

Acceptor-extended donor-acceptor COFs enable charge-polarization tuning for efficient photocatalytic C–H oxidation

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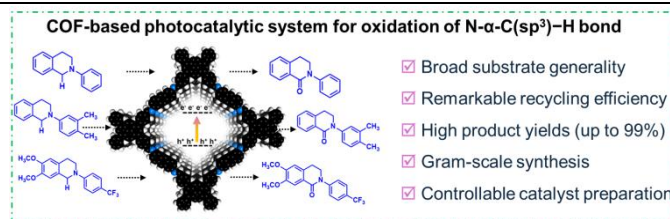
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Efficient COF-based photocatalytic system for synthesis of isoquinolinones and its derivatives by direct oxidation of the *N*- α -C(sp³)-H bond in tetrahydroisoquinolines.

Acceptor-extended donor-acceptor COFs enable charge-polarization tuning for efficient photocatalytic C–H oxidation

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ABSTRACT: Rational modulation of charge polarization in covalent organic frameworks constitutes a fundamental strategy for optimizing photocatalytic performance, yet achieving precise and systematic control over these parameters remains a significant challenge. Moreover, the interplay in covalent organic frameworks between molecular dipole moments, electronic structure, and catalytic activity is poorly understood. Here, we demonstrate that controlled extension of the acceptor unit in donor–acceptor (D–A) type COFs provides an effective handle for tuning charge polarization. By systematically elongating the acceptor linker from phenylene to naphthalene and anthracene, we achieve progressive modulation of the molecular dipole moment, accompanied by narrowed bandgaps and suppressed charge recombination, as confirmed by combined spectroscopic and density functional theory analyses. When evaluated in the photocatalytic oxidation of tetrahydroisoquinolines, the anthracene-linked Aa-COF delivers near-quantitative product yield (98%) under mild conditions, with scalability demonstrated via gram-scale synthesis and solar-driven operation. Mechanistic studies implicate superoxide and singlet oxygen as the primary reactive species, while Fukui analysis identifies enhanced nucleophilicity as a key factor facilitating oxygen activation. This work establishes acceptor extension as a viable design principle for polarization-modulated COF photocatalysts, offering a generalizable approach for selective organic transformations under sustainable conditions.

KEYWORDS: covalent-organic frameworks, pore engineering, photocatalytic oxidation, tetrahydroisoquinolines, density functional theory (DFT)

1 Instruction

The direct oxidation of the $N\text{--}\alpha\text{--C}(\text{sp}^3)\text{--H}$ bond in tetrahydroisoquinoline (THIQ) derivatives has attracted considerable attention, as the resulting isoquinolinone heterocyclic scaffold is widely present in various natural alkaloids, bioactive compounds, and drug molecules, and holds significant structural significance (Figure 1a)[1–4]. Although the conversion of tetrahydroisoquinoline to dihydroisoquinoline ketone has been reported in cross-dehydrogenative coupling reactions, this transformation typically occurs only as a side reaction, unsatisfactory product yield, insufficient catalyst reusability (Figure 1b), and stringent oxidizing conditions, efficient selective control remains challenging to achieve[5–8]. Consequently, the development of an efficient and general protocol for the direct oxidation of the $N\text{--}\alpha\text{--C}(\text{sp}^3)\text{--H}$ bond in tetrahydroisoquinolines under mild conditions remains a compelling objective in synthetic chemistry.

To address these challenges, covalent organic frameworks (COFs) have emerged as promising photocatalysts by virtue of

their structural periodicity, synthetic tunability, and extended π -conjugation[9–12]. Unlike conventional photocatalysts, the modular construction of COFs allows the electronic structure and pore environment to be independently tailored at the molecular level[13–15]. Among the various design parameters, charge polarization originating from the spatial separation of electron-rich and electron-deficient units within the framework has recently come into focus as a key factor governing exciton dissociation, charge carrier dynamics, and the energetics of reactive oxygen species generation[16–18]. Despite this potential, the relationship between molecular-level polarization and macroscopic photocatalytic activity remains poorly understood, largely owing to the lack of systematic structural series that enable controlled modulation of dipole moments while minimizing confounding variables[19–22]. Clarifying this structure–property relationship is essential for the rational development of COF photocatalysts with enhanced performance in selective oxidative transformations.

Herein, we report a systematic strategy for tuning charge polarization in D–A COFs through controlled elongation of the

acceptor linker (Figure 1c). Specifically, three pyrene-based frameworks are constructed by condensing a common tetraphenylpyrene donor node with three different aromatic diamines—phenylene (Pa), naphthalene (Na), and anthracene (Aa) (Figure 1d), to achieve incremental extension of the acceptor unit. This design enables progressive modulation of the dipole moment and charge density distribution while simultaneously affording systematic variation in pore dimensions, allowing us to disentangle the contributions of electronic and steric factors to photocatalytic activity. Through a combination of experimental characterization and DFT calculations, we establish a clear correlation between acceptor length, charge polarization, and catalytic performance in the

photocatalytic oxidation of tetrahydroisoquinolines, a transformation of synthetic relevance that exemplifies the challenges of selective C–H functionalization. The anthracene-linked Aa-COF delivers exceptional activity (98% yield) under mild conditions (Figure 1e), with mechanistic studies implicating superoxide and singlet oxygen as the key reactive species. Notably, the anthracene-linked Aa-COF exhibits the lowest average local ionization energy (ALIE) value (Figure 1f)[23, 24], reflecting its superior electron-donating capacity for O₂ activation. Collectively, these findings establish a direct correlation between linker extension, charge polarization, and photocatalytic efficiency, providing a design principle for COF-based C–H functionalization.

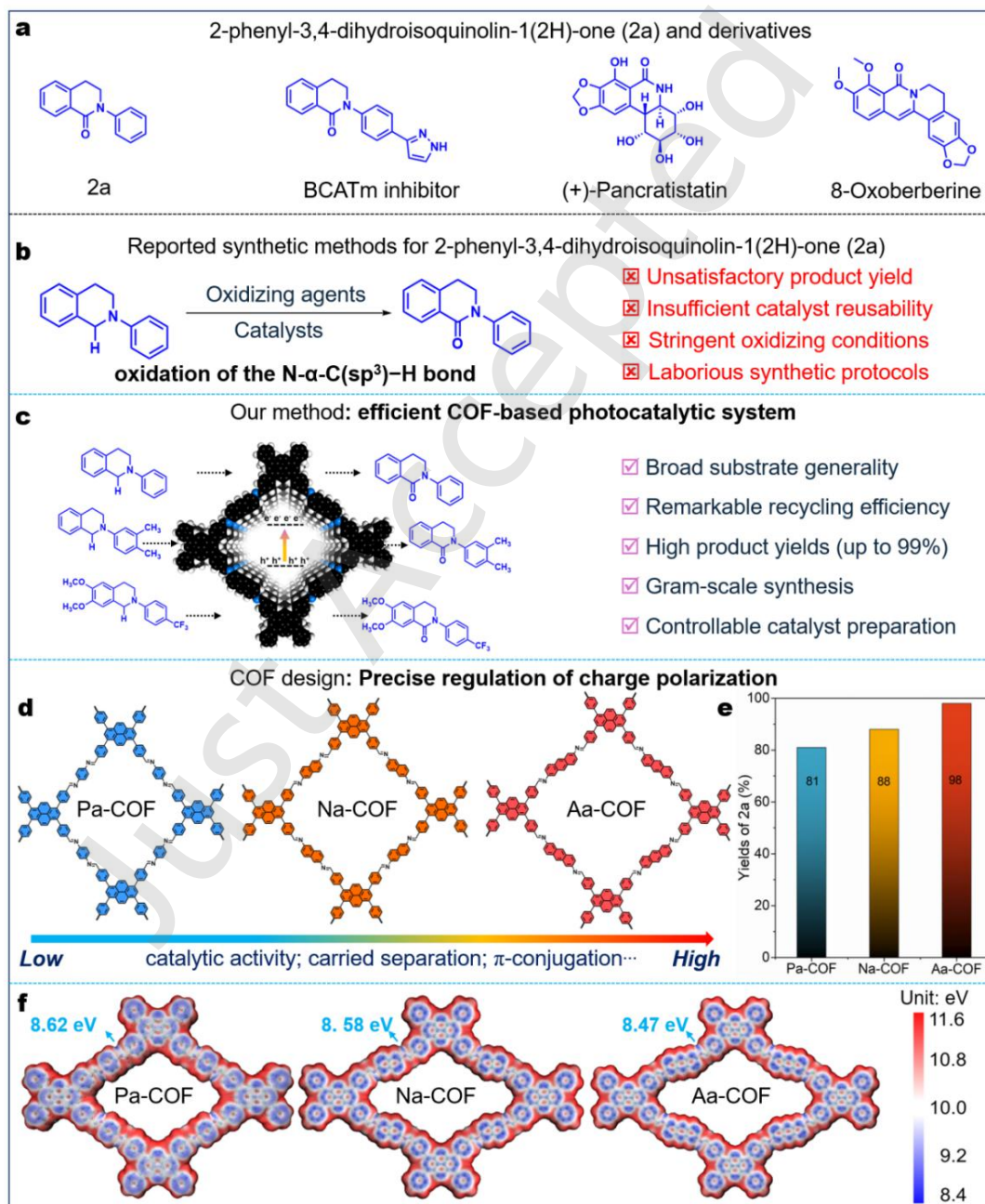


Figure 1. (a) The chemical structures of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one and derivatives. (b) The reported synthesis method of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one by oxidation of the N- α -C(sp³)-H bond and challenges. (c) The designed photocatalytic system based on COF for synthesis of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one. (d) Chemical structure of various pore size Pa-COF, Na-COF and Aa-COF photocatalysts. (e) Yield of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one comparison with Pa-COF, Na-COF and Aa-COF photocatalysts. (f) Average local ionization energy of Pa-COF, Na-COF, and Aa-COF.

2 Experimental

2.1 Materials

All the starting materials and solvents, unless otherwise noted, are used without purification. 1,3,6,8-Tetrakis(4-formylphenyl)pyrene (TFPPy), *p*-Phenylenediamine (Pa), naphthalene-2,6-diamine (Na) and anthracene-2,6-diamine (Aa) were purchased from the Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. 1,2-Dichlorobenzene, *n*-butanol, CH₃COOH (6.0 M), anhydrous acetonitrile (purity ≥99.9%, water content <50 ppm) without further purification, were obtained from Shanghai Titan Scientific Co. Ltd. Liquid N₂ were obtained from Kunming PENGYIDA Gas Products Co. Ltd. All tetrahydroisoquinoline derivatives employed for photocatalytic performance evaluation were self-synthesized following the reported literature procedures[25].

2.1 synthesis of Pa-COF, Na-COF and Aa-COF

A Pyrex tube was charged with 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde (12.3 mg, 0.02 mmol) and the corresponding linkers (1,4-diaminobenzene: 4.3 mg, 0.04 mmol; naphthalene-2,6-diamine: 6.4 mg, 0.04 mmol; anthracene-2,6-diamine: 8.3 mg, 0.04 mmol). A 1 mL mixed solution of *n*-butanol/1,2-dichlorobenzene (1:1, v/v) was then added to the tube, followed by sonication for 10.0 min. Acetic acid (0.2 mL, 6 M) was subsequently added to the resulting mixture. The tube was frozen in a liquid nitrogen bath and sealed under vacuum conditions. After sealing, the tube was placed in an oven maintained at 120 °C for 3 days. Upon cooling to room temperature, the resulting solid product was collected by filtration and thoroughly washed with tetrahydrofuran (THF) several times. The obtained solid was immersed in anhydrous THF for 24 h, with the solvent replaced six times daily using fresh anhydrous THF. Finally, the activated samples were dried under vacuum at 120 °C for 12 h to afford Pa-COF, Na-COF, and Aa-COF powders (yield with 85%), respectively.

2.3 The oxidation of N- α -C(sp³)-H bond in tetrahydroisoquinolines

An oven-dried 10 mL Schlenk tube fitted with a magnetic stir bar was charged sequentially with tetrahydroisoquinolines (0.2 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.3 mmol), photocatalyst (Pa-COF, 10 mg; Na-COF, 10 mg; or Aa-COF, 10 mg), and acetonitrile (CH₃ CN, 4 mL). The reaction system was then exposed to N₂ and stirred at room temperature for a period of 24 hours, while being irradiated by a 100 W white LED at a distance of 8 cm. Once the reaction was complete, the mixture was diluted with H₂O and ethyl acetate, the layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na₂SO₄), filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography using a gradient eluent of *n*-hexane/ethyl acetate (v/v = 10:1 to 1:1) to afford the corresponding oxidation products **2a–2k** as pure compounds.

2.4 Characterizations

The microstructures of prepared COFs were studied by scanning electron microscope (SEM, Zeiss Sigma 300) and transmission electron micrographs images (TEM, JEM-F200). The

crystallinity of obtained COFs was measured by powder X-ray diffraction (PXRD) and recorded using a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA over 2° to 40° 2 θ range with a Cu K α radiation. The porosity of synthesized COFs was investigated by nitrogen adsorption-desorption isotherms measured at 77 K on an Autosorb IQ2 absorptiometer (Quantachrome Instruments). Solid-state nuclear magnetic resonance (NMR) experiments were conducted using an Agilent VNMRs 600 MHz NMR spectrometer at room temperature. X-ray photoelectron spectroscopy (XPS) was conducted to demonstrate the chemical component in an Escalab 250Xi instrument from Thermo Scientific equipped with an Al K α microfocused X-ray source, and the C 1 s peak at 284.8 eV was used as an internal standard. Variable temperature electron paramagnetic resonance (EPR) spectra were recorded by an A300 (Bruker EMXplus-6/1) spectrometer. Fourier transform infrared (FT-IR) spectroscopy was performed with a Thermo NICOLET iS50 FT-IR. UV-visible absorption spectra were obtained via the Kubelka–Munk transformation from the diffuse reflectance spectra (DRS) measured on an UV-visible spectrophotometer (UV-2600, Japan) equipped with an integrating sphere. The steady-state photoluminescence (PL) emission spectra were obtained by directly detecting powder samples via a fluorescence spectrometer (FL4500, Japan) with an excitation wavelength of 505 nm. All air- and moisture-sensitive solutions and chemicals were handled under an argon atmosphere. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel60 F₂₅₄ plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker Avance III 400 at 400 MHz. Carbon-13 nuclear magnetic resonance (¹³C-NMR) was recorded on Bruker Avance III 400 spectrometer at 100 MHz. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz.

2.5 Theoretical calculation simulation

All theoretical calculations were conducted using Materials Studio. Three COF models (Pa-COF, Na-COF, Aa-COF) were constructed with the Forcite module. Geometry optimization was performed using the CASTEP and DMol3 modules. On the basis of the optimized structures, Mulliken atomic charges, electron density, electrostatic potential, density of states, Fukui functions, electron localization function, average local ionization energy, adsorption energy, and frontier orbitals (HOMO-LUMO) were further calculated. The accuracy of the computational model was ensured by accurately describing electronic exchange and correlation energies within the generalized gradient approximation (GGA) framework using the Perdew-Burke-Ernzerhof (PBE) functional[26]. The Grimme method accounted for van der Waals interactions, with the kinetic energy cutoff set at 570 eV[27, 28]. The energy convergence value between two consecutive steps was chosen to be 1 × 10⁻⁵ eV/atom, with the maximum allowable force below 0.03 eV/Å and the maximum allowable displacement below 0.005 Å. The average local

ionization energy was visualized through Multiwfn and VMD, with corresponding results presented in graphical form[29, 30].

3 Results and discussion

3.1 COFs photocatalysts synthesis and characterization

To implement the designed synthetic strategy, 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) is judiciously selected as the tetrahedral node to construct π -electron-rich covalent organic frameworks (COFs). This core unit is subsequently condensed with a series of linear aromatic diamines of varying lengths—namely, *p*-phenylenediamine (Pa), naphthalene-2,6-diamine (Na), and anthracene-2,6-diamine (Aa)—to systematically modulate the pore dimensions and π -conjugation extent of the resulting frameworks. Through this approach, three distinct COF materials, designated as Pa-COF, Na-COF, and Aa-COF, are successfully synthesized in *n*-butanol/1,2-dichlorobenzene (Figure S1). These frameworks exhibit tunable pore architectures and progressively expanded conjugated domains, providing an ideal platform for investigating the effects of linker length on the structural and electronic properties of pyrene-based COFs. The phase purity and completeness of the condensation reactions for the as-synthesized COFs are confirmed by comparing their powder X-ray diffraction (PXRD) profiles with those of the corresponding monomeric precursors (Figures S2–S4). The absence of diffraction peaks attributable to the starting materials in the patterns of the frameworks, coupled

with the emergence of distinct new reflections characteristic of the extended crystalline lattices, unequivocally demonstrates the successful conversion into the desired porous architectures. The sharp reflections of Pa-COF, Na-COF, and Aa-COF in PXRD (Figure S5) can be observed at 2θ in 3.78° ($d=23.36 \text{ \AA}$), 3.46° ($d=25.51 \text{ \AA}$) and 3.16° ($d=27.94 \text{ \AA}$) [31]. The progressive shift of these primary reflections toward lower angles along the series from Pa-COF to Aa-COF is indicative of an increasing unit cell dimension, which directly correlates with the expanding pore apertures resulting from the employment of elongated diamine linkers. This systematic variation in the diffraction profiles corroborates the successful construction of frameworks with tunable pore architectures. To gain deeper insight into the molecular packing configurations of the Pa-COF, Na-COF, and Aa-COF—representative AA and AB stacking models are constructed and are presented in Figures S6–S8. The simulated structures reveal that all three frameworks preferentially adopt a highly ordered AA-stacking arrangement characterized by square topology, which is in excellent agreement with the experimental PXRD patterns. Such an eclipsed stacking geometry is widely recognized for promoting effective charge carrier transport across adjacent layers and imparting enhanced structural robustness[32]. These favorable attributes are likely to play a pivotal role in underpinning the photocatalytic behavior of the COFs.

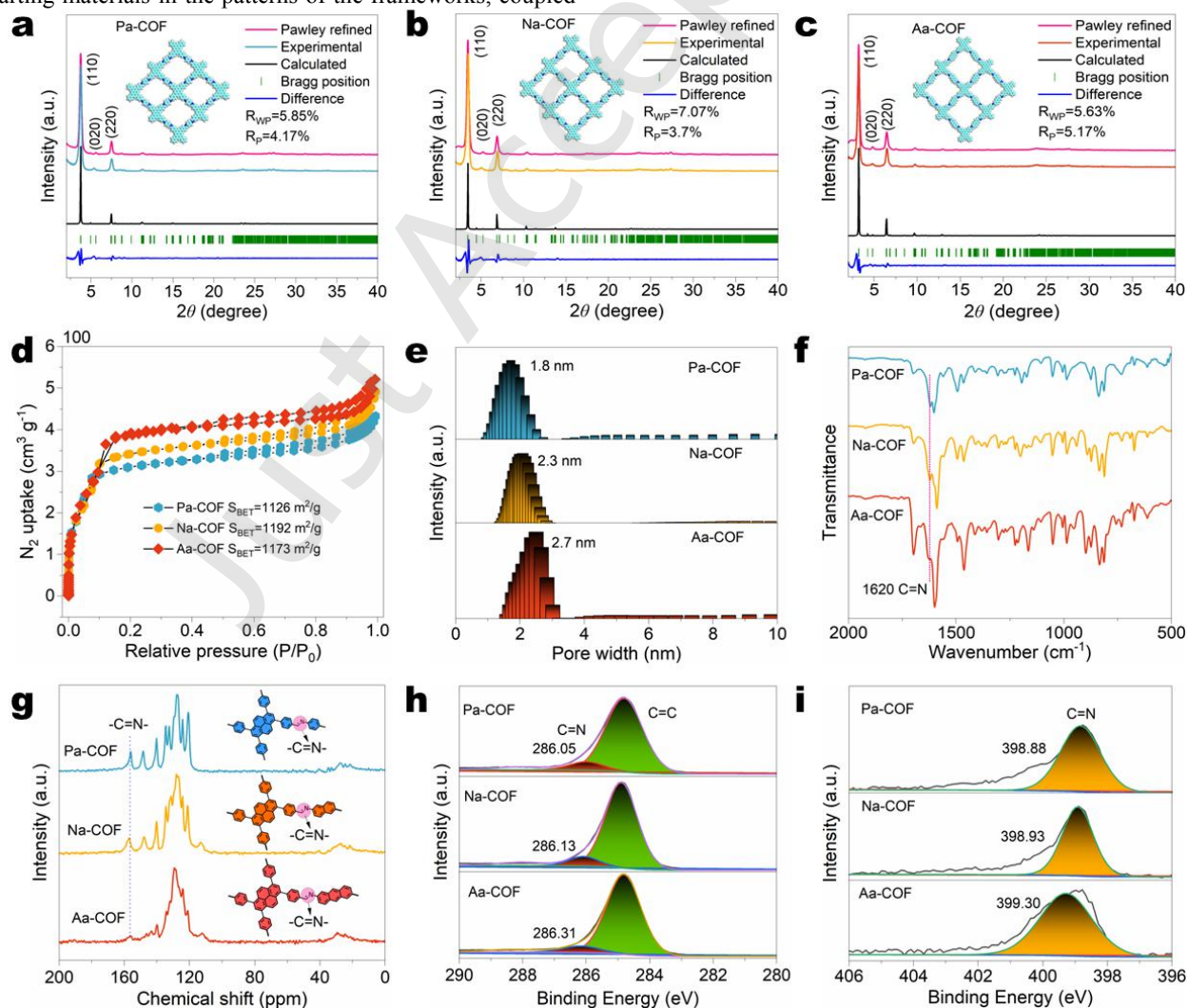


Figure 2. PXRD and Pawley refinement patterns of (a) Pa-COF, (b) Na-COF, and (c) Aa-COF. (d) N_2 adsorption-desorption isotherms and BET surface area of

Pa-COF, Na-COF, and Aa-COF. (e) Pore size distribution of Pa-COF, Na-COF, and Aa-COF. (f) FT-IR spectra of Pa-COF, Na-COF, and Aa-COF. (g) Solid-state ^{13}C NMR spectra of Pa-COF, Na-COF, and Aa-COF. High-resolution (h) XPS C 1s and (i) N 1s of Pa-COF, Na-COF, and Aa-COF.

To validate the structural models, Pawley refinement is conducted against the experimental PXRD profiles, yielding excellent agreement between the observed and simulated patterns. For Pa-COF, the refinement converges with residual factors of $R_p = 4.17\%$ and $R_{wp} = 5.85\%$ (Figure 2a). Similarly, Na-COF shows $R_p = 3.70\%$ and $R_{wp} = 7.07\%$ (Figure 2b), while Aa-COF exhibits $R_p = 5.17\%$ and $R_{wp} = 5.63\%$ (Figure 2c). The low magnitudes of these residuals confirm the reliability of the proposed structural models. Furthermore, the refined patterns distinctly reveal well-resolved diffraction peaks corresponding to the (110), (020), and (220) crystallographic planes, which are characteristic of the adopted structural symmetry. The presence of these higher-order reflections substantiates the existence of extended in-plane periodicity and long-range structural coherence within the frameworks, underscoring the high crystallinity and architectural regularity achieved across the series.

To elucidate the textural properties of the as-synthesized

frameworks, nitrogen physisorption measurements were performed at 77 K. The Brunauer–Emmett–Teller (BET) surface areas were calculated to be $1126\text{ m}^2\cdot\text{g}^{-1}$ for Pa-COF, $1192\text{ m}^2\cdot\text{g}^{-1}$ for Na-COF, and $1173\text{ m}^2\cdot\text{g}^{-1}$ for Aa-COF (Figure 2d). These values, which are closely comparable across the series, indicate the formation of highly porous structures with fully accessible pore channels. Pore size distributions, derived from the adsorption branches using non-local density functional theory (NLDFT), reveal mean diameters centered at approximately 1.8, 2.3, and 2.7 nm for Pa-COF, Na-COF, and Aa-COF, respectively (Figure 2e). The progressive enlargement of the pore aperture along the series is consistent with the increasing molecular length of the diamine linkers employed, confirming that the pore dimensions can be systematically modulated through judicious selection of the building blocks. This tunability underscores the versatility of the synthetic strategy in generating COFs with tailored porosity.

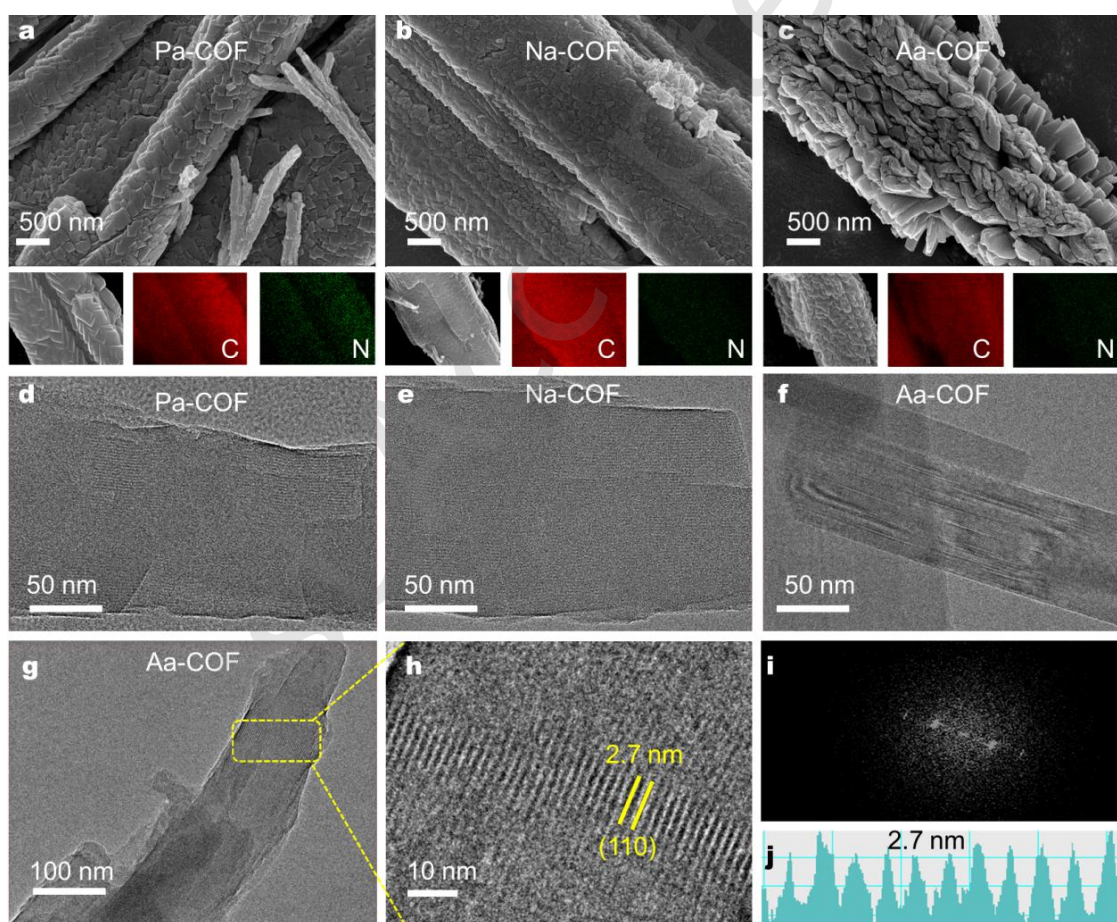


Figure 3. SEM images of (a) Pa-COF, (b) Na-COF, and (c) Aa-COF. TEM images of (d) Pa-COF, (e) Na-COF, and (f, g) Aa-COF. (h) High-resolution TEM image of Aa-COF. (i) FFT patterns and (j) pore size distribution.

The formation of imine linkages in the synthesized COFs is confirmed by Fourier-transform infrared (FT-IR) and solid-state ^{13}C NMR spectroscopy. FT-IR spectra (Figure 2f) display a characteristic C=N stretching vibration at approximately 1620 cm^{-1} , along with the complete disappearance of the N–H stretches (3316 cm^{-1}) from the diamine monomers and the aldehyde C=O stretch (1690 cm^{-1}), indicating exhaustive polycondensation (Figures S9–S11)[33–35]. Solid-state ^{13}C

NMR spectra further corroborate this, exhibiting a distinct resonance at around 157 ppm (Figure 2g) attributable to the C=N. Thermogravimetric analysis (TGA) demonstrates outstanding thermal stability, with the frameworks remaining intact above $300\text{ }^{\circ}\text{C}$ under nitrogen (Figure S12). X-ray photoelectron spectroscopy (XPS) survey spectra confirm the presence of C, N, and O elements in all three frameworks without detectable impurities (Figure S13). High-resolution XPS

reveals systematic shifts in the binding energies of the C=N moiety: from 286.05 eV to 286.31 eV in the C 1s spectrum (Figure 2h) and from 398.88 eV to 399.30 eV in the N 1s spectrum (Figure 2i) across the Pa-COF to Aa-COF series. This progressive increase suggests that larger pore diameters facilitate enhanced electron transfer from the pyrene core to the ligands. Chemical stability tests were further conducted by immersing Aa-COF in acidic (HCl), basic (NaOH), and common organic solvents (DMF, methanol) for 24 h. PXRD patterns after all treatments remained essentially unchanged (Figure S14), confirming that the framework retains its crystallinity and structural integrity under these conditions. Collectively, these analyses confirm the successful synthesis of the three COF photocatalysts.

The morphological features of the three frameworks are examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As presented in Figure 3a–c, the SEM images reveal that Pa-COF, Na-COF, and Aa-COF all adopt rod-like architectures assembled from smaller granular or cubic building units. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping confirms the uniform distribution of C and N throughout the frameworks, indicating homogeneous chemical composition. The rod-like morphology is further corroborated by TEM imaging (Figure 3d–f), which demonstrates consistent structural characteristics across the series, in good agreement with the proposed framework architectures. High-resolution TEM coupled with fast Fourier transform (FFT) analysis is performed to gain deeper insight into the periodic ordering[36–38]. For Aa-COF (Figure 3g–j), well-resolved lattice fringes corresponding to an interplanar spacing of approximately 2.7 nm are clearly observed,

assignable to the (110) crystallographic plane and indicative of highly ordered one-dimensional nanochannels. Similarly, Pa-COF and Na-COF exhibit distinct lattice spacings of 1.8 nm and 2.4 nm, respectively (Figures S15 and S16), which align closely with the pore dimensions derived from nitrogen sorption measurements. These TEM observations collectively affirm the high crystallinity of the synthesized COFs and demonstrate excellent consistency with the pore size distributions obtained from gas adsorption analyses. The well-defined and tunable pore architectures established herein provide a solid foundation for systematically investigating the influence of pore size on photocatalytic performance[39,40].

3.2 Study of charge density and electronic configuration of photocatalysts

To elucidate the correlation between pore architecture and photophysical properties, the solid-state ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy is employed to systematically investigate the light-harvesting behavior of the COF materials across varying pore dimensions. A pronounced bathochromic shift is observed in the absorption profile of Aa-COF relative to its counterparts. As depicted in Figure 4a, Aa-COF exhibits a maximum absorption wavelength ($\lambda_{\max}$) at 520 nm, in contrast to Pa-COF and Na-COF, whose absorption maxima are centered around 500 nm. Quantitative analysis via Tauc plots reveals a progressive narrowing of the optical bandgap (E_g) with increasing pore size. Specifically, Na-COF and Pa-COF display bandgaps of approximately 2.34 eV and 2.32 eV, respectively, whereas Aa-COF demonstrates a substantially narrower bandgap of 2.15 eV (Figure S17).

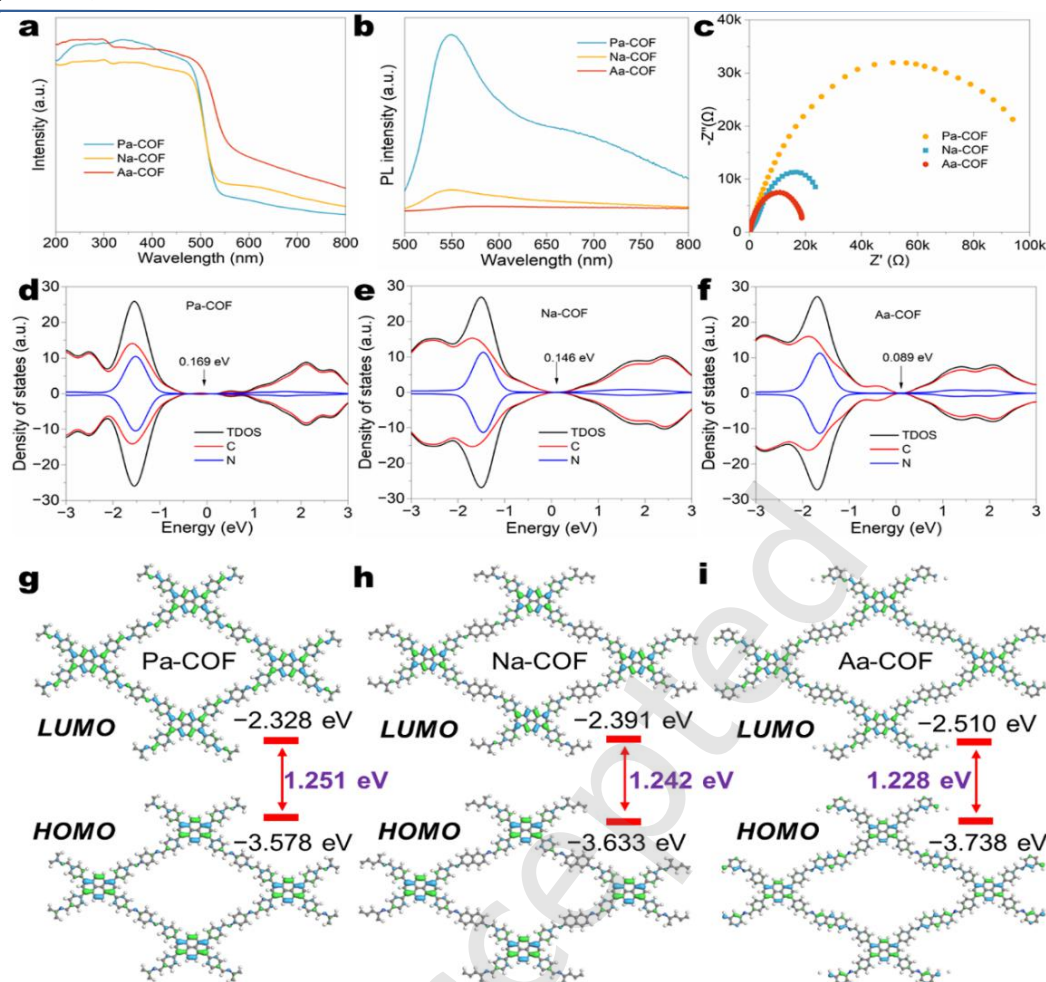


Figure 4. (a) UV/Vis absorption of Pa-COF, Na-COF and Aa-COF. (b) PL emission spectra of Pa-COF, Na-COF and Aa-COF. (c) EIS Nyquist plots of Pa-COF, Na-COF and Aa-COF. The TDOSs and PDOSs of C and N for (d) Pa-COF, (e) Na-COF, and (f) Aa-COF. Kohn–Sham LUMOs and HOMOs of (g) Pa-COF, (h) Na-COF and (i) Aa-COF.

To further elucidate the impact of pore architecture on photogenerated charge carrier dynamics, photoluminescence (PL) spectroscopy is conducted. A marked attenuation in PL intensity is observed for Aa-COF compared to Pa-COF and Na-COF (Figure 4b). This significant quenching effect is indicative of a more efficient donor-acceptor (D-A) configuration within the Aa-COF framework, which effectively suppresses radiative recombination and promotes charge separation[41,42]. Time-resolved PL decay measurements revealed an average lifetime of 3.8 ns for Aa-COF (Figure S18), confirming an extended exciton lifetime and suppressed non-radiative recombination. Electrochemical impedance spectroscopy (EIS) analysis further corroborated the superior charge transfer kinetics of Aa-COF. The Nyquist plot revealed that Aa-COF possesses the smallest semicircular diameter (Figure 4c), corresponding to a charge transfer resistance (R_{ct}). This minimal R_{ct} value is unequivocally attributed to the formation of an efficient D-A architecture, induced by the integration of anthracene units, which substantially facilitates interfacial electron transport. Collectively, these findings underscore that the integration of a larger pore size within the COF skeleton not only narrows the optical bandgap but also facilitates intramolecular charge transfer. Such synergistic effects are critically beneficial for enhancing the kinetics of oxidation of C–H, positioning Aa-COF as a more promising candidate for photocatalytic applications.

To gain deeper insight into the origin of the enhanced conductivity, partial density of states (PDOS) calculations are

performed (Figure 4d–f). The results demonstrate that functionalization with anthracene moieties in Aa-COF leads to a more delocalized electronic distribution near the Fermi level, yielding a significantly narrower bandgap of 0.089 eV. This value is markedly lower than those calculated for Pa-COF (0.169 eV) and Na-COF (0.146 eV). The reduced bandgap facilitates more efficient electron excitation and intrachain charge transport. Collectively, these computational insights corroborate the experimental impedance data and underscore that strategic incorporation of conjugated functional groups serves as an effective approach to modulate the electronic band structure and optimize the charge transport properties of covalent organic frameworks. To gain quantum-chemical insight into the photoactivity, the frontier molecular orbitals of the three frameworks are evaluated via theoretical simulations[41], with the results presented in Figures 4g–i. While Pa-COF and Na-COF exhibit HOMO and LUMO both centered on the pyrene unit, Aa-COF features a distinctive orbital distribution: the HOMO is localized on the pyrene donor, and the LUMO is concentrated on the anthracene acceptor. This spatial separation, together with the narrowest HOMO–LUMO gap of 1.228 eV, confirms the formation of a typical D-A system that facilitates efficient intramolecular charge transfer[39,40]. The enhanced charge separation, corroborated by the computed energy levels, directly translates to superior photocatalytic performance, positioning Aa-COF as the most effective candidate among the series for the oxidative activation of C–H bonds.

3.3 Research on electronic environment and charge state of

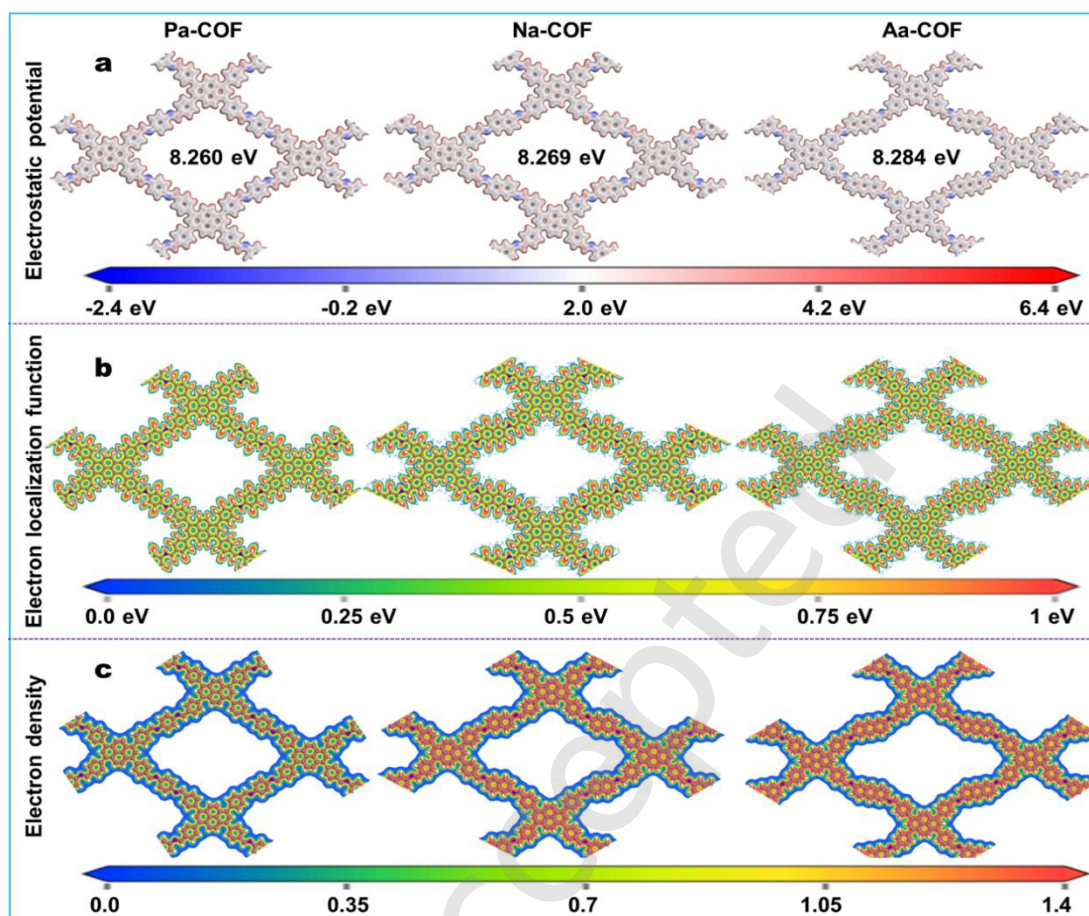


Figure 5. (a) Electrostatic potential surface maps of Pa-COF, Na-COF, and Aa-COF. (b) Electron localization function of Pa-COF, Na-COF, and Aa-COF. (c) Electron density distribution of Pa-COF, Na-COF, and Aa-COF.

The influence of pendant functional groups on the electronic properties of the COFs is systematically interrogated using DFT-based computational tools. Electrostatic potential (ESP) mapping is conducted to characterize the molecular surface polarity (Figure 5a)[43]. The calculated dipole moments exhibit a gradual increase from Pa-COF (8.26 eV) to Na-COF (8.269 eV) and Aa-COF (8.284 eV), confirming that the introduced substituents effectively perturb the charge equilibrium and polarize the electron distribution. To further elucidate the spatial organization of charge density, electron localization function (ELF) analysis is performed (Figure 5b). The resulting of ELF isosurfaces reveal notably enhanced electron localization in the vicinity of the anthracene unit within Aa-COF, creating distinct electron-enriched domains[44, 45]. These localized regions are postulated to function as catalytically active centers that facilitate substrate activation and promote interfacial charge transfer during C–H bond oxidation. These findings underscore that the judicious selection of functional units with tailored conjugation lengths and pore architectures enables precise control over the electronic structure, thereby optimizing the material's catalytic potential. Moreover, a comprehensive analysis of the electronic density distribution across the three COF materials reveals a distinct structure-dependent trend: Aa-COF, characterized by its enlarged pore dimensions and superior π -conjugation, demonstrates the most advantageous electronic configuration and the highest charge density among the series (Figure 5c). This enhanced electronic characteristic, consistently supported by both experimental evidence and computational validation, renders Aa-COF exceptionally responsive to

photoirradiation[40]. Under light excitation, the photoinduced electrons within its conjugated framework are efficiently mobilized and transferred to adsorbed oxygen species. This process promotes the reductive activation of O_2 to generate superoxide radicals ($O_2^{\cdot-}$), a key reactive intermediate that subsequently participates in the oxidative functionalization of C–H bonds[46–48]. These findings underscore that the concurrent increase in pore size and conjugation length serves as an effective design strategy to modulate the electronic structure and boost the photocatalytic efficiency of COF-based systems. The pore diameters of Pa-COF, Na-COF, and Aa-COF are 1.8, 2.3, and 2.7 nm, respectively, all substantially larger than the THIQ substrate (~ 0.8 – 1.0 nm). Thus, steric exclusion or diffusion limitation cannot explain the activity trend (Aa-COF > Na-COF > Pa-COF). We note that extending the acceptor linker simultaneously enlarges the pore aperture, narrows the optical bandgap, and enhances charge polarization. These three effects are intrinsically linked and cannot be fully decoupled in the current series. Therefore, we do not attribute the activity enhancement of Aa-COF solely to charge polarization. Instead, we propose a synergistic mechanism: the enlarged pores reduce mass-transfer limitations, the narrowed bandgap improves light harvesting, and the enhanced polarization facilitates exciton dissociation and charge separation. Together, these factors contribute to the superior photocatalytic performance of Aa-COF.

3.4 Study on photocatalytic performance

To verify the significant catalytic performance of COF materials designed and prepared in organic transformation reactions, 2-

phenyl-1,2,3,4-THIQ (**1a**) was selected as the model substrate. The reaction was performed using Aa-COF as the catalyst, potassium *tert*-butoxide (^tBuOK) as the base, O₂ as the oxidant,

and *N,N*-dimethylformamide (DMF) as the solvent. The reaction proceeded under irradiation with a 100 W white LED light for 24 h, and the results are summarized in Table 1.

Table 1 Optimization of the oxidation of the *N*- α -C(sp³)-H bond in THIQs^{a,b,c}.

Entry	Photocatalyst (mg)	Base	h ν (100 W)	Gaseous atmosphere	solvent	Yield (%)
1	Aa-COF (5)	^t BuOK	White LED	O ₂	DMF	75
2	-	^t BuOK	White LED	O ₂	DMF	7
3	Aa-COF (5)	-	White LED	O ₂	DMF	7
4	-	-	White LED	O ₂	DMF	6
5	Aa-COF (5)	^t BuOK	-	O ₂	DMF	2
6	Aa-COF (5)	^t BuOK	White LED	Air	DMF	60
7	Aa-COF (5)	^t BuOK	White LED	vacuum	DMF	57
8	Aa-COF (5)	^t BuOK	White LED	N ₂	DMF	80
9	Aa-COF (5)	N(CH ₂ CH ₃) ₃	White LED	N ₂	DMF	9
10	Aa-COF (5)	Imidazole	White LED	N ₂	DMF	6
11	Aa-COF (5)	DABCO	White LED	N ₂	DMF	15
12	Aa-COF (5)	NaN(SiMe ₃) ₂	White LED	N ₂	DMF	13
13	Aa-COF (5)	Pyridine	White LED	N ₂	DMF	25
14	Aa-COF (5)	DBU	White LED	N ₂	DMF	88
15	Aa-COF (5)	DBU	White LED	N ₂	CH ₃ OH	66
16	Aa-COF (3)	DBU	White LED	N ₂	toluene	83
17	Aa-COF (5)	DBU	White LED	N ₂	acetone	82
18	Aa-COF (5)	DBU	White LED	N ₂	DMSO	61
19	Aa-COF (5)	DBU	White LED	N₂	MeCN	100 (98)^d
20	Aa-COF (3)	DBU	White LED	N ₂	MeCN	79
21 ^e	Aa-COF (5)	DBU	White LED	N ₂	MeCN	94
22 ^f	Aa-COF (5)	DBU	White LED	N ₂	MeCN	50

^a Reactions conducted on a 0.1 mmol scale using 1 equiv. of **1a** and 1.5 equiv. of base. ^b assay yield determined by ¹H NMR spectroscopy of the crude reaction mixtures using C₂H₂Cl₄ as an internal standard. ^c The light source is white LED (100 W, 400-750 nm, Lamp-flask separation 8 cm). ^d Isolated yield after chromatographic purification. ^e 0.1 M. ^f 12 h.

To further verify the superior photocatalytic activity of Aa-COF, a comprehensive performance comparison with previously reported photocatalysts was conducted, and the relevant results are summarized in Table 2. Although several referenced catalysts can achieve comparable product yields within a shorter reaction duration, Aa-COF delivers a maximum product yield of 98% at a reaction time of 24 h. Notably, most of the previously

reported catalytic systems require air or pure oxygen as the reaction atmosphere, while the Aa-COF-based catalytic system exhibits excellent catalytic performance under a nitrogen atmosphere. These comparative results firmly demonstrate that Aa-COF serves as a highly competitive and promising photocatalyst for the target reaction.

Table 2 Compares the photocatalytic performance of our catalytic system with that of previously reported analogous systems.

Entry	Photocatalyst	Reaction conditions	Yield (%)	Ref.
1	Aa-COF	white LED (100 W), ^t BuOK, DBU, MeCN, N ₂ , r.t., 24 h	98	This work
2	TRO-OMe	white LED (110 mW cm ⁻²), ^t BuOH, DBN, MeCN, O ₂ , r.t., 2 h	91	[49]
3	TFPA-TAPP-COF	Xe lamp (40 W), MeCN, r.t., air, 18 h.	83	[50]
4	PHEMA-Eosin Y	Green LED (30 W), DABCO, MeCN, r.t., air, 4.5 h.	96	[51]
5	SOF(MVDPY-NATPE-CB[8])	UV LEDs (365–367 nm), r.t., air, 24 h.	83	[52]
6	Ta–Th-6	blue LED (18 W), DBN, DMSO, O ₂ , r.t., 12 h	91	[53]
7	Quinazolinone-based BF ₂ Photocatalysts	Blue LED (4 W 405 nm), DBN, DMSO, air, r.t., 5 h	84	[54]
8	Cu-Cl-bpyc	450 nm LED, NaAc, MeCN, O ₂ , r.t., 12 h	95	[55]
9	PATT-CB[7]-SBE-b-CD+EY+SR101	360-365 nm LED, H ₂ O, air, r.t., 36 h	85	[56]

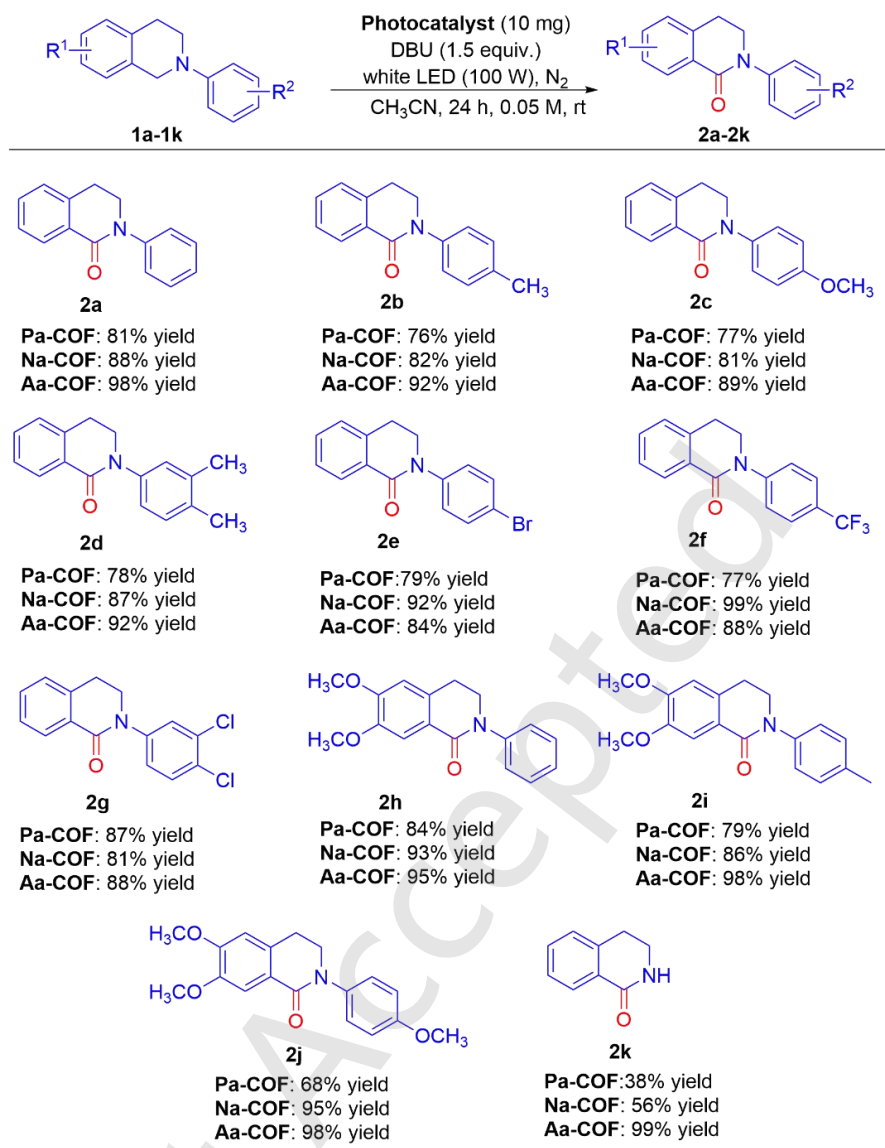
First, systematic control experiments were performed to explore the roles of the catalyst Aa-COF, base ^tBuOK, and light irradiation. It was found that the highest yield (75%) of the product **2a** via *N*- α -C(sp³)-H bond oxidation of substrate **1a** was achieved only when all three reaction parameters (Aa-COF

catalyst, ^tBuOK base and light irradiation) were present simultaneously (Table 1, entry 1). In contrast, extremely low yields were observed under other control conditions (Table 1, entries 2-5). These results unambiguously verify the excellent photocatalytic activity of Aa-COF. Under the aforementioned

reaction conditions (Table 1, entry 1), the effects of different gas atmospheres (air, vacuum, and N_2) on the reaction system were investigated, and the results showed that the nitrogen atmosphere provided the optimal reaction performance, affording the target oxidation product **2a** in 80% yield, whereas under the other atmospheres, the yields ranged from 57% to 60% (Table 1, entries 6-8). To further optimize the reaction conditions, a systematic screening of bases was performed in the reaction system by substituting $tBuOK$ with triethylamine ($N(CH_2CH_3)_3$), imidazole, 1,4-Diazabicyclo[2.2.2]Octane (DABCO), $NaN(SiMe_3)_2$, pyridine, and 1,8-Diazabicyclo[5.4.0]-7-Undecene (DBU), respectively, and the results demonstrated that the use of DBU as the base led to an increased yield of product **2a**, reaching 88%, whereas the yields obtained with the other five bases were significantly lower and thus less favorable (Table 1, entries 9-14). Given that the yield of product **2a** remained improvable, we subsequently investigated the effects of five different solvents, namely methanol (CH_3OH), toluene, acetone, dimethyl sulfoxide (DMSO), and acetonitrile (MeCN), on the reaction performance (Table 1, entries 15-19). Surprisingly, when MeCN was

employed as the solvent, the assay yield of product **2a** reached 100%, and the corresponding isolated yield was determined to be 98% (Table 1, entry 19). By contrast, markedly lower yields were afforded in the other tested solvents. From the perspective of economic efficiency and cost control, we further optimized the reaction conditions by reducing the catalyst loading, decreasing solvent dosage, and shortening the reaction time. Unfortunately, these adjustments led to moderate to significant declines in the yield of product **2a** (Table 1, entries 20-22). Based on the analysis of the experimental results, this study has identified the reaction conditions corresponding to entry 19 in Table 1 as the optimal conditions for the oxidation of $N-\alpha-C(sp^3)-H$ bond in THIQs, which will be employed in subsequent research work.

During the process of optimal condition screening, we found that the pore size of the photocatalyst COF has an impact on the catalytic performance of this oxidation reaction. In order to further explore the structure-activity relationship of this photocatalyst, this study selected three COFs (Pa-COF, Na-COF and Aa-COF), and systematically investigated their substrate scope (Table 3).

Table 3 Substrate scope for the oxidation of the *N*- α -C(sp³)-H bond in THIQs ^a.

^a Reactions conducted on a 0.2 mmol scale. Lamp-flask separation 8 cm. Isolated yield after chromatographic purification.

When 2-phenyl-THIQ (**1a**) was employed as the substrate, the Pa-COF, Na-COF, and Aa-COF-catalyzed reactions afforded the corresponding product **2a** in 81%, 88%, and 98% yield, respectively. When the *N*-aryl group of *N*-aryl THIQ was substituted with electron-donating groups (-CH₃, -OCH₃), the isolated yields of product **2b** are 76%, 82% and 92% respectively when Pa-COF, Na-COF and Aa-COF were used as catalysts. Correspondingly, the isolated yields of product **2c** were 77%, 81% and 89%, respectively. To further enhance the spatial steric hindrance effect of the substrate, reactions employing substrate **1d** afforded product **2d** in yields of 78%, 87%, and 92%, respectively. Similarly, upon introduction of electron-withdrawing substituents onto the *N*-aryl ring, the three photocatalysts (Na-COF, Aa-COF, and Pa-COF) exhibited certain differences in catalytic performance. In the transformations of substrates **1e** and **1f**, Na-COF demonstrated superior catalytic activity, affording the corresponding products **2e** and **2f** in isolated yields of 92% and 99%, respectively. Aa-COF displayed moderate activity, whereas Pa-COF exhibited the lowest activity under identical conditions. This observation can be rationalized by the more efficient charge-carrier separation and favorable substrate-catalyst interaction of Na-COF, which

facilitates the single electron transfer (SET) process with electron-deficient substrates **1e** and **1f**. Notably, when substrate **1g** was employed, the catalytic efficiencies of all three catalysts converged, with the isolated yield of product **2g** ranging from 81% to 88% across the series. Furthermore, when two methoxy substituents were introduced onto the quinoline ring of the *N*-aryl THIQ, the yields of product **2h** obtained by the three catalysts were 84%, 93%, and 95% respectively. Meanwhile, when substituents were introduced simultaneously on the *N*-aryl group and the quinoline ring of *N*-aryl THIQ to further increase the steric hindrance, the three catalysts could catalyze the reaction differently, and the yield of product **2i** could reach 79%-98%, while the yield of product **2j** was 68% - 98%. Finally, when unsubstituted THIQ was employed as the substrate, the Na-COF, Aa-COF, and Pa-COF catalytic systems afforded the target product **2k** in yields of 38%, 56%, and 99%, respectively. Based on the substrate extension experiments described above, a systematic structure-performance correlation has been established for the three photocatalysts Pa-COF, Na-COF, and Aa-COF, with substrates bearing electron-withdrawing groups displaying atypical reactivity trends while all other substrate classes exhibit a consistent catalytic activity ranking of Aa-

COF > Na-COF > Pa-COF. The reusability and stability of Aa-COF were evaluated through five consecutive photocatalytic runs. The product yields remained consistently high (98% to 95%), demonstrating excellent recyclability. Post-reaction characterizations by PXRD and FT-IR confirmed that the crystallinity, imine linkages and porous structure were all well preserved (Figure S19). These results collectively establish Aa-

COF as a robust and recyclable heterogeneous photocatalyst.

3.5 Research on photocatalytic kinetics

To elucidate the underlying reaction kinetics governing the photocatalytic oxidation of tetrahydroisoquinoline, theoretical calculations are employed to probe the adsorption behavior of both the oxidant (O_2) and the substrate on the COF catalysts.

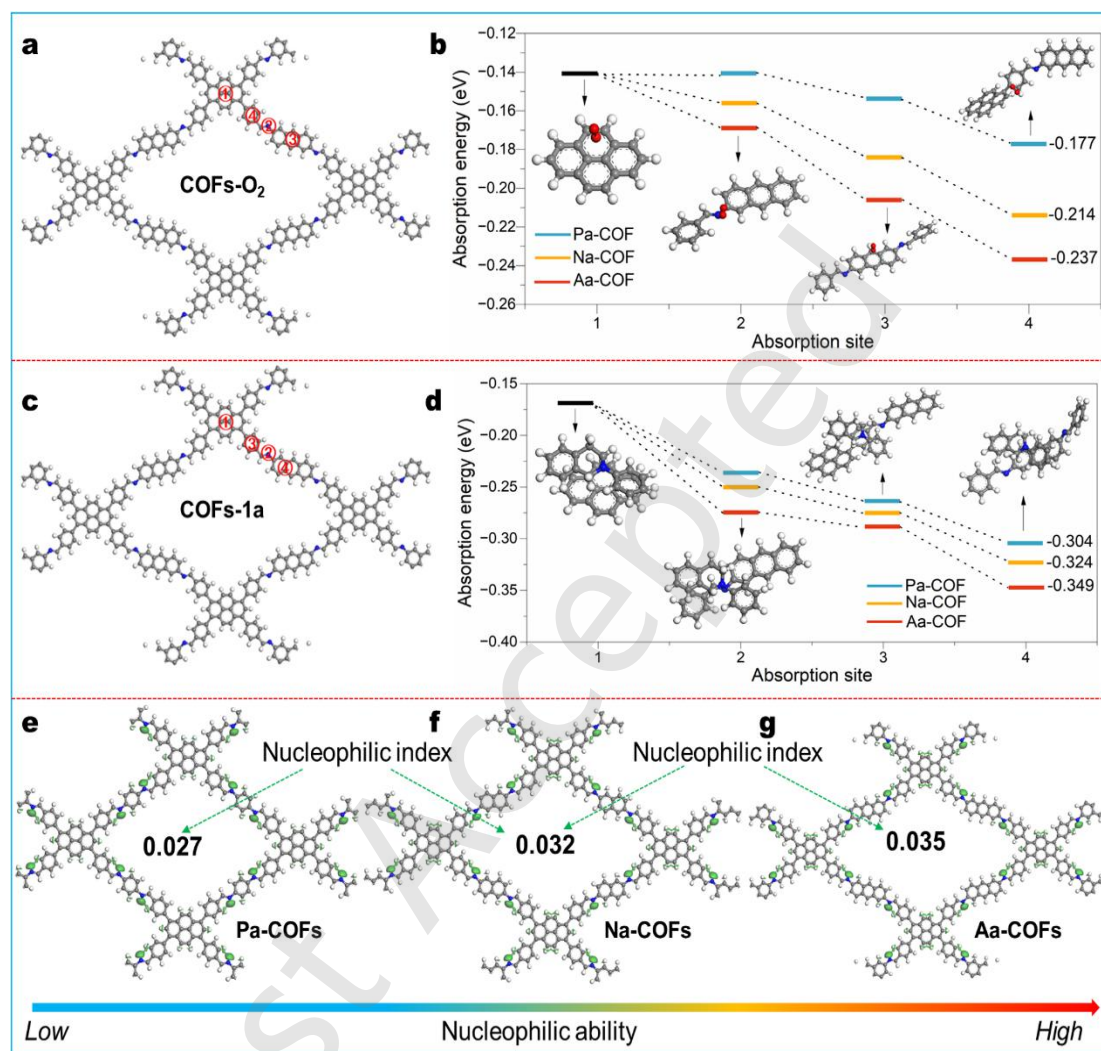


Figure 6. (a) Study of absorption site for COFs towards O_2 at four different positions. (b) absorption energy for four different positions. (c) Study of absorption site for COFs towards isoquinoline at four different positions. (d) absorption energy for four different positions. Orbit weight Fukui function for nucleophilic ability of (e) Pa-COF, (f) Na-COF, and (g) Aa-COF.

Initial investigations identified four potential oxygen adsorption sites within the COF framework (Figure 6a, Figure S20-21). The computational results reveal that the region proximal to the pyridine moiety on the phenyl ring exhibits the most favorable affinity for oxygen, with a calculated adsorption energy of -0.237 eV—substantially higher than that of the other three sites (Figure 6b, Table S1). A comparative analysis across the three frameworks demonstrated that Aa-COF, benefiting from its enlarged pore architecture and extended π -conjugation, possesses a markedly enhanced adsorption capacity for O_2 . Although the photocatalytic oxidation reaction was performed under a nitrogen atmosphere without exogenous oxygen injection, the pre-adsorbed oxygen species on the porous COF surface can act as the oxygen source. As demonstrated by our theoretical calculations, Aa-COF possesses excellent O_2 adsorption and activation capability. The porous structure and

enhanced π -conjugation of Aa-COF can efficiently capture and concentrate trace oxygen from the reaction system, which is further photochemically activated to generate $O_2^{\cdot-}$ as the dominant active intermediate to drive the oxidation reaction. Therefore, even trace oxygen in the closed N_2 system is sufficient to support the photocatalytic oxidation process, which well explains the observed reaction kinetics and catalytic activity.

This trend is consistently observed in the adsorption of tetrahydroisoquinoline, where Aa-COF again exhibited the highest adsorption energy among the series (Figure 6c-d, Figure S22-23, Table S2). The calculated adsorption energies for both O_2 and the substrate fall in the physisorption regime, indicating that strong chemisorption is not required for the reaction. Instead, the photocatalytic cycle relies on diffusional encounters within the confined pore environment, where weak binding facilitates product desorption and catalyst turnover. These findings indicate

that the synergistic effect of increased pore size and improved conjugation in Aa-COF creates a more favorable microenvironment for the co-adsorption of both oxidant and reactant. This dual-affinity characteristic effectively concentrates the reactive species within the porous framework, increasing their proximity and collision probability, thereby facilitating the subsequent oxidation reaction. Consequently, Aa-COF demonstrates the highest reaction yield and the most rapid kinetics in the photocatalytic oxidation of tetrahydroisoquinoline, underscoring the critical role of pore-conjugation engineering in optimizing catalytic performance.

To provide a more granular understanding of the distinct photocatalytic kinetics observed among the three frameworks, Fukui function analysis is conducted to evaluate their nucleophilic reactivity—a key descriptor governing electron donation to electrophilic oxidants. The calculated nucleophilic indices reveal clear difference: Aa-COF exhibits the highest value (0.035), significantly exceeding those of Pa-COF (0.027) and Na-COF (0.032)[57] (Figures 6e-g). This enhanced nucleophilicity is of particular significance given that O_2 , functioning as an electrophilic species, preferentially accepts electrons from nucleophilic centers. The superior electron-donating capability of Aa-COF thus facilitates the reductive activation of O_2 to generate $O_2^{\cdot-}$, which serve as the primary reactive intermediates driving the subsequent oxidation of tetrahydroisoquinoline. This Fukui-derived insight not only corroborates the previously discussed advantages in electronic configuration and adsorption behavior but also provides a quantitative rationale for the accelerated reaction kinetics observed with Aa-COF.

3.6 Practical application and reaction mechanism analysis

To bridge the gap between fundamental catalytic performance and practical implementation, the scalability of the Aa-COF photocatalytic system was assessed through a gram-scale synthesis of the $N-\alpha-C(sp^3)-H$ oxidation product. Capitalizing on the superior catalytic efficacy demonstrated in smaller-scale reactions, a preparative experiment was conducted using 6.0 mmol of 2-phenyl-THIQ (**1a**) as the substrate, with 300 mg of Aa-COF under the previously optimized conditions. The reaction successfully afforded 1.25 g of the desired oxidized product **2a**, corresponding to an isolated yield of 93% (Figure 7a). This high yield on an enlarged scale not only confirms the robustness and retained activity of the Aa-COF framework under increased substrate loading but also underscores its promising industrial applicability. The favorable mass balance and minimal catalytic deactivation observed suggest that this photocatalytic platform possesses the requisite stability and efficiency for continuous or batch-scale manufacturing processes, paving the way for its integration into the pharmaceutical and fine chemical synthesis sectors.

To evaluate the translational potential of the Aa-COF photocatalytic system beyond controlled laboratory settings, a comparative study was undertaken utilizing natural sunlight as the irradiation source for the $N-\alpha-C(sp^3)-H$ oxidation of tetrahydroisoquinoline, conducted outdoors over a 12-hour period beginning January 14th, 2026. We further recorded the kinetic profile under outdoor natural sunlight (Figure 7b). Strikingly, exposure to natural sunlight not only preserved the catalytic efficiency but also markedly accelerated the reaction

kinetics. The target product **2a** is isolated in 97% yield after only 12 hours, reducing the required reaction time by half relative to the 24-hour artificial illumination. This substantial rate enhancement is attributed to the superior spectral match and increased irradiance of sunlight, which promote more efficient photon harvesting and charge carrier generation within the Aa-COF framework. The demonstrated compatibility with solar irradiation carries profound implications for industrial scale-up, suggesting that Aa-COF-based processes could be effectively deployed in solar reactor configurations, thereby eliminating the capital and operational expenditures associated with artificial lighting systems and enhancing the overall economic viability of photocatalytic manufacturing.

To elucidate the intrinsic mechanism underlying the enhanced photocatalytic performance of Aa-COF materials, it is essential to systematically analyze the conversion pathway of the $N-\alpha-C(sp^3)-H$ bond in THIQ molecules during the oxidation reaction. For this purpose, this study employed the representative substrate **1a** to conduct mechanistic investigation experiments. By introducing specific radical quenchers or trapping agents into the reaction system and analyzing the changes in the yield of product **2a** along with the results of control experiments, the key active intermediates involved in the catalytic cycle are identified (Figure S24). Compared with the standard conditions, when *tert*-butanol (TBA) was added as a scavenger of hydroxyl radicals ($\cdot OH$), the reaction yields of product **2a** was 91%. Furthermore, upon the addition of photogenerated hole scavengers ammonium oxalate (AO) and potassium iodide (KI), the yields of product **2a** were 96% and 72%, respectively, indicating the involvement of photogenerated holes in the reaction process. Additionally, upon the introduction of electron scavenger (potassium persulfate, $K_2S_2O_8$), superoxide radical ($O_2^{\cdot-}$) scavenger (2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO), and singlet oxygen (1O_2) scavenger (2,2,6,6-tetramethylpiperidine, TEMP), the photocatalytic efficiency of the $N-\alpha-C(sp^3)-H$ bond oxidation in THIQs catalyzed by Aa-COF was significantly reduced, with the yield of product **2a** decreasing to 19%, 75%, and 65%, respectively. These scavenging experiments demonstrate that photogenerated electrons, $O_2^{\cdot-}$, and 1O_2 are all key active intermediates in the functionalization of the $N-\alpha-C(sp^3)-H$ bond, each playing an indispensable role in the catalytic transformation process. In addition, EPR spin-trapping measurements were performed to identify reactive oxygen species. Upon illumination, time-dependent characteristic signals of the DMPO- $O_2^{\cdot-}$ adduct were recorded (Figure S25), indicating superoxide radical generation via electron transfer from photoexcited Aa-COF to adsorbed O_2 . A typical three-line signal assignable to TEMPO radical was also observed with 4-oxo-TEMP (Figure S26), demonstrating singlet-oxygen formation through energy transfer. These observations reveal that both $O_2^{\cdot-}$ and 1O_2 can be generated even under N_2 atmosphere, where the oxygen originates from dissolved/adsorbed O_2 confined inside COF pores instead of gaseous O_2 .

Based on experimental results, theoretical calculations, and relevant literature reports[49,58,59], this study proposes a plausible reaction mechanism for the $N-\alpha-C(sp^3)-H$ bond oxidation reaction in THIQ derivatives (Figure 7c). Under light irradiation, the [Pa/Na/Aa-COF] photocatalysts absorbed photon

energy and were promoted to their excited state $[\text{Pa}/\text{Na}/\text{Aa-COF}]^*$. These excited species then mediated a SET process with THIQ derivatives, affording the reduced radical anion $[\text{Pa}/\text{Na}/\text{Aa-COF}]^{\cdot-}$ and a nitrogen-centered radical cation intermediate **A**. Subsequently, $[\text{Pa}/\text{Na}/\text{Aa-COF}]^{\cdot-}$ interacted with molecular oxygen through two mechanisms: first, via an energy transfer pathway that generated $^1\text{O}_2$; second, through a SET process that produced superoxide anion radicals $\text{O}_2^{\cdot-}$, regardless of the pathway, $[\text{Pa}/\text{Na}/\text{Aa-COF}]^{\cdot-}$ were regenerated to their ground state $[\text{Pa}/\text{Na}/\text{Aa-COF}]$, thereby enabling the sustained progression of the photocatalytic cycle. Next, intermediate **A**

underwent a hydrogen atom transfer (HAT) process with the $\text{O}_2^{\cdot-}$, followed by elimination of the peroxide hydrogen anion (HO_2^-), to yield the Schiff base-derived nitrogen cation intermediate **B**. Thereafter, the HO_2^- served as a nucleophile and underwent nucleophilic addition with intermediate **B**, affording intermediate **C**. Finally, in the presence of the base DBU, intermediate **C** underwent a cascade reaction involving deprotonation, electron transfer, and elimination of a hydroxide ion (OH^-), ultimately achieving the selective oxidation of the $N-\alpha\text{-C}(\text{sp}^3)\text{-H}$ bond in THIQs and obtaining the target products **2**.

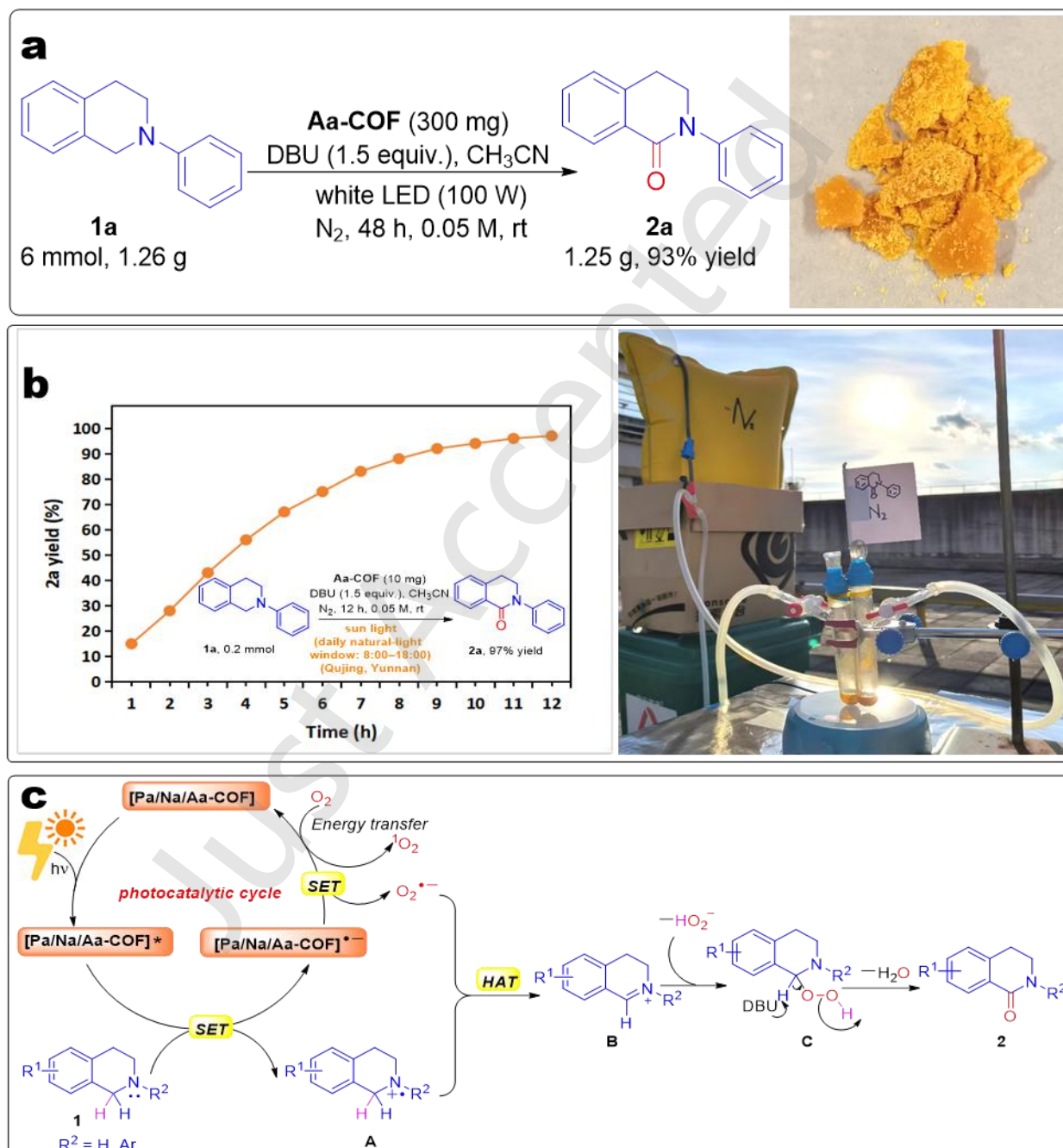


Figure 7. (a) Gram-scale synthesis of **2a**. (b) Photocatalytic experiment of synthesis **2a** conducted in an outdoor environment and kinetic profile (Note: 8:00–18:00 represents the daily time window for outdoor natural sunlight. The total effective irradiation time of 12 h was accumulated over two consecutive days. After partial outdoor irradiation on the first day, the reaction vessel was transferred indoors, tightly wrapped with tin foil and kept in dark conditions. The photocatalytic reaction was completely terminated during the transfer and dark-storage period.). (c) Proposed mechanism for the oxidation of the $N-\alpha\text{-C}(\text{sp}^3)\text{-H}$ bond in THIQs catalyzed by $\text{Pa}/\text{Na}/\text{Aa-COF}$.

4 Conclusions

In summary, we have demonstrated that controlled acceptor extension provides an effective strategy for tuning charge

polarization in D–A COFs, leading to enhanced photocatalytic performance in the selective oxidation of tetrahydroisoquinolines. Systematic elongation of the acceptor linker from phenylene to anthracene progressively modulates the molecular dipole moment and electron density distribution, as evidenced by spectroscopic characterization and DFT calculations. The anthracene-linked Aa-COF, featuring the most extended acceptor unit and the lowest average local ionization energy, exhibits superior electron-donating capacity for O₂ activation, affording the desired isoquinolinone in near-quantitative yield (98%) under mild conditions. Mechanistic studies identify superoxide and singlet oxygen as the primary reactive oxygen species driving the oxidation cascade. Collectively, this work establishes acceptor extension as a viable design principle for polarization-modulated COF photocatalysts and provides a generalizable platform for selective C–H functionalization under sustainable conditions.

Electronic Supplementary Material: Supplementary material is available in the online version of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors reports no conflict of interests in this work.

Author contribution statement

Z. F. L. and J. H. C.: Validation, writing manuscript. X. P. T.: Funding acquisition, review manuscript. C. S. Z.: Data curation. J. L.: Formal analysis. X. D. J.: Investigation. F. N. C.: Project administration. S. F. J.: Data curation. G. F. Z.: Project administration, review manuscript. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Acceptor-extended donor-acceptor COFs enable charge-polarization tuning for efficient photocatalytic C–H oxidation

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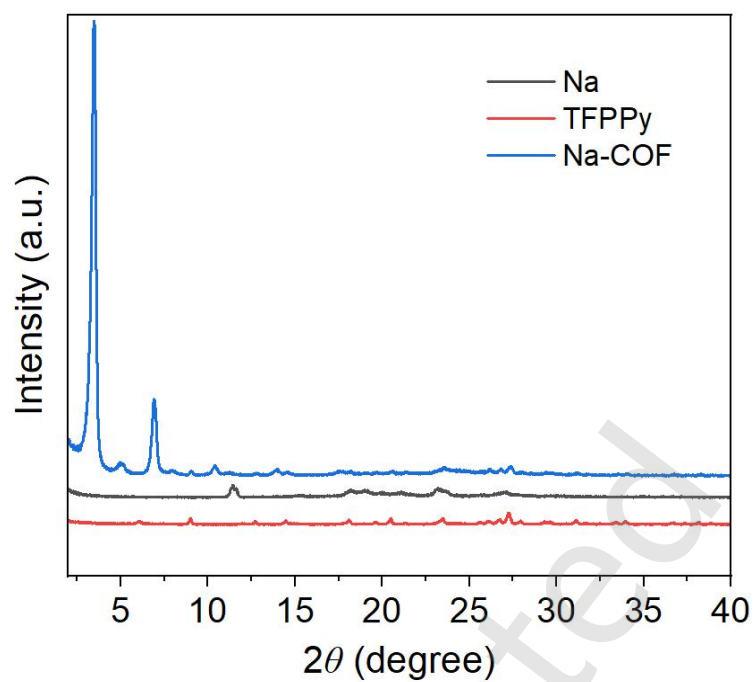


Figure S3. PXRD patterns of synthesized Na-COF and starting materials of Na and TFPPy.

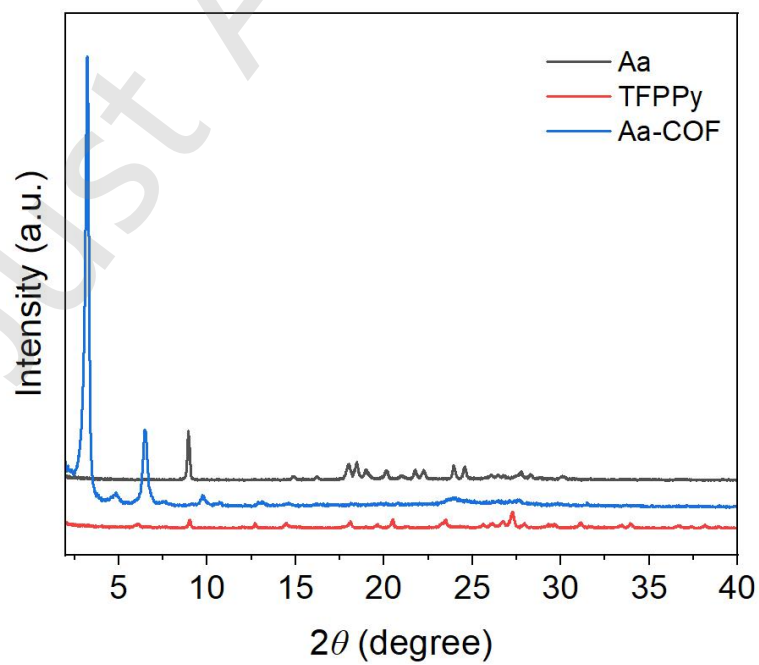


Figure S4. PXRD patterns of synthesized Aa-COF and starting materials of Aa and TFPPy.

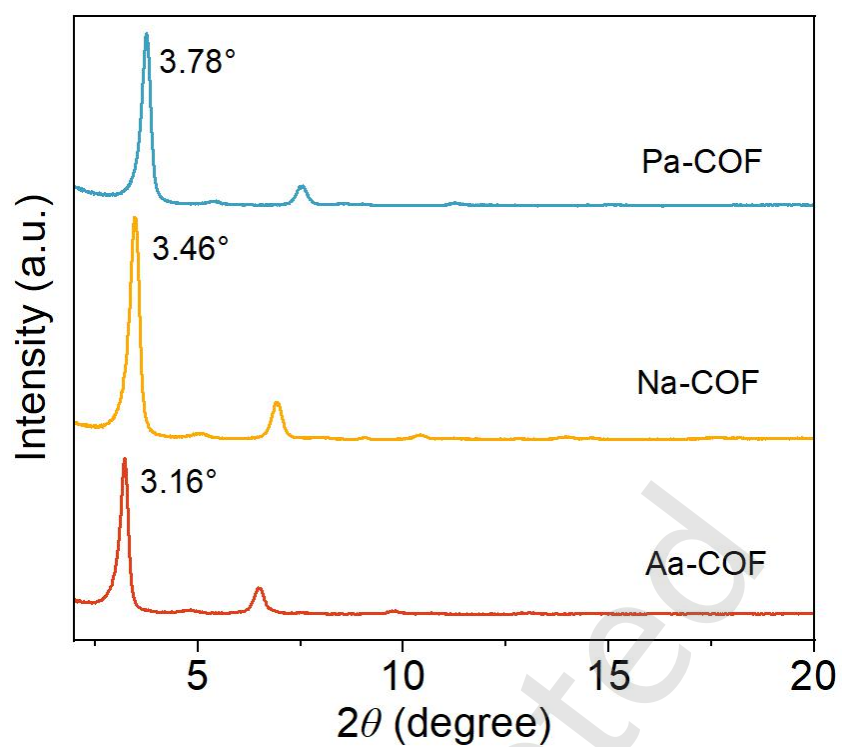


Figure S5. PXRD patterns of synthesized Pa-COF, Na-COF and Aa-COF.

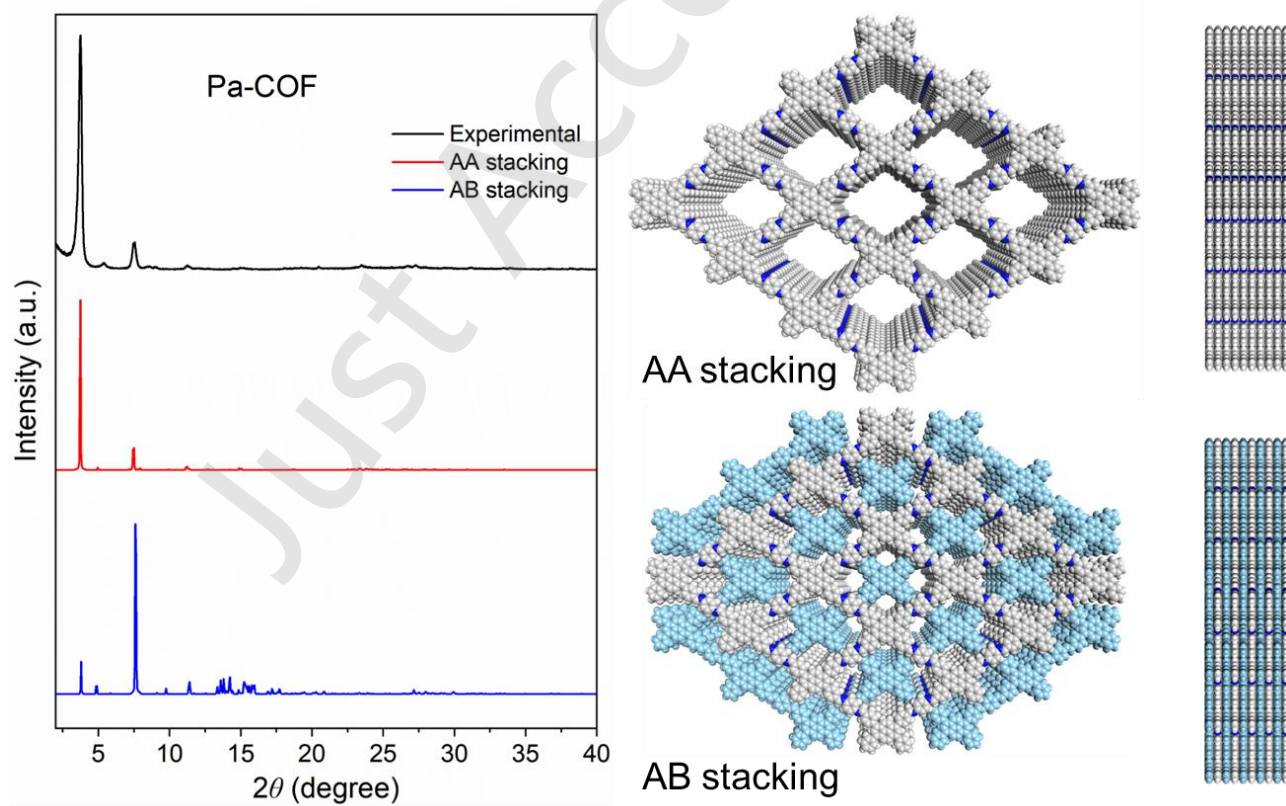


Figure S6. PXRD patterns of synthesized Pa-COF, AA stacking and AB stacking.

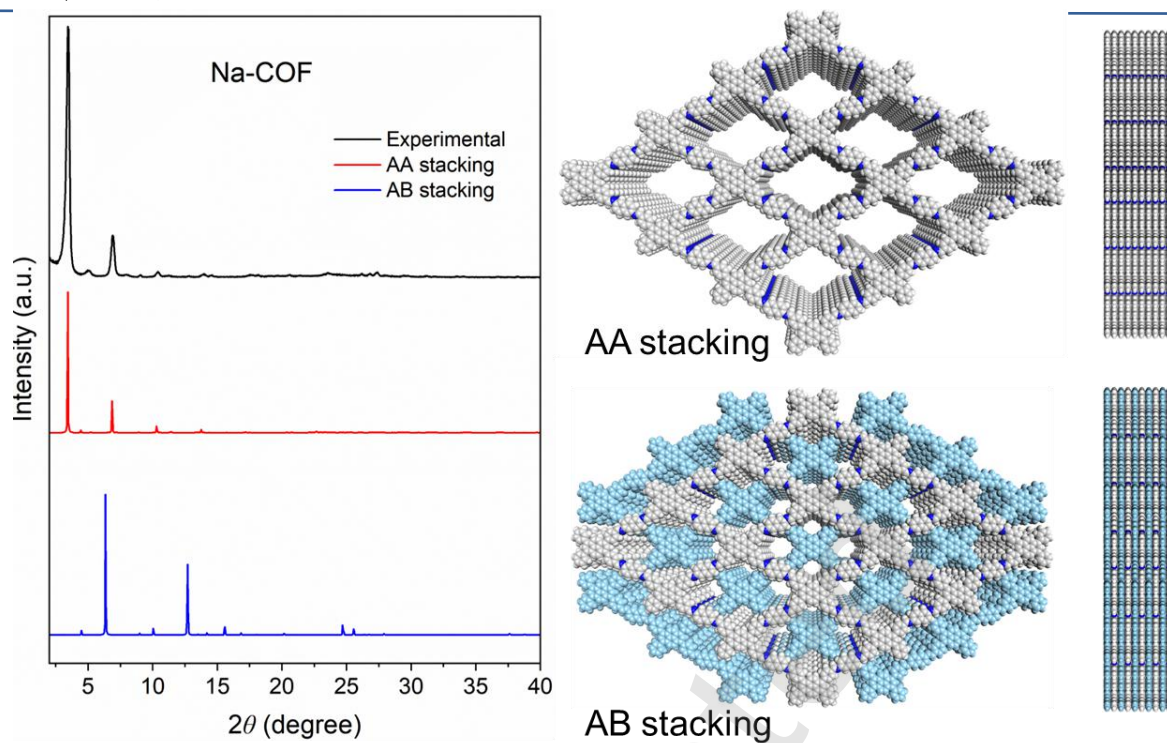


Figure S7. PXRD patterns of synthesized Na-COF, AA stacking and AB stacking.

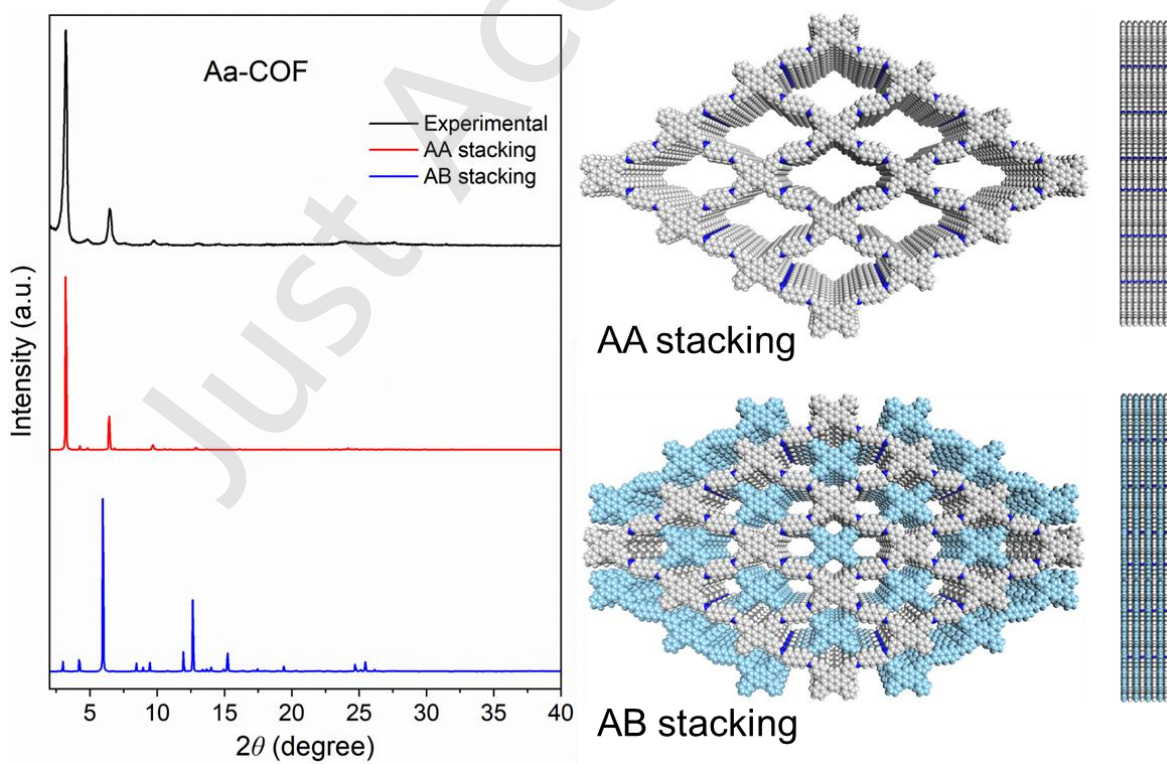


Figure S8. PXRD patterns of synthesized Aa-COF, AA stacking and AB stacking.

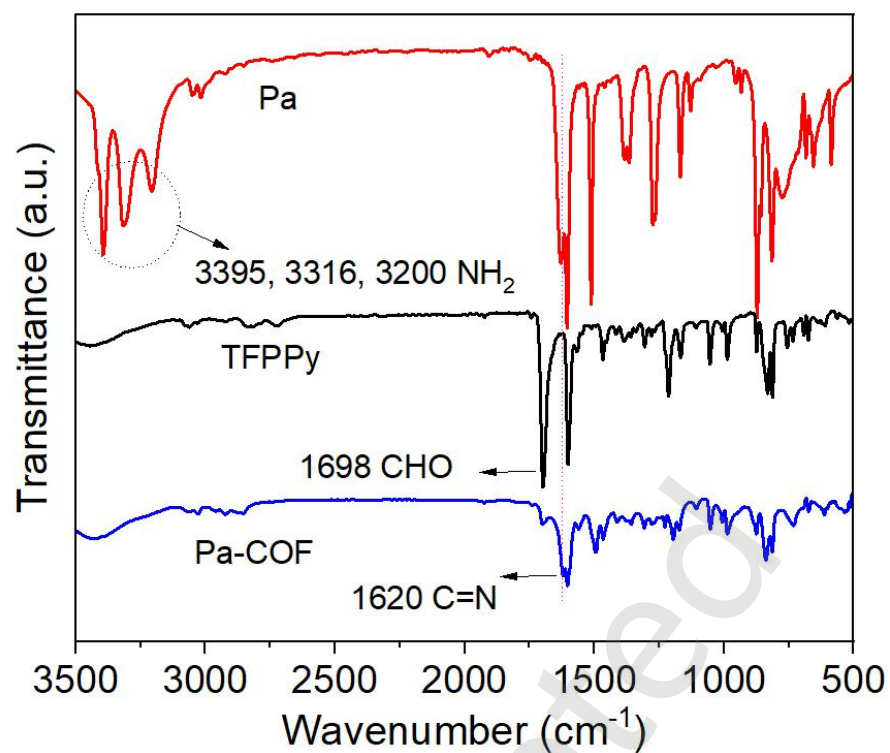


Figure S9. FT-IR spectra of starting materials of Pa, TFPPy and as-prepared Pa-COF.

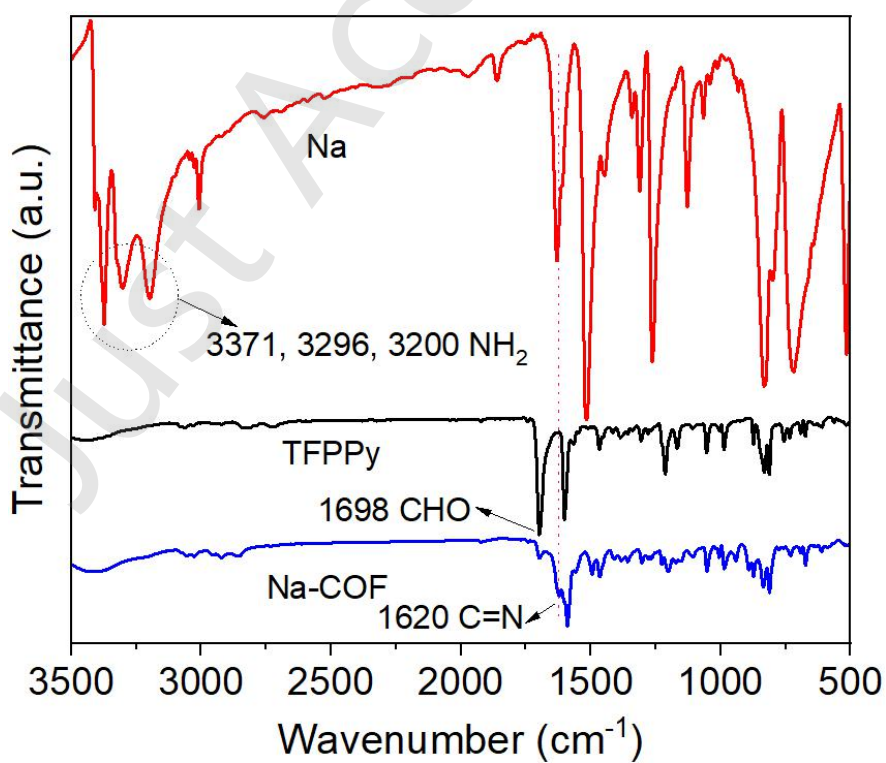


Figure S10. FT-IR spectra of starting materials of Na, TFPPy and as-prepared Na-COF.

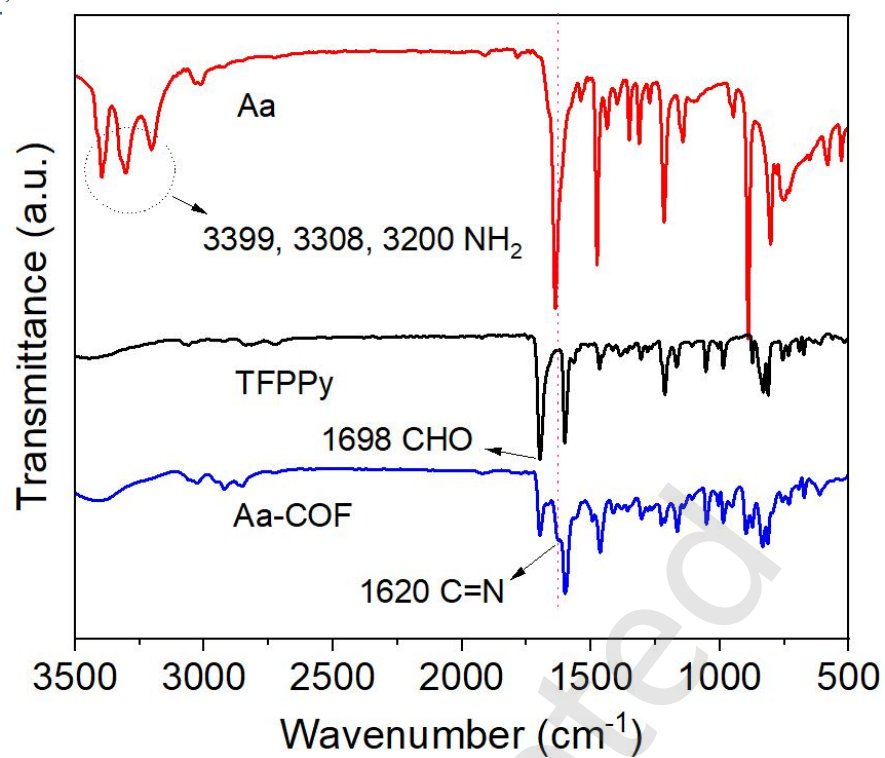


Figure S11. FT-IR spectra of starting materials of Aa, TFPPy and as-prepared Aa-COF.

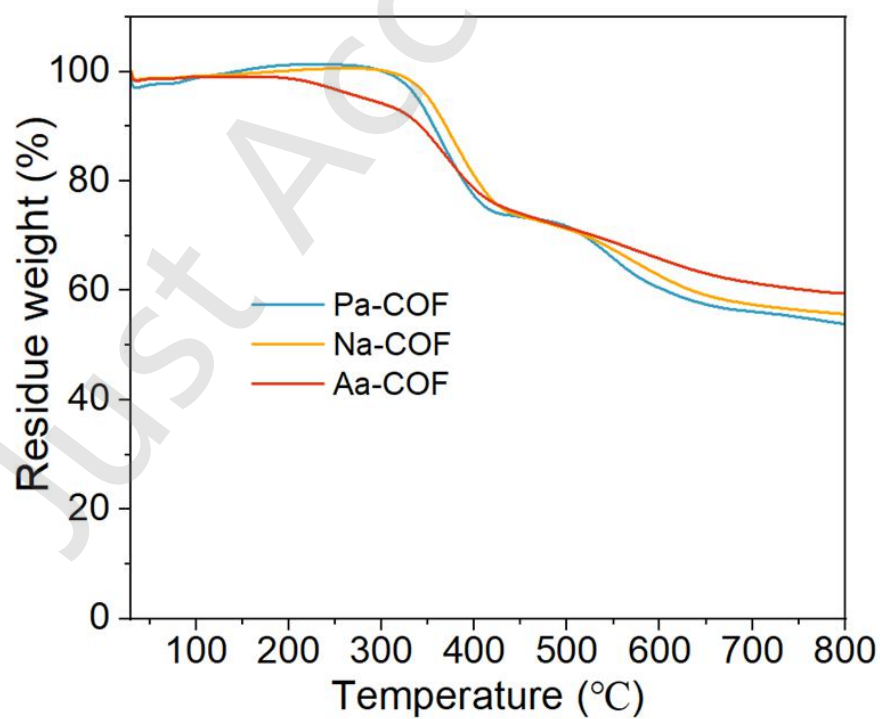


Figure S12. TGA curves of Pa-COF, Na-COF and Aa-COF.

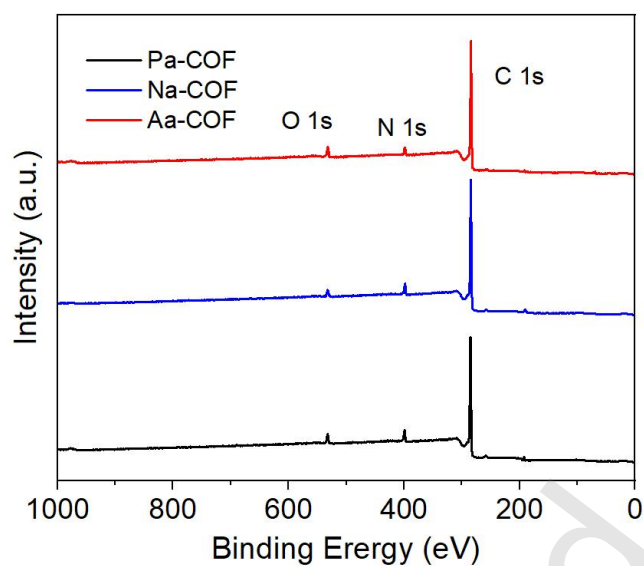


Figure S13. XPS survey spectra of Pa-COF, Na-COF, and Aa-COF.

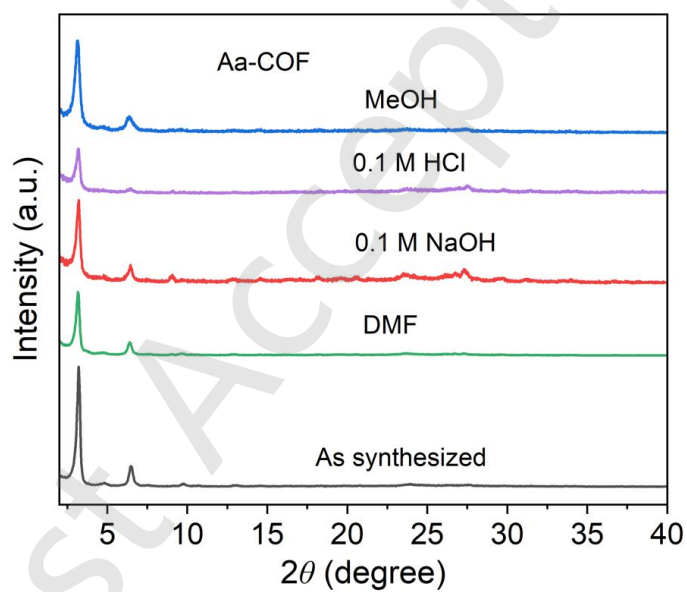


Figure S14. PXRD patterns of Aa-COF at various chemical conditions.

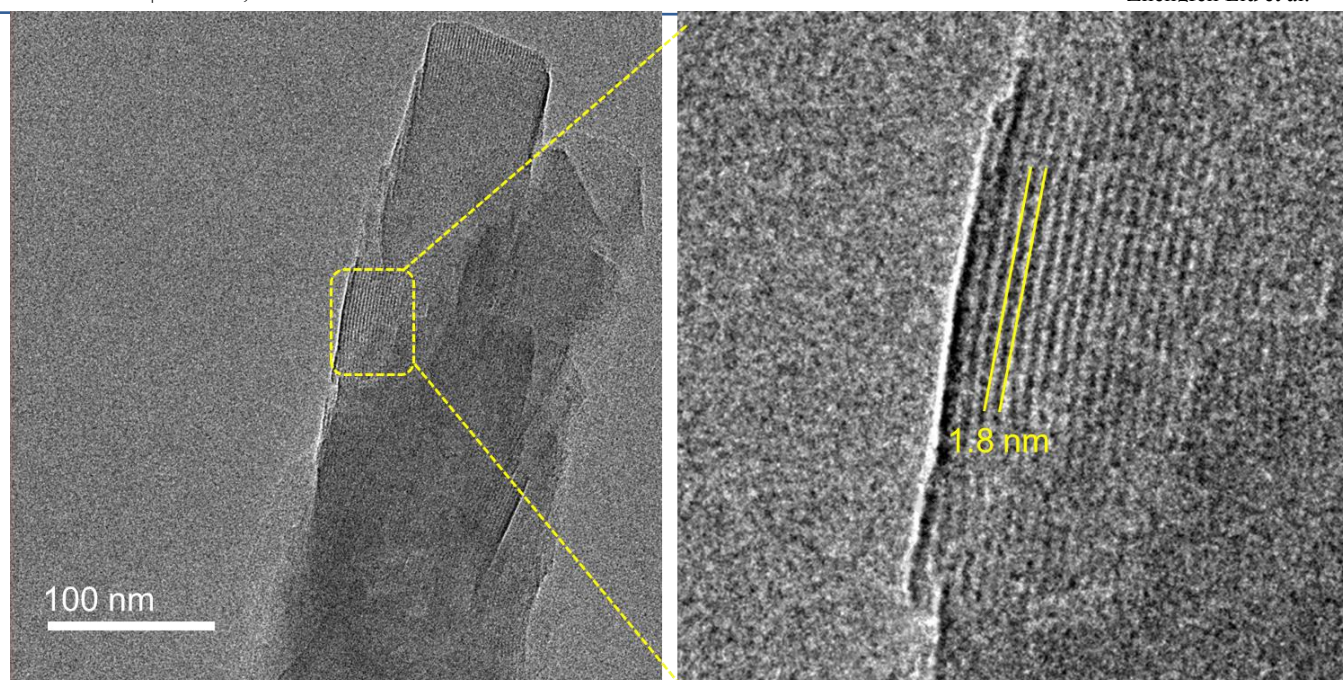


Figure S15. TEM images of Pa-COF.

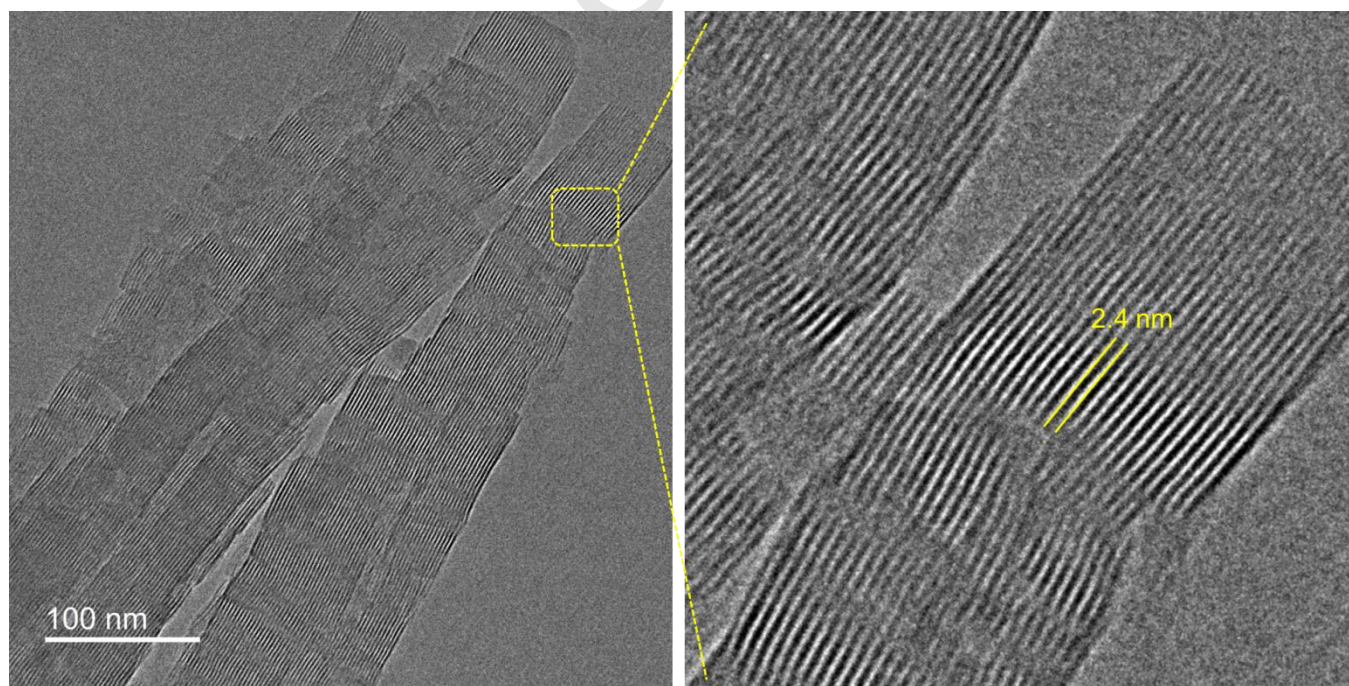


Figure S16. TEM images of Na-COF.

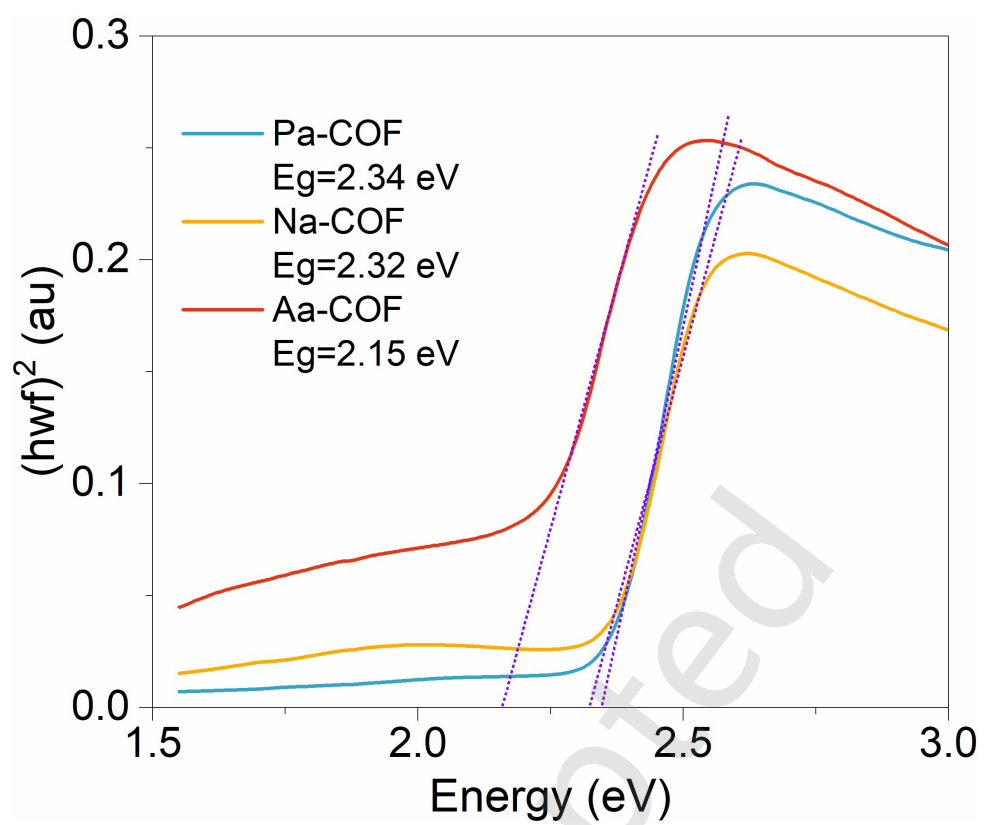


Figure S17. Tauc plots of Pa-COF, Na-COF and Aa-COF.

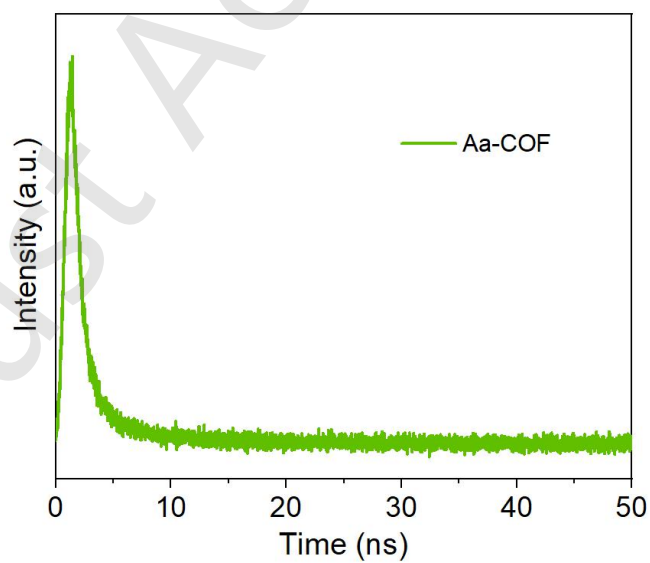


Figure S18. Fluorescence lifetime of Aa-COF.

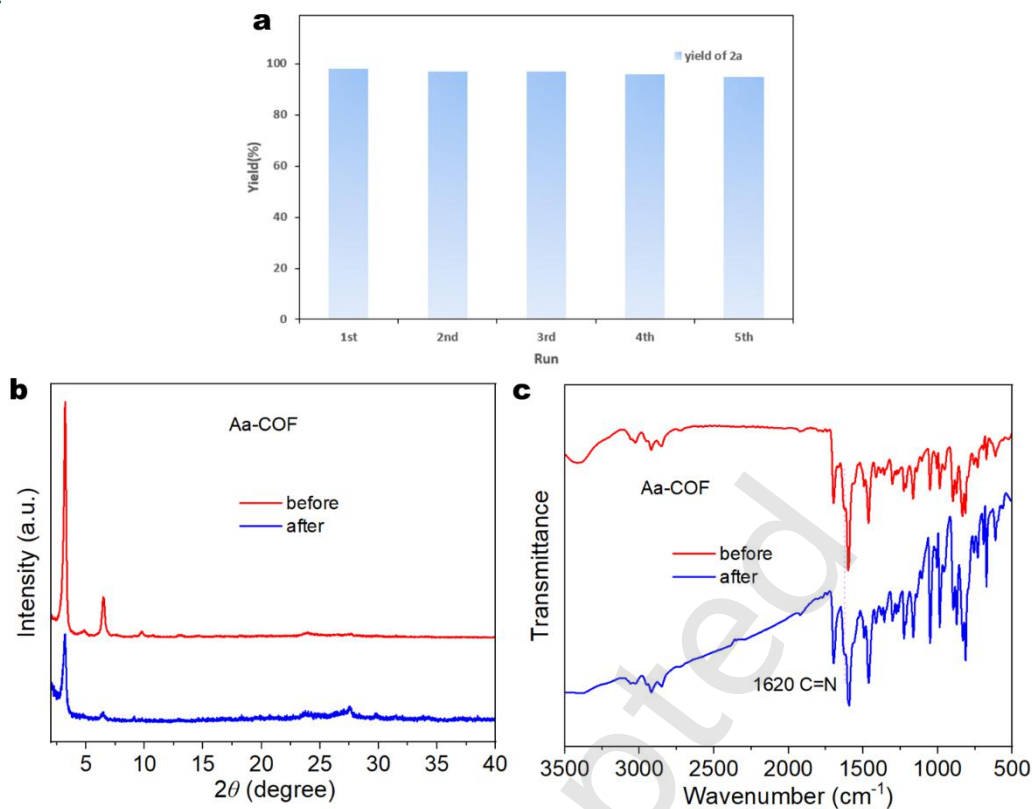


Figure S19. (a) Recyclability of Aa-COF in the oxidation of the *N*- α -C(sp³)-H bond in THIQs over five consecutive cycles. (b) PXRD patterns of Aa-COF before and after tests. (c) FT-IR patterns of Aa-COF before and after tests.

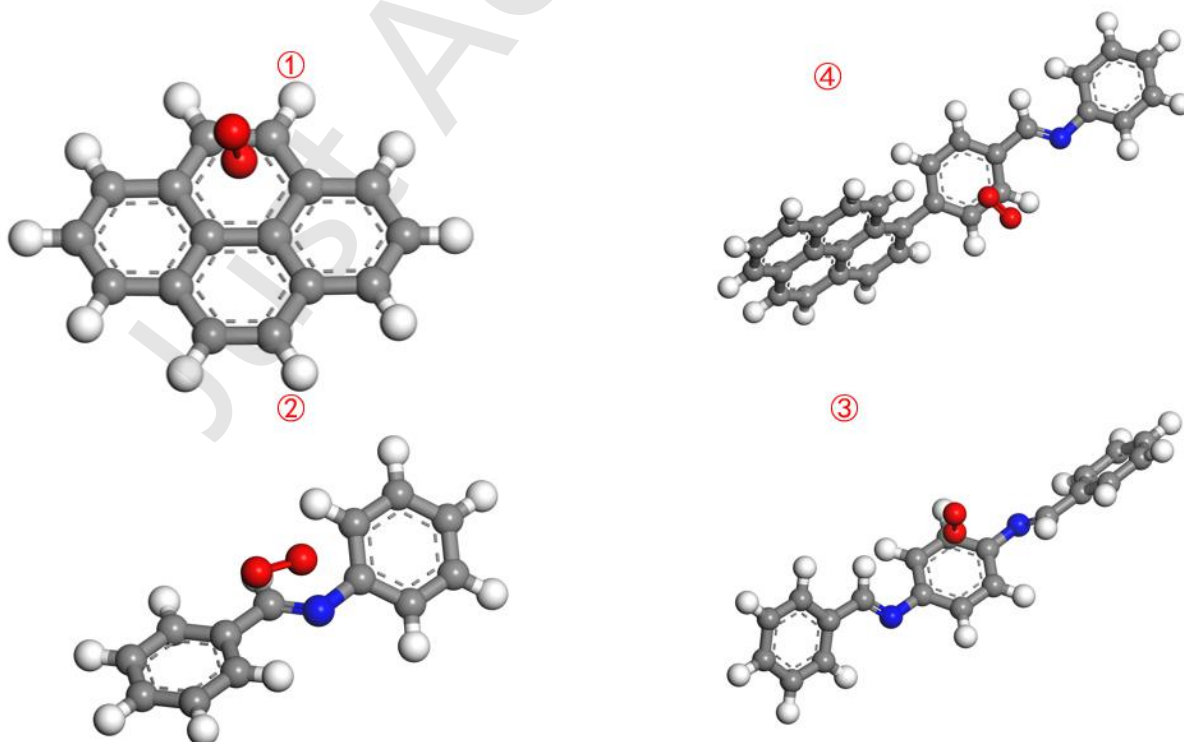


Figure S20. Various adsorption site of Pa-COF towards O₂.

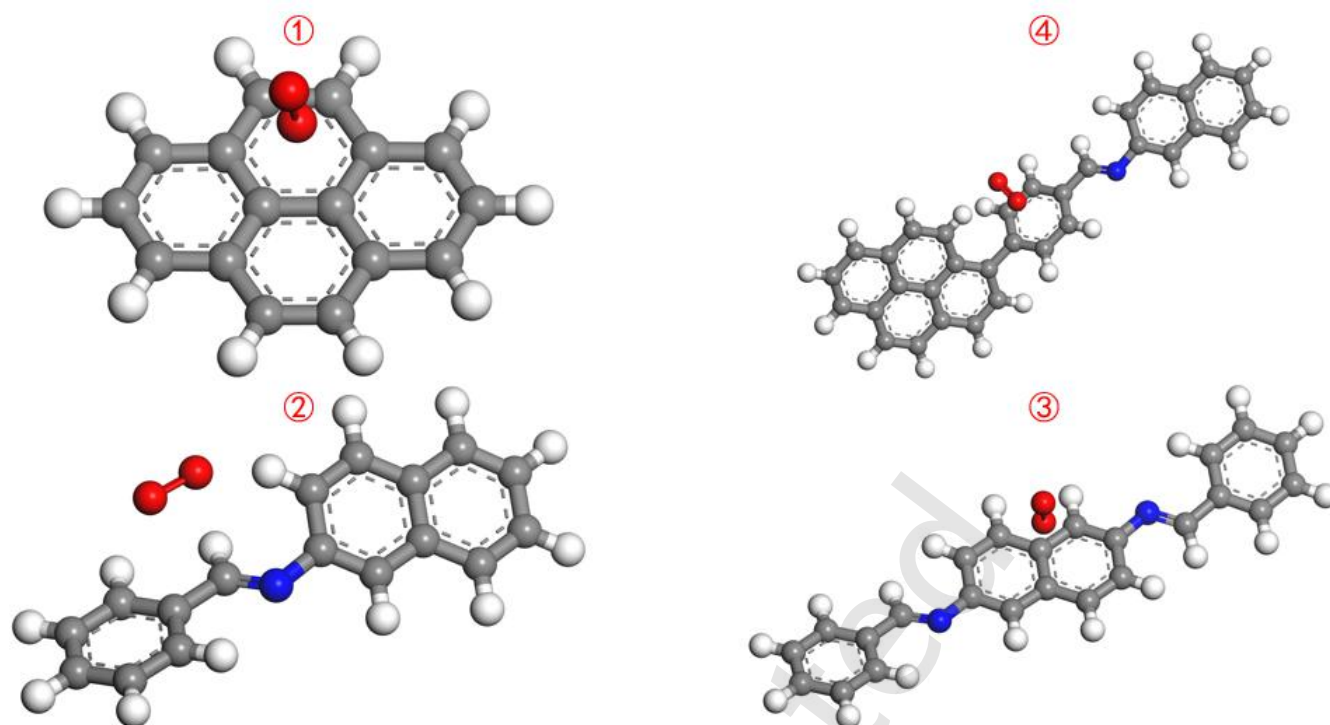


Figure S21. Various adsorption site of Na-COF towards O_2 .

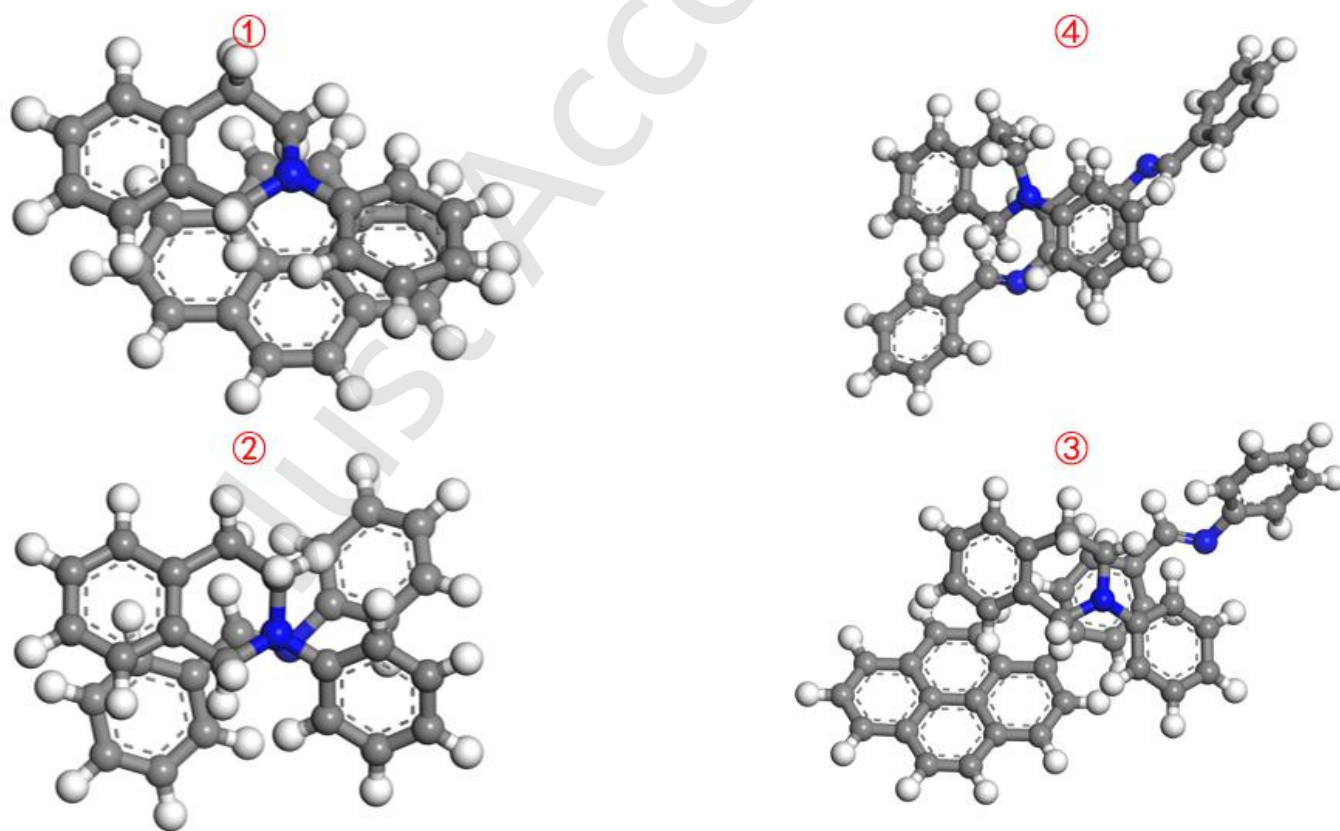


Figure S22. Various adsorption site of Pa-COF towards compound **1a**.

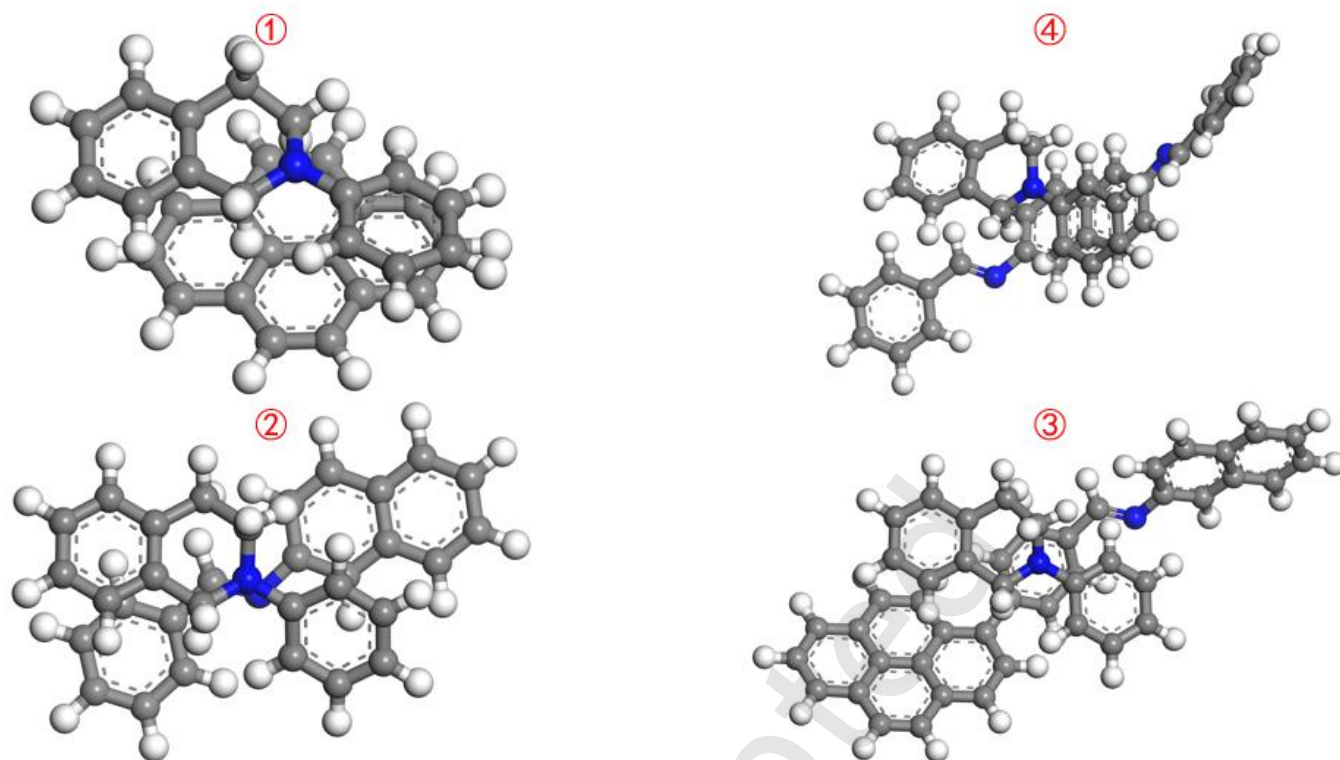


Figure S23. Various adsorption site of Na-COF towards compound **1a**.

Table S1. Adsorption energy of O₂ at different positions on the COF framework.

COFs	①	②	③	④
Pa-COF	−0.141 eV	−0.141 eV	−0.154 eV	−0.177 eV
Na-COF	−0.141 eV	−0.156 eV	−0.184 eV	−0.214 eV
Aa-COF	−0.141 eV	−0.169 eV	−0.206 eV	−0.237 eV

Table S2. Adsorption energy of tetrahydroisoquinoline at different positions on the COF framework.

COFs	①	②	③	④
Pa-COF	−0.169 eV	−0.236 eV	−0.265 eV	−0.304 eV
Na-COF	−0.169 eV	−0.251 eV	−0.275 eV	−0.324 eV
Aa-COF	−0.169 eV	−0.274 eV	−0.288 eV	−0.349 eV

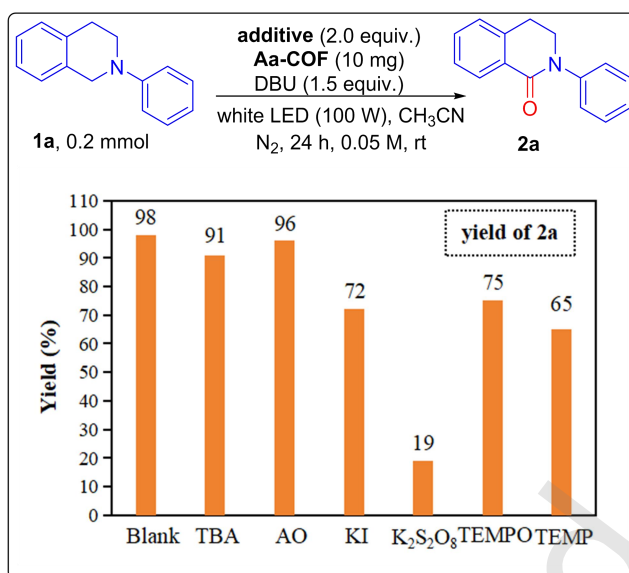


Figure S24. Yields of **2a** in the presence of different scavengers.

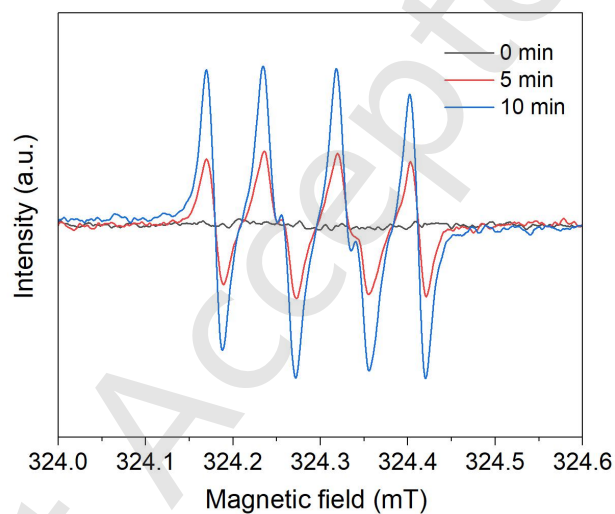


Figure S25. EPR spectra of $\text{O}_2^{\cdot -}$ trapped by DMPO for Aa-COF.

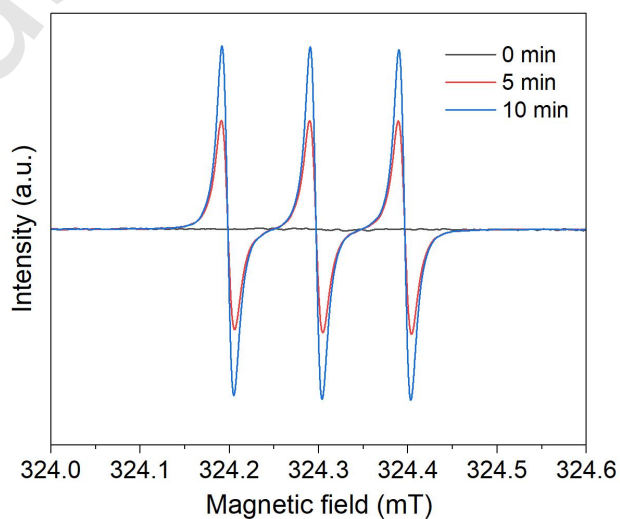


Figure S26. EPR spectra of $^1\text{O}_2$ trapped by 4-oxo-TEMP for Aa-COF.

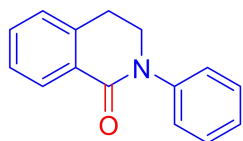
Procedure and characterization for the oxidation of N - α -C(sp³)-H bond in tetrahydroisoquinolines

General Procedure: The oxidation of N - α -C(sp³)-H bond in tetrahydroisoquinolines

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with tetrahydroisoquinolines (0.2 mmol), DBU (0.3 mmol), photocatalyst Aa-COF (10 mg), and CH₃CN (4 mL). The reaction system was then exposed to N₂ and stirred at room temperature for a period of 24 hours, while being irradiated by a 100 W white LED at a distance of 8 cm. Once the reaction was complete, the mixture was diluted with H₂O and ethyl acetate, the layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na₂SO₄), filtered and concentrated *in vacuo*. The crude products were purified by column chromatography on silica gel (eluting with hexanes:ethyl acetate = 10:1→1:1) to give the corresponding oxidation products **2a-2k**.

Product Characterization:

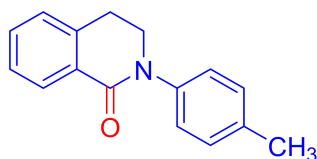
2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (**2a**):



The reaction was performed following the General Procedure with 2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2a** (43.76 mg, 98% yield) as a white solid. The characterization data for this compound match the literature data.[1]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, J = 7.6, 1.2 Hz, 1H), 7.38 – 7.25 (m, 6H), 7.17 – 7.13 (m, 2H), 3.88 (dd, J = 6.4, 2.0 Hz, 2H), 3.03 (t, J = 6.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, Chloroform-*d*) δ 164.2, 143.1, 138.4, 132.1, 129.7, 128.9, 127.2, 128.7, 127.2, 127.0, 126.3, 125.3, 49.4, 28.6 ppm.

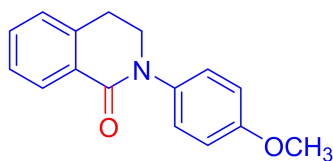
2-(*p*-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (**2b**):



The reaction was performed following the General Procedure with 2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline **1b** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1) to give the product **2b** (43.66 mg, 92% yield) as a pale yellow solid. The characterization data for this compound match the literature data.[2]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, J = 7.6, 1.6 Hz, 1H), 7.36 (td, J = 7.6, 1.6 Hz, 1H), 7.27 (td, J = 7.6, 1.2 Hz, 1H), 7.21 – 7.11 (m, 5H), 3.85 (dd, J = 7.2, 6.4 Hz, 2H), 3.02 (t, J = 6.4 Hz, 2H), 2.27 (s, 3H) ppm; ¹³C NMR (100 MHz, Chloroform-*d*) δ 164.3, 140.6, 138.4, 136.1, 132.0, 129.8, 129.6, 128.7, 127.2, 127.0, 125.2, 49.5, 28.6, 21.1 ppm.

2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (**2c**):

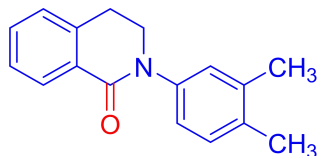


The reaction was performed following the General Procedure with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **1c** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2c** (45.09 mg, 89% yield) as a white solid. The characterization data for this compound match the literature data.[1]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, J = 8.0, 1.6 Hz, 1H), 7.38 (td, J = 9.6, 1.6 Hz, 1H), 7.29 (td, J = 7.6, 1.6 Hz, 1H),

7.23 – 7.18 (m, 2H), 7.15 (dd, $J = 7.6, 1.2$ Hz, 1H), 6.89 – 6.84 (m, 2H), 3.86 (t, $J = 6.4$ Hz, 2H), 3.74 (s, 3H), 3.05 (t, $J = 6.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 164.5, 157.9, 138.4, 136.1, 132.0, 129.8, 128.7, 127.2, 127.0, 126.7, 114.3, 55.6, 49.8, 28.7 ppm.

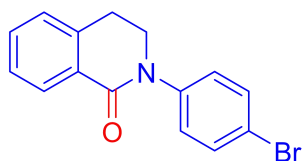
2-(3,4-dimethylphenyl)-3,4-dihydroisoquinolin-1(2H)-one (2d):



The reaction was performed following the General Procedure with 2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline **1d** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2d** (46.24 mg, 92% yield) as a white solid. The characterization data for this compound match the literature data.[2]

^1H NMR (400 MHz, Chloroform- d) δ 8.15 (dd, $J = 7.6, 2.0$ Hz, 1H), 7.46 (td, $J = 7.2, 1.2$ Hz, 1H), 7.37 (td, $J = 7.6, 1.2$ Hz, 1H), 7.23 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.17 (dd, $J = 6.0, 3.6$ Hz, 2H), 7.09 (dd, $J = 8.0, 2.4$ Hz, 1H), 3.95 (t, $J = 10.0$ Hz, 2H), 3.13 (t, $J = 6.4$ Hz, 2H), 2.28 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 164.4, 141.0, 138.4, 137.4, 135.0, 132.0, 130.2, 130.0, 128.8, 127.3, 127.0, 126.9, 122.8, 49.7, 28.8, 20.08, 19.5 ppm.

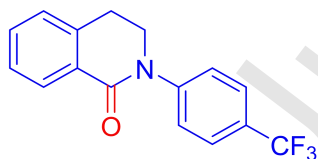
2-(4-bromophenyl)-3,4-dihydroisoquinolin-1(2H)-one (2e):



The reaction was performed following the General Procedure with 2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline **1e** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2e** (50.76 mg, 84% yield) as a white solid. The characterization data for this compound match the literature data.[2]

^1H NMR (400 MHz, Chloroform- d) δ 8.14 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.54 – 7.51 (m, 2H), 7.48 (td, $J = 7.2, 1.6$ Hz, 1H), 7.38 (td, $J = 8.4, 1.2$ Hz, 1H), 7.30 – 7.23 (m, 3H), 3.97 (td, $J = 6.0, 1.6$ Hz, 2H), 3.14 (t, $J = 6.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 164.3, 142.2, 138.3, 132.4, 132.0, 129.5, 128.9, 127.4, 127.1, 127.0, 119.5, 49.4, 28.6 ppm.

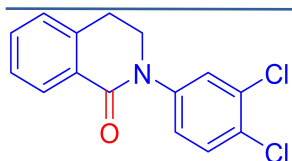
2-(4-(trifluoromethyl)phenyl)-3,4-dihydroisoquinolin-1(2H)-one (2f):



The reaction was performed following the General Procedure with 2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline **1f** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2f** (51.26 mg, 88% yield) as a white solid. The characterization data for this compound match the literature data.[2]

^1H NMR (400 MHz, Chloroform- d) δ 8.16 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.67 (dd, $J = 6.0, 2.0$ Hz, 2H), 7.55 – 7.52 (m, 2H), 7.50 (td, $J = 7.2, 1.2$ Hz, 1H), 7.39 (td, $J = 7.6, 1.2$ Hz, 1H), 7.27 – 7.25 (m, 1H), 4.03 (td, $J = 6.0, 1.6$ Hz, 2H), 3.17 (t, $J = 6.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 164.3, 146.1, 138.4, 132.6, 129.3, 129.0, 127.9 (q, $J_{\text{C-F}} = 32.7$ Hz), 127.5, 127.2, 126.0 (q, $J_{\text{C-F}} = 4.2$ Hz), 125.2, 124.1 (q, $J_{\text{C-F}} = 270$ Hz), 49.2, 28.6 ppm.

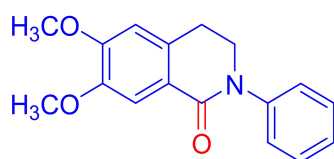
2-(3,4-dichlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one (2g):



The reaction was performed following the General Procedure with 2-(3,4-dichlorophenyl)-1,2,3,4-tetrahydroisoquinoline **1g** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2g** (51.42 mg, 88% yield) as a white solid.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, J = 8.0, 1.6 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.38 (td, J = 7.6, 1.2 Hz, 1H), 7.28 – 7.24 (m, 2H), 3.96 (td, J = 6.0, 1.2 Hz, 2H), 3.15 (t, J = 6.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.3, 142.4, 138.3, 132.6, 130.4, 129.9, 129.2, 128.9, 127.5, 127.20, 127.17, 124.7, 49.3, 28.5 ppm.

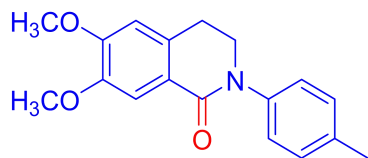
6,7-dimethoxy-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (2h):



The reaction was performed following the General Procedure with 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline **1h** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2h** (53.83 mg, 95% yield) as a yellow solid. The characterization data for this compound match the literature data.[3]

^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.43 – 7.35 (m, 4H), 7.26 – 7.22 (m, 1H), 6.69 (s, 1H), 3.98 (t, J = 6.6 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 3.07 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.3, 152.2, 148.1, 143.4, 132.2, 129.0, 126.2, 125.4, 122.3, 110.9, 109.3, 56.2, 49.7, 28.4 ppm.

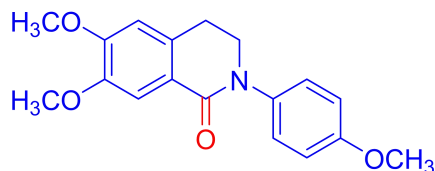
6,7-dimethoxy-2-(*p*-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (2i):



The reaction was performed following the General Procedure with 6,7-dimethoxy-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline **1i** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2i** (58.28 mg, 98% yield) as a red solid. The characterization data for this compound match the literature data.[4]

^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.24 – 7.19 (m, 4H), 6.68 (s, 1H), 3.93 (d, J = 6.0 Hz, 8H), 3.05 (t, J = 6.4 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.4, 152.1, 148.1, 140.8, 136.0, 132.2, 129.6, 125.3, 122.3, 110.9, 109.3, 77.4, 56.2, 49.8, 28.3, 21.2 ppm.

6,7-dimethoxy-2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (2j):

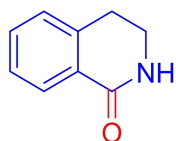


The reaction was performed following the General Procedure with 6,7-dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **1j** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→7:1) to give the product **2j** (61.42 mg, 98% yield) as a red solid. The characterization data for this compound match the literature data.[5]

^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, J = 1.2 Hz, 1H), 7.29 – 7.27 (m, 2H), 6.94 – 6.92 (m, 2H), 6.69 (s, 1H), 3.94 – 3.91 (m,

8H), 3.82 (d, $J = 0.8$ Hz, 3H), 3.06 (t, $J = 6.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 164.5, 157.8, 152.1, 148.1, 136.4, 132.1, 126.8, 122.3, 114.3, 110.9, 109.3, 77.4, 56.2, 55.6, 50.0, 28.4 ppm.

3,4-dihydroisoquinolin-1(2H)-one (**2k**):



The reaction was performed following the General Procedure with 1,2,3,4-tetrahydroisoquinoline **1k** (0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 1:1) to give the product **2k** (29.14 mg, 99% yield) as a red oil.

^1H NMR (400 MHz, Chloroform- d) δ 8.34 (t, $J = 1.6$ Hz, 1H), 7.35 (td, $J = 7.2, 2.0$ Hz, 1H), 7.32 – 7.25 (m, 2H), 7.15 (dq, $J = 7.6, 0.8$ Hz, 1H), 3.79 – 3.75 (m, 2H), 2.77 – 2.73 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform- d) δ 160.4, 136.4, 131.1, 128.5, 127.5, 127.3, 127.1, 47.4, 25.0 ppm.

Supplementary references

- [1] Zeng, R.; Yan, P.; Xu, B.; Jing, Z.-L.; Liu, H.; Lai, W.-J.; Xie, H.-T.; Niu, S.-L.; Yang, S.-M.; Ouyang, Q. Red-light-induced high-efficiency oxidation and functionalization of tetrahydroisoquinoline derivatives using chlorophyll as a photocatalyst. *New J. Chem.* **2025**, *49*, 4421-4426.
- [2] Wei, L. L.; Chen, Q.; Wang, J. Y.; Sun, J.; Chen, Y.; Zhou, M. D. Dye molecule-containing polymeric photosensitizer as a high-performance photocatalyst for aerobic chemical conversion. *Catal. Sci. Technol.* **2025**, *15*, 4567-4574.
- [3] Ye, T.; Li, Y.; Zhao, F.; Song, A.; Zhong, Z.; Tan, S.; Li, F. Visible-Light-Mediated Aerobic α -Oxygenation of Tetrahydroisoquinolines and Isoindolines Without External Photocatalysts. *Molecules* **2025**, *30*, 743.
- [4] Thatikonda, T.; Deepake, S. K.; Das, U. α -Angelica lactone in a new role: facile access to *N*-aryl tetrahydroisoquinolinones and isoindolinones via organocatalytic α -CH₂ oxygenation. *Org. Lett.* **2019**, *21*, 2532-2535.
- [5] Zhang, H.; Yuan, T.; Zhumabay, N.; Ruan, Z.; Qian, H.; Rueping, M. Ketone-functionalized conjugated organic polymers boost red-light-driven molecular oxygen-mediated oxygenation. *Chem. Sci.* **2024**, *15*, 17435-17443.

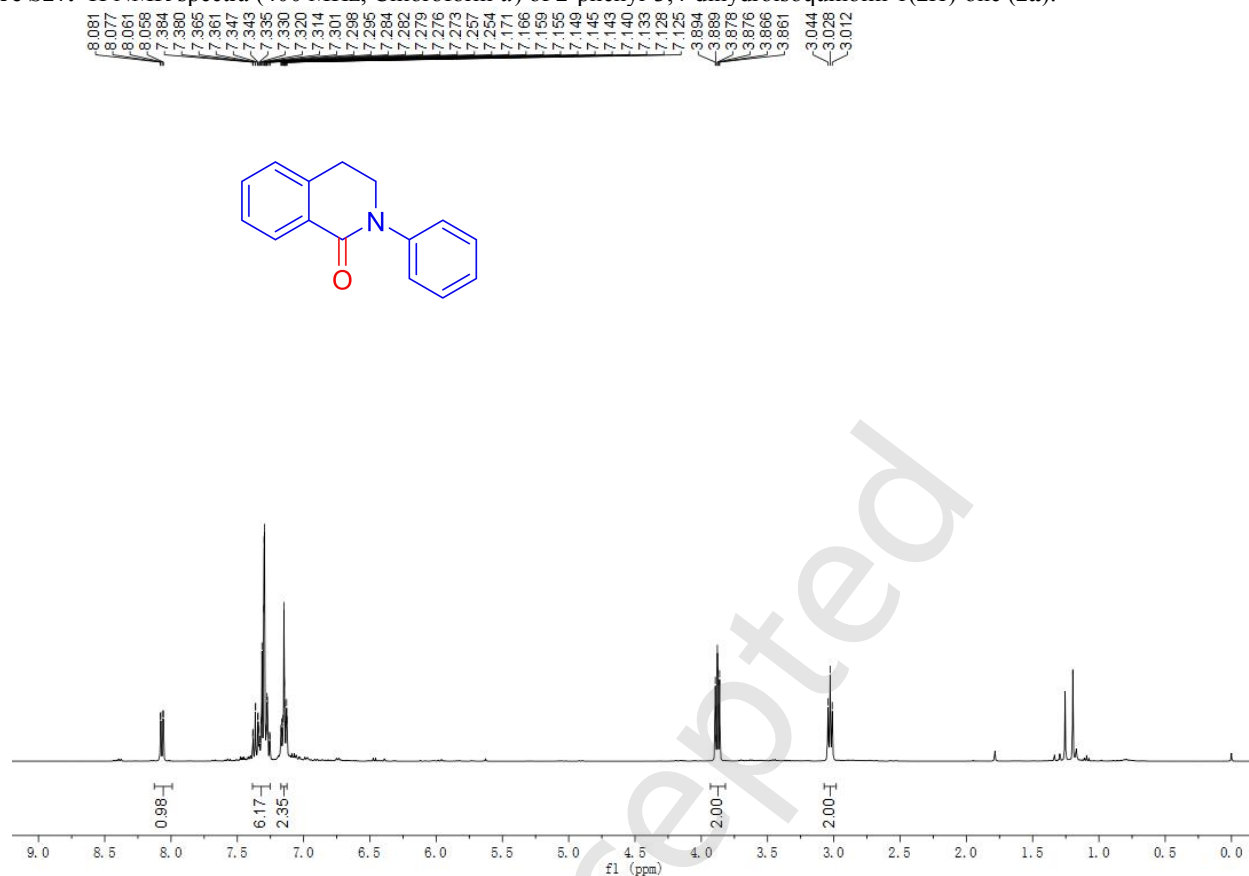
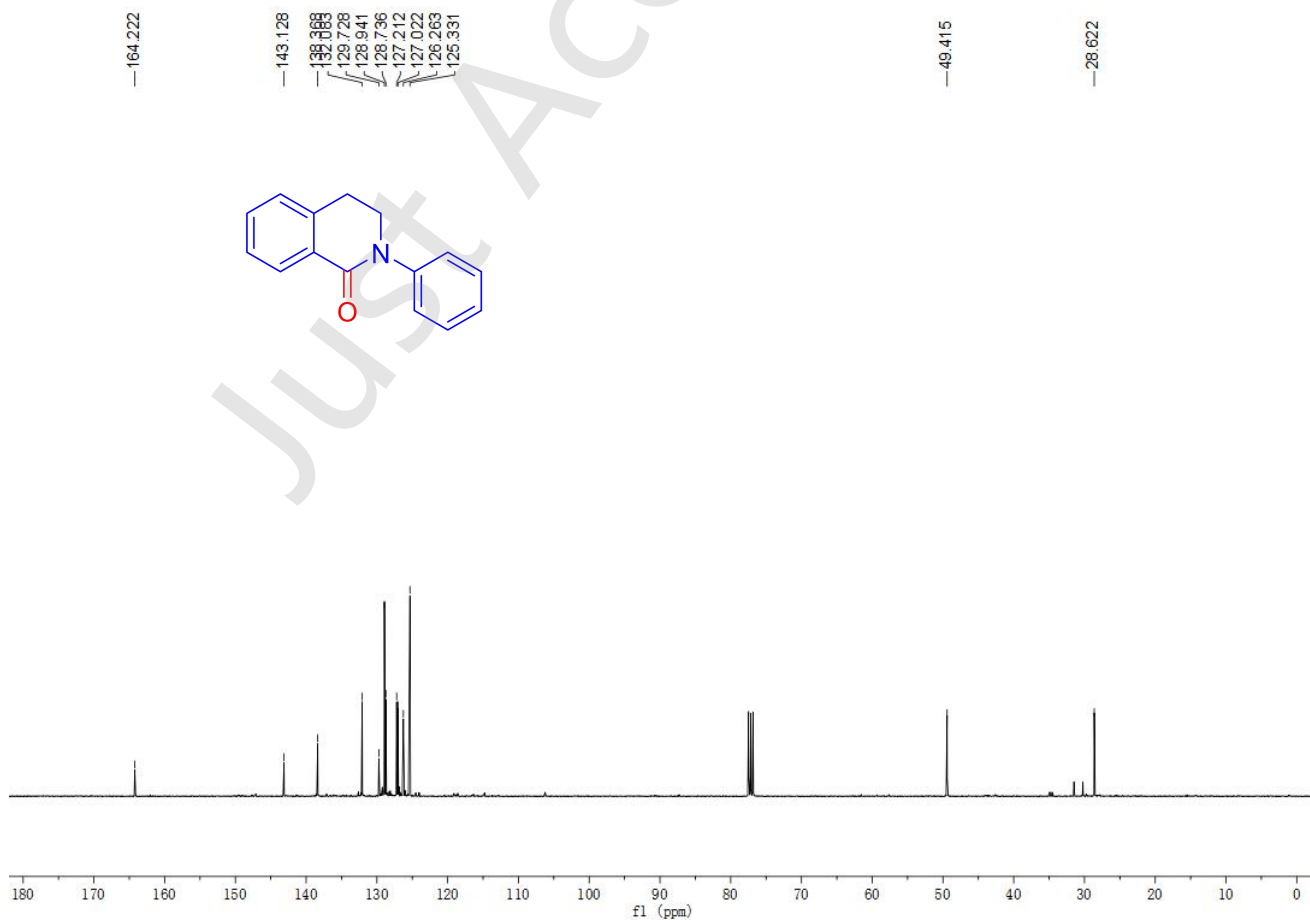
NMR Spectra**Figure S27.** ^1H NMR spectra (400 MHz, Chloroform- d) of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (**2a**):**Figure S28.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform- d) of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (**2a**):

Figure S29. ^1H NMR spectra (400 MHz, Chloroform- d) of 2-(p -tolyl)-3,4-dihydroisoquinolin-1($2H$)-one (**2b**):

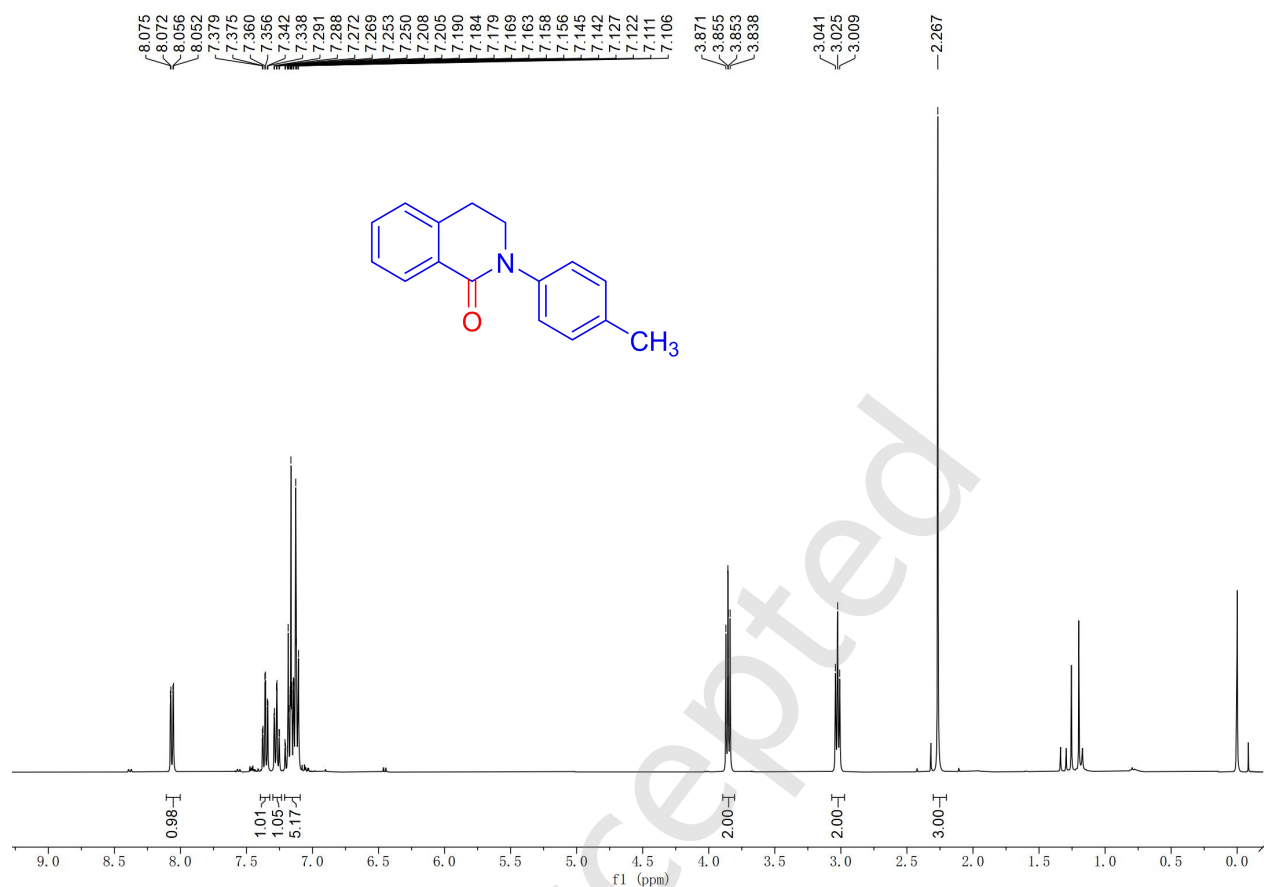


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform- d) of 2-(p -tolyl)-3,4-dihydroisoquinolin-1($2H$)-one (**2b**):

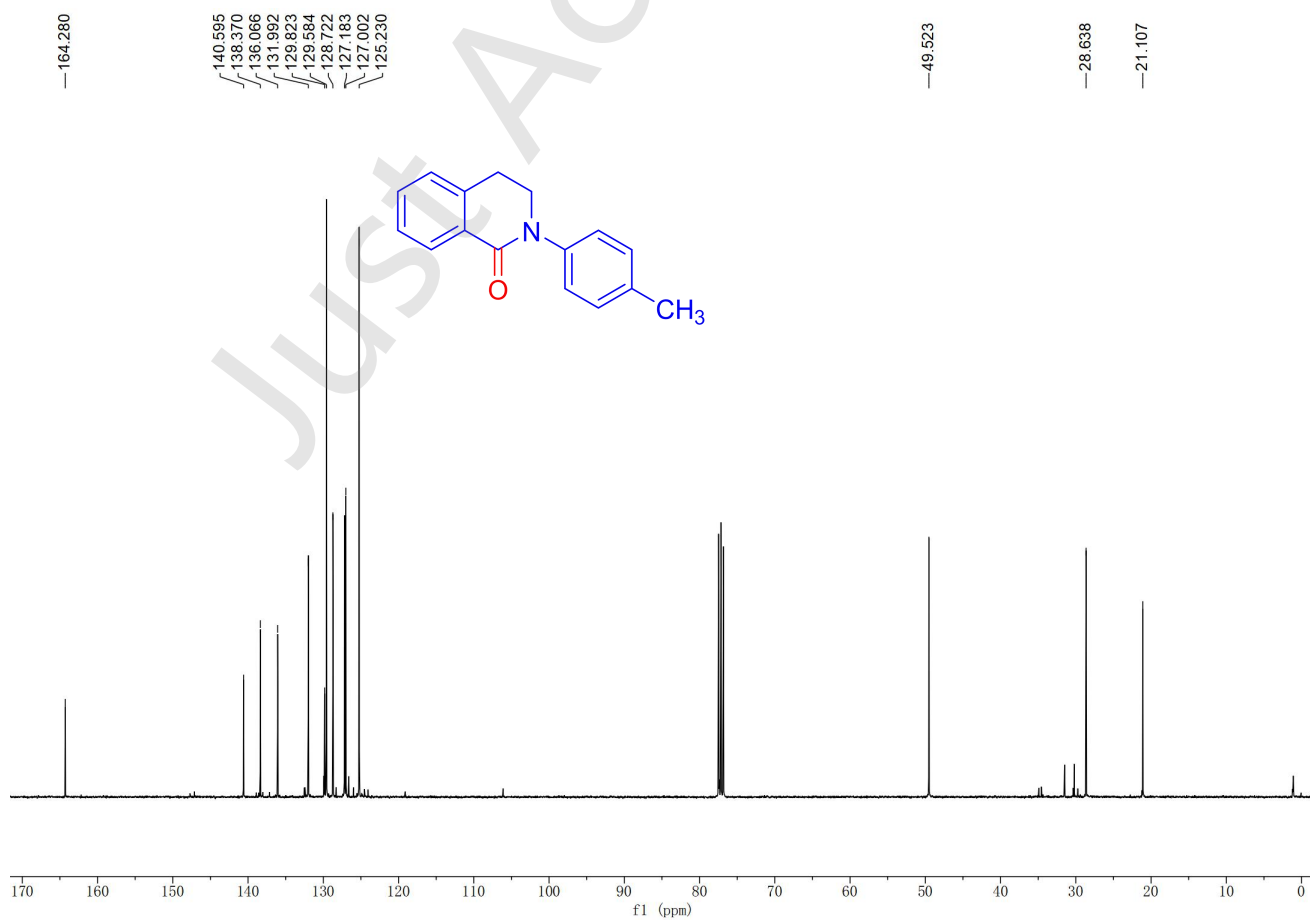
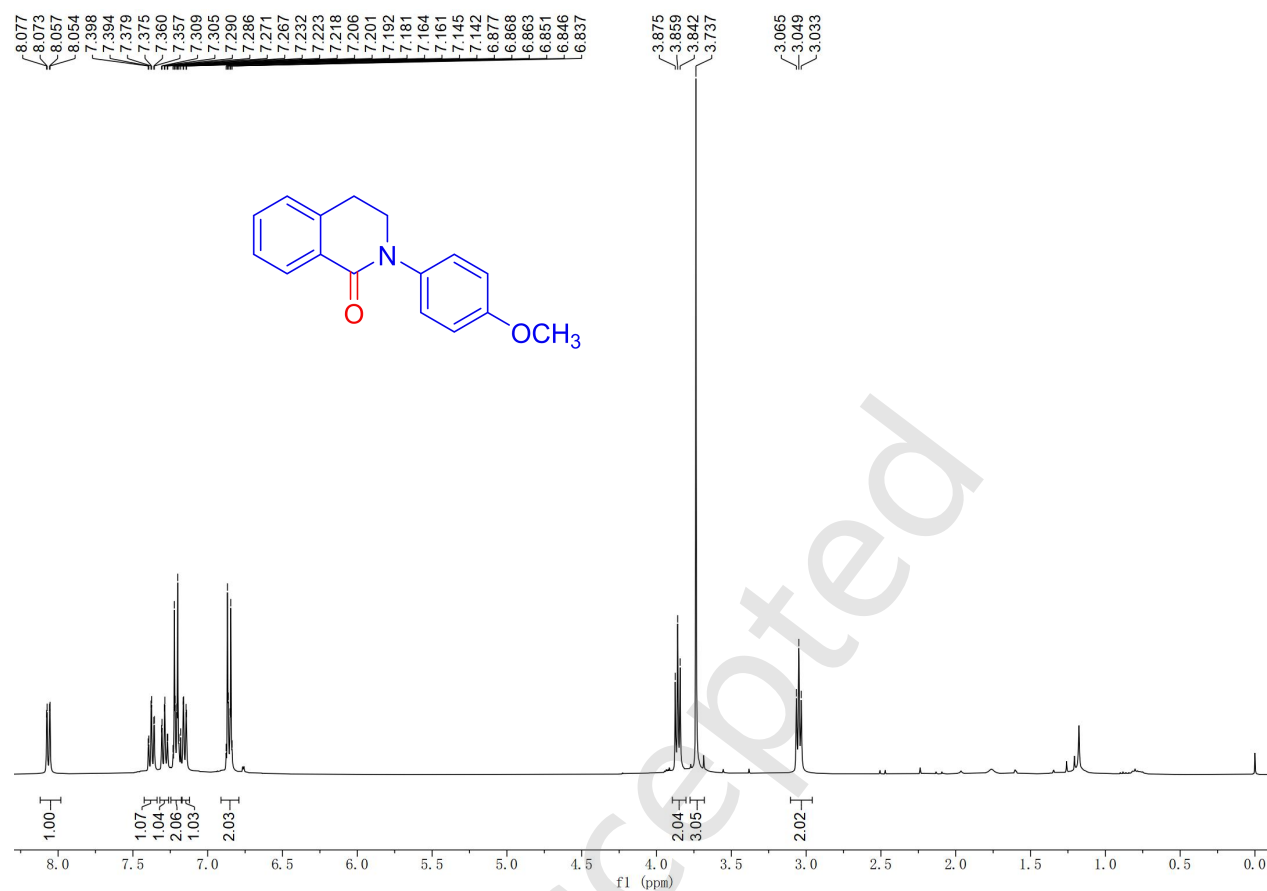


Figure S31. ^1H NMR spectra (400 MHz, Chloroform- d) of 2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (**2c**):**Figure S32.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform- d) of 2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (**2c**):

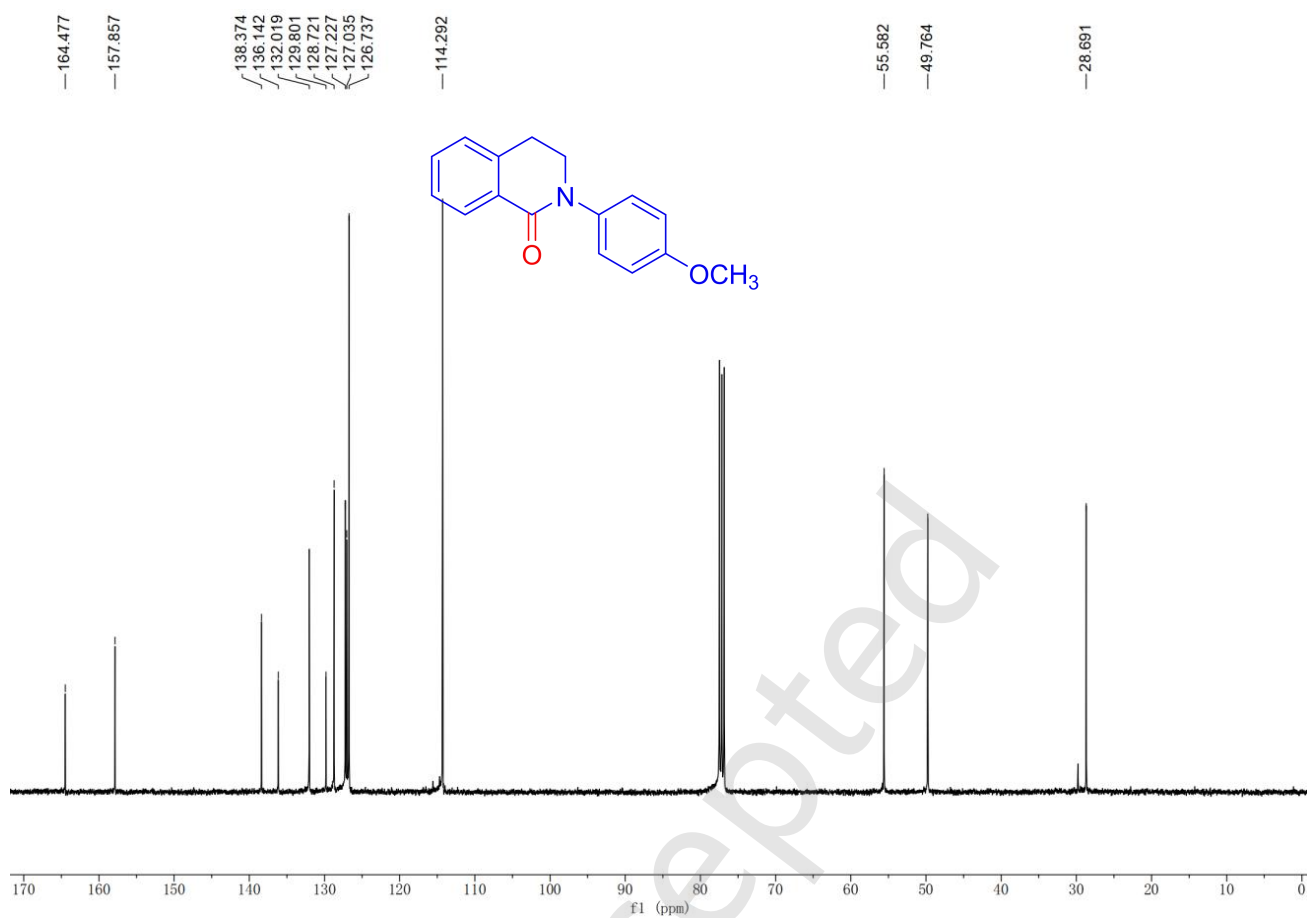


Figure S33. ¹H NMR spectra (400 MHz, Chloroform-*d*) of 2-(3,4-dimethylphenyl)-3,4-dihydroisoquinolin-1(2H)-one (**2d**):

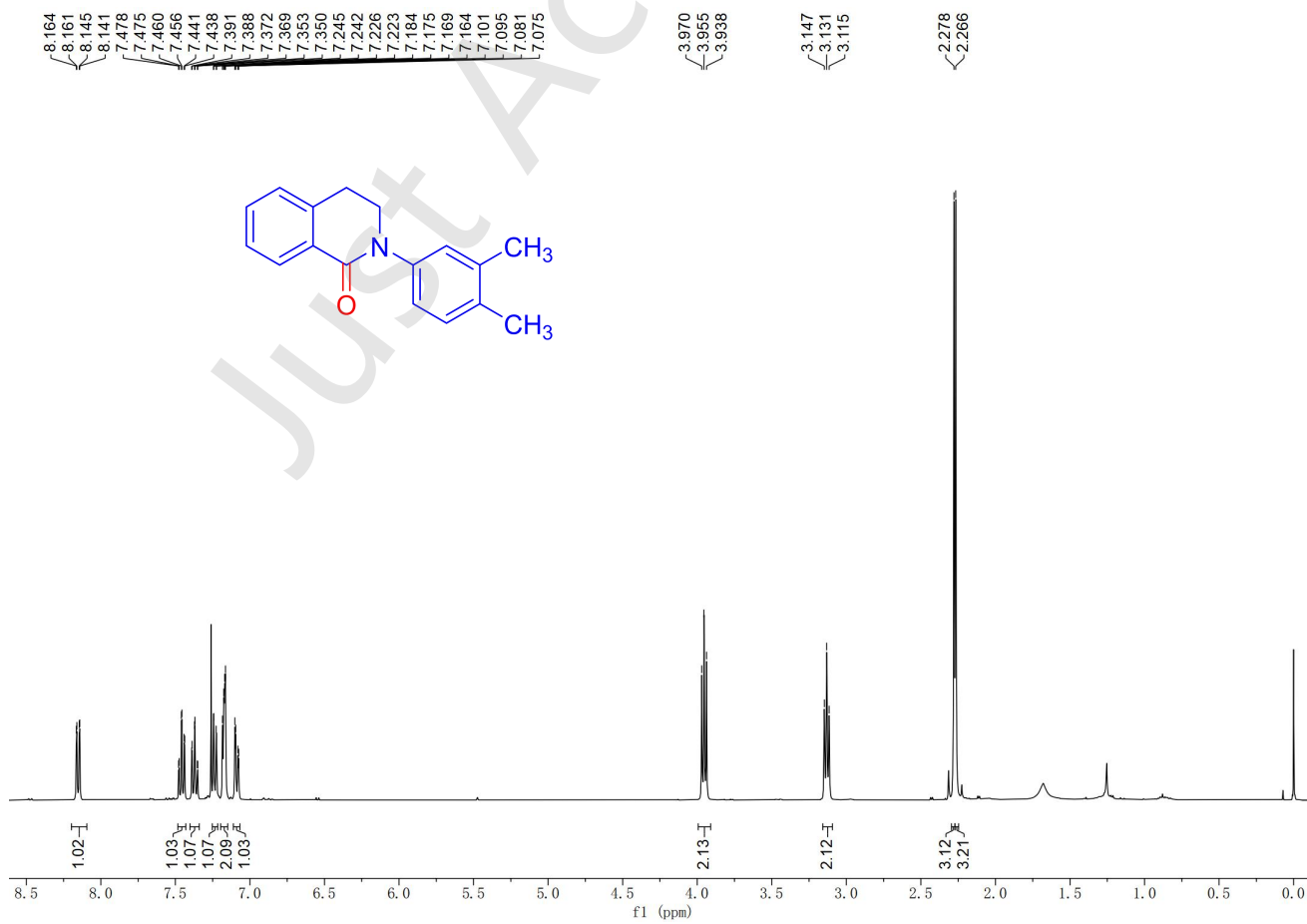


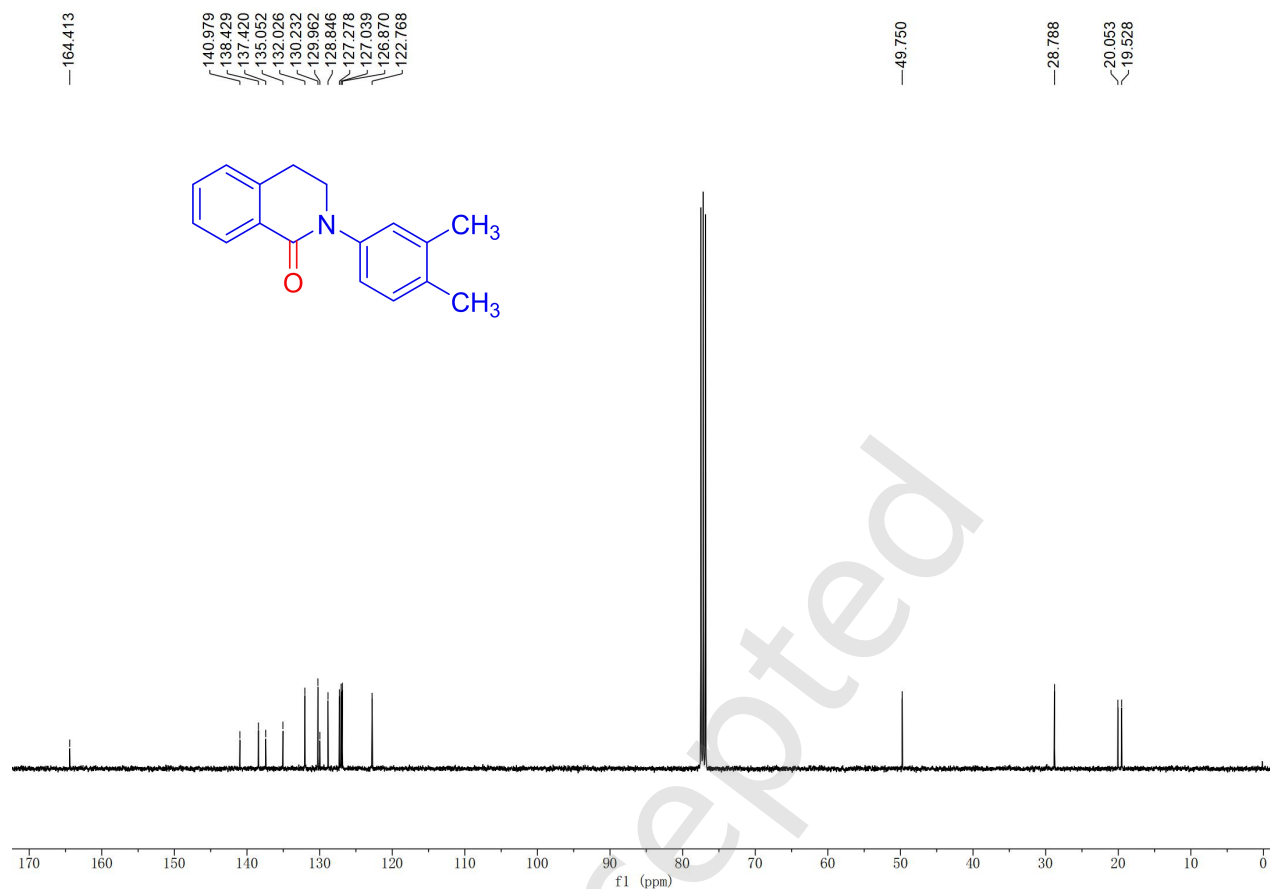
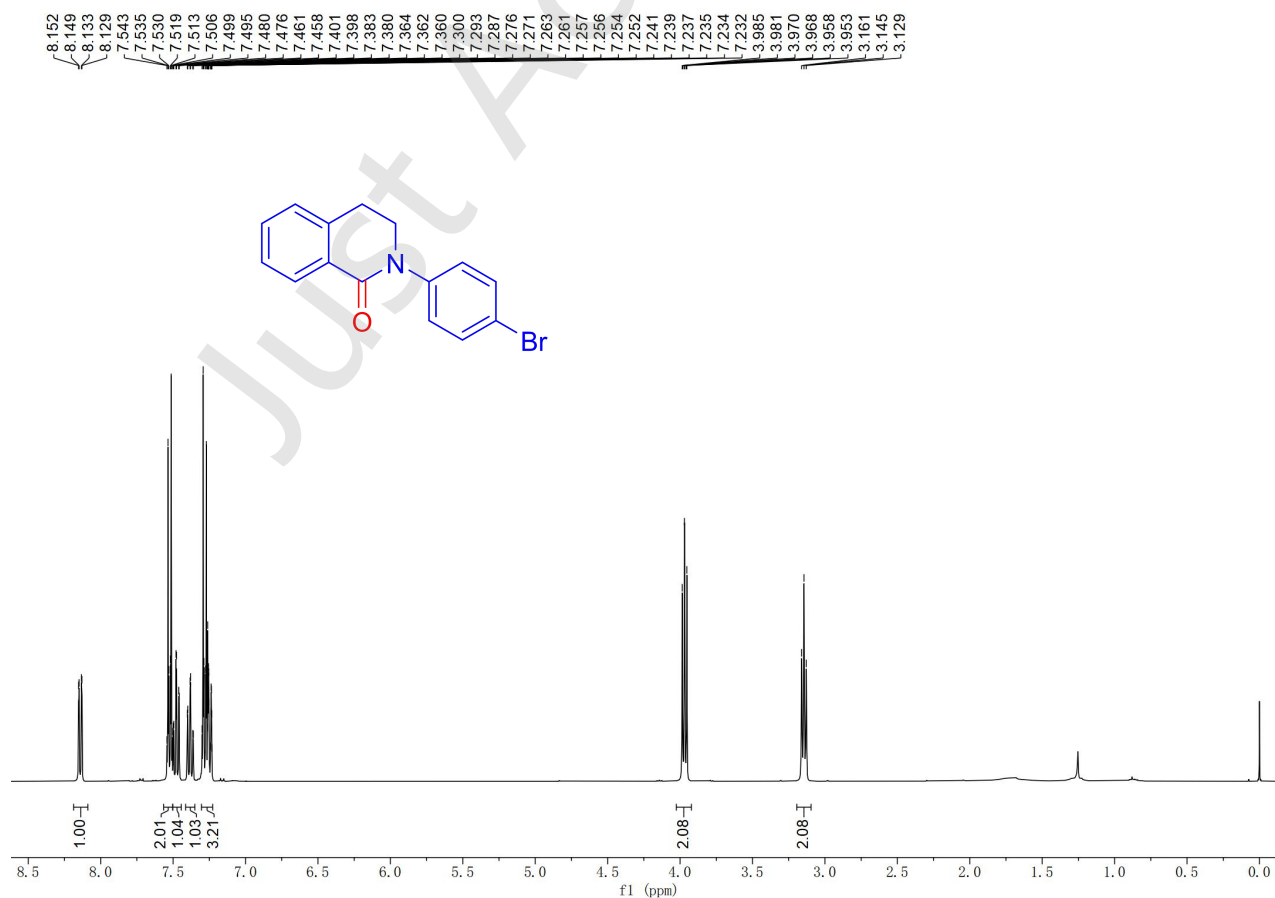
Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of 2-(3,4-dimethylphenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2d**):**Figure S35.** ^1H NMR spectra (400 MHz, Chloroform-*d*) of 2-(4-bromophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2e**):

Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of 2-(4-bromophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2e**):

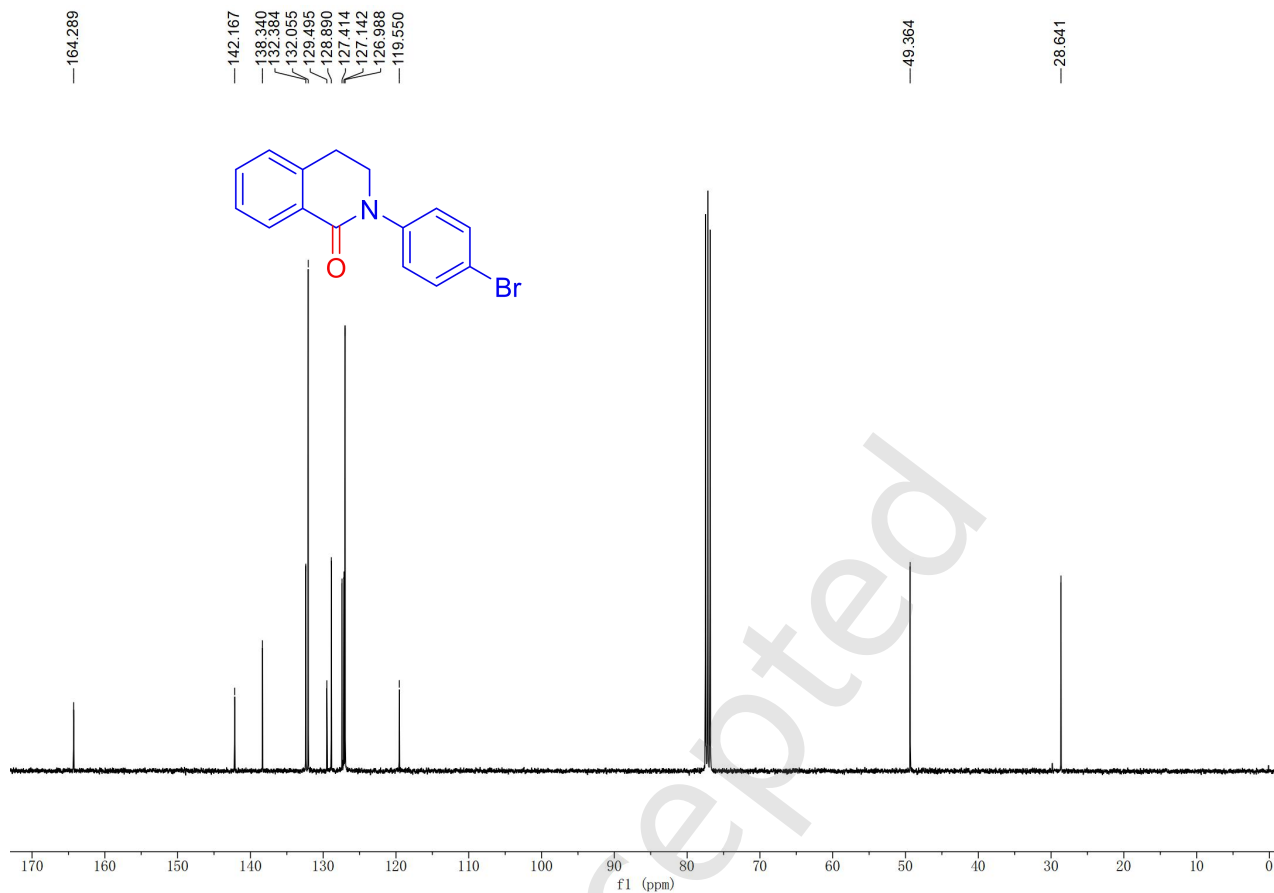


Figure S37. ^1H NMR spectra (400 MHz, Chloroform-*d*) of 2-(4-(trifluoromethyl)phenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2f**):

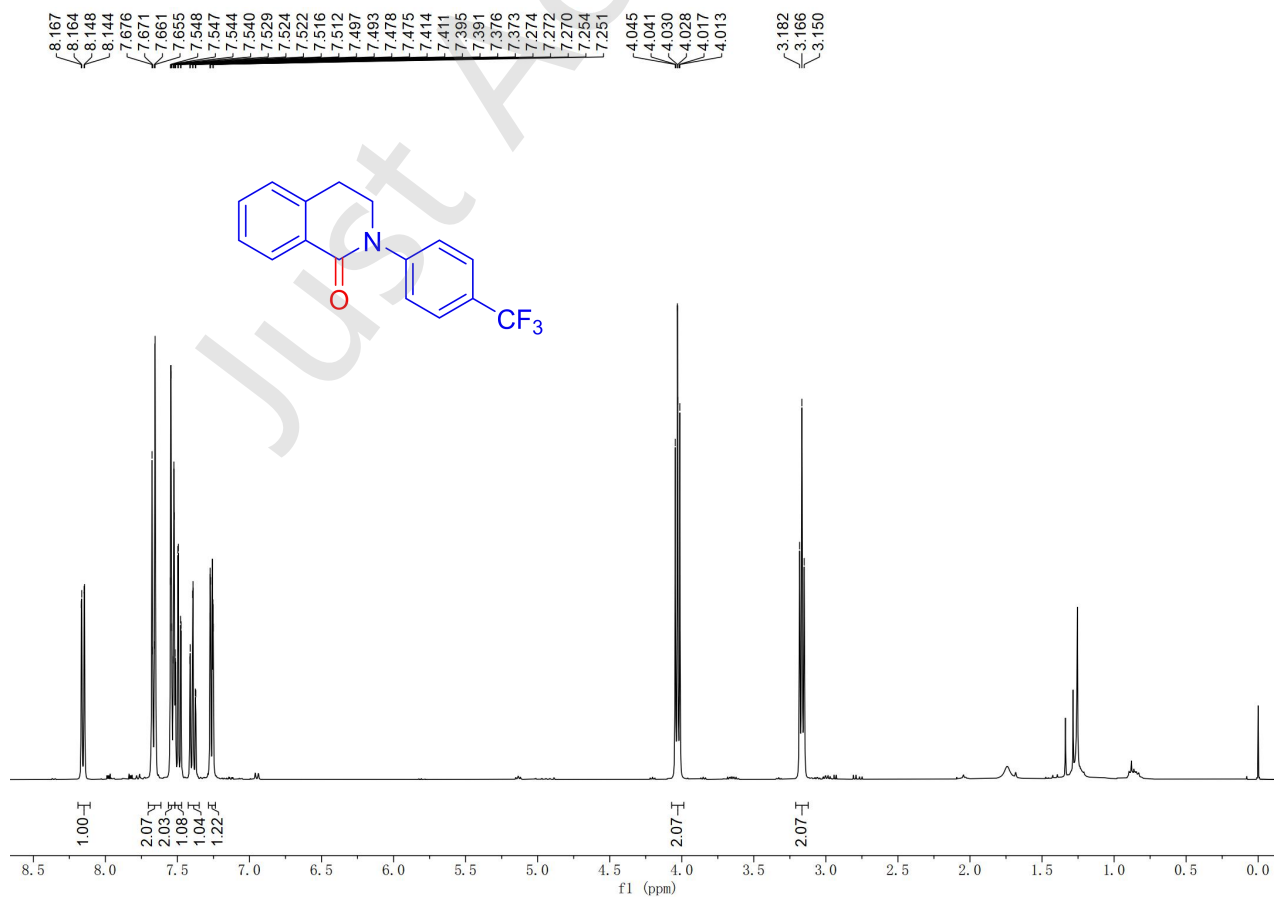
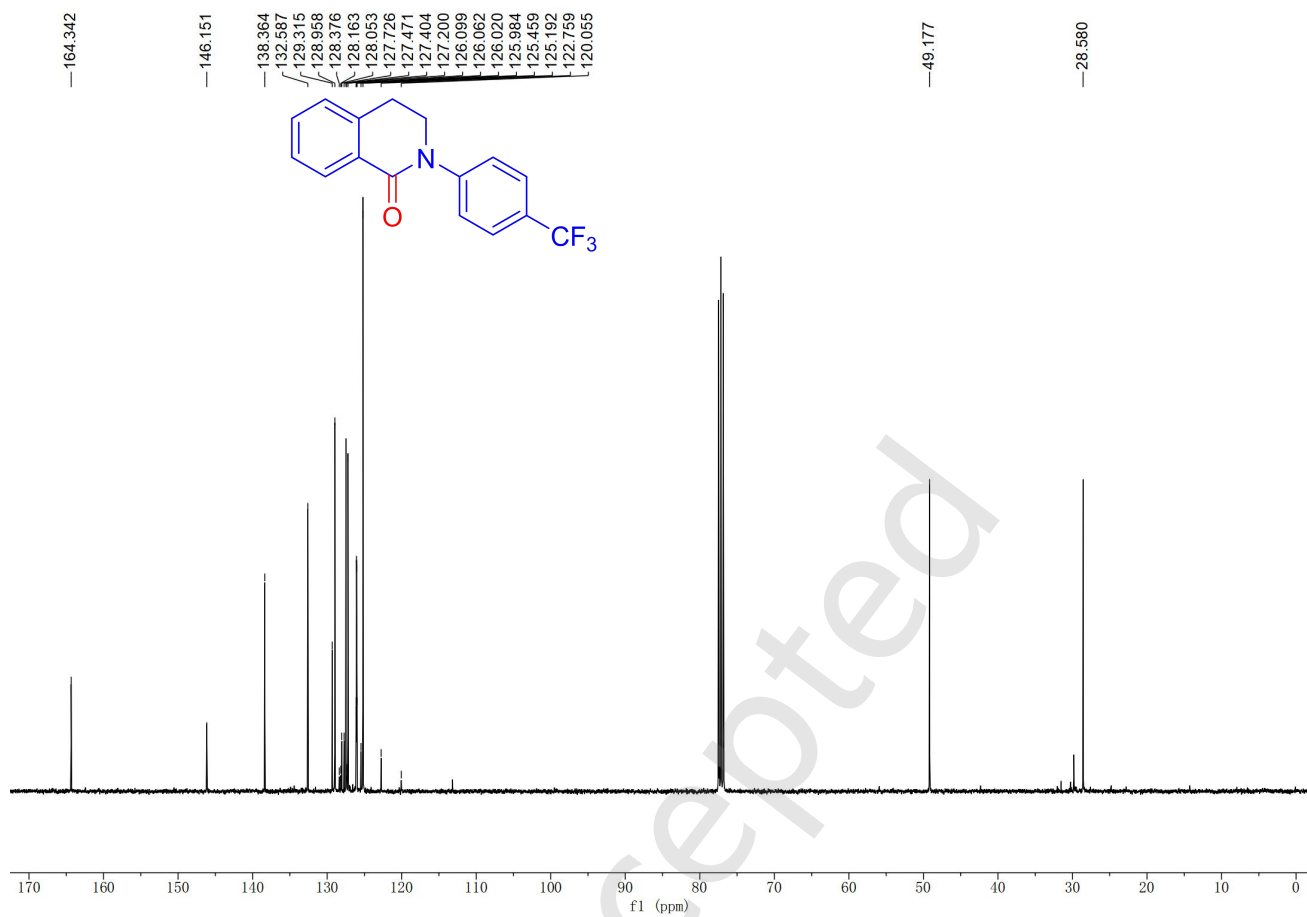


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of 2-(4-(trifluoromethyl)phenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2f**):**Figure S39.** ^1H NMR spectra (400 MHz, Chloroform-*d*) of 2-(3,4-dichlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2g**):

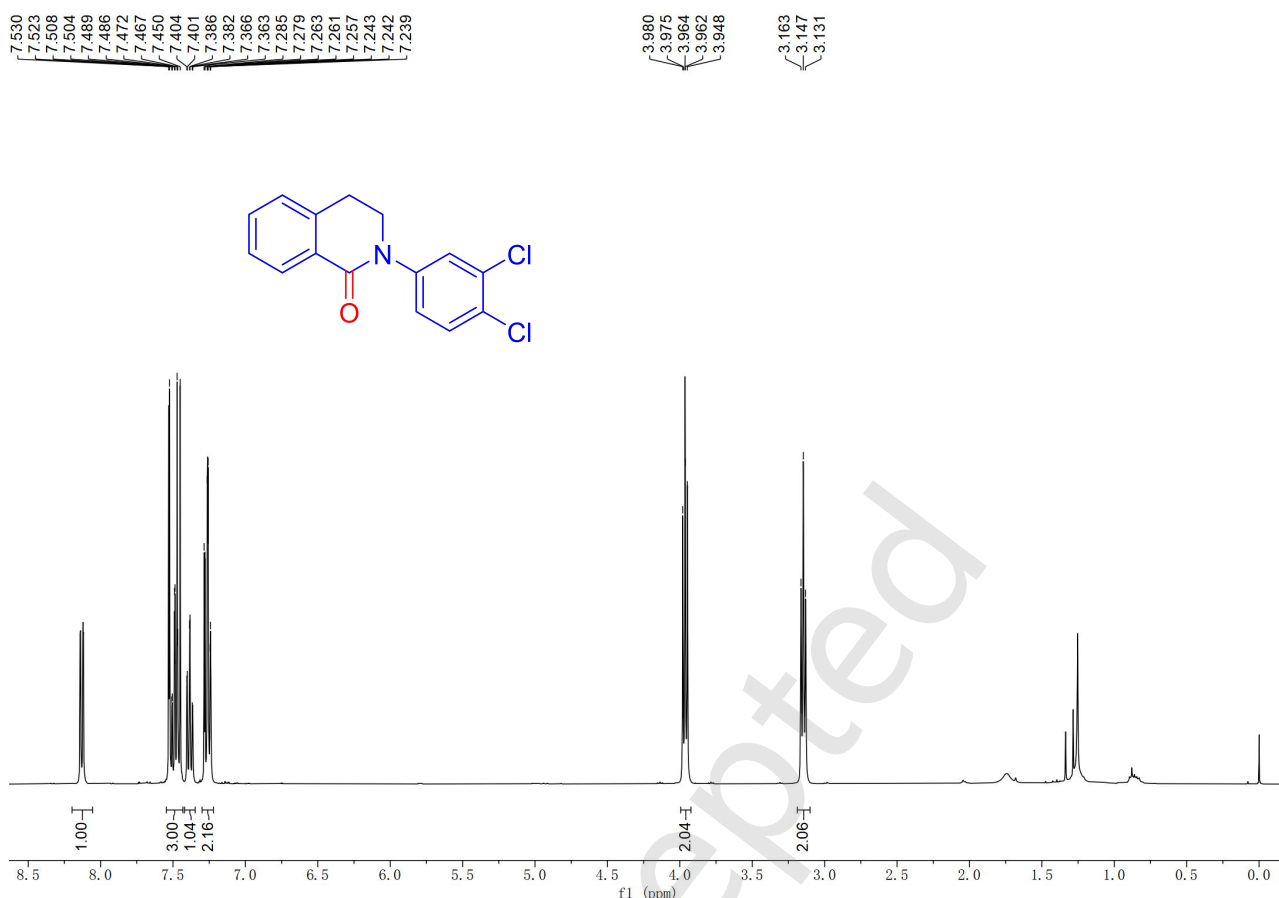


Figure S40. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of 2-(3,4-dichlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one (**2g**):

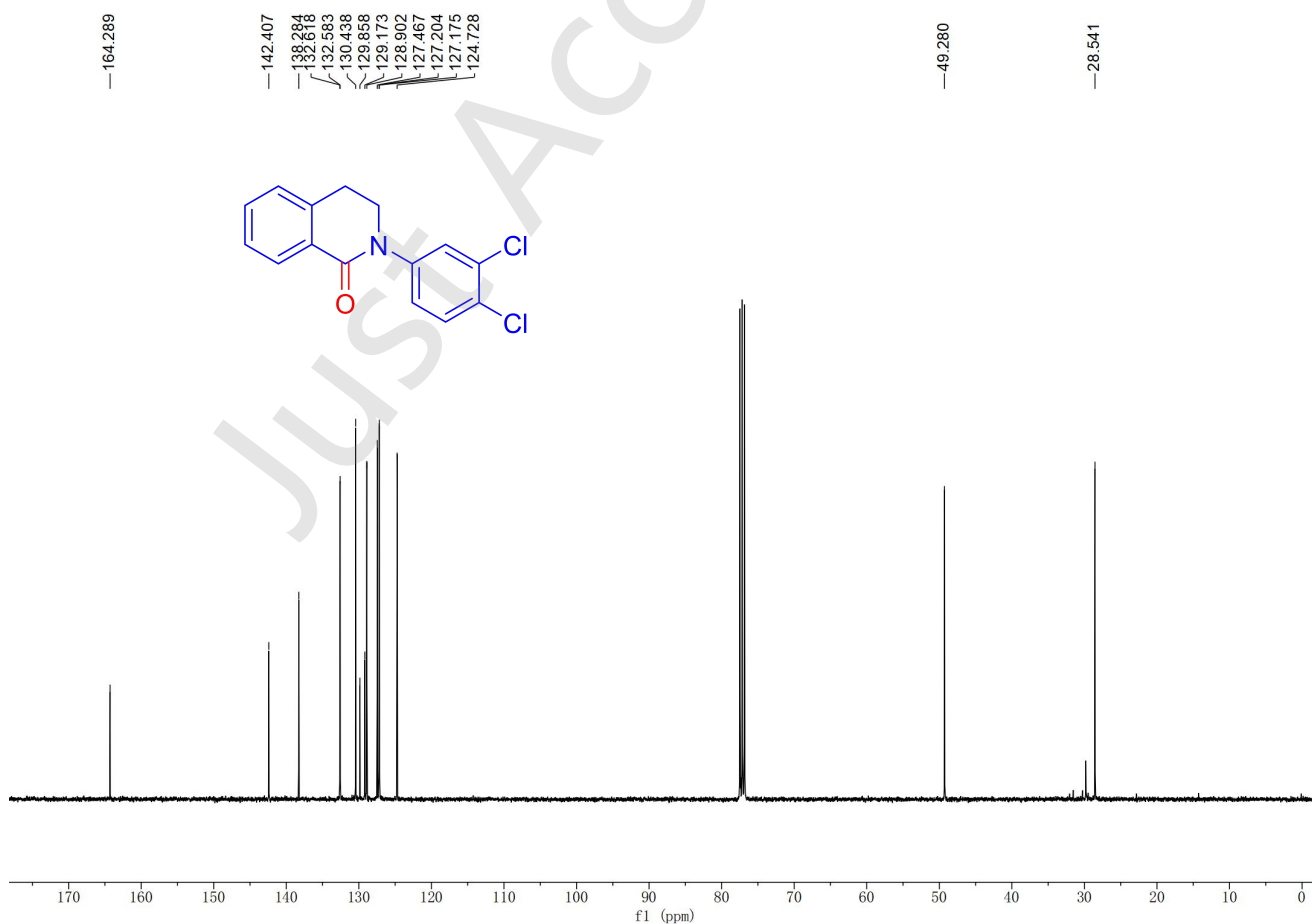


Figure S41. ^1H NMR spectra (400 MHz, Chloroform-*d*) of 6,7-dimethoxy-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (**2h**):

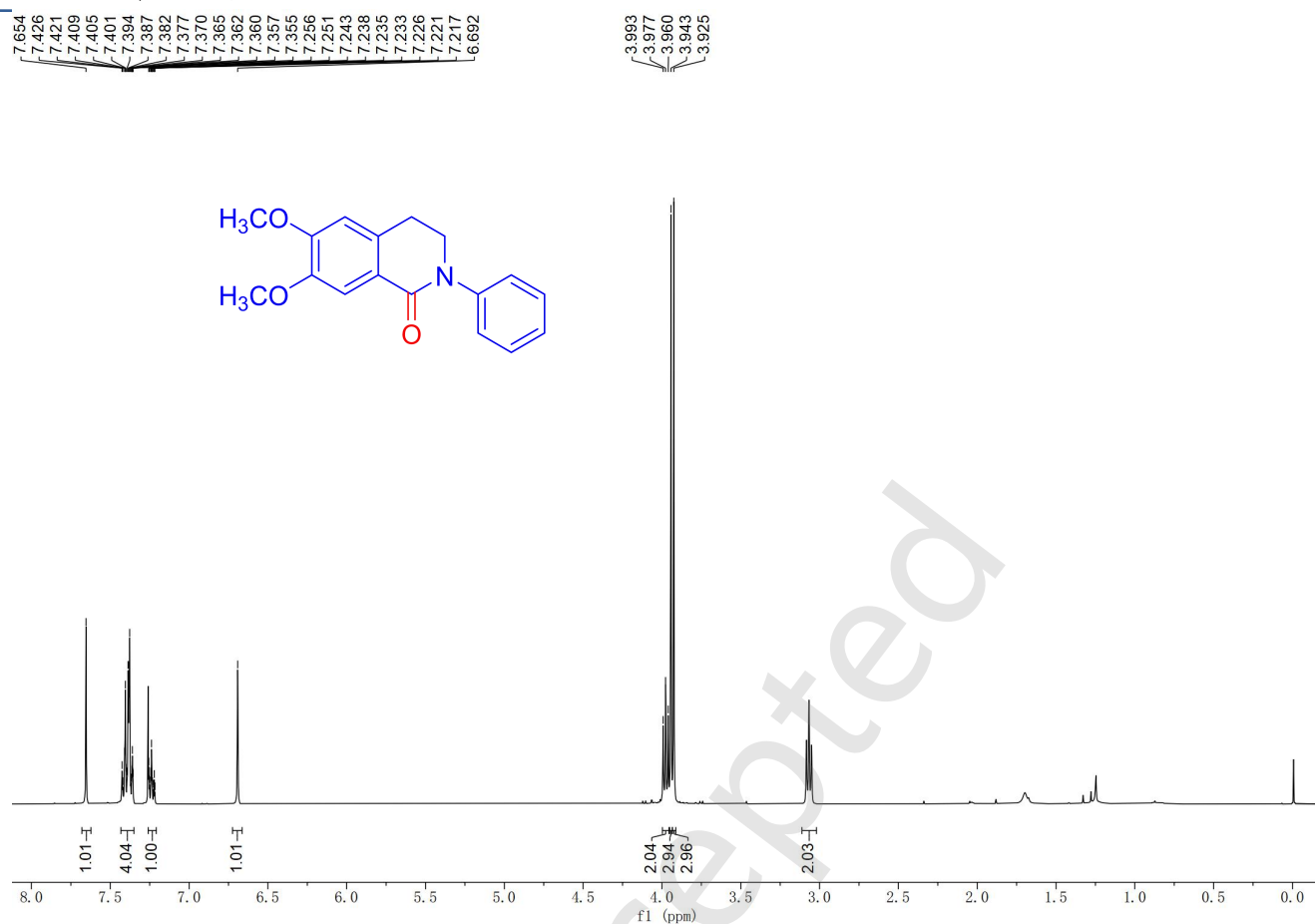


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of 6,7-dimethoxy-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (2h):

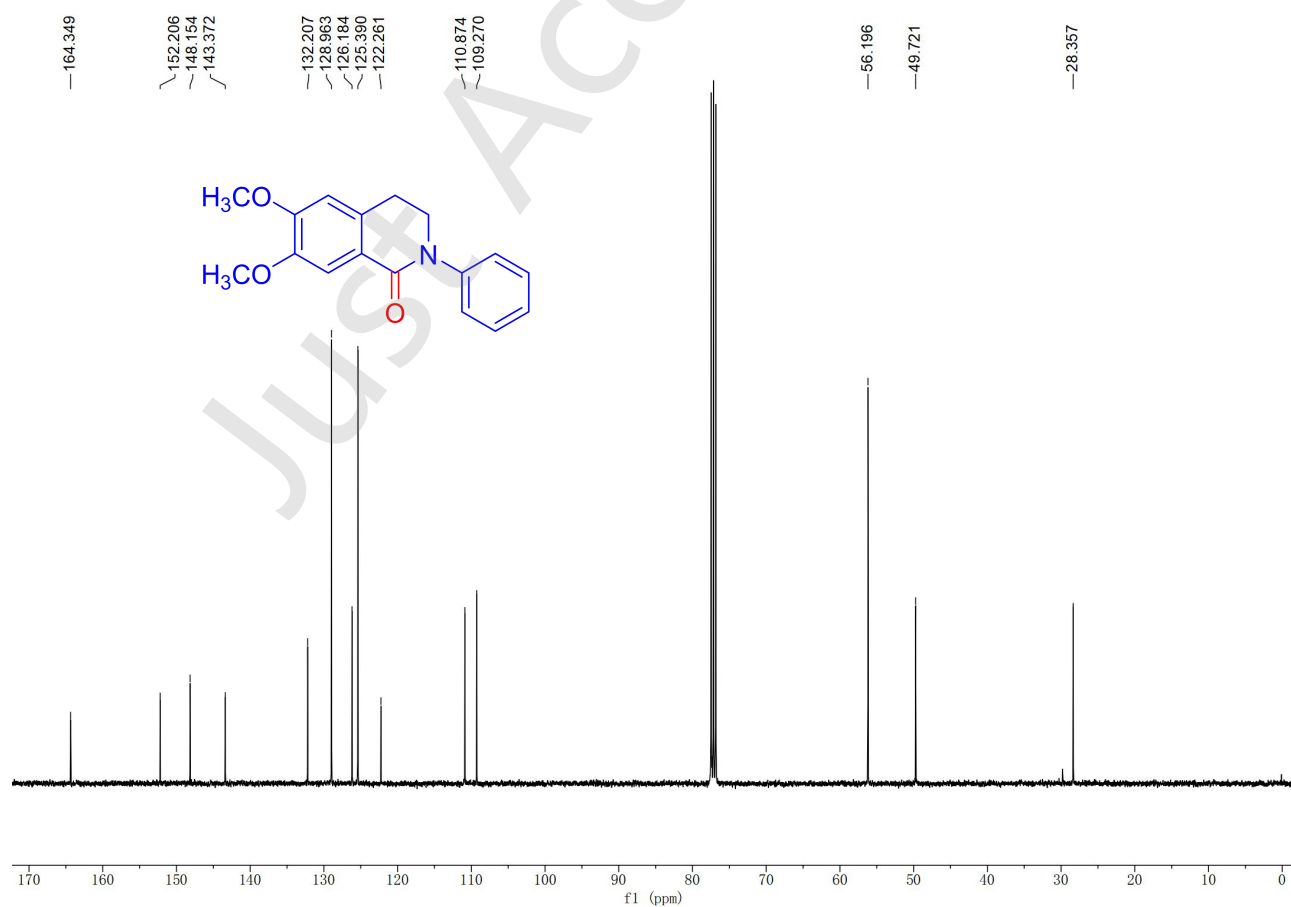


Figure S43. ^1H NMR spectra (400 MHz, Chloroform-*d*) of 6,7-dimethoxy-2-(p-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (2i):

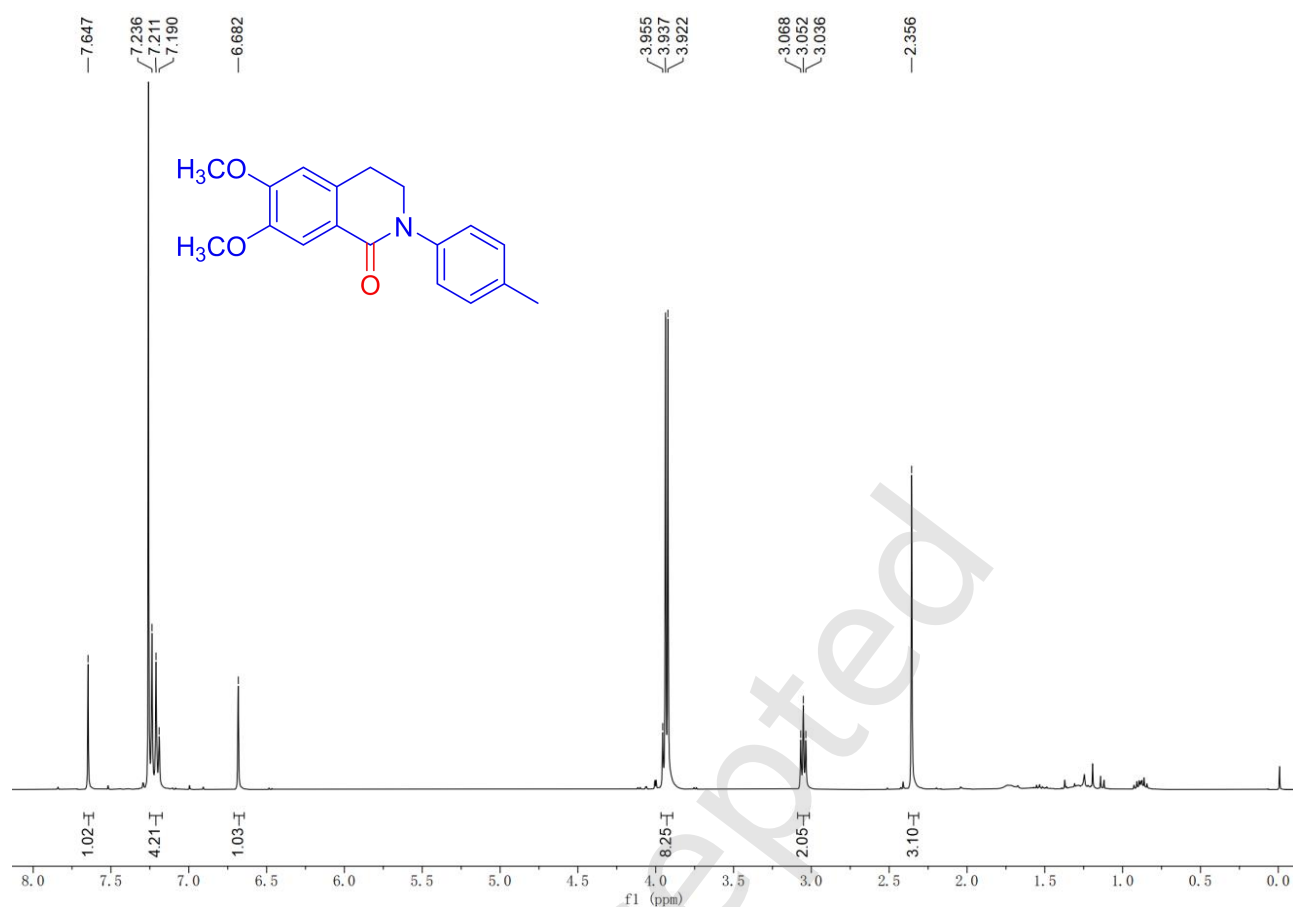


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of 6,7-dimethoxy-2-(*p*-tolyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**2i**):

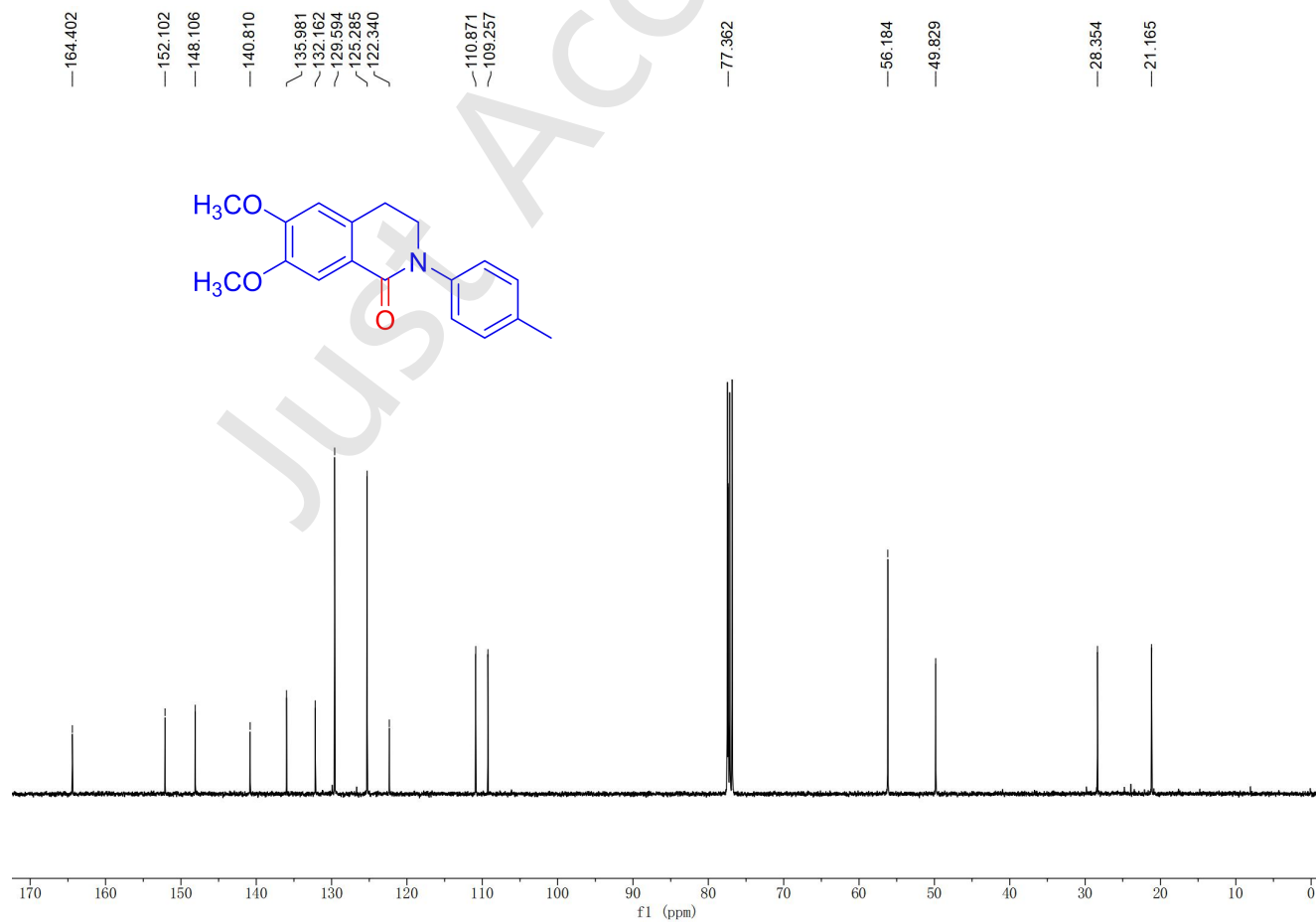


Figure S45. ^1H NMR spectra (400 MHz, Chloroform- d) of 6,7-dimethoxy-2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (2j):

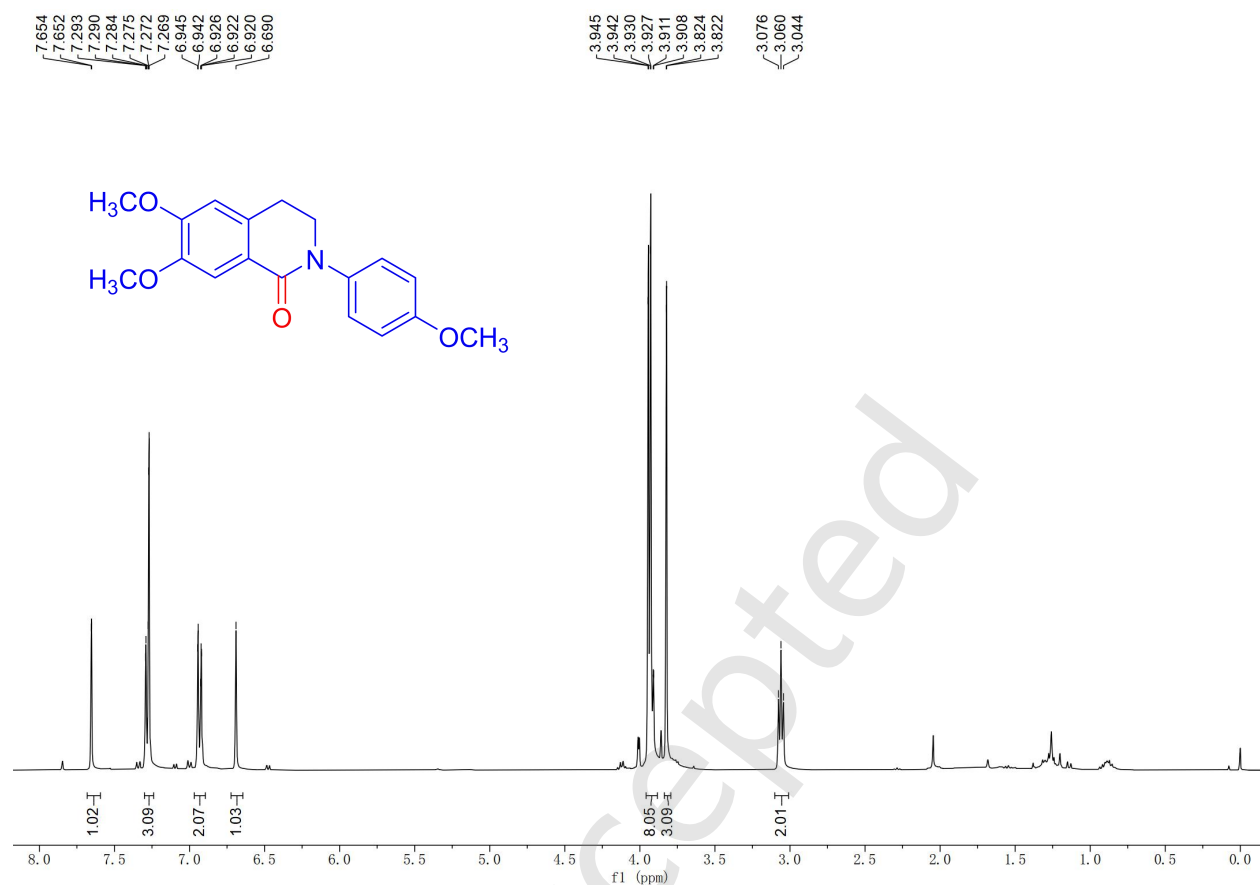


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform- d) of 6,7-dimethoxy-2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (2j):

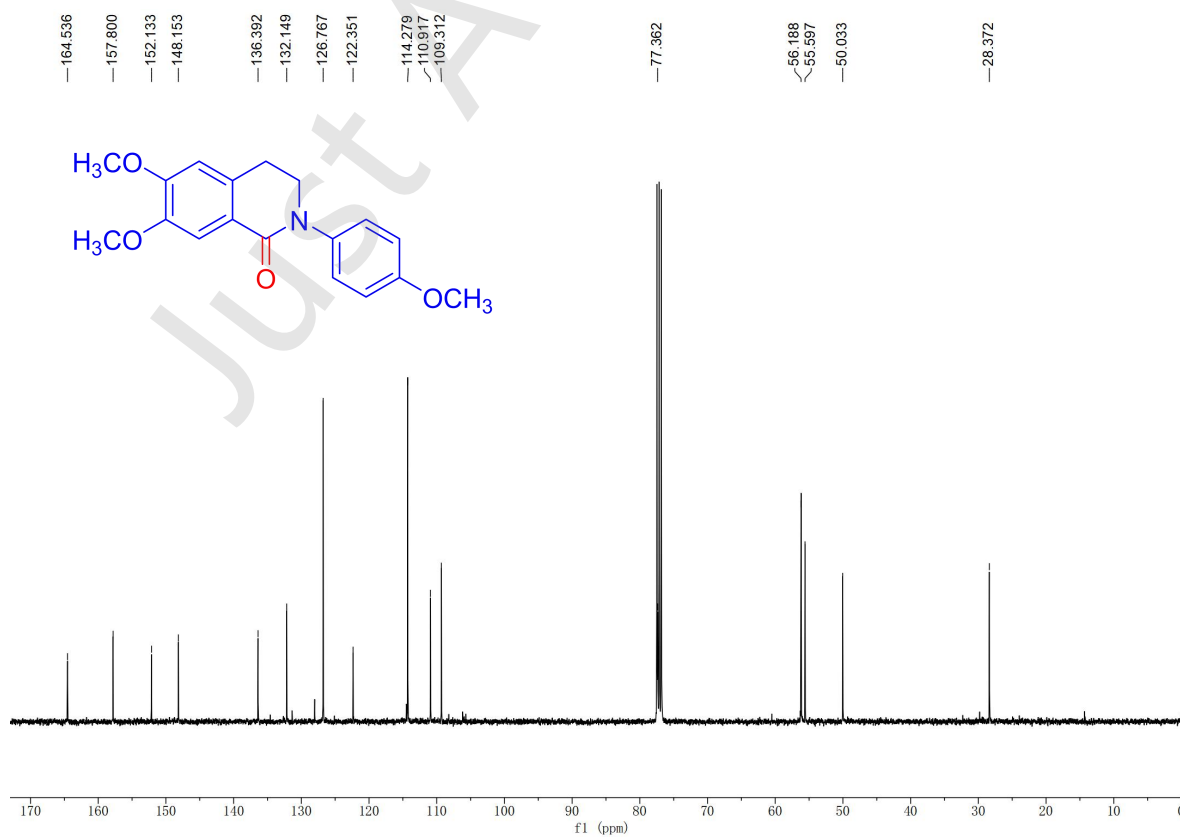


Figure S47. ^1H NMR spectra (400 MHz, Chloroform- d) of 3,4-dihydroisoquinolin-1(2H)-one (**2k**):

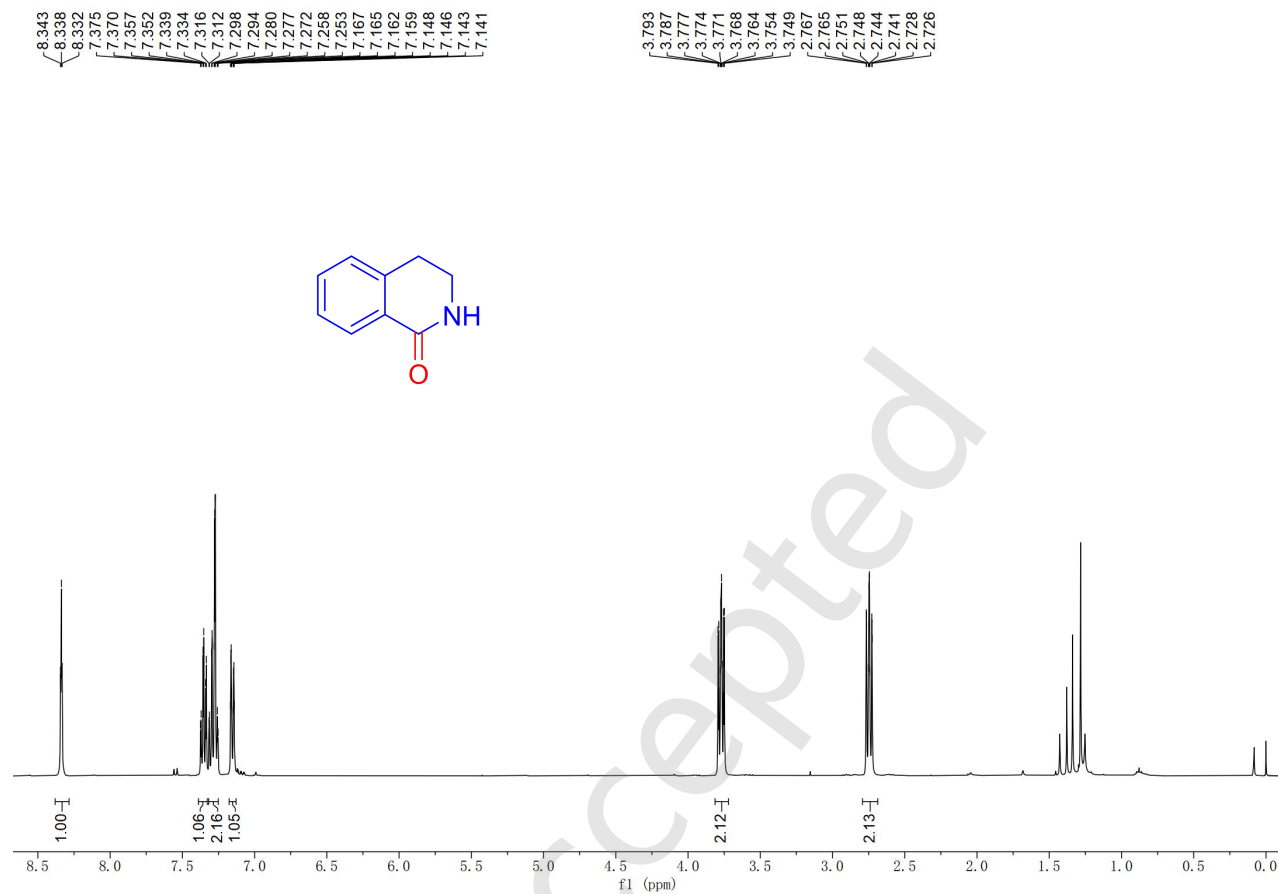
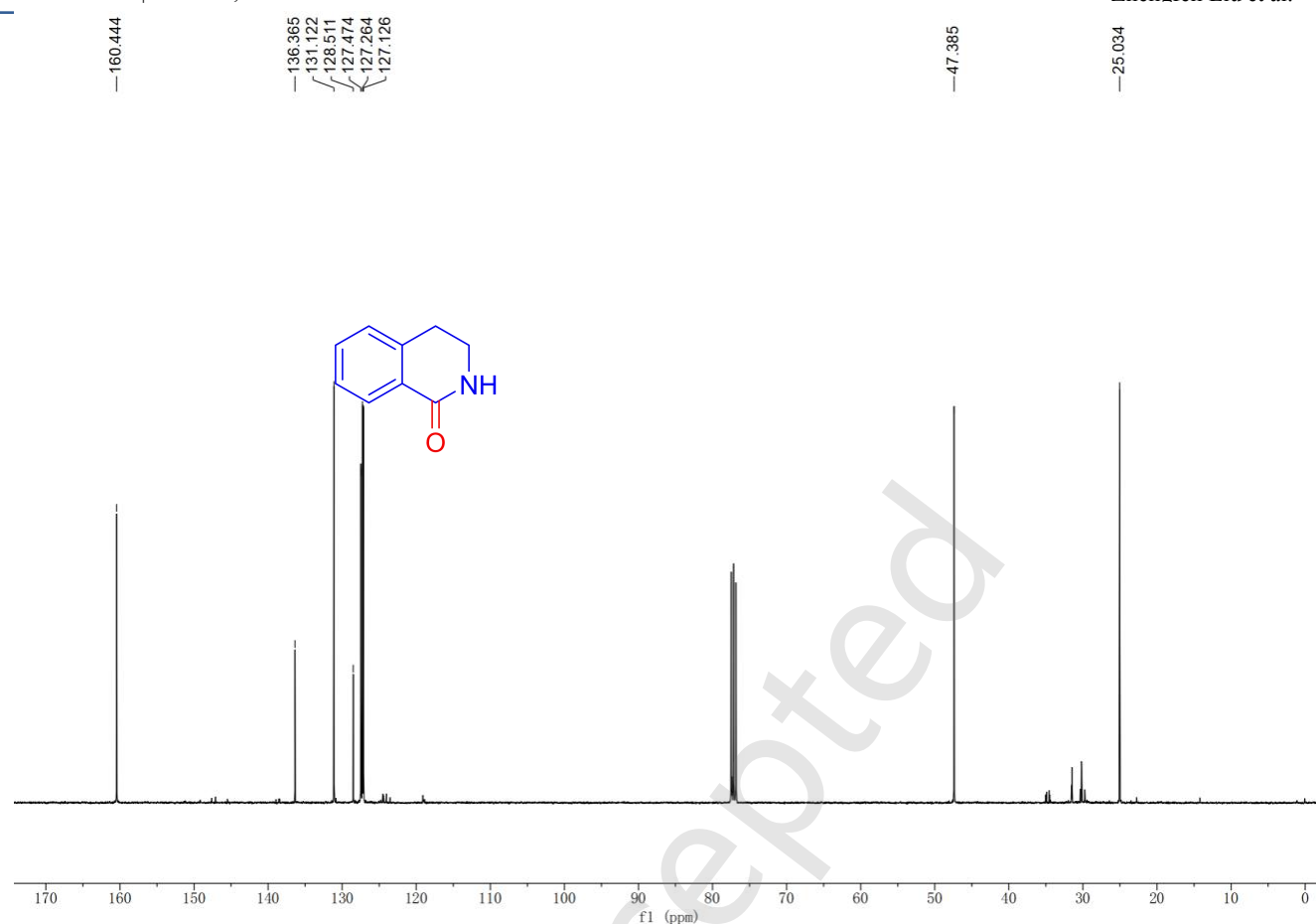


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform- d) of 3,4-dihydroisoquinolin-1(2H)-one (**2k**):

**Table S3.** Atomic coordinates for Pa- COF.

Name: Pa- COF	Space group: <i>P1</i>	Cell parameter: $a = 24.2790 \text{ \AA}$, $b = 24.7072 \text{ \AA}$, $c = 3.8205 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$	
Atom	x	y	z
C1	1.42975	-1.92501	0.06127
N2	1.39309	-1.88519	0.04154
C3	1.40746	-1.82608	0.00711
C4	1.46227	-1.80815	-0.01279
C5	1.47382	-1.75275	-0.03582
C6	1.37611	-1.73309	-0.02517
C7	1.36468	-1.78832	-0.00319
C8	1.44677	-1.29487	-0.05238
C9	1.50377	-1.28229	-0.04357
C10	1.5192	-1.22809	-0.09787
C11	1.48042	-1.18684	-0.10589
C12	1.4243	-1.19753	-0.05313
C13	1.40695	-1.25239	-0.05627
C14	1.42935	-1.34963	-0.0635
C15	1.4685	-1.39186	-0.01535
C16	1.52402	-1.37793	0.03128
C17	1.54307	-1.32447	0.00465
C18	1.35	-1.26493	-0.07493
C19	1.33498	-1.31863	-0.1456
C20	1.37358	-1.36001	-0.13594
C21	1.3847	-1.1556	-0.01153
C22	1.32906	-1.17007	0.01812

C23	1.31039	-1.22308	-0.03527
C24	1.39805	-1.09629	0.00108
C25	1.60399	-1.31532	0.04053
C26	1.4436	-1.07581	0.18715
C27	1.4547	-1.02024	0.19434
C28	1.41834	-0.98356	0.038
C29	1.37179	-1.00343	-0.13872
C30	1.3624	-1.05898	-0.16213
C31	1.64182	-1.35197	-0.10937
C32	1.69865	-1.34441	-0.07104
C33	1.71898	-1.29936	0.11205
C34	1.68165	-1.26322	0.26453
C35	1.6251	-1.27191	0.23649
C36	1.77847	-1.28853	0.14568
C37	1.45385	-1.45081	0.00226
N38	1.81505	-1.32149	0.01833
C39	1.40749	-1.46884	0.18878
C40	1.39418	-1.52364	0.20543
C41	1.42833	-1.56239	0.04961
C42	1.47598	-1.54525	-0.12679
C43	1.48831	-1.49003	-0.15284
C44	1.41297	-1.61998	0.07644
N45	1.44437	-1.65807	-0.04685
C46	1.431	-1.71472	-0.03429
C47	1.24929	-1.23147	-0.05054
C48	1.21623	-1.19344	-0.22756
C49	1.15907	-1.19878	-0.23528
C50	1.13341	-1.24303	-0.07466
C51	1.16588	-1.2812	0.10327
C52	1.22304	-1.27463	0.12287
C53	1.07293	-1.24768	-0.09261
C54	1.98856	-1.29664	0.02378
C55	1.95273	-1.25196	0.04067
C56	1.89579	-1.2596	0.03917
C57	1.87347	-1.31215	0.02665
C58	1.90921	-1.35656	0.01013
C59	1.96632	-1.3489	0.0135
N60	1.04738	-1.29021	0.02438

Table S4. Atomic coordinates for Na⁺ COF.

Name: Na ⁺ COF	Space group: <i>P1</i>	Cell parameter: $a=b=26.6898 \text{ \AA}$, $c=4.0032 \text{ \AA}$; $\alpha=\beta=\gamma=90^\circ$	
Atom	x	y	z
C1	1.40803	-2.78474	-0.00167
C2	1.45582	-2.7698	-0.11717
C3	1.4688	-2.71887	-0.11827
C4	1.38682	-2.6977	0.10088
C5	1.37393	-2.74841	0.10923
C6	1.445	-2.29526	0

C7	1.4964	-2.28161	-0.0073
C8	1.50842	-2.2306	-0.03467
C9	1.47184	-2.19392	-0.02296
C10	1.42062	-2.206	-0.02381
C11	1.40705	-2.25731	0
C12	1.43135	-2.34666	0.0073
C13	1.46901	-2.38437	-0.01223
C14	1.51944	-2.3697	0
C15	1.53411	-2.31927	0.01223
C16	1.35574	-2.27088	0.02382
C17	1.34366	-2.3221	0.02296
C18	1.38034	-2.35868	0.03467
C19	1.38272	-2.16847	-0.04573
C20	1.3326	-2.18286	0
C21	1.31821	-2.23298	0.04574
C22	1.39355	-2.11418	-0.11982
C23	1.589	-2.30794	0.05087
C24	1.43119	-2.10037	-0.34779
C25	1.4447	-2.05034	-0.392
C26	1.41827	-2.01223	-0.22942
C27	1.37755	-2.02507	-0.02457
C28	1.36563	-2.07545	0.03221
C29	1.62546	-2.33695	-0.11556
C30	1.67645	-2.32563	-0.08591
C31	1.69204	-2.28407	0.10215
C32	1.65623	-2.25608	0.27622
C33	1.60568	-2.2692	0.26186
C34	1.74493	-2.26833	0.11251
C35	1.45768	-2.43926	-0.05087
N36	1.78059	-2.29858	0.02326
C37	1.41894	-2.45594	-0.26186
C38	1.40582	-2.50649	-0.27623
C39	1.43381	-2.5423	-0.10216
C40	1.47537	-2.52671	0.0859
C41	1.48669	-2.47572	0.11556
C42	1.41807	-2.59519	-0.11253
N43	1.44832	-2.63085	-0.02326
C44	1.43419	-2.68265	-0.01558
C45	1.26392	-2.24381	0.11983
C46	1.22519	-2.21589	-0.0322
C47	1.17481	-2.22781	0.02457
C48	1.16197	-2.26853	0.22943
C49	1.20008	-2.29496	0.39201
C50	1.25011	-2.28146	0.34779
C51	1.10956	-2.28473	0.27464
C52	1.93448	-2.25829	0.00167
C53	1.89815	-2.22419	-0.10923
C54	1.84744	-2.23708	-0.10089
C55	1.83239	-2.28445	0.01558
C56	1.86861	-2.31906	0.11826

C57	1.91954	-2.30608	0.11717
N58	1.07338	-2.26423	0.10594
C59	1.39516	-2.83571	4.50E-04
C60	1.42882	-2.87188	-0.11714
C61	1.47652	-2.85667	-0.22942
C62	1.48977	-2.80605	-0.22984
N63	1.41397	-2.92364	-0.10594
C64	1.43447	-2.95982	-0.27464
C65	1.95579	-2.34003	0.22984
C66	2.00641	-2.32678	0.22943
C67	2.02162	-2.27908	0.11714
C68	1.98545	-2.24542	-0.00045

Table S5. Atomic coordinates for Aa- COF.

Name: Aa- COF	Space group: <i>P1</i>	Cell parameter: $a=28.6671 \text{ \AA}$, $a=28.6667 \text{ \AA}$ $c=4.0806 \text{ \AA}$; $\alpha=\beta=\gamma=90^\circ$	
Atom	x	y	z
C1	1.27934	-1.68963	-0.16364
C2	1.32131	-1.6738	-0.01964
C3	1.33327	-1.62641	-0.0385
C4	1.26222	-1.61069	-0.34063
C5	1.25015	-1.65781	-0.32389
C6	1.32554	-1.23796	-0.05504
C7	1.37257	-1.2244	-0.10825
C8	1.38476	-1.17769	-0.05176
C9	1.35227	-1.1452	0.05231
C10	1.30556	-1.15739	0.10876
C11	1.29201	-1.20442	0.05552
C12	1.31199	-1.28499	-0.10831
C13	1.34569	-1.31853	-0.20896
C14	1.39187	-1.30428	-0.25804
C15	1.40612	-1.2581	-0.20889
C16	1.24498	-1.21798	0.10873
C17	1.23279	-1.26469	0.05223
C18	1.26527	-1.29717	-0.05186
C19	1.27186	-1.12385	0.2094
C20	1.22568	-1.1381	0.25852
C21	1.21143	-1.18428	0.20938
C22	1.28272	-1.07335	0.25969
C23	1.45661	-1.24723	-0.25924
C24	1.31963	-1.05936	0.46244
C25	1.33068	-1.01237	0.50174
C26	1.30428	-0.97793	0.34473
C27	1.2659	-0.99135	0.15202
C28	1.25518	-1.03868	0.11062
C29	1.49129	-1.27477	-0.11026
C30	1.53861	-1.26405	-0.15176
C31	1.55203	-1.22566	-0.34446
C32	1.51758	-1.19926	-0.50135
C33	1.47059	-1.21031	-0.46197

C34	1.60122	-1.21154	-0.38089
C35	1.33482	-1.36902	-0.25942
N36	1.63376	-1.22986	-0.20041
C37	1.2979	-1.38299	-0.46215
C38	1.28685	-1.42998	-0.50166
C39	1.31326	-1.46444	-0.34489
C40	1.35164	-1.45103	-0.15219
C41	1.36237	-1.40371	-0.11057
C42	1.29913	-1.51363	-0.38143
N43	1.31748	-1.54618	-0.20123
C44	1.30417	-1.59459	-0.19974
C45	1.16094	-1.19515	0.25971
C46	1.12626	-1.1676	0.11075
C47	1.07894	-1.17831	0.15225
C48	1.06552	-1.2167	0.34494
C49	1.09996	-1.24311	0.50181
C50	1.14695	-1.23207	0.46242
C51	1.01632	-1.23081	0.38139
C52	1.7772	-1.19171	-0.16273
C53	1.74538	-1.16252	-0.32296
C54	1.69826	-1.17459	-0.33972
C55	1.68216	-1.21654	-0.19885
C56	1.71398	-1.24564	-0.03756
C57	1.76137	-1.23368	-0.0187
N58	0.98379	-1.21251	0.20074
C59	1.2671	-1.73691	-0.14401
C60	1.2963	-1.7686	0.0183
C61	1.33828	-1.75277	0.16227
C62	1.35052	-1.7055	0.14264
C63	1.79307	-1.26289	0.14357
C64	1.84035	-1.25065	0.16313
C65	1.85617	-1.20868	0.01913
C66	1.82448	-1.17947	-0.14313
C67	1.28434	-1.81599	0.03723
C68	1.31344	-1.84781	0.19854
C69	1.3554	-1.83172	0.33932
C70	1.36748	-1.7846	0.3225
N71	1.30011	-1.89621	0.20023
C72	1.3184	-1.92873	0.38105
C73	1.87217	-1.27985	0.32329
C74	1.91929	-1.26778	0.34001
C75	1.93539	-1.22582	0.1992
C76	1.90357	-1.19672	0.03797