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Electronic Supplementary Information

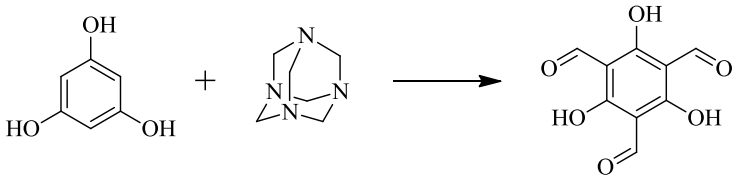
Bifunctional Covalent Organic Framework as an Efficient Platform for Cascade Catalysis

Qi Sun, Briana Aguila, and Shengqian Ma*

Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, Florida 33620, United States

E-mail: sqma@usf.edu

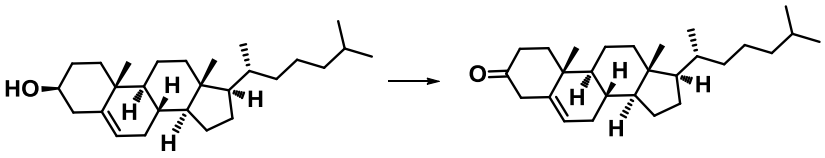
Material synthesis



Reagents: CF_3COOH, HCl.

Synthesis of triformylphloroglucinol (Tp): Hexamethylenetetraamine (15.1 g, 108 mmol), phloroglucinol (6.0 g, 49 mmol) and trifluoroacetic acid (90 mL) were refluxed at 100 °C under N_2 for 2.5 h. After that, 3 M HCl (150 mL) was added slowly, and the mixture was heated at 100 °C for another 1 h. After cooling to room temperature, the solution was filtered through Celite, extracted with an excess of CH_2Cl_2, dried over $MgSO_4$, and the solution was evaporated under reduced pressure to afford the product as light yellow solid. Yield: 1.53 g (14.5%). ^{1}H NMR (400 MHz, d_6-DMSO, 298K, TMS): δ 9.99 (s, 3H), 6.88 (br, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K, TMS) 103.62, 173.76, 191.92 ppm.[1]

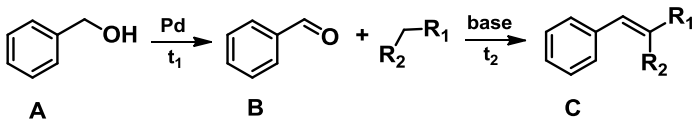
Table S1. Aerobic oxidation of cholesterol over Pd/COF-TpPa-Py and Pd/pyridine.[a]



Entry	Catalyst	Conv.(%)
1	Pd/COF-TpPa-Py	8%
2	Pd/pyridine	87%

[a] Reaction conditions: the mixture of cholesterol (1 mmol) toluene (10 mL), and catalyst was stirred at 80 °C under O_2 (1 atm) for 4 h in the presence of Pd/COF-TpPa-Py (65 mg containing 0.025 mmol Pd and 0.2 mmol pyridine moieties) or $Pd(OAc)_2$ (5.6 mg) and pyridine (15.8 mg, 0.2 mmol).

Table S2. Pd/COF-TpPa-Py catalyzed cascade oxidation-Knoevenagel condensation reactions from alcohols to α,β-unsaturated dinitriles.[a]



A B C

Entry	R_1	R_2	Time (h)	Conv.(%)	Yield (%)	
			[t_1 + t_2]	A	B	C
1	CN	CN	4 + 1.5	99	trace	99
2	CN	CH_3CH_2COO	4 + 5	99	trace	97
3	CH_3CH_2COO	CH_3CH_2COO	4 + 8	99	95	4

[a] Reaction conditions: The mixture of benzyl alcohol (1 mmol), toluene (10 mL), and Pd/COF-TpPa-Py was stirred at 80 °C under O_2 (1 atm) for t_1 (4 h) and then methylene compounds (1.05 mmol) was introduced, and the reaction continued for t_2 h.

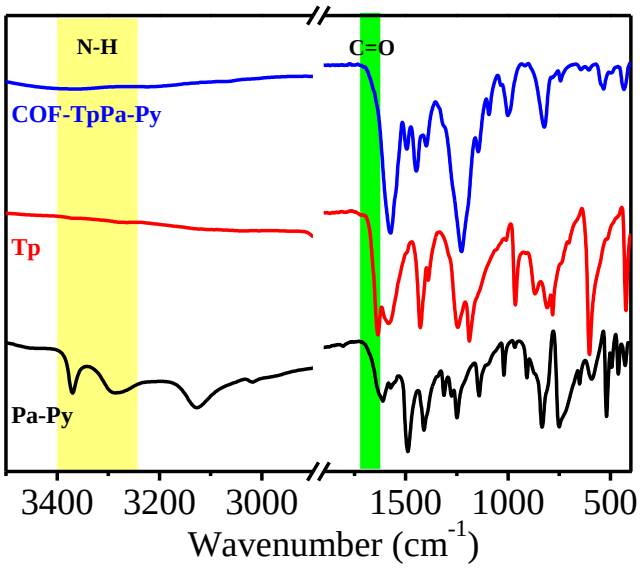


Fig. S1 IR spectra of COF-TpPa-Py and corresponding monomers.

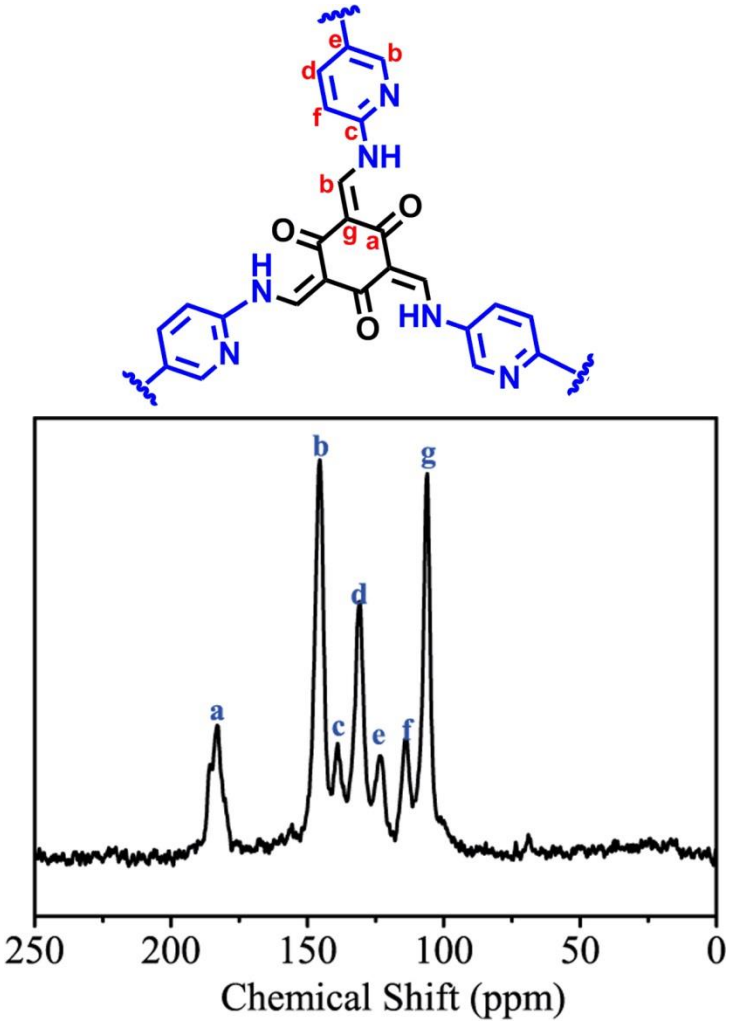


Fig. S2 Detailed assignment of ^{13}C MAS NMR spectrum of COF-TpPa-Py.

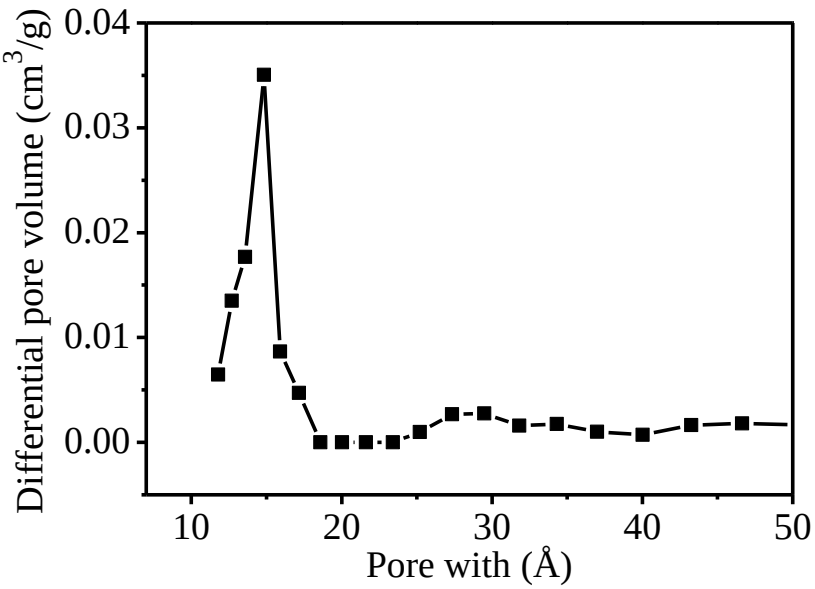


Fig. S3 Pore size distribution of COF-TpPa-Py calculated based upon NLDFT.

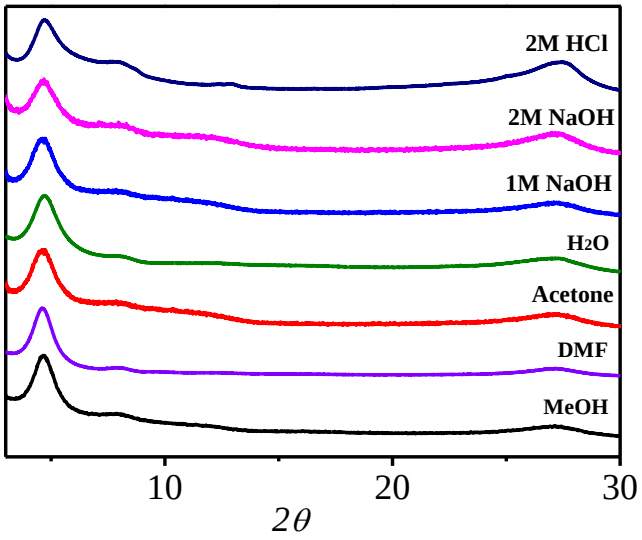


Fig. S4 PXRD patterns of COF-TpPa-Py after treatment for 24 h in various solvents as well as acid and base aqueous solutions.

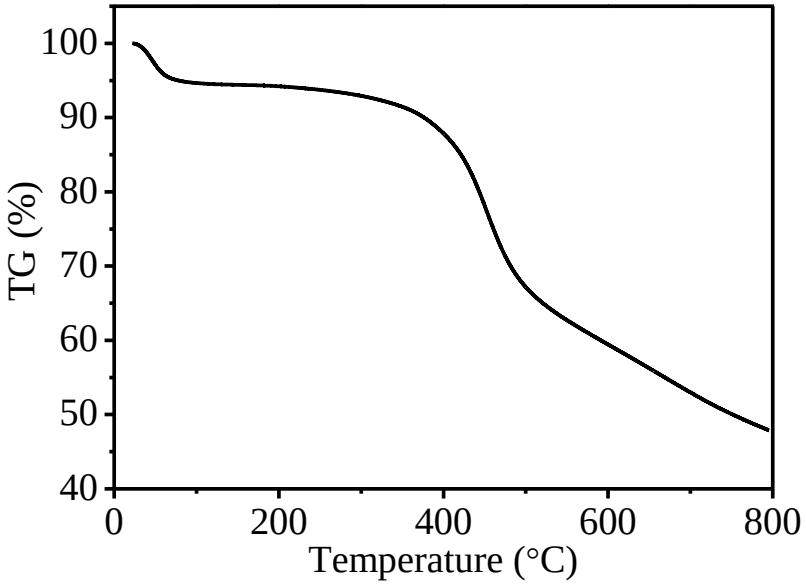


Fig. S5 TG curve of COF-TpPa-Py tested under N_2 atmosphere.

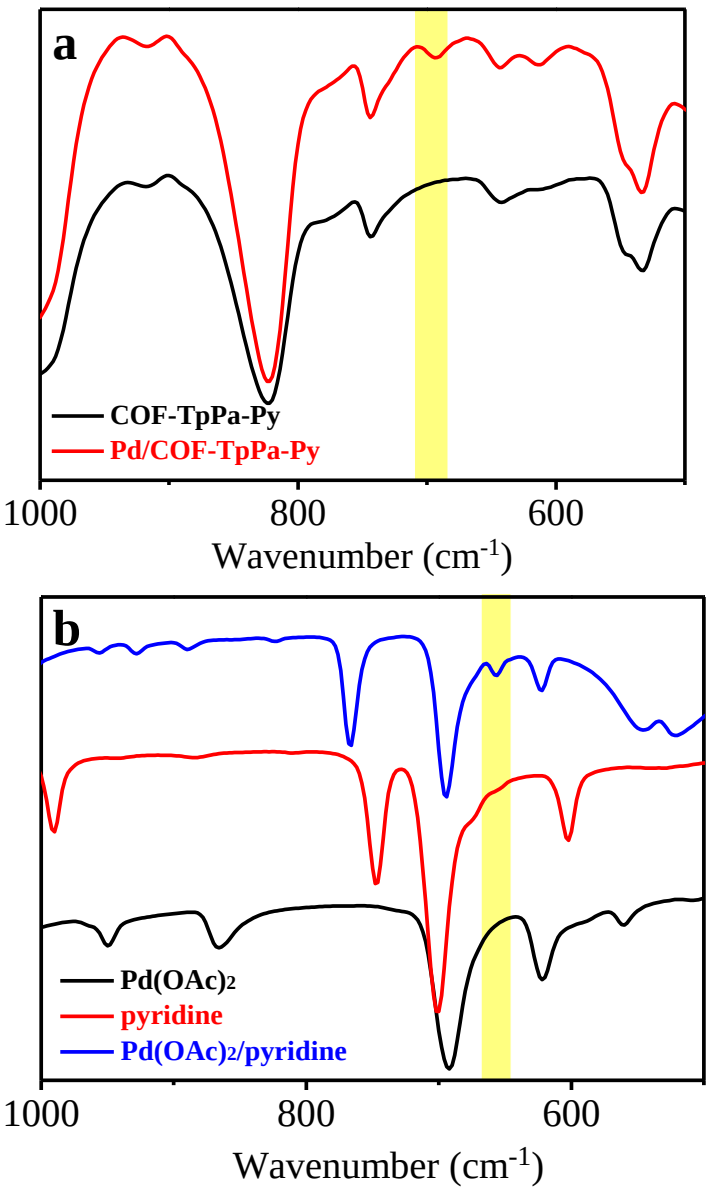


Fig. S6 IR spectra.

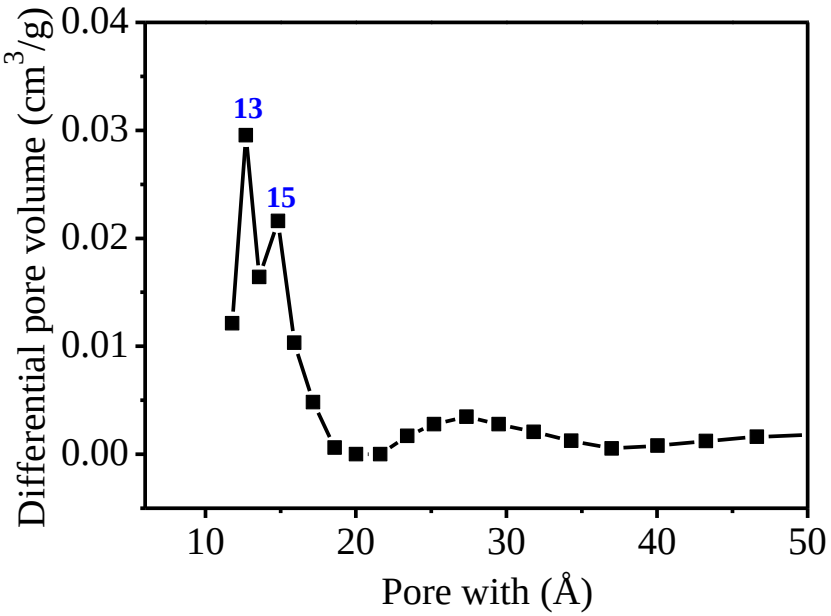


Fig. S7 Pore size distribution of COF-TpPa-Py calculated based upon NLDFT.

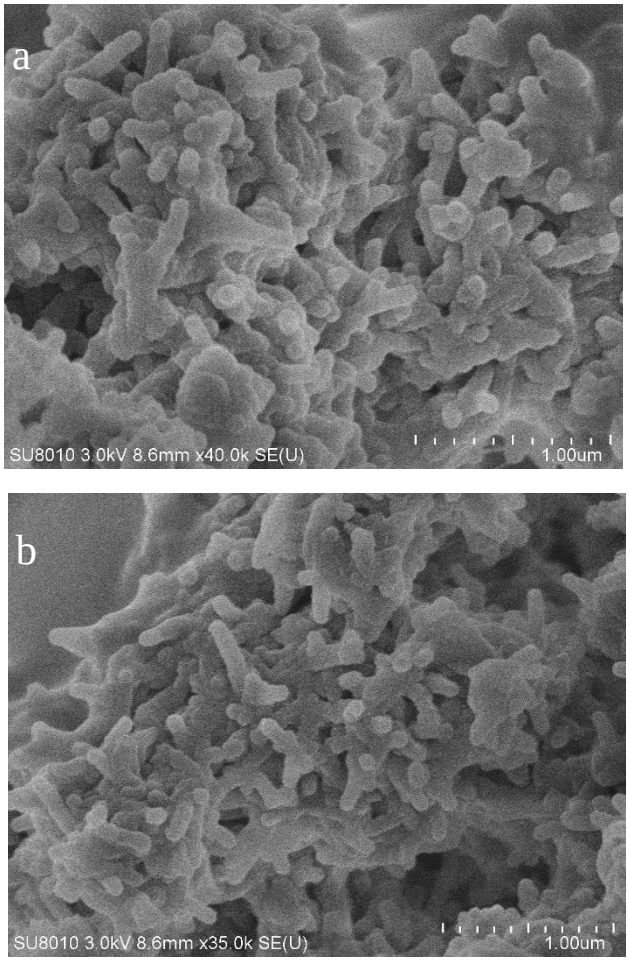


Fig. S8 SEM images of (a) COF-TpPa-Py and (b) Pd/COF-TpPa-Py.

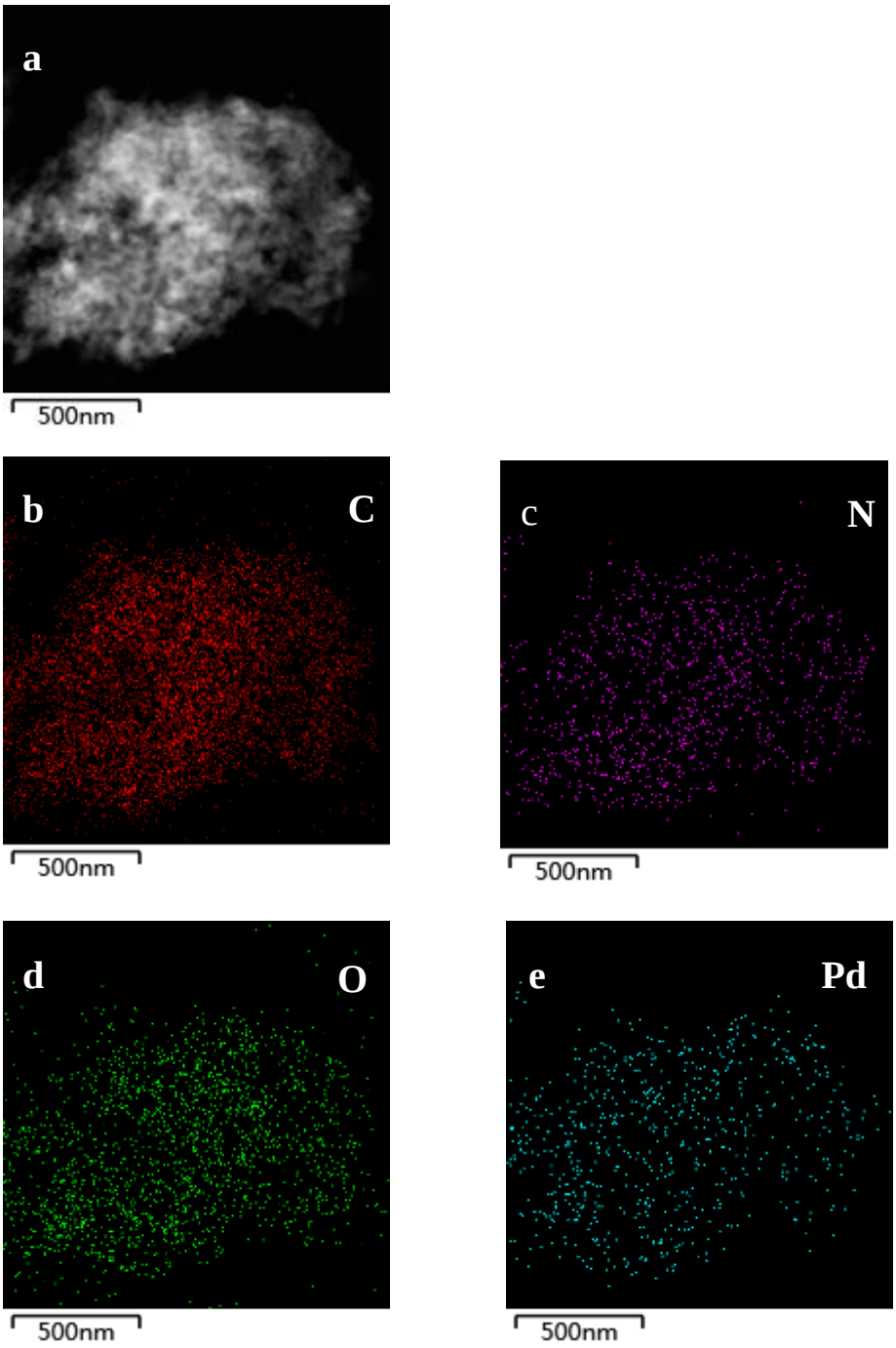


Fig. S9 (a) HADDF-STEM image of Pd/COF-TpPa-Py and corresponding EDX mapping of (b) C, (c) N, (d) O, and (e) Pd. EDX mapping results revealed that Pd species are homogeneously distributed throughout the material and no aggregated Pd nanoparticles are observed.

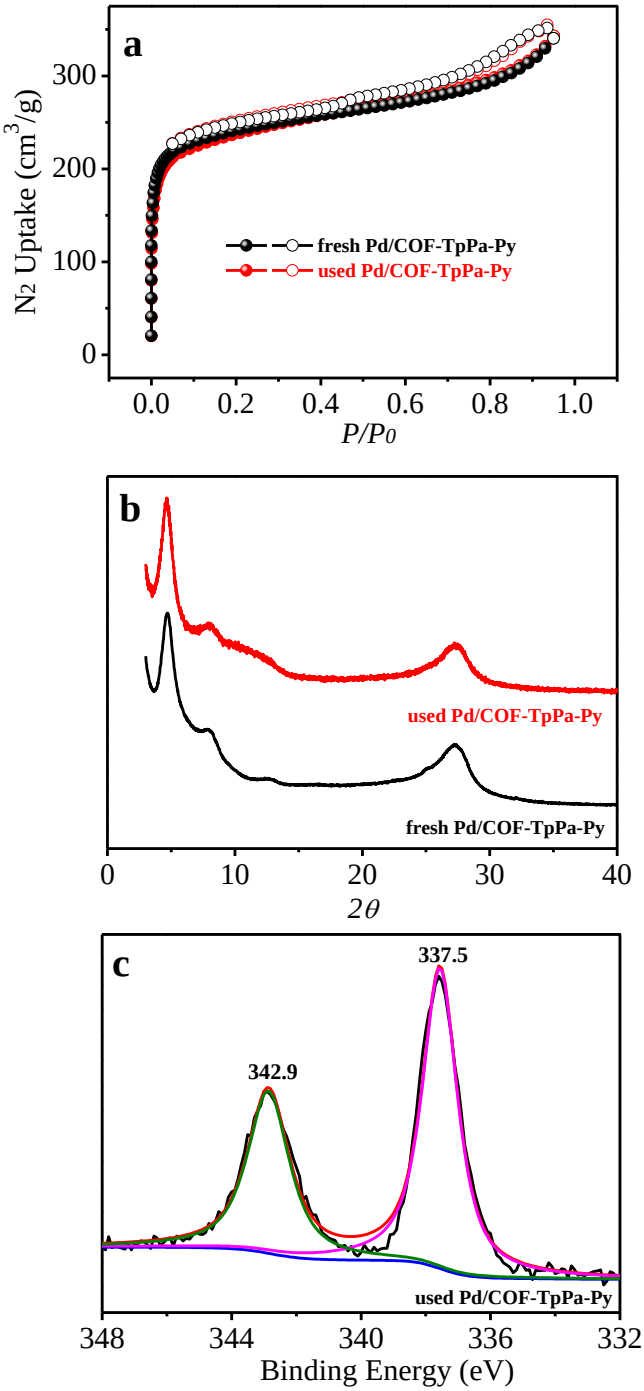


Fig. S10 (a) N_2 sorption isotherms, (b) XRD patterns, and (c) Pd 3d XPS spectra of fresh Pd/COF-TpPa-Py and used Pd/COF-TpPa-Py after cascade oxidation-Knoevenagel reaction from benzyl alcohol to benzylidene malononitrile. These results indicate that the pore structure, crystallinity, and chemical state of Pd species in Pd/COF-TpPa-Py catalyst are well-retained.

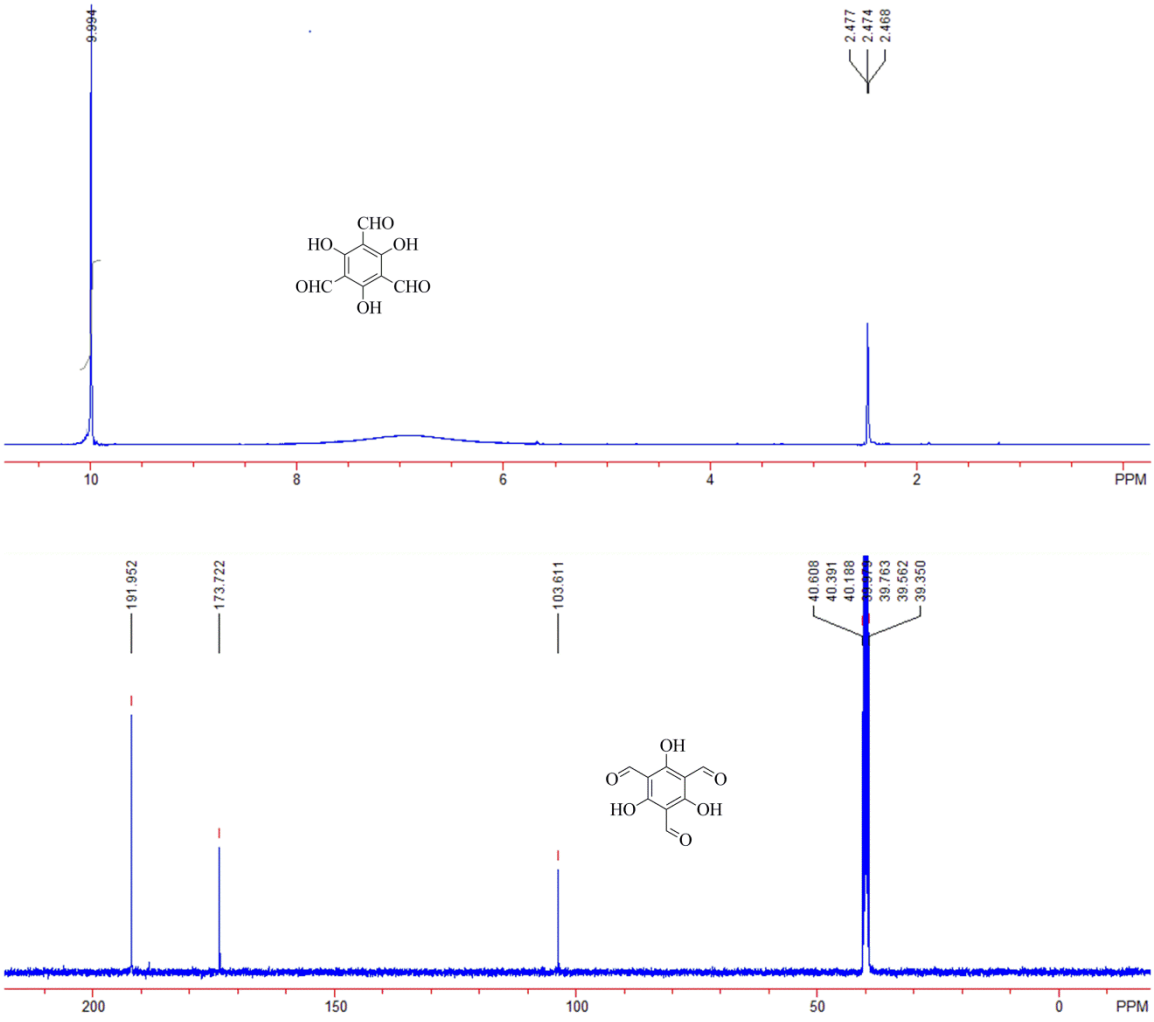


Fig. S11 Liquid NMR spectra of various compounds.