SUPPORTING INFORMATION

Designing potentially singlet fission materials with an Anti–Kasha

behaviour

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Table S1. Values of energies (in cm^{-1}) of excited states of interest using different methods with the Tamm-Damcoff approximation.

Tamm-Damcoff approximation	T_1	S_1	S_2	S_2-2T_1
	H→L	H→L	H-1→L; H→L+1	(Eq 2)
Experimental	13900	14300	28800	1000
DFT/MRCI	14180	15400	27900	−460
CASSCF-NEVPT2	15383	15450	31446	680
B3LYP	16348	20149	30585	−2112
BHandHLYP	17456	21551	31967	−2946
CAM-B3LYP	16540	20642	31732	−1348
M06	16469	19923	29786	−3152
M06-2X	16907	20591	32578	−1236
M06-HF	17521	21090	34468	−573
M11L	17191	20268	28717	−5664
BP86	15857	19469	29507	−2207
TPSS	16232	19927	29938	−2526
WB97XD	16643	20661	31678	−1608
B97D	15905	19510	29334	−2477
PBE	15841	19473	29591	−2091
PBE0	16388	20436	31126	−1649
HSEH1PBE	16379	20399	31017	−1741
LC-BLYP	16955	21249	32930	-981
LC-ωHPBE	16552	21004	32822	−282

Table S2. Excitation energies computed at the TD-LC-ωHPBE/6-311G(d,p)//B3LYP/6-311G(d,p) level for substituted azulenes. The numbers in the first column indicate the carbon atom containing the substituent.

Position[a]	Excitation energies								
	in eV			in cm^{-1}					
	T_1	S_1	S_2	T_1	S_1	S_2	S_2-S_1	S_2-2T_1	S_2-2T_1[b]
Experimental[c1]	1.72	1.77	3.57	13900	14300	28800	14500	1000	-
DFT/MRCI[c1]	1.76	1.91	3.46	14180	15400	27900	12500	−460	-
CASSCF-NEVPT2[d2]	1.91	1.92	3.90	15383	15450	31446	15996	680	-
Azulene	1.86	2.38	3.87	14982	19164	31208	12044	1245	0
CN1	2.01	2.49	3.85	16183	20102	31086	10984	−1279	−2524
CN2	1.78	2.34	3.87	14349	18848	31227	12379	2528	1283
CN6	1.56	2.15	3.71	12620	17349	29922	12573	4682	3438
CN7	1.87	2.38	3.68	15069	19169	29691	10521	−447	−1691
CN8	1.61	2.14	3.66	13005	17291	29480	12189	3471	2226
CN12	1.90	2.44	3.85	15312	19701	31037	11336	414	−831
CN13	2.13	2.59	3.87	17151	20891	31198	10307	−3104	−4348
CN47	1.60	2.13	3.50	12921	17176	28233	11056	2391	1146
CN48	1.40	1.94	3.50	11310	15679	28200	12521	5581	4337
CN57	1.89	2.36	3.54	15209	19061	28586	9525	−1832	−3077
CN67	1.55	2.15	3.55	12522	17367	28620	11253	3576	2332
CN68	1.38	1.97	3.52	11147	15921	28420	12498	6127	4882
CN78	1.65	2.16	3.47	13294	17413	27980	10567	1393	148
CN123	1.99	2.53	3.85	16040	20384	31088	10704	−992	−2237
CN457	1.64	2.14	3.36	13219	17227	27074	9847	637	−607
CN458	1.42	1.95	3.33	11455	15763	26841	11078	3930	2686
CN467	1.35	1.96	3.38	10905	15777	27270	11493	5461	4217
CN468	1.21	1.81	3.38	9784	14611	27283	12673	7715	6470
CN567	1.56	2.14	3.42	12598	17230	27620	10391	2424	1179
CN678	1.40	1.99	3.35	11279	16044	27053	11009	4495	3250
CN4578	1.44	1.95	3.20	11582	15757	25787	10030	2623	1378
CN4678	1.21	1.82	3.23	9763	14640	26014	11374	6487	5243
CN5678	1.38	1.96	3.25	11136	15789	26186	10397	3914	2670
CN45678	1.21	1.80	3.10	9799	14549	24997	10447	5399	4155
OH1a	1.41	1.99	3.72	11405	16087	30019	13932	7208	5964
OH1b	1.38	1.97	3.67	11126	15903	29578	13675	7327	6082
OH2	2.18	2.68	3.72	17577	21620	29982	8362	−5172	−6417
OH6a	2.22	2.63	3.85	17895	21236	31048	9813	−4742	−5986
OH6b	2.22	2.63	3.85	17897	21233	31047	9814	−4747	−5991
OH7a	1.45	2.17	3.84	11714	17465	30939	13474	7512	6268
OH7b	1.49	2.14	3.84	12004	17259	30951	13691	6943	5698
OH8a	1.96	2.58	3.92	15826	20801	31632	10831	−20	−1265
OH8b	2.11	2.71	4.02	16998	21868	32445	10577	−1551	−2796

OH12a	1.66	2.29	3.59	13384	18475	28967	10492	2199	954
OH12b	1.90	2.46	3.58	15300	19814	28852	9038	−1749	−2993
OH13	1.08	1.68	3.67	8691	13561	29597	16037	12216	10972
OH48	2.36	2.92	4.13	19016	23520	33312	9792	−4720	−5964
OH56a	1.92	2.43	3.78	15469	19631	30472	10841	−466	−1711
OH56b	1.73	2.33	3.76	13936	18775	30340	11565	2469	1224
OH57	1.26	2.00	3.87	10130	16161	31225	15064	10966	9721
OH58	1.48	2.30	3.84	11949	18558	30989	12431	7091	5847
OH68	2.27	2.84	3.96	18348	22942	31974	9033	−4722	−5967
OH78	1.75	2.41	3.87	14121	19472	31177	11706	2935	1691
OH123	1.46	2.04	3.48	11757	16461	28090	11629	4576	3331
OH456	2.21	2.74	3.95	17839	22136	31870	9734	−3809	−5053
OH457a	1.45	2.29	3.92	11718	18431	31622	13190	8185	6940
OH458a	1.84	2.73	4.08	14864	22001	32869	10868	3142	1897
OH467	1.87	2.64	3.93	15086	21268	31736	10468	1565	320
OH468	2.85	3.30	4.31	23015	26616	34734	8118	−11296	−12540
OH478	2.02	2.72	4.05	16304	21944	32630	10686	21	−1224
OH567	1.57	2.19	3.74	12634	17696	30176	12481	4909	3664
OH568	2.11	2.78	3.98	16997	22459	32093	9633	−1902	−3146
OH578	1.43	2.21	3.84	11507	17841	30947	13106	7932	6688
OH678	2.07	2.60	3.87	16680	20987	31238	10250	−2121	−3366
OH4567	1.77	2.46	3.87	14265	19874	31217	11343	2687	1443
OH4568a	2.29	2.90	4.08	18502	23397	32932	9536	−4072	−5317
OH4578	1.56	2.43	3.94	12616	19590	31809	12218	6577	5332
OH4678	2.20	2.99	4.11	17766	24102	33110	9008	−2422	−3667
OH5678	1.82	2.45	3.83	14691	19779	30882	11103	1499	255
OH45678	2.03	2.69	3.99	16342	21728	32183	10455	−502	−1746

[a] In the OH-substituted compounds, isomers a and b are observed, these are relative to the position of the hydrogen in −OH, but do not change considerably the final result. [b] Equation 2 (S_2–$2T_1$) relative to Azulene. [c] Ref. 37. [d] Ref. 22.

Table S3. Dipole moments at levels of theory used in this work.

Level of Theory	Dipole Moment (Debye)			
	S_0	T_1	S_1	S_2
Adiabatic B3LYP-6-311G(d,p)	1.04	0.53	0.30	0.56
Vertical LC-ωHPBE/6-311G(d,p)	1.40	0.64	0.70	0.70
Adiabatic LC-ωHPBE/6-311G(d,p)	1.40	0.96	0.84	0.80

Table S4. Values obtained for –OH compounds from equation 2 (relative to azulene) and those obtained from the sum of the monosubstituted compounds (additive approach).

Compound	Eq 2[a]	Additive app.	Compound	Eq 2[a]	Additive app.
OH12a	954	−453	OH467	320	−983
OH12b	−2993	−335	OH468	−12540	−10046
OH13	10972	11927	OH478	−1224	107
OH48	−5964	−5591	OH567	3664	5975
OH56a	−1711	−288	OH568	−3146	−2519
OH56b	1224	277	OH578	6688	9171
OH57	9721	12535	OH678	−3366	−2519
OH58	5847	5003	OH4567	1443	4146
OH68	−5967	−7251	OH4568a	−5317	−5310
OH78	1691	3472	OH4578	5332	5806
OH123	3331	5510	OH4678	−3667	−3779
OH456	−5053	−8520	OH5678	255	2615
OH457a	6940	11271	OH45678	−1746	−186
OH458a	1897	3738			

[a] Values relative to Azulene following: $S_{2,X}-2T_{1,X}-S_{2,Azulene}-2T_{1,Azulene}$, where S_x and T_x represent the respective excited state values for X designed compound.

Figure S1. Frontier Molecular orbitals for Azulene and selected derivatives.
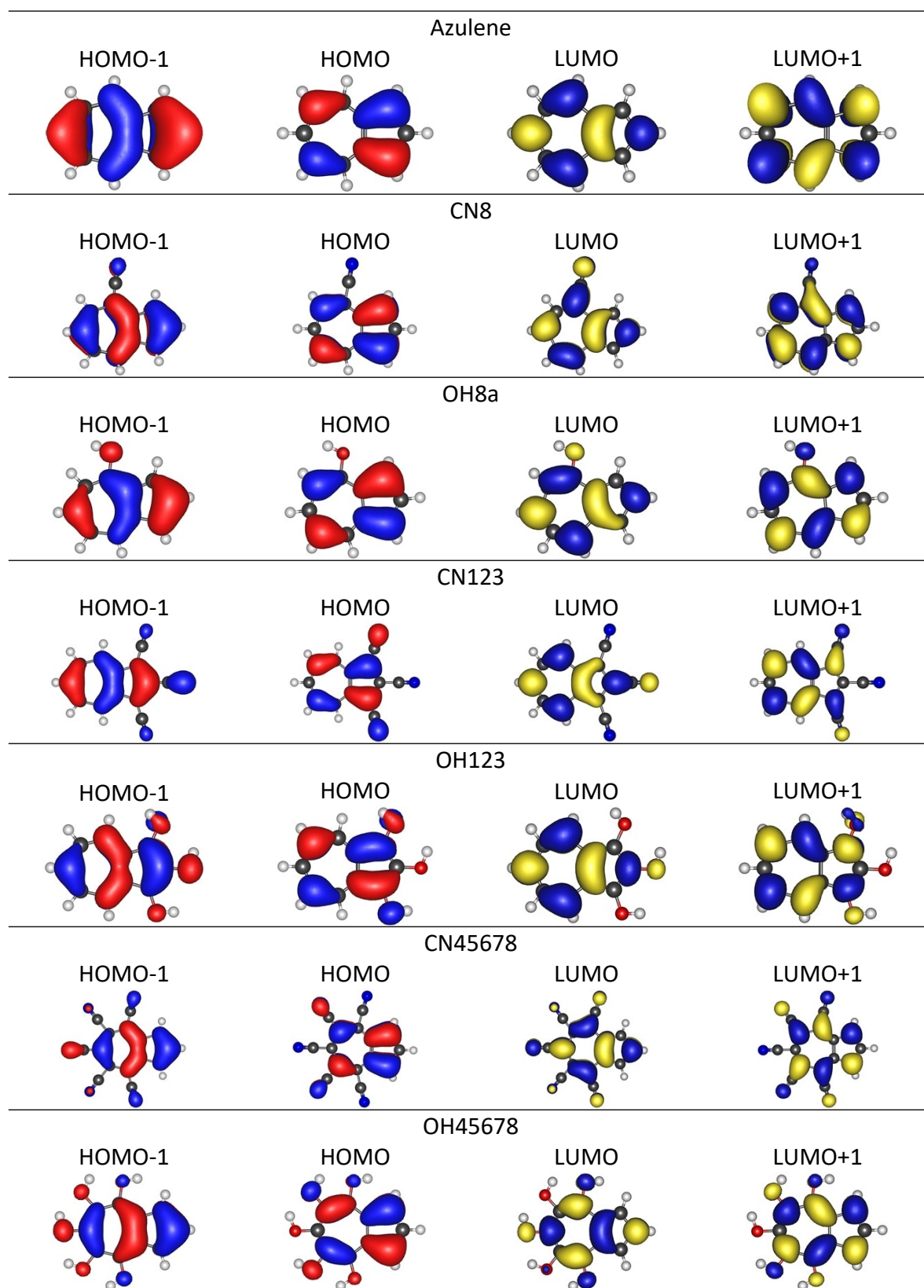
		Azulene	
HOMO-1	HOMO	LUMO	LUMO+1

		CN8	
HOMO-1	HOMO	LUMO	LUMO+1

		OH8a	
HOMO-1	HOMO	LUMO	LUMO+1

		CN123	
HOMO-1	HOMO	LUMO	LUMO+1

		OH123	
HOMO-1	HOMO	LUMO	LUMO+1

		CN45678	
HOMO-1	HOMO	LUMO	LUMO+1

		OH45678	
HOMO-1	HOMO	LUMO	LUMO+1

Figure S2. Excited state energies calculated for azulene a) for substituted –CN compounds and b) for substituted –OH compounds at the TD-LC-ωHPBE/6-311G(d,p)//B3LYP/6-311G(d,p) level.
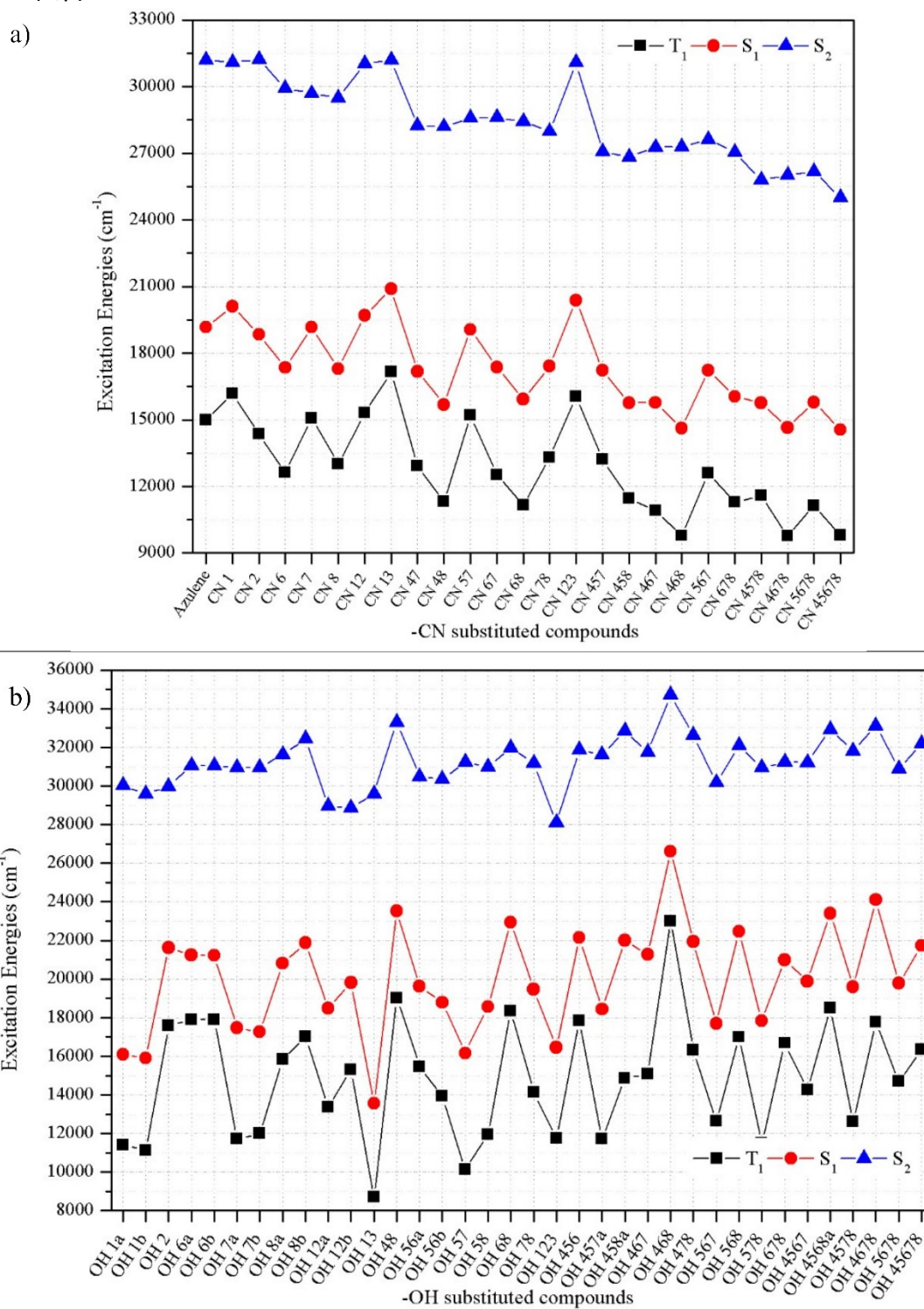
Figure S3. Computed vs. predicted values using the additive scheme for S_2–$2T_1$ relative to azulene for the substituted -CN compounds.
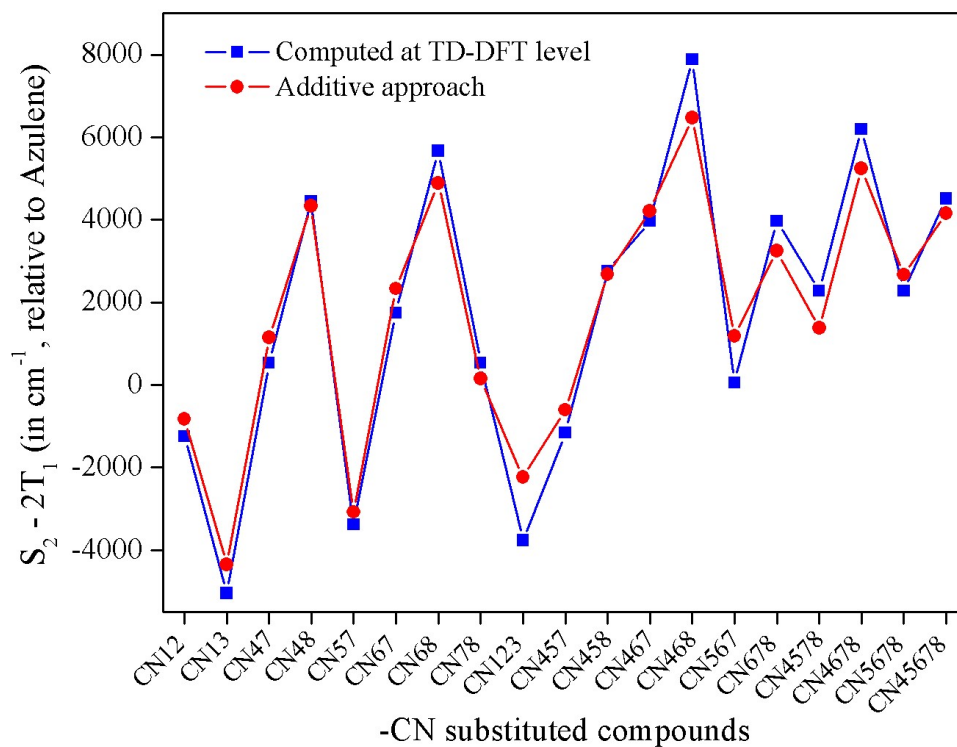

Figure S4. Correlation between Computed vs. predicted values using the additive scheme for S_2–$2T_1$ relative to azulene for the substituted -CN compounds.

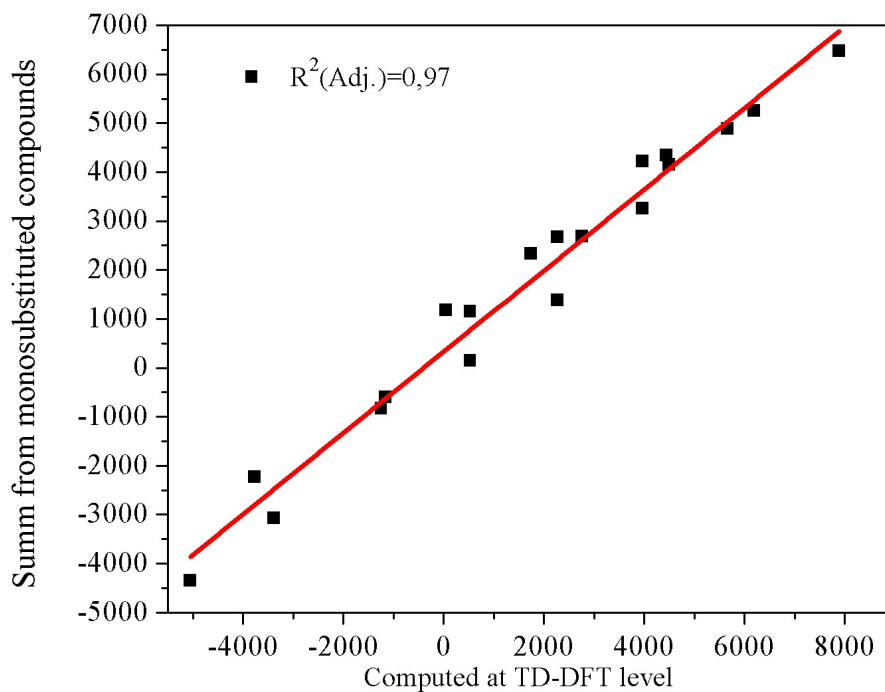**Figure S5.** Computed vs. predicted values using the additive scheme for S_2–$2T_1$ relative to azulene for the substituted –OH compounds.
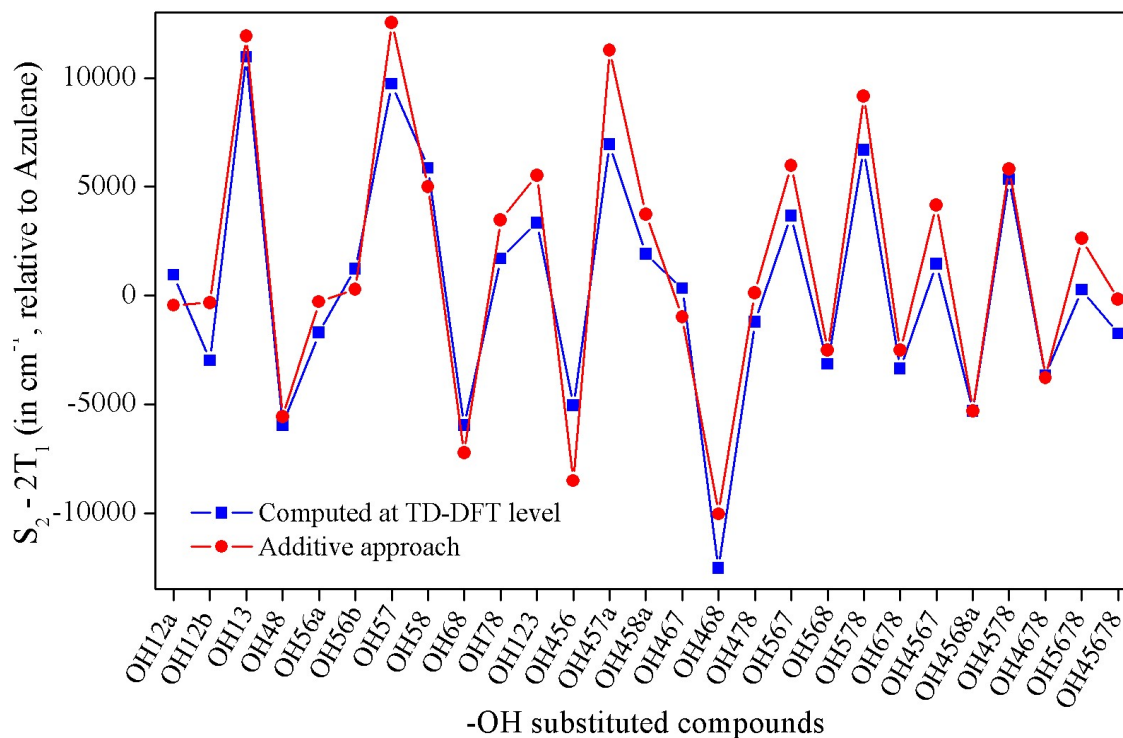

Figure S6. Correlation between Computed vs. predicted values using the additive scheme for S_2–$2T_1$ relative to azulene for the substituted –OH compounds.