Electronic Supporting Information for

New insights into the photocyclization reaction of a popular diarylethene switch - a nonadiabatic molecular dynamics study

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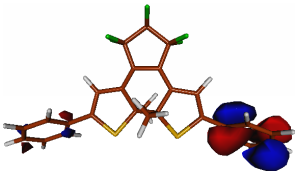
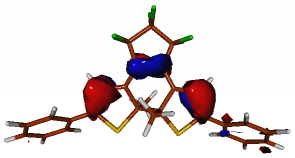
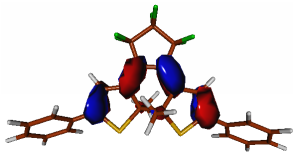


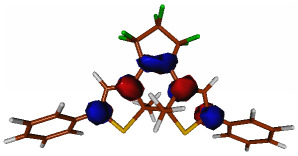
(a) H2 orbital of **PT-CF**



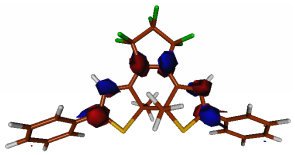
(b) H1 orbital of **PT-CF**



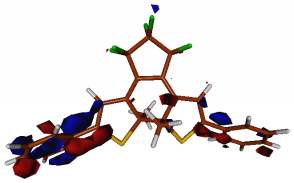
(c) HOMO orbital of **PT-CF**



(d) LUMO orbital of **PT-CF**

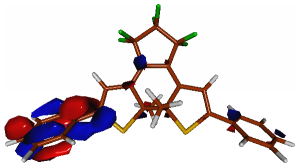


(e) L1 orbital of **PT-CF**



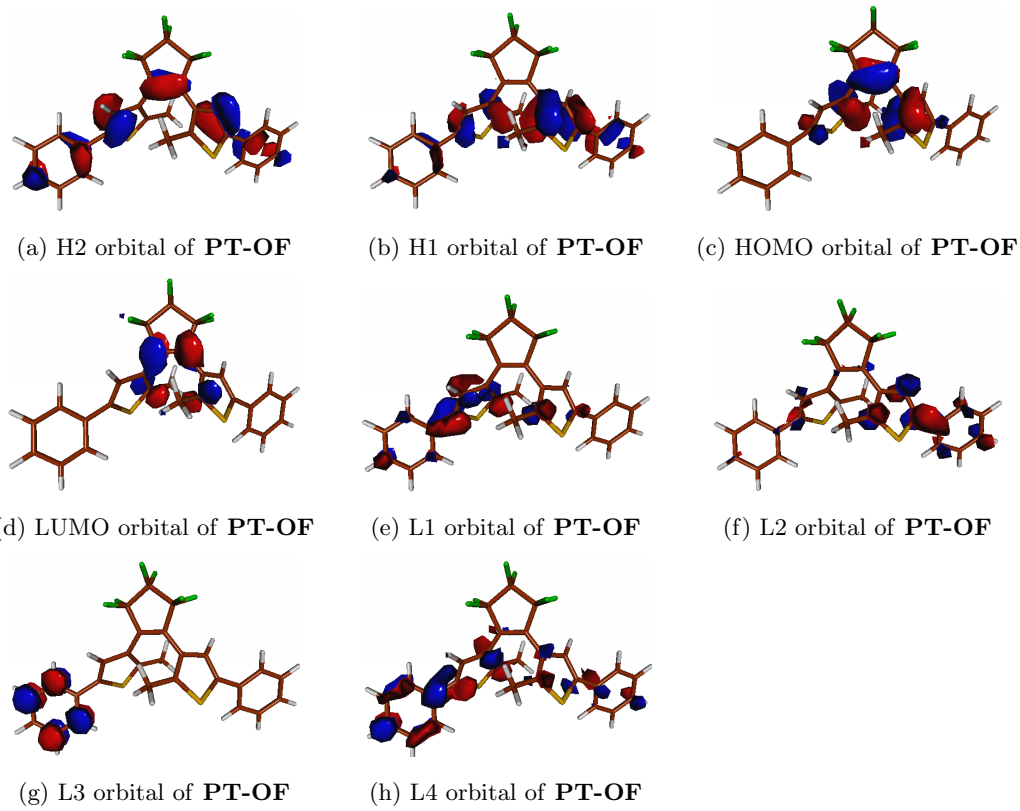
(f) L2 orbital of **PT-CF**

(g) L3 orbital of **PT-CF**



(h) L4 orbital of **PT-CF**

Figure S1: Active space orbitals of **PT-CF** used in ODM2/MRCI calculations. These orbitals have been optimized for an open-shell singlet configuration, with the HOMO and LUMO orbitals each occupied by one electron (H-L).

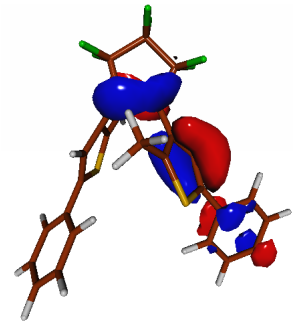


(a) H2 orbital of **PT-OF** (b) H1 orbital of **PT-OF** (c) HOMO orbital of **PT-OF**

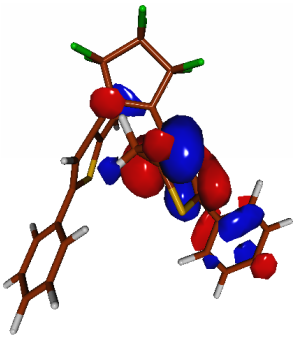
(d) LUMO orbital of **PT-OF** (e) L1 orbital of **PT-OF** (f) L2 orbital of **PT-OF**

(g) L3 orbital of **PT-OF** (h) L4 orbital of **PT-OF**

Figure S2: Active space orbitals of **PT-OF** used in ODM2/MRCI calculations. These orbitals have been optimized for an open-shell singlet configuration, with the HOMO and LUMO orbitals each occupied by one electron (H-L).



(a) H2 orbital of **PT**-*twist*.



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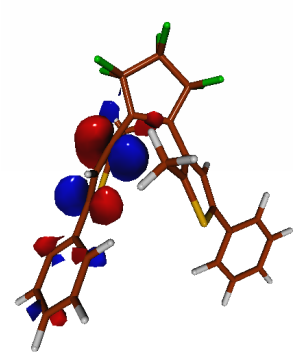
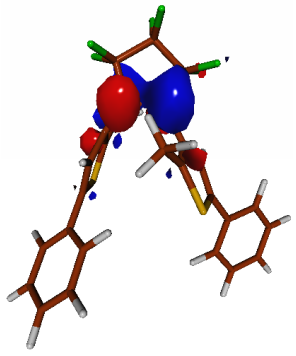
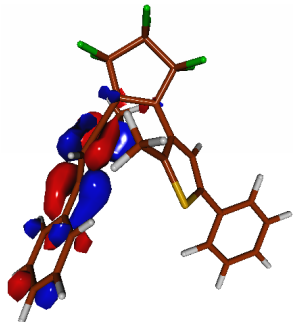


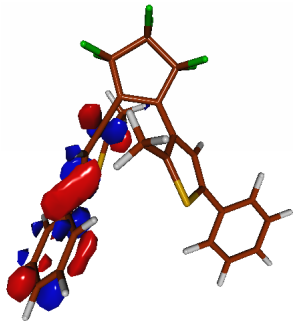
(c) HOMO orbital of **PT**-*twist*.



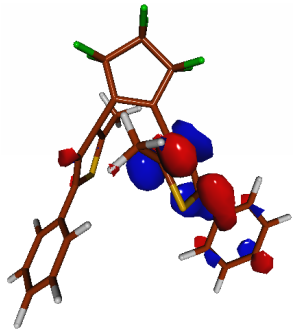
(d) LUMO orbital of **PT**-*twist*.



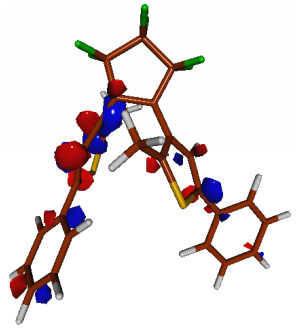
(e) L1 orbital of **PT**-*twist*.



(f) L2 orbital of **PT**-*twist*.

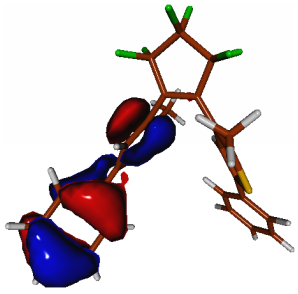


(g) L3 orbital of **PT**-*twist*.

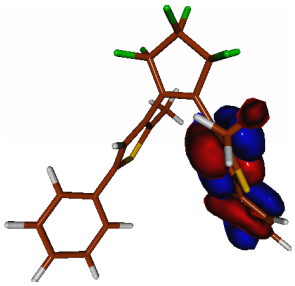


(h) L4 orbital of **PT**-*twist*.

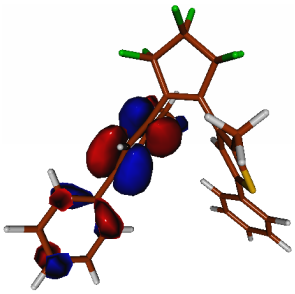
Figure S3: Active space orbitals of **PT**-*twist*, at the S_1 local minimum, used in ODM2/MRCI calculations. These orbitals have been optimized for an open-shell singlet configuration, with the HOMO and LUMO orbitals each occupied by one electron (H-L).



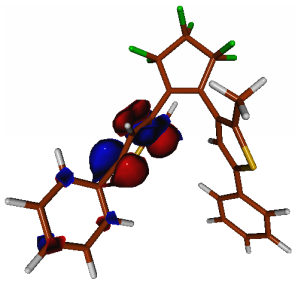
(a) H2 orbital of **PT**-*twist*.



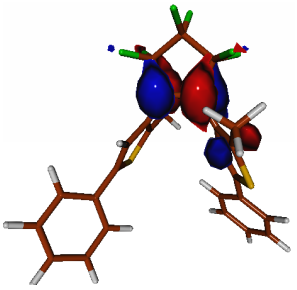
(b) H1 orbital of **PT**-*twist*.



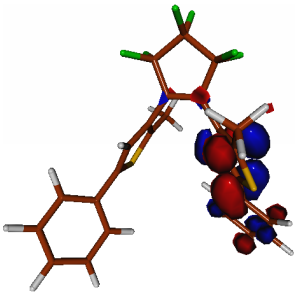
(c) HOMO orbital of **PT**-*twist*.



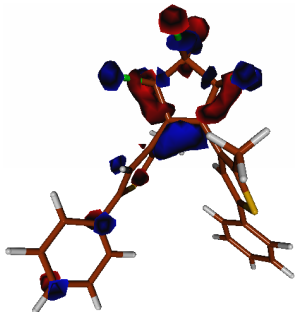
(d) LUMO orbital of **PT**-*twist*.



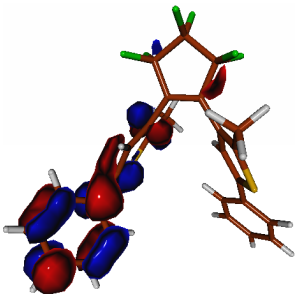
(e) L1 orbital of **PT**-*twist*.



(f) L2 orbital of **PT**-*twist*.

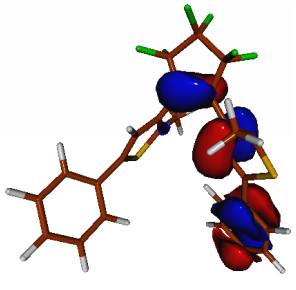


(g) L3 orbital of **PT**-*twist*.

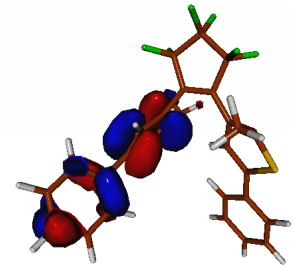


(h) L4 orbital of **PT**-*twist*.

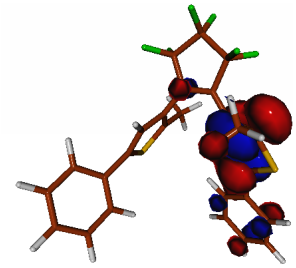
Figure S4: Active space orbitals of **PT**-*twist*, at the S_0 local minimum, used in ODM2/MRCI calculations. These orbitals have been optimized for an open-shell singlet configuration, with the HOMO and LUMO orbitals each occupied by one electron (H-L).



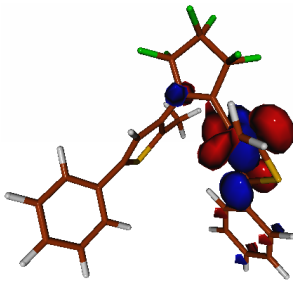
(a) H2 orbital of **PT**-*twist*.



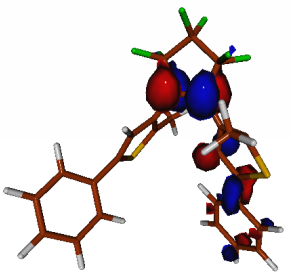
(b) H1 orbital of **PT**-*twist*.



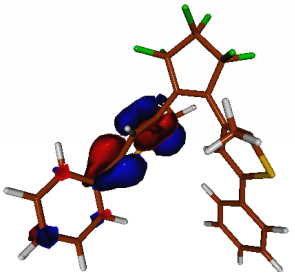
(c) HOMO orbital of **PT**-*twist*.



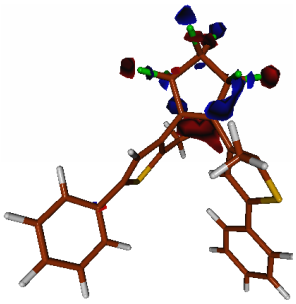
(d) LUMO orbital of **PT**-*twist*.



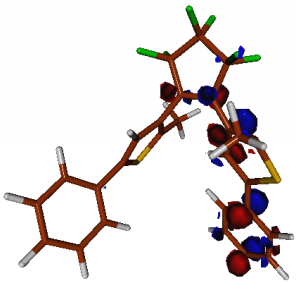
(e) L1 orbital of **PT**-*twist*.



(f) L2 orbital of **PT**-*twist*.



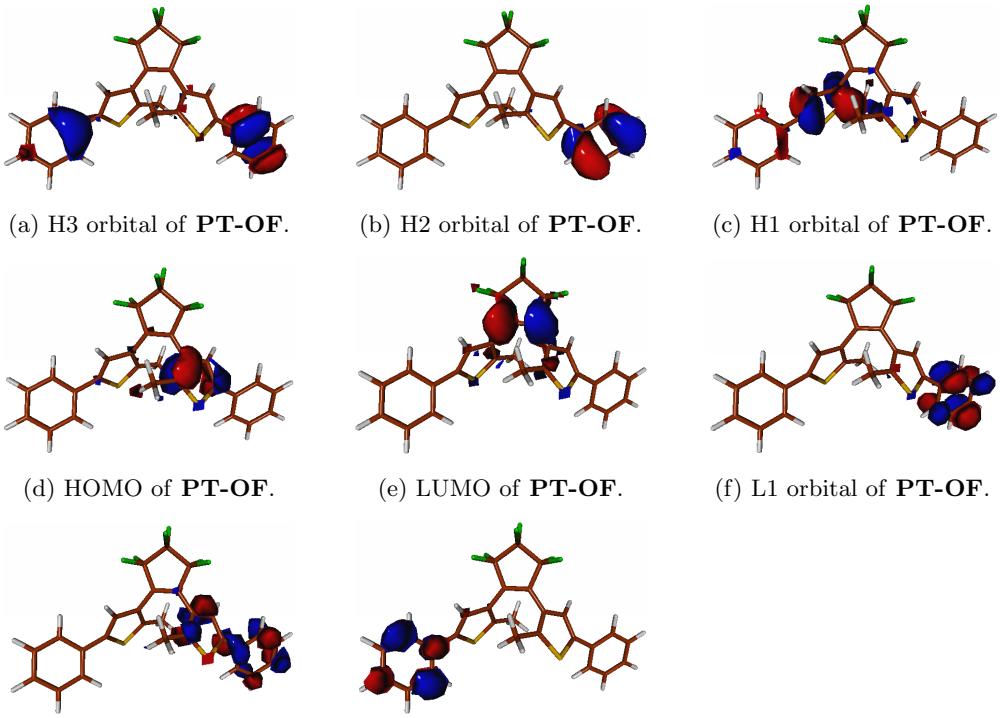
(g) L3 orbital of **PT**-*twist*.



(h) L4 orbital of **PT**-*twist*.

Figure S5: Active space orbitals of **PT**-*twist*, at the T_1 local minimum, used in ODM2/MRCI calculations. These orbitals have been optimized for an open-shell singlet configuration, with the HOMO and LUMO orbitals each occupied by one electron (H-L).

S2 Orbital active spaces (AS) used in QD-NEVPT2 calculations

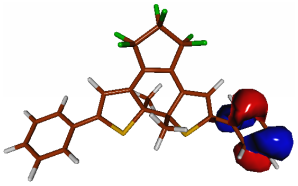


(a) H3 orbital of **PT-OF**. (b) H2 orbital of **PT-OF**. (c) H1 orbital of **PT-OF**.

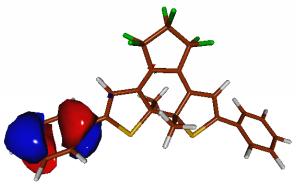
(d) HOMO of **PT-OF**. (e) LUMO of **PT-OF**. (f) L1 orbital of **PT-OF**.

(g) L2 orbital of **PT-OF**. (h) L3 orbital of **PT-OF**.

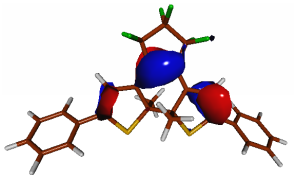
Figure S6: Active space orbitals of **PT-OF** used in QD-NEVPT2 calculations. The averaging was performed over the three lowest singlet states with equal weights.



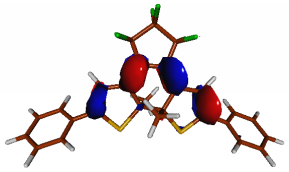
(a) H3 orbital of **PT-CF**.



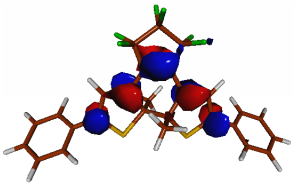
(b) H2 orbital of **PT-CF**.



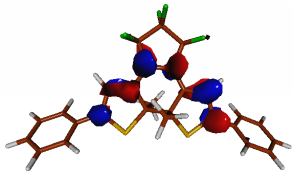
(c) H1 orbital of **PT-CF**.



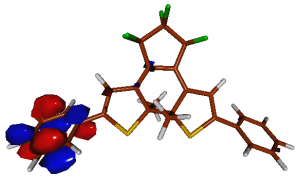
(d) HOMO of **PT-CF**.



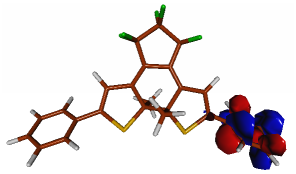
(e) LUMO of **PT-CF**.



(f) L1 orbital of **PT-CF**.

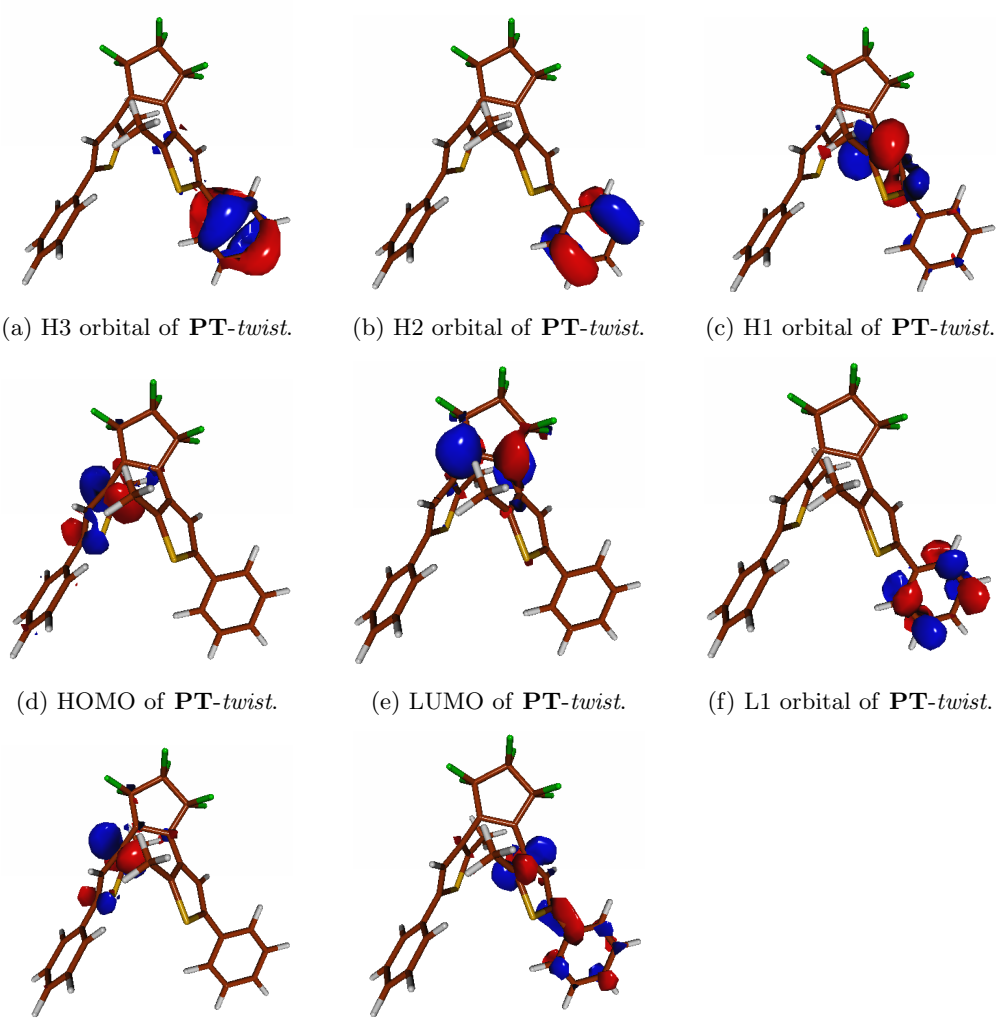


(g) L2 orbital of **PT-CF**.



(h) L3 orbital of **PT-CF**.

Figure S7: Active space orbitals of **PT-CF** used in QD-NEVPT2 calculations. The averaging was performed over the three lowest singlet states with equal weights.



(a) H3 orbital of **PT**-*twist*. (b) H2 orbital of **PT**-*twist*. (c) H1 orbital of **PT**-*twist*.

(d) HOMO of **PT**-*twist*. (e) LUMO of **PT**-*twist*. (f) L1 orbital of **PT**-*twist*.

(g) L2 orbital of **PT**-*twist*. (h) L3 orbital of **PT**-*twist*.

Figure S8: Active space orbitals of **PT**-*twist* used in QD-NEVPT2 calculations. The averaging was performed over the three lowest singlet states with equal weights.

S3 DFT benchmark calculations

S3.1 Geometry optimisations

The two relevant ground-state minima - **PT-OF** and **PT-CF** were reoptimised using DFT, with the ωb97XD functional, and the Dunning correlation-consistent double-ζ basis set. These

calculations confirm the global-minimum character of **PT-OF**, which is stabilised by 0.49 eV with respect to the closed form. The C_1–C_6 distance takes the value of 1.54 Åfor **PT-CF** and 3.50 Å for **PT-OF**. The tiophene dihedral angles are equal to $\varphi_1 = 49$ and $\varphi_2 = 50$ degrees for the open-ring isomer, and $\varphi_1 = 9$ and $\varphi_2 = 6$ degrees for **PT-CF**.

TD-DFT calculations at the same level of theory predict the first absorption maximum of **PT-OF** at 4.37 eV (271 nm) and 2.72 eV (456 nm) for **PT-CF**. While the predicted $S_0 -> S_1$ transition energy is accurate with respect to the experimental data for **PT-OF**, the predicted transition energy of **PT-CF** is off by about 0.6 eV with respect to the experiment, replicating ODM2/MRCI-SD results. TD-DFT predicts the S_1 state of both switching forms to be of HOMO-LUMO character, which agrees with both the QD-NEVPT2 and semi-empirical results.

Optimisations at the DFT level of theory confirm the existence of a ground state **PT**-*twist*minimum. The tiophene dihedral angles take the values of $\varphi_1 = 60$ and $\varphi_2 = 79$ degrees. However, unlike ODM2/MRCI-SD, DFT/ωb97XD predicts this structure as higher-energy then **PT-OF**, by 0.28 eV. The relative energies of all optimised DFT minima can be found in table S1.

Excited state optimisation at the TDA TD-DFT/ωb97XD level of theory yield an S_1 minimum of **PT**-*twist* in which the positions of the side tiophene groups are slightly differnt, with respect to ODM2/MRCI-SD results. The relevant dihedral angles take the values of $\varphi_1 = 12$ degrees and $\varphi_2 = 25$ degrees, indicating a situation where both the tiophene rings and the central cyclopentane rings are much more in-plane. However, such behaviour is expected, as the conformation of these side-rings will be influenced mostly by dispersion interactions, which are modelled in a significantly different way in the semi-empirical and DFT calculations. Nevertheless, the overall twisted, and potentially unreactive character of **PT**-*twist* is maintained.

Table S1: Relative energies of the DFT-optimised minima of **PT**.

Form	Relative energy (eV)
PT-OF	0
PT-CF	0.49
PT-*twist* (S0)	0.28
PT-*twist* (S1)	3.95
MECI-PT product (S0)	1.04

S3.2 Cartesian coordinates

Table S2: Cartesian coordinates of **PT-CF**, optimised at the DFT/ωb97x-D level of theory, with the cc-pVDZ basis set.

C	6.327409	4.943451	0.825962
C	6.381775	3.818623	-0.009488
C	7.370627	3.757885	-1.000630
C	8.271320	4.805448	-1.164704
C	8.202942	5.924200	-0.336590
C	7.230705	5.988212	0.660966
C	5.394961	2.733827	0.135942
S	5.864593	1.078409	-0.280425
C	4.265581	0.403849	0.366180
C	3.360736	1.631996	0.508929
C	4.107535	2.863183	0.540309
C	3.593686	-0.607084	-0.585311
C	2.197519	-0.940948	-0.048595
C	1.459621	0.088280	0.420715
C	2.030519	1.416666	0.590521
C	0.930127	2.390451	0.869325
C	-0.210172	1.493626	1.424489
C	-0.004695	0.120077	0.730321
C	1.874384	-2.337097	-0.185037
C	2.938833	-3.116843	-0.497240
S	4.462456	-2.238830	-0.673661
F	-0.757122	0.086143	-0.403742
F	-0.431007	-0.902159	1.511359
F	0.494105	3.009308	-0.262711
F	1.260115	3.365065	1.749013
F	-1.430943	2.004853	1.216946
F	-0.025398	1.342435	2.753969
C	4.519271	-0.154665	1.779665
C	3.410191	-0.074649	-2.019781
C	2.936365	-4.583773	-0.653863
C	2.134403	-5.374126	0.181372
C	2.121995	-6.758187	0.041161

C	2.909207	-7.370478	-0.932991
C	3.710049	-6.591731	-1.766779
C	3.729411	-5.207531	-1.626108
H	0.871260	-2.731680	-0.027824
H	3.647026	3.821877	0.774292
H	1.536458	-4.895893	0.959735
H	1.500827	-7.363873	0.703975
H	2.901994	-8.457079	-1.039508
H	4.325899	-7.066344	-2.533182
H	4.350030	-4.596706	-2.285556
H	2.844451	-0.809201	-2.609011
H	2.843488	0.868357	-2.005576
H	4.378391	0.102736	-2.504465
H	5.227459	-0.992473	1.753845
H	3.575992	-0.505206	2.224777
H	4.931132	0.640234	2.416001
H	7.421067	2.890410	-1.662874
H	9.029647	4.746352	-1.947724
H	8.912239	6.744202	-0.465214
H	7.178870	6.856414	1.320777
H	5.583693	4.988351	1.624076

Table S3: Cartesian coordinates of **PT-OF**, optimised at the DFT/ωb97x-D level of theory, with the cc-pVDZ basis set.

C	2.909611	4.710908	1.710266
C	1.550364	4.431127	1.496424
C	0.593576	5.182195	2.197034
C	0.983851	6.181784	3.086298
C	2.337512	6.445002	3.297942
C	3.297815	5.704046	2.607178
C	1.146530	3.355674	0.570987
S	-0.364038	3.426142	-0.296773
C	-0.108267	1.880212	-1.042262

C	1.096897	1.336825	-0.639265
C	1.811352	2.197613	0.263999
C	1.621408	0.020128	-1.056284
C	1.001119	-1.186794	-1.046611
C	1.907138	-2.268080	-1.607665
C	3.097328	-1.493602	-2.242288
C	3.055366	-0.113504	-1.529885
C	-0.341702	-1.525248	-0.525616
C	-1.314436	-2.264623	-1.284633
C	-2.509627	-2.437753	-0.637748
S	-2.441949	-1.723623	0.950443
C	-0.813850	-1.168662	0.724670
C	-3.725084	-3.117016	-1.125268
C	-3.617452	-4.231803	-1.971875
C	-4.758337	-4.868396	-2.456404
C	-6.026887	-4.411322	-2.095598
C	-6.145404	-3.309543	-1.247713
C	-5.005469	-2.665562	-0.769004
C	-0.129377	-0.438442	1.838138
F	3.441966	0.883400	-2.354060
F	3.922716	-0.115247	-0.474226
F	2.870172	-1.318599	-3.561195
F	4.271284	-2.125084	-2.086888
F	1.287536	-3.044612	-2.535651
F	2.355593	-3.100409	-0.635017
C	-1.135081	1.345467	-1.991954
H	-0.678023	0.643965	-2.703336
H	-1.601152	2.158092	-2.567379
H	-1.936887	0.808928	-1.459981
H	-0.352988	0.640041	1.812182
H	0.960151	-0.556045	1.764809
H	-0.449049	-0.822918	2.816900
H	-0.469178	4.969430	2.056949
H	0.223405	6.752230	3.623915

H	2.643717	7.226322	3.996650
H	4.360002	5.906728	2.759982
H	3.668381	4.155501	1.155215
H	-5.109116	-1.790197	-0.122825
H	-7.133272	-2.941949	-0.961901
H	-6.920208	-4.914153	-2.471948
H	-4.654541	-5.735638	-3.112069
H	-2.628605	-4.613045	-2.234967
H	2.772875	1.928376	0.700988
H	-1.132862	-2.617379	-2.298756

Table S4: Cartesian coordinates of **PT**-*twist*, optimised at the DFT/ωb97x-D level of theory, with the cc-pVDZ basis set, in the ground state.

C	-0.164677	5.018172	1.168765
C	0.022506	3.628422	1.232420
C	-0.282177	2.970627	2.436171
C	-0.745768	3.680871	3.541412
C	-0.931032	5.062105	3.464162
C	-0.642186	5.725708	2.271466
C	0.501112	2.855573	0.069175
S	0.212003	3.386670	-1.564896
C	0.960558	1.978316	-2.250382
C	1.147607	1.647278	0.057012
C	1.411316	1.130666	-1.257489
C	2.015338	-0.212090	-1.470179
C	1.528078	-1.377395	-0.987191
C	2.367284	-2.564563	-1.401983
C	3.598398	-1.961921	-2.154984
C	3.341111	-0.416093	-2.177689
C	0.283403	-1.555243	-0.190389
C	-1.032533	-1.516482	-0.765976
C	-2.039980	-1.616936	0.156230
S	-1.377666	-1.786429	1.759130

C	0.258490	-1.709695	1.178791
C	-3.503061	-1.586634	-0.069132
C	-4.099599	-2.462648	-0.988473
C	-5.474550	-2.418919	-1.219492
C	-6.274075	-1.502825	-0.534854
C	-5.690695	-0.630621	0.385523
C	-4.316730	-0.672919	0.618673
C	1.404186	-1.779874	2.142664
F	3.337244	0.038592	-3.457691
F	4.336711	0.239126	-1.533574
F	3.686251	-2.450236	-3.405029
F	4.739745	-2.244889	-1.501589
F	1.667283	-3.393627	-2.215728
F	2.772988	-3.307281	-0.339966
C	0.988068	1.827888	-3.741566
H	0.074053	2.239504	-4.192392
H	1.066269	0.771555	-4.026317
H	1.848117	2.353940	-4.183189
H	2.358924	-1.755726	1.602939
H	1.378476	-2.710076	2.729290
H	1.385696	-0.941993	2.857026
H	-0.181096	1.885338	2.497987
H	-0.978760	3.147392	4.465801
H	-1.304093	5.616795	4.327835
H	-0.785990	6.805820	2.198176
H	0.072721	5.554965	0.246825
H	-3.861901	0.025208	1.325331
H	-6.307318	0.095015	0.920509
H	-7.350439	-1.469026	-0.717416
H	-5.924985	-3.111843	-1.933562
H	-3.480200	-3.194143	-1.511945
H	1.455053	1.132967	0.966729
H	-1.217871	-1.386080	-1.832434

Table S5: Cartesian coordinates of **PT**-*twist*, optimised at the TDA TD-DFT/B3LYP level of theory, with the cc-pVDZ basis set, in the S_1 state.

C	-0.818801	4.666525	0.501231
C	-0.655355	3.272740	0.530231
C	-1.259208	2.544148	1.569793
C	-1.995536	3.195053	2.553824
C	-2.149216	4.580236	2.516712
C	-1.559687	5.312095	1.485087
C	0.113348	2.559363	-0.494920
S	0.264761	3.164754	-2.130223
C	1.155093	1.808063	-2.661186
C	0.745126	1.356139	-0.387916
C	1.316186	0.855131	-1.618097
C	1.882559	-0.455334	-1.711361
C	1.780962	-1.434915	-0.668197
C	2.982721	-2.310771	-0.704251
C	3.440190	-2.242572	-2.182700
C	2.901134	-0.882072	-2.711881
C	0.626091	-1.647009	0.139555
C	-0.689933	-1.200723	-0.261583
C	-1.656432	-1.362477	0.684745
S	-0.974802	-2.114863	2.115085
C	0.595661	-2.195921	1.446964
C	-3.060140	-0.934726	0.641473
C	-3.410413	0.202630	-0.104961
C	-4.732879	0.630067	-0.161035
C	-5.725691	-0.063452	0.529778
C	-5.386654	-1.190072	1.279396
C	-4.066372	-1.624033	1.335192
C	1.737587	-2.707308	2.256234
F	2.414384	-1.064188	-3.983256
F	3.930378	0.007806	-2.850751
F	2.859020	-3.255089	-2.858819
F	4.770969	-2.351529	-2.325799

F	2.754455	-3.599841	-0.337843
F	4.015492	-1.870500	0.094109
C	1.594993	1.729726	-4.082783
H	1.293369	2.623098	-4.644754
H	1.170901	0.839036	-4.570155
H	2.688843	1.626473	-4.140651
H	2.630840	-2.090190	2.076193
H	2.001977	-3.733871	1.959002
H	1.505431	-2.702527	3.329718
H	-1.169640	1.455505	1.589935
H	-2.464600	2.610662	3.347944
H	-2.731047	5.089116	3.287750
H	-1.673476	6.397392	1.449531
H	-0.346766	5.252122	-0.292101
H	-3.813345	-2.518798	1.909910
H	-6.159382	-1.739870	1.820480
H	-6.762870	0.274920	0.487818
H	-4.986468	1.520411	-0.739823
H	-2.631852	0.767282	-0.623415
H	0.846376	0.830797	0.559356
H	-0.886668	-0.796329	-1.254049

Table S6: Cartesian coordinates of the alternative photoproduct of **PT** cyclization, formed via the proton transfer **MECI**, optimised at the DFT/ωb97x-D level of theory, with the cc-pVDZ basis set.

C	2.563371	5.107970	1.042316	0.000000
C	1.295515	4.522007	1.181667	0.000000
C	0.385799	5.087658	2.088705	0.000000
C	0.739460	6.201015	2.847884	0.000000
C	2.004580	6.771849	2.706801	0.000000
C	2.913419	6.222969	1.800128	0.000000
C	0.928001	3.335645	0.386813	0.000000
S	-0.773926	3.066661	-0.011197	0.000000

C	-0.342794	1.634994	-0.982153	0.000000
C	1.076663	1.254048	-0.745746	0.000000
C	1.752382	2.364764	-0.079244	0.000000
C	1.659629	0.057194	-1.038035	0.000000
C	0.995471	-1.249509	-1.494625	0.000000
C	2.151662	-2.274003	-1.512563	0.000000
C	3.413608	-1.427108	-1.793114	0.000000
C	3.160976	-0.134325	-0.974381	0.000000
C	-0.256358	-1.705594	-0.756402	0.000000
C	-1.451838	-2.052211	-1.472369	0.000000
C	-2.528655	-2.346946	-0.676502	0.000000
S	-2.062314	-2.248614	0.997828	0.000000
C	-0.432820	-1.778507	0.608838	0.000000
C	-3.915620	-2.640172	-1.087469	0.000000
C	-4.177748	-3.237941	-2.331212	0.000000
C	-5.486836	-3.462166	-2.753390	0.000000
C	-6.562070	-3.108403	-1.936580	0.000000
C	-6.314563	-2.527869	-0.692401	0.000000
C	-5.005798	-2.292372	-0.273294	0.000000
C	0.524983	-1.531735	1.735040	0.000000
F	3.874998	0.902025	-1.483342	0.000000
F	3.624646	-0.324313	0.301456	0.000000
F	3.434080	-1.107874	-3.110956	0.000000
F	4.560519	-2.045828	-1.480064	0.000000
F	1.971607	-3.231775	-2.449159	0.000000
F	2.313194	-2.895677	-0.317610	0.000000
C	-1.187441	1.157019	-1.905317	0.000000
H	0.726187	-1.160918	-2.562087	0.000000
H	-0.907327	0.339497	-2.564562	0.000000
H	-2.177338	1.594382	-2.045838	0.000000
H	0.724082	-2.461277	2.290056	0.000000
H	0.119480	-0.796518	2.446605	0.000000
H	1.485072	-1.157300	1.364877	0.000000
H	-0.604203	4.641854	2.213693	0.000000

H	0.022108	6.623928	3.554223	0.000000
H	2.280692	7.647076	3.298607	0.000000
H	3.901118	6.671328	1.675036	0.000000
H	3.270306	4.698473	0.318127	0.000000
H	-4.827190	-1.811338	0.691582	0.000000
H	-7.148006	-2.244270	-0.045763	0.000000
H	-7.587565	-3.286776	-2.267125	0.000000
H	-5.667805	-3.924872	-3.726116	0.000000
H	-3.344899	-3.542605	-2.968369	0.000000
H	2.819397	2.352238	0.131534	0.000000
H	-1.518352	-2.036019	-2.562018	0.000000

S4 Ground-state population fitting

To obtain the timescales of **PT-OF** photo-cyclization the ground-state population data was fitted with a double sigmoid function:

$$P(t) = \frac{A}{1 + e^{-B(t-\tau_1)}} + \frac{C}{1 + e^{-D(t-\tau_2)}}. \tag{S1}$$

The timescales are denoted as τ_1 and τ_2, while A and C measures the portion of trajectories relaxing on each timescale. The parameters B and D can be interpreted as the steepness of the growth curve on each timescale. Fit parameters for **PT-OF** dynamics can be seen in table S1, and the fitted function, along with the simulation data, in figure S9.

Table S7: Parameters of the function $P(t)$ fitted to the S_0 population rise in **PT-OF** dynamics.

Parameter	
A	0,5315 ± 0,0052
B	(0,01815 ± 0.00021) 1/fs
C	0,4107 ± 0,0055
D	(0,00583 ± 0.00001) 1/fs
τ_1	(342,06 ± 0,52) fs
τ_2	(766,3 ± 4,8) fs

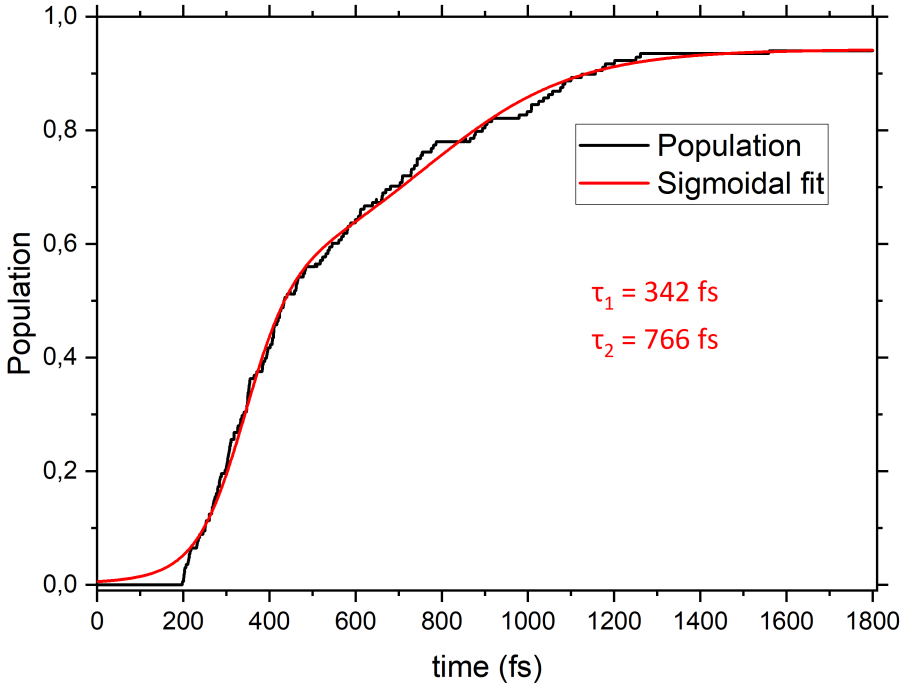


Figure S9: Ground state population rise, and the fitted double sigmoid function in **PT-OF** dynamics.

S5 Dynamic sampling procedure

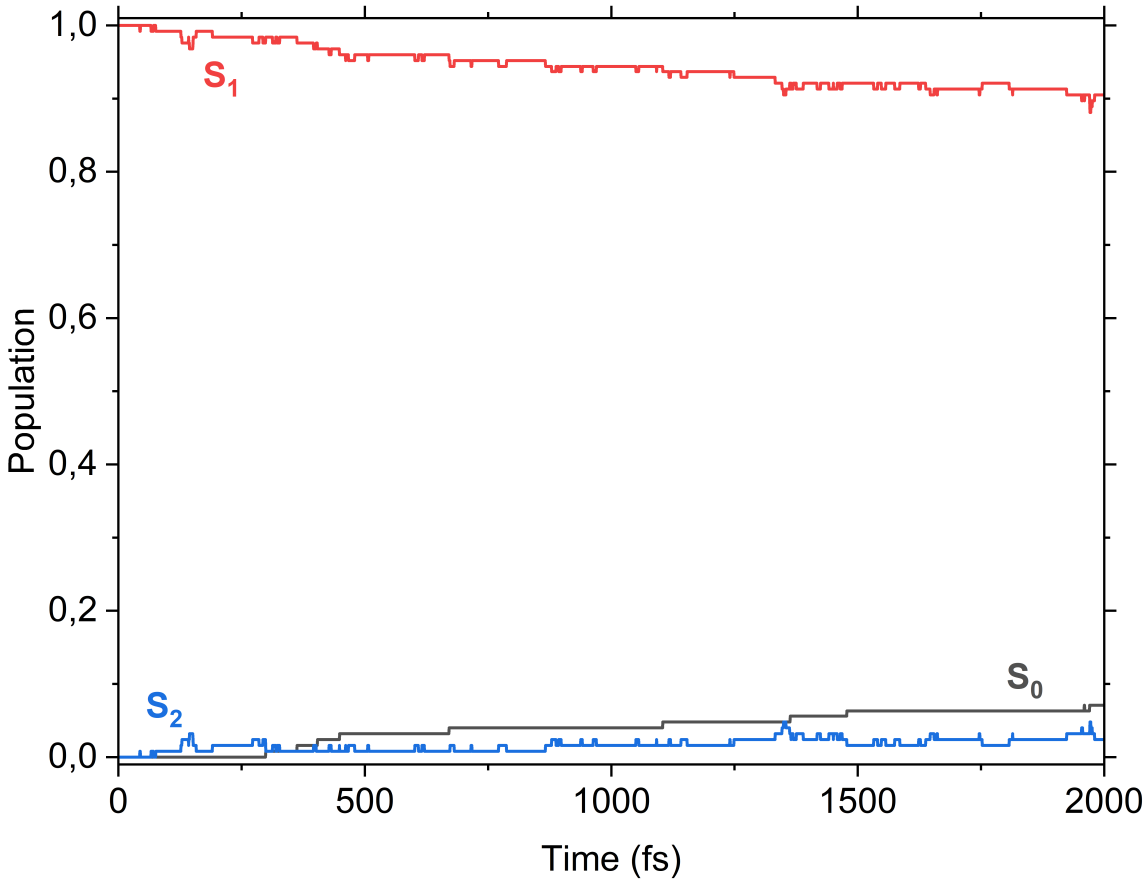


Figure S10: Electronic state population evolution in the photo-cyclization dynamics of **PT**-*twist*. The states S_0, S_1 and S_2 have been marked respectively in black, red, and blue.

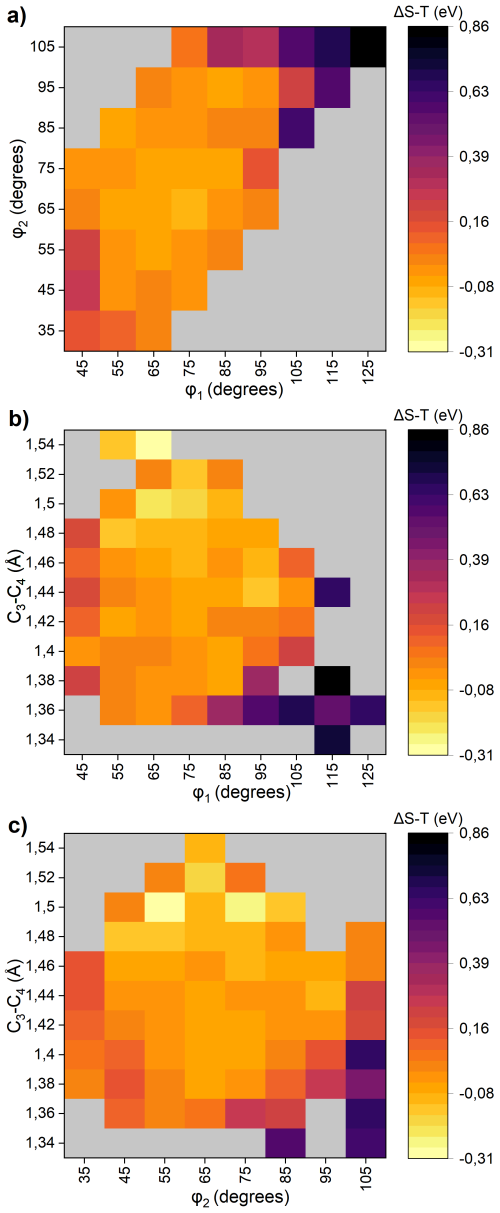


Figure S11: Heatmaps displaying the magnitude of the energy gap between S_1 and T_1 parametrized by geometric parameters of **PT-OF**; (a) dihedral angles φ_1 and φ_2; (b) dihedral angle φ_1 and the C_3–C_4 distance; (c) dihedral angle φ_2 and the C_3–C_4 distance.

S6 Solvent shifts

Table S8: Electronic transition energies of the studied **PT** forms computed at the ODM2/MRCI-SD level of theory, with the environment accounted for under the conductor-like screening model (COSMO), for several solvents commonly used in DAE experimental studies.

Molecule	Gas phase	Cyclohexane	Chloroform	Acetonitrile
$S_0 \rightarrow S_1$				
PT-OF	4.11	4.02	3.95	3.88
PT-CF	2.77	2.78	2.78	2.79
PT-*twist* **(S0-opt)**	4.90	4.46	4.35	4.16
PT-*twist* **(S1-opt)**	2.15	1.88	1.64	1.43
$S_0 \rightarrow T_1$				
PT-*twist* **(S1-opt)**	2.04	1.80	1.58	1.37

S7 Cartesian coordinates of key forms of PT optimised at the ODM2/MRCI-SD level

Table S9: Cartesian coordinates of **PT-CF**.

C	6.616614	4.620270	1.113910
C	6.389554	3.798816	-0.001449
C	7.067057	4.023255	-1.210042
C	7.971767	5.071965	-1.293007
C	8.205636	5.893344	-0.186085
C	7.525484	5.663553	1.013491
C	5.405806	2.715413	0.106516
S	5.921121	1.043370	-0.164388
C	4.306433	0.397603	0.372145
C	3.377673	1.617978	0.454146
C	4.087626	2.866780	0.439365
C	3.679094	-0.623622	-0.598377
C	2.261749	-0.943546	-0.093250
C	1.488737	0.067774	0.370533

C	2.036539	1.411003	0.518044
C	0.944719	2.401639	0.746065
C	-0.353971	1.558191	0.957192
C	0.038829	0.055330	0.747411
C	1.933369	-2.342092	-0.196082
C	3.020489	-3.121571	-0.480022
S	4.544645	-2.229285	-0.649666
F	-0.750532	-0.537738	-0.190005
F	-0.212223	-0.684893	1.865090
F	0.804560	3.302069	-0.270784
F	1.183657	3.201070	1.822744
F	-1.332346	1.936777	0.101136
F	-0.882902	1.770813	2.186387
C	4.412723	-0.148181	1.804727
C	3.512119	-0.063501	-2.018337
C	2.991339	-4.588203	-0.602396
C	2.593429	-5.345755	0.499111
C	2.535029	-6.732289	0.375330
C	2.866846	-7.343922	-0.828739
C	3.267362	-6.575438	-1.916576
C	3.338006	-5.188481	-1.811422
H	0.939706	-2.726406	-0.032012
H	3.613541	3.816930	0.627504
H	2.338815	-4.858908	1.445039
H	2.217500	-7.339734	1.229304
H	2.815329	-8.432594	-0.919595
H	3.534316	-7.059713	-2.863107
H	3.651775	-4.579521	-2.663461
H	2.887476	-0.740526	-2.613649
H	3.014509	0.913601	-1.973332
H	4.478310	0.052286	-2.517065
H	5.175657	-0.926704	1.878599
H	3.445809	-0.567168	2.108202
H	4.669259	0.664714	2.495548

H	6.882150	3.376580	-2.070121
H	8.509520	5.254282	-2.228330
H	8.923433	6.715890	-0.257989
H	7.711077	6.308945	1.877477
H	6.086808	4.427915	2.050303

Table S10: Cartesian coordinates of **PT-OF.**

C	2.516248	4.887625	1.485273
C	1.254613	4.285051	1.479589
C	0.248532	4.721983	2.348295
C	0.508151	5.780253	3.212589
C	1.756518	6.398216	3.210954
C	2.757781	5.948830	2.353751
C	0.999393	3.177855	0.552155
S	-0.478960	3.156667	-0.396055
C	-0.033192	1.626145	-1.107797
C	1.198781	1.176434	-0.618773
C	1.800199	2.077737	0.314611
C	1.770630	-0.075964	-1.049471
C	1.143881	-1.280070	-1.077230
C	2.004148	-2.344172	-1.739211
C	3.294583	-1.596997	-2.216653
C	3.197317	-0.175529	-1.567218
C	-0.168498	-1.582183	-0.543852
C	-1.228450	-2.170345	-1.304499
C	-2.386999	-2.294189	-0.563794
S	-2.188300	-1.747171	1.089176
C	-0.533825	-1.286041	0.767864
C	-3.683361	-2.798083	-1.030286
C	-3.729959	-3.976935	-1.784559
C	-4.963312	-4.468389	-2.198077
C	-6.134911	-3.791580	-1.875930
C	-6.078006	-2.606472	-1.142564

C	-4.854925	-2.105701	-0.715624
C	0.319531	-0.682981	1.822527
F	3.521457	0.810785	-2.436473
F	4.103170	-0.030661	-0.559705
F	3.347914	-1.511590	-3.568641
F	4.427773	-2.251199	-1.871482
F	1.363758	-2.961661	-2.768803
F	2.316219	-3.362955	-0.898291
C	-0.883329	0.963676	-2.126926
H	-0.267477	0.277982	-2.727661
H	-1.347973	1.695872	-2.800679
H	-1.670711	0.386120	-1.621492
H	0.170080	0.407440	1.821526
H	1.375454	-0.899251	1.603048
H	0.072300	-1.083766	2.814816
H	-0.731825	4.240158	2.349213
H	-0.273970	6.132522	3.892224
H	1.953629	7.236026	3.887239
H	3.739456	6.433509	2.357418
H	3.295352	4.539351	0.801542
H	-4.812227	-1.181743	-0.133295
H	-7.003312	-2.075192	-0.898251
H	-7.102769	-4.187050	-2.198000
H	-5.012016	-5.400243	-2.772381
H	-2.808022	-4.512555	-2.023800
H	2.748302	1.902674	0.802035
H	-1.144018	-2.451359	-2.344445

Table S11: Cartesian coordinates of **PT-twist**, at the S_1 local minimum.

C	-0.346727	4.845187	1.180672
C	-0.047951	3.483530	1.282668
C	-0.201030	2.785230	2.487874
C	-0.700182	3.465439	3.590466

C	-1.013802	4.820213	3.499141
C	-0.824049	5.510303	2.304863
C	0.479217	2.735723	0.144463
S	-0.152982	2.915294	-1.501832
C	0.937626	1.686643	-2.047426
C	1.742796	1.093235	-0.947549
C	1.473684	1.779501	0.253608
C	2.356896	-0.183712	-1.087118
C	1.400007	-1.233022	-1.274071
C	2.053431	-2.393516	-1.919624
C	3.530038	-1.961046	-2.224378
C	3.627160	-0.467450	-1.773441
C	0.214641	-1.296011	-0.443274
C	-1.123102	-1.394406	-0.947272
C	-2.075320	-1.289084	0.048122
S	-1.370513	-1.092266	1.642780
C	0.235813	-1.141404	0.941284
C	-3.532310	-1.364002	-0.109902
C	-4.066964	-2.451114	-0.809084
C	-5.445420	-2.562502	-0.951941
C	-6.284325	-1.595082	-0.406396
C	-5.746453	-0.504458	0.270518
C	-4.368118	-0.377459	0.419004
C	1.450962	-1.125741	1.791673
F	3.916268	0.379321	-2.828658
F	4.707250	-0.236655	-0.960115
F	3.852143	-2.107771	-3.537839
F	4.435853	-2.742720	-1.582583
F	1.426853	-2.735181	-3.100282
F	1.997669	-3.576512	-1.236404
C	1.044536	1.211564	-3.434846
H	0.361332	1.720054	-4.120465
H	0.836072	0.134934	-3.425484
H	2.082512	1.352716	-3.757621

H	2.332246	-1.067375	1.142954
H	1.494107	-2.052728	2.383770
H	1.445413	-0.264164	2.484748
H	0.021884	1.717534	2.547755
H	-0.850497	2.933223	4.532199
H	-1.424079	5.336288	4.373119
H	-1.060182	6.574891	2.246084
H	-0.198760	5.384253	0.242852
H	-3.938942	0.479422	0.947695
H	-6.413488	0.253703	0.694799
H	-7.369476	-1.692572	-0.507464
H	-5.872913	-3.418055	-1.484062
H	-3.400473	-3.213585	-1.219841
H	1.985165	1.563909	1.172753
H	-1.361905	-1.540209	-1.992358

Table S12: Cartesian coordinates of **PT-twist**, at the S_0 local minimum.

C	-0.140028	4.924989	1.269332
C	-0.019390	3.529644	1.274969
C	-0.347593	2.798391	2.423389
C	-0.779531	3.468773	3.563565
C	-0.894055	4.856484	3.564661
C	-0.577381	5.579038	2.417853
C	0.464575	2.792262	0.104260
S	0.204497	3.368960	-1.533170
C	1.003961	1.957376	-2.184787
C	1.454522	1.109631	-1.179807
C	1.134653	1.582470	0.129275
C	2.056667	-0.189877	-1.423279
C	1.495811	-1.366942	-1.062189
C	2.326894	-2.557169	-1.496682
C	3.576174	-1.947460	-2.217091
C	3.392630	-0.393675	-2.115012

C	0.255751	-1.511241	-0.313298
C	-1.047594	-1.526318	-0.899965
C	-2.043938	-1.523671	0.058948
S	-1.409816	-1.566353	1.689495
C	0.230700	-1.539398	1.077395
C	-3.494971	-1.485663	-0.185386
C	-4.073320	-2.450112	-1.019165
C	-5.440184	-2.396535	-1.278115
C	-6.226114	-1.391595	-0.713592
C	-5.642705	-0.437250	0.118806
C	-4.277681	-0.477671	0.390394
C	1.403850	-1.603982	1.990150
F	3.480501	0.210520	-3.328891
F	4.413891	0.166947	-1.414154
F	3.661898	-2.362157	-3.504403
F	4.735075	-2.360294	-1.649015
F	1.647225	-3.406202	-2.311618
F	2.688413	-3.341715	-0.444868
C	1.160217	1.754903	-3.647583
H	0.401261	2.308000	-4.218843
H	1.067062	0.679571	-3.875027
H	2.162179	2.102776	-3.946396
H	2.330078	-1.554737	1.398812
H	1.386092	-2.551125	2.546905
H	1.384928	-0.764627	2.702010
H	-0.277855	1.706895	2.422811
H	-1.039247	2.899747	4.461859
H	-1.235139	5.377096	4.465788
H	-0.669969	6.670703	2.416560
H	0.115836	5.500773	0.377107
H	-3.819426	0.275908	1.034783
H	-6.264529	0.352236	0.554774
H	-7.301960	-1.356162	-0.918341
H	-5.901023	-3.151799	-1.922376

H	-3.456111	-3.243454	-1.449248
H	1.410453	1.057055	1.034706
H	-1.234335	-1.503640	-1.965280

Table S13: Cartesian coordinates of **PT** CC-MECI.

C	0.843636	5.476272	1.491310
C	1.410697	4.201454	1.590973
C	2.338566	3.915262	2.601724
C	2.695932	4.909843	3.504914
C	2.132596	6.180061	3.409975
C	1.207618	6.458976	2.405450
C	1.092543	3.139442	0.636460
S	-0.565574	2.930485	0.022859
C	-0.111013	1.488354	-0.872147
C	1.340505	1.259233	-0.757122
C	1.974840	2.262556	0.076717
C	1.840295	-0.003126	-1.002680
C	1.059892	-1.163710	-1.114672
C	1.760393	-2.264582	-1.792173
C	3.237883	-1.773170	-1.963710
C	3.293862	-0.346674	-1.317527
C	-0.305202	-1.144014	-0.702915
C	-1.278615	-2.033955	-1.213384
C	-2.558970	-1.716974	-0.748044
S	-2.626511	-0.329970	0.280049
C	-0.826531	-0.041456	0.126786
C	-3.763882	-2.460547	-1.131561
C	-3.670769	-3.851600	-1.233301
C	-4.796835	-4.583186	-1.597942
C	-5.996389	-3.930046	-1.869784
C	-6.079665	-2.545325	-1.772295
C	-4.967049	-1.797970	-1.396971
C	-0.174409	-0.038971	1.501607

F	3.891589	0.563458	-2.127294
F	4.066341	-0.332543	-0.196724
F	3.609222	-1.722578	-3.267131
F	4.134092	-2.616617	-1.395775
F	1.219337	-2.631909	-3.005229
F	1.707755	-3.453270	-1.115765
C	-0.797589	1.265072	-2.194025
H	-1.886906	1.315782	-2.116048
H	-0.505252	0.302600	-2.626098
H	-0.450796	2.063783	-2.866359
H	-0.318799	-0.990967	2.037900
H	-0.591141	0.777466	2.101977
H	0.903445	0.121976	1.378397
H	2.770856	2.913584	2.682056
H	3.418712	4.691399	4.298522
H	2.414206	6.958865	4.125395
H	0.765831	7.458633	2.334346
H	0.123248	5.702011	0.701774
H	-5.032500	-0.710498	-1.327917
H	-7.024078	-2.037309	-1.987158
H	-6.878021	-4.510172	-2.159742
H	-4.736266	-5.671778	-1.670714
H	-2.731716	-4.362432	-1.005137
H	3.034553	2.233073	0.301882
H	-1.067742	-2.875528	-1.851250

Table S14: Cartesian coordinates of **PT** PT-MECI.

C	1.410176	5.823534	1.125248
C	1.530696	4.461552	1.422533
C	1.883893	4.035584	2.710083
C	2.122583	4.984694	3.697826
C	2.012976	6.343128	3.406924
C	1.656187	6.758741	2.125309

C	1.331517	3.437340	0.394937
S	-0.009838	3.554805	-0.770890
C	0.441764	2.050103	-1.523210
C	1.561102	1.433213	-0.775215
C	2.109794	2.323319	0.213987
C	1.723230	0.071184	-0.909407
C	0.731371	-0.761324	-1.589169
C	1.517153	-1.966358	-2.080134
C	2.996224	-1.897440	-1.550653
C	3.058463	-0.635992	-0.637989
C	-0.424495	-1.203388	-0.748704
C	-1.523954	-1.850357	-1.400034
C	-2.556131	-2.147064	-0.532339
S	-2.218795	-1.627318	1.105520
C	-0.647774	-1.018562	0.608186
C	-3.809149	-2.814101	-0.897842
C	-3.747381	-3.888531	-1.792022
C	-4.926042	-4.503965	-2.202709
C	-6.154412	-4.054319	-1.725858
C	-6.208648	-2.990543	-0.828981
C	-5.038998	-2.363860	-0.408918
C	0.228311	-0.361200	1.608294
F	4.120224	0.173198	-0.895849
F	3.222048	-0.955335	0.672576
F	3.916227	-1.793762	-2.540905
F	3.368532	-3.003626	-0.862570
F	1.554747	-2.000481	-3.449708
F	0.998779	-3.188424	-1.779705
C	-0.063554	1.409588	-2.683546
H	0.138399	0.148246	-2.348783
H	0.665895	1.455416	-3.503795
H	-1.029272	1.774921	-3.026143
H	-0.003936	-0.691556	2.628846
H	0.097960	0.733650	1.552574

H	1.277828	-0.614566	1.397478
H	1.957318	2.968634	2.939414
H	2.395958	4.661980	4.706987
H	2.204553	7.085706	4.187502
H	1.568349	7.826357	1.902628
H	1.136165	6.152460	0.120357
H	-5.085000	-1.526081	0.290729
H	-7.176860	-2.642508	-0.453266
H	-7.079260	-4.540161	-2.054042
H	-4.885748	-5.345611	-2.902259
H	-2.780108	-4.245994	-2.154696
H	2.988888	2.090833	0.796699
H	-1.537397	-2.084274	-2.456206

Table S15: Cartesian coordinates of the alternative photoproduct of **PT** cyclization, formed *via* the proton transfer MECI

C	2.357323	5.275836	0.911107
C	1.317634	4.485257	1.424116
C	0.630144	4.844348	2.586921
C	0.964413	6.039284	3.223567
C	1.961695	6.862943	2.690131
C	2.656062	6.481302	1.544446
C	0.910651	3.306971	0.645097
S	-0.706259	3.320403	-0.060275
C	-0.400087	1.775642	-0.871526
C	0.951543	1.264846	-0.551872
C	1.656390	2.220151	0.292186
C	1.522619	0.102188	-0.989482
C	0.894306	-1.034748	-1.744399
C	1.999818	-2.097817	-1.943999
C	3.359284	-1.444799	-1.560970
C	2.984651	-0.171690	-0.743442
C	-0.263744	-1.633587	-1.010784

C	-1.490484	-1.957417	-1.664537
C	-2.442761	-2.432871	-0.783891
S	-1.862425	-2.523678	0.851490
C	-0.301512	-1.899567	0.356527
C	-3.851600	-2.702084	-1.125833
C	-4.256168	-3.985205	-1.478595
C	-5.582048	-4.193587	-1.862362
C	-6.465704	-3.123561	-1.914853
C	-6.049870	-1.845038	-1.565406
C	-4.733549	-1.625245	-1.159659
C	0.795535	-1.733971	1.345997
F	3.785535	0.879566	-1.081616
F	3.280626	-0.350581	0.579062
F	4.066552	-1.116434	-2.671821
F	4.172637	-2.283792	-0.874624
F	2.021626	-2.551925	-3.230854
F	1.795777	-3.224776	-1.214278
C	-1.316663	1.249465	-1.703142
H	0.580937	-0.692797	-2.765204
H	-1.169309	0.300547	-2.187971
H	-2.253847	1.747247	-1.911294
H	0.536487	-2.169656	2.318937
H	0.995975	-0.662262	1.480264
H	1.698290	-2.234050	0.969049
H	-0.164460	4.207717	2.979326
H	0.430102	6.350424	4.125189
H	2.193797	7.817980	3.175172
H	3.427945	7.133212	1.126426
H	2.890192	4.967846	0.009410
H	-4.396844	-0.626872	-0.873315
H	-6.754597	-1.010319	-1.606125
H	-7.500730	-3.288326	-2.233240
H	-5.918577	-5.200412	-2.123640
H	-3.547206	-4.814368	-1.441435

H	2.669940	2.073342	0.628118
H	-1.668504	-1.865321	-2.729278

Table S16: Cartesian coordinates of **PT-twist**, at the optimised local minimum of the T_1 state.

C	-0.159445	4.937430	1.205940
C	0.053807	3.542054	1.209414
C	-0.351416	2.791188	2.330904
C	-0.934868	3.420427	3.420380
C	-1.138657	4.801674	3.411884
C	-0.754395	5.547956	2.300031
C	0.700182	2.878215	0.104351
S	1.076071	3.712260	-1.416631
C	1.473054	2.170477	-2.218333
C	1.545427	1.091017	-1.168379
C	1.005638	1.490139	0.041190
C	2.005295	-0.231416	-1.460955
C	1.483058	-1.388969	-0.965140
C	2.252613	-2.608949	-1.420908
C	3.407247	-2.061660	-2.325007
C	3.195435	-0.509283	-2.366277
C	0.277902	-1.510612	-0.158151
C	-1.027544	-1.561486	-0.738850
C	-2.021697	-1.576174	0.221118
S	-1.383625	-1.584247	1.852537
C	0.253016	-1.506050	1.230235
C	-3.466135	-1.549043	-0.047596
C	-4.007013	-2.521993	-0.889785
C	-5.358295	-2.455463	-1.220728
C	-6.152298	-1.423821	-0.729391
C	-5.606838	-0.463051	0.115800
C	-4.260306	-0.522966	0.468810
C	1.434242	-1.561344	2.130246
F	3.008438	-0.081827	-3.646032

F	4.311396	0.153396	-1.970395
F	3.378505	-2.607682	-3.564188
F	4.631086	-2.383448	-1.841586
F	1.474343	-3.502474	-2.086899
F	2.734317	-3.335607	-0.373754
C	0.746566	1.822748	-3.474117
H	0.733756	2.670845	-4.167372
H	-0.289996	1.533353	-3.241860
H	1.249727	0.977336	-3.953567
H	2.279919	-1.041080	1.656850
H	1.706513	-2.616227	2.283773
H	1.225157	-1.098623	3.103893
H	-0.219048	1.703123	2.351084
H	-1.241915	2.828784	4.288237
H	-1.599558	5.297453	4.271620
H	-0.920034	6.630384	2.292257
H	0.143357	5.551792	0.356334
H	-3.828972	0.230597	1.131772
H	-6.234599	0.344756	0.505055
H	-7.211400	-1.373323	-1.002898
H	-5.796078	-3.221852	-1.867836
H	-3.379847	-3.328996	-1.276308
H	0.861481	0.831669	0.888705
H	-1.209278	-1.565795	-1.805238