Electronic Supplementary Information

Cyclo[4]pyrrole with α–β direct linkages

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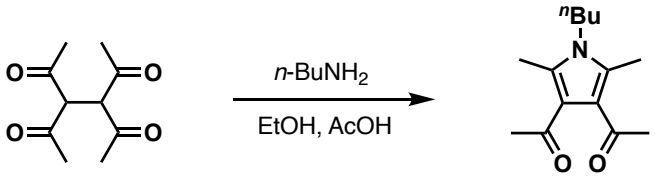
1. General Information

Solvents and reagents were purchased from Fujifilm WAKO Pure Chemical Industries Ltd., TCI Co., Ltd., Kanto Chemical Co., Inc., or Sigma-Aldrich Co., and used without further purification unless otherwise mentioned. Tetraacetylethane was synthesized according to the reported procedure[S1]. All ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-ECS400 spectrometers, and chemical shifts were reported in parts per million (ppm) relative to an internal standard tetramethylsilane (δ = 0.00 ppm for ^{1}H NMR in $CDCl_3$) or a solvent residual peak (δ = 77.16 ppm for ^{13}C NMR in $CDCl_3$, δ = 2.50 ppm for ^{1}H NMR in DMSO-d_6, 39.52 ppm for ^{13}C NMR in DMSO-d_6, and δ = 2.05 ppm for ^{1}H NMR in Acetone-d_6). Infrared spectra were measured using a JASCO Co. FT/IR-4600. ESI-TOF-MS spectra were recorded on a Thermo Scientific Executive spectrometer. Elemental analyses were carried out using an Exceter Analytical, Inc. CE440. Melting points were recorded using Yanaco MP-S3. Thin layer chromatography (TLC) was performed on silica gel sheets, MERCK silica gel 60 F_{254}. Preparative scale separations were performed by means of gravity column chromatography over silica gel (Cica-Reagent, 60N, 63-210 μm). UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescence emission spectra were recorded on a JASCO FP-8550 spectrophotometer. Fluorescence lifetime was recorded on EDINBURGH INSTRUMENTS FLS1000 photoluminescence spectrometer. Quantum yields were measured using a HAMAMATSU Quantaurus-QY Absolute PL quantum yield spectrometer: C11347-01. Analytical HPLC chromatograms were recorded using a JASCO MD-2018 photodiode array detector quipped with a JASCO PU-2089 pump, JASCO AS-2059 sampler, JASCO CO-2060 column thermostat. Recycling HPLC LaboACE LC-5060 equipped with two JAIGEL-2HR columns. Cyclic voltammograms were recorded by ALS Model660E electrochemical analyzer with an electrochemical system utilizing the three-electrode configuration consisting of platinum (working electrode), platinum wire (counter electrode) and $Ag/AgNO_3$ (reference electrode) in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. Spectroelectrochemical measurements were conducted on a JASCO V-770 spectrophotometer using a CH Instrument Model 700E (ALS) in dichloromethane solutions with 0.3 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte. Measurements were made with an optically transparent thin-layer electrode cell containing a degassed sample solution using a Pt mini-grid as a working electrode, a Pt wire as a counter electrode, and an Ag/AgCl wire as a reference electrode. Single crystal X-ray diffraction data were obtained using Rigaku XtaLAB P200 diffractometer equipped with a PILATUS200K detector, which uses a multilayer mirror (MoKα radiation λ = 0.71073 Å). All structures were solved using a dual-space algorithm (SHELXT[S2]) and refined using full-matrix least-squares method (SHELXL[S3]).

2. Synthetic Procedures

2-1 Synthesis of 3,4-diacetyl-1-butyl-2,5-dimethylpyrrole (6)

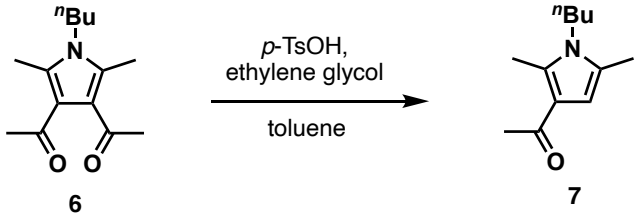


6

Tetraacetylethane[S1] (7.93 g, 40.0 mmol) was dissolved in a 1:1 (v/v) mixture (200 mL) of EtOH and AcOH in a 500 mL round bottom flask equipped with a reflux condenser. To the solution, *n*-butylamine (4.00 mL, 40.0 mol) was added, and the mixture was refluxed overnight. After cooling the reaction mixture to room temperature, the solvent was removed with a rotary evaporator. 200 mL of saturated aqueous $NaHCO_3$ solution was added to the residue, and the products were extracted by washing with dichloromethane (50 mL × 3). The combined organic layer was dried over Na_2SO_4 followed by rotary evaporation to dryness. The residue was chromatographed on a silica gel column (diameter: 6 cm, height: 15 cm, eluent: ethyl acetate/hexane = 1:1) to give compound **6** (7.56 g, 32.1 mmol) in 80% yield as a colorless solid.

R_f = 0.30 (silica gel, ethyl acetate/hexane = 1:1), m.p.: 45-48 ºC; ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ = 3.83 (t, J = 7.6 Hz, 2H, methylene), 2.29 (s, 6H, methyl), 2.26 (s, 6H, methyl), 1.52 (m, 2H, methylene), 1.33 (sext, J = 7.6 Hz, 2H, methylene) , 0.92 ppm (t, J = 7.2 Hz, 3H, methyl); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 298 K): δ = 196.4, 131.5, 122.5, 42.8, 31.9, 30.8, 19.4, 13.5, 10.9 ppm; IR(ATR, neat) 2956, 2933, 2864, 1664, 1639, 1415, 1384, 1365, 1342, 1155, 593 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{14}H_{21}NO_2Na^+$: 258.1465 [M+Na]$^+$; found: 258.1459; elemental analysis calcd (%) for $C_{14}H_{21}NO_2$: C, 71.44; H, 9.00; N, 5.95; found: C, 71.38; H, 9.04; N, 5.93.

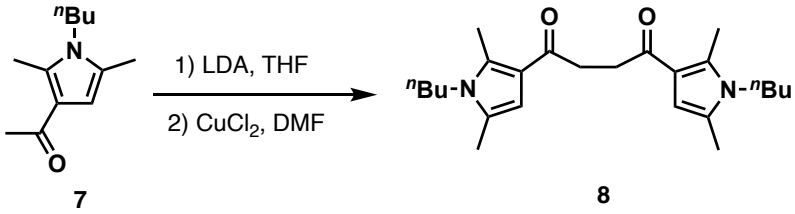
2-2 Synthesis of 3-acetyl-1-butyl-2,5-dimethylpyrrole (7)



In a 300 mL round bottom flask equipped with a refluxing condenser, compound **6** (4.71 g, 20.0 mmol), ethylene glycol (1.12 mL, 20.0 mmol), *p*-toluenesulfonic acid monohydrate (0.38 g, 2.0 mmol) were dissolved in 100 mL of toluene. After refluxing the mixture for 1 h, the reaction solution was cooled to room temperature. The reaction solution was poured into a saturated aqueous $NaHCO_3$ solution (100 mL), and the organic layer was then separated. The aqueous layer was extracted with dichloromethane (50 mL × 2), and the combined organic layer was dried over anhydrous Na_2SO_4. After the removal of the solvent by rotary evaporator, the crude product was chromatographed on a silica gel column (diameter: 5.5 cm, height: 11 cm, eluent: ethyl acetate/hexane = 1:2) to give compound **7** (3.23 g, 16.7 mmol) in 84% yield as a pale yellow solid.

R_f = 0.46 (silica gel: ethyl acetate/hexane = 1:2), m.p.: 46-48 ºC; ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ = 6.20 (s, 1H, pyrrole), 3.77 (t, J = 7.2 Hz, 2H, methylene), 2.44 (s, 3H, methyl), 2.22 (s, 3H, methyl), 2.17 (s, 3H, methyl), 1.51 (quint, J = 7.5 Hz, 2H, methylene), 1.30 (sext, J = 7.4 Hz, 2H, methylene), 0.90 ppm (t, J = 7.2 Hz, 3H, methyl); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 298 K): δ = 193.3, 133.5, 127.0, 119.3, 108.0, 42.5, 32.0, 28.3, 19.5, 13.6, 11.8, 11.4 ppm; IR(ATR, neat) 2961, 2954, 2871, 1643, 1518, 1417, 1362, 1343, 1232, 1214, 1184, 945, 923, 774, 623 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{12}H_{19}NONa^+$: 216.1359 [M+Na]$^+$; found: 216.1356; elemental analysis calcd (%) for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25; found: C, 74.62; H, 9.95; N, 7.23.

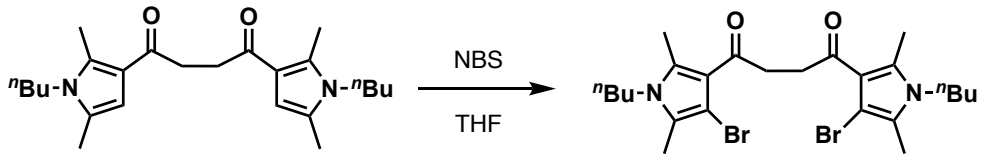
2-3 Synthesis of compound 8



Compound **7** (1.74 g, 9.00 mmol) was added into a dropping funnel that equipped on a 200 mL three-neck flask. After the flask was cooled to −78ºC with N_2 atmosphere, lithium diisopropylamide (LDA) solution (2M, 5.80 mL, 11.7 mmol) was added. Then anhydrous THF (15 mL) was added into the dropping funnel and the result solution of **7** was slowly added into flask over 15 min. After stirring for 15 min, a solution of $CuCl_2$ (2.42 g, 18.0 mmol) in anhydrous DMF (40 mL) was added all at once. The reaction mixture was stirred for 1.5 h while kept the temperature at –78 ºC. The mixture was quenched by saturated NH_4Cl aqueous solution (90 mL) after warming to room temperature and extracted by ether (90 mL × 3). The combined ether layer was washed by water (90 mL) and dried over Na_2SO_4, then concentrated by rotary evaporation to provide the residue. The crude was chromatographed by a silica gel column (diameter: 4 cm, height: 15 cm, eluent: ethyl acetate/hexane = 1:3) to give compound **8** (0.67 g, 1.7 mmol) in 39% as pale yellow solid.

R_f = 0.29 (silica gel: ethyl acetate/hexane = 1:3), m.p.: 136-139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.31 (s, 2H, pyrrole), 3.74 (t, J = 7.6 Hz, 4H, methylene), 3.11 (s, 4H, ethylene), 2.54 (s, 6H, methyl), 2.20 (s, 6H, methyl), 1.36 (sext, J = 7.5 Hz, 4H, methylene), 0.96 ppm (t, J = 7.2 Hz, 6H, methyl), one methylene peak was overlapped with water peak; ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ = 6.26 (s, 2H, pyrrole), 3.78 (t, J = 7.8 Hz, 4H, methylene), 2.90 (s, 4H, ethylene), 2.44 (s, 6H, methyl), 2.18 (s, 6H, methyl), 1.52 (m, 4H, methylene), 1.31 (sext, J = 7.4 Hz, 4H, methylene), 0.91 ppm (t, J = 7.4 Hz, 6H, methyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 196.3, 134.7, 127.3, 119.6, 107.9, 43.3, 34.8, 32.7, 20.2, 13.9, 12.4, 12.0 ppm; IR(ATR, neat) 2967, 2918, 2872, 2856, 1635, 1519, 1417, 1361, 774, 418 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{24}H_{36}N_2O_2Na^+$: 407.2669 [M+Na]$^+$; found: 407.2657; elemental analysis calcd (%) for $C_{24}H_{36}N_2O_2$: C, 74.96; H, 9.44; N, 7.28; found: C, 75.12; H, 9.48; N, 7.24; UV-Vis (MeCN): λ_{max} (ε) = 212 (3.0 × 10^4), 250 (2.1 × 10^4), 285 nm (1.6 × 10^4 L mol^{-1} cm^{-1}).

2-4 Synthesis of compound 9

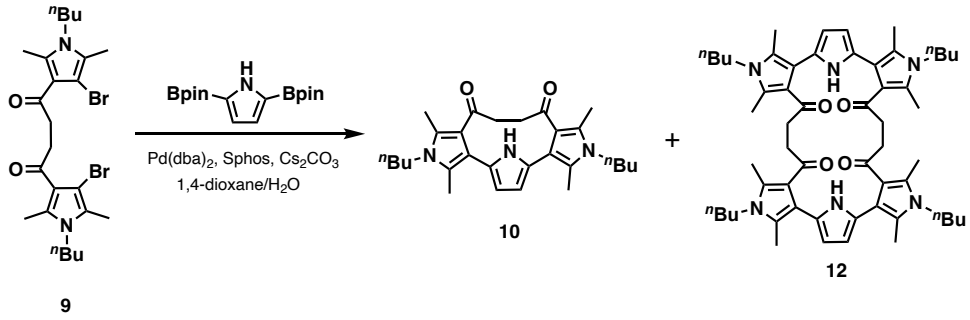


8 **9**

Compound **8** (461 mg, 1.20 mmol) was added to a 50 mL round bottom flask and dissolved in 12 mL THF (with 0.03% stabilizer). Then, a solution of 428 mg N-bromosuccinimide (NBS) (2.40 mmol) in 12 mL THF (with 0.03% stabilizer) was added dropwise. After keeping stirring 15 min, the solvent was removed by rotary evaporation. The residue was ultrasonic dispersed in EtOH (2.4 mL) and filtered. The result solid was washed by EtOH (1 mL) and water (10 mL) to provide compound **9** as pale solid (569 mg, 1.05 mmol) in 88%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.78 (t, J = 7.8 Hz, 4H, methylene), 3.38 (s, 4H, ethylene), 2.48 (s, 6H, methyl), 2.23 (s, 6H, methyl), 1.36 (sext, J = 7.5 Hz, 4H, methylene), 0.96 ppm(t, J = 7.2 Hz, 6H, methyl), one methylene peak was overlapped with water peak; ^{1}H NMR (400 MHz, acetone-d_6, 298 K): δ = 3.92 (t, J = 7.8 Hz, 4H, methylene), 3.27 (s, 4H, ethylene), 2.44 (s, 6H, methyl), 2.25 (s, 6H, methyl), 1.62 (m, 4H, methylene), 1.39 (sext, J = 7.4 Hz, 4H, methylene), 0.95 ppm (t, J = 7.2 Hz, 6H, methyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 196.2, 134.9, 126.4, 119.9, 94.8, 44.3, 37.2, 32.7, 20.1, 13.9, 12.5, 11.3 ppm; IR(ATR, neat) 2953, 2931, 2863, 1638, 1499, 1412, 1392, 1193, 968, 424 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{24}H_{34}Br_2N_2O_2Na^+$: 565.0859 [$M$+Na]$^+$; found: 565.0850; elemental analysis calcd (%) for $C_{24}H_{34}Br_2N_2O_2$: C, 53.15; H, 6.32; N, 5.17; found: C, 53.17; H, 6.30; N, 5.04; UV-Vis (MeCN): λ_{max} (ε) = 212 (2.5 × 10^4), 254 (1.8 × 10^4), 279 nm (1.2 × 10^4 L mol^{-1} cm^{-1}).

2-5 Synthesis of compounds 10 and 12



9 10 12

To a 50 mL 2-necked flask equipped with a reflux condenser, compound **9** (245 mg, 0.450 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole[S4] (156 mg, 0.490 mmol), bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) (26 mg, 0.045 mmol), dicyclohexyl(2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phosphane (Sphos) (37 mg, 0.090 mmol), Cs_2CO_3 (880 mg, 2.70 mmol) were added. Fill the flask with N_2 atmosphere then added degassed 1,4-dioxane (1.5 mL) and water (75 μL). The mixture was heated to 100 °C for 1 h, then remove the solvent under reduced pressure. Added 10 mL water into the flask and extracted by dichloromethane (10 mL × 3). The combined dichloromethane layer provided the crude after drying by Na_2SO_4 and rotary evaporation. The crude was chromatographed on a silica gel column (diameter: 3 cm, height: 15 cm, eluent: ethyl acetate/hexane = 2:3) to provide the two fractions (R_f = 0.21 and R_f = 0.35). Fraction (R_f = 0.21) provided 97 mg mixture containing compound **10** and pure compound **10** (48 mg, 0.107 mmol, 24%) as grey powder was obtained by recrystallization in MeOH (7.5 mL). Fraction (R_f = 0.35) required further GPC-HPLC separation followed a short silica gel column purification to provide small amount of compound **12** (c.a. 1 mg).

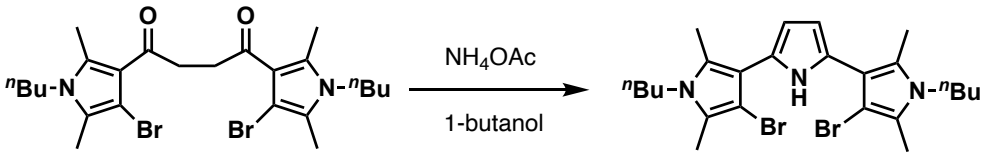
Compound 10

R_f = 0.21 (silica gel: ethyl acetate/hexane = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.15 (br, 1H, pyrrole), 6.09 (d, J = 2.8 Hz, 2H, pyrrole), 3.79 (t, J = 8.0 Hz, 4H, methylene), 2.40 (s, 6H, methyl), 2.35 (s, 4H, ethylene), 2.34 (s, 6H, methyl), 1.41 (sext, J = 7.4Hz, 4H, methylene), 0.98 ppm (t, J = 7.4Hz, 6H, methyl), one methylene peak was overlapped with water peak; ^{1}H NMR (400 MHz, acetone-d_6, 328 K): δ = 9.81 (br, 1H, pyrrole), 6.00 (d, J = 2.0 Hz, 2H, pyrrole), 3.91 (t, J = 7.8 Hz, 4H, methylene), 2.39 (s, 6H, methyl), 2.34 (s, 6H, methyl), 2.25 (s, 4H, ethylene), 1.68 (m, 4H, methylene), 1.45 (sext, J = 7.4Hz, 4H, methylene), 1.00 ppm (t, J = 7.4Hz, 6H, methyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 199.8, 134.4, 125.4, 125.3, 123.4, 112.5, 110.8, 43.8, 40.1, 32.8, 20.3, 13.9, 11.7, 10.6 ppm; IR(ATR, neat) 3338, 2957, 2929, 2869, 1646, 1606, 1508, 1407, 784, 769 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{28}H_{37}N_3O_2Na^+$: 470.2778 [M+Na]$^+$; found: 470.2768; elemental analysis calcd (%) for $C_{28}H_{37}N_3O_2$: C, 75.13; H, 8.33; N, 9.39; found: C, 74.96; H, 8.39; N, 9.30; UV-Vis (MeCN): λ_{max} (ε) = 241 nm (2.6 × 10^4 L mol^{-1} cm^{-1}).

Compound 12

R_f = 0.35 (silica gel: ethyl acetate/hexane = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 10.16 (br, 2H, pyrrole), 6.09 (d, J = 2.4 Hz, 4H, pyrrole), 3.76 (t, J = 7.6 Hz, 8H, methylene), 2.61 (s, 8H, methylene), 2.35 (s, 12H, methyl), 2.22 (s, 12H, methyl), 1.38 (sext, J = 7.4Hz, 8H, methylene), 0.96 ppm (t, J = 7.2Hz, 12H, methyl), one methylene peak overlap with water peak; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 198.4, 133.8, 126.9, 125.6, 120.7, 113.8, 109.0, 43.6, 36.1, 32.9, 20.3, 13.9, 12.2, 11.1 ppm; HRMS(ESI): *m/z* calcd for $C_{56}H_{74}N_6O_4Na^+$: 917.5664 [M+Na]$^+$; found: 917.5654.

2-6 Synthesis of compound 11

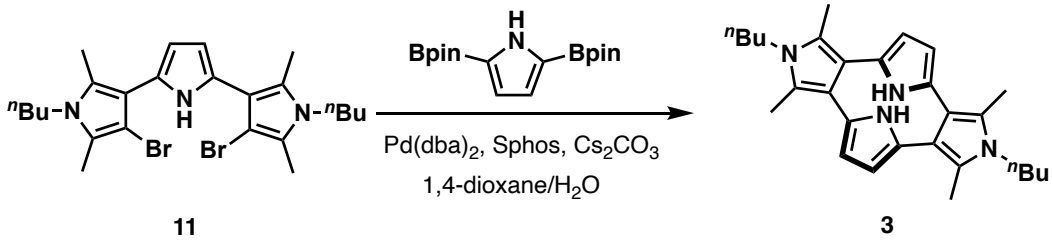


9 **11**

To a 100 mL Schlenk flask with flat stopper, compound **9** (864 mg, 1.60 mmol), NH_4OAc (2.47g, 32.0 mmol) and 1-butanol (27 mL) were added. Heating the flask to 105 °C then closed the switch and kept 90 min. The solution was cooled to room temperature and washed by 120 mL saturated $NaHCO_3$ aqueous solution. The organic layer was separated and extracted the aqueous layer by dichloromethane (40 mL × 2). The combined organic layer was dried over Na_2SO_4 and followed by rotary evaporation to obtain the concentrated residue. After a silica gel column chromatograph (diameter: 3 cm, height: 10 cm, eluent: dichloromethane/hexane = 1:2), compound **11** (500 mg, 0.955 mmol) in 60% yield as a colorless solid.

R_f = 0.35 (silica gel: dichloromethane/hexane = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.88 (br, 1H, pyrrole), 6.19 (d, J = 2.0 Hz, 2H, pyrrole), 3.79 (t, J = 7.8 Hz, 4H, methylene), 2.36 (s, 6H, methyl), 2.25 (s, 6H, methyl), 1.61 (m, 4H, methylene), 1.38 (sext, J = 7.4 Hz, 4H, methylene), 0.97 ppm (t, J = 7.4 Hz, 6H, methyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 125.00, 124.98, 124.5, 112.6, 107.4, 93.8, 44.7, 33.2, 20.2, 14.0, 11.6, 11.1 ppm; IR(ATR, neat) 3442, 2956, 2926, 2861, 1337, 1046, 762, 527 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{24}H_{32}Br_2N_3^-$: 522.0948 [*M*–H]$^-$; found: 522.0960; elemental analysis calcd (%) for $C_{24}H_{33}Br_2N_3$: C, 55.08; H, 6.36; N, 8.03; found: C, 55.02; H, 6.35; N, 7.89; UV-Vis (MeCN): λ_{max} (ε) = 278 nm (1.8×10^4 L mol^{-1} cm^{-1}).

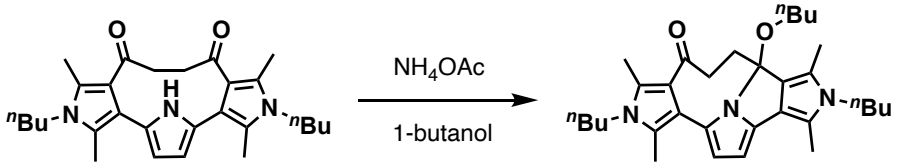
2-7 Synthesis of compound 3



To a 50 mL 2-necked flask equipped with a reflux condenser, compound **11** (418 mg, 0.80 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole[S4] (281 mg, 0.88 mmol), bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) (46 mg, 0.080 mmol), dicyclohexyl(2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phosphane (Sphos) (66 mg, 0.16 mmol), 1.56 g Cs_2CO_3 (4.80 mmol) were added. Fill the flask with N_2 then added degassed 1,4-dioxane (2.67 mL) and water (130 μL) into the flask by syringe. The mixture was heated to 100 °C for 90 min then remove the solvent under reduced pressure. Added 25 mL water into the flask and extracted the aqueous layer by dichloromethane (20 mL × 3). The combined dichloromethane layer was dried over Na_2SO_4 followed rotary evaporation to provide the crude. The crude was chromatographed on a silica gel column (diameter: 3 cm, height: 19 cm, eluent: dichloromethane/hexane = 2:1) to give compound **3** (87 mg, 0.20 mmol) in 25% yield as colorless solid.

R_f = 0.70 (silica gel: dichloromethane/hexane = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.34 (br, 2H, pyrrole), 6.21 (d, J = 2.0 Hz, 4H, pyrrole), 3.77 (m, 4H, methylene), 2.40 (s, 12H, methyl), 1.69 (quint, J = 7.5 Hz, 4H, methylene), 1.44 (sext, J = 7.4 Hz, 4H, methylene), 1.00 ppm (t, J = 7.4 Hz, 6H, methyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 130.1, 122.9, 116.5, 113.5, 44.0, 33.4, 20.4, 14.0, 10.9 ppm; IR(ATR, neat) 3422, 2950, 2925, 2864, 1595, 1473, 1403, 1031, 762 cm^{-1}; HRMS(ESI): *m/z* calcd for $C_{28}H_{36}N_4Na^+$: 451.2833 [M+Na]$^+$; found: 451.2822; UV-Vis (MeCN): λ_{max} (ε) = 276 nm (4.3×10^4 L mol^{-1} cm^{-1}).

2-8 Paal-Knorr condition for compound 10



10 **13**

In a 10 mL Schlenk flask with flat stopper, compound **10** (48.0 mg, 0.100 mmol), NH_4OAc (154 mg, 2.00 mmol) and 1-butanol (1.70 mL) were added. Heating the flask to 115 °C then closed the switch and kept 6 h. The solution was cooled to room temperature and washed by 100 mL saturated $NaHCO_3$ aqueous solution. The organic layer was separated and extracted the aqueous layer by dichloromethane (5 mL × 3). The combined organic layer was dried over Na_2SO_4 and followed by rotary evaporation to obtain the concentrated residue. After a silica gel column chromatograph (diameter: 2 cm, height: 13 cm, eluent: ethyl acetate/hexane = 2:3), compound **13** (13.0 mg, 0.0258 mmol, 26%) was obtained as yellow oil.

Characterization data for compound 13

R_f=0.61 (silica gel: ethyl acetate/hexane = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.14 (d, J = 3.2 Hz, 1H, pyrrole), 6.00 (d, J = 3.6 Hz, 1H, pyrrole), 3.86-3.75 (m, 2H, methylene), 3.67 (t, J = 7.4 Hz, 2H, methylene), 3.18-3.10 (m, 1H, ethylene), 3.07-3.02 (m, 1H, ethylene), 2.89-2.81 (m, 1H, ethylene), 2.67-2.61 (m, 1H, ethylene), 2.59 (s, 3H, methyl), 2.30 (s, 6H, methyl), 2.21-2.16 (m, 2H, methylene), 2.14 (s, 3H, methyl), 1.45-1.31 (m, 6H, methylene), 0.99-0.92 (m, 6H, methyl), 0.59 ppm (t, J = 7.0 Hz, 3H, methyl), one methylene peak overlap with water peak; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ=199.0, 133.8, 132.5, 127.8, 125.4, 124.9, 120.1, 119.7, 115.8, 115.7, 113.6, 112.0, 95.9, 95.2, 63.6, 43.5, 41.8, 37.6, 33.3, 32.9, 31.5, 20.3, 20.2, 19.0, 14.0, 13.94, 13.92, 11.9, 11.8, 11.4, 10.4 ppm, one pyrrolic carbon peak may overlapped; HRMS(ESI): *m/z* calcd for $C_{32}H_{45}N_3O_2Na^+$: 526.3404 [M+Na]$^+$; found: 526.3394.

3. Single Crystal X-ray Diffraction Analysis

3-1 Crystallographic data for compound 10

Single crystals suitable for X-ray diffraction analysis were grown by vapor diffusion of hexane into a chloroform solution of compound **10**.

$C_{28}H_{37}N_3O_2$, M = 447.60, crystal size: 0.68 × 0.35 × 0.22 mm^3, monoclinic, space group $P2_1/n$, a = 12.8130(5), b = 13.3344(5), c = 14.2787(6) Å, α = 90, β = 91.632(4), γ = 90º, V = 2438.58(17) Å^3, Z = 4, T = 123(2) K, μ = 0.077 mm^{-1}, D_{calc} = 1.219 g/cm^3, 2.090 ≤ θ ≤ 27.498, 4750 unique reflections out of 5478 with I > 2σ(*I*), GOF = 1.004, R_1 = 0.0419 and wR_2 = 0.1063 for all data, CCDC deposit number: 2382890.

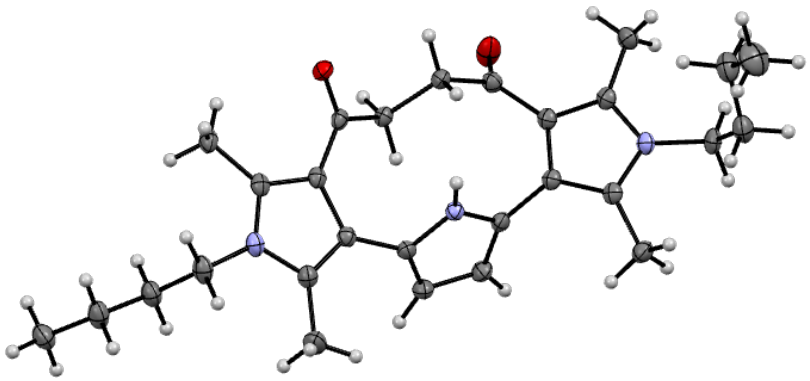


Fig. S1 ORTEP drawing of crystal structure of compound **10** at the 50% thermal probability level.

3-2 Crystallographic data for compound 3

Single crystals suitable for X-ray diffraction analysis were grown by vapor diffusion of hexane into a dichloromethane solution of compound **3**.

$C_{28}H_{36}N_4$, M = 428.61, crystal size: 0.50 × 0.15 × 0.04 mm^3, triclinic, space group P-1, a = 9.0906(8), b = 9.1054(5), c = 9.2735(5) Å, α = 62.149(6), β = 61.589(7), γ = 65.472(7)º, V = 578.30(9) $Å^3$, Z = 1, T = 123(2) K, μ = 0.073 mm^{-1}, D_{calc} = 1.231 g/cm^3, 2.612 ≤ θ ≤ 26.999°, 2268 unique reflections out of 2469 with I > 2$\sigma(I)$, GOF = 1.039, R_1 = 0.0407 and wR_2 = 0.1035 for all data. CCDC deposit number: 2382889.

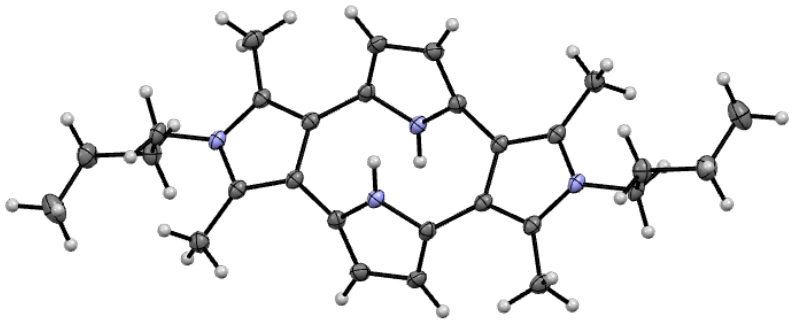


Fig. S2 ORTEP drawing of crystal structure of compound **3** at the 50% thermal probability level.

4. StrainViz Analysis

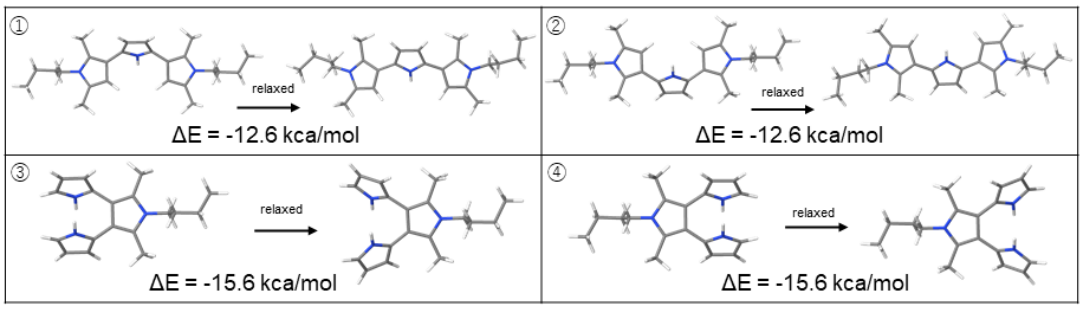
4-1 Computational details

Geometry optimization and vibration analysis of the three compounds (**3**, **4**, and **10**) were performed by the global reaction route mapping (GRRM) program.[S5] The initial structures were prepared from the crystal structures determined in the present work for **3** and **10** and that[S6] determined by Morimoto et al. for **4**. The vibrational frequencies were computed to confirm whether the optimized geometry corresponded to stationary or saddle points on potential energy surface. The density functional theory (DFT) calculations were carried out at the M06-2X[S7]/6-311+G(2d,p) level of theory implemented in the Gaussian 16 program.[S8]

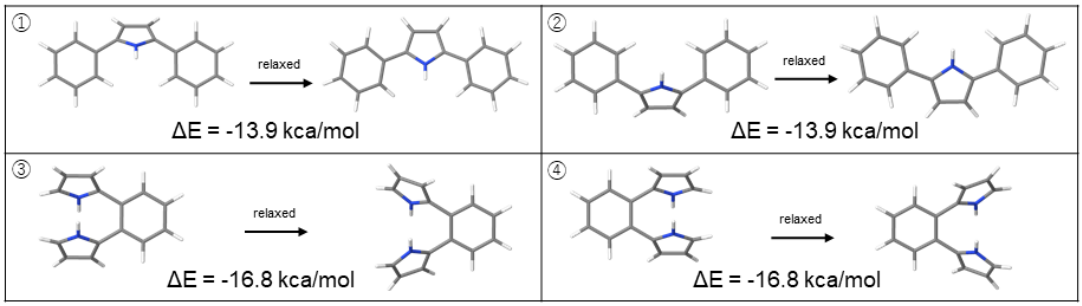
Strains of each macrocycle were computed by the StrainViz program[S9] at the same DFT level of theory as the geometry optimization calculations. The DFT structure was divided into four fragments with same manner to evaluate four types of strain (total, bond, angle, and dihedral). The strain representation was visualized by the visual molecular dynamics (VMD) software.[S10] For **3** and **4**, the StrainViz analyses at the B3LYP+D3[S11-15]/6-311+G(2d,p) level of theory were additionally examined to confirm influences of the adopted functionals.

Structural and energy changes of the four fragments used in the StrainViz analysis are supplementary summarized in Fig. S3.

(a) Compound 3



(b) Compound 4



(c) Compound 10

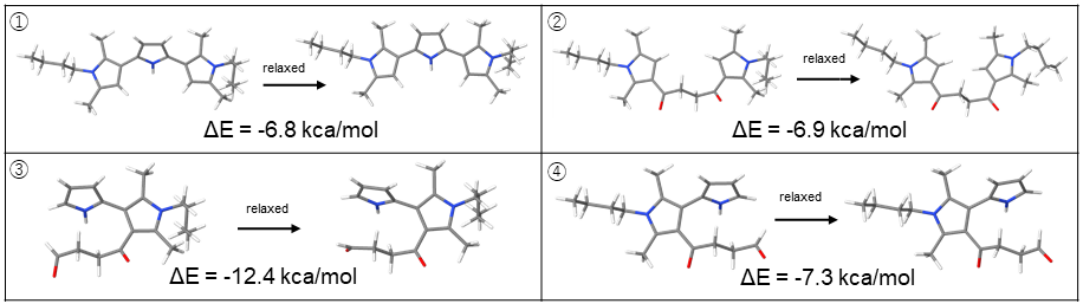


Fig. S3 Fragmentation manner of each macrocycle. Structural and energy changes of the four fragments through strain release are also shown. Atom colors are assigned as follows: white (hydrogen), gray (carbon), blue (nitrogen), and red (oxygen).

4-2 Major contribution of total strain

From Fig. 3d in the main text, it is found that the dihedral strain is a major contribution of the total strain. Fig. S4 (b and c) show visualized comparison of dihedral and total strains. For each macrocycle, the distribution pattern of dihedral strain is similar to that of total one. Particularly, the larger strains are likely to appear at the C–C bonds linking the subrings.

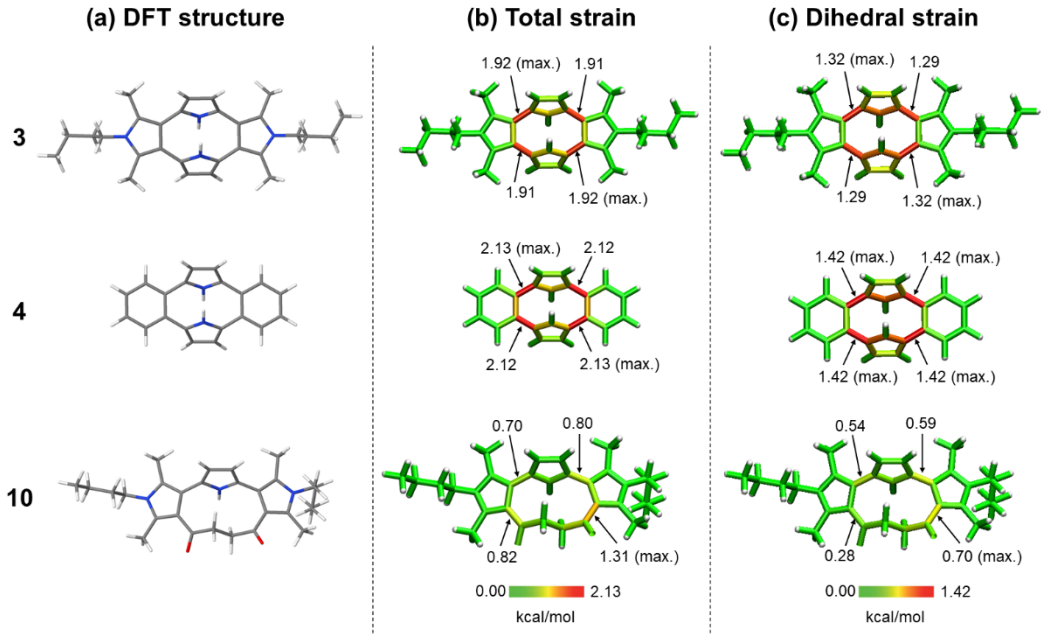
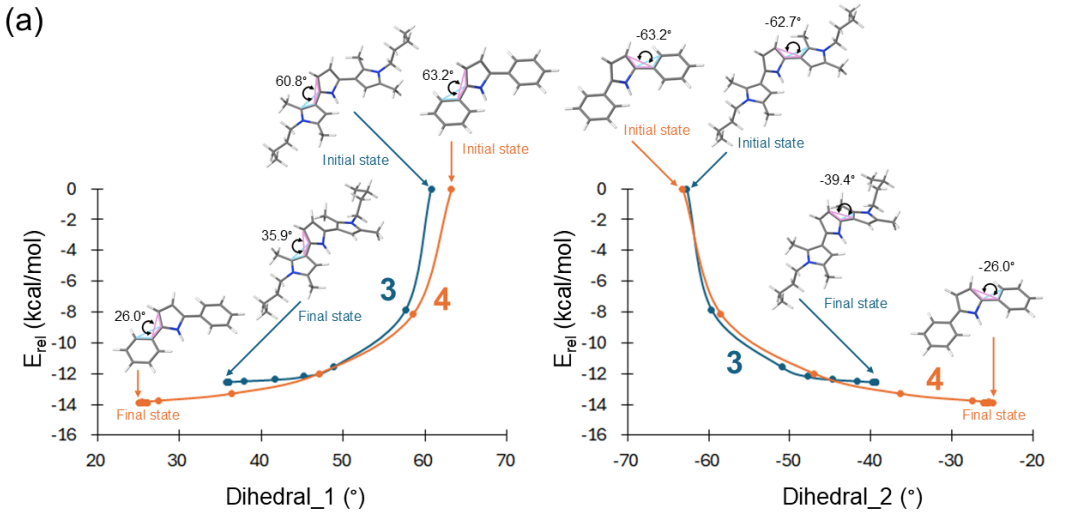


Fig. S4 Visualized comparison of dihedral and total strains. (a) DFT structure, (b) total strain, and (c) dihedral strain. In (a), atom colors are assigned as follows: white (hydrogen), gray (carbon), blue (nitrogen), and red (oxygen).

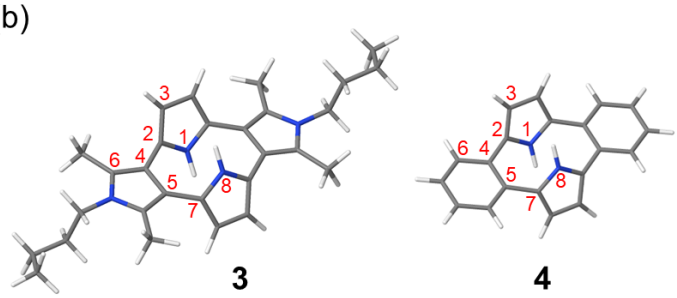
4-3 Rationalization for difference of total/dihedral strain between 3 and 4

The total strain of **3** is slightly smaller than that of **4**. The individual fragment shown in Fig. S3 also exhibits larger strains at the C-C bonds between two aromatic rings. Especially, dihedral strains of the fragment 1 (or 2) are identified as major contributions at the strained C-C bonds. Fig. S5a shows relative energy changes for the structural relaxation of fragment 1. For **3**, the steric effect between methyl groups and pyrrole might affect the strain energy and torsional motion, which resulted in less strain.

Fig. S5b shows selected geometrical parameters for the macrocycles of **3** and **4**. Judging from the parameters, **4** has the narrower cavity than that of **3**, which resulted in a larger total strain.



(b)



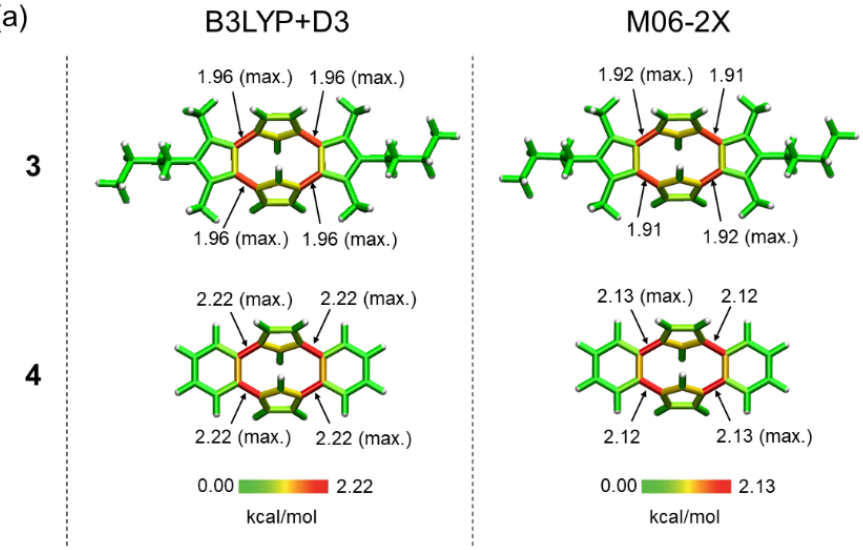
	3	4
Bond (Å)		
N1-N8	2.581	2.510
C2-C7	3.053	2.918
Angle (°)		
C2-C4-C5	122.8	120.1
C4-C5-C7	122.7	120.1
Dihedral (°)		
C2-C4-C5-C7	-14.0	-11.7

Fig. S5 Differences in geometrical and energy changes between **3** and **4**. (a) relative energy changes as a function of dihedral angle through the structural relaxation of fragment 1. (b) selected geometrical parameters of macrocycles.

4-4 DFT dependency of computed strains

In Fig. S6, computed strains by the B3LYP+D3 method are compared to those by the M06-2X method. In (a), the strain distribution and maximum values of each macrocycle are found to be the similar manner between the two evaluations. In (b), although the computed values by the B3LYP+D3 method are slightly larger than those by the M06-2X method, there is no change for the order of total strains between **3** and **4** and the contribution of individual strain. Therefore, the selection of functionals does not influence the present evaluation.

(a)



(b)

	B3LYP+D3		M06-2X	
	3	**4**	**3**	**4**
Total strain	21.5	23.8	20.8	22.7
Bond strain	1.1	1.4	0.9	1.2
Angle strain	4.4	5.3	4.2	4.8
Dihedral strain	16.0	17.1	15.7	16.7

Fig. S6 Comparison of StrainViz analyses computed at two different DFT methods. (a) Visualization of the total strain of **3** and **4**. (b) Calculated total, bond, angle, and dihedral strain energies (in kcal/mol) of **3** and **4**.

5. UV-Vis Absorption Spectra

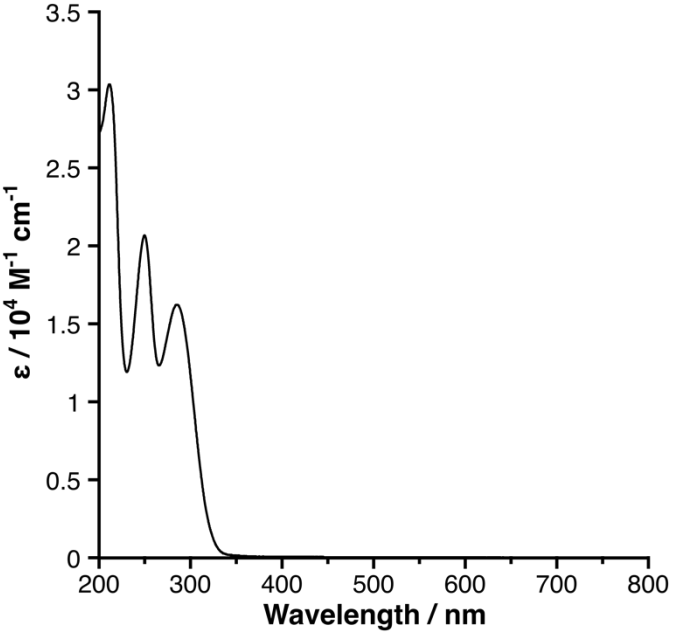


Fig. S7 UV-Vis absorption spectrum of compound **8** in MeCN (λ_{max} = 212, 250, 285 nm).

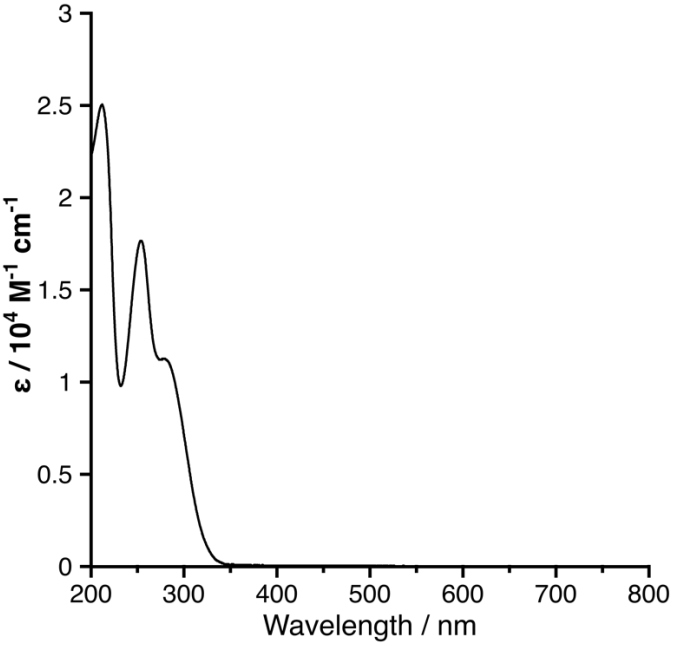


Fig. S8 UV-Vis absorption spectrum of compound **9** in MeCN (λ_{max} = 212, 254, 279 nm).

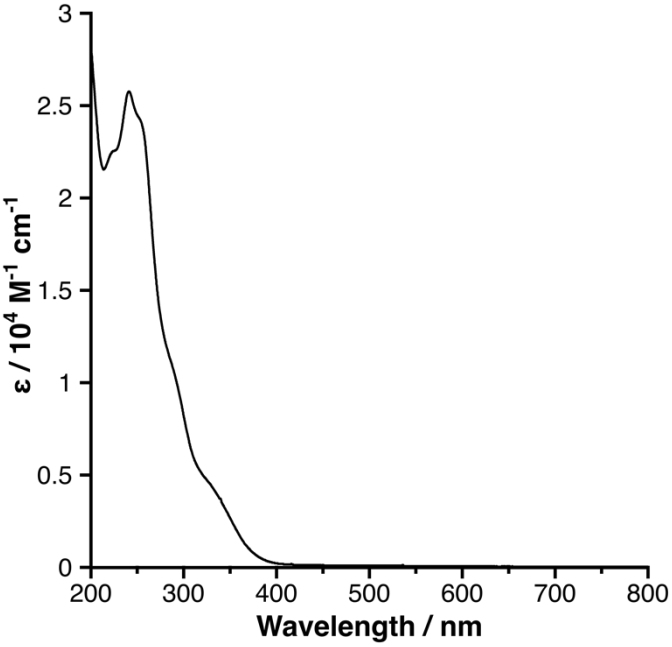


Fig. S9 UV-Vis absorption spectrum of compound **10** in MeCN (λ_{max} = 241 nm).

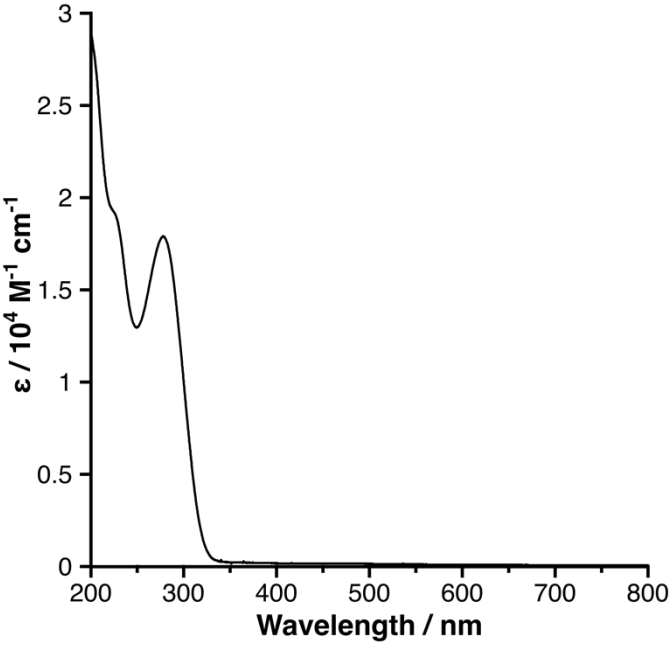
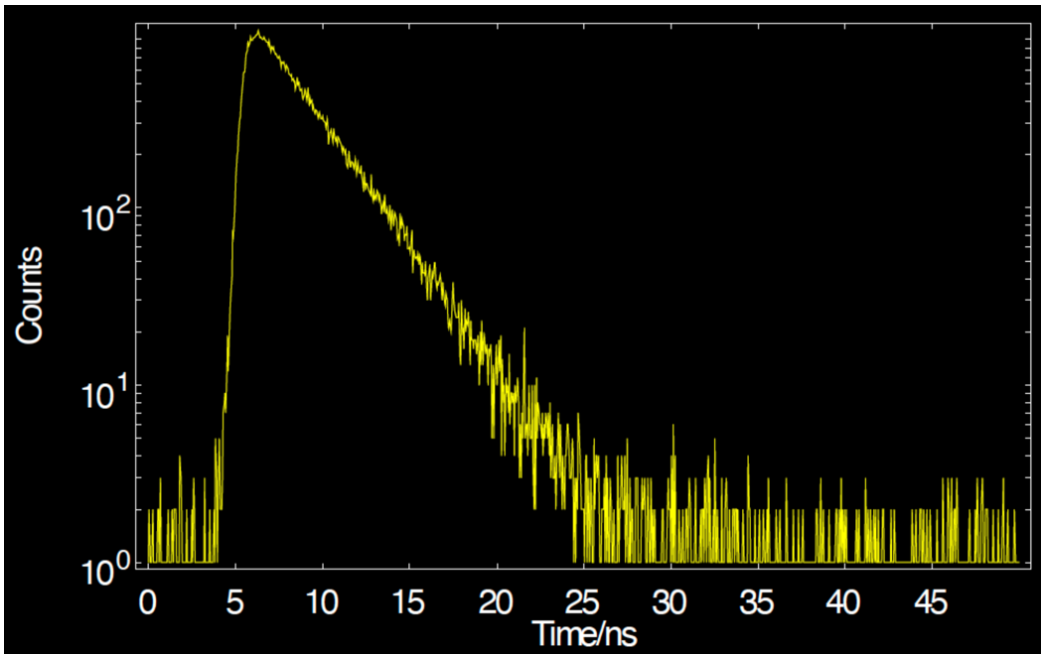


Fig. S10 UV-Vis absorption spectrum (solid line) of compound **11** in MeCN (λ_{max} = 278 nm).

6. Fluorescence Lifetime Measurement

a)



b)

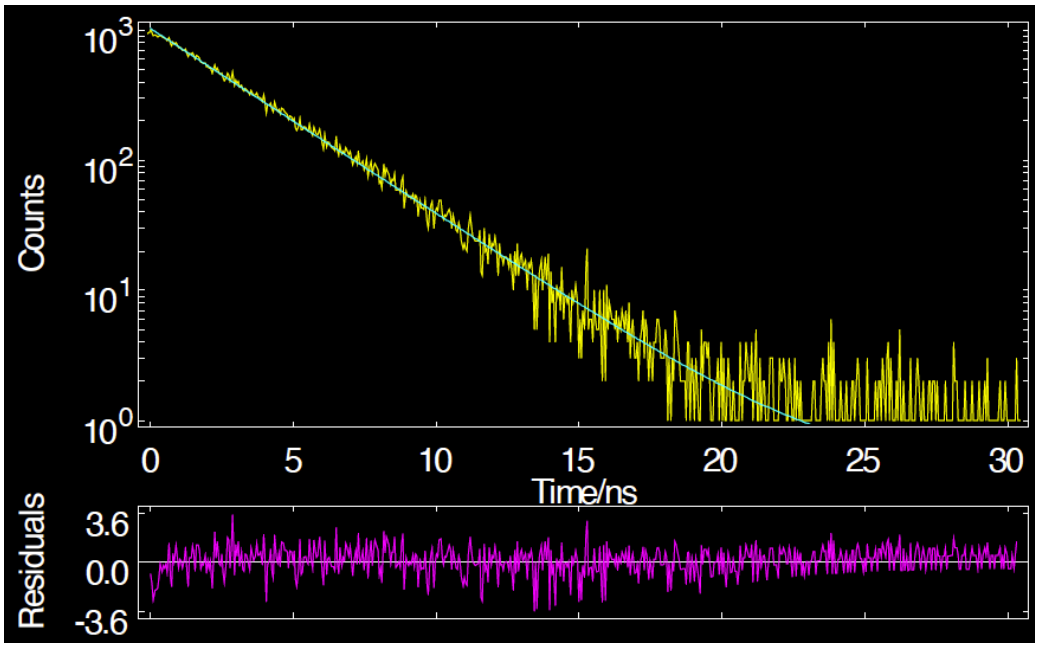


Fig. S11 (a) Emission decay and (b) fitting analysis of compound **3** in CH_3CN (τ = 3.05 ns, χ^2 = 1.004, λ_{ex}: 270 nm, λ_{obs}: 435 nm).

7. Electrochemical Measurement

7-1 Cyclic voltammetry

Three-electrode system; solvent: CH_2Cl_2; electrolyte: 0.1 M *n*-Bu_4NPF_6; working electrode: Pt; counter electrode: Pt wire; reference electrode: $Ag/AgNO_3$; scan rate: 0.05 V/s; The three-electrode system was purged with N_2. Ferrocene (Fc) was used as external standards.

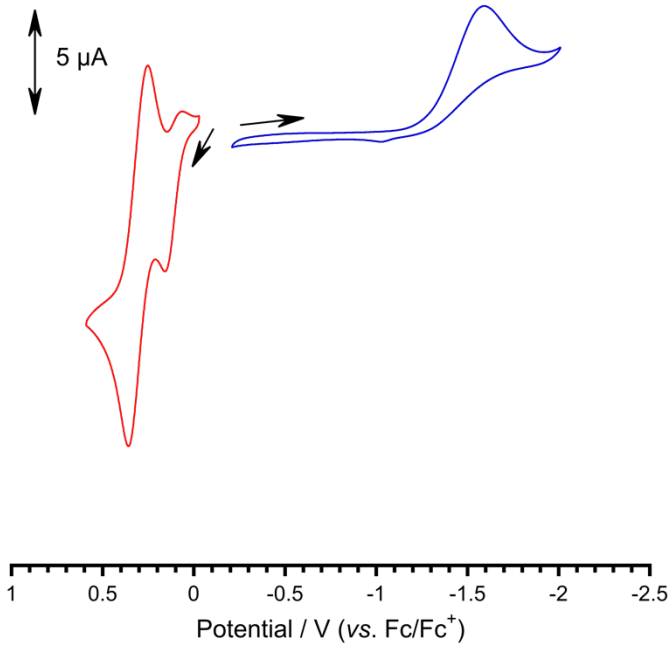


Fig. S12 Cyclic voltammetry curves of compound **10** (red: oxidation; blue: reduction).

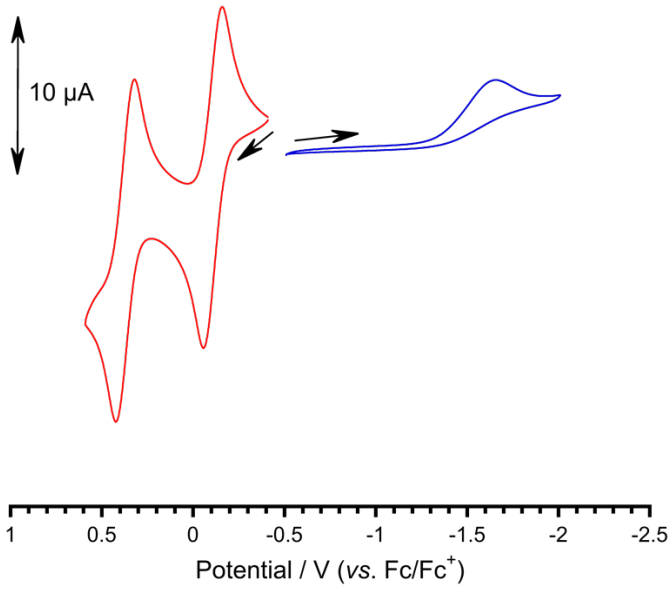


Fig. S13 Cyclic voltammetry curves of compound **11** (red: oxidation; blue: reduction).

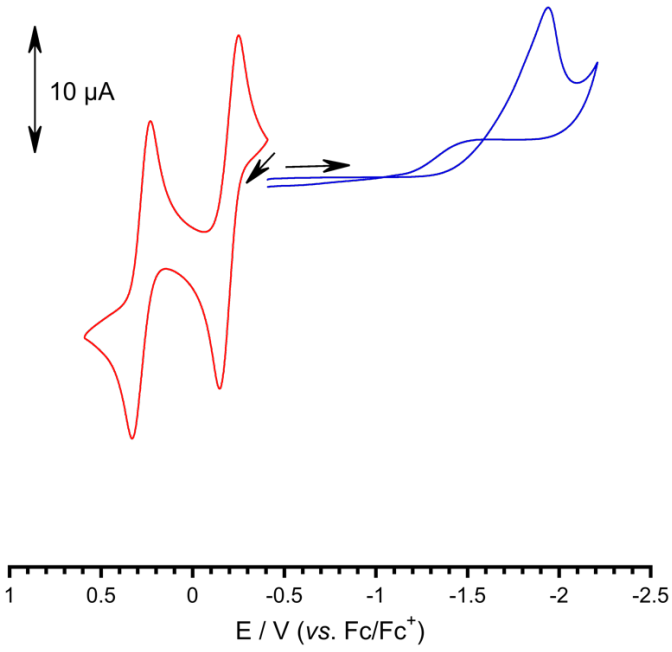


Fig. S14 Cyclic voltammetry curves of compound **3** (red: oxidation; blue: reduction).

8. DFT Calculation

8-1 Computational details

All calculations were carried out using the *Gaussian 16* program.[S8] The calculations were performed by the density functional theory (DFT) method with the indicated functional (B3LYP, ωB97XD, or CAM-B3LYP), employing a basis set 6-311G(d) for C, H, and N. SMD solvation model with CH_2Cl_2 as a continuum description of the solvent was applied for the relative energy comparison and simulation of the UV/Vis spectra via time-dependent DFT method. All structures were fully optimized without any symmetry restriction. Calculated frequencies were used to verify the nature of all stationary points as minima (no imaginary frequencies). The NICS values were obtained with the GIAO method. The ring centers for the NICS values were designated at the nonweighted means of the carbon and nitrogen coordinates. [S15,S16] The anisotropy of the induced current density (ACID) calculation was conducted with the CSGT method, in which the external magnetic field was applied in the direction from the back of the paper to the surface.[S17,S18]

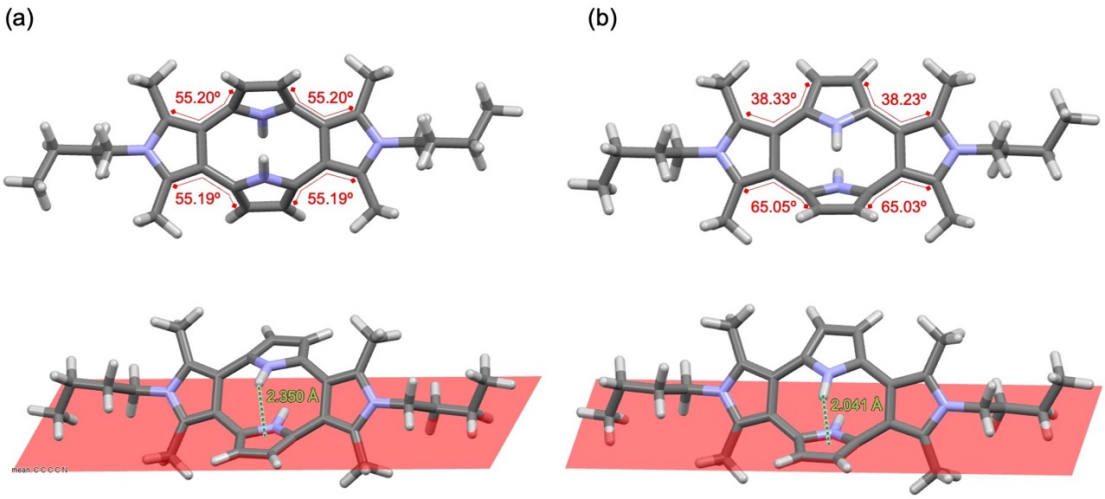


Fig. S15 Optimized structures and structural details of (a) **3** and (b) $\mathbf{3}^{\bullet+}$ at (U)B3LYP/6-311G(d,p) level.

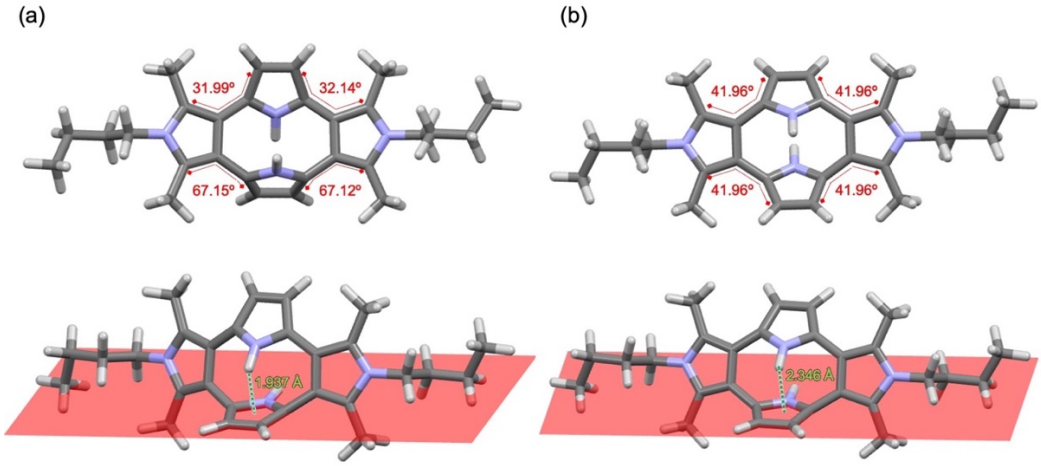


Fig. S16 Optimized structures and structural details of $\mathbf{3}^{2+}$. (a) Closed-shell singlet with (R)B3LYP/6-311G(d,p) level and (b) open-shell triplet with (U)B3LYP/6-311G(d,p) level.

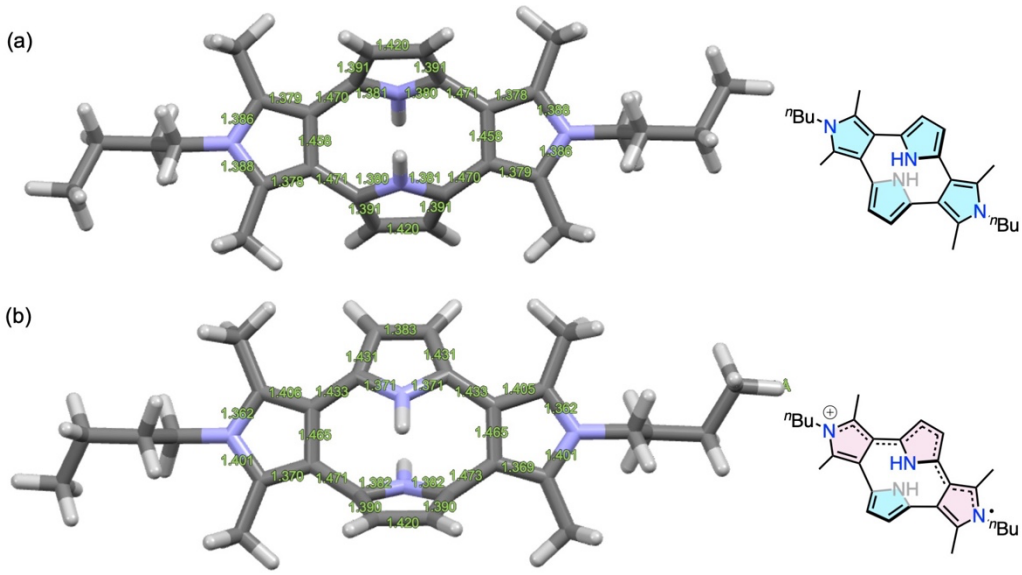


Fig. S17 Selected bond lengths (in Å) of the optimized structures of (a) **3** and (b) $\mathbf{3}^{\bullet+}$.

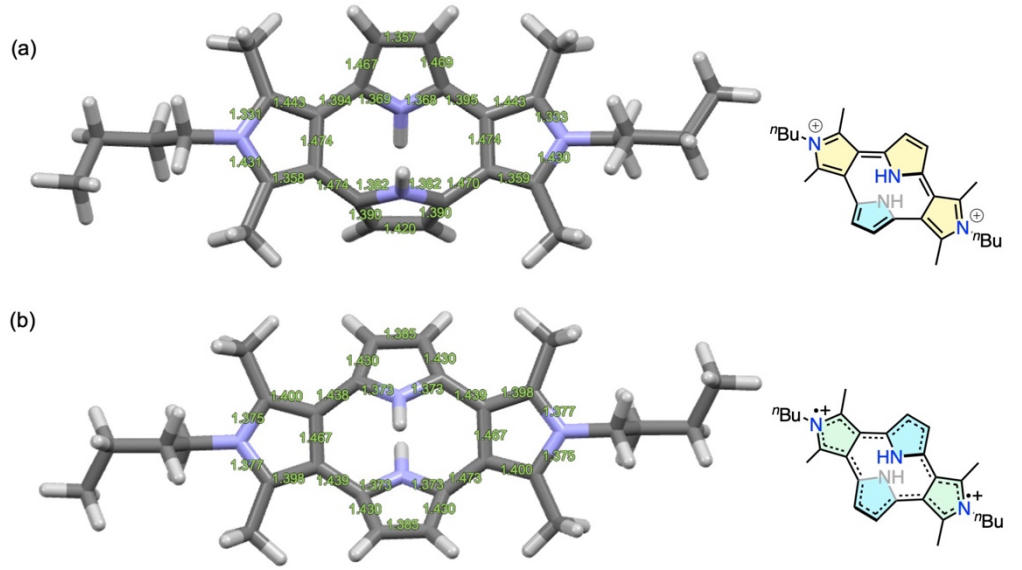


Fig. S18 Selected bond lengths (in Å) of the optimized structures of $\mathbf{3}^{2+}$. (a) Closed-shell singlet with (R)B3LYP/6-311G(d,p) level and (b) open-shell triplet with (U)B3LYP/6-311G(d,p) level.

Table S1. Comparison of the total energy (sum of electronic and zero-point energies) of $\mathbf{3}^{2+}$ with various functional. The basis set was set at 6-311G(d,p) level.

Relative energy	(R/U)B3LYP	(R/U)ωB97XD	(R/U)CAM-B3LYP
CS, singlet	+0.50 kcal/mol	+0.33 kcal/mol	+0.31 kcal/mol
OS, singlet	+1.64 kcal/mol	+1.64 kcal/mol	+1.73 kcal/mol
OS, triplet	0 kcal/mol	0 kcal/mol	0 kcal/mol

Table S2. Comparison of the total energy (sum of electronic and zero-point energies) of $\mathbf{3}^{2+}$ with various functional with SMD continuum solvation model (CH_2Cl_2). The basis set was set at 6-311G(d,p) level.

Relative energy	(R/U)B3LYP	(R/U)ωB97XD	(R/U)CAM-B3LYP
CS, singlet	+1.14 kcal/mol	0 kcal/mol	+0.46 kcal/mol
OS, singlet	+1.39 kcal/mol	+1.32 kcal/mol	+1.30 kcal/mol
OS, triplet	0 kcal/mol	+0.12 kcal/mol	0 kcal/mol

8-2 TD-DFT Calculations

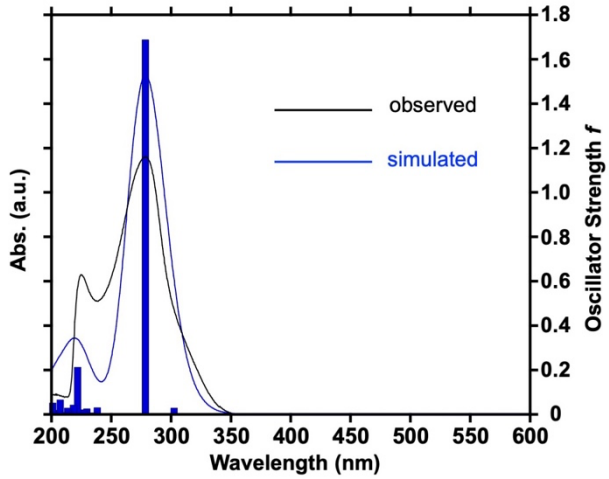


Fig. S19 Calculated UV/Vis absorption spectra of **3** at (R)B3LYP/6-311G(d,p) level. SMD solvation model (CH_2Cl_2) was applied.

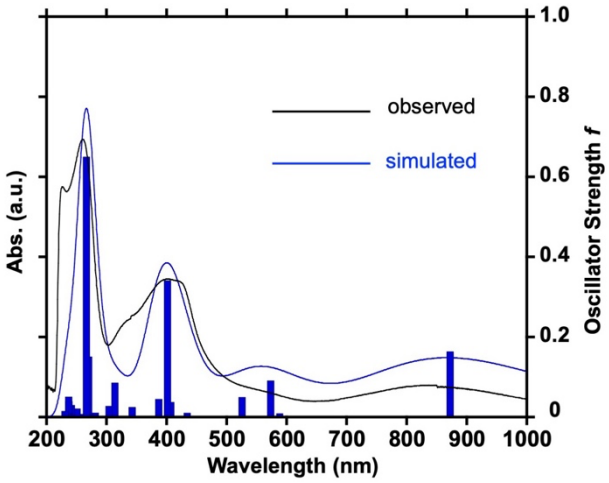


Fig. S20 Calculated UV/Vis absorption spectra of $\mathbf{3}^{\bullet+}$ at (U)B3LYP/6-311G(d,p) level. SMD solvation model (CH_2Cl_2) was applied.

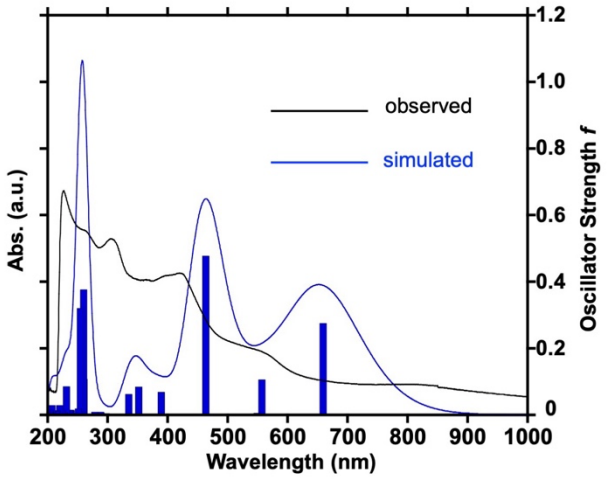


Fig. S21 Calculated UV/Vis absorption spectra of $\mathbf{3}^{2+}$ (closed-shell) at (R)B3LYP/6-311G(d,p) level. SMD solvation model (CH_2Cl_2) was applied.

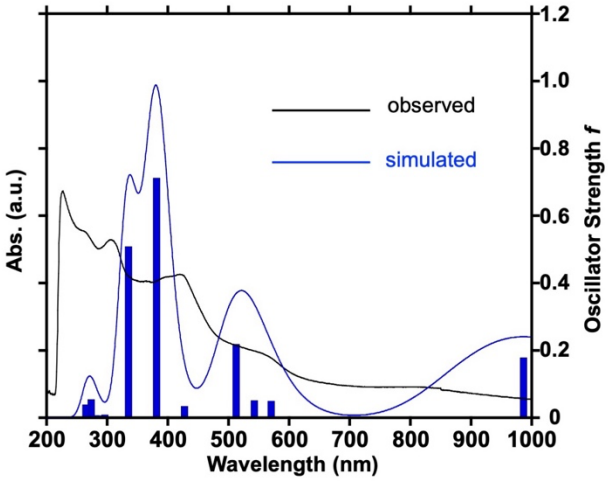


Fig. S22 Calculated UV/Vis absorption spectra of $\mathbf{3}^{2+}$ (open-shell, triplet) at (U)B3LYP/6-311G(d,p) level. SMD solvation model (CH_2Cl_2) was applied.

8-3 ACID Isosurface

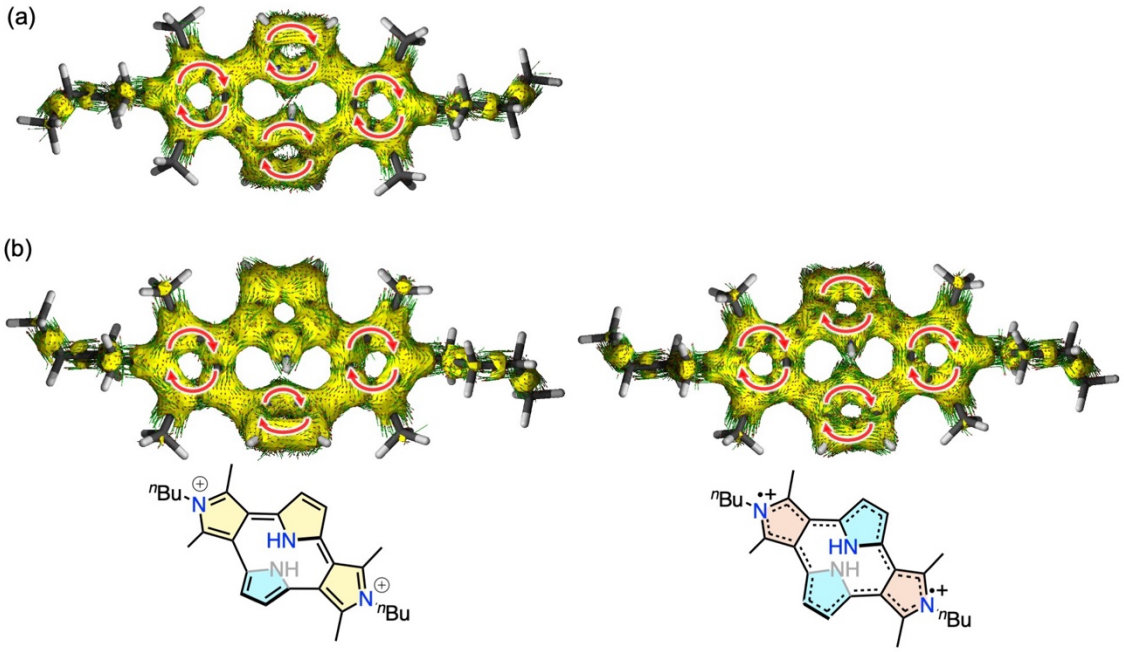


Fig. S23 ACID isosurfaces for (a) **3** and (b) $\mathbf{3}^{2+}$ (left: closed-shell, right: open-shell triplet). Isosurface value: 0.05.

8-4 NICS Calculations

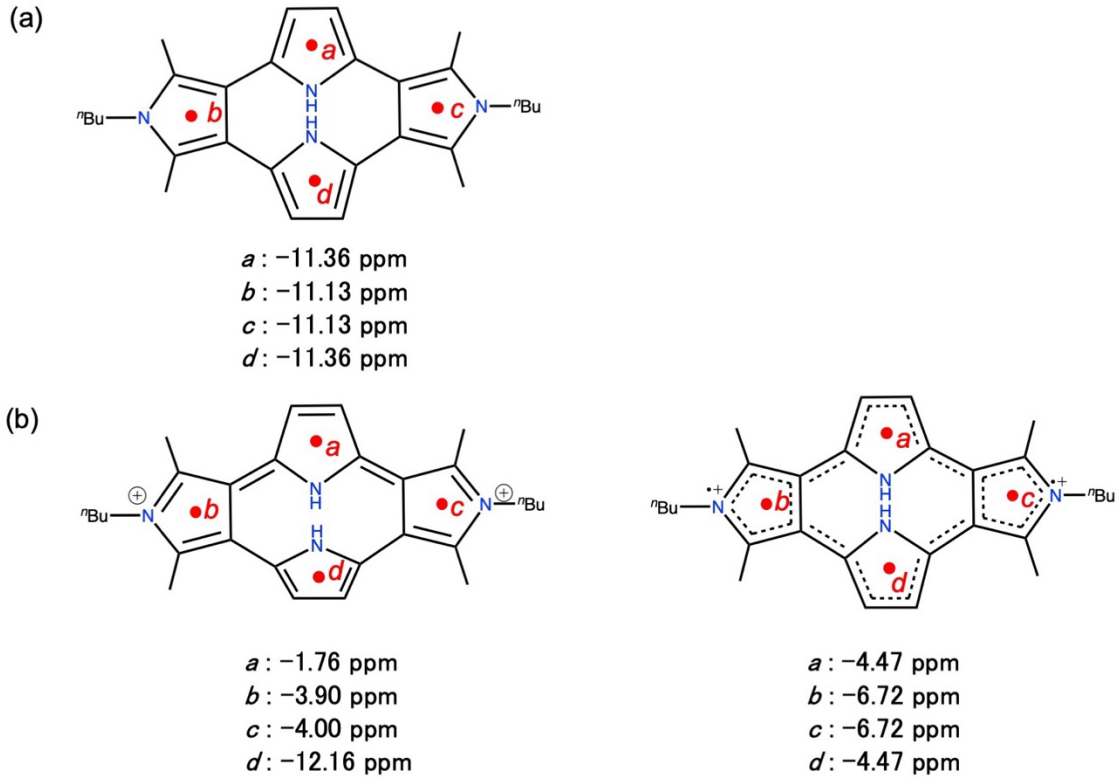


Fig. S24 NICS(0) values for (a) **3** and (b) $\mathbf{3}^{2+}$ (left: closed-shell, right: open-shell triplet).

9. Chemical Oxidation

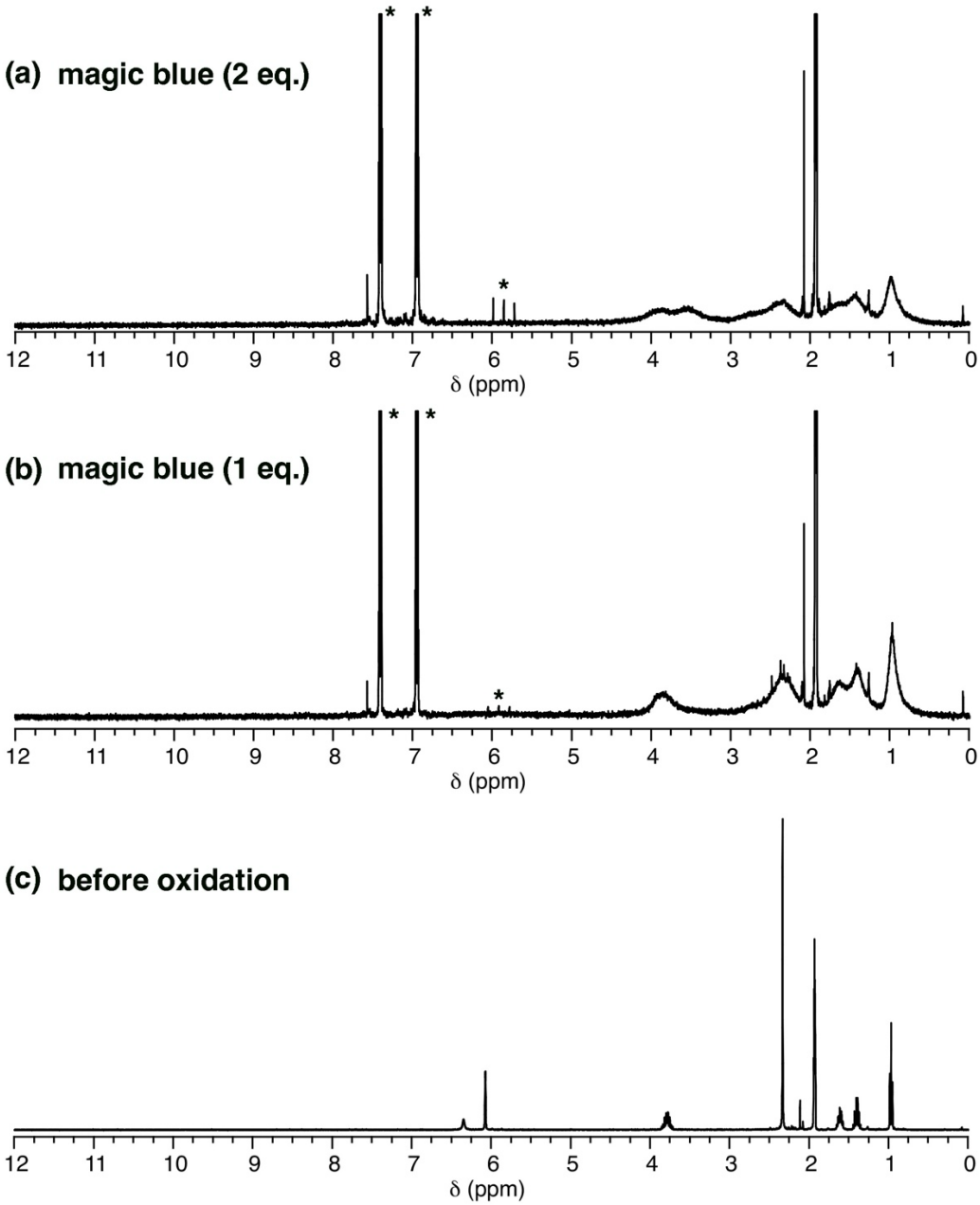


Fig. S25 ^{1}H NMR spectra of cyclo[4]pyrrole **3** with (a) 2, (b) 1, and (c) 0 equivalent(s) of magic blue recorded in CD_3CN (400 MHz at 25 ºC). Asterisks (*) indicate impurities derived from magic blue.

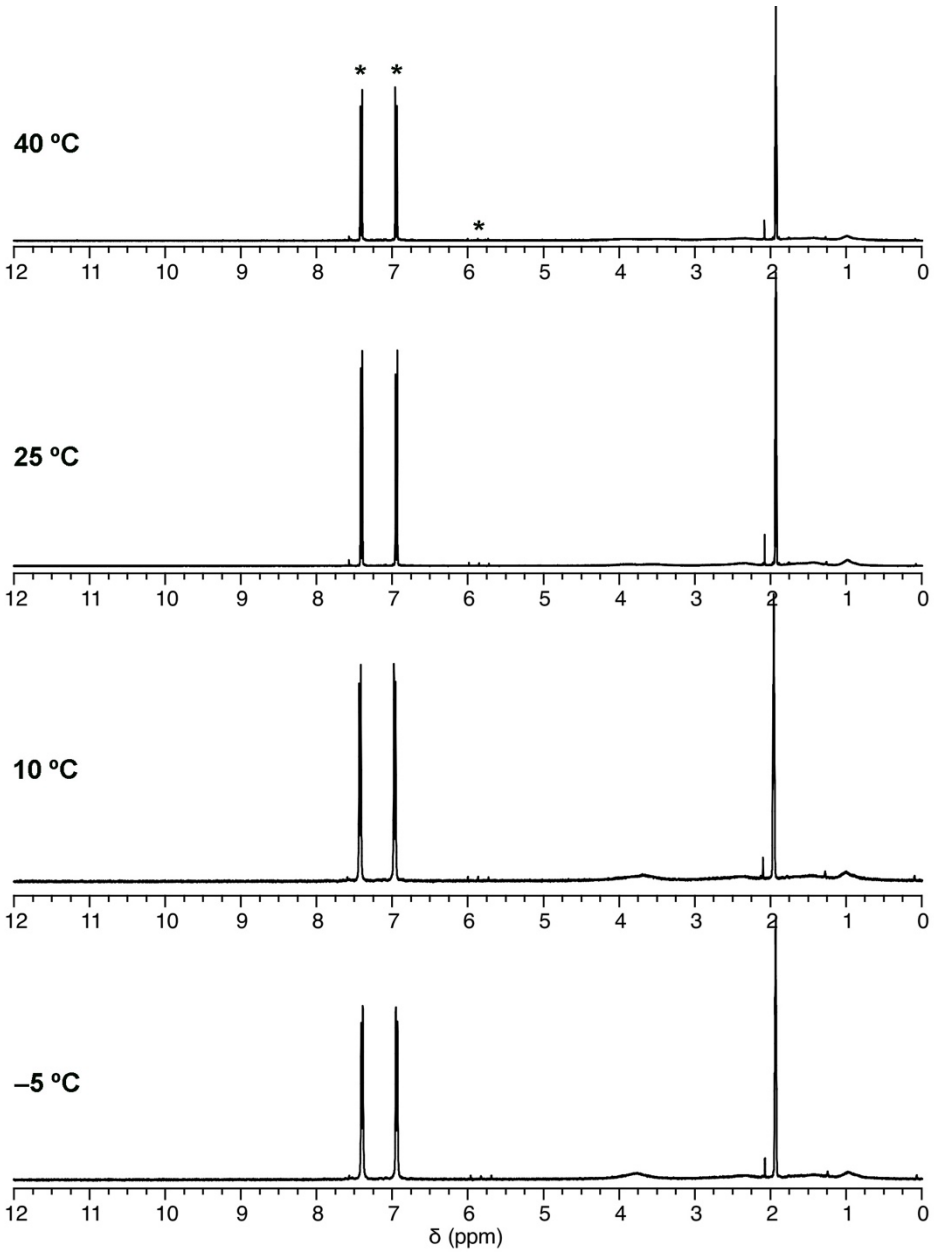


Fig. S26 Variable temperature 400 MHz ^{1}H NMR spectra of cyclo[4]pyrrole **3** after addition of 2 equivalent of magic blue in CD_3CN. Asterisks (*) indicate impurities derived from magic blue.

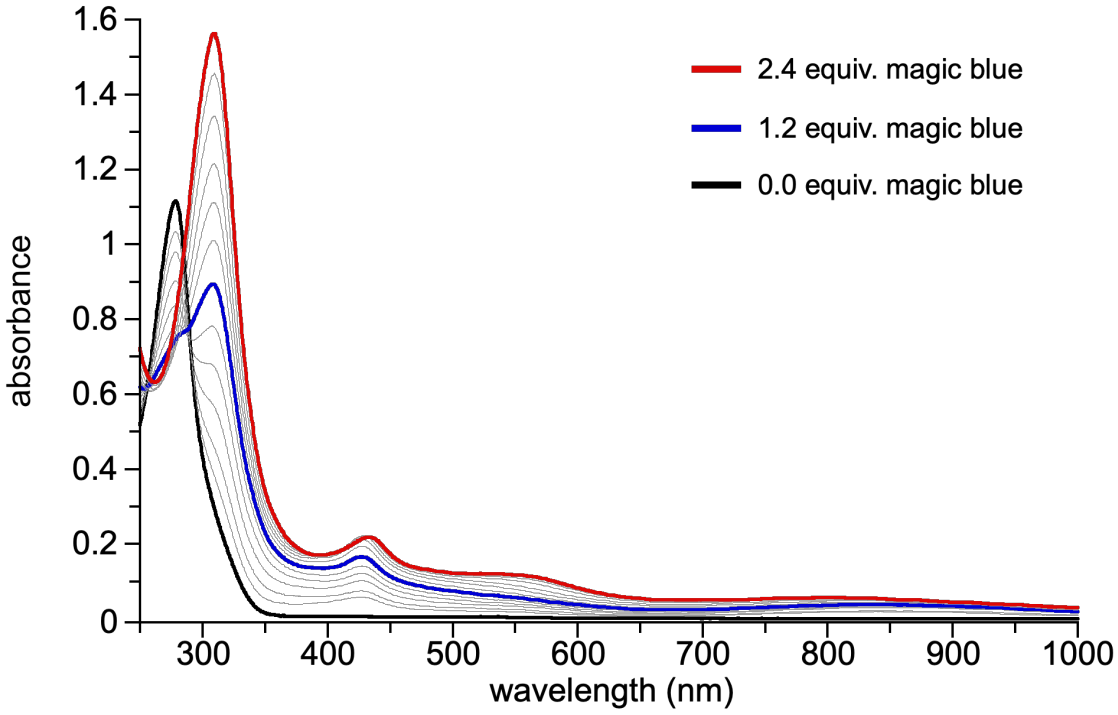


Fig. S27 UV-vis absorption spectra of cyclo[4]pyrrole **3** during titration with magic blue (0 to 2.4 equiv.) in CH_2Cl_2. The absorption band at 309 nm is attributed to tris(4-bromophenyl)amine which was generated upon oxidation with magic blue.

10. NMR Spectra

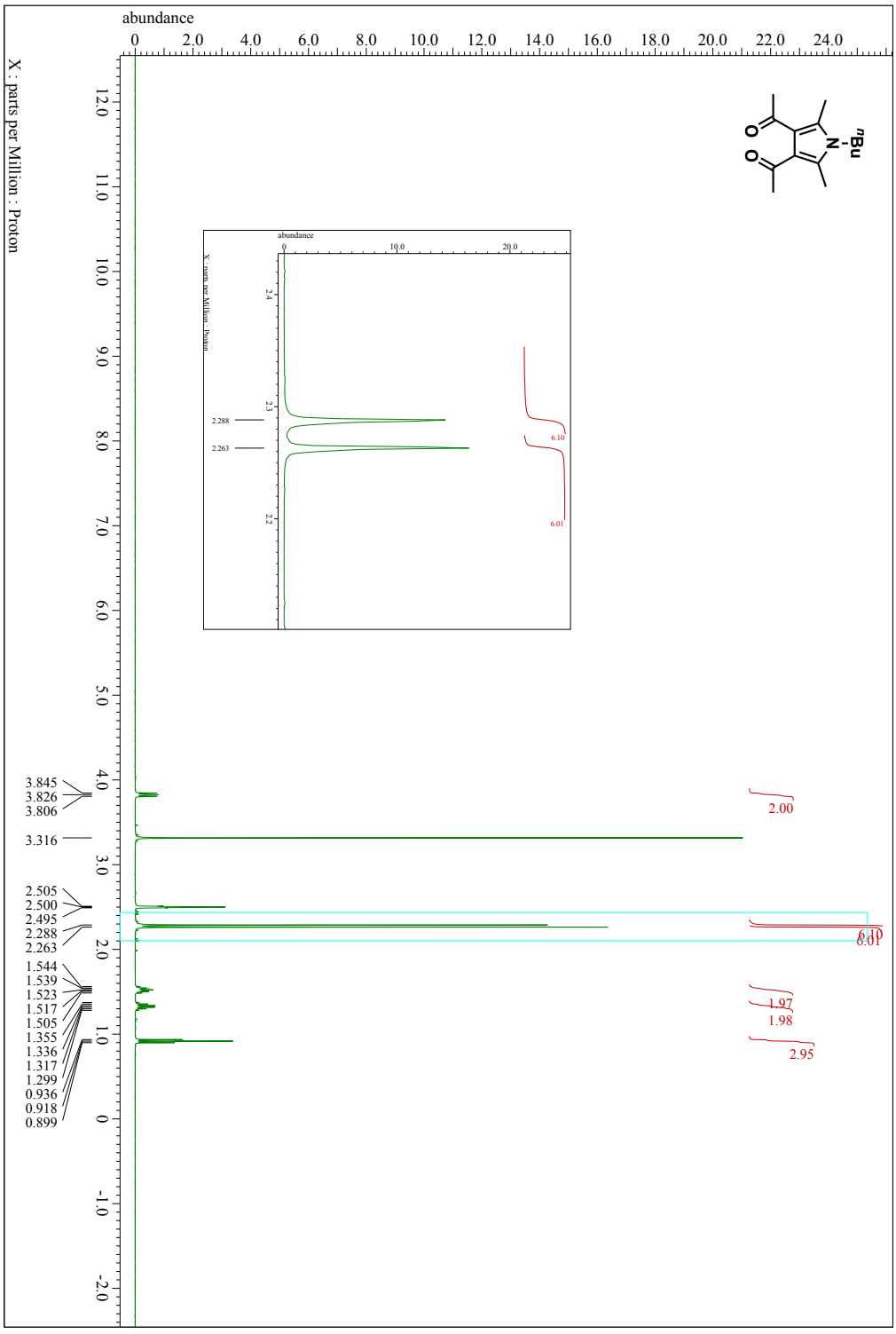


Fig. S28 ^{1}H NMR spectrum of compound **6** (400 MHz, DMSO-d_6, 298 K).

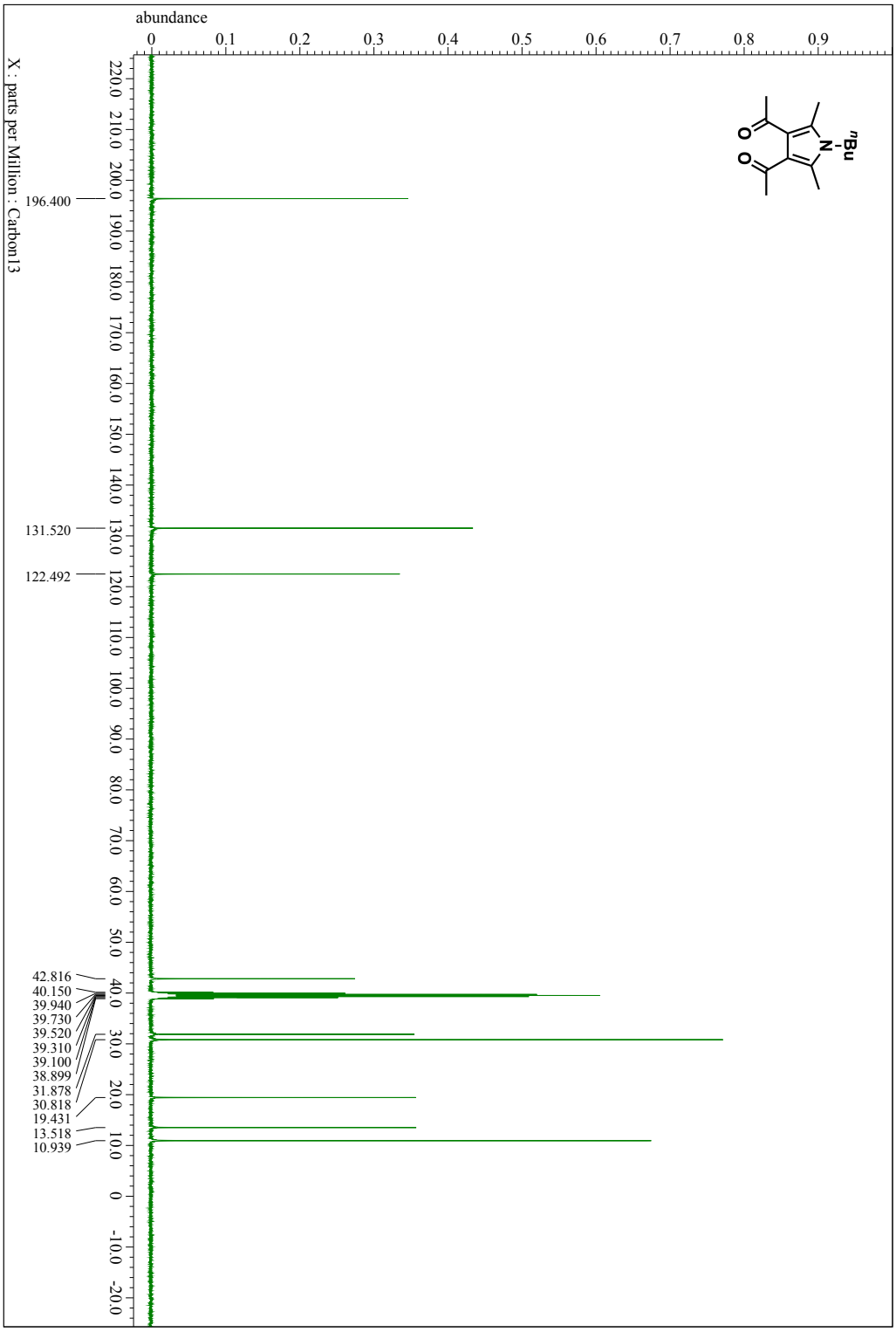


Fig. S29 $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** (100 MHz, DMSO-d_6, 298 K).

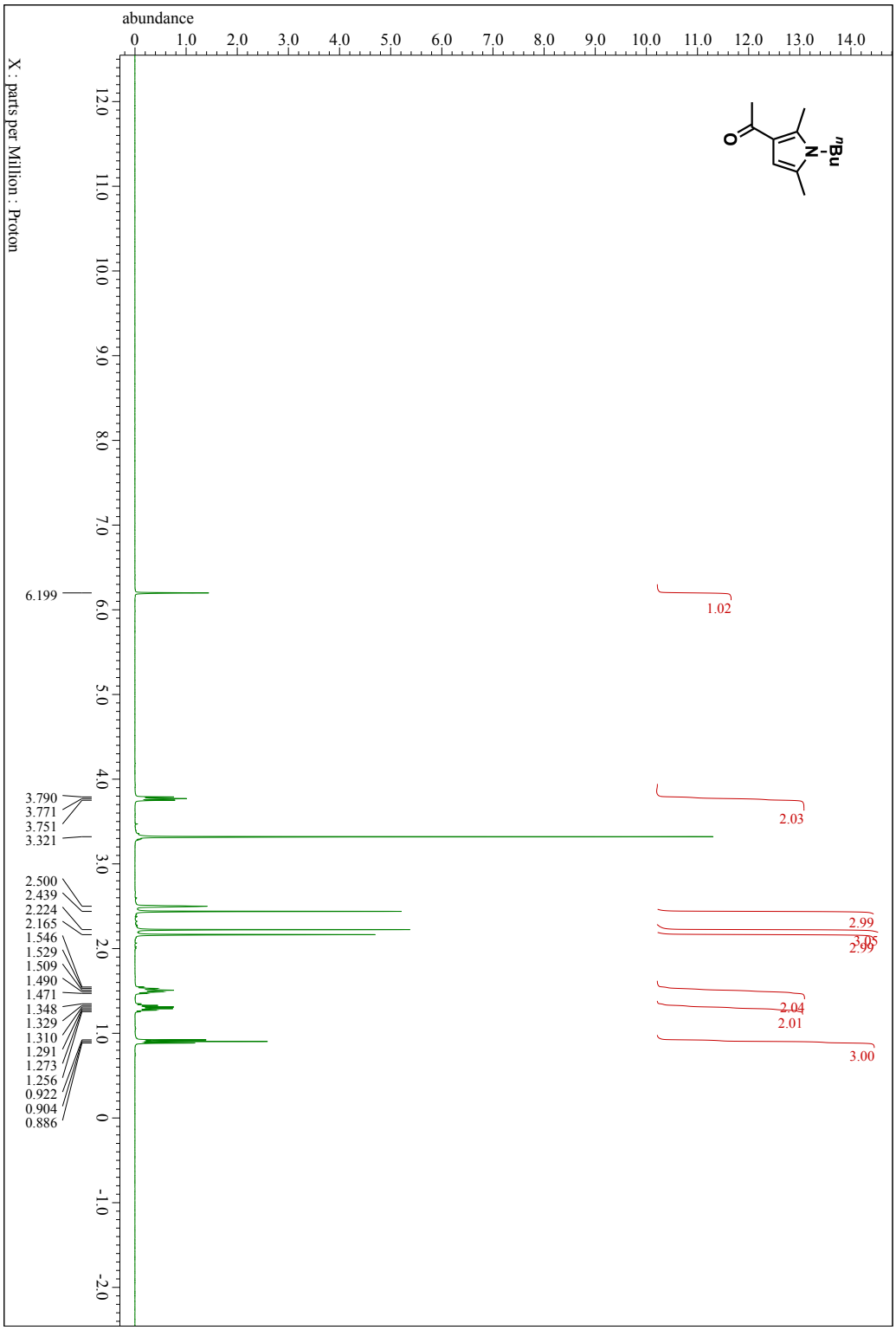


Fig. S30 ^{1}H NMR spectrum of compound **7** (400 MHz, DMSO-d_6, 298 K).

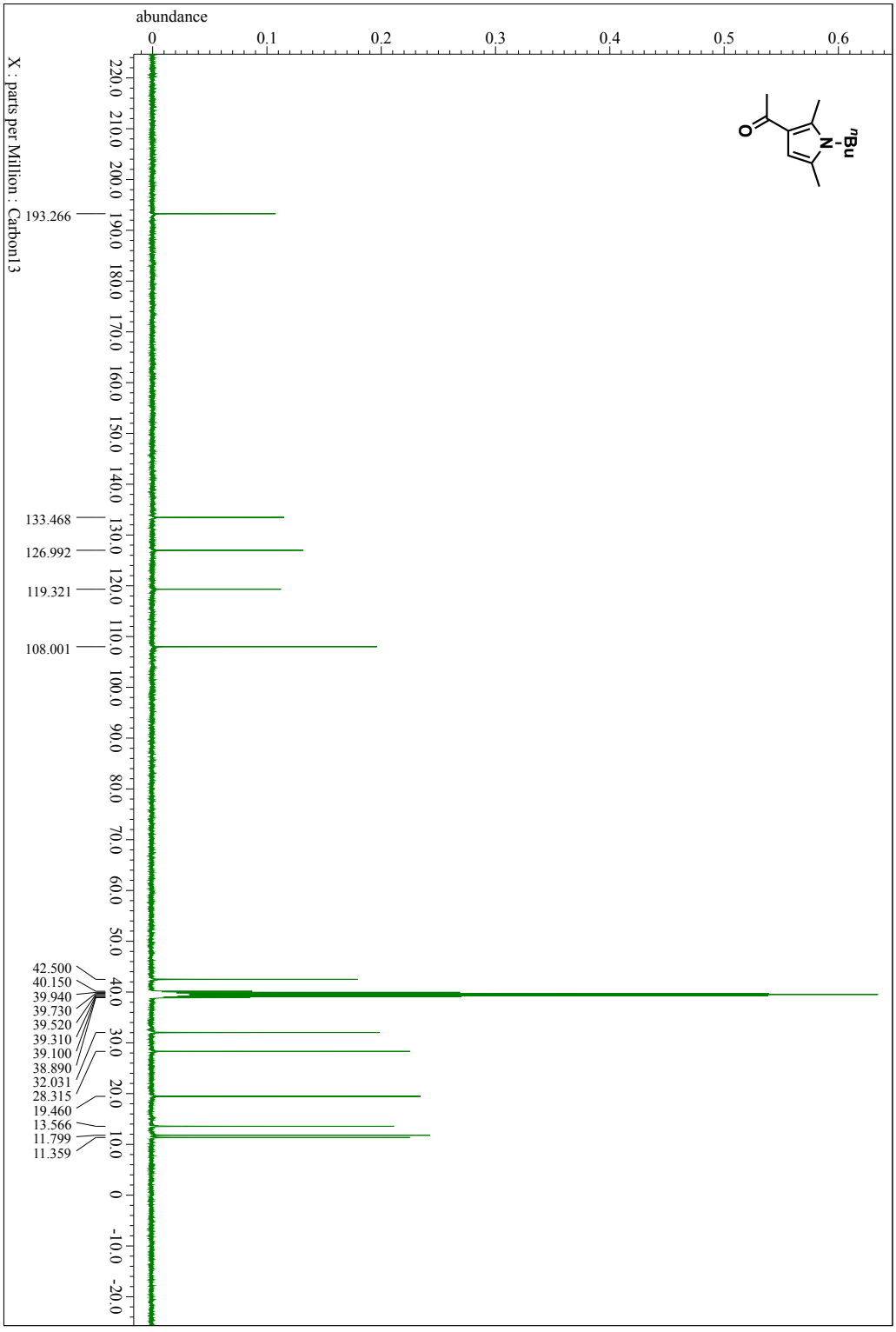


Fig. S31 $^{13}C\{^{1}H\}$ NMR spectrum of compound **7** (100 MHz, DMSO-d_6, 298 K).

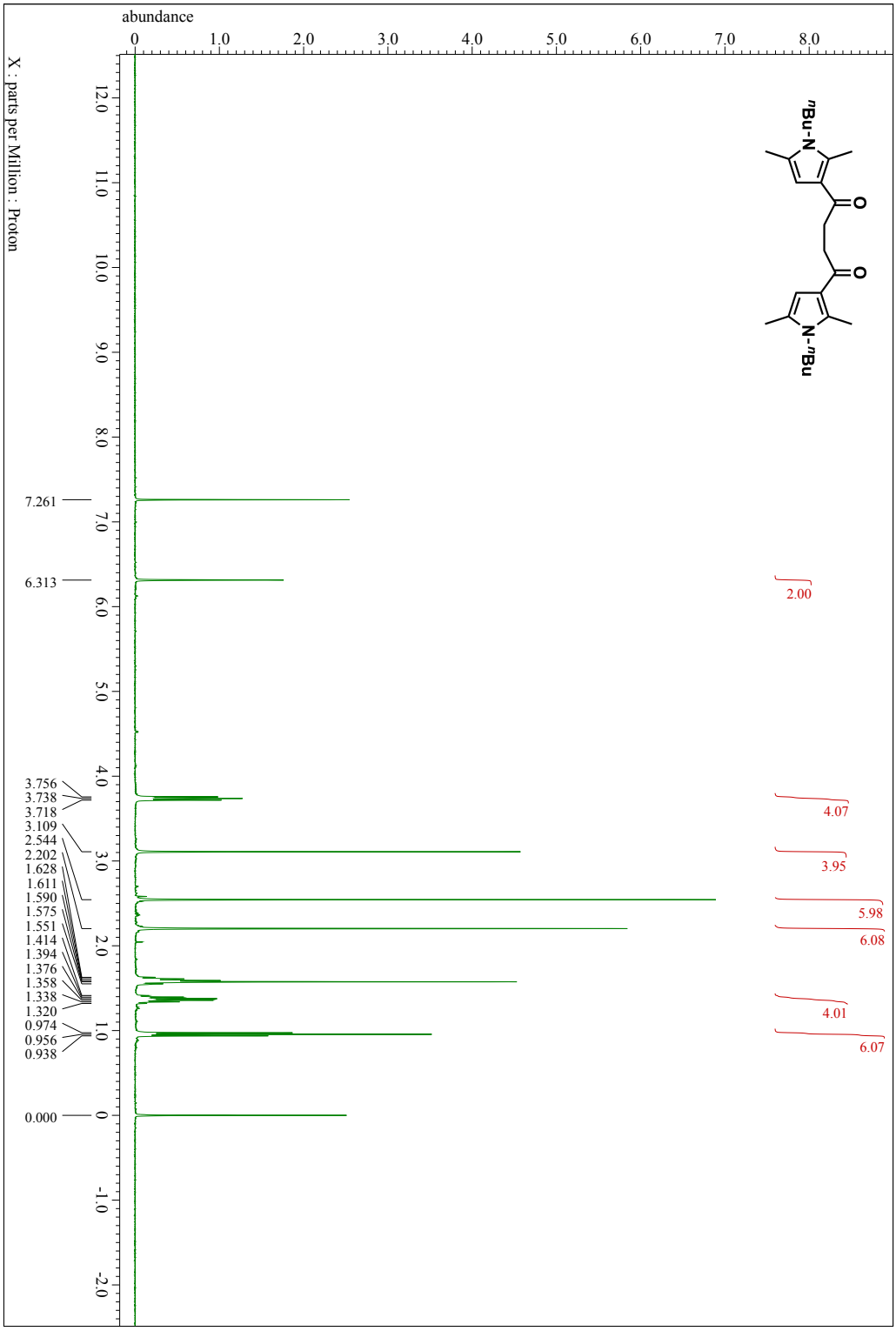


Fig. S32 ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$, 298 K).

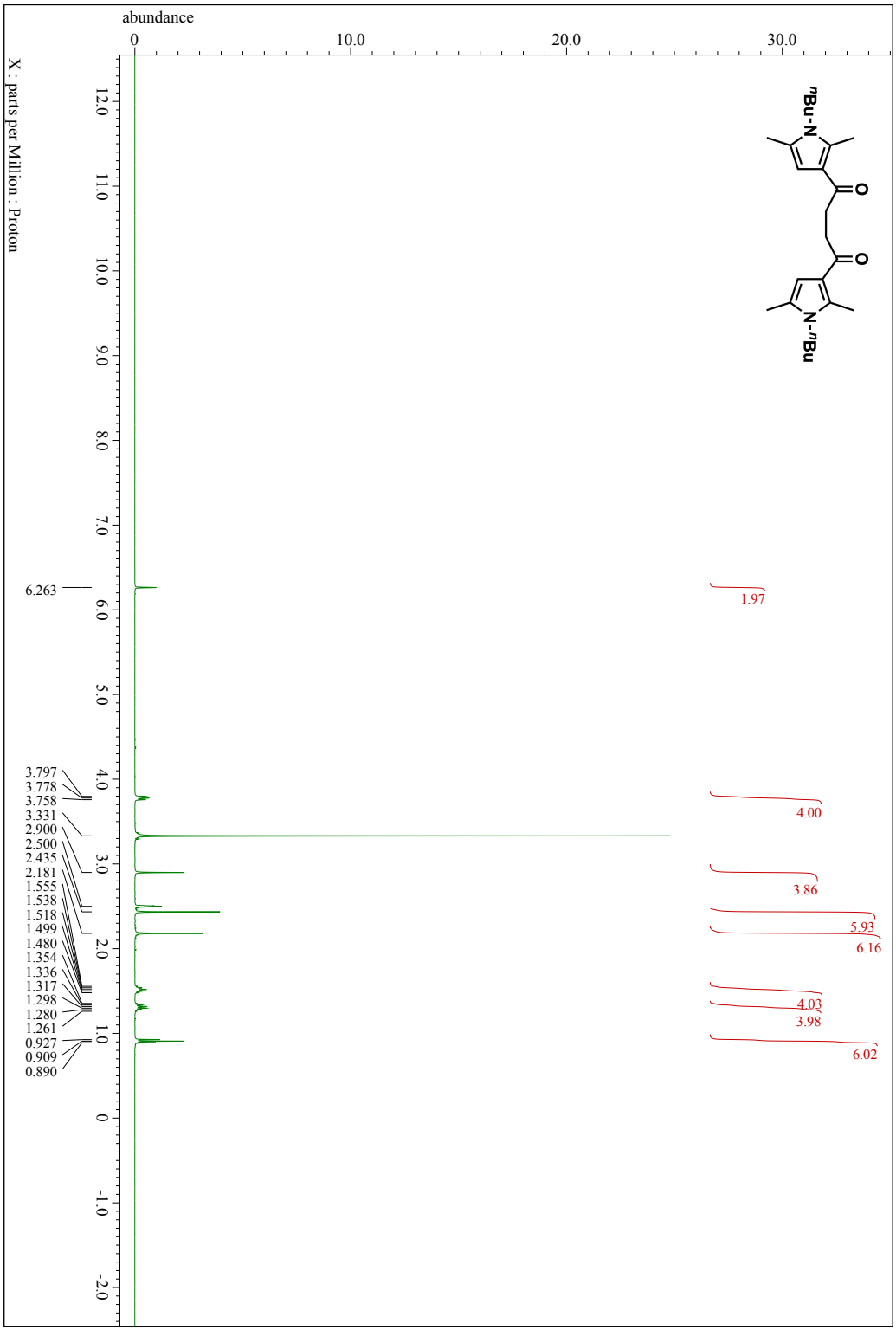


Fig. S33 ^{1}H NMR spectrum of compound **8** (400 MHz, DMSO-d_6, 298 K).

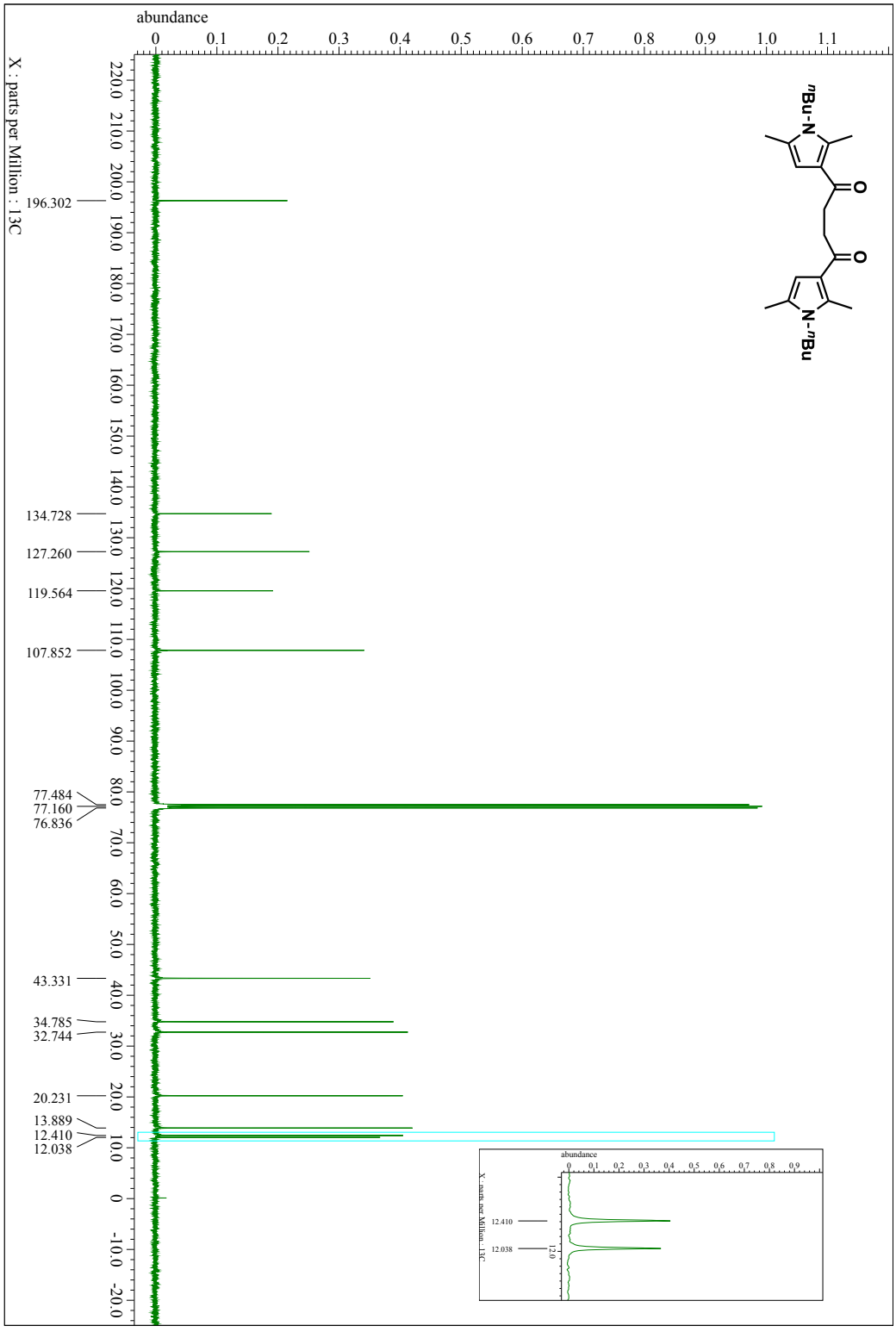


Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** (100 MHz, $CDCl_3$, 298 K).

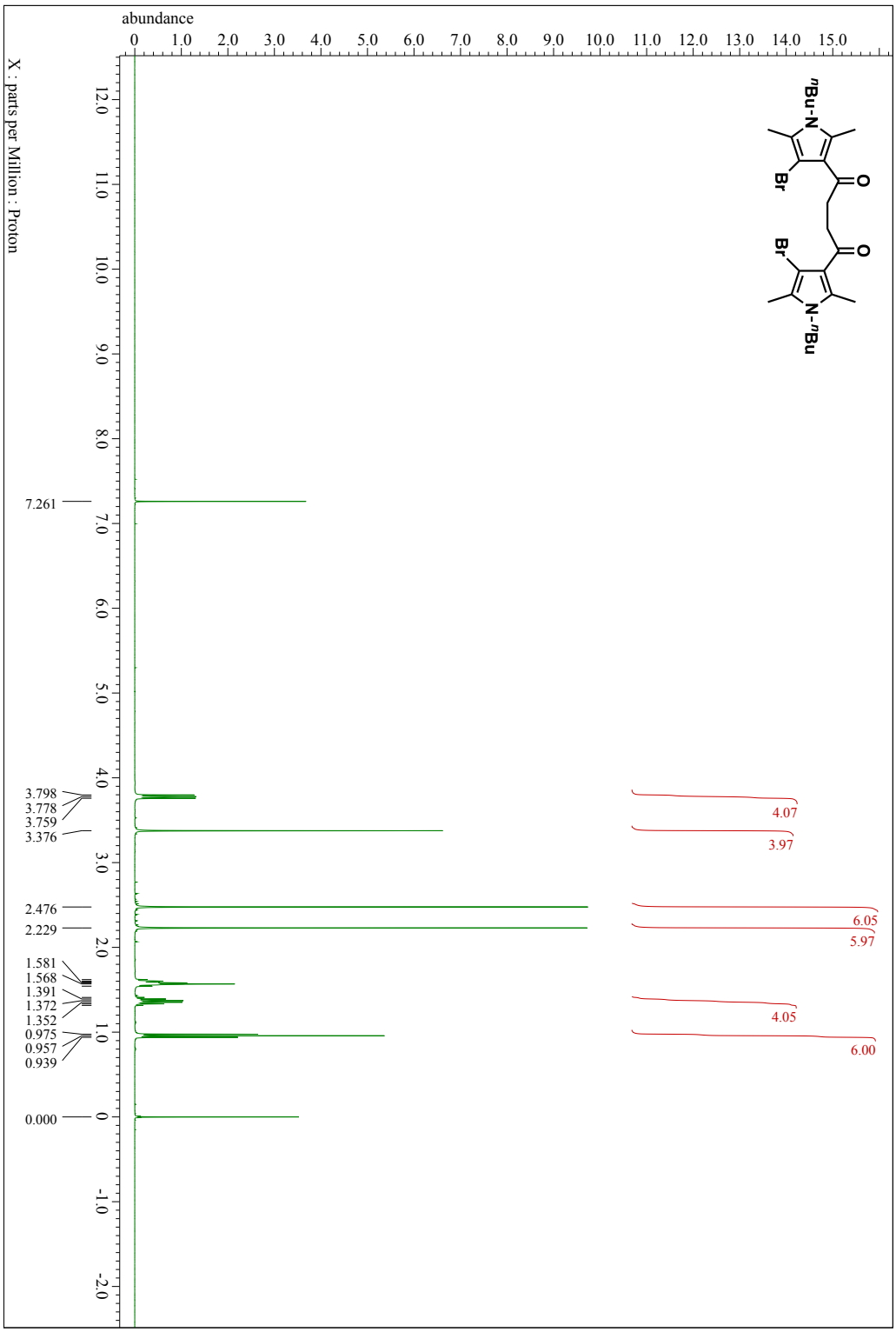


Fig. S35 ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$, 298 K).

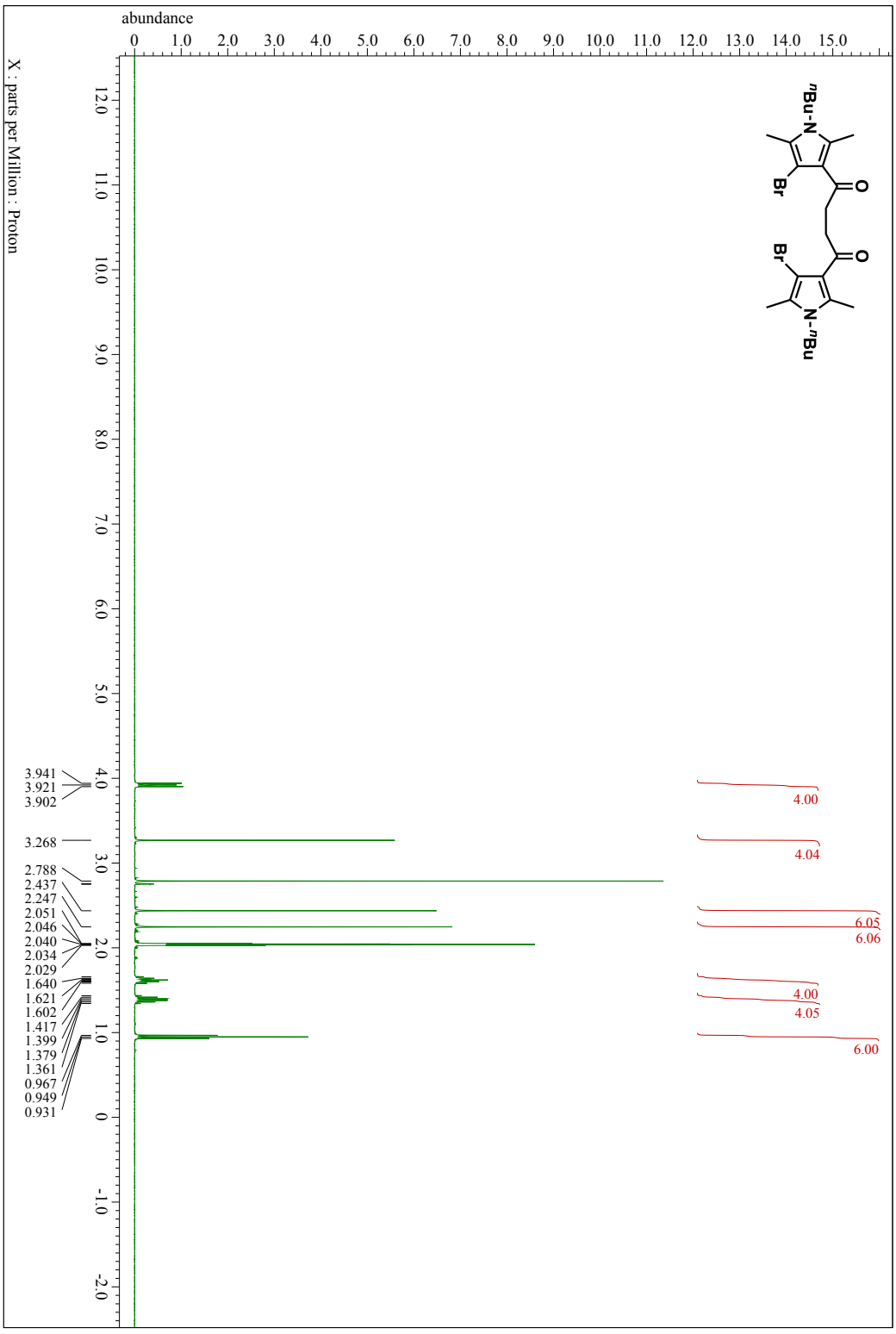


Fig. S36 ^{1}H NMR spectrum of compound **9** (400 MHz, acetone-d_6, 298 K).

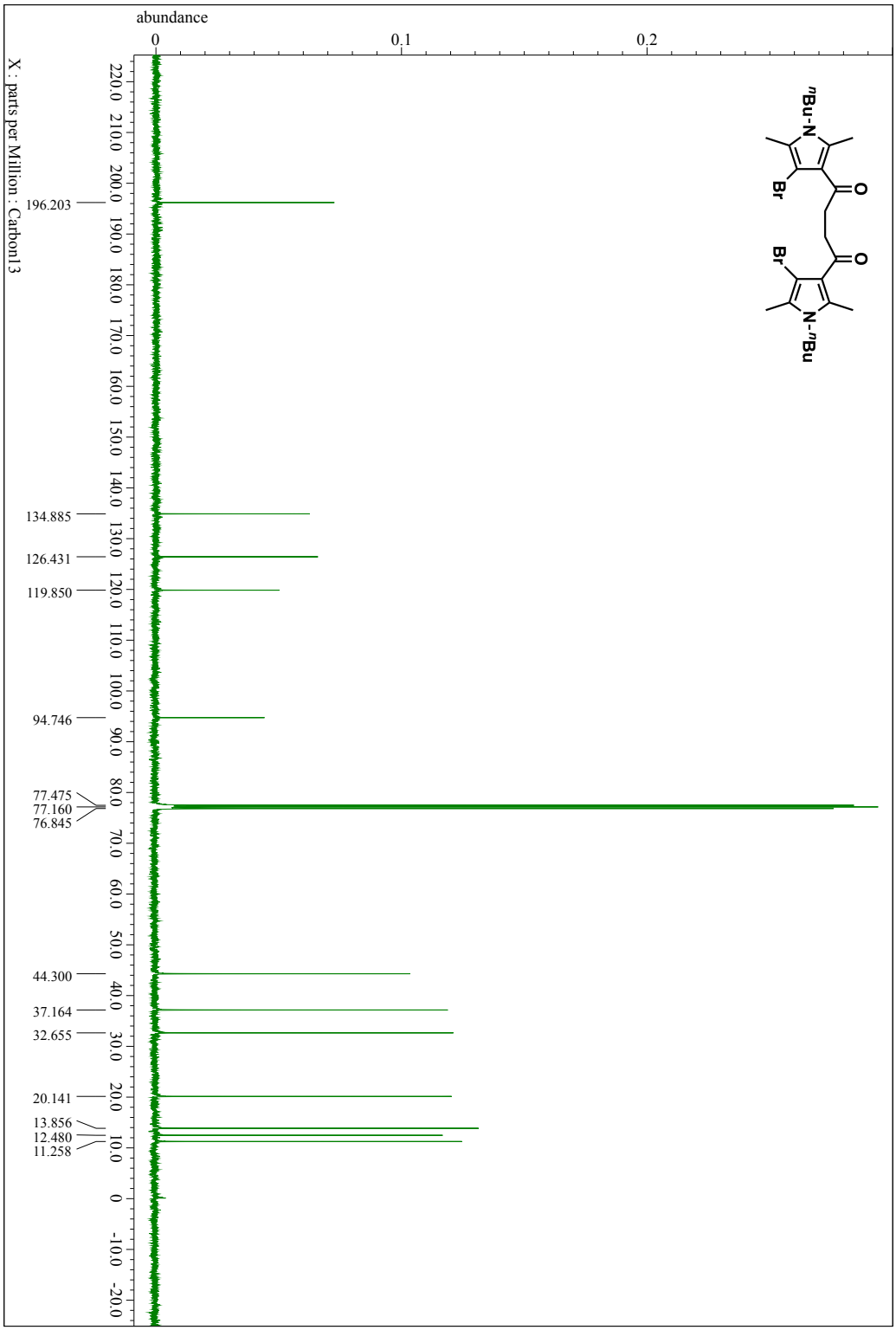


Fig. S37 $^{13}C\{^{1}H\}$ NMR spectrum of compound **9** (100 MHz, $CDCl_3$, 298 K).

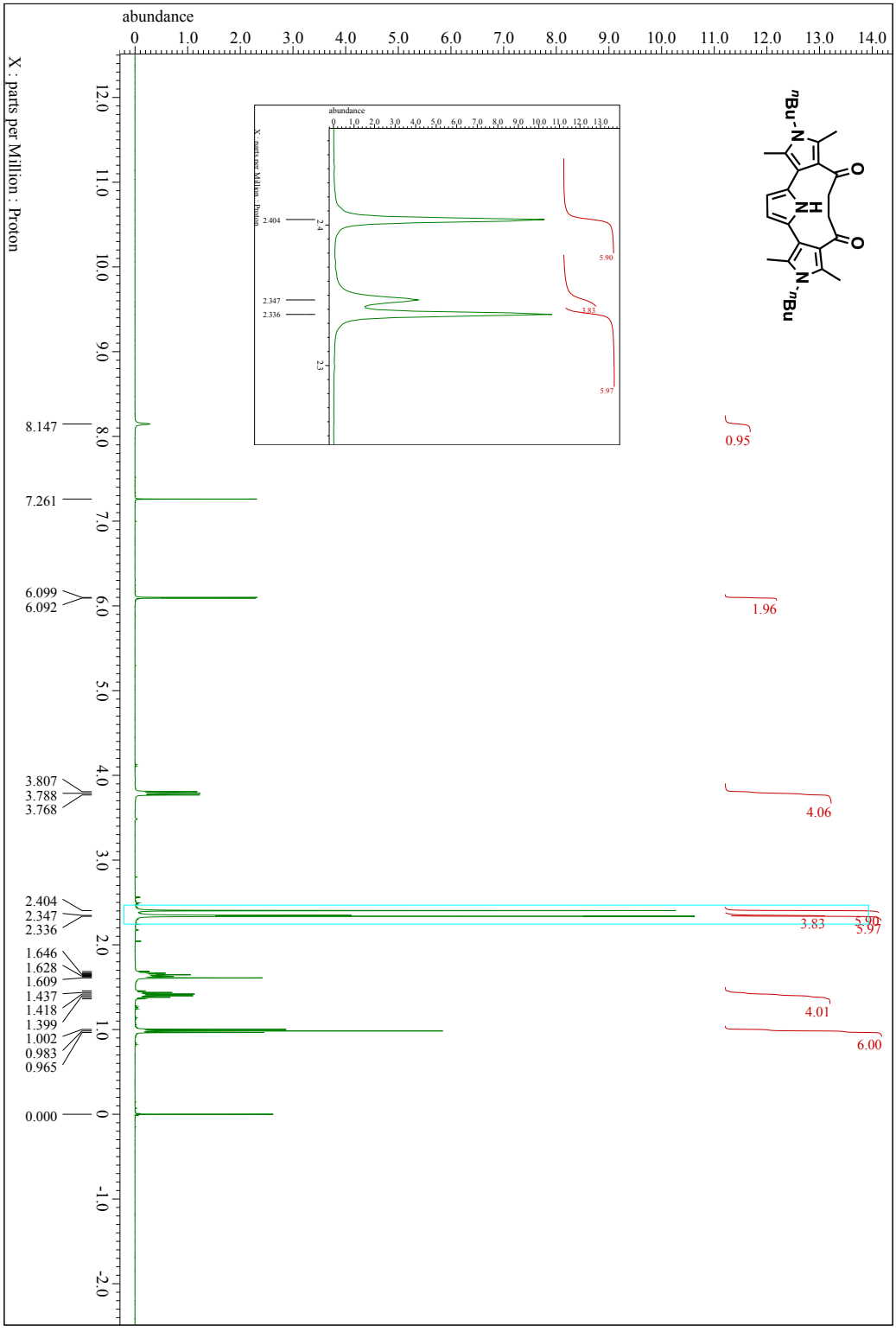


Fig. S38 ^{1}H NMR spectrum of compound **10** (400 MHz, $CDCl_3$, 298 K).

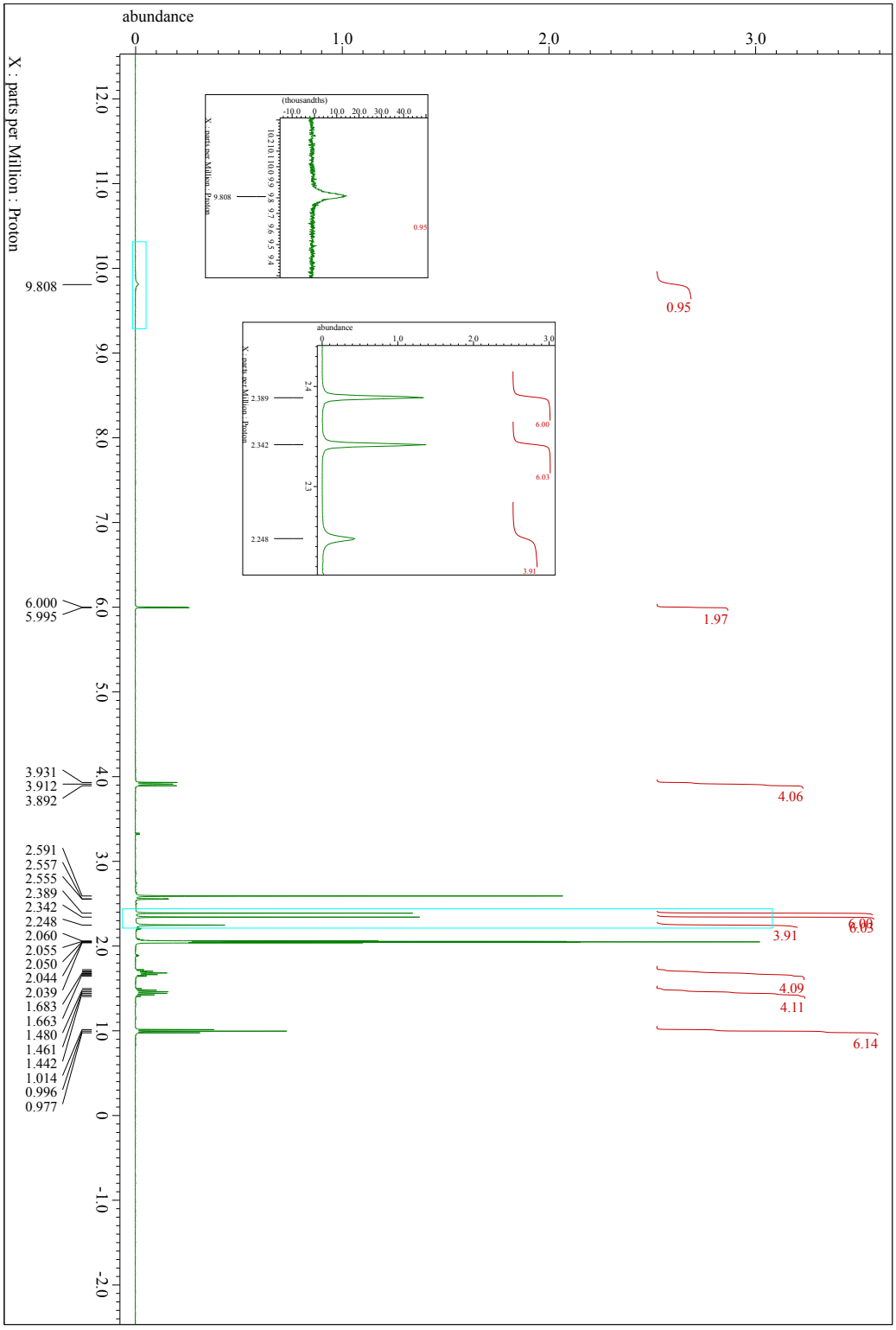


Fig. S39 ^{1}H NMR spectrum of compound **10** (400 MHz, acetone-d_6, 328 K).

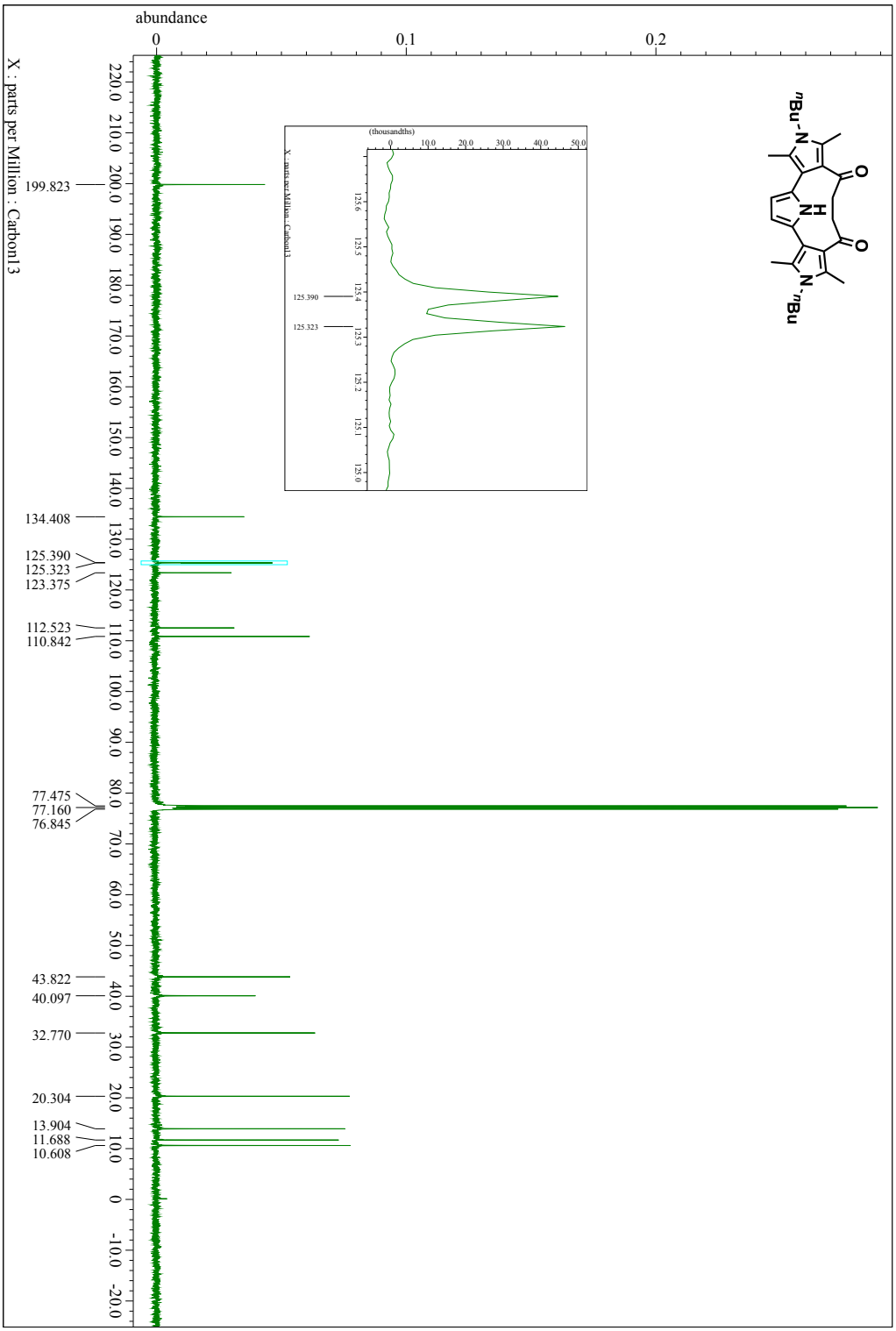


Fig. S40 $^{13}C\{^{1}H\}$ NMR spectrum of compound **10** (100 MHz, $CDCl_3$, 298 K).

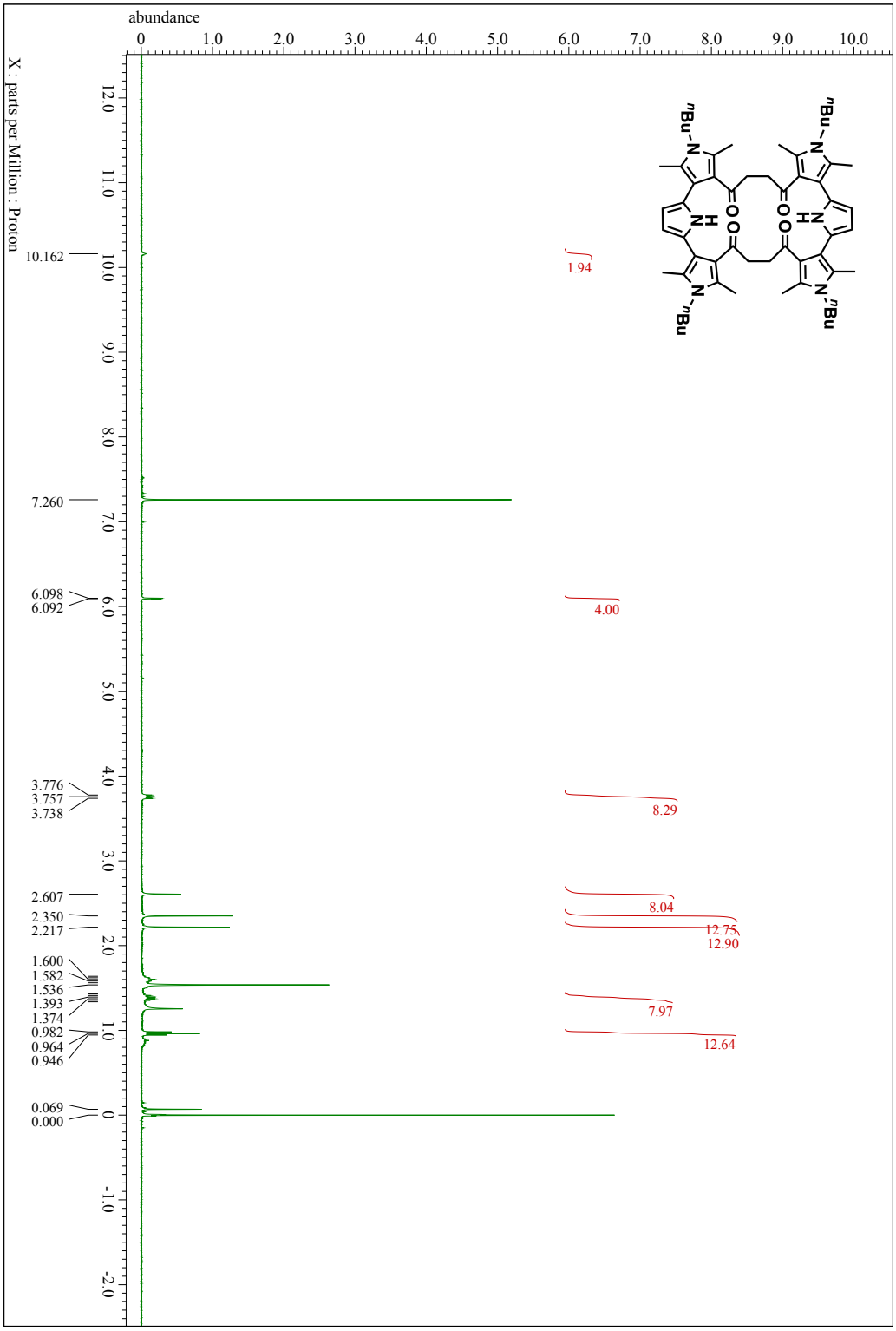


Fig. S41 ^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$, 298 K).

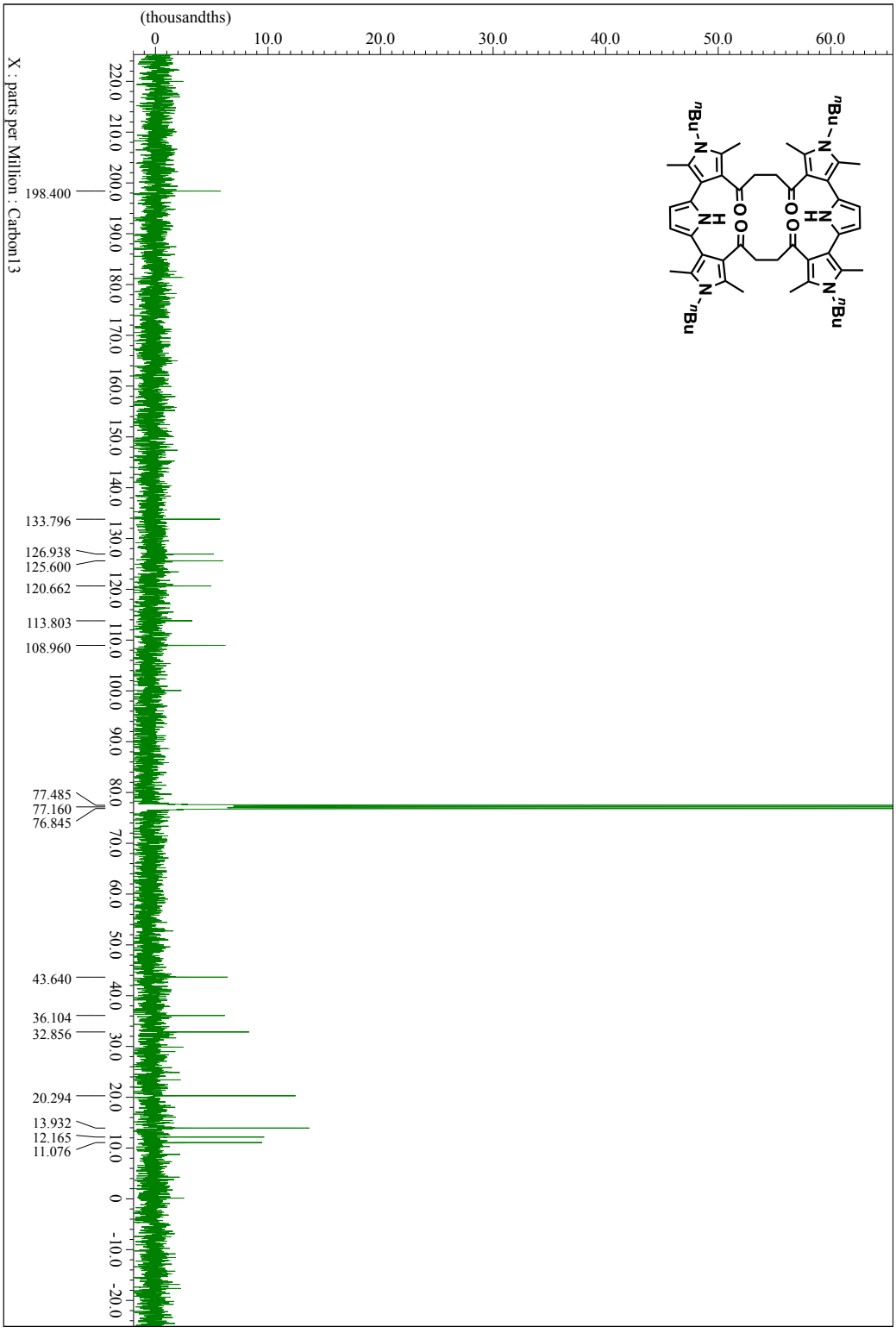


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum of compound **12** (100 MHz, $CDCl_3$, 298 K).

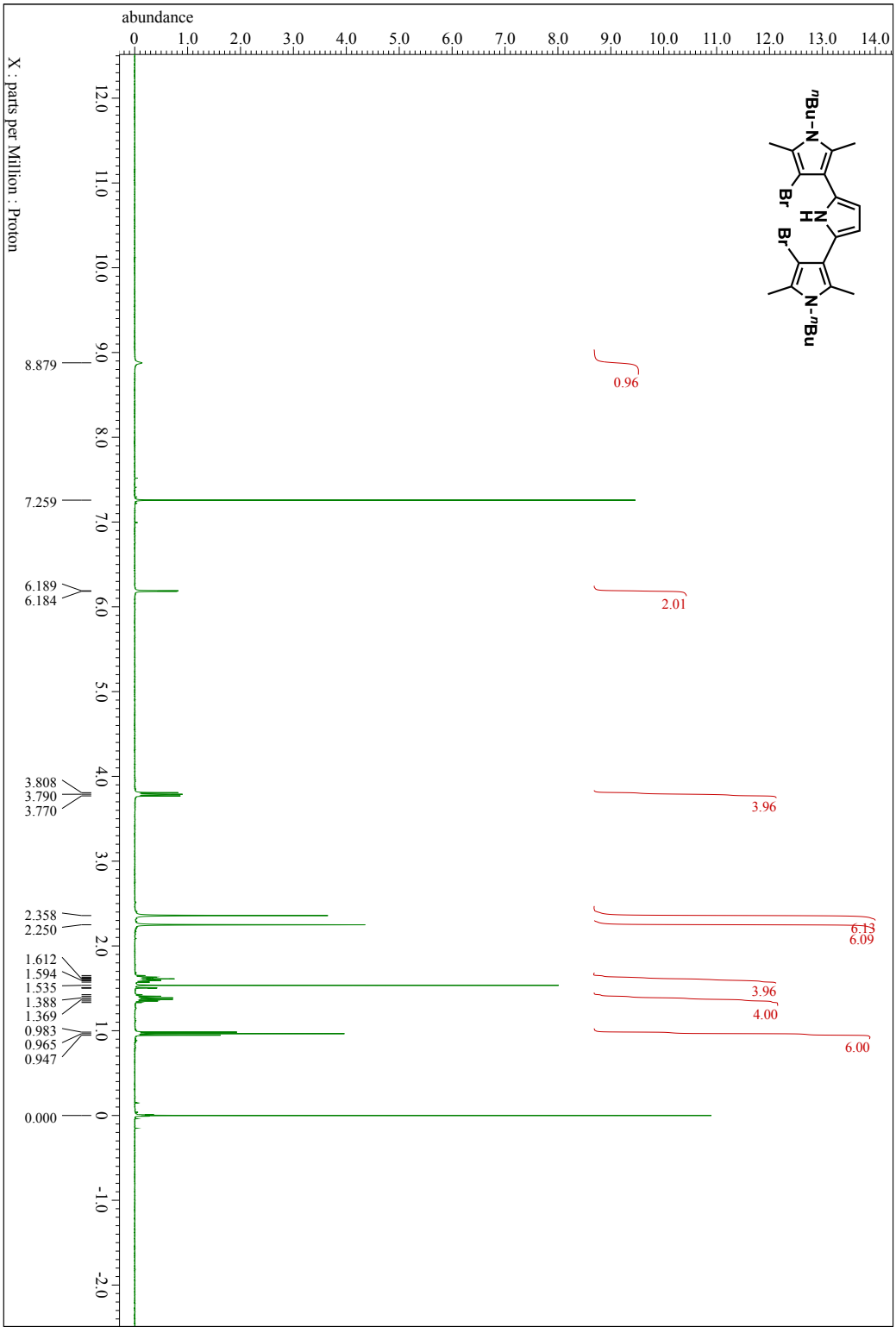


Fig. S43 ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$, 298 K).

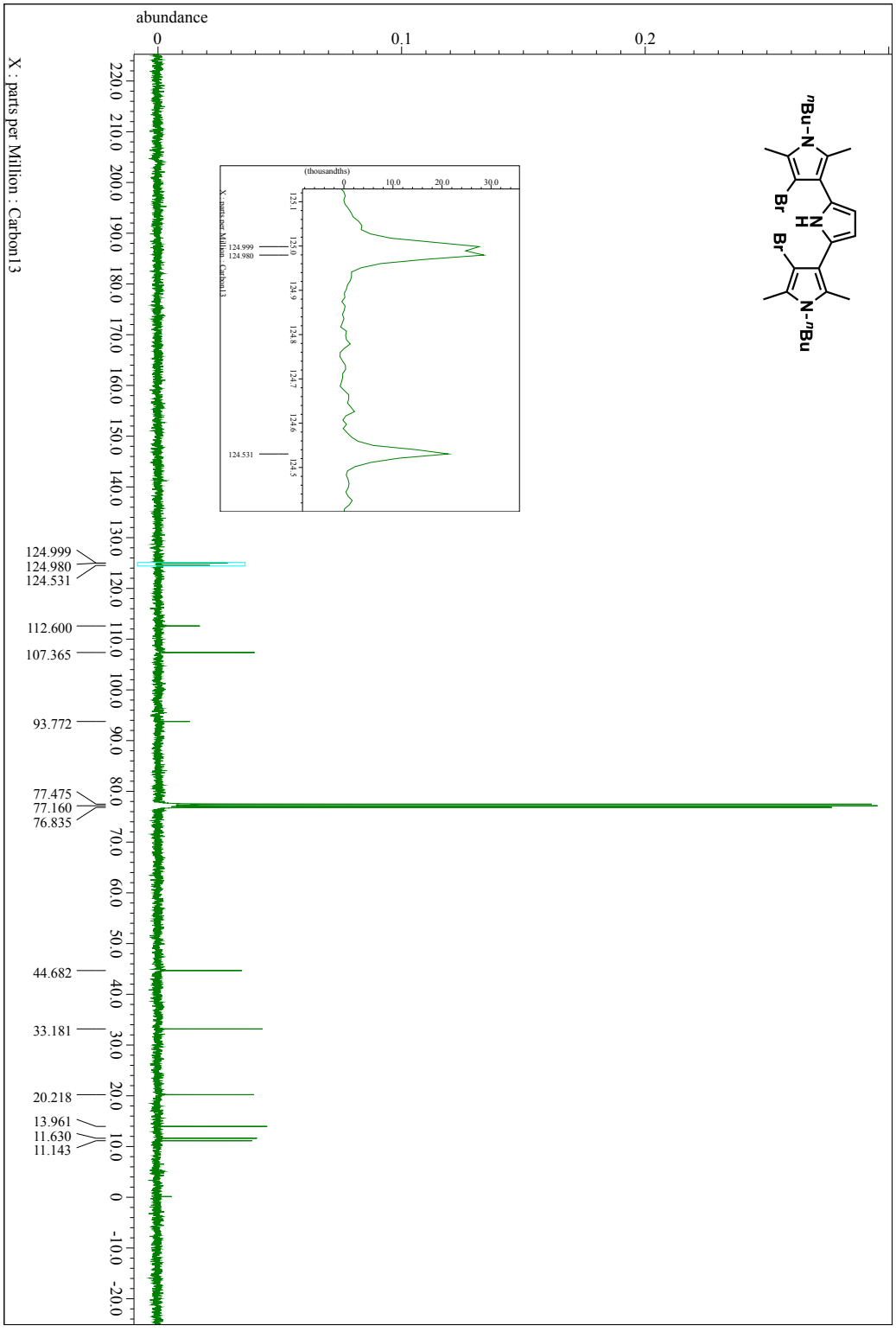


Fig. S44 $^{13}C\{^{1}H\}$ NMR spectrum of compound **11** (100 MHz, $CDCl_3$, 298 K).

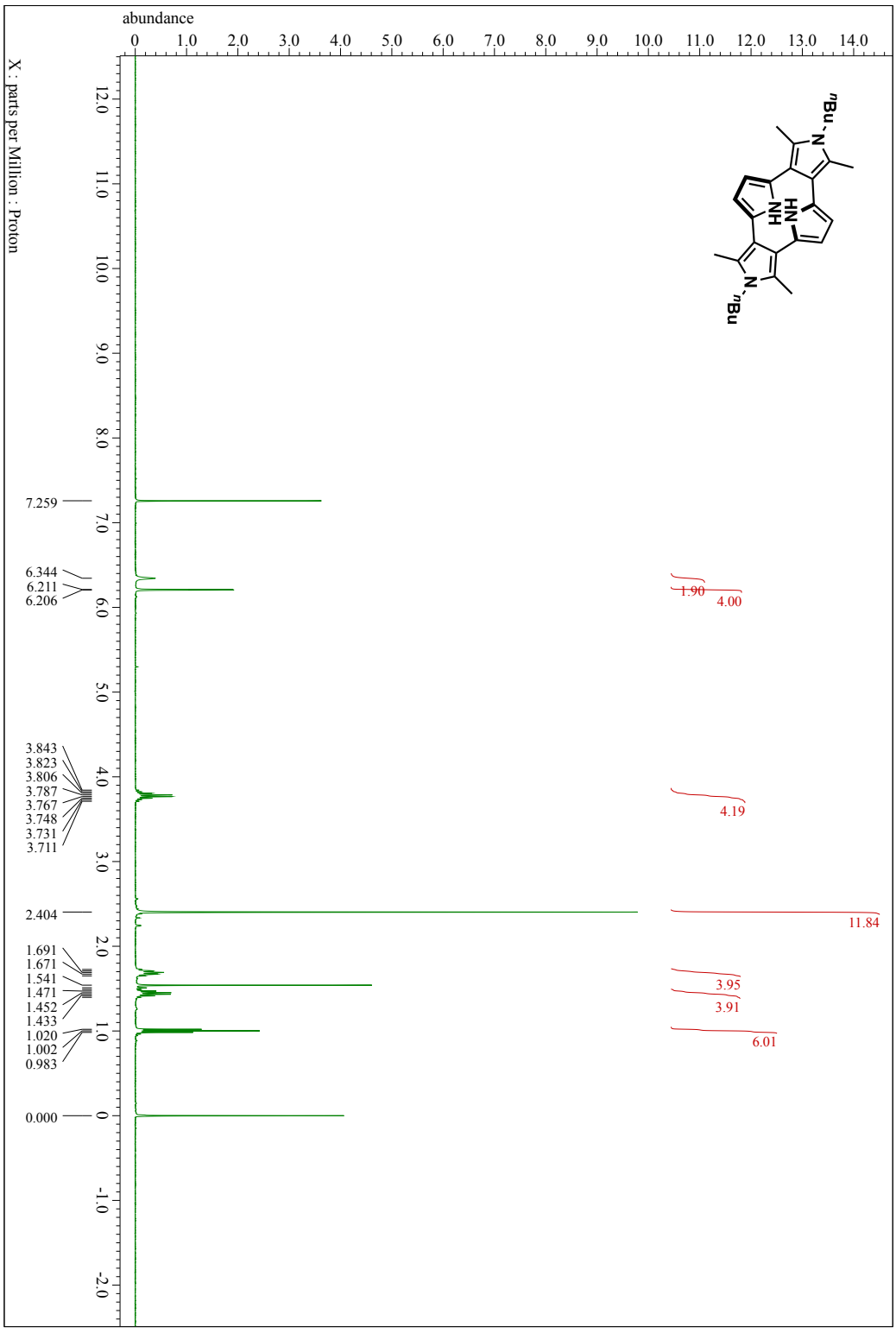


Fig. S45 ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$, 298 K).

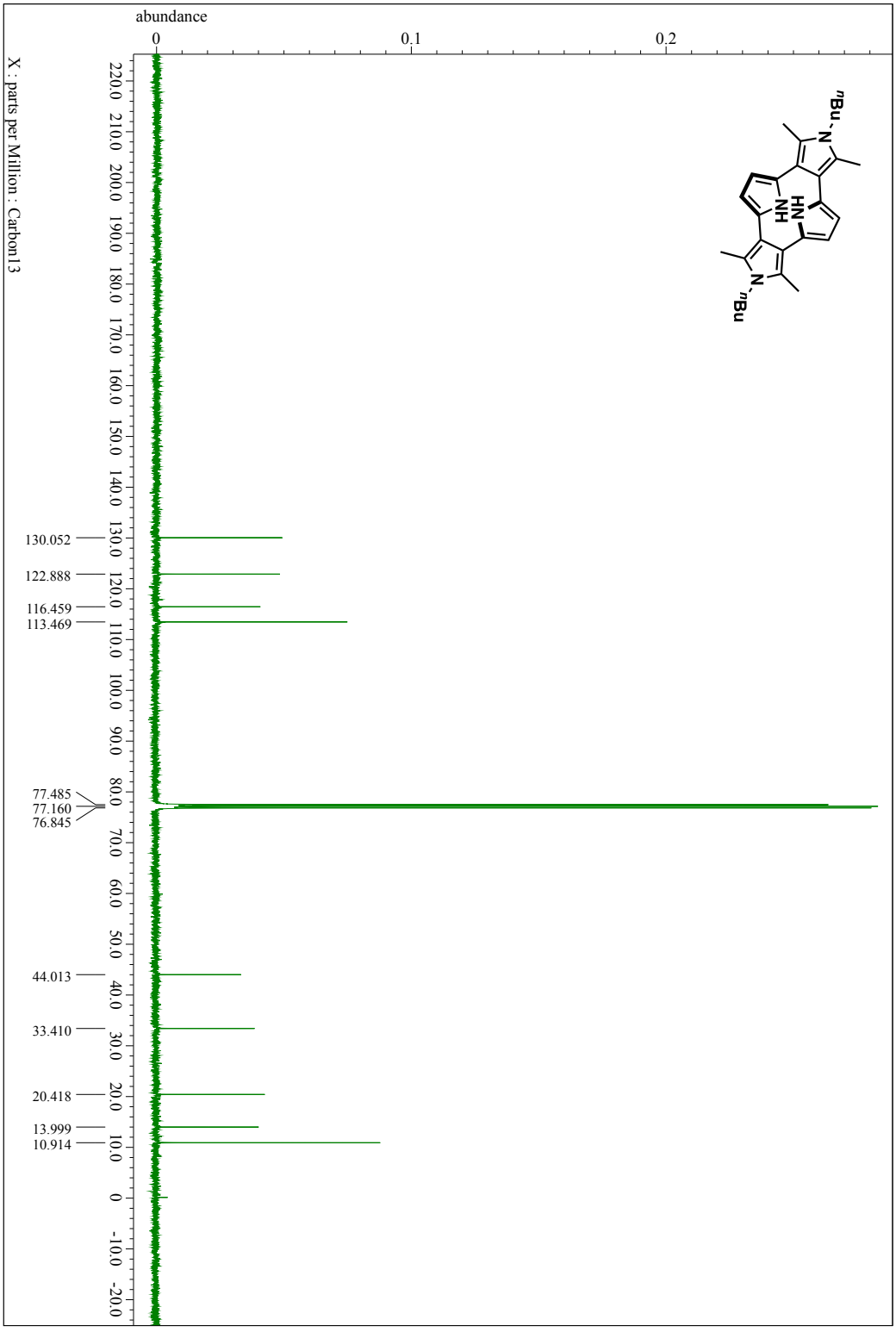


Fig. S46 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** (100 MHz, $CDCl_3$, 298 K).

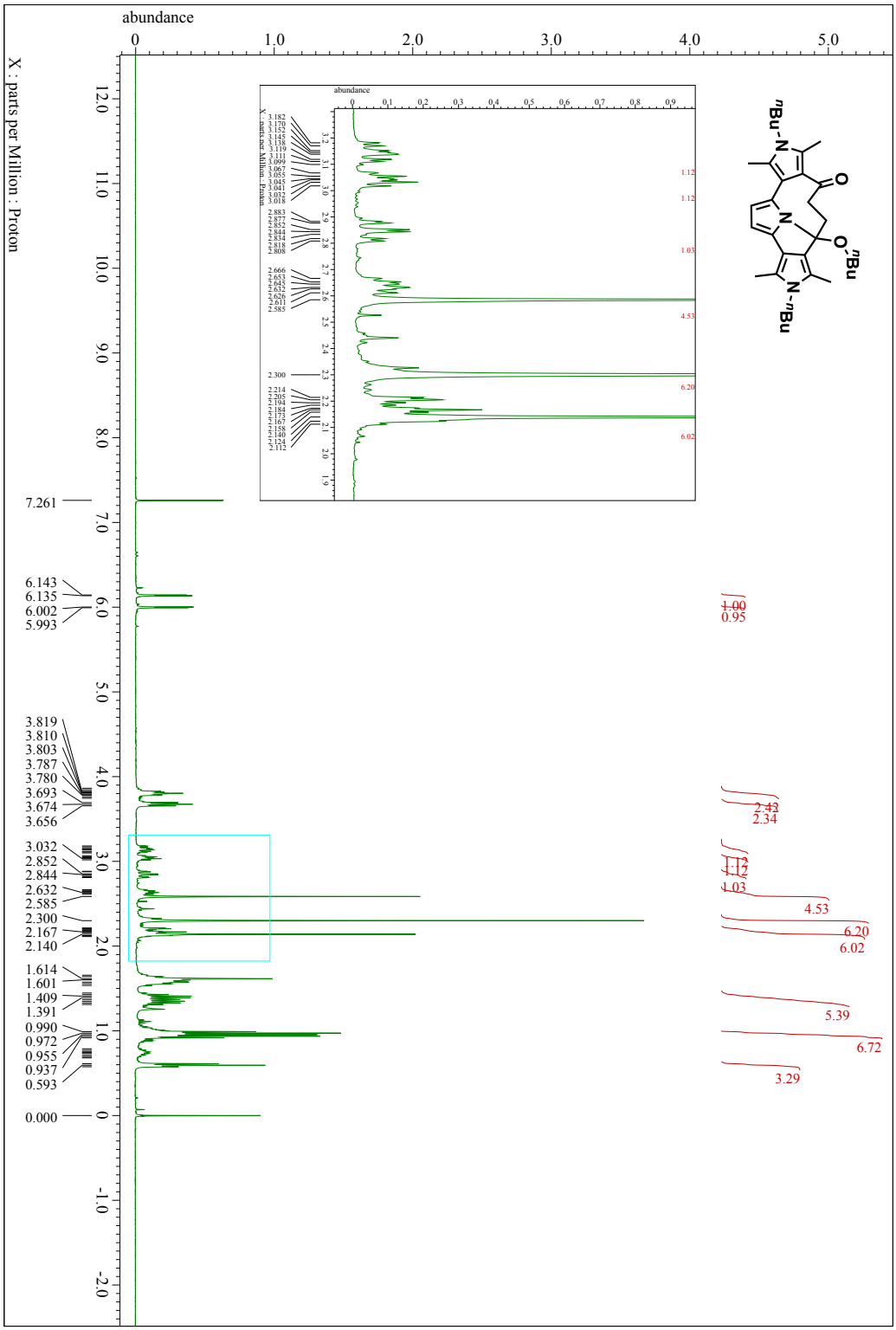


Fig. S47 ^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$, 298 K).

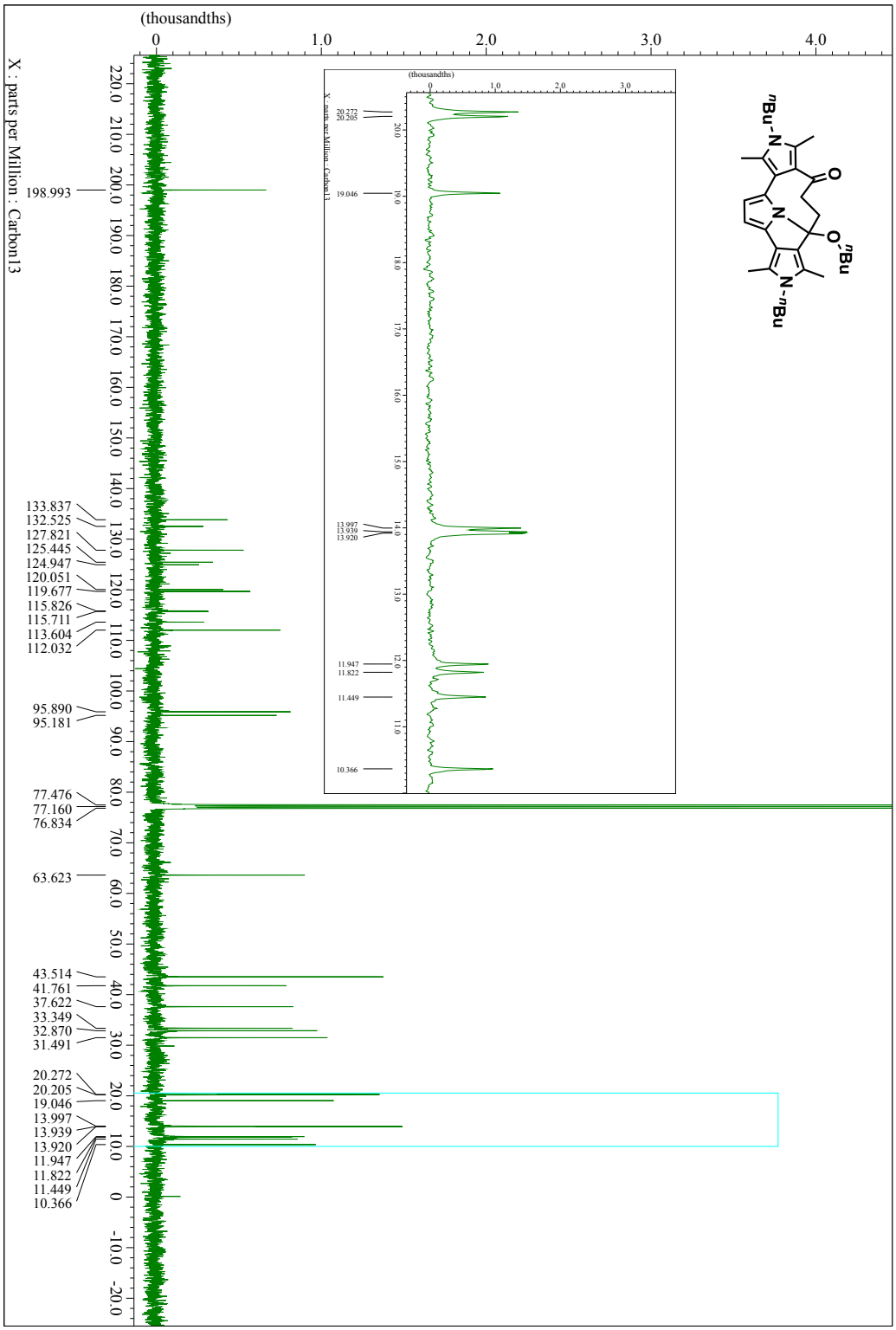


Fig. S48 $^{13}C\{^{1}H\}$ NMR spectrum of compound **13** (100 MHz, $CDCl_3$, 298 K).

11. Cartesian Coordinates for Optimized Structures

Coordinate and total energy of the lowest energy conformer of each compound shown in **Figs. S3**–**S6**.

compound **3**
68 atoms
E_{tot} = -1307.477985 hartree

C	9.640853135	6.106863752	2.496612626
C	14.087168412	4.265660126	2.727531661
C	10.909958596	5.900531967	2.972353407
C	11.100944942	6.808788222	4.086271620
C	9.933135198	7.510511829	4.239538839
C	11.993301221	5.071035059	2.429398798
C	13.975673465	4.673468193	1.411631499
C	12.662257441	5.179073705	1.224781772
C	7.758546955	7.677287436	3.007400755
C	7.861351832	8.865999930	2.053181956
C	8.931469740	5.438623346	1.368699197
C	9.575677757	8.544041776	5.252431181
C	6.518755611	9.549284826	1.801752351
C	5.496375867	8.647457292	1.112720593
C	16.732506378	4.924973668	5.182507944
C	12.286170291	6.766111617	4.951625228
C	15.463361580	5.131205647	4.706834659
C	15.272439405	4.223050639	3.592826230
C	16.440344952	3.521509592	3.439413256
C	14.379989577	5.960640892	5.249815486
C	12.397581587	6.358218509	6.267504479
C	13.710970553	5.852550600	6.454391039
C	18.615125260	3.355098049	4.671348316
C	18.512845082	2.165973587	5.625101634
C	17.441848469	5.593149346	6.310486249
C	16.797940259	2.488250023	2.426296317
C	19.856146155	1.484506592	5.877821255
C	20.875660666	2.386878981	6.570391381
N	12.838604774	4.404612261	3.282958179
N	9.048975184	7.074746188	3.277795914
N	13.534754395	6.627145643	4.396252676
N	17.324475270	3.957262103	4.401188516
H	12.671393660	4.338104214	4.278360103
H	14.789511806	4.709106460	0.704720805
H	12.278799024	5.675541455	0.347410072
H	7.318830491	7.994775363	3.956025879
H	7.106939452	6.906392953	2.595298252
H	8.286833443	8.520560972	1.105682195

H	8.574632802	9.581827453	2.470013868
H	8.027862708	4.923907354	1.705902032
H	9.596943553	4.696717995	0.928799219
H	8.640567757	6.142200552	0.583780208
H	10.465801728	8.787916019	5.831533588
H	8.808935810	8.188358192	5.946520742
H	9.206416546	9.463644024	4.791482547
H	6.111442474	9.909124550	2.752101879
H	6.689030498	10.435760407	1.186656462
H	5.910699337	8.225035999	0.193937926
H	4.597151345	9.204629601	0.848133607
H	5.189070773	7.818314476	1.751859117
H	13.702007261	6.693679107	3.400859771
H	11.583704573	6.322572105	6.974369912
H	14.094369642	5.356024668	7.331755776
H	19.054978468	3.038146405	3.722616421
H	19.266401894	4.126105203	5.083735017
H	18.085799073	2.510554920	6.572235322
H	17.800997527	1.449281332	5.207250310
H	18.345269634	6.108199656	5.973295423
H	16.776225350	6.334765662	6.750648255
H	17.733054522	4.889457281	7.095194131
H	15.907817422	2.244280551	1.847231932
H	17.564527024	2.844251324	1.732198170
H	17.167463592	1.568645815	2.887023201
H	20.265856612	1.127017556	4.927617034
H	19.686279120	0.596670587	6.491058925
H	20.459119304	2.806185361	7.489621142
H	21.775720531	1.831004896	6.834899199
H	21.182096234	3.218249134	5.933696546

compound **4**

36 atoms

E_{tot} = -879.933251 hartree

C	0.794872812	7.535137126	2.641712052
C	1.669335333	7.294321469	1.600795156
C	2.595212644	6.312953171	2.038119239
C	2.264603565	5.977386491	3.335919080
C	3.179395148	5.465138822	4.380997834
C	3.823257609	4.242833647	4.221461356
C	4.771613760	3.805446917	5.137611516
C	5.087633377	4.593279681	6.233451760
C	4.462135208	5.821652778	6.405720281
C	3.516919486	6.281418078	5.495168304
N	1.102525353	6.640947695	3.634423972
C	2.767556492	7.531462718	5.754056969
C	1.893093971	7.772278379	6.794973864
C	0.967216663	8.753646679	6.357649778
C	1.297825745	9.089213357	5.059849937
C	0.383034163	9.601461026	4.014771183
C	-0.260828290	10.823766206	4.174307657
C	-1.209184444	11.261152935	3.258157500
C	-1.525204073	10.473320164	2.162317264
C	-0.899705910	9.244947064	1.990048745
C	0.045509817	8.785181766	2.900600717
N	2.459903954	8.425652148	4.761345047
H	1.698488209	7.849256184	0.676727712
H	3.472859154	5.968609254	1.514817240
H	3.560532538	3.625711449	3.370742419
H	5.255829143	2.847622549	4.996054382
H	5.824884148	4.258556047	6.952007364
H	4.714989488	6.449277900	7.251720678
H	0.726021176	6.703621722	4.571475182
H	1.863941093	7.217343667	7.719041309
H	0.089570154	9.097990600	6.880951775
H	0.001896790	11.440888407	5.025026589
H	-1.693399820	12.218977307	3.399714630
H	-2.262454849	10.808043797	1.443761664
H	-1.152560199	8.617321939	1.144048354
H	2.836408132	8.362978120	3.824293838

compound **10**
70 atoms
E_{tot} = -1403.804178 hartree

C	6.501226286	6.373077891	11.430540817
C	5.447129605	6.381429558	12.318494571
C	4.332159845	6.967928395	11.663690102
C	4.730576496	7.303631751	10.388774351
C	3.972671130	7.607944228	9.179558597
C	3.185419914	8.701583236	8.945187035
C	2.918190369	9.882579048	9.813620726
C	1.700760949	9.499625740	7.092956478
C	0.259934424	9.119426959	7.418344913
C	-0.741644361	10.092347171	6.806769158
C	-2.183871608	9.718499816	7.131110369
C	3.106941911	7.428045662	7.086836054
C	2.678174748	7.023122028	5.716496457
C	3.936113223	6.783252233	7.995979855
C	4.564335487	5.477171453	7.720994087
C	5.110298343	4.595575836	8.843606423
C	6.635770785	4.451904889	8.662642667
C	7.324204409	3.694817815	9.790419827
C	8.099231071	4.436263461	10.813724560
C	9.303858199	3.990339076	11.321430868
C	10.084745585	2.763047308	10.990607024
C	11.006435239	4.882016729	12.945567225
C	12.040122786	5.818416794	12.319532597
C	12.427142869	5.454906623	10.890289505
C	13.397076909	6.466136092	10.288461008
C	8.798591594	5.913193450	12.380054738
C	8.909634167	6.986621303	13.408834700
C	7.784304603	5.669180527	11.490943762
N	6.057756896	6.986217989	10.290500608
N	2.664969600	8.578639311	7.671047966
N	9.726117622	4.900130015	12.255473421
O	4.660541590	5.064062364	6.578944544
O	7.287932205	2.481511036	9.793149717
H	5.469888488	5.945212491	13.304254821
H	3.325419556	7.053671325	12.039938327
H	6.609479995	7.129100343	9.461244680
H	3.453045364	9.750703267	10.753288066
H	1.855600028	9.997931835	10.041960736
H	3.264273716	10.812067656	9.353844488
H	1.855254145	9.529172668	6.013520321
H	1.919279531	10.499343720	7.471925995
H	0.136775330	9.087956073	8.505344964
H	0.066231682	8.104734611	7.057182002

H	-0.531913211	11.103497945	7.169533365
H	-0.602767151	10.119234337	5.721419461
H	-2.420618880	8.721757523	6.753797219
H	-2.887900839	10.422077768	6.686001298
H	-2.350408275	9.713208157	8.210117760
H	1.660011710	7.350077491	5.502498711
H	2.736652786	5.942575258	5.620131534
H	3.341966387	7.444846499	4.957100034
H	4.662518819	3.609286438	8.707065524
H	4.842290070	4.953438999	9.835147687
H	6.807961560	3.876282762	7.752428814
H	7.110056013	5.422991779	8.524023029
H	11.115522325	2.995654790	10.719610570
H	9.606470431	2.245068984	10.163932858
H	10.103477438	2.073014362	11.838332633
H	11.373959676	3.855266762	12.942931694
H	10.832302071	5.160363162	13.986611764
H	11.653326217	6.841276963	12.335860980
H	12.931459120	5.811924962	12.954917534
H	11.524665547	5.396225571	10.274254570
H	12.882843592	4.459940774	10.880602219
H	12.949485859	7.461673160	10.258657383
H	13.675527093	6.193707640	9.270152175
H	14.312123619	6.530515026	10.881233212
H	8.053576685	7.652707636	13.310292297
H	9.819361356	7.580471838	13.300936574
H	8.899825251	6.574747643	14.421650969

Coordinate and total energy of the lowest energy conformer of each compound shown in **Figure S15**–**S18**.

Macrocycle **3**

68 atoms

E_{tot} = -1307.981311 hartree

C	-1.060179000	-1.595921000	0.0301230
C	-0.494079000	-2.539439000	-0.8210040
C	0.917584000	-2.459556000	-0.6887790
C	-1.207437000	1.467883000	-0.2426150
C	-2.377787000	0.584386000	-0.3482940
C	-2.321089000	-0.849931000	-0.0902530
C	-3.613676000	-1.324956000	-0.1538190
C	-3.702375000	0.908695000	-0.5501390

C	-4.111406000	-2.723426000	0.0171170
C	-4.305470000	2.235829000	-0.8774670
C	-5.903137000	-0.327992000	-0.5110000
C	-6.597681000	-0.116548000	0.8441300
C	-8.842720000	0.822952000	-0.0227980
H	0.112062000	0.249609000	-1.3440970
H	-1.037052000	-3.133117000	-1.5407370
H	1.647433000	-2.981476000	-1.2889900
H	-4.876547000	2.211460000	-1.8126220
H	-3.504847000	2.966405000	-0.9985350
H	-4.976725000	2.605141000	-0.0937110
H	-3.278102000	-3.360403000	0.3162740
H	-4.527567000	-3.137362000	-0.9093350
H	-4.885780000	-2.802989000	0.7876250
H	-6.175131000	-1.306232000	-0.9159840
H	-6.241643000	0.414346000	-1.2356240
H	-8.562999000	0.805889000	-1.0796780
N	-0.010485000	-1.056501000	0.7467450
N	-4.449197000	-0.254642000	-0.4362870
H	-8.608602000	1.818833000	0.3664030
C	-8.125455000	-0.265771000	0.7844510
H	-6.336774000	0.875426000	1.2293870
H	-6.189627000	-0.839134000	1.5576830
H	-8.377322000	-1.251975000	0.3748680
H	-8.511384000	-0.259541000	1.8090870
H	-9.927265000	0.695401000	0.0267640
C	8.125448000	0.265771000	-0.7844840
H	6.336757000	-0.875414000	-1.2294110
H	6.189617000	0.839150000	-1.5576900
H	8.377323000	1.251975000	-0.3749060
H	8.511363000	0.259538000	-1.8091250
H	9.927265000	-0.695399000	-0.0268160
H	8.608601000	-1.818833000	-0.3664400
C	1.060180000	1.595919000	-0.0301160
C	0.494078000	2.539438000	0.8210110
C	-0.917584000	2.459563000	0.6887750

C	1.207439000	-1.467884000	0.2426190
C	2.377789000	-0.584388000	0.3483030
C	2.321090000	0.849930000	0.0902630
C	3.613675000	1.324958000	0.1538400
C	3.702377000	-0.908697000	0.5501420
C	4.111405000	2.723429000	-0.0170810
C	4.305472000	-2.235830000	0.8774780
C	5.903141000	0.327987000	0.5109910
C	6.597673000	0.116554000	-0.8441470
C	8.842721000	-0.822952000	0.0227580
H	-0.112059000	-0.249608000	1.3441000
H	1.037051000	3.133113000	1.5407470
H	-1.647435000	2.981489000	1.2889780
H	4.876519000	-2.211463000	1.8126520
H	3.504850000	-2.966412000	0.9985150
H	4.976755000	-2.605131000	0.0937410
H	3.278103000	3.360408000	-0.3162380
H	4.527560000	3.137359000	0.9093770
H	4.885784000	2.802998000	-0.7875830
H	6.175137000	1.306223000	0.9159830
H	6.241650000	-0.414359000	1.2356060
H	8.563011000	-0.805889000	1.0796400
N	0.010487000	1.056497000	-0.7467370
N	4.449199000	0.254640000	0.4362880

Macrocycle **3**$^{\bullet+}$

68 atoms

E_{tot} = -1307.776599 hartree

C	1.060000000	-1.703000000	0.3330000
C	0.492000000	-2.454000000	1.3560000
C	-0.920000000	-2.374000000	1.2280000
C	1.199000000	1.356000000	0.6390000
C	2.356000000	0.515000000	0.5530000
C	2.316000000	-0.933000000	0.3320000
C	3.612000000	-1.351000000	0.1920000
C	3.709000000	0.892000000	0.5300000

C	4.135000000	-2.726000000	-0.0550000
C	4.316000000	2.237000000	0.7570000
C	5.910000000	-0.275000000	0.2040000
C	6.402000000	-0.067000000	-1.2360000
C	8.718000000	0.930000000	-0.6720000
H	-0.099000000	-0.071000000	1.4860000
H	1.036000000	-2.917000000	2.1640000
H	-1.649000000	-2.766000000	1.9200000
H	5.040000000	2.215000000	1.5770000
H	3.546000000	2.957000000	1.0280000
H	4.837000000	2.609000000	-0.1300000
H	3.295000000	-3.407000000	-0.1940000
H	4.727000000	-3.096000000	0.7880000
H	4.763000000	-2.776000000	-0.9490000
H	6.246000000	-1.242000000	0.5820000
H	6.320000000	0.484000000	0.8710000
H	8.592000000	0.908000000	0.4150000
N	0.009000000	-1.284000000	-0.4610000
N	4.447000000	-0.234000000	0.3260000
H	8.411000000	1.919000000	-1.0260000
C	7.928000000	-0.179000000	-1.3750000
H	6.070000000	0.915000000	-1.5930000
H	5.922000000	-0.809000000	-1.8810000
H	8.255000000	-1.158000000	-1.0050000
H	8.169000000	-0.167000000	-2.4420000
H	9.787000000	0.828000000	-0.8710000
C	-8.167000000	0.360000000	0.1520000
H	-6.485000000	-0.798000000	0.8800000
H	-6.364000000	0.919000000	1.2100000
H	-8.340000000	1.348000000	-0.2920000
H	-8.699000000	0.364000000	1.1080000
H	-9.842000000	-0.583000000	-0.8610000
H	-8.608000000	-1.722000000	-0.3260000
C	-1.057000000	1.483000000	0.4340000
C	-0.495000000	2.681000000	-0.1110000
C	0.880000000	2.603000000	0.0140000

C	-1.207000000	-1.576000000	0.1270000
C	-2.349000000	-0.670000000	-0.0900000
C	-2.266000000	0.775000000	0.1340000
C	-3.539000000	1.303000000	-0.1420000
C	-3.634000000	-0.941000000	-0.4790000
C	-4.015000000	2.715000000	-0.0560000
C	-4.240000000	-2.242000000	-0.8830000
C	-5.782000000	0.377000000	-0.7910000
C	-6.668000000	0.192000000	0.4500000
C	-8.765000000	-0.725000000	-0.7500000
H	0.115000000	-0.633000000	-1.2240000
H	-1.044000000	3.439000000	-0.6460000
H	1.598000000	3.290000000	-0.4060000
H	-4.618000000	-2.215000000	-1.9100000
H	-3.481000000	-3.022000000	-0.8270000
H	-5.070000000	-2.534000000	-0.2330000
H	-3.257000000	3.340000000	0.4160000
H	-4.228000000	3.131000000	-1.0470000
H	-4.927000000	2.802000000	0.5400000
H	-5.957000000	1.356000000	-1.2400000
H	-6.017000000	-0.366000000	-1.5530000
H	-8.335000000	-0.717000000	-1.7550000
N	-0.006000000	0.818000000	1.0110000
N	-4.347000000	0.265000000	-0.4960000

Macrocycle $\mathbf{3}^{2+}$ (closed shell, singlet)

68 atoms

E_{tot} = -1307.441161 hartree

C	1.056524000	-1.760222000	0.4574100
C	0.492133000	-2.454262000	1.5214080
C	-0.920035000	-2.374929000	1.3954490
C	1.190751000	1.281412000	0.8011670
C	2.321391000	0.482446000	0.6234470
C	2.306482000	-0.978314000	0.4219150
C	3.591946000	-1.361417000	0.2040020
C	3.698388000	0.896936000	0.5092030

C	4.146716000	-2.712275000	-0.0726120
C	4.291842000	2.249854000	0.6961040
C	5.887037000	-0.230203000	0.0863370
C	6.291257000	-0.041215000	-1.3852610
C	8.622882000	0.981731000	-0.9348690
H	-0.097071000	-0.203814000	1.5649660
H	1.035052000	-2.885154000	2.3484860
H	-1.644939000	-2.734568000	2.1093420
H	5.064106000	2.230877000	1.4707550
H	3.541429000	2.971037000	1.0099150
H	4.763150000	2.609242000	-0.2234250
H	3.326879000	-3.422702000	-0.1764920
H	4.786142000	-3.058563000	0.7459550
H	4.739680000	-2.734202000	-0.9903300
H	6.242293000	-1.188852000	0.4638910
H	6.318876000	0.545991000	0.7167720
H	8.564637000	0.958174000	0.1574510
N	0.006308000	-1.365776000	-0.3499920
N	4.421745000	-0.199010000	0.2838640
H	8.288160000	1.967166000	-1.2733220
C	7.812337000	-0.138706000	-1.5940730
H	5.932255000	0.931911000	-1.7383340
H	5.790382000	-0.800486000	-1.9933270
H	8.165300000	-1.114154000	-1.2408580
H	7.993894000	-0.127657000	-2.6722910
H	9.678949000	0.890948000	-1.1948780
C	-8.135799000	0.399368000	-0.0837410
H	-6.496074000	-0.747659000	0.7513170
H	-6.399234000	0.974677000	1.0765150
H	-8.289842000	1.387757000	-0.5317420
H	-8.717741000	0.396588000	0.8419540
H	-9.741816000	-0.552441000	-1.1875200
H	-8.534864000	-1.685699000	-0.5890210
C	-1.058564000	1.406993000	0.5998350
C	-0.496671000	2.705125000	0.2089630
C	0.852854000	2.629859000	0.3292230

C	-1.207173000	-1.633252000	0.2554370
C	-2.336536000	-0.717303000	0.0085500
C	-2.221313000	0.738201000	0.2171600
C	-3.496311000	1.305872000	-0.1493240
C	-3.593132000	-0.953418000	-0.4511190
C	-3.941553000	2.726912000	-0.1007410
C	-4.219197000	-2.226186000	-0.8952030
C	-5.710373000	0.421265000	-0.8921820
C	-6.656129000	0.239959000	0.3065500
C	-8.672196000	-0.689004000	-1.0189900
H	0.112125000	-0.804471000	-1.1816790
H	-1.052824000	3.520426000	-0.2248530
H	1.562377000	3.374578000	0.0067160
H	-4.521988000	-2.182494000	-1.9457480
H	-3.501113000	-3.038023000	-0.7832490
H	-5.105193000	-2.473997000	-0.3040080
H	-3.251115000	3.335754000	0.4785800
H	-4.013197000	3.147211000	-1.1104530
H	-4.925786000	2.819704000	0.3617620
H	-5.847542000	1.400360000	-1.3515620
H	-5.901363000	-0.324733000	-1.6620130
H	-8.193506000	-0.673653000	-2.0027760
N	-0.007844000	0.712813000	1.1363850
N	-4.285327000	0.297626000	-0.5146510

Macrocycle **3**$^{2+}$ (open shell, singlet)

68 atoms

E_{tot} = -1307.438116 hartree

C	1.063305000	-1.601895000	-0.0884580
C	0.495870000	-2.719639000	0.6035050
C	-0.879521000	-2.646114000	0.4782130
C	1.191695000	1.482060000	0.2946060
C	2.334900000	0.609744000	0.2872240
C	2.270423000	-0.854869000	0.1350560
C	3.581596000	-1.323776000	0.2324060
C	3.681597000	0.934668000	0.4509810

C	4.093068000	-2.716953000	0.1122890
C	4.301028000	2.259256000	0.7304880
C	5.879031000	-0.311514000	0.5118560
C	6.573469000	-0.170290000	-0.8514400
C	8.789034000	0.837865000	0.0193110
H	-0.112780000	0.211186000	1.3572380
H	1.044237000	-3.407128000	1.2282890
H	-1.601052000	-3.265591000	0.9874770
H	4.813221000	2.262229000	1.6975810
H	3.540065000	3.037469000	0.7614340
H	5.037403000	2.528801000	-0.0316350
H	3.287917000	-3.396045000	-0.1642540
H	4.520481000	-3.064161000	1.0589410
H	4.872328000	-2.798270000	-0.6492150
H	6.128156000	-1.266354000	0.9752880
H	6.198031000	0.469743000	1.2005230
H	8.510067000	0.858066000	1.0770550
N	0.014779000	-1.008580000	-0.7474560
N	4.404446000	-0.236855000	0.4166820
H	8.550700000	1.813906000	-0.4143330
C	8.103417000	-0.295406000	-0.7508160
H	6.311317000	0.796338000	-1.2953140
H	6.188446000	-0.939087000	-1.5287580
H	8.360200000	-1.261653000	-0.3016840
H	8.496871000	-0.325946000	-1.7705260
H	9.873668000	0.722181000	-0.0179430
C	-8.103417000	0.295409000	0.7508140
H	-6.311318000	-0.796335000	1.2953140
H	-6.188445000	0.939090000	1.5287550
H	-8.360200000	1.261655000	0.3016790
H	-8.496871000	0.325952000	1.7705230
H	-9.873669000	-0.722178000	0.0179430
H	-8.550702000	-1.813904000	0.4143360
C	-1.063305000	1.601894000	0.0884570
C	-0.495871000	2.719639000	-0.6035050
C	0.879520000	2.646111000	-0.4782190

C	-1.191694000	-1.482060000	-0.2946080
C	-2.334900000	-0.609745000	-0.2872240
C	-2.270423000	0.854869000	-0.1350550
C	-3.581596000	1.323775000	-0.2324050
C	-3.681597000	-0.934669000	-0.4509770
C	-4.093067000	2.716952000	-0.1122890
C	-4.301028000	-2.259257000	-0.7304830
C	-5.879030000	0.311514000	-0.5118570
C	-6.573469000	0.170292000	0.8514390
C	-8.789035000	-0.837863000	-0.0193100
H	0.112781000	-0.211184000	-1.3572370
H	-1.044239000	3.407129000	-1.2282870
H	1.601050000	3.265586000	-0.9874860
H	-4.813222000	-2.262231000	-1.6975750
H	-3.540066000	-3.037470000	-0.7614270
H	-5.037403000	-2.528801000	0.0316420
H	-3.287916000	3.396044000	0.1642540
H	-4.520480000	3.064160000	-1.0589410
H	-4.872327000	2.798270000	0.6492150
H	-6.128155000	1.266353000	-0.9752900
H	-6.198029000	-0.469744000	-1.2005230
H	-8.510068000	-0.858067000	-1.0770540
N	-0.014779000	1.008580000	0.7474560
N	-4.404445000	0.236854000	-0.4166820

Macrocycle $\mathbf{3}^{2+}$ (open shell, triplet)

68 atoms

E_{tot} = -1307.440678 hartree

C	-1.063244000	1.601772000	-0.0885180
C	-0.495927000	2.715073000	0.6072640
C	0.880577000	2.641448000	0.4816910
C	-1.192139000	-1.481723000	0.2948790
C	-2.333832000	-0.606010000	0.2866050
C	-2.269496000	0.851516000	0.1352700
C	-3.583933000	1.322453000	0.2314770
C	-3.684002000	-0.932286000	0.4513570

C	-4.092616000	2.715504000	0.1086490
C	-4.300630000	-2.256713000	0.7332570
C	-5.883764000	0.312232000	0.5113750
C	-6.578317000	0.170876000	-0.8513930
C	-8.793073000	-0.839499000	0.0188200
H	0.112716000	-0.210523000	1.3565470
H	-1.043257000	3.401593000	1.2340360
H	1.601504000	3.259975000	0.9929810
H	-4.804247000	-2.260721000	1.7050500
H	-3.540156000	-3.035547000	0.7553850
H	-5.045155000	-2.522820000	-0.0222240
H	-3.285329000	3.394183000	-0.1621440
H	-4.526501000	3.061467000	1.0529530
H	-4.867713000	2.797272000	-0.6572350
H	-6.132316000	1.267240000	0.9748540
H	-6.202417000	-0.468373000	1.2009130
H	-8.513851000	-0.860426000	1.0764790
N	-0.014626000	1.008406000	-0.7474380
N	-4.408507000	0.237518000	0.4164120
H	-8.554245000	-1.815026000	-0.4157250
C	-8.108391000	0.294859000	-0.7506130
H	-6.315765000	-0.795469000	-1.2957650
H	-6.194168000	0.940008000	-1.5288700
H	-8.365764000	1.260586000	-0.3006790
H	-8.502086000	0.325897000	-1.7701720
H	-9.877785000	-0.724516000	-0.0180980
C	8.108392000	-0.294858000	0.7506110
H	6.315766000	0.795471000	1.2957620
H	6.194168000	-0.940006000	1.5288700
H	8.365764000	-1.260585000	0.3006790
H	8.502087000	-0.325894000	1.7701710
H	9.877786000	0.724516000	0.0180940
H	8.554245000	1.815026000	0.4157210
C	1.063243000	-1.601772000	0.0885210
C	0.495927000	-2.715074000	-0.6072610
C	-0.880577000	-2.641447000	-0.4816910

C	1.192139000	1.481723000	-0.2948790
C	2.333832000	0.606010000	-0.2866050
C	2.269496000	-0.851516000	-0.1352680
C	3.583933000	-1.322453000	-0.2314760
C	3.684002000	0.932285000	-0.4513580
C	4.092616000	-2.715504000	-0.1086460
C	4.300629000	2.256713000	-0.7332600
C	5.883764000	-0.312233000	-0.5113760
C	6.578317000	-0.170875000	0.8513910
C	8.793074000	0.839498000	-0.0188240
H	-0.112717000	0.210523000	-1.3565450
H	1.043258000	-3.401595000	-1.2340320
H	-1.601504000	-3.259973000	-0.9929820
H	4.804246000	2.260720000	-1.7050530
H	3.540156000	3.035547000	-0.7553870
H	5.045156000	2.522820000	0.0222210
H	3.285330000	-3.394183000	0.1621490
H	4.526500000	-3.061468000	-1.0529500
H	4.867713000	-2.797271000	0.6572380
H	6.132316000	-1.267241000	-0.9748540
H	6.202416000	0.468372000	-1.2009160
H	8.513851000	0.860425000	-1.0764830
N	0.014626000	-1.008406000	0.7474400
N	4.408507000	-0.237518000	-0.4164120

12. References

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