

# **Supplementary Information: Activating Hydrogen Evolution Reaction on Carbon Nanotube via Aryl Functionalization: The Role of Hybrid $sp^2$ - $sp^3$ Interface and Curvature**

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## Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for 4,4 Armchair

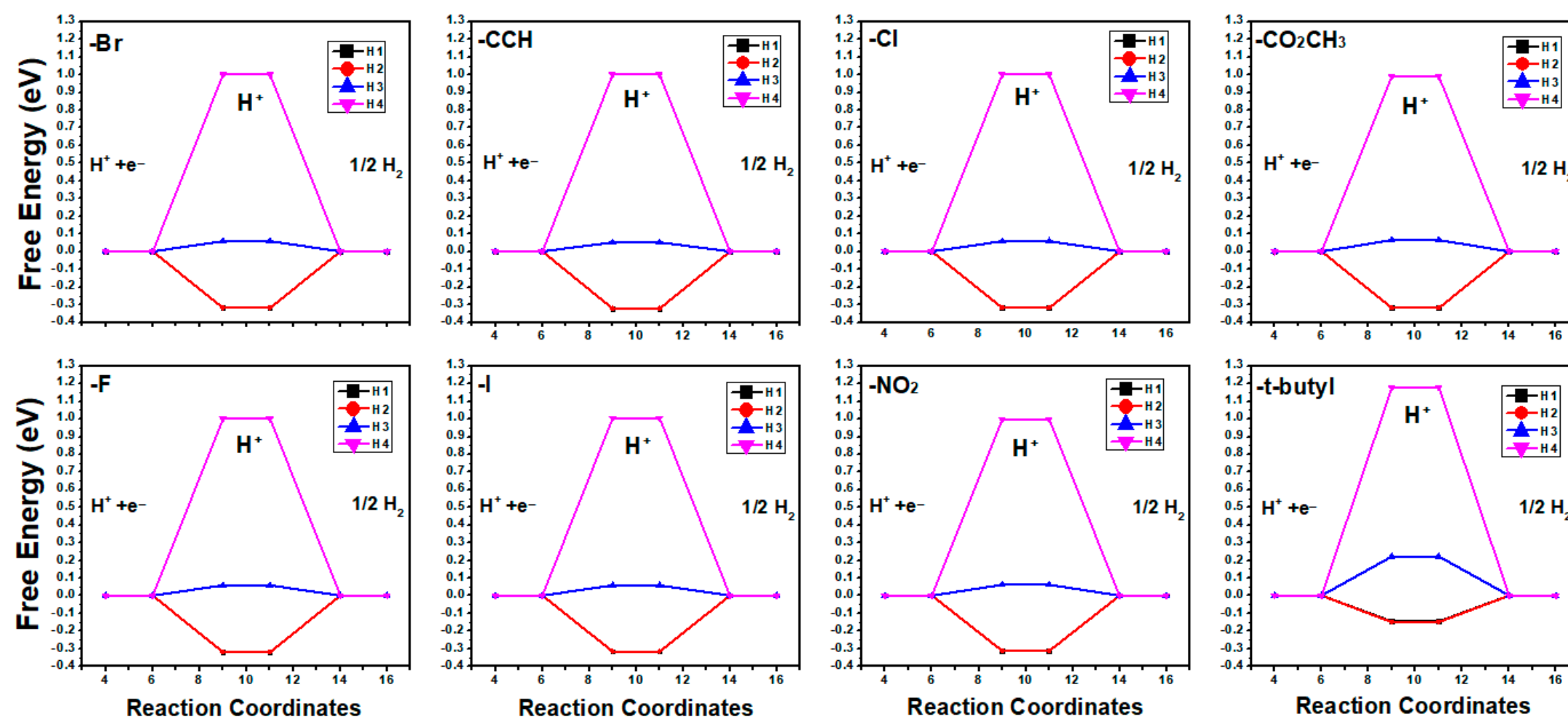


Figure S1. Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for (4,4) armchair SWCNT

## Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for 6,6 Armchair

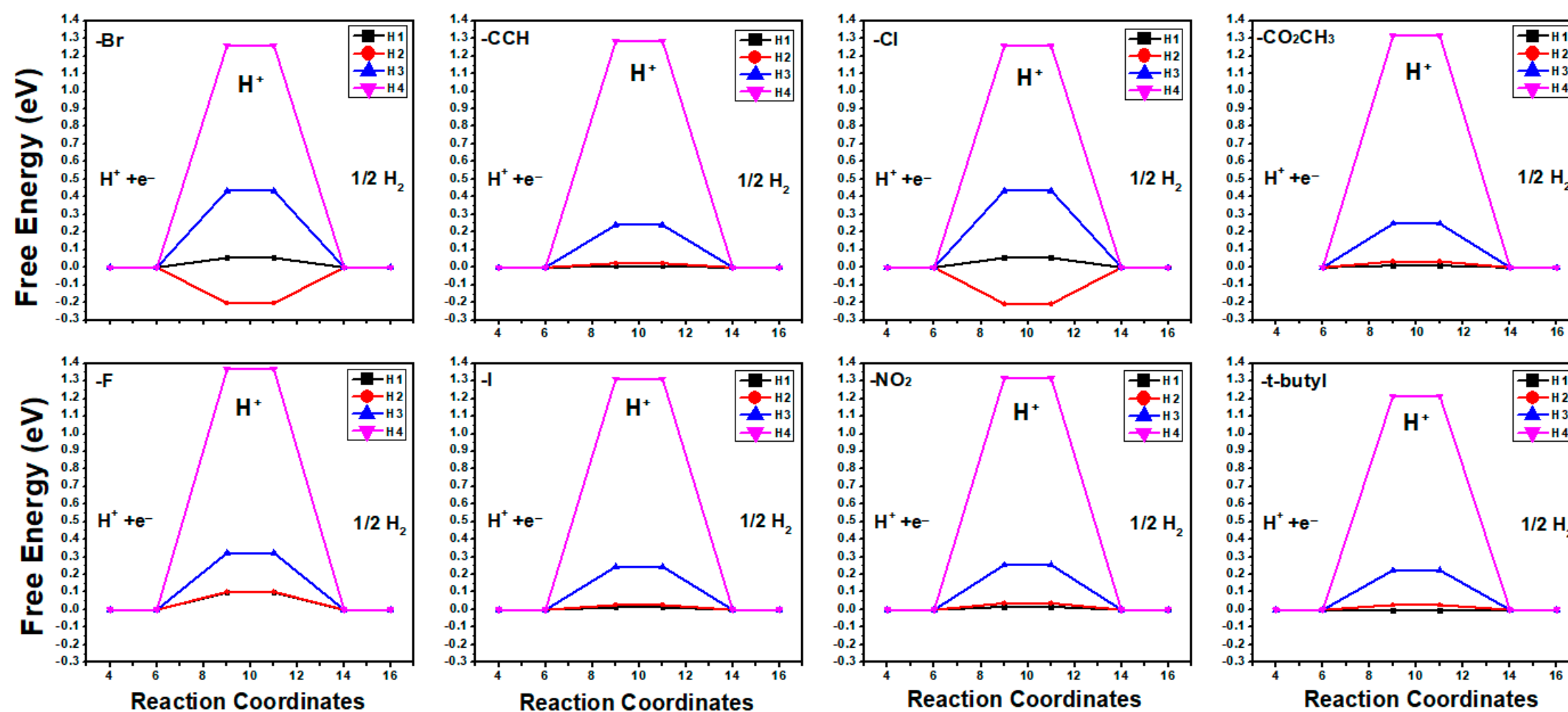


Figure S2. Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for (6,6) armchair SWCNT.

### Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for 8,8 Armchair

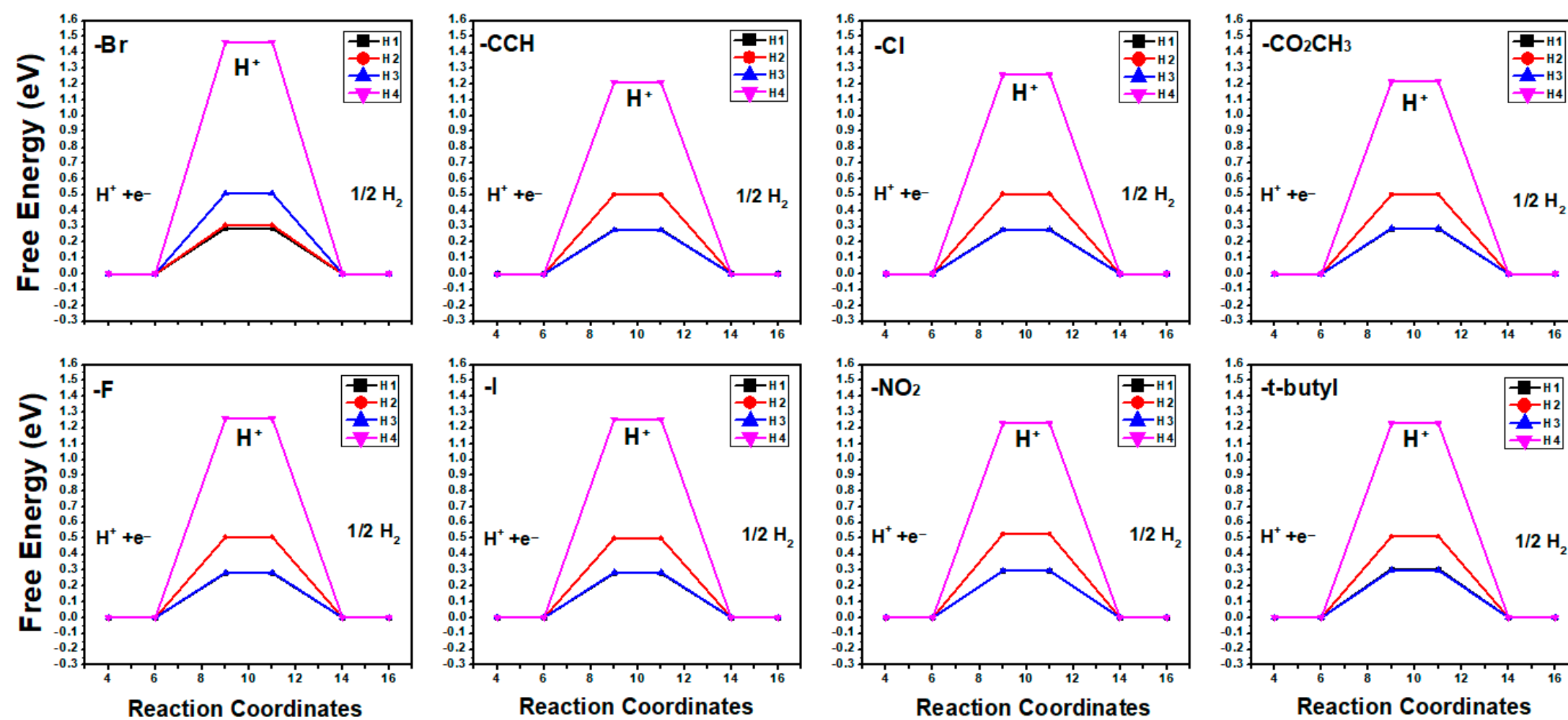


Figure S3. Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for (8,8) armchair SWCNT.

Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for 10,10 Armchair

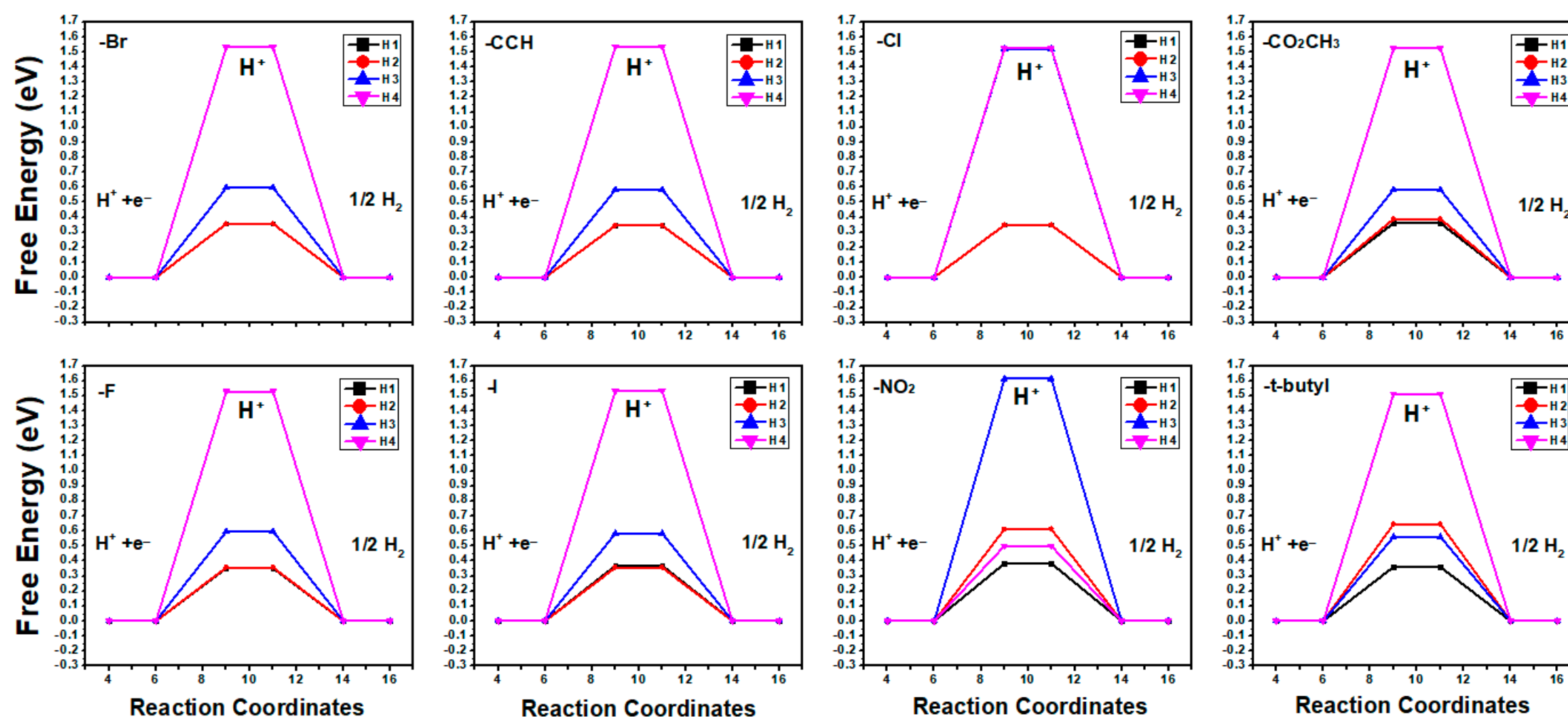
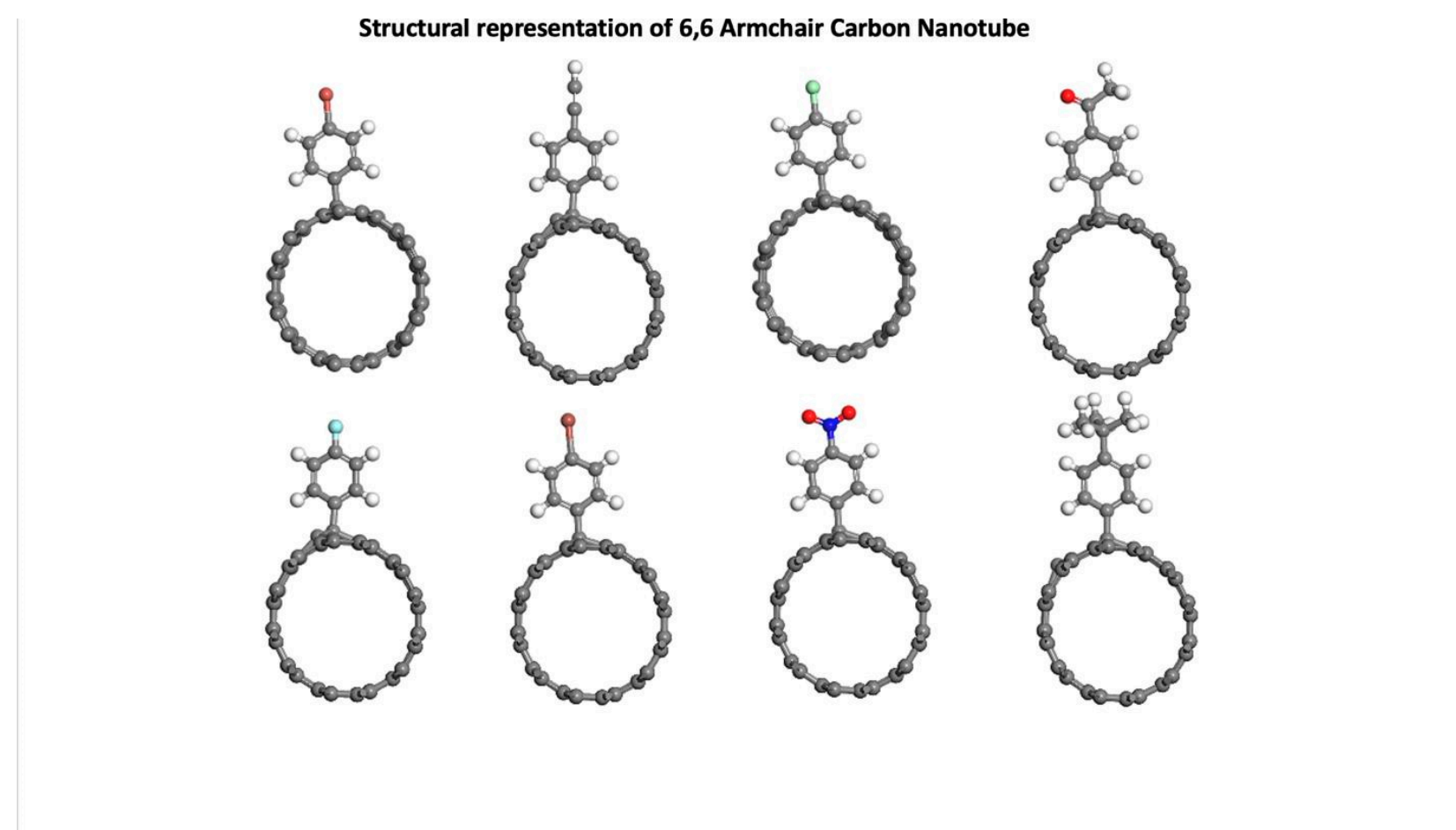


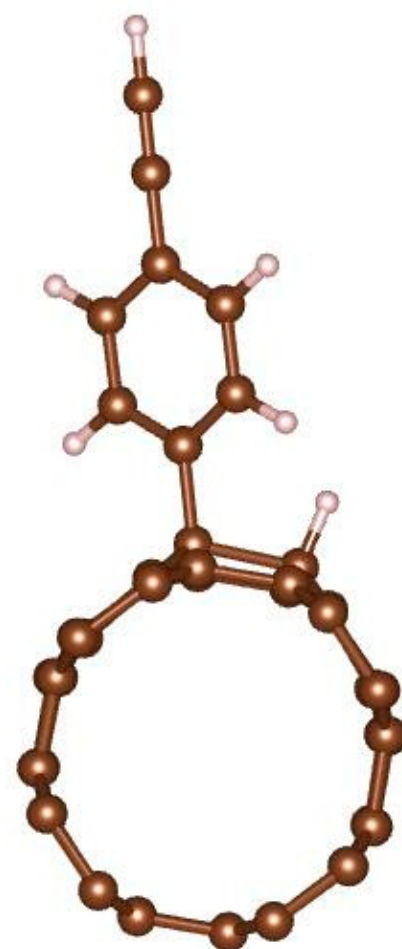
Figure S4. Graphical representation of Gibbs Free Energy ( $\Delta G$ ) for (10,10) armchair SWCNT.

Optimized geometrics for the various intermediates which are formed during the aryl functionalized single walled carbon nanotube



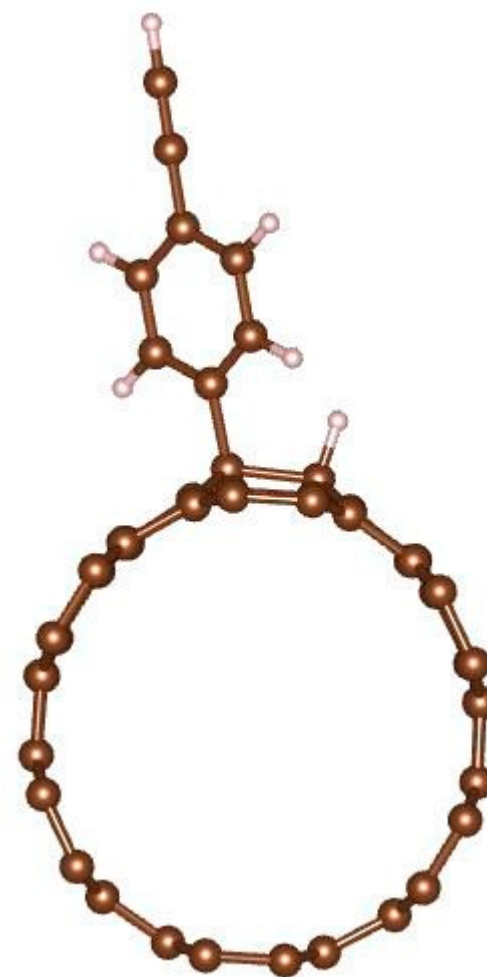
**Figure S5.** Structural representation of 6,6 armchair SWCNT.

Final optimized geometry of Aryl-CCH@SWCNT-4,4 Armchair



**Figure S6.** Final optimized geometry of Aryl-CCH@SWCNT-4,4 Armchair.

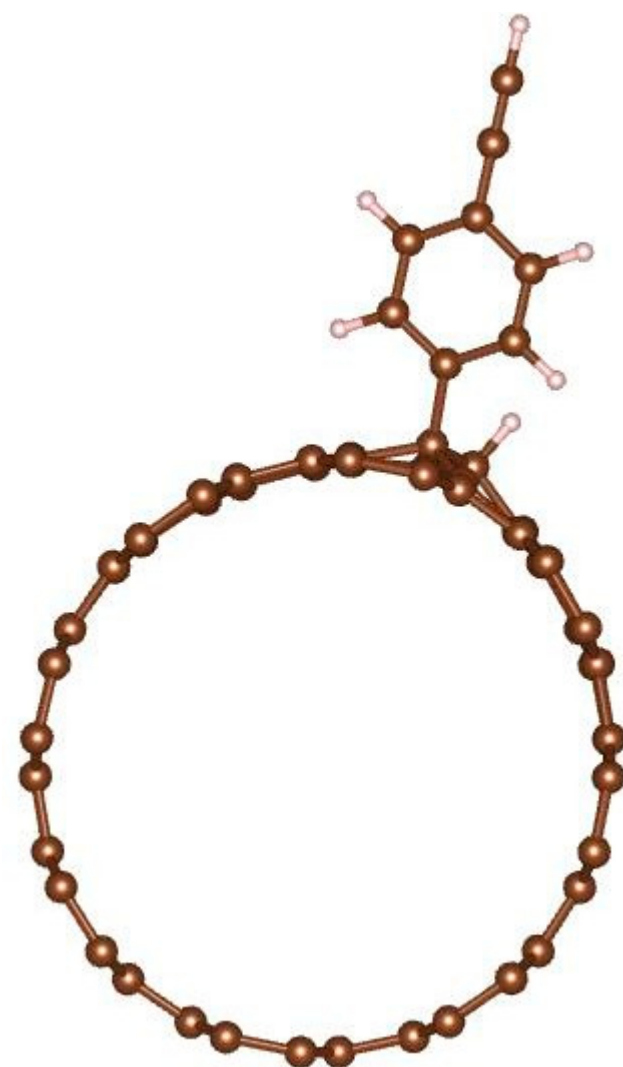
Final optimized geometry of Aryl-CCH@SWCNT-6,6 Armchair



**Figure S7.** Final optimized geometry of Aryl-CCH@SWCNT-6,6 Armchair.

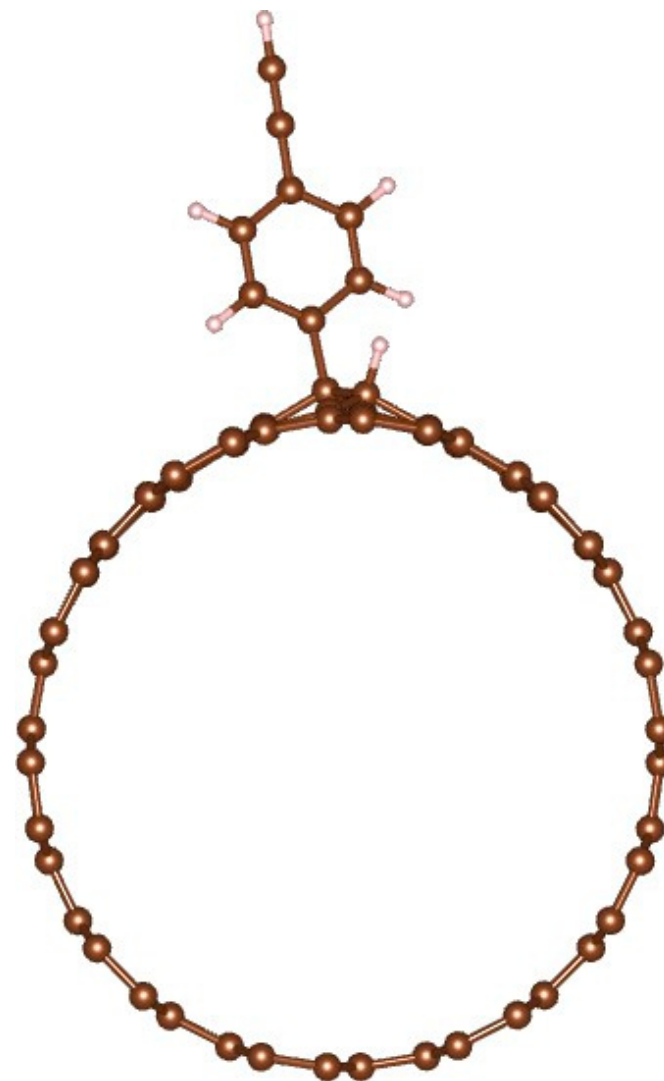


Final optimized geometry of Aryl-CCH@SWCNT-8,8 Armchair

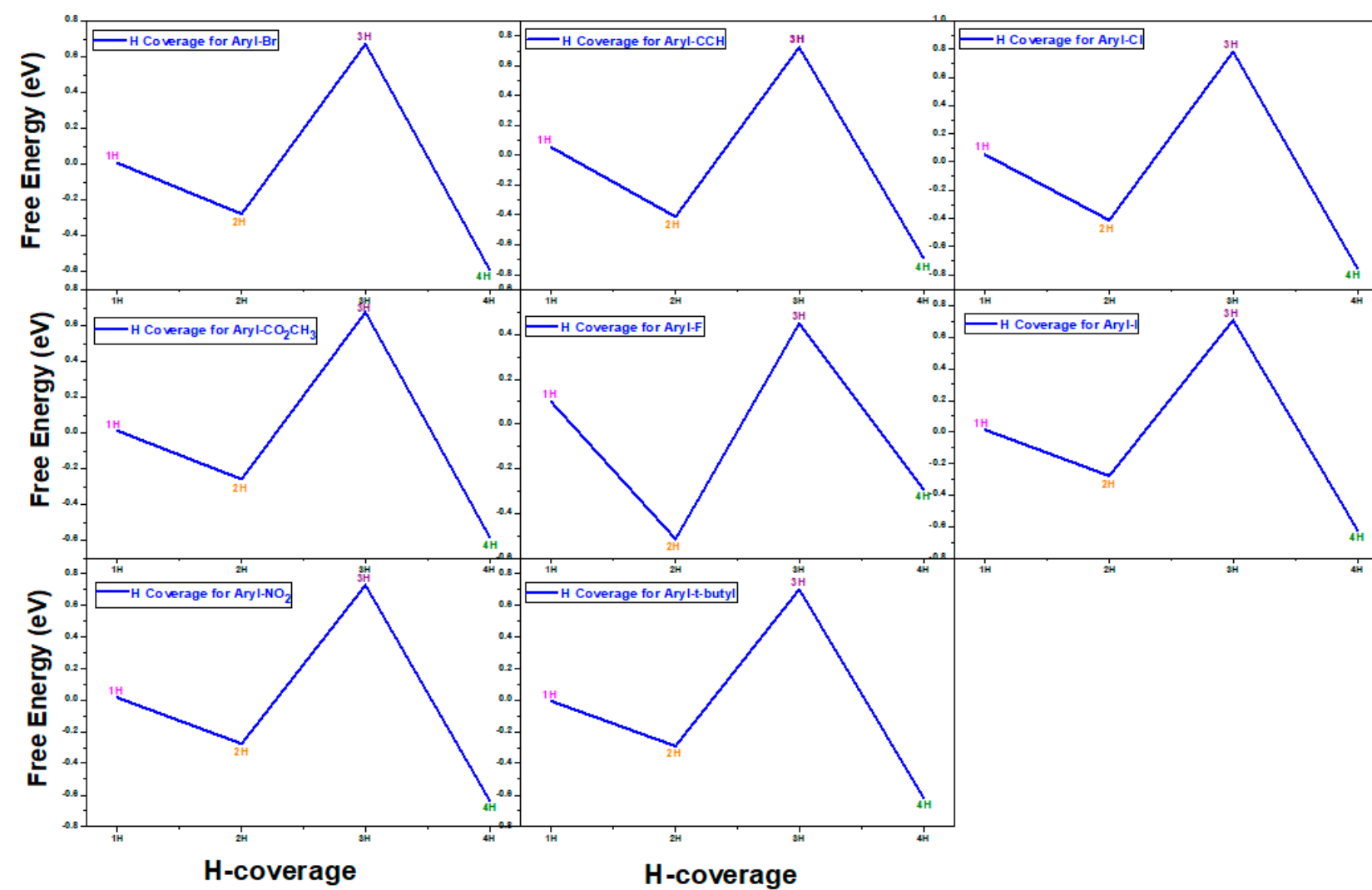


**Figure S8.** Final optimized geometry of Aryl-CCH@SWCNT-8,8 Armchair.

Final optimized geometry of Aryl-CCH@SWCNT-10,10 Armchair



**Figure S9.** Final optimized geometry of Aryl-CCH@SWCNT-10,10 Armchair.



**Figure S10.** Influence of H coverage on the Aryl-SWCNT-6,6 armchair. H1, H2, H3, and H4 represent 1 H atom, 2 H atoms, 3 H atoms, and 4 H atoms respectively.

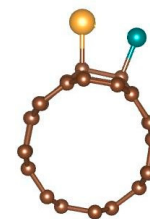
Aryl	Charge	Bader charge
Br	0.907	-0.092
CCH	0.934	<b>-0.066</b>
Cl	0.92	-0.08
CO <sub>2</sub> CH <sub>3</sub>	0.89	-0.107
F	0.90	-0.092
I	0.89	-0.105
NO <sub>2</sub>	0.897	-0.102
t-butyl	0.91	-0.09

**Table S1.** Bader charge analysis for Aryl-CCH@SWCNT taking 6,6 armchair nanotube.

Aryl Functional Group	Without solvation	Solvated Surface with Water Solvent (implicit)
CCH	0.005888 eV	0.011488 eV
Cl	0.053388 eV	0.047888 eV
CO <sub>2</sub> CH <sub>3</sub>	0.010988 eV	-0.044112 eV
F	0.099488 eV	0.107388 eV
NO <sub>2</sub>	0.017188 eV	0.013888 eV
t-butyl	-0.005812 eV	-0.072712 eV

**Table S2.** Effect of the solvated surface with water solvent (implicit) on six of the newly discovered aryl catalysts.

4,4



6,6



8,8





**10,10**

