

Supplementary Information

One-Pot Cascade Construction of Nonsubstituted Quinoline-Bridged Covalent Organic Frameworks

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1. General information

1.1 Reagents

Unless otherwise noted, all the chemicals and reagents were purchased in analytical purity from commercial suppliers and used directly without further purification. 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde (**D**), 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2-methoxybenzaldehyde) (**E**), and 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline (**3**) were synthesized following the reported procedures.^[1]

1.2 Characterization methods

Powder X-ray diffraction (PXRD) patterns were collected 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). Liquid-state ¹H NMR, ¹³C NMR, and ¹⁹F NMR were recorded on Bruker Advance 600 MHz, 150 MHz, and 376 MHz spectrometers at 298 K, respectively, and chemical shift (δ) was reported in ppm with residual solvent peak as the reference. Peaks are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, 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. 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 (HRTEM) 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

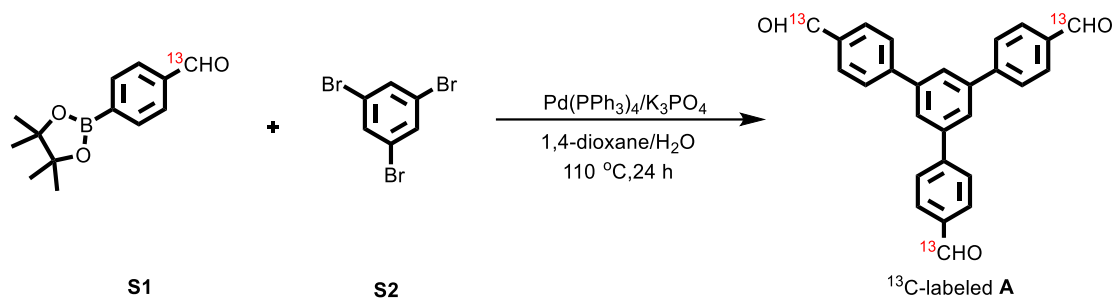
photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer with non-monochromatic Al K α x-rays as the excitation source and C 1s (284.8 eV) as the reference line. Solid-state diffuse reflectance Ultraviolet–visible spectroscopy (UV-vis) spectra were collected on a Shimadzu UV 3600 Spectrophotometer with BaSO₄ as the reference. Thermal stability was investigated on a DSC 200 PC (NETZSCH) thermogravimetric analyzer with temperature ranging from 303 to 1073 K under N₂ atmosphere at a heating rate of 5 K min⁻¹. The generation of O₂^{•-} was determined by electron paramagnetic resonance (EPR) spectra, which was recorded on a JES-FA200 spectrometer under visible light irradiation using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trapper.

1.3 Electrochemical measurements

Electrochemical measurements were performed on the CHI660E workstation (Chenhua Instruments, China), and the standard three-electrode system included a platinum plate as the counter electrode, a commercial Ag/AgCl electrode as the reference electrode, and a working electrode. The working electrode was prepared as follows: 15 mg of sample was thoroughly mixed with 200 μ L isopropanol containing 5% Nafion, and the resulting suspension was carefully loaded on the ITO glass substrate (10 $\times$ 25 $\times$ 1.1 mm) and dried at 60 °C under vacuum for 1 h. 0.1 M Na₂SO₄ aqueous solution was employed as the electrolyte for the photocurrent test while the aqueous solution containing 0.1 M KCl and 0.005 M K₃[Fe(CN)₆] was employed as the electrolyte for the electrochemical impedance spectroscopy (EIS) measurement. For Mott-Schottky tests, the perturbation was 5 mV with frequencies of 100, 500, and 1000

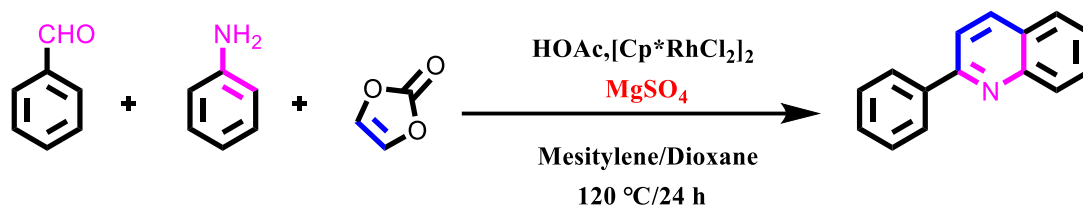
Hz.

2. Synthesis of small molecules



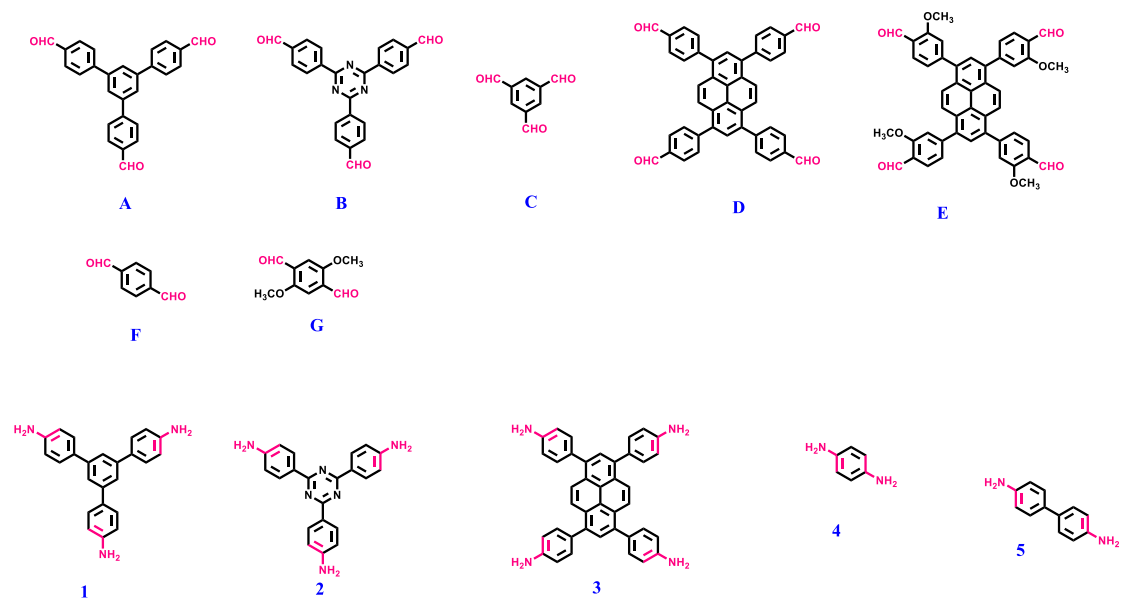
¹³C-labeled A: A round-bottom flask was charged with ¹³C-labeled **S1**^[1] (464 mg, 2 mmol), 1,3,5-tribromobenzene (157 mg, 0.5 mmol), Pd(PPh₃)₄ (28.89 mg, 0.025 mmol) and K₃PO₄ (0.743 g, 3.5 mmol), and a mixed solvent of 1,4-dioxane (15 mL), distilled water (2 mL). After being degassed with Ar for 10 min, the mixture was stirred at 110 °C under an Ar atmosphere for 24 h. After cooling down, water was added to quench the reaction, and the mixture was extracted with ethyl acetate (EA) three times. The combined organic phases were washed with brine and dried over anhydrous Na₂SO₄. The concentrated residue was purified by flash chromatography on silica gel with CH₂Cl₂ as the eluent to afford the product ¹³C-labeled **A** as a white solid (180 mg, 93%).

¹H NMR (600 MHz, CDCl₃) δ 10.25-9.96 (dd, 3H), 8.03-8.01 (m, 6H), 7.91 (s, 3H), 7.88 (d, *J* = 8.2 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 191.9, 146.4, 141.7, 136.0, 130.6, 128.1, 126.6.



Model reaction for the synthesis of 2-phenylquinoline: A 10 mL Schlenk pressure tube was charged with benzaldehyde (31.8 mg, 0.30 mmol), aniline (27.9 mg, 0.30 mmol), vinylene carbonate (51.6 mg, 0.60 mmol), [Cp*RhCl₂]₂ (4 mg, 0.003 mmol), and mesitylene (1 mL) and dioxane (1 mL). After being sonicated for 5 minutes, the tube was degassed by three freeze-pump-thaw cycles (liquid nitrogen) and sealed under vacuum. Subsequently, the reaction mixture was stirred at 120 °C for 24 h. After cooling down, the concentrated residue was purified by flash chromatography on silica gel with PE/EA as the eluent to afford the product **2-phenylquinoline** (58.5 mg, 0.28 mmol, 95%). ¹H NMR (CDCl₃, 600 MHz) δ 8.25-8.17 (m, 4H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.55-7.52 (m, 3H), 7.48 (t, *J* = 7.5 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 157.3, 148.2, 139.6, 136.7, 129.7, 129.6, 129.3, 128.8, 127.5, 127.4, 127.1, 126.2, 118.9.

3. One-pot synthesis of NQ-COFs



Supplementary Scheme 1. Chemical structures of the building blocks for synthesis of NQ-COFs

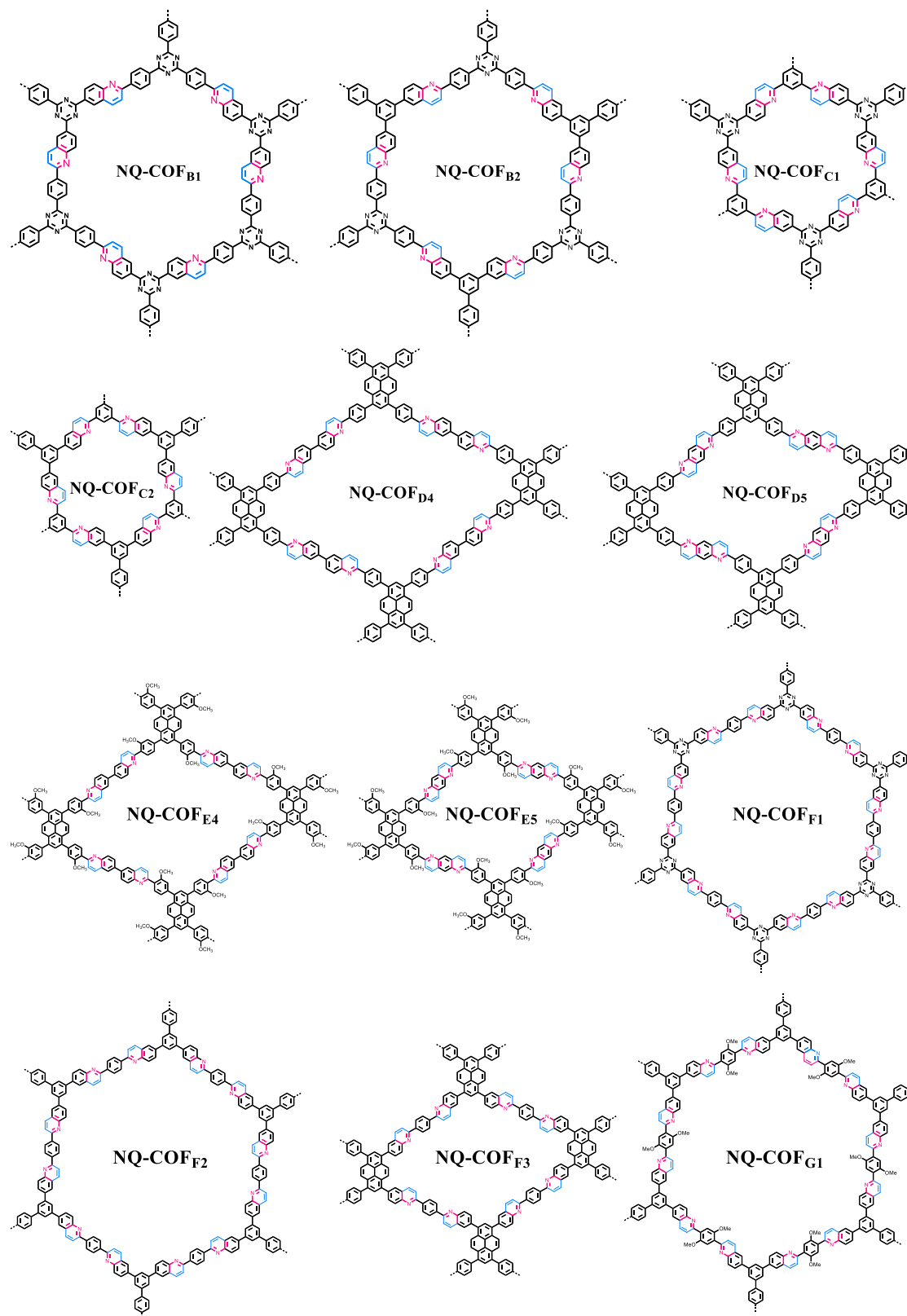
Supplementary Table 1. Condition optimization for the synthesis of NQ-COF_{A1}-**OPR.^a**

Entry	Solvent	Catalyst	MgSO ₄ (mg)	Crystallinity
1	<i>o</i> -DCB 1 mL	HOAc 50μL	72	Low
2	<i>o</i> -DCB 1 mL	HOAc 50μL	-	No
3	<i>o</i> -DCB 1 mL	6 M HOAc 100 μL	72	No
4	<i>o</i> -DCB 1 mL	6 M HOAc 100 μL	-	No
5	<i>o</i> -DCB 1 mL	TFA 50 μL	72	Low
6	<i>o</i> -DCB 1 mL	TFA 50 μL	-	No
7	Dioxane 1mL	HOAc 50 μL	72	No
8	Dioxane 1mL	HOAc 50 μL	-	No
9	Dioxane 1mL	6 M HOAc 100 μL	72	No
10	Dioxane 1mL	6 M HOAc 100 μL	-	No
11	Dioxane 1mL	TFA 50 μL	72	No
12	Dioxane 1mL	TFA 50 μL	-	No
13	Mesitylene: Dioxane=1:1	HOAc 50 μL	72	Moderate
14	Mesitylene: Dioxane=1:1	HOAc 50 μL	-	No
15	Mesitylene: Dioxane=1:1	6 M HOAc 100 μL	72	No
16	Mesitylene: Dioxane=1:1	6 M HOAc 100 μL	-	No
17	Mesitylene: Dioxane=1:1	TFA 50 μL	72	Low
18	Mesitylene: Dioxane=1:1	TFA 50 μL	-	No
19	Mesitylene: Dioxane=1:2	HOAc 50 μL	72	High
10	Mesitylene: Dioxane=1:2	HOAc 50 μL	-	No
21	Mesitylene: Dioxane=1:2	6 M HOAc 100 μL	72	No
22	Mesitylene: Dioxane=1:2	6 M HOAc 100 μL	-	No
23	Mesitylene: Dioxane=1:2	TFA50 μL	72	No
24	Mesitylene: Dioxane=1:2	TFA50 μL	-	No
25	Mesitylene: Dioxane=2:1	HOAc 50 μL	72	Low
26	Mesitylene: Dioxane=2:1	HOAc 50 μL	-	No
27	Mesitylene: Dioxane=2:1	6 M HOAc 100 μL	72	Low
28	Mesitylene: Dioxane=2:1	6 M HOAc 100 μL	-	No
29	Mesitylene: Dioxane=2:1	TFA50 μL	72	No
30	Mesitylene: Dioxane=2:1	TFA50 μL	-	No
31	<i>o</i> -DCB: <i>n</i> -BuOH =1:1	HOAc 50 μL	72	Low
32	<i>o</i> -DCB: <i>n</i> -BuOH =1:1	HOAc 50 μL	-	No
33	<i>o</i> -DCB: <i>n</i> -BuOH =1:1	6 M HOAc 100 μL	72	No
34	<i>o</i> -DCB: <i>n</i> -BuOH =1:1	6 M HOAc 100 μL	-	No
35	<i>o</i> -DCB: <i>n</i> -BuOH =1:1	TFA50 μL	72	Low
36	<i>o</i> -DCB: <i>n</i> -BuOH =1:1	TFA50 μL	-	No
37	<i>o</i> -DCB: <i>n</i> -BuOH =1:2	HOAc 50 μL	72	Moderate
38	<i>o</i> -DCB: <i>n</i> -BuOH =1:2	HOAc 50 μL	-	No

39	<i>o</i> -DCB: <i>n</i> -BuOH =1:2	6 M HOAc 100 μ L	72	Low
40	<i>o</i> -DCB: <i>n</i> -BuOH =1:2	6 M HOAc 100 μ L	-	No
41	<i>o</i> -DCB: <i>n</i> -BuOH =1:2	TFA50 μ L	72	No
42	<i>o</i> -DCB: <i>n</i> -BuOH =1:2	TFA50 μ L	-	No
43	<i>o</i> -DCB: <i>n</i> -BuOH =2:1	HOAc 50 μ L	72	Low
44	<i>o</i> -DCB: <i>n</i> -BuOH =2:1	HOAc 50 μ L	-	No
45	<i>o</i> -DCB: <i>n</i> -BuOH =2:1	6 M HOAc 100 μ L	72	Low
46	<i>o</i> -DCB: <i>n</i> -BuOH =2:1	6 M HOAc 100 μ L	-	No
47	<i>o</i> -DCB: <i>n</i> -BuOH =2:1	TFA50 μ L	72	Low
48	<i>o</i> -DCB: <i>n</i> -BuOH =2:1	TFA50 μ L	-	No
49	<i>o</i> -DCB: <i>i</i> -PrOH =1:1	HOAc 50 μ L	72	No
50	<i>o</i> -DCB: <i>i</i> -PrOH =1:1	HOAc 50 μ L	-	No
51	<i>o</i> -DCB: <i>i</i> -PrOH =1:1	6 M HOAc 100 μ L	72	No
52	<i>o</i> -DCB: <i>i</i> -PrOH =1:1	6 M HOAc 100 μ L	-	No
53	<i>o</i> -DCB: <i>i</i> -PrOH =1:1	TFA50 μ L	72	No
54	<i>o</i> -DCB: <i>i</i> -PrOH =1:1	TFA50 μ L	-	No
55	DMAc: Mesitylene: Dioxane=2:2:1	HOAc 50 μ L	72	Moderate
56	DMAc: Mesitylene: Dioxane=2:2:1	HOAc 50 μ L	-	No
57	DMAc: Mesitylene: Dioxane=2:2:1	6 M HOAc 100 μ L	72	Low
58	DMAc: Mesitylene: Dioxane=2:2:1	6 M HOAc 100 μ L	-	No
59	DMAc: Mesitylene: Dioxane=2:2:1	TFA50 μ L	72	Low
60	DMAc: Mesitylene: Dioxane=2:2:1	TFA50 μ L	-	No
61	Mesitylene: Dioxane: <i>n</i> - BuOH=1:1:1	HOAc 50 μ L	72	Low
62	Mesitylene: Dioxane: <i>n</i> - BuOH=1:1:1	HOAc 50 μ L	-	No
63	Mesitylene: Dioxane: <i>n</i> - BuOH=1:1:1	6 M HOAc 100 μ L	72	No
64	Mesitylene: Dioxane: <i>n</i> - BuOH=1:1:1	6 M HOAc 100 μ L	-	No
65	Mesitylene: Dioxane: <i>n</i> - BuOH=1:1:1	TFA50 μ L	72	Low
66	Mesitylene: Dioxane: <i>n</i> - BuOH=1:1:1	TFA50 μ L	-	No

^a Aldehyde A, amine 1, vinylene carbonate (3 equiv), 120 °C, 3 d.

One-pot synthesis of 12 other NQ-COFs: The synthetic condition is similar to that of NQ-COF_{A1}-OPR with only the amount of building blocks, types of catalyst, and solvent changed, and the optimized reaction conditions were demonstrated in Table S2.



Supplementary Scheme 2. Chemical structures of different NQ-COFs.

Supplementary Table 2. Optimized reaction conditions for one-pot synthesis of different NQ-COFs.

Entry	Aldehyde	Amine	Acid	Solvent 1	Solvent 2	Solvent 3	Yield
NQ-COF_{B1}	19.7 mg 0.05 mmol	17.6 mg 0.05 mmol	HOAc (0.05 mL)	Mesitylene (1.0 mL)	Dioxane (0.5 mL)	-	36.2 mg 95%
NQ-COF_{B2}	19.7 mg 0.05 mmol	17.7 mg 0.05 mmol	HOAc (0.05 mL)	<i>o</i> -DCB (0.5 mL)	<i>i</i> -PrOH (0.5 mL)	-	36.0 mg 94%
NQ-COF_{C1}	8.1 mg 0.05 mmol	17.6 mg 0.05 mmol	HOAc (0.05 mL)	<i>o</i> -DCB (0.5 mL)	<i>n</i> -BuOH (1.0 mL)	-	24.5 mg 92%
NQ-COF_{C2}	8.1 mg 0.05 mmol	17.7 mg 0.05 mmol	HOAc (0.05 mL)	<i>o</i> -DCB (0.5 mL)	<i>n</i> -BuOH (1.0 mL)	-	24.0 mg 90%
NQ-COF_{D4}	30.9 mg 0.05 mmol	10.8 mg 0.10 mmol	HOAc (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	39.5 mg 92%
NQ-COF_{D5}	30.9 mg 0.05 mmol	18.4 mg 0.10 mmol	TFA (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	46.6 mg 92%
NQ-COF_{E4}	36.9 mg 0.05 mmol	10.8 mg 0.10 mmol	TFA (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	43.5 mg 89%
NQ-COF_{E5}	36.9 mg 0.05 mmol	18.4 mg 0.10 mmol	TFA (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	49.2 mg 87%
NQ-COF_{F1}	10.6 mg 0.075 mmol	17.6 mg 0.05 mmol	TFA (0.05 mL)	Mesitylene (0.5 mL)	Dioxane (0.5 mL)	<i>n</i> -BuOH (0.5 mL)	25.9 mg 92%
NQ-COF_{F2}	10.6 mg 0.075 mmol	17.7 mg 0.05 mmol	HOAc (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	26.2 mg 93%
NQ-COF_{F3}	13.4 mg 0.10 mmol	28.3 mg 0.05 mmol	TFA (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	38.6 mg 90%
NQ-COF_{G1}	14.6 mg 0.075 mmol	17.6 mg 0.05 mmol	HOAc (0.05 mL)	<i>o</i> -DCB (1.0 mL)	-	-	30.3 mg 93%

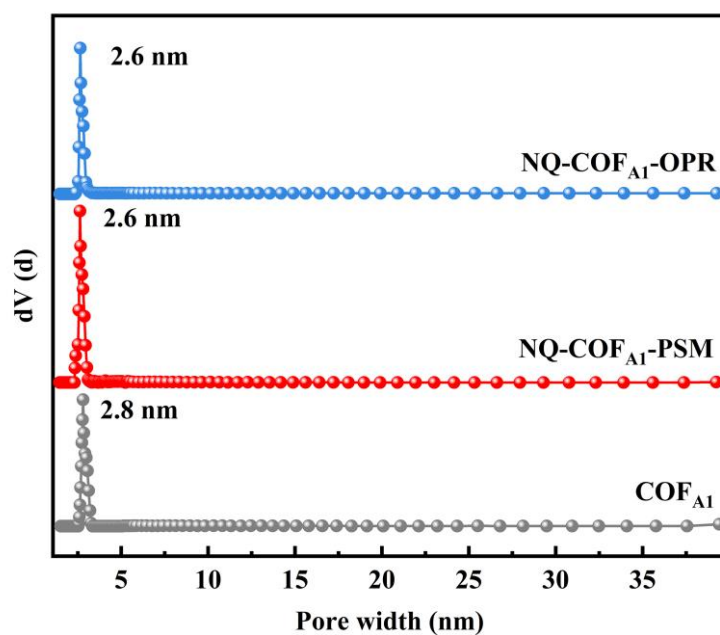
4. Structure Modeling and PXRD Refinement of NQ-COFs

Supplementary Table 3. The Pawley refinement results including unit cell parameters and final related refinement factors for NQ-COFs

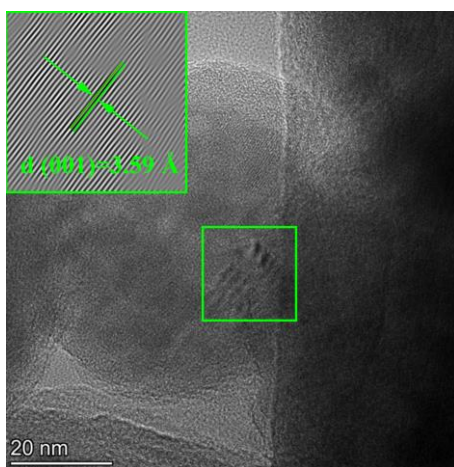
NQ-COF	Unit cell parameters	Space group	Refinement factors
NQ-COF_{A1}-OPR	a = 25.47 Å b = 26.22 Å	<i>PI</i>	Rwp = 1.49 %
	c = 3.59 Å		Rp = 1.11 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{B1}	a = 25.16 Å b = 26.27 Å	<i>PI</i>	Rwp = 1.66 %
	c = 3.51 Å		Rp = 1.45 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{B2}	a = 25.87 Å b = 25.89 Å	<i>PI</i>	Rwp = 1.48 %
	c = 3.53 Å		Rp = 0.83 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{C1}	a = 19.04 Å b = 17.79 Å	<i>PI</i>	Rwp = 1.30 %
	c = 3.35 Å		Rp = 1.21 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{C2}	a = 18.62 Å b = 18.61 Å	<i>PI</i>	Rwp = 2.38 %
	c = 3.63 Å		Rp = 1.53 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{D4}	a = 28.05 Å b = 28.52 Å	<i>PI</i>	Rwp = 1.65 %
	c = 3.74 Å		Rp = 1.28 %
	$\alpha = \beta = \gamma = 90^\circ$		

NQ-COF_{D5}	a = 23.93 Å b = 24.23 Å	<i>PI</i>	Rwp = 1.32 %
	c = 3.75 Å		Rp = 1.19 %
	$\alpha = \beta = \gamma = 90^\circ$		
NQ-COF_{E4}	a = 28.17 Å b = 28.65 Å	<i>PI</i>	Rwp = 1.27 %
	c = 3.81 Å		Rp = 1.19 %
	$\alpha = \beta = \gamma = 90^\circ$		
NQ-COF_{E5}	a = 23.85 Å b = 24.15 Å	<i>PI</i>	Rwp = 1.21 %
	c = 3.85 Å		Rp = 1.09 %
	$\alpha = \beta = \gamma = 90^\circ$		
NQ-COF_{F1}	a = 34.21 Å b = 36.72 Å	<i>PI</i>	Rwp = 4.60 %
	c = 4.92 Å		Rp = 3.61 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{F2}	a = 37.68 Å b = 36.15 Å	<i>PI</i>	Rwp = 1.34 %
	c = 3.62 Å		Rp = 1.17 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		
NQ-COF_{F3}	a = 23.43 Å b = 23.82 Å	<i>PI</i>	Rwp = 1.91 %
	c = 3.83 Å		Rp = 1.51 %
	$\alpha = \beta = \gamma = 90^\circ$		
NQ-COF_{G1}	a = 37.30 Å b = 36.95 Å	<i>PI</i>	Rwp = 3.78 %
	c = 3.79 Å		Rp = 2.93 %
	$\alpha = \beta = 90^\circ \gamma = 120^\circ$		

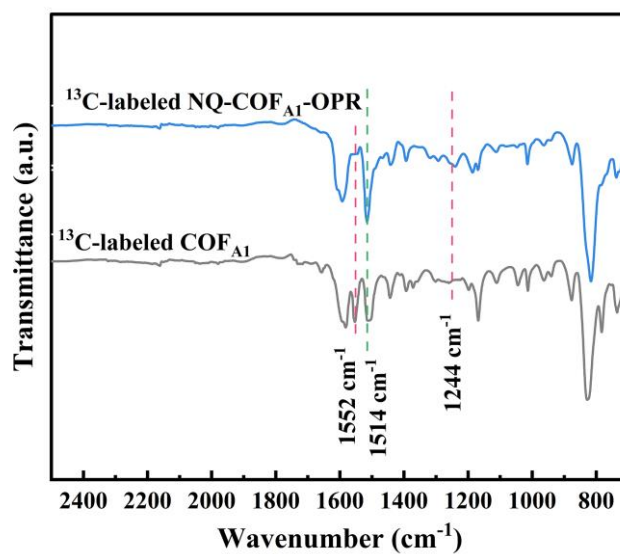
5. Characterization of NQ-COFs



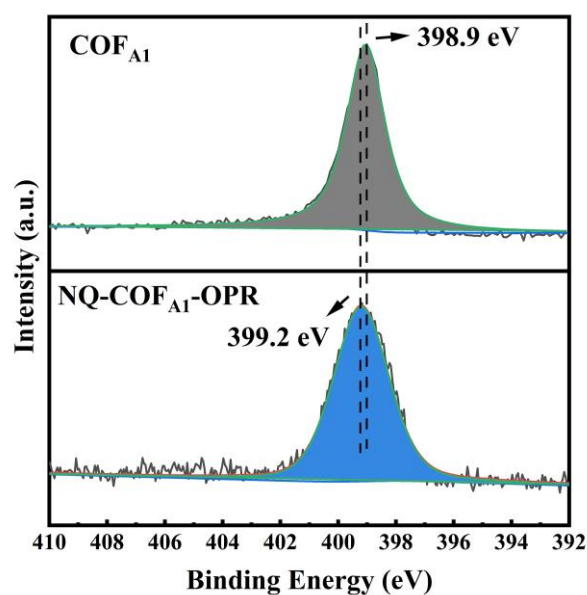
Supplementary Fig. 1 Pore size distribution profiles of COF_{A1}, NQ-COF_{A1}-PSM, and NQ-COF_{A1}-OPR.



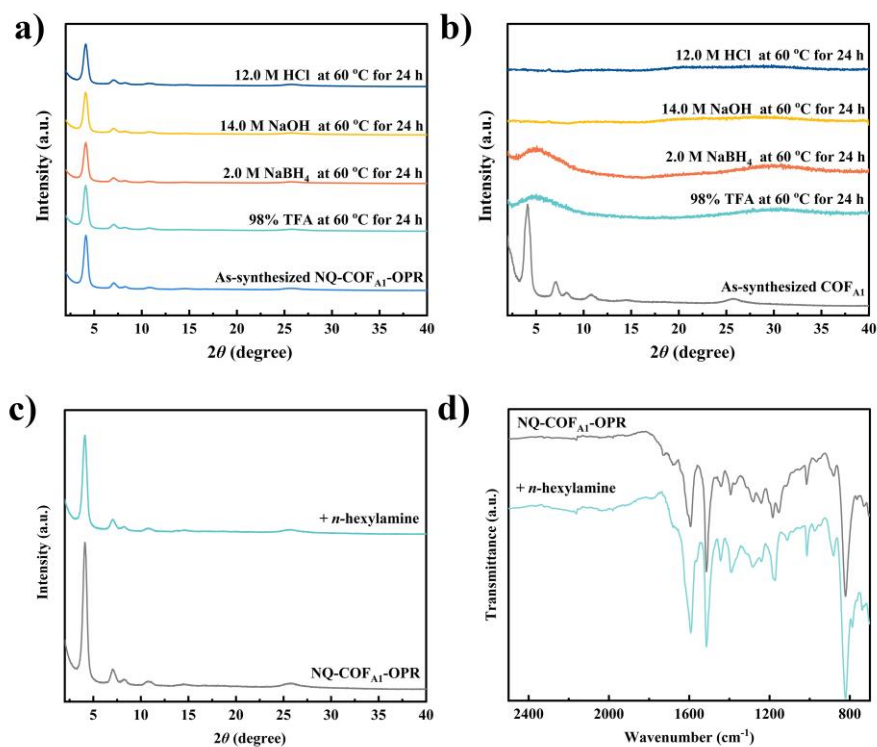
Supplementary Fig. 2 HRTEM image of NQ-COF_{A1}-OPR (the inset shows the enlarged image of the selected area).



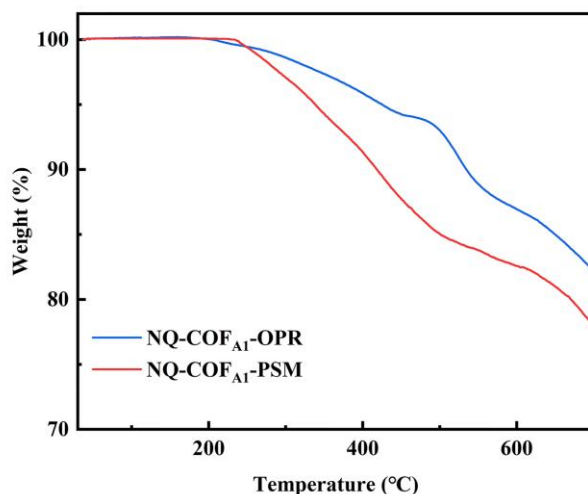
Supplementary Fig. 3 FT-IR spectra of isotopically ^{13}C -labelled COF_{A1} and $\text{NQ-COF}_{\text{A1-OPR}}$.



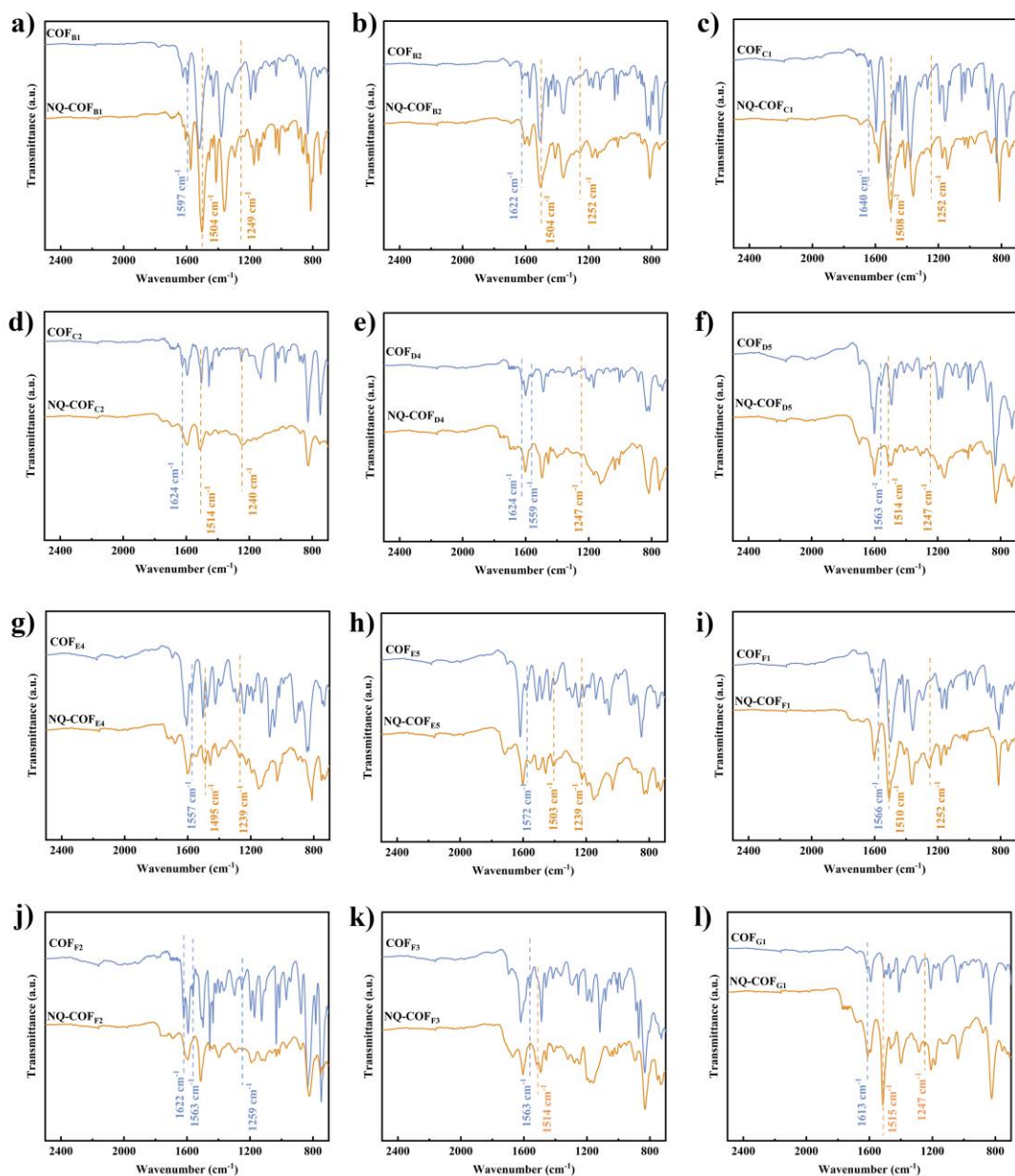
Supplementary Fig. 4 High resolution N 1s XPS spectra of COF_{A1} and $\text{NQ-COF}_{\text{A1-OPR}}$.



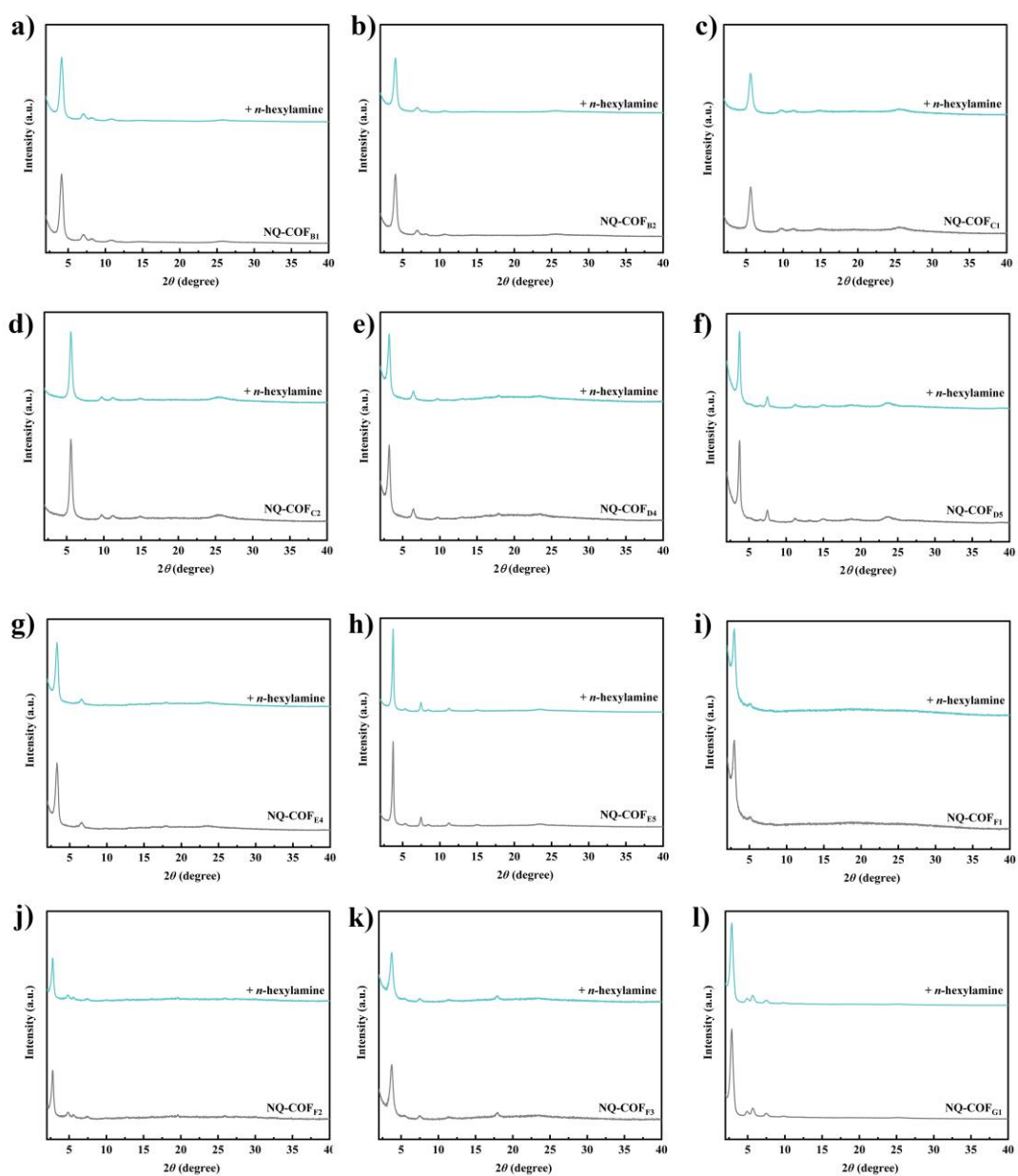
Supplementary Fig. 5 Chemical stability test. PXRD patterns of (a) NQ-COF_{A1}-OPR and (b) COF_{A1} after treatment under different harsh chemical conditions. (c) (d) PXRD patterns and FT-IR spectra of NQ-COF_{A1}-OPR before and after treatment in n-hexylamine solution for 24 h.



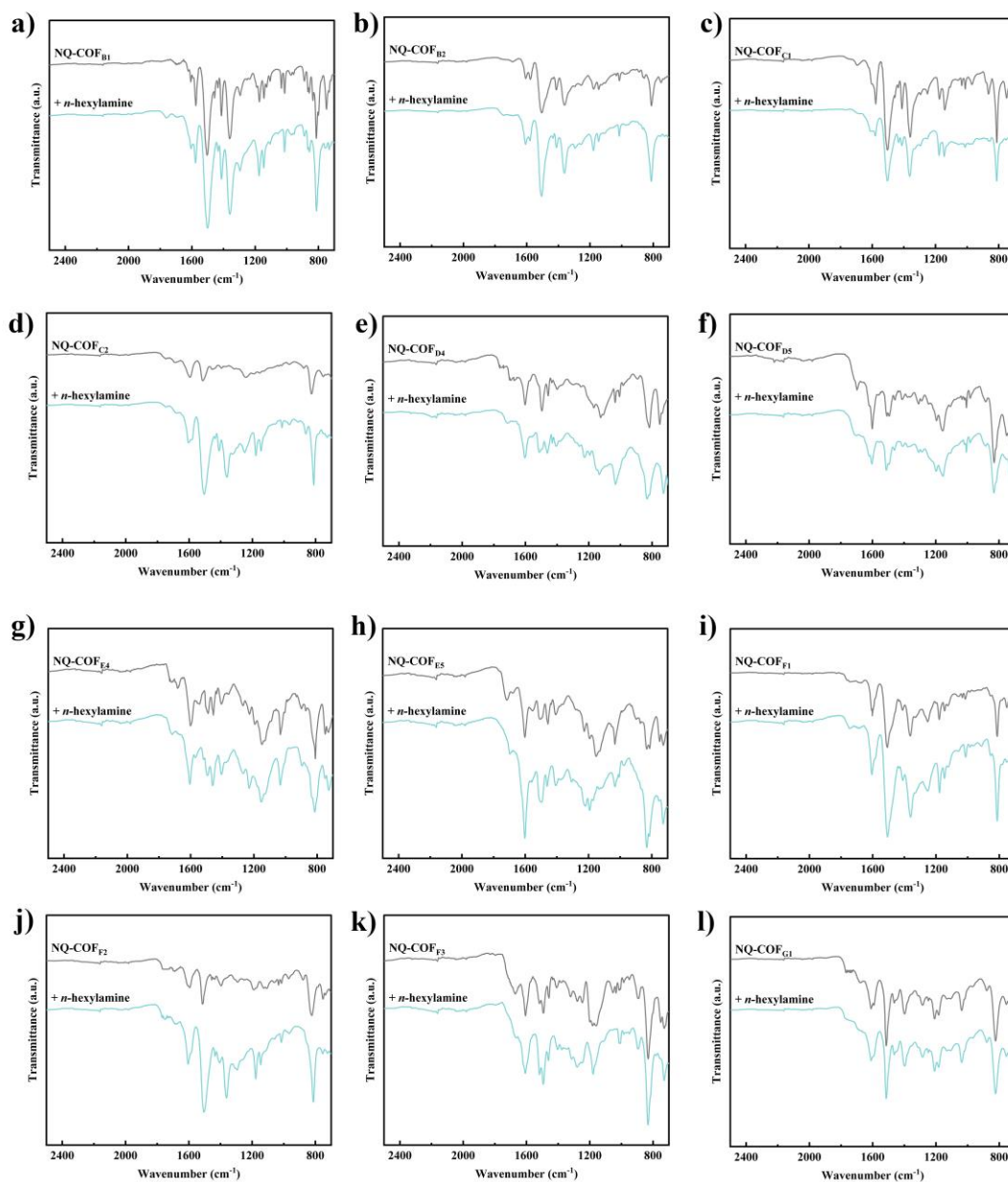
Supplementary Fig. 6 Thermal stability evaluation by TGA measurement.



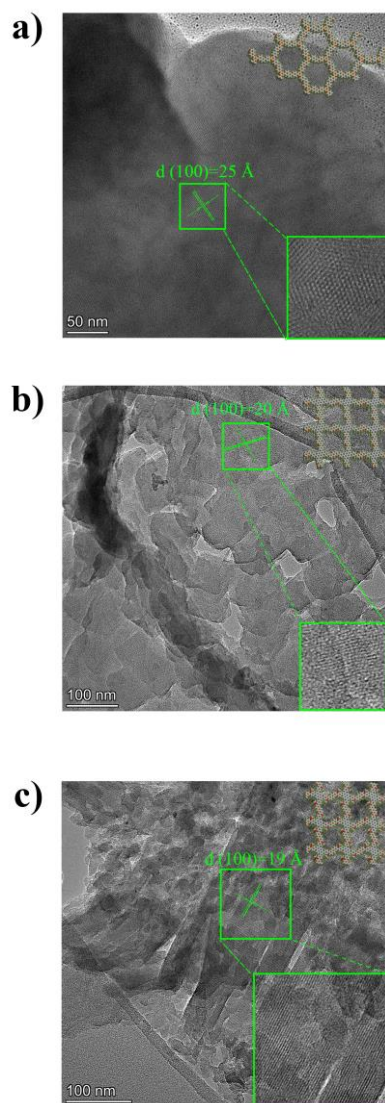
Supplementary Fig. 7 FT-IR spectra of different COFs and NQ-COFs.



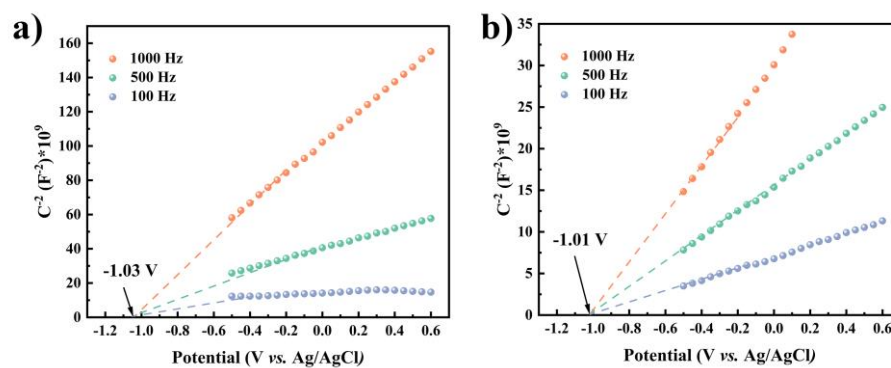
Supplementary Fig. 8 PXRD patterns of different NQ-COFs before and after treatment in *n*-hexylamine solution for 24 h.



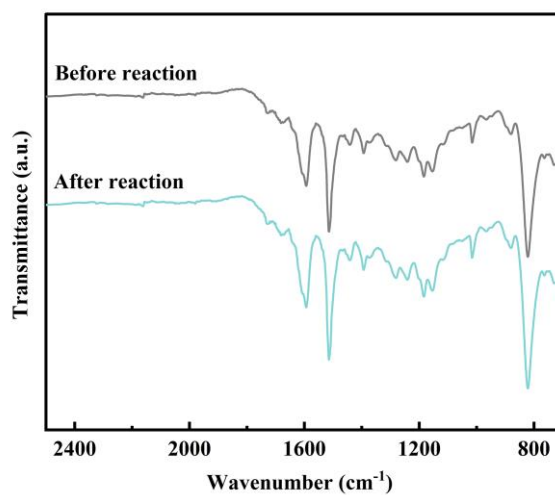
Supplementary Fig. 9 FT-IR spectra of different COFs and NQ-COFs before and after treatment in *n*-hexylamine solution for 24 h.



Supplementary Fig. 10 HRTEM images of (a) NQ-COF_{B1}, (b) NQ-COF_{D5}, and (c) NQ-COF_{E5}. The insets show the enlarged image of the selected area.

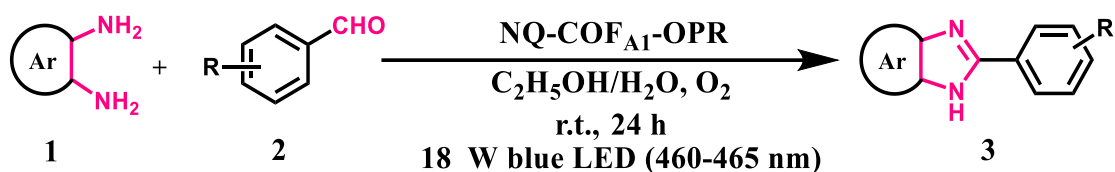


Supplementary Fig. 11 Mott-Schottky plots of (a) COFA1 and (b) NQ-COFA1-PSM .



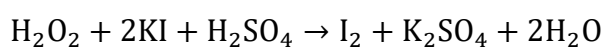
Supplementary Fig. 12 FT-IR spectra of NQ-COFA1-OPR before and after the five runs of the photocatalytic reaction.

6. Photocatalytic synthesis of 2-benzimidazole based derivatives

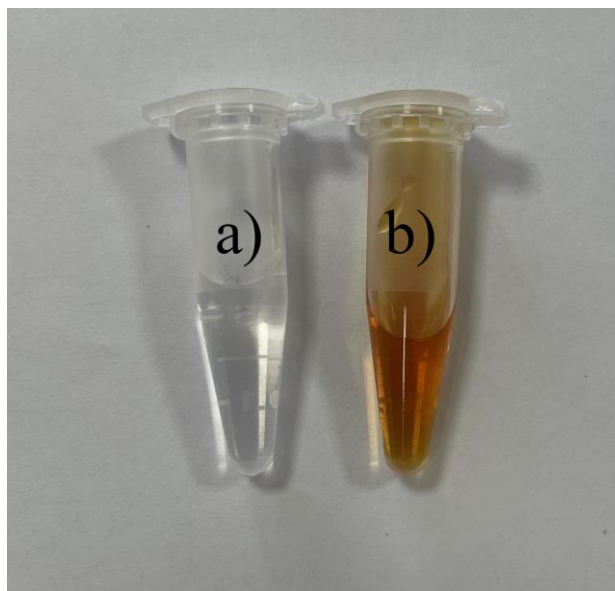


Detection of H₂O₂:

The generation of H₂O₂ in the photocatalytic reaction was detected by the following mechanism:

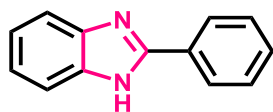


Typical procedure: after finishing the synthesis of 2-phenyl-1H-benzo[d]imidazole (**3a**), 0.5 mL aliquot of the filtrate was diluted with 5 mL distilled water. Subsequently, 5 mL of 3.5 M H₂SO₄ solution, 1 mL of 0.1 M KI solution, and 1 mL of 0.4 M Potassium bipthalate solution were successively added to the above solution to evaluate the generation of H₂O₂.

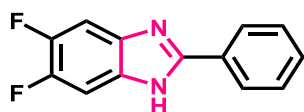


Supplementary Fig. 13 (a) Photo image of potassium iodide, potassium bipthalate, and 3.5 M H₂SO₄ mixture solution, which was changed to dark yellow (b) after addition

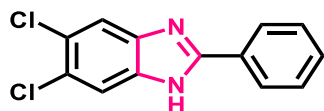
of 0.5 mL aliquot of the filtrate 3a.



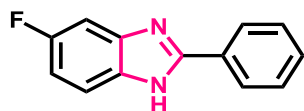
2-phenyl-1H-benzo[d]imidazole (3a): 96 mg, 0.495 mmol, 99 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.93 (br s, 1H), 8.19 (d, $J = 7.2$ Hz, 2H), 7.61 (s, 2H), 7.56-7.48 (m, 3H), 7.22-7.19 (m, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 151.2, 130.1, 129.9, 128.9, 126.4, 122.1.



5,6-difluoro-2-phenyl-1H-benzo[d]imidazole (3b): 108 mg, 0.47 mmol, 94 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.17 (br s, 1H), 8.15 (d, $J = 8.4$ Hz, 2H), 7.68-7.49 (m, 5H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 153.3, 130.2, 129.7, 129.0, 126.4; ^{19}F NMR (564 MHz, DMSO- d_6): δ -140.9, -142.9.

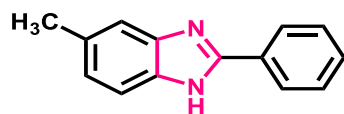


5,6-dichloro-2-phenyl-1H-benzo[d]imidazole (3c): 115 mg, 0.44 mmol, 88 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.26 (br s, 1H), 8.17 (d, $J = 8.4$ Hz, 2H), 7.94 (s, 1H), 7.76 (s, 1H), 7.59-7.52 (m, 3H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 154.3, 131.1, 129.7, 125.6, 127.2.

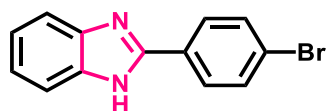


5-fluoro-2-phenyl-1H-benzo[d]imidazole (3d): 87 mg, 0.41 mmol, 82 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.05 (br s, 1H), 8.17 (d, $J = 7.4$ Hz, 2H), 7.69-7.33 (m, 5H), 7.06 (s, 1H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 159.7, 158.1, 152.9, 131.7, 130.1,

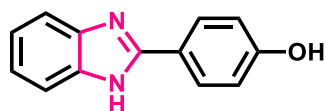
128.8, 126.5, 119.7, 111.9, 110.6, 104.4. ^{19}F NMR (564 MHz, DMSO- d_6) δ -119.6, -121.4.



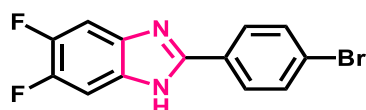
5-methyl-2-phenyl-1H-benzo[d]imidazole (3e): 89 mg, 0.43 mmol, 85 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.74 (br s, 1H), 8.16 (d, J = 7.1 Hz, 2H), 7.63-7.32 (m, 5H), 7.03 (s, 1H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 133.3, 130.8, 130.1, 129.7, 129.4, 126.8, 119.0, 111.5, 21.8.



2-(4-bromophenyl)-1H-benzo[d]imidazole (3f): 121 mg, 0.45 mmol, 89 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.96 (br s, 1H), 8.12 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.60 (s, 2H), 7.34-7.20 (m, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 150.7, 132.4, 129.9, 128.8, 123.7, 122.8.

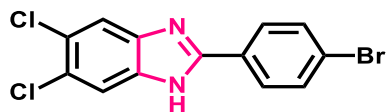


4-(1H-benzo[d]imidazol-2-yl) phenol (3g): 96 mg, 0.46 mmol, 92 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.65 (br s, 1H), 9.98 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.54 (s, 2H), 7.16-7.14 (m, 2H), 6.92 (d, J = 8.4 Hz, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 159.6, 152.3, 128.6, 122.1, 121.6, 116.1.

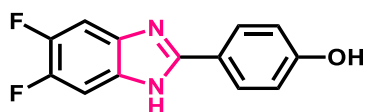


2-(4-bromophenyl)-5,6-difluoro-1H-benzo[d]imidazole (3h): 144 mg, 0.47 mmol, 94 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.26 (br s, 1H), 8.08 (d, J = 8.6 Hz,

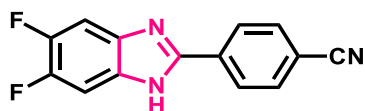
2H), 7.77 (d, $J = 8.6$ Hz, 2H), 7.65 (s, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 152.7, 132.5, 129.3, 128.8, 124.1; ^{19}F NMR (564 MHz, DMSO- d_6) δ -143.0, -144.8.



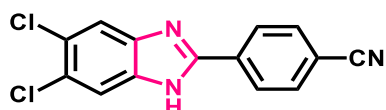
2-(4-bromophenyl)-5,6-dichloro-1H-benzo[d]imidazole (3i): 137 mg, 0.40 mmol, 80 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.36 (br s, 1H), 8.10 (d, $J = 8.4$ Hz, 2H), 7.87-7.78 (m, 4H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 153.3, 132.6, 129.1, 128.9, 124.5.



4-(5,6-difluoro-1H-benzo[d]imidazol-2-yl) phenol (3j): 109 mg, 0.45 mmol, 89 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.91 (br s, 1H), 10.04 (s, 1H), 7.96 (d, $J = 7.0$ Hz, 2H), 7.57 (s, 2H), 6.91 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 170.8, 159.8, 154.3, 147.8, 147.7, 146.2, 146.1, 128.6, 121.1, 116.2; ^{19}F NMR (564 MHz, DMSO- d_6) δ -144.5, -145.8.

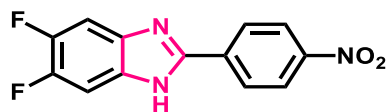


4-(5,6-difluoro-1H-benzo[d]imidazol-2-yl) benzonitrile (3k): 108 mg, 0.43 mmol, 85 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.41 (br s, 1H), 8.30 (d, $J = 8.4$ Hz, 2H), 8.03 (d, $J = 8.3$ Hz, 2H), 7.72 (s, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 134.2, 133.5, 127.5, 119.0, 112.6. ^{19}F NMR (564 MHz, DMSO- d_6) δ -141.8, -143.7.

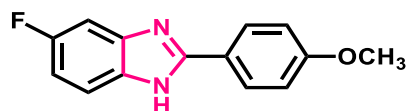


4-(5,6-dichloro-1H-benzo[d]imidazol-2-yl) benzonitrile (3l): 115 mg, 0.4 mmol, 80 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.55 (br s, 1H), 8.33 (d, $J = 8.6$ Hz, 2H), 8.05

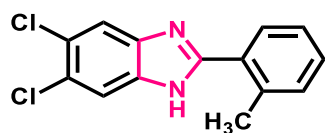
(d, $J = 8.6$ Hz, 2H), 7.93 (s, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 152.5, 133.9, 133.6, 127.8, 113.0.



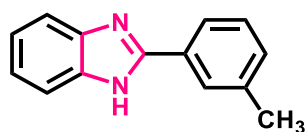
5,6-difluoro-2-(4-nitrophenyl)-1H-benzo[d]imidazole (3m): 114 mg, 0.42 mmol, 83 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 13.49 (br s, 1H), 8.41-8.37 (m, 2H), 7.73-7.70 (m, 2H), 5.75 (s, 2H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 151.5, 148.4, 135.9, 127.9, 124.8. ^{19}F NMR (564 MHz, DMSO- d_6) δ -142.2, -144.1.



5-fluoro-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3n): 98 mg, 0.41 mmol, 81 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.87 (br s, 1H), 8.10 (s, 2H), 7.61-7.02 (m, 5H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 161.2, 128.5, 122.9, 119.7, 114.9, 112.0, 110.5, 55.8. ^{19}F NMR (564 MHz, DMSO- d_6) δ -120.2, -121.8.

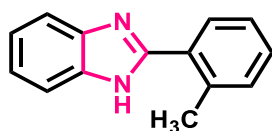


5,6-dichloro-2-(o-tolyl)-1H-benzo[d]imidazole (3o): 129 mg, 0.46 mmol, 93 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.97 (br s, 1H), 7.85 (s, 2H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.44-7.37 (m, 3H), 2.59 (s, 3H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 155.0, 137.7, 131.9, 130.4, 130.0, 129.6, 126.5, 21.4.



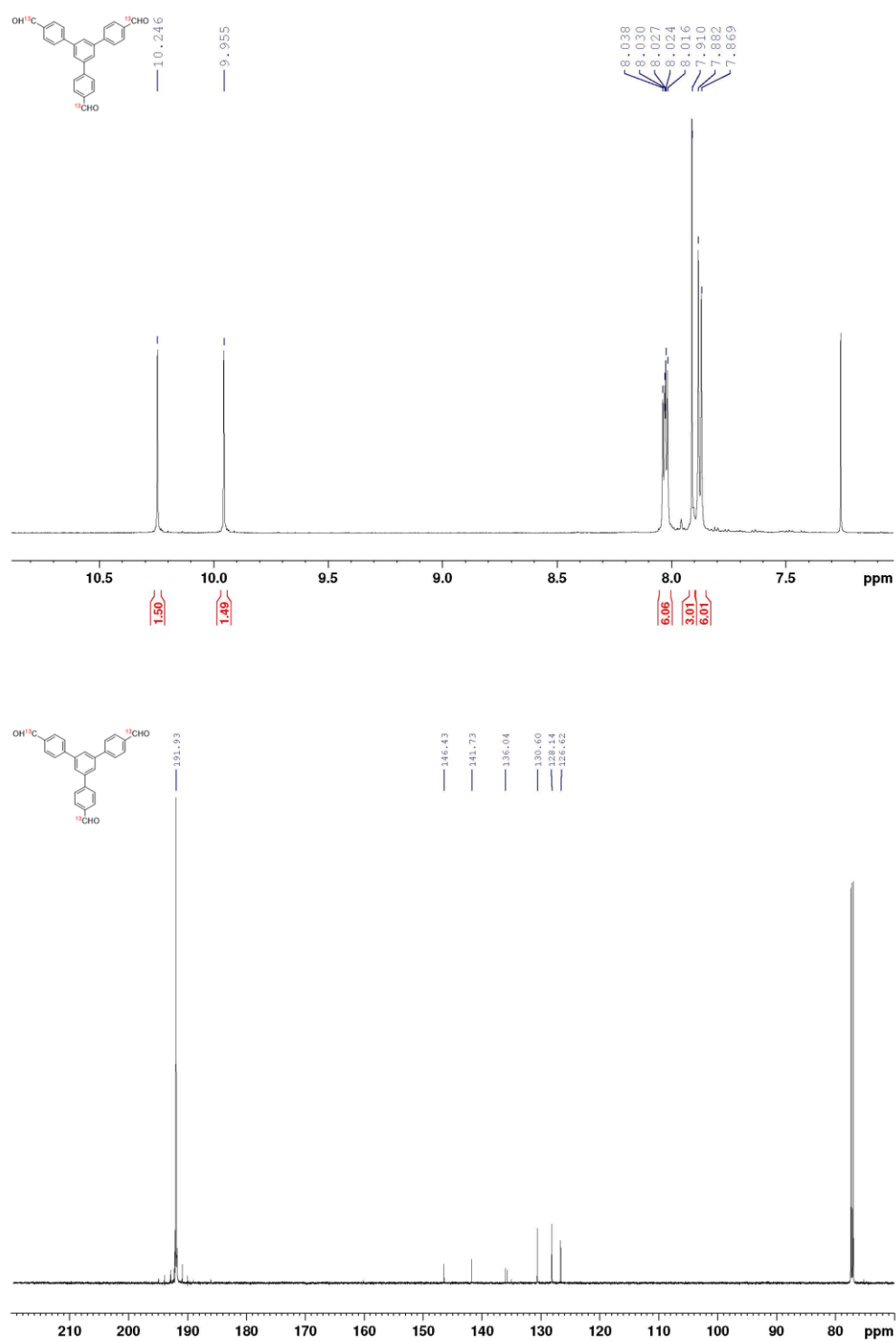
2-(m-tolyl)-1H-benzo[d]imidazole (3p): 93 mg, 0.44 mmol, 89 % yield. ^1H NMR (600

MHz, DMSO- d_6) δ 13.30 (br s, 1H), 8.09 (s, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 7.60-7.58 (m, 2H), 7.42-7.40 (t, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.19-7.17 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 151.8, 138.5, 130.9, 130.6, 129.3, 127.6, 124.2, 122.4, 21.5.

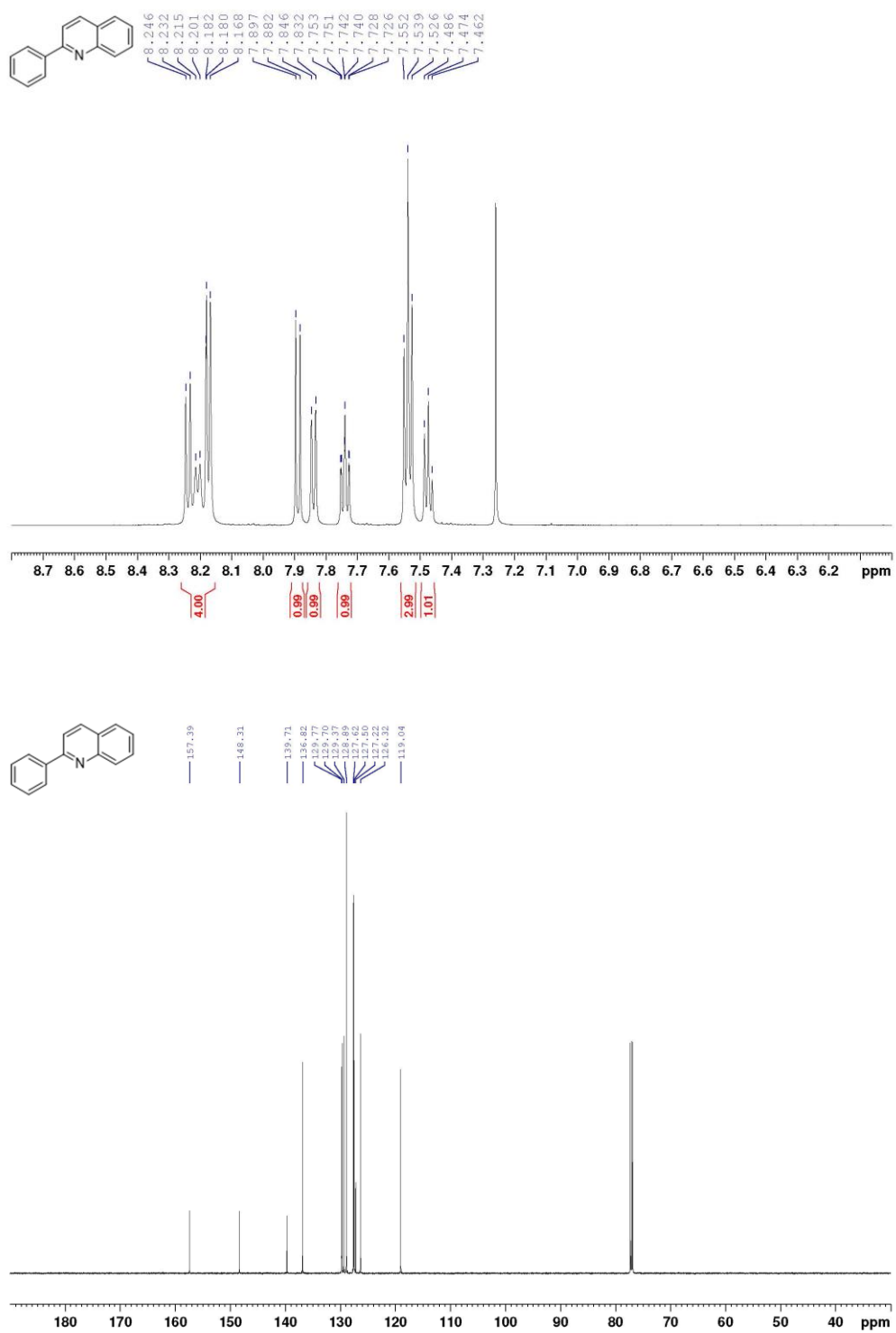


2-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (3q): 96 mg, 0.46 mmol, 92 % yield. ^1H NMR (600 MHz, DMSO- d_6) δ 12.61 (br s, 1H), 7.74 (d, $J = 7.4$ Hz, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.52 (d, $J = 7.7$ Hz, 1H), 7.40-7.36 (m, 3H), 7.23-7.19 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 152.4, 144.2, 137.5, 134.9, 131.7, 130.5, 129.9, 129.8, 126.4, 122.8, 121.9, 119.4, 111.7, 21.5.

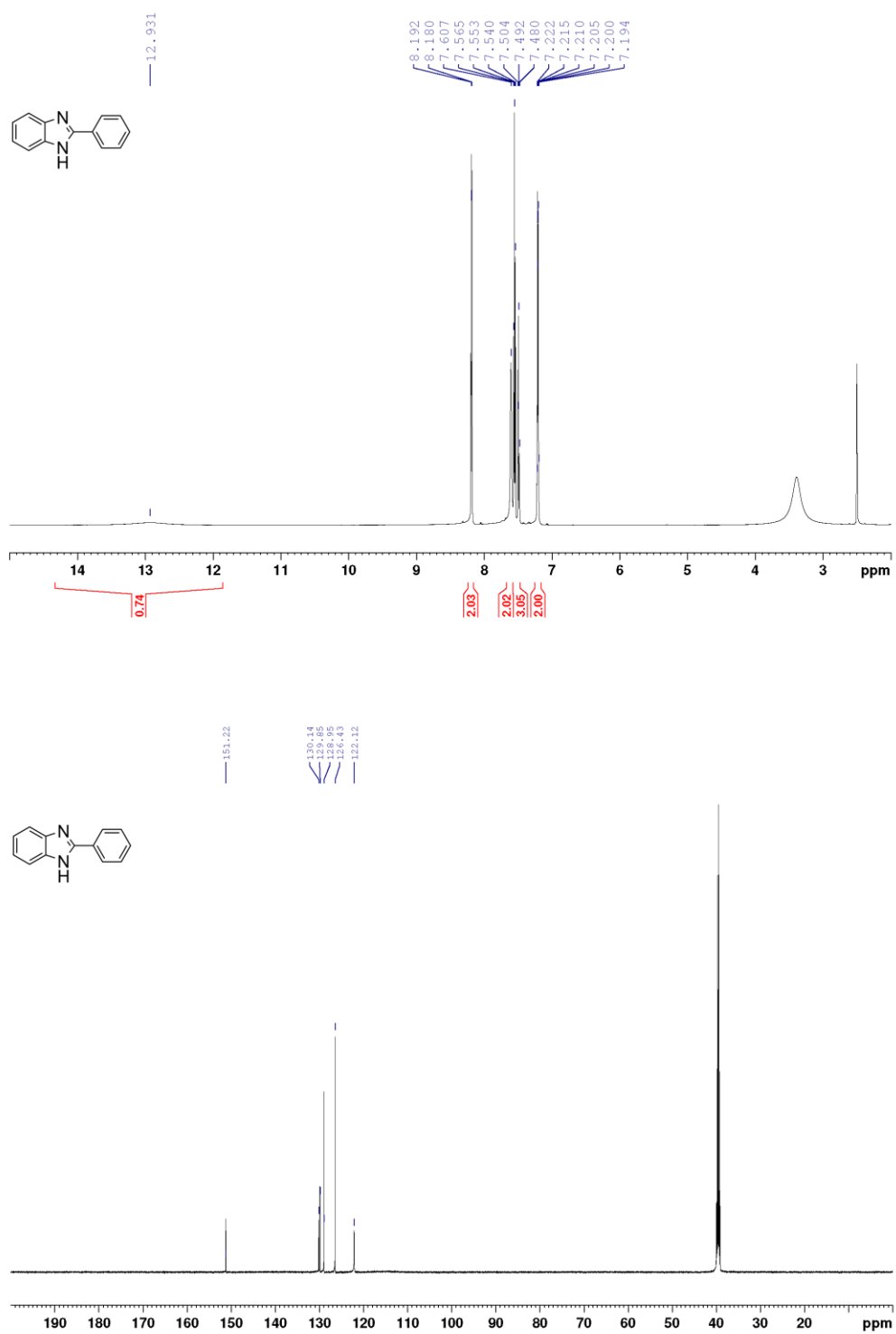
7. Copies of NMR spectra



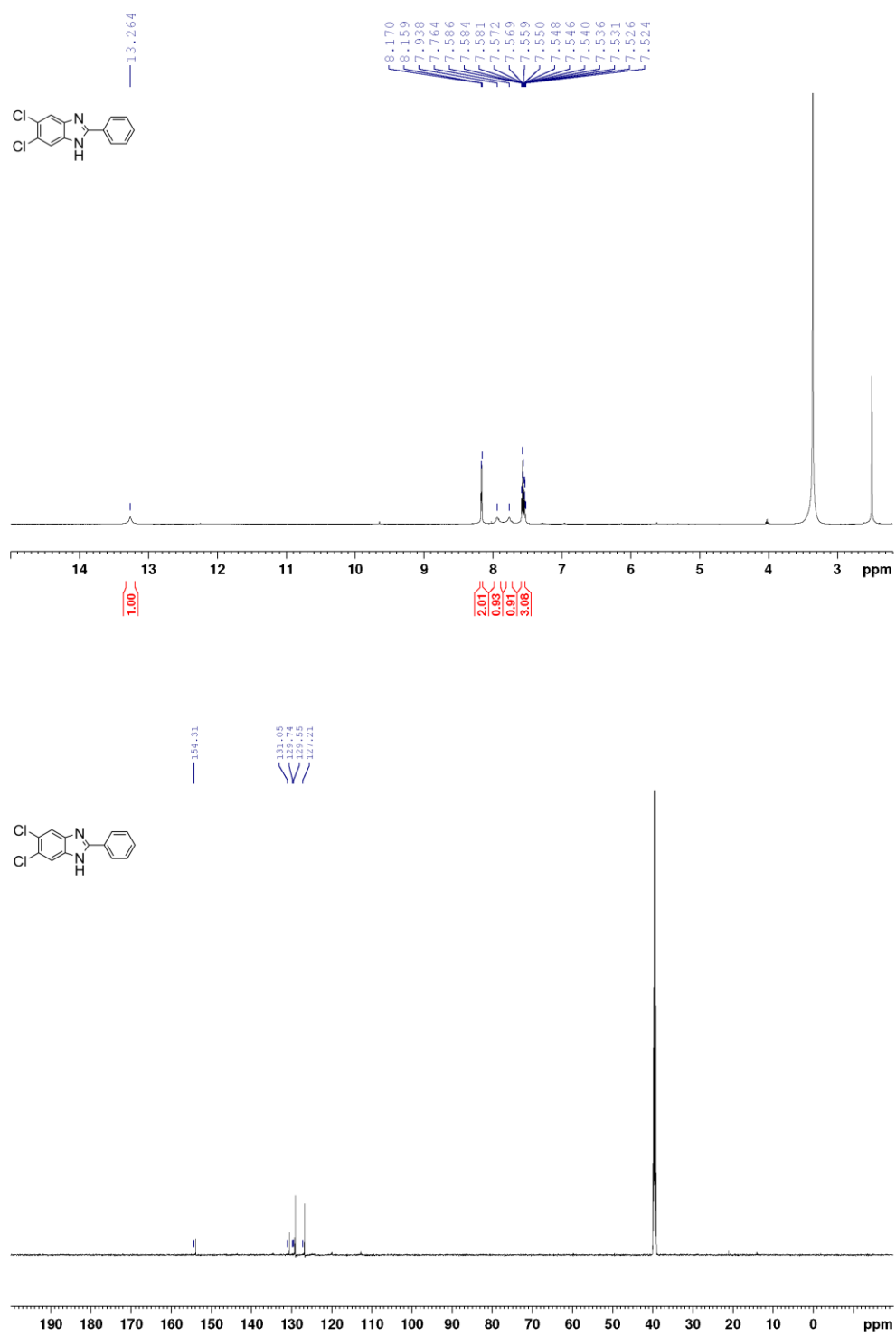
Supplementary Fig. 14 ^1H NMR and ^{13}C NMR spectra of ^{13}C -labeled A.



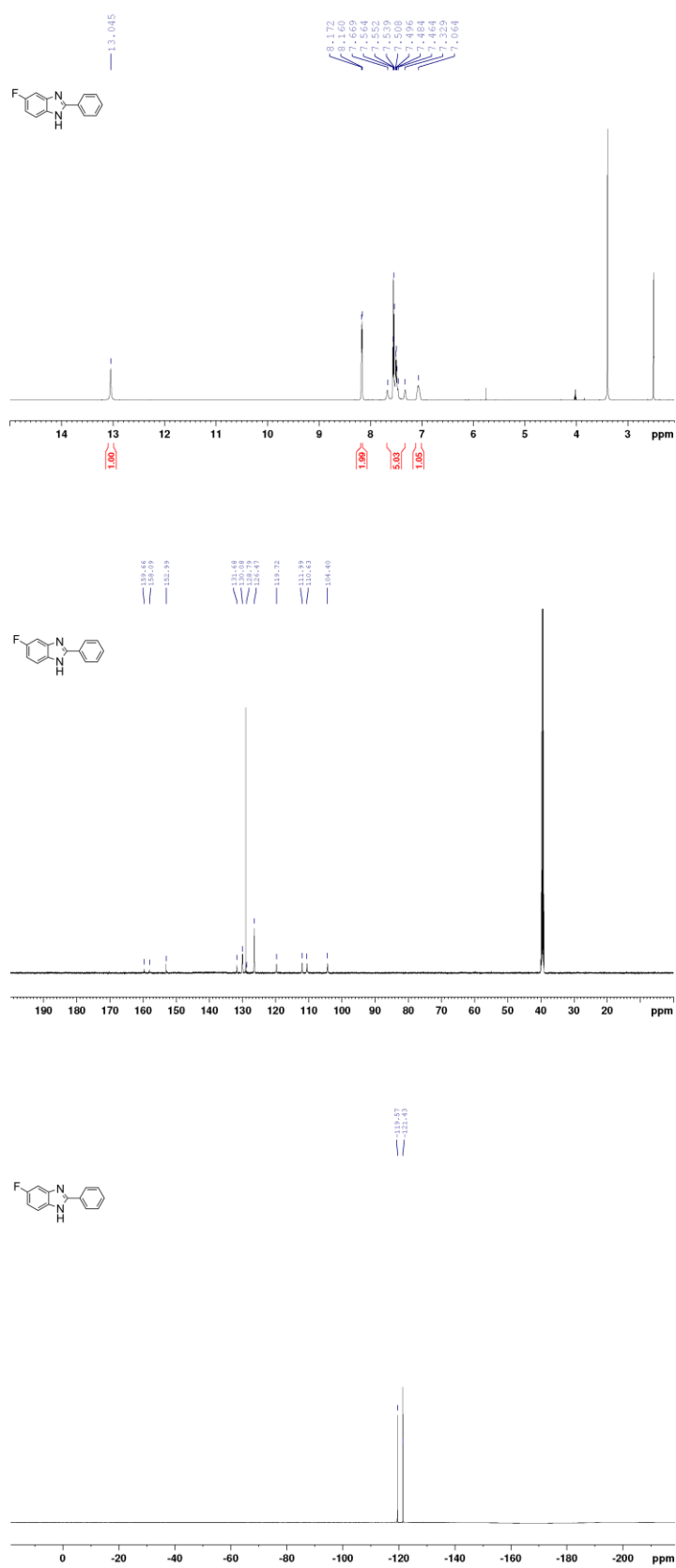
Supplementary Fig. 15 ^1H NMR and ^{13}C NMR spectra of 2-phenylquinoline.



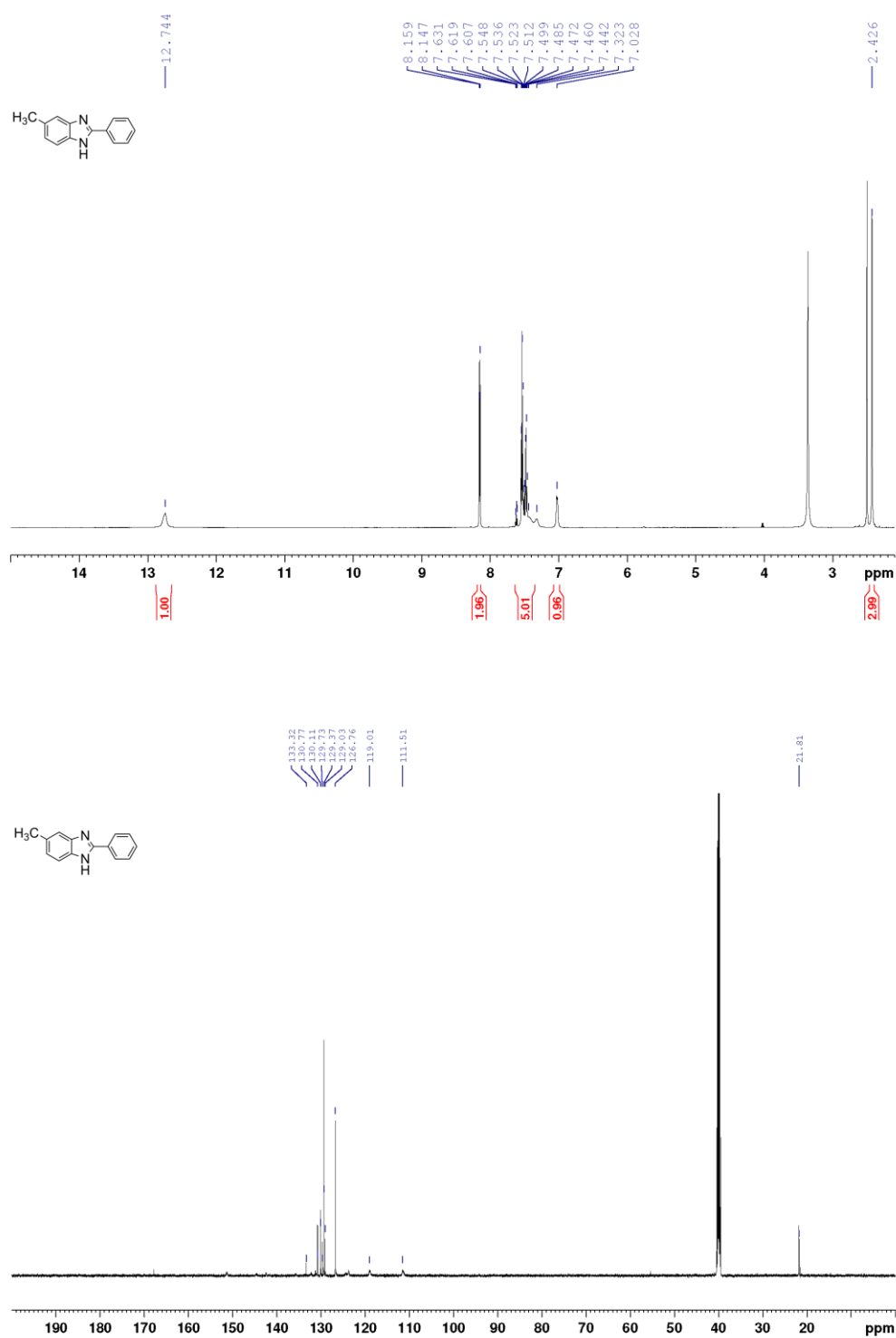
Supplementary Fig. 16 ¹H NMR and ¹³C NMR spectra of 3a.



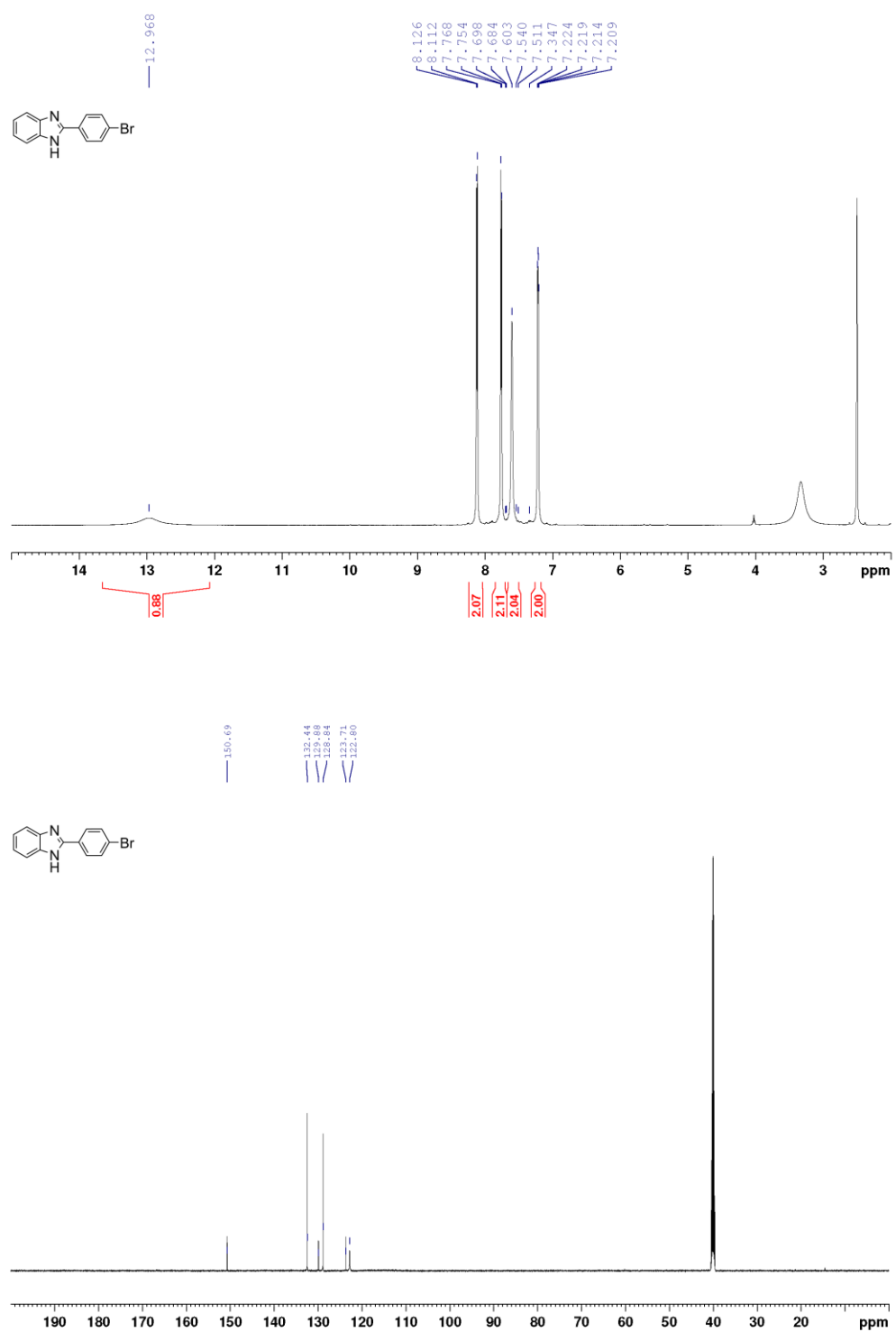
Supplementary Fig. 18 ^1H NMR and ^{13}C NMR spectra of **3c**.



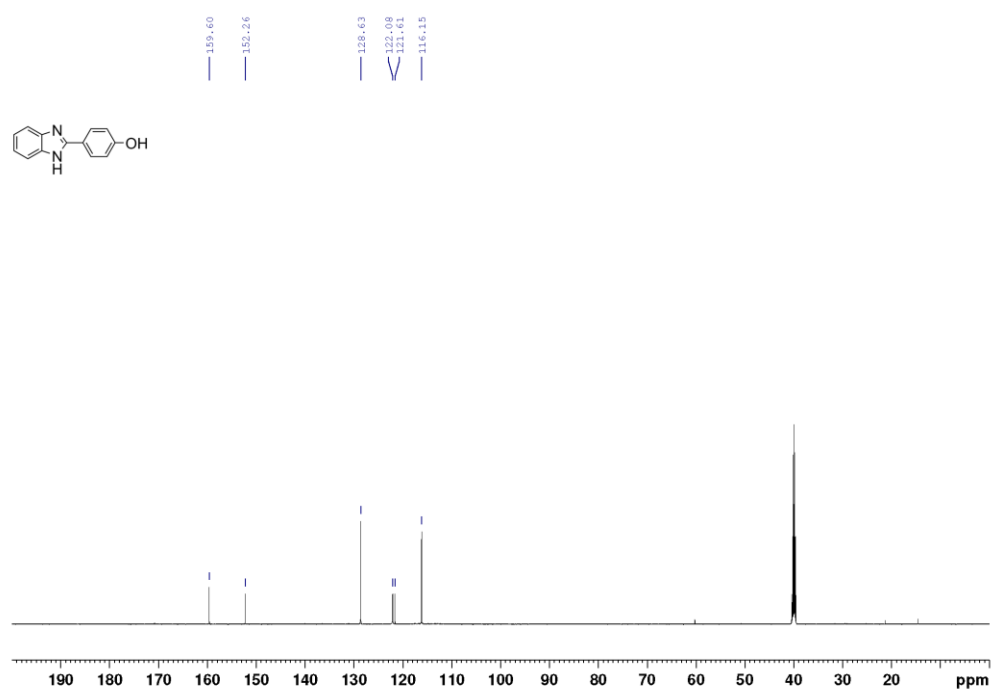
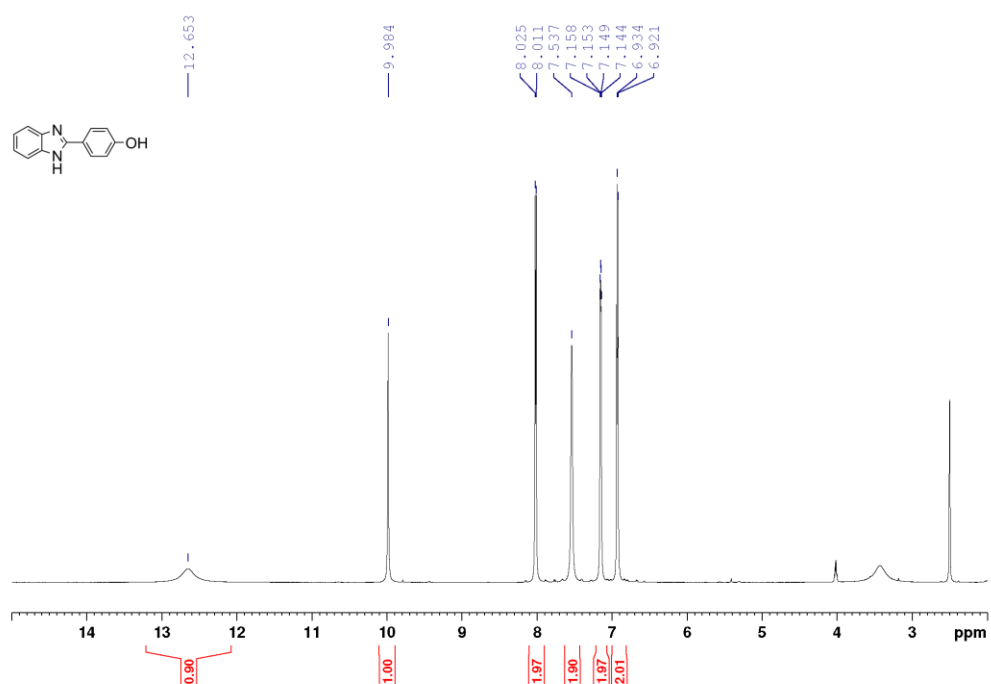
Supplementary Fig. 19 ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra of 3d.



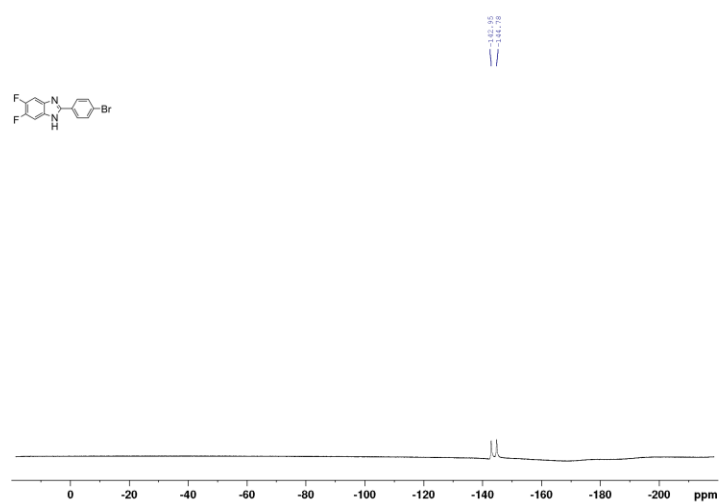
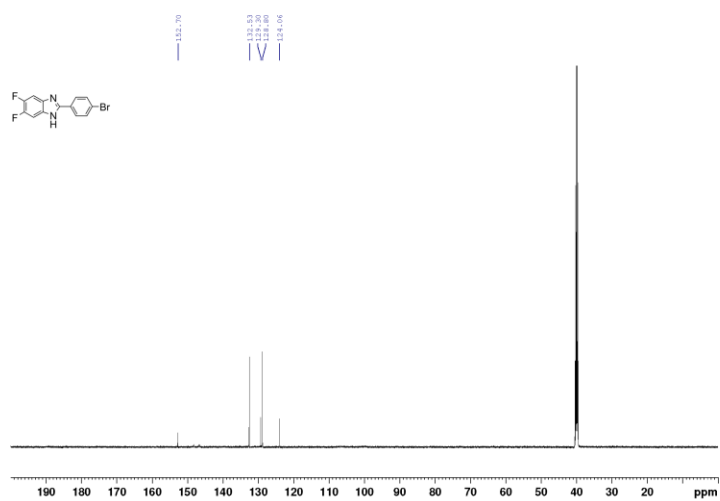
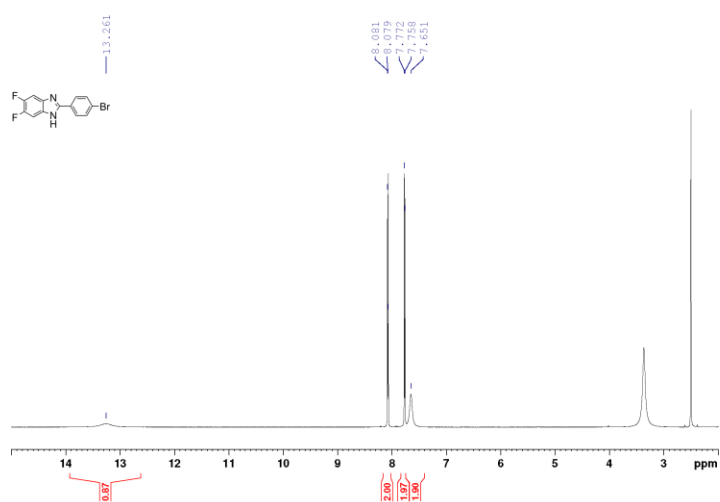
Supplementary Fig. 20 ¹H NMR and ¹³C NMR spectra of 3e.



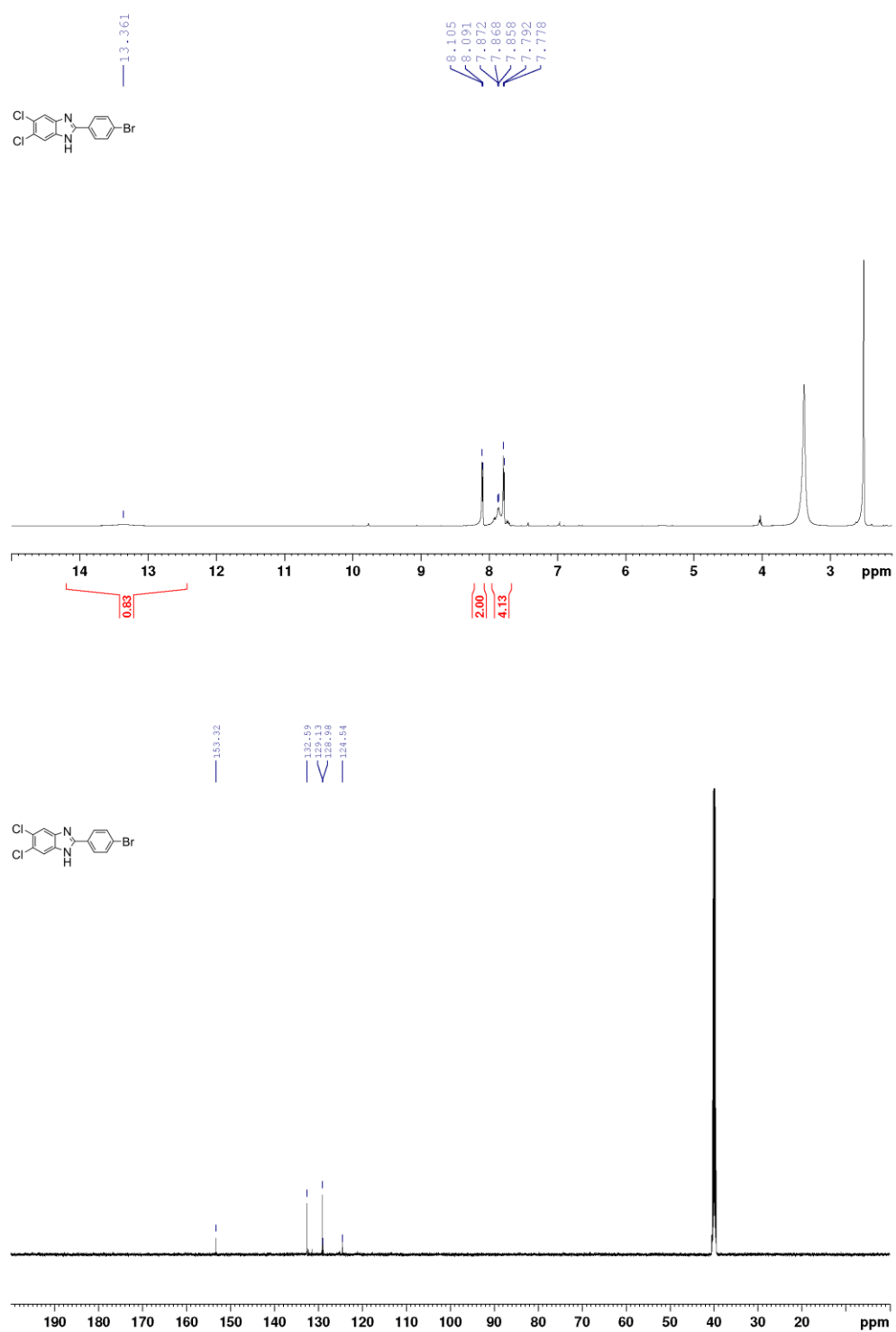
Supplementary Fig. 21 ¹H NMR and ¹³C NMR spectra of 3f.



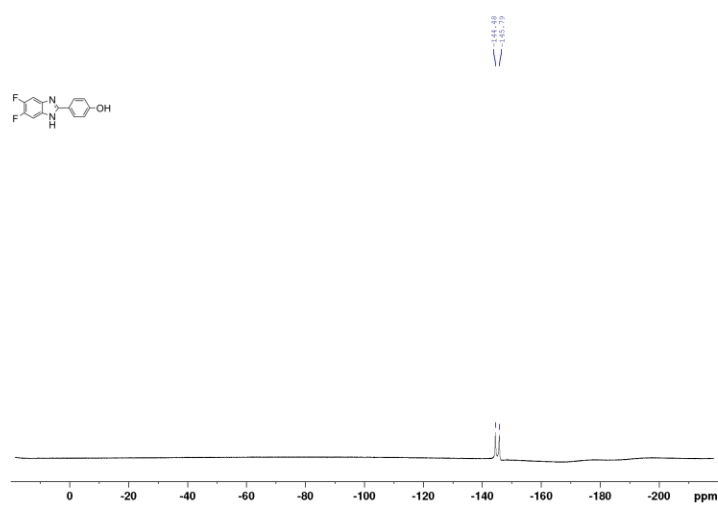
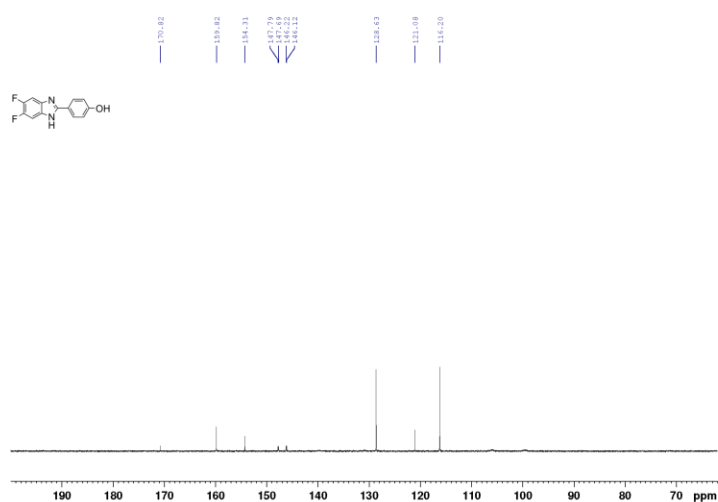
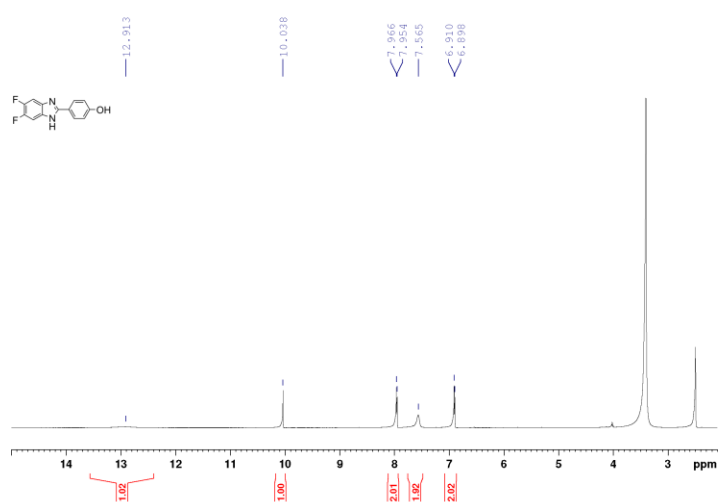
Supplementary Fig. 22 ¹H NMR and ¹³C NMR spectra of 3g.



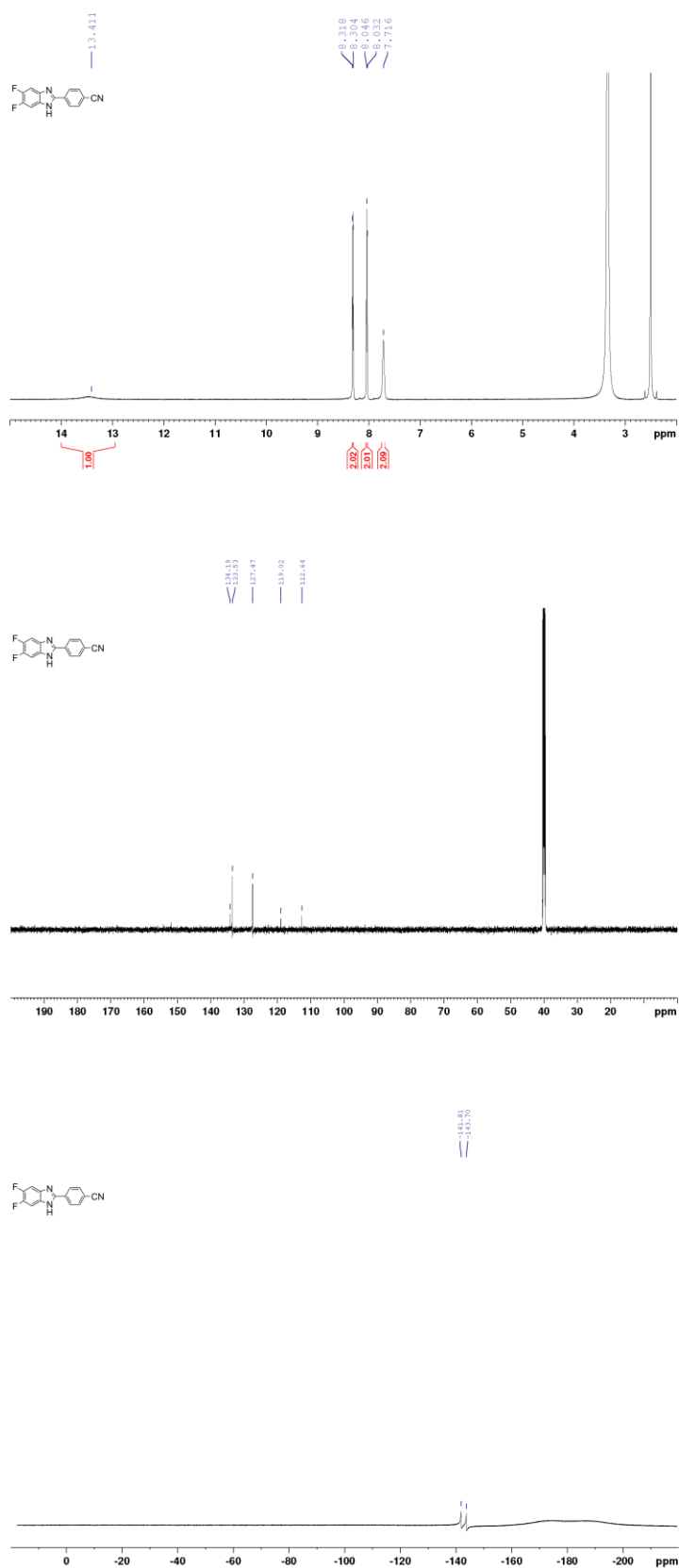
Supplementary Fig. 23 ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra of **3h**.



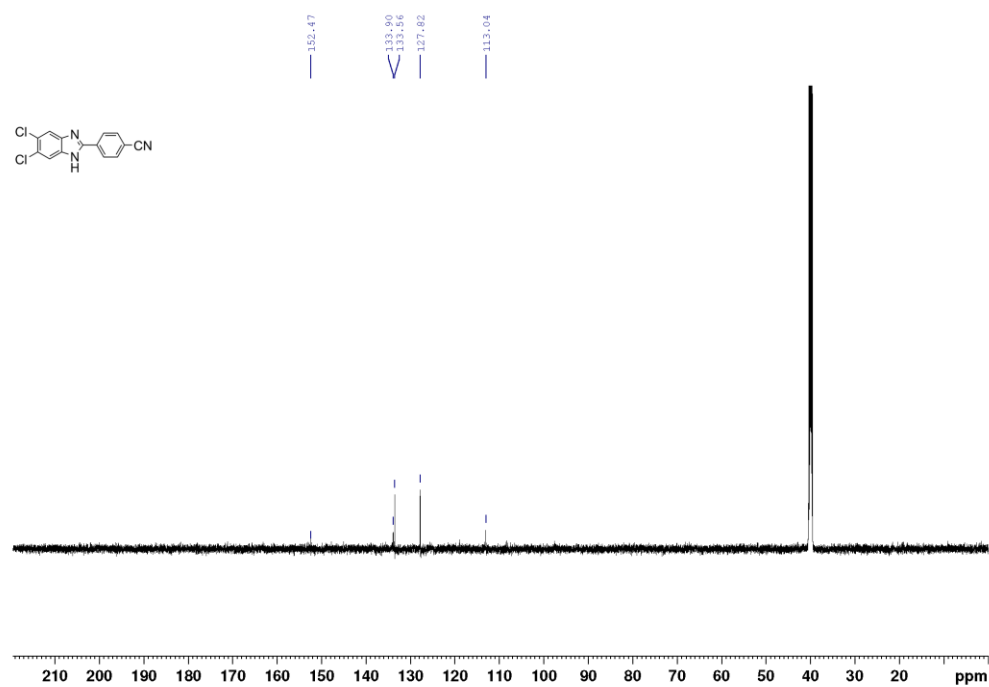
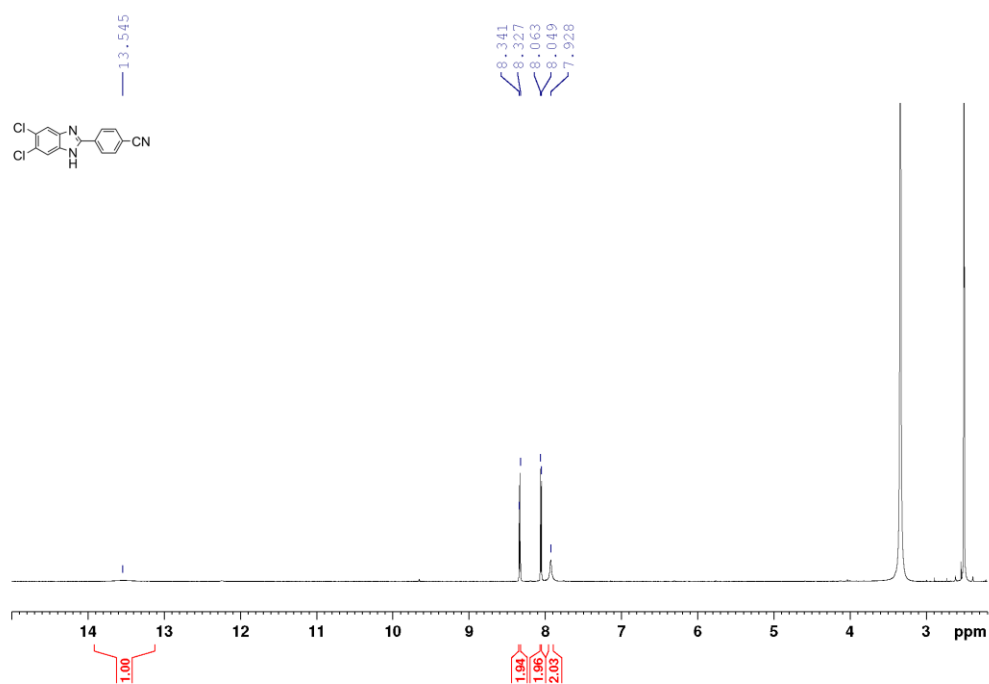
Supplementary Fig. 24 ¹H NMR and ¹³C NMR spectra of **3i**.



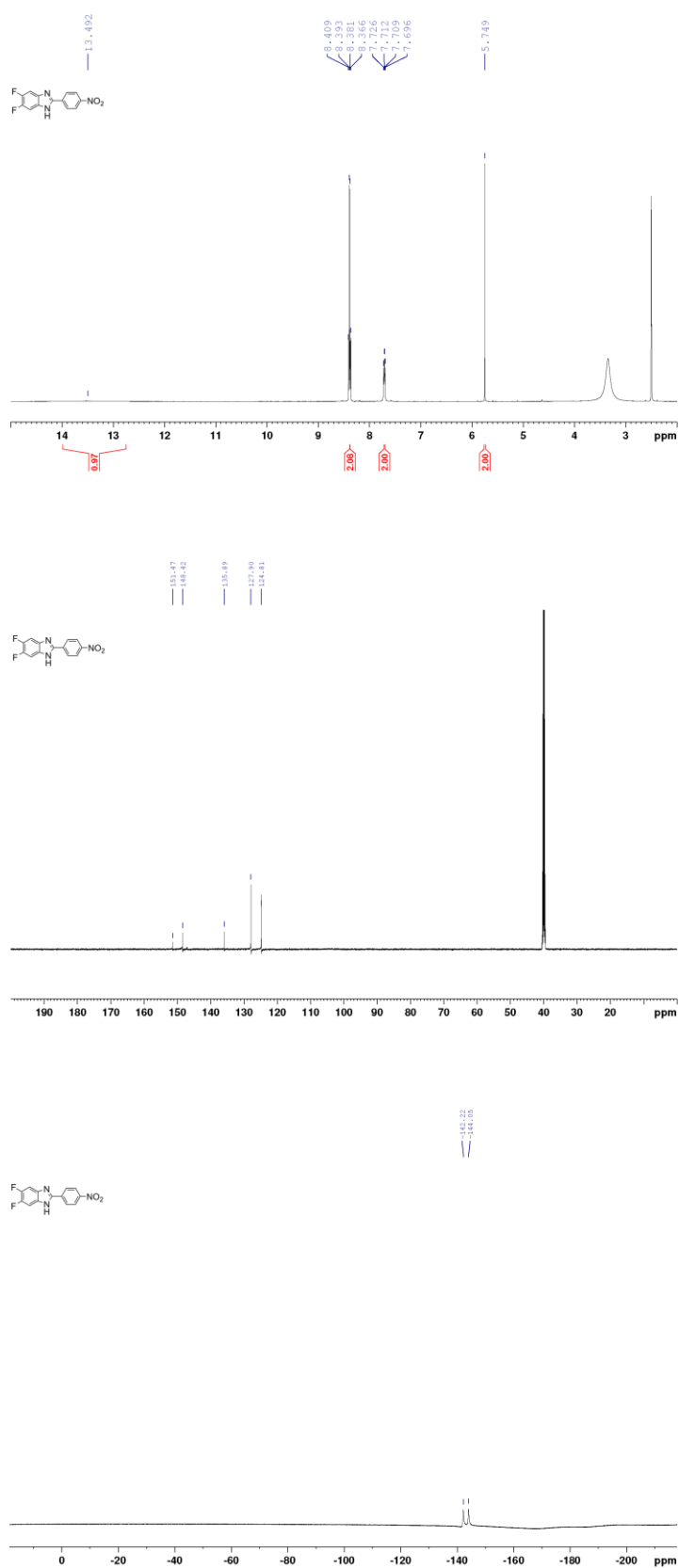
Supplementary Fig. 25 ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra of **3j**.



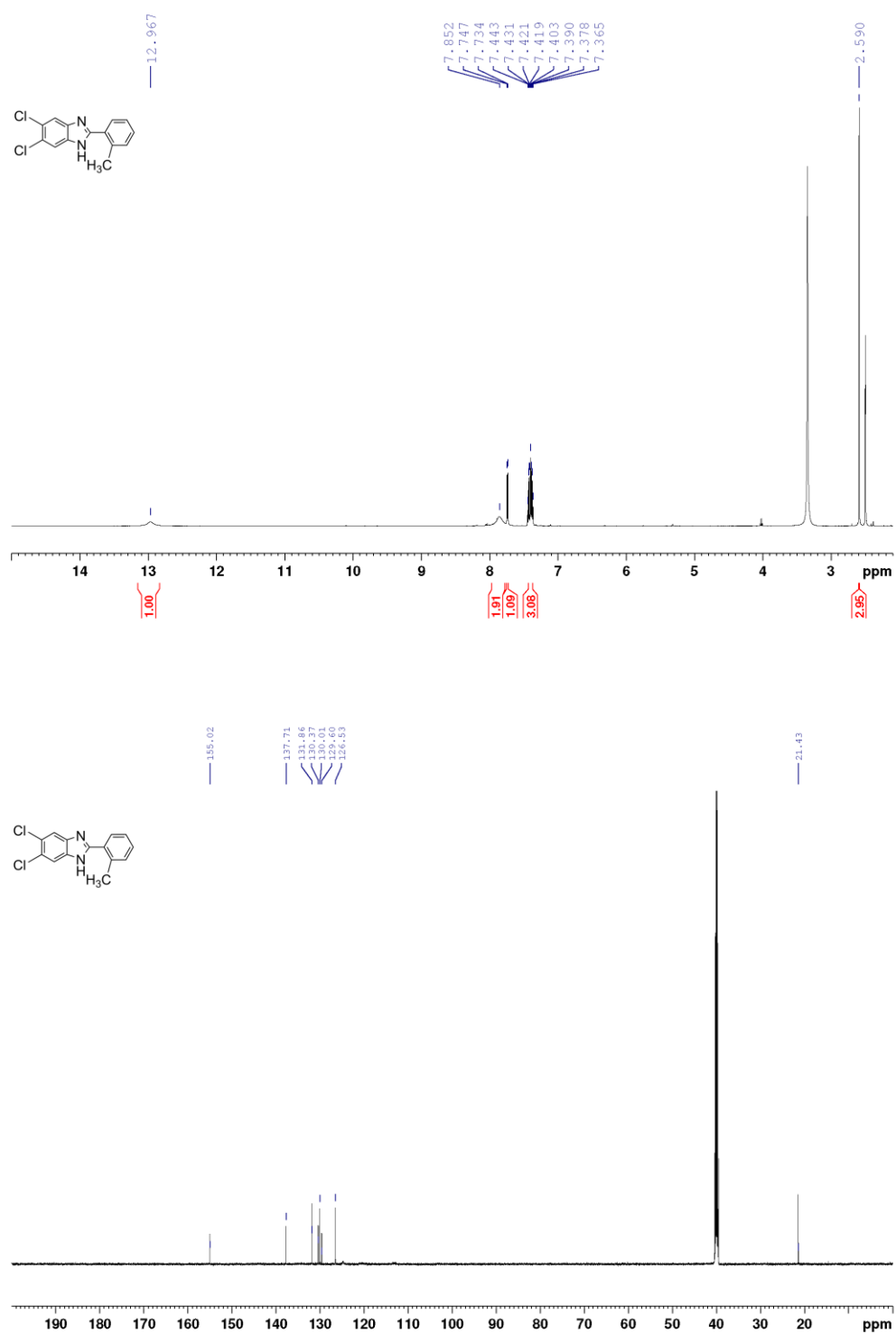
Supplementary Fig. 26 ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra of **3k**.



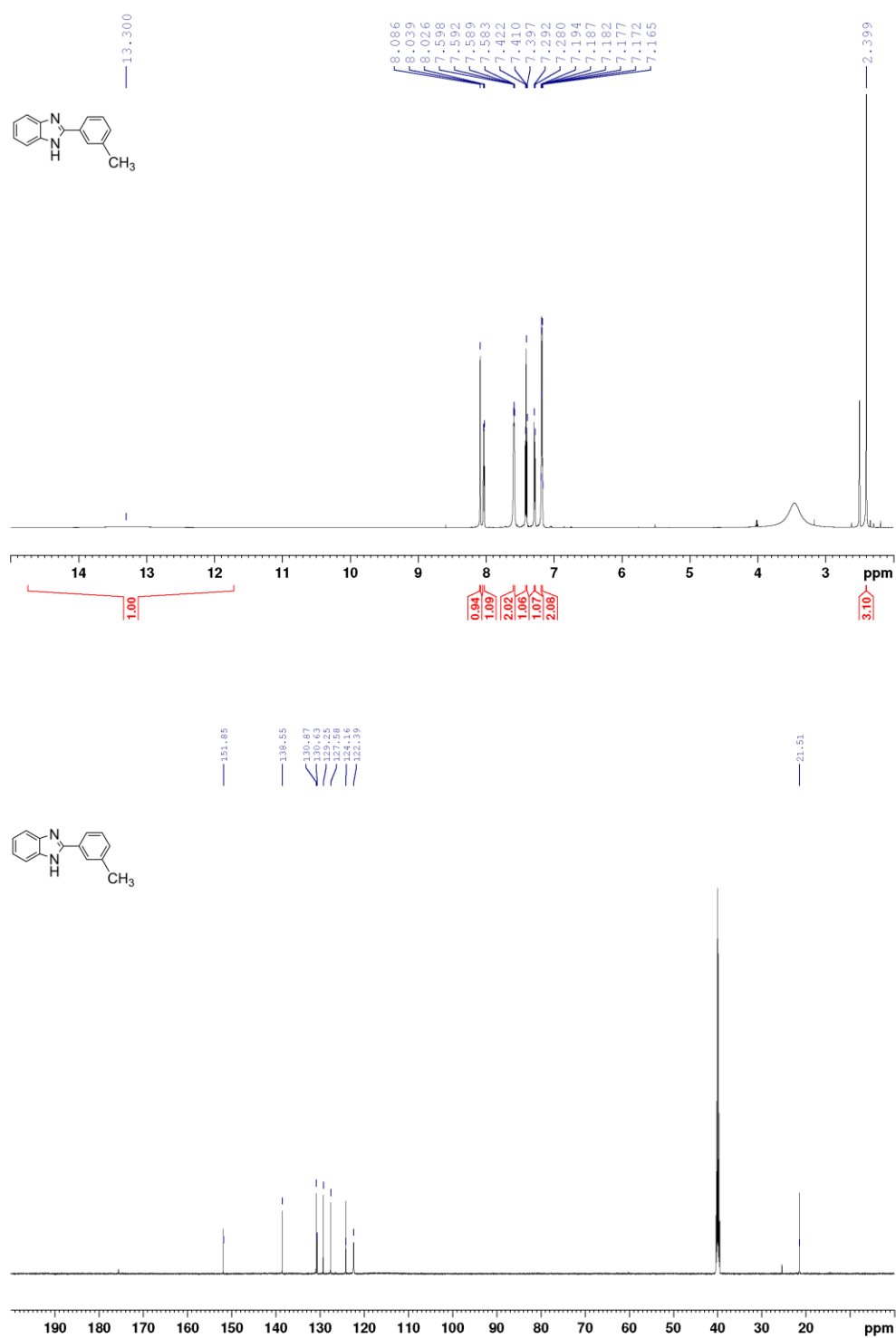
Supplementary Fig. 27 ¹H NMR and ¹³C NMR spectra of 3l.



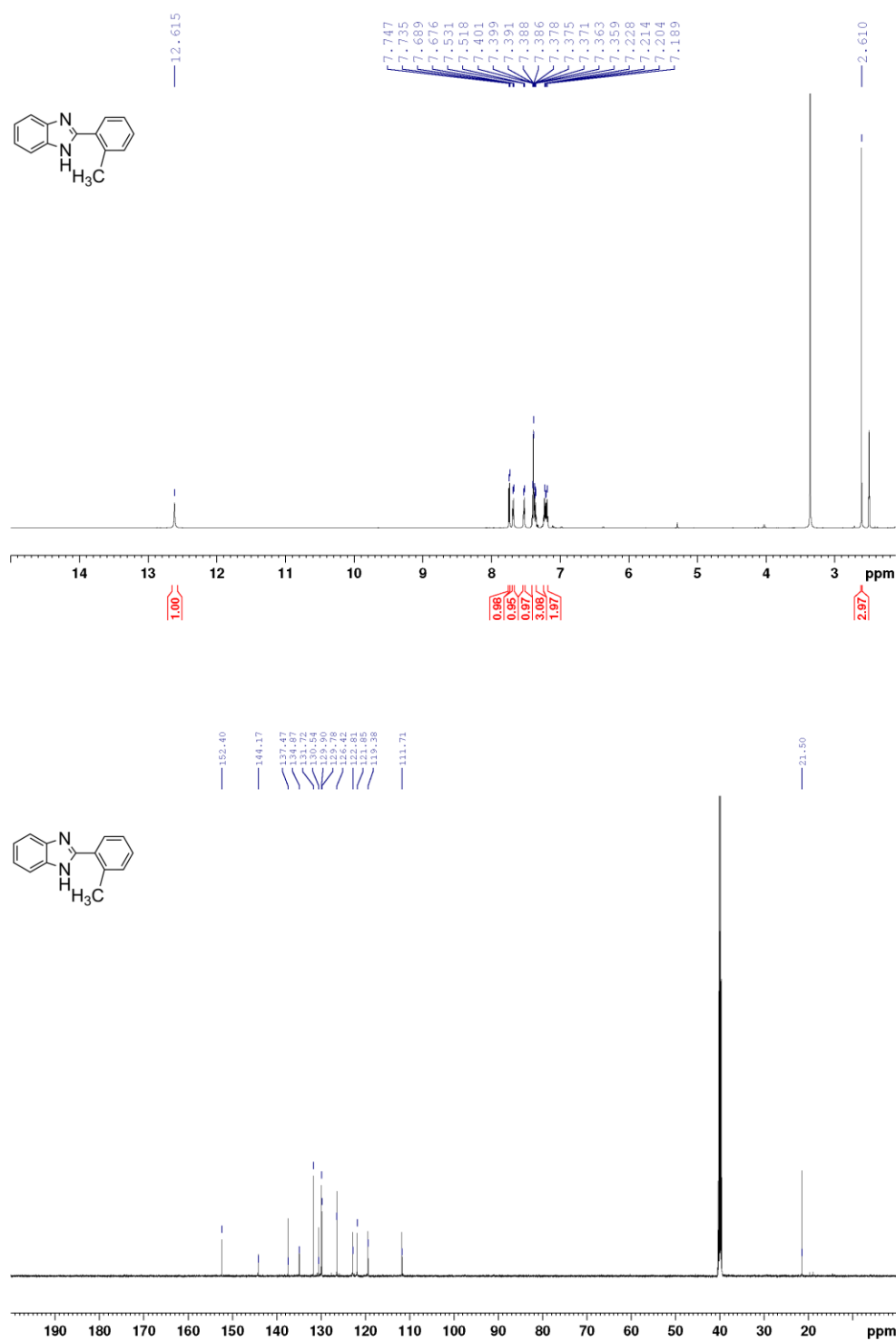
Supplementary Fig. 28 ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra of 3m.



Supplementary Fig. 30 ¹H NMR and ¹³C NMR spectra of **30**.



Supplementary Fig. 31 ¹H NMR and ¹³C NMR spectra of 3p.



Supplementary Fig. 32 ¹H NMR and ¹³C NMR spectra of 3q.

1. References

- [1] X. Zhao, H. Pang, D. Huang, G. Liu, J. Hu, Y. Xiang, *Angew. Chem. Int. Ed.* **2022**, e202208833.