Supplementary Information for

Synthesis of a Macrocyclic Oligomer of Pyridylbenzoxazole Utilizing Dynamic Covalent Bonds and Its Unsymmetric Conversion

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1. Materials and methods

Unless otherwise noted, solvents and reagents were purchased from Tokyo Chemical Industry Co., Ltd., Fujifilm Wako Pure Chemical Co., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Japan G.K., and used without further purification. Dry THF and DMF were purified by Glass Contour Ultimate Solvent System. Silica gel for column chromatography was purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, 63–210 μm)). Automated flash chromatography purifications were performed using a Biotage Isolera One system with Biotage Sfär Silica (HC D 20 μm) columns.

Measurements were performed at 298 K unless otherwise noted. ^{1}H, ^{13}C, and other 2D NMR spectra were recorded on Bruker AVANCE III-400 and 600 spectrometers. Negative values were depicted in red in the spectra. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for ^{1}H and ^{13}C NMR measurements when $CDCl_3$ was used as a solvent. The assignments of the ^{1}H and ^{13}C signals were based on ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC experiments.

MALDI TOF mass data were recorded on an AB SCIEX TOF/TOF 5800 system. ESI TOF mass data were recorded on an AB SCIEX TripleTOF 4600 system. UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer. Emission spectra were recorded on a JASCO FP-8600 fluorescence spectrophotometer. Absolute fluorescence quantum yields were determined with a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02. Melting points were measured by a MPA100 OptiMelt Automated Melting Point System.

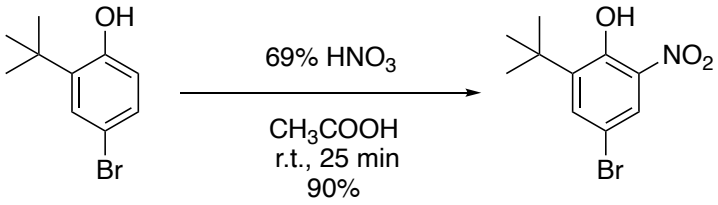
Single-crystal X-ray crystallographic measurements were performed using Bruker APEX II ULTRA with Mo K_α radiation at 100 K. Obtained data were collected using Bruker APEX2[S1a] and processed using Bruker APEX3[S1b] and Yadokari-XG[S2] crystallographic software package. The initial structures were solved using SHELXT-2018[S3], and refined using SHELXL-2018[S4]. We appreciate Prof. Takahiro Sasamori (Univ. of Tsukuba) for the support in the X-ray diffraction measurements.

Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Masao Sasaki (Univ. of Tsukuba) for the measurements.

We appreciate the Chemical Analysis Division, Research Facility Center for Science and Technology (Univ. of Tsukuba) for the MALDI TOF mass measurements. We appreciate the Organization for Open Facility Initiatives (Univ. of Tsukuba) for the NMR, MALDI TOF mass, and ESI TOF mass measurements.

2. Synthesis of Bifunctional Monomer and Macrocycles

Synthesis of **7**



6 **7**

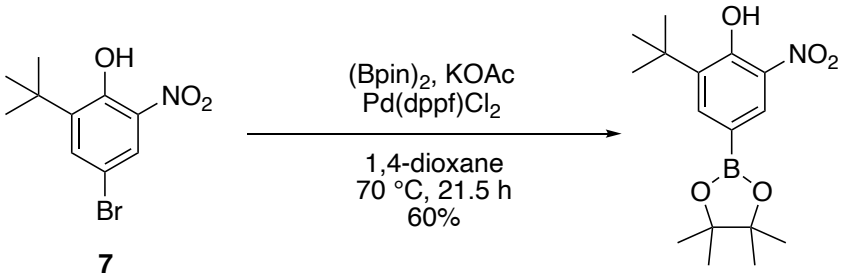
Scheme S1. Synthesis of **7**

In a 100 mL eggplant flask, to a solution of **6** (3.8964 g, 17.007 mmol, 1.0 eq.) in AcOH (36 mL) was added a solution of 69% HNO_3 aq (1.6263 g, 18 mmol, 1.0 eq.) in AcOH (4 mL) with stirring at 0 °C, and then the mixture was stirred at room temperature for 25 min. The reaction was quenched by adding 0.1 M NaOH aq (40 mL) to the reaction mixture, and the aqueous layer was extracted with $CHCl_3$ (80 mL × 1, then 40 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by automated column chromatography (*n*-hexane/$CHCl_3$ = 95/5–50/50) and dried in vacuo to give **7**[S5] as yellow solid (4.1858 g, 15.27 mmol, 90%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.46 (s, 1H), 8.15 (d, J = 2.5 Hz, 1H), 7.64 (d, J = 2.5 Hz, 1H), 1.43 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1, 143.1, 137.6, 134.7, 125.2, 111.3, 35.9, 29.2.

Synthesis of **8**



7 **8**

Scheme S2. Synthesis of **8**

In a 300 mL 3-necked round bottom flask, to a mixture of **7** (6.0344 g, 22.379 mmol, 1.0 eq.), bis(pinacolato)diboron (6.1649 g, 24.277 mmol, 1.1 eq.), and KOAc (6.4581 g, 65.798 mmol, 2.9 eq.) in dry 1,4-dioxane (90 mL) was added $Pd(dppf)Cl_2$ (0.9950 g, 1.360 mmol, 6.1 mol%), and the mixture was stirred at 70 °C for 6 h under Ar atmosphere. **7** remained in the reaction mixture, and then additional bis(pinacolato)diboron (3.0679 g, 12.081 mmol, 0.54 eq.) was added, and the mixture was stirred at 70 °C for another 15.5 h under Ar atmosphere. The reaction mixture was concentrated in vacuo. Sat. $NaHCO_3$ aq was added to the residue, and the aqueous layer was extracted with $CHCl_3$ (100 mL × 5). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was passed through silica gel column ($CHCl_3$), and concentrated in vacuo. The combined materials were recrystallized from *n*-hexane/$CHCl_3$ (20 mL/4.5 mL). The solid was collected by filtration and dried in vacuo. **8** was obtained as a pale yellow crystal (3.2969 g). The filtrate was concentrated in vacuo, and was purified by automated column chromatography (*n*-hexane/$CHCl_3$/AcOEt = 70/30/0–50/50/0–0/0/100) and dried in vacuo to give **8** as pale yellow solid (1.0056 g) (total: 4.3025 g, 13.389 mmol, 60%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.74 (s, 1H), 8.46 (d, J = 1.2 Hz, 1H), 7.94 (d, J = 1.2 Hz, 1H), 1.46 (s, 9H), 1.34 (s, 12H);

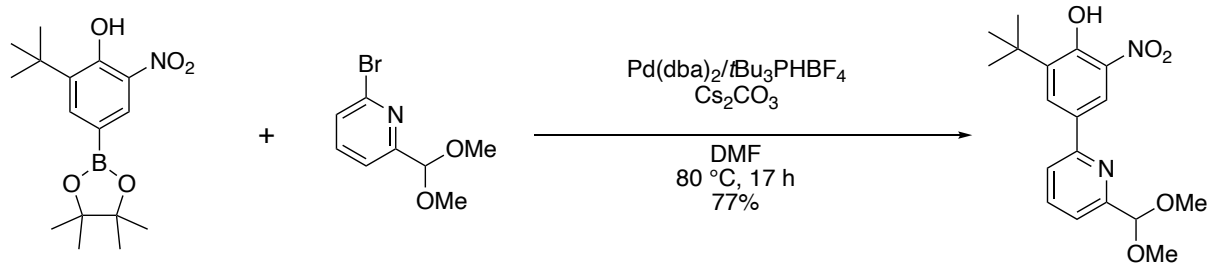
^{13}C NMR (151 MHz, $CDCl_3$): δ 157.0, 140.2, 139.7, 134.1, 130.3, 84.2, 35.5, 29.4, 24.9;

m.p.: 188.7–190.9 °C (decomp.);

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{23}BNO_5$ ([**8**–H]$^-$): 319.1706; found: 319.1694;

Elemental analysis: calcd for $C_{16}H_{24}BNO_5$ (**8**); C, 59.83; H, 7.53; N, 4.36. found: C, 59.82; H, 7.32; N, 4.43.

Synthesis of **10**



8 **9** **10**

Scheme S3. Synthesis of **10**

In a 300 mL 3-necked round bottom flask, to a mixture of **8** (4.0725 g, 12.680 mmol, 1.0 eq.), **9**[S6] (4.6136 g, 19.965 mmol, 1.6 eq.), and Cs_2CO_3 (14.1366 g, 43.3878 mmol, 3.4 eq.) in dry DMF (70 mL) was added *t*Bu_3PHBF_4 (1.227 g, 4.229 mmol, 33 mol%) and $Pd_2(dba)_3$ (0.9314 g, 1.017 mmol, 8.0 mol%), and the mixture was stirred at 80 °C for 17 h under Ar atmosphere. The reaction mixture was concentrated in vacuo. 1 M NH_4Cl aq (200 mL) was added to the residue, and aqueous layer was extracted with $CHCl_3$ (100 mL × 3). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was passed through silica gel column ($CHCl_3$/AcOEt = 100/1), and concentrated in vacuo. The residue was purified by column chromatography on silica gel ($CHCl_3$) and dried in vacuo to give **10** as a yellow solid (3.3864 g, 9.7830 mmol, 77%).

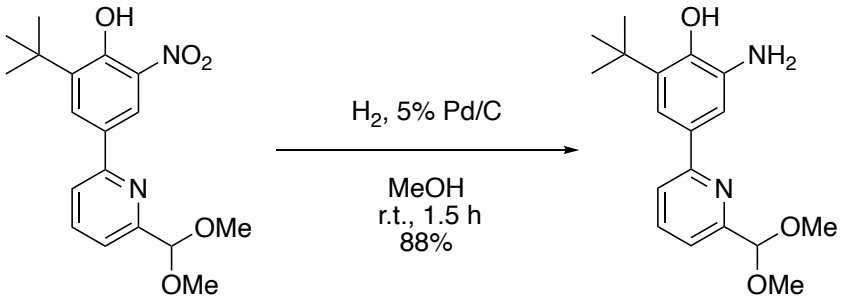
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.67 (s, 1H), 8.64 (d, *J* = 2.2 Hz, 1H), 8.35 (d, *J* = 2.2 Hz, 1H), 7.82 (dd, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 5.42 (s, 1H), 3.49 (s, 6H), 1.51 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.6, 155.4, 154.5, 140.9, 137.6, 134.4, 133.4, 130.4, 121.2, 119.7, 104.8, 54.2, 35.8, 29.3;

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{23}N_2O_5$ ([**10**+H]$^+$): 347.1607; found: 347.1590;

Elemental analysis: calcd for $C_{18}H_{22}N_2O_5$ (**10**); C, 61.61; H, 6.46; N, 7.98. found: C, 61.70; H, 6.55; N, 7.94.

Synthesis of **1**



10 **1**

Scheme S4. Synthesis of **1**

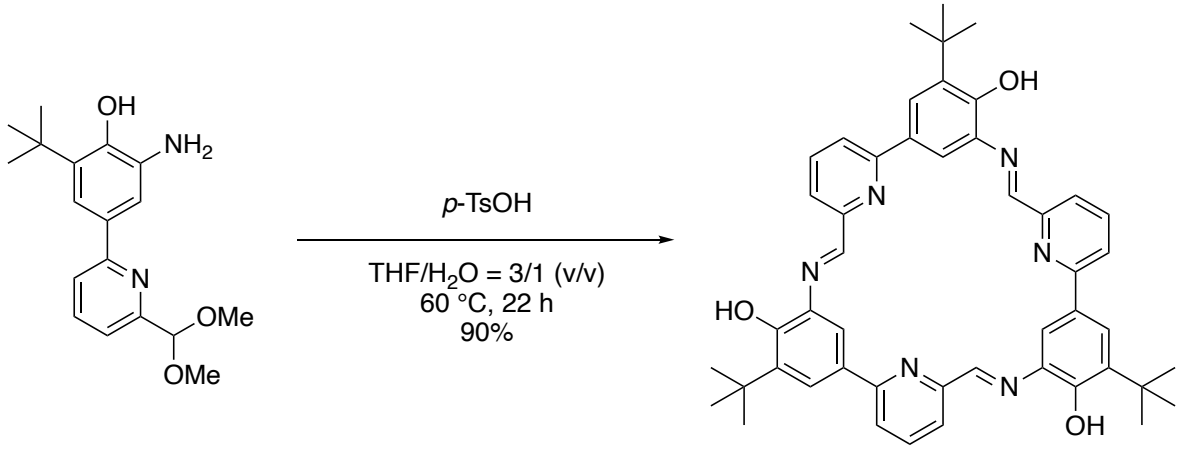
A mixture of **10** (1.0176 g, 2.9378 mmol, 1.0 eq.) and 5% Pd/C (0.6581 g) in dry MeOH (100 mL) was stirred at room temperature for 1 h under H_2 atmosphere in a 200 mL eggplant flask. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by automated column chromatography ($CHCl_3$/AcOEt = 100/0–80/20) and dried in vacuo to give **1** as white solid (0.82 g, 2.6 mmol, 88%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.57 (s, 1H), 7.52 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 6.24 (br, 1H), 5.41 (s, 1H), 3.46 (s, 6H), 1.46 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.12, 156.95, 148.5, 137.1, 135.9, 132.8, 130.7, 119.6, 118.41, 118.29, 104.9, 54.0, 34.6, 29.7;

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{25}N_2O_3$ ([**1**+H]$^+$): 317.1865; found: 317.1853.

Synthesis of **2**



1 **2**

Scheme S5. Synthesis of **2**

In a 100 mL Schlenk flask, to a solution of **1** (0.7556 g, 2.388 mmol, 1.0 eq.) and *p*-TsOH·H_2O (0.4966 g, 2.611 mmol, 1.1 eq.) in dry THF (36 mL) was added H_2O (12 mL), and the mixture was stirred at 60 °C for 22 h under Ar atmosphere. The reaction mixture was filtrated, and the collected solid was washed with water. The solid was dried in vacuo to give **2**·1.75H_2O as a pale yellow solid (0.5660 g, 0.7178 mmol, 90%).

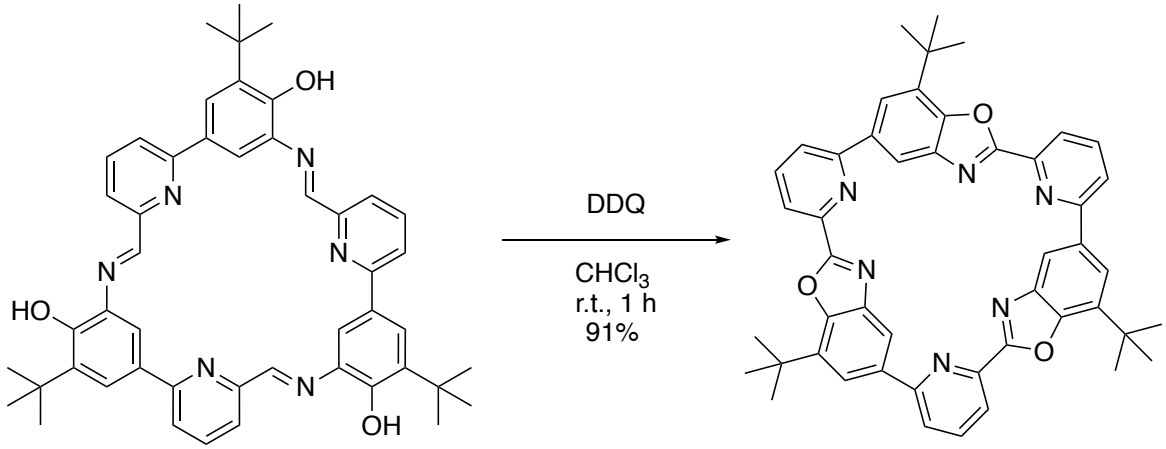
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.34 (s, 3H), 8.76 (d, *J* = 1.7 Hz, 3H), 8.43 (s, 3H), 8.17 (t, *J* = 4.3 Hz, 3H), 7.89–7.88 (m, 6H), 7.82 (d, *J* = 1.7 Hz, 3H), 1.56 (s, 27H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.7, 156.7, 154.1, 153.2, 137.2, 136.2, 134.5, 129.0, 124.7, 120.3, 118.6, 112.5, 35.0, 29.4;

MALDI-MS: *m*/*z* calcd for $C_{48}H_{49}N_6O_3$ ([**2**+H]$^+$): 757.39, found: 757.40;

Elemental analysis: calcd for $C_{48}H_{51.5}N_6O_{4.75}$ (**2**·1.75H_2O); C, 73.12; H, 6.58; N, 10.66. found: C, 73.05; H, 6.84; N, 10.36.

Synthesis of **3**



2 **3**

Scheme S6. Synthesis of **3**

DDQ (0.5098 g, 2.246 mmol, 5.5 eq.) was add to a solution of **2** (0.3088 g, 0.4080 mmol, 1.0 eq.) in $CHCl_3$ (150 mL), and the mixture was stirred at room temperature for 1 h in a 300 mL eggplant flask. The reaction mixture was washed with sat. $NaHCO_3$ aq (200 mL × 1, then 100 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. $CHCl_3$ (10 mL) was added to the residue, and the mixture was filtered. The obtained solid was washed with $CHCl_3$ (10 mL × 2). The solid was dried in vacuo to give **3**·3.4$CHCl_3$ (amount of $CHCl_3$ was determined from ^{1}H NMR in benzene-d_6 and elemental analysis) as a white solid (0.2793 g, 0.3720 mmol, 91%).

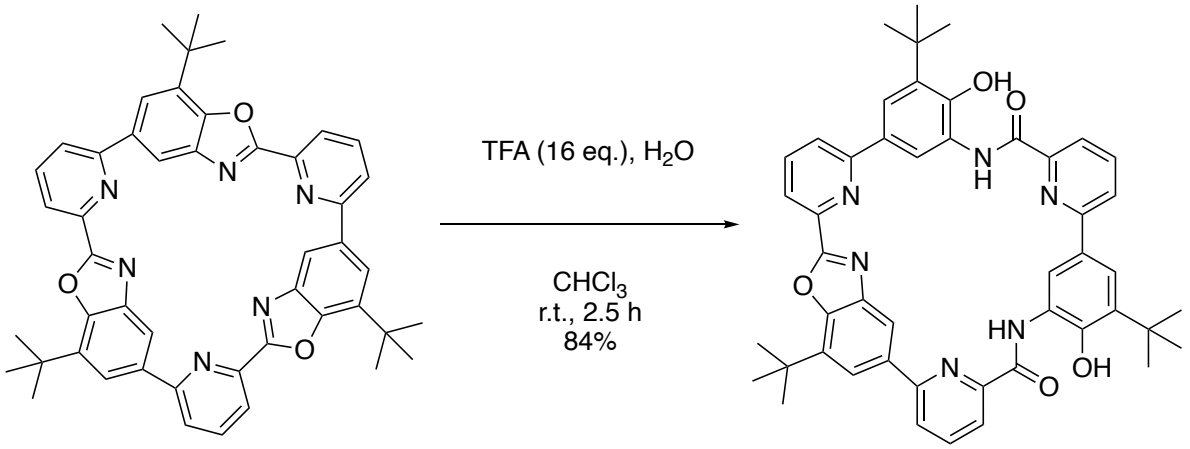
^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD = 10/1): δ 9.15 (d, J = 1.7 Hz, 3H), 8.00 (t, J = 7.6 Hz, 3H), 7.95 (d, J = 7.6 Hz, 3H), 7.90 (d, J = 7.6 Hz, 3H), 7.61 (d, J = 1.7 Hz, 3H), 1.57 (s, 27H);

^{13}C NMR (151 MHz, $CDCl_3$/CD_3OD = 10/1): δ 163.7, 158.2, 151.6, 146.0, 143.7, 138.4, 137.4, 135.2, 122.9, 120.44, 120.34, 119.1, 34.7, 30.2;

HRMS (ESI): m/z calcd for $C_{48}H_{42}N_6O_3Na$ ([**3**+Na]$^+$): 773.3216; found: 773.3194.

Elemental analysis: calcd for $C_{51.4}H_{54.4}N_6O_3Cl_{10.2}$ (**3**·3.4$CHCl_3$); C, 53.37; H, 3.96; N, 7.27. found: C, 53.51; H, 3.89; N, 7.35.

Synthesis of **4**



3 **4**

Scheme S7. Synthesis of **4**

A solution of **3**·$(CHCl_3)_3$ (0.1535 g, 0.1384 mmol, 1.0 eq.) and TFA (170 μL, 2.22 mmol, 16 eq.) in $CHCl_3$ (70 mL) with H_2O (100 μL) was stirred at room temperature for 2.5 h in a 200 mL eggplant flask. The reaction mixture was washed with sat. $NaHCO_3$ aq (100 mL × 1). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by automated column chromatography ($CHCl_3$/MeOH = 100/0–95/5) and dried in vacuo to give **4**·$(CHCl_3)_{1.5}$·H_2O as white solid (0.1148 g, 0.1167 mmol, 84%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.67 (s, 1H), 10.02 (s, 1H), 9.02 (d, *J* = 1.7 Hz, 1H), 8.94 (s, 2H), 8.68 (d, *J* = 2.0 Hz, 1H), 8.43 (dd, *J* = 7.8, 0.9 Hz, 1H), 8.23 (dd, *J* = 7.4, 0.8 Hz, 1H), 8.10 (d, *J* = 7.4 Hz, 1H), 8.06 (t, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.95–7.97 (m, 3H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 1.64 (s, 9H), 1.56 (s, 9H), 1.54 (s, 8H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.8, 164.0, 163.1, 160.6, 156.6, 155.0, 151.9, 151.1, 150.4, 148.5, 147.7, 144.4, 143.3, 141.9, 140.9, 139.2, 138.1, 137.8, 135.7, 134.6, 132.9, 128.82, 128.72, 127.5, 127.1, 126.4, 122.37, 122.34, 122.1, 120.7, 120.0, 119.1, 77.33, 77.23, 77.0, 76.7, 35.57, 35.52, 34.7, 30.1, 29.82, 29.74;

HRMS (ESI): *m*/*z* calcd for $C_{48}H_{47}N_6O_5$ ([**4**+H]$^+$): 787.3608; found: 787.3604.

Elemental analysis: calcd for $C_{49.5}H_{49.5}N_6O_6Cl_{4.5}$ (**4**·1.5$CHCl_3$·H_2O); C, 60.42; H, 5.07; N, 8.54. found: C, 60.18; H, 5.00; N, 8.26.

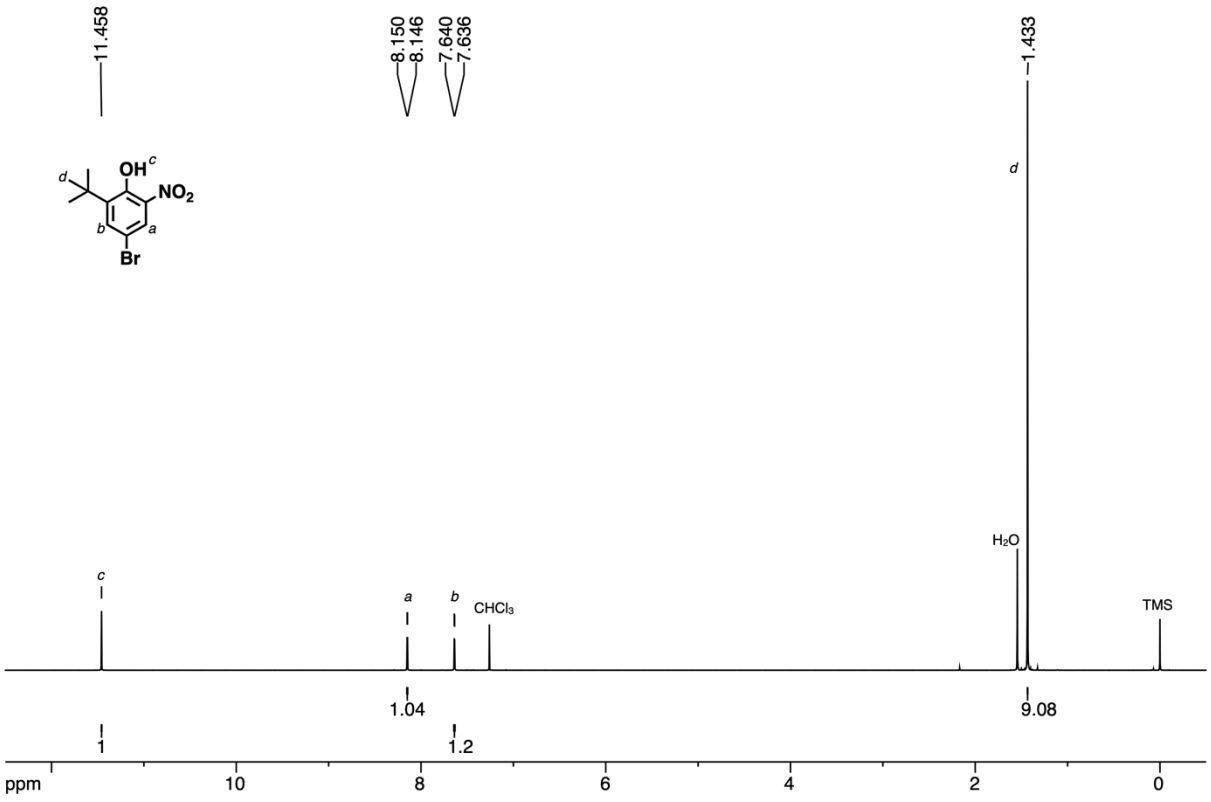


Figure S1. ^{1}H NMR spectrum of **7** ($CDCl_3$, 600 MHz)

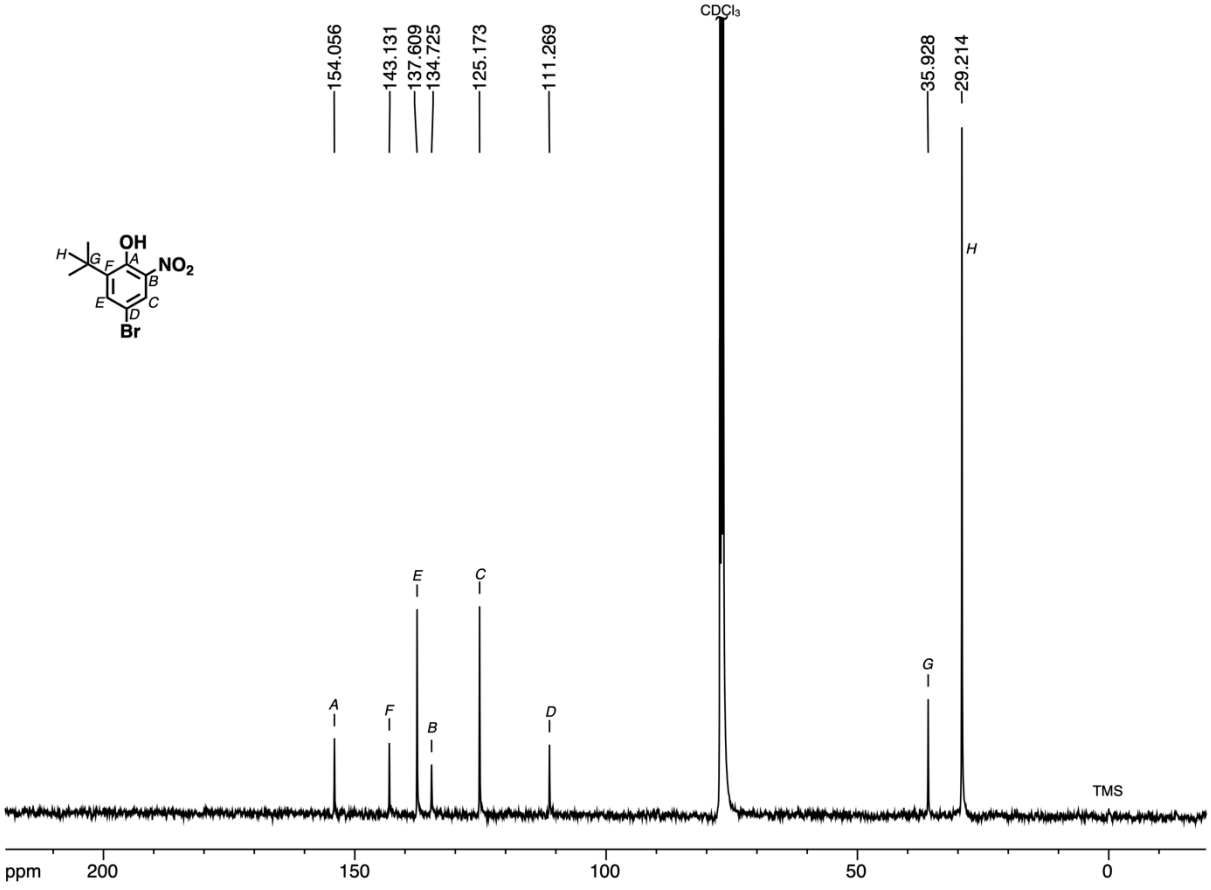


Figure S2. ^{13}C NMR spectrum of **7** ($CDCl_3$, 101 MHz)

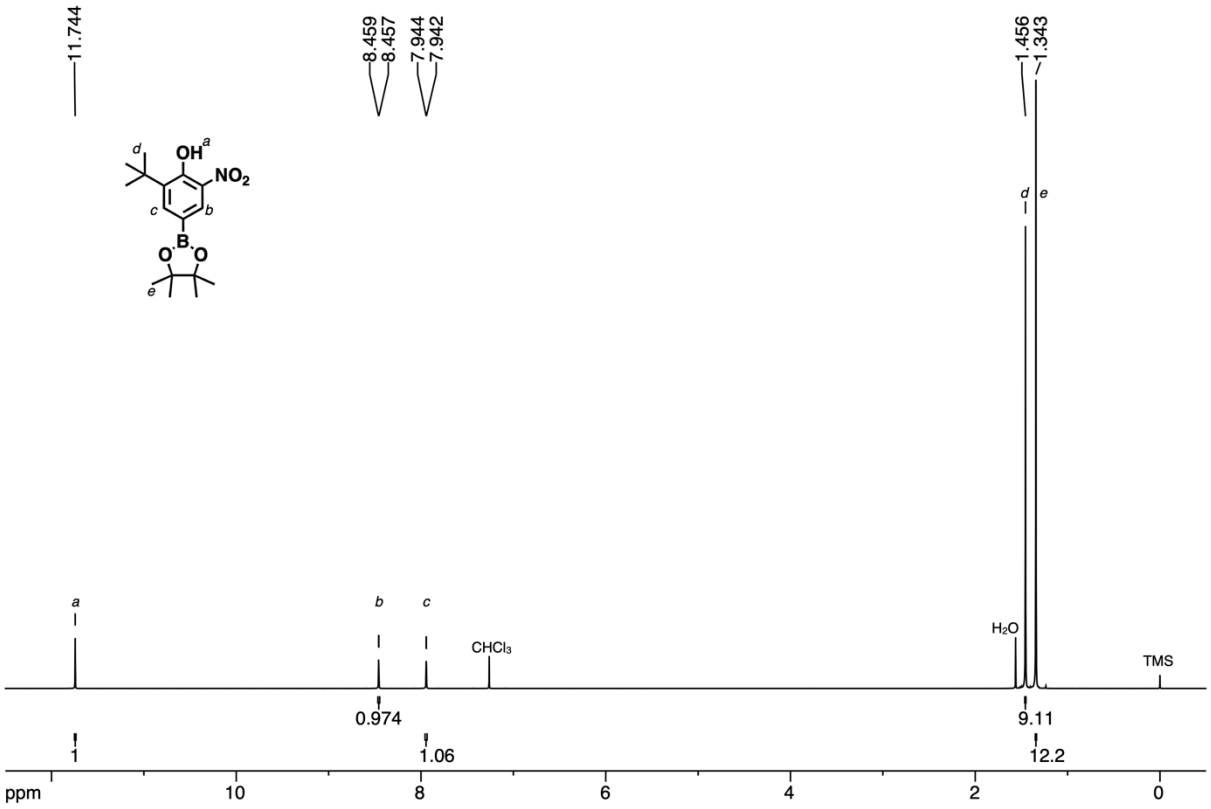


Figure S3. ^{1}H NMR spectrum of **8** ($CDCl_3$, 600 MHz)

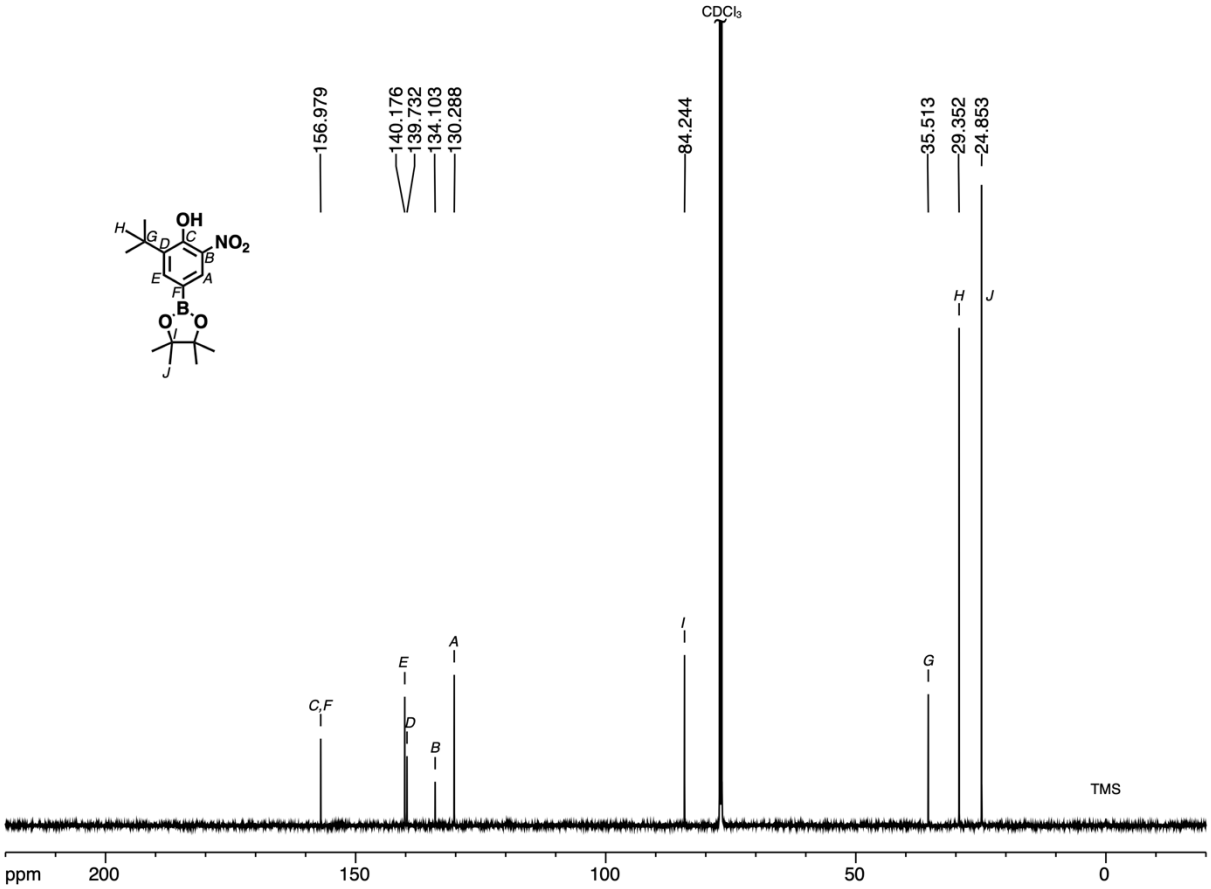


Figure S4. ^{13}C NMR spectrum of **8** ($CDCl_3$, 151 MHz)

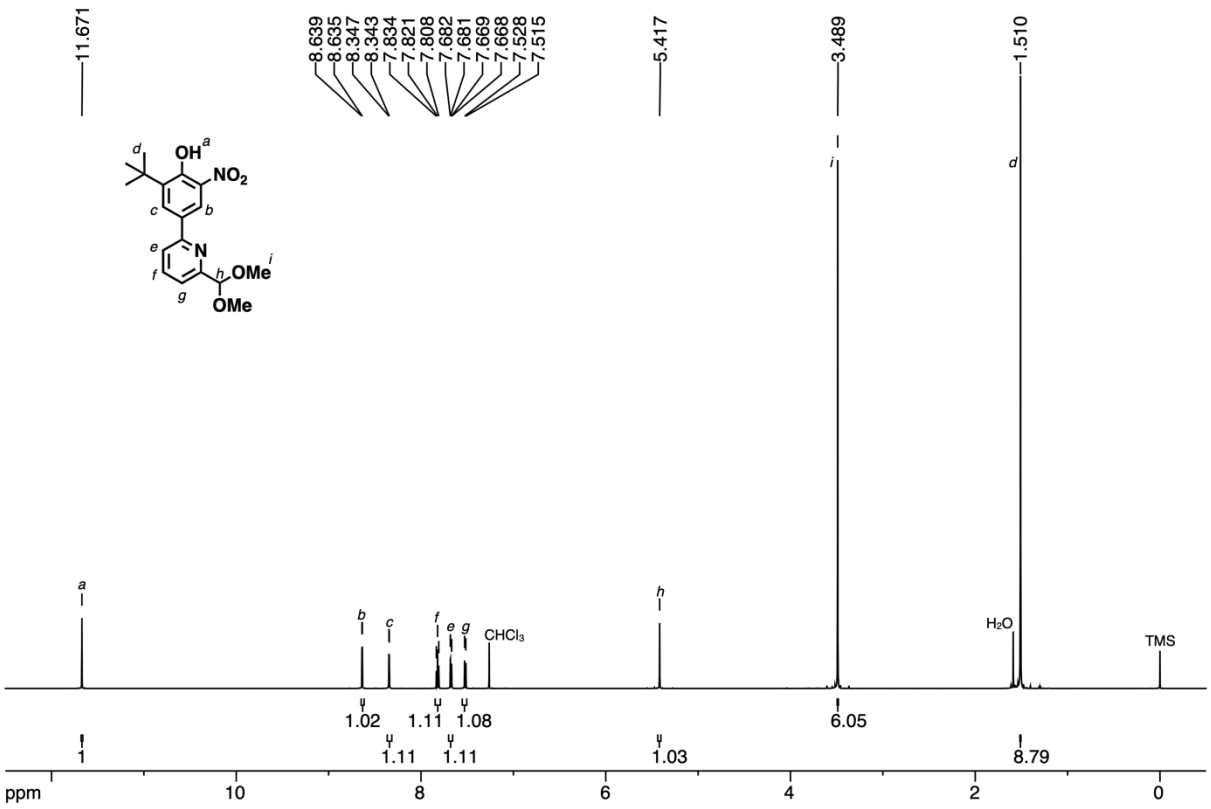


Figure S5. ^{1}H NMR spectrum of **10** ($CDCl_3$, 600 MHz)

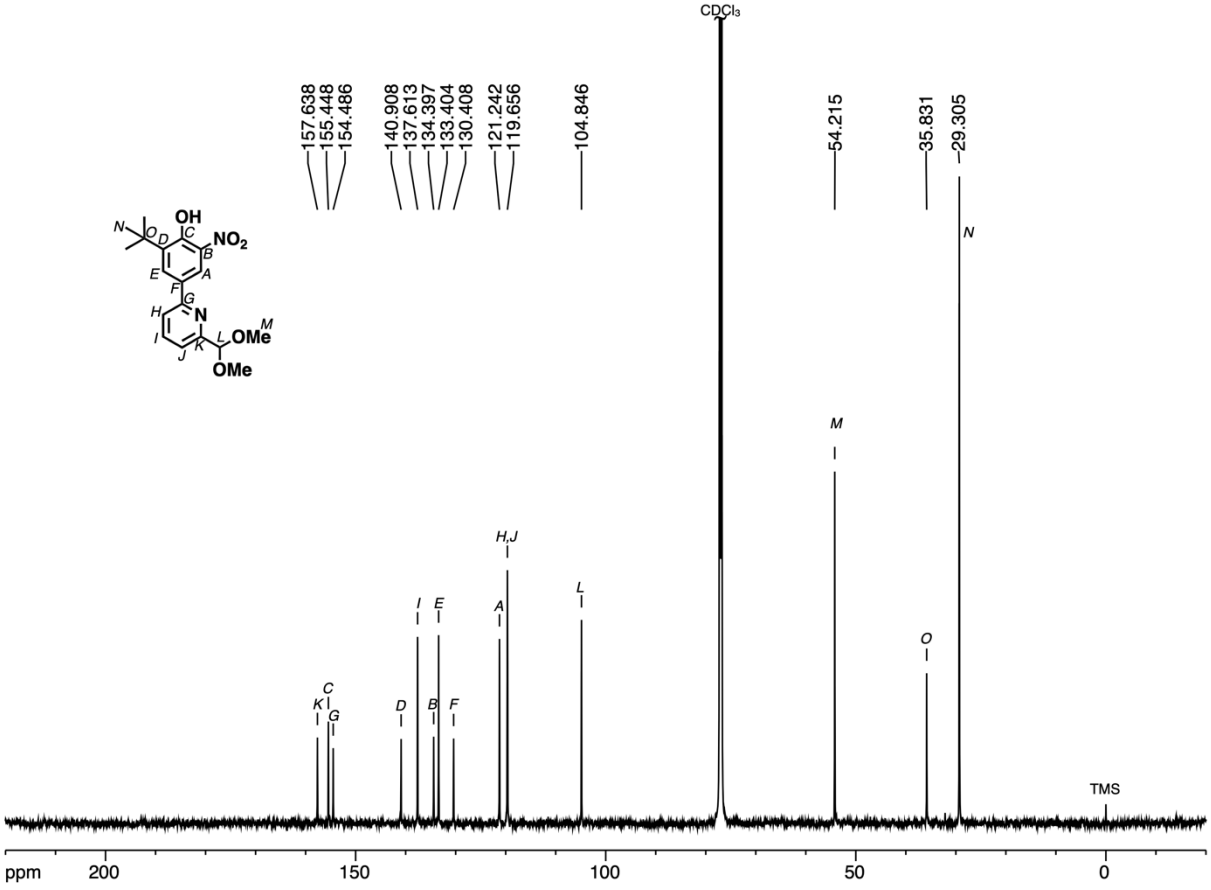


Figure S6. ^{13}C NMR spectrum of **10** ($CDCl_3$, 151 MHz)

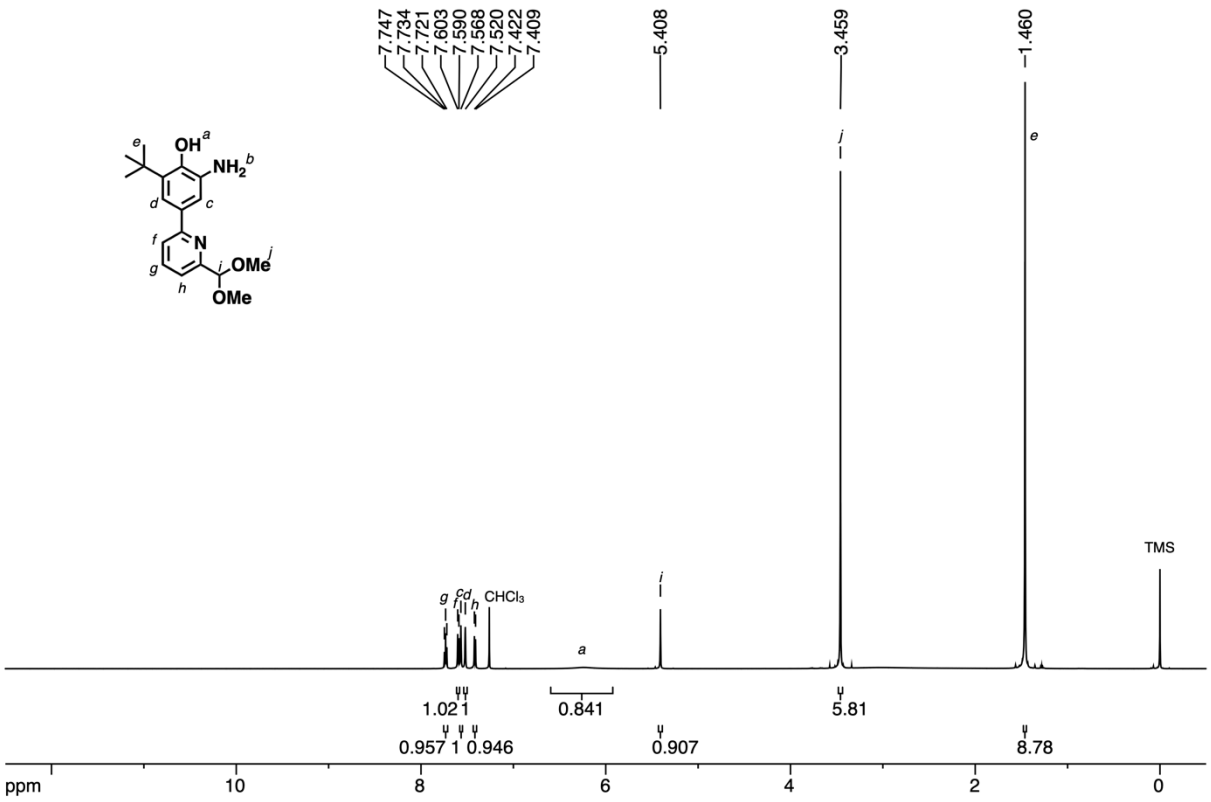


Figure S7. ^{1}H NMR spectrum of **1** ($CDCl_3$, 600 MHz)

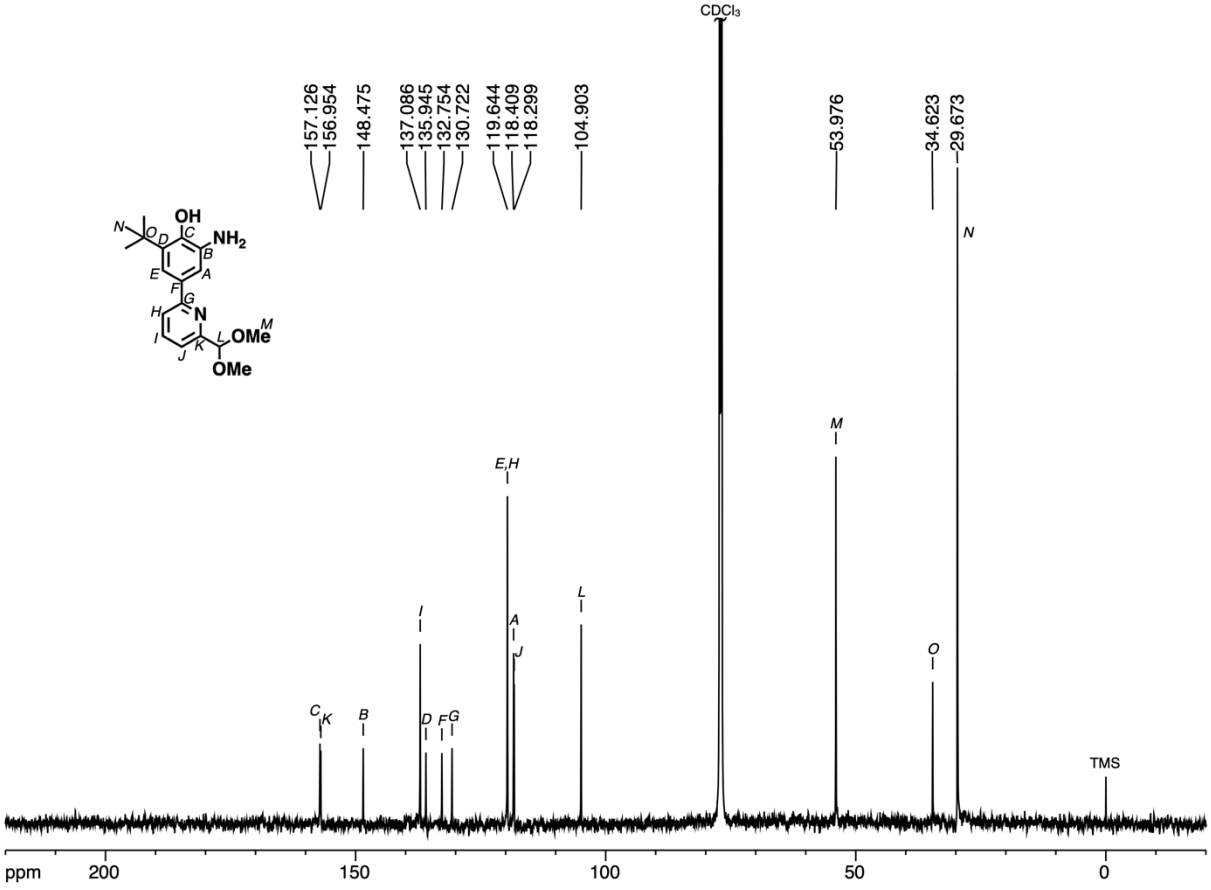


Figure S8. ^{13}C NMR spectrum of **1** ($CDCl_3$, 151 MHz)

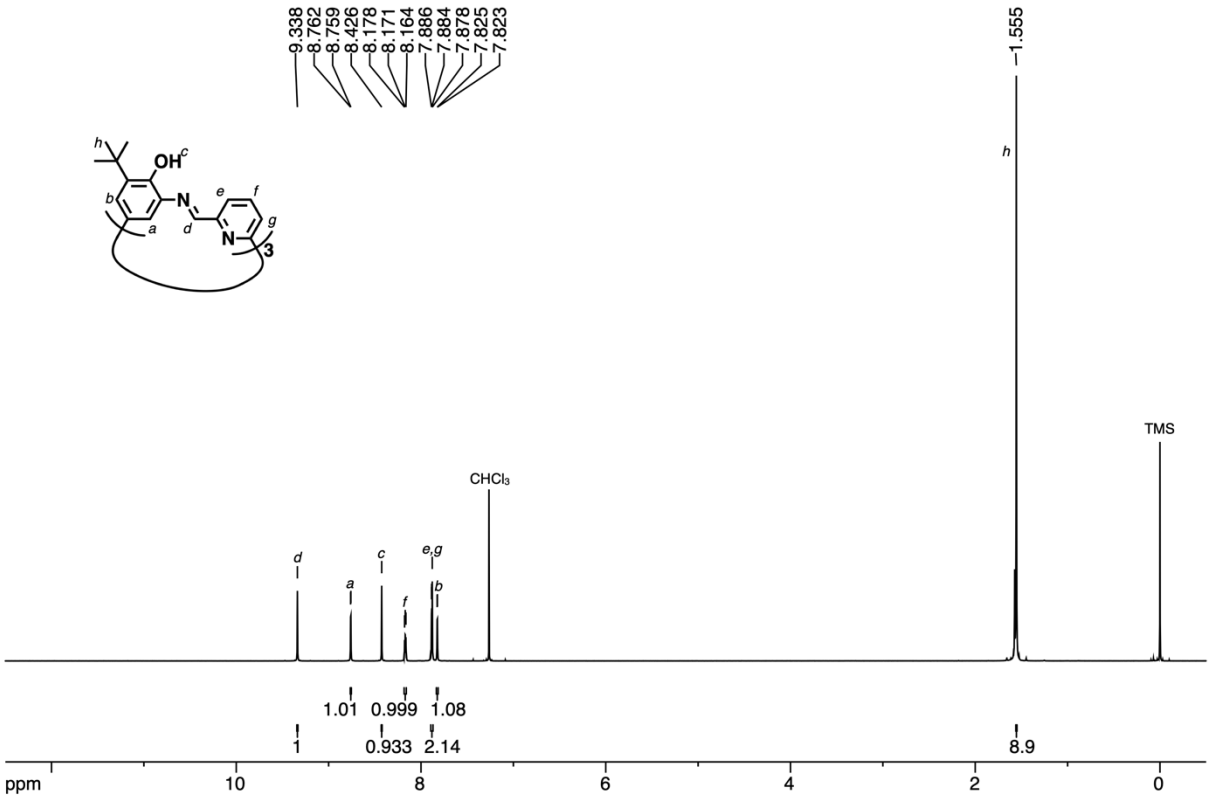


Figure S9. ^{1}H NMR spectrum of **2** ($CDCl_3$, 600 MHz)

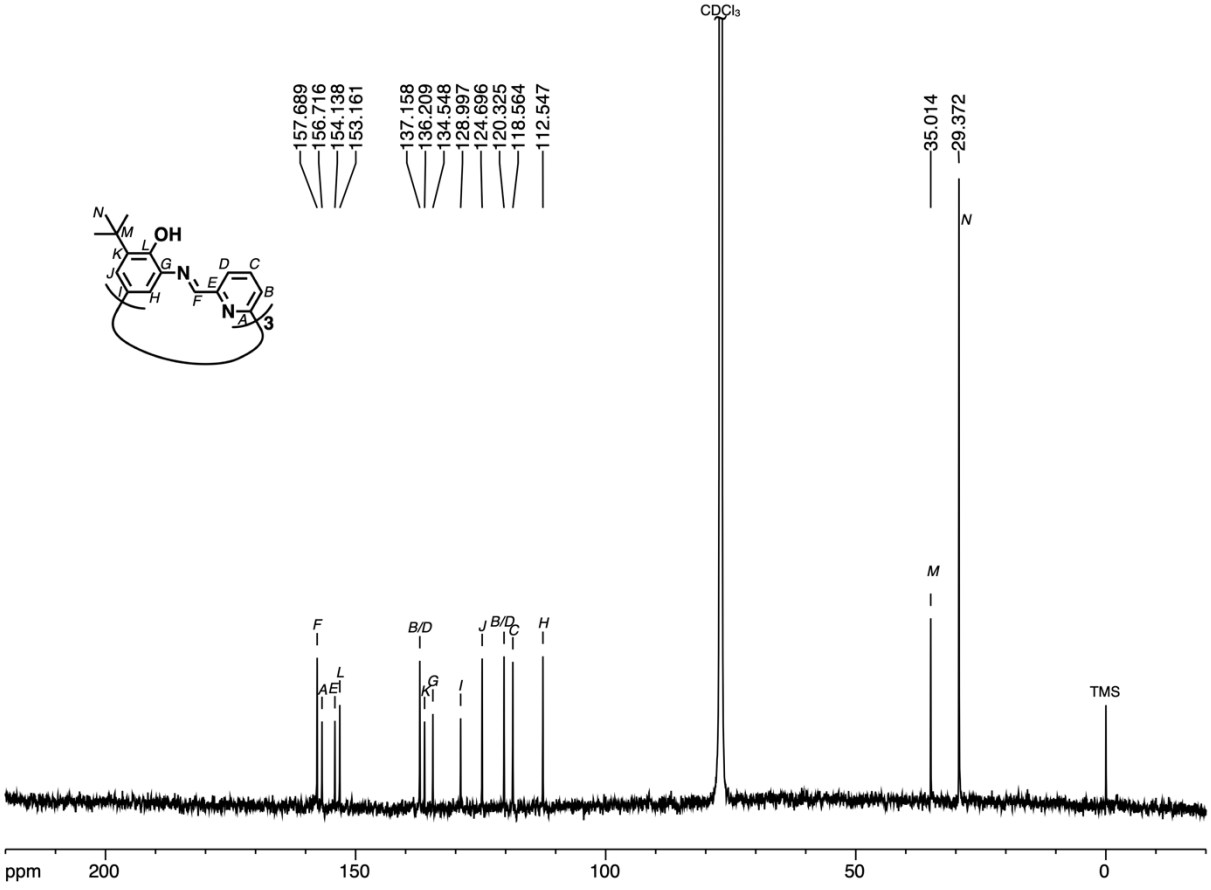


Figure S10. ^{13}C NMR spectrum of **2** ($CDCl_3$, 151 MHz)

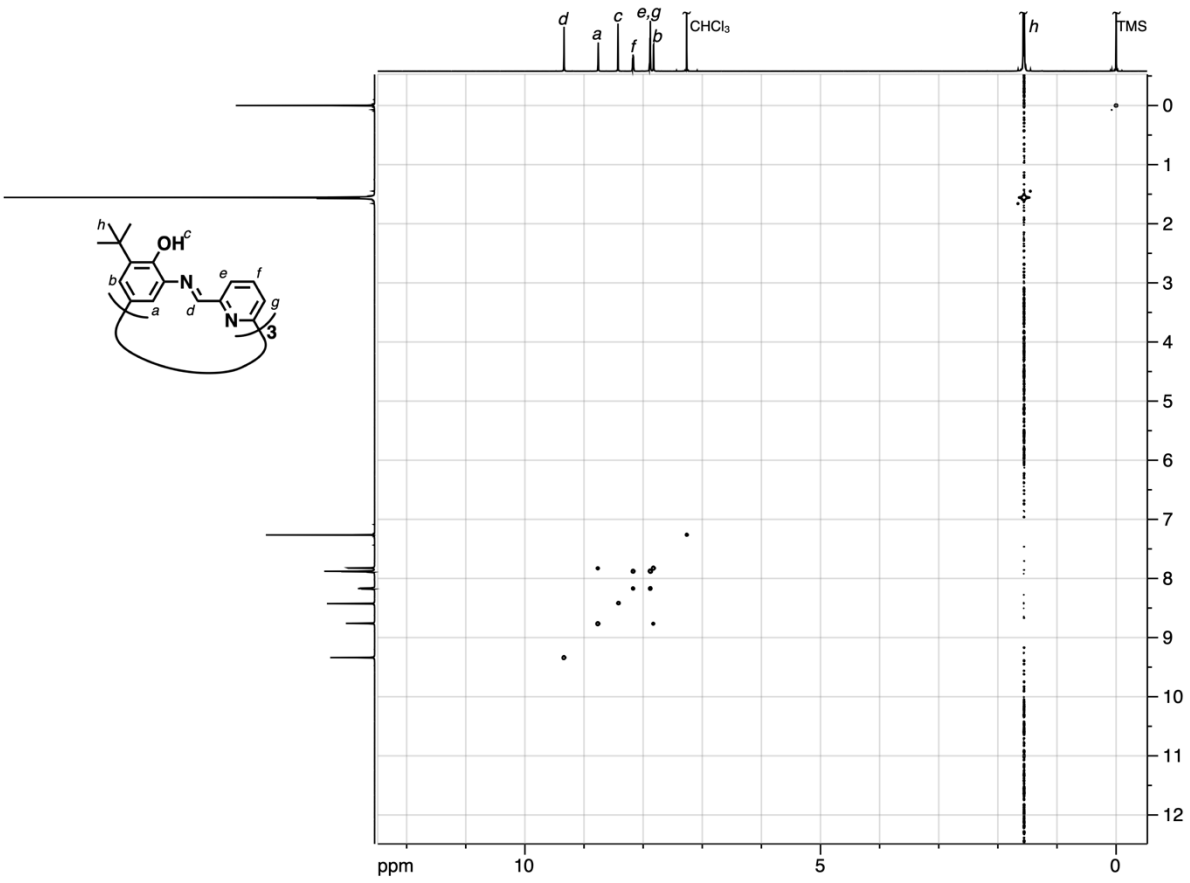


Figure S11. ^{1}H–^{1}H COSY spectrum of **2** ($CDCl_3$, 600 MHz)

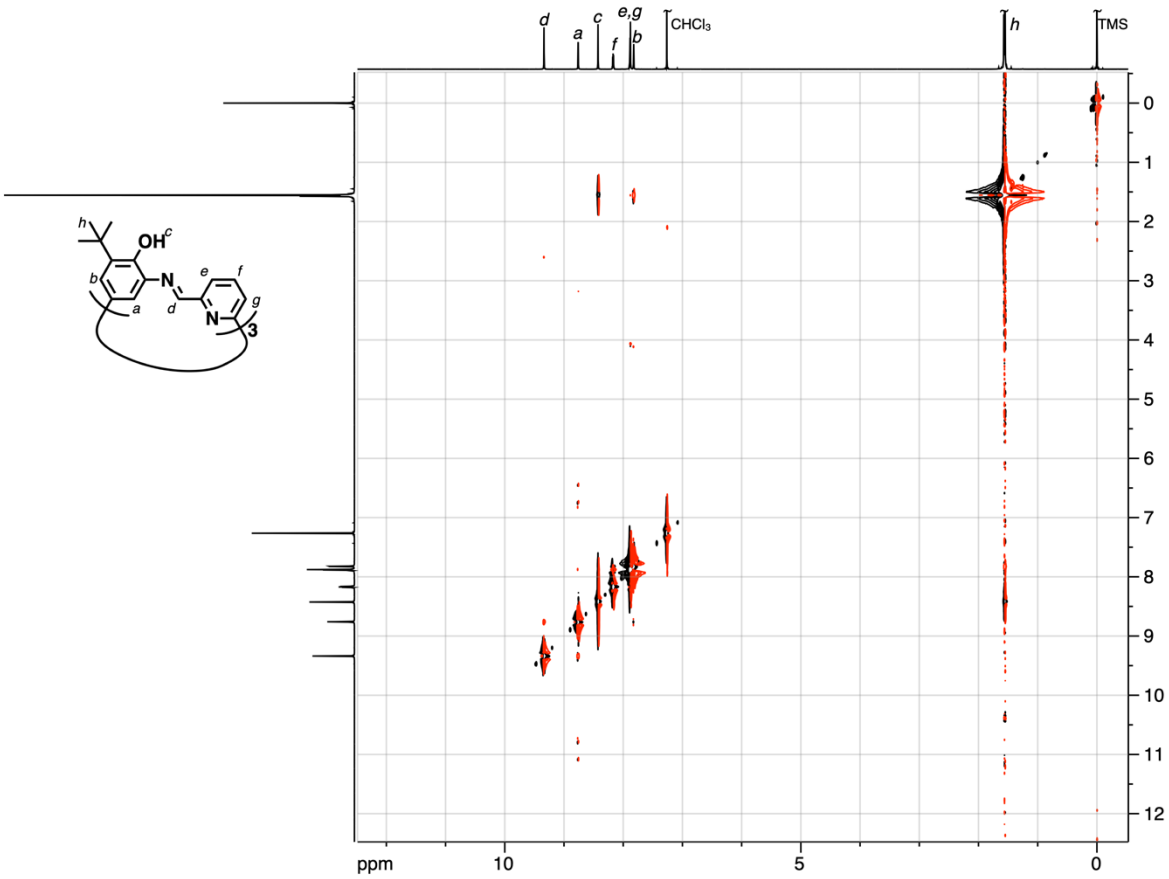


Figure S12. ^{1}H–^{1}H NOESY spectrum of **2** ($CDCl_3$, 600 MHz)

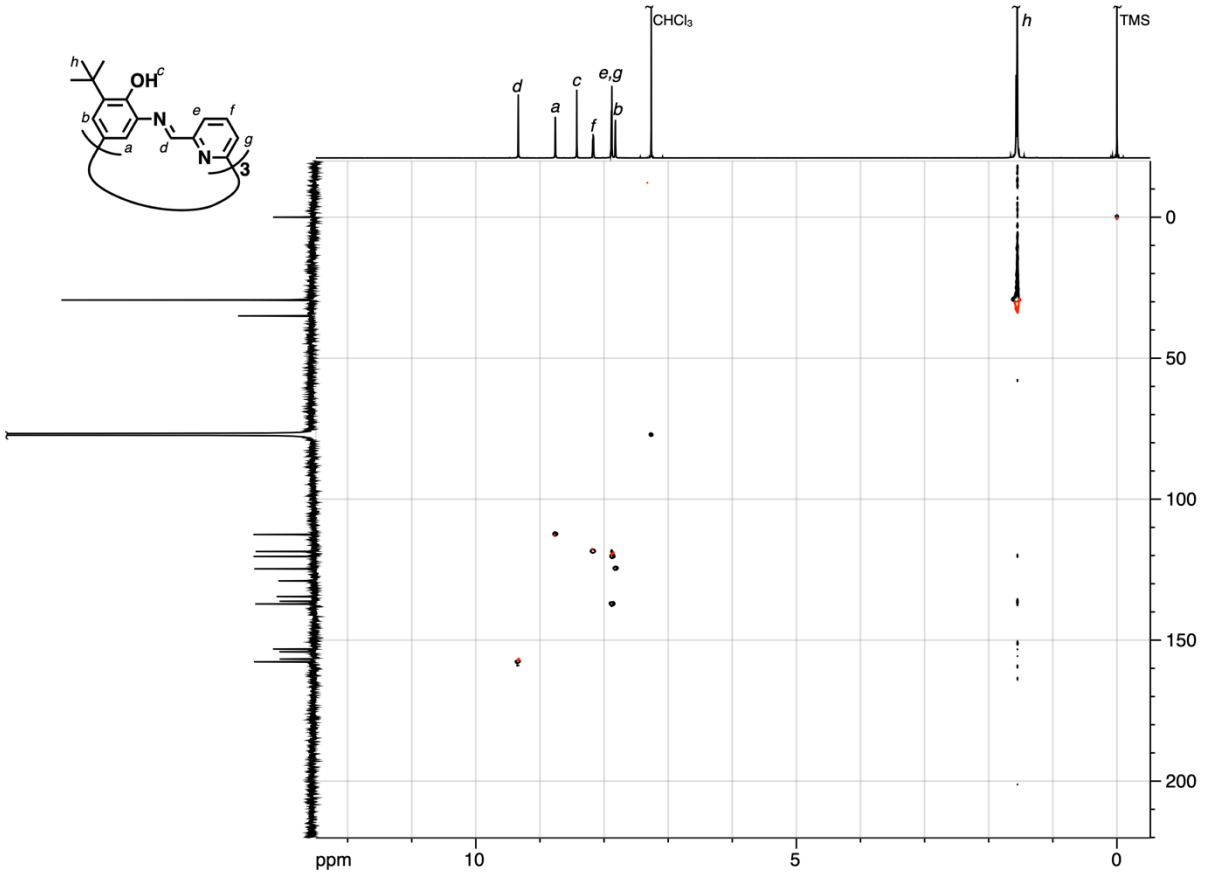


Figure S13. ^{1}H–^{13}C HSQC spectrum of **2** ($CDCl_3$, 600 MHz)

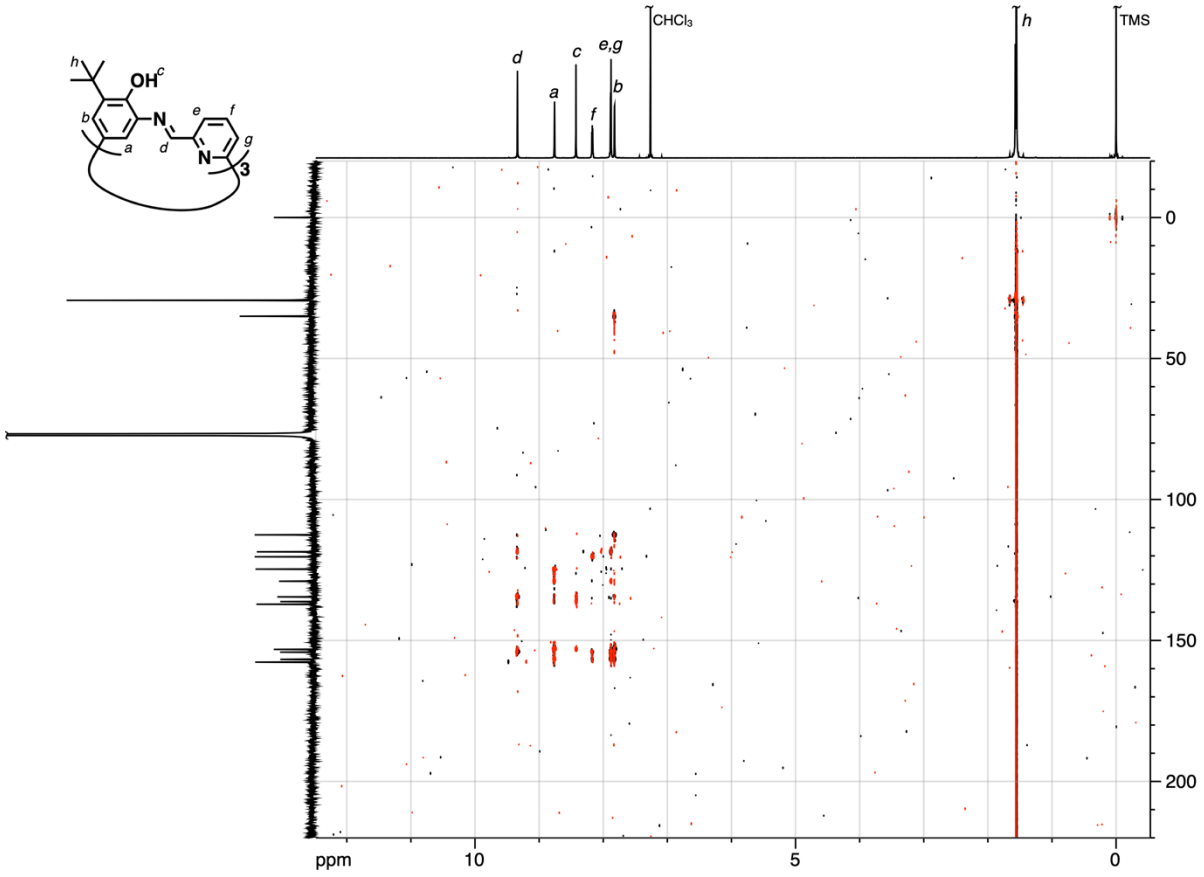


Figure S14. ^{1}H–^{13}C HMBC NMR spectrum of **2** ($CDCl_3$, 600 MHz)

A single crystal of **2**·0.64$CH_3COOC_2H_5$ suitable for an X-ray diffraction analysis was obtained by AcOEt vapor diffusion into THF solution of **2**.

Crystal data: $C_{50.56}H_{53.12}N_6O_{4.28}$, Fw = 813.31, yellow octahedron, 0.15 × 0.14 × 0.13 mm^3, hexagonal, space group $P6_5$ (No. 170), a = 18.9446(9) Å, c = 22.0233(11) Å, V = 6845.2(7) $Å^3$, Z = 6, T = 100 K, λ(Mo K_α) = 0.71073 Å, θ_{max} = 26.508°, R_1 ($I > 2\sigma$) = 0.0709, wR_2 (all) = 0.2160, GOF = 1.548, Flack parameter = 0.1(3). CCDC 2307866.

Absolute configuration was assigned by anomalous-dispersion effects in diffraction measurements on the crystal. The occupancy of AcOEt was optimized.

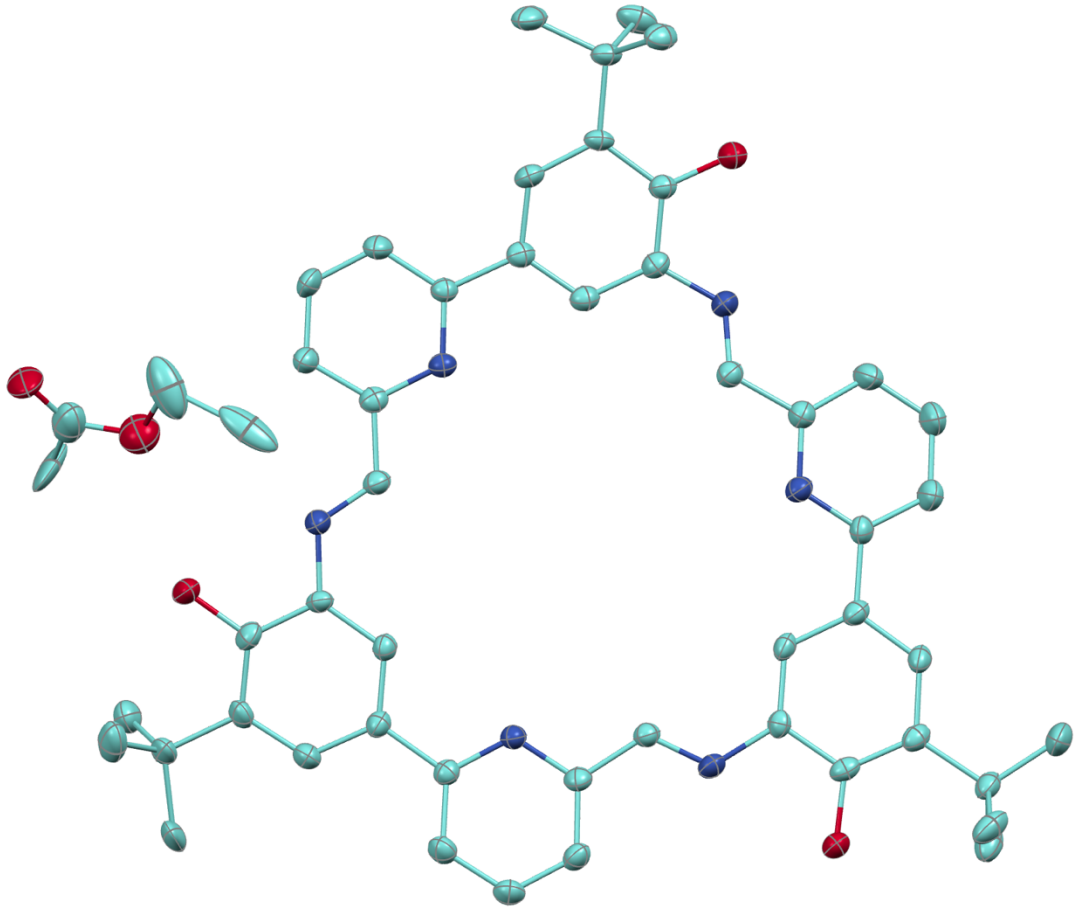


Figure S15. The molecular structure of **2**·0.64$CH_3COOC_2H_5$ determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red.

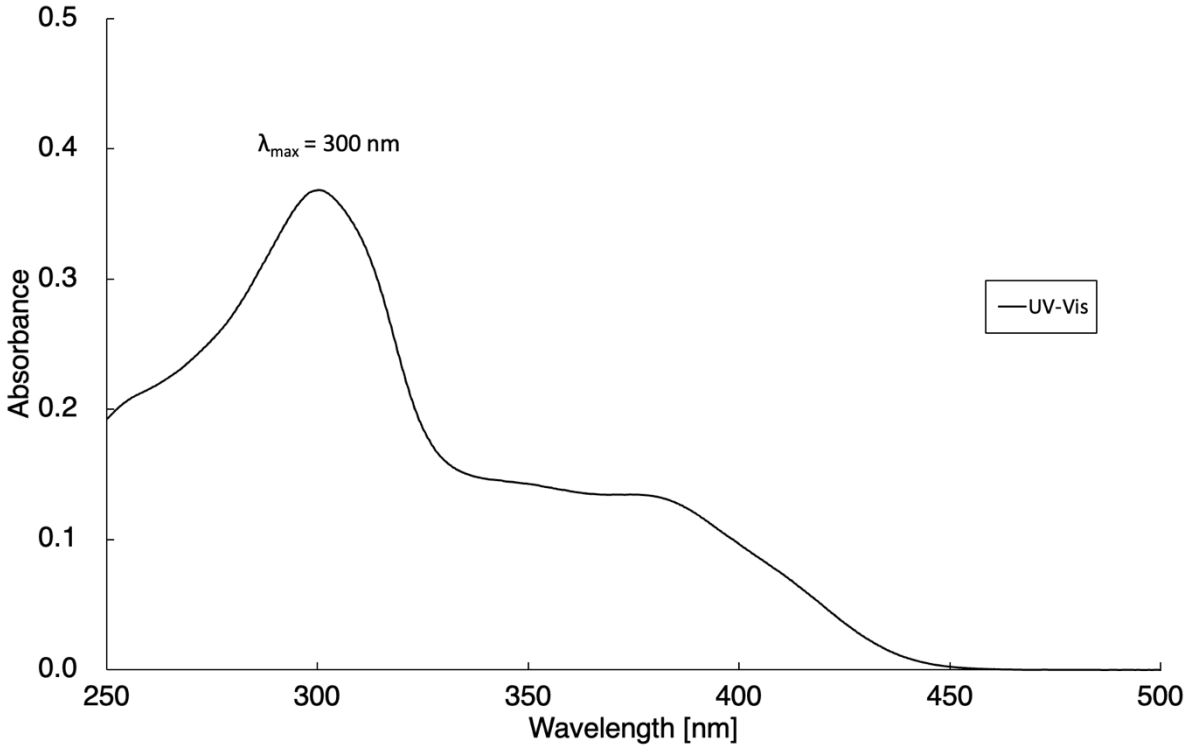


Figure S16. The UV-vis absorbance spectrum of **2** (5.0 μM, $CHCl_3$, l = 1 cm)

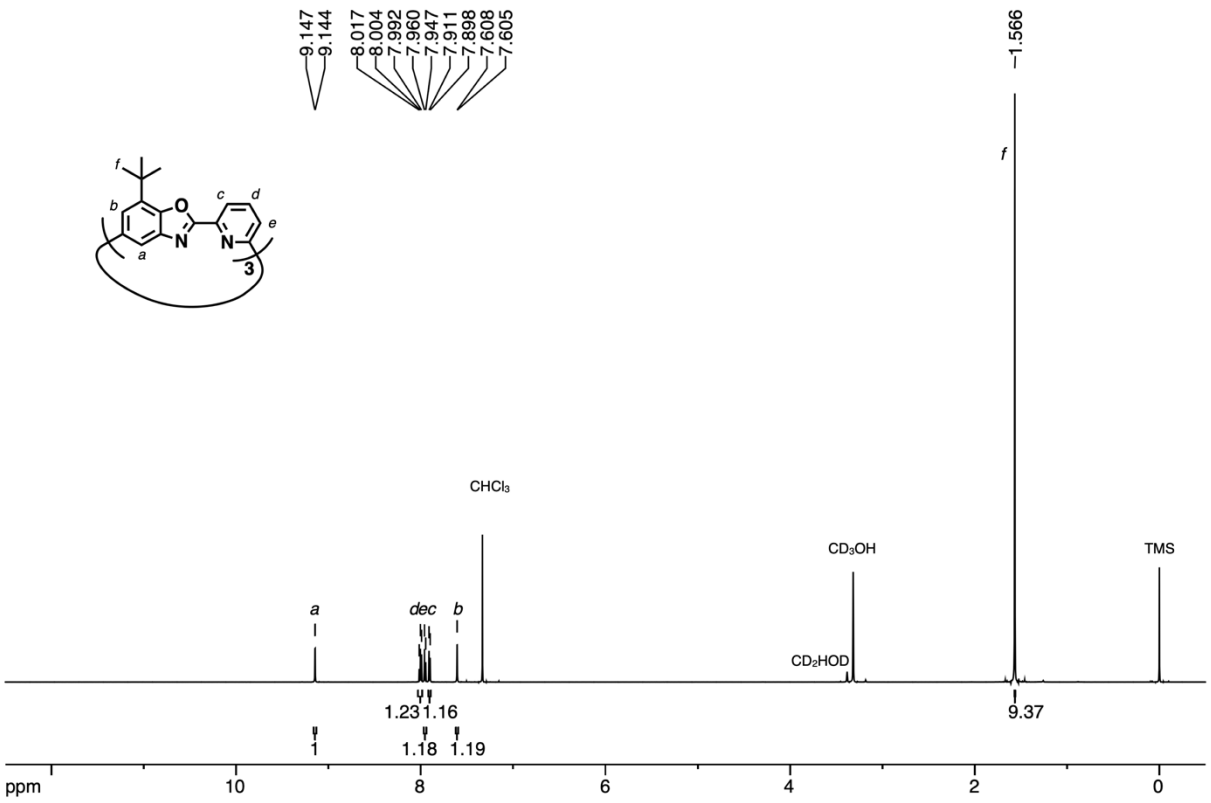


Figure S17. ^{1}H NMR spectrum of **3** ($CDCl_3/CD_3OD$ = 10/1, 600 MHz)

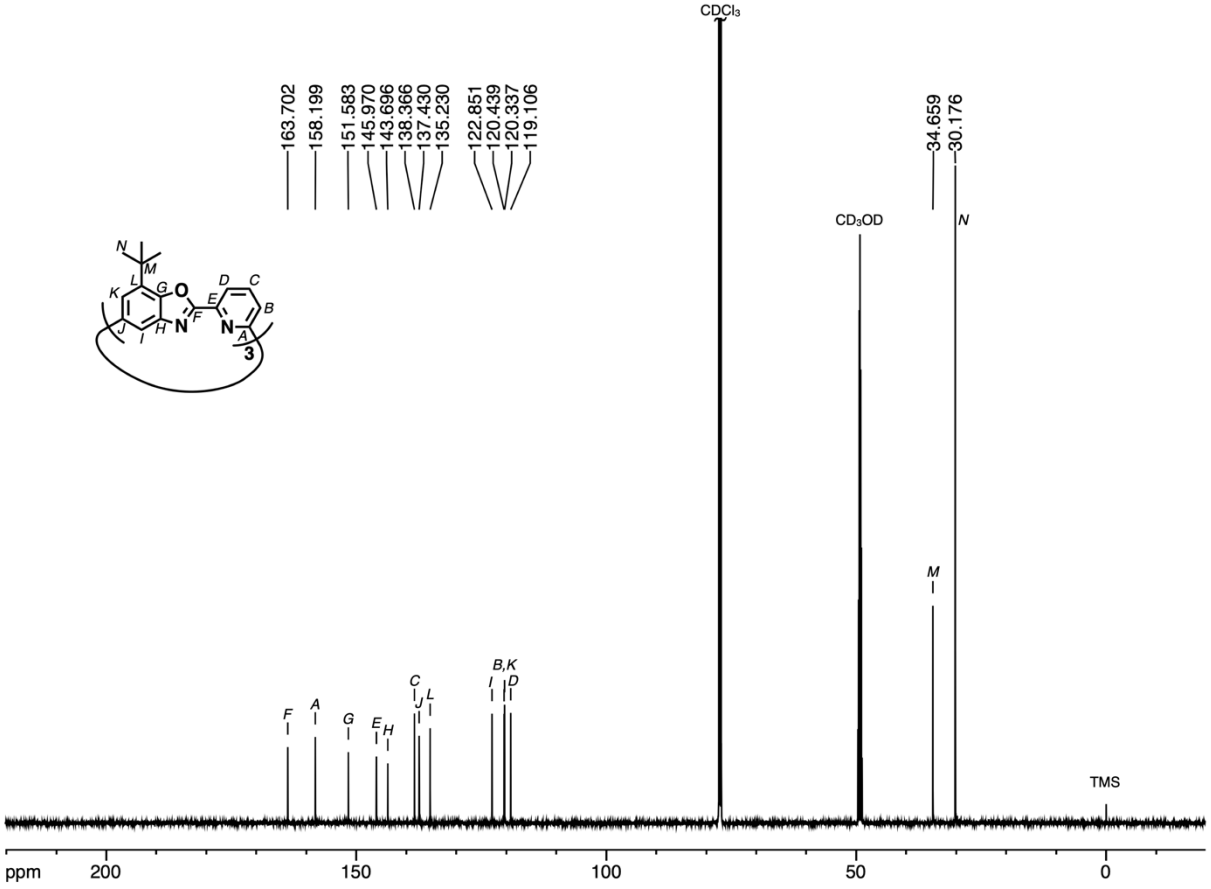


Figure S18. ^{13}C NMR spectrum of **3** ($CDCl_3/CD_3OD$ = 10/1, 151 MHz)

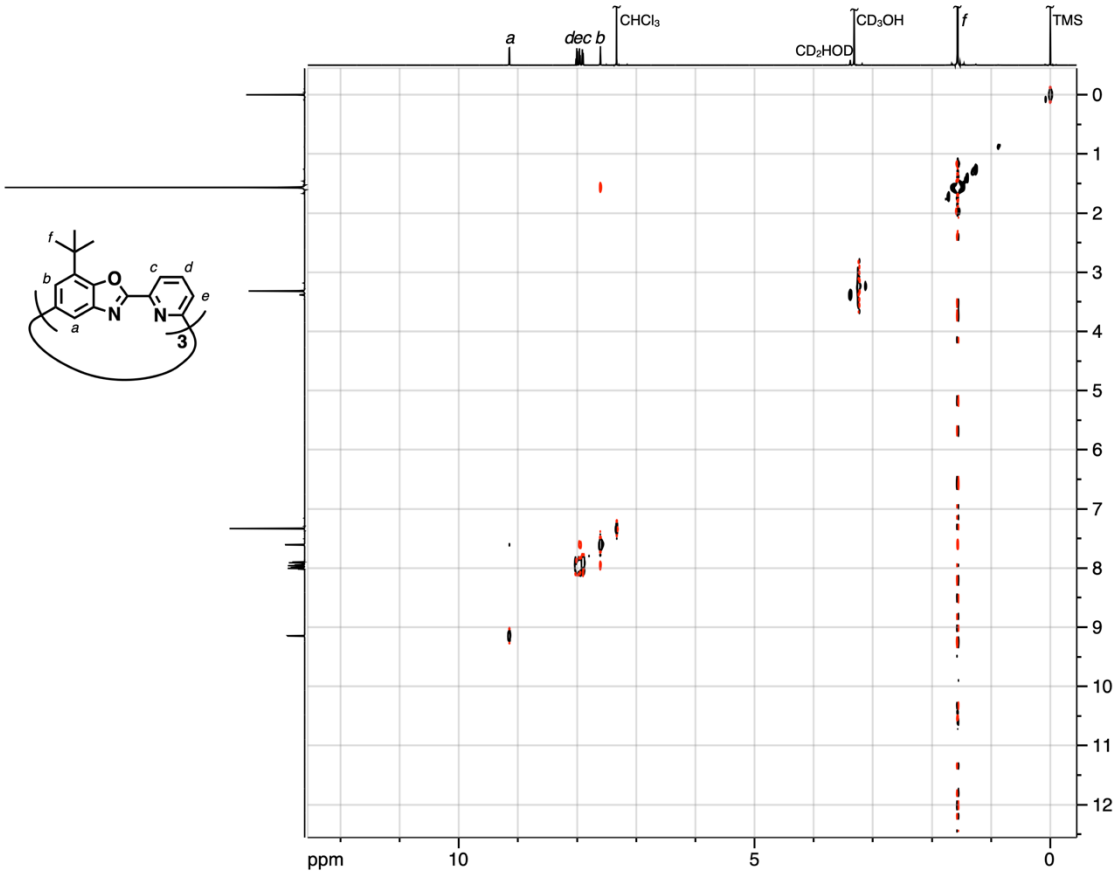


Figure S19. ^{1}H–^{1}H NOESY spectrum of **3** ($CDCl_3/CD_3OD$ = 10/1, 600 MHz)

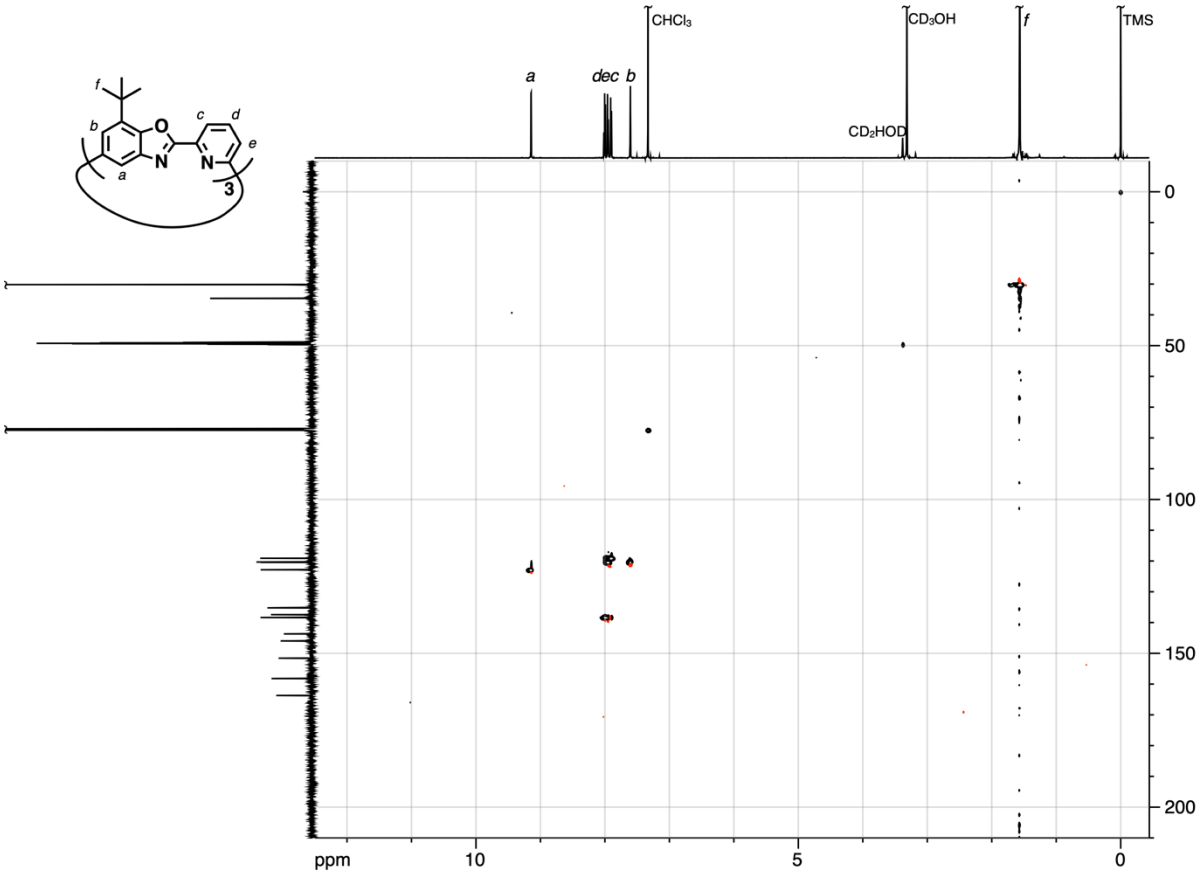


Figure S20. ^{1}H–^{13}C HSQC spectrum of **3** ($CDCl_3/CD_3OD$ = 10/1, 600 MHz)

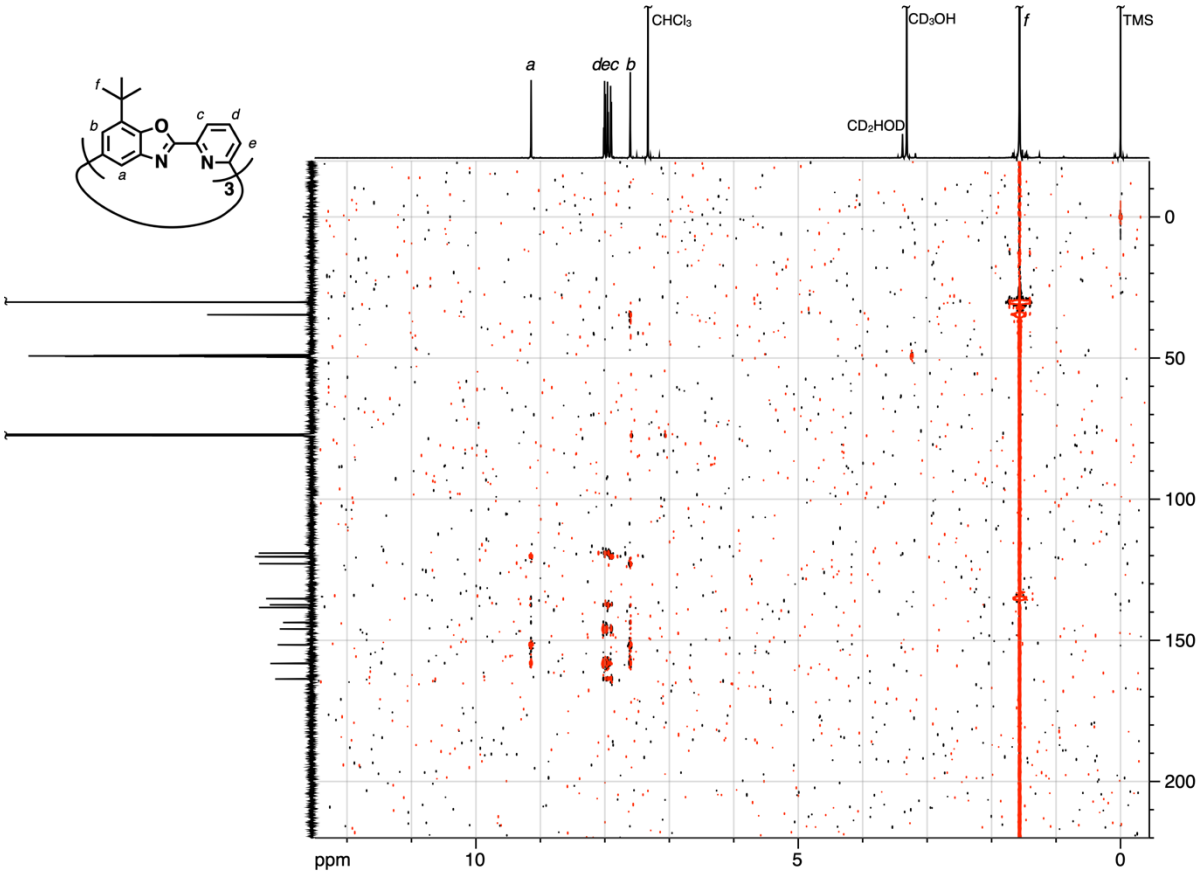


Figure S21. ^{1}H–^{13}C HMBC NMR spectrum of **3** ($CDCl_3/CD_3OD$ = 10/1, 600 MHz)

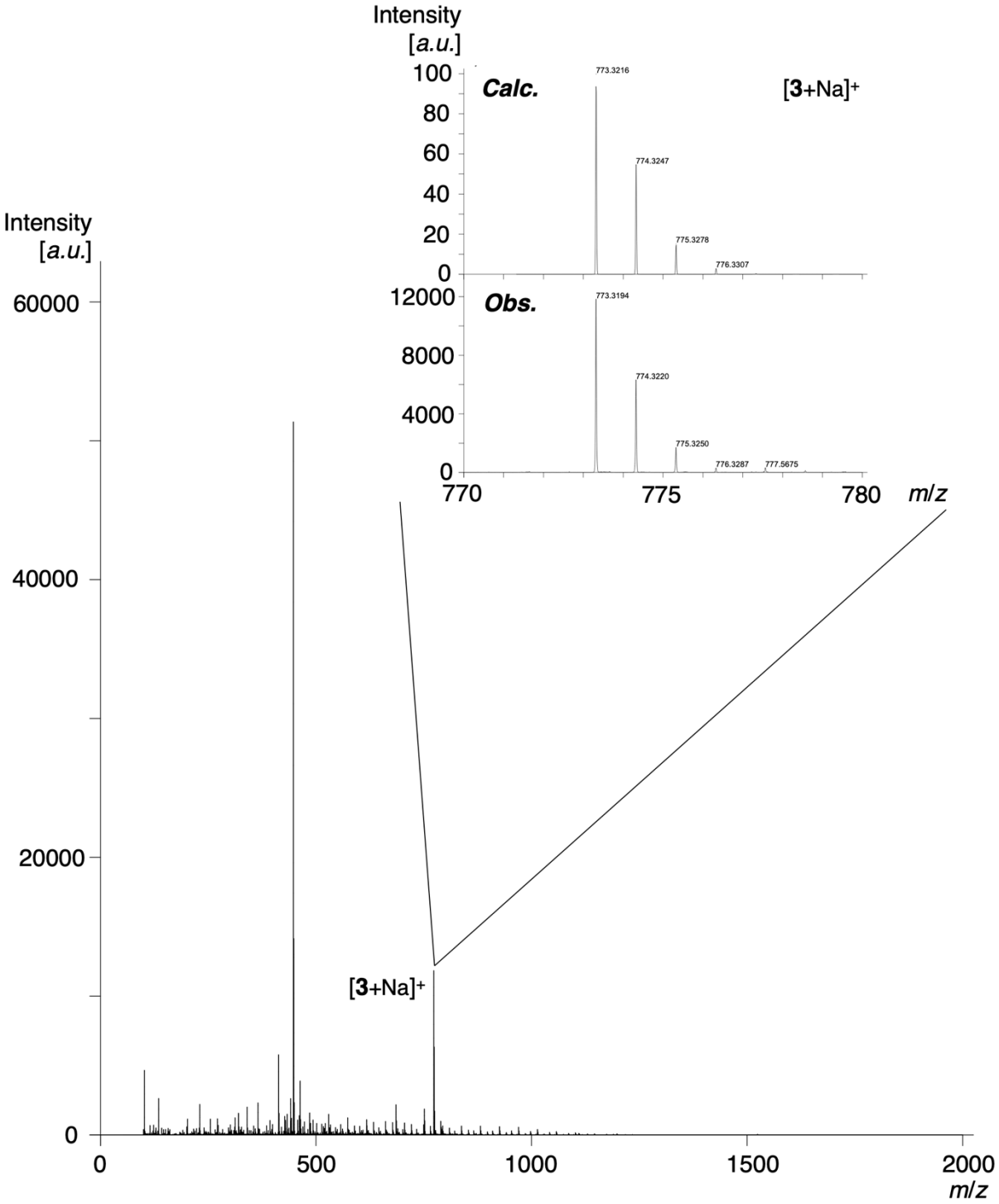


Figure S22. ESI-TOF mass spectrum of **3** (positive, MeOH).

A single crystal of **3**·2H_2O suitable for an X-ray diffraction analysis was obtained by recrystallization from toluene.

Crystal data: $C_{48}H_{42}N_6O_5$, Fw = 789.93, colorless block, 0.82 × 0.27 × 0.15 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 16.082(4) Å, b = 17.555(5) Å, c = 17.564(5) Å, V = 4959(2) $Å^3$, Z = 4, T = 100 K, λ(Mo K_α) = 0.71073 Å, θ_{max} = 23.255°, R_1 ($I > 2\sigma$) = 0.1644, wR_2 (all) = 0.3766, GOF = 2.440. Chemical absolute configuration is unknown. CCDC 2307867.

Solvent accessible voids of 1247 cubic angstroms (25.1% of the unit cell volume) were found, where toluene solvent molecules were heavily disordered. Refinements were performed using reflection data of 0.90 angstrom resolution, since the values of R-merge and mean $F_o^2/s(F_o^2)$ in the resolution shell between 1.00 and 0.90 angstrom were 25.63% and 4.00, respectively. The weak diffractions are probably due to the poor quality of the crystal, the large molecular size and the disordered solvents.

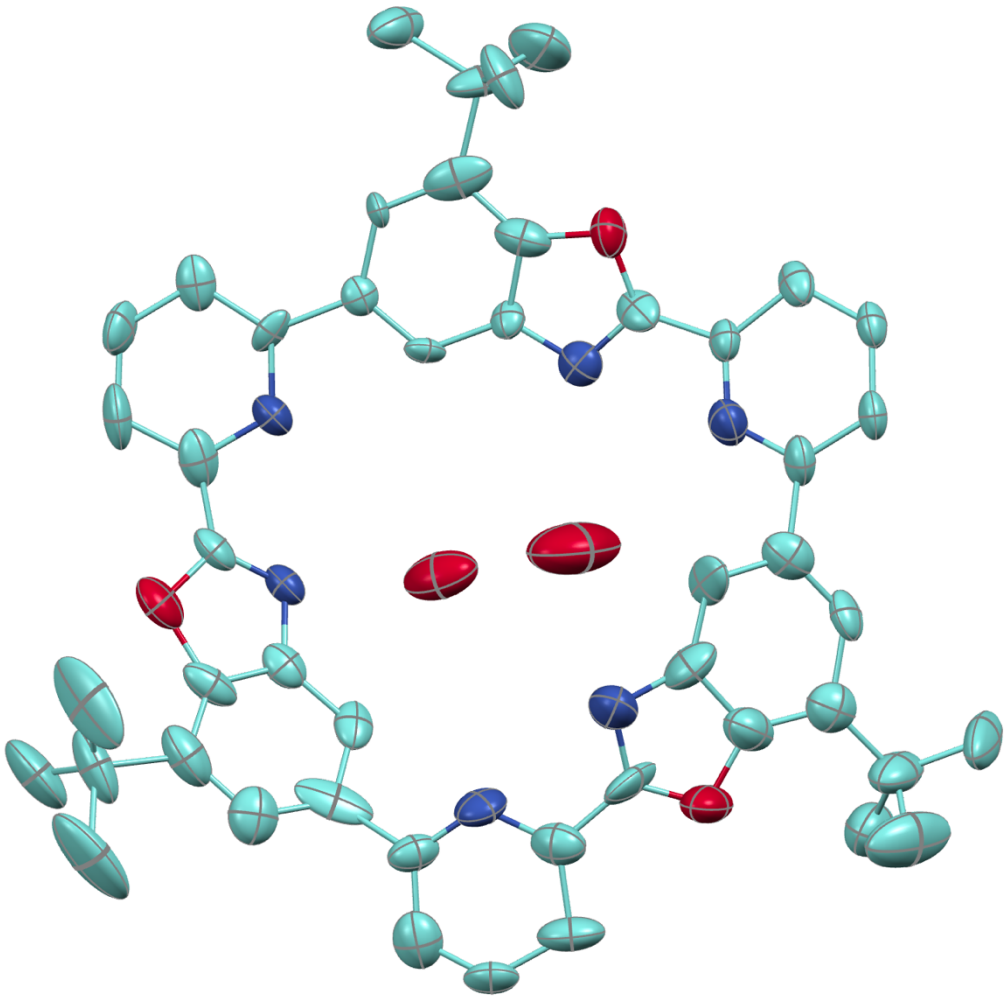


Figure S23. The molecular structure of **3**·2(H_2O) determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red.

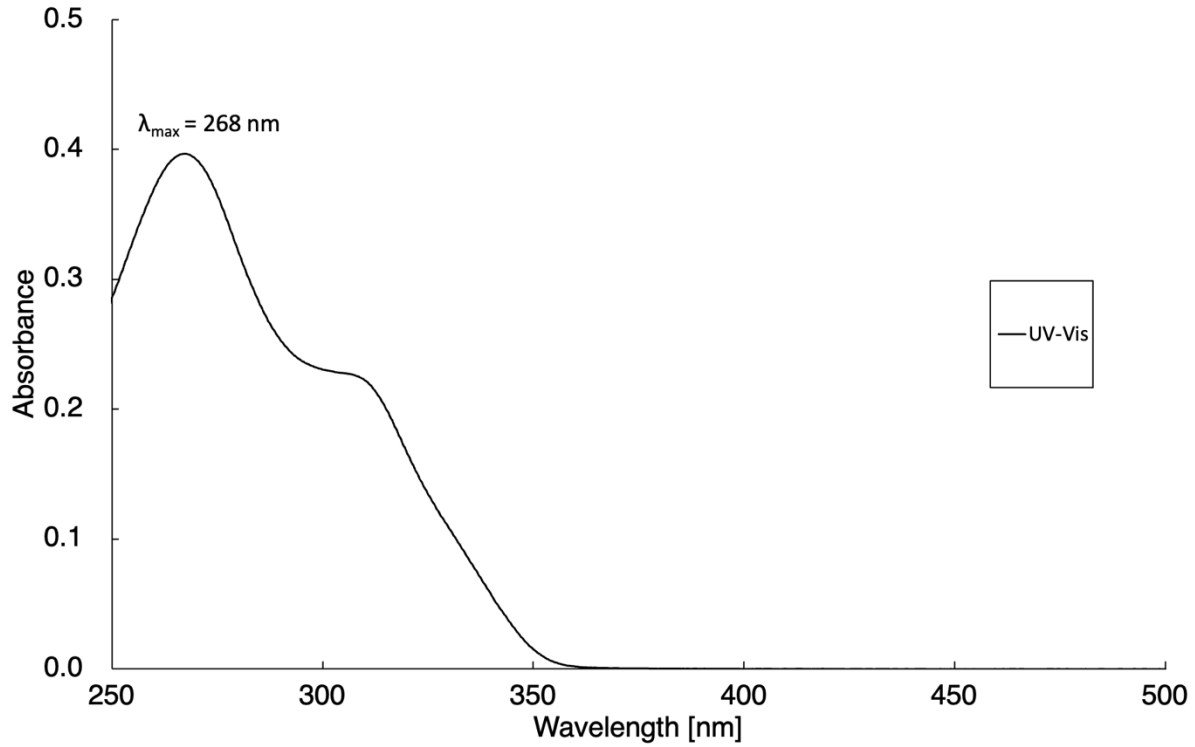


Figure S24. UV-vis absorption spectrum of **3** (5.0 μM, $CHCl_3$, l = 1 cm).

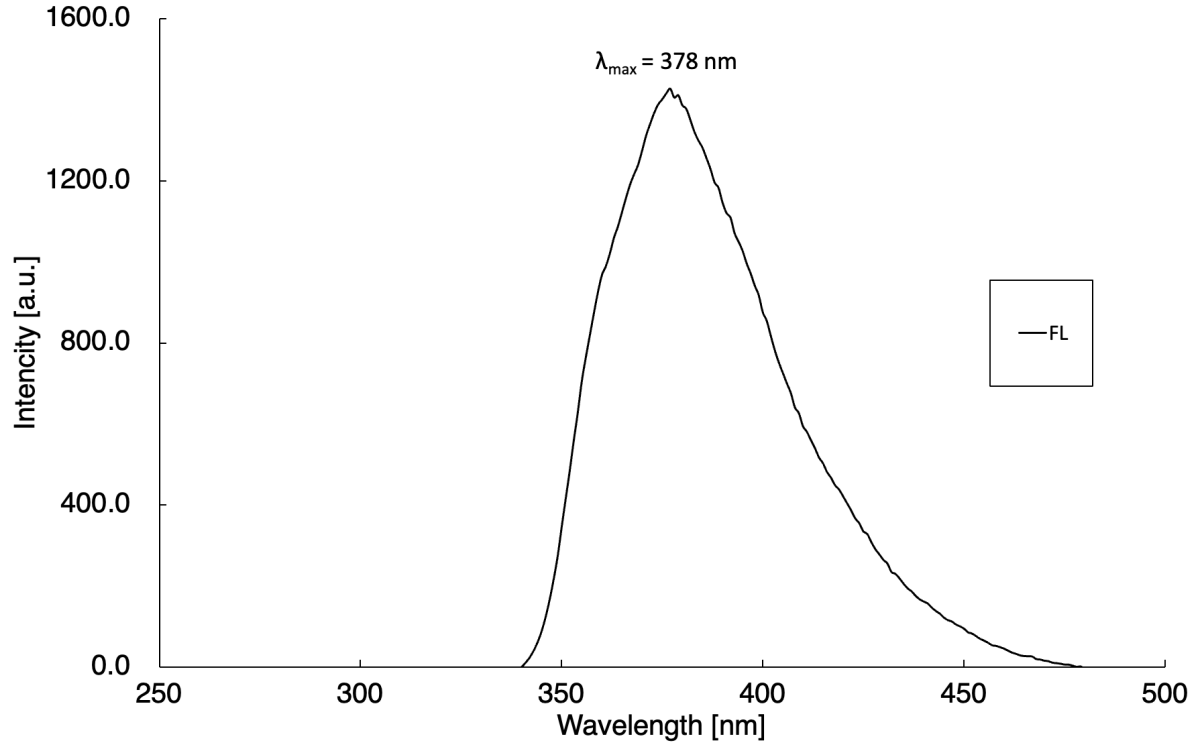


Figure S25. Emission spectrum of **3** (5.0 μM, $CHCl_3$, l = 1 cm, λ_{ex} = 268 nm)
Absolute fluorescence quantum yield of this solution was 2.6%.

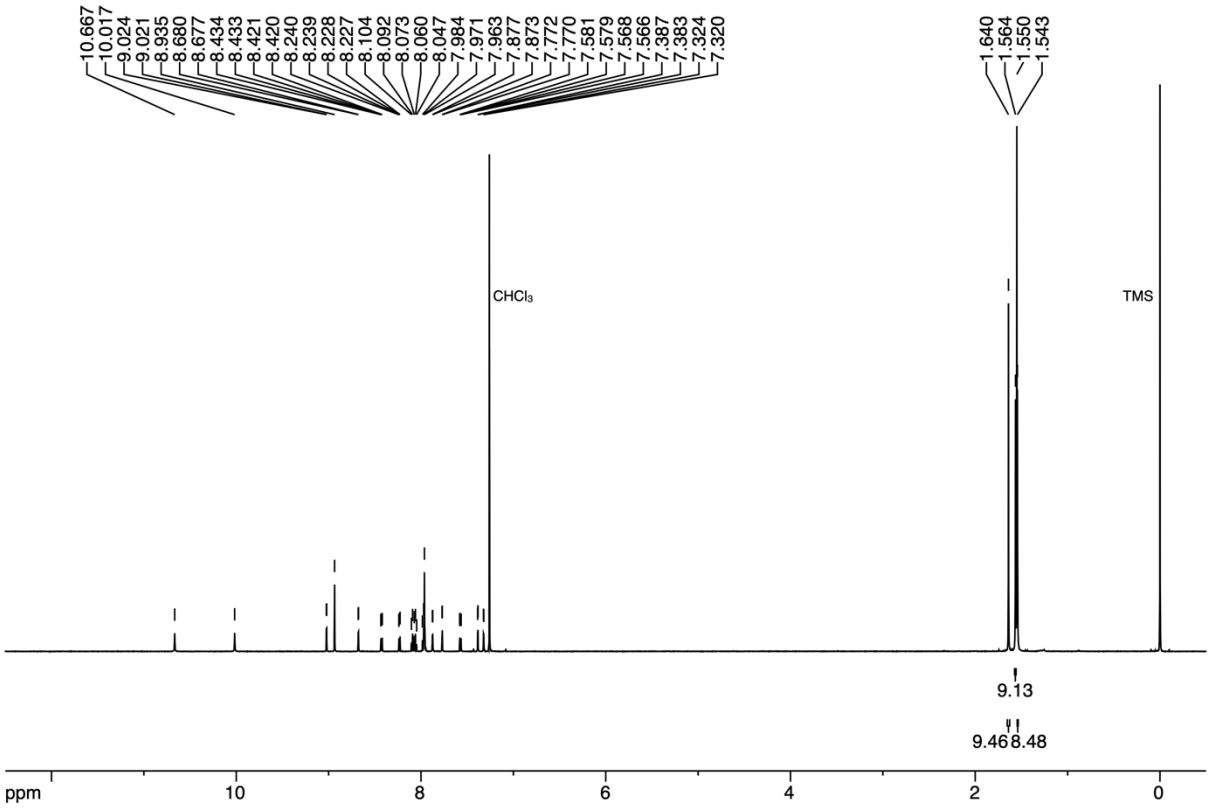


Figure S26. ^{1}H NMR spectrum of **4** ($CDCl_3$, 600 MHz). Assignments are shown in the main text.

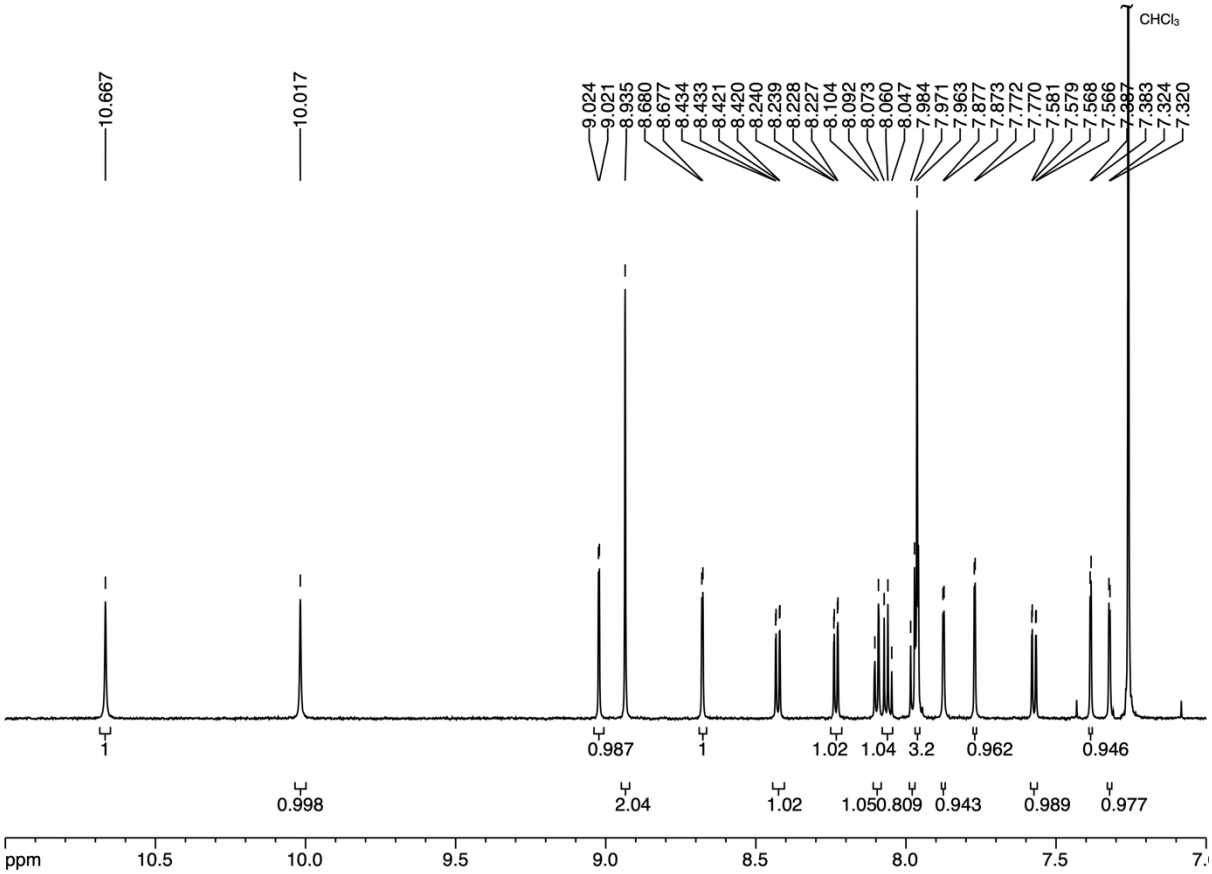


Figure S27. ^{1}H NMR spectrum (aromatic region (7.0–11.0 ppm)) of **4** ($CDCl_3$, 600 MHz).

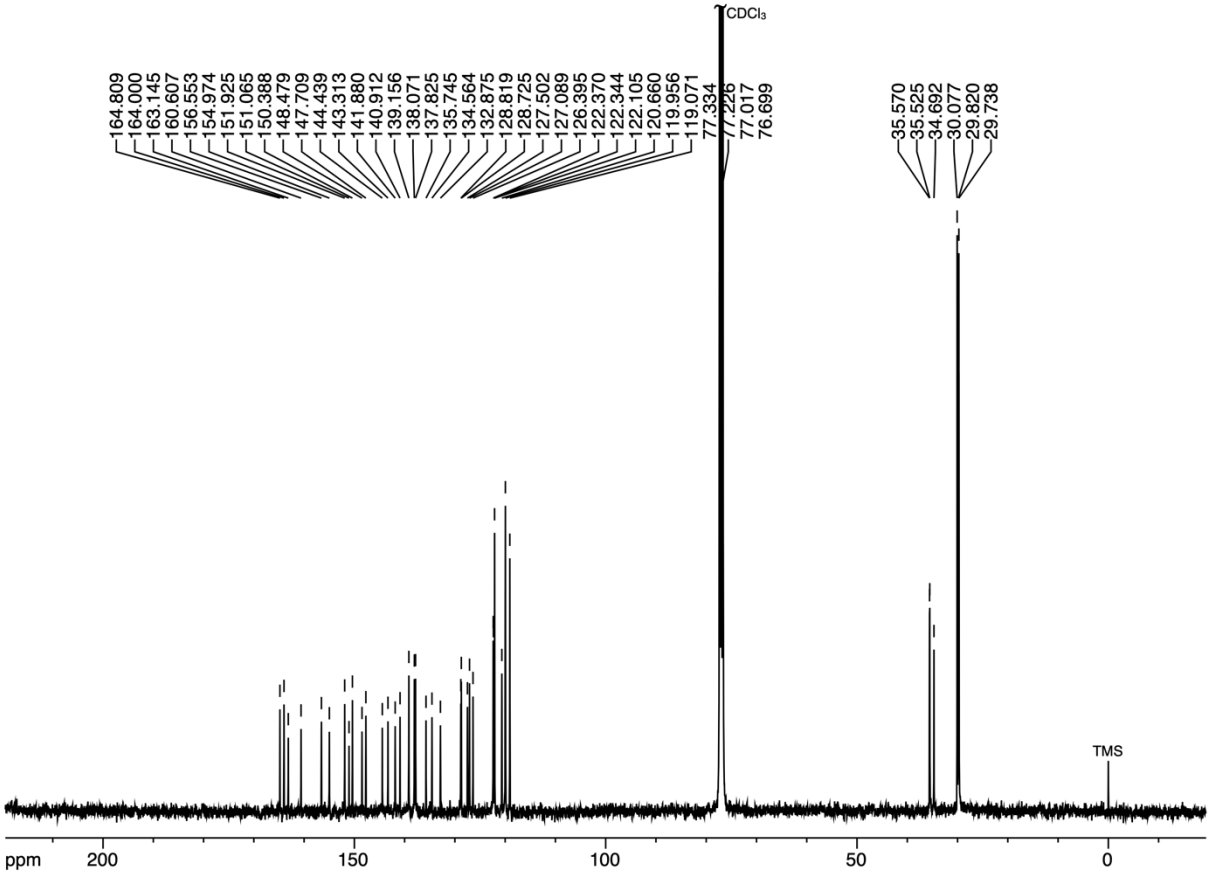


Figure S28. ^{13}C NMR spectrum of **4** ($CDCl_3$, 100 MHz)

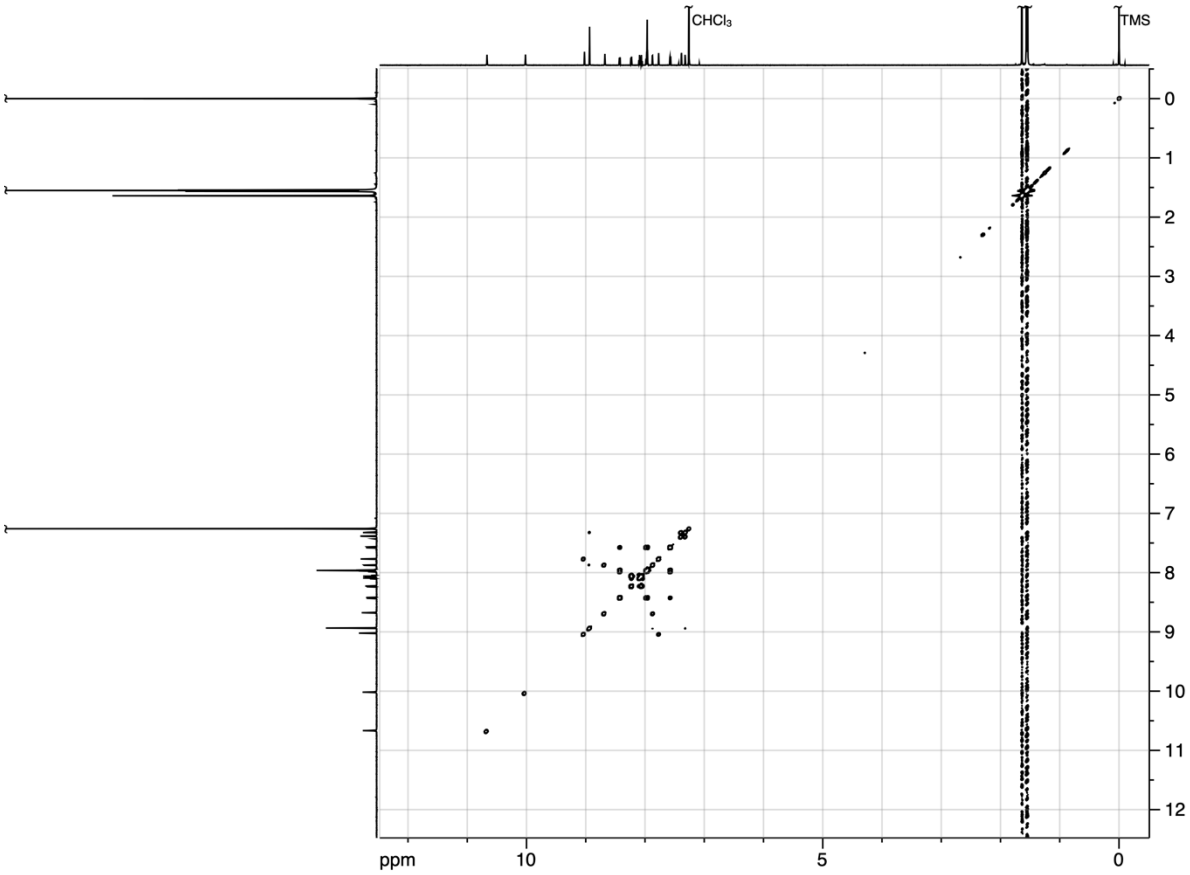


Figure S29. ^{1}H–^{1}H COSY spectrum of **4** ($CDCl_3$, 400 MHz)

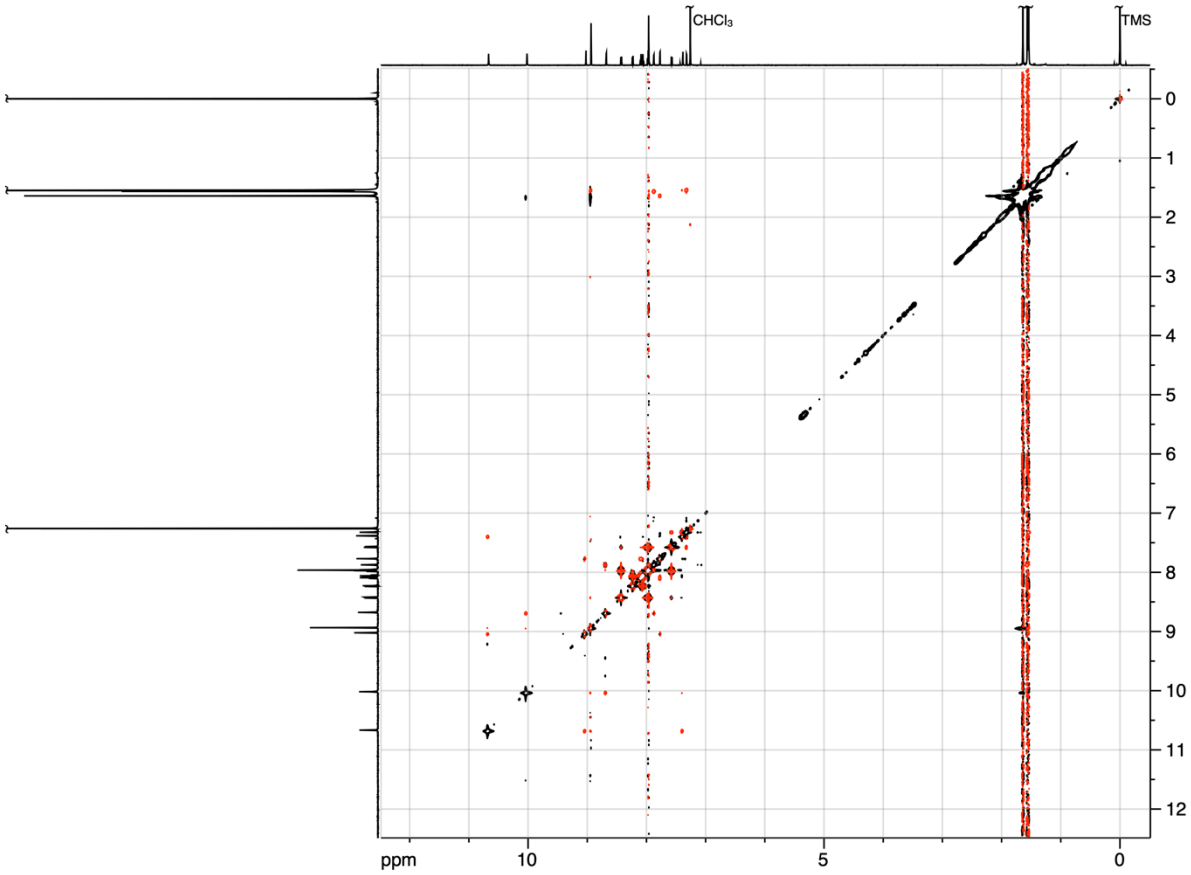


Figure S30. ^{1}H–^{1}H NOESY spectrum of **4** ($CDCl_3$, 400 MHz)

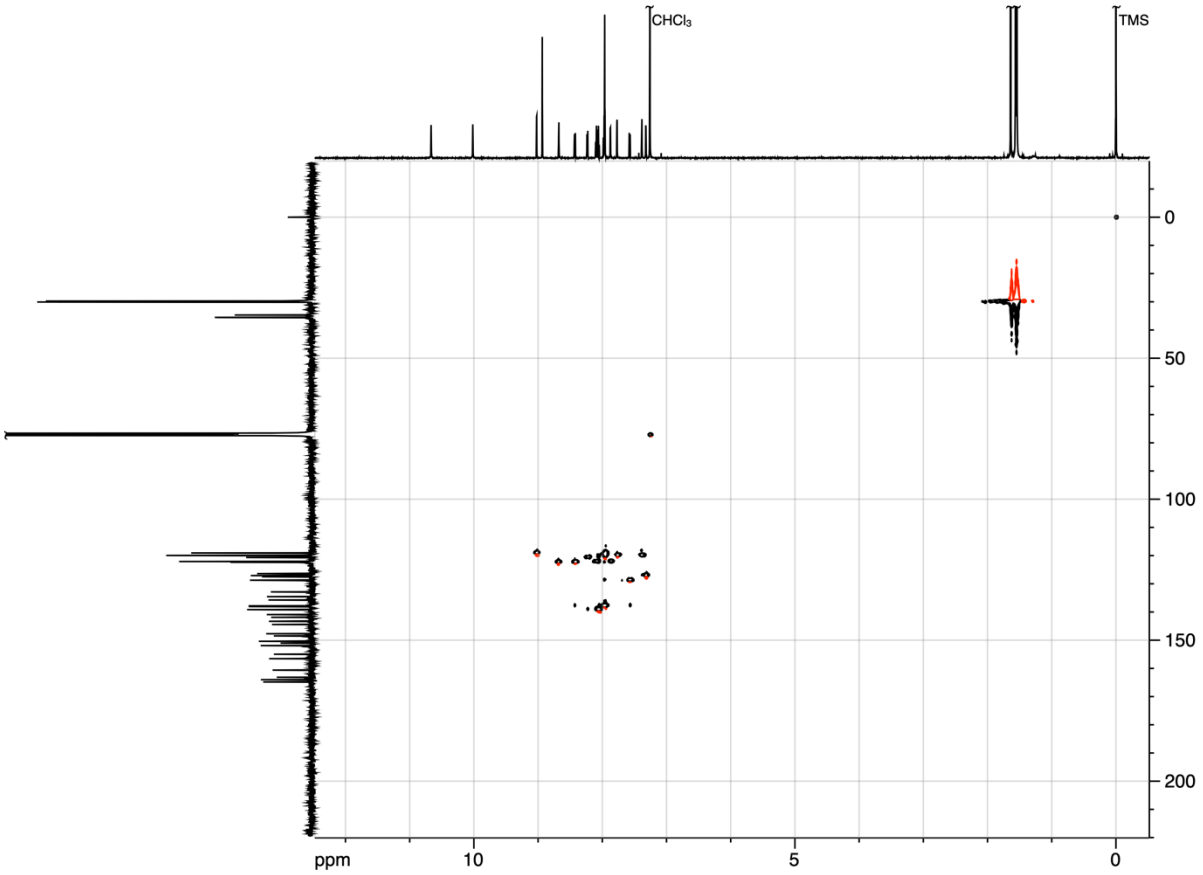


Figure S31. ^{1}H–^{13}C HSQC spectrum of **4** ($CDCl_3$, 400 MHz)

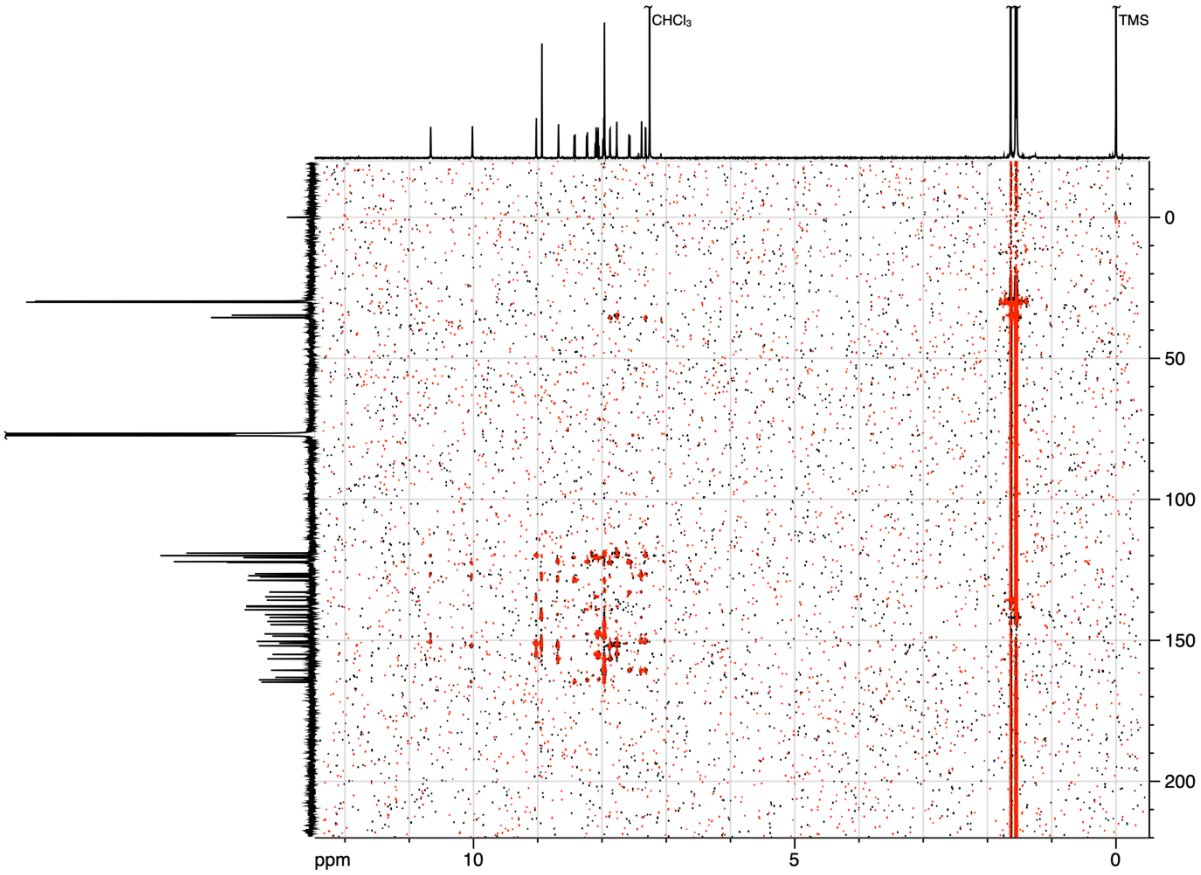


Figure S32. ^{1}H–^{13}C HMBC NMR spectrum of **4** ($CDCl_3$, 400 MHz)

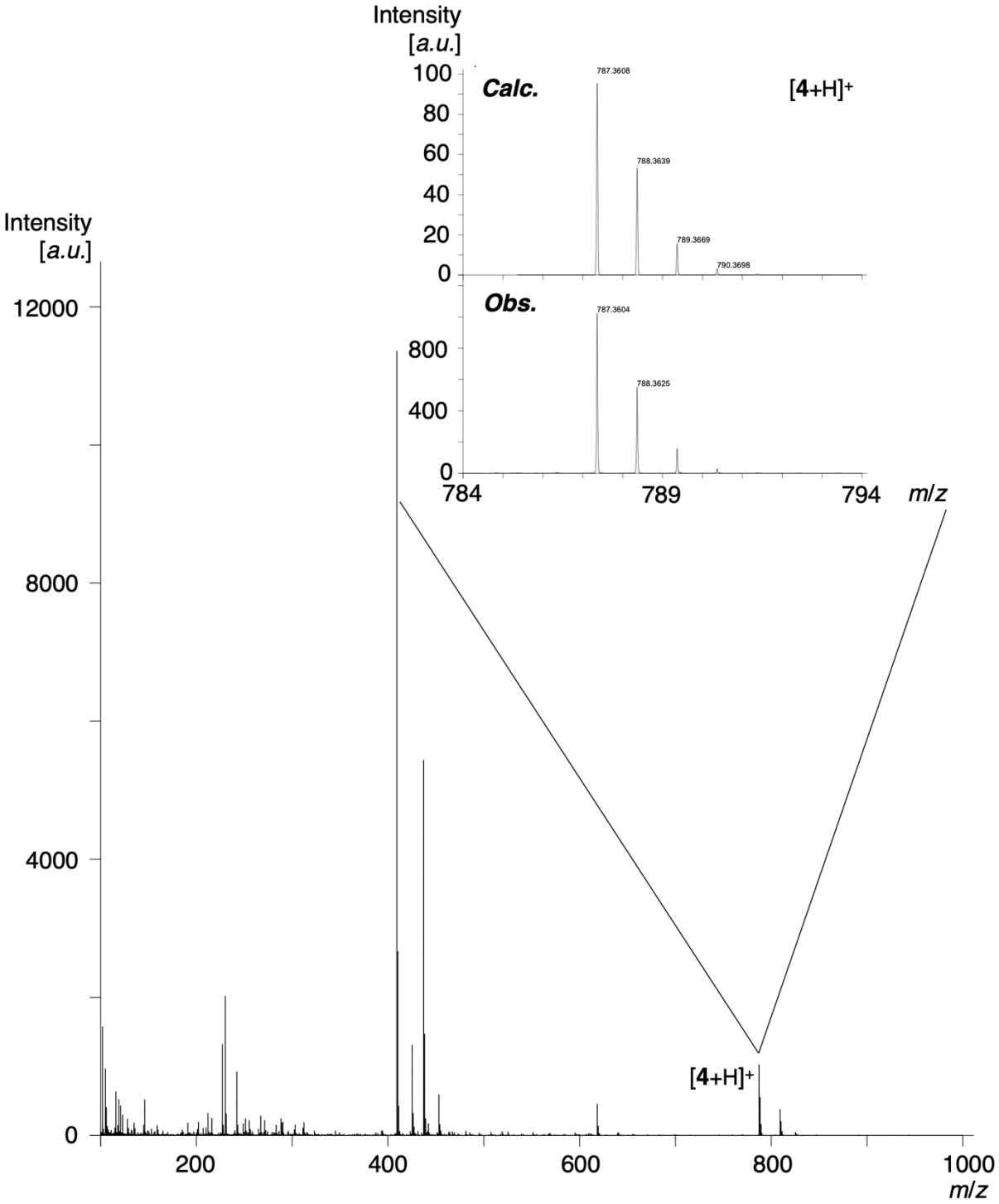


Figure S33. ESI-TOF mass spectrum of **4** (positive, MeOH).

A single crystal of **4**·$(C_2H_5)_2O$·C_4H_8O suitable for an X-ray diffraction analysis was obtained by Et_2O vapor diffusion into THF solution of **4**.

Crystal data: $C_{56}H_{64}N_6O_7$, *Fw* = 933.13, colorless plate, 0.30 × 0.80 × 0.20 mm^3, triclinic, space group *P*–1 (No. 2), *a* = 11.244(5) Å, *b* = 12.917(5) Å, *c* = 17.778(7) Å, α = 86.525(4)°, β = 87.331(5)°, γ = 75.394(4)°, *V* = 2492.8(18) Å^3, *Z* = 2, *T* = 100 K, λ(Mo K$_\alpha$) = 0.71073 Å, θ_{max} = 26.850°, R_1 (*I* > 2σ) = 0.0983, wR_2 (all) = 0.2639, GOF = 1.085. CCDC 2307868.

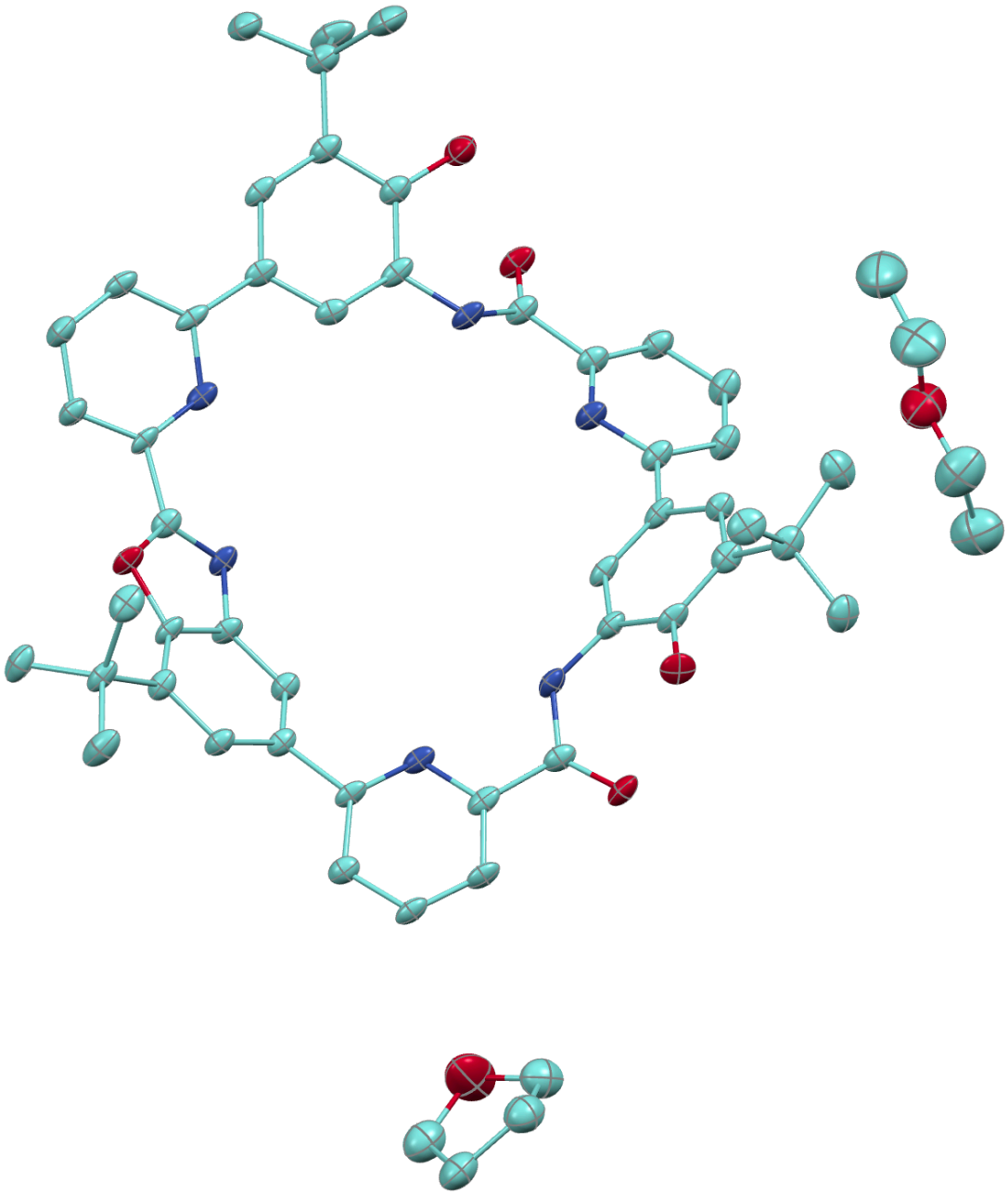


Figure S34. The molecular structure of **4**·$(C_2H_5)_2O$·C_4H_8O determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red.

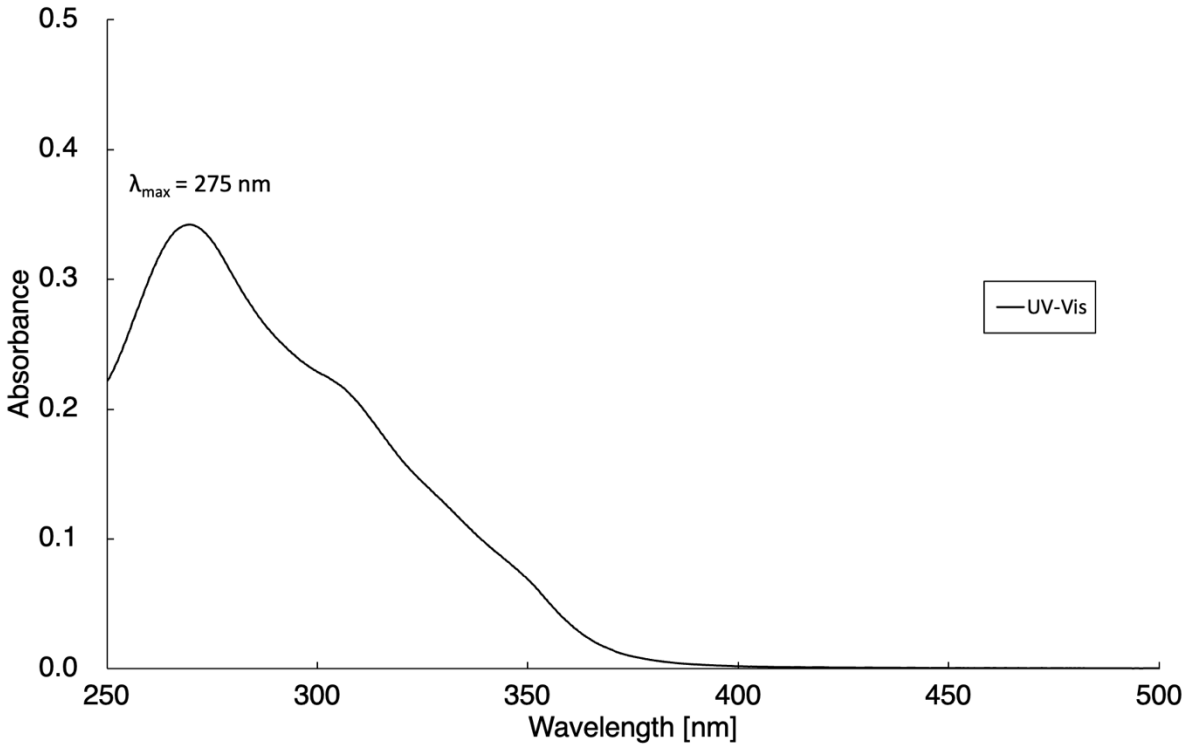
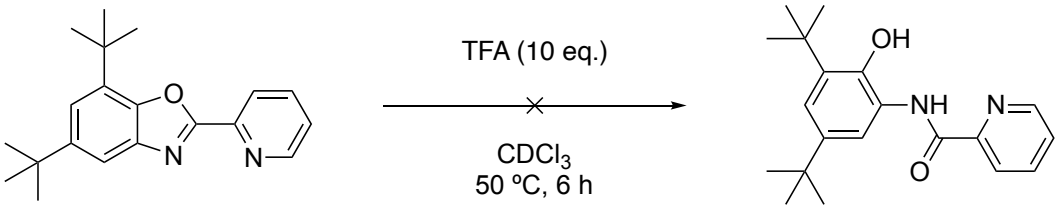


Figure S35. The UV-vis absorbance spectrum of **4** (5.0 μM, $CHCl_3$, l = 1 cm)

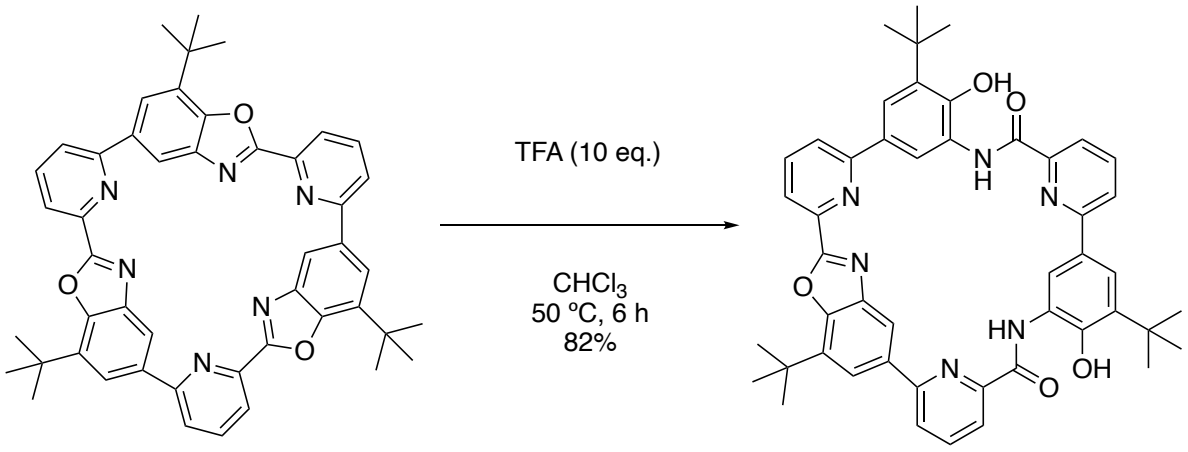
Checking stability of benzoxazole in an acidic condition



5 **11**

Scheme S8. Benzoxazole monomer **5** in acidic condition.

TFA (4.4 μL, 57 μmol, 10 eq.) was added to a solution of **5**[S7] (1.75 mg, 5.67 μmol 1.0 eq.) in $CDCl_3$ (500 μL) in NMR tube and ^1H NMR measurement was performed. After the mixture was heated at 50 °C for 6 h, the ^1H NMR spectrum did not change.



3 **4**

Scheme S9. Pbo trimer **3** in acidic condition.

A solution of **3** (0.0509 g, 0.0678 mmol, 1.0 eq.) and TFA (52 μL, 0.679 mmol, 10 eq.) in $CHCl_3$ (10 mL) was stirred at 50 °C for 6 h in a 30 mL eggplant flask. The reaction mixture was concentrated in vacuo. The residue was purified by automated column chromatography ($CHCl_3$/MeOH = 100/0–95/5) and dried in vacuo to give **4** as pale yellow solid (0.0437 g, 0.0555 mmol, 82%).

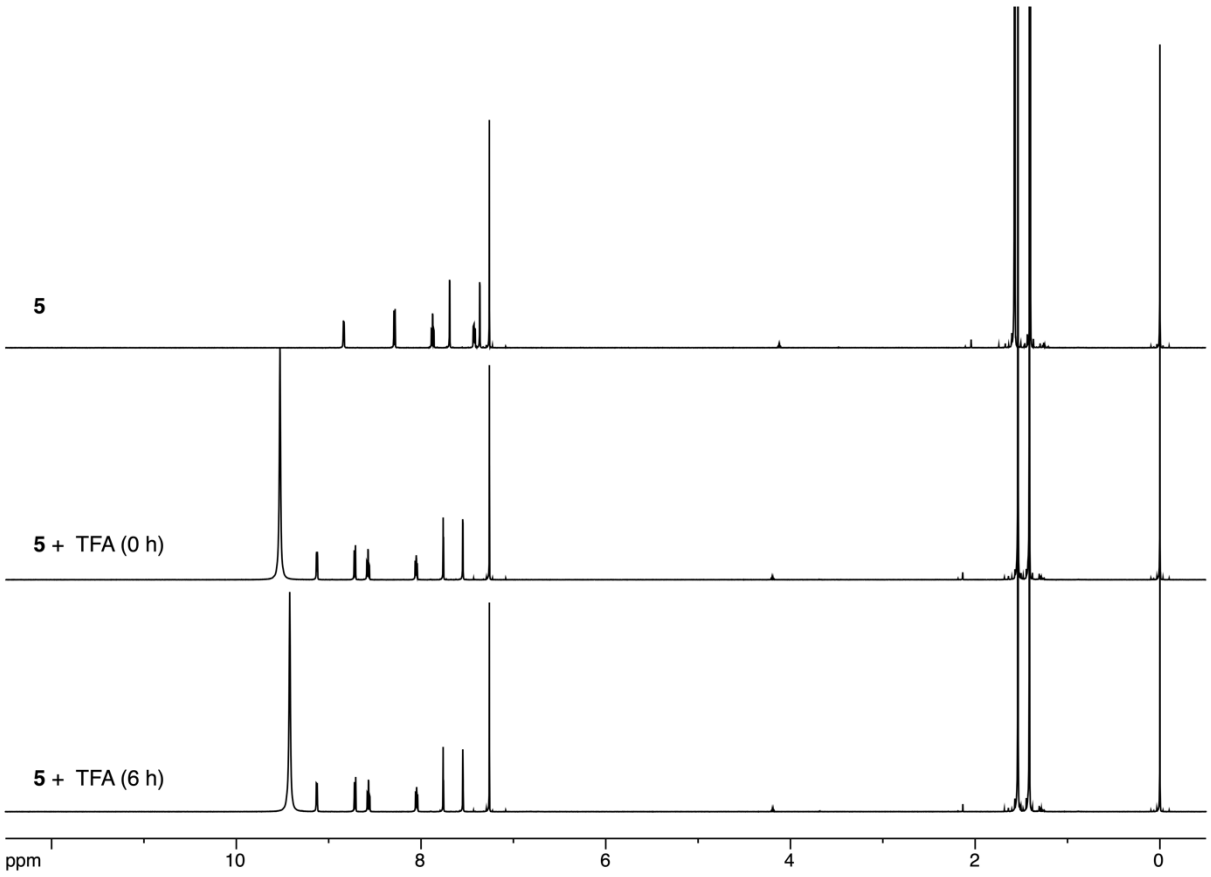


Figure S36. ^{1}H NMR spectra of pbo monomer **5** in acidic condition ($CDCl_3$, 600 MHz).

3. Formation of Zinc Complex

^{1}H NMR titration experiments of $Zn(OTf)_2$ against **4**

4 (1.24 mg, 1.58 μmol, 1.0 eq.) was weighed in an NMR tube and dissolved in $CDCl_3/CD_3OD$ = 10/1 (550 μL). $Zn(OTf)_2$ (5.12 mg, 14.1 μmol) was weighed in another microtube and dissolved in $CDCl_3/CD_3OD$ = 10/1 (893 μL). 10 μL each of the $Zn(OTf)_2$ solution (0.16 μmol, 0.1 equiv) was titrated into the solution of the ligand, and ^{1}H NMR measurements were carried out during the titration. The formation of a single species was confirmed when 0.5 equiv. of $Zn(OTf)_2$ was added, and the product was characterized by NMR.

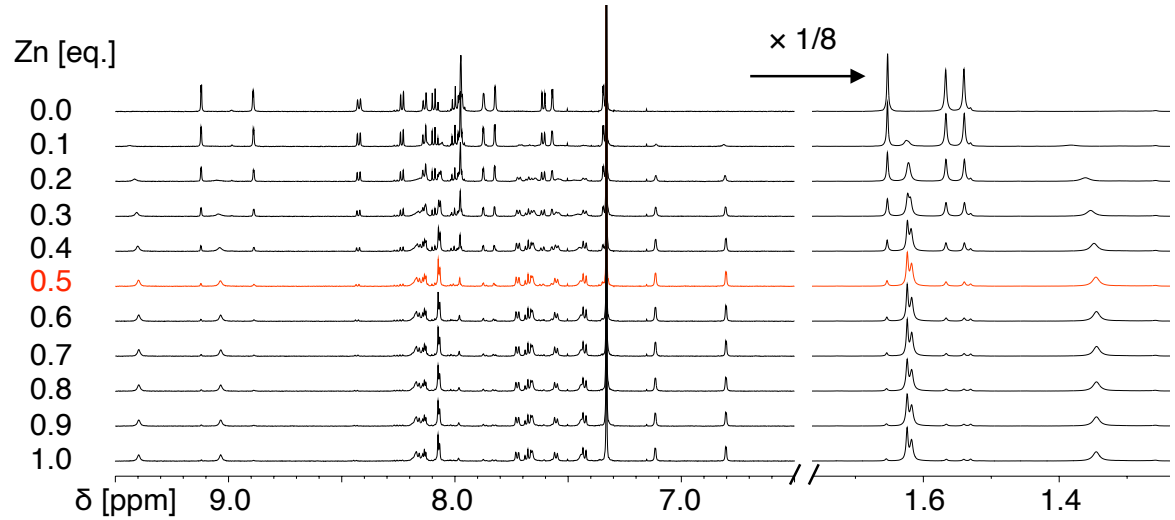


Figure S37. A titration experiment of $Zn(OTf)_2$ against **4** (^{1}H NMR, 600 MHz, $CDCl_3/CD_3OD$ = 10/1).

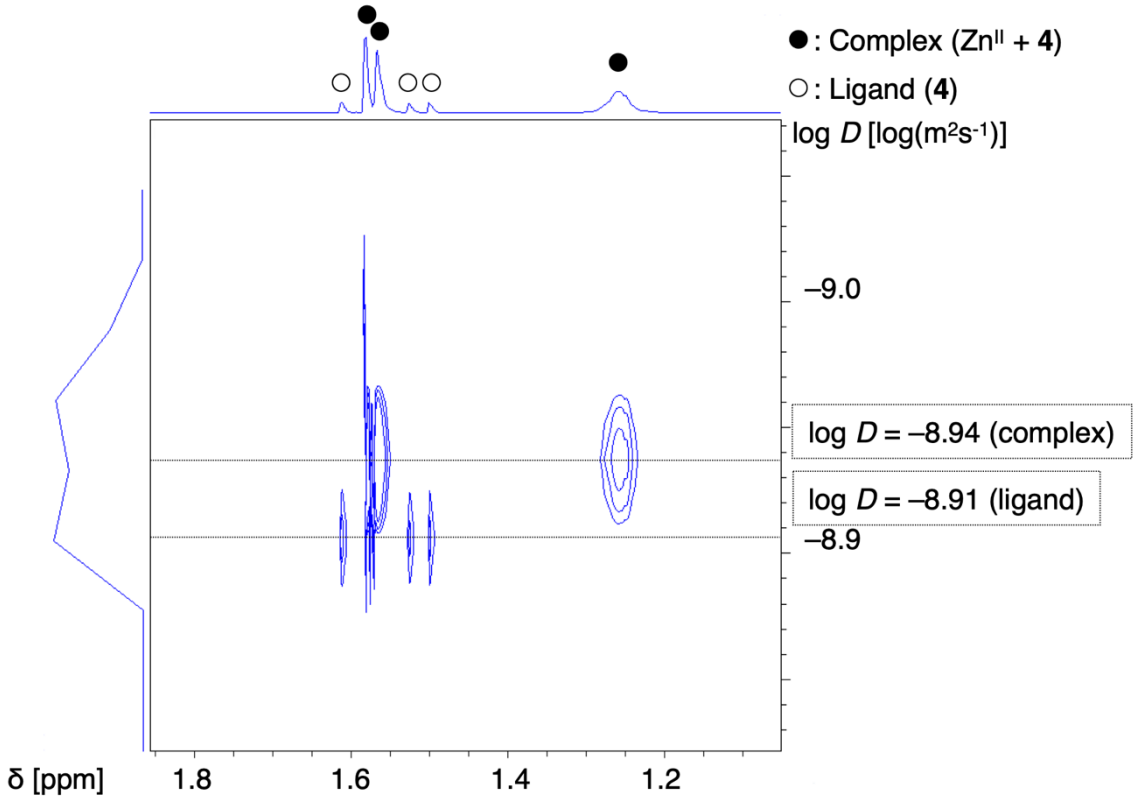


Figure S38. A ^{1}H DOSY NMR spectrum of the mixture of **4** and its Zn^{II} complex (the sample at **4** : $Zn(OTf)_2$ = 1 : 0.4) (600 MHz, $CDCl_3/CD_3OD$ = 10/1).

A single crystal of $[Zn\mathbf{4}_2(H_2O)_2]\cdot 2CF_3SO_3\cdot 6CHCl_3\cdot 2CH_3OH$ suitable for an X-ray diffraction analysis was obtained by slow evaporation from chloroform/methanol solution of **4** and $Zn(OTf)_2$.

Crystal data: $C_{106}H_{110}Cl_{18}F_6N_{12}O_{20}S_2Zn$, $Fw = 2753.64$, colorless block, 0.18 × 0.08 × 0.50 mm^3, triclinic, space group $P\text{–}1$ (No. 2), $a = 16.0885(5)$ Å, $b = 20.1668(6)$ Å, $c = 21.6212(7)$ Å, $\alpha = 103.611(2)°$, $\beta = 101.577(2)°$, $\gamma = 109.328(2)°$, $V = 6129.8(3)$ $Å^3$, $Z = 2$, $T = 100$ K, $\lambda(Mo\ K_\alpha) = 0.71073$ Å, $\theta_{max} = 27.500°$, R_1 ($I > 2\sigma$) = 0.0991, wR_2 (all) = 0.3074, GOF = 1.032. CCDC 2307869.

Triflate anion and chloroform solvent molecules were disordered in the crystal. DFIX and RIGU restraints were applied for triflate anion and chloroform. Calculated residual density with 3.68 $eÅ^{-3}$ was found at 0.97 Å from S3 atom. Here, the presence of a disordered triflate anion with low occupancy is suggested, but further analysis was difficult.

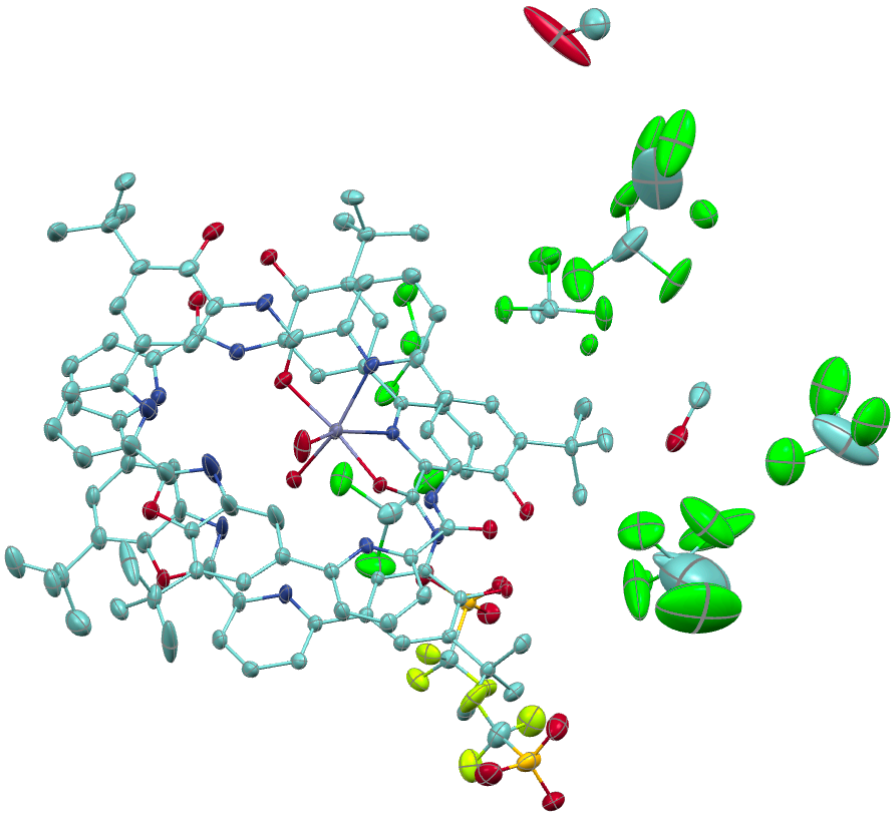


Figure S39. The molecular structure of $[Zn\mathbf{4}_2(H_2O)_2]\cdot 2CF_3SO_3\cdot 6CHCl_3\cdot 2CH_3OH$ determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; Cl, green; F, yellow green; N, blue; O, red; S, orange; Zn, purple.

4. References for the Supplementary Information

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