Supporting Information For Publication: Substitution enables significant new decay channels in non-canonical amino acid

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S1 Computational details

The ground state geometries of Ind and 7F-Ind are optimized with resolution of identity Moller Plesset perturbation (RI-MP2) theory at the cc-PVTZ basis. These are also optimized with (10o,8e) active space for Ind and (11o,8e) active space for 7F-Ind at SA-CASSCF/6-311++G(d,p) level of theory for comparison. The Cartesian coordinates of the optimized geometries of Ind and 7F-Ind are given in section S6 of Supporting Information (SI).

The vertical excitation energies (VEEs) have been calculated at different levels of theories: (i) equation of motion couple cluster single and doubles (EOM-EE-CCSD), (ii) state-averaged complete active space self-consistent field theory (SA-CASSCF), and (iii) multi-state complete active space self-consistent including second-order perturbation theory (MS-CASPT2). All calculations are performed with 6-311++G(d,p) basis set. For Ind, we have used a (10o,8e) active space and for 7F-Ind, a (11o,8e) active space is used. Both the active spaces consist of four π orbitals, five $\pi^\star$ orbitals and one $\sigma^\star$ orbital (for Ind) and two $\sigma^\star$ orbitals (for 7F-Ind) [given in section S2 and S3 of SI]. SA-CASSCF calculations have also been done with the lowest five state averaging for the larger active spaces and three state averaging for the smallest active space that is used for dynamics. To incorporate the dynamic correlation, MS-CASPT2 calculations have been done with 0.3 a.u. level shift by which the intruder state problem can be avoided. No IEPA shift is used in these calculations. The first excited state (S_1) of Ind and 7F-Ind have been optimized with (10o,8e) and (11o,8e) CASSCF/6-311++G(d,p) level of theories, respectively.

The minimum energy crossing points (MECPs) of Ind and 7F-Ind have been optimized with (5o,4e) SA-CASSCF/6-311++G(d,p) level of theories. These are also re-optimized with (10o,8e) active space for Ind and (11o,8e) active space for 7F-Ind at 6-311++G(d,p) basis set for comparison [Figs. S5 and S6]. The orbitals taken in (5o,4e) active space and (10o,8e) and (11o,8e) active spaces are given in SI [section S2 and S3].

The surface hoping dynamics have been performed with SHARC quantum chemistry package with its interface to the Molpro package.[2, 3, 4] The initial conditions are obtained by sampling 100 initial geometries generated from Wigner distribution along the normal modes calculated at the SA-CASSCF(3o,2e)/6-31G level of theory. The trajectories are generated with a 0.5 fs time step and sampled over 500 fs each. The energies and gradients are obtained on the fly using the same SA-CASSCF level of theory. The small active space used in this case contains the π, $\pi^\star$ and $\sigma^\star$ orbitals involved in the lowest two excited states which are in close proximity to each other and expected to be involved in the deactivation processes.

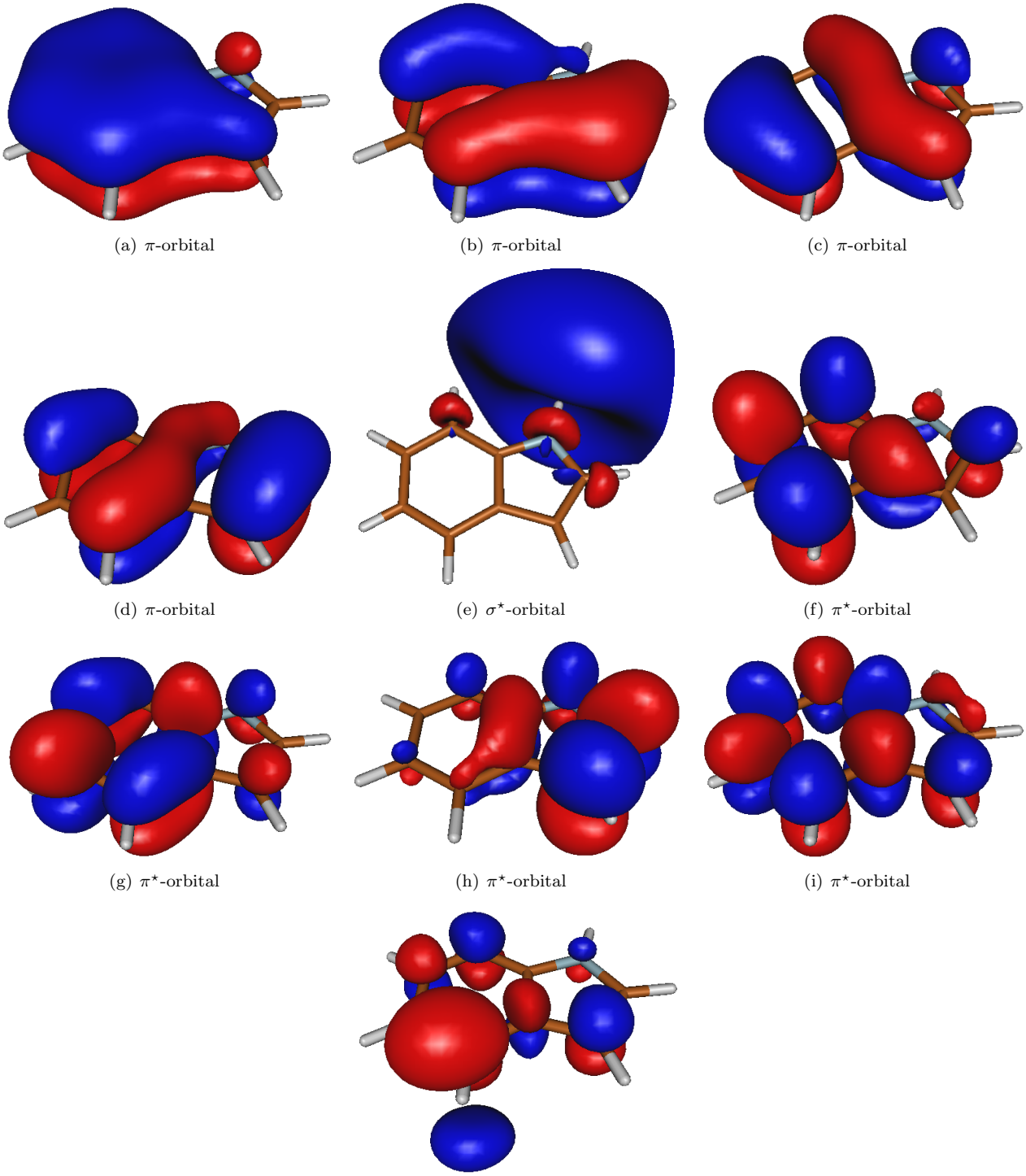
The minimum energy pathways (MEPs) have been constructed by constrained optimization of excited state at TDDFT/cam-b3lyp level of theory with 6-311++G(d,p) basis set followed by single point (10o,8e) active space for Ind and (11o,8e) active space for 7F-Ind at MS-CASPT2/6-311++G(d,p) levels of theories. For Ind, we have constrained the NH bond length whereas for 7F-Ind, we have constrained three different reaction coordinates such as CF bond

length, NH bond length and CN bond length for three MEPs. The CASPT2 MEPs of Ind and 7F-Ind with larger active space and smaller active space are given in section S5 of SI for the comparison.

The ground state geometry optimization with RI-MP2 method, calculation of VEEs with EOM-EE-CCSD method, TDDFT optimization of excited states for MEPs are performed in the quantum chemistry software package Q-Chem and the active space based calculations are performed with Molpro.

S2 CASSCF natural orbitals used in different calculations for Ind

S2.1 (10o,8e)/6-311++G(d,p) active space to calculate VEEs



(a) π-orbital (b) π-orbital (c) π-orbital

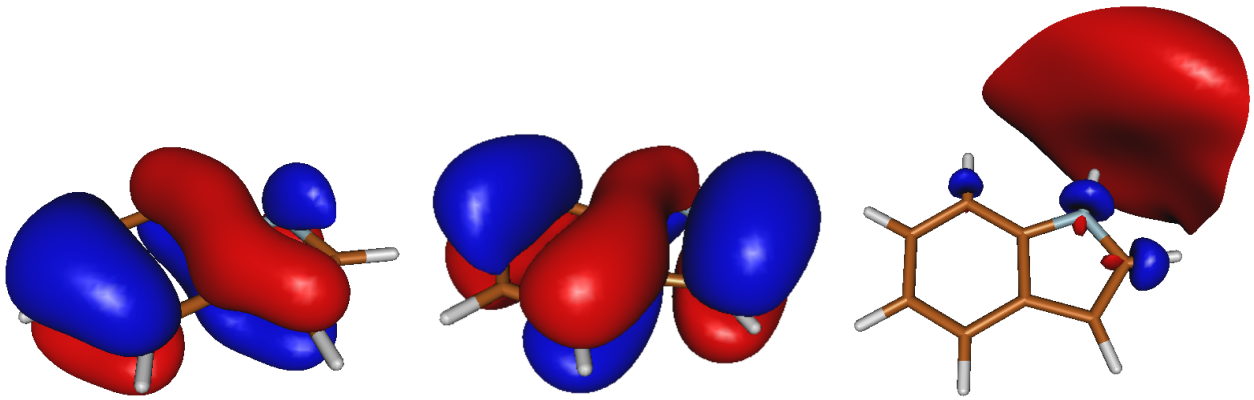
(d) π-orbital (e) $\sigma^\star$-orbital (f) $\pi^\star$-orbital

(g) $\pi^\star$-orbital (h) $\pi^\star$-orbital (i) $\pi^\star$-orbital

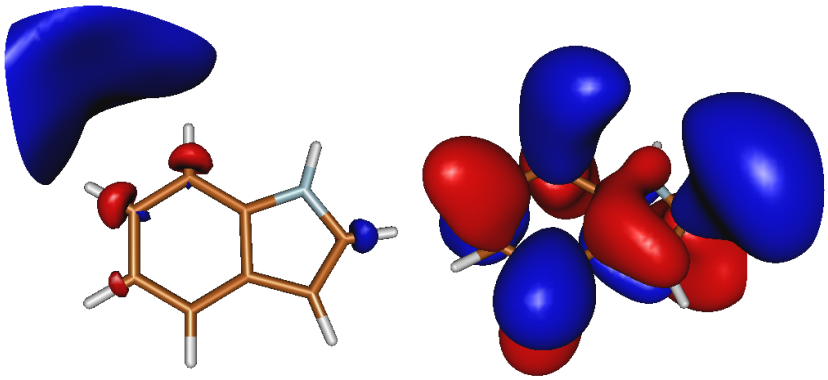
(j) $\pi^\star$-orbital

Figure S1: CASSCF natural orbitals used to calculate VEEs for Ind. This active space is also used to evaluate the MECPs for comaprison.

S2.2 (5o,4e)/6-311++G(d,p) active space to find MECPs



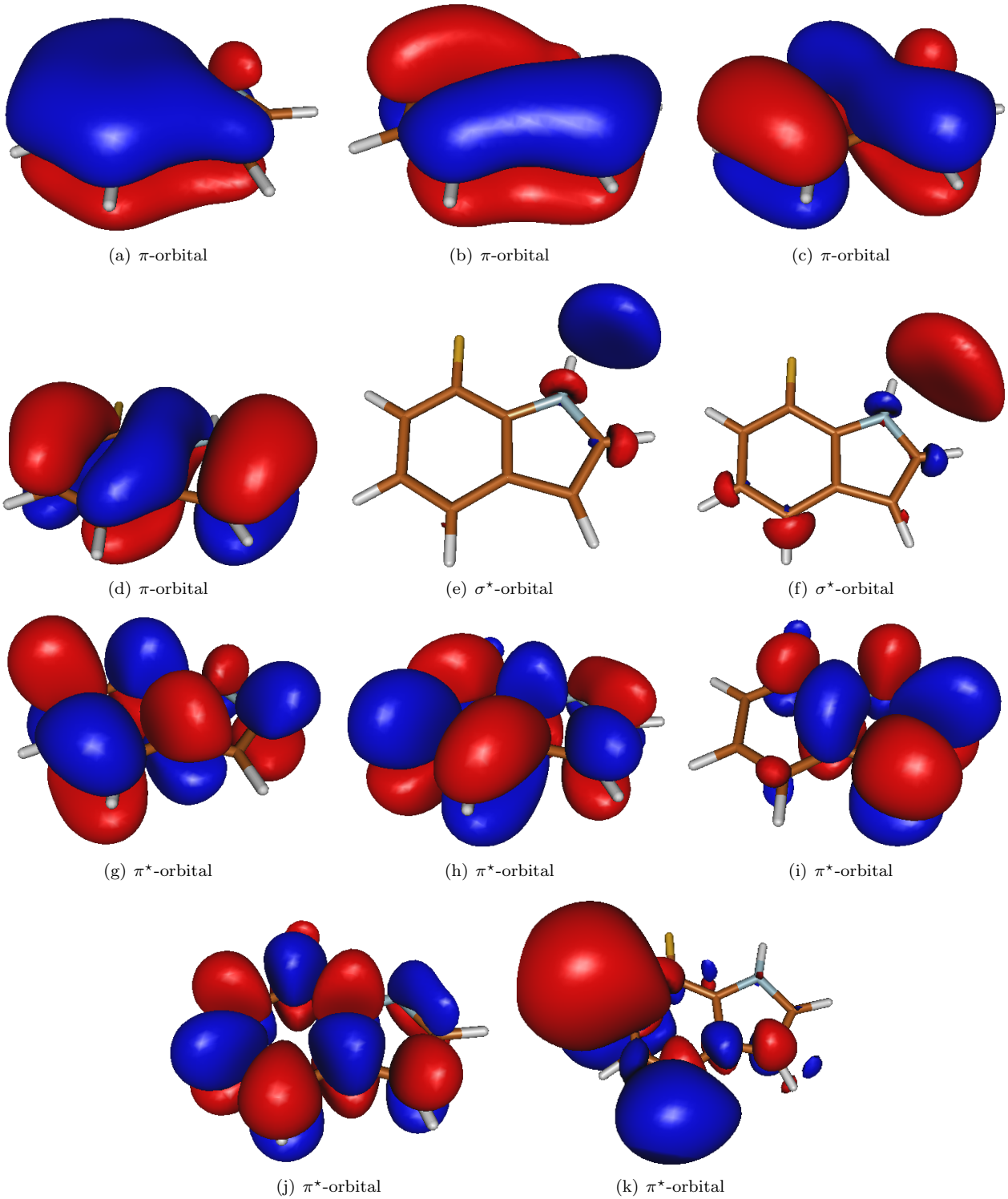
(a) π-orbital (b) π-orbital (c) $\sigma^\star$-orbital



(d) $\sigma^\star$-orbital (e) $\pi^\star$-orbital

Figure S2: Hartree-Fock orbitals used to find MECPs for Ind

S2.3 (11o,8e)/6-311++G(d,p) active space to calculate VEEs



(a) π-orbital (b) π-orbital (c) π-orbital

(d) π-orbital (e) $\sigma^\star$-orbital (f) $\sigma^\star$-orbital

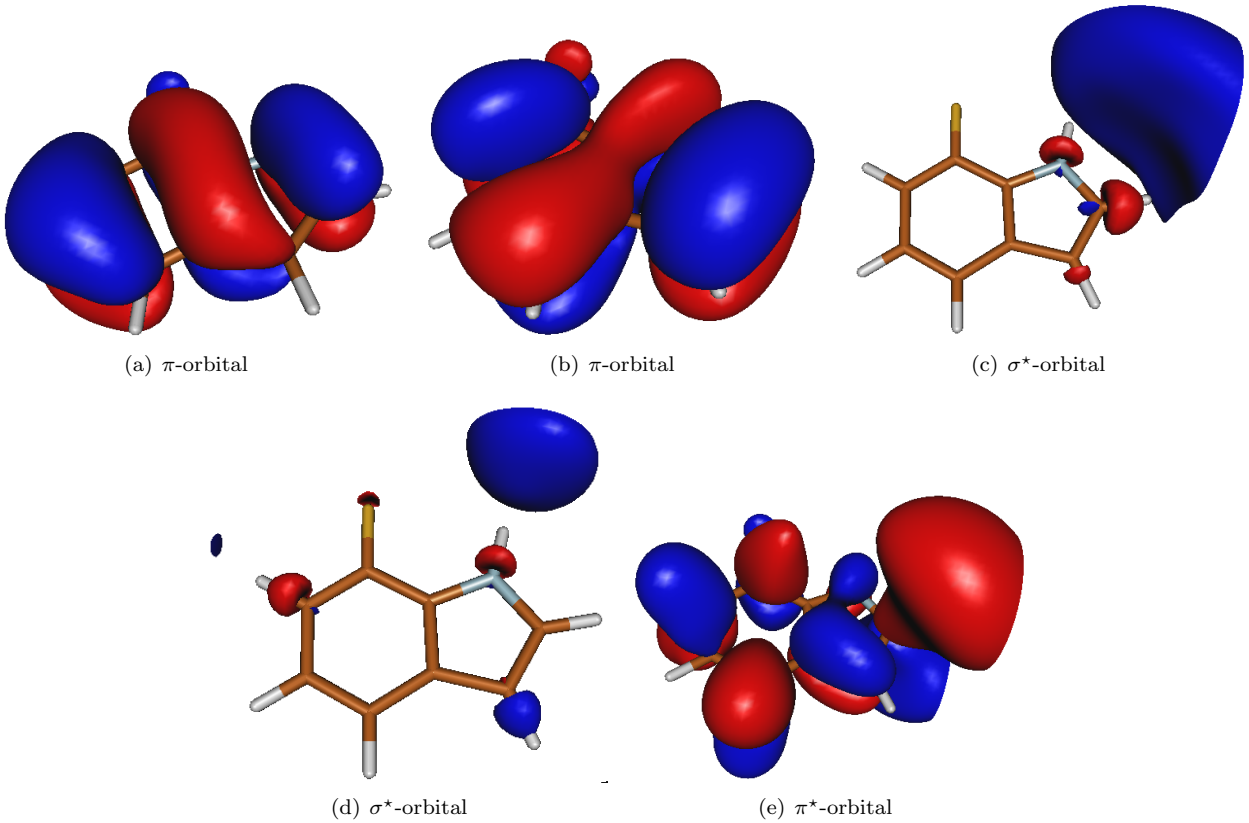
(g) $\pi^\star$-orbital (h) $\pi^\star$-orbital (i) $\pi^\star$-orbital

(j) $\pi^\star$-orbital (k) $\pi^\star$-orbital

Figure S3: CASSCF natural orbitals used to calculate VEEs for 7F-Ind. This active space is also used to evaluate the MECPs for comaprison.

S3 CASSCF natural orbitals used in different calculations for 7F-Ind

S3.1 (5o,4e)/6-311++G(d,p) active space to find MECPs



(a) π-orbital (b) π-orbital (c) $\sigma^\star$-orbital

(d) $\sigma^\star$-orbital (e) $\pi^\star$-orbital

Figure S4: Hartree-Fock orbitals used to find MECPs for 7F-Ind

S4 Comparison of MECPs found with (5o,4e) and (10o,8e) or (11o,8e) and (3o,2e) active space

We have computed the MECPs of Ind and 7F-Ind with (5o,4e) active space at CASSCF/6-311++G(d,p) level of theory. We have also re-optimized the MECPs with higher active spaces like (10o,8e) for Ind and (11o,8e) for 7F-Ind for comparison. (10o,8e) and (11o,8e) active spaces consist of those orbitals which we have used to calculate VEEs of Ind and 7F-Ind, respectively.

S4.1 Indole

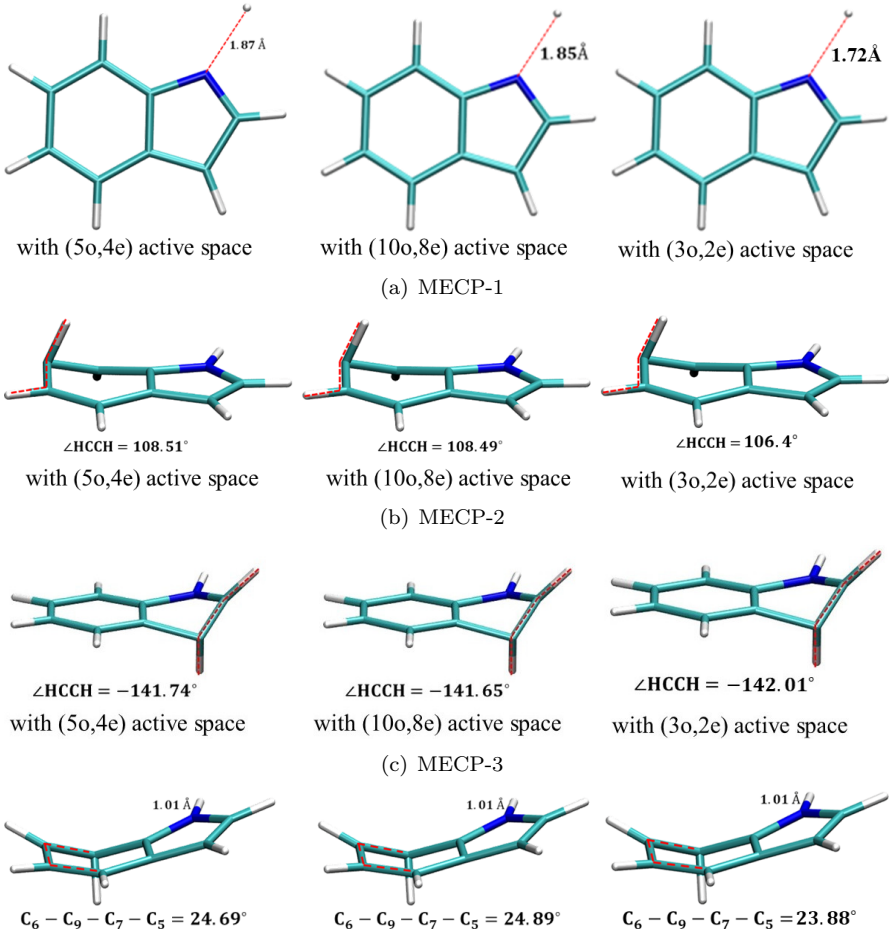
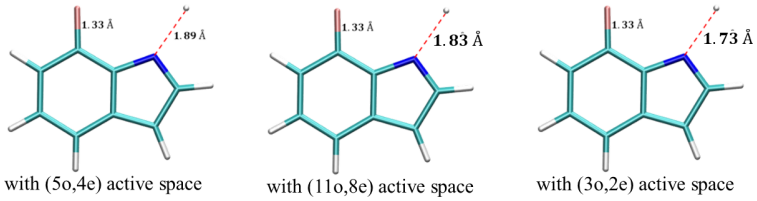


Figure S5: Comparison of MECPs of Ind optimized with (5o,4e) active space and (10o,8e) active space at SA-CASSCF/6-311++G(d,p) level of theories.

The MECP geometries (4 in nos) of Indole optimized with two different active spaces shows that the geometries are in excellent agreement and therefore, choosing the smaller active space for our dynamical calculations is adequate.

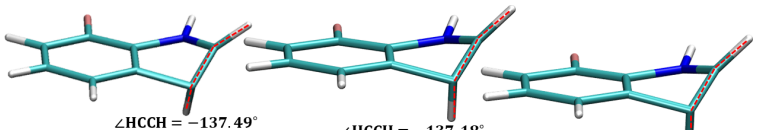
S4.2 7F-Indole

Figure S6: Comparison of MECPs of Ind optimized with (5o,4e) active space and (11o,8e) active space at SA-CASSCF/6-311++G(d,p) level of theories.



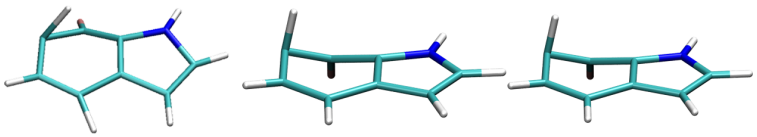
with (5o,4e) active space | with (11o,8e) active space | with (3o,2e) active space

(a) MECP(i)



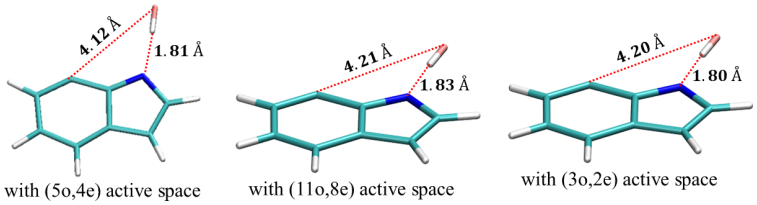
with (5o,4e) active space | with (11o,8e) active space | with (3o,2e) active space

(b) MECP(ii)



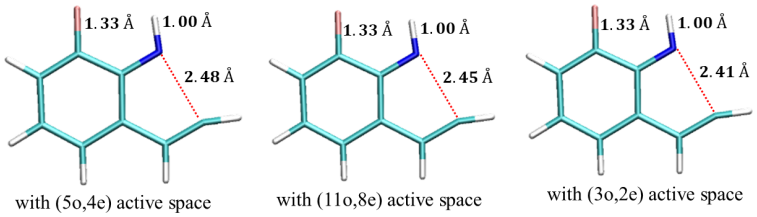
with (5o,4e) active space | with (11o,8e) active space | with (3o,2e) active space

(c) MECP(iii)



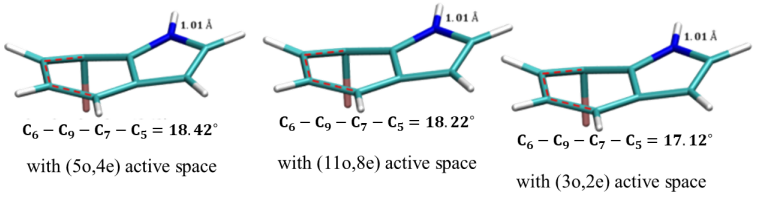
with (5o,4e) active space | with (11o,8e) active space | with (3o,2e) active space

(d) MECP(iv)



with (5o,4e) active space | with (11o,8e) active space | with (3o,2e) active space

(e) MECP(v)



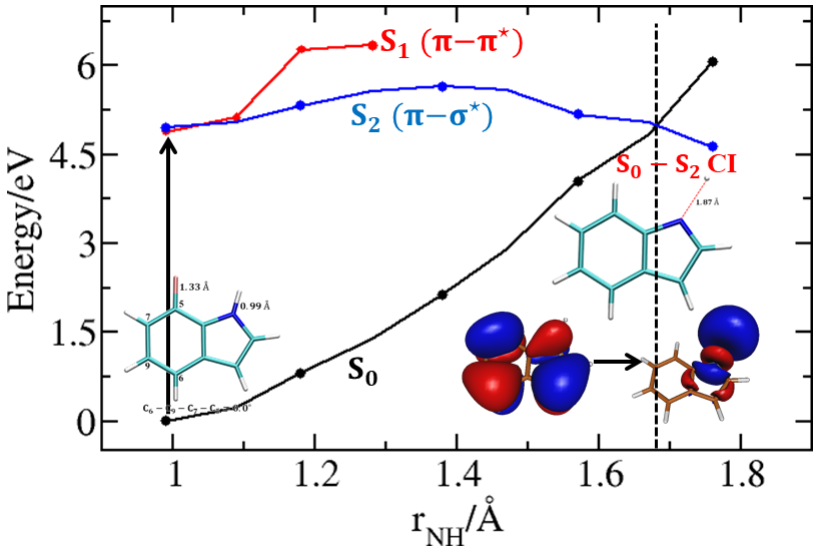
with (5o,4e) active space | with (11o,8e) active space | with (3o,2e) active space

(f) MECP(vi)

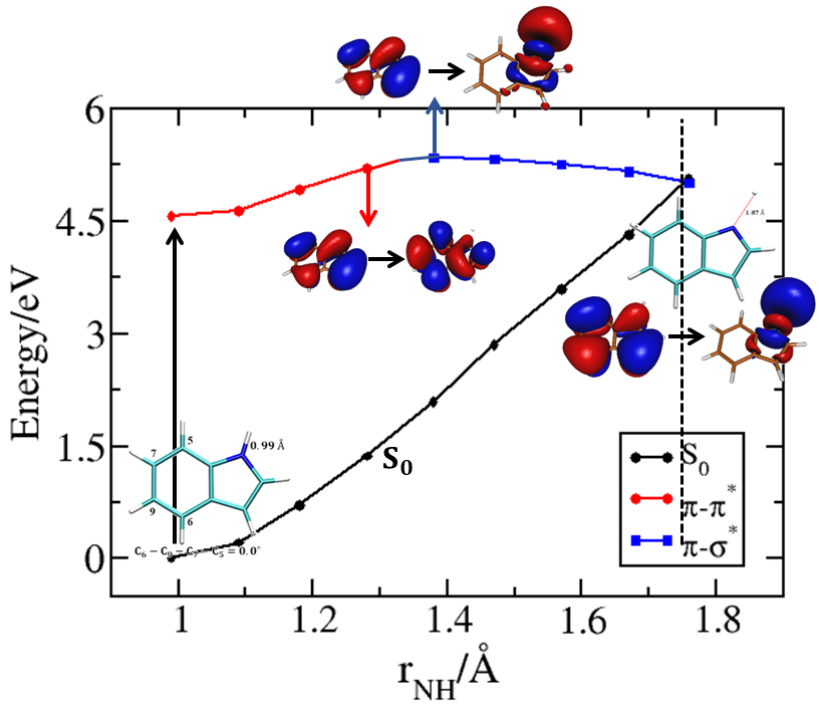
In case of 7F-Indole we have found 6 low energy MECPs, which are again optimized at both the active spaces and compared to prove the efficacy of the small active space for the dynamical calculations.

S5 CASPT2 MEP PESs along lower energy accessible CIs

S5.1 Indole



(g) 11o,8e



(h) 3o,2e

Figure S7: CASPT2 MEP PES of Ind along NH elongated lower energy accessible MECP-1: The energy barrier along this pathway is 17.53 kcal/mol (11o,8e) active space and 8.07 kcal/mol (3o,2e) active space.

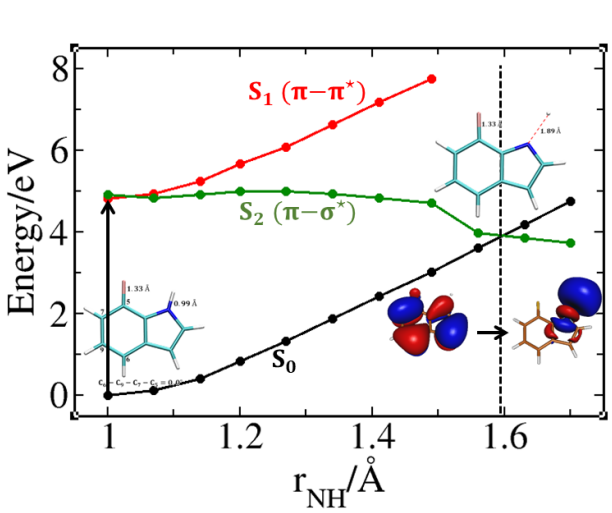
The relative energies of the MECPs calculated for Indole are (i) -4.61 kcal/mol [MECP-1 Fig. 5(a)], (ii) 19.6 kcal/mol [MECP-2 Fig. 5(b)], (iii) 30.44 kcal/mol [MECP-3 Fig. 5(c)], and (iv) 36.21 kca/mol [MECP-4 Fig. 5(d)] with respect to S_1 minima (see Fig. 3a). Therefore, the structures (ii)-(iv) are energetically unfeasible (significantly) and therefore, the deactivation pathway and effective barrier is calculated for the MECP-1 (given in Fig. 5(a)) only.

S5.2 7F-Indole

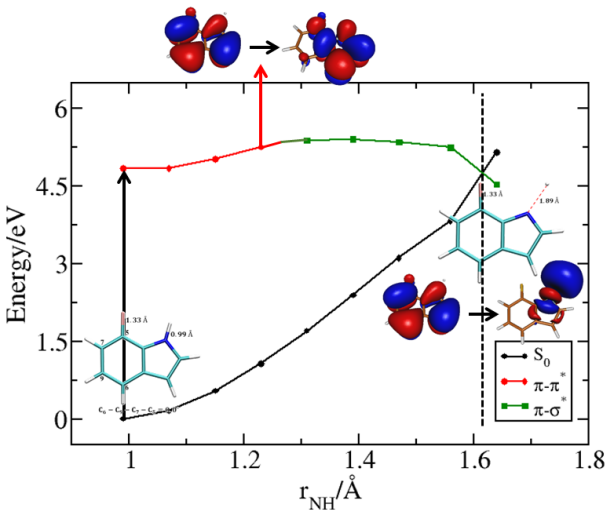
7F-indole has a few lower energy accessible MECPs [shown in the manuscript (Fig 3b)]: (i) along NH bond elongation [MECP(i)] [(3.69 kcal/mol lower in energy than S_1 minima] (ii) 5 membered ring puckering [MECP(ii)] [17.98 kcal/mol higher in energy] (iii) 6 membered ring puckering [MECP(iii)] [41.05 kcal/mol higher in energy] (iv) along CF bond elongation along with NH elongation [MECP(iv)] [13.84 kcal/mol lower in energy than S_1 minima], (v) Ring opening [MECP(v)] [11.3 kcal/mol lower in energy], (vi) both 5 and 6 membered ring puckering [MECP(vi)] [9.22 kcal/mol higher in energy].

Therefore, we notice that MECP(i), MECP(iv) and MECP(v) are energetically feasible and those channels of deactivation pathways are studied.

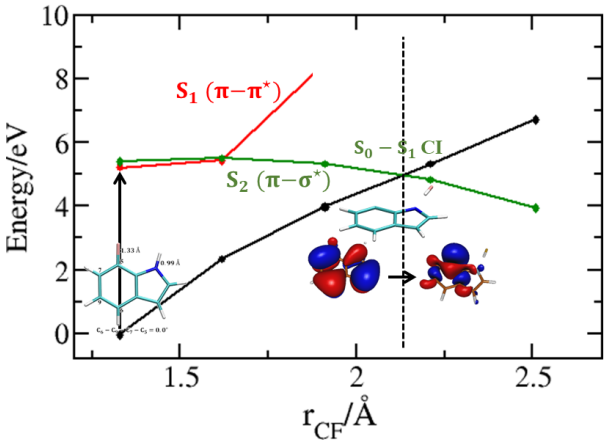
The following MEP PESs represent the nonradiative pathways along MECP(i), MECP(iv) and MECP(v). The PES along MECP(i) is minimum energy optimized pathway along NH bond elongation [Fig. 8(a)] which has 4.38 kcal/mol barrier. For MECP(iv), we have optimized the S_2 state by constraining C-F and N-H bond distances [Fig. 8(c)] which is barrierless. Fig. 8(e) represents the CASPT2 MEP PES along MECP(v) which has ∼6 kcal/mol energy barrier.



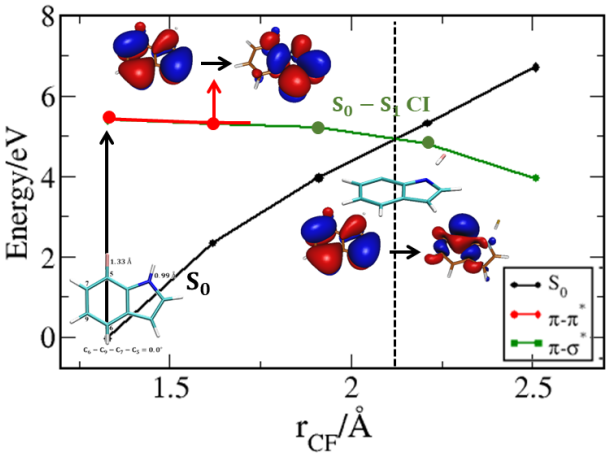
(a) Pathway along MECP(i): 11o,8e



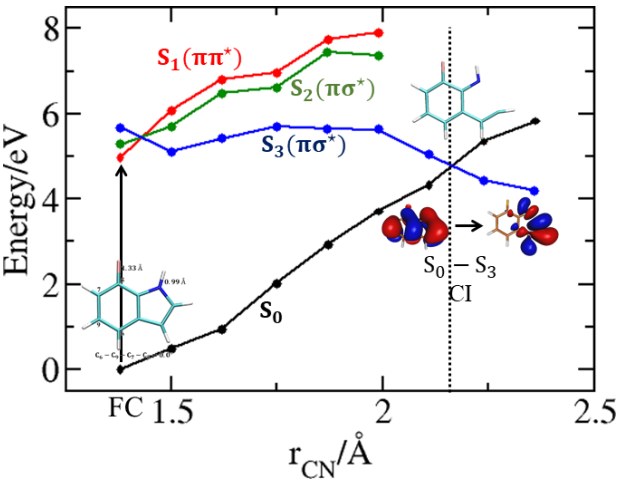
(b) Pathway along MECP(i): 3o,2e



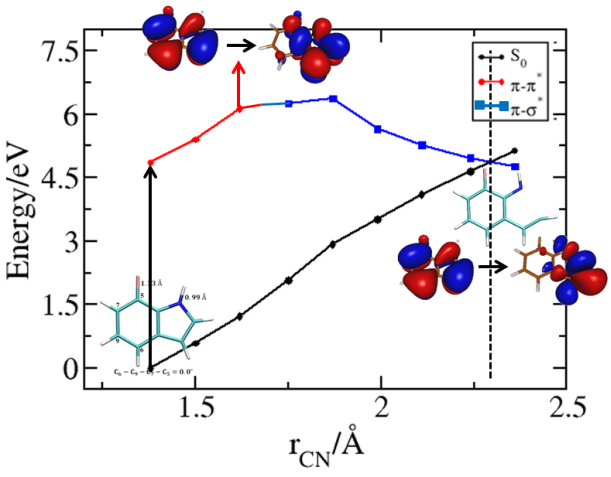
(c) Pathway along MECP(iv): 11o,8e



(d) Pathway along MECP(iv): 3o,2e



(e) Pathway along MECP(v): 11o,8e



(f) Pathway along MECP(v): 3o,2e

Figure S8: The non-radiative pathways for low-energy accessible MECPs of 7F-Ind. (a) 4.38 kcal/mol (11o,8e) and 1 kcal/mol (3o,2e) barrier pathway to MECP(i), (b) barrierless pathway to MECP(iv), and (c) pathway to MECP(v) which has energy barrier of $\sim$ 6 kcal/mol (11o,8e) and 23 kcal/mol (3o,2e).

S6 Optimized ground state of indole and 7F-Ind at different methods

S6.1 RI-MP2/CC-pVTZ level of theory: Ind

C	2.3753544958	-0.1028537058	-0.0003557665
C	0.2634898098	0.6539451547	-0.0000110577
C	0.2234074230	-0.7669302410	-0.0002795046
H	1.9249565596	-2.2401314629	-0.0013061777
C	-0.8939445761	1.4367202004	0.0007281246
C	-1.0269169903	-1.4078631973	0.0003268566
C	-2.1109667296	0.7732809151	0.0011803614
H	-0.8457520715	2.5177965882	0.0008943440
C	-2.1755283059	-0.6345281522	0.0010155429
H	-1.0894700620	-2.4882002393	0.0001788141
C	1.5762753235	-1.2216760374	-0.0005207569
N	1.5856146983	1.0224254683	-0.0001543522
H	1.9251741233	1.9674433272	0.0008334256
H	3.4489291428	-0.0187514083	-0.0004877295
H	-3.0279437644	1.3465905377	0.0017625464
H	-3.1437941187	-1.1159954505	0.0014739360

S6.2 (10o,8e) SA-CASSCF/6-311++G(d,p) level of theory: Ind

C	2.3833879881	-0.0320192500	0.0000000000
C	0.2519960866	0.6680939958	0.0000000000
C	0.2465477996	-0.7386321186	0.0000000000
H	1.9965754102	-2.1668057148	0.0000000000
C	-0.9314390607	1.4150581393	0.0000000000
C	-0.9812876025	-1.4238399994	0.0000000000
C	-2.1337465699	0.7197171912	0.0000000000
H	-0.9146930237	2.4907357254	0.0000000000
C	-2.1591399168	-0.6908154471	0.0000000000
H	-1.0077677139	-2.4992410377	0.0000000000
C	1.6275108250	-1.1618128617	0.0000000000
N	1.5637887066	1.0817434804	0.0000000000
H	1.8744373155	2.0215496648	0.0000000000
H	3.4483666145	0.0756208341	0.0000000000
H	-3.0609180889	1.2644721482	0.0000000000
H	-3.1062256996	-1.2001592598	0.0000000000

S6.3 RI-MP2/CC-pVTZ level of theory: 7F-Ind

C	2.4616825437	0.4802375344	0.0006477639
C	0.2309903574	0.4410709245	0.0001033272
C	0.6799201380	-0.9048783338	0.0000594174
H	2.7911312978	-1.6788441532	-0.0005479951
C	-1.1284564593	0.7426271529	0.0001692170
C	-0.2696067973	-1.9428602679	0.0000931046
C	-2.0535884822	-0.2751186787	0.0002161624
C	-1.6141839905	-1.6166045971	0.0001773690
H	0.0451534937	-2.9773109267	-0.0000333056
C	2.1067149504	-0.8481161823	-0.0002509334
N	1.3270331824	1.2578080362	-0.0001225117
H	1.2993760744	2.2618400436	-0.0000370107

H	3.4366585364	0.9368690735	0.0010242345
H	-3.1056939071	-0.0300544877	0.0002149353
H	-2.3565271227	-2.4024363137	0.0001399837
F	-1.5066919555	2.0376694784	0.0001425611

S6.4 (11o,8e) SA-CASSCF/6-311++G(d,p) level of theory

C	2.4744075023	0.4144746246	0.0000000000
C	0.2399473319	0.4378673275	0.0000000000
C	0.6426176264	-0.9100957263	0.0000000000
H	2.7445473134	-1.7412045651	0.0000000000
C	-1.1131749616	0.7728327952	0.0000000000
C	-0.3330032401	-1.9260399792	0.0000000000
C	-2.0719478361	-0.2100256604	0.0000000000
C	-1.6670615155	-1.5730896074	0.0000000000
H	-0.0432617748	-2.9614450015	0.0000000000
C	2.0906534306	-0.8938152127	0.0000000000
N	1.3565517490	1.2317861710	0.0000000000
H	1.3585181386	2.2219155834	0.0000000000
H	3.4572342600	0.8373119040	0.0000000000
H	-3.1108843137	0.0615875407	0.0000000000
H	-2.4245681797	-2.3356399955	0.0000000000
F	-1.4523998707	2.0616331717	0.0000000000

S7 Cartesian coordinates of excited states minima of Ind and 7F-Ind

S7.1 S_1 minima of Ind optimized at (10o,8e)/6-311++G(d,p) SA-CASSCF level of theory

C	2.4075446121	-0.0301069737	0.0000069326
C	0.2569183146	0.6929806362	0.0000016405
C	0.2648585438	-0.7664526569	0.0000025836
H	1.9997442921	-2.1739615328	0.0000076854
C	-0.9297884404	1.4600303119	0.0000060301
C	-0.9672395002	-1.4726201927	0.0000021033
C	-2.1653038959	0.7396004545	0.0000100237
H	-0.9163495315	2.5323670186	0.0000101903
C	-2.1849591442	-0.6985812618	0.0000257808
H	-1.0017633758	-2.5446506834	0.0000450765
C	1.6301033050	-1.1689067690	0.0000050752
N	1.5727147031	1.0850821333	0.0000002213
H	1.8869139789	2.0217476042	0.0000021735
H	3.4700292331	0.0772806262	-0.0000028718
H	-3.0946933287	1.2754169017	0.0000445522
H	-3.1313366960	-1.2055601259	0.0000528031

S7.2 S_1 minima of 7F-Ind optimized at (11o,8e)/6-311++G(d,p) SA-CASSCF level of theory

C	2.4965849325	0.4246364663	0.0000653368
C	0.2377505216	0.4654464445	0.0000125416
C	0.6735205482	-0.9298529242	0.0000140315
H	2.7497495699	-1.7462924399	0.0000594617

C	-1.1180787484	0.8035662436	-0.0000133345
C	-0.3025474176	-1.9589357028	0.0000091215
C	-2.1115891662	-0.2052584824	0.0000038346
C	-1.6992010614	-1.5846548632	0.0000047943
H	-0.0250821071	-2.9946290930	0.0000072990
C	2.0932894396	-0.9006417460	0.0000218237
N	1.3694894301	1.2408577450	0.0000211375
H	1.3758923729	2.2292148341	0.0000635061
H	3.4800984984	0.8406777410	0.0000039398
H	-3.1484211706	0.0644127094	0.0000138624
H	-2.4497913056	-2.3504705878	0.0000047681
F	-1.4734886762	2.0899770254	0.0000278760

S8 Cartesian coordinates of MECPs of Ind and 7F-Ind

S8.1 Ind

S8.1.1 MECP1

C	2.3095174654	0.1265601066	0.0226168575
C	0.2123913154	0.6376444753	0.0693089329
C	0.2215253726	-0.7766061898	0.0185229307
H	2.0168919307	-2.1221013563	-0.0540519056
C	-0.9764344365	1.3564757916	0.1111572524
C	-1.0150912588	-1.4941566713	0.0095352256
C	-2.1458238396	0.6417829992	0.1013762695
H	-0.9722136717	2.4297022205	0.1496003421
C	-2.1646402875	-0.7843649199	0.0505041030
H	-1.0231865974	-2.5687082955	-0.0288625504
C	1.5839754278	-1.1432204754	-0.0130193778
N	1.5297430143	1.1307281281	0.0691316077
H	2.1105513459	2.6644650565	0.1163673853
H	3.3783805524	0.2415116038	0.0122725470
H	-3.0843433704	1.1661996259	0.1328723621
H	-3.1138177455	-1.2889163523	0.0452617091

S8.1.2 MECP2

C	0.1610637576	1.3562902486	0.8935207138
C	-0.9422669100	0.7469693991	0.1762817540
C	-0.9307645655	-0.6576921347	-0.0553612102
C	0.2823998837	-1.3095418069	0.1004565372
C	1.4866377483	-0.6344638481	0.4146774398
C	1.4542692603	0.7366328412	0.5746669624
C	-2.1884064651	-0.9800065596	-0.6997022503
C	-2.8564882108	0.1780545079	-0.8267629020
N	-2.0858860728	1.2196229986	-0.3027021987
H	-2.5394311795	-1.9436837027	-1.0093152458
H	-3.8179562866	0.3779320142	-1.2506592138
H	-0.0114198603	0.6657055710	1.7556206504
H	0.3451649453	-2.3564250221	-0.1513948048
H	-2.3339199017	2.1821441401	-0.2748416996
H	2.3646382315	1.3077929951	0.4872436111
H	2.4143726454	-1.1733098317	0.3210303562

S8.1.3 MECP3

C	2.4606466838	0.4216522471	0.0200496013
C	0.2501368060	0.5073704109	0.2049411925
C	0.6055685857	-0.8229429721	-0.0872369093
H	2.6328613317	-1.7010947805	-0.4212543839
C	-1.0852592237	0.8793438624	0.1119295297
C	-0.3936606219	-1.8475516416	-0.2763193851
C	-2.0596268745	-0.1361171547	0.3940658242
C	-1.7046681342	-1.5151023661	-0.0382166385
H	-0.1034019014	-2.8213281303	-0.6286743488
C	2.0170312707	-0.8546090480	-0.1991569030
N	1.4223510790	1.2462470620	0.2414097485
H	1.4923345221	2.2097829078	0.4665569487
H	3.4667443234	0.7907316302	0.0248561252
H	-1.5524864064	-0.3800637817	1.3744383251
H	-2.4609027962	-2.2813279269	-0.0593064203
H	-1.3534704642	1.8838112316	-0.1927692962

S8.1.4 MECP4

C	2.4627210550	0.3854532418	0.2309830829
C	0.2291910695	0.4013643099	-0.0365569244
C	0.6313642647	-0.9624519584	-0.0237841439
H	1.9529533995	-0.5260307172	-1.4170353485
C	-1.0682462663	0.8065944863	-0.0254051364
C	-0.3282358821	-1.9214914048	0.0759441970
C	-2.0436596770	-0.2073664477	0.0853508870
C	-1.6834236202	-1.5270137831	0.1514445971
H	-0.0620397746	-2.9624781561	0.0774959467
C	2.1138535232	-0.8912229877	-0.3918052911
N	1.4294998409	1.1976810707	0.0068290791
H	1.4111521677	2.1819783376	0.1774823839
H	3.2321478456	0.6586687256	0.9350636105
H	-3.0823126712	0.0681365565	0.1192438736
H	-2.4448026123	-2.2802761586	0.2484758060
H	-1.3549873724	1.8398024750	-0.1076106592

S8.1.5 MECP5

C	2.9831579536	-0.0080240760	0.1558775296
C	0.2526941786	0.6238003513	0.0147168194
C	0.6957006063	-0.7629301888	0.0845901328
H	2.4606333252	-2.0069761856	0.2063916537
C	-1.1965156809	0.8506980428	-0.0562108428
C	-0.2506174224	-1.8109280387	0.0819968442
C	-2.0641185101	-0.2025063792	-0.0552108996
C	-1.5775906752	-1.5641585428	0.0156105381
H	0.1053309139	-2.8255022108	0.1345073631
C	2.0991571264	-0.9886064126	0.1535164542
N	1.1428208109	1.5363321133	0.0198289436
H	0.7626741482	2.4629435371	-0.0304817604
H	3.9138345159	0.4953348413	0.1776982879
H	-3.1234892721	-0.0266174156	-0.1074680380
H	-2.2848366853	-2.3731491381	0.0146578171

H	-1.5500873532	1.8650842725	-0.1086183329

S8.2 7F-Ind

S8.2.1 MECP1

C	2.0500366129	0.5920716222	-0.0740005779
C	-0.0591433307	0.3063452770	-0.0271098266
C	0.5308373963	-1.0395370503	0.0323219667
H	2.7379979888	-1.4714583666	0.0204344628
C	-1.4286063708	0.1867366520	-0.0000018783
C	-0.2441728094	-2.1626178157	0.1013548992
C	-2.3069264565	-0.8660156365	0.0670694126
C	-1.6615907984	-2.0825639964	0.1190454690
H	0.2179252299	-3.1326318097	0.1436306919
C	1.9426019953	-0.7551146839	-0.0038116171
N	0.8337708688	1.2482470348	-0.0887312994
H	0.4622733575	2.9796168762	-0.1711043442
H	2.9516035060	1.1704267388	-0.1172758385
H	-3.3731188235	-0.7560243695	0.0777665408
H	-2.2475611163	-2.9816515654	0.1737635351
F	0.1967114251	3.8604606271	-0.2117930041

S8.2.2 MECP2

C	0.1385585518	1.4399522698	0.9094148461
C	-0.9332124008	0.7015943607	0.1987778219
C	-0.9526585324	-0.7288786501	-0.0088075882
C	0.2549201713	-1.3280806180	-0.0062482447
C	1.4850169390	-0.6052586639	0.3126336278
C	1.4466693042	0.7085083692	0.5713484622
C	-2.2303532848	-1.0298934296	-0.6512925773
C	-2.8390573708	0.1405895673	-0.8415549816
N	-2.0178289054	1.1789270193	-0.3362810746
H	-2.6136615578	-1.9926320474	-0.9221155224
H	-3.7839438991	0.3699333808	-1.2871728898
H	0.3460928727	-2.3469597920	-0.3487328110
H	-2.2087765359	2.1583803580	-0.3335399296
H	2.3704900698	1.2532701340	0.6572444832
H	2.4132112514	-1.1383074669	0.2101194352
F	-0.1082584233	0.7922720488	2.2085818528

S8.2.3 MECP3

C	2.4573069004	0.4561219431	0.2045695466
C	0.2522561311	0.4282674719	-0.0777469903
C	0.6635819182	-0.9332745986	-0.0093085029
H	1.9148701712	-0.4499208682	-1.3220997162
C	-1.0550453171	0.7812931033	-0.1163131921
C	-0.2903261225	-1.9054118798	0.0722353576
C	-2.0325569363	-0.2105190843	-0.0245405862
C	-1.6460370712	-1.5244840219	0.0804771192
H	-0.0108799550	-2.9411232792	0.1124070021
C	2.1621220476	-0.8617054063	-0.3186122000
N	1.4276979104	1.2483310397	-0.0463549768

H	1.3988167989	2.2420794836	0.0197701588
H	3.2801513413	0.8078381144	0.8055162679
H	-3.0676138662	0.0756627602	-0.0293011732
H	-2.4032251565	-2.2829055280	0.1666162725
F	-1.4052653483	2.0595004922	-0.2430482711

S8.2.4 MECP4

C	2.4520877087	0.3812952362	0.2295108083
C	0.2417747124	0.3969661915	-0.0091561448
C	0.6323982446	-0.9723017412	0.0057374622
H	1.8653468669	-0.4645700308	-1.3152059145
C	-1.0601956046	0.7711833751	-0.0099005087
C	-0.3352357942	-1.9318043103	0.0740639578
C	-2.0515458435	-0.2079691006	0.0684068226
C	-1.6842298985	-1.5305149122	0.1220645300
H	-0.0717457574	-2.9724648565	0.0740134250
C	2.1255576719	-0.9134953667	-0.3310985000
N	1.4306021518	1.1972710517	0.0258960951
H	1.4190258340	2.1885552714	0.1256851969
H	3.2920323363	0.6998670565	0.8252637870
H	-3.0817646386	0.0941341891	0.0939048727
H	-2.4517038265	-2.2796315536	0.1980026361
F	-1.3922416674	2.0581528205	-0.0870824159

S8.2.5 MECP5

C	2.586035544	0.395573358	0.025223269
C	0.184099467	0.517518356	0.323591302
C	0.555891156	-0.840989553	0.057536567
H	2.391769253	-1.714802657	-0.733299215
C	-1.044718831	0.894344991	0.041507089
C	-0.480945523	-1.912049538	-0.225227609
C	-2.080515015	-0.258433634	0.346922475
C	-1.816403301	-1.745031747	0.041838497
H	0.244388065	-2.860205597	-0.701807066
C	2.050611279	-0.855189581	-0.311888555
N	1.447962562	1.183372910	0.486098650
H	1.601169465	2.219758032	0.490762450
H	3.415478875	1.012984989	0.148933798
H	-1.427622768	-0.015077828	1.474876674
H	-2.677559073	-2.254399483	-0.090218111
F	-1.389440891	2.065729881	-0.576753958

S8.2.6 MECP6

C	2.9992991744	-0.0253908993	0.1572434460
C	0.2373370872	0.6139310620	0.0145601087
C	0.6853141685	-0.7356911416	0.0831488839
H	2.4449870405	-2.0124796237	0.2058434772
C	-1.1808996722	0.8019236766	-0.0535592011
C	-0.2392107286	-1.7905512174	0.0817346490
C	-2.0640357206	-0.2139393826	-0.0545464643
C	-1.5801492707	-1.5416926505	0.0148065713

H	0.1191973720	-2.8030160633	0.1341718216
C	2.1167919572	-0.9808553547	0.1539470260
N	1.1160170052	1.5844149909	0.0171298288
H	0.6826285593	2.4875895145	-0.0345350670
H	3.9572424310	0.4278122451	0.1822779942
H	-3.1166470218	-0.0064858477	-0.1075530155
H	-2.2826826424	-2.3547284231	0.0141262012
F	-1.6079866620	2.0567415548	-0.1177422721

S9 Amplitudes of EOM-EE-CCSD transitions

States	Orbitals involved	EOM-EE-CCSD amplitudes
S_1	HOMO-1 → LUMO+7	-0.5433
S_2	HOMO → LUMO	-0.5754
S_3	HOMO → LUMO+7	0.5396
S_4	HOMO-1 → LUMO	-0.5422

Table S1: Ind

States	Orbitals involved	EOM-EE-CCSD amplitudes
S_1	HOMO-1 → LUMO+7	-0.5191
S_2	HOMO → LUMO	-0.5538
S_3	HOMO → LUMO+7	0.5250
S_4	HOMO-1 → LUMO	0.5627

Table S2: 7F-Ind

S10 Occupancy of energetically ordered MCSCF orbitals

MCSCF orbital	Occupancy for state S_1	Occupancy for state S_2	Occupancy for state S_3	Occupancy for state S_4
HOMO-3 (π)	1.8724370	1.9401894	1.9388559	1.9288678
HOMO-2 (π)	1.8718469	1.9084856	1.9019279	1.9214634
HOMO-1 (π)	1.3691368	1.8681243	1.8655302	1.0383105
HOMO (π)	1.5728989	1.0327559	1.0503120	1.8509177
LUMO ($\sigma^\star$)	0.0000089	0.9565613	0.0587459	0.9654426
LUMO+1 ($\pi^\star$)	0.3953969	0.0776266	0.4219112	0.0770269
LUMO+2 ($\pi^\star$)	0.1688927	0.0479305	0.4639246	0.0557511
LUMO+3 ($\pi^\star$)	0.3137626	0.0603500	0.1532024	0.0520486
LUMO +4 ($\pi^\star$)	0.2770756	0.0614584	0.0765724	0.0612601
LUMO+5 ($\pi^\star$)	0.1585437	0.0465180	0.0690175	0.0489113

Table S3: Ind

Most important configurations in the occupation number formalism are :
$S_1 = |2212000100\rangle$, $|2212010000\rangle$, $|2212001000\rangle$, $|2210000001\rangle$ and so on
$S_2 = |2221100000\rangle$
$S_3 = |2221010000\rangle$, $|2221000100\rangle$, $|2221000001\rangle$ and so on
$S_4 = |2212100000\rangle$.

MCSCF orbital	Occupancy for state S_1	Occupancy for state S_2	Occupancy for state S_3	Occupancy for state S_4
HOMO-3 (π)	1.8739265	1.9409763	1.9304906	1.9318820
HOMO-2 (π)	1.8761542	1.9038398	1.9204157	1.9085210
HOMO-1 (π)	1.4025818	1.8519060	1.2352377	1.6891904
HOMO (π)	1.5298384	1.0543239	1.6542321	1.2308738
LUMO ($\sigma^\star$)	0.0000057	0.9858620	0.0309191	0.2025933
LUMO+1 ($\sigma^\star$)	0.0000058	0.0141423	0.0572143	0.7974095
LUMO+2 ($\pi^\star$)	0.1696029	0.0280068	0.4389621	0.0284847
LUMO+3 ($\pi^\star$)	0.1362584	0.0468700	0.5610401	0.0483366
LUMO +4 ($\pi^\star$)	0.4955209	0.0842754	0.0723775	0.0741229
LUMO+5 ($\pi^\star$)	0.1381606	0.0301369	0.0336782	0.0323821
LUMO+6 ($\pi^\star$)	0.3779449	0.0596607	0.0654325	0.0562037

Table S4: 7F-Ind

The most important configurations in the occupation no formalism are :
$S_1 = |22120000100\rangle$, $|22120000001\rangle$, $|22210000100\rangle$, $|22210000001\rangle$ and so on
$S_2 = |22211000000\rangle$
$S_3 = |221200001000\rangle$, $|221200010000\rangle$ and so on
$S_4 = |22210100000\rangle$, $|22211000000\rangle$, $|22121000000\rangle$ and so on.

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