**Supporting Information**

**Enhanced Catalytic Activity in the Oxidative Synthesis of Benzoxazoles by Tuning Local Electronic structures in N-doped sp3@sp2 Hybrid Nanocarbon**

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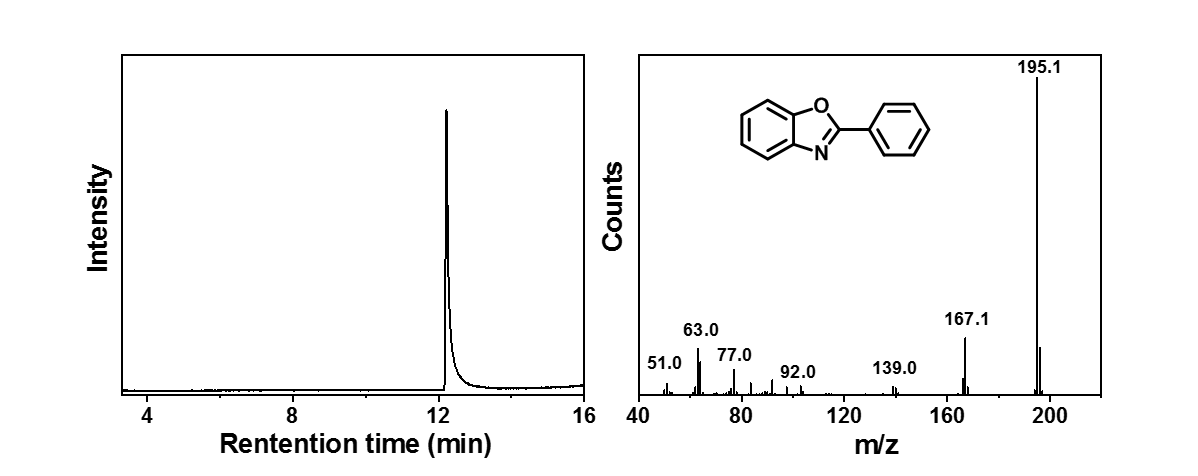
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| **Figure S1**. Schematic illustration of the synthesis of N-doped sp2@sp3 nanocarbons hybrids. |

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| **Figure S2**. STEM-HAADF image of NC@ND-900 and corresponding EDS spectrum and elemental mapping of C, N and O. |

**Table S1** Optimization of the reaction temperature and time.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Catalyst** | **Temp.**  **(oC)** | **Time**  **(h)** | **Con. A\***  **(%)** | **Sel. P\***  **(%)** | **Sel. I\***  **(%)** | **Yield P\***  **(%)** |
| **1** | **/** | 140 | 2 | 96.1 | 0 | 99.8 | 0 |
| **2** | NC@ND-900 | 140 | 2 | 100 | 27.7 | 70.9 | 27.7 |
| **3** | NC@ND-900 | 120 | 2 | 100 | 8.8 | 90.1 | 8.8 |
| **4** | NC@ND-900 | 100 | 2 | 100 | 3.5 | 95.6 | 3.5 |
| **5** | NC@ND-900 | 140 | 12 | 100 | 79.0 | 20.2 | 79.0 |
| **6** | NC@ND-900 | 140 | 28 | 100 | 97.4 | 0 | 97.4 |
| **7** | NC@ND-900 | 120 | 12 | 100 | 35.6 | 63.0 | 35.6 |
| **8** | NC@ND-900 | 100 | 12 | 100 | 16.9 | 82.3 | 16.9 |

**Reaction Conditions:** 2 mmol 2-aminophenol (A); 2.2 mmol benzaldehyde (B); 10 mL xylene; 120 mg catalyst; T= 140 oC ; \*GC analysis, nitrobenzene was used as internal standard;

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**Figure S3**. Product structure identification by GC-MS spectrum.

**Table S2** Comparison between the catalytic activity of N-doped sp3@sp2 hybrids and other reported catalysts in the synthesis of benzoazoles, benzothiazoles, and benzimidazoles

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | | | | | |
| **Entry** | **X** | **Catalysts** | **Oxidants** | **Additives** | **Temp ( oC)** | **Time (h)** | **Yield (%)** | **Ref** |
| **1** | O | NC@ND-900 | O2 | / | 140 | 30 | 97.4 | this work |
| **2** | S | NC@ND-900 | O2 | / | 140 | 100 | 74.8 | this work |
| **3** | NH | NC@ND-900 | O2 | / | 140 | 100 | 79.2 | this work |
| **4** | O | / | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone | / | 45 | 12 | 93 | [1](#_ENREF_1) |
| **5** | O | 2,6-di-*tert*-butyl-4-methylpyridine | thianthrene cation radical perchlorate | / | RT |  | 97 | [2](#_ENREF_2) |
| **6** | NH | / | oxone | / | RT |  | 90 | [3](#_ENREF_3) |
| **7** | NH | Ru(PPh3)3(CO)H2/ Xantphos | / | p-TsOH/ piperidinium acetate | 111 | 8 | 98 | [4](#_ENREF_4) |
| **8** | O | [Cp\*IrI2]2 | / | crotononitrile | 111 | 24 | 100 | [4](#_ENREF_4) |
| **9** | S | [Cp\*IrI2]2 | / | crotononitrile | 111 | 24 | 68 | [4](#_ENREF_4) |
| **10** | NH | CuCl/Bpy | air | TEMPO | r.t. | 12 | 95 | [5](#_ENREF_5) |
| **11** | O | CuCl/Bpy | air | TEMPO | r.t. | 12 | 89 | [5](#_ENREF_5) |
| **12** | S | CuCl/Bpy | air | TEMPO | r.t. | 13 | 93 | [5](#_ENREF_5) |
| **13** | O | Au/TiO2 | / | / | 111 | 24 | 90 | [6](#_ENREF_6) |
| **14** | O | Polymer-Incarcerated Pt nanoclusters | O2 | K2CO3 | 30 | 20 | 72 | [7](#_ENREF_7) |
| **15** | S | Polymer-Incarcerated Pt nanoclusters | O2 | K2CO3 | 30 | 20 | 83 | [7](#_ENREF_7) |
| **16** | O | AgPd NPs/WO2.72 | HCOOH | / | 80 | 8 | 99 | [8](#_ENREF_8) |
| **17** | O | N-hydroxyphthalimide | O2 | / | 150 | 15 | 71 | [9](#_ENREF_9) |
| **18** | O | 4-methoxy-TEMPO | O2 | / | 120 | 15 | 96 | [9](#_ENREF_9) |
| **19** | O | Darco KB | O2 | / | 120 | 4 | 78 | [10](#_ENREF_10) |
| **20** | O | MIL-101(Cr) | O2 | / | 120 | 9 | 87 | [11](#_ENREF_11) |
| **21** | NH | MIL-101(Cr) | O2 | / | 55 | 2 | 94 | [11](#_ENREF_11) |
| **22** | S | MIL-101(Cr) | O2 | / | 60 | 2.5 | 87 | [11](#_ENREF_11) |
| **23** | NH | SiO2-OSO3H | air | / | 80 | 0.5 | 92 | [12](#_ENREF_12) |
| **24** | NH | Pt/TiO2 | / | / | 165 | 24 | 94 | [13](#_ENREF_13) |
| **25** | S | Pt/Al2O3 | / | / | 165 | 24 | 89 | [13](#_ENREF_13) |
| **26** | O | molecular sieve | O2 | / | 180 | 48 | 86 | [14](#_ENREF_14) |
| **27** | O | Ru2Cl4(CO)6/PFMN | / | DABCO | 120 | 24 | 72 | [15](#_ENREF_15) |
| **28** | O | Fe3O4@SiO2@PPh2 | / | DABCO | 110 | 12 | 10 | [15](#_ENREF_15) |
| **29** | NH | CoSO4⋅7 H2O | air | CF3COOH | r.t./20 mA | 2.5 | 93 | [16](#_ENREF_16) |
| **30** | S | CoSO4⋅7 H2O | air | CF3COOH | r.t./20 mA | 2.5 | 86 | [16](#_ENREF_16) |
| **31** | O | CoSO4⋅7 H2O | air | CF3COOH | r.t./10 mA | 6 | 40 | [16](#_ENREF_16) |
| **32** | O | copper ferrite NPs | / | / | 130 | 16 | 92 | [17](#_ENREF_17) |
| **33** | S | AgPd NPs/WO2.72 | HCOOH | / | 80 | 8 | 87 | [18](#_ENREF_18) |
| **34** | NH | AgPd NPs/WO2.72 | HCOOH | / | 80 | 8 | 83 | [18](#_ENREF_18) |
| **35** | O | CuFe2O4 | O2 | / | 110 |  | 92 | [19](#_ENREF_19) |
| **36** | S | CuFe2O4 | O2 | / | 110 |  | 93 | [19](#_ENREF_19) |
| **37** | NH | CuFe2O4 | O2 | / | 110 |  | 89 | [19](#_ENREF_19) |

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**Figure S4**. Plot of conversion of aminophenol and yield of 2-phenylbenzoxazole after five runs on NC@ND-900. Reaction conditions: 2 mmol 2-aminophenol; 2.2 mmol benzaldehyde; 10 mL xylene; 120 mg catalyst; T= 140 oC; Time = 12 h

**Table S3** The catalytic performance of NC@ND-900, purified and Fe loaded NC@ND-900.

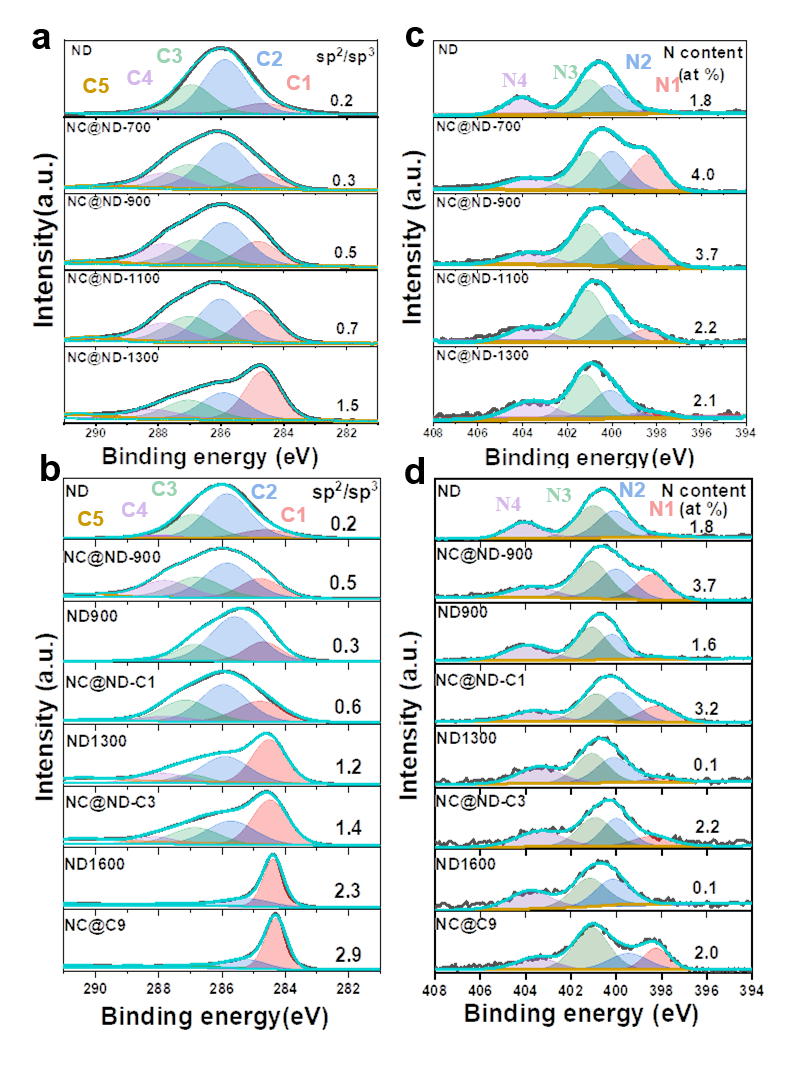
|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Catalyst** | **Temp.**  **(oC)** | **Time**  **(h)** | **Con.A\***  **(%)** | **Sel.P\***  **(%)** | **Sel.I\***  **(%)** | **Yie.P\***  **(%)** |
| **1** | NC@ND-900 | 140 | 2 | 100 | 27.7 | 70.9 | 27.7 |
| **2** | NC@ND-900-HCl | 140 | 2 | 100 | 26.5 | 72.3 | 26.5 |
| **3** | Fe/NC@ND-900 | 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 oC.

**Table S4** The ICP results of various samples.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Sample** | **Fe (wt.%)** | **Ca (wt.%)** | **Ba (wt.%)** | **Ni (wt.%)** |  |
| **1** | NDs | 0.37 | 0.02 | 0.35 | / |  |
| **2** | ND-purified | 0.01 | 0.13 | / | / |  |
| **3** | NC@ND-700 | 0.02 | 0.02 | / | / |  |
| **4** | NC@ND-900 | 0.09 | 0.02 | / | / |  |
| **5** | NC@ND-1100 | 0.04 | 0.01 | / | / |  |
| **6** | NC@ND-1300 | 0.08 | 0.01 | / | / |  |
| **7** | NC@ND-900-HCl | 0.09 | 0.03 | 0.02 | / |  |
| **8** | Fe/NC@ND-900 | 0.42 | 0.02 | 0.02 | / |  |

**Measure conditions:** 25 mg sample was mixed with 30 mL HNO3 in 100 mL autoclave under 200 oC for 2 days, and then was diluted with DI water to 50 mL.



**Figure S5**. High resolution C1s (a, b) and N1s (c, d) XPS spectra of NDs and different N-doped sp3@sp2 nanocarbon. C1: sp2 C; C2: sp3 C; C3: C-O, C-N; C4: C=O; C5: O-C=O. N1: pyridinic N; N2: pyrrolic N; N3: graphitic N; N4: N oxide.

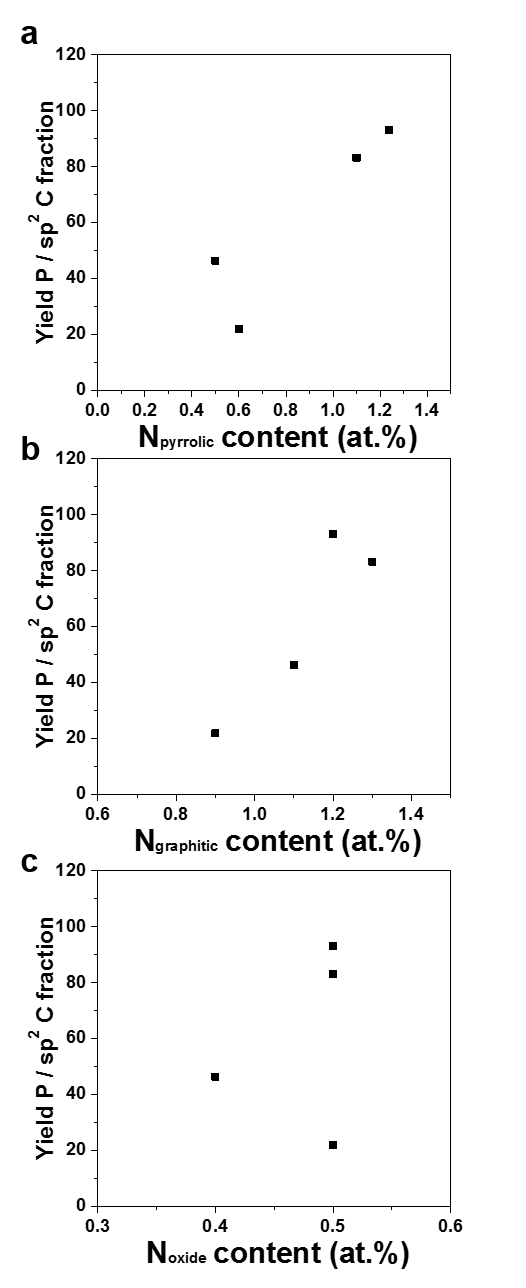
|  |
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**Table S5** Summary of XPS N1s data of various samples

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 |
| **NC@ND-700** | 4.0 | 25.8 | 31.0 | 30.4 | 12.8 | 1.0 | 1.24 | 1.2 | 0.5 |
| **NC@ND-900** | 3.7 | 22.5 | 28.5 | 35.5 | 13.4 | 0.8 | 1.1 | 1.3 | 0.5 |
| **NC@ND-1100** | 2.2 | 10.8 | 22.4 | 48.9 | 18.0 | 0.2 | 0.5 | 1.1 | 0.4 |
| **NC@ND-1300** | 2.1 | 5.4 | 28.0 | 41.1 | 25.5 | 0.1 | 0.6 | 0.9 | 0.5 |
| **ND900** | 1.6 | 3.9 | 29.0 | 40.9 | 26.3 | 0.1 | 0.5 | 0.7 | 0.4 |
| **NC@ND-C1** | 3.2 | 20.6 | 33.2 | 32.2 | 14.0 | 0.7 | 1.1 | 1.0 | 0.4 |
| **ND1300** | 0.1 | 5.6 | 32.3 | 35.5 | 26.7 | 0.01 | 0.01 | 0.04 | 0.03 |
| **NC@ND-C3** | 2.2 | 17.9 | 26.0 | 32.9 | 23.2 | 0.4 | 0.6 | 0.7 | 0.5 |
| **ND1600** | 0.1 | 0 | 37.3 | 29.0 | 33.7 | 0 | 0.04 | 0.03 | 0.03 |
| **NC@ND-C9** | 2.0 | 17.5 | 20.2 | 47.2 | 15.2 | 0.4 | 0.4 | 0.9 | 0.3 |

**Table S6** Summary of XPS C1s data of various samples

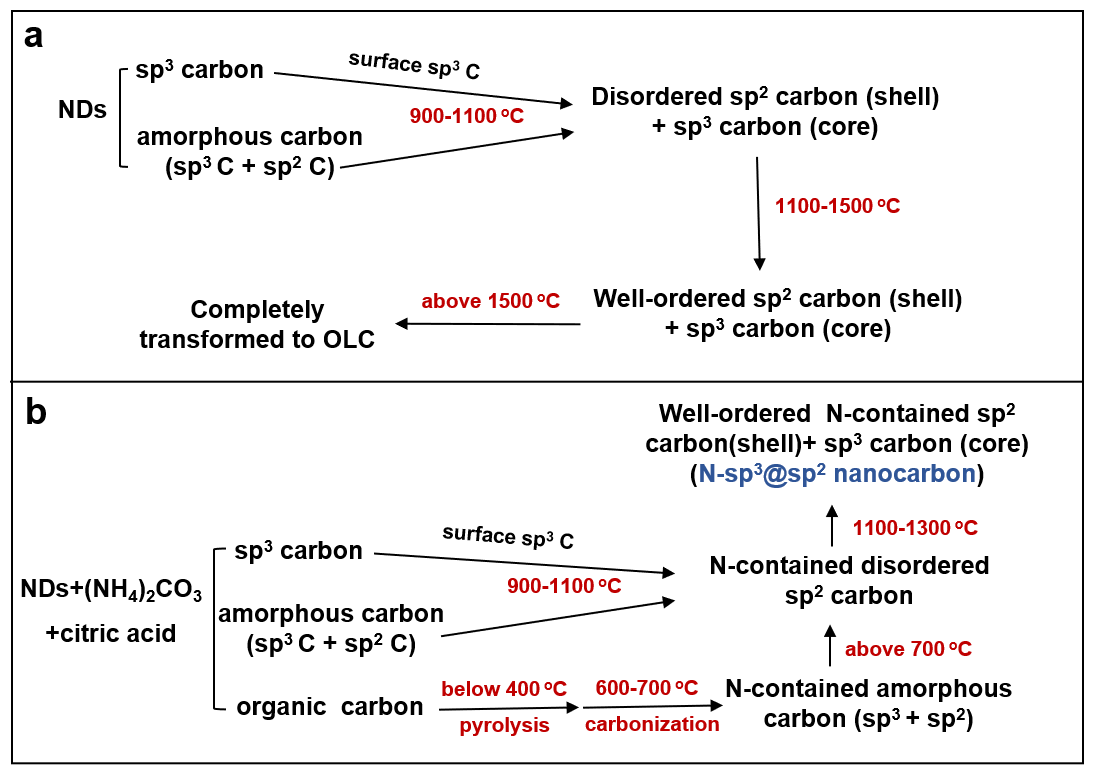
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **C**  **(at%)** | **N**  **(at%)** | **O**  **(at%)** | **sp2/sp3** | **sp2 carbon**  **fraction (%)** |
| **ND** | 87.6 | 1.8 | 10.5 | 0.2 | 16.7 |
| **NC@ND-700** | 89.9 | 4.0 | 6.1 | 0.3 | 23.1 |
| **NC@ND-900** | 92.3 | 3.7 | 4.0 | 0.5 | 33.3 |
| **NC@ND-1100** | 93.0 | 2.2 | 4.8 | 0.7 | 41.2 |
| **NC@ND-1300** | 93.7 | 2.1 | 4.2 | 1.5 | 60 |
| **ND900** | 95.4 | 1.6 | 3.0 | 0.3 | 23.1 |
| **NC@ND-C1** | 93.3 | 3.2 | 3.5 | 0.6 | 37.5 |
| **ND1300** | 98.9 | 0.1 | 1.0 | 1.2 | 54.5 |
| **NC@ND-C3** | 96.5 | 2.2 | 1.3 | 1.8 | 65.5 |
| **ND1600** | 98.8 | 0.1 | 1.1 | 2.9 | 74.5 |
| **NC@ND-C9** | 96.9 | 2.0 | 1.1 | 3.8 | 79.2 |

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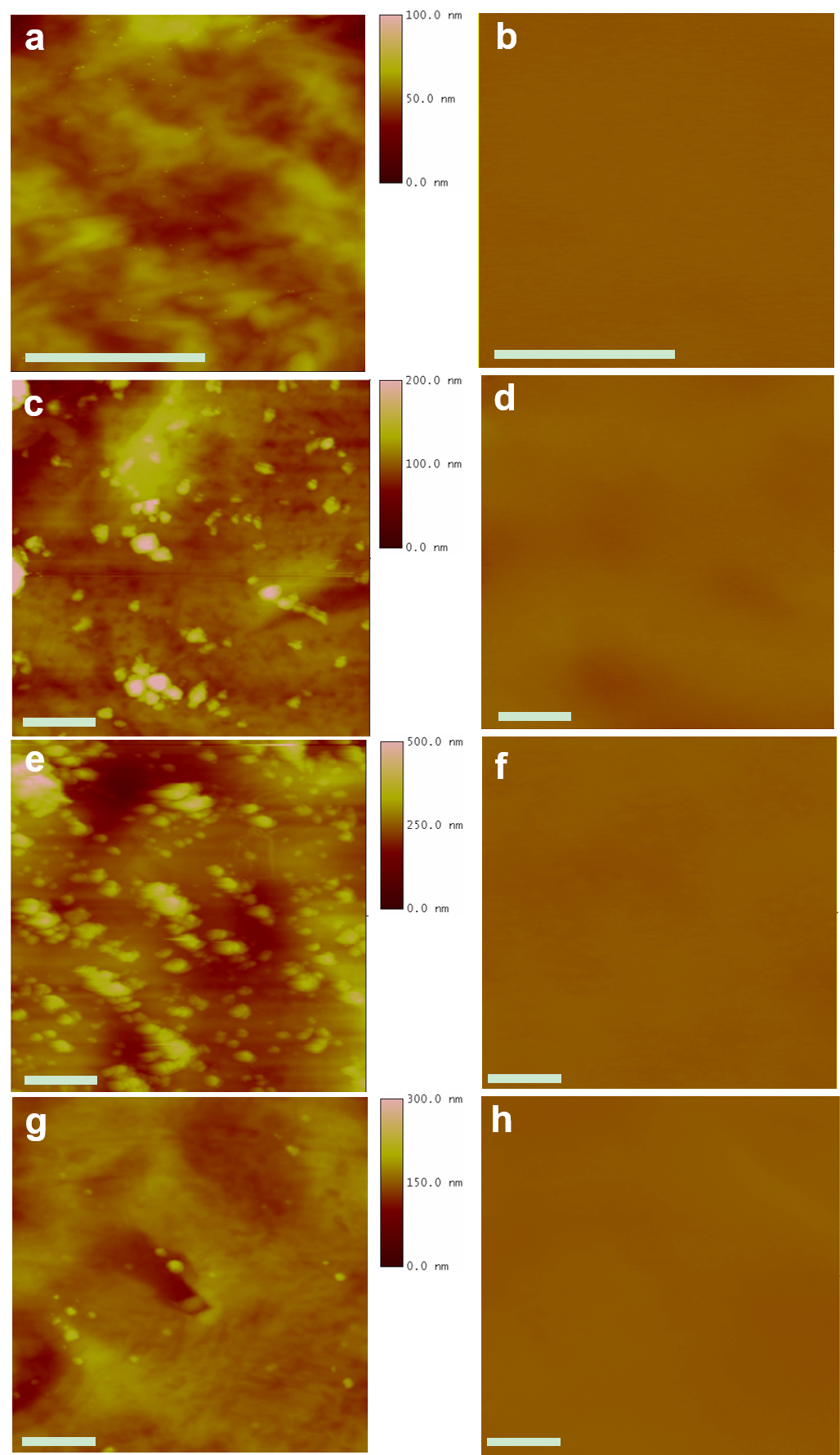
**Figure S6**. Relationships between pyrrolic N (a), graphitic N (b) and N oxide(c) content and yield of 2-phenylbenzoxazole normalized by sp2 carbon fraction.

**Table S7** Summary of Raman peaks assignments.

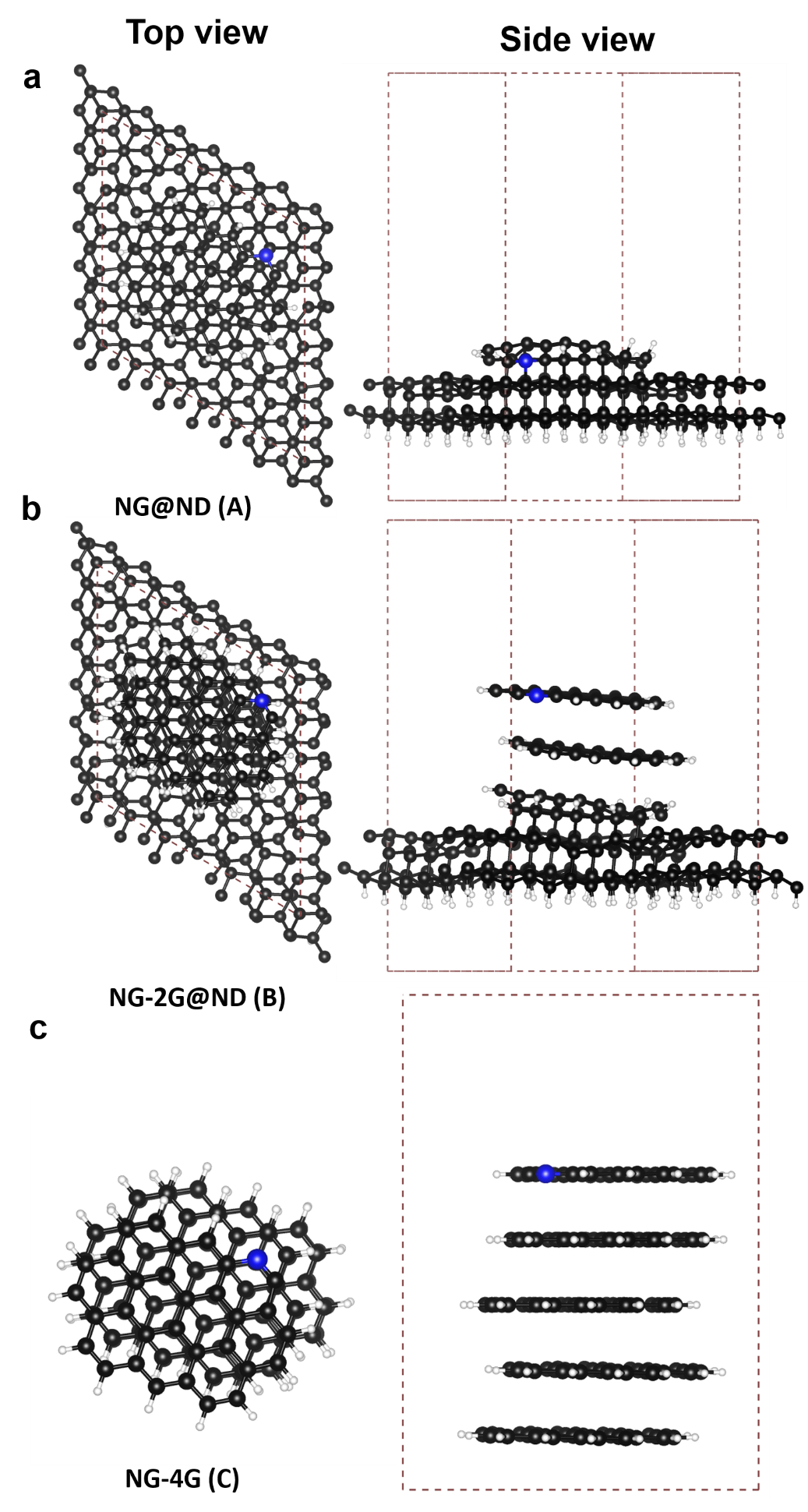
|  |  |
| --- | --- |
| **Position** | **Assignment** |
| 1324 cm-1 | Diamond peak |
| 1400 cm-1 | Disorder-induced D band |
| 1590 cm-1 | G band |
| 1640 cm-1 | O-H bending vibrations |

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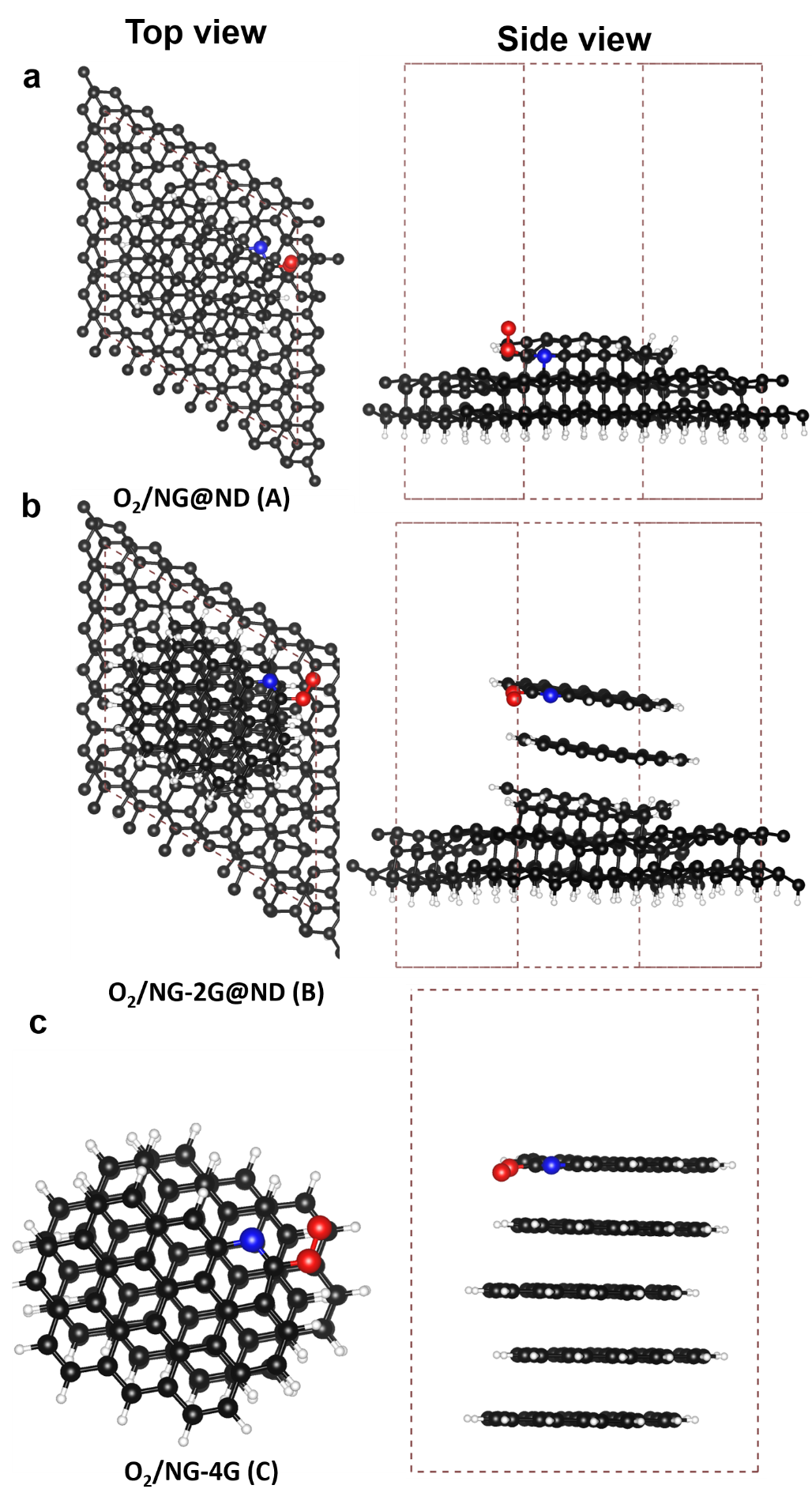
**Figure S7**. The proposed structure evolution process of (a) NDs and (b)N-sp3@sp2 nanocarbon.

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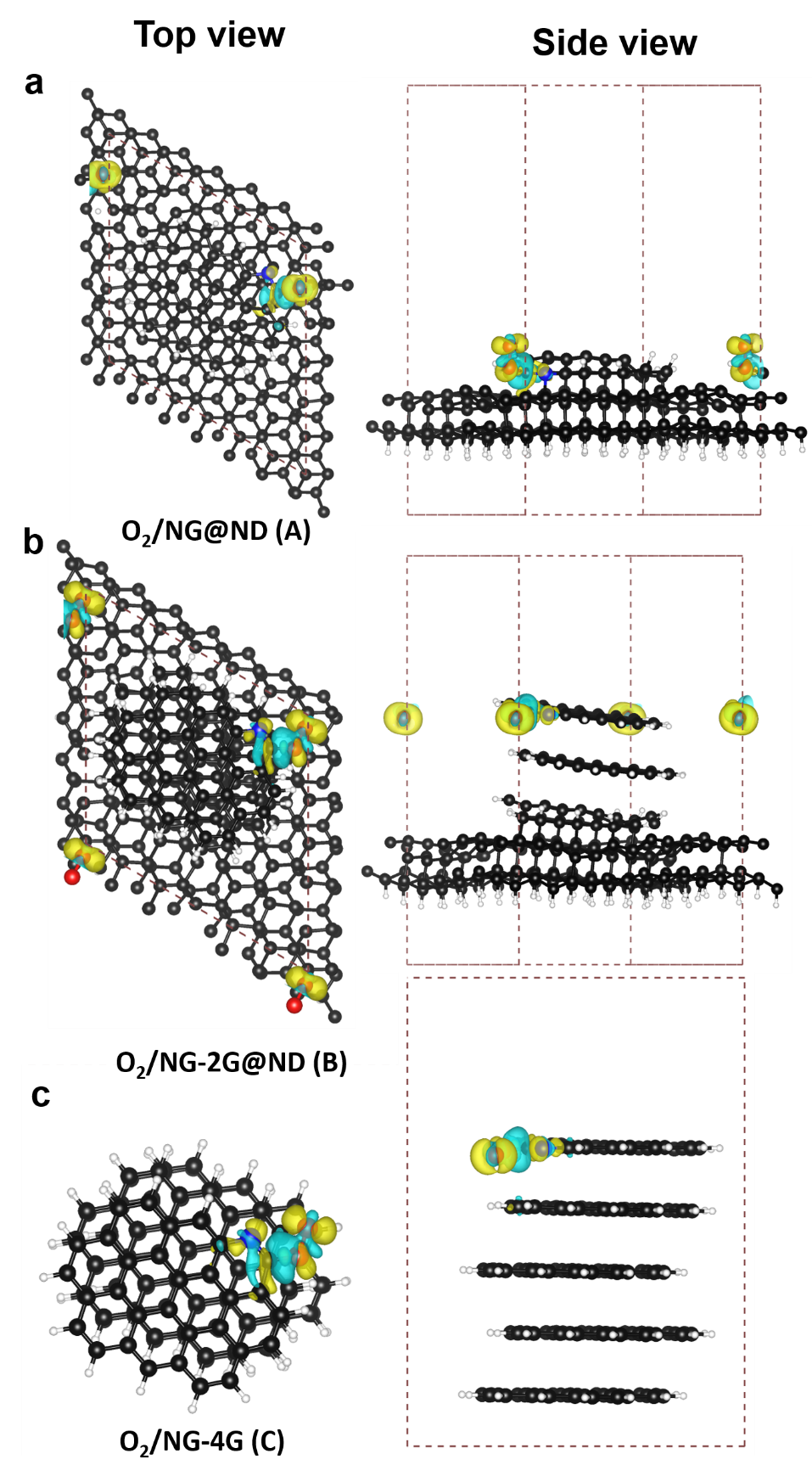
**Figure S8**. Topography and CPD images of the NC@ND-900 (a, b), NC@ND-C1 (c, d), NC@ND-C3 (e, f) and NC@C9(g, h). The scale bar at the bottom left of the figures is 1μm.



**Fig. S9** The top and side view of optimized configurations of (a) NG@ND, (b) NG-2G@ND and (c) NG-4G.

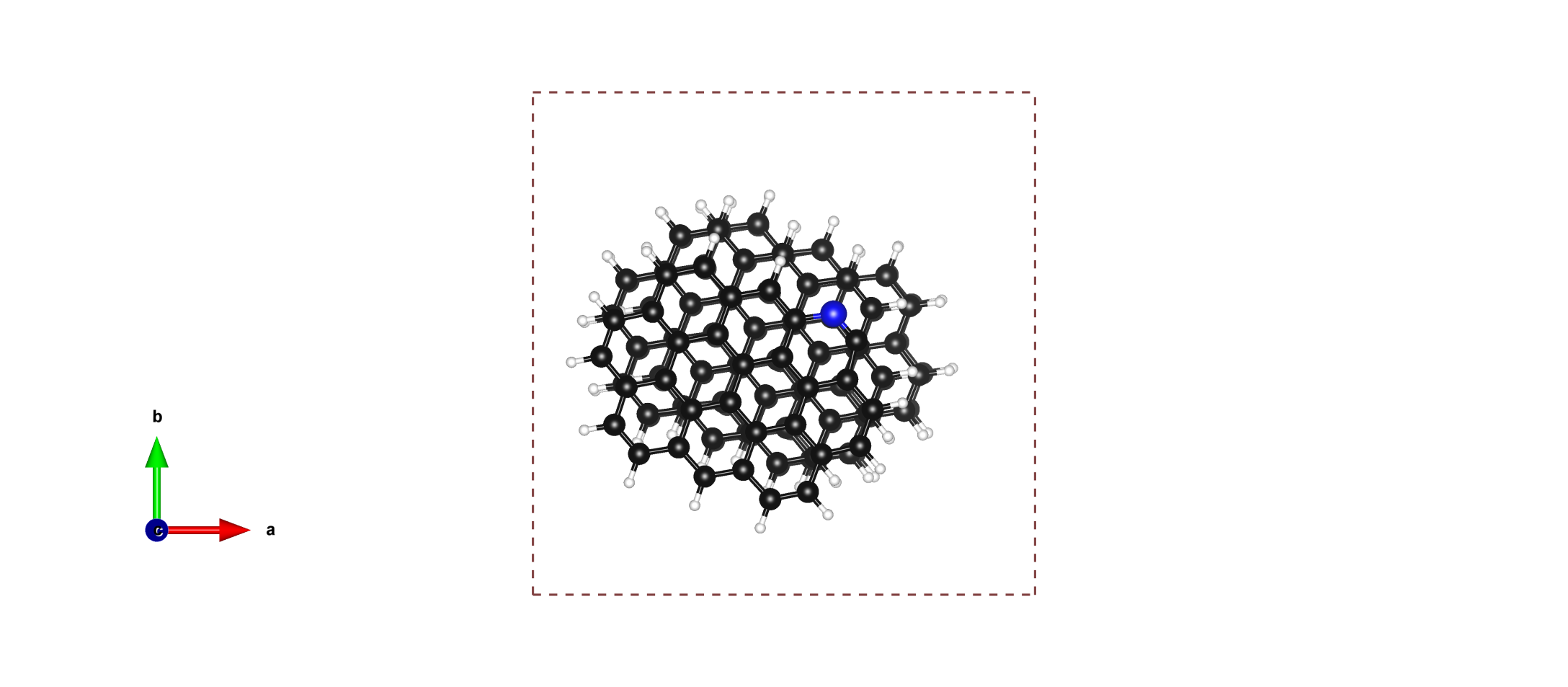


**Fig. S10** The top and side view of optimized configurations of (a) O2/NG@ND, (b) O2/NG-2G@ND and (c) O2/NG-4G.



**Fig. S11** The top and side view of charge density difference for (a) O2/NG@ND, (b) O2/NG-2G@ND and (c) O2/NG-4G. The yellow areas mean that the accumulation of electrons and the blue region exhibits the depletion of electrons (the isosurface value is ±0.002 e/ A3).

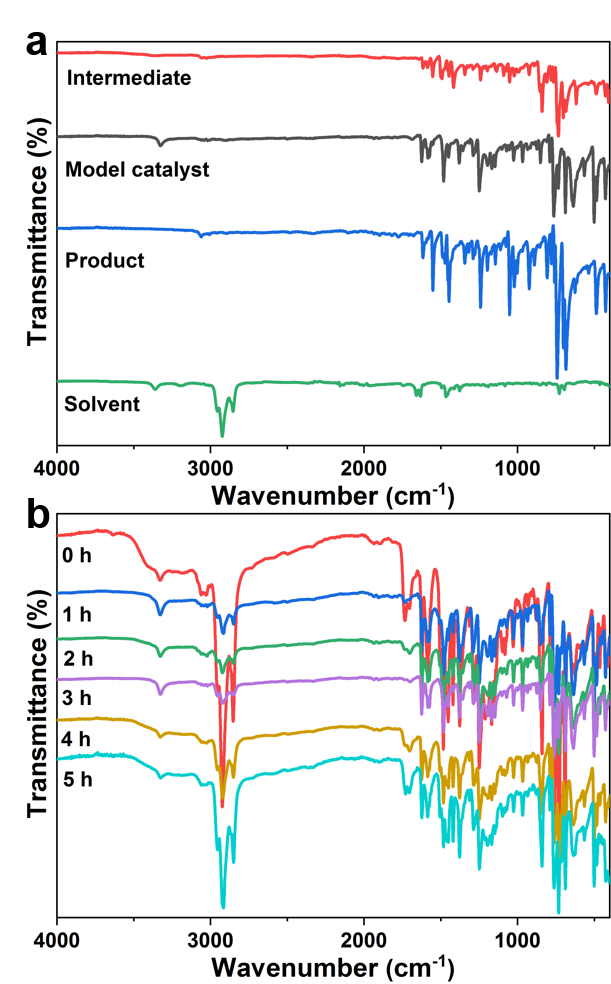
**Table S8** Atom charge for the C atoms that adjacent to the doped-N from Bader charge analysis.



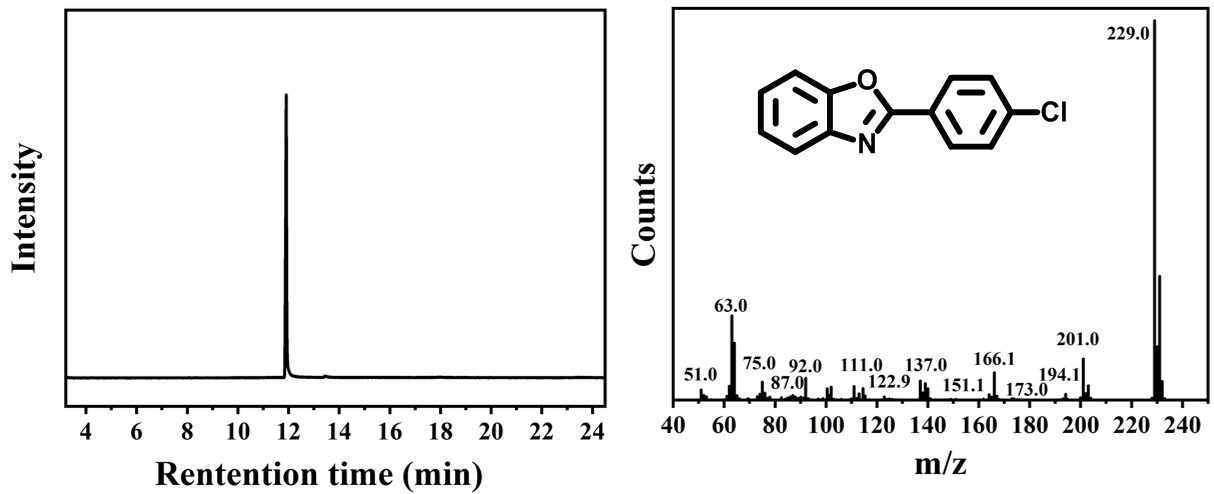
**C1**

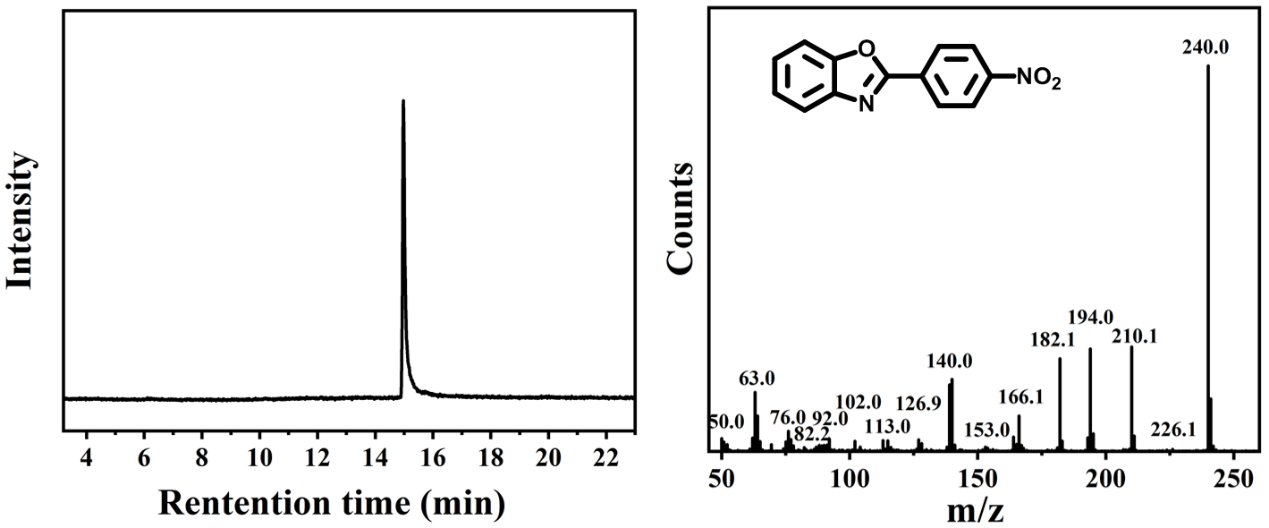
**C2**

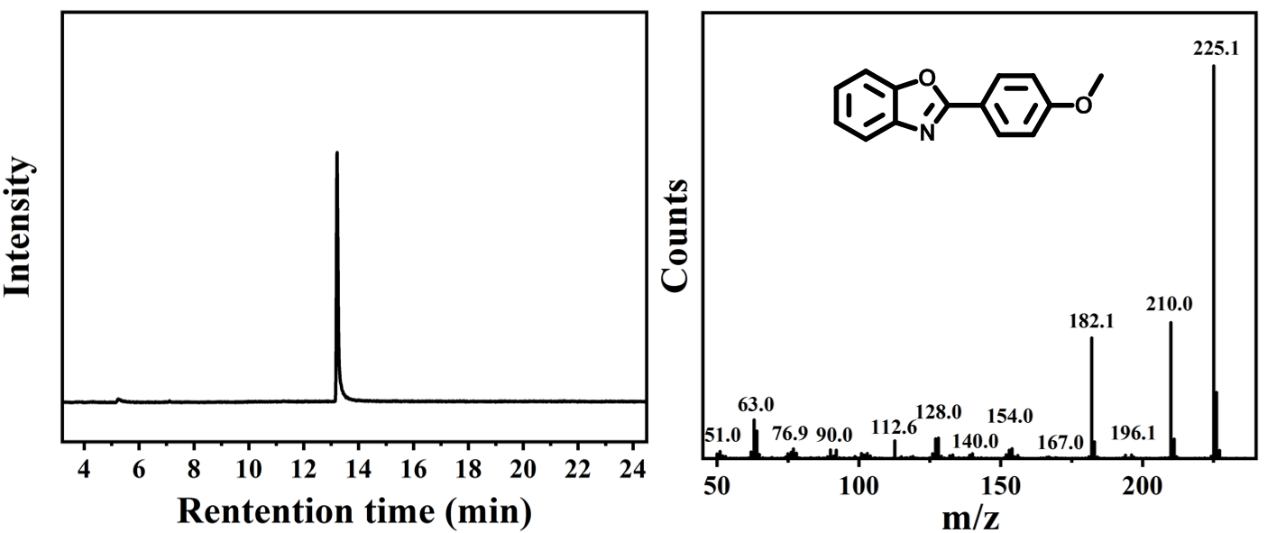
|  |  |
| --- | --- |
| **Atom** | **Charge** |
| C1 in NG@ND | 0.23 |
| C2 in NG@ND | 0.31 |
| C1 in NG-2G@ND | 0.47 |
| C2 in NG-2G@ND | 0.58 |
| C1 in NG-4G | 0.37 |
| C2 in NG-4G | 0.60 |

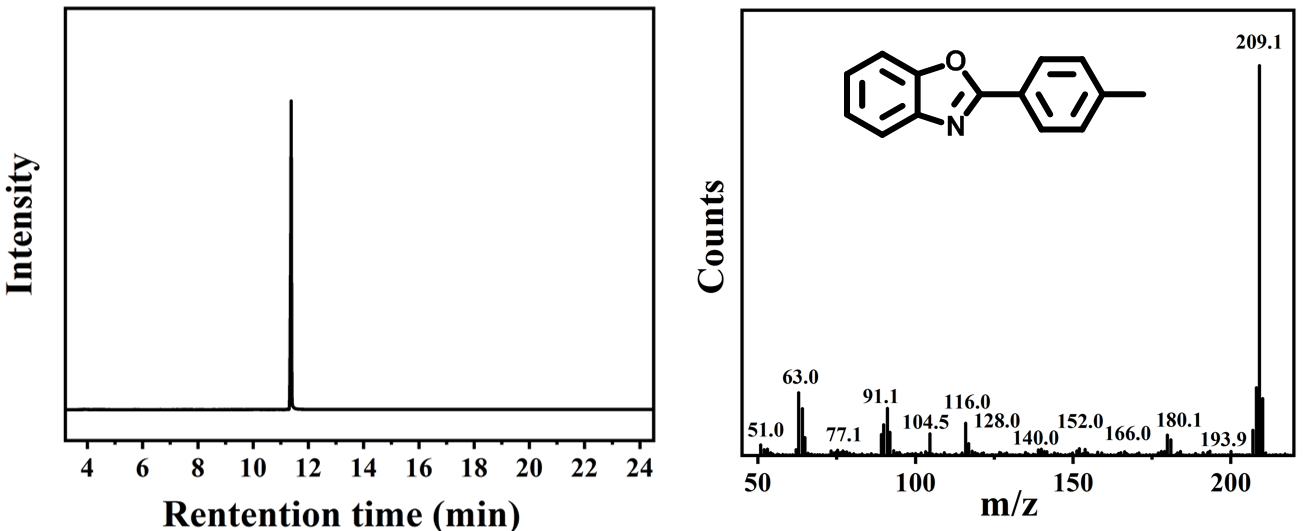


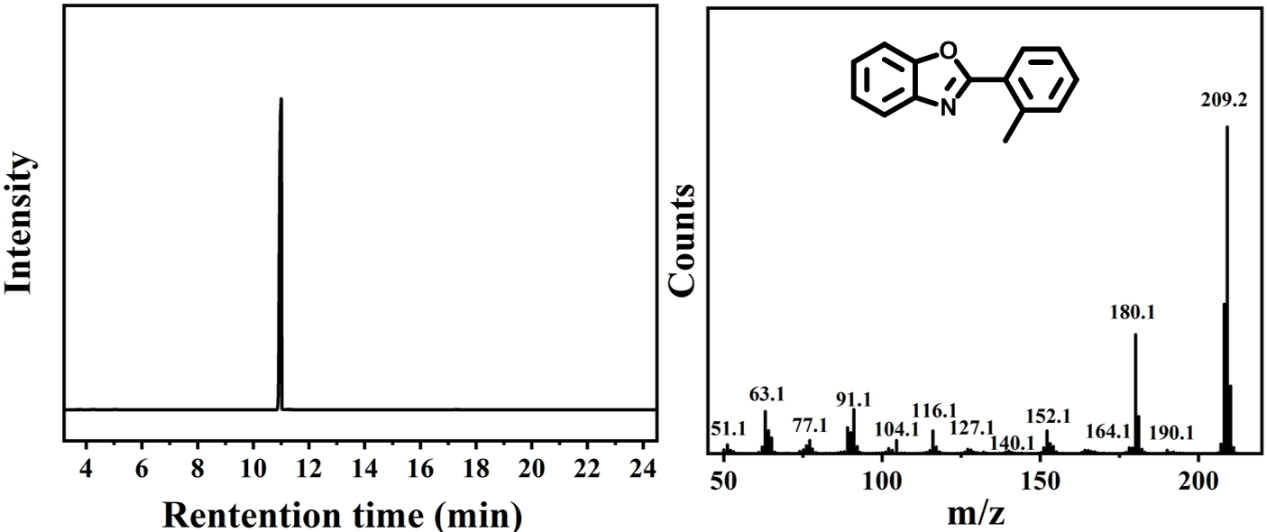
**Fig. S12** ATR-IR spectra of (a) reference samples including **I** (2-(benzylideneamino)phenol), model catalyst (1,10-phenanthroline), product (2-phenylbenzoxazole) and solvent (toluene); (b) catalytic systems with the mixture of **I** (as reactant), model catalyst and toluene under 140 oC in oxygen for 1, 2, 3, 4 and 5 h, respectively.

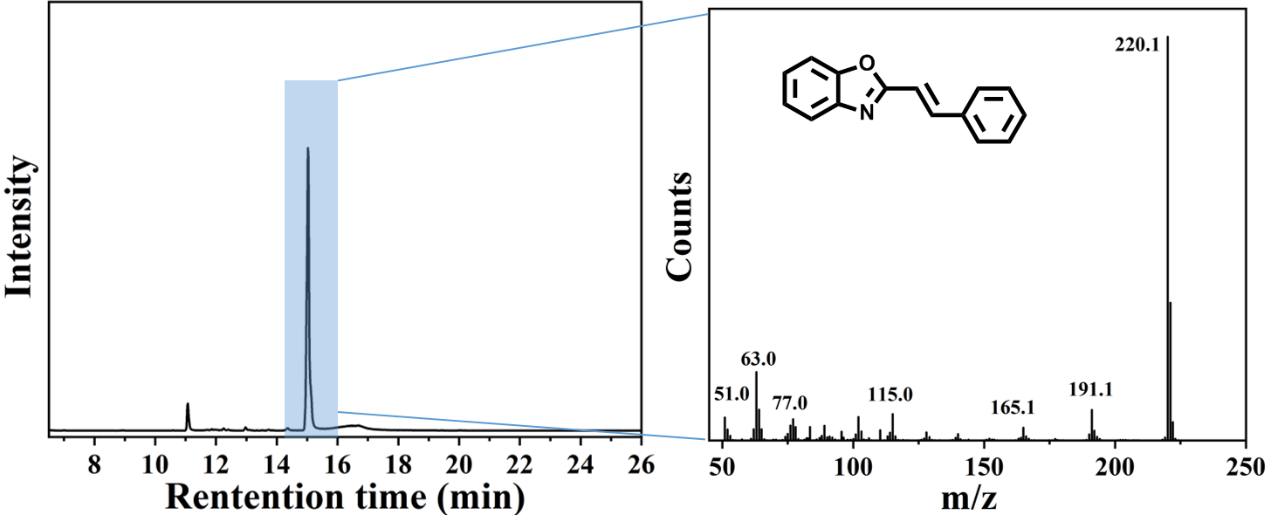


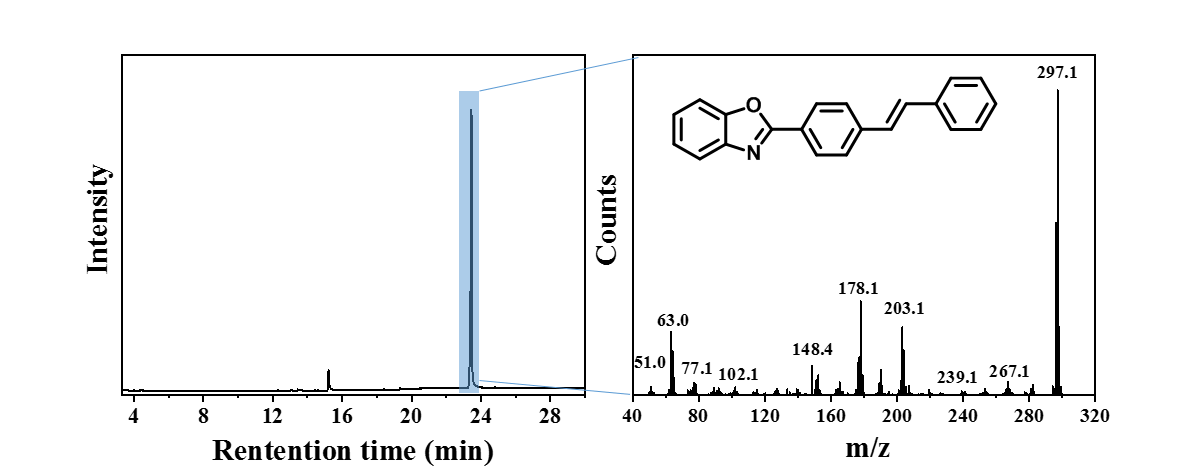


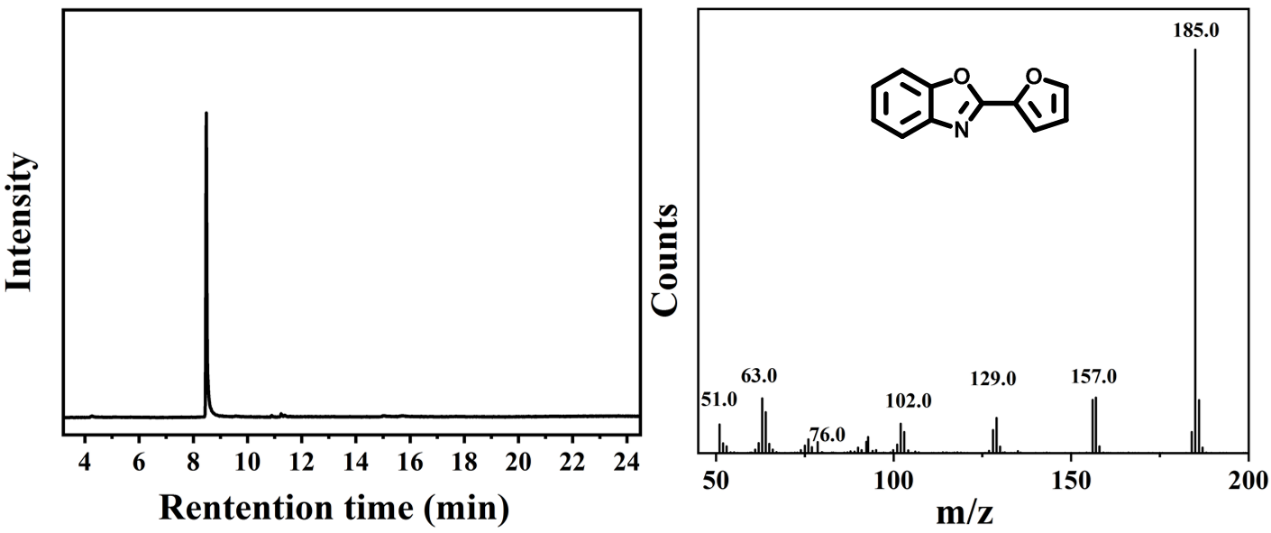


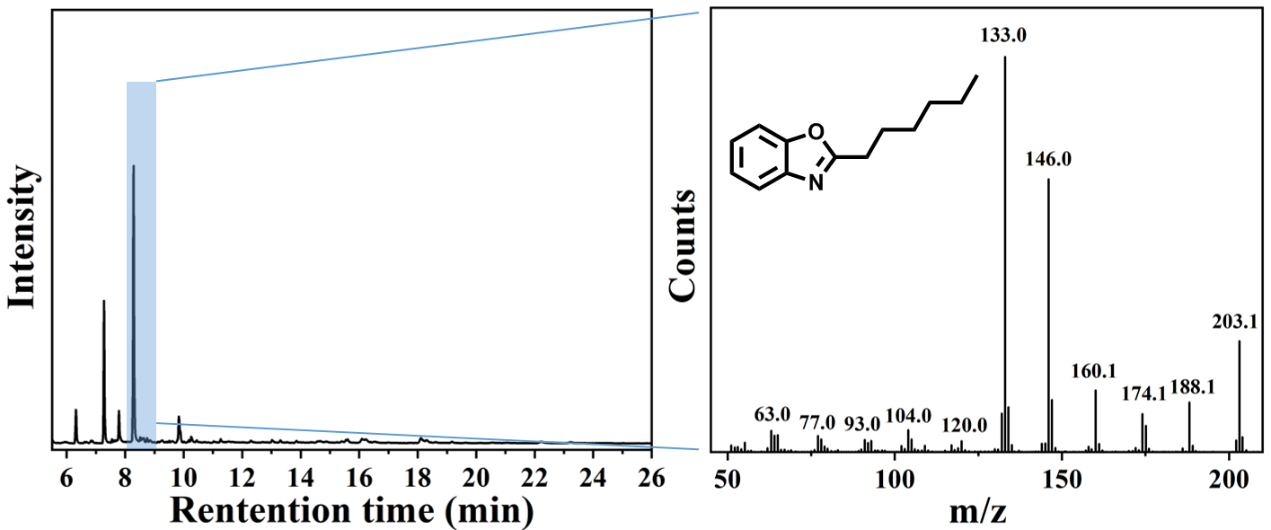


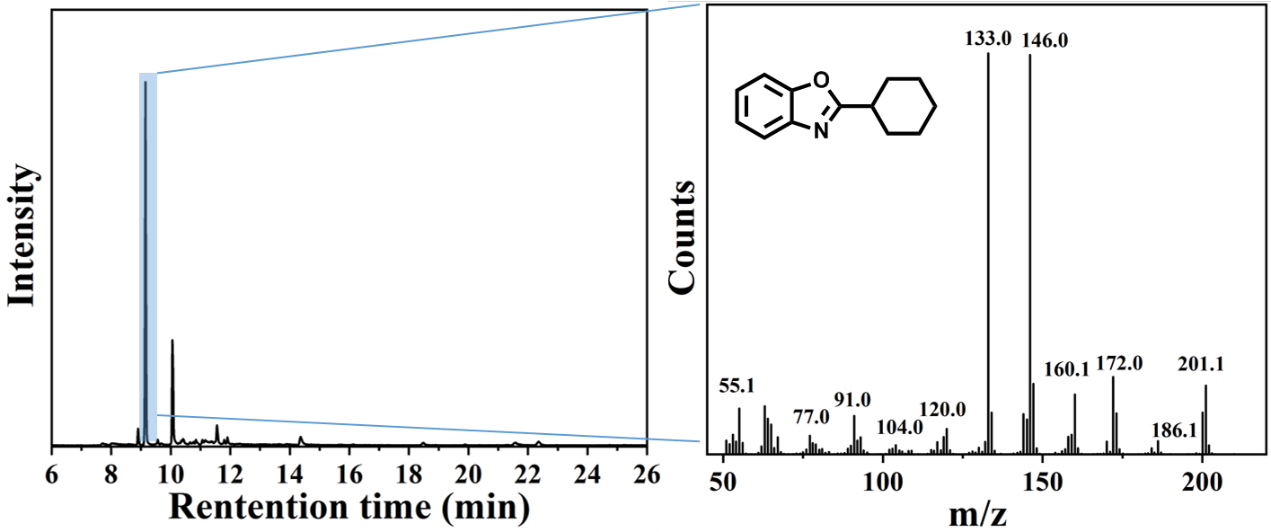


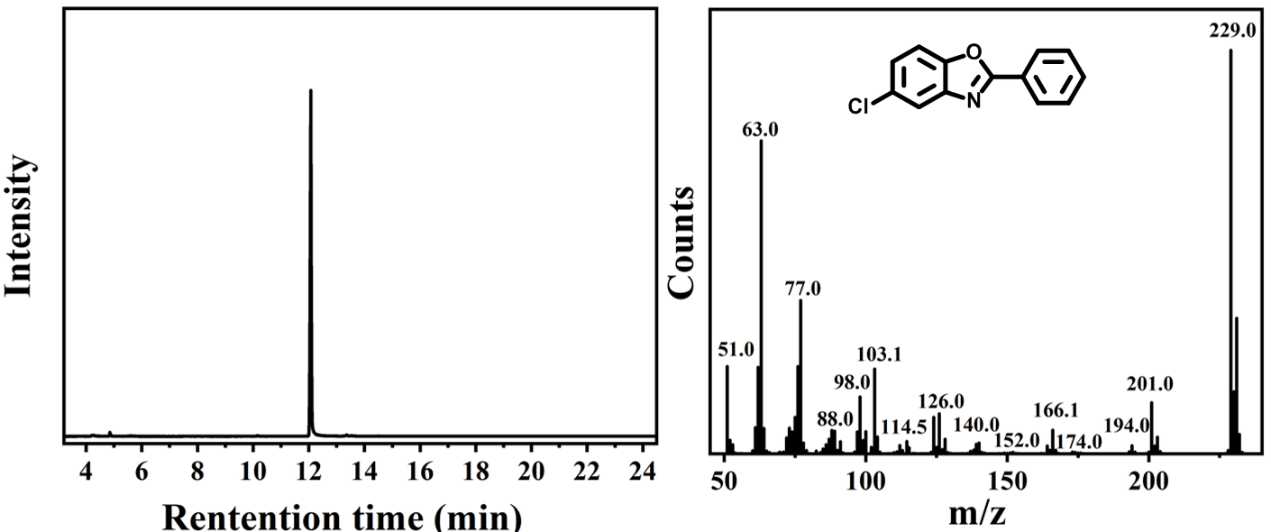


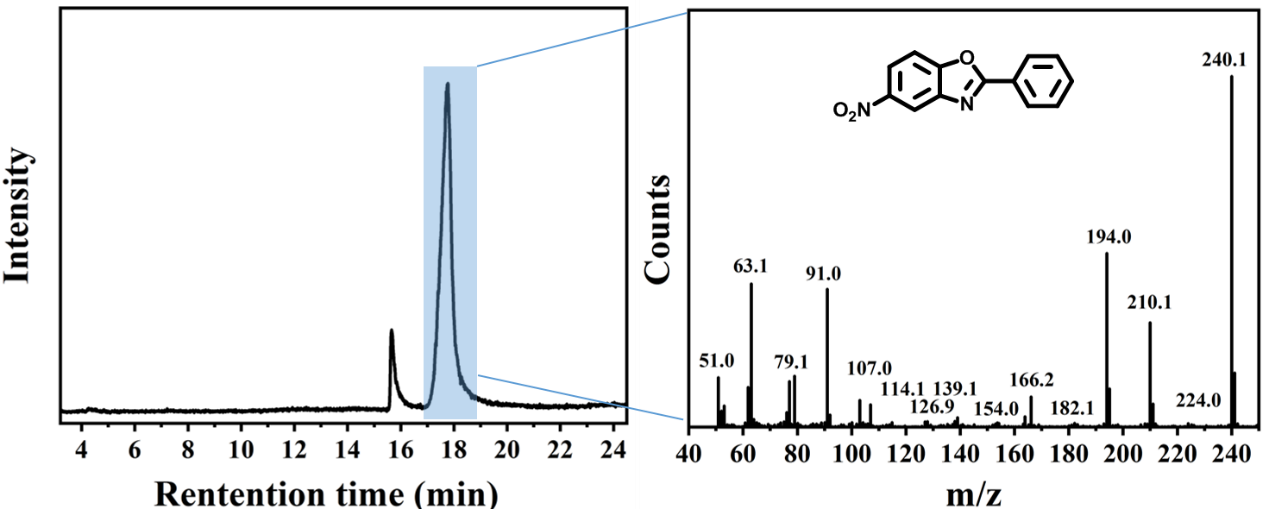


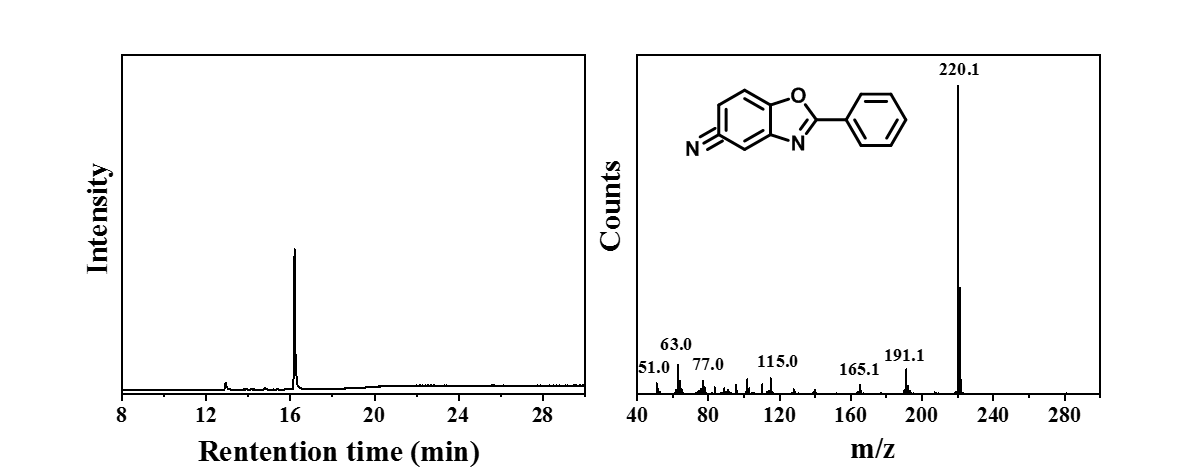


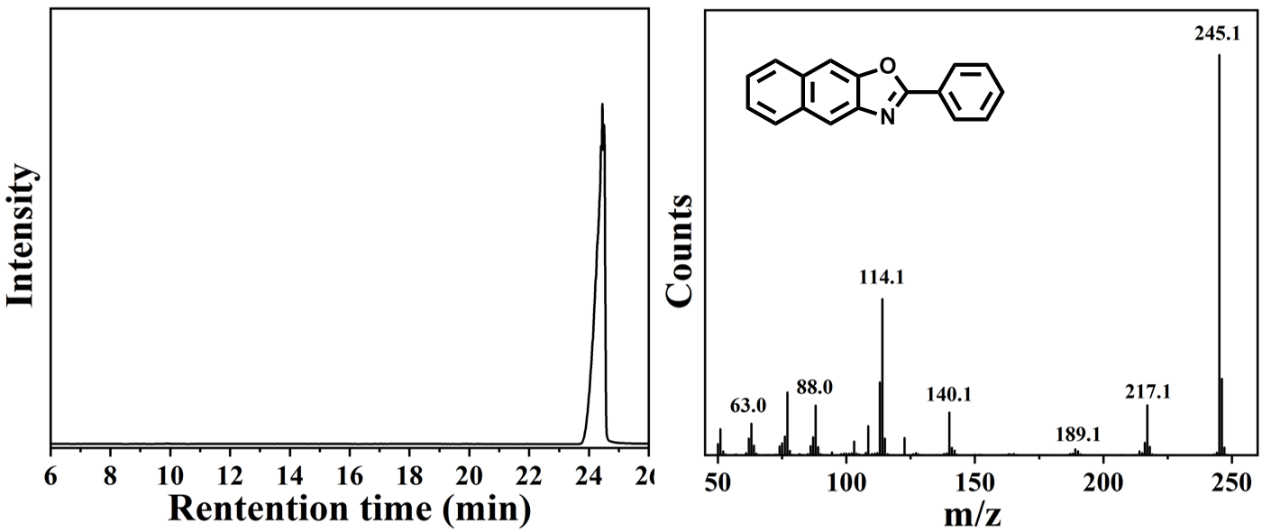


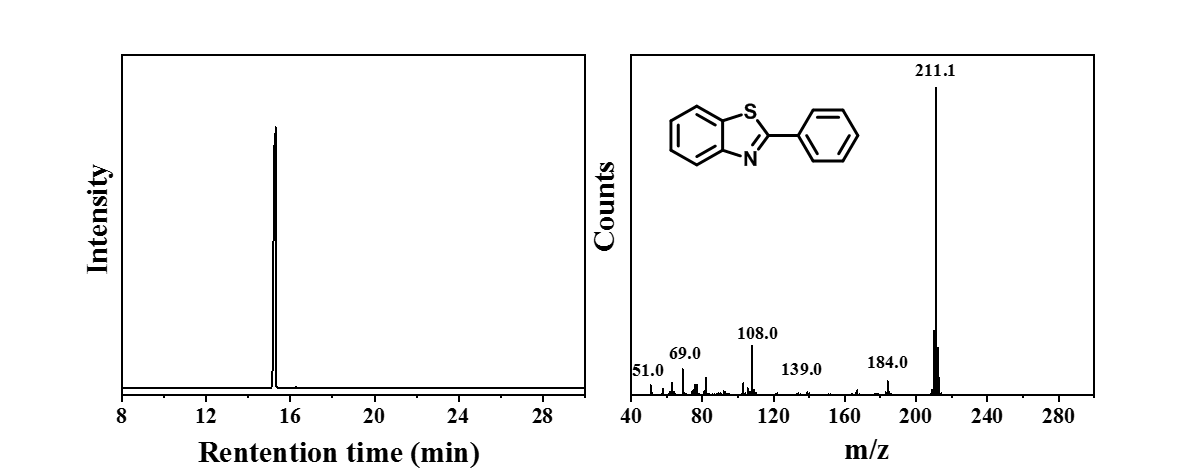


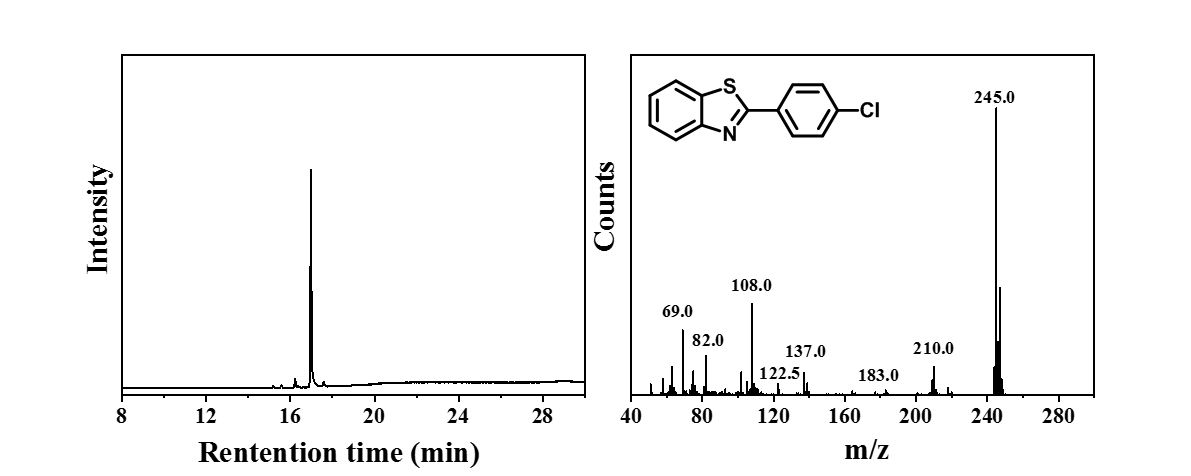


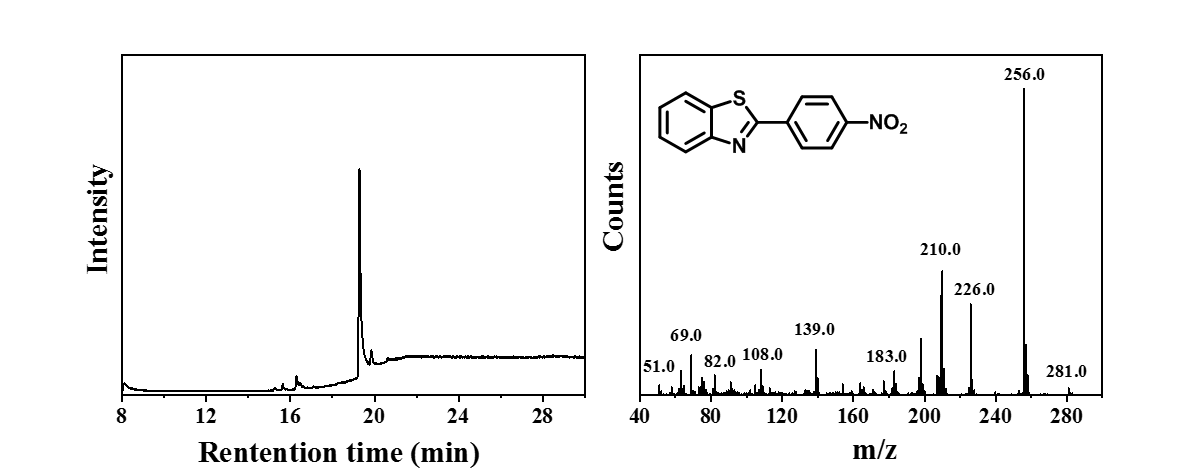


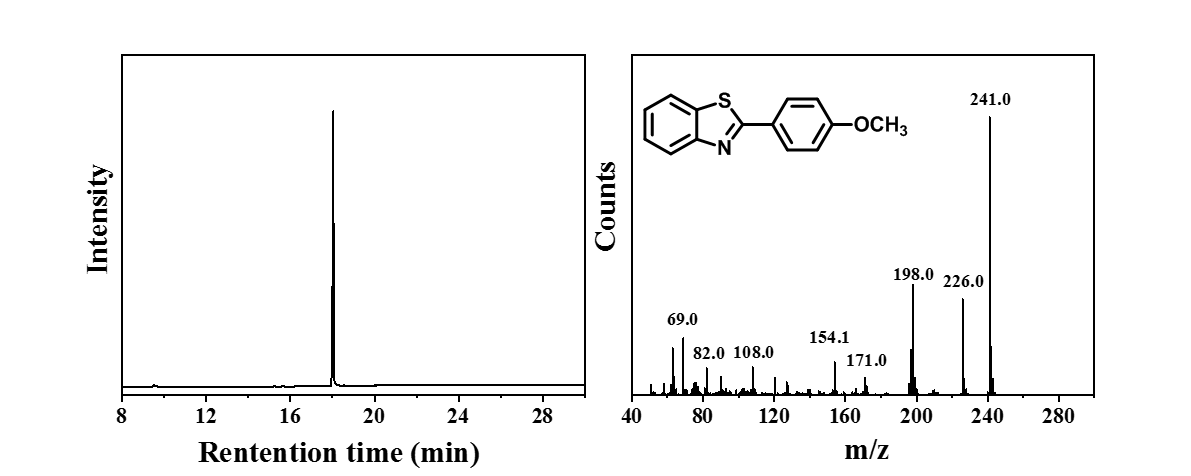


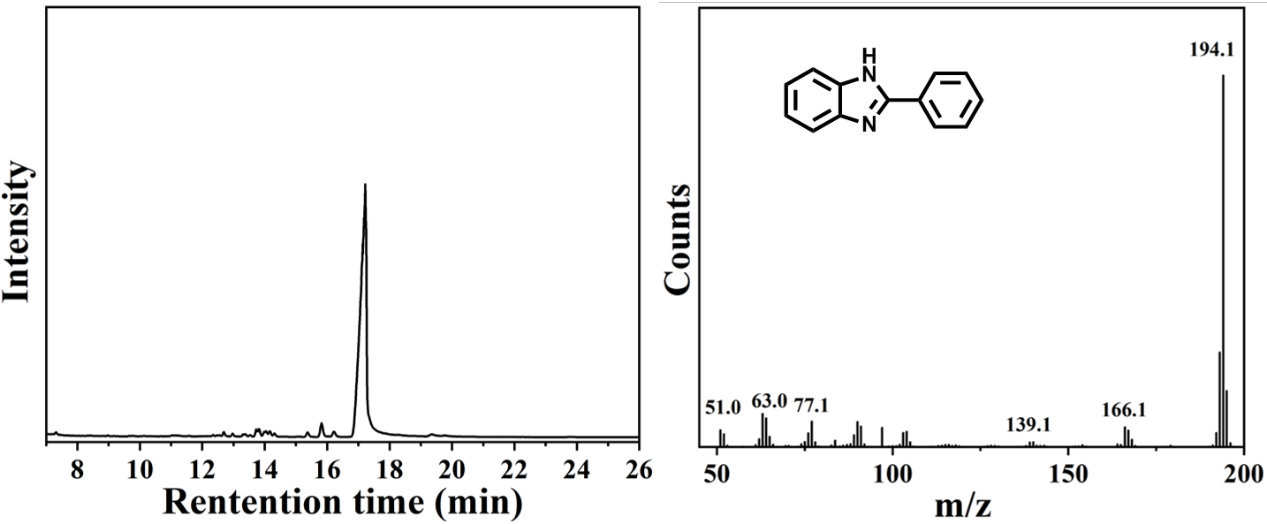


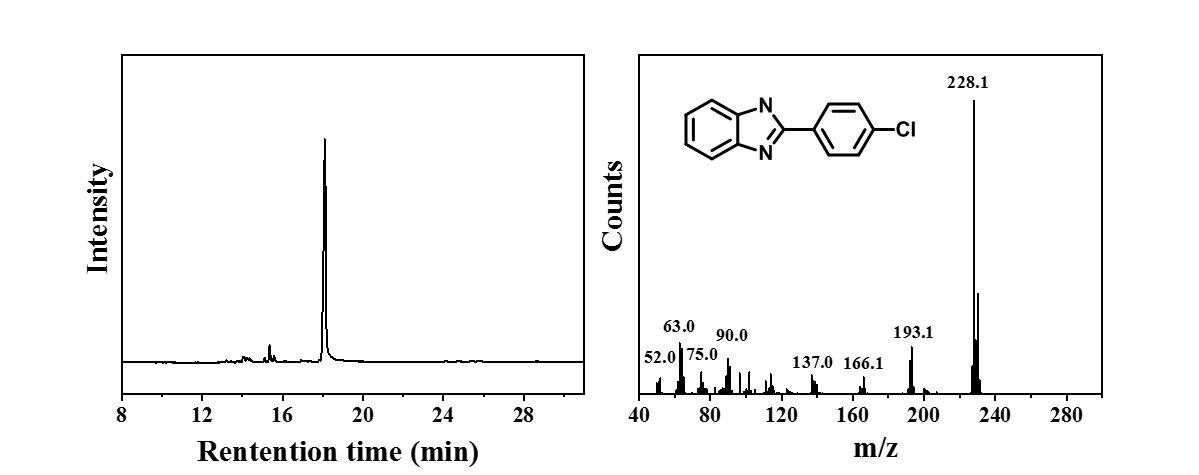


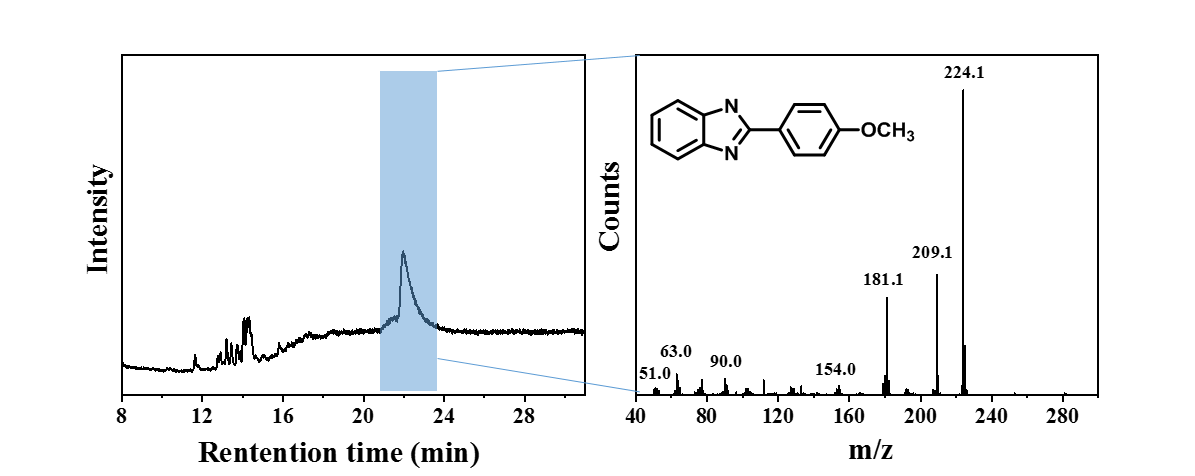












**Fig. S13** GC-MS analysis of products (**P1**-**P23**) in substrate scope experiments.

**References**

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