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Supplementary Information

Mechanistic insights into the catalytic elimination of tar and the Promotional effect of Boron on it: First principles study using Toluene as a model compound

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1. Comparison between energies calculated using optB88-vdW and PBE functional.

Table T1. Activation barriers and reaction energies calculated using optB88-vdW and PBE functionals.

	Functional	**optB88-vdW**		**PBE**	
	Energy (kJ/mol)	**E_a**	**ΔE**	**E_a**	**ΔE**
Adsorption			-174		-90
Step 1					
1-1	CH_3-C_6H_5 → *CH_2-C_6H_5 + H*	72	-13	71	-12
1-2	CH_3-C_6H_5 → *CH_3 + C_6H_5*	163	+106	167	+101
1-3	CH_3-C_6H_5 → CH_3-C_6H_4* + H* (*ortho*)	141	+75	138	+73
1-4	CH_3-C_6H_5 → CH_3-C_6H_4* + H* (*meta*)	131	+70	130	+68
1-5	CH_3-C_6H_5 → CH_3-C_6H_4* + H* (*para*)	142	+76	140	+74
1-6	Ring opening at *ortho* position	123	+110	124	+108
1-7	Ring opening at *meta* position	159	+149	157	+146
1-8	Ring opening at *para* position	116	+93	115	+89
Step 2					
2-1	*CH_2-C_6H_5 → *CH-C_6H_5 + H*	104	+41	105	+38
2-2	*CH_2-C_6H_5 → *CH_2 + C_6H_5*	191	+119	192	+116
2-3	*CH_2-C_6H_5 → *CH_2-C_6H_4* + H* (*ortho*)	130	+74	127	+71
2-4	*CH_2-C_6H_5 → *CH_2-C_6H_4* + H* (*meta*)	133	+70	132	+68
2-5	*CH_2-C_6H_5 → *CH_2-C_6H_4* + H* (*para*)	146	+88	143	+85
2-6	Ring opening at *ortho* position	118	+99	114	+94
2-7	Ring opening at *meta* position	159	+141	156	+142
2-8	Ring opening at *para* position	122	+99	118	+96
Step 3					
3-1	*CH-C_6H_5 → *C-C_6H_5 + H*	80	+5	76	+1
3-2	*CH-C_6H_5 → *CH + C_6H_5*	113	+47	113	+48
3-3	*CH-C_6H_5 → *CH-C_6H_4* + H* (*ortho*)	116	+61	119	+64

3-4	*CH-C_6H_5 → *CH-C_6H_4* + H* (*meta*)	138	+93	135	+86
3-5	*CH-C_6H_5 → *CH-C_6H_4* + H* (*para*)	143	+91	145	+85
3-6	Ring opening at *ortho* position	101	+74	106	+67
3-7	Ring opening at *meta* position	168	+130	159	+125
3-8	Ring opening at *para* position	123	+107	130	+103
Step 4					
4-1	*C-C_6H_5 → *C + C_6H_5*	168	+92	170	+97
4-2	*C-C_6H_5 → *C-C_6H_4* + H* (*ortho*)	112	+65	112	+62
4-3	*C-C_6H_5 → *C-C_6H_4* + H* (*meta*)	148	+93	151	+89
4-4	*C-C_6H_5 → *C-C_6H_4* + H* (*para*)	144	+89	145	+84
4-5	Ring opening at *ortho* position	122	+104	120	+97
4-6	Ring opening at *meta* position	167	+128	166	+125
4-7	Ring opening at *para* position	123	+103	122	+96
Step 5					
5-1	*C-C_6H_4* → *C + C_6H_4*	158	+66	159	+70
5-2	*C-C_6H_4* → *C-C_6H_3* + H* (at C_3 position)	100	-7	98	-7
5-3	*C-C_6H_4* → *C-C_6H_3* + H* (at C_4 position)	142	+87	138	+81
5-4	*C-C_6H_4* → *C-C_6H_3* + H* (at C_5 position)	154	+137	153	+129
5-5	*C-C_6H_4* → *C-C_6H_3* + H* (at C_6 position)	124	+65	121	+62
5-6	Ring opening at C_1 position	84	+33	85	+29
5-7	Ring opening at C_2 position	136	+78	137	+71
5-8	Ring opening at C_3 position	112	+58	115	+50
5-9	Ring opening at C_4 position	130	+104	126	+99
5-10	Ring opening at C_5 position	167	+145	167	+141
5-11	Ring opening at C_6 position	159	+109	159	+102

2. Model of p(4x8) Ni(111) with four missing row to create B5 and F4 step site.

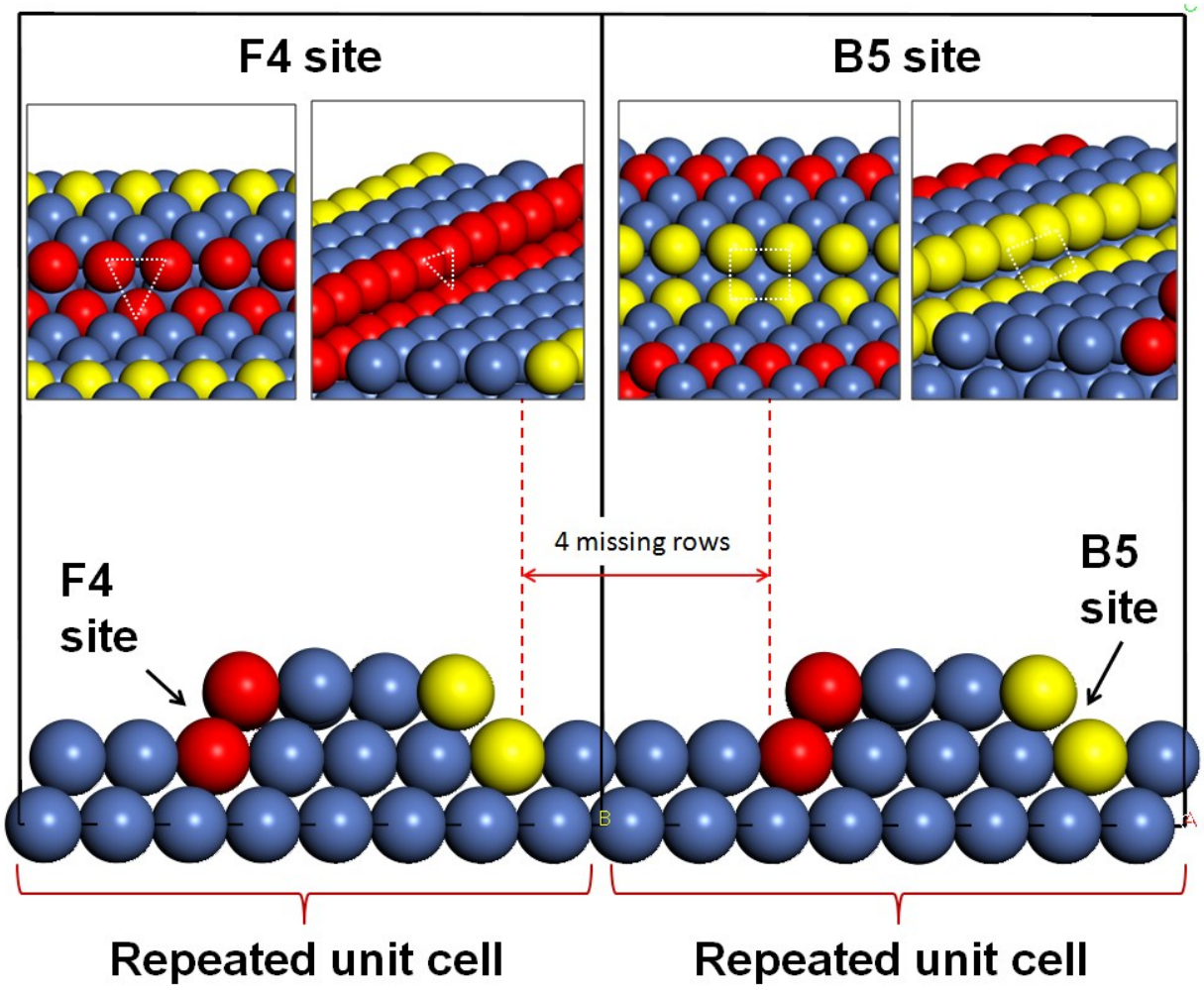

Figure S1. Generation of B5 and F4 step site in the p(4x8) Ni(111) with 4 missing row on the top layer. Atoms at B5 step site are highlighted in yellow color, and atoms at F4 step site are highlighted in red color. B5 and F4 sites are indicated by square and triangles, respectively.

3. Different adsorption configurations of toluene on Ni(111) surface and their relative stability.

There are different high symmetry sites for the adsorption of toluene: bridge (30), bridge (0), hollow (0), hollow (30), named from the site where the center of the ring bound to the surface (hollow or bridge site) and the orientation of the C-C bond at two opposite corner relative to the horizontal axis (0 or 30 degree).

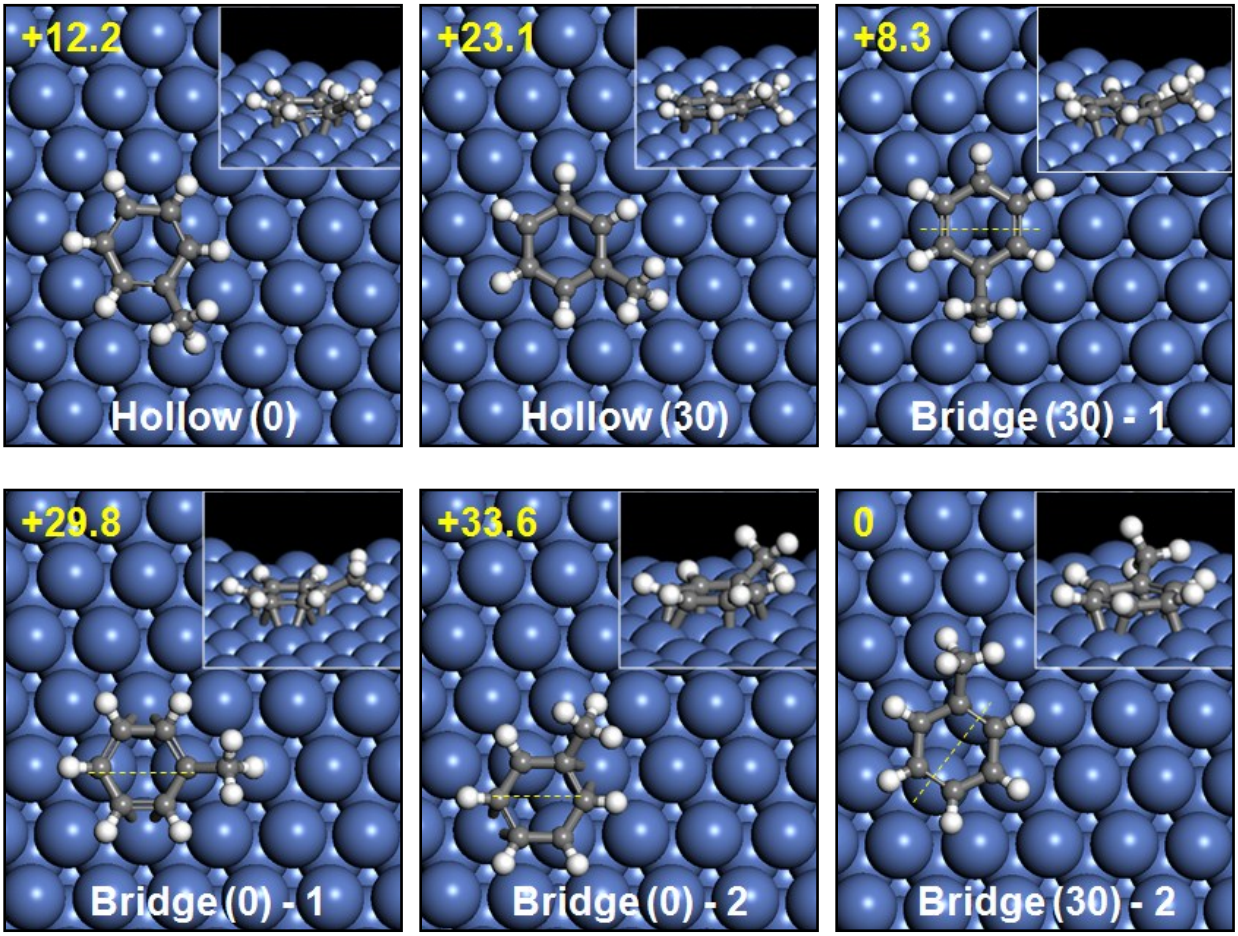

Figure S2. Different adsorption configurations of toluene on Ni(111) surface. Relative energies to the energy of the most stable configuration (bridge (30)-2) are inserted in kJ/mol. Bridge-1 and Bridge-2 differs by the position of toluene coordinates across the *meta* position (bridge-1) and *ortho* position (bridge-2)

4. Decomposition of Toluene on Ni(111) surface:

4.1. Step 1.

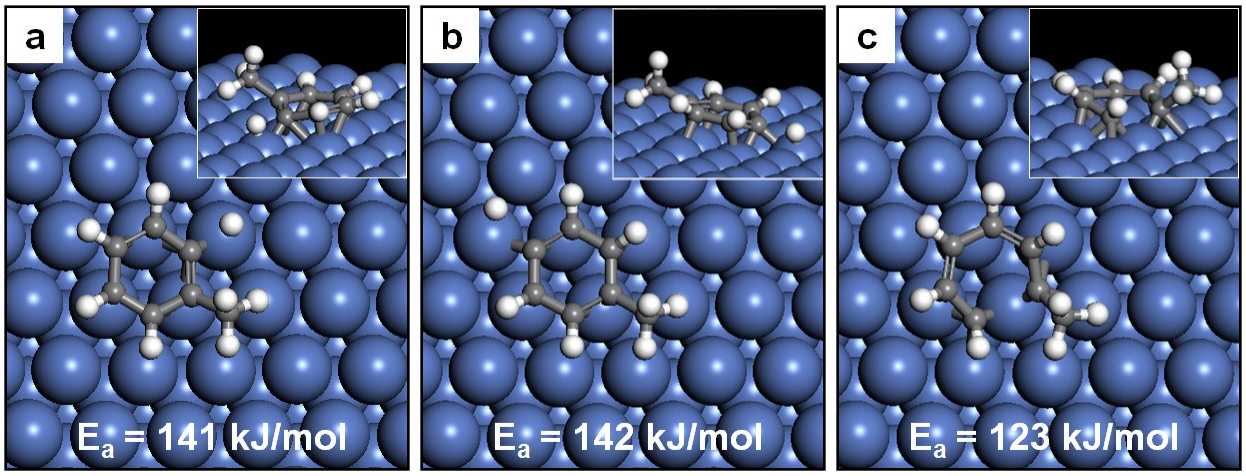

Figure S3. Initial activations of Toluene on Ni(111) surface: (a) aromatic C-H activation at *ortho* position; (b) aromatic C-H activation at *para* position; (c) ring opening at *ortho* position. Insertion are side view of the structures. Adsorption energy, activation barrier and distance are also shown.

4.2. Step 2

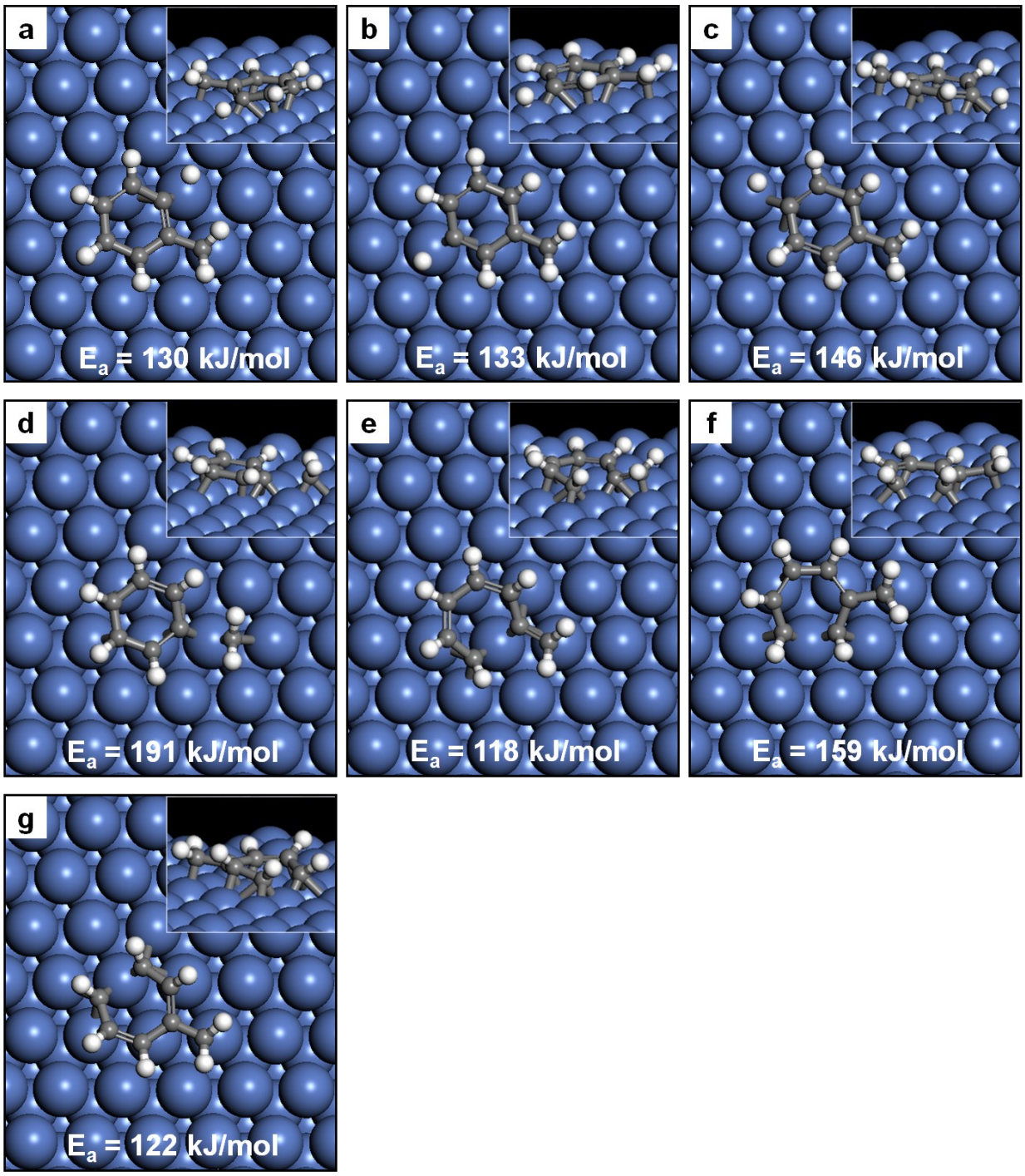

Figure S4. Decomposition of Toluene on Ni(111) surface in Step 2: (a) aromatic C-H activation at *ortho* position; (b) aromatic C-H activation at *meta* position; (c) aromatic C-H activation at *para* position; (d) aliphatic C-C dissociation; (e) ring opening at *ortho* position; (f) ring opening at *meta* position; (g) ring opening at *para* position.

4.3. Step 3

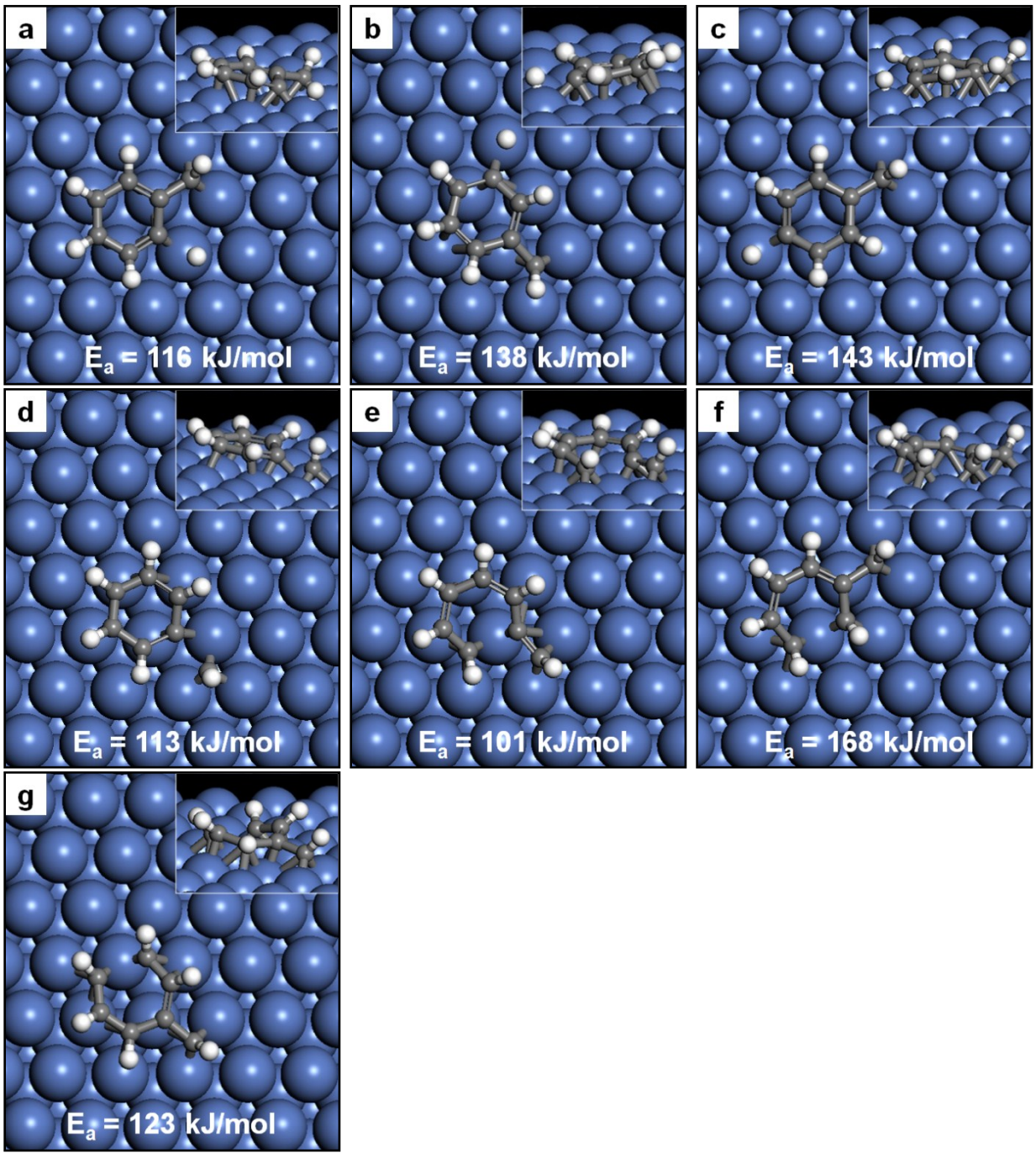

Figure S5. Decomposition of Toluene on Ni(111) surface in Step 3 (a) aromatic C-H activation at *ortho* position; (b) aromatic C-H activation at *meta* position; (c) aromatic C-H activation at *para* position; (d) aliphatic C-C dissociation; (e) ring opening at *ortho* position; (f) ring opening at *meta* position; (g) ring opening at *para* position.

4.4. Step 4

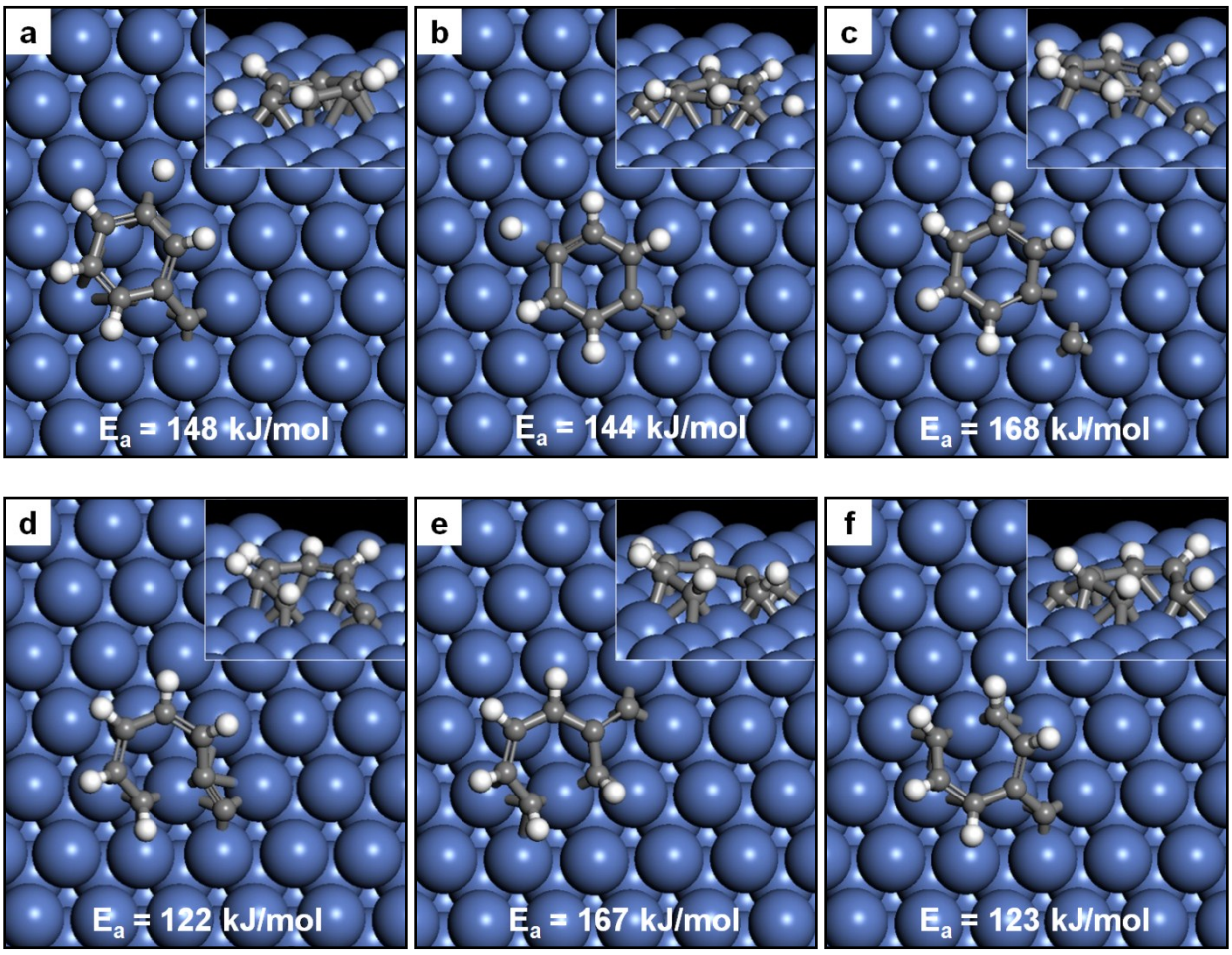

Figure S6. Decomposition of Toluene on Ni(111) surface in Step 4: (a) aromatic C-H activation at *meta* position; (b) aromatic C-H activation at *para* position; (c) aliphatic C-C dissociation; (d) ring opening at *ortho* position; (e) ring opening at *meta* position; (f) ring opening at *para* position.

4.5. Step 5

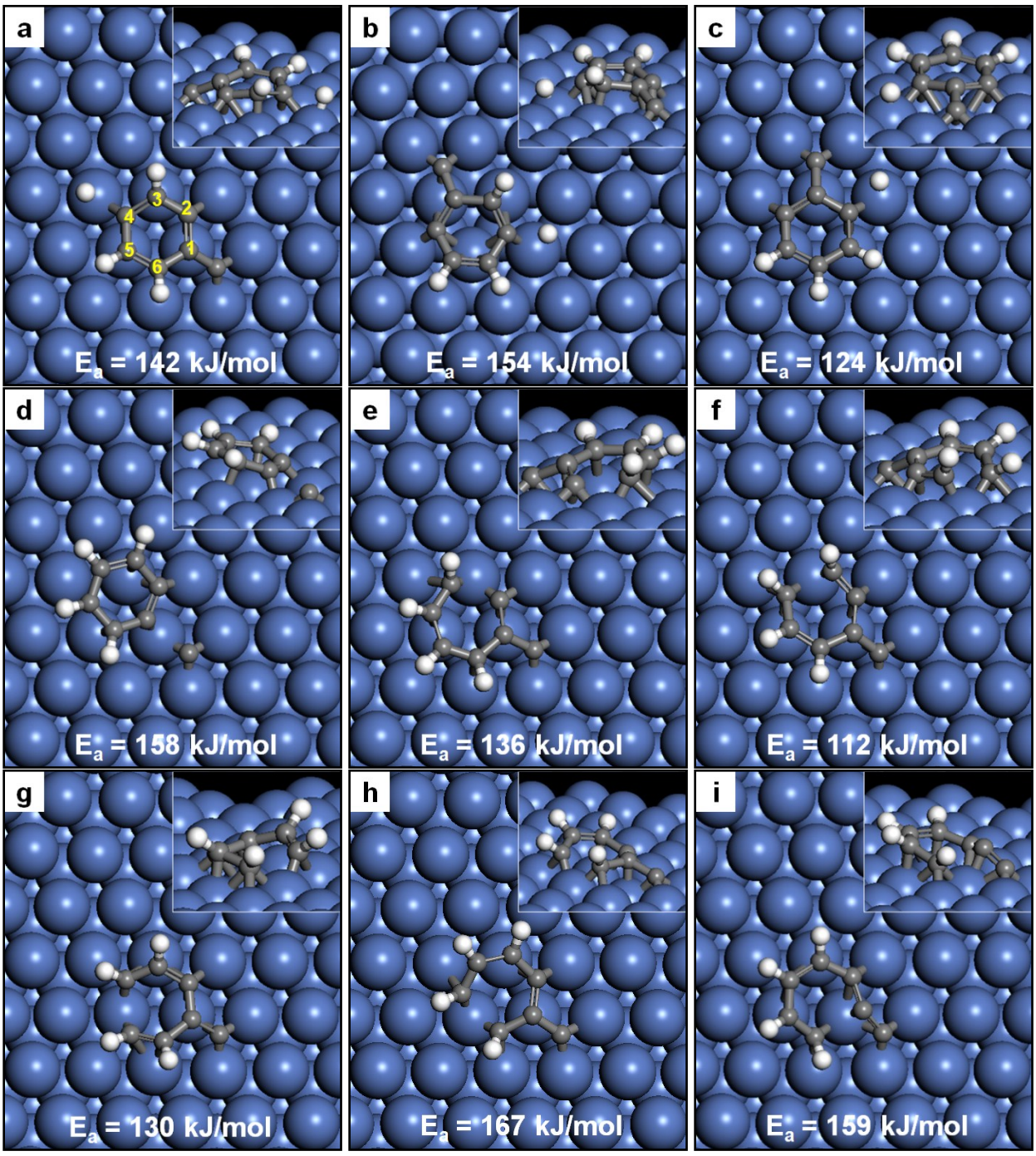

Figure S7. Decomposition of Toluene on Ni(111) surface in Step 5: (a) ring C-H activation at C_4 position; (b) ring C-H activation at C_5 position; (c) ring C-H activation at C_6 position; (d) aliphatic C-C dissociation; (e) ring opening at C_2 position; (f) ring opening at C_3 position; (g) ring opening at C_4 position; (h) ring opening at C_5 position; (i) ring opening at C_6 position.

5. Decomposition of Toluene on B-Ni surface

5.1. Step 1.

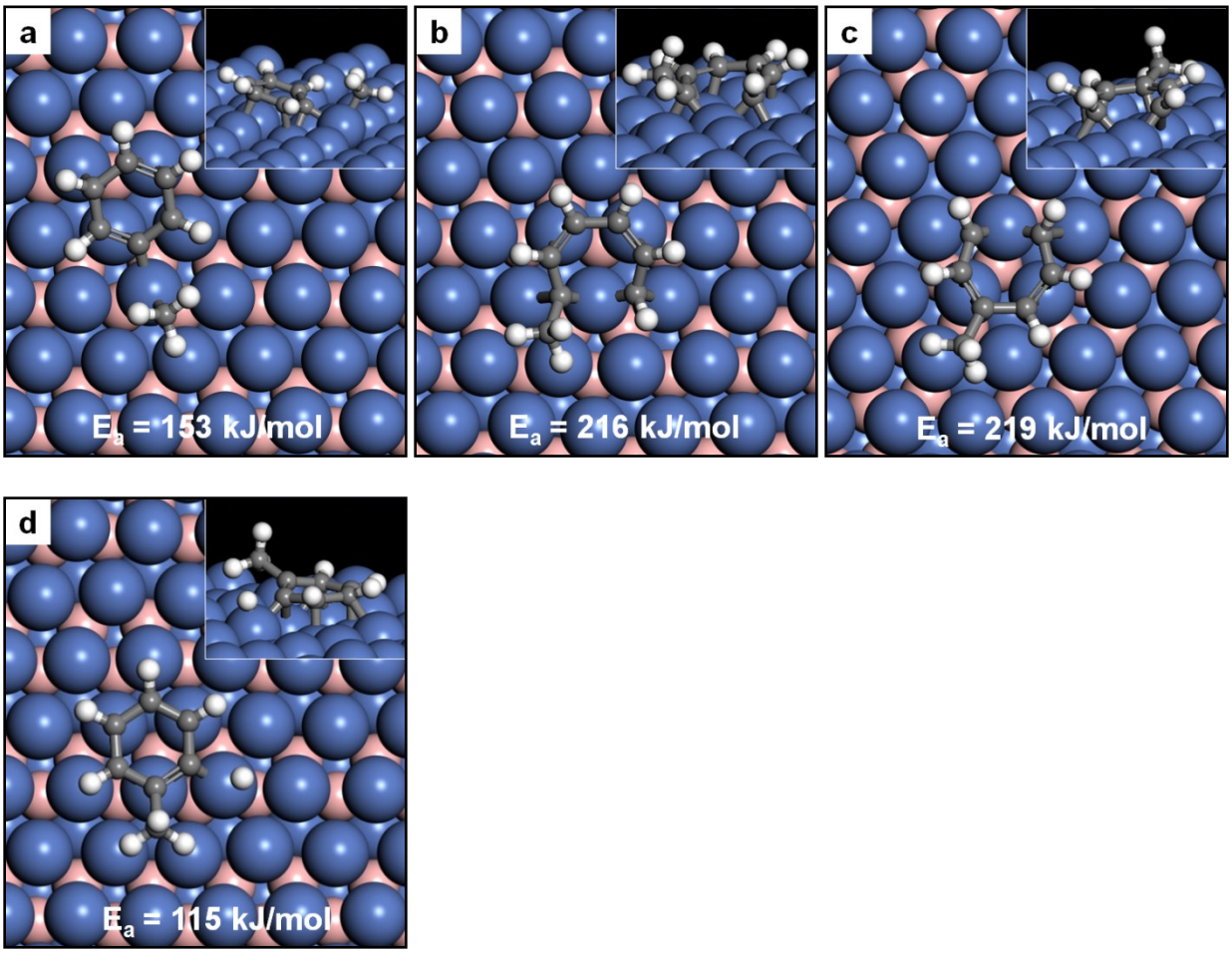

Figure S8. Initial activations of Toluene on B-Ni surface: (a) aliphatic C-C dissociation; (b) ring opening at *ortho* position; (c) ring opening at *para* position; (d) aromatic C-H activation at *ortho* position.

5.2. Step 2

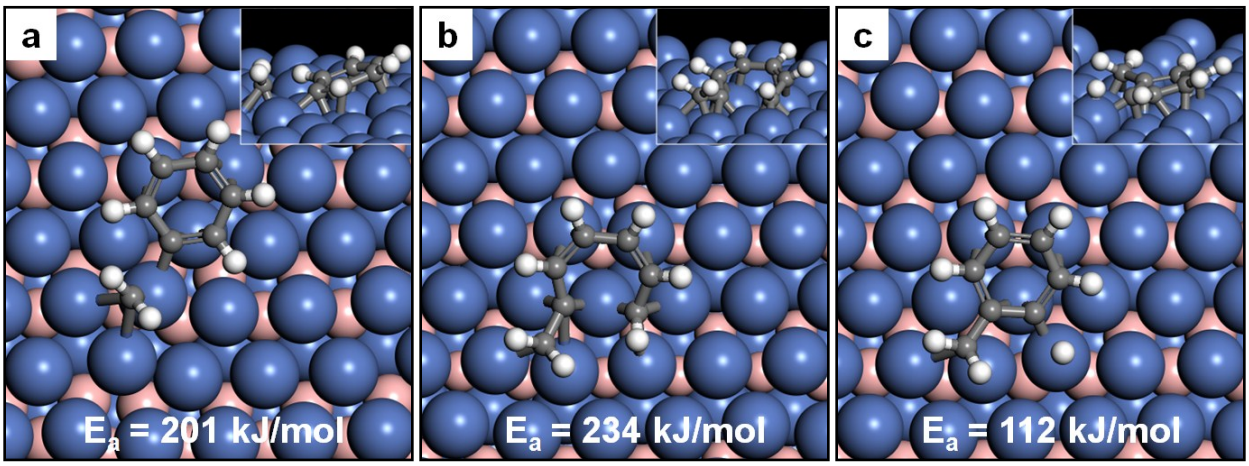

Figure S9. Activations of Toluene on B-Ni surface in Step 2: (a) aliphatic C-C dissociation; (b) ring opening at *ortho* position; (c) aromatic C-H activation at *ortho* position.

5.3. Step 3 and Step 4.

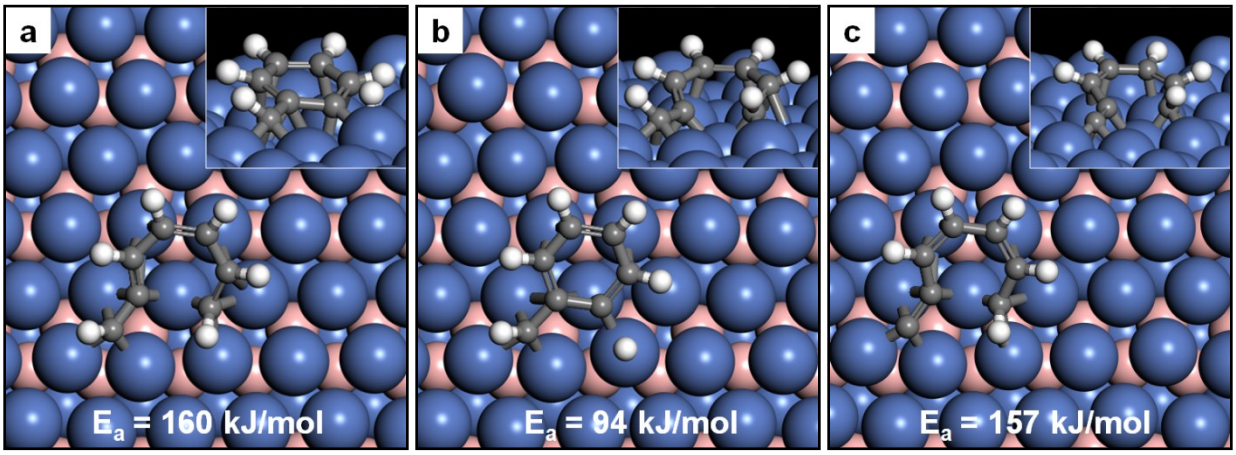

Figure S10. Activations of Toluene on B-Ni surface in Step 3: (a) ring opening at *ortho* position; (b) aromatic C-H activation at *ortho* position and (c) ring opening at *ortho* position in Step 4.

6. Adsorption of toluene on the p(4x8) Ni(111) with four missing row.

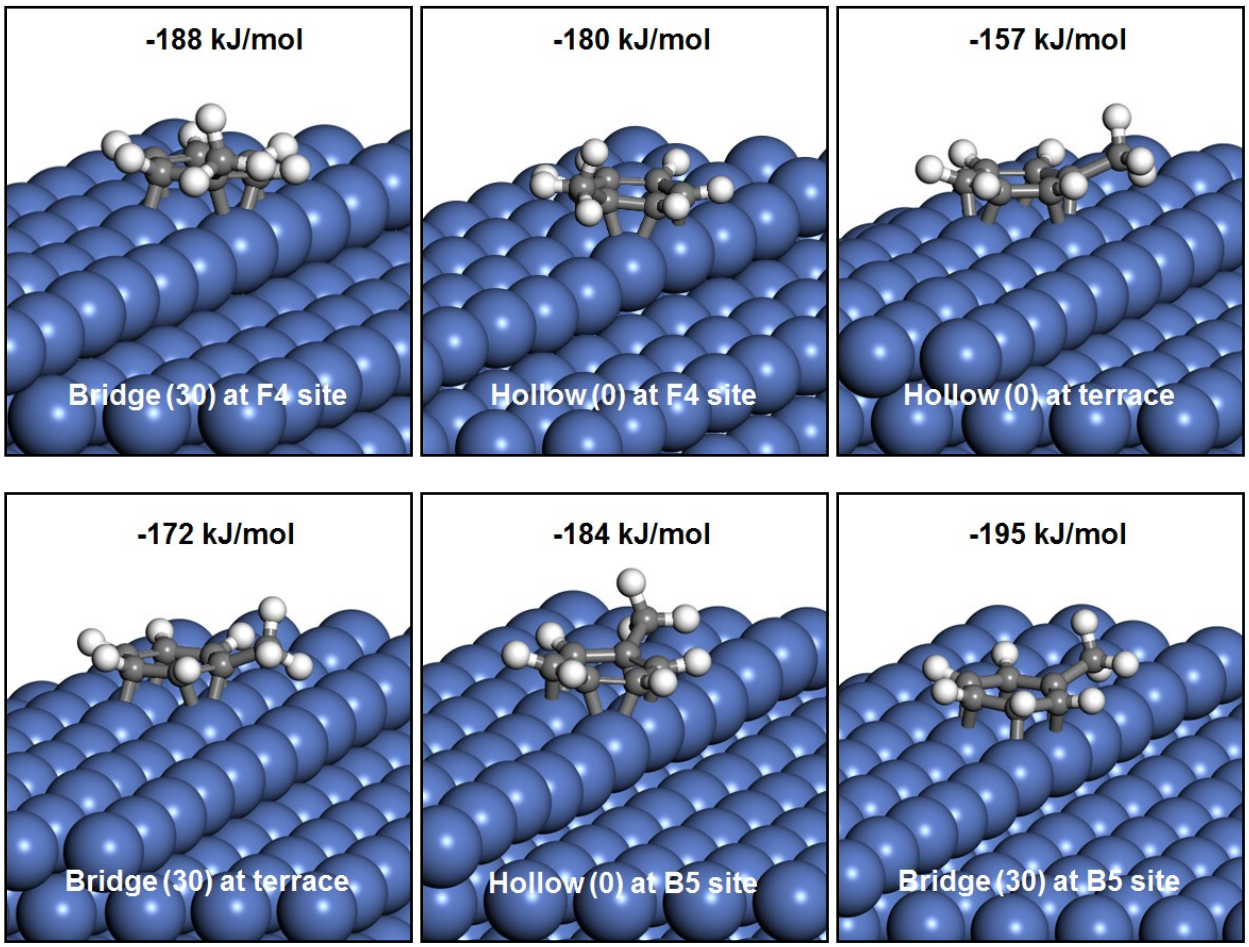

Figure S11. Adsorption of toluene on the p(4x8) Ni(111) with four missing row at different positions. The adsorption energies are also shown.