

Supplementary Information

Synthesis of fully fused tetrapyrazinoporphyrazine polymers bearing three-dimensional structures controlled by steric repulsion

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1. Experimental Section

General

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) for reactions were purified by passing through a solvent purification system (Glass Contour). All work-up and purification procedures were carried out with reagent-grade solvents in air. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The chromatogram was analyzed using a UV lamp (254 and 365 nm). Silica gel column chromatography was performed with KANTO Silica Gel 60N (spherical, neutral, 40-100 μm). Synthesis of monomers was performed according to reported procedures with modification.^{S1}

High-resolution and EI mass spectra (HRMS) were obtained using a JEOL JMS-T100GC AccuTOFTM GC-TOFMS equipped with Agilent 6890N GC. Fourier-transform infrared spectroscopy (FT-IR) were performed from a JASCO FT/IR-460plus spectrometer in the ATR mode in air. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-400 (¹H 400 MHz, ¹³C 100 MHz) spectrometer. The ¹H NMR chemical shifts were expressed in parts per million (ppm) relative to residual CHCl₃ (δ 7.26 ppm) or DMSO (δ 2.50 ppm). Chemical shifts for ¹³C NMR are expressed in ppm relative to CDCl₃ (δ 77.16 ppm). The data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constant (Hz), and integration. Thermogravimetric analysis (TGA) was carried out using a Rigaku TG-DTA8122. Samples were heated at a rate of 25 °C/min under a dry nitrogen gas flow. Diffuse reflectance measurements were carried out using a HITACHI U-4100 spectrophotometer with an integrating sphere. Gas adsorption measurements were conducted on a BELSORP-max volumetric gas adsorption analyzer with a cryostatic temperature controller. Samples **4a** and **4b** were heated at 120 °C for 1 h, evacuated at 120 °C for 6 h, and activated under dynamic vacuum at 120 °C for 12 h prior to the measurement. Grade 1 CO₂ gas was used (>99.995 vol.%).

2. Computational Study

The Gaussian 16 program^{S2} running on a NEC LX 110Rh system was used for all calculations. Structures were optimized at B3LYP/LANL2DZ for Zn and 6-31G(d) for others.^{S3,4} Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency). Cartesian coordinates of optimized structures are included in CartesianCoordinates.xyz file.

Table S1. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).^a

	E	$E + ZPE$	H	G
DiMes	-12058.9700922	-12055.665266	-12055.408868	-12056.017188
DiEtPr	-9925.01408569	-9922.002441	-9921.787996	-9921.787996
DiBuPh	-14810.6751434	-14805.371690	-14805.032007	-14805.805617

a) E : electronic energy; ZPE : zero-point energy; $H (= E + ZPE + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} + RT)$: sum of electronic and thermal enthalpies; $G (= H - TS)$: sum of electronic and thermal free energies.

The Quantum Espresso program^{S5,6} running on a NEC LX 110Rh system was used for variable-cell relaxation (vc-relax) and self-consistent field (SCF) calculations. The vc-relax calculation was completed with the cell_dofree = 'ibrav' input to maintain consistency in the lattice structure while relaxing the unit cell axis. We used optimized norm-conserving Vanderbilt pseudopotentials^{S7,8} to construct wavefunctions with a plane-wave kinetic energy cutoff of 140 Ry and a Gamma-point-centered k-point grid of 2×2×4.

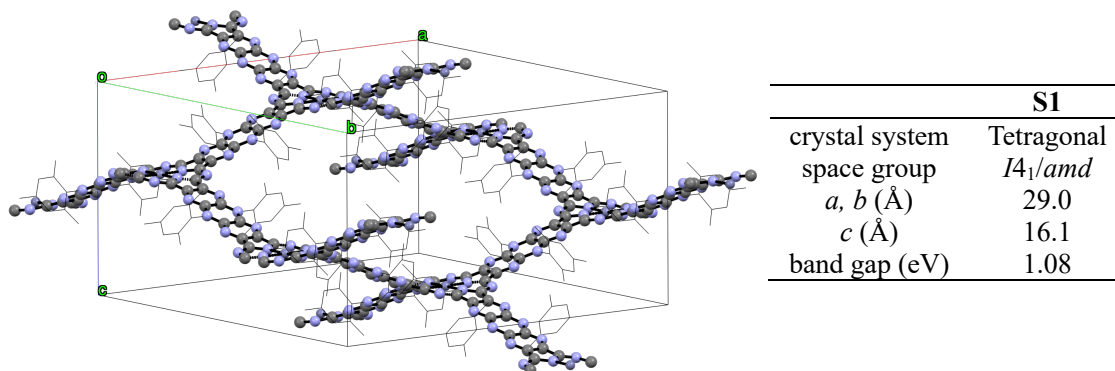
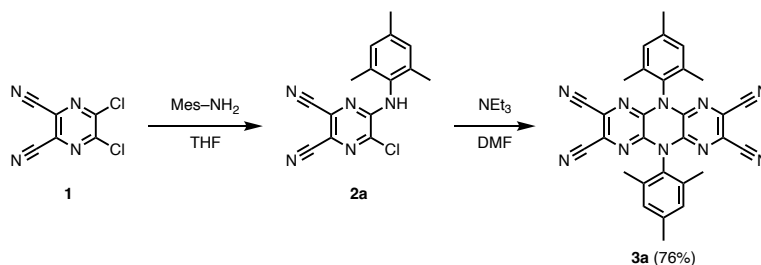


Figure S1. Optimized structure, cell parameter, and band gap of 3D periodic structure **S1**.

3. Synthesis

Synthesis of **3a**

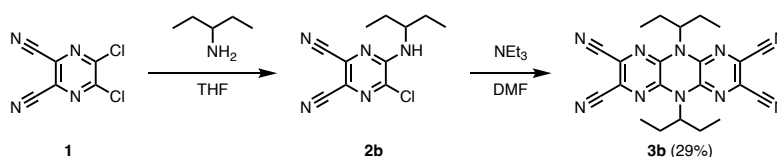


To a 100-mL two-necked flask containing a magnetic stirring bar were added 5,6-dichloro-2,3-dicyanopyrazine (2.00 g, 10.1 mmol, 1.0 equiv.) and THF (20 mL). Mesitylamine (2.83 mL, 20.1 mmol, 2.0 equiv.) was added at 0 °C and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water (200 mL) and filtered. The residual solid was washed with water, and dried in vacuo to obtain pale yellow powder containing **2a**, which was used to the next step without further purification.

To a 100-mL two-necked flask containing a magnetic stirring bar were added **2a**, *N,N*-dimethylformamide (DMF; 20 mL), and triethylamine (3.08 mL, 22.1 mmol, 2.2 equiv.). The mixture was heated at 140 °C for 10 h. The reaction mixture was quenched with 1M HCl (200 mL) and filtered. The residual solid was washed with water, then dissolved in chloroform. The solution was dried with anhydrous Na_2SO_4 , and passed through a silica (eluent: chloroform), and concentrated under reduced pressure. The mixture was further purified by recrystallization with chloroform/hexane. The resulting solid was filtered and washed with hexane to obtain **3a** as a yellow solid (1.99 g, 76%). The single crystals suitable for X-ray crystallography were obtained by cooling a hot DMAc solution of **3a** to room temperature.

^1H NMR (CDCl_3 , 400 MHz): δ 7.07 (s, 4H), 2.39 (s, 6H), 2.18 (s, 12H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 144.1 (4°), 140.8 (4°), 134.2 (4°), 130.6 (CH), 127.9 (4°), 126.9 (4°), 112.6 (4°), 21.3 (CH_3), 18.1 (CH_3); HRMS (GC-TOF MS): calcd. for $\text{C}_{30}\text{H}_{22}\text{N}_{10}$ ($[\text{M}]^+$): 522.2023, found: 522.2033.

Synthesis of **3b**

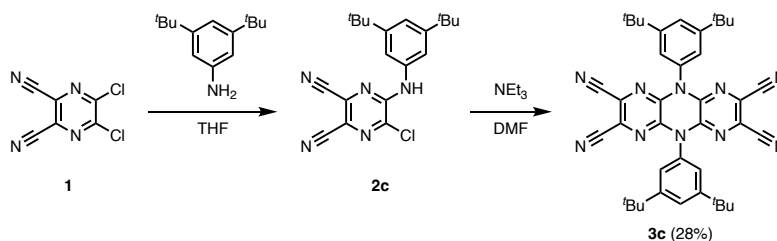


To a 37-mL screw cap test tube containing a magnetic stirring bar were added 5,6-dichloro-2,3-dicyanopyrazine (500 mg, 2.51 mmol, 1.0 equiv.), and THF (5.0 mL). 3-aminopentane (0.58 mL, 5.0 mmol, 2.0 equiv.) was added at 0 °C and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water (50 mL), and filtered. The residual solid was washed with water, and dried in vacuo to obtain pale yellow powder containing **2b**, which was used to the next step without further purification.

To a 37-mL screw cap test tube containing a magnetic stirring bar were added **2b**, DMF (5.0 mL), and triethylamine (0.77 mL, 5.5 mmol, 2.2 equiv.). The mixture was heated at 140 °C for 10 h. The reaction mixture was quenched with 1M HCl (50 mL), and filtered. The residual solid was washed with water, then dissolved in chloroform. The solution was dried with anhydrous Na₂SO₄, and passed through a silica (eluent: chloroform), and concentrated under reduced pressure. The mixture was further purified by recrystallization with chloroform/hexane. The resulting solid was filtered and washed with hexane to obtain **3b** as a brown crystalline solid (157 mg, 29%). The single crystals suitable for X-ray crystallography were obtained by cooling a hot ethyl acetate solution of **3b** to room temperature.

¹H NMR (CDCl₃, 400 MHz): δ 4.88 (tt, *J* = 6.0 Hz, 9.6 Hz, 2H), 2.06 (ddq, ²*J*_{HH} = 14.8 Hz, ³*J*_{HH} = 7.6 Hz, 9.6 Hz, 4H), 1.85 (ddq, ²*J*_{HH} = 14.8 Hz, ³*J*_{HH} = 6.0 Hz, 7.6 Hz, 4H), 0.93 (t, *J* = 7.6 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz): δ 144.6 (4°), 125.2 (4°), 112.9 (4°), 61.4 (CH), 23.5 (CH₂), 11.3 (CH₃); HRMS (GC-TOF MS): calcd. for C₂₂H₂₂N₁₀ ([M]⁺): 426.2023, found: 426.2030.

Synthesis of **3c**

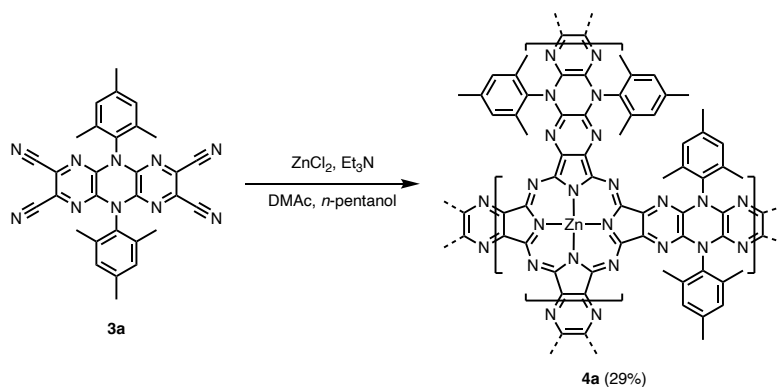


To a 37-mL screw cap test tube containing a magnetic stirring bar were added 5,6-dichloro-2,3-dicyanopyrazine (500 mg, 2.51 mmol, 1.0 equiv.), and THF (3.0 mL). 3,5-di-*tert*-butylaniline (1.03 g, 5.03 mmol, 2.0 equiv.) in THF (2.0 mL) was added at 0 °C and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water (50 mL), and filtered. The residual solid was washed with water, and dried in vacuo to obtain pale yellow powder containing **2c**, which was used to the next step without further purification.

To a 37-mL screw cap test tube containing a magnetic stirring bar were added **2c**, DMF (5.0 mL), and triethylamine (0.77 mL, 5.5 mmol, 2.2 equiv.). The mixture was heated at 140 °C for 10 h. The reaction mixture was quenched with 1M HCl (50 mL), and filtered. The residual solid was washed with water, then dissolved in chloroform. The solution was dried with anhydrous Na₂SO₄, and passed through a silica (eluent: chloroform), and concentrated under reduced pressure. The mixture was further purified by recrystallization with chloroform/hexane. The resulting solid was filtered and washed with hexane to obtain **3c** as a yellow solid (229 mg, 28%). The single crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a chloroform solution of **3c**.

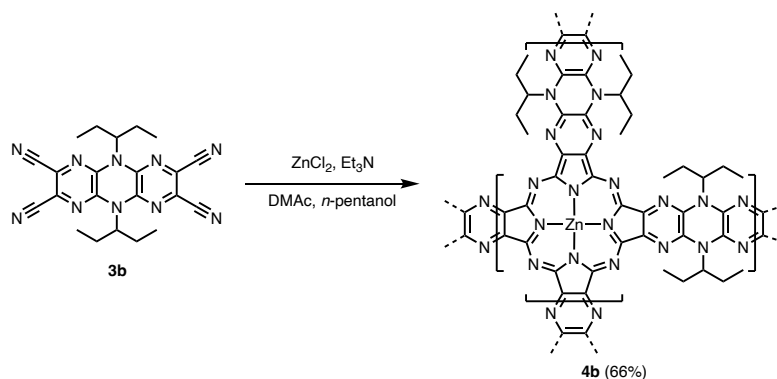
¹H NMR (CDCl₃, 400 MHz): δ 7.57 (t, *J* = 1.6 Hz, 2H), 6.94 (d, *J* = 1.6 Hz, 4H), 1.36 (s, 36H); ¹³C NMR (CDCl₃, 100 MHz): δ 153.7 (4°), 145.0 (4°), 131.3 (4°), 126.3 (4°), 124.4 (CH), 121.5 (CH), 112.8 (4°), 35.3 (4°), 31.4 (CH₃); HRMS (FAB MS): calcd. for C₄₀H₄₂N₁₀ ([M]⁺): 662.3588, found: 662.3588.

Synthesis of **4a**



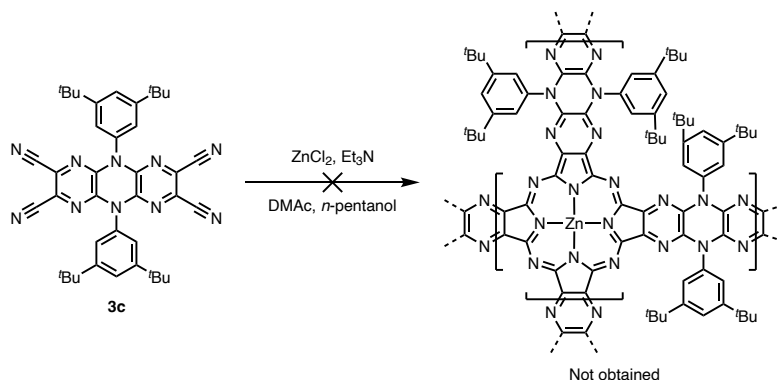
To a 37-mL screw cap test tube filled by argon gas were added **3a** (30.0 mg, 57.4 μmol , 1.0 equiv.), anhydrous ZnCl_2 (3.9 mg, 29 μmol , 0.5 equiv.), *N,N*-dimethylacetamide (DMAC; 2.0 mL), *n*-pentanol (0.2 mL), and triethylamine (10 μL). Five more test tubes were prepared in the same manner. The six test tubes in total were sonicated for 3 minutes and heated without stirring, started at 100 $^\circ\text{C}$ and the temperature was increased by 10 $^\circ\text{C}$ per day up to 200 $^\circ\text{C}$. All reaction mixtures were combined, then filtered and washed with DMAC, hexane, acetone, water, methanol, ethyl acetate, chloroform, dichloromethane, and diethyl ether, and dried in vacuo to obtain **4a** as a metallic black solid (54.7 mg, 29%). Elem. Anal. Calcd for $(\text{C}_{60}\text{H}_{44}\text{N}_{20}\text{Zn}) \cdot (\text{C}_4\text{H}_9\text{NO})_3 \cdot (\text{H}_2\text{O})_6$: C 58.39, H 5.65, N 21.83. Found, C 58.50, H 5.37, N 20.24.

Synthesis of 4b



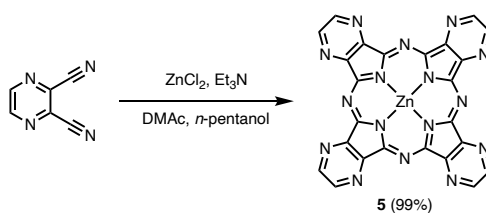
To a 37-mL screw cap test tube filled by argon gas were added **3b** (30.0 mg, 70.3 μmol , 1.0 equiv.), anhydrous ZnCl_2 (4.8 mg, 35 μmol , 0.5 equiv.), DMAC (2.0 mL), *n*-pentanol (0.2 mL), and triethylamine (10 μL). Five more test tubes were prepared in the same manner. The six test tubes in total were sonicated for 3 minutes and heated without stirring, started at 100 $^\circ\text{C}$ and the temperature was increased by 10 $^\circ\text{C}$ per day up to 200 $^\circ\text{C}$. All reaction mixtures were combined, then filtered and washed with DMAC, hexane, acetone, water, methanol, ethyl acetate, chloroform, dichloromethane, and diethyl ether, and dried in vacuo to obtain **4b** as a metallic black solid (129 mg, 66%). Elem. Anal. Calcd for $(\text{C}_{44}\text{H}_{44}\text{N}_{20}\text{Zn}) \cdot (\text{C}_4\text{H}_9\text{NO})_3 \cdot (\text{H}_2\text{O})$: C 56.10, H 6.14, N 26.97. Found, C 56.15, H 5.86, N 26.55.

Attempt for the synthesis of 4c



To a 37-mL screw cap test tube filled by argon gas were added **3c** (30.0 mg, 45.3 μmol , 1.0 equiv.), anhydrous ZnCl_2 (3.1 mg, 23 μmol , 0.5 equiv.), *N,N*-dimethylacetamide (2.0 mL), *n*-pentanol (0.2 mL), and triethylamine (10 μL). The test tube was sonicated for 3 minutes and heated without stirring, started at 100 $^\circ\text{C}$ and the temperature was increased by 10 $^\circ\text{C}$ per day up to 200 $^\circ\text{C}$. The reaction mixture was filtered to obtain no insoluble solid.

Synthesis of **5**



To a 37-mL screw cap test tube containing a magnetic stirring bar were added 2,3-dicyanopyrazine (200 mg, 1.54 mmol, 1.0 equiv.), anhydrous ZnCl_2 (52.4 mg, 384 μmol , 0.25 equiv.), DMAc (4.0 mL), *n*-pentanol (0.4 mL), and triethylamine (80 μL). The mixture was stirred at 140 °C for 24 h. The reaction mixture was filtered and the resulting solid was washed with DMAc, hexane, acetone, water, methanol, ethyl acetate, chloroform and dichloromethane to obtain **5** as a dark blue solid. The filtrate of the reaction mixture was evaporated and the resulting solid was washed with chloroform with sonication and grinding to obtain **5** as a dark blue solid. In total, 233 mg of **5** (99%) was obtained. The single crystals suitable for X-ray crystallography were obtained by slow diffusion of methanol into a DMSO solution of **5**.

^1H NMR ($\text{DMSO-}d_6$, 400 MHz, 140 °C): δ 9.54 (8H). ^{13}C NMR signals could not be recorded because of low solubility.

4. X-ray Crystallography and Powder XRD

Details of the crystal data and a summary of the intensity data collection parameters for **3a**·2DMAc, **3b**, **3c** and **5**·2DMSO are listed in Table S2. Suitable crystals were mounted with mineral oil on a MiTeGen MicroMounts and transferred to the goniometer of the kappa goniometer of a RIGAKU XtaLAB Synergy Custom system with equipped with mirror monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and HyPix-6000HEIC detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Rigaku Oxford Diffraction, 2018). The structures were solved by dual methods using SHELXT^{S9} and refined by full-matrix least-squares techniques against F^2 with SHELXL-2018/3^{S10} using Olex2 software package.^{S11} The intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically as riding model.

Powder XRD patterns of **4a** and **4b** were acquired using Rigaku MiniFlex 600-C diffraction system with 600 W X-ray tube (Cu K α).

Table S2. Crystallographic data and structure refinement details of **3a**, **3b**, and **3c**.

	3a ·2DMAc	3b	3c
formula	C ₃₀ H ₂₂ N ₁₀ ·2(C ₄ H ₉ NO)	C ₂₂ H ₂₂ N ₁₀	C ₄₀ H ₄₂ N ₁₀
Fw	696.82	426.49	662.83
<i>T</i> (K)	143	143	143
λ (Å)	0.71073	0.71073	0.71073
cryst syst	Triclinic	Orthorhombic	Monoclinic
space group	<i>P</i> -1	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.9056(6)	8.6557(5)	17.1684(8)
<i>b</i> (Å)	10.0760(6)	14.4716(8)	9.2231(4)
<i>c</i> (Å)	10.9491(5)	17.0096(9)	12.1013(6)
α (deg)	107.517(5)	90	90
β (deg)	91.562(4)	90	108.561(5)
γ (deg)	116.601(6)	90	90
<i>V</i> (Å ³)	914.85(10)	2137.7(2)	1816.52(16)
<i>Z</i>	1	4	2
cryst size (mm)	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.04	0.10 × 0.05 × 0.01
2 θ range (deg)	5.064 to 62.67	5.63 to 62.85	5.006 to 62.572
reflns collected	13568	11471	20618
indep reflns/ <i>R</i> _{int}	4973/0.0461	2981/0.0371	5050/0.0618
params	299	166	232
GOF on F^2	1.057	1.051	1.034
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0539, 0.1242	0.0520, 0.1253	0.0587, 0.1317
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0860, 0.1379	0.0815, 0.1374	0.1199, 0.1529
CCDC Number	2403177	2403178	2403179

Table S3. Crystallographic data and structure refinement details of **5**.

5·2DMSO	
formula	$C_{24}H_8N_{16}Zn \cdot 2(C_2H_6OS)$
Fw	742.09
<i>T</i> (K)	143
λ (Å)	0.71073
cryst syst	Monoclinic
space group	$P2_1/n$
<i>a</i> (Å)	9.3572(5)
<i>b</i> (Å)	13.3654(5)
<i>c</i> (Å)	11.4576(7)
α (deg)	90
β (deg)	99.790(6)
γ (deg)	90
<i>V</i> (Å ³)	1412.05(13)
<i>Z</i>	2
cryst size (mm)	0.10 × 0.10 × 0.05
2 θ range (deg)	5.208 to 60.81
reflns collected	8653
indep reflns/ <i>R</i> _{int}	3630/0.0408
params	225
GOF on <i>F</i> ²	1.074
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0571, 0.1460
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0859, 0.1634
CCDC Number	2404808

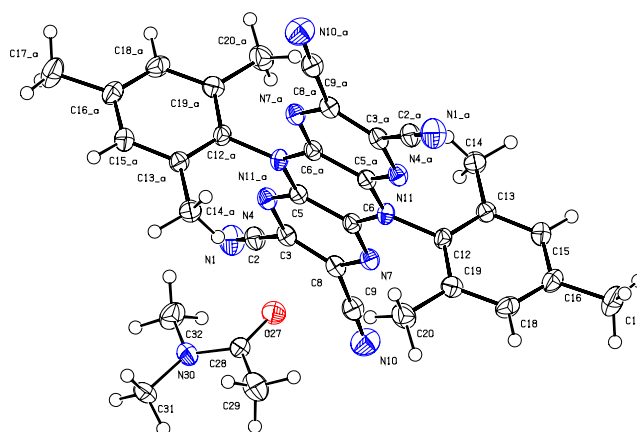


Figure S2. ORTEP drawing of **3a**·2DMAC with thermal ellipsoids at 50% probability.

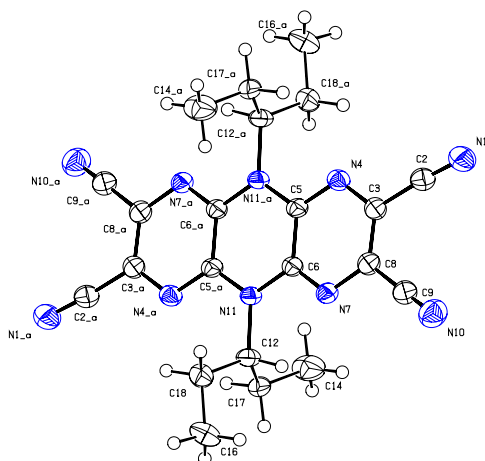


Figure S3. ORTEP drawing of **3b** with thermal ellipsoids at 50% probability.

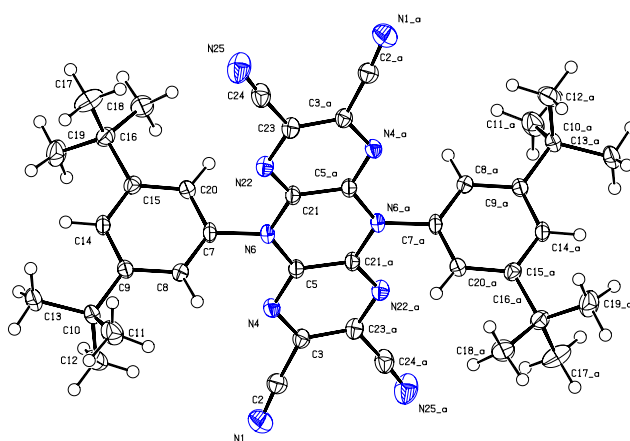


Figure S4. ORTEP drawing of **3c** with thermal ellipsoids at 50% probability.

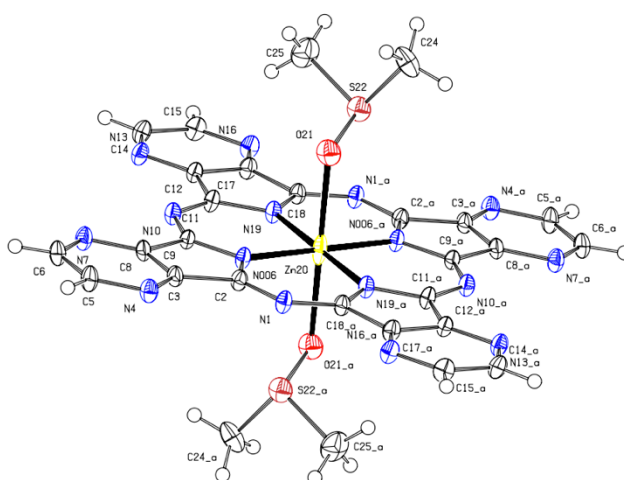


Figure S5. ORTEP drawing of **5·2DMSO** with thermal ellipsoids at 50% probability.

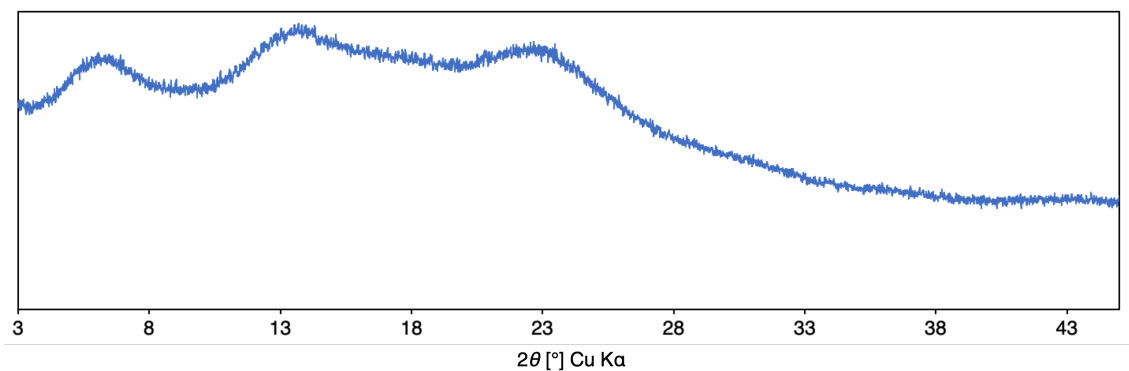


Figure S6. PXRD patterns of **4a**.

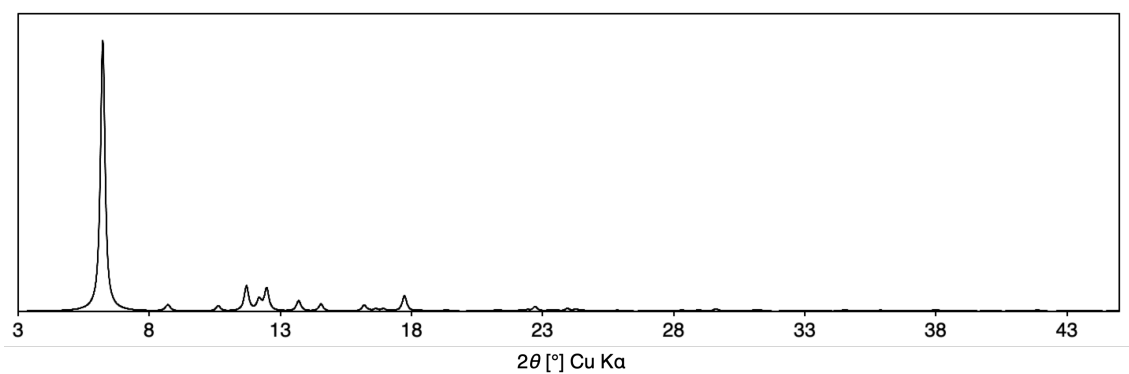


Figure S7. Simulated PXRD patterns of calculated structure **S1**.

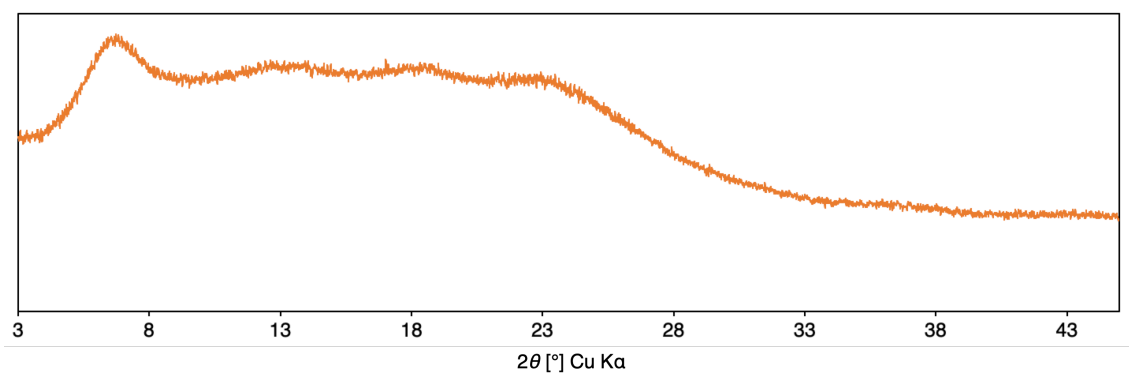


Figure S8. PXRD patterns of **4b**.

5. Solid-state NMR Spectroscopy

Solid-state ^{13}C NMR spectra using cross polarization magic angle spinning with total suppression of sidebands^{S12} (CP-MAS TOSS) method were measured at 150 MHz with a JEOL JNM-ECZ600II spectrometer and 3.2 mm ^1H -X double resonance MAS probe. Samples **4a** and **4b** were heated at 120 °C for 1 h, evacuated at 120 °C for 6 h, and evacuated under dynamic vacuum at 120 °C for 12 h prior to the measurements. Spectra were acquired at a spin rate of 20 kHz \pm 5 Hz, 3 ms contact time, and with a recycle delay of 1 s. Carbon spectral referencing is relative to tetramethylsilane, carried out by setting the high-frequency signal from an external sample of adamantane to 29.5 ppm. ^1H Heteronuclear decoupling during the detection period was achieved using two pulse phase modulation (TPPM)^{S13} with a ^1H RF field of 105 kHz. Initial magnetizations of rare nuclei were enhanced by using ^1H - ^{13}C cross-polarization with 11% amplitude sweep of the ^1H spin locking field.^{S14} FIDs were apodized with trapezoid window functions prior to Fourier transformation. The assignments of the observed signals are shown in Figs. S9 and S10 in comparison with previous reports.^{S15,16}

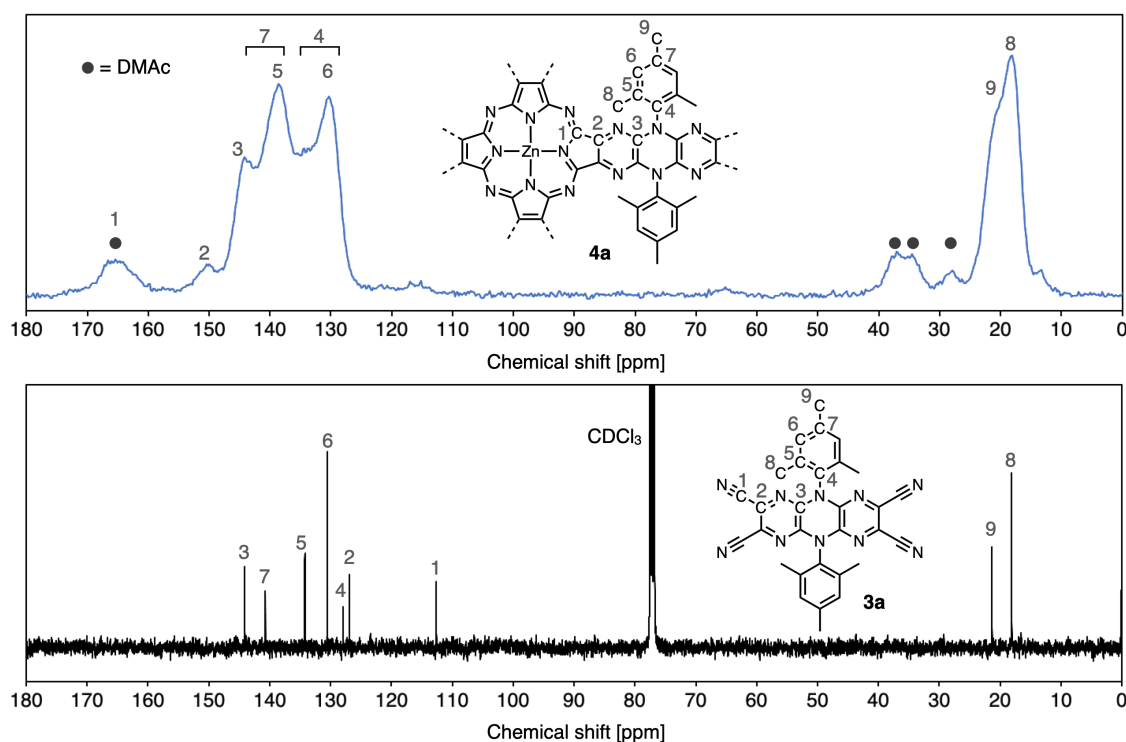


Figure S9. The solid-state ^{13}C NMR spectrum of **4a**, and the solution-state ^{13}C NMR spectrum of **3a** in CDCl_3 .

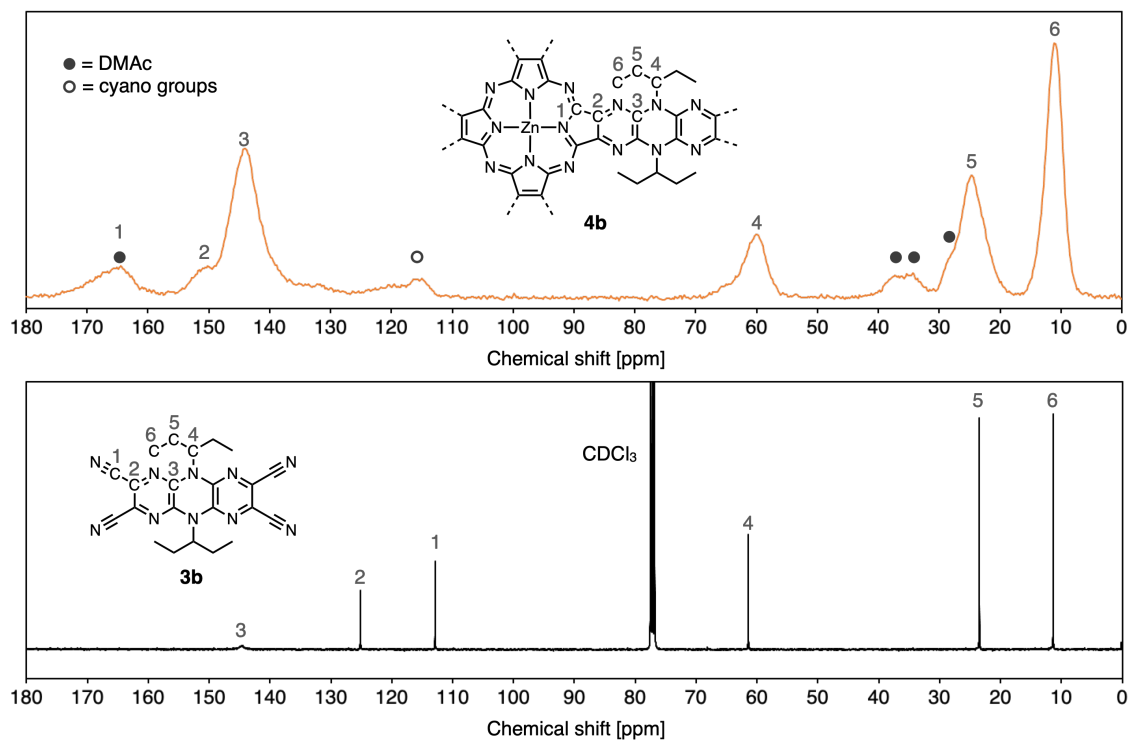


Figure S10. The solid-state ^{13}C NMR spectrum of **4b**, and the solution-state ^{13}C NMR spectrum of **3b** in CDCl_3 .

6. EDS Maps

Schottky emission scanning electron microscopy (SEM) was performed on a Hitachi SU-6600 operating at an accelerating voltage of 5.0 kV. Energy dispersive spectroscopy (EDS) was carried out using a BrukerAXS XFlash[®] 5060FQ.

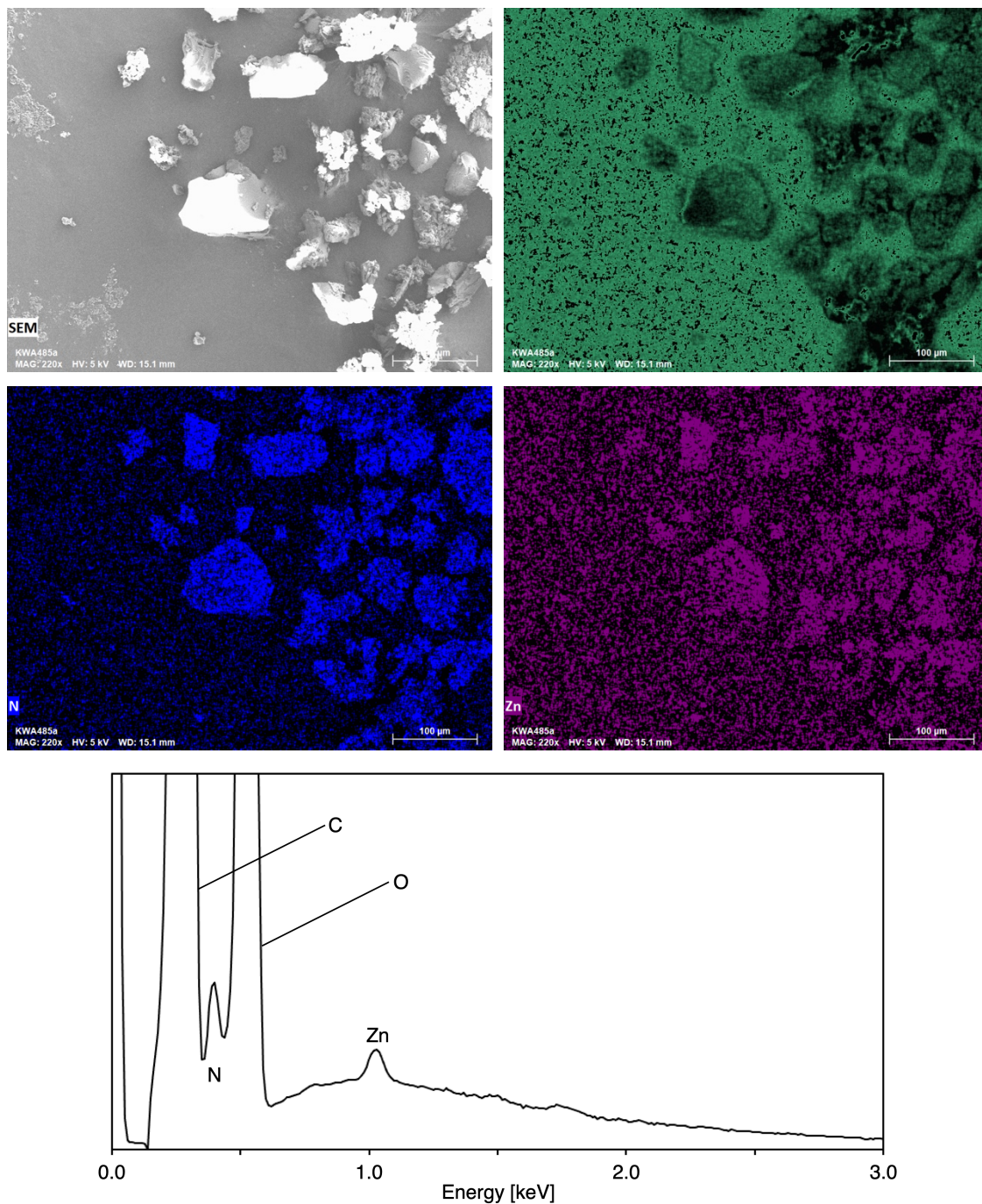


Figure S11. EDS maps and energy dispersive spectrum of 4a.

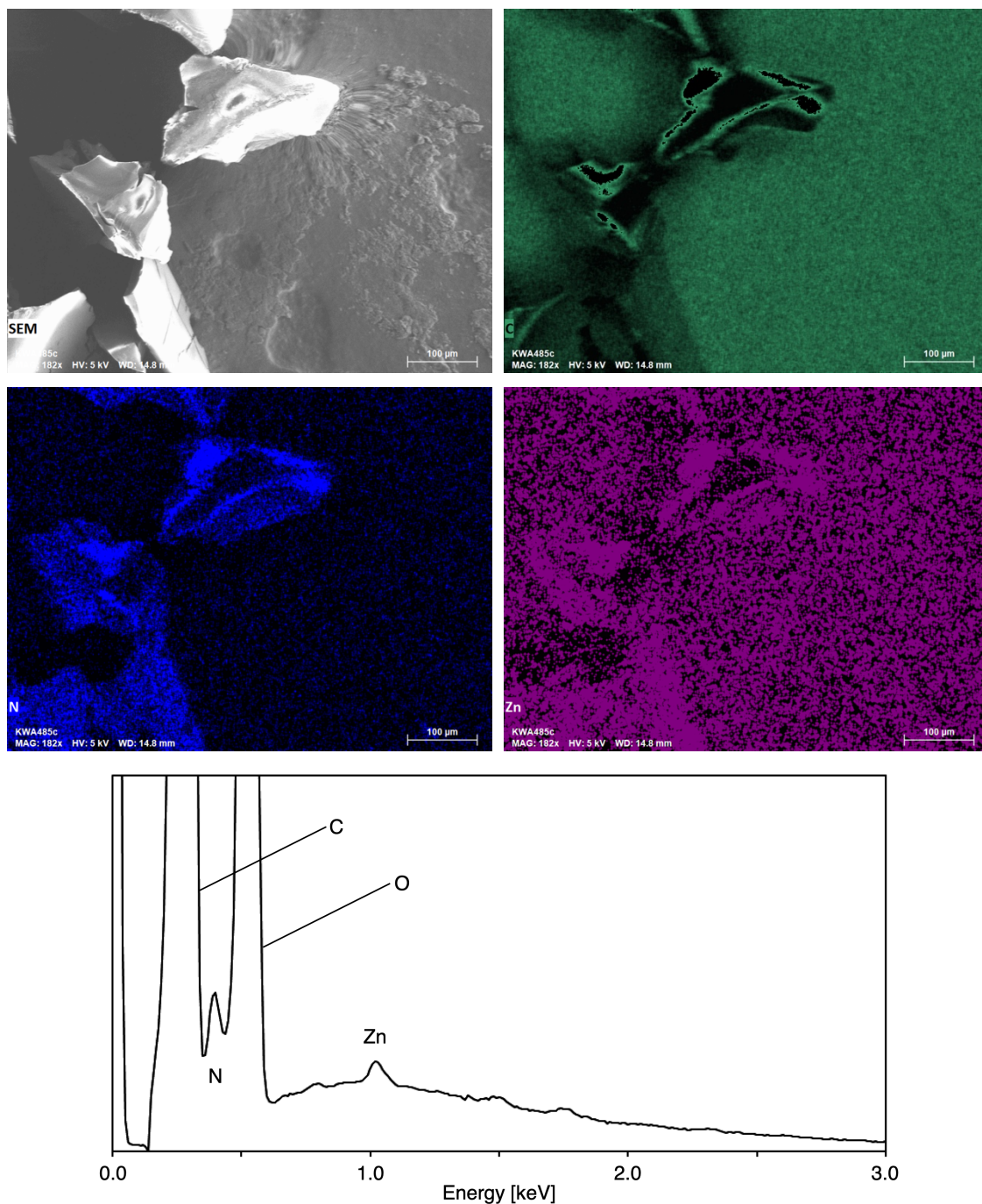


Figure S12. EDS maps and energy dispersive spectrum of 4b.

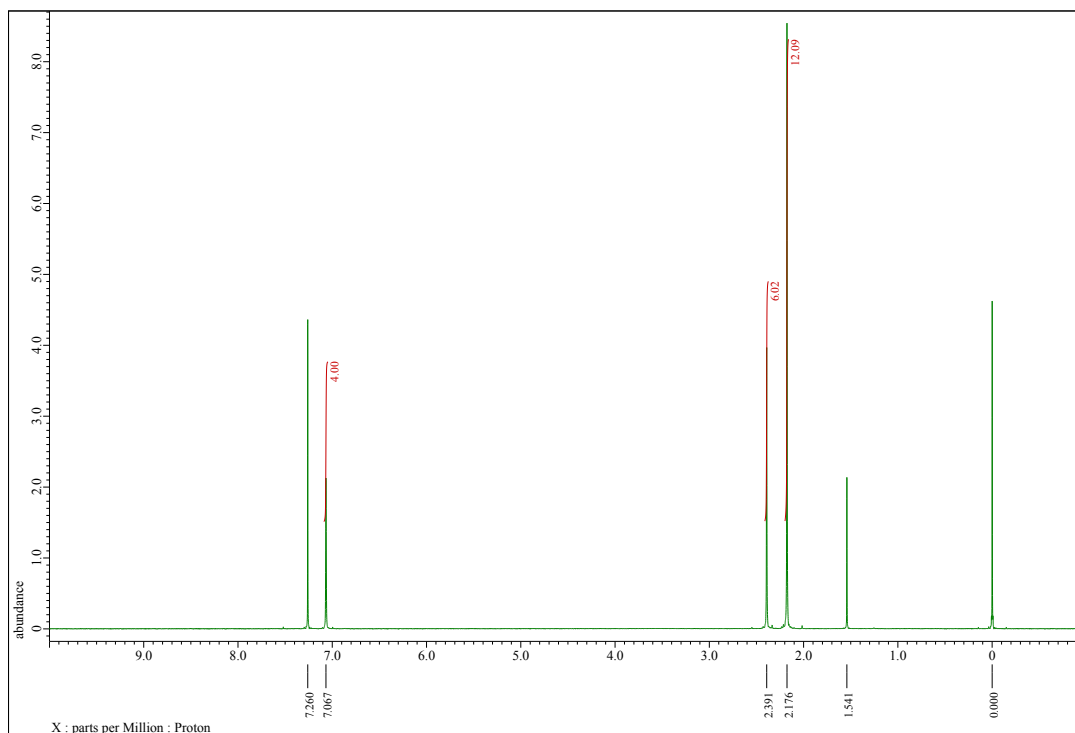
7. References

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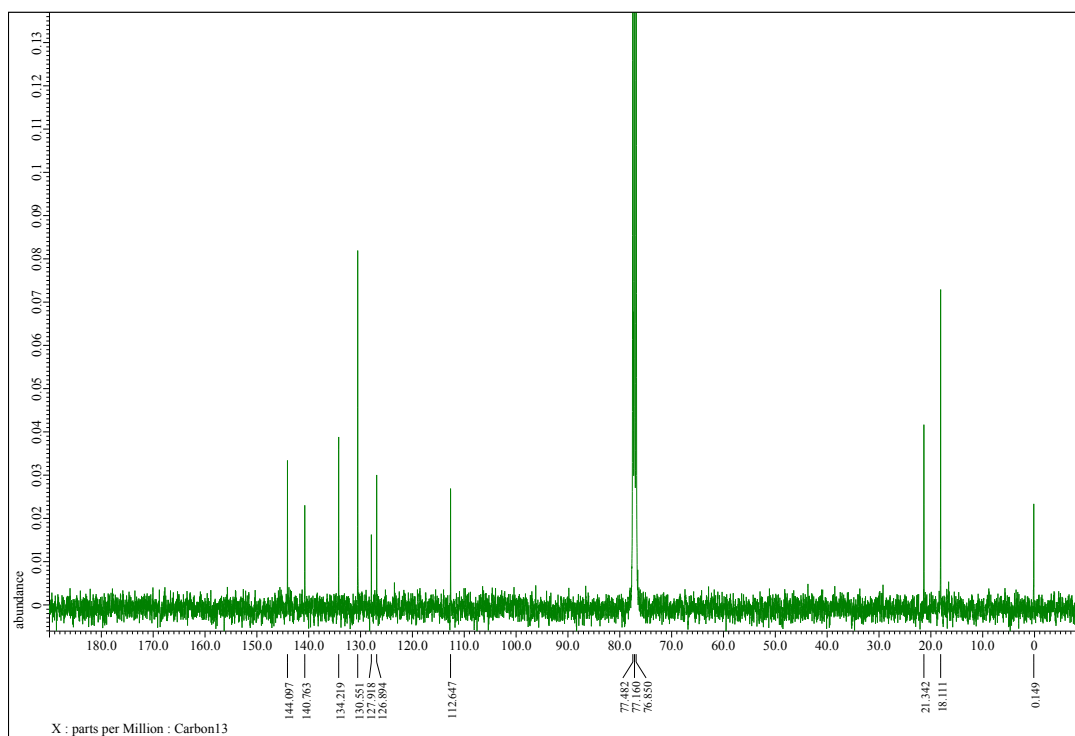
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8. NMR Spectra of Products

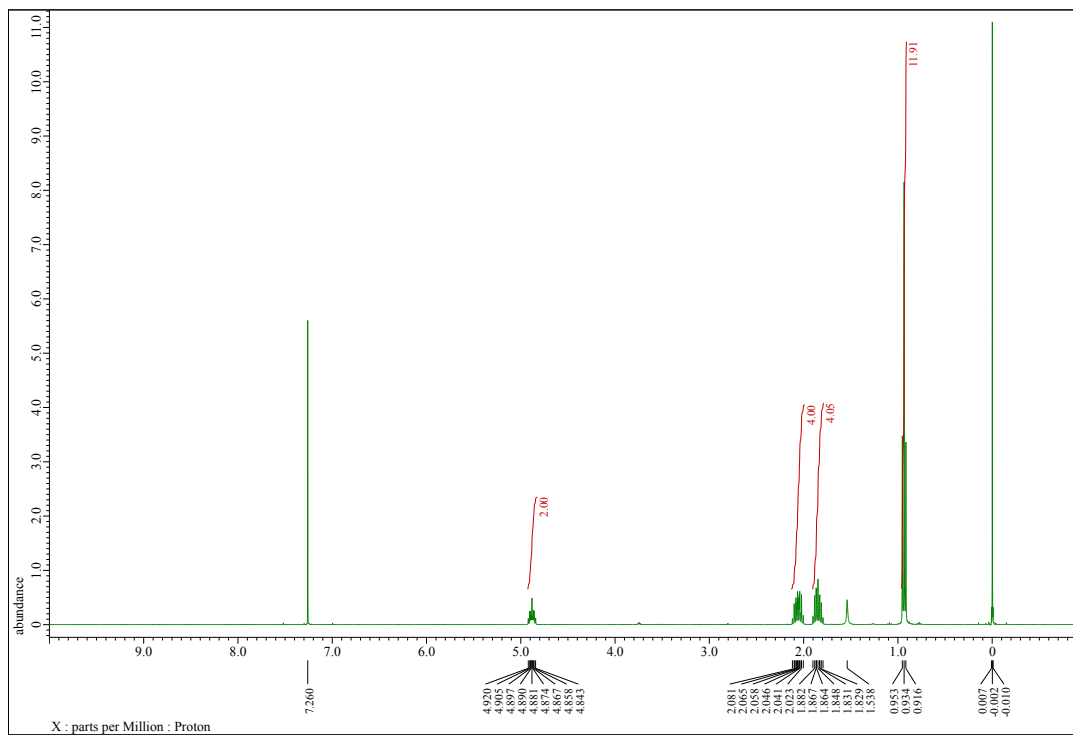
^1H NMR spectrum of **3a** (400 MHz, CDCl_3)



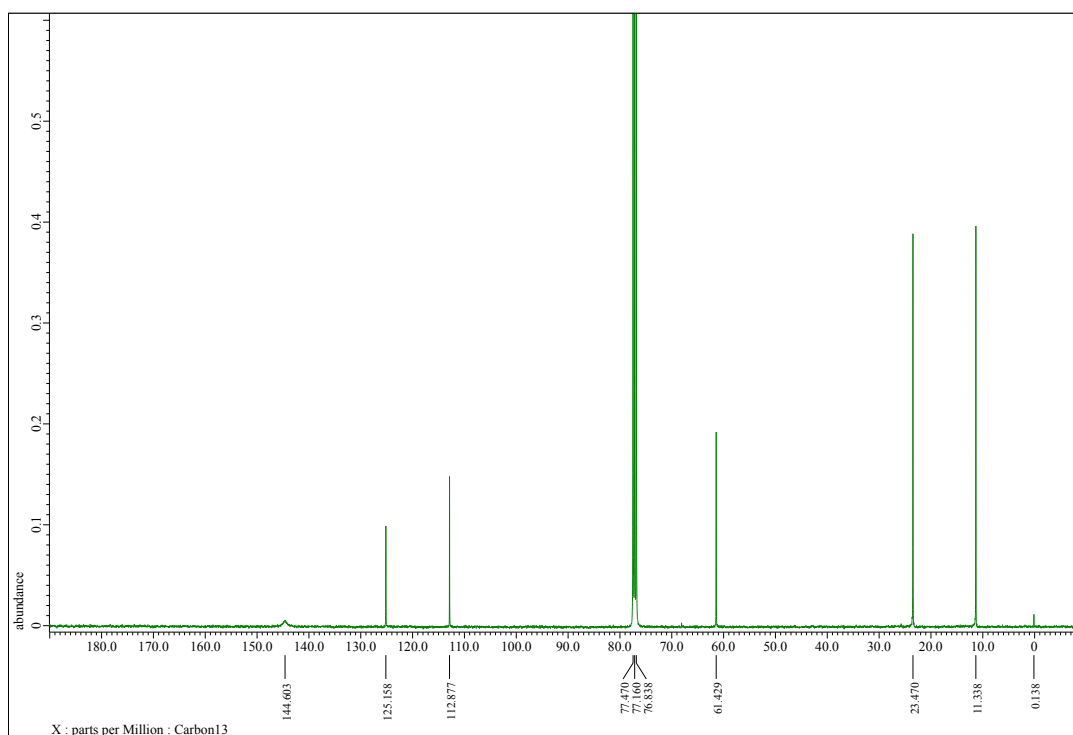
^{13}C NMR spectrum of **3a** (100 MHz, CDCl_3)



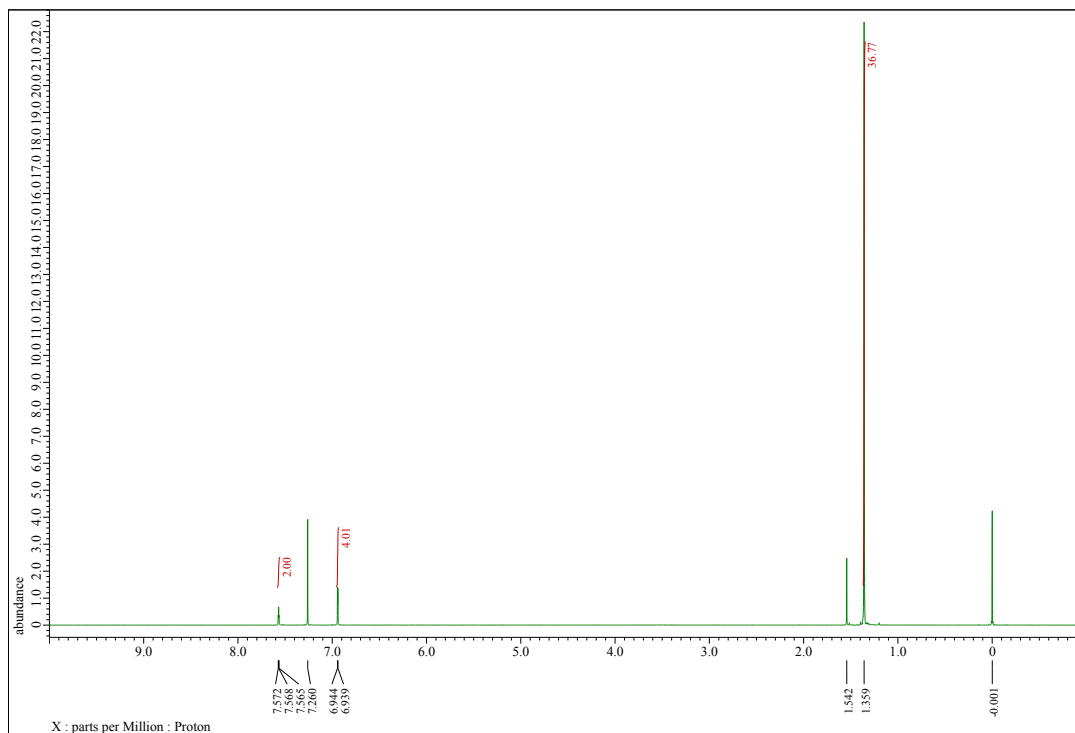
^1H NMR spectrum of **3b** (400 MHz, CDCl_3)



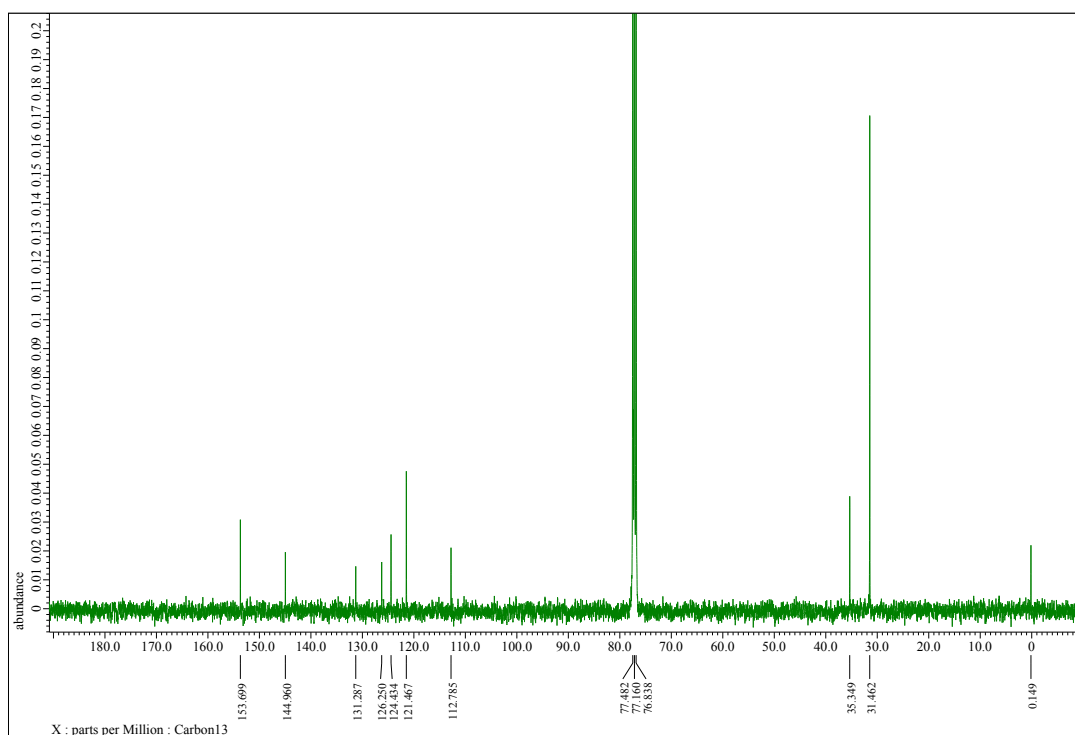
^{13}C NMR spectrum of **3b** (100 MHz, CDCl_3)



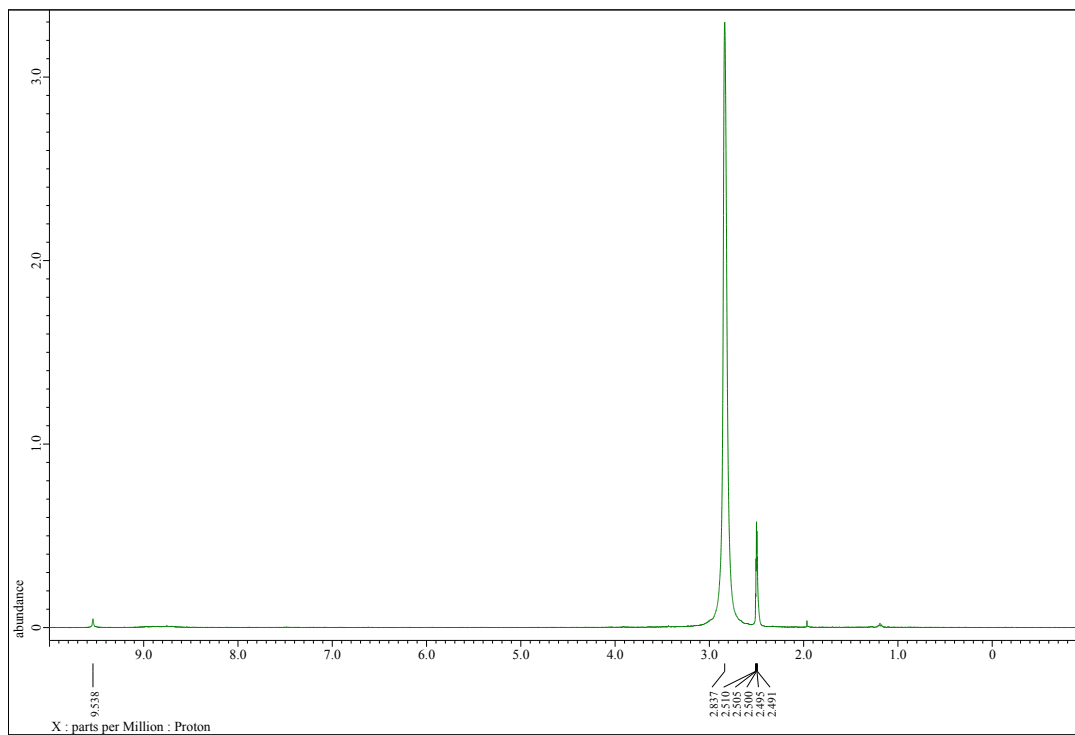
^1H NMR spectrum of **3c** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3c** (100 MHz, CDCl_3)

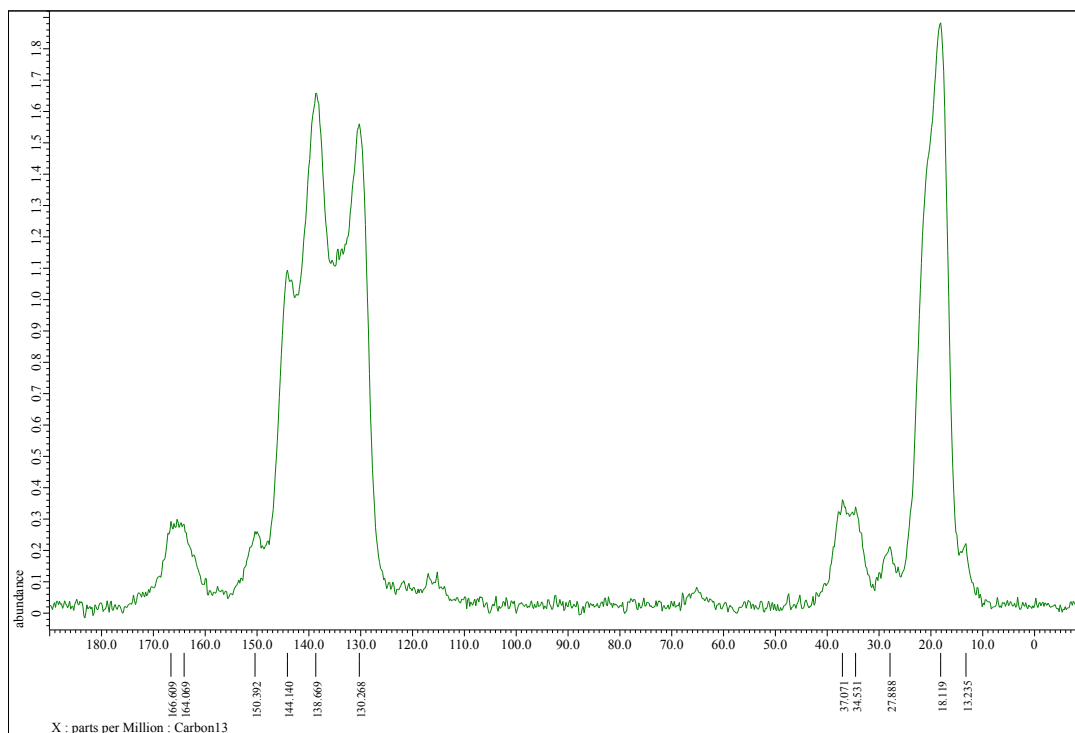


^1H NMR spectrum of **5** (400 MHz, $\text{DMSO-}d_6$, 140 °C)



8. Solid-state NMR Spectra of Products

^{13}C NMR spectrum of **4a** (150 MHz)



^{13}C NMR spectrum of **4b** (150 MHz)

