Supporting information for

Optimizing the NRR activity of single and double boron atom catalysts using suitable support: A first principles investigation

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Table of contents

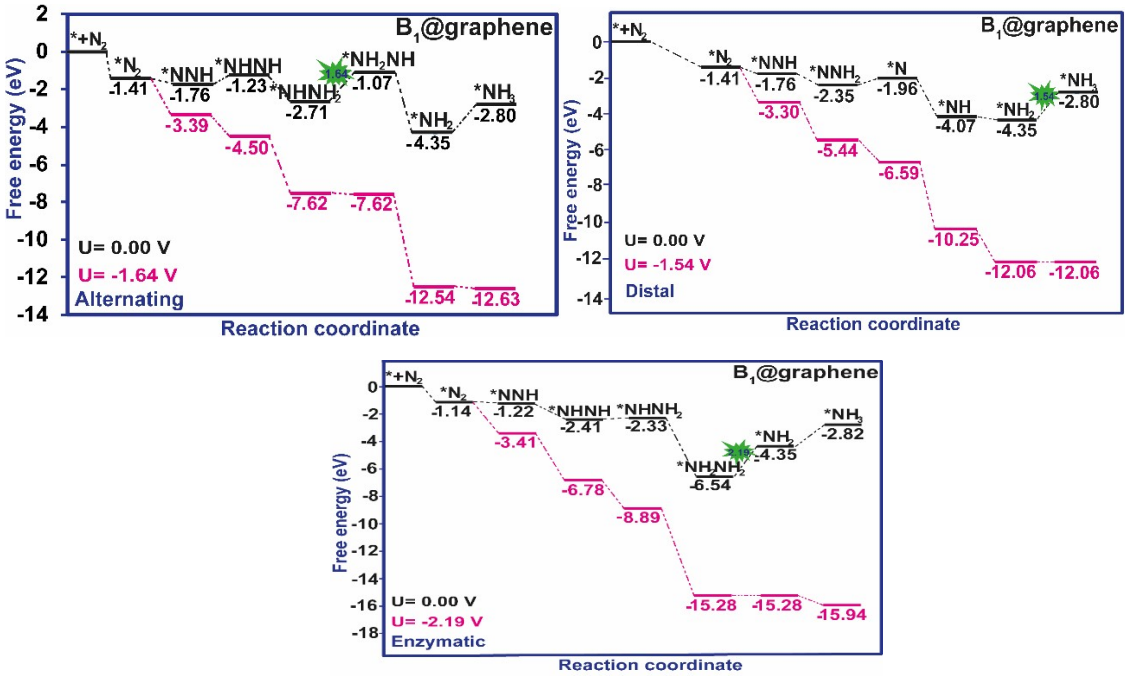
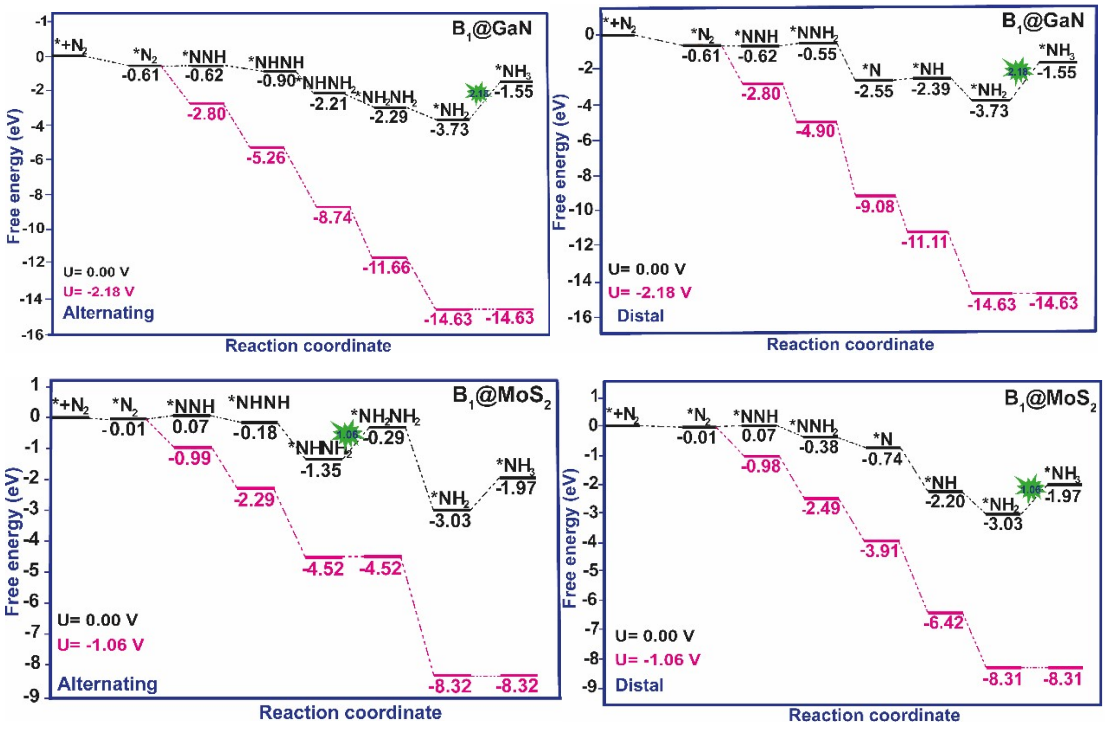


Fig. S1. *Free energy profile for NRR on B_1@graphene along alternating, distal and enzymatic pathways.*



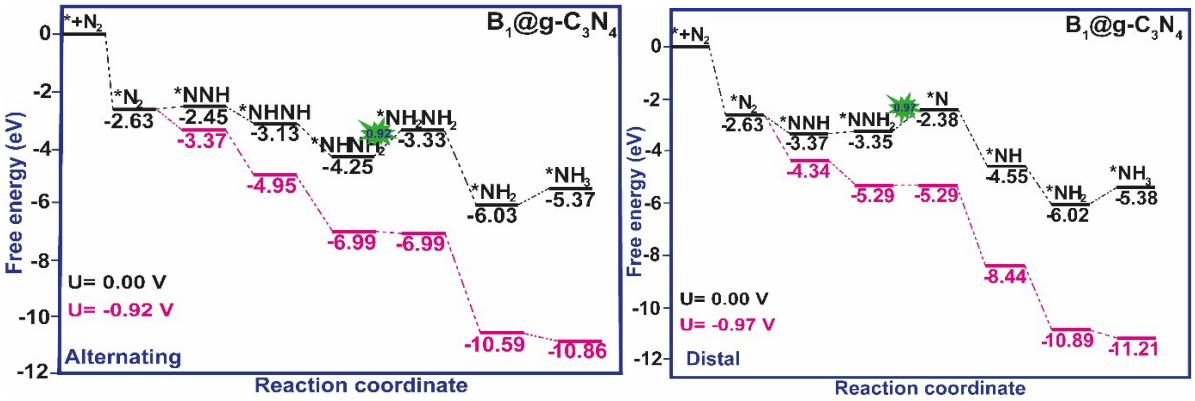


Fig. S2. *Free energy profile for NRR on B_1@GaN, B_1@MoS_2, and B_1@g-C_3N_4 along alternating and distal pathways.*

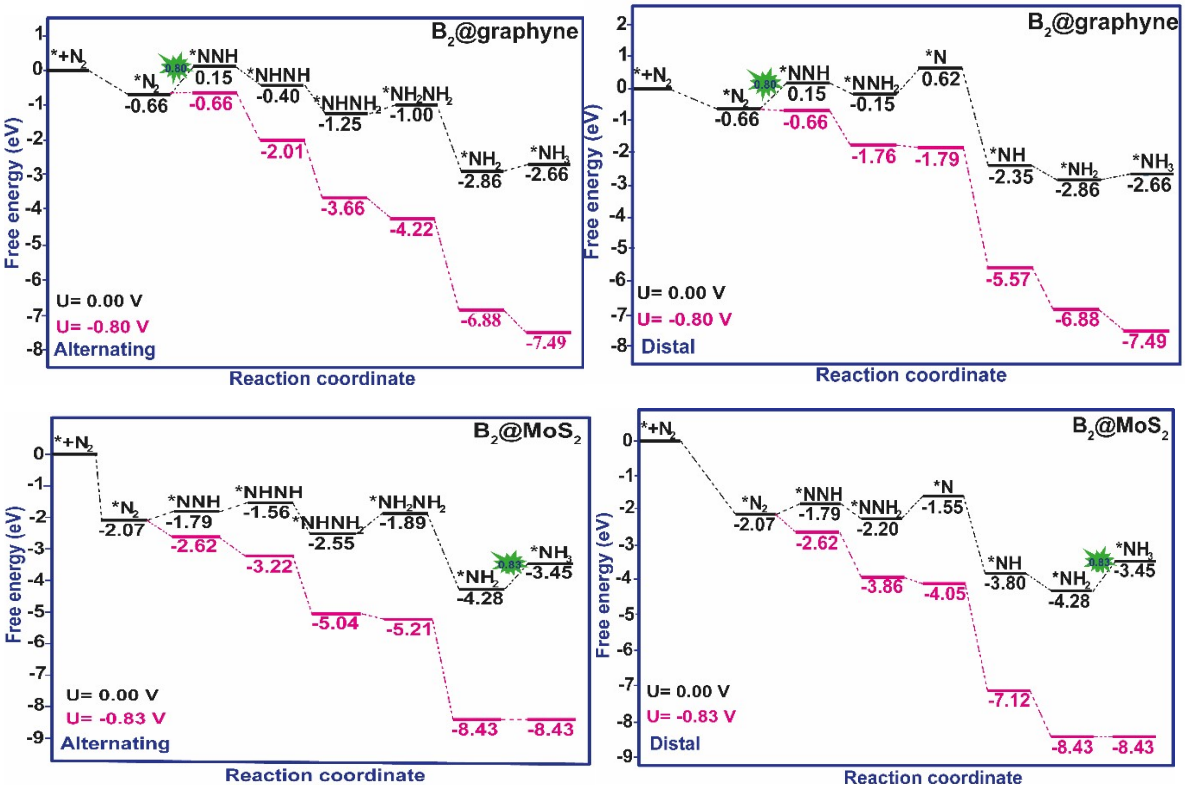
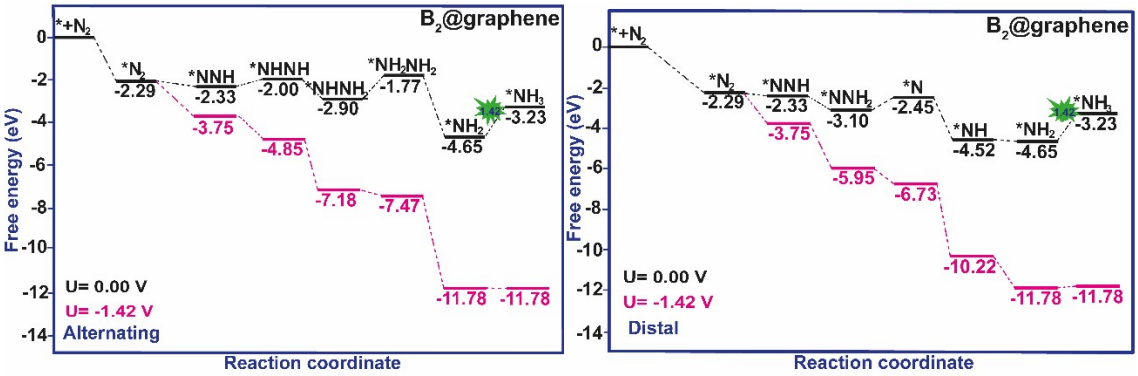


Fig. S3. *Free energy profile for NRR on B_2@graphyne and $B_{2@}MoS_2$ catalysts along alternating and distal pathways.*



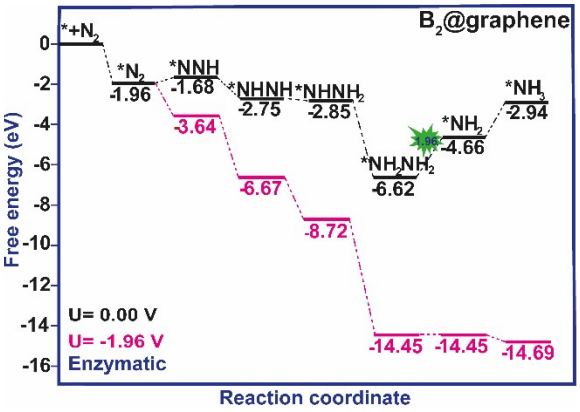


Fig. S4. *Free energy profile for NRR on B_2@graphene catalyst along alternating, distal and enzymatic pathways.*

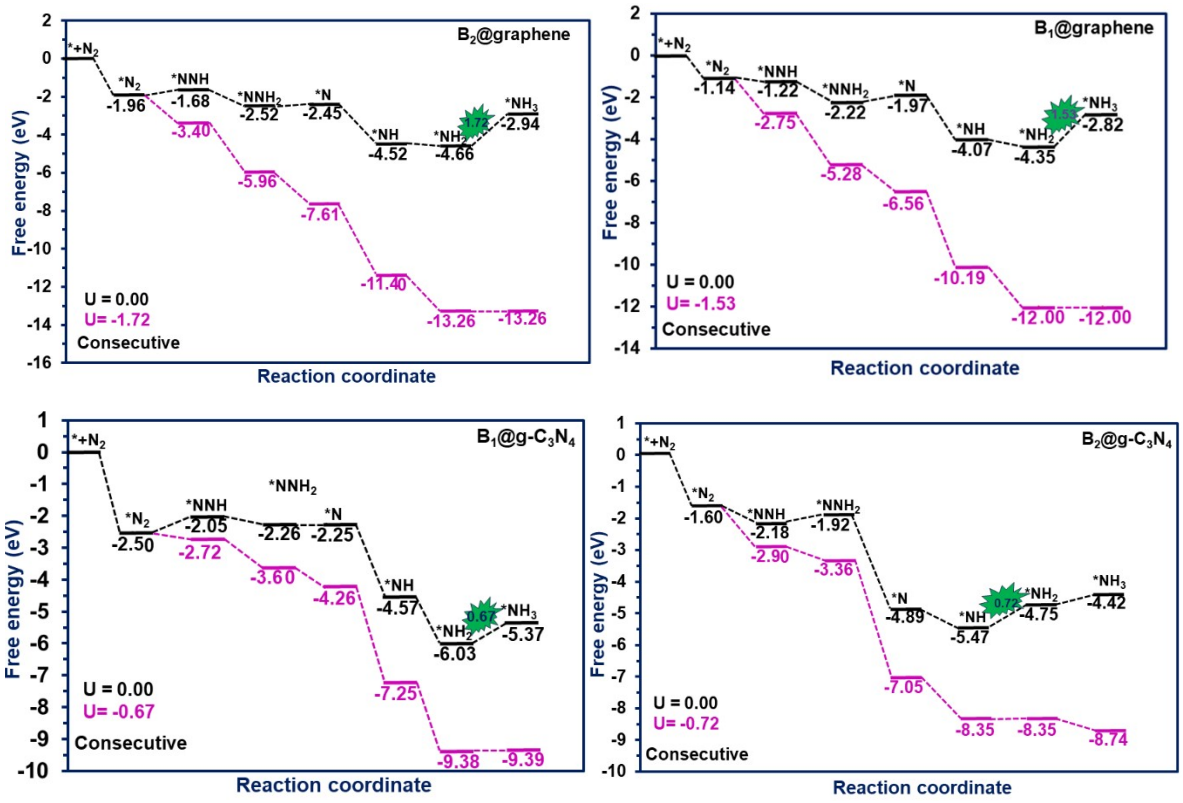


Fig. S5. *Free energy profile for NRR on B_1@graphene, B_2@graphene, B_1@g-C_3N_4 and B_2@g-C_3N_4 catalyst along Consecutive pathway.*

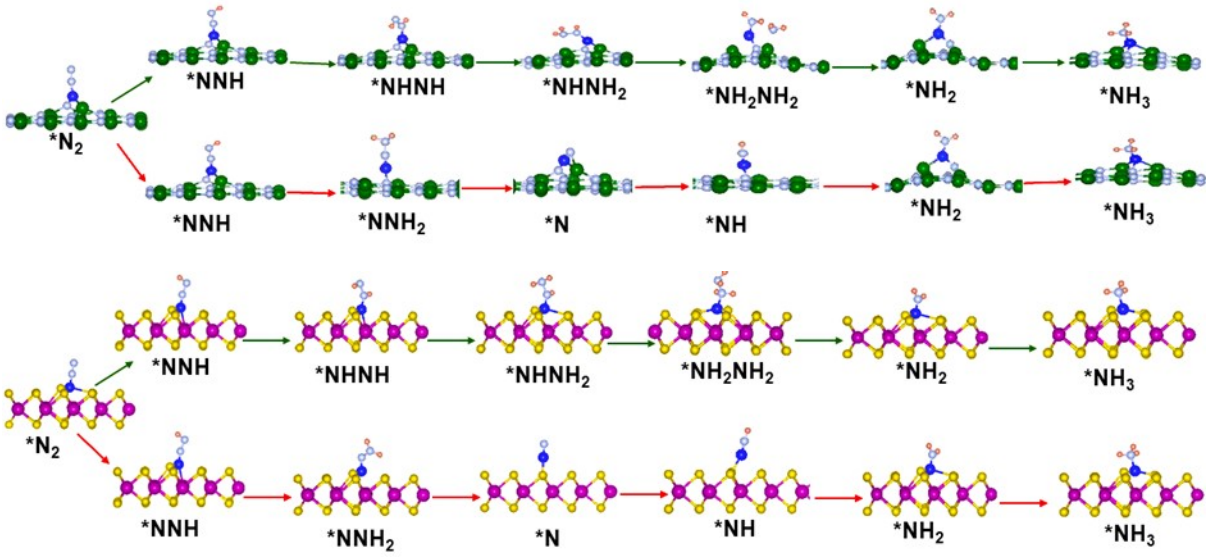


Fig. S6. *Truncated side views of the optimized NRR intermediates on B_1@GaN and B_1@MoS_2 catalysts along alternating and distal pathways. Green and red coloured arrows indicate alternating and distal pathway respectively.*

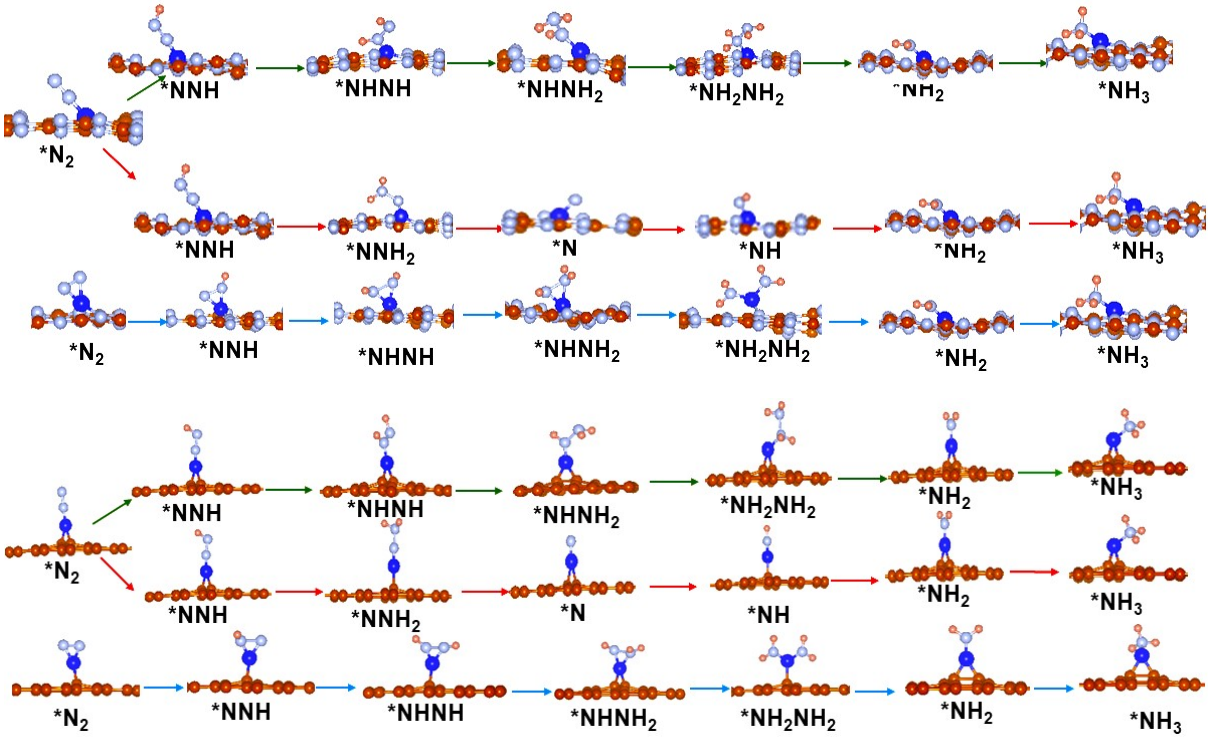


Fig. S7. *Truncated side views of the optimized NRR intermediates on B_1@g-C_3N_4 and B_1@graphene catalysts along alternating, distal and enzymatic pathways. Green, red and cyan coloured arrows indicate alternating, distal and enzymatic pathway respectively.*

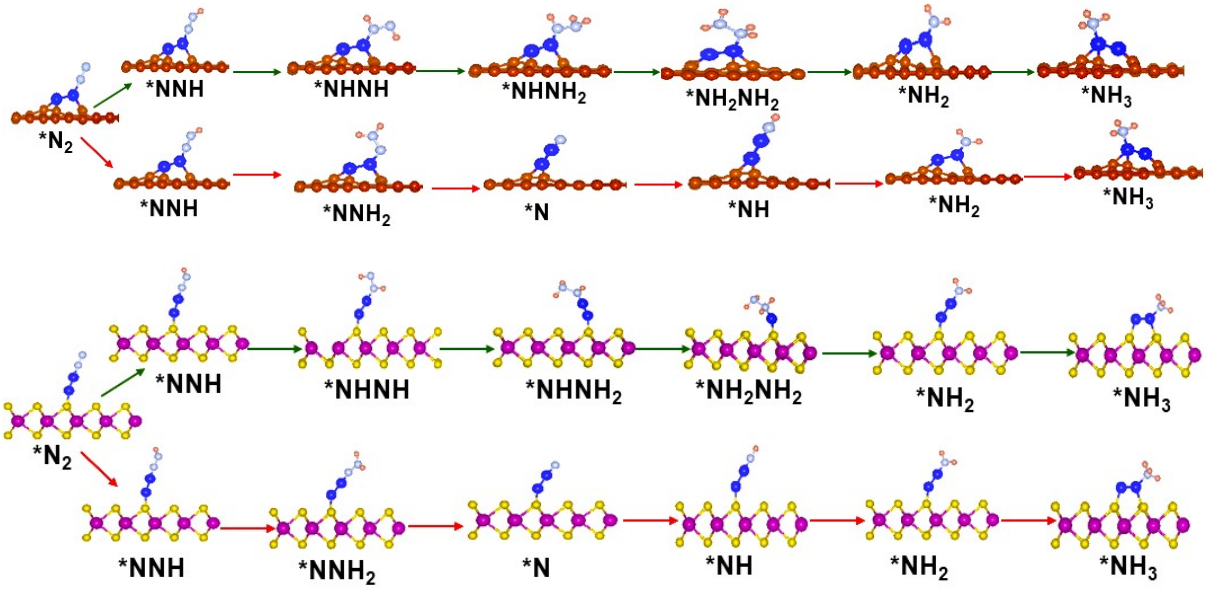


Fig. S8. *Truncated side views of the optimized NRR intermediates on B_2@graphyne and B_2@MoS_2 catalyst s along alternating and distal pathways. Green and red coloured arrows indicate alternating and distal pathway respectively.*

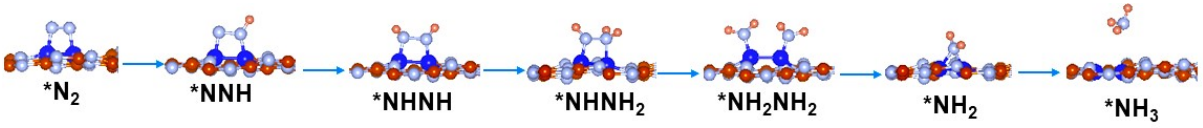


Fig. S9. *Truncated side views of the optimized NRR intermediates on B_2@g-C_3N_4 catalyst along enzymatic pathway. Cyan coloured arrow indicates enzymatic pathway.*

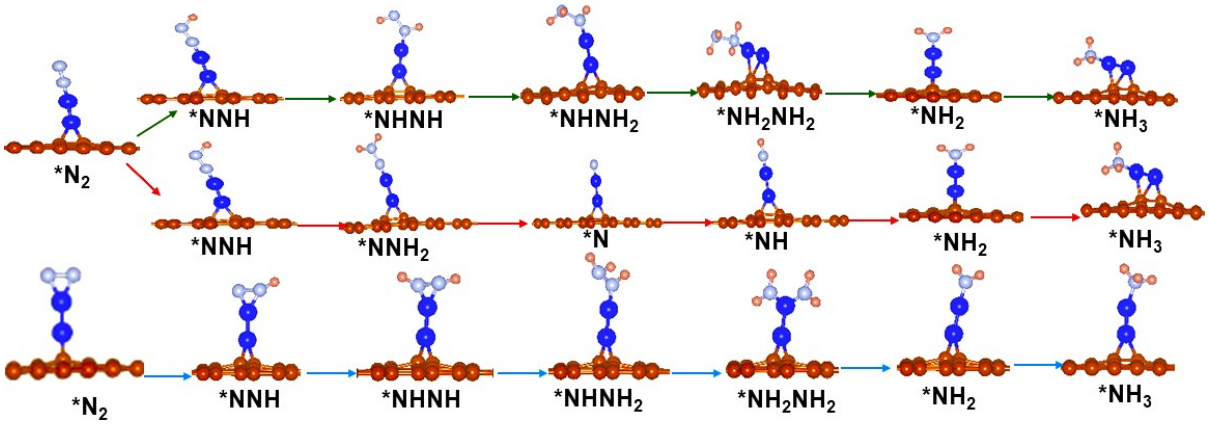


Fig. S10. *Truncated side views of the optimized NRR intermediates on B_2@graphene catalyst along alternating, distal and enzymatic pathways**.** Green, red and cyan coloured arrows indicate alternating, distal, and enzymatic pathway respectively.*

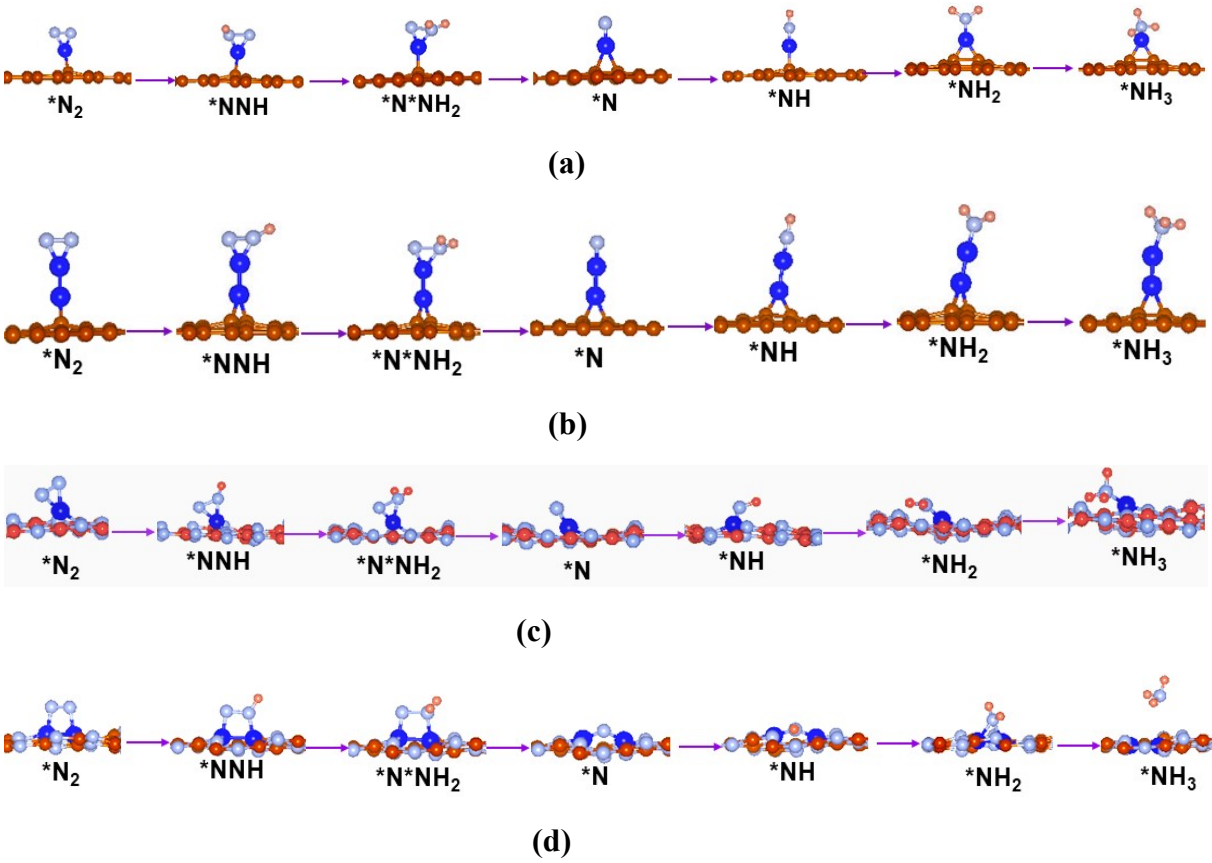


Fig. S11. *Truncated side views of the optimized NRR intermediates on (a)B_1@graphene (b) B_2@graphene (c) B_1@g-C_3N_4 and (d) B_2@ g-C_3N_4 catalysts along consecutive pathway.*

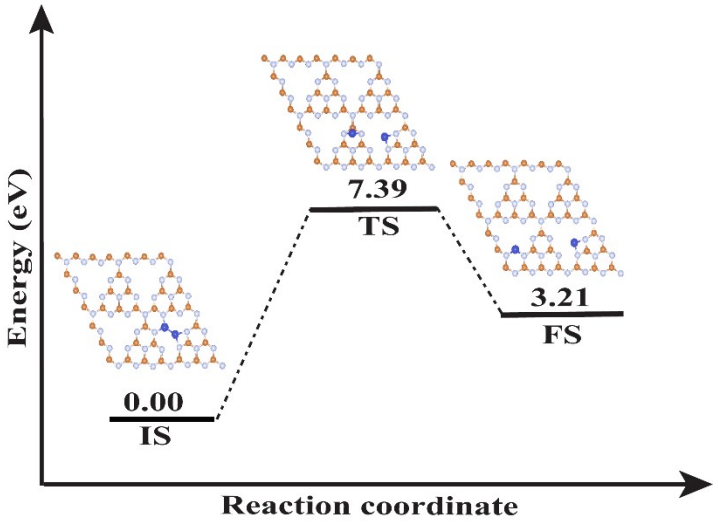


Fig. S12. *Dissociation barrier for the double boron atom catalysts supported on the g-C_3N_4 monolayer as obtained from nudged elastic band calculations.*

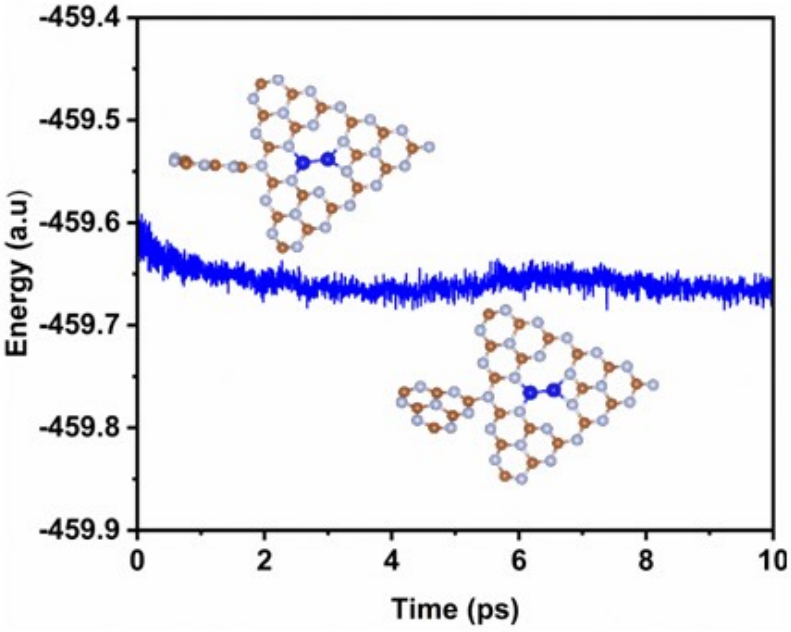


Fig. S13. *Variations of energy versus the AIMD simulation time for B_2@g-C_3N_4 at 350 K.*

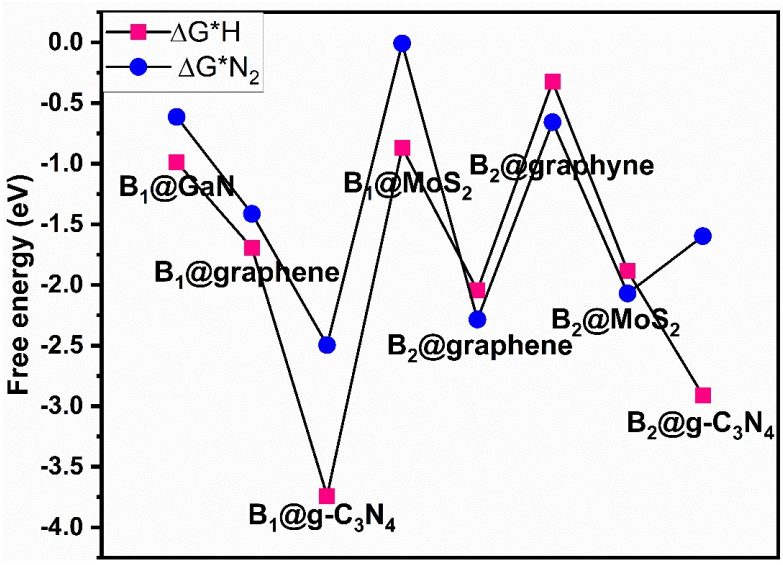


Fig. S14*. Calculated adsorption free energies of N_2 molecule and H atom on the single and double boron atom adsorbed on GaN, graphene, g-C_3N_4, MoS_2 and graphyne supports.*

Table S1. Energy, ZPE, TS, G and ΔG of reaction steps of NRR on B_1@GaN and B_1@MoS_2 along alternating and distal pathway.

Alternating NRR pathway on B_1@GaN

Reaction step	**Energy**	**ZPE**	**TS**	**G**	**ΔG**
*N_2	-310.65	0.21	0.15	-310.59	-0.61
*NNH	-314.24	0.52	0.16	-313.88	-0.62
C*NHNH	-318.13	0.84	0.16	-317.44	-0.90
*$NHNH_2$	-323.10	1.20	0.13	-322.03	-2.21
*NH_2NH_2	-327.25	1.37	0.17	-326.05	-2.94
*NH_2	-311.97	0.73	0.09	-311.33	-3.73
*NH_3	-313.37	1.05	0.11	-312.43	-1.55

Distal NRR pathway on B_1@GaN

Reaction step	**Energy**	**ZPE**	**TS**	**G**	**ΔG**
*N_2	-310.65	0.21	0.15	-310.59	-0.61
*NNH	-314.24	0.52	0.16	-313.88	-0.62
*NNH_2	-317.76	0.83	0.16	-317.09	-0.55
*N	-303.65	0.12	0.03	-303.57	-2.55
*NH	-306.95	0.37	0.12	-306.70	-2.39
*NH_2	-311.97	0.73	0.09	-311.33	-3.73
*NH_3	-313.37	1.05	0.11	-312.43	-1.55

Alternating pathway on B_1@MoS_2

Reaction	**Energy**	**ZPE**	**TS**	**G**	**ΔG**

step					
*N_2	-579.91	0.22	0.13	-579.82	-0.01
*NNH	-583.41	0.52	0.14	-583.03	0.07
*NHNH	-587.28	0.85	0.14	-586.56	-0.18
*$NHNH_2$	-592.06	1.18	0.18	-591.01	-1.35
*NH_2NH_2	-594.60	1.53	0.17	-593.24	-0.29
*NH_2	-581.12	0.74	0.07	-580.46	-3.03
*NH_3	-583.69	1.09	0.09	-582.69	-1.97

Distal pathway on B_1@MoS_2

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-579.91	0.22	0.13	-579.82	-0.01
*NNH	-583.41	0.52	0.14	-583.03	0.07
*NNH_2	-587.23	0.57	0.09	-586.76	-0.38
*N	-571.60	0.08	0.09	-571.60	-0.74
*NH	-576.62	0.28	0.002	-576.35	-2.20
*NH_2	-581.12	0.74	0.07	-580.46	-3.02
*NH_3	-583.69	1.09	0.09	-582.69	-1.97

Table S2. Energy, ZPE, TS, G and ΔG of reaction steps of NRR on B_1@graphene and B_1@g-C_3N_4 along alternating, distal and enzymatic pathway.

Alternating NRR pathway on B_1@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-483.26	0.21	0.15	-483.20	-1.41
*NNH	-487.19	0.52	0.15	-486.82	-1.76
*NHNH	-490.23	0.82	0.17	-489.58	-1.23
*$NHNH_2$	-495.31	1.18	0.21	-494.34	-2.71
*NH_2NH_2	-497.36	1.51	0.14	-495.99	-1.07
*NH_2	-484.39	0.73	0.09	-483.75	-4.35
*NH_3	-486.46	1.07	0.10	-485.49	-2.80

Distal Pathway on B_1@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-483.26	0.21	0.15	-483.20	-1.41
*NNH	-487.19	0.52	0.15	-486.82	-1.76
*NNH_2	-491.36	0.80	0.15	-490.70	-2.35
*N	-474.79	0.08	0.09	-474.79	-1.96
*NH	-480.48	0.38	0.10	-480.19	-4.07
*NH_2	-484.39	0.73	0.09	-483.75	-4.35
*NH_3	-486.46	1.07	0.10	-485.49	-2.80

Enzymatic pathway on B_1@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-482.99	0.20	0.13	-482.92	-1.14
*NNH	-486.61	0.47	0.15	-486.29	-1.22
*NHNH	-491.40	0.81	0.16	-490.76	-2.41
*$NHNH_2$	-495.01	1.18	0.14	-493.97	-2.33
*NH_2NH_2	-502.73	1.45	0.18	-501.46	-6.54
*NH_2	-484.40	0.73	0.09	-483.75	-4.35
*NH_3	-486.46	1.06	0.11	-485.50	-2.82

Alternating pathway on B_1@g-C_3N_4

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-497.56	0.23	0.11	-497.44	-2.63
*NNH	-500.92	0.51	0.13	-500.54	-2.45
*NHNH	-505.25	0.86	0.11	-504.50	-3.13
*$NHNH_2$	-509.99	1.20	0.12	-508.91	-4.25
*NH_2NH_2	-512.68	1.52	0.12	-511.28	-3.33
*NH_2	-499.14	0.74	0.06	-498.45	-6.03
*NH_3	-502.06	1.04	0.06	-501.08	-5.38

Distal pathway on B_1@g-C_3N_4

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-497.56	0.23	0.11	-497.44	-2.63
*NNH	-500.92	0.51	0.13	-500.54	-2.45
*NNH_2	-505.44	0.85	0.13	-504.72	-3.35
*N	-488.26	0.084	0.06	-488.23	-2.38
*NH	-494.03	0.39	0.06	-493.69	-4.55
*NH_2	-499.14	0.75	0.06	-498.45	-6.03
*NH_3	-502.06	1.04	0.06	-501.08	-5.38

Enzymatic pathway on B_1@g-C_3N_4

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-497.42	0.21	0.10	-497.30	-2.50
*NNH	-500.50	0.48	0.12	-500.14	-2.05
*NHNH	-505.41	0.85	0.10	-504.66	-3.29
*$NHNH_2$	-509.24	1.19	0.11	-508.17	-3.51
*NH_2NH_2	-515.37	1.46	0.15	-514.06	-6.12
*NH_2	-499.14	0.74	0.06	-498.45	-6.03
*NH_3	-502.05	1.04	0.06	-501.08	-5.37

Table S3. Energy, ZPE, TS, G and ΔG of reaction steps of NRR on B_2@MoS_2 and B_2@graphyne along alternating, and distal pathway.

Alternating pathway on B_2@MoS_2

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-585.48	0.22	0.151758	-585.41	-2.07
*NNH	-588.72	0.49	0.183362	-588.41	-1.79
*NHNH	-592.13	0.85	0.18366	-591.47	-1.56
*$NHNH_2$	-596.68	1.16	0.215264	-595.74	-2.55
*NH_2NH_2	-599.70	1.53	0.196183	-598.37	-1.89
*NH_2	-585.79	0.69	0.145497	-585.24	-4.28
*NH_3	-588.65	1.07	0.121049	-587.70	-3.45

Distal pathway on B_2@MoS_2

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-585.48	0.22	0.15	-585.41	-2.07
*NNH	-588.72	0.49	0.18	-588.41	-1.79
*NNH_2	-592.80	0.83	0.14	-592.11	-2.20
*N	-575.93	0.08	0.10	-575.95	-1.55
*NH	-581.75	0.38	0.10	-581.48	-3.80
*NH_2	-585.79	0.69	0.15	-585.24	-4.28
*NH_3	-588.65	1.07	0.12	-587.70	-3.45

Alternating pathway on B_2@graphyne

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-442.16	0.23	0.14	-442.07	-0.66
*NNH	-444.91	0.52	0.15	-444.55	0.15
*NHNH	-449.12	0.88	0.14	-448.38	-0.40
*$NHNH_2$	-453.51	1.18	0.18	-452.52	-1.25
*NH_2NH_2	-456.88	1.53	0.20	-455.55	-1.00
*NH_2	-442.56	0.74	0.08	-441.89	-2.86
*NH_3	-445.94	1.07	0.15	-444.98	-2.67

Distal pathway on B_2@graphyne

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-442.16	0.23	0.14	-442.07	-0.66
*NNH	-444.91	0.52	0.15	-444.55	0.15
*NNH_2	-449.13	0.85	0.14	-448.13	-0.15
*N	-432.01	0.08	0.08	-431.85	0.62
*NH	-438.58	0.38	0.10	-438.10	-2.35
*NH_2	-442.56	0.74	0.08	-441.89	-2.86
*NH_3	-445.94	1.07	0.11	-444.98	-2.67

Table S4. Energy, ZPE, TS, G and ΔG of reaction steps of NRR on B_2@g-C_3N_4 along Enzymatic pathway**.**

Enzymatic pathway on B_2@g-C_3N_4

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-504.25	0.22	0.07	-504.11	-1.60
*NNH	-508.43	0.54	0.08	-507.97	-2.18
*NHNH	-512.90	0.86	0.08	-512.12	-3.04
*$NHNH_2$	-516.59	1.21	0.10	-515.48	-3.12
*NH_2NH_2	-522.07	1.45	0.14	-520.75	-5.11
*NH_2	-505.59	0.75	0.05	-504.88	-4.75
*NH_3	-508.51	0.95	0.27	-507.83	-4.42

Table S5. Energy, ZPE, TS, G and ΔG of reaction steps of NRR on B_2@graphene along alternating, distal and enzymatic pathway.

Alternating pathway on B_2@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-488.76	0.22	0.09	-488.63	-2.29
*NNH	-492.28	0.50	0.17	-491.95	-2.32
*NHNH	-495.58	0.84	0.18	-494.91	-2.00
*$NHNH_2$	-500.06	1.16	0.21	-499.10	-2.90
*NH_2NH_2	-502.57	1.51	0.19	-501.25	-1.76
*NH_2	-489.20	0.68	0.10	-488.62	-4.65
*NH_3	-491.45	1.07	0.10	-490.48	-3.23

Distal pathway on B_2@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-488.76	0.22	0.09	-488.63	-2.29
*NNH	-492.28	0.50	0.17	-491.95	-2.32
*NNH_2	-496.68	0.85	0.18	-496.01	-3.10
*N	-479.81	0.08	0.11	-479.85	-2.45
*NH	-485.49	0.38	0.09	-485.20	-4.52
*NH_2	-489.20	0.68	0.10	-488.62	-4.65
*NH_3	-491.45	1.07	0.10	-490.48	-3.23

Enzymatic pathway on B_2@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-488.36	0.20	0.14	-488.31	-1.96
*NNH	-491.63	0.48	0.15	-491.31	-1.68
*NHNH	-496.33	0.82	0.15	-495.68	-2.75
*$NHNH_2$	-499.91	1.16	0.20	-499.05	-2.85
*NH_2NH_2	-507.35	1.44	0.19	-506.10	-6.62
*NH_2	-489.21	0.70	0.12	-488.63	-4.66
*NH_3	-491.10	1.05	0.14	-490.19	-2.94

Table S6. Energy, ZPE, TS, G and ΔG of reaction steps of NRR on B_1@graphene, B2@graphene, B1@g-C3N4 and B2@g-C3N4 catalysts along consecutive pathway.

Consecutive pathway on B_1@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-482.99	0.20	0.13	-482.92	-1.14
*NNH	-486.61	0.47	0.15	-486.29	-1.22
*NNH_2	-491.28	0.85	0.15	-490.57	-2.22
*N	-474.80	0.08	0.09	-474.81	-1.97
*NH	-480.47	0.38	0.10	-480.18	-4.07
*NH_2	-484.40	0.73	0.09	-483.75	-4.35
*NH_3	-486.46	1.06	0.11	-485.50	-2.82

Consecutive pathway on B_2@graphene

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-488.36	0.20	0.14	-488.31	-1.96
*NNH	-491.63	0.48	0.15	-491.31	-1.68
*NNH_2	-496.12	0.85	0.16	-495.43	-2.52
*N	-479.82	0.08	0.11	-479.85	-2.45
*NH	-485.49	0.38	0.09	-485.20	-4.52
*NH_2	-489.21	0.70	0.12	-488.63	-4.66
*NH_3	-491.10	1.05	0.14	-490.19	-2.94

Consecutive pathway on B_1@g-C_3N_4

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-497.42	0.21	0.10	-497.30	-2.50
*NNH	-500.50	0.48	0.12	-500.14	-2.05
*NNH_2	-504.37	0.84	0.11	-503.64	-2.26
*N	-488.12	0.08	0.07	-488.11	-2.25
*NH	-494.05	0.40	0.06	-493.71	-4.57
*NH_2	-499.14	0.74	0.06	-498.45	-6.03
*NH_3	-502.05	1.04	0.06	-501.08	-5.37

Consecutive pathway on B_2@g-C_3N_4

Reaction step	Energy	ZPE	TS	G	ΔG
*N_2	-504.25	0.22	0.07	-504.11	-1.60
*NNH	-508.43	0.54	0.08	-507.97	-2.18
*NNH_2	-511.78	0.87	0.09	-511.00	-1.92
*N	-498.57	0.14	0.02	-498.45	-4.89
*NH	-502.75	0.45	0.02	-502.32	-5.47
*NH_2	-505.59	0.75	0.05	-504.88	-4.75
*NH_3	-508.51	0.95	0.27	-507.83	-4.42