.6025237893	0.2535896571	0.0130939560
C	-1.6394569240	0.4247544266	-0.2118419005
H	-0.7291548432	-1.2041953001	2.3812290426
H	0.3543393855	-2.8471066664	0.5687924478
SI	-0.0341198181	1.1918352864	0.4898546167
C	0.1712628200	2.7390300226	-0.6343417687
H	-0.7155875750	3.3886193132	-0.5254238868
H	1.0432413147	3.3621353558	-0.3709287485
H	0.2524667509	2.4847689453	-1.7051013921
C	-0.0230995258	2.0453636143	2.1794172231
H	-0.9452859795	2.6398379921	2.2921636378
H	0.0376058301	1.3479479663	3.0247328886
H	0.8205313974	2.7523932215	2.2398478611
C	-2.8343459135	-1.6528708156	0.2427572427
H	-2.9120794096	-2.6125647592	0.7599058153
C	-3.8405768967	-1.2388389408	-0.6312075274
H	-4.7092086782	-1.8793647906	-0.7995583899
C	-3.7494383009	-0.0119036274	-1.2911065870
H	-4.5478036127	0.2911061473	-1.9723861938
C	-2.6509603333	0.8248326063	-1.0864701162
H	-2.5961417549	1.7876133234	-1.5998892895
C	2.7141045479	-1.9495394314	-0.2956107810
H	2.6674399000	-3.0362984288	-0.2036471341
C	2.7428112220	0.8397833063	-0.5398074860
H	2.7734097223	1.9173604501	-0.6954225221
C	3.8340408344	-1.3279440485	-0.8006277864
H	4.6991588758	-1.9089214439	-1.1226695278
C	3.8416422121	0.0706794517	-0.9169529017
H	4.7246041825	0.5655424991	-1.3313653156

**Table S7: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{TS})$  of noPh for XMS (Å)**

	x	y	z
C	-0.640865	-1.553761	1.126133
C	0.647439	-1.946699	0.617887
C	1.709550	-1.150598	0.127363
C	-1.770274	-0.990314	0.333389
C	1.590693	0.266892	-0.027138
C	-1.613203	0.338590	-0.159059
H	-0.969509	-2.218729	1.937648
H	0.852441	-3.028210	0.528455
Si	-0.024037	1.160625	0.457418
C	0.084027	2.781196	-0.541278
H	-0.811954	3.396932	-0.352423
H	0.951892	3.398381	-0.255027
H	0.138180	2.606570	-1.628697
C	-0.032057	1.790048	2.242165
H	-0.955743	2.361376	2.430996
H	0.020877	0.973832	2.975507
H	0.818106	2.470729	2.410462
C	-2.970778	-1.687269	0.077060
H	-3.104601	-2.699564	0.466274
C	-3.980324	-1.095038	-0.663799
H	-4.905365	-1.642219	-0.857397
C	-3.821552	0.199657	-1.162471
H	-4.619222	0.655398	-1.752969
C	-2.652185	0.907773	-0.902449
H	-2.554149	1.927115	-1.282858
C	2.918987	-1.809498	-0.244563
H	2.984062	-2.893007	-0.125977
C	2.698418	0.947987	-0.540620
H	2.638097	2.025408	-0.696053
C	3.991036	-1.097784	-0.725672
H	4.918048	-1.605076	-0.997002
C	3.877056	0.292063	-0.878248
H	4.719548	0.862839	-1.276987

**Table S8: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{TS})$  of noPh for STEOM (Å)**

	x	y	z
C	-0.636037	-1.522330	1.149083
C	0.641047	-1.937788	0.629904
C	1.706724	-1.151118	0.132255
C	-1.770051	-0.982268	0.343176
C	1.591448	0.266010	-0.024190
C	-1.614626	0.340817	-0.161892
H	-0.959884	-2.167537	1.978498
H	0.832333	-3.021864	0.537326
Si	-0.024995	1.162057	0.457928
C	0.087731	2.775983	-0.552832
H	-0.808279	3.393762	-0.370464
H	0.955320	3.394973	-0.269459
H	0.143846	2.593699	-1.638944
C	-0.033136	1.810314	2.235948
H	-0.957308	2.383012	2.418342
H	0.020683	1.002890	2.978809
H	0.815991	2.494230	2.396316
C	-2.964736	-1.687706	0.088056
H	-3.096679	-2.696601	0.486656
C	-3.972858	-1.106185	-0.664135
H	-4.894853	-1.658704	-0.857190
C	-3.816583	0.184031	-1.174532
H	-4.613364	0.630664	-1.773167
C	-2.651132	0.899576	-0.916393
H	-2.554637	1.915376	-1.306559
C	2.910795	-1.816428	-0.243957
H	2.971402	-2.900106	-0.124707
C	2.699851	0.942232	-0.542444
H	2.642890	2.019434	-0.700206
C	3.984227	-1.109251	-0.729053
H	4.908380	-1.620164	-1.003254
C	3.874916	0.280827	-0.882182
H	4.718614	0.847837	-1.283856

**Table S9: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{TS})$  of noPh for TD (Å)**

	x	y	z
C	-0.593736	-1.264841	1.293675
C	0.585674	-1.859527	0.719142
C	1.681771	-1.153333	0.172327
C	-1.763154	-0.917120	0.412685
C	1.596469	0.260431	-0.007054
C	-1.624880	0.356552	-0.189078
H	-0.877143	-1.749342	2.240517
H	0.666476	-2.959081	0.620749
Si	-0.032781	1.177118	0.450323
C	0.114352	2.736211	-0.651121
H	-0.781331	3.367878	-0.518370
H	0.980253	3.368292	-0.391021
H	0.184603	2.495060	-1.725222
C	-0.041152	1.962458	2.172393
H	-0.968096	2.544299	2.306934
H	0.017901	1.223019	2.982037
H	0.801399	2.665876	2.273037
C	-2.912887	-1.688883	0.182357
H	-3.026111	-2.667984	0.654426
C	-3.914411	-1.196261	-0.645642
H	-4.812758	-1.791184	-0.824211
C	-3.781708	0.055388	-1.248288
H	-4.574866	0.427200	-1.900699
C	-2.646307	0.829174	-1.017760
H	-2.564906	1.813905	-1.483740
C	2.845499	-1.870356	-0.222762
H	2.870147	-2.953900	-0.091123
C	2.712735	0.894902	-0.558578
H	2.683579	1.969052	-0.739960
C	3.932226	-1.202133	-0.735789
H	4.835101	-1.743153	-1.022374
C	3.860938	0.188572	-0.903163
H	4.716112	0.723009	-1.325554

**Table S10:** Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{TS})$  of noPh for TDA (Å)

	x	y	z
C	-0.590073	-1.243875	1.302480
C	0.580958	-1.852739	0.725730
C	1.679620	-1.153353	0.175571
C	-1.762239	-0.911848	0.417650
C	1.596811	0.260094	-0.006094
C	-1.625650	0.357651	-0.191541
H	-0.870085	-1.715355	2.256968
H	0.652899	-2.953130	0.628046
Si	-0.033426	1.178511	0.448968
C	0.116254	2.733111	-0.659324
H	-0.779377	3.365705	-0.530387
H	0.982044	3.366157	-0.401099
H	0.187534	2.487425	-1.732355
C	-0.041759	1.973946	2.166414
H	-0.968864	2.556383	2.297361
H	0.017618	1.239801	2.980799
H	0.800363	2.678529	2.262513
C	-2.908452	-1.688779	0.190309
H	-3.019899	-2.665301	0.668121
C	-3.909794	-1.203492	-0.642735
H	-4.806282	-1.801772	-0.819466
C	-3.779261	0.044852	-1.252631
H	-4.572378	0.410536	-1.908560
C	-2.646203	0.823193	-1.025158
H	-2.566225	1.805232	-1.497033
C	2.840287	-1.874540	-0.220024
H	2.862037	-2.957964	-0.086967
C	2.713870	0.891037	-0.559926
H	2.687008	1.964844	-0.743495
C	3.928232	-1.209614	-0.734985
H	4.829511	-1.753112	-1.021870
C	3.860033	0.181050	-0.904103
H	4.716250	0.712715	-1.327936

**Table S11:** Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{D104})$  of noPh (Å)

	x	y	z
C	-0.557263	-1.064263	1.362066
C	0.539318	-1.791958	0.778015
C	1.660493	-1.152538	0.203000
C	-1.752403	-0.866722	0.456659
C	1.599481	0.257843	0.000151
C	-1.632135	0.366071	-0.213784
H	-0.807427	-1.424391	2.372456
H	0.535868	-2.896861	0.691232
Si	-0.039119	1.190868	0.434064
C	0.131062	2.706936	-0.730092
H	-0.764077	3.346344	-0.632684
H	0.995956	3.347809	-0.487775
H	0.210605	2.423802	-1.793475
C	-0.046797	2.067754	2.111507
H	-0.975037	2.654479	2.213121
H	0.015093	1.377898	2.963255
H	0.792044	2.780461	2.170090
C	-2.868751	-1.686612	0.259664
H	-2.963360	-2.640118	0.785287
C	-3.870504	-1.264765	-0.610800
H	-4.751179	-1.891280	-0.768540
C	-3.760241	-0.045814	-1.281338
H	-4.554400	0.267078	-1.962934
C	-2.647052	0.770536	-1.084114
H	-2.580526	1.728547	-1.604973
C	2.795876	-1.909199	-0.192037
H	2.792750	-2.990997	-0.045255
C	2.724125	0.857887	-0.571234
H	2.717217	1.928194	-0.774536
C	3.895018	-1.273201	-0.721574
H	4.783235	-1.838048	-1.007693
C	3.853399	0.116560	-0.908044
H	4.719138	0.623846	-1.342739

**Table S12:** Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{FC})$  of *p*-Ph (Å)

	x	y	z		x	y	z
C	-0.67385100	-0.24377600	1.77767300	H	8.39028000	-3.10051900	-0.40809500
C	2.53625100	1.70876100	-0.89921800	C	0.67385100	-0.24377500	1.77767300
H	2.43658900	2.58596700	-1.54154700	C	1.67192500	0.25376700	0.81358200
C	3.88405000	-0.15763600	-0.16137000	C	-1.67192500	0.25376600	0.81358200
C	3.69824500	0.95411500	-0.99040300	C	1.50647200	1.39442100	-0.00240500
H	4.48539800	1.25113200	-1.68543600	C	-1.50647100	1.39442000	-0.00240500
C	-5.12750700	-0.96771300	-0.22851100	H	-1.12604800	-0.79301600	2.60991300
C	-5.72244100	-1.26744100	-1.46000400	H	1.12604900	-0.79301400	2.60991300
C	-5.73454000	-1.45095700	0.93704700	Si	0.00000000	2.49849700	0.15069400
C	-6.88522300	-2.02832400	-1.52454500	C	0.00000000	3.77168400	-1.22299000
H	-5.25291900	-0.91838300	-2.38131900	H	-0.88542900	4.42318400	-1.15265400
C	-6.89802700	-2.21061600	0.87374400	H	0.88542900	4.42318500	-1.15265400
H	-5.29955200	-1.20853500	1.90817100	H	0.00000000	3.30645800	-2.22102100
C	-7.47817200	-2.50336700	-0.35775300	C	-0.00000100	3.37903700	1.80470400
H	-7.32763100	-2.25810600	-2.49568300	H	-0.89169900	4.01901500	1.90149600
H	-7.35908500	-2.57088300	1.79528900	H	-0.00000100	2.66709800	2.64256700
H	-8.39028100	-3.10051700	-0.40809400	H	0.89169700	4.01901600	1.90149800
C	5.12750700	-0.96771300	-0.22851100	C	-2.86412100	-0.48093400	0.73349800
C	5.72243800	-1.26744500	-1.46000400	H	-2.98029900	-1.36006400	1.37109400
C	5.73454200	-1.45095400	0.93704700	C	-3.88405000	-0.15763600	-0.16137000
C	6.88522000	-2.02832800	-1.52454600	C	-3.69824400	0.95411400	-0.99040400
H	5.25291400	-0.91838900	-2.38131900	H	-4.48539700	1.25113100	-1.68543700
C	6.89802800	-2.21061300	0.87374400	C	-2.53625000	1.70876000	-0.89921800
H	5.29955600	-1.20852900	1.90817100	H	-2.43658800	2.58596700	-1.54154700
C	7.47817100	-2.50336800	-0.35775400	C	2.86412100	-0.48093400	0.73349800
H	7.32762500	-2.25811300	-2.49568400	H	2.98029800	-1.36006300	1.37109400
H	7.35908800	-2.57087800	1.79528900				

**Table S13: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  of *p*-Ph (Å)**

	x	y	z		x	y	z
C	-0.70876900	-1.17912400	0.72457500	H	2.59619300	2.90025500	-0.61284000
C	0.70672800	-1.18089600	0.71849500	C	4.14413600	-0.10019500	-0.13594200
C	1.72613000	-0.27156300	0.36095900	C	3.94656400	1.25918500	-0.48715400
C	-1.72809500	-0.26945500	0.36773700	H	4.79321500	1.86238100	-0.81798900
C	1.55848500	1.13402700	0.04867700	C	-5.49039700	-0.71650800	-0.23469400
C	-1.55860200	1.13450700	0.04933600	C	-6.34232900	-0.39088000	-1.29791800
H	-1.10408000	-2.15933900	1.00729600	C	-5.94225000	-1.63788500	0.71843200
H	1.10189100	-2.16290700	0.99512500	C	-7.60088300	-0.97214700	-1.40918600
Si	-0.00005800	2.08108000	0.43297300	H	-6.00225100	0.30995400	-2.06218300
C	-0.00032900	3.73109600	-0.45636900	C	-7.20134800	-2.21896700	0.60834200
H	-0.88115800	4.32798500	-0.17372500	H	-5.30562900	-1.88442100	1.56986800
H	0.88661800	4.32334300	-0.18337800	C	-8.03646000	-1.88908600	-0.45631100
H	-0.00637300	3.60727600	-1.55020700	H	-8.24433000	-0.70979800	-2.25108300
C	0.00127900	2.36870600	2.30227000	H	-7.53665100	-2.92948200	1.36622500
H	-0.89200400	2.93352500	2.61154500	H	-9.02471200	-2.34420300	-0.54204600
H	-0.00180800	1.40253500	2.82922100	C	5.48931600	-0.71937700	-0.23801300
H	0.89876500	2.92712100	2.61095600	C	6.35037500	-0.38135000	-1.29003600
C	-3.05221900	-0.81944900	0.29523900	C	5.93373100	-1.65179800	0.70791700
H	-3.17533100	-1.87553000	0.54394400	C	7.61044900	-0.96025300	-1.39671300
C	-4.14529300	-0.09732600	-0.13116100	H	6.01749600	0.32814000	-2.04954400
C	-3.94545100	1.25943200	-0.49095200	C	7.19421000	-2.23052800	0.60247600
H	-4.79078700	1.86105000	-0.82806000	H	5.29048200	-1.90903200	1.55121200
C	-2.68866400	1.83971300	-0.37375900	C	8.03875700	-1.88742800	-0.45051500
H	-2.59278900	2.89857100	-0.62315000	H	8.26085500	-0.68765800	-2.23001300
C	3.04927900	-0.82327300	0.28406900	H	7.52315200	-2.94923400	1.35543800
H	3.17036400	-1.88073600	0.52762200	H	9.02846900	-2.34009200	-0.53227300
C	2.69018400	1.84002100	-0.36873000				

**Table S14:** Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{Con})$  of *p*-Ph (Å)

	x	y	z		x	y	z
C	-0.59386100	0.85539600	1.75756200	H	2.82250900	2.90919100	-0.94907900
C	0.39447000	-0.14091800	1.41618400	C	3.81772900	-0.24471100	-0.04531400
C	1.57004200	0.24575600	0.73282900	C	3.84133500	1.06503000	-0.56893900
C	-1.77196600	0.67073600	0.81308300	H	4.73268600	1.39994800	-1.10141000
C	1.58114400	1.55969900	0.18766800	C	-4.96654300	-1.08218700	-0.20438500
C	-1.61774800	1.62311200	-0.20335300	C	-5.93033300	-1.01293200	-1.22173700
H	-0.84762400	0.86012500	2.82615800	C	-5.12233700	-2.06213300	0.78478900
H	0.24609400	-1.22032200	1.59464600	C	-7.00906700	-1.88955800	-1.24691100
Si	-0.04773300	2.60475600	0.25943600	H	-5.81748200	-0.27561400	-2.01476200
C	0.20009600	3.69783400	-1.29881800	C	-6.20039800	-2.94274900	0.76142200
H	-0.67814200	4.35540800	-1.42691500	H	-4.39781800	-2.12452600	1.59872900
H	1.07624200	4.36620700	-1.22962900	C	-7.14804100	-2.86100600	-0.25651500
H	0.30149200	3.10927500	-2.22712400	H	-7.74209500	-1.81992500	-2.05343300
C	-0.13203400	3.93404000	1.60018500	H	-6.30208000	-3.69347600	1.54388300
H	-1.16689600	4.31487700	1.66343100	H	-7.99516100	-3.54881300	-0.27707300
H	0.13892900	3.54245800	2.59026200	C	4.99498200	-1.14316300	-0.17518000
H	0.51805800	4.79219400	1.35798000	C	6.16365100	-0.70603200	-0.81005900
C	-2.84283100	-0.21760000	0.82717200	C	4.96368100	-2.44491100	0.33821300
H	-2.93411300	-0.96878000	1.61614400	C	7.26539500	-1.54558000	-0.92789200
C	-3.81407800	-0.14264400	-0.18153800	H	6.21955900	0.31390500	-1.20133700
C	-3.66586100	0.82148100	-1.19212800	C	6.06701200	-3.28158600	0.21753100
H	-4.42988800	0.89902800	-1.96665500	H	4.05735300	-2.81650400	0.81761600
C	-2.58386700	1.69816800	-1.20848600	C	7.22212600	-2.83922200	-0.41292500
H	-2.50248000	2.44279900	-2.00361800	H	8.16998800	-1.18091300	-1.42206000
C	2.64990500	-0.65556400	0.57717600	H	6.01949200	-4.29847000	0.62411100
H	2.57248000	-1.65274100	1.00773900	H	8.08704900	-3.49610500	-0.50900900
C	2.75408500	1.92861100	-0.47475100				

**Table S15: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{TS})$  of *p*-Ph (Å)**

	x	y	z		x	y	z
C	-0.680259	-0.031120	1.781952	H	2.687978	2.860985	-0.916165
C	0.601645	-0.569720	1.393990	C	3.981377	-0.190278	-0.087633
C	1.678181	0.050911	0.714633	C	3.878575	1.117884	-0.603947
C	-1.787144	0.288915	0.832931	H	4.729778	1.548848	-1.132999
C	1.583064	1.374866	0.186514	C	-5.224874	-0.932936	-0.258897
C	-1.599518	1.414896	-0.020729	C	-6.099976	-0.768056	-1.342217
H	-1.023657	-0.455132	2.733549	C	-5.557438	-1.878055	0.720232
H	0.769107	-1.640265	1.587895	C	-7.264016	-1.521793	-1.442921
Si	-0.020424	2.386531	0.347932	H	-5.850436	-0.055014	-2.127347
C	0.113975	3.626267	-1.091699	C	-6.721603	-2.634436	0.621160
H	-0.772208	4.283530	-1.102919	H	-4.904096	-2.008692	1.584695
H	0.990885	4.288890	-0.998280	C	-7.579722	-2.460285	-0.462268
H	0.169380	3.130401	-2.075216	H	-7.925830	-1.380699	-2.299901
C	-0.071467	3.502541	1.872849	H	-6.962177	-3.360321	1.397816
H	-1.074287	3.952989	1.967696	H	-8.493793	-3.051332	-0.541353
H	0.130826	2.935334	2.792489	C	5.234482	-0.974378	-0.238339
H	0.659796	4.323847	1.790800	C	6.249650	-0.541452	-1.100175
C	-2.978195	-0.458475	0.748635	C	5.432420	-2.160684	0.478209
H	-3.111867	-1.326478	1.398920	C	7.423432	-1.272986	-1.242420
C	-3.980528	-0.126447	-0.159059	H	6.120942	0.385544	-1.664802
C	-3.780291	0.979604	-1.000963	C	6.606837	-2.890658	0.334077
H	-4.562743	1.264428	-1.705564	H	4.653692	-2.521315	1.151590
C	-2.618344	1.736350	-0.922954	C	7.607909	-2.452115	-0.524443
H	-2.509515	2.601955	-1.580195	H	8.202782	-0.915147	-1.919767
C	2.869286	-0.711081	0.546831	H	6.740666	-3.815333	0.904519
H	2.900538	-1.719730	0.958563	H	8.529052	-3.025006	-0.637890
C	2.714396	1.863769	-0.472880				

**Table S16:** Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{FC})$  of *m*-Ph (Å)

	x	y	z		x	y	z
C	0.03937658	-3.25728850	-0.67405868	H	-0.83683830	1.02049328	2.42211874
C	0.03937504	-3.25728818	0.67405794	C	0.90094687	-1.49403391	3.85736324
C	0.07823738	-2.17061736	1.66600321	H	1.47015465	-1.73607148	4.75638223
C	0.07823970	-2.17061687	-1.66600286	C	0.34593878	-0.21846001	3.70514276
C	-0.51866777	-0.90054751	1.50582527	C	0.48872922	0.81534278	4.76110610
C	-0.51866553	-0.90054711	-1.50582408	C	0.67494326	2.16272599	4.42665996
H	0.11319636	-4.25096153	-1.12792591	C	0.44194672	0.47116732	6.11797460
H	0.11319351	-4.25096150	1.12792543	C	0.80789730	3.13298682	5.41442402
SI	-1.56473492	-0.50484528	-0.00000002	H	0.74046916	2.45049222	3.37613692
C	-2.03483482	1.30841114	-0.00000021	C	0.57660845	1.44033406	7.10665340
H	-2.64421143	1.55085165	-0.88502062	H	0.27405846	-0.56887507	6.40260452
H	-2.64421381	1.55085101	0.88501869	C	0.75961157	2.77623435	6.75937742
H	-1.15555274	1.97083887	0.00000111	H	0.95898648	4.17601433	5.13001842
C	-3.13041570	-1.53318127	-0.00000272	H	0.53011913	1.14973930	8.15784401
H	-3.73779290	-1.30987644	-0.89169587	H	0.86460231	3.53704229	7.53475798
H	-2.90878181	-2.61018190	-0.00000373	C	0.48872957	0.81534303	-4.76110547
H	-3.73779589	-1.30987859	0.89168890	C	0.67495667	2.16272454	-4.42665995
C	0.75839429	-2.44737964	-2.86238560	C	0.44193360	0.47116815	-6.11797361
H	1.20853076	-3.43318394	-2.99973199	C	0.80791010	3.13298479	-5.41442478
C	0.90094919	-1.49403330	-3.85736290	H	0.74049203	2.45048940	-3.37613707
H	1.47015699	-1.73606971	-4.75638229	C	0.57659472	1.44033430	-7.10665307
C	0.34594014	-0.21845995	-3.70514199	H	0.27403575	-0.56887309	-6.40260239
C	-0.36215340	0.04326063	-2.52746101	C	0.75961081	2.77623304	-6.75937791
H	-0.83683731	1.02049327	-2.42211726	H	0.95900941	4.17601109	-5.13002010
C	0.75839166	-2.44738023	2.86238604	H	0.53009480	1.14974030	-8.15784343
H	1.20852784	-3.43318458	2.99973251	H	0.86460110	3.53704050	-7.53475898
C	-0.36215516	0.04326047	2.52746183				

**Table S17: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{Flu})$  of *m*-Ph (Å)**

	x	y	z		x	y	z
C	-0.71950368	-2.03376398	0.70528818	H	2.50859677	1.74908220	-1.32905586
C	0.68744916	-2.02123371	0.74759845	C	4.09109852	-1.08882725	-0.35190898
C	1.70472143	-1.19197089	0.22399039	H	5.06665441	-1.57500817	-0.36108612
C	-1.71877290	-1.22370525	0.12015788	C	3.92146665	0.17113288	-0.98733570
C	1.53830192	0.13071118	-0.33384490	C	5.02963577	0.85135904	-1.65608884
C	-1.54531383	0.10218238	-0.42794686	C	4.80088028	1.80549157	-2.67045532
H	-1.12873409	-2.94337593	1.15549782	C	6.37175106	0.58005488	-1.31555835
H	1.08497856	-2.92388118	1.22174958	C	5.85300563	2.45213969	-3.30225119
SI	-0.02280892	1.12224311	-0.05988919	H	3.78038943	2.01666740	-2.99087861
C	-0.00278390	2.67751911	-1.10400758	C	7.42105043	1.23146879	-1.94730282
H	-0.90026155	3.28590753	-0.91239718	H	6.59380349	-0.12928418	-0.51805983
H	0.86720997	3.30317089	-0.85099834	C	7.17191906	2.17232978	-2.94604966
H	0.03682344	2.45611147	-2.18197749	H	5.64262364	3.17682593	-4.09124347
C	-0.08257929	1.59052858	1.76111209	H	8.44805390	1.00812491	-1.65190056
H	-0.97492826	2.19858785	1.97901383	H	7.99864854	2.68149018	-3.44412822
H	-0.12454225	0.68750352	2.38876723	C	-4.96222782	0.75163679	-1.96373284
H	0.81088137	2.16632867	2.04961194	C	-4.68971107	1.71436263	-2.95902989
C	-3.03408331	-1.79068938	0.04489597	C	-6.31737191	0.44840543	-1.71301024
H	-3.19580489	-2.77499752	0.48989427	C	-5.71257862	2.33924555	-3.65719978
C	-4.06730149	-1.16836963	-0.60009145	H	-3.65571793	1.94992655	-3.21195792
H	-5.03058347	-1.67377323	-0.66847967	C	-7.33758964	1.07810202	-2.41098968
C	-3.88453261	0.09477749	-1.22557001	H	-6.57528677	-0.26882335	-0.93359148
C	-2.61476190	0.69480331	-1.08205593	C	-7.04525592	2.02819909	-3.38905167
H	-2.48600369	1.70201143	-1.47970280	H	-5.46734486	3.07173485	-4.42870686
C	3.03308117	-1.73269909	0.22864999	H	-8.37634035	0.82978572	-2.18466155
H	3.18723716	-2.71456140	0.68173494	H	-7.84898817	2.52035812	-3.93914825
C	2.63342841	0.74489496	-0.92250474				

**Table S18: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{Con})$  of *m*-Ph (Å)**

	x	y	z		x	y	z
C	-0.53586777	-0.92269894	1.32229295	H	2.64896434	1.88115659	-0.82033335
C	0.49005650	-1.76804273	0.75912420	C	3.83857466	-1.31368032	-0.79111266
C	1.64565245	-1.17905547	0.22136838	H	4.69417075	-1.91446149	-1.09007681
C	-1.74929041	-0.80741788	0.41964477	C	3.81713532	0.08201737	-1.04234627
C	1.60100563	0.23144634	0.01254515	C	4.93673612	0.73921198	-1.76782476
C	-1.64045956	0.43718275	-0.20955456	C	4.87015067	2.09237718	-2.13847195
H	-0.75298876	-1.16140995	2.37754195	C	6.09387369	0.02918212	-2.12624782
H	0.39708688	-2.86603751	0.64737368	C	5.90663090	2.70346808	-2.83198942
SI	-0.02867129	1.17257077	0.50597532	H	3.99296199	2.68833499	-1.89451861
C	0.17431921	2.74572166	-0.58889012	C	7.13063547	0.63807757	-2.82213639
H	-0.70614366	3.39772178	-0.44791723	H	6.20204824	-1.02097224	-1.86200492
H	1.05321645	3.36046581	-0.32698649	C	7.04310574	1.97964895	-3.18086006
H	0.23305819	2.51578115	-1.66702140	H	5.82251119	3.75679640	-3.10345178
C	0.00246141	1.99754262	2.21096986	H	8.01478382	0.05590655	-3.08649716
H	-0.90836023	2.60740520	2.33588408	H	7.85519057	2.45818497	-3.73046079
H	0.05172534	1.28364955	3.04314441	C	-4.88481289	0.58573752	-2.19619869
H	0.85923700	2.68801232	2.28213597	C	-4.83966116	1.86298157	-2.77564702
C	-2.84672247	-1.62611833	0.16394007	C	-6.02000411	-0.19279771	-2.46767536
H	-2.94919468	-2.60788820	0.63285345	C	-5.86957591	2.33767414	-3.57944516
C	-3.84441947	-1.16568980	-0.69381930	H	-3.98719408	2.51591769	-2.59742133
H	-4.70240939	-1.81431822	-0.86917292	C	-7.05065257	0.27652370	-3.27515692
C	-3.77932023	0.09287688	-1.31753341	H	-6.11661879	-1.19003364	-2.04120905
C	-2.64302094	0.88059268	-1.06650825	C	-6.98452696	1.54698711	-3.83817921
H	-2.53761153	1.86102941	-1.53010268	H	-5.79739617	3.34050764	-4.00487794
C	2.76938777	-1.93531068	-0.19917147	H	-7.91686061	-0.36113605	-3.46231099
H	2.78449894	-3.01501116	-0.03121707	H	-7.79322221	1.91714527	-4.47047545
C	2.69294271	0.81398382	-0.62177603				

**Table S19: Cartesian coordinates of  $\mathbf{R}^{\text{DFT}}(\text{TS})$  of *m*-Ph (Å)**

	x	y	z		x	y	z
C	0.615132	3.073552	0.104737	H	-2.555338	-0.835323	0.992588
C	-0.655179	3.050000	-0.572240	C	-3.932116	1.417249	-1.147442
C	-1.713673	2.129920	-0.431630	H	-4.822898	1.603776	-1.744090
C	1.753951	2.132631	-0.088385	C	-3.823196	0.234197	-0.375963
C	-1.598382	0.966739	0.391704	C	-4.892453	-0.787464	-0.388352
C	1.591228	0.832496	0.463395	C	-4.689935	-2.063729	0.167687
H	0.932868	4.106053	0.314506	C	-6.147640	-0.528173	-0.967307
H	-0.832074	3.795175	-1.366284	C	-5.689077	-3.027321	0.146553
SI	-0.024515	0.686531	1.440250	H	-3.729452	-2.321128	0.611368
C	-0.133495	-1.171343	1.867779	C	-7.146816	-1.492164	-0.988881
H	0.742237	-1.462877	2.472504	H	-6.360647	0.447575	-1.401190
H	-1.022617	-1.418687	2.471982	C	-6.924616	-2.749396	-0.433002
H	-0.142211	-1.815402	0.972350	H	-5.497763	-4.008533	0.584092
C	-0.088619	1.486569	3.151380	H	-8.110504	-1.256928	-1.443790
H	0.808043	1.204678	3.727980	H	-7.708445	-3.508243	-0.452787
H	-0.131262	2.583159	3.102101	C	4.915203	-0.811155	-0.411439
H	-0.966242	1.125062	3.711767	C	4.722789	-2.138636	0.009681
C	2.966727	2.437106	-0.737369	C	6.183456	-0.481711	-0.920326
H	3.124483	3.429983	-1.165342	C	5.739249	-3.081994	-0.070279
C	3.970219	1.490120	-0.841640	H	3.756706	-2.450951	0.403623
H	4.888859	1.767315	-1.358373	C	7.200777	-1.424840	-1.002792
C	3.828149	0.194895	-0.310264	H	6.392891	0.535671	-1.248448
C	2.617768	-0.098629	0.340285	C	6.987812	-2.733656	-0.578328
H	2.478402	-1.083464	0.785914	H	5.550808	-4.102707	0.268130
C	-2.907064	2.324139	-1.186363	H	8.173860	-1.130225	-1.400590
H	-2.999158	3.220012	-1.805041	H	7.786501	-3.474433	-0.642754
C	-2.652507	0.060433	0.383180				

## Cartesian coordinates obtained using XMS-CASPT2 calculations

**Table S20:** Cartesian coordinates of R<sup>XMS</sup>(Flu) of noPh (Å)

	x	y	z
C	-0.71608000	-2.04488600	0.38862100
C	0.71594900	-2.04494700	0.38832000
C	1.73153900	-1.11968100	0.05171300
C	-1.73164900	-1.11962000	0.05198900
C	1.55049700	0.30649300	-0.18036500
C	-1.55042300	0.30646700	-0.18051400
H	-1.10940900	-3.03934800	0.62988200
H	1.10926200	-3.03946700	0.62933200
Si	-0.00002600	1.18496300	0.40014900
C	-0.00010200	2.97713400	-0.17448800
H	-0.88524500	3.50720800	0.20651600
H	0.88482200	3.50753400	0.20657000
H	-0.00017500	3.05379500	-1.27147100
C	0.00021300	1.09983500	2.28872900
H	-0.89395500	1.587778100	2.70476800
H	0.00010900	0.04832400	2.61043600
H	0.89491700	1.58729900	2.70424600
C	-3.06031000	-1.66098100	-0.08884500
H	-3.21439000	-2.72147900	0.13171300
C	-4.11998600	-0.89084000	-0.52751600
H	-5.10808800	-1.34134600	-0.64788900
C	-3.91878000	0.47676600	-0.82769200
H	-4.74723000	1.08717300	-1.19836100
C	-2.65528500	1.05324800	-0.62049300
H	-2.53694400	2.12353600	-0.81149800
C	3.06014300	-1.66114400	-0.08937100
H	3.21412400	-2.72172700	0.13084700
C	2.65544300	1.05330500	-0.62006100
H	2.53719000	2.12367200	-0.81070100
C	4.11992000	-0.89095400	-0.52770900
H	5.10797900	-1.34153300	-0.64819000
C	3.91890300	0.47678400	-0.82739000
H	4.74743500	1.08721800	-1.19783600

**Table S21:** Cartesian coordinates of  $\mathbf{R}^{\text{XMS}}(\text{Con})$  of noPh (Å)

	x	y	z
C	-0.55694500	-0.72698200	1.57142300
C	0.36386400	-1.65453300	0.92058200
C	1.51208800	-1.16215600	0.24473900
C	-1.69990700	-0.76326700	0.57661400
C	1.59136900	0.25354700	0.05135300
C	-1.56046600	0.37414600	-0.26195400
H	-0.81414300	-0.98327500	2.61368100
H	0.18147100	-2.74587400	0.86326500
Si	-0.01145800	1.29773000	0.37053900
C	0.22192300	2.65118800	-0.97763700
H	-0.66047500	3.31232800	-0.99437600
H	1.09379600	3.29790600	-0.78743000
H	0.33321600	2.22350200	-1.98710100
C	-0.08464000	2.37006700	1.93069900
H	-1.05024400	2.90048900	1.95326500
H	0.01120500	1.78147500	2.85025800
H	0.70561000	3.13744400	1.90216900
C	-2.75251100	-1.66286100	0.41362800
H	-2.85038200	-2.54394500	1.05569300
C	-3.73630300	-1.37835100	-0.55382700
H	-4.58830400	-2.05191800	-0.68021000
C	-3.63294500	-0.22935000	-1.35917500
H	-4.41256800	-0.02277400	-2.09698800
C	-2.55702800	0.65552300	-1.21364700
H	-2.49693700	1.55082000	-1.83776000
C	2.54818700	-2.03520100	-0.18188000
H	2.44046200	-3.11540600	-0.05214100
C	2.78115900	0.75423500	-0.49087000
H	2.89014400	1.82428800	-0.67890300
C	3.73086000	-1.49149600	-0.68676800
H	4.55931700	-2.14138200	-0.97494100
C	3.84044700	-0.10616900	-0.83316300
H	4.76334100	0.31806600	-1.23672600

**Table S22:** Cartesian coordinates of  $\mathbf{R}^{\text{XMS}}(\text{TS})$  of noPh (Å)

	x	y	z
C	-0.72535500	-1.78331100	0.98984500
C	0.51221900	-1.98015000	0.24173200
C	1.60595200	-1.15213800	-0.07860500
C	-1.73982600	-1.02716300	0.37883200
C	1.62853200	0.27297200	0.15478000
C	-1.42284400	0.21476700	-0.33094900
H	-1.04499500	-2.66999000	1.55097300
H	0.66526200	-3.02757400	-0.07025800
Si	0.00730400	1.22804000	0.32496900
C	0.18857300	2.82513100	-0.65992000
H	-0.73359200	3.42250900	-0.60555600
H	1.00481600	3.44460700	-0.25992000
H	0.40565200	2.61981700	-1.71812500
C	-0.34039000	1.62672200	2.13465300
H	-1.23633200	2.25859600	2.22516000
H	-0.50414800	0.69728900	2.69668800
H	0.50948000	2.16029800	2.58622200
C	-3.12136800	-1.44229300	0.41950400
H	-3.39101200	-2.30860500	1.03035600
C	-4.06565900	-0.82390400	-0.37333200
H	-5.09835600	-1.18196100	-0.36234200
C	-3.71004400	0.26956700	-1.21371800
H	-4.46369400	0.73656800	-1.85175600
C	-2.40444700	0.78576400	-1.15651400
H	-2.17778100	1.69878700	-1.71497500
C	2.78940300	-1.79261500	-0.57158700
H	2.75619400	-2.86080200	-0.80343900
C	2.85876400	0.93145200	0.06976800
H	2.91191600	2.00768700	0.25750600
C	3.98778100	-1.09334000	-0.67509700
H	4.88853700	-1.60469200	-1.02142800
C	4.03160700	0.26718400	-0.33938400
H	4.96840600	0.82302800	-0.42871900

**Table S23:** Cartesian coordinates of  $\mathbf{R}_r^{\text{XMS}}(\text{Flu})$  of *p*-Ph ( $\text{\AA}$ )<sup>a</sup>

	x	y	z		x	y	z
C	-0.71535600	-1.12527800	0.84094800	H	2.55481700	2.87222900	-0.81446100
C	0.71535300	-1.12547300	0.84004300	C	4.13906600	-0.09423500	-0.17511400
C	1.73286400	-0.24496700	0.40461800	C	3.92812800	1.23434400	-0.62719300
C	-1.73278800	-0.24511000	0.40478800	H	4.76885900	1.80976800	-1.02442800
C	1.55174900	1.14284100	0.00305600	C	-5.47628500	-0.71446800	-0.25790200
C	-1.55100800	1.14192500	0.00075800	C	-6.27514100	-0.54339600	-1.40256100
H	-1.10810200	-2.08543200	1.19398300	C	-5.97708100	-1.48645100	0.80520000
H	1.10815500	-2.08608500	1.19177300	C	-7.53850600	-1.13326100	-1.48346600
Si	-0.00026800	2.08897100	0.45822800	H	-5.88876100	0.03717700	-2.24315000
C	-0.00022700	3.78780100	-0.35016100	C	-7.23835200	-2.08088500	0.72120500
H	-0.88490300	4.36369200	-0.04274900	H	-5.37761900	-1.60034600	1.71112700
H	0.88414700	4.36396300	-0.04235300	C	-8.02411500	-1.90495900	-0.42249600
H	0.00008000	3.71758600	-1.44719700	H	-8.14334300	-0.99785500	-2.38246400
C	-0.00193400	2.25585500	2.34088900	H	-7.61550300	-2.67253600	1.55789800
H	-0.89641600	2.79477600	2.68652700	H	-9.01160000	-2.36595800	-0.48621200
H	-0.00217900	1.25732800	2.80100700	C	5.47651000	-0.71434600	-0.25741500
H	0.89180600	2.79497700	2.68815400	C	6.27619300	-0.54028300	-1.40098500
C	-3.05669600	-0.79930700	0.33508100	C	5.97616000	-1.48988600	0.80357500
H	-3.20042000	-1.83808000	0.64680100	C	7.53923100	-1.13071200	-1.48289700
C	-4.13853400	-0.09488900	-0.17662300	H	5.89072700	0.04312900	-2.23998500
C	-3.92661400	1.23230400	-0.63242200	C	7.23709300	-2.08489600	0.71854300
H	-4.76678600	1.80689400	-1.03205100	H	5.37605500	-1.60619100	1.70871700
C	-2.66147100	1.82690000	-0.51160300	C	8.02368000	-1.90598500	-0.42405200
H	-2.55274400	2.86946900	-0.82232400	H	8.14471600	-0.99291900	-2.38104200
C	3.05653800	-0.79963300	0.33376300	H	7.61331800	-2.67936800	1.55360900
H	3.19967000	-1.83926800	0.64285000	H	9.01089300	-2.36745600	-0.48856900
C	2.66302200	1.82893600	-0.50602000				

<sup>a</sup> This geometry was obtained by fully-relaxed optimization.

**Table S24:** Cartesian coordinates of  $\mathbf{R}_c^{\text{XMS}}(\text{Flu})$  of *p*-Ph ( $\text{\AA}$ )<sup>a</sup>

	x	y	z		x	y	z
C	-0.71602800	-1.01889500	0.99191900	H	2.53718300	2.73930900	-1.17407700
C	0.71600100	-1.01898300	0.99167800	C	4.11997500	-0.11888200	-0.17477500
C	1.73158000	-0.20171300	0.44257600	C	3.91893500	1.13672800	-0.79441200
C	-1.73160800	-0.20169300	0.44274100	H	4.74746400	1.64025700	-1.30069600
C	1.55051200	1.12686900	-0.12548500	C	-5.47141900	-0.74233400	-0.18715200
C	-1.55040800	1.12671400	-0.12570200	C	-6.62175800	0.03926300	-0.01700000
H	-1.10934100	-1.92623100	1.46511700	C	-5.63175000	-2.12232200	-0.36817500
H	1.10933000	-1.92641100	1.46466800	C	-7.88726900	-0.53888000	-0.01914500
Si	-0.00005000	2.11906700	0.22683300	H	-6.52135000	1.11488300	0.14213900
C	-0.00015000	3.72058900	-0.76170800	C	-6.89650700	-2.70182800	-0.37162800
H	-0.88531800	4.32667200	-0.51929900	H	-4.75187500	-2.74764200	-0.53217600
H	0.88474900	4.32705500	-0.51928000	C	-8.03044500	-1.91262000	-0.19631300
H	-0.00019000	3.53134300	-1.84496000	H	-8.76916000	0.08938700	0.12470400
C	0.00013100	2.49035500	2.08051200	H	-6.99736200	-3.77902100	-0.52209100
H	-0.89406200	3.06396500	2.36705500	H	-9.02355600	-2.36688100	-0.20044700
H	0.00004100	1.54699000	2.64551900	C	5.47142000	-0.74231500	-0.18718800
H	0.89481000	3.06342700	2.36670900	C	6.62179200	0.03914900	-0.01664300
C	-3.06025100	-0.76107500	0.43611800	C	5.63166100	-2.12225500	-0.36864400
H	-3.21431300	-1.73747900	0.90509800	C	7.88726000	-0.53908200	-0.01885200
C	-4.11993100	-0.11897600	-0.17482400	H	6.52142700	1.11471900	0.14285200
C	-3.91874800	1.13639900	-0.79490000	C	6.89637700	-2.70184700	-0.37216300
H	-4.74720100	1.63979700	-1.30143600	H	4.75174500	-2.74744500	-0.53291900
C	-2.65527300	1.74582100	-0.73230000	C	8.03034900	-1.91277300	-0.19647000
H	-2.53695100	2.73883000	-1.17494700	H	8.76919000	0.08905900	0.12530200
C	3.06020200	-0.76117200	0.43580200	H	6.99718200	-3.77899700	-0.52297100
H	3.21420100	-1.73773200	0.90448000	H	9.02342900	-2.36710400	-0.20064600
C	2.65545500	1.74614200	-0.73176000				

<sup>a</sup> This geometry was optimized at TD-CAM-B3LYP/def2-SVP level with the skeleton of **noPh** fixed at  $\mathbf{R}^{\text{XMS}}(\text{Flu})$ .

**Table S25:** Cartesian coordinates of  $\mathbf{R}_c^{\text{XMS}}(\text{TS})$  of *p*-Ph ( $\text{\AA}$ )<sup>a</sup>

	x	y	z		x	y	z
C	-0.70427500	-0.46391800	1.57818400	H	2.81798700	3.07817500	-0.20646500
C	0.59404200	-0.82308400	1.01659700	C	4.08981000	-0.07765600	0.05198200
C	1.67379800	-0.08465000	0.49380400	C	4.05132700	1.31551300	-0.10048800
C	-1.69947800	-0.02972700	0.68639000	H	4.96834900	1.86736300	-0.32200200
C	1.61930500	1.33275900	0.22196000	C	5.38191000	-0.80645100	-0.07803200
C	-1.38087500	0.91316300	-0.38883500	C	5.45066900	-2.04144800	-0.73533000
H	-1.02888100	-1.12462600	2.39140600	C	6.56301300	-0.27444400	0.45459900
H	0.81384200	-1.90172300	1.09459200	C	6.65784400	-2.72287700	-0.85383200
Si	-0.04841400	2.18054500	-0.04161400	H	4.54668600	-2.46313100	-1.17960600
C	0.14132100	3.35367700	-1.50494100	C	7.77109400	-0.95495400	0.33760800
H	-0.80628400	3.87216900	-1.71330100	H	6.53001000	0.67773200	0.98816100
H	0.89814000	4.12437100	-1.29695100	C	7.82390700	-2.18260300	-0.31734400
H	0.44711400	2.81408400	-2.41290800	H	6.68897200	-3.68101100	-1.37747200
C	-0.54988300	3.14946400	1.49608500	H	8.67812700	-0.52473400	0.76816600
H	-1.47556300	3.71435200	1.31119100	H	8.77189400	-2.71675200	-0.41048300
H	-0.71749500	2.45915400	2.33389400	C	-5.35269600	-0.78780000	-0.13053400
H	0.24005000	3.85941300	1.78396600	C	-5.99414700	-1.31998600	-1.25621400
C	-3.06166500	-0.49528200	0.78812800	C	-6.04887500	-0.77749600	1.08490200
H	-3.34111600	-1.11665400	1.64378500	C	-7.28623800	-1.82889400	-1.16921900
C	-3.96731800	-0.24775100	-0.22241600	H	-5.46425800	-1.35672400	-2.21029800
C	-3.59407200	0.51387100	-1.36653500	C	-7.34157900	-1.28399000	1.17295500
H	-4.31538000	0.68474300	-2.16883600	H	-5.57659800	-0.34552500	1.96962700
C	-2.31922700	1.10264700	-1.41583500	C	-7.96588900	-1.81270000	0.04596300
H	-2.08853900	1.78289800	-2.24100800	H	-7.76364300	-2.24743800	-2.05801000
C	2.91706800	-0.77623200	0.32119600	H	-7.86866600	-1.25815700	2.12928200
H	2.94604900	-1.85914100	0.47069600	H	-8.98070500	-2.21024800	0.11443200
C	2.82405700	2.00147800	-0.01401100				

<sup>a</sup> This geometry was optimized at TD-CAM-B3LYP/def2-SVP level with the skeleton of **noPh** fixed at  $\mathbf{R}^{\text{XMS}}(\text{TS})$ .

**Table S26:** Cartesian coordinates of  $\mathbf{R}_r^{\text{XMS}}(\text{Flu})$  of *m*-Ph (Å)<sup>a</sup>

	x	y	z		x	y	z
C	0.71332800	3.08886300	-0.50149800	H	-2.49299300	-1.09722700	0.65331200
C	-0.70990400	3.09051100	-0.49585800	C	-4.09103200	1.58065000	-0.72331000
C	-1.71737300	2.11430400	-0.31344900	H	-5.06498100	1.89037900	-1.10830100
C	1.71968400	2.11524600	-0.31317000	C	-3.89979500	0.23950600	-0.28426800
C	-1.53646600	0.78069300	0.23238600	C	-4.98014100	-0.73934800	-0.31623900
C	1.53900900	0.78461700	0.23332900	C	-4.70943600	-2.11373700	-0.50608900
H	1.11379700	4.05986600	-0.81395100	C	-6.32871400	-0.34721900	-0.15730400
H	-1.11033500	4.06271700	-0.80475100	C	-5.74069400	-3.05229000	-0.52866800
Si	0.00059400	0.34707400	1.21245700	H	-3.68068900	-2.43945800	-0.67164200
C	0.00644500	-1.47936500	1.66371000	C	-7.35751300	-1.28794800	-0.18405900
H	0.89272200	-1.72864400	2.26501300	H	-6.56538900	0.70287300	0.02385100
H	-0.87718200	-1.73297300	2.26704800	C	-7.07068100	-2.64591000	-0.36885300
H	0.00671300	-2.11957500	0.76992500	H	-5.50733200	-4.10735600	-0.68692100
C	0.00462900	1.41268700	2.76914600	H	-8.39086200	-0.96205200	-0.04783200
H	0.89582800	1.20942000	3.38124600	H	-7.87732500	-3.38114100	-0.38916100
H	0.01175700	2.47661000	2.49290600	C	4.97655800	-0.74082000	-0.31725600
H	-0.89202900	1.22078300	3.37686700	C	4.70035800	-2.11700300	-0.48984200
C	3.05336200	2.48368600	-0.72858800	C	6.32788200	-0.35064400	-0.17412600
H	3.21320100	3.49826200	-1.10394500	C	5.72861500	-3.05845300	-0.50895400
C	4.09763800	1.58777500	-0.73111300	H	3.66971500	-2.44160600	-0.64514200
H	5.07150600	1.89232500	-1.11816800	C	7.35341300	-1.29485900	-0.19604900
C	3.90006800	0.23999800	-0.28654300	H	6.56979000	0.70064800	-0.00800100
C	2.61838600	-0.09653600	0.21829500	C	7.06098800	-2.65400100	-0.36287000
H	2.49504500	-1.09101600	0.65549700	H	5.49132900	-4.11449900	-0.65390600
C	-3.04707300	2.47980600	-0.72428100	H	8.38867800	-0.97066900	-0.07126000
H	-3.21361400	3.49407500	-1.09876400	H	7.86527300	-3.39190900	-0.38022000
C	-2.61503200	-0.10168400	0.21916800				

<sup>a</sup> This geometry was obtained by fully-relaxed optimization.

**Table S27:** Cartesian coordinates of  $\mathbf{R}_c^{\text{XMS}}(\text{Flu})$  of *m*-Ph (Å)<sup>a</sup>

	x	y	z		x	y	z
C	0.71613100	3.05734000	-0.42607000	H	-2.53713400	-1.17038700	0.54429300
C	-0.71589800	3.05723000	-0.42643300	C	-4.11983900	1.60386700	-0.66882100
C	-1.73148300	2.08471700	-0.27264900	H	-5.10788600	1.93964400	-0.99257100
C	1.73170500	2.08484100	-0.27220800	C	-3.91882500	0.26219100	-0.26829600
C	-1.55044800	0.72467400	0.21532500	C	5.03224400	-0.69942300	-0.31197800
C	1.55047200	0.72466400	0.21533500	C	4.80282600	-2.08137600	-0.46756400
H	1.10946100	4.04418200	-0.69681700	C	6.37221100	-0.27747900	-0.19992000
H	-1.10921000	4.04399200	-0.69746500	C	5.85304800	-2.98866200	-0.50478900
Si	0.00003500	0.23747800	1.14885000	H	3.78310100	-2.44752300	-0.59524000
C	0.00011600	-1.60870800	1.51447500	C	7.42114700	-1.18645000	-0.23329700
H	0.88523300	-1.88780300	2.10463900	H	6.59537700	0.77986900	-0.05100900
H	-0.88483400	-1.88808400	2.10475700	C	7.17065500	-2.54917000	-0.38655500
H	0.00024200	-2.20726200	0.59198800	H	5.64142100	-4.05205500	-0.63803800
C	-0.00029600	1.22696900	2.75971600	H	8.44785700	-0.82769100	-0.13099200
H	0.89384500	1.00170200	3.36011800	H	7.99633600	-3.26315600	-0.41567700
H	-0.00019400	2.30268800	2.53168200	C	-5.03229300	-0.69936500	-0.31191800
H	-0.89502700	1.00184800	3.35933900	C	-6.37228300	-0.27733100	-0.20012500
C	3.06037900	2.49020000	-0.65763400	C	-4.80297000	-2.08138200	-0.46705800
H	3.21446200	3.52477600	-0.97849800	C	-7.42127300	-1.18624900	-0.23342800
C	4.12006700	1.60396500	-0.66819100	H	-6.59543700	0.78004200	-0.05149900
H	5.10818100	1.93975400	-0.99171500	C	-5.85325700	-2.98860900	-0.50421000
C	3.91885800	0.26215800	-0.26818300	H	-3.78327200	-2.44769600	-0.59440000
C	2.65534600	-0.14177000	0.19231700	C	-7.17085000	-2.54901800	-0.38632200
H	2.53700000	-1.17059100	0.54377900	H	-8.44795800	-0.82736500	-0.13131300
C	-3.06007300	2.49001100	-0.65847400	H	-5.64163600	-4.05203800	-0.63718400
H	-3.21405200	3.52449300	-0.97969200	H	-7.99656600	-3.26296500	-0.41542400
C	-2.65538200	-0.14167700	0.19246100				

<sup>a</sup> This geometry was optimized at TD-CAM-B3LYP/def2-SVP level with the skeleton of **noPh** fixed at  $\mathbf{R}^{\text{XMS}}(\text{Flu})$ .

**Table S28:** Cartesian coordinates of  $\mathbf{R}_c^{\text{XMS}}(\text{TS})$  of *m*-Ph (Å)<sup>a</sup>

	x	y	z		x	y	z
C	0.68430300	3.00945300	0.02299500	H	-2.88947200	-0.73399300	1.18595000
C	-0.42039900	2.64126900	-0.85682300	C	-3.73688800	1.14223600	-1.53530900
C	-1.47238500	1.70828900	-0.77112200	H	-4.56218600	1.28741800	-2.23573200
C	1.76132800	2.11259800	0.12259800	C	-3.86368200	0.23948500	-0.47012700
C	-1.56420900	0.69485900	0.25379200	C	5.03585900	-0.67540200	-0.30494000
C	1.52604600	0.67202800	0.24931300	C	6.32513800	-0.39994600	0.18102500
H	0.93625800	4.07648600	-0.01152000	C	4.84102900	-1.88783000	-0.98827400
H	-0.49923200	3.29162600	-1.74489900	C	7.37024000	-1.29714000	-0.00462900
Si	-0.01088600	0.13938400	1.17473400	H	6.50712100	0.51962400	0.73970800
C	-0.07883400	-1.73953100	1.31121300	C	5.88660300	-2.78380900	-1.17599300
H	0.80984800	-2.12405700	1.83331200	H	3.85853700	-2.11768800	-1.40433400
H	-0.96089800	-2.06165400	1.88410400	C	7.15771100	-2.49427000	-0.68467300
H	-0.12790700	-2.21093900	0.31902300	H	8.36009100	-1.06216200	0.39294900
C	0.04863200	0.90555200	2.89643100	H	5.70892800	-3.71431200	-1.71975300
H	0.90509400	0.51259300	3.46407800	H	7.97947700	-3.19816300	-0.83193300
H	0.14743900	1.99657500	2.81610800	C	-5.12174200	-0.51917600	-0.28517200
H	-0.87242600	0.68059800	3.45495000	C	-5.57624200	-0.86949400	0.99717200
C	3.13024900	2.56876700	0.09789800	C	-5.90511700	-0.91129200	-1.38317700
H	3.32477000	3.64505700	0.10813400	C	-6.75841200	-1.57893800	1.17348900
C	4.16880200	1.67121200	-0.03804500	H	-5.00681400	-0.55465500	1.87358100
H	5.19615300	2.03928800	-0.10016600	C	-7.08684700	-1.62218400	-1.20757100
C	3.91871100	0.27088200	-0.10818400	H	-5.56860100	-0.67935400	-2.39525000
C	2.60756800	-0.20390900	0.06442400	C	-7.52122700	-1.96051000	0.07192600
H	2.44645000	-1.28404700	0.12930900	H	-7.09244000	-1.82865000	2.18313400
C	-2.55168900	1.85145500	-1.70300500	H	-7.67071300	-1.92243000	-2.08064600
H	-2.45813800	2.57878400	-2.51425200	H	-8.44992500	-2.51812500	0.21010400
C	-2.78271400	0.02714500	0.40773200				

<sup>a</sup> This geometry was optimized at TD-CAM-B3LYP/def2-SVP level with the skeleton of **noPh** fixed at  $\mathbf{R}^{\text{XMS}}(\text{TS})$ .