Supporting Information

Visible Light-Catalytic Hydroxylation of Aryl Halides with Water to Phenols by Carbon Nitride and Nickel Complex Cooperative Catalysis

Kaixuan Wang, [a, b] Min Tong, [b] Yanan Yang, [b] Bingyu Zhang, [b] Helong Liu, [b] Hexing Li* [a, b] and Fang Zhang* [b]

[a]School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, 200237, Shanghai, China

[b]The Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, China

* Email: hexing-li@ shnu.edu.cn; zhangfang@shnu.edu.cn;

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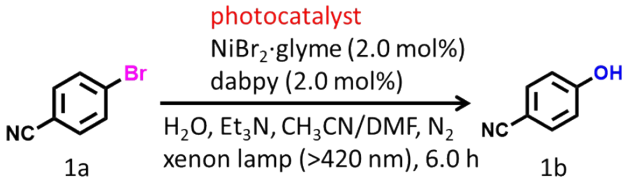
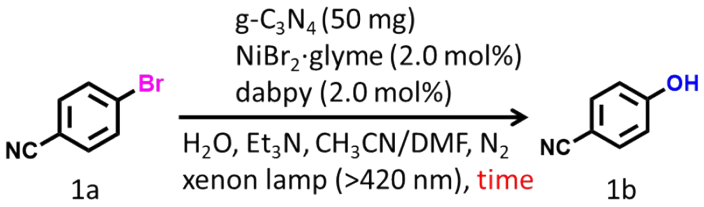
Table S1. Catalytic performances of different photocatalyst in the synthesis of phenol from 4-bromobenzonitrile.[a]



Entry	PC	Conversion (%)	Yield (%)[b]
1	Cu_2O	trace	trace
2	WO_3	trace	trace
3	α-Fe_2O_3	trace	trace
4	CdS	5.10	4.20
5	g-C_3N_4	67.1	66.5

[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), photocatalyst (50 mg), DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C. [b]Determined by HPLC anlysis against an internal standard.

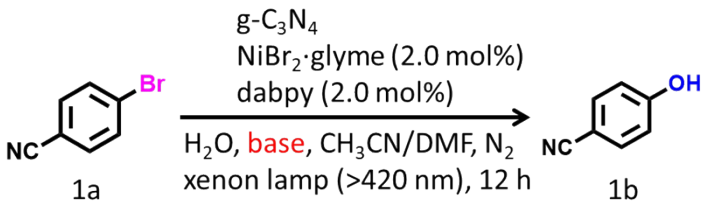
Table S2. Catalytic performances of different time in the synthesis of phenol from 4-bromobenzonitrile. [a]



Entry	Time (h)	Conversion (%)	Yield (%) [b]
1	2	18.3	17.1
2	4	34.6	31.0
3	6	67.1	66.5
4	8	81.9	81.6
5	10	94.3	94.0
6	12	99.9	99.9

[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4, DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), [b]Determined by HPLC anlysis against an internal standard.

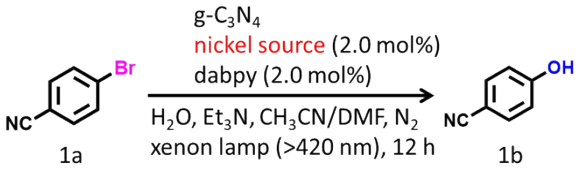
Table S3. Catalytic performances of different base in the synthesis of phenol from 4-bromobenzonitrile. [a]



Entry	Catalyst	Addition agent	Conversion (%)	Yield (%) [b]
1	$NiBr_2$·glyme	DIPEA	46.0	34.0
2	$NiBr_2$·glyme	dimethylphenylamine	9.50	trace
3	$NiBr_2$·glyme	TEOA	2.52	1.95
4	$NiBr_2$·glyme	Et_3N	99.9	99.9
5	$NiBr_2$·glyme	DABCO	trace	trace
6	$NiBr_2$·glyme	2,6-lutidine	trace	trace
7	$NiBr_2$·glyme	K_2CO_3	12.2	trace
8	$NiBr_2$·glyme	Cs_2CO_3	trace	trace

[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4 (50 mg), DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 µL, 20 equiv), base (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C, 12 h. [b]Determined by HPLC anlysis against an internal standard.

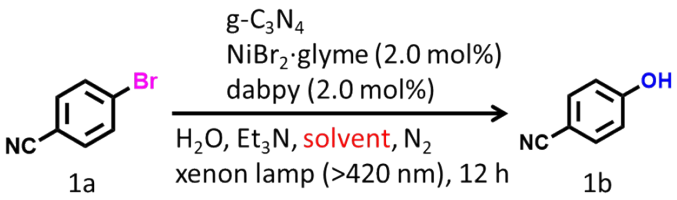
Table S4. Catalytic performances of different nickel source in the synthesis of phenol from 4-bromobenzonitrile. [a]



Entry	Catalyst	Conversion (%)	Yield (%) [b]
1	$NiBr_2 \cdot glyme$	99.9	99.9
2	$NiCl_2$	50.5	50.1
3	$NiCl_2 \cdot 6H_2O$	98.6	98.0
4	$NiBr_2 \cdot 3H_2O$	59.2	58.1
5	$NiBr_2$	23.2	23.0

[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), Ni(II) (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4 (50 mg), DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C, 12 h. [b]Determined by HPLC anlysis against an internal standard.

Table S5. Catalytic performances of different solvent in the synthesis of phenol from 4-bromobenzonitrile. [a]



Entry	Catalyst	Solvent	Conversion (%)	Yield (%) [b]
1	$NiBr_2$·glyme	DMF/CH_3CN	99.9	99.9
2	$NiBr_2$·glyme	DMF	65.9	64
3	$NiBr_2$·glyme	DMA/MeOH	82.1	79.1
4	$NiBr_2$·glyme	H_2O	80.8	79.7

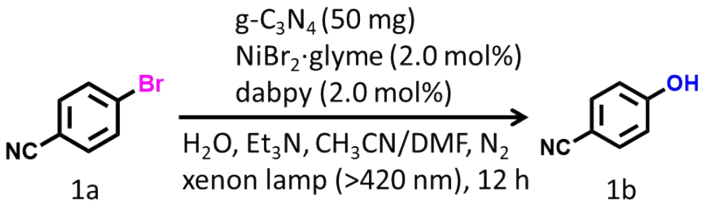
[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4 (50 mg), solvent (3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C, 12 h. [b]Determined by HPLC anlysis against an internal standard.

Table S6. Catalytic performances of different amount of solvent in the synthesis of phenol from 4-bromobenzonitrile. [a]

Entry	Amount of solvent (mL)	Conversion (%)	Yield (%)[b]
1	2.0	31.3	28.1
2	3.0	99.9	99.9
3	4.0	87.5	85.8
4	5.0	44.2	43.1

[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4 (50 mg), DMF/CH_3CN (1:1), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C, 12 h. [b]Determined by HPLC anlysis against an internal standard.

Table S7. Catalytic performances of different dosage of photocatalyst in the synthesis of phenol from 4-bromobenzonitrile. [a]



Entry	$g\text{-}C_3N_4$ dosage (mg)	Conversion (%)	Yield (%) [b]
1	20	51.9	50.4
2	30	74.1	73.8
3	40	88.3	86.2
4	50	99.9	99.9
5*	50	34.3	33.1

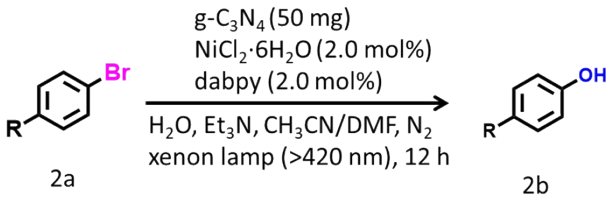
[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), $g\text{-}C_3N_4$, DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C, 12 h. [b]Determined by HPLC anlysis against an internal standard. * $NiBr_2$·glyme (1.0 mol%)

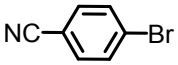
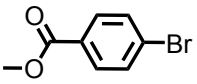
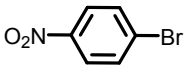
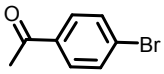
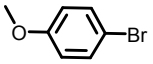
Table S8. Catalytic performances of light intensity in the synthesis of phenol from 4-bromobenzonitrile. [a]

Entry	Power (W)	Conversion (%)	Yield (%) [b]
1	100	12.1	11.5
3	150	20.4	20.1
4	200	58.1	57.6
5	300	99.9	99.9

[a]Reaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), $NiBr_2$·glyme (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4 (50 mg), DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25 °C, 12 h. [b]Determined by HPLC anlysis against an internal standard.

Table S9 Reaction scope of Nidabpy/g-C_3N_4 catalyzed hydroxylation of aromatic halides. [a]



Entry	Substrate	Conversion (%)	Yield (%)[b]
1		98.6	98.0
2		91.1	88.2
3		29.5	22.1
4		50.1	49.0
5		44.9	41.7

[a]Reaction conditions: aromatic halide (2a) (0.5 mmol, 1.0 equiv), $NiCl_2·6H_2O$ (2.0 mol%), dabpy (2.0 mol%), g-C_3N_4 (50 mg), DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 μL, 20 equiv), Et_3N (0.75 mmol, 1.5 equiv), N_2, xenon lamp (>420 nm), 25°C, 12 h. [b]Determined by HPLC anlysis against an internal standard.

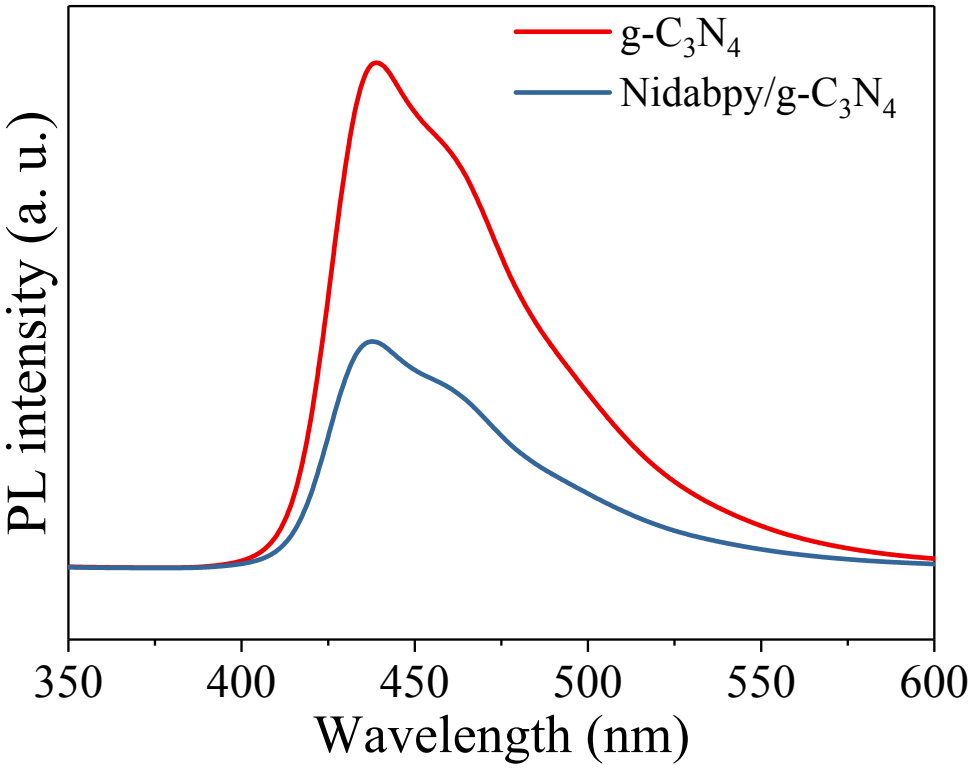


Figure S1 Photoluminescence (PL) spectra of Nidabpy/g-C_3N_4 and g-C_3N_4 samples.

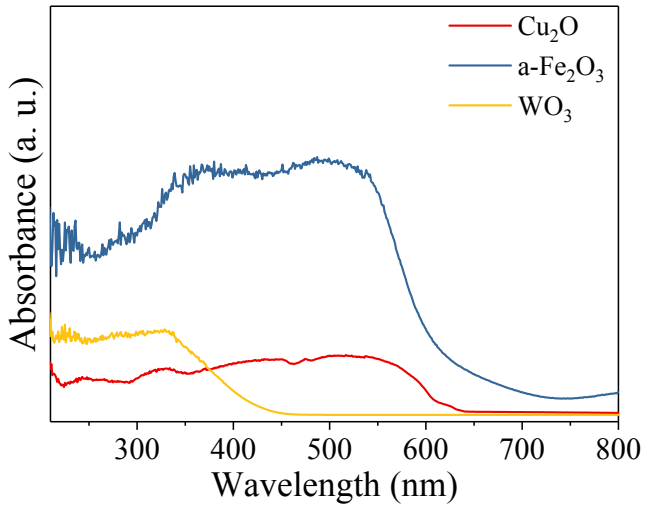


Figure S2. UV-Vis spectra of Cu_2O, a-Fe_2O_3 and WO_3 samples.

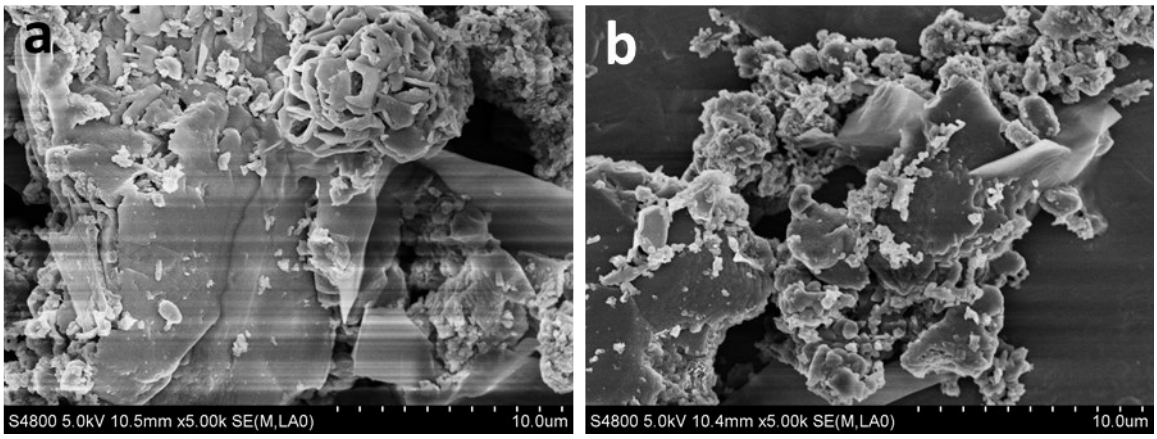
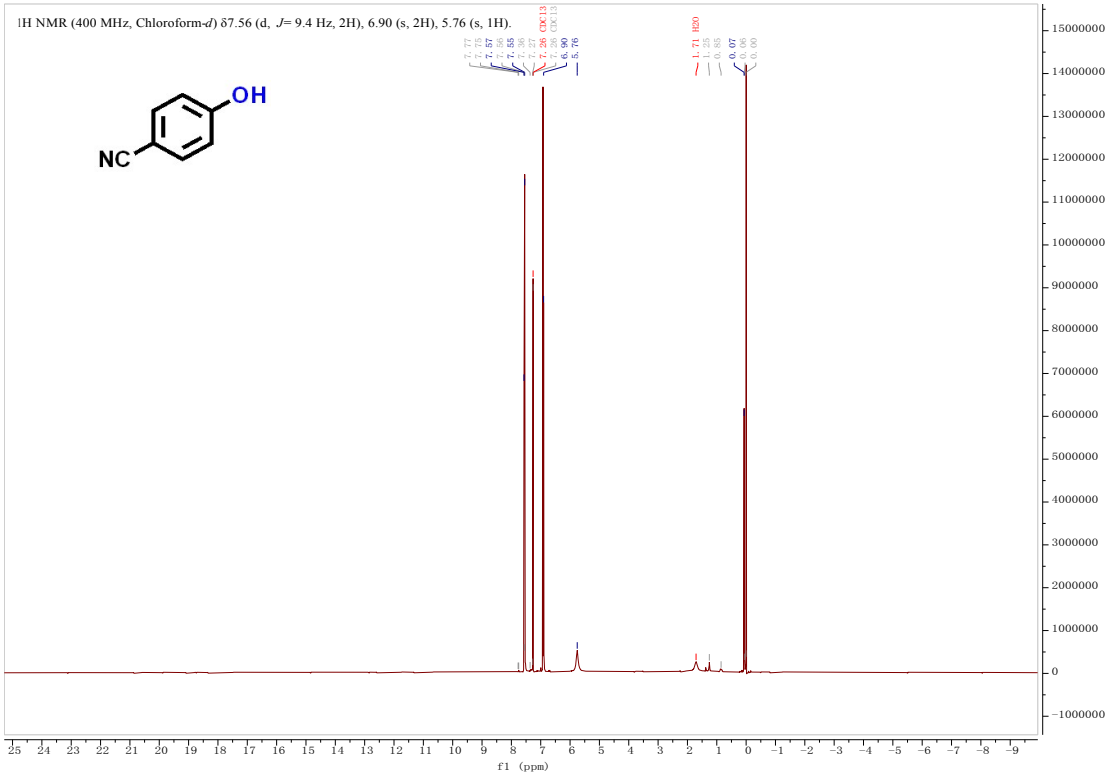
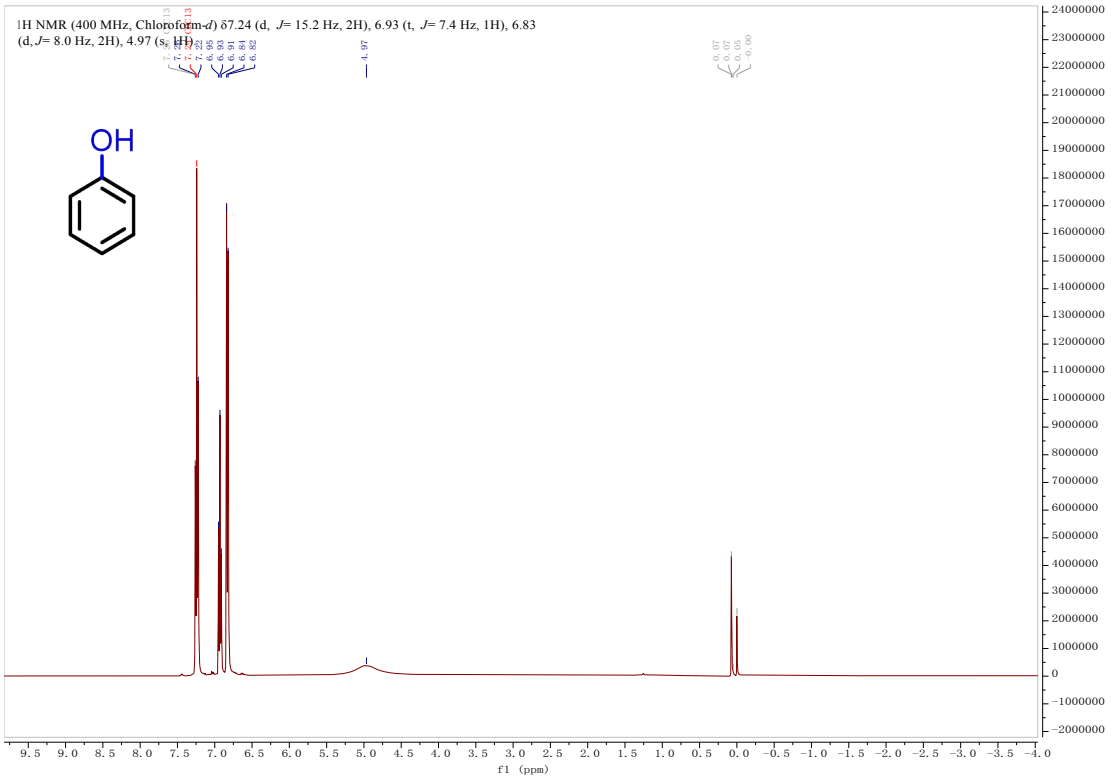
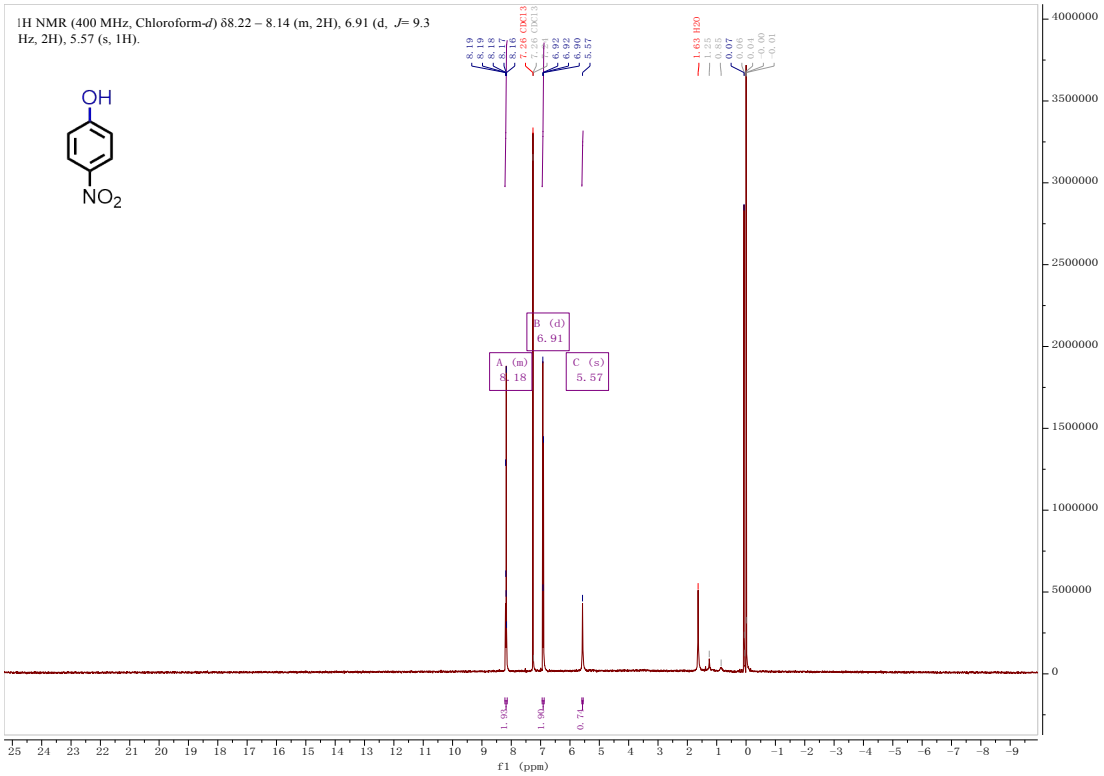


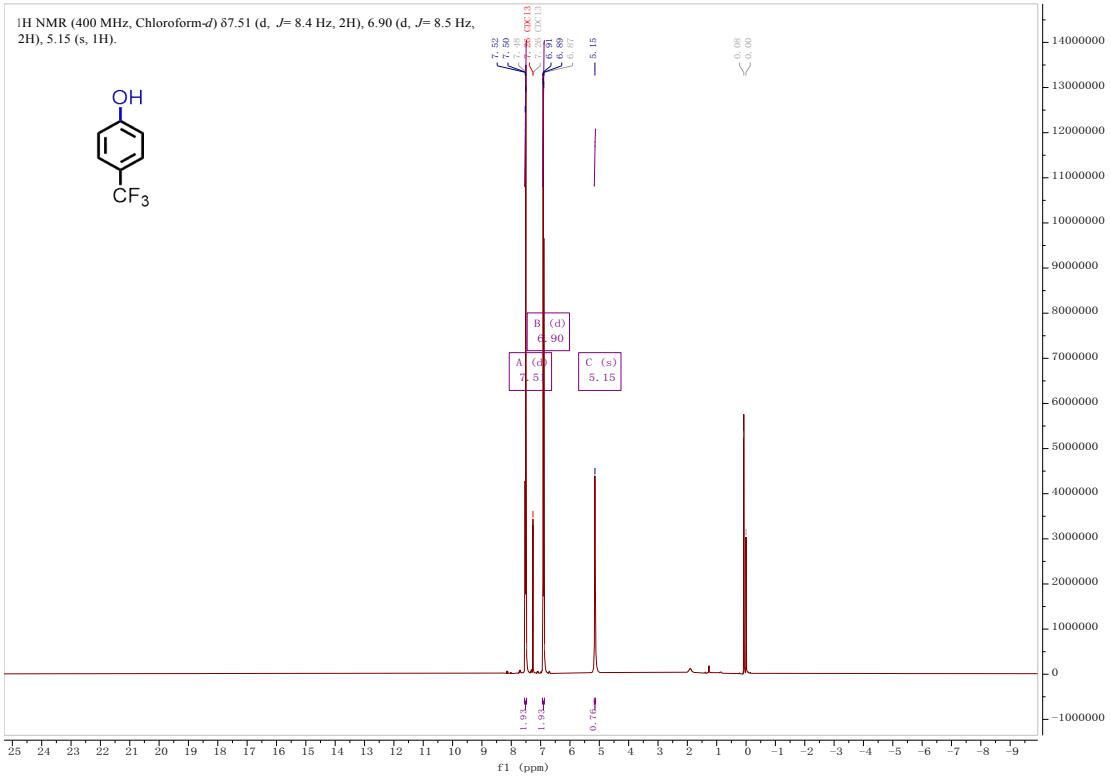
Figure S3. SEM images of g-C_3N_4 before and after the reaction.

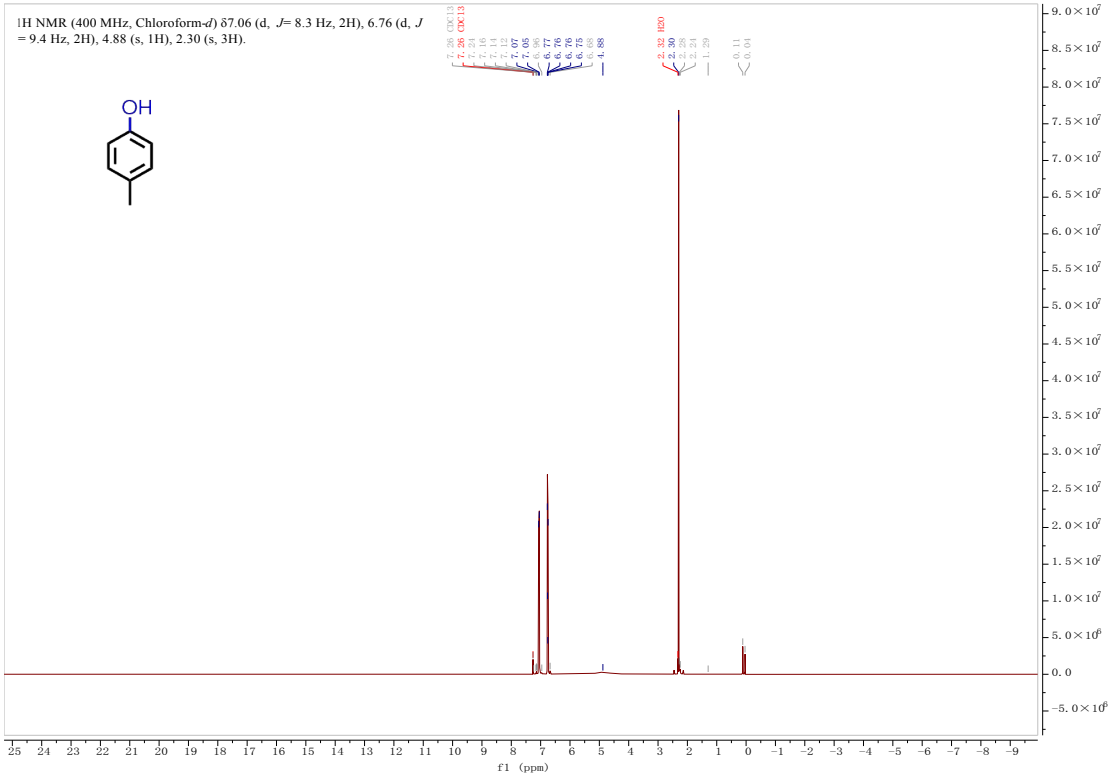
NMR spectra of the compounds

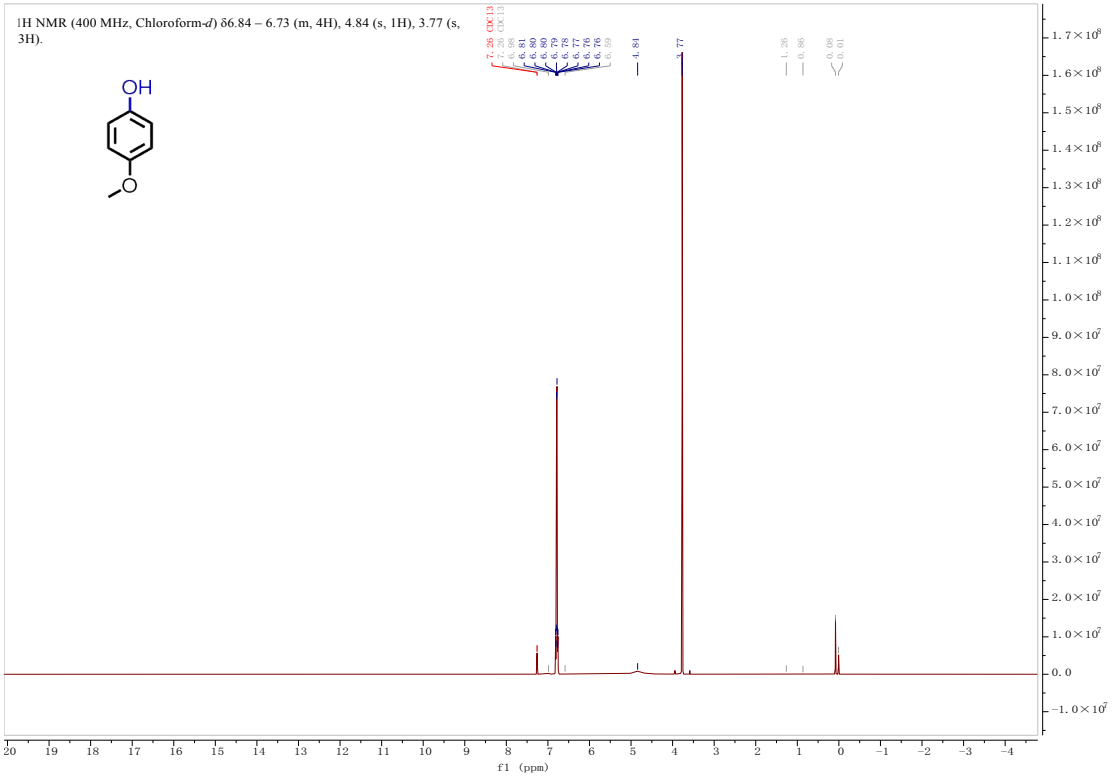


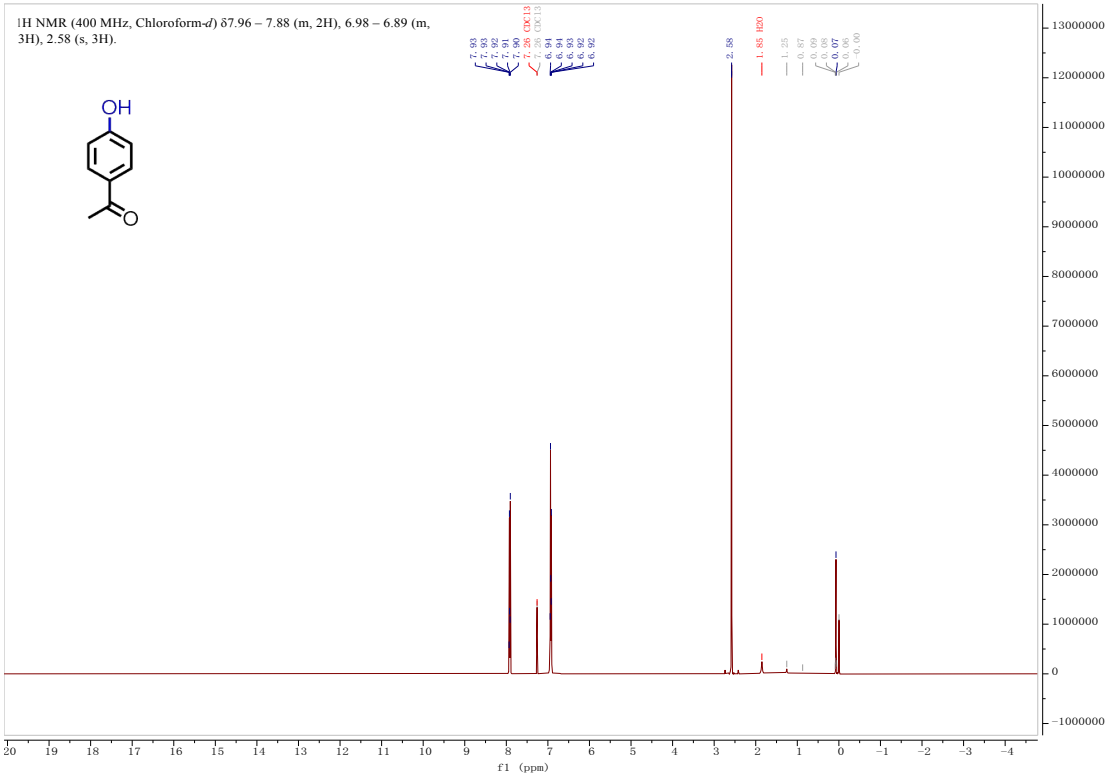

1H NMR (400 MHz, Chloroform-d) δ7.24 (d, J= 15.2 Hz, 2H), 6.93 (t, J= 7.4 Hz, 1H), 6.83 (d, J= 8.0 Hz, 2H), 4.97 (s, 1H)
OH
f1 (ppm)

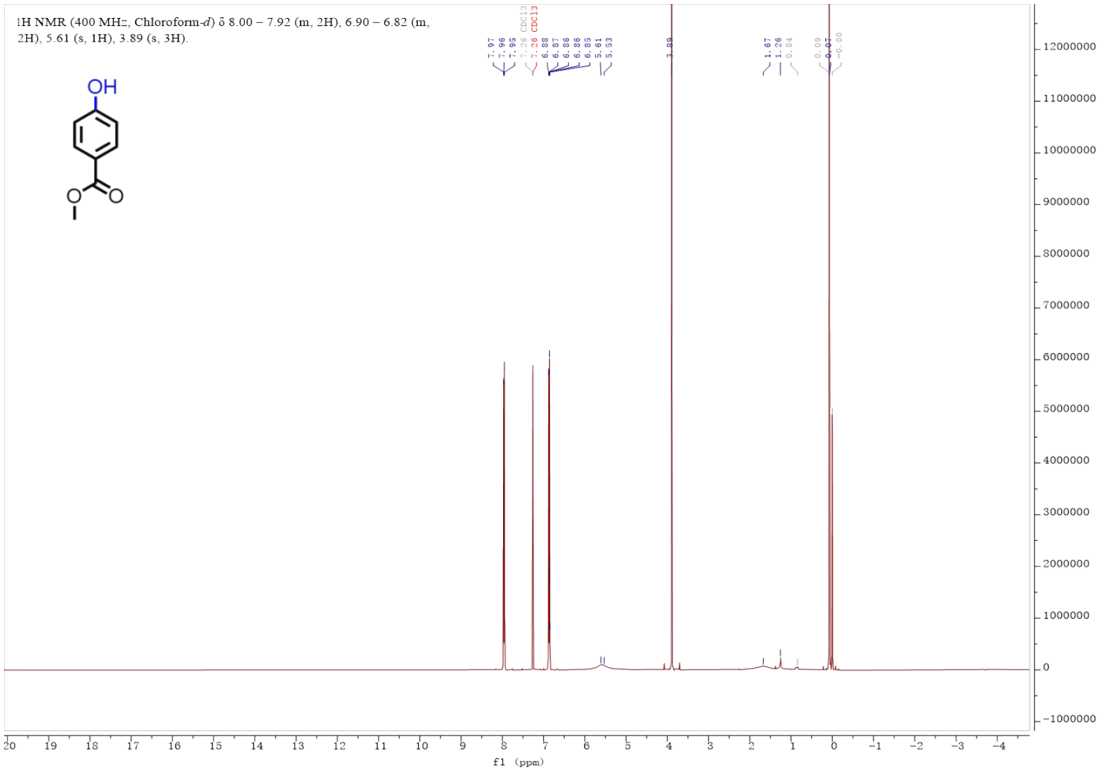

1H NMR (400 MHz, Chloroform-d) δ8.22 – 8.14 (m, 2H), 6.91 (d, J= 9.3 Hz, 2H), 5.57 (s, 1H).
OH
NO2
8.19
8.19
8.17
8.17
8.16
7.26 CDCl3
6.92
6.92
6.90
6.90
5.57
1.63 H2O
1.25
0.85
0.07
0.06
0.04
0.00
-0.01
B (d) 6.91
A (m) 8.18
C (s) 5.57
1.93
1.90
0.71
f1 (ppm)

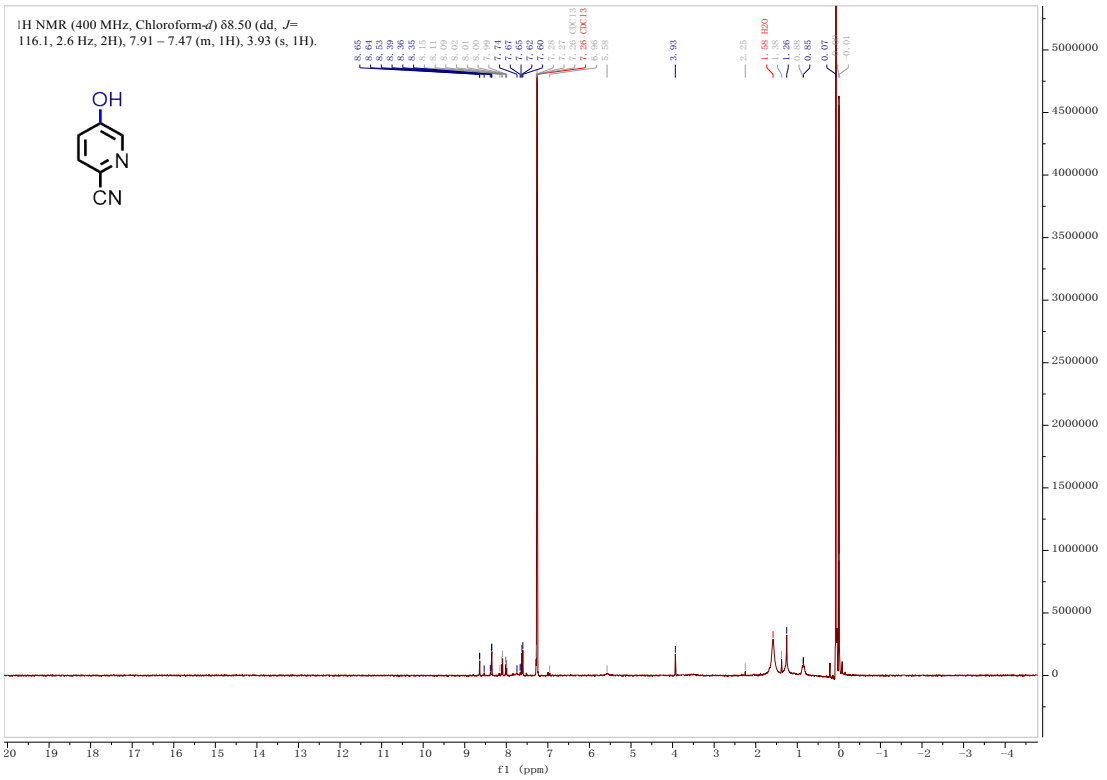

1H NMR (400 MHz, Chloroform-d) δ7.51 (d, J= 8.4 Hz, 2H), 6.90 (d, J= 8.5 Hz, 2H), 5.15 (s, 1H).
OH
CF3
B (d) 6.90
A (d) 7.51
C (s) 5.15
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ7.06 (d, J= 8.3 Hz, 2H), 6.76 (d, J = 9.4 Hz, 2H), 4.88 (s, 1H), 2.30 (s, 3H).
OH
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ6.84 – 6.73 (m, 4H), 4.84 (s, 1H), 3.77 (s, 3H).
OH
O
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ7.96 – 7.88 (m, 2H), 6.98 – 6.89 (m, 3H), 2.58 (s, 3H).
OH
O
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ 8.00 – 7.92 (m, 2H), 6.90 – 6.82 (m, 2H), 5.61 (s, 1H), 3.89 (s, 3H).
OH
O
O
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ8.50 (dd, J= 116.1, 2.6 Hz, 2H), 7.91 – 7.47 (m, 1H), 3.93 (s, 1H).
OH
N
CN
f1 (ppm)