

Construction of quinoline-4-carboxylic esters linked covalent organic framework *via* Doebner–von Miller reaction

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Contents

1. General information	1
1.1 Materials	1
1.2 Characterization techniques.....	1
2. Synthetic procedures.....	3
2.1 Model reaction.....	3
2.1.1 Synthesis of methyl-2-phenylquinoline-4-carboxylate.....	3
2.1.2 Synthesis of (L)-menthyl pyruvate	3
2.1.3 Synthesis of (L)-menthyl-2-phenylquinoline-4-carboxylate	4
2.2 Synthesis of Im-COFs	4
2.2.1 Synthesis of Im-COF _{F3}	4
2.2.2 Synthesis of Im-COF _{G1}	5
2.3 Synthesis of QCE-COFs.....	5
2.3.1 Typical synthetic procedure of QCE-COF _{F3} -Me.....	5
2.3.2 Synthesis of QCE-COF _{F3} -Men	6
3. Characterization of COFs	7
4. Copies of NMR spectra.....	15
5. References	18

1. General information

1.1 Materials

All the chemicals and reagents were purchased in analytical purity from commercial suppliers and used directly without further purification, except that 1,3,6,8-tetrakis(4-aminophenyl)pyrene (Tappy) and ¹³C-labeled terephthalaldehyde were synthesized according to the reported procedures.^{1,2}

1.2 Characterization techniques

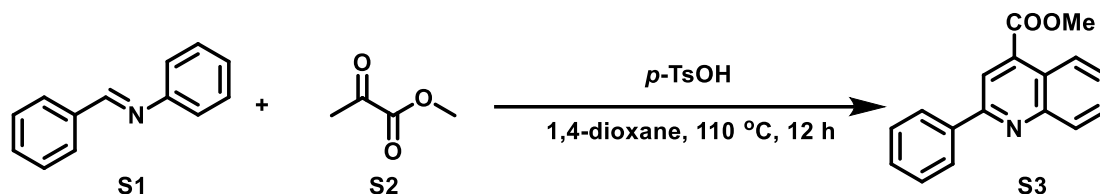
¹H NMR and ¹³C NMR were recorded on a Bruker Avance 600 MHz and 151 Hz spectrometers at 298 K, respectively. Chemical shift (δ) was reported in ppm relative to the residual solvent peaks. Peaks were reported as: s = singlet, d = doublet, td = triple doublet, m = multiplet or unresolved, with coupling constants in Hz. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 6700 spectrometer (Thermo Scientific, USA) equipped with an ATR cell. Powder X-ray diffraction (PXRD) analysis was conducted on a Bruker D8 Advance diffractometer with Cu K α radiation (2θ range: 2-40°; Scan step size: 0.02°; Time per step: 1 s). The specific Brunauer-Emmett-Teller (BET) surface area and pore size distribution were measured using a Micrometrics ASAP 2040 instrument at 77 K. High resolution transmission electron microscope (HR-TEM) images were obtained on a JEM-2100F instrument at an accelerating voltage of 200 kV. Solid-state ¹³C cross polarization magic angle spinning (¹³C-CP/MAS) NMR spectra were collected on a Bruker Avance III HD 400 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer with non-monochromatic Al K α x-rays as the excitation source and C 1s (284.8 eV) as the reference line. Thermal stability was investigated on a DZ-STA200 thermogravimetric analyzer with temperature ranging from 303 to 1073 K under N₂ atmosphere at a heating rate of 10 K min⁻¹. Thermogravimetric analysis (TGA) measurements were investigated on a DZ-STA200 thermogravimetric analyzer with temperature ranging from 303 to 1073 K under air atmosphere at a heating rate of 10 K min⁻¹. Circular dichroism (CD) spectra were carried out on a JASCO J-1500 spectropolarimeter in the

range of 200-400 nm using a 1 mm path length quartz cell (scan speed: 200 nm min⁻¹, band width: 4 nm). Samples were prepared by dispersing them in ethanol.

2. Synthetic procedures

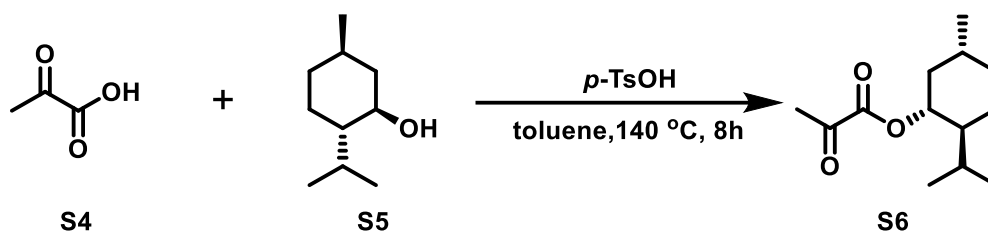
2.1 Model reaction

2.1.1 Synthesis of methyl-2-phenylquinoline-4-carboxylate



A 10 mL Schlenk tube was charged with *N*-Benzylideneaniline (S1, 38 mg, 0.20 mmol), methyl pyruvate (S2, 41 mg, 0.40 mmol), *p*-TsOH (7 mg, 0.04 mmol), and 2 mL of 1,4-dioxane. The mixture was stirred at 110 °C under an O₂ atmosphere for 12 hours. After cooling, the mixture was concentrated, and then purified by flash column chromatography on silica gel using the eluent (PE : EtOAc = 50 : 1) to yield methyl-2-phenylquinoline-4-carboxylate (S3, 45 mg, 86 %) as a colorless liquid. ¹H NMR (600 MHz, CDCl₃): δ 8.76 (d, *J* = 8.5 Hz, 1H), 8.41 (s, 1H), 8.24-8.20 (m, 3H), 7.79-7.76 (m, 1H), 7.65-7.62 (m, 1H), 7.56-7.54 (m, 2H), 7.50-7.48 (m, 1H), 4.08 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.9, 156.8, 149.3, 138.8, 135.6, 130.3, 130.0, 129.8, 129.0, 127.9, 127.5, 125.4, 124.0, 120.4, 52.8.

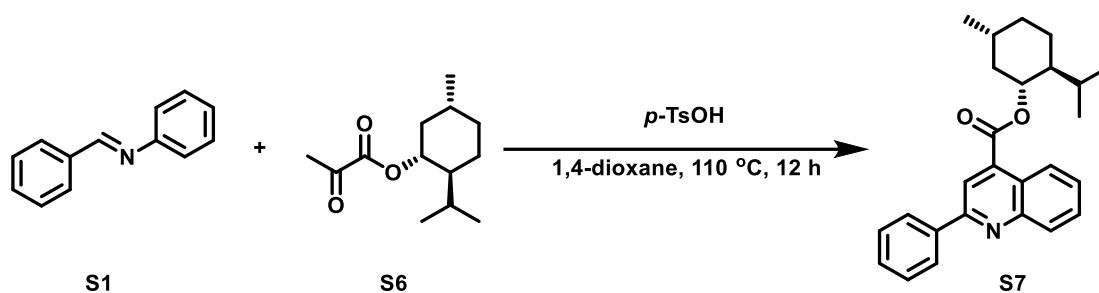
2.1.2 Synthesis of L-menthyl pyruvate



A round-bottom flask was charged with pyruvic acid (S4, 1.76 g, 20 mmol), L-menthol (S5, 3.43 g, 22 mmol), *p*-TsOH (344 mg, 2 mmol), and toluene (90 mL), and the mixture was reacted at 140 °C for 8 hours using a water separator. After cooling, the reaction was quenched by adding saturated NaHCO₃, and the mixture was then extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under vacuum. The resulting residue was then purified by flash column chromatography on silica gel using the eluent (PE :

EtOAc = 20 : 1) to yield product **S6** (2.45 g, 54 %) as a yellow oil. ¹H NMR (600 MHz, CDCl₃): δ 4.83 (td, *J* = 10.9 Hz, *J* = 4.4 Hz, 1H), 2.46 (s, 3H), 2.03-2.00 (m, 1H), 1.88-1.83 (m, 1H), 1.73-1.68 (m, 2H), 1.55-1.48 (m, 2H), 1.33-1.23 (m, 2H), 1.14-1.06 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 192.4, 160.6, 74.7, 40.4, 34.0, 31.4, 26.8, 26.2, 23.3, 21.9, 20.7, 16.2.

2.1.3 Synthesis of L-menthyl-2-phenylquinoline-4-carboxylate



A 10 mL Schlenk tube was charged with *N*-Benzylideneaniline (**S1**, 38 mg, 0.20 mmol), **S6** (155 mg, 0.40 mmol), *p*-TsOH (7 mg, 0.04 mmol), and 2 mL of 1,4-dioxane. The mixture was stirred at 110 °C under an O₂ atmosphere for 12 hours. After cooling, the mixture was concentrated, and then purified by flash column chromatography on silica gel using the eluent (PE : EtOAc = 50 : 1) to yield L-menthyl-2-phenylquinoline-4-carboxylate (**S7**, 56.8 mg, 73 %) as a colorless liquid. ¹H NMR (600 MHz, CDCl₃): δ 8.73 (d, *J* = 9.3 Hz, 1H), 8.35 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.21 (m, 2H), 7.79-7.76 (m, 1H), 7.65-7.62 (m, 1H), 7.58-7.55 (m, 2H), 7.51-7.49 (m, 1H), 5.17 (td, *J* = 11.0 Hz, *J* = 4.5 Hz, 1H), 2.29-2.25 (m, 1H), 2.04-1.99 (m, 1H), 1.81-1.76 (m, 2H), 1.66-1.61 (m, 2H), 1.30-1.16 (m, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.1, 156.8, 149.3, 139.0, 136.7, 130.3, 129.9, 129.7, 129.0, 127.7, 127.5, 125.4, 124.1, 119.9, 47.2, 41.0, 34.2, 31.6, 26.6, 23.5, 22.1, 20.8, 16.4.

2.2 Synthesis of Im-COFs

2.2.1 Synthesis of Im-COF_{F3}

1,3,6,8-tetrakis(4-aminophenyl)pyrene (Tappyl) (29 mg, 0.05 mmol) and terephthalaldehyde (14 mg, 0.10 mmol) were sequentially added to a Pyrex glass tube

along with a mixed solution of *o*-DCB (0.7 mL) and *n*-BuOH (0.7 mL). The tube was then sonicated for 15 minutes. After adding aqueous acetic acid (6 M, 0.1 mL), the glass tube underwent three freeze-pump-thaw cycles to degas before being sealed under vacuum. Subsequently, the sealed tube was heated in an oven at 120 °C for 3 days. Upon cooling, the resulting suspension was centrifuged to separate the solid material, which was then washed repeatedly with THF and MeOH until the solvent became colorless. The final product, **Im-COF_{F3}**, was obtained as a yellow powder (35 mg, 91 % yield) after being dried under vacuum at 60 °C.

2.2.2 Synthesis of Im-COF_{G1}

1,3,5-Tris(4-aminophenyl)benzene (18 mg, 0.05 mmol) and 2,5-Dimethoxy-1,4-benzenedicarboxaldehyde (15 mg, 0.075 mmol) were sequentially added to a Pyrex glass tube along with a mixed solution of Mesitylene (0.6 mL) and 1,4-Dioxane (0.6 mL). The tube was then sonicated for 15 minutes. After adding aqueous acetic acid (6 M, 0.1 mL), the glass tube underwent three freeze-pump-thaw cycles to degas before being sealed under vacuum. Subsequently, the sealed tube was heated in an oven at 120 °C for 3 days. Upon cooling, the resulting suspension was centrifuged to separate the solid material, which was then washed repeatedly with THF and MeOH until the solvent became colorless. The final product, **Im-COF_{G1}**, was obtained as a yellow powder (26 mg, 89 % yield) after being dried under vacuum at 60 °C.

2.3 Synthesis of QCE-COFs

2.3.1 Typical synthetic procedure of QCE-COF_{F3}-Me

A 10 mL Schlenk tube was charged with **Im-COF_{F3}** (38 mg, theoretically containing 0.20 mmol of imine linkages), methyl pyruvate (**S2**, 51 mg, 0.5 mmol), *p*-TsOH (7 mg, 0.04 mmol), and 2 mL of 1,4-dioxane. The mixture was stirred at 110 °C under an O₂ atmosphere for 36 hours. After cooling, the solid was filtered under reduced pressure and washed sequentially with CH₃OH, aqueous ammonia, water, and CH₃OH. The final product, **QCE-COF_{F3}-Me**, was obtained as an orange powder (47 mg, 85 % yield) after being dried under vacuum at 60 °C.

QCE-COF_{F3}-Et, **QCE-COF_{G1}-Me** and **QCE-COF_{G1}-Et** were synthesized similarly following the procedure for the synthesis of **QCE-COF_{F3}-Me**.

2.3.2 Synthesis of **QCE-COF_{F3}-Men**

A 10 mL Schlenk tube was charged with **Im-COF_{F3}** (38 mg), L-menthyl pyruvate (**S7**, 113 mg, 0.5 mmol), *p*-TsOH (7 mg, 0.04 mmol), and 2 mL of 1,4-dioxane. The mixture was stirred at 110 °C under an O₂ atmosphere for 72 hours. After cooling, the solid was filtered under reduced pressure and washed sequentially with CH₃OH, aqueous ammonia, water, and CH₃OH. The final product, **QCE-COF_{F3}-Men**, was obtained as an orange powder (50 mg, 62 % yield) after being dried under vacuum at 60 °C.

3. Characterization of COFs

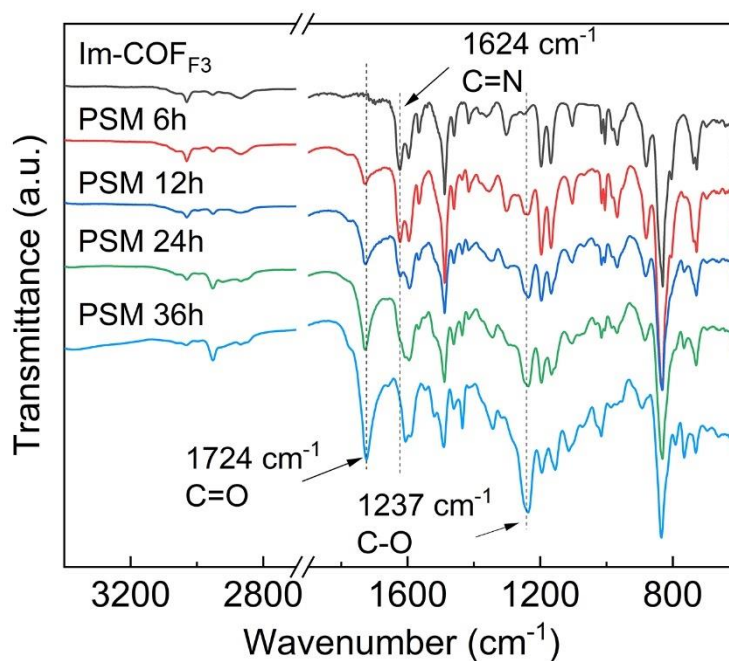


Fig. S1 FT-IR monitoring of the synthesis of QCE-COF_{F3}-Me.

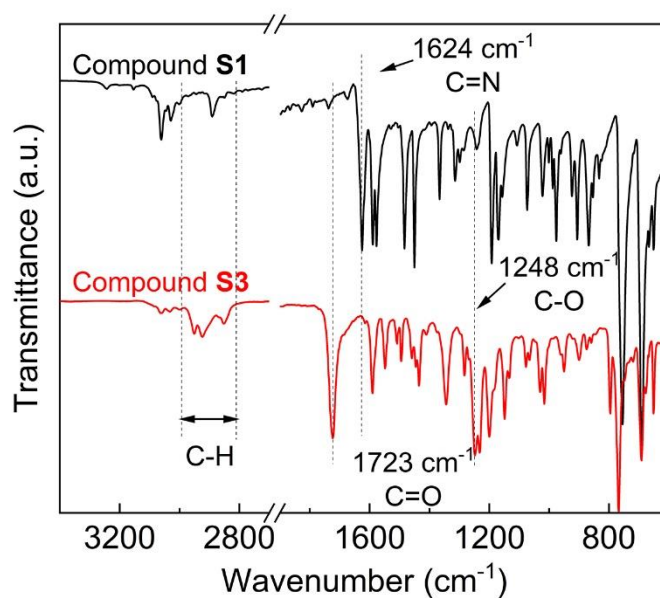


Fig. S2 FT-IR spectra of model reactant S1 and model product S3 in the model reaction.

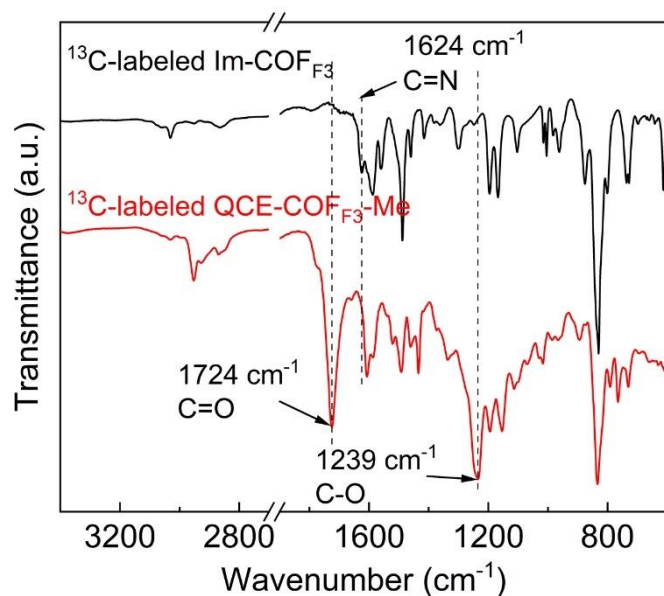


Fig. S3 FT-IR spectra of ^{13}C labeled $\text{Im-COF}_{\text{F}_3}$ and $\text{QCE-COF}_{\text{F}_3}\text{-Me}$.

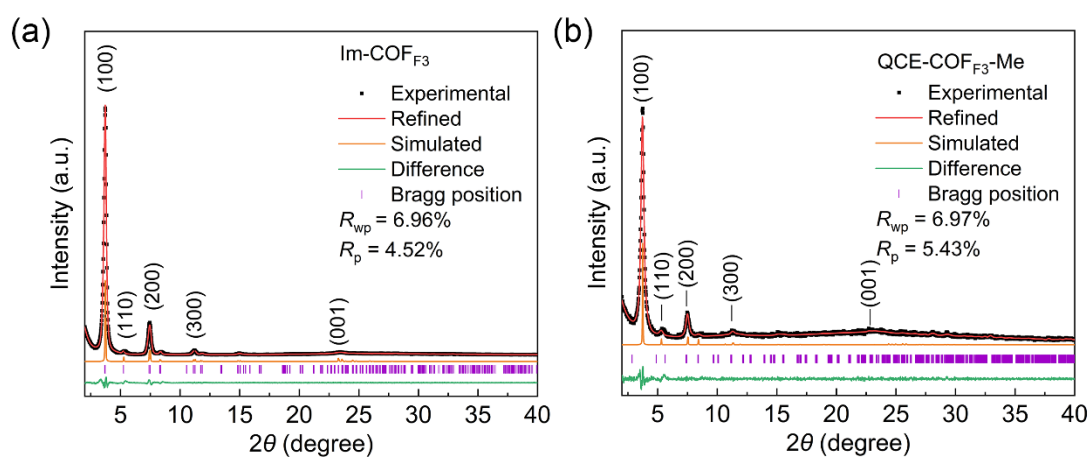


Fig. S4 PXRD patterns of $\text{Im-COF}_{\text{F}_3}$ (a) and $\text{QCE-COF}_{\text{F}_3}\text{-Me}$ (b).

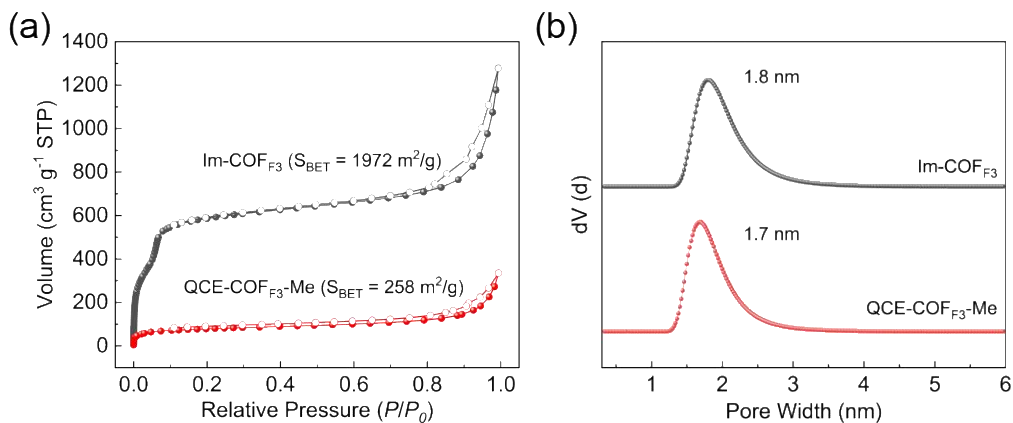


Fig. S5 (a) N_2 sorption isotherm curves. (b) Pore size distribution.

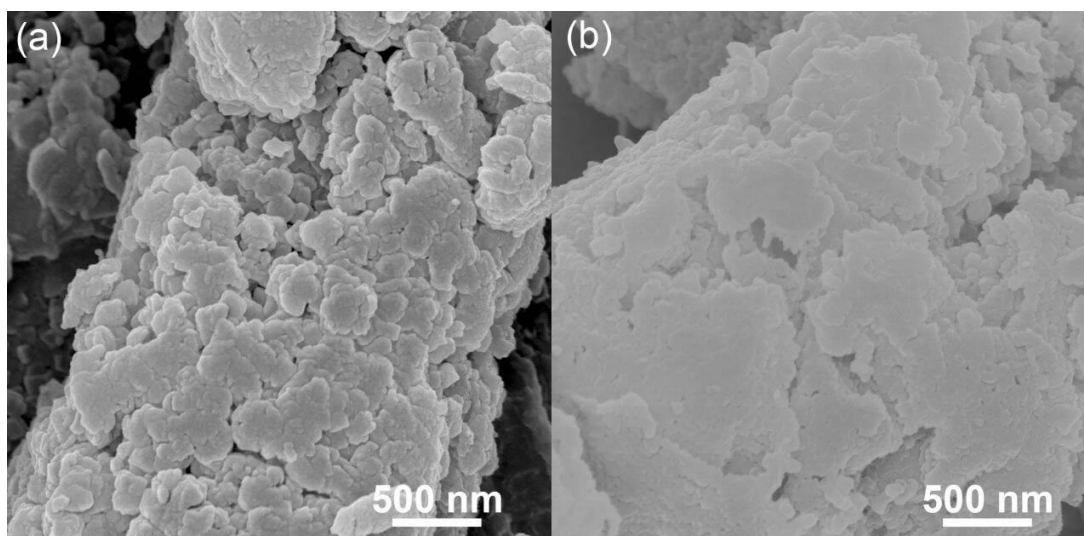


Fig. S6 SEM images of (a) **Im-COF_{F3}** and (b) **QCE-COF_{F3}-Me**.

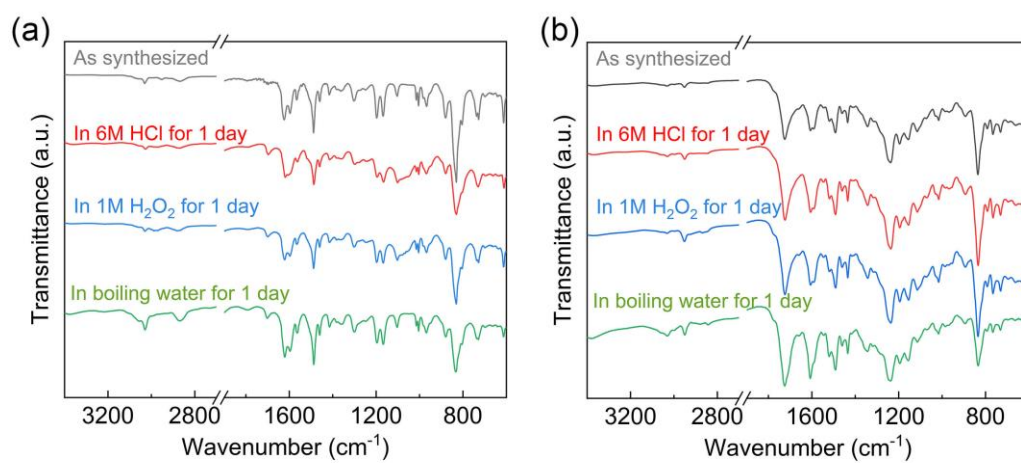


Fig. S7 FT-IR spectra of **Im-COF_{F3}** (a) and **QCE-COF_{F3}-Me** (b) before and after treatment with 6M HCl, 1M H₂O₂ and 100 °C H₂O for 1 day.

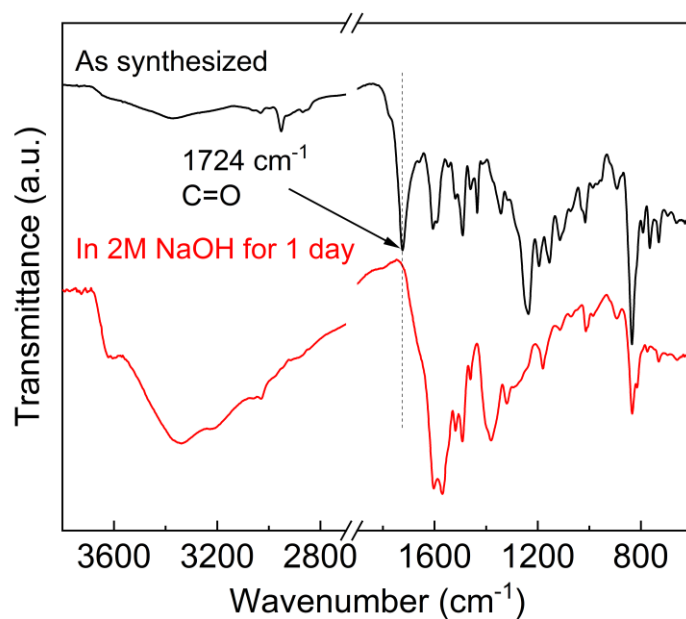


Fig. S8 FT-IR spectra of **QCE-COF_{F3}-Me** before and after treatment with 2M NaOH for 1 day.

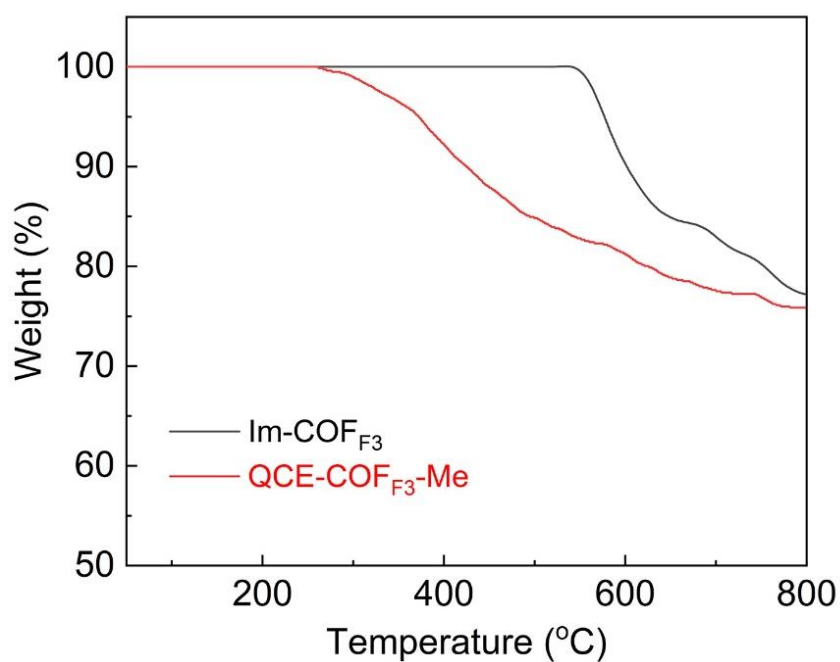


Fig. S9 Thermal stability of **Im-COF_{F3}** and **QCE-COF_{F3}-Me** under N₂ atmosphere.

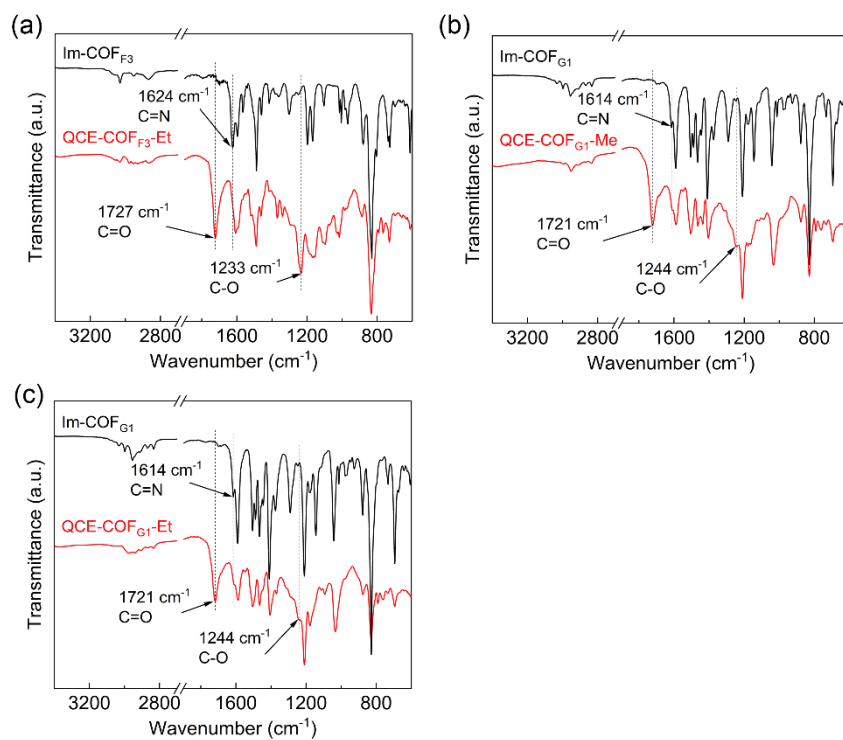


Fig. S10 FT-IR spectra. (a) **Im-COF_{F3}** and **QCE-COF_{F3}-Et**. (b) **Im-COF_{G1}** and **QCE-COF_{G1}-Me**. (c) **Im-COF_{G1}** and **QCE-COF_{G1}-Et**.

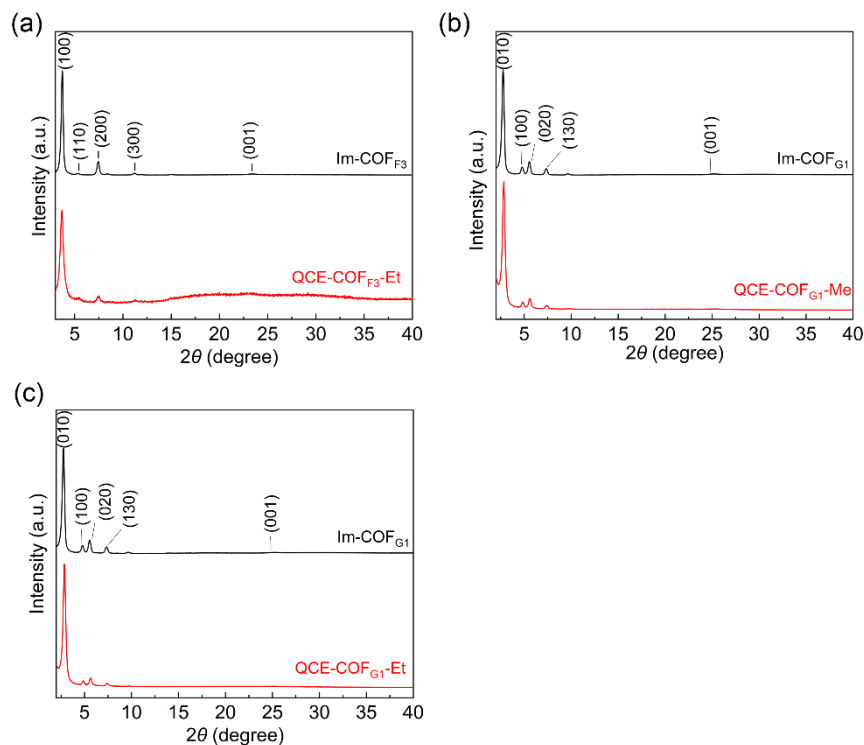


Fig. S11 Experimental PXRD patterns. (a) **Im-COF_{F3}** and **QCE-COF_{F3}-Et**. (b) **Im-COF_{G1}** and **QCE-COF_{G1}-Me**. (c) **Im-COF_{G1}** and **QCE-COF_{G1}-Et**.

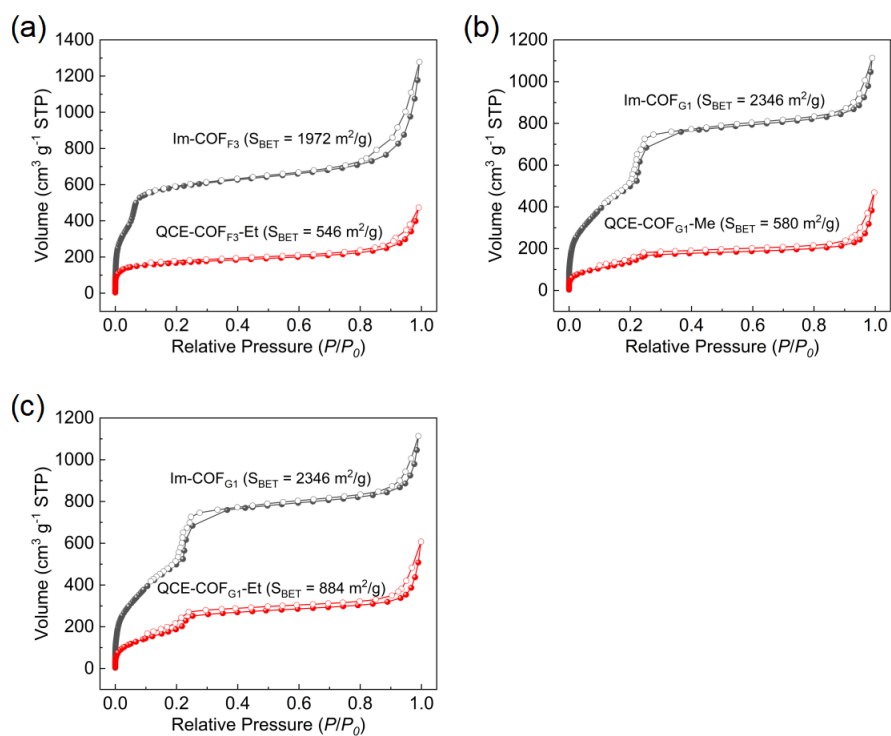


Fig. S12 N₂ sorption isotherm curves.

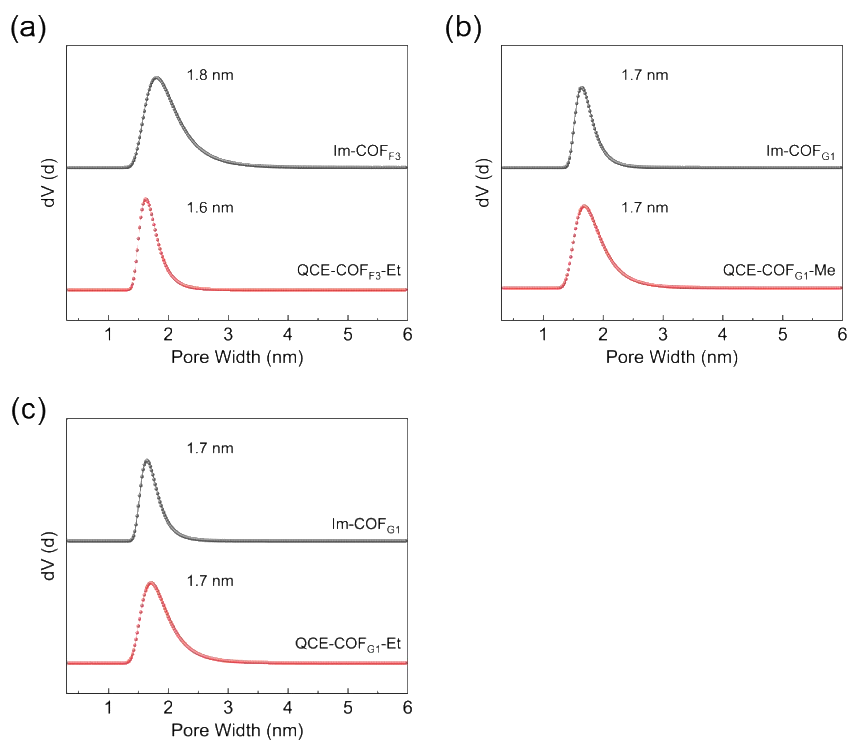


Fig. S13 Pore size distribution.

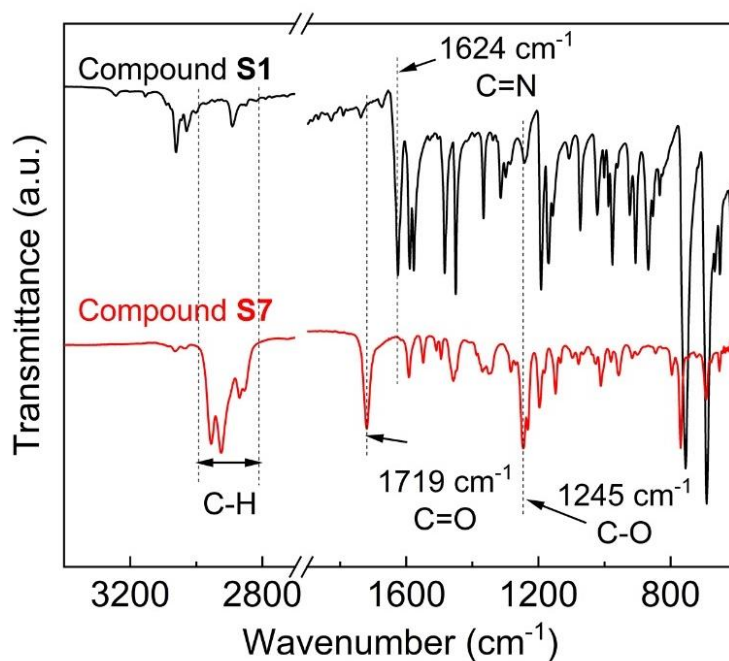


Fig. S14 FT-IR spectra of model reactant **S1** and model product **S7** in the model reaction.

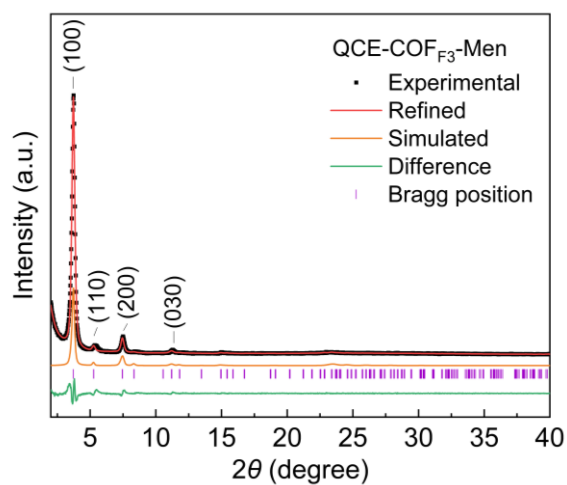


Fig. S15 PXRD patterns of **QCE-COF₃-Men**.

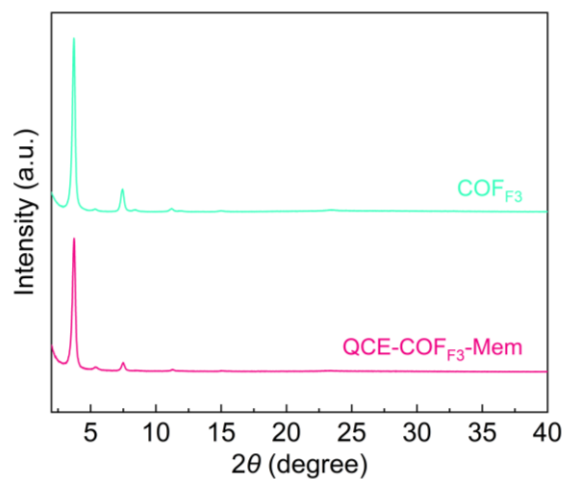


Fig. S16 Experimental PXRD patterns.

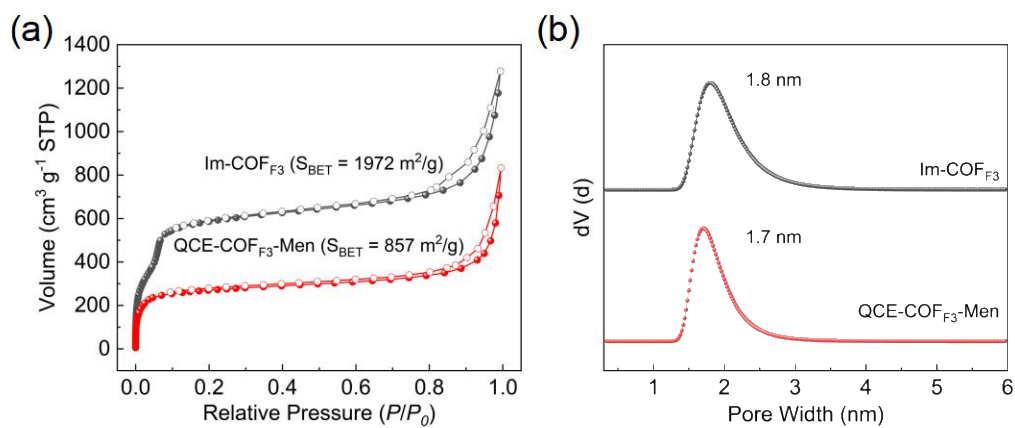


Fig. S17 (a) N_2 sorption isotherm curves. (b) Pore size distribution.

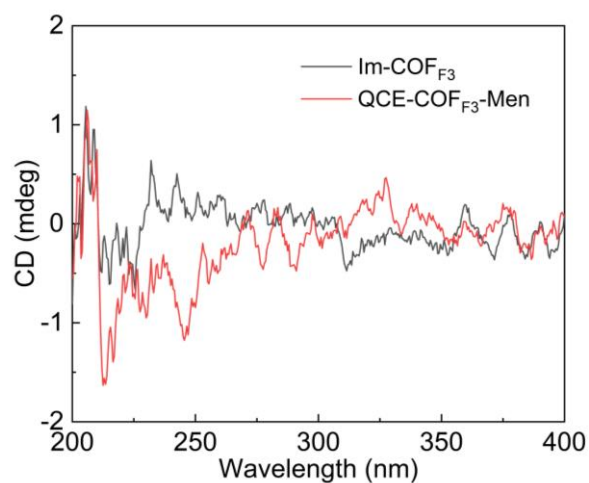


Fig. S18 CD spectra of **Im-COF_{F3}** and **QCE-COF_{F3}-Men**.

4. Copies of NMR spectra

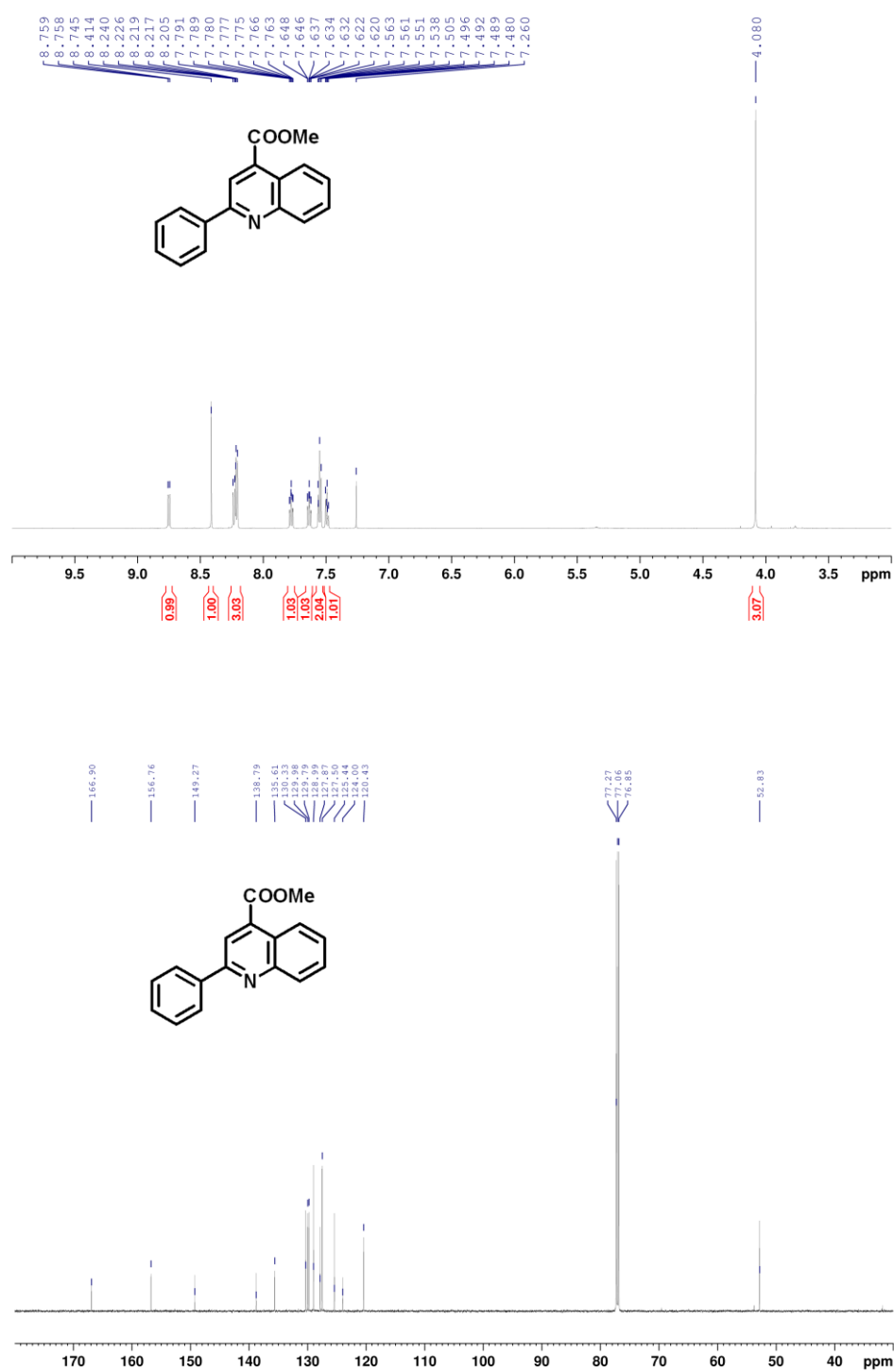


Fig. S19 ¹H NMR and ¹³C NMR spectra of methyl-2-phenylquinoline-4-carboxylate.

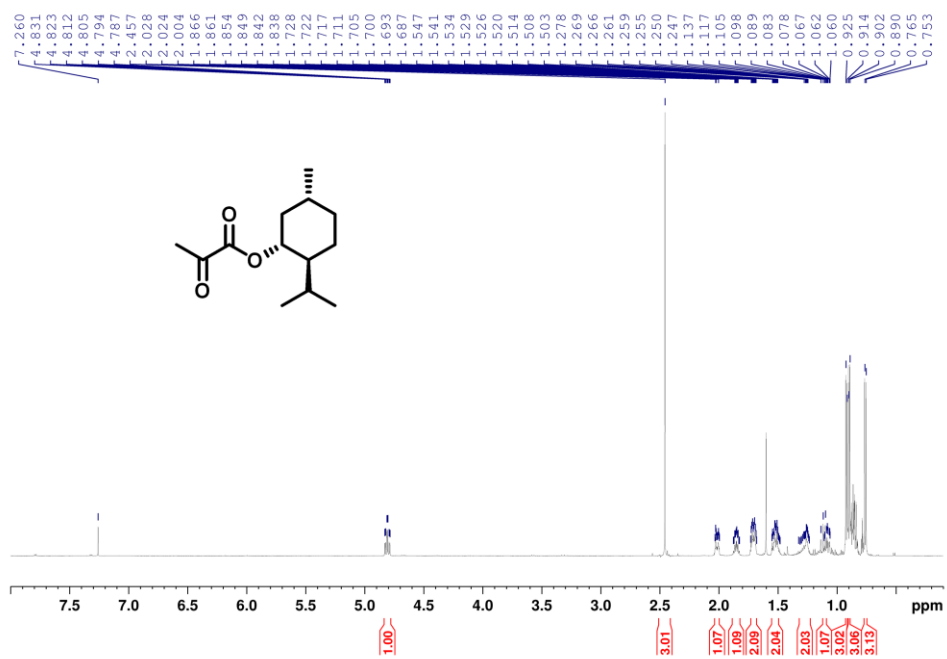


Fig. S20 ¹H NMR and ¹³C NMR spectra of L-menthyl pyruvate.

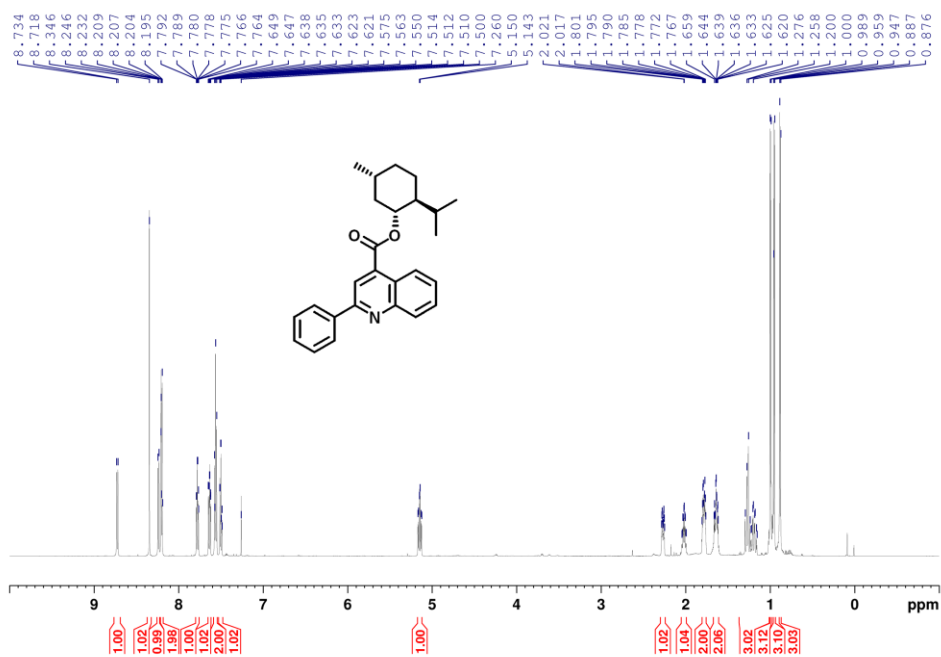
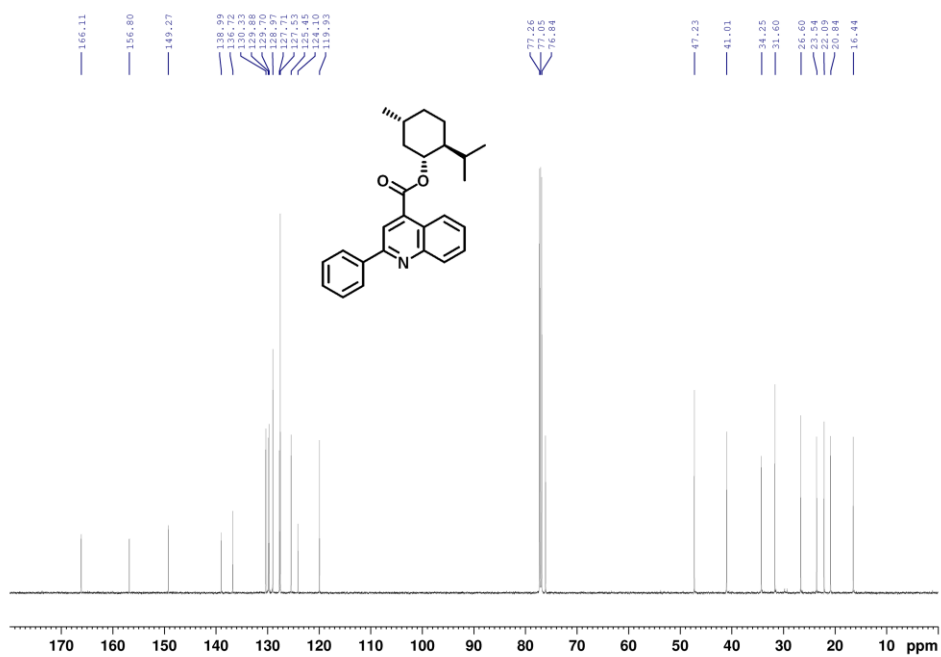


Fig. S21 ¹H NMR and ¹³C NMR spectra of L-menthyl-2-phenylquinoline-4-carboxylate.

5. References

1. Zhao, X.; Pang, H.; Huang, D.; Liu, G.; Hu, J.; Xiang, Y. *Angew. Chem. Int. Ed.* 2022, **61**, e202208833.
2. Zhu, Y.; Huang, D.; Wang, W.; Liu, G.; Ding, C.; Xiang, Y. *Angew. Chem. Int. Ed.* 2024, **63**, e202319909.