

Supporting Information

Synergized Molecular Oxygen Activation in an Enzyme-Mimicking Metal–Organic Framework for Boosted C–H Bond Oxidation

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1. General remarks

All the reagents and solvents were used as received from commercial sources, unless otherwise specified, or prepared as described in the literature. All the manipulations of air- and/or moisture-sensitive compounds were performed using standard Schlenk-line techniques or in a glove box under an inert atmosphere of argon.

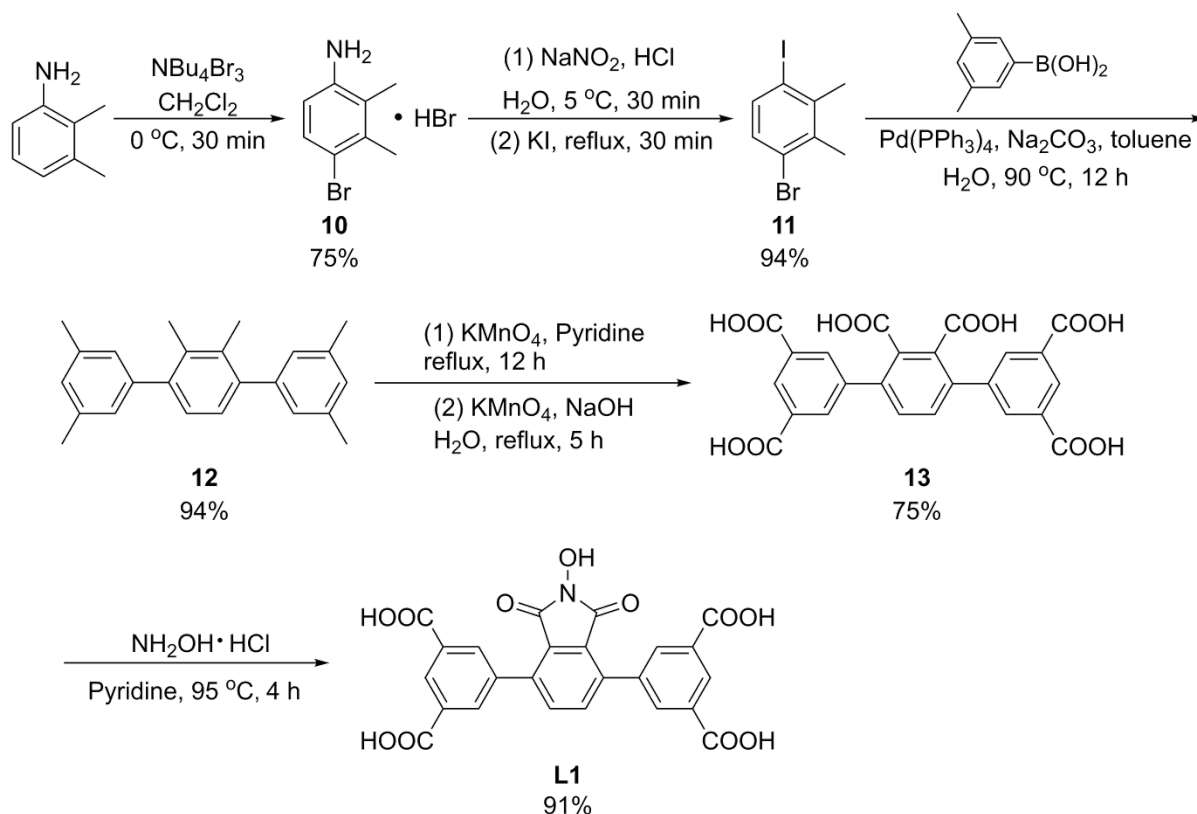
^1H and ^{13}C nuclear magnetic resonance (NMR) data were obtained by Bruker ARX400 and ARX600 spectrometer (400 MHz/600 MHz). The samples were dissolved in DMSO- d_6 , CDCl_3 or CD_3OD to conduct the NMR measurements. Single crystal X-ray diffraction data collection was carried out using a Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on Bruker D8 VENTURE or RIGAKU XtaLab P200 CCD system with VariMax Mo Optic or the MX1 beamline at the Australian Synchrotron using silicon double crystal chromated radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal parameters and details of refinements are given in Table S1. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer at 40 mA, 40 kV on Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) at room temperature with 2° min^{-1} at a range of $5\text{--}40^\circ$. Thermal gravimetric analysis (TGA) was conducted on a differential thermal analyzer (TA, Q500) by heating the samples from 20°C to 600°C with a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 atmosphere (60 mL min^{-1}). Scanning electron microscopy (SEM) images were performed on a Zeiss Sigma 300 instrument. The upper solution of the stored MOF crystals was replaced with fresh acetone once a day for totally 3 days. The MOF crystals were collected and dried under vacuum at 120°C for 12 h prior to sorption analysis. Essentially, the activation process was performed without exposure to the air. Gas adsorption

measurements were conducted using the gas adsorption equipment TRISTAR 3020. The catalytic performance tests were carried out on Ruicheng Ts100 oscillator with constant temperatures and oscillation frequencies. The reaction products of aerobic oxidation were analyzed by gas chromatography mass spectrometry (GC–MS, SHIMADZU GCMS–QP2010 SE W) using SH–Rxi–5Sil MS column with a combination of the NMR spectra. Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker A300–10/12 spectrometer set with the following experimental parameters: (1) frequency, 9.852609 GHz; power, 18.26 mW; modulation amplitude, 0.1 G; modulation frequency, 100 kHz; sweep time, 41.94 s; center field, 3510 G; sweep width, 50 G. (2) frequency, 9.822866 GHz; power, 6.325 mW; modulation amplitude, 1.000 G; modulation frequency, 100.00 kHz; sweep time, 30.00 s; center field, 3499.00 G; sweep width, 100.00 G.

2. Synthesis of ligands

Compound **10**, **11**, **12** and **13** were synthesized according to the literatures with slight modifications.^[1, 2] The MOF **NOTT-101** was synthesized according to the literature.^[3]

Synthesis of ligand L1



Scheme S1. Synthetic scheme of **L1**

Synthesis of compound 10. To a solution of 2,3-dimethylaniline (15 mL, 127 mmol) in CH_2Cl_2 (250 mL) was added NBu_4Br_3 (59 g, 127 mmol) at $0\text{ }^\circ\text{C}$ under argon, and then the solution was stirred at $0\text{ }^\circ\text{C}$ for 30 min. The precipitated colorless crystals of **10** (26.7 g, 75% yield) were isolated by filtration, washed with Et_2O and dried under vacuum. ^1H NMR (CD_3OD , 400 MHz): δ 2.36 (s, 3H), 2.48(s, 3H), 7.13 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H). ^{13}C NMR (CD_3OD , 100 MHz): δ 140.5, 134.4, 132.7, 130.5, 127.3, 123.6, 20.7, 15.6.

Synthesis of compound 11. A solution of **10** (23.1 g, 82 mmol) in a mixture of 150 mL of water and 75 mL of concentrated HCl was cooled to 0 °C using an external ice bath, and to this solution was added 6.14 g (86 mmol) of NaNO₂ in 45 mL of water dropwise and stirring continued for 30 min after the addition was completed. The resulting diazonium salt was treated with an aqueous solution (80 mL) of KI (40.8 g, 246 mmol), leading to the formation of a brown emulsion that was allowed to stand for several minutes before warming to 80 °C. During this process gas evolution could be observed. The reaction mixture was heated to reflux for 30 min. After cooling to room temperature, NaHSO₃ (aq.) was subsequently added to quench the reaction. The reaction mixture was extracted by 3 × 200 mL portions of EA. The combined organic layers were dried over anhydrous MgSO₄, followed by filtration and removal of the ethyl acetate solvent. The resulting paste was subjected to silica gel column chromatography using hexane as eluent to give **11** (23.9 g, 94% yield) as a white solid. ¹H NMR (CDCl₃, 600 MHz): δ 7.51 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 2.51 (s, 3H), 2.47 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 141.13, 137.53, 137.08, 131.44, 125.83, 100.66, 26.90, 21.58.

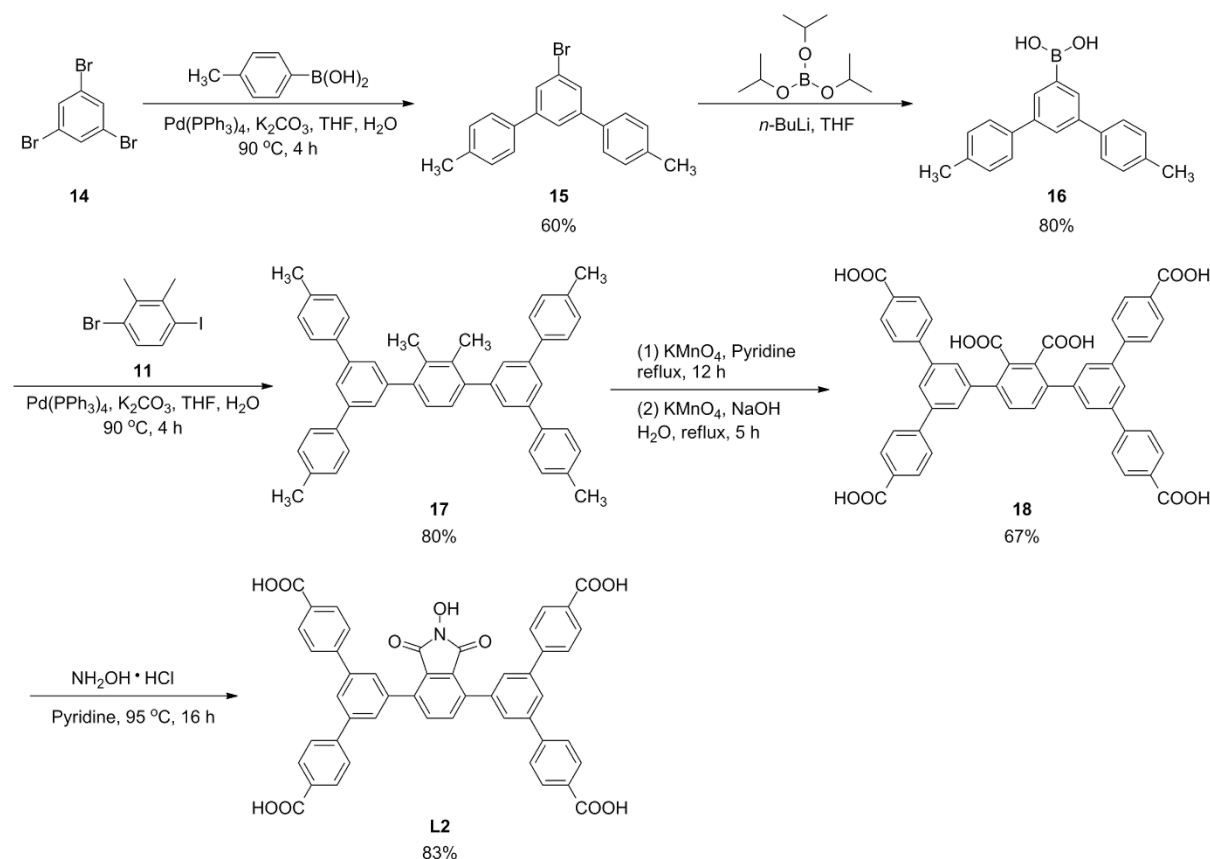
Synthesis of compound 12. To a deoxygenated mixture of compound **11** (7.80 g, 25.1 mmol), 3,5-dimethylphenylboronic acid (9.75 g, 65.0 mmol), Na₂CO₃ (10.6 g, 100 mmol) and Pd(PPh₃)₄ (1.45 g, 1.25 mmol) was added a solution mixture of degassed toluene (150 mL) and water (50 mL). The reaction mixture was heated at 90 °C for 6 h under argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with H₂O

(30 mL) and subsequently extracted with EA (3 × 100 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, and then evaporated to dryness. The resulting solid was subjected to silica gel column chromatography using PE as eluent to give **12** (7.40 g, 94% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.12 (s, 2H), 7.01 (s, 2H), 6.98 (s, 4H), 2.39 (s, 12H), 2.24(s, 6H). ¹³C NMR (151 MHz, CDCl₃): δ 142.62, 141.37, 137.40, 134.39, 128.17, 127.32, 126.89, 21.36, 17.79. HRMS (ESI–TOF): *m/z* calculated for C₂₄H₂₇ [M+H]⁺: 315.2107, found: 315.2103.

Synthesis of compound 13. To a solution of compound **12** (6.1 g, 19.4 mmol) in pyridine (150 ml) and water (40 ml) was added KMnO₄ (27.5 g, 174.5 mmol). The reaction mixture was heated to reflux for 3 h, and then additional KMnO₄ (12.3 g, 77.8 mmol) was added by portions. The reaction mixture was further refluxed for 9 h. Upon cooling, the reaction mixture was concentrated, and then dissolved in an aqueous solution of NaOH (2 M, 200 mL). The reaction mixture was heated to 100 °C and another portion of KMnO₄ (12.3 g, 77.8 mmol) was added carefully. After the reaction mixture was stirring for 5 h, the brown solid was removed by hot filtration. The filtrate was allowed to room temperature and carefully acidified with an aq. HCl solution (6 M). The produced precipitate was filtered and washed with water and dried in vacuum to afford **13** (7.2 g, 75% yield) as white powder. ¹H NMR (DMSO-*d*₆, 400 MHz): δ 13.37 (s, 6H), 8.50 (s, 2H), 8.19 (s, 4H) , 7.69 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 168.95, 166.47, 140.48, 137.44, 133.16, 133.09, 131.81, 131.60, 129.39. HRMS (ESI–TOF): *m/z* calculated for C₂₄H₁₄NaO₁₂ [M+Na]⁺: 517.0377, found: 517.0414.

Synthesis of L1 A mixture of compound **13** (2.4 g, 4.85 mmol), hydroxylamine hydrochloride (369 mg, 5.34 mmol), pyridine (50 mL) was heated at 95 °C for 4 h. After cooling to room temperature, pyridine was removed by a rotary evaporator and 20 mL of 1 M HCl was added. The resulting mixture was subjected to a short period of ultrasonication and the precipitate was filtered and washed with water thoroughly and dried in vacuum to afford **L1** (2.1 g, 91%) as a yellow solid. ¹H NMR (DMSO-*d*₆, 400 MHz): δ 13.44 (s, 4H), 10.84 (s, 1H), 8.57 (s, 2H), 8.38 (s, 4H), 7.89 (s, 2H). ¹³C NMR (DMSO-*d*₆ 151 MHz): δ 166.45, 163.19, 137.03, 136.73, 135.99, 134.33, 131.19, 129.90, 126.08. HRMS (ESI–TOF): *m/z* calculated for C₂₄H₁₄NO₁₁ [M+H]⁺: 492.0561, found: 492.0569.

Synthesis of ligand L2



Scheme S2. Synthetic scheme of **L2**

Synthesis of compound 15. To a deoxygenated mixture of compound **14** (12.0 g, 40.0 mmol), 4-methylphenylboronic acid (11.9 g, 80.0 mmol), K_2CO_3 (26.3 g, 190.0 mmol) and $\text{Pd(PPh}_3)_4$ (3.24 g, 2.8 mmol) was added a mixture of degassed THF (150 mL) and water (50 mL). The reaction mixture was heated at 90 °C for 6 h under argon atmosphere. After cooling to room temperature, the reaction mixture was extracted with DCM (3 $\times$ 100 mL). The combined organics were washed with brine, dried over anhydrous MgSO_4 , and then evaporated to dryness. The resulting solid was subjected to silica gel column chromatography using PE as eluent to give **15** (7.70 g, 60% yield) as a white solid. ^1H NMR (600 MHz, CDCl_3)

δ 7.55 (d, 3H), 7.36 (d, 4H), 7.14 (d, 4H), 2.28 (s, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 143.63, 137.93, 137.02, 129.74, 128.52, 127.13, 124.50, 123.31, 21.26. GC-MS (ESI): m/z calculated for $\text{C}_{20}\text{H}_{17}\text{Br}$ $[\text{M}+\text{H}]^+$: 336.0514, found: 336.0533.

Synthesis of compound 16. To a 250 mL three-necked flask equipped with dropping funnel were added compound **15** (8.00 g, 20.0 mmol) and dry THF (100 mL). The solution was cooled to $-78\text{ }^\circ\text{C}$ and *n*-butyllithium (12.5 mL, 30.0 mmol) was then added dropwise into the solution. After the reaction mixture was stirred for 1.5 h at $-78\text{ }^\circ\text{C}$, triisopropyl borate (27.9 mL, 120 mmol) was added dropwise in 15 min. The reaction mixture was allowed to room temperature and stirred overnight, and then quenched by 1 M HCl aq. solution. The reaction mixture was extracted with EA ($3 \times 100\text{ mL}$). And the combined organics were washed with brine, dried over anhydrous MgSO_4 , and then evaporated to dryness. The resulting solid was subjected to silica gel column chromatography (PE/EA =3:1) to give **16** (5.80 g, 80% yield) as a white solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.25 (s, 2H), 8.05 (s, 2H), 7.87 (s, 1H), 7.65 (d, 4H), 7.30 (d, 4H), 2.35 (s, 6H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 139.80, 137.68, 136.65, 131.19, 129.51, 126.73, 126.23, 20.70. HRMS (ESI-TOF): m/z calculated for $\text{C}_{20}\text{H}_{19}\text{NaBO}_2$ $[\text{M}+\text{Na}]^+$: 325.1376, found: 325.1393.

Synthesis of compound 17. To a deoxygenated mixture of compound **16** (2.50 g, 8.04 mmol), compound **11** (1.00 g, 3.20 mmol), K_2CO_3 (4.40 g, 32.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.45 g, 0.39 mmol) was added a mixture of degassed THF (80 mL) and water (16 mL). The reaction mixture was heated at $90\text{ }^\circ\text{C}$ for 4 h under argon atmosphere. After cooling to room

temperature, the reaction mixture was extracted with EA (3 × 50 mL). The combined organics were washed with brine, dried over anhydrous MgSO₄, and then evaporated to dryness. The resulting solid was subjected to silica gel column chromatography (PE/DCM = 20:1) to give **17** (1.58 g, 80% yield) as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 7.69 (s, 2H), 7.50 (d, 8H), 7.47 (s, 4H), 7.19 (d, 10H), 2.31 (s, 12H), 2.26 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 143.61, 141.64, 141.56, 138.41, 137.37, 135.01, 129.70, 127.35, 127.28, 127.02, 124.23, 21.28, 18.16. HRMS (ESI-TOF): m/z calculated for C₄₈H₄₃ [M+H]⁺: 619.3359, found: 619.3372.

Synthesis of compound 18. To a solution of compound **17** (1.44 g, 2.34 mmol) in pyridine (30 ml) and water (8 ml) was added KMnO₄ (3.30 g, 21.1 mmol). The reaction mixture was heated to reflux for 3 h, and then additional KMnO₄ (1.47 g, 9.36 mmol) was added by portions. The reaction mixture was further refluxed for 9 h. Upon cooling, the reaction mixture was concentrated, and then dissolved in an aqueous solution of NaOH (2 M, 40 mL). The reaction mixture was heated to 100 °C and another portion of KMnO₄ (1.47 g, 9.36 mmol) was added carefully. After stirring for 5 h, the brown solid was removed by hot filtration. After cooling to room temperature, the filtrate was acidified with 6 M HCl aqueous solution. The resulting precipitate was filtered, washed thoroughly with water and dried in vacuum to afford **18** (1.26 g, 67% yield) as pale yellow powder. ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.11 (s, 6H), 8.29 (s, 1H), 8.19 (s, 1H), 8.08 (m, 20H), 7.84 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 167.20, 162.46, 143.86, 143.81, 141.13, 140.22, 139.89, 137.99, 137.68, 136.48,

134.49, 133.12, 130.12, 130.11, 130.04, 129.51, 128.69, 128.14, 127.40, 127.38, 126.85.

HRMS (ESI–TOF): m/z calculated for $C_{48}H_{30}NaO_{12}$ $[M+Na]^+$: 821.1629, found: 821.1612.

Synthesis of L2 A mixture of compound **10** (0.48 g, 0.60 mmol), hydroxylamine hydrochloride (40 mg, 0.66 mmol), pyridine (6 mL) was heated at 95 °C for 16 h. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and to the residue 10 mL of 1 M HCl aqueous solution was added. The mixture was subjected to a short period of ultrasonication and the resulting precipitate was filtered, washed with water and dried in vacuum to afford **L2** (0.40 g, 83%) as a yellow solid. 1H NMR (600 MHz, DMSO- d_6) δ 13.07 (s, 4H), 10.88 (s, 1H), 8.15 (s, 2H), 8.09 – 8.01 (m, 22H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 167.20, 166.72, 163.44, 143.97, 139.65, 138.27, 137.27, 136.33, 134.48, 130.01, 129.51, 127.37, 125.95, 124.60. HRMS (ESI–TOF): m/z calculated for $C_{48}H_{30}NO_{11}$ $[M+H]^+$: 796.1813, found: 796.1804.

3. Synthesis of MOFs

Synthesis of the TJU-101-NHPI

L1 (10.0 mg) and $Cu(NO_3)_2 \cdot 2.5 H_2O$ (12.0 mg) were dissolved in DMF (2.0 mL) by sonication and charged into a 10 mL Pyrex vial. And then MeOH (0.5 mL) and HBF_4 aqueous solution (40%, 12 μ L) were added sequentially followed by sonication to give a clear solution. The Pyrex vial was capped and heated at 55 °C for 12 h to yield blue-green block crystals (yield 72%).

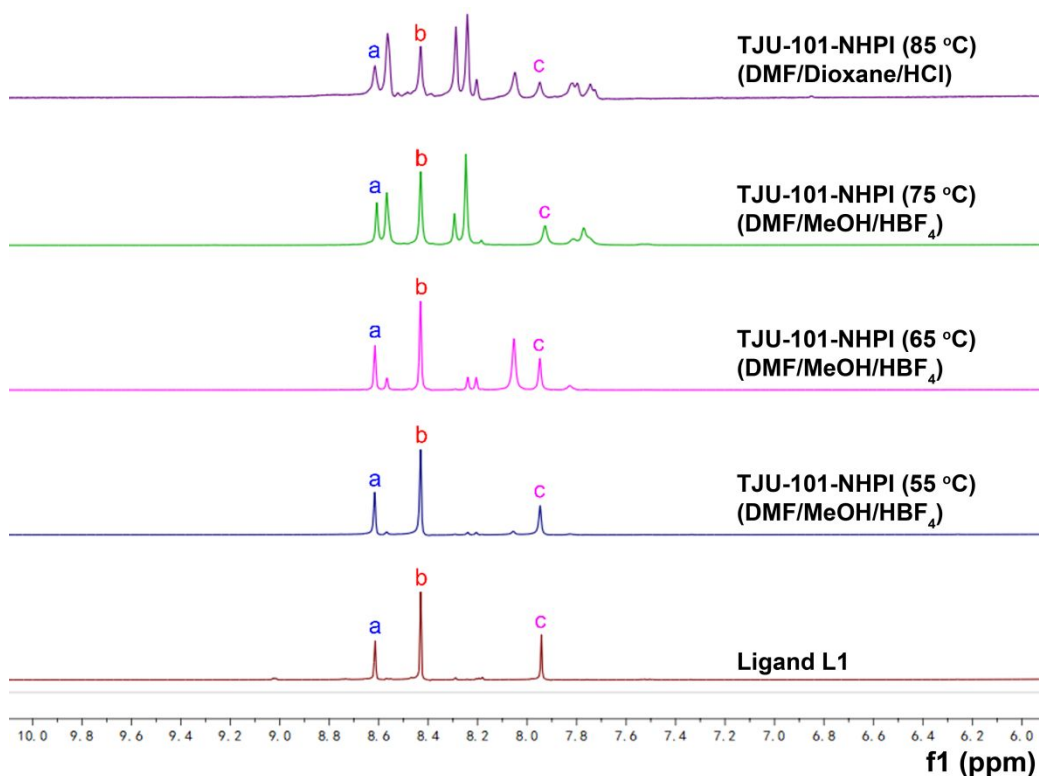


Figure S1. ^1H NMR spectra of ligand **L1** and the digested **TJU-101-NHPI** synthesized under different conditions with DCl in $\text{DMSO}-d_6$.

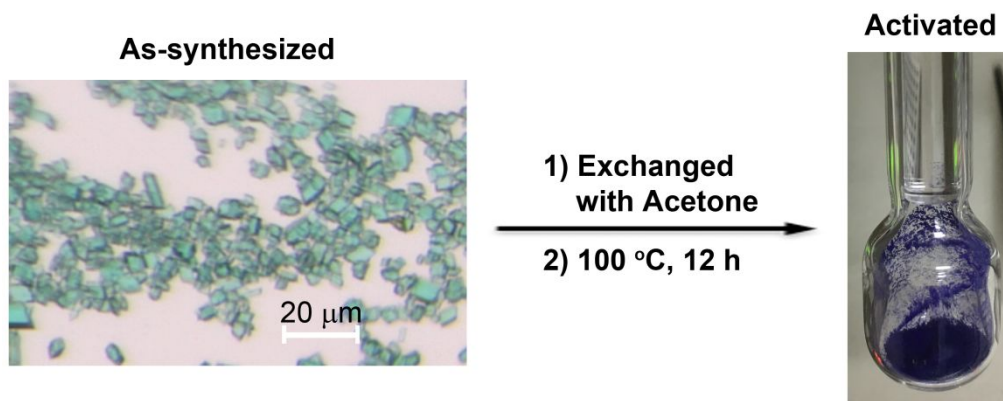


Figure S2. The photos of the as-synthesized and activated **TJU-101-NHPI** crystals.

Note: The as-synthesized **TJU-101-NHPI** crystals show homogeneously small sizes and blue-green color. The activated **TJU-101-NHPI** crystals exhibit distinct purple-blue color, indicating the coordinated H_2O molecules onto the Cu(II) paddle-wheel nodes were

successfully removed.^[4]

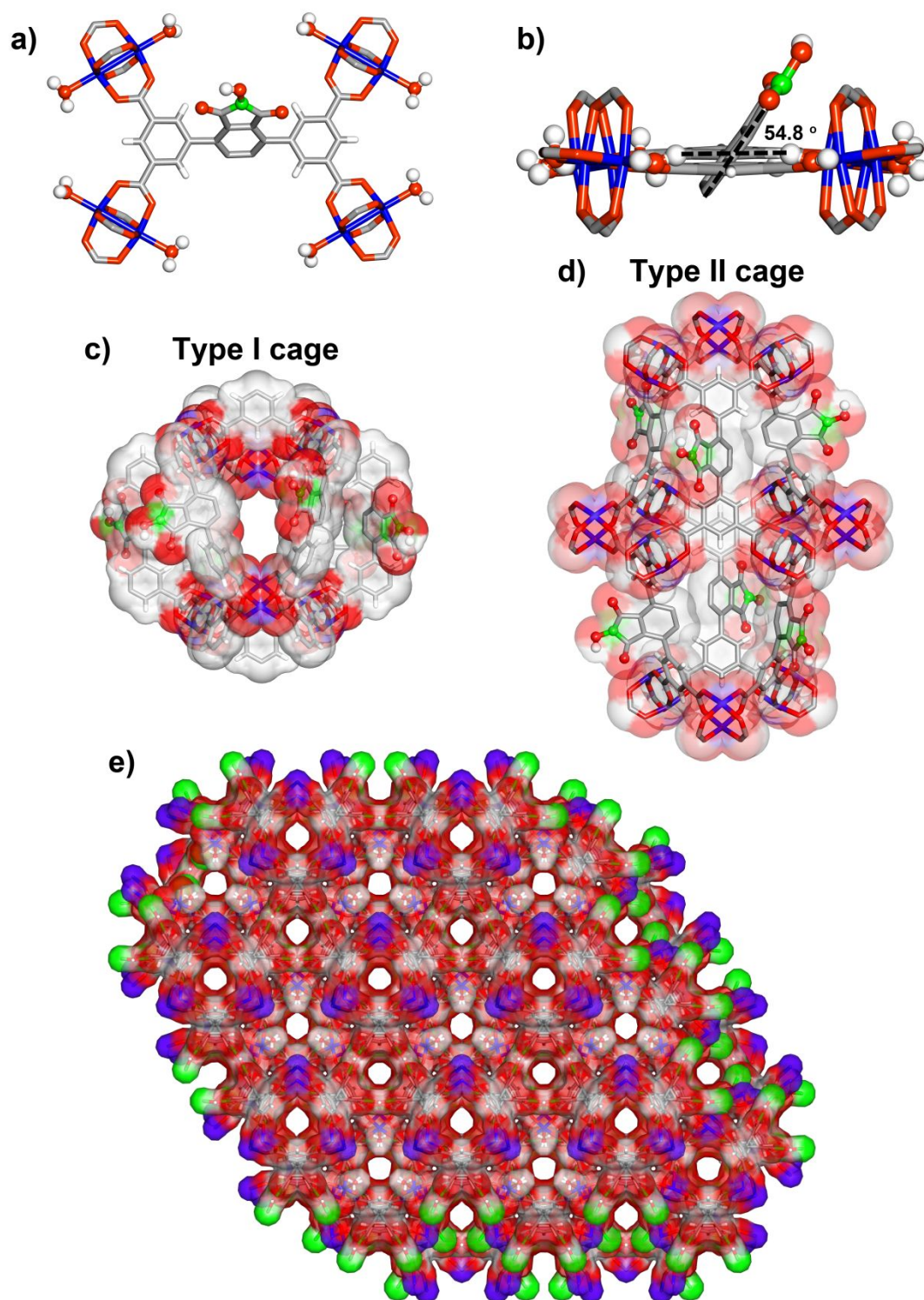


Figure S3. The crystal structure of the **TJU-101-NHPI**. (a) The Cu(II) paddle-wheel nodes coordinated with H₂O molecules. (b) The dihedral angle between the NHPI plane and

adjacent phenyl rings. (c–e) The two types of cages and structural view along the *c*-axis with the Van der Waals surface. Atom colors: C (gray), H (white), O (red), N (green), Cu (blue).

Synthesis of RMOF-NHPI

L2 (4.0 mg) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{ H}_2\text{O}$ (8.6 mg) were dissolved in DMF (2.5 mL) by sonication and charged into a 10 mL Pyrex vial. And then MeCN (0.4 mL) and HBF_4 aqueous solution (40%, 20 μL) were added sequentially followed by sonication to give a clear solution. The Pyrex vial was capped and heated at 55 °C for 4 days to yield blue-green plate crystals (yield 48%).

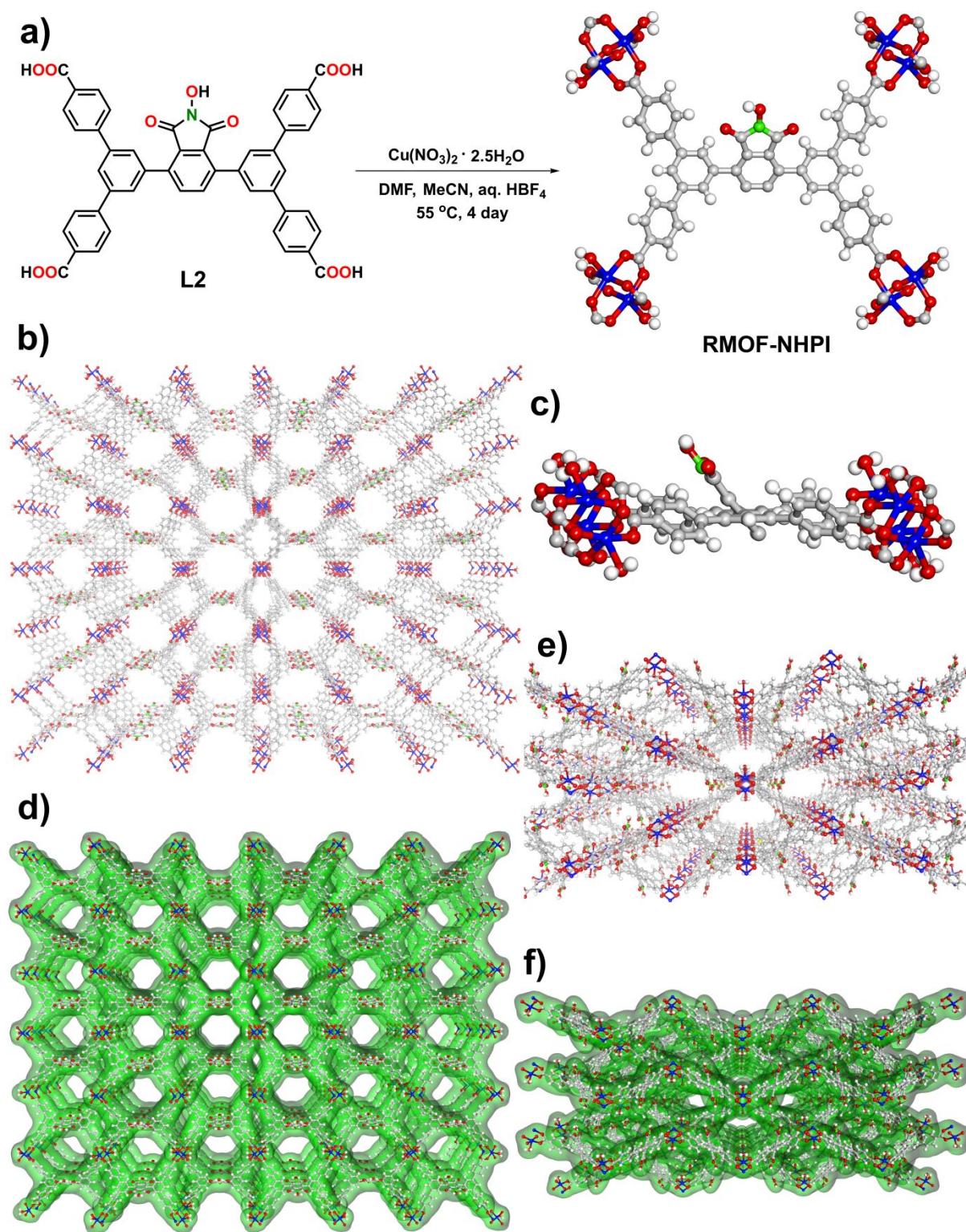


Figure S4. The synthesis and structure of the **RMOF-NHPI**. (a) The synthetic scheme of the **RMOF-NHPI** showing the ligand and the Cu(II) paddle-wheel nodes coordinated with H_2O molecules. (b) The structural view along the c -axis (d) with the Van der Waals surface. (c) (e) (f)

The structural torsion between the NHPI plane and adjacent phenyl rings. (e–f) The structural view along the *b*-axis with the Van der Waals surface. Atom colors: C (gray), H (white), O (red), N (green), Cu (blue).

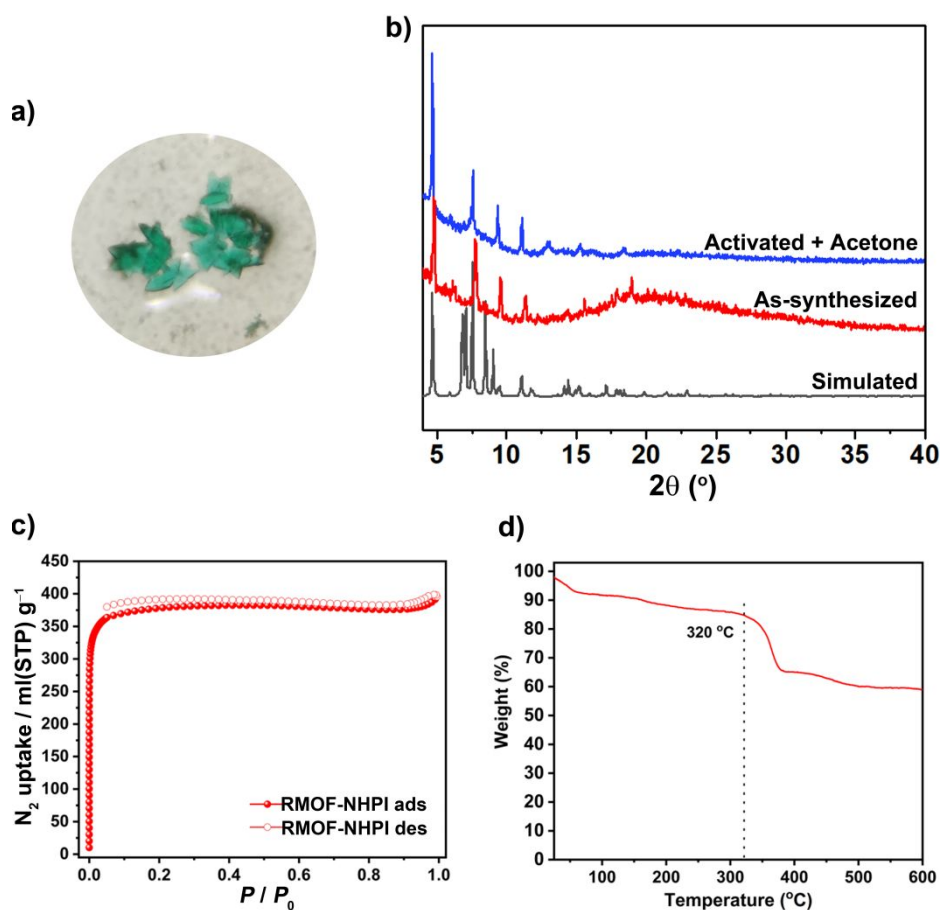


Figure S5. (a) The photo of the **RMOF-NHPI** crystals. (b) The PXRD patterns of the simulated, as-synthesized, and activated **RMOF-NHPI** samples. (c) The sorption isotherm of N_2 (77 K) on the **RMOF-NHPI**. STP and P_0 denote the standard temperature and pressure and the saturated vapor pressure, respectively. (d) The TGA curve of the **RMOF-NHPI** sample.

Table S1 Crystal data and structure refinements for **TJU-101-NHPI** and **RMOF-NHPI**.

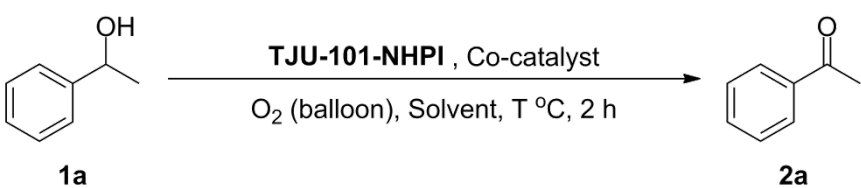
Compound	TJU-101-NHPI	RMOF-NHPI
CCDC No.	2313352	2313257
Empirical formula	C ₂₄ H ₁₃ Cu ₂ NO ₁₃	C ₄₈ H ₂₉ Cu ₂ NO ₁₃
Formula weight	650.43	954.80
Temperature/K	293(2)	293(2)
Crystal system	Trigonal	Orthorhombic
Space group	R-3m	Imma
a/Å	18.448(2)	29.676(3)
b/Å	18.448(2)	37.692(4)
c/Å	39.013(4)	14.0810(14)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	120	90
Volume/Å ³	11498(3)	15750(3)
Z	9	4
$\rho_{\text{calc}} \text{ g/cm}^3$	0.845	0.403
μ/mm^{-1}	0.868	0.289
F(000)	2934	1944
Crystal size/mm ³	0.10 × 0.08 × 0.05	0.15 × 0.12 × 0.05
Radiation/Å	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	2.208 to 25.494	2.570 to 27.238
Index ranges	−19 ≤ h ≤ 0, 0 ≤ k ≤ 22, 0 ≤ l ≤ 47	−24 ≤ h ≤ 24, −31 ≤ k ≤ 31, −11 ≤ l ≤ 11
Reflections collected	2615	50046
Independent reflections	2615	2503
Data/restraints/parameters	2615/187/129	2503/379/166
Goodness-of-fit on F ²	1.081	1.093
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0707, wR ₂ = 0.1357	R ₁ = 0.0446, wR ₂ = 0.1139
Final R indexes [all data]	R ₁ = 0.1227, wR ₂ = 0.1448	R ₁ = 0.0559, wR ₂ = 0.1187
Largest diff. peak/hole/e Å ^{−3}	0.689/−0.619	0.224/−0.279

4. Catalytic reactions

Representative procedure for the catalytic oxidation by TJU-101-NHPI and TBN using **1a** as model substrate.

To a 10 mL glass tube were added **TJU-101-NHPI** (0.005 mmol, 0.05 mol%) and CH₃CN (0.5 mL) in glove box. And then the 1-phenylethanol **1a** (0.1 mmol) and TBN (x mol%) were added to the mixture under air. The glass tube was sealed with rubber stopper and connected to an O₂ balloon through a needle. After gently discharging the air in the glass tube by O₂ bubbling, the glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 600 rpm for 2 h, and the yields were checked by GC–MS and/or ¹H NMR spectroscopy. For the reusability test, the catalyst in the reaction mixture was separated by centrifugation, washed with CH₃CN (3 × 5 mL), and directly used for the next cycle under the same reaction condition.

Table S2 Catalytic oxidation of **1a** by the **TJU-101-NHPI** with different co-catalyst. ^a

 1a TJU-101-NHPI , Co-catalyst 2a O₂ (balloon), Solvent, T °C, 2 h					
Entry	Catalyst (amount)	Co-catalyst (amount)	Solvent	Temp. (°C)	Yield (%) ^b
1	TJU-101-NHPI (5 mol%)	/	MeCN	80	3%
2	TJU-101-NHPI (5 mol%)	Co(OAc) ₂ (30 mol%)	MeCN	80	trace

3	TJU-101-NHPI (5 mol%)	VO(acac) ₂ (30 mol%)	MeCN	80	12%
4	TJU-101-NHPI (5 mol%)	Mn(OAc) ₂ (30 mol%)	MeCN	80	trace
5	TJU-101-NHPI (5 mol%)	Co(NO ₃) ₂ (30 mol%)	MeCN	80	48%
6	TJU-101-NHPI (5 mol%)	AIBN (30 mol%)	MeCN	80	33%
7	TJU-101-NHPI (5 mol%)	Ethanal (30 mol%)	MeCN	80	18%
8	TJU-101-NHPI (5 mol%)	DDQ (30 mol%)	MeCN	80	21%
9	TJU-101-NHPI (5 mol%)	DMG (30 mol%)	MeCN	80	31%
10	TJU-101-NHPI (5 mol%)	TBN (30 mol%)	MeCN	80	100%
11	/	TBN (30 mol%)	MeCN	80	8%
12	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	MeCN	80	78%
13	TJU-101-NHPI (5 mol%)	TBN (15 mol%)	MeCN	80	57%
14	TJU-101-NHPI (3 mol%)	TBN (30 mol%)	MeCN	80	92%
15	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	MeCN	70	82%
16	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	MeCN	60	65%
17	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	DMSO	80	trace
18	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	DMF	80	27%

19	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	CH ₃ OH	80	20%
20	TJU-101-NHPI (5 mol%)	TBN (20 mol%)	THF	80	71%
21	L1 (5 mol%)	TBN (30 mol%)	MeCN	80	41%
22	L1 + Cu(NO ₃) ₂ (5 mol%)	TBN (30 mol%)	MeCN	80	45%
23 ^c	TJU-101-NHPI (5 mol%)	TBN (30 mol%)	MeCN	80	2%

^a Reaction condition: **1a** (0.1 mmol), catalyst, co-catalyst, solvent (0.5 mL), O₂ (balloon).

^b GC–MS yield. (AIBN: azodiisobutyronitrile; DDQ: 2,3-dichloro-5,6-dicyanobenzoquinone; DMG: dimethylglyoxime) ^c Under argon.

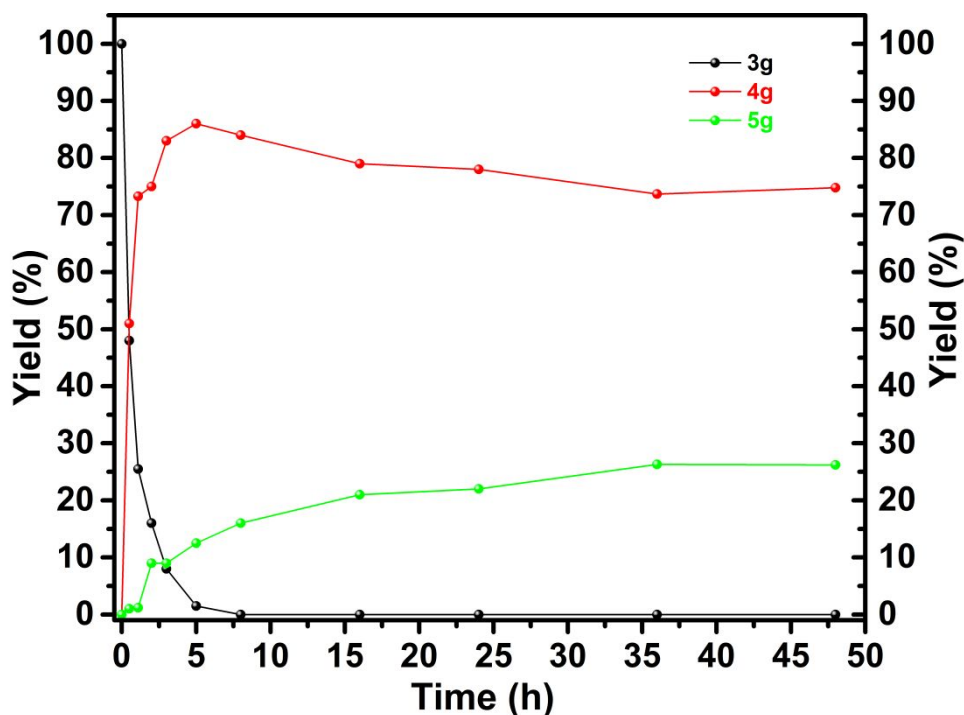


Figure S6. The Time–Yield chart of the catalytic oxidation of **3g** under a sluggish condition (TJU-101-NHPI (10 mol%), TBN (5 mol%), O₂ (balloon), MeCN, 80 °C).

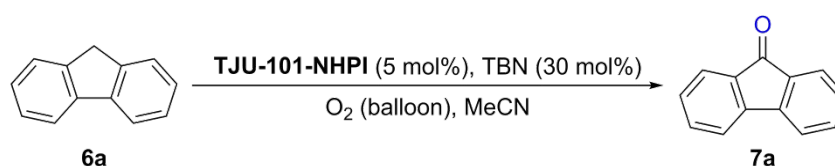
Note: In the first *ca.* 1 h, with the existence of a large amount of alcohol **3g** as inhibitor for the further oxidation of the aldehyde **4g**, trace amount of acid **5g** could be produced, resulting in a specific time dependent selectivity of this reaction.

General procedure for the catalytic oxidation by TJU-101-NHPI and TBN using **6a as model substrate.**

To a 10 mL glass tube were added **TJU-101-NHPI** (0.005 mmol, 5 mol%) and MeCN (0.5 mL) in glove box. And then the fluorene **6a** (0.1 mmol) and TBN (0.03 mmol, 30 mol%) were added to the mixture under air. The glass tube was sealed with rubber stopper and connected to an O₂ balloon through a needle. After gently discharging the air in the glass tube by O₂ bubbling, the glass tube was fixed in a thermoshaker and heated at different

temperature with a shaking speed of 600 rpm for 5 h, and the yields were checked by GC–MS. For the reusability test, the catalyst in the reaction mixture was separated by centrifugation, washed with CH₃CN (3 × 5 mL), and directly used for the next cycle under the same reaction condition.

Table S3 Catalytic oxidation of **6a** by the **TJU-101-NHPI** (5 mol%) and TBN (30 mol%) under different reaction conditions.^a



Entry	Time (h)	Temperature (°C)	Yield (%) ^b
1	4	80	88
2	5	80	100
3	5	60	100
4	5	40	57
5 ^c	5	60	5

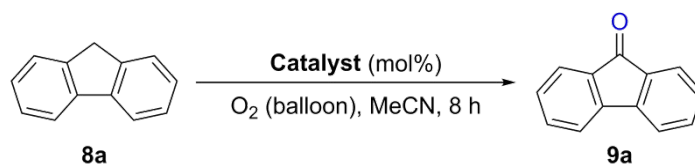
^a Reaction condition: **6a** (0.1 mmol), TJU-101-NHPI (5 mol%), TBN (30 mol%), MeCN (0.5 mL), O₂ (balloon). ^b GC–MS yield. ^c Under argon.

Representative procedure for the catalytic oxidation by TJU-101-NHPI alone using **8a** as model substrate.

To a 10 mL glass tube were added **TJU-101-NHPI** (x mol%) and MeCN (0.5 mL) in glove box. And then the fluorene **8a** (0.1 mmol) was added to the mixture under air. The glass tube was sealed with rubber stopper and connected to an O₂ balloon through a needle. After gently discharging the air in the glass tube by O₂ bubbling, the glass tube was fixed in a

thermoshaker and heated at different temperature with a shaking speed of 600 rpm for 8 h, and the yields were checked by GC–MS. For the reusability test, the catalyst in the reaction mixture was separated by centrifugation, washed with CH₃CN (3 × 5 mL), and directly used for the next cycle under the same reaction condition.

Table S4 Catalytic oxidation of **8a** by the **TJU-101-NHPI** alone or other organic small molecular catalyst under different reaction conditions.^a



Entry	Catalyst (mol%)	Temperature (°C)	Yield (%) ^b
1	TJU-101-NHPI (5)	80	26
2	TJU-101-NHPI (10)	80	78
3	TJU-101-NHPI (15)	80	94
4	TJU-101-NHPI (20)	80	100
5	TJU-101-NHPI (20)	60	100
6	TJU-101-NHPI (20)	40	73
7 ^c	TJU-101-NHPI (20)	60	trace
8	L1 (20)	60	trace
9	NHPI (20)	60	5

^a Reaction condition: **8a** (0.05 mmol), MeCN (0.5 mL), O₂ (balloon). ^b GC–MS yield. ^c Under argon.

Procedure for verification of the heterogeneous characteristics of the catalytic oxidation system.

Taking the catalytic oxidation of 1a as an example: To a 10 mL glass tube were added **TJU-101-NHPI** (0.005 mmol, 5 mol%) and CH₃CN (1.0 mL) in glove box. And then the 1-phenylethanol **1a** (0.1 mmol) and TBN (0.03 mmol, 30 mol%) were added to the mixture under air. The glass tube was sealed with rubber stopper and connected to an O₂ balloon through a needle. After gently discharging the air in the glass tube by O₂ bubbling, the glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 600 rpm for 1 h, and the yields were checked by GC–MS. The hot reaction mixture was filtered to remove the solid catalyst and the filtrate was collected in another glass tube. The glass tube was sealed and connected to an O₂ balloon through a needle. After gently discharging the air in the glass tube by O₂ bubbling, the glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 600 rpm again. The yields were checked by GC–MS in every 0.5 h.

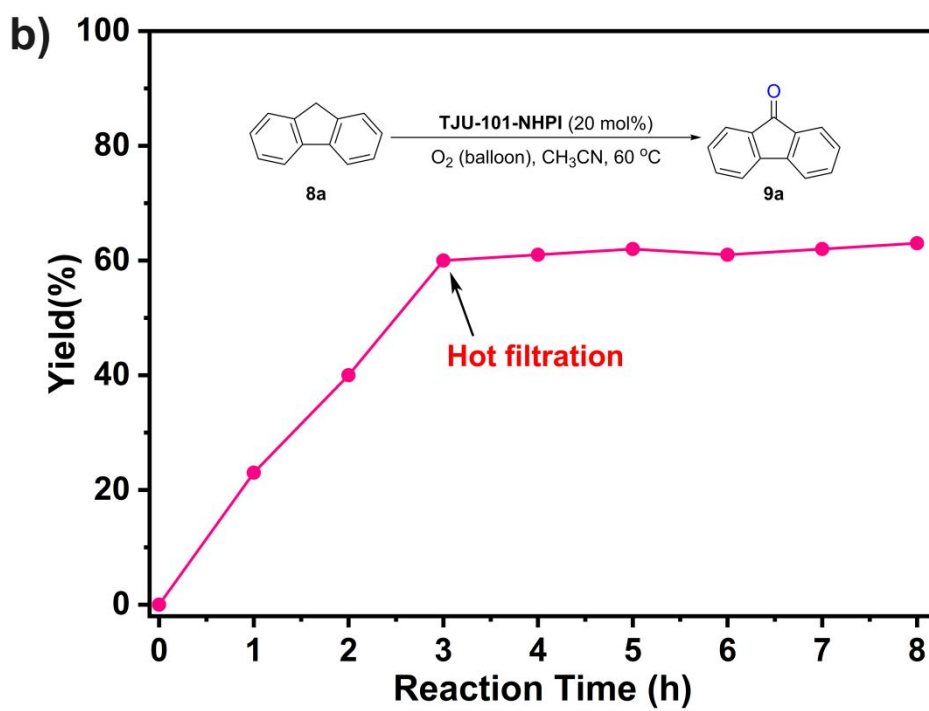
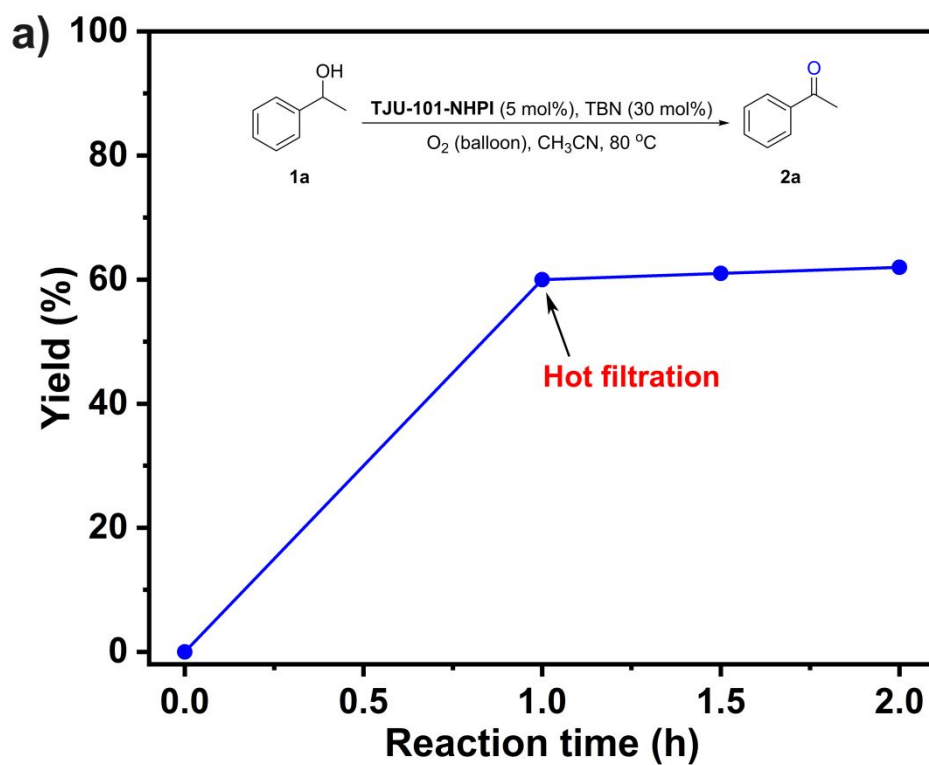


Figure S7. The plots of conversion vs. reaction time for the catalytic oxidation of the **1a** (a) and **8a** (b).

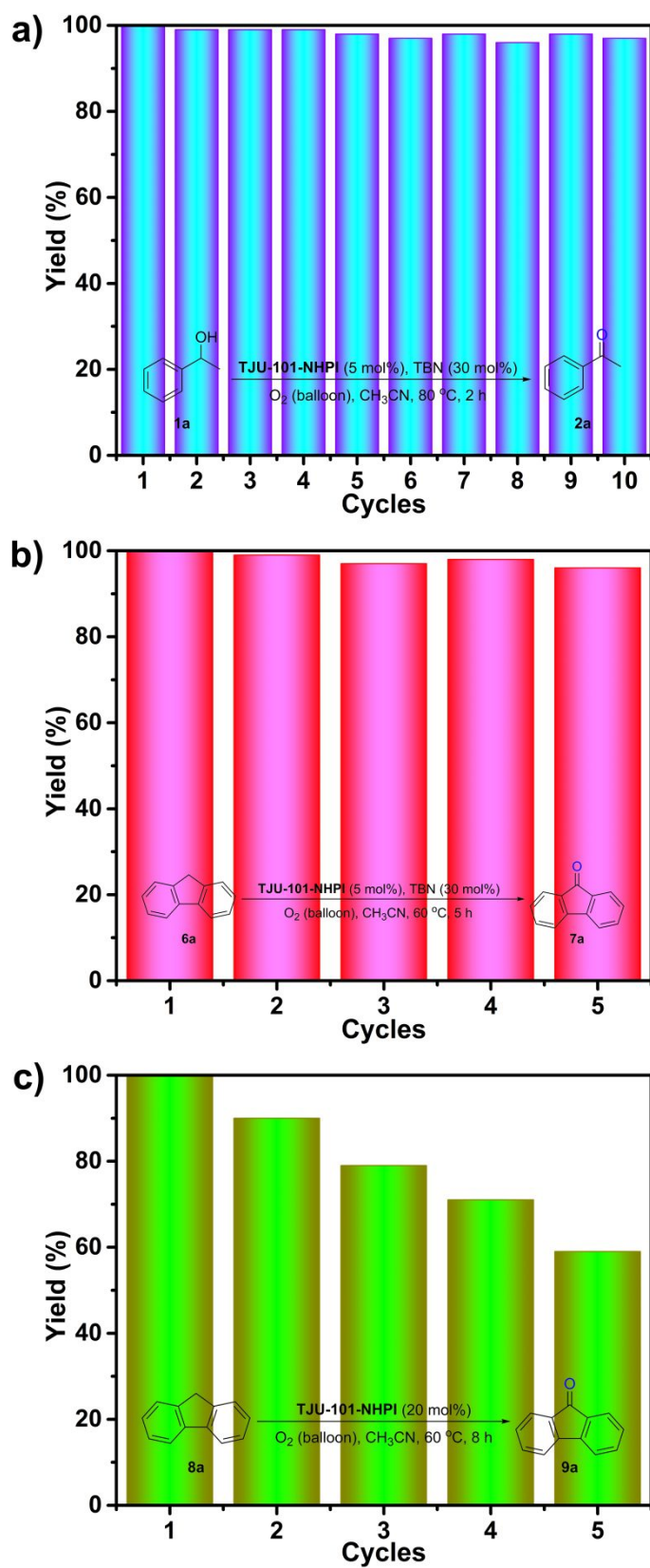
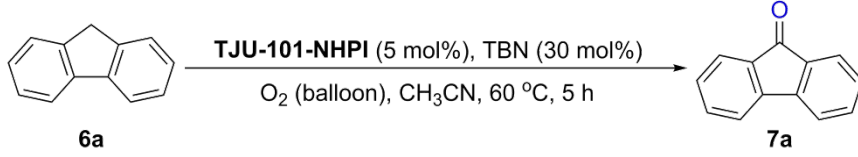
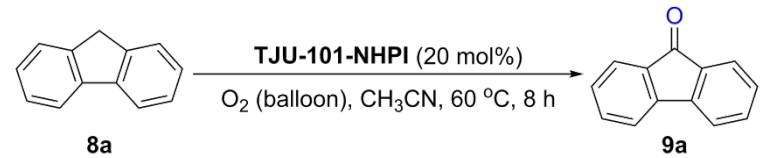


Figure S8. The recycling tests of the heterogeneously catalytic oxidation of **1a** (a), **6a** (b), and **8a** (c) by the TJU-101-NHPI.

Table S5 The weight percentage (wt%) of Cu determined by ICP-OES in the reaction solution after the catalytic reactions.

Entry	Reaction	Cu (wt%)
1	 <chem>c1ccc2c(c1)ccc3ccccc23</chem> 6a $\xrightarrow[\text{O}_2 \text{ (balloon), CH}_3\text{CN, 60 }^\circ\text{C, 5 h}]{\text{TJU-101-NHPI (5 mol\%), TBN (30 mol\%)}}$ <chem>O=C1C=CC2=CC=CC=C2C1C3=CC=CC=C3</chem> 7a	0.057
2	 <chem>c1ccc2c(c1)ccc3ccccc23</chem> 8a $\xrightarrow[\text{O}_2 \text{ (balloon), CH}_3\text{CN, 60 }^\circ\text{C, 8 h}]{\text{TJU-101-NHPI (20 mol\%)}}$ <chem>O=C1C=CC2=CC=CC=C2C1C3=CC=CC=C3</chem> 9a	0.130

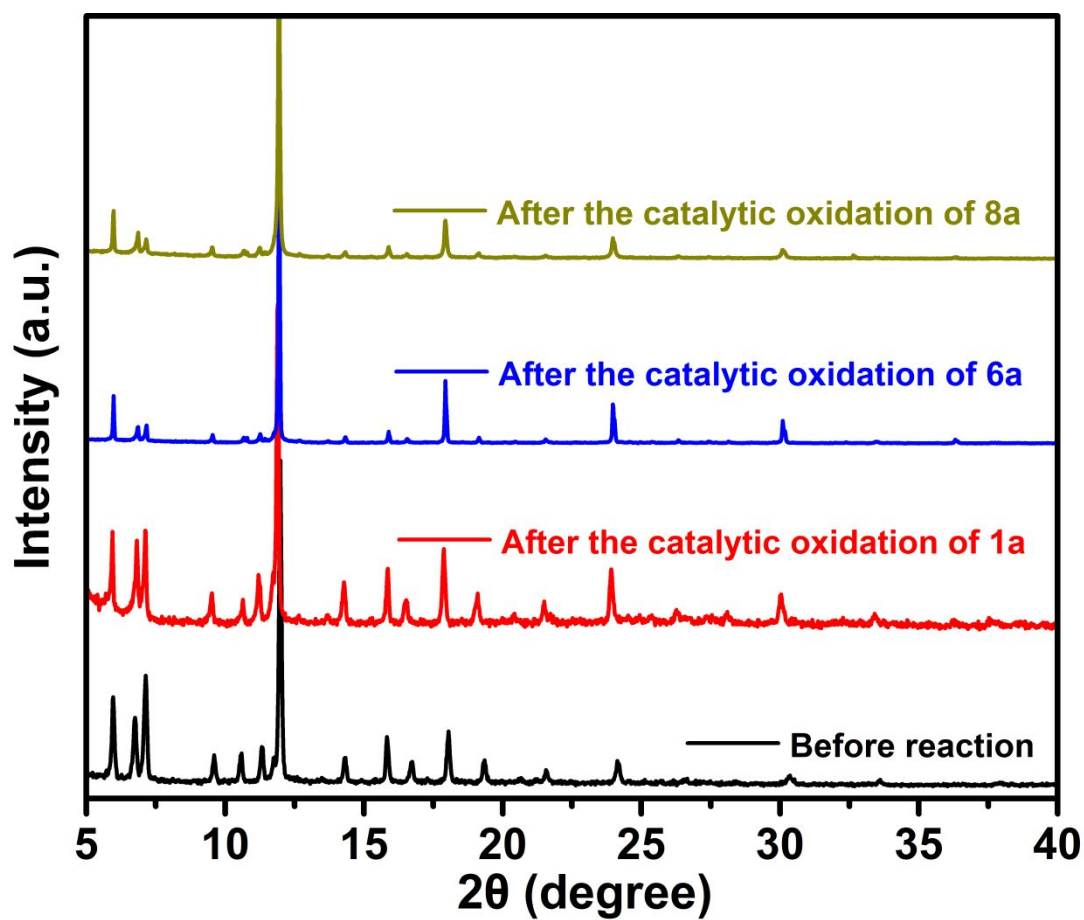


Figure S9. The PXRD patterns of the TJU-101-NHPI catalyst before and after the 5th catalytic oxidation reactions.

5. Mechanistic studies

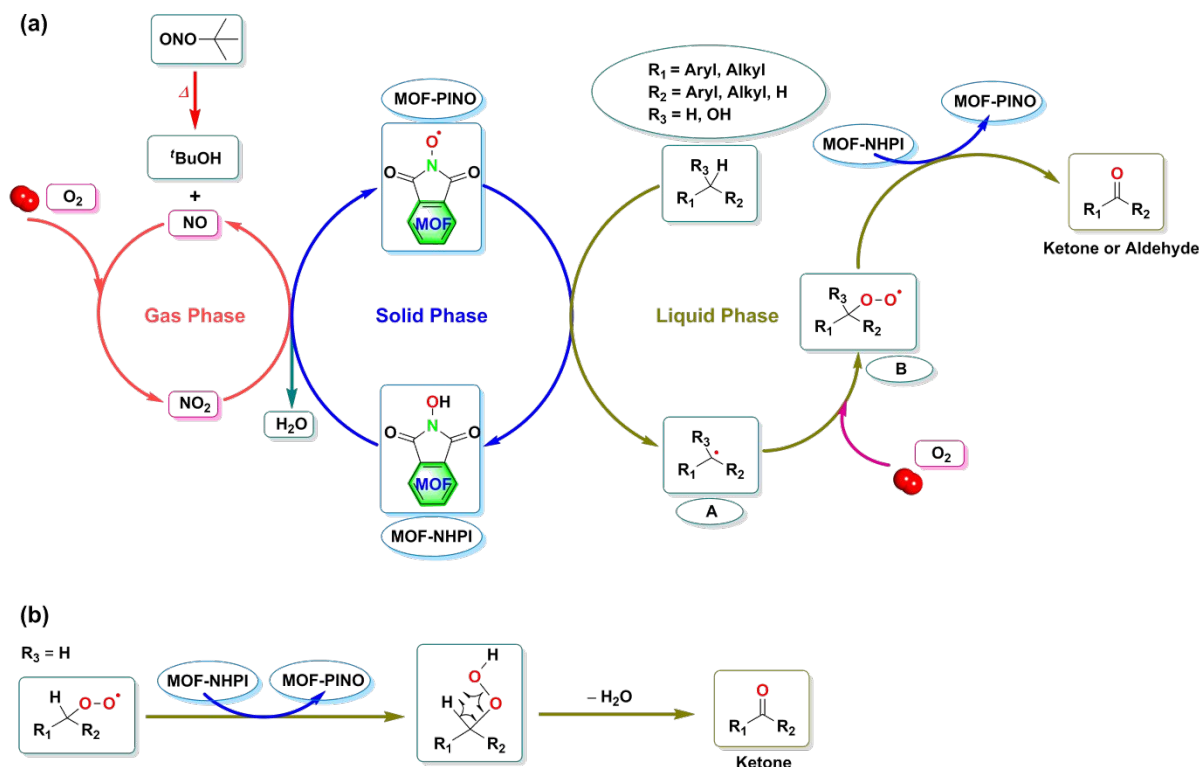
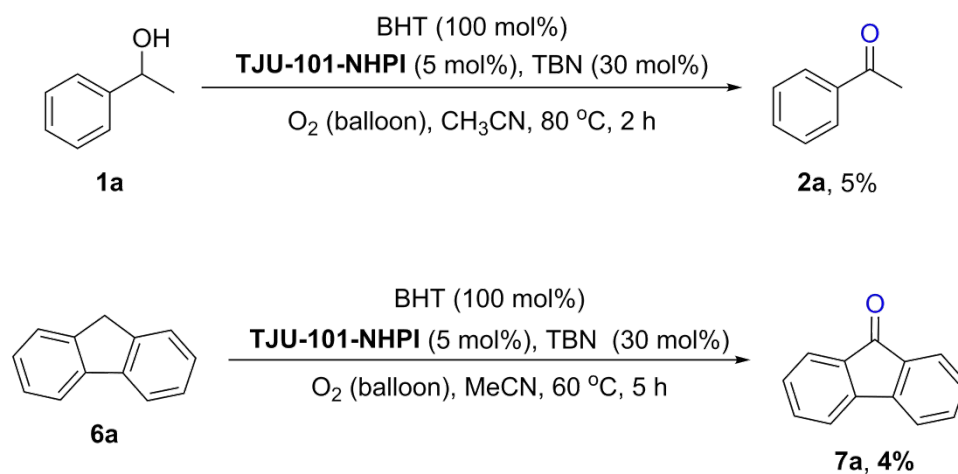


Figure S10. (a) The plausible mechanism of the catalytic oxidation involved in the MOF-101-NHPI/TBN/O₂ system. (b) The plausible mechanism of the catalytic oxidation of the alkylarenes (R₃ = H) directly to the ketones.

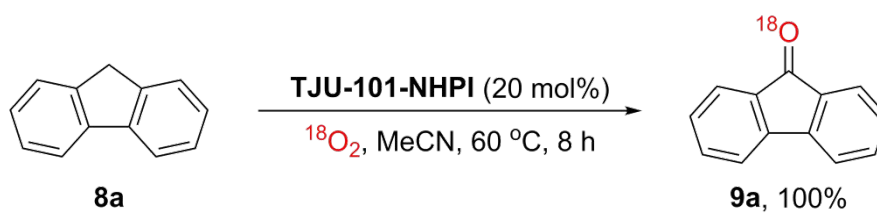
Procedure for radical inhibition experiments

The representative procedure for the catalytic oxidation of 1a: To a 10 mL glass tube were added **TJU-101-NHPI** (0.005 mmol, 0.05 equiv.) and CH₃CN (0.5 mL) in glove box. And then the 1-phenylethanol **1a** (0.1 mmol, 1.0 equiv.), TBN (0.03 mmol, 0.3 equiv.) 2,6-di-*tert*-butyl-4-methylphenol (BHT, 0.1 mmol, 1.0 equiv.) were added to the mixture under air. The glass tube was sealed with rubber stopper and connected to an O₂ balloon

through a long needle. The glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 900 rpm, and the yield was checked by GC–MS.



Scheme S3. Radical inhibition experiments with BHT of the **1a** and **6a** oxidation catalyzed by **TJU-101-NHPI** and co-catalyst TBN.



Scheme S4. The ¹⁸O labeled experiment of catalytic oxidation of **8a**.

Procedure of *in-situ* verifying the PINO radicals in the catalytic system by EPR spectra.

To a 10 mL glass tube were added **TJU-101-NHPI** (13 mg, 0.02 mmol) and CH₃CN (0.5 mL) in glove box. And then, TBN (14 μ L, 0.12 mmol) was added to the mixture under air. The glass tube was sealed with rubber stopper and connected to an O₂ balloon through a long needle. After gently degassing with oxygen gas, the reaction mixture was transferred into an EPR tube and heated at 80 °C for 1 h. Subsequently the EPR spectrum was recorded at ambient temperature.

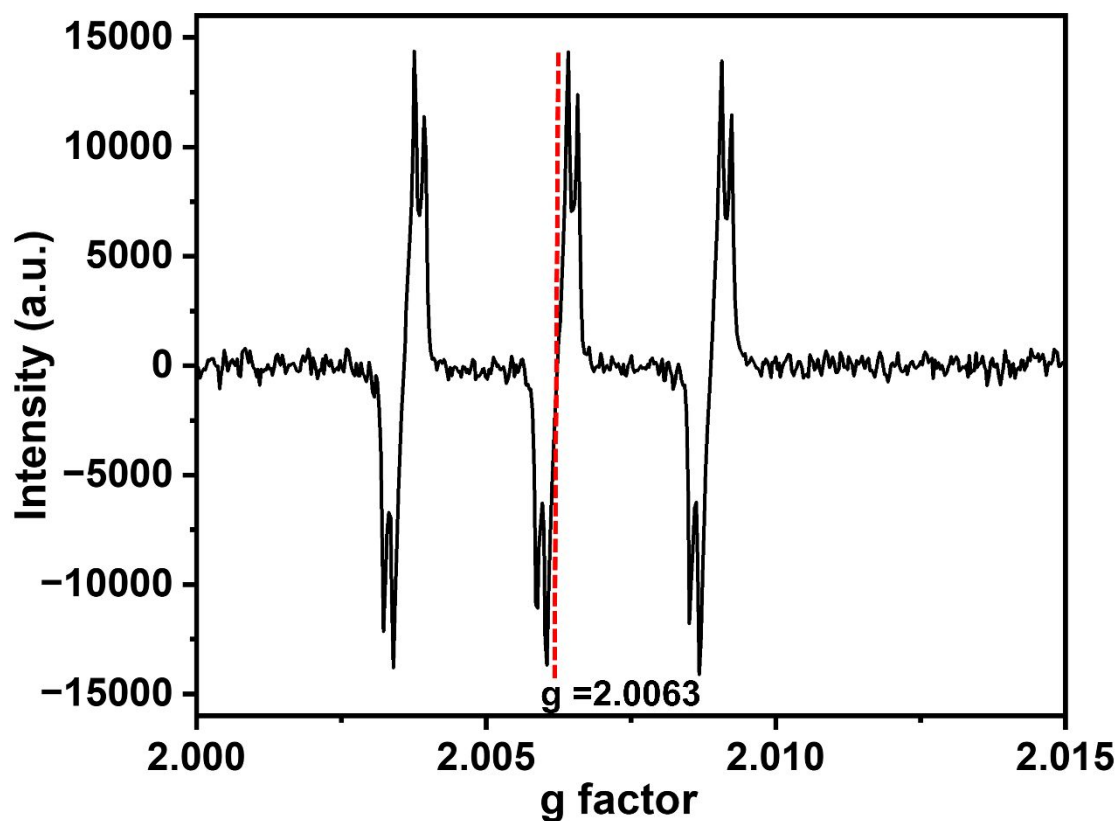


Figure S11. The EPR spectrum of the **TJU-101-NHPI** in the catalysis assisted by the TBN co-catalyst.

Procedure of *in-situ* detection of the reactive oxygen species by EPR spectra.

To a 10 mL glass tube was added **TJU-101-NHPI** (8 mg) and CH₃CN (0.5 mL). And the glass tube was sealed with rubber stopper and connected to an O₂ balloon through a long needle. After gently bubbled with oxygen for 5 min, the reaction mixture was transferred into an EPR tube. The EPR tube was then heated at 80 °C for 1 h and cooled by the ice water bath immediately. After careful addition of the DMPO (30 ul, 100 mM in MeCN), the EPR spectrum was subsequently recorded.

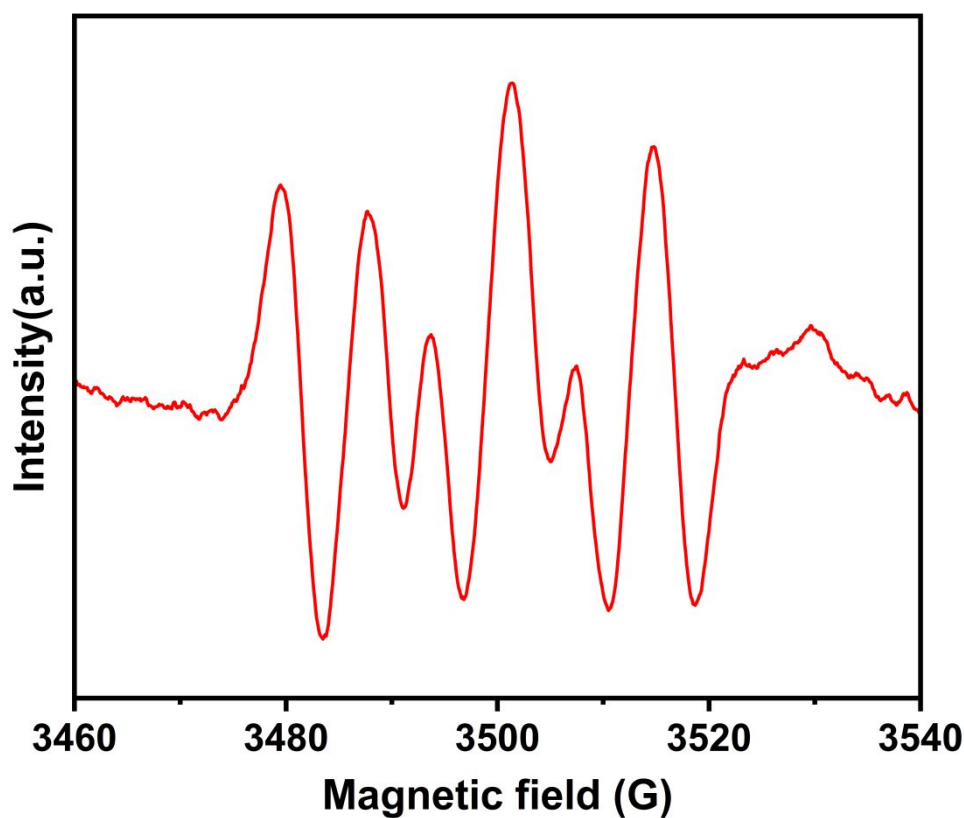


Figure S12. The EPR spectrum of the O₂ activation by **TJU-101-NHPI** alone trapped by DMPO.

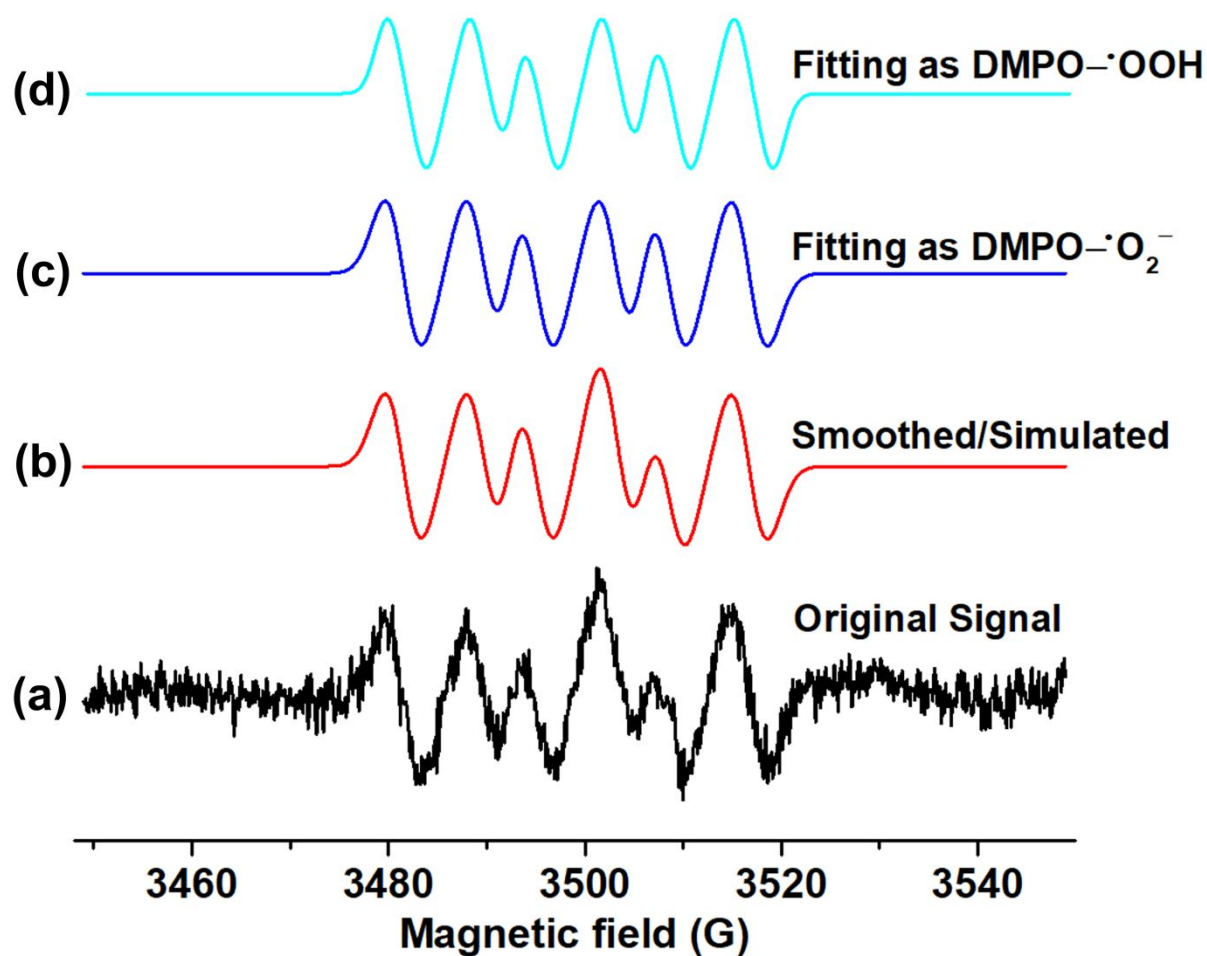


Figure S13. The EPR spectrum analyses of the O_2 activation by TJU-101-NHPI alone trapped by DMPO. (a) The original signal of the EPR spectrum. (b) The smoothed and simulated spectrum based on the original signal. (c) The EPR spectrum fitted as $\text{DMPO}-\bullet\text{O}_2^-$ adduct ($g = 2.0056$, $A_{\text{N}} = 13.4859$, $A_{\text{H}\beta} = 8.42464$). (d) The EPR spectrum fitted as $\text{DMPO}-\bullet\text{O}_2\text{H}$ adduct ($g = 2.00569$, $A_{\text{N}} = 13.4544$, $A_{\text{H}\beta} = 8.37288$, $A_{\text{H}\gamma} = 1.95816$).

6. Computational studies

All the computational studies were conducted on the popular quantum chemistry software Gaussian 16 package, Revision A.03.^[5] The geometrical structures of intermediate (IN) species in gas-phase were fully optimized by using the B3LYP functional.^[6-8] The 6-31+G(d) basis set was used for C, H, and O, and LanL2DZ (Lanl-2-double-zeta) was used for Cu. Squeezed self-consistent field (SCF) convergence standard was adopted in all the calculations. The single point energy calculation was based on def2TZVP basis set to ensure accuracy and the corresponding thermal correction calculation was based on the 6-31+G(d) basis set. The model structures used for calculation were constructed based on the single crystal structures and considered the key moieties. In optimization processes, Cu-metal clusters frozen to constrain the structures of supported Cu sites on the MOFs or unfrozen were considered respectively.

The different adsorption configurations and adsorption energy (kcal/mol) of O₂ over **TJU-101-NHPI** were carried out using Materials Studio 2019. Spin-polarized density functional theory (DFT) calculations were carried out by using a Cambridge Sequential Total Energy Package (CasteP)^[9] based on the generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) functional.^[10] The many-body dispersion^[11] (MBD@rsSCS) van der Waals method was adopted to improve the description of van der Waals interactions in all calculations.

The computational studies on the TJU-101-NHPI

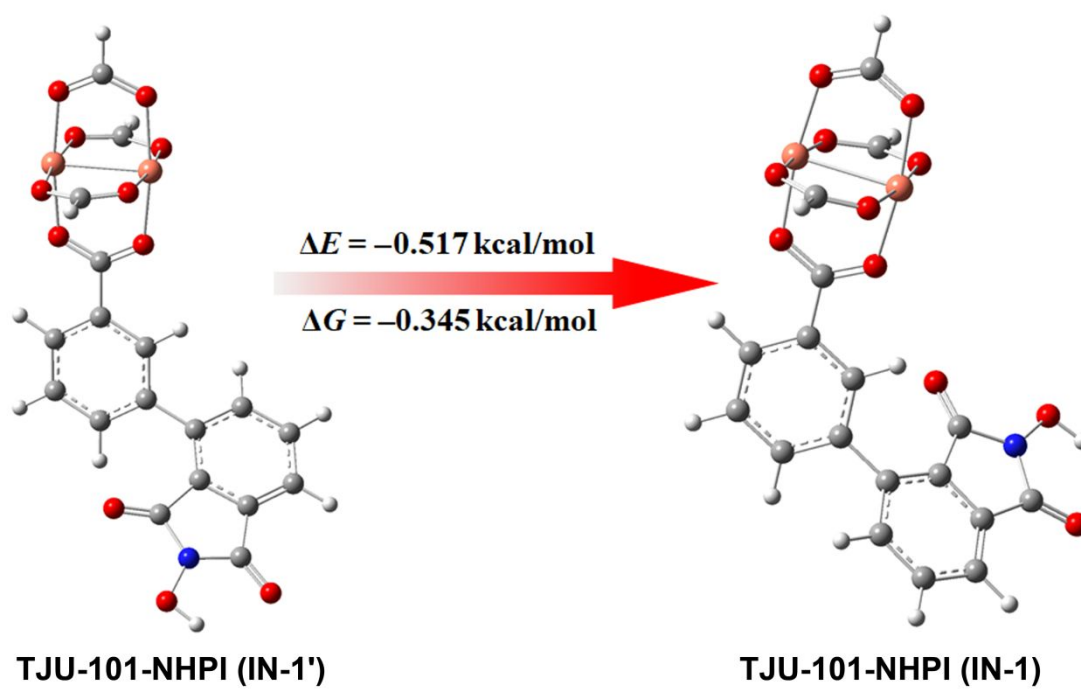


Figure S14. The two configurations **IN-1'** and **IN-1** of the **TJU-101-NHPI** structural models optimized by DFT calculations.

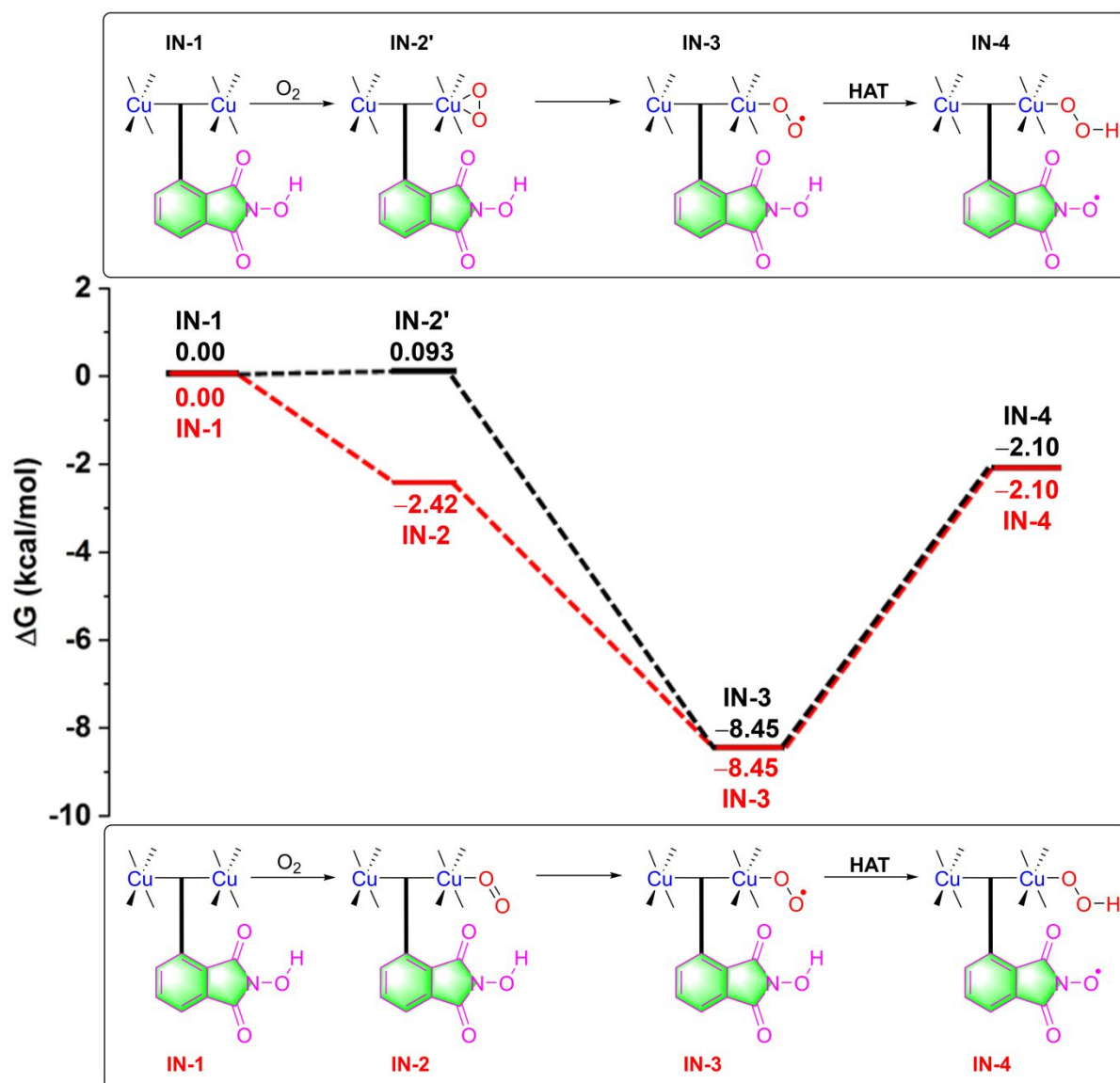


Figure S15. Energy profiles of different O_2 activation processes on the TJU-101-NHPI.

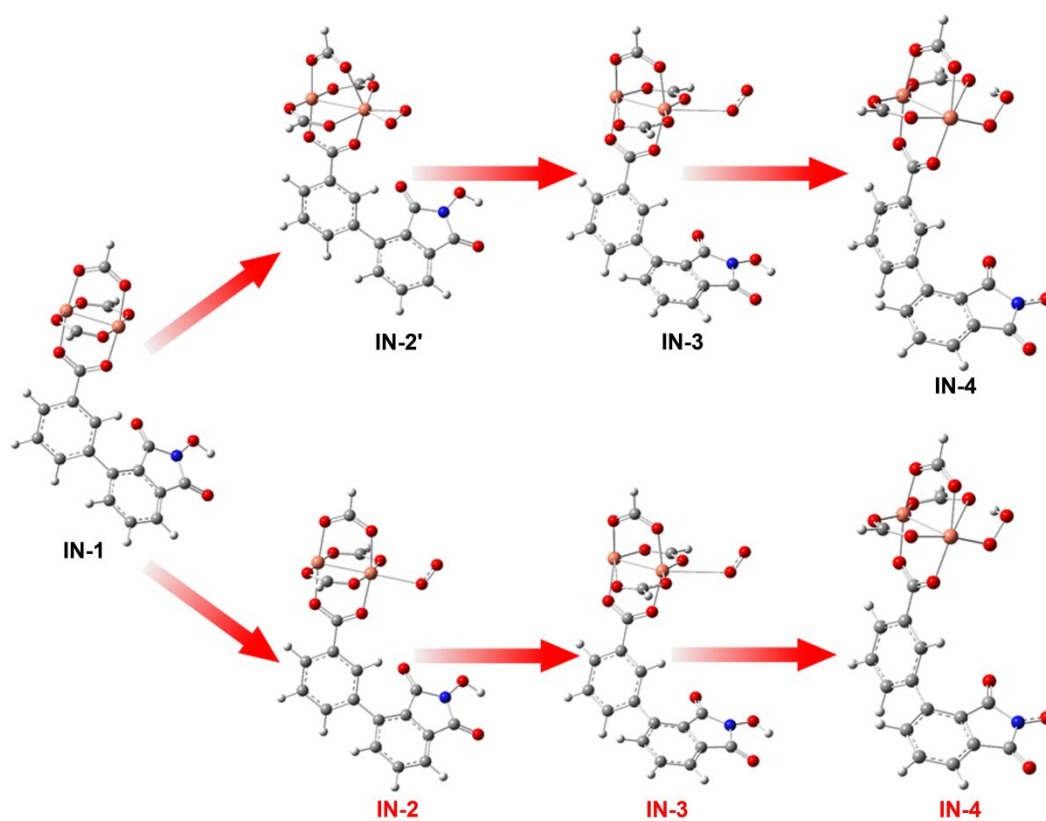


Figure S16. The configurations of the key intermediate structural models of the different O_2 activation processes on the TJU-101-NHPI.

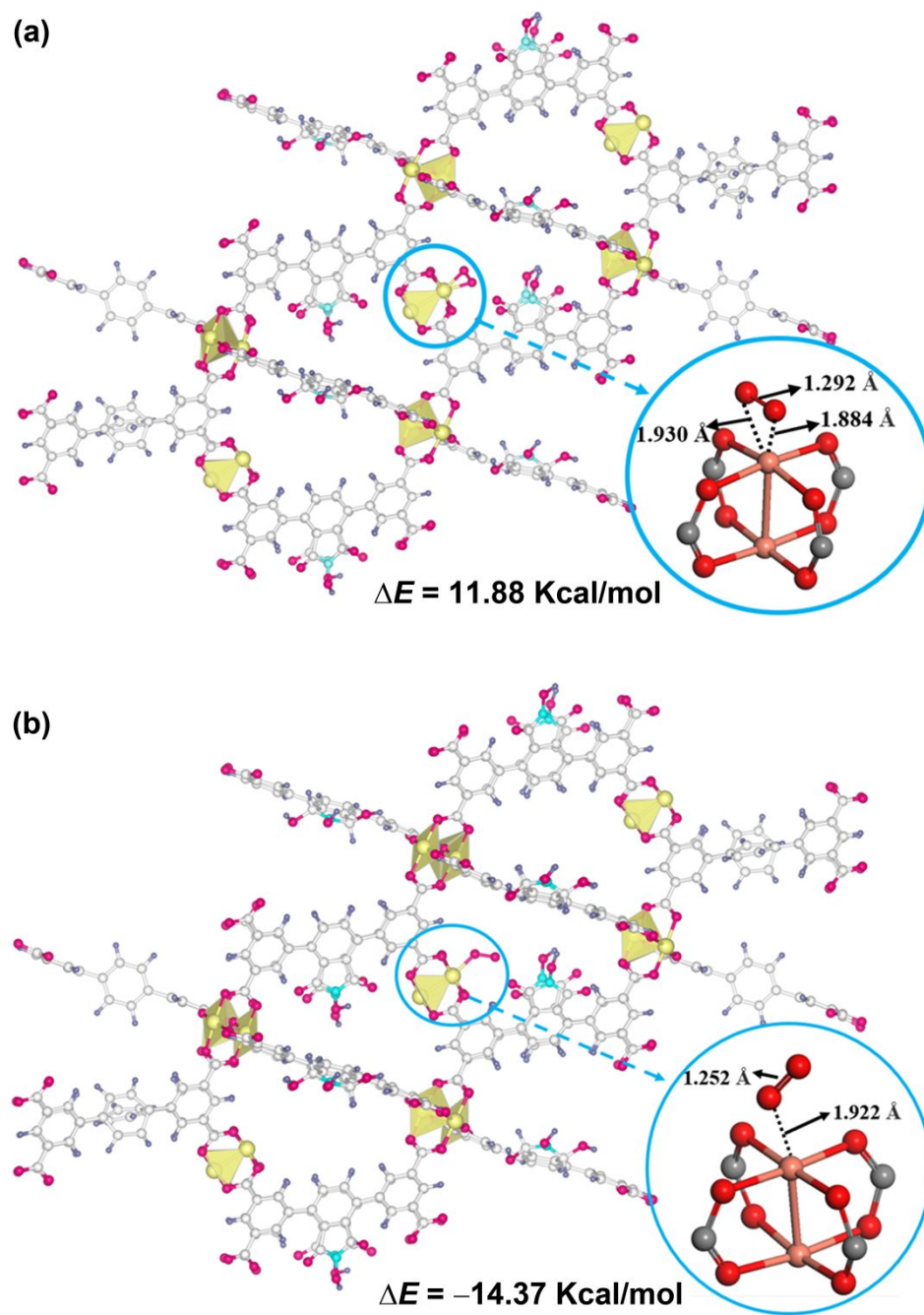


Figure S17. The (a) side-on and (b) end-on adsorption configurations with the calculated adsorption energies of the O₂ on TJU-101-NHPI.

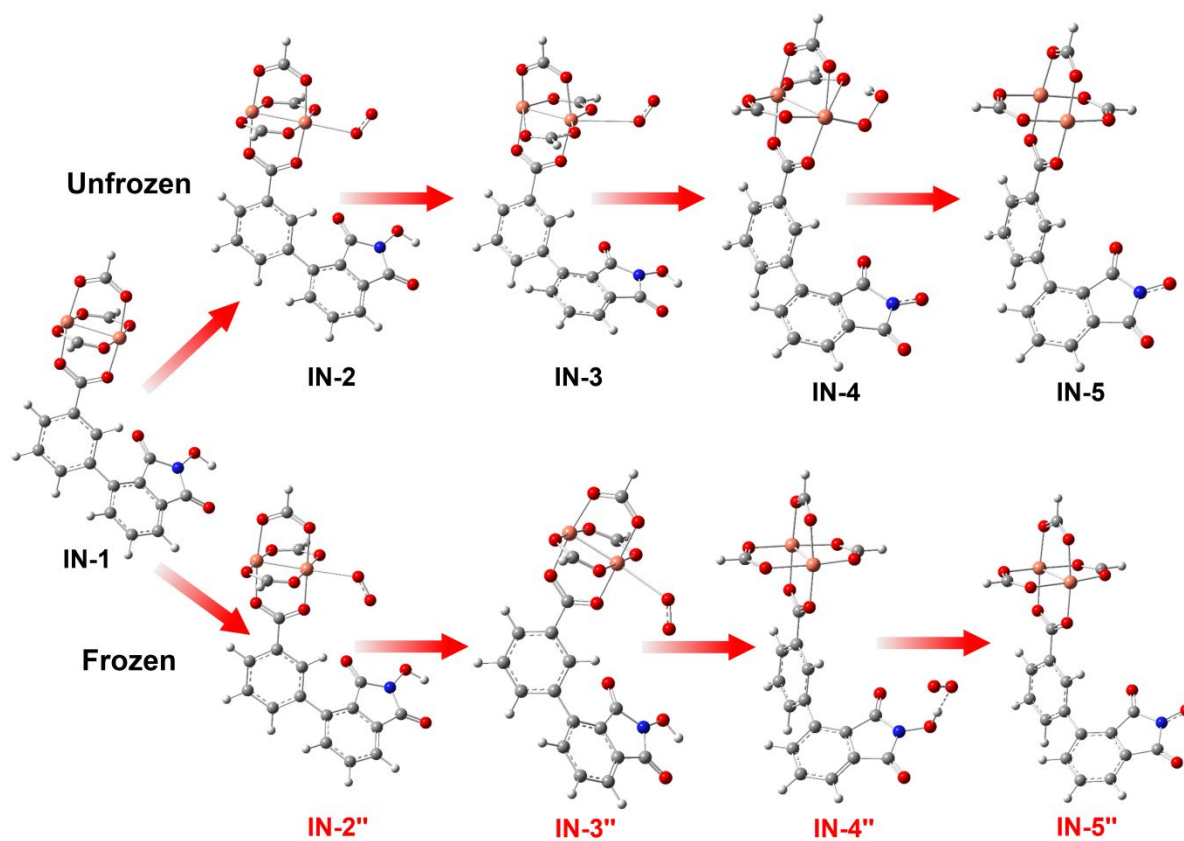


Figure S18. The configurations of the key intermediate structural models (unfrozen and frozen) of the O₂ activation processes on the **TJU-101-NHPI**.

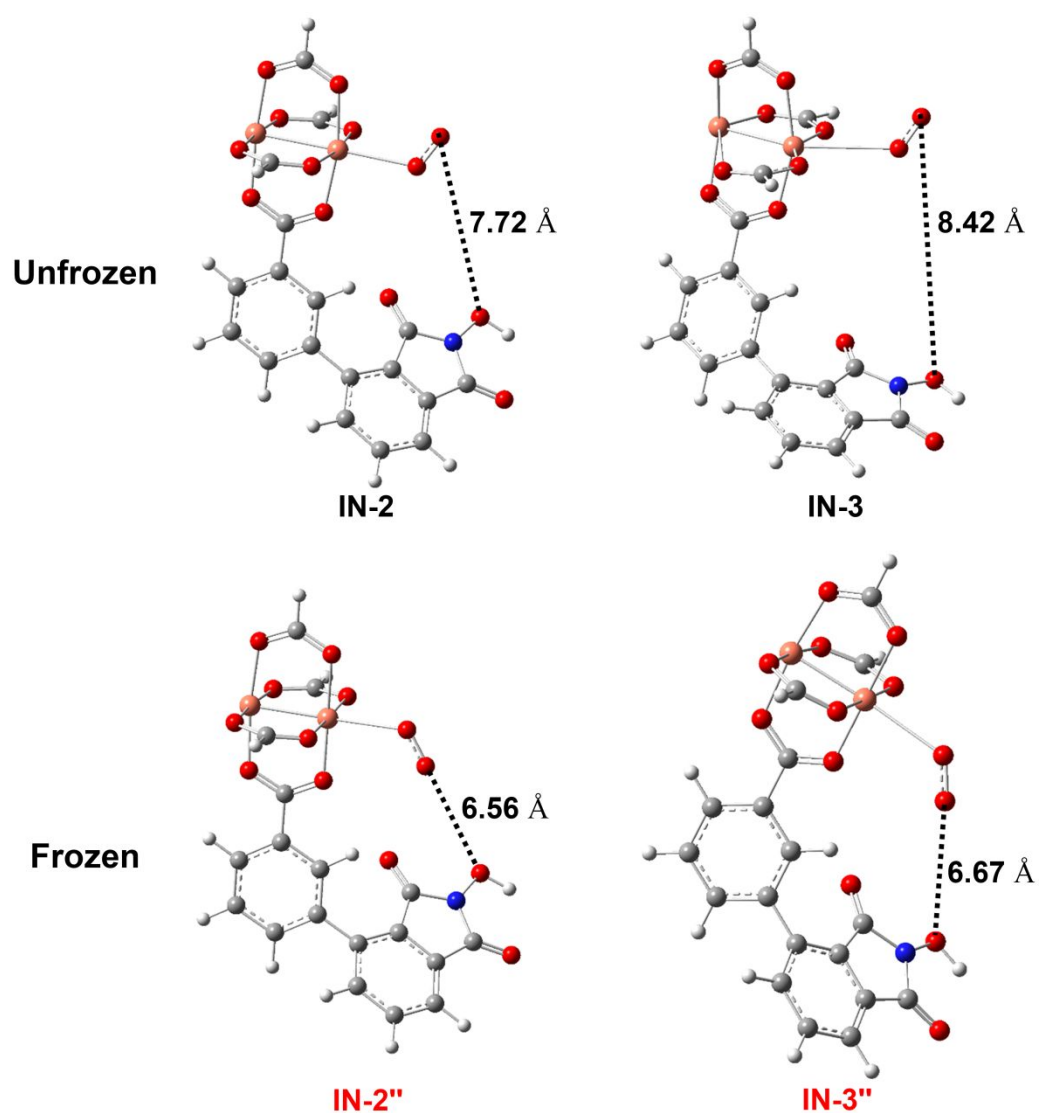


Figure S19. The O₂...HO and O₂•...HO distances of the key intermediate structural models (unfrozen and frozen) of the O₂ activation processes on the **TJU-101-NHPI**.

The computational studies on the RMOF-NHPI

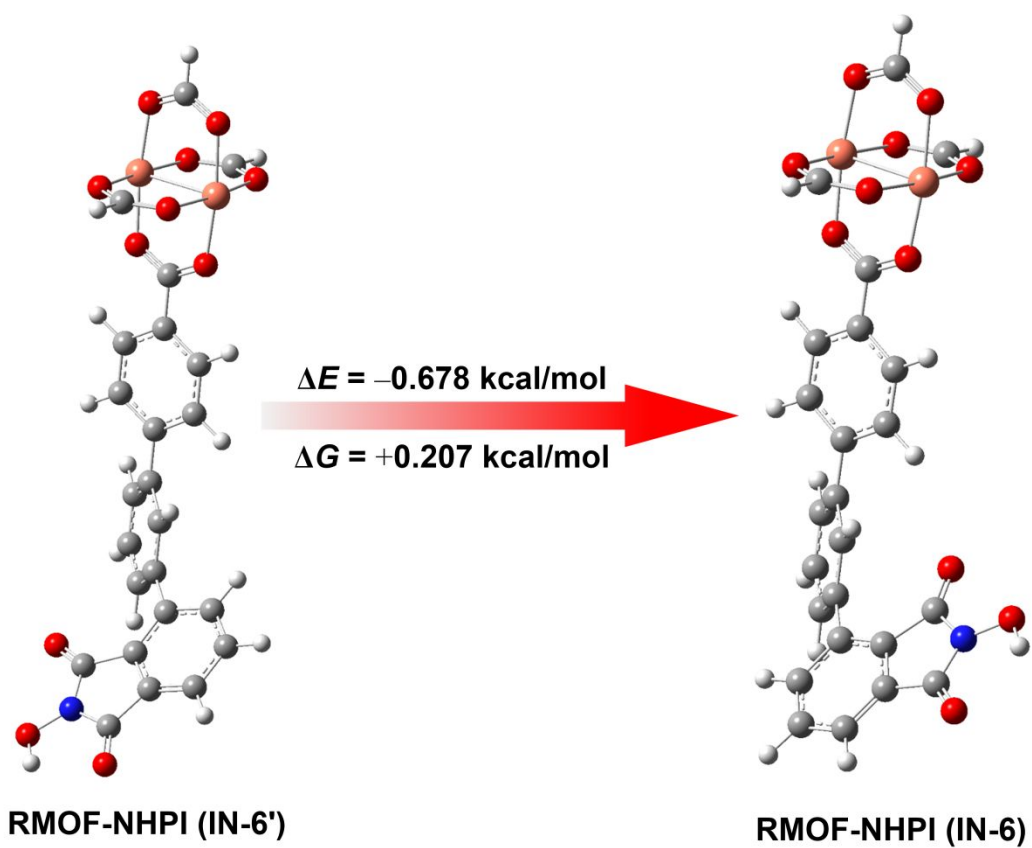


Figure S20. The two configurations **IN-6'** and **IN-6** of the **RMOF-NHPI** structural models optimized by DFT calculations.

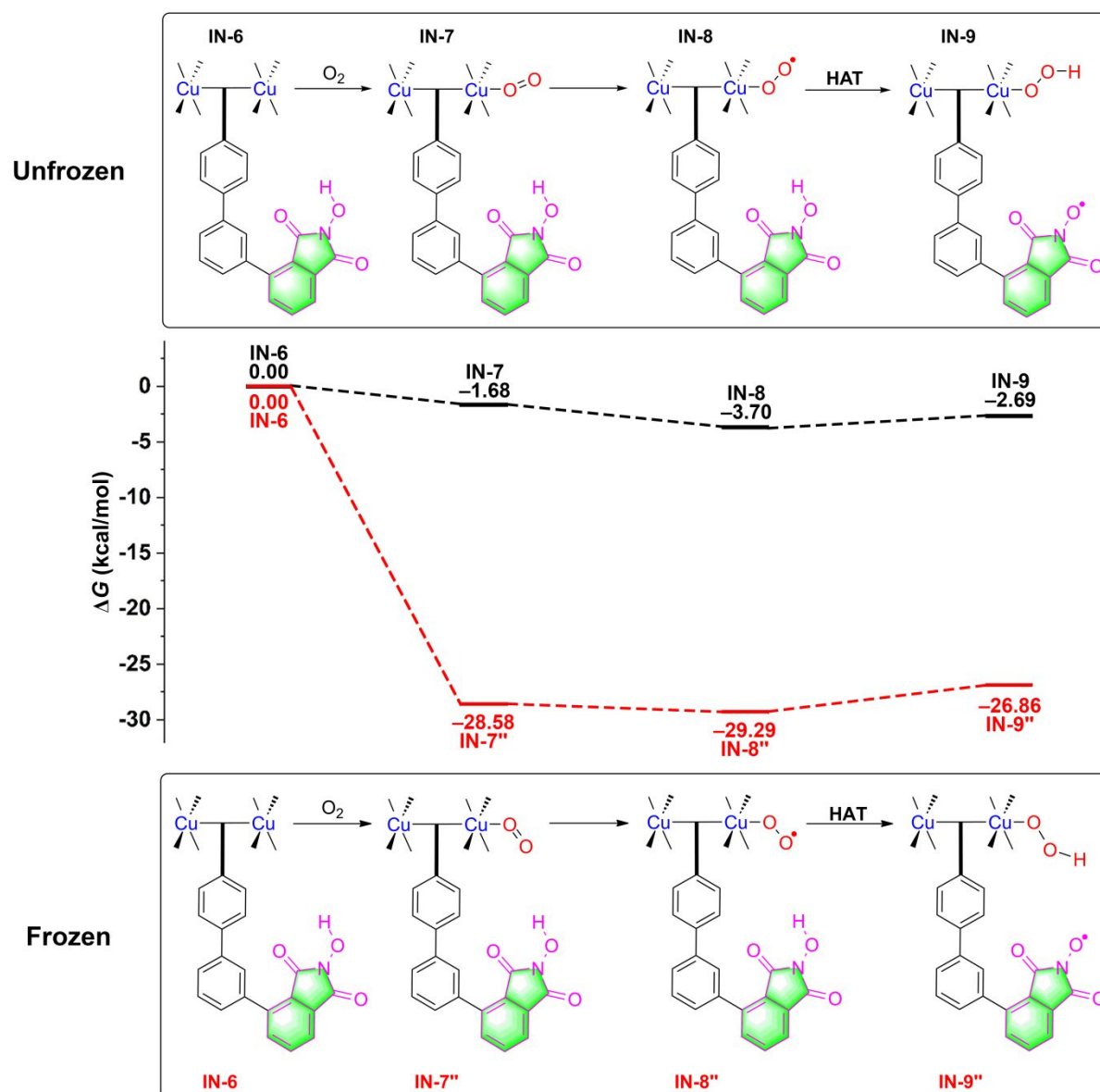


Figure S21. Energy profiles of the O₂ activation processes (unfrozen and frozen) on the RMOF-NHPI.

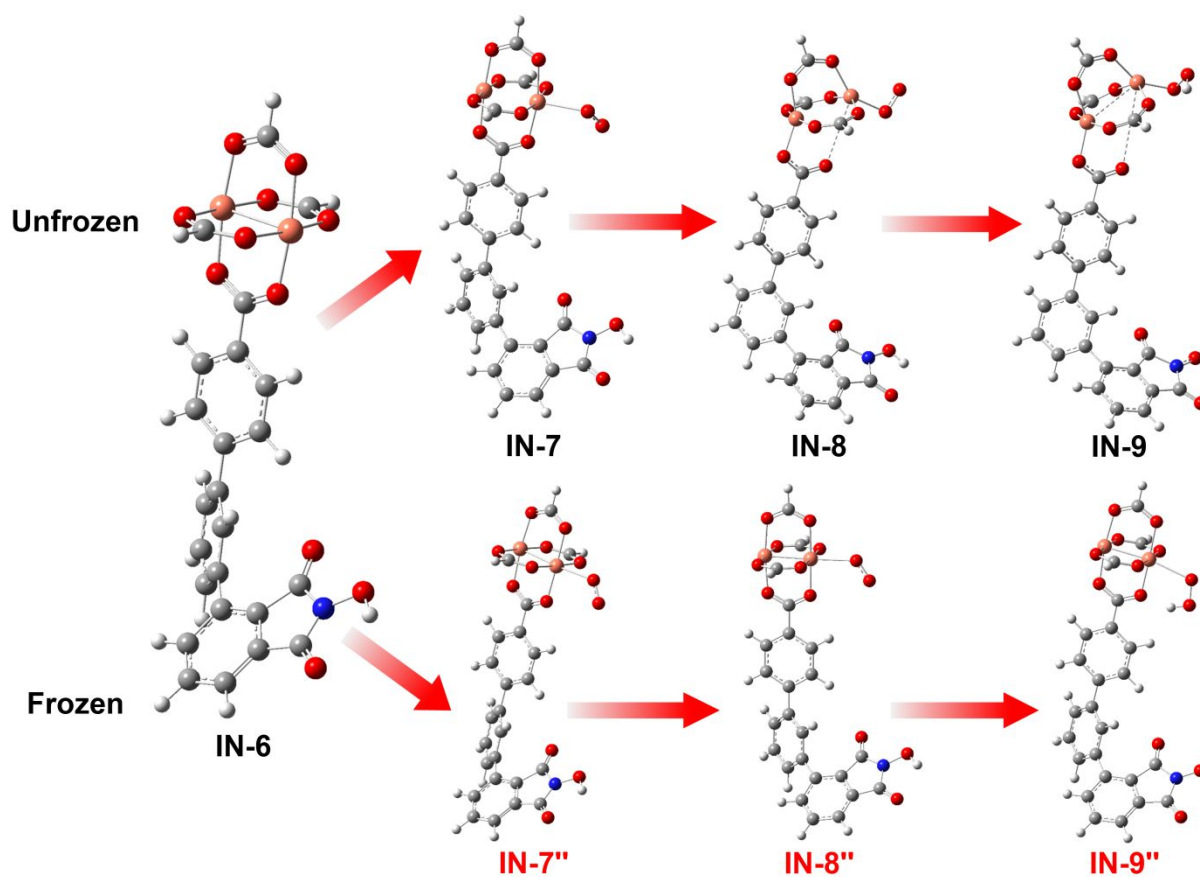


Figure S22. The configurations of the key intermediate structural models (unfrozen and frozen) of the O_2 activation processes on the **RMOF-NHPI**.

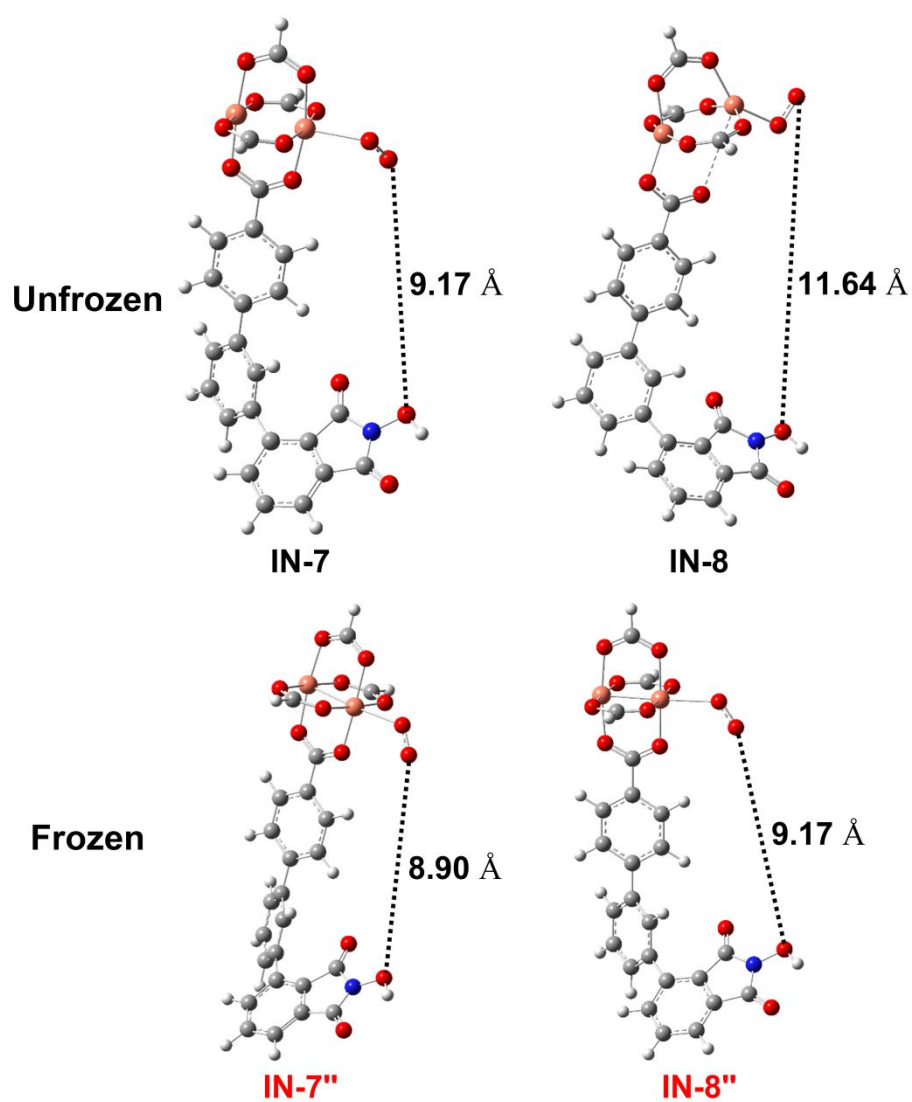


Figure S23. The $\text{O}_2 \cdots \text{HO}$ and $\text{O}_2^\bullet \cdots \text{HO}$ distances of the key intermediate structural models (unfrozen and frozen) of the O_2 activation processes on the **RMOF-NHPI**.

7. Supplementary figures of the selected NMR spectra

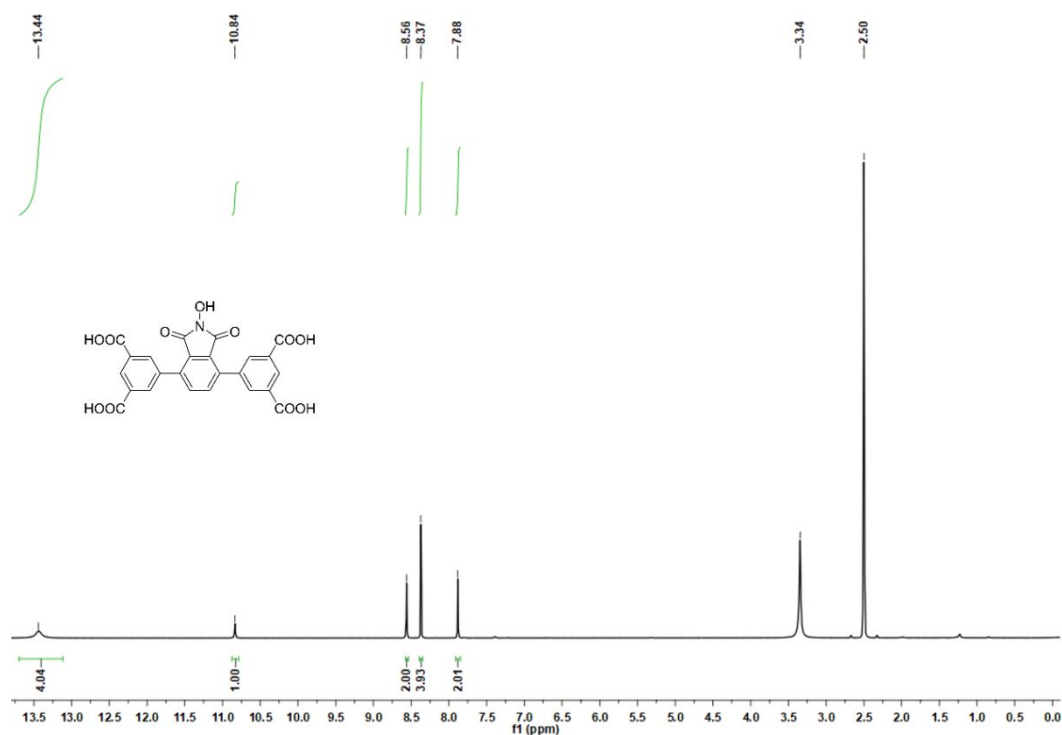


Figure S24. ^1H NMR spectrum of the ligand **L1** in $\text{DMSO}-d_6$.

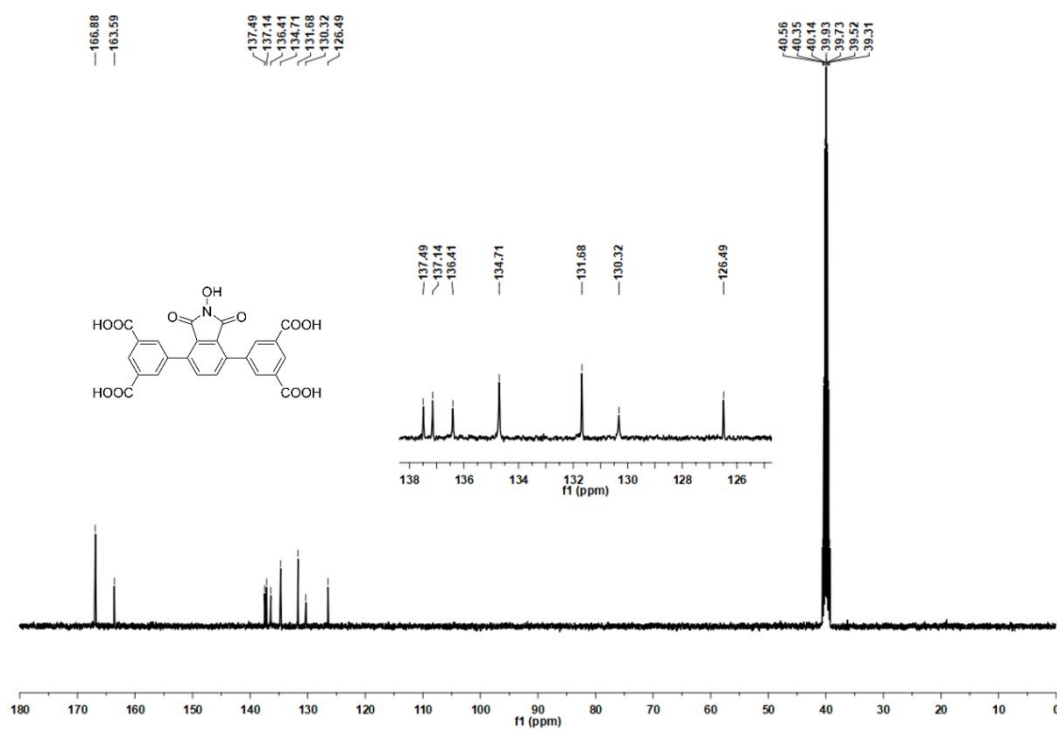


Figure S25. ^{13}C NMR spectrum of the ligand **L1** in $\text{DMSO}-d_6$.

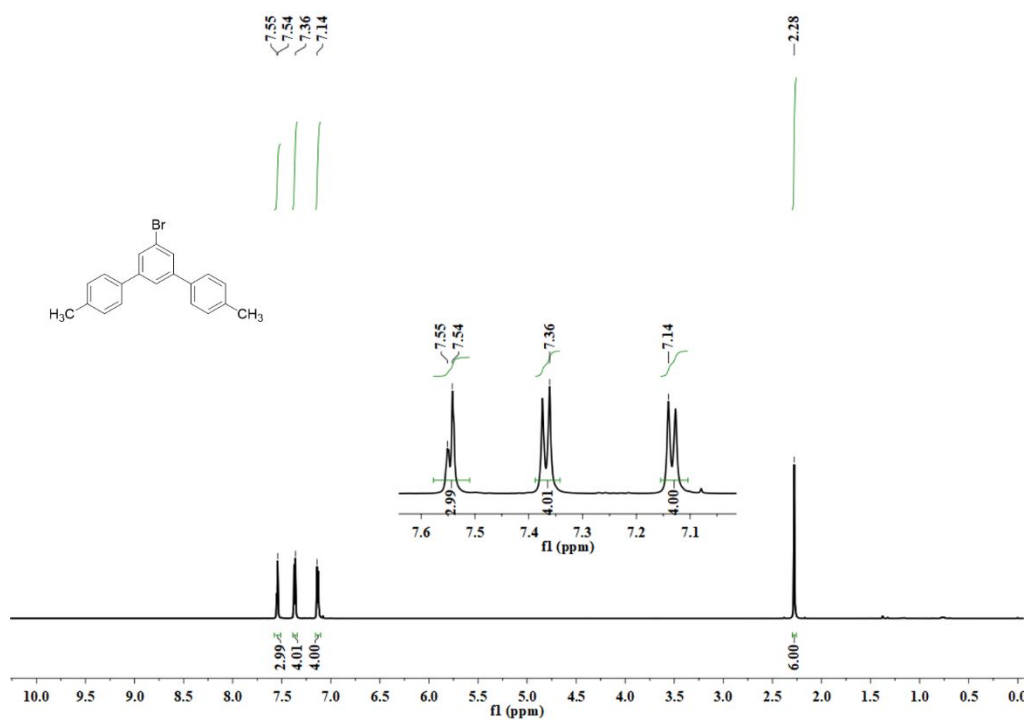


Figure S26. ^1H NMR spectrum of compound **15** in CDCl₃.

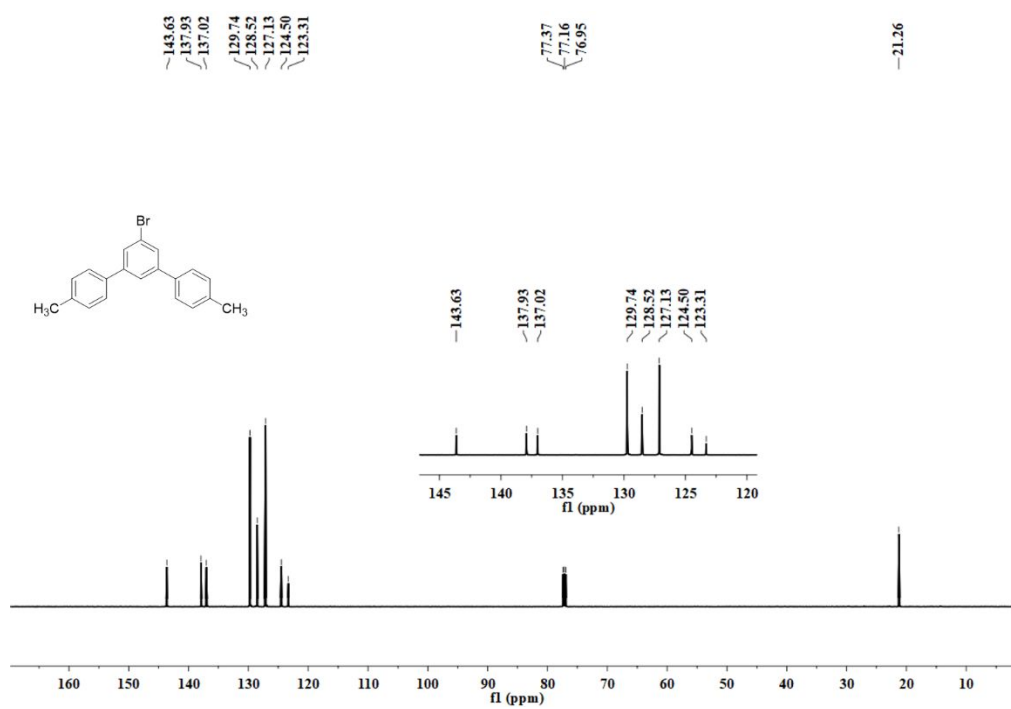


Figure S27. ^{13}C NMR spectrum of compound **15** in CDCl₃.

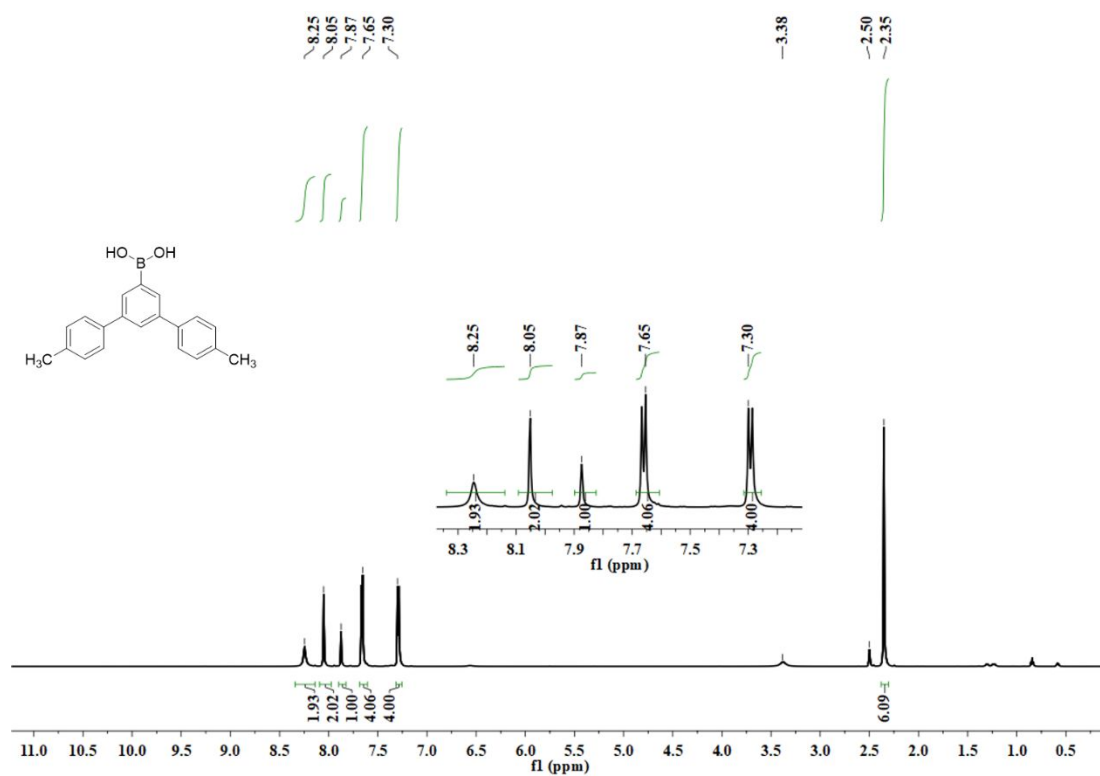


Figure S28. ^1H NMR spectrum of compound **16** in DMSO- d_6 .

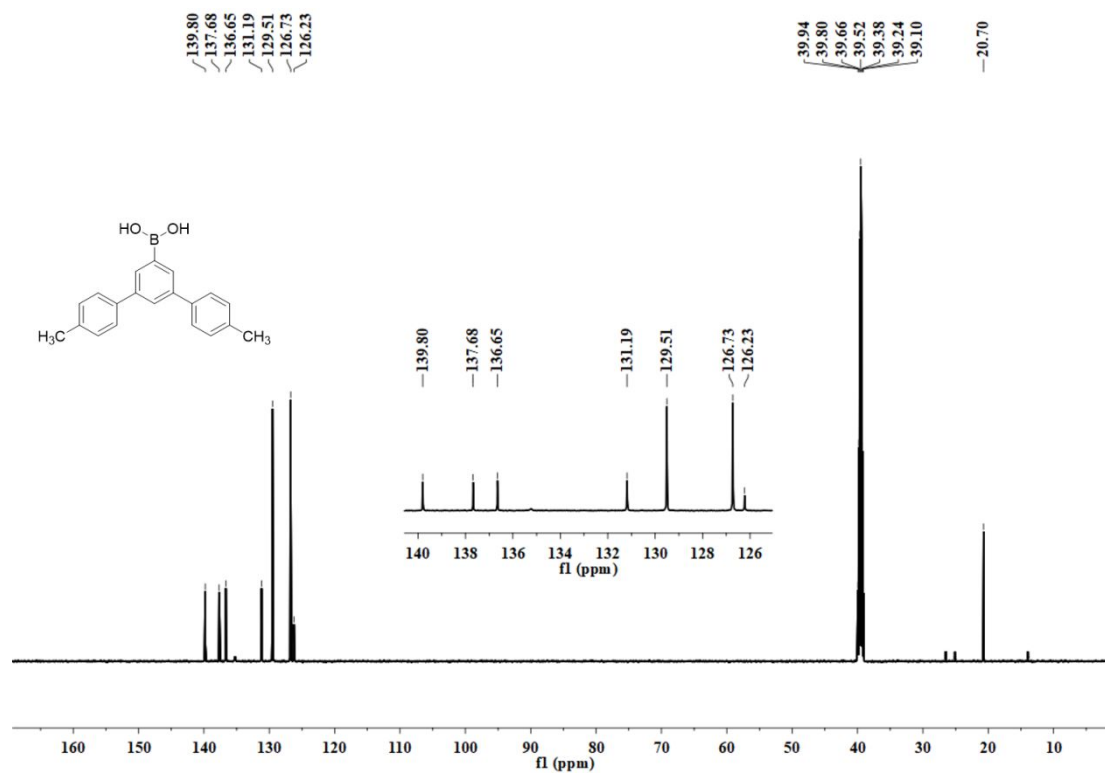


Figure S29. ^{13}C NMR spectrum of compound **16** in DMSO- d_6 .

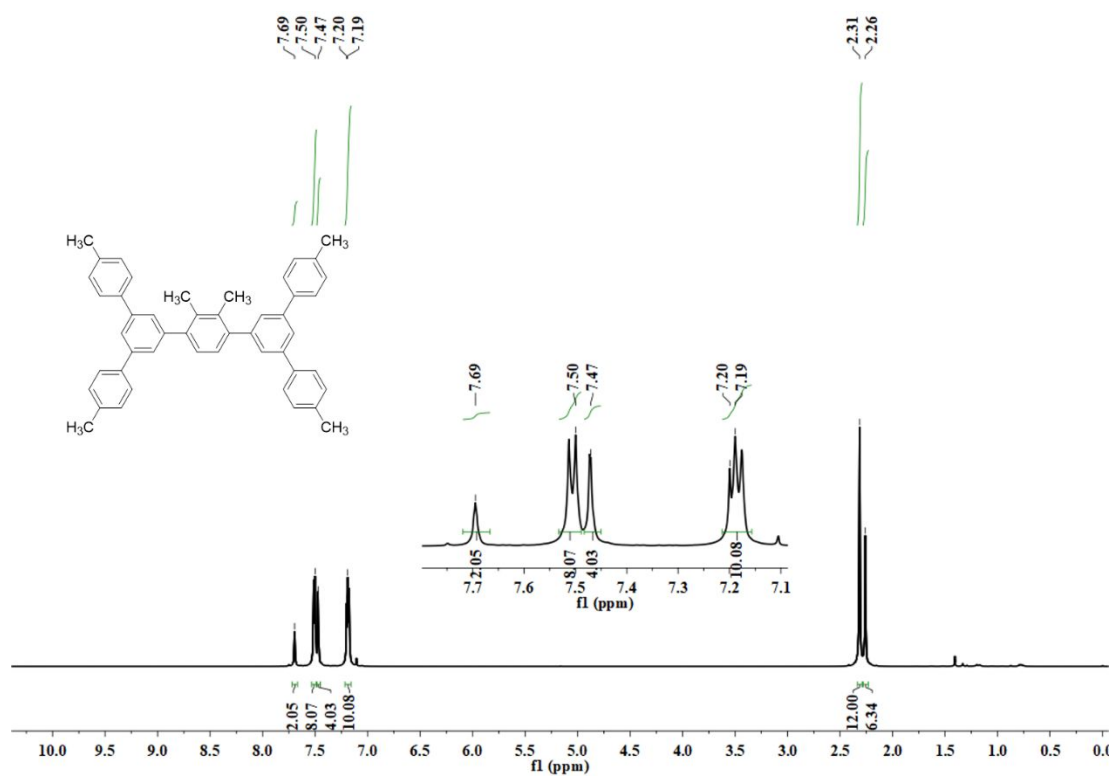


Figure S30. ¹H NMR spectrum of compound **17** in CDCl₃.

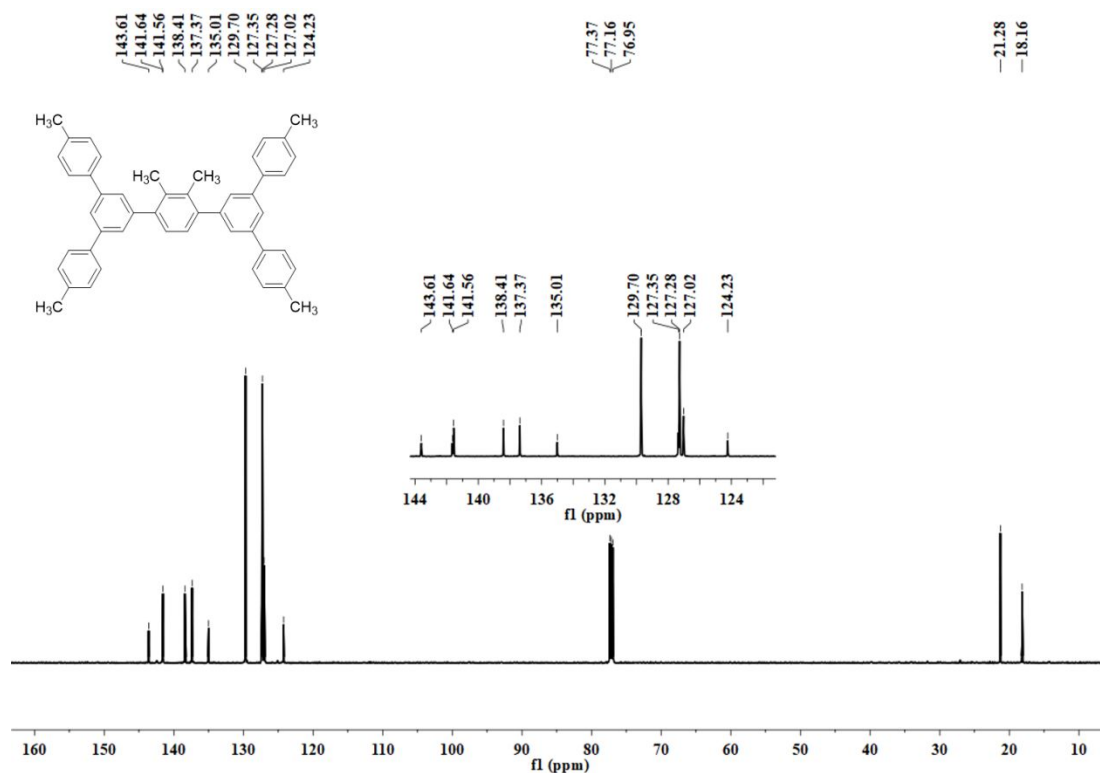


Figure S31. ¹³C NMR spectrum of compound **17** in CDCl₃.

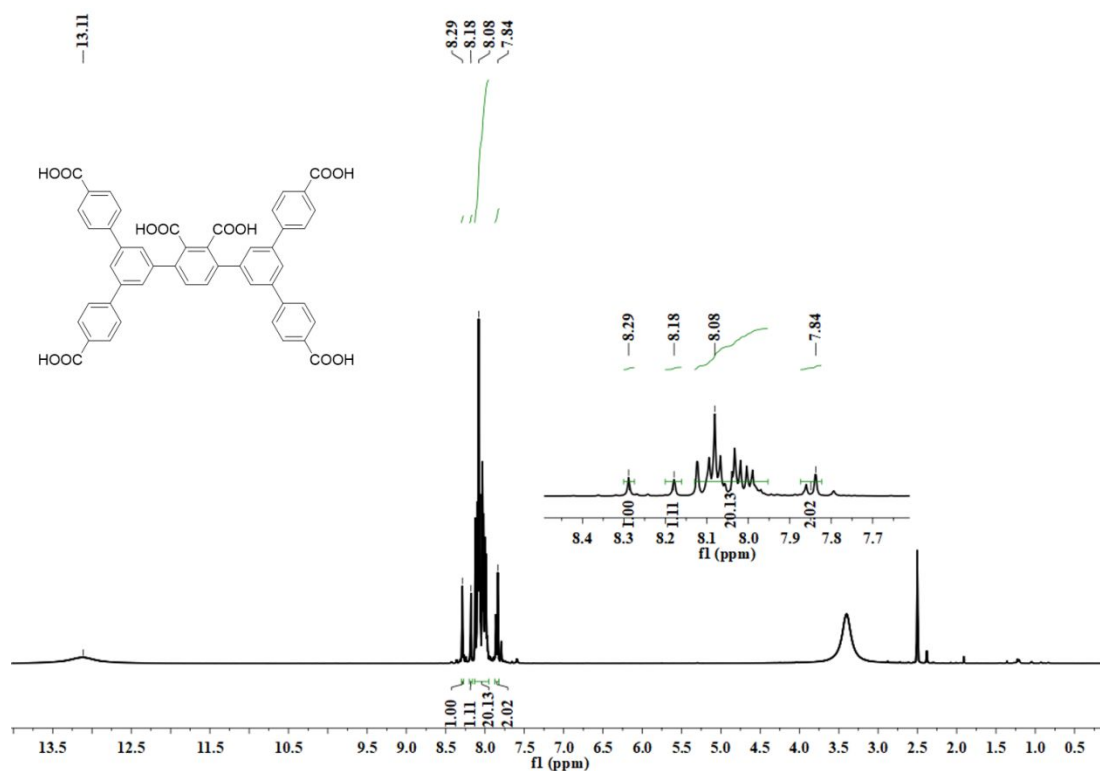


Figure S32. ^1H NMR spectrum of compound **18** in $\text{DMSO}-d_6$.

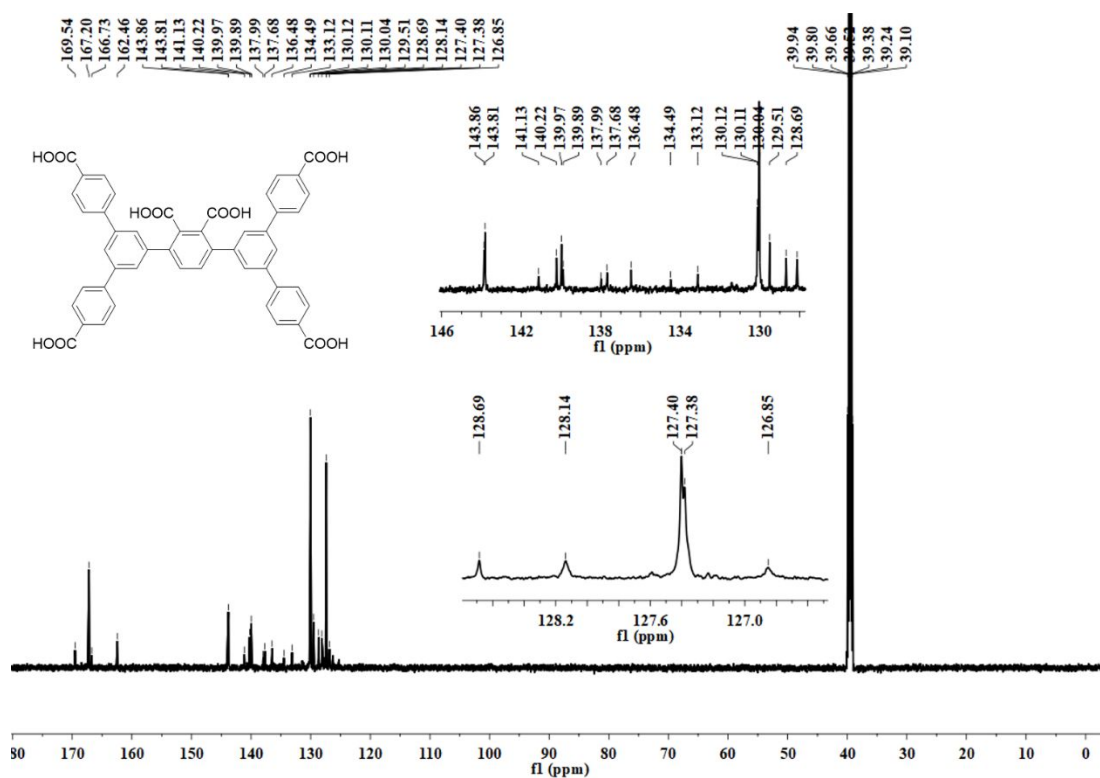


Figure S33. ^{13}C NMR spectrum of compound **18** in $\text{DMSO}-d_6$.

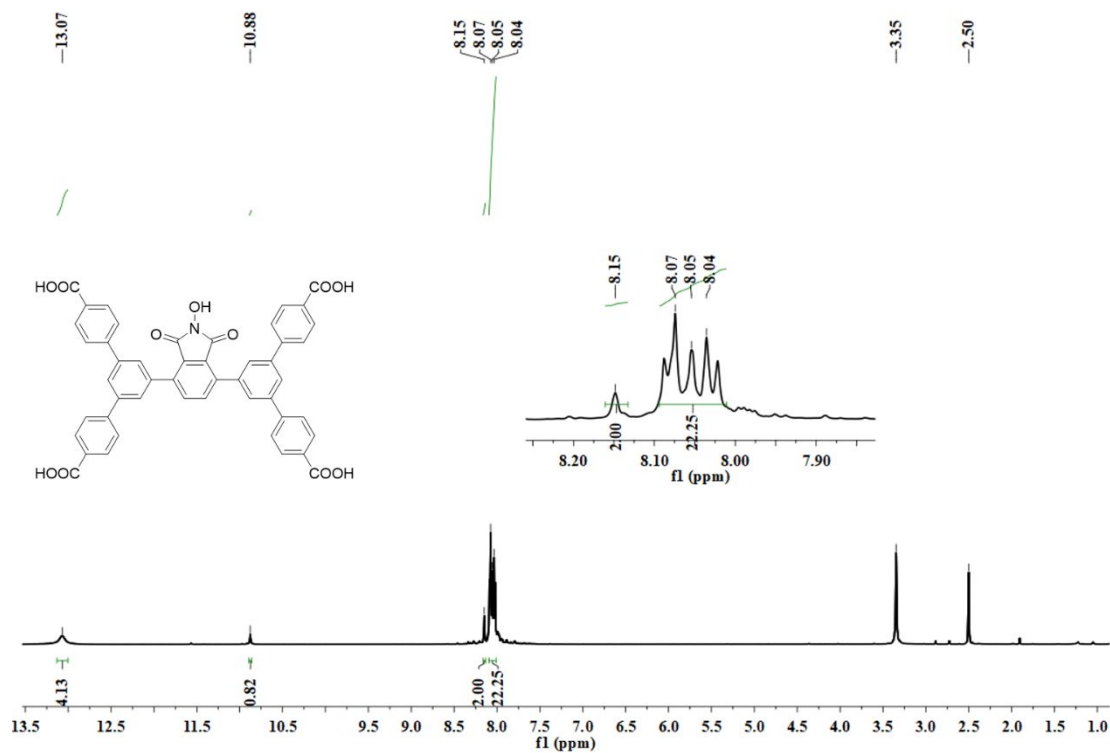


Figure S34. ^1H NMR spectrum of the ligand **L2** in $\text{DMSO}-d_6$.

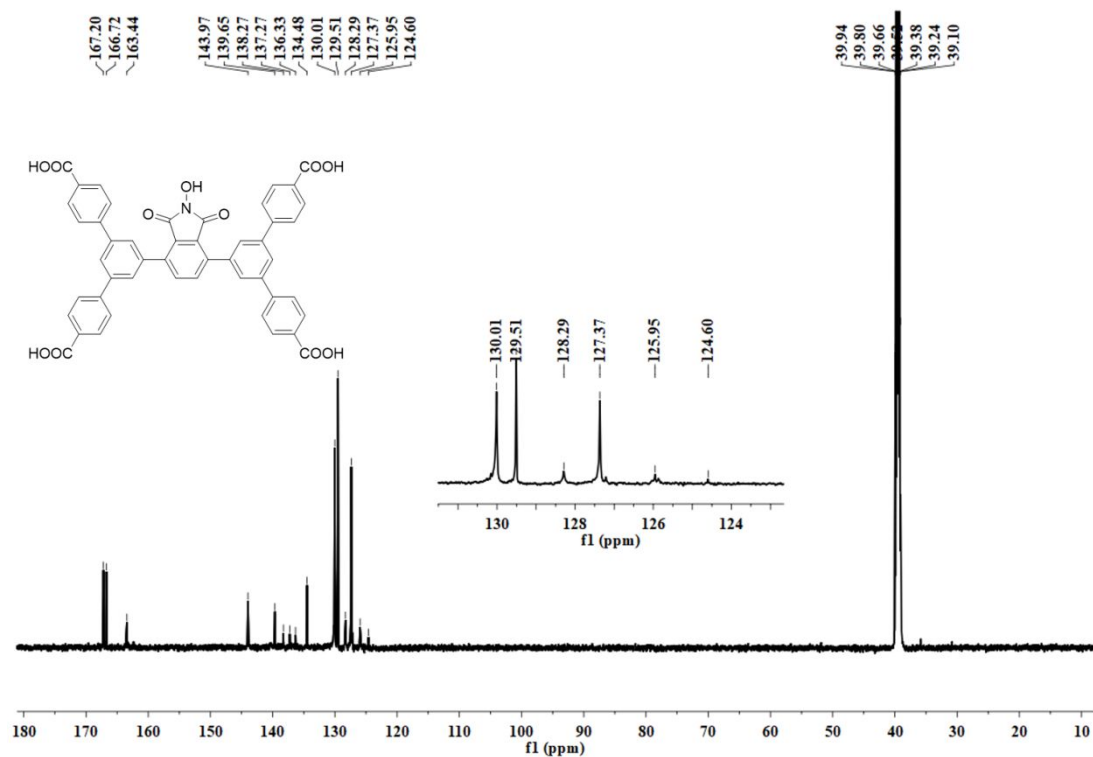


Figure S35. ^{13}C NMR spectrum of the ligand **L2** in $\text{DMSO}-d_6$.

8. References

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Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman J. B.; Fox, D. J. Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.

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