

Supplementary Information

A Mechanochemical Route to Triazatrinaphthylenes: Building Block for π -Extended, Nitrogen-Enriched Two-Dimensional Metal-Organic Framework

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Section S1: General Information Materials:

For the synthesis of TNP derivatives, 1,3,5-tribromo-2,4,6-trimethylbenzene, aniline precursors and all solvents were purchased from TCI Chemicals and used without further purification.

Methods:

Nitrogen adsorption experiments (0 to 1 bar) were performed using the Quantachrome Quadrasorb automatic instrument. The nitrogen adsorption isotherms were collected at 77 K using a liquid nitrogen bath. Before performing gas adsorption experiments, the materials were degassed at 120 °C for 8 hrs under a vacuum. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) model applied between P/P₀ values of 0.02 and 0.225. Corresponding pore size distributions were calculated using the quenched solid density functional theory (QSDFT).

Fourier transform infrared (FT-IR): FT-IR spectra of the solid samples were recorded on a Bruker Optics ALPHA II spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory. All the data have been reported in wavenumber (cm⁻¹) scale.

Scanning Electron Microscopy (SEM): SEM images were obtained using JEOL JSM-IT800 microscope operating at 10 kV using tungsten filament as the electron source. Before the imaging, the samples were sputtered with platinum (nano-sized film) using an SCD 040 Balzers Union sputterer to avoid charging during SEM analyses. The samples were prepared simply by putting a drop of dispersed samples in isopropanol on a clean piece of Silicon wafer.

Transmission Electron Microscopy (TEM): TEM images were obtained using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. Samples for TEM imaging were prepared by direct drop-casting onto copper grids TEM Window (TED PELLA, INC. 200 mesh).

Electron Paramagnetic Resonance (EPR) spectroscopy: EPR was studied on the metal organic framework by a conventional Bruker spectrometer (Bruker, EMXmicro) operating at X-band frequency and magnetic field modulation of 100 kHz, with a microwave power of 2.25 mW and modulation amplitude of 1 G at room temperature.

X-ray Photoelectron Spectroscopy (XPS): XPS analyses were performed using ULVAC-PHI 5000 Versa Probe III in a standard high vacuum chamber (5×10⁻¹⁰ mbar). An Al K α X-ray source (100 microns 250 Watts 15 kV) was used, and the pass energy of the analyzer was set at 26 eV, with a step size of 0.1 eV. The XPS stage is prepared in the glove box under inert conditions and loaded into a transfer module for transferring into the XPS chamber.

Solution NMR details: ¹H, ¹³C NMR spectra were collected using BRUKER (¹H: 500 MHz, ¹³C: 126 MHz) and JEOL (¹H: 400 MHz, ¹³C: 100 MHz) instrument. NMR data was taken in the ppm unit and referenced against the solvent residual peaks. Coupling constants (J) are

reported in Hertz (Hz). Coupling patterns are indicated as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), or m (multiplet).

High-resolution electrospray ionization mass spectrometry (ESI-HRMS): The experiments were performed in Bruker micrOTOF-Q II Spectrometer. The samples were prepared simply by dissolving solid substrates in MeOH or CH₃CN (10^{-3} to 10^{-5} M).

Supplementary Text

Section S2: Synthetic Procedures of Starting Materials:

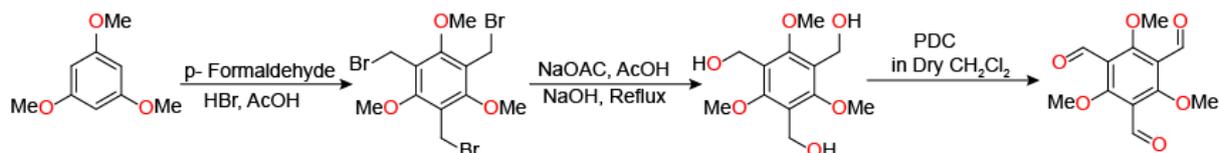


Fig. S1: Schematic representation of the synthesis of 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde.

1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene:

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde was synthesized according to a previously reported procedure. Paraformaldehyde (8.5 g), 1,3,5-trimethoxybenzene (11.5 g), and glacial acetic acid (25 mL) were combined in a 100 mL tube and stirred for 30 min to achieve a homogeneous mixture. Subsequently, 33% HBr in acetic acid (75 mL) was added dropwise under stirring at 70 °C. The resulting reaction mixture was then heated to 90 °C and maintained at that temperature for 3 h, during which it gradually turned orange. After completion, the reaction mixture was poured into water and washed thoroughly with water several times to remove residual acid. The resulting white solid was extracted with dichloromethane (DCM), dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure to yield a sticky oil. The crude product was purified by column chromatography using 5% ethyl acetate in hexane as the eluent to afford the desired product. ¹H NMR (CDCl₃): δ 4.59 (s, 6H), 4.13 (s, 9H).

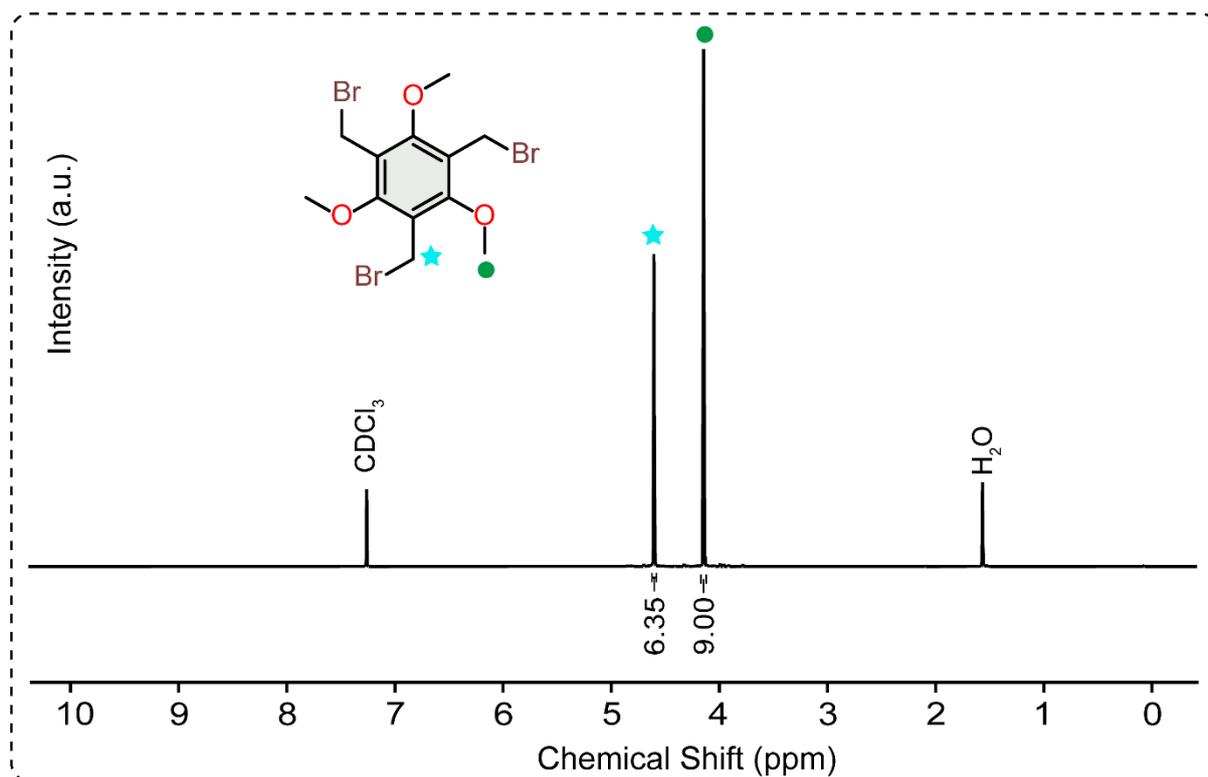


Fig. S2 ^1H NMR spectra of *1,3,5*-tris(bromomethyl)-*2,4,6*-trimethoxybenzene CDCl_3 . ^1H NMR (400 MHz, CDCl_3) δ 4.59 (s, 6H), 4.13 (s, 9H)

Synthesis of *1,3,5*-tris-hydroxymethyl-*2,4,6*-trimethoxybenzene:

1,3,5-Tris(bromomethyl)-*2,4,6*-trimethoxybenzene (1.00 g, 2.24 mmol) and anhydrous sodium acetate (2.27 g, 27.7 mmol) were suspended in glacial acetic acid (20 mL) in a round-bottom flask. The reaction mixture was heated to reflux under an open system for 4-6 h. After cooling to room temperature, the resulting suspension was filtered, and the filtrate was extracted with ethyl acetate. The organic layer was successively washed with saturated aqueous NaHCO_3 , water, and brine, then dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to afford the crude triacetate (0.860 g, quantitative yield) as a white solid. ^1H NMR (CDCl_3): δ 5.16 (s, 6H), 3.83 (d, 9H), 2.07 (s, 9H) ppm.

The as-synthesized triacetate was dissolved in ethanol (8 mL), and an aqueous solution of sodium hydroxide (1.50 g, 37.5 mmol in 10 mL of water) was added. The resulting mixture was heated to reflux for 12-18 h. After completion, ethanol was removed under reduced pressure, and the remaining aqueous phase was neutralized with 1.0 M HCl, followed by saturation with NaCl. The mixture was then extracted with ethyl acetate, and the combined organic layers were dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to yield the triol (0.48 g, 83%) as a white solid.: ^1H NMR ($\text{DMSO}-d_6$): δ 3.87 (s, 9H), 4.45-4.46 (d, 6H), 4.76-4.78 (t, 3H) ppm.

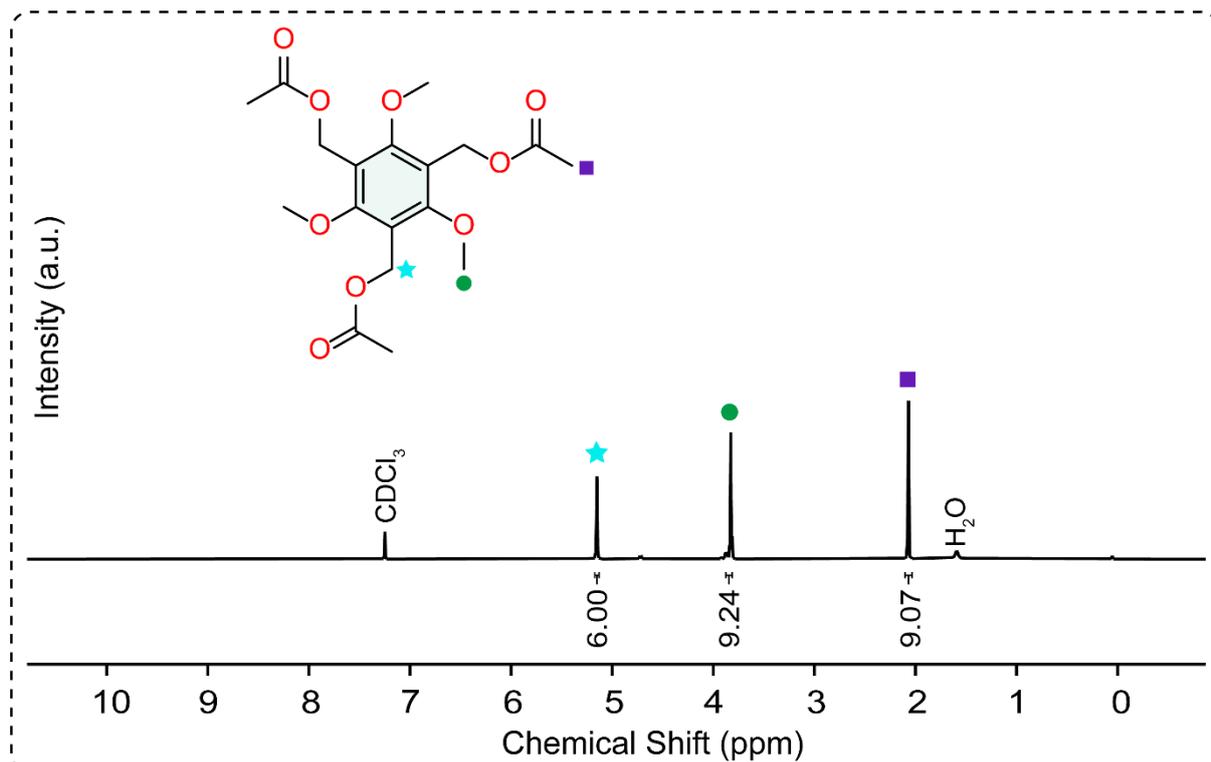


Fig. S3 ¹H NMR spectra of (2,4,6-trimethoxybenzene-1,3,5-triyl) tris(methylene)triacetate in CDCl₃. ¹H NMR (400 MHz, CDCl₃) δ 5.16 (s, 6H), 3.83 (d, 9H), 2.07 (s, 9H).

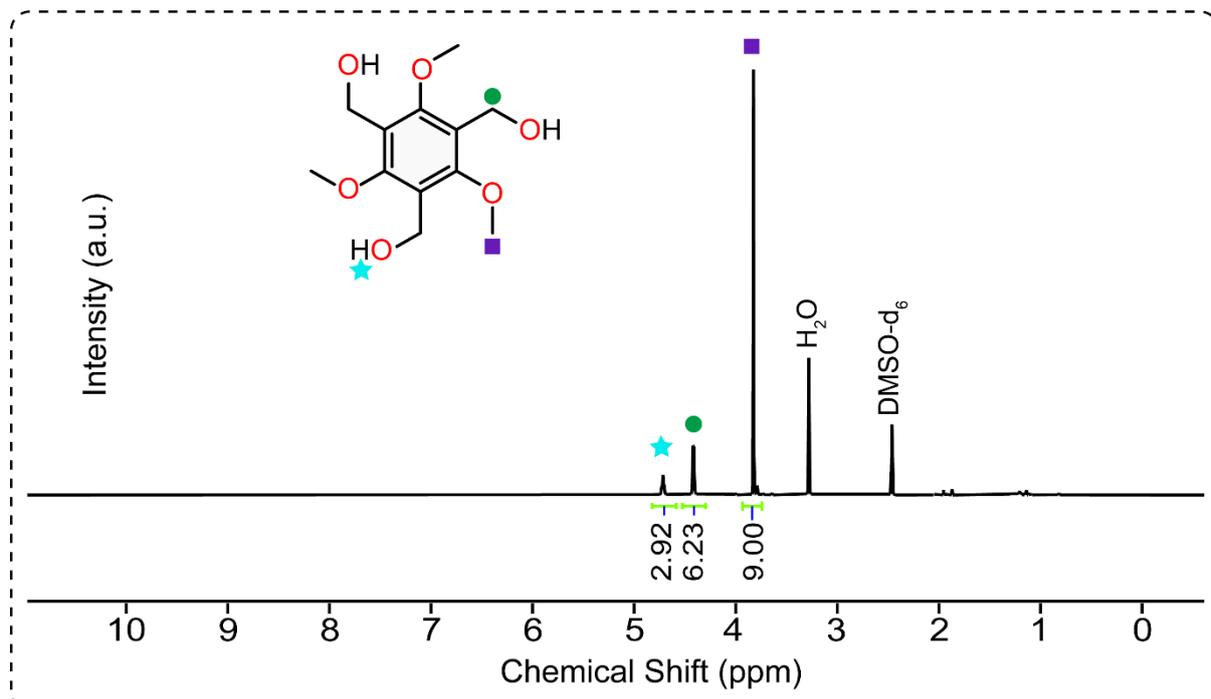


Fig. S4 ¹H NMR spectra of 1,3,5-tris-hydroxymethyl-2,4,6-trimethoxybenzene in DMSO-d₆. ¹H NMR (500 MHz, DMSO-d₆) δ 4.72 (t, 3H), 4.41 (d, 6H), 3.82 (s, 9H).

Synthesis of 2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde:

To a stirred solution of 1,3,5-tris(hydroxymethyl)-2,4,6-trimethoxybenzene (750 mg) in dry dichloromethane (35 mL) containing 3 Å molecular sieves, pyridinium dichromate (PDC, 5.5 g) was added under an argon atmosphere. The resulting suspension was stirred overnight. After completion, the mixture was diluted with dichloromethane (100 mL), and the solids were removed by suction filtration through a pad of Celite. The filtrate was concentrated under reduced pressure, and the crude residue was purified by column chromatography (ethyl acetate/hexane) to afford the trialdehyde as a colorless solid (75% yield). $^1\text{H NMR}$ (CDCl_3): δ 10.33 (s, 3H), 4.01 (s, 9H) ppm.

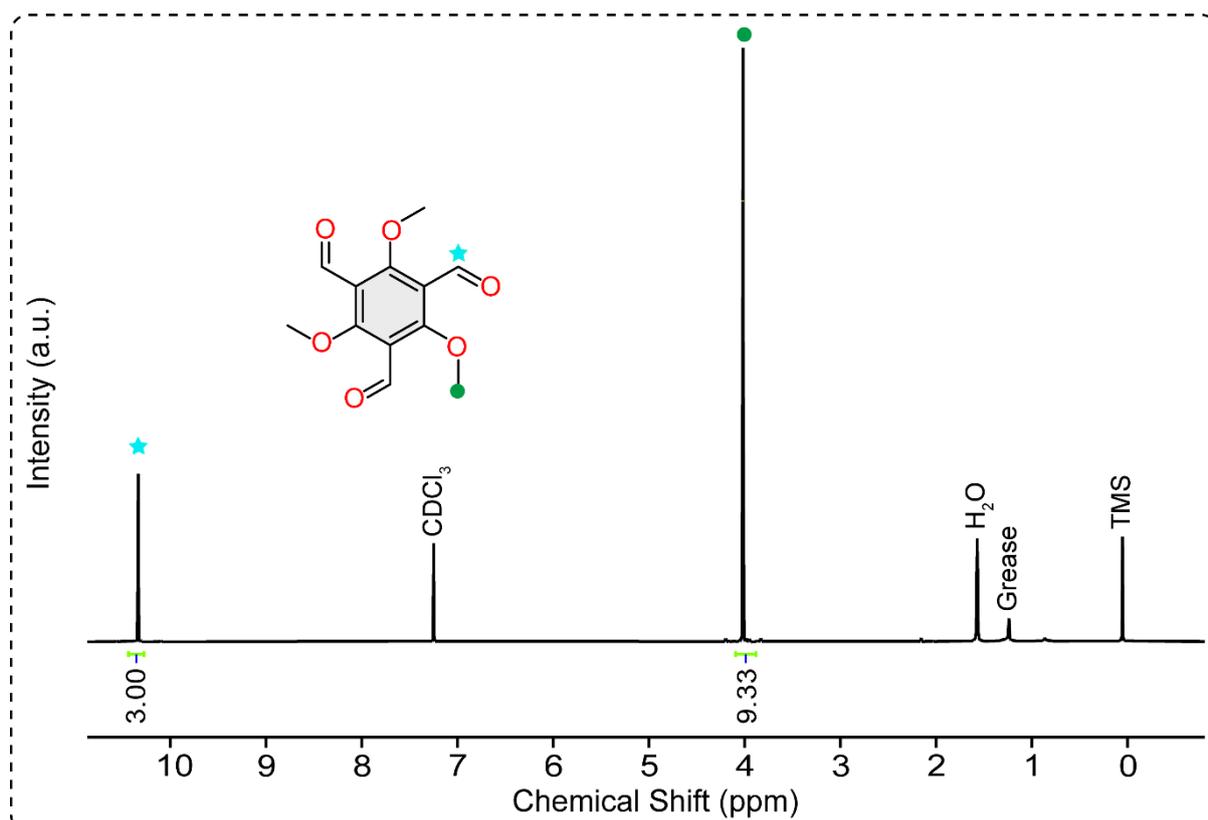


Fig. S5 $^1\text{H NMR}$ spectra of 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde in CDCl_3 . $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.33 (s, 3H), 4.01 (s, 9H).

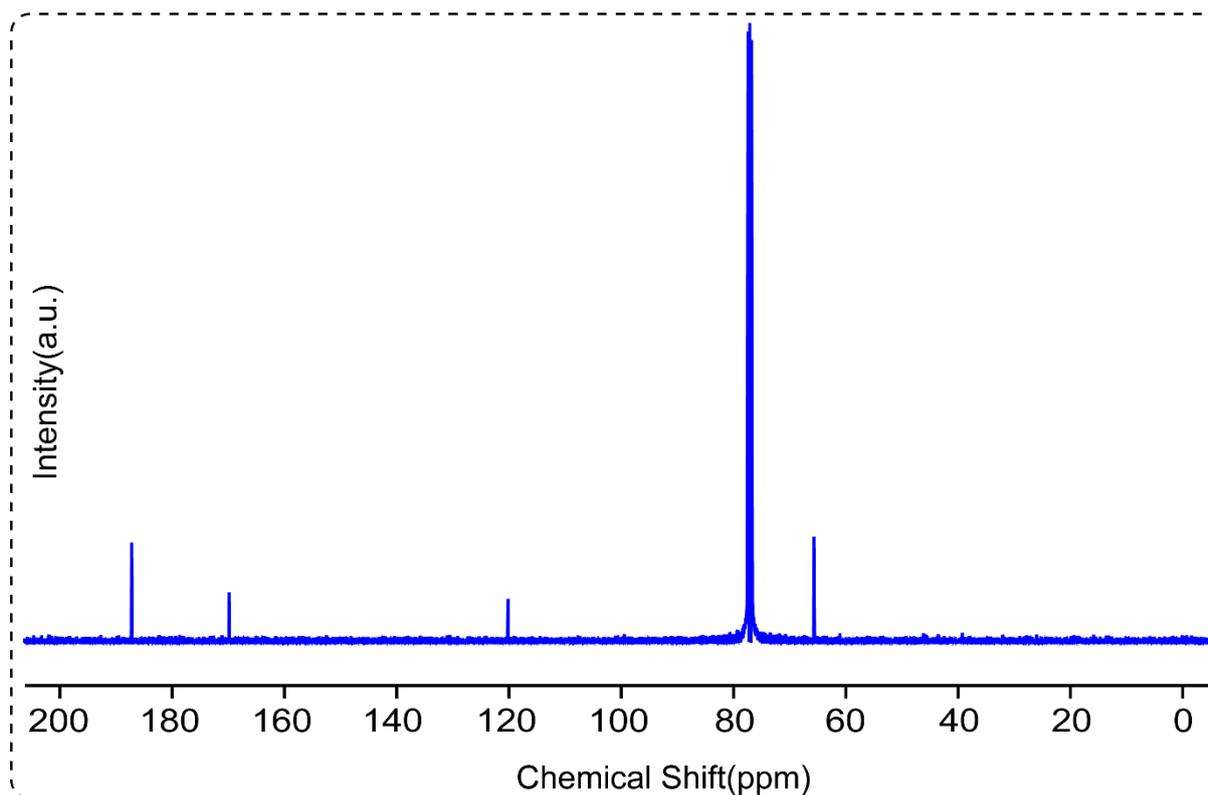


Fig. S6 ¹³C NMR (101 MHz, Chloroform-d) δ 187.23, 169.86, 120.18, 65.68.

Section S3: Reaction Optimization

The mechanochemical reaction was optimized using 4-aminylaniline and 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde. In a typical procedure, 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) was placed in a mortar, followed by the addition of 4-aminylaniline. The mixture was ground manually for 25 minutes in the presence of a catalyst and subsequently maintained at a specified temperature for 24 h. The crude product was purified by column chromatography using an ethyl acetate/hexane eluent to isolate the desired product. Reaction parameters, including amine equivalents, solvent system, catalyst identity, catalyst loading, reaction temperature, and reaction time, were systematically optimized as detailed below.

Optimization : Catalysts

No	Catalyst	Catalyst Concentration	Catalyst Volume	Temperature	Time	Yield(%)
1	Triflic Acid	Concentrated	500 μ L	120 $^{\circ}$ C	24 h	0 %
2	HCl	12 (M)	500 μ L	120 $^{\circ}$ C	24 h	0 %
3	CF ₃ COOH(TFA)	Concentrated	500 μ L	120 $^{\circ}$ C	24 h	0 %
4	<i>p</i> -Toluene sulphonic acid (PTSA)	Concentrated	500 μ L	120 $^{\circ}$ C	24 h	52 %
5	CH ₃ COOH (AcOH)	17.4	500 μ L	120 $^{\circ}$ C	24 h	95 %
6	NaOH	6(M)	500 μ L	120 $^{\circ}$ C	24 h	0 %

Table 1 Optimization of catalysts for the synthesis of TNP-*p*-Amyl keeping other conditions constant

Optimization : Catalyst's Concentration

No	Catalyst	Catalyst Concentration	Catalyst Volume	Temperature	Time	Yield(%)
1	CH ₃ COOH (AcOH)	3 (M)	500 μ L	120 $^{\circ}$ C	24 h	65 %
2	CH ₃ COOH (AcOH)	6 (M)	500 μ L	120 $^{\circ}$ C	24 h	72 %
3	CH ₃ COOH (AcOH)	9 (M)	500 μ L	120 $^{\circ}$ C	24 h	80 %
4	CH ₃ COOH (AcOH)	12 (M)	500 μ L	120 $^{\circ}$ C	24 h	87 %
5	CH ₃ COOH (AcOH)	15 (M)	500 μ L	120 $^{\circ}$ C	24 h	94 %
6	CH ₃ COOH (AcOH)	17.4 (M)	500 μ L	120 $^{\circ}$ C	24 h	95 %

Table 2 Optimization of catalyst's concentration for the synthesis of TNP- *p*-Amyl keeping other conditions constant.

Optimization : Catalyst's Volume

No	Catalyst	Catalyst Concentration	Catalyst Volume	Temperature	Time	Yield(%)
1	CH ₃ COOH (AcOH)	17.4 (M)	2 μL	120 °C	24 h	38 %
2	CH ₃ COOH (AcOH)	17.4 (M)	5 μL	120 °C	24 h	57 %
3	CH ₃ COOH (AcOH)	17.4 (M)	20 μL	120 °C	24 h	67 %
4	CH ₃ COOH (AcOH)	17.4 (M)	30 μL	120 °C	24 h	79 %
5	CH ₃ COOH (AcOH)	17.4 (M)	50 μL	120 °C	24 h	85 %
6	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	120 °C	24 h	95 %
7	CH ₃ COOH (AcOH)	17.4 (M)	500 μL	120 °C	24 h	94 %

Table 3 Optimization of catalyst's volume for the synthesis of TNP- *p*-Amyl keeping other conditions constant

Optimization : Temperature

No	Catalyst	Catalyst Concentration	Catalyst Volume	Temperature	Time	Yield(%)
1	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	25 °C	24 h	55 %
2	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	70 °C	24 h	75 %
3	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	80 °C	24 h	85 %
4	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	24 h	95 %
5	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	120 °C	24 h	93 %

Table 4 Optimization of temperature for the synthesis of TNP- *p*-Amyl keeping other conditions constant

Optimization : Time

No	Catalyst	Catalyst Concentration	Catalyst Volume	Temperature	Time	Yield(%)
1	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	2 h	59 %
2	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	6 h	64 %
3	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	12 h	78 %
4	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	18 h	89 %
5	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	24 h	95 %
6	CH ₃ COOH (AcOH)	17.4 (M)	100 μL	90 °C	36 h	94 %

Table 5 Optimization of time for the synthesis of TNP- *p*-Amyl keeping other conditions constant

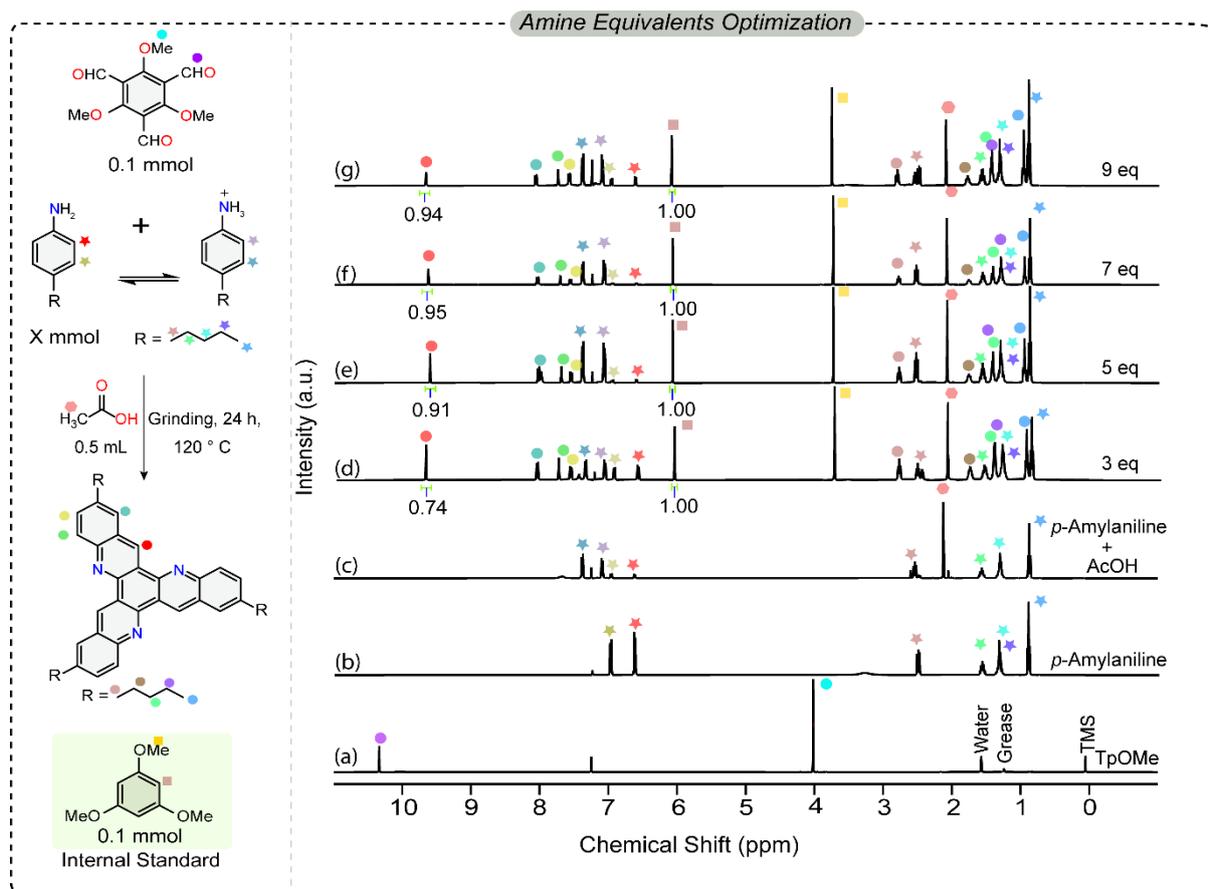


Fig. S7 $^1\text{H NMR}$ of (a) TP-OMe (b) *p*-Amylaniline, (c) *p*-Amylaniline in the presence of glacial AcOH, (d) NMR yield of reaction in the presence of 3eq of *p*-Amylaniline (e) NMR yield of reaction in the presence of 5eq of *p*-Amylaniline (f) NMR yield of reaction in the presence of 7eq of *p*-Amylaniline (g) NMR yield of reaction in the presence of 9eq of *p*-Amylaniline.

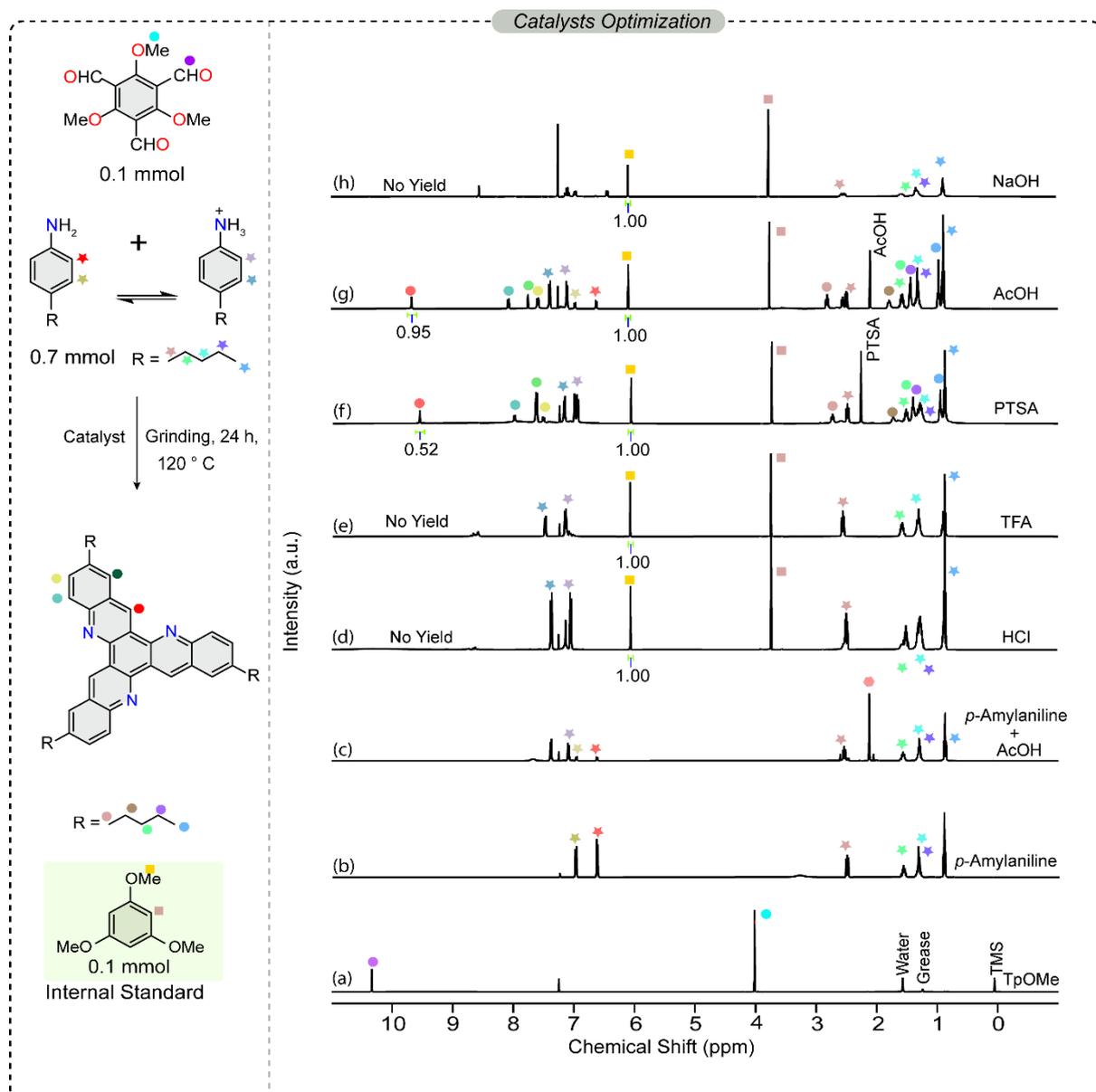


Fig. S8 ^1H NMR of (a) TP-OMe, (b) *p*-Amylaniline, (c) *p*-Amylaniline in the presence of glacial AcOH, (d) NMR yield of reaction in the presence of HCl, (e) NMR yield of reaction in the presence of TFA, (f) NMR yield of reaction in the presence of PTSA, (g) NMR yield of reaction in the presence of AcOH, (h) NMR yield of reaction in the presence of NaOH

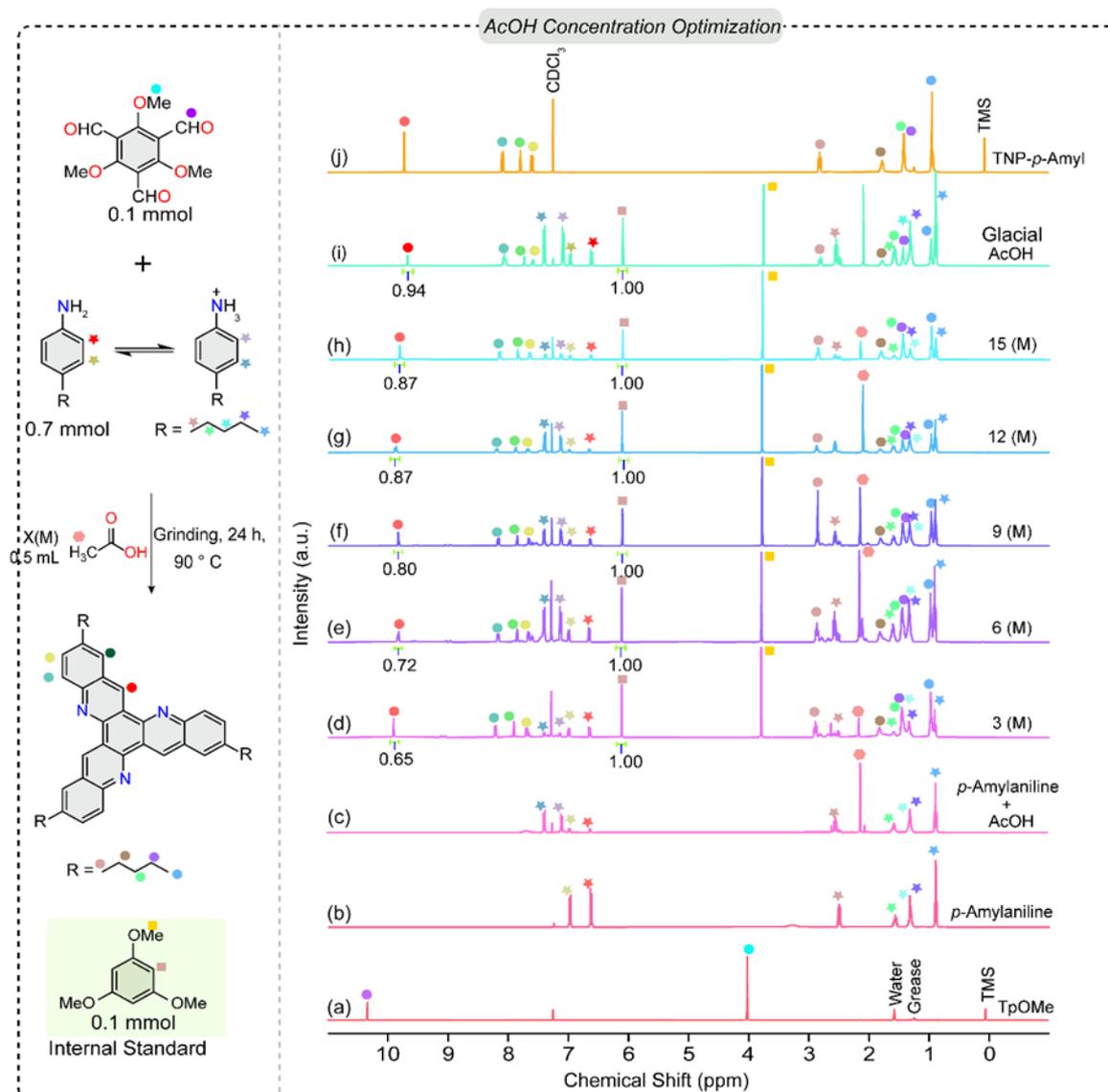


Fig. S9 ^1H NMR of (a) TP-OMe (b) *p*- Amylaniline (c) *p*- Amylaniline in presence of glacial AcOH (d) NMR yield of reaction in presence of 3 (M) AcOH (e) NMR yield of reaction in presence of 6 (M) AcOH (f) NMR yield of reaction in presence of 9 (M) AcOH (g) NMR yield of reaction in presence of 12 (M) AcOH (h) NMR yield of reaction in presence of 15 (M) AcOH (i) NMR yield of reaction in presence of glacial AcOH

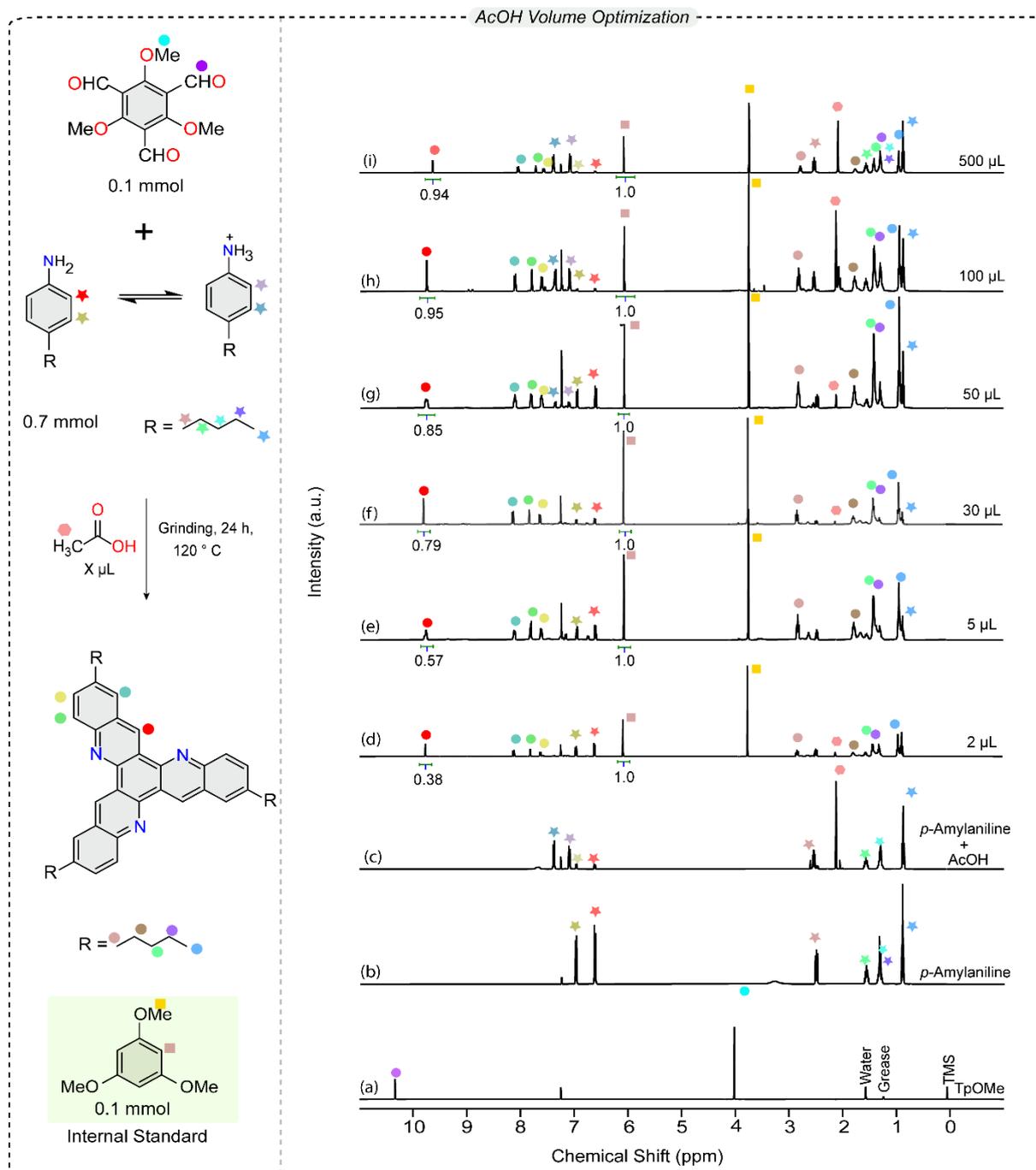


Fig. S10 ^1H NMR of (a) TP-OMe (b) *p*- Amylaniline (c) *p*- Amylaniline in presence of glacial AcOH (d) NMR yield of reaction in presence of 2 μL of 17.4 (M) AcOH (e) NMR yield of reaction in presence of 5 μL of 17.4 (M) AcOH (f) NMR yield of reaction in presence of 20 μL of 17.4 (M) AcOH (g) NMR yield of reaction in presence of 30 μL of 17.4 (M) AcOH (h) NMR yield of reaction in presence of 50 μL of 17.4 (M) AcOH (i) NMR yield of reaction in presence of 100 μL of 17.4 (M) AcOH (j) NMR yield of reaction in presence of 500 μL of 17.4 glacial AcOH

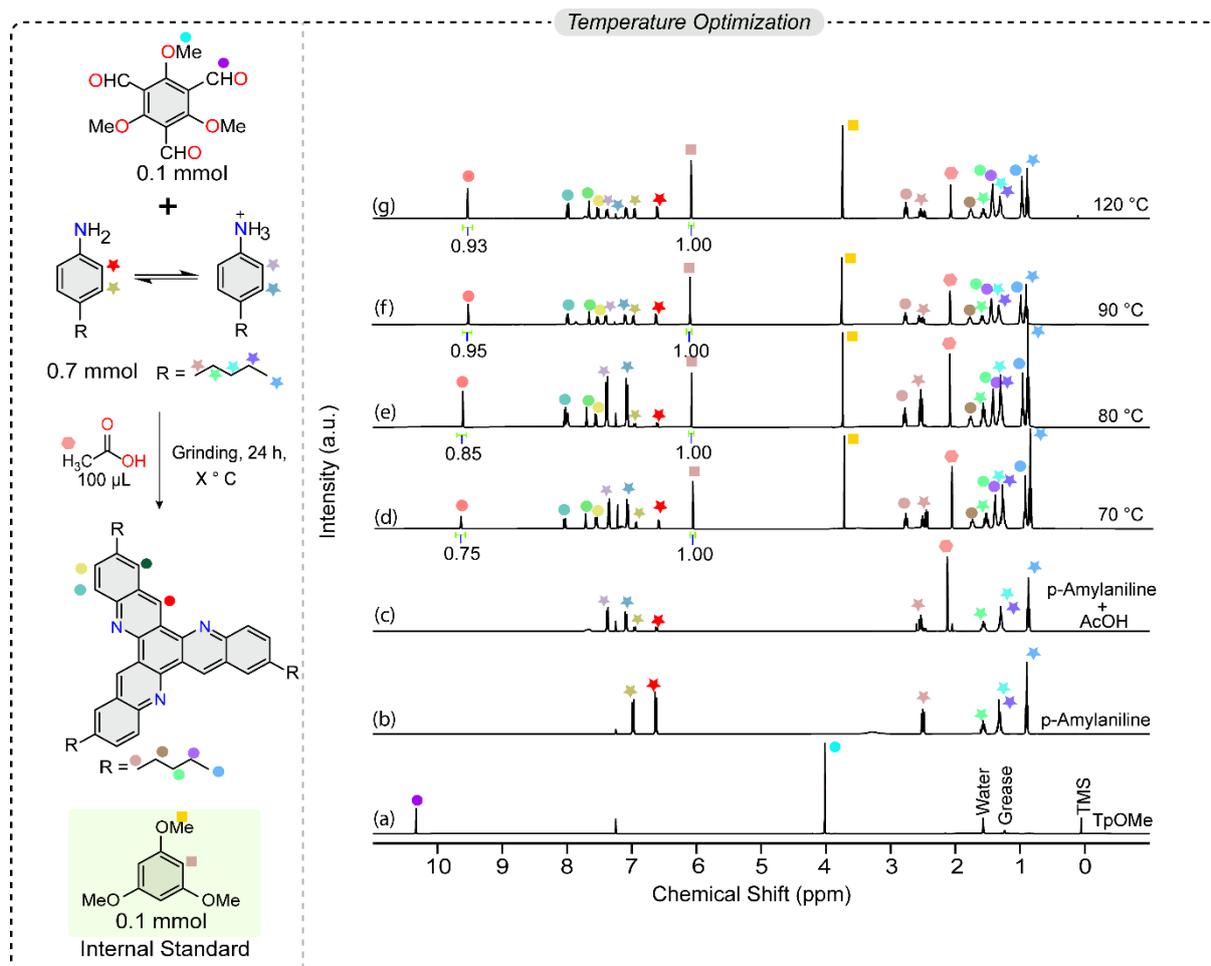


Fig. S11 ^1H NMR of a) TP-OMe b) *p*- Amylaniline c) ^1H NMR of *p*- Amylaniline in presence of glacial AcOH d) NMR yield of reaction at 25 °C (e) NMR yield of reaction at 70 °C (f) NMR yield of reaction at 80 °C (g) NMR yield of reaction at 90 °C (h) NMR yield of reaction at 120 °C

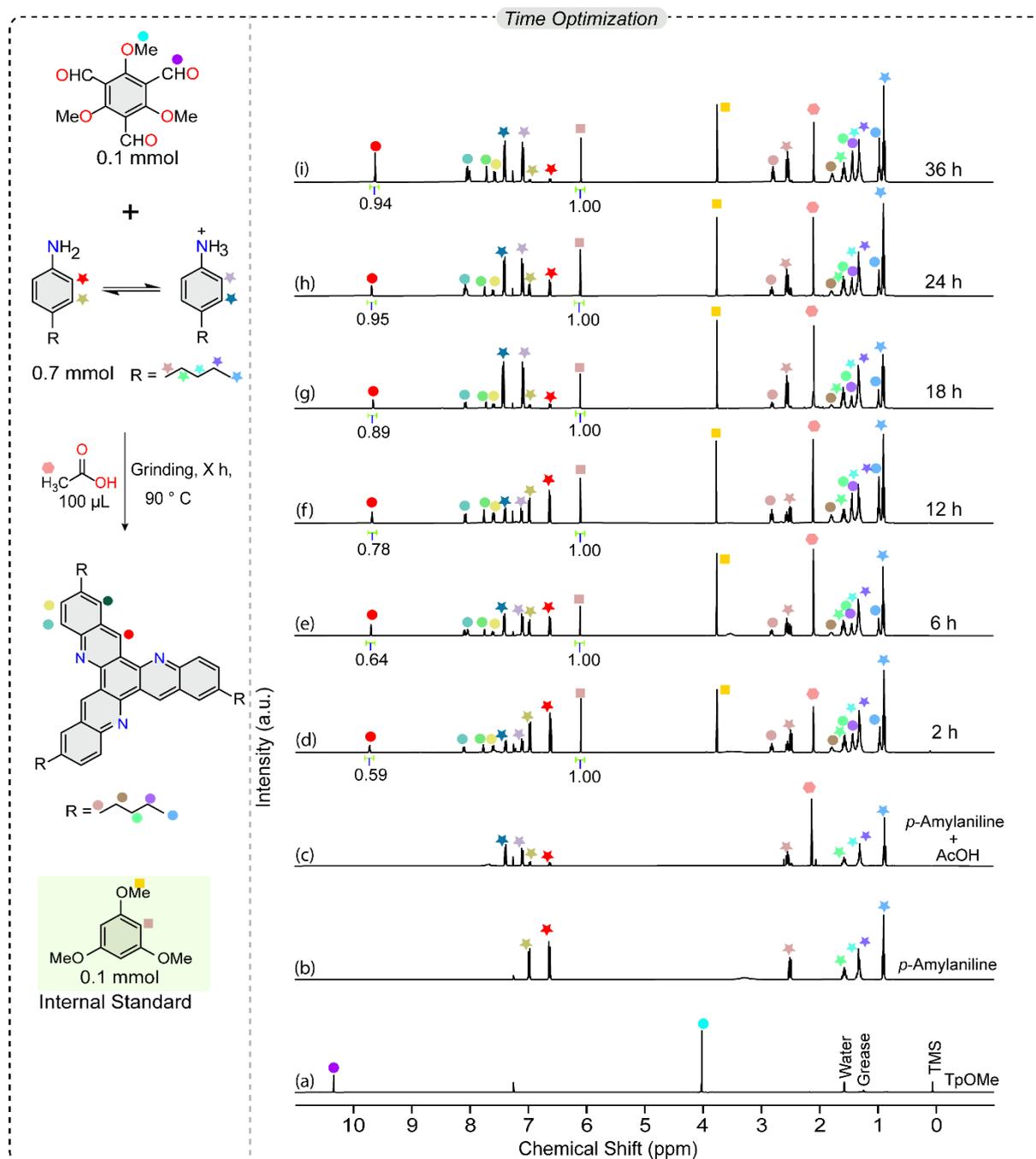


Fig. S12 ^1H NMR of a) TP-OMe b) *p*- Amylaniline c) *p*- Amylaniline in presence of glacial AcOH d) NMR yield of reaction after 2 h (e) NMR yield of reaction after 6 h (f) NMR yield of reaction after 12 h (g) NMR yield of reaction after 18 h (h) NMR yield of reaction after 24 h (i) NMR yield of reaction after 36 h

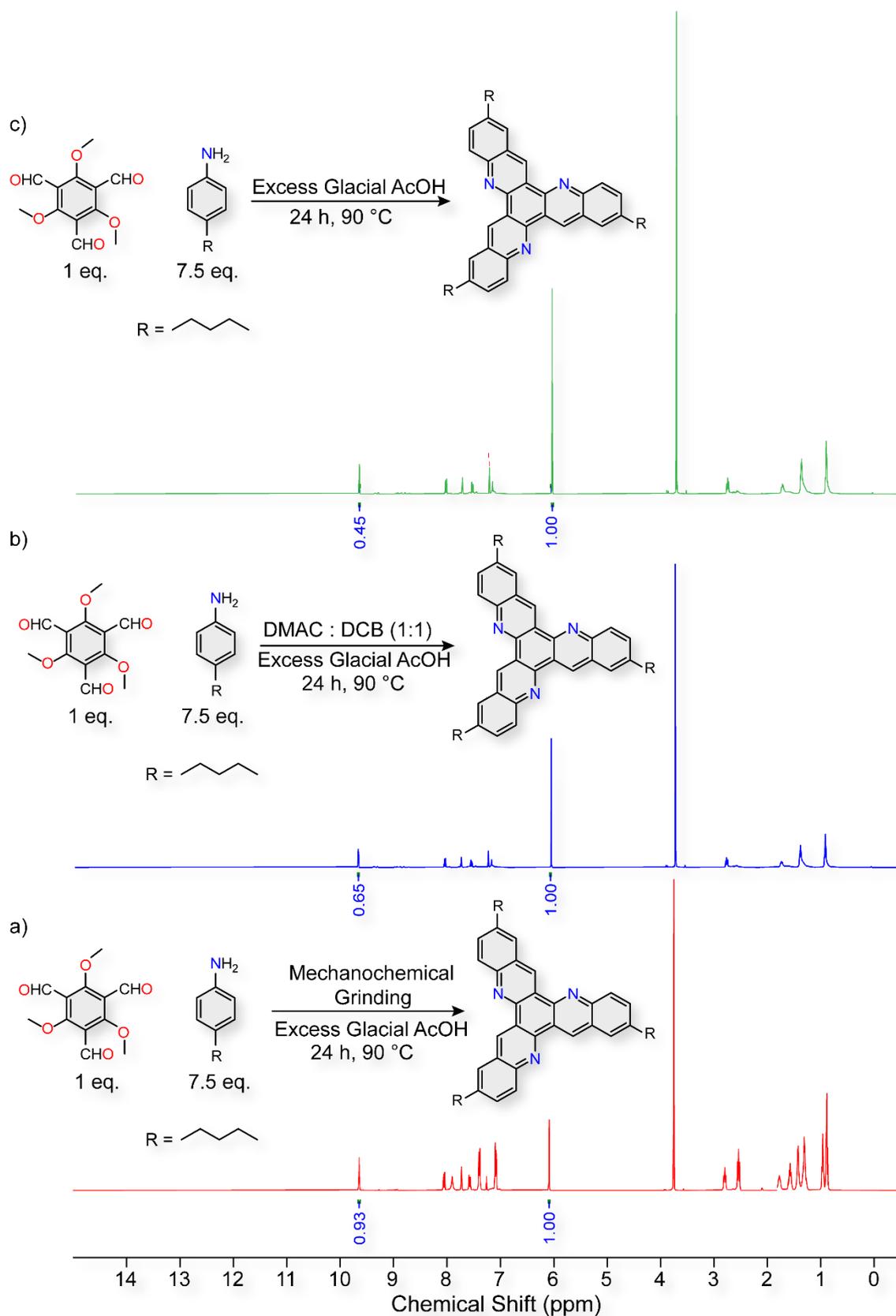


Fig. S13 ^1H NMR yield of the TNP-*p*-Amyl product under a) mechanochemical condition, b) traditional solvothermal condition, c) in the presence of excess AcOH.

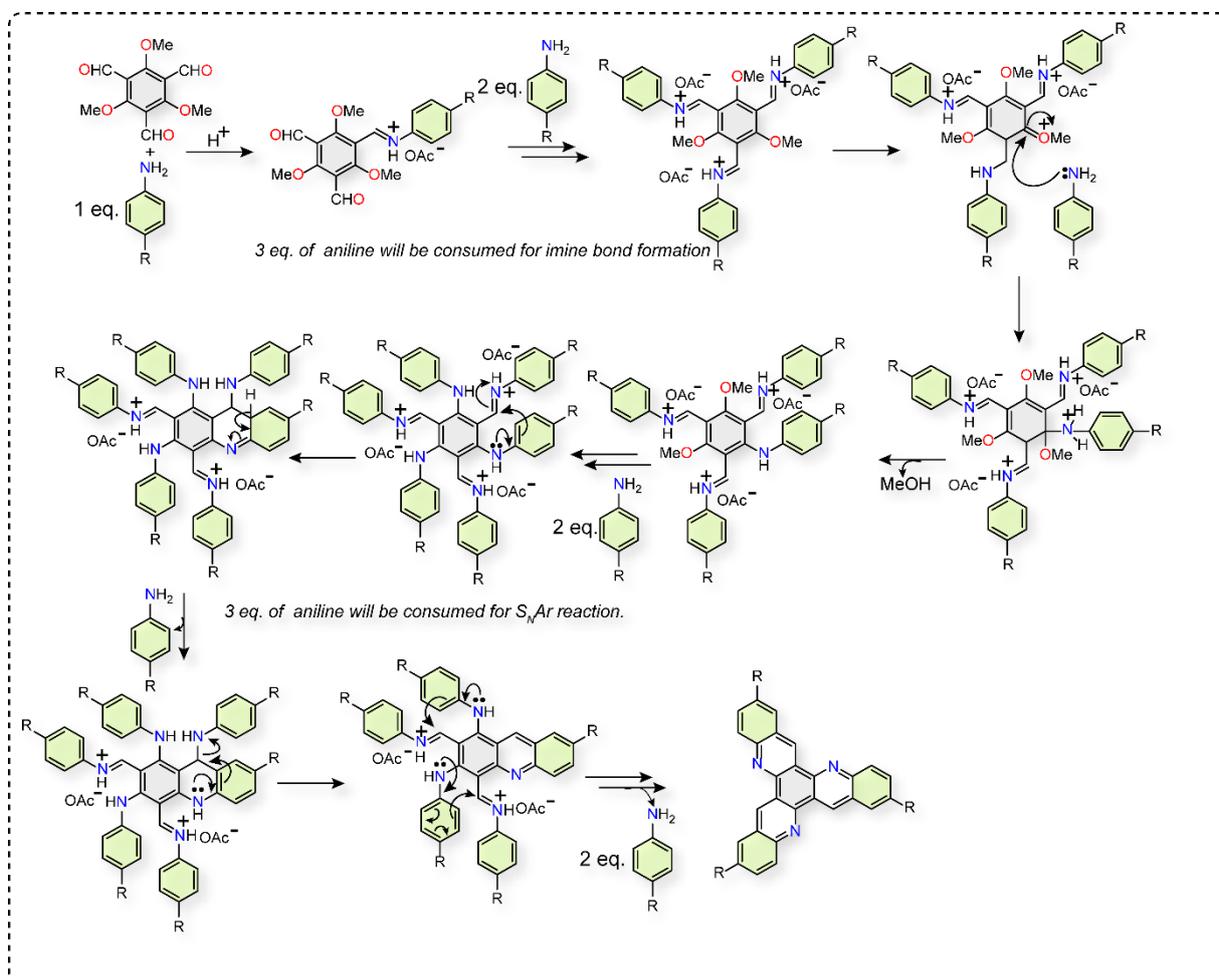


Fig. S14 Schematic representation of the mechanism to understand the requirement of the stoichiometry of *p*-amyl aniline.

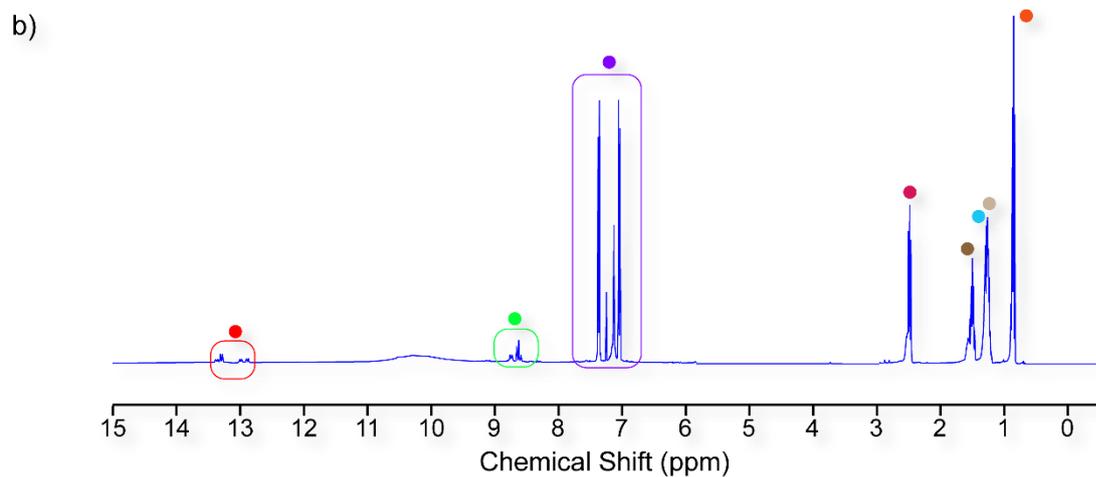
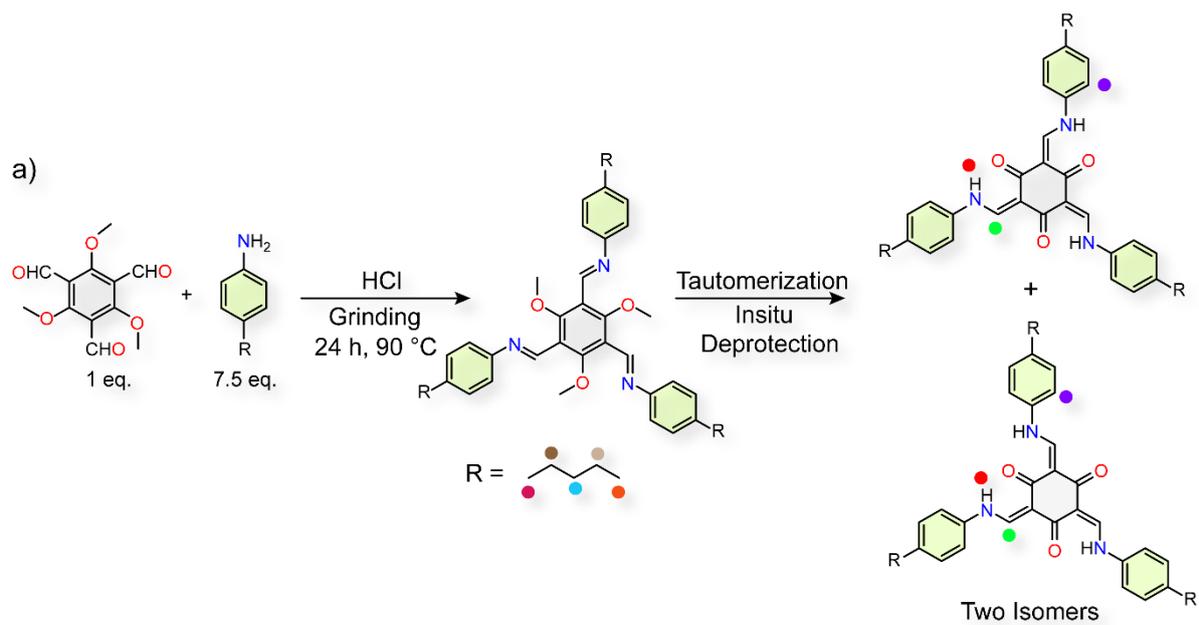


Fig. S15 Reaction scheme of TP-OMe and *p*-aryl aniline in presence of HCl and ^1H NMR spectroscopy

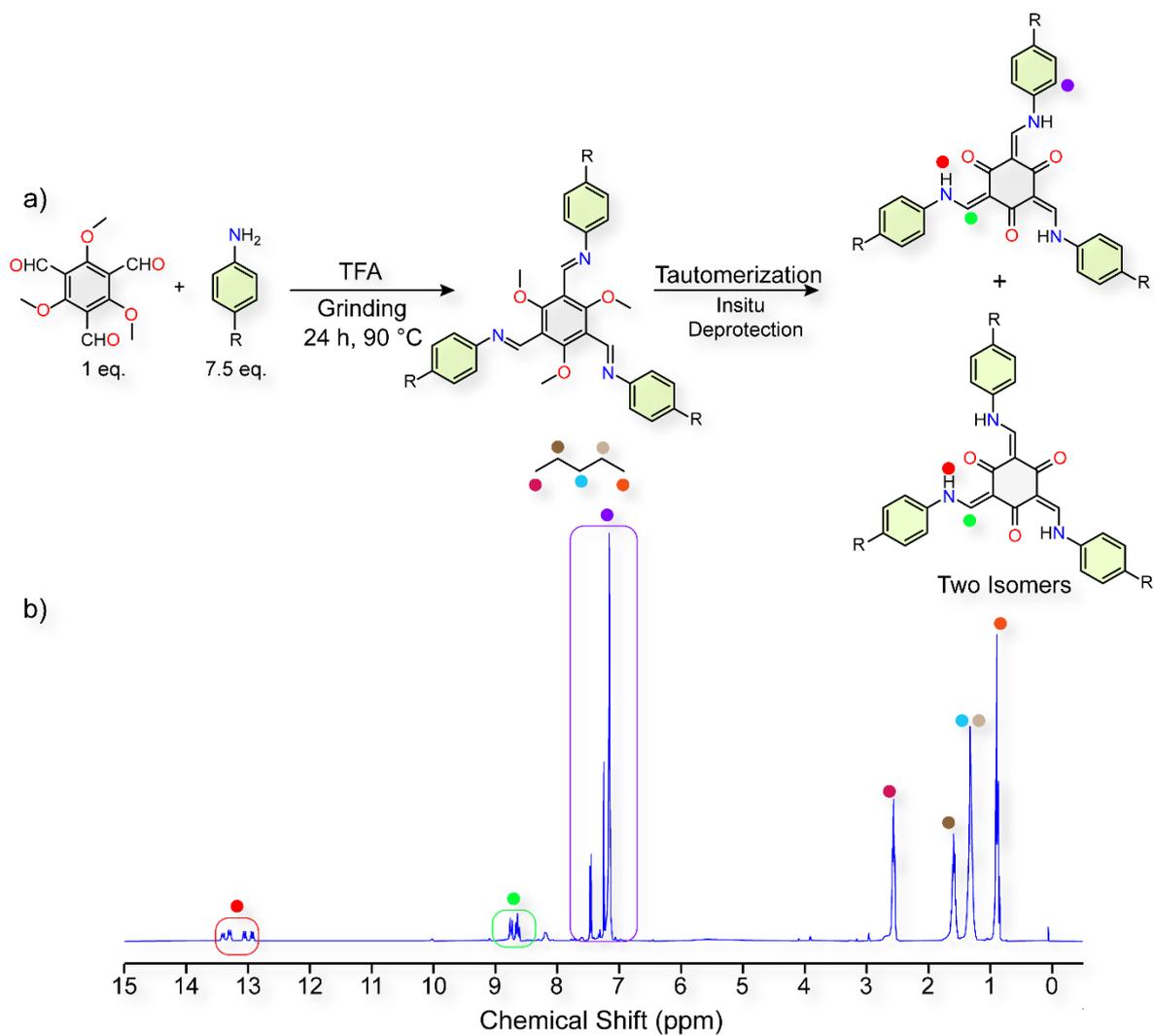


Fig. S16 Reaction scheme of TP-OMe and *p*-aryl aniline in presence of TFA and ^1H NMR spectroscopy

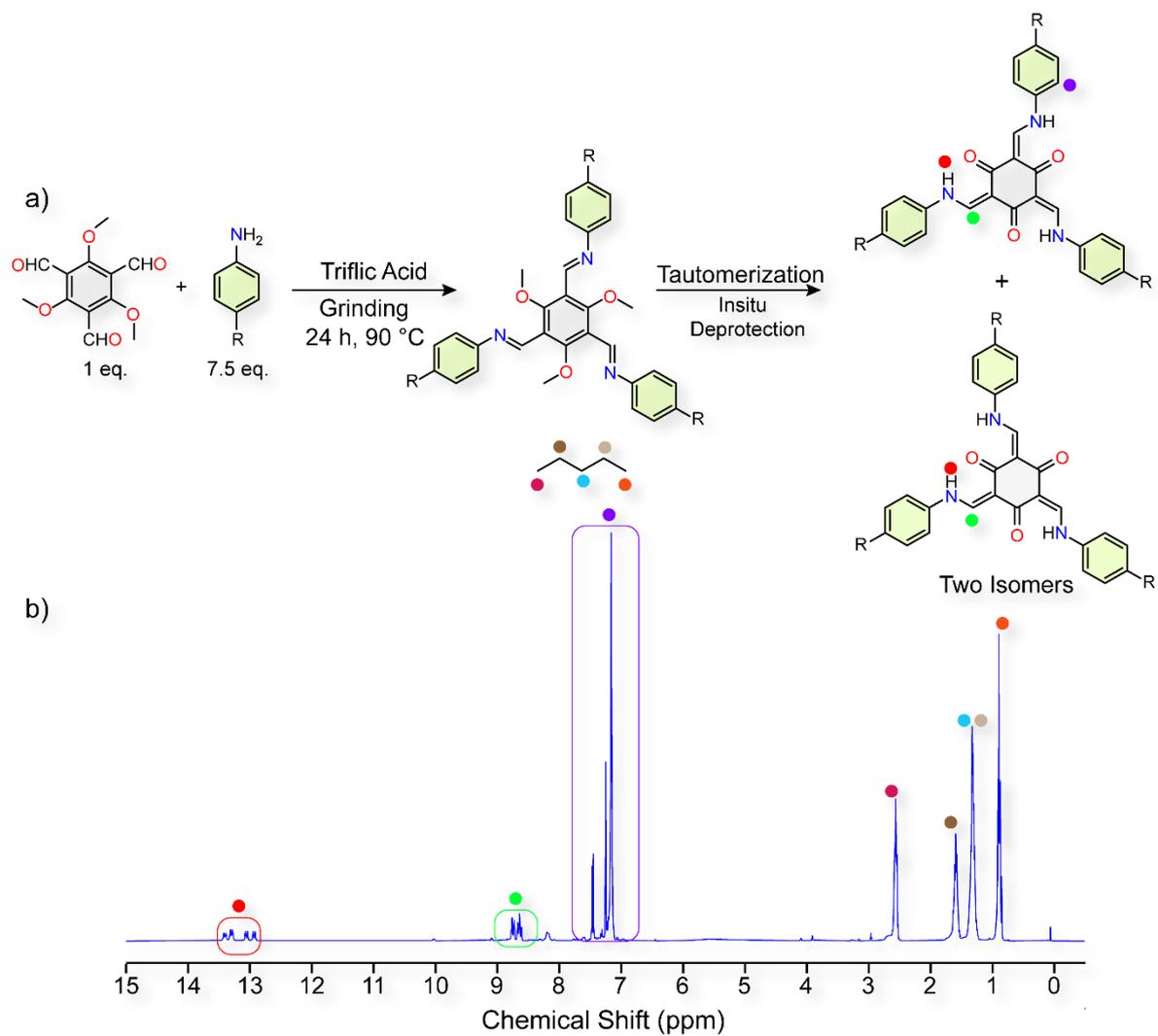


Fig. S17 Reaction scheme of TP-OMe and *p*- aryl aniline in presence of TFOH and ^1H NMR spectroscopy

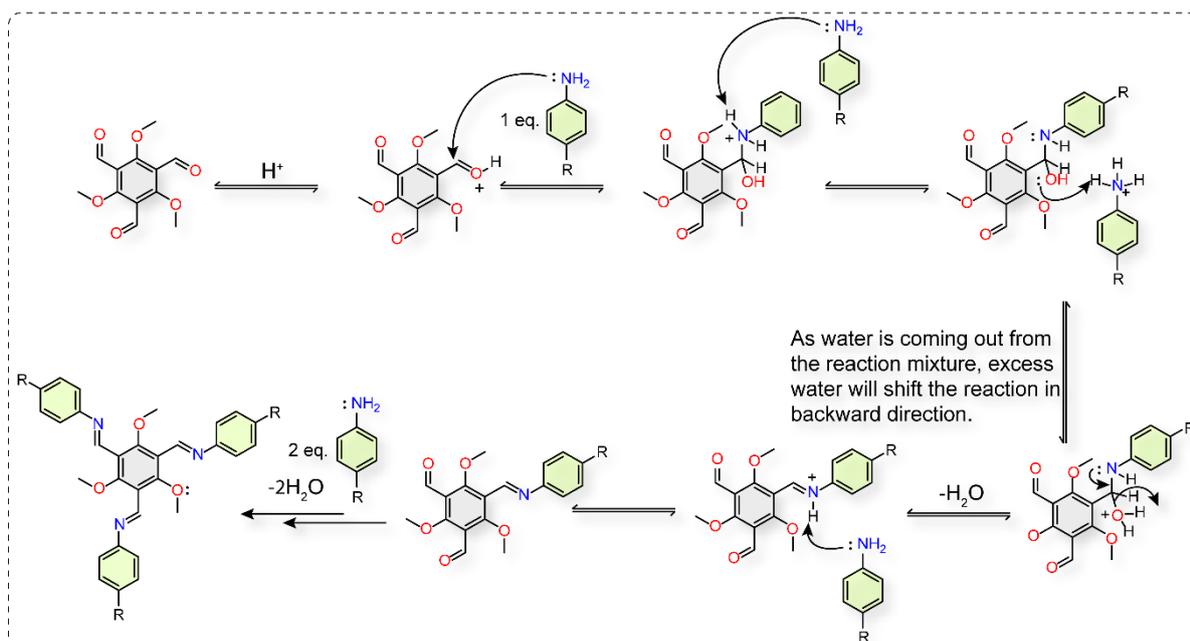


Fig. S18 Schematic representation of the formation of tri-imine compound and the effect of water.

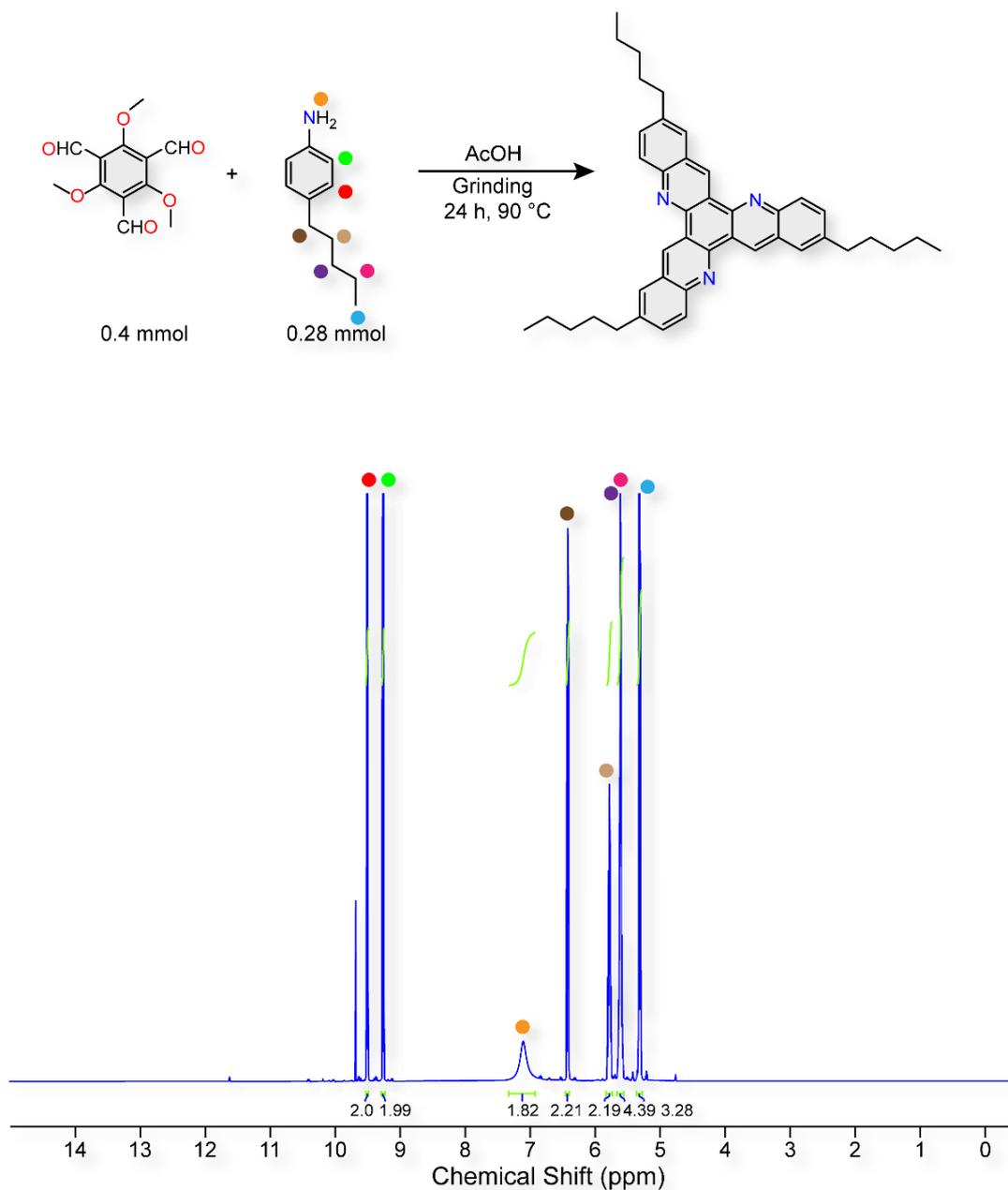


Fig. S19 ¹H NMR of the recovered *p*-Amyl aniline after the reaction.

Section S4: Characterization of TNP-Derivatives

TNP

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and aniline (64 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L). The mixture was ground manually for 25 minutes, transferred to an open-mouthed glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the residue was washed several times with acetone to afford the crude product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.13 (s, 3H) 8.37 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 7.4 Hz, 2H), 7.91 (ddd, J = 8, 8, 1.5 Hz, 3H), 7.89 (d, J = 1.7 Hz, 1H), 7.70 – 7.65 (m, 3H). HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{15}\text{N}_3$ 382.1344; Found 382.1317.

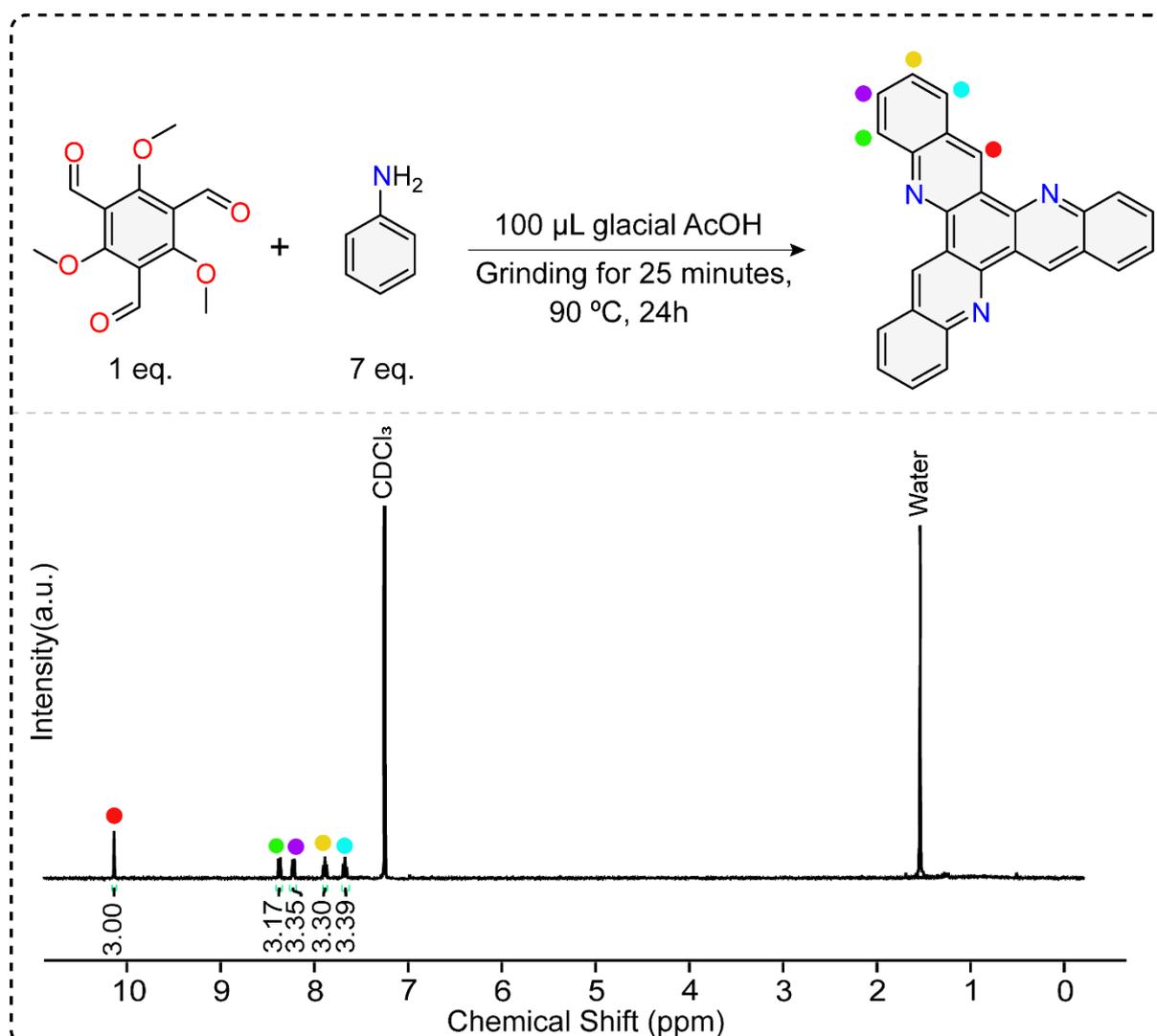


Fig. S20 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.13 (s, 3H) 8.37 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 7.4 Hz, 2H), 7.91 (ddd, J = 8, 8, 1.5 Hz, 3H), 7.89 (d, J = 1.7 Hz, 1H), 7.70 – 7.65 (m, 3H).

As the TNP compound is not soluble enough in any deuterated solvent (CDCl_3 , DMSO-d_6 , DMF-d_7 , THF-d_8 , CD_2Cl_2), $^{13}\text{C NMR}$ has not been provided.

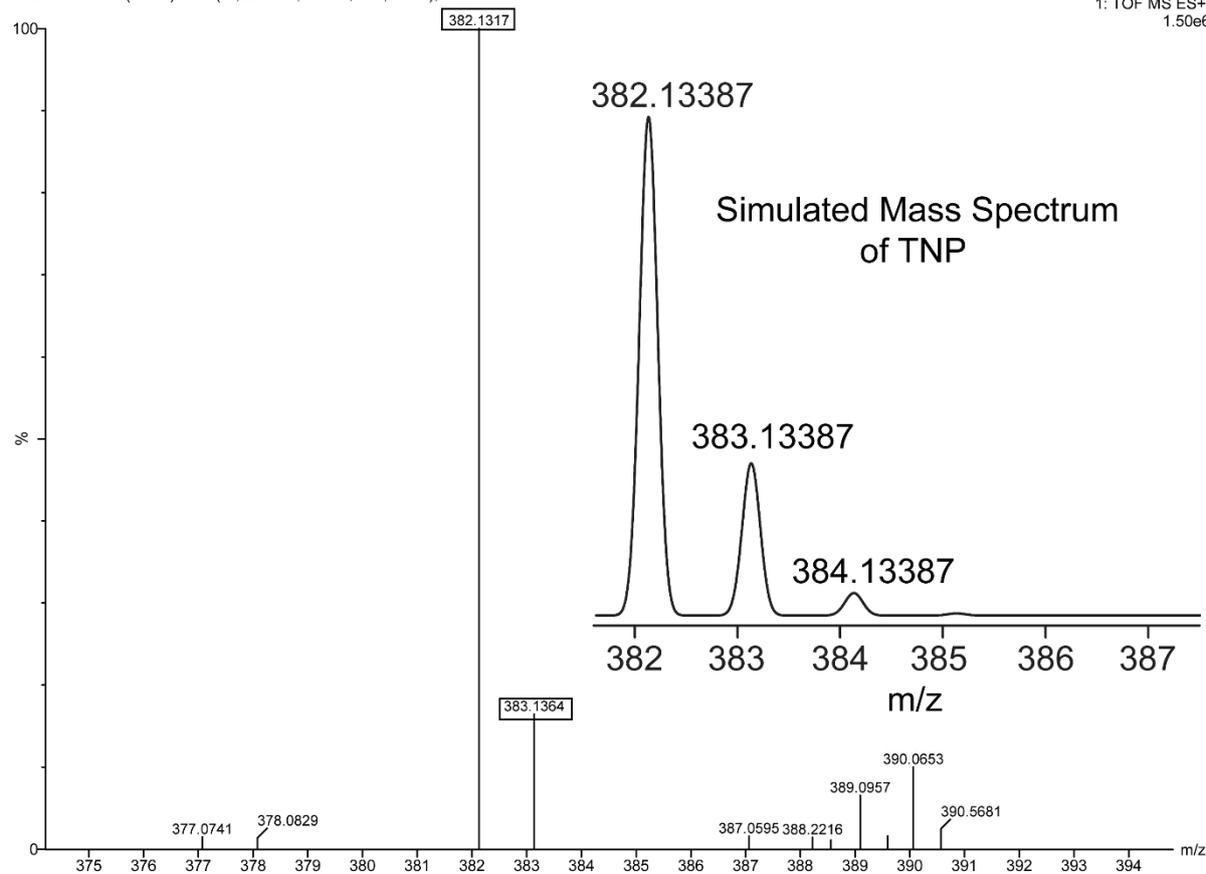


Fig. S21 High resolution mass spectrum of TNP m/z $[M+H]^+$ calculated for $C_{27}H_{15}N_3$ 382.13387; found 382.1317

TNP-*p*-amyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-amylaniline (121.48 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.67 (s, 3H) 8.06 (d, J = 8.06 Hz, 1H), 7.76 (s, 3H), 7.58 (dd, J = 8, 1.92 Hz, 3H), 2.81 (t, J = 8 Hz, 6H), 1.78 (m, J = 8 Hz, 6H) 1.42 (m, J = 4Hz, 12H) 0.96 (m, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*D*) δ 147.85, 147.52, 141.26, 133.11, 132.36, 128.99, 127.87, 126.93, 124.89, 36.06, 31.68, 30.81, 22.72, 14.22. **HRMS**: m/z : $[M+H]^+$ calculated for $\text{C}_{42}\text{H}_{45}\text{N}_3$ 592.3692; Found 592.3691.

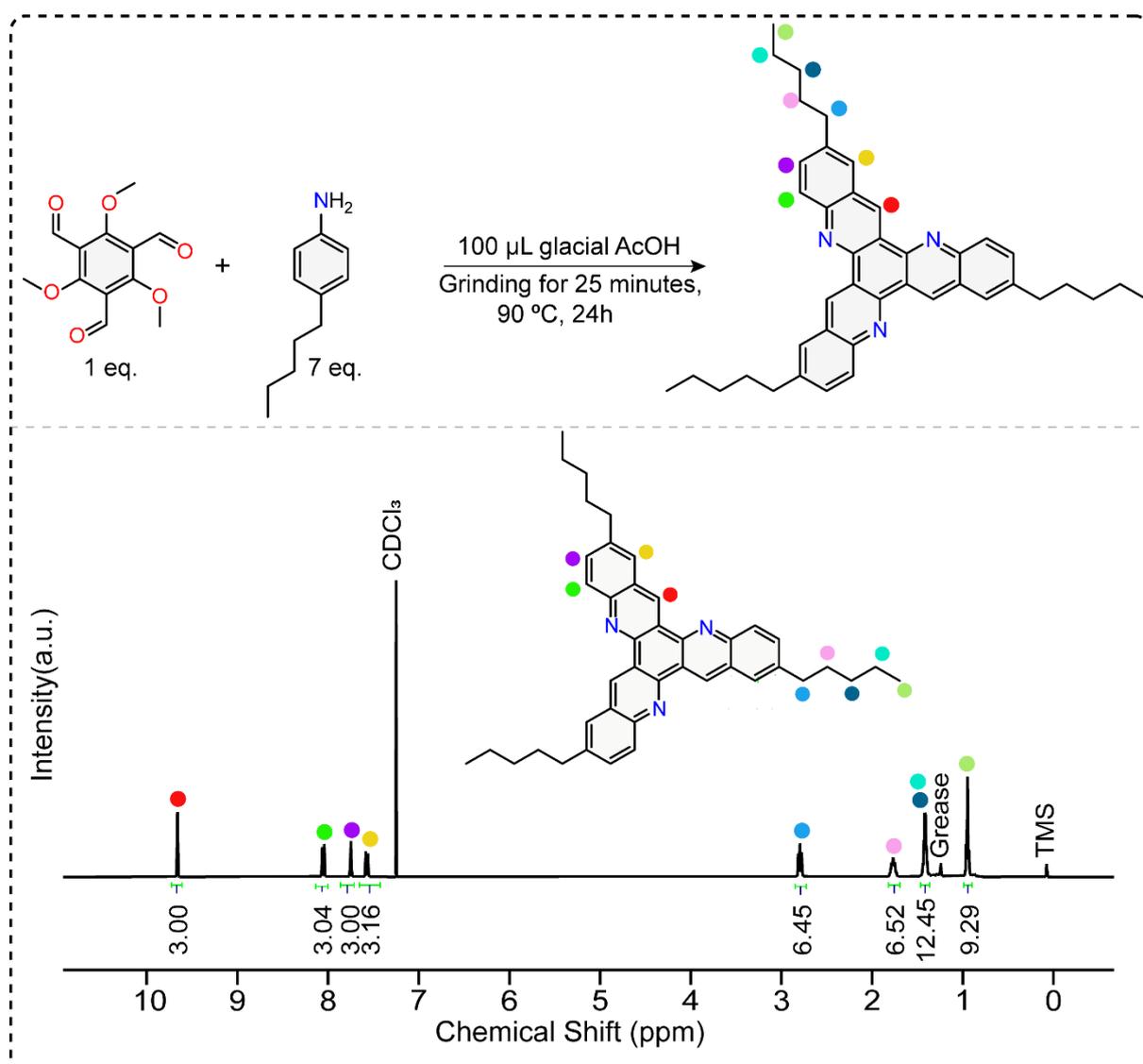


Fig. S22 $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.67 (s, 3H) 8.06 (d, J = 8.06 Hz, 1H), 7.76 (s, 3H), 7.58 (dd, J = 8, 1.92 Hz, 3H), 2.81 (t, J = 8 Hz, 6H), 1.78 (m, J = 8 Hz, 6H) 1.42 (m, J = 4Hz, 12H) 0.96 (m, 9H).

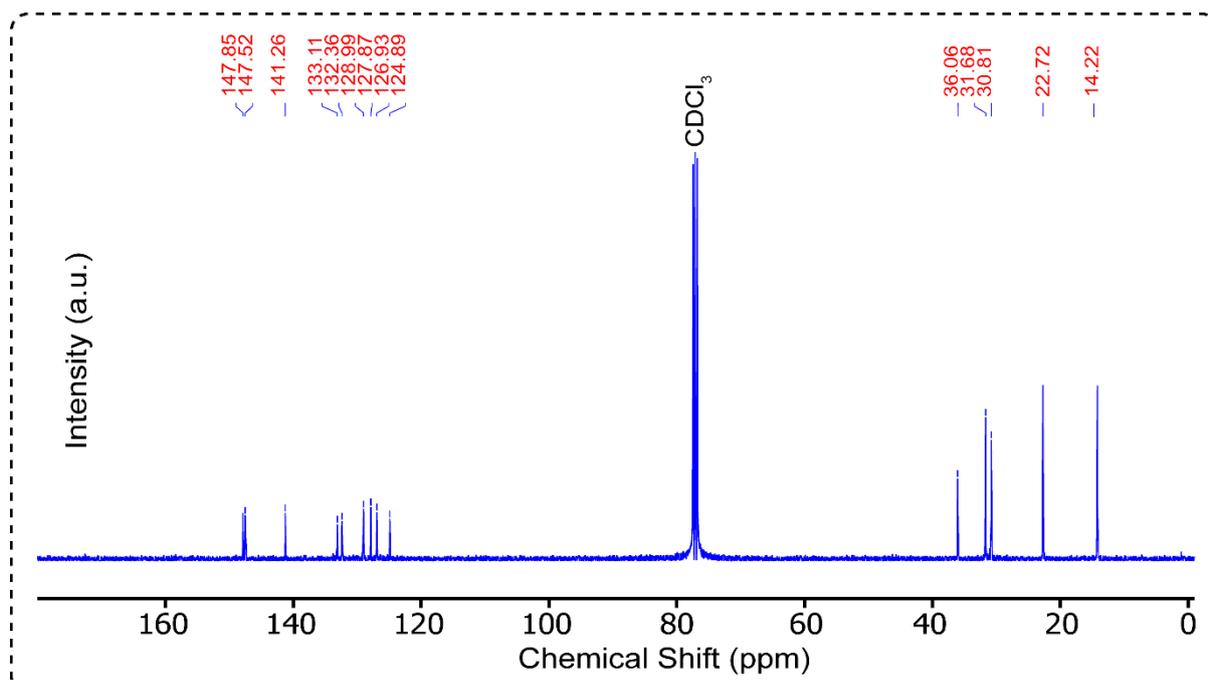


Fig. S23 ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.85, 147.52, 141.26, 133.11, 132.36, 128.99, 127.87, 126.93, 124.89, 36.06, 31.68, 30.81, 22.72, 14.22.

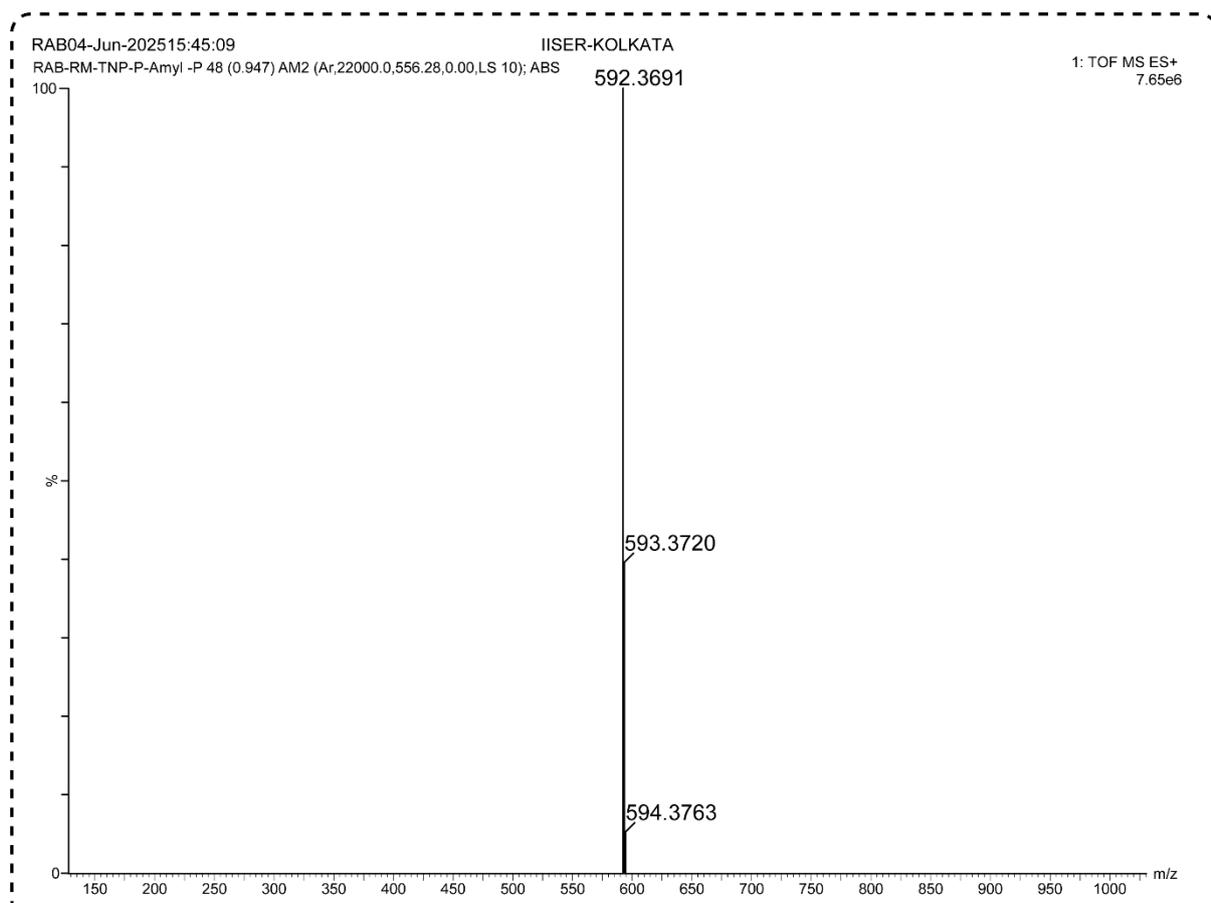


Fig. S24 High-resolution mass spectra of TNP-*p*-Amyl. *m/z*: [M+H]⁺ calculated for C₄₂H₄₅N₃ 592.3692; Found 592.3691.

TNP-*p*-butyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-butylaniline (110.45 μL , 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μL) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.81 (s, 3H) 8.14 (d, $J = 8$ Hz, 3H), 7.84 (d, $J = 4$ Hz, 3H), 7.64 (dd, $J = 8$ Hz, 2 Hz, 3H), 2.85 (t, $J = 8$ Hz, 6H), 1.77 (m, $J = 4$ Hz, 6H) 1.46 (m, $J = 4$ Hz, 6H), 1.00 (t, $J = 8$ Hz). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.01, 147.63, 141.31, 133.16, 132.44, 129.06, 127.00, 125.03, 35.80, 33.30, 22.51, 14.1. HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{40}\text{N}_3$ 550.3222; Found 550.3224.

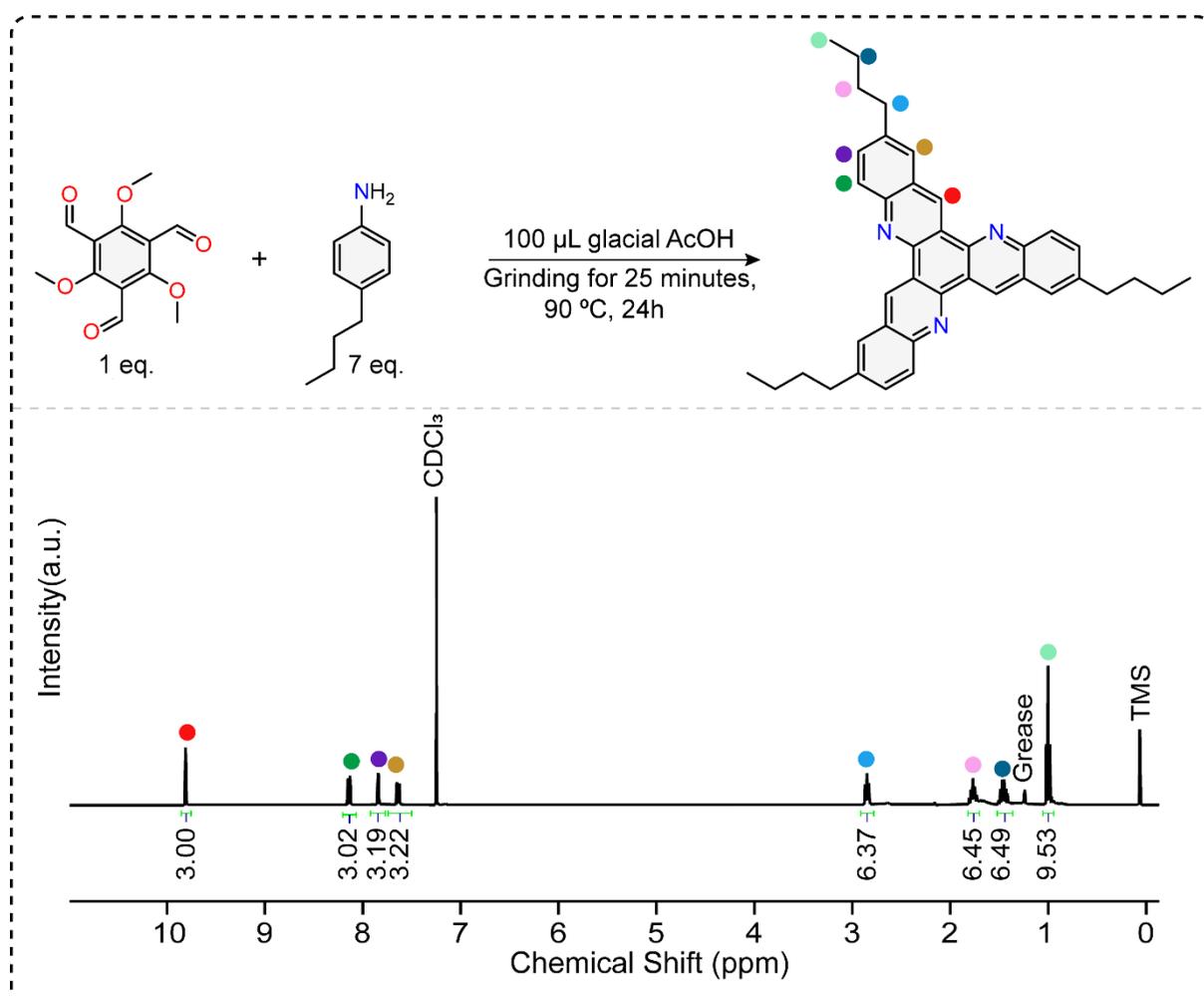


Fig. S25 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.81 (s, 3H) 8.14 (d, $J = 8$ Hz, 3H), 7.84 (d, $J = 4$ Hz, 3H), 7.64 (dd, $J = 8$ Hz, 2 Hz, 3H), 2.85 (t, $J = 8$ Hz, 6H), 1.77 (m, $J = 4$ Hz, 6H) 1.46 (m, $J = 4$ Hz, 6H), 1.00 (t, $J = 8$ Hz).

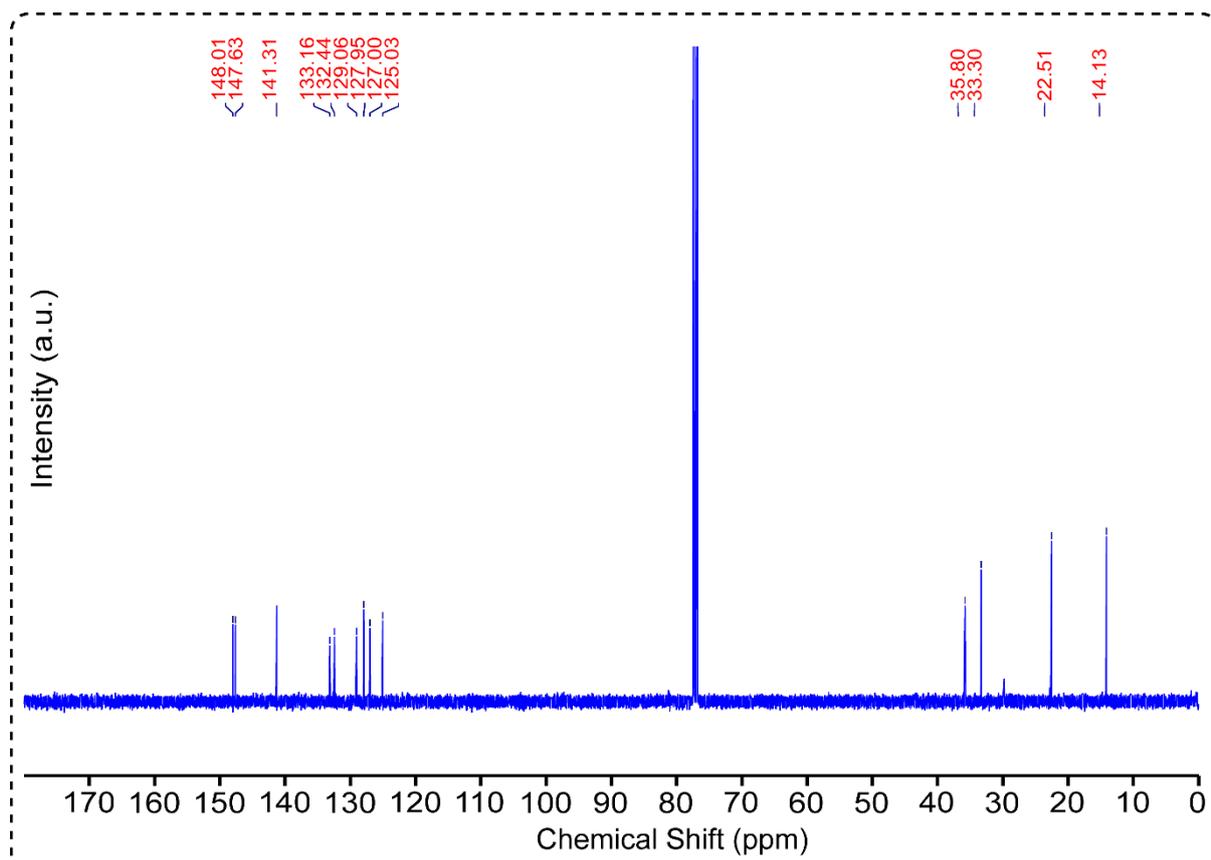


Fig. S26 ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.01, 147.63, 141.31, 133.16, 132.44, 129.06, 127.00, 125.03, 35.80, 33.30, 22.51, 14.13

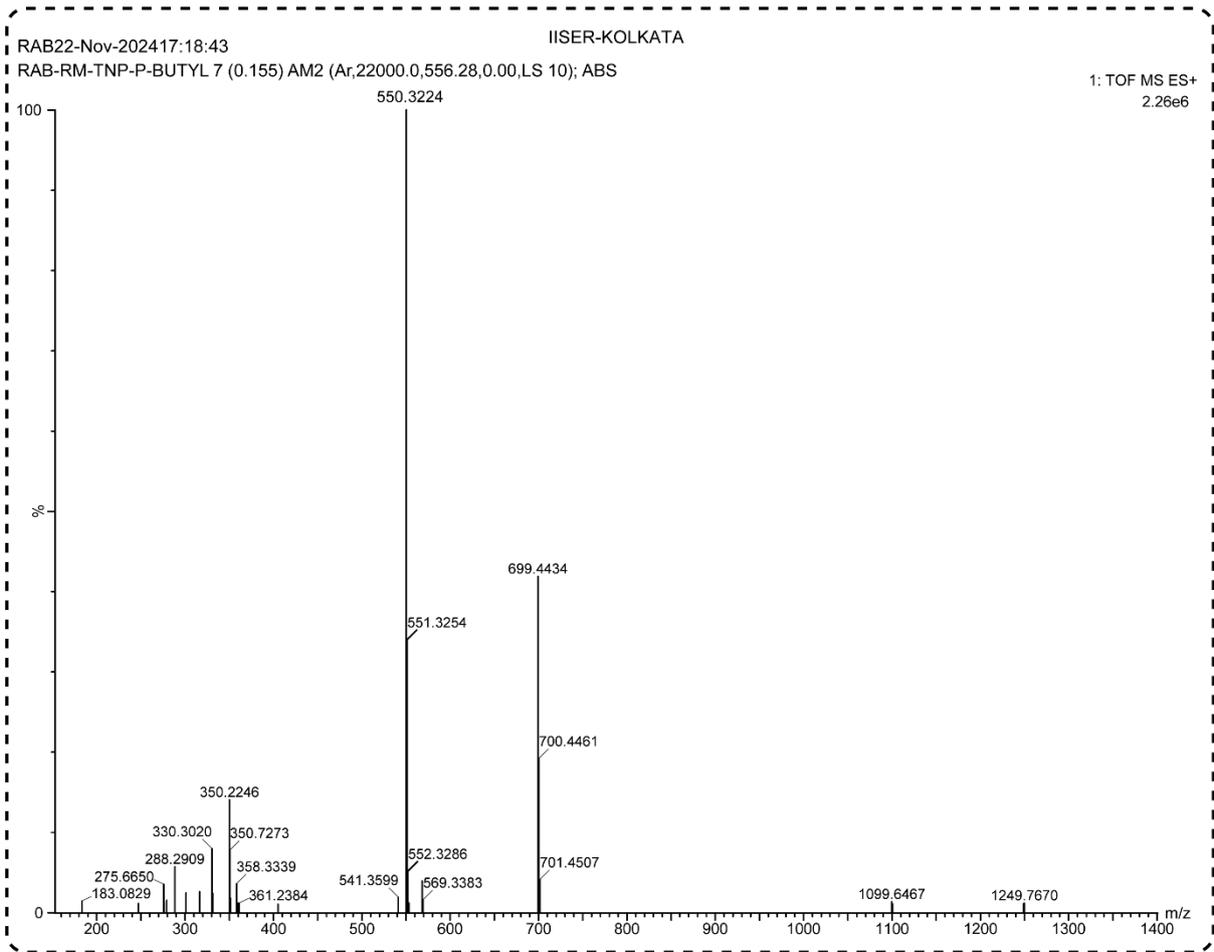


Fig. S27 High-resolution mass spectra of TNP-*p*-Butyl. m/z : $[M+H]^+$ calculated for $C_{39}H_{40}N_3$ 550.3222; Found 550.3224.

TNP-*p*-propyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-propylaniline (147.01, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.93 (s, 3H) 8.21 (d, $J = 8$ Hz, 3H), 7.91 (d, $J = 2$ Hz, 3H), 7.68 (dd, $J = 8$ Hz, 2 Hz, 3H), 2.86 (t, $J = 8$ Hz, 6H), 1.83 (m, $J = 8$ Hz, 6H) 1.04 (t, $J = 8$ Hz, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.17, 147.78, 141.22, 133.32, 132.57, 129.12, 127.92, 127.18, 125.19, 38.19, 24.29, 13.95. **HRMS**: m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{33}\text{N}_3$ 508.2753; Found 550.2702.

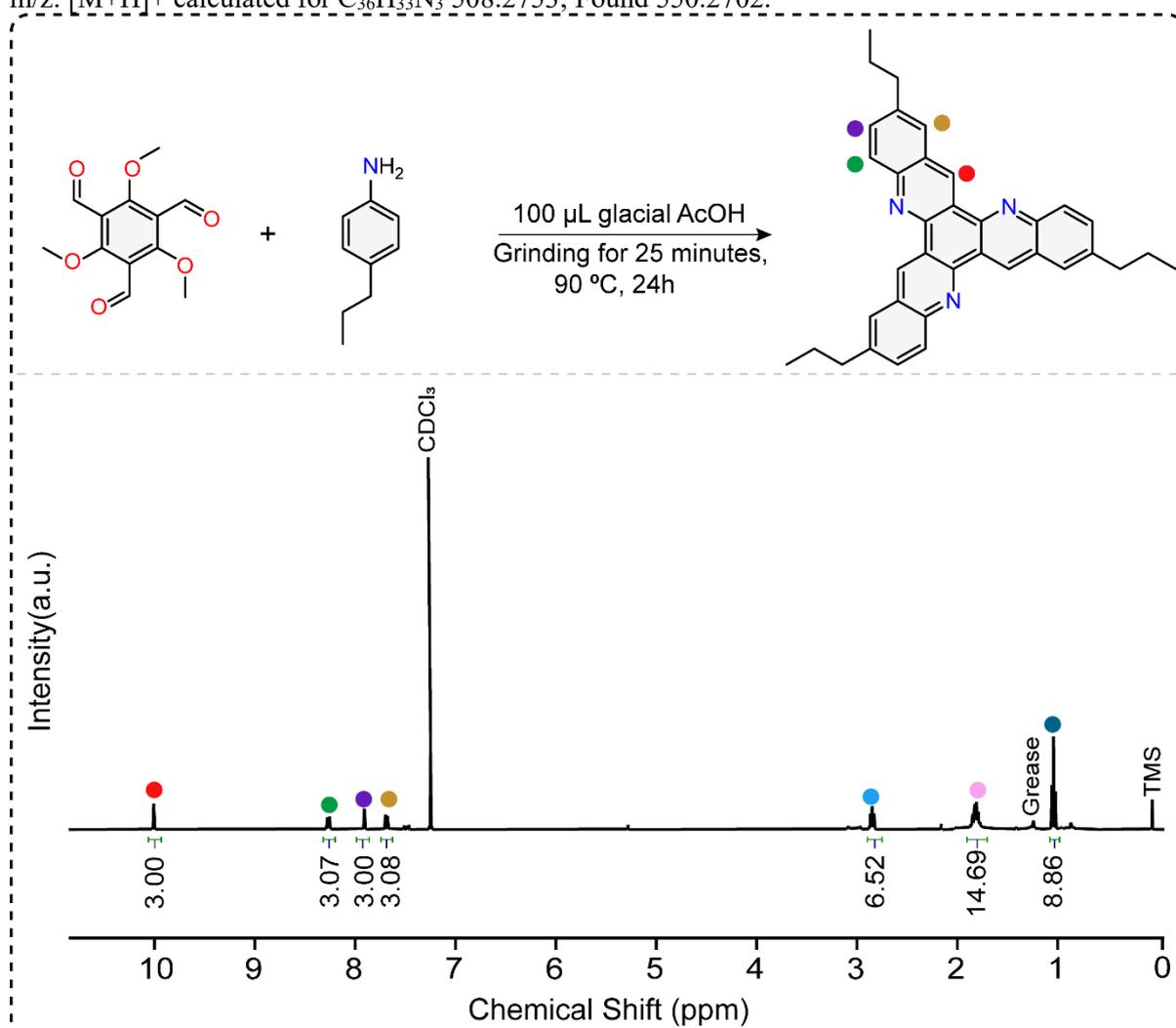


Fig. S28 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.93 (s, 3H) 8.21 (d, $J = 8$ Hz, 3H), 7.91 (d, $J = 2$ Hz, 3H), 7.68 (dd, $J = 8$ Hz, 2 Hz, 3H), 2.86 (t, $J = 8$ Hz, 6H), 1.83 (m, $J = 8$ Hz, 6H) 1.04 (t, $J = 8$ Hz, 9H).

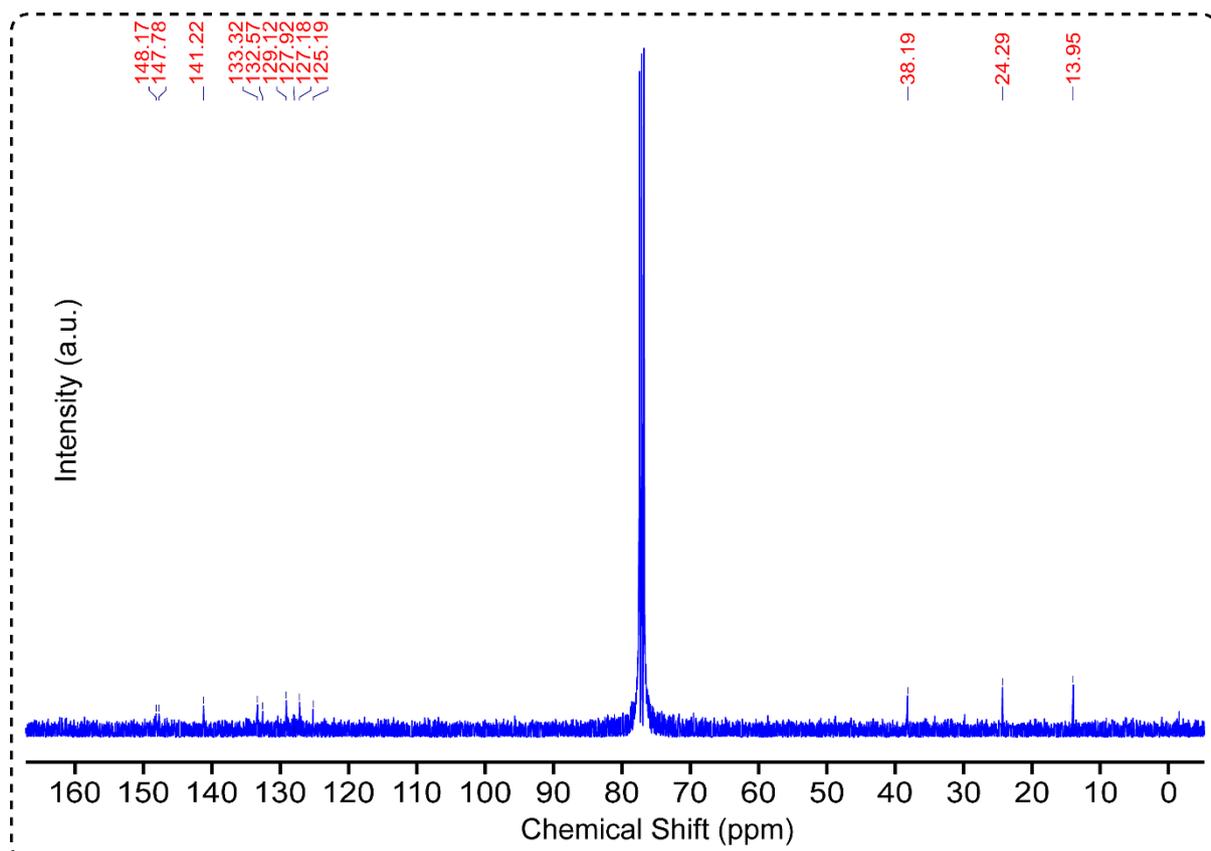


Fig. S29 ¹³C NMR (101 MHz, Chloroform-d) δ 148.17, 147.78, 141.22, 133.32, 132.57, 129.12, 127.92, 127.18, 125.19, 38.19, 24.29, 13.95.

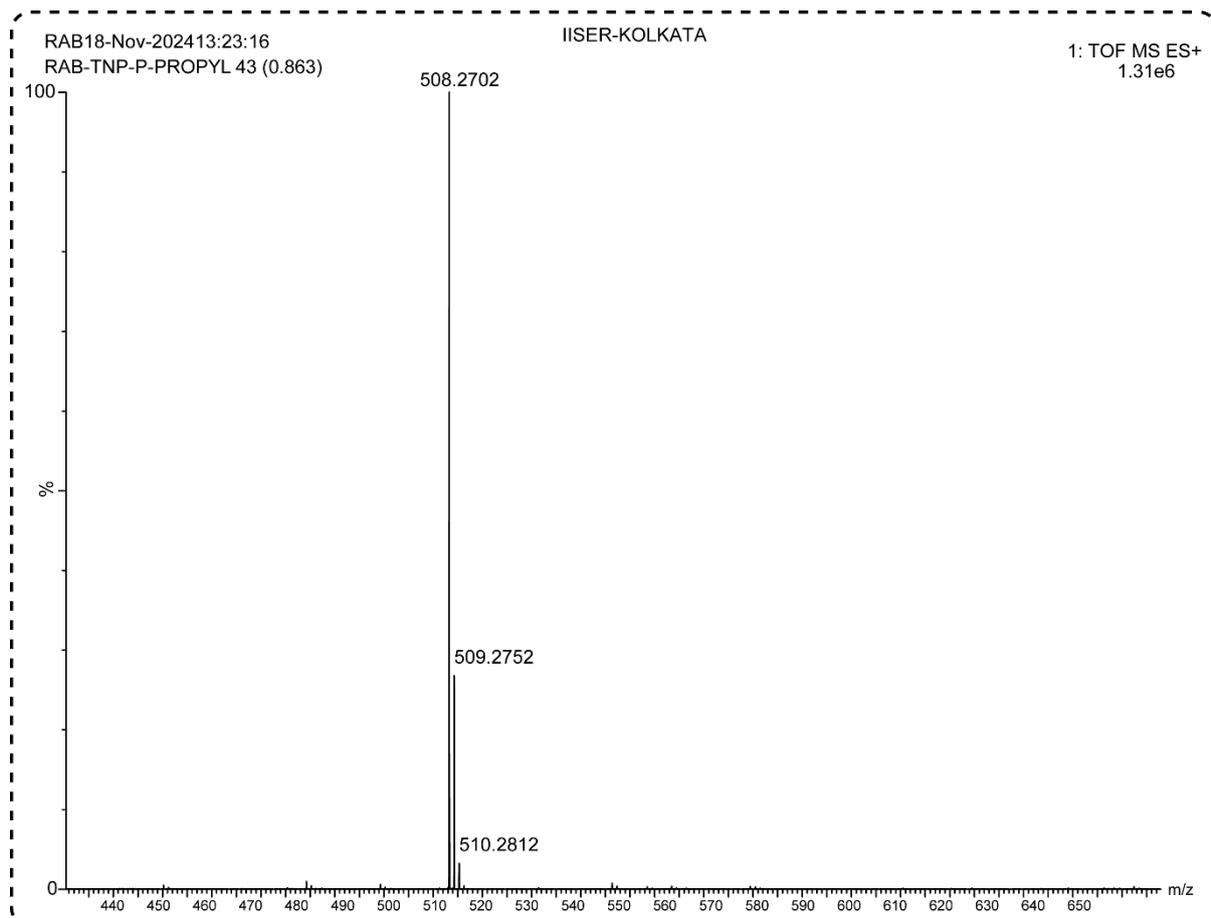


Fig. S30 High-resolution mass spectra of TNP-*p*-propyl. m/z : $[M+H]^+$ calculated for $C_{36}H_{33}N_3$ 508.2753; Found 508.2702.

TNP-*p*-Ethyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-ethylaniline (87 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.05 (s, 3H) 8.28 (d, J = 12 Hz, 3H), 7.97 (d, J = 2 Hz, 3H), 7.73 (dd, J = 4 Hz, 3H), 2.94 (q, J = 8 Hz, 6H), 1.42 (t, J = 8 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) 148.02, 147.77, 142.75, 133.35, 132.40, 129.16, 127.26, 126.28, 125.18, 29.07, 15.29. HRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{27}\text{N}_3$ 466.2239; Found 466.2283

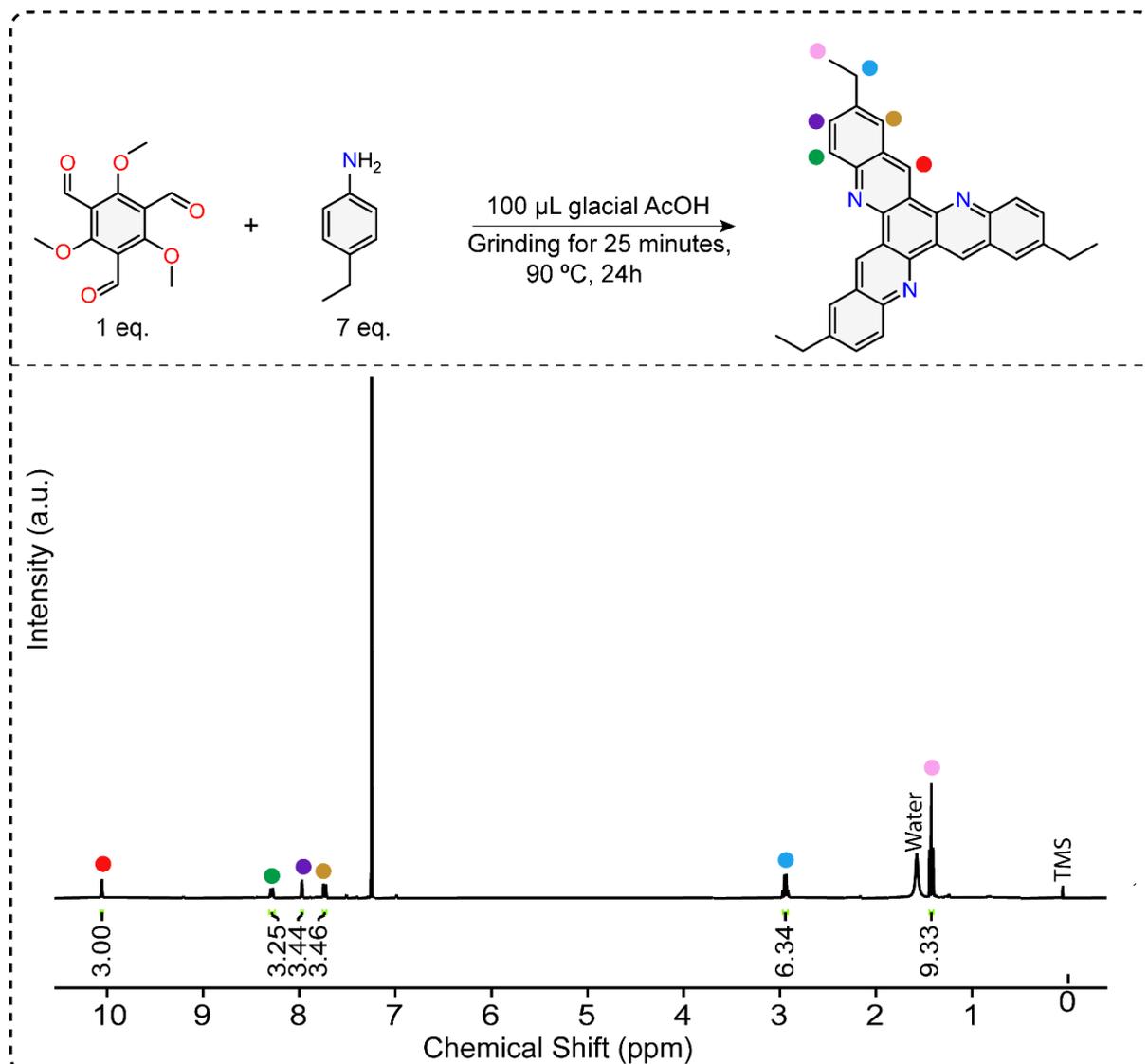


Fig. S31 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.05 (s, 3H) 8.28 (d, J = 12 Hz, 3H), 7.97 (d, J = 2 Hz, 3H), 7.73 (dd, J = 4 Hz, 3H), 2.94 (q, J = 8 Hz, 6H), 1.42 (t, J = 8 Hz, 6H).

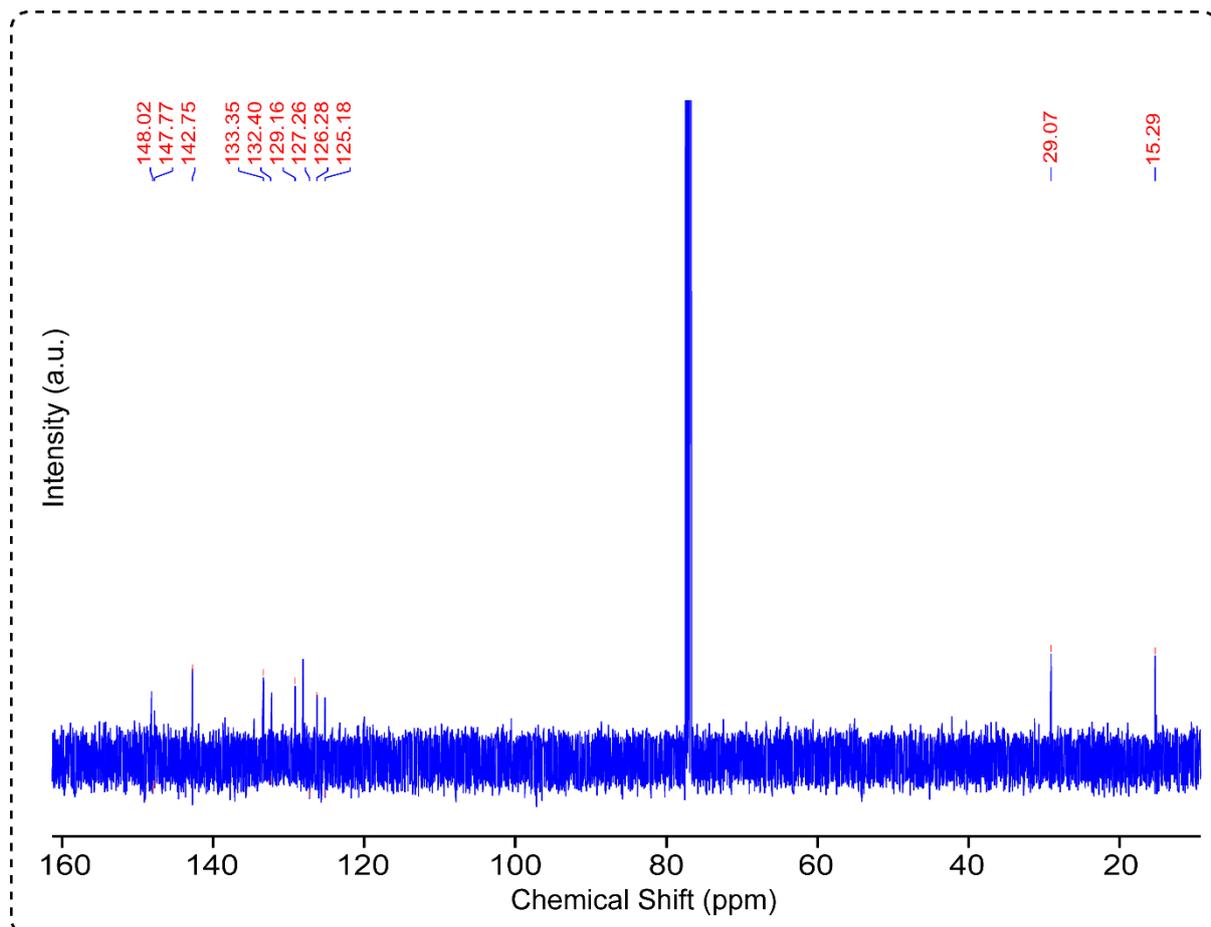


Fig. S32 ¹³C NMR (101 MHz, Chloroform-*d*) 148.02, 147.77, 142.75, 133.35, 132.40, 129.16, 127.26, 126.28, 125.18, 29.07, 15.29.

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RAB-RM-TNP-P-ET 4 (0.104)

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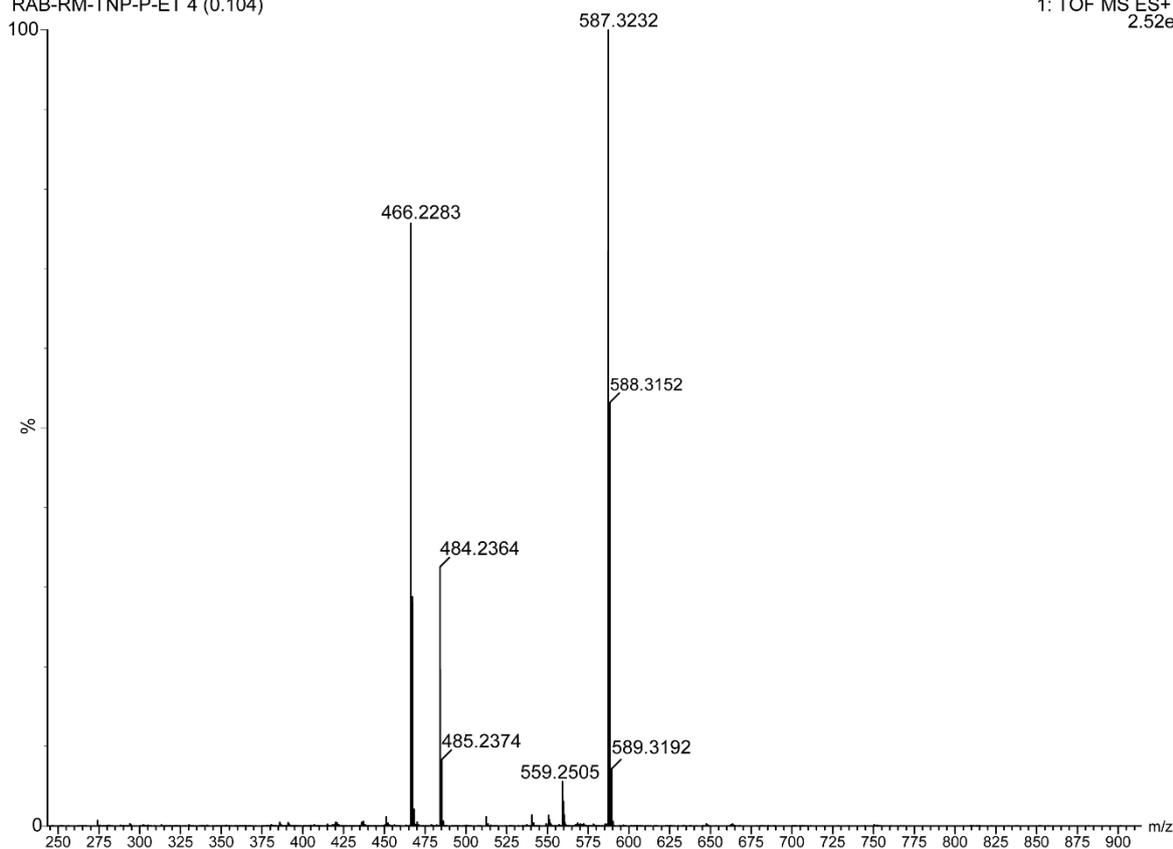


Fig. S33 High-resolution mass spectra of TNP-*p*-Et. m/z: [M+H]⁺ calculated for C₃₃H₂₇N₃ 466.2283; Found 466.2283

TNP-*p*-methyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-methylaniline (75 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by continuous washing with acetone. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.98 (s, 3H) 8.25 (d, J = 8 Hz, 3H), 7.97 (d, J = 2 Hz, 3H), 7.73 (dd, J = 4 Hz, 3H), 2.94 (q, J = 8 Hz, 6H), 1.42 (t, J = 8 Hz, 6H). **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{21}\text{N}_3$ 424.1814; Found 424.1841

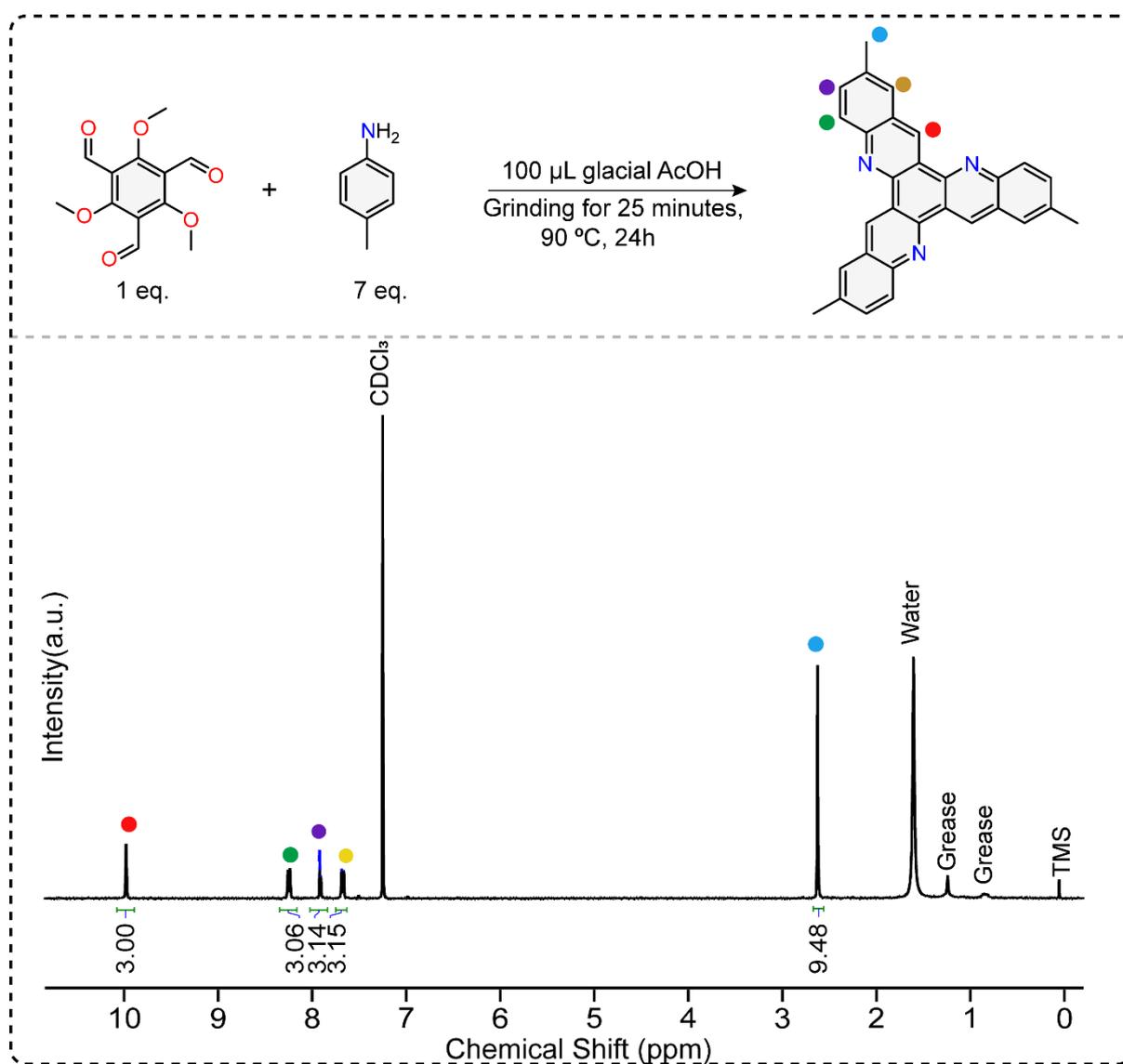


Fig. S34 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.98 (s, 3H) 8.25 (d, J = 8 Hz, 3H), 7.97 (d, J = 2 Hz, 3H), 7.73 (dd, J = 4 Hz, 3H), 2.94 (q, J = 8 Hz, 6H), 1.42 (t, J = 8 Hz, 6H).

As the TNP-Me compound is not soluble enough in any deuterated solvent (CDCl_3 , $\text{DMSO-}d_6$, $\text{DMF-}d_7$, $\text{THF-}d_8$, CD_2Cl_2), $^{13}\text{C NMR}$ has not been provided.

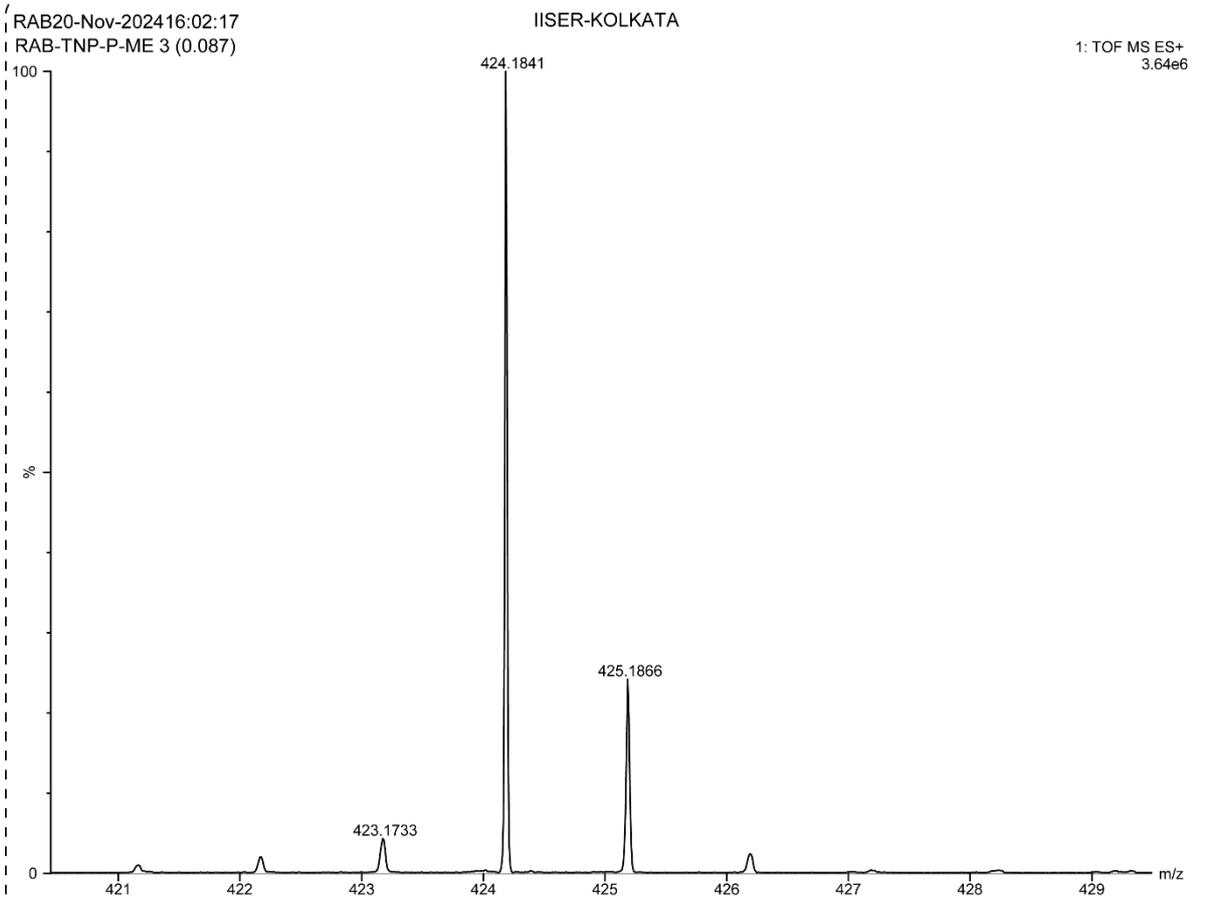


Fig. S35 High-resolution mass spectra of TNP-*p*-Me. m/z : $[M+H]^+$ calculated for $C_{30}H_{21}N_3$ 424.1814; Found 424.1841

TNP-*p*-tBu

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-tertbutylaniline (112 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.85 (s, 3H) 8.19 (d, J = 8 Hz, 3H), 8.05 (d, J = 4Hz, 3H), 7.95 (dd, J = 8 Hz, 2.2Hz, 3H), 2.94 (q, J = 8 Hz, 6H), 1.42 (t, J = 8 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) 149.34, 148.11, 147.36, 133.80, 129.92, 128.81, 127.66, 124.93, 123.91, 35.18, 31.34. HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{39}\text{N}_3$ 550.3222; Found 550.3234.

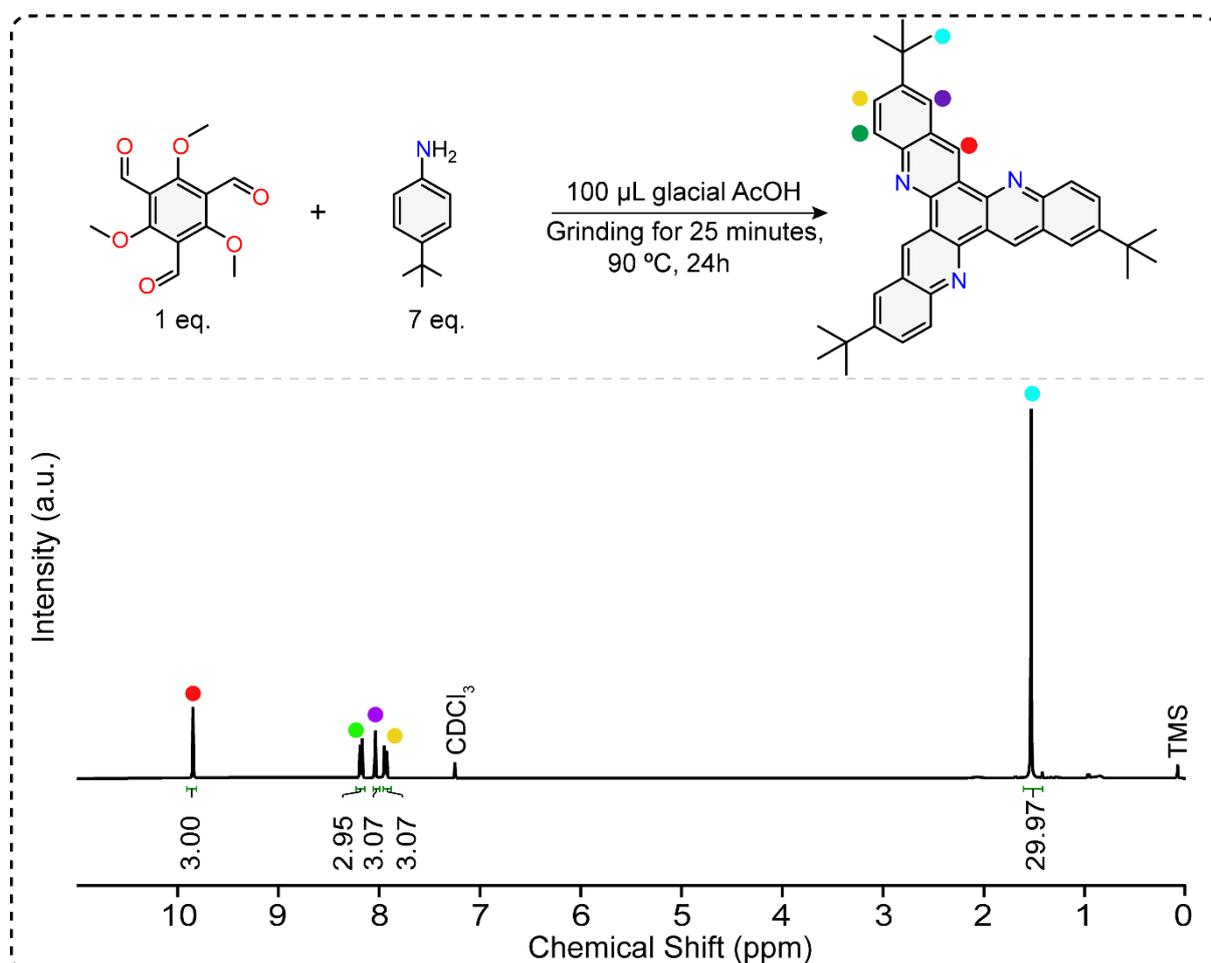


Fig. S36 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.85 (s, 3H) 8.19 (d, J = 8 Hz, 3H), 8.05 (d, J = 4Hz, 3H), 7.95 (dd, J = 8 Hz, 2.2Hz, 3H), 2.94 (q, J = 8 Hz, 6H), 1.42 (t, J = 8 Hz, 6H).

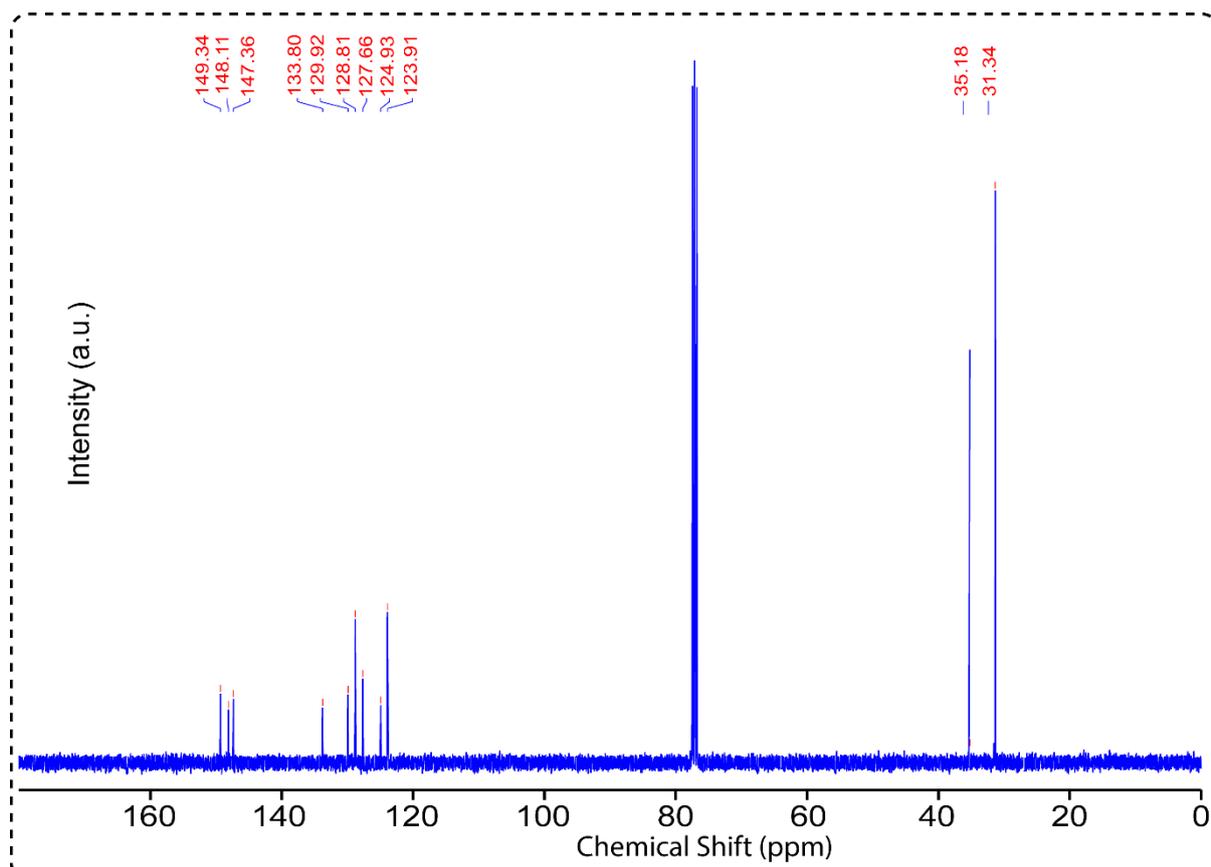


Fig. S37 ^{13}C NMR (101 MHz, Chloroform-*d*) 149.34, 148.11, 147.36, 133.80, 129.92, 128.81, 127.66, 124.93, 123.91, 35.18, 31.34.

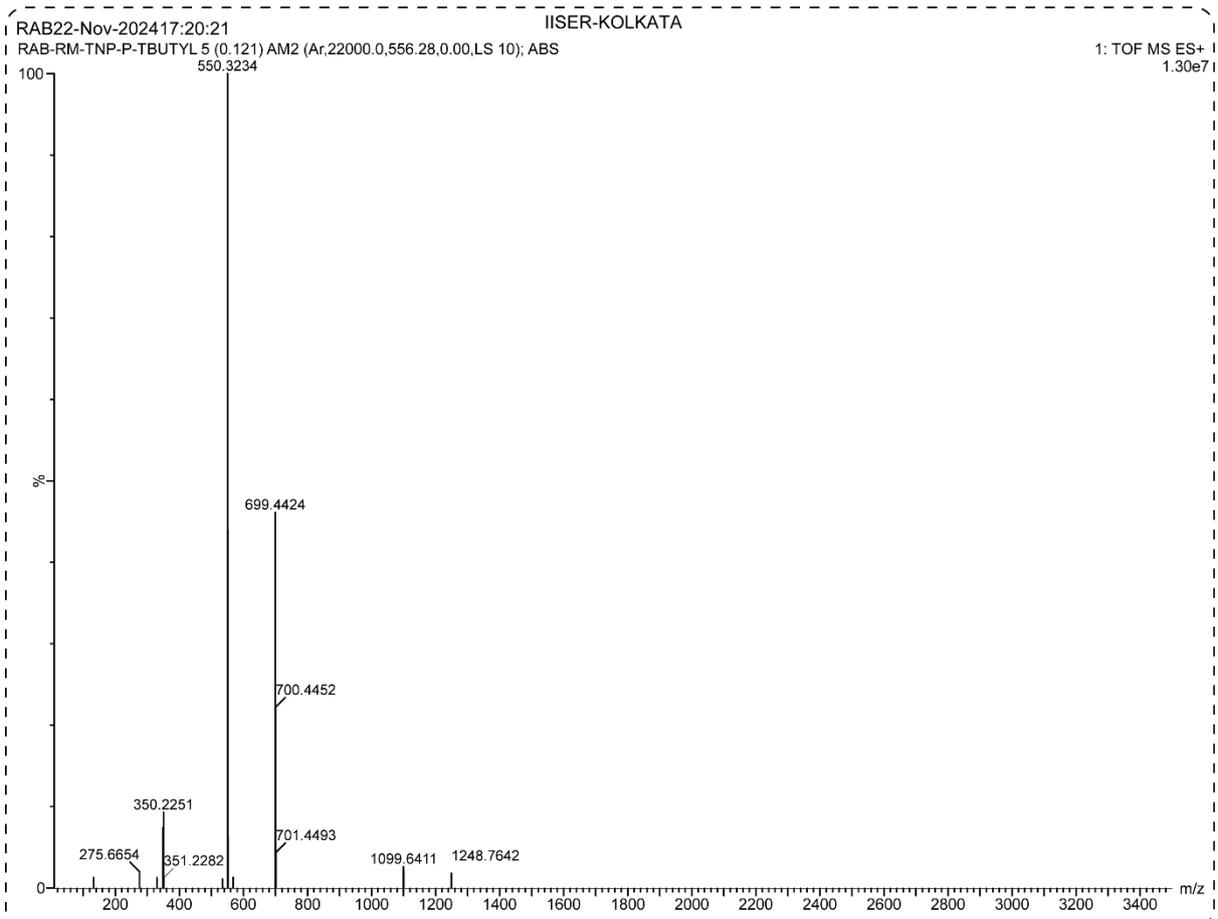


Fig. S38 High-resolution mass spectra of TNP-*p*-tBu. m/z: [M+H]⁺ calculated for C₃₉H₃₉N₃ 550.3222; Found 550.3234.

TNP-*p*-iPr

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-isopropylaniline (96 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. : $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.97 (s, 3H) 8.24 (d, J = 8 Hz, 3H), 7.97 (d, J = 2Hz, 3H), 7.77 (dd, J = 8 Hz, 2 Hz, 3H), 3.20 (hept, J = 6.83 Hz, 6H), 1.42 (t, J = 6.97 Hz, 6H) $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.14, 147.83, 147.15, 133.44, 130.94, 129.20, 128.01, 125.10, 124.87, 34.26, 23.94. **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{33}\text{N}_3$ 508.2753; Found 508.2747. **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{34}\text{N}_3$ 508.2753; Found 508.2747.

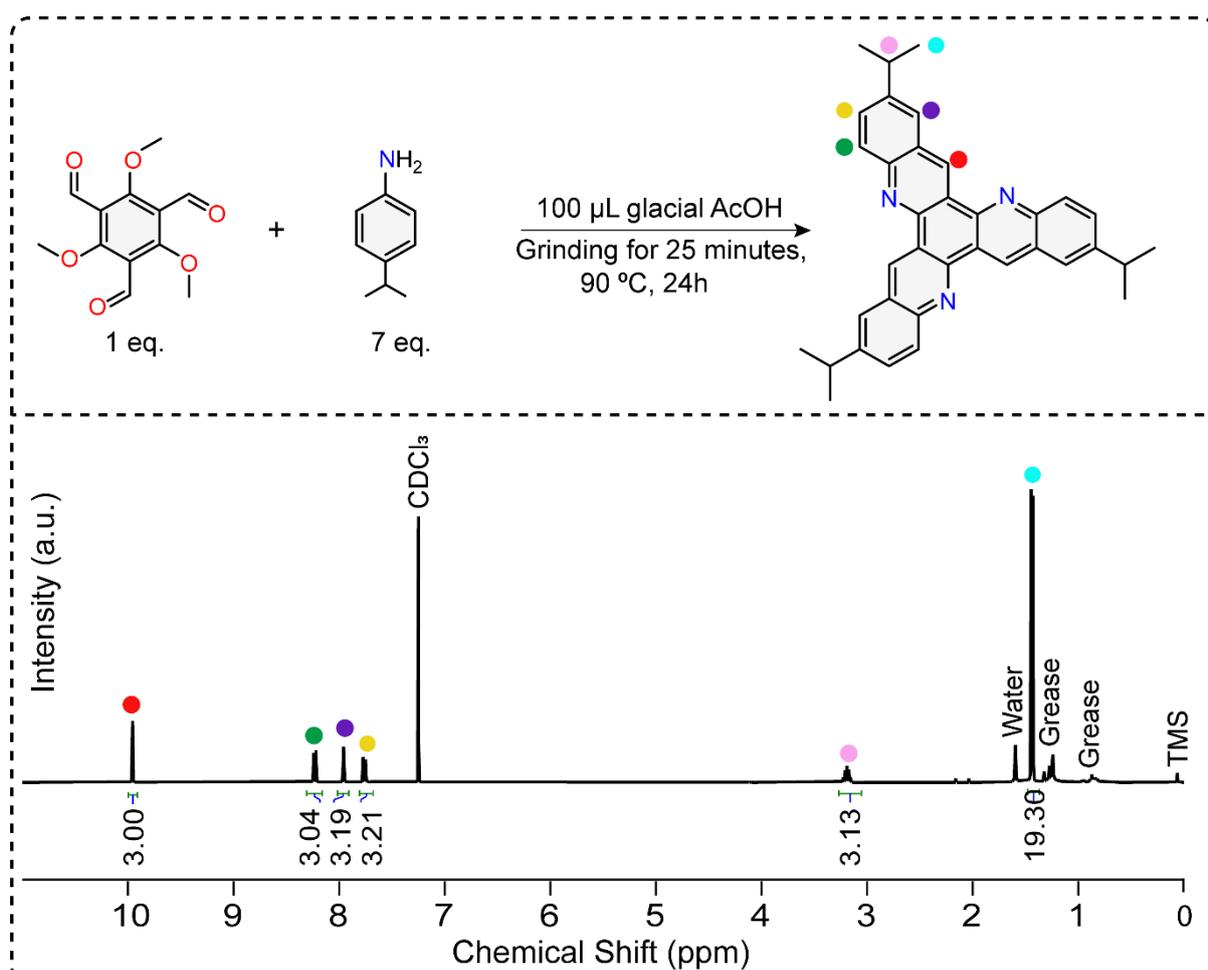


Fig. S39 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.97 (s, 3H) 8.24 (d, J = 8 Hz, 3H), 7.97 (d, J = 2Hz, 3H), 7.77 (dd, J = 8 Hz, 2 Hz, 3H), 3.20 (hept, J = 6.83 Hz, 6H), 1.42 (t, J = 6.97 Hz, 6H).

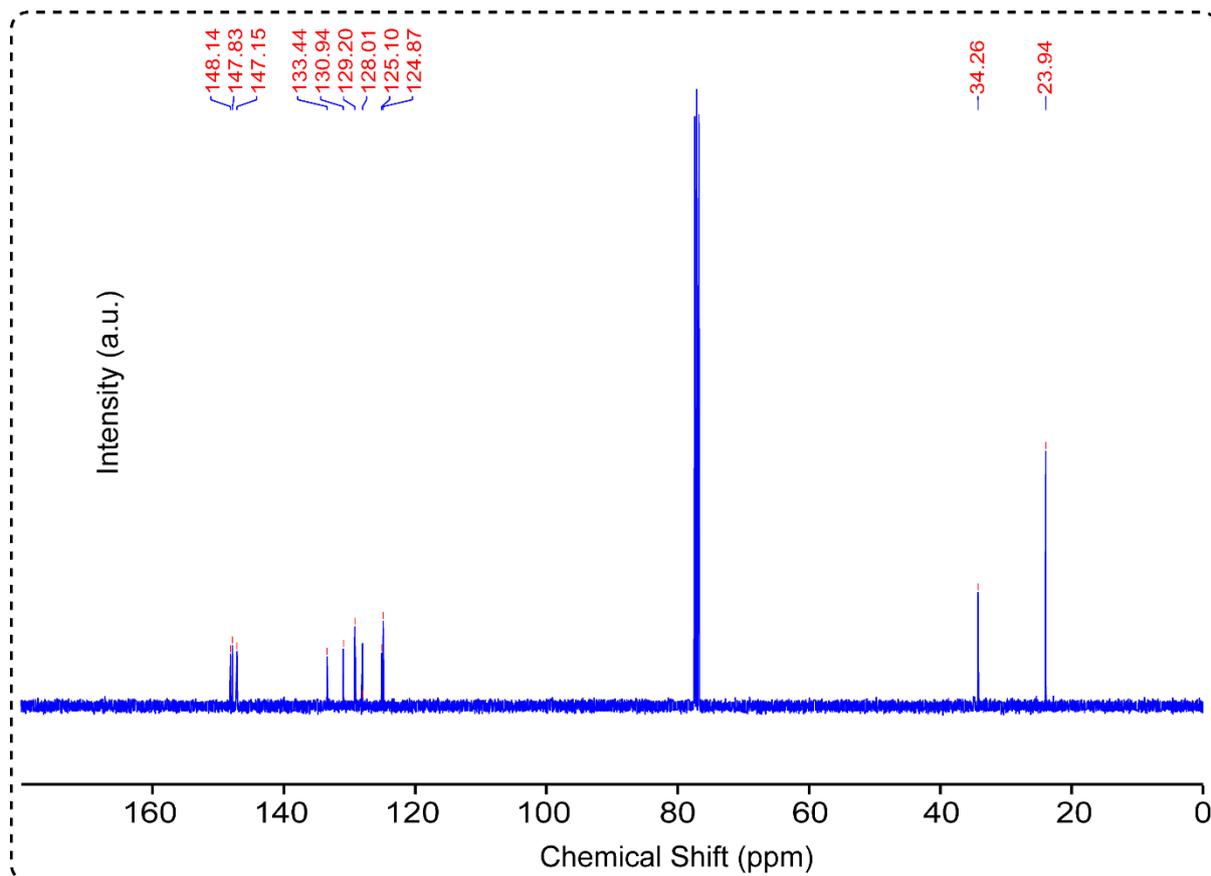


Fig. S40 ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.14, 147.83, 147.15, 133.44, 130.94, 129.20, 128.01, 125.10, 124.87, 34.26, 23.94.

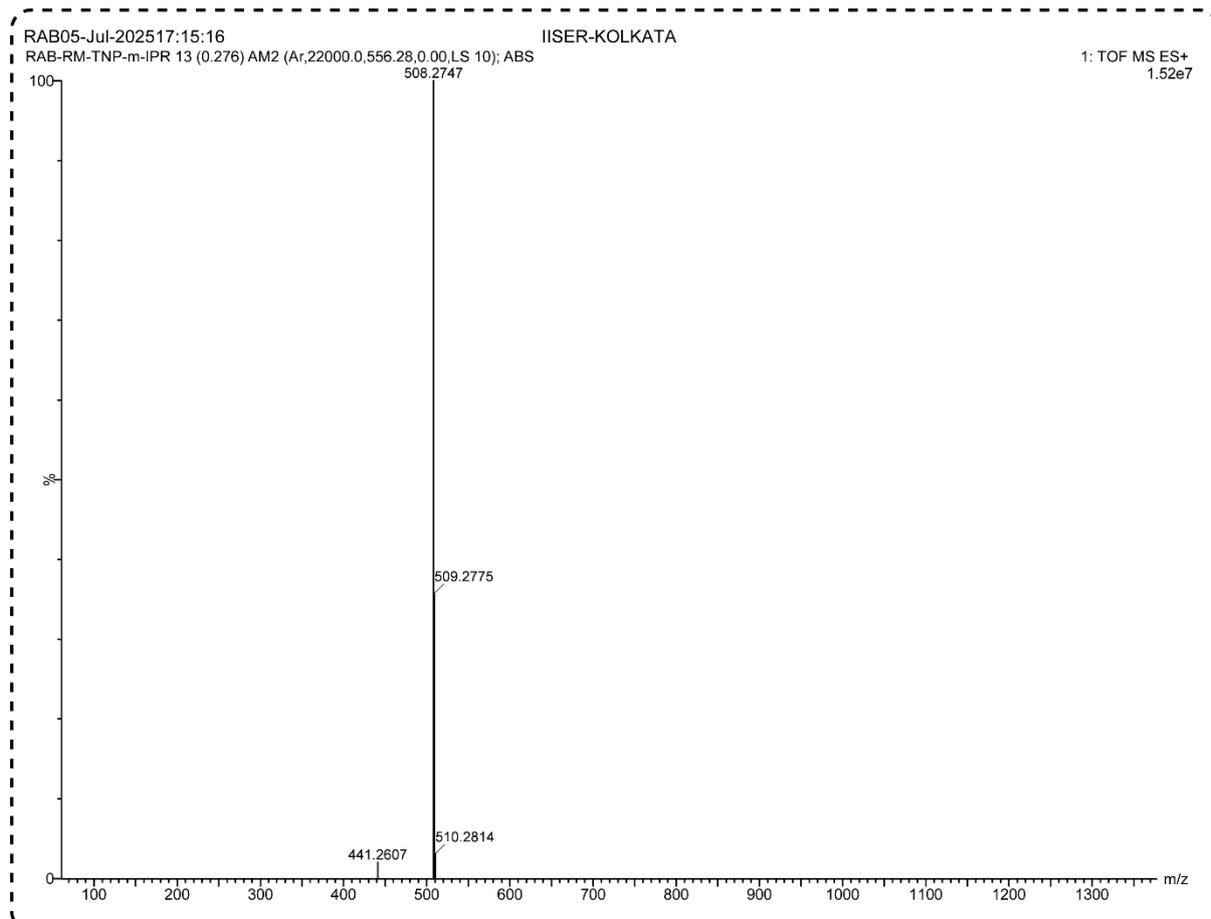


Fig. S41 High-resolution mass spectra of TNP-*p-m-iPr*. m/z: [M+H]⁺ calculated for C₃₆H₃₄N₃ 508.2753; Found 508.2747.

TNP-*p*-Anisidine

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-methoxyaniline (86.205 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.63 (s, 3H) 8.24 (d, $J = 9.26$ Hz, 3H), 7.33 (dd, $J = 9.2$ Hz, 2.7 Hz, 3H), 7.08 (d, $J = 2.6$ Hz, 3H), 3.97 (s, 6H). **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{21}\text{N}_3\text{O}_3$ 472.1661; Found 472.1656.

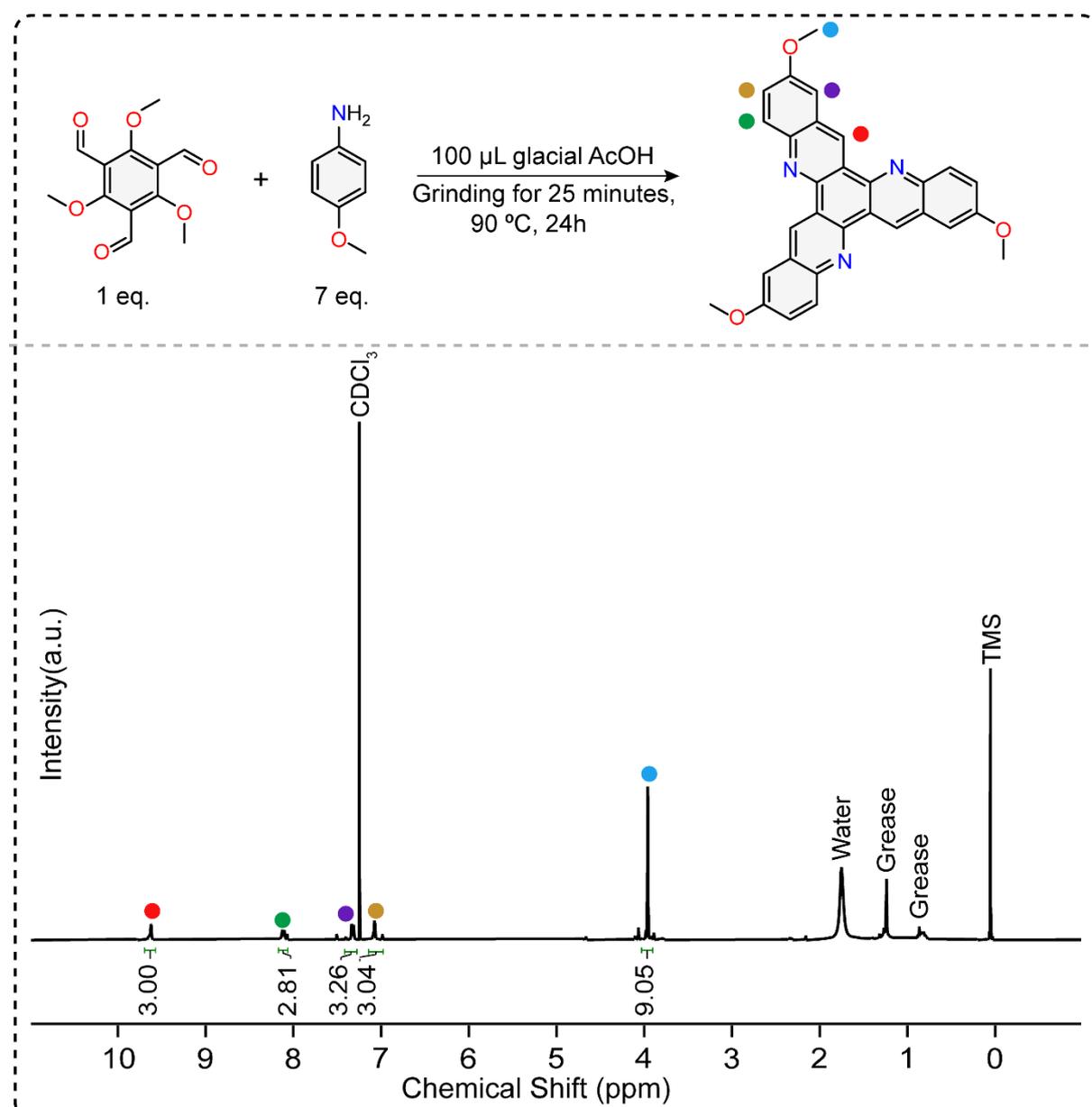


Fig. S42 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.63 (s, 3H) 8.24 (d, $J = 9.26$ Hz, 3H), 7.33 (dd, $J = 9.2$ Hz, 2.7 Hz, 3H), 7.08 (d, $J = 2.6$ Hz, 3H), 3.97 (s, 6H).

As the TNP-*p*-OMe compound is not soluble enough in any deuterated solvent (CDCl_3 , $\text{DMSO-}d_6$, $\text{DMF-}d_7$, $\text{THF-}d_8$, CD_2Cl_2), $^{13}\text{C NMR}$ has not been provided.

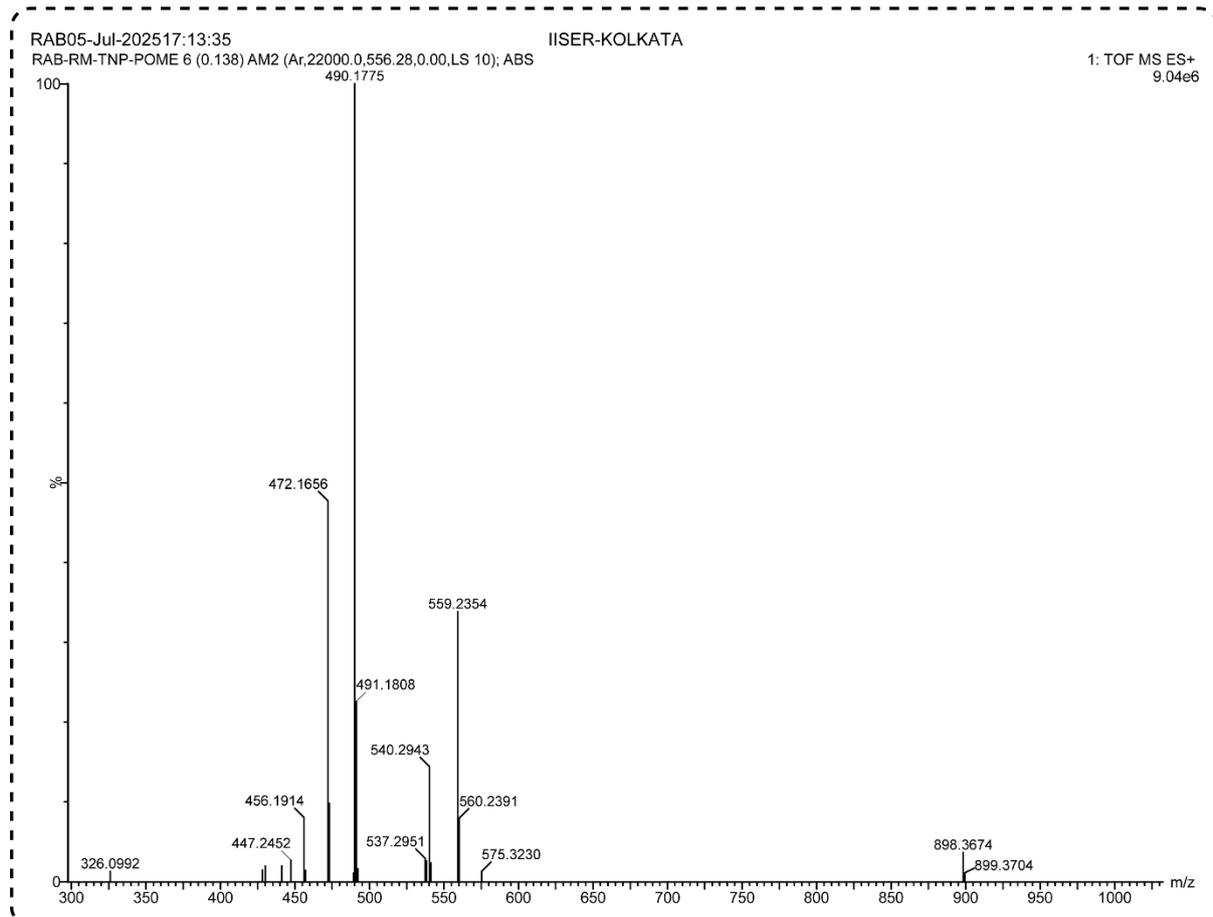


Fig. S43 High-resolution mass spectra of TNP-*p*-OMe. m/z: [M+H]⁺ calculated for C₃₀H₂₁N₃O₃ 472.1661; Found 472.1656.

TNP-*p*-OCF₃

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-trifluoromethoxyaniline (94 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.48 (s, 3H) 7.88 (d, J = 8.9 Hz, 3H), 7.35 (dd, J = 9.2 Hz, 2.7 Hz, 3H), 7.08 (d, J = 2.6 Hz, 3H), 3.97 (s, 6H), 1.42. **HRMS.** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{12}\text{F}_9\text{N}_3\text{O}_3$ 634.0813; Found 634.0768.

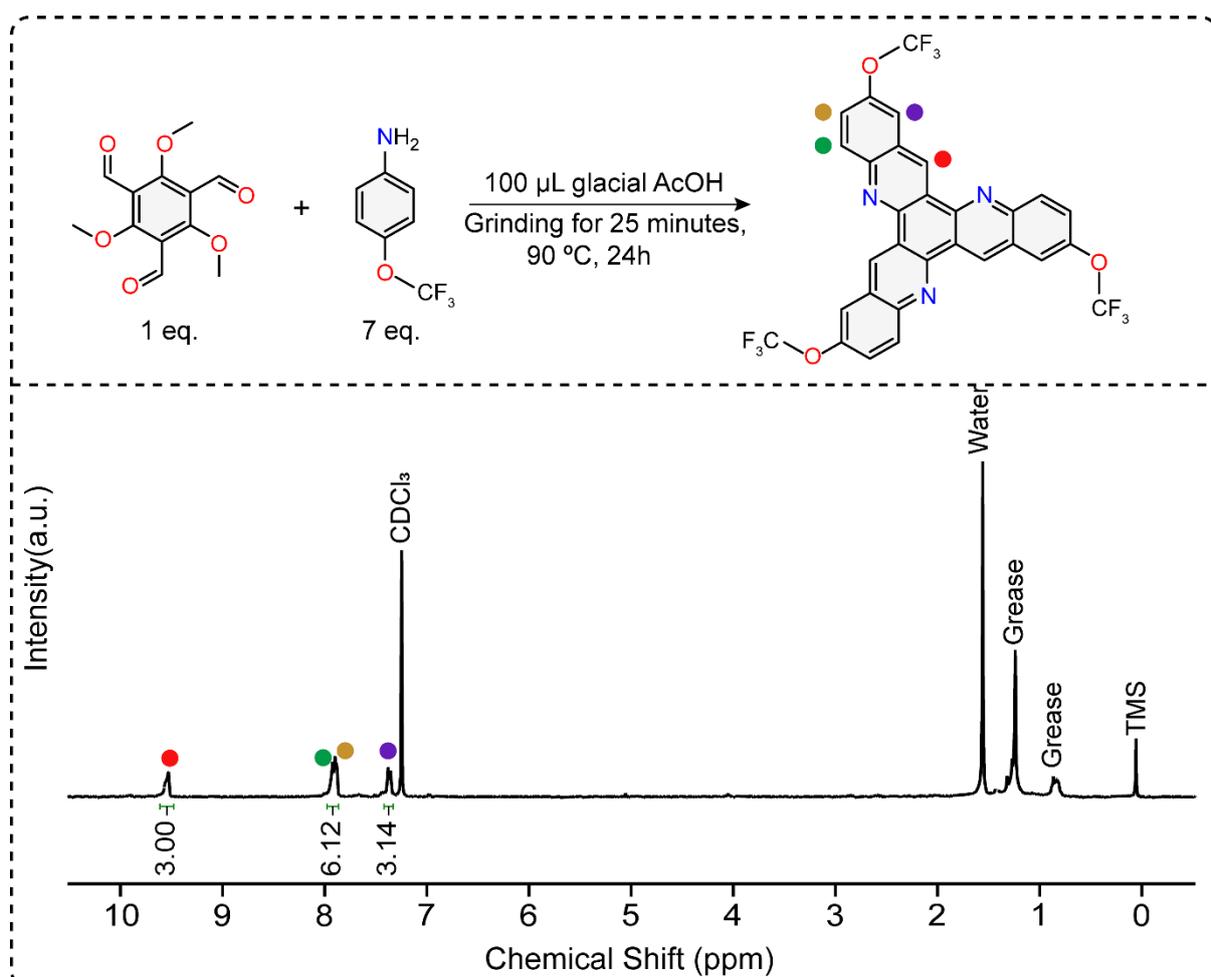


Fig. S44 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.48 (s, 3H) 7.88 (d, J = 8.9 Hz, 3H), 7.35 (dd, J = 9.2 Hz, 2.7 Hz, 3H), 7.08 (d, J = 2.6 Hz, 3H), 3.97 (s, 6H), 1.42.

As the TNP-*p*-OCF₃ compound is not soluble enough in any deuterated solvent (CDCl₃, DMSO-*d*₆, DMF-*d*₇, THF-*d*₈, CD₂Cl₂), $^{13}\text{C NMR}$ has not been provided.

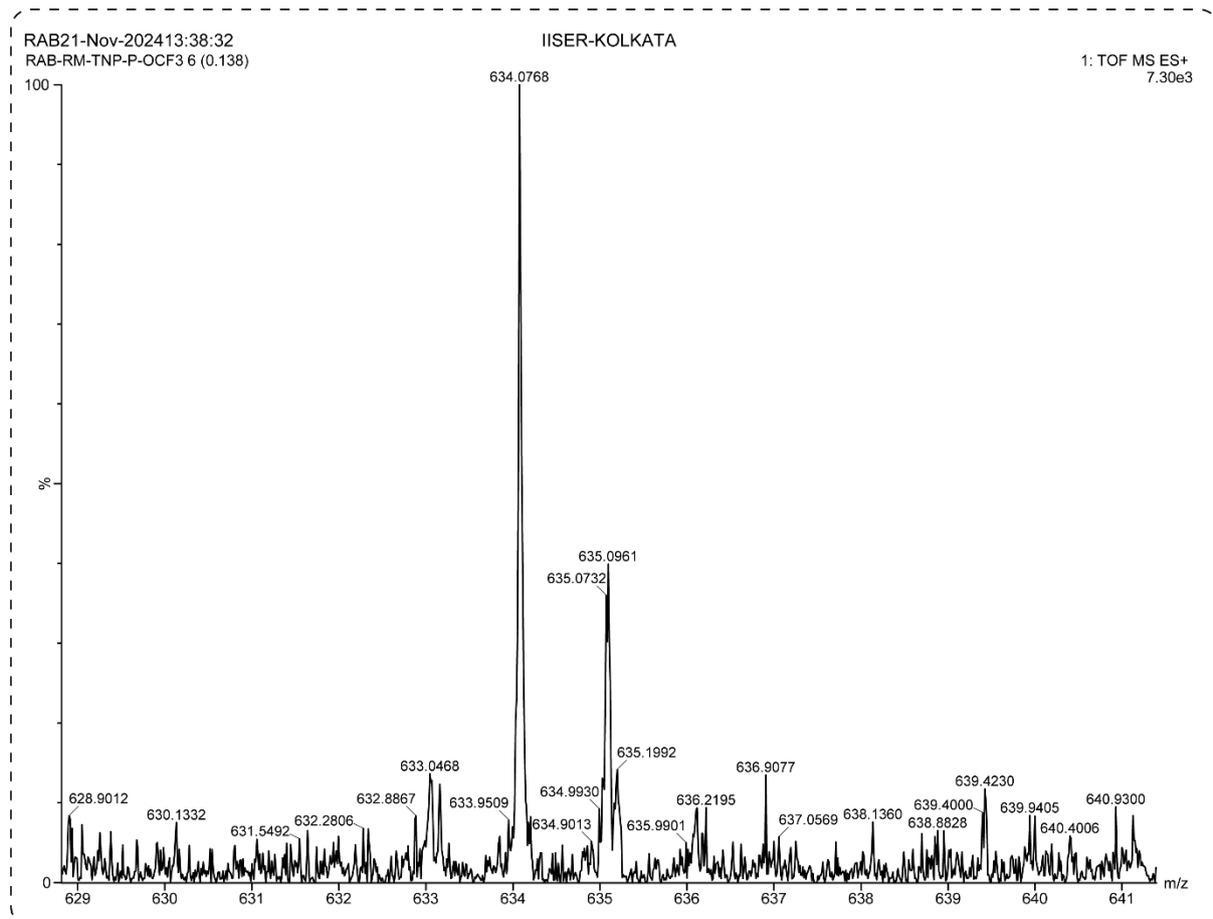


Fig. S45 High-resolution mass spectra of TNP-*p*-OCF₃. m/z: [M+H]⁺ calculated for C₃₀H₁₂F₉N₃O₃ 634.0768; Found 634.0768.

TNP-*p*-CF₃

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-trifluoromethylaniline (88 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 °C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. **HRMS.** m/z : $[M+H]^+$ calculated for C₃₀H₁₂F₉N₃ 586.0966; Found 586.0969.

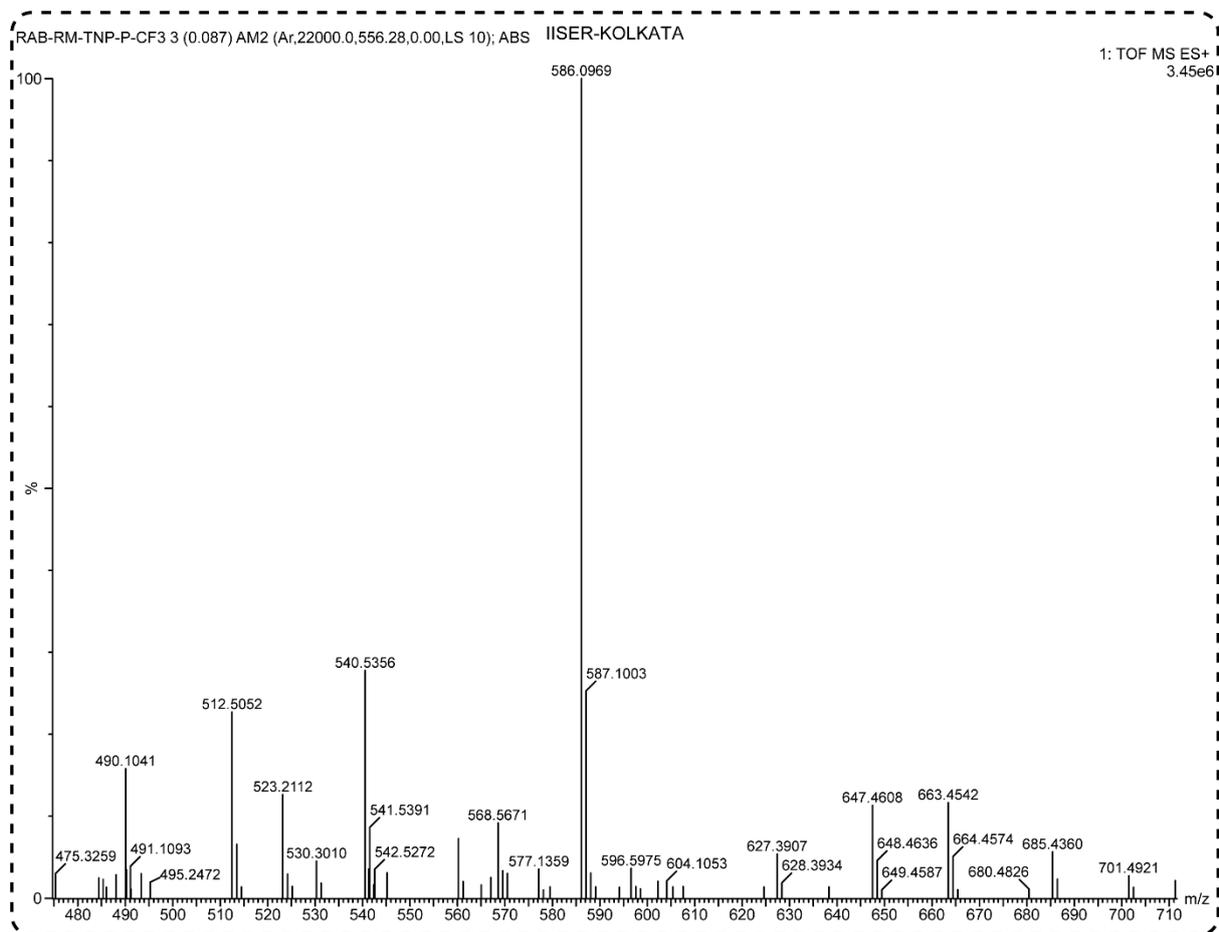


Fig. S46 High-resolution mass spectra of TNP-*p*-CF₃. m/z : $[M+H]^+$ calculated for C₃₀H₁₂F₉N₃ 586.0966; Found 586.0969.

As the TNP-CF₃ compound is not soluble enough in any deuterated solvent (CDCl₃, DMSO-*d*₆, DMF-*d*₇, THF-*d*₈, CD₂Cl₂), ¹H, ¹³C NMR has not been provided.

TNP-*p*-OPh

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-phenoxyaniline (130 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.07 (s, 3H) 8.43 (d, J = 8.9 Hz, 3H), 7.68 (dd, J = 9.2 Hz, 2.7 Hz, 3H), 7.52 (d, J = 2.5 Hz, 3H). **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{45}\text{H}_{27}\text{N}_3\text{O}_3$ 658.2131; Found 658.2131.

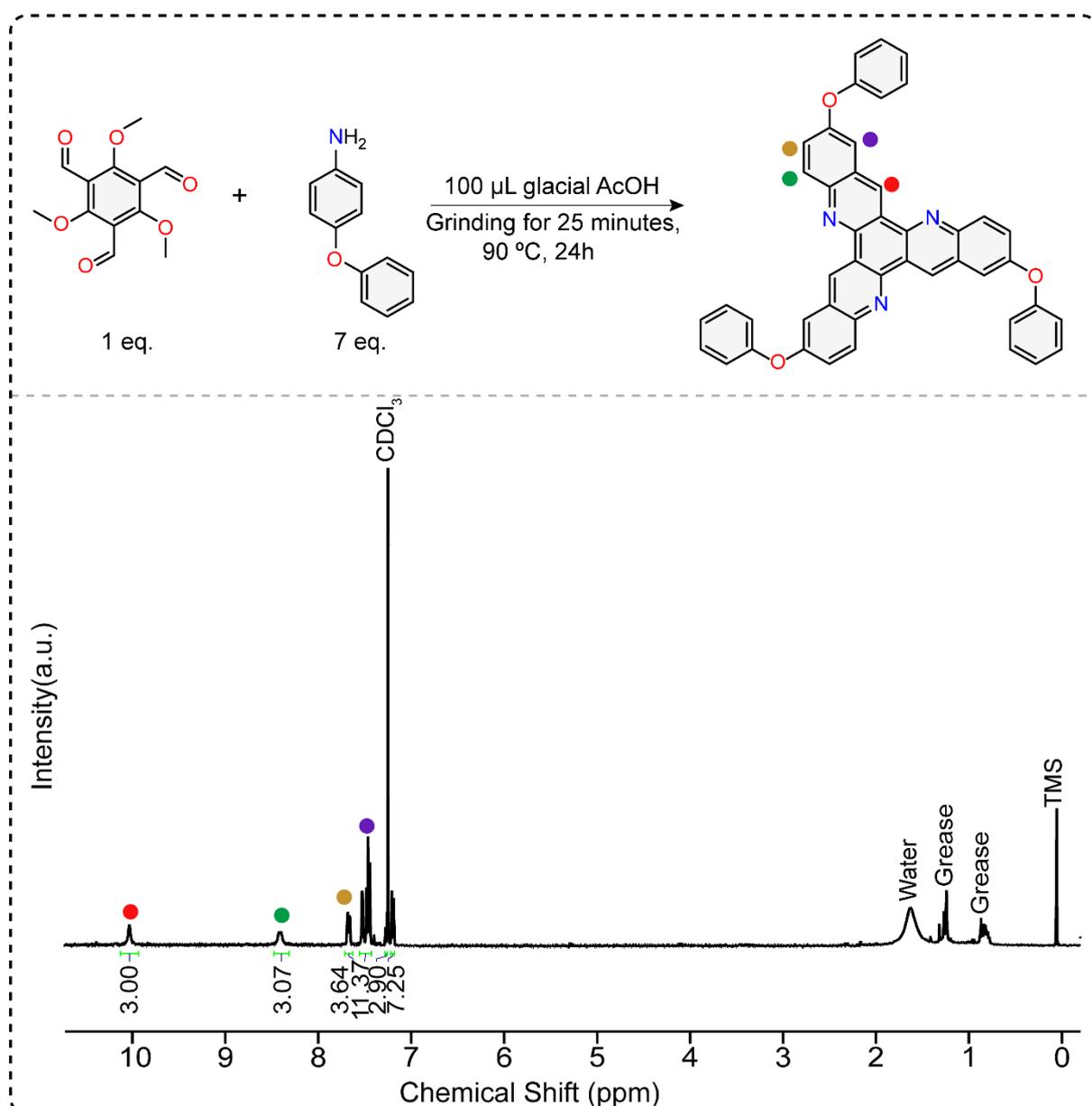


Fig. S47 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.07 (s, 3H) 8.43 (d, J = 8.9 Hz, 3H), 7.68 (dd, J = 9.2 Hz, 2.7 Hz, 3H), 7.52 (d, J = 2.5 Hz, 3H).

As the TNP-*p*-OPh compound is not soluble enough in any deuterated solvent (CDCl_3 , DMSO-d_6 , DMF-d_7 , THF-d_8 , CD_2Cl_2), $^{13}\text{C NMR}$ has not been provided.

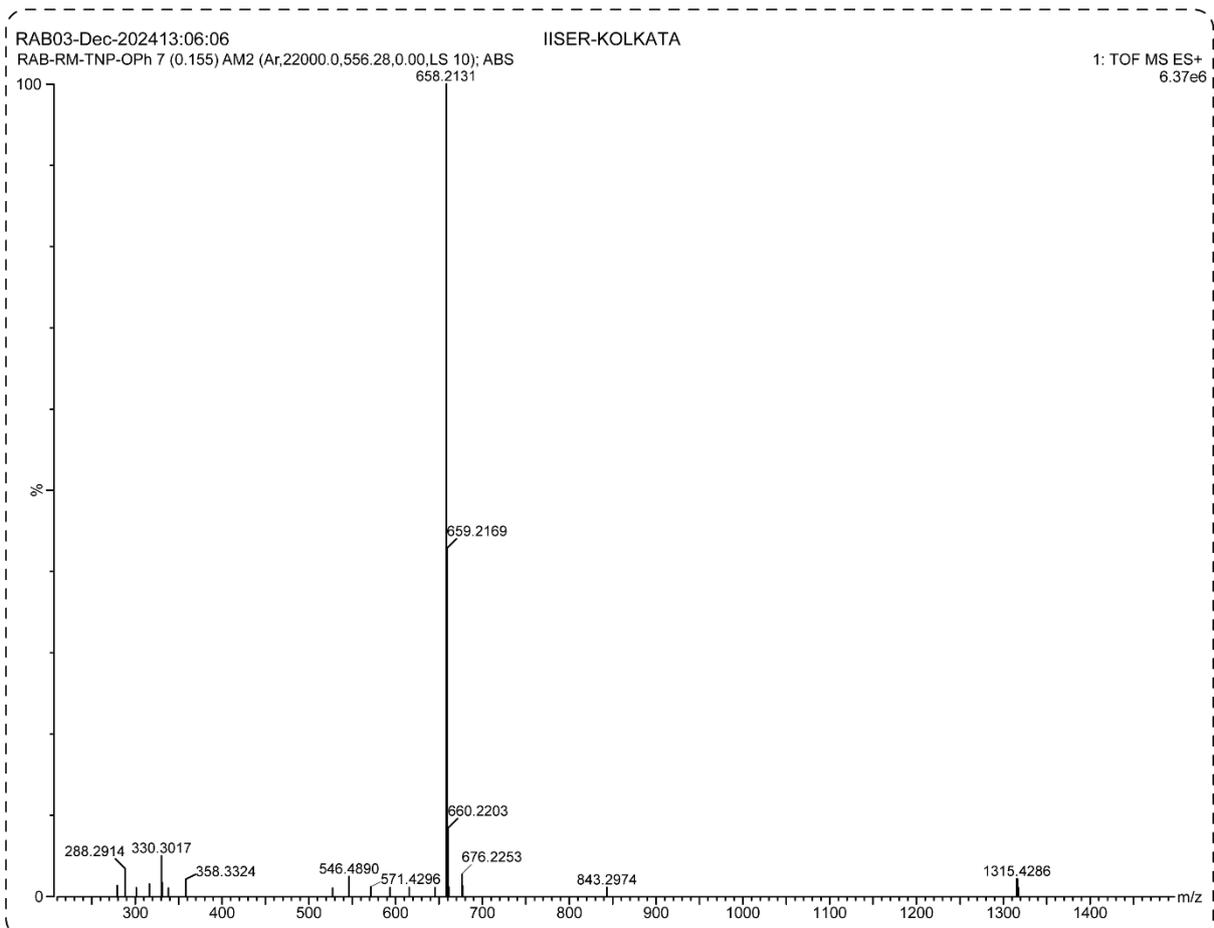


Fig. S48 High-resolution mass spectra of TNP-*p*-Oph. m/z : $[M+H]^+$ calculated for $C_{45}H_{27}N_3O_3$ 658.2131; Found 658.2131.

TNP-*p*-Mor

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-morpholinoaniline (124.761 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.84 (s, 3H) 8.21 (d, J = 9.25 Hz, 3H), 7.62 (dd, J = 9.4 Hz, 2.8 Hz, 3H), 7.34 (d, J = 2.8 Hz, 3H), 3.97 (t, J = 4.8 Hz, 3H), 3.38 (t, J = 4.9 Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 149.23, 146.39, 144.71, 131.53, 130.16, 129.15, 125.73, 123.82, 123.49, 66.97, 49.42. HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{36}\text{N}_6\text{O}_3$ 637.2927; Found 637.2928.

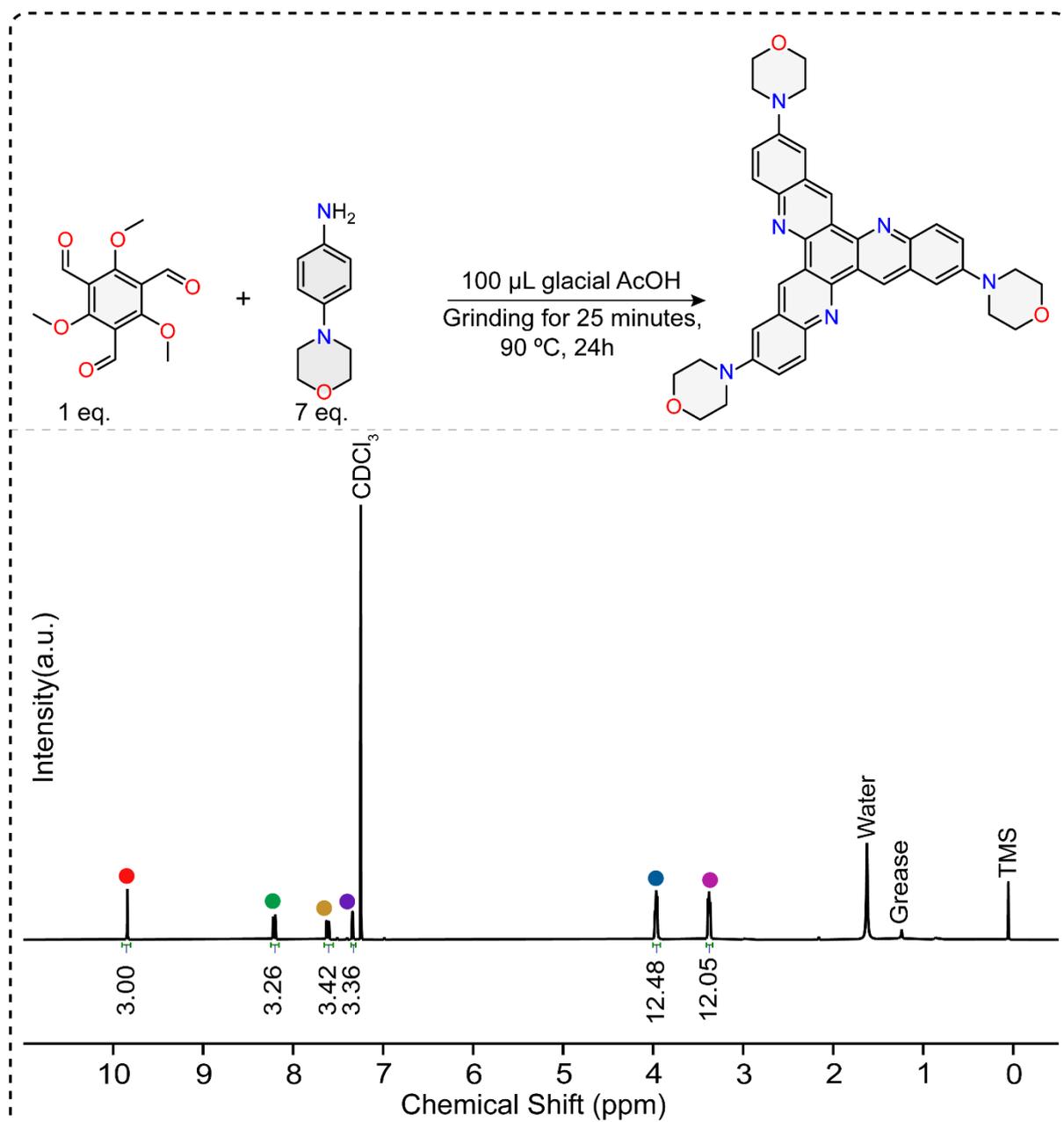


Fig. S49 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.84 (s, 3H) 8.21 (d, J = 9.25 Hz, 3H), 7.62 (dd, J = 9.4 Hz, 2.8 Hz, 3H), 7.34 (d, J = 2.8 Hz, 3H), 3.97 (t, J = 4.8 Hz, 3H), 3.38 (t, J = 4.9 Hz, 2H).

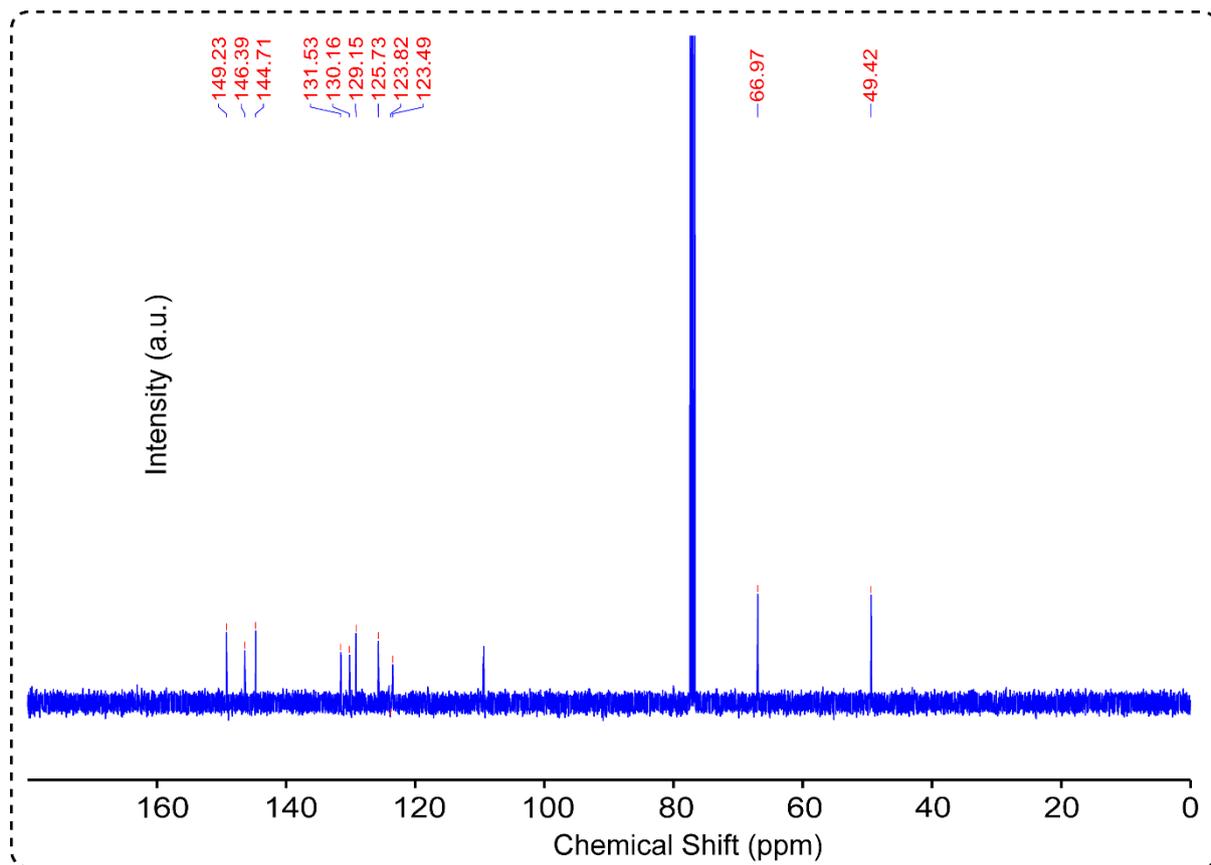


Fig. S50 ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.23, 146.39, 144.71, 131.53, 130.16, 129.15, 125.73, 123.82, 123.49, 66.97, 49.42.

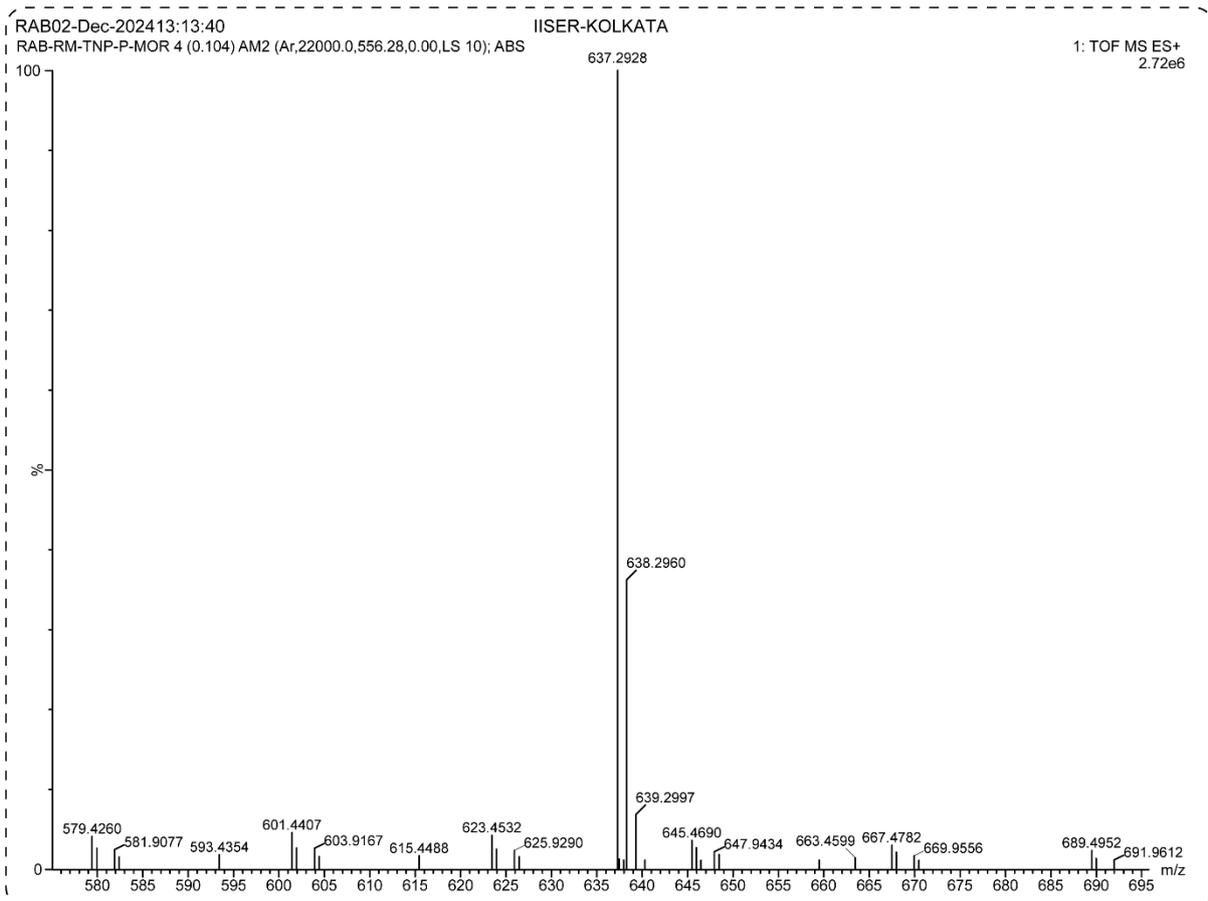


Fig. S51 High-resolution mass spectra of TNP-*p*-Mor. m/z : $[M+H]^+$ calculated for $C_{39}H_{36}N_6O_3$ 637.2927; Found 637.2928.

TNP-*p*-NMe₂

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and N,N-Dimethyl-*p*-phenylenediamine (95.3 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. : ¹H NMR (400 MHz, Chloroform-*D*) δ 9.72 (s, 3H), 8.18 (d, J = 9.1 Hz, 3H), 7.43 (dd, J = 9.3, 2.8 Hz, 3H), 7.01 (d, J = 2.9 Hz, 3H), 3.14 (s, 18H). HRMS m/z : [M+H]⁺ calculated for C₃₃H₃₀N₆ 511.2610; Found 511.2615.

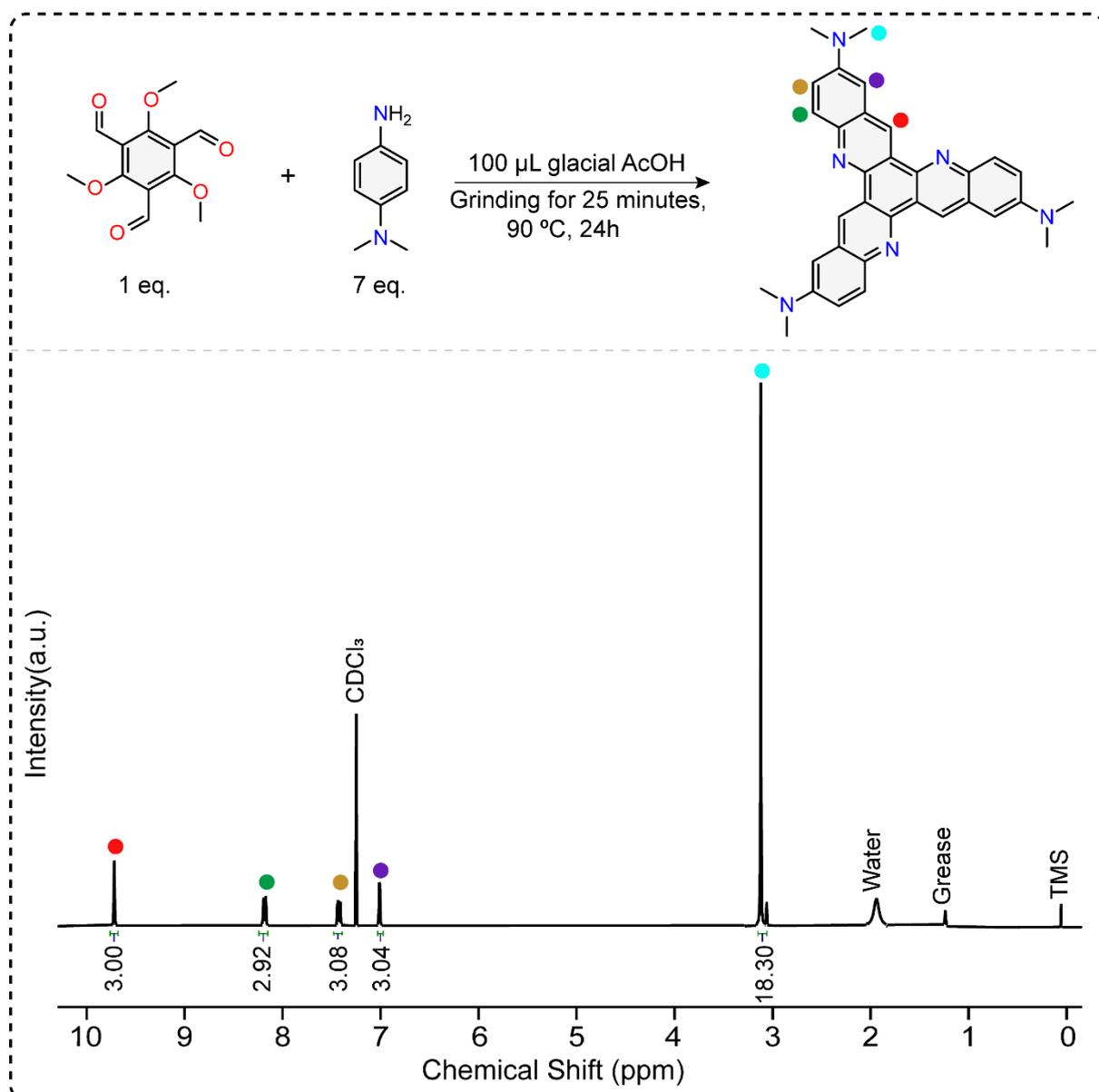


Fig. S52 ¹H NMR (400 MHz, Chloroform-*D*) δ 9.72 (s, 3H), 8.18 (d, J = 9.1 Hz, 3H), 7.43 (dd, J = 9.3, 2.8 Hz, 3H), 7.01 (d, J = 2.9 Hz, 3H), 3.14 (s, 18H).

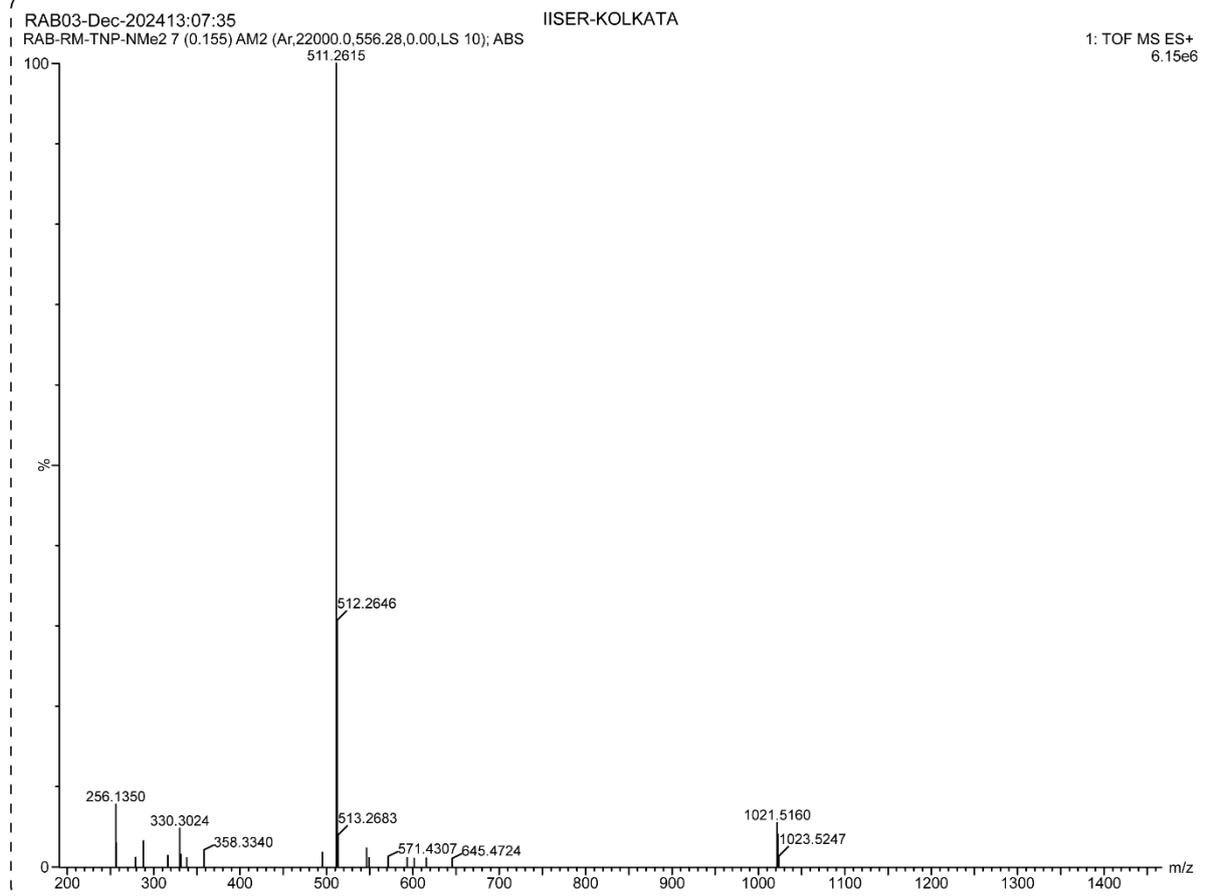


Fig. S53 High-resolution mass spectra of TNP-*p*-NMe₂. m/z: [M+H]⁺ calculated for C₃₀H₂₁N₃ 511.2610; Found 511.2615.

TNP-*p*-SMe

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-(methylthio)aniline (97.33 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. **HRMS** m/z : $[M+H]^+$ calculated for $C_{33}H_{21}N_3S_3$ 511.2610; Found 511.2615.

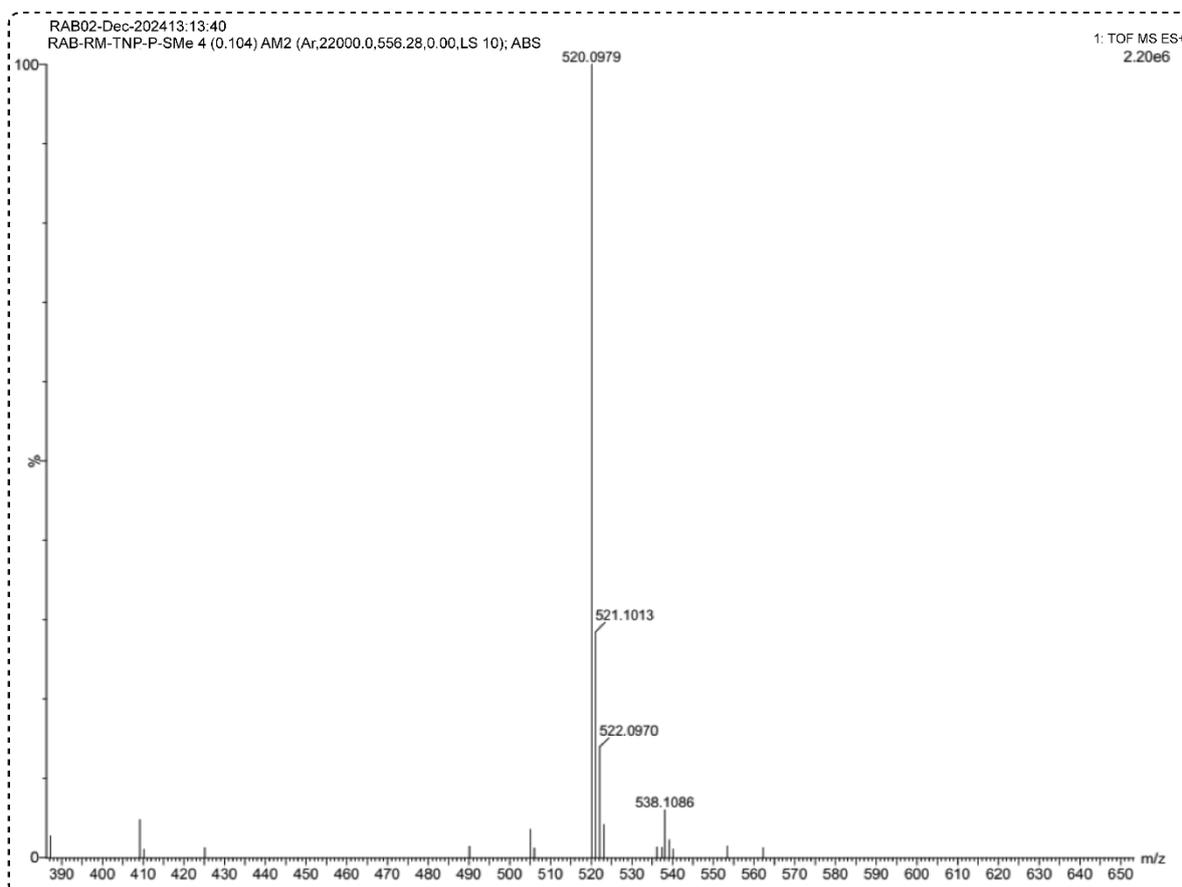


Fig. S54 High-resolution mass spectra of TNP-*p*-SMe. m/z : $[M+H]^+$ calculated for $C_{30}H_{21}N_3S_3$ 520.0976; Found 520.0979.

TNP-*m*-tBu

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3-tert-butylaniline aniline (112.3 μL , 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μL) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. : ^1H NMR (400 MHz, Chloroform-*D*) δ 9.94 (s, 1H), 8.27 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.6 Hz, 1H), 7.74 (dd, J = 8.6, 1.9 Hz, 1H), 1.55 (s, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.26, 149.05, 148.83, 133.55, 128.56, 126.04, 125.93, 124.57, 124.36, 35.56, 31.26. HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{39}\text{N}_3$ 550.3178; Found 550.3234.

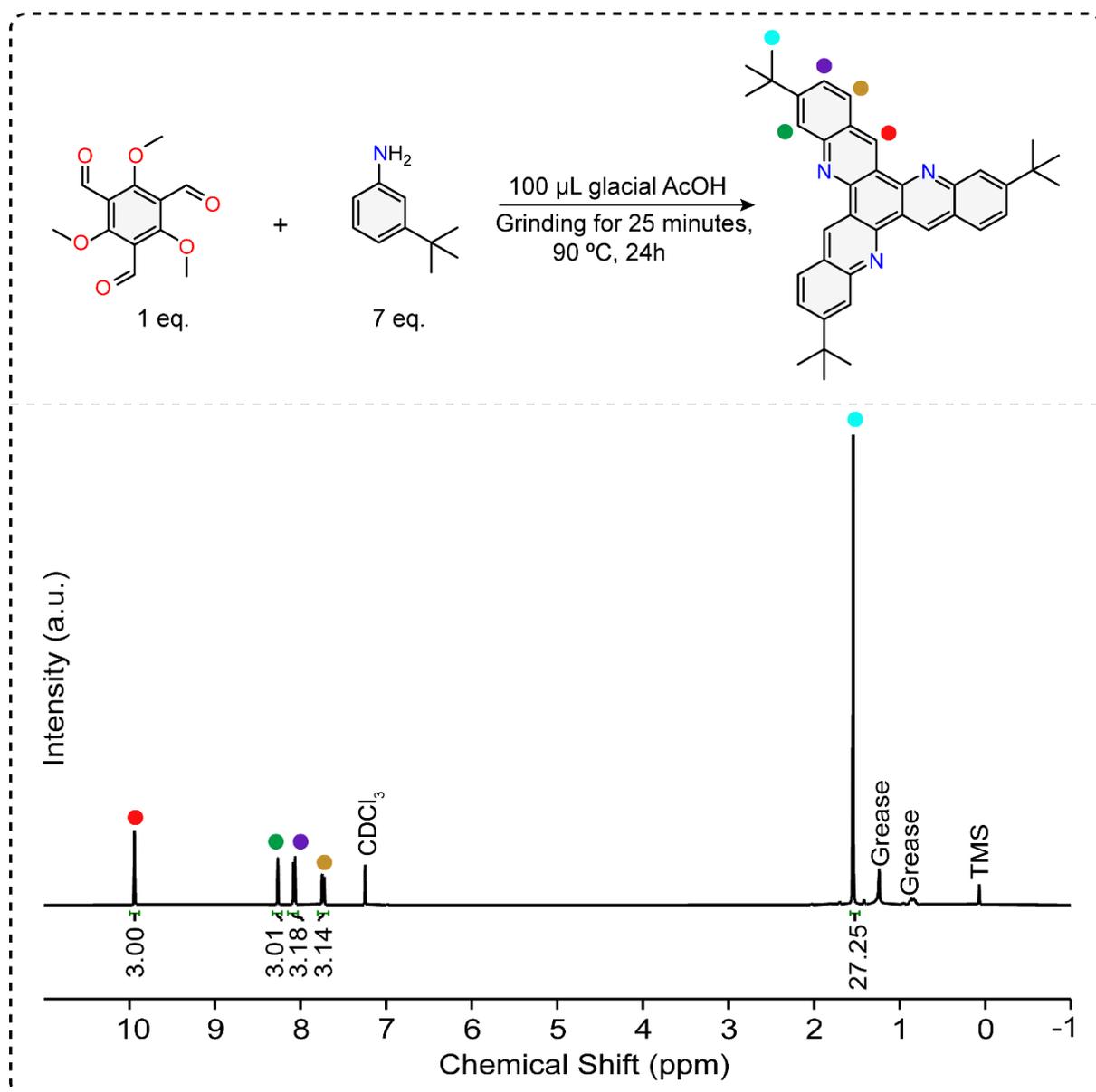


Fig. S55 ^1H NMR (400 MHz, Chloroform-*D*) δ 9.94 (s, 1H), 8.27 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.6 Hz, 1H), 7.74 (dd, J = 8.6, 1.9 Hz, 1H), 1.55 (s, 8H).

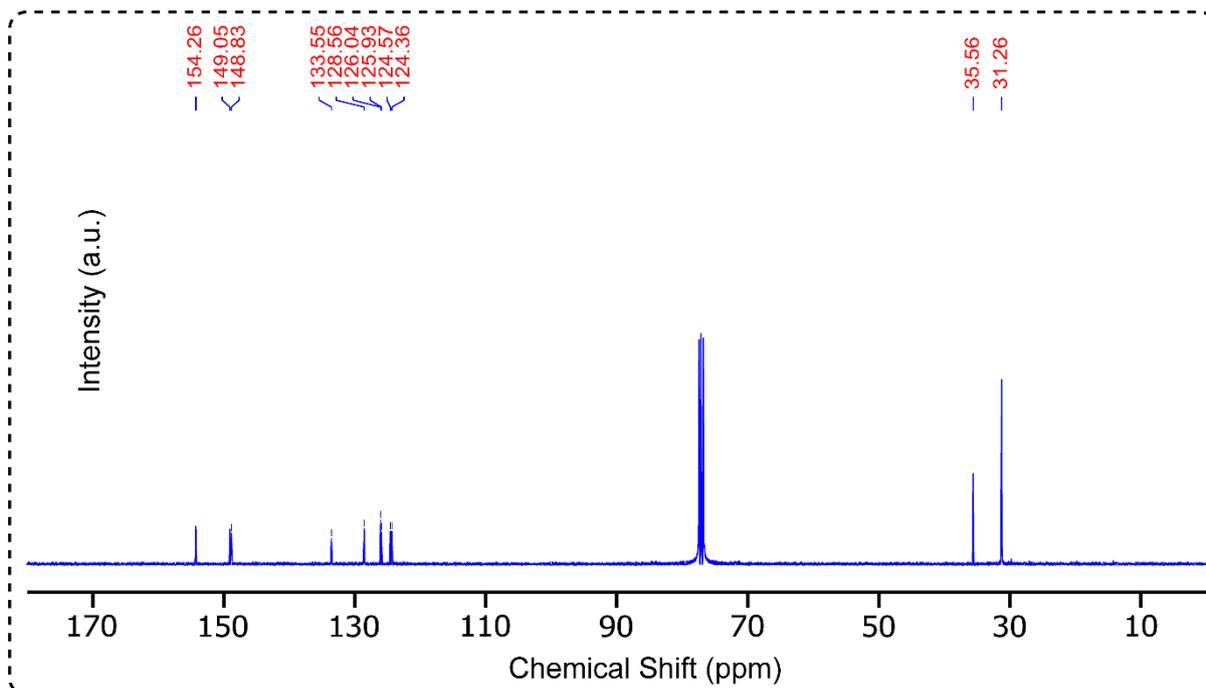


Fig. S56 ^{13}C NMR (101 MHz, Chloroform-*D*) δ 154.26, 149.05, 148.83, 133.55, 128.56, 126.04, 125.93, 124.57, 124.36, 35.56, 31.26.

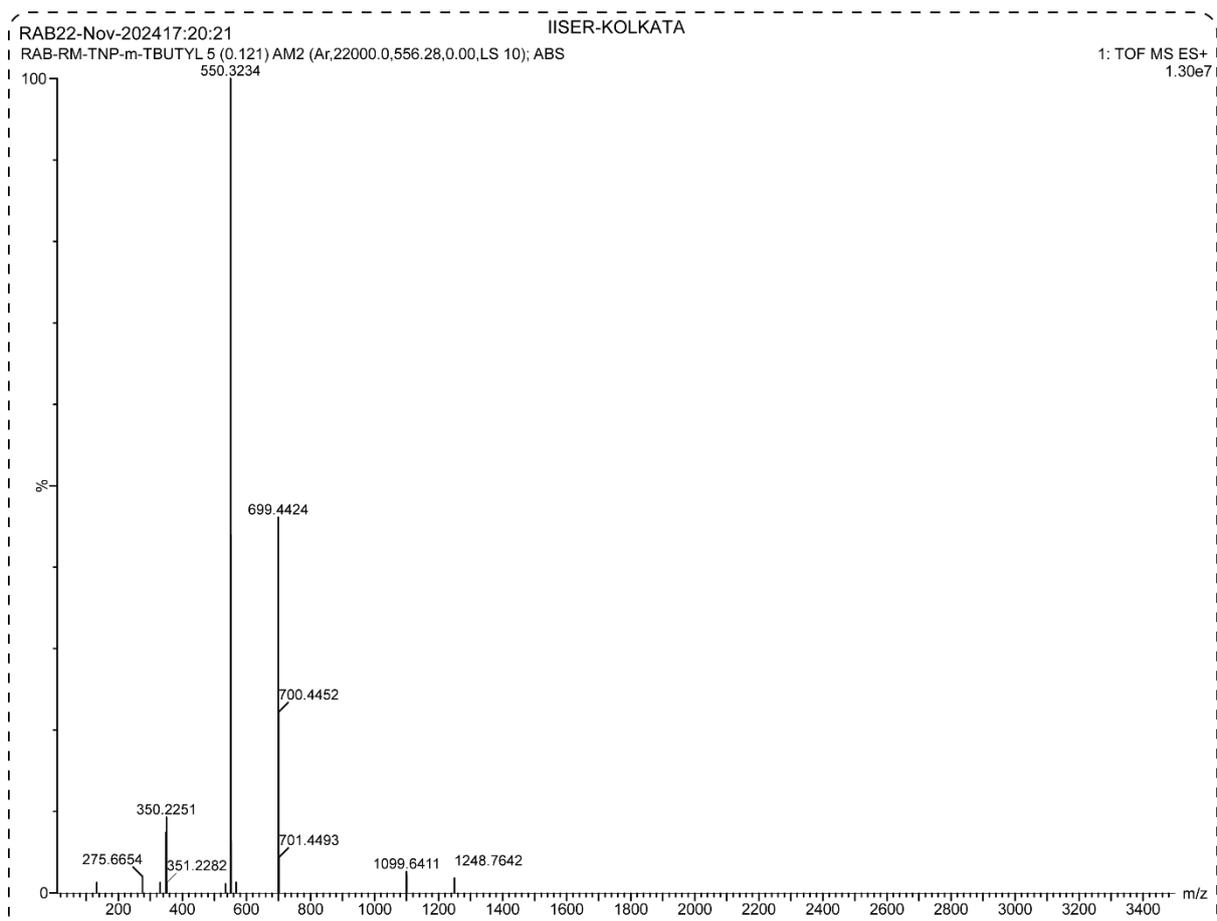


Fig. S57: High-resolution mass spectra of TNP-*m*-tBu. m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{39}\text{N}_3$ 550.3178; Found 550.3234.

TNP-*m*-iPr

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3-isopropyl aniline (98.6 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.03 (s, 1H), 8.18 (s, 3H), 8.12 (d, $J = 8.4$ Hz, 3H), 7.57 (dd, $J = 8.5, 1.8$ Hz, 3H), 3.23 (p, $J = 6.7$ Hz, 3H), 1.47 (d, $J = 6.9$ Hz, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.22, 149.27, 148.91, 133.86, 128.90, 127.23, 126.50, 125.26, 124.48, 34.72, 23.80. HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{33}\text{N}_3$ 508.2753; Found 508.2747.

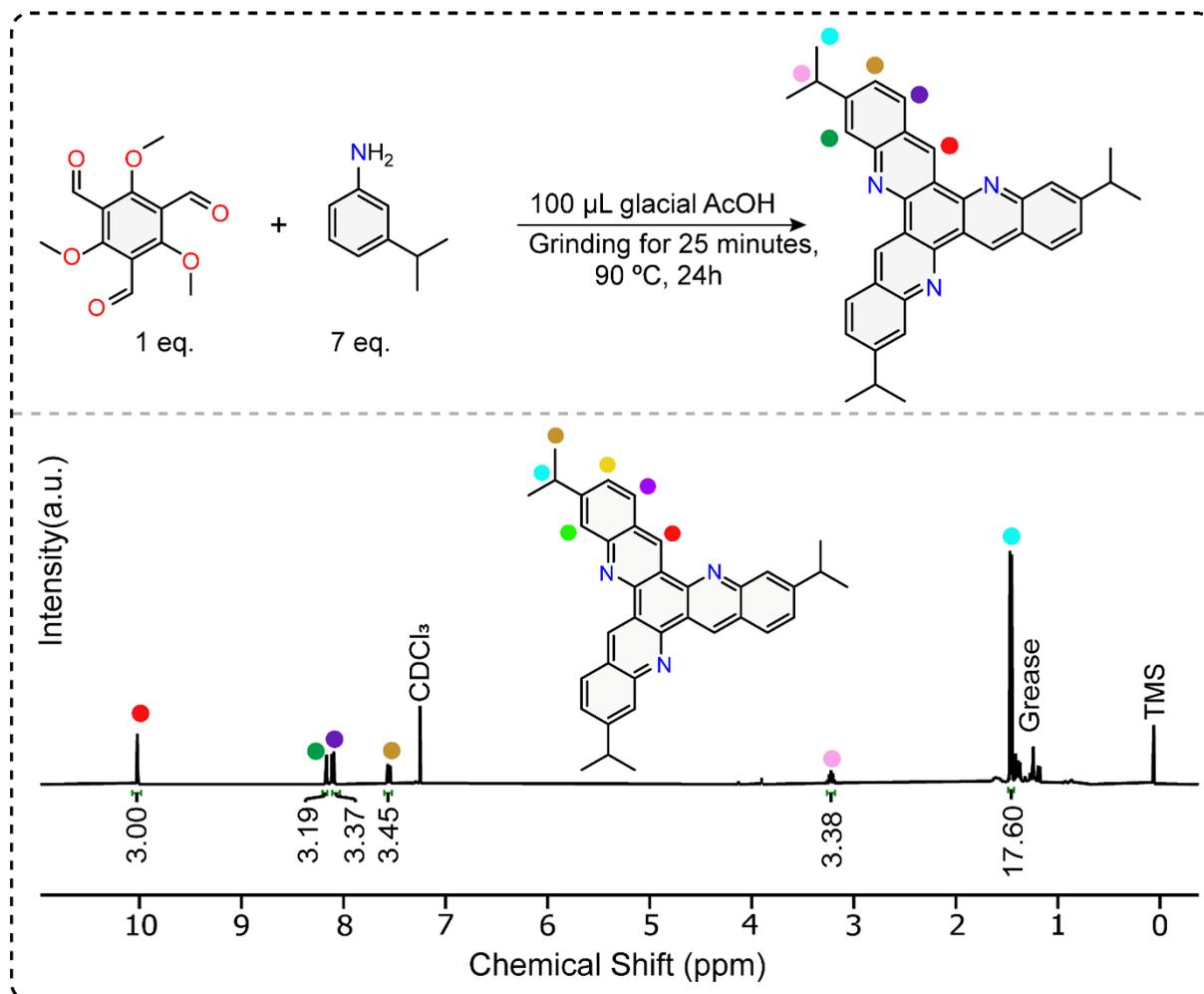


Fig. S58 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.03 (s, 1H), 8.18 (s, 3H), 8.12 (d, $J = 8.4$ Hz, 3H), 7.57 (dd, $J = 8.5, 1.8$ Hz, 3H), 3.23 (p, $J = 6.7$ Hz, 3H), 1.47 (d, $J = 6.9$ Hz, 18H).

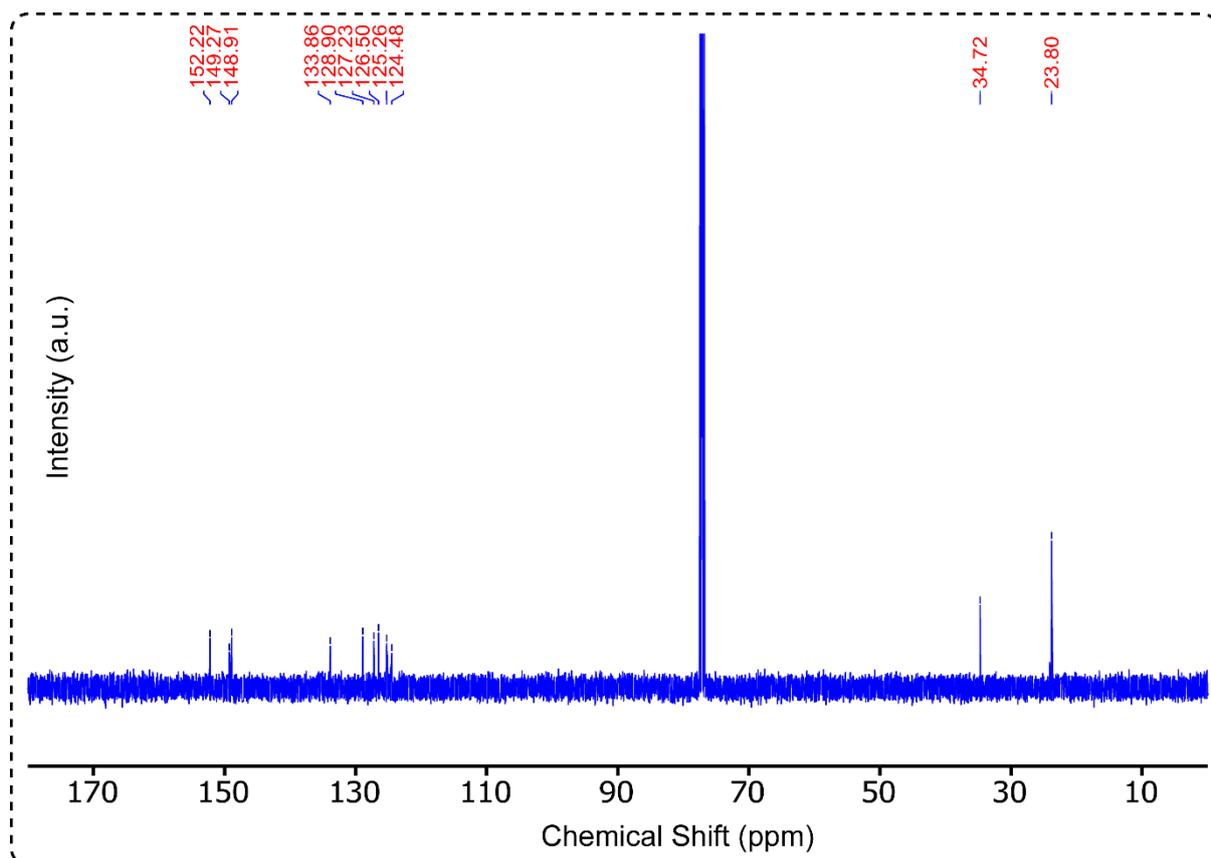


Fig. S59 ¹³C NMR (101 MHz, CDCl₃) δ 152.22, 149.27, 148.91, 133.86, 128.90, 127.23, 126.50, 125.26, 124.48, 34.72, 23.80.

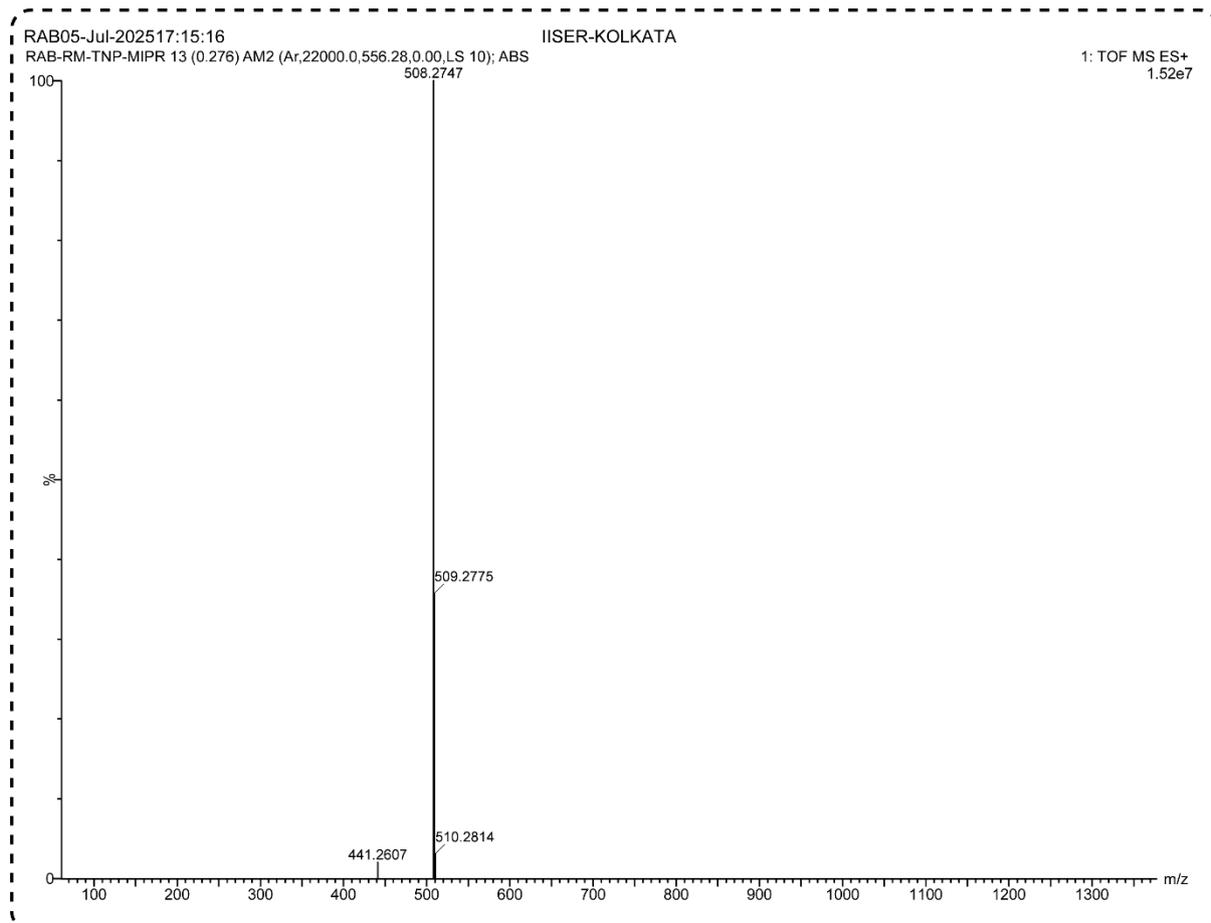


Fig. S60 High-resolution mass spectra of TNP-*p*-*m*-*i*Pr. m/z: [M+H]⁺ calculated for C₃₆H₃₃N₃ 508.2753; Found 508.2747.

TNP-*m*-OMe

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3-methoxy aniline (78.65 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.35 (s, 1H), 9.86 (s, 3H), 7.99 (d, J = 9.0 Hz, 3H), 7.87 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.55 (s, 3H), 7.27 (s, 3H), 6.89 (d, J = 7.8 Hz, 1H), 4.14 (s, 3H), 4.06 (s, J = 5.1 Hz, 9H). **HRMS** $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{21}\text{N}_3\text{O}_3$ 472.1661; Found 472.1656.

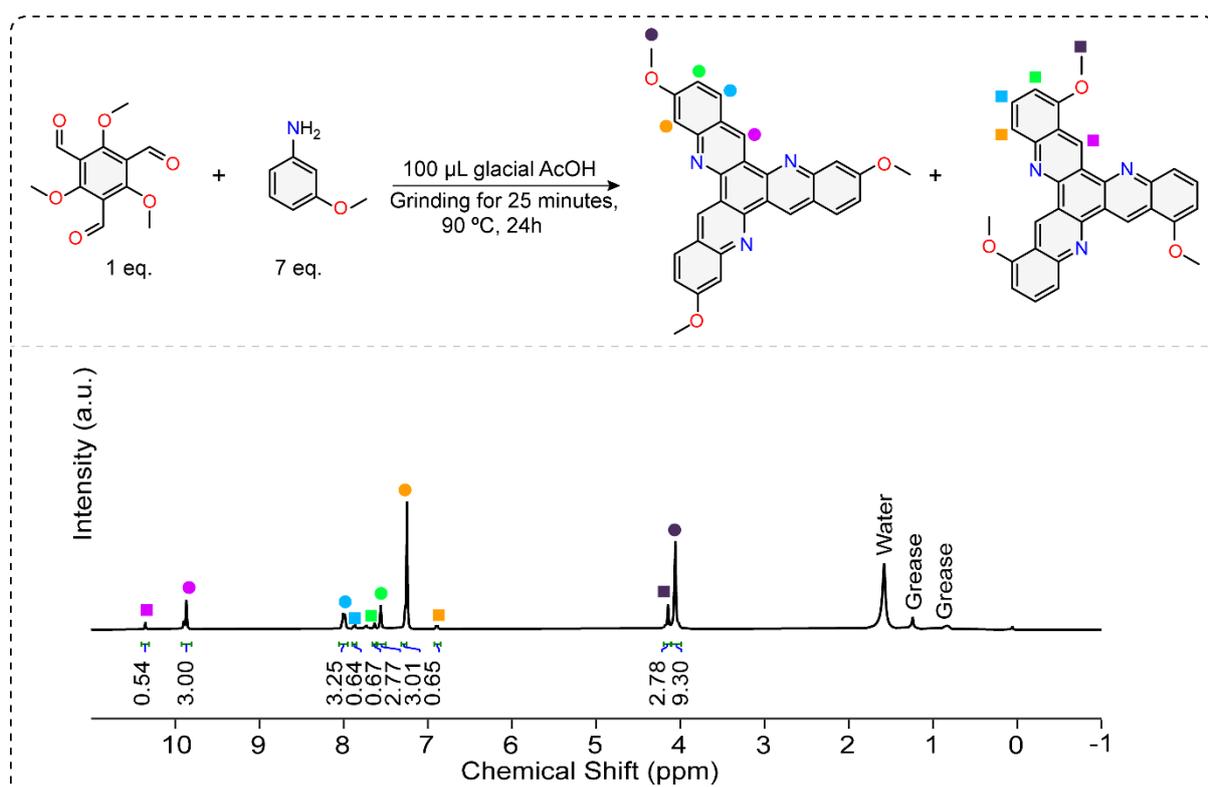


Fig. S61 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.35 (s, 1H), 9.86 (s, 3H), 7.99 (d, J = 9.0 Hz, 3H), 7.87 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.55 (s, 3H), 7.27 (s, 3H), 6.89 (d, J = 7.8 Hz, 1H), 4.14 (s, 3H), 4.06 (s, J = 5.1 Hz, 9H).

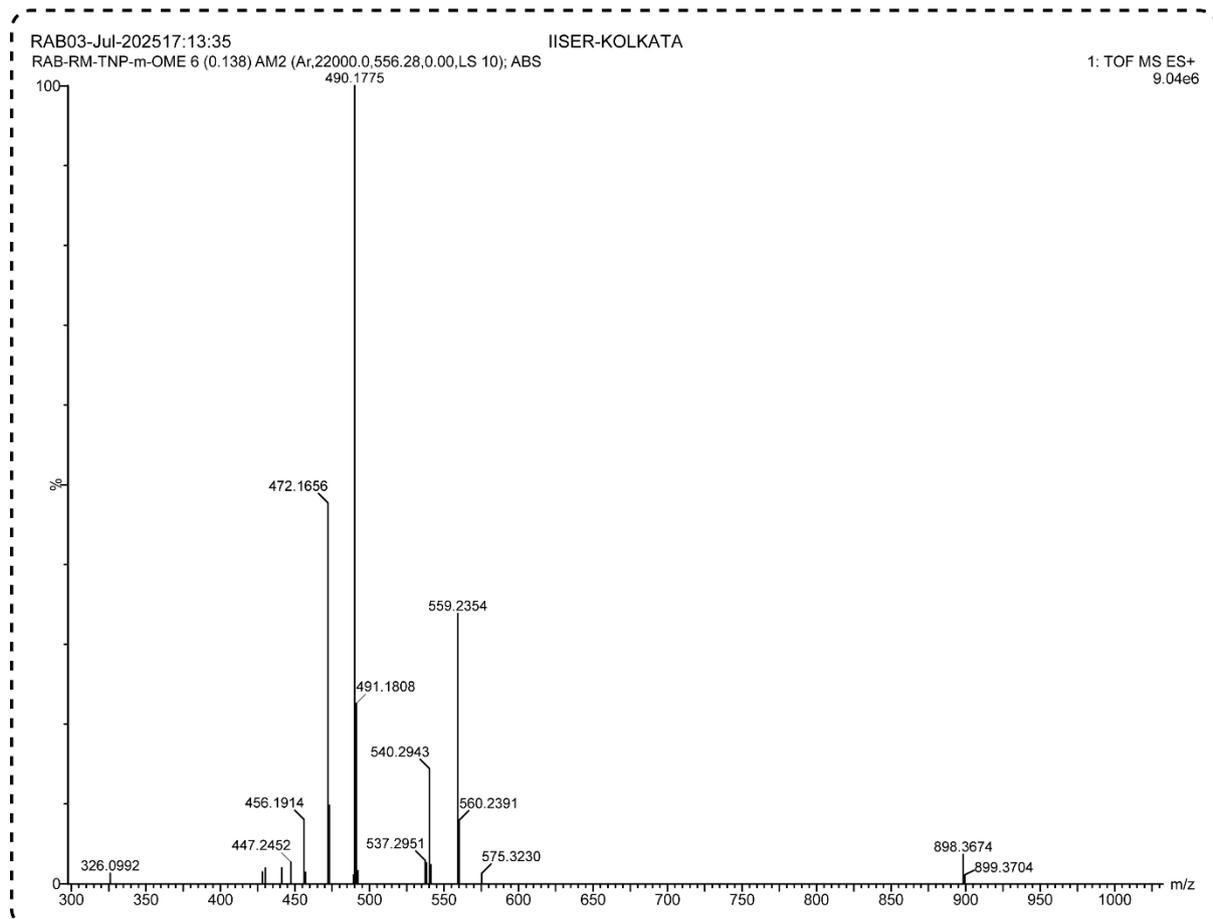


Fig. S62 High-resolution mass spectra of TNP-*m*-OMe. m/z: [M+H]⁺ calculated for C₃₀H₂₁N₃O₃ 472.1661; Found 472.1656.

TNP-*m*-Me

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3-methyl aniline (75.08 μL , 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μL) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. $^1\text{H NMR}$ (400 MHz, CHLOROFORM-*D*) δ 10.18 (s, 1H), 9.96 (s, 3H), 8.18 – 8.17 (m, 0H), 8.16 – 8.12 (m, 2H), 8.08 (td, $J = 1.6, 0.8$ Hz, 3H), 8.04 (d, $J = 8.4$ Hz, 3H), 7.73 – 7.69 (m, 1H), 7.48 – 7.42 (m, 3H), 2.97 (s, 3H), 2.66 (d, 9H). HRMS m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{21}\text{N}_3$ 424.1769; Found 424.1841

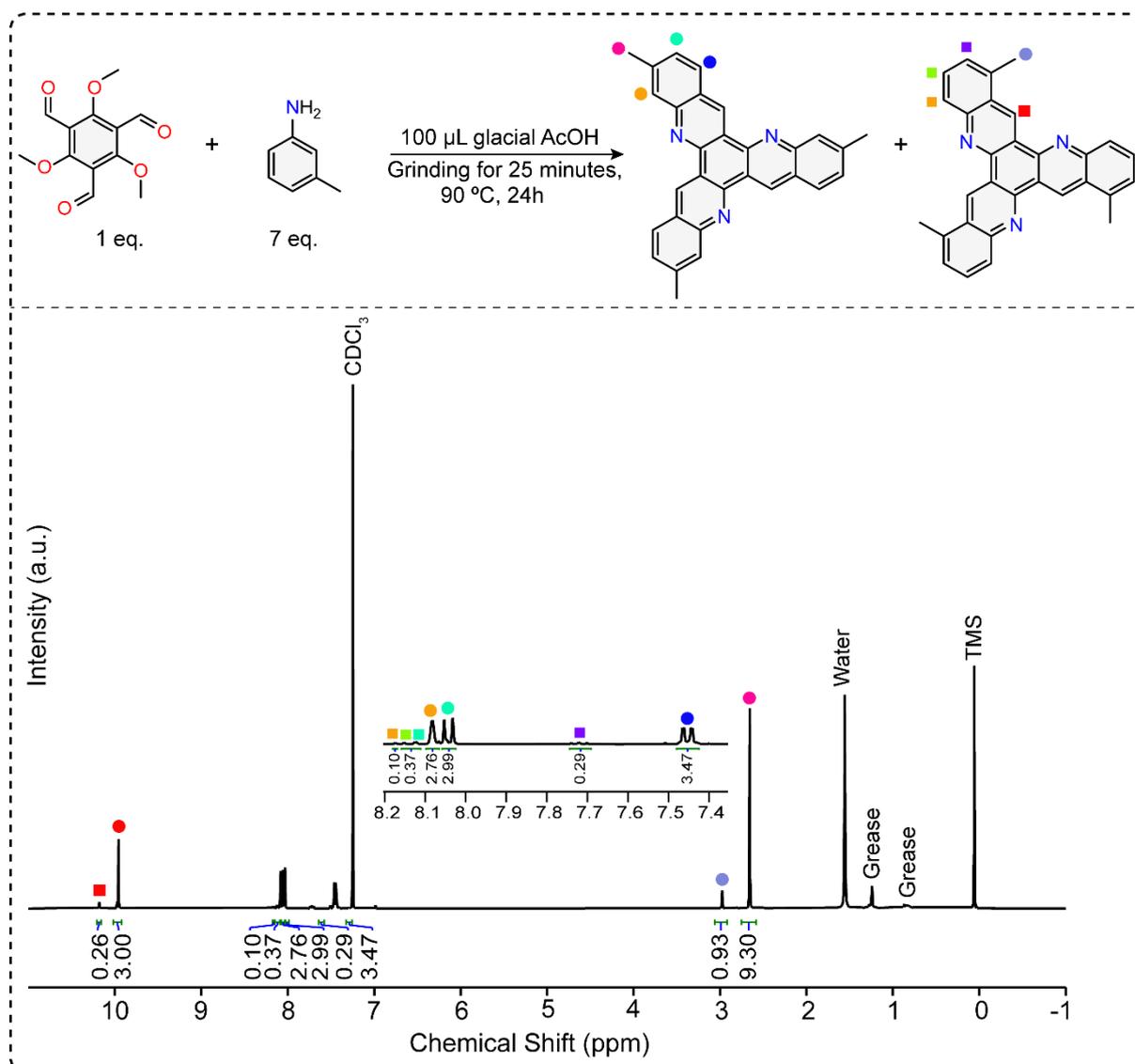


Fig. S63 $^1\text{H NMR}$ (400 MHz, CHLOROFORM-*D*) δ 10.18 (s, 1H), 9.96 (s, 3H), 8.18 – 8.17 (m, 0H), 8.16 – 8.12 (m, 2H), 8.08 (td, $J = 1.6, 0.8$ Hz, 3H), 8.04 (d, $J = 8.4$ Hz, 3H), 7.73 – 7.69 (m, 1H), 7.48 – 7.42 (m, 3H), 2.97 (s, 3H), 2.66 (d, 9H).

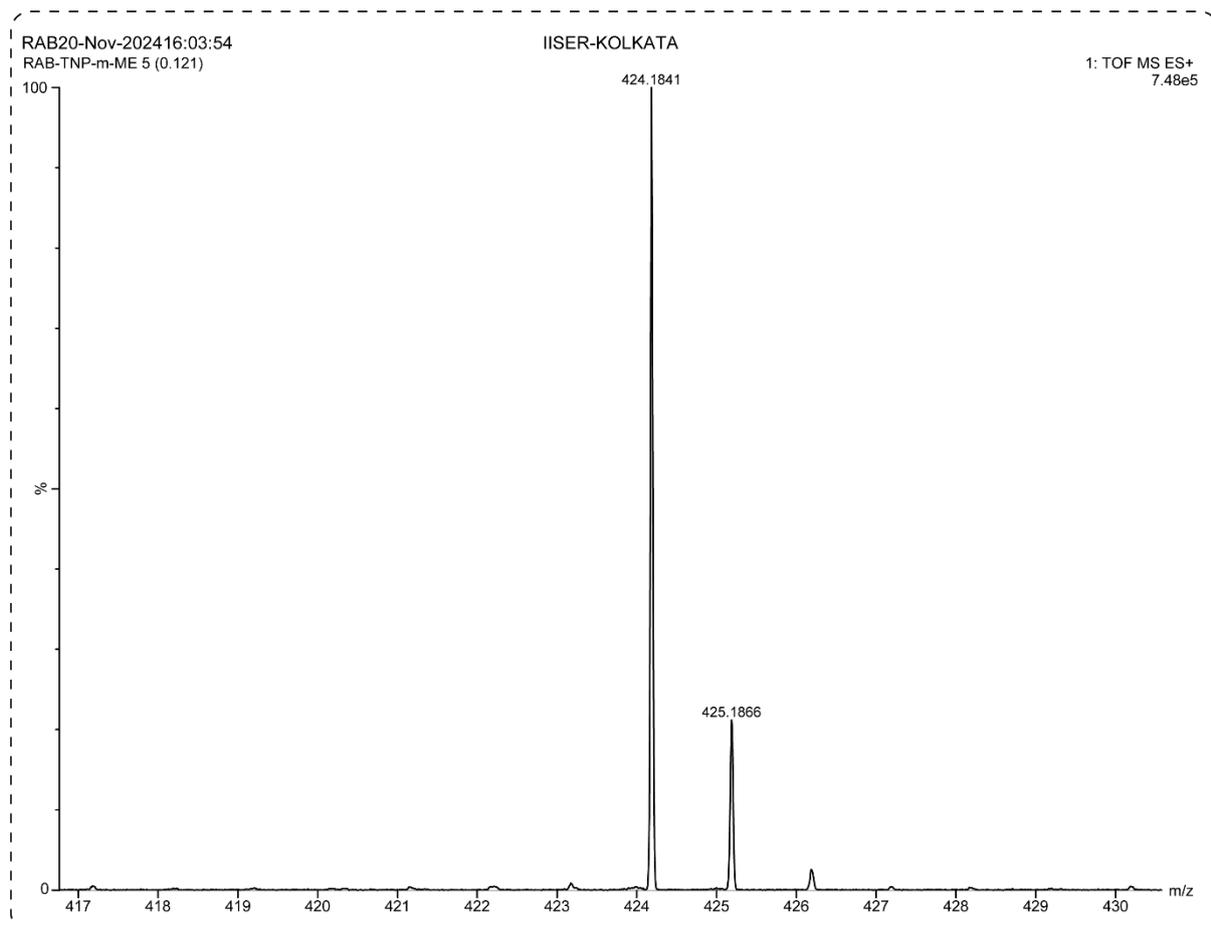


Fig. S64 High-resolution mass spectra of TNP-*m*-Me. m/z : $[M+H]^+$ calculated for $C_{30}H_{21}N_3$ 424.1769; Found 424.1841

TNP-*o*-Me

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 2-methyl aniline (75.08 μL , 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μL) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.00 (s, 1H), 8.03 (d, $J = 8.2$ Hz, 1H), 7.70 (d, $J = 7.4$ Hz, 1H), 7.55 (dd, $J = 7.4$ Hz, 1.7 Hz, 1H), 3.09 (s, 3H). **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{21}\text{N}_3$ 424.1769; Found 424.1841

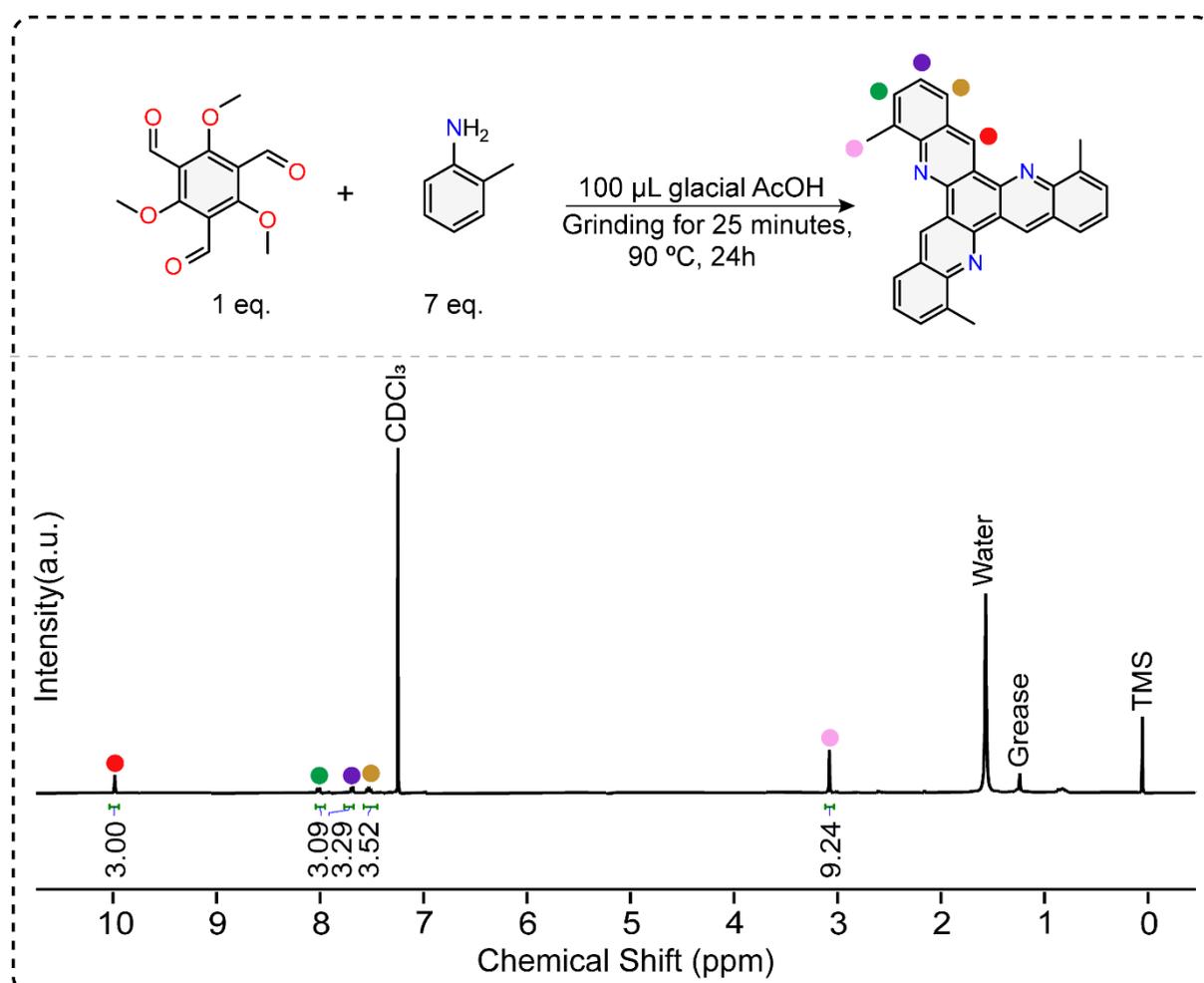


Fig. S65 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 10.00 (s, 1H), 8.03 (d, $J = 8.2$ Hz, 1H), 7.70 (d, $J = 7.4$ Hz, 1H), 7.55 (dd, $J = 7.4$ Hz, 1.7 Hz, 1H), 3.09 (s, 3H).

As the TNP-*o*-Me compound is not soluble enough in any deuterated solvent (CDCl_3 , DMSO-d_6 , DMF-d_7 , THF-d_8 , CD_2Cl_2), $^{13}\text{C NMR}$ has not been provided.

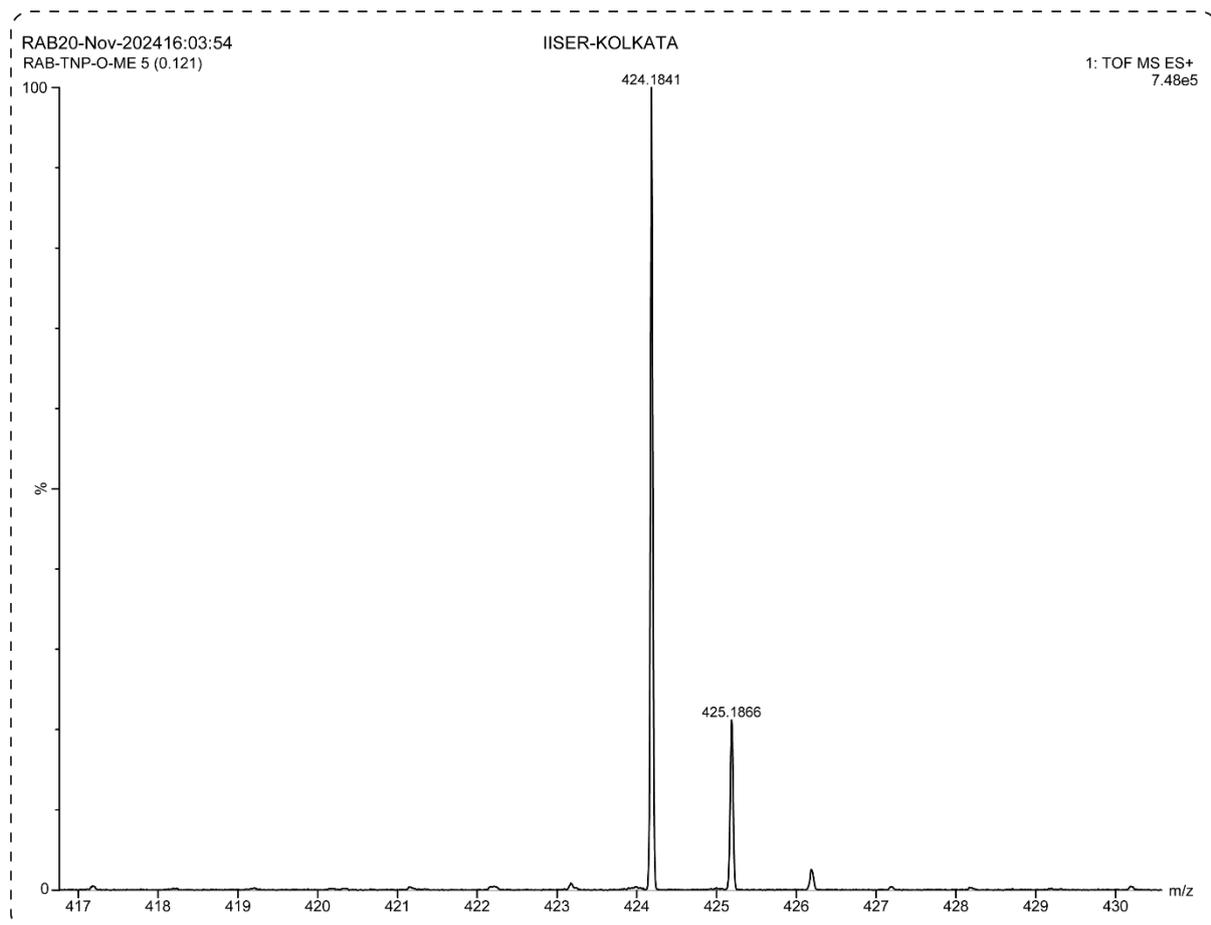


Fig. S66 High-resolution mass spectra of TNP-*o*-Me. m/z : $[M+H]^+$ calculated for $C_{30}H_{21}N_3$ 424.1769; Found 424.1841

TNP-*o*-Et

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 2-ethyl aniline (75.08 μL , 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μL) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. : $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.84 (s, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.65 (d, $J = 6.9$ Hz, 2H), 7.51 (d, $J = 7.3$ Hz, 1H), 3.55 (q, $J = 7.5$ Hz, 4H), 1.57 (t, $J = 7.5$ Hz, 5H). **HRMS** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{27}\text{N}_3$ 466.2239; Found 466.2283

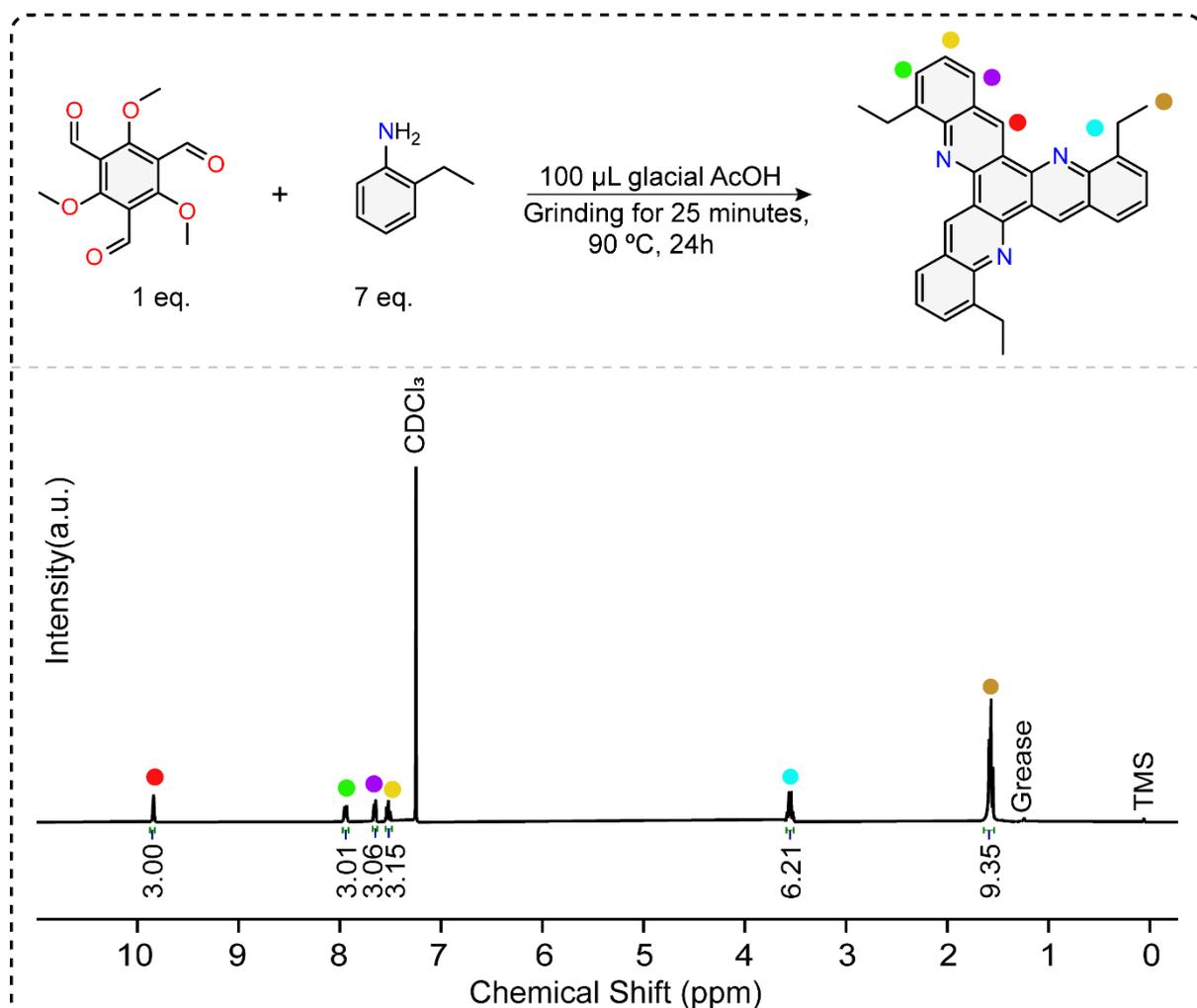


Fig. S67 $^1\text{H NMR}$ (400 MHz, Chloroform-*D*) δ 9.84 (s, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.65 (d, $J = 6.9$ Hz, 2H), 7.51 (d, $J = 7.3$ Hz, 1H), 3.55 (q, $J = 7.5$ Hz, 4H), 1.57 (t, $J = 7.5$ Hz, 5H).

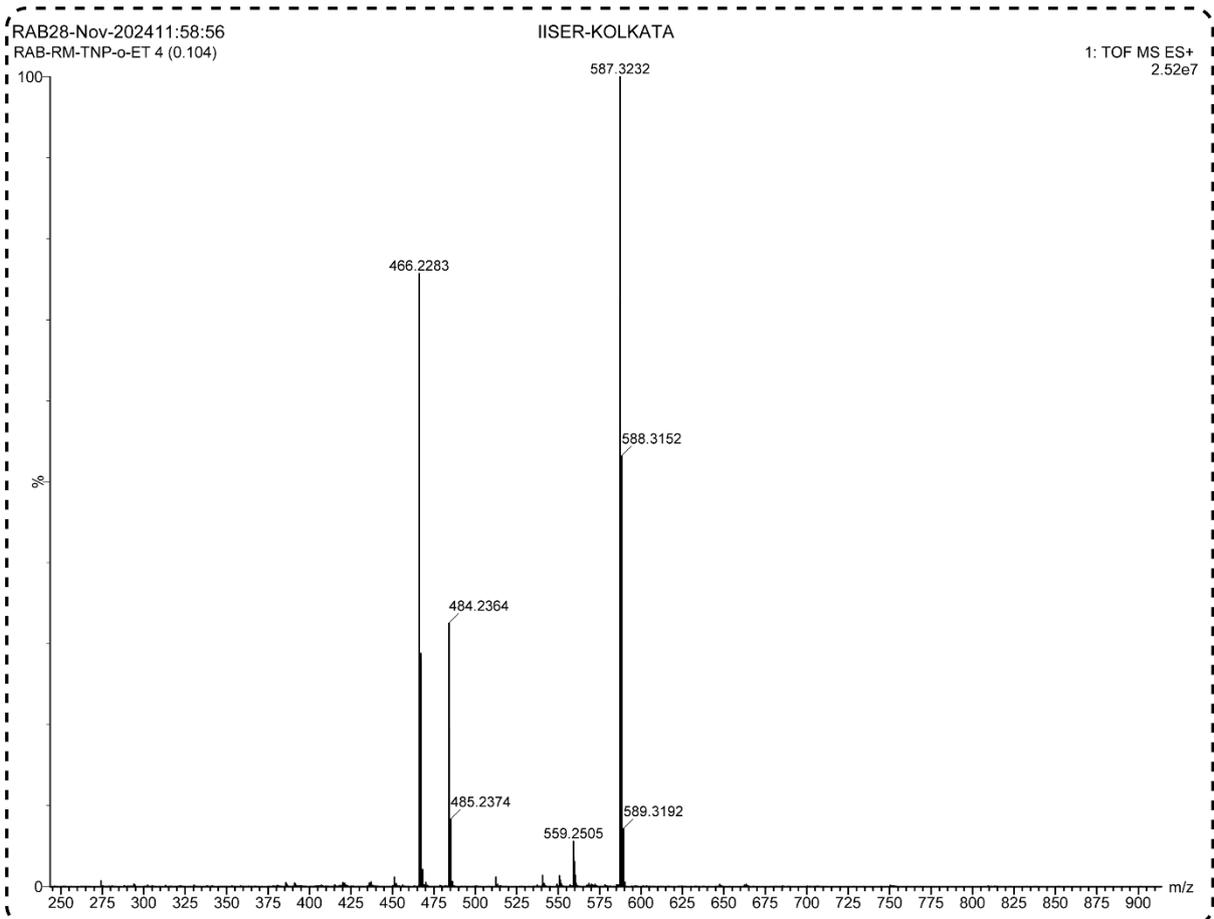


Fig. S68 High-resolution mass spectra of TNP-*o*-Et. m/z: [M+H]⁺ calculated for C₃₃H₂₇N₃ 466.2283; Found 466.2283

TNP-Me₂

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3,4-dimethylaniline (84.8 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. HRMS m/z : $[M+H]^+$ calculated for C₃₃H₂₇N₃ 466.2283; Found 466.2283

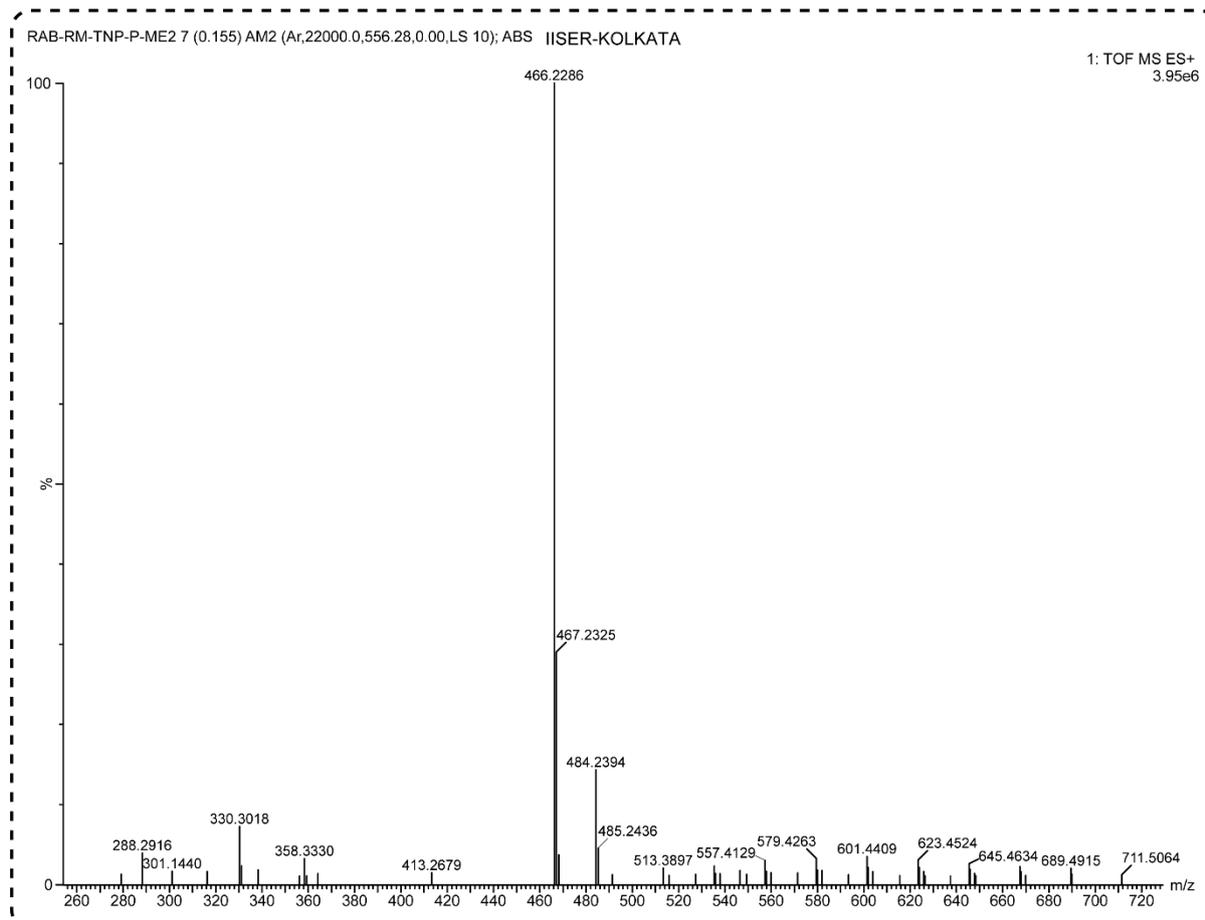


Fig. S69 High-resolution mass spectra of TNP-Me₂. m/z : $[M+H]^+$ calculated for C₃₃H₂₇N₃ 466.2283; Found 466.2286

TNP-(OMe)₆

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3,4-dimethoxyaniline (107.226 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. **HRMS** m/z : $[M+H]^+$ calculated for C₃₃H₂₇N₃O₆ 562.1978; Found 424.1974

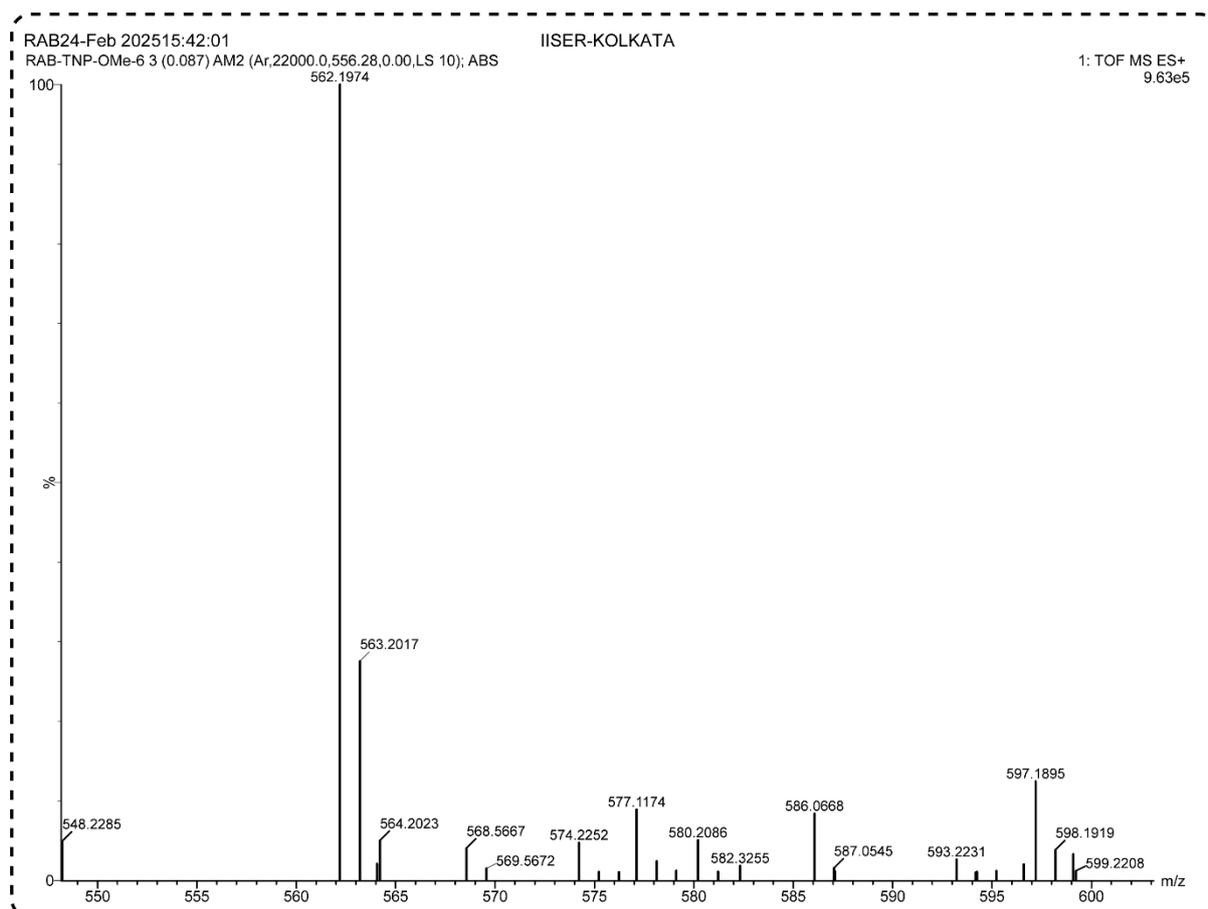


Fig. S70 High-resolution mass spectra of TNP-(OMe)₆ m/z : $[M+H]^+$ calculated for C₃₃H₂₇N₃O₆ 562.1978; Found 424.1974

TNP-NAP

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 1-naphthylaniline (100.1 mg, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by washing with acetone to afford the desired product. **HRMS**: m/z : $[M+H]^+$ calculated for $C_{39}H_{22}N_3$ 532.1814; Found 532.1808

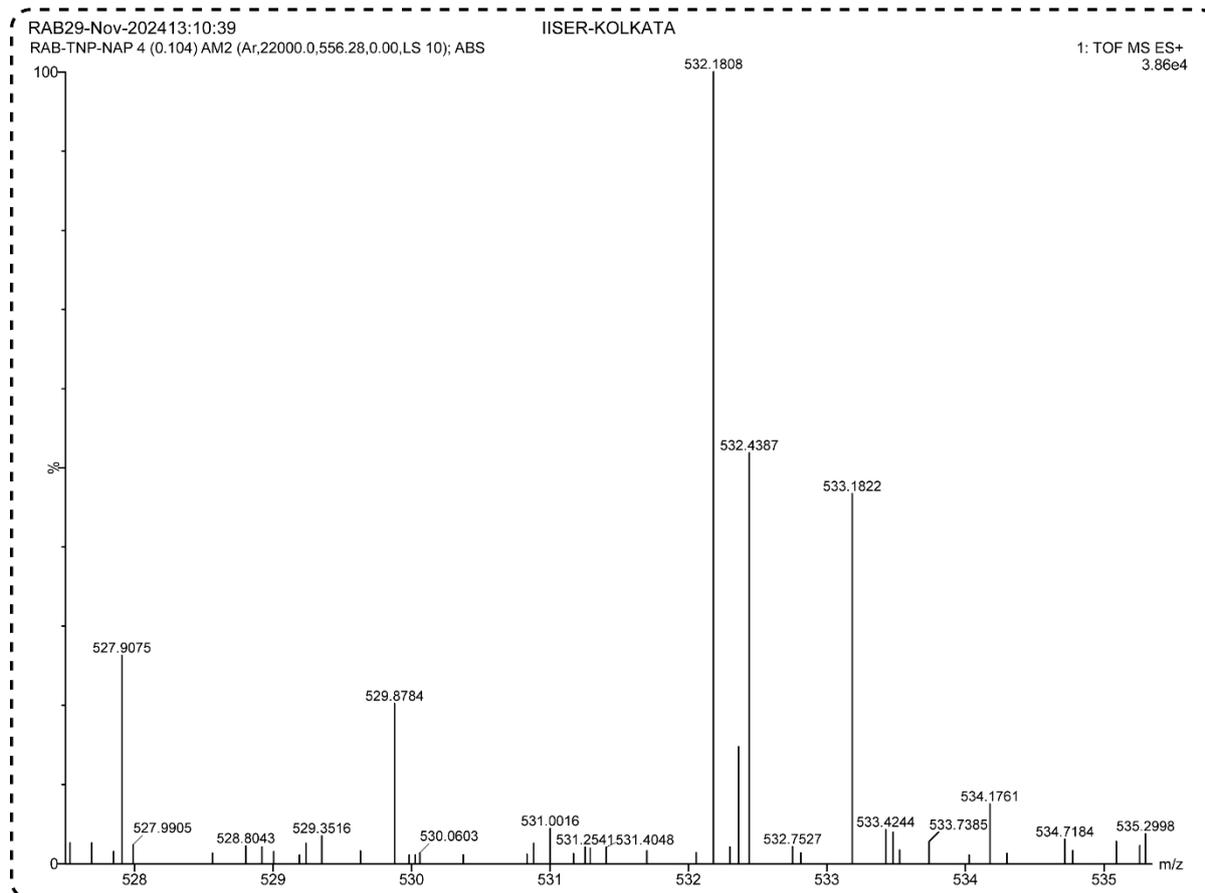


Fig. S71 High-resolution mass spectra of TNP-Nap m/z : $[M+H]^+$ calculated for $C_{39}H_{22}N_3$ 532.1814; Found 532.1808

Section S5: NMR Yield of TNP Compounds

We have performed the experiment with 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde with aniline having different substituents. After getting the product using optimized conditions, we have calculated the NMR yield in the presence of 1,3,5-trimethoxybenzene as an internal standard. And we have done the NMR yield calculation only for those TNP compounds that are fairly soluble in deuterated solvent.

TNP-*p*-Amyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-amylaniline (121.48 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*p*-Amyl at 9.65 ppm and aromatic C-H of 1,3,5 trimethoxybenzene as an internal standard. The calculated NMR yield was 95%.

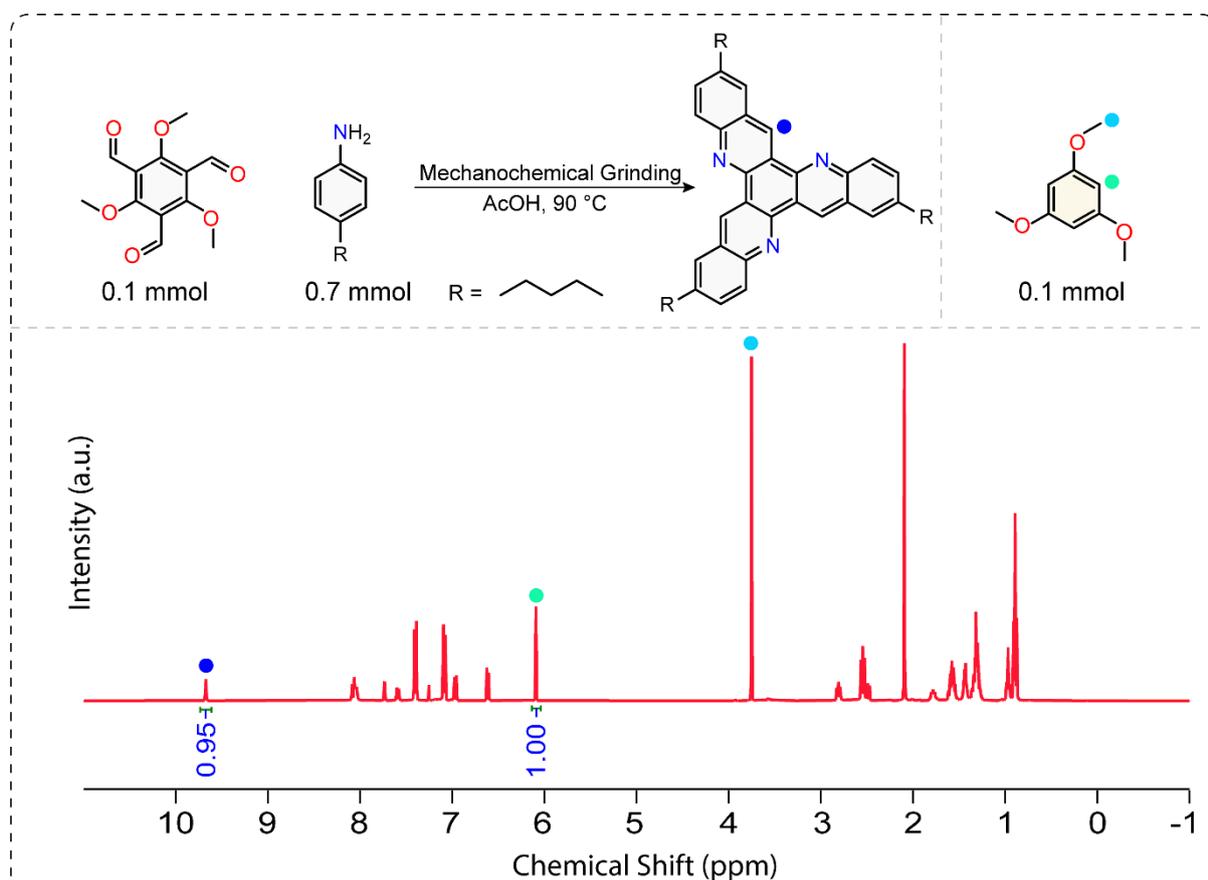


Fig. S72 ^1H NMR yield calculation of TNP-*p*-Amyl. 0.1 mmol of 1,3,5 trimethoxy benzene was taken as internal standard. The reaction was done in presence of 0.1 mmol of TP-OMe and 0.7 mmol of *p*-amylaniline. The calculated yield was 95%.

TNP-*p*-Butyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-butylaniline (110.45 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*p*-Amyl at 9.68 ppm and aromatic C-H of 1,3,5-trimethoxybenzene as an internal standard. The calculated NMR yield was 82%.

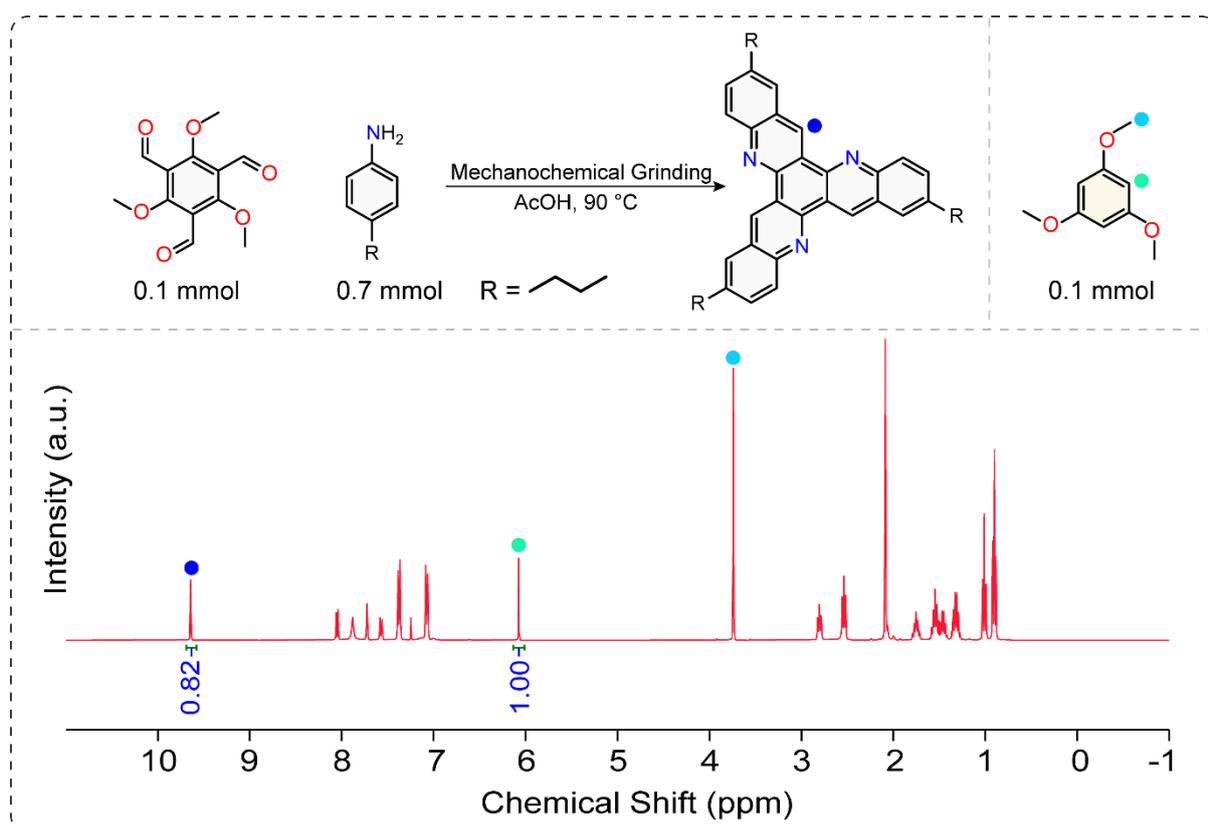


Fig. S73 1 H NMR yield calculation of TNP-*p*-Butyl. 0.1 mmol of 1,3,5 trimethoxy benzene was taken as internal standard. The reaction was done in presence of 0.1 mmol of TP-OMe and 0.7 mmol of *p*-butylaniline. The calculated yield was 82%.

TNP-*p*-Propyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-propylaniline (147.01 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*p*-Propyl at 9.66 ppm and aromatic C-H of 1,3,5-trimethoxybenzene as an internal standard. The calculated NMR yield was 93%.

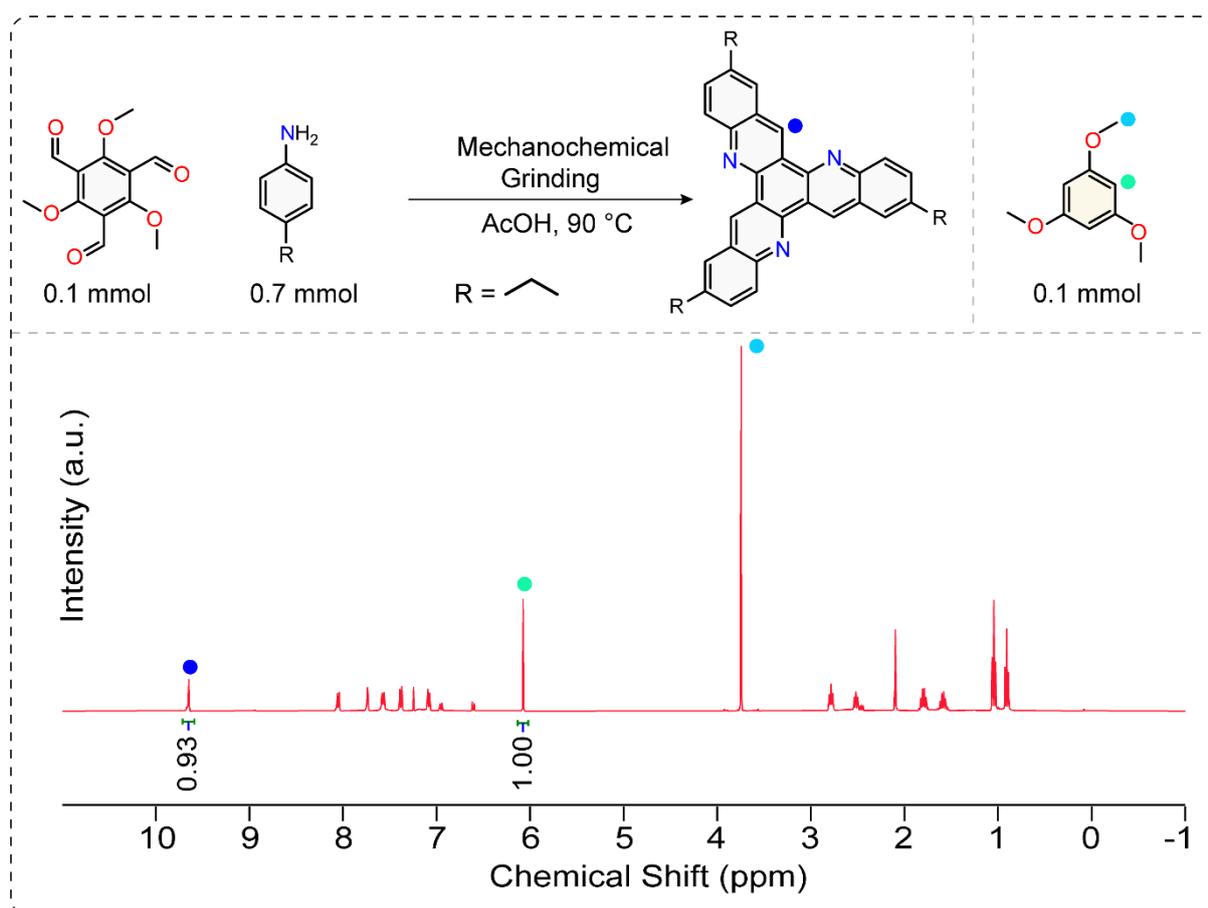


Fig. S74 ^1H NMR yield calculation of TNP-*p*-Prop. 0.1 mmol of 1,3,5-trimethoxybenzene was taken as an internal standard. The reaction was done in the presence of 0.1 mmol of TP-OME and 0.7 mmol of *p*-propylaniline. The calculated yield was 93%.

TNP-*p*-Ethyl

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and *p*-ethylaniline (87 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of the area under the pyridinic C-H of TNP-*p*-Propyl at 9.62 ppm and the aromatic C-H of 1,3,5-trimethoxybenzene as an internal standard. The calculated NMR yield was 84%.

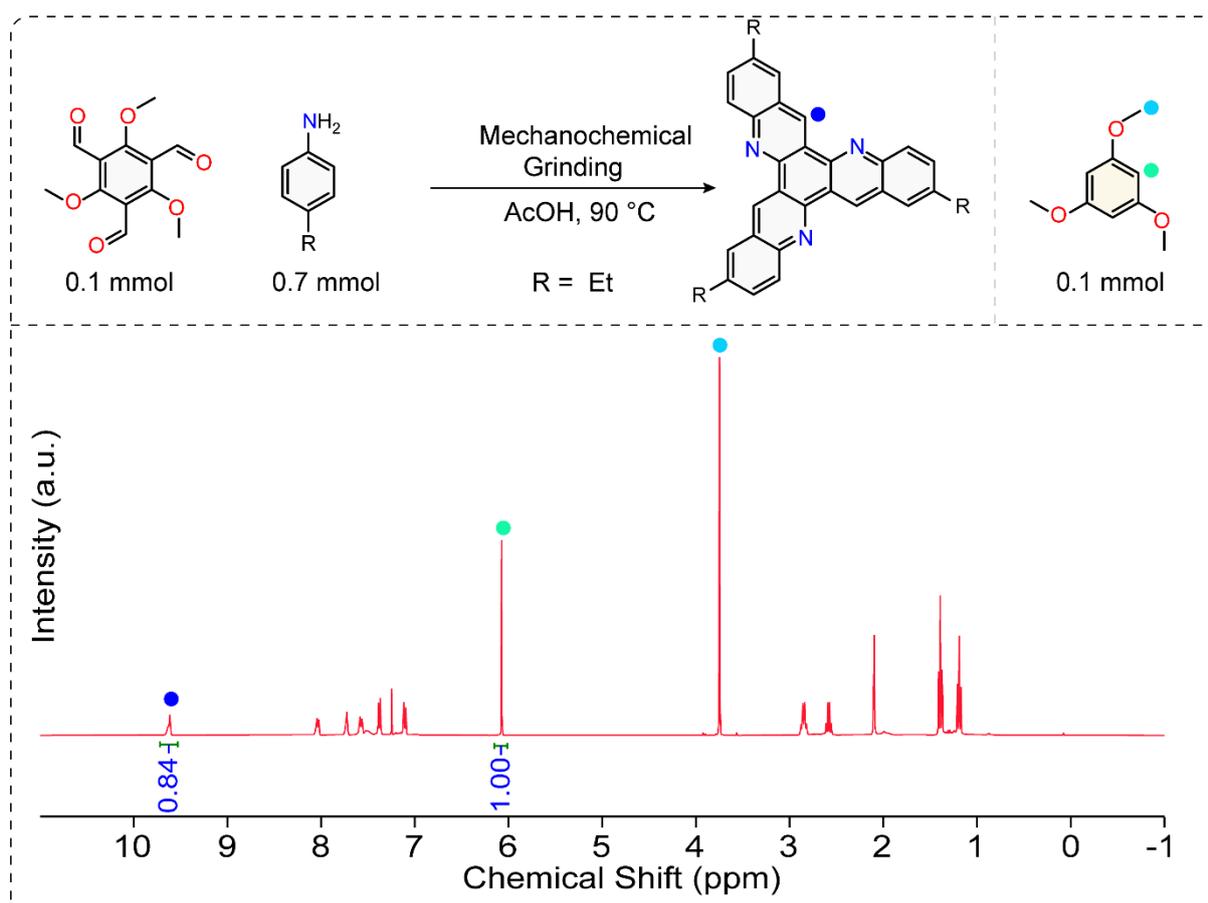


Fig. S75 1 H NMR yield calculation of TNP-*p*-Ethyl. 0.1 mmol of 1,3,5 trimethoxy benzene was taken as internal standard. The reaction was done in the presence of 0.1 mmol of TP-OMe and 0.7 mmol of *p*-ethylaniline. The calculated yield was 84%.

TNP-*p*-iPr

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-isopropyl aniline (98.6 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*p*-Propyl at 9.81 ppm and aromatic C-H of 1,3,5-trimethoxybenzene as an internal standard. The calculated NMR yield was 94%.

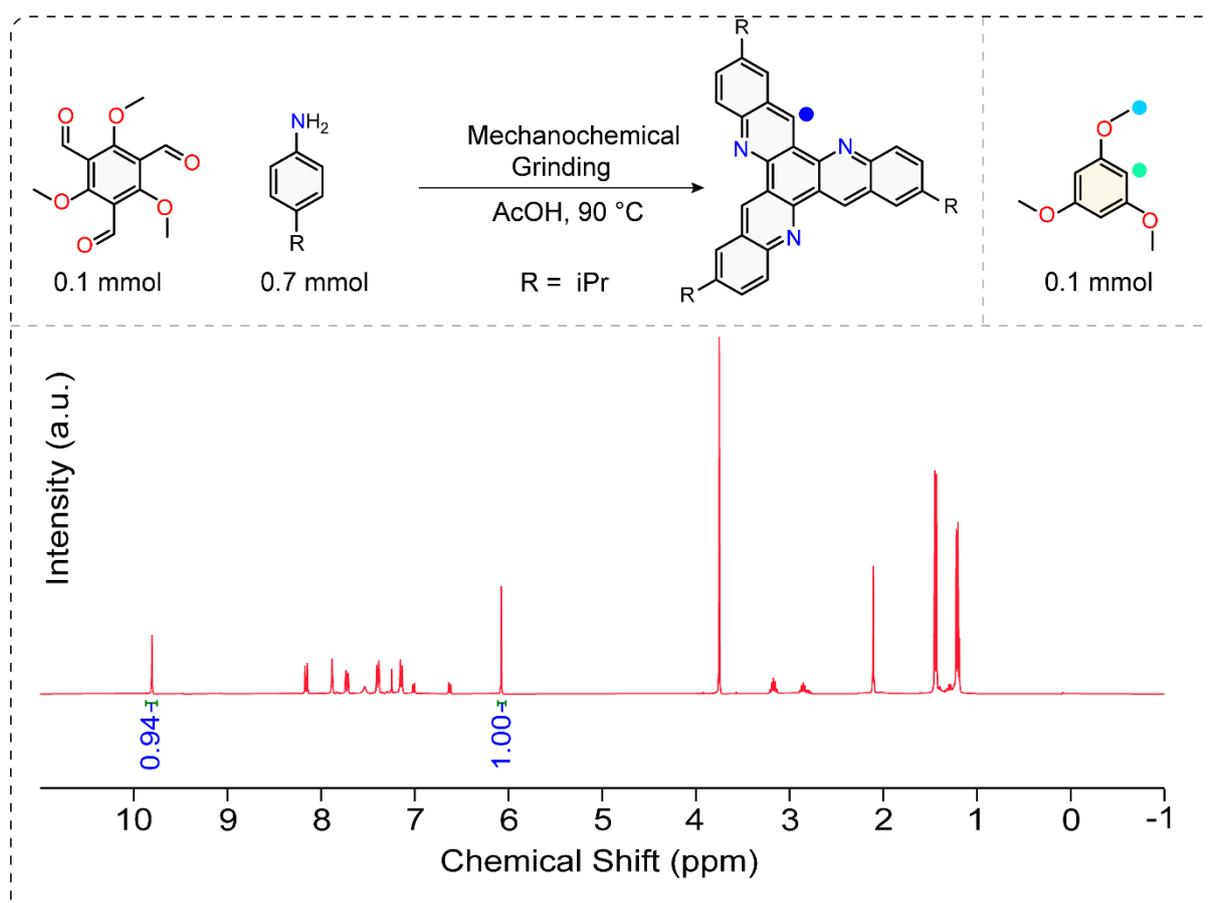


Fig. S76 ^1H NMR yield calculation of TNP-*p*-iPr. 0.1 mmol of 1,3,5 trimethoxybenzene was taken as internal standard. The reaction was done in the presence of 0.1 mmol of TP-OMe and 0.7 mmol of *p*-iso-propylaniline. The calculated yield was 94%.

TNP-*m*-iPr

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3-isopropyl aniline (98.6 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*p*-Propyl at 9.81 ppm and aromatic C-H of 1,3,5-trimethoxybenzene as an internal standard. The calculated NMR yield was 94%.

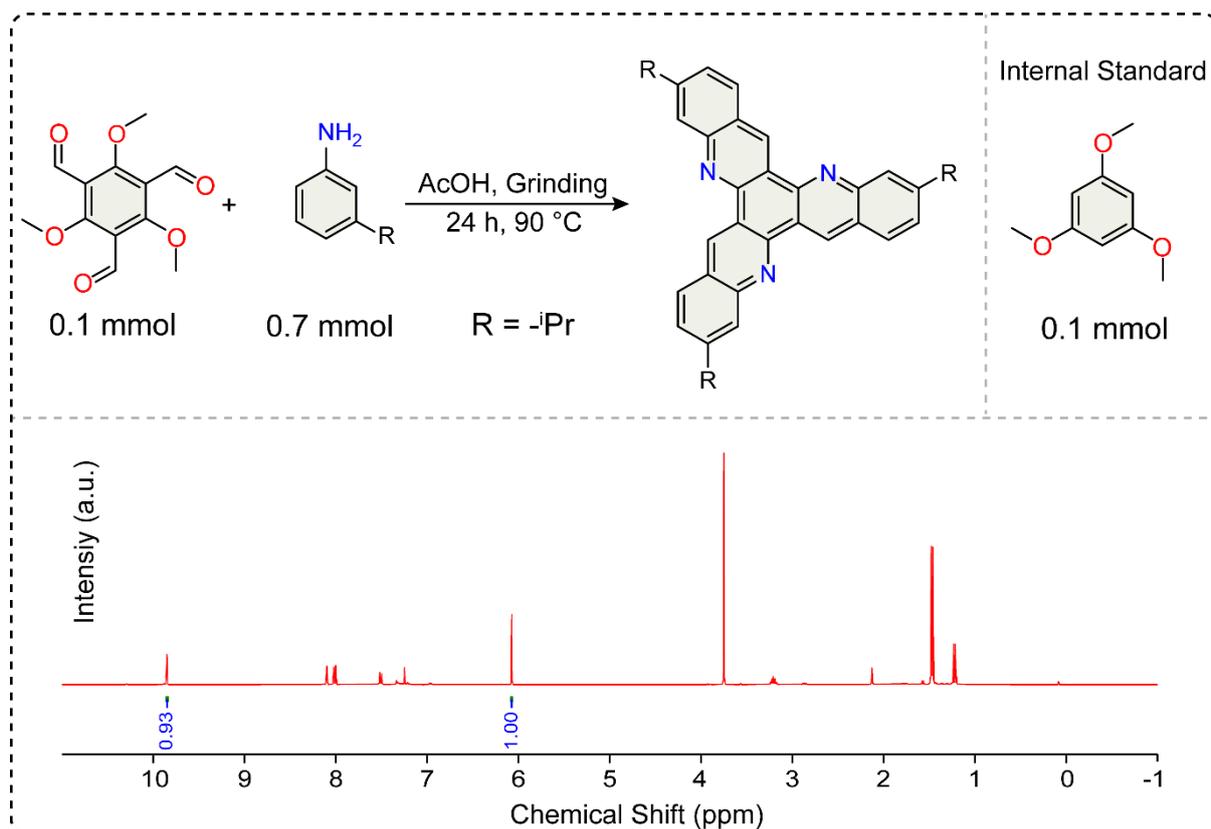


Fig. S77 ¹H NMR yield calculation of TNP-*m*-iPr. 0.1 mmol of 1,3,5-trimethoxybenzene was taken as an internal standard. The reaction was done in the presence of 0.1 mmol of TP-OMe and 0.7 mmol of 3-isopropyl aniline. The calculated yield was 95%.

TNP-*p*-^tBu

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 4-tertbutylaniline (112 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*p*-*t*Bu at 9.93 ppm and aromatic C-H of 1,3,5 trimethoxybenzene as an internal standard. The calculated NMR yield was 95%.

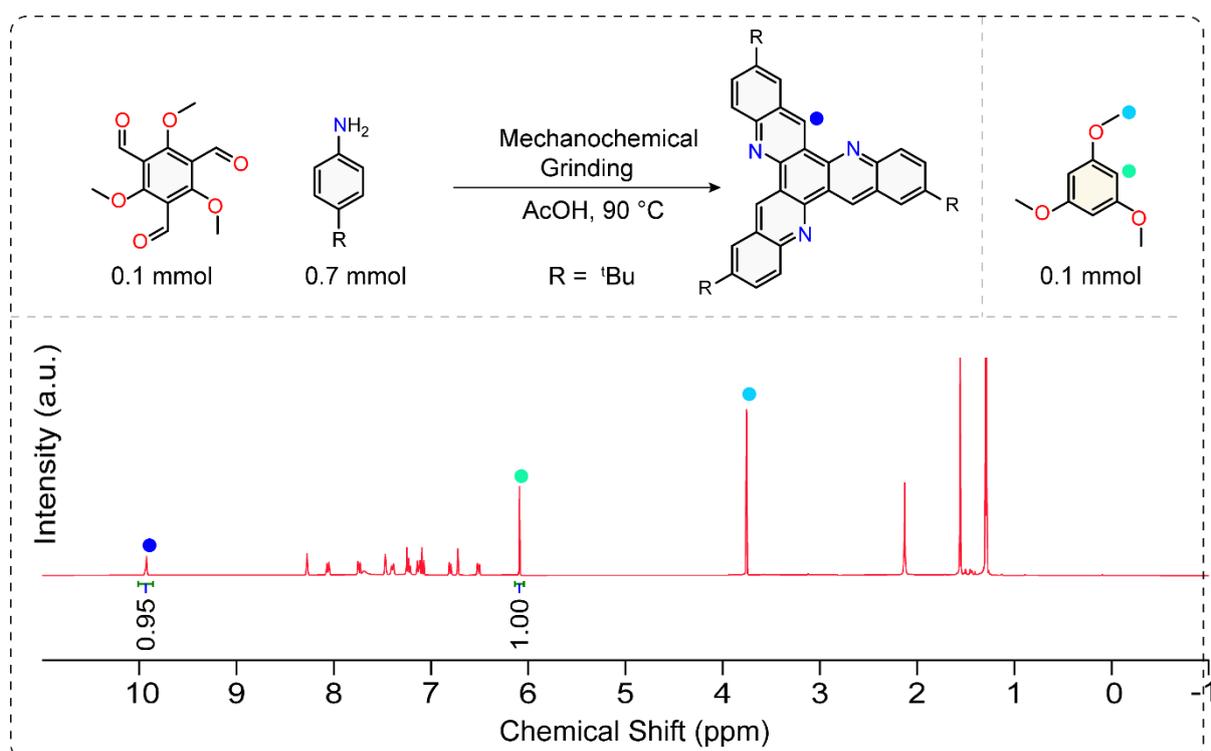


Fig. S78 ¹H NMR yield calculation of TNP-*p*-*t*Bu. 0.1 mmol of 1,3,5 trimethoxy benzene was taken as internal standard. The reaction was done in the presence of 0.1 mmol of TP-OMe and 0.7 mmol of *p*-tert-butylaniline. The calculated yield was 95%.

TNP-*m*-^tBu

2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (25.2 mg, 0.1 mmol) and 3-tertbutylaniline (112 μ L, 0.7 mmol) were placed in a mortar, followed by the addition of glacial acetic acid (100 μ L) as a catalyst. The mixture was ground manually for 25 minutes, transferred to a glass vial, and heated at 90 $^{\circ}$ C for 24 h. After cooling to room temperature, the crude reaction mixture was purified by column chromatography (hexane/ethyl acetate) to afford the desired product. Here, the NMR yield was calculated taking the ratio of area under the pyridinic C-H of TNP-*m*-^tBu at 9.88 ppm and aromatic C-H of 1,3,5 trimethoxybenzene as an internal standard. The calculated NMR yield was 94%.

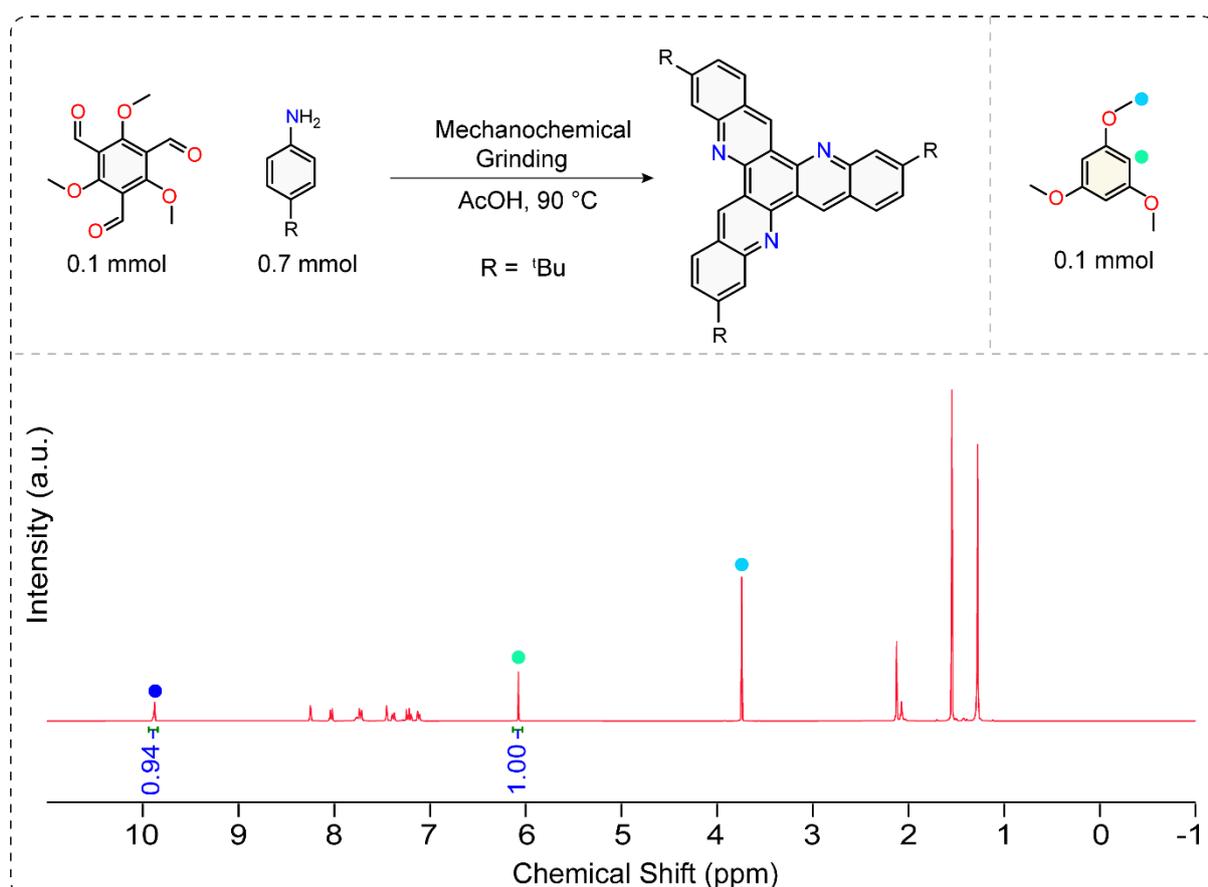


Fig. S79 1 H NMR yield calculation of TNP-*m*-^tBu. 0.1 mmol of 1,3,5-trimethoxybenzene was taken as an internal standard. The reaction was done in the presence of 0.1 mmol of TP-OMe and 0.7 mmol of *m*-tert-butylaniline. The calculated yield was 94%.

Section S6: Mechanistic Investigation

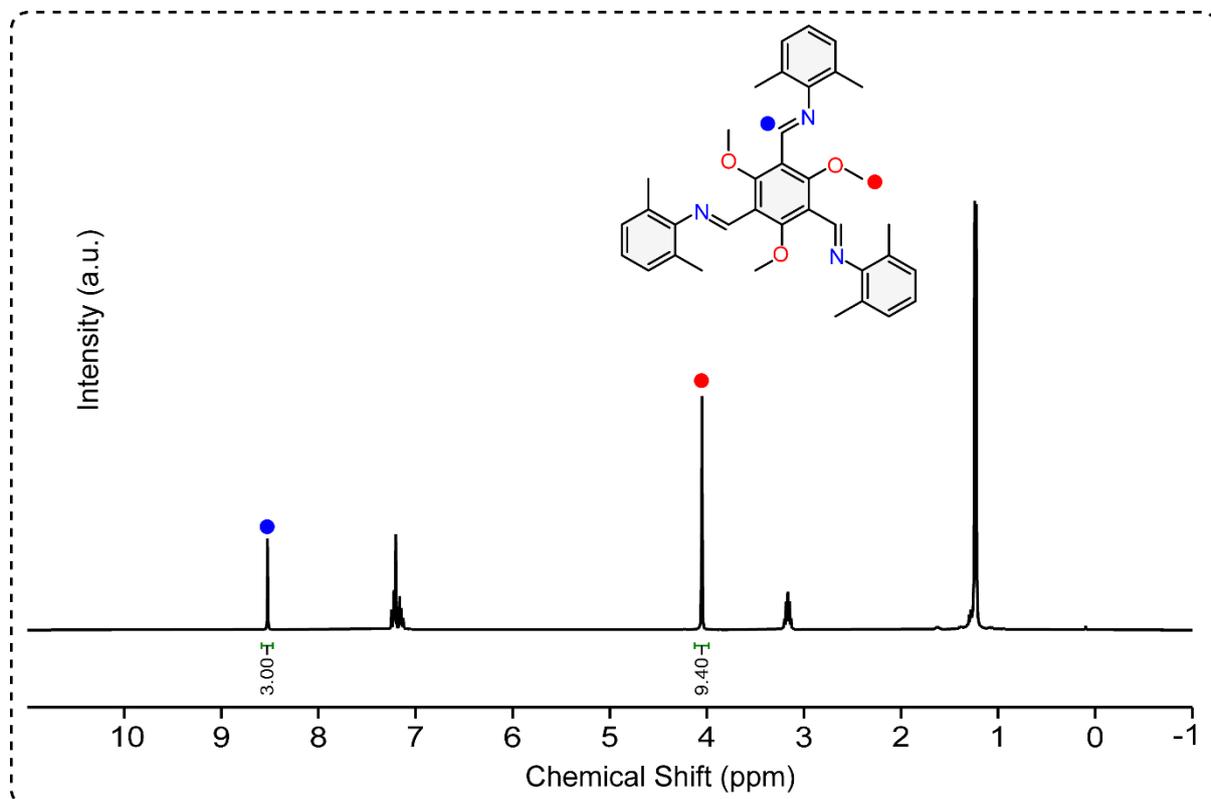


Fig. S80 ^1H NMR (400 MHz, Chloroform-*D*) of tri-imine complex

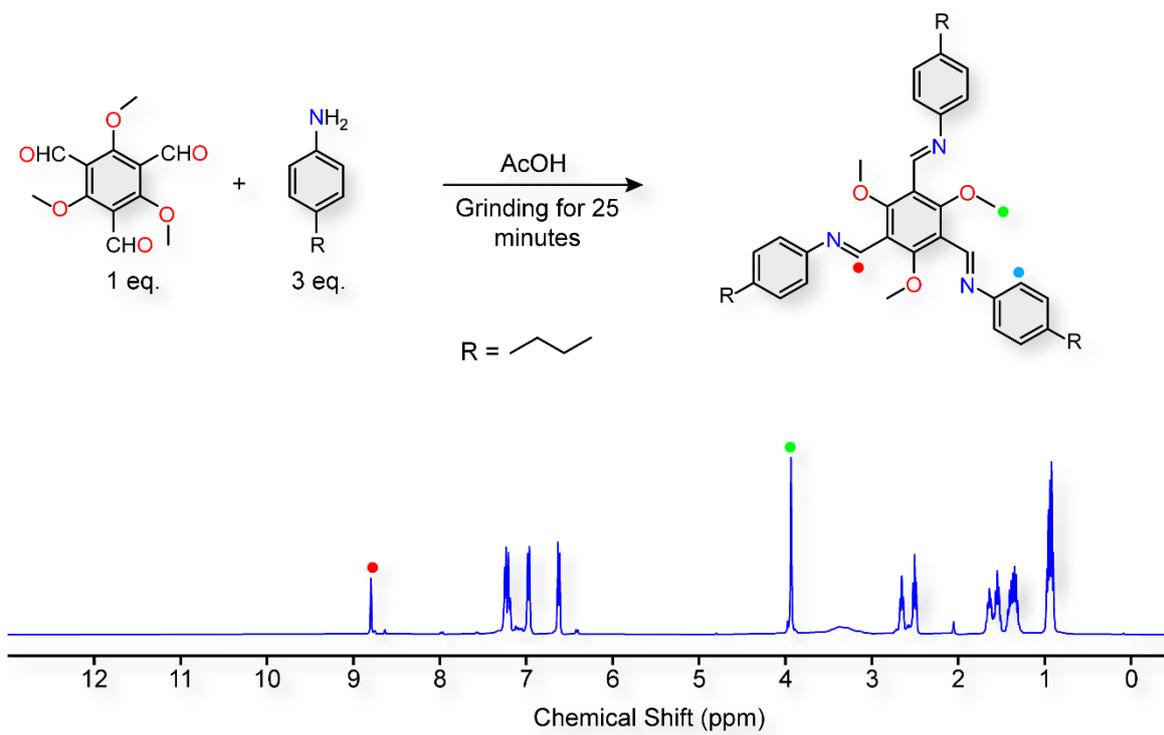


Fig. S81 ¹H NMR of the obtained product immediately after the grinding.

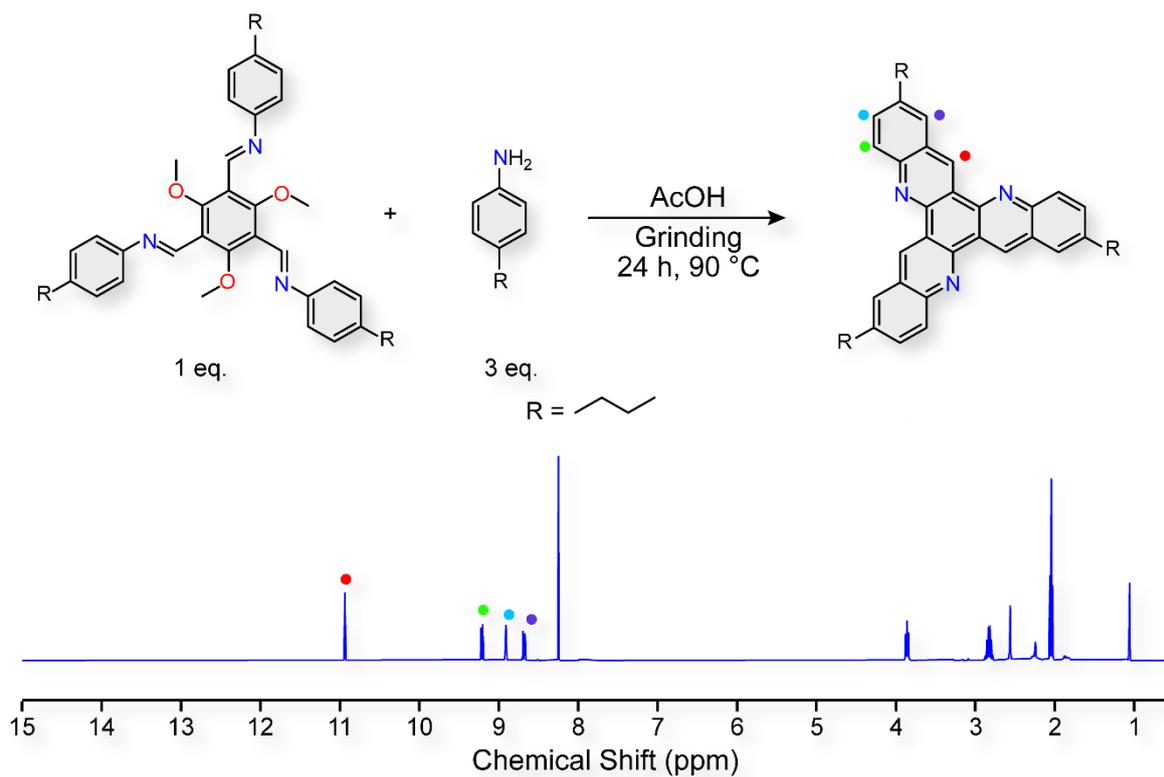


Fig. S82 ¹H NMR of tri-imine complex with *p*-butyl aniline

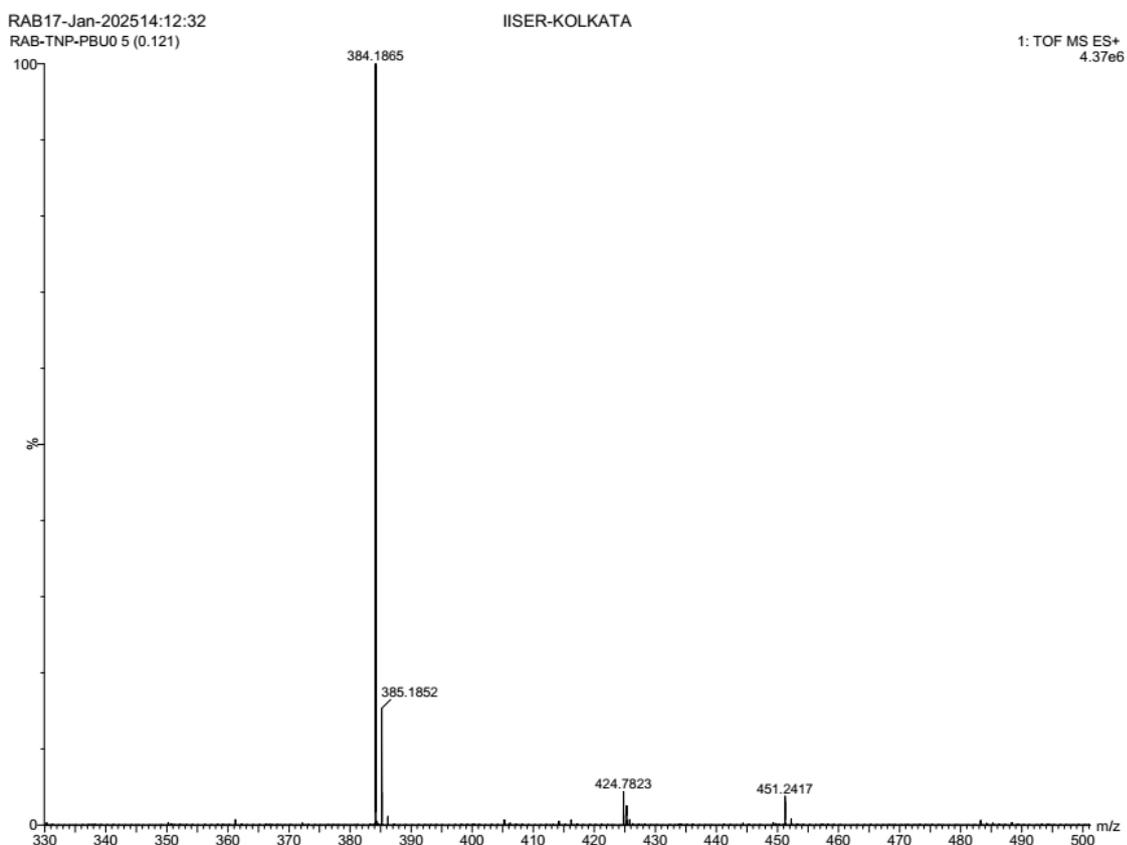


Fig. S83 High-resolution mass spectra of monoimine complex with *p*-butylaniline m/z: [M+H]⁺ calculated for C₂₂H₂₅NO₅ 384.1805; Found 384.1865

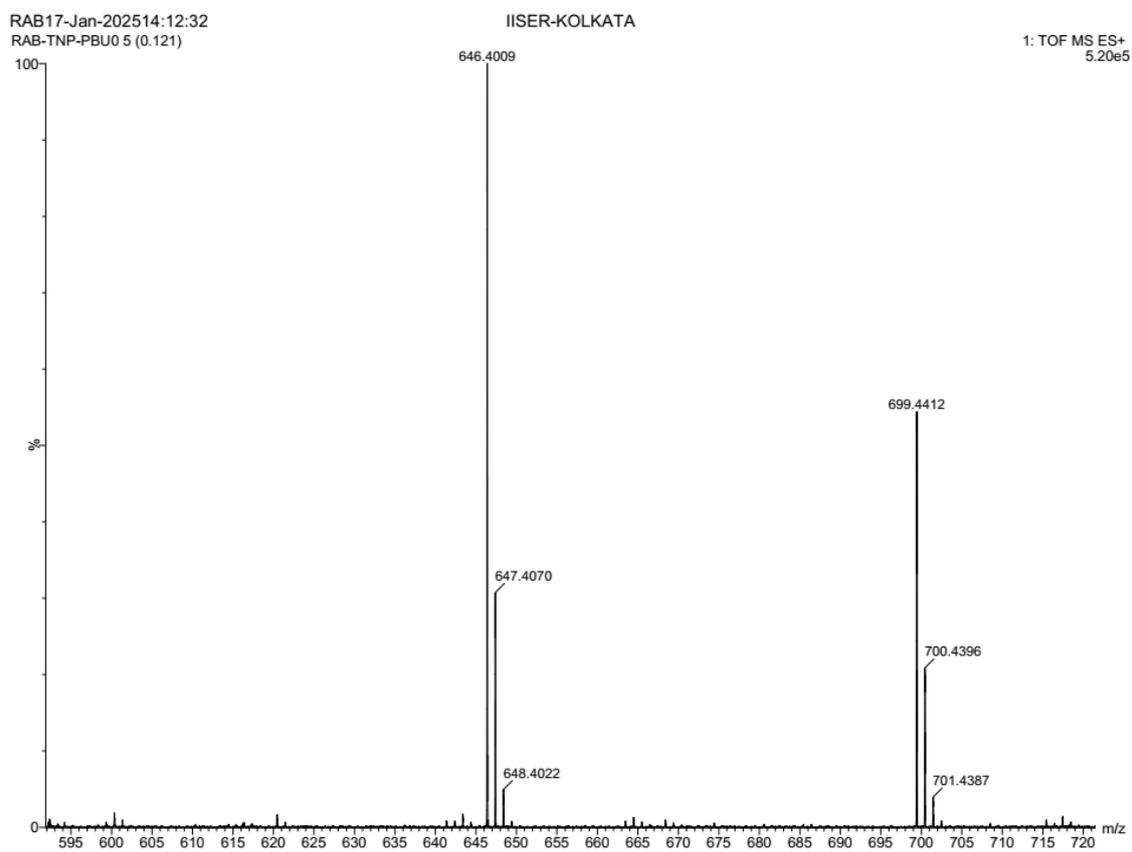


Fig. S84 High-resolution mass spectra of tri-immine complex with p-butylaniline m/z: $[M+H]^+$ calculated for $C_{42}H_{51}N_3O_3$ 646.4003; Found 646.4009

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RAB-TNP-PBU0 6 (0.138)

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1: TOF MS ES+
2.31e6

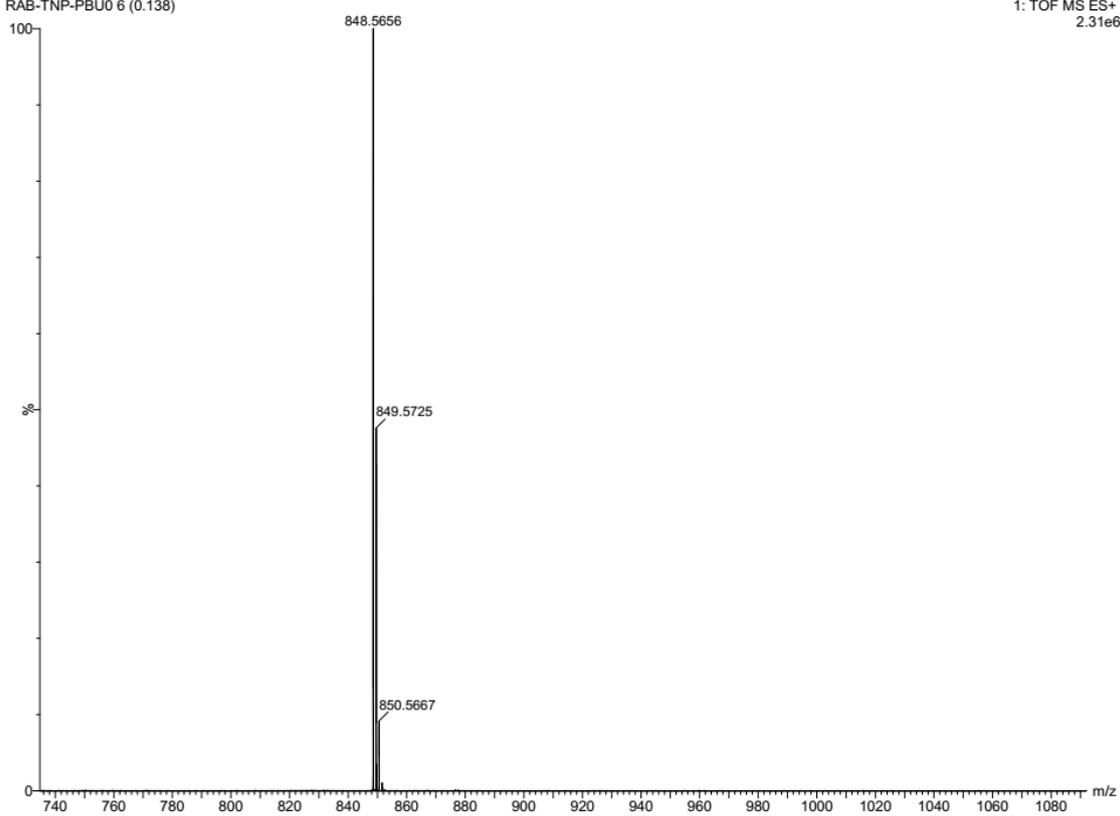


Fig. S85 High-resolution mass spectra of intermediate after one side ring cyclization
 $m/z: [M+H]^+$ calculated for $C_{59}H_{69}N_5$ 848.5625; Found 848.5656

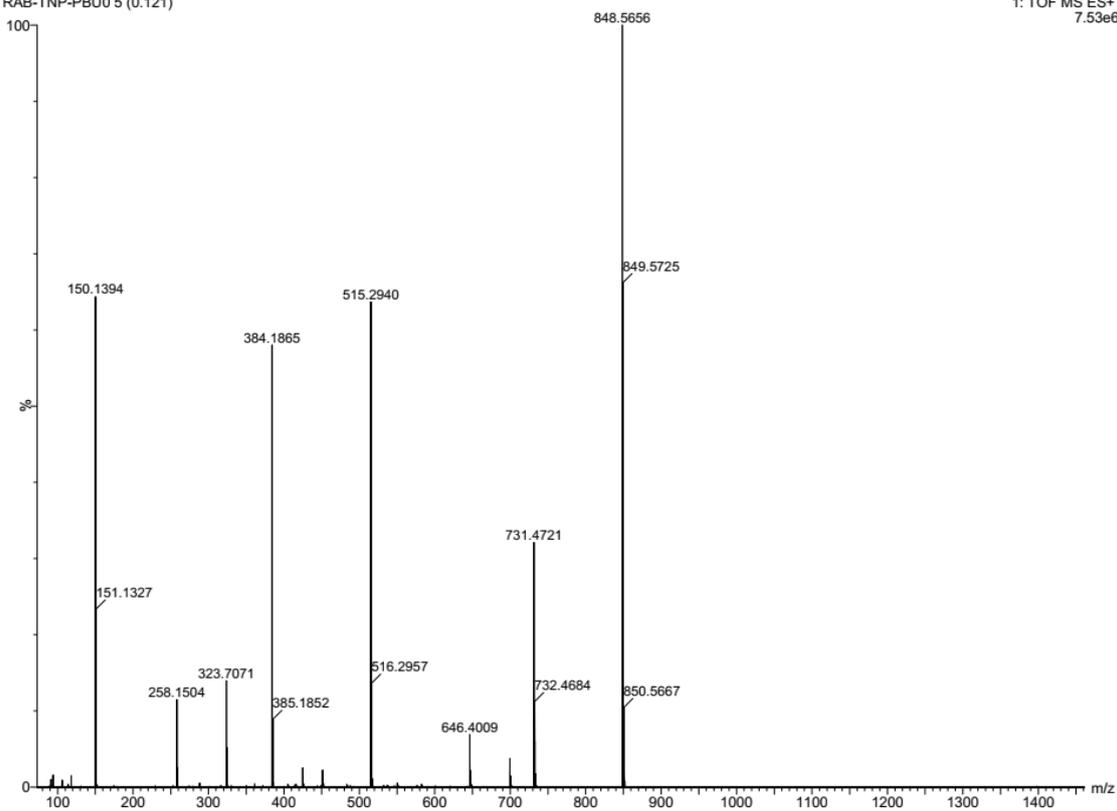


Fig. S86 Full range High-resolution mass spectra of three intermediates.

Section S7: Synthesis of TNP-Hexa-hydroxy ligand and Metal Organic Framework

Synthesis of TNP(OH)₆:

TNP(OMe)₆ (0.09 mmol) was treated with pyridine hydrochloride (1.8 mmol), and the mixture was subjected to thermal treatment at 180 °C for 4 hours. Upon completion of the reaction, the mixture was thoroughly washed with copious amounts of water to remove excess pyridine hydrochloride. The resulting solid was then dried under vacuum to yield the demethylated product. ¹H NMR (400 MHz, DMSO-*D*₆) δ 10.42 (s, 1H), 10.05 (s, 1H), 9.59 (s, 1H), 7.47 (s, 3H), 7.45 (s, 3H).

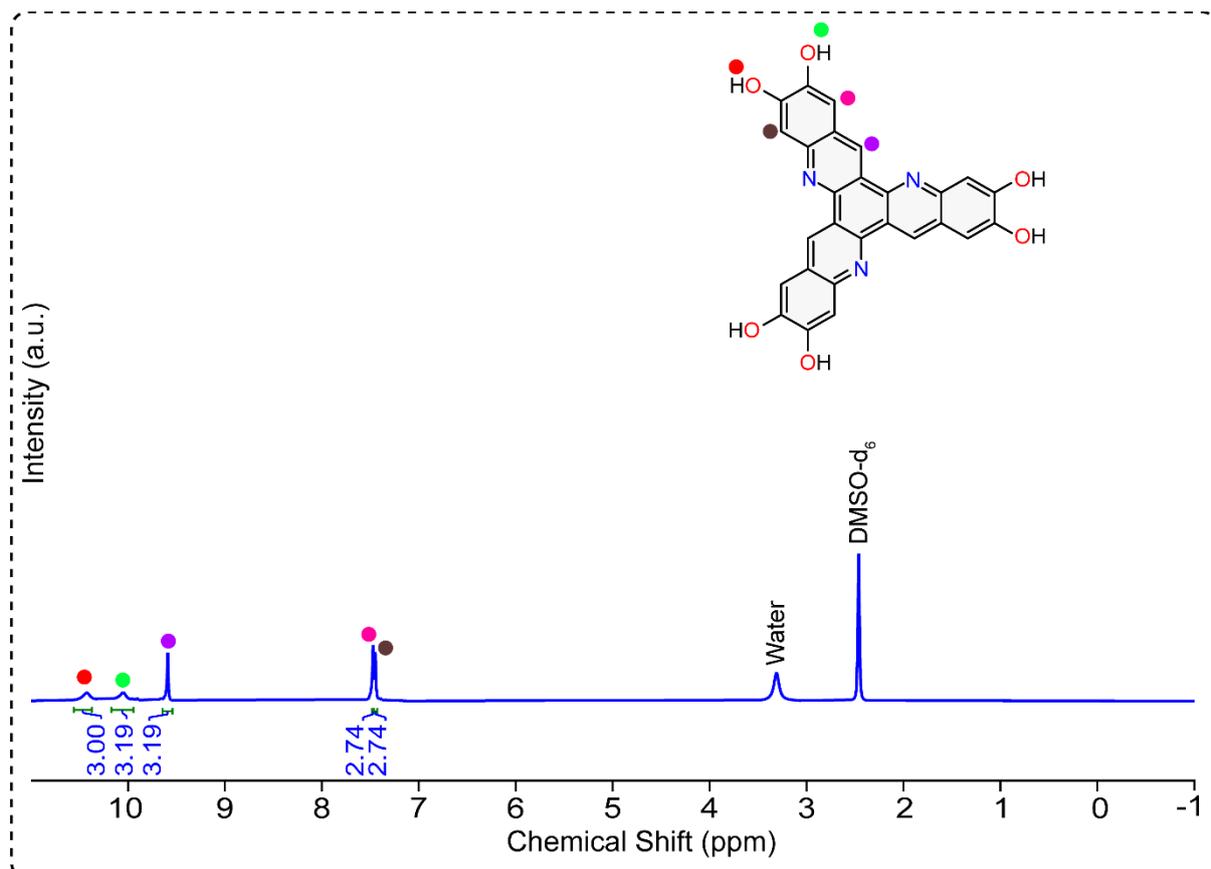


Fig. S87 ¹H NMR (400 MHz, DMSO-*D*₆) δ 10.42 (s, 1H), 10.05 (s, 1H), 9.59 (s, 1H), 7.47 (s, 3H), 7.45 (s, 3H).

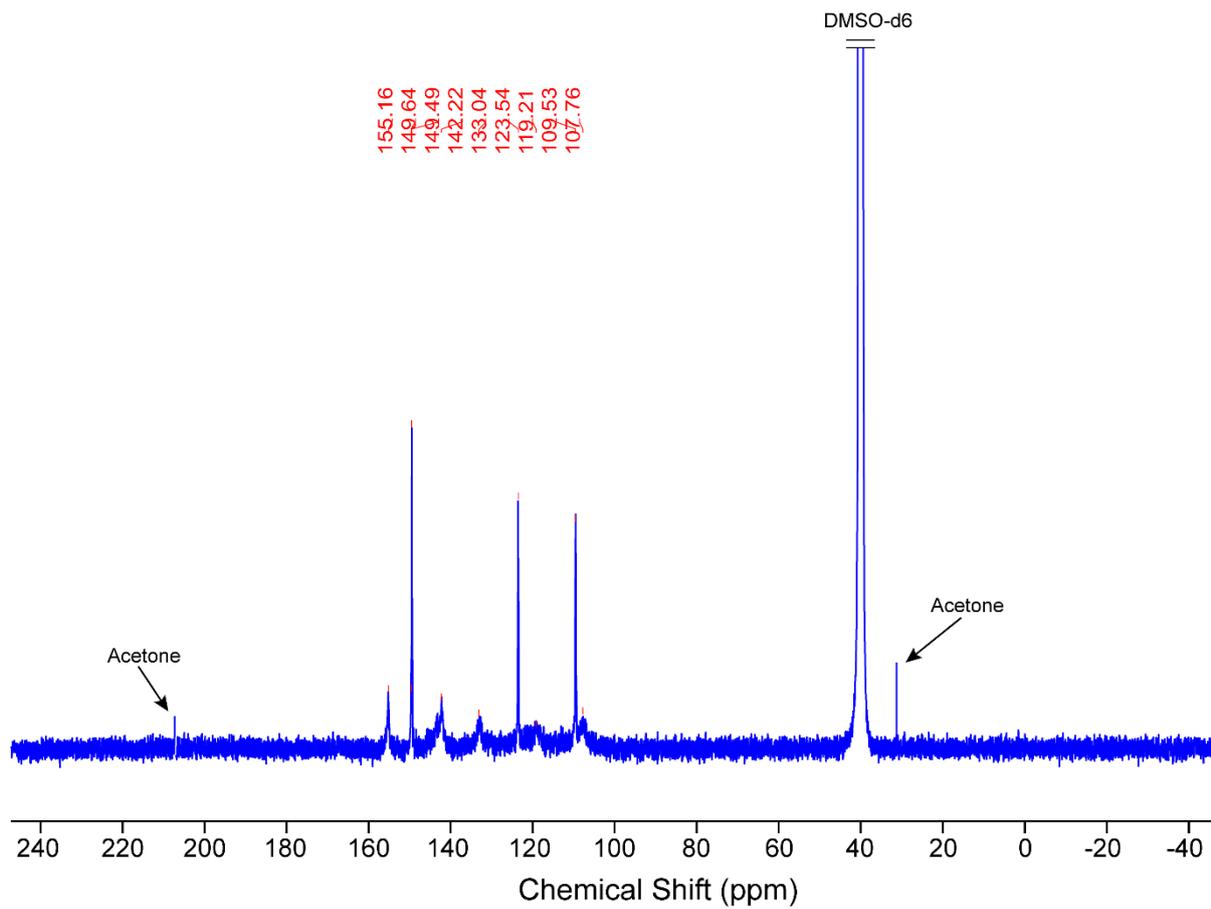


Fig. S88 ^{13}C NMR (101 MHz, CDCl_3) δ 156.16, 149.64, 149.49, 142.22, 133.04, 123.54, 119.21, 109.53., 107.76.

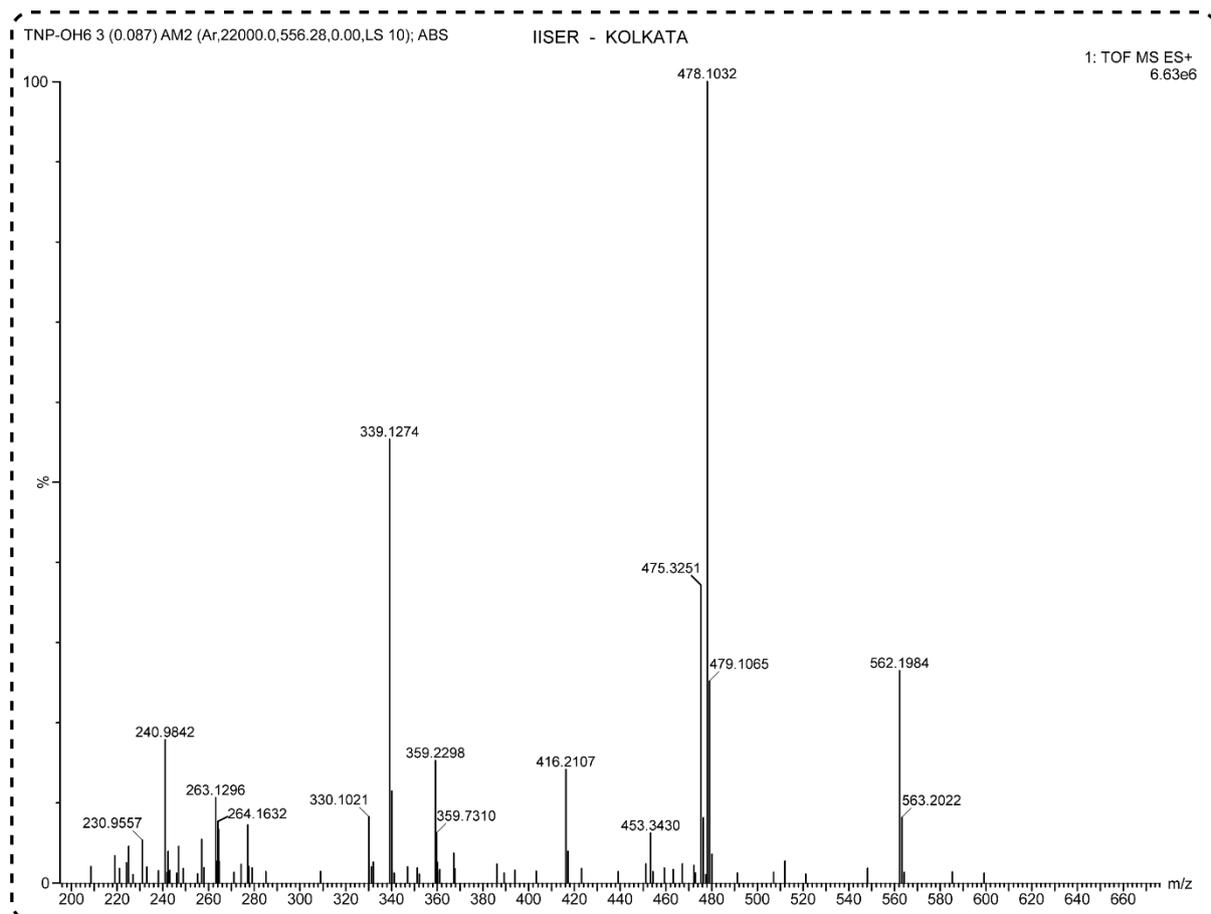


Fig. S89 High-resolution mass spectra of TNP(OH)₆. m/z: [M+H]⁺ calculated for C₂₇H₁₆N₃O₆ 478.1039; Found 478.1032.

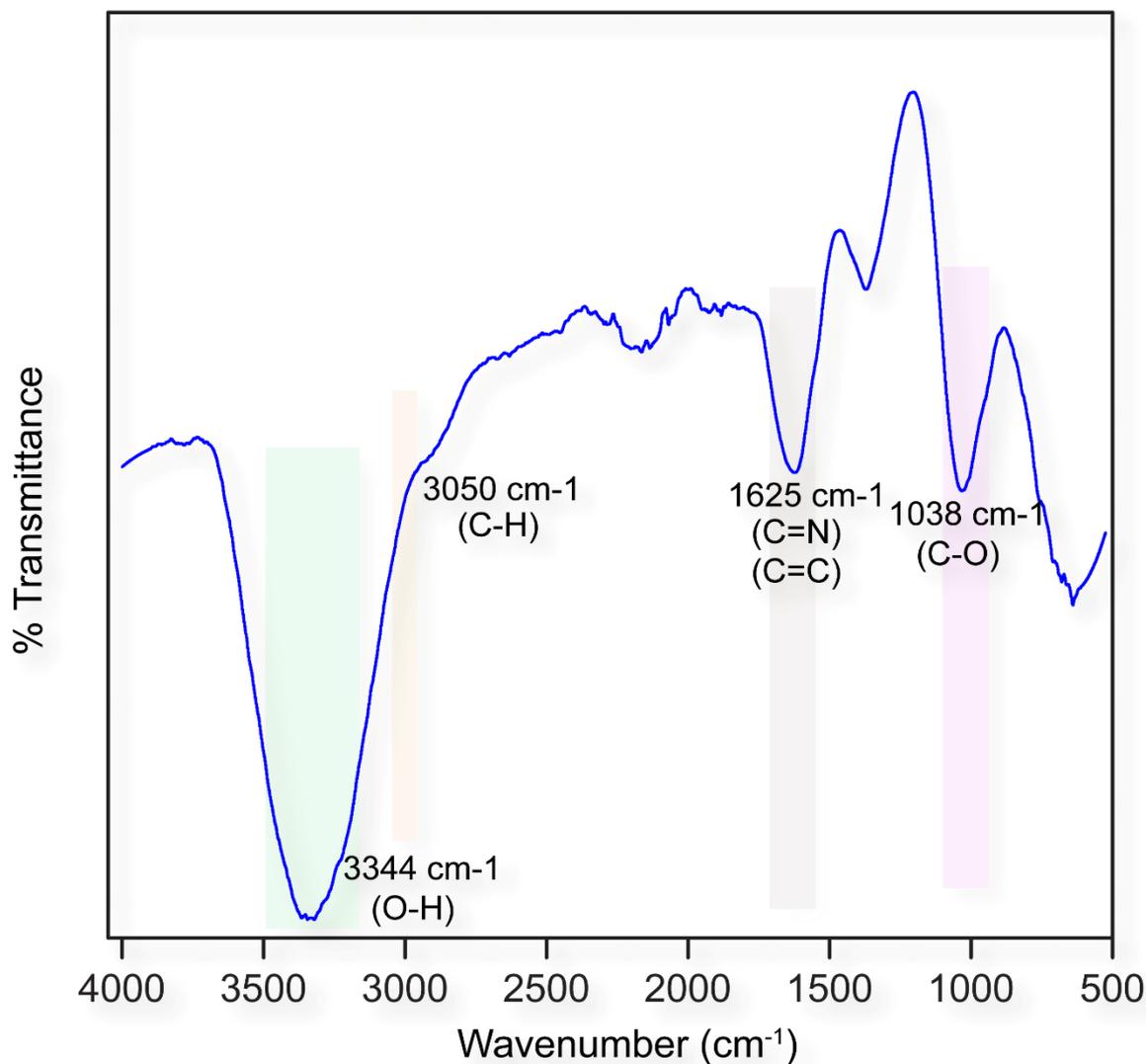


Fig. S90 IR spectra of TNP(OH)₆

Synthesis of MOF:

TNP(OH)₆ (30 mg, 0.067 mmol, 1.0 equiv) was dissolved in 0.2 mL of DMSO. To this solution, an aqueous solution of CuSO₄·5H₂O (41.6 mg, 0.167 mmol, 2.5 equiv in 1.6 mL deionized water) was added dropwise under ambient conditions, resulting in the immediate formation of a black precipitate. The resulting suspension was transferred to a sealed glass vial and subjected to treatment at 150 °C for 12 h. After cooling to room temperature, the solid product was isolated by vacuum filtration, washed thoroughly with hot DMSO and acetone to remove unreacted starting materials and byproducts, and subsequently dried in a hot-air oven.

Section S8: Structural Characterization of Metal-Organic Framework

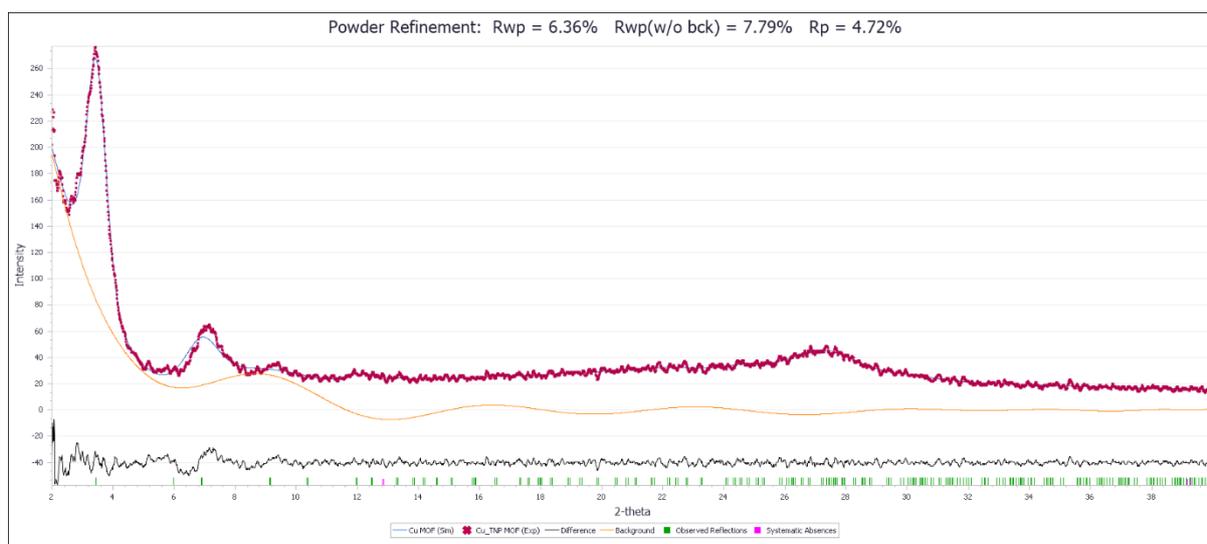


Fig. S91 Experimental (Red) compared with refined (Blue) PXRD profiles Cu-TNP-MOF difference plot is given in (black).

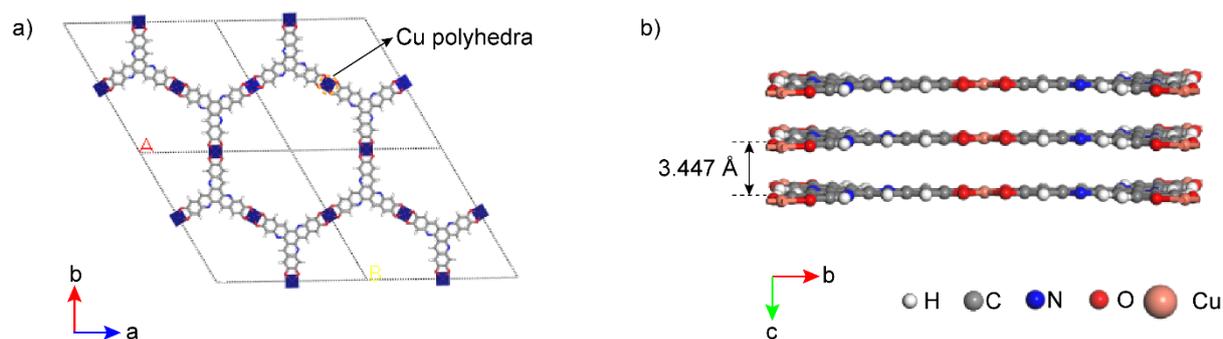


Fig. S92 (a) Top view of the crystal structure showing the two-dimensional framework in the *ab* plane, highlighting the arrangement of the organic linkers and the coordination environment of the Cu polyhedra. (b) Side view of the layered structure along *a* axis, illustrating the π - π stacked layers with an interlayer separation of 3.447 Å. Atom colors: H (light grey), C (grey), N (blue), O (red), and Cu (orange).

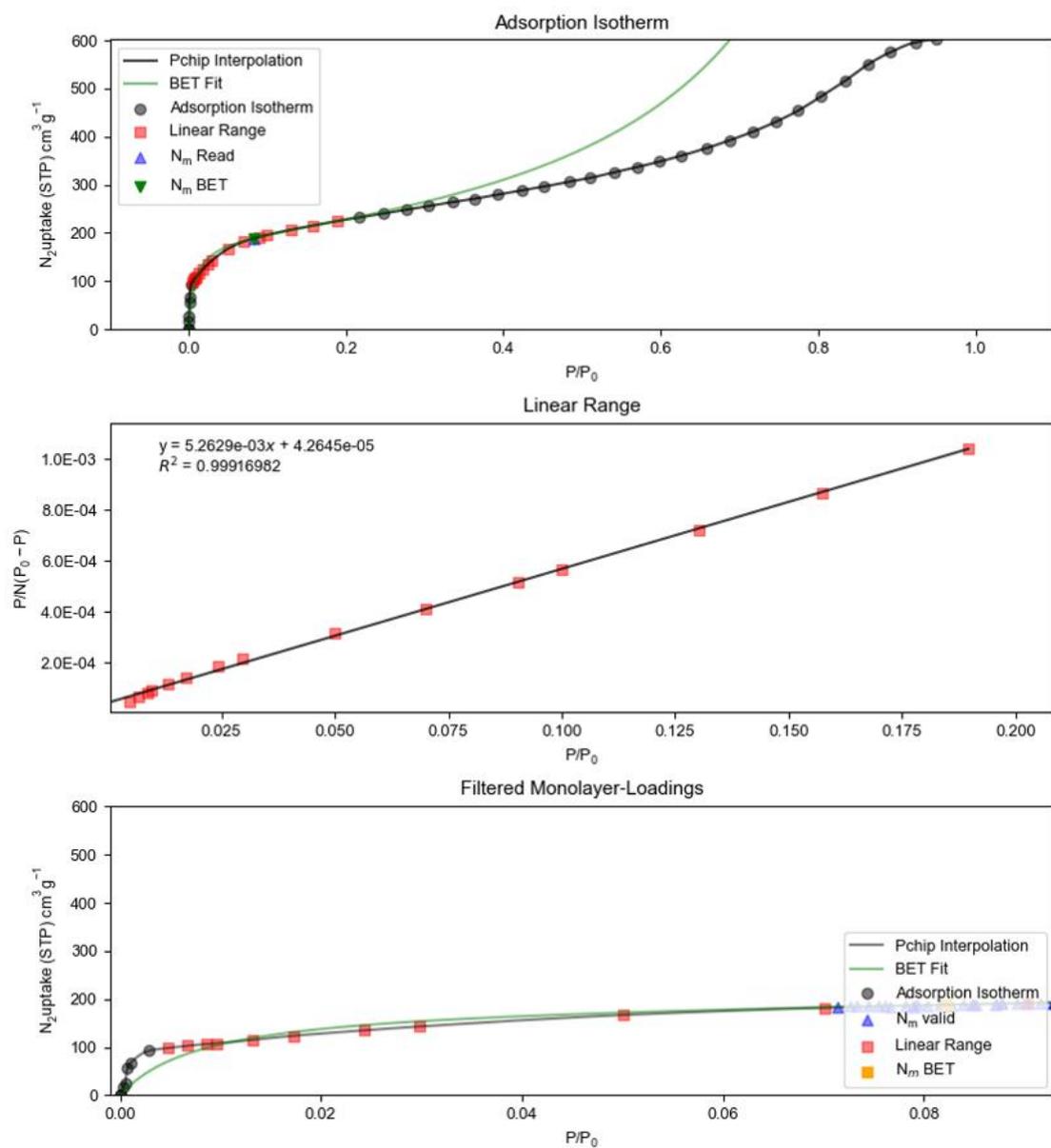


Fig. S93 a) Adsorption isotherm b) Linear fitting c) Filtered monolayer loading of Cu-TNP MOF

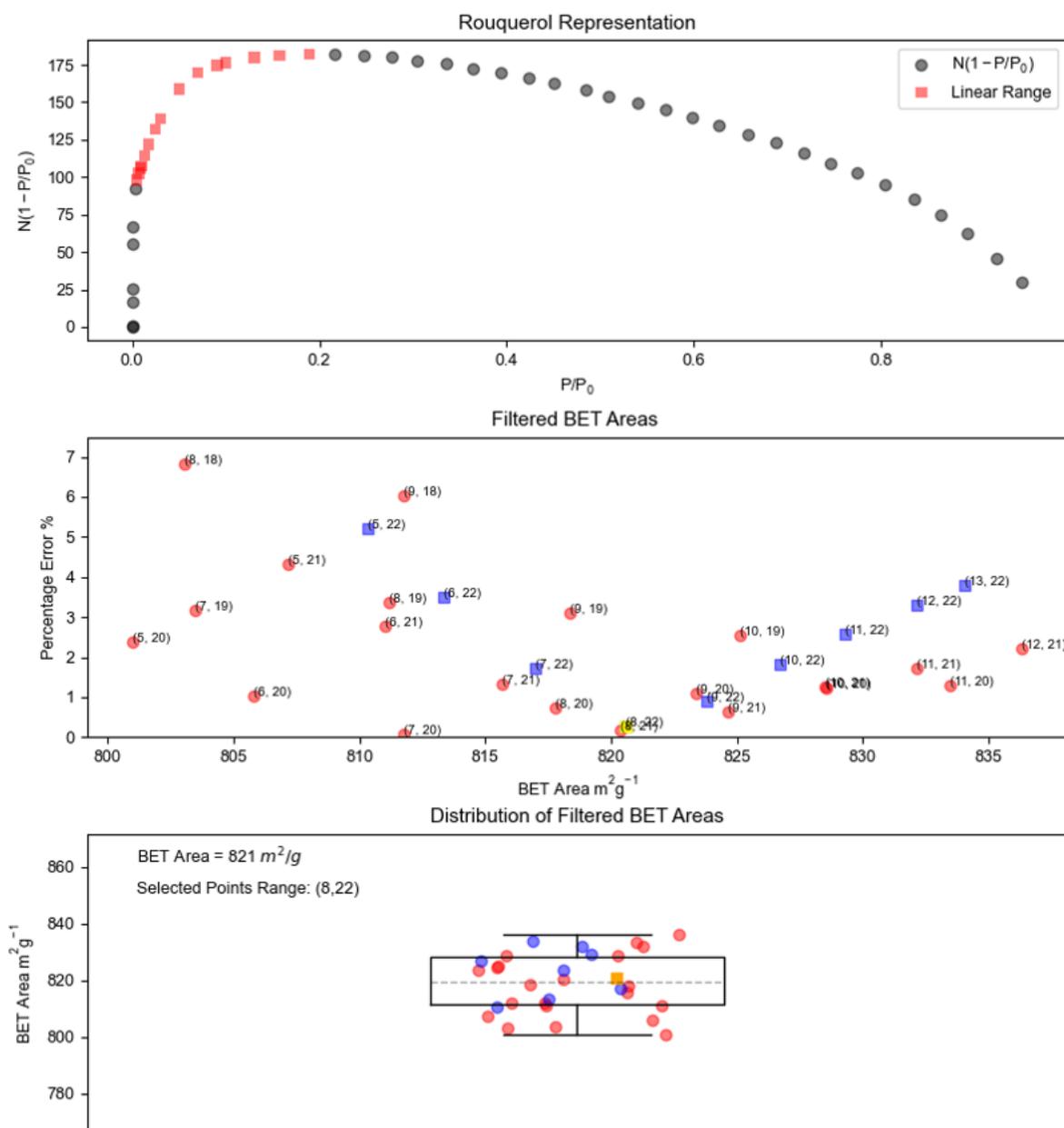


Fig. S94 BET Rouquerol details of Cu-TNP MOF

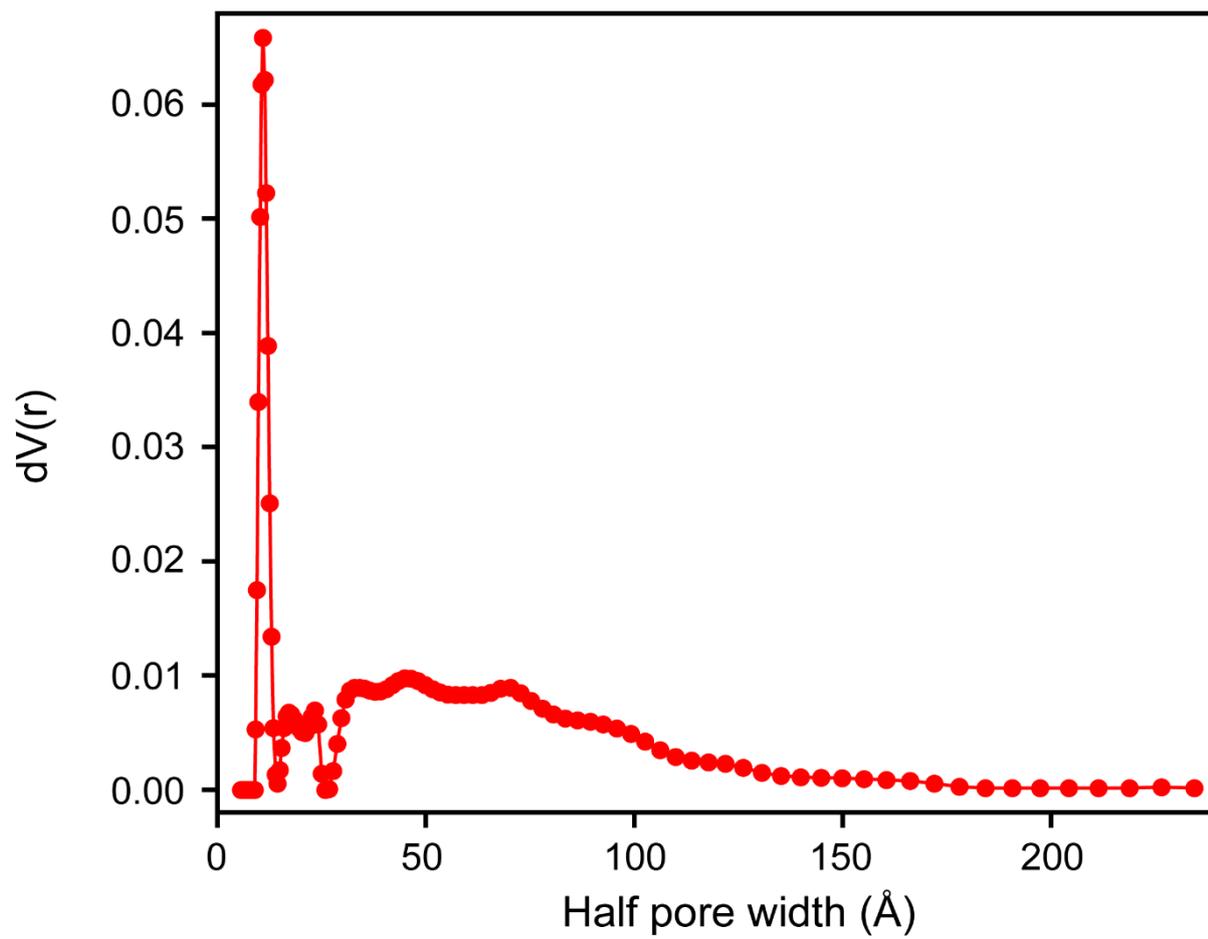


Fig. S95 Pore size distribution Cu-TNP MOF and TNP(OH)₆ MOF.

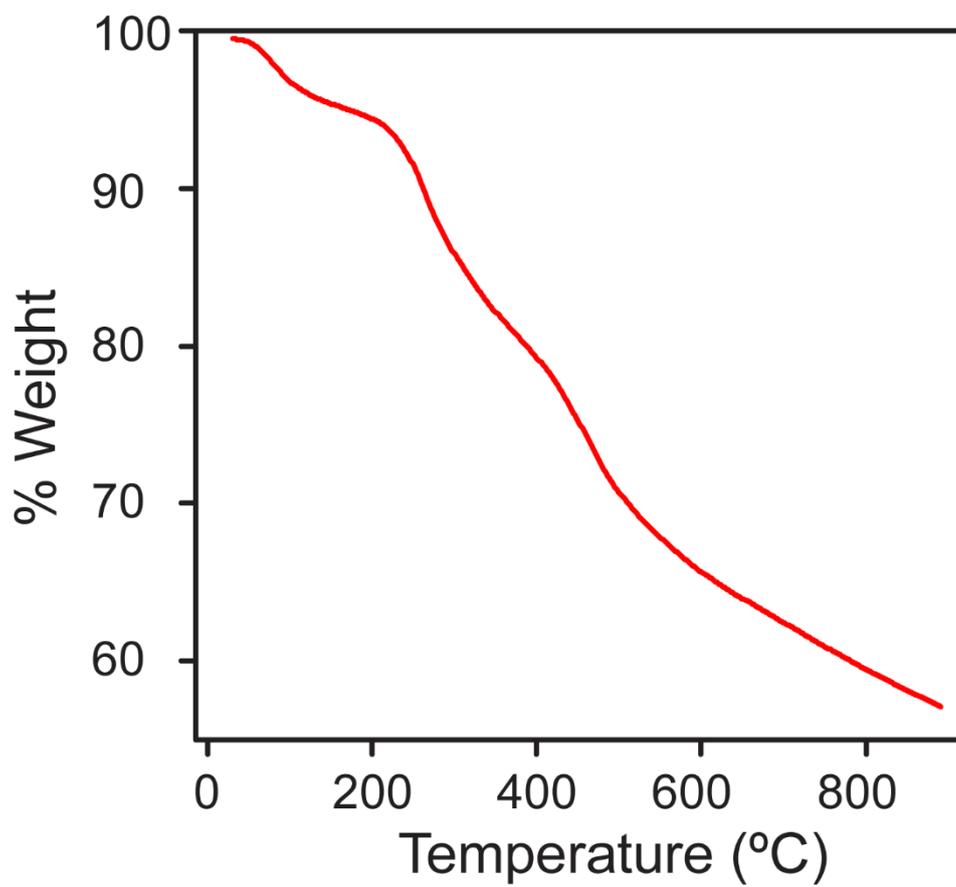


Fig. S96 Thermogravimetric Analysis (TGA) of Cu-TNP(OH)₆ MOF

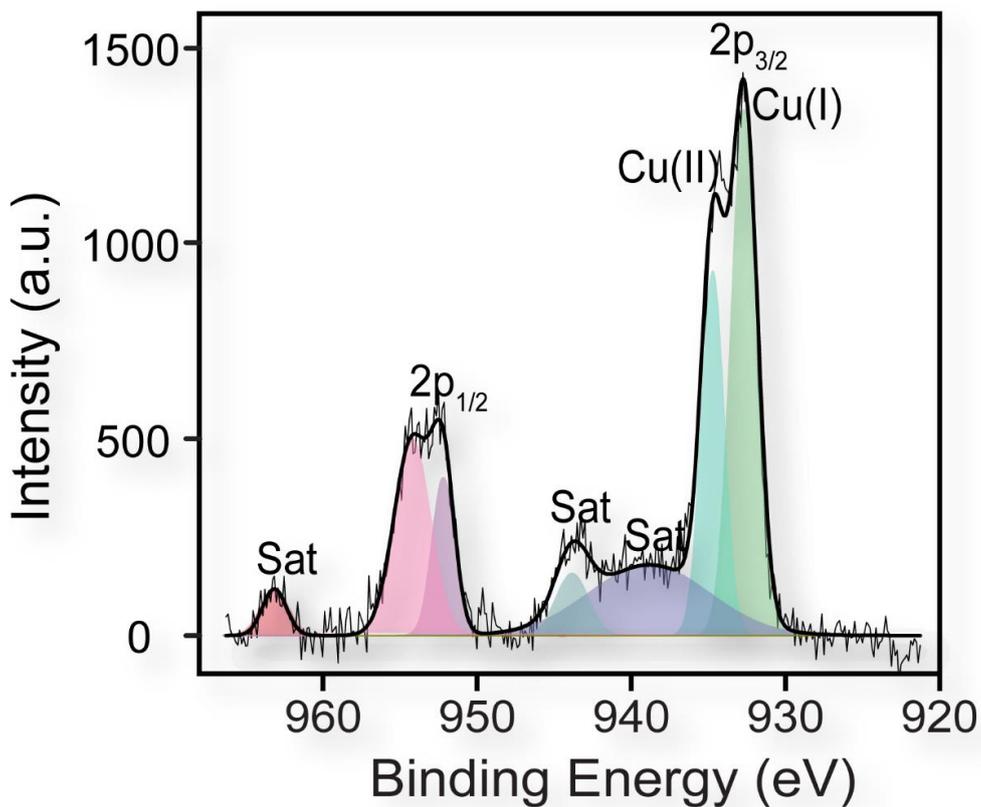


Fig. S97 XPS spectra of TNP-Cu-MOF showing the presence of mixed Cu(I) and Cu(II) oxidation states, with characteristic Cu 2p_{3/2} binding energies at 932.78 eV and 934.71 eV, respectively.

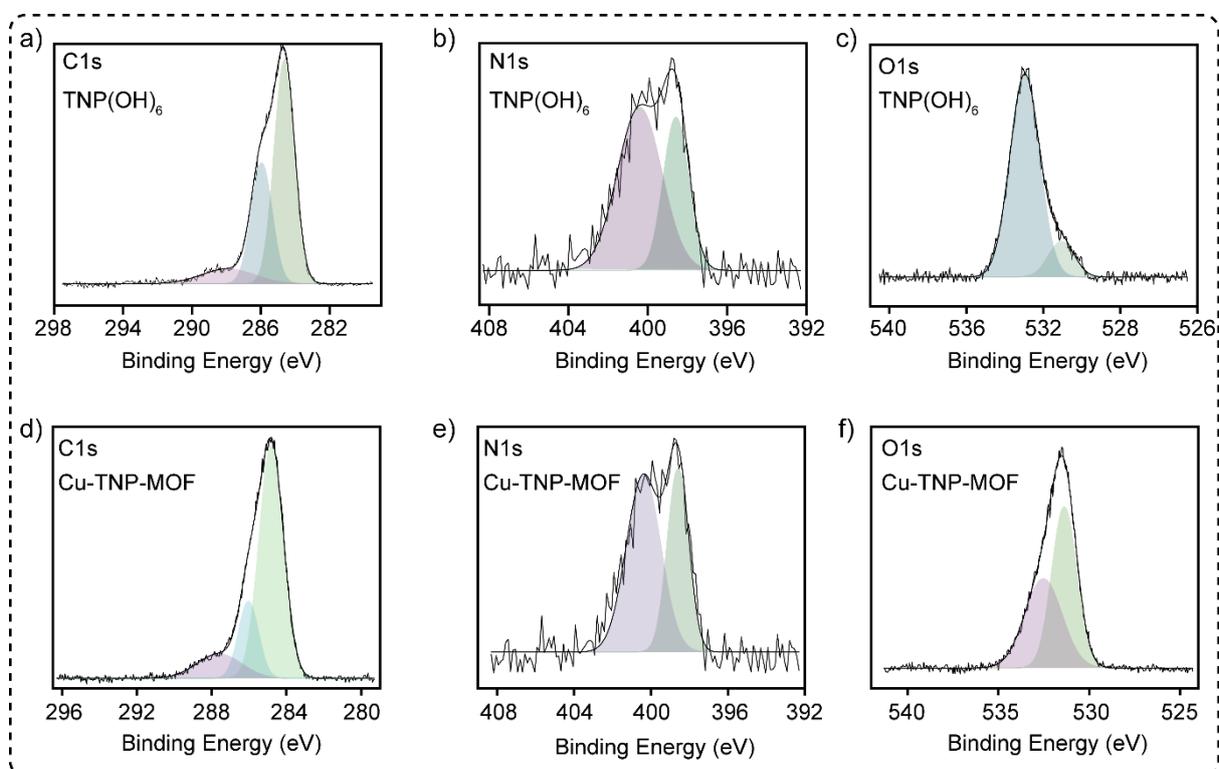


Fig. S98 XPS spectra of a) C 1s b) N 1s c) O 1s of TNP(OH)₆ ligand d) C 1s e) N 1s f) O 1s of Cu-TNP MOF

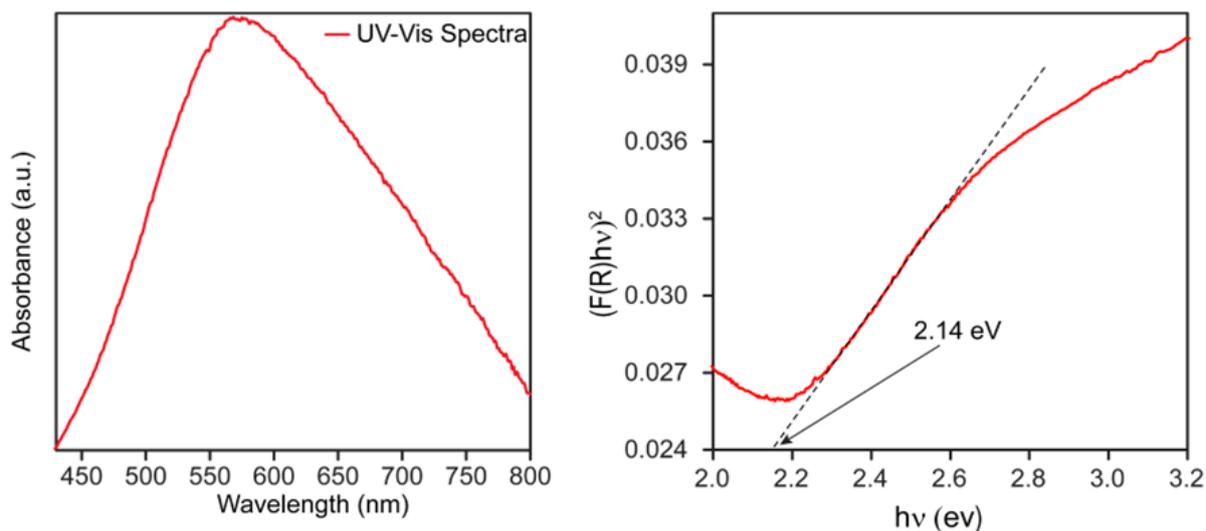


Fig. S99 a) UV-Visible spectra of Cu-TNP-MOF b) Optical band gap of Cu-TNP-MOF

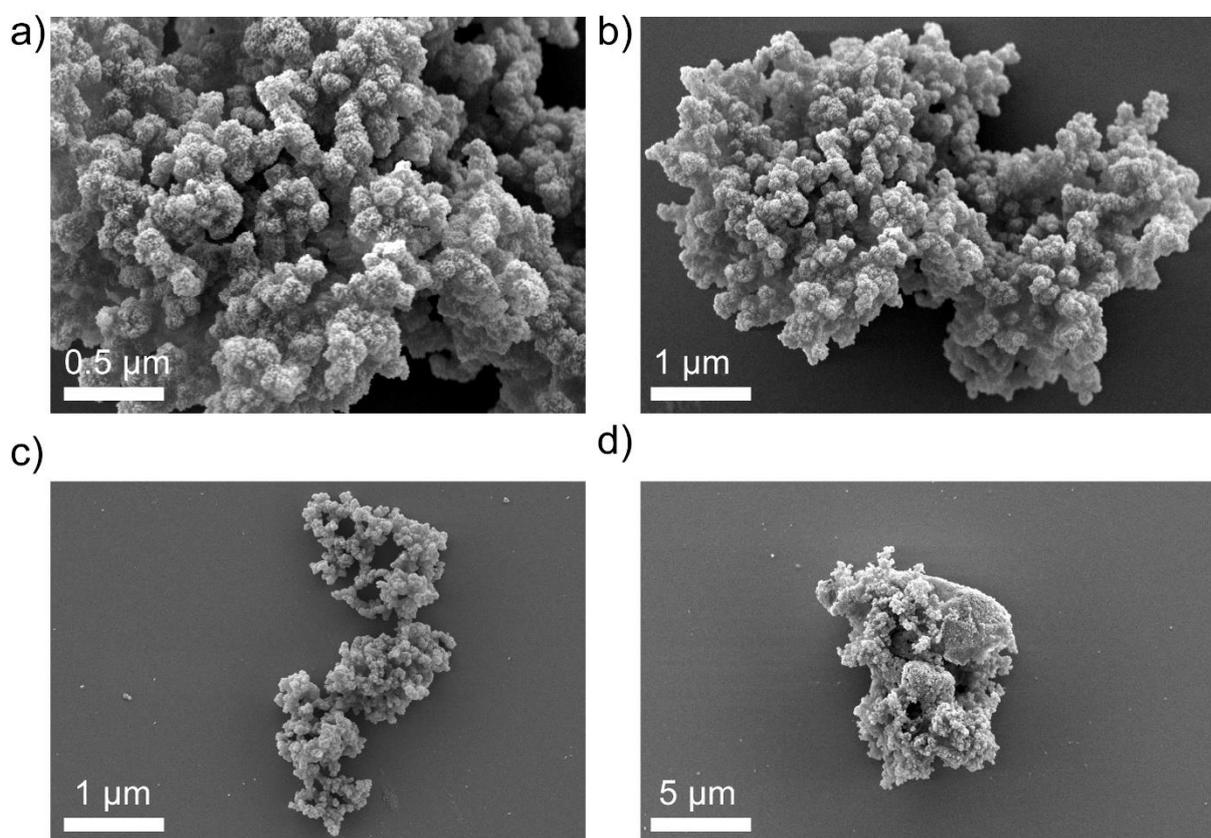


Fig. S100 SEM images of the as-synthesized material recorded at different magnifications. (a) High-magnification image showing densely packed, nanosized primary particles with a rough surface texture. (b) Aggregation of these nanoparticles into larger, hierarchical clusters. (c) Lower-magnification view highlighting elongated, chain-like agglomerates formed by particle coalescence. (d) A very low-magnification image reveals micrometer-scale secondary aggregates with an overall flower-like, porous morphology.

Traditional Synthesis				
Reaction Condition	% Yield	Substrate Scopes	Mechanism	Referene
Pd ₂ (dba) ₃ , Brettphos, K ₂ CO ₃ , t-BuOH, 100 °C, 24 h	~75%	TNP with R = Ph and Tol	C-N coupling	<i>Org. Lett.</i> 2021, 24 , 344-348
Pd(OAc) ₂ , P(^t Bu) ₃ , Cs ₂ CO ₃ , toluene, 40 h; ii) 5 % NaOH (aq), acetone, 16h, room temp.; iii) POCl ₃ , 16h, reflux; iv) R ₂ NH ₂ , 3d, reflux	~50%	TNP with R = H, Me	C-N coupling	<i>Chem. Eur. J.</i> 2011, 17 , 4529-4539
Pd(OAc) ₂ , P(^t Bu) ₃ , Cs ₂ CO ₃ , toluene, reflux, 72h; ii) 5 % NaOH, acetone, reflux, 16 h; iii) POCl ₃ , reflux; iv) LiAlH ₄ , THF, reflux, 16 h; v) FeCl ₃ ·6 H ₂ O, EtOH/H ₂ O (2:1), reflux, 16 h.	~50%	TNP with R = OR	C-N coupling	<i>Chem. Eur. J.</i> 2013, 19 , 14654-14664
Pd(OAc) ₂ /BINAP/Cs ₂ CO ₃ /dioxane; ii) P(O)Cl ₃ , reflux; iii) LiAlH ₄ , THF, reflux, then FeCl ₃ /NH ₄ OH.	~22%	TNP with R = Me	C-N coupling	<i>J. Mater. Chem.</i> 2005, 15 , 3175-3180
DMAC:DCB (1:1) 3(M) AcOH, 120 °C, 24 h.	~70%	25	S _N Ar	<i>Nat. Synth.</i> 2024, 3 , 1266-1274.
Mechanochemical Synthesis				

Reaction Condition	% Yield	Substrate Scopes	Mechanism	Reference
Glacial Acetic Acid	~70%-95%	25	S _N Ar	This Work

Table 6: Comparison of synthetic conditions, product yields, and substrate scope between the present method and the conventional solvothermal approach.