**A comprehensive benchmark of the XMS-CASPT2 Method for the Photochemistry of a Retinal Chromophore Model**

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**Figure S1.** Energy profiles (in kcal mol-1) along the BLA pathway at various methods relative to *cis*-PSB3 ground state energy using (A) SS-SR and (B) MS-MR contraction schemes for MRPT2 calculations. The solid line represents the diabatic *Ψ*DIR state while the dashed line the *Ψ*CT state. The positions of the transition states (TSCT and TSDIR) and the conical intersection along the BLA coordinate (CIBLA) are indicated by the vertical dashed lines in gray. The approximate position of the surface crossings at each method is indicated by a filled circle.

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**Figure S2.** Energy profiles (in kcal mol-1) along the MEPCT pathway at various methods relative to *cis*-PSB3 ground state energy using (A) SS-SR and (B) MS-MR contraction schemes for MRPT2 calculations.

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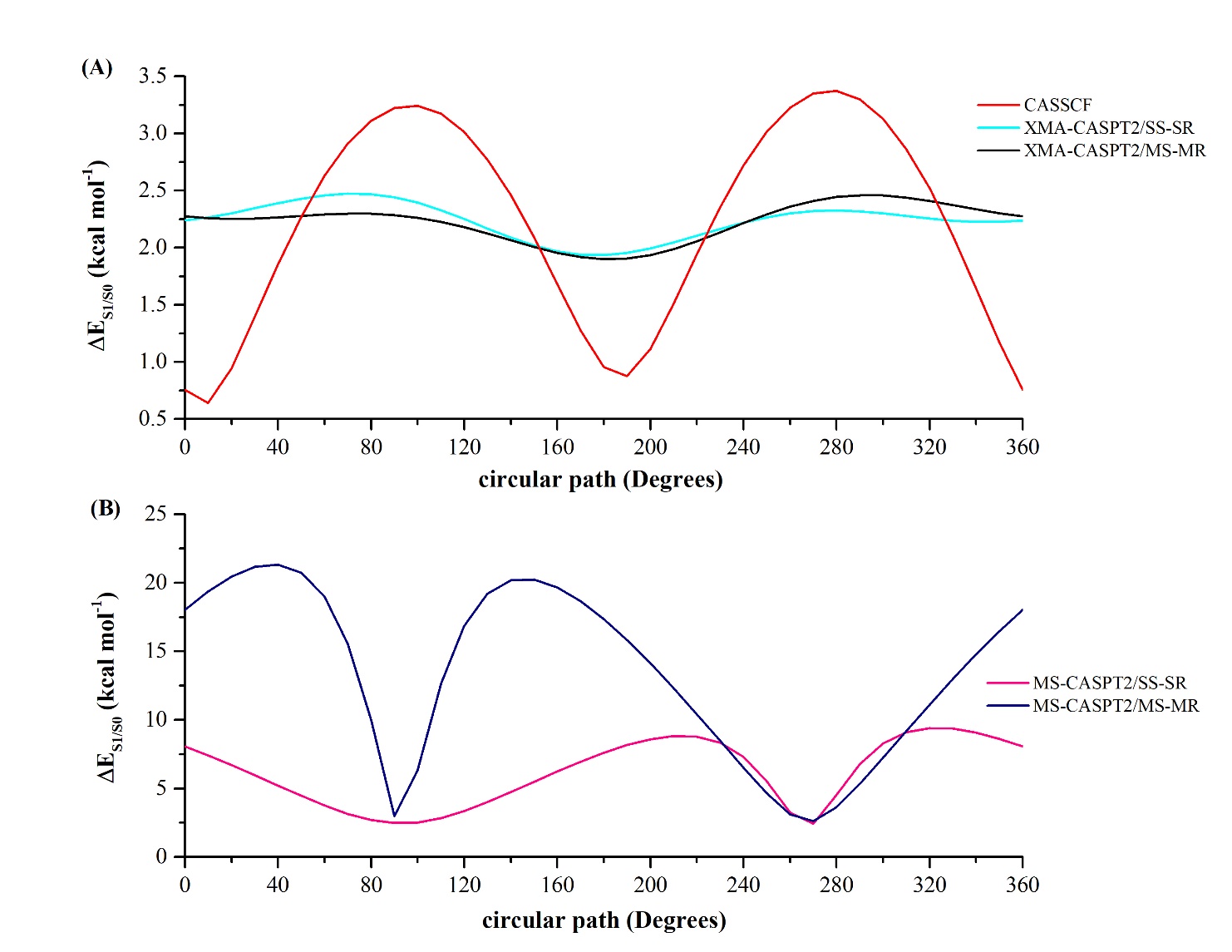
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**Figure S3.** Energy profiles (in kcal mol-1) along the MEPDIR pathway at various methods relative to *cis*-PSB3 ground state energy using (A) SS-SR and (B) MS-MR contraction schemes for MRPT2 calculations.

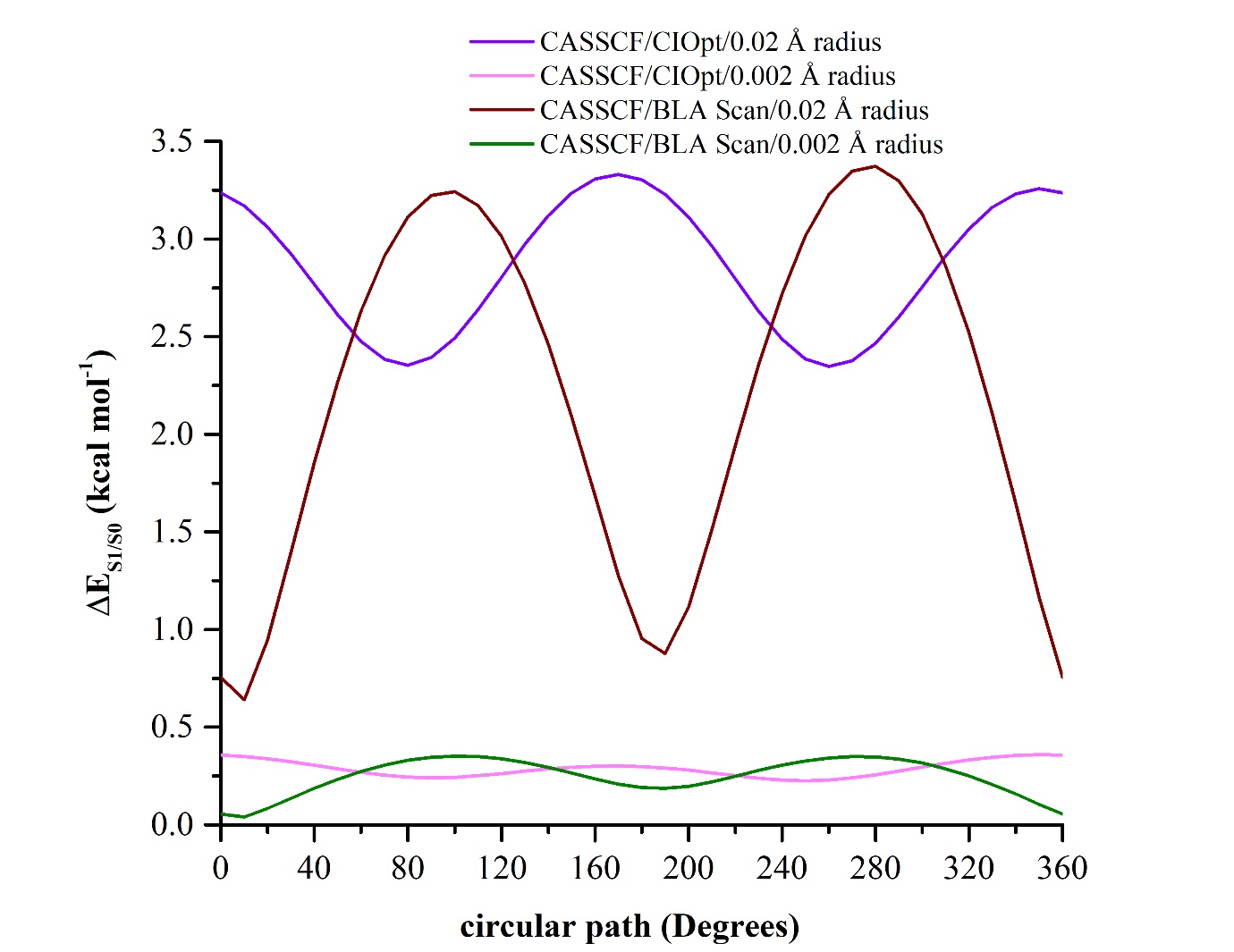
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**Figure S4.** Energy profiles (in kcal mol-1) along the composite CASSCF paths comprising MEPCIS, CI seam and MEPTRANS pathways relative to *trans*-PSB3 ground state energy using (A) SS-SR and (B) MS-MR contraction schemes for MRPT2 calculations. The insets show the 12 points nearest to each of the *cis*- and *trans*-PSB3, and the CI seam.



**Figure** **S5**. S1–S0 energy profiles (in kcal mol-1) of PSB3 along the circular loop centered around the crossing point along BLA scan at (A) CASSCF (red), XMS-CASPT2/SSSR (cyan), XMS-CASPT2/MSMR (black), and (B) MS-CASPT2/SSSR (pink) and MS-CASPT2/MSMR (navy) methods.



**Figure** **S6**. S1–S0 energy profiles (in kcal mol-1) of PSB3 along the circular loop centered around the optimized conical intersection and crossing point along BLA scan at CASSCF method for two different circle radius.