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Electronic Supplementary Information for

Modulating photocatalytic decarbonylative Minisci alkylation through conjugation engineering in pyrene-based hydrogen-bonded organic frameworks

Rong-Xin Zhu, Guang-Lu Li, Hui Liu, Shengsheng Yu* and Ling-Bao Xing*

School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255000, P. R. China

*Corresponding author: Tel. /fax: +86 533 2781664. E-mail: ssyu@sdut.edu.cn; lbxing@sdut.edu.cn.

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1. Experimental section

1.1 Materials

Unless specifically mentioned, the chemicals used are commercially available.

1.2 Characterizations

UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer in a quartz cell (light path 10 mm) at 298 K. Steady-state fluorescence measurements were carried out using a Hitachi 4500 spectrophotometer. The images of materials were carried out on scanning electron microscopy (SEM, Malvern, U.K.). X-ray diffraction (XRD) is tested using D8ADVANCE models of X-ray diffractometers, the pattern is recorded on a ray diffractometer with Cu radiation (Bruker, U.S.A.). Hamamatsu absolute quantum yield measuring instrument Quantaurus-QY was used to obtain fluorescence quantum yields. The time-resolved fluorescence decay curve was obtained by the FLS5 Steady-State/Transient Fluorescence Spectrometer. The N_2 adsorption-desorption isotherms of powder samples were measured with a Micromeritics ASAP 2020 adsorption apparatus at 77 K up to 1 bar. Before the measurement, the samples were outgassed at 373 K over a period of 12 h. Electron paramagnetic resonance (EPR) spectrum was obtained on A300 Bruker Co., Germany.

2. The molecular orbitals of different carboxylate tectons.

A single-point DFT calculation was run with ORCA v5.0.3 program[5] in all default settings, using B3LYP[6] hybrid functional and def2-TZVP[7] basis set. CPCM[8] implicit solvation models were used to simulate water solution.The HOMO-LUMO Fig. result was calculated by Gaussian 16 program[9], using B3LYP/def2-TZVP, and PCM[10] implicit solvation models.

3. Detection of $^1O_2$ production in solution.

Compound 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used as an indicator for detection of $^1O_2$ in solution (Fig. S4). 5 mg of photocatalyst was dissolved in 3.0 mL solution containing 100 μM of ABDA. The mixture was then placed in a cuvette and irradiated with a blue LED (400-410 nm). The absorption change of the sample at 378 nm was recorded by the UV-Vis absorption spectrophotometer.

4. General procedure for the decarbonylation Minisci alkylation reaction.

The 4-methylquinoline derivatives (0.2 mmol) and pivalaldehyde derivatives (0.4 mmol) were added in the newly produced aqueous solution of HOFs (5 mg). The reaction was irradiated with Blue LED (400-410 nm, 10 W) at room temperature under the ambient air condition for 36 h. Then the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was removed in vacuo and purified by rapid column chromatography to obtain the corresponding product.

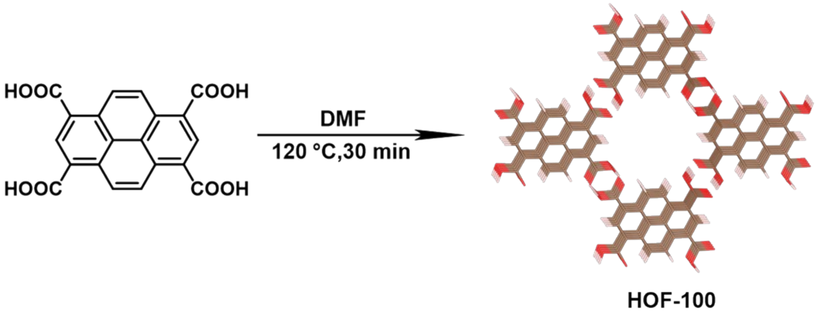
5. Calculation of the quenching constant

$$I_0/I = 1 + k_{SV}\,[Q] = 1 + k_q\,\tau_0\,[Q] \quad (S1)$$

where τ_0 is the lifetime of the excited state, and I_0 and I are the emission intensities in the absence and in the presence of the quencher Q, respectively, k_{SV} is the Stern-Volmer constant and k_q is the quenching constant.

6. Synthesis of HOF

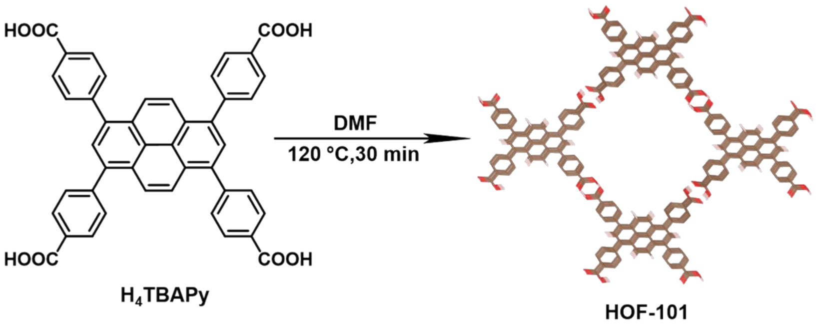
6.1 Synthesis of HOF-100



Scheme S1 Synthesis of HOF-100.

H_4TCPy (200 mg, 0.3 mmol) was dissolved in 10 mL of DMF under heating at 120˚C for 30 min to get a clear solution. After cooling down to room temperature, the solution was poured into 160 mL of acetone under stirring (400 rpm) within 1 min. The suspension was kept stirring for 12 h and isolated by centrifugation at 8000 rpm for 5 min. The obtained brown powder was further washed with acetone (2 × 45 mL), and then dried in at room temperature (yield 150 mg, 75%).

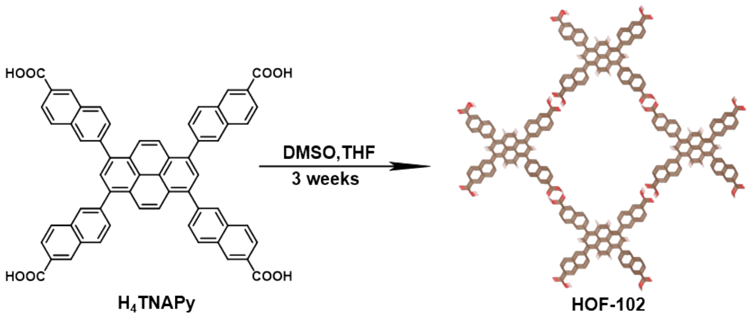
6.2 Synthesis of HOF-101



Scheme S2 Synthesis of HOF-101.

H_4TBAPy (200 mg, 0.3 mmol) was dissolved in 10 mL of DMF under heating at 120˚C for 30 min to get a clear yellow solution. After cooling down to room temperature, the solution was poured into 160 mL of acetone under stirring (400 rpm) within 2 min. The suspension was kept stirring for 12h and isolated by centrifugation at 8000 rpm for 5 min. The obtained yellow powder was further washed with acetone (4 × 45 mL), and then dried in at room temperature (yield 180 mg, 90%).

6.3 Synthesis of HOF-102



Scheme S3 Synthesis of HOF-102.

Scheme S3. The synthetic route of the TPPB target molecule.

H_4TNAPy (200 mg, 0.225 mmol) was dissolved in 0.2 mL of DMSO in a 5 mL uncapped vial. The vial was put in a 20 mL vial containing 10 mL THF and the large vial was sealed. The yellow needle like crystals of HOF-102 suitable for single crystal X-ray diffraction analysis were grown by slow vapor diffusion for about 3 weeks at room temperature (yield 170 mg, 85%).

7. The FTIR spectra of HOFs

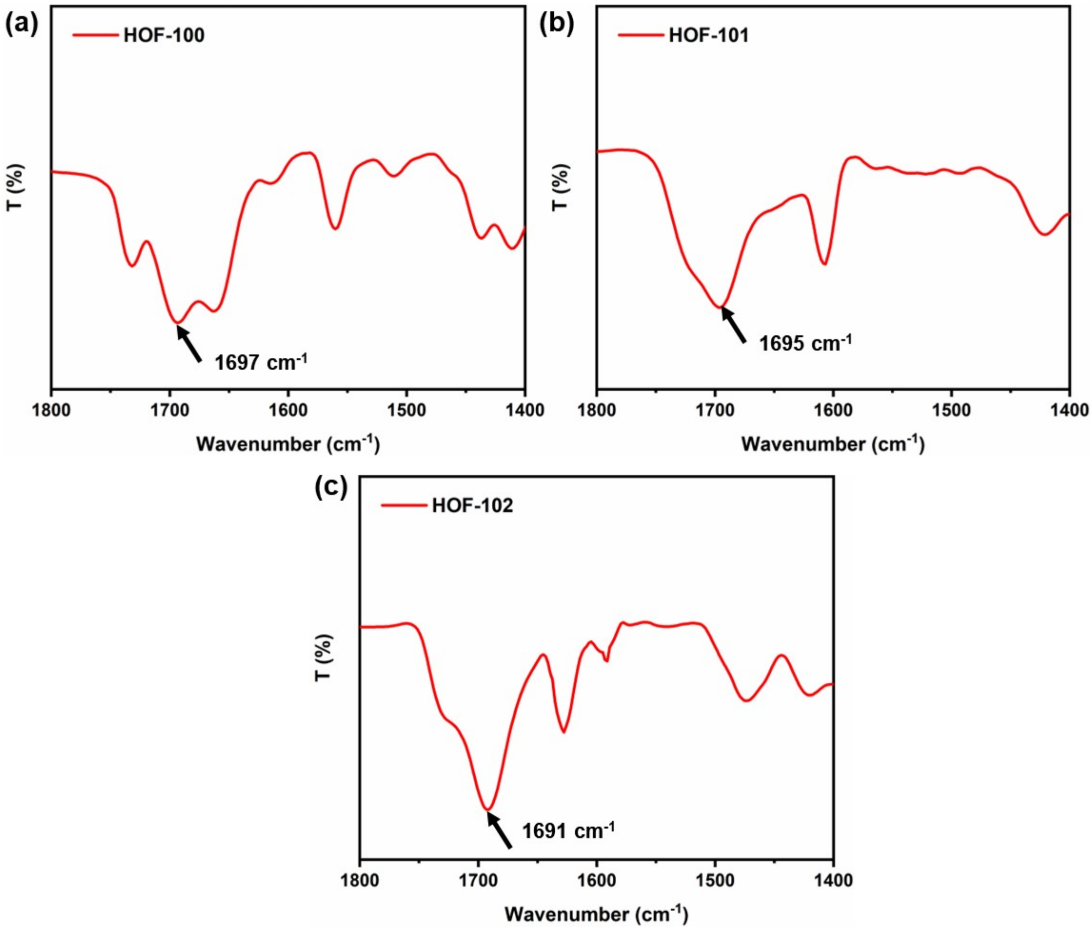


Fig. S1 The FTIR spectra of HOF-100, HOF-101 and HOF-102.

8. N_2 adsorption-desorption isotherms of HOFs

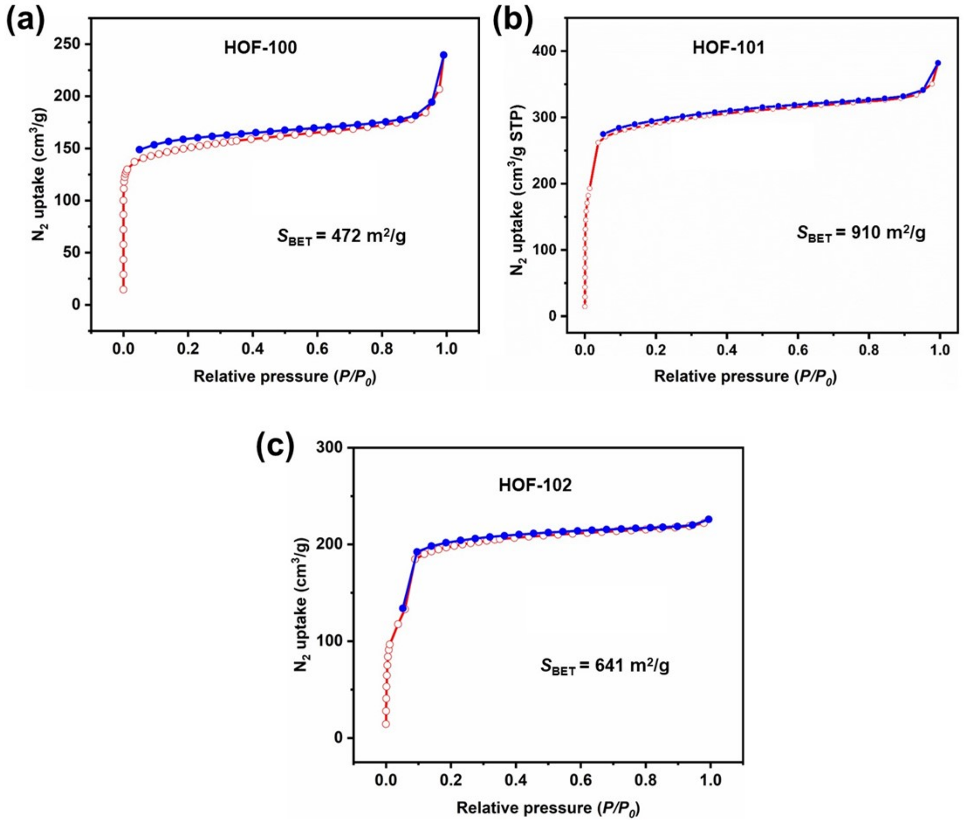


Fig. S2 N_2 adsorption-desorption isotherms of (a) HOF-100, (b) HOF-101 and (c) HOF-102.

9. UV-vis spectra

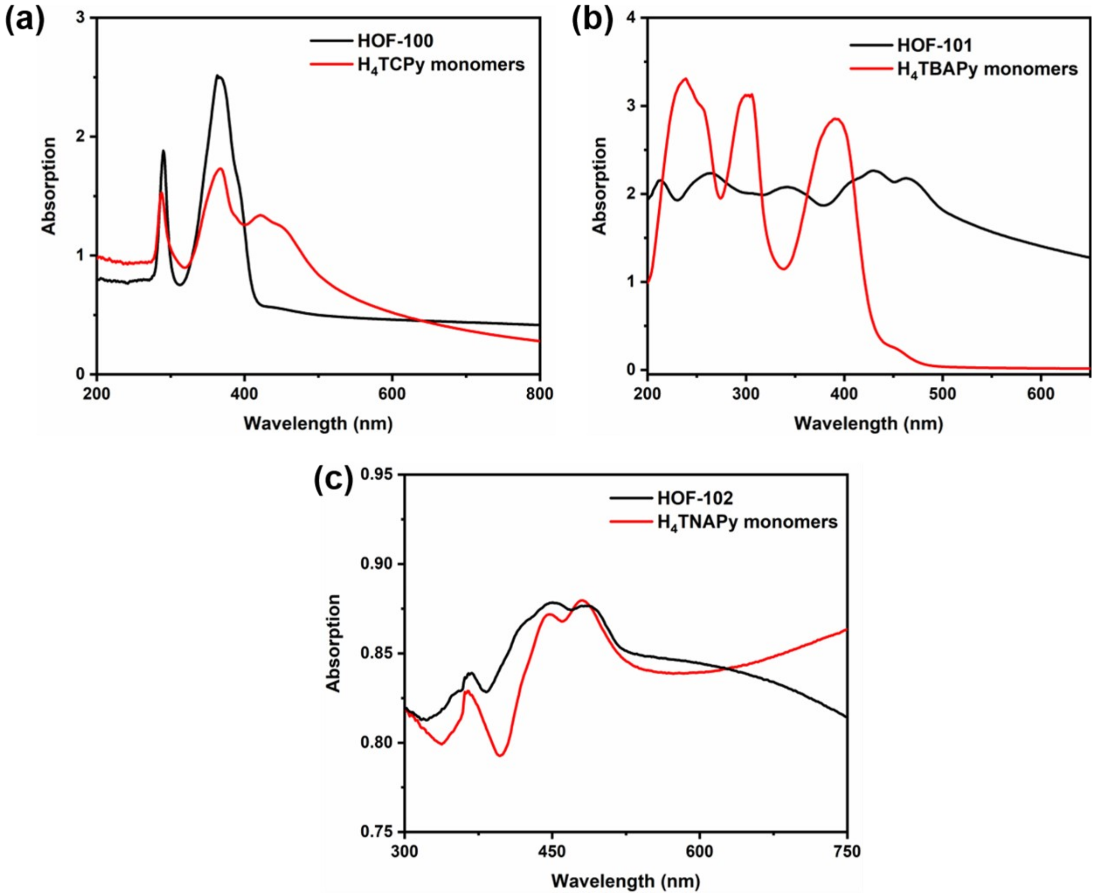


Fig. S3 (a) UV-vis absorption spectra of H_4TCPy monomers and HOF-100 in aqueous solution; (b) UV-vis absorption spectra of H_4TBAPy monomers and HOF-101 in aqueous solution; (c) UV-vis absorption spectra of H_4TNAPy monomers and HOF-102 in aqueous solution.

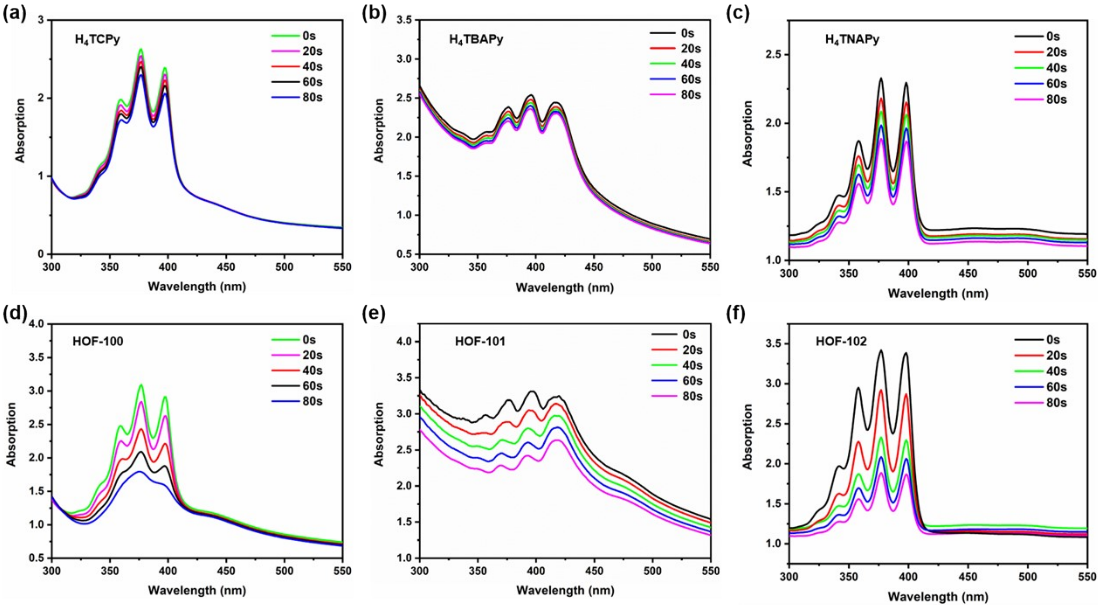
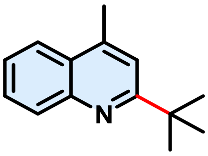


Fig. S4 The absorption spectra of ABDA (100 μM) after irradiation (400-410 nm, 10 W) for different time in the presence of (a) H_4TCPy monomers (5 mg); (b) H_4TBAPy monomers (5 mg); (c) H_4TNAPy monomers (5 mg); (d) HOF-100 (5 mg); (e) HOF-101 (5 mg); (f) HOF-102 (5 mg).

10. ^{1}H NMR spectra and data of 3a-3l

3a. 2-(tert-butyl)-4-methylquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.89-7.84 (m, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.28 (s, 1H), 2.62 (s, 3H), 1.39 (s, 9H).

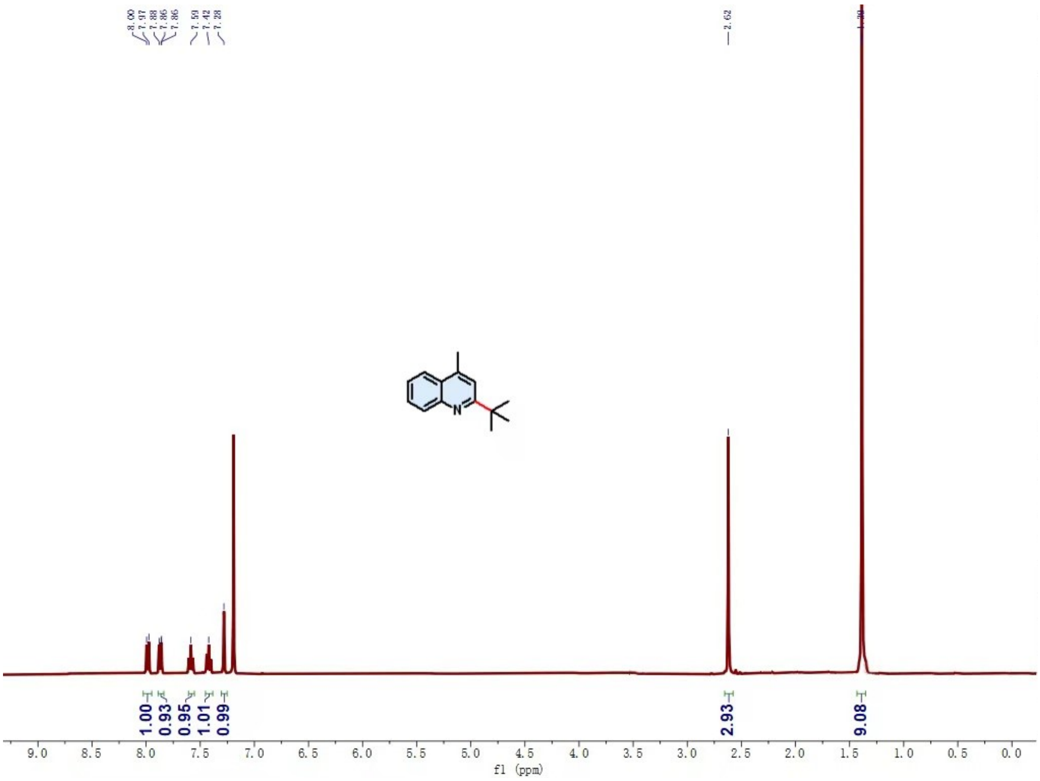
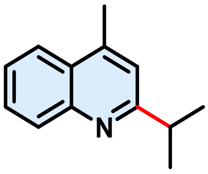


Fig. S5 ^{1}H NMR spectra of **3a** in $CDCl_3$.

3b. **2-isopropyl-4-methylquinoline**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 1H), 8.03-7.93 (m, 1H), 7.69-7.64 (m, 1H), 7.55-7.49 (m, 1H), 7.17 (d, *J* = 1.2 Hz, 1H), 3.30-3.10 (m, 1H), 2.68 (s, 3H), 1.38 (s, 6H).

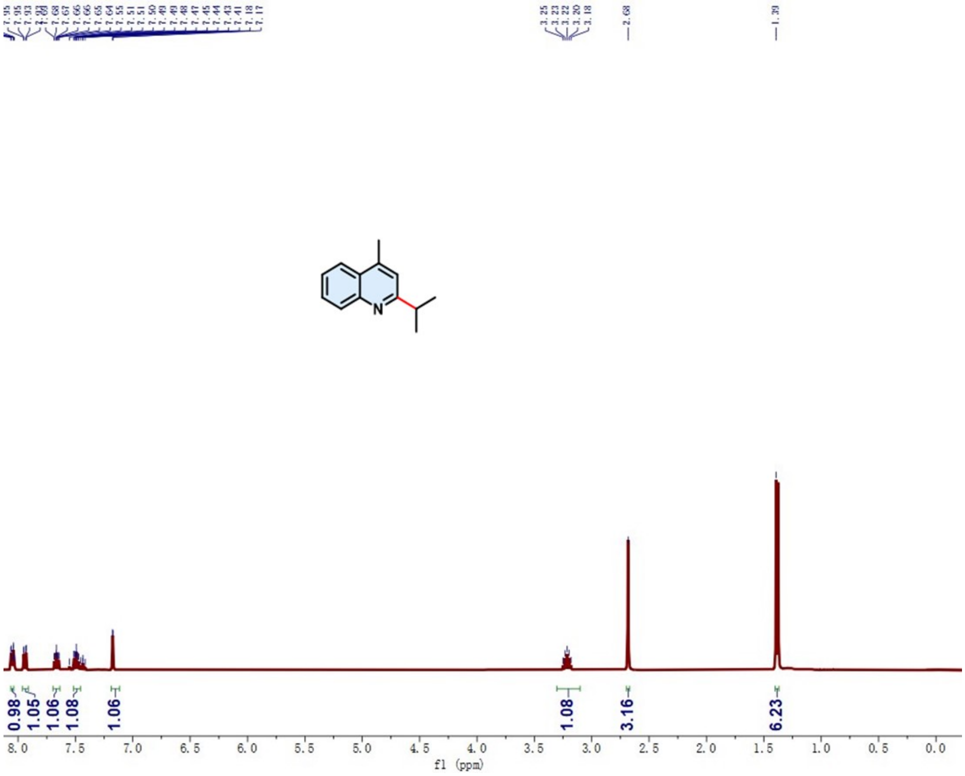
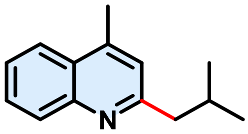


Fig. S6 ^{1}H NMR spectra of **3b** in $CDCl_3$.

3c. 2-isobutyl-4-methylquinoline



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 1.1 Hz, 1H), 7.78-7.75 (m, 1H), 7.66-7.65 (m, 1H), 3.27 (d, J = 7.0 Hz, 2H), 2.76 (s, 3H), 2.40-2.33 (m, 1H), 1.04 (s, 6H).

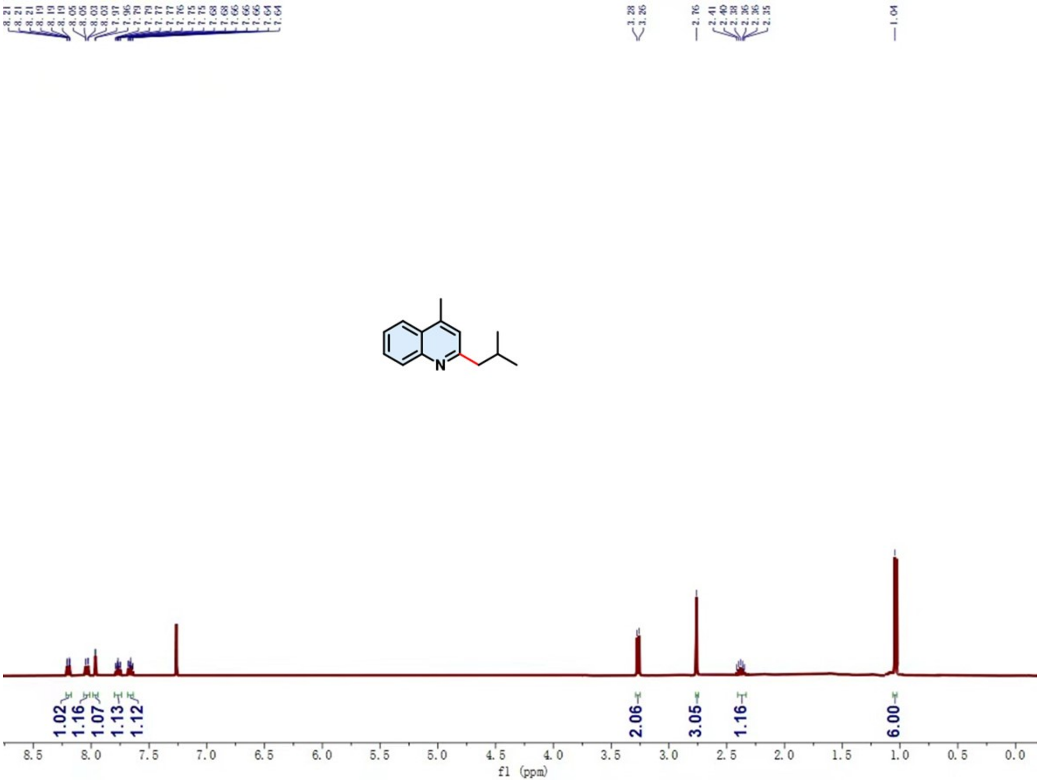
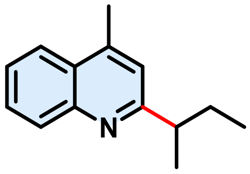


Fig. S7 ^{1}H NMR spectra of **3c** in CDCl$_3$.

3d. **2-(sec-butyl)-4-methylquinoline**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.69-7.62 (m, 1H), 7.55-7.49 (m, 1H), 7.14 (d, J = 1.1 Hz, 1H), 3.00-2.88 (m, 1H), 2.69 (s, 3H), 1.87-1.80 (m, 1H), 1.70-1.68 (m, 1H), 1.35 (s, 3H), 0.91 (s, 3H).

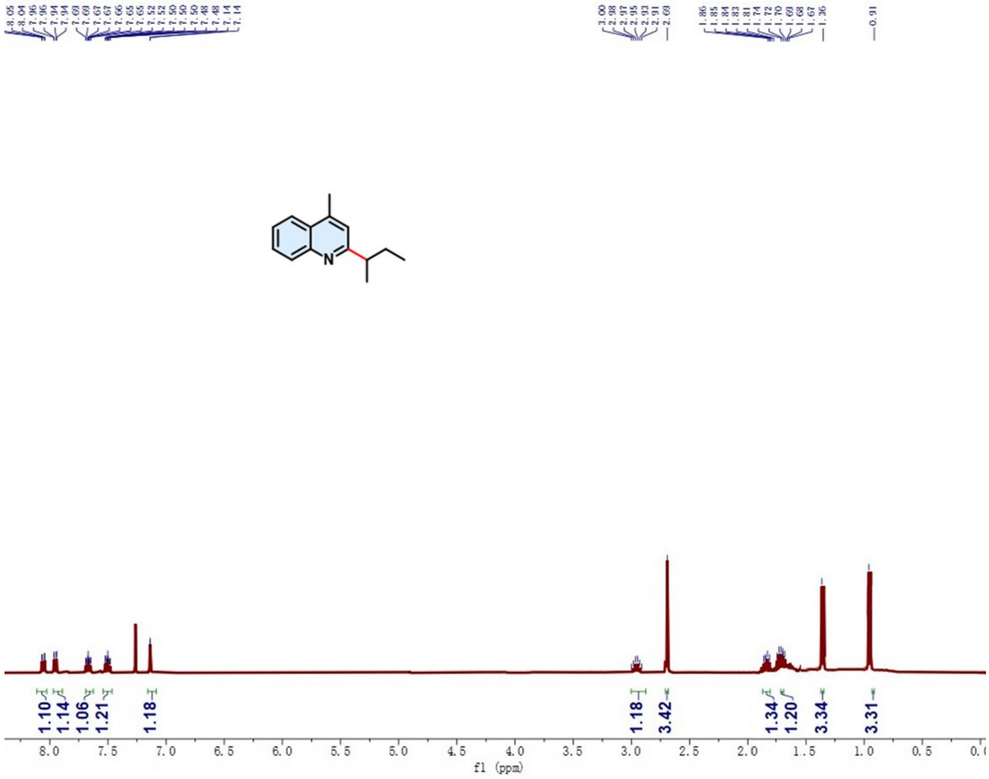
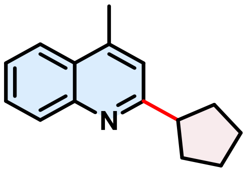


Fig. S8 ^{1}H NMR spectra of **3d** in CDCl$_3$.

3e. **2-cyclopentyl-4-methylquinoline**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.4, 1H), 7.94 (d, J = 8.3, 1H), 7.70-7.66 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 3.38-3.29 (m, 1H), 2.68 (s, 3H), 2.22-2.11 (m, 2H), 1.92-1.87 (m, 4H), 1.78-1.71 (m, 2H).

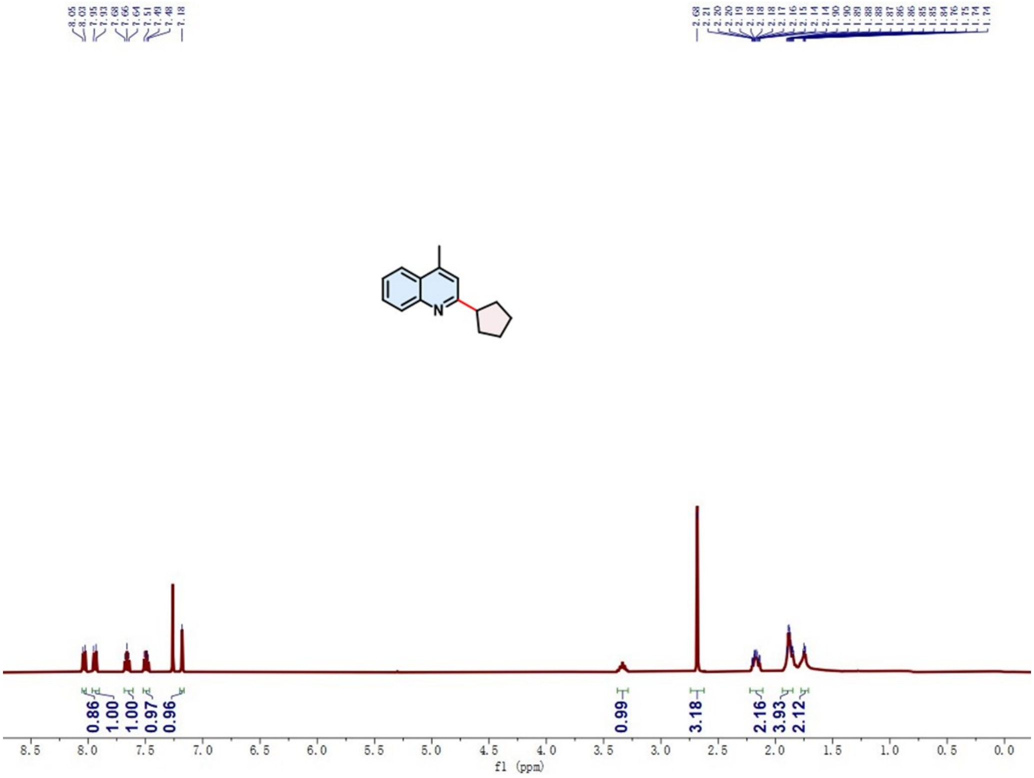
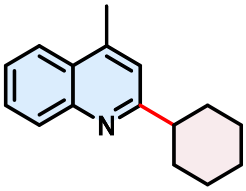


Fig. S9 ^{1}H NMR spectra of **3e** in CDCl$_3$.

3f. **2-cyclohexyl-4-methylquinoline**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.66 (t, J = 8.4 Hz, 1H), 7.49 (t, J = 8.2 Hz, 1H), 7.17 (s, 1H), 2.94-2.81 (m, 1H), 2.69 (s, 3H), 2.03 (d, J = 13.0 Hz, 2H), 1.91 (d, J = 9.8 Hz, 2H), 1.80 (s, 1H), 1.68-1.58 (m, 2H), 1.52-1.41 (m, 2H), 1.38-1.32 (m, 1H).

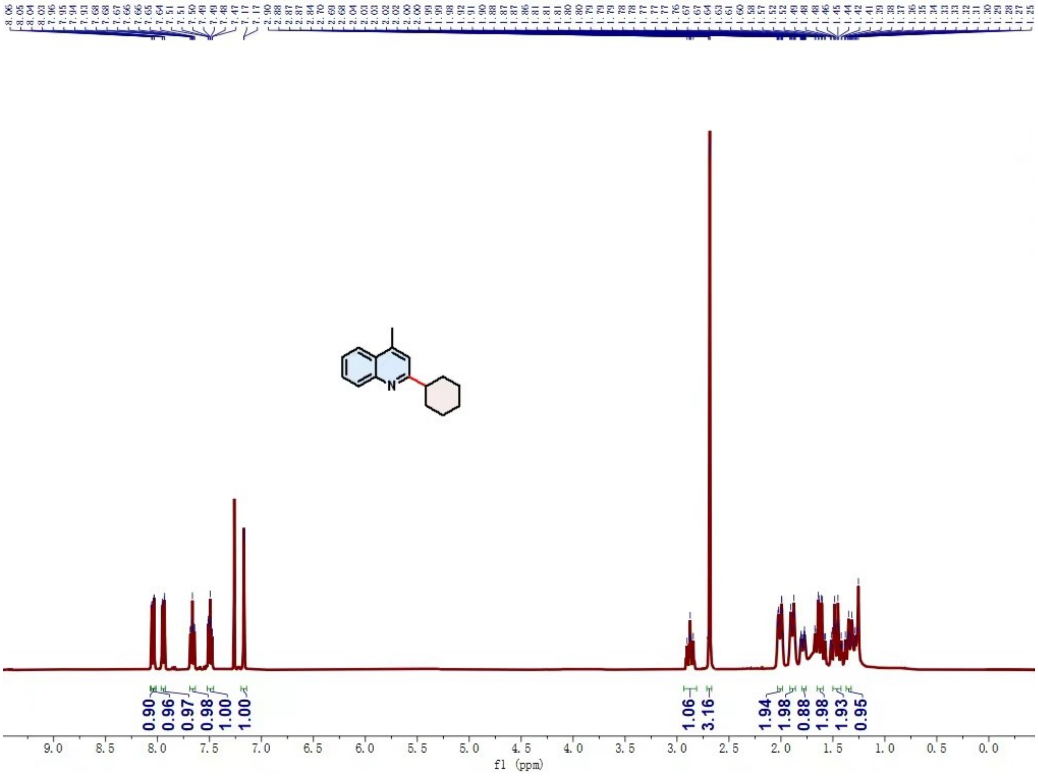
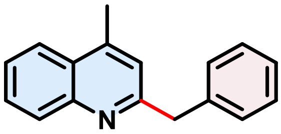


Fig. S10 ^{1}H NMR spectra of **3f** in CDCl$_3$.

3g. **2-benzyl-4-methylquinoline**



^{1}H NMR (400 MHz, CDCl$_3$) δ 9.44 (s, 1H), 7.27-7.19 (m, 4H), 7.16-7.09 (m, 5H), 6.61 (t, J = 6.9 Hz, 1H), 3.58 (s, 2H), 2.75 (s, 3H).

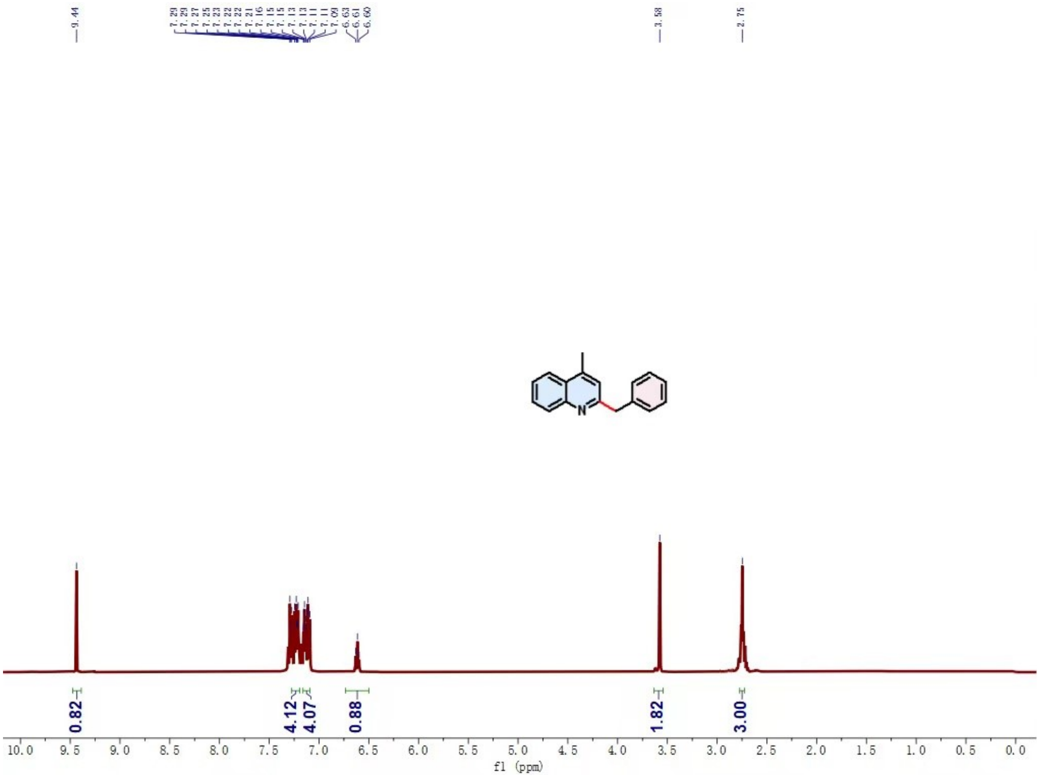
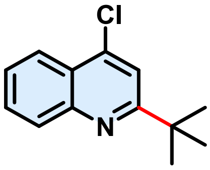


Fig. S11 ^{1}H NMR spectra of **3g** in CDCl$_3$.

3h. 2-(tert-butyl)-4-chloroquinoline



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, J = 8.4, Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.71 (t, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.58 (t, J = 7.6 Hz, 1H), 1.45 (s, 9H).

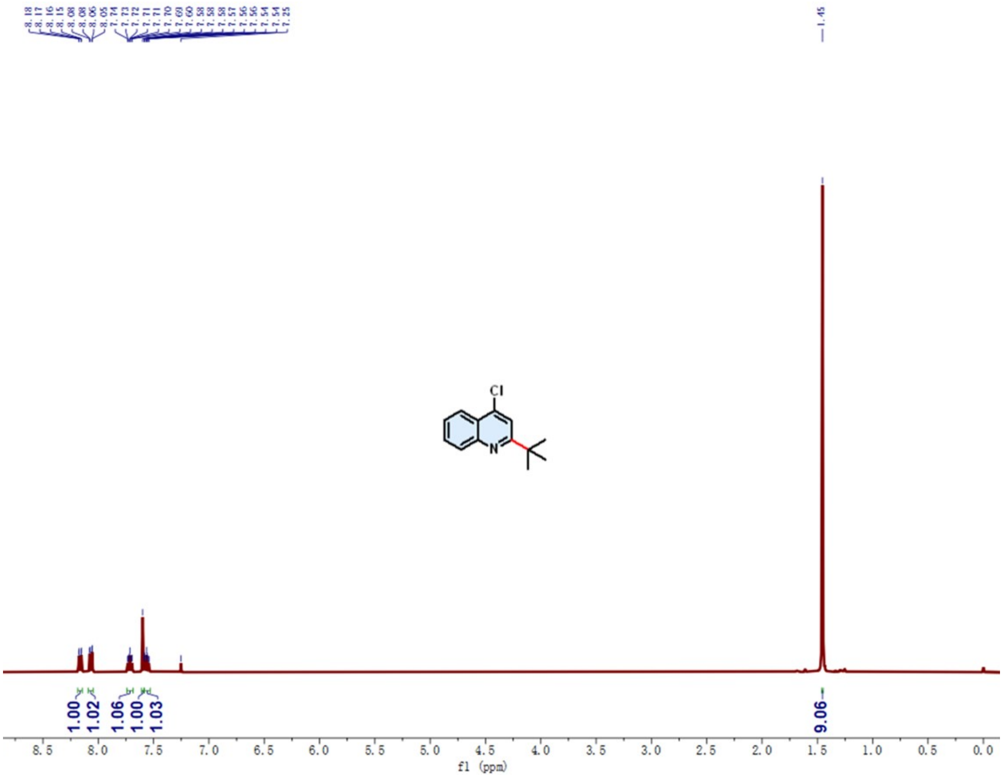
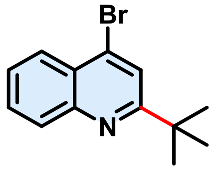


Fig. S12 ^{1}H NMR spectra of **3h** in CDCl$_3$.

3i. **4-bromo-2-(tert-butyl)quinoline**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.57 (t, J = 8.2 Hz, 1H), 1.46 (s, 9H).

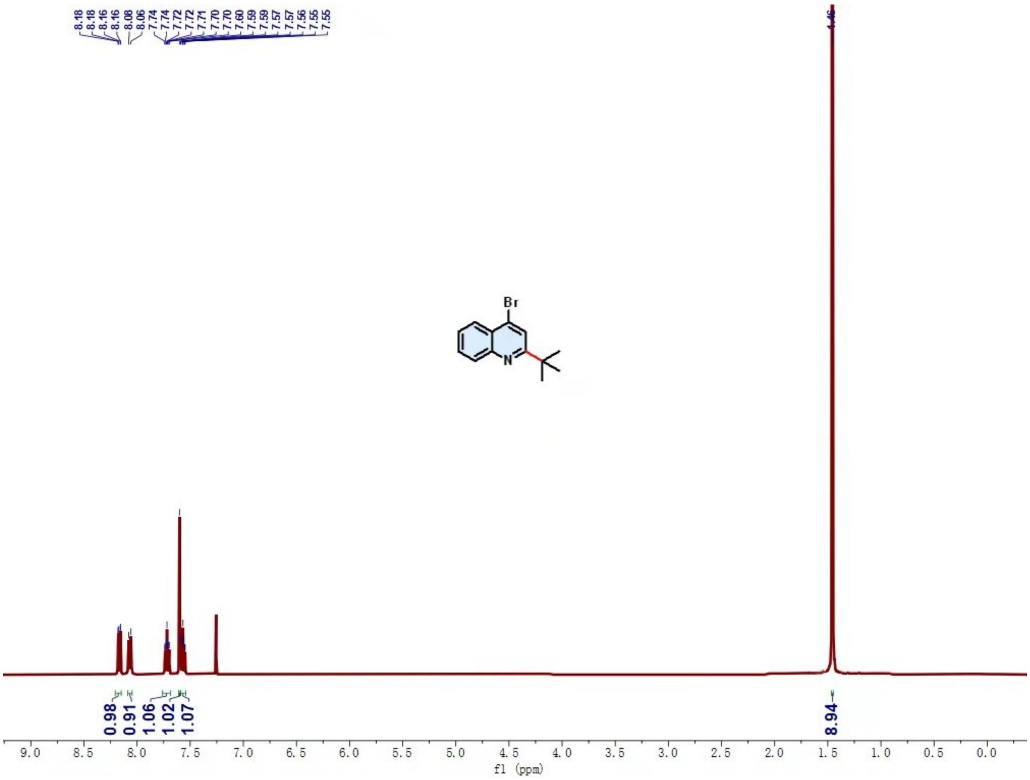
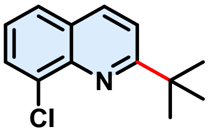


Fig. S13 ^{1}H NMR spectra of **3i** in CDCl$_3$.

3j. 2-(tert-butyl)-8-chloroquinoline



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12-7.98 (m, 2H), 7.69 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.43-7.41 (m, 1H), 1.45 (s, 9H).

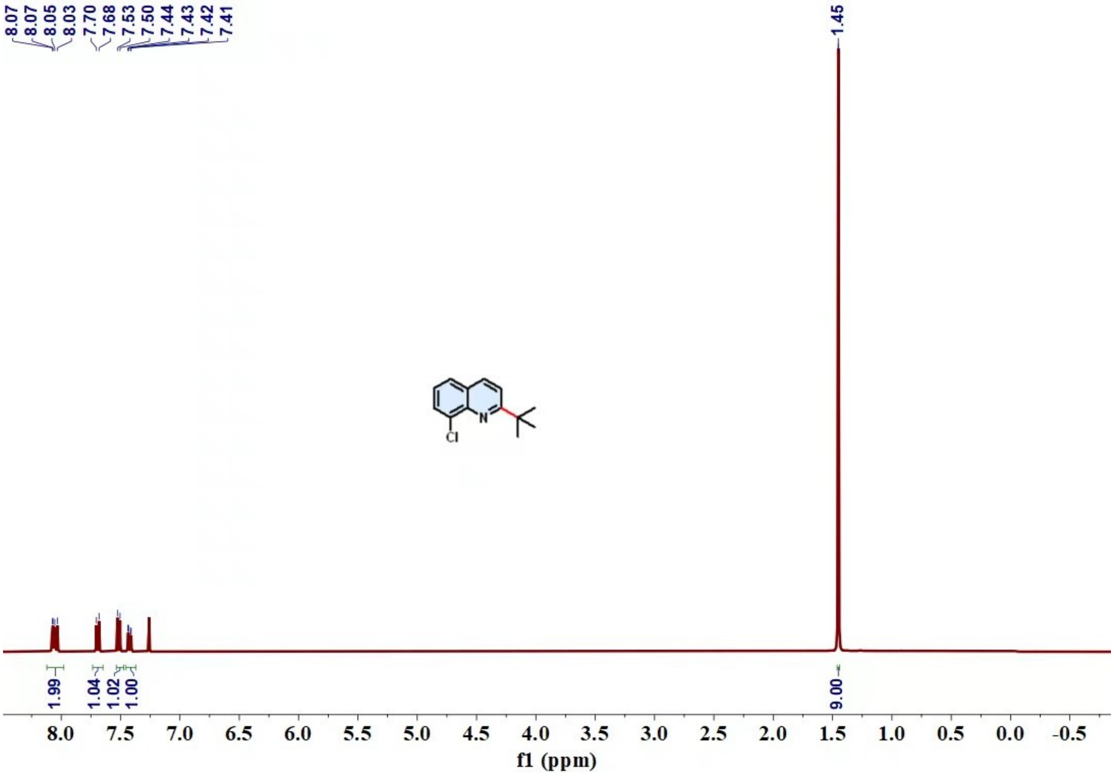
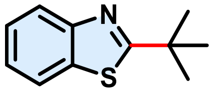


Fig. S14 ^{1}H NMR spectra of **3j** in CDCl$_3$.

3k. **2-(tert-butyl)benzo[d]thiazole**



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 7.9b Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 1H), 1.53 (s, 9H).

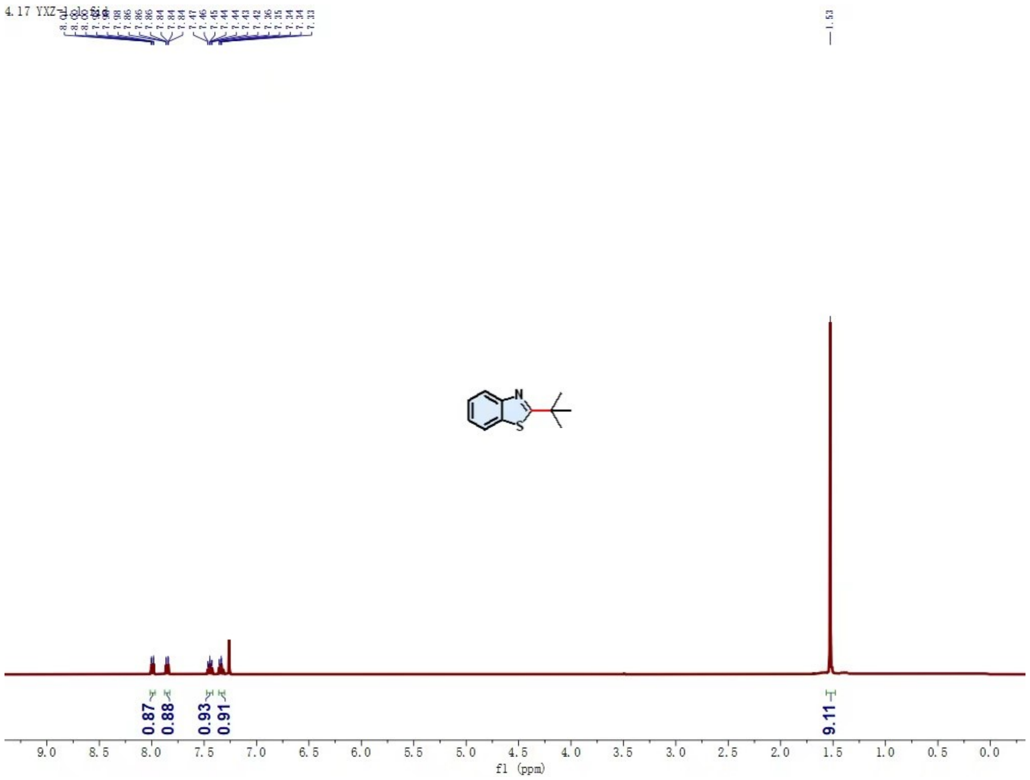
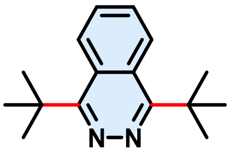


Fig. S15 ^{1}H NMR spzzectra of **3k** in CDCl$_3$.

3l. 1,4-di-tert-butylphthalazine



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.53-5.50 (m, 2H), 7.80-7.78 (m, 2H), 1.71 (s, 18H).

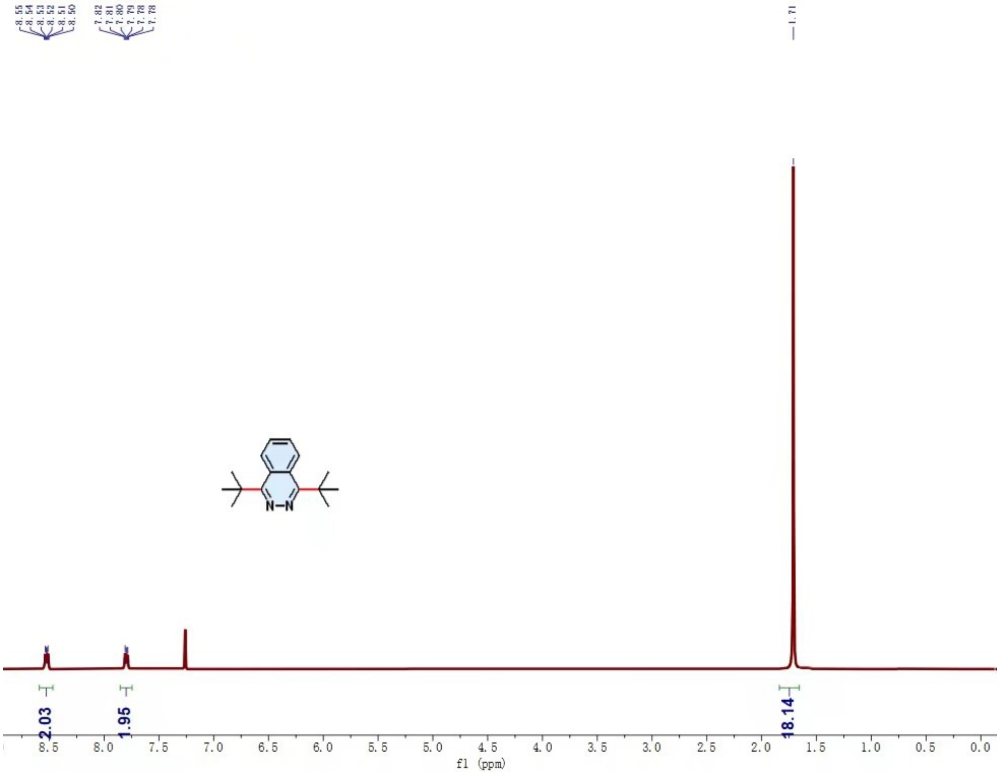
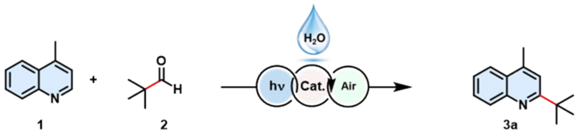


Fig. S16 ^{1}H NMR spectra of **3l** in CDCl$_3$.

11. Yields and characterizations after five cycles.

Table S1 Product yield of pyrene-based HOFs over five cycles.



Cycle Number	HOF-102 Yield (%)	HOF-101 Yield (%)	HOF-100 Yield (%)
1st	91	71	65
2nd	88	67	60
3rd	84	63	58
4th	79	59	52
5th	75	55	49

12. Characterization of HOFs after five cycles.

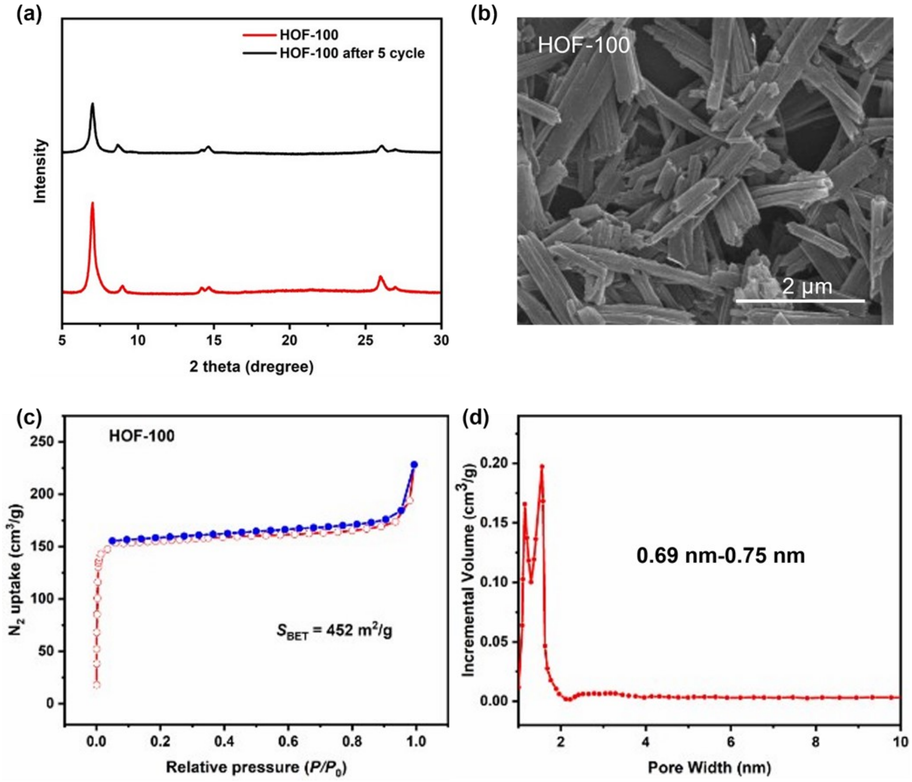


Fig. S17 The (a) XRD, (b) SEM image, (c) N_2 adsorption-desorption isotherms, and (d) NLDFT pore size distribution of HOF-100 after recycling 5 times.

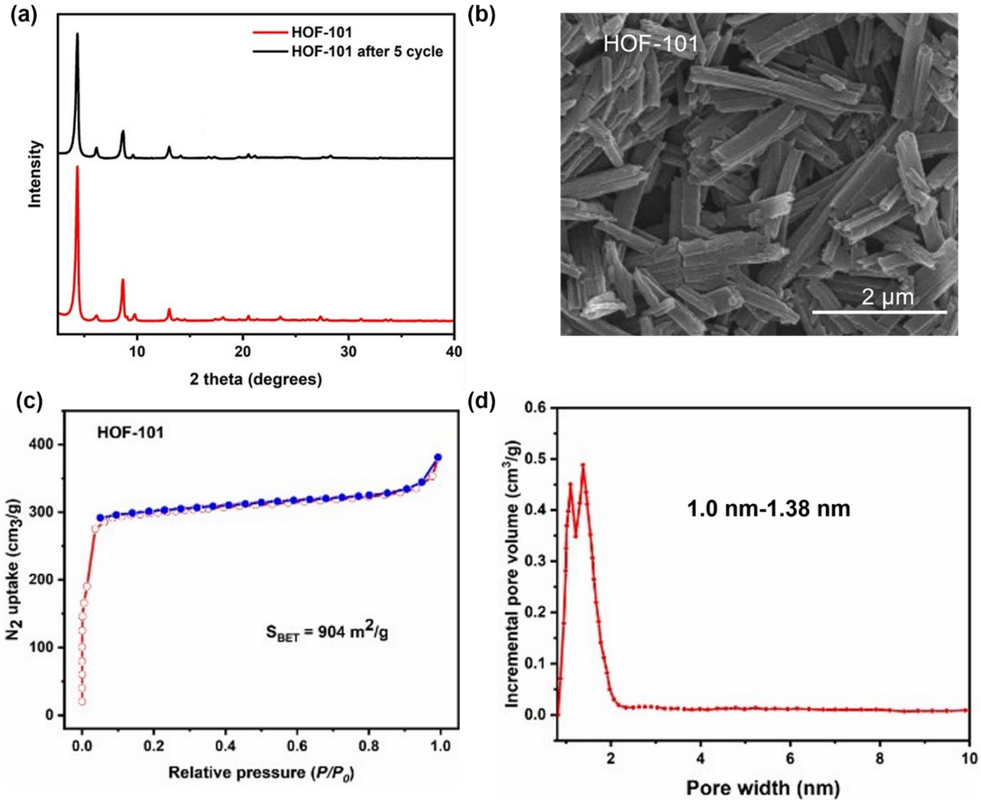


Fig. S18 The (a) XRD, (b) SEM image, (c) N_2 adsorption-desorption isotherms, and (d) NLDFT pore size distribution of HOF-101 after recycling 5 times.

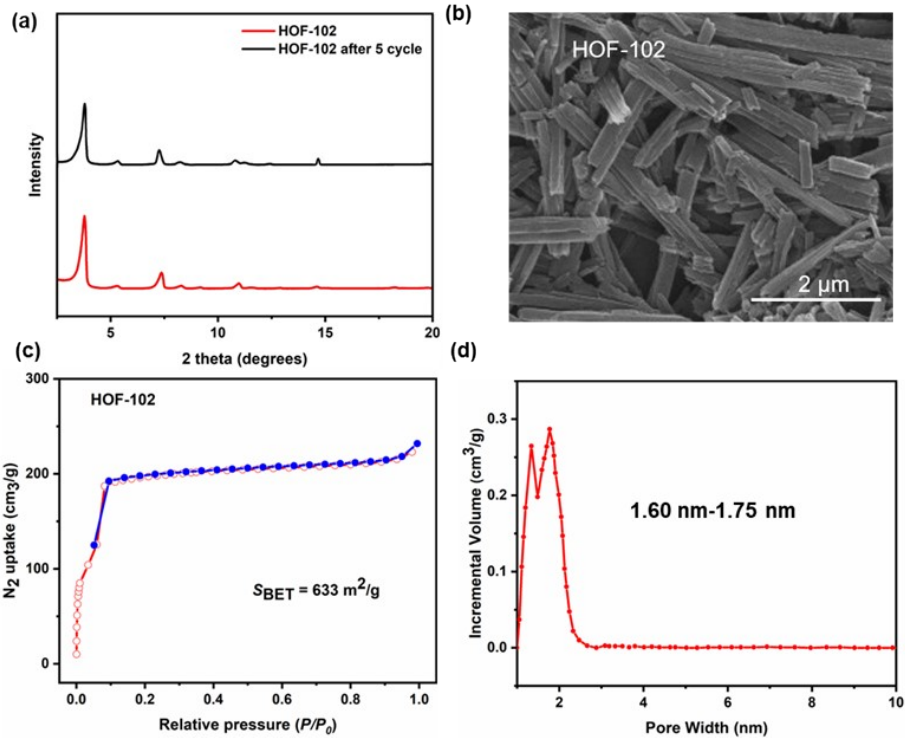


Fig. S19 The (a) XRD, (b) SEM image, (c) N_2 adsorption-desorption isotherms, and (d) NLDFT pore size distribution of HOF-102 after recycling 5 times.

13. UV-vis DRS of HOFs and monomers.

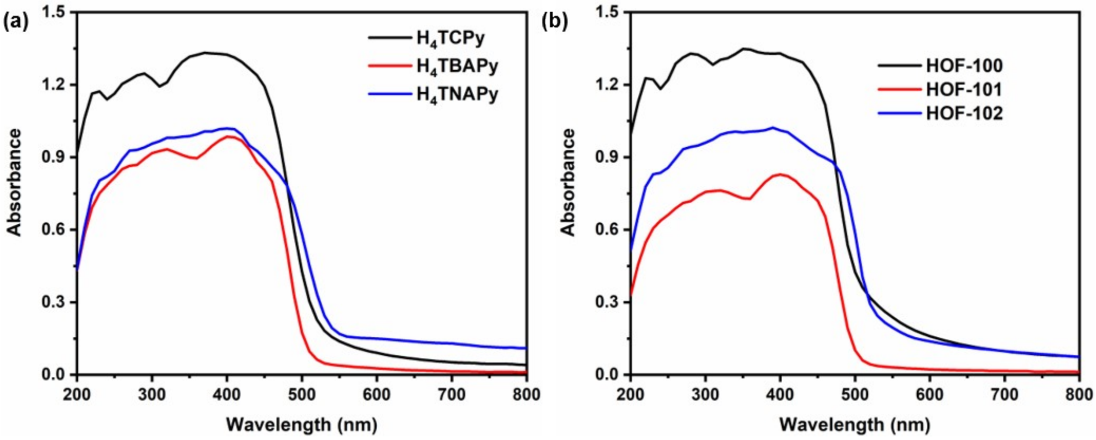


Fig. S20 UV-vis DRS of (a) H_4TCPy, H_4TBAPy, and H_4TNAPy; and (b) HOF-100, HOF-101, and HOF-102.

14. EPR spectra of TEMP-$^1O_2$.

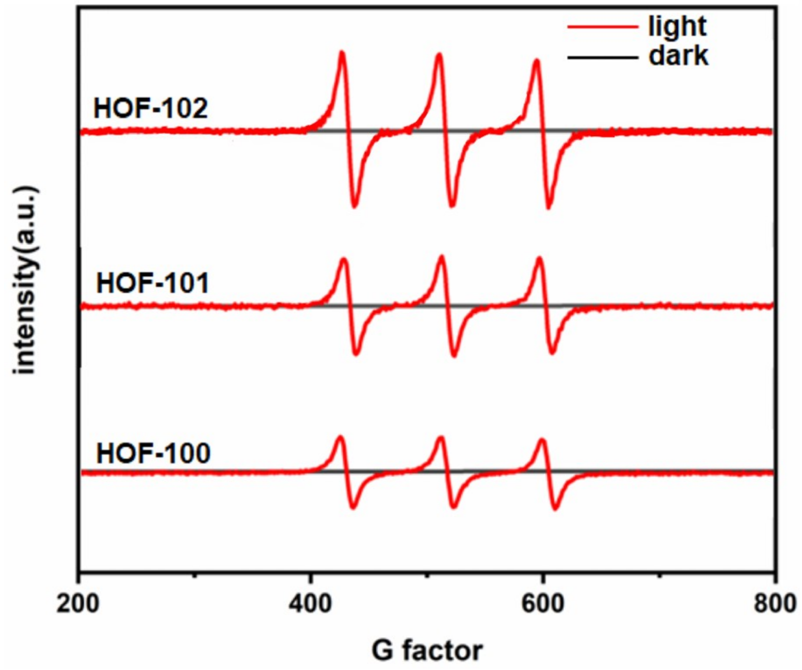


Fig. S21 EPR spectra of TEMP-$^1O_2$.