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Supplementary Information

Mechanistic Insight into Catalytic Transfer Hydrogenation of Furfural to Furfuryl Alcohol over N-Doped Carbon-Supported Ni Single Atom Catalyst from First Principles

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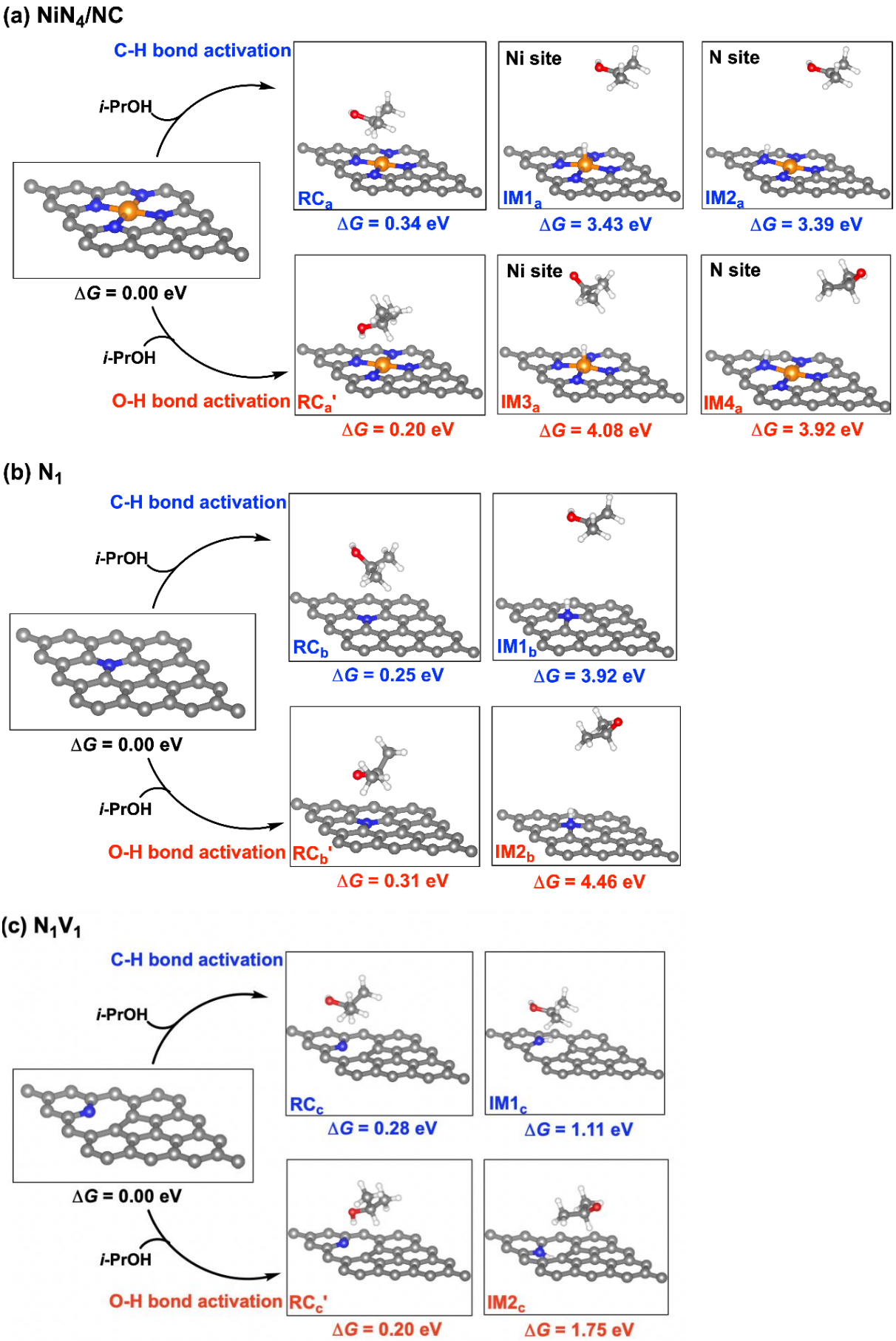
(a) NiN4/NC
C-H bond activation
i-PrOH
RCa
ΔG = 0.34 eV
Ni site
IM1a
ΔG = 3.43 eV
N site
IM2a
ΔG = 3.39 eV
ΔG = 0.00 eV
i-PrOH
O-H bond activation
RCa'
ΔG = 0.20 eV
Ni site
IM3a
ΔG = 4.08 eV
N site
IM4a
ΔG = 3.92 eV
(b) N1
C-H bond activation
i-PrOH
RCb
ΔG = 0.25 eV
IM1b
ΔG = 3.92 eV
ΔG = 0.00 eV
i-PrOH
O-H bond activation
RCb'
ΔG = 0.31 eV
IM2b
ΔG = 4.46 eV
(c) N1V1
C-H bond activation
i-PrOH
RCc
ΔG = 0.28 eV
IM1c
ΔG = 1.11 eV
ΔG = 0.00 eV
i-PrOH
O-H bond activation
RCc'
ΔG = 0.20 eV
IM2c
ΔG = 1.75 eV

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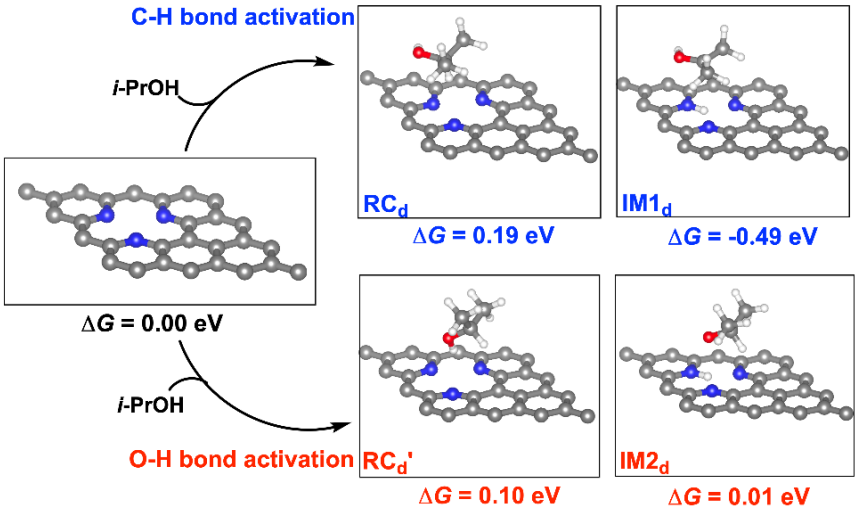
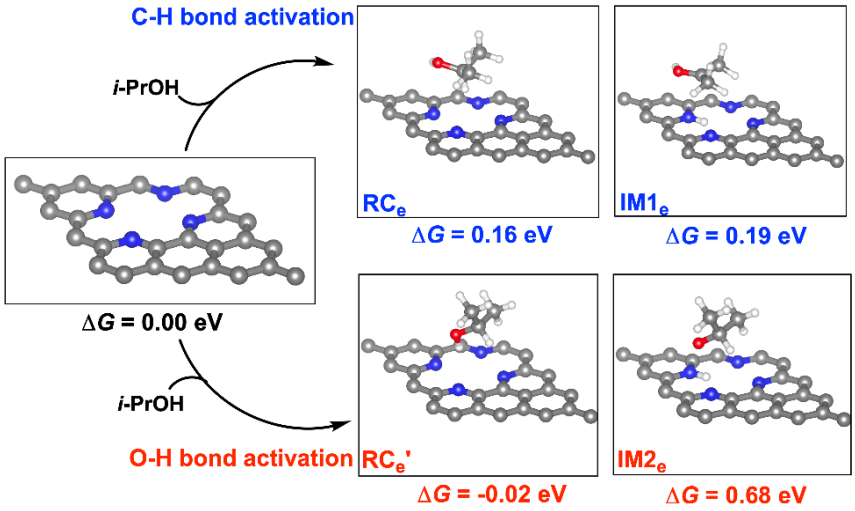
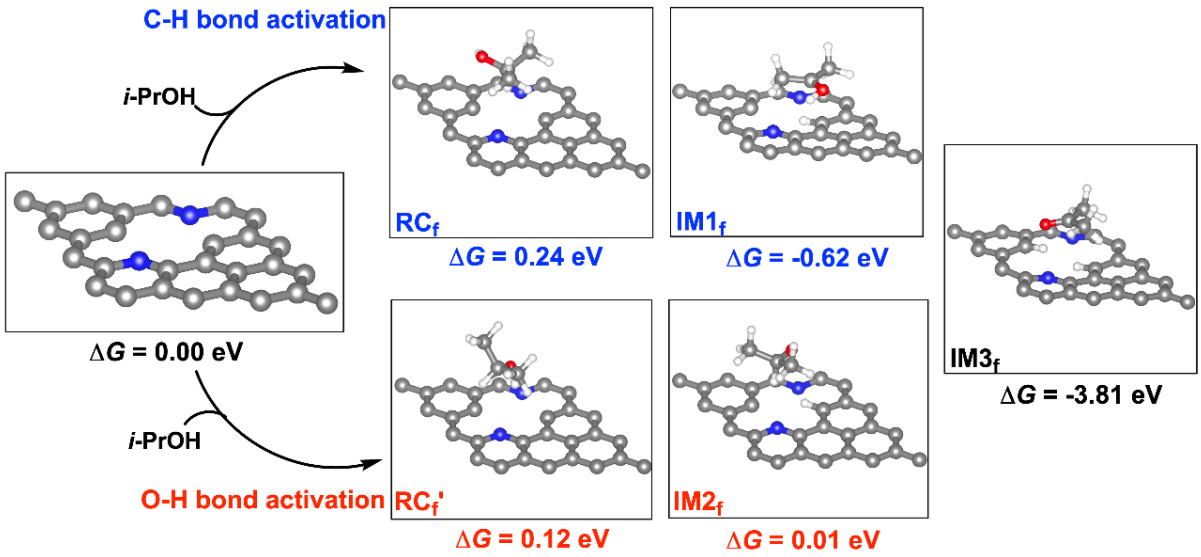
(d) pyridinic N_3V_1



(e) pyridinic N_4V_2



(f) pyridinic N_2V_2



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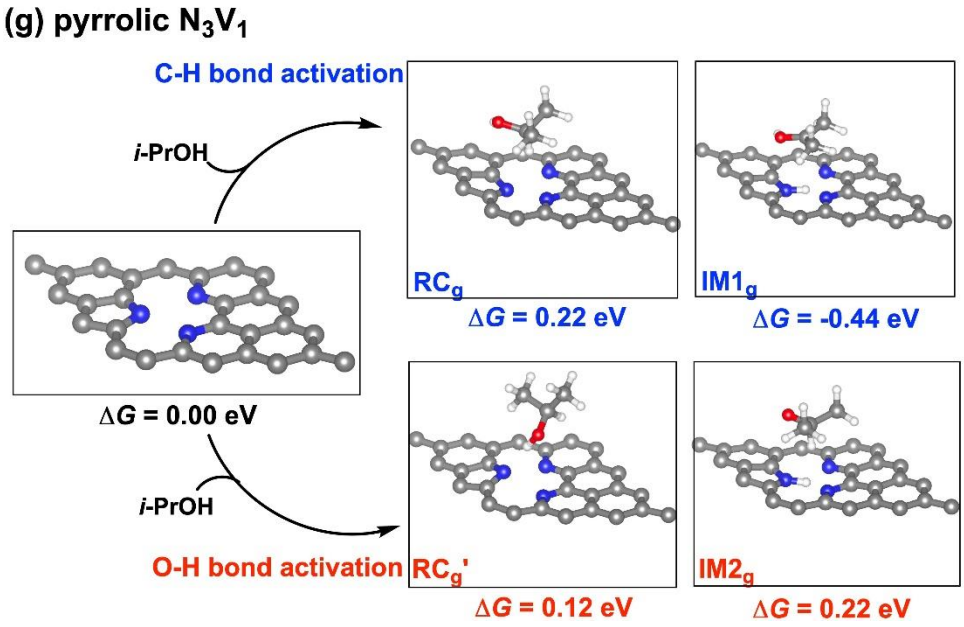

Fig. S1. Reaction pathway for the initial C-H/O-H bond activation of *i*-PrOH over different carbon materials: (a) NiN_4/NC, (b) N_1, (c) N_1V_1, (d) pyridinic N_3V_1, (e) pyridinic N_4V_2, (f) pyridinic N_2V_2 and (g) pyrrolic N_3V_1, respectively.

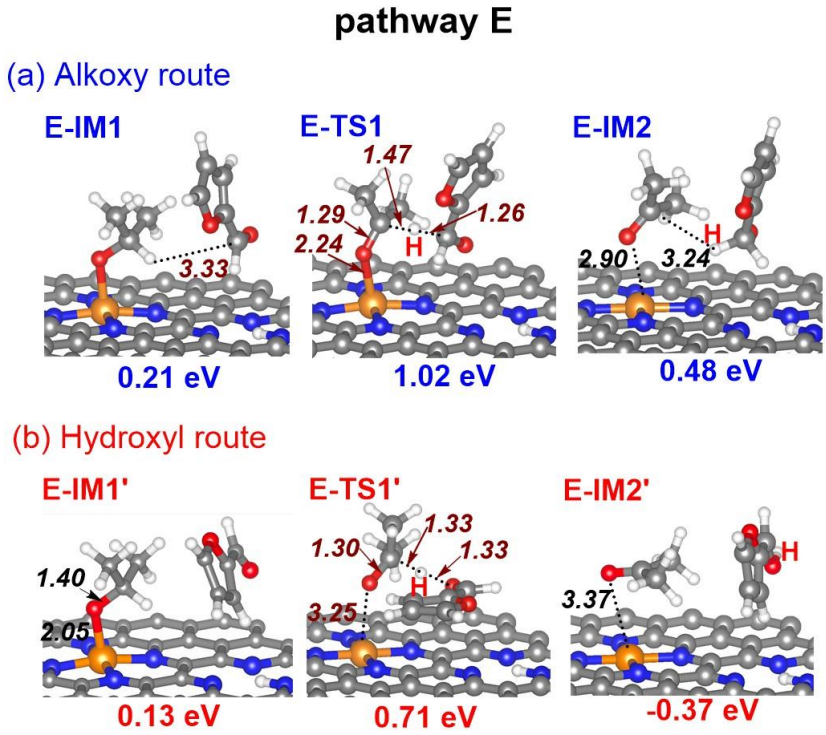

Fig. S2. Possible reaction pathways for the direct H transfer. The energies relative to **B-IM2'** and the isolated FF are given in eV.

Absolute and Relative Energies of Involved Species

The detail of each intermediates' relative electron energy (E_{DFT}), zero-point energy (ZPE), thermodynamic energy ($\Delta U_{(0->T)}$), entropy contribution ($T*S$) and Gibbs free energy (G) were shown in tables below.

$H_{gas} = E_{DFT} + ZPE + \Delta U_{(0->T)} + P*V$;

$H_{ads} = E_{DFT} + ZPE + \Delta U_{(0->T)}$

$G_{gas} = E_{DFT} + ZPE + \Delta U_{(0->T)} + P*V - T*S$;

$G_{ads} = E_{DFT} + ZPE + \Delta U_{(0->T)} - T*S$

Table S1. The electronic energy, thermodynamic corrections, enthalpy and free energies of the isolated molecules and carbon materials.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	$P*V$ (eV)	H (eV)	$T*S$ (eV)	G (eV)
i-PrOH	-63.656	2.85	0.24	0.0339	-60.530	1.24	-61.765
Acetone	-56.042	2.20	0.23		-53.575	1.26	-54.831
FF	-72.047	2.09	0.25		-69.668	1.32	-70.984
FA	-79.637	2.71	0.39		-76.601	1.42	-78.024
NiN_4/NC	-279.135	5.00	0.65	-	-273.486	1.07	-264.513
N_1	-294.557	5.38	0.62		-288.561	0.99	-289.549
N_1V_1	-281.112	5.12	0.63		-275.358	1.06	-276.422
pyridinic N_3V_1	-280.835	4.99	0.61		-275.237	0.99	-276.224
pyridinic N_4V_2	-270.603	4.88	0.60		-265.117	1.00	-266.113
pyridinic N_2V_2	-268.966	4.88	0.63		-263.453	1.06	-264.513
pyrrolic N_3V_1	-279.185	5.08	0.65		-273.460	1.10	-274.561
NiN_4-N_3V_1/NC	-633.981	11.42	1.56		-620.999	2.71	-623.704
H&H*	-641.582	11.89	1.59		-628.102	2.73	-630.829

Table S2. The energies[a] of the key species involved in Fig. 2a.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	$T*S$ (eV)	G (eV)	ΔG (eV)
NiN_4-N_3V_1/NC +*i*-PrOH	-697.637	14.27	1.80	-681.529	0.00	3.94	-685.469	0.00
A-RC	-698.032	14.29	1.89	-681.853	-0.32	3.43	-685.283	0.19
A-TS1$_{N5}$	-697.120	14.17	1.84	-681.109	0.42	3.26	-684.365	1.10
A-IM1$_{N5}$	-698.508	14.27	1.88	-682.362	-0.83	3.41	-685.769	-0.30
A-TS1$_{N6}$	-697.178	14.18	1.84	-681.156	0.37	3.26	-684.416	1.05
A-IM1$_{N6}$	-698.474	14.23	1.88	-682.356	-0.83	3.42	-685.778	-0.31
A-TS1$_{N7}$	-697.108	14.17	1.84	-681.096	0.43	3.26	-684.357	1.11
A-IM1$_{N7}$	-698.464	14.27	1.88	-682.318	-0.79	3.40	-685.718	-0.25
A-IM2	-698.540	14.25	1.87	-682.417	-0.89	3.38	-685.796	-0.33
A-TS2	-698.277	14.17	1.83	-681.996	-0.47	3.27	-683.457	-0.08
A-IM3	-698.635	14.31	1.86	-682.028	-0.50	3.37	-682.457	-0.37
A-TS2'	-697.960	14.11	1.85	-682.274	-0.75	3.31	-685.308	0.16
A-IM3'	-698.010	14.09	1.90	-682.466	-0.94	3.44	-685.465	0.00

[a]$\Delta H_{INT} = H_{INT} - (H_{NiN_4-N_3V_1/NC} + H_{i-PrOH})$, where H_{INT}, $H_{NiN_4-N_3V_1/NC}$ and H_{i-PrOH} are the enthalpy of intermediates, NiN_4-N_3V_1/NC and *i*-PrOH molecule, respectively;

$\Delta G_{INT} = G_{INT} - (G_{NiN_4-N_3V_1/NC} + G_{i-PrOH})$, where G_{INT}, $G_{NiN_4-N_3V_1/NC}$ and G_{i-PrOH} are the free energies of intermediates, NiN_4-N_3V_1/NC and *i*-PrOH molecule, respectively.

Table S3. The energies [a] of the key species involved in Fig. 2b.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	$T*S$ (eV)	G (eV)	ΔG (eV)
NiN_4-N_3V_1/NC +*i*-PrOH	-697.637	14.27	1.80	-681.529	0.00	3.94	-685.469	0.00
B-RC	-698.207	14.30	1.87	-682.033	-0.50	3.38	-685.416	0.05
B-TS1$_{N5}$	-697.480	14.21	1.80	-681.467	0.06	3.18	-684.646	0.82
B-IM1$_{N5}$	-697.842	14.25	1.83	-681.765	-0.24	3.28	-685.047	0.42
B-TS1$_{N6}$	-697.425	14.19	1.84	-681.391	0.14	3.29	-684.677	0.79
B-IM1$_{N6}$	-697.887	14.22	1.83	-681.835	-0.31	3.27	-685.109	0.36
B-TS1$_{N7}$	-697.508	14.20	1.83	-681.469	0.06	3.27	-684.739	0.73
B-IM1$_{N7}$	-697.877	14.23	1.83	-681.817	-0.29	3.28	-685.096	0.37
B-IM2	-698.054	14.21	1.86	-681.987	-0.46	3.32	-685.311	0.16
B-TS2	-697.795	14.12	1.85	-681.827	-0.30	3.29	-685.120	0.35
B-IM3	-698.013	14.13	1.89	-681.995	-0.47	3.43	-685.429	0.04
B-IM4	-697.625	14.09	1.85	-682.280	-0.75	3.98	-685.660	-0.19
B-IM2'	-698.415	14.29	1.85	-681.377	0.15	3.29	-685.567	-0.10
B-TS2'	-697.350	14.14	1.84	-682.430	-0.90	3.27	-684.644	0.83
B-IM3'	-698.554	14.29	1.84	-681.469	0.06	3.31	-685.739	-0.27
H&H* +acetone	-697.625	14.09	1.82	-681.678	-0.15	3.98	-685.660	-0.19

[a] $\Delta H_{INT} = H_{INT} - (H_{NiN_4-N_3V_1/NC} + H_{i-PrOH})$,where H_{INT}, $H_{NiN_4-N_3V_1/NC}$, H_{i-PrOH} are the enthalpy of intermediates, NiN_4-N_3V_1/NC and *i*-PrOH molecule, respectively;

$\Delta G_{INT} = G_{INT} - (G_{NiN_4-N_3V_1/NC} + G_{i-PrOH})$, where G_{INT}, $G_{NiN_4-N_3V_1/NC}$, G_{i-PrOH} are the free energies of intermediates, NiN_4-N_3V_1/NC and *i*-PrOH molecule, respectively.

Table S4. The energies [a] of the key species involved in Fig. 4.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	$T*S$ (eV)	G (eV)	ΔG (eV)
C-IM1	-714.090	14.00	1.92	-698.164	0.00	3.48	-701.642	0.00
C-IM2	-714.327	14.07	1.86	-698.394	-0.23	3.31	-701.709	-0.07
C-IM1'	-714.140	14.01	1.92	-698.211	0.00	3.48	-701.688	0.00
C-IM2'	-710.435	13.91	1.94	-694.585	3.63	3.52	-698.106	3.58
D-IM1	-714.048	14.00	1.89	-698.154	0.00	3.40	-701.552	0.00
D-IM2	-715.050	14.15	1.91	-698.995	-0.84	3.44	-702.432	-0.88
D-IM1'	-714.140	14.01	1.92	-698.210	0.00	3.48	-701.686	0.00
D-IM2'	-711.355	13.91	1.94	-695.505	2.71	3.52	-699.026	2.66

[a] $\Delta H_{INT} = H_{INT} - H_{IM1/IM1'}$, where H_{INT}, and$H_{IM1/IM1'}$,are the enthalpy of intermediates and **IM1**/**IM1'**, respectively;

$\Delta G_{INT} = G_{INT} - G_{IM1/IM1'}$, where G_{INT}, and$G_{IM1/IM1'}$,are the free energies of intermediates and **IM1**/**IM1'**, respectively.

Table S5. The energies[a] of the key species involved in Fig. 5a.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	T*S (eV)	G (eV)	ΔG (eV)
H&H* +FF	-713.629	13.98	1.80	-697.770	0.00	4.04	-701.813	0.00
C-IM1	-714.090	14.00	1.92	-698.164	-0.39	3.48	-701.642	0.17
C-TS1	-714.040	13.98	1.88	-698.174	-0.40	3.36	-701.534	0.28
C-IM2	-714.327	14.07	1.86	-698.394	-0.62	3.31	-701.709	0.10
C-IM3	-714.154	14.10	1.90	-698.158	-0.39	3.42	-701.581	0.23
C-TS2	-713.746	14.07	1.87	-697.805	-0.03	3.35	-701.153	0.66
C-IM4	-714.423	14.17	1.91	-698.344	-0.57	3.45	-701.795	0.02
NiN_4-N_3V_1/NC + FA	-713.618	14.13	1.95	-697.600	0.17	4.13	-701.728	0.08

[a]$\Delta H_{INT} = H_{INT} - (H_{H\&H*} + H_{FF})$, where H_{INT}, $H_{H\&H*}$ and H_{FF} are the enthalpy of intermediates, H&H* and FF molecule, respectively;

$\Delta G_{INT} = G_{INT} - (G_{H\&H*} + G_{FF})$, where G_{INT}, $G_{H\&H*}$ and G_{FF} are the free energies of intermediates, H&H* and FF molecule, respectively.

Table S6. The energies[a] of the key species involved in Fig. 5b.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	T*S (eV)	G (eV)	ΔG (eV)
H&H* +FF	-713.629	13.98	1.80	-697.770	0.00	4.04	-701.813	0.00
D-IM1	-714.048	14.00	1.89	-698.154	-0.38	3.40	-701.552	0.26
D-TS2	-714.013	13.99	1.86	-698.166	-0.40	3.31	-701.474	0.34
D-IM2	-715.050	14.15	1.91	-698.995	-1.23	3.44	-702.432	-0.62
D-IM3	-715.002	14.15	1.91	-698.938	-1.17	3.45	-702.391	-0.58
D-TS2	-713.428	14.03	1.86	-697.543	0.23	3.28	-700.820	0.99
D-IM4	-714.161	14.16	1.93	-698.075	-0.31	3.51	-701.589	0.22
NiN_4-N_3V_1/NC + FA	-713.618	14.13	1.95	-697.600	0.17	4.13	-701.728	0.08

[a]$\Delta H_{INT} = H_{INT} - (H_{H\&H*} + H_{FF})$, where H_{INT}, $H_{H\&H*}$ and H_{FF} are the enthalpy of intermediates, H&H* and FF molecule, respectively;

$\Delta G_{INT} = G_{INT} - (G_{H\&H*} + G_{FF})$, where G_{INT}, $G_{H\&H*}$ and G_{FF} are the free energies of intermediates, H&H* and FF molecule, respectively.

Table S7. The energies[a] of the key species involved in Fig. S1.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	$T*S$ (eV)	G (eV)	ΔG (eV)
NiN_4/NC + *i*-PrOH	-342.791	7.84	0.90	-334.015	0.00	2.30	-336.320	0.00
RC$_a$	-343.099	7.85	0.93	-334.324	-0.31	1.66	-335.983	0.34
IM1$_a$	-339.665	7.57	0.96	-331.136	2.88	1.76	-332.895	3.43
IM2$_a$	-339.911	7.76	0.96	-331.190	2.83	1.74	-332.926	3.39
RC$_a$'	-343.154	7.86	0.98	-334.310	-0.29	1.81	-336.123	0.20
IM3$_a$	-339.125	7.59	0.90	-330.634	3.38	1.60	-332.238	4.08
IM4$_a$	-339.453	7.75	0.91	-330.799	3.22	1.60	-332.402	3.92
N_1 + *i*-PrOH	-358.213	8.23	0.86	-349.091	0.00	2.22	-351.314	0.00
RC$_b$	-358.522	8.25	0.94	-349.327	-0.24	1.74	-351.064	0.25
IM1$_b$	-354.840	8.23	0.93	-345.681	3.41	1.71	-347.394	3.92
RC$_b$'	-358.532	8.25	0.91	-349.369	-0.28	1.64	-351.009	0.31
IM2$_b$	-353.953	7.94	0.96	-345.050	4.04	1.80	-346.853	4.46
N_1V_1 + *i*-PrOH	-344.769	7.97	0.88	-335.888	0.00	2.30	-338.187	0.00
RC$_c$	-345.088	7.98	0.93	-336.171	-0.28	1.73	-337.905	0.28
IM1$_c$	-344.316	8.00	0.93	-335.390	0.50	1.68	-337.073	1.11
RC$_c$'	-345.158	7.99	0.95	-336.214	-0.33	1.77	-337.989	0.20
IM2$_c$	-343.653	7.97	0.92	-334.761	1.13	1.68	-336.439	1.75
pyridinic N_3V_1 + *i*-PrOH	-344.491	7.84	0.85	-335.767	0.00	2.22	-337.990	0.00
RC$_d$	-344.897	7.91	0.95	-336.039	-0.27	1.76	-337.797	0.19
IM1$_d$	-345.671	7.92	0.91	-336.841	-1.07	1.64	-338.480	-0.49
RC$_d$'	-345.068	7.94	0.92	-336.202	-0.44	1.68	-337.886	0.10
IM2$_d$	-345.105	7.93	0.94	-336.230	-0.46	1.75	-337.978	0.01
pyridinic N_4V_2 + *i*-PrOH	-334.260	7.73	0.85	-325.646	0.00	2.23	-327.878	0.00
RC$_e$	-334.685	7.76	0.93	-326.001	-0.35	1.72	-327.718	0.16
IM1$_e$	-334.681	7.74	0.92	-326.028	-0.38	1.66	-327.689	0.19
RC$_e$'	-334.837	7.77	0.94	-326.124	-0.48	1.77	-327.896	-0.02
IM2$_e$	-334.121	7.72	0.94	-325.460	0.19	1.74	-327.202	0.68
pyridinic N_2V_2 + *i*-PrOH	-332.622	7.73	0.88	-323.983	0.00	2.30	-326.279	0.00
RC$_f$	-332.997	7.75	0.93	-324.322	-0.34	1.71	-326.037	0.24
IM1$_f$	-333.869	7.75	0.93	-325.195	-1.21	1.71	-326.901	-0.62
RC$_f$'	-333.073	7.75	0.95	-324.368	-0.39	1.79	-326.159	0.12
IM2$_f$	-333.180	7.72	0.94	-324.514	-0.53	1.76	-326.273	0.01
IM3$_f$	-337.057	7.81	0.94	-328.307	-3.98	1.78	-330.086	-3.81

Continued **Table S7**

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	T*S (eV)	G (eV)	ΔG (eV)
pyrrolic N_3V_1 + *i*-PrOH	-342.841	7.92	0.89	-333.989	0.00	2.34	-336.326	0.00
RC$_g$	-343.203	7.95	0.97	-334.284	-0.29	1.82	-336.107	0.22
IM1$_g$	-343.869	7.96	0.98	-334.928	-0.94	1.84	-336.764	-0.44
RC$_g$'	-343.371	7.96	0.95	-334.465	-0.48	1.74	-336.209	0.12
IM2$_g$	-343.209	7.94	0.96	-334.306	-0.32	1.80	-336.109	0.22

[a]$\Delta H_{INT} = H_{INT} - (H_{catalyst} + H_{i-PrOH})$, where H_{INT}, $H_{catalyst}$ and H_{i-PrOH} are the enthalpy of intermediates, free catalyst and *i*-PrOH molecule, respectively;

$\Delta G_{INT} = G_{INT} - (G_{catalyst} + G_{i-PrOH})$, where G_{INT}, $G_{catalyst}$ and G_{i-PrOH} are the free energies of intermediates, free catalyst and *i*-PrOH molecule, respectively.

Table S8. The energies[a] of the key species involved in Fig. S2.

INT	E_{DFT} (eV)	ZPE (eV)	$\Delta U_{(0->T)}$ (eV)	H (eV)	ΔH (eV)	T*S (eV)	G (eV)	ΔG (eV)
B-IM2' + FF	-770.462	16.38	2.10	-751.045	0.00	4.60	-756.551	0.00
E-IM1	-770.878	16.40	2.18	-752.295	-1.25	4.05	-756.344	0.21
E-TS1	-770.062	16.30	2.14	-751.616	-0.57	3.92	-755.533	1.02
E-IM2	-770.509	16.32	2.17	-752.017	-0.97	4.06	-756.078	0.48
E-IM1'	-770.967	16.41	2.18	-752.382	-1.34	4.04	-756.425	0.13
E-TS1'	-770.291	16.26	2.16	-751.868	-0.82	3.98	-755.844	0.71
E-IM2'	-771.379	16.37	2.19	-752.814	-1.77	4.11	-756.925	-0.37

[a]$\Delta H_{INT} = H_{INT} - (H_{B-IM2'} + H_{FF})$, where H_{INT}, $H_{B-IM2'}$ and H_{FF} are the enthalpy of intermediates, **B-IM2'** and FF molecule, respectively;

$\Delta G_{INT} = G_{INT} - (G_{B-IM2'} + G_{FF})$, where G_{INT}, $G_{B-IM2'}$ and G_{FF} are the free energies of intermediates, **B-IM2'** and FF molecule, respectively.