Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Nonadiabatic molecular dynamic simulation for ultrafast photoisomerization of dMe-OMe-NAIP based on TDDFT on-the-fly potential energy surfaces

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Table S1 Energies (in eV) for equilibriums, transition states, and conical intersections in ground state S_0 and the first singlet excited S_1 state. E_{diff} is the energy gap between S_0 and S_1 states. All geometries are listed in Table 1. Exp is experiment value for E_{diff} from Ref.25.

Geometry	Energy	E_{diff}	Exp[a]
Z-S_1-L	3.00	2.58	
ZT-CI-L	7.34	0.02	
Z-S_0-L	0.10	3.14	3.1
Rot-CI-L	6.01	0.10	
TS-S_0-L	1.20	0.70	
ET-CI-L	7.06	0.01	
E-S_1-L	3.12	2.81	
E-S_0-L	0.00	3.25	3.18

[a]Ref.25

Table S2 Cartesian coordinates for L-form geometries listed in Table 1 calculated at TD-B3LYP/6-32G* level.

Table S2.1: Z-S_1-L

	X	Y	Z
C	-2.17646700	-1.34657300	-0.07579700
N	-3.47823000	-1.63446500	-0.20715800
C	-4.05311800	-2.96383600	-0.26237500
H	-3.26720600	-3.69789000	-0.45058000
H	-4.79178500	-3.01667400	-1.06969900
H	-4.55503600	-3.21100100	0.68336800
C	-4.32549100	-0.44260000	-0.10258500
C	-3.32663100	0.73616500	-0.10810800
H	-3.41227300	1.30658100	-1.03780100
H	-3.52629500	1.42894800	0.71347900
C	-1.94941900	0.08580800	0.01394700
C	-0.74260300	0.67913500	0.16509000
C	-0.32625400	2.15463900	0.09440800
C	-1.31180100	3.11337400	-0.58569800
H	-0.83644200	4.09323600	-0.70730600
H	-2.21631800	3.26915700	0.00901900
H	-1.60144800	2.76067400	-1.58134300
C	-0.00343400	2.66486600	1.52143100
H	-0.90793400	2.68440000	2.13794400
H	0.40027800	3.68304700	1.47646500
H	0.73448800	2.03247600	2.02732200
C	0.99733500	2.05797100	-0.74113600
H	1.67266400	2.89636700	-0.53818400
H	0.76906100	2.08071900	-1.81767400
C	1.58300100	0.71940400	-0.36912200
C	2.90035600	0.29978400	-0.42143000
H	3.67460700	0.95101800	-0.81140800
C	3.21403500	-0.97995700	0.08978700
O	4.43522700	-1.53039800	0.07750900
C	5.53126800	-0.85100300	-0.54932700
H	6.38141000	-1.52502700	-0.45512300
H	5.74299000	0.09195400	-0.03314600
H	5.31349100	-0.66225800	-1.60586400
C	2.20649300	-1.78719900	0.68500200
H	2.49470800	-2.75955400	1.06995500
C	0.89018500	-1.33256200	0.75486500
H	0.14558100	-1.93274100	1.26787200
C	0.56469200	-0.09841400	0.19046200
H	-4.90756100	-0.49233800	0.82789300
H	-5.03529600	-0.41797100	-0.93689500
H	-1.43877000	-2.13269700	-0.13473200

Table S2.2: ZT-CI-L

	X	Y	Z
C	-2.036628378	-1.464082869	0.483094960
N	-2.762884896	-1.659079078	-0.684173575
C	-2.881247036	-3.025771432	-1.222231505
H	-3.932772337	-3.259907533	-1.243546836
H	-2.405527616	-3.666511546	-0.459707625
H	-2.403596493	-3.054699699	-2.166199581
C	-3.641394209	-0.617192436	-1.086474866
C	-3.425245638	0.610409323	-0.133638802
H	-3.234368561	1.426640257	-0.888152950
H	-4.215445053	0.820673844	0.608423889
C	-1.976672503	0.146044749	0.441469746
C	-0.885038409	0.863329921	0.564858194
C	-0.345285197	2.364121940	0.282247139
C	-1.213146677	3.469384246	-0.454022474
H	-0.910201298	4.538606464	-0.328602661
H	-2.240508696	3.381247239	-0.145026250
H	-1.057544681	3.010371985	-1.493186579
C	-0.068293983	2.934552610	1.586355613
H	-0.918089201	3.104363144	2.317607764
H	0.541264003	3.855233354	1.586468599
H	0.584834598	2.151324326	2.122329727
C	1.045397875	2.213756035	-0.411790294
H	1.629386557	3.171557851	-0.514908704
H	0.926943462	2.297714792	-1.613443730
C	1.443478314	0.847479141	-0.064616952
C	2.675076166	0.162670163	-0.363035332
H	3.502850237	0.701450647	-0.899379422
C	2.938446171	-1.119356978	0.214067837
O	3.877776665	-1.891832574	-0.239776976
C	4.599752085	-1.689875239	-1.426172729
H	4.358635927	-2.676296061	-2.081347781
H	5.698033116	-1.746238643	-1.334822227
H	4.143508842	-0.755153382	-1.845971727
C	2.001985200	-1.623759635	1.236478090
H	2.242615637	-2.508428721	1.783192631
C	0.832890564	-0.959538158	1.434399148
H	0.192795493	-1.300981637	2.305250037
C	0.443383397	0.170403401	0.592430849
H	-4.641127077	-0.876936003	-1.337087977
H	-3.302750582	-0.185767606	-2.060865013
H	-2.289502787	-2.072981063	1.332574500

Table S2.3: Z-S_0-L

	X	Y	Z
C	2.22293500	-1.30585200	-0.23374800
N	3.50721600	-1.59862600	-0.14697300
C	4.12486100	-2.89598000	-0.37719500
H	3.36341300	-3.61856900	-0.67568000
H	4.87685700	-2.81526000	-1.16903700
H	4.61456500	-3.24396400	0.53888900
C	4.29422900	-0.42372800	0.28613000
C	3.29350700	0.74902300	0.15485800
H	3.53191200	1.35071200	-0.72738100
H	3.33771500	1.40892600	1.02426100
C	1.93533000	0.05289500	0.00360500
C	0.66299300	0.60658200	0.01534100
C	0.35231700	2.11360200	-0.01641800
C	1.25410500	2.96051800	-0.93103400
H	0.80043800	3.94876800	-1.06340600
H	2.24856800	3.12442100	-0.50872100
H	1.36379400	2.51042800	-1.92409500
C	0.40703000	2.65944100	1.43492900
H	1.40770300	2.55678700	1.86745300
H	0.15129800	3.72449900	1.43571100
H	-0.30017000	2.13523900	2.08561300
C	-1.12346000	2.14519000	-0.52810500
H	-1.71033700	2.93990800	-0.05475300
H	-1.14107200	2.33797900	-1.60933800
C	-1.65508200	0.77191500	-0.23558400
C	-2.97505700	0.34564600	-0.25296100
H	-3.77148200	1.03849600	-0.49869200
C	-3.25102500	-0.99613600	0.06361300
O	-4.47516700	-1.54043900	0.08543600
C	-5.61522100	-0.73260200	-0.22856000
H	-6.47404800	-1.39777800	-0.14453400
H	-5.71678500	0.09346900	0.48371900
H	-5.54840700	-0.34268200	-1.25011400
C	-2.19890500	-1.87638900	0.42622500
H	-2.46346500	-2.88597600	0.72180800
C	-0.89223400	-1.44169900	0.44127000
H	-0.12273000	-2.11839600	0.79717600
C	-0.59084700	-0.10697400	0.07344500
H	4.63146900	-0.58687400	1.31699700
H	5.17756900	-0.32133800	-0.35019400
H	1.52115800	-2.07761700	-0.52522500

Table S2.4: Rot-CI-L

	X	Y	Z
C	-2.744878666	-0.390474846	0.635945995
N	-3.977594420	-0.912157132	0.023796910
C	-5.283195663	-0.891662279	0.588069164
H	-5.475826403	-0.104342490	1.409098966
H	-5.450354481	-1.795753386	1.257129364
H	-5.978259064	-1.049498945	-0.318815921
C	-3.549270968	-1.576621872	-1.241887408
C	-2.168280248	-0.865209184	-1.652594103
H	-1.385656948	-1.518549586	-2.058304375
H	-2.527257094	-0.092051282	-2.404568148
C	-1.790528009	-0.400894427	-0.284865513
C	-0.551473372	0.325964273	0.014135372
C	-0.521174553	1.792290726	-0.007036874
C	-1.494063564	2.395616406	-1.051847225
H	-2.252584685	1.686103985	-1.361080283
H	-1.076435206	2.685617994	-2.016093378
H	-1.892853112	3.367678013	-0.785600403
C	-0.843727221	2.382069783	1.359819580
H	-0.411651218	3.363561206	1.195554783
H	-0.420847395	1.804431052	2.153349795
H	-1.931951706	2.539027369	1.632321398
C	0.934152863	1.859364678	-0.478330379
H	1.561612507	2.661630373	-0.184359043
H	1.067883428	1.618402914	-1.564647656
C	1.671086004	0.694311210	0.135426756
C	3.036520869	0.524782661	0.108646874
H	3.578129534	1.333656412	-0.477292430
C	3.581323842	-0.752963270	0.345899127
O	4.757114260	-1.275340752	-0.011298465
C	5.663358773	-0.201829937	-0.334180078
H	6.691059831	-0.595273802	-0.101027246
H	5.451217341	0.706105619	0.113940341
H	5.750805833	-0.144557733	-1.450028737
C	2.517553043	-1.691010898	0.807836055
H	3.070854385	-2.471395894	1.253678246
C	1.178575511	-1.450718214	0.969134268
H	0.505134712	-2.251335460	1.040925615
C	0.575780784	-0.238810971	0.419014543
H	-4.298061341	-1.522675227	-2.007551044
H	-3.409896098	-2.628109792	-0.968090989
H	-2.883615452	0.055146707	1.591678125

Table S2.5: TS-S_0-L

	X	Y	Z
C	-2.63311400	-0.65623200	0.79967600
N	-3.72104900	-1.35734700	0.32874800
C	-4.92690500	-1.51797900	1.12621100
H	-4.65476500	-1.74600900	2.16035000
H	-5.51226400	-2.35617900	0.73736300
H	-5.55970700	-0.61599700	1.11602600
C	-3.86547900	-1.03374200	-1.10057600
C	-2.45443600	-0.56764400	-1.52898000
H	-1.87238700	-1.39467000	-1.96098700
H	-2.49371800	0.22811100	-2.27861800
C	-1.85588400	-0.13389000	-0.17918900
C	-0.55935500	0.51993000	-0.05093100
C	-0.38016100	2.02670400	0.05970100
C	-1.09333100	2.75929700	-1.09921800
H	-0.93786000	3.83856800	-1.00073700
H	-2.16987600	2.56756000	-1.07426900
H	-0.70535800	2.44756000	-2.07509100
C	-0.98350100	2.49614500	1.41020700
H	-2.04807200	2.25139600	1.46267100
H	-0.87568300	3.58210700	1.49705000
H	-0.47523500	2.03190100	2.26247800
C	1.16633800	2.22334800	0.02711600
H	1.53301500	2.80468500	0.88117300
H	1.47953500	2.76839300	-0.87269700
C	1.73694600	0.83431900	0.02020800
C	3.05366900	0.42880700	0.05592500
H	3.86104300	1.14994700	0.10515400
C	3.32154800	-0.96088600	0.02331900
O	4.53514300	-1.48663100	0.04965700
C	5.70474100	-0.64688500	0.11551700
H	6.54786200	-1.33562000	0.12373000
H	5.69681200	-0.05303500	1.03415000
H	5.75886000	0.00146000	-0.76387700
C	2.26437200	-1.92783900	-0.04082200
H	2.54703100	-2.97478800	-0.05775700
C	0.96069900	-1.52443200	-0.07307900
H	0.14897600	-2.24387600	-0.11007300
C	0.67314800	-0.12406500	-0.04289000
H	-4.59641800	-0.21743000	-1.22141000
H	-4.22099700	-1.89948200	-1.66632800
H	-2.46036900	-0.60985300	1.87004500

Table S2.6: ET-CI-L

	X	Y	Z
C	-3.304643214	0.112071807	0.629207897
N	-3.687106853	-0.766751675	-0.312411574
C	-4.542664875	-0.612127552	-1.387702686
H	-3.997631747	-0.490550810	-2.280876384
H	-5.091575028	0.294876306	-1.364707911
H	-5.206046420	-1.584186362	-1.168114518
C	-3.181970425	-2.140669077	0.074592480
C	-2.122124102	-1.819714524	1.299947805
H	-2.571751093	-1.835647164	2.370779919
H	-1.107056711	-2.252695867	1.378082934
C	-1.900841754	-0.309868383	0.991016847
C	-0.827231405	0.320785513	0.409560878
C	-0.509134356	1.769691773	0.120108869
C	0.081375629	2.156296236	-1.302696732
H	0.345435756	3.125783171	-0.985429532
H	-0.712656463	2.468982952	-2.092344129
H	0.837155896	1.477888385	-1.923651608
C	-1.539889437	2.822523216	0.563243779
H	-1.423381763	3.033383157	1.678554305
H	-2.506851391	2.776356149	0.025140192
H	-1.173229538	3.828182585	0.237276242
C	0.832086611	1.941371608	0.808078052
H	0.716520245	2.196854012	1.886552397
H	1.449331092	2.746080064	0.374103513
C	1.523040109	0.651727424	0.556189598
C	2.843038151	0.491705804	0.367530523
H	3.466410279	1.379730534	0.559076540
C	3.300854605	-0.732890813	-0.135498160
O	4.529915507	-1.046777459	-0.620462570
C	5.289614291	-0.015197529	-1.338332040
H	6.216037946	-0.565339750	-1.601548656
H	5.725051117	0.564881072	-0.438956895
H	4.796829824	0.556826007	-2.140908795
C	2.401191325	-1.778460921	-0.334782522
H	2.700447891	-2.546991751	-1.018886028
C	0.999541781	-1.473193760	-0.092417702
H	0.369222268	-2.227273663	-0.398269736
C	0.511908336	-0.361718183	0.458717831
H	-2.697995177	-2.701413531	-0.734489859
H	-4.051485972	-2.744949677	0.277109395
H	-3.922780113	0.425921239	1.482390717

Table S2.7: E-S_1-L

	X	Y	Z
C	3.20208300	0.18917900	0.06002400
N	4.09256800	-0.79488600	-0.12919900
C	5.52835600	-0.63309000	-0.24349500
H	5.81277300	0.36947500	0.08154500
H	5.85402500	-0.77866600	-1.28275800
H	6.03882100	-1.37136300	0.38502400
C	3.44002500	-2.08101700	-0.39204100
C	1.97777100	-1.83673600	0.03297200
H	1.26767700	-2.30025000	-0.65701400
H	1.80610200	-2.27148600	1.02575400
C	1.84586600	-0.31247100	0.08710600
C	0.68553400	0.39185600	0.16224500
C	0.44275200	1.90935000	0.11416500
C	0.21670000	2.42805100	1.55799800
H	-0.04702900	3.49204300	1.54019900
H	1.12600100	2.31110900	2.15673600
H	-0.59165400	1.88915300	2.06424900
C	1.51480100	2.76247600	-0.57985600
H	2.39271700	2.92217800	0.05396100
H	1.10511200	3.75549200	-0.79560300
H	1.83739600	2.31840100	-1.52816300
C	-0.90094100	1.98874100	-0.68361500
H	-0.69744600	2.00492900	-1.76684400
H	-1.46318500	2.90058300	-0.45247600
C	-1.63280800	0.72479700	-0.32819900
C	-2.99007600	0.45233300	-0.40892300
H	-3.68134200	1.19926200	-0.78247900
C	-3.43878400	-0.80579300	0.02463500
O	-4.71484500	-1.22810800	0.00632800
C	-5.74051900	-0.36946000	-0.50167200
H	-6.66607700	-0.93705300	-0.41499200
H	-5.54935300	-0.11926400	-1.55154700
H	-5.80595500	0.54795300	0.09490800
C	-2.51927000	-1.74969700	0.56096200
H	-2.90768800	-2.70676700	0.89295200
C	-1.14828000	-1.44465600	0.65684800
H	-0.48083700	-2.17237700	1.10310400
C	-0.69784500	-0.22534500	0.17652400
H	3.93633000	-2.87629800	0.17319800
H	3.52805600	-2.32158000	-1.46165600
H	3.54415400	1.20247300	0.20160300

Table S2.8: E-S_0-L

	X	Y	Z
C	-3.08999300	0.15973200	-0.00010300
N	-4.05062800	-0.74647100	0.00015100
C	-5.48388200	-0.49558000	-0.00078900
H	-5.67009800	0.57971700	-0.00021000
H	-5.94132000	-0.94185500	0.88876600
H	-5.93999200	-0.94069700	-0.89162400
C	-3.50499500	-2.11818500	0.00052300
C	-1.97119800	-1.90730100	0.00038000
H	-1.51588400	-2.36734300	0.88307300
H	-1.51601700	-2.36764700	-0.88222800
C	-1.79247900	-0.38535500	0.00012400
C	-0.60255100	0.33147700	0.00014700
C	-0.50053600	1.87637600	0.00010400
C	-1.12156900	2.49443100	-1.27475200
H	-0.93280600	3.57315900	-1.28866300
H	-2.20431200	2.35255200	-1.33675100
H	-0.67738400	2.06238200	-2.17794600
C	-1.12244600	2.49483800	1.27426800
H	-2.20532300	2.35353600	1.33531300
H	-0.93326200	3.57349900	1.28818700
H	-0.67929000	2.06278700	2.17796300
C	1.03762900	2.15091000	0.00057800
H	1.33898900	2.73615800	0.87809400
H	1.33937600	2.73701200	-0.87623300
C	1.69075500	0.80264700	0.00019800
C	3.05149100	0.53614900	0.00010100
H	3.76821800	1.34924000	0.00018300
C	3.47324800	-0.80435000	-0.00009100
O	4.75087800	-1.20376500	-0.00022100
C	5.79974500	-0.22818600	-0.00017000
H	6.72722700	-0.79984500	-0.00034100
H	5.75108500	0.39708600	0.89791100
H	5.75091700	0.39736600	-0.89804500
C	2.51751900	-1.85309500	-0.00013500
H	2.88607100	-2.87327200	-0.00023200
C	1.16956800	-1.57916100	-0.00004900
H	0.47737100	-2.40958300	-0.00010100
C	0.72109200	-0.23002000	0.00008500
H	-3.87050300	-2.64862500	-0.88519000
H	-3.87035600	-2.64806700	0.88663400
H	-3.36371800	1.20589100	-0.00036300

Table S3 Vertical excitation energies at E-S_0-L and Z-S_0-L calculated by three functionals, (TD-B3LYP, TD-BHandHLYP and TD-Cam-B3LYP)/6-31G* in comparison with experimental values.

Geometries	Vertical excitation energies/eV			Exp[a]
	TD-B3LYP	TD-BHandHLYP	TD-CAM-B3LYP	
E-S_0-L	3.25	3.50	3.39	3.18
Z-S_0-L	3.04	3.31	3.23	3.1

[a]Ref.25

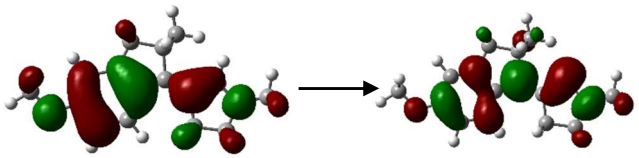
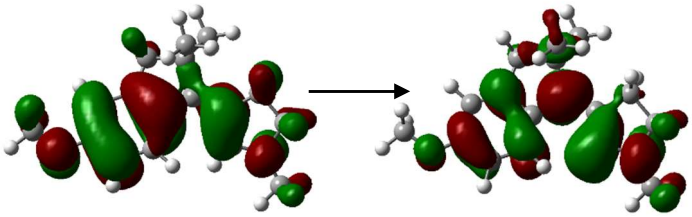
Geometries	Electronic state	Hole state
E-S_0-L		
Z-S_0-L		

Fig. S1 Calculated natural transition orbitals of $S_0 \rightarrow S_1$ vertical excitations by TD-B3LYP/6-31g* at the ground state geometries

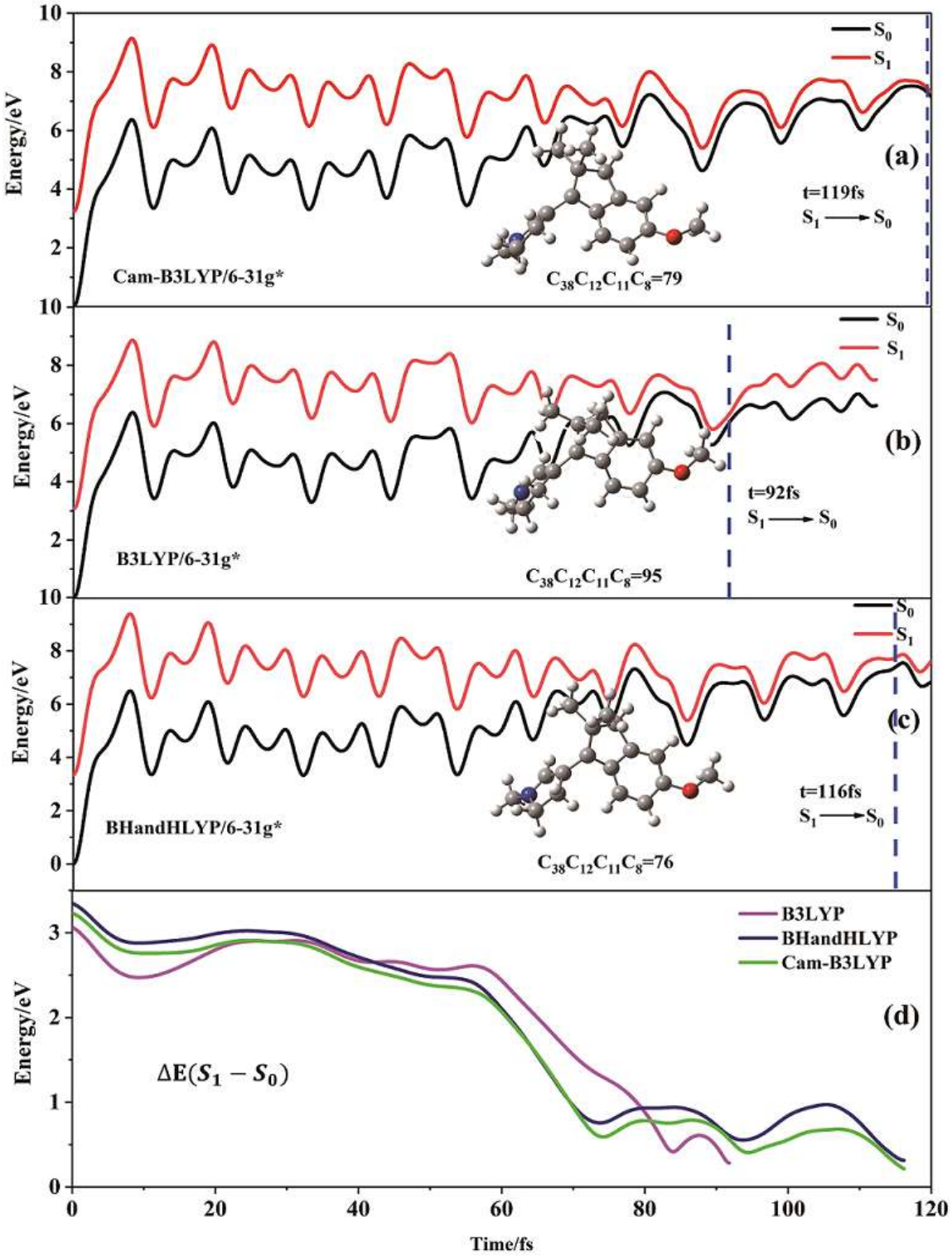


Fig. S2 One trajectory evolution with the same initial condition starting from Z-isomer and calculated by three functionals with the same basis set 6-31g*, (a) TD-CAM-B3LYP, (b) TD-B3LYP and (c) TD-BHandHLYP. (d) Comparison of potential energy differences between first excited and ground states calculate by the three functionals.

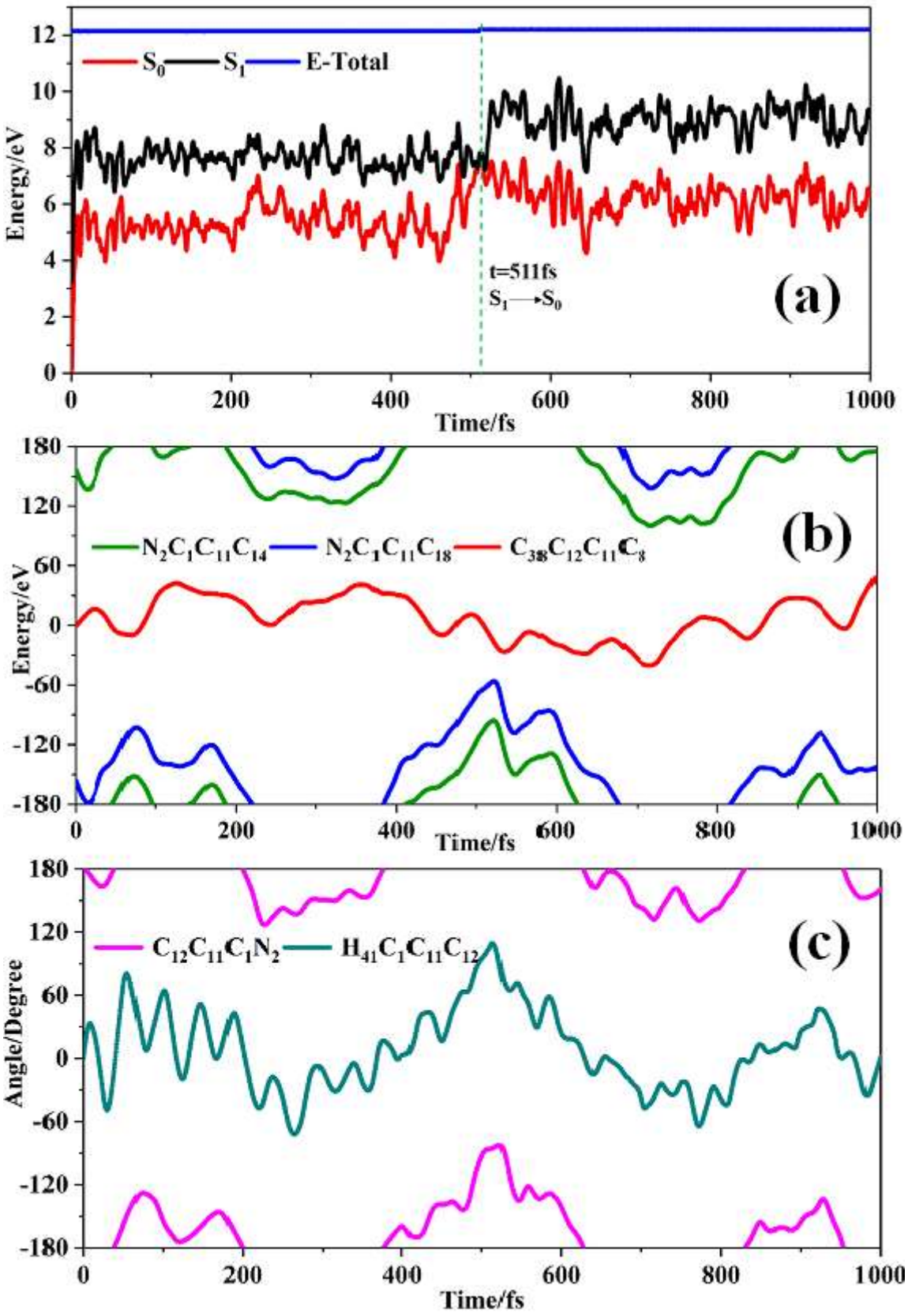


Fig. S3 A selected clockwise non-reactive trajectory goes via ET-CI starting from E-isomer as function of time.

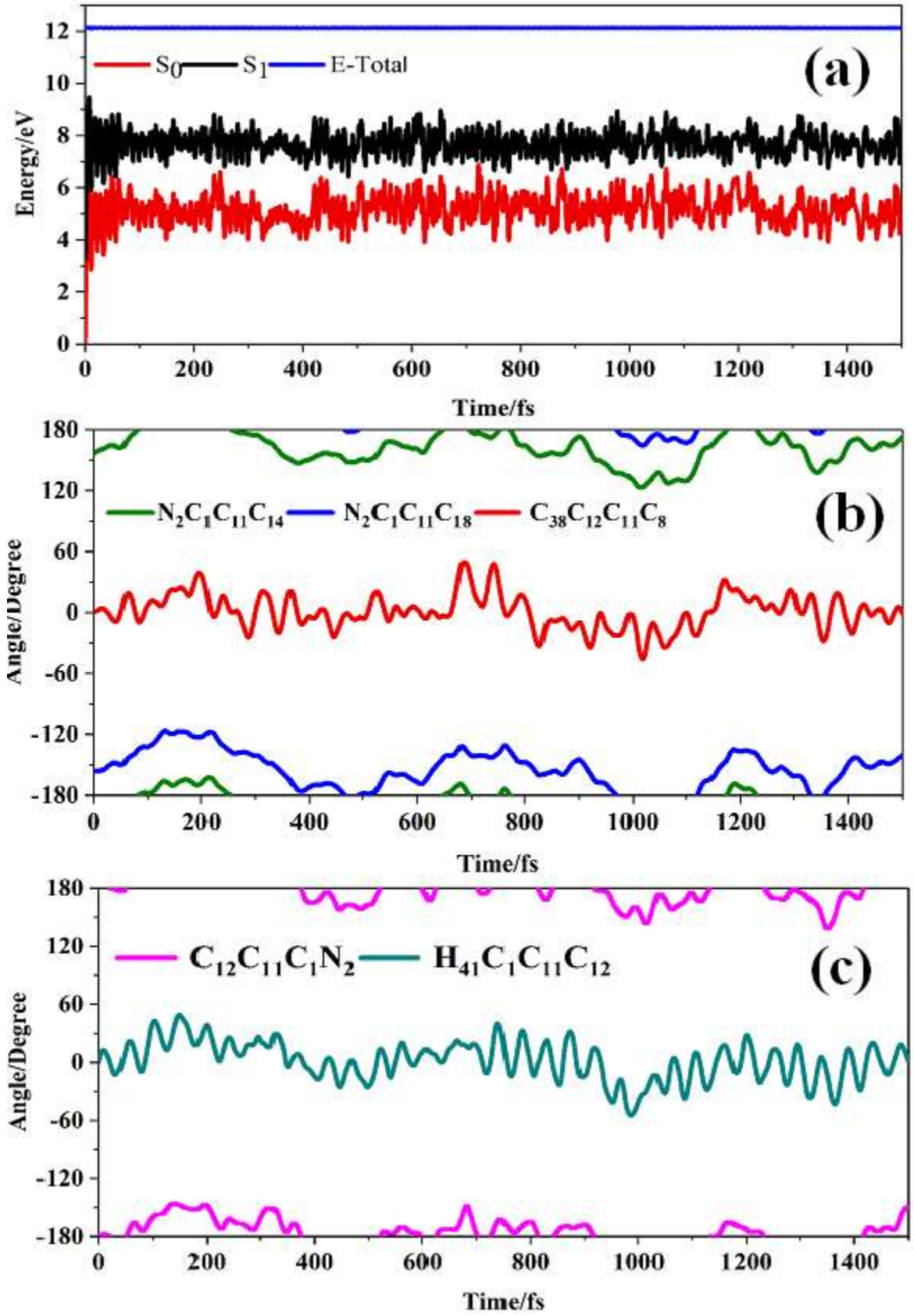


Fig. S4 A selected resonance trajectory starting from E-isomer as function of time.

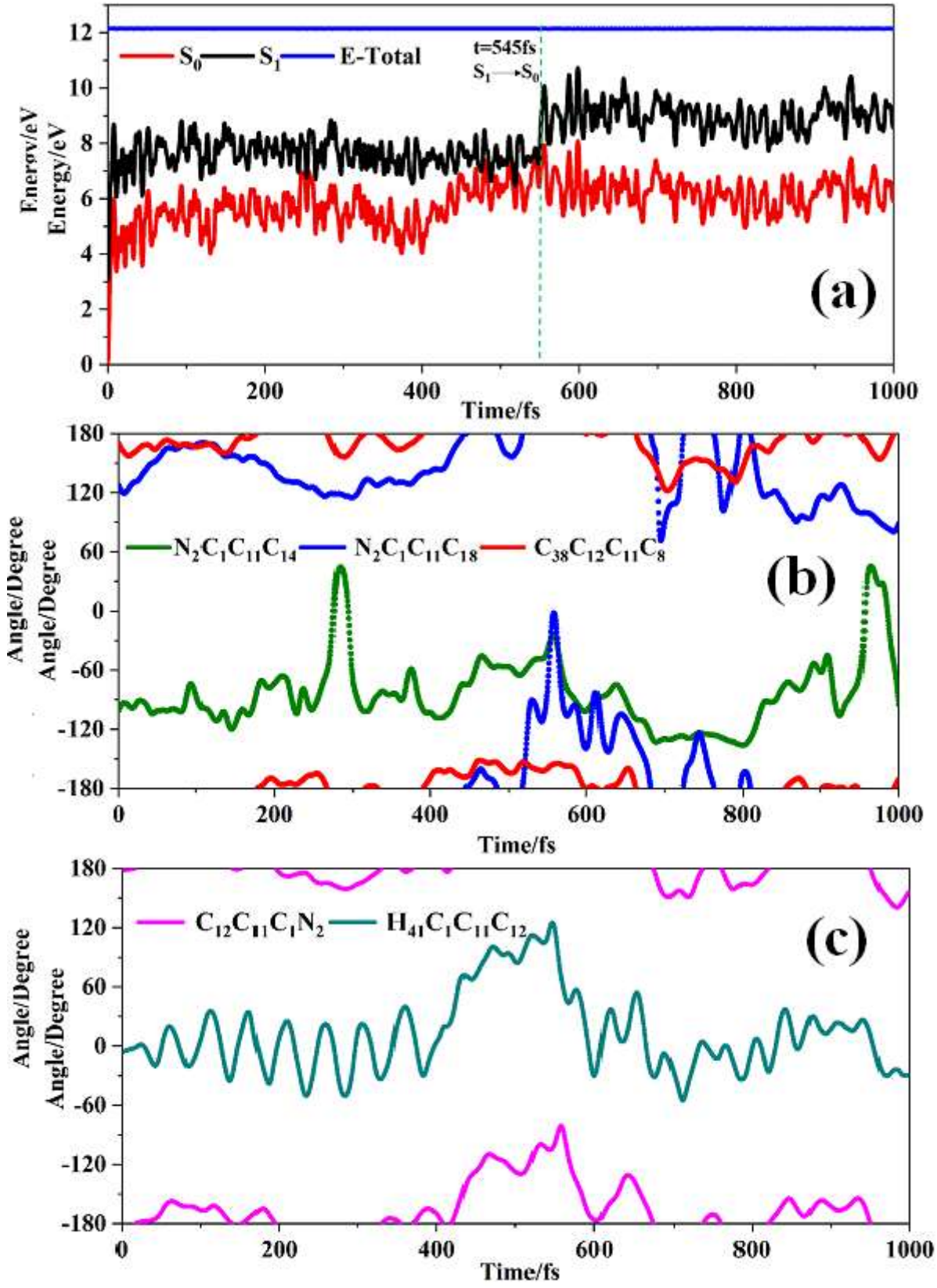


Fig. S5 A selected counterclockwise non-reactive trajectory goes via ZT-CI starting from Z-isomer as function of time.

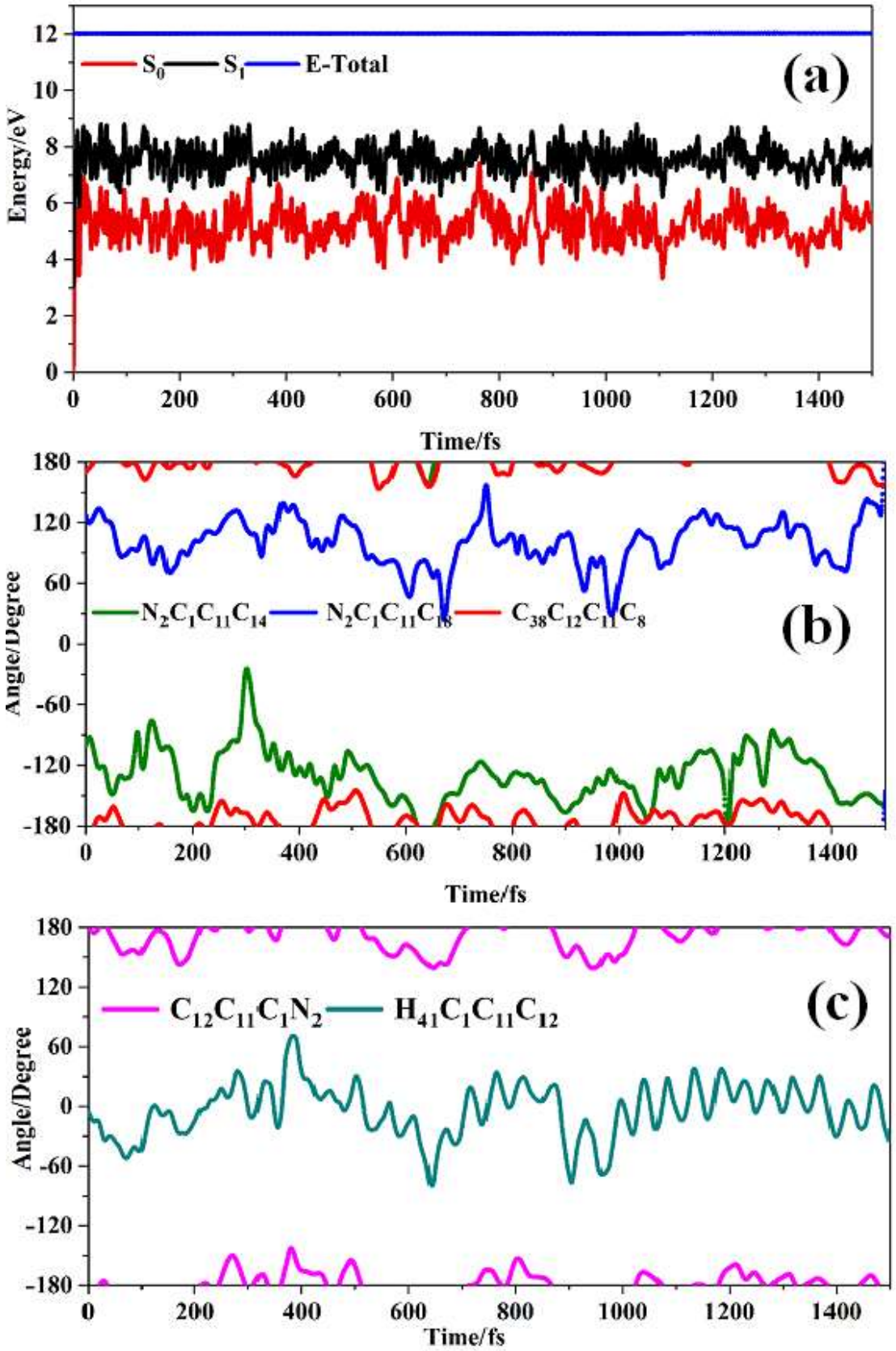


Fig. S6 A selected resonance trajectory starting from Z-isomer as function of time.