Supporting Information

Prediction of a Kinetic Pathway for Fabricating Narrowest Zigzag Graphene Nanoribbons on Cu(111)

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Contents of Supplemental Figures

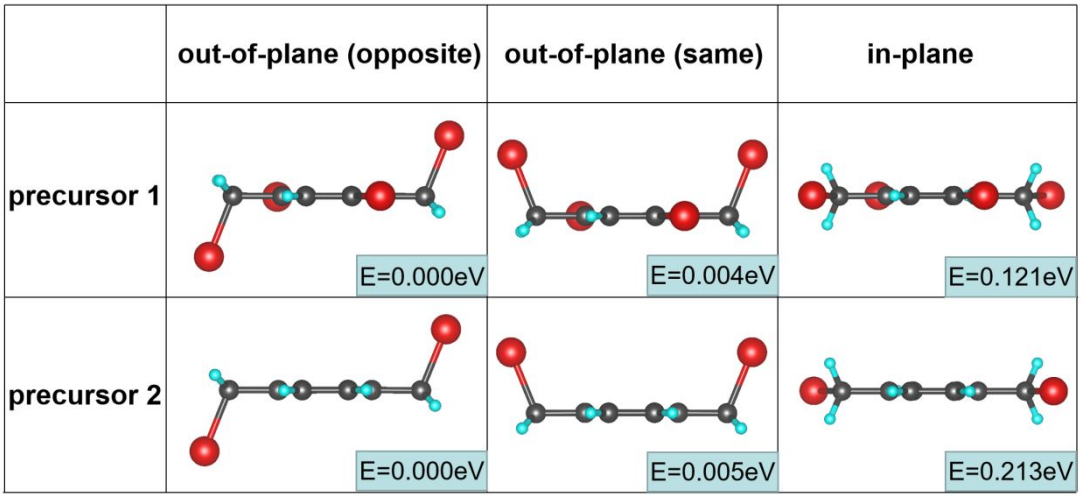


Figure S1. Side views of two precursors in gas phase with out-of-plane and in-plane structures. In the out-of-plane configurations, the two Br atoms in the bromomethyl groups locate either on the opposite sides of the benzene plane (opposite) or same side (same). For each precursor, the energies of the different configurations relative to that of the most stable configuration (out-of-plane (opposite)) are indicated.

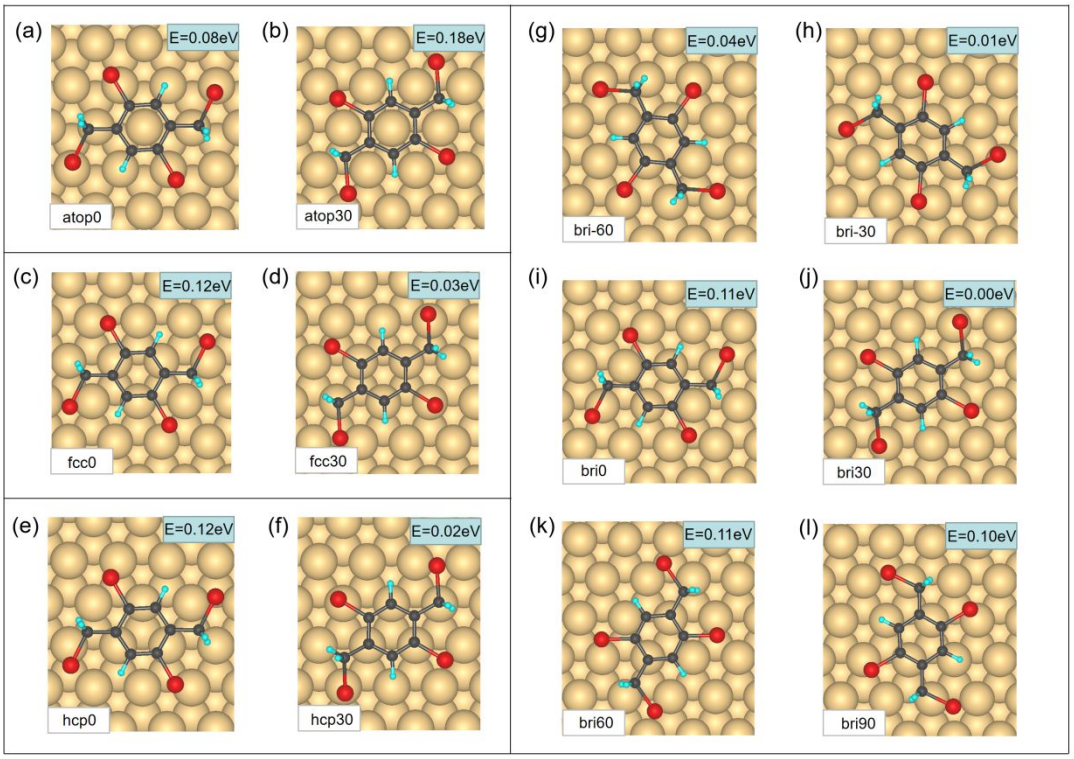


Figure S2. (a)-(l) Optimized adsorption configurations of precursor **1** on Cu(111). For each configuration, the energy relative to that of the most stable configuration (bri30) is indicated.

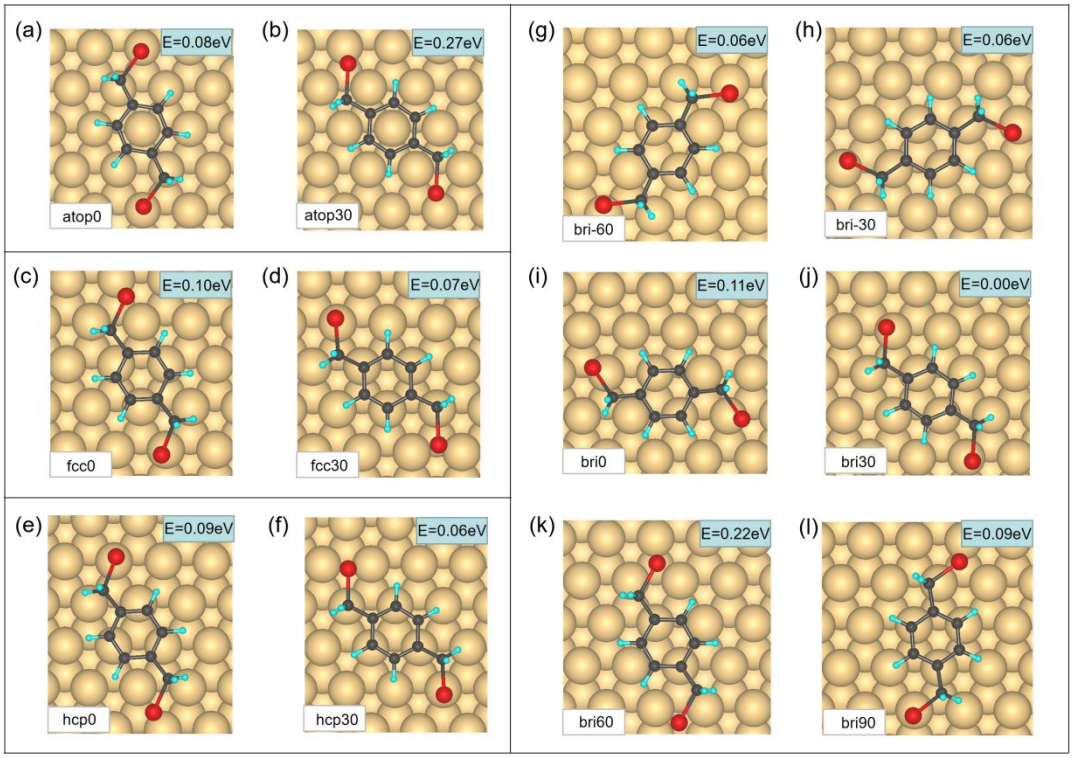


Figure S3. (a)-(l) Optimized adsorption configurations of precursor **2** on Cu(111). For each configuration, the energy relative to that of the most stable configuration (bri30) is indicated.

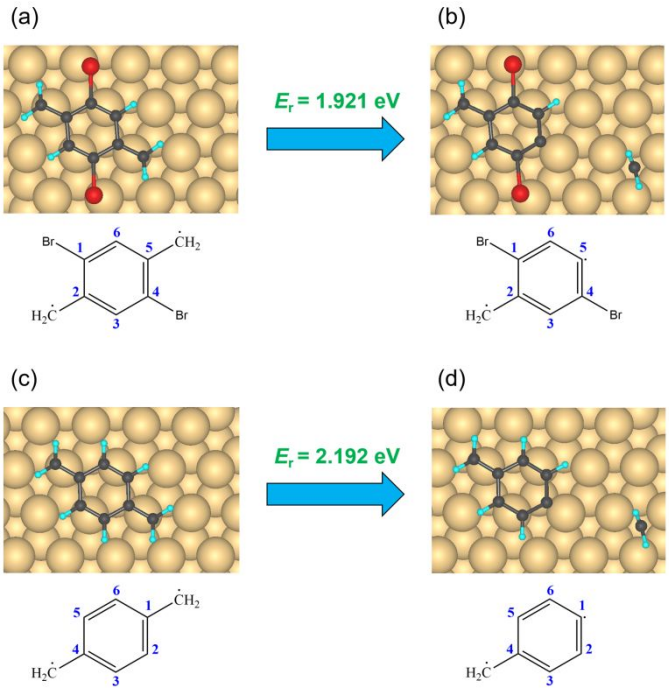


Figure S4. (a)-(b) Detachment of one $-CH_2$ group of molecule **1b**. (c)-(d) Detachment of one $-CH_2$ group of molecule **2b**. The corresponding reaction energies (E_r) and molecule structures are also illustrated. The black dots represent the unpaired electrons on the C atoms.

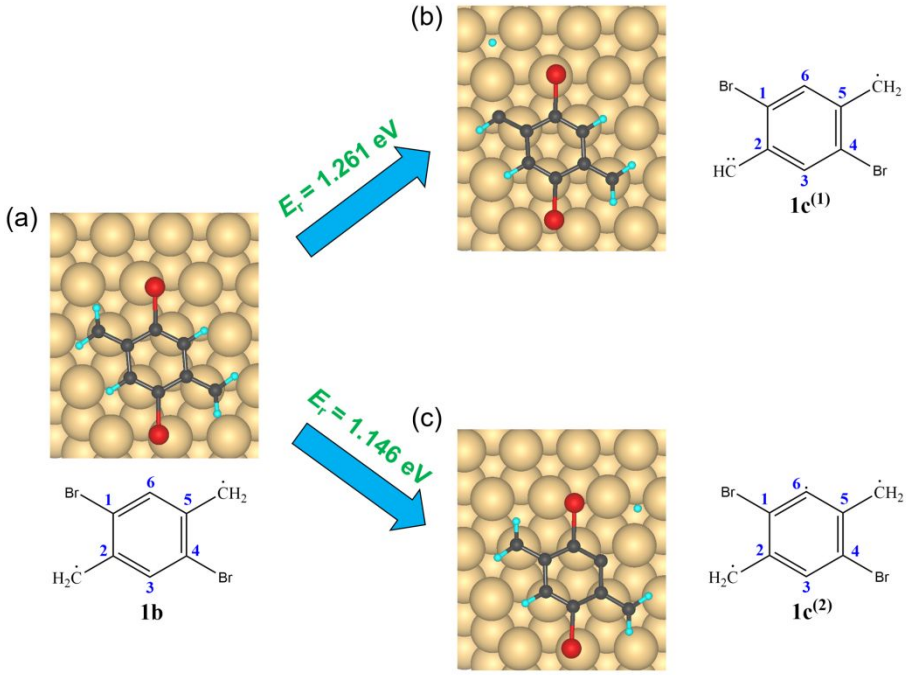


Figure S5. (a)-(b) Detachment of one benzylic H atom of molecule **1b**. (a)-(c) Detachment of one phenylic H atom of molecule **1b**. The corresponding reaction energies (E_r) and molecule structures are also illustrated. The black dots represent the unpaired electrons on the C atoms.

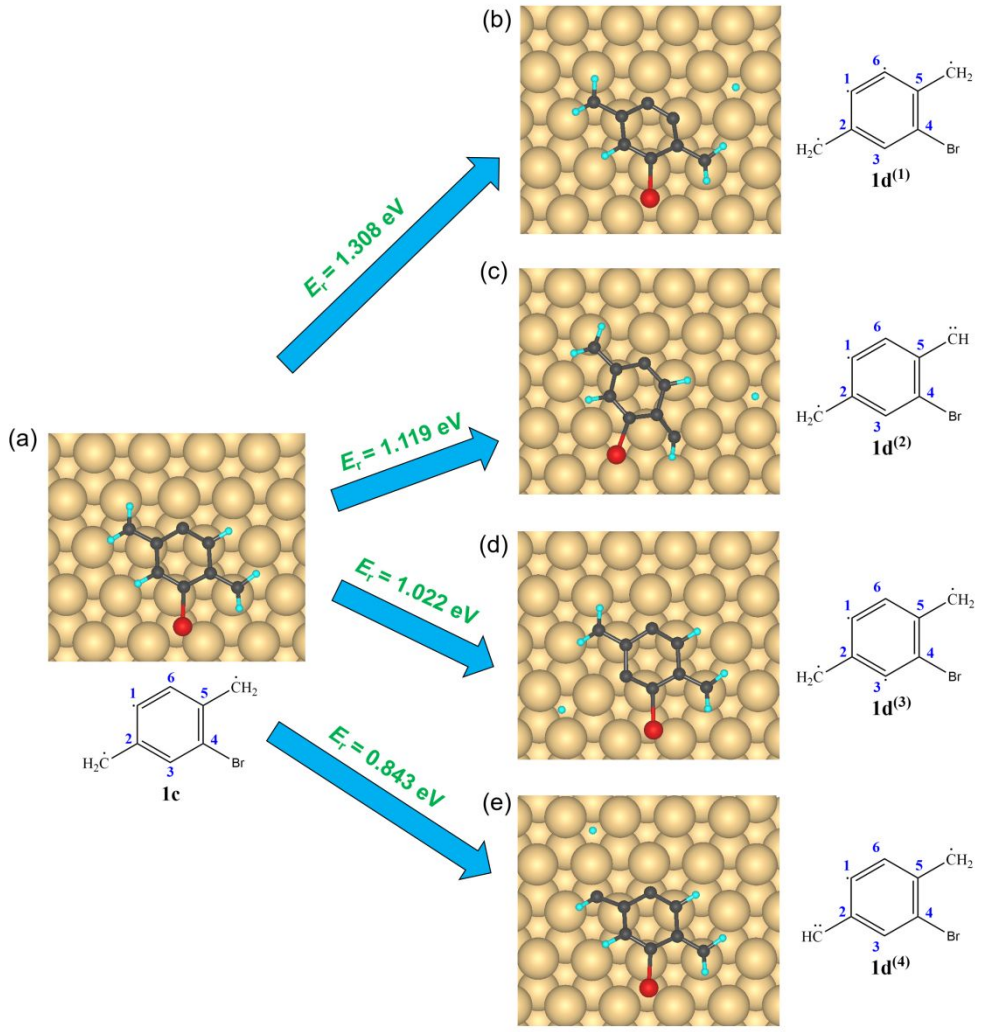


Figure S6. (a)-(b) Detachment of one phenylic H atom (on site 6) of molecule **1c**. (a)-(c) Detachment of one benzylic H atom (in the $-CH_2$ group on site 5) of molecule **1c**. (a)-(d) Detachment of one phenylic H atom (on site 3) of molecule **1c**. (a)-(e) Detachment of one benzylic H atom (in the $-CH_2$ group on site 2) of molecule **1c**. The corresponding reaction energies (E_r) and molecule structures are also illustrated. The black dots represent the unpaired electrons on the C atoms.

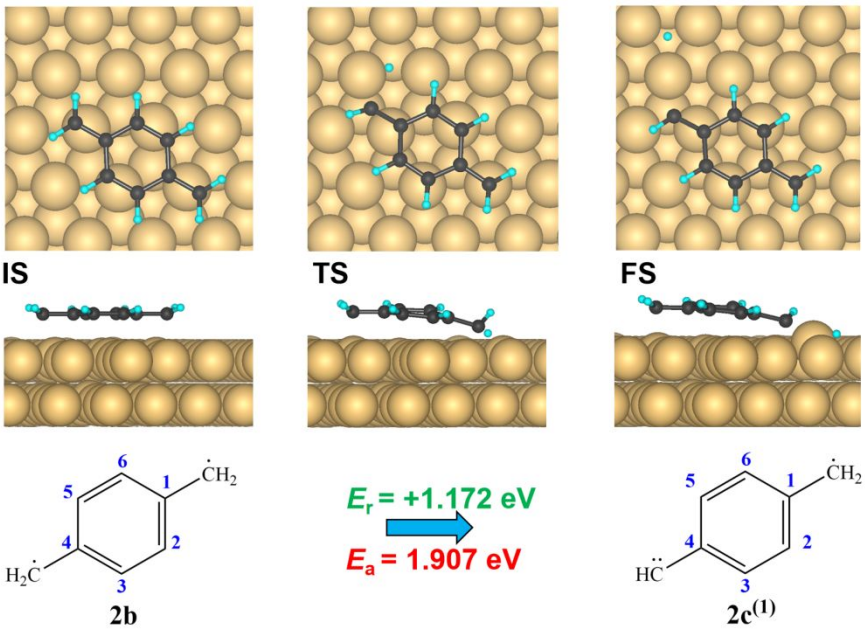


Figure S7. Detachment of one H atom in the −CH_2 group of molecule **2b**. The top (upper panel) and side (middle panel) views of the initial state (IS), transition state (TS), and final state (FS) are depicted. The molecular structures of the IS and FS associated with the E_r and E_a are also given in the lower panel, with the black dots on top of the C atoms representing the unpaired electrons.

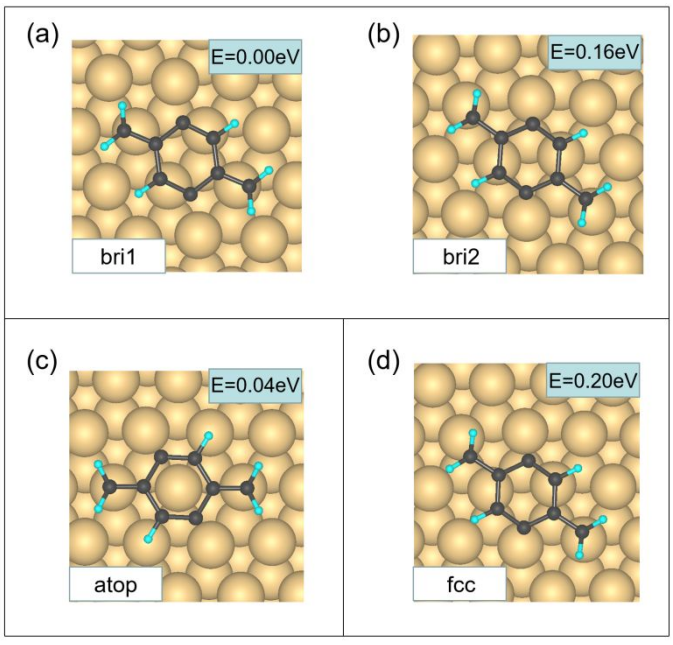


Figure S8. (a)-(d) Optimized adsorption configurations of a C_8H_6 radical on Cu(111). For each configuration, the energy relative to that of the most stable configuration (bri1) is indicated.

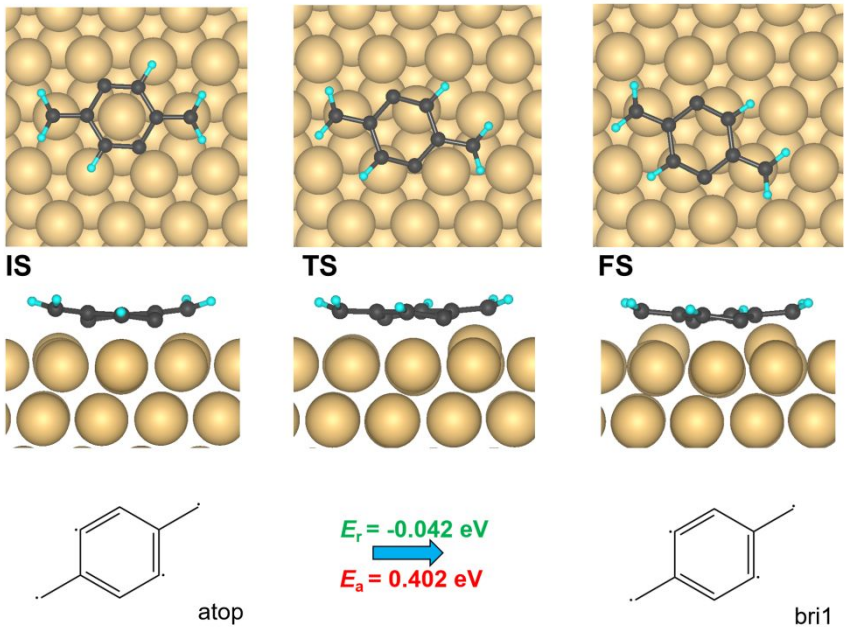


Figure S9. Transition of a C_8H_6 radical from an atop site to its nearest bri1 site on Cu(111). The top (upper panel) and side (middle panel) views of the IS, TS, and FS are depicted. The molecular structures of the IS and FS structures associated with the E_r and E_a are also given in the lower panel, with the black dots representing the unpaired electrons on the C atoms.

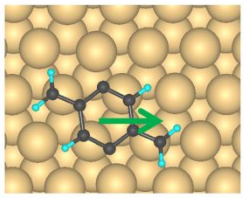
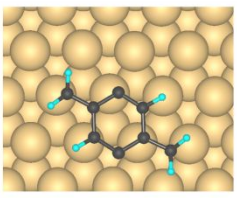
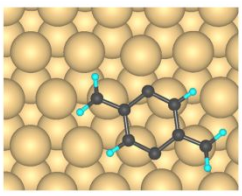
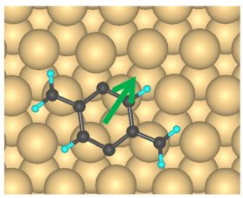
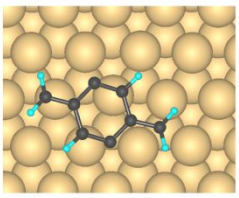
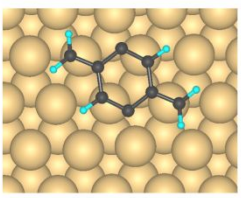
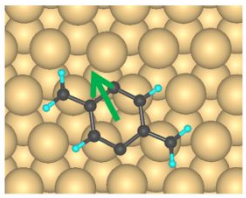
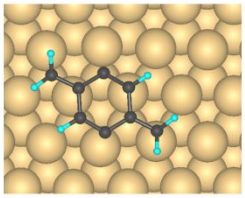
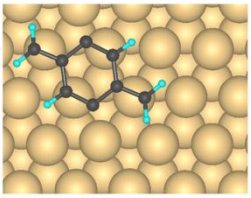
mode	IS	TS	FS	E_a / eV
D1				0.635
D2				0.458
D3				0.267

Figure S10. Reaction pathways of three diffusional motions of a C_8H_6 radical on a bri1 site, with the corresponding energy barriers indicated. The green arrows represent the diffusion directions.

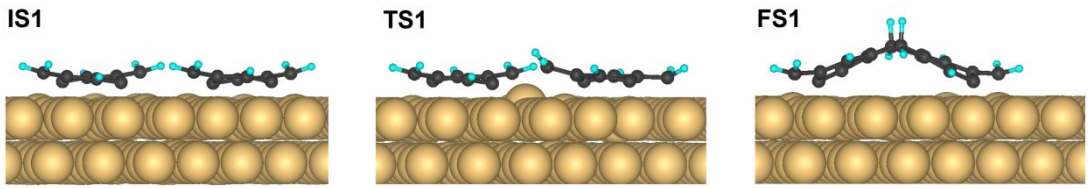


Figure S11. Side views of the optimized structures for the recombination process of two radicals on atop sites, corresponding to IS1-FS1 in Figure 6 in the main text.

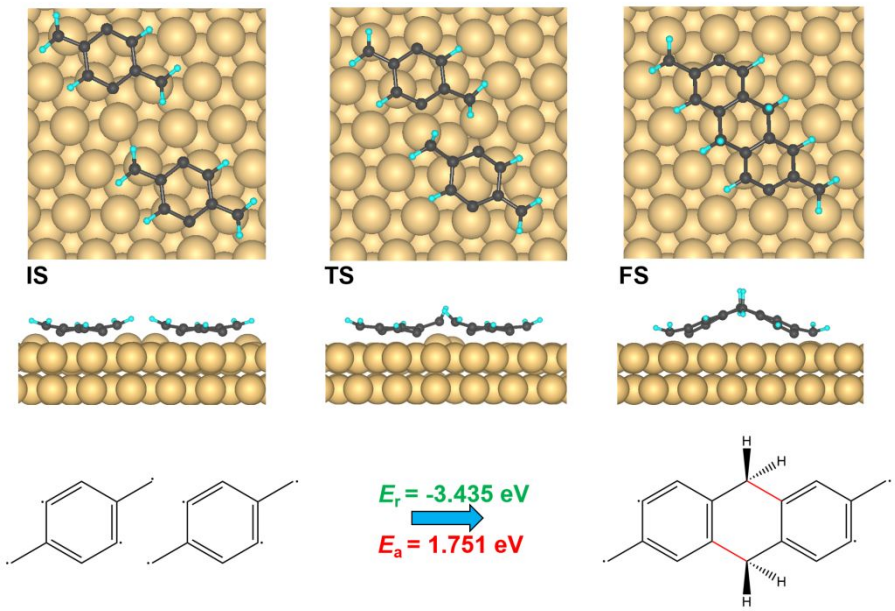


Figure S12. Recombination of two radicals on bri1 sites to form an nZGNR-like dimer. The top (upper panel) and side (middle panel) views of the IS, TS, and FS are depicted. The molecular structures of the IS and FS structures associated with the E_r and E_a are also given in the lower panel, where the bonds in red are newly formed upon coupling and the black dots represent the unpaired electrons on the C atoms.

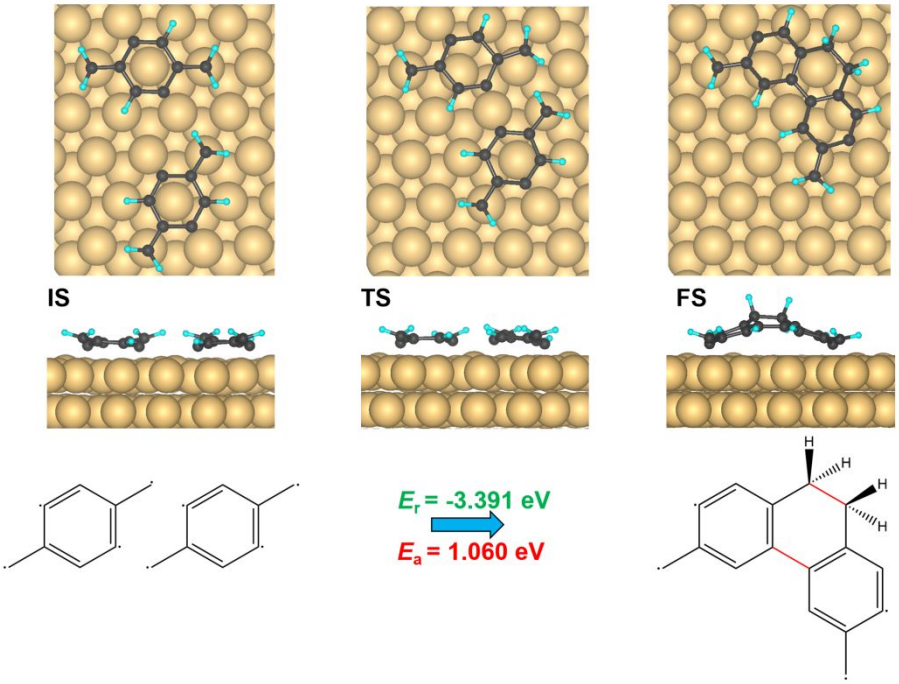


Figure S13. Recombination of two radicals on atop sites to form a chGNR dimer. The top (upper panel) and side (middle panel) views of the IS, TS, and FS are depicted. The molecular structures of the IS and FS structures associated with the E_r and E_a are also given in the lower panel, where the bonds in red are newly formed upon coupling and the black dots represent the unpaired electrons on the C atoms.

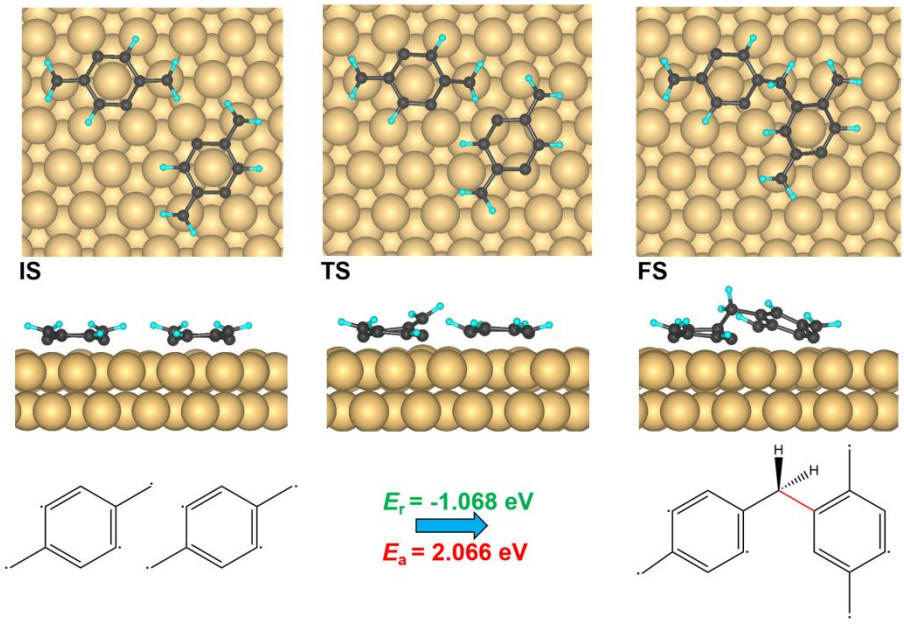


Figure S14. Recombination of two radicals on atop sites to form the first bp dimer. The top (upper panel) and side (middle panel) views of the IS, TS, and FS are depicted. The molecular structures of the IS and FS structures associated with the E_r and E_a are also given in the lower panel, where the bond in red is newly formed upon coupling and the black dots represent the unpaired electrons on the C atoms.

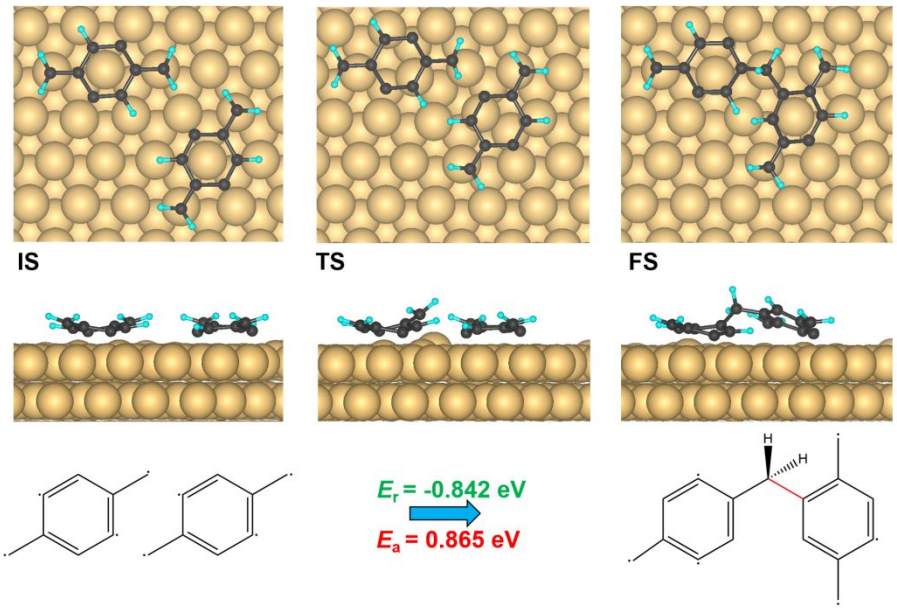


Figure S15. Recombination of two radicals on atop sites to form the second bp dimer. The top (upper panel) and side (middle panel) views of the IS, TS, and FS are depicted. The molecular structures of the IS and FS structures associated with the E_r and E_a are also given in the lower panel, where the bond in red is newly formed upon coupling and the black dots represent the unpaired electrons on the C atoms.

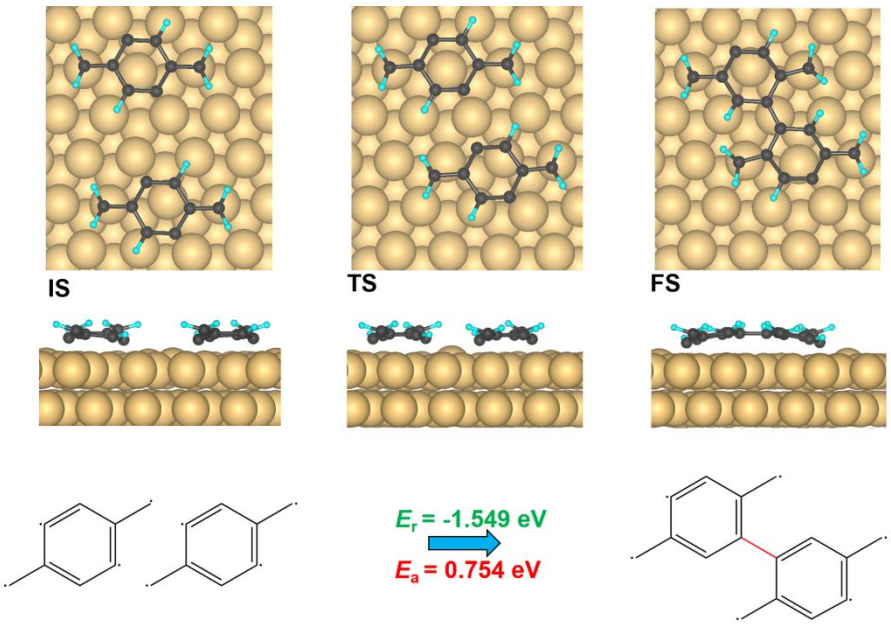


Figure S16. Recombination of two radicals on atop sites to form a pp dimer. The top (upper panel) and side (middle panel) views of the IS, TS, and FS are depicted. The molecular structures of the IS and FS structures associated with the E_r and E_a are also given in the lower panel, where the bond in red is newly formed upon coupling and the black dots represent the unpaired electrons on the C atoms.