Supplementary Materials

Nanodiamond derived N-doped sp^3@sp^2 hybrid carbocatalysts for the aerobic oxidative synthesis of 2-substituted benzoxazoles

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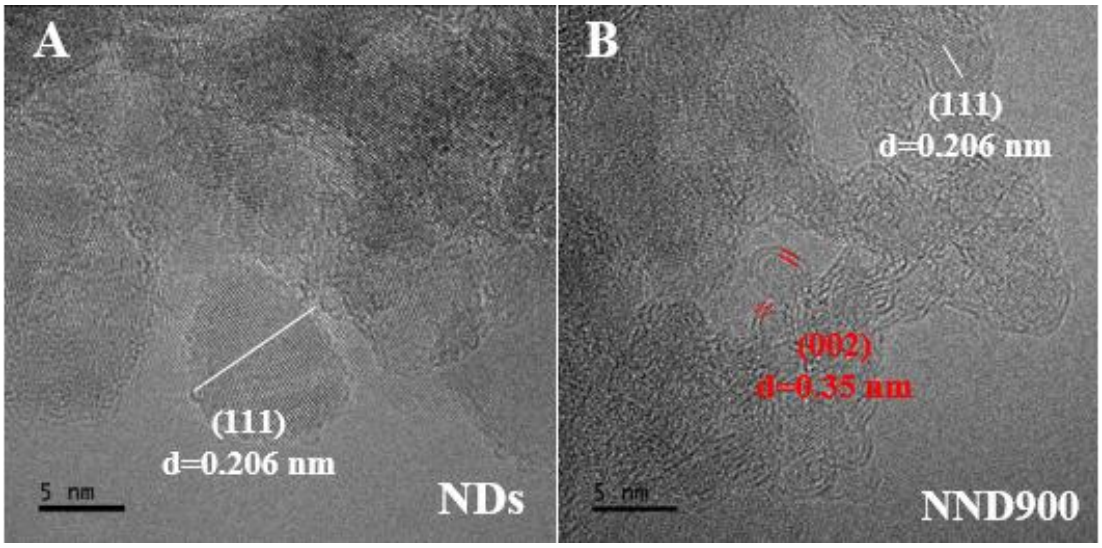
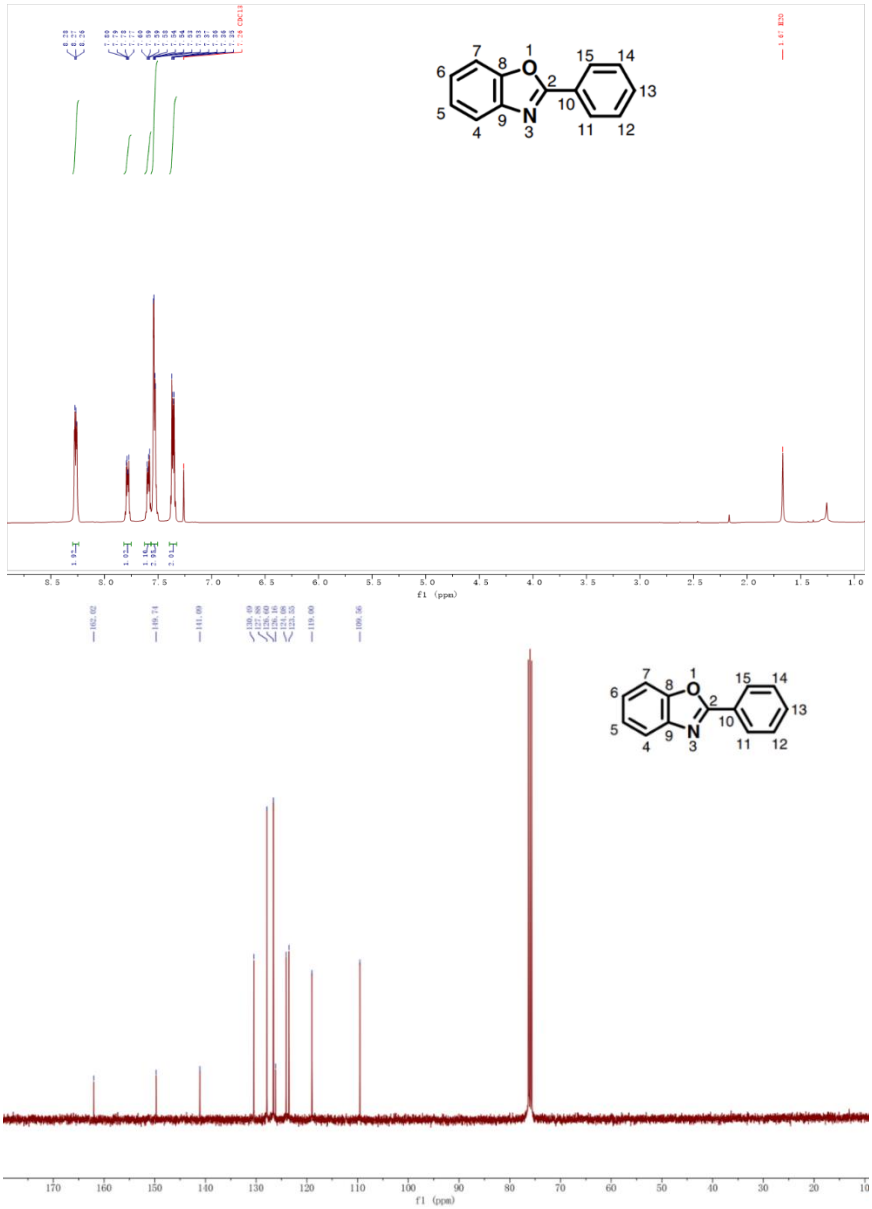


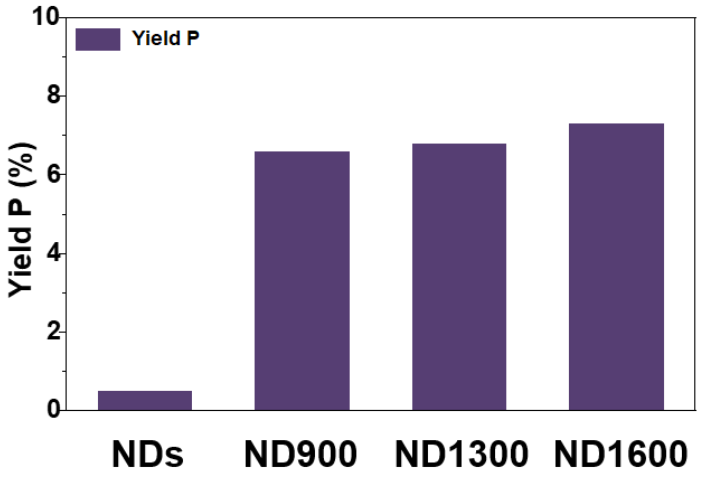
Supplementary Figure 1. HR-TEM images of pristine NDs (A) and NND900 (B).



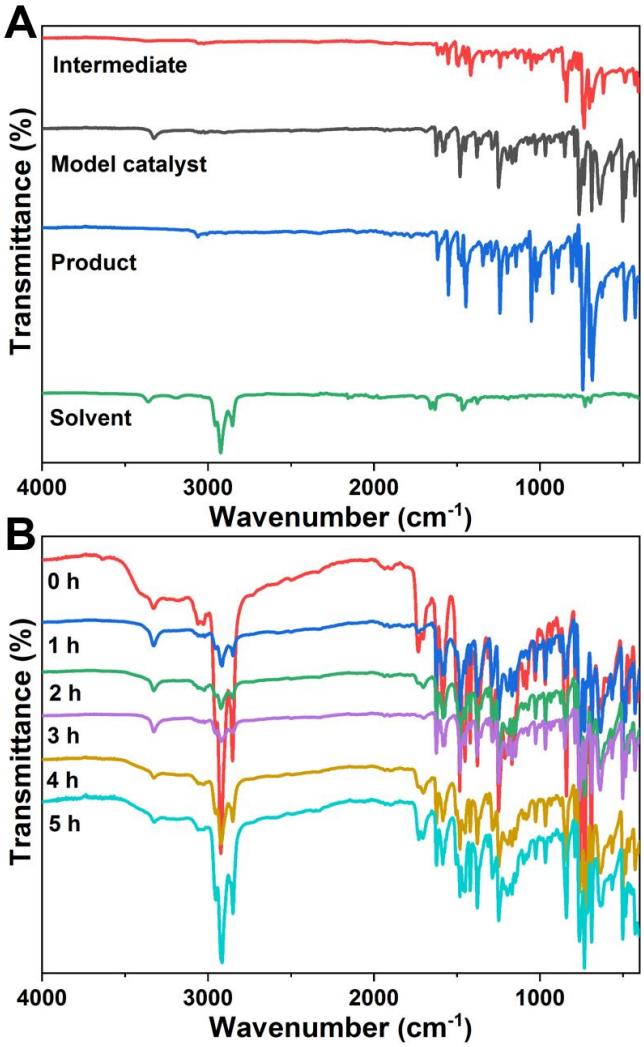
R_f 0.68 (30:1 hexane: ethylacetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28-8.26 (m, 2H), 7.80-7.77 (m, 1H), 7.60-7.58 (m, 1H), 7.54-7.52 (m, 3H), 7.37-7.34 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.06 (C-2), δ 150.79 (C-8), δ 142.14 (C-9), δ131.53 (C-10), δ 128.93 (C-12,C-14), δ 127.65 (C-11,C-15), δ 127.20 (C-13), δ 125.12 (C-5), δ 124.59 (C-6), δ 120.05 (C-4), δ 110.61 (C-7).

Supplementary Figure 2. Product structure identification by ^{1}H NMR and ^{13}C NMR.

 Gu *et al. Chem Synth* 2023;Volume:Number | http://dx.doi.org/10.20517/cs.2023.xx

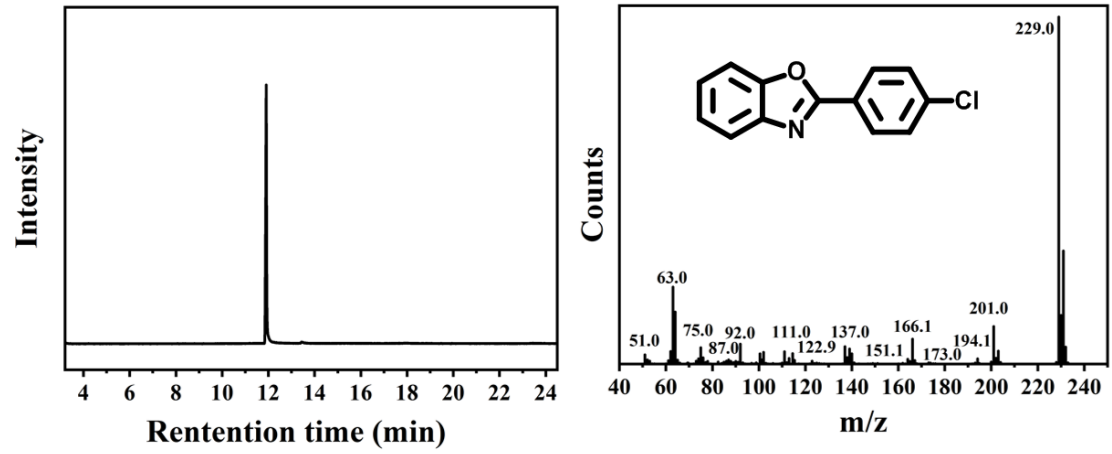


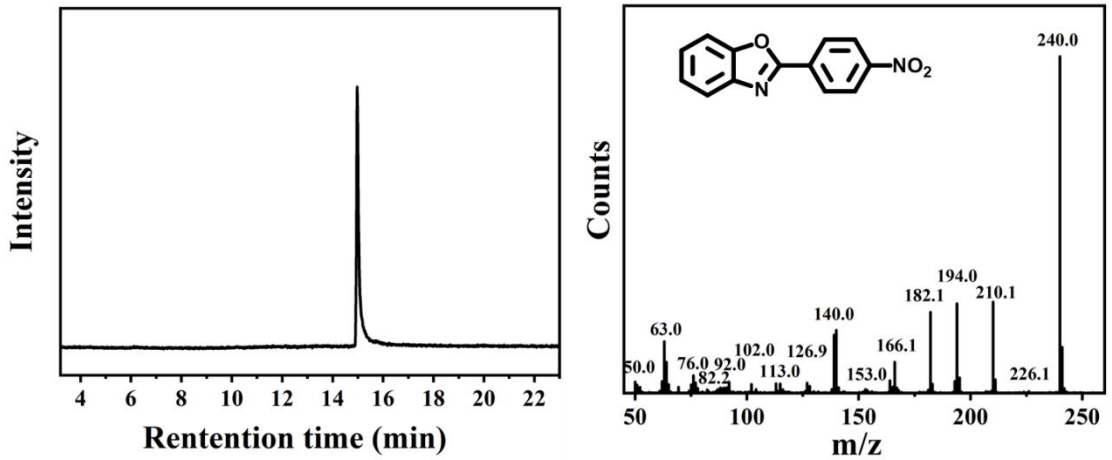
Supplementary Figure 3. Catalytic performance of NDs under different annealing temperatures. Reaction Conditions: 2 mmol aminophenol, 2.2 mmol benzaldehyde, 10 mL xylene, 120 mg catalyst, 140 °C, t = 2 h, 1 atm O_2. Quantitative analysis was determined by GC-FID using nitrobenzene as an internal standard.

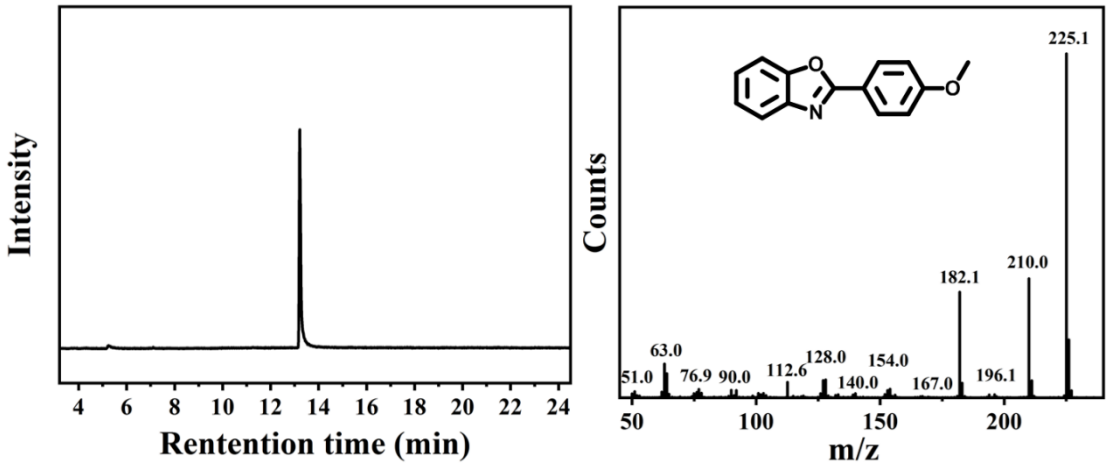


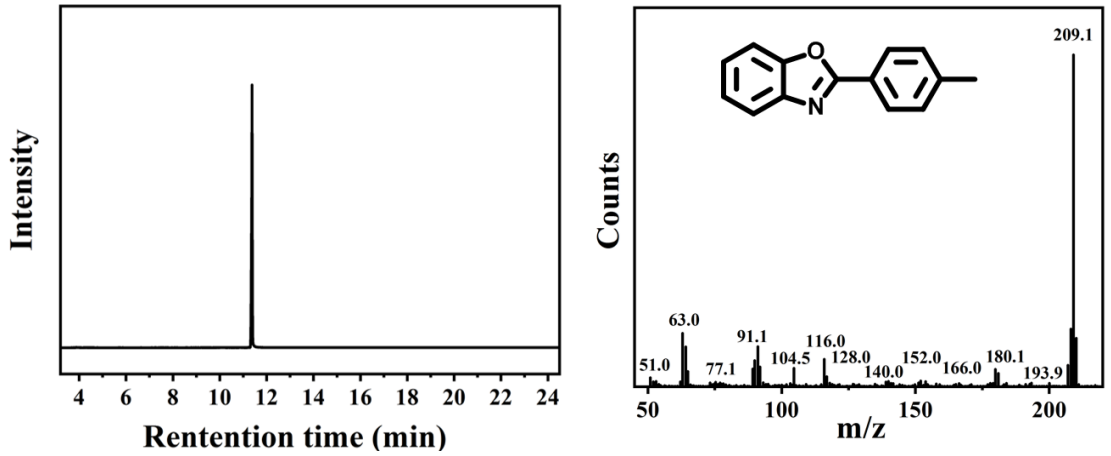
Supplementary Figure 4. ATR-IR spectra of (a) reference samples including **I** (2-(benzylidene amino)phenol), model catalyst (1,10-phenanthroline), product (2-phenyl benzoxazole) and solvent (toluene); (b) catalytic systems with the mixture of **I** (as reactant), model catalyst and toluene under 140 ºC in oxygen for 1, 2, 3, 4 and 5 h, respectively.

Gu *et al. Chem Synth* 2023;Volume:Number | http://dx.doi.org/10.20517/cs.2023.xx





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140.0
152.0
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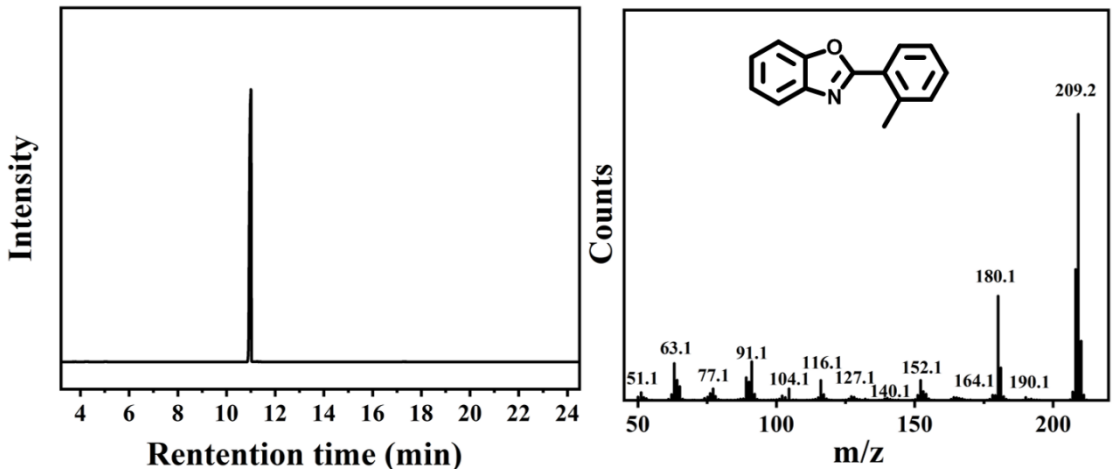
180.1
193.9
50 100 150 200
m/z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164.1
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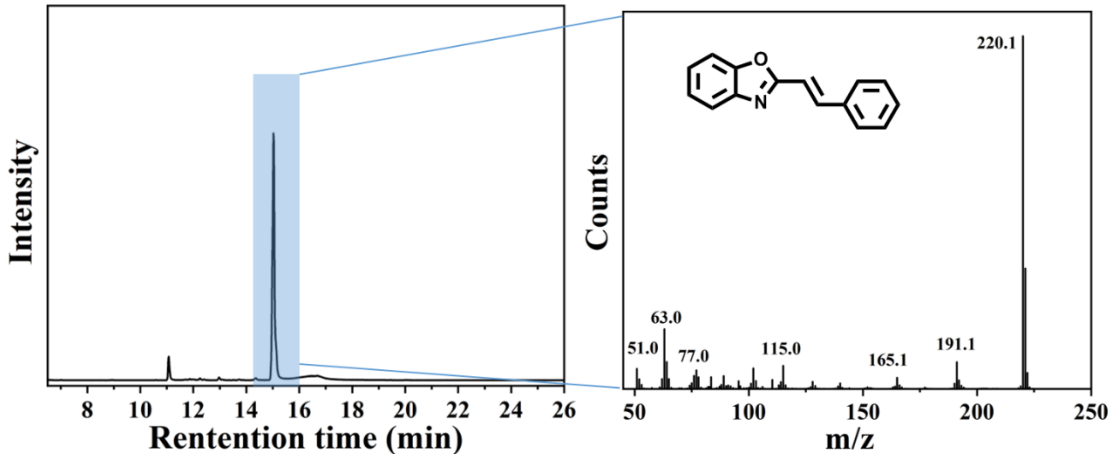
m/z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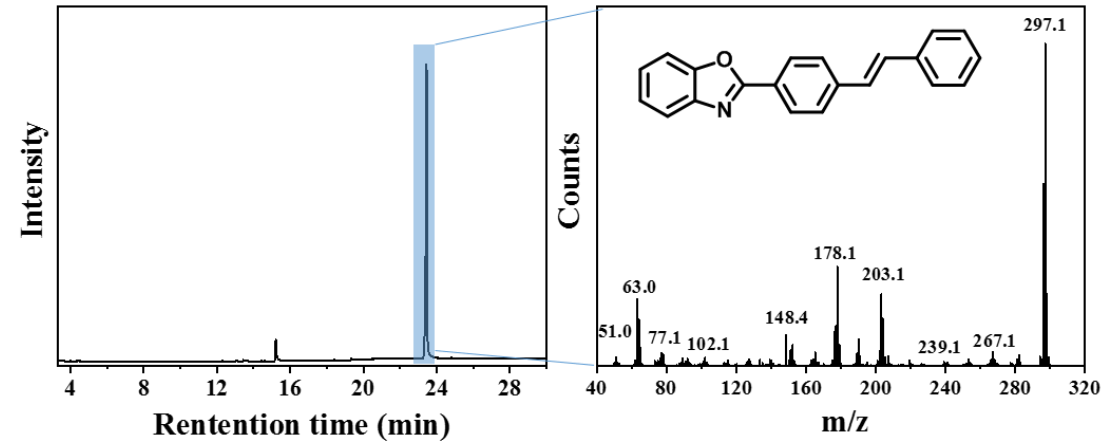
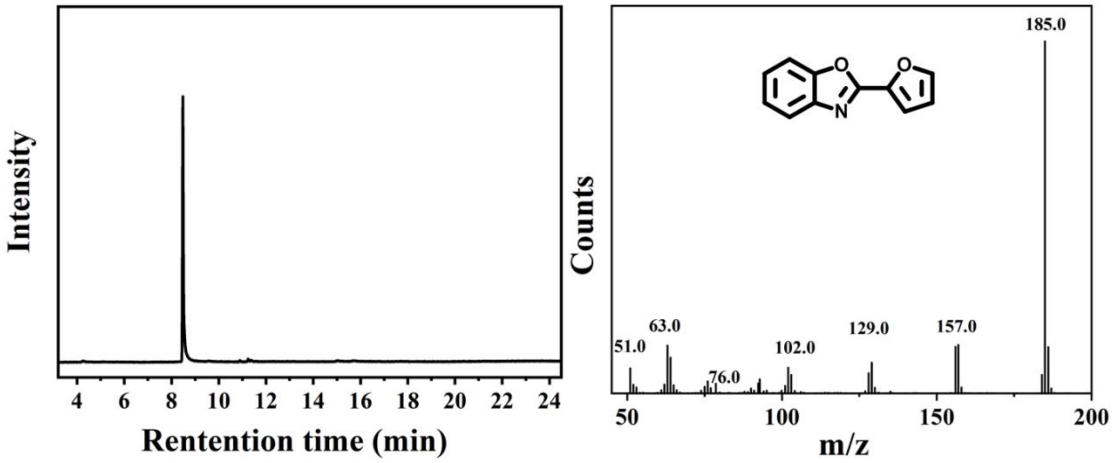
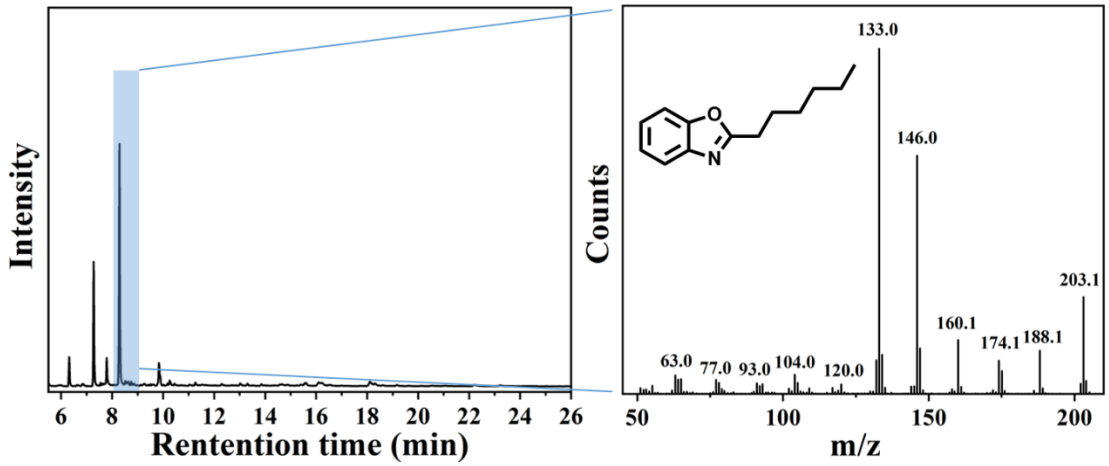
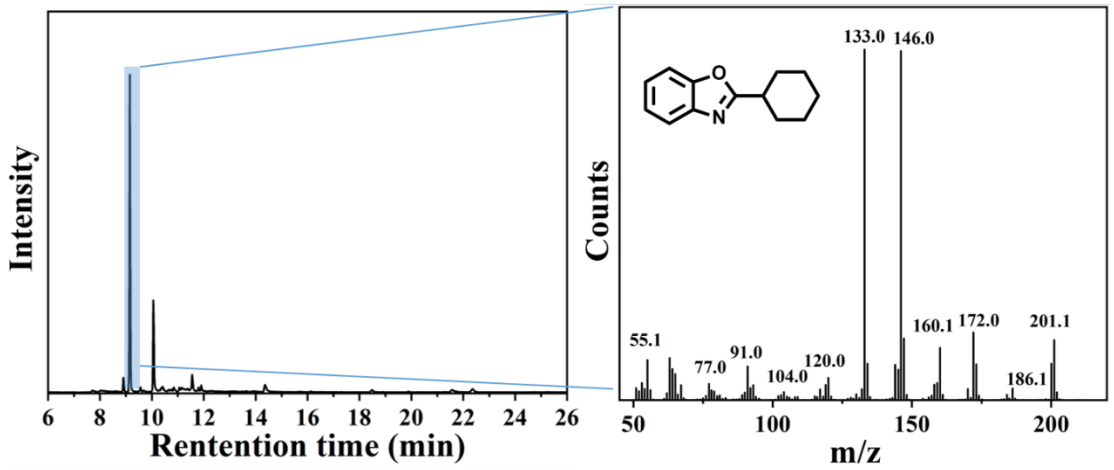
m/z

Gu *et al. Chem Synth* 2023;Volume:Number | http://dx.doi.org/10.20517/cs.2023.xx





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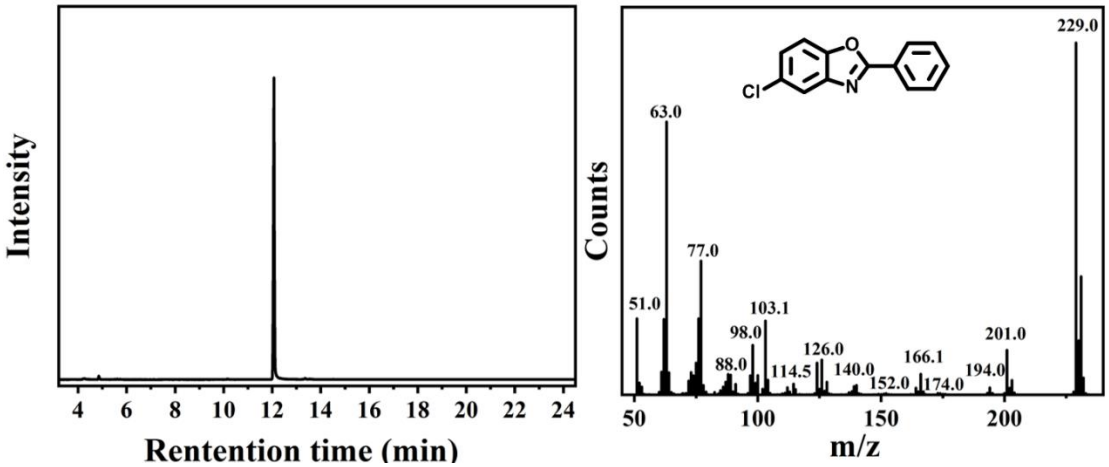
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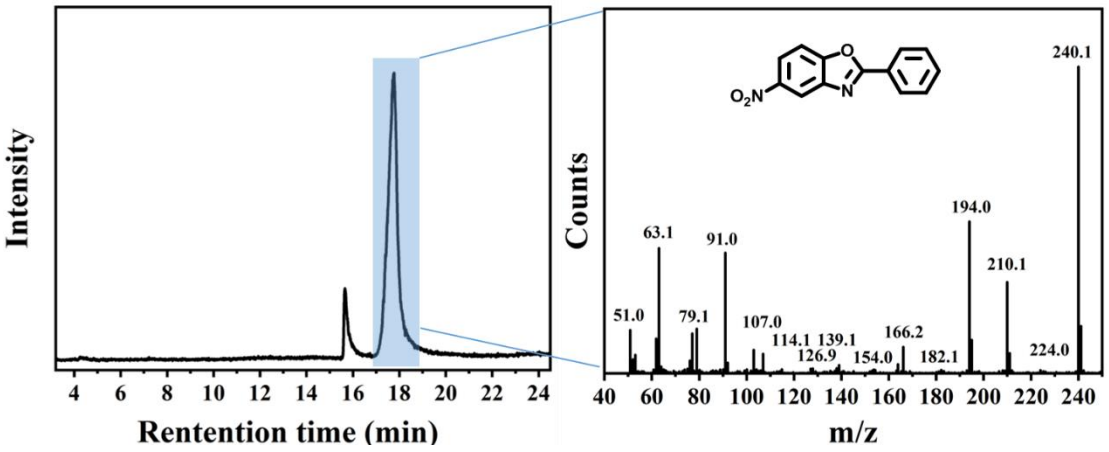
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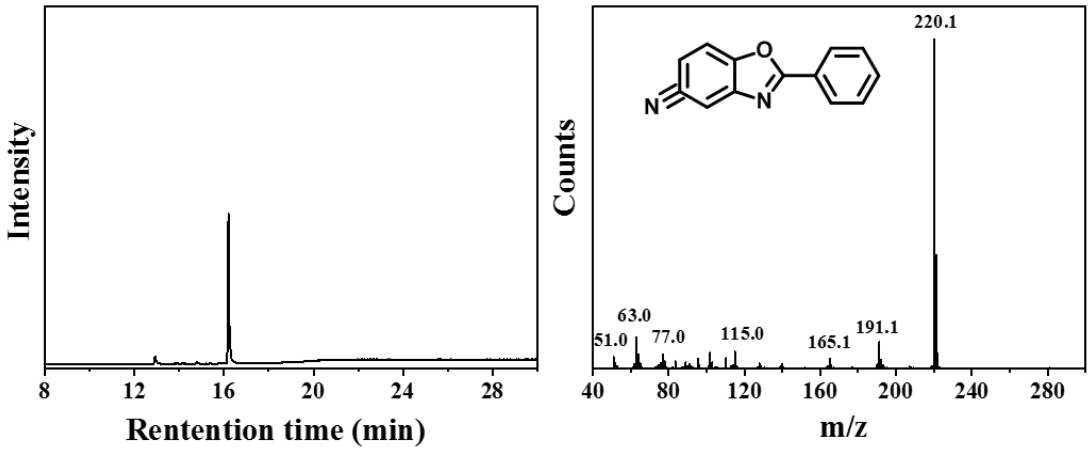
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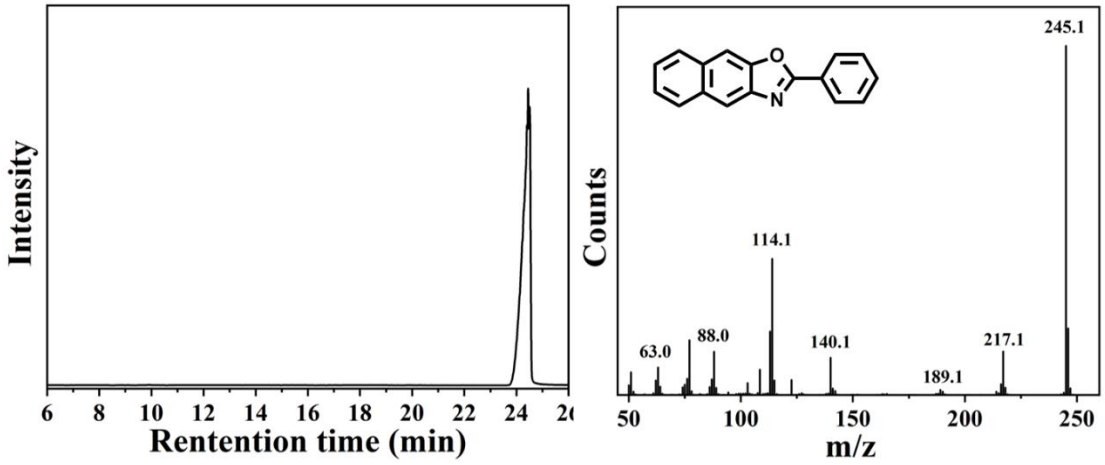
N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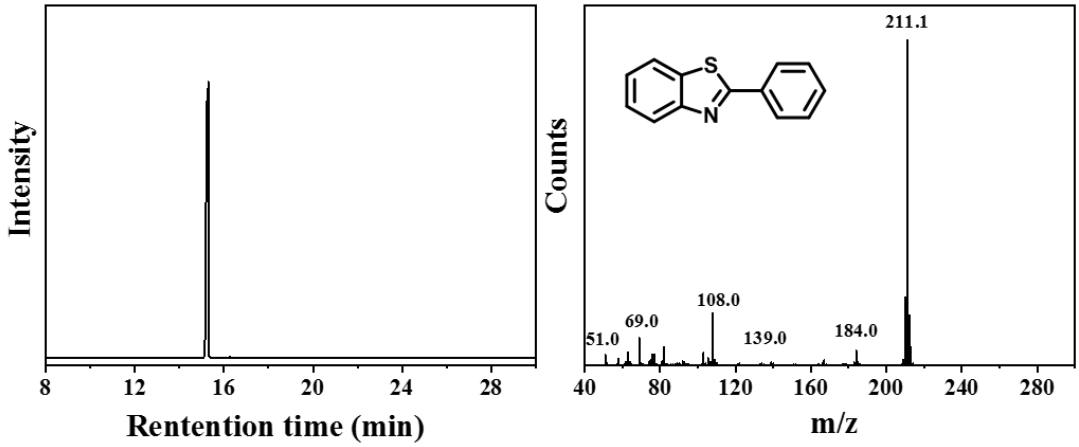
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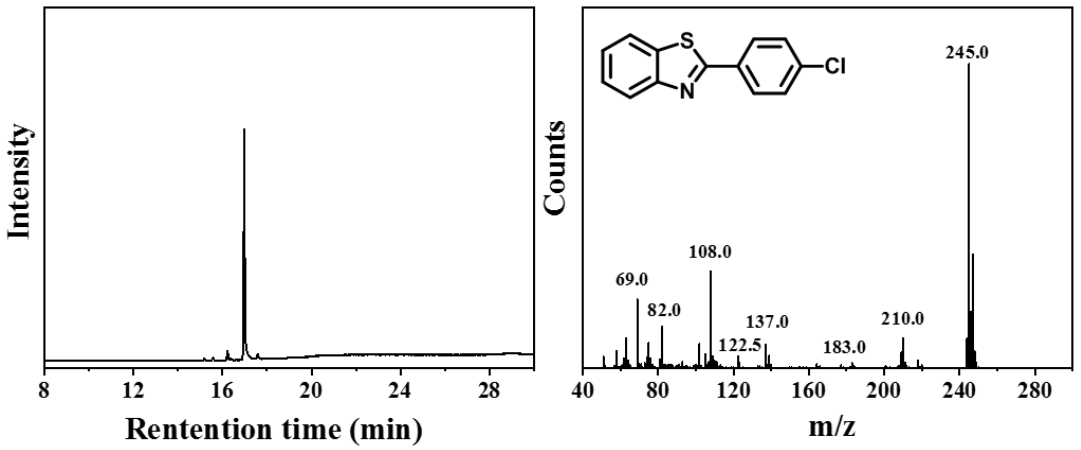
N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Rentention time (min)
Counts
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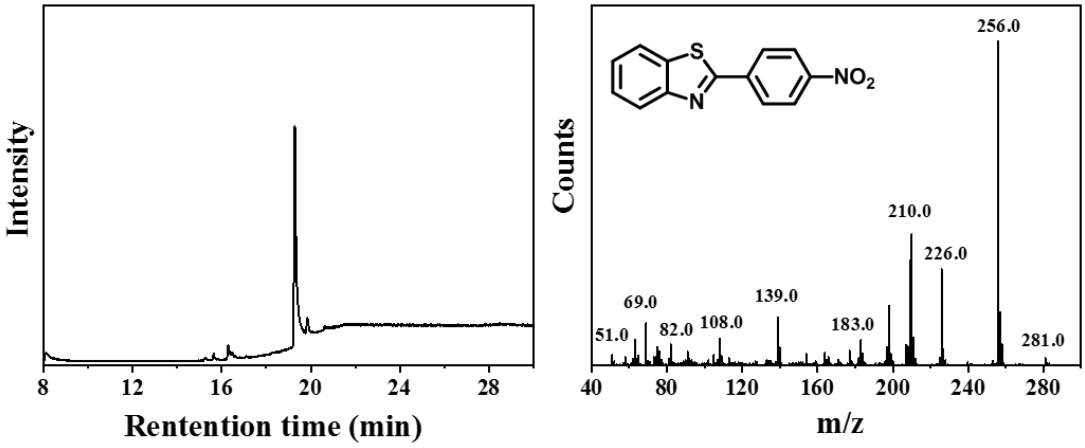
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Rentention time (min)
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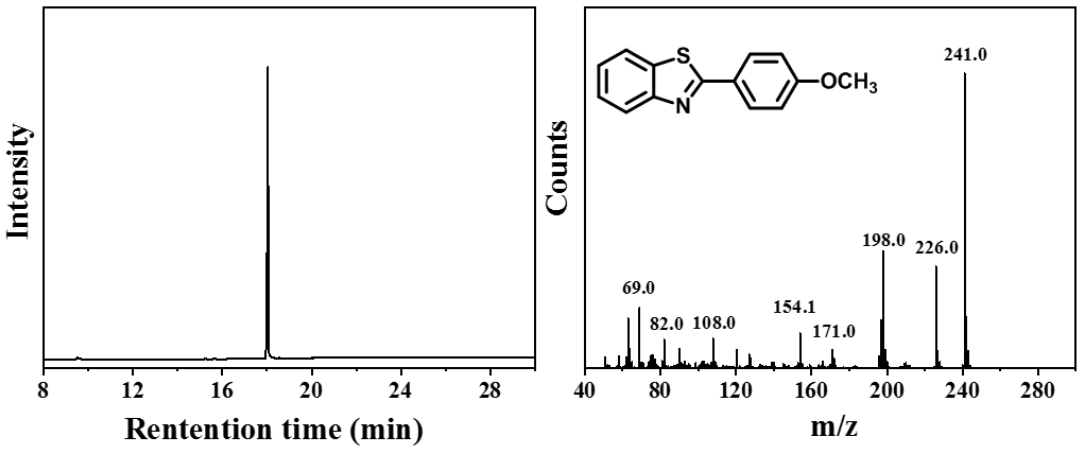
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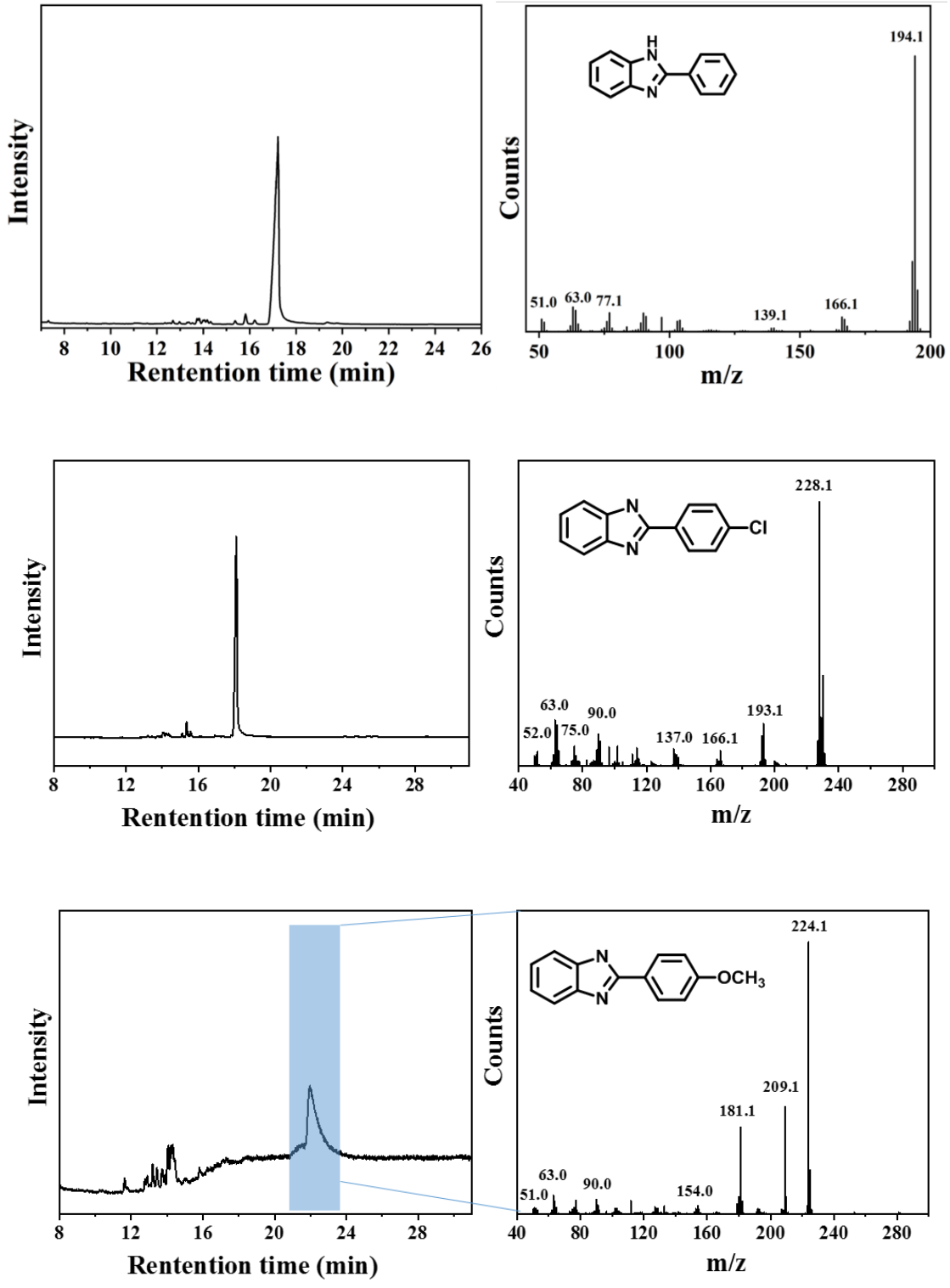


Supplementary Figure 5. GC-MS analysis of products (**P1**-**P23**) in substrate scope and experiments.

Supplementary Table 1. Summary of XPS C1s data of various samples

Sample	C (at%)	N (at%)	O (at%)	sp^2/sp^3	sp^2 carbon fraction (%)
ND	87.6	1.8	10.5	0.2	16.7
NND900	92.3	3.7	4.0	0.5	33.3
ND900	95.4	1.6	3.0	0.3	23.1

C1: sp^2 C; C2: sp^3 C; C3: C-O, C-N; C4: C=O; C5: O-C=O.

Supplementary Table 2. Summary of Raman peaks assignments

Position	Assignment
1324 cm^{-1}	Diamond peak
1400 cm^{-1}	Disorder-induced D band
1590 cm^{-1}	G band
1640 cm^{-1}	O-H bending vibrations

Supplementary Table 3. The specific surface area of different NDs-based samples.

Entry	Samples	Surface area (m^2g^{-1})*
1	NDs	312
2	oND900	360
3	NoND900	360
4	NND900	366

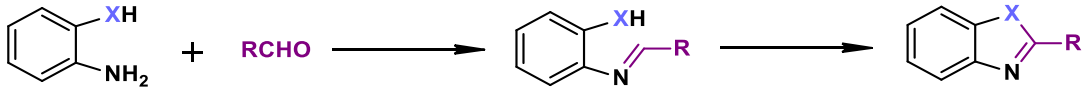
* Determined by N_2 adsorption-desorption experiment

Supplementary Table 4. Optimization of the reaction temperature and time

Entry	Catalyst	Temp. (°C)	Time (h)	Con. A* (%)	Sel. P* (%)	Sel. I* (%)	Yield P* (%)	Normalized r_P (mmol h^{-1} g^{-1})*
1	/	140	2	96.1	0	99.8	0	/
2	NND900	140	2	100	27.7	70.9	27.7	2.3
3	NND900	120	2	100	8.8	90.1	8.8	0.7
4	NND9000	100	2	100	3.5	95.6	3.5	0.3
5	NND9000	140	12	100	79.0	20.2	79.0	1.1
6	NND9000	140	28	100	97.4	0	97.4	0.6
7	NND900	120	12	100	35.6	63.0	35.6	0.5
8	NND900	100	12	100	16.9	82.3	16.9	0.2

Reaction Conditions: 2 mmol 2-aminophenol (**A**); 2.2 mmol benzaldehyde (**B**); 10 mL xylene; 120 mg catalyst; T= 140 °C; *GC analysis, nitrobenzene was used as internal standard; Catalyst mass normalized formation rate of product **P**: $r_P = \frac{n_P}{m_{Cat.}*t}(mmol \cdot h^{-1} \cdot g^{-1})$.

Supplementary Table 5. Comparison between the catalytic activity of N-doped sp^3@sp^2 hybrids and other reported catalysts in the synthesis of benzoxazoles, benzothiazoles, and benzimidazoles



Entry	X	Catalysts	Oxidants	Additives	Temp (°C)	Time (h)	Yield (%)	Normalized r_P (mmol h^{-1} g^{-1})*	Ref
1 [a]	O	NND900	O_2	/	140	28	97.4	0.6	this work
2 [a]	S	NND900	O_2	/	140	100	74.8	0.1	this work
3[a]	NH	NND900	O_2	/	140	100	79.2	0.1	this work
4	O	/	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	/	45	12	93	/	[1]
5	O	2,6-di-*tert*-buty l-4-methylpyridine	thianthrene cation radical perchlorate	/	RT		97	/	[2]
6	NH	/	oxone	/	RT		90	/	[3]
7	NH	$Ru(PPh_3)_3(CO)H_2$/ Xantphos	/	p-TsOH/piperidinium acetate	111	8	98	2.5 h^{-1}	[4]
8	O	$[Cp^*IrI_2]_2$	/	crotononitrile	111	24	100	4.2 h^{-1}	[4]
9	S	$[Cp^*IrI_2]_2$	/	crotononitrile	111	24	68	2.8 h^{-1}	[4]
10	NH	CuCl/Bpy	air	TEMPO	r.t.	12	95	1.6 h^{-1}	[5]
11	O	CuCl/Bpy	air	TEMPO	r.t.	12	89	1.5 h^{-1}	[5]
12	S	CuCl/Bpy	air	TEMPO	r.t.	13	93	1.4 h^{-1}	[5]
13	O	Au/TiO_2	/	/	111	24	90	1.9 h^{-1}	[6]

14	O	Polymer-Incarcerated Pt nanoclusters	O_2	K_2CO_3	30	20	72	0.9	[7]
15	S	Polymer-Incarcerated Pt nanoclusters	O_2	K_2CO_3	30	20	83	1.0	[7]
16	O	AgPd NPs/$WO_{2.72}$	HCOOH	/	80	8	99	4.1 h^{-1}	[8]
17	O	N-hydroxyphthalimide	O_2	/	120	15	71	0.5 h^{-1}	[9]
18	O	4-methoxy-TEMPO	O_2	/	120	15	96	0.6 h^{-1}	[9]
19 [b]	O	Darco KB	O_2	/	120	4	78	1. 6	[10]
20	O	MIL-101(Cr)	O_2	/	120	9	87	9. 7	[11]
21	NH	MIL-101(Cr)	O_2	/	55	2	94	47.0	[11]
22	S	MIL-101(Cr)	O_2	/	60	2.5	87	34.8	[11]
23	NH	SiO_2-OSO_3H	air	/	80	0.5	92	12.3	[12]
24	NH	Pt/TiO_2	/	/	165	24	94	3.9 h^{-1}	[13]
25	S	Pt/Al_2O_3	/	/	165	24	89	3.7 h^{-1}	[13]
26	O	molecular sieve	O_2	/	180	48	86	0.005	[14]
27	O	$Ru_2Cl_4(CO)_6$/PFMN	/	DABCO	120	24	78	0.7	[15]
28	O	Fe_3O_4@SiO_2@PPh_2	/	DABCO	110	12	10	0.2	[15]
29	NH	$CoSO_4 \cdot 7H_2O$	air	CF_3COOH	r.t./20 mA	2.5	93	18.6 h^{-1}	[16]
30	S	$CoSO_4 \cdot 7H_2O$	air	CF_3COOH	r.t./20 mA	2.5	86	17.2 h^{-1}	[16]
31	O	$CoSO_4 \cdot 7H_2O$	air	CF_3COOH	r.t./10 mA	6	40	3.3 h^{-1}	[16]
32	O	copper ferrite NPs	/	/	130	16	92	0.6 h^{-1}	[17]
33	O	$CuFe_2O_4$	O_2	/	110		92	/	[18]
34	S	$CuFe_2O_4$	O_2	/	110		93	/	[18]
35	NH	$CuFe_2O_4$	O_2	/	110		89	/	[18]

[a] 60 mg catalyst per 1 mmol aminophenol (**A**); [b] 125 mg catalyst per 8 mmol aminophenol (**A**);Catalyst mass normalized formation rate of product **P**: $r_P = \frac{n_P}{m_{Cat.}*t}(mmol \cdot h^{-1} \cdot g^{-1})$; Catalyst (in some cases, metal) moles normalized formation rate of product **P**: $r_P = \frac{n_P}{n_{Cat.}*t}(h^{-1})$.

Supplementary Table 6. The catalytic performance of NND900, purified and Fe loaded NND900.

Entry	Catalyst	Temp. (°C)	Time (h)	Con.A* (%)	Sel.P* (%)	Sel.I* (%)	Yie.P* (%)
1	NND900	140	2	100	27.7	70.9	27.7
2	NND900-HCl	140	2	100	26.5	72.3	26.5
3	Fe/NND900	140	2	100	26.1	72.9	26.1

Reaction Conditions: 2 mmol 2-aminophenol; 2.2 mmol benzaldehyde; 10 mL xylene; 120 mg catalyst; T= 140 °C.

Supplementary Table 7. ICP results of various samples

Entry	Sample	Fe (wt.%)	Ca (wt.%)	Ba (wt.%)	Ni (wt.%)
1	NDs	0.37	0.02	0.35	/
2	NDs-purified	0.01	0.13	/	/
3	NND900	0.09	0.02	/	/

Supplementary Table 8. Summary of XPS N1s data of various samples

Sample	N (at%)	N1/N (%)	N2/N (%)	N3/N (%)	N4/N (%)	N1 (at%)	N2 (at%)	N3 (at%)	N4 (at%)
NDs	1.8	2.7	33.8	41.9	21.7	0	0.6	0.8	0.4
NND900	3.7	22.5	28.5	35.5	13.4	0.8	1.1	1.3	0.5
ND900	1.6	3.9	29.0	40.9	26.3	0.1	0.5	0.7	0.4

N1: pyridinic N; N2: pyrrolic N; N3: graphitic N; N4: N oxide.

Supplementary Table 9. Catalytic performance of model catalysts 1,10-phenanthroline and carbazole.

Entry	Catalyst	Temp. (°C)	Time (h)	Con.A (%)	Sel.P (%)	Sel.I (%)	Yie.P (%)
1	1,10-phenanthroline	140	12	100	13.7	84.9	13.7
2	carbazole	140	12	100	7.0	92.0	7.0

Reaction Conditions: 2 mmol 2-aminophenol; 2.2 mmol benzaldehyde; 10 mL xylene; 120 mg catalyst; T= 140 °C.

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