

Electronic Supplementary Information (ESI) for

**Self-assembled dimethyldihydropyrene-pyridyl substituted ligands
with zinc (II) *meso*-tetraphenylporphyrin *via* axial coordination**

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1. Additional NMR spectra

Figure ESI 1 : ^1H NMR spectrum of 2_c

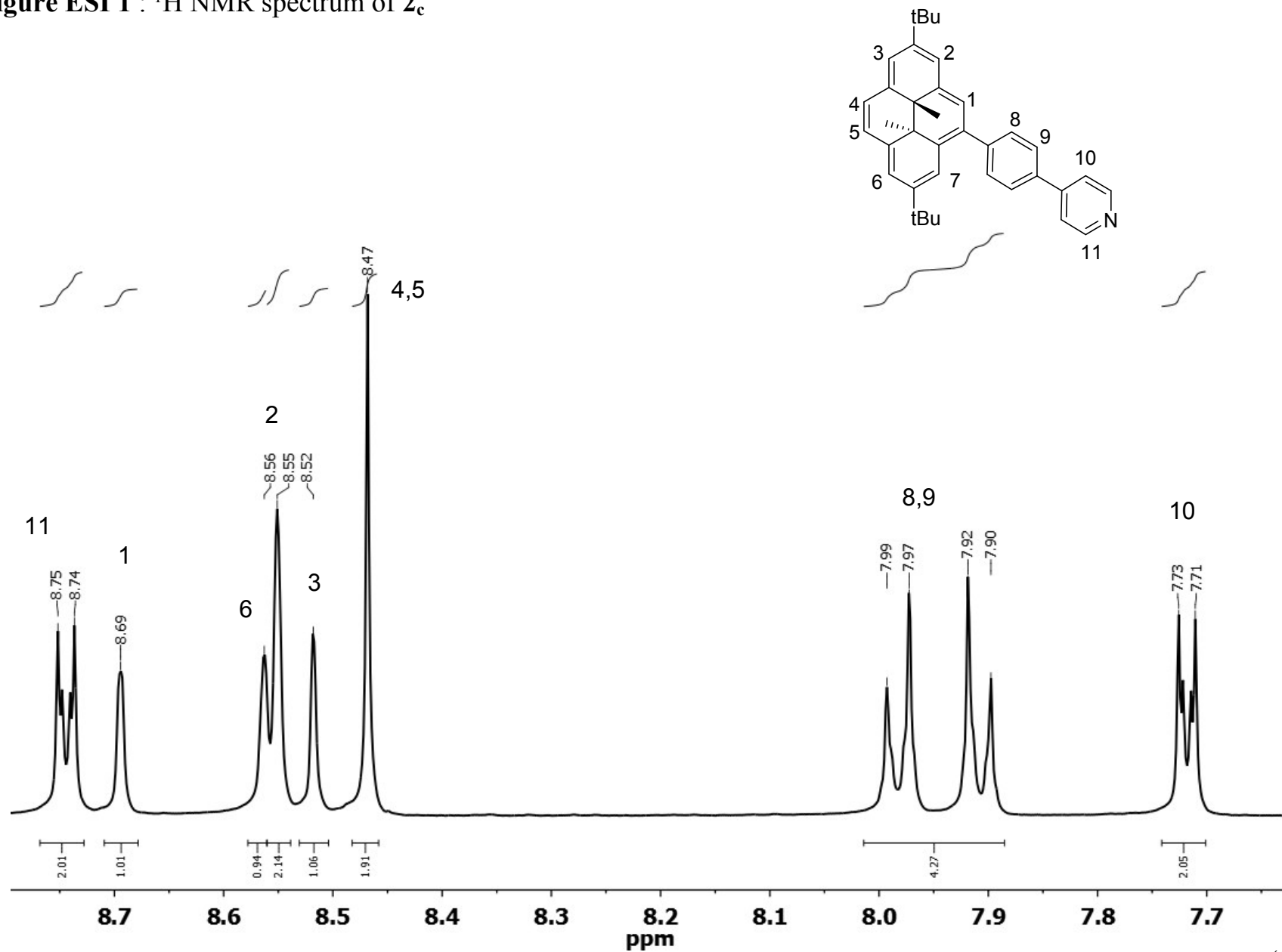


Figure ESI 2 : ^1H NMR spectrum of 3_c^+

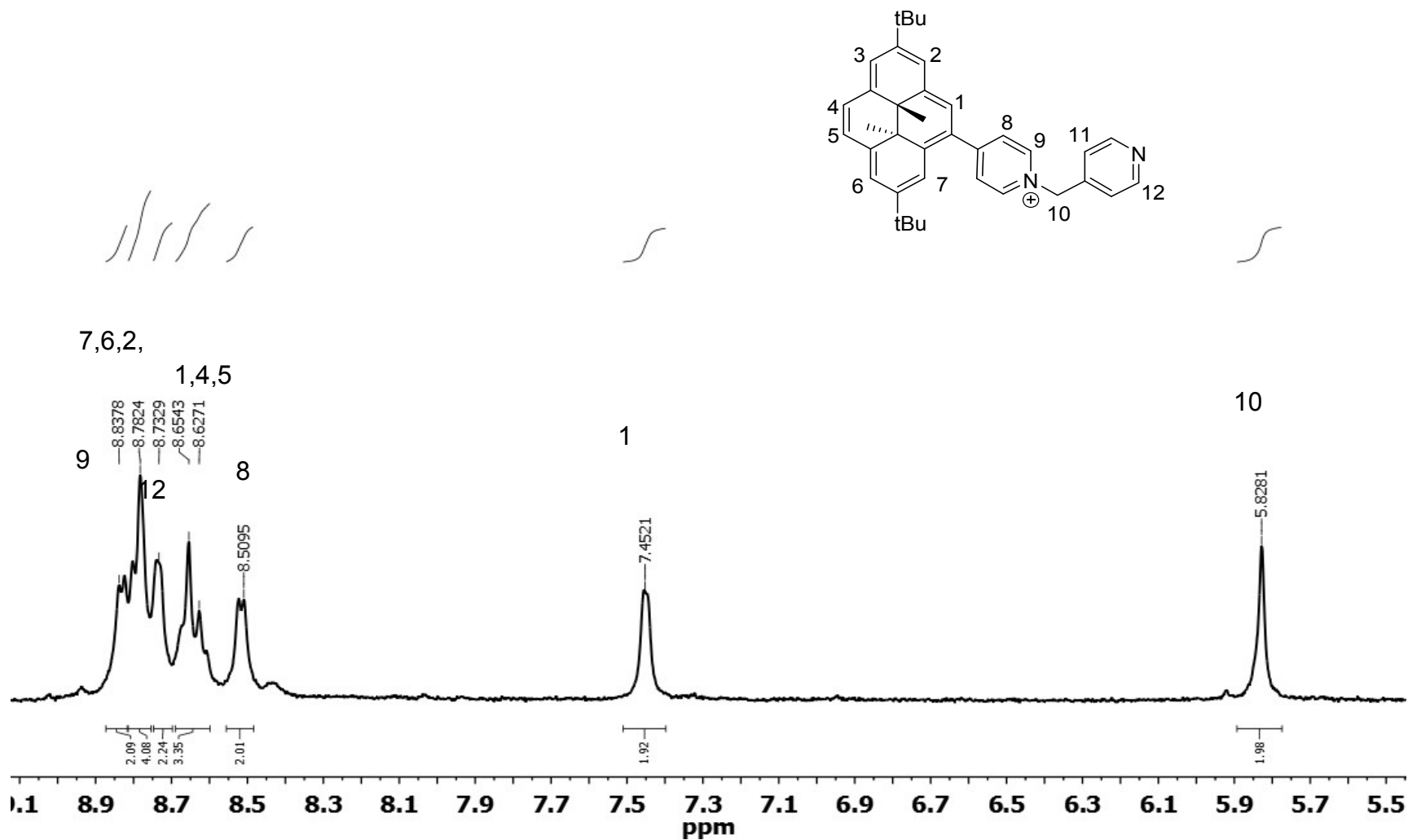


Figure ESI 3 : ^1H NMR spectrum of the titration (TPP)Zn with 1_c (0-4 eq, in red the (TPP)Zn spectrum)

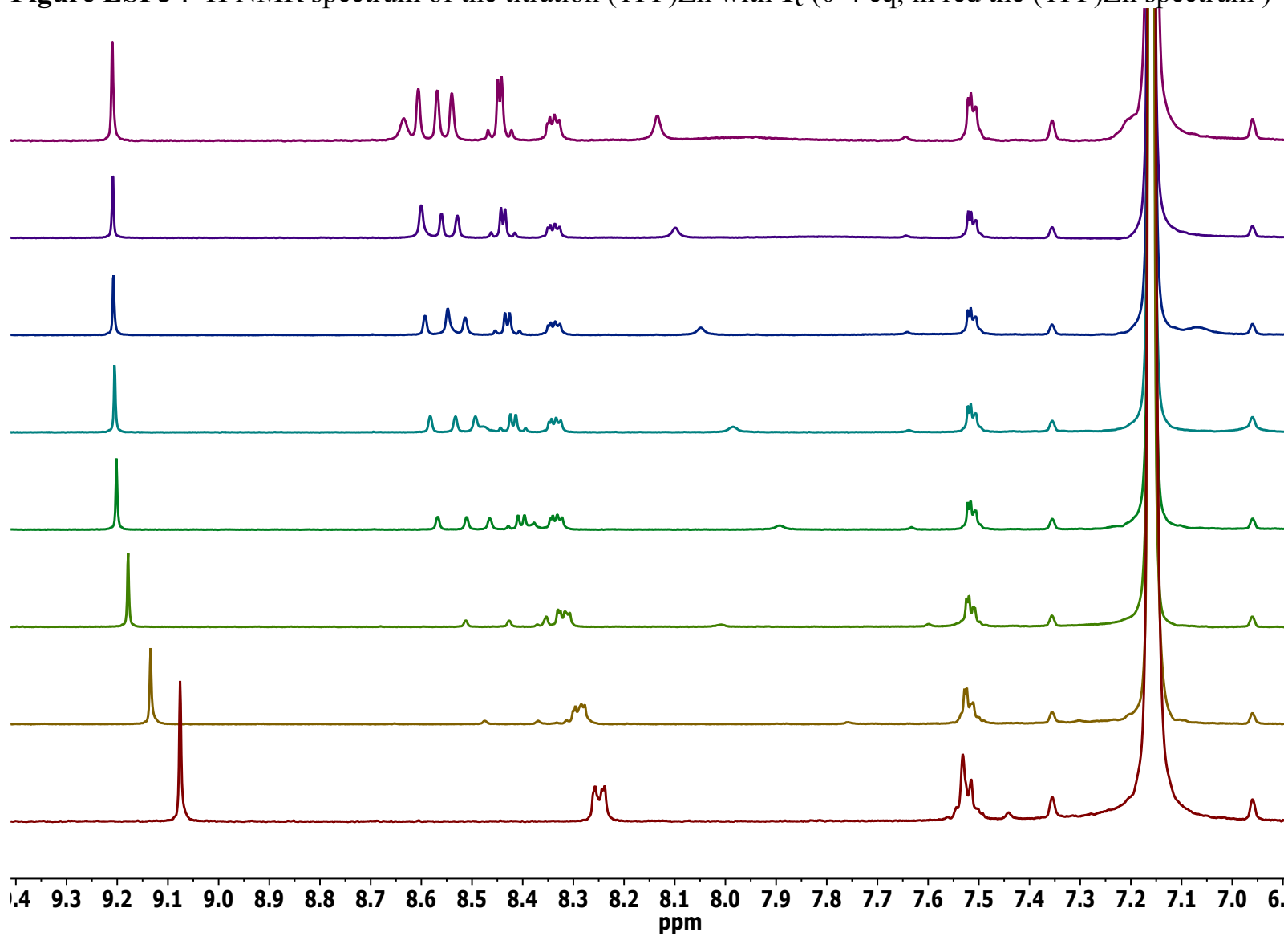


Figure ESI 4 : ^1H NMR spectrum of the titration (TPP)Zn with 2_c (0-4 eq, in red the (TPP)Zn spectrum)

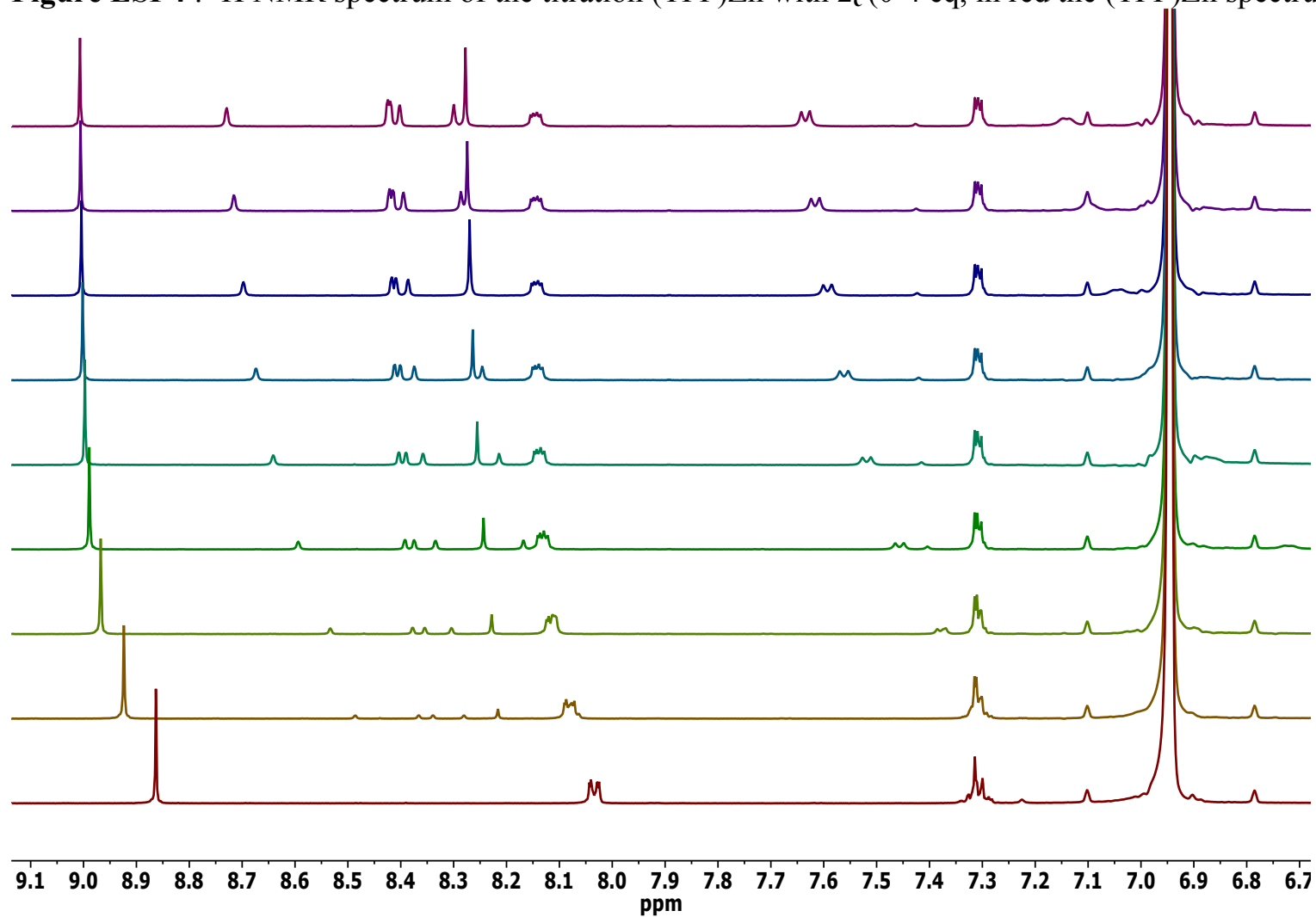
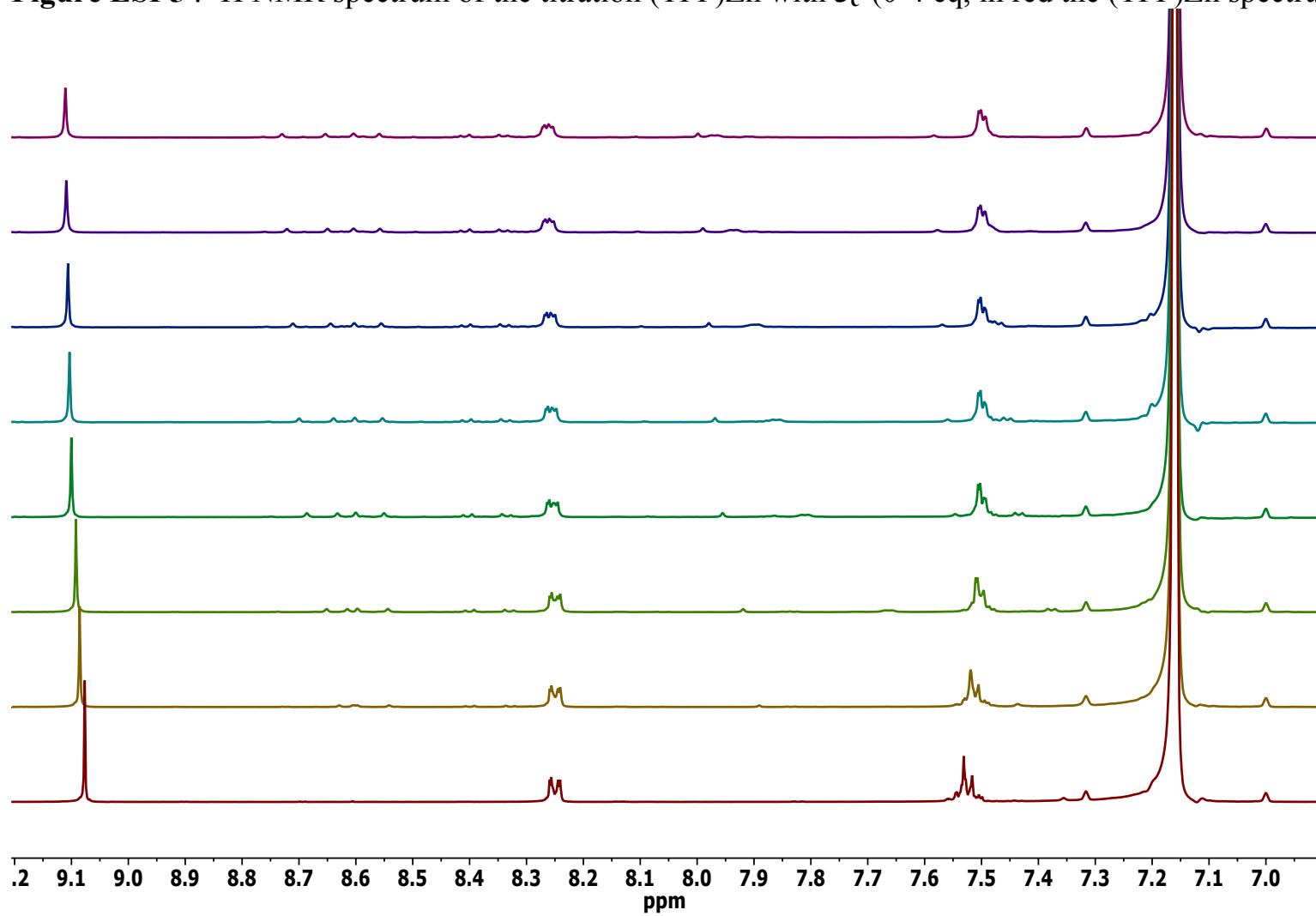
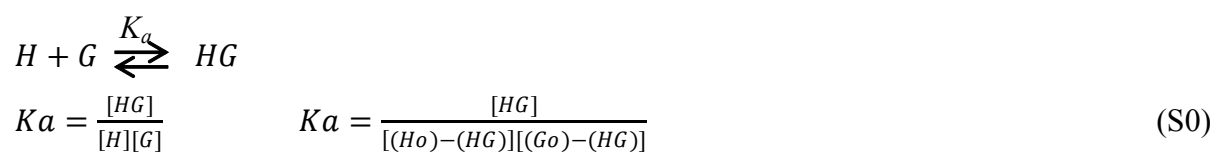


Figure ESI 5 : ^1H NMR spectrum of the titration (TPP)Zn with 3_c^+ (0-4 eq, in red the (TPP)Zn spectrum)



2. Binding constants

The binding constants of the complexations were determined by fitting of data obtained from ^1H NMR titrations with equation S0 in OriginPro 8.6.0 (OriginLab Corporation)



$$\Delta A = \frac{l(\Delta\varepsilon)}{2} \left([H_0] + [G_0] + \frac{1}{K_a} \right) - \frac{1}{2} \sqrt{\left([H_0] + [G_0] + \frac{1}{K_a} \right)^2 - 4[H_0][G_0]}$$

3. Crystal data

Table S1. Crystal Data and Structure Refinement for **2_c**

Formula	C ₃₇ H ₃₉ N
Fw (g mol ⁻¹)	497.69
Crystal system	orthorhombic
Space group	Pbca
<i>a</i> (Å)	10.102(2)
<i>b</i> (Å)	19.058(4)
<i>c</i> (Å)	31.626(6)
α (deg.)	90.00
β (deg.)	90.00
γ (deg.)	90.00
<i>V</i> (Å ³) / <i>Z</i>	6089(2)
<i>D_x</i> (g cm ⁻³)	1.086
μ (cm ⁻¹)	0.062
Crystal dim. (mm)	0.45x0.17x0.07
<i>T</i> (K)	200.0
θ range for coll. (deg.)	2.50 -25.00
nb. of rflns. coll.	67156
Data/restraints/parameters	5336/84/382
R (<i>I</i>) ^a all/R[<i>I</i> >2 σ (<i>I</i>)]	11.26% / 7.51%
Goodness of fit <i>S</i>	1.137
$\Delta\rho_{\min}/\Delta\rho_{\max}$ (e Å ⁻³)	-0.236 / 0.208

$$^a R = \frac{\sum ||I_o| - |I_c||}{\sum |I_o|}$$

4. TD-DFT values

Table S2. B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0 $\mathbf{1}_{c,model}$.

C	0.36359130	2.94151696	1.47429523	B3LYP energy:
C	0.38823624	3.02363910	2.86975665	
C	0.27407823	1.88991580	3.68033408	$E(S_0) = -942.815812$ a.u.
C	0.05974885	0.62736946	3.13410904	
C	0.14894074	1.72827285	0.82467666	
C	0.01528821	-0.55364984	3.88131802	
C	-0.16045232	-1.79951821	3.27630129	
C	-0.13641009	-1.96142623	1.88702917	CAM-B3LYP energy:
C	-0.38271034	-3.17248230	1.24639826	
C	-0.45391457	-3.24965756	-0.14436506	$E(S_0) = -942.261355$ a.u.
C	-0.32594169	-2.12107505	-0.96394081	
C	-0.04318085	-0.86233626	-0.44239426	
C	0.04309636	0.32812635	-1.20252710	
C	0.20128353	1.56840981	-0.56068266	
C	-0.29044154	0.52730774	1.65055922	
C	0.30475391	-0.76308982	1.04774205	
C	-1.85895009	0.53246171	1.59163522	
C	1.87260357	-0.77491399	1.10559564	
H	0.56105382	3.83060561	0.88319148	
H	0.40150678	1.98654331	4.75430229	
H	-0.58189697	-4.05700559	1.84382331	
H	-0.50291999	-2.23129183	-2.02665317	
H	0.56700781	3.98641614	3.33578277	
H	-0.68280399	-4.20344134	-0.60701987	
H	0.08938295	-0.49028030	4.96271786	
H	-0.30091967	-2.67888156	3.89758973	
H	0.37416953	2.44813490	-1.17293997	
H	-2.27643339	-0.29506150	2.16637058	
H	-2.21203878	0.46103407	0.56187326	
H	2.22771404	-0.70628950	2.13460337	
H	2.29418124	0.05038966	0.53038785	
H	-2.22504920	1.46798685	2.01776268	
H	2.23346624	-1.71284318	0.67968451	
C	0.00833242	0.31870008	-2.68976018	
C	0.86728494	-0.47985825	-3.45622558	
C	-0.86272649	1.15804858	-3.39571158	
C	0.81176753	-0.40647968	-4.84455876	
H	1.58448950	-1.13464269	-2.97631755	
C	-0.84162779	1.15373766	-4.78732991	
H	-1.55964124	1.79646539	-2.86524812	
N	-0.02463544	0.38971088	-5.51837651	
H	1.47945036	-1.01612138	-5.44772690	
H	-1.51924726	1.79625577	-5.34348676	

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0 $\mathbf{1}_{o,model}$.

C	-0.651162807228	2.781060847659	1.401160275209
C	-0.305597831276	2.998551420332	2.731243091924
C	-0.111190730632	1.896644989878	3.560009482994
C	-0.441685550084	0.605024839297	3.121565125818
C	-0.983192195503	1.494719532877	0.941965535869
C	0.195319217845	-0.550204207823	3.808905966332
C	0.911692523473	-1.518807399555	3.195238735139
C	0.932197562256	-1.779048730736	1.727746264568
C	0.548915823333	-3.054162848157	1.290907393968
C	0.159765159320	-3.270658397960	-0.028473736374
C	-0.013702643517	-2.172607842523	-0.863653905317
C	0.379566383763	-0.888772244872	-0.450558951799
C	-0.201462918541	0.296300754711	-1.169993639799
C	-0.906827845551	1.265781599102	-0.521644980409
C	-1.114610441345	0.452085655650	1.888289346898
C	1.065976092439	-0.742041951109	0.773473680763
C	-1.978898477536	-0.752571278829	1.619245768384
C	1.931269608157	0.465089822688	1.041139803573
H	-0.615329788620	3.600846836399	0.691124195623
H	0.348999847674	2.022625210239	4.534685854934
H	0.504144210130	-3.866404710407	2.009337267403
H	-0.492502727046	-2.295669263286	-1.828479409064
H	-0.086491381937	3.999156472162	3.085166025650
H	-0.105941607042	-4.265391213382	-0.366960941099
H	0.218895424124	-0.525545893408	4.895856868997
H	1.389535828549	-2.260920773531	3.830607091235
H	-1.280804333333	2.081716152999	-1.134855057733
H	-1.926509120582	-1.110739907510	0.593630444178
H	-1.757923289109	-1.575618403886	2.295512739759
H	1.787264361635	1.237412876045	0.287375025528
H	1.786048567853	0.905612274510	2.025157824041
H	-3.017574241940	-0.451170802766	1.802396048102
H	2.977299750085	0.142075585501	0.983954009135
C	-0.076928123869	0.349406073551	-2.648691541337
C	1.091854736719	-0.090104046213	-3.286198358570
C	-1.092002095966	0.844060993036	-3.480279007234
C	1.197951974597	0.010190786340	-4.669307213748
H	1.911616540918	-0.498826556060	-2.707767528972
C	-0.886785308694	0.897323670008	-4.854744695878
H	-2.042073016665	1.159958873382	-3.066363971112
N	0.235063876547	0.494609012117	-5.460334182908
H	2.105625245907	-0.317673239973	-5.169049342183
H	-1.670821809307	1.275021923505	-5.505860832492

B3LYP energy:

$E(S_0) = -942.783809$ a.u.

Table S2 (continued). UB3LYP/6-311G(d,p) Cartesian coordinates and energies for S_0 transition state between $\mathbf{1}_{c,model}$ and $\mathbf{1}_{o,model}$.

C	-0.651162807228	2.781060847659	1.401160275209
C	-0.305597831276	2.998551420332	2.731243091924
C	-0.111190730632	1.896644989878	3.560009482994
C	-0.441685550084	0.605024839297	3.121565125818
C	-0.983192195503	1.494719532877	0.941965535869
C	0.195319217845	-0.550204207823	3.808905966332
C	0.911692523473	-1.518807399555	3.195238735139
C	0.932197562256	-1.779048730736	1.727746264568
C	0.548915823333	-3.054162848157	1.290907393968
C	0.159765159320	-3.270658397960	-0.028473736374
C	-0.013702643517	-2.172607842523	-0.863653905317
C	0.379566383763	-0.888772244872	-0.450558951799
C	-0.201462918541	0.296300754711	-1.169993639799
C	-0.906827845551	1.265781599102	-0.521644980409
C	-1.114610441345	0.452085655650	1.888289346898
C	1.065976092439	-0.742041951109	0.773473680763
C	-1.978898477536	-0.752571278829	1.619245768384
C	1.931269608157	0.465089822688	1.041139803573
H	-0.615329788620	3.600846836399	0.691124195623
H	0.348999847674	2.022625210239	4.534685854934
H	0.504144210130	-3.866404710407	2.009337267403
H	-0.492502727046	-2.295669263286	-1.828479409064
H	-0.086491381937	3.999156472162	3.085166025650
H	-0.105941607042	-4.265391213382	-0.366960941099
H	0.218895424124	-0.525545893408	4.895856868997
H	1.389535828549	-2.260920773531	3.830607091235
H	-1.280804333333	2.081716152999	-1.134855057733
H	-1.926509120582	-1.110739907510	0.593630444178
H	-1.757923289109	-1.575618403886	2.295512739759
H	1.787264361635	1.237412876045	0.287375025528
H	1.786048567853	0.905612274510	2.025157824041
H	-3.017574241940	-0.451170802766	1.802396048102
H	2.977299750085	0.142075585501	0.983954009135
C	-0.076928123869	0.349406073551	-2.648691541337
C	1.091854736719	-0.090104046213	-3.286198358570
C	-1.092002095966	0.844060993036	-3.480279007234
C	1.197951974597	0.010190786340	-4.669307213748
H	1.911616540918	-0.498826556060	-2.707767528972
C	-0.886785308694	0.897323670008	-4.854744695878
H	-2.042073016665	1.159958873382	-3.066363971112
N	0.235063876547	0.494609012117	-5.460334182908
H	2.105625245907	-0.317673239973	-5.169049342183
H	-1.670821809307	1.275021923505	-5.505860832492

UB3LYP energies:

$$E(S_0) = -942.745791 \text{ a.u.}$$

$$\langle S^2 \rangle = 1.020695$$

$$E(T_1) = -942.739932 \text{ a.u.}$$

$$\langle S^2 \rangle = 2.040388$$

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_1(\text{LE}) \mathbf{1}_{\text{c,model}}$.

C	0.35255954	2.94377381	1.47287614	TD-CAM-B3LYP energy:
C	0.39521780	3.02858701	2.86457892	
C	0.28086467	1.89465875	3.66944396	
C	0.05021066	0.63293574	3.11451024	$E(S_1) = -942.183822 \text{ a.u.}$
C	0.11917812	1.72416763	0.82965573	
C	0.02929682	-0.54922935	3.86269496	
C	-0.12890090	-1.79680620	3.25966077	
C	-0.10929432	-1.95832892	1.86886518	
C	-0.38443537	-3.17235858	1.23771931	
C	-0.48617754	-3.25035856	-0.14917941	
C	-0.35528155	-2.12325160	-0.96297174	
C	-0.03441611	-0.86908431	-0.43568576	
C	0.04478325	0.32101850	-1.19732627	
C	0.18185233	1.56434761	-0.55465386	
C	-0.30189487	0.52681677	1.64632030	
C	0.31381670	-0.76425207	1.03864148	
C	-1.85702696	0.47005937	1.57057264	
C	1.86928333	-0.71313857	1.11488823	
H	0.54207275	3.82702072	0.87344960	
H	0.41231439	1.98109214	4.74215826	
H	-0.57581115	-4.05069708	1.84381932	
H	-0.55266779	-2.22030524	-2.02170906	
H	0.57869920	3.98976199	3.32946881	
H	-0.73233473	-4.20006945	-0.60870040	
H	0.12483924	-0.48547775	4.94124975	
H	-0.27142051	-2.67467478	3.88066177	
H	0.37099682	2.44082286	-1.16490818	
H	-2.23771865	-0.37977132	2.13706158	
H	-2.18615086	0.37854042	0.53517054	
H	2.19939871	-0.62358281	2.14975230	
H	2.25439442	0.13452039	0.54809786	
H	-2.27479057	1.38558343	1.99029379	
H	2.28307760	-1.63111567	0.69601715	
C	0.00940452	0.31372091	-2.67666091	
C	0.82016315	-0.52811356	-3.43940203	
C	-0.80705142	1.19949791	-3.37978279	
C	0.77348949	-0.44850999	-4.82142112	
H	1.49709362	-1.22318640	-2.95961392	
C	-0.78330938	1.19618556	-4.76552921	
H	-1.46804465	1.87452264	-2.85041771	
N	-0.01204365	0.39178670	-5.49116875	
H	1.40709702	-1.09249776	-5.42408331	
H	-1.42184676	1.87609174	-5.32183865	

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_2(Z)$ $\mathbf{1}_{c,model}$ (CPD*).

C	0.349769	2.926431	1.480958
C	0.448252	3.013753	2.869680
C	0.353762	1.864519	3.661080
C	0.058639	0.634673	3.108753
C	0.061131	1.727505	0.846669
C	0.058381	-0.578374	3.862742
C	-0.045982	-1.805120	3.269909
C	-0.086920	-1.956264	1.848416
C	-0.434536	-3.142175	1.229106
C	-0.592505	-3.220326	-0.155775
C	-0.463938	-2.081078	-0.954361
C	-0.071392	-0.864108	-0.428297
C	-0.003258	0.358792	-1.199198
C	0.076727	1.579537	-0.567602
C	-0.335232	0.537850	1.664006
C	0.319729	-0.771920	1.019855
C	-1.883289	0.393781	1.585946
C	1.868901	-0.634741	1.103382
H	0.530198	3.808864	0.875977
H	0.549544	1.930205	4.726276
H	-0.628573	-4.017396	1.840391
H	-0.710139	-2.150797	-2.006074
H	0.666230	3.968486	3.331758
H	-0.880766	-4.160391	-0.609506
H	0.147690	-0.507904	4.941895
H	-0.118762	-2.697658	3.881549
H	0.220284	2.471410	-1.167503
H	-2.214284	-0.474836	2.154870
H	-2.200653	0.278056	0.549190
H	2.186460	-0.518170	2.139508
H	2.205369	0.230732	0.533014
H	-2.352101	1.286329	2.002094
H	2.334664	-1.530689	0.690806
C	0.010957	0.330588	-2.678692
C	0.848242	-0.525792	-3.395624
C	-0.785406	1.198623	-3.424990
C	0.852453	-0.469014	-4.779725
H	1.504944	-1.213647	-2.879058
C	-0.710639	1.171492	-4.808702
H	-1.470831	1.875690	-2.930921
N	0.089886	0.357888	-5.491340
H	1.508019	-1.122166	-5.347972
H	-1.331542	1.838067	-5.399918

TD-CAM-B3LYP energy:

$E(S_2) = -942.176817$ a.u.

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0
 $Z_{c,model}$

C	-0.183430468160	1.026278419886	0.030090620899
C	0.663012407019	3.126908805625	0.915752441385
H	1.319414295860	3.645828575950	1.605050389692
C	-0.258424804938	-0.460137051796	0.049839667098
C	0.897631182247	-1.272335897673	-0.039040062262
C	2.179051595867	-0.802927786140	-0.310757834289
H	2.334219435080	0.255845159601	-0.477674361556
C	-0.099999179585	5.346983884682	0.022270137840
C	-0.953352291816	3.155950752626	-0.859108318189
H	-1.594227469119	3.697493248525	-1.545579136334
C	-1.525393862395	-1.051643600811	0.194556068422
H	-2.378969506405	-0.404424720394	0.371521173319
C	-0.129536729695	3.865204137767	0.025465846687
C	-0.983553461904	1.766812383370	-0.851965479929
H	-1.630942855915	1.243063738887	-1.546308428794
N	-0.044444707422	8.176285106082	0.015466048210
C	3.272822653579	-1.668465712850	-0.440512309210
C	1.896899685328	-3.645791717528	-0.149339941951
C	0.731490912155	-2.835568556685	1.860807776263
H	1.684480010608	-2.453811566338	2.231606701652
H	0.616863089378	-3.864364832672	2.204541459245
H	-0.071256059286	-2.229931119639	2.283410501489
C	-1.745317610024	-2.428086433065	0.123562468007
C	0.639459665382	1.737914902812	0.915556074766
H	1.257032694853	1.193987911176	1.620541792021
C	-0.569437922548	-3.225734053149	-1.884197756147
H	-1.519865517279	-3.607513580312	-2.260707687013
H	0.235643565359	-3.831329918823	-2.301951297976
H	-0.451134320823	-2.196385193190	-2.225689980482
C	3.135758848699	-3.055212126246	-0.382658824071
H	3.994982206417	-3.688279946935	-0.582878564344
C	-2.987074309893	-3.026813776098	0.322681695776
H	-3.851124547267	-2.399856140286	0.520898067118
C	-3.129614498970	-4.417722601746	0.331501738989
C	1.675493361235	-5.026335125214	-0.188781713863
H	2.528112346719	-5.683614259211	-0.330777080485
C	0.403437409668	-5.579135221148	-0.027248750624
H	0.293346095345	-6.657568359146	0.034977014702
C	-2.031461911110	-5.275644093988	0.216386202809
H	-2.175651970922	-6.345751550131	0.330997661428
C	-0.185704979400	6.082848077473	-1.166754285566
H	-0.251254342884	5.580880913272	-2.124771462133
C	0.037340221450	7.474220006884	1.149888293752
H	0.119365090537	8.054526622800	2.065112824736
C	0.732624592235	-2.760284189019	0.293821000959
C	0.014687685996	6.084581200798	1.207765124271
H	0.060488313909	5.585211836676	2.168273909518
C	-0.744673789194	-4.782414878709	0.017301473052
C	-0.578133953284	-3.300811533575	-0.316262272577
C	-0.153864080756	7.472569009298	-1.115591566110
H	-0.213231096672	8.051261087014	-2.033577859152
H	4.246644326779	-1.244963059856	-0.660848912605
H	-4.113055504039	-4.843445308829	0.498242821557

B3LYP energy:

$E(S_0) = -1173.925574$ a.u.

CAM-B3LYP energy:

$E(S_0) = -1173.236255$ a.u.

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0
 $Z_{o,model}$

C	-1.030621375378	2.696397666717	2.945165551317
C	-0.678332802410	3.037263684590	4.247219381467
C	-0.301006211432	2.023890347593	5.124604511612
C	-0.456319550322	0.675645798364	4.767448259371
C	-1.188251271986	1.351712783155	2.566516785391
C	0.363317735581	-0.335549235405	5.487411505987
C	1.191408801698	-1.226180193534	4.896531569392
C	1.200634078024	-1.565489462308	3.445137968645
C	0.991236026212	-2.905414612313	3.092447722653
C	0.594480035263	-3.251169412789	1.803243860111
C	0.237614040812	-2.239230564602	0.918966306424
C	0.453906424628	-0.890366238992	1.247083679948
C	-0.314866044468	0.155462622122	0.487602373194
C	-1.128777295402	1.051996013190	1.114720648700
C	-1.139367078778	0.358058735901	3.571441061590
C	1.151771444813	-0.577094427755	2.432783541065
C	-1.829319942298	-0.970967544789	3.401672883432
C	1.842544438858	0.754126013193	2.601026719237
H	-1.135813819820	3.470762127333	2.192248486590
H	0.167729140027	2.269704864304	6.071985623897
H	1.087531118475	-3.672512154985	3.854165838281
H	-0.248932305418	-2.484132893895	-0.018302495830
H	-0.594571637681	4.077663055956	4.539057359228
H	0.464148482246	-4.291593408892	1.528778749493
H	0.419443776714	-0.244899847948	6.569712718790
H	1.792180815713	-1.854720797551	5.549862344681
H	-1.634325460866	1.772258340237	0.476596726908
H	-1.757356679036	-1.378472302982	2.395927637808
H	-1.471526943125	-1.712656819395	4.112734593835
H	1.564397821768	1.452513367269	1.813483757871
H	1.666679674853	1.226365005724	3.565123960099
H	-2.894495673400	-0.809832690510	3.608521706457
H	2.921917699995	0.580065175206	2.519759571910
C	-0.252338684529	0.130112631483	-0.995861942709
C	0.955353163050	-0.165688587946	-1.648250356089
C	-1.369780941642	0.410086310246	-1.798477303929
C	1.050276597704	-0.146183500047	-3.032959536371
H	1.829774757121	-0.411692359052	-1.057196414210
C	-1.277277351524	0.420031666827	-3.183793512636
H	-2.327817058737	0.604535989406	-1.330683394160
H	1.996552128434	-0.389471040570	-3.502532395551
H	-2.157382950743	0.655219883329	-3.771431032881
C	-0.063956793989	0.148404503351	-3.831795502541
C	0.035067030207	0.160445183673	-5.309875358734
C	1.176172608568	0.639005459969	-5.967127071770
C	-1.006383202508	-0.304366524904	-6.123773980841
C	1.219961606291	0.630400883609	-7.357350522846
H	2.012216330696	1.037810274029	-5.405006081285
C	-0.862453178025	-0.269400150589	-7.506826507943
H	-1.910000082552	-0.713134708304	-5.687452887693
N	0.226217239757	0.187180514779	-8.133652509257
H	2.098706506352	1.005617082974	-7.875178675352
H	-1.662846287793	-0.633820194472	-8.145351022757

B3LYP energy:

$$E(S_0) = -1173.893604 \text{ a.u.}$$

Table S2 (continued). UB3LYP/6-311G(d,p) Cartesian coordinates and energies for S_0 transition state between $\mathbf{Z}_{c,model}$ and $\mathbf{Z}_{o,model}$.

C	0.446665567088	1.980811733462	5.230429634508
C	-0.007072840765	0.752741947789	4.772176825890
C	-0.580174883661	0.660361601735	3.429441333881
C	-0.277062363162	1.753647139421	2.509804194496
C	0.178453527302	2.965055825254	3.028892568395
C	0.472349833577	3.107114282623	4.389399180016
C	-0.297965316414	1.522233701361	1.079499769868
C	-0.139328397708	0.303028297754	0.465913881354
C	-0.010695612692	-0.937969703132	1.265538791780
C	-0.584042791715	-2.132909542087	0.847035104412
C	-0.658245244930	-3.247697994887	1.695821411144
C	-0.290837388710	-3.122325324717	3.042052661525
C	0.256953814079	-1.942793282200	3.528740412121
C	0.571754739641	-0.859440129540	2.600317971184
H	0.827996249982	2.059761811321	6.244068510487
C	0.203296958699	-0.473170066669	5.535542351968
H	0.350052157142	3.796795327020	2.352235779388
H	0.808420299867	4.062340290459	4.774589802219
H	-0.306124359588	2.406913056368	0.449832801311
H	-1.007346161127	-2.196618341321	-0.148913441310
H	-1.079700074423	-4.176839436032	1.331399007823
H	-0.483857388883	-3.939073351790	3.731175138445
C	0.358108553220	-1.698763627977	4.966365709431
C	-1.981368042386	0.065032919015	3.330682458555
C	1.971519403839	-0.259226288311	2.706115510431
H	0.488016766340	-2.561892384301	5.613068040693
H	0.307818113033	-0.380537874313	6.612809885268
H	-2.691573421980	0.793585972989	3.736560463008
H	-2.076350102894	-0.852975931523	3.909493161704
H	-2.263964458560	-0.137564951554	2.297962468167
H	2.068920471010	0.651773718609	2.116916177593
H	2.687788433437	-0.990317511457	2.315861852714
H	2.245801772129	-0.041935500497	3.737544748019
C	-0.116301218255	0.231017903197	-1.012380210952
C	0.775840457735	-0.621544621880	-1.685151062422
C	-0.960118315886	1.033358037308	-1.798879685364
C	0.836807585484	-0.651648443837	-3.071202863338
H	1.434447344581	-1.260756913111	-1.109431870782
C	-0.905097857917	0.995990049205	-3.185436730793
H	-1.679944644803	1.681927965653	-1.313253821464
H	1.531005695312	-1.328856137177	-3.555621418600
H	-1.561976855994	1.640033355288	-3.758963304391
C	-0.002578995003	0.155799187653	-3.853075163055
C	0.057942400327	0.117167799208	-5.332459278626
C	1.270663965883	-0.041207794301	-6.016430286990
C	-1.093379454726	0.237988720731	-6.122008954296
C	1.274178778295	-0.070094543615	-7.406998594715
H	2.206081976924	-0.115673260324	-5.474758155214
C	-0.981201989226	0.196551678551	-7.507766563214
H	-2.070550690051	0.337566600960	-5.664633442207
N	0.175747585519	0.045410575501	-8.159901746355
H	2.211226408808	-0.186159190586	-7.945153718348
H	-1.870028777794	0.283208178703	-8.127153135359

UB3LYP energies:

$$E(S_0) = -1173.855626 \text{ a.u.}$$

$$\langle S^2 \rangle = 1.021174$$

$$E(T_1) = -1173.849743 \text{ a.u.}$$

$$\langle S^2 \rangle = 2.040356$$

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_1(\text{LE}) \mathbf{2}_{\text{c,model}}$.

C	-0.177087051600	1.020091749140	0.023899700330	TD-CAM-B3LYP energy:
C	0.706453480836	3.110060526671	0.869220130354	
H	1.393053595953	3.629615516436	1.526921446844	
C	-0.250874672178	-0.458349558180	0.047215209186	$E(S_1) = -1173.159098$ a.u.
C	0.904631392947	-1.272042587633	-0.029057771470	
C	2.183332262427	-0.797071082280	-0.336099583197	
H	2.326049297191	0.257948903459	-0.525701917326	
C	-0.100402349829	5.324179286606	0.025365697744	
C	-0.990536102709	3.142129147843	-0.815403214190	
H	-1.663101691758	3.686302213796	-1.467649462557	
C	-1.521966377019	-1.049211800267	0.167349980588	
H	-2.372683559633	-0.403686738086	0.357070209402	
C	-0.127752706545	3.843986444922	0.025303265794	
C	-1.018908310190	1.758251221811	-0.810949891434	
H	-1.698125754314	1.235116709801	-1.473506169805	
N	-0.049535499793	8.136387634563	0.025081616232	
C	3.275436387556	-1.657249018157	-0.463343788443	
C	1.894271844601	-3.621089004246	-0.114222750146	
C	0.662804058181	-2.832145844921	1.859202540071	
H	1.594541191087	-2.458683082000	2.285656721547	
H	0.523745577742	-3.865009791474	2.178487606576	
H	-0.162394444815	-2.231427567893	2.241578502314	
C	-1.741586356338	-2.424440746866	0.087700351433	
C	0.685709569066	1.726790771616	0.865720464153	
H	1.337529133478	1.181023772949	1.536520710300	
C	-0.500311221637	-3.201988111952	-1.882681107577	
H	-1.429570271604	-3.575994262877	-2.313431461786	
H	0.326862603616	-3.803003847271	-2.260306017054	
H	-0.358423318168	-2.168748610962	-2.200660981538	
C	3.136807980945	-3.040619128266	-0.372622663314	
H	3.990062683160	-3.682636873345	-0.560608144778	
C	-2.990325388238	-3.016629338797	0.301875335862	
H	-3.848851859486	-2.381063097600	0.487426795729	
C	-3.136120853420	-4.403746017327	0.330883579852	
C	1.672858960032	-5.003513417996	-0.147516532450	
H	2.524288510504	-5.660987181616	-0.286924175607	
C	0.398570191093	-5.552737126050	-0.007222797456	
H	0.286987757624	-6.628331012006	0.078026335887	
C	-2.037158236751	-5.256167801492	0.221316634546	
H	-2.171177420650	-6.325179665609	0.342893269446	
C	-0.224443850002	6.057049937877	-1.153427620359	
H	-0.321326430338	5.556678622405	-2.108717323242	
C	0.068688955060	7.436725194401	1.150135793809	
H	0.179033020616	8.014698844034	2.062843459727	
C	0.732996147682	-2.743405857539	0.305311315621	
C	0.050141791964	6.052307313767	1.204034472214	
H	0.128792575024	5.549103926616	2.159500129911	
C	-0.750345845483	-4.754341791981	0.008332999911	
C	-0.576666075294	-3.289058647876	-0.329137235705	
C	-0.193008275322	7.441271858227	-1.099822717769	
H	-0.282469319417	8.022681268447	-2.012636197837	
H	4.246284237253	-1.237661270011	-0.698325479440	
H	-4.118610023110	-4.827829112811	0.500003839097	

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_2(Z)$ $Z_{c,model}$ (CPD*).

C	-0.215957	1.023236	-0.054135
C	0.718385	3.079409	0.822757
H	1.431702	3.571467	1.473152
C	-0.304525	-0.450764	-0.064647
C	0.893600	-1.279260	-0.101850
C	2.124256	-0.818681	-0.505340
H	2.236249	0.223716	-0.776254
C	-0.089341	5.326540	0.070989
C	-1.025924	3.179403	-0.809344
H	-1.708560	3.749087	-1.428538
C	-1.543176	-1.045976	-0.023857
H	-2.418532	-0.414264	0.084855
C	-0.133483	3.847939	0.027792
C	-1.067960	1.796806	-0.847586
H	-1.763584	1.302168	-1.514642
N	-0.007346	8.137530	0.154302
C	3.241544	-1.666213	-0.609013
C	1.898112	-3.589889	-0.034151
C	0.541544	-2.756344	1.865526
H	1.419070	-2.331369	2.354578
H	0.415976	-3.784019	2.204817
H	-0.338148	-2.180161	2.153263
C	-1.746558	-2.451538	-0.026264
C	0.683753	1.697934	0.777805
H	1.353829	1.127116	1.408530
C	-0.378958	-3.284425	-1.909149
H	-1.255690	-3.709070	-2.399587
H	0.500704	-3.863675	-2.191339
H	-0.248933	-2.257020	-2.249278
C	3.110924	-3.032382	-0.405691
H	3.958556	-3.687495	-0.578348
C	-2.979409	-3.028300	0.264895
H	-3.836443	-2.380874	0.417950
C	-3.120516	-4.399828	0.397775
C	1.690363	-5.003994	0.031625
H	2.562566	-5.648843	0.001027
C	0.445994	-5.555421	0.099641
H	0.334342	-6.629658	0.198981
C	-1.993586	-5.242145	0.340027
H	-2.107922	-6.298955	0.557951
C	-0.249913	6.097185	-1.079208
H	-0.388050	5.628001	-2.045168
C	0.145901	7.402165	1.252068
H	0.297364	7.950478	2.177121
C	0.738536	-2.712576	0.322306
C	0.114043	6.017118	1.264499
H	0.223173	5.484324	2.200719
C	-0.743393	-4.751427	0.055980
C	-0.581335	-3.319552	-0.367076
C	-0.201246	7.478619	-0.984758
H	-0.318918	8.088605	-1.875484
H	4.196326	-1.252104	-0.908296
H	-4.093239	-4.824274	0.612976

TD-CAM-B3LYP energy:

$E(S_1-Z)^* = -1173.152551$ a.u.

* The Z state has just crossed the LE state at the CPD* geometry.

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0 $3c^+$,_{model}

C	0.187532128763	3.065171427096	2.630057446225	B3LYP energy:
C	0.367455086935	3.476407085887	3.945308039581	
C	0.446741076798	2.553451989489	5.001080459214	
C	0.267263401310	1.194570469356	4.788263574092	$E(S_0) = -1229.672840$ a.u.
C	0.000165340943	1.713739604604	2.305205012393	
C	0.416036117988	0.228674594133	5.792434616228	
C	0.279773315348	-1.130965418360	5.523367467270	
C	0.147789429006	-1.617255901278	4.216618271308	CAM-B3LYP energy:
C	-0.107830075647	-2.956990389143	3.928346520980	
C	-0.380162382763	-3.361002726355	2.627226685468	
C	-0.420285748013	-2.459215372936	1.549385842345	$E(S_0) = -1228.956615$ a.u.
C	-0.107517539483	-1.118052561363	1.699338059556	
C	-0.172171058022	-0.128085765842	0.6678437676840	
C	-0.071922453177	1.248507672372	1.004059258153	
C	-0.243968875610	0.722182238061	3.429805784693	
C	0.388628116426	-0.643073862772	3.069102010352	
C	-1.802530113518	0.621512734229	3.575072178227	
C	1.950616647899	-0.554705804742	2.922593731330	
H	0.231970755672	3.798533350246	1.831022032920	
H	0.699318446487	2.905012341769	5.996131601953	
H	-0.168353381445	-3.674891005924	4.739198796036	
H	-0.768826614702	-2.835840181483	0.596065846612	
H	0.517802371390	4.528863294095	4.154702123927	
H	-0.633013280719	-4.398716200459	2.441219577887	
H	0.611733961193	0.556351730316	6.808196790304	
H	0.286514614282	-1.841647234384	6.342943978127	
H	0.009638008302	1.976299852240	0.203618715128	
H	-2.082056173791	-0.058024562788	4.380588138361	
H	-2.258790568639	0.273764863624	2.646502845945	
H	2.406251764885	-0.204994186313	3.849402117054	
H	2.234657673847	0.120667975663	2.115272907701	
H	-2.205377072628	1.608812957698	3.804977566911	
H	2.345950884749	-1.547491120009	2.701680597396	
C	-0.279502969394	-0.464995514969	-0.741861432450	
C	0.341596034151	-1.597231019147	-1.327482791782	
C	-0.976452969943	0.377643818336	-1.648376927819	
C	0.252344170355	-1.839936437748	-2.673714047411	
H	0.940240147616	-2.266921330096	-0.727624098971	
C	-1.043932805284	0.088390136642	-2.984787880705	
H	-1.500951384797	1.251915958886	-1.288852257283	
N	-0.437955368625	-1.013299217543	-3.502898889851	
H	0.738003826639	-2.686875091131	-3.138857549290	
H	-1.580293702643	0.711534599476	-3.687079102047	
C	-0.570741267384	-1.324875745247	-4.956060195652	
H	-1.608712726437	-1.607385364400	-5.143136662545	
H	0.050361402170	-2.201675601742	-5.141812392879	
C	-0.159504306823	-0.175507997652	-5.847625941541	
C	-1.079537792816	0.423540337388	-6.705709903620	
C	1.153575298520	0.300697933152	-5.856032642178	
C	-0.650605397652	1.468209384822	-7.526781950426	
H	-2.109176045202	0.085506213695	-6.751231084660	
C	1.477587723318	1.350449430644	-6.710580997325	
H	1.917287952638	-0.132130887821	-5.218896354558	
N	0.598813592247	1.931915541445	-7.533002181514	
H	-1.346241144059	1.950164653058	-8.207048442336	
H	2.490577429335	1.740036543224	-6.740046993672	

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0 3_0^+ ,model.

C	-0.328918210539	3.026180969714	2.425020953419
C	0.278855068448	3.536314718827	3.563347001010
C	0.520602766451	2.678041522178	4.635901517195
C	-0.009362393758	1.378087618680	4.666694586296
C	-0.835794615072	1.707396333256	2.417813639792
C	0.560687791465	0.398115178796	5.631347586615
C	1.029970823136	-0.826166607835	5.305968436934
C	0.783812842143	-1.504525259168	4.003109349628
C	0.145969734176	-2.752610833945	4.024940574603
C	-0.496989314873	-3.245259342988	2.893448276180
C	-0.639417133738	-2.410591255918	1.789196835476
C	0.028614265360	-1.177801188233	1.733203328185
C	-0.431204079043	-0.159788925287	0.725795871578
C	-0.915884472805	1.076799671147	1.104879726068
C	-0.900485255228	0.990483022649	3.644797475780
C	0.917167294296	-0.822928948142	2.771725369271
C	-1.957998726351	-0.053281834616	3.864697032662
C	1.983321260899	0.228747753937	2.581114538894
H	-0.351432723223	3.609729650763	1.510915897085
H	1.147630738788	3.008183269198	5.457232489673
H	0.103447426052	-3.308472666531	4.955487633306
H	-1.308598340644	-2.696392745367	0.984344915739
H	0.649341020771	4.553659421480	3.580262135689
H	-0.974592386758	-4.217358265695	2.912848192718
H	0.741125483473	0.753065612979	6.642209862725
H	1.490060610575	-1.414121553173	6.095396123454
H	-1.158382580569	1.767314036162	0.300938257268
H	-2.224944106504	-0.592399813338	2.957400827999
H	-1.701653195297	-0.762095516122	4.647350077296
H	1.637054883773	1.128312912198	2.074816109698
H	2.437569597370	0.515644254859	3.527026618297
H	-2.859255954833	0.479340000761	4.192712614667
H	2.777252158232	-0.205124683296	1.962345484356
C	-0.370118117935	-0.492029101968	-0.688686233103
C	0.526161465186	-1.482677052676	-1.160969698940
C	-1.174798039257	0.123933955413	-1.682999875624
C	0.617141955873	-1.779562022324	-2.496348178730
H	1.162595056430	-2.013130585340	-0.466348631517
C	-1.046661188724	-0.208669058758	-3.004820570664
H	-1.931093780975	0.849423007008	-1.418487138785
N	-0.156292113040	-1.149646464688	-3.417865662746
H	1.305415335667	-2.522466381111	-2.875671571811
H	-1.645500258558	0.251683683609	-3.778551906809
C	-0.082758537032	-1.524272904216	-4.861860747213
H	-1.004429024431	-2.051144196258	-5.116656763104
H	0.741586202887	-2.231833252211	-4.954702288593
C	0.123801476392	-0.333855015591	-5.769787776858
C	-0.838601542739	0.015297420939	-6.715167711971
C	1.290110138849	0.431996233519	-5.705048189891
C	-0.596584990844	1.110746631673	-7.546435547192
H	-1.756464020089	-0.553034125897	-6.820210542759
C	1.431728491260	1.507288521758	-6.577448099237
H	2.080554417948	0.201973358113	-4.998747734451
N	0.510465887398	1.850018657800	-7.483205876653
H	-1.327998918623	1.402233668677	-8.294082348048
H	2.328386948184	2.118940354598	-6.551982234861

B3LYP energy:

$E(S_0) = -1229.640038$ a.u.

Table S2 (continued). UB3LYP/6-311G(d,p) Cartesian coordinates and energies for S_0 transition state between 3_c^+ ,_{model} and 3_o^+ ,_{model}.

C	0.423925384456	2.661513967979	4.834530205084	UB3LYP energies:
C	0.140087947674	1.315106449604	4.724049014147	
C	-0.574773706902	0.830093065178	3.540861616270	$E(S_0) = -1229.607144$ a.u.
C	-0.590042864231	1.717696962409	2.375809169545	$\langle S^2 \rangle = 0.924463$
C	-0.312413736686	3.085606630024	2.561244875825	
C	0.129989784041	3.561745059257	3.785016681487	
C	-0.712037486417	1.194179012325	1.056765003757	$E(T_1) = -1229.603931$ a.u.
C	-0.413199604027	-0.110768496191	0.678016996146	$\langle S^2 \rangle = 2.035871$
C	-0.060194635467	-1.113417950289	1.725431921799	
C	-0.575590951621	-2.399208492110	1.695518458993	
C	-0.398408618384	-3.288095929129	-2.769418967949	
C	0.161859415123	-2.826351241495	3.964701373807	
C	0.634253551311	-1.525268582248	4.077452625751	
C	0.670163678247	-0.659071579056	2.901344812385	
H	0.907347115556	3.032076485117	5.732205607302	
C	0.632328204674	0.345863766774	5.702248114568	
H	-0.397301633875	3.761260083207	1.716516766568	
H	0.333611818731	4.617663960116	3.913406488398	
H	-0.871883113277	1.928951415062	0.274267362980	
H	-1.147656453387	-2.727462767411	0.834371023756	
H	-0.769655123374	-4.302756171603	2.698462783925	
H	0.178838796564	-3.473009094384	4.835680450870	
C	0.908780338542	-0.945059259565	5.392907255685	
C	-1.882650603242	0.091004630368	3.813854519410	
C	1.976688740638	0.093754094062	2.653440498445	
H	1.265432517463	-1.608601984467	6.174336340296	
H	0.851158269007	0.708114253858	6.701368724678	
H	-2.621378210854	0.824042989117	4.152734080277	
H	-1.773380795699	-0.659048569425	4.595427045846	
H	-2.273724367414	-0.383546601232	2.914002958386	
H	1.868560052842	0.863437506375	1.889980986319	
H	2.721881239305	-0.626287223260	2.301165443772	
H	2.363902288076	0.551601372799	3.561839515601	
C	-0.406580956623	-0.464837419381	-0.718927417246	
C	0.369490674002	-1.546676216967	-1.221076237238	
C	-1.153394743235	0.247273628368	-1.702550889146	
C	0.401288997342	-1.839764686328	-2.556956388718	
H	0.972124489337	-2.142961432057	-0.550996431284	
C	-1.091813417697	-0.088359646721	-3.024694288059	
H	-1.816306961064	1.052583327305	-1.419066637212	
N	-0.318028690946	-1.122565166236	-3.464761775952	
H	1.001620614813	-2.646707783080	-2.954337452565	
H	-1.652580318946	0.440586981729	-3.782877752611	
C	-0.314519975466	-1.486840316909	-4.907146143180	
H	-1.305378886087	-1.868830321410	-5.162620784107	
H	0.394170978169	-2.308357818335	-5.018669668708	
C	0.058960425672	-0.331047053521	-5.808587912966	
C	-0.826888464508	0.127062031716	-6.781574945324	
C	1.305361117465	0.291667825761	-5.710876463158	
C	-0.432286017297	1.181730290416	-7.606891855253	
H	-1.803764740015	-0.326340175213	-6.910507275229	
C	1.599473383651	1.338035302390	-6.580092617881	
H	2.040842125095	-0.025727858191	-4.979602630243	
N	0.752842096012	1.784242814723	-7.513367749106	
H	-1.102785899775	1.555491728262	-8.374865951042	
H	2.561408422709	1.838968511912	-6.528353103798	

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_1(\text{CT-Z}) \mathbf{3}_c^+$,_{model} (CPD*).

C	0.086765715523	3.055693671001	2.641776725057	TD-CAM-B3LYP energy:
C	0.366584536399	3.455685521621	3.955871601697	
C	0.525774025331	2.539731393134	4.987218350075	
C	0.362940253532	1.171875020545	4.763851258068	$E(S_1) = -1228.890115$ a.u.
C	-0.124839787313	1.721605099861	2.341214483551	
C	0.616186080689	0.193298468003	5.737718811417	
C	0.502167192527	-1.155658431410	5.448414909166	
C	0.266035346959	-1.625582357615	4.144230926961	
C	-0.059282016241	-2.947432757022	3.875183552376	
C	-0.467359891379	-3.328286816369	2.605658861134	
C	-0.575141149993	-2.401422146326	1.557237861595	
C	-0.202303101089	-1.083900205717	1.703263546689	
C	-0.318900612650	-0.086925721412	0.660446419875	
C	-0.273445893981	1.259852936367	1.022110762266	
C	-0.230958089459	0.716581351634	3.453202716459	
C	0.404546257899	-0.633333510174	3.014134447282	
C	-1.761685319893	0.534754452700	3.719471094590	
C	1.935445641032	-0.465220191707	2.762310025012	
H	0.079405926006	3.793299655140	1.848135735237	
H	0.820758249348	2.883875156826	5.971268637050	
H	-0.064696650357	-3.669502689486	4.683483415090	
H	-1.002340790696	-2.738757543702	0.621985562417	
H	0.517071046688	4.508596191539	4.160898051126	
H	-0.771345984985	-4.352843927078	2.430083871827	
H	0.879435421850	0.508788656172	6.740302908353	
H	0.581457592205	-1.881827463356	6.249937324071	
H	-0.275953299611	2.010606074105	0.240100140232	
H	-1.926404057157	-0.197762177940	4.509150820370	
H	-2.269299998811	0.200738860061	2.815013220584	
H	2.444882619047	-0.150046213061	3.671750841793	
H	2.115121698622	0.274603261296	1.981312177923	
H	-2.194023779204	1.485896496345	4.029050167449	
H	2.359904225037	-1.417989328071	2.444689649632	
C	-0.408176815392	-0.423366178213	-0.742929536072	
C	0.226948289747	-1.556778512693	-1.313619832567	
C	-1.106768417906	0.404061138437	-1.664092494926	
C	0.165973081850	-1.802949377387	-2.650218385812	
H	0.812317320126	-2.226260893826	-0.700620805697	
C	-1.151894308294	0.108471251175	-2.989029023013	
H	-1.654600071003	1.269877598969	-1.320368853175	
N	-0.522839438990	-0.988844175638	-3.497539638044	
H	0.668257879057	-2.646015827908	-3.103363587699	
H	-1.688743487855	0.719086312823	-3.701496151245	
C	-0.635312285809	-1.296390479523	-4.932754523489	
H	-1.681205102846	-1.510434870598	-5.162112900835	
H	-0.070716307341	-2.212464893031	-5.107586792101	
C	-0.120577718178	-0.184930797760	-5.814852939642	
C	-0.897498551222	0.313054764040	-6.849490229749	
C	1.150394912790	0.349552281256	-5.636039441771	
C	-0.373338638088	1.315960892838	-7.657196063473	
H	-1.894482634817	-0.068198913531	-7.037249736838	
C	1.578213317839	1.349937765538	-6.494154103638	
H	1.804476462625	0.000110128768	-4.845696369599	
N	0.837052580907	1.831896338403	-7.488578154387	
H	-0.960189852891	1.722050309858	-8.474713678378	
H	2.566021879817	1.784327582098	-6.379644084271	

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_2(\text{CT-LE}) \mathbf{3c}^+$,_{model}.

C	0.174132433228	3.084548913372	2.638838753619	TD-CAM-B3LYP energy:
C	0.393575311007	3.477615915818	3.926947035420	
C	0.498954970641	2.521601919666	4.977248602421	
C	0.287271845774	1.187135616379	4.754219299425	$E(S_2) = -1228.877172$ a.u.
C	-0.018602534580	1.711828924682	2.302132556812	
C	0.458426532871	0.202196583655	5.753442914246	
C	0.323134553790	-1.145800165606	5.477078947084	
C	0.167938757697	-1.614744168437	4.162059115308	
C	-0.123195031165	-2.947520879449	3.871890166704	
C	-0.418334550140	-3.357873704960	2.576822873546	
C	-0.458015844397	-2.434387706994	1.525563722764	
C	-0.106386258775	-1.097158951977	1.690387500917	
C	-0.186330783526	-0.115844655916	0.666492647555	
C	-0.086281105027	1.266747810375	1.008084672070	
C	-0.243981426948	0.720135323825	3.414244394117	
C	0.417398408705	-0.632321636494	3.038613956525	
C	-1.784601283052	0.571823508570	3.568707093619	
C	1.961905380565	-0.488107478618	2.903196432263	
H	0.173213667111	3.818929127993	1.840804249159	
H	0.785664056861	2.858015892696	5.967609650804	
H	-0.174593262667	-3.660980436585	4.686856180895	
H	-0.831002287664	-2.775977141353	0.568587875901	
H	0.545857812240	4.524926901776	4.153517619158	
H	-0.691966346807	-4.387774931850	2.389491034831	
H	0.682362125369	0.523373037042	6.764843265667	
H	0.341232245853	-1.863304374639	6.289403318135	
H	-0.002140966343	1.993597905597	0.208153761601	
H	-2.035728391773	-0.135712022250	4.358376833930	
H	-2.233624107526	0.227433008690	2.636930560525	
H	2.412869763052	-0.136742881443	3.830461143051	
H	2.218570354271	0.210716625465	2.107151454919	
H	-2.219270204676	1.538852997447	3.823100592244	
H	2.393910691238	-1.459820685027	2.661306005781	
C	-0.303094578904	-0.446422950414	-0.740562217394	
C	0.336420311032	-1.565996085934	-1.325549086899	
C	-1.031547397356	0.377450544611	-1.633603251627	
C	0.230619266206	-1.816121271577	-2.661815974996	
H	0.959305341578	-2.216153147506	-0.728995458568	
C	-1.112316077141	0.081929390149	-2.959947881401	
H	-1.567000395748	1.242216245504	-1.267473463840	
N	-0.490777951637	-1.010268937542	-3.481305940204	
H	0.724607003435	-2.655413517274	-3.131316180027	
H	-1.668281659799	0.690590302505	-3.659318310595	
C	-0.633677077485	-1.314887738827	-4.919231710590	
H	-1.680541361276	-1.552984211587	-5.116350753155	
H	-0.050658099803	-2.215299155667	-5.111968609468	
C	-0.172293563612	-0.183908902447	-5.804615944588	
C	-1.020443537320	0.360168434416	-6.756803814077	
C	1.117751235315	0.325999479061	-5.708378930194	
C	-0.545248335266	1.384992644864	-7.567835257181	
H	-2.034078684937	-0.003005299234	-6.880404379114	
C	1.492585086255	1.351235357077	-6.561893716776	
H	1.827582023535	-0.062050659962	-4.986974757204	
N	0.682493865115	1.878267440705	-7.476624739430	
H	-1.187217017562	1.827161832324	-8.322781255197	
H	2.493260580168	1.767834245308	-6.511681048489	

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0 $1_{C,model-Zn}$.

N	-2.196041721321	2.337581125971	-0.559925630188
N	-2.423984969117	-0.129488112713	-2.091616623160
N	-2.532895458624	0.830205017102	1.910796227267
N	-2.685520398724	-1.645145331306	0.383143013325
C	-2.153736820539	2.146577804772	-3.026969245861
C	-2.146772814470	2.871619441566	-1.819955703612
C	-2.281637421295	0.748280480983	-3.135804477864
C	-2.202117393777	3.384998129376	0.322187160574
C	-2.541160630895	-1.384969763563	-2.630724425082
C	-2.278078524237	3.285564013713	1.724662180193
C	-2.731155752896	-2.579934479883	-1.908359778062
C	-2.122276301483	4.316744222341	-1.730834561373
C	-2.277122521617	0.013928229727	-4.382310348960
C	-2.038219121296	2.929813535076	-4.299991726827
C	-2.430063577542	2.087346442643	2.449040085703
C	-2.826595882939	-2.676262619066	-0.506891916834
C	-2.156324940882	4.633155460890	-0.410664009530
C	-2.436942703374	-1.299958212468	-4.071185656217
C	-2.863813987824	-1.439091424429	2.842988320628
C	-2.695570911306	-0.045222093917	2.953955372648
C	-2.887060691669	-2.162341746183	1.635044046231
C	-2.215863712413	4.562033724738	2.508320983608
C	-2.868563017227	-3.847000473748	-2.696059124498
C	-2.499078024614	1.998567183765	3.891377639999
C	-3.131355942265	-3.895778749030	0.212091483064
C	-2.662649607123	0.685119596354	4.202408617881
C	-3.168564347265	-3.579037052151	1.532132241336
C	-3.056830675516	-2.213764732674	4.111801274525
C	-0.824878788180	3.52633870907	-4.664949261983
C	-3.140411780353	3.085394670685	-5.149947099465
C	-3.356351581804	5.073022275146	3.140529610471
C	-1.015066558949	5.273651372099	2.621876755304
C	-1.848415451973	-4.806398512859	-2.691546426771
C	-4.020893442053	-4.102493452152	-3.450001183570
C	-0.714881322652	4.254835371687	-5.847380732407
C	-3.032604668701	3.816115207874	-6.331148791353
C	-2.049134550054	-3.058008788555	4.5945282856659
C	-4.249001188528	-2.113699436859	4.839980032945
C	-1.818917659864	4.402355561525	-6.684362370722
C	-3.297874320857	6.260869943726	3.866042040852
C	-0.954482433337	6.460197096096	3.349433258842
C	-1.974240946389	-5.985834754362	-3.422317509863
C	-4.149333269545	-5.28269962594	-4.178950592803
C	-2.096207872425	6.957879582145	3.973909797471
C	-3.125691290377	-6.227950763725	-4.168459899446
C	-2.226126352393	-3.779308402805	5.773278836655
C	-4.428451923508	-2.836601525358	6.017263727376
C	-3.416924004965	-3.671056625971	6.488460314174
H	-2.104689370531	4.994602397178	-2.568981752079
H	-2.162846665501	0.446892052458	-5.363029200350
H	-2.171903243339	5.617379426550	0.029060687660
H	-2.477008570902	-2.135119198789	-4.751774804998
H	-2.427938206622	2.830396492343	4.573501177848
H	-3.314683031376	-4.857972980130	-0.238334628966
H	-2.749108871358	0.249252928811	5.184680838684
H	-3.387633660162	-4.234637512258	2.359467445345
H	0.036535342118	3.411525289880	-4.016626639464
H	-4.087665872651	2.635731503117	-4.874657028935
H	-4.294169595577	4.536275655066	3.053084345798
H	-0.124648285890	4.887573886956	2.138539115534
H	-0.950550624930	-4.619783134096	-2.1134149770981
H	-4.821790106466	-3.371893876954	-3.454913987089
H	0.234513247814	4.705629626787	-6.115040661593
H	-3.898879283662	3.930123379935	-6.973558058881
H	-1.12055550754	-3.142645833066	4.041320627126
H	-5.040263810427	-1.470195502754	4.472469479648
H	-1.734530186554	4.970540810449	-7.603967978747
H	-4.193094241807	6.643343480043	4.343961663988
H	-0.014247153528	6.994806041412	3.429427258505
H	-1.171439864429	-6.714954835588	-3.409591350931
H	-5.051724711959	-5.464789746634	-4.752219722861
H	-2.050272287595	7.882093563471	4.539018205878
H	-3.225114372013	-7.146340193785	-4.736171253727
H	-1.432248348483	-4.424511208858	6.133380583630
H	-5.360899416132	-2.750125007355	6.564203827351
H	-3.556062027976	-4.233287443012	7.405067098352
Zn	-2.195070351026	0.319153190614	-0.075202796837
C	7.062425903969	1.771523573780	1.686598605631
C	8.453503233667	1.731640370527	1.816007135229
C	9.211083351940	0.658981998829	1.334613539854
C	8.605897672453	-0.456983454169	0.763860444212
C	6.356056248376	0.704639628005	1.135342125774
C	9.307807697109	-1.523800324148	0.193861202932
C	8.649744283575	-2.59335556925	-0.404797730431
C	7.267067870943	-2.599240311121	-0.618443136444
C	6.567375504317	-3.683474016480	-1.140170441045
C	5.175531520620	-3.667100241626	-1.226360879413
C	4.409283704454	-2.590760042243	-0.761571472405
C	4.996158120106	-1.435751624764	-0.253923602595
C	4.288347509795	-0.334776507650	0.284958958713
C	4.981395245653	0.723123762893	0.899684963546
C	7.090483280457	-0.605046270454	0.886183287513
C	6.518162501188	-1.290358298538	-0.373241708188
C	6.858735200342	-1.465889758242	2.177968929315
C	6.747801918488	-0.435259871186	-1.668665303086
H	6.524190368180	2.668146763859	1.978414692033
H	10.294969930559	0.716060273661	1.362855663227
H	7.112207568879	-4.577828922741	-1.426618025701
H	3.331042862941	-2.691480701792	-0.754507283065
H	8.965903642138	2.586814404756	2.242653454166
H	4.661781333557	-4.543985734410	-1.604684565939
H	10.392142990402	-1.524178230152	0.248892242836
H	9.224613045504	-3.458848513335	-0.735868675077
H	4.420570556018	1.601902401347	1.202640386276
H	7.359176287314	-2.431816113215	2.101275934614
H	5.794607722229	-1.632230372796	2.351773288962
H	7.811224842318	-0.269184809365	-1.845138046588
H	6.246547979129	0.530774669540	-1.596864733091
H	7.268927343145	-0.931895505651	3.036619161918
H	6.338001482532	-0.974737794204	-2.524374962027
C	2.809193229581	-0.226294068888	0.194104491299
C	2.116507565776	-0.373084796921	-1.015478599305
C	2.039730786906	0.085010430680	1.322979774649
C	0.738323174736	-0.214011696305	-1.043932784661
H	2.648991735686	-0.587528360478	-1.933254814727
C	0.663784623511	0.223632809272	1.204875673990
H	2.508838291511	0.203860070116	2.291957615407
N	0.011125719632	0.077561773974	0.043895194010
H	0.183882281205	-0.315453557566	-1.969551072231
H	0.049642500035	0.457925007893	2.066499745721

B3LYP energy:

$E(S_0) = -4635.239887$ a.u.

CAM-B3LYP energy:

$E(S_0) = -4633.680231$ a.u.

Table S2 (continued). B3LYP/6-311G(d,p) Cartesian coordinates and energy for S_0 $1_{o,model-Zn}$.

N	-2.353983449048	1.764632615062	-1.362120533084
N	-2.212510509311	-1.076473025922	-1.992270339278
N	-2.789276375881	1.116404135267	1.444118822788
N	-2.571764464938	-1.722377482312	0.825251268488
C	-2.054090124761	0.785827342744	-3.615282770338
C	-2.228613408363	1.860416503169	-2.722372288618
C	-2.048168488036	-0.576502482313	-3.258635529310
C	-2.541078944783	3.034046477429	-0.883788507003
C	-2.170121655629	-2.443896890338	-2.087924810857
C	-2.745116172932	3.389001689914	0.463464471367
C	-2.320649831076	-3.350872935458	-1.021180345093
C	-2.342072388498	3.247972311857	-3.12077250621
C	-1.863538568534	-1.671236472542	-4.186324722294
C	-1.885062814071	1.119469719761	-5.067105612493
C	-2.856186903078	2.483144482467	1.536169435003
C	-2.536158849095	-2.996392247150	0.324360365158
C	-2.535005894895	3.971265673128	-1.987723626006
C	-1.939037715300	-2.821442445103	-3.465344534416
C	-2.995625612518	-0.747550256064	3.060114090840
C	-2.968220287217	0.615855597421	2.708337245561
C	-2.839472598329	-1.822713987591	2.164432649415
C	-2.877601332420	4.848919149346	0.777149566995
C	-2.270925415312	-4.813356714324	-1.347296179523
C	-3.054512792229	2.861492958953	2.918427721594
C	-2.792845101856	-3.941501023058	1.391056178829
C	-3.123322966216	1.711383451174	3.640376848185
C	-2.979505850101	-3.218191513745	2.525180933256
C	-3.234498614805	-1.083387138124	4.501539614478
C	-0.697062558254	1.694863165872	-5.534720481828
C	-2.911152945562	0.867060637644	-5.986243040706
C	-4.116740197692	5.397962160001	1.130181159192
C	-1.764467425051	5.696829659032	0.720099787579
C	-1.170056357637	-5.593143561565	-0.971677168034
C	-3.324793120651	-5.432419715321	-2.031028539983
C	-0.537415503000	2.006298818431	-6.88237997782
C	-2.753911420671	1.180564710070	-7.334511662632
C	-2.201619561474	-1.594140945522	5.297442534195
C	-4.495200594437	-0.898230279007	5.082749559467
C	-1.565845072942	1.750309508113	-7.787672768136
C	-4.239409028525	6.755400664698	1.418427887304
C	-1.885108600595	7.053979515627	1.010840434350
C	-1.121979384186	-6.952424531017	-1.273368793307
C	-3.279352415525	-6.792148360533	-2.330852010200
C	-3.123532604647	7.587835608375	1.360826215474
C	-2.177073169996	-7.556532427382	-1.953812075951
C	-2.421076523990	-1.907979453717	6.636946046253
C	-4.716835328026	-1.214263099332	6.421329878519
C	-3.679991249219	-1.719245183078	7.203273337105
H	-2.302247577127	3.612597629405	-4.134569911476
H	-1.695143918669	-1.571137672241	-5.246479902082
H	-2.682110647775	5.036058067961	-1.904808196530
H	-1.843533174022	-3.831708654984	-3.829461475270
H	-3.12722811706	3.872330135785	3.286173033746
H	-2.845094953607	-5.012428879902	1.278332926835
H	-3.262465972450	1.612161013300	4.704858248939
H	-3.212651190586	-3.588915954608	3.510335218797
H	0.105832302352	1.892931023904	-4.833541418163
H	-3.838963811067	4.029520902584	-5.635519682848
H	-4.988001791168	4.754069341405	1.169611217423
H	-0.799141190483	5.283781685038	0.449729113525
H	-0.346426945359	-5.125229823147	-0.444205590603
H	-4.186401409902	-4.841447270155	-2.320250808007
H	0.391795953703	2.447403527398	-7.227068033220
H	-3.562013841362	0.982578615063	-8.030136987173
H	-1.220376294366	-1.740057127916	4.859966274907
H	-5.305488797163	-0.511531573787	4.475165478682
H	-1.442928517706	1.993788960692	-8.837077735071
H	-5.208583179252	7.162871861980	1.684473288230
H	-1.010554606100	7.693773255247	0.965306884708
H	-0.258670845491	-7.538762380503	-0.978177966884
H	-4.107702264453	-7.254638097297	-2.856261242021
H	-3.218601692255	8.644254916617	1.585698050216
H	-2.141072842275	-8.614666701596	-2.187671463881
H	-1.60736155093	-2.298415119089	7.23293100339
H	-5.701542497521	-1.069078288119	6.85189966304
H	-3.852053741752	-1.964716227909	8.245276837442
Zn	-2.217148710624	0.028746231363	-0.232278791859
C	6.648785296280	2.903468135128	0.753197087400
C	7.975868577047	3.132957695022	0.404342643054
C	8.868951583258	2.065075227219	0.433523723670
C	8.491201215174	0.830383602090	0.983649761790
C	6.249885011938	1.672733384553	1.302855026809
C	9.264078465248	-0.377405484050	0.587388120167
C	8.731069742911	-1.495563693982	0.045680952790
C	7.281672093709	-1.843331795235	0.037174911723
C	6.901745312990	-3.050934973677	0.637930223318
C	5.583836826286	-3.271013795990	1.029977495684
C	4.685035094368	-2.211372551662	0.979175573400
C	5.040549914063	-0.999595667705	0.363905063514
C	4.238132881967	0.227049665239	0.697047557583
C	4.805640797875	1.346605601494	1.229965648262
C	7.245929965957	0.728103580301	1.643515174183
C	6.277691875256	-0.907172918719	-0.308194421652
C	7.012825678758	-0.312332446857	2.707834739746
C	6.509157679153	0.134999465281	-1.374617750628
H	5.897112084570	3.659794665512	0.552339838577
H	9.850695423065	2.164237201788	-0.018053170452
H	7.661096023108	-3.797285151921	0.847999289560
H	3.713676894987	-2.302629048830	1.452088734568
H	8.282542114438	4.096650001208	0.015046126020
H	5.291271569967	-4.218671084945	1.466837792201
H	10.348058734712	-0.291200251432	0.587637179150
H	9.422892352005	-2.272109447162	-0.272023967607
H	4.136517495903	2.180148168109	1.427816457813
H	6.005530351116	-0.722664977259	2.706674488820
H	7.730092887960	-1.128114177230	2.650431588309
H	5.723615547504	0.888744773512	-1.380095315392
H	7.472892606758	0.634251353562	-1.303215246997
H	7.158185610720	0.180787364297	3.676797574454
H	6.481162431531	-0.373715472749	-2.345319152687
C	2.766838012844	0.172972344640	0.517631504694
C	2.201811864253	-0.525184029275	-0.559535674633
C	1.869659037722	0.811516608143	1.386811799696
C	0.825809231315	-0.530991582293	-0.733822903293
H	2.832764289861	-1.054950417785	-1.261971663350
C	0.506505861094	0.750410571533	1.139024494504
H	2.225014370527	1.331612487912	2.267387089495
N	-0.021289250497	0.094700343391	0.095687687058
H	0.371399261865	-1.054072671914	-1.567032190976
H	-0.202557774475	1.232555439214	1.801732165649

B3LYP energy:

$E(S_0) = -4635.207965$ a.u.

Table S2 (continued). UB3LYP/6-311G(d,p) Cartesian coordinates and energies for S_0 transition state between $\mathbf{1}_{c,model-Zn}$ and $\mathbf{1}_{o,model-Zn}$.

N	-2.72279501120	1.455558137914	-0.988704998278
N	-2.031089758253	-1.099694293729	-2.205062565130
N	-2.903112538716	0.162272440847	1.615565218005
N	-2.136850688089	-2.377262355881	0.410992006031
C	-2.324470765786	1.049804847294	-3.397275900116
C	-2.677070815308	1.855368466699	-2.297559946756
C	-2.025070463239	-0.324981044126	-3.336640130553
C	-3.143275857050	2.530982012559	-0.252756835917
C	-1.711839415744	-2.377469016532	-2.587191248685
C	-3.358586053985	2.548368554833	1.138678139157
C	-1.630109351441	-3.497095762209	-1.736899375056
C	-3.087149270052	3.240902628026	-2.393396183070
C	-1.656826307439	-1.139944808163	-4.473932558819
C	-2.287699991303	1.705066109580	-4.745119967572
C	-3.240497829918	1.436263654929	1.994798824529
C	-1.860862822160	-3.483118614891	-0.347941473597
C	-3.374577625307	3.657284598163	-1.133189251373
C	-1.464036081770	-2.404176239526	-4.012344758923
C	-2.662902277181	-1.998586980127	2.799338221898
C	-2.926582368425	-0.616217698500	2.744363585874
C	-2.326499748304	-2.807584919824	1.697059153921
C	-3.769302873397	3.852089566174	1.754158828812
C	-1.293184054579	-4.816350229206	-2.364309661781
C	-3.455468841505	1.469751051560	3.425123732950
C	-1.877741785157	-4.661895291982	0.493059287977
C	-3.262198043962	0.205566655911	3.886777632221
C	-2.164709284305	-4.245546596307	1.753449881060
C	-2.771457550818	-2.668774135466	4.135942198093
C	-1.265673198143	2.603694576954	-5.075490823114
C	-3.275145767710	1.436768481897	-5.701382995842
C	-5.076923297471	4.048129746502	2.216006697636
C	-2.853896573307	4.904819379868	1.877039019824
C	-0.042046372616	-5.409375320669	-2.154413548064
C	-2.222088556889	-5.486402520595	-3.170287715720
C	-1.229354948899	3.214504737003	-6.327102187583
C	-3.241640416728	2.049058409250	-6.952294928724
C	-1.625942685121	-3.110749508468	4.809491224587
C	-4.019349742398	-2.871053007273	4.738707163468
C	-2.217777711869	2.939249164676	-7.269694181481
C	-5.458190784155	5.261293658918	2.784893223282
C	-3.233037581105	6.117618211181	2.448241948719
C	0.273418982245	-6.635523273367	-2.735781917788
C	-1.909051960310	-6.713889951183	-3.750037530575
C	-4.536990898376	6.299883110948	2.903975424678
C	-0.659620924524	-7.292100646812	-3.535474440563
C	-1.724035289051	-3.734064268662	6.051586725594
C	-4.119158065300	-3.496731326236	5.979425653667
C	-2.971484460949	-3.929355884169	6.640608127538
H	-3.165396503653	3.808041975942	-3.30623276481
H	-1.555905037796	-0.789218151910	-5.488384401318
H	-3.731347900988	4.627452655132	-0.826960227775
H	-1.177070970830	-3.273816284453	-4.581293633636
H	-3.715518736556	2.344929346590	3.998484757402
H	-1.714448942003	-5.672856490065	0.155974760642
H	-3.335769848279	-0.139256701065	4.905597490943
H	-2.279260991410	-4.853464795333	2.636419830871
H	-0.493944699284	2.818025347332	-4.344725028408
H	-4.076475844961	0.749441397300	-5.454965740082
H	-5.797705344961	3.244230731172	2.118714127882
H	-1.838005243537	4.765115073755	1.524932299585
H	0.686700959473	-4.899439289085	-1.534389951977
H	-3.197285143257	-5.042014968056	-3.333892216034
H	-0.427213646174	3.904260917265	-6.565913776189
H	-0.418398682612	1.832744910675	-7.677543166748
H	-0.653685051493	-2.958142083427	4.354579477324
H	-4.914542800727	-2.541219613803	4.223827376713
H	-2.191063815546	3.415432060879	-8.243442388974
H	-6.476944395128	5.395672322257	3.131597481189
H	-2.508519767398	6.919616200367	2.538459890800
H	1.249333859095	-7.076727960115	-2.565305490347
H	-2.643726484842	-7.219978235420	-4.366676296335
H	-4.833075002877	7.244014777888	3.347201528280
H	-0.415488414889	-8.247139247982	-3.987068243512
H	-0.824958269714	-4.065538570001	6.559641371495
H	5.094927181317	-3.649260658992	6.427461412435
H	-3.048799614847	-4.415758435796	7.606566287145
Zn	-2.187146790777	0.409512130662	-0.250558277454
C	8.372822668563	3.632682408430	1.398738209184
C	8.203173048771	2.265489469477	1.239255667745
C	6.916133606432	1.661846098685	1.583744404578
C	5.774901035125	2.567048338958	1.688869001165
C	6.007041935863	3.93300620126	1.845579448738
C	7.300149166575	4.461114387934	1.773295139703
C	4.433756008870	2.067768179192	1.468374974252
C	4.112158228109	0.946681660436	0.741863495849
C	5.168453522417	0.074175952938	0.177315955626
C	5.028915529168	-1.307891551521	0.146012337784
C	6.106523268933	-2.146014246588	-0.178634805542
C	7.389834891298	-1.603529034600	-0.324478471761
C	7.599176913387	-0.231957616627	-0.267480082951
C	6.451346888854	0.667917171085	-0.180961679983
H	9.342412321758	4.073965769100	1.188911896130
C	9.223858476460	1.437609900808	0.604420517723
H	5.160781399985	4.60097106358	1.980065969394
H	7.460815909005	5.523019392541	1.915035757660
H	3.621685028441	2.712643293915	1.790549496771
H	4.074053891711	-1.752053946143	0.403572432811
H	5.960009256535	-3.218060772908	-0.230252610440
H	8.244535295192	-2.264571598279	-0.431527289756
C	8.945103870599	0.316470738901	-0.113133603061
C	6.954103960049	0.508119476552	2.581311137841
C	6.419516535124	1.826210437201	-1.174995237437
H	9.769266629860	-0.252313650111	-0.533974491402
H	10.252507757103	1.782301317624	0.657060425301
H	7.183159900795	0.919127470108	3.570370703141
H	7.726075490566	-0.219678353858	2.334410996433
H	5.994113815374	-0.003455058286	2.646624812679
H	5.642551732909	2.550216873121	-0.932490021122
H	6.200883053778	1.418851467189	-2.167835198856
H	7.376594619829	2.343027637212	-1.230429184598
C	2.688540199783	0.611127353918	0.530243689252
C	2.227207244613	0.089300802919	-0.688987930496
C	1.718519829878	0.821701092869	1.523262870128
C	0.876321988103	-0.169884726954	-0.862747046045
H	2.915893142406	-0.099423206578	-1.502390475379
C	0.387836099111	0.531038086870	1.263796757476
H	2.001506385940	1.186334282438	2.502696035671
N	-0.041986215455	0.042826728585	0.091416583380
H	0.500501504426	-0.561700074835	-1.800641792835
H	-0.373266274563	0.681803710624	2.020400143373

UB3LYP energies:

$$E(S_0) = -4635.170076 \text{ a.u.}$$

$$\langle S^2 \rangle = 1.019107$$

$$E(T_1) = -4635.164298 \text{ a.u.}$$

$$\langle S^2 \rangle = 2.040284$$

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_1(\text{LE})$ $1_{\text{c,model}}\text{-Zn}$.

N	-2.179434131898	2.320272338092	-0.558201436505
N	-2.403021791553	-0.135144083221	-2.077013417494
N	-2.512133309435	0.825700554593	1.899613548815
N	-2.675003602578	-1.636537201139	0.384048357326
C	-2.122999703374	2.126298762277	-3.011549499756
C	-2.117746609584	2.848314670597	-1.811915388639
C	-2.256829954850	0.736146781732	-3.116198587579
C	-2.177923940637	3.363107844584	0.317559192638
C	-2.525030442478	-1.384052442659	-2.611377459526
C	-2.255704186369	3.268055217464	1.712345560814
C	-2.716593584181	-2.570991364320	-1.892895326642
C	-2.077872425820	4.290058500777	-1.726633470717
C	-2.256248519380	0.003291194956	-4.359558798738
C	-1.999135761039	2.904542584602	-4.282474649574
C	-2.410648795652	2.076973339819	2.432758103703
C	-2.811392447954	-2.664145085038	-0.499060456922
C	-2.115202874057	4.607357576922	-0.414246000575
C	-2.421656720299	-1.302484043653	-4.048673562124
C	-2.840963384660	-1.430192697818	2.831527988411
C	-2.674408268940	-0.043689495361	2.937979115768
C	-2.866955900686	-2.149866125625	1.630727908783
C	-2.191042302018	4.542013358139	2.492709135167
C	-2.855253600637	-3.836532205747	-2.677357563086
C	-2.482200488931	1.991962446805	3.871765072193
C	-3.105432428335	-3.882273198485	0.220176058016
C	-2.644507922054	0.685844479630	4.182934017647
C	-3.1392606635243	-3.565366699956	1.532782890338
C	-3.029462878358	-2.201213380032	4.098874438903
C	-0.782660882610	3.477240829513	-4.648901312761
C	-3.097203185033	3.075850575490	-5.123461992329
C	-3.329270879568	5.059455196765	3.108453352206
C	-0.990769211736	5.239221512429	2.616642721769
C	-1.835802276864	-4.786693911170	-2.680083970269
C	-4.007654729817	-4.093279318650	-3.418016949034
C	-0.665158112986	4.200567399819	-5.827244435732
C	-2.982243411882	3.800672600352	-6.301048841298
C	-2.017284170357	-3.026348971215	4.585434307415
C	-4.221050597139	-2.113381293548	4.816373903182
C	-1.765221297573	4.364569583263	-6.656958768064
C	-3.269205486368	6.242947488462	3.830244565740
C	-0.928179175471	6.421839694902	3.339784636754
C	-1.962736506149	-5.962147952046	-3.406471685768
C	-4.137422778901	-5.268980794152	-4.143350924776
C	-2.067854481514	6.927381879596	3.948900665030
C	-3.114586756140	-6.206827992261	-4.140507045151
C	-2.189832134005	-3.743629229782	5.760683933179
C	-4.396303892251	-2.831526226169	5.990609758346
C	-3.380508433593	-3.648321998478	6.466851985648
H	-2.046764204263	4.964123893704	-2.566997561646
H	-2.140689559131	0.436765847693	-5.339508278773
H	-2.120694922709	5.591122365073	0.025882481134
H	-2.466947216077	-2.139301163050	-4.726330635255
H	-2.413219529307	2.826219332148	4.550581803992
H	-3.282414336240	-4.845433452486	-0.229866742942
H	-2.733292167013	0.249510317969	5.164401067474
H	-3.348978663181	-4.219289675253	2.363410978107
H	0.077200172743	3.348922315441	-4.002029789894
H	-0.4049076346114	2.640084633917	-4.844001156313
H	-4.268837550535	4.528429807120	3.012276761089
H	-0.100179129522	4.844693114878	2.141812658804
H	-0.935728239291	-4.596137789747	-2.107531613627
H	-4.809012887389	-3.364008883675	-3.416845144366
H	0.289508387380	4.636008738784	-6.098175029858
H	-3.847725887517	3.927696244443	-6.940679683285
H	-1.086735480632	-3.100677355489	4.035149034504
H	-5.016620634634	-1.479748248442	4.442715370122
H	-1.674825905228	4.930302686794	-7.576579265846
H	-4.165256836860	6.632924701734	4.298563183160
H	0.014493306409	6.949044122571	3.428437940561
H	-1.158434399876	-6.688441440202	-3.399689024703
H	-5.042541586203	-5.453880517798	-4.709812898816
H	-2.020381715466	7.851395292217	4.512696582639
H	-3.215305395035	-7.124907727995	-4.706985505294
H	-1.390582284556	-4.377699338885	6.126136615126
H	-5.331233042247	-2.754759054144	6.533136148865
H	-3.516730136502	-4.208978919791	7.383931667631
Zn	-2.185398520064	0.314671964739	-0.073889635579
C	6.999351166682	1.758870197142	1.734906092450
C	8.389291553794	1.735954037644	1.849223886361
C	9.146190390689	0.675702056319	1.349691154945
C	8.535978245649	-0.441173948086	0.772353676560
C	6.302569827368	0.681315131929	1.179238306360
C	9.245866140135	-1.482167008427	0.163942419459
C	8.595663261460	-2.542137031583	-0.467169593238
C	7.211022715058	-2.547617155513	-0.675257871600
C	6.522358619243	-3.646557843029	-1.190799790617
C	5.131426701408	-3.654225795048	-1.249204919982
C	4.366533352077	-2.589137929261	-0.767981777303
C	4.957562293996	-1.422408851000	-0.276755463658
C	4.241679366945	-0.337300994485	0.285400579406
C	4.929493989992	0.702717494990	0.936429681848
C	7.036316563567	-0.605773100602	0.893115043821
C	6.462952945166	-1.261202720894	-0.394174280141
C	6.793753478766	-1.530730467365	2.123316424754
C	6.704957687174	-0.340602051081	-1.627981122750
H	6.447882222894	2.639609909367	2.043754829915
H	10.228694713585	0.731220592075	1.370426703155
H	7.080934251356	-4.524546993693	-1.494781202708
H	3.291045609151	-2.696606519497	-0.735745906499
H	8.897141138862	2.58774507158	2.285154182190
H	4.622489794266	-4.534109809942	-1.623837987030
H	10.329693537429	-1.465638482026	0.200360838447
H	9.173718193087	-3.393278342684	-0.810619643356
H	4.368979104724	1.580307698280	1.239777649076
H	7.291927461190	-2.490349084794	1.985523784267
H	5.727067635532	-1.705540564220	2.266035870551
H	7.771058676413	-0.166562593059	-1.772484446971
H	6.206779887362	0.619756097060	-1.494996923883
H	7.192320365107	-1.055200047339	3.019836526962
H	6.306763746747	-0.820498224028	-2.522633190698
C	2.770375797935	-0.232655250774	0.197621437648
C	2.076078361423	-0.425468145565	-0.998648348233
C	2.009495809161	0.125408388635	1.311731208552
C	0.704815638452	-0.261998225854	-1.028813872126
H	2.604407986805	-0.678268421784	-1.098070938628
C	0.639320658355	0.262251457467	1.193342559802
H	2.481795235549	0.279795346825	2.273225722968
N	-0.012873002185	0.073150916848	0.045625663404
H	0.145845971943	-0.395926140140	-1.947327934584
H	0.027627624303	0.530603508264	2.046524055307

TD-CAM-B3LYP energy:

$$E(S_1) = -4633.605217 \text{ a.u.}$$

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_2(Q)$ $1_{c,model-Zn}$.

N	-2.181743787396	2.343485358953	-0.557790845163
N	-2.421112865013	-0.126165985500	-2.069537589977
N	-2.550019478024	0.828692315991	1.895808232037
N	-2.672178401792	-1.653726472619	0.390912455801
C	-2.126173502366	2.139266140104	-3.014875148929
C	-2.151887242290	2.877090435156	-1.813115530711
C	-2.231640340976	0.743116774626	-3.11187063934
C	-2.214352484246	3.389347439374	0.317653307355
C	-2.485030339726	-1.384786222764	-2.606103828161
C	-2.268108726050	3.278752370223	1.722707349812
C	-2.694086322542	-2.577179488492	-1.896031742326
C	-2.177412144706	4.313843772911	-1.729238461330
C	-2.137059445116	0.000662751783	-4.344345803581
C	-1.993504992450	2.910901331858	-4.282490308710
C	-2.403837712210	2.078429747388	2.437107900163
C	-2.827808526609	-2.679044121773	-0.49558985294
C	-2.215767140912	4.630770865734	-0.411045908842
C	-2.292472461368	-1.307937818958	-4.033638917522
C	-2.859403969424	-1.435017032215	2.840378047562
C	-2.673288784180	-0.047662985789	2.941414694232
C	-2.903496776844	-2.165242264836	1.634456679777
C	-2.194395970935	4.544175522086	2.505767736264
C	-2.805638728802	-3.838349150152	-2.681395184363
C	-2.398819955424	1.980237977023	3.876235330717
C	-3.180852857077	-3.881646857687	0.212379635136
C	-2.564927575251	0.672827743730	4.186448052472
C	-3.227809820878	-3.563718678741	1.530086235810
C	-3.043676487743	-2.200993776279	4.104966774881
C	-0.827286499962	3.623397646004	-4.563006447276
C	-3.032372304587	2.942654340399	-5.212870051181
C	-3.283234835407	4.984841102487	3.258187778652
C	-1.034476748554	5.319365564146	2.497427877440
C	-1.851432773751	-4.847255165441	-2.547034213585
C	-3.868117132915	-4.041444407413	-3.562232926203
C	-0.699973297714	3.409089512109	-5.743082851584
C	-2.908396779198	3.665098506703	-6.390666618345
C	-2.098893797286	-3.144439693035	4.509595769814
C	-4.165562962698	-1.996403589689	4.908340488388
C	-1.740976938990	4.364939384693	-6.660738549965
C	-3.213896584968	6.165791870681	3.982789135062
C	-0.962048382990	6.497117191077	3.226292752184
C	-1.951720167053	-6.021841834379	-3.277672140032
C	-3.972631633441	-5.218395060792	-4.289094477166
C	-2.052351040734	6.924890030029	3.971024136875
C	-3.013634407997	-6.211768839422	-4.150951660313
C	-2.266688021602	-3.857553622390	5.687270216000
C	-4.337369255552	-2.713596454008	6.08327637481
C	-3.387489740820	-3.64507726493	6.477854435190
H	-2.191204085801	4.989148368455	-2.568511999302
H	-1.961102712357	0.426933255259	-5.318123777422
H	-2.267108328178	5.613395189292	0.027625792153
H	-2.267074633775	-2.148812006729	-4.706798492670
H	-2.271676468767	2.804676031990	4.558153767732
H	-3.391835918329	-4.835593835963	-0.241579933570
H	-2.598513055800	0.231158080163	5.168644456272
H	-3.483808393487	-4.209491062955	2.353521913536
H	-0.012959568080	3.605031080365	-3.848507719690
H	-3.947035994698	2.402164406678	-5.000961895360
H	-4.193283465778	4.397129040629	3.263410822454
H	-0.181939059807	4.986588196933	1.917427531913
H	-1.021381582627	-4.700645870610	-1.866246885359
H	-4.621585543216	-3.270082129679	-3.666541595063
H	0.216691707622	4.881753874304	-5.946999476891
H	-3.729168552491	3.683876052583	-7.097967196029
H	-1.222581827897	-3.311019161602	3.894531158269
H	-4.911484147416	-1.274318810144	4.598775722724
H	-1.643274141721	4.927711503519	-7.581397459516
H	-4.072731428859	6.4955388551768	4.55467924854
H	-0.049822619980	7.082004456897	3.213451059775
H	-1.196655248487	-6.791045506099	-3.165295507460
H	-4.809285057847	-5.360772311729	-4.962907795603
H	-1.997476305882	7.846391568832	4.538207576590
H	-3.094243140092	-7.130360772896	-4.719768901565
H	-1.518019753867	-4.508590302333	5.98067457204
H	-5.219155331895	-2.546129498650	6.690535992095
H	-3.520615410427	-4.203976753102	7.296429725016
Zn	-2.190724897042	0.319269723677	-0.069575074849
C	7.000542273228	1.755460195801	1.646311529836
C	8.409330829622	1.711832456931	1.778145370673
C	9.148033509972	0.656961045822	1.307547409717
C	8.529185209779	-0.463769528224	0.718298963924
C	6.304008626802	0.702302719538	1.122829535386
C	9.214714627839	-1.500429569808	0.135881675685
C	8.537975657967	-2.589789807025	-0.456610931849
C	7.178917254480	-2.576840793541	-0.651384364503
C	6.458612006346	-3.663217178996	-1.186572793939
C	5.091386054018	-3.647280356723	-1.231695367857
C	4.331723825496	-2.564211714873	-0.721210981206
C	4.925759468709	-1.433057946867	-0.237996210710
C	4.221249836745	-0.316135400067	0.316734060287
C	4.906230177672	0.715476641986	0.917135993628
C	7.022731437912	-0.604270847759	0.861108688783
C	6.434415519597	-1.277571950977	-0.387403563033
C	6.804682202812	-1.464493136311	2.143130489220
C	6.637479201476	-0.416823160245	-1.670306563488
H	6.470543973664	2.658440603049	1.930353711333
H	10.231564846178	0.696427150166	1.342566672714
H	7.003391485671	-4.543507336387	-1.510692830301
H	3.254839596715	-2.667744952456	-0.684070259996
H	8.918092439976	2.566976520551	2.207206965109
H	4.561574072952	-4.511895016507	-1.613760306615
H	10.299300357828	-1.496224702778	0.158279257744
H	9.106810946785	-3.454113267655	-0.782592261862
H	4.353841626128	1.588159810752	1.249683894638
H	7.291452127152	-2.434781477800	2.049030035377
H	5.743472174262	-1.619464166249	2.338361864842
H	7.696471591689	-0.241767914190	-1.858322478048
H	6.130295162061	0.544362081549	-1.587596178330
H	7.238567094557	-0.941426908512	2.995848982895
H	6.221394206575	-0.954138917709	-2.523402256433
C	2.744009046374	-0.211042221280	0.220427937385
C	2.06752379763	-0.334751163909	-0.992694962858
C	1.97278536396	0.068218219311	1.346748261365
C	0.695202844914	-0.178237668474	-1.028702805708
H	2.608377462756	-0.533947783164	-1.908162113303
C	6.02295001901	0.206664575046	1.222748506190
H	2.436406663909	0.164904335291	2.319874928169
N	-0.034556194603	0.086316934334	0.057458313499
H	0.147004086245	-0.261527062828	-1.959382521085
H	-0.018889354771	0.420136513380	2.084061563824

TD-CAM-B3LYP energy:

$E(S_1-Q)^* = -4633.603322$ a.u.

* The Q state has crossed the LE state at its optimized geometry (see Fig. 8a).

Table S2 (continued). TD-CAM-B3LYP/6-311G(d,p) Cartesian coordinates and energy for $S_4(Z)$ $1_{c,model}Zn$ (CPD*).

N	-2.175062072205	2.324324357642	-0.547589511115
N	-2.377449615870	-0.129930906163	-2.071453480104
N	-2.533891514786	0.826825334475	1.904447673881
N	-2.674662175230	-1.634270167780	0.384588714837
C	-2.088672912641	2.132757748819	-3.000293620211
C	-2.098527317331	2.853583545744	-1.799994721228
C	-2.220085889639	0.742637584804	-3.107953614336
C	-2.185679038714	3.366415092190	0.329066519368
C	-2.492773849765	-1.378322659295	-2.608646127400
C	-2.280249045217	3.269948751347	1.722696412161
C	-2.690605888642	-2.566301422501	-1.893779358336
C	-2.061289321056	4.295266282309	-1.712927789727
C	-2.205363607645	0.011239896905	-4.352068356071
C	-1.950491614860	2.912464853963	-4.268869130810
C	-2.441374618869	2.077808092352	2.440032690542
C	-2.799857338214	-2.661194377978	-0.501038797677
C	-2.115391422666	4.611358061523	-0.400835789847
C	-2.373543800700	-1.294980570708	-4.044595667444
C	-2.867349156150	-1.430906886548	2.830392120111
C	-2.705411015956	-0.04411185834	2.940078318870
C	-2.878703642933	-2.149381424101	1.628666272813
C	-2.227330500316	4.543205135663	2.505070383961
C	-2.819528919686	-3.831030925443	-2.681164944564
C	-2.528760889731	1.991037392529	3.878030153475
C	-3.098826966510	-3.880680088006	0.213748677083
C	-2.691193956605	0.684162292842	4.186001093506
C	-3.146947896446	-3.565315339617	1.526303834419
C	-3.067768631817	-2.203704920369	4.094835231466
C	-0.729813715095	3.485057424479	-4.621142330924
C	-3.039186549173	3.085253082776	-5.121636408055
C	-3.373791285597	5.057631983181	3.107930245198
C	-1.030005659615	5.242672700381	2.643931219375
C	-1.797638575244	-4.778531876313	-2.677064116794
C	-3.965153532181	-4.089410203619	-3.431671876885
C	-0.959069837078	4.209781475310	-5.797231348442
C	-2.910984712561	3.811482268364	-6.296987952140
C	-2.058724617790	-3.026414688243	4.591874697530
C	-4.267542166226	-2.119969752318	4.799049780124
C	-1.689880009939	4.375287610333	-6.638776544460
C	-3.324633880570	6.240409492229	3.831712896732
C	-0.978346473308	6.424569843055	3.369106150507
C	-1.915604663408	-5.953098811887	-3.406397470487
C	-4.085978165539	-5.264255706071	-4.159932351165
C	-2.126149810499	6.927109089696	3.965305830272
C	-3.060797777069	-6.199494048992	-4.150204264876
C	-2.242321897533	-3.745343046474	5.764438228058
C	-4.453834969428	-2.839773493387	5.970566003123
C	-3.441082180606	-3.654133053289	6.457340997249
H	-2.020422544393	4.970098606855	-2.552257088180
H	-2.079176313107	0.445963251975	-5.330149079301
H	-2.127520039821	5.594723714264	0.040044175974
H	-2.410917072396	-2.131062043821	-4.723646736137
H	-2.469386356076	2.824722613654	4.558451890255
H	-3.269052352716	-4.843691379115	-0.239217524351
H	-2.789732506414	0.246556593471	5.165968481874
H	-3.363932545553	-4.220599805416	2.353988971290
H	0.122837868909	3.355535569242	-3.965036346942
H	-3.994247257682	2.649521602144	-4.853207313630
H	-4.311085718411	4.524834324739	3.000091344997
H	-0.133053415526	4.850519032149	2.179212191306
H	-0.902667564716	-4.586573795115	-2.097028441155
H	-4.768292791545	-3.362109817062	-3.435971037639
H	0.358702952322	4.645120760602	-6.057125436938
H	-3.769315461661	3.939647345710	-6.945956424411
H	-1.121857552799	-3.097516206649	4.051982005668
H	-5.060698458671	-1.488233943054	4.417139527310
H	-1.589131889597	4.942103909723	-7.556650486051
H	-4.226928013431	6.628044917317	4.289873750075
H	-0.037849505817	6.953546947622	3.469490478087
H	-1.109461111487	-6.672720458769	-3.394335071570
H	-4.985913879600	-5.450503829498	-4.734153543379
H	-2.087190776654	7.850554390703	4.530678876883
H	-3.154498726844	-7.116870379735	-4.719017411483
H	-1.445389366564	-4.377469103668	6.138210983551
H	5.394971816153	-2.766204457391	6.502697956716
H	-3.585923053185	-4.216070421013	7.272310738999
Zn	-2.185286554604	0.318483869682	-0.065799226316
C	7.043858661513	1.773642534872	1.616605018050
C	8.438208546117	1.788571413832	1.642737920606
C	9.168131821421	0.714839998258	1.123092873454
C	8.539718217534	-0.426910621343	0.667408685157
C	6.335706768611	0.669642657532	1.165542429901
C	9.237207326595	-1.493872432314	0.025648519461
C	8.587142306094	-2.522516634412	-0.597763692597
C	7.161973759337	-2.556110318608	-0.707368997189
C	6.465496695100	-3.68581878358	-1.092448964027
C	5.069461345466	-3.728310314472	-1.057875462492
C	4.334642223197	-2.642706793020	-0.578218354648
C	4.943538876753	-1.452230681275	-0.221046152201
C	4.237266873568	-0.336530131432	0.365069939601
C	4.924262893787	0.671939849355	1.007112197612
C	7.062959428783	-0.606202235424	0.871779245893
C	6.423287445520	-1.278355795667	-0.426062844034
C	6.852192032089	-1.565505576568	2.078972876955
C	6.638646661259	-0.323764110432	-1.636822253794
H	6.493630320029	2.654956289529	1.929317213413
H	10.247335934212	0.790761155218	1.041790079088
H	7.021701225440	-4.569546398198	-1.386513654982
H	3.264906621310	-2.752952013519	-0.453526061951
H	8.958009754492	2.665460152404	2.007640685410
H	4.553752545099	-4.635386948222	-1.347126895073
H	10.322156316148	-1.473701129308	0.037814181968
H	9.153764071532	-3.352021849781	-1.005818516872
H	4.377028608826	1.542466986596	1.351174869459
H	7.361145992692	-2.513631883850	1.906149248891
H	5.789455768474	-1.758668292484	2.229107618002
H	7.700104196867	-0.121946176183	-1.781269180098
H	6.120960340200	0.621146908704	-1.473245406646
H	7.259212746146	-1.108083258566	2.981435769535
H	6.242465216846	-0.788899390853	-2.540327675179
C	2.766445525929	-0.225146465091	0.265613198202
C	2.086889739051	-0.437352135873	-0.935206403844
C	1.995304514258	0.143161220774	1.368518421870
C	0.716107198581	-0.271038053761	-0.982844542420
H	2.625988932207	-0.710329289162	-1.832375457657
C	0.626802854531	0.280952745392	1.232506919532
H	2.458037954162	0.303392776334	2.333474636024
N	-0.011912754230	0.079706086575	0.079235450315
H	0.166404184983	-0.418014616402	-1.904923156227
H	0.005227287025	0.558607098224	2.075459993486

TD-CAM-B3LYP energy:

$E(S_2-Z)^* = -4633.598123$ a.u.

* The Z state has crossed the Q states at its optimized geometry (see Fig. 8b).

Figure ESI6. Computed absorption spectrum of $1_{c,model}$ at the TD-CAM-B3LYP/6-311G(d,p) level.

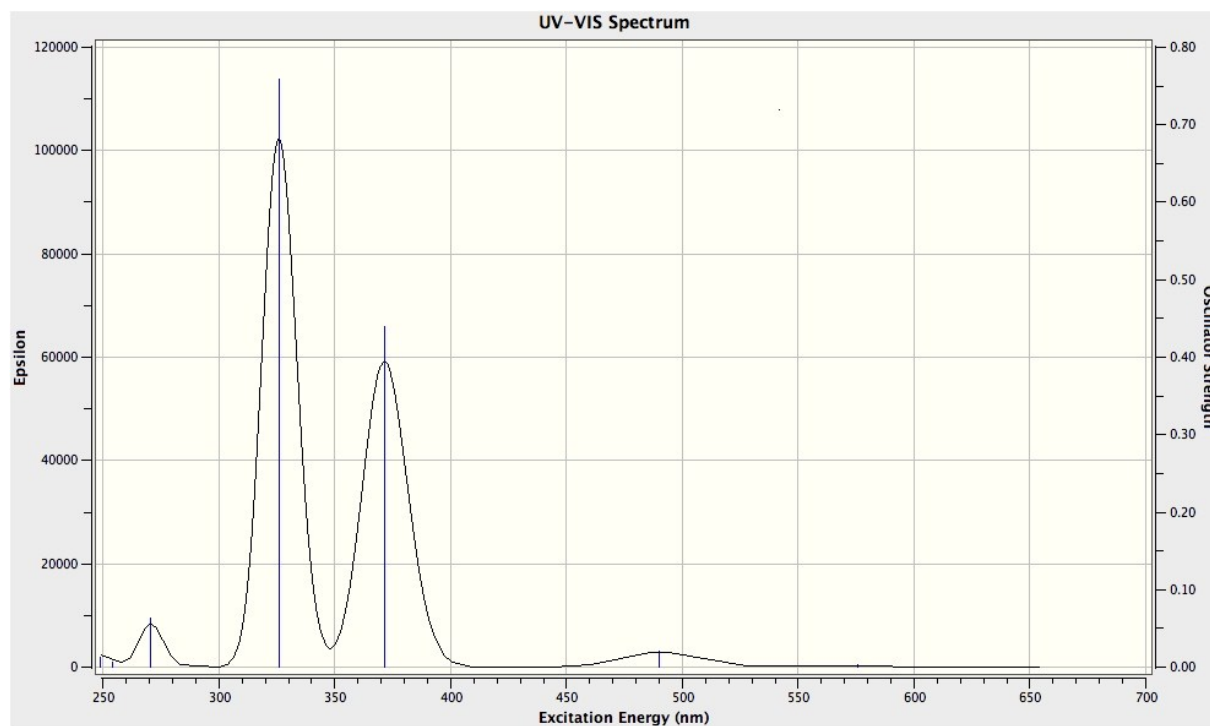


Figure ESI 7. Computed absorption spectrum of $2_{c,model}$ at the TD-CAM-B3LYP/6-311G(d,p) level.

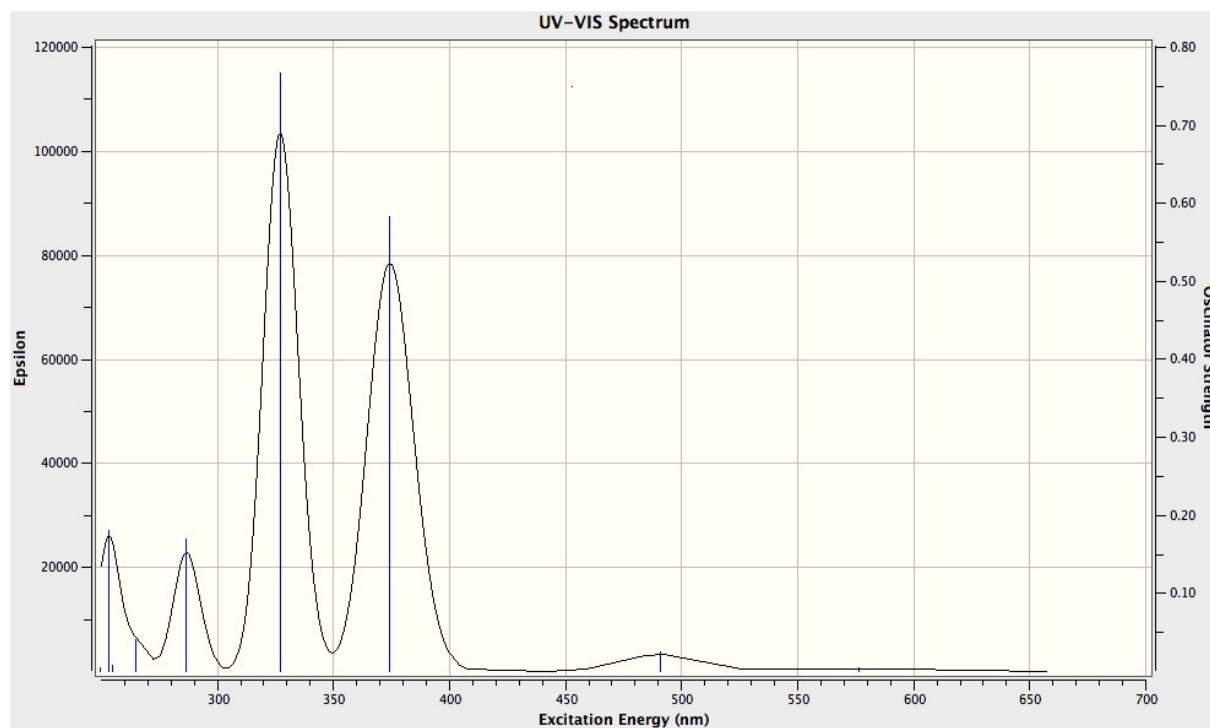


Figure ESI8. Computed absorption spectrum of 3_c^+ ,_{model} at the TD-CAM-B3LYP/6-311G(d,p) level.

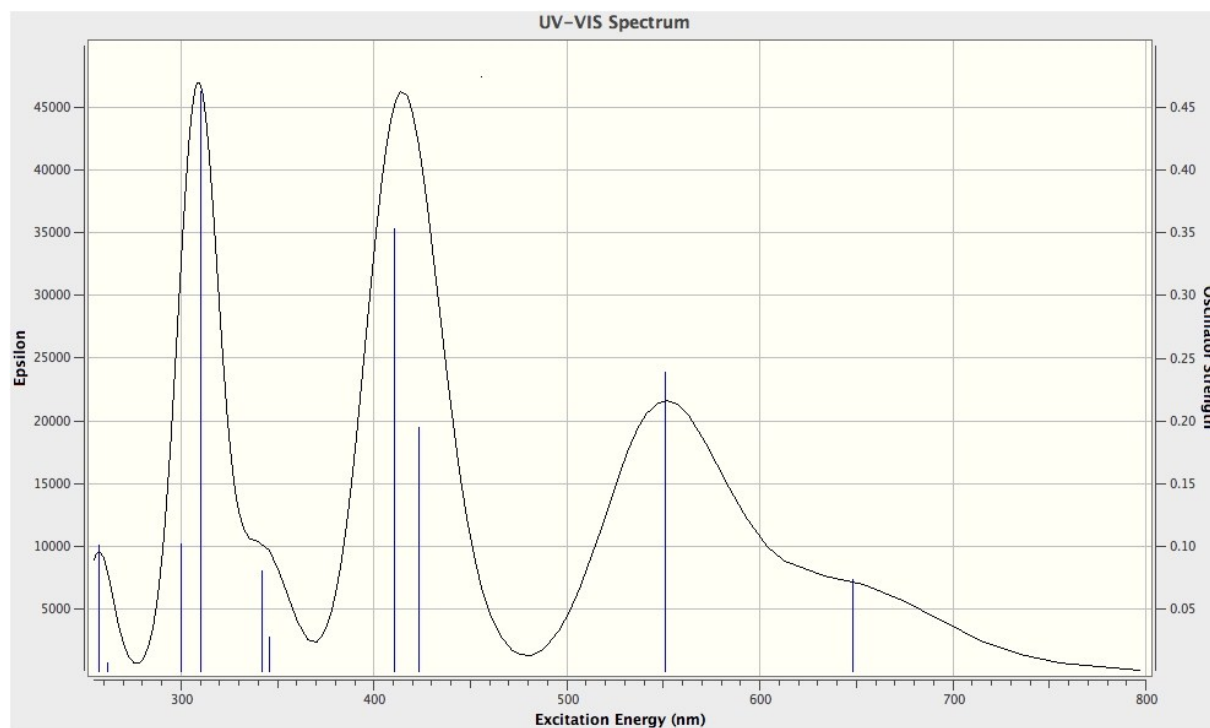
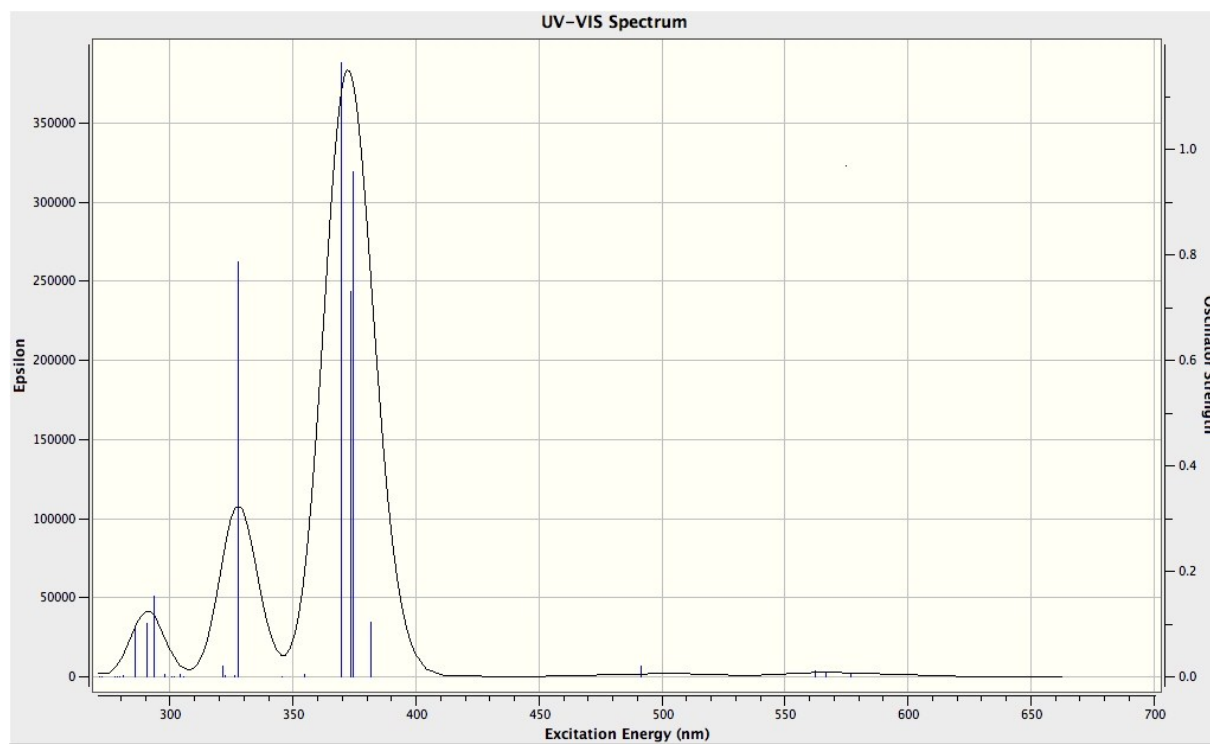


Figure ESI9. Computed absorption spectrum of $\mathbf{1}_{c,model-Zn}$ at the TD-CAM-B3LYP/6-311G(d,p) level.



5. Photo-isomerisation quantum yield

Potassium ferrioxalate actinometer was used as a primary standard to determine the photoisomerisation quantum yield of this secondary standard, $\phi_{c/o} = 1.4 \cdot 10^{-3}$.

The change in absorption upon irradiation at 480 nm (band-pass filter) during specific time periods for 2,7-di-*t*-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene was compared to the change in absorption for the actinometer irradiated at the same wavelength. The monitoring wavelengths were 235, 476, and 643 nm for 2,7-di-*t*-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene. The compounds were dissolved in acetonitrile; the concentration was such that the absorbance at 480 nm was higher than 1.9. The solution of the primary actinometer was 0.15 M in a 0.05 M H₂SO₄ aqueous solution. After each irradiation, 8 μ L of the irradiated solution was placed into a 2 mL volumetric flask. A 100 μ L amount of sodium acetate buffer solution (pH = 3.5) and 16 μ L of 0.01 M 1,10-phenanthroline aqueous solution were then added, and the volume was completed with distilled water. The photoreduction of the actinometer was followed at 510 nm. The absorption spectra for each compound were recorded after each irradiation time without further handling, and the total time was such that the isomerization of the compound was less than 10%. The ring-opening quantum yields ϕ_x were calculated according to classical equations reminded in the experimental part.