

Novel Products From $C_6H_5 + C_6H_6/C_6H_5$ Reactions

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Supporting Information:

Figure S1. Temperature profiles of the pyrolysis zone of the reaction tube recorded at three different supplied voltages. Typically the length of the heater was 22 cm, and was fixed in between 2 and 24 cm in the above profiles. Measurement of temperature was performed from the point 2 cm before the pyrolysis zone to 3 cm after the pyrolysis zone by carefully moving the K-type thermocouple from up towards down-stream zone.

Figure S2. Geometries of transition states, TS0 – TS13 in figure 4(a), calculated by UB3LYP/6-311G(d,p). Values in parentheses denote $\langle s^2 \rangle$ (actual eigenvalue of the s^2 operator), bond distances (r) in angstroms, angles (a) and dihedral angles (d) in degrees.

Figure S3. Details of the reaction channels involved in the isomerization of biphenyl into cyclopenta[a]indene + H₂ (H-atoms have been omitted frequently for clarity). A conrotatory pathway is preferred in the electrocyclic ring-closing reactions of benzofluvene, according to the Woodward-Hoffman rules. Dihydrocyclopenta[a]indenes interconvert into each-others because of frequent interchanging of 1,5-hydrogen atoms. Alphabets A, B, and C on the shoulder correspond to those in figure 4(b). See text for an asterisk on the right shoulder of numerals.

Figure S4. Details of the reaction channels showing the conversion of dihydrocyclopenta[a]indenes, dihydro-as-indacenes, and spiro[H-pentalene-cyclopentadiene]s into acenaphthylene + H₂ (H-atoms have been omitted for clarity). Rearrangement of carbon-carbon framework is typically due to 1,5- and 1,9-hydrogen shifting reactions. Alphabets D and E on the shoulder and channels F, G correspond to those in figure 4(b). See text for an asterisk on the right shoulder of numerals.

Figure S5. Details of the reaction channels showing the conversion of dihydro-as-indacenes into naphthalene + acetylene and as-indacene + H₂ (H-atoms have been omitted frequently for clarity). Alphabet J on the shoulder and channel H correspond to those in figure 4(b). The result of IRC (intrinsic reaction coordinate) calculations at the employed level of theory shows that 3a,8a-dihydro-as-indacene is converted to Im1 via TS1 and Im1 is further converted to 1,4-dihydro-1,4-ethenonaphthalene via Im2. Finally, 1,4-dihydro-1,4-ethenonaphthalene is dissociated into naphthalene + acetylene via TS4. See also figure S4 and S6 for molecular hydrogen elimination from dihydro-as-indacenes. As for the magnitude of enthalpy with an asterisk on the right shoulder of numerals, the reference state of Im2, TS2, and TS3 is Im1. See main text for details.

Figure S6. Details of the reaction channels showing the conversion of dihydro-as-indacenes into dihydro-s-indacenes followed by dissociation to s-indacene + H₂ (H-atoms have been omitted frequently for clarity). Alphabet K on the shoulder and channels I correspond to those in figure 4(b). See text for an asterisk on the right shoulder of numerals.

Figure S7. Details of the reaction channels showing the conversion of biphenyl radical to acenaphthylene + H (H-atoms omitted frequently for clarity). Channels A, B, C and D correspond to those in figure 5(b).

Temperature profiles shown in figure S1 clearly show that highest temperature is just before the pinhole and there is some thermal stability just before and after the pinhole. It should be noted that the tip of K-type thermocouple was adjusted just in front of the pinhole to record the reaction temperature at which the gaseous mixture was sampled into the ionization region of Mass spectrometer for the analysis of the composition by the TOF-MS.

However, in figure S2, intermediate species representing the transition states TS0 to TS13 in figure 4 (a) of the main text, have been shown with some characteristic features. Among many pathways connecting to two wells in figure 4(b) of the main text, intentionally details of some specific channels involving the lowest potential barrier have been presented here in figures S3-S6. Briefly, figure S3 shows preferred production of cyclopenta[a]indene, figure S4 shows the preferred production of acenaphthylene, figure S5 shows the preferred production of naphthalene + C₂H₂, and figure S6 shows the production of s-indacene + H₂.

Similarly, among many reaction channels representing the conversion of *o*-biphenyl radical into biphenylene, cyclopenta[a]indene and acenaphthylene as can be seen in figure 5(b) of main text, only energetically the most preferred pathways producing acenaphthylene from *o*-biphenyl radical is included in figure S7.

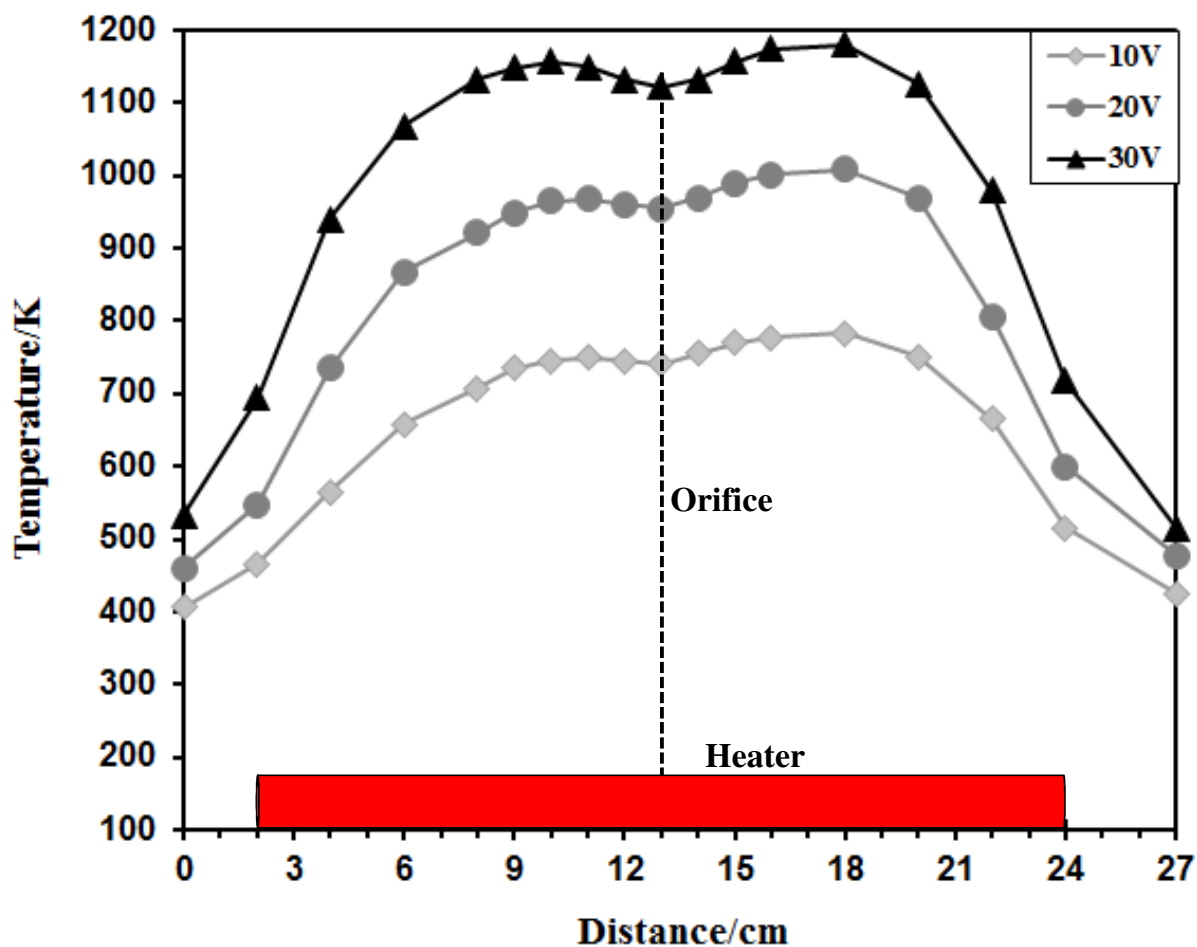


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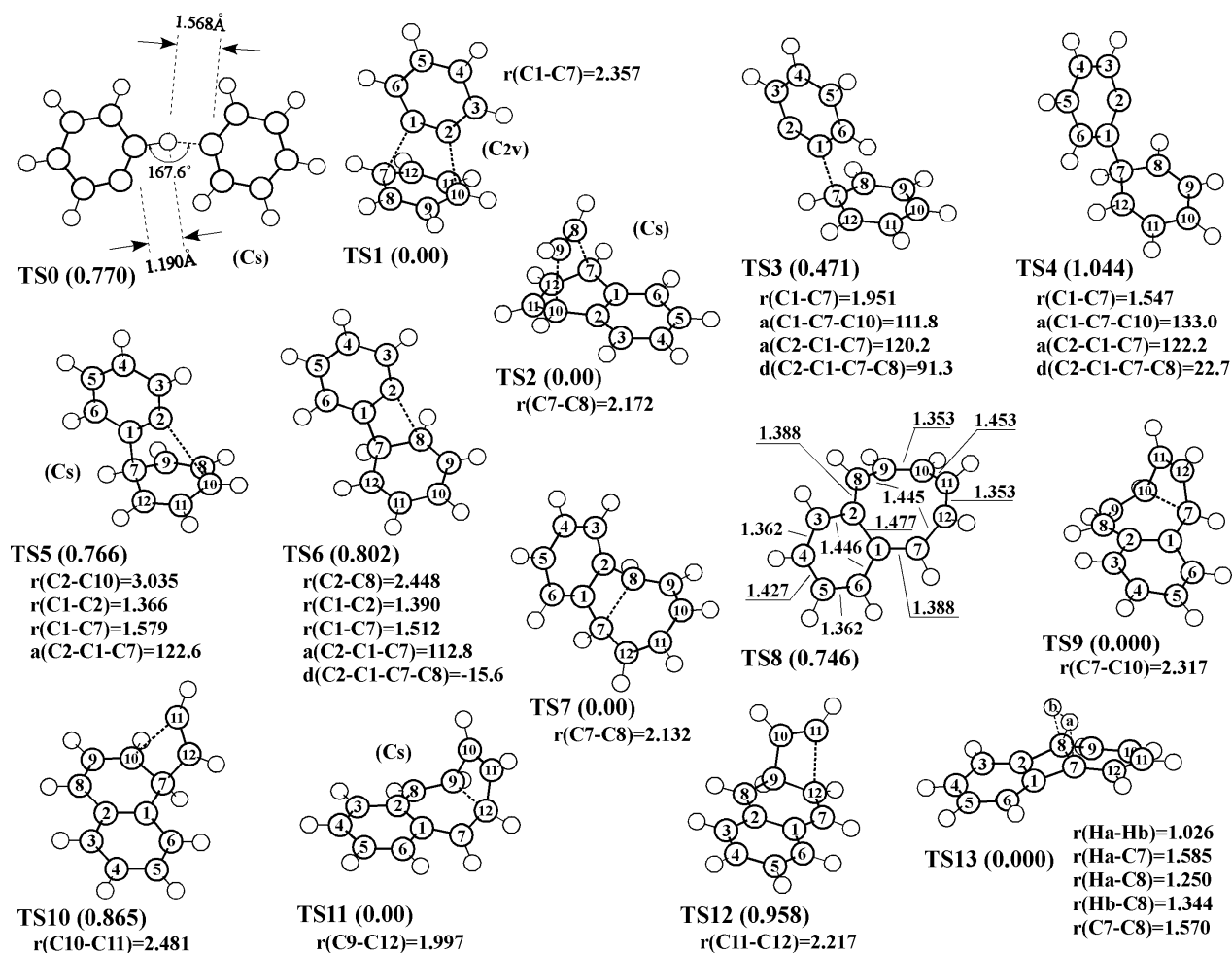


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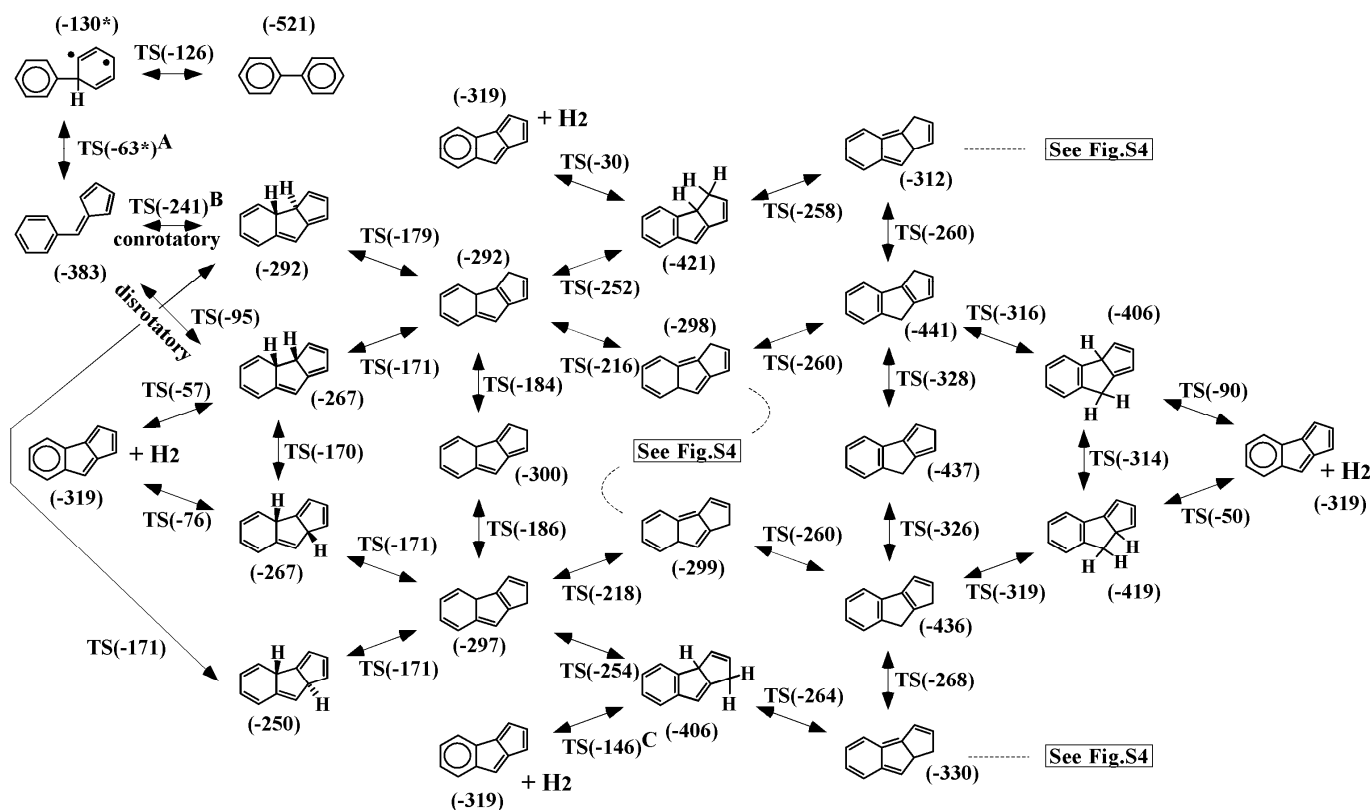


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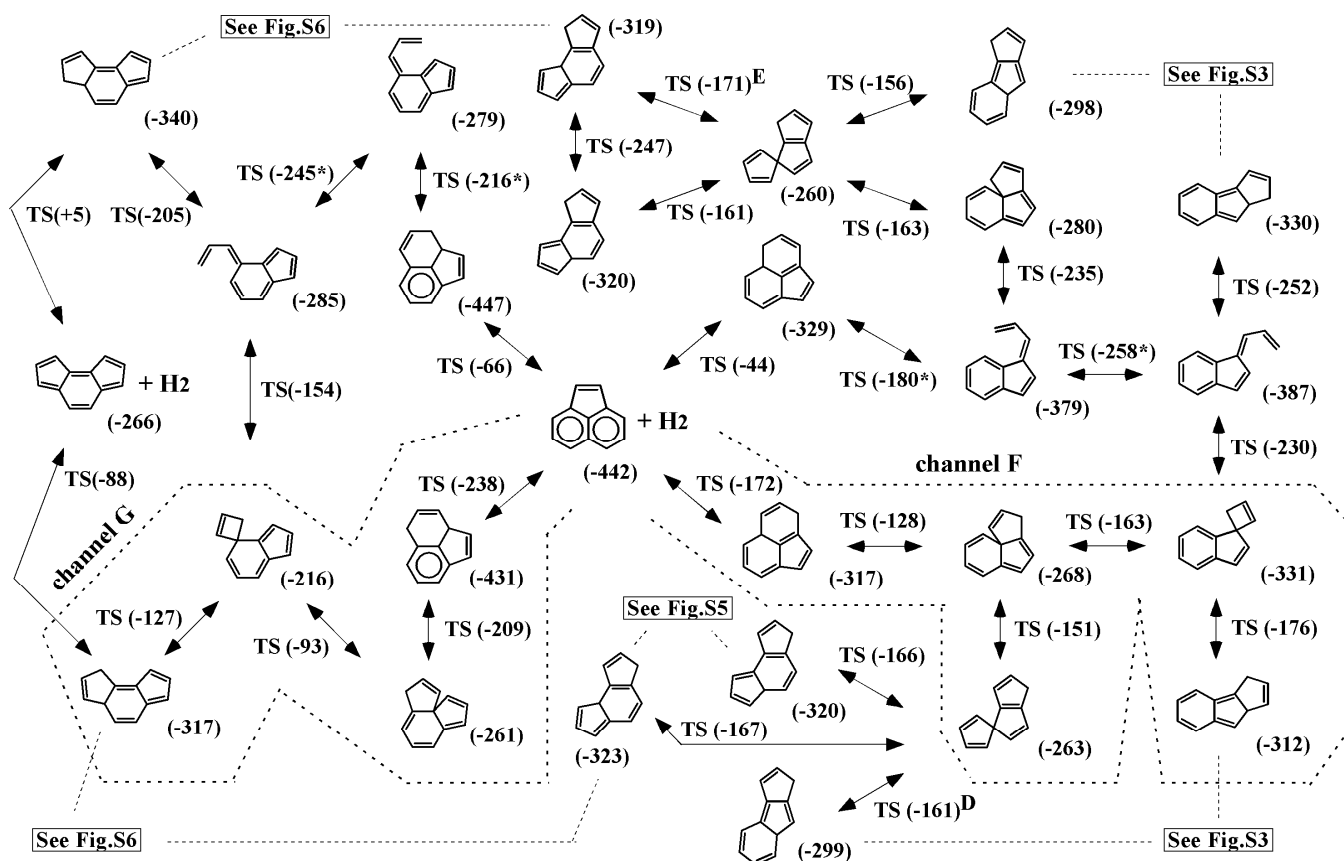


Figure S4. Details of the reaction channels showing the conversion of dihydrocyclopenta[a]indenes, dihydro-as-indacenes, and spiro[H-pentalene-cyclopentadiene]s into acenaphthylene + H₂ (H-atoms have been omitted for clarity). Rearrangement of carbon-carbon framework is typically due to 1,5- and 1,9-hydrogen shifting reactions. Alphabets D and E on the shoulder and channels F, G correspond to those in figure 4(b). See text for an asterisk on the right shoulder of numerals.

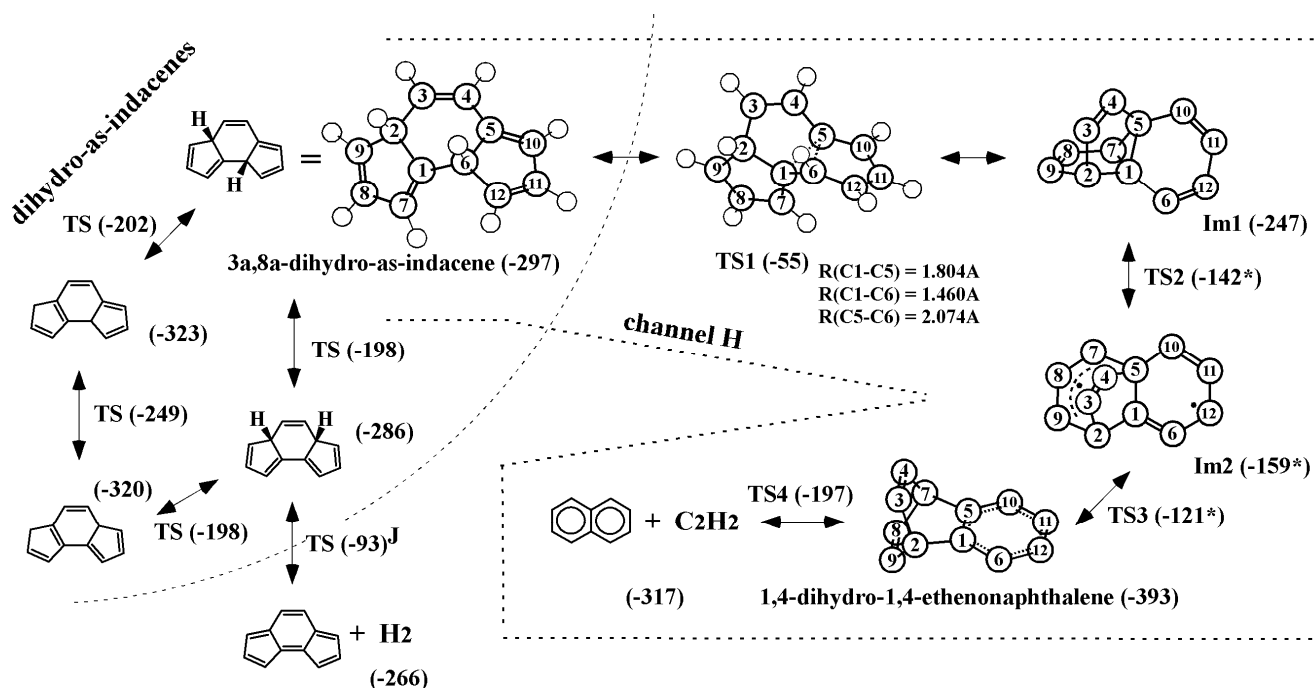


Figure S5. Details of the reaction channels showing the conversion of dihydro-as-indacenes into naphthalene + acetylene and as-indacene + H₂ (H-atoms have been omitted frequently for clarity). Alphabet J on the shoulder and channel H correspond to those in figure 4(b). The result of IRC (intrinsic reaction coordinate) calculations at the employed level of theory shows that 3a,8a-dihydro-as-indacene is converted to Im1 via TS1 and Im1 is further converted to 1,4-dihydro-1,4-ethenonaphthalene via Im2. Finally, 1,4-dihydro-1,4-ethenonaphthalene is dissociated into naphthalene + acetylene via TS4. See also figure S4 and S6 for molecular hydrogen elimination from dihydro-as-indacenes. As for the magnitude of enthalpy with an asterisk on the right shoulder of numerals, the reference state of Im2, TS2, and TS3 is Im1. See main text for details.

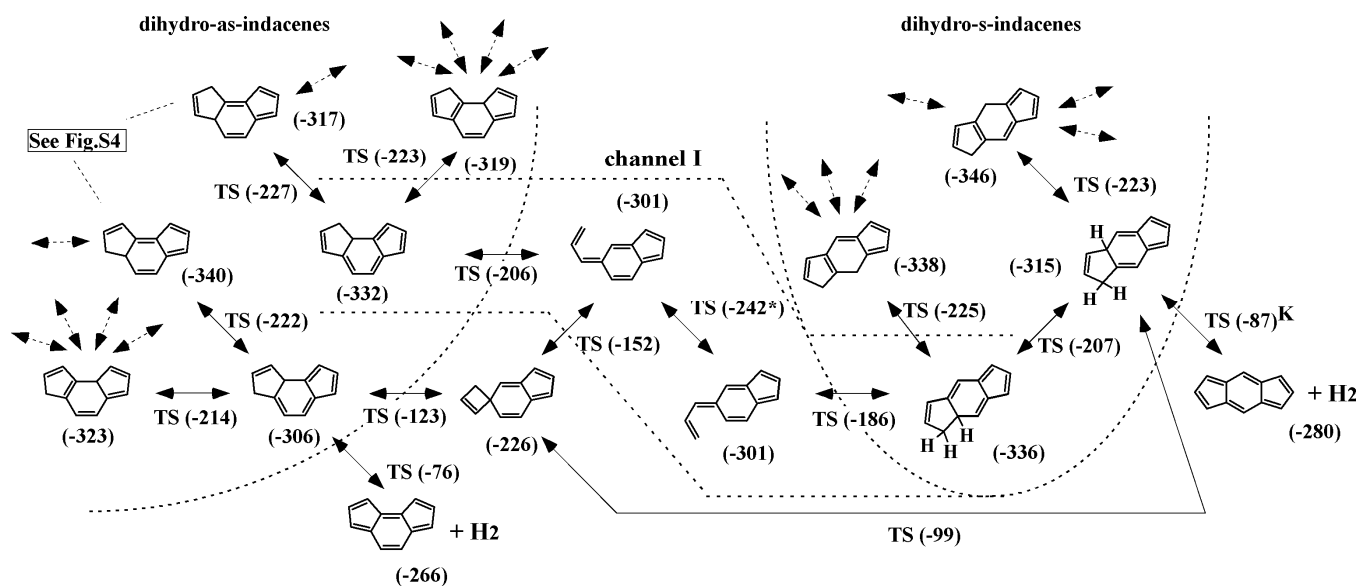


Figure S6. Details of the reaction channels showing the conversion of dihydro-as-indacenes into dihydro-s-indacenes followed by dissociation to s-indacene + H₂ (H-atoms have been omitted frequently for clarity). Alphabet K on the shoulder and channels I correspond to those in figure 4(b). See text for an asterisk on the right shoulder of numerals.

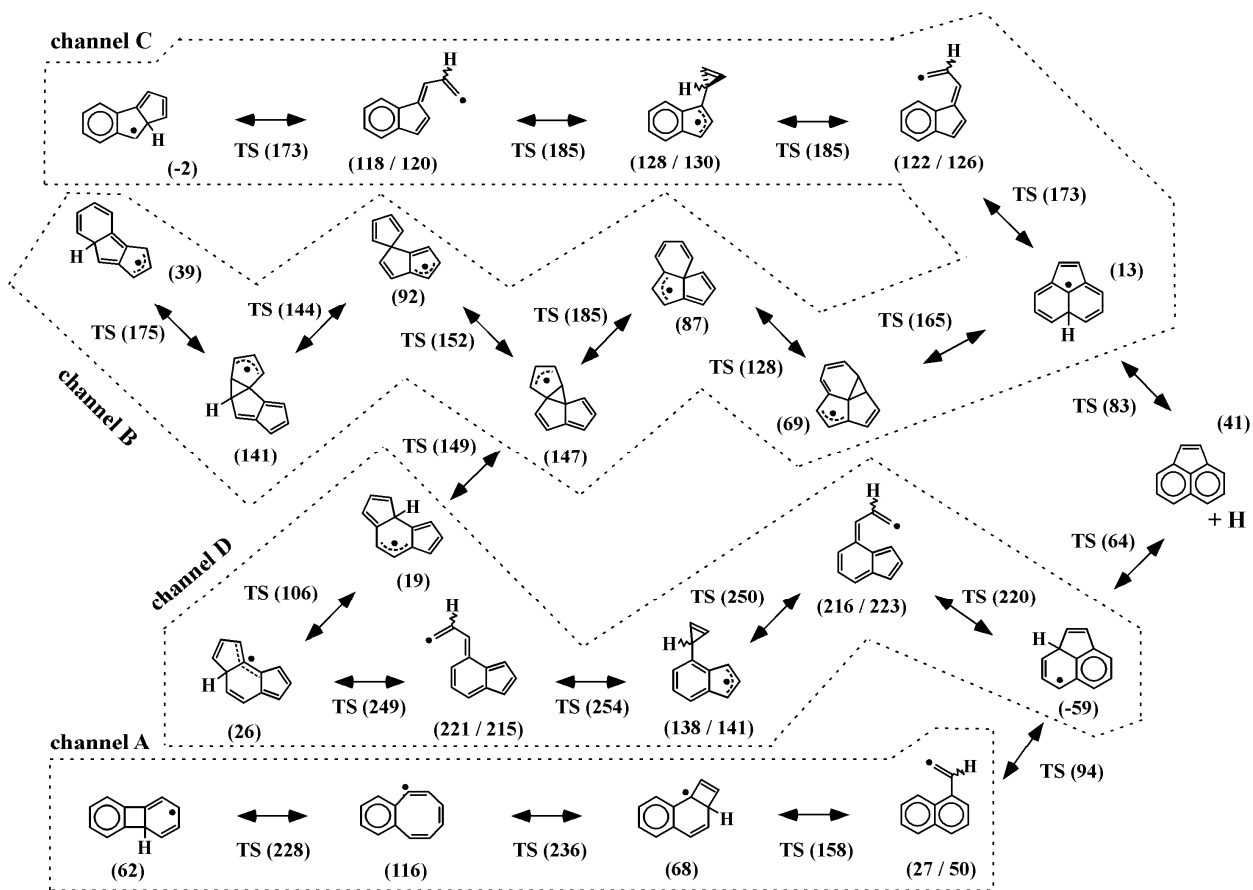


Figure S7. Details of the reaction channels showing the conversion of biphenyl radical to acenaphthylene + H (H-atoms have been omitted frequently for clarity). Channels A, B, C and D correspond to those in figure 5(b).