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Supporting information

Flexible vs. Rigid Covalent Organic Frameworks: Catalytic Performance in the Knoevenagel Reaction

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I. Characterization Methods

Chemicals were obtained from Energy Chemical or Aladdin, and used without further purification unless otherwise noted. The solvents were dried and distilled according to conventional procedures.

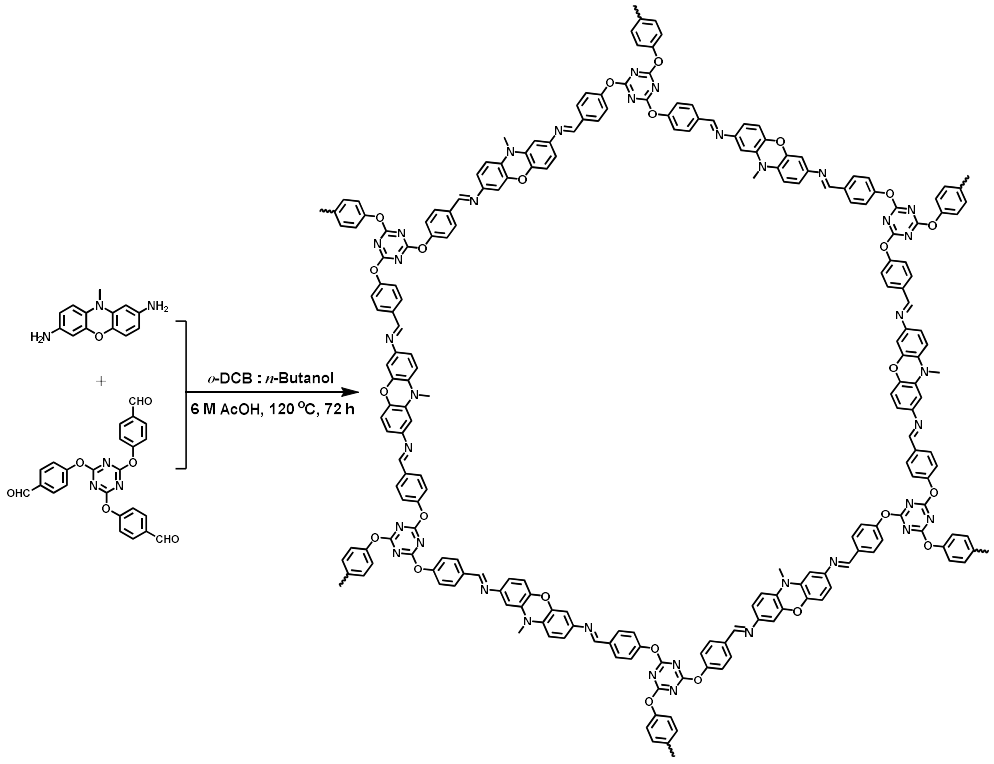
^{1}H spectra was recorded in $CDCl_3$ or DMSO-d_6 on Bruker Advance or Joel 400 MHz spectrometers. Fourier transform infrared (FT-IR) spectra were obtained with KBr plates by using a IS10 FT-IR Spectrometer (Themo Fisher Corporation). Powder X-ray diffraction (PXRD) patterns were recorded on a Smart Lab 3Kw (Rigaku Corporation). Nitrogen gas adsorption experiments were performed on a Quanta chrome Autosorb-iQ3 automatic volumetric instrument. The samples were sputtered with Au (nano-sized film) prior to imaging. Thermogravimetric analyses (TGA) were carried out on a STA449 analyzer (Netzsch Corporation) under N_2 atmosphere at a heating rate of 10 °C min^{-1} within a temperature range of 30-800 °C. Solid-state ^{13}C CP/MAS NMR spectra were recorded on a Bruker AdvanceIII-400 MHz spectrometer. The particle size distribution was measured by the Laser Particle Size Analyzer Omini. Transmission electron microscope (TEM) samples were examined by using a JEM-ARM200F and JEOL 1400Plus operating at 200 kV. The reaction autoclave used in the experiment was purchased from Beijing Laibei Scientific Instrument Co., Ltd.

II. Synthetic Precursors

2,7-diamino-10-methylphenoxazine(DAPO),[1] tri(4-formylphenoxy)-cyanurate (TFPC)[2] and 1,3,5-triazine(4-aldehyde benzene)triazine (TFPT)[3] were synthesized according to the reported procedures. Their ^{1}H NMR spectra match well with those reported previously.

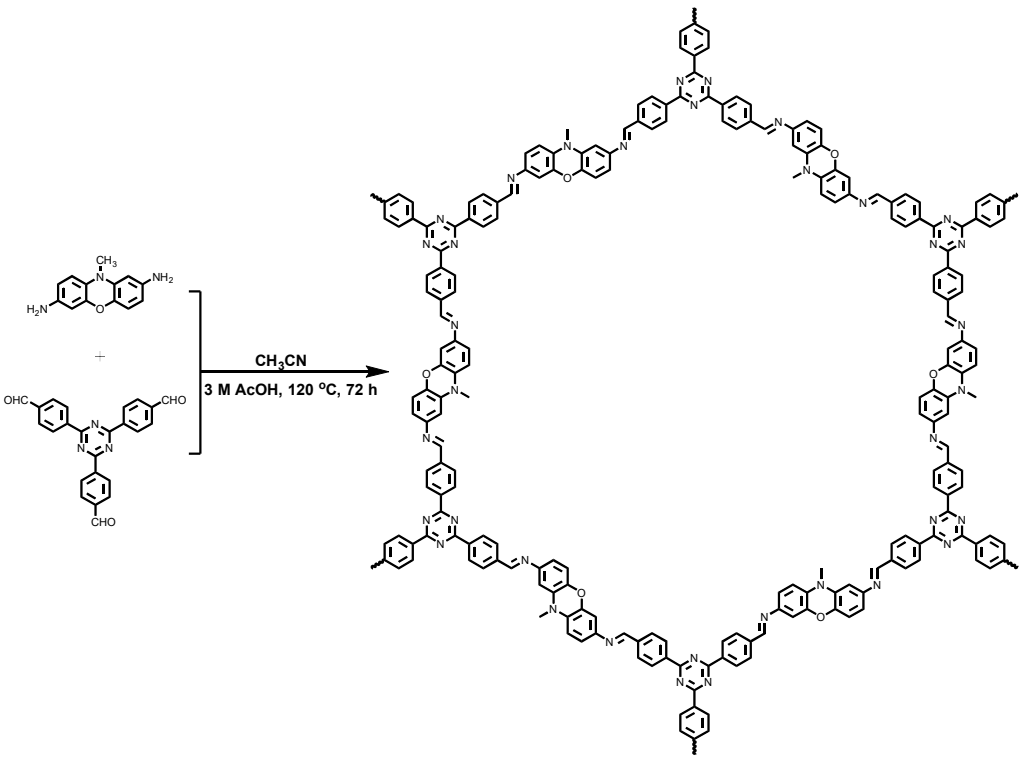
III. Synthetic COFs

Synthesis of DAPO-TFPC-COF.



10-methyl-phenoxazine-2,7-diamine (DAPO, 34.1 mg, 0.15 mmol) and tri(4-formylphenoxy)cyanurate (TFPC, 44.1 mg, 0.1 mmol) were mixed in a Schlenk tube filled with nitrogen. Subsequently, o-DCB (1 mL) and n-Butanol (1 mL) were added, placed in the ultrasonic machine for 15 minutes to blend well; After it, added the catalyst AcOH (0.3 mL , 6 mol/L), froze the mixture in liquid nitrogen, removed vacuum and the reaction system was degassed through three freezing-vacuum-melting cycles. Take the mixture froze and seal the tube with a flamethrower, and put it in oven for 3 days at 120 °C. The solid was filtered then washed with DMF, THF, and acetone. The solid was vacuum-dried at 80 °C for 12 h to afford yellow crystalline powder (69.2 mg, 87%).

Synthesis of DAPO-TFPT-COF.



2,7-diamino-10-methylphenoxazine (DAPO, 30.6 mg, 0.135 mmol) and 1,3,5-triazine (4-aldehyde benzene) triazine (TFPT, 35.4 mg, 0.09 mmol) were dissolved in 3 mL of acetonitrile in Schleck tube. Ultrasonic treatment for 15 minutes promoted dispersive dissolution. After it, added the catalyst AcOH (0.9 mL, 3 mol/L), froze the mixture in liquid nitrogen, removed vacuum and the reaction system was degassed through three freezing-vacuum-melting cycles. The reaction mixture is sealed and heated at 120 °C for 3 days. Take the mixture froze and seal the tube with a flamethrower, and put it in oven for 3 days at 120 °C. The solid was filtered then washed with DMF, THF, and acetone. The solid was vacuum-dried at 80 °C for 12 h to afford red crystalline powder (56 mg, 89%).

IV. Structural Refinements

Figure S1. DAPO-TFPC-COF and DAPO-TFPT-COF experimental powder PXRD and Pawley refinement (upper), Rietveld refinement (lower).

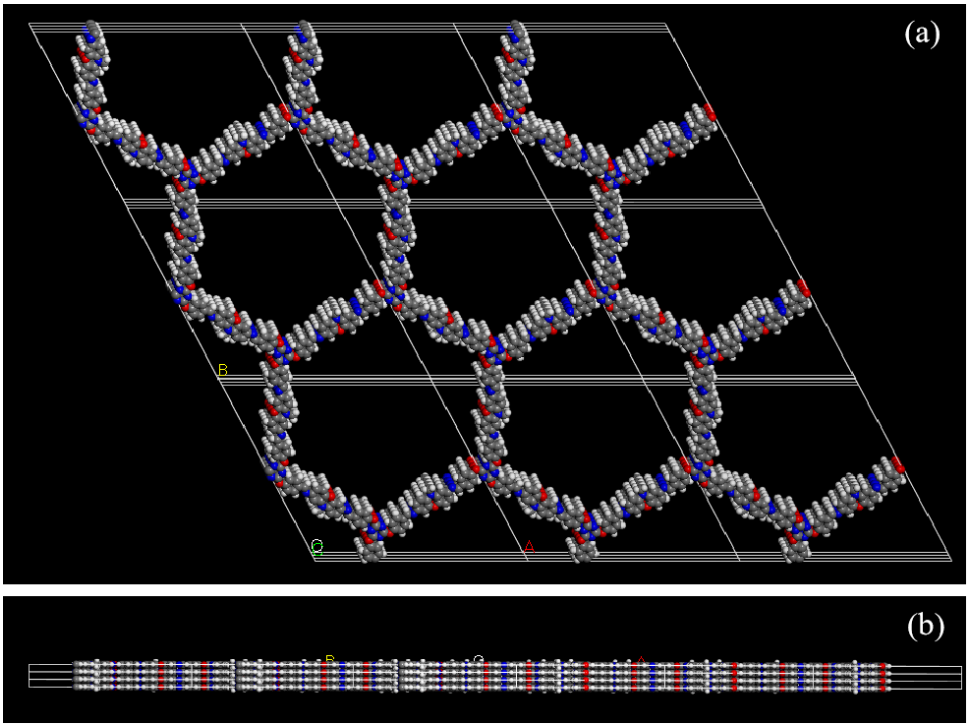


Figure S2. The computationally determined structures of DAPO-TFPC-COF. (a) Top and (b) side view of the theoretical structure of DAPO-TFPC-COF with eclipsed (AA) stacking arrangement.

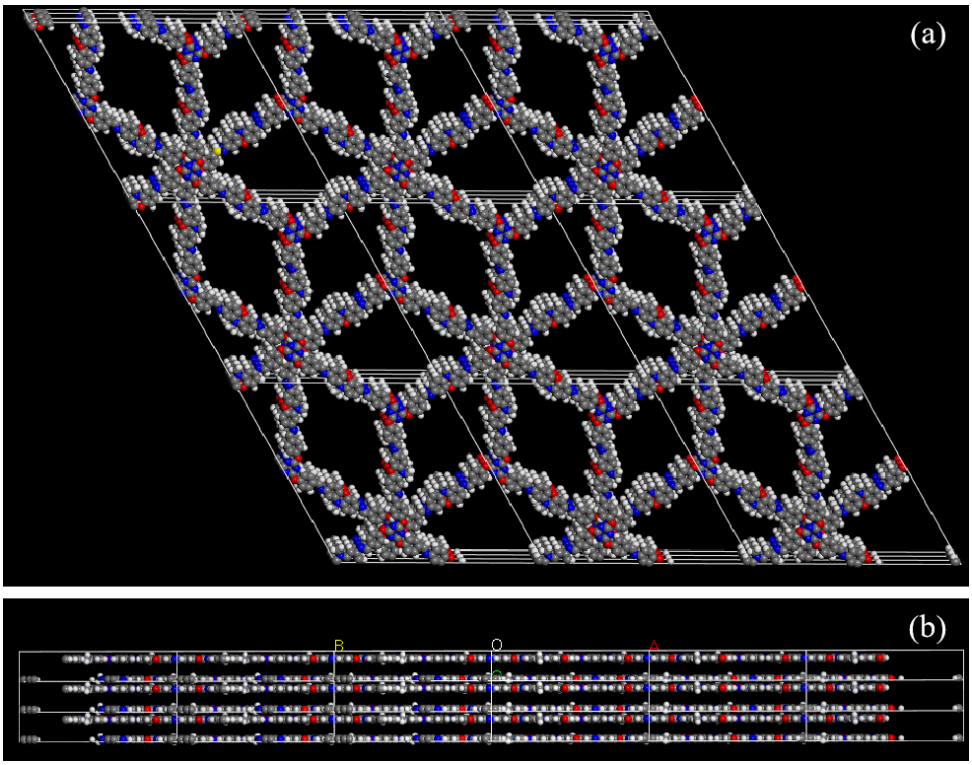


Figure S3. The computationally determined structures of DAPO-TFPC-COF. (a) Top and (b) side view of the theoretical structure of DAPO-TFPC-COF with eclipsed (AB) stacking arrangement.

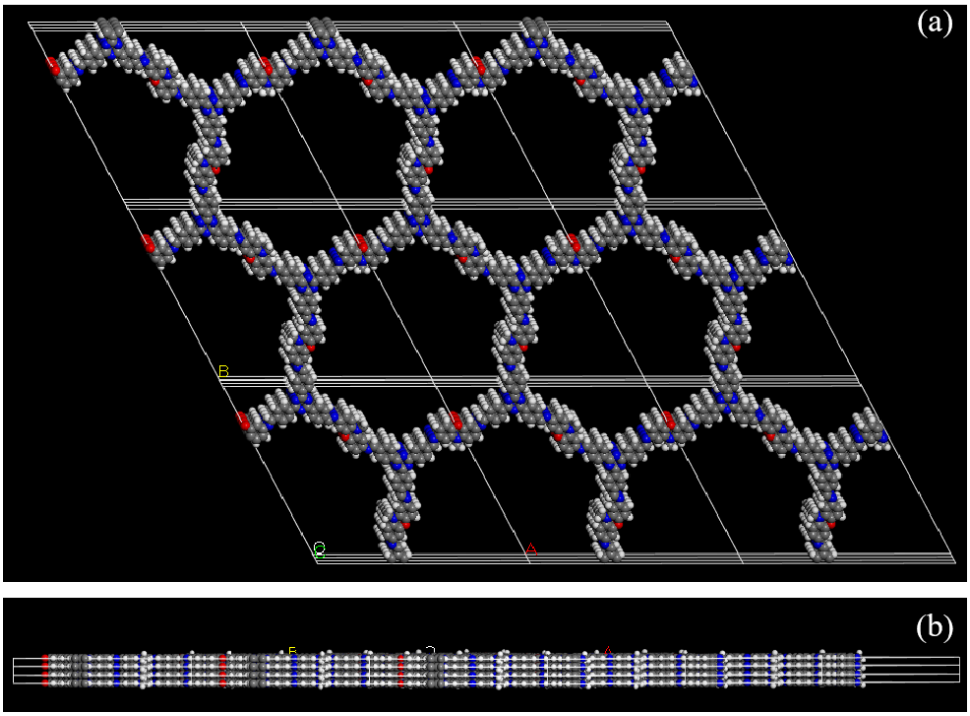


Figure S4. The computationally determined structures of DAPO-TFPT-COF. (a) Top and (b) side view of the theoretical structure of DAPO-TFPT-COF with eclipsed (AA) stacking arrangement.

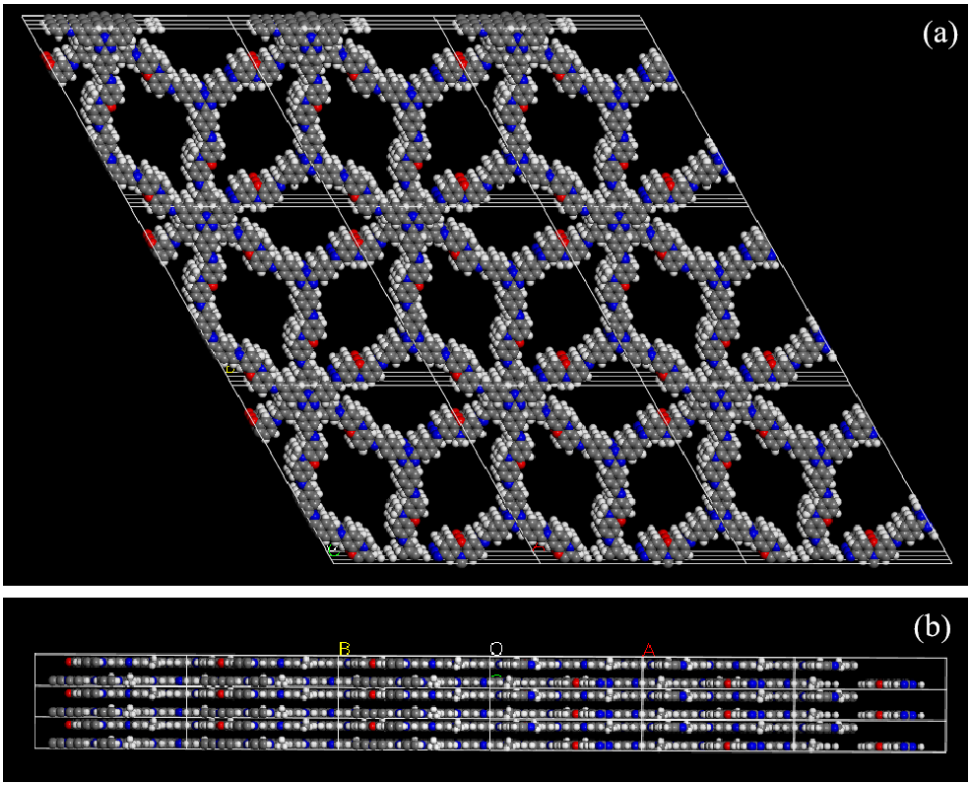


Figure S5. The computationally determined structures of DAPO-TFPT-COF. (a) Top and (b) side view of the theoretical structure of DAPO-TFPT-COF with eclipsed (AB) stacking arrangement.

V. BET Plot for N_2 Isotherm

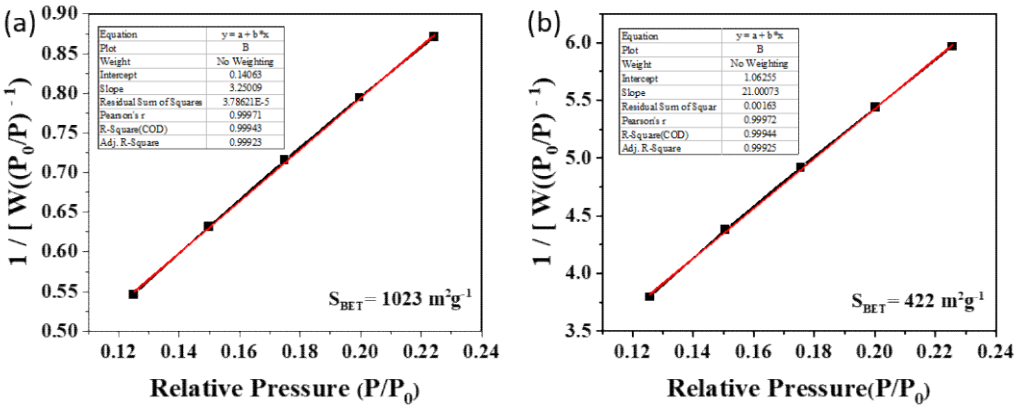


Figure S6 BET plot for (a)DAPO-TFPC-COF; (b)DAPO-TFPT-COF.

VI. Solid-State ^{13}C CP-MAS NMR Spectra

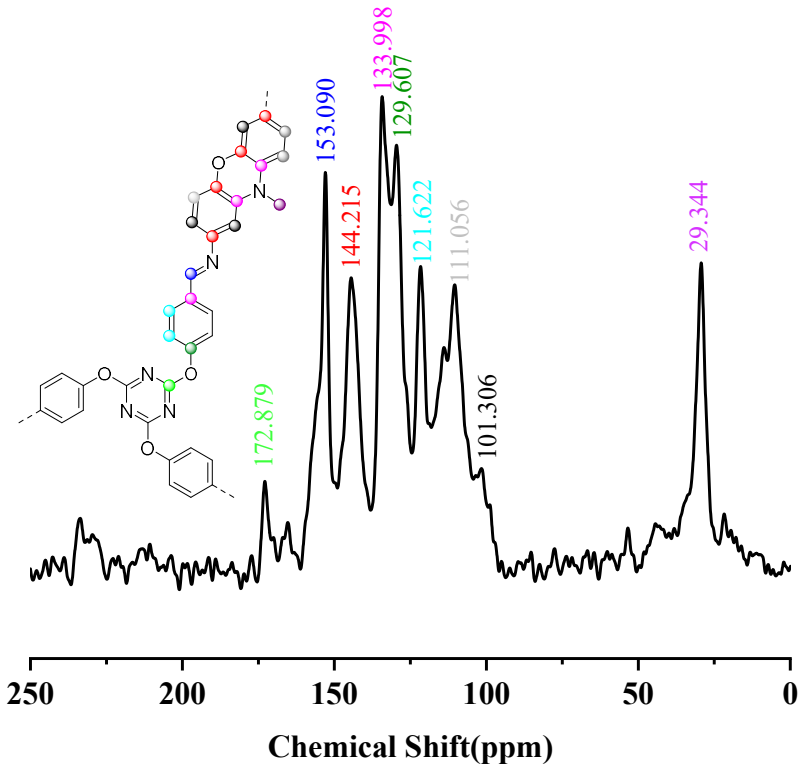


Figure S7. Solid-state ^{13}C CP-MAS NMR spectra of DAPO-TFPC-COF.[4]

VII. Chemical Stability Tests

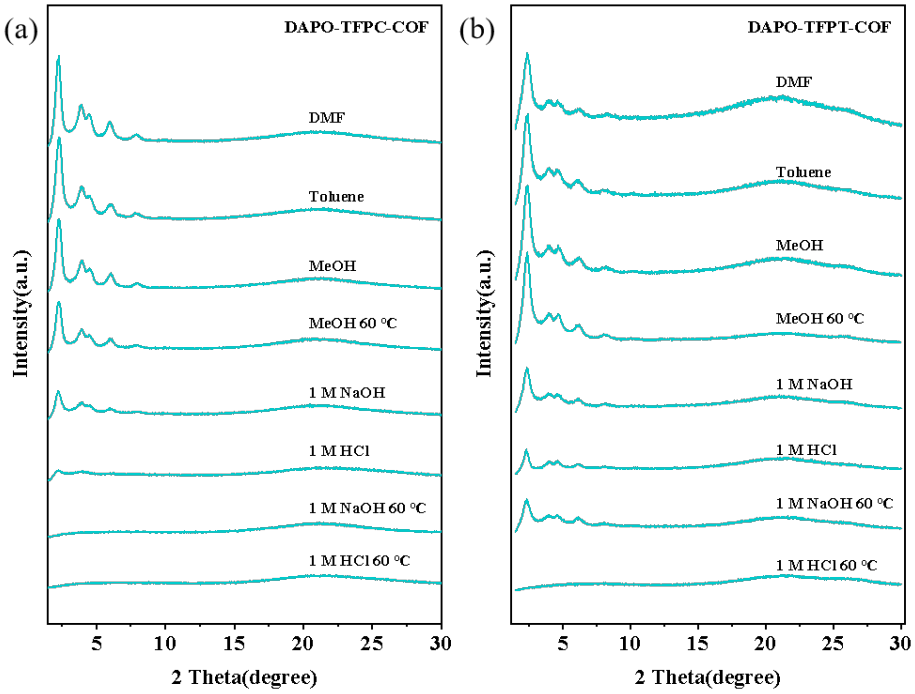


Figure S8. Chemical stability tests of the DAPO-TFPC-COF (a) and DAPO-TFPT-COF (b). The DAPO-TFPC-COF and DAPO-TFPT-COF samples were each exposed to identical conditions for 24 h.

VIII. The Catalytic Activity of the Monomer

Table S1 The catalytic activities of the three monomers for the Knoevenagel Condensation[a].

Catalyst	Am.(mg)[b]	Yield%
TFPC	3.6	＜1
TFPT	3.4	＜1
DAPO	1.9	81

[a] Reaction conditions: Catalyst, benzaldehyde (0.50 mmol), malononitrile (0.60 mmol), Yield (%) was determined using the normalization method with ^{1}H NMR spectroscopy. [b] The mass of each monomer catalyst was determined based on the proportion of each monomer in the corresponding 5.5 mg COF.

IX. Mechanism of Knoevenagel Condensation Reaction

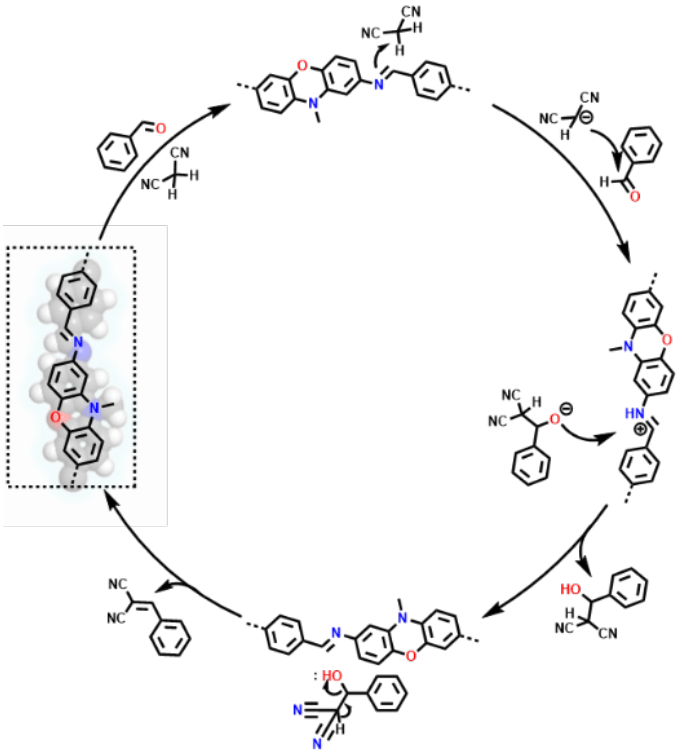


Figure S9. Mechanism of the catalytic Knoevenagel condensation reaction.

X. SEM Image after Five Cycles

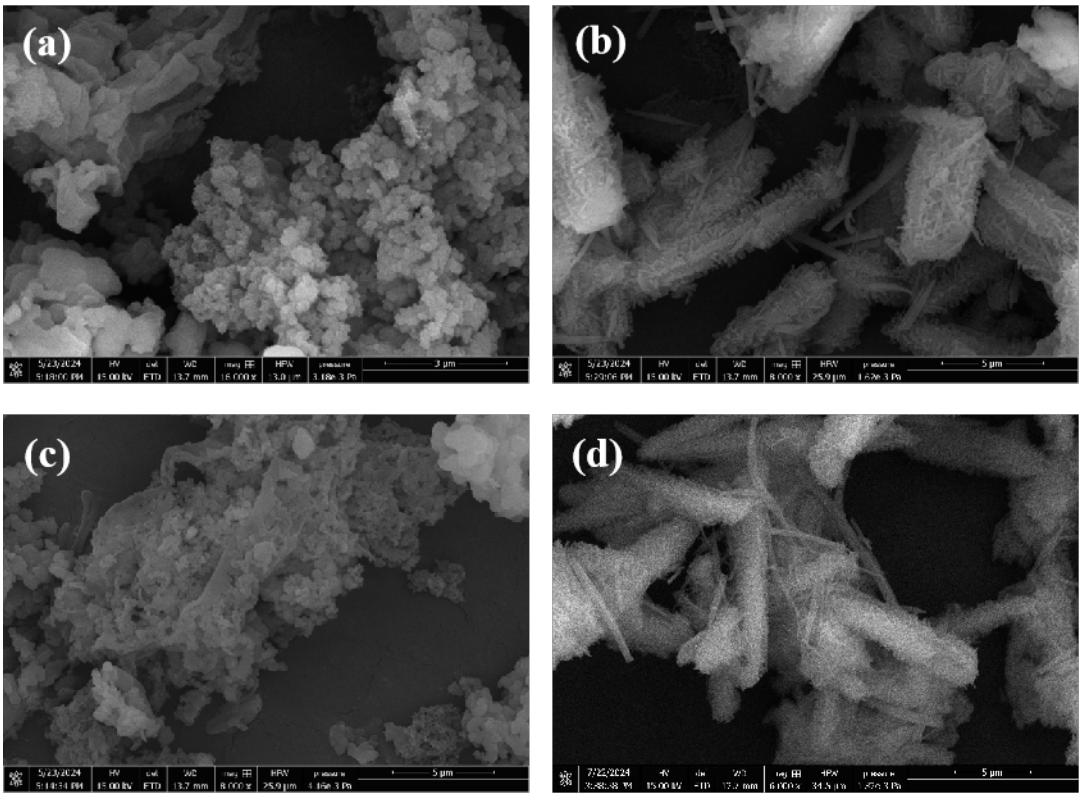


Figure S10. SEM image after five cycles of DAPO-TFPC-COF (a) (c) and DAPO-TFPT-COF (b) (d).

XI. Study on the Cycling Stability of Catalysts

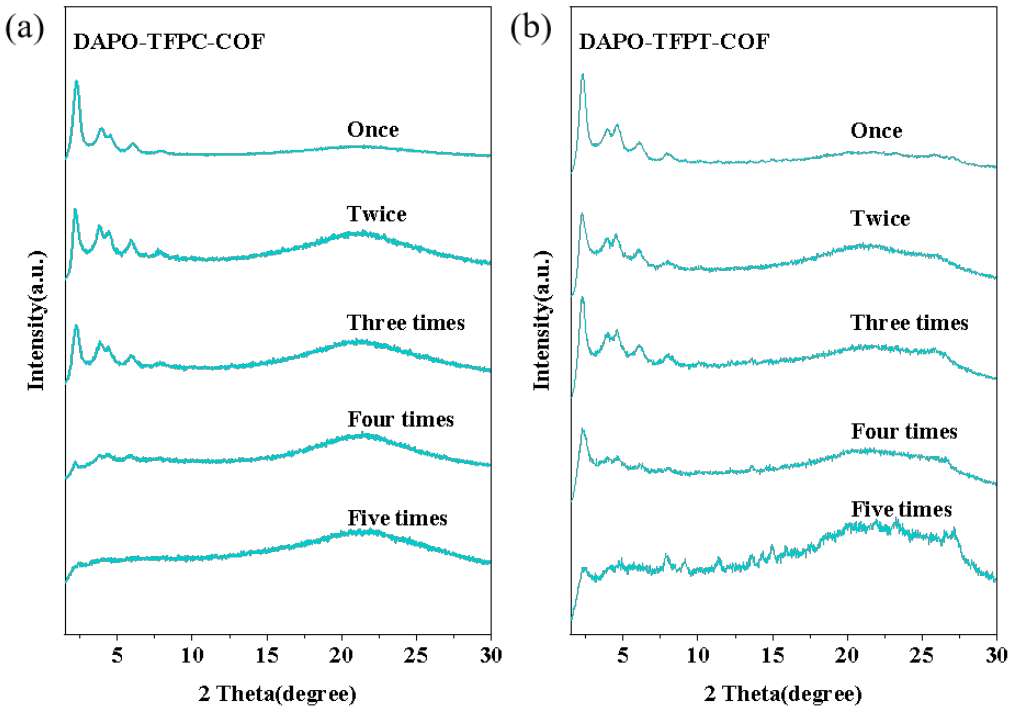


Figure S11. (a) PXRD of DAPO-TFPC-COF cycling five times; (b) PXRD of DAPO-TFPT-COF cycling five times.

XII. FT-IR Comparison Chart before and after Five Cycles

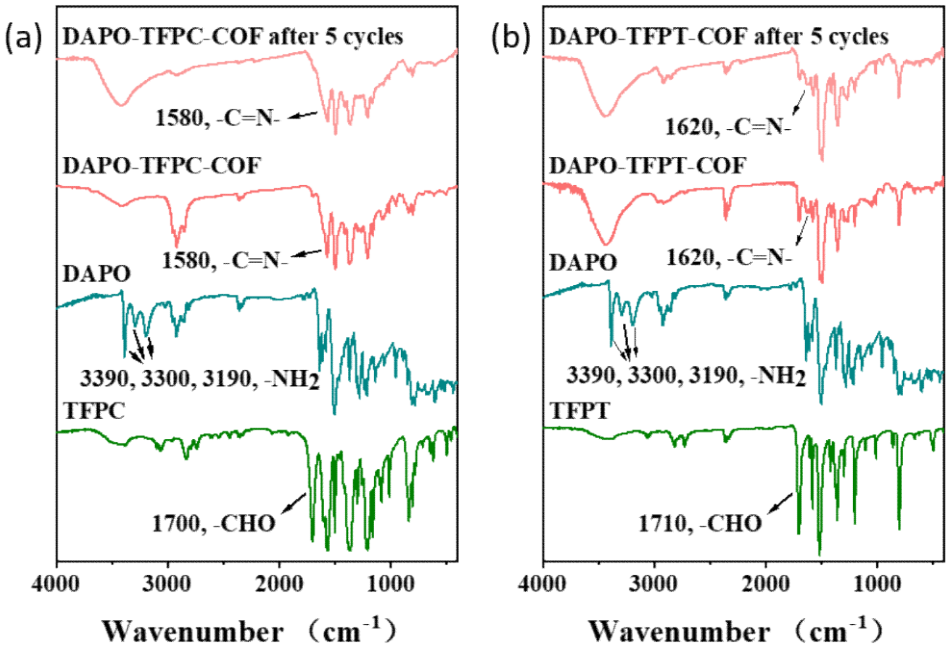
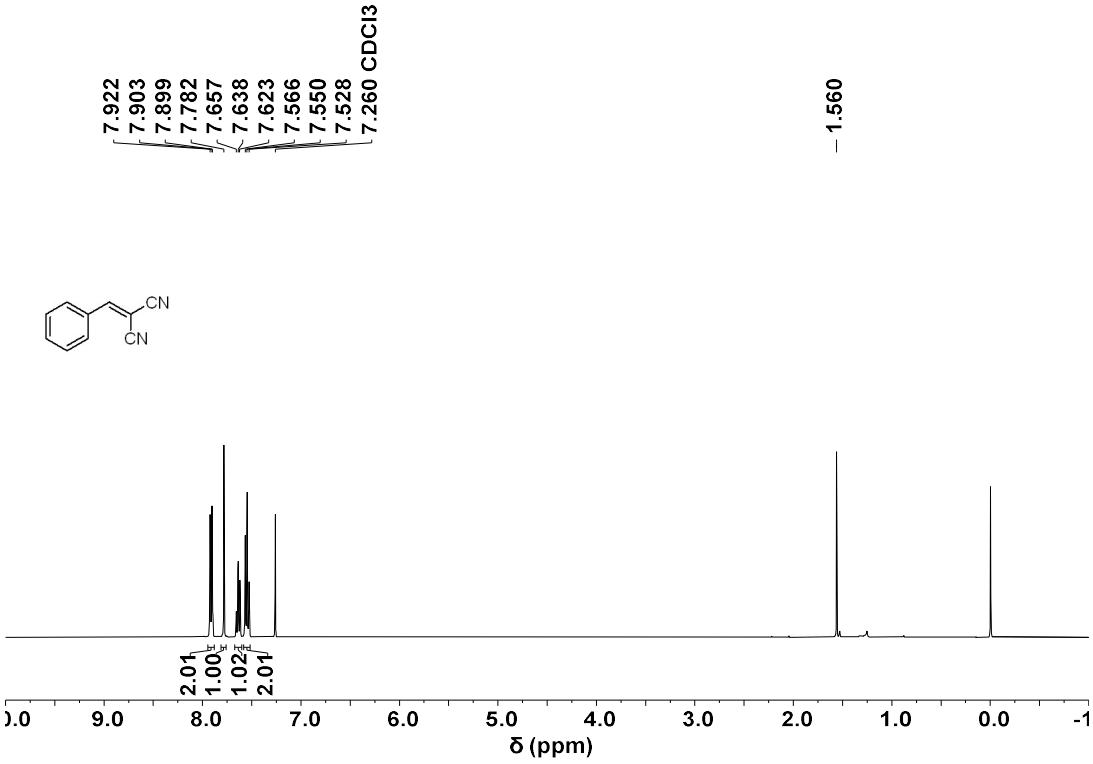
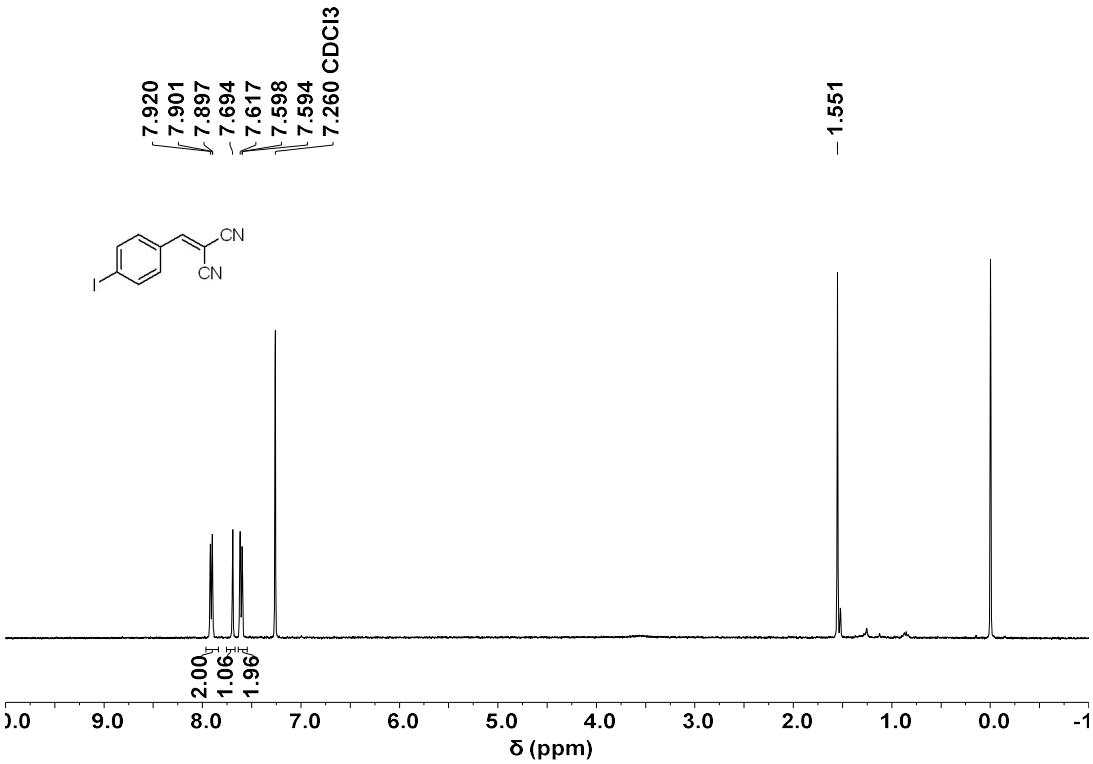
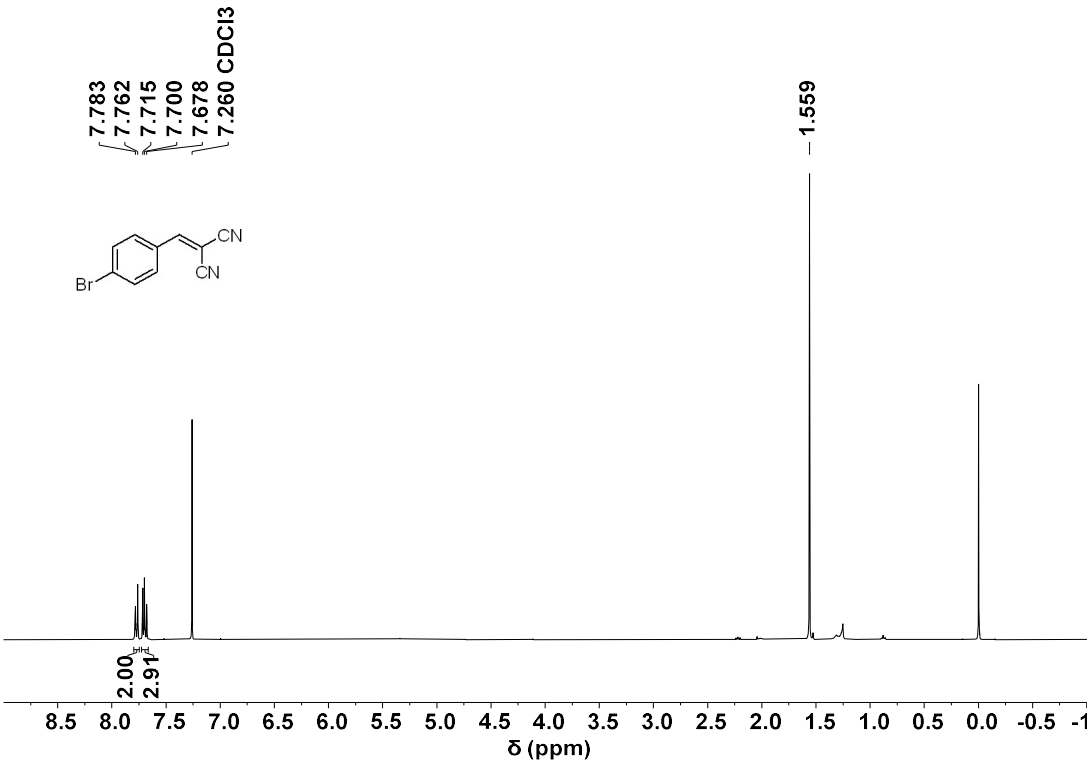


Figure S12. The FT-IR comparison chart before and after 5 cycles of DAPO-TFPC-COF (a) and DAPO-TFPT-COF (b).

XIII. NMR Spectra



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CN
Br
2.00
2.91
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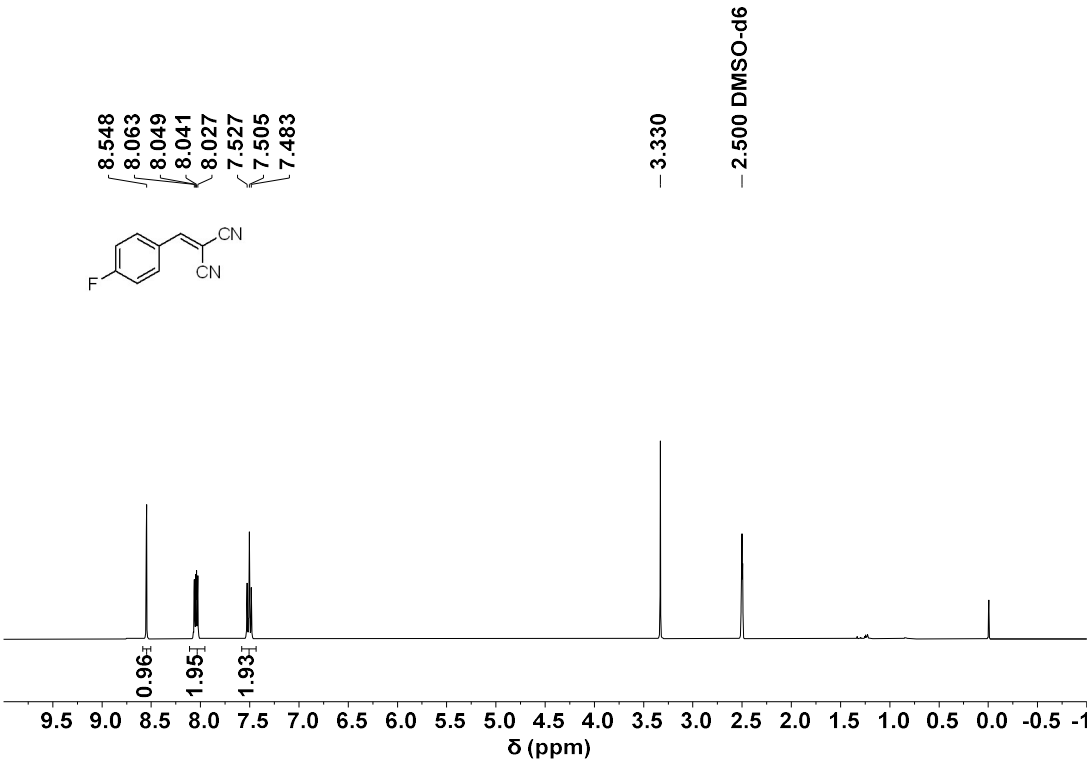
δ (ppm)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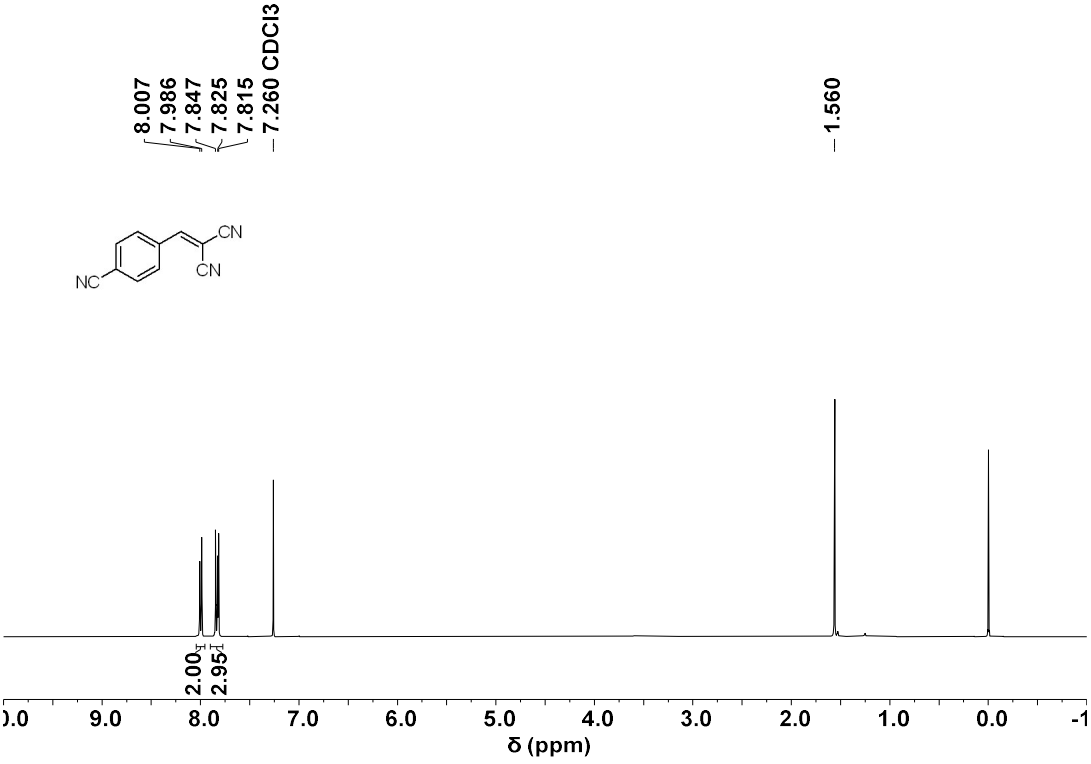
F
0.96
1.95
1.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
δ (ppm)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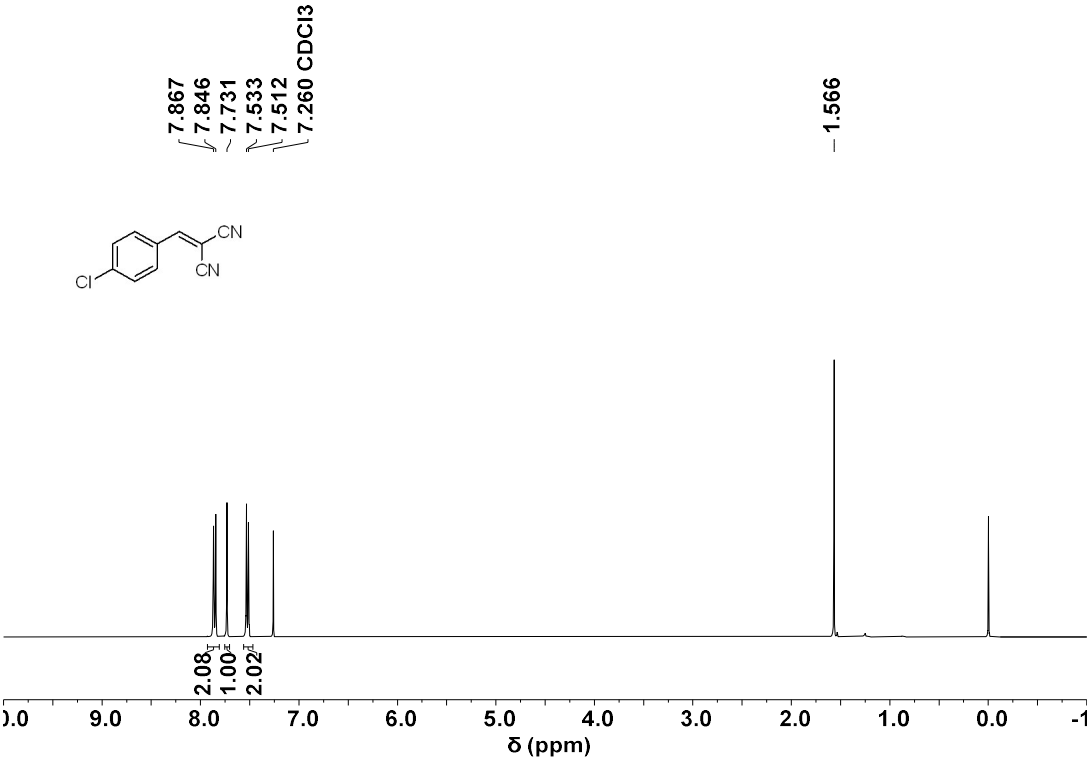
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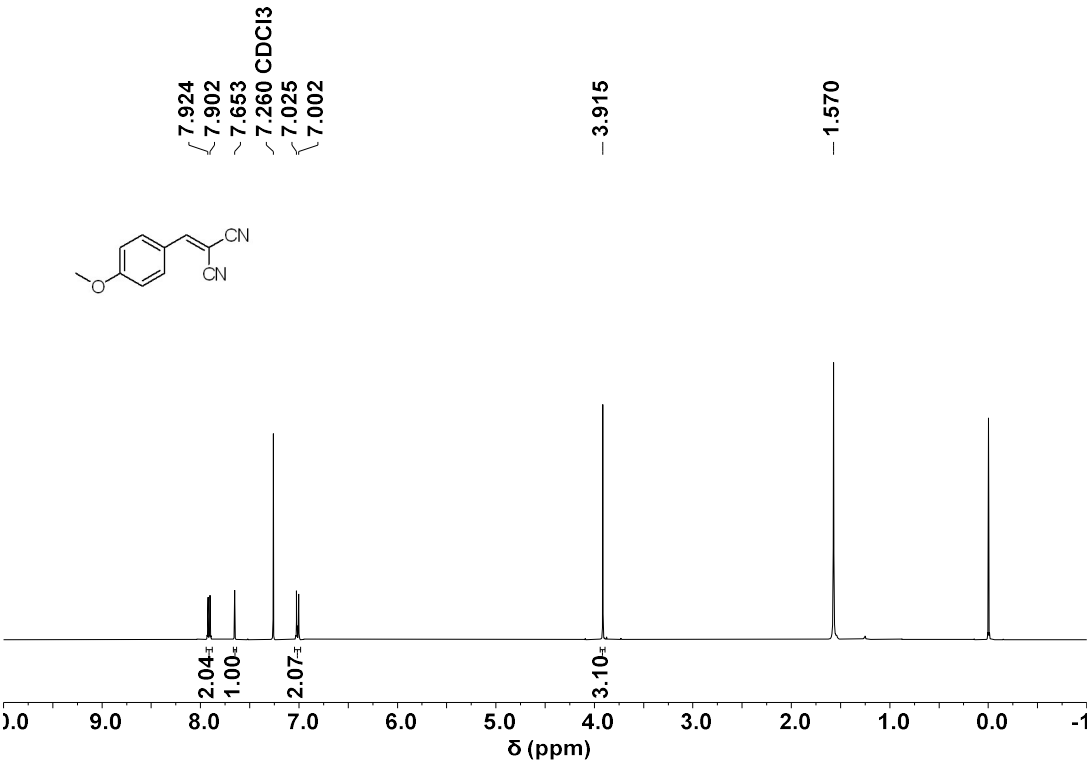
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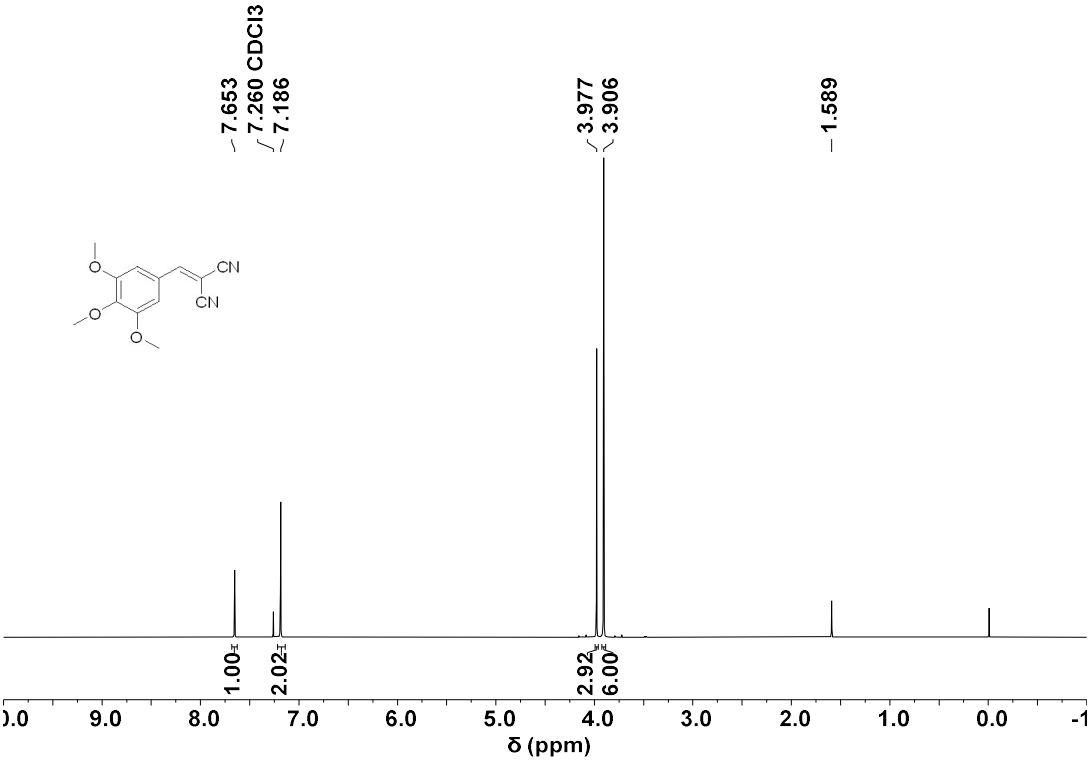
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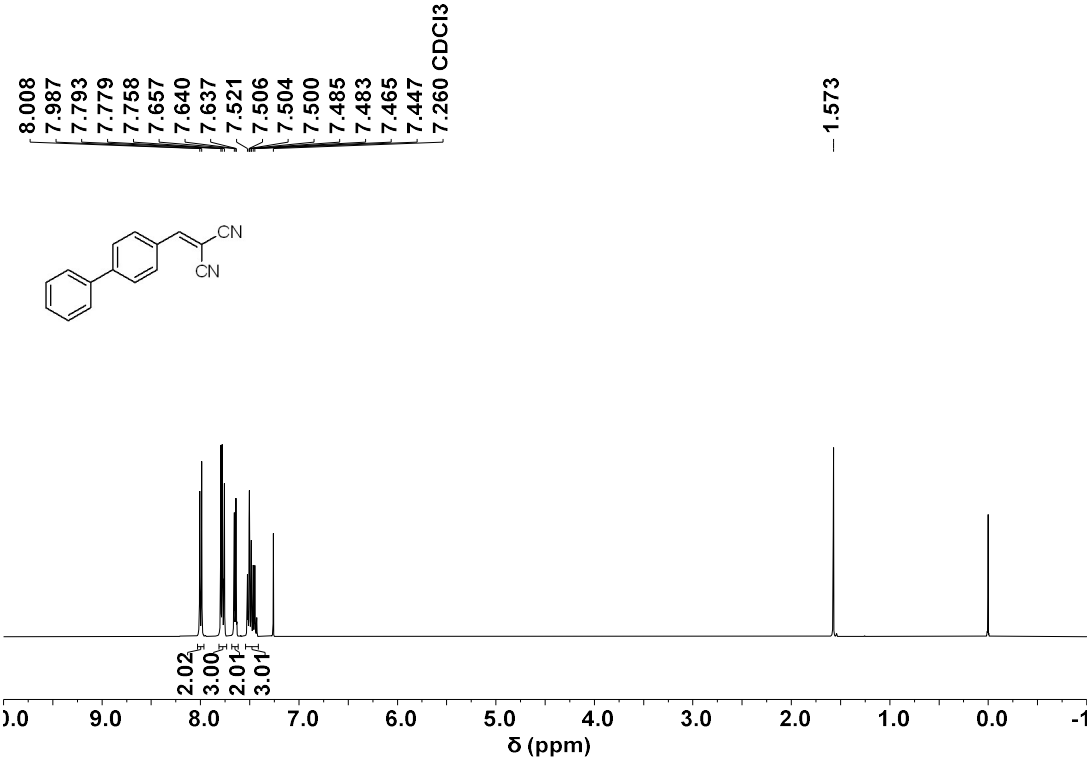
δ (ppm)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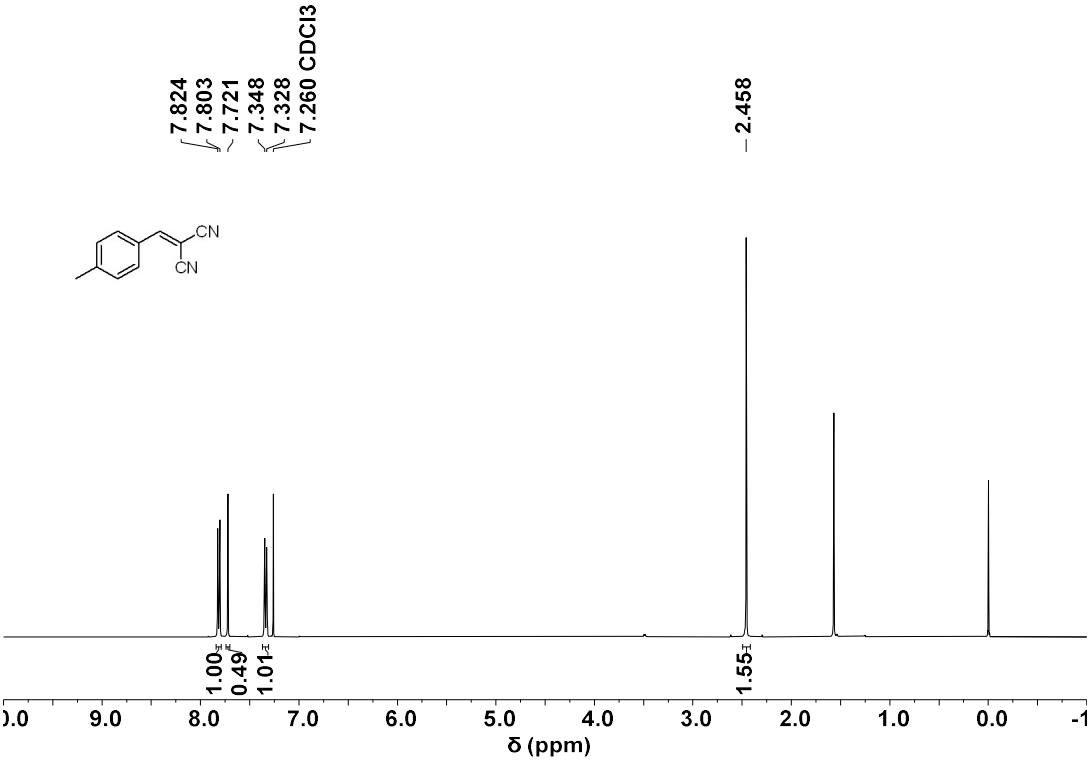
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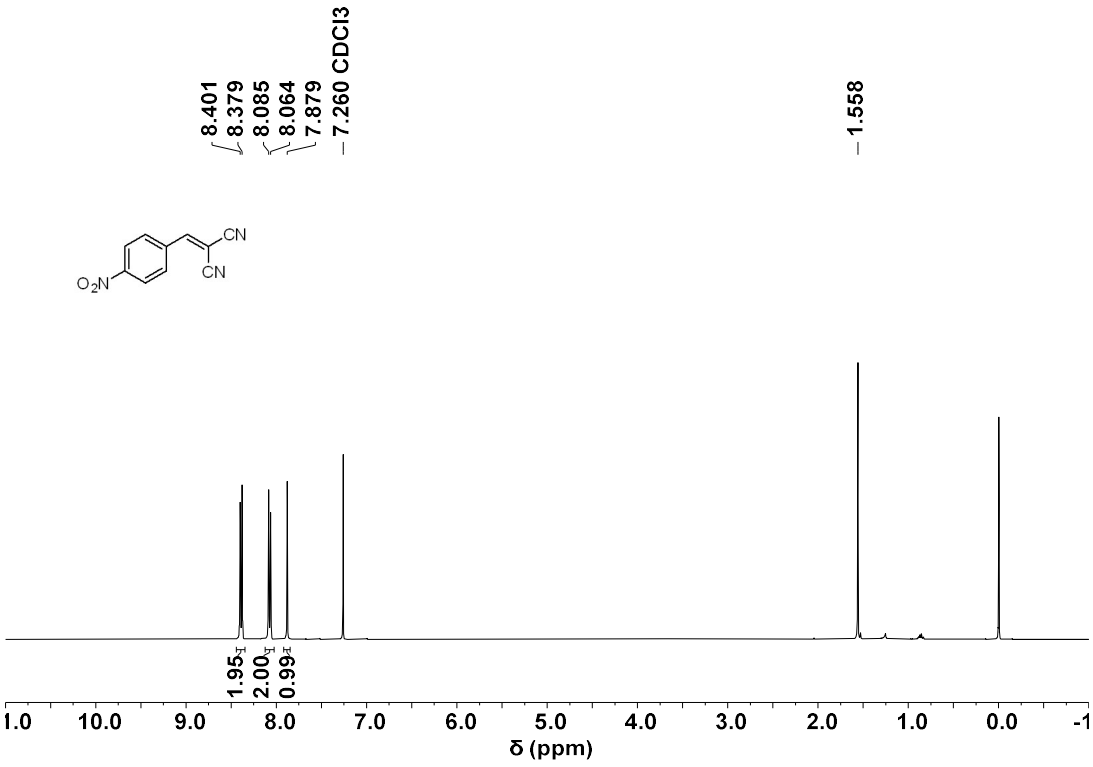
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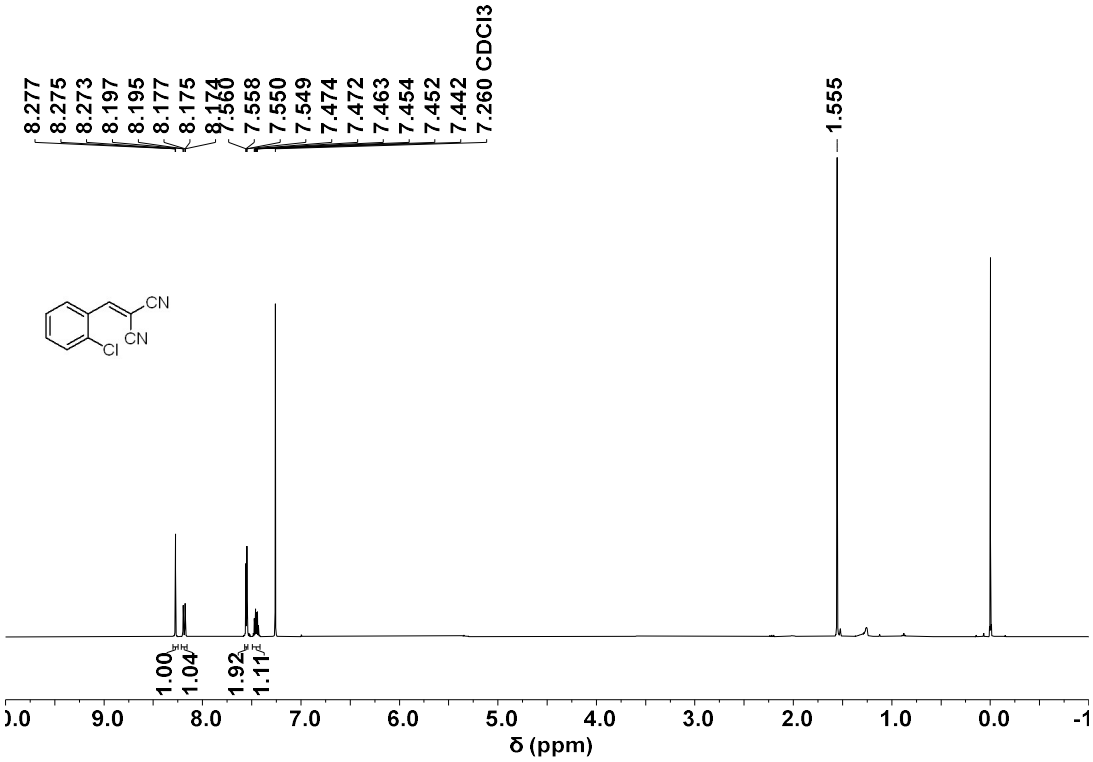
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CN
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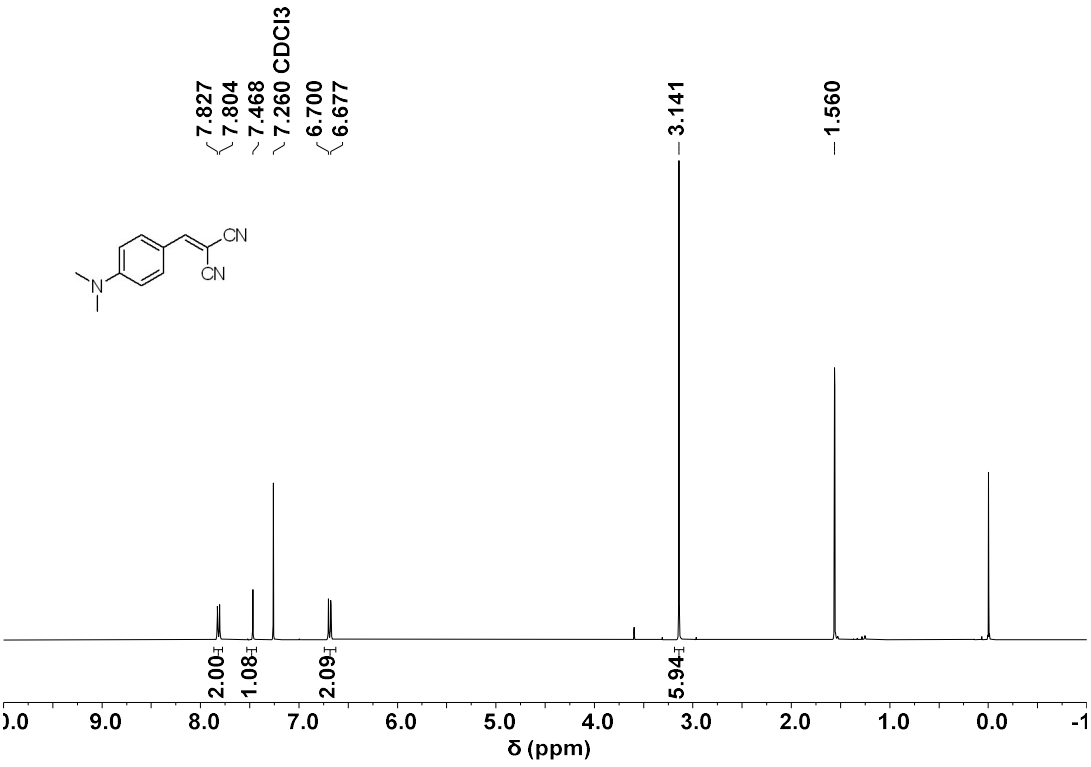
δ (ppm)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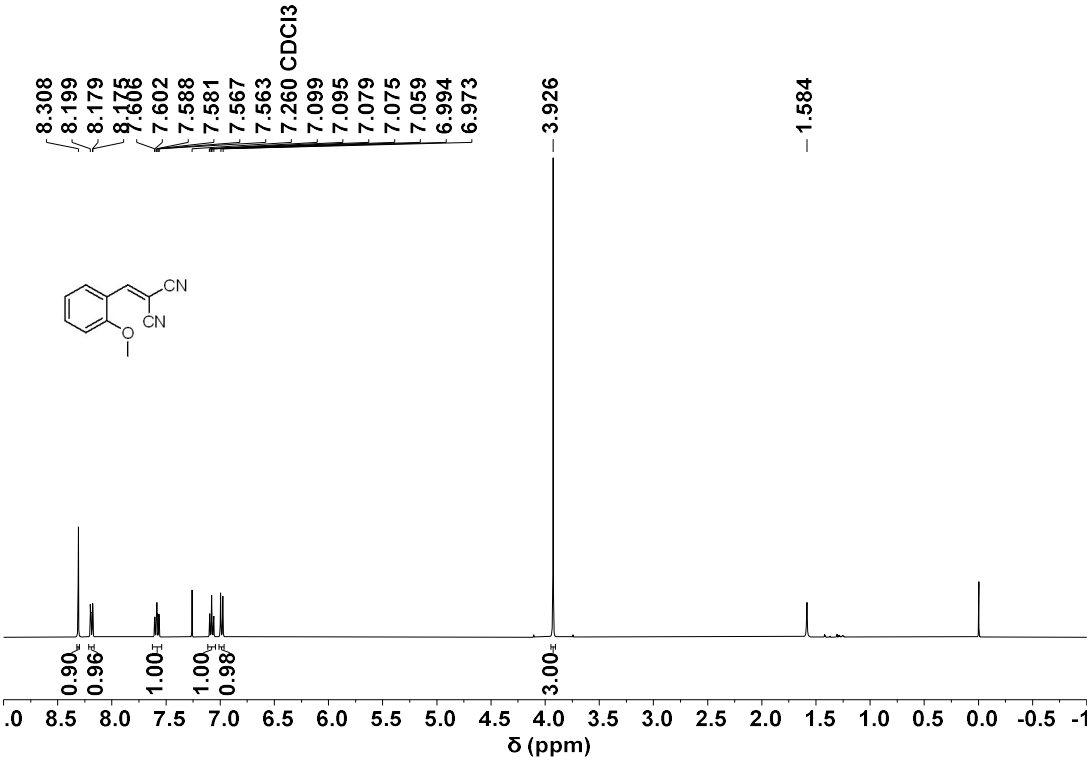
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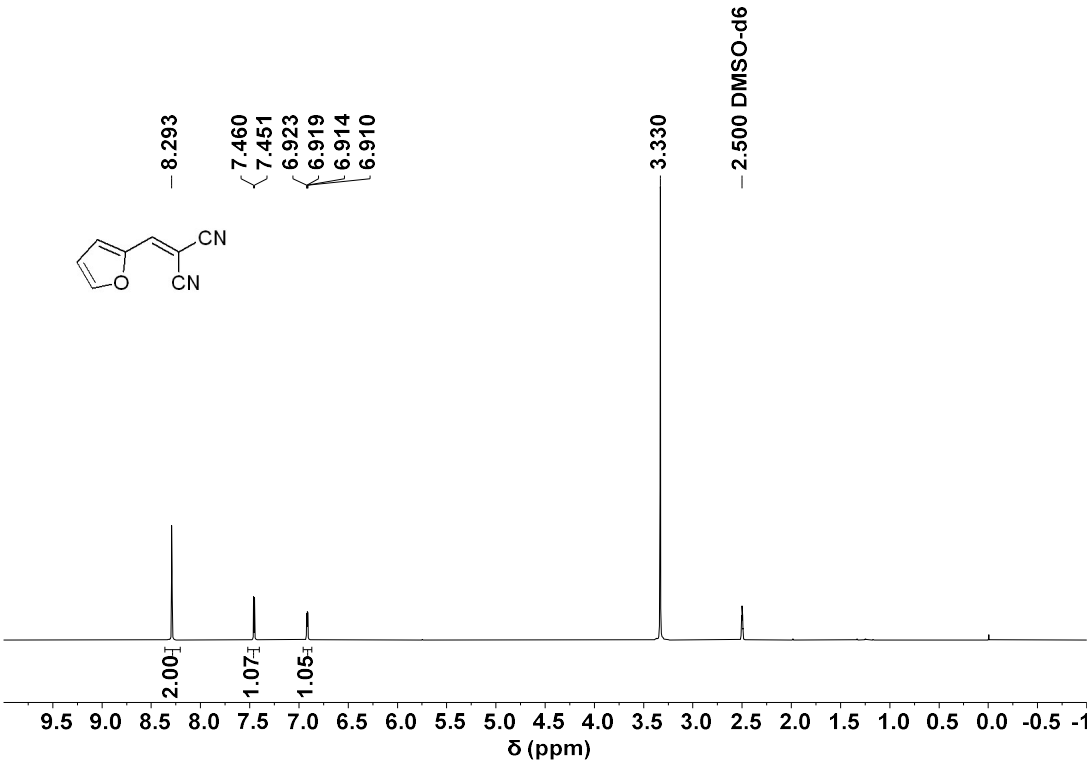
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CN
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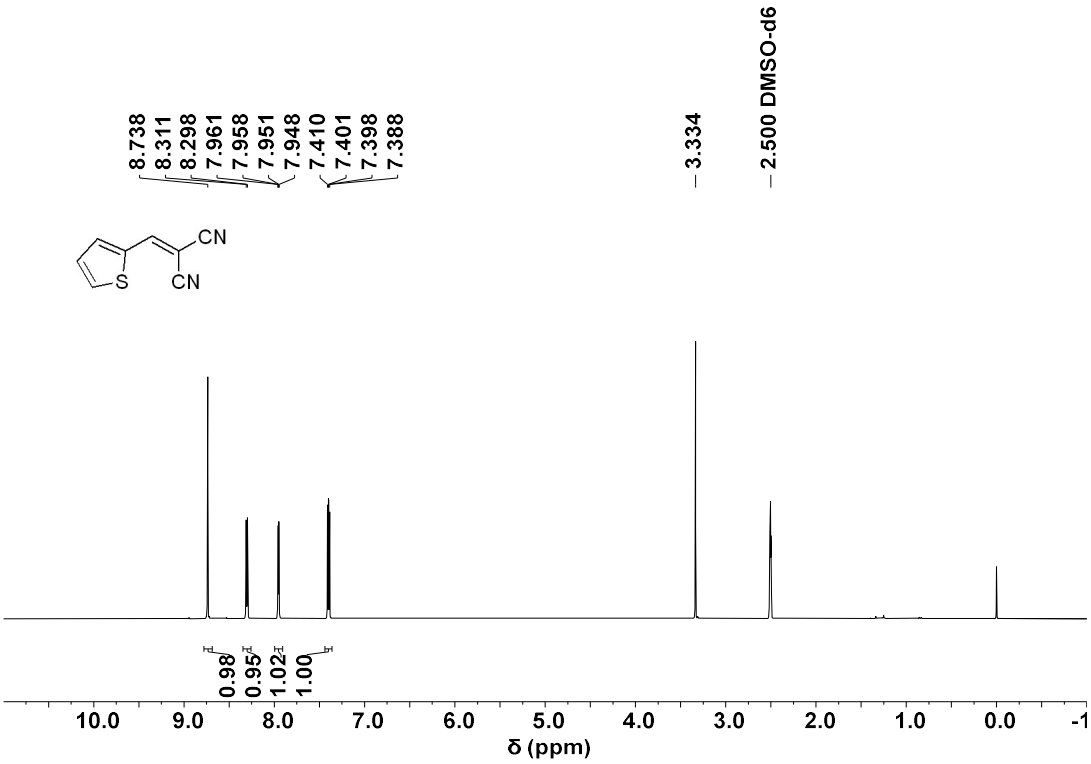
1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
δ (ppm)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CN
CN
S
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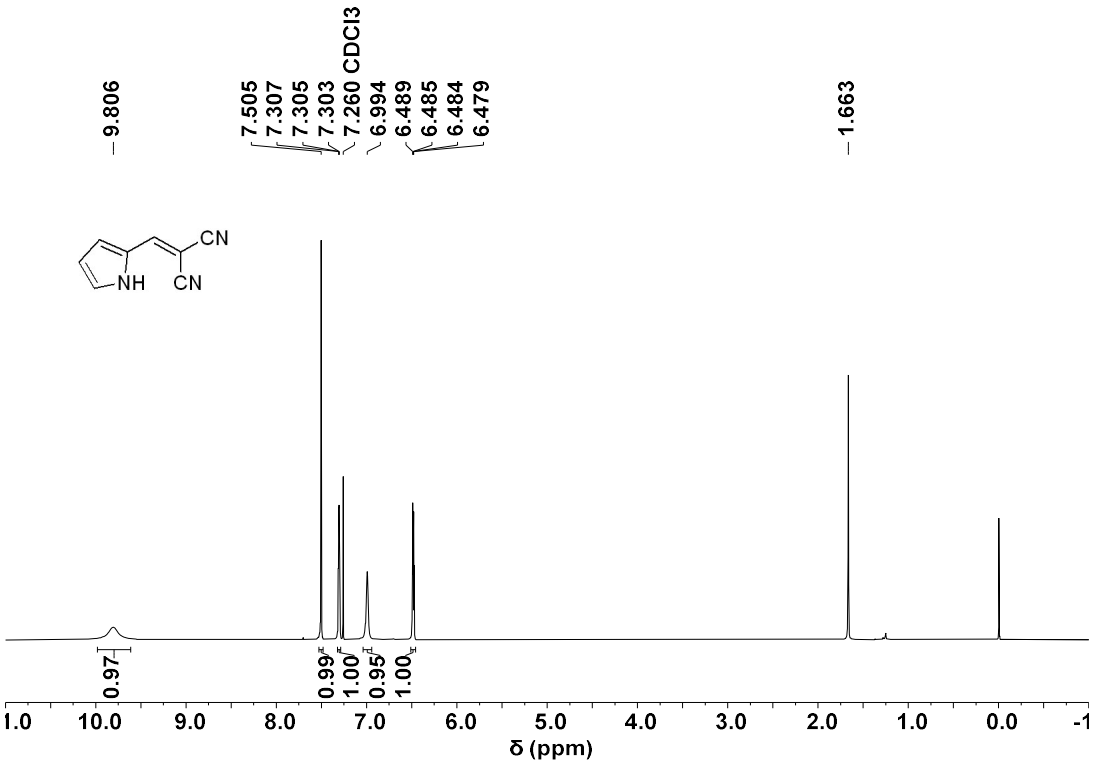
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0.95
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

XIV. References

1. Z. Meng, Y. Zhang, M. Dong, Y. Zhang, F. Cui, T.-P. Loh, Y. Jin, W. Zhang, H. Yang, Y. Du, *J. Mater. Chem. A,* 2021, **9** (17), 10661-10665.
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3. J. Yang, X. Zhang, W. Si, Y. Cao, J. Qian, Y. Li, B. Li, W. Qin, *ACS Catal.,* 2024, **14** (3), 2022-2030.
4. L. Liu, C. Yin, Y. Li, H. Yang, Y. Du, Y. Wang, *Ind. Eng. Chem. Res.,* 2023, **62** (49), 21304-21310.