

Ultrafast Raman observation of the perpendicular intermediate phantom state of stilbene photoisomerization

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1. Synthesis

General information

^1H spectra were recorded by a commercial NMR spectrometer (AVANCE-400, Bruker). ^1H chemical shifts were referenced to residual solvent peaks. Elemental analyses (C and H) were carried out using an elemental analyzer (Vario EL CHNOS, Elementar). Mass spectra (GC-MS) were acquired on a gas chromatograph mass spectrometer (PARVUM2, SHIMADZU) using an Rxi®-5ms column (30 m, 0.25 mm I.D.).

Materials

Acetophenone, Zinc (Powder), Titanium (IV) Chloride, Tetrahydrofuran (THF) Anhydrous, *n*-hexane, and *n*-pentane were purchased from FUJIFILM Wako Chemicals. Acetophenone- α - ^{13}C (99 atom % ^{13}C) was purchased from ISOTECHTM.

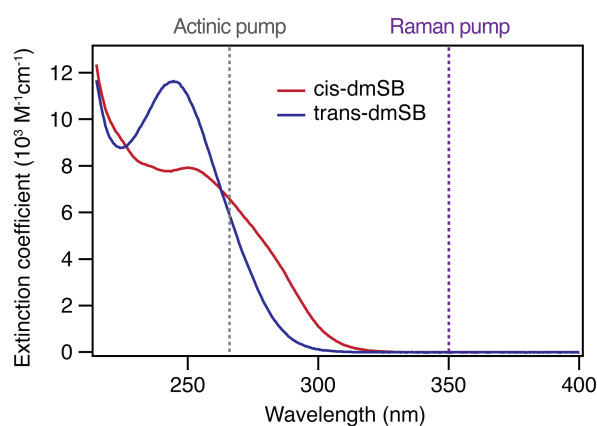
1, 1'-dimethylstilbene (dmSB)

TiCl_4 (1.50 mL, 13.7 mmol) was added dropwise to a 100 mL two-necked flask charged with Zinc (1.80 g, 28.4 mmol) and anhydrous THF (70 mL) under a nitrogen atmosphere at 0 °C. After stirring for 10 min, acetophenone (1.05 mL, 9.00 mmol) was added. The dark brown solution was refluxed for 24 h. The mixture was cooled to room temperature. A solution of saturated aqueous NaCO_3 (50 mL) was added to the reaction mixture, and then the product was extracted with diethyl ether (3×50 mL). The combined organic extracts were dried over MgSO_4 . The drying agent was removed by filtration, and the solvent was removed *in vacuo* to give a pale-yellow oil. The residue was purified by column chromatography on silica gel (*n*-hexane, 35 mm in diameter and 350 mm in length) to afford trans-dmSB ($R_f = 0.37$), 109 mg (12%) as a colorless solid and cis-dmSB ($R_f = 0.23$), 702 mg (75%) as a colorless viscous liquid. Colorless crystals of cis- and trans-dmSB recrystallized from *n*-pentane at -20 °C were used for the spectroscopic measurements. trans-dmSB: ^1H NMR (400 MHz,

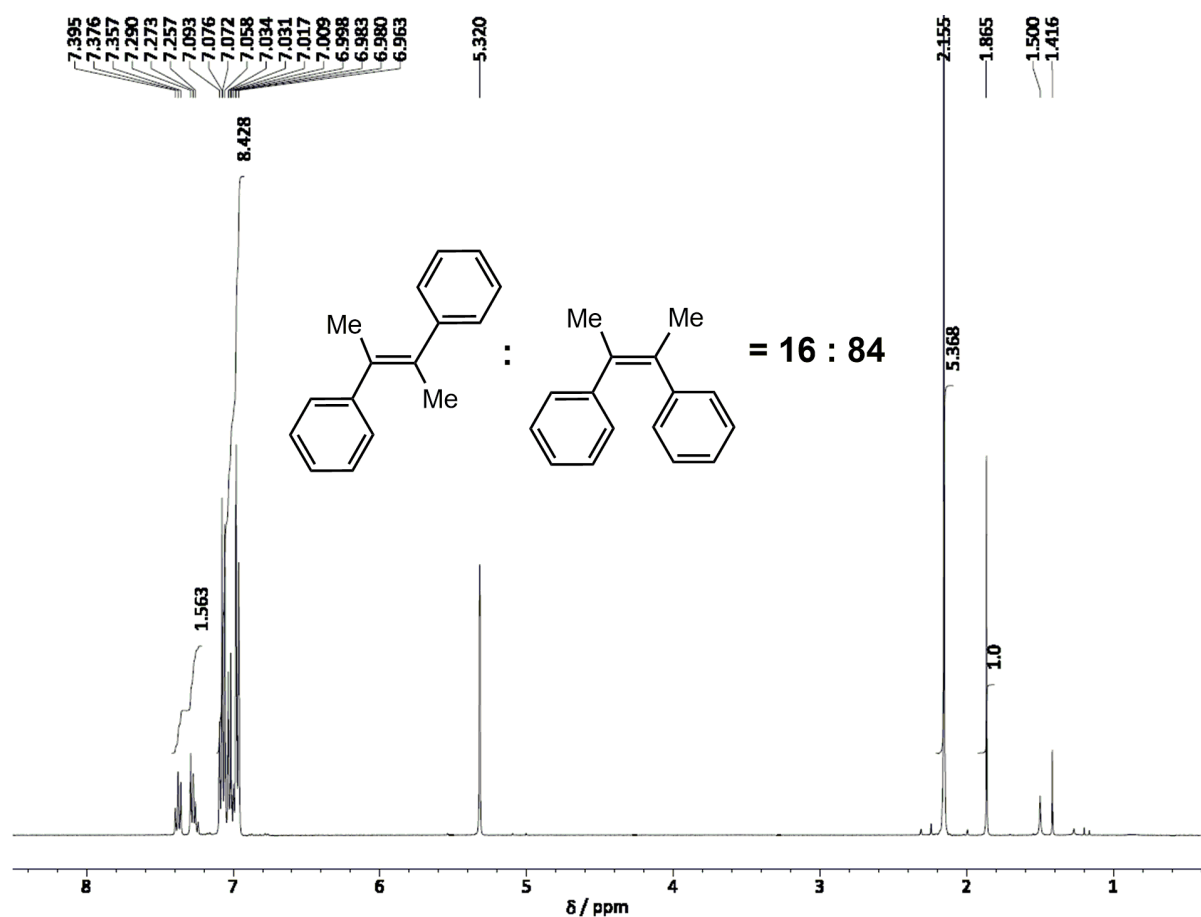
CD₂Cl₂, 293 K): δ 1.86 (s, 6H), 7.24-7.29 (m, 6H) 7.37 (t, J = 7.5 Hz, 4H). GC-MS m/z : M^+ = 208.30 calculated for C₁₆H₁₆; Found 208.30. Elemental analysis: found: C, 92.03; H, 7.65; calc. for C₁₆H₁₆: C, 92.26; H, 7.74%. *cis*-dmSB: ¹H NMR (400 MHz, CD₂Cl₂, 293 K): δ 2.16 (s, 6H), 7.96-7.04 (m, 6H) 7.06-7.09 (m, 4H). GC-MS m/z : M^+ = 208.30 calculated for C₁₆H₁₆; Found 208.30. Elemental analysis: found: C, 92.15; H, 7.82; calc. for C₁₆H₁₆: C, 92.26; H, 7.74%.

1, 1'-dimethylstilbene-1, 1'-¹³C (¹³C dmSB)

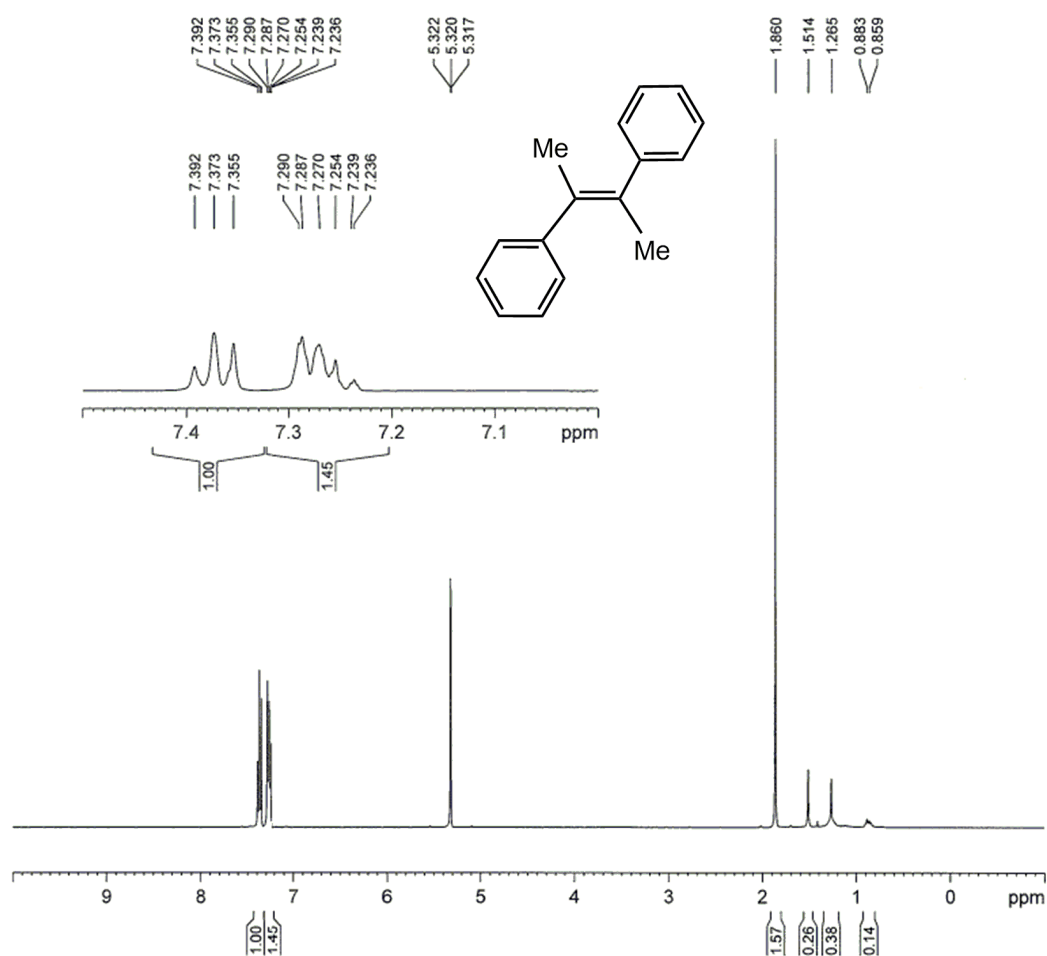
The ¹³C isotopomers of dmSB were prepared similarly to dmSB, except that acetophenone- α -¹³C (1.06 mL, 9.00 mmol) was used instead of acetophenone. The analytically pure sample was obtained by recrystallization from *n*-pentane at -20 °C. ¹³C *trans*-dmSB: ¹H NMR (400 MHz, CD₂Cl₂, 293 K): δ 1.87 (s, 6H), 7.24-7.30 (m, 6H) 7.38 (t, J = 7.5 Hz, 4H). GC-MS m/z : M^+ = 210.29 calculated for C₁₄¹³C₂H₁₆; Found 210.29. Elemental analysis: found: C, 92.41; H, 7.65; calc. for C₁₄¹³C₂H₁₆: C, 92.33; H, 7.67%. ¹³C *cis*-dmSB: ¹H NMR (400 MHz, CD₂Cl₂, 293 K): δ 2.17 (s, 6H), 7.97-7.05 (m, 6H) 7.07-7.10 (m, 4H). GC-MS m/z : M^+ = 210.29 calculated for C₁₄¹³C₂H₁₆; Found 210.29. Elemental analysis: found: C, 92.39; H, 7.59; calc. for C₁₄¹³C₂H₁₆: C, 92.33; H, 7.67%.



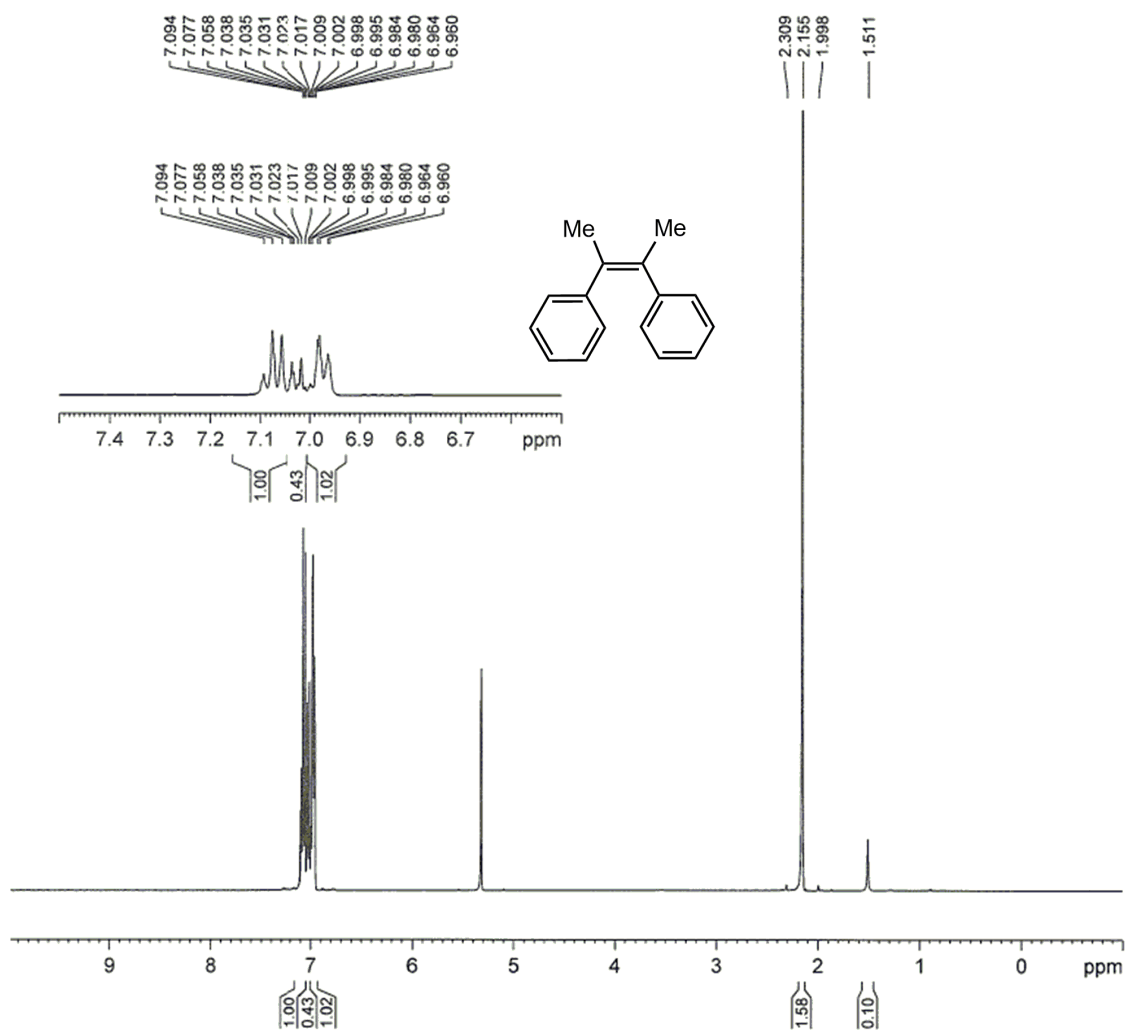
Supplementary Figure 1. Molar absorption coefficient spectra of *trans*- and *cis*-dmSB in acetonitrile.



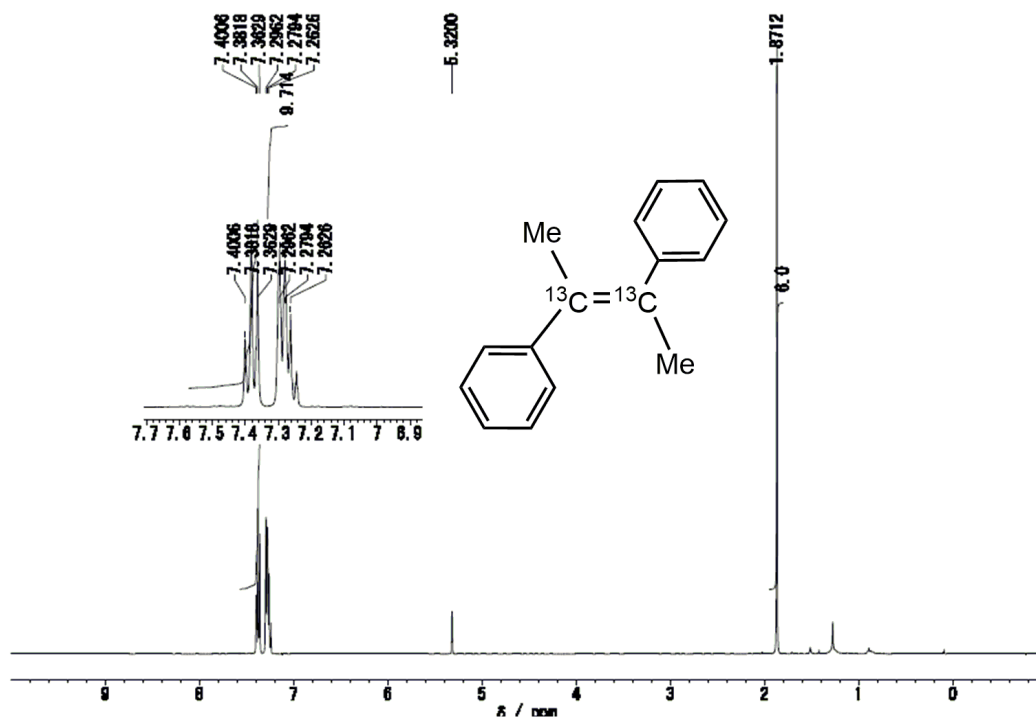
Supplementary Figure 2. ¹H NMR spectrum of the crude product before purification using column chromatography in CD₂Cl₂ at 293 K.



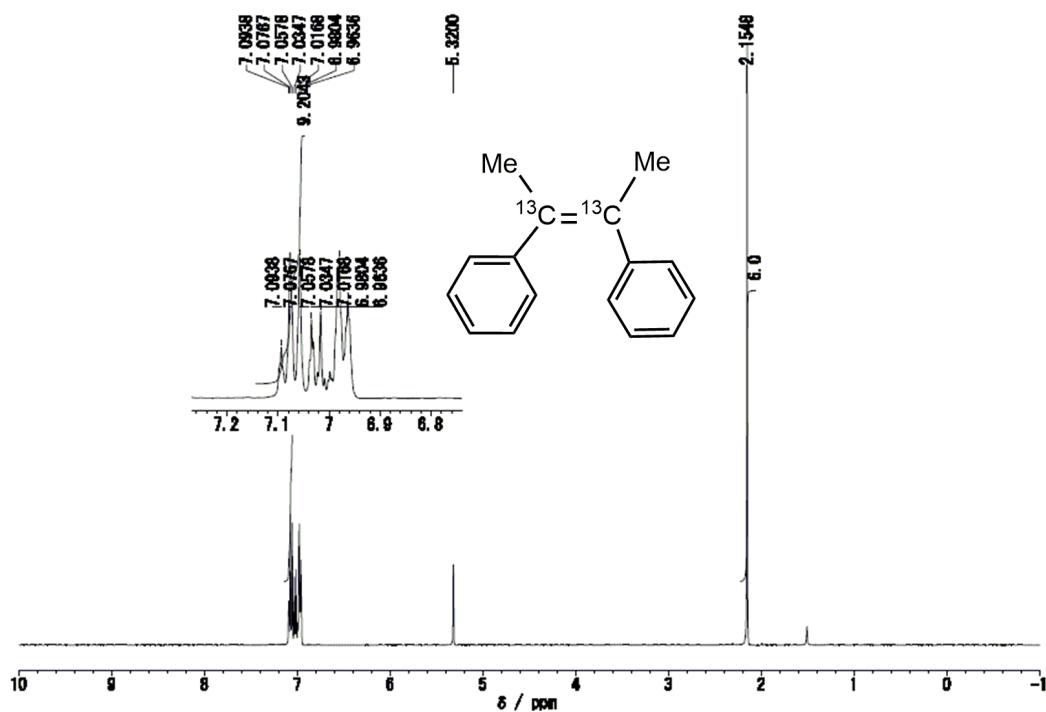
Supplementary Figure 3. ^1H NMR spectrum of trans-dmSB in CD_2Cl_2 at 293 K.



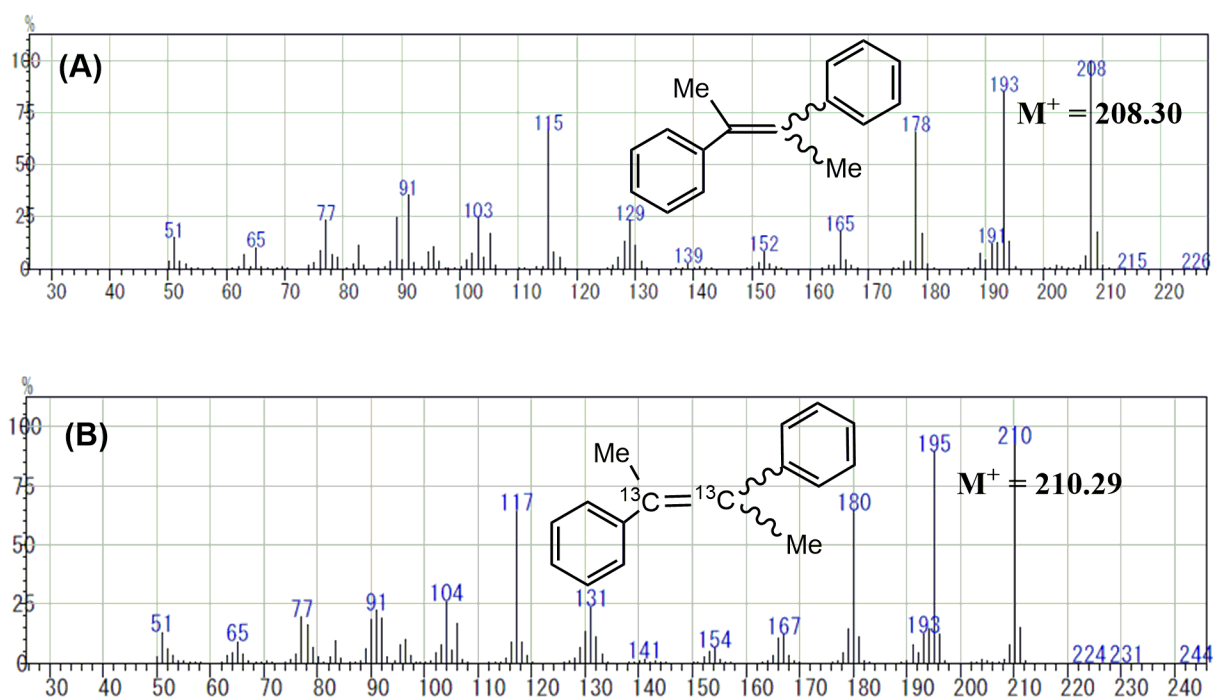
Supplementary Figure 4. ^1H NMR spectrum of *cis*-dmSB in CD_2Cl_2 at 293 K.



Supplementary Figure 5. ¹H NMR spectrum of ¹³C trans-dmSB in CD₂Cl₂ at 293 K.



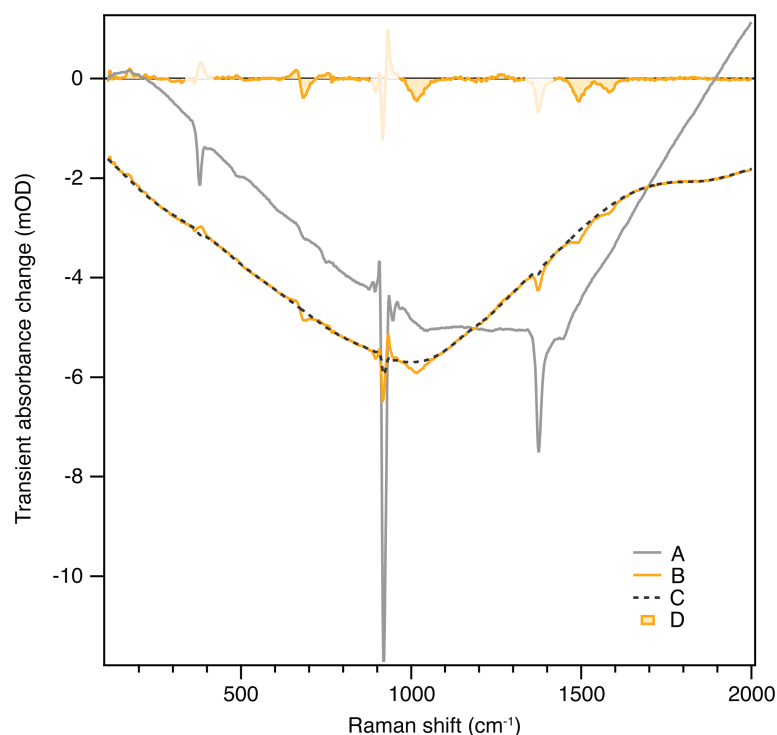
Supplementary Figure 6. ¹H NMR spectrum of ¹³C cis-dmSB in CD₂Cl₂ at 293 K.



Supplementary Figure 7. GC-MS spectra of dmSB (A) and ^{13}C dmSB (B).

2. Baseline subtraction procedure for the FSRS measurements

A typical raw UV-FSRS spectrum of *cis*-dmSB is shown in Supplementary Fig. 8 (A). A raw spectrum obtained in FSRS measurements contains Raman signals not only from the transients but also from the ground state molecule, solvent, and quartz cell. These additional signals were carefully subtracted with adequate scaling factors (B). Then, the sloping background due to the bleaching of the UV transient absorption was modeled by a spline function to smoothly connect the frequency regions where no band features exist (C). Subtracting this modeled background curve, we obtained a UV-FSRS spectrum of the transient as negative absorbance changes (D). In the main text, we present the FSRS spectra as a positive stimulated Raman gain spectrum in the mOD unit after inverting the sign.

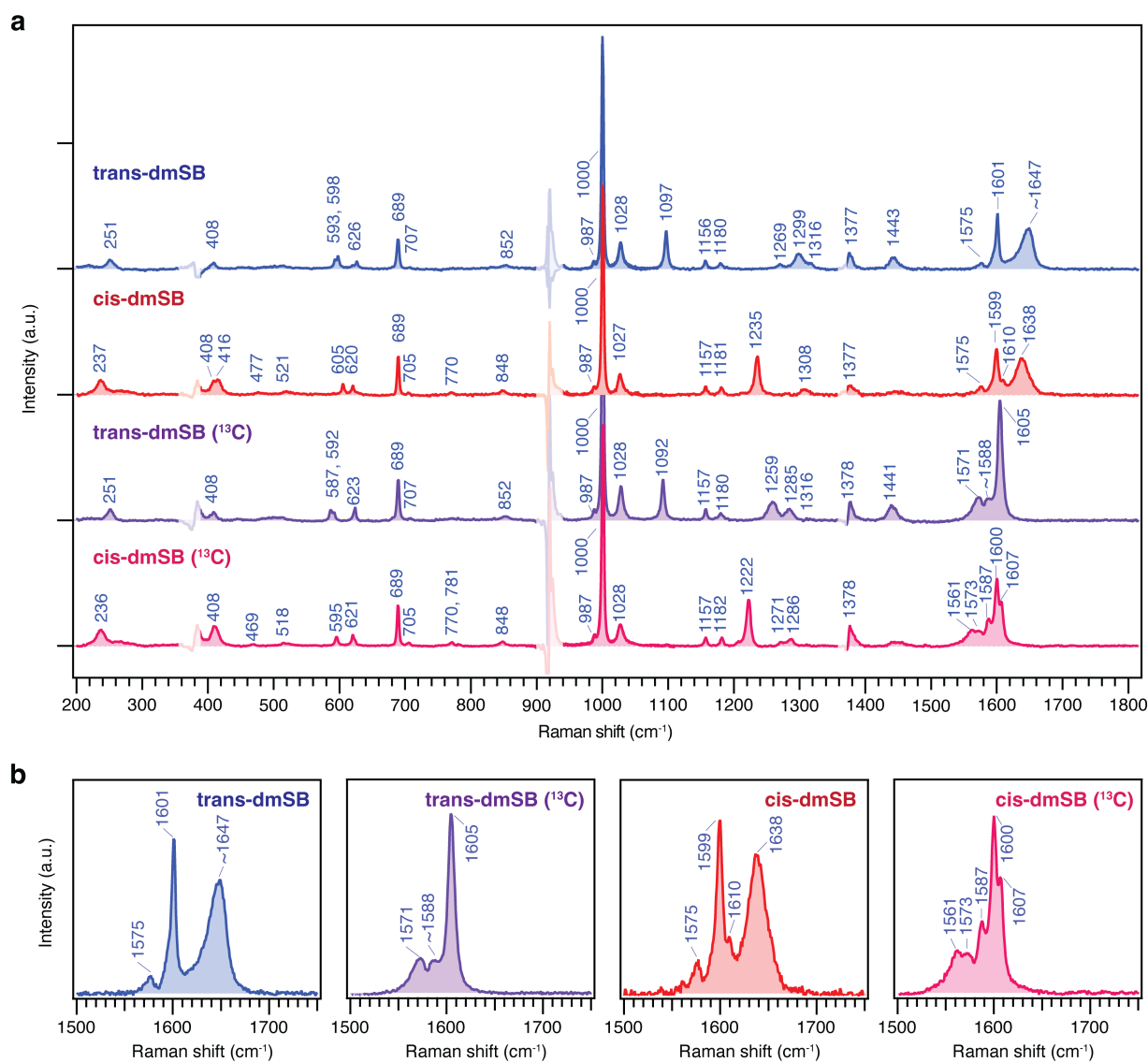


Supplementary Figure 8. Procedure to extract a UV-FSRS spectrum of the transient. (A) The raw UV-FSRS spectrum of cis-dmSB at a delay time of 0.3 ps ($\times 0.5$), (B) the spectrum obtained after subtracting the signals due to the ground state, solvent, and quartz cell, (C) the sloping background modeled with a spline curve, and (D) the final spectrum ($\times 2$) obtained after subtraction of the sloping background. The white-shaded region in (D) indicates the disturbed spectral region by the imperfect subtraction of the solvent Raman signal.

3. Steady-state Raman spectra of dmSB

Supplementary Fig. 9a shows steady-state Raman spectra of trans- and cis-dmSB and their ^{13}C isotopomers in acetonitrile, obtained under excitation with a He–Ne laser (632.8-nm, 14 mW). Trans- and cis-dmSB provide similar Raman spectra but exhibit several distinctly different Raman bands reflecting their different conformations. For example, the trans spectrum shows bands at 1097 and 1443 cm^{-1} , but they are absent in the cis spectrum. Conversely, the cis spectrum exhibits a band at 1235 cm^{-1} , which is absent in the trans spectrum. Many other bands are commonly seen in both

spectra, but their frequencies often differ slightly between trans and cis forms. Upon the ^{13}C labeling of the ethylenic carbons, several bands show noticeable frequency shifts in both spectra of trans- and cis-dmSB. The most prominent spectral changes are recognized in the CC double bond stretch region ($1500 - 1700\text{ cm}^{-1}$), which is magnified in Supplementary Fig. 9b. The band of the trans form around 1647 cm^{-1} and the band of the cis form around 1638 cm^{-1} disappear and appear to be merged into the sets of bands around 1580 cm^{-1} with the ^{13}C substitution. These ^{13}C shifts allow us to assign the $\sim 1647\text{-cm}^{-1}$ band of trans-dmSB and the 1638-cm^{-1} band of cis-dmSB to the $\text{C}_{\text{et}}\text{C}_{\text{et}}$ stretch mode of each form in the S_0 state.



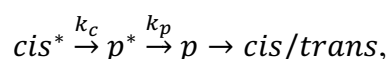
Supplementary Figure 9. (a) Steady-state spontaneous Raman spectra of trans- and cis-dmSB and their ^{13}C isotopomers in acetonitrile obtained with 632.8-nm excitation. These spectra are shown after the subtraction of the solvent bands and the baseline correction. The white-shaded regions are obscured by the imperfect subtraction of the solvent Raman signal. (b) Magnified view of the CC double bond stretch region.

4. UV-FSRS spectrum of parent cis-stilbene

As shown in Extended Data Fig. 2, the UV-FSRS spectrum of parent cis-stilbene exhibits significantly broadened bands around ~ 790 and $\sim 1540\text{ cm}^{-1}$. Although precise evaluation is difficult, the bandwidths of the transient Raman band of parent cis-stilbene can be estimated to be $100 - 150\text{ cm}^{-1}$. This very broad bandwidth suggests that the lifetime of the perpendicular state of parent cis-stilbene is much shorter than that of cis-dmSB and that the lifetime broadening is the major origin of the bandwidth. Indeed, a previous *ab initio* molecular dynamics simulation indicated that the perpendicular state of parent cis-stilbene is closely located to the conical intersection, and the perpendicular state decays to the ground state very rapidly¹. Note that the spectral pattern for parent cis-stilbene is slightly different from that of cis-dmSB, and this difference is likely attributable to the difference in the perpendicular-state structure. In fact, a previous quantum chemical calculation indicated that the perpendicular state structures ($(S_1)_{\text{twist}}$) of dmSB and parent stilbene are similar but different in the dihedral angle d_{C3C1C2C4} (103° for dmSB and 113° for parent stilbene) and the distance r_{C5C6} ($3.8\text{ \AA}$ for dmSB and $4.1\text{ \AA}$ for parent stilbene)^{1,2}.

5. Inverted kinetics of transient UV absorption band of parent cis-stilbene

The photoisomerization of cis-stilbenes can be represented by the following sequential scheme,

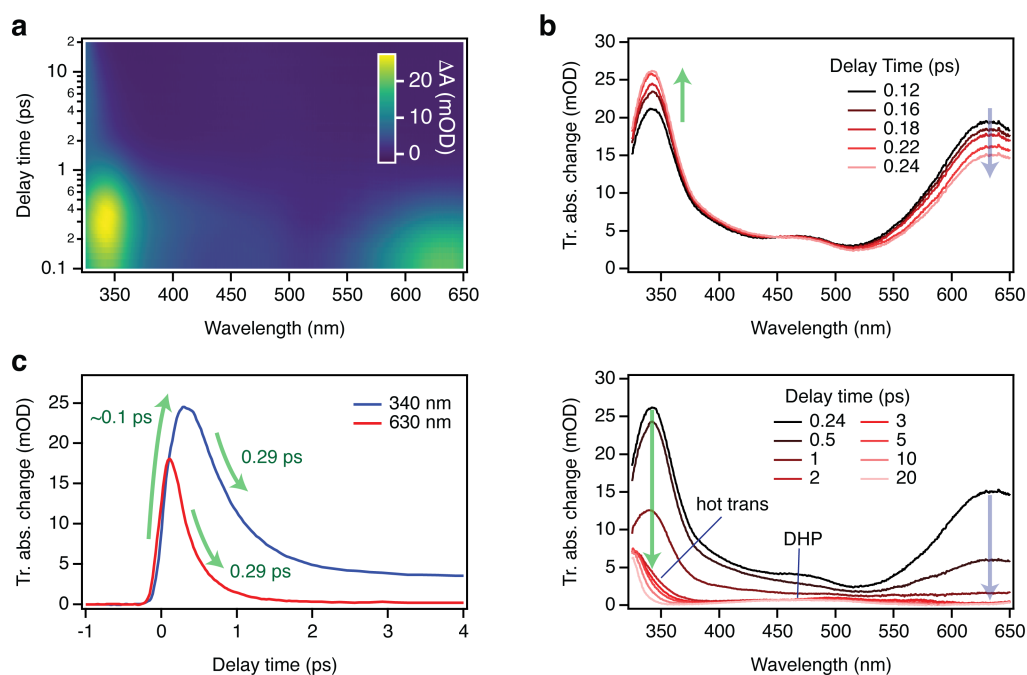


where cis^* , p^* , p , and $cis/trans$ represent the excited-state cis , the excited-state perpendicular state, the ground-state perpendicular state, and the ground-state $cis/trans$, respectively. k_c and k_p represent the decay rate constants of cis^* and p^* , respectively. (Here, we ignored the reaction path to form DHP that competes with the isomerization for simplicity.) Based on this scheme, we obtain the kinetics of cis^* and p^* as follows,

$$[cis^*] = [cis^*]_0 \exp(-k_c t)$$

$$[p^*] = \frac{k_c}{k_c - k_p} [cis^*]_0 (\exp(-k_p t) - \exp(-k_c t)),$$

where $[cis^*]_0$ represents the initial population of cis^* formed upon photoexcitation. When k_c is larger than k_p , $[p^*]$ simply shows the temporal change that grows with k_c and decays with k_p . On the other hand, when k_p is larger than k_c , the sign of the pre-exponential factor becomes negative, and as a result, $[p^*]$ grows with k_p and decays with k_c . This counter-intuitive situation is called inverted kinetics. In the case of parent cis -stilbene, the decay of cis^* ($k_c = (0.29 \text{ ps})^{-1}$) is considered to be slower than the decay of the perpendicular p^* state (k_p) in acetonitrile, which is estimated to be $(\sim 100 \text{ fs})^{-1}$ from the bandwidth of the p^* Raman bands (Extended Data Fig. 2). This situation satisfies the condition for the inverted kinetics of $[p^*]$. In fact, the temporal profile of the transient UV absorption band of cis -stilbene, i.e., the absorption band of the perpendicular p^* state, grows and decays with ~ 0.1 and ~ 0.3 ps time constants (Supplementary Fig. 10), respectively, and the latter agrees well with the lifetime of cis^* . These observations indicate that the perpendicular p^* state of parent cis -stilbene exhibits inverted kinetics.

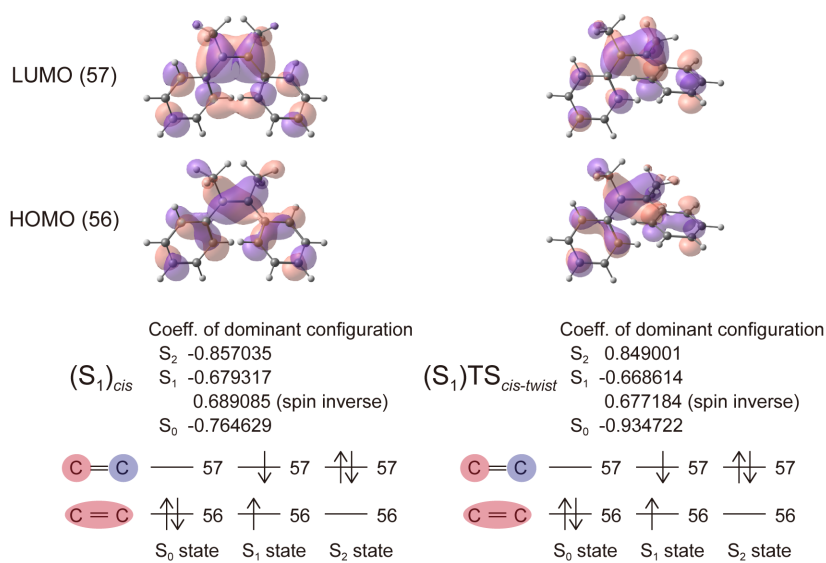
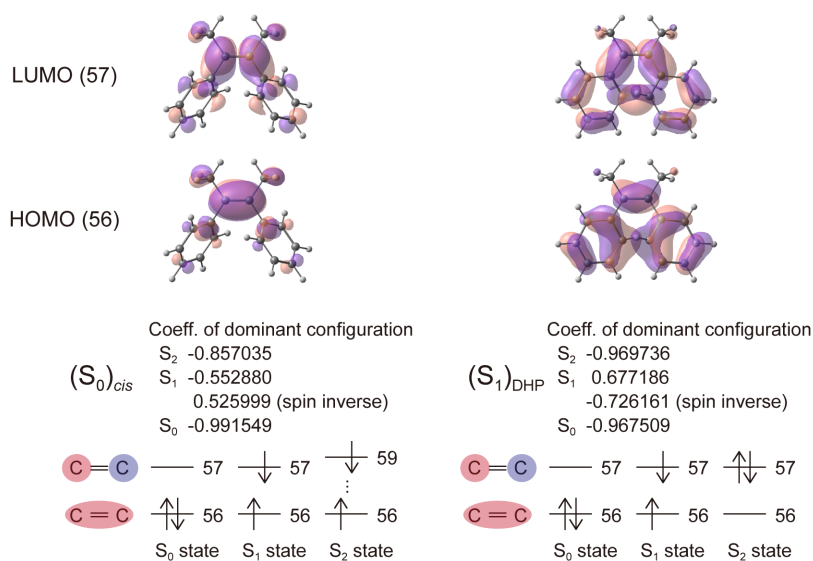


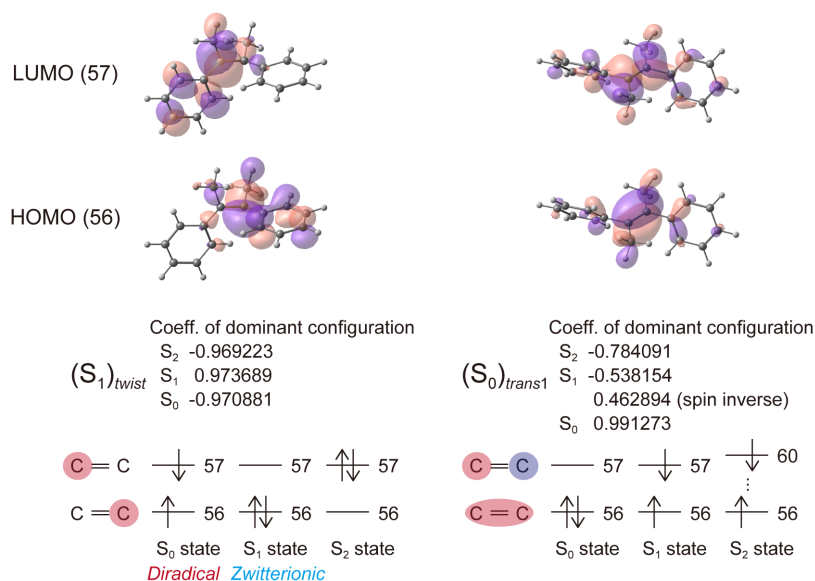
Supplementary Figure 10. Femtosecond time-resolved absorption data of parent cis-stilbene in acetonitrile (1 mM). (a) Two-dimensional plot of the time-resolved absorption data. (b) Time-resolved absorption spectra in the time ranges relevant to the formation (top) and decay (bottom) of the perpendicular state. (c) Temporal profiles of the time-resolved absorption signals around the excited-state absorption and p* absorption maxima (630 and 340 nm, respectively).

6. Nature of the electronic structure of the perpendicular state

As shown in Extended Data Fig. 1, we analyzed the dipole moment along the reaction pathways from the Franck-Condon (FC) region of the trans and cis forms to the twist minimum ($(S_1)_{\text{twist}}$) structure in the S_1 state for dmSB, and the result indicates that the perpendicular state is a zwitterionic state. Supplementary Fig. 11 shows the molecular orbitals and dominant electron configurations that describe the ground and excited states (S_0 , S_1 , and S_2) in the key structures. While descending from the FC region to the twist region, the S_1 state is mainly characterized by HOMO-LUMO (H-L) single excitation. However, at $(S_1)_{\text{twist}}$, the electron distributions in the HOMO and LUMO are localized in the left and right sides of the central $C_{\text{et}}C_{\text{et}}$ bond, respectively, and the S_1

state becomes a zwitterionic state with the ground-state configuration, whereas the S_0 state is a diradical state with H-L single excitation.

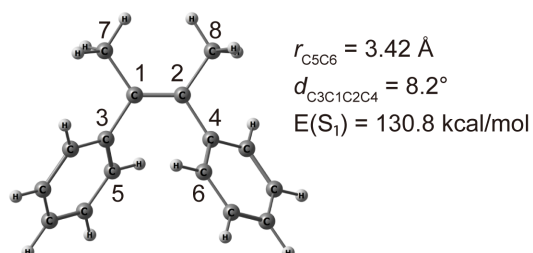




Supplementary Figure 11. Dominant electron configurations for the S_0 , S_1 , and S_2 states and related molecular orbitals in the key structures.

7. Molecular structures and Cartesian coordinates (in Å) for the S_0 and S_1 minima and S_1/S_0 minimum energy conical intersections of dmSB optimized at SF-TDDFT(BHHLYP)/6-31G(d) level

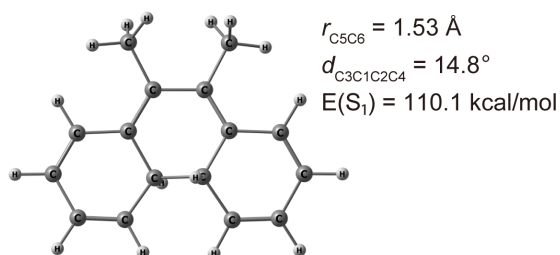
$(S_0)_{\text{cis}}$



C	0.000000000000	0.000000000000	0.000000000000
C	-0.000000000003	-0.000000000002	1.345827404429
C	1.253465600759	0.000000000000	-0.802617066533
C	1.240650002850	-0.178733872508	2.147315977555
C	2.227039968066	0.981708995240	-0.617795903799

C	2.078285983435	-1.275357854022	1.941553388046
C	-1.246488930454	0.065026866093	-0.844932362814
C	-1.243069195986	0.121773888360	2.189260941218
C	1.459707514996	-0.945441076234	-1.807891180982
C	2.605064736809	-0.923900347138	-2.586103416213
C	3.563709224581	0.057319187156	-2.388256351661
C	3.367811760705	1.011399187043	-1.401351129396
C	1.567440510883	0.708595118195	3.173643191712
C	2.699700297421	0.520576798517	3.949111884833
C	3.523602221898	-0.571514112390	3.727800138667
C	3.205137418529	-1.470154039947	2.720997263942
H	-1.291034820123	1.010347572013	-1.385249719492
H	-1.237576466642	-0.716963860455	-1.601158404605
H	-2.161860201306	-0.044501970348	-0.278273499800
H	-1.387433388297	-0.777761941157	2.786630000067
H	-1.148327469111	0.944929813793	2.894646234666
H	-2.142558797310	0.294189576870	1.613105018045
H	0.725567009394	-1.718138082548	-1.971336693500
H	2.747535643423	-1.673462113880	-3.348064201812
H	4.452570176764	0.079521734471	-2.997769685627
H	4.104000806332	1.782972886550	-1.242422835746
H	2.082036772779	1.725774281127	0.147129513888
H	1.838454597566	-1.980047704823	1.163260681125
H	3.833896162952	-2.327898317654	2.542973786066
H	4.401980073350	-0.722469964264	4.334315108887
H	2.936586126924	1.228434011648	4.727463338207
H	0.941002684193	1.566687807868	3.358397772746

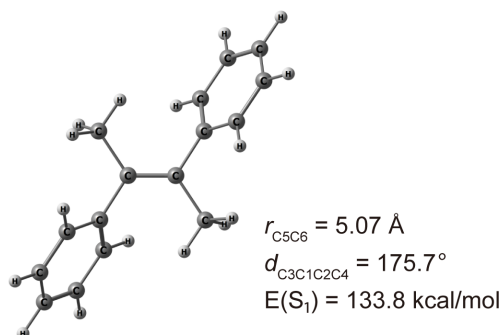
$(S_0)_{DHP}$



C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000094	0.000000000012	1.456113883894
C	1.170263069925	0.000000000000	-0.693212576188
C	1.131737226592	-0.298185730158	2.149118183923

C	2.491709513546	0.030602865529	0.050293632139
C	2.398938358101	-0.671742204586	1.404450820270
C	-1.337427139704	0.038588901244	-0.695848248810
C	-1.303143900965	0.305838519230	2.151183193983
C	1.236491454174	0.104499911804	-2.137684540304
C	2.374651545401	-0.114219887761	-2.811707771734
C	3.578581468855	-0.524694177396	-2.113953507134
C	3.628580556805	-0.501624751246	-0.784794197615
C	1.171996082876	-0.409025753233	3.594020622427
C	2.329195387343	-0.488571597621	4.266353230075
C	3.597182146892	-0.411719764961	3.566054884681
C	3.637143611318	-0.454536073122	2.237052697269
H	-1.278345868266	-0.324094750512	-1.713876612438
H	-2.061872377194	-0.585836083766	-0.181127283313
H	-1.752906212596	1.046230205449	-0.727026909447
H	-1.155475278756	0.632250378100	3.172439041147
H	-1.838003104672	1.101595964051	1.640784869414
H	-1.966588176106	-0.559051039690	2.172638839379
H	0.344981770463	0.353517839857	-2.686092105394
H	2.393302523265	-0.034941587541	-3.886685738280
H	4.423820482979	-0.866860472434	-2.690025947898
H	4.522478295733	-0.826613812817	-0.278811154807
H	2.715810278798	1.090513694523	0.258934138708
H	2.337808263768	-1.753177373679	1.195216357474
H	4.584524853364	-0.379863056737	1.729424280118
H	4.503589829957	-0.300295239806	4.140050764449
H	2.328415428618	-0.562661853864	5.341884584524
H	0.247911352869	-0.415537835848	4.144876845041

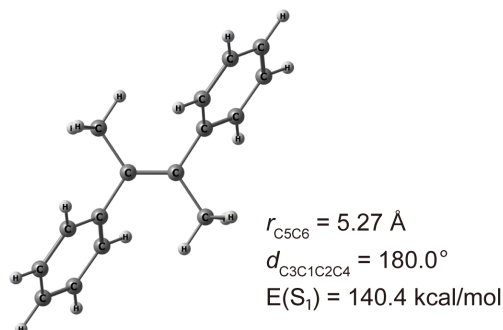
(S₀)_{trans1}



C	0.000000000000	0.000000000000	0.000000000000
C	-0.000000000036	-0.000000000006	1.345664597288
C	1.255545712642	0.000000000000	-0.796353557858
C	-1.252398190640	0.095211594686	2.142144503408

C	2.186143370444	1.031764546691	-0.676412571103
C	-2.088947357857	1.206939093180	2.048238432449
C	-1.256908336062	-0.009264069453	-0.830316834470
C	1.249836437028	-0.111620458277	2.179334741242
C	1.514713586603	-1.011600621105	-1.721777137160
C	2.668981410897	-1.001726324862	-2.486139155828
C	3.586023850809	0.029836580087	-2.352392641972
C	3.338839851154	1.047734741775	-1.444890707221
C	-1.599199076659	-0.911234853425	3.043915381483
C	-2.747800905385	-0.818850571888	3.810989610309
C	-3.570883360421	0.292017779334	3.704009364655
C	-3.235607923634	1.305431625402	2.820071138690
H	-1.215721700241	-0.804147029678	-1.572653346288
H	-2.148097084927	-0.152377589146	-0.232310791528
H	-1.362263624807	0.921875266296	-1.386950881875
H	1.433144380567	0.809853647876	2.732018827710
H	1.137333361094	-0.896280806058	2.925035351935
H	2.127546523280	-0.333447589395	1.585324665690
H	0.814110506279	-1.823937556047	-1.830186563862
H	2.853544625352	-1.801044395822	-3.185903873840
H	4.482544314265	0.040321086933	-2.950805541906
H	4.041516697101	1.858476745143	-1.337304072604
H	1.994245631788	1.831088057472	0.020862864880
H	-0.971825445898	-1.783961566601	3.131382414455
H	-3.000774835707	-1.615602593748	4.492106699007
H	-4.462872389649	0.367084892492	4.304621717757
H	-3.864953155147	2.176833379196	2.733486979606
H	-1.829786134801	2.002581193093	1.368431013524

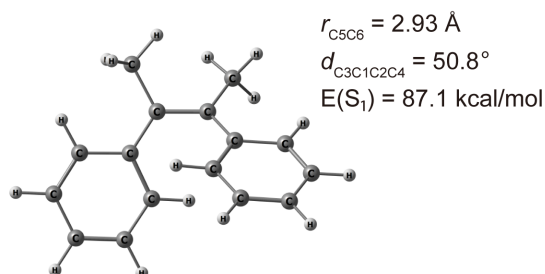
(S₀)_{trans2}



C	0.000000000000	0.000000000000	0.000000000000
C	-0.000000000012	0.000000000003	1.344873989432
C	1.253337409850	0.000000000000	-0.802742753773
C	-1.253339326021	0.000011956040	2.147617028044

C	2.163156979530	1.053425679379	-0.728836649544
C	-1.515921981732	1.032922018855	3.047004587267
C	-1.251684829177	0.046081751877	-0.837753414057
C	1.251679426415	-0.046089446615	2.182634293142
C	1.515902949877	-1.032875179536	-1.702175979370
C	2.657302933030	-1.022988245301	-2.486540773644
C	3.556126981025	0.028935173507	-2.397036730181
C	3.303648291909	1.068238674354	-1.515735018096
C	-2.163143863862	-1.053429633169	2.073751732995
C	-3.303637651334	-1.068226082632	2.860647433913
C	-3.556132876193	-0.028889097750	3.741905279480
C	-2.657324413779	1.023051450494	3.831367268368
H	-1.188829173624	0.864210116156	-1.553498608646
H	-1.369297775255	-0.865630127863	-1.423323774573
H	-2.145861294576	0.178835412718	-0.241955864843
H	1.369303377741	0.865628584127	2.768193271356
H	1.188806341331	-0.864207286560	2.898389914844
H	2.145857083103	-0.178865681676	1.586843632284
H	0.826225572727	-1.858452852395	-1.777420001603
H	2.845481099786	-1.837681471786	-3.167368582054
H	4.442583360861	0.039225287510	-3.010276669880
H	3.991899754612	1.895100441329	-1.443228121794
H	1.965464451896	1.870408204639	-0.053921672118
H	-0.826256391790	1.858513349607	3.122214973292
H	-2.845515771345	1.837771067396	4.512160134496
H	-4.442590336320	-0.039165352460	4.355144184063
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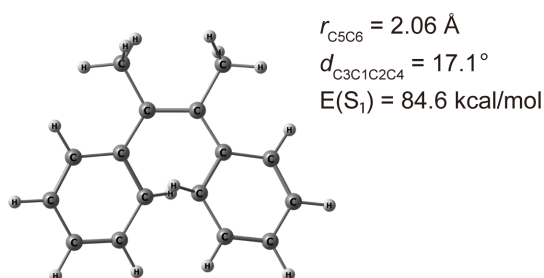
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C	0.744908824095	-0.913895074570	2.182222829537
C	2.473785795551	0.135965511751	-0.146416127573

C	1.460072805750	-2.001735385585	1.574359089572
C	-1.329836184805	0.037822713267	-0.709559843053
C	-0.869431898403	1.006887502057	2.138387329393
C	1.163090271129	-0.139569997929	-2.180257125747
C	2.318954918816	-0.178373481565	-2.907267822907
C	3.570707482972	-0.062306311882	-2.280569508246
C	3.625668655881	0.105565175677	-0.907078226664
C	0.842090015821	-0.814670482319	3.608584133626
C	1.608380400185	-1.681715136146	4.334692104576
C	2.314575262318	-2.721295598946	3.707060553243
C	2.216781984070	-2.871442909527	2.333927326367
H	-1.404615652844	0.869007030964	-1.411593986402
H	-1.491611850965	-0.875676561020	-1.285092998388
H	-2.151142417581	0.113407379859	-0.006792235984
H	-1.592455557220	0.536767537330	2.806776974878
H	-0.266741895572	1.679079324199	2.751230437865
H	-1.413183710995	1.626673170681	1.435211945405
H	0.221094748353	-0.237588790402	-2.690577751685
H	2.269317473170	-0.299573296730	-3.977776681119
H	4.474500796875	-0.091664003968	-2.866082319569
H	4.579835428764	0.222822028274	-0.418394114724
H	2.540115564799	0.329629965699	0.906380290298
H	1.351213656022	-2.176059682910	0.521717904520
H	2.731322873476	-3.683221365278	1.844731606387
H	2.913564203558	-3.399602523165	4.291514061588
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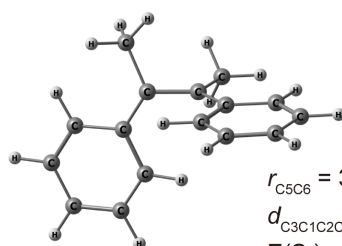
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C	1.153923159087	-0.354130981186	2.145427525011
C	2.464334978574	0.324345980370	-0.056034291290
C	2.257956584740	-1.037585608838	1.469045023422

C	-1.319905311761	0.042932672269	-0.725078072107
C	-1.274740911072	0.345711230719	2.137810599567
C	1.294298452683	-0.415815728791	-2.083847669037
C	2.496823603303	-0.570963144340	-2.718307732481
C	3.710230870583	-0.276451234370	-2.053571740210
C	3.683523501396	0.197489918285	-0.775238313323
C	1.362846244621	0.022348260545	3.494555412647
C	2.558378692511	-0.183718427897	4.128143514675
C	3.628425473833	-0.828423774333	3.464204669409
C	3.460386746008	-1.277198083711	2.187427442303
H	-1.197944886354	0.242937438558	-1.782135848265
H	-1.879370458184	-0.888241686250	-0.622238447881
H	-1.953682260317	0.833230609113	-0.329106069304
H	-1.210518811281	0.139050581395	3.198623786817
H	-1.548859303381	1.394603243676	2.015771160646
H	-2.107435477879	-0.241191335277	1.756000406081
H	0.394574393202	-0.680055386913	-2.612184768809
H	2.520790451732	-0.925114697420	-3.736020253479
H	4.646519057407	-0.388357975021	-2.575972742866
H	4.598230225975	0.486423053890	-0.282058668395
H	2.426564310380	1.118298782137	0.673841465186
H	1.985667188338	-1.784990163032	0.739888700580
H	4.247116222868	-1.826863978988	1.695091687038
H	4.556524773442	-0.998882102888	3.985287378781
H	2.687238865864	0.152058777850	5.144140809488
H	0.583025832856	0.544248464808	4.021665616538

$(S_1)_{twist}$

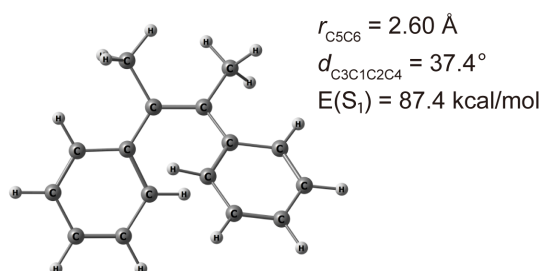


$r_{C5C6} = 3.84 \text{ \AA}$
 $d_{C3C1C2C4} = 103.1^\circ$
 $E(S_1) = 84.6 \text{ kcal/mol}$

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C	1.235861134925	0.000000000000	-0.672853936525
C	-0.273024888950	-1.171415659107	2.200847359944
C	2.454489587018	-0.417987215505	-0.058319840998
C	-0.455805839265	-2.386481224947	1.502411411763
C	-1.226889710073	0.652226249821	-0.598663949823

C	0.294588669489	1.293767311009	2.114560484113
C	1.358536631655	0.410795456434	-2.033058190584
C	2.564234082207	0.378315097914	-2.695073605869
C	3.737394678094	-0.037121162760	-2.069480119347
C	3.652487848917	-0.430490056742	-0.739775323595
C	-0.356196438649	-1.190839623974	3.615971061745
C	-0.614669686707	-2.361603837248	4.283226068658
C	-0.788048708810	-3.547080296957	3.566638546511
C	-0.705814999601	-3.559182448682	2.180938983925
H	-1.142430411575	1.738097537327	-0.754278567259
H	-1.454114273881	0.217218943922	-1.571225799254
H	-2.113202077065	0.490516756892	0.014965509146
H	-0.378174444147	2.044528371180	1.703580992132
H	0.257401869812	1.323783973874	3.196711609883
H	1.289153280108	1.581515557278	1.773887269392
H	0.484836234218	0.757880290278	-2.558536983791
H	2.596321325011	0.697332906922	-3.726746687616
H	4.675747410355	-0.052907822425	-2.597593413117
H	4.540954341538	-0.760945550744	-0.221666242139
H	2.443571496861	-0.765717935615	0.964126096166
H	-0.383693880824	-2.341464470286	0.431294655145
H	-0.835930738820	-4.480670535972	1.639512668633
H	-0.986745305705	-4.462930385743	4.099173787236
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H	-0.223833556609	-0.287750959974	4.181948014781

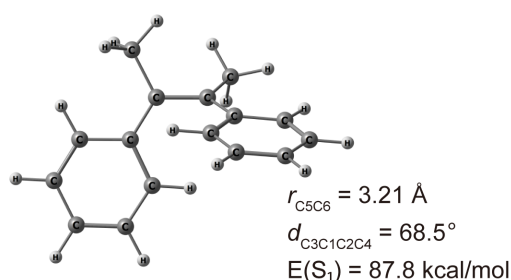
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C	2.477411356945	0.224677746378	-0.108274177293
C	1.826743070784	-1.687081539153	1.526370216253
C	-1.309456754251	0.008142603094	-0.749614751200
C	-1.042093876605	0.793414104175	2.166058084992

C	1.219431691520	-0.246741019500	-2.147679472904
C	2.392331396145	-0.350147274273	-2.832514095812
C	3.635944044047	-0.179860763704	-2.181107964499
C	3.655696669528	0.128945382689	-0.840869637817
C	1.124636626778	-0.536955404523	3.563158488405
C	2.118826016448	-1.168650808648	4.247487507346
C	2.996885663857	-2.066439761392	3.596974965466
C	2.820402715347	-2.328199576330	2.258066360174
H	-1.394849035774	0.852547390396	-1.433541494701
H	-1.413650695745	-0.895883654914	-1.350383437667
H	-2.159031676852	0.029216962891	-0.078803534453
H	-1.591694311522	0.187659125586	2.886040570174
H	-0.576628300933	1.605592764295	2.726104218751
H	-1.757194021634	1.253511470302	1.496165205171
H	0.292956865872	-0.391612753097	-2.674871901069
H	2.373816327209	-0.565057551855	-3.889151010849
H	4.552674806477	-0.260520712727	-2.741167335200
H	4.593442583886	0.320934233886	-0.344060618807
H	2.509361213429	0.648037081490	0.876008337268
H	1.591252879368	-2.043407795802	0.543065482253
H	3.445209341034	-3.053518741000	1.761687634461
H	3.773302297013	-2.561198258040	4.156402462993
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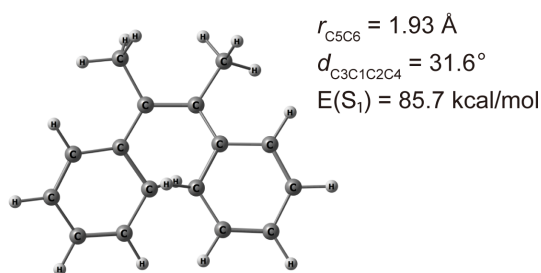
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C	0.000000000007	0.000000000001	1.437686038539
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C	0.436692049565	-1.106969569165	2.187185875256
C	2.482563791771	-0.087904452907	-0.115984679397
C	0.830075594878	-2.302722030853	1.515317576136
C	-1.332232030482	0.133482788483	-0.692421731625
C	-0.493937969747	1.250914451671	2.097653427897
C	1.193833084481	0.087266792234	-2.161111356004

C	2.359142812821	0.063779449805	-2.882304896371
C	3.602879625332	-0.031755480039	-2.251084993744
C	3.639512542541	-0.099537009680	-0.865072585726
C	0.559245651421	-1.096893324198	3.609094265267
C	1.025272841482	-2.190710644810	4.287891509529
C	1.387804640228	-3.354987019506	3.600143135824
C	1.282055097308	-3.398968355546	2.217611252920
H	-1.469891294030	-0.636297731728	-1.453483964612
H	-1.455658367491	1.096126276276	-1.198927182954
H	-2.153512914953	0.030282369370	0.011146124227
H	0.254310158758	2.038825822715	1.983561914073
H	-0.724691500429	1.145324159678	3.151538248210
H	-1.385145081765	1.613029154826	1.588943431143
H	0.257294318123	0.172971543609	-2.684264041357
H	2.311827847038	0.125071169001	-3.958756248740
H	4.511713356822	-0.047835348809	-2.828984008173
H	4.589614152042	-0.163996506830	-0.357429139853
H	2.553562636407	-0.133108882821	0.955533321031
H	0.746517869881	-2.336907115958	0.445429572071
H	1.561481994832	-4.293042655628	1.684540282984
H	1.750646563512	-4.210962303224	4.144787729004
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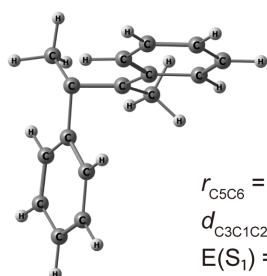
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C	1.199686115048	0.000000000000	-0.701390989291
C	1.049100307113	-0.646217870521	2.092516467578
C	2.396514002310	0.256847446508	0.117648683737
C	2.255523819333	-1.151000801266	1.427604862587
C	-1.311983855244	0.025579184157	-0.717037505705
C	-1.208503588464	0.434754167122	2.211712938697
C	1.360662430683	-0.439343797810	-2.041978494084
C	2.574469628601	-0.495899345794	-2.652960901653

C	3.704318260489	-0.066211836546	-1.905771489148
C	3.652260884971	0.276771099654	-0.593118663129
C	1.049802645709	-0.836437741859	3.503316926883
C	2.238799100090	-1.047710365463	4.161510947808
C	3.472706606017	-1.275574439660	3.530652703077
C	3.410217876553	-1.451806673222	2.171691529115
H	-1.221554747351	-0.129044984679	-1.783896426523
H	-1.999763858269	-0.703273776607	-0.296010540177
H	-1.764119239330	1.005321534182	-0.569668932804
H	-0.913106518163	1.009818598941	3.089055288143
H	-1.855124891241	1.082465684215	1.627620145787
H	-1.831361339394	-0.388804530509	2.573726864528
H	0.488006452405	-0.760059225553	-2.587395725085
H	2.679318152785	-0.802187745389	-3.678112144245
H	4.655746645629	0.012943489758	-2.412587018322
H	4.538110014313	0.610281088117	-0.078765703387
H	2.239407100082	1.027739439467	0.867116711871
H	2.097639329068	-1.805947036098	0.582783655058
H	4.263004508294	-1.826759973579	1.624240404690
H	4.375613768049	-1.406271970396	4.098871386590
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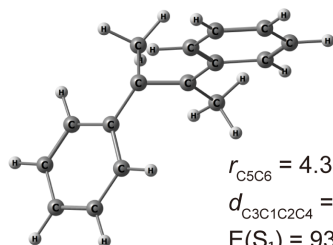
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C	2.243775510288	-1.085207212636	0.412779832074
C	-1.227627936432	-2.111851335721	1.442362612880
C	-0.582291893668	1.311076966847	-0.533715555750
C	0.508217603668	1.145383638830	2.267865459896
C	2.247691438643	1.026794296797	-0.717331393408
C	3.614202759577	0.930718475917	-0.873752512895
C	4.323956857891	-0.143513718022	-0.344476821448

C	3.623604859575	-1.146522466692	0.303466728380
C	-0.558867699180	-1.183847154556	3.580590168927
C	-1.198519144497	-2.213096872946	4.226467199814
C	-1.862021990720	-3.190652014144	3.482511552112
C	-1.882197049041	-3.137155397576	2.097897242525
H	-0.185401052467	2.264291257077	-0.143913327083
H	-0.433158445020	1.334849364665	-1.611334994322
H	-1.659319237238	1.331833568972	-0.373886762301
H	-0.357444230115	1.593143877593	2.758152164362
H	1.195088900941	0.838935448073	3.049809961098
H	0.987589614669	1.891801242851	1.653404803712
H	1.740563487841	1.881911997630	-1.127738044227
H	4.142118840549	1.712528908295	-1.398483768880
H	5.394754714489	-0.200549356576	-0.453559047961
H	4.149011083312	-1.999613540214	0.704734081203
H	1.719959488793	-1.921352230263	0.845269616755
H	-1.188571215933	-2.013253640874	0.373942564829
H	-2.397732459643	-3.896973422725	1.535134887312
H	-2.360239633682	-3.997436307051	3.995761284237
H	-1.190453095767	-2.268107931353	5.302019380971
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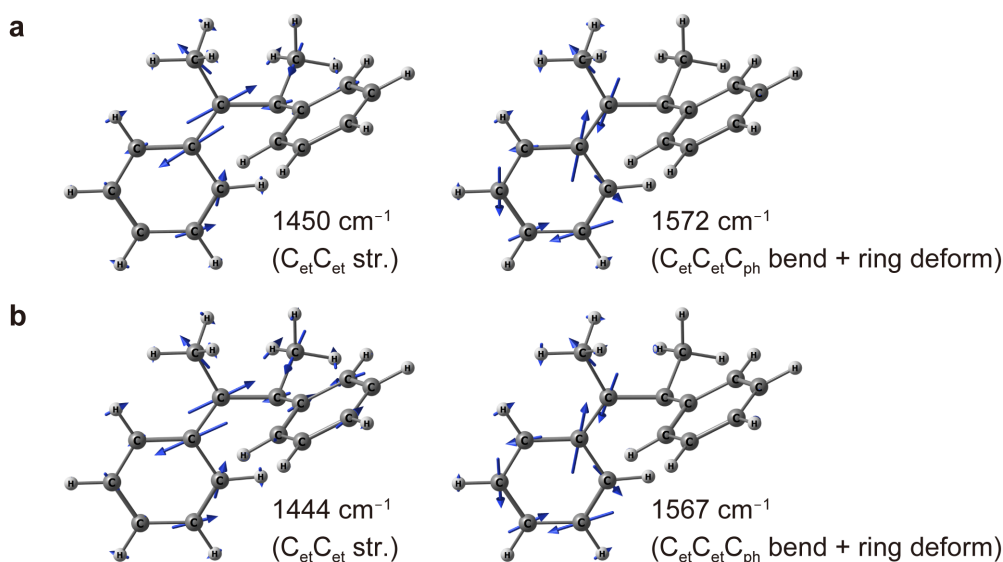
$(S_1/S_0)_{twist2}$



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C	-0.830633414704	-0.926707671457	2.153481617812
C	2.248257147016	-0.920885602942	-0.486274933777
C	-1.538250295839	-1.913801179777	1.453054071261
C	-0.709370997032	1.433830908198	0.000739195113
C	0.837075278625	0.954582708448	2.212324474317
C	1.442646145237	0.842834367539	-1.880980394486
C	2.599770450089	0.757021482347	-2.637780261063
C	3.598938442187	-0.150849106501	-2.330381421254
C	3.401618349834	-0.988653488132	-1.238644973522

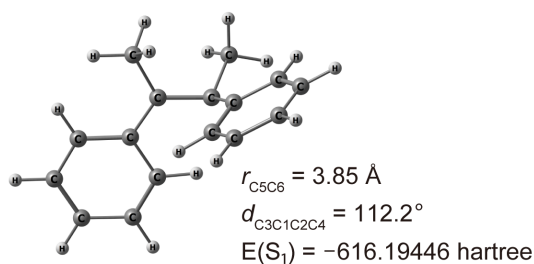
C	-0.912102893309	-0.901043671185	3.558482214068
C	-1.658012871570	-1.841317653166	4.232000379601
C	-2.341029704788	-2.823071763481	3.518119249050
C	-2.276333800398	-2.862344329762	2.133048428492
H	-0.047785403604	2.300530147925	0.063106403184
H	-1.197714615007	1.407701448461	-0.970159113492
H	-1.522659299545	1.562309272254	0.713490011357
H	0.283721750156	1.520055583156	2.956186810027
H	1.553701604361	0.330851827435	2.747602959661
H	1.393054265144	1.623229098871	1.572312295043
H	0.697985688554	1.567633669756	-2.165613941729
H	2.720620509821	1.423636029842	-3.478568567043
H	4.499732848951	-0.207641814745	-2.918566020994
H	4.159754367026	-1.708827883754	-0.968845900259
H	2.120145571755	-1.607105510770	0.337878458142
H	-1.472949674439	-1.880147834696	0.381466263865
H	-2.809264276941	-3.624033352993	1.589316648228
H	-2.925663245805	-3.556352311975	4.049748522348
H	-1.714479710123	-1.817538252930	5.307326803930
H	-0.382448782014	-0.155159887749	4.123168805331

8. Normal mode vectors including the movement of the central ethylenic carbons for the $(S_1)_{twist}$ and ^{13}C isotopomer, and Cartesian coordinates for $(S_1)_{twist}$



Supplementary Figure 12. Normal mode vectors including the movement of the central ethylenic carbons for (a) $(S_1)_{\text{twist}}$ and (b) its ^{13}C isotopomer: the $\text{C}_{\text{et}}\text{C}_{\text{et}}$ stretching mode and $\text{C}_{\text{et}}\text{C}_{\text{et}}\text{C}_{\text{ph}}$ bending mode with ring deformation calculated with SS-CASPT2/cc-pVDZ.

Cartesian coordinates (in Å) of $(S_1)_{\text{twist}}$ optimized at the SS-CASPT2/cc-pVDZ level



C	0.000000000000	0.000000000000	0.000000000000
C	-0.000000000084	-0.000000000079	1.467046158733
C	1.225410514901	0.000000000000	-0.735398722548
C	-0.488634370010	-1.262591604528	2.000005781805
C	2.433703017016	-0.070085228550	0.028079678753
C	-0.229592475447	-2.509826841745	1.344959844807
C	-1.329352267600	0.012815301291	-0.711799925707
C	-0.634869544415	1.288447881209	2.016069168203
C	1.292671914090	0.055025477681	-2.164070292230
C	2.531130116509	0.053304287841	-2.798076435479
C	3.719499081610	-0.014279332087	-2.030751141885
C	3.671058321296	-0.078524744562	-0.623467662615
C	-1.223067180160	-1.332550395049	3.223252280051
C	-1.645272172298	-2.557902131806	3.744586966920
C	-1.394879164327	-3.771121118422	3.082765013920
C	-0.682153374553	-3.721870260320	1.874992494357
H	-1.884523675868	0.886908253827	-0.343383044369
H	-1.308031189025	0.017278920554	-1.804245753964
H	-1.871037958817	-0.868684054564	-0.342888937110
H	-1.742848531491	1.319122151952	1.981477556860
H	-0.345069391781	1.422038466213	3.063902230250
H	-0.262065617512	2.174975154931	1.487435485297
H	0.394822512577	0.104167080657	-2.740308346341
H	2.583839545193	0.101256043610	-3.868933154622
H	4.658367658538	-0.016952100562	-2.542620470613
H	4.581665789836	-0.134419650890	-0.055402448177

H	2.313525888731	-0.109123269810	1.096962233046
H	0.352838546002	-2.516855681015	0.439361929186
H	-0.464524616267	-4.638239525474	1.343146468307
H	-1.729112075596	-4.697240892259	3.486411890660
H	-2.192961604604	-2.557609267250	4.678897309045
H	-1.446126664087	-0.427387491249	3.754661845897

9. Details of *ab initio* molecular dynamics (AIMD) simulation

The AIMD simulations, shown in Fig. 4b, were performed according to the flowchart in Supplementary Fig. 13. The initial samplings were conducted by the normal mode sampling, which samples the initial energy generated by the Boltzmann distribution at 300 K for initial coordinate displacements and velocities to their respective normal modes. The coordinate and velocity were developed by the velocity-Verlet algorithm:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t - \frac{1}{2} \frac{\mathbf{g}(t)}{\mathbf{M}} \Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) - \frac{1}{2} \frac{\mathbf{g}(t) + \mathbf{g}(t + \Delta t)}{\mathbf{M}} \Delta t$$

where $\mathbf{r}(t)$, $\mathbf{v}(t)$, and $\mathbf{g}(t)$ are vectors for molecular coordinates, velocities, and potential gradients at time t , respectively; Δt is the simulation timestep; $\mathbf{M}$ is the atomic mass matrix. The generated initial coordinates and velocities of the *trans*- and *cis*-side simulations are shown as follows.

Trans-side

Initial coordinate (in Å)

C	-0.01762014035546	-0.12027230132934	0.04194695189707
C	-0.02596418548114	-0.11462783152395	-1.35823252934360
C	-1.30091636494489	-0.12031463031740	0.75421839329448
C	1.26302785347056	-0.17558715959168	-2.16226716412392
C	-2.45476020192780	-0.94565269842751	0.52215331721314
C	2.29156372065162	-1.14663531000708	-1.88241239569217

C	1.25390376852594	-0.12851068506400	0.82054298207549
C	-1.19331241988284	0.16521390590665	-2.24957393384841
C	-1.43454637610807	0.86554487732974	1.72613177924153
C	-2.54442034563997	0.98528295528133	2.60905570666170
C	-3.56194014388228	0.06900886722383	2.50634214216932
C	-3.53232342806967	-0.85855020470989	1.46312986001297
C	1.47089299763496	0.71641944190179	-3.17784387384773
C	2.57813624177622	0.68553640916351	-4.00998714578651
C	3.63614961291924	-0.22751971129272	-3.67726841966243
C	3.49421858026356	-1.14535824504700	-2.64806019827989
H	1.17014047165648	0.61550982458780	1.60915042269464
H	2.14362263372790	0.05038730951355	0.20566188563246
H	1.44241288062887	-1.10676873285490	1.22378242486042
H	-1.03261436587861	1.11199586904334	-2.81931824024150
H	-2.07893551270876	0.24355862218835	-1.59620504020879
H	-1.36510650941827	-0.62631131892347	-3.02098198938372
H	-0.61134738266599	1.64674560729836	1.84595625346055
H	-2.58290081171703	1.86020055099223	3.25088132382468
H	-4.40975562830792	0.07894398573117	3.13584056825216
H	-4.53491704043767	-1.43480214982722	1.23698837580503
H	-2.41999194953989	-1.66277619950227	-0.28542784826500
H	2.12410689527586	-1.88707346703772	-1.05628603754049
H	4.37678402037792	-1.83523818681855	-2.30673357347191
H	4.60592245534773	-0.23756533260926	-4.26902516167740
H	2.53732007466182	1.37729218446938	-4.91751842995532
H	0.69611297454686	1.50922002077071	-3.48449963792140

Initial velocity (in atomic units)

C	0.00003743331672	0.00007367912838	0.00025317608071
C	-0.00002680792146	-0.00006820373828	-0.00002810764035
C	-0.00007413521380	0.00004474771260	-0.00006606167349
C	0.00000484511917	-0.00022310507049	0.00000847762468
C	0.00006201103348	-0.00007829689721	-0.00002864120128
C	0.00008842649932	-0.00020286962528	-0.00002366709137
C	0.00003130748147	-0.00037315072656	-0.00005506754548
C	0.00004425324723	0.00017962760989	-0.00012412541533
C	0.00000870789114	0.00000677620607	0.00006377896365
C	0.00004240318510	0.00020990660243	-0.00010907422189
C	-0.00010247415667	0.00003061763739	0.00003423240104
C	0.00006814224319	-0.00013041892347	0.00018780826788
C	-0.00019672722216	0.00000242106635	-0.00005325437529
C	-0.00009872349969	-0.00009281645361	-0.00000099158457
C	0.00003083746992	0.00002211776436	0.00018612175048

C	0.00006418764925	0.00037984482542	-0.00010411355569
H	-0.00012801462959	0.00032645217180	-0.00054324938485
H	0.00023182681173	0.00021767766990	0.00032253701489
H	-0.00047618373093	-0.00019369435121	0.00001755400114
H	0.00039699225692	0.00013158247770	-0.00037565575226
H	-0.00017297791960	0.00026386137526	-0.00056475630544
H	0.00012988591682	0.00045874533034	-0.00008945640320
H	0.00006209073081	0.00000977006518	-0.00016243885268
H	0.00003635036097	0.00036116831228	-0.00005496651867
H	-0.00036913198311	0.00014417552374	-0.00044373424933
H	0.00005400832002	0.00002267543870	0.00053474723619
H	-0.00032599416934	0.00046995029231	-0.00022589755693
H	0.00045373218577	-0.00029445826939	0.00013164326517
H	0.00036268575904	0.00054409706001	-0.00009513817247
H	-0.00022120224632	-0.00002828692835	-0.00015553703371
H	0.00021158329154	0.00047303333018	0.00029719553534
H	-0.00005141631361	-0.00029769088181	-0.00026564651651

Cis-side

Initial coordinate (in Å)

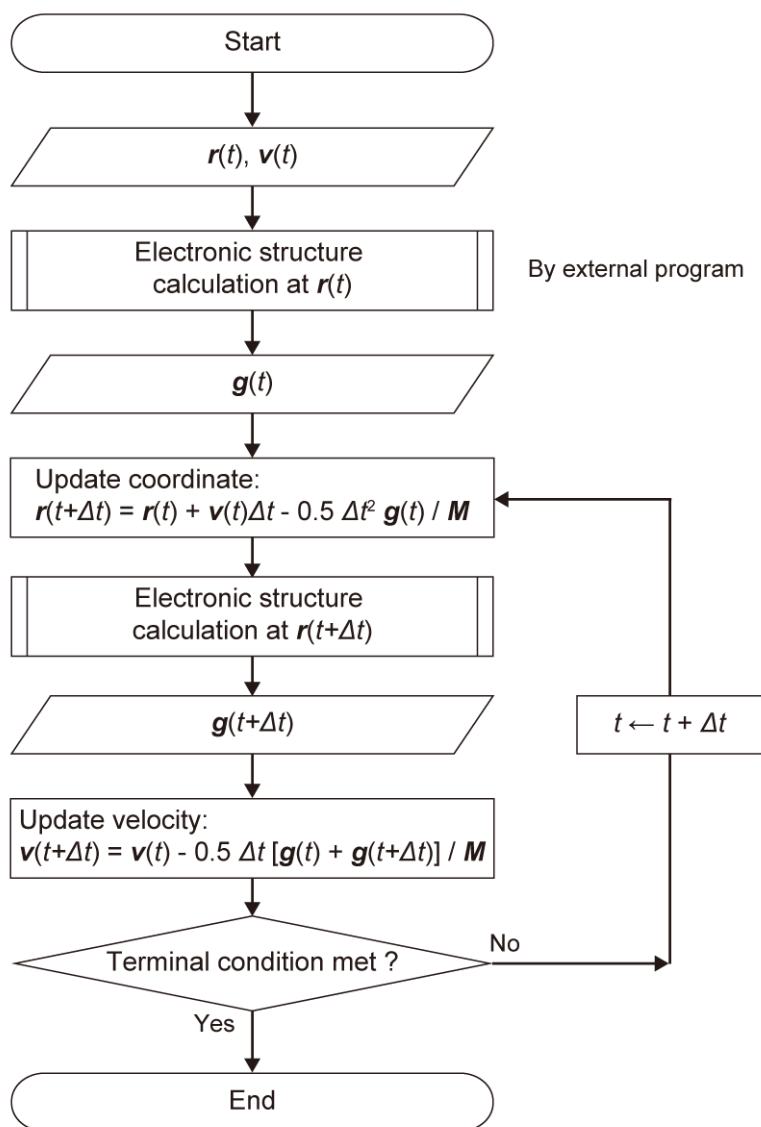
C	0.68004098865267	1.34162732346954	0.90434835255135
C	-0.56724656717103	1.60820724591186	0.43872305454524
C	1.31324963229959	0.01934325357792	0.75804097315157
C	-1.27580100469649	0.72069437274125	-0.52838969351425
C	-1.31789228192007	2.90674036175145	0.85166652089615
C	1.43334640659349	2.28814040646421	1.80116810454878
C	0.63754229647627	-1.09911334318389	1.19624167953358
H	2.93653441871295	-3.40149341354862	0.39218050630080
H	0.73228486958217	-3.30685717972668	1.27401828782433
C	3.17762639187150	-1.32701532649470	0.09153925113315
H	-0.33105463659398	-1.00175279648564	1.78092830477280
H	4.14987988978832	-1.33546060210933	-0.26835151527600
C	2.57099052846633	-0.09339386114850	0.20262506283393
C	2.48466685264637	-2.45886667569952	0.43947341337672
C	1.19959519235271	-2.35058906835700	0.98256346064130
C	-2.57542478195168	0.30900908388881	-0.26707891609861
C	-0.62240573761256	0.19384565254612	-1.66354082201609
C	-1.31336566213169	-0.73159601420481	-2.43552797577009
C	-3.23756796544147	-0.68898271390139	-0.97089423520589
C	-2.61032789201436	-1.16563092786279	-2.10168294635661
H	0.32326015000738	0.59937170065073	-1.99696129436154

H	-0.84554900666012	-1.17326886456781	-3.29475947062094
H	-4.21099904337151	-1.07814766158485	-0.74236039048693
H	-3.13469248939041	-1.85381324645102	-2.73301935905513
H	-0.99493476076002	3.24361148346682	1.91675639348518
H	-1.05369010738415	3.74314399499448	0.05717445368212
H	-2.50329328231074	2.64828955845640	0.70664775594129
H	1.78013190128430	1.86544167684901	2.75787532234668
H	2.35816265484901	2.48559729770450	1.30472671622881
H	1.05235373976879	3.28168062668601	1.94215241426508
H	-3.05623855068311	0.76881392559732	0.61100818179355
H	3.07162208317539	0.80166943107755	-0.12444867297294

Initial velocity (in atomic units)

C	0.00010933355588	0.00016518349261	-0.00016651400631
C	-0.00001546242551	-0.00006493392732	0.00022244830639
C	-0.00016151229950	-0.00013529839515	0.00030144026465
C	0.00000166666181	0.00010248805416	-0.00018568370360
C	-0.00006172499039	0.00004409783586	0.00010412127398
C	0.00005836631330	-0.00004363177958	0.00034182084103
C	0.00005002448770	0.00008514493528	0.00021777142163
H	-0.00029939159885	0.00040274656293	-0.00001268285006
H	0.00061993200893	0.00024482614355	-0.00051165996781
C	-0.00010387264087	-0.00019035390831	-0.00008744209043
H	-0.00067355645646	-0.00037772486059	0.00080745688990
H	-0.00144276707149	-0.00066754313989	-0.00057958888025
C	-0.00017047227514	-0.00002499567927	-0.00046470298668
C	0.00004560936070	0.00018939901735	-0.00014094566194
C	0.00010482939953	-0.00038169138096	0.00021022314031
C	-0.00004704230367	0.00015661296086	0.00024776934433
C	-0.00018150258869	-0.00018235542114	0.00000898344846
C	0.00007861053857	-0.00008997897897	-0.00026955028661
C	0.00013036656929	-0.00004621936706	-0.00003702562586
C	0.00019084785928	-0.00004030497530	-0.00015005700884
H	0.00011915974330	-0.00040052991423	0.00092523418249
H	0.00038038129245	0.00013059862884	0.00018663803533
H	-0.00042542782253	0.00122729573444	-0.00053610941831
H	0.00075041540502	-0.00058148451131	0.00005494703025
H	0.00012871131555	0.00080450387155	-0.00030364206465
H	0.00098134939727	-0.00064179304849	0.00068404640675
H	0.00085405260137	0.00003472746895	-0.00061960443269
H	0.00070233666282	0.00096651542444	-0.00064589946677
H	-0.00029482851534	0.00162208893609	0.00060351027105
H	-0.00082193022653	0.00111353874862	-0.00103650962947

H	0.00000212036386	0.00068991857478	-0.00044280751155
H	-0.00091499306267	0.00087616661721	-0.00039244408662



Supplementary Figure 13. Flowchart of velocity-Verlet algorithm in the SPPR program³.

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