Electronic Supplementary Information

Reactivity and Mechanism Investigation for Selective Hydrogenation of 2,3,5-Trimethylbenzoquinone on *in-situ* Generated Metallic Cobalt

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Content

Catalysts Preparation Method.

The CoO_x@CN catalyst was prepared by thermal condensation of GAH, melamine, and $Co(CH_3COO)_2{\bullet}4H_2O$. In typical, a mixture of 1g GAH, 40 g melamine and 0.814 g cobalt acetate were dissolved in diluted water and stirred under 80 ^oC. Then the dried solid were grinded into powder and directly calcined under a N_2 flow of 400 mL min^{-1}. The temperature was increased to 900 ^oC and held for 1h after the furnace was firstly heated to 600 ^oC and kept for 1h. Afterwards, the sample was cooled down to room temperature. Finally, the product was ground in the crucible and CoO_x@CN was obtained. The CoO_x@CN-800, and CoO_x@CN-1000 were prepared under the method except that the pyrolysis temperature was 800 ^oC and 1000 ^oC, respectively. In similar, CoO_x@M, CoO_x@G and CN were made from mixtures of cobalt acetate & melamine, cobalt acetate & GAH and melamine & GAH at 900 ^oC. The way to fabricate CoO_x@GL catalyst was the same as CoO_x@CN, except that glucose was used as carbon source. The sample of CoO_x@NCNTs and CoO_x@CN-S were synthesized by applying cobalt nitrate and cobalt sulfate as cobalt source via the same pyrolysis process as CoO_x@CN. The preparation way of CoO_x@NCNTs was in line with paper.[1] The AT-CoO_x@CN catalysts were acquired by acid treatment of CoO_x@CN with 2 M HCl solution for 3 days at 50 ^oC. Co_3O_4/SiO_2, Co_3O_4/ZrO_2 and Co_3O_4/TiO_2 were all obtained by impregnation method. In typical, 1g SiO_2 and 1.56g cobalt nitrate were dissolved in 15 mL deionized water. Then the mixture was heated at 80 ^oC with stirring to remove water. After the dried solid was grounded finely, it was roasted in the muffle at 450 ^oC for 2h. Finally, the corresponding supported cobalt oxide (named as Co_3O_4/SiO_2) was obtained.

Figure S1. TEM images of CoOx@M (a) and CoOx@G (b); BET (c) and Nitrogen content (d) analysis of CoOx@M, CoOx@G and CoOx@CN.

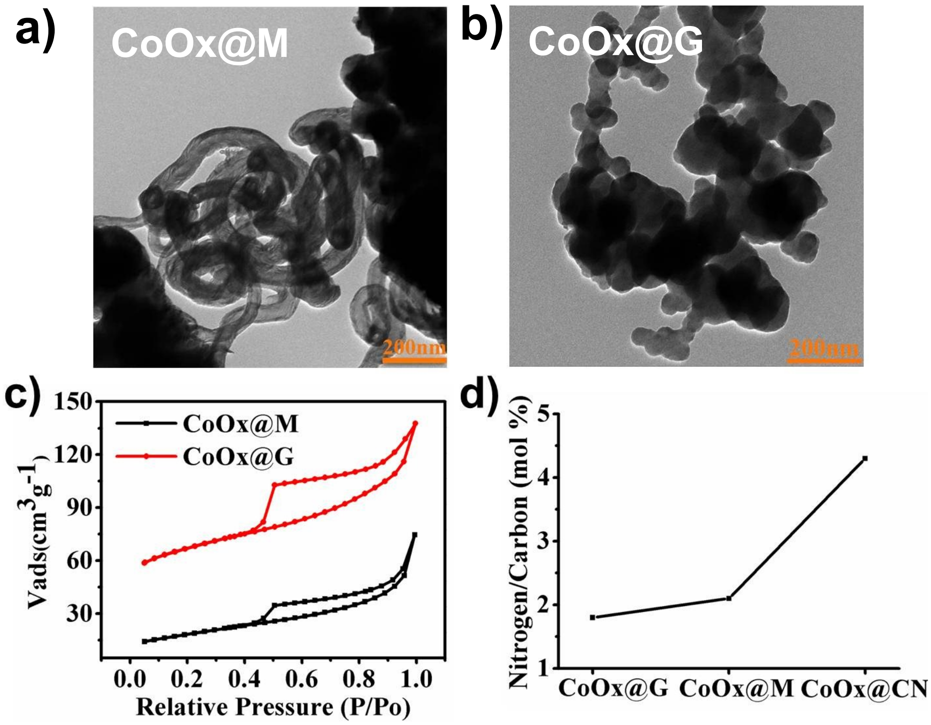
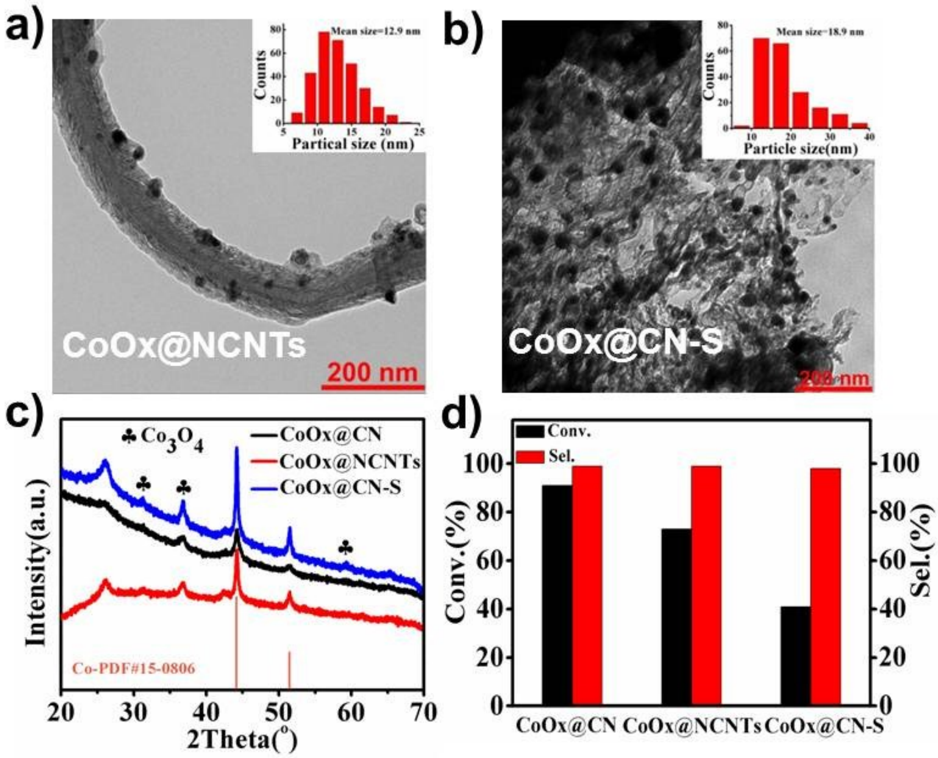


Figure S2. TEM images of CoO_x@NCNTs (a) and CoO_x@CN-S (b); XRD pattern (c) of CoO_x@NCNTs and CoO_x@CN-S; Catalytic performance under the same reaction condition (6.7 mmol TMBQ, 1.6 mol% Co to substrate, 15mL i-propanol, 120 ^oC, 2 MPa H_2 , 6 h).



Note: The average size of CoOx@NCNTs and CoOx@CN-S is 12.9 nm and 18.9 nm, respectively.

Figure S3. TEM images of the catalysts pyrolyzed at 800 ^oC (a) and 1000 ^oC (b); (c) and (d) are BET and XRD patterns.

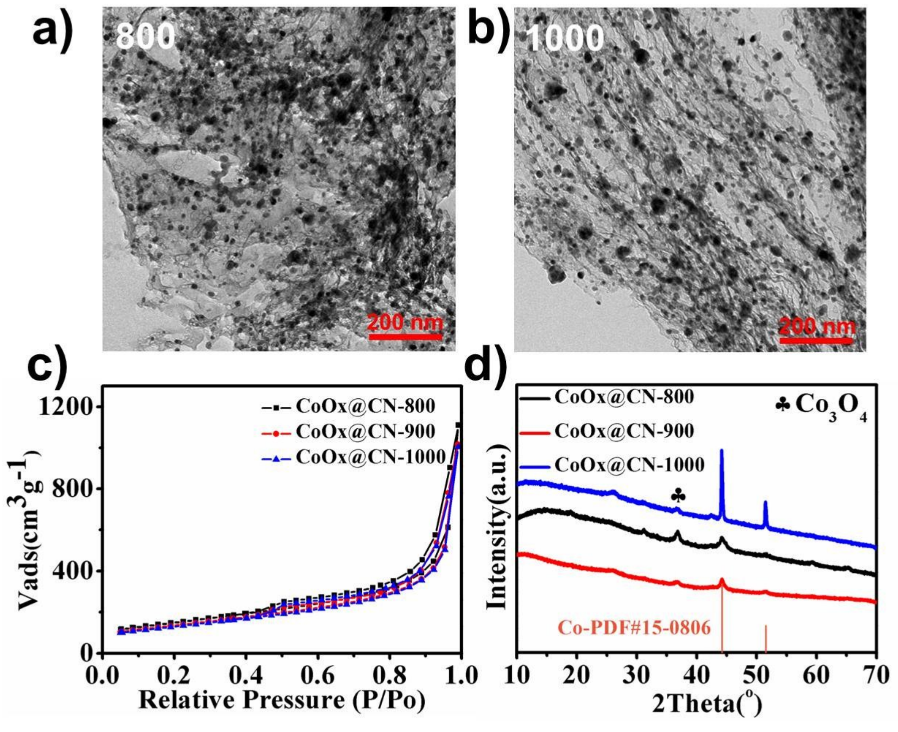


Figure S4. TEM characterization (a), XRD plots (b), BET analysis (c) and Nitrogen content (d) of CoOx@GL.

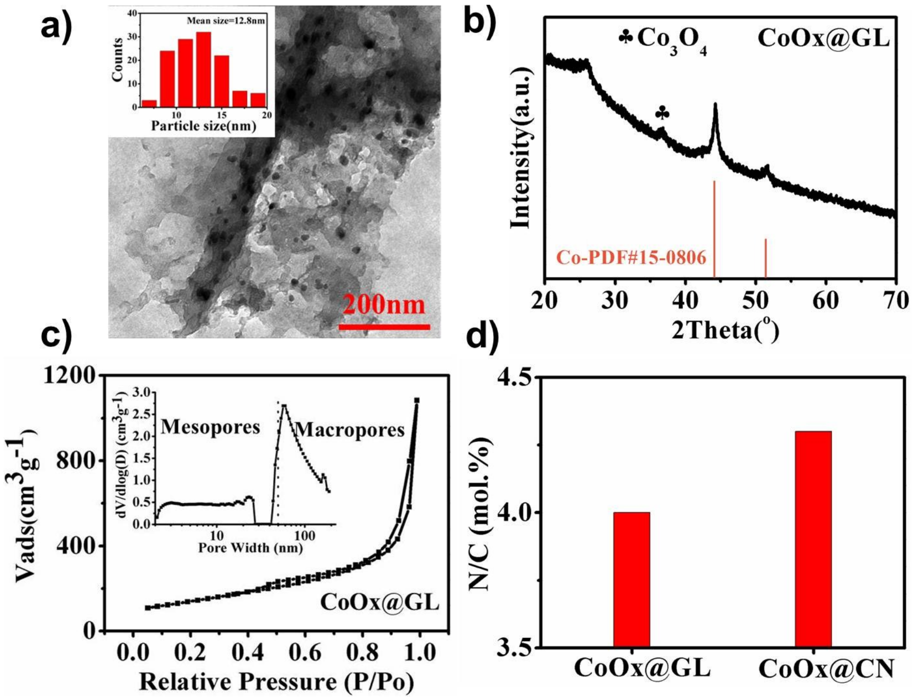


Figure S5. XRD patterns (a) of the three supported cobalt oxide catalysts before and after reaction;TEM pictures (b) of the three supported cobalt oxide catalysts.

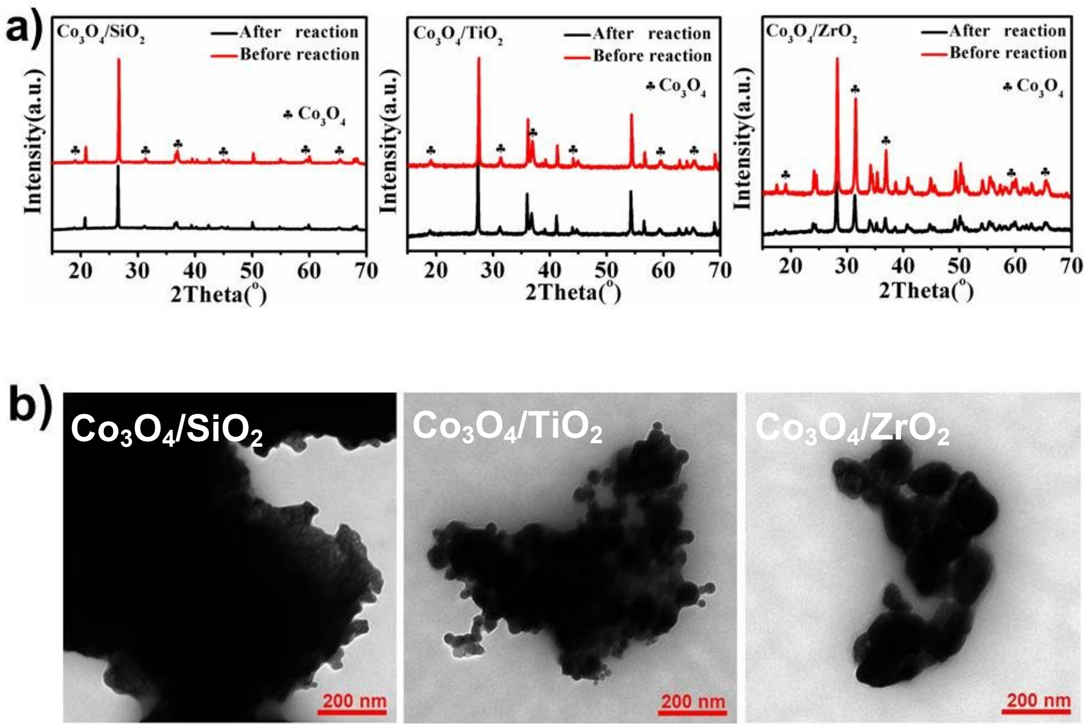


Figure S6. (a) XRD and (b) HRTEM image of AT-CoOx@CN

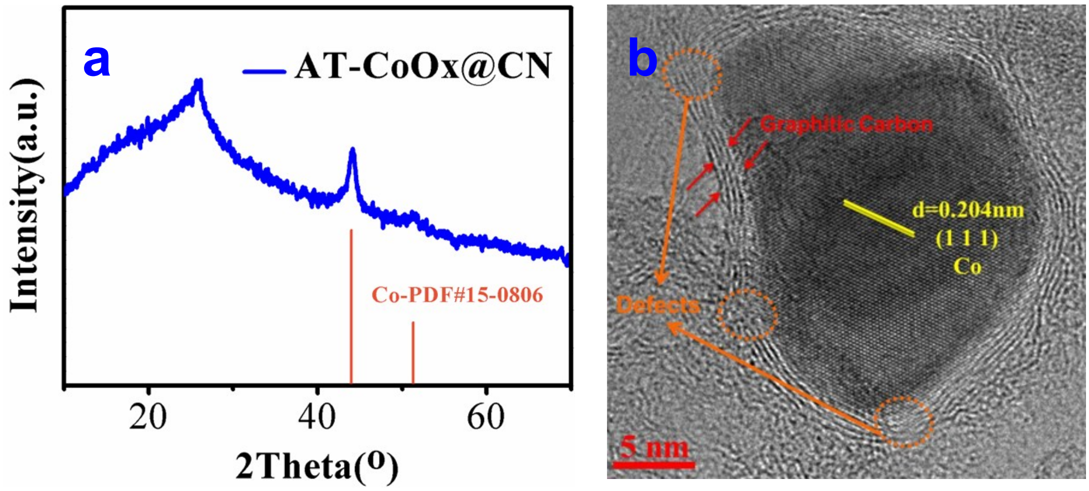


Figure S7. The energy changes as TMBQ closing to Co (1 1 1) surface gradually.

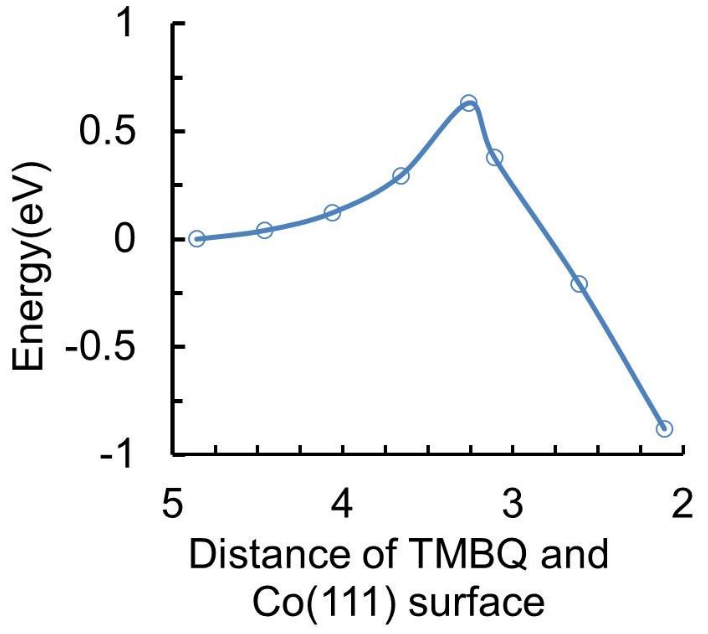
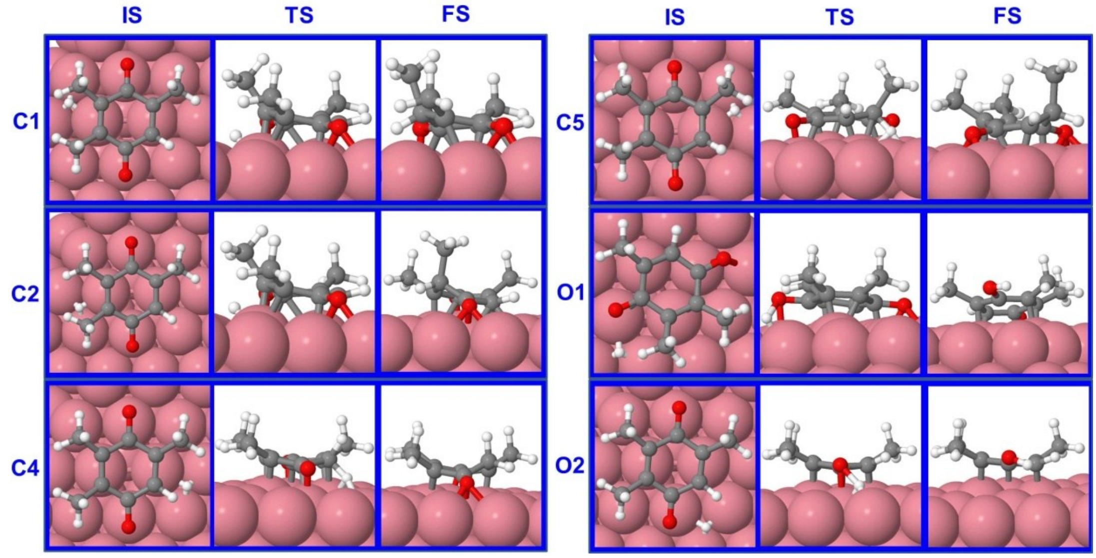


Figure S8. Configurations during the first-step hydrogenation of TMBQ.



Note: IS, TS and FS mean Initial State, Transition State and Final State.

Table S1. K-point tests.

K-point	E_{ads}/eV	ΔE_{C2}/eV
1×1×1	-0.88	0.16
2×2×1	-0.67	-
3×3×1	-0.51	-0.19

E_{ads} means the adsorption energy of the most stable configuration for TMBQ on Co (111) surface. ΔE_{C2} means the enthalpy change for the first hydrogenation on C2 atom. The energy changes of E_{ads} andΔE_{C2} under 1×1×1 and 3×3×1 k-point meshes are 0.37 and 0.34 eV respectively, with the random error of about 0.03 eV. These results indicate that 1×1×1 k-point mesh is barely tolerable.

Table S2. BET analysis.

	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Pore Size (nm)
CoO_x@M	65	0.12	6.5
CoO_x @G	217	0.21	4.8
CoO_x @CN	484	1.57	11.8
CoO_x @NCNTs	254	0.67	9.6
CoO_x @CN-S	272	0.68	8.0
CoO_x @CN-800	531	1.72	11.7
CoO_x @CN-1000	464	1.55	11.3
CoOx @GL	500	1.68	12.1

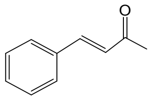
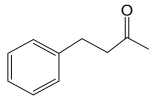
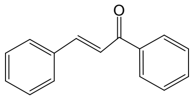
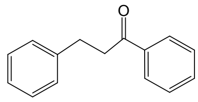
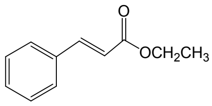
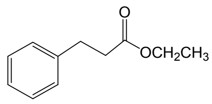
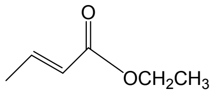
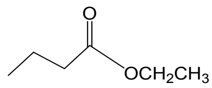
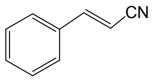
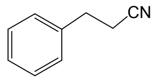
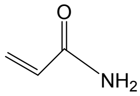
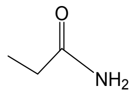
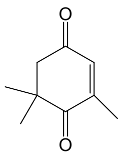
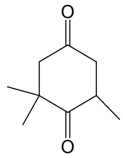
Note:

1) CoO_x@M and CoO_x@G were made from mixtures of cobalt acetate & melamine and cobalt acetate & GAH, respectively.
2) The cobalt resource of CoO_x @NCNTs and CoO_x @CN-S were cobalt nitrate and cobalt sulfate.
3) CoO_x @CN-800 and CoO_x @CN-1000 prepared at 800 ^oC and 1000 ^oC, respectively.
4) CoO_x @GL was synthesized by using glucose as carbon source.

Table S3. ICP results.

Sample	**Co (wt %)**
CoO_x@CN-800	33.6
CoO_x@CN-900	31.6
CoO_x@CN-1000	32
AT-CoO_x@CN	10.8
CoO_x@G	44.3
CoO_x@M	43
CoO_x@GL	29.3
Co_3O_4/SiO_2	23.1
Co_3O_4/ZrO_2	22.7
Co_3O_4/TiO_2	23.3

Table S4. Hydrogenation of various α,β-unsaturated carbonyls over $CoO_x@CN$ [a]

Entry	Substrate	Product	Time (h)	Conv.(%)	Yield (%)
1			3.5	99	99
2			2.5	99	99
3			1.5	99	99
4			1.5	99	99
5			2.5	99	99
6			1	99	99
7[b]			2	97	94

[a]Reaction conditions: 0.5 mmol reactant, 16 mol% Co to substrate, 15 mL ethanol, 100 °C, 2 MPa H_2; [b]Reaction conditions: 0.5 mmol reactant, 16 mol% Co to substrate, 15 mL ethanol, 80 °C, 2 MPa H_2. All the results were determined by GC and GC-MS.

Table S5. The optimized stable configurations with the corresponding adsorption energies.

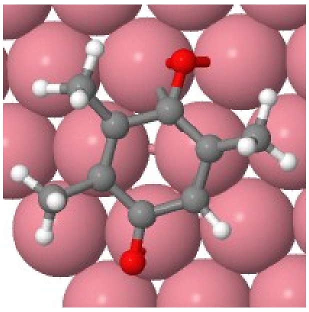
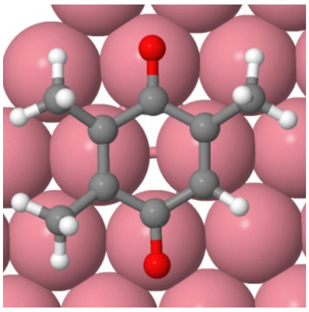
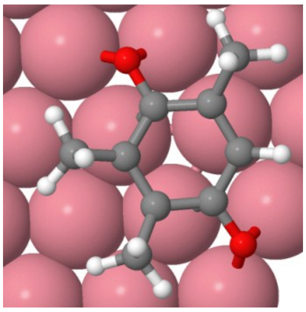
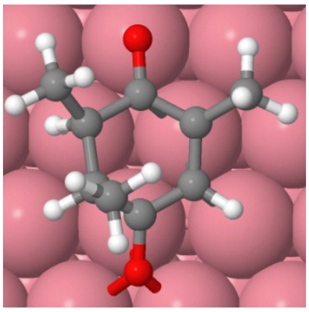
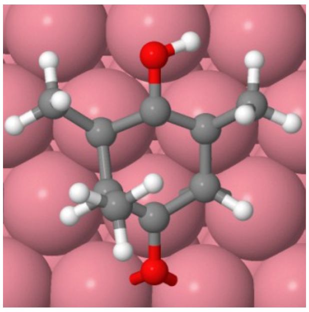
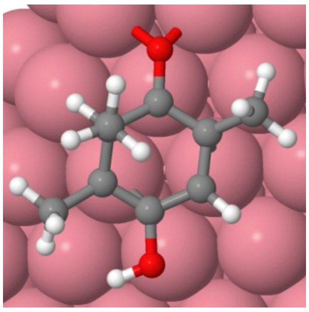
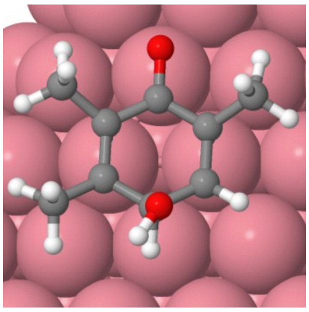
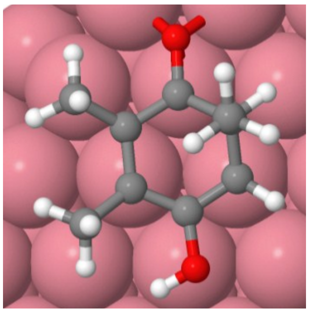
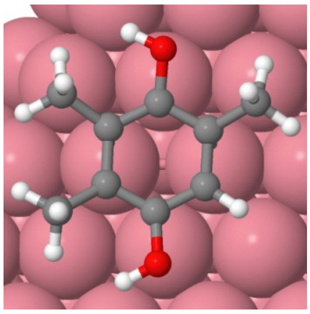
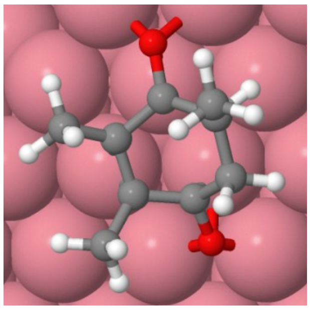
Stable Configurations	Energy (eV)
	-0.76
	-0.88
	-0.87

Table S6. Energy of the first hydrogen adatom added to TMBQ.

Position	$E_{initial}$ (eV)	E_{final} (eV)	Ea (eV)
C1	0.31	0.70	0.73
C2	0.32	0.47	0.77
C4	0.37	0.76	0.81
C5	0.38	0.49	0.69
O1	0.30	0.57	0.86
O2	0.37	0.56	0.69

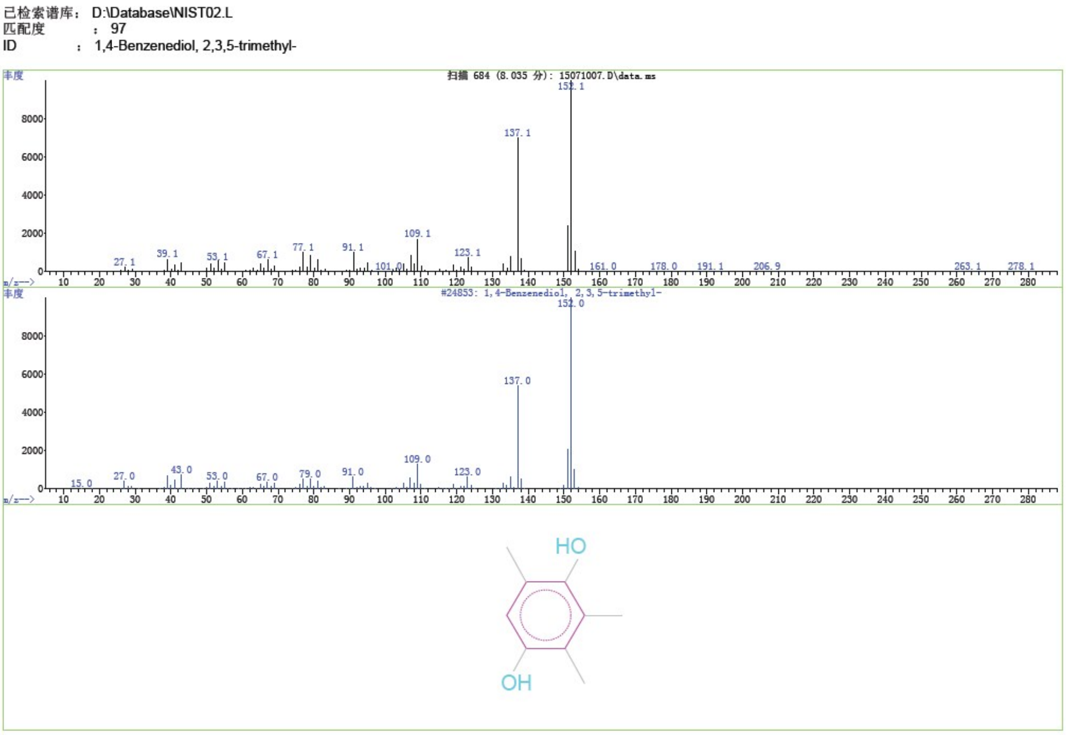
Table S7. Energy of two hydrogen adatom added to TMBQ.

First Hydrogenated atom	Second Hydrogenated atom	Energy (eV)	Configurations
C2	C1	0.76	
	O1	0.90	
O2	C1	1.16	
	C3	1.30	
	C5	1.20	

O2	O1	1.28	
C5	C4	0.92	

GC-MS results:

1.



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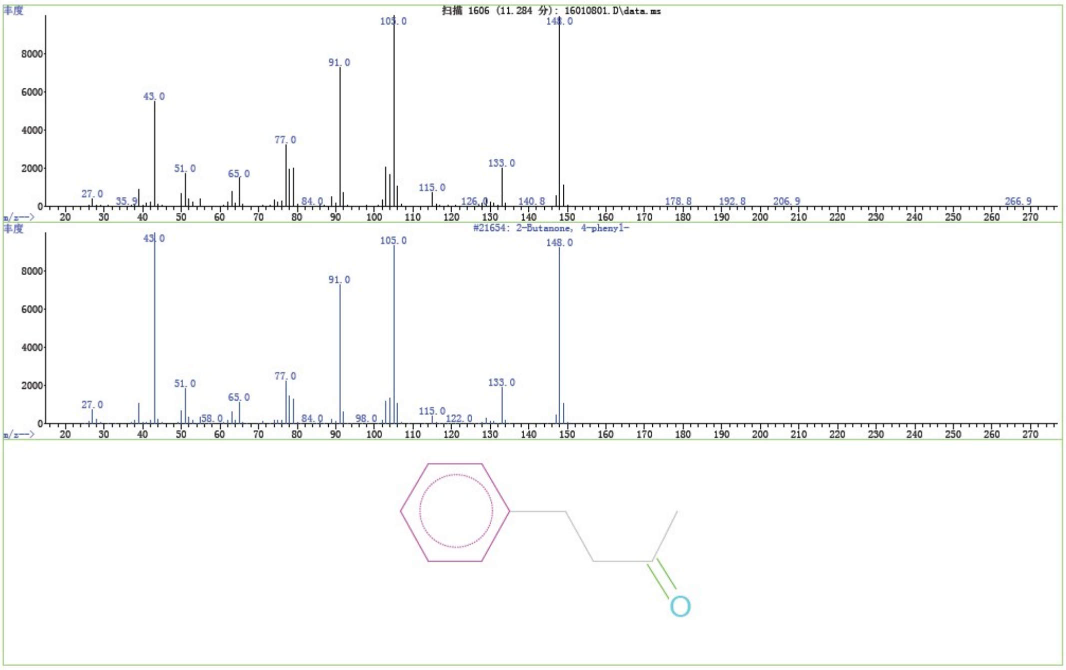

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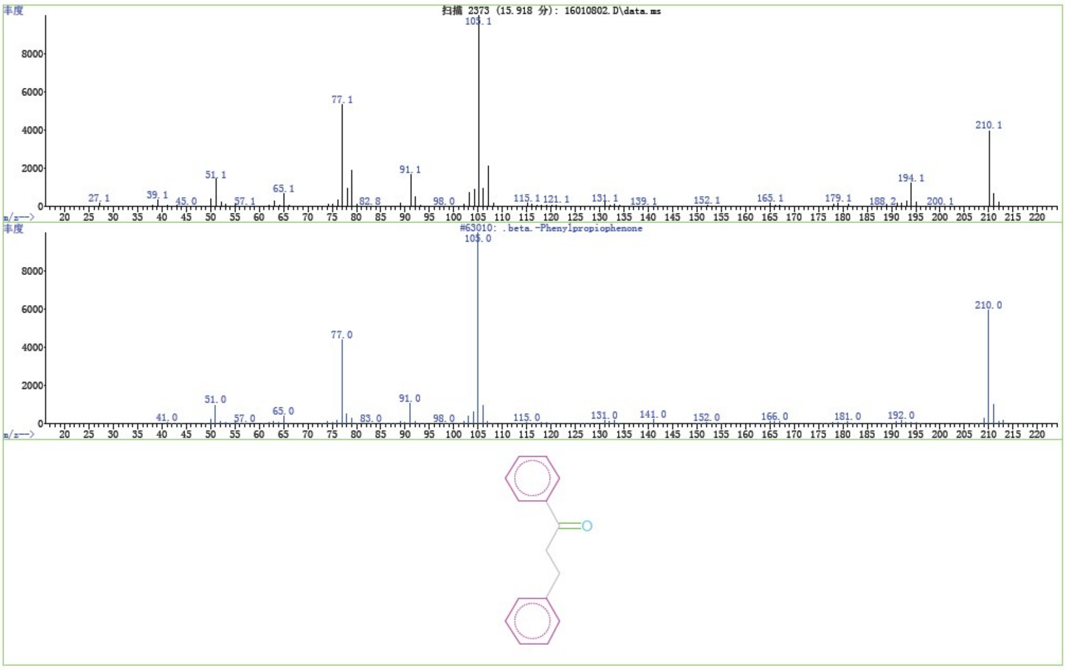

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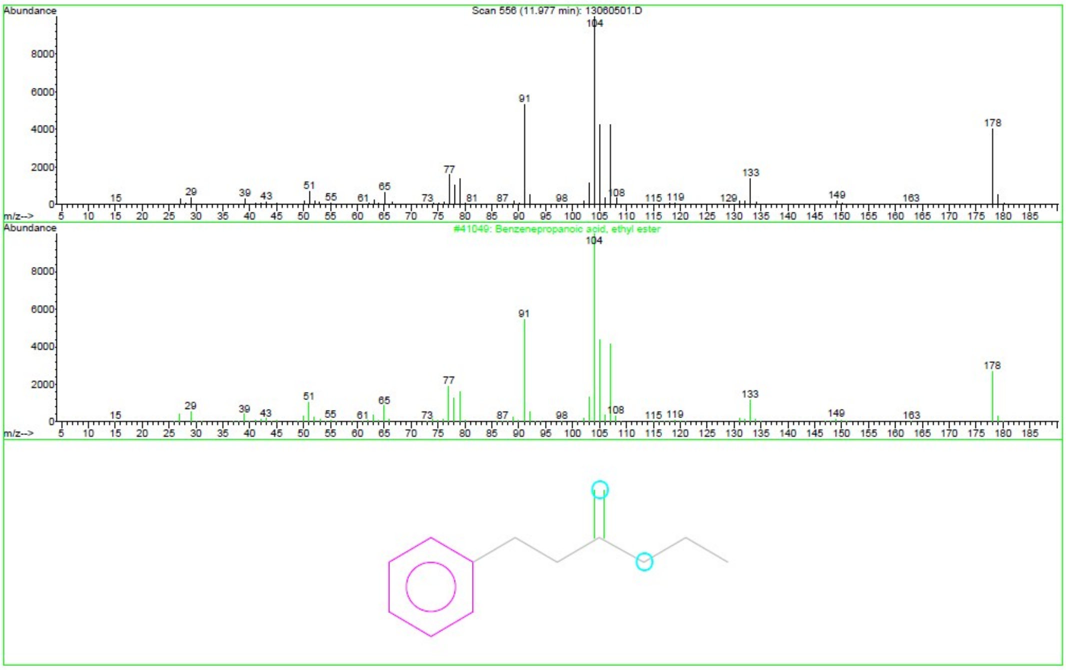

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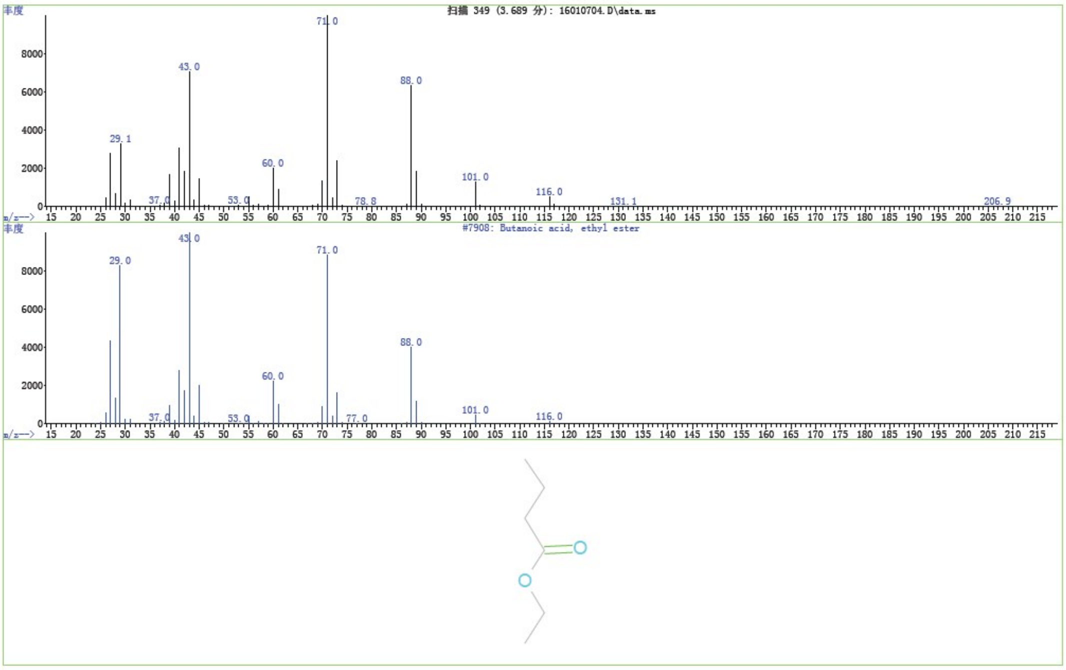

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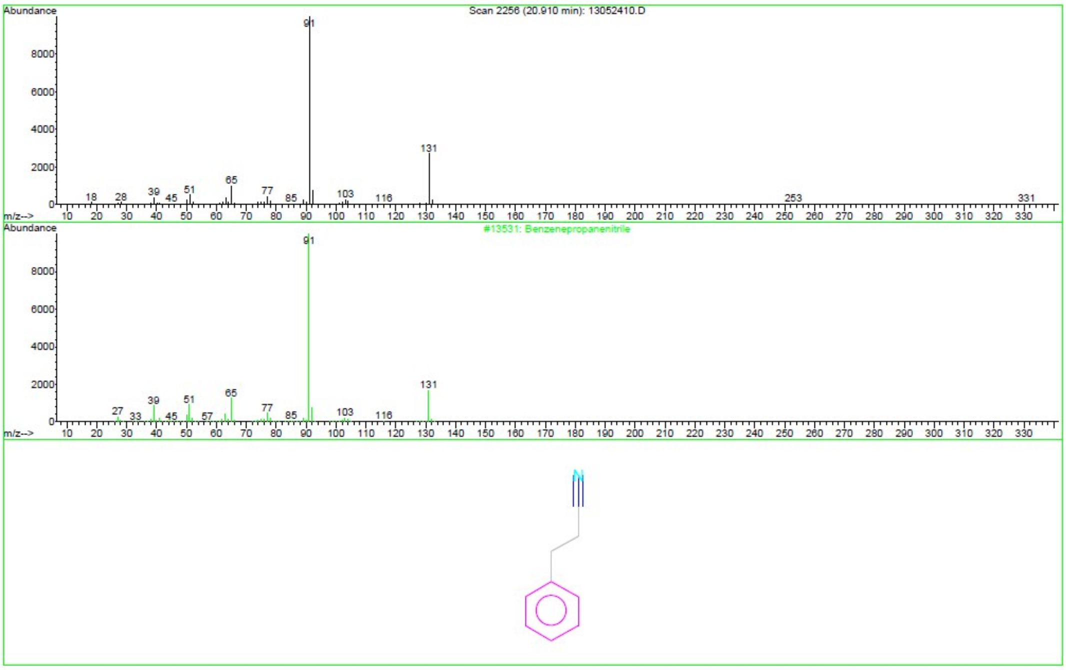

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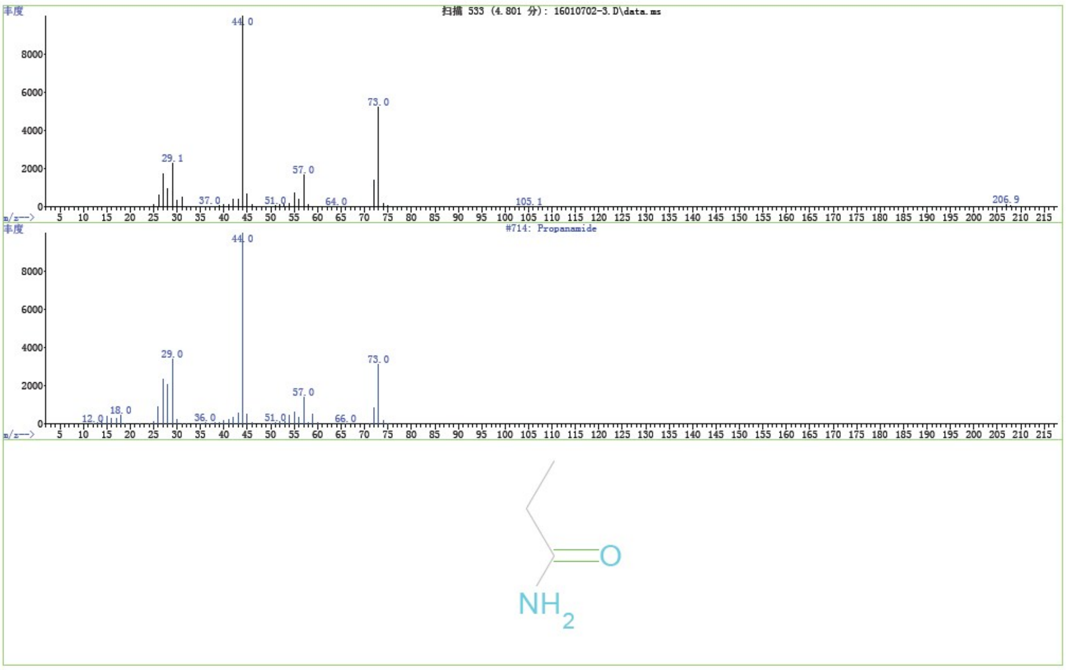

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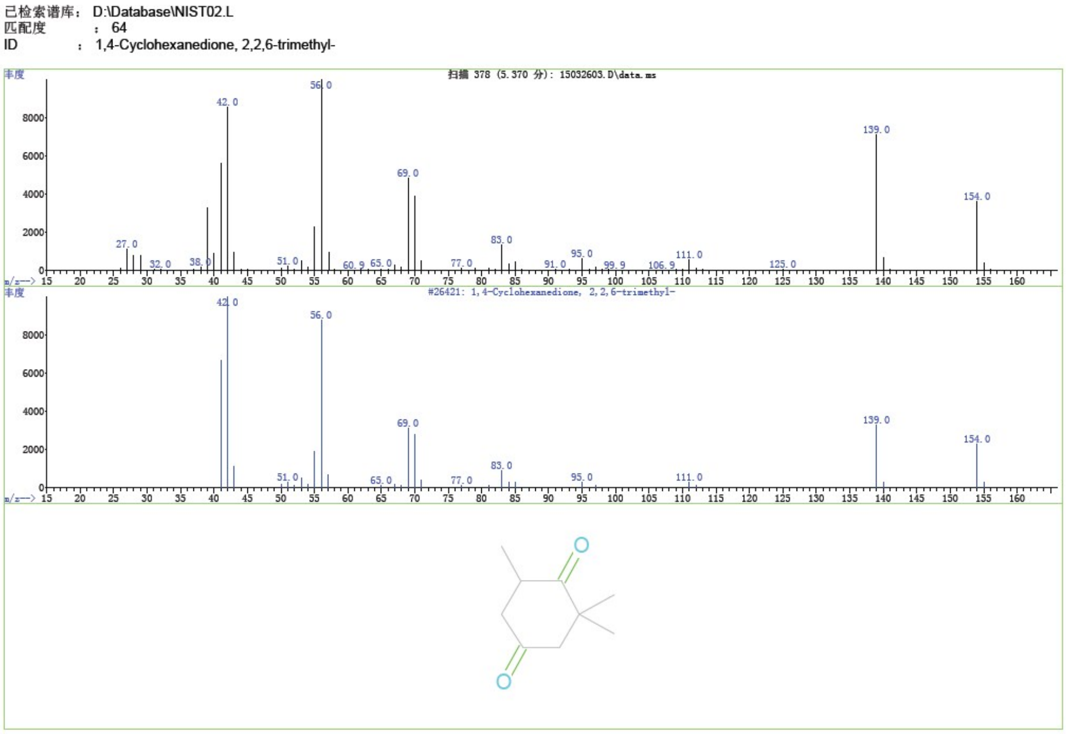

Reference

1 Z. Wei, J. Wang, S. Mao, D. Su, H. Jin, Y. Wang, F. Xu, H. Li and Y. Wang, *ACS Catal.*, 2015, 4783-4789.

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