Supporting Information for

"Regulation of Transition Metal Atoms Supported on Defective h-BN by Adjacent Monovacancies for Electrochemical CO_2 Reduction: Mechanism and d-band Spin-Polarization Effect"

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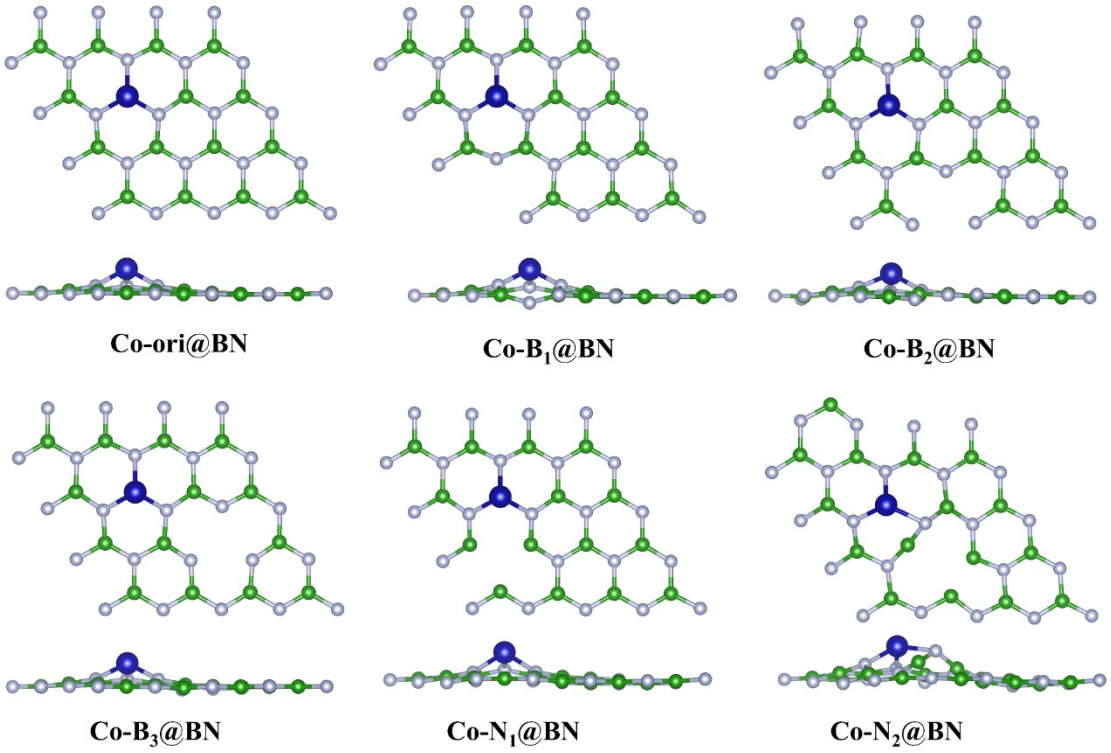

Figure S1. Top and side views of on various Co-vac@BN. Boron, nitrogen, and Co atoms are denoted by green, light blue, and dark blue balls, respectively.

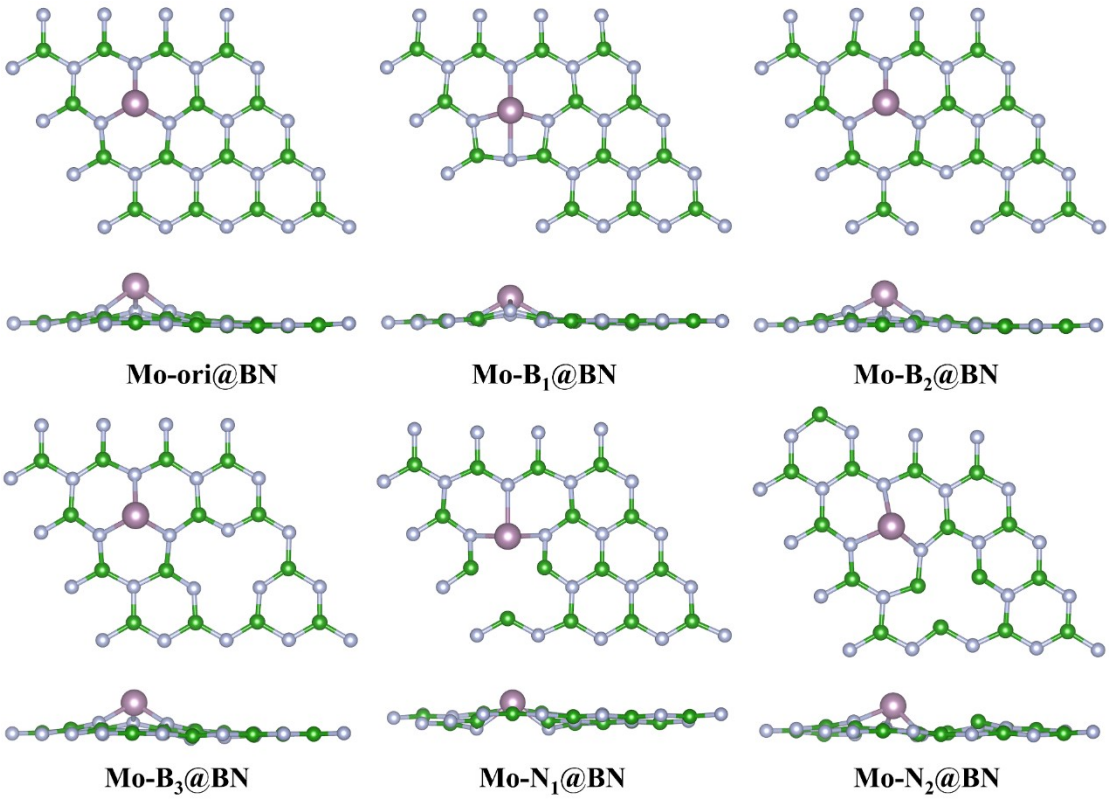

Figure S2. Top and side views of on various Mo-vac@BN. Boron, nitrogen, and Mo atoms are denoted by green, light blue, and light purple balls, respectively.

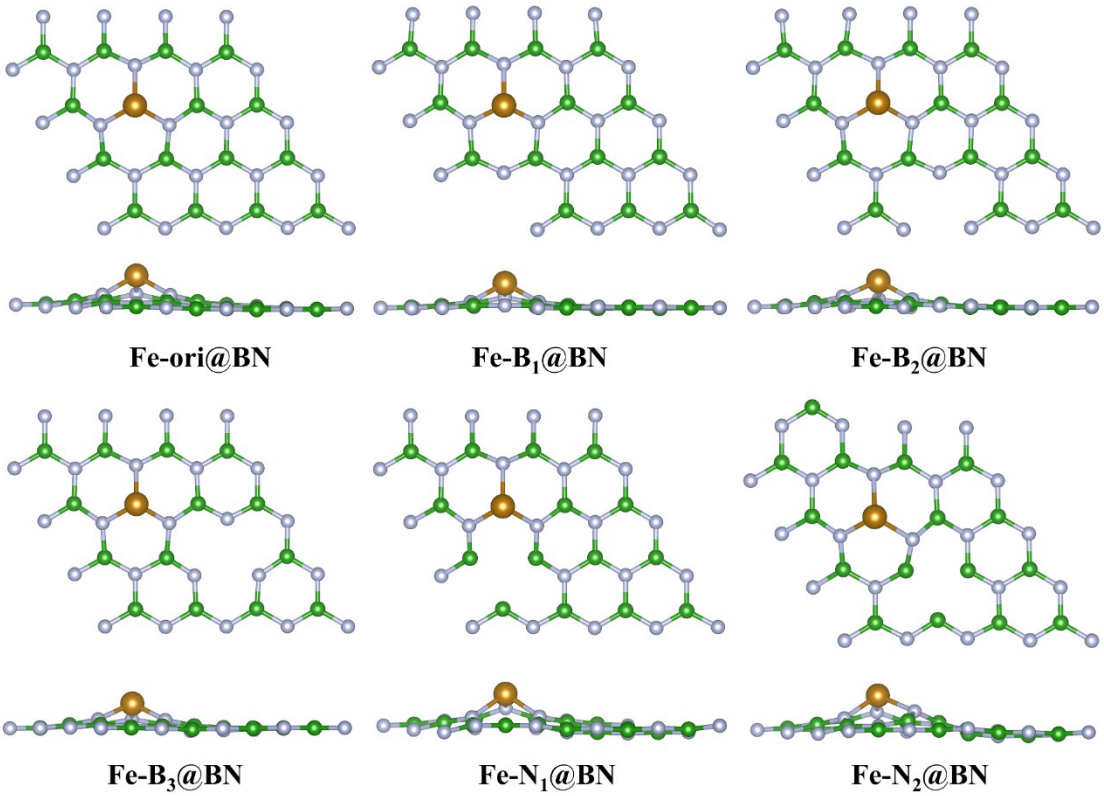

Figure S3. Top and side views of on various Fe-vac@BN. Boron, nitrogen, and Fe atoms are denoted by green, light blue, and light brown balls, respectively.

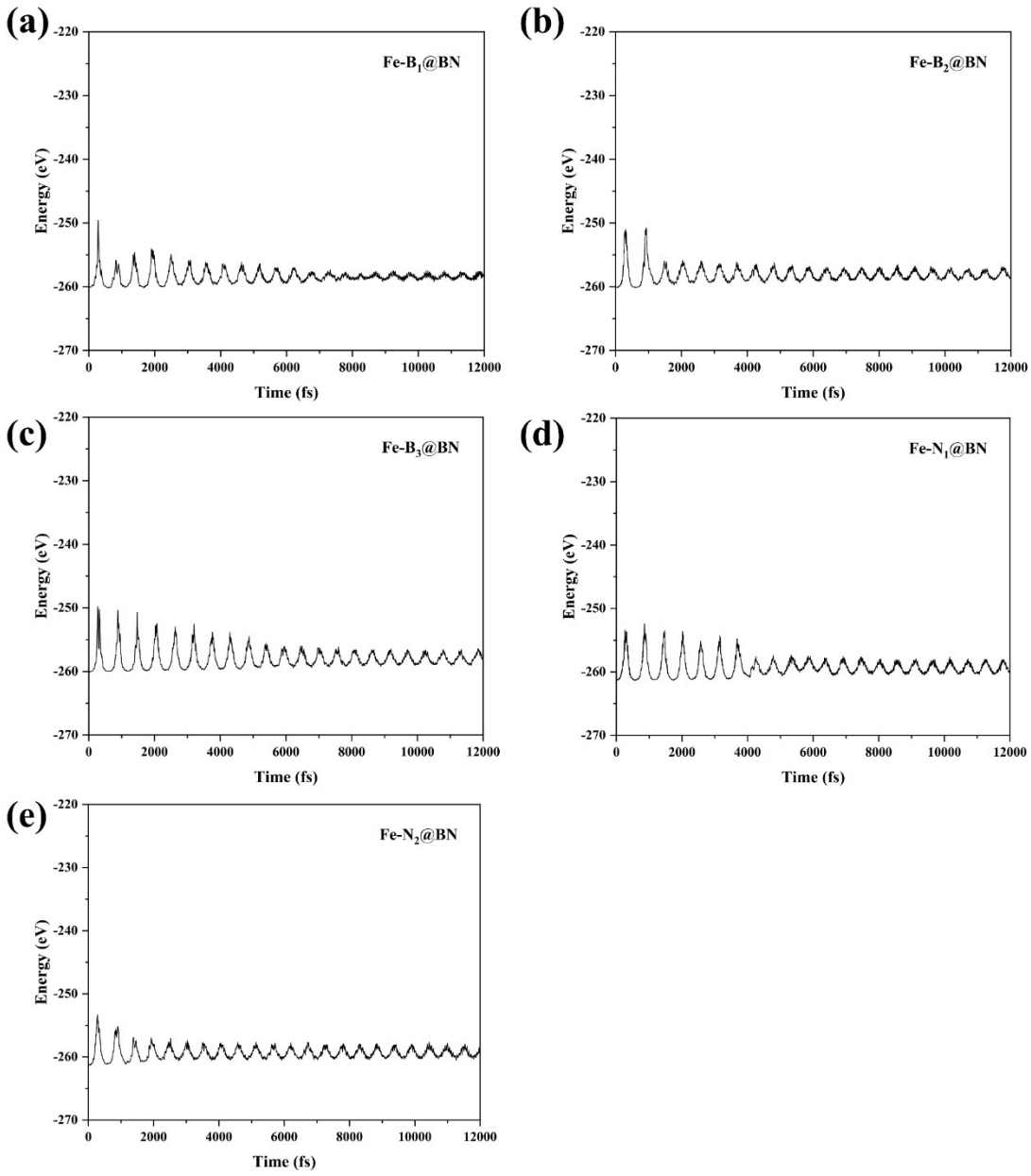

Figure S4. Energies of various Fe-vac@BN during the time progression of AIMD simulations at 500 K.

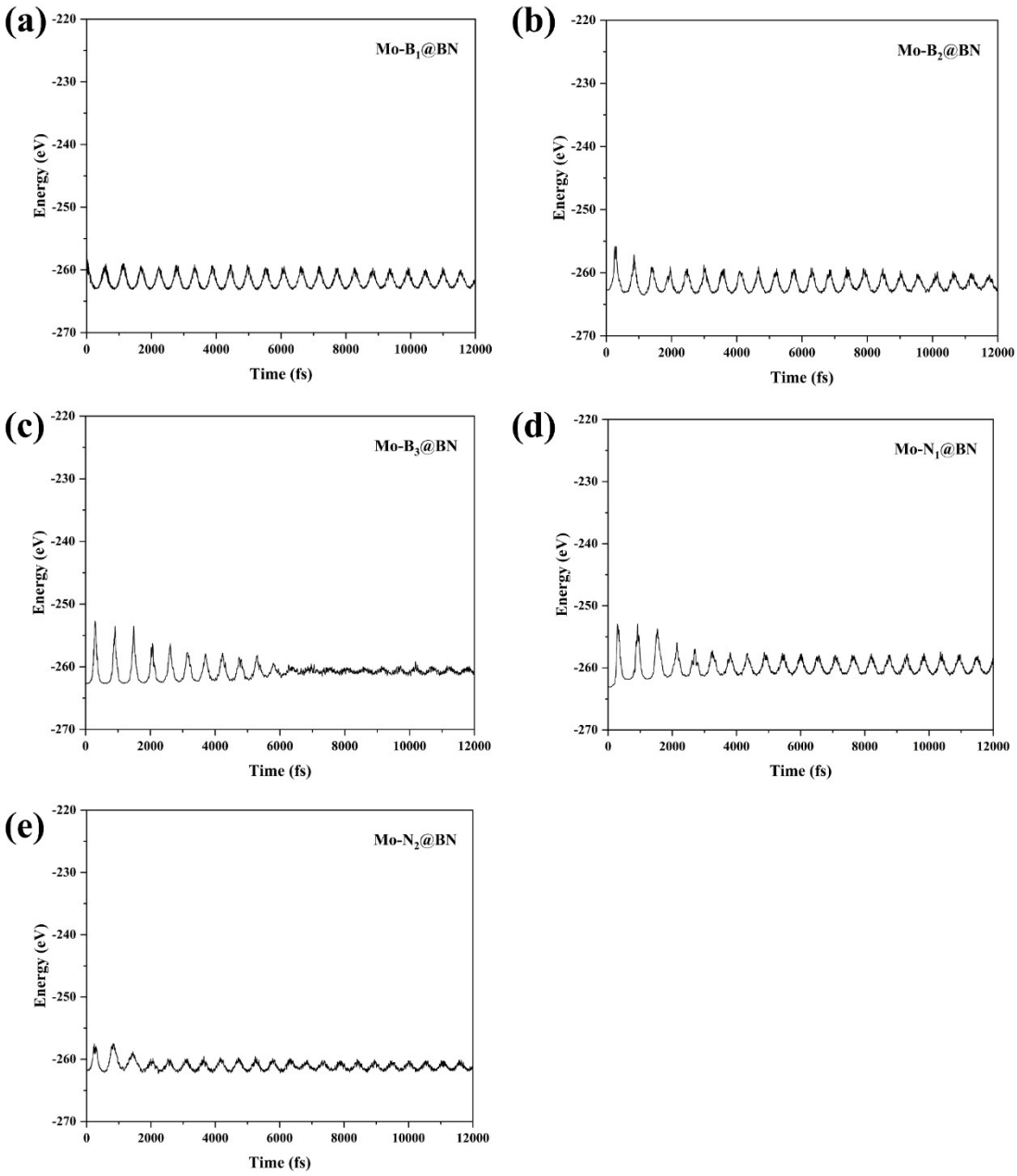

Figure S5. Energies of various Mo-vac@BN during the time progression of AIMD simulations at 500 K.

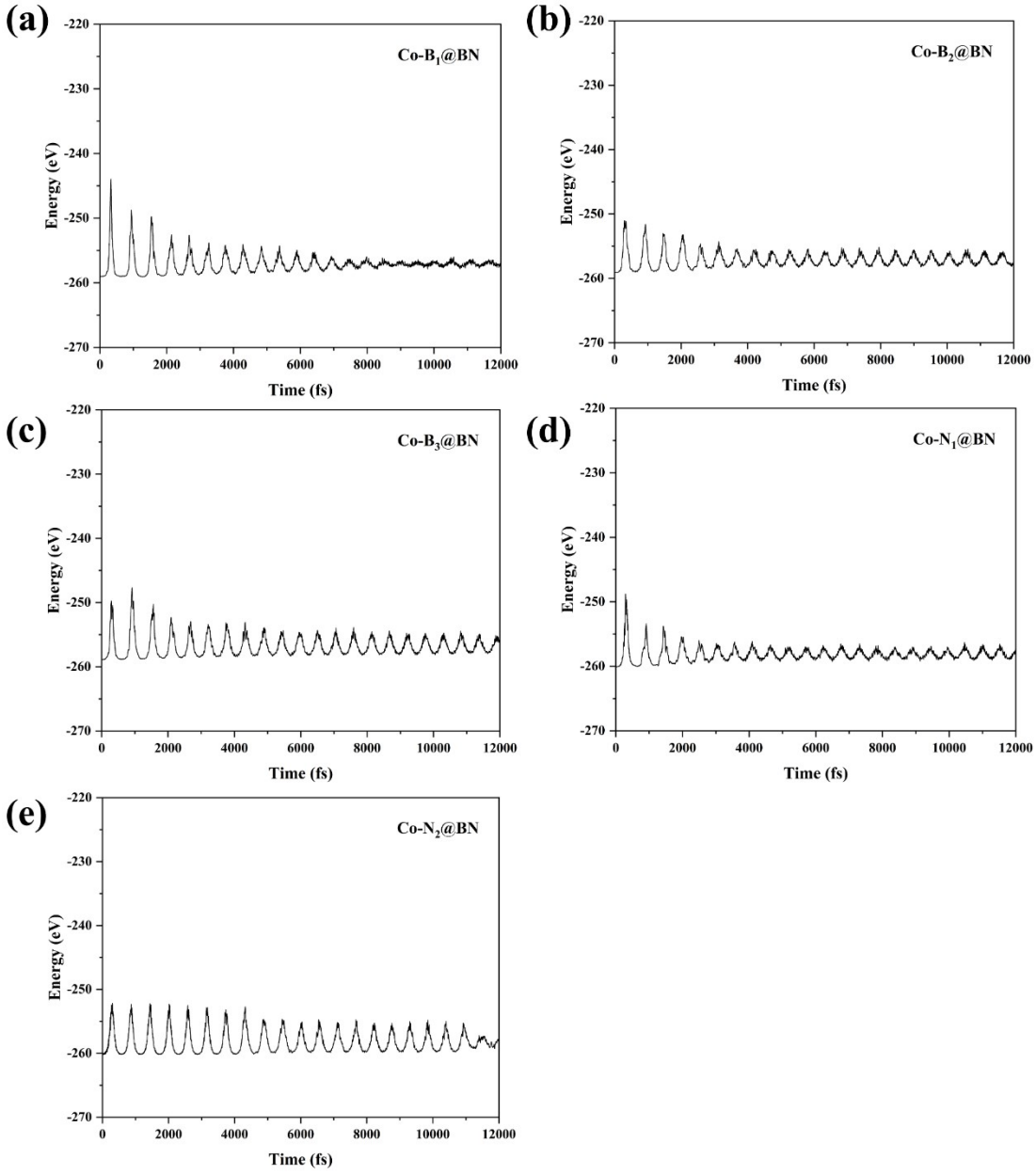

Figure S6. Energies of various Co-vac@BN during the time progression of AIMD simulations at 500 K.

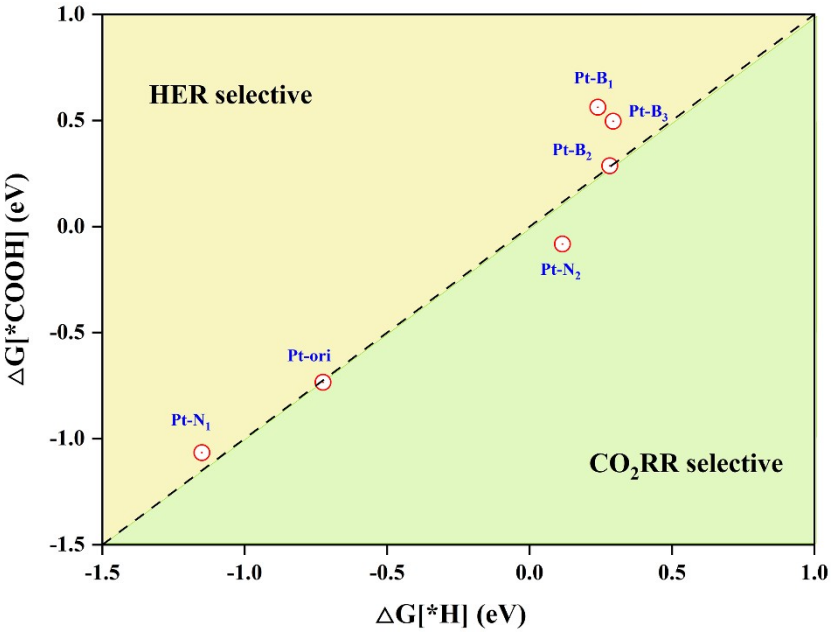

Figure S7. Gibbs free energies of the initial protonation steps of HER and CO_2RR on various Pt-vac@BN.

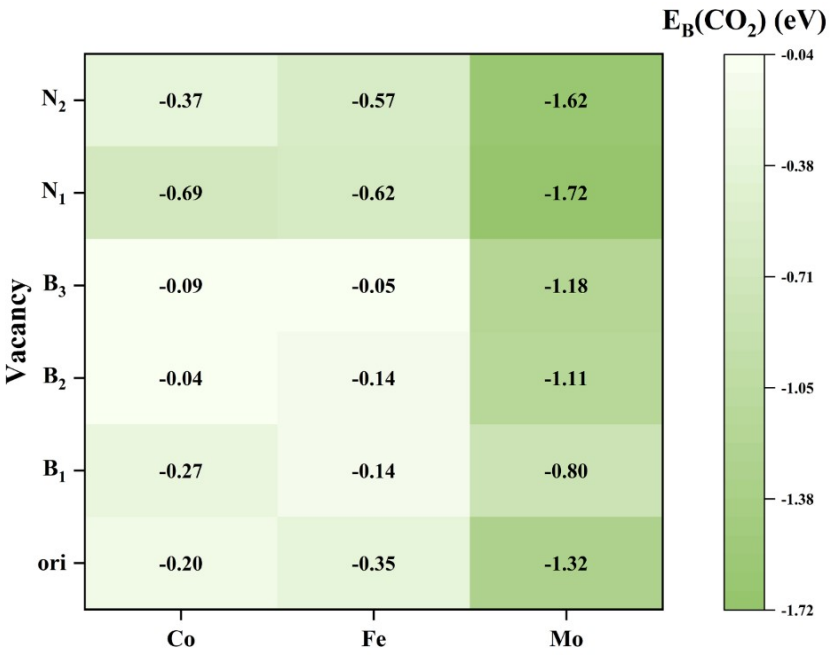

Figure S8. Calculated $E_B(CO_2)$ of various M-vac@BN.

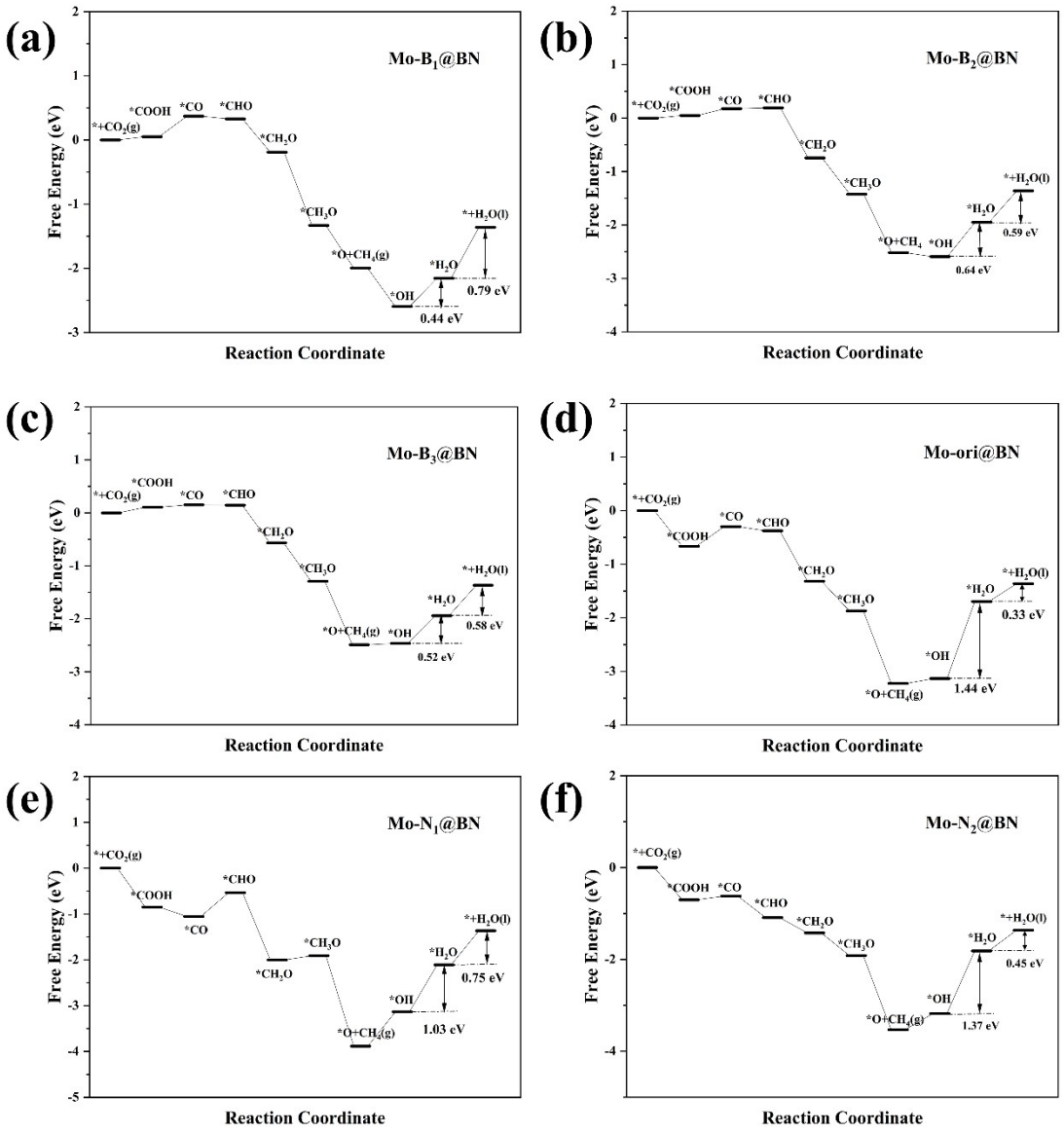

Figure S9. Free-energy profiles for the CO_2RR on various Mo-vac@BN at 0 V (*vs.* RHE).

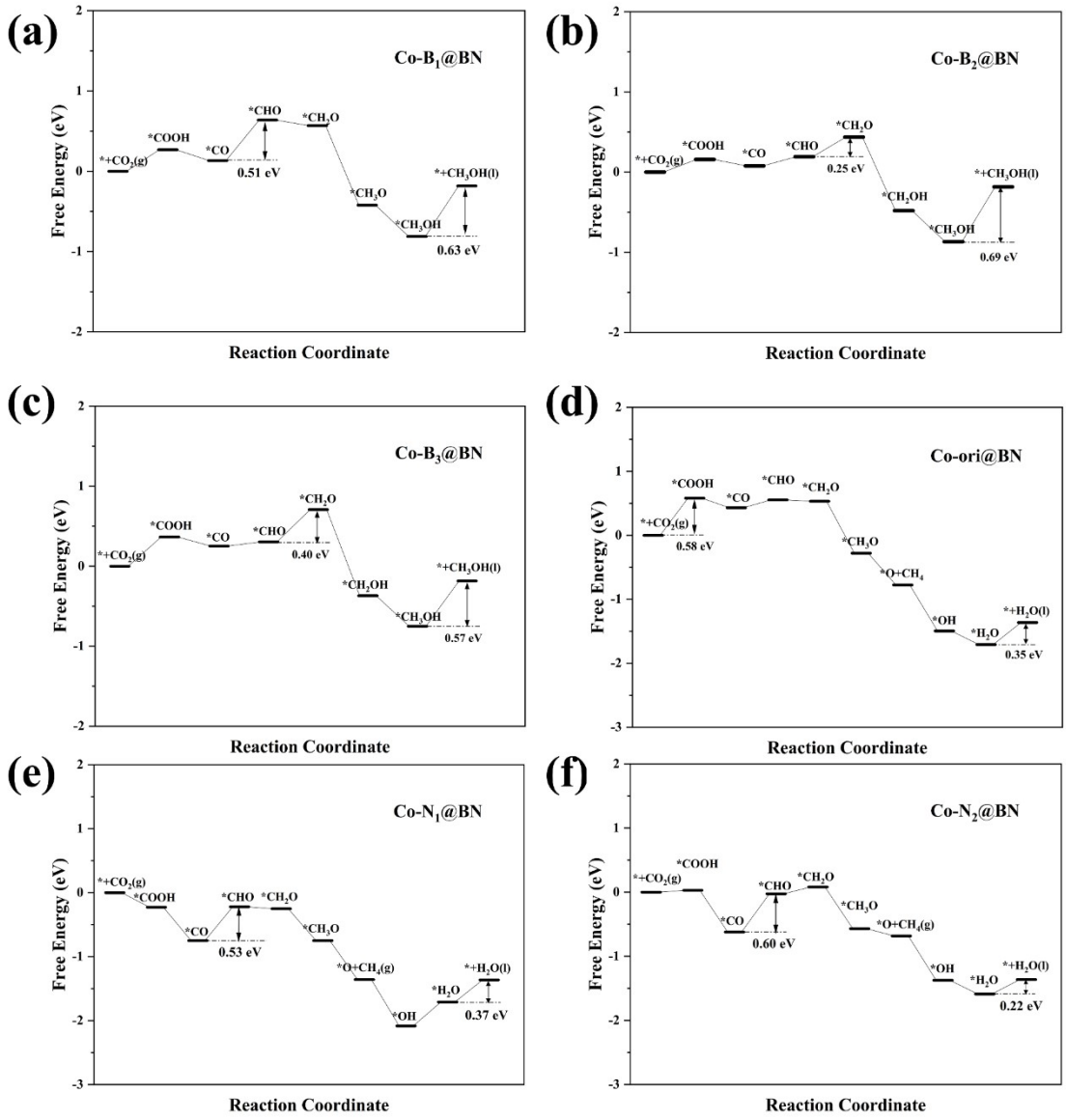

Figure S10. Free-energy profiles for the CO_2RR on various Co-vac@BN at 0 V (*vs.* RHE).

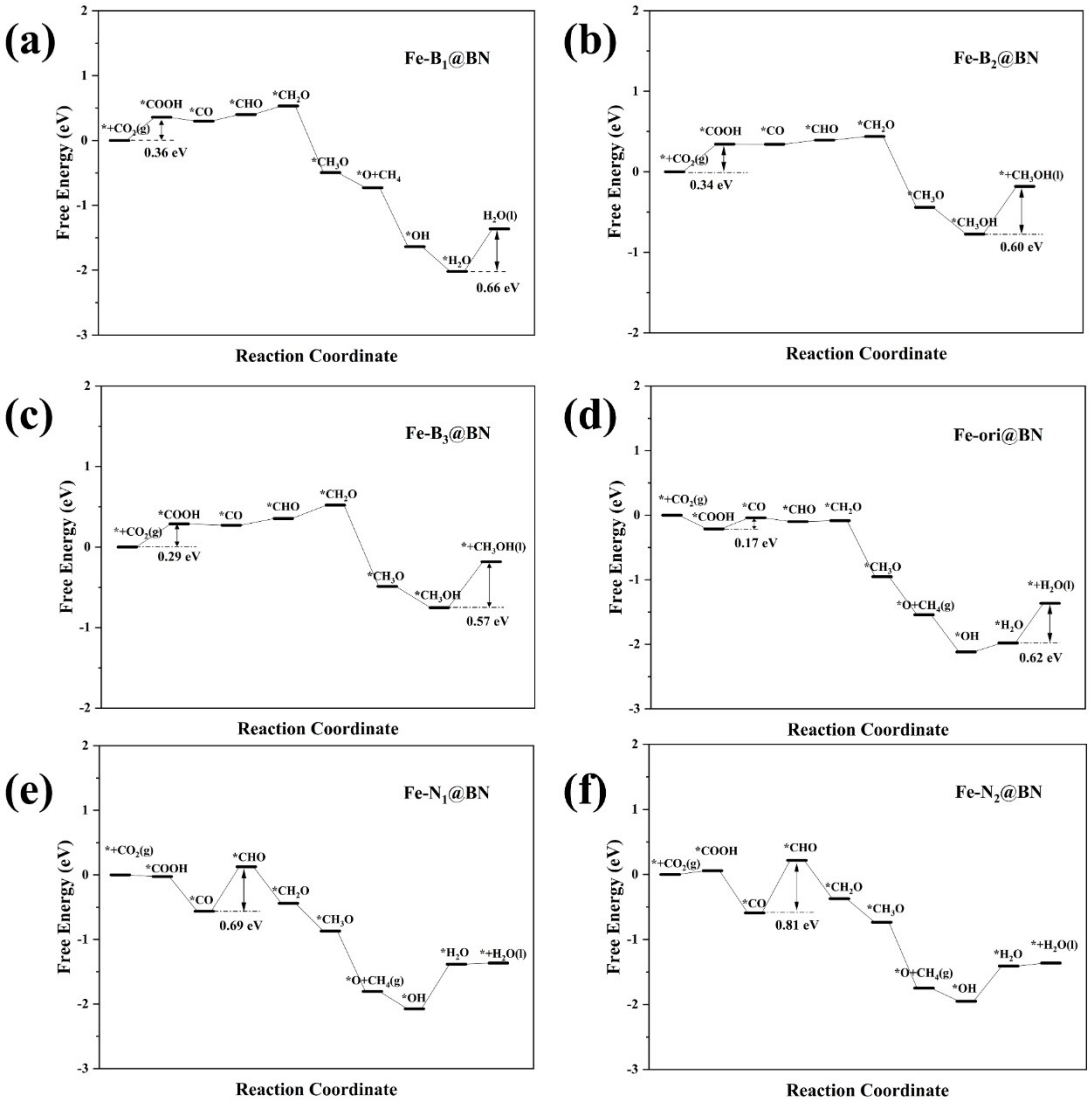

Figure S11. Free-energy profiles for the CO_2RR on various Fe-vac@BN at 0 V (*vs.* RHE).

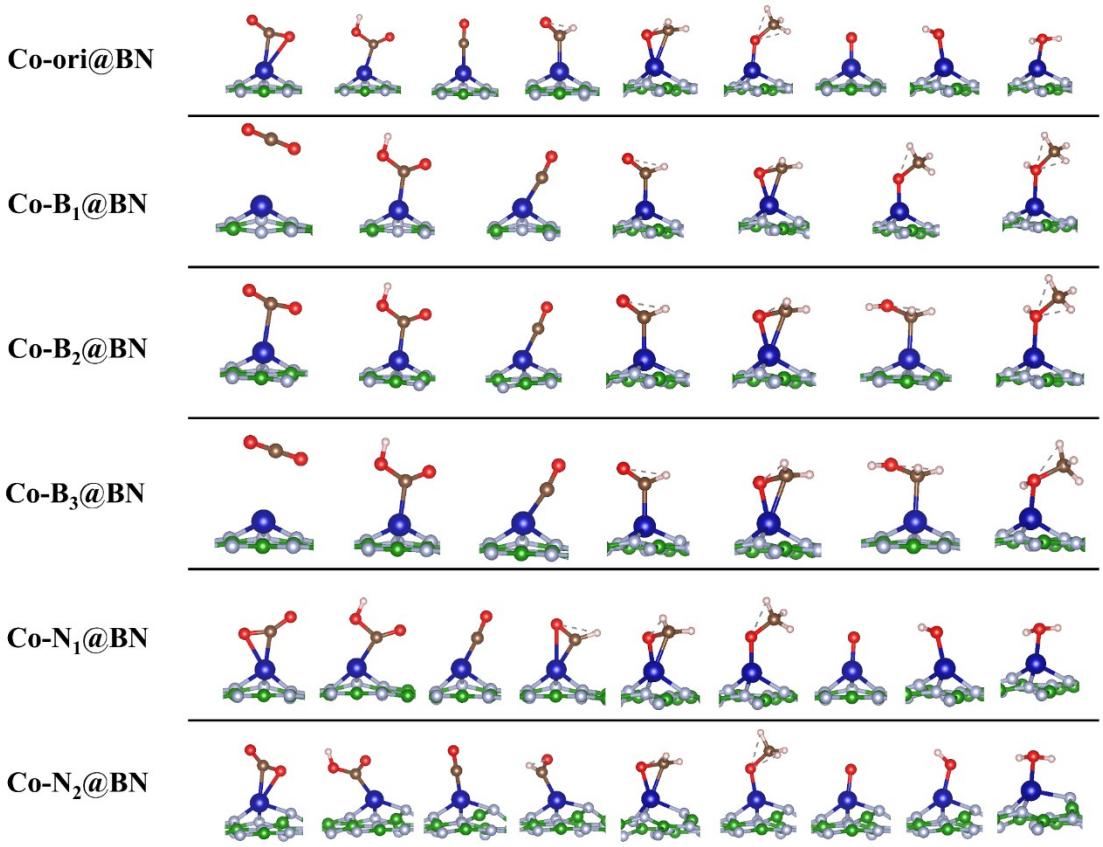

Figure S12. The intermediate structures along the reaction pathways of CO_2RR on various Co-vac@BN. Boron, nitrogen, carbon, oxygen, hydrogen, and Co atoms are denoted by green, light blue, dark brown, red, white, and blue balls, respectively.

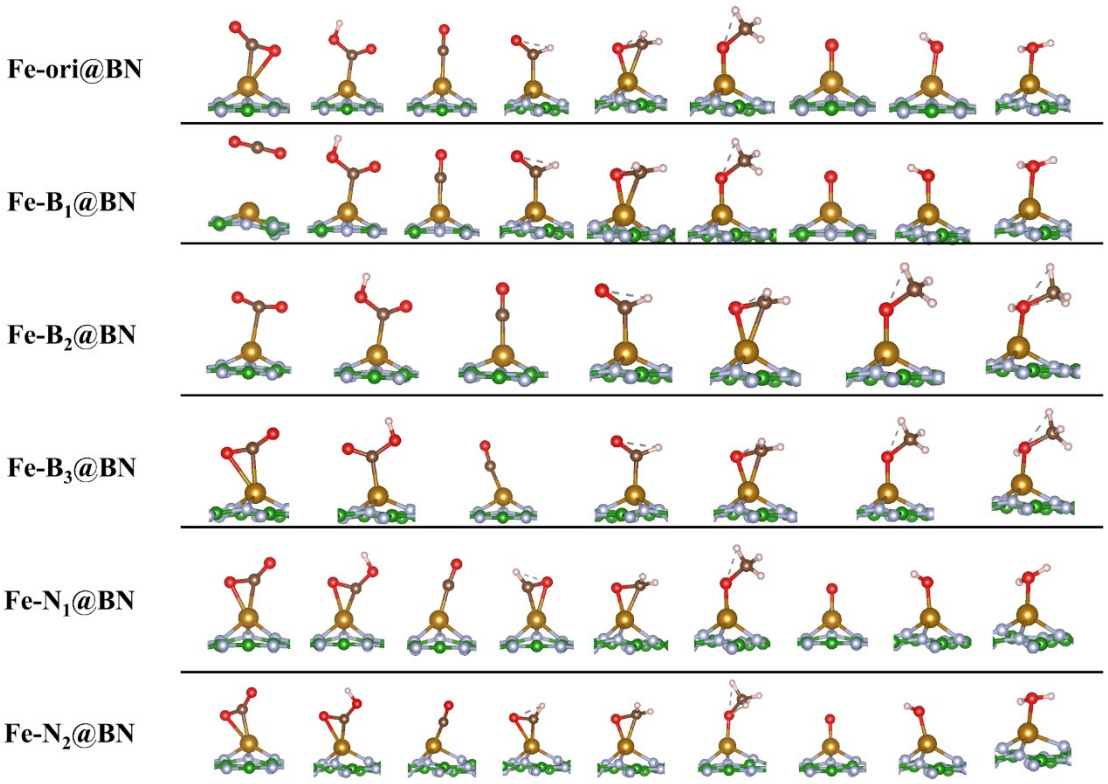

Figure S13. The intermediate structures along the reaction pathways of CO_2RR on various Fe-vac@BN. Boron, nitrogen, carbon, oxygen, hydrogen, and Fe atoms are denoted by green, light blue, dark brown, red, white, and brown balls, respectively.

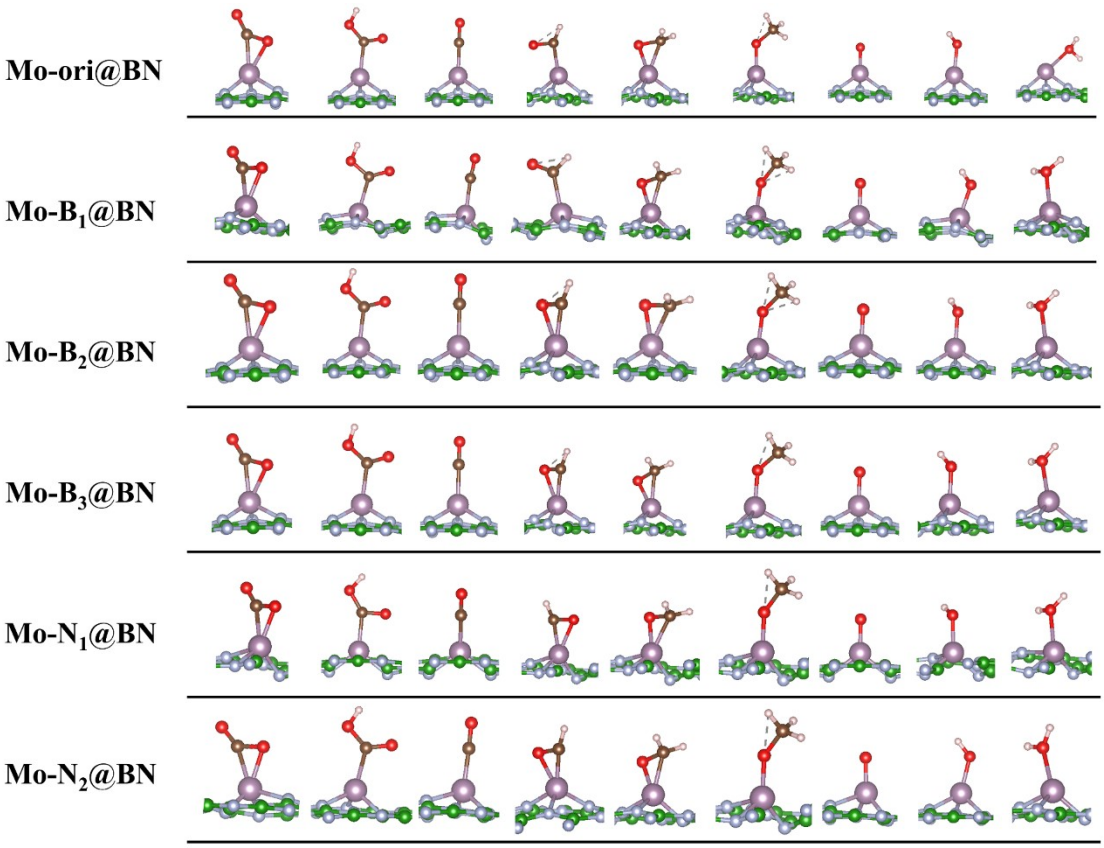

Figure S14. The intermediate structures along the reaction pathways of CO_2RR on various Mo-vac@BN. Boron, nitrogen, carbon, oxygen, hydrogen, and Mo atoms are denoted by green, light blue, dark brown, red, white, and light purple balls, respectively.

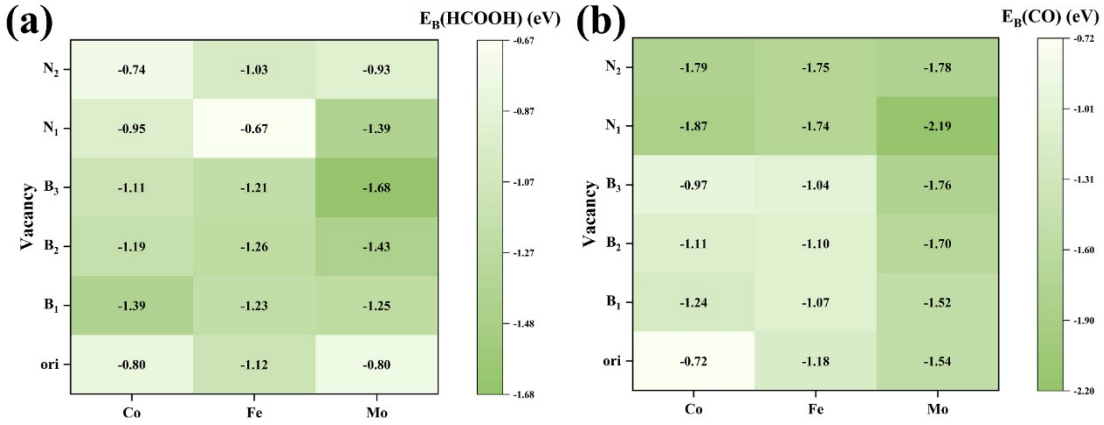

Figure S15. (a) Calculated E_B(HCOOH) of various M-vac@BN. (b) Calculated E_B(CO) of various M-vac@BN.

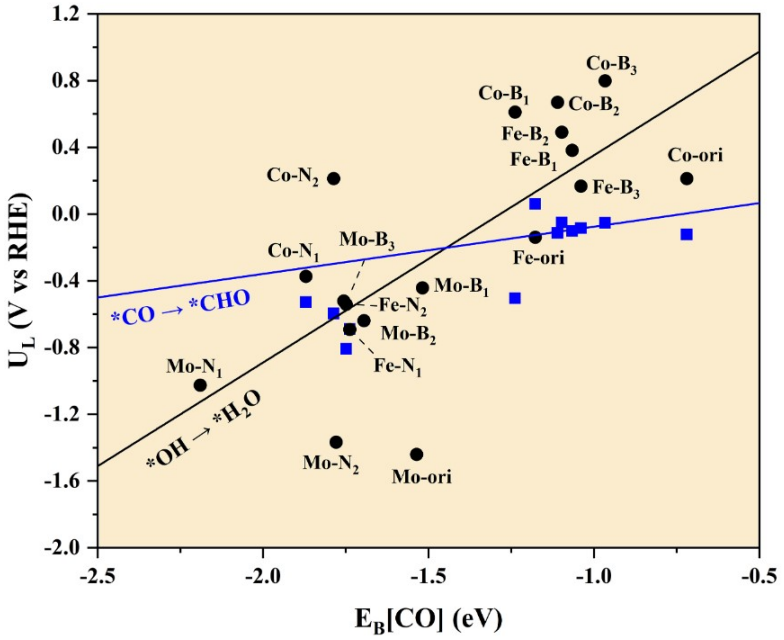

Figure S16. Correlation between the U_L for (*CO → *CHO) and (*OH → *H_2O) and the E_B(CO) of various M-vac@BN.

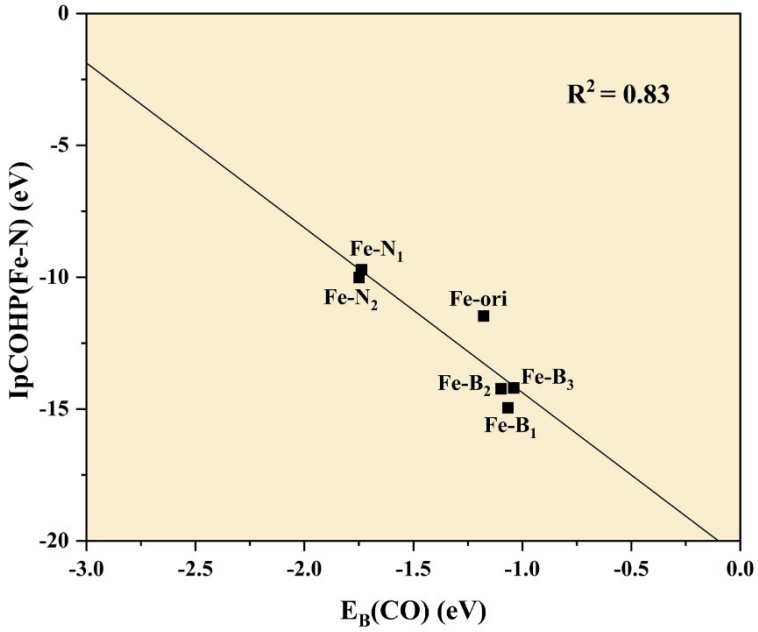

Figure S17. Correlation between the IpCOHP(Fe-N) and the E_B(CO) of Fe-vac@BN.

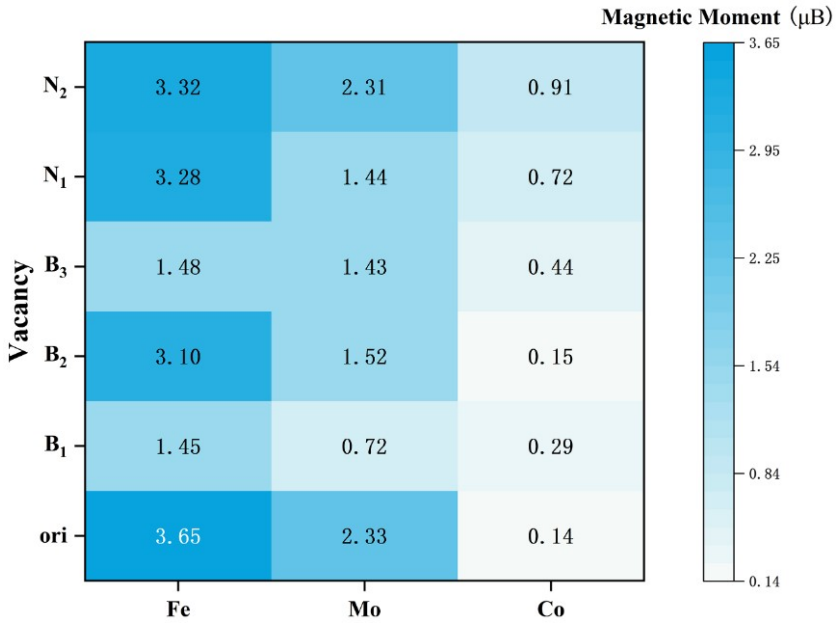

Figure S18. Calculated magnetic moments of the metal atoms in various M-vac@BN.

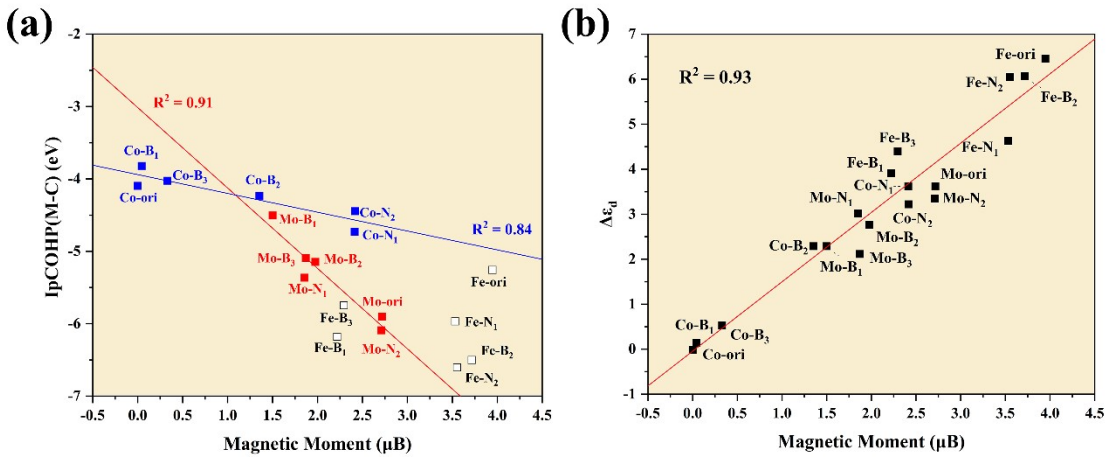

Figure S19. (a) Correlation between the IpCOHP(M-C) and calculated magnetic moments of the metal atoms M in various M-vac@BN after considering DFT+U. (b) Correlation between the calculated magnetic moments and $\Delta\varepsilon_d$ of metal atoms M in various M-vac@BN after considering DFT+U.

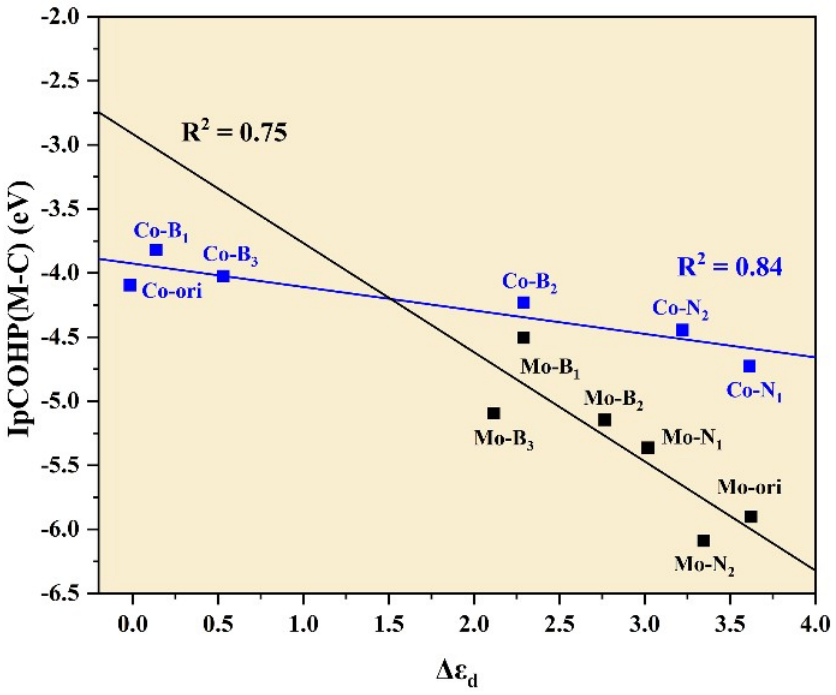

Figure S20. Correlation between IpCOHP(M-C) and $\Delta\varepsilon_d$ for M-vac@BN (M= Co, Mo) after considering DFT+U.

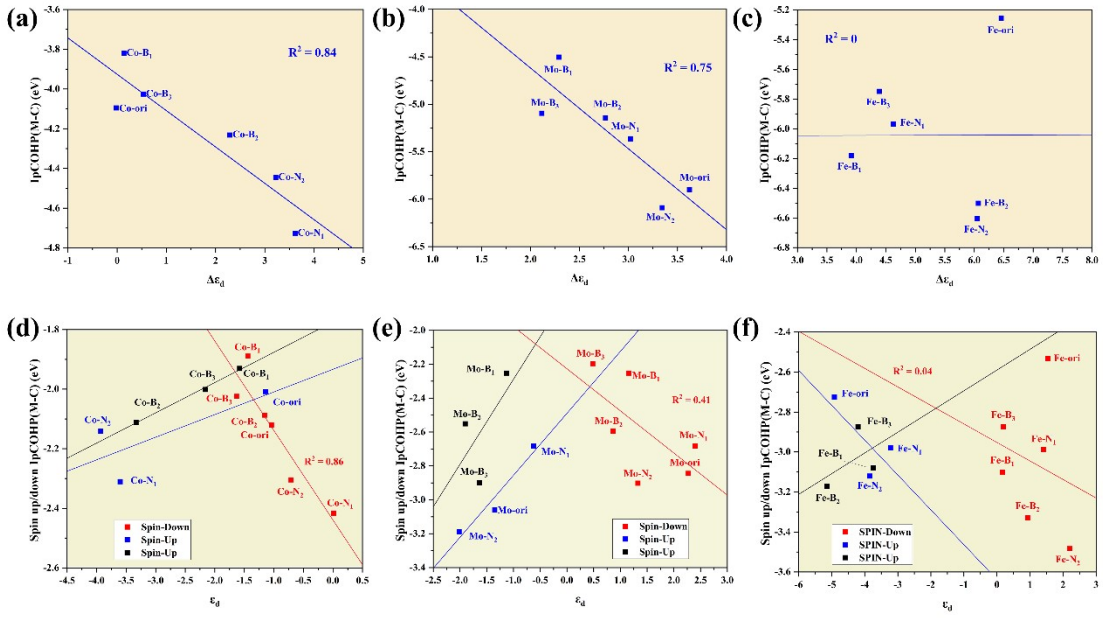

Figure S21. Correlation between IpCOHP(M-C) and $\Delta\varepsilon_d$ for (a) Co-vac@BN, (b) Mo-vac@BN, and (c) Fe-vac@BN, respectively, after considering DFT+U; Correlation between spin up/down IpCOHP(M-C) and spin up/down ε_d for (d) Co-vac@BN, (e) Mo-vac@BN, and (f) Fe-vac@BN, respectively, after considering DFT+U.

Table S1. Calculated limiting potential (U_L), overpotential (η), final products, and PDS of CO_2RR on various M-vac@BN.

Catalysts	Products	PDS	U_L (V *vs.* RHE)	η (V)
Co-ori@BN	CH_4	$*+CO_2 \rightarrow *COOH$	-0.58	0.75
Co-B_1@BN	CH_3OH	$*CO \rightarrow *CHO$	-0.51	0.54
Co-B_2@BN	CH_3OH	$*CHO \rightarrow *CH_2O$	-0.25	0.28
Co-B_3@BN	CH_3OH	$*CHO \rightarrow *CH_2O$	-0.40	0.43
Co-N_1@BN	CH_4	$*CO \rightarrow *CHO$	-0.53	0.70
Co-N_2@BN	CH_4	$*CO \rightarrow *CHO$	-0.60	0.77
Fe-ori@BN	CH_4	$*COOH \rightarrow *CO$	-0.17	0.34
Fe-B_1@BN	CH_4	$*+CO_2 \rightarrow *COOH$	-0.36	0.53
Fe-B_2@BN	CH_3OH	$*+CO_2 \rightarrow *COOH$	-0.34	0.37
Fe-B_3@BN	CH_3OH	$*+CO_2 \rightarrow *COOH$	-0.29	0.32
Fe-N_1@BN	CH_4	$*CO \rightarrow *CHO$	-0.69	0.86
Fe-N_2@BN	CH_4	$*CO \rightarrow *CHO$	-0.81	0.98
Mo-ori@BN	CH_4	$*OH \rightarrow *H_2O$	-1.44	1.61
Mo-B_1@BN	CH_4	$*OH \rightarrow *H_2O$	-0.44	0.61
Mo-B_2@BN	CH_4	$*OH \rightarrow *H_2O$	-0.64	0.81
Mo-B_3@BN	CH_4	$*OH \rightarrow *H_2O$	-0.52	0.69
Mo-N_1@BN	CH_4	$*OH \rightarrow *H_2O$	-1.03	1.20
Mo-N_2@BN	CH_4	$*OH \rightarrow *H_2O$	-1.37	1.54

Table S2. Limiting potential (U_L) and final products of CO_2RR on various catalysts reported in related researches.

Catalysts	U_L (V *vs.* RHE)	Products
Fe/defective BN [1]	-0.52	CH_4

Co/defective BN [1]	-0.68	CH_4
Pt/defective BN [1]	-0.60	CH_4
Mo@BN [2]	-0.45	CH_4
Co-DVBN [3]	-0.58	CH_3OH
Fe-DVBN [3]	-1.90	CH_4
Mo-DVBN [3]	-2.02	CH_4
Ni-DVBN [3]	-0.48	CH_3OH
Pd-DVBN [3]	-0.56	CH_3OH
Fe_2@BN [4]	-0.47	CH_4
Co_2@BN [4]	-0.75	CH_4
Ni_2@BN [4]	-0.39	CH_4
CuMn@BN [4]	-0.61	CH_4

Table S3. Calculated corrections of Gibbs free energy for the adsorbates on various M-vac@BN. All values are given in eV.

Adsorbate (Fe-ori@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.20	-0.01	0.01
*COOH	0.61	-0.24	0.11
*CO	0.19	-0.18	0.08
*HCOOH	0.93	-0.23	0.11
*CHO	0.46	-0.12	0.06

*COH	0.49	-0.17	0.08
*CHOH	0.78	-0.19	0.09
*CH_2O	0.77	-0.17	0.08
*CH_2OH	1.09	-0.21	0.10
*CH_3O	1.09	-0.18	0.08
*CH_3OH	1.41	-0.27	0.12
*O	0.07	-0.07	0.04
*OH	0.35	-0.11	0.05
*H_2O	0.65	-0.17	0.08
Adsorbate (Fe-B_1@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.19	-0.01	0.01
*COOH	0.61	-0.25	0.11
*CO	0.20	-0.17	0.07
*HCOOH	0.92	-0.23	0.11
*COH	0.48	-0.16	0.08
*CHO	0.46	-0.19	0.09
*CHOH	0.80	-0.17	0.08
*CH_2O	0.79	-0.15	0.08
*CH_2OH	1.09	-0.21	0.10
*CH_3O	1.09	-0.18	0.08
*CH_3OH	1.41	-0.27	0.12
*O	0.08	-0.06	0.03
*OH	0.33	-0.13	0.06
*H_2O	0.65	-0.19	0.09
Adsorbate (Fe-B_2@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.19	-0.02	0.01
*COOH	0.61	-0.25	0.11
*CO	0.20	-0.16	0.07
*HCOOH	0.93	-0.23	0.11

*COH	0.48	-0.17	0.08
*CHO	0.45	-0.19	0.09
*CHOH	0.77	-0.21	0.10
*CH_2O	0.79	-0.17	0.08
*CH_2OH	1.09	-0.22	0.10
*CH_3O	1.09	-0.18	0.08
*CH_3OH	1.42	-0.26	0.12
*O	0.08	-0.06	0.03
*OH	0.34	-0.11	0.06
*H_2O	0.65	-0.18	0.08
Adsorbate (Fe-B_3@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.20	-0.01	0.01
*COOH	0.61	-0.25	0.11
*HCOOH	0.92	-0.23	0.11
*CO	0.20	-0.17	0.07
*COH	0.49	-0.17	0.08
*CHO	0.46	-0.18	0.09
*CHOH	0.79	-0.13	0.07
*CH_2O	0.77	-0.18	0.09
*CH_2OH	1.09	-0.20	0.10
*CH_3O	1.09	-0.18	0.08
*CH_3OH	1.42	-0.26	0.12
*O	0.06	-0.10	0.04
*OH	0.34	-0.13	0.06
*H_2O	0.65	-0.18	0.08
Adsorbate (Fe-N_1@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.16	-0.03	0.02
*COOH	0.61	-0.24	0.11
*CO	0.20	-0.17	0.07

*HCOOH	0.93	-0.24	0.11
*COH	0.46	-0.20	0.09
*CHO	0.44	-0.19	0.09
*CHOH	0.77	-0.14	0.07
*CH_2O	0.78	-0.17	0.08
*CH_2OH	1.08	-0.20	0.10
*CH_3O	1.08	-0.24	0.11
*CH_3OH	1.40	-0.24	0.11
*O	0.08	-0.06	0.03
*OH	0.33	-0.13	0.06
*H_2O	0.65	-0.15	0.08
Adsorbate (Fe-N_2@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.17	-0.02	0.01
*COOH	0.60	-0.25	0.11
*CO	0.21	-0.15	0.07
*HCOOH	0.92	-0.26	0.12
*COH	0.46	-0.19	0.09
*CHO	0.46	-0.16	0.08
*CHOH	0.78	-0.19	0.09
*CH_2O	0.77	-0.17	0.08
*CH_2OH	1.06	-0.24	0.11
*CH_3O	1.07	-0.20	0.09
*CH_3OH	1.40	-0.25	0.11
*O	0.08	-0.06	0.03
*OH	0.34	-0.12	0.06
*H_2O	0.66	-0.15	0.08
Adsorbate (Co-ori@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.19	-0.01	0.01
*COOH	0.60	-0.19	0.09

*CO	0.19	-0.17	0.08
*HCOOH	0.93	-0.24	0.11
*COH	0.47	-0.18	0.09
*CHO	0.44	-0.14	0.07
*CHOH	0.81	-0.16	0.08
*CH_2O	0.77	-0.18	0.09
*CH_2OH	1.08	-0.23	0.11
*CH_3O	1.08	-0.14	0.06
*CH_3OH	1.41	-0.19	0.10
*O	0.08	-0.06	0.03
*OH	0.35	-0.11	0.06
*H_2O	0.65	-0.15	0.08
Adsorbate (Co-B_1@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.18	-0.02	0.01
*COOH	0.61	-0.26	0.12
*CO	0.21	-0.16	0.07
*HCOOH	0.93	-0.23	0.11
*COH	0.48	-0.17	0.08
*CHO	0.46	-0.19	0.09
*CHOH	0.78	-0.17	0.08
*CH_2O	0.77	-0.19	0.09
*CH_2OH	1.10	-0.21	0.10
*CH_3O	1.08	-0.18	0.08
*CH_3OH	1.40	-0.23	0.11
*O	0.08	-0.06	0.03
*OH	0.35	-0.10	0.05
*H_2O	0.66	-0.16	0.08
Adsorbate (Co-B_2@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.18	-0.02	0.01

*COOH	0.61	-0.25	0.11
*HCOOH	0.93	-0.23	0.11
*CO	0.21	-0.15	0.07
*COH	0.47	-0.18	0.08
*CHO	0.45	-0.14	0.07
*CHOH	0.77	-0.15	0.07
*CH_2O	0.77	-0.19	0.09
*CH_2OH	1.10	-0.21	0.10
*CH_3O	1.09	-0.18	0.08
*CH_3OH	1.39	-0.18	0.09
*O	0.08	-0.06	0.03
*OH	0.34	-0.12	0.06
*H_2O	0.66	-0.17	0.08
*CH	0.32	-0.09	0.05
*CH_2	0.60	-0.12	0.07

Adsorbate (Co-B_3@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.19	-0.02	0.01
*COOH	0.61	-0.19	0.09
*CO	0.21	-0.14	0.07
*HCOOH	0.92	-0.22	0.11
*COH	0.46	-0.13	0.06
*CHO	0.46	-0.19	0.09
*CHOH	0.80	-0.16	0.08
*CH_2O	0.77	-0.19	0.09
*CH_2OH	1.10	-0.21	0.10
*CH_3O	1.08	-0.18	0.08
*CH_3OH	1.42	-0.26	0.12
*O	0.08	-0.06	0.03
*OH	0.34	-0.11	0.06

*H_2O	0.66	-0.16	0.08
*CH	0.31	-0.09	0.05
*CH_2	0.59	-0.08	0.05
Adsorbate (Co-N_1@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.21	-0.01	0.01
*COOH	0.60	-0.24	0.11
*CO	0.22	-0.15	0.06
*HCOOH	0.93	-0.23	0.11
*COH	0.48	-0.17	0.08
*CHO	0.47	-0.17	0.08
*CHOH	0.80	-0.16	0.08
*CH_2O	0.77	-0.17	0.08
*CH_2OH	1.07	-0.17	0.08
*CH_3O	1.08	-0.25	0.11
*CH_3OH	1.40	-0.24	0.11
*O	0.06	-0.09	0.04
*OH	0.35	-0.11	0.05
*H_2O	0.66	-0.14	0.07
Adsorbate (Co-N_2@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.22	-0.01	0.01
*COOH	0.62	-0.23	0.11
*CO	0.22	-0.15	0.07
*HCOOH	0.93	-0.23	0.11
*COH	0.47	-0.18	0.08
*CHO	0.46	-0.18	0.08
*CHOH	0.79	-0.14	0.07
*CH_2O	0.77	-0.18	0.09
*CH_2OH	1.08	-0.23	0.10
*CH_3O	1.08	-0.19	0.09

*CH_3OH	1.40	-0.25	0.11
*O	0.07	-0.06	0.03
*OH	0.35	-0.05	0.03
*H_2O	0.66	-0.14	0.08
Adsorbate (Mo-ori@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.17	-0.02	0.01
*COOH	0.59	-0.27	0.12
*CO	0.19	-0.16	0.07
*HCOOH	0.86	-0.26	0.12
*CO	0.19	-0.16	0.07
*COH	0.47	-0.18	0.09
*CHO	0.45	-0.18	0.08
*CHOH	0.77	-0.19	0.09
*CH_2O	0.78	-0.16	0.08
*CH_2OH	1.07	-0.20	0.10
*CH_3O	1.08	-0.21	0.09
*CH_3OH	1.39	-0.25	0.11
*O	0.07	-0.07	0.04
*OH	0.33	-0.13	0.06
*H_2O	0.65	-0.15	0.08
Adsorbate (Mo-B_1@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.19	-0.01	0.01
*COOH	0.60	-0.26	0.12
*CO	0.19	-0.17	0.08
*HCOOH	0.91	-0.17	0.08
*COH	0.52	-0.12	0.06
*CHO	0.45	-0.20	0.09
*CHOH	0.78	-0.20	0.09
*CH_2O	0.79	-0.13	0.07

*CH_2OH	1.08	-0.23	0.10
*CH_3O	1.08	-0.21	0.09
*CH_3OH	1.41	-0.22	0.10
*O	0.08	-0.06	0.03
*OH	0.34	-0.11	0.06
*H_2O	0.65	-0.19	0.09
Adsorbate (Mo-B_2@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.17	-0.02	0.01
*COOH	0.59	-0.27	0.12
*HCOOH	0.91	-0.26	0.12
*CO	0.19	-0.17	0.08
*COH	0.46	-0.19	0.09
*CHO	0.47	-0.14	0.07
*CHOH	0.78	-0.19	0.09
*CH_2O	0.79	-0.14	0.07
*CH_2OH	1.07	-0.17	0.08
*CH_3O	1.08	-0.21	0.09
*CH_3OH	1.40	-0.19	0.09
*O	0.08	-0.06	0.03
*OH	0.32	-0.09	0.05
*H_2O	0.65	-0.19	0.09
Adsorbate (Mo-B_3@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.18	-0.01	0.01
*COOH	0.60	-0.27	0.12
*HCOOH	0.91	-0.23	0.11
*CO	0.19	-0.16	0.08
*COH	0.47	-0.18	0.09
*CHO	0.47	-0.14	0.07
*CHOH	0.78	-0.19	0.09

*CH_2O	0.79	-0.14	0.07
*CH_2OH	1.07	-0.22	0.10
*CH_3O	1.08	-0.22	0.09
*CH_3OH	1.40	-0.25	0.11
*O	0.07	-0.06	0.03
*OH	0.33	-0.12	0.06
*H_2O	0.65	-0.18	0.09
Adsorbate (Mo-N_1@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.17	-0.03	0.02
*COOH	0.60	-0.25	0.11
*HCOOH	0.91	-0.25	0.12
*CO	0.20	-0.15	0.07
*COH	0.46	-0.20	0.09
*CHO	0.45	-0.15	0.08
*CHOH	0.78	-0.19	0.09
*CH_2O	0.80	-0.14	0.07
*CH_2OH	1.08	-0.20	0.10
*CH_3O	1.08	-0.26	0.11
*CH_3OH	1.40	-0.27	0.12
*O	0.08	-0.06	0.03
*OH	0.36	-0.10	0.05
*H_2O	0.66	-0.15	0.07
Adsorbate (Mo-N_2@BN)	**Zero Point Energies**	**-TS**	$\int C_p dT$
*H	0.17	-0.02	0.01
*COOH	0.59	-0.27	0.12
*HCOOH	0.90	-0.25	0.12
*CO	0.19	-0.16	0.07
*COH	0.48	-0.17	0.08
*CHO	0.48	-0.12	0.06

*CHOH	0.78	-0.19	0.09
*CH_2O	0.78	-0.16	0.08
*CH_2OH	1.08	-0.20	0.10
*CH_3O	1.08	-0.21	0.09
*CH_3OH	1.38	-0.19	0.09
*O	0.07	-0.07	0.04
*OH	0.32	-0.14	0.07
*H_2O	0.61	-0.15	0.08

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