

Interfacial coupling of transition-metal composites with nitrogen doped carbon as efficient catalysts for nitro-compounds hydrogenation †

Yingping Li,^a Zhiqiang Chen,^c Jieryue Wang,^a Mingyue Wang,^a Wenhai Wang,^a Mingfu Ye,^a Dehong Wu,^{*,b} Binbin Jiang^{*,d} and Konglin Wu^{*,a}

a. Institute of Clean Energy and Advanced Nanocatalysis (iClean), Anhui International Joint Research Center for Green Manufacturing and Biotechnology of Energy Materials, School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243032, China. E-mails: klwuchem@ahut.edu.cn

b. Emergency Management Bureau of Jiangan County, Yibin 644200, China. E-mail: wudehong511523@163.com

c. Beijing Key Laboratory of Research and Application for Aerospace Green Propellants, Aerospace Liquid Propellant Research Center, Beijing Institute of Aerospace Testing Technology, Beijing 100074, China

d. School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Photoelectric-Magnetic Functional Materials, Anqing Normal University, Anqing 246001, China. E-mail: jiangbb@aqnu.edu.cn

1. Experimental section

1.1 Chemicals and materials

$C_8H_{12}ClNO_2$ (98%), nitrobenzene and other nitroarenes were purchased from Aladdin Industrial Corporation. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Na_2WO_4\cdot 2H_2O$, NH_4VO_3 , $K_2Cr_2O_7$, $N_2H_4\cdot H_2O$ (85%), $NH_3\cdot H_2O$ and ethanol were supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as purchased without further purification.

1.2 The synthesis of catalysts

1.2.1. Synthesis of Cr_2O_3/NC and NC

1.25 g of $C_8H_{12}ClNO_2$ and 0.18 g of $K_2Cr_2O_7$ were dissolved into 30 mL of ultrapure water by ultrasonication for 0.5 h, named as solution A. Meanwhile, 1.9 mL of ammonia was slowly added to a mixture of 100 mL ethanol and 225 mL water, named as solution B. Then, the solution A was added into solution B with continuous stirring. After stirring with 24 h, the product was being filtered and washed with deionized water and ethanol for several times, the Cr_2O_3/PDA precursors were achieved with freeze-drying. The last, the Cr_2O_3/PDA precursors were heated in a tube furnace and annealed at 700 °C for 3 h under N_2 flow with a ramp rate of 3 °C·min⁻¹, and the black catalyst was obtained named Cr_2O_3/NC . NC was synthesized by the similar method except that no $K_2Cr_2O_7$ was added.

1.2.2. Synthesis of Cr_2O_3

5 g of $K_2Cr_2O_7$ was measured in crucible and calcined at 900 °C in a muffle furnace for 2.5 h. After calcination, the material was washed with deionized water and acetone for several times. After washing, Cr_2O_3 were achieved and dried at 80 °C overnight.

1.2.3. Synthesis of Mo_2C/NC

Mo_2C/NC was synthesized by the same procedure of the synthesis of Cr_2O_3/NC . The pyrolysis temperatures were 800 °C.

1.2.4. Synthesis of V_2O_5/NC

V_2O_5/NC was synthesized by the same procedure of the synthesis of Cr_2O_3/NC . The pyrolysis temperatures were 800 °C.

1.2.5. Synthesis of WO_x/NC

WO_x/NC was synthesized by the same procedure of the synthesis of Cr_2O_3/NC . The pyrolysis temperatures were 900 °C.

1.3 Characterization

The achieved nanocomposites were characterized by X-ray powder diffraction (XRD, Rigaku Ultima IV), Transmission electron microscopy (TEM, Hitachi H-7700), Scanning electron microscopy (SEM, JSM-6700F), high resolution TEM (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping by energy-dispersive X-ray spectrometry (EDS, JEOL JEM-2100F), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi), Raman spectrometer (Jobin Yvon LabRam HR evolution). The metal contents in achieved product were detected by ICP-OES (Agilent 720). The catalytic process performance was directed by GC (QP2030 NX) equipped with a FID detector and a Rtx-1 column (30 m×0.32 mm×0.25 mm). The structure of the product was confirmed by comparison with a standard sample and by GC-MS (QP2030 NX).

1.4 Catalytic hydrogenation of nitrobenzene

The hydrogenation of nitrobenzene was carried out in a 15 ml pressure bottle. Typically, 1 mmol nitrobenzene, 10 mg Cr₂O₃/NC catalyst, and 5 mL of ethanol were refluxed and were allowed to stir at 40 °C, followed by the addition of 2 mL N₂H₄·H₂O (85 wt%). Reaction samples were collected every 5 min using an injection syringe and filtered, then the crude mixture was diluted with ethanol, followed by gas chromatography-mass spectrometry (GCMS-QP2020 NX) analysis. Nitrobenzene was completely transferred to aniline within 1 hour.

To demonstrate the high efficiency of the prepared catalyst, the selective hydrogenation of different nitro-compound substrates was carried out under the same conditions as mentioned above.

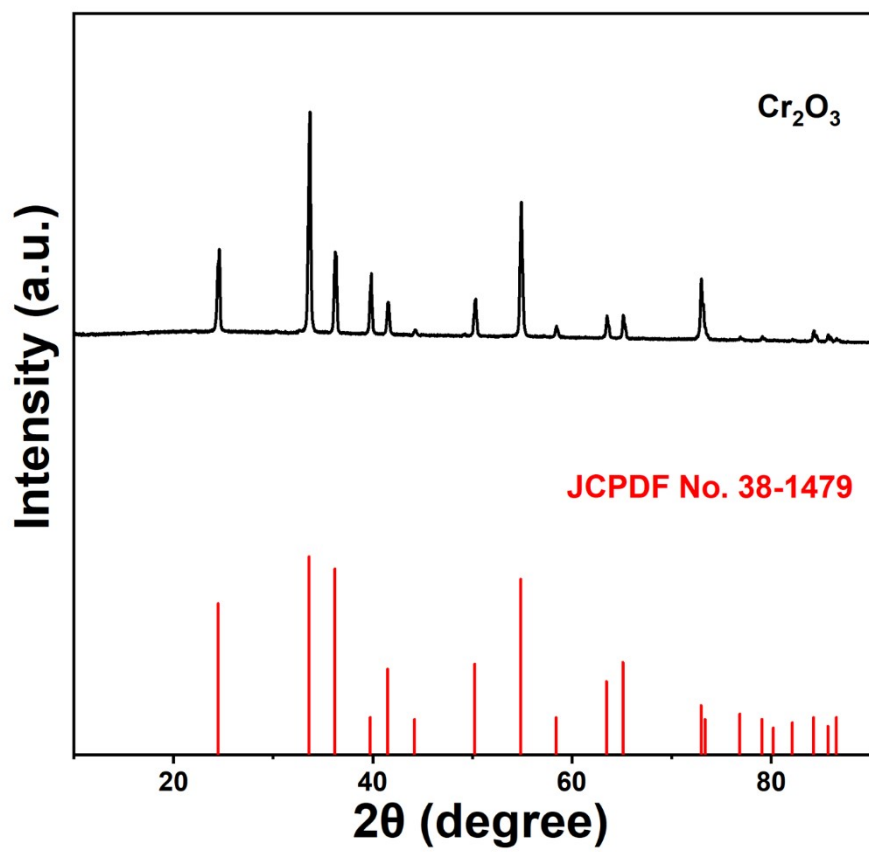


Fig. S1. XRD pattern of Cr_2O_3 .

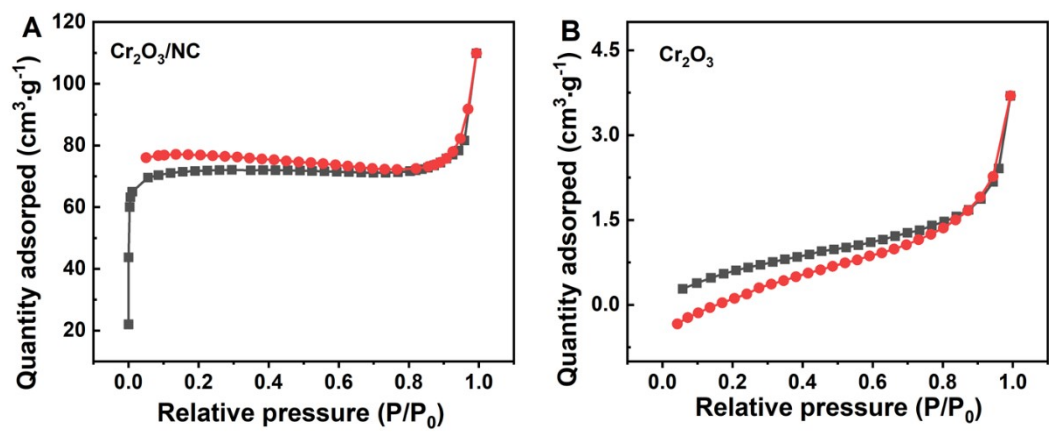


Fig. S2. BET surface area of (A) $\text{Cr}_2\text{O}_3/\text{NC}$ and (B) Cr_2O_3 .

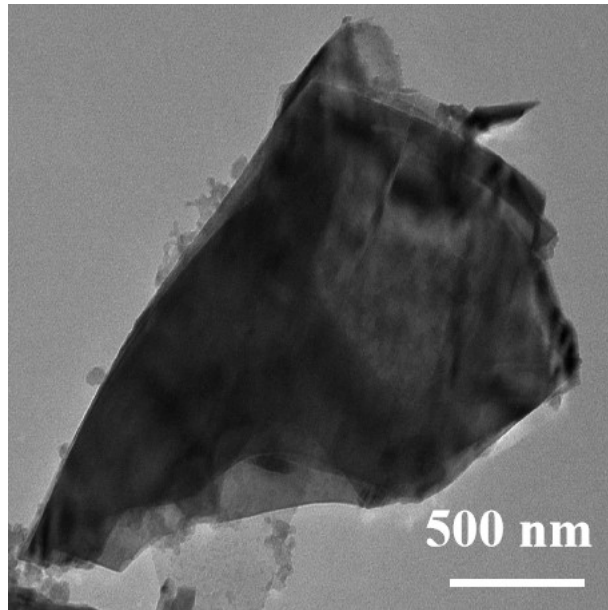


Fig. S3. The TEM image of Cr₂O₃.

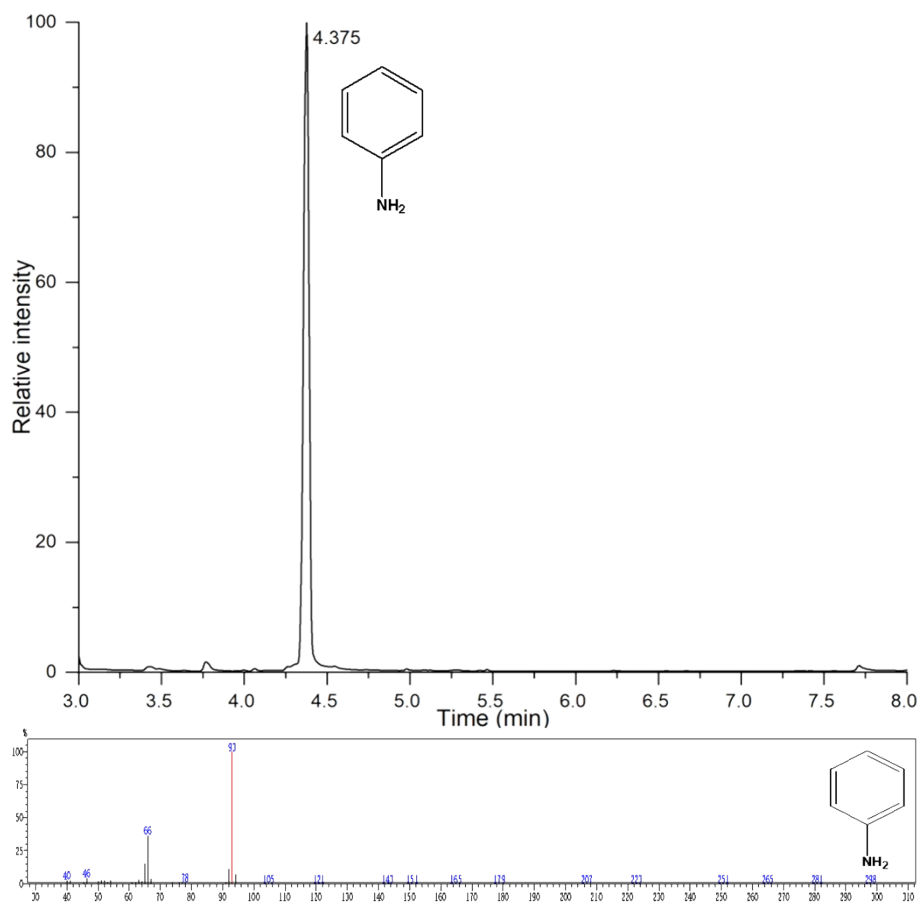


Fig. S4. GC-MS data of hydrogenation of nitrobenzene to aniline results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

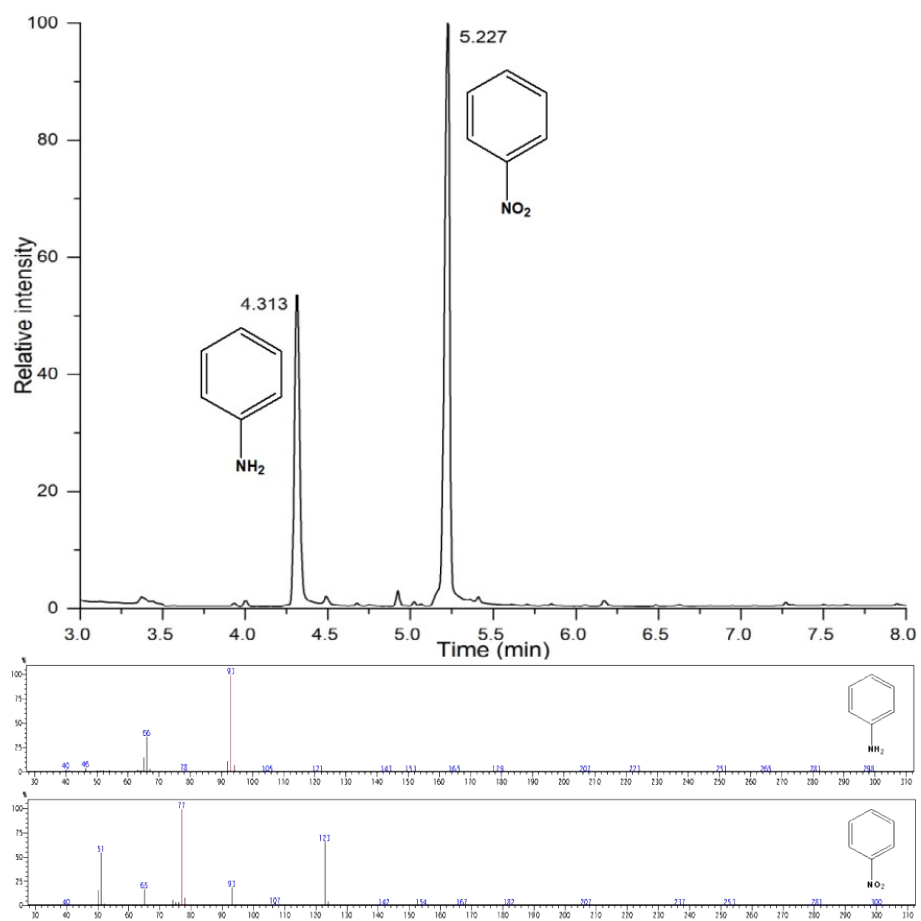


Fig. S5. GC-MS data of hydrogenation of nitrobenzene to aniline results by using Cr_2O_3 as catalysts.

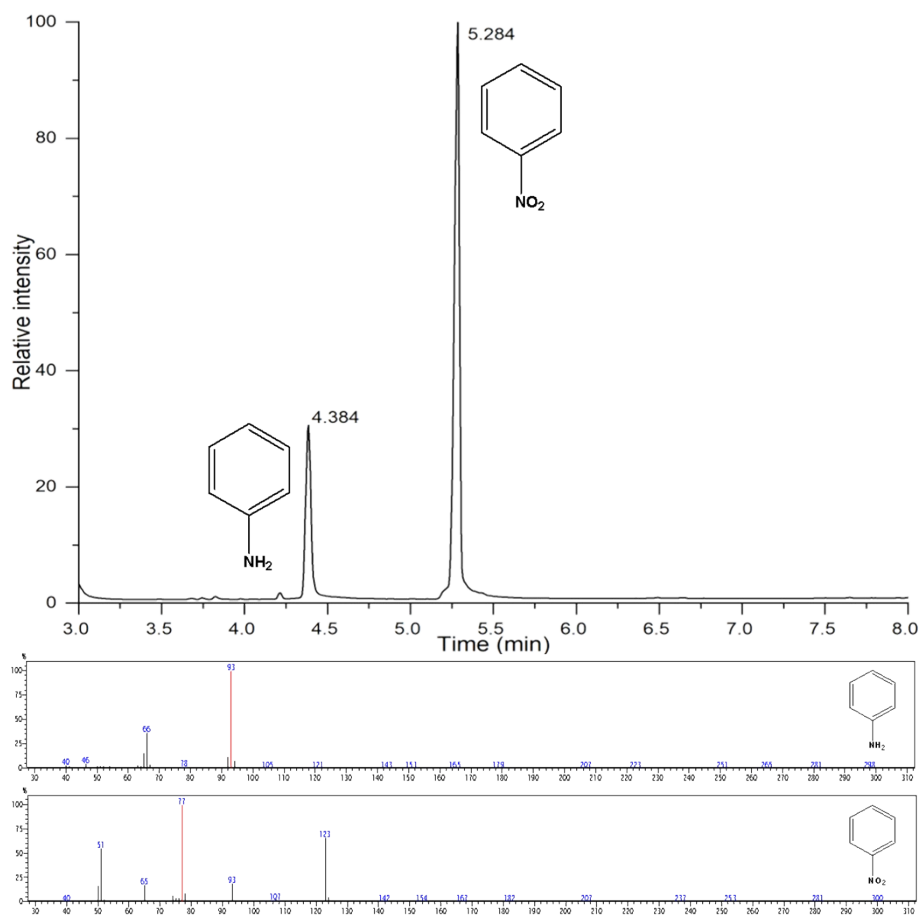


Fig. S6. GC-MS data of hydrogenation of nitrobenzene to aniline results by using NC as catalysts.

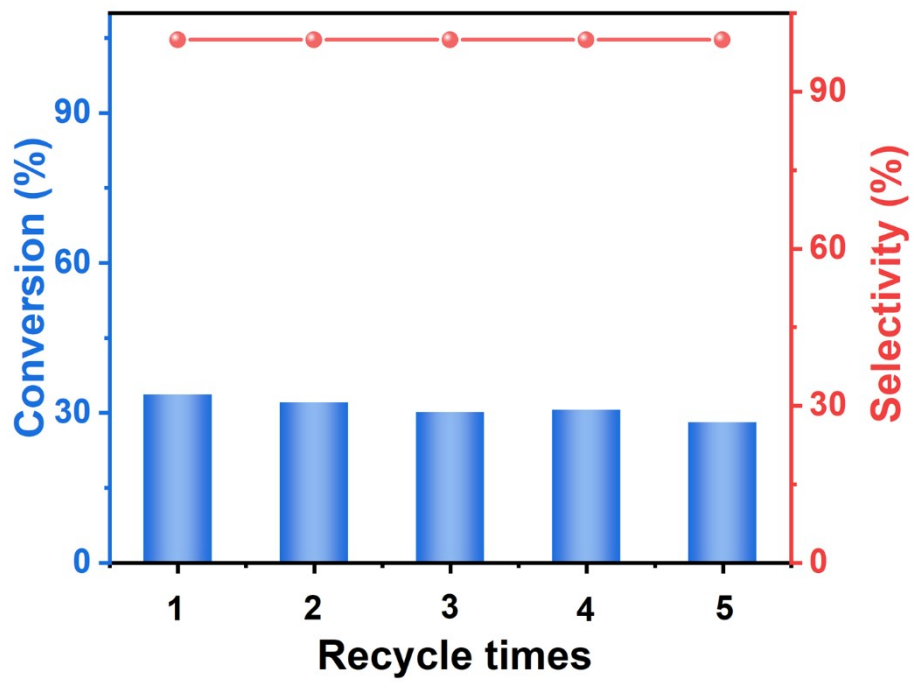


Fig. S7. The stability activities of Cr_2O_3 with 5 cycles.

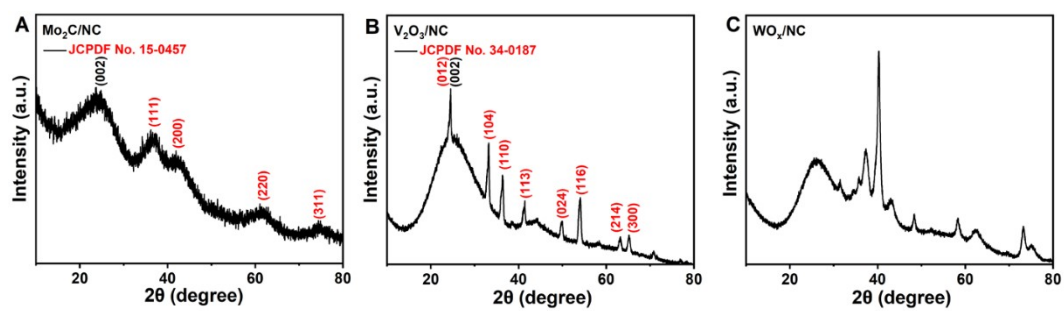


Fig. S8. The XRD patterns of $\text{Mo}_2\text{C}/\text{NC}$, $\text{V}_2\text{O}_3/\text{NC}$ and WO_x/NC .

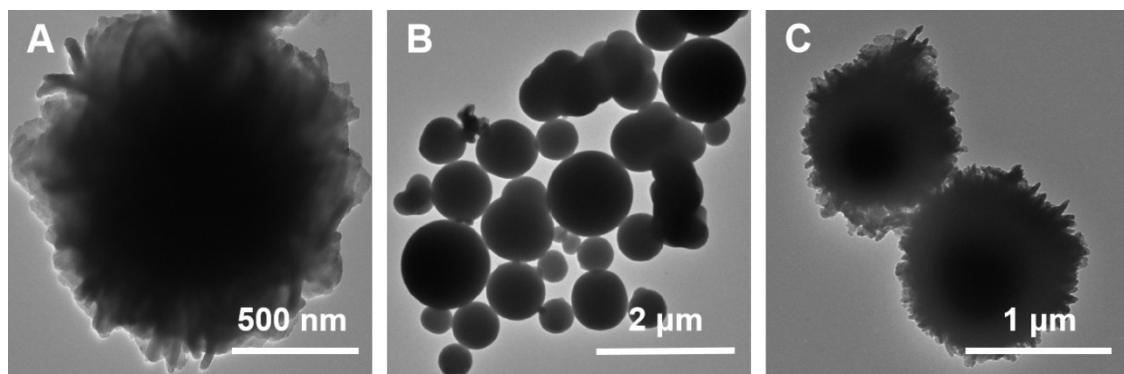


Fig. S9. The TEM image of Mo₂C/NC, V₂O₃/NC, WO_x/NC.

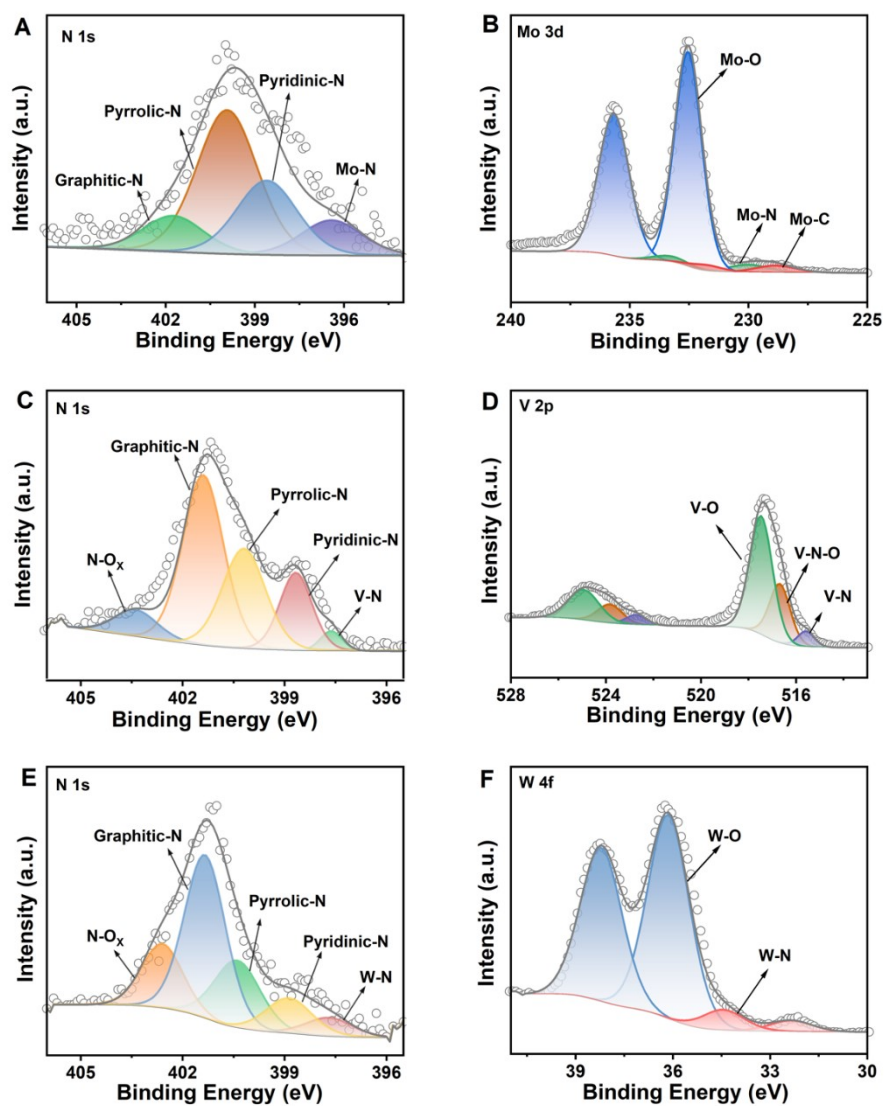


Fig. S10. The high resolution XPS spectra of (A) N 1s, (B) Mo 3d of Mo₂C/NC, (C) N 1s, (D) V 2p of V₂O₃/NC, (E) N 1s and (F) W 4f of WO_x/NC.

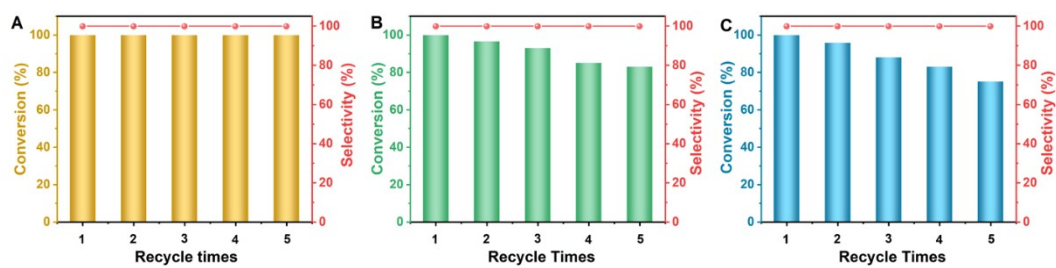


Fig. S11. Stability activities of Mo₂C/NC, V₂O₃/NC, WO_x/NC with 5 recycle times.

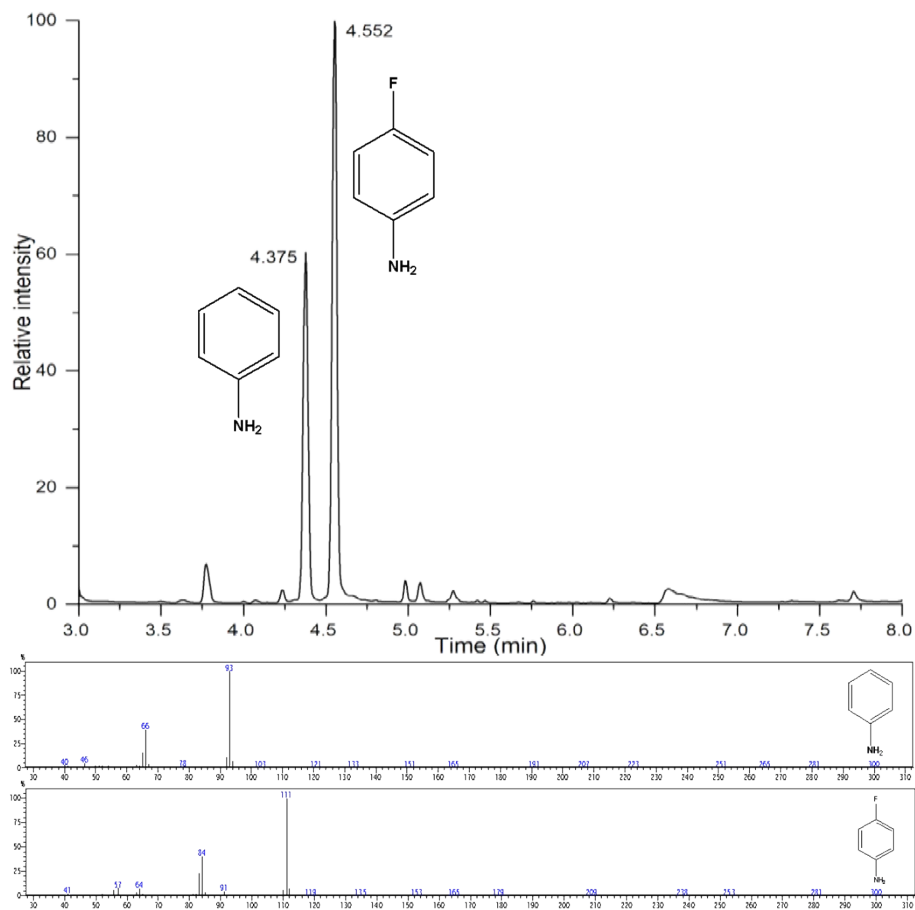


Fig. S12. GC-MS data of 1-Fluoro-4-nitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

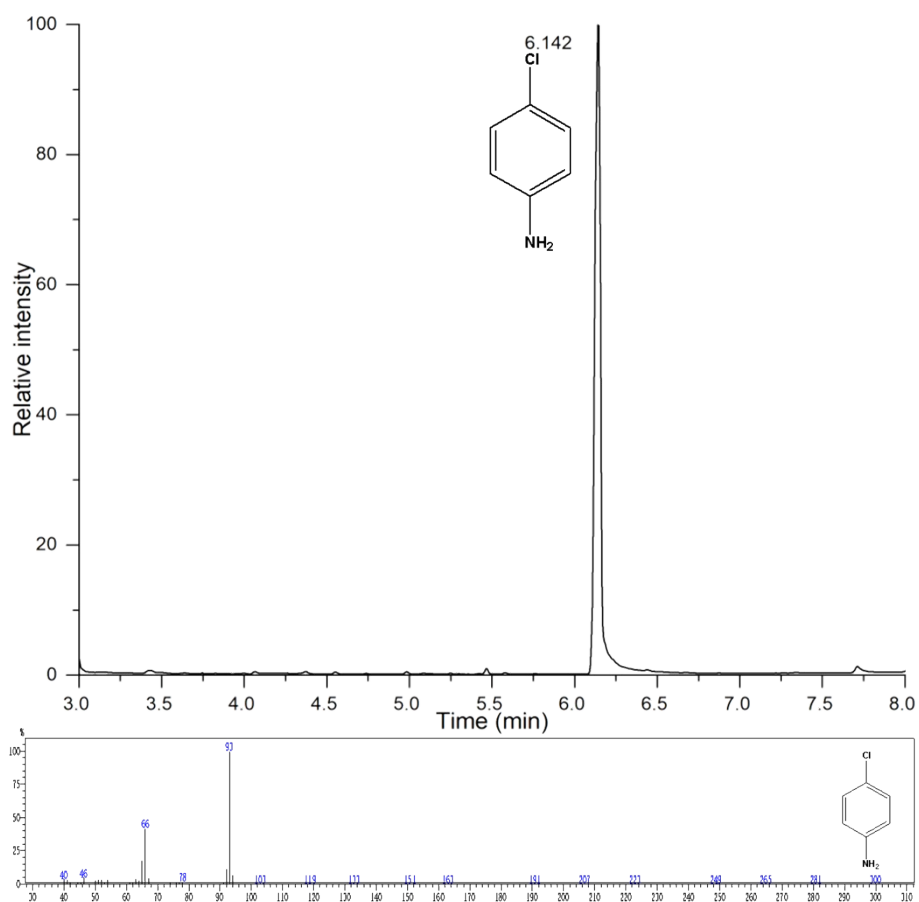


Fig. S13. GC-MS data of 1-Chloro-4-nitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

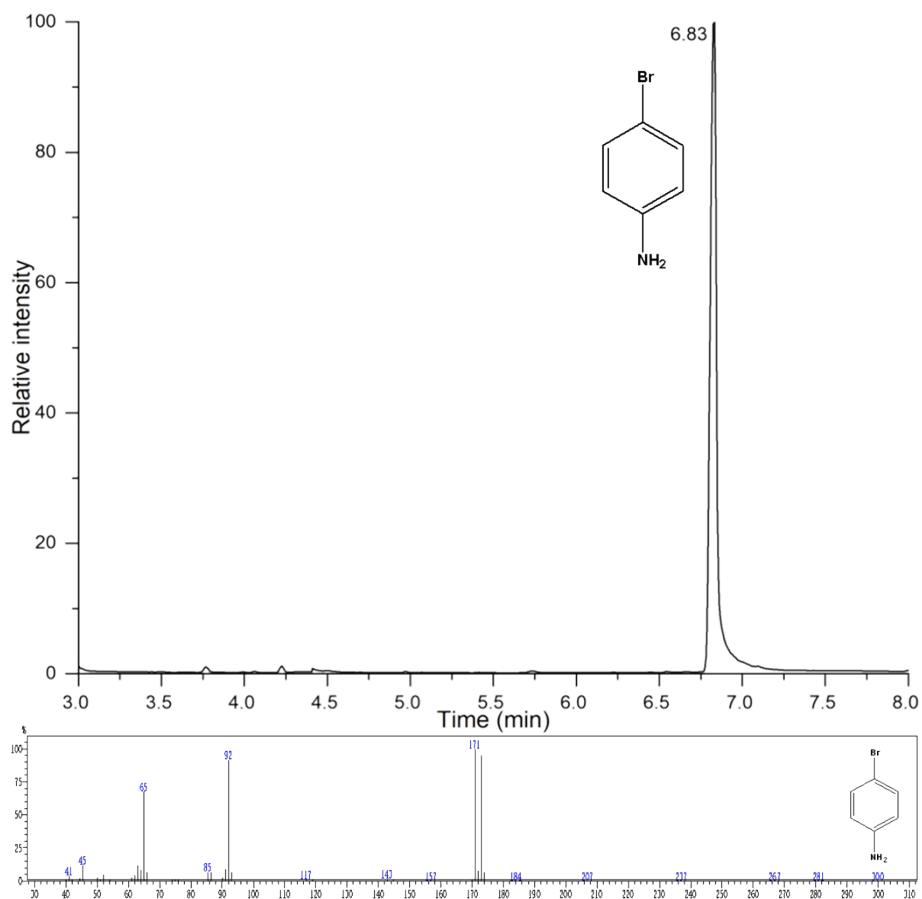


Fig. S14. GC-MS data of 1-Bromo-4-nitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

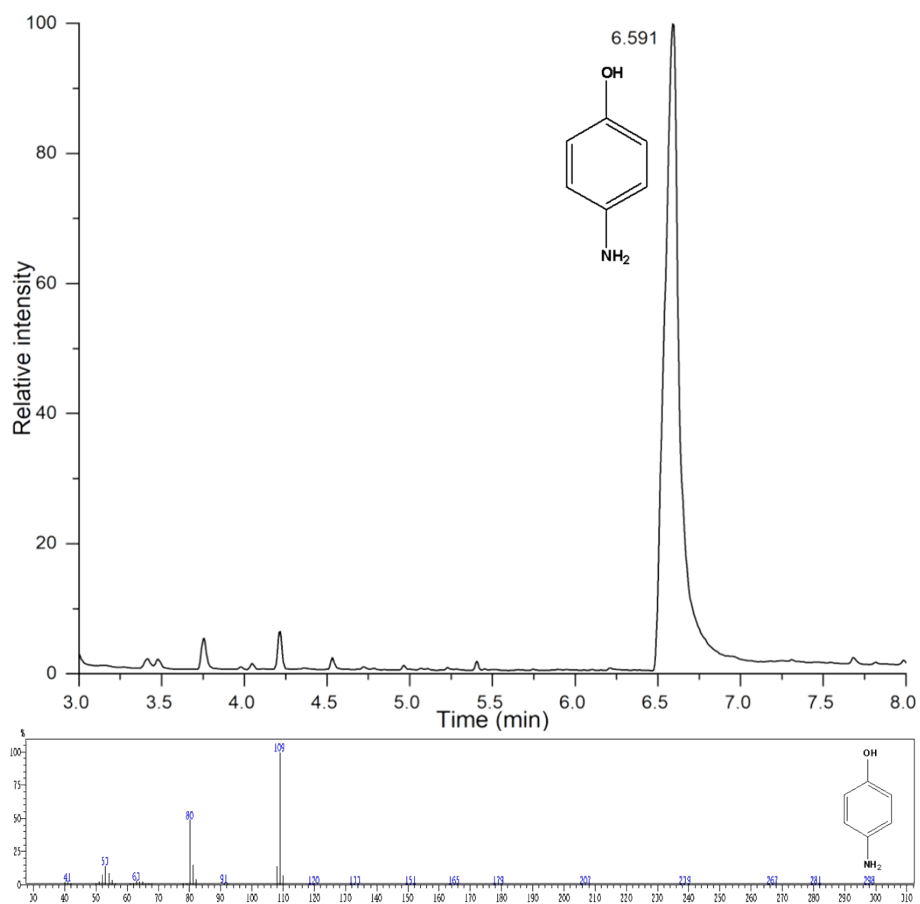


Fig. S15. GC-MS data of P-Nitrophenol reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

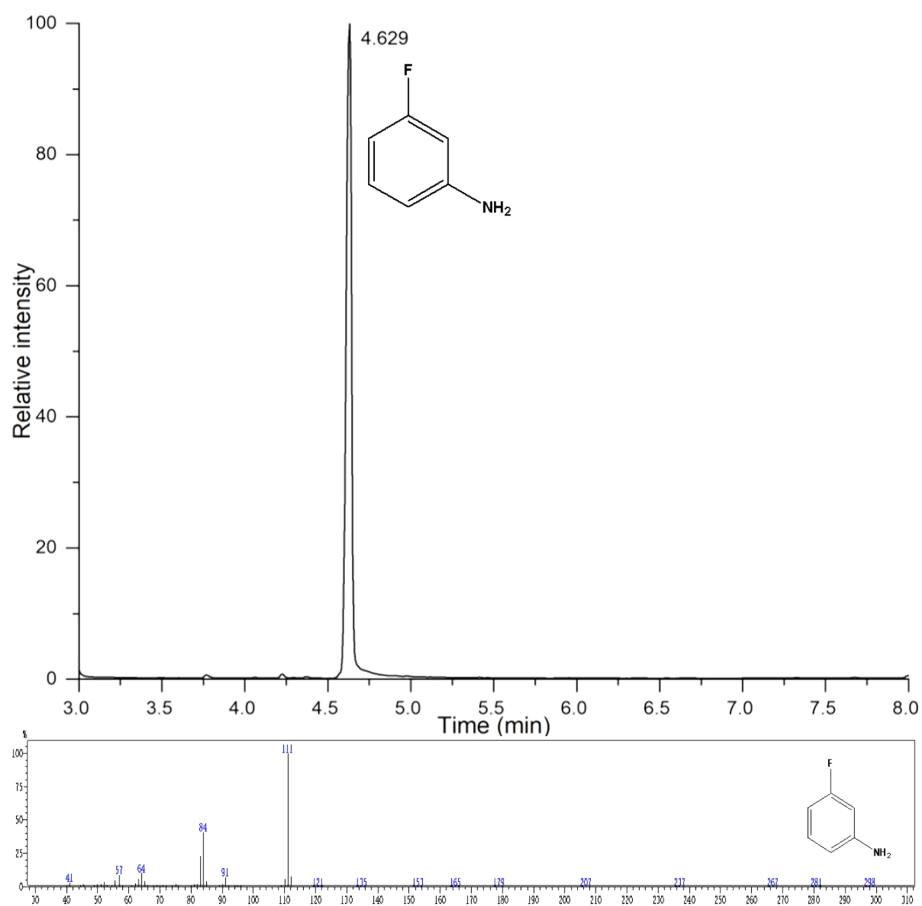


Fig. S16. GC-MS data of 1-Fluoro-3-nitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

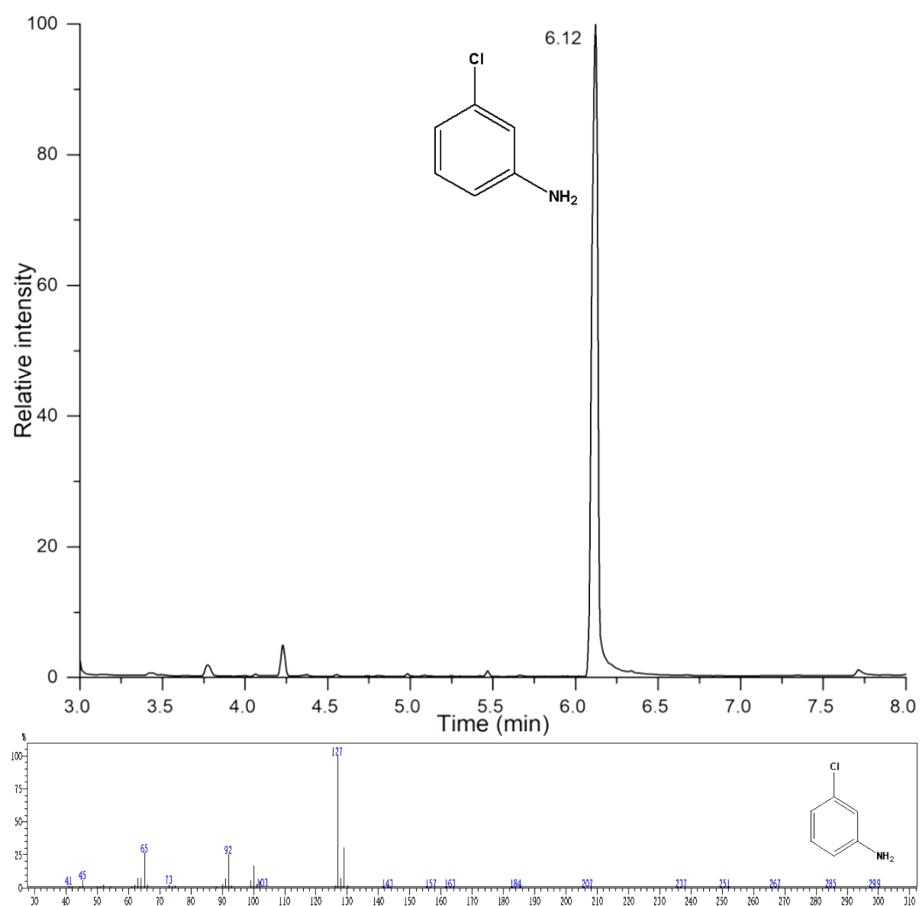


Fig. S17. GC-MS data of 1-Chloro-3-nitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

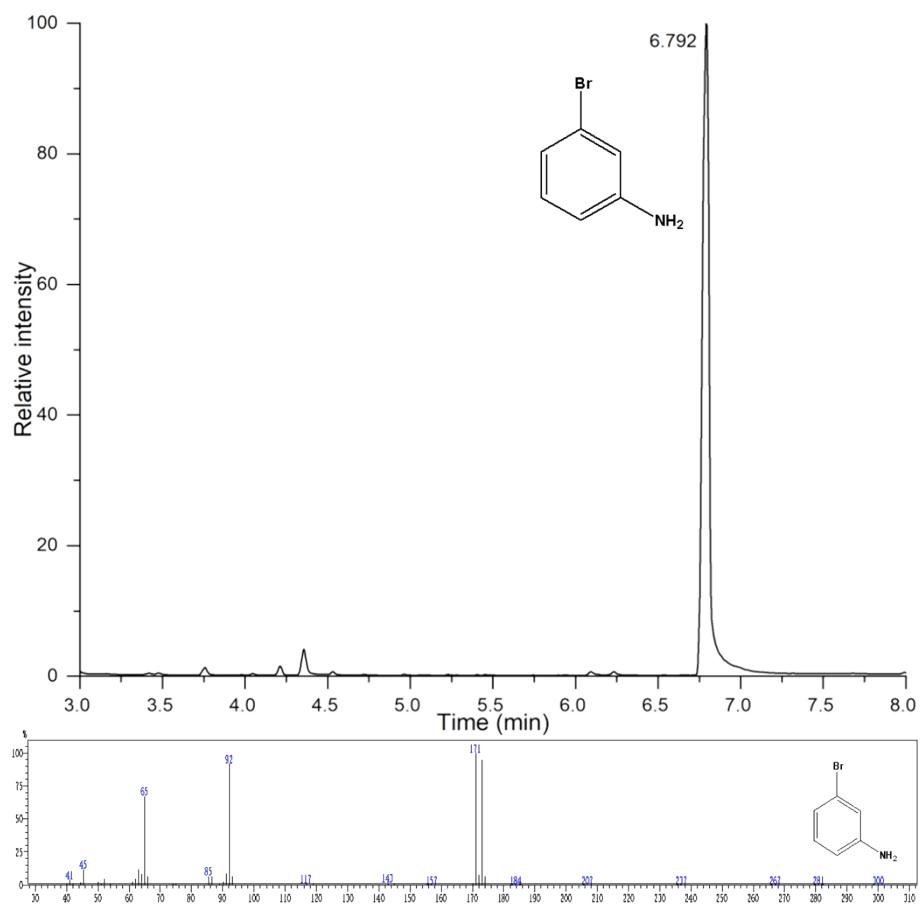


Fig. S18. GC-MS data of 3-Bromonitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

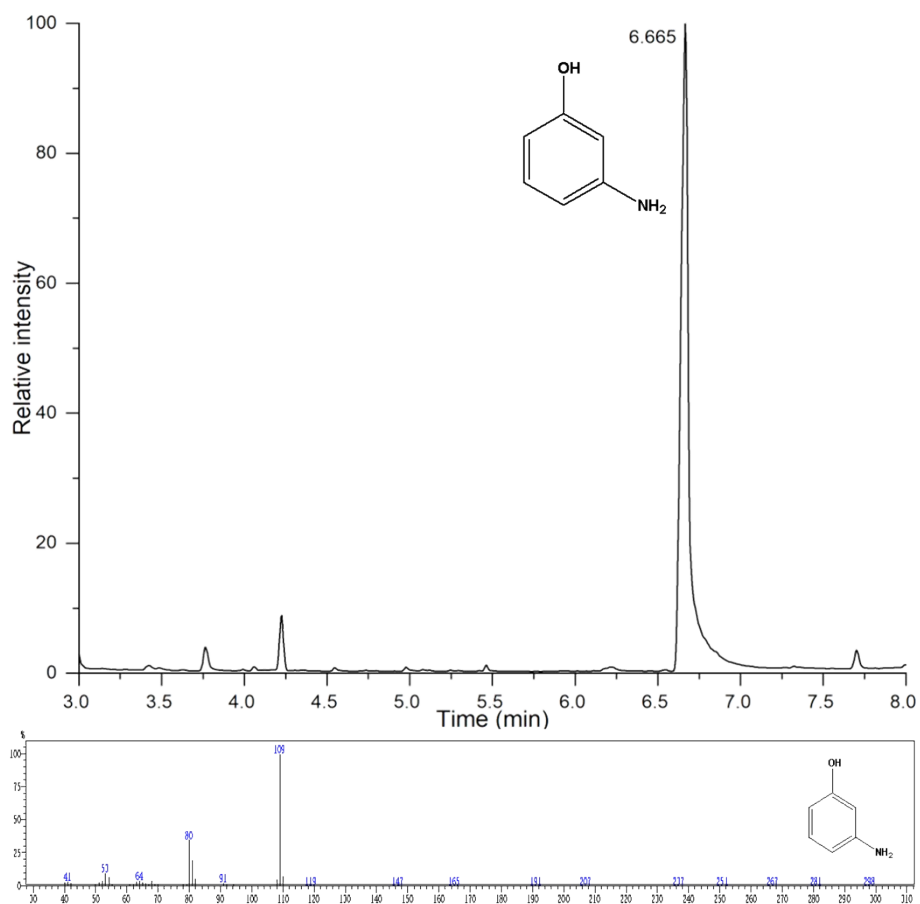


Fig. S19. GC-MS data of 3-Nitrophenol reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

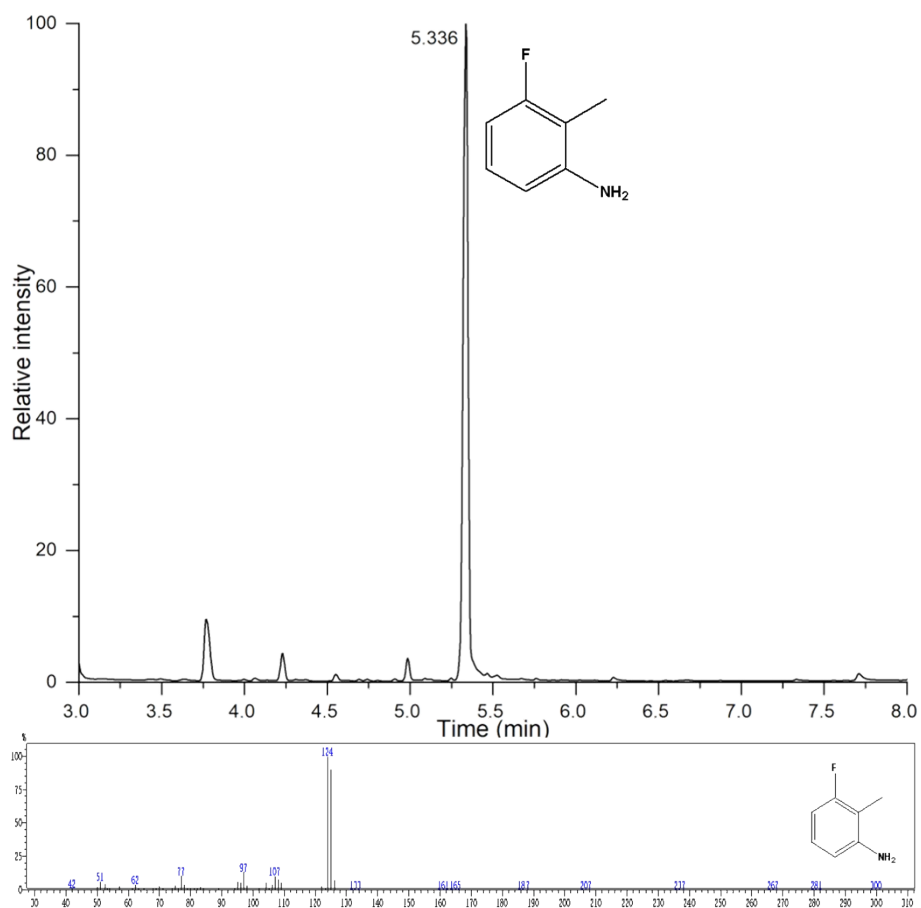


Fig. S20. GC-MS data of 2-Fluoro-6-nitrotoluene reaction results by using Cr₂O₃/NC as catalysts.

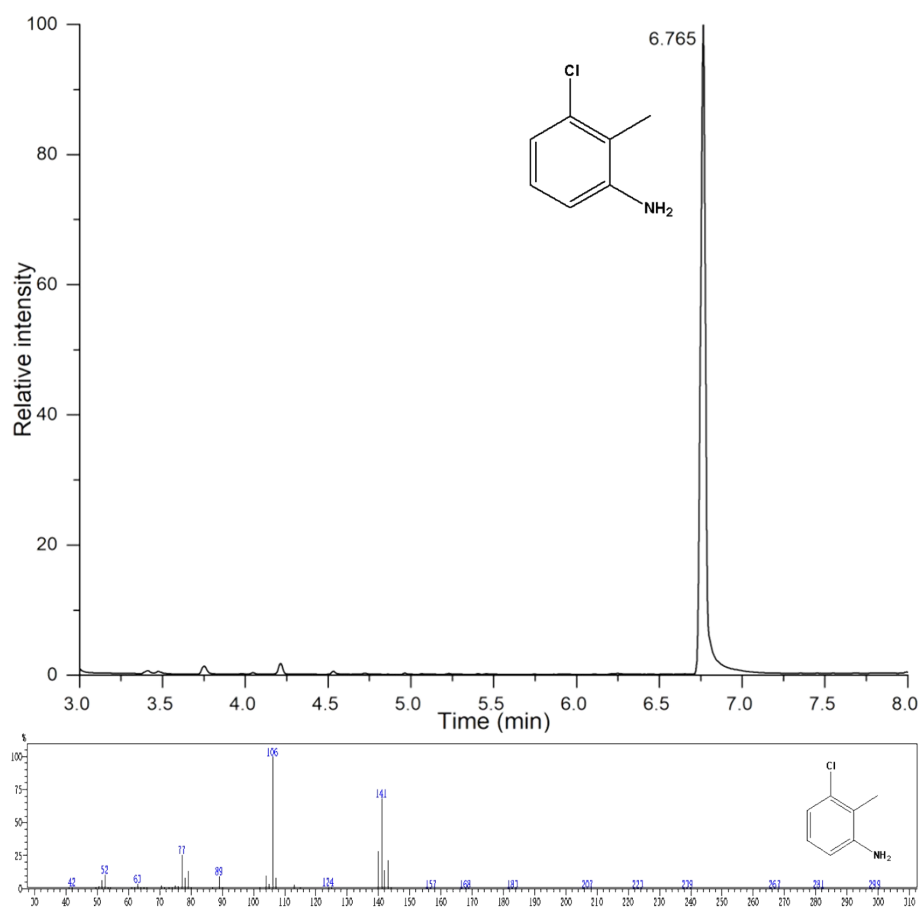


Fig. S21. GC-MS data of 2-Chloro-6-nitrotoluene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

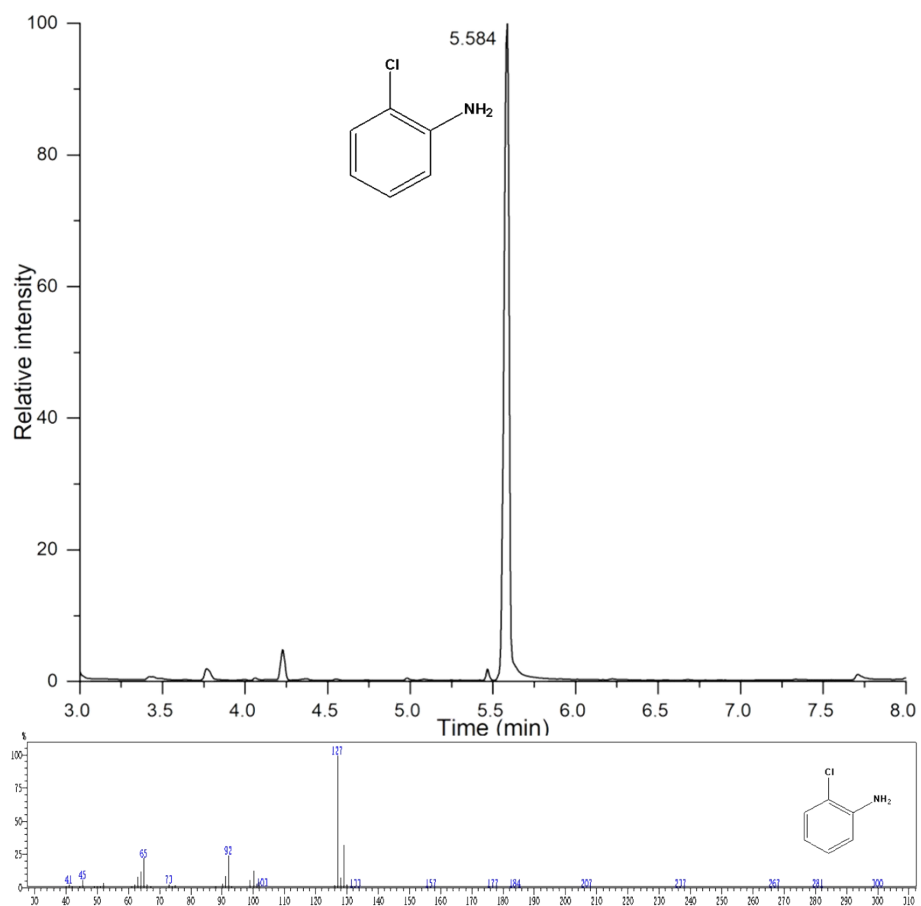


Fig. S22. GC-MS data of 2-Chloronitrobenzene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

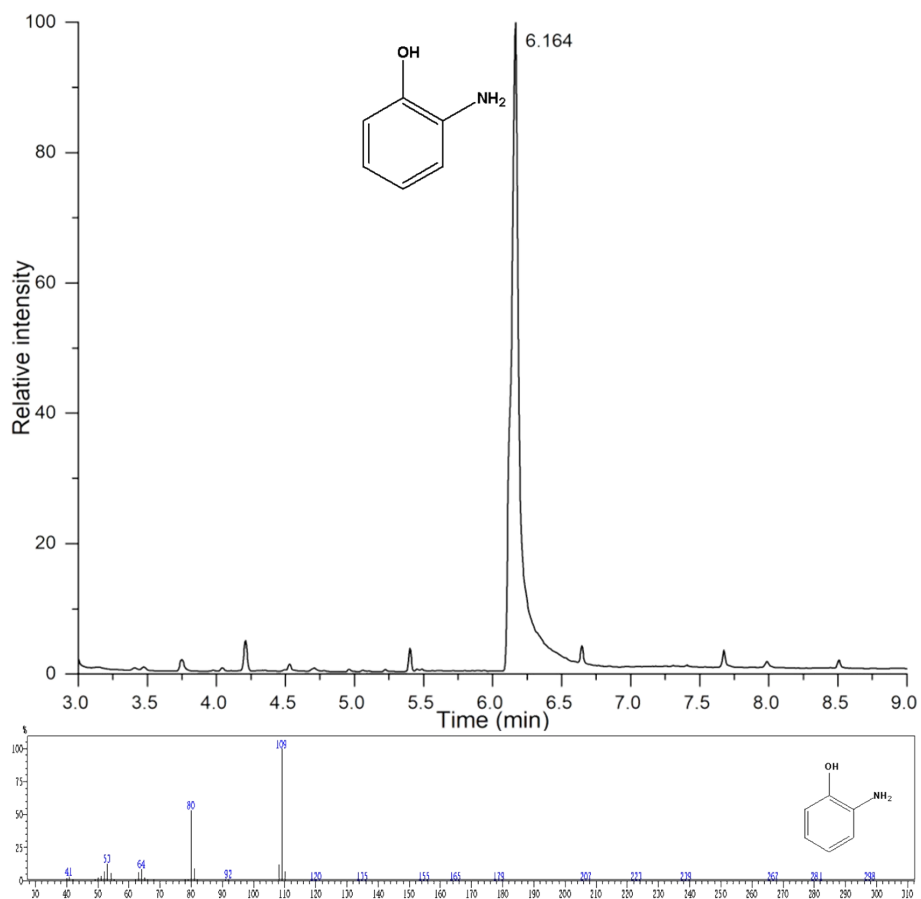


Fig. S23. GC-MS data of 2-Nitrophenol reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

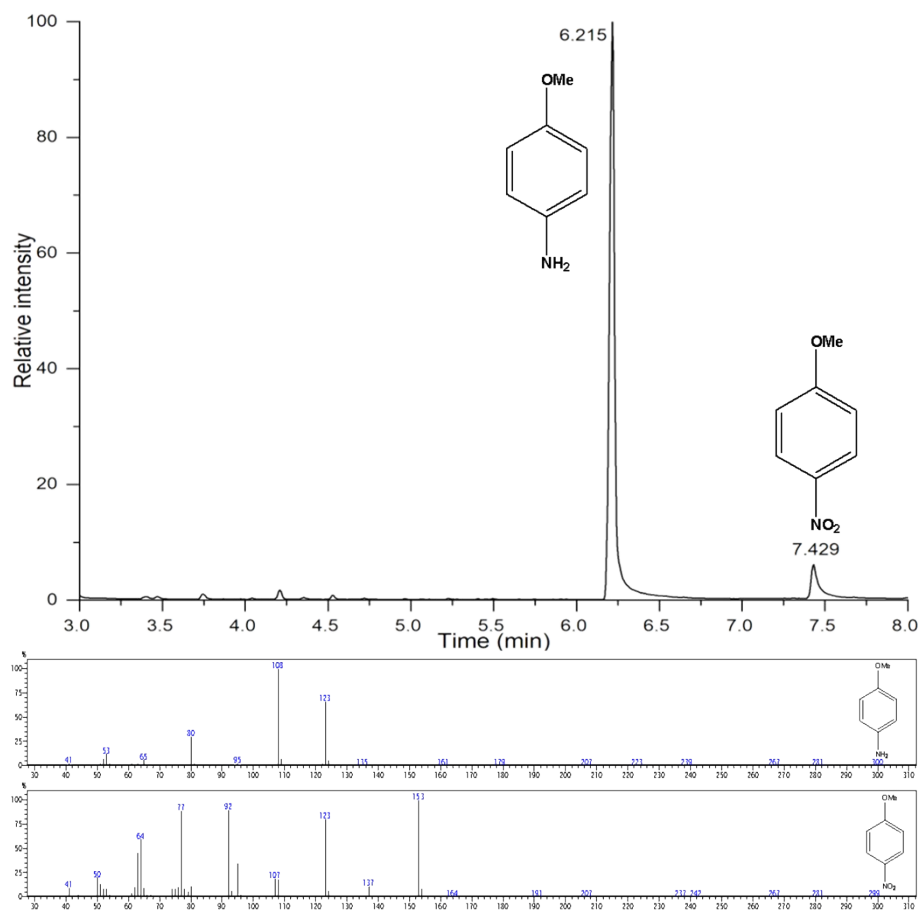


Fig. S24. GC-MS data of 4-Nitroanisole reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

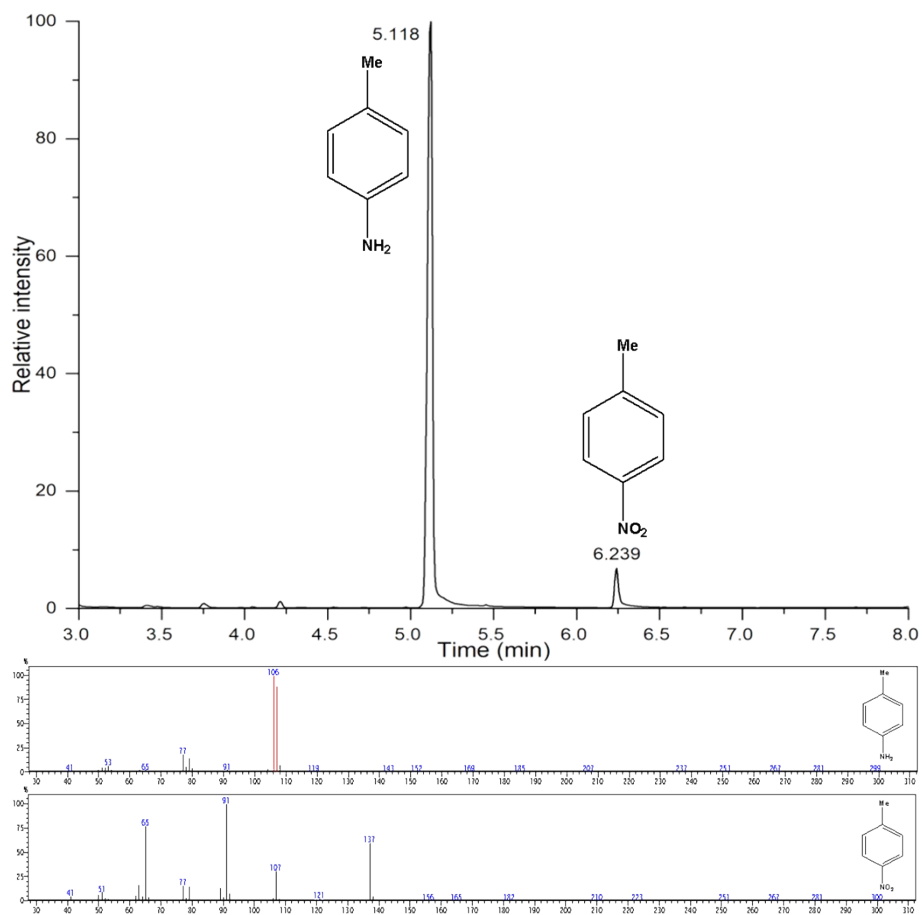


Fig. S25. GC-MS data of 4-Nitrotoluene reaction results by using Cr₂O₃/NC as catalysts.

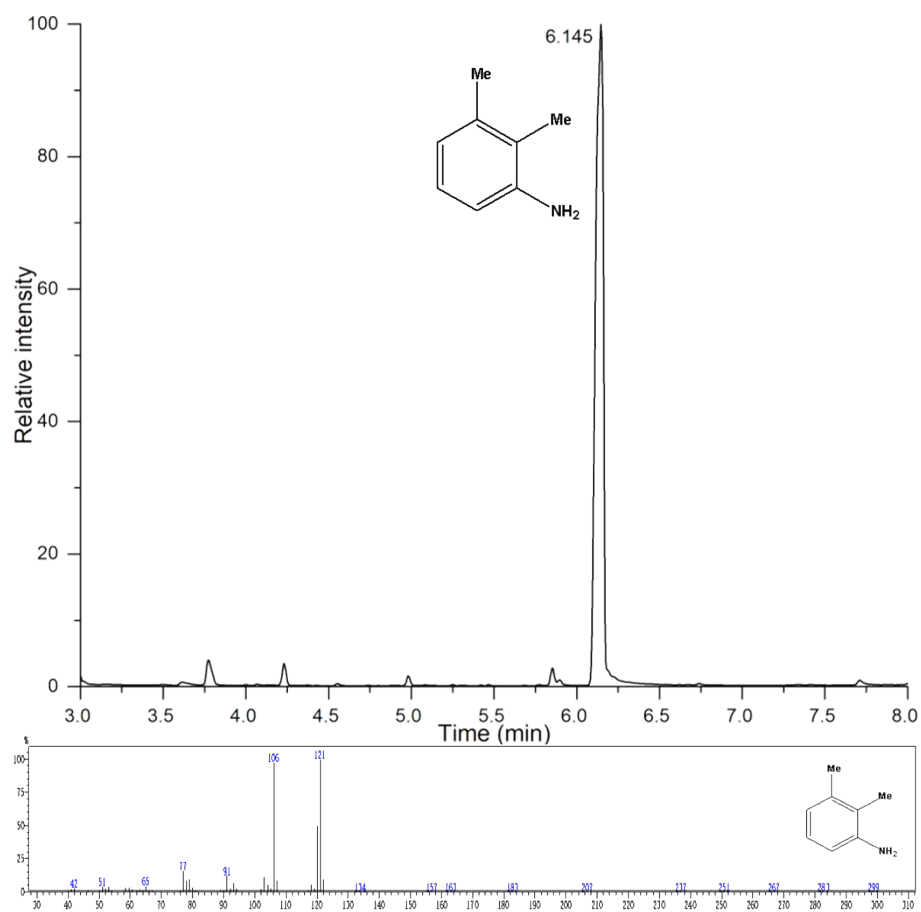


Fig. S26. GC-MS data of 3-Nitro-o-xylene reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

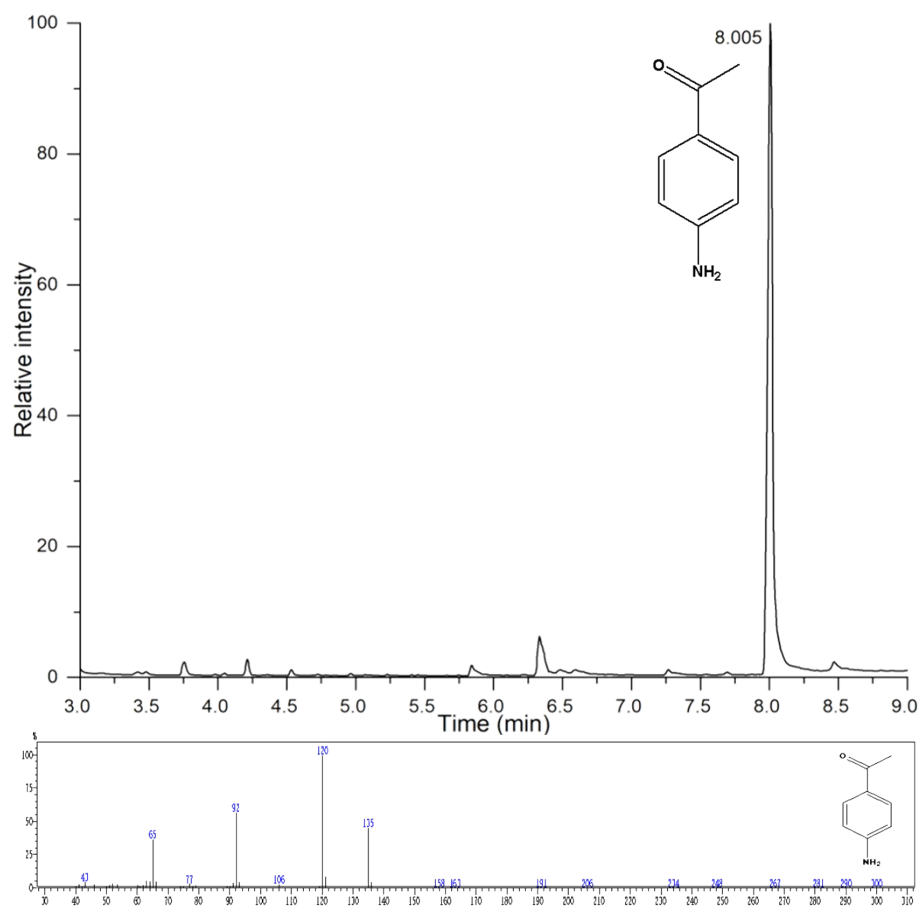


Fig. S27. GC-MS data of p-Nitroacetophenone reaction results by using $\text{Cr}_2\text{O}_3/\text{NC}$ as catalysts.

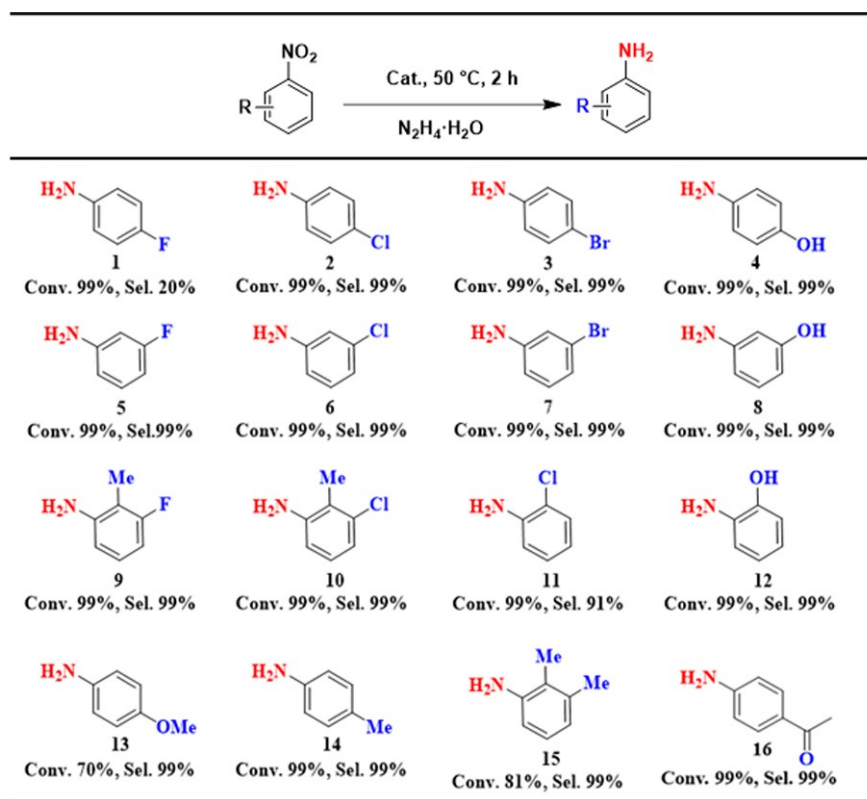


Fig. S28. Hydrogenation of various substituted nitrobenzene compounds over the Mo₂C/NC catalyst. The conversion (conv.) and selectivity (sel.) are evaluated by GC and GC-MS analysis with dodecane as an internal standard).

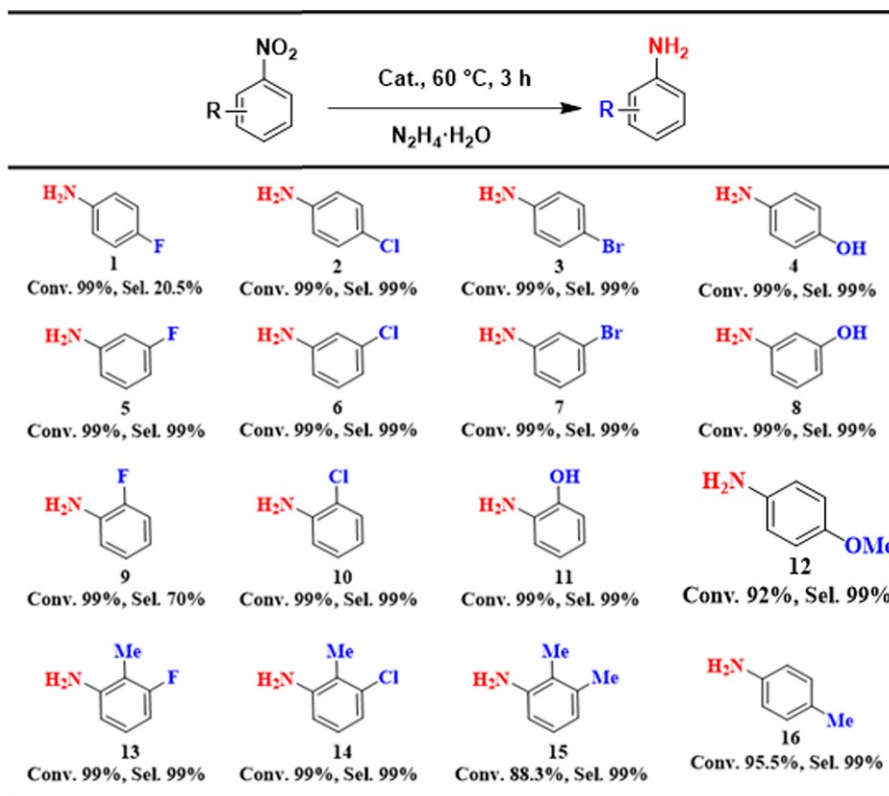


Fig. S29. Hydrogenation of various substituted nitrobenzene compounds over V_2O_3/NC catalyst. The conversion (conv.) and selectivity (sel.) are evaluated by GC and GC-MS analysis with dodecane as an internal standard).

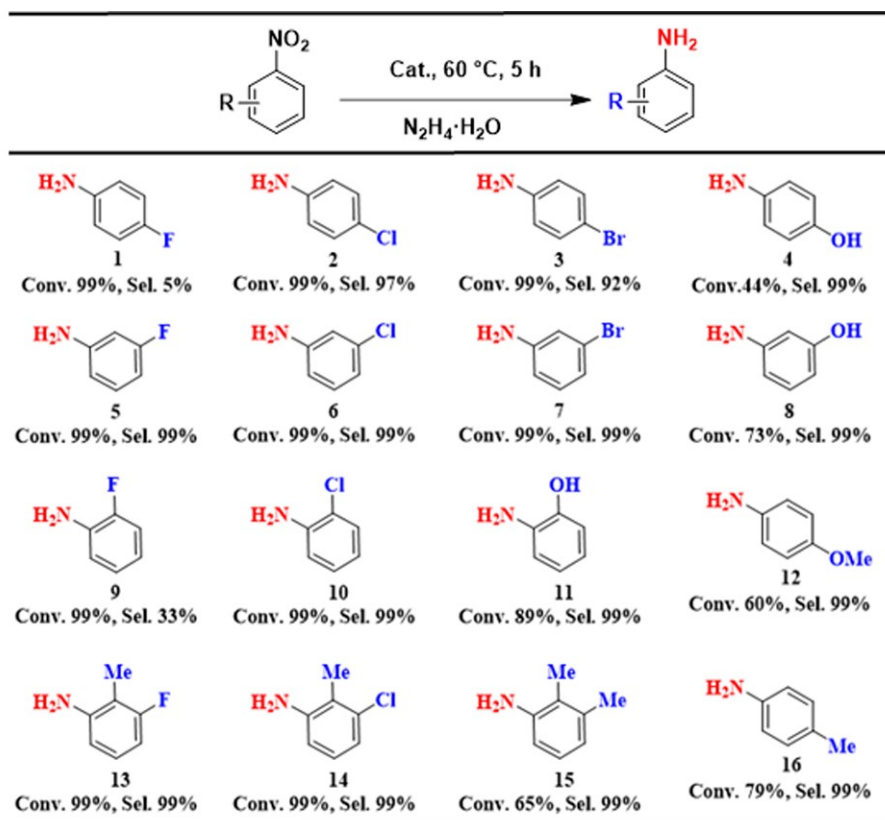


Fig. S30. Hydrogenation of various substituted nitrobenzene compounds over the WO_x/NC catalyst. The conversion (conv.) and selectivity (sel.) are evaluated by GC and GC-MS analysis with dodecane as an internal standard).