Supporting Information: PAH growth in flames and space: phenalenyl radical from acenaphthylene

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Reaction schemes for CH insertion

As there are three unique H atoms on the six-membered rings of ACYN, C-H bond insertion may proceed via three distinct pathways, each leading to a unique tropzyl-like RSR intermediate. One of these pathways, for CH insertion at the 1-position, was presented in Figure 7. The pathways (and corresponding tropyl-like intermediates) for CH insertion at the 2-position and 3-position are shown below in Figures S1 and S2.

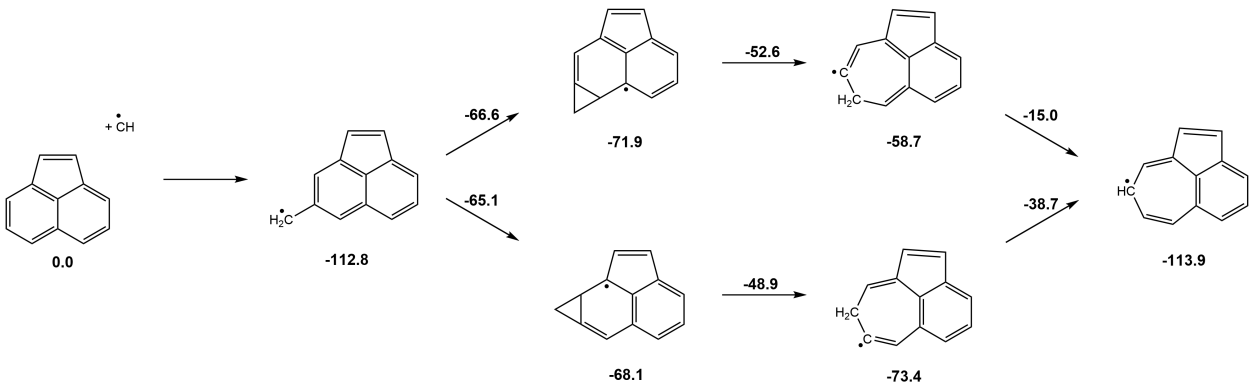

Figure S1: Reaction scheme for CH insertion at the 2-position, forming the second tropyl-like RSR. Calculations were performed at MO6-2X/6-31G(2df,p) level of theory. The energies are in kcal/mol.

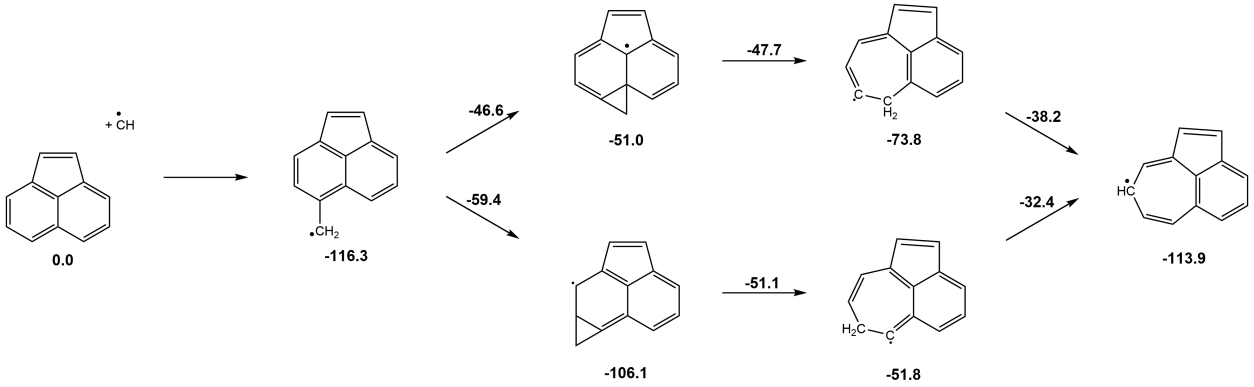

Figure S2: Reaction scheme for CH insertion at the 3-position, forming the third tropyl-like RSR. Calculations were performed at MO6-2X/6-31G(2df,p) level of theory. The energies are in kcal/mol.