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Electronic supplementary information

Highly stable Mo-doped Fe_2P and Fe_3P monolayers as low-onset-potential electrocatalysts for nitrogen fixation

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Table S1 Convergence test

		Fe_2P	Fe_3P
k point (Orbital cutoff: 5.0 Å)	5 x 5	-1.41	-1.69
	6 x 6	-1.42	-1.67
	7 x 7	-1.42	-1.69
Orbital cutoff (*k* point: 6 x 6)	4.8	-1.47	-1.63
	5.0	-1.42	-1.67
	5.2	-1.44	-1.62

Table S2 The average energy difference (in eV per atom) between FM and AFM states.

	E_{AFM1} - E_{FM}	E_{AFM2} - E_{FM}	E_{AFM3} - E_{FM}
Fe_2P	0.015	0.017	0.018
Fe_3P	0.041	0.041	0.052

Table S3 Calculated vibrational frequencies, zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on Fe_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	Vibrational Frequencies (cm^{-1})					E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*N≡N	80.70	84.21	386.62	386.98	440.45	0.2157	0.1358	0.001
	2092.05							
*N=NH	56.15	81.46	247.63	323.61	391.20	0.4744	0.1693	0.003
	546.92	1047.21	1672.06	3266.77				
*N-NH_2	102.79	184.25	337.23	435.72	457.81	0.8434	0.1264	0.004
	494.25	563.50	1213.26	1219.12	1569.86			
	3427.97	3564.05						
*N-NH_3	151.08	160.57	169.07	437.05	484.69	1.2289	0.1308	0.006
	495.54	925.58	1086.52	1104.27	1455.87			
	1568.81	1569.54	3314.24	3418.42	3430.05			
*N	403.06	416.98	651.39			0.0915	0.0287	0.001
*NH	428.72	430.76	661.03	662.82	684.45	0.3925	0.0355	0.002
	3446.86							
*NH_2	184.56	362.16	544.99	583.84	608.84	0.7005	0.0673	0.004
	672.21	1500.06	3367.13	3446.28				
*NH_3	144.94	153.92	155.00	441.99	580.65	1.0483	0.1254	0.005
	639.62	1206.87	1578.96	1583.25	3384.91			
	3495.91	3499.18						
*NH=NH	292.79	295.16	332.20	514.86	517.16	0.8606	0.0794	0.004
	665.25	719.67	1055.83	1203.95	1368.13			
	3433.09	3447.56						
*NH-NH_2	234.91	277.49	403.49	473.88	558.48	1.2221	0.0839	0.006
	658.93	743.00	871.42	1093.04	1207.76			
	1323.37	1575.08	3373.75	3404.25	3462.38			
*NH_2-NH_2	117.61	153.57	234.08	431.12	484.10	1.5564	0.1386	0.008
	494.92	548.22	852.28	1140.86	1151.44			
	1168.74	1351.56	1549.62	1610.90	3390.36			
	3407.79	3469.80	3482.81					
*N≡*N	98.98	173.78	295.87	343.39	442.19	0.1936	0.1204	0.001
	1760.07							
*N=*NH	97.18	227.54	284.49	480.47	519.53	0.4997	0.1134	0.003
	576.70	1259.14	1271.00	3224.13				
*NH=*NH	297.03	297.23	330.82	514.62	525.27	0.8577	0.0788	0.004
	672.04	715.31	1027.36	1221.89	1348.69			
	3417.36	3430.78						
*NH=NH_2	236.99	276.05	389.19	467.15	556.46	1.2177	0.0856	0.006
	649.61	706.43	858.40	1087.62	1211.85			
	1316.61	1581.61	3380.59	3406.21	3466.66			
NH_2=NH_2	149.72	161.85	234.90	427.48	489.68	1.5656	0.1285	0.008
	561.49	583.77	844.36	1140.35	1151.90			
	1184.02	1346.83	1561.98	1591.13	3396.03			
	3404.58	3473.59	3484.38					

Table S4 Calculated vibrational frequencies, zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on Fe_3P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	Vibrational Frequencies (cm^{-1})					E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*N≡N	80.99	110.83	381.91	446.10	458.91	0.2231	0.1256	0.001
	2110.11							
*N=NH	70.77	104.93	286.25	422.56	454.58	0.4935	0.1449	0.003
	582.76	1029.88	1715.12	3273.27				
*N-NH_2	89.70	96.87	233.92	269.96	513.44	0.8079	0.1594	0.004
	564.01	571.40	1180.68	1352.54	1541.27			
	3121.51	3461.92						
*N-NH_3	147.95	166.37	182.55	285.67	436.22	1.1772	0.1410	0.006
	464.91	826.92	1060.60	1092.47	1434.77			
	1549.98	1561.27	2942.87	3361.11	3425.54			
*N	188.50	223.77	1036.10			0.0900	0.0549	0.001
*NH	171.02	352.11	396.32	690.64	719.41	0.3544	0.0665	0.002
	3372.12							
*NH_2	167.21	336.00	525.33	598.34	672.11	0.7108	0.0070	0.004
	679.20	1487.70	3433.19	3536.74				
*NH_3	9.65	84.80	102.82	363.88	565.05	1.0258	0.2244	0.005
	608.59	1202.41	1573.87	1580.36	3391.43			
	3507.66	3512.72						
*NH=NH	141.44	264.68	329.02	400.97	488.30	0.8421	0.1065	0.004
	551.62	706.28	1204.45	1284.85	1390.13			
	3382.98	3403.86						
*NH-NH_2	108.91	173.00	207.63	365.56	443.06	1.1791	0.1396	0.006
	597.40	648.13	863.81	1042.83	1150.10			
	1393.16	1594.89	3419.56	3437.73	3523.82			
*NH_2-NH_2	54.30	107.58	176.52	321.78	343.76	1.5367	0.1861	0.008
	470.38	556.95	909.68	1127.70	1156.13			
	1163.35	1378.58	1560.38	1589.09	3400.06			
	3412.94	3488.55	3505.03					

Table S5 Calculated vibrational frequencies, zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on Mo-doped Fe_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	Vibrational Frequencies (cm^{-1})					E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*N≡N	66.86	82.86	379.76	401.57	449.42	0.2152	0.1402	0.001
	2081.11							
*N=NH	195.56	260.40	321.55	466.72	528.30	0.5008	0.0904	0.003
	612.62	1053.13	1266.79	3351.93				
*N-NH_2	176.19	255.13	351.98	480.03	505.74	0.8659	0.0944	0.005
	601.04	852.92	1063.23	1183.49	1548.58			
	3401.96	3511.06						
*N-NH_3	16.57	107.97	115.31	387.29	427.67	1.1232	0.2267	0.006
	454.64	582.20	594.70	623.07	1203.65			
	1565.77	1585.69	3389.96	3503.42	3513.07			
*N	370.66	410.01	608.67			0.0864	0.0314	0.001
*NH	386.25	410.69	631.26	647.30	705.42	0.3871	0.0388	0.002
	3447.38							
*NH_2	184.45	364.07	548.09	593.38	624.77	0.7033	0.0663	0.004
	685.95	1503.45	3365.58	3445.69				
*NH_3	140.87	154.65	163.73	438.93	626.44	1.0510	0.1237	0.005
	640.31	1244.26	1582.65	1587.18	3374.57			
	3480.92	3494.75						
*N≡*N	99.10	246.08	267.13	301.09	394.59	0.1852	0.1193	0.001
	1672.33							
*N=*NH	291.35	319.68	402.08	467.50	564.80	0.5241	0.0696	0.003
	723.49	1004.72	1253.72	3405.07				
*NH=*NH	303.77	348.26	421.64	543.56	572.77	0.8512	0.0701	0.004
	624.10	717.82	860.19	1181.60	1317.45			
	3389.88	3413.92						
*NH=NH_2	226.43	282.21	392.03	467.46	569.13	1.2178	0.0853	0.006
	654.18	716.26	863.03	1115.79	1206.09			
	1320.96	1560.76	3359.35	3412.42	3446.77			
NH_2=NH_2	109.53	185.19	238.35	432.38	497.72	1.5627	0.1336	0.008
	518.52	565.54	860.52	1136.48	1164.60			
	1201.51	1356.21	1553.86	1621.25	3377.60			
	3390.32	3457.73	3473.93					

Table S6 Calculated vibrational frequencies, zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on Mo-doped Fe_3P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	Vibrational Frequencies (cm^{-1})					E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*N≡N	55.55	73.92	316.95	353.20	358.14	0.2011	0.1584	0.001
	2077.77							
*N=NH	65.91	85.78	257.81	354.61	374.91	0.4741	0.1624	0.003
	519.91	1142.17	1576.48	3250.29				
*N-NH_2	73.07	78.53	197.53	280.66	364.63	0.8126	0.1861	0.004
	380.60	557.89	1200.77	1393.98	1583.75			
	3417.05	3545.11						
*N-NH_3	78.86	151.87	242.04	285.10	290.33	1.1373	0.1559	0.006
	613.53	891.62	1053.66	1102.36	1427.58			
	1506.11	1550.87	2878.61	2899.57	3325.11			
*N	147.95	207.55	983.61			0.0832	0.0628	0.001
*NH	149.64	159.82	399.23	469.34	881.38	0.3461	0.0914	0.002
	3508.37							
*NH_2	122.90	159.96	252.33	470.41	579.10	0.6696	0.1032	0.004
	638.06	1449.28	3415.36	3523.05				
*NH_3	98.80	111.93	135.76	420.72	627.73	1.0469	0.1547	0.005
	678.45	1259.32	1580.85	1590.35	3401.67			
	3505.37	3522.62						
*NH=NH	62.63	70.74	121.13	260.97	428.12	0.8165	0.1940	0.004
	462.31	990.79	1295.76	1367.31	1497.76			
	3263.03	3315.41						
*NH-NH_2	57.90	102.26	188.36	290.80	308.92	1.1487	0.1861	0.006
	556.73	591.24	718.03	1153.89	1183.35			
	1464.59	1587.13	3359.37	3431.08	3487.99			
*NH_2-NH_2	56.65	99.07	161.41	207.29	340.31	1.5283	0.1980	0.008
	451.35	654.14	903.05	1095.15	1121.95			
	1233.69	1437.85	1591.66	1621.55	3313.91			
	3391.97	3420.57	3485.84					
*N≡*N	131.49	202.54	288.54	324.00	382.75	0.1862	0.1141	0.001
	1667.13							
*N=*NH	139.23	224.80	299.35	482.75	515.53	0.5080	0.1034	0.003
	585.02	1236.60	1330.58	3358.66				
*NH=*NH	137.56	247.26	329.28	447.39	504.47	0.8437	0.1069	0.004
	539.29	688.02	1192.60	1242.71	1394.42			
	3414.20	3436.76						
*NH=NH_2	122.91	206.62	217.41	427.20	449.36	1.1909	0.1275	0.006
	600.50	640.89	920.52	1060.08	1155.62			
	1393.32	1579.92	3410.92	3463.11	3511.43			
NH_2=NH_2	92.08	121.02	171.87	331.59	445.04	1.5496	0.1624	0.008
	523.55	586.56	905.16	1136.47	1143.66			
	1162.14	1359.66	1550.73	1584.23	3407.65			
	3414.99	3490.49	3503.70					

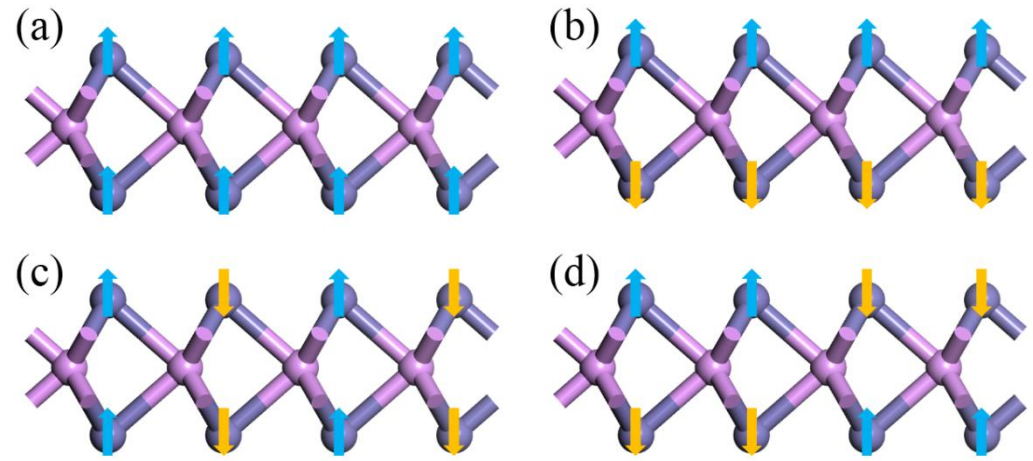

Fig. S1 Side views of four considered magnetic configurations of the Fe_2P monolayer: (a) FM, (b) AFM1, (c) AFM2, and (d) AFM3.

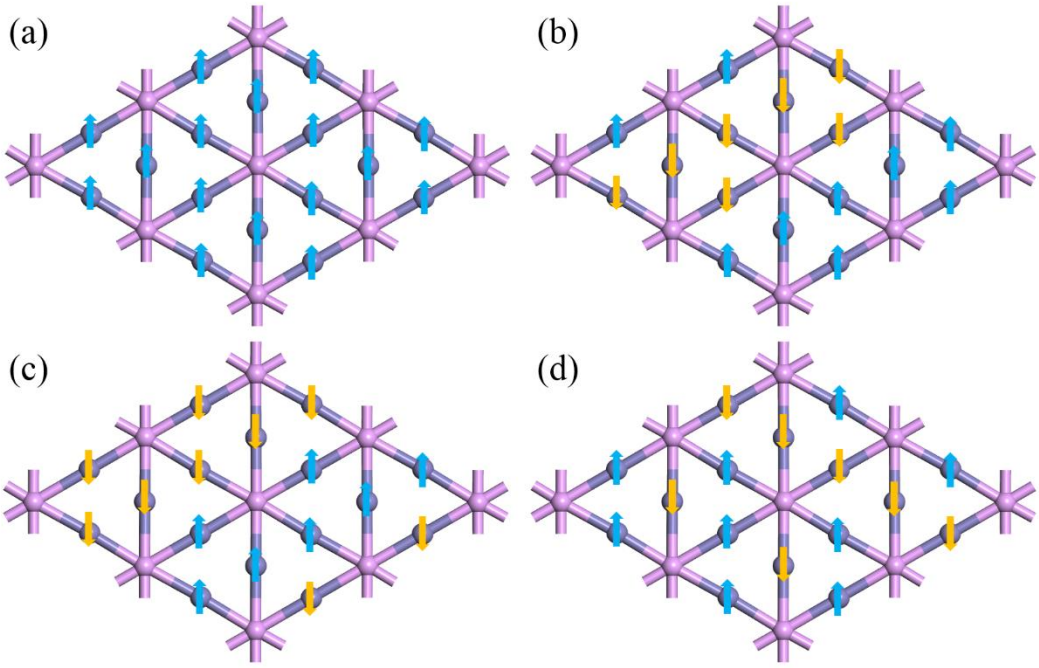

Fig. S2 Top views of four considered magnetic configurations of the Fe_3P monolayer: (a) FM, (b) AFM1, (c) AFM2, and (d) AFM3.

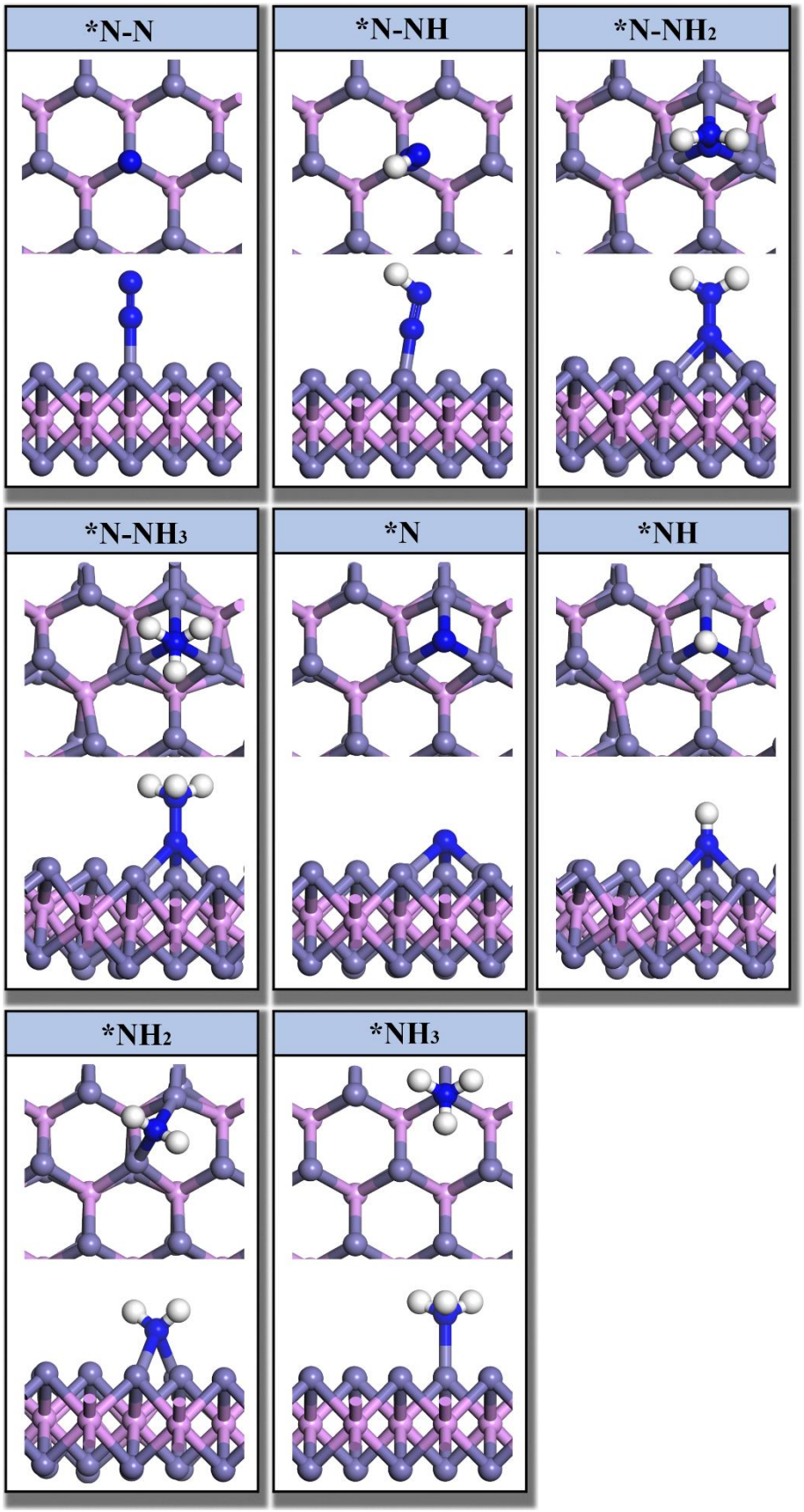

Fig. S3 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_2P monolayer through the distal pathway.

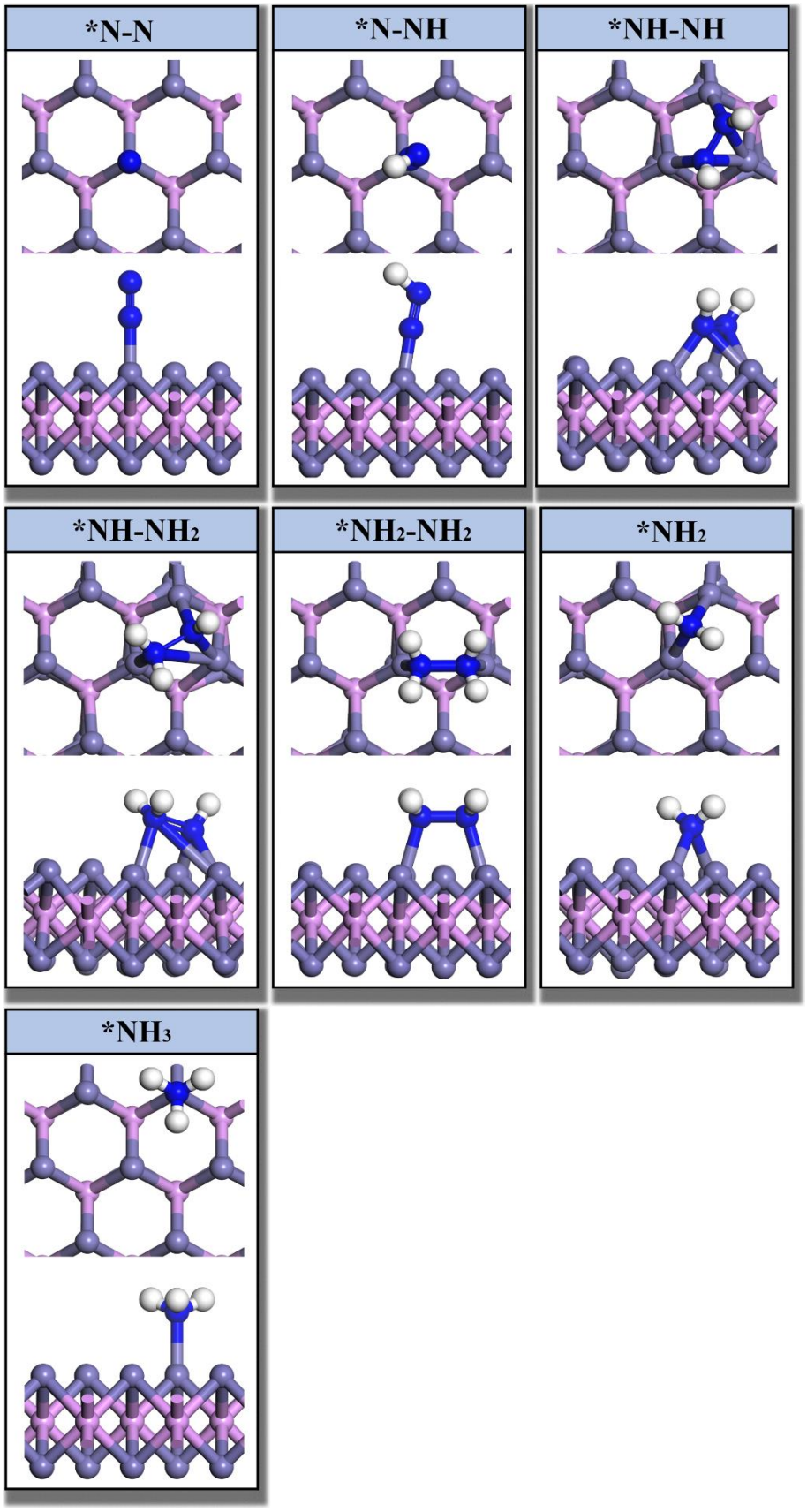

Fig. S4 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_2P monolayer through the alternating pathway.

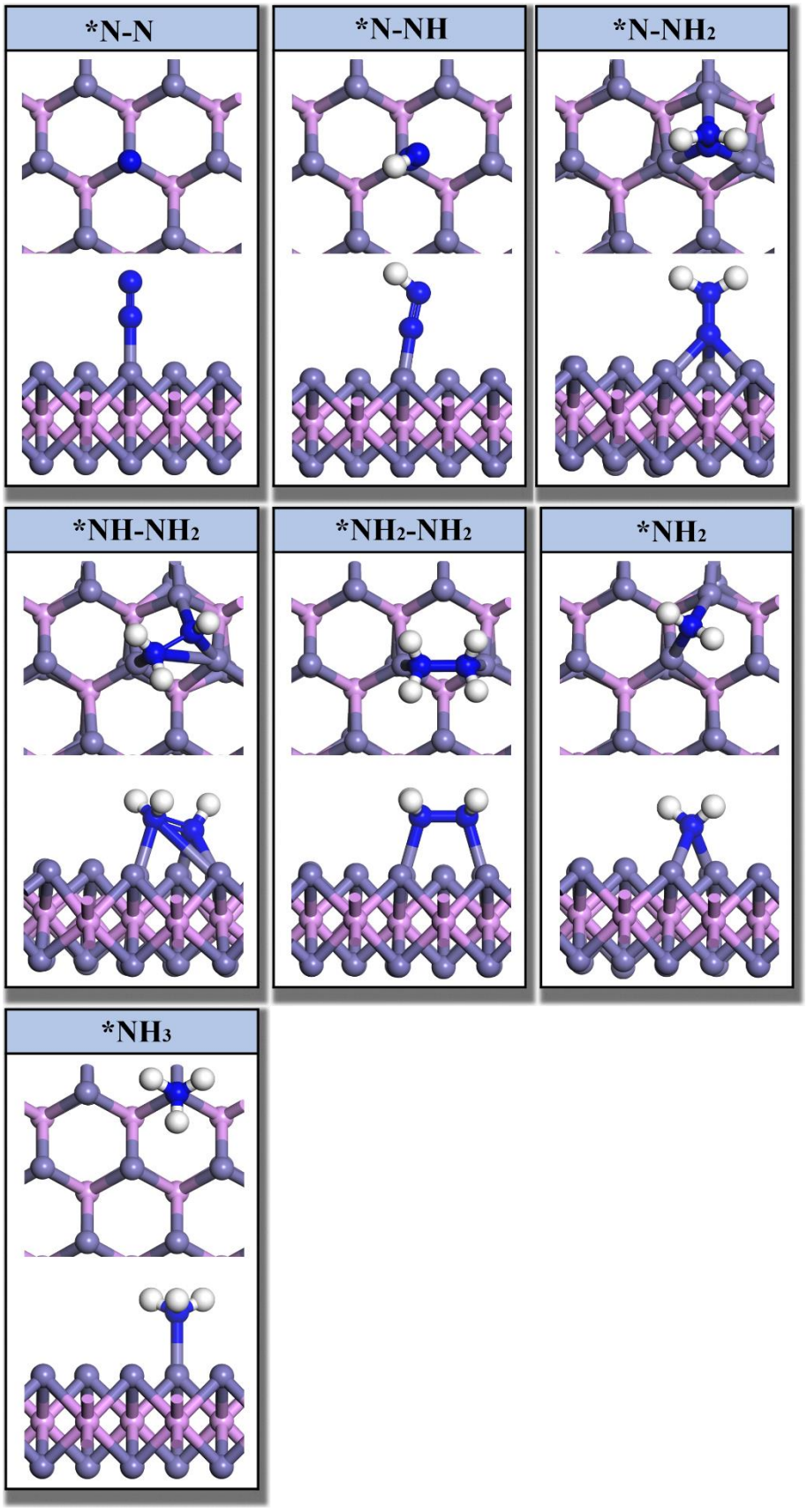

Fig. S5 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_2P monolayer through the mix pathway.

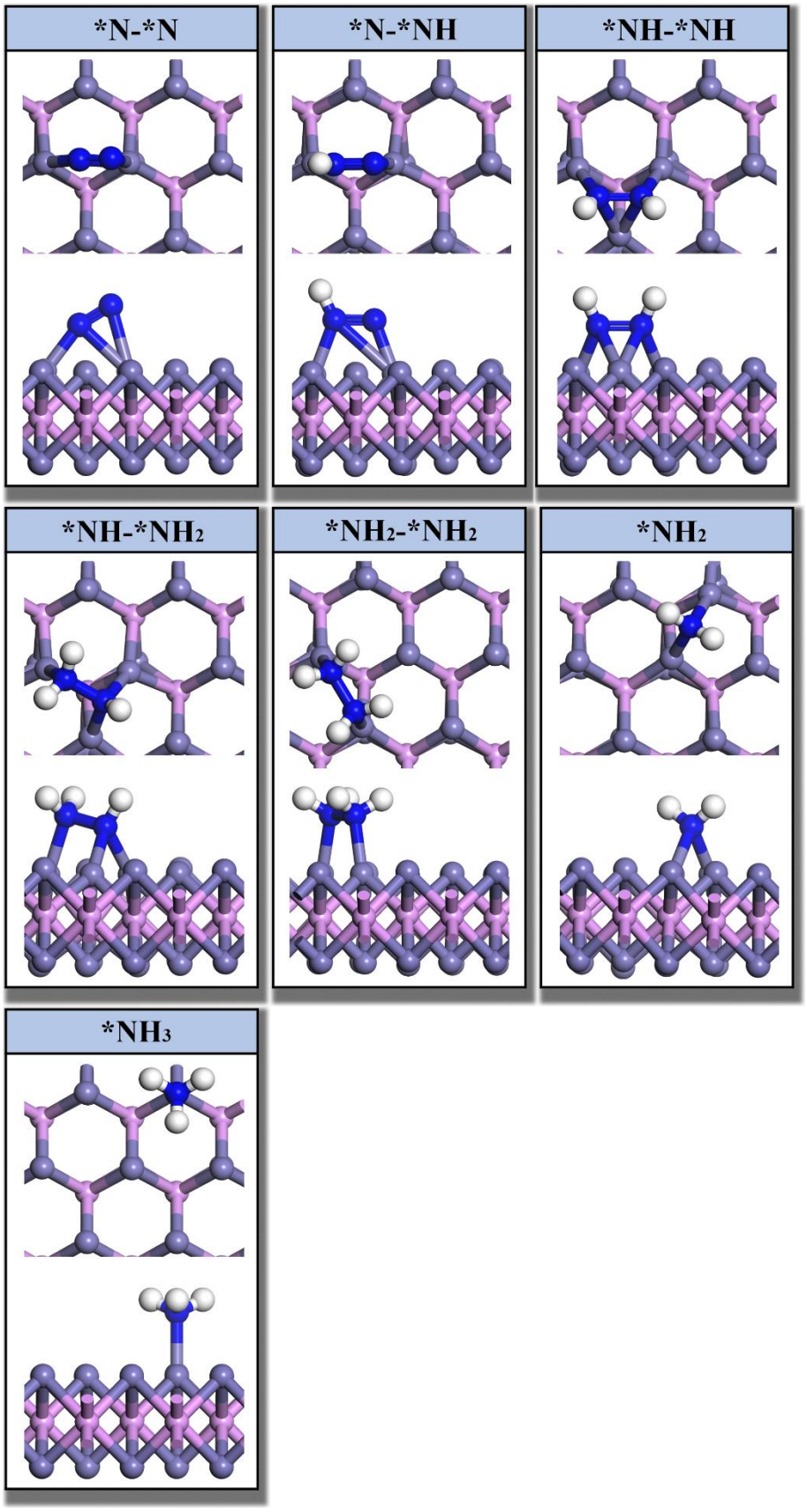

Fig. S6 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_2P monolayer through the enzymatic pathway.

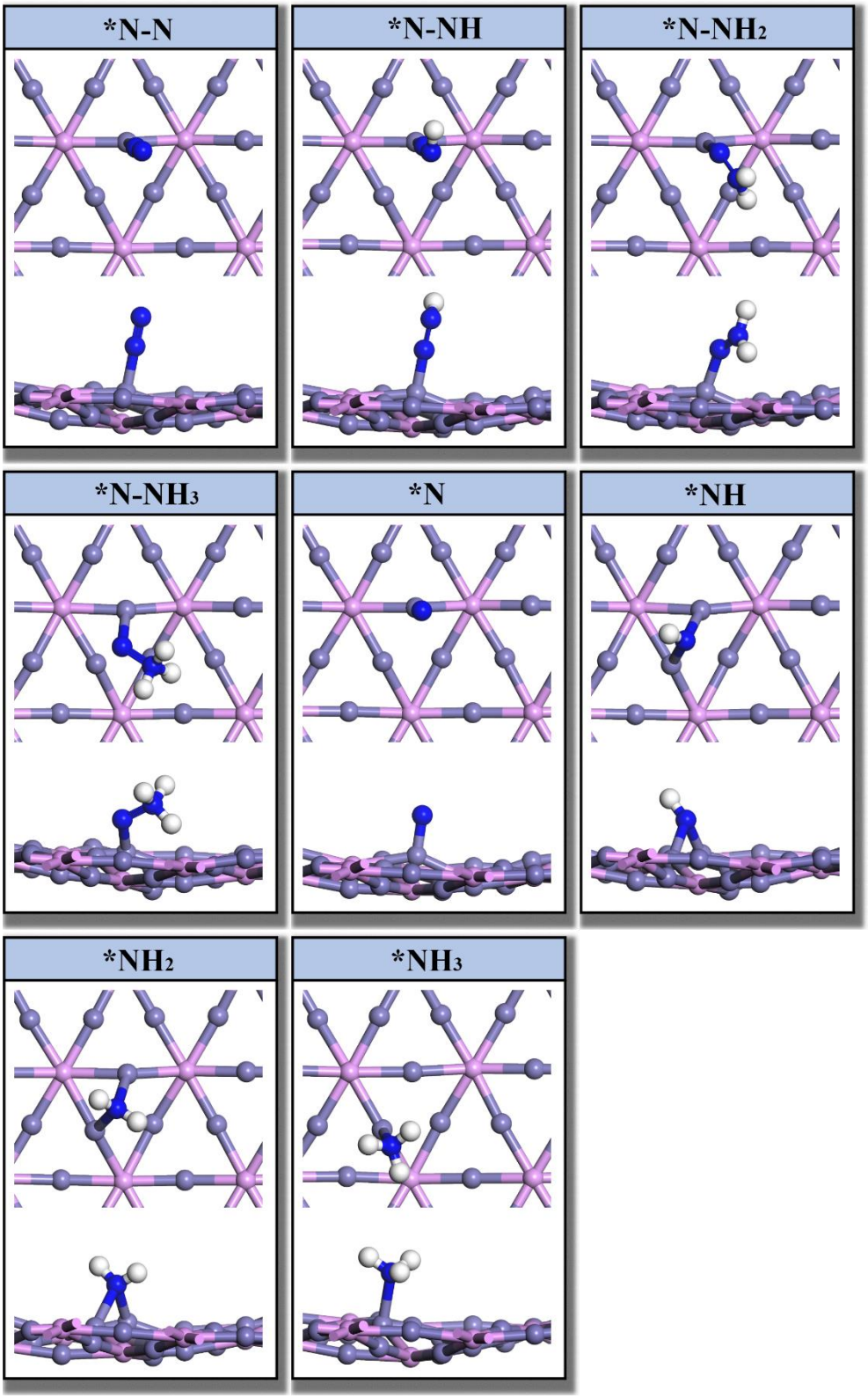

Fig. S7 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_3P monolayer through the distal pathway.

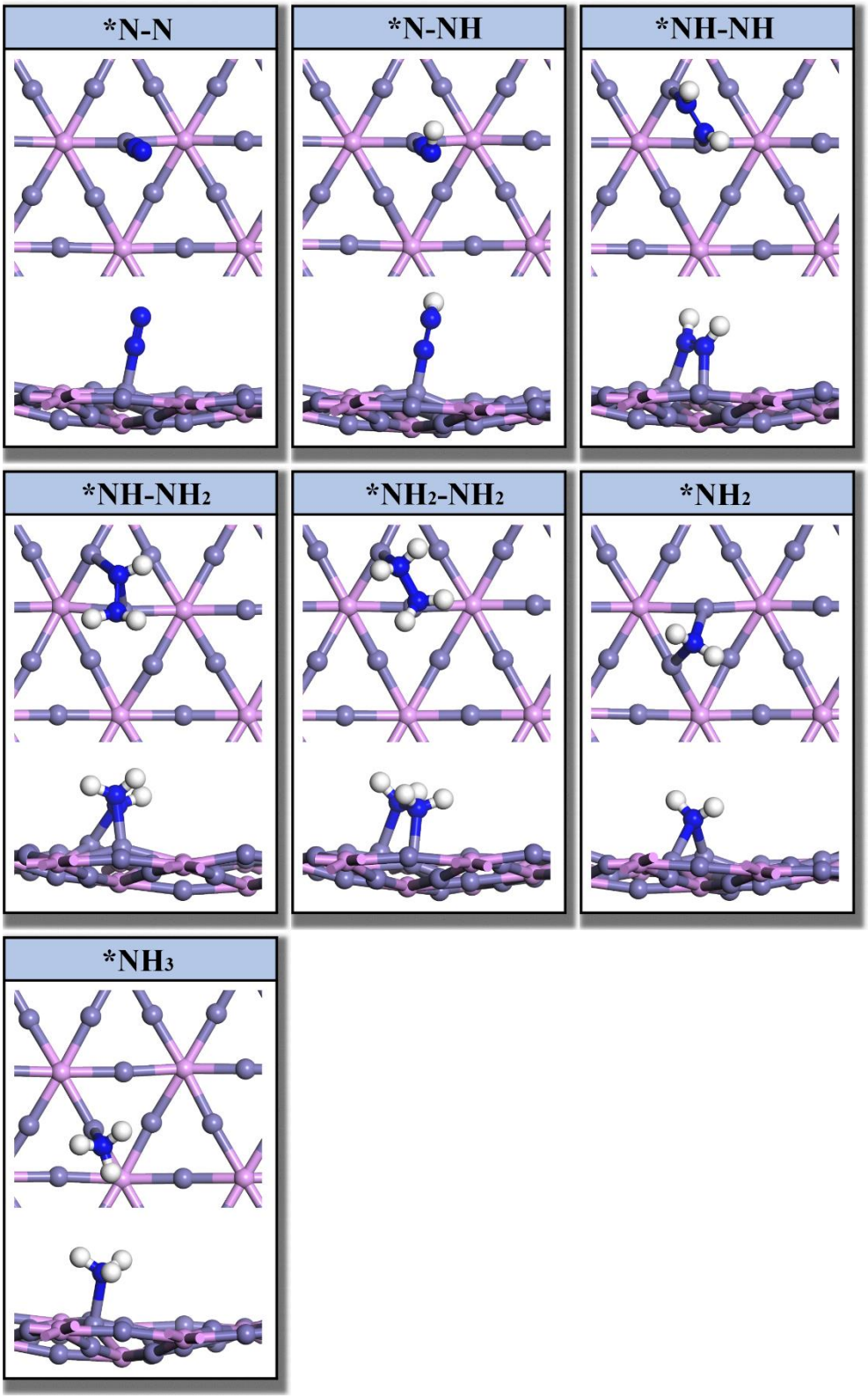

Fig. S8 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_3P monolayer through the alternating pathway.

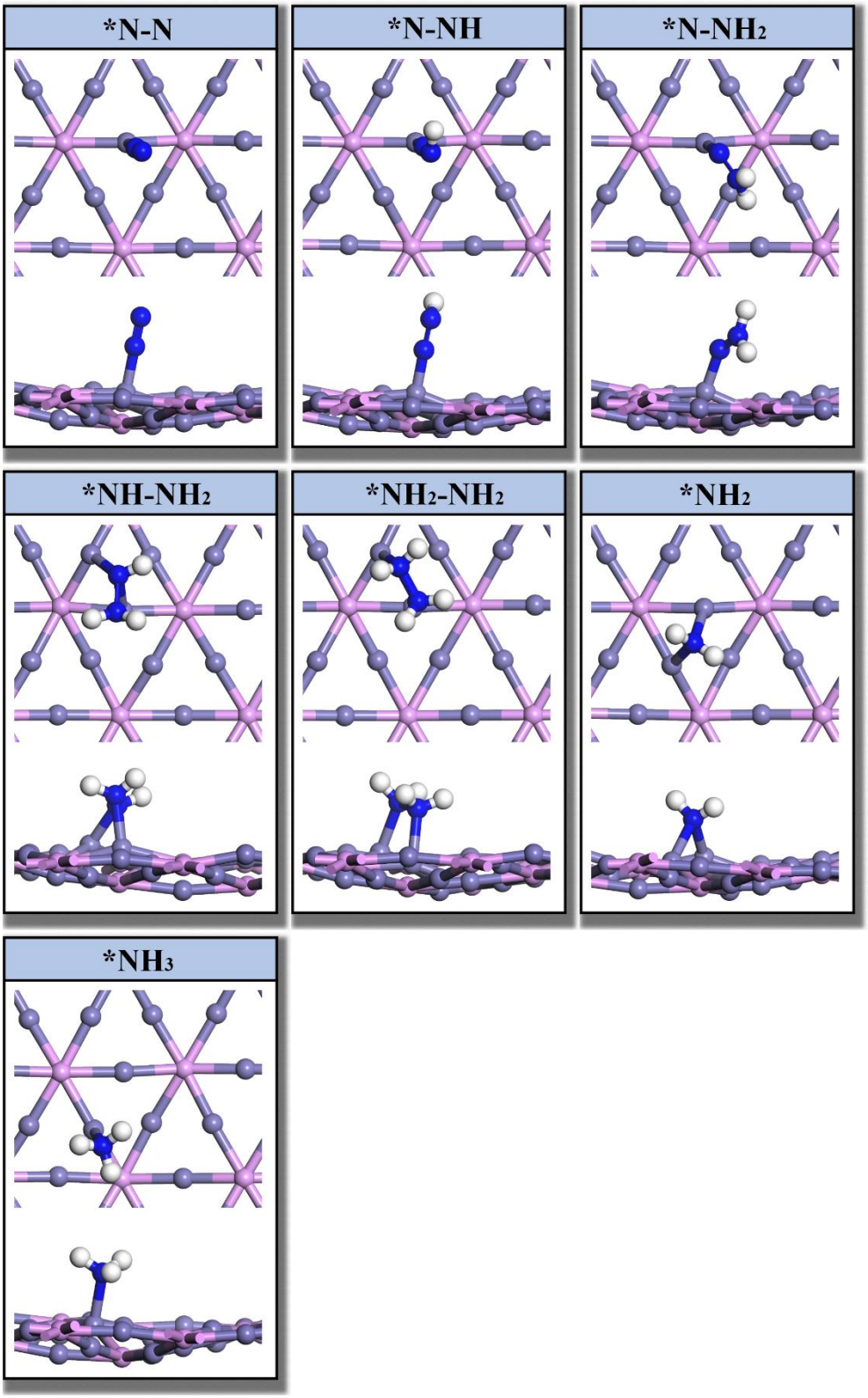

Fig. S9 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Fe_3P monolayer through the mix pathway.

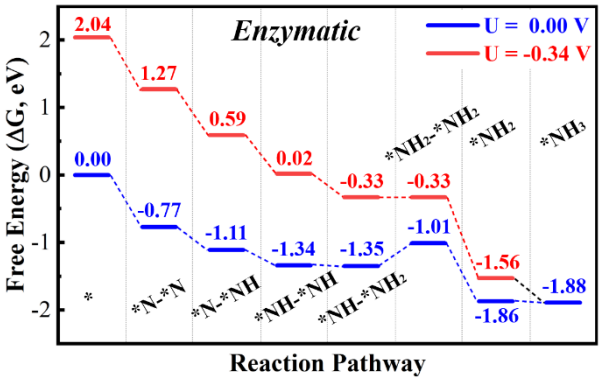

Fig. S10 Free energy diagrams for NRR on the Mo-doped Fe_2P monolayer through enzymatic pathway at different electrode potentials.

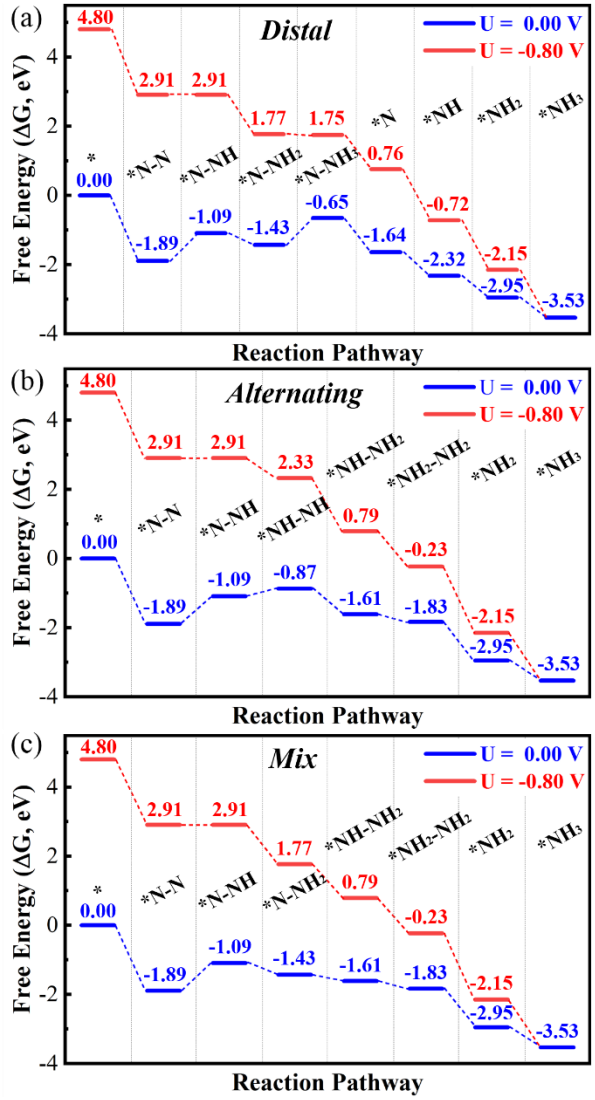

Fig. S11 Free energy diagrams for NRR on the Mo-doped Fe_3P monolayer through (a) distal, (b) alternating, and (c) mixed pathways at different electrode potentials.

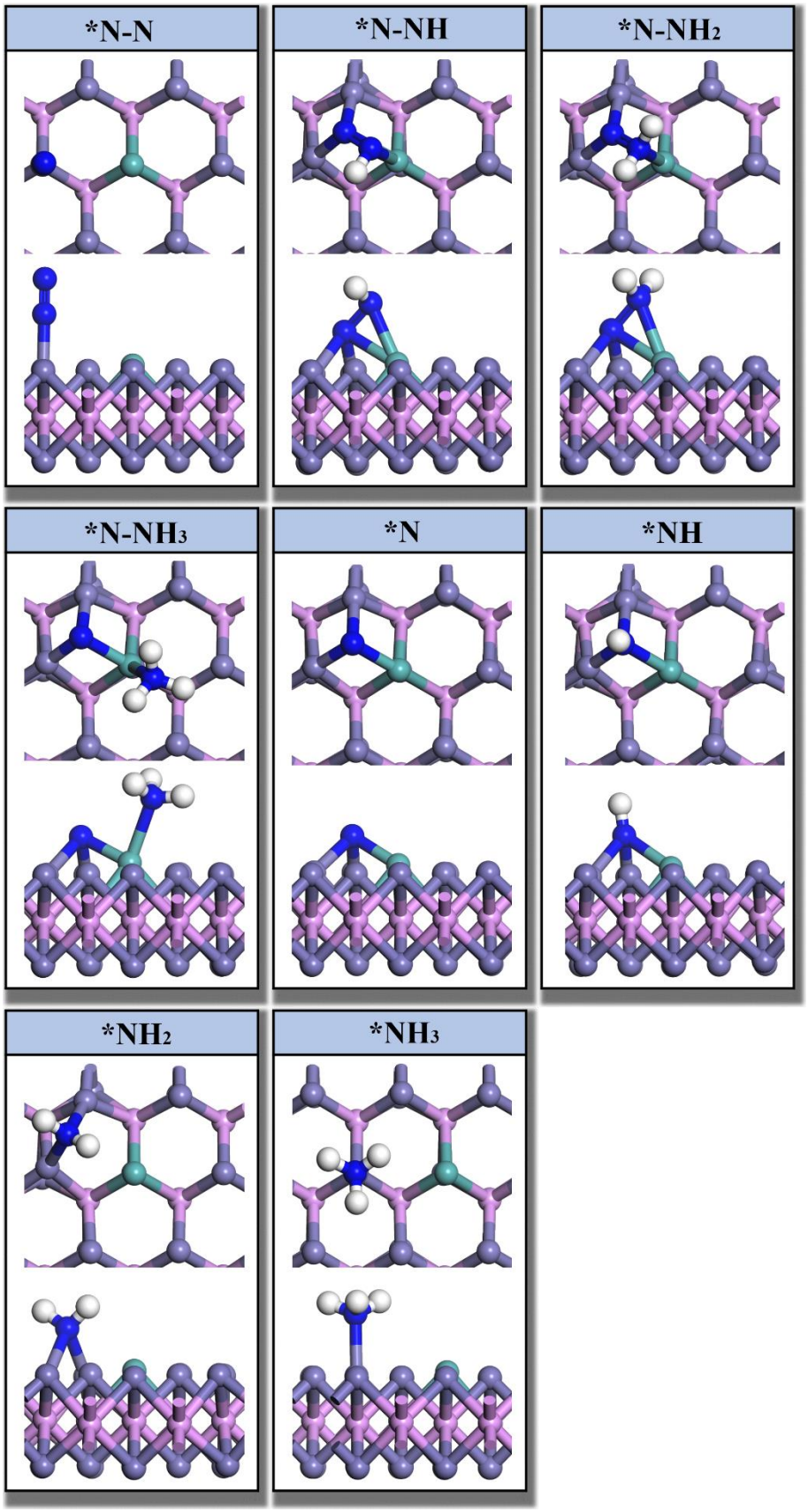

Fig. S12 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Mo-doped Fe_2P monolayer through the distal pathway.

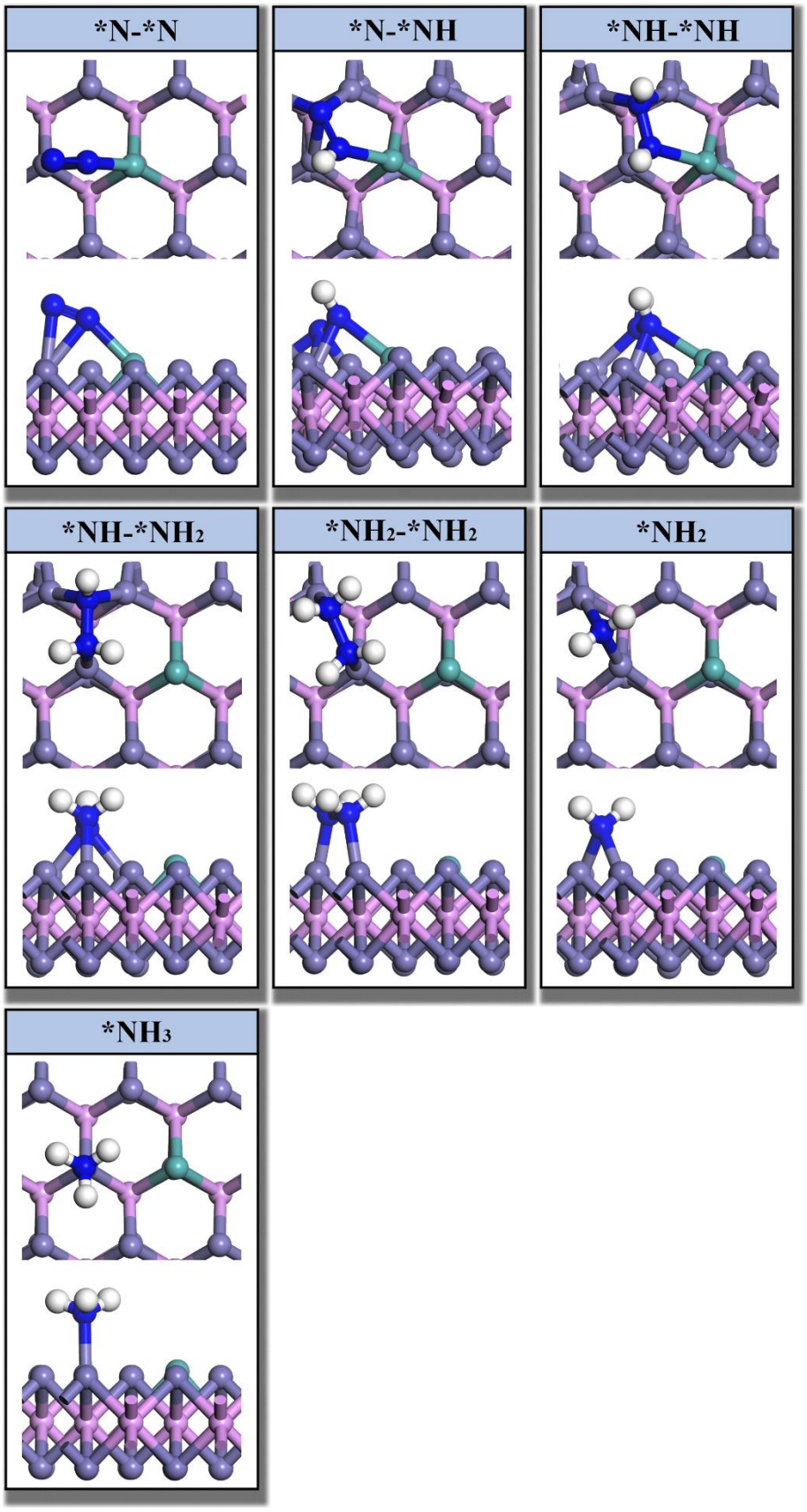

Fig. S13 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Mo-doped Fe_2P monolayer through the enzymatic pathway.

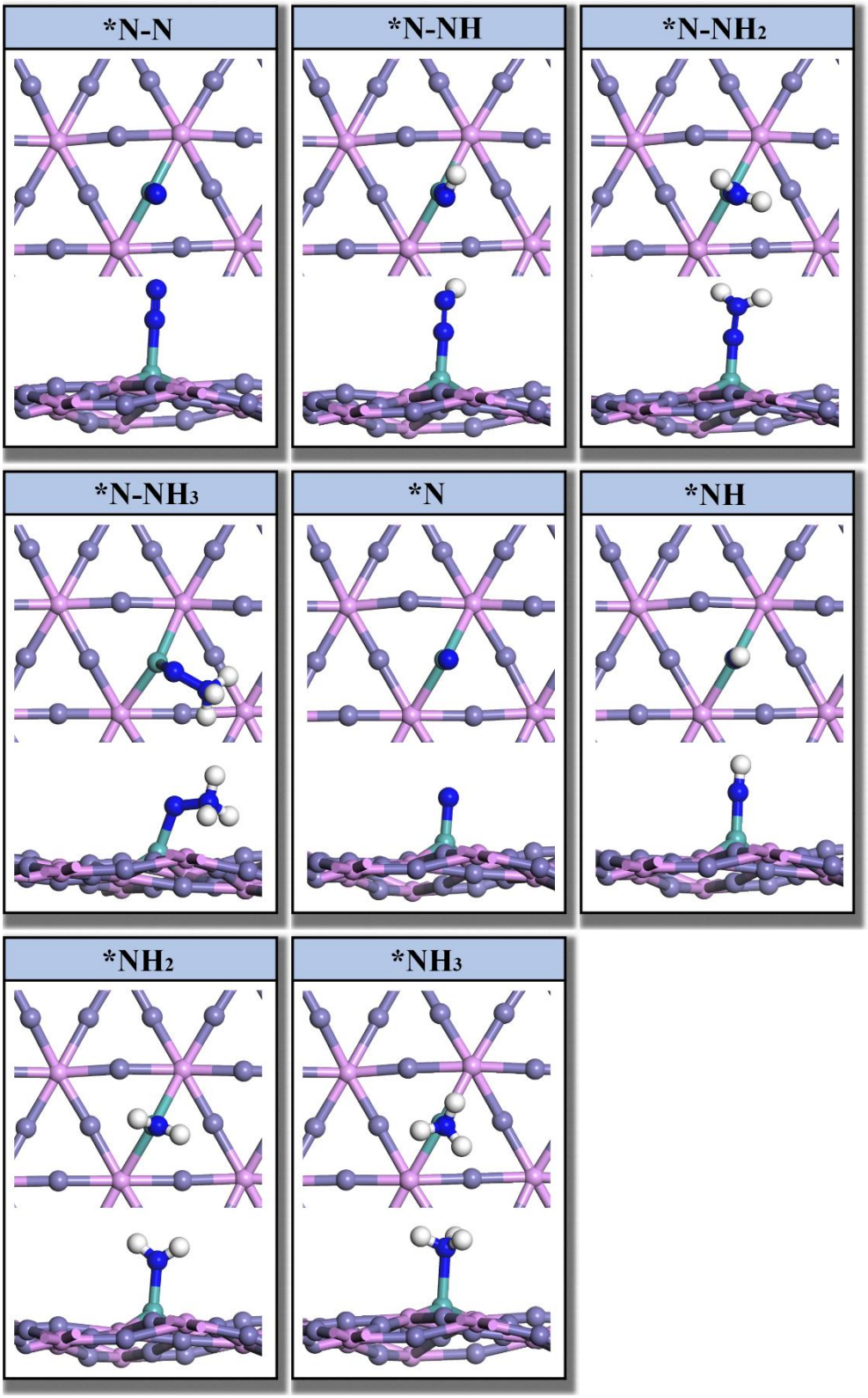

Fig. S14 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Mo-doped Fe_3P monolayer through the distal pathway.

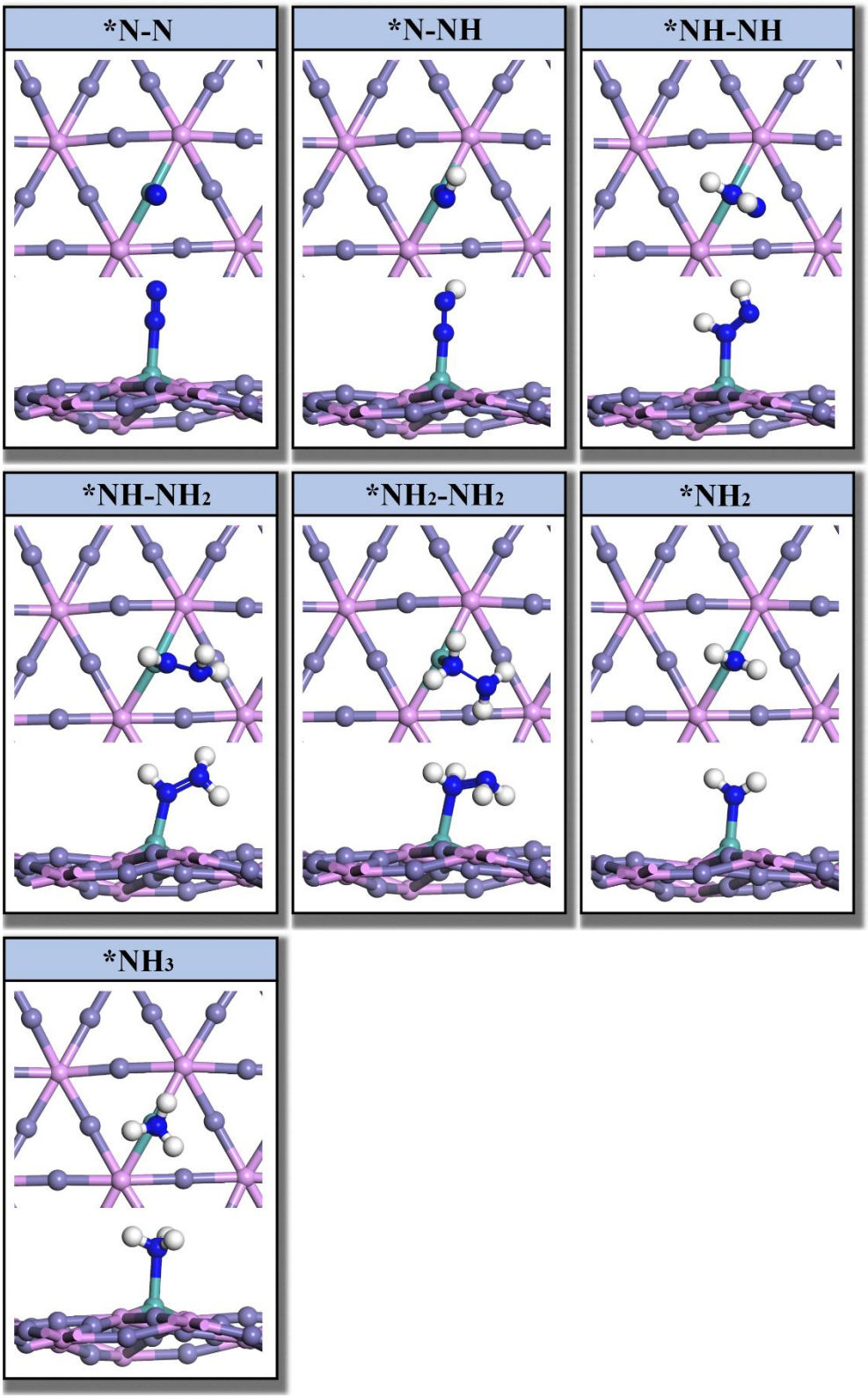

Fig. S15 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Mo-doped Fe_3P monolayer through the alternating pathway.

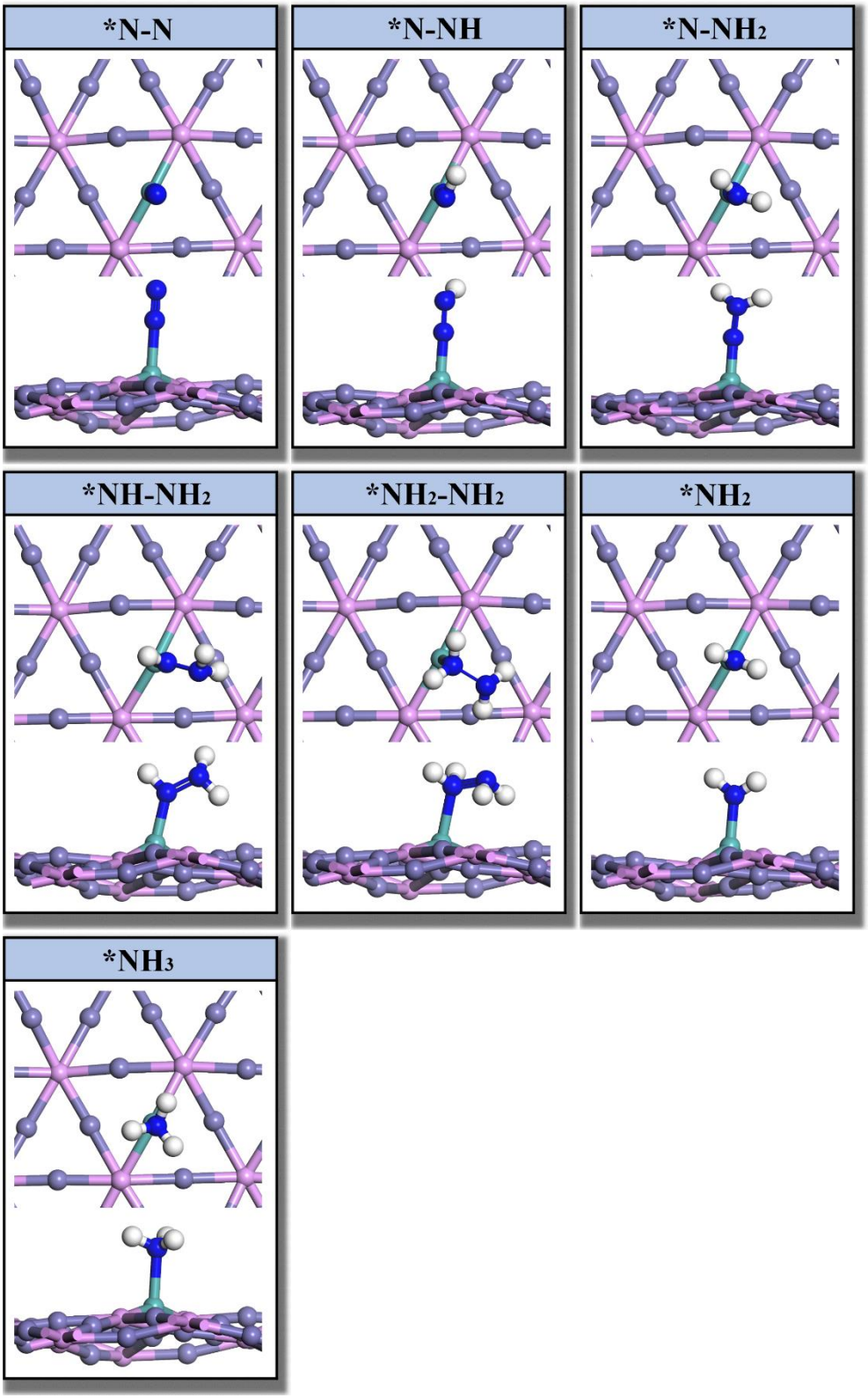

Fig. S16 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Mo-doped Fe_3P monolayer through the mixed pathway.

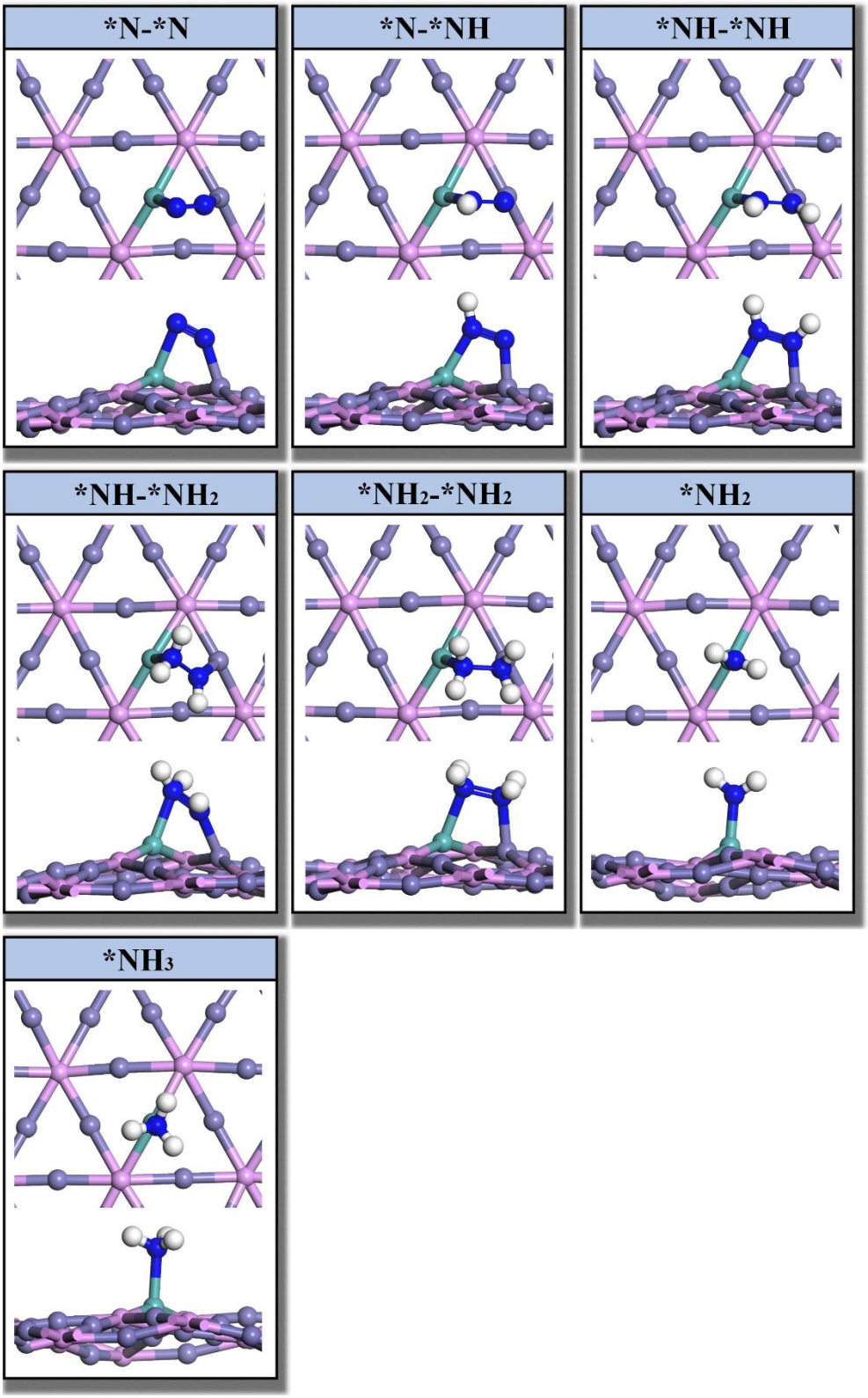

Fig. S17 Optimized adsorption structures of the reaction intermediates for N_2 reduction on the Mo-doped Fe_3P monolayer through the enzymatic pathway.

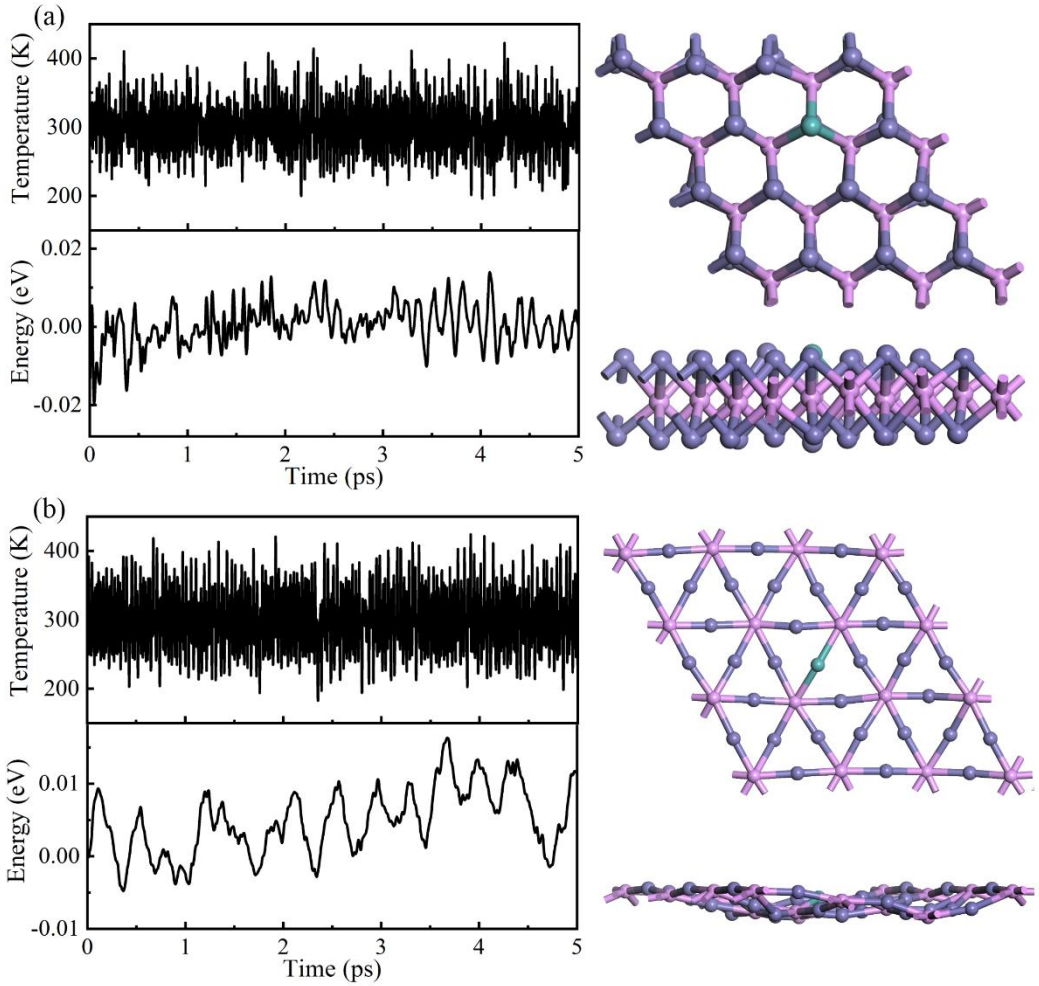

Fig. S18 Variations of temperature and relative energy against the time for AIMD simulations of (a) Mo-doped Fe_2P, and (b) Mo-doped Fe_3P monolayers. Inserts are top and side views of the final atomic structures after annealing. The AIMD simulations were performed in a canonical ensemble (*NVT*) and the system temperature was controlled at around 300 K by using Nosé-Hoover chain method.[1, 2] Lower accuracy calculations were adopted for AIMD simulations. The Brillouin zone was represented by 3 × 3 × 1 *k*-points grids and the convergence tolerance for self-consistent calculation was 1.0×10^{-6} Ha. The total simulation time was set as 5 ps with a time step 2 fs.

REFERENCES

1. W. G. Hoover, *Phys. Rev. A*, 1985, **31**, 1695-1697.

2. S. Nose, *J. Chem. Phys.*, 1984, **81**, 511-519.