Supplementary Materials

A Comparative Analysis of Isomerization Pathways in 3- and 4-Styrylpyridines

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IDPP interpolation

A brief description of IDPP interpolation method is shown below. The image-dependent pair potential (IDPP) is an interpolation algorithm which provides an improved initial guess for the minimum energy path computations. In contrast to the simple linear interpolation in atomic coordinates approach which may result in overlapping atoms or unphysical distortions, the IDPP approach refines the process by generating atomic configurations through interpolation of pairwise atom separations between reactant and product minima.[1] Following the two-stage approach developed by Halgren and Lipscomb,[2] all pairwise atomic distances are interpolated for each intermediate configuration, producing target values that the pathway seeks to reproduce as accurately as possible. For each image, an objective function is introduced to assess the deviation between the actual atomic separations and the interpolated targets, assigning higher importance to shorter distances.

Table S1: Cartesian coordinates of 3-T1 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	2.824779	-1.290755	-0.000684	C	2.823265	-1.337710	0.000016
C	1.938097	-0.186157	-0.000017	C	1.885883	-0.232682	-0.000028
C	2.492832	1.119249	0.000673	C	2.434440	1.112659	-0.000066
C	3.884634	1.306902	0.000606	C	3.821207	1.306821	-0.000084
C	4.755897	0.196596	-0.000055	C	4.711633	0.207831	-0.000018
C	4.220087	-1.104573	-0.000678	C	4.197115	-1.122810	0.000076
H	2.412850	-2.306325	-0.001228	H	2.422169	-2.357830	-0.000049
H	1.838927	1.996409	0.001314	H	1.767021	1.978419	-0.000063
H	4.294121	2.322252	0.001042	H	4.223698	2.325349	-0.000153
H	5.840081	0.347612	-0.000094	H	5.793344	0.377810	-0.000051
H	4.885529	-1.973895	-0.001136	H	4.884963	-1.974416	0.000237
C	0.482702	-0.451839	-0.000047	C	0.496845	-0.500123	-0.000033
H	0.212764	-1.514967	-0.000319	H	0.192719	-1.552330	-0.000157
C	-0.509532	0.482365	0.000144	C	-0.515474	0.515961	0.000071
H	-0.241709	1.546297	0.000191	H	-0.204675	1.566951	0.000188
C	-1.963503	0.212978	0.000152	C	-1.908257	0.262041	0.000058
C	-2.873089	1.294936	-0.000705	C	-2.862869	1.342769	0.000075
C	-4.253815	1.037763	-0.000761	C	-4.222044	1.055789	0.000002
H	-2.497666	2.324514	-0.001318	H	-2.502022	2.377981	0.000149
H	-4.980943	1.855460	-0.001488	H	-4.969175	1.855697	0.000100
C	-4.690286	-0.298311	0.000111	C	-4.641682	-0.305508	-0.000134
H	-5.759002	-0.537830	0.000138	H	-5.707578	-0.558747	-0.000217
N	-3.844517	-1.357487	0.001028	N	-3.780181	-1.354559	-0.000161
C	-2.522786	-1.091146	0.001052	C	-2.465131	-1.080420	-0.000030
H	-1.872458	-1.971978	0.001841	H	-1.801220	-1.950873	0.000031

Table S2: Cartesian coordinates of 3-T2 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	0.4010175	0.3897927	0.000409	C	0.4103353	0.4288392	-0.0001617
C	1.8525207	0.1041821	0.0001885	C	1.8032428	0.1426816	-0.0002064
C	2.7549341	1.1958326	-0.0025461	C	2.7485494	1.234012	-0.000345
C	4.1474067	0.9895906	-0.0028576	C	4.1220457	1.0022542	-0.0003718
C	4.6642653	-0.3192476	-0.0004402	C	4.6193532	-0.3307803	-0.0002742
C	3.777055	-1.4168867	0.0023514	C	3.7160849	-1.4185826	-8.98E-05
C	2.3880871	-1.2091953	0.0027683	C	2.3323928	-1.2029666	-8.76E-05
C	-0.6049265	-0.5292528	-0.0001141	C	-0.6190371	-0.5598799	4.03E-05
C	-2.0517004	-0.2304028	-2.17E-05	C	-1.999005	-0.2551215	0.0001726
C	-4.8087418	0.0668353	-0.0008578	C	-4.7613327	0.0605697	0.0005877
C	-3.9979116	1.2199731	0.0024761	C	-3.945287	1.2131748	0.0003791
C	-2.6039585	1.0727129	0.0030059	C	-2.5463377	1.0911972	0.0001302
H	0.1443582	1.4568317	0.0007101	H	0.1179591	1.4849641	-0.0002447
H	2.3577409	2.2173405	-0.0046946	H	2.3606064	2.2590831	-0.000408
H	4.8254841	1.8491392	-0.004936	H	4.8198833	1.8456874	-0.0005492
H	5.7461708	-0.4859054	-0.0006338	H	5.6988822	-0.5136605	-0.0003457
H	4.1717413	-2.4380631	0.0044131	H	4.1037599	-2.4426128	5.36E-05
H	1.7213202	-2.0765762	0.0052051	H	1.6535324	-2.0599662	9.61E-05
H	-0.3564851	-1.5975339	-0.0008775	H	-0.3424957	-1.6202359	0.0001082
H	-5.9006844	0.1539964	-0.0011067	H	-5.8525105	0.1566997	0.0008388
H	-4.4579569	2.2128478	0.0046973	H	-4.4209428	2.1996272	0.0004301
H	-1.9605163	1.9577018	0.0058687	H	-1.8997848	1.9725564	-0.000101
N	-4.3121213	-1.190116	-0.0036783	N	-4.2782181	-1.2291588	0.0005486
C	-2.9667394	-1.3120475	-0.0031152	C	-2.9453999	-1.346032	0.0003766
H	-2.5827102	-2.3397971	-0.0052169	H	-2.5486269	-2.370597	0.0004203

Table S3: Cartesian coordinates of 3-C1 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	0.6309899	2.067535	0.2008907	C	0.6596648	2.2339986	0.146163
C	1.3689031	0.9077128	0.7656277	C	1.2861678	1.0420701	0.7120928
C	0.7549192	0.007589	1.6703798	C	0.3972443	-0.0710356	1.1544334
C	1.4751153	-1.0819508	2.1905109	C	1.0802788	-1.3234386	1.5195172
C	2.8202131	-1.2867329	1.8207634	C	2.4505231	-1.456913	1.4119145
C	3.4461757	-0.3840314	0.9392686	C	3.2795331	-0.3596128	1.0009873
C	2.7273229	0.7109361	0.423545	C	2.6776704	0.8658536	0.658815
C	-0.660054	2.0715632	-0.2327171	C	-0.6438613	2.232363	-0.2922448
C	-1.5519172	0.8868288	-0.3255295	C	-1.4314118	0.995405	-0.2706289
C	-3.1331224	-1.3678367	-0.5606137	C	-2.71738	-1.4454729	0.0938983
C	-3.6978924	-0.200362	-0.0162169	C	-3.4848836	-0.2427467	0.0473349
C	-2.8967475	0.9490762	0.0957732	C	-2.8181655	0.9870813	-0.1460522
H	1.1875439	3.0118615	0.1380781	H	1.263428	3.1454751	0.0551132
H	-0.2853232	0.1680327	1.9696905	H	-0.3672093	0.2362277	1.891625
H	0.9885032	-1.7702934	2.8891802	H	0.4679234	-2.1670184	1.8529456
H	3.3779717	-2.1380294	2.2239962	H	2.9187084	-2.4125741	1.6738009
H	4.4934719	-0.5309023	0.6555104	H	4.3660543	-0.4805046	0.9390868
H	3.217262	1.4132871	-0.2604924	H	3.3016392	1.6999936	0.3134793
H	-1.0856259	3.0275894	-0.5640962	H	-1.118866	3.1561642	-0.6448057
H	-3.7302699	-2.2809444	-0.6594593	H	-3.2312163	-2.4043517	0.2433457
H	-4.7425649	-0.1955541	0.3099727	H	-4.5706408	-0.2860999	0.1727844
H	-3.3020747	1.877368	0.5138477	H	-3.3750493	1.9319387	-0.1603879
N	-1.8551893	-1.4437701	-1.003839	N	-1.4048328	-1.5105169	-0.0833022
C	-1.0977015	-0.3339934	-0.882984	C	-0.6840898	-0.2972308	-0.2246652
H	-0.0700403	-0.4088201	-1.2543799	H	0.0786391	-0.3928962	-1.0185432

Table S4: Cartesian coordinates of 3-C2 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	2.9518054	-1.2921497	1.6994812	C	2.5224787	-1.4879433	1.2877972
C	3.4642153	-0.3936264	0.7432634	C	3.2970425	-0.3824553	0.8006858
C	2.6846225	0.6960602	0.3100019	C	2.6556647	0.8448464	0.5409564
C	1.3770316	0.8906191	0.8124958	C	1.2756527	1.0087612	0.7306014
C	0.8784221	-0.0054285	1.7888131	C	0.438178	-0.1242312	1.2223155
C	1.6597369	-1.0892783	2.2267653	C	1.1679747	-1.36475	1.5326812
H	3.558328	-2.1375563	2.039979	H	3.0243993	-2.437147	1.5076021
H	4.4708225	-0.5391417	0.3375886	H	4.3728324	-0.4939502	0.6312694
H	3.08613	1.3951967	-0.432401	H	3.2386909	1.6906656	0.1550954
H	-0.1210673	0.1548958	2.2052358	H	-0.2822727	0.1671876	2.0059022
H	1.264076	-1.7733715	2.9846884	H	0.6085767	-2.2072574	1.9554908
C	0.5622192	2.0407822	0.3380429	C	0.5816029	2.2048933	0.2574934
H	1.0732299	3.0107725	0.2812178	H	1.1520666	3.1372787	0.1642663
C	-0.7528805	2.0017652	-0.0136089	C	-0.7509337	2.1800804	-0.0854402
H	-1.239039	2.9505229	-0.2744632	H	-1.2785667	3.1036318	-0.3524412
C	-1.6040122	0.7878198	-0.1009759	C	-1.4909273	0.9164446	-0.0846093
C	-3.3406338	-1.3592983	-0.230643	C	-2.9151711	-1.4373589	0.2375495
H	-4.0503792	-2.1931484	-0.2653832	H	-3.5250887	-2.3399692	0.3547155
C	-2.0149984	-1.5295025	-0.6767876	C	-1.5501497	-1.5407027	0.037593
H	-1.6896339	-2.4970405	-1.071498	H	-1.0886001	-2.5326091	-0.0112192
C	-1.131903	-0.4416875	-0.6147668	C	-0.7113647	-0.3488409	-0.1079589
H	-0.0986938	-0.5360771	-0.9617016	H	0.0169189	-0.41331	-0.9372477
N	-3.8237439	-0.1892925	0.2450822	N	-3.6111007	-0.249181	0.2624459
C	-2.9605917	0.8502186	0.2929892	C	-2.878203	0.8786431	0.0978048
H	-3.3705777	1.7936232	0.6742983	H	-3.4372155	1.8229505	0.1343646

Table S5: Cartesian coordinates of 3-CYC-1 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	3.2228722	-2.9728372	-0.5105912	C	3.2042386	-3.0987988	-0.4285938
C	2.9631428	-1.6705837	-0.1434957	C	2.9228705	-1.7256661	0.0034869
C	4.0351755	-0.8570057	0.568916	C	3.9442541	-1.0488665	0.8581507
C	2.7194305	1.0812187	0.2334153	C	2.744224	0.9705803	0.6685715
C	4.5380701	-3.5541366	-0.3237615	C	4.4943079	-3.5748809	-0.4329581
C	5.6158606	-2.773681	0.0372343	C	5.6319156	-2.7286077	-0.0817807
C	5.4491175	-1.258819	0.1231697	C	5.4285296	-1.2508534	-0.0766627
C	6.5136721	-0.5924578	0.9716548	C	6.5355159	-0.4590376	0.4858801
C	7.6968565	-1.2123879	1.2353692	C	7.6619473	-1.0619844	1.0095904
C	7.9504322	-2.5858445	0.7821692	C	7.8352155	-2.4863356	0.9709492
C	6.945414	-3.3358245	0.2263984	C	6.8142571	-3.2881132	0.4271295
H	2.4099379	-3.5910717	-0.9106515	H	2.3721992	-3.7288829	-0.7661705
H	3.9356728	-1.0708449	1.6620483	H	4.2286323	-1.6351596	1.7506126
H	2.6231135	2.1749028	0.1794921	H	2.6692784	2.0362022	0.9227256
H	4.680223	-4.6283001	-0.4898037	H	4.6859702	-4.6250058	-0.686107
H	5.5649521	-0.8681868	-0.9200681	H	5.0541159	-0.849793	-1.0364933
H	6.3201816	0.4311697	1.3060078	H	6.4315985	0.6302082	0.5079647
H	8.4714121	-0.6958586	1.8121718	H	8.4542914	-0.4379751	1.4383396
H	8.9389337	-3.028412	0.945056	H	8.7443273	-2.9436586	1.3750134
H	7.1122016	-4.3879934	-0.03274	H	6.9244828	-4.3799827	0.4229558
C	1.6474062	-1.0667532	-0.251743	C	1.8345541	-0.996207	-0.4671343
H	0.7948525	-1.6806292	-0.5658731	H	1.0891449	-1.4785237	-1.1111474
N	3.9150225	0.6141054	0.4358227	N	3.7676971	0.3162334	1.2003424
C	1.5092664	0.2723471	0.0004053	C	1.7338224	0.3753001	-0.1451787
H	0.5395822	0.7740391	-0.076779	H	0.9054116	0.9859634	-0.5156618

Table S6: Cartesian coordinates of 3-CYC-2 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	3.2207345	-2.9198129	-0.4741208	C	3.2189541	-3.0184444	-0.453908
C	2.9965464	-1.6167477	-0.0978964	C	2.9912826	-1.6312894	-0.0437454
C	4.0805981	-0.8412089	0.6363767	C	4.0379991	-0.9644403	0.773977
C	3.8034881	0.6445446	0.5265019	C	3.7668229	0.4566036	1.0028118
C	2.5795651	1.112997	0.1681119	C	2.6669364	1.0771587	0.4380804
C	4.5204054	-3.5324188	-0.2675896	C	4.4856684	-3.5550555	-0.415722
C	5.6171723	-2.7680264	0.067282	C	5.6528548	-2.7457077	-0.0708821
C	5.4810586	-1.244597	0.1352022	C	5.5138756	-1.2628198	-0.1617916
C	6.5925127	-0.6019652	0.9460389	C	6.6549786	-0.4859501	0.3501875
C	7.7666967	-1.2460403	1.1884076	C	7.7327409	-1.0995903	0.9598584
C	7.9749553	-2.6337846	0.755346	C	7.829164	-2.5288982	1.0440722
C	6.936245	-3.3633843	0.2393021	C	6.7887471	-3.3201504	0.5183229
H	2.4078624	-3.5046605	-0.9212095	H	2.3672069	-3.6155537	-0.8011953
H	4.0242805	-1.1332483	1.7152769	H	4.3161464	-1.5193737	1.6888013
H	4.5845703	1.3635934	0.7927755	H	4.4482176	1.0397596	1.6312404
H	2.3816613	2.1875848	0.122249	H	2.4858804	2.1436588	0.6118565
H	4.6405448	-4.6114294	-0.4182964	H	4.6343367	-4.6198153	-0.6340146
H	5.575233	-0.8724706	-0.9170722	H	5.151473	-0.9127473	-1.1436639
H	6.4627618	0.431287	1.2838077	H	6.6297804	0.6053572	0.2505645
H	8.5672442	-0.7382473	1.7364414	H	8.5506915	-0.4843016	1.351793
H	8.9553692	-3.0983538	0.9028113	H	8.7003584	-2.9969915	1.5134979
H	7.0667879	-4.4239444	-0.0056075	H	6.8483781	-4.4134444	0.5916939
N	1.4593174	0.3005978	-0.1763521	N	1.7156711	0.4348857	-0.3232001
C	1.6973778	-0.9774413	-0.3095208	C	1.9092647	-0.8897357	-0.5325103
H	0.8600518	-1.6117695	-0.6353125	H	1.1556108	-1.3920609	-1.1531711

Table S7: Cartesian coordinates of 4-T1 in the S_0 and S_1 states optimized at SCS-RI-MP2/aug-cc-pVDZ and SCS-RI-ADC(2)/aug-cc-pVDZ levels of theory, respectively.

S_0				S_1			
Atom	x	y	z	Atom	x	y	z
C	2.8811326	1.2534822	-0.0069651	C	2.8893383	1.3031312	-0.1669529
C	1.9658235	0.1904809	0.000898	C	1.9154802	0.2505096	-0.0781741
C	2.4721587	-1.1203107	0.008421	C	2.4017091	-1.0900069	0.1222633
C	3.8429163	-1.3521408	0.0074973	C	3.7606899	-1.3345918	0.2133102
C	4.7423461	-0.2825636	-0.0007903	C	4.6864205	-0.2867154	0.1108078
C	4.255524	1.0228199	-0.0079706	C	4.2365081	1.0387292	-0.0773961
H	2.5071355	2.2700532	-0.01247	H	2.5367545	2.3166609	-0.3144806
H	1.7961427	-1.9643772	0.0158385	H	1.6979575	-1.9036264	0.2249204
H	4.2129994	-2.3687831	0.0137321	H	4.1139611	-2.345833	0.3660072
H	5.8079375	-0.4678995	-0.0012797	H	5.7465072	-0.4929355	0.176526
H	4.9415335	1.8592375	-0.0142747	H	4.9536979	1.8449661	-0.1509763
C	0.5328284	0.5017074	0.0014292	C	0.5531053	0.5515539	-0.1794453
H	0.2983082	1.5606185	0.0039293	H	0.2808706	1.5949624	-0.2896113
C	-0.480458	-0.3863115	-0.0017195	C	-0.4879666	-0.421879	-0.1791292
H	-0.2566397	-1.4469353	-0.0058443	H	-0.220489	-1.4644206	-0.3051785
C	-1.9086068	-0.0565987	-0.0007644	C	-1.848152	-0.1147419	-0.0640901
C	-2.8533213	-1.0893112	-0.0073606	C	-2.8517425	-1.1326537	-0.1508943
C	-4.2128563	-0.7872248	-0.0061987	C	-4.1842193	-0.8006835	-0.0417738
H	-2.5319789	-2.1230485	-0.0133242	H	-2.5580752	-2.163198	-0.3103238
H	-4.9456557	-1.5852042	-0.0111317	H	-4.9404909	-1.5738645	-0.1107652
C	-2.4172463	1.2503339	0.0068006	C	-2.3478794	1.215196	0.1484059
H	-1.7618817	2.1097933	0.0127932	H	-1.6741185	2.0545145	0.2539426
C	-3.7921781	1.4491806	0.0071819	C	-3.7140321	1.4213504	0.2461449
N	-4.7010352	0.4596578	0.0009554	N	-4.6529372	0.4607393	0.1497145
H	-4.1911301	2.4563542	0.0128312	H	-4.0890992	2.4258472	0.4093625

Table S8: Cartesian coordinates of 4-C1 and 4-CYC-1 in the S_0 state optimized at SCS-RI-MP2/aug-cc-pVDZ level of theory, respectively.

4-C1				4-CYC-1			
Atom	x	y	z	Atom	x	y	z
C	-2.5533019	-0.295688	1.8100338	C	-2.5180444	-0.1123753	1.7891254
C	-1.3312586	0.3654862	1.5455185	C	-1.2149288	-0.3180486	1.1734826
C	-1.3632281	1.669179	0.9942319	C	-0.9982099	0.1948224	-0.2491455
C	-2.5901266	2.281555	0.6839296	C	-2.288763	0.2251326	-1.0498777
C	-3.8031427	1.6036422	0.9238957	C	-3.5028224	0.2803582	-0.4354374
C	-3.7815782	0.3149598	1.4922413	C	-3.6130025	0.204508	1.0257339
C	-0.0435429	-0.2993779	1.8776128	C	0.1115341	-0.5797393	-0.984488
C	1.072983	-0.3273427	1.0983342	C	1.3107963	-0.8822203	-0.10016
C	1.1983201	0.2057174	-0.2825089	C	1.1421358	-1.0458864	1.2559567
C	0.1767288	0.0602183	-1.2484673	C	-0.1537483	-0.8488158	1.8761881
C	0.3772466	0.572652	-2.5408053	C	0.562824	0.1552765	-2.2393399
C	2.4836487	1.331385	-2.0160025	C	2.6986075	-0.7417076	-2.1032127
C	2.3848303	0.8463571	-0.6989324	C	2.5616543	-1.1290291	-0.7965096
H	-0.7584057	-0.4499376	-1.0004339	H	-0.3086868	-1.5652298	-1.3100146
H	-0.4049667	0.4650071	-3.3004522	H	-0.1528852	0.8216124	-2.7406643
H	3.3955361	1.8404695	-2.3479222	H	3.6197912	-0.9244068	-2.6630287
H	3.2223262	0.9754227	-0.0046954	H	3.4011858	-1.5949535	-0.2686189
H	-0.4235593	2.200648	0.8140539	H	-0.6439611	1.2521486	-0.1399096
H	-2.6016336	3.2907476	0.259352	H	-2.2293691	0.255438	-2.143491
H	-4.7575856	2.0809435	0.6796535	H	-4.4183811	0.3461025	-1.0326725
H	-4.7201263	-0.2129881	1.6906525	H	-4.593997	0.3309347	1.4953218
H	-2.5389847	-1.2974747	2.2542513	H	-2.6182133	-0.2719814	2.8690816
N	1.5041494	1.2103627	-2.9406694	N	1.7361177	0.0526835	-2.7860249
H	1.9735888	-0.7966151	1.514787	H	-0.2886399	-1.1113417	2.931946
H	0.0076819	-0.802901	2.8518851	H	1.9908088	-1.3702236	1.8694519

Table S9: Cartesian coordinates of conical intersection structures, 3-CI1 and 3-CI2 at SA-3-CASSCF(12,10)/6-31G* level of theory.

3-CI1				3-CI2			
Atom	x	y	z	Atom	x	y	z
C	-2.1173955	-0.5741274	1.0879451	C	3.0628167	-0.7640522	-0.4383604
C	-1.0233105	0.3020205	1.0115074	C	1.8243561	-0.0277396	-0.2106980
C	-1.2857797	1.6682542	0.9374527	C	0.8208072	-0.1779431	-1.2544638
C	-2.6130661	2.0860124	0.9564162	C	1.0512813	-1.0230039	-2.3876940
C	-3.5999745	1.1293712	1.0370877	C	2.2219253	-1.6622420	-2.5462187
N	-3.3640764	-0.1828299	1.1047523	C	3.2587931	-1.4928870	-1.5477252
C	0.3455705	-0.1931259	1.1100669	C	1.5302809	0.6171070	1.0409803
C	1.5249598	0.6294345	1.0142974	C	0.3692435	-0.2245592	1.1233943
C	1.8036172	-0.0614296	-0.2182139	C	-1.0296435	0.2341452	1.0272281
C	0.8600411	-0.1649271	-1.2951355	C	-2.0886677	-0.6649968	1.0500034
C	1.1097563	-0.9681688	-2.4378857	C	-3.3805477	-0.1723522	1.0328936
C	2.2703379	-1.6444975	-2.5757034	C	-3.5608428	1.1951639	0.9956978
C	3.2638259	-1.5507899	-1.5375244	N	-2.5655187	2.0669971	0.9764361
C	3.0277711	-0.8417634	-0.4012151	C	-1.3196026	1.5889409	0.9830962
H	2.2835365	0.3170071	1.7208910	H	2.2988372	0.3025436	1.7370187
H	-0.0091950	0.4574458	-1.2959994	H	-0.0211079	0.4795844	-1.2724742
H	0.3599157	-1.0097759	-3.2080641	H	0.2734768	-1.1118605	-3.1254920
H	2.4679049	-2.2396454	-3.4481935	H	2.4101007	-2.2836358	-3.4020621
H	4.1958515	-2.0745141	-1.6564113	H	4.2022717	-1.9880424	-1.6977607
H	3.7723253	-0.7912927	0.3723035	H	3.8407312	-0.6715373	0.2978440
H	0.3927090	-1.2603493	1.3174354	H	0.4426528	-1.2812375	1.3750789
H	-0.4589184	2.3489090	0.8768425	H	-0.5146009	2.2966822	0.9597406
H	-2.8713234	3.1270352	0.9062677	H	-4.5532783	1.6103745	0.9806551
H	-4.6361935	1.4160563	1.0474276	H	-1.9036364	-1.7243515	1.0821081
H	-1.9478373	-1.6364833	1.1430039	H	-4.2288871	-0.8309457	1.0536539

Table S10: Cartesian coordinates of conical intersection structure, 3-CI3 and 3-CI4 at SA-3-CASSCF(12,10)/6-31G* level of theory.

3-CI3				**3-CI4**			
Atom	x	y	z	Atom	x	y	z
C	-1.0086547	0.5590038	0.2817574	C	-2.4778760	-0.5913321	1.8940844
C	-0.0151598	-0.7450420	-0.8168190	C	-1.2027404	-0.0603189	1.6401354
C	1.1353293	-0.8701570	0.0441916	C	-0.9993311	0.7040978	0.4211634
C	1.1001189	-0.7825500	1.4552913	N	-2.1101394	1.2296429	-0.2246444
C	-0.1380859	-0.7185709	2.1025401	C	-3.2702801	0.7645981	0.1416256
C	-1.2613603	-0.1680038	1.5221706	C	-3.5433897	-0.2253825	1.1249557
C	0.1311767	-0.6957163	-2.2354568	C	-0.0261107	-0.5951287	2.1685127
C	1.3551790	-0.7119079	-2.8404170	C	1.1955690	-0.4966431	1.5007208
C	2.4626759	-0.9339218	-1.9807199	C	1.0960308	-0.7751758	0.1043901
C	2.3797221	-1.0595774	-0.6246851	C	-0.0917405	-0.6017755	-0.7172930
C	-2.2339209	1.0007892	-0.3783543	C	0.0059270	-0.6001010	-2.1369462
C	-3.4264382	0.7731255	0.2296571	C	1.2034640	-0.7285552	-2.7895868
N	-3.6712120	0.0408838	1.3733691	C	2.3029886	-1.0702755	-1.9695590
C	-2.5999446	-0.3936284	1.9498790	C	2.2481333	-1.2051611	-0.6039908
H	1.9764066	-1.0749805	2.0002171	H	2.0805545	-0.8538893	1.9930403
H	-0.8934462	-1.2795769	-0.4941628	H	-0.9479555	-1.1618784	-0.3815227
H	-0.7685226	-0.6311100	-2.8235329	H	-0.9112020	-0.4862724	-2.6870814
H	1.4942125	-0.5934330	-3.8970376	H	1.3163989	-0.6250934	-3.8506050
H	3.4412988	-1.0098740	-2.4253708	H	3.2571613	-1.2405262	-2.4401803
H	3.2675550	-1.2367102	-0.0472610	H	3.1306382	-1.4895945	-0.0630234
H	-0.2287465	-1.1387183	3.0949796	H	-0.0932782	-1.1274452	3.1106790
H	-2.1804999	1.6071149	-1.2627637	H	-4.1084401	1.2104641	-0.3728748
H	-4.3029910	1.2213415	-0.2065528	H	-2.6036409	-1.2740337	2.7196762
H	-2.7366176	-0.9909545	2.8396272	H	-0.1324777	1.3479213	0.4448191
H	-0.1615887	1.2302843	0.3002528	H	-4.5501297	-0.5320726	1.3268700

Table S11: Cartesian coordinates of conical intersection structures, 4-CI1 and 4-CI2 at SA-3-CASSCF(12,10)/6-31G* level of theory.

4-CI1				4-CI2			
Atom	x	y	z	Atom	x	y	z
C	3.0363706	-0.8401812	-0.4108822	C	-2.5880937	-0.4985790	1.9548016
C	1.8193217	-0.0472516	-0.2196801	C	-1.2494305	-0.1676581	1.5460459
C	0.8615854	-0.1425597	-1.2862006	C	-1.0206317	0.5846283	0.3216021
C	1.0923045	-0.9627750	-2.4234361	C	-2.2140054	1.0691755	-0.3729552
C	2.2462228	-1.6498951	-2.5585110	C	-3.4394402	0.7843303	0.1319016
C	3.2453731	-1.5543096	-1.5267114	C	-3.6660884	-0.0577321	1.2918395
C	1.5432802	0.6447462	1.0130017	C	-0.1039039	-0.6923502	2.1000826
C	0.3768983	-0.1945622	1.1024183	C	1.1349954	-0.6774576	1.4327911
C	-1.0077208	0.2696460	1.0054395	C	1.1397930	-0.8012702	0.0405327
C	-2.0751594	-0.6264642	1.0753687	C	2.3625054	-0.9642721	-0.7103425
C	-3.3712544	-0.1251377	1.0795861	C	2.3610416	-0.7234844	-2.0532960
N	-3.6478413	1.1777748	1.0171690	N	1.2865352	-0.4959914	-2.8607380
C	-2.6275328	2.0300384	0.9535804	C	0.1521979	-0.6154579	-2.2267402
C	-1.2928565	1.6295405	0.9431804	C	-0.0217187	-0.7296495	-0.8259337
H	2.3071914	0.3550108	1.7220909	H	2.0355442	-0.9033848	1.9705083
H	0.0119917	0.5061078	-1.2907919	H	-0.8937098	-1.2931251	-0.5407673
H	0.3380704	-1.0037922	-3.1890623	H	-0.7397992	-0.6043953	-2.8337432
H	2.4355334	-2.2555412	-3.4254887	H	-0.1779045	-1.1647206	3.0704091
H	4.1703132	-2.0898867	-1.6516829	H	-0.1517260	1.2229073	0.3473179
H	3.7853522	-0.7960663	0.3588125	H	-2.0940445	1.7028684	-1.2307928
H	0.4446349	-1.2546618	1.3362775	H	-4.2941737	1.2253768	-0.3522224
H	-0.4856041	2.3333401	0.8957909	H	-4.6675619	-0.2768534	1.6062940
H	-2.8824537	3.0731529	0.9116637	H	-2.6991812	-1.1223693	2.8260797
H	-1.9032919	-1.6863249	1.1247919	H	3.2881897	-1.1528927	-0.1995066
H	-4.2146180	-0.7888171	1.1349960	H	3.3101190	-0.7131705	-2.5628352

Table S12: Vertical Excitation Energies (VEEs in eV) for the First Three Singlet Excited States at CASPT2 and SCS-RI-ADC(2) levels. The main character of each excited state is also shown.

	S_1				S_2				S_3			
	CASPT2		RI-ADC(2)		CASPT2		RI-ADC(2)		CASPT2		RI-ADC(2)	
3-STPY:												
3-T1	4.77	$\pi\pi^*$	4.38	$\pi\pi^*$	5.21	$\pi\pi^*$	4.59	$\pi\pi^*$	5.64	$\pi\pi^*$	4.61	$\pi\pi^*$
3-T2	4.42	$\pi\pi^*$	4.26	$\pi\pi^*$	5.24	$\pi\pi^*$	4.57	$\pi\pi^*$	5.92	$\pi\pi^*$	4.75	$\pi\pi^*$
3-C1	4.91	$\pi\pi^*$	4.59	$\pi\pi^*$	5.11	$\pi\pi^*$	4.78	$\pi\pi^*$	5.70	$\pi\pi^*$	4.88	$\pi\pi^*$
3-C2	4.98	$\pi\pi^*$	4.62	$\pi\pi^*$	5.22	$\pi\pi^*$	4.73	$\pi\pi^*$	5.73	$\pi\pi^*$	4.89	$\pi\pi^*$
3-CYC-1	3.62	$\pi\pi^*$	2.97	$\pi\pi^*$	4.06	$\pi\pi^*$	4.08	$n\pi^*$	4.70	$\pi\pi^*$	4.28	$\pi\pi^*$
3-CYC-2	3.76	$\pi\pi^*$	3.02	$\pi\pi^*$	3.99	$\pi\pi^*$	4.01	$n\pi^*$	4.84	$\pi\pi^*$	4.25	$\pi\pi^*$
4-STPY:												
4-T1	4.44	$\pi\pi^*$	4.38	$\pi\pi^*$	5.43	$\pi\pi^*$	4.59	$\pi\pi^*$	5.73*	$\pi\pi^*$	4.63	$\pi\pi^*$
4-C1	4.96	$\pi\pi^*$	4.6	$\pi\pi^*$	5.57	$\pi\pi^*$	4.78	$\pi\pi^*$	6.06*	$\pi\pi^*$	4.85	$\pi\pi^*$
4-CYC-1	3.68	$\pi\pi^*$	3.14	$\pi\pi^*$	4.20	$\pi\pi^*$	4.16	$\pi\pi^*$	4.81*	$\pi\pi^*$	4.21	$n\pi^*$

* The aug-cc-pVDZ basis set is used. The characters of the excited states are listed in the right column, adjacent to the corresponding energy values.

Table S13: Energy gap between the S_1 and S_0 states(in eV) at the CASSCF/6-31G(d,p) and CASPT2/6-31G(d,p) levels.

	CASSCF(ΔE)	CASPT2 (ΔE)
3-STPY:		
3-CI1	0.00	0.53
3-CI2	0.00	0.42
3-CI3	0.00	0.33
3-CI4	0.00	0.11
4-STPY:		
4-CI1	0.00	0.43
4-CI2	0.00	0.32

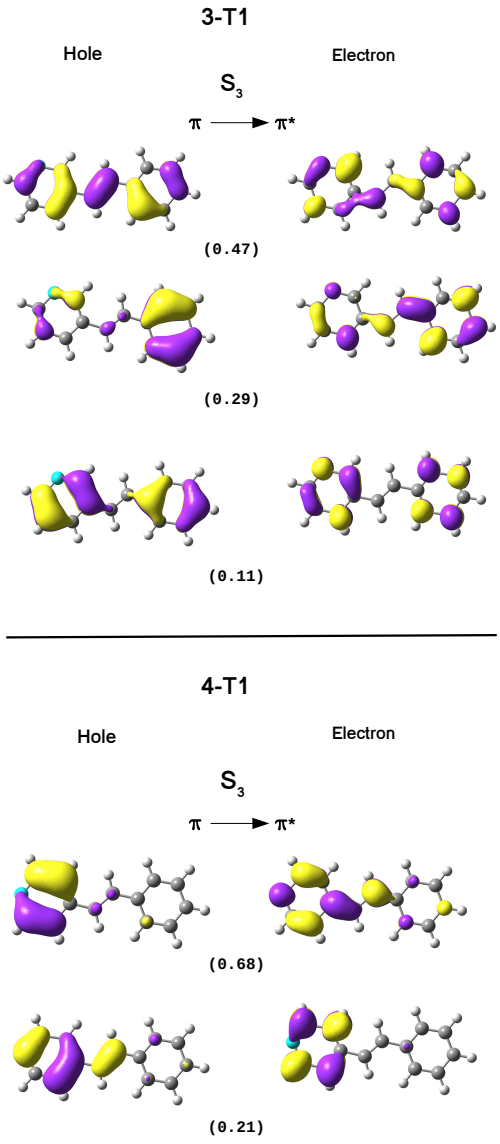

Figure S1: Dominant NTOs involved in the transitions from S_0 to S_3 state for **3-T1** and **4-T1**.

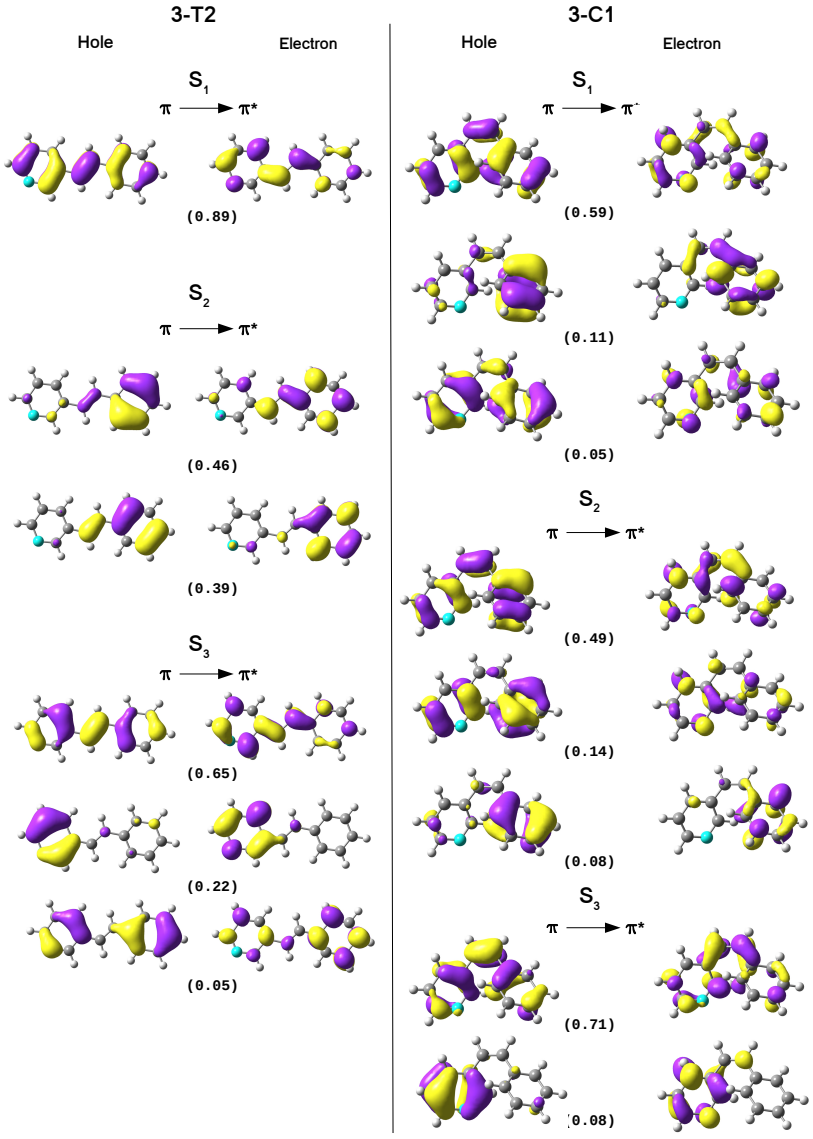

Figure S2: Dominant NTOs involved in the transitions from S_0 to S_1, S_2 and S_3 states for **3-T2** and **3-C1**. The values in parentheses indicate the weight of a configuration.

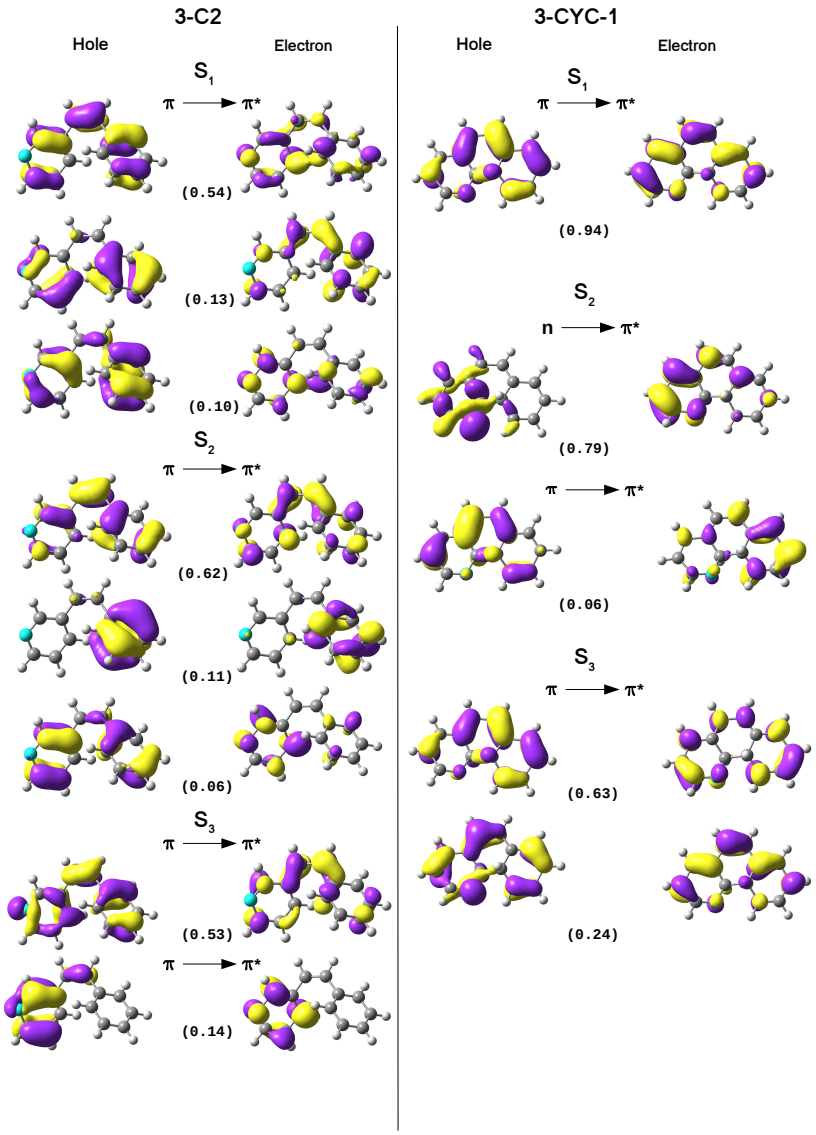

Figure S3: Dominant NTOs involved in the transitions from S_0 to S_1, S_2 and S_3 states for **3-C2** and **3-CYC-1**. The values in parentheses indicate the weight of a configuration.

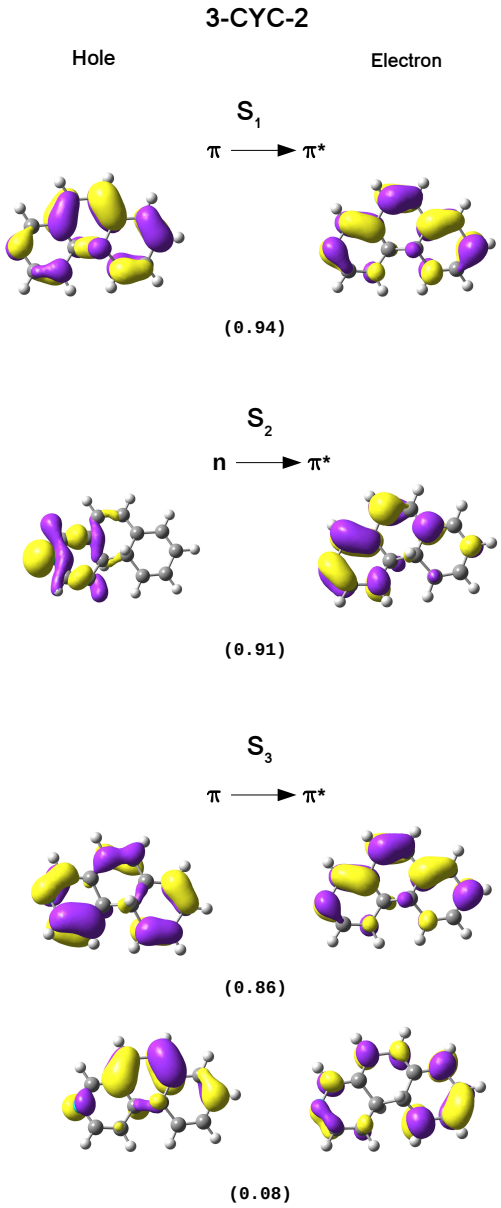

Figure S4: Dominant NTOs involved in the transitions from S_0 to S_1, S_2 and S_3 states for **3-CYC-2**. The values in parentheses indicate the weight of a configuration.

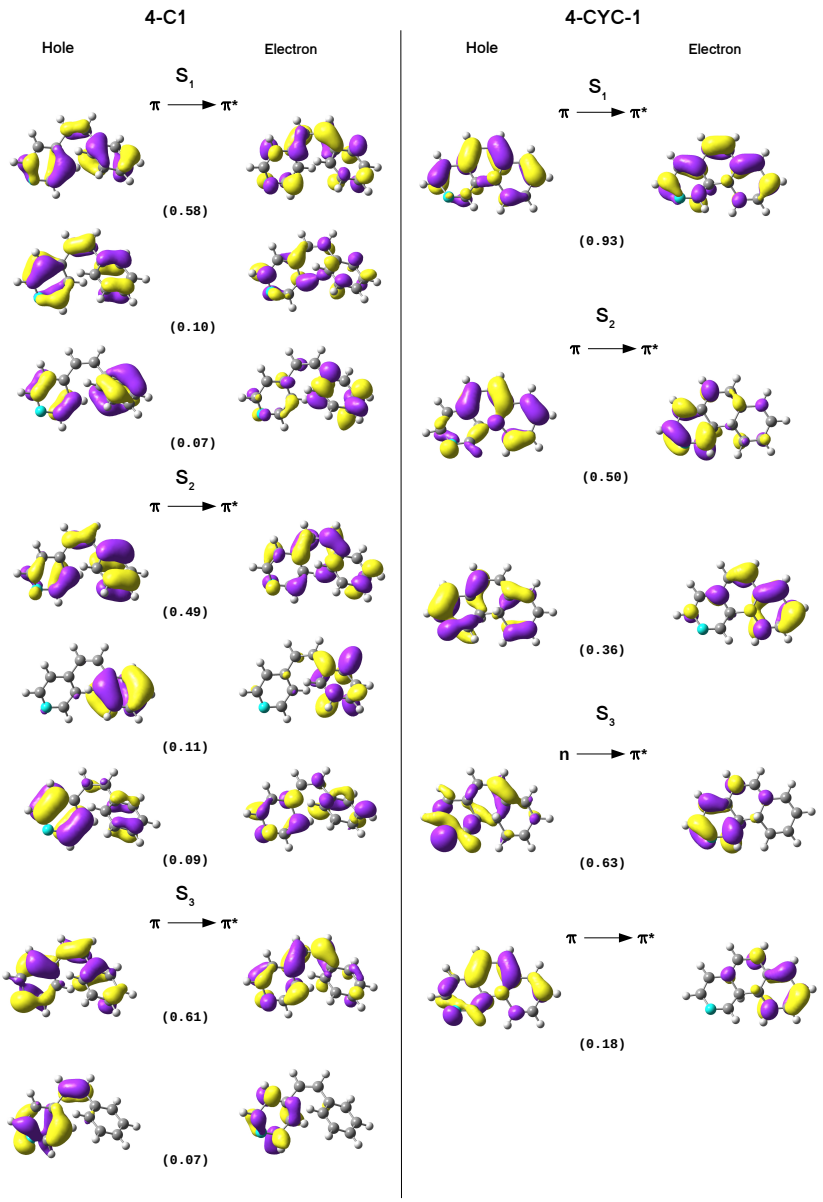

Figure S5: Dominant NTOs involved in the transitions from S_0 to S_1, S_2 and S_3 states for **4-C1** and **4-CYC-1**. The values in parentheses indicate the weight of a configuration.

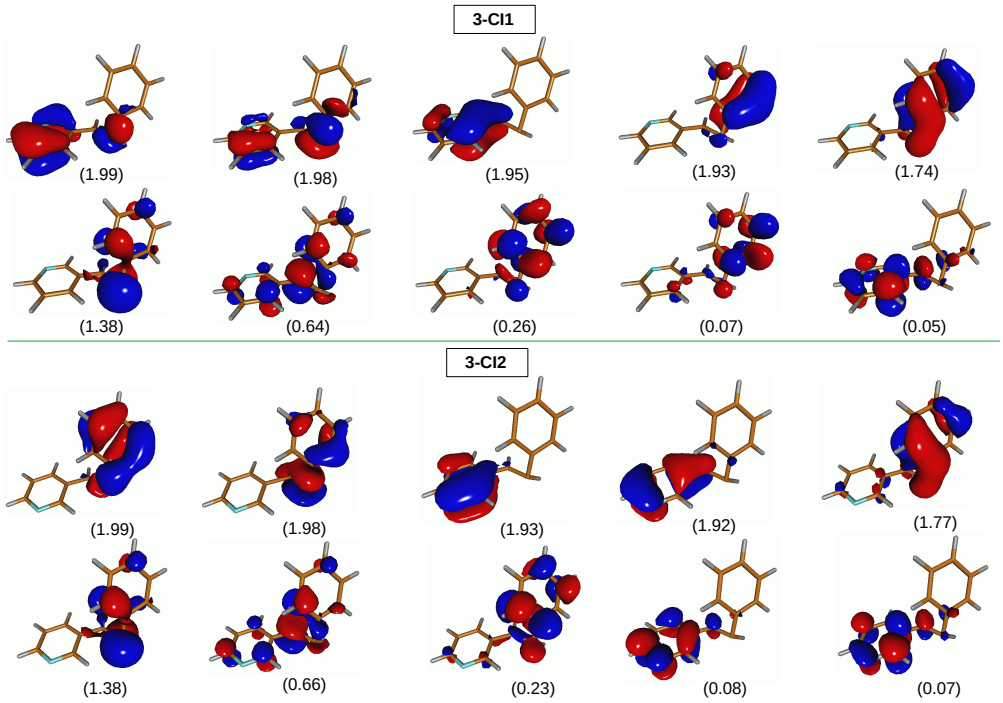

Figure S6: The orbitals in the active space for **3-CI1** and **3-CI2** structures calculated at SA-3-CASSCF(12,10)/6-31G* level. The numbers in the parentheses depict the orbital occupation number.

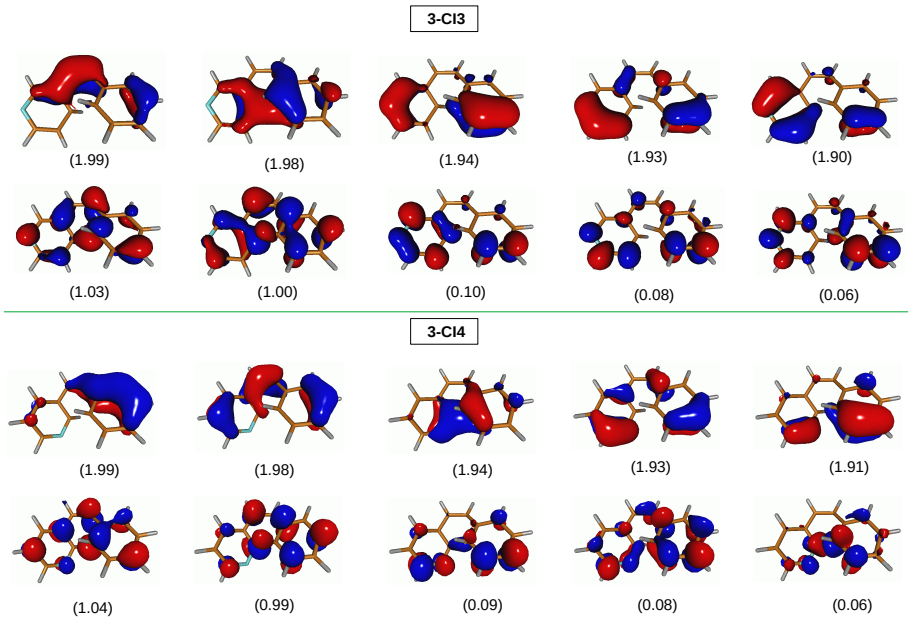

Figure S7: The orbitals in the active space for **3-CI3** and **3-CI4** structures calculated at SA-3-CASSCF(12,10)/6-31G* level. The numbers in the parentheses depict the orbital occupation number.

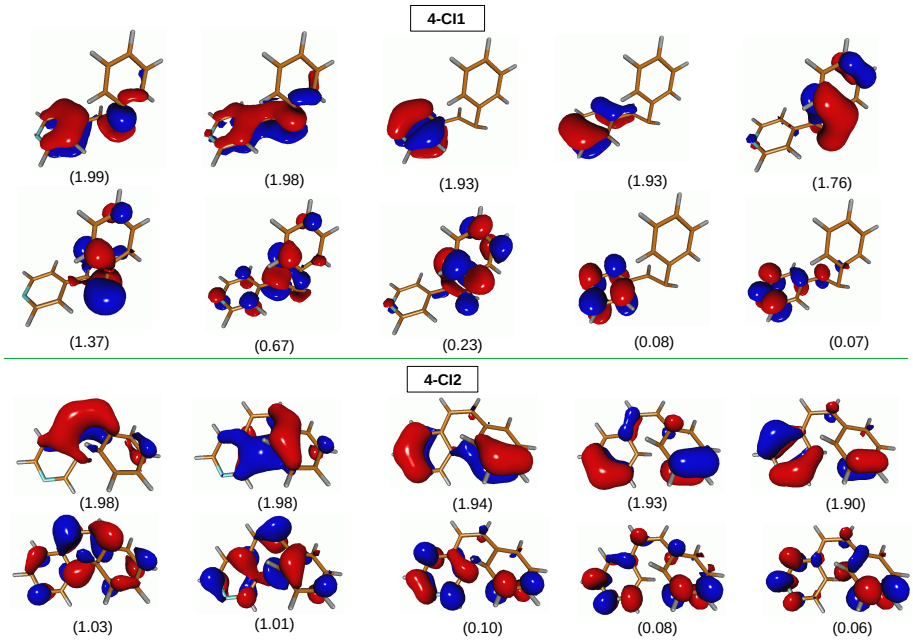

Figure S8: The orbitals in the active space for **4-C1** and **4-CI2** structures calculated at SA-3-CASSCF(12,10)/6-31G* level. The numbers in the parentheses depict the orbital occupation number.

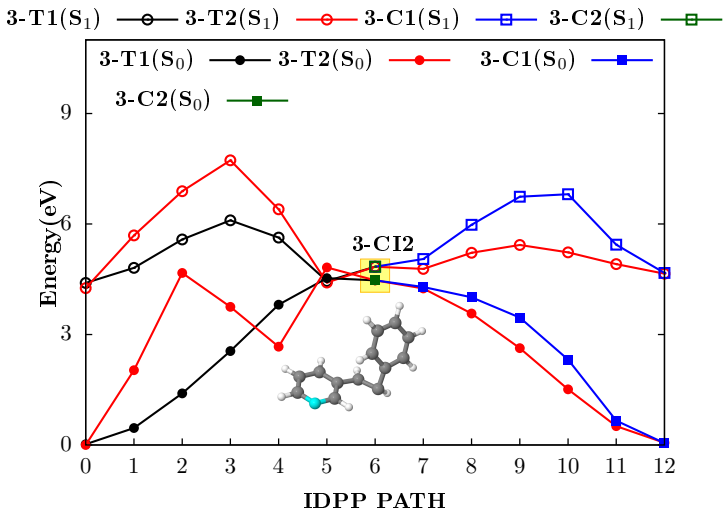

Figure S9: Potential energy profiles along the IDPP pathways linking the 3-STPY *trans* and *cis* conformers via **3-CI2**, computed at SCS-RI-ADC(2)/aug-cc-pVDZ level of theory. Energies are relative to the ground state of **3-T2**. The molecular structure of **3-CI2** is depicted within the figure. The highlighted portion indicates the **3-CI1** point.

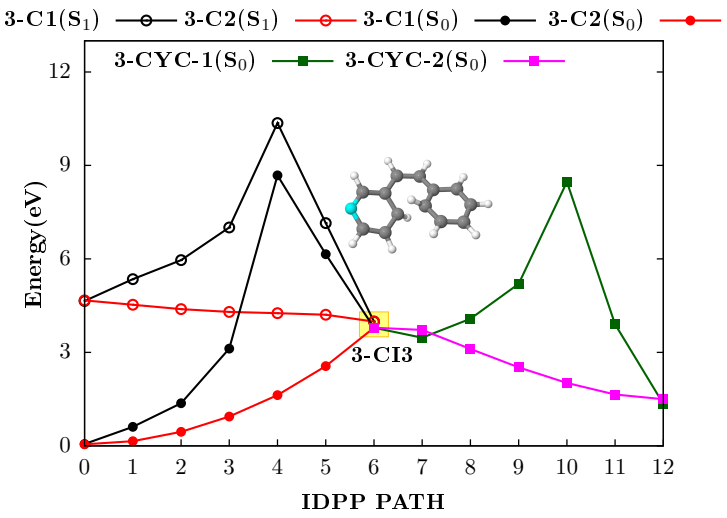

Figure S10: Potential energy profiles along the IDPP pathways linking the 3-STPY *trans* conformers via **3-CI3**, computed at SCS-RI-ADC(2)/aug-cc-pVDZ level of theory. Energies are relative to the ground state of **3-T2**. The molecular structure of **3-CI3** is depicted within the figure. The highlighted portion indicates the **3-CI3** point.

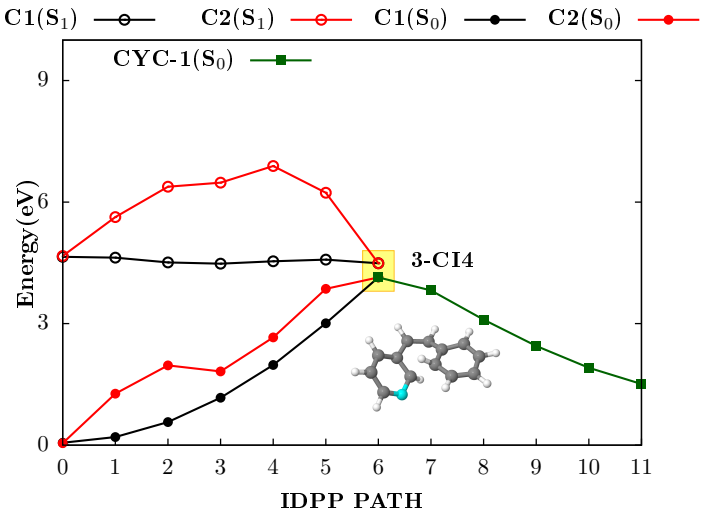

Figure S11: Potential energy profiles along the IDPP pathways linking the 3-STPY *cis* and cyclized conformers via **3-CI4**, computed at SCS-RI-ADC(2)/aug-cc-pVDZ level of theory. Energies are relative to the ground state of **3-T2**. The molecular structure of **3-CI4** is depicted within the figure. The highlighted portion indicates the **3-CI4** point.

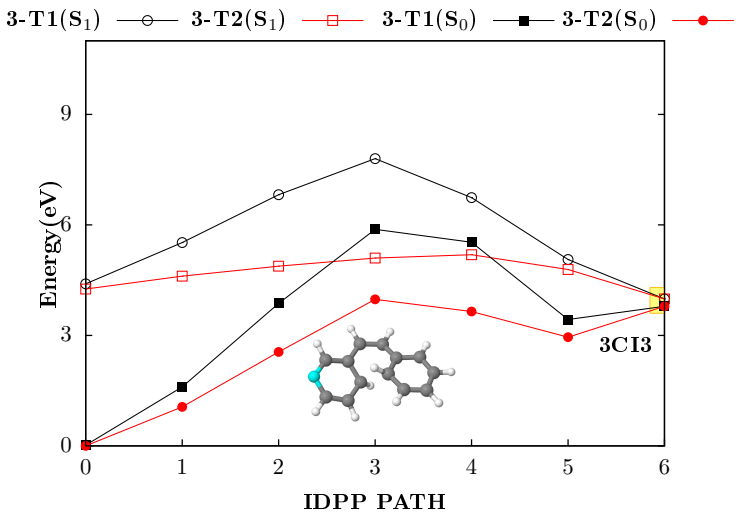

Figure S12: Potential energy profiles along the IDPP pathways linking the 3-STPY *trans* conformers via **3-CI3**, computed at SCS-RI-ADC(2)/aug-cc-pVDZ level of theory. Energies are relative to the ground state of **3-T2**. The molecular structure of **3-CI3** is depicted within the figure. The highlighted portion indicates the **3-CI3** point.

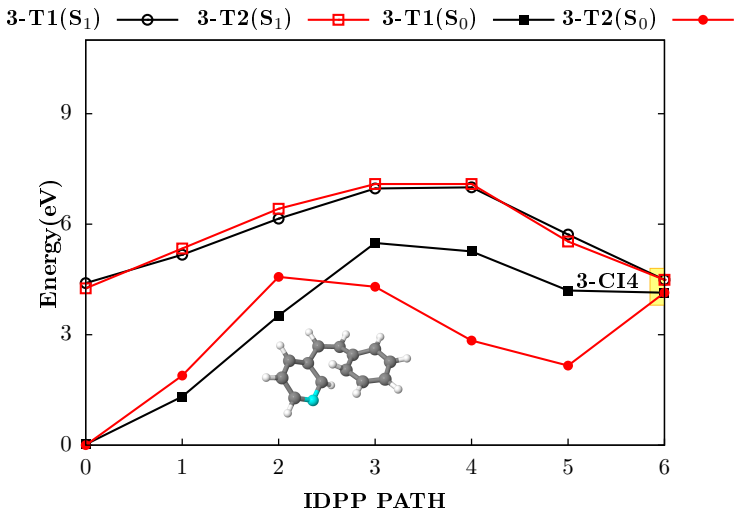

Figure S13: Potential energy profiles along the IDPP pathways linking the 3-STPY *trans* conformers via **3-CI4**, computed at SCS-RI-ADC(2)/aug-cc-pVDZ level of theory. Energies are relative to the ground state of **3-T2**. The molecular structure of **3-CI4** is depicted within the figure. The highlighted portion indicates the **3-CI4** point.

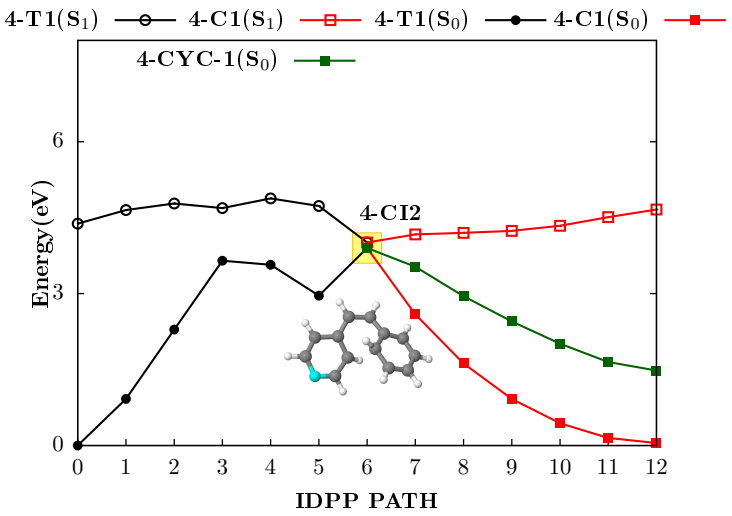

Figure S14: Potential energy profiles along the IDPP pathways linking the 4-STPY *cis* and cyclized conformers via **4-CI2**, computed at SCS-RI-ADC(2)/aug-cc-pVDZ level of theory. Energies are relative to the ground state of **3-T2**. The molecular structure of **4-CI2** is depicted within the figure. The highlighted portion indicates the **4-CI2** point.

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