Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Supporting Information

Deprotection of benzyl unit induces 22π aromatic macrocycle of 3-oxypyripentaphyrin(0.1.1.1.0) with strong NIR absorption.

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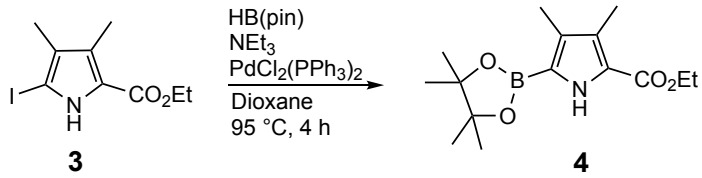
1. General Information

All reagents were of the commercial grade and were used without further purification except where noted. The spectroscopic grade dichloromethane was used as a solvent for all spectroscopic studies. Silica gel column chromatography was performed on Wakogel C-200 and C-400. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck 5554). UV/Visible absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. ^{1}H and ^{19}F NMR spectra were recorded on a JEOL ECZ-400 and a ECZ-600 spectrometer (operating as 399.78 MHz and 600.17 MHz for ^{1}H, 376.17 MHz for ^{19}F) using tetramethylsilane(TMS) as the internal reference for ^{1}H (δ = 0 ppm). Hexafluorobenzene for ^{19}F (δ = –162.9 ppm) was employed as external references. High-resolution electrospray-ionization time-of-flight mass spectroscopy (HR-ESI-TOF-MS) was recorded on a BRUKER micrOTOF model or Thermo scientific Exactive spectrometer using positive or negative mode for methanol solutions of samples.

2. Synthesis and Characterization

ethyl 3,4-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-pyrrole-2-carboxylate 4.



3 **4**

Scheme S1. Synthesis of **4**

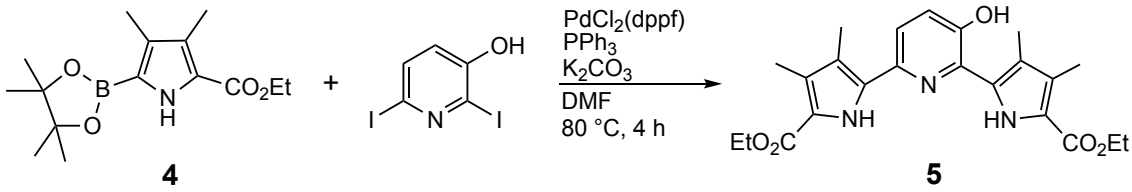
To a 500 mL two-necked flask purged with nitrogen gas, 2-ethoxycarbonyl-5-iodo-3,4-dimethylpyrrole **3** (24.3 g, 82.9 mmol), $PdCl_2(PPh_3)_2$ (1.46 g, 2.1 mmol), triethylamine (9.6 mL, 20.7 mmol), pinacolborane (24.6 mL, 168 mmol) and 330 mL of dry dioxane was placed. The resultant solution was stirred for 4 h at 95 ˚C oil bath. After the reaction mixture was cooled to room temperature, the reaction mixture was filtered with 200 mL of dioxane. The filtrate was evaporated to leave crude products as a brown oil. The oil was chromatographed twice on silica gel column using dichloromethane and 1:5 mixture of ethyl acetate/hexane. The obtained fraction was evaporated to leave brown solid. The solid was recrystallized with 130 mL of methanol to give ethyl 3,4-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-pyrrole-2-carboxylate **4** (17.5 g, 72 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.31 (s, 12H, pinacol-CH_3), 1.36 (t, J = 7.2 Hz, 3H, -CH_2CH_3), 2.18 (s, 3H, pyrrole-CH_3), 2.26 (s, 3H, pyrrole-CH_3), 4.32 (q, 2H, J = 7.2 Hz, -OCH_2CH_3), 9.06 (s, 1H, NH).

^{13}C NMR (98.51 MHz, $CDCl_3$, 298 K): δ (ppm) = 10.2, 10.5, 14.7, 60.1, 83.8, 122.9, 126.8, 131.8, 161.5.

ESI-TOF-MS *m/z* (obsd.) = 294.1872 $[M+H]^+$, (calcd) = 294.1871 for $C_{15}H_{25}BNO_4^+$.

diethyl 5,5'-(3-hydroxypyridine-2,6-diyl)bis(3,4-dimethylpyrrole-2-carboxylate) 5.



4 **5**

Scheme S2. Synthesis of **5**

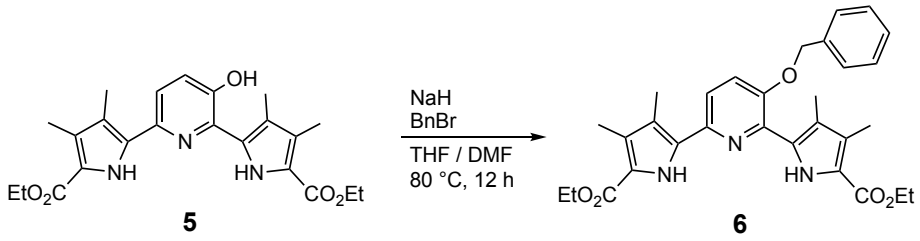
Compound **4** (8.03 g, 28.7 mmol) and 2,6-diiodopyridin-3-ol (3.95 g, 11.4 mmol) and PPh_3 (517 mg, 1.97 mmol) and $PdCl_2$(dppf) (700 mg, 957 μmol) in dry DMF (105 mL) was placed in 300 mL two-necked flask. The resultant solution was stirred for 10 min under an atmosphere of nitrogen at 80 ˚C oil bath. A solution of K_2CO_3 (3.95 g, 27 mmol) in water (21 mL) was added and heating was continued for 4 h. The reaction was quenched with 300 mL of saturated aqueous NH_4Cl and the products were extracted with a mixture of $CHCl_3$/THF = 10:1 (100 mL) for five times. The organic phase was washed with brine and dried over anhydrous Na_2SO_4 followed by evaporation of solvent under reduced pressure. After 40 mL of CH_2Cl_2 was added, the precipitate was collected and washed with CH_2Cl_2 to give white solids of **5** (3.0 g, 61%).

^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ (ppm) = 1.31 (t, J = 7.2 Hz, 3H, -OCH$_2$CH_3), 1.32 (t, J = 7.2 Hz, 3H, OCH$_2$CH_3), 2.19 (s, 3H, -CH_3), 2.20 (s, 3H, -CH_3), 2.25 (s, 3H, -CH_3) , 2.27 (s, 3H, -CH_3), 4.26 (q, J = 7.2 Hz, 2H, -OCH_2CH$_3$), 4.28 (q, J = 7.2 Hz, 2H, -OCH_2CH$_3$), 7.36 (d, J = 8.8 Hz, 1H, pyridine-H), 7.50 (d, J = 8.8 Hz, 1H, pyridine-H), 10.76 (s, 1H, NH or OH) , 10.89 (s, 1H, NH or OH), 11.19 (s, 1H, NH or OH).

^{13}C NMR (98.51 MHz, DMSO-d_6, 298 K): δ (ppm) = 10.3, 10.4, 10.4, 11.2, 14.5, 14.5, 59.4, 59.4, 117.0, 117.9, 118.0, 119.9, 120.8, 123.9, 126.0, 126.9, 130.2, 132.1, 138.2, 141.0, 149.5, 161.0, 161.0.

ESI-TOF-MS *m/z* (obsd.) 424.1879 $[M–H]^–$, (calcd) = 424.1878 for $C_{23}H_{26}N_3O_5^+$.

diethyl 5,5'-(3-hydroxypyridine-2,6-diyl)bis(3,4-dimethylpyrrole-2-carboxylate) 6.



Scheme S3. Synthesis of **6**.

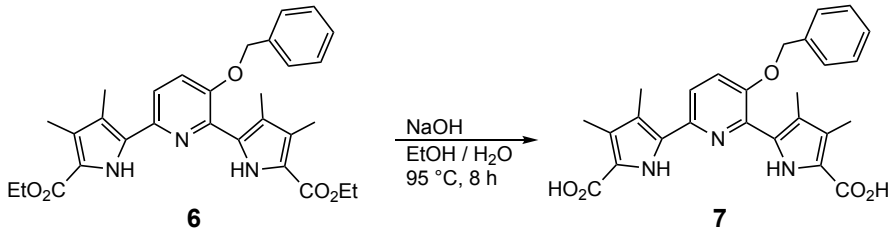
Compound **5** (3.00 g, 7.1 mmol) in 300 mL two-necked flask was added into dry THF/DMF = 1:1 mixture (120 mL) and stirred solution was heated in N_2 atmosphere for 5 min at 80 ˚C oil bath to dissolve them. NaH (abt. 60%, 339 mg, 8.5 mmol) was added and heating was continued for 20 min. After that, BnBr (1.70 mL, 14.3 mmol) was added and the resulting solution was heated for further 12 h. The reaction solution was cooled to room temperature and quenched with a solution of K_2CO_3 (3.0 g 2.2 mmol) in MeOH (300 mL) and water (300 mL) on ice bath. The white precipitate is filtered was collected by filtration and washed with 200 mL of water/MeOH = 1:1 mixture. Drying the residue for 3 hours at 50 ˚C gave pure solids of compound **6** (3.64 g, 3.5 mmol, 99%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21 (t, *J* = 7.2 Hz, 3H, -OCH_2CH_3), 1.40 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.29 (s, 3H, -CH_3), 2.36 (s, 3H, -CH_3), 2.37 (s, 3H, -CH_3) , 2.53 (s, 3H, -CH_3), 4.21 (q, *J* = 7.2 Hz, 2H, -OCH_2CH_3), 4.34 (q, *J* = 7.2 Hz, 2H, -OCH_2CH_3), 5.23 (s, 2H, -OCH_2Ph), 7.36-7.50 (m, 7H, phenyl-H and pyridyl-H), 9.88 (s, 1H, NH) , 10.27 (s, 1H, NH).

^{13}C NMR (98.51 MHz, $CDCl_3$, 298 K): δ (ppm) = 10.3, 10.4, 11.0, 12.3, 14.6, 14.6, 59.8, 60.0, 71.5, 117.8, 117.8, 118.6, 118.8, 120.5, 122.6, 127.7, 128.0, 128.5, 128.5, 128.8, 129.1, 130.8, 135.4, 140.6, 142.4, 150.0, 161.3, 161.5.

ESI-TOF-MS *m/z* (obsd.) = 516.2497 $[M+H]^+$, (calcd) = 516.2493 for $C_{30}H_{34}N_3O_5^+$

5,5'-(3-(benzyloxy)pyridine-2,6-diyl)bis(3,4-dimethyl-1H-pyrrole-2-carboxylic acid) 7.



6 **7**

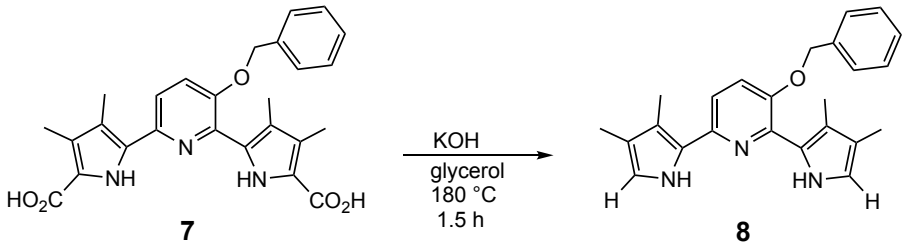
Scheme S4. Synthesis of **7**.

Compound **6** (1.80 g, 3.49 mmol) was added into EtOH (216 mL) and stirred under reflux for 5 min. A solution of NaOH (1.08 g 27 mmol) in water (54 mL) was added and refluxed for 8 h. The reaction solution was cooled to room temperature and the reaction mixture was neutralized by addition of hydrochloric acid. After addition of water (270 mL). The precipitate was collected by filtration and washed with water. Drying the resulting solid for 2 h at 50 ˚C gave pure compound **7** (1.61 g, 3.49 mmol, quant.).

^{1}H NMR (400 MHz, DMSO-*d6*, 298 K): δ (ppm) = 1.98 (s, 3H, -C*H*$_3$), 2.19 (s, 3H, -C*H*$_3$), 2.20 (s, 3H, -C*H*$_3$), 2.25 (s, 3H, -C*H*$_3$), 5.21 (s, 2H, -C*H*$_2$Ph), 7.32-7.42 (3H, phenyl-H), 7.47 (d, *J* = 7.6 Hz, 2H, phenyl-H), 7.58 (d, *J* = 9.0 Hz, 1H, pyridine-H), 7.66 (d, *J* = 9.0 Hz, 1H, pyridine-H), 11.15 (s, 1H, NH), 11.34 (s, 1H, NH), 12.35 (brs, 2H, COOH).

^{13}C NMR (98.51 MHz, DMSO-*d6*, 298 K): δ (ppm) = 10.3, 10.4, 11.2, 70.1, 117.1, 119.0, 119.5, 119.7, 120.5, 120.9, 125.5, 126.4, 128.1, 128.1, 128.5, 129.4, 131.5, 136.3, 140.2, 142.2, 150.5, 162.7, 162.8. ESI-TOF-MS *m/z* (obsd.) = 458.1727 $[M–H]^-$, (calcd) = 458.1721 for $C_{26}H_{24}N_3O_5^-$

3-(benzyloxy)-2,6-bis(3,4-dimethyl-1H-pyrrol-2-yl)pyridine 8.



7 **8**

Scheme S5. Synthesis of **8**.

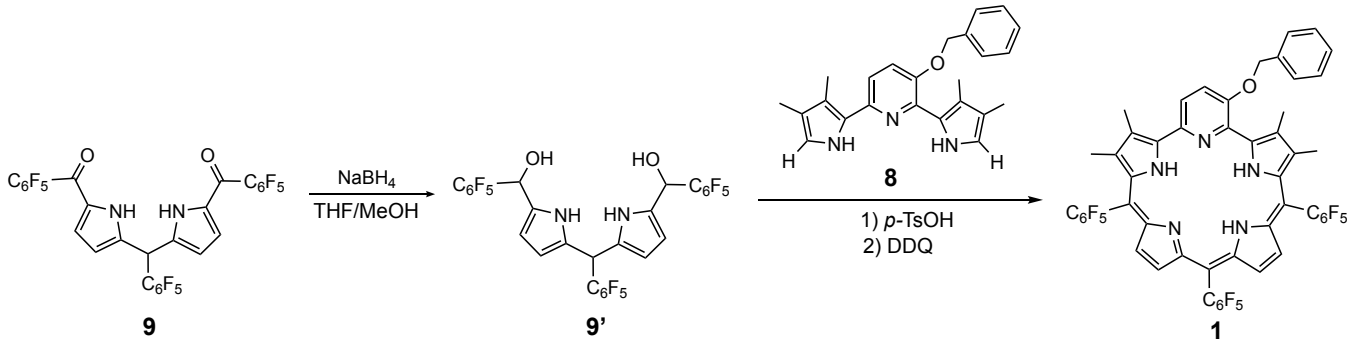
Compound **7** (800 mg, 1.74 mmol) was added to a solution of KOH (2.40 g, 42.8 mmol) in dry glycerol (40 mL) and the resultant mixture was stirred in N_2 atmosphere at 180 ˚C for 1.5 h. After cooling to room temperature, the reaction mixture was added into 500 mL water and neutralized by addition of acetic acid (10 mL). The reaction mixture was extracted with 500mL dichloromethane and the organic phase was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of solvent under reduced pressure, silica gel column chromatography using CH_2Cl_2 and recrystallization with hexane afforded compound **8** (274 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.09 (s, 3H, -C*H*$_3$), 2.10 (s, 3H, -C*H*$_3$), 2.29 (s, 3H, -C*H*$_3$), 2.51 (s, 3H, -C*H*$_3$), 5.15 (s, 2H, --C*H*$_2$Ph), 6.57 (d, *J* = 2.4 Hz, 1H, pyrrole-H), 6.64 (d, *J* = 2.0 Hz, 1H, pyrrole-H), 7.24 (d, *J* = 8.6 Hz, 1H, pyridine-H), 7.26 (d, *J* = 8.4 Hz, 1H, pyridine-H), 7.35-7.46 (5H, phenyl-H), 9.17 (s, 1H, NH), 9.55 (s, 1H, NH).

^{13}C NMR (98.51 MHz, $CDCl_3$, 298 K): δ (ppm) = 10.4, 10.5, 11.2, 12.6, 71.4, 114.9, 115.8, 115.8, 116.3, 119.8, 120.3, 120.5, 120.7, 125.7, 127.8, 128.1, 128.6, 129.0, 136.3, 141.6, 143.9, 148.2.

ESI-TOF-MS *m/z* (obsd.) = 372.2070 $[M+H]^+$, (calcd) = 372.2070 for $C_{24}H_{26}N_3O^+$.

2-benzyloxy-7,8,22,23-tetramethyl-10,15-20-tris(pentafluorophenyl)-pyripentaphyrin(0.1.1.1.0) 1



Scheme S6. Synthesis of **1**.

5-Pentafluorophenyl-1,9-bis(pentafluorobenzoyl)dipyrromethene **9** (280 mg, 0.40 mmol) was reduced with $NaBH_4$ (303 mg, 20 eq) in a 10:1 mixture solution of THF and methanol (44 mL). After 1 h, the reaction was quenched with water (60 mL) and extracted with ethyl acetate(60 mL). The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield di-carbinol **9'** quantitatively, which was unstable at ambient temperature and hence had to be used immediately. The di-carbinol **9'** was added to a solution of **8** (149 mg, 0.40 mmol) in CH_2Cl_2 (200 mL). After the resultant solution was stirred in N_2 atmosphere for 5 min, *p*-toluenesulfonic acid monohydrate (98.8 mg, 1.3 eq) was added and stirring was continued for 1 h. DDQ (272 mg, 3.0 eq) was added and the resulting solution was stirred for further 20 min. The reaction mixture with 200 mL of ethyl acetate was passed through a basic alumina column followed by evaporation of solvent under reduced pressure. The residue was purified twice by silica gel column chromatography using 3:1 mixture of hexane: ethyl acetate and 20:1 mixture of CH_2Cl_2: ethyl acetate. After collection of the green band, recrystallization from CH_2Cl_2/hexane afforded pure pyripentaphyrin **1** (77.2 mg, 74.5 μmol, 19%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.69 (s, 3H, -*CH*$_3$), 1.77 (s, 3H, -*CH*$_3$), 2.18 (s, 3H, -*CH*$_3$), 2.57 (s, 3H, -*CH*$_3$), 5.06 (brs, 3H, NH, merged with protons of water), 5.37 (s, 2H, -*CH*$_2$-), 6.41 (d, *J* = 4.8 Hz, 1H, *β*-H), 6.51 (d, *J* = 6.0 Hz, 1H, *β*-H), 6.75 (d, *J* = 4.8 Hz, 1H, *β*-H), 6.80 (d, *J* = 4.8 Hz, 1H, *β*-H), 7.34-7.46 (5H, phenyl-H), 7.75 (d, *J* = 9.2 Hz, 1H, pyridine-H), 8.31 (d, *J* = 9.2 Hz, 1H, pyridine-H).

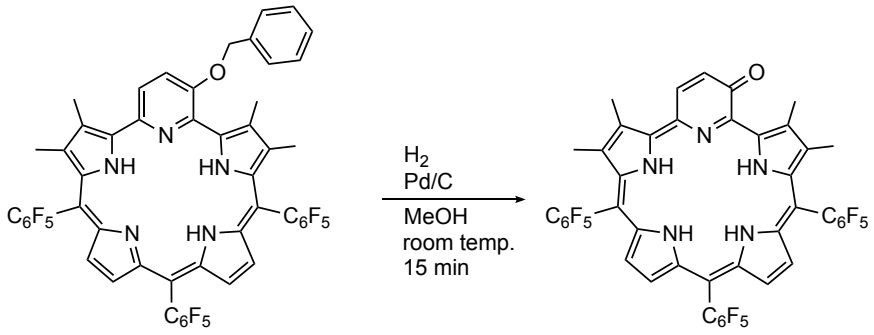
^{13}C NMR (98.51 MHz, $CDCl_3$, 298 K): δ (ppm) = 10.4, 11.1, 12.0, 14.3, 72.0, 93.2, 98.6, 114.0, 119.9, 120.7, 121.3, 12-2.0, 122.3, 126.2, 127.0, 127.7, 128.3, 128.5, 128.6, 128.9, 129.2, 129.3, 129.9, 134.0, 136.0, 136.1, 138.68, 138.75, 141.8, 148.2, 150.7, 153.7, 162.8. (^{13}C NMR (98.51 MHz, $CDCl_3$, 298 K): δ (ppm) = 10.4, 10.5, 11.2, 12.6, 71.4, 114.9, 115.8, 115.8, 116.3, 119.8, 120.3, 120.5, 120.7, 125.7, 127.8, 128.1, 128.6, 129.0, 136.3, 141.6, 143.9, 148.2. (The signals for pentafluorophenyl carbons were not clearly observed because of their complicated ^{13}C–F coupling.)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ (ppm) = –139.20 (d, *J* = 24 Hz, 2F, *o*-F), –139.59 (d, *J* = 24 Hz, 2F, *o*-F), –139.88 (d, *J* = 24 Hz, 2F, *o*-F), –154.22 (t, *J* = 22 Hz, 1F, *p*-F), –154.63 (t, *J* = 22 Hz, 1F, *p*-F), –155.35 (t, *J* = 22 Hz, 1F, *p*-F), –162.83 - –162.93 (6F, *m*-F).

UV/Vis/NIR (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])= 348 (3.2×10^4), 435 (3.7×10^4), 705 (1.2×10^4).

ESI-TOF-MS *m/z* (obsd.) = 1036.2133 $[M+H]^+$, (calcd) = 1036.2128 for $C_{53}H_{29}N_5F_{15}O_1^+$.

2-oxy-7,8,22,23-tetramethyl-10,15-20-tris(pentafluorophenyl)-pyripentaphyrin(0.1.1.1.0) 2.



Scheme S7. Synthesis of **2**.

Palladium-activated carbon (Pd 10%, 5.0 mg) was added to a solution of compound **1** (25.0 mg, 24.1 μmol) in MeOH (20 mL) and the resultant mixture was stirred in H_2 atmosphere for 15 min at room temperature. Palladium-activated carbon was filtered off and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using 1:1 mixture of hexane/ethyl acetate. After collection of the brown band, recrystallization from CH_2Cl_2/hexane afforded pure pyripentaphyrin **2** (17.8 mg, 18.8 μmol, 78%).

^{1}H NMR (400 MHz, CD_3OD, 298 K): δ (ppm) = 2.29 (s, 3H, -CH_3), 2.44 (s, 3H, -CH_3), 3.00 (s, 3H, -CH_3), 3.27 (s, 3H, -CH_3), 7.87 (1H, brs, *β*-H), 7.90 (1H, brs, *β*-H), 8.07 (d, *J* = 8.4 Hz, 1H, pyridine-H), 8.16 (1H, *β*-H), 8.23 (1H, *β*-H), 9.6 (d, *J* = 6.8 Hz, 1H, pyridine-H).

^{13}C NMR spectra in $CDCl_3$ or methanol-d_3 were too broad or weak to analysis because of the keto-enol equilibrium and low solubility (in methanol) of **2**.

^{19}F NMR (376 MHz, CD_3OD, 298 K): δ (ppm) = –142.79 (d, *J* = 18 Hz, 2F, *o*-F), –143.10 (d, *J* = 12 Hz, 2F, *o*-F), –143.26 (d, *J* = 24 H z, 2F, *o*-F), –156.08 (br, 1F, *p*-F), –156.32 (br, 1F, *p*-F), –157.95 (br, 1F, *p*-F), –165.64 (t, *J* = 18 Hz, 2F, *m*-F), –165.89 (t, *J* = 18 Hz, 2F, *m*-F), –166.14 (m, 2F, *m*-F).

UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [$M^{-1}cm^{-1}$]) = 344 (3.2×10^4), 437 (5.0×10^4), 497 (3.2×10^4), 519 (3.2×10^4), 519 (3.2×10^4), 716 (1.9×10^4), 842 (1.3×10^4); (MeOH): λ_{max}[nm] (ε[$M^{-1}cm^{-1}$]) = 349 (4.1×10^4), 431 (8.4×10^4), 502 (4.3×10^4), 530 (5.0×10^4), 704(2.9×10^4), 761(1.9×10^4), 852 (4.2×10^4).

ESI-TOF-MS *m/z* (obsd.) = 946.1663 $[M+H]^+$, (calcd) = 946.1691 for $C_{46}H_{22}N_5F_{15}O_1^+$.

3. NMR Spectra

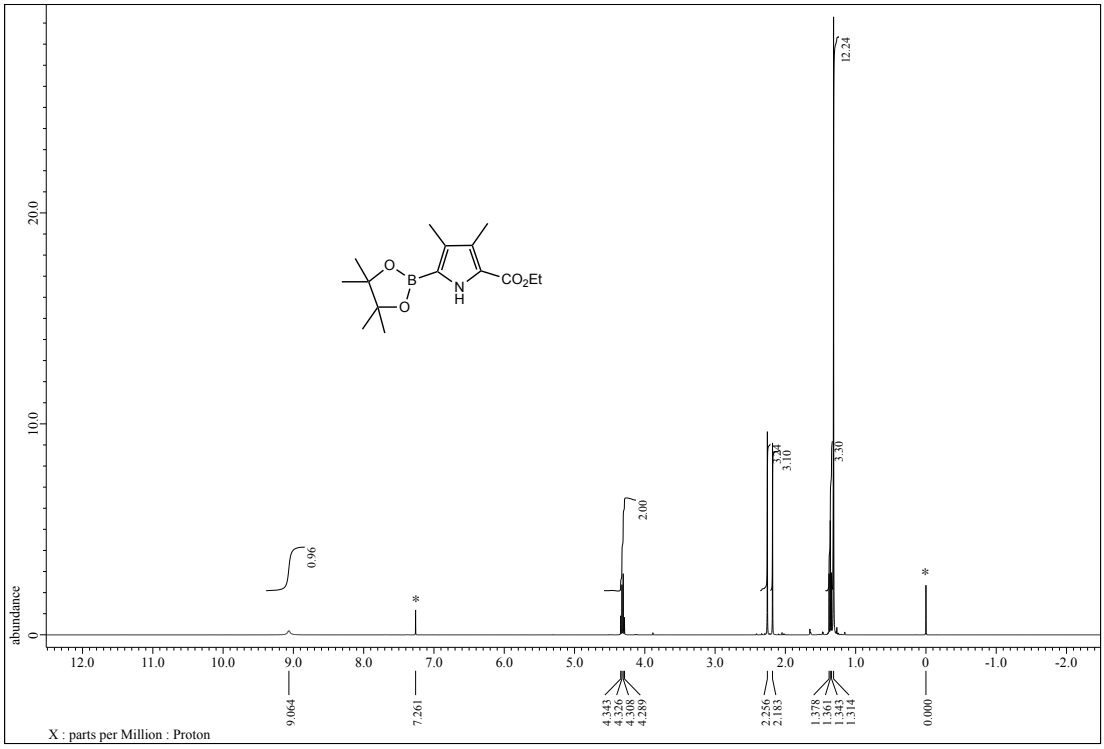


Fig. S1. ^{1}H NMR spectrum of **4** in $CDCl_3$ at 25 °C. * indicates $CHCl_3$ and TMS.

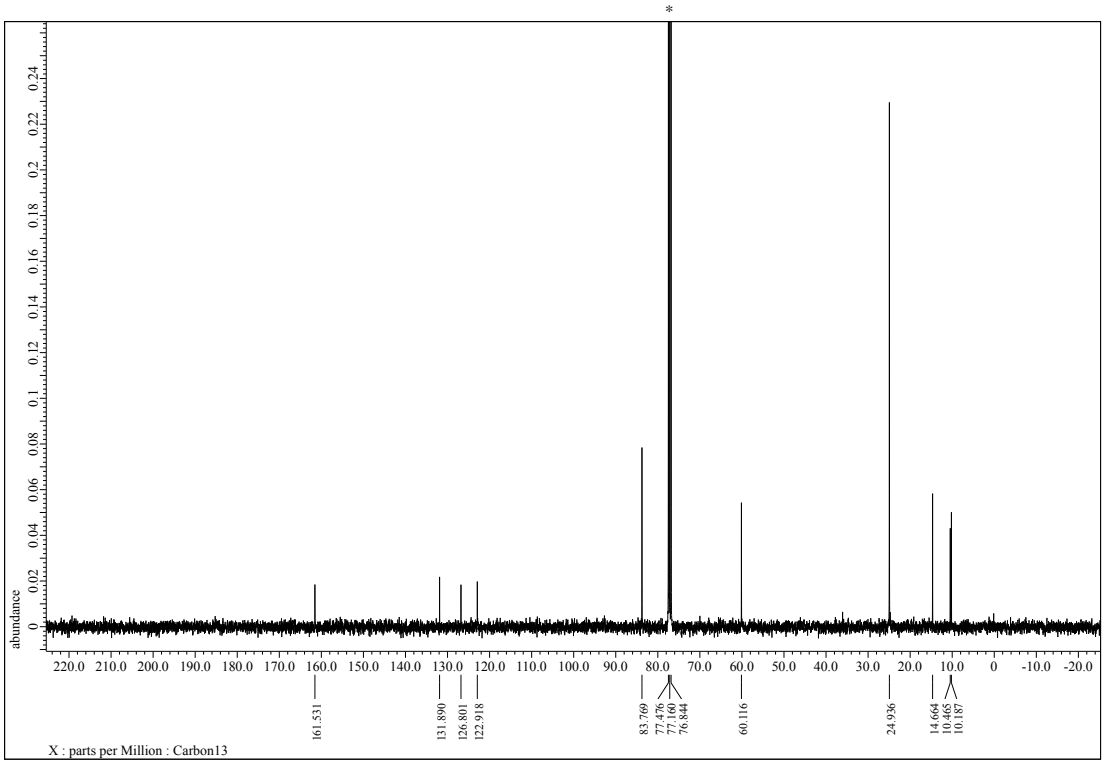


Fig. S2. ^{13}C NMR spectrum of **4** in $CDCl_3$ at 25 °C. * indicates solvent.

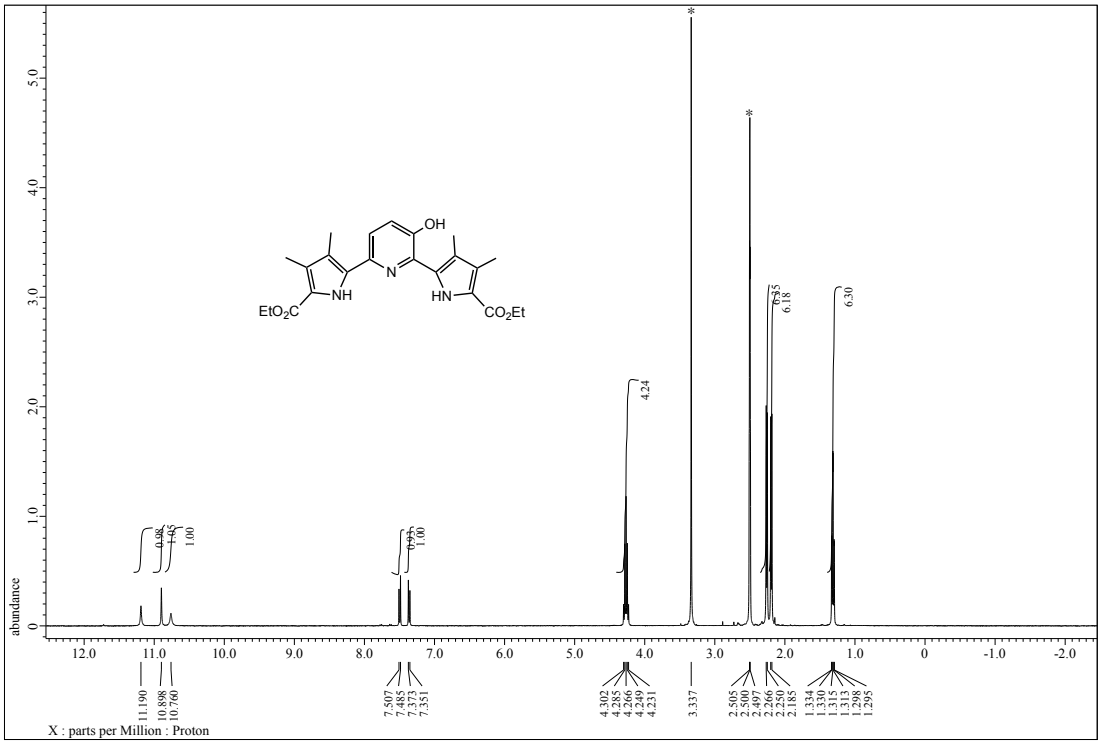


Fig. S3. ^{1}H NMR spectrum of **5** in DMSO-*d*6 at 25 °C. * indicates residual solvents.

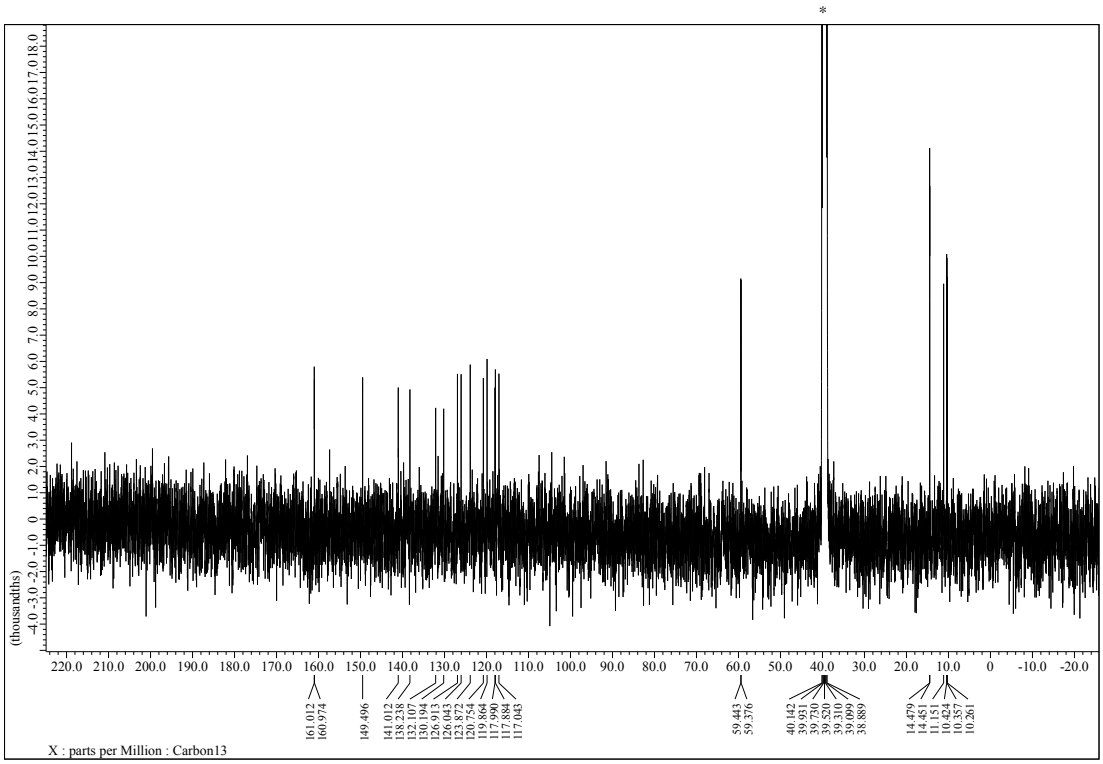


Fig. S4. ^{13}C NMR spectrum of **5** in DMSO-*d*6 at 25 °C. * indicates DMSO-*d*6.

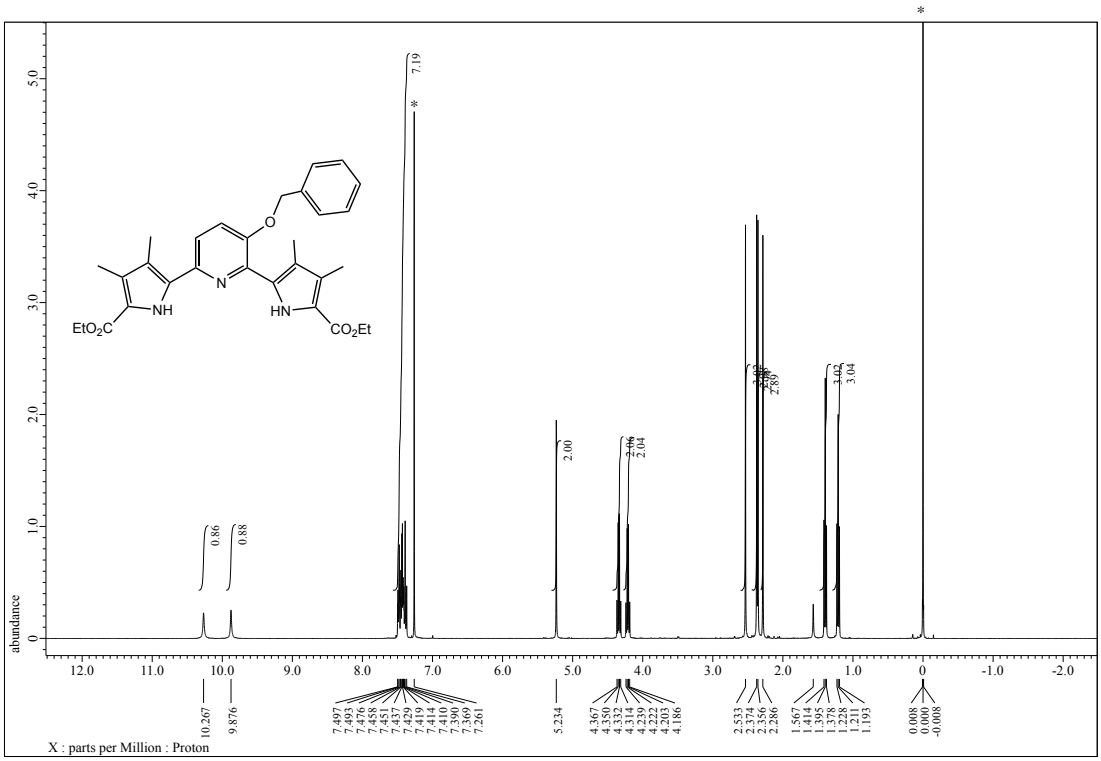


Fig. S5. ^{1}H NMR spectrum of **6** in $CDCl_3$ at 25 °C. * indicates $CHCl_3$ and TMS.

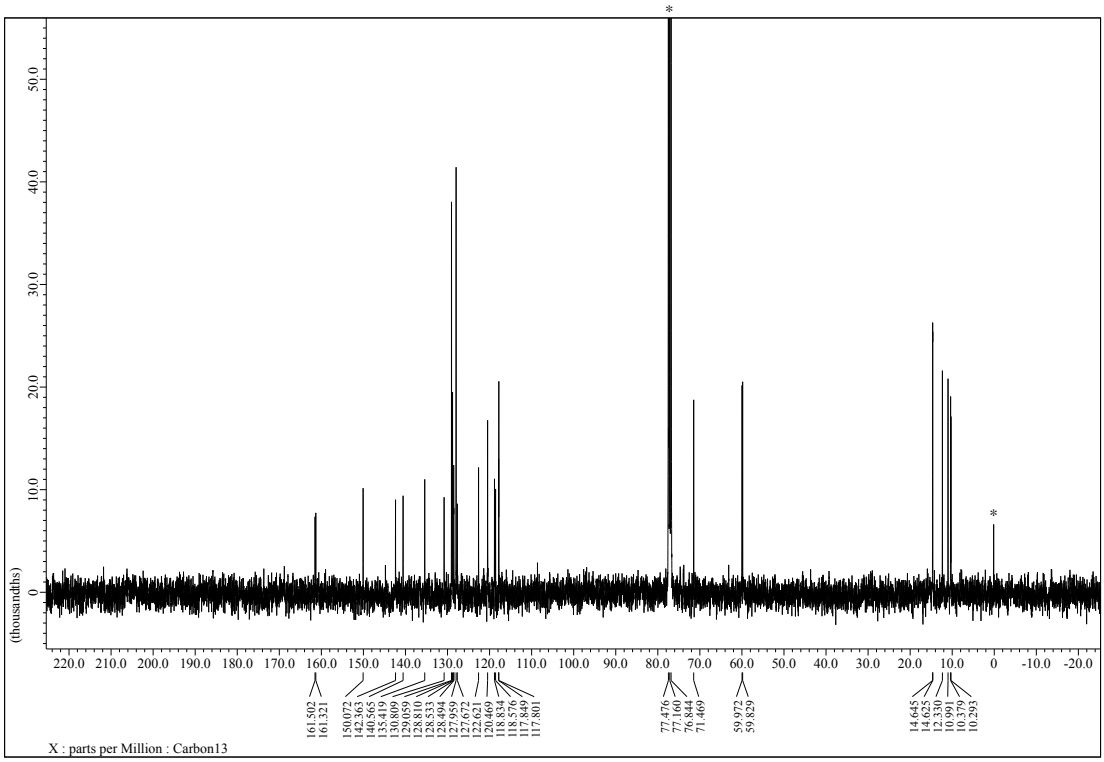


Fig. S6. ^{13}C NMR spectrum of **6** in $CDCl_3$ at 25 °C. * indicates $CDCl_3$ and TMS.

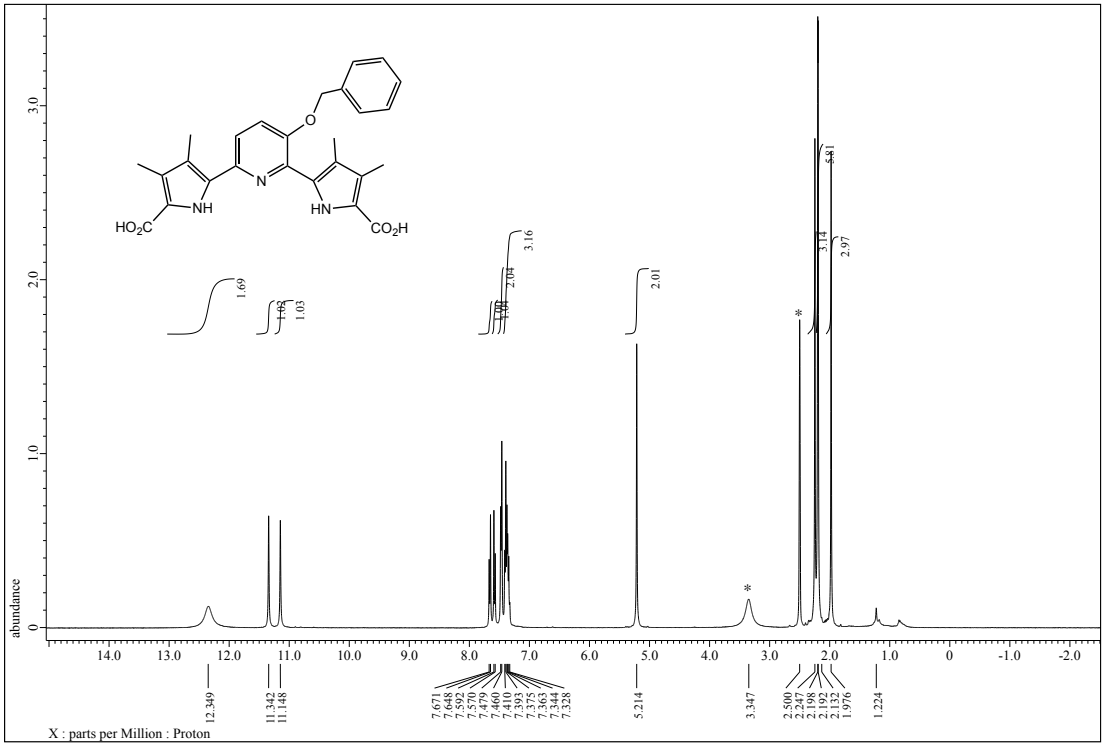


Fig. S7. ^{1}H NMR spectrum of **7** in DMSO-*d*6 at 25 °C. * indicates residual solvents.

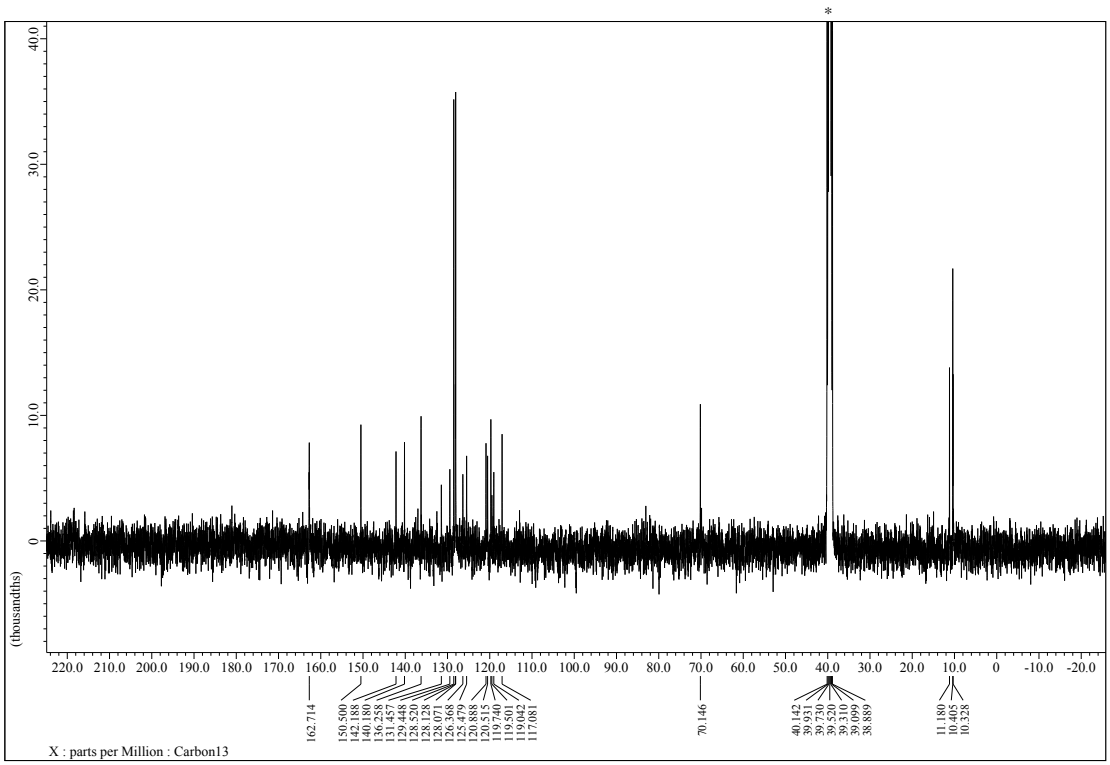


Fig. S8. ^{13}C NMR spectrum of **7** in DMSO-*d*6 at 25 °C. * indicates residual DMSO-*d*6.

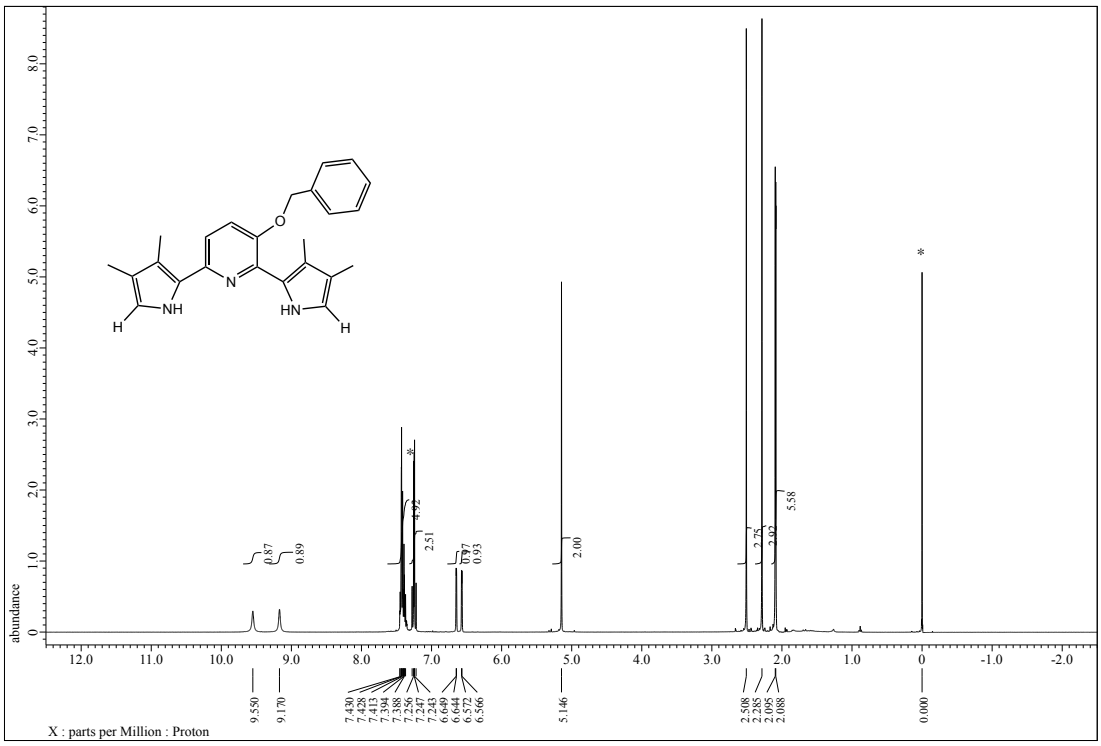


Fig. S9. ^{1}H NMR spectrum of **8** in $CDCl_3$ at 25 °C. * indicates $CHCl_3$ and TMS.

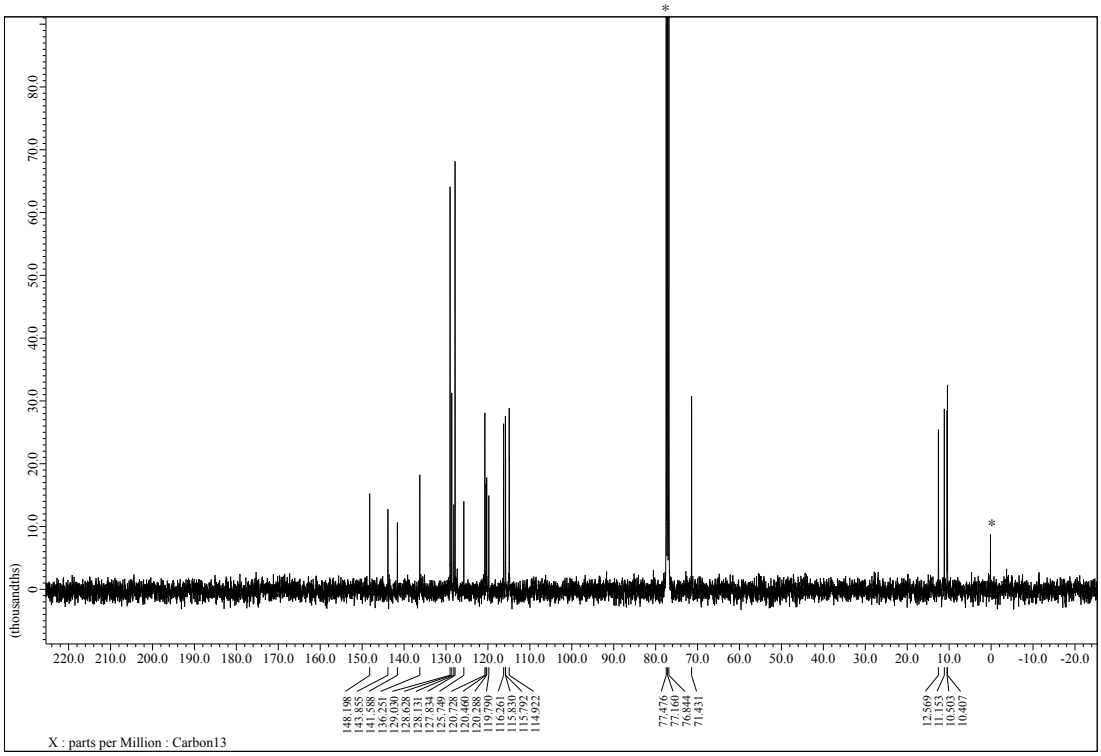


Fig. S10. ^{13}C NMR spectrum of **8** in $CDCl_3$ at 25 °C. * indicates $CDCl_3$ and TMS.

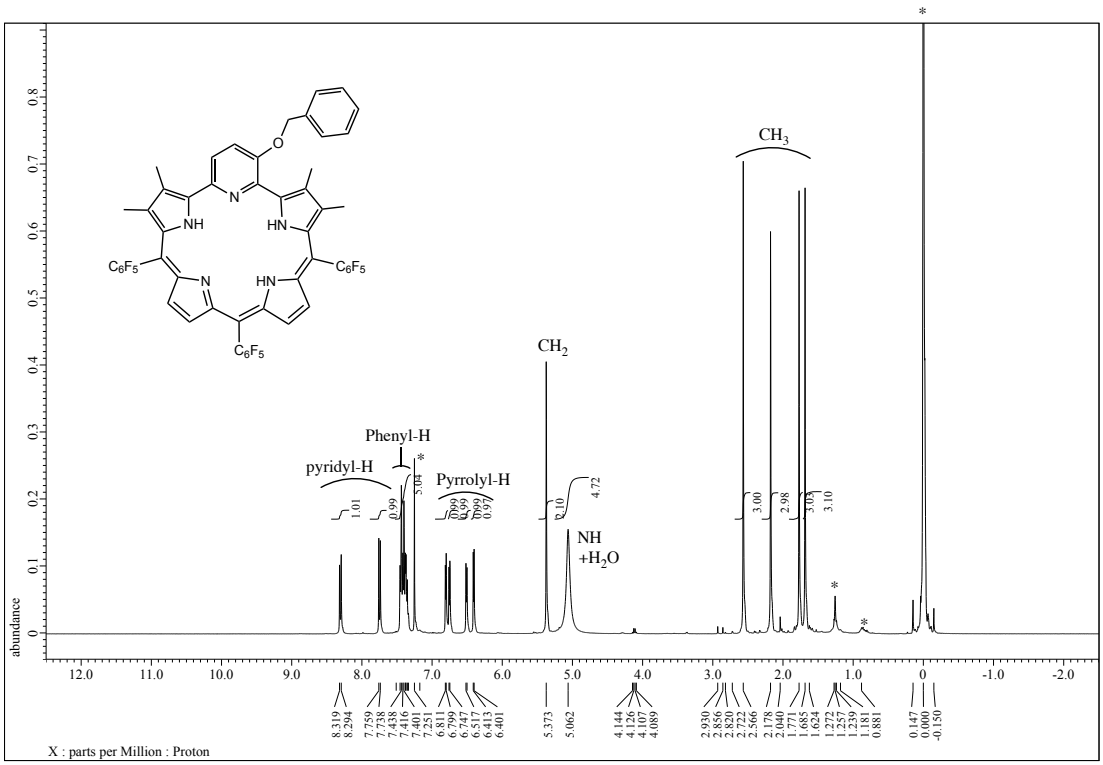


Fig. S11. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 °C. * indicates residual solvents and TMS.

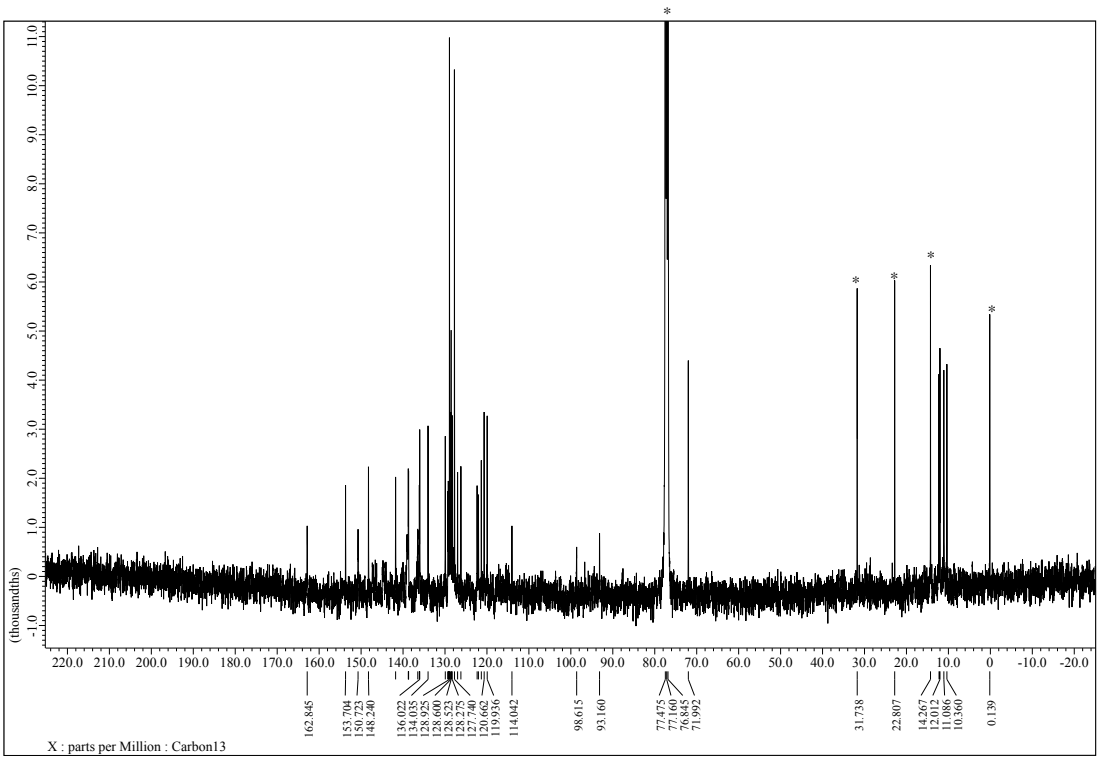


Fig. S12. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ at 25 °C. * indicates residual solvents and TMS.

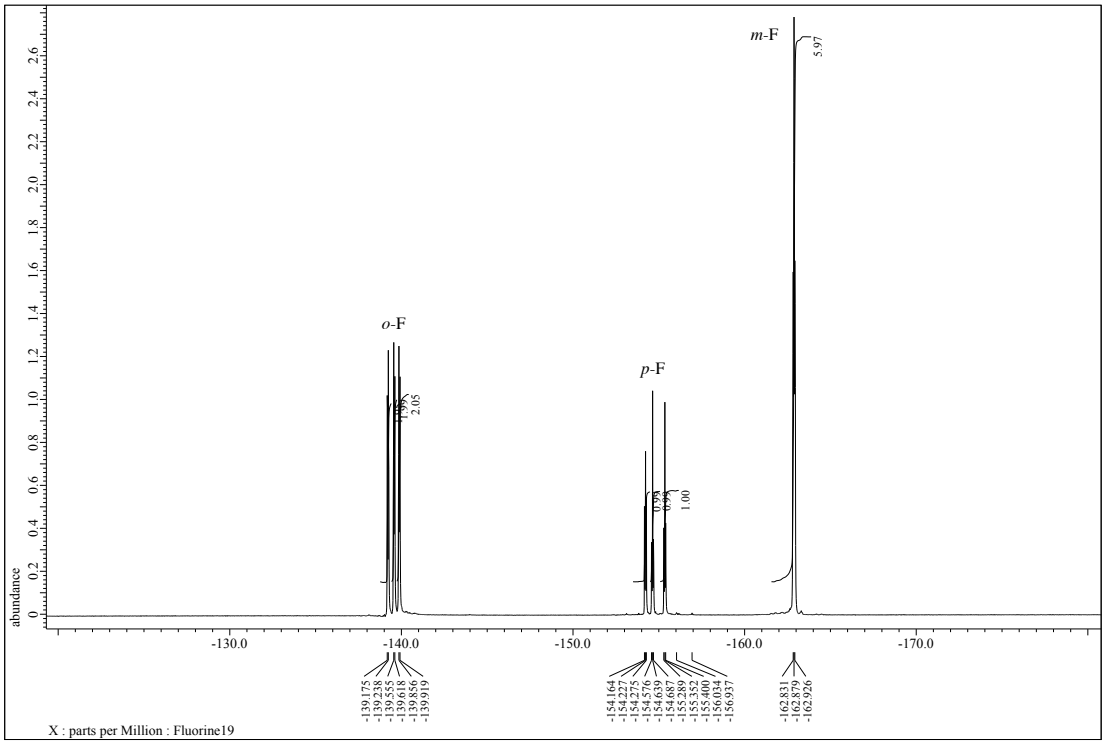


Fig. S13. ^{19}F NMR spectrum of **1** in $CDCl_3$ at 25 °C.

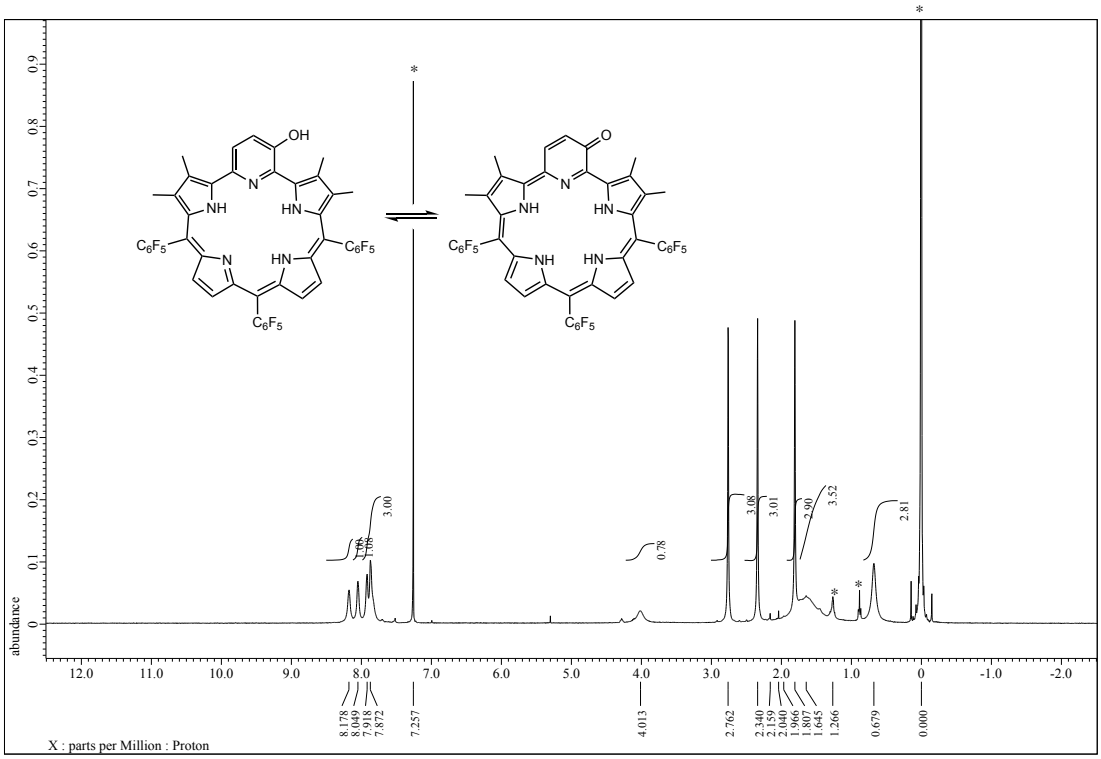


Fig. S14. ^{1}H NMR spectrum of **2** in $CDCl_3$ at 25 °C. * indicate residual solvents and TMS.

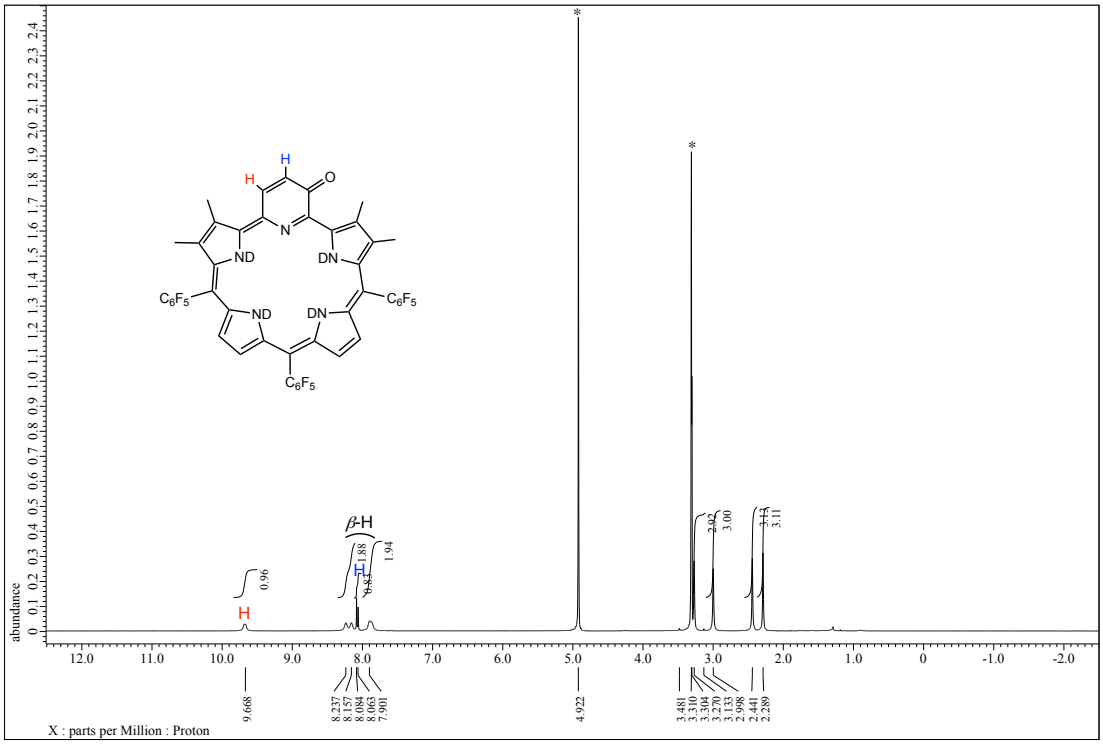


Fig. S15. ^{1}H NMR spectrum of **2** in methanol-*d*4 at 25 °C. * indicates residual solvents.

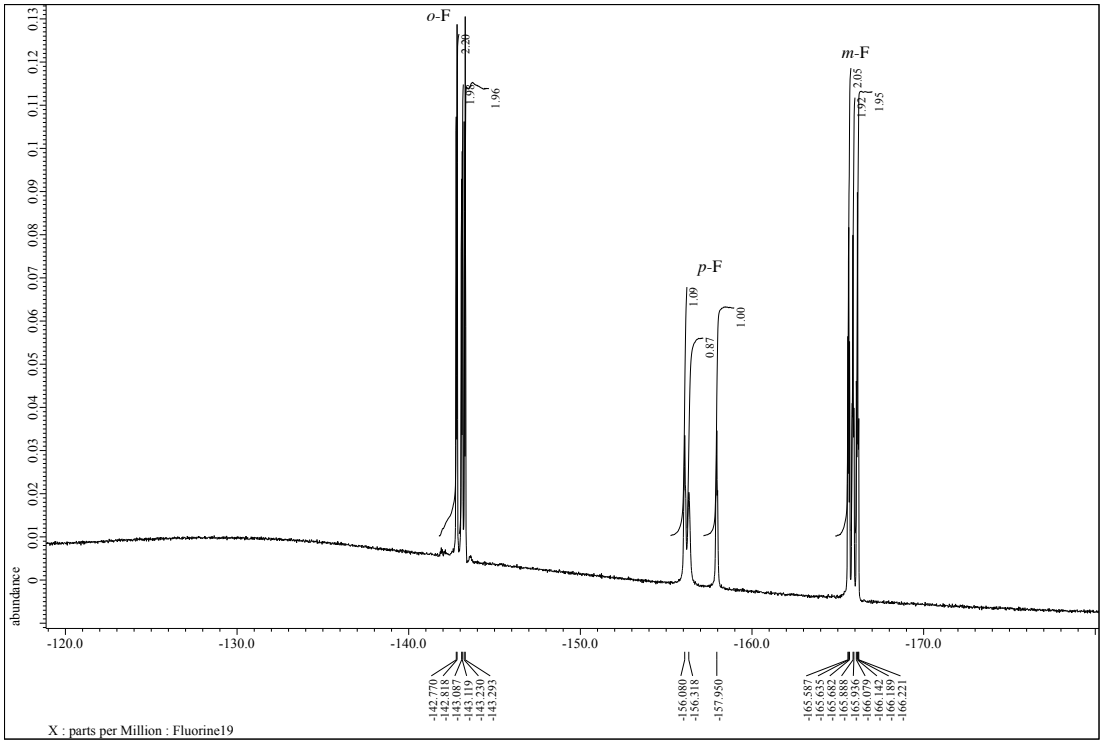
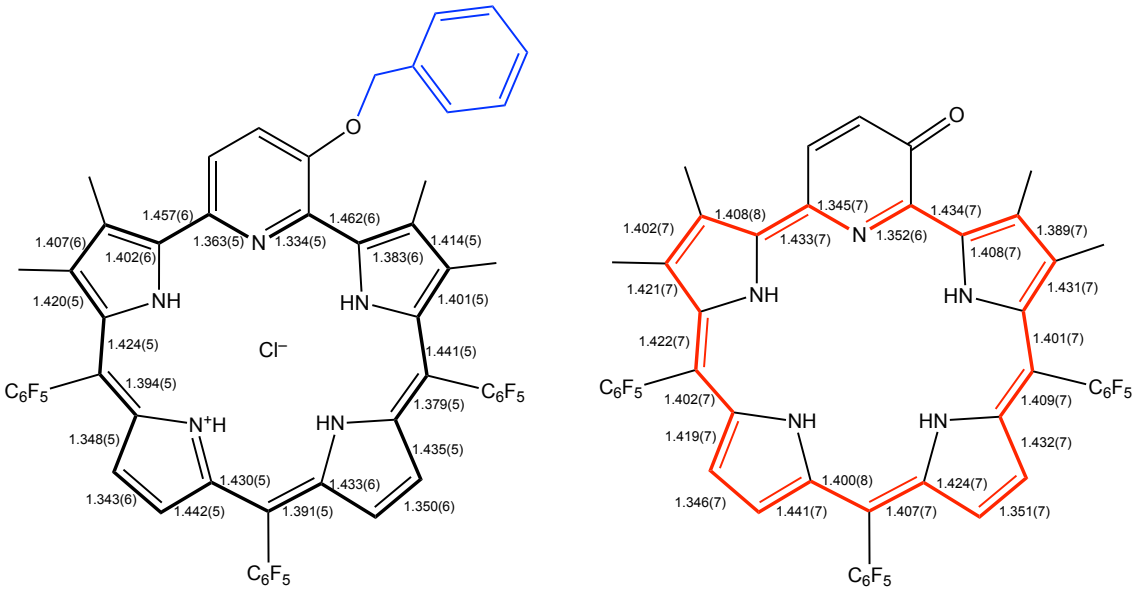


Fig. S16. ^{19}F NMR spectrum of **2** in methanol-*d*4 at 25 °C.

3. X-Ray Crystallographic Analysis

Data for single crystal X-ray diffraction analyses were collected on a Rigaku R-AXIS RAPID diffractometer using a graphite monochromator with CuK_α radiation (λ = 1.54187 Å). Data collection and reduction were performed using *RAPID AUTO*. The structures for crystallography were solved by direct methods using *SHELXL97* and were refined using *SHELXL97* on *Yadokari-XG* program.



HOMA = 0.562 HOMA = 0.713

Fig. S17. Selected bond lengths of **1**(left) and **2**(right) shown in Å.

4. Cyclic Voltammograms

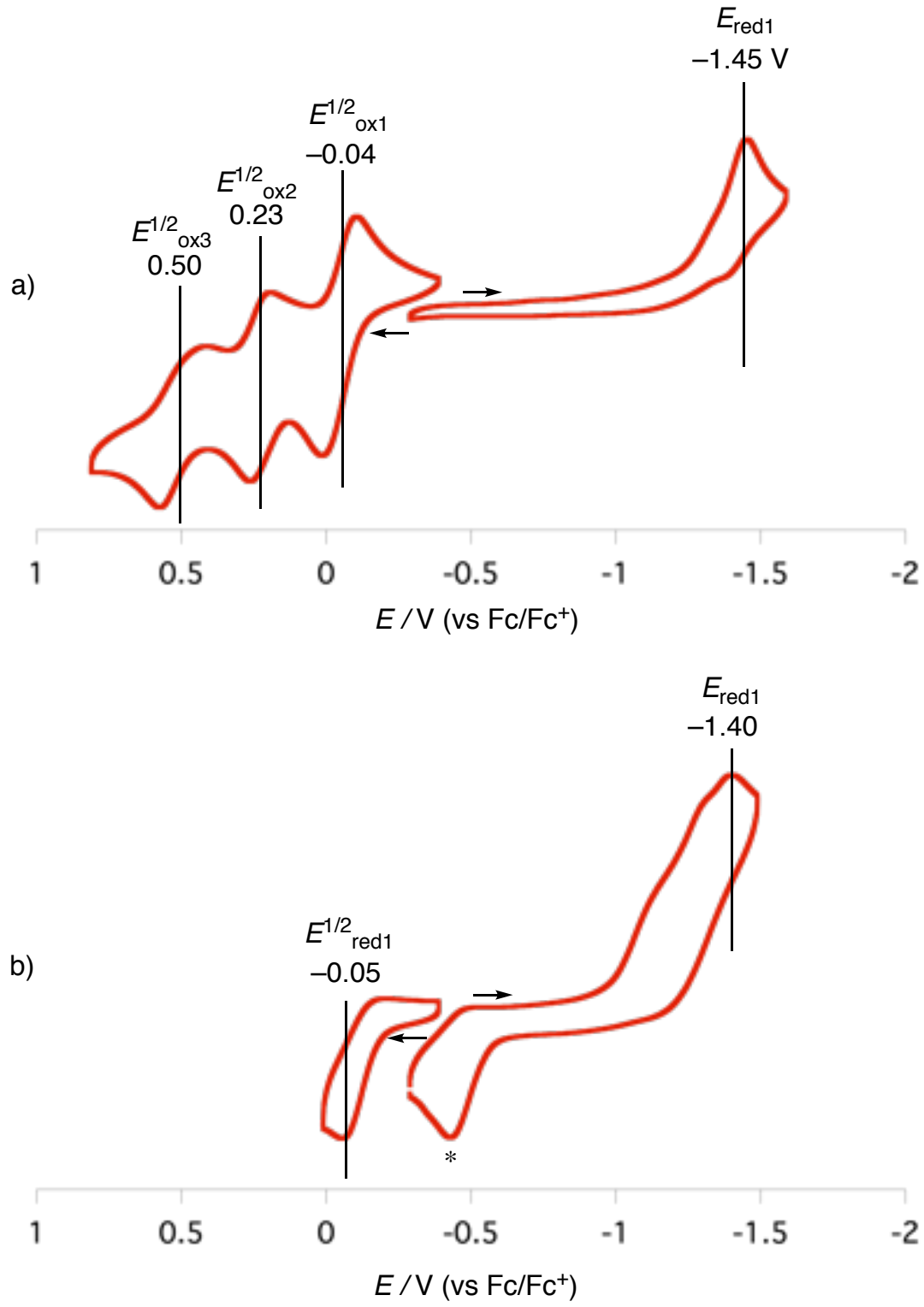


Fig. S18. Cyclic Voltammograms of a) **1** and b) **2** measured in dichloromethane using tetrabutylammonium hexafluorophosphate (0.10 M) as supporting electrolyte (*E*/V vs ferrocene/ferrocenium cation, scan rate 0.05 Vs^{-1}). The * peak is derived from the irreversibly reduced anion radical species.

5. DFT Calculations

All calculations were carried out using the *Gaussian 16* program.[S1] All structures were fully optimized without any symmetry restriction. The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level, employing a basis set 6-31G(d) for C, H, N, O, and F. The NICS values and absolute ^{1}H shielding values were obtained with the GIAO method. The ^{1}H chemical shift values were calculated relative to $CHCl_3$ (δ = 7.26 ppm, absolute shielding: 24.94 ppm). The global ring centers for the NICS values were designated at the nonweighted means of the carbon and nitrogen coordinates on the peripheral positions of conjugated macrocycles. In addition, NICS values were also calculated on centers of other local cyclic structures as depicted in the figures.

Table S1 Summary of DFT calculations of **1** and keto-form and enol-form of **2**

	1	**2**(keto-form)	**2**(enol-form)
Total energy (kJ/mol)	−1019450	−9484740.5	−9484723.8
HOMO-KUMO gap (eV)	1.99	1.97	2.00
NICS(0) (ppm)	−0.66	−10.91	+0.73

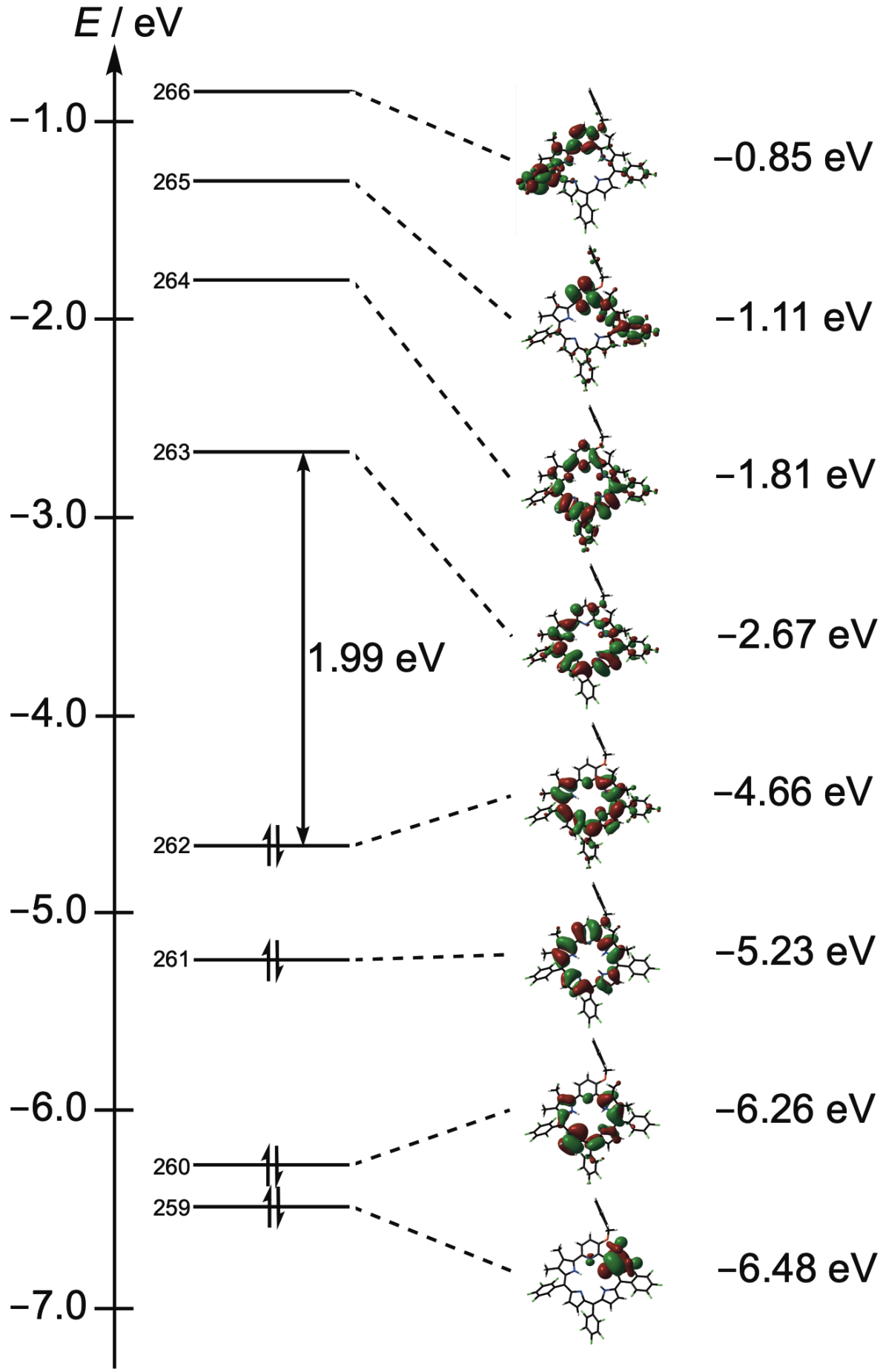


Fig. S19. Kohn-Sham orbital diagrams of **1** of the optimized structures.

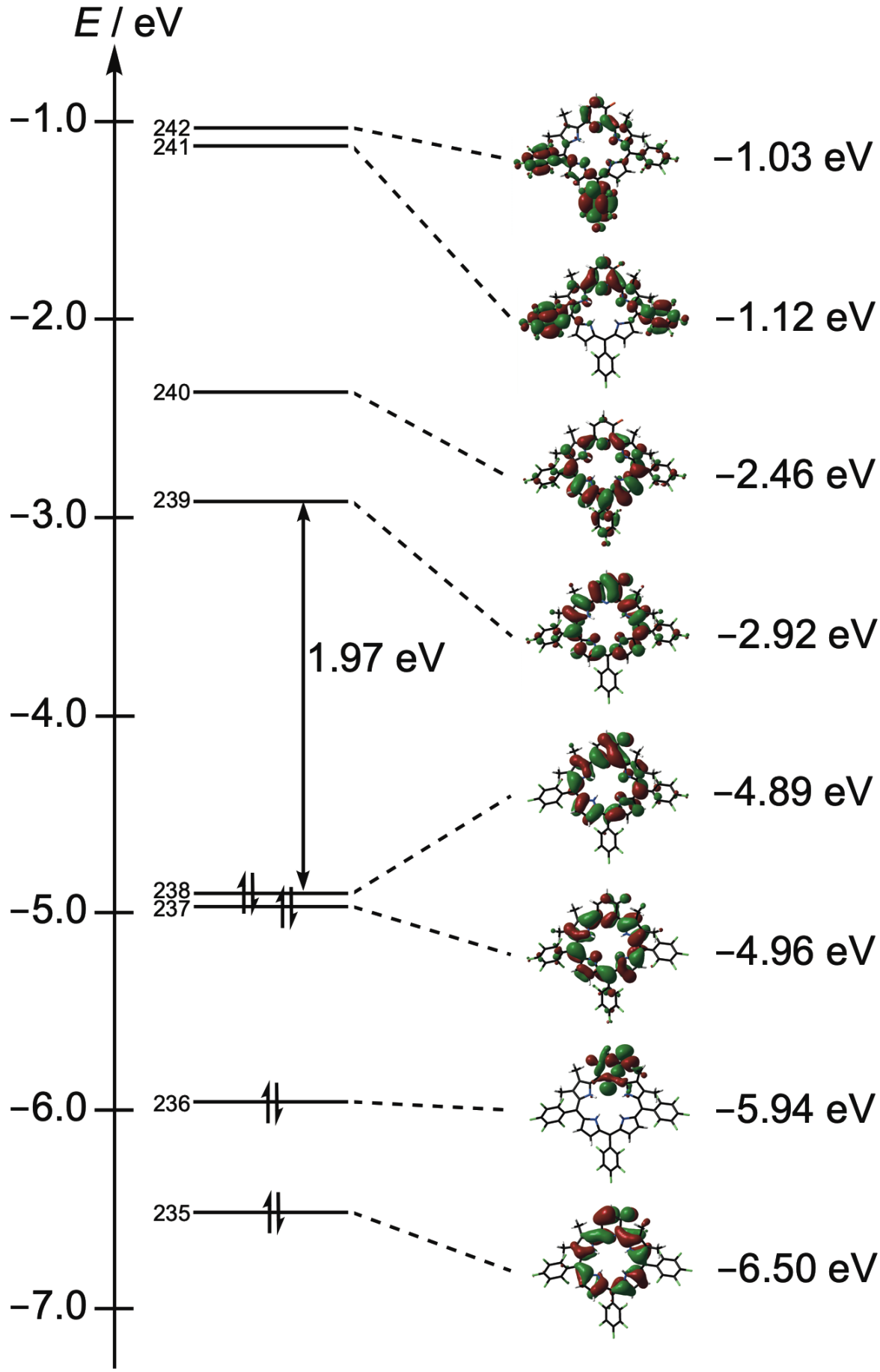


Fig. S20. Kohn-Sham orbital diagrams of keto-form of **2** of the optimized structures.

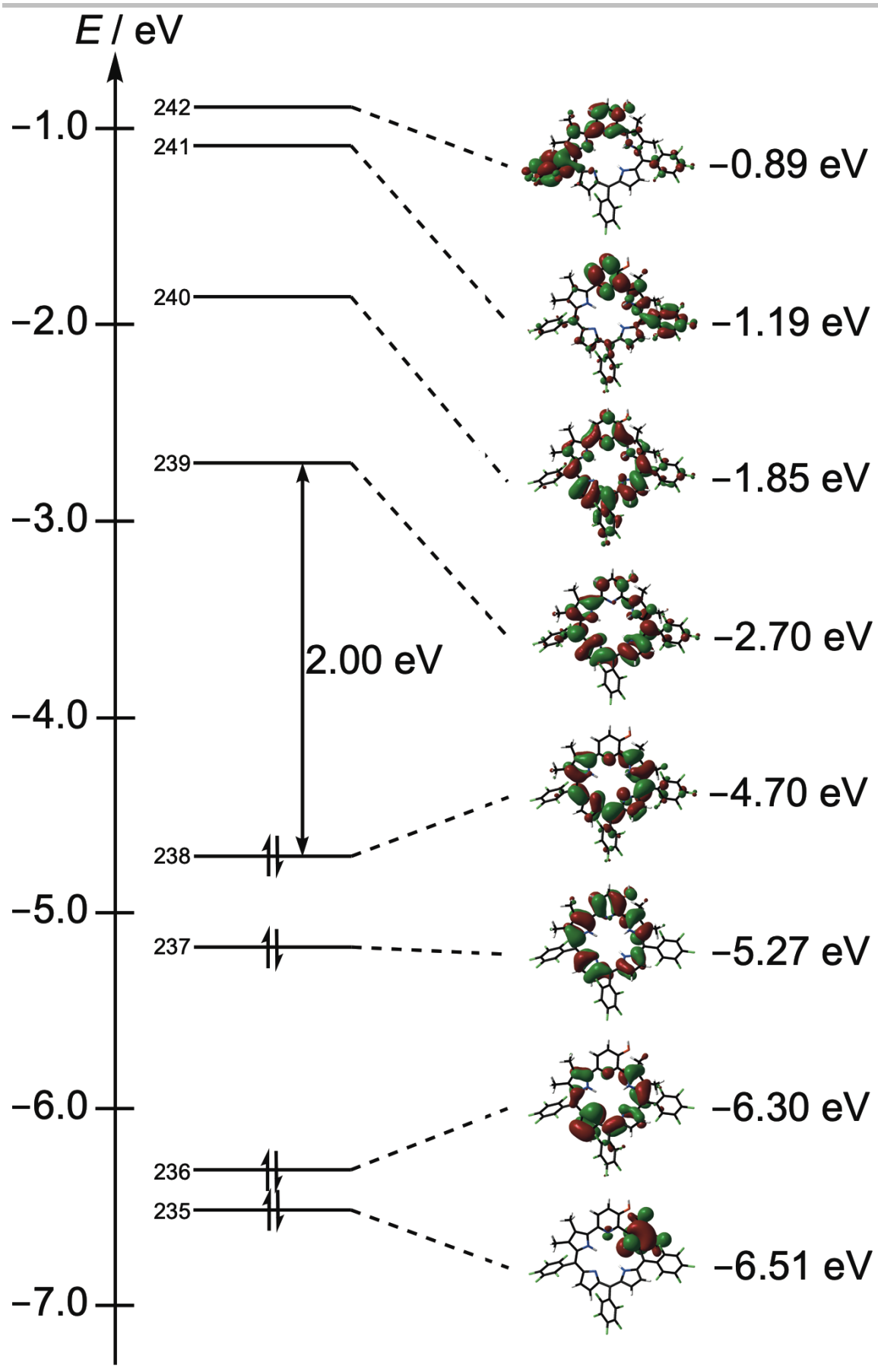
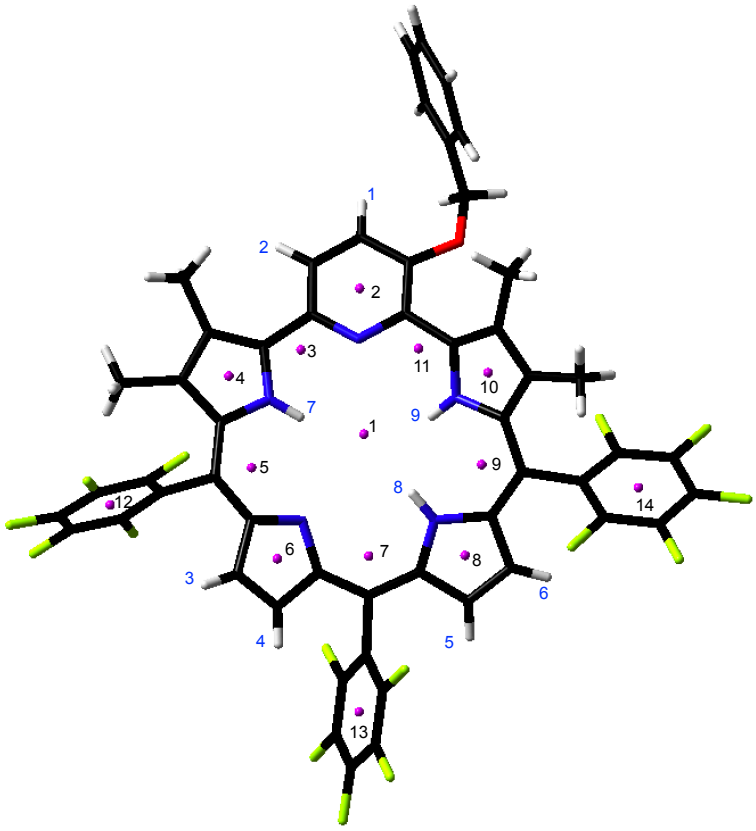
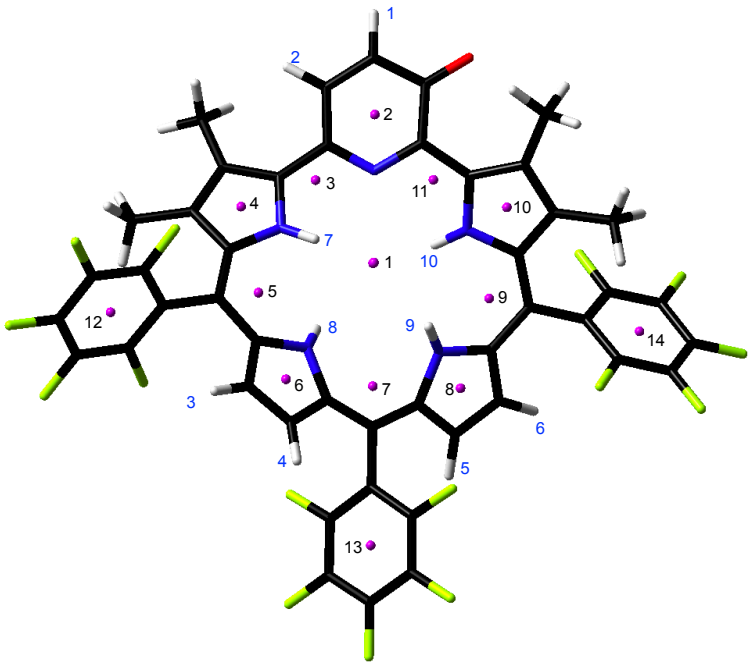


Fig. S21. Kohn-Sham orbital diagrams of enol-form of **2** of the optimized structures.



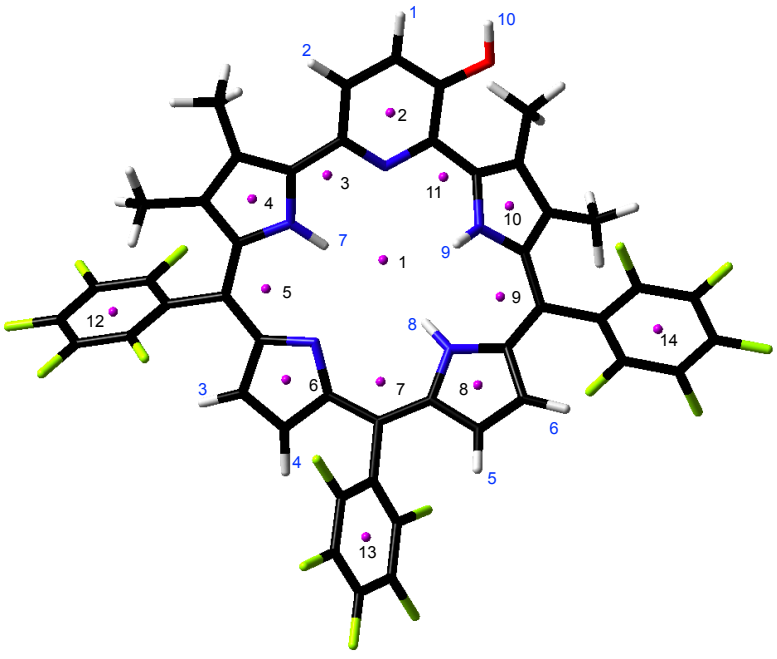
position	NICS (ppm)	^{1}H	δ (ppm)
1	–0.66	1	4.43
2	–9.73	2	5.04
3	–7.37	3	3.98
4	–10.33	4	3.23
5	–3.42	5	3.94
6	–2.69	6	4.19
7	–5.41	7	2.47
8	–6.28	8	–0.20
9	–6.17	9	0.53
10	–11.30		
11	–10.59		
12	–15.29		
13	–15.10		
14	–15.00		

Fig. S22. NICS values at various positions and simulated chemical shifts of **1** based on the optimized structure.



position	NICS (ppm)	^{1}H	δ (ppm)
1	–10.91	1	7.77
2	+4.08	2	9.56
3	–23.45	3	7.77
4	–14.23	4	7.90
5	–19.30	5	7.85
6	–14.99	6	7.87
7	–19.54	7	6.10
8	–14.64	8	–6.98
9	–19.33	9	–7.00
10	–13.44	10	–6.64
11	–24.09	11	–0.59
12	–14.08		
13	–13.99		
14	–14.05		

Figure S23. NICS values at various positions and simulated chemical shifts of keto-form of **2** based on the optimized structure.



position	NICS (ppm)	^{1}H	δ (ppm)
1	+0.73	1	7.04
2	–9.98	2	8.11
3	–8.12	3	6.56
4	–10.61	4	6.18
5	–3.14	5	6.40
6	–3.09	6	6.54
7	–5.70	7	7.65
8	–6.24	8	4.29
9	–6.05	9	4.84
10	–11.84	10	4.33
11	–10.32		
12	–15.12		
13	–14.92		
14	–14.81		

Figure S24. NICS values at various positions and simulated chemical shifts of enol-form of **2** based on the optimized structure.

6. References

[S1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009.**