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

Supporting Information

Probing the π→π* photoisomerization mechanism of *trans*-azobenzene by multi-state *ab initio* on-the-fly trajectory dynamics simulation

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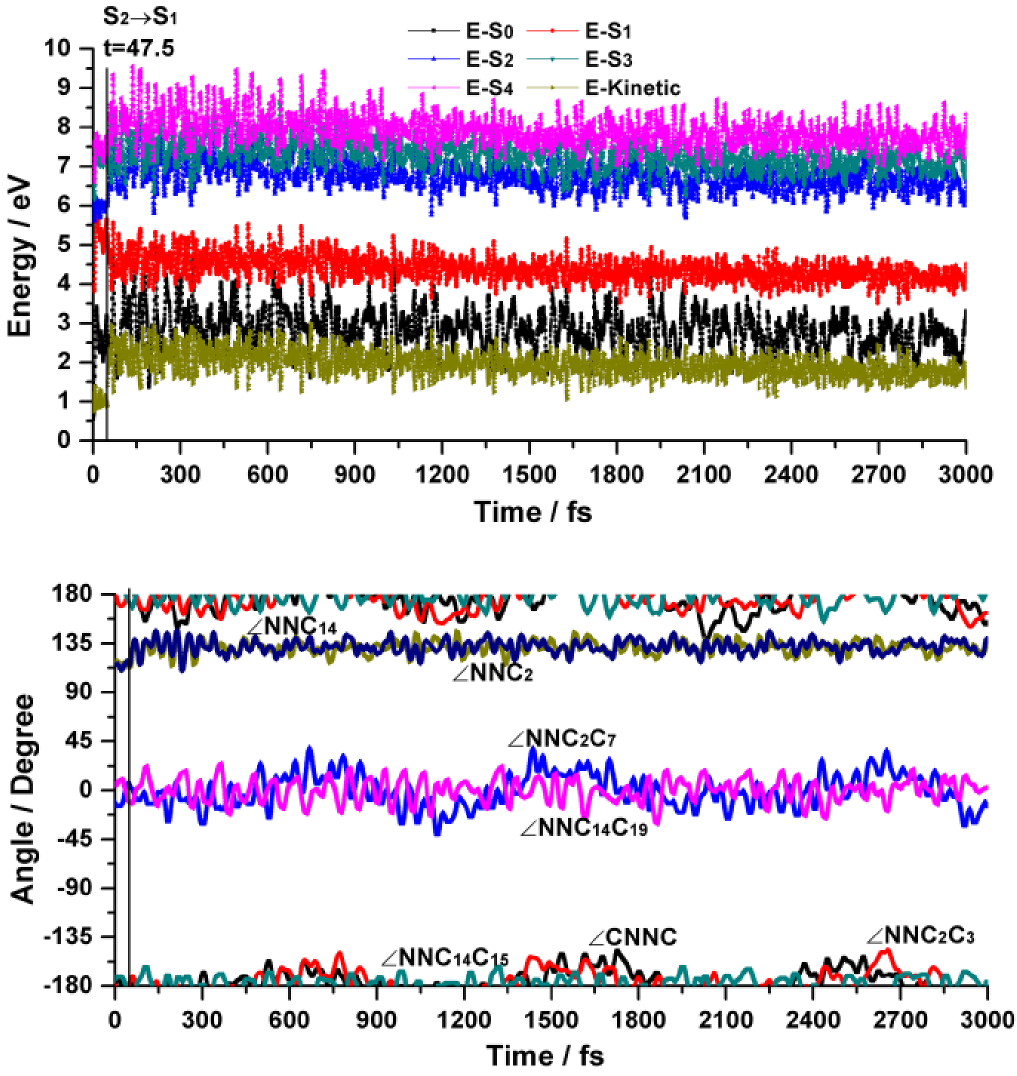

Fig. S1 Typical resonance trajectory starts from Franck-Condon region on S_2 state of *trans*-azobenzene and ends in Franck-Condon region of S_1 state. Upper panel is for evolution of potential energy profile and lower panel is for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles.

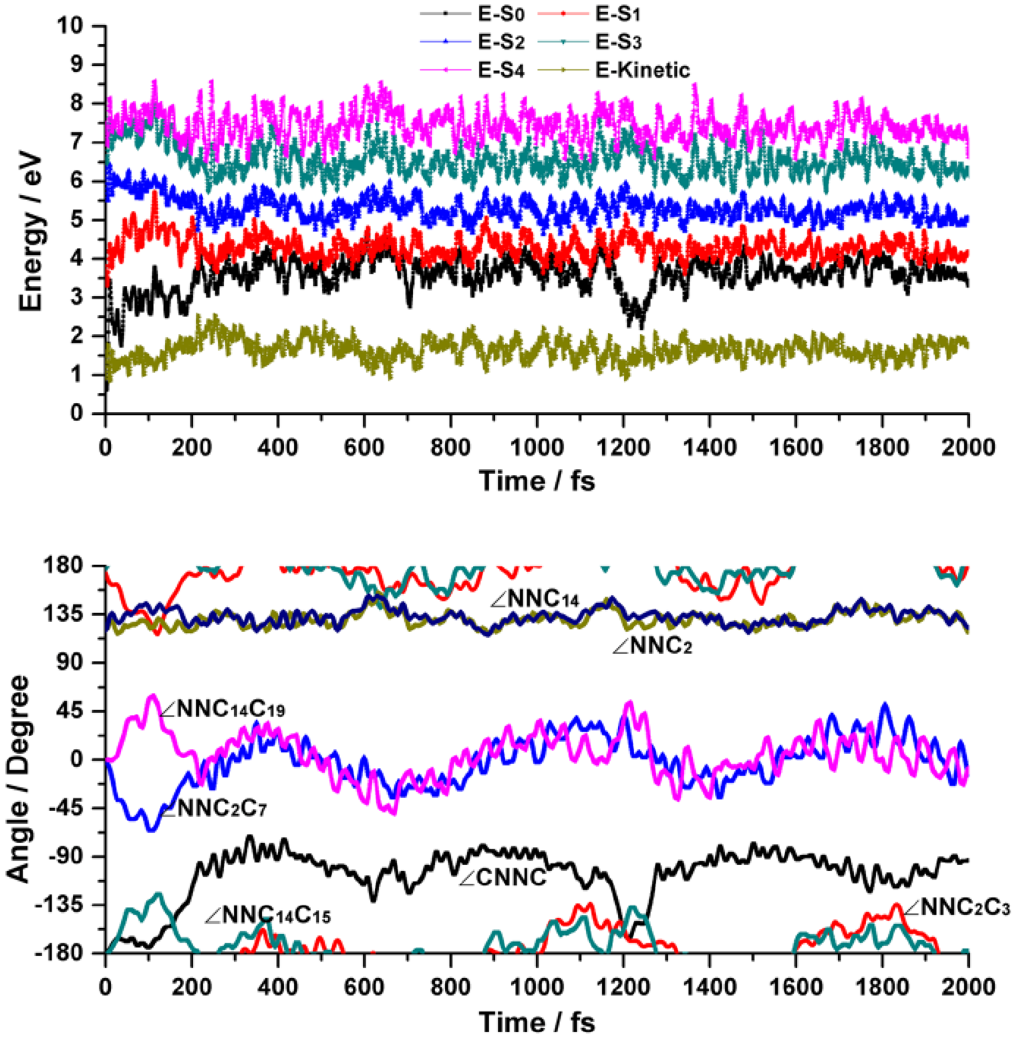

Fig. S2 Typical resonance trajectory starts from Franck-Condon region on S_2 state of *trans*-azobenzene and ends in *rot* S_2 state. Upper panel is for evolution of potential energy profile and lower panel is for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles.

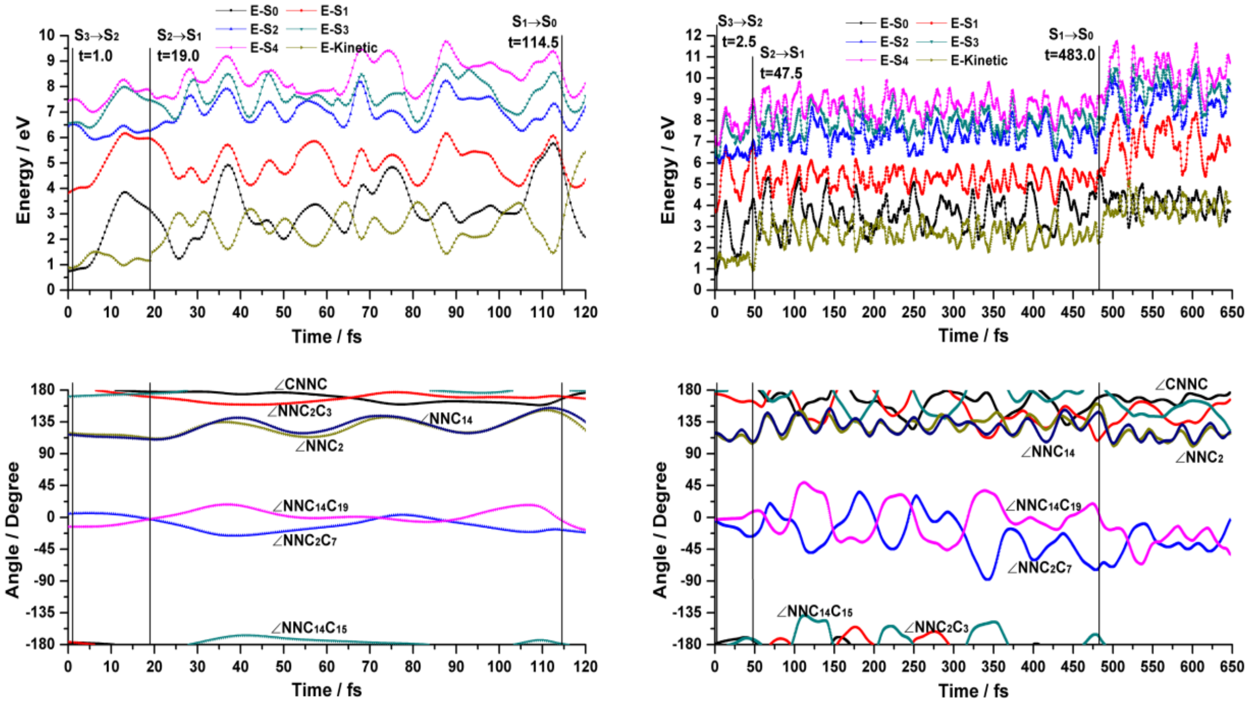

Fig. S3 The *trans*-1 case (starting from S_3 state of *trans*-azobenzene) with upper panels for evolution of potential energy profiles and lower panels for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles. The left (right) panels represent one typical fast (slow) nonreactive trajectory.

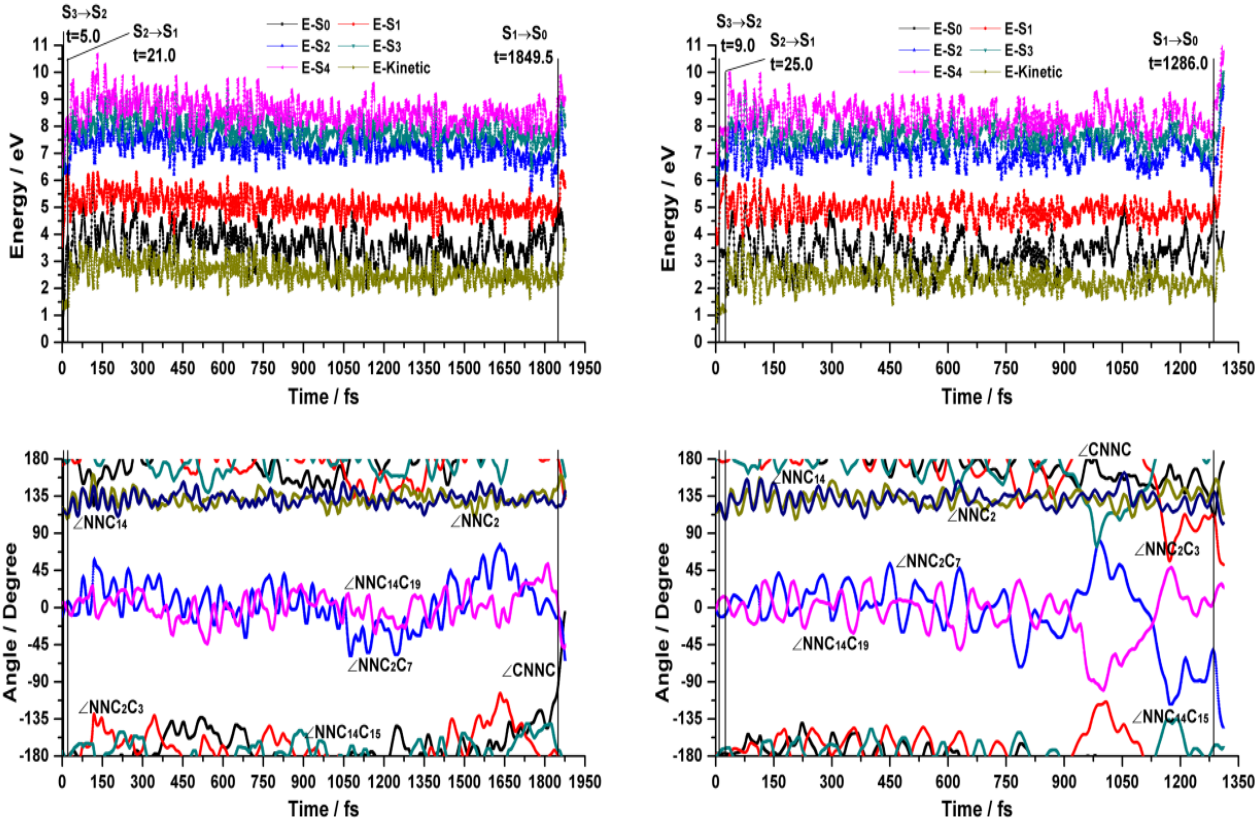

Fig. S4 The *trans*-2 case (starting from S_3 state of *trans*-azobenzene) with upper panels for evolution of potential energy profiles and lower panels for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles. The left (right) panels represent one typical reactive (nonreactive) trajectory.

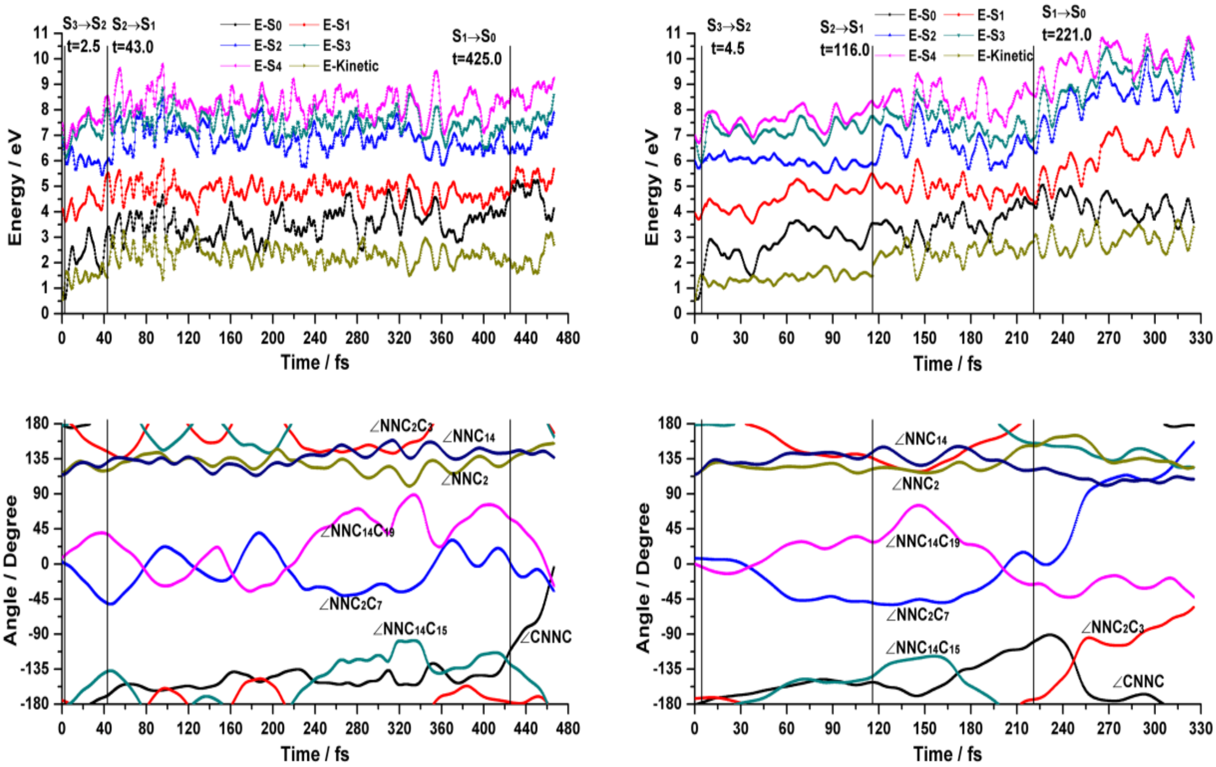

Fig. S5 The *trans*-3 case (starting from S_3 state of *trans*-azobenzene) with upper panels for evolution of potential energy profiles and lower panels for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles. The left (right) panels represent one typical reactive (nonreactive) trajectory.

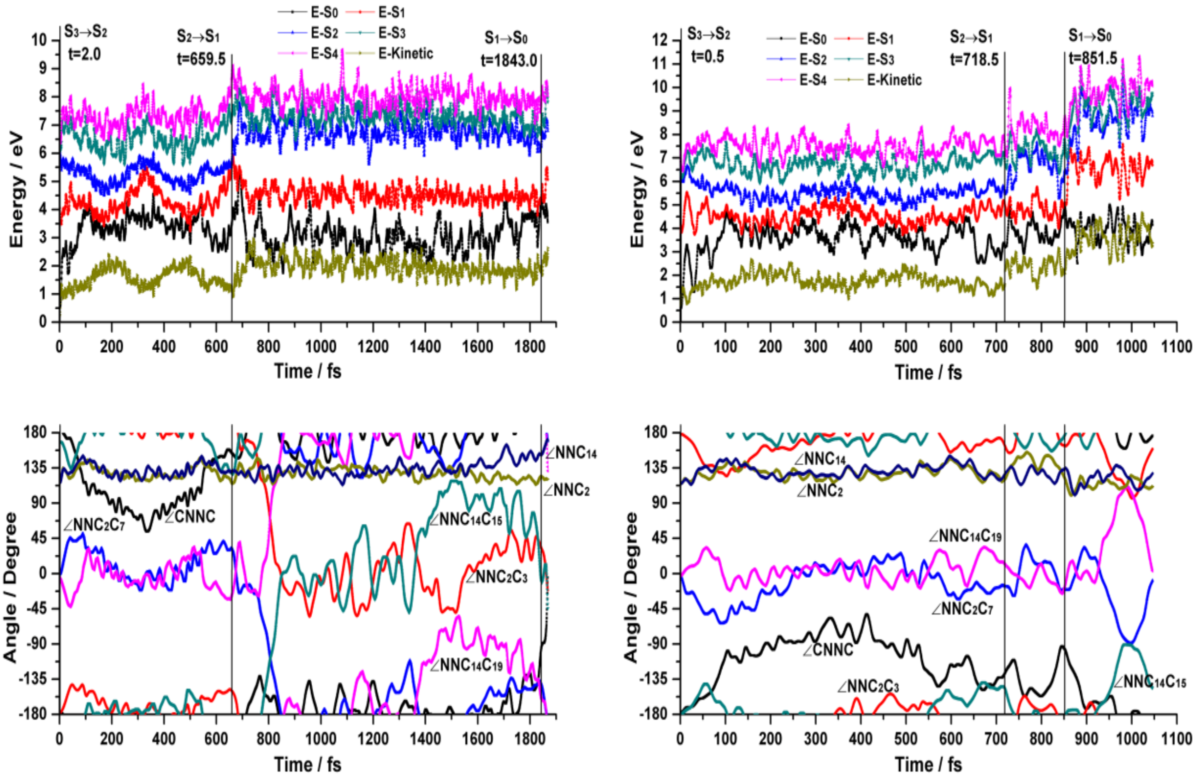

Fig. S6 The *trans*-4 case (starting from S$_3$ state of *trans*-azobenzene) with upper panels for evolution of potential energy profiles and lower panels for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles. The left (right) panels represent one typical reactive (nonreactive) trajectory.

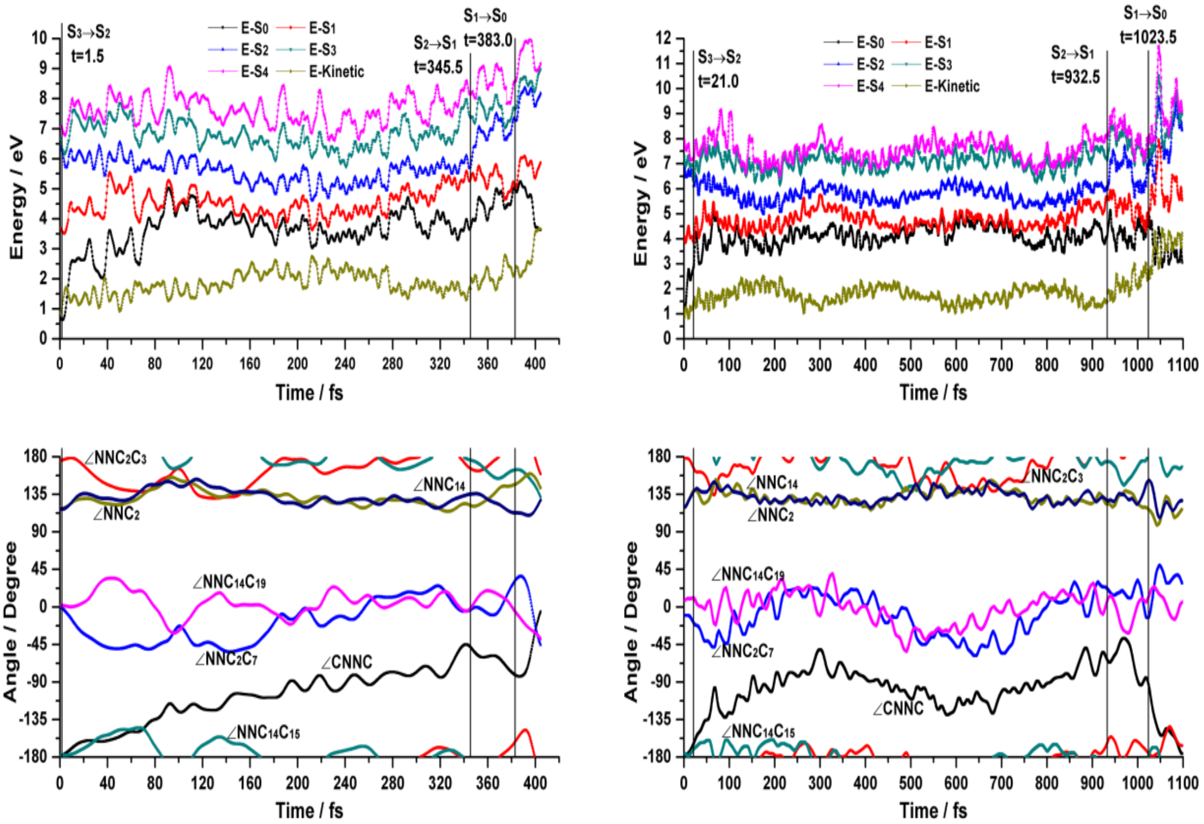

Fig. S7 The *trans*-5 case (starting from S_3 state of *trans*-azobenzene) with upper panels for evolution of potential energy profiles and lower panels for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles. The left (right) panels represent one typical reactive (nonreactive) trajectory.

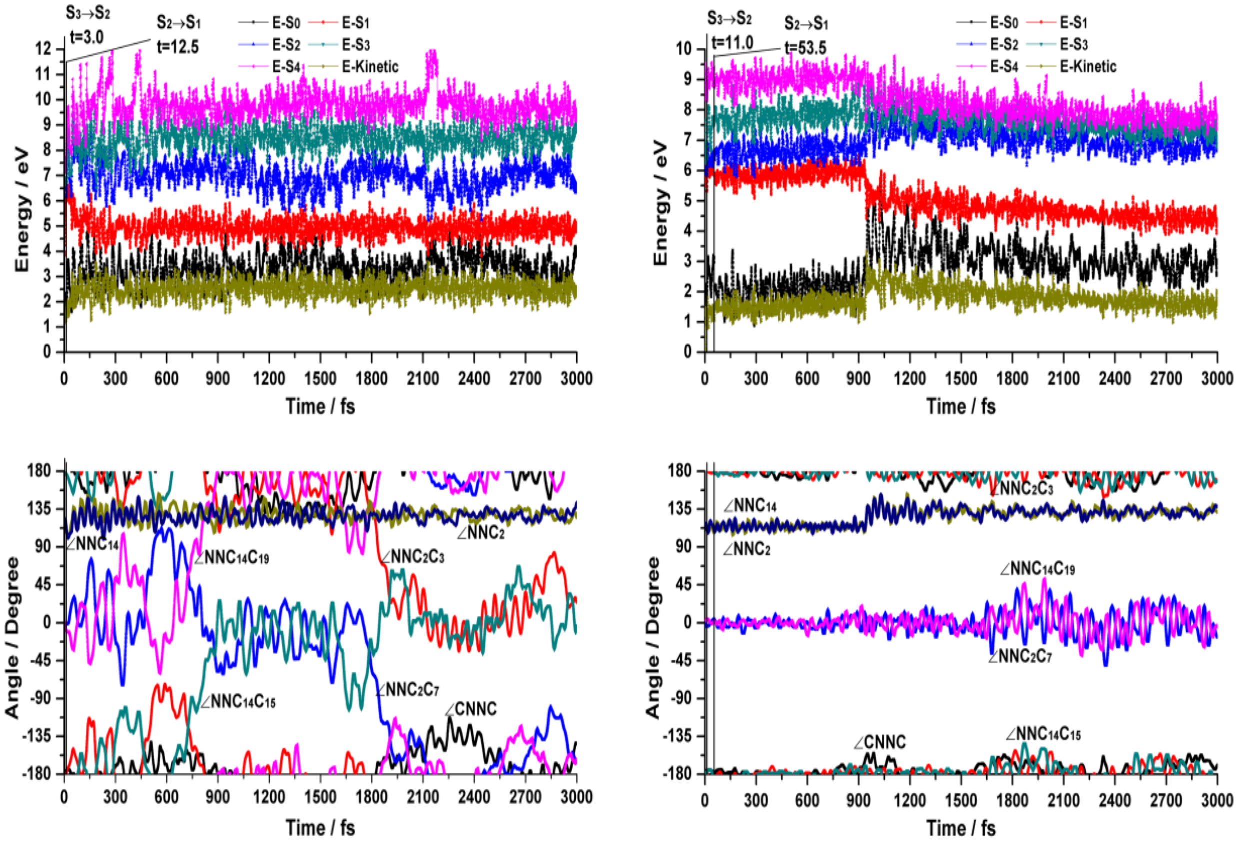

Fig. S8 Typical resonance trajectory starts from Franck-Condon region on S_3 state of *trans*-azobenzene and ends in Franck-Condon region of S_1 state. Upper panel is for evolution of potential energy profile and lower panel is for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles.

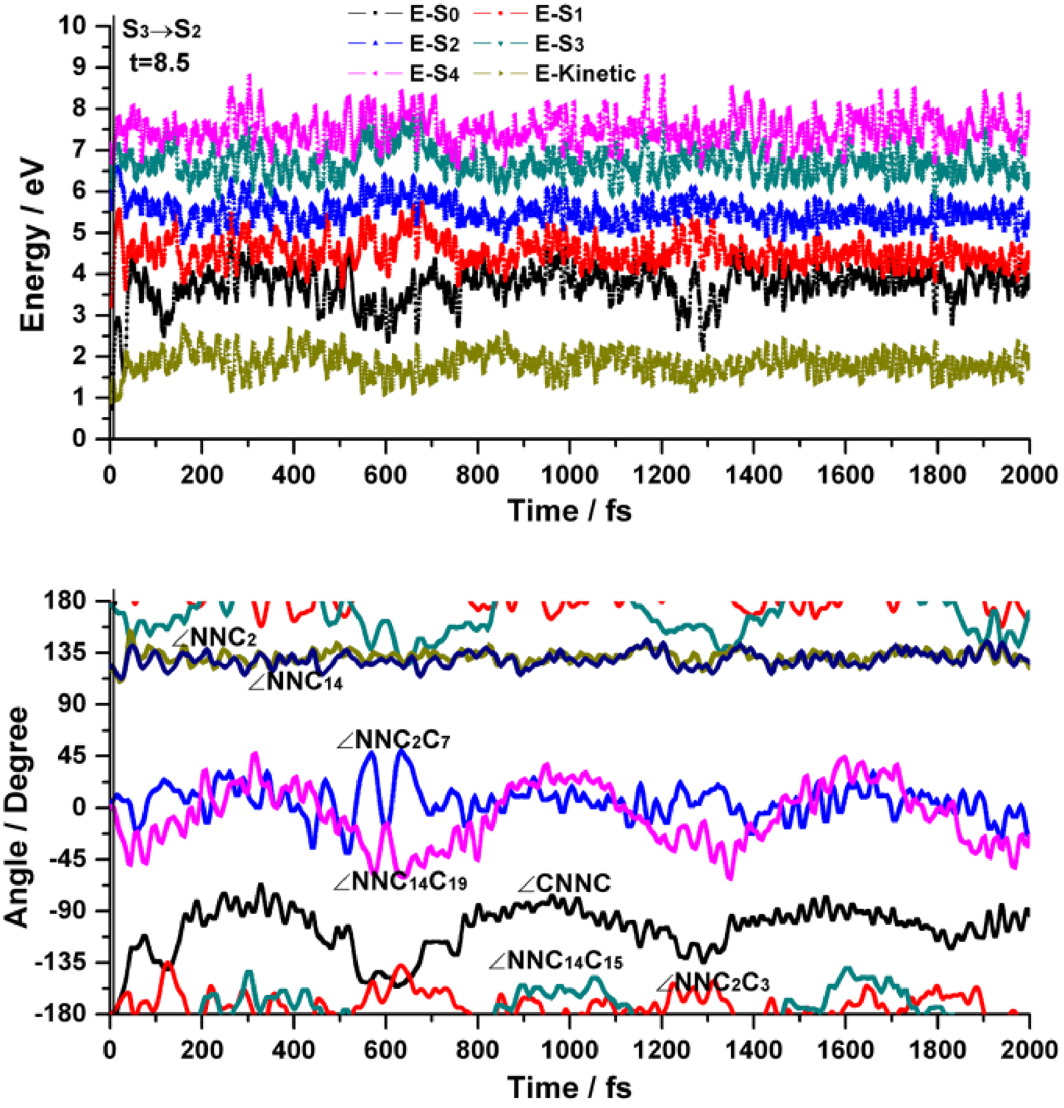

Fig. S9 Typical resonance trajectory starts from Franck-Condon region on S_3 state of *trans*-azobenzene and ends in *rot* S_2 state. Upper panel is for evolution of potential energy profile and lower panel is for evolution of two NNC bond angles, CNNC and four NNCC dihedral angles.