

***Supplementary Information for***

**Non-metal boron atoms on CuB<sub>12</sub> monolayer as efficient catalytic  
sites for urea production**

Changyan Zhu,<sup>a</sup> Chaoxia Wen,<sup>a</sup> Miao Wang,<sup>a</sup> Min Zhang,<sup>\*a</sup>

Yun Geng,<sup>a</sup> Zhongmin Su<sup>\*ab</sup>

<sup>a</sup>Institute of Functional Material Chemistry, Faculty of Chemistry, National & Local  
United Engineering Laboratory for Power Batteries, Northeast Normal University,  
Changchun 130024, China

<sup>b</sup>School of Chemistry and Environmental Engineering, Changchun University of  
Science and Technology, Changchun 130022, China

Email: [mzhang@nenu.edu.cn](mailto:mzhang@nenu.edu.cn); [zmsu@nenu.edu.cn](mailto:zmsu@nenu.edu.cn)

## Supplementary Methods

**Global-minimum structure searching:** The model searching for the global-minimum structures of the CuB<sub>12</sub> monolayer was performed by employing a particle-swarm optimization (PSO) algorithm<sup>1</sup> within the evolutionary scheme as implemented in the Crystal structure AnaLYsis by Particles Swarm Optimization (CALYPSO) code,<sup>2</sup> which can efficiently and rapidly find reliable structures via the input of chemical composition. Its validity has been confirmed by the application of a diverse variety of two-dimensional B-containing monolayers, such as MM'B<sub>7</sub>,<sup>3</sup> Ni<sub>2</sub>B<sub>5</sub>,<sup>4</sup> B<sub>7</sub>P<sub>2</sub>,<sup>5</sup> ScB<sub>12</sub>,<sup>6</sup> FeB<sub>2</sub>,<sup>7</sup> FeB<sub>6</sub>,<sup>8</sup> Cu<sub>2</sub>B<sub>2</sub>,<sup>9</sup> AlB<sub>6</sub>,<sup>10</sup> and TiB<sub>4</sub>.<sup>11</sup> In our PSO simulation, the number of generation and the population size was set to be 30 and 50 for the CuB<sub>12</sub> monolayer. In the first step, random structures with certain symmetry are constructed, in which atomic coordinates are generated by the crystallographic symmetry operations. Then the structure optimizations are performed using the VASP code, in which the plane-wave cutoff energy, the energy converged, the force converged are set to be 400 eV, 10<sup>-5</sup> eV and 10<sup>-1</sup> eV Å<sup>-1</sup>, respectively. After processing the first generation structures, 60% of them with the lower Gibbs free energies are selected to construct the next generation structure by PSO, and 40% of the structures in the new generation are again randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that these identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency.

**Electrochemical reaction computations:** The Gibbs free energy change ( $\Delta G$ ) for each elementary step in the electrochemical synthesis of urea was obtained by the

computational hydrogen electrode (CHE) model proposed by Nørskov et al,<sup>12,13</sup> which can be computed by:

$$\Delta G = \Delta E + \Delta E_{\text{zpe}} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}}$$

where  $\Delta E$  is the electronic energy difference between the free standing and adsorption states of reaction intermediates, which can be directly obtained from DFT calculations.  $\Delta E_{\text{zpe}}$  and  $\Delta S$  are the changes between the adsorbed species and the gas phase molecules in zero-point energy and entropy, respectively, which can be obtained from the vibrational frequency. For each adsorbed species, its  $E_{\text{zpe}}$  and  $TS$  can be calculated by the following equations,<sup>14,15</sup> respectively:

$$E_{\text{zpe}} = 1/2 \sum \hbar \nu_i$$

$$TS = k_{\text{B}} T \left[ \sum_i \ln \left( \frac{1}{1 - e^{-\hbar \nu_i / k_{\text{B}} T}} \right) + \sum_i \frac{\hbar \nu_i}{k_{\text{B}} T} \frac{1}{e^{\hbar \nu_i / k_{\text{B}} T} - 1} + 1 \right]$$

where  $k_{\text{B}}$  is the Boltzmann's constant;  $h$  represents the Planck constant;  $\nu_i$  denotes the frequency of the normal mode of the adsorbed species;  $T$  is the thermodynamic temperature of the reaction (298.15 K). Moreover, the corresponding  $E_{\text{zpe}}$  and  $S$  of the gas phase molecules are taken from the NIST database (Supplementary Table 1).<sup>16</sup> Furthermore, the corrections for zero point energy and entropy of reaction intermediates are only needed for the adsorbed species because the contribution of the substrate can be offset, which has been verified in the previous report.  $\Delta G_{\text{U}}$  is the free energy contribution related to applied potential  $U$ , and  $U$  is the operating electrochemical potential relative to the reversible hydrogen electrode (RHE), which is determined by the potential-limiting step with the most positive  $\Delta G_{\text{max}}$  value ( $U = -\Delta G_{\text{max}}/e$ ).  $\Delta G_{\text{pH}} = 2.303 \times k_{\text{B}} \times T \times \text{pH}$ , which represents the free energy correction due

to the variations in the H concentration. Moreover, the pH will not change the overpotential, and in this work the value of pH was assumed to be zero in a highly acidic solution.

**Table S1.** Total energy ( $E_{\text{tot}}$ ), zero-potential correction energy ( $E_{\text{zpe}}$ ), entropy contribution (TS, T=298.15 K) of free molecules from NIST database.

| Specie                           | $E_{\text{tot}}$ (eV) | $E_{\text{zpe}}$ (eV) | TS (eV) |
|----------------------------------|-----------------------|-----------------------|---------|
| $\text{H}_2(\text{g})$           | -6.67                 | 0.27                  | 0.40    |
| $\text{H}_2\text{O}(\text{l})$   | -14.54                | 0.56                  | 0.58    |
| $\text{N}_2(\text{g})$           | -16.32                | 0.14                  | 0.59    |
| $\text{NH}_3(\text{g})$          | -19.73                | 0.60                  | 0.89    |
| $\text{CO}(\text{g})$            | -14.78                | 0.13                  | 0.61    |
| $\text{CH}_3\text{OH}(\text{g})$ | -30.44                | 1.35                  | 0.74    |
| $\text{CH}_4(\text{g})$          | -24.03                | 1.18                  | 0.58    |

**Table S2.** Structural information of the global-minimum  $\text{CuB}_{12}$  monolayer.

| Phase             | Space Group | Lattice Parameters ( $\text{\AA}$ , $^\circ$ )                   | Coordinates                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|-------------------|-------------|------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{CuB}_{12}$ | P4/MMM      | $a=b=6.183863$<br>$c=20.00000$<br>$\alpha=\beta=\gamma=90.00000$ | Cu(0.500000000,0.500000000,0.500000000)<br>B(0.857930005,0.500000000,0.500000000)<br>B(0.142069995,0.500000000,0.500000000)<br>B(0.500000000,0.857930005,0.500000000)<br>B(0.500000000,0.142069995,0.500000000)<br>B(0.257779986,0.257779986,0.500000000)<br>B(0.742220044,0.742220044,0.500000000)<br>B(0.742220044,0.257779986,0.500000000)<br>B(0.257779986,0.742220044,0.500000000)<br>B(0.737800002,0.000000000,0.500000000)<br>B(0.262199998,0.000000000,0.500000000)<br>B(0.000000000,0.737800002,0.500000000)<br>B(0.000000000,0.262199998,0.500000000) |

**Table S3.** Total energy ( $E_{\text{tot}}$ ), zero-potential correction energy ( $E_{\text{zpe}}$ ) and entropy contribution (TS, T=298.15 K) of the optimized intermediates for urea production on the CuB<sub>12</sub> monolayer.

| Intermediates                                      | $E_{\text{tot}}$ (eV) | $E_{\text{ZPE}}$ (eV) | TS (eV) |
|----------------------------------------------------|-----------------------|-----------------------|---------|
| *CO <sub>2</sub> +*N <sub>2</sub>                  | -355.19               | 0.58                  | 0.18    |
| *CO <sub>2</sub> +*NNH                             | -359.71               | 0.94                  | 0.17    |
| *CO <sub>2</sub> +*NHNH                            | -364.00               | 1.23                  | 0.21    |
| *CO <sub>2</sub> +*NNH <sub>2</sub>                | -363.07               | 1.27                  | 0.18    |
| *CO <sub>2</sub> +*NHNH <sub>2</sub>               | -368.12               | 1.61                  | 0.19    |
| *CO <sub>2</sub> +*NH <sub>2</sub> NH <sub>2</sub> | -372.96               | 1.78                  | 0.27    |
| *OCOH+*NNH                                         | -363.18               | 1.26                  | 0.17    |
| *OCOH+*NHNH                                        | -367.70               | 1.59                  | 0.17    |
| *OCOH+*NNH <sub>2</sub>                            | -366.52               | 1.59                  | 0.19    |
| *OCOH+*NHNH <sub>2</sub>                           | -371.37               | 1.93                  | 0.20    |
| *OCOH+*NH <sub>2</sub> NH <sub>2</sub>             | -376.46               | 2.12                  | 0.28    |
| *OCOH+*N <sub>2</sub>                              | -358.76               | 0.91                  | 0.17    |
| *CO+*N <sub>2</sub>                                | -347.19               | 0.45                  | 0.16    |
| *CO+*NNH                                           | -351.60               | 0.80                  | 0.17    |
| *CO+*NHNH                                          | -356.39               | 1.15                  | 0.14    |
| *CO+*NNH <sub>2</sub>                              | -355.79               | 1.18                  | 0.13    |
| *CO+*NHNH <sub>2</sub>                             | -359.93               | 1.48                  | 0.18    |
| *CO+*NH <sub>2</sub> NH <sub>2</sub>               | -365.46               | 1.72                  | 0.20    |
| *NCON                                              | -348.13               | 0.48                  | 0.14    |
| *NCONH                                             | -353.59               | 0.81                  | 0.16    |
| *NHCONH                                            | -358.79               | 1.17                  | 0.16    |
| *NCONH <sub>2</sub>                                | -357.65               | 1.15                  | 0.18    |
| *NHCONH <sub>2</sub>                               | -362.26               | 1.52                  | 0.19    |
| *NH <sub>2</sub> CONH <sub>2</sub>                 | -365.35               | 1.81                  | 0.24    |

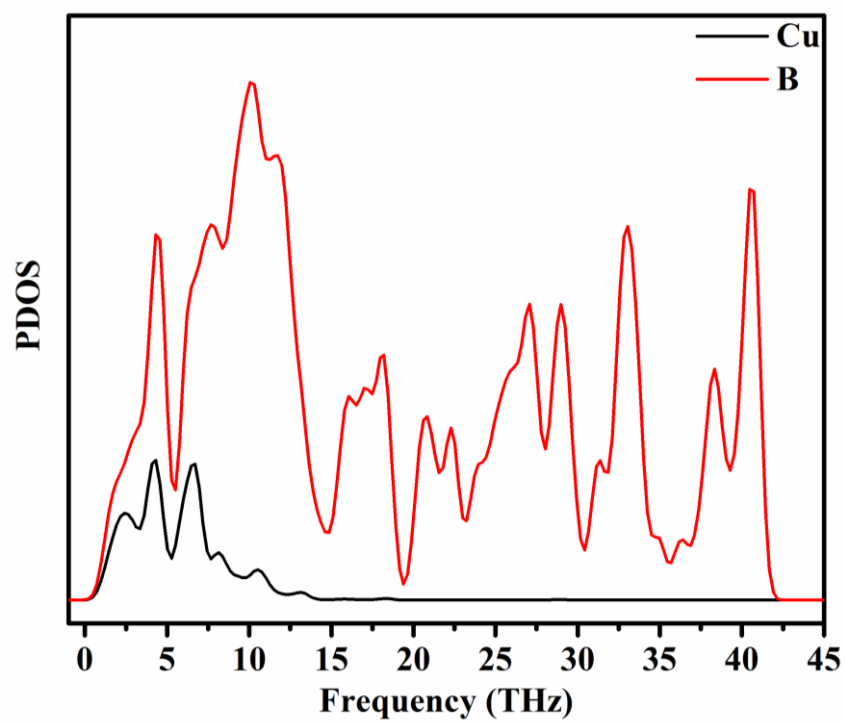
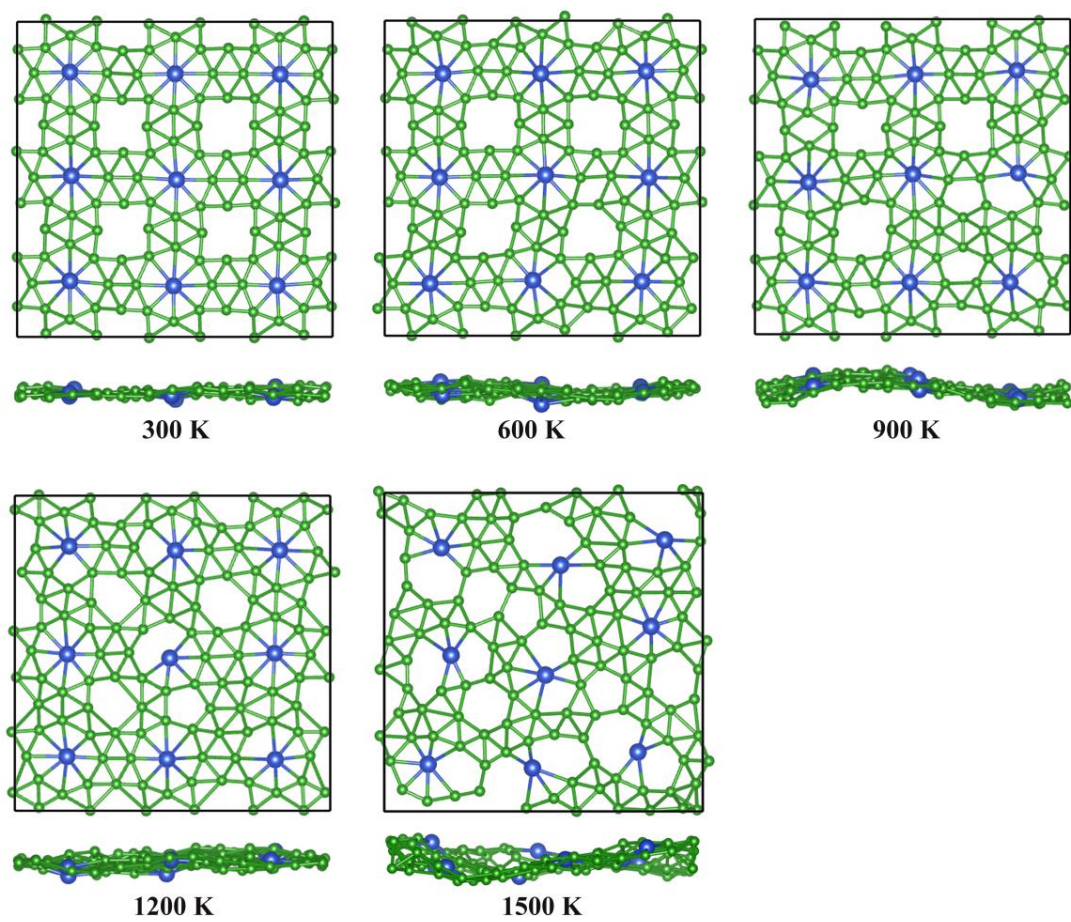
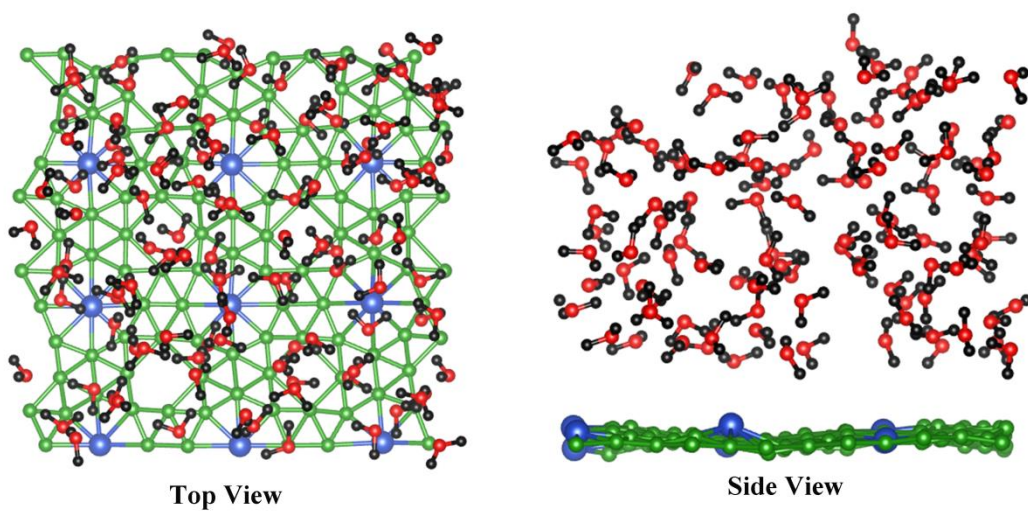


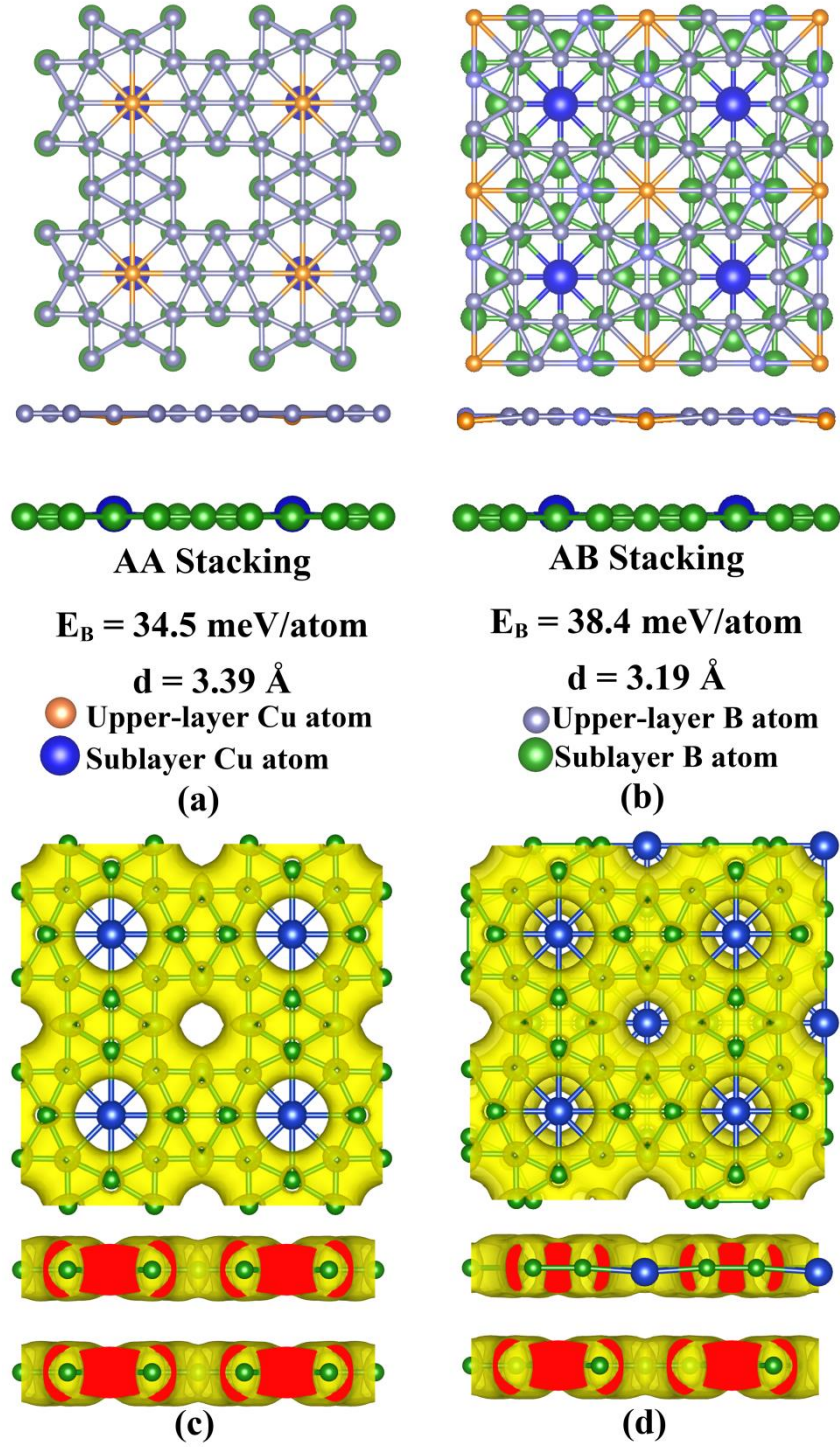
Figure S1. The phonon densities of states (PDOS) of the CuB<sub>12</sub> monolayer using PBE functional.



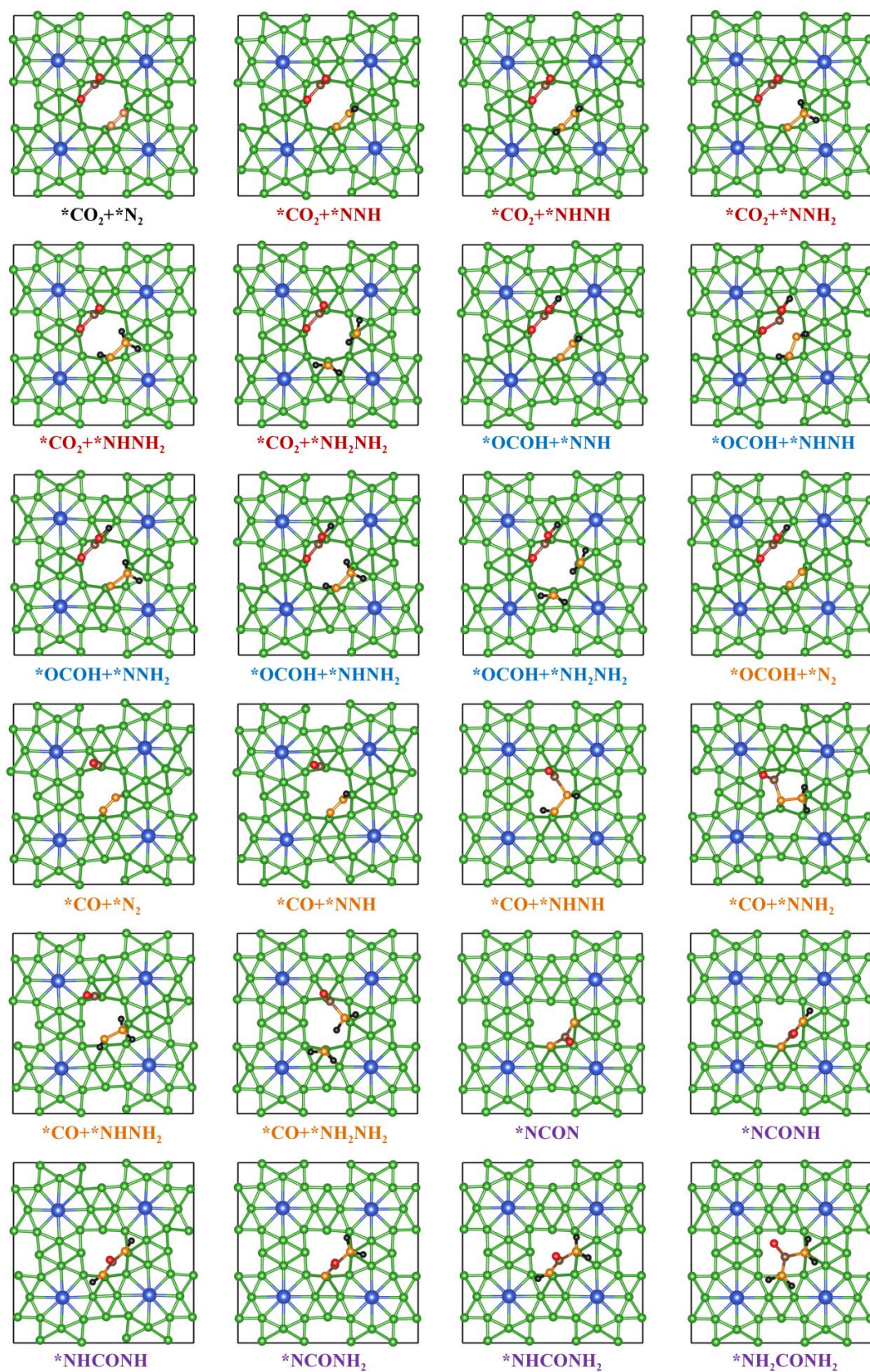
**Figure S2.** Snapshots of the  $\text{CuB}_{12}$  monolayer equilibrium structures at 300 K, 600 K, 900 K, 1200 K and 1500 K at the end of 10 *ps* AIMD simulations.



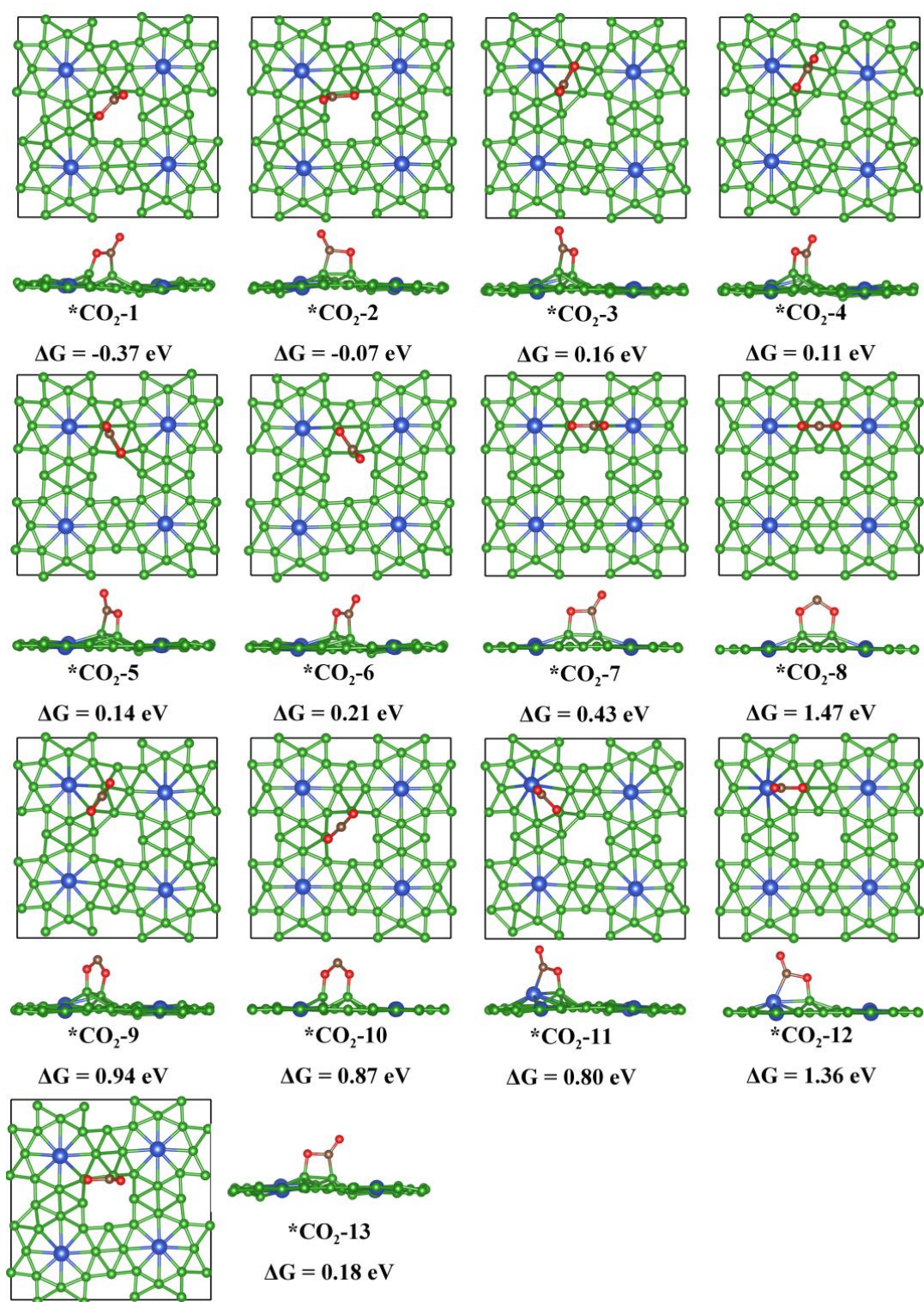
**Figure S3.** Snapshots of the  $\text{CuB}_{12}$  monolayer equilibrium structures at 300 K at the end of 5 *ps* AIMD simulations.



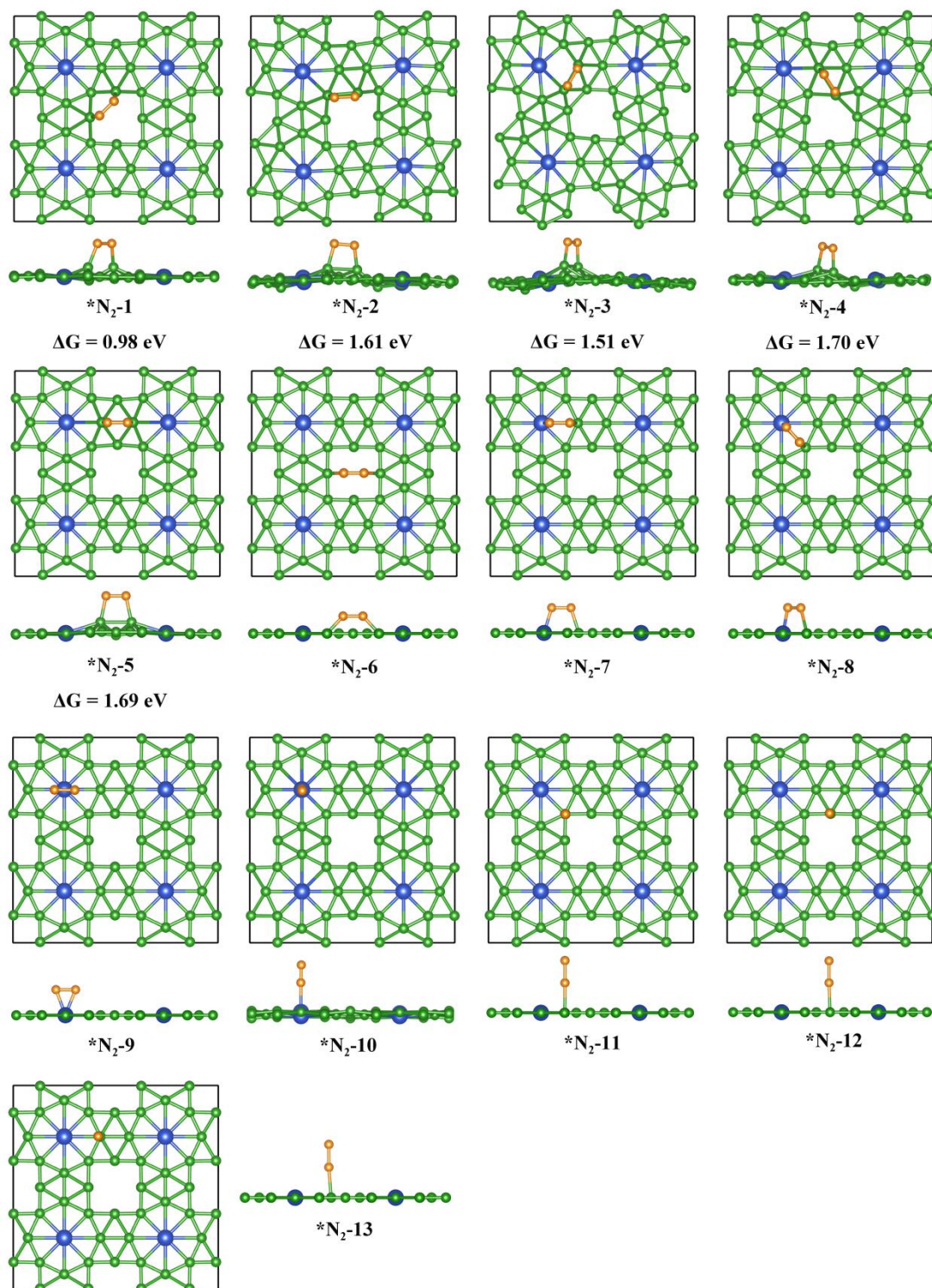
**Figure S4.** (a-b) Geometries, interlayer interaction energies and the shortest interlayer distance of the CuB<sub>12</sub> bilayer with AA and AB stacking patterns. The interlayer interaction energies are defined as  $E_B = (2E_{\text{CuB}_{12}} - E_T)/n$ , in which the  $E_{\text{CuB}_{12}}$  and  $E_T$  are the energies of the CuB<sub>12</sub> monolayer and bilayer,  $n$  is the number of atoms in CuB<sub>12</sub> bilayer. (c-d) Isosurface of ELF plotted with a value of 0.50 for the AA and AB stacked bilayers.



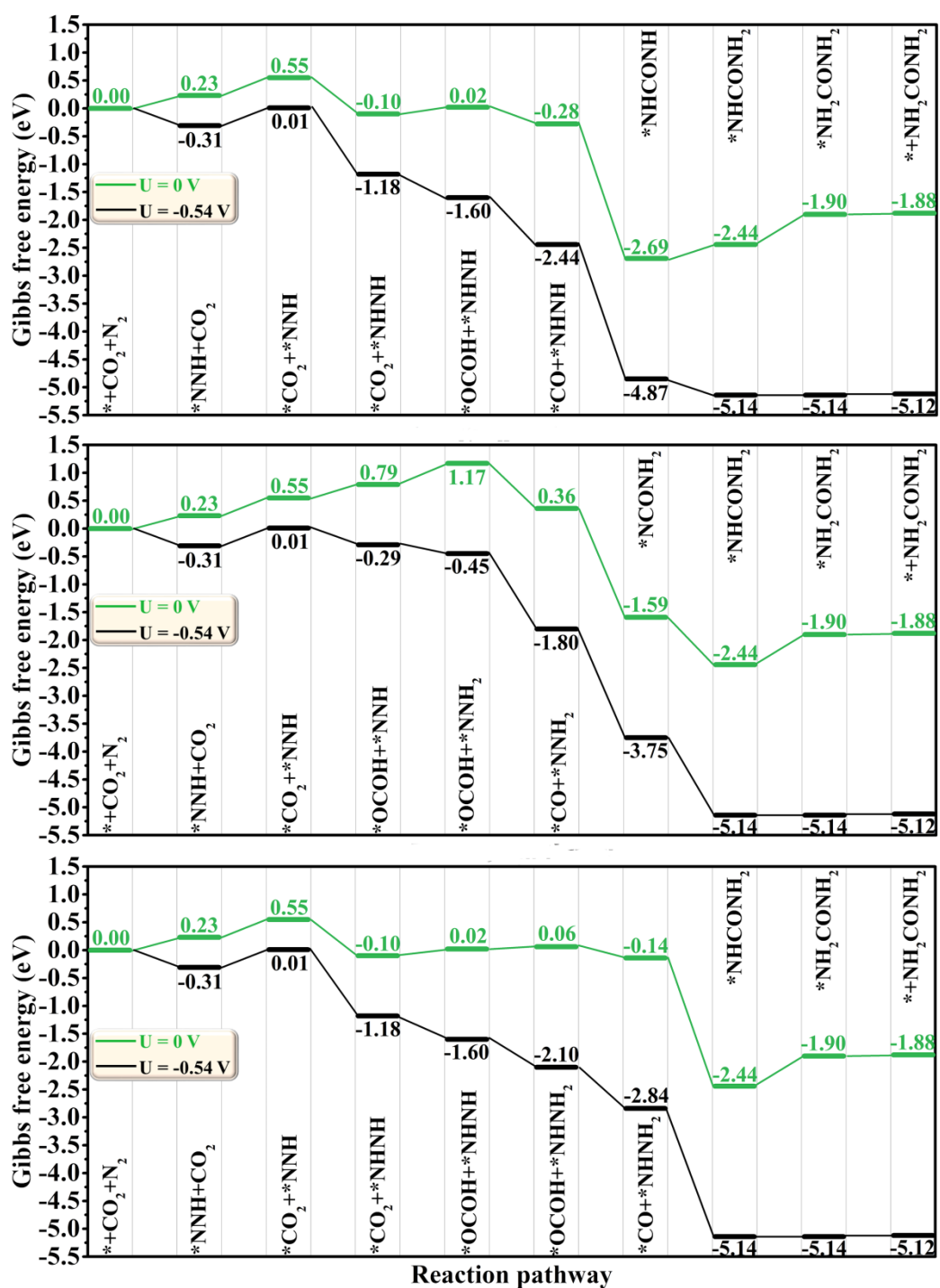
**Figure S5.** Top view of all optimized possible reaction intermediates for urea production on the CuB<sub>12</sub> monolayer.



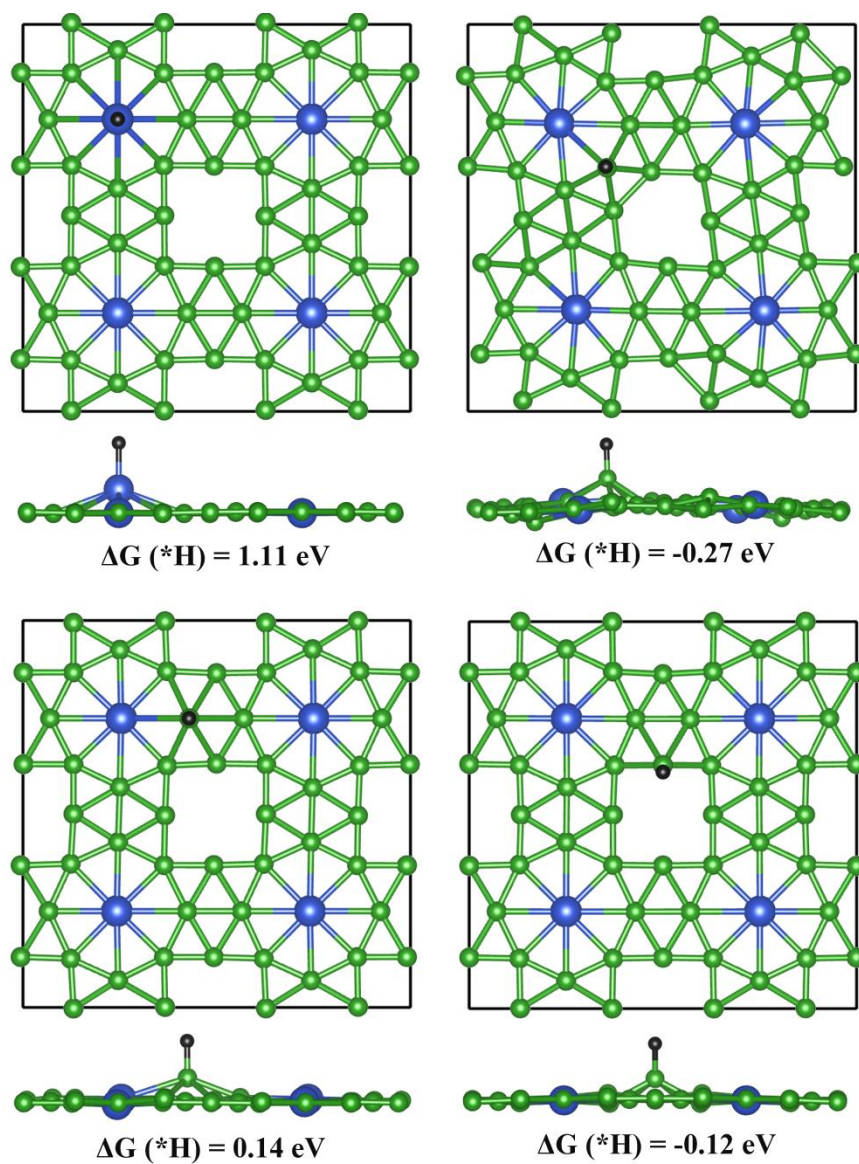
**Figure S6.** Thirteen possible configurations and computed Gibbs free energy change values ( $\Delta G$ ) of CO<sub>2</sub> adsorbed on the CuB<sub>12</sub> monolayer.



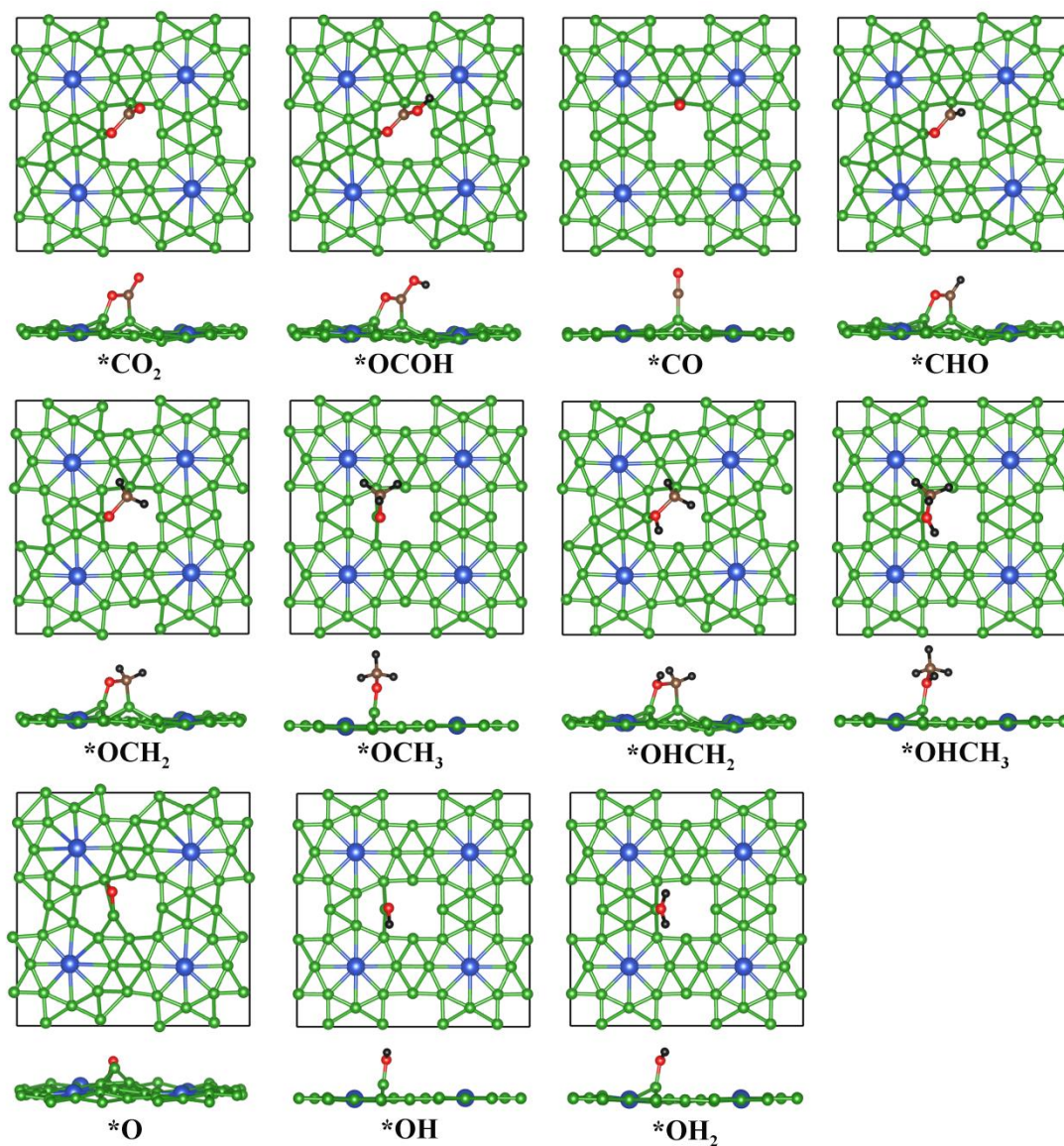
**Figure S7.** Thirteen possible configurations of N<sub>2</sub> adsorbed on the CuB<sub>12</sub> monolayer. The first five N<sub>2</sub> configurations are the final structures after optimizing, and the computed Gibbs free energy change values ( $\Delta G$ ) are also shown. The last eight N<sub>2</sub> configurations are the initial structures, and the N<sub>2</sub> removes away the surface after optimizing.



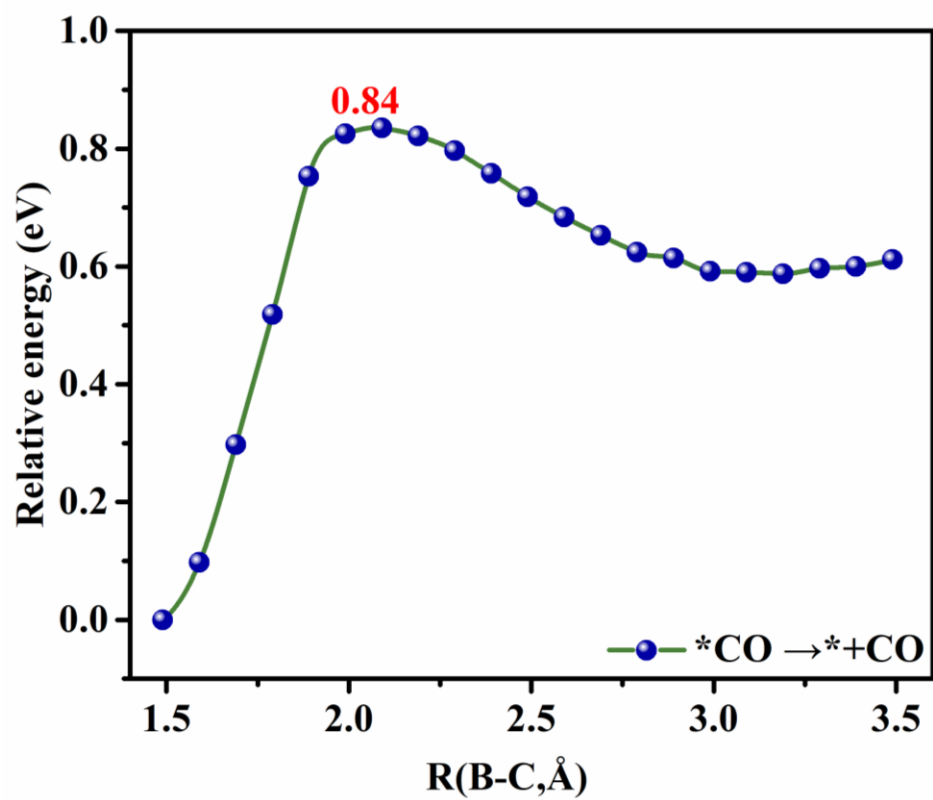
**Figure S8.** Gibbs free energy diagrams for urea production through three possible mixed pathways on the CuB<sub>12</sub> monolayer at different applied potentials.



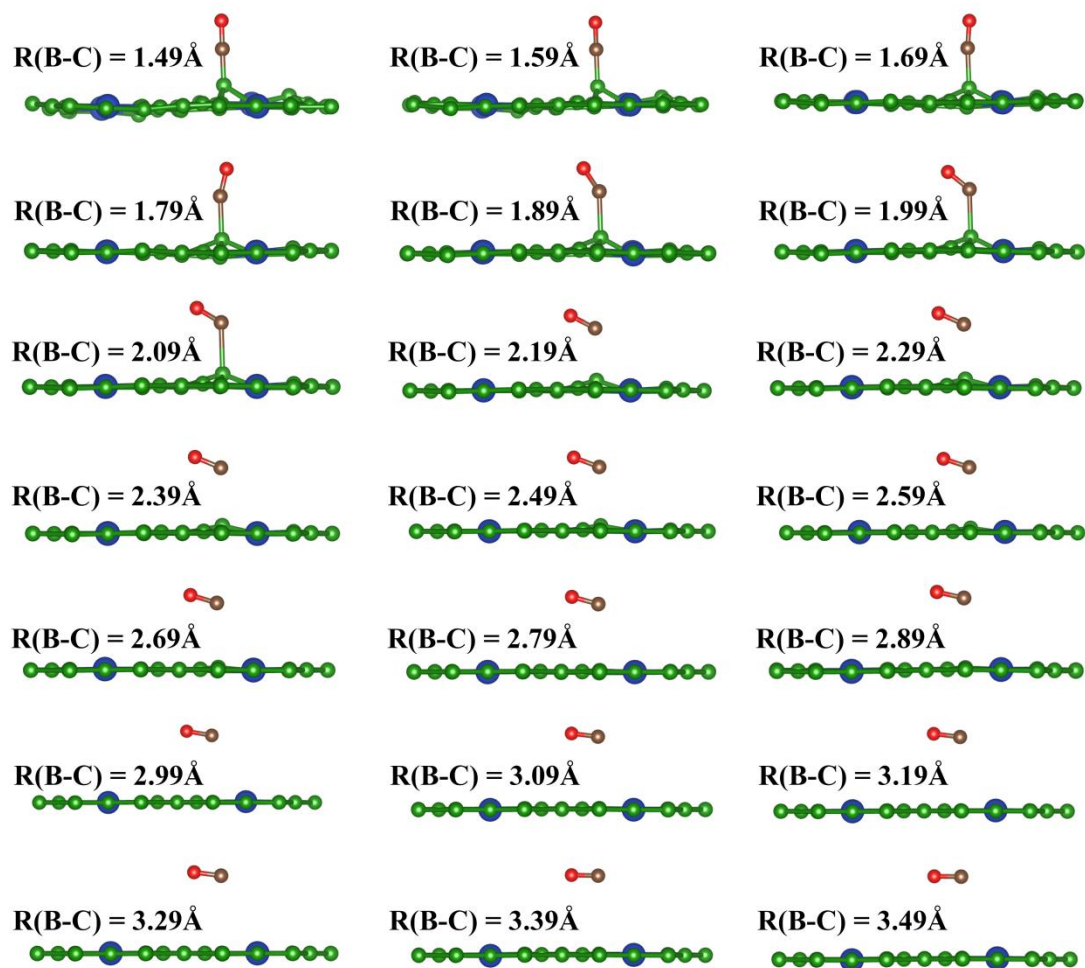
**Figure S9.** Four possible configurations and computed Gibbs free energy change values ( $\Delta G$ ) of H adsorbed on the CuB<sub>12</sub> monolayer.



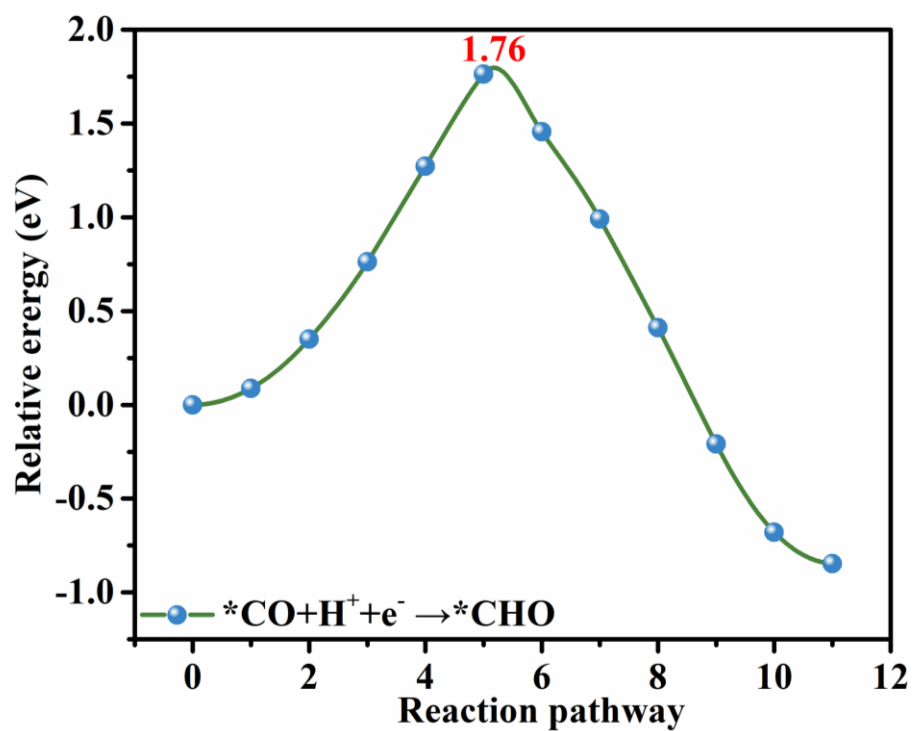
**Figure S10.** Top and side views of all optimized possible reaction intermediates for  $\text{CO}_2$  reduction reaction to C1 products ( $\text{CO}_2\text{RR-C1}$ ) on the  $\text{CuB}_{12}$  monolayer.



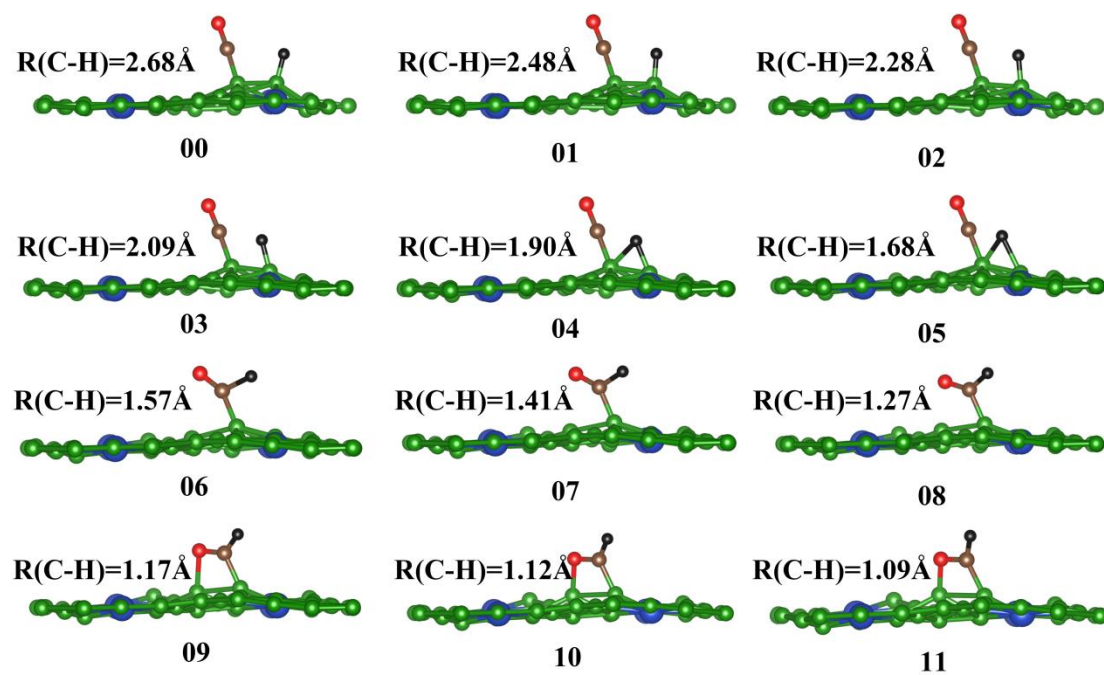
**Figure S11.** Kinetic energy barrier for CO desorption from the CuB<sub>12</sub> monolayer.



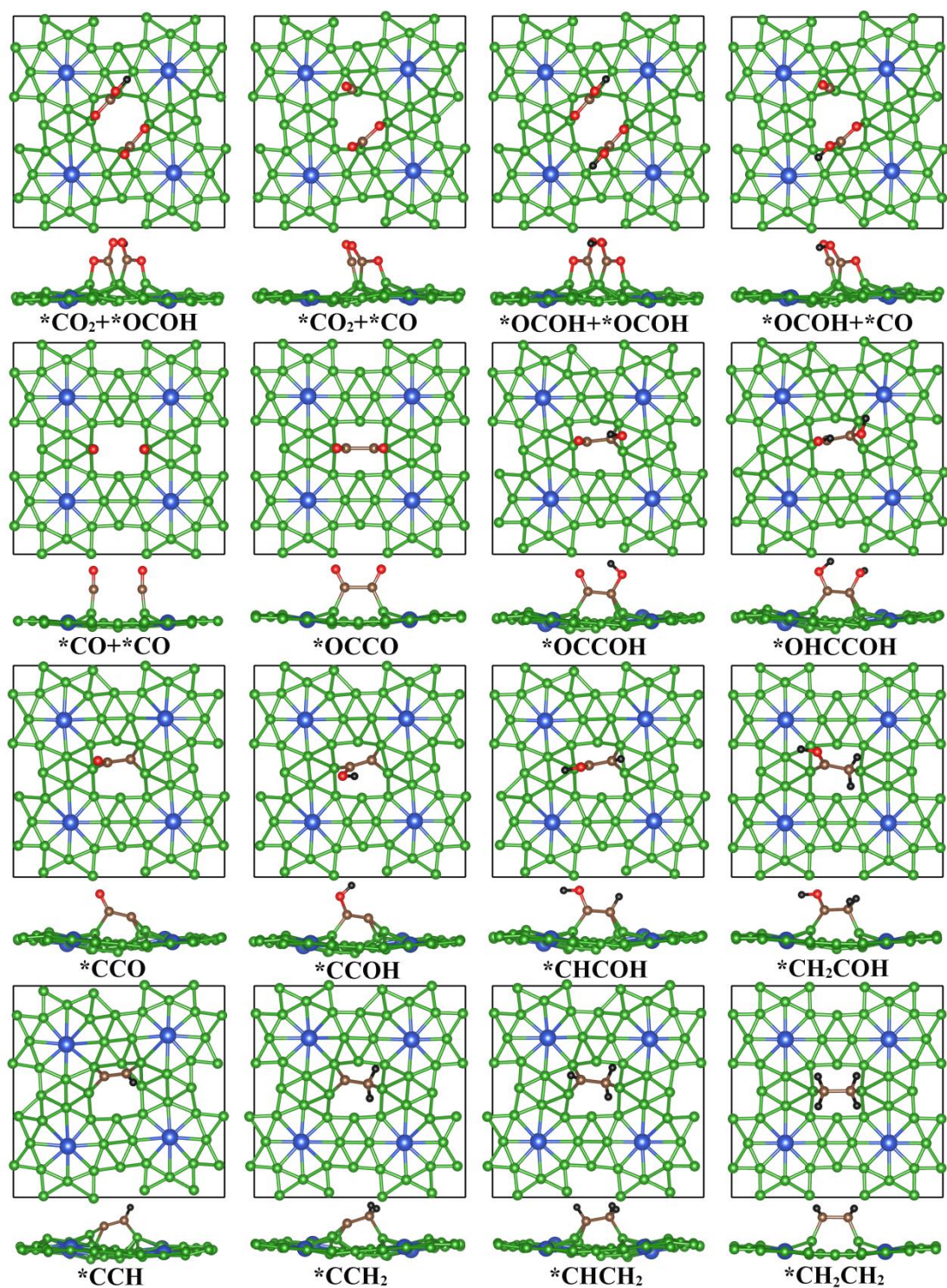
**Figure S12.** The optimized structures for the process of CO desorption from the  $\text{CuB}_{12}$  monolayer. The corresponding distances of B-C are presented.



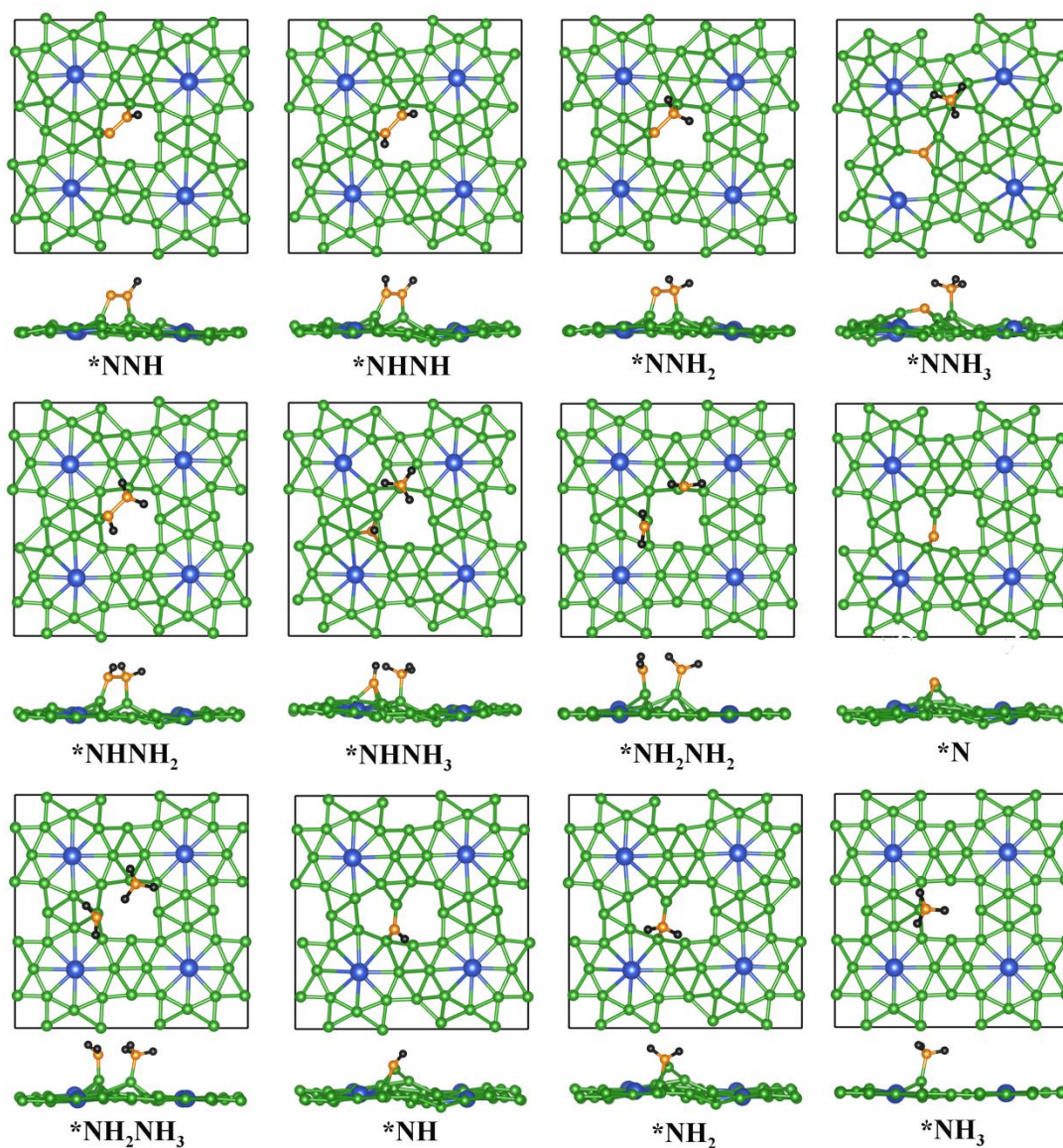
**Figure S13.** Kinetic energy barrier→on the CuB<sub>12</sub> monolayer.



**Figure S14.** The structures for reduction process of  $*\text{CO} + \text{H}^+ + \text{e}^- \rightarrow * \text{CHO}$ . The corresponding distances of C-H are presented.



**Figure S15.** Top and side views of all optimized possible reaction intermediates for  $\text{CO}_2$  reduction reaction to  $\text{C}_2$  products ( $\text{CO}_2\text{RR-C}_2$ ) on the  $\text{CuB}_{12}$  monolayer.



**Figure S16.** Top and side views of all optimized possible reaction intermediates for  $\text{N}_2$  reduction reaction (NRR) on the  $\text{CuB}_{12}$  monolayer.

## Supplementary References

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