

Supporting Information for

Efficient Modulation of Catalytic Performance of Electrocatalytic Nitrogen Reduction with Transition Metal Anchored N/O-codoped Graphene by Coordination Engineering

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Figure S1. The results from high-throughput screening for TM-O₁N₃@Gra (a, a', a''), TM-O₂N₂^α@Gra (b, b', b''), TM-O₂N₂^β@Gra (c, c', c''), TM-O₂N₂^γ@Gra (d, d', d''), TM-O₃N₁@Gra (e, e', e''), and TM-O₄@Gra (f, f', f''). The navy and orange dotted lines refer to 0 eV, and the magenta, violet, pink and olive dashed lines refer to 0.50 eV.

Figure S2. Gibbs free energy diagrams of eNRR on 21 potential candidates that meet three screening criteria at zero potential.

Figure S3. The geometry configurations of reaction intermediates on V-N₄@Gra (a), Tc-N₄@Gra (b), V-O₁N₃@Gra (c), V-O₂N₂^α@Gra (d), V-O₂N₂^β@Gra (e), V-O₂N₂^γ@Gra (f), V-O₃N₁@Gra (g), Mo-O₃N₁@Gra (h), V-O₄@Gra (i), and Ru-O₄@Gra (j) along the most favorable reaction pathways.

Figure S4. The evolution of N-N bond length along the most favorable pathways on the 10 selected catalysts.

Figure S5. The charge distribution on different fragments (i.e., N₂-TM-O_xN_yC_z, here C_z are those C atoms directly connected to O/N in TM-O_xN_y) of the 10 selected catalysts. The positive and negative charge values represent gain and loss of electrons, respectively.

Figure S6. Total density of states (TDOS) and projected density of states (PDOS) before and after N₂ adsorption on the 10 selected catalysts. The Fermi level is set at 0 eV.

Figure S7. The relationships between the charge difference (ΔQ) of TM atom and the d-band center difference (ΔE_d) between before N₂ adsorption and after N₂ adsorption of the 10 selected catalysts.

Figure S8. We attempt to obtain the relationship between catalytic activity (can be indicated by ΔG_{max} of the PDS) and adsorption energy of different intermediate species (such as, *N₂, *NNH, *N, *NH₂) for 21 selected catalyst materials (showed as 21 points in a-d), but from the obtained data, there is no clear functional relationship between them (such as linear relationship or volcanic curve) because the obtained data are randomly distributed. (a) ΔG_{max} vs. ΔE_{ads}(*N₂), (b) ΔG_{max} vs. ΔE_{ads}(*NNH), (c) ΔG_{max} vs. ΔE_{ads}(*N), and (d) ΔG_{max} vs. ΔE_{ads}(*NH₂).

Table S1. The lattice parameters (Å), space groups, point groups, and magnetic moments (TM and total) of optimized crystal structures of 210 TM-O_xN_y@Gra monolayers.

Table S2. ΔG(*N₂), ΔG(*N₂→*NNH) and ΔG(*NH₂→*NH₃) through side-on and/or end-on modes on TM-O_xN_y@Gra. ^a represents that the TM atom cannot be embedded into substrate. "—" represents the side-on configuration transforms to end-on configuration after structure optimization. "/" represents that the configuration is excluded since ΔG in the previous step is higher than the threshold set in high-throughput screening.

Table S3. The ΔG_{max}, PDS, the most favorable pathway, ΔE_{ads}(*N₂), ΔE_{ads}(*NNH), ΔE_{ads}(*N), ΔE_{ads}(*NH₂), and the linear combination of adsorption energy of different intermediates (labeled as ΔE_{ads}) of 21 potential candidates that meet three screening criteria. ΔE_{ads}(*N_xH_y) = E(*N_xH_y) - E(*) - x/2×E(N₂) - y/2×E(H₂), where E(*N_xH_y), E(*), E(N₂) and E(H₂) stand for the energy of intermediate of N_xH_y, catalyst, free molecules N₂ and H₂, respectively. ΔE_{ads} = [ΔE_{ads}(*N₂) - ΔE_{ads}(*N)] + [ΔE_{ads}(*NNH) - ΔE_{ads}(*N)] + [ΔE_{ads}(*NH₂) - ΔE_{ads}(*N)]. The

unit of the values in the table is eV.

Table S4. Thermal corrections (in eV) of reaction intermediates along the most favorable pathways on the 10 selected catalysts. ^a represents that thermal corrections of the gas-phase molecules (N₂, H₂, and NH₃) are taken from the NIST database.

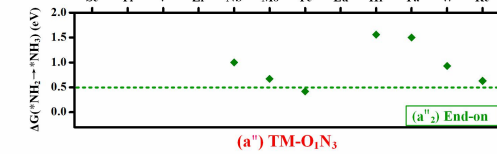
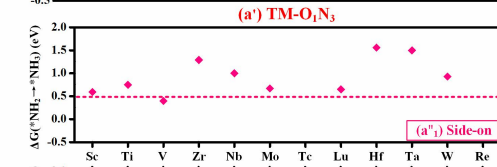
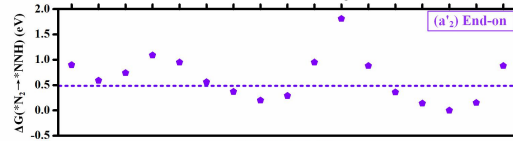
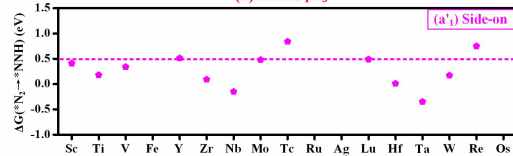
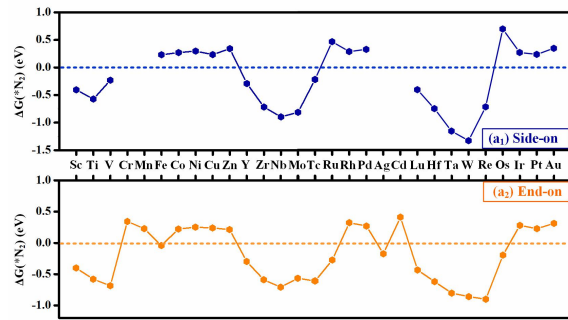
Table S5. Charge variation of the three moieties along the most favorable reaction pathway on the 10 selected catalysts. The positive and negative charge values represent gain and loss of electrons, respectively. The charge distribution on the bare catalyst is used as a reference to evaluate the charge variation.

Table S6. The N-N bond length (Å) of free N₂ (g), *N₂, *NNH, and *NNH₂ on the 10 selected TM-O_xN_y@Gra catalysts.

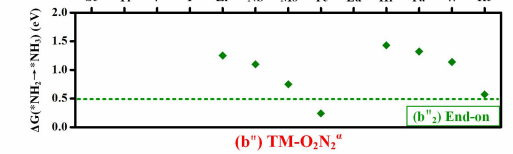
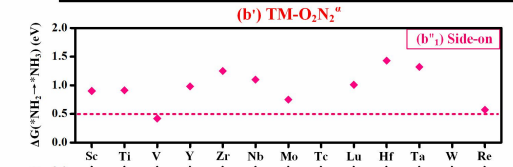
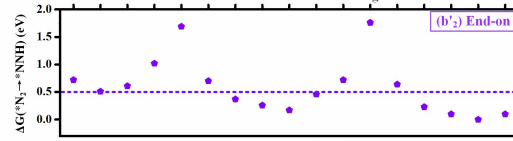
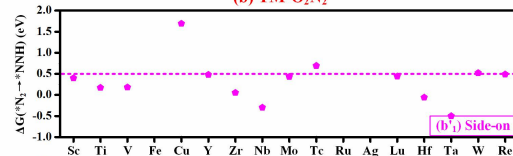
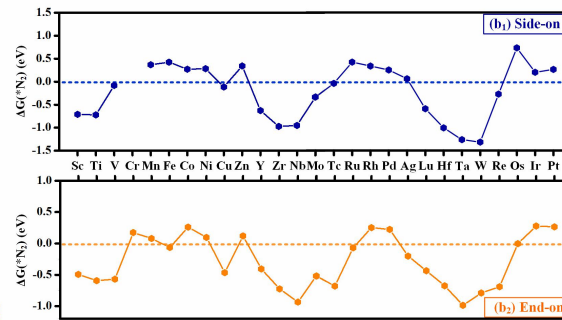
Table S7. The Bader charge and magnetic moment before and after N₂ adsorption. (*) and (*N₂) stand for before and after N₂ adsorption on 10 selected catalysts, respectively. The positive and negative charge values represent gain and loss of electrons, respectively.

Table S8. The d-band center of 10 selected catalysts before and after N₂ adsorption.

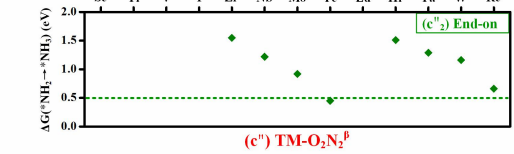
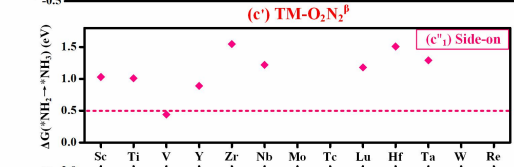
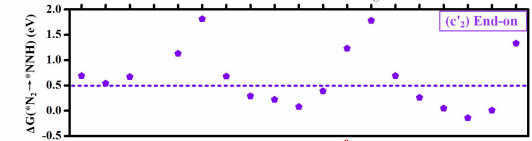
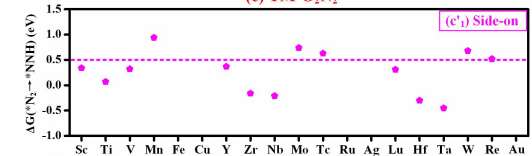
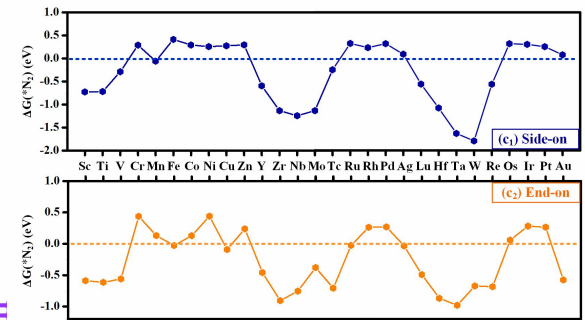
Table S9. ΔG(*N₂) versus ΔG(*H) on the 10 selected catalysts.



High-Throughput Screening



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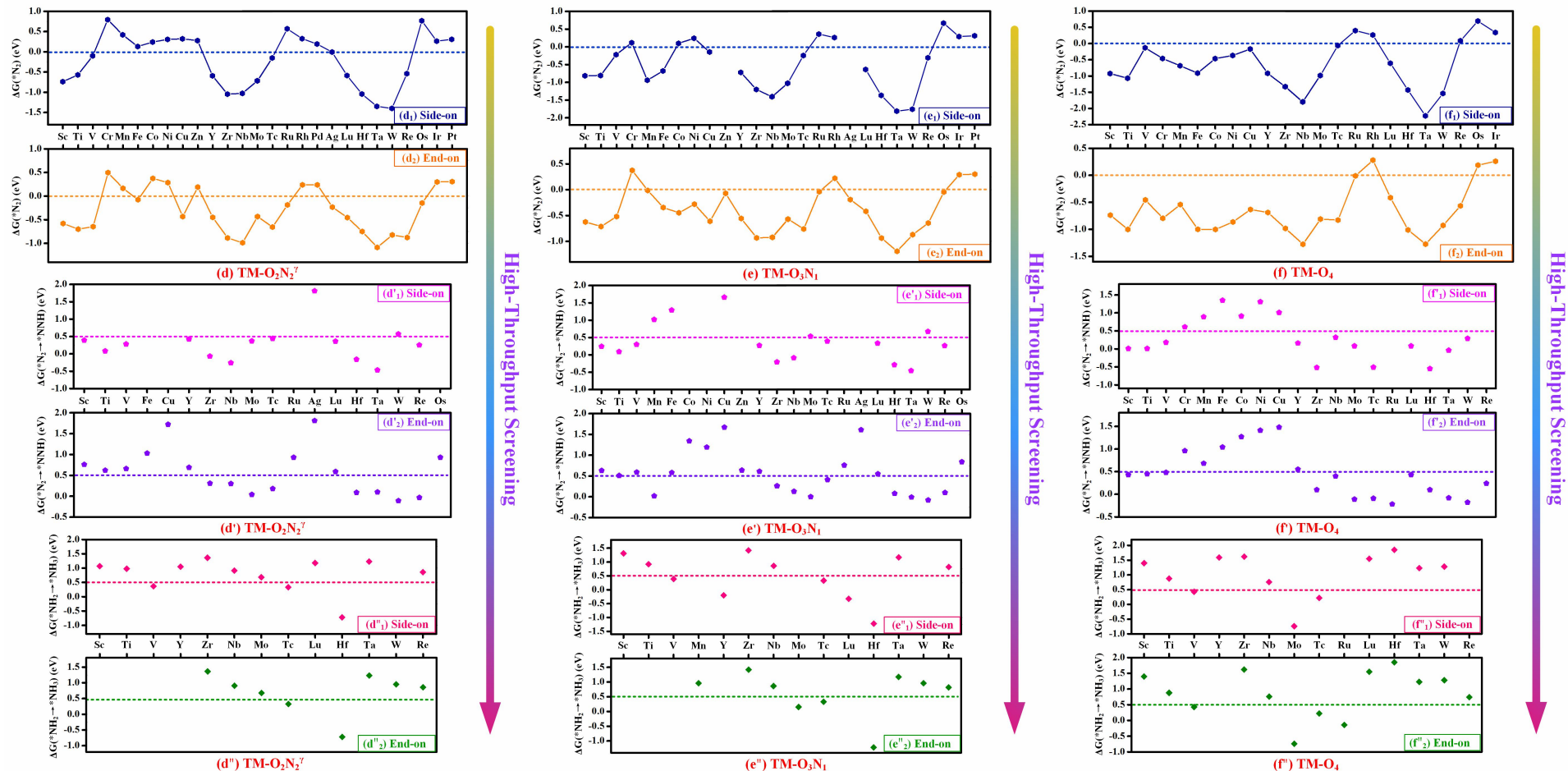
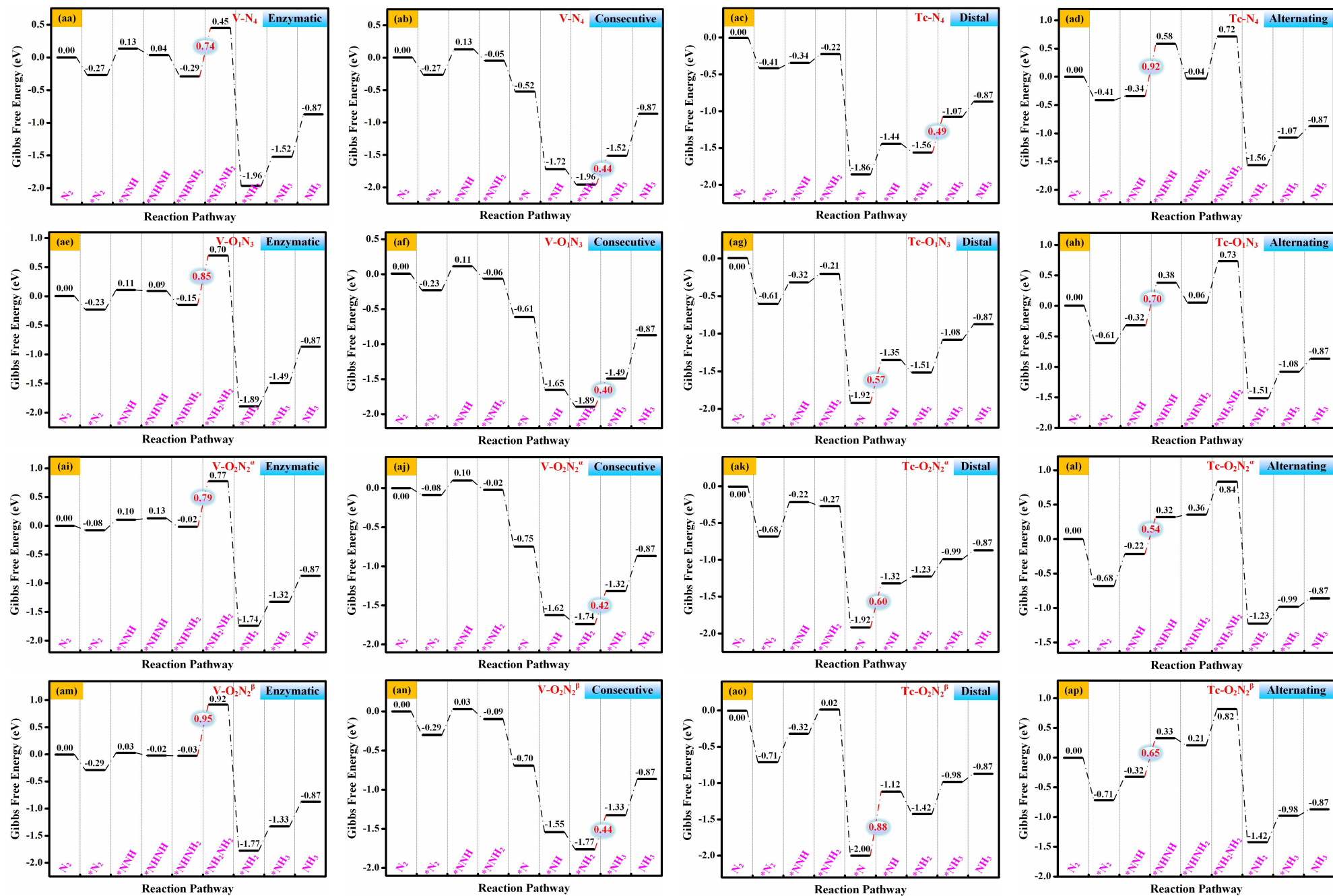
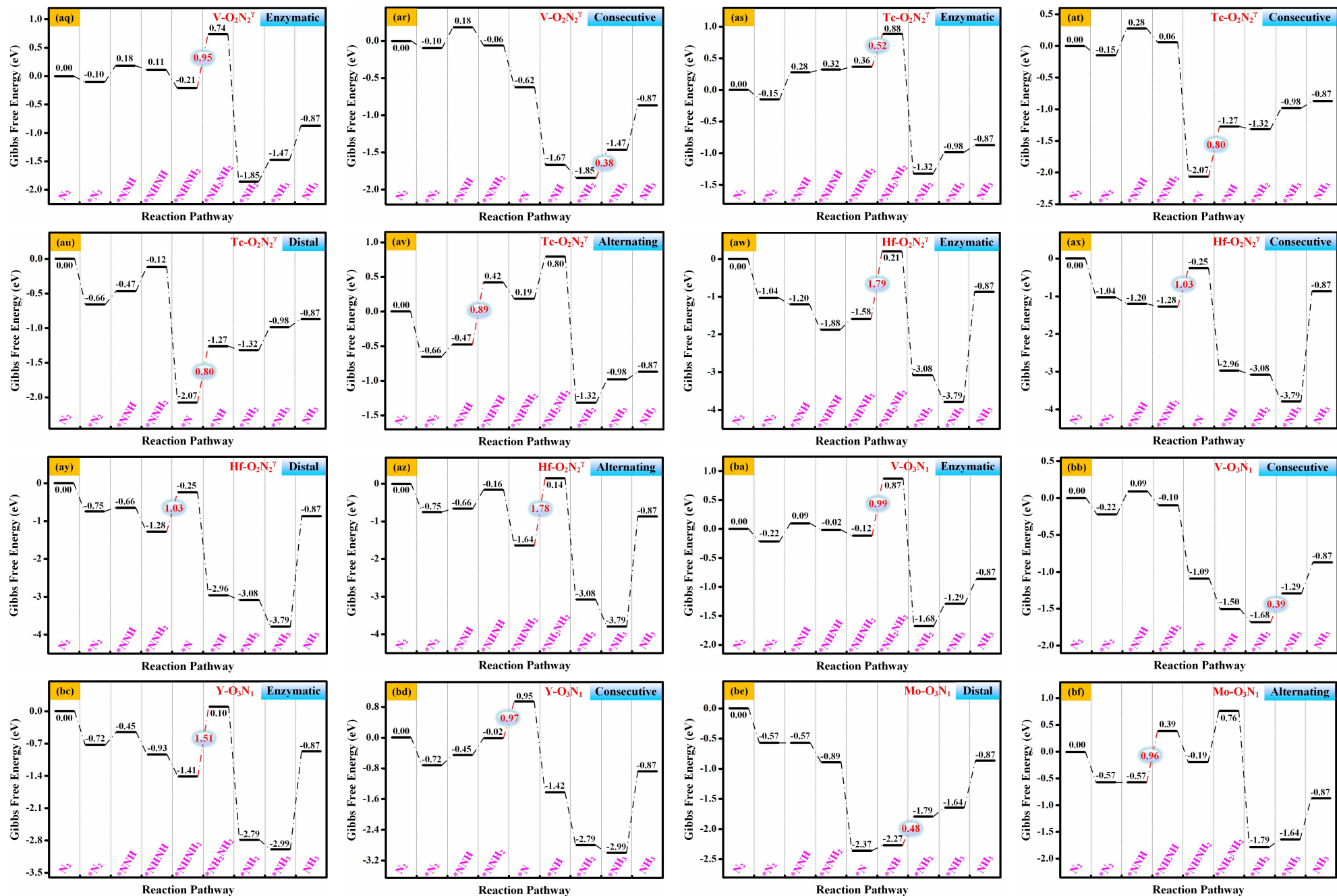
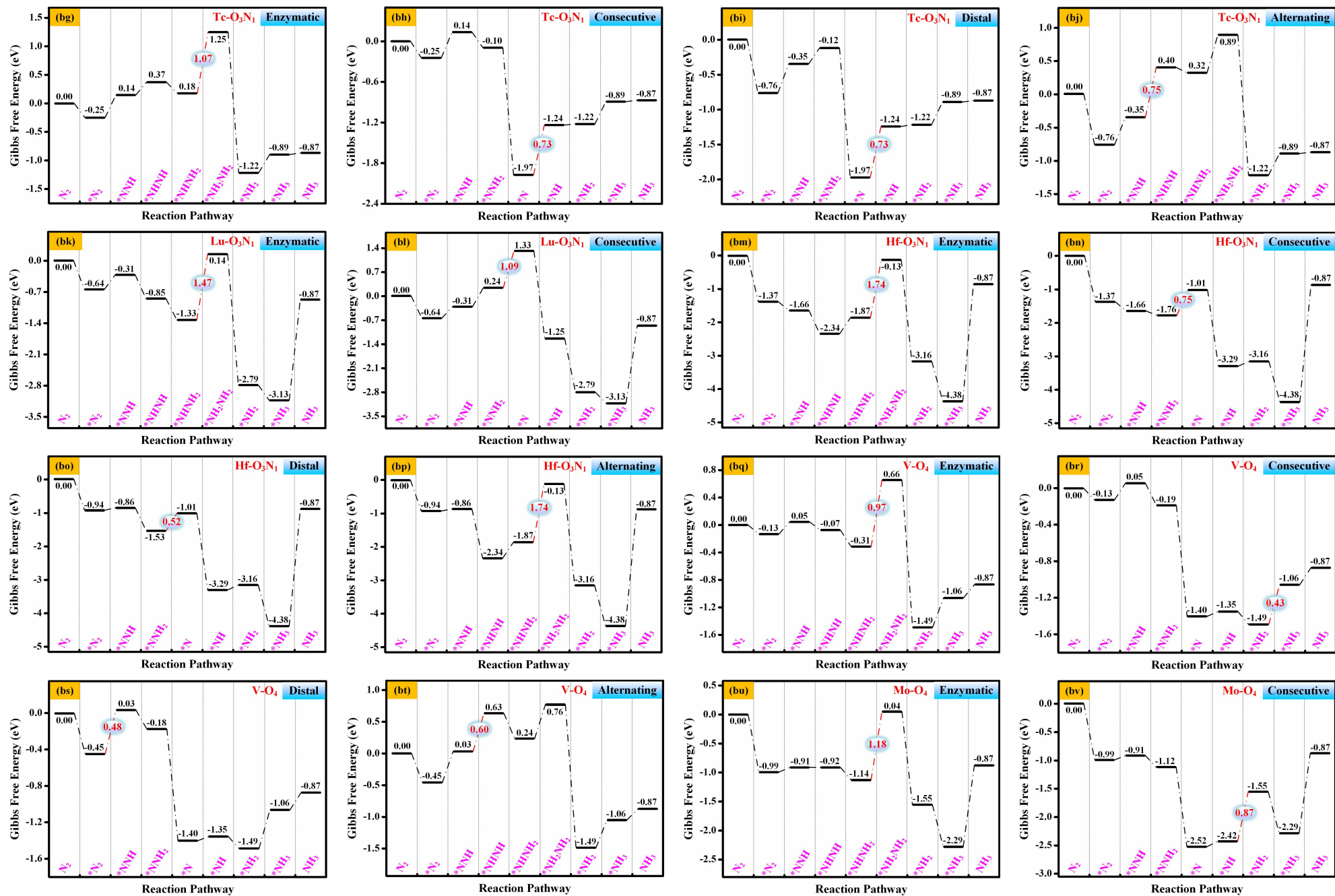


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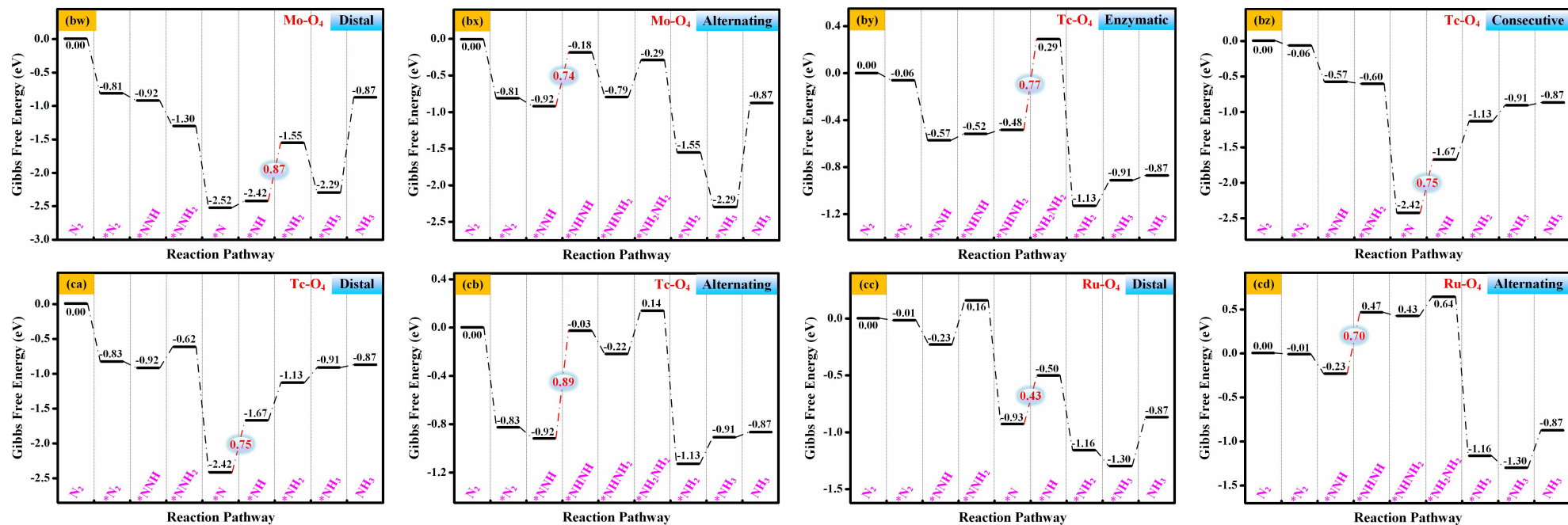
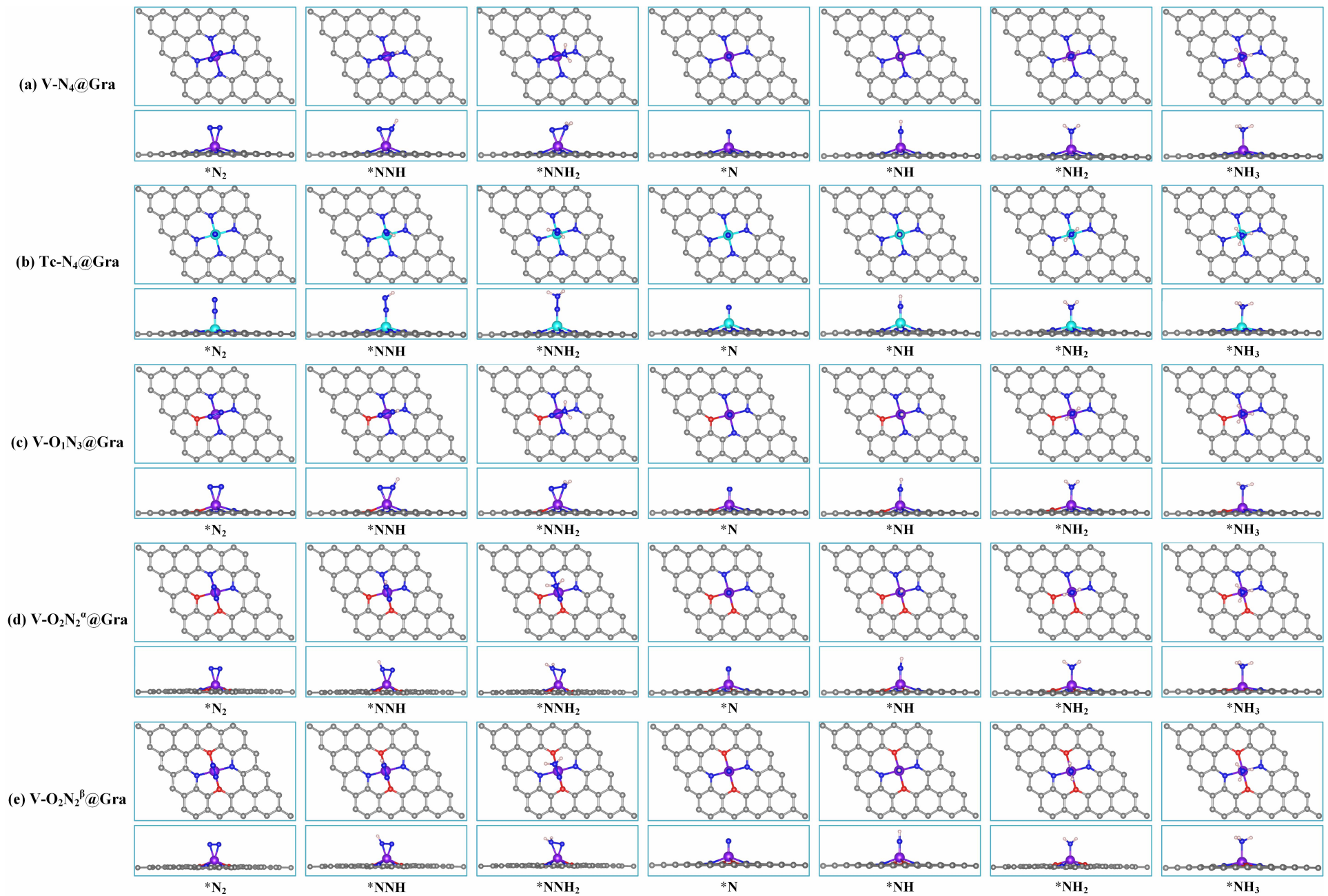


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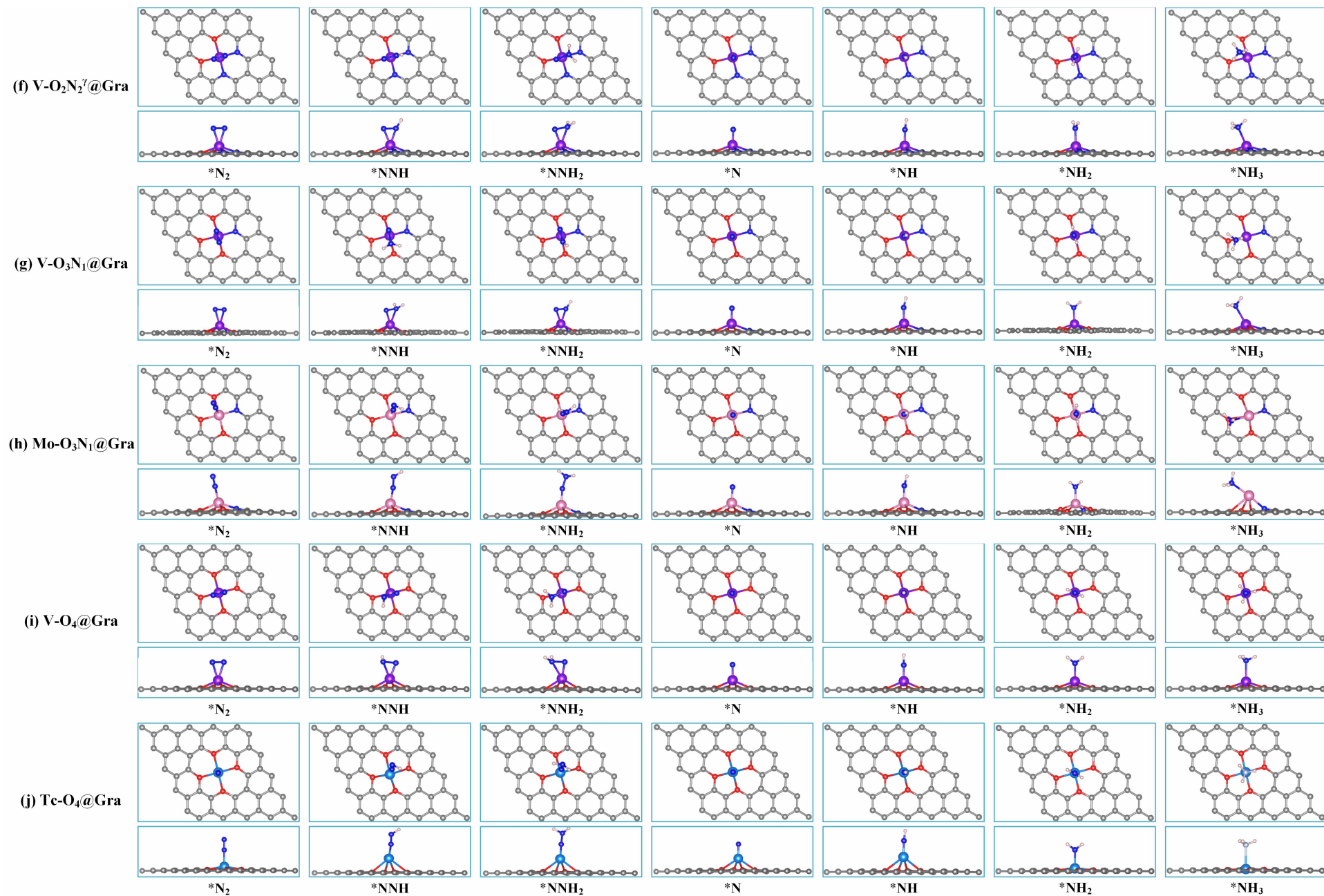


Figure S3. The geometry configurations of reaction intermediates on $\text{V-N}_4\text{@Gra}$ (a), $\text{Tc-N}_4\text{@Gra}$ (b), $\text{V-O}_1\text{N}_3\text{@Gra}$ (c), $\text{V-O}_2\text{N}_2^\alpha\text{@Gra}$ (d), $\text{V-O}_2\text{N}_2^\beta\text{@Gra}$ (e), $\text{V-O}_2\text{N}_2^\gamma\text{@Gra}$ (f), $\text{V-O}_3\text{N}_1\text{@Gra}$ (g), $\text{Mo-O}_3\text{N}_1\text{@Gra}$ (h), $\text{V-O}_4\text{@Gra}$ (i), and $\text{Ru-O}_4\text{@Gra}$ (j) along the most favorable reaction pathways.

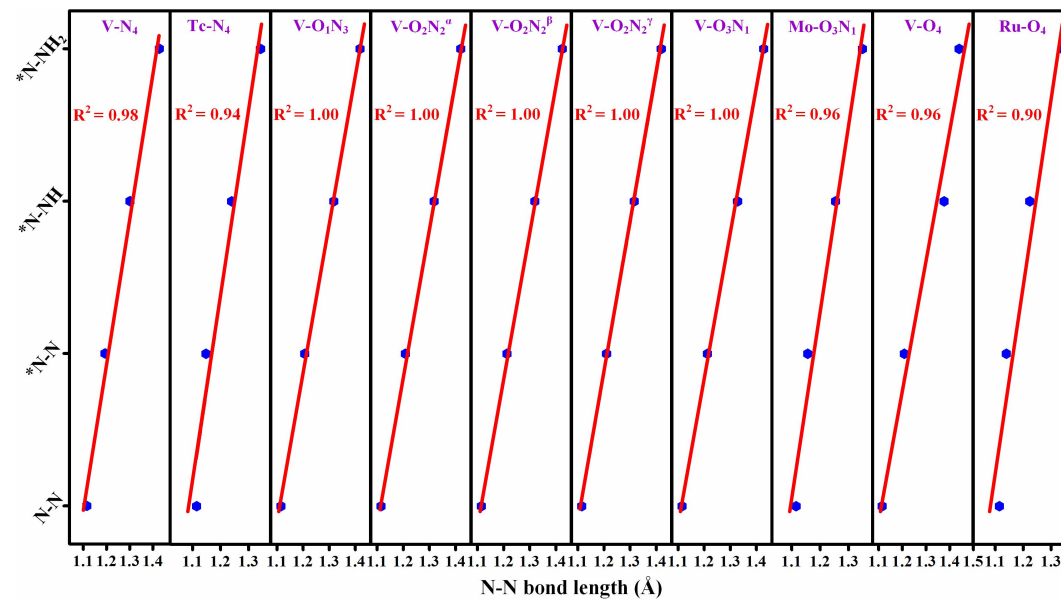


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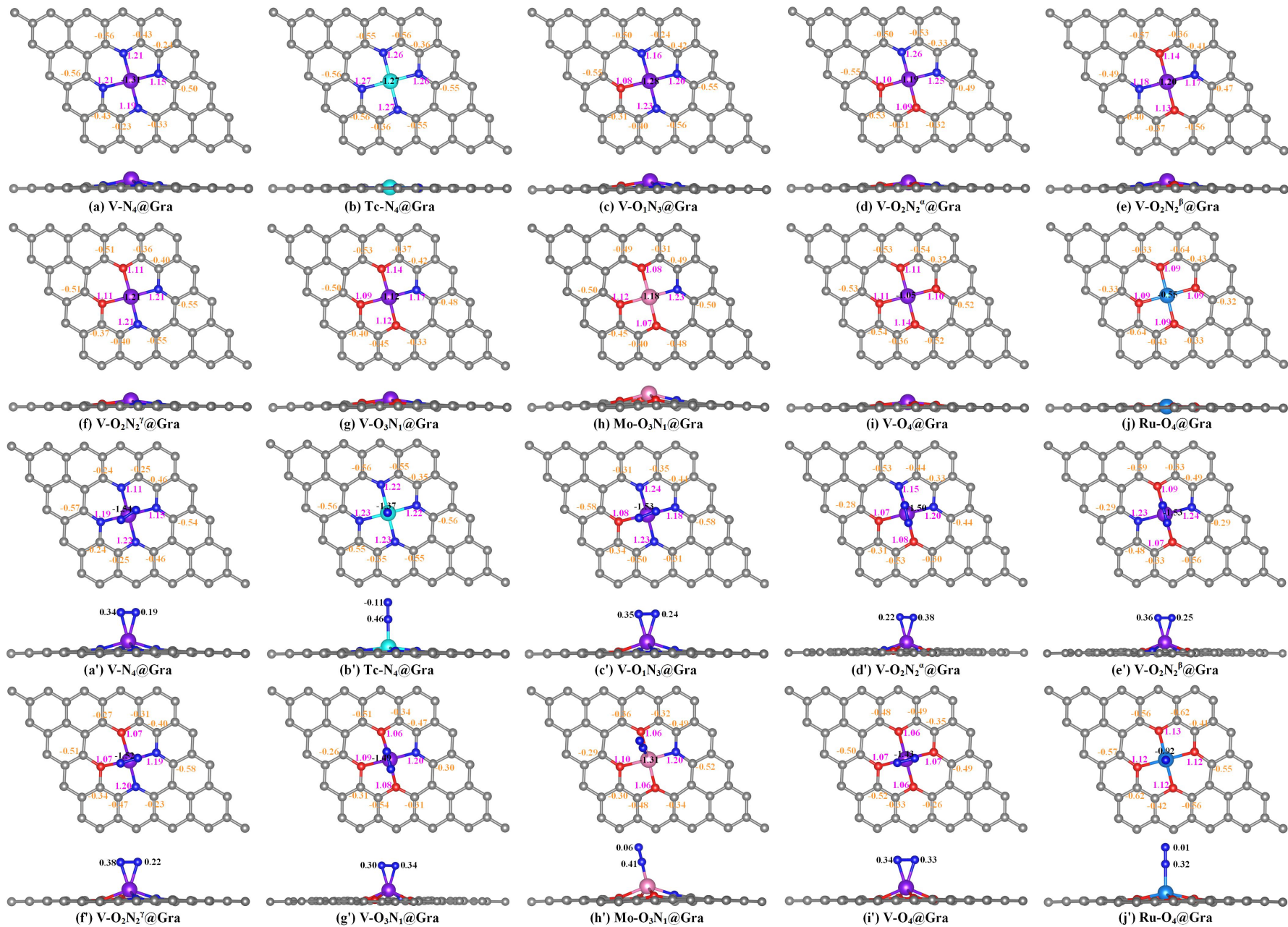


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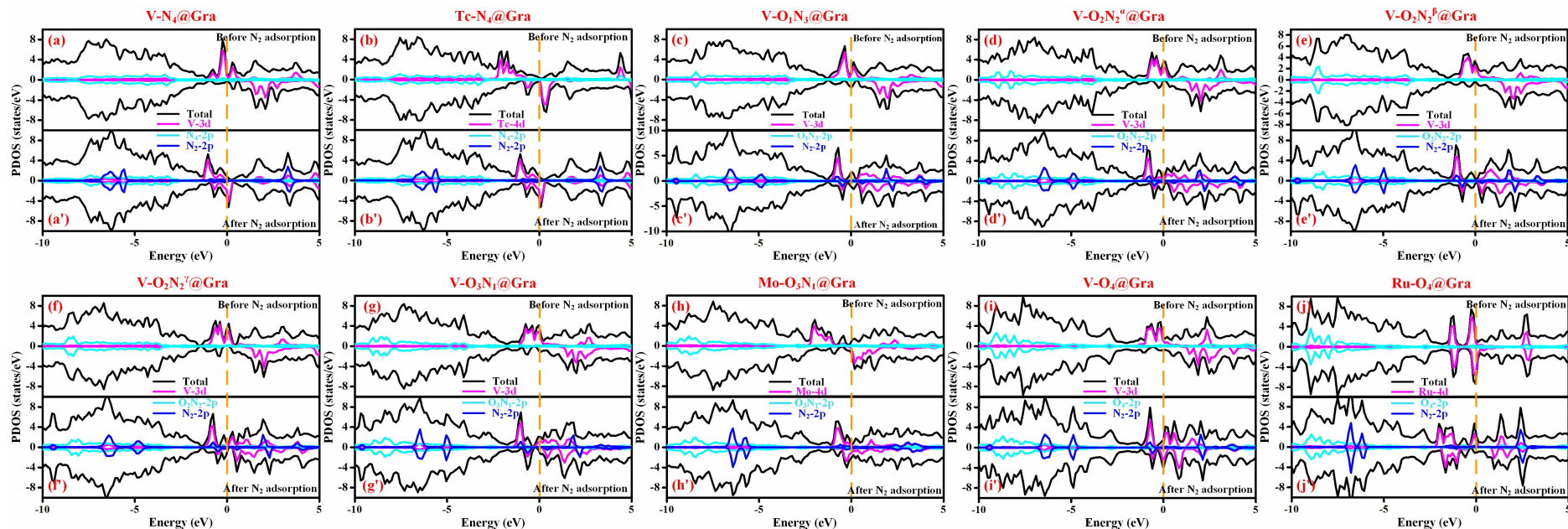


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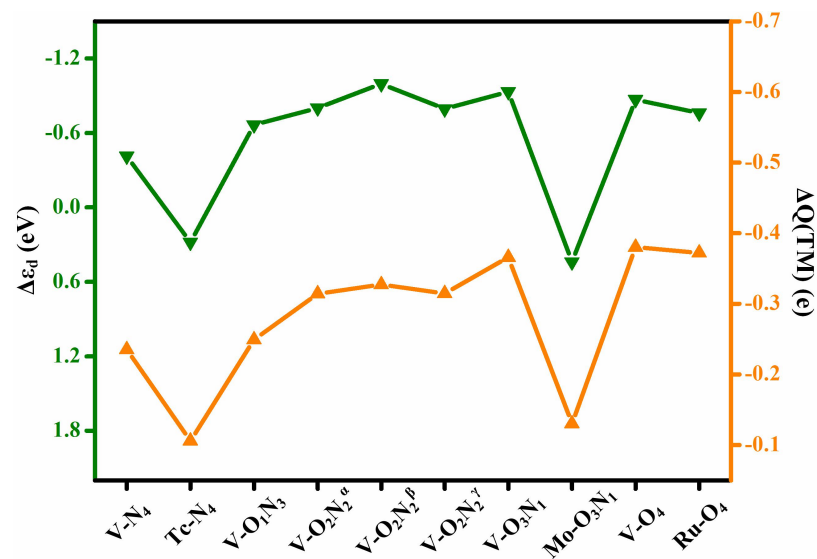


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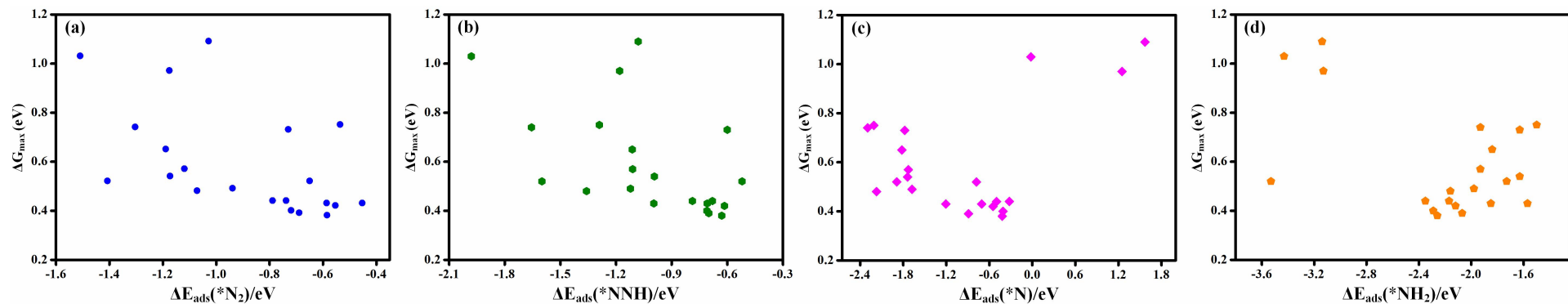
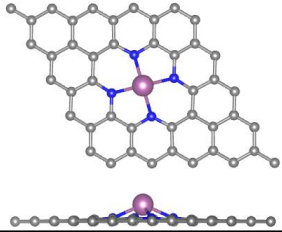
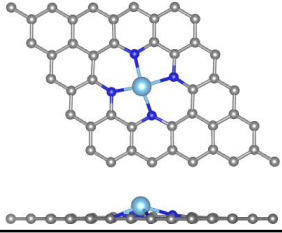
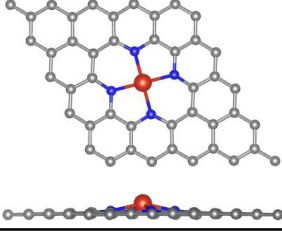
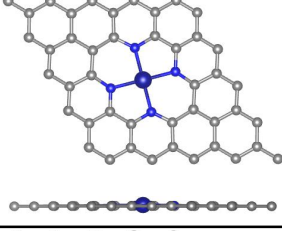
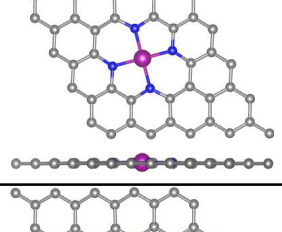
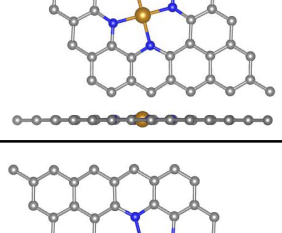
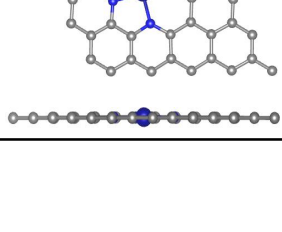
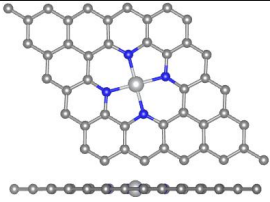
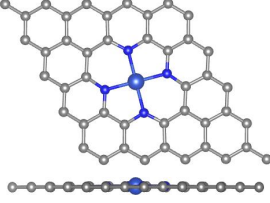
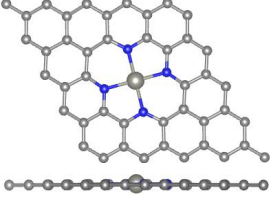
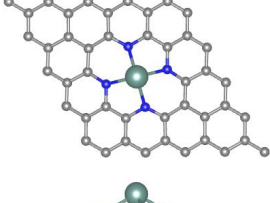
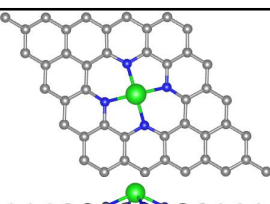
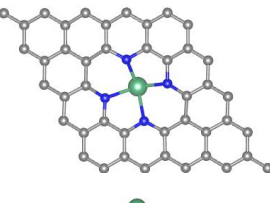
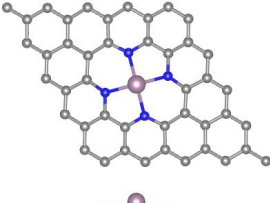
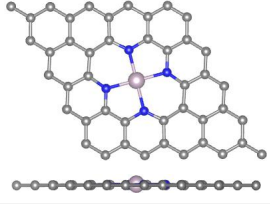
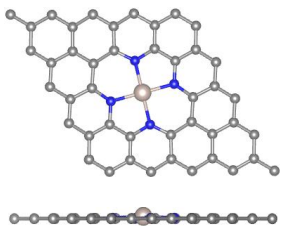
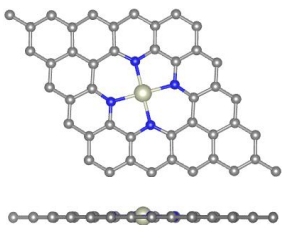
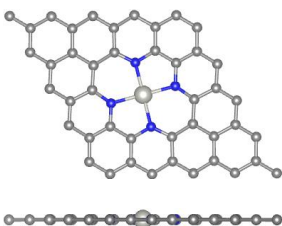
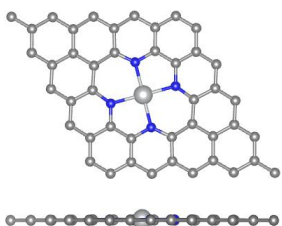
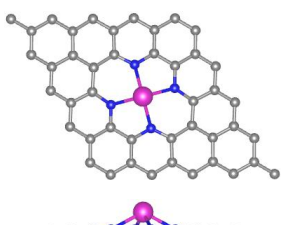
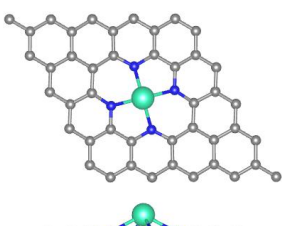
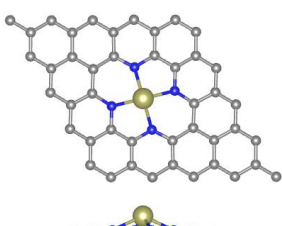


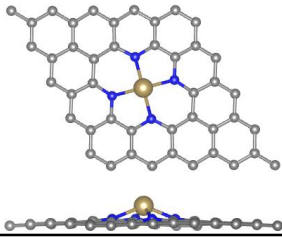
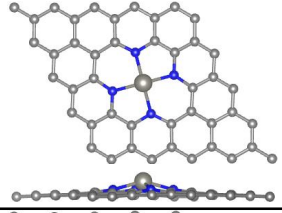
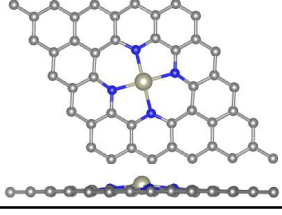
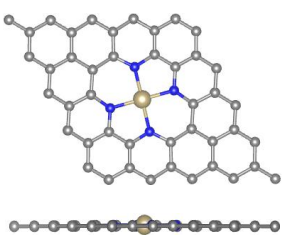
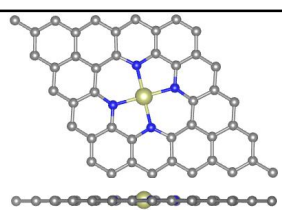
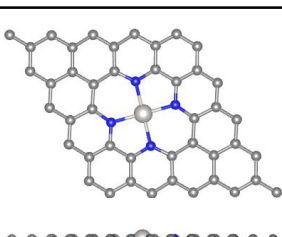
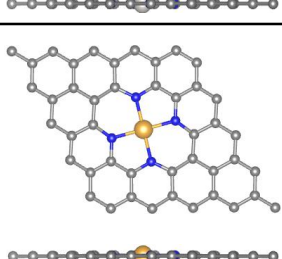
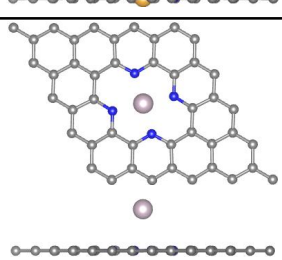
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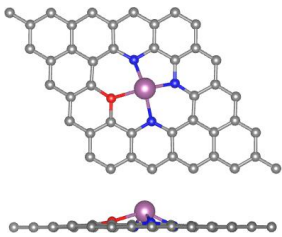
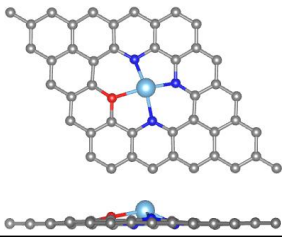
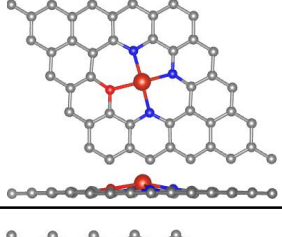
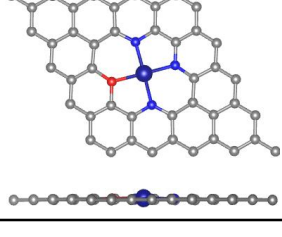
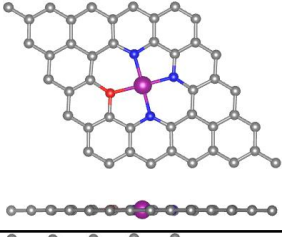
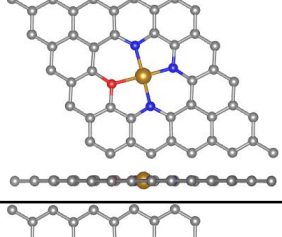
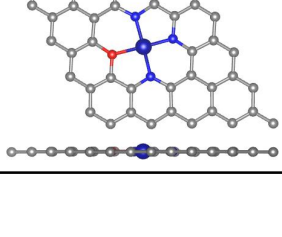
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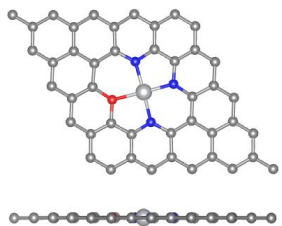
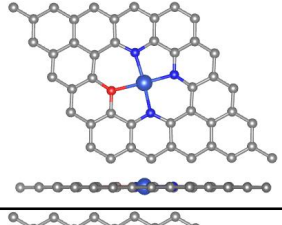
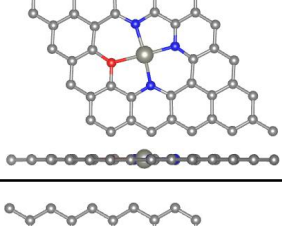
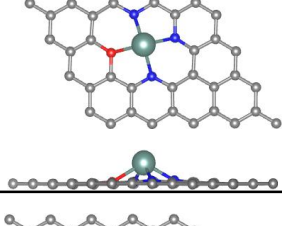
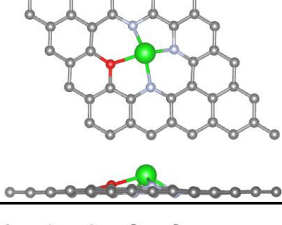
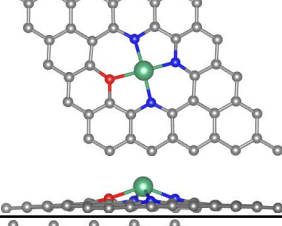
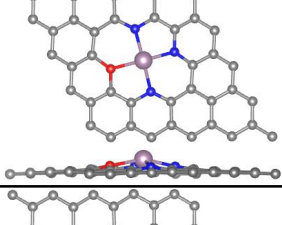
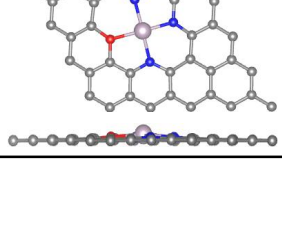
TM-N ₄ @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.29 b = 12.29 c = 15.02	Cmm2 (#35)	C _{2v}	0	0
Ti		a = 12.28 b = 12.28 c = 15.03	Cm (#8)	C _s	1.12	1.19
V		a = 12.28 b = 12.28 c = 15.01	Cmm2 (#35)	C _{2v}	2.35	2.41
Cr		a = 12.29 b = 12.29 c = 14.97	Cmm2 (#35)	C _{2v}	3.45	3.50
Mn		a = 12.27 b = 12.27 c = 15.03	Cmm2 (#35)	C _{2v}	3.00	2.80
Fe		a = 12.25 b = 12.25 c = 15.06	Cmmm (#65)	D _{2h}	1.91	1.84
Co		a = 12.23 b = 12.23 c = 15.11	Cmmm (#65)	D _{2h}	0.66	0.69

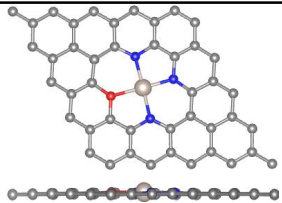
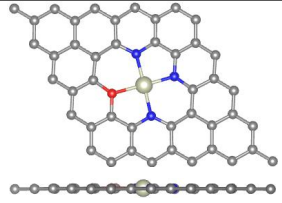
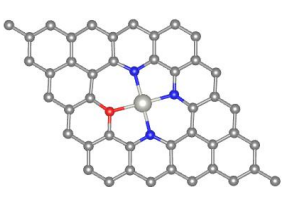
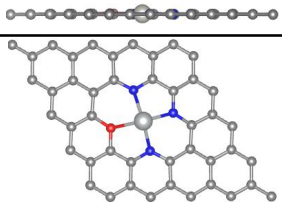
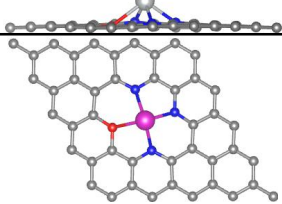
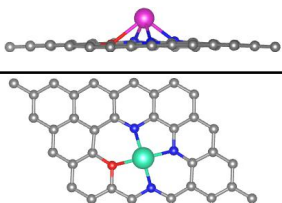
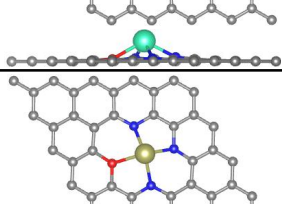
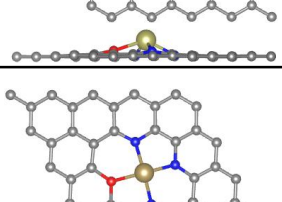
Ni		a = 12.23 b = 12.23 c = 15.12	Cmmm (#65)	D _{2h}	0	0
Cu		a = 12.26 b = 12.26 c = 15.03	Cmmm (#65)	D _{2h}	0.53	0.93
Zn		a = 12.29 b = 12.29 c = 14.97	Cmm2 (#35)	C _{2v}	0	0
Y		a = 12.30 b = 12.30 c = 14.99	Cmm2 (#35)	C _{2v}	0	0
Zr		a = 12.29 b = 12.29 c = 15.01	Cmm2 (#35)	C _{2v}	0.35	0.37
Nb		a = 12.28 b = 12.28 c = 15.05	P1 (#1)	C ₁	1.04	0.91
Mo		a = 12.29 b = 12.29 c = 14.98	Cmm2 (#35)	C _{2v}	2.67	2.82
Tc		a = 12.31 b = 12.31 c = 14.91	Cmm2 (#35)	C _{2v}	2.58	2.63

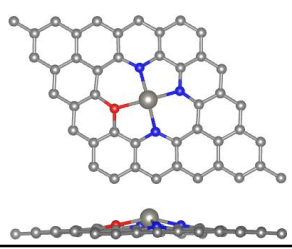
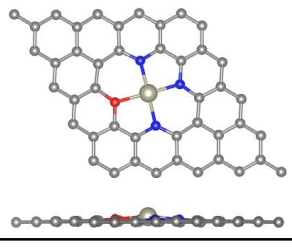
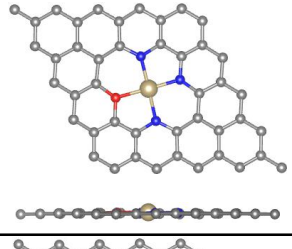
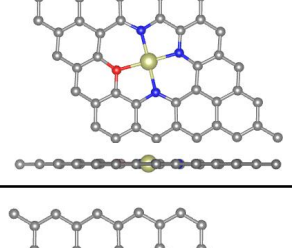
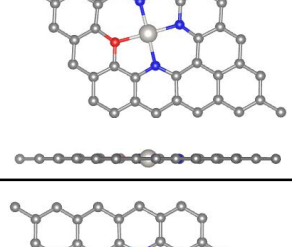
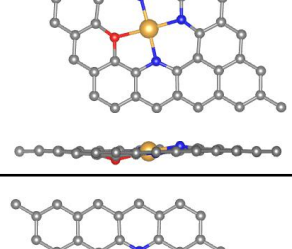
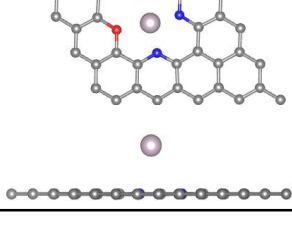
Ru		a = 12.28 b = 12.28 c = 14.95	Cmm2 (#35)	C _{2v}	1.24	1.29
Rh		a = 12.27 b = 12.27 c = 14.98	Cmmm (#65)	D _{2h}	0	0
Pd		a = 12.28 b = 12.28 c = 14.98	Cmmm (#65)	D _{2h}	0	0
Ag		a = 12.31 b = 12.31 c = 14.90	Cmmm (#65)	D _{2h}	0.29	0.66
Cd		a = 12.29 b = 12.29 c = 14.99	Cmm2 (#35)	C _{2v}	0	0
Lu		a = 12.29 b = 12.29 c = 15.00	Cmm2 (#35)	C _{2v}	0.05	0.05
Hf		a = 12.29 b = 12.29 c = 15.01	Cmm2 (#35)	C _{2v}	0.49	0.54

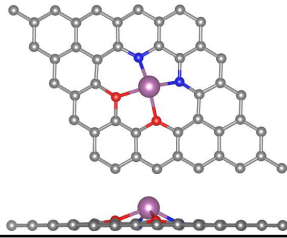
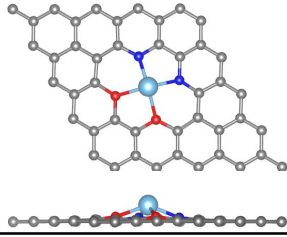
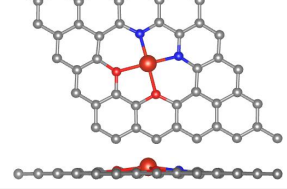
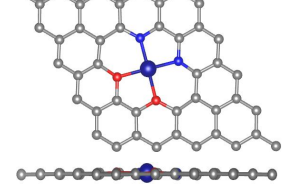
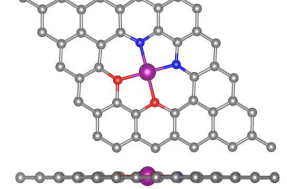
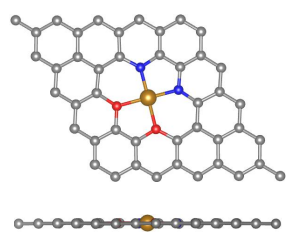
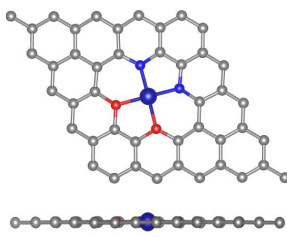
Ta		a = 12.27 b = 12.27 c = 15.04	Cmm2 (#35)	C _{2v}	1.46	1.72
W		a = 12.28 b = 12.28 c = 15.00	Cmm2 (#35)	C _{2v}	1.84	1.77
Re		a = 12.30 b = 12.30 c = 14.92	Cmm2 (#35)	C _{2v}	2.43	2.50
Os		a = 12.28 b = 12.28 c = 14.94	Cmm2 (#35)	C _{2v}	0.33	0.33
Ir		a = 12.27 b = 12.27 c = 14.96	Cmmm (#65)	D _{2h}	0.07	0.08
Pt		a = 12.28 b = 12.28 c = 14.97	Cmmm (#65)	D _{2h}	0.00	0.00
Au		a = 12.29 b = 12.29 c = 14.95	Cmmm (#65)	D _{2h}	0.00	0.00
Hg		a = 12.26 b = 12.26 c = 15.06	Cmm2 (#35)	C _{2v}	0.00	0.00

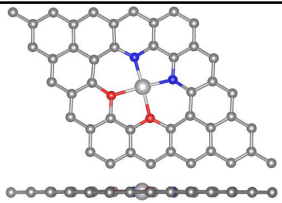
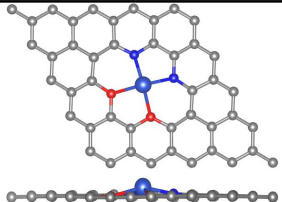
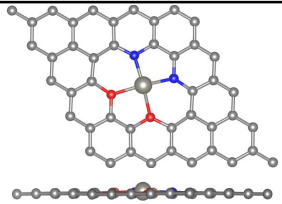
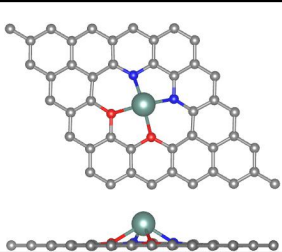
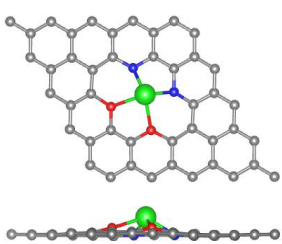
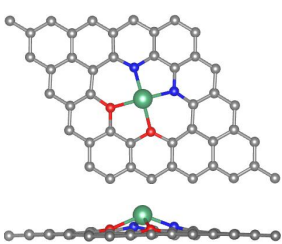
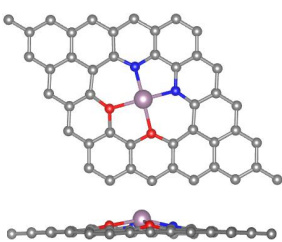
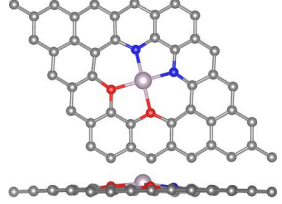
TM-O ₁ N ₃ @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.31 b = 12.28 c = 15.01	P1 (#1)	C ₁	0.00	0.00
Ti		a = 12.30 b = 12.28 c = 15.02	P1 (#1)	C ₁	1.13	0.95
V		a = 12.29 b = 12.28 c = 14.99	P1 (#1)	C ₁	2.44	2.31
Cr		a = 12.29 b = 12.28 c = 14.97	P1 (#1)	C ₁	3.39	3.16
Mn		a = 12.27 b = 12.26 c = 15.02	Pm (#6)	C _s	2.72	2.56
Fe		a = 12.25 b = 12.24 c = 15.05	Pm (#6)	C _s	1.51	1.36
Co		a = 12.24 b = 12.23 c = 15.10	Pm (#6)	C _s	0.15	0.13

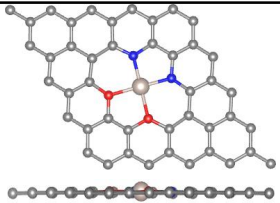
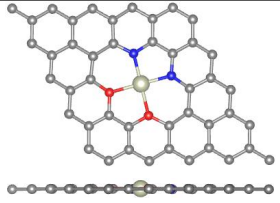
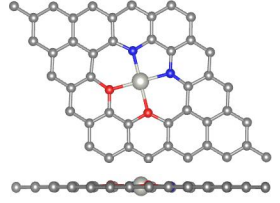
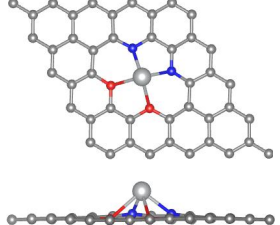
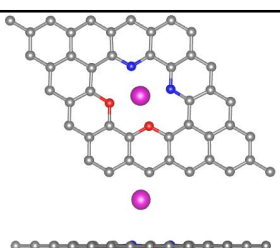
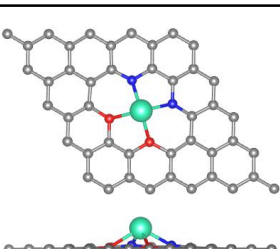
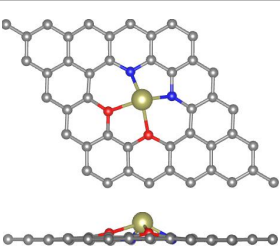
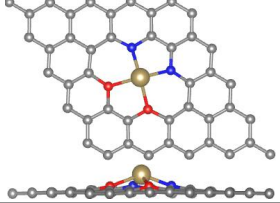
Ni		a = 12.25 b = 12.24 c = 15.08	Pm (#6)	C _s	0.20	0.27
Cu		a = 12.30 b = 12.26 c = 14.99	Pm (#6)	C _s	-0.37	-0.56
Zn		a = 12.31 b = 12.27 c = 14.96	Pm (#6)	C _s	0.00	0.00
Y		a = 12.31 b = 12.29 c = 14.98	P1 (#1)	C ₁	0.03	0.02
Zr		a = 12.31 b = 12.28 c = 15.01	P1 (#1)	C ₁	0.43	0.44
Nb		a = 12.30 b = 12.26 c = 15.02	P1 (#1)	C ₁	1.64	1.55
Mo		a = 12.31 b = 12.29 c = 14.95	P1 (#1)	C ₁	2.71	2.61
Tc		a = 12.30 b = 12.30 c = 14.91	P1 (#1)	C ₁	2.05	2.05

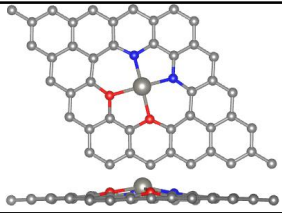
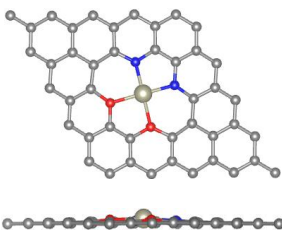
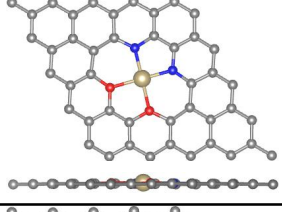
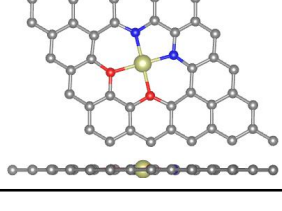
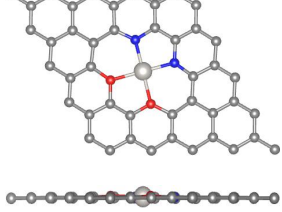
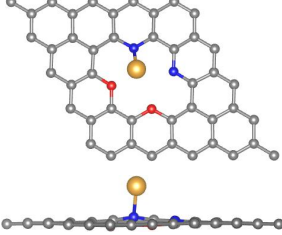
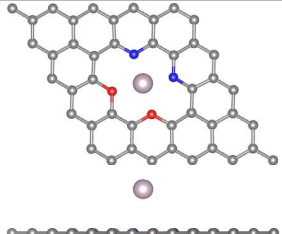
Ru		a = 12.28 b = 12.28 c = 14.95	P1 (#1)	C ₁	0.89	0.94
Rh		a = 12.28 b = 12.27 c = 14.97	Pm (#6)	C _s	0.00	0.00
Pd		a = 12.29 b = 12.28 c = 14.97	Pm (#6)	C _s	0.00	0.00
Ag		a = 12.28 b = 12.27 c = 15.03	P1 (#1)	C ₁	0.00	0.00
Cd		a = 12.28 b = 12.26 c = 15.05	P1 (#1)	C ₁	0.20	0.29
Lu		a = 12.30 b = 12.29 c = 15.00	P1 (#1)	C ₁	0.10	0.11
Hf		a = 12.31 b = 12.29 c = 15.00	P1 (#1)	C ₁	0.52	0.53
Ta		a = 12.29 b = 12.26 c = 15.02	P1 (#1)	C ₁	1.55	1.53

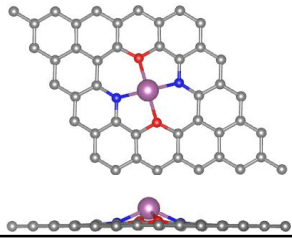
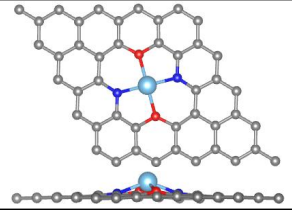
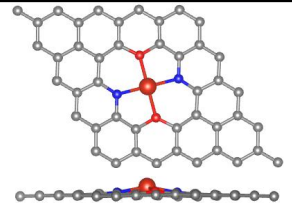
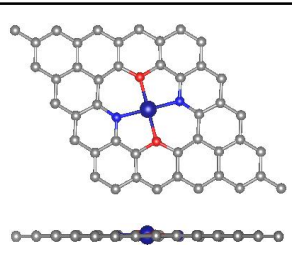
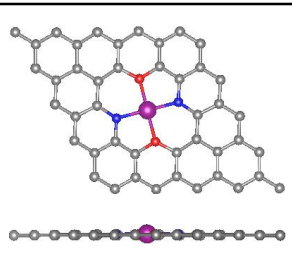
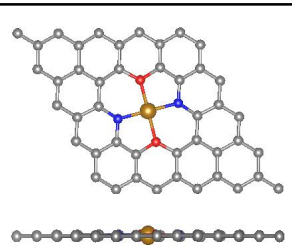
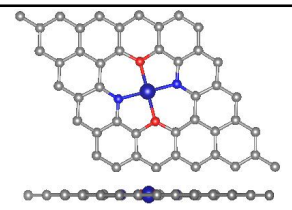
W		$a = 12.30$ $b = 12.28$ $c = 14.96$	P1 (#1)	C ₁	2.43	2.43
Re		$a = 12.31$ $b = 12.31$ $c = 14.88$	P1 (#1)	C ₁	2.01	2.02
Os		$a = 12.28$ $b = 12.28$ $c = 14.94$	P1 (#1)	C ₁	0.76	0.85
Ir		$a = 12.28$ $b = 12.27$ $c = 14.96$	Pm (#6)	C _s	0.00	0.00
Pt		$a = 12.28$ $b = 12.28$ $c = 14.95$	Pm (#6)	C _s	0.00	0.00
Au		$a = 12.32$ $b = 12.29$ $c = 14.90$	P1 (#1)	C ₁	0.32	0.54
Hg		$a = 12.26$ $b = 12.26$ $c = 15.08$	P1 (#1)	C ₁	0.00	0.00

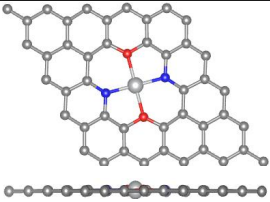
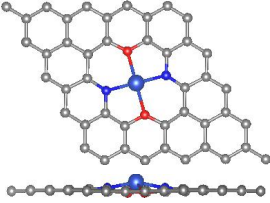
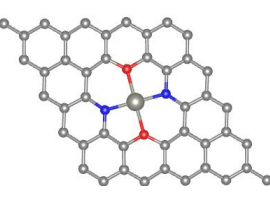
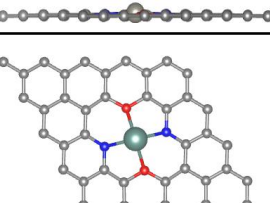
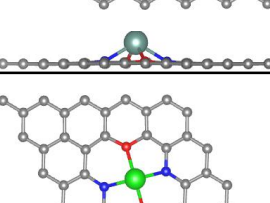
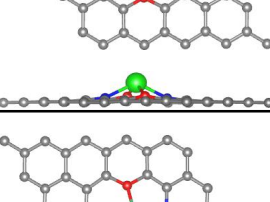
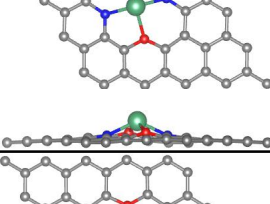
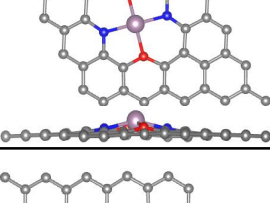
TM-O ₂ N ₂ ^a @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.30 b = 12.30 c = 15.00	Cm (#8)	C _s	0.40	0.43
Ti		a = 12.29 b = 12.29 c = 15.01	Cm (#8)	C _s	1.56	1.58
V		a = 12.30 b = 12.30 c = 14.95	Cm (#8)	C _s	2.67	2.60
Cr		a = 12.30 b = 12.30 c = 14.96	Cm (#8)	C _s	3.45	3.42
Mn		a = 12.27 b = 12.27 c = 15.00	Cm (#8)	C _s	2.47	2.38
Fe		a = 12.25 b = 12.25 c = 15.05	Amm2 (#38)	C _{2v}	1.34	1.22
Co		a = 12.24 b = 12.24 c = 15.08	Amm2 (#38)	C _{2v}	0.00	0.00

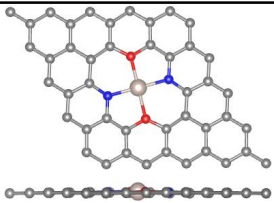
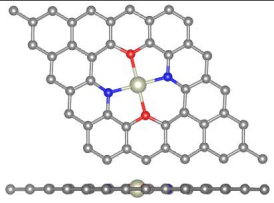
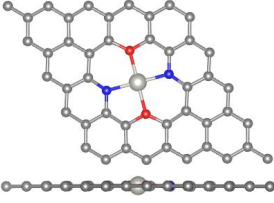
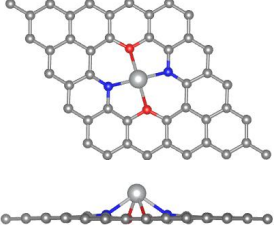
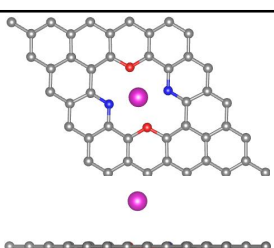
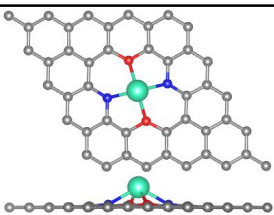
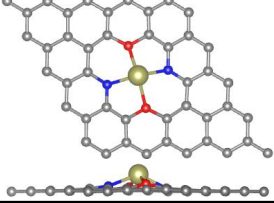
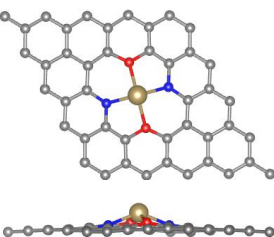
Ni		a = 12.27 b = 12.27 c = 15.00	Amm2 (#38)	C _{2v}	-0.85	-1.07
Cu		a = 12.29 b = 12.29 c = 14.99	Cm (#8)	C _s	0.00	0.00
Zn		a = 12.30 b = 12.30 c = 14.96	Cm (#8)	C _s	0.00	0.00
Y		a = 12.30 b = 12.30 c = 14.99	Cm (#8)	C _s	0.22	0.257
Zr		a = 12.30 b = 12.30 c = 15.00	Cm (#8)	C _s	0.56	0.54
Nb		a = 12.29 b = 12.29 c = 14.99	Cm (#8)	C _s	1.84	1.85
Mo		a = 12.31 b = 12.31 c = 14.92	Cm (#8)	C _s	2.78	2.74
Tc		a = 12.30 b = 12.30 c = 14.92	Cm (#8)	C _s	1.77	1.75

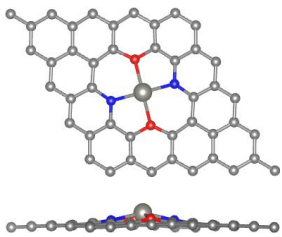
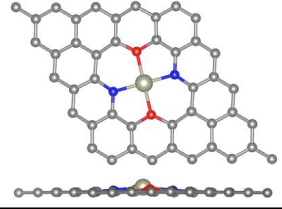
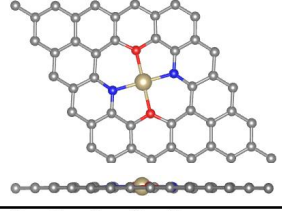
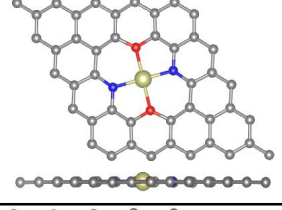
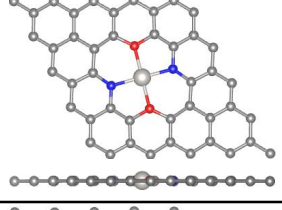
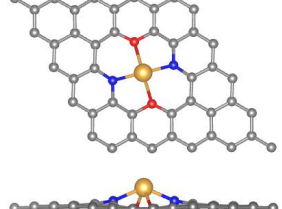
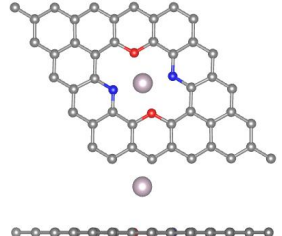
Ru		a = 12.28 b = 12.28 c = 14.95	Cm (#8)	C _s	0.67	0.69
Rh		a = 12.28 b = 12.28 c = 14.96	Amm2 (#38)	C _{2v}	0.00	0.00
Pd		a = 12.29 b = 12.29 c = 14.95	Cm (#8)	C _s	0.00	0.00
Ag		a = 12.27 b = 12.27 c = 15.06	Cm (#8)	C _s	0.00	0.00
Cd		a = 12.26 b = 12.26 c = 15.10	Cm (#8)	C _s	0.00	0.00
Lu		a = 12.30 b = 12.30 c = 15.00	Cm (#8)	C _s	0.19	0.22
Hf		a = 12.30 b = 12.30 c = 14.99	Cm (#8)	C _s	0.54	0.54
Ta		a = 12.29 b = 12.29 c = 14.98	Cm (#8)	C _s	1.63	1.62

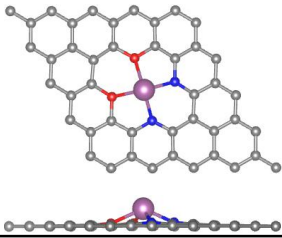
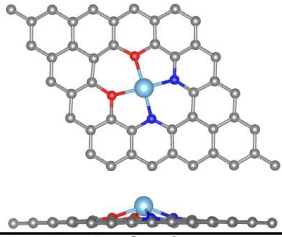
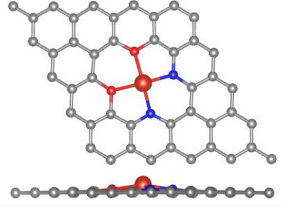
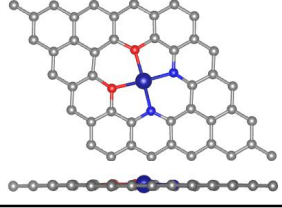
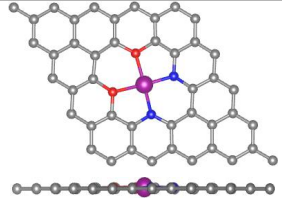
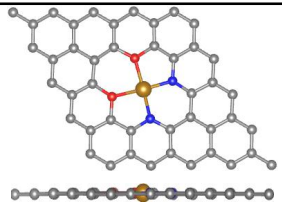
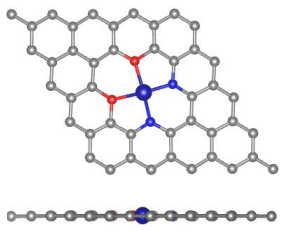
W		a = 12.30 b = 12.30 c = 14.92	Cm (#8)	C _s	2.58	2.56
Re		a = 12.30 b = 12.30 c = 14.91	Cm (#8)	C _s	1.51	1.55
Os		a = 12.29 b = 12.29 c = 14.93	Cm (#8)	C _s	0.66	0.72
Ir		a = 12.28 b = 12.28 c = 14.94	Amm2 (#38)	C _{2v}	0.00	0.00
Pt		a = 12.30 b = 12.30 c = 14.93	Cm (#8)	C _s	0.00	0.00
Au		a = 12.26 b = 12.25 c = 15.12	P1 (#1)	C ₁	0.26	0.43
Hg		a = 12.26 b = 12.26 c = 15.11	Cm (#8)	C _s	0.00	0.00

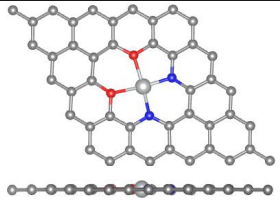
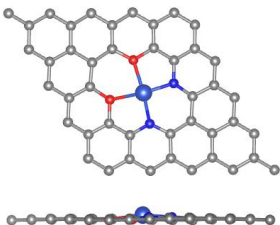
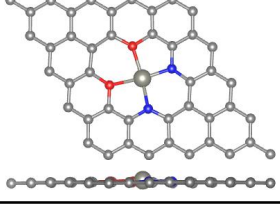
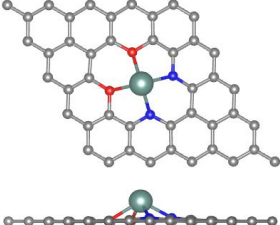
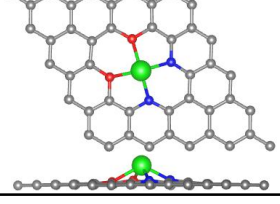
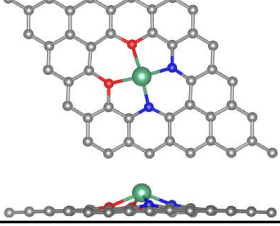
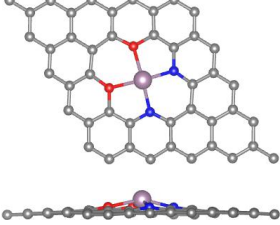
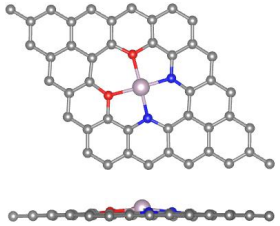
TM-O ₂ N ₂ ^β @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.27 b = 12.32 c = 15.00	P2 (#3)	C ₂	0.41	0.41
Ti		a = 12.26 b = 12.30 c = 15.01	P2 (#3)	C ₂	1.57	1.55
V		a = 12.28 b = 12.31 c = 14.97	P2 (#3)	C ₂	2.65	2.55
Cr		a = 12.29 b = 12.30 c = 14.96	P2/m (#10)	C _{2h}	3.41	3.24
Mn		a = 12.26 b = 12.28 c = 15.00	P2 (#3)	C ₂	2.44	2.31
Fe		a = 12.24 b = 12.26 c = 15.05	P2/m (#10)	C _{2h}	1.41	1.36
Co		a = 12.23 b = 12.25 c = 15.08	P2/m (#10)	C _{2h}	0.00	0.00

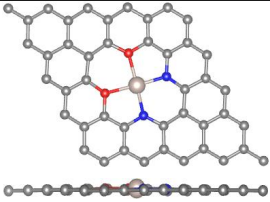
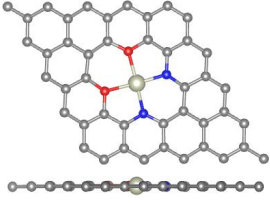
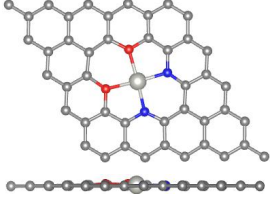
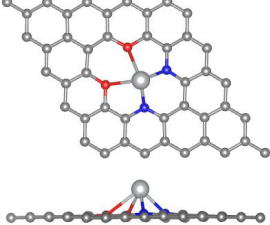
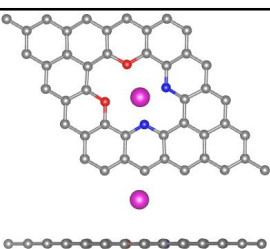
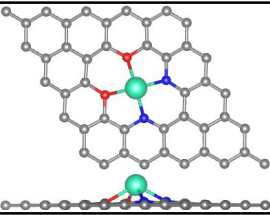
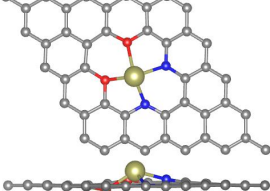
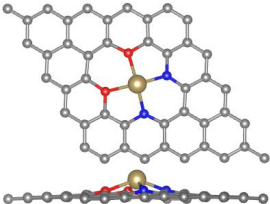
Ni		a = 12.24 b = 12.30 c = 15.01	P2/m (#10)	C _{2h}	0.93	1.11
Cu		a = 12.24 b = 12.32 c = 15.01	P2 (#3)	C ₂	0.00	0.00
Zn		a = 12.25 b = 12.34 c = 14.96	P2 (#3)	C ₂	0.00	0.00
Y		a = 12.28 b = 12.32 c = 14.99	P2 (#3)	C ₂	-0.20	-0.21
Zr		a = 12.27 b = 12.32 c = 15.00	P2 (#3)	C ₂	0.84	0.92
Nb		a = 12.24 b = 12.33 c = 15.00	P2 (#3)	C ₂	2.01	2.00
Mo		a = 12.29 b = 12.32 c = 14.93	P2 (#3)	C ₂	2.82	2.75
Tc		a = 12.29 b = 12.31 c = 14.92	P2 (#3)	C ₂	1.78	1.74

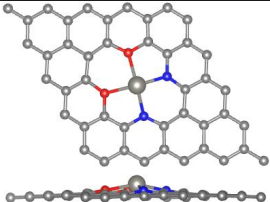
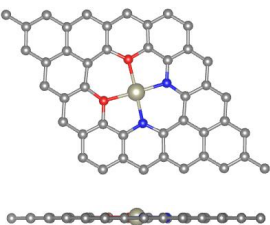
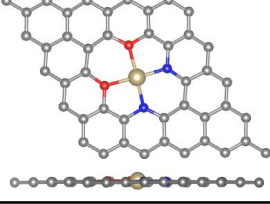
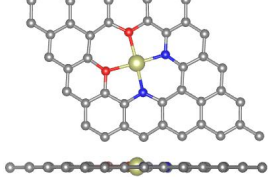
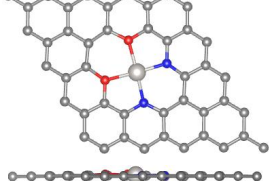
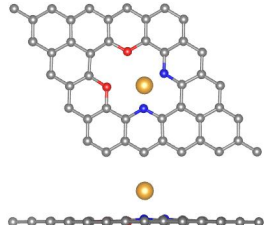
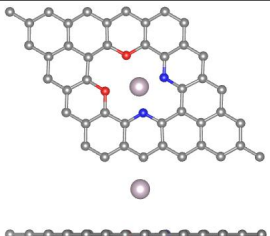
Ru		a = 12.27 b = 12.29 c = 14.95	P2 (#3)	C ₂	0.52	0.52
Rh		a = 12.27 b = 12.29 c = 14.96	P2/m (#10)	C _{2h}	0.00	0.00
Pd		a = 12.29 b = 12.32 c = 14.93	P2/m (#10)	C _{2h}	0.10	0.15
Ag		a = 12.25 b = 12.29 c = 15.05	P2 (#3)	C ₂	0.00	0.00
Cd		a = 12.25 b = 12.26 c = 15.10	P2 (#3)	C ₂	0.00	0.00
Lu		a = 12.28 b = 12.32 c = 15.00	P2 (#3)	C ₂	0.18	0.20
Hf		a = 12.28 b = 12.32 c = 14.99	P1 (#1)	C ₁	0.58	0.57
Ta		a = 12.25 b = 12.31 c = 15.00	P2 (#3)	C ₂	1.77	1.72

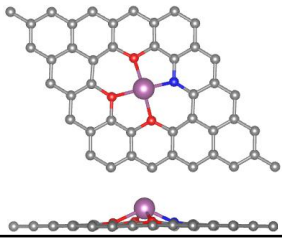
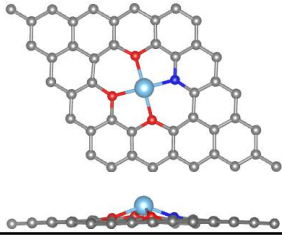
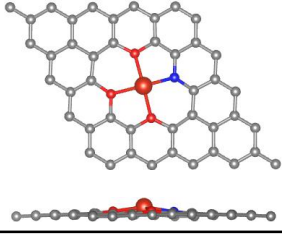
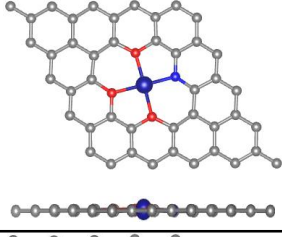
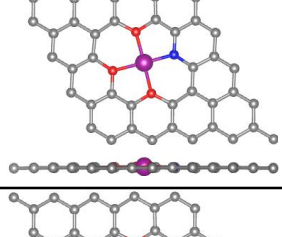
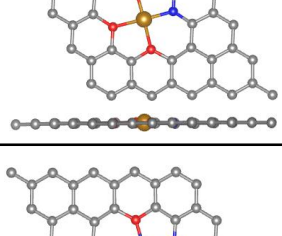
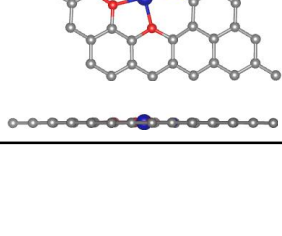
W		a = 12.28 b = 12.32 c = 14.94	P2 (#3)	C ₂	2.59	2.53
Re		a = 12.28 b = 12.30 c = 14.92	P2 (#3)	C ₂	1.30	1.28
Os		a = 12.28 b = 12.30 c = 14.93	P2 (#3)	C ₂	0.53	0.55
Ir		a = 12.28 b = 12.29 c = 14.95	P2/m (#10)	C _{2h}	0.00	0.00
Pt		a = 12.29 b = 12.30 c = 14.93	P2/m (#10)	C _{2h}	0.00	0.00
Au		a = 12.24 b = 12.29 c = 15.04	P2 (#3)	C ₂	0.00	0.00
Hg		a = 12.25 b = 12.26 c = 15.11	P2 (#3)	C ₂	0.00	0.00

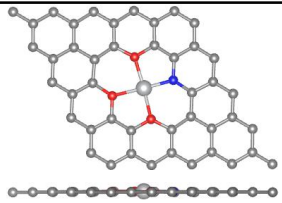
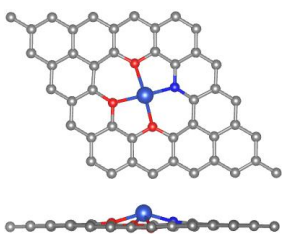
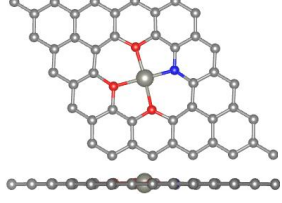
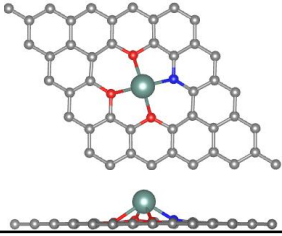
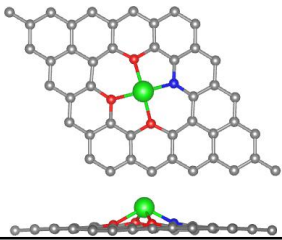
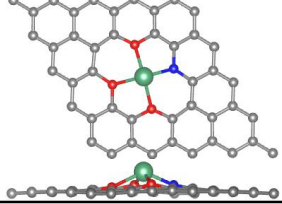
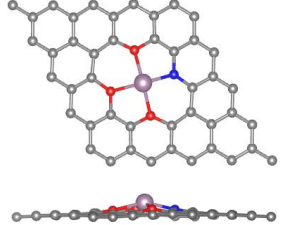
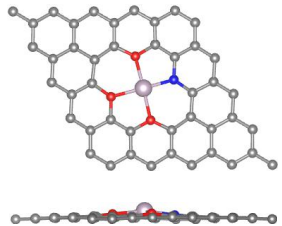
TM-O ₂ N ₂ ^γ @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.29 b = 12.29 c = 15.00	Cm (#8)	C _s	0.44	0.47
Ti		a = 12.28 b = 12.28 c = 15.01	Cm (#8)	C _s	1.58	1.60
V		a = 12.30 b = 12.30 c = 14.96	Cm (#8)	C _s	2.63	2.58
Cr		a = 12.30 b = 12.30 c = 14.96	Cm (#8)	C _s	3.48	3.53
Mn		a = 12.28 b = 12.28 c = 15.00	Cm (#8)	C _s	2.60	2.64
Fe		a = 12.26 b = 12.26 c = 15.04	Cm (#8)	C _s	1.51	1.58
Co		a = 12.24 b = 12.24 c = 15.08	Amm2 (#38)	C _{2v}	0.00	0.00

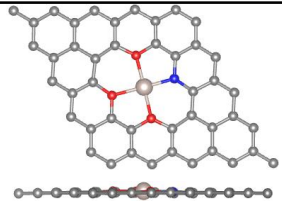
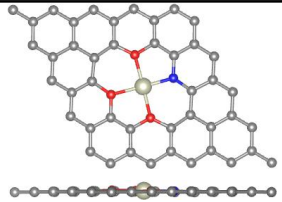
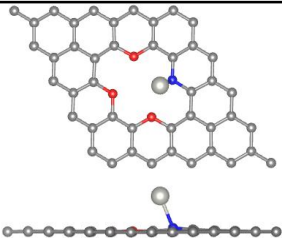
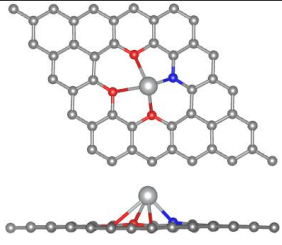
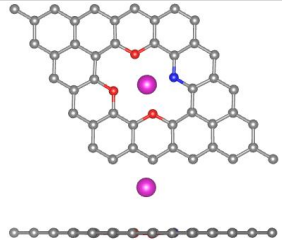
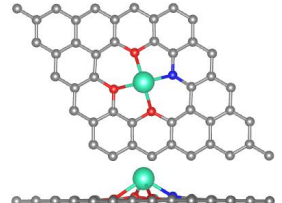
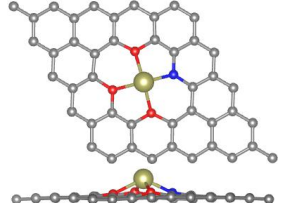
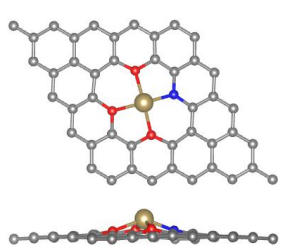
Ni		a = 12.27 b = 12.27 c = 15.02	Amm2 (#38)	C _{2v}	-0.54	-0.83
Cu		a = 12.28 b = 12.29 c = 14.98	Cm (#8)	C _s	-0.27	-0.49
Zn		a = 12.29 b = 12.29 c = 14.95	Cm (#8)	C _s	0.00	0.00
Y		a = 12.30 b = 12.30 c = 14.99	Cm (#8)	C _s	0.21	0.230
Zr		a = 12.29 b = 12.29 c = 15.00	P1 (#1)	C ₁	0.89	1.03
Nb		a = 12.29 b = 12.29 c = 14.99	Cm (#8)	C _s	1.93	2.12
Mo		a = 12.31 b = 12.31 c = 14.93	Cm (#8)	C _s	2.96	3.19
Tc		a = 12.30 b = 12.30 c = 14.91	Cm (#8)	C _s	1.90	1.96

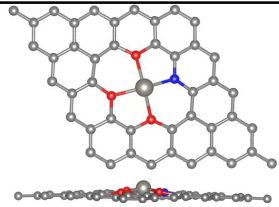
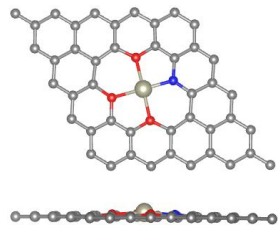
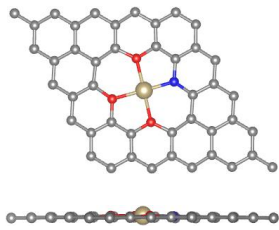
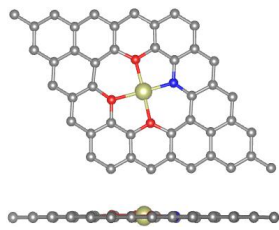
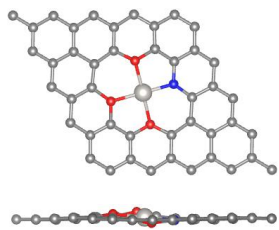
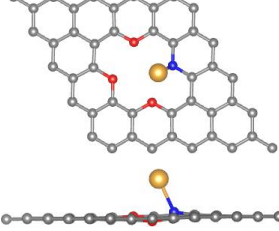
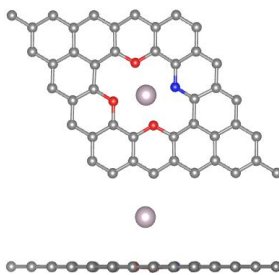
Ru		a = 12.29 b = 12.29 c = 14.94	Cm (#8)	C _s	0.79	0.87
Rh		a = 12.28 b = 12.28 c = 14.96	Amm2 (#38)	C _{2v}	0.00	0.00
Pd		a = 12.30 b = 12.30 c = 14.95	Cm (#8)	C _s	0.00	0.00
Ag		a = 12.27 b = 12.27 c = 15.05	Cm (#8)	C _s	0.00	0.00
Cd		a = 12.25 b = 12.25 c = 15.10	Cm (#8)	C _s	0.00	0.00
Lu		a = 12.29 b = 12.29 c = 15.00	Cm (#8)	C _s	0.19	0.22
Hf		a = 12.29 b = 12.31 c = 15.00	P1 (#1)	C ₁	0.61	0.64
Ta		a = 12.29 b = 12.29 c = 14.99	Cm (#8)	C _s	1.69	1.71

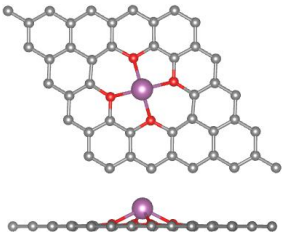
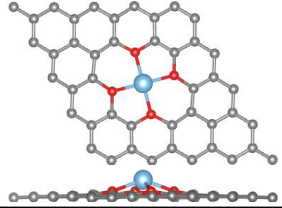
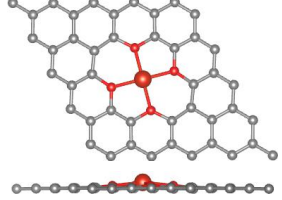
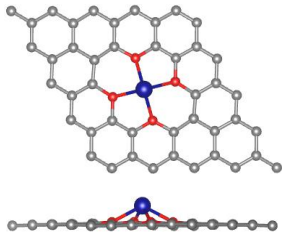
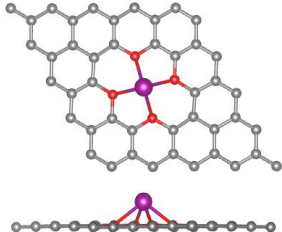
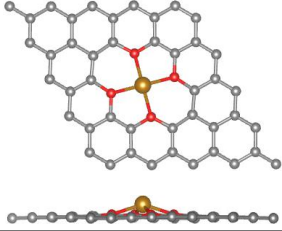
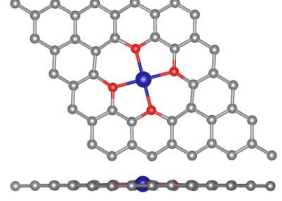
W		a = 12.31 b = 12.31 c = 14.92	Cm (#8)	C _s	2.70	2.87
Re		a = 12.32 b = 12.32 c = 14.85	Cm (#8)	C _s	1.81	1.84
Os		a = 12.29 b = 12.29 c = 14.92	Cm (#8)	C _s	0.75	0.85
Ir		a = 12.28 b = 12.28 c = 14.95	Amm2 (#38)	C _{2v}	0.00	0.00
Pt		a = 12.30 b = 12.30 c = 14.94	Cm (#8)	C _s	0.00	0.00
Au		a = 12.26 b = 12.26 c = 15.08	Cm (#8)	C _s	0.00	0.00
Hg		a = 12.26 b = 12.26 c = 15.10	Cm (#8)	C _s	0.00	0.00

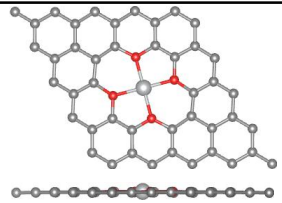
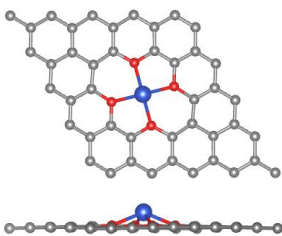
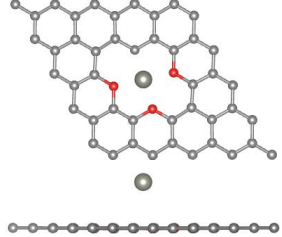
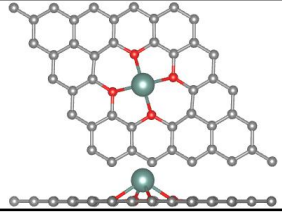
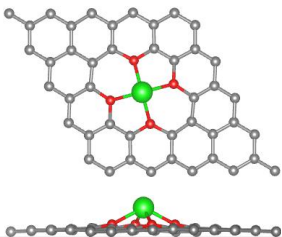
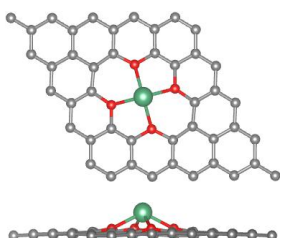
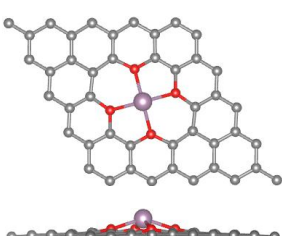
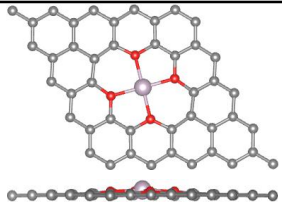
TM-O ₃ N ₁ @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.28 b = 12.30 c = 15.00	P1 (#1)	C ₁	0.58	0.57
Ti		a = 12.27 b = 12.29 c = 15.01	P1 (#1)	C ₁	1.74	1.70
V		a = 12.29 b = 12.31 c = 14.96	P1 (#1)	C ₁	2.85	2.79
Cr		a = 12.30 b = 12.31 c = 14.94	P1 (#1)	C ₁	3.49	3.44
Mn		a = 12.27 b = 12.28 c = 14.99	P1 (#1)	C ₁	2.38	2.34
Fe		a = 12.25 b = 12.27 c = 15.03	P1 (#1)	C ₁	1.20	1.07
Co		a = 12.25 b = 12.26 c = 15.06	Pm (#6)	C _s	-0.03	-0.03

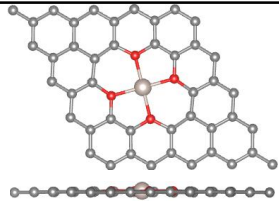
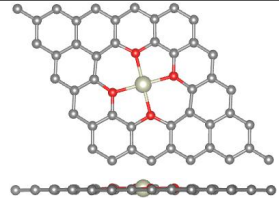
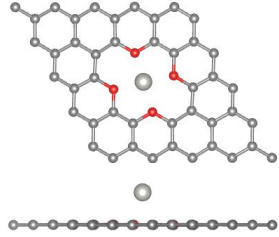
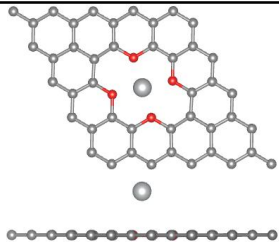
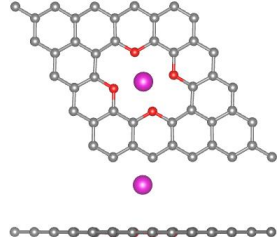
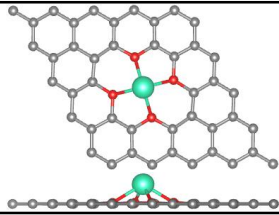
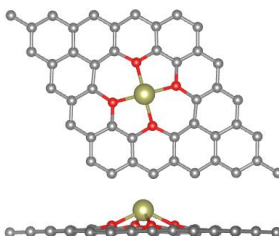
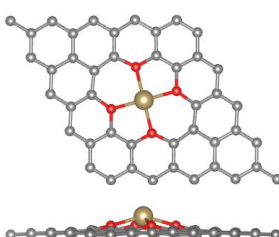
Ni		a = 12.27 b = 12.29 c = 15.00	Pm (#6)	C _s	0.91	1.03
Cu		a = 12.26 b = 12.30 c = 15.03	P1 (#1)	C ₁	0.00	0.00
Zn		a = 12.28 b = 12.32 c = 14.94	Pm (#6)	C _s	0.00	0.00
Y		a = 12.29 b = 12.31 c = 15.00	P1 (#1)	C ₁	0.29	0.30
Zr		a = 12.27 b = 12.30 c = 15.01	P1 (#1)	C ₁	1.08	1.08
Nb		a = 12.27 b = 12.32 c = 14.98	P1 (#1)	C ₁	2.22	2.22
Mo		a = 12.30 b = 12.32 c = 14.93	P1 (#1)	C ₁	2.98	2.99
Tc		a = 12.29 b = 12.30 c = 14.92	P1 (#1)	C ₁	1.70	1.74

Ru		a = 12.28 b = 12.30 c = 14.94	P1 (#1)	C ₁	0.41	0.45
Rh		a = 12.29 b = 12.30 c = 14.95	P1 (#1)	C ₁	0.00	0.00
Pd		a = 12.25 b = 12.27 c = 15.11	P1 (#1)	C ₁	0.00	0.00
Ag		a = 12.25 b = 12.27 c = 15.09	P1 (#1)	C ₁	0.04	0.01
Cd		a = 12.25 b = 12.26 c = 15.12	P1 (#1)	C ₁	0.00	0.00
Lu		a = 12.28 b = 12.30 c = 15.01	P1 (#1)	C ₁	0.25	0.30
Hf		a = 12.28 b = 12.30 c = 14.99	P1 (#1)	C ₁	1.06	1.09
Ta		a = 12.27 b = 12.31 c = 14.97	P1 (#1)	C ₁	2.10	2.12

W		a = 12.31 b = 12.32 c = 14.96	P1 (#1)	C ₁	2.65	2.68
Re		a = 12.29 b = 12.30 c = 14.95	P1 (#1)	C ₁	0.86	0.89
Os		a = 12.28 b = 12.29 c = 14.93	P1 (#1)	C ₁	0.17	0.17
Ir		a = 12.29 b = 12.30 c = 14.93	P1 (#1)	C ₁	0.00	0.00
Pt		a = 12.29 b = 12.30 c = 14.94	P1 (#1)	C ₁	0.00	0.00
Au		a = 12.24 b = 12.26 c = 15.13	P1 (#1)	C ₁	0.10	0.02
Hg		a = 12.25 b = 12.26 c = 15.12	P1 (#1)	C ₁	0.00	0.00

TM-O ₄ @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment (TM)	Magnetic moment (total)
Sc		a = 12.29 b = 12.29 c = 14.99	Cmm2 (#35)	C _{2v}	0.86	0.85
Ti		a = 12.29 b = 12.29 c = 14.99	Cmm2 (#35)	C _{2v}	1.94	1.92
V		a = 12.31 b = 12.31 c = 14.93	Cmm2 (#35)	C _{2v}	3.06	3.04
Cr		a = 12.28 b = 12.28 c = 15.02	Cmm2 (#35)	C _{2v}	4.20	4.23
Mn		a = 12.26 b = 12.26 c = 15.08	Cmm2 (#35)	C _{2v}	4.67	4.77
Fe		a = 12.28 b = 12.28 c = 15.00	Cmm2 (#35)	C _{2v}	2.92	3.02
Co		a = 12.29 b = 12.29 c = 14.98	Cmm2 (#35)	C _{2v}	1.91	2.07

Ni		a = 12.29 b = 12.29 c = 14.99	Cmmm (#65)	D _{2h}	0.93	1.09
Cu		a = 12.28 b = 12.28 c = 15.02	Cmm2 (#35)	C _{2v}	0.00	0.00
Zn		a = 12.25 b = 12.25 c = 15.13	Cmm2 (#35)	C _{2v}	0.00	0.00
Y		a = 12.30 b = 12.30 c = 14.99	Cmm2 (#35)	C _{2v}	0.37	0.39
Zr		a = 12.29 b = 12.29 c = 14.99	Cmm2 (#35)	C _{2v}	1.20	1.22
Nb		a = 12.30 b = 12.30 c = 14.98	Cmm2 (#35)	C _{2v}	2.58	2.69
Mo		a = 12.31 b = 12.31 c = 14.93	Cmm2 (#35)	C _{2v}	2.78	2.93
Tc		a = 12.31 b = 12.31 c = 14.89	Cmm2 (#35)	C _{2v}	1.69	1.63

Ru		a = 12.29 b = 12.29 c = 14.94	Cmm2 (#35)	C _{2v}	0.29	0.27
Rh		a = 12.30 b = 12.30 c = 14.93	Cmm2 (#35)	C _{2v}	0.00	0.00
Pd		a = 12.26 b = 12.26 c = 15.12	Cmm2 (#35)	C _{2v}	0.00	0.00
Ag		a = 12.25 b = 12.25 c = 15.13	Cmm2 (#35)	C _{2v}	0.34	0.37
Cd		a = 12.25 b = 12.25 c = 15.13	Cmm2 (#35)	C _{2v}	0.00	0.00
Lu		a = 12.30 b = 12.30 c = 14.99	Cmm2 (#35)	C _{2v}	0.27	0.31
Hf		a = 12.29 b = 12.29 c = 14.98	Cmm2 (#35)	C _{2v}	1.28	1.33
Ta		a = 12.30 b = 12.30 c = 14.93	Cmm2 (#35)	C _{2v}	2.43	2.54

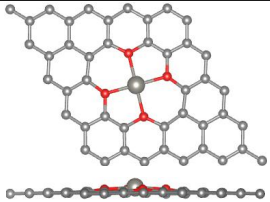
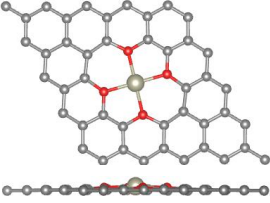
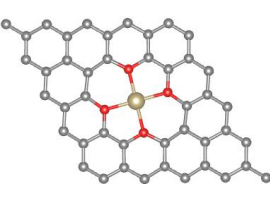
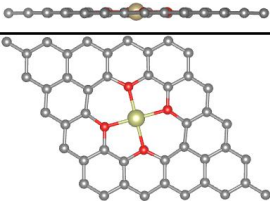
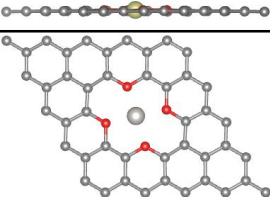
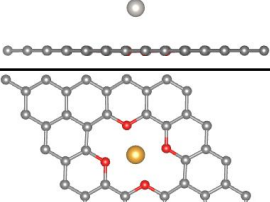
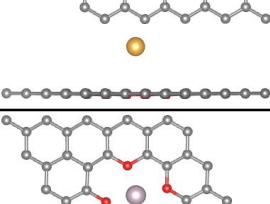
W		$a = 12.32$ $b = 12.32$ $c = 14.87$	Cmm2 (#35)	C_{2v}	2.25	2.33
Re		$a = 12.31$ $b = 12.31$ $c = 14.89$	Cmm2 (#35)	C_{2v}	1.28	1.32
Os		$a = 12.30$ $b = 12.30$ $c = 14.91$	Cmm2 (#35)	C_{2v}	0.28	0.28
Ir		$a = 12.30$ $b = 12.30$ $c = 14.92$	Cmm2 (#35)	C_{2v}	0.00	0.00
Pt		$a = 12.25$ $b = 12.25$ $c = 15.14$	Cmm2 (#35)	C_{2v}	1.24	1.296
Au		$a = 12.24$ $b = 12.24$ $c = 15.15$	Cmm2 (#35)	C_{2v}	0.28	0.29
Hg		$a = 12.25$ $b = 12.25$ $c = 15.12$	Cmm2 (#35)	C_{2v}	0.00	0.00

Table S2. $\Delta G(^*N_2)$, $\Delta G(^*N_2 \rightarrow ^*NNH)$ and $\Delta G(^*NH_2 \rightarrow ^*NH_3)$ through side-on and/or end-on modes on TM-O_xN_y@Gra. ^a represents that the TM atom cannot be embedded into substrate. "—" represents the side-on configuration transforms to end-on configuration after structure optimization. "/" represents that the configuration is excluded since ΔG in the previous step is higher than the threshold set in high-throughput screening.

TM-N ₄ @Gra	Side-on			End-on		
	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$
Sc	-0.26	0.54	/	-0.35	0.98	/
Ti	-0.62	0.33	0.75	-0.63	0.67	/
V	-0.27	0.40	0.44	-0.65	0.68	/
Cr	0.62	/	/	0.15	/	/
Mn	0.31	/	/	0.30	/	/
Fe	0.83	/	/	-0.04	1.22	/
Co	0.25	/	/	0.25	/	/
Ni	0.30	/	/	0.24	/	/
Cu	0.30	/	/	0.33	/	/
Zn	0.33	/	/	0.27	/	/
Y	-0.13	0.68	/	-0.18	1.06	/
Zr	-0.74	0.24	1.15	-0.60	0.56	/
Nb	-0.82	-0.04	1.28	-0.63	0.33	1.28
Mo	-0.75	0.19	0.79	-0.78	0.25	0.79
Tc	-0.06	0.53	/	-0.41	0.07	0.49
Ru	0.17	/	/	-0.69	1.32	/
Rh	0.24	/	/	0.23	/	/
Pd	0.23	/	/	0.32	/	/
Ag	0.38	/	/	0.30	/	/
Cd	—	/	/	0.22	/	/
Lu	-0.28	0.64	/	-0.37	1.05	/
Hf	-0.80	0.16	1.40	-0.68	0.48	1.40
Ta	-0.98	-0.35	1.46	-0.77	-0.03	1.46
W	-1.15	-0.07	0.97	-1.01	0.03	0.97
Re	-0.56	0.47	0.74	-0.82	0.10	0.74
Os	0.25	/	/	-0.68	0.92	/
Ir	0.30	/	/	0.32	/	/
Pt	0.35	/	/	0.25	/	/
Au	0.30	/	/	0.27	/	/
Hg ^a	/	/	/	/	/	/

TM-O ₁ N ₃ @Gra	Side-on			End-on		
	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$
Sc	-0.41	0.41	0.59	-0.40	0.90	/
Ti	-0.57	0.18	0.75	-0.58	0.59	/
V	-0.23	0.34	0.40	-0.68	0.74	/
Cr	—	/	/	0.34	/	/
Mn	—	/	/	0.23	/	/
Fe	0.23	/	/	-0.04	1.09	/
Co	0.27	/	/	0.22	/	/
Ni	0.30	/	/	0.25	/	/
Cu	0.23	/	/	0.24	/	/
Zn	0.34	/	/	0.21	/	/
Y	-0.29	0.51	/	-0.30	0.95	/
Zr	-0.72	0.09	1.29	-0.59	0.56	/
Nb	-0.90	-0.15	1.00	-0.71	0.37	1.00
Mo	-0.81	0.48	0.67	-0.57	0.20	0.67
Tc	-0.22	0.84	/	-0.61	0.29	0.42
Ru	0.47	/	/	-0.27	0.95	/
Rh	0.29	/	/	0.32	/	/
Pd	0.33	/	/	0.27	/	/
Ag	—	/	/	-0.17	1.81	/
Cd	—	/	/	0.41	/	/
Lu	-0.40	0.49	0.65	-0.43	0.88	/
Hf	-0.75	0.01	1.56	-0.62	0.36	1.56
Ta	-1.16	-0.35	1.50	-0.80	0.14	1.50
W	-1.33	0.17	0.93	-0.86	0.00	0.93
Re	-0.72	0.75	/	-0.90	0.15	0.63
Os	0.70	/	/	-0.19	0.88	/
Ir	0.27	/	/	0.28	/	/
Pt	0.24	/	/	0.23	/	/
Au	0.35	/	/	0.31	/	/
Hg ^a	/	/	/	/	/	/

TM-O ₂ N ₂ ^a @Gra	Side-on			End-on		
	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$
Sc	-0.71	0.40	0.90	-0.49	0.72	/
Ti	-0.72	0.17	0.91	-0.59	0.51	/
V	-0.08	0.18	0.42	-0.57	0.61	/
Cr	—	/	/	0.17	/	/
Mn	0.37	/	/	0.08	/	/
Fe	0.42	/	/	-0.06	1.02	/
Co	0.27	/	/	0.26	/	/
Ni	0.28	/	/	0.10	/	/
Cu	-0.11	1.69	/	-0.47	1.69	/
Zn	0.34	/	/	0.12	/	/
Y	-0.63	0.48	0.98	-0.41	0.70	/
Zr	-0.97	0.05	1.25	-0.72	0.37	1.25
Nb	-0.95	-0.30	1.10	-0.93	0.26	1.10
Mo	-0.34	0.43	0.75	-0.52	0.17	0.75
Tc	-0.04	0.69	/	-0.68	0.46	0.24
Ru	0.42	/	/	-0.07	0.72	/
Rh	0.34	/	/	0.25	/	/
Pd	0.25	/	/	0.22	/	/
Ag	0.06	/	/	-0.20	1.76	/
Cd ^a	/	/	/	/	/	/
Lu	-0.59	0.44	1.01	-0.43	0.64	/
Hf	-1.01	-0.06	1.43	-0.67	0.23	1.43
Ta	-1.26	-0.50	1.32	-0.99	0.10	1.32
W	-1.32	0.52	/	-0.79	0.00	1.14
Re	-0.27	0.49	0.57	-0.69	0.10	0.57
Os	0.73	/	/	0.00	/	/
Ir	0.20	/	/	0.28	/	/
Pt	0.26	/	/	0.26	/	/
Au ^a	/	/	/	/	/	/
Hg ^a	/	/	/	/	/	/

TM-O ₂ N ₂ ^β @Gra	Side-on			End-on		
	$\Delta G(*N_2)$	$\Delta G(*N_2 \rightarrow *NNH)$	$\Delta G(*NH_2 \rightarrow *NH_3)$	$\Delta G(*N_2)$	$\Delta G(*N_2 \rightarrow *NNH)$	$\Delta G(*NH_2 \rightarrow *NH_3)$
Sc	-0.73	0.34	1.03	-0.59	0.69	/
Ti	-0.72	0.07	1.01	-0.61	0.54	/
V	-0.29	0.32	0.44	-0.56	0.67	/
Cr	0.29	/	/	0.44	/	/
Mn	-0.06	0.94	/	0.13	/	/
Fe	0.41	/	/	-0.03	1.13	/
Co	0.29	/	/	0.13	/	/
Ni	0.26	/	/	0.44	/	/
Cu	0.28	/	/	-0.09	1.81	/
Zn	0.30	/	/	0.24	/	/
Y	-0.59	0.37	0.89	-0.46	0.68	/
Zr	-1.13	-0.16	1.55	-0.91	0.29	1.55
Nb	-1.24	-0.21	1.22	-0.75	0.22	1.22
Mo	-1.13	0.74	/	-0.38	0.08	0.92
Tc	-0.25	0.63	/	-0.71	0.39	0.45
Ru	0.32	/	/	-0.02	1.23	/
Rh	0.23	/	/	0.26	/	/
Pd	0.32	/	/	0.27	/	/
Ag	0.09	/	/	-0.03	1.78	/
Cd ^a	/	/	/	/	/	/
Lu	-0.56	0.31	1.18	-0.49	0.69	/
Hf	-1.08	-0.30	1.51	-0.87	0.26	1.51
Ta	-1.63	-0.45	1.29	-0.98	0.05	1.29
W	-1.79	0.68	/	-0.67	-0.14	1.16
Re	-0.56	0.52	/	-0.68	0.01	0.66
Os	0.32	/	/	0.06	/	/
Ir	0.30	/	/	0.28	/	/
Pt	0.25	/	/	0.27	/	/
Au	0.08	/	/	-0.58	1.33	/
Hg ^a	/	/	/	/	/	/

TM-O ₂ N ₂ ^γ @Gra	Side-on			End-on		
	$\Delta G(*N_2)$	$\Delta G(*N_2 \rightarrow *NNH)$	$\Delta G(*NH_2 \rightarrow *NH_3)$	$\Delta G(*N_2)$	$\Delta G(*N_2 \rightarrow *NNH)$	$\Delta G(*NH_2 \rightarrow *NH_3)$
Sc	-0.74	0.39	1.07	-0.58	0.76	/
Ti	-0.57	0.08	0.98	-0.70	0.62	/
V	-0.10	0.28	0.37	-0.64	0.66	/
Cr	0.79	/	/	0.50	/	/
Mn	0.42	/	/	0.16	/	/
Fe	0.13	/	/	-0.07	1.03	/
Co	0.24	/	/	0.37	/	/
Ni	0.31	/	/	0.29	/	/
Cu	0.32	/	/	-0.43	1.72	/
Zn	0.28	/	/	0.19	/	/
Y	-0.59	0.42	1.05	-0.45	0.69	/
Zr	-1.05	-0.07	1.36	-0.88	0.31	1.36
Nb	-1.03	-0.26	0.91	-0.99	0.30	0.91
Mo	-0.72	0.37	0.68	-0.43	0.04	0.68
Tc	-0.15	0.44	0.33	-0.66	0.18	0.33
Ru	0.57	/	/	-0.19	0.93	/
Rh	0.32	/	/	0.24	/	/
Pd	0.19	/	/	0.24	/	/
Ag	-0.01	1.81	/	-0.23	1.81	/
Cd ^a	/	/	/	/	/	/
Lu	-0.59	0.36	1.18	-0.45	0.59	/
Hf	-1.04	-0.16	-0.72	-0.75	0.09	-0.72
Ta	-1.35	-0.47	1.23	-1.09	0.10	1.23
W	-1.40	0.57	/	-0.82	-0.11	0.95
Re	-0.54	0.25	0.86	-0.88	-0.03	0.86
Os	0.77	/	/	-0.15	0.93	/
Ir	0.26	/	/	0.30	/	/
Pt	0.31	/	/	0.31	/	/
Au ^a	/	/	/	/	/	/
Hg ^a	/	/	/	/	/	/

TM-O ₃ N ₁ @Gra	Side-on			End-on		
	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$
Sc	-0.81	0.24	1.31	-0.62	0.63	/
Ti	-0.81	0.09	0.92	-0.71	0.51	/
V	-0.22	0.30	0.39	-0.52	0.59	/
Cr	0.12	/	/	0.37	/	/
Mn	-0.94	1.02	/	-0.01	0.02	0.96
Fe	-0.68	1.29	/	-0.35	0.58	/
Co	0.10	/	/	-0.45	1.34	/
Ni	0.24	/	/	-0.28	1.19	/
Cu	-0.14	1.66	/	-0.61	1.67	/
Zn	—	/	/	-0.07	0.64	/
Y	-0.72	0.27	-0.20	-0.56	0.61	/
Zr	-1.20	-0.21	1.42	-0.93	0.26	1.42
Nb	-1.41	-0.09	0.86	-0.92	0.13	0.86
Mo	-1.03	0.53	/	-0.57	0.00	0.15
Tc	-0.25	0.39	0.33	-0.76	0.41	0.33
Ru	0.36	/	/	-0.04	0.76	/
Rh	0.26	/	/	0.22	/	/
Pd ^a	/	/	/	/	/	/
Ag	—	/	/	-0.19	1.61	/
Cd ^a	/	/	/	/	/	/
Lu	-0.64	0.33	-0.33	-0.42	0.55	/
Hf	-1.37	-0.29	-1.22	-0.94	0.08	-1.22
Ta	-1.81	-0.46	1.17	-1.19	-0.01	1.17
W	-1.76	0.67	/	-0.87	-0.08	0.96
Re	-0.31	0.26	0.82	-0.65	0.10	0.82
Os	0.66	/	/	-0.04	0.84	/
Ir	0.28	/	/	0.29	/	/
Pt	0.31	/	/	0.30	/	/
Au ^a	/	/	/	/	/	/
Hg ^a	/	/	/	/	/	/

TM-O ₄ @Gra	Side-on			End-on		
	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$	$\Delta G(^*N_2)$	$\Delta G(^*N_2 \rightarrow ^*NNH)$	$\Delta G(^*NH_2 \rightarrow ^*NH_3)$
Sc	-0.93	0.01	1.40	-0.74	0.43	1.40
Ti	-1.07	0.01	0.88	-1.00	0.45	0.88
V	-0.13	0.18	0.43	-0.45	0.48	0.43
Cr	-0.46	0.61	/	-0.80	0.96	/
Mn	-0.68	0.89	/	-0.54	0.68	/
Fe	-0.91	1.35	/	-1.00	1.04	/
Co	-0.47	0.91	/	-1.00	1.27	/
Ni	-0.37	1.31	/	-0.86	1.41	/
Cu	-0.17	1.01	/	-0.63	1.48	/
Zn ^a	/	/	/	/	/	/
Y	-0.92	0.16	1.59	-0.69	0.55	/
Zr	-1.33	-0.52	1.62	-0.98	0.10	1.62
Nb	-1.80	0.32	0.76	-1.28	0.40	0.76
Mo	-0.99	0.08	-0.74	-0.81	-0.11	-0.74
Tc	-0.06	-0.51	0.22	-0.83	-0.09	0.22
Ru	0.40	/	/	-0.01	-0.22	-0.14
Rh	0.26	/	/	0.28	/	/
Pd ^a	/	/	/	/	/	/
Ag ^a	/	/	/	/	/	/
Cd ^a	/	/	/	/	/	/
Lu	-0.61	0.08	1.55	-0.41	0.43	1.55
Hf	-1.43	-0.55	1.85	-1.01	0.10	1.85
Ta	-2.23	-0.04	1.23	-1.27	-0.08	1.23
W	-1.54	0.29	1.28	-0.93	-0.18	1.28
Re	0.08	/	/	-0.56	0.24	0.74
Os	0.69	/	/	0.19	/	/
Ir	0.34	/	/	0.26	/	/
Pt ^a	/	/	/	/	/	/
Au ^a	/	/	/	/	/	/
Hg ^a	/	/	/	/	/	/

Table S3. The $\Delta G_{\max}$, PDS, the most favorable pathway, $\Delta E_{\text{ads}}(^*\text{N}_2)$, $\Delta E_{\text{ads}}(^*\text{NNH})$, $\Delta E_{\text{ads}}(^*\text{N})$, $\Delta E_{\text{ads}}(^*\text{NH}_2)$, and the linear combination of adsorption energy of different intermediates (labeled as ΔE_{ads}) of 21 potential candidates that meet three screening criteria. $\Delta E_{\text{ads}}(^*\text{N}_x\text{H}_y) = E(^*\text{N}_x\text{H}_y) - E(^*) - x/2 \times E(\text{N}_2) - y/2 \times E(\text{H}_2)$, where $E(^*\text{N}_x\text{H}_y)$, $E(^*)$, $E(\text{N}_2)$ and $E(\text{H}_2)$ stand for the energy of intermediate of N_xH_y , catalyst, free molecules N_2 and H_2 , respectively. $\Delta E_{\text{ads}} = [\Delta E_{\text{ads}}(^*\text{N}_2) - \Delta E_{\text{ads}}(^*\text{N})] + [\Delta E_{\text{ads}}(^*\text{NNH}) - \Delta E_{\text{ads}}(^*\text{N})] + [\Delta E_{\text{ads}}(^*\text{NH}_2) - \Delta E_{\text{ads}}(^*\text{N})]$. The unit of the values in the table is eV.

TM-O _x N _y @Gra	$\Delta G_{\max}$	PDS	Pathway	$\Delta E_{\text{ads}}(^*\text{N}_2)$	$\Delta E_{\text{ads}}(^*\text{NNH})$	$\Delta E_{\text{ads}}(^*\text{N})$	$\Delta E_{\text{ads}}(^*\text{NH}_2)$	ΔE_{ads}
V-N ₄ @Gra	0.44	*NH ₂ →*NH ₃	consecutive	-0.74	-0.68	-0.32	-2.35	-2.79
Tc-N ₄ @Gra	0.49	*NH ₂ →*NH ₃	distal	-0.94	-1.12	-1.68	-1.98	0.99
V-O ₁ N ₃ @Gra	0.40	*NH ₂ →*NH ₃	consecutive	-0.72	-0.71	-0.41	-2.29	-2.48
Tc-O ₁ N ₃ @Gra	0.57	*N→*NH	distal	-1.12	-1.11	-1.73	-1.93	1.04
V-O ₂ N ₂ ^α @Gra	0.42	*NH ₂ →*NH ₃	consecutive	-0.55	-0.62	-0.55	-2.12	-1.65
Tc-O ₂ N ₂ ^α @Gra	0.54	*NNH→*NHNH	alternating	-1.17	-0.99	-1.74	-1.63	1.43
V-O ₂ N ₂ ^β @Gra	0.44	*NH ₂ →*NH ₃	consecutive	-0.79	-0.79	-0.50	-2.17	-2.25
Tc-O ₂ N ₂ ^β @Gra	0.65	*NNH→*NHNH	alternating	-1.19	-1.11	-1.82	-1.84	1.32
V-O ₂ N ₂ ^γ @Gra	0.38	*NH ₂ →*NH ₃	consecutive	-0.58	-0.63	-0.42	-2.26	-2.20
Tc-O ₂ N ₂ ^γ @Gra	0.52	*NHNH ₂ →*NH ₂ NH ₂	enzymatic	-0.65	-0.52	-1.89	-1.73	2.77
Hf-O ₂ N ₂ ^γ @Gra	1.03	*NNH ₂ →*N+NH ₃ (g)	consecutive	-1.51	-1.98	-0.02	-3.43	-6.86
V-O ₃ N ₁ @Gra	0.39	*NH ₂ →*NH ₃	consecutive	-0.69	-0.70	-0.89	-2.07	-0.79
Y-O ₃ N ₁ @Gra	0.97	*NNH ₂ →*N+NH ₃ (g)	consecutive	-1.17	-1.18	1.25	-3.13	-9.23
Mo-O ₃ N ₁ @Gra	0.48	*NH→*NH ₂	distal	-1.07	-1.36	-2.17	-2.16	1.93
Tc-O ₃ N ₁ @Gra	0.73	*N→*NH	consecutive	-0.73	-0.60	-1.78	-1.63	2.37
Lu-O ₃ N ₁ @Gra	1.09	*NNH ₂ →*N+NH ₃ (g)	consecutive	-1.03	-1.08	1.57	-3.14	-9.97
Hf-O ₃ N ₁ @Gra	0.52	*NNH ₂ →*N+NH ₃ (g)	distal	-1.41	-1.60	-0.78	-3.53	-4.21
V-O ₄ @Gra	0.43	*NH ₂ →*NH ₃	consecutive	-0.59	-0.71	-1.21	-1.85	0.47
Mo-O ₄ @Gra	0.74	*NNH→*NHNH	alternating	-1.30	-1.66	-2.30	-1.93	2.00
Tc-O ₄ @Gra	0.75	*N→*NH	consecutive	-0.53	-1.29	-2.21	-1.50	3.30
Ru-O ₄ @Gra	0.43	*N→*NH	distal	-0.45	-1.00	-0.71	-1.57	-0.89

Table S4. Thermal corrections (in eV) of reaction intermediates along the most favorable pathways on the 10 selected catalysts. ^a represents that thermal corrections of the gas-phase molecules (N₂, H₂, and NH₃) are taken from the NIST database.

N _x H _y	V-N ₄ @Gra			Tc-N ₄ @Gra			V-O ₁ N ₃ @Gra			V-O ₂ N ₂ ^a @Gra			V-O ₂ N ₂ ^b @Gra		
	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT
N ₂ ^a	0.14	0.59	0.09	0.14	0.59	0.09	0.14	0.59	0.09	0.14	0.59	0.09	0.14	0.59	0.09
H ₂ ^a	0.27	0.40	0.09	0.27	0.40	0.09	0.27	0.40	0.09	0.27	0.40	0.09	0.27	0.40	0.09
NH ₃ ^a	0.89	0.60	0.10	0.89	0.60	0.10	0.89	0.60	0.10	0.89	0.60	0.10	0.89	0.60	0.10
*N ₂	0.19	0.16	0.08	0.21	0.09	0.05	0.19	0.13	0.07	0.19	0.14	0.07	0.20	0.12	0.06
*NNH	0.48	0.13	0.07	0.49	0.16	0.08	0.49	0.12	0.07	0.46	0.21	0.09	0.49	0.12	0.07
*NNH ₂	0.84	0.14	0.07	0.81	0.19	0.09	0.84	0.13	0.07	0.84	0.14	0.07	0.85	0.13	0.07
*N	0.09	0.06	0.03	0.09	0.05	0.03	0.09	0.06	0.03	0.08	0.07	0.03	0.08	0.06	0.03
*NH	0.35	0.08	0.05	0.35	0.08	0.05	0.35	0.08	0.05	0.35	0.09	0.05	0.35	0.08	0.05
*NH ₂	0.65	0.12	0.07	0.68	0.10	0.06	0.66	0.11	0.06	0.66	0.12	0.07	0.67	0.10	0.06
*NH ₃	1.03	0.17	0.08	1.03	0.18	0.08	1.02	0.18	0.08	1.02	0.19	0.08	1.03	0.17	0.08

N _x H _y	V-O ₂ N ₂ ^γ @Gra			V-O ₃ N ₁ @Gra			Mo-O ₃ N ₁ @Gra			V-O ₄ @Gra			Ru-O ₄ @Gra		
	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT	ZPE	TS	∫C _p dT
N ₂ ^a	0.14	0.59	0.09	0.14	0.59	0.09	0.14	0.59	0.09	0.14	0.59	0.09	0.14	0.59	0.09
H ₂ ^a	0.27	0.40	0.09	0.27	0.40	0.09	0.27	0.40	0.09	0.27	0.40	0.09	0.27	0.40	0.09
NH ₃ ^a	0.89	0.60	0.10	0.89	0.60	0.10	0.89	0.60	0.10	0.89	0.60	0.10	0.89	0.60	0.10
*N ₂	0.19	0.14	0.07	0.19	0.15	0.07	0.21	0.13	0.07	0.17	0.15	0.08	0.19	0.19	0.08
*NNH	0.49	0.13	0.07	0.47	0.13	0.07	0.48	0.15	0.08	0.46	0.15	0.08	0.46	0.14	0.07
*NNH ₂	0.85	0.13	0.07	0.84	0.14	0.07	0.82	0.17	0.09	0.83	0.16	0.08	0.78	0.15	0.08
*N	0.09	0.06	0.03	0.09	0.06	0.03	0.09	0.06	0.03	0.09	0.06	0.03	0.08	0.09	0.04
*NH	0.35	0.08	0.05	0.35	0.09	0.05	0.35	0.08	0.05	0.35	0.09	0.05	0.33	0.10	0.05
*NH ₂	0.67	0.10	0.06	0.66	0.12	0.06	0.66	0.14	0.07	0.63	0.11	0.06	0.68	0.11	0.06
*NH ₃	1.03	0.16	0.08	1.02	0.17	0.08	1.02	0.16	0.08	1.02	0.11	0.06	1.03	0.14	0.07

Table S5. Charge variation of the three moieties along the most favorable reaction pathway on the 10 selected catalysts. The positive and negative charge values represent gain and loss of electrons, respectively. The charge distribution on the bare catalyst is used as a reference to evaluate the charge variation.

*N _x N _y	Moiety	V-N ₄ @Gra	Tc-N ₄ @Gra	V-O ₁ N ₃ @Gra	V-O ₂ N ₂ ^a @Gra	V-O ₂ N ₂ ^b @Gra	V-O ₂ N ₂ ^γ @Gra	V-O ₃ N ₁ @Gra	Mo-O ₃ N ₁ @Gra	V-O ₄ @Gra	Ru-O ₄ @Gra
*N ₂	TM-O _x N _y	-0.32	-0.25	-0.19	-0.53	-0.33	-0.44	-0.46	-0.25	-0.58	-0.23
	C _{all}	-0.21	-0.10	-0.39	-0.08	-0.28	-0.16	-0.18	-0.21	-0.09	-0.10
	N ₂	0.53	0.35	0.59	0.61	0.61	0.60	0.64	0.46	0.67	0.33
*NNH	TM-O _x N _y	-0.49	-0.54	-0.33	-0.63	-0.43	-0.52	-0.54	-0.30	-0.58	-0.19
	C _{all}	-0.09	0.10	-0.29	0.01	-0.18	-0.08	-0.10	-0.27	-0.23	-0.22
	NNH	0.59	0.44	0.62	0.63	0.61	0.60	0.64	0.58	0.81	0.42
*NNH ₂	TM-O _x N _y	-0.39	-0.99	-0.46	-0.69	-0.41	-0.63	-0.51	-0.48	-0.56	-0.12
	C _{all}	-0.16	0.62	-0.06	0.18	-0.10	0.14	-0.01	0.02	0.00	-0.16
	NNH ₂	0.55	0.37	0.52	0.51	0.51	0.50	0.51	0.45	0.56	0.28
*N	TM-O _x N _y	-0.13	-0.73	-0.19	-0.52	-0.28	-0.40	-0.47	-0.37	-0.47	-0.51
	C _{all}	-0.53	0.03	-0.55	-0.29	-0.44	-0.39	-0.34	-0.40	-0.26	0.04
	N	0.66	0.71	0.74	0.80	0.72	0.79	0.81	0.77	0.73	0.47
*NH	TM-O _x N _y	-0.62	-0.83	-0.59	-0.69	-0.42	-0.57	-0.56	-0.56	-0.70	-0.33
	C _{all}	-0.01	0.40	-0.02	0.13	-0.12	-0.02	0.02	0.02	0.10	-0.14
	NH	0.63	0.43	0.62	0.56	0.54	0.59	0.54	0.54	0.60	0.47
*NH ₂	TM-O _x N _y	-0.46	-0.85	-0.36	-0.53	-0.22	-0.45	-0.46	-0.45	-0.64	-0.31
	C _{all}	0.12	0.61	-0.03	0.17	-0.15	0.09	0.07	0.08	0.25	0.02
	NH ₂	0.35	0.24	0.39	0.35	0.37	0.36	0.39	0.37	0.39	0.29
*NH ₃	TM-O _x N _y	-0.22	-0.39	-0.17	-0.15	-0.27	-0.07	-0.16	0.28	-0.44	-0.12
	C _{all}	0.35	0.60	0.27	0.30	0.37	0.17	0.25	-0.20	0.52	0.27
	NH ₃	-0.13	-0.21	-0.11	-0.15	-0.11	-0.10	-0.08	-0.08	-0.08	-0.14

Table S6. The N-N bond length (Å) of free N₂ (g), *N₂, *NNH, and *NNH₂ on the 10 selected TM-O_xN_y@Gra catalysts.

TM-O _x N _y @Gra	N ₂ (g)	*N ₂	*NNH	*NNH ₂
V-N ₄ @Gra	1.115	1.194	1.302	1.428
Tc-N ₄ @Gra	1.115	1.148	1.240	1.343
V-O ₁ N ₃ @Gra	1.115	1.206	1.318	1.418
V-O ₂ N ₂ ^α @Gra	1.115	1.208	1.318	1.420
V-O ₂ N ₂ ^β @Gra	1.115	1.213	1.320	1.424
V-O ₂ N ₂ ^γ @Gra	1.115	1.210	1.316	1.419
V-O ₃ N ₁ @Gra	1.115	1.213	1.328	1.428
Mo-O ₃ N ₁ @Gra	1.115	1.156	1.254	1.349
V-O ₄ @Gra	1.115	1.209	1.377	1.440
Ru-O ₄ @Gra	1.115	1.140	1.224	1.340

Table S7. The Bader charge and magnetic moment before and after N₂ adsorption. (*) and (*N₂) stand for before and after N₂ adsorption on 10 selected catalysts, respectively. The positive and negative charge values represent gain and loss of electrons, respectively.

TM-O _x N _y @Gra	Bader (*)/e			Bader (*N ₂)/e				Magnetic moment (*)/μ _B				Magnetic moment (*N ₂)/μ _B				
	TM	O _x N _y	C _{all}	TM	O _x N _y	C _{all}	N ₂	TM	O _x N _y	C _{all}	total	TM	O _x N _y	C _{all}	N ₂	total
V-N ₄ @Gra	-1.31	4.76	-3.45	-1.54	4.68	-3.67	0.53	2.35	-0.12	0.19	2.42	1.07	-0.08	0.00	0.00	0.99
Tc-N ₄ @Gra	-1.27	5.05	-3.79	-1.37	4.91	-3.89	0.35	2.58	-0.06	0.11	2.63	0.79	-0.02	0.05	-0.02	0.80
V-O ₁ N ₃ @Gra	-1.28	4.68	-3.40	-1.53	4.74	-3.80	0.59	2.44	-0.18	0.05	2.31	1.07	-0.04	0.11	-0.01	1.13
V-O ₂ N ₂ ^α @Gra	-1.19	4.72	-3.53	-1.50	4.50	-3.60	0.61	2.67	-0.18	0.11	2.60	1.22	-0.08	-0.02	-0.03	1.09
V-O ₂ N ₂ ^β @Gra	-1.20	4.62	-3.42	-1.53	4.62	-3.70	0.61	2.66	-0.17	0.06	2.55	1.04	-0.07	0.01	-0.03	0.95
V-O ₂ N ₂ ^γ @Gra	-1.21	4.65	-3.44	-1.52	4.53	-3.60	0.60	2.63	-0.18	0.13	2.58	1.11	-0.08	-0.02	-0.03	0.98
V-O ₃ N ₁ @Gra	-1.12	4.53	-3.41	-1.49	4.43	-3.58	0.64	2.85	-0.15	0.10	2.80	1.37	-0.06	0.13	-0.04	1.40
Mo-O ₃ N ₁ @Gra	-1.18	4.50	-3.32	-1.31	4.38	-3.53	0.46	2.98	0.00	0.01	2.99	0.86	0.00	-0.01	0.04	0.89
V-O ₄ @Gra	-1.05	4.46	-3.41	-1.43	4.26	-3.51	0.67	3.06	-0.10	0.08	3.04	0.66	-0.02	0.00	-0.04	0.60
Ru-O ₄ @Gra	-0.55	4.36	-3.81	-0.92	4.50	-3.91	0.33	0.29	0.03	-0.05	0.27	0.75	0.04	0.01	0.03	0.83

Table S8. The d-band center of 10 selected catalysts before and after N₂ adsorption.

TM-O _x N _y @Gra	Before N ₂ adsorption			After N ₂ adsorption		
	spin up	spin down	average	spin up	spin down	average
V-N ₄ @Gra	-0.22	1.59	0.67	-0.16	0.68	0.26
Tc-N ₄ @Gra	-2.03	-0.34	-1.20	-1.16	-0.68	-0.92
V-O ₁ N ₃ @Gra	-0.34	1.54	0.58	-0.50	0.35	-0.08
V-O ₂ N ₂ ^α @Gra	-0.34	1.69	0.66	-0.63	0.35	-0.15
V-O ₂ N ₂ ^β @Gra	-0.31	1.72	0.68	-0.73	0.10	-0.32
V-O ₂ N ₂ ^γ @Gra	-0.37	1.64	0.61	-0.62	0.27	-0.18
V-O ₃ N ₁ @Gra	-0.38	1.78	0.67	-0.81	0.30	-0.26
Mo-O ₃ N ₁ @Gra	-1.83	0.17	-0.85	-0.70	-0.12	-0.41
V-O ₄ @Gra	-0.49	1.81	0.63	-0.51	0.03	-0.24
Ru-O ₄ @Gra	-1.10	-0.92	-1.01	-2.02	-1.52	-1.77

Table S9. ΔG(*N₂) versus ΔG(*H) on the 10 selected catalysts.

ΔG	V-N ₄ @Gra	Tc-N ₄ @Gra	V-O ₁ N ₃ @Gra	V-O ₂ N ₂ ^α @Gra	V-O ₂ N ₂ ^β @Gra	V-O ₂ N ₂ ^γ @Gra	V-O ₃ N ₁ @Gra	Mo-O ₃ N ₁ @Gra	V-O ₄ @Gra	Ru-O ₄ @Gra
ΔG(*N ₂)	-0.27	-0.41	-0.23	-0.08	-0.29	-0.10	-0.22	-0.57	-0.13	-0.01
ΔG(*H)	-0.19	-0.35	-0.15	-0.13	-0.16	-0.13	-0.16	-0.40	-0.20	-0.34

Appendix

During the peer-review process, a reviewer required us to compare our calculated results in the present study with the previous experiments reported results. The reviewer's question was as follows: In the previous experimental studies, Mn-O₃N₁/PC catalyst (Ref 20: ACS Catal., 2021, 11, 509-516) and W-N₂O₂/NC (Ref21: Adv. Mater., 2021, 2100429) have been investigated as efficient catalysts for eNRR. Please compare the calculation results on the corresponding models in this work with the experimental results in the literature and provide some discussion.

Following the referee's comments, we have carefully read the two experimental references (refs. 20 and 21), done additional calculations and made a comprehensive comparison between the two experimental works and the current computational study from various aspects (including computational methods, level, model, functional, accuracy, parameters, calculated results, etc). We are aware that the experimental catalyst structures are somewhat different from our computational models. And the computational methods, accuracy, parameters are also somewhat different. Thus, what we can do is to make qualitative comparisons, discussions, comments, and get some general conclusions.

Let's discuss and analyze the Mn-O₃N₁/PC catalyst (Ref 20: ACS Catal., 2021, 11, 509-516) first. The experimental results show that the catalytic performance of Mn-O₃N₁/PC is better than that of Mn-N₄/PC. Our calculated results agree well with the experimental results. Both experiments and calculations show that the best reaction pathway follows the distal mechanism. The free energy profiles of both experiments and calculations are compared and shown in below Fig. R1. In the left part of Fig. R1, the free energy profile of Mn-N₄ and Mn-O₃N₁ are shown in (a) and (b), respectively. In the right part of Fig. R1, the free energy profile of Mn-N₄@Gra and Mn-O₃N₁@Gra are displayed in (c) and (d), respectively. Both (a) and (c) are non-spontaneous paths as $\Delta G(*N_2) > 0$, thus excluded. Whereas, the (b) and (d) are spontaneous processes since $\Delta G(*N_2) < 0$. This means that the catalytic performance of Mn-O₃N₁ is better than that of Mn-N₄.

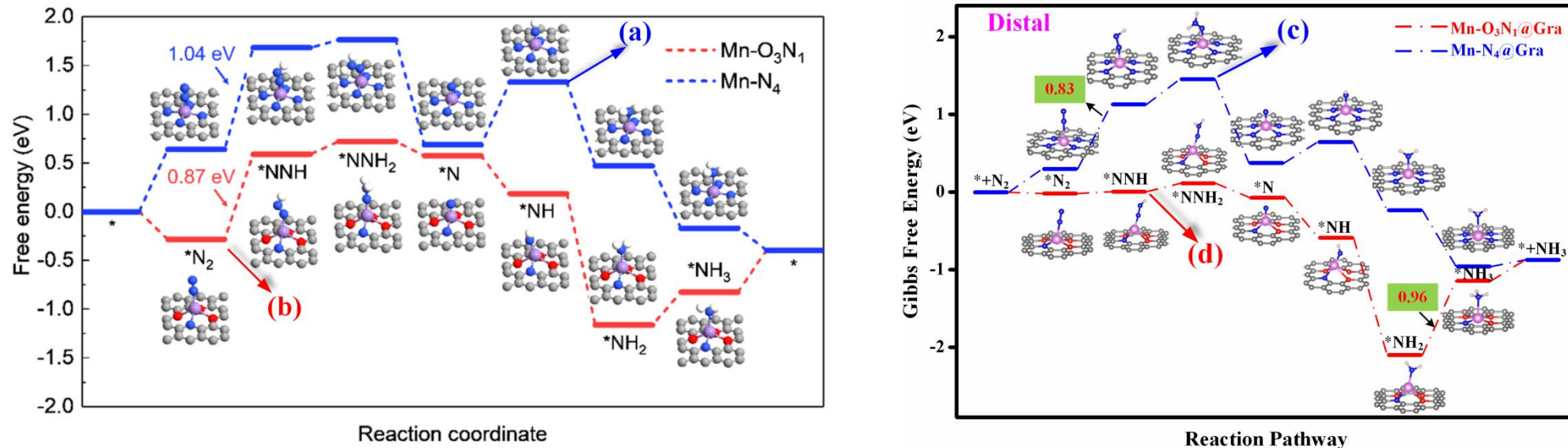


Fig. R1. The free energy profiles of distal pathway for both experiments (Mn-N₄ (a) and Mn-O₃N₁ (b)) and calculations (Mn-N₄@Gra (c) and Mn-O₃N₁@Gra (d)).

Besides the distal pathway, we also considered and calculated other three typical pathways, i.e., alternating, enzymatic, consecutive. The free energy profiles are shown in below Fig. R2. All these pathways demonstrate that the catalytic performance of Mn-O₃N₁@Gra is better than that of Mn-N₄.

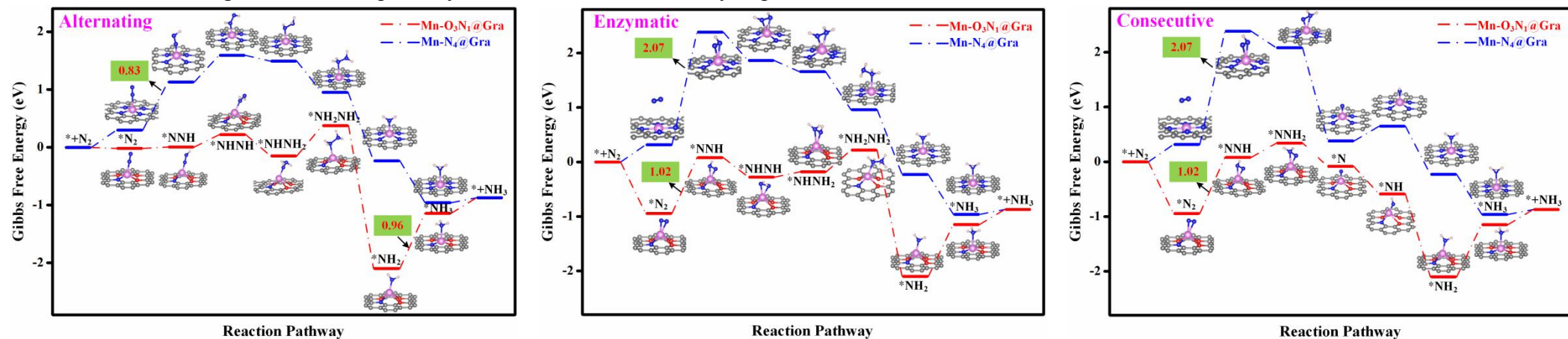
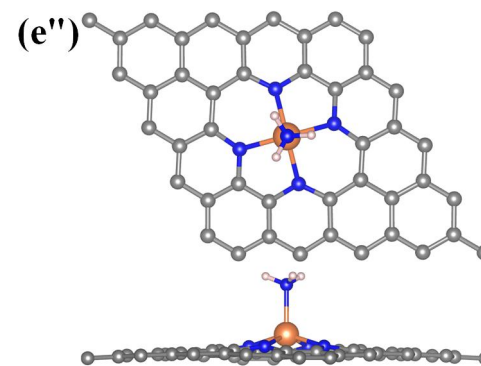
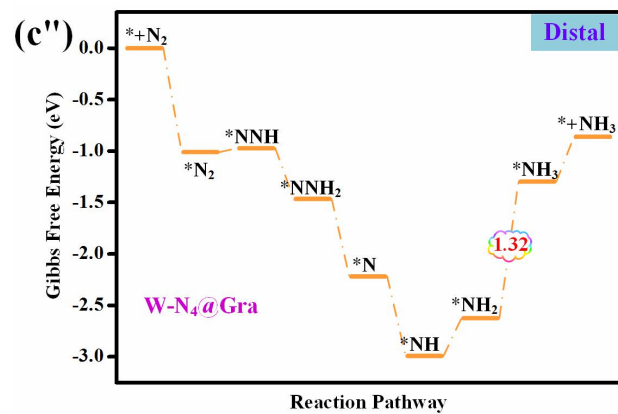
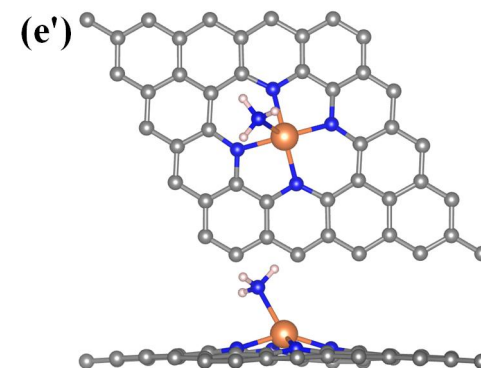
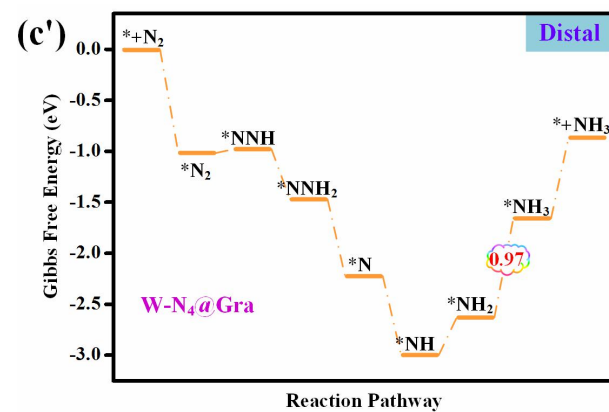
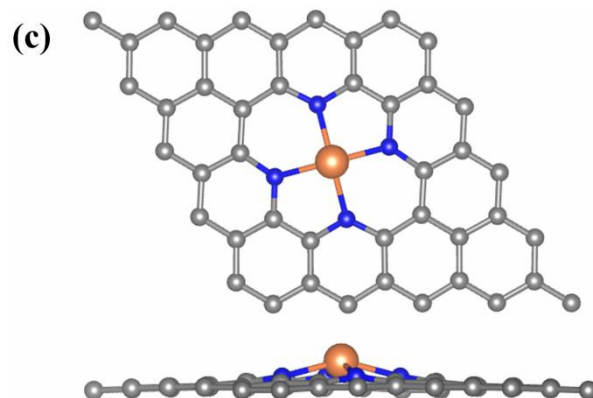
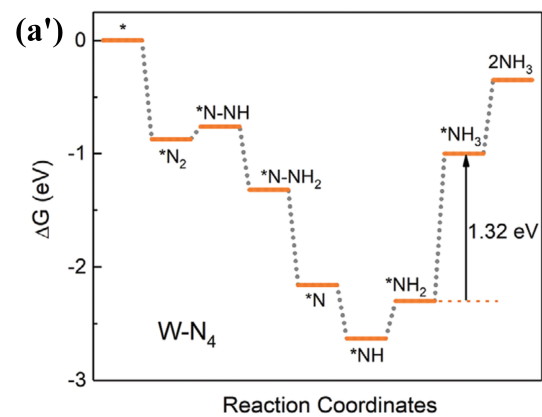
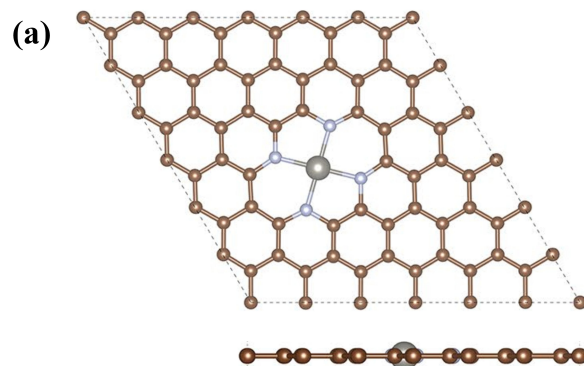


Fig. R2. The free energy profiles of alternating, enzymatic, consecutive pathways for the calculated Mn-N₄@Gra and Mn-O₃N₁@Gra.

Now, let's turn to discuss and analyze the experimental catalyst W-N₂O₂/NC (Ref21: Adv. Mater., 2021, 2100429). The experimental results are shown in (a), (a'), (b), and (b'). The comparison between (a') and (b') shows that the catalytic performance of W-N₂O₂/NC is better than that of W-N₄/NC. Our computational results are displayed in (c), (c'), (c''), (d), and (d'). (c') and (c'') are the free energy profiles of NRR for W-N₄@Gra. (d') is the free energy profile for W-O₂N₂@Gra, whose local coordination environment is the same as that of experimental structure W-N₂O₂/NC. Note that (c') and (c'') are different reaction paths for the same structure model W-N₄@Gra. The only difference between (c') and (c'') are the configuration (also the energy) of intermediate specie *NH₃. There is no imaginary frequency of intermediate specie *NH₃ in (e'). However, there is an imaginary frequency (−101 cm^{−1}) of intermediate specie *NH₃ in (e''). After we remove the imaginary frequency (−101 cm^{−1}) of intermediate specie *NH₃ in (e'') by following the vibration direction of imaginary frequency, we get (e'). Surprisingly and unexpectedly, the potential-determining step (PDS) of (c'') agrees well with that of (a'), whereas, the PDS of (c') is a bit different from that of (a').



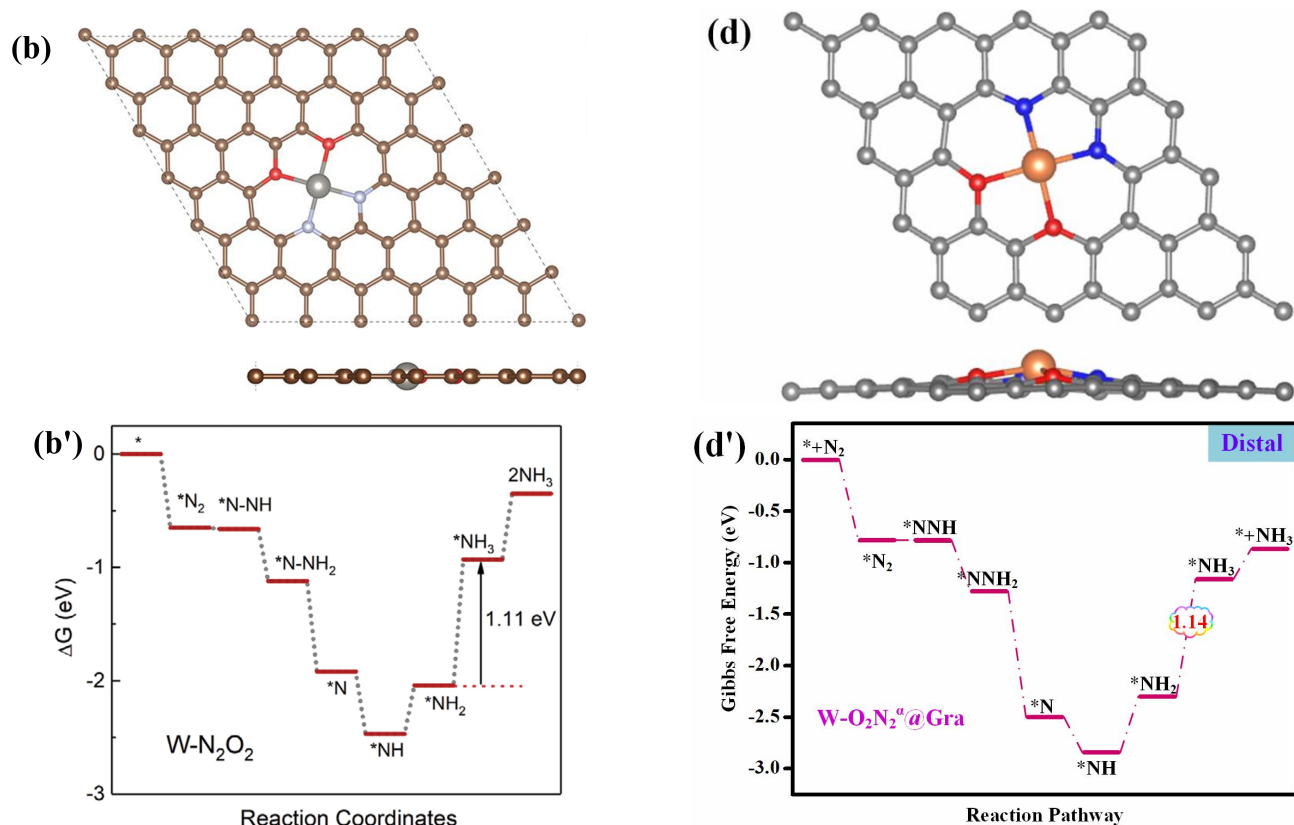
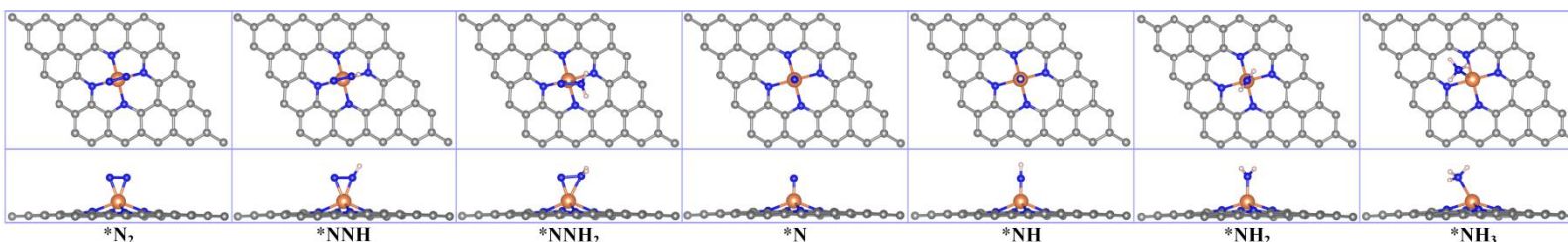
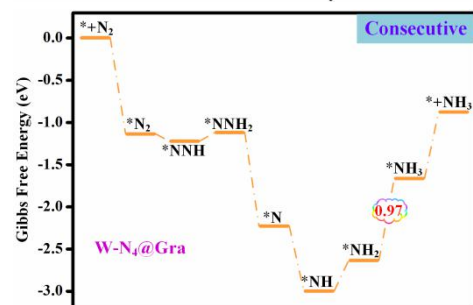
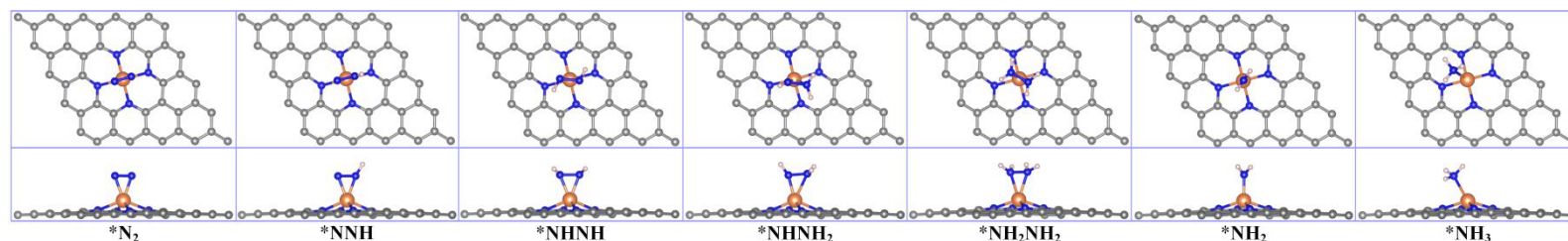
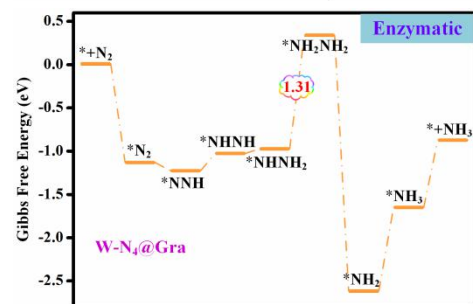
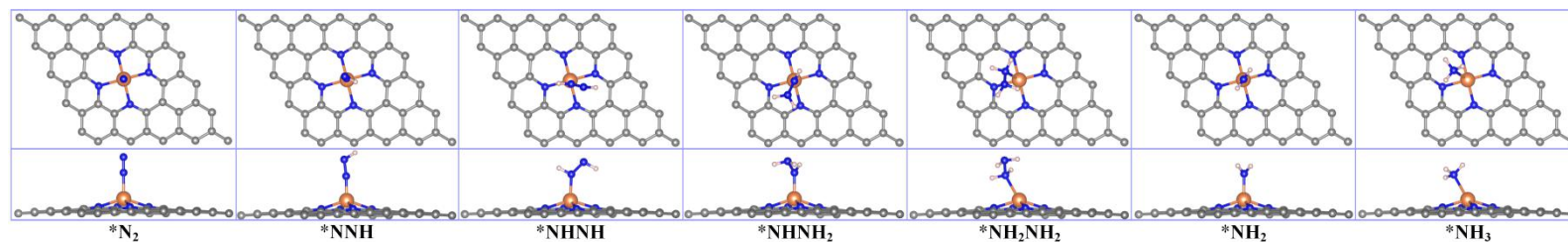
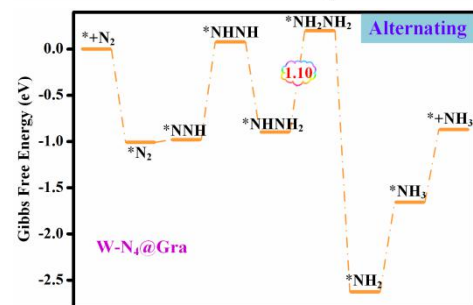
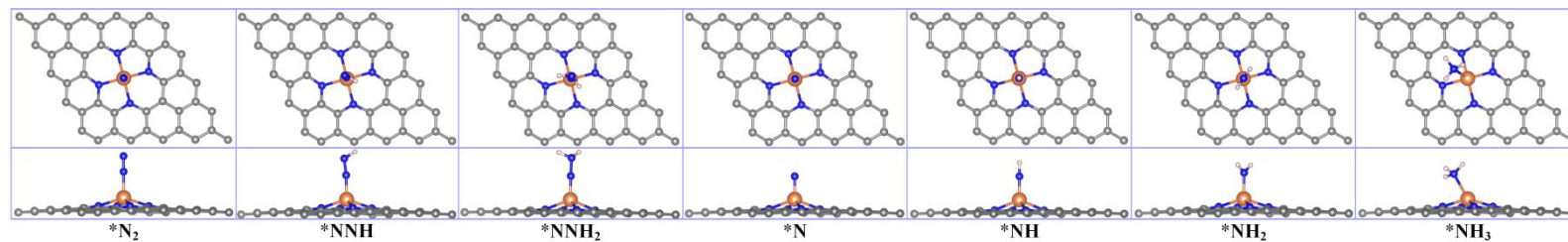
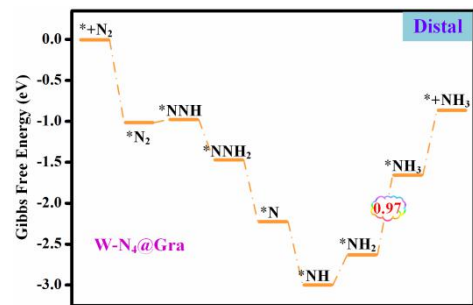
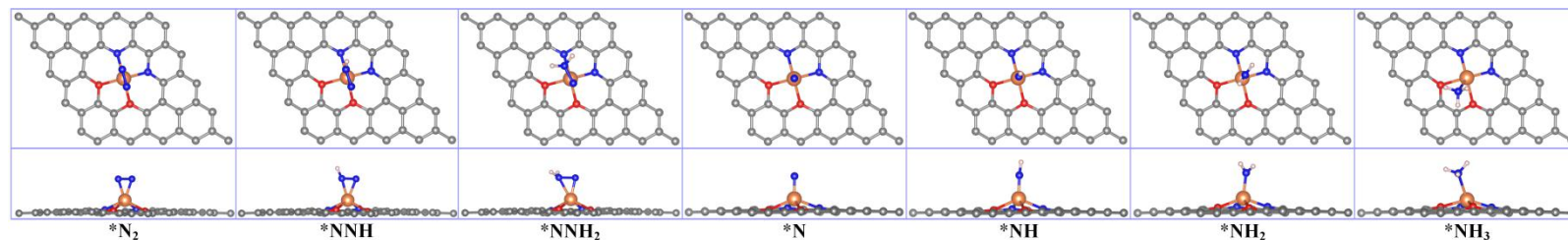
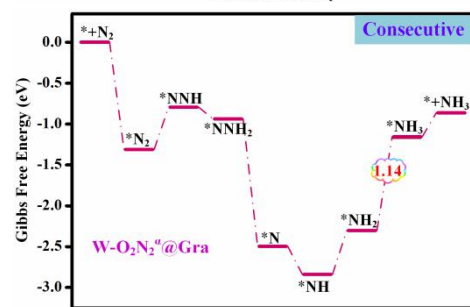
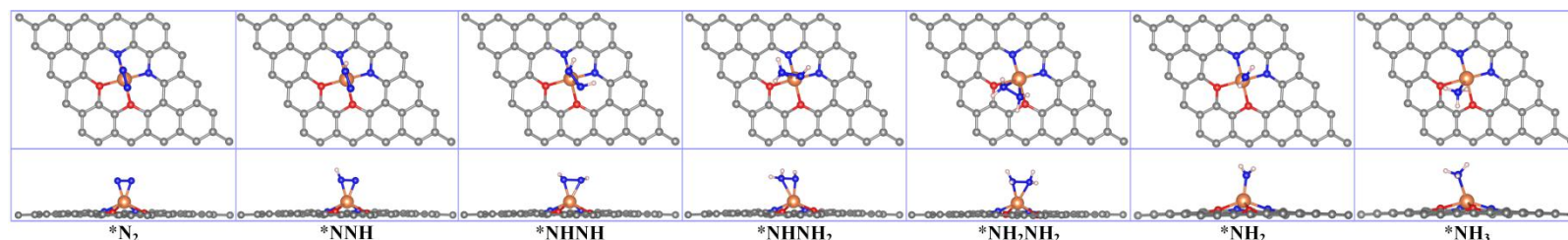
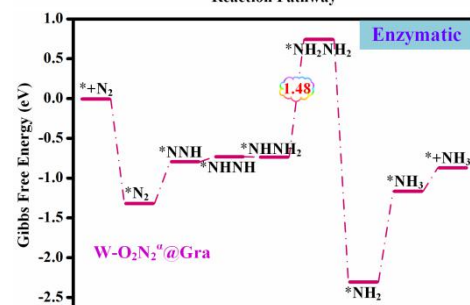
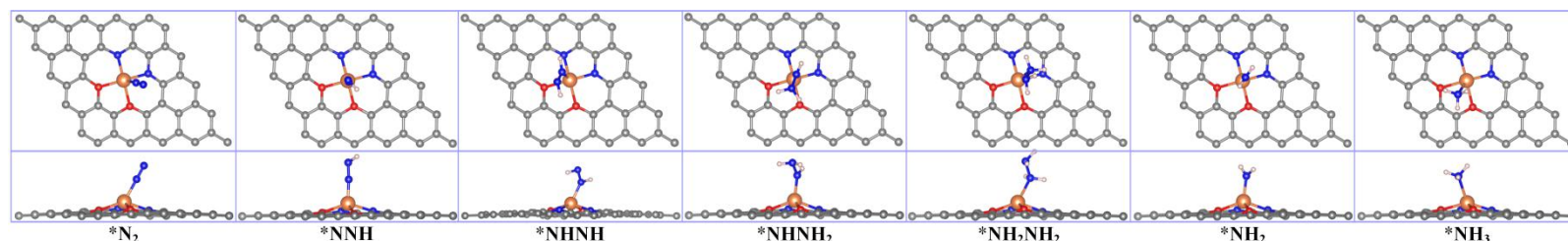
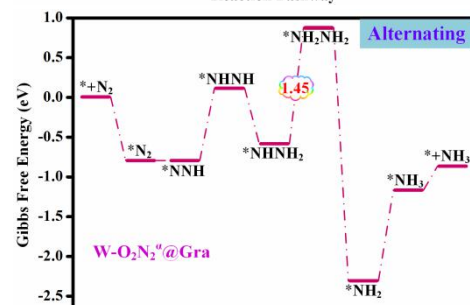
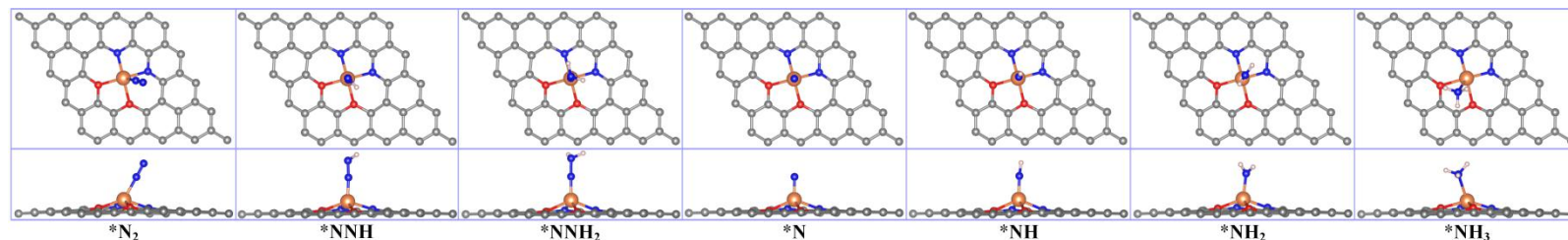
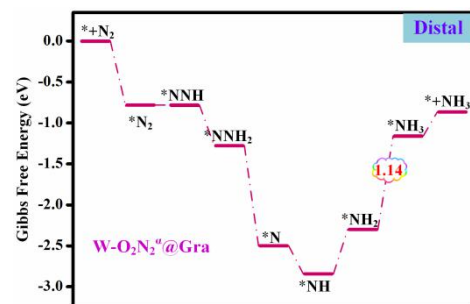
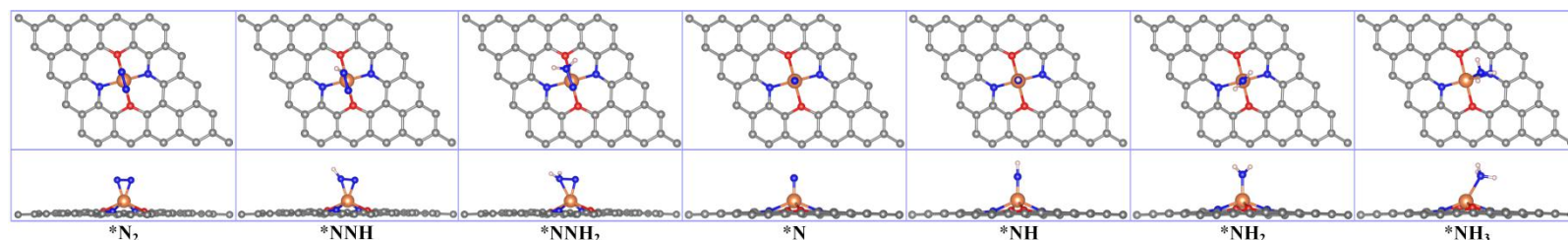
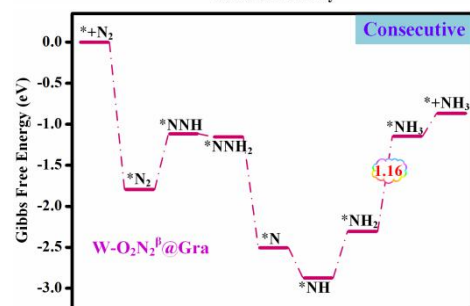
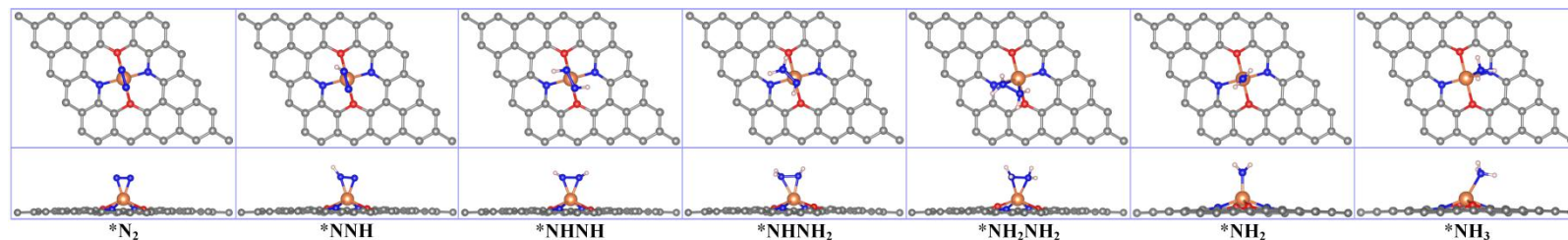
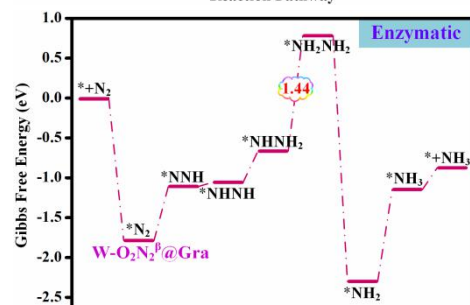
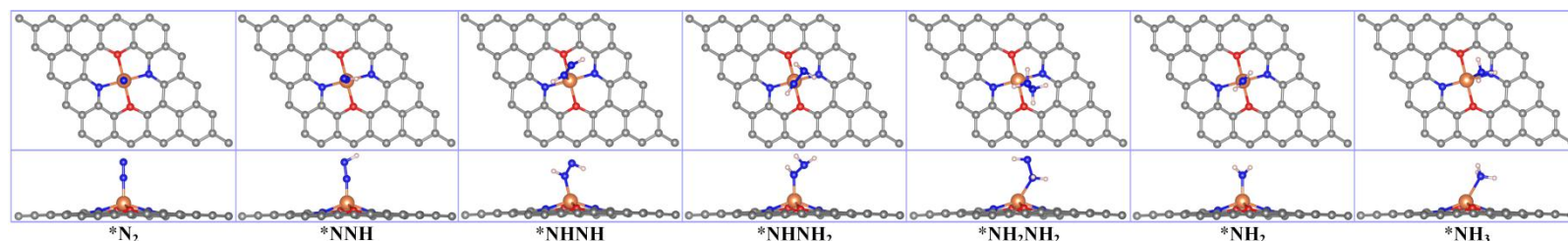
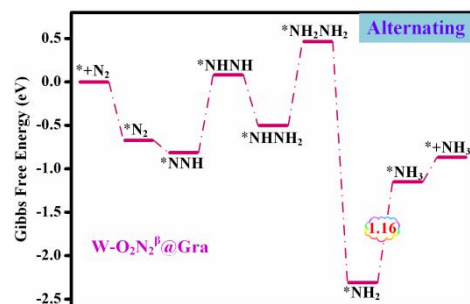
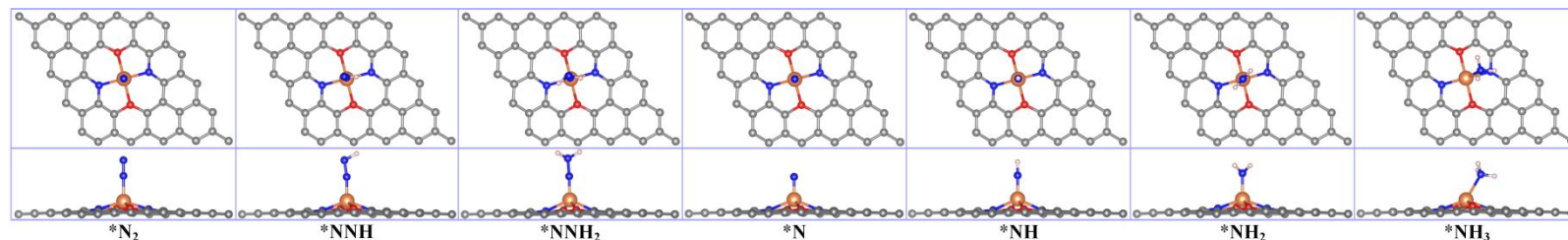
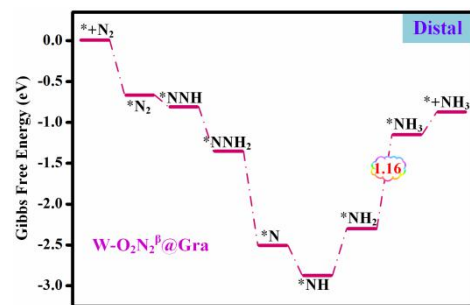


Fig. R3 The free energy profiles of distal pathways for the calculated W-N₄@Gra and W-O₂N₂@Gra.

Besides the above structure models and free energy profiles in Fig. R3, we also made comprehensive explorations on different structure models with diverse local coordination environments and different reaction pathways so as to get a full picture of reaction profiles for W-N₄@Gra, W-O₂N₂^a@Gra, W-O₂N₂^b@Gra, W-O₂N₂^c@Gra and the detailed results are displayed in below Fig. R4. From Fig. R4, we can clearly see different reaction pathways and the relevant intermediate species, also the best reaction path and the corresponding onset potential (this can be derived from the potential-determining step (PDS)).







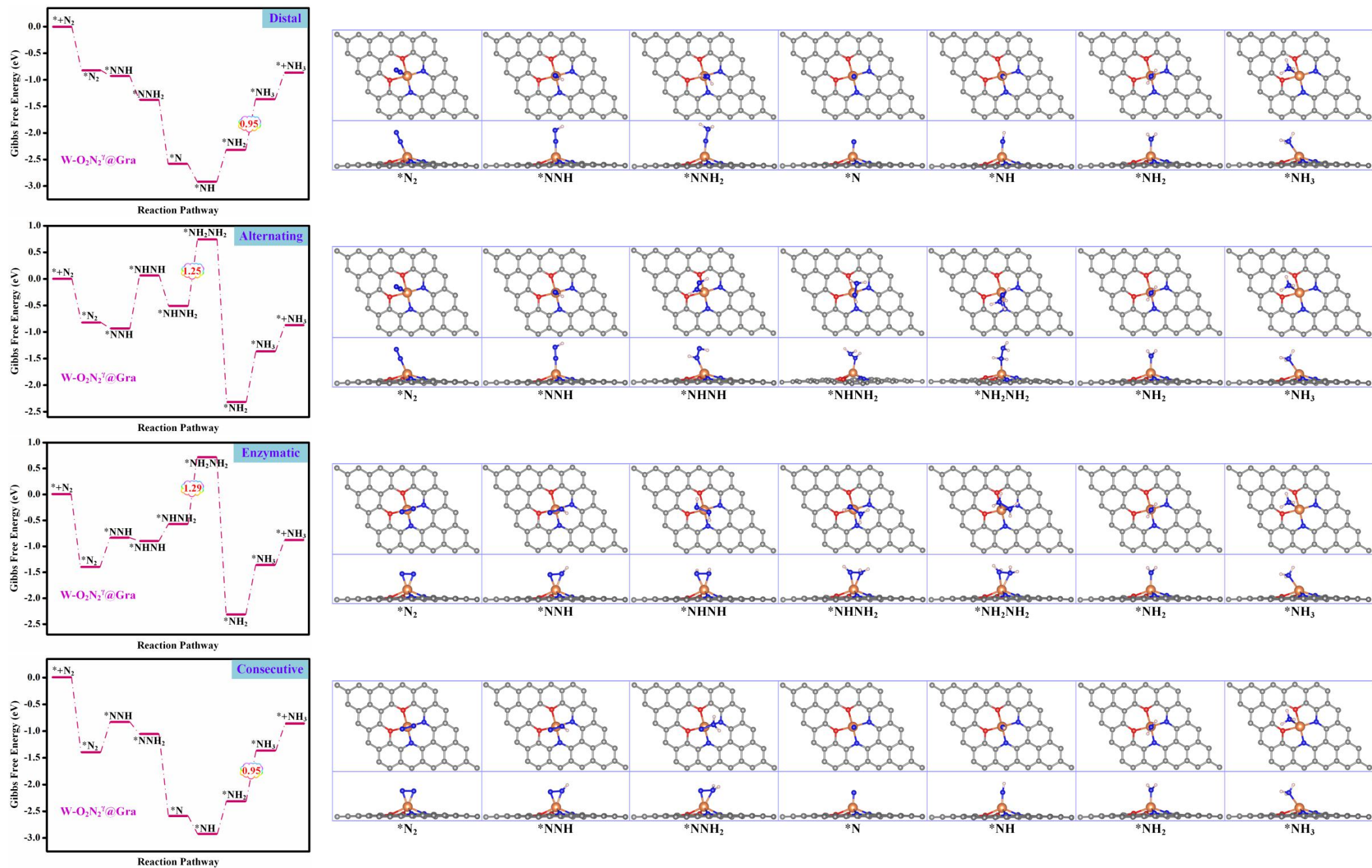


Fig. R4 The free energy profiles and the relevant intermediate species of different reaction pathways for $W-N_4@Gra$, $W-O_2N_2^a@Gra$, $W-O_2N_2^b@Gra$, and $W-O_2N_2^c@Gra$.