

Supporting Information

***meso*-Alkyl Substituted *meso-meso* Linked Diporphyrins and *meso*-Alkyl Substituted *meso-meso*, β - β , β - β Triply Linked Diporphyrins**

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General

All reagents and solvents were of the commercial reagent grade and used without further purification except where noted. Dry toluene was obtained by distillation over CaH₂. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-400) and size exclusion gel permeation chromatography (Bio-Red Bio-Beads S-X1, packed with CHCl₃ or THF in a 4 x 100 cm gravity flow column).

5-(4-Methoxycarbonylbutyl)dipyrromethane. (DM3)

A mixture of methyl 6-oxohexanoate (2.58 g, 17.9 mmol) and pyrrole (50 mL) was degassed by bubbling with argon for 5 min, and then trifluoroacetic acid (0.134 mL, 1.81 mmol) was added. The reaction mixture was stirred for 20 min at room temperature. After the reaction was quenched with addition of a 0.1 M NaOH aqueous solution, the resulting mixture was diluted with ethyl acetate and washed with water twice. After the organic layer was dried over anhydrous Na₂SO₄, the solvent was removed under reduced pressure, and the unreacted pyrrole was removed by vacuum distillation. The residue was purified by silica-gel column chromatography with hexane:ethyl acetate = 4:1 solution as an eluent. Recrystallization from dichloromethane/hexane gave a colorless solid in 52% (2.48g, 9.52 mmol) yield. ¹H NMR (CDCl₃) δ 1.35 (m, 2H), 1.66 (m, 2H), 1.97 (m, 2H), 2.28 (m, 2H), 3.65 (s, 3H, OCH₃), 4.00 (t, J = 7.8 Hz, 1H), 6.05 (m, 2H), 6.14 (m, 2H), and 7.85 ppm (br, 2H). ESI HRMS obsd m/z 261.1591 ([M+H]⁺), calcd for C₁₅H₂₁O₂N₂⁺ 261.1598; mp 90 - 91 °C.

5,15-Dihexylporphyrin. (1)

A solution of *meso*-free dipyrromethane (**DM1**) (1.07 g, 7.43 mmol) and heptanal (0.843 g, 7.38 mmol) in CH₂Cl₂ (1.4 L) was degassed by argon for 5 min in a 2 L round-bottom flask, to which was added trifluoroacetic acid (0.055 mL, 0.743 mmol). The mixture was stirred overnight at room temperature and then DDQ (2.54 g, 11.2 mmol) was added. The mixture was stirred for additional 1 h, and then quenched with triethylamine and filtered through a short alumina column. The solvent was removed and purification by silica-gel column chromatography with CH₂Cl₂ gave 5,15-dihexyl substituted porphyrin in 20% yield (351 mg, 0.734 mmol). ¹H NMR (CDCl₃) δ -2.92 (br s, 2H), 0.95 (t, J = 7.7 Hz, 6H), 1.42 (m, J = 7.3 Hz, 4H), 1.54 (m, J = 7.8 Hz, 4H), 1.83 (m, J = 7.3 Hz, 4H), 2.57 (m, J = 7.8 Hz, 4H), 5.01 (m, J = 8.2 Hz, 4H), 9.43 (d, J = 4.6 Hz, 4H), 9.59 (d, J = 4.6 Hz, 4H), and 10.2

ppm (s, 2H); UV-vis (CHCl_3) λ_{max} = 403, 503, 535, and 577 nm; ESI HRMS obsd m/z 479.3172 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{32}\text{H}_{38}\text{N}_4^+$ 479.3168; mp >300 °C decomp.

AgPF₆-promoted oxidation of zinc(II) 5,15-dihexylporphyrin

A solution of **Zn-1** (49.8 mg, 91.9 μmol) in CHCl_3 was shielded from light and cooled to 0°C. A solution of AgPF_6 (0.36 mL, 0.12 M solution in acetonitrile) was added and the mixture was stirred. After 2 h, the reaction was quenched with water. The organic phase was washed with water and dried over anhydrous Na_2SO_4 . The solvent was removed by a rotary evaporator. The residue was dissolved in CHCl_3 and treated with a solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in methanol, and the mixture was refluxed for 2 h. The reaction mixture was quenched with saturated $\text{NaHCO}_3(\text{aq})$, and extracted with CHCl_3 . The combined organic extract was washed with water and dried over anhydrous Na_2SO_4 . The solvent was removed by a rotary evaporator. Size-exclusion column chromatography (SEC) with CHCl_3 as an eluent gave recovered monomer (18.7 mg, 42%), dimer (2.6 mg, 6%) and other oligomers (<1% respectively). The diporphyrin fraction was found to be a 4.5:1 mixture of *meso-meso* linked diporphyrin **2** and *meso- β* linked diporphyrin **3** by the ^1H -NMR (Supporting Figure 3) and FAB-MS measurements (Figure 4). FAB-MS (free-base) obsd m/z 954.82, calcd for $\text{C}_{64}\text{H}_{74}\text{N}_8$ 954.60.

5,10,15-Trihexyl zinc(II)-porphyrin. (Zn-4)

A solution of *meso*-free dipyrromethane (**DM1**) (1.18 g, 8.08 mmol), *meso*-hexyl dipyrromethane (**DM2**) (1.89 g, 8.18 mmol) and heptanal (2.24 mL, 16.4 mmol) in dichloromethane (1.6 L) was degassed by argon for 5 min in a 2 L round- flask, to which was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.66 mL, 2.5 M

solution in CH₂Cl₂). The mixture was stirred for 15 min at room temperature and was added DDQ (5.58 g, 24.5 mmol). After an additional stirring for 1 h the reaction was quenched with triethylamine and filtered through a short alumina column. The solvent was removed by a rotary evaporator and the residue was purified by silica-gel column chromatography with ethyl acetate:hexane = 1:10 solution as an eluent gave 5,10,15-trihexylporphyrin **4** as the second fraction. Then, the product was dissolved in CHCl₃, and a saturated solution of Zn(OAc)₂·2H₂O in methanol was added to the solution. The resulting mixture was refluxed for 2 h. After the complete metalation was confirmed by MALDI TOF-MS and UV analyses, the mixture was poured into water and extracted with CHCl₃ twice. The organic layer was dried over anhydrous Na₂SO₄ and evaporated. Recrystallization with CHCl₃/methanol afforded **Zn-4** as purple solids in 8% yield (418 mg, 0.668 mmol). ¹H NMR (CDCl₃) δ 0.98 (m, 9H), 1.43 (m, 6H), 1.54 (m, 6H), 1.83 (m, 6H), 2.46 (m, 6H), 4.69–4.75 (m, 6H), 9.06 (d, *J* = 4.6 Hz, 2H), 9.28–9.34 (m, 6H) and 9.62 ppm (s, 2H). UV-vis (CHCl₃) λ_{max}(ε) = 415 (365000) and 549 (13200) nm. ESI HRMS obsd *m/z* 659.2837 ([M + Cl]⁺), calcd for C₃₈H₅₀N₄ZnCl 659.2864; mp >300 °C decomp.

***meso*-Hexyl *meso-meso* linked zinc(II)-diporphyrin (**5**).^[1]**

A solution of **4** (188 mg, 0.298 mmol) in CHCl₃ (150 mL) with 0.5% *N,N*-dimethylacetamide was degassed by argon for 5 min, then AgPF₆ (2.98 mL, 0.12 M solution in acetonitrile) was added. The mixture was stirred for 1 h at room temperature, then quenched with water. The solution was extracted with CHCl₃ three times. The combined organic extract was washed with water and brine, and dried over anhydrous Na₂SO₄. SEC chromatography with CHCl₃ as an eluent afforded **5** in 70% yield (131 mg, 0.105 mmol). ¹H NMR (CDCl₃) δ 0.88–1.02 (m, 18H), 1.36–1.61 (m, 24H), 1.82–1.94 (m, 12H), 2.57–2.65 (m, 12H), 4.92–5.07 (m, 12H), 8.08 (d, *J* = 4.6 Hz, 4H), 9.21 (d, *J* = 5.0 Hz, 4H), 9.61 (d, *J* = 4.6

Hz, 4H), and 9.65 ppm (d, $J = 4.6$ Hz, 4H); UV-vis (THF) $\lambda_{\text{max}}(\epsilon) = 421$ (186000), 458 (281000), 572 (41200), and 616 nm (17500); ESI HRMS obsd m/z 1250.6211 ($[M]^+$), calcd for $C_{76}H_{94}N_8Zn_2^+$ 1250.6158; mp $>300^\circ\text{C}$ decomp.

***meso*-Hexyl *meso-meso*, β - β , β - β , triply linked zinc(II)-diporphyrin (**6**).^[2]**

A solution of **5** (29.7 mg, 23.8 μmol) in dry toluene (50 mL) was degassed by argon and warmed up to 50°C . Then DDQ (27.2 mg, 120 μmol) and $\text{Sc}(\text{OTf})_3$ (79.5 mg, 160 μmol) were added and the resulting mixture was stirred at 50°C . After 12 h, the mixture was diluted with THF and filtered through a short neutral alumina. The elution was evaporated and the residue was dissolved in THF with pyridine. Separation by SEC chromatography with THF as an eluent and recrystallization from THF/methanol gave **6** (18.6 mg, 14.5 μmol) as light red solids in 61% yield. ^1H NMR ($\text{C}_5\text{D}_5\text{N}$): δ 0.80 (m, 18H), 1.23 (m, 12H), 1.49 (m, 24H), 2.11 (m, 12H), 3.88–4.00 (m, 6H), 8.37 (s, 4H), 8.55 (d, $J = 5.0$ Hz, 4H), and 8.60 ppm (d, $J = 4.6$ Hz, 4H). UV-vis (THF) $\lambda_{\text{max}}(\epsilon) = 418$ (71600), 480 (41600), 556 (67000), 578 (67000), and 1127 nm (24800). ESI HRMS obsd m/z 1246.5855 ($[M]^+$), calcd for $C_{76}H_{90}N_8Zn_2^+$ 1246.5845; mp: $>240^\circ\text{C}$ decomp.

5,10,15-Tris(4-methoxycarbonylbutyl) zinc(II)-porphyrin (Zn-7).

A solution of *meso*-free dipyrromethane (1.10 g, 7.53 mmol), **DM3** (1.96 g, 7.53 mmol), methyl 6-oxohexanoate (2.16 g, 15.0 mmol) in dichloromethane (1.6 L) was degassed by argon for 5 min in a 2 L round- flask, to which was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.60 mL, 2.5 M solution in CH_2Cl_2). The mixture was stirred for 15 min at room temperature and was added DDQ (5.13 g, 22.6 mmol). The mixture was

stirred for an additional 1 h and then quenched with triethylamine and filtered through a short alumina column. Purification by silica-gel column chromatography using dichloromethane:ethyl acetate = 10:1 as an eluent afforded purple solid as the second fraction. Then, the crude product was dissolved in CHCl_3 , and a saturated solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in methanol was added to the solution. The resulting mixture was refluxed for 2 h. After the complete metalation was confirmed by MALDI TOF-MS and UV analyses, the mixture was poured into water and extracted with CHCl_3 twice. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. Recrystallization with CHCl_3 /hexane afforded **Zn-7** as purple solids in 6% yield (342 mg, 0.478 mmol). ^1H NMR (CDCl_3) δ 2.17 (m, 6H), 2.53 (m, 12H), 3.69 (m, 15H), 4.96 (m, 6H), 9.28 (d, J = 4.6 Hz, 2H), 9.52 (m, J = 4.6 Hz, 6H), and 9.88 ppm (s, 1H); UV-vis (CHCl_3) $\lambda_{\text{max}}(\epsilon)$ = 416 (276000), 549 (11600) and 591 (4500) nm; ESI HRMS obsd m/z 737.2274 ($[\text{M} + \text{Na}]^+$), calcd for $\text{C}_{38}\text{H}_{42}\text{O}_6\text{N}_4\text{ZnNa}^+$ 737.2288; mp >300 °C decomp.

***meso*-(4-Methoxycarbonylbutyl) *meso-meso* linked zinc(II)-diporphyrin (8).**

A solution of **7** (100 mg, 140 μmol) and AgPF_6 (1.40 mL, 0.120 M in acetonitrile solution) was stirred for 30 min under argon atmosphere. Purification by SEC chromatography gave **8** in 61% yield (61.0 mg, 42.6 μmol). ^1H NMR (CDCl_3): δ 2.11–2.23 (m, 12H), 2.43–2.65 (m, 24H), 3.58–3.71 (m, 18H), 4.93–5.07 (m, 12H), 8.08 (d, J = 4.6 Hz, 4H), 9.19 (d, J = 4.6 Hz, 4H), 9.57 (d, J = 4.6 Hz, 4H), and 9.61 ppm (d, J = 4.6 Hz, 4H); UV-vis (CHCl_3) $\lambda_{\text{max}}(\epsilon)$ = 422 (194000), 456 (159000) and 564 (26000) nm; ESI HRMS obsd m/z 1453.4455 ($[\text{M} + \text{Na}]^+$), calcd for $\text{C}_{76}\text{H}_{82}\text{N}_8\text{O}_{12}\text{Zn}_2\text{Na}^+$ 1453.4508; mp >300 °C decomp.

***meso*-(4-(2-Ethylhexyloxy)carbonylbutyl) *meso-meso* linked zinc(II)-diporphyrin (9).**

A solution of **8** (60.0 mg, 41.9 μmol), 2-ethyl-1-hexanol (0.15 mL, 0.96 mmol), and a distannoxane catalyst (10.1 mg, 9.62 μmol) in toluene was refluxed under argon atmosphere for 5 days. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was dissolved to CHCl_3 and purification by silica-gel column chromatography with CHCl_3 gave **9** in 80 % yield as a purple solid. Without further purification, the product was used for the next reaction: FAB MS obsd m/z 2018.98, calcd for $\text{C}_{118}\text{H}_{166}\text{N}_8\text{O}_{12}\text{Zn}_2$ 2018.12.

meso-(4-(2-Ethylhexyloxy)carbonylbutyl) meso-meso, β - β , β - β , triply linked zinc(II)-diporphyrin (10).

This compound was subjected to the conditions similar to those of the compound **6**. A solution of **9** (40.0 mg, 19.8 μmol), DDQ (22.5 mg, 99.1 μmol) and $\text{Sc}(\text{OTf})_3$ (68.4 mg, 139 μmol) were stirred for 12 h at 50 $^\circ\text{C}$. Purification by silica-gel column chromatography with CHCl_3 gave **10** as a red solid in 38% yield (15.1 mg, 7.49 μmol). ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 0.91–3.54 (m, 72H), 4.03–4.09 (m, 12H), 7.56 (br, 4H), 7.89 (br, 4H), and 7.93 ppm (br, 4H); UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\epsilon) = 400$ (139000), 470 (65600), 543 (133000), 948 (21500), and 1059 nm (22600); ESI HRMS obsd m/z 2016.0963 ($[\text{M} + \text{H}]^+$), calcd for $\text{C}_{118}\text{H}_{163}\text{N}_8\text{O}_{12}\text{Zn}_2^+$ 2016.0969; mp >300 $^\circ\text{C}$ decomp.

References

- (1) Yoshida, N.; Aratani, N.; Osuka, A. *Chem. Commun.* **2000**, 197-198.
- (2) Tsuda, A.; Osuka, A. *Science* **2001**, 293, 79.

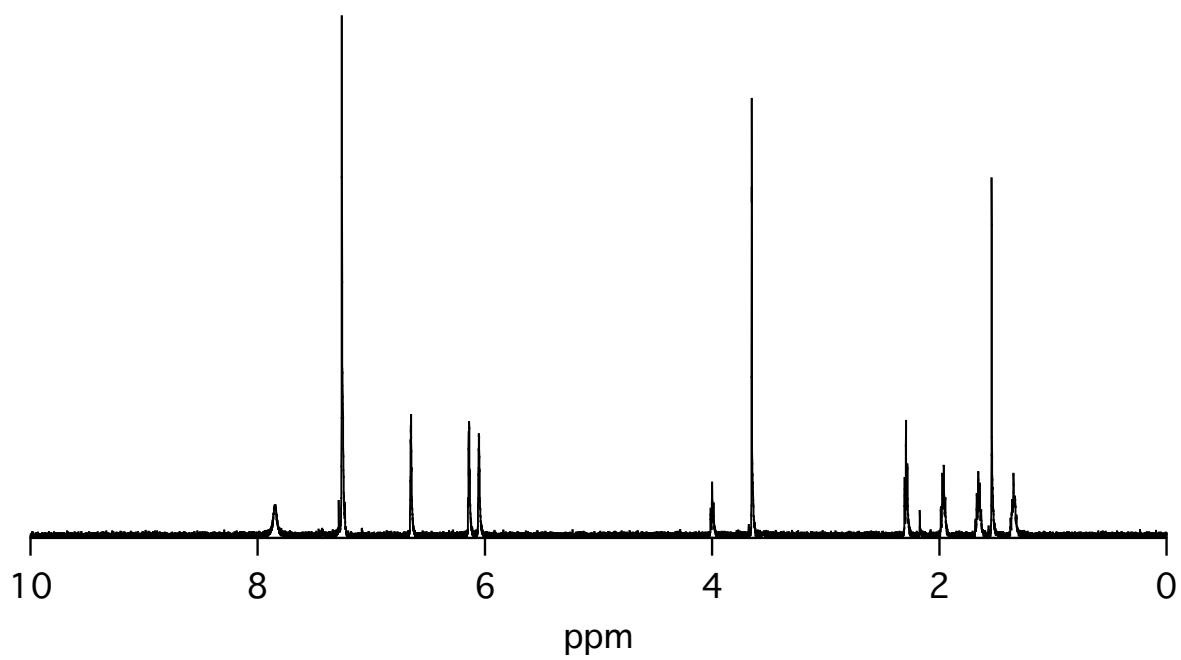


Figure S1. ^1H NMR spectrum of **DM3** in CDCl_3

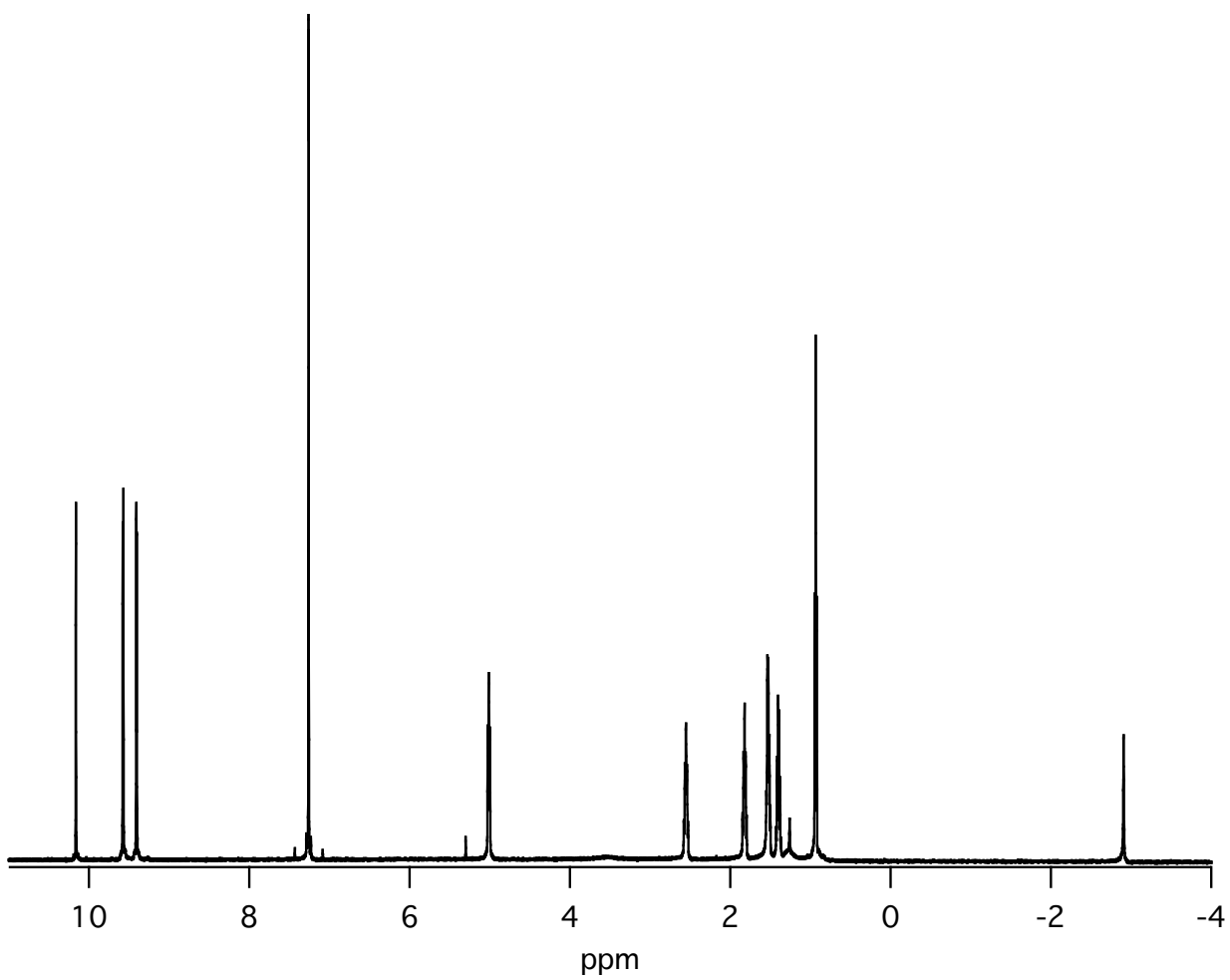


Figure S2. ^1H NMR spectrum of **1** in CDCl_3 .

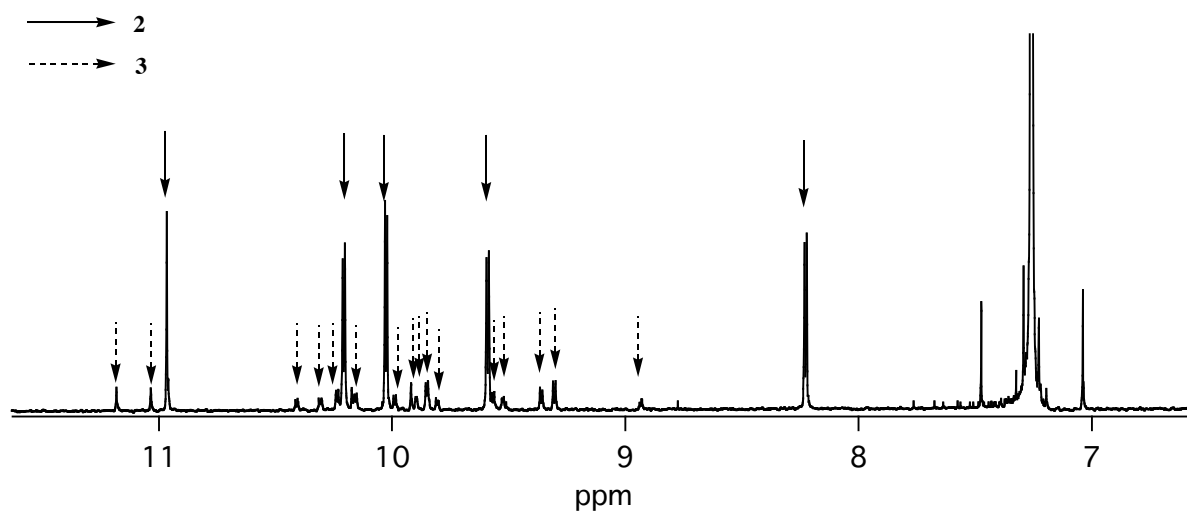


Figure S3. ^1H NMR spectrum of the diporphyrin products (**2** and **3**).

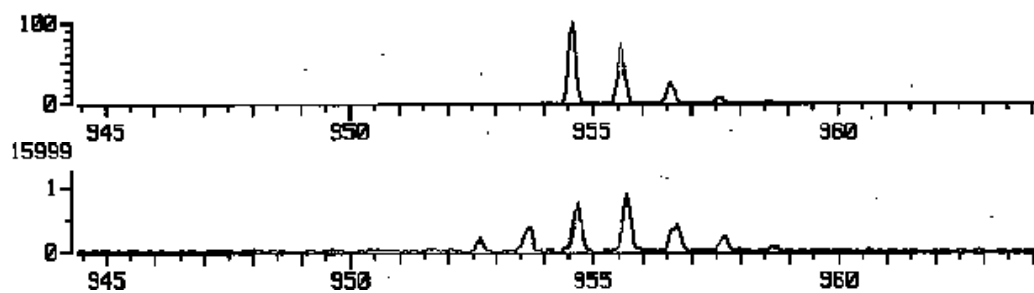


Figure S4. FAB-MS of the diporphyrin products (**2** and **3**).

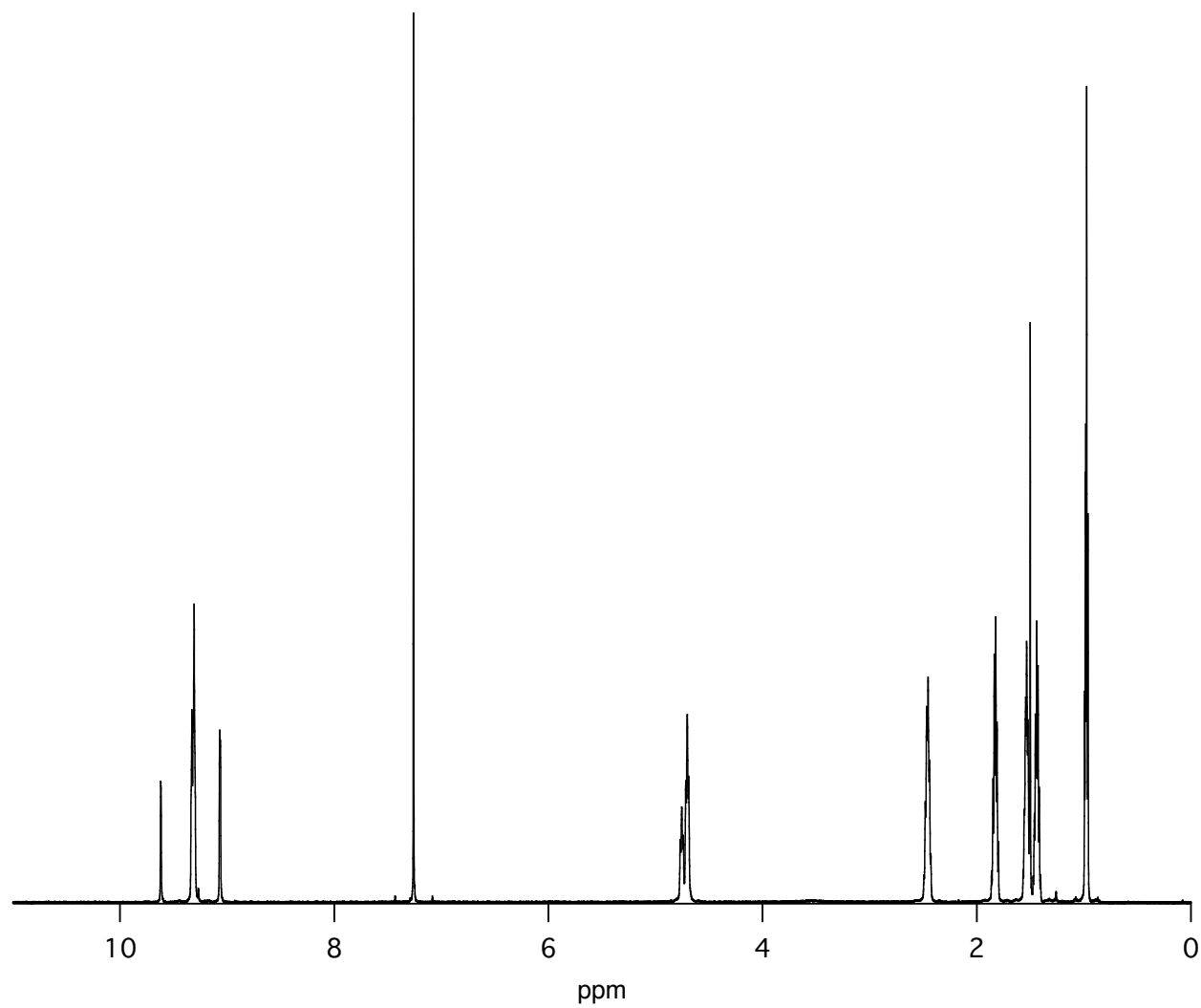


Figure S5. ^1H NMR spectrum of **Zn-4** in CDCl_3 .

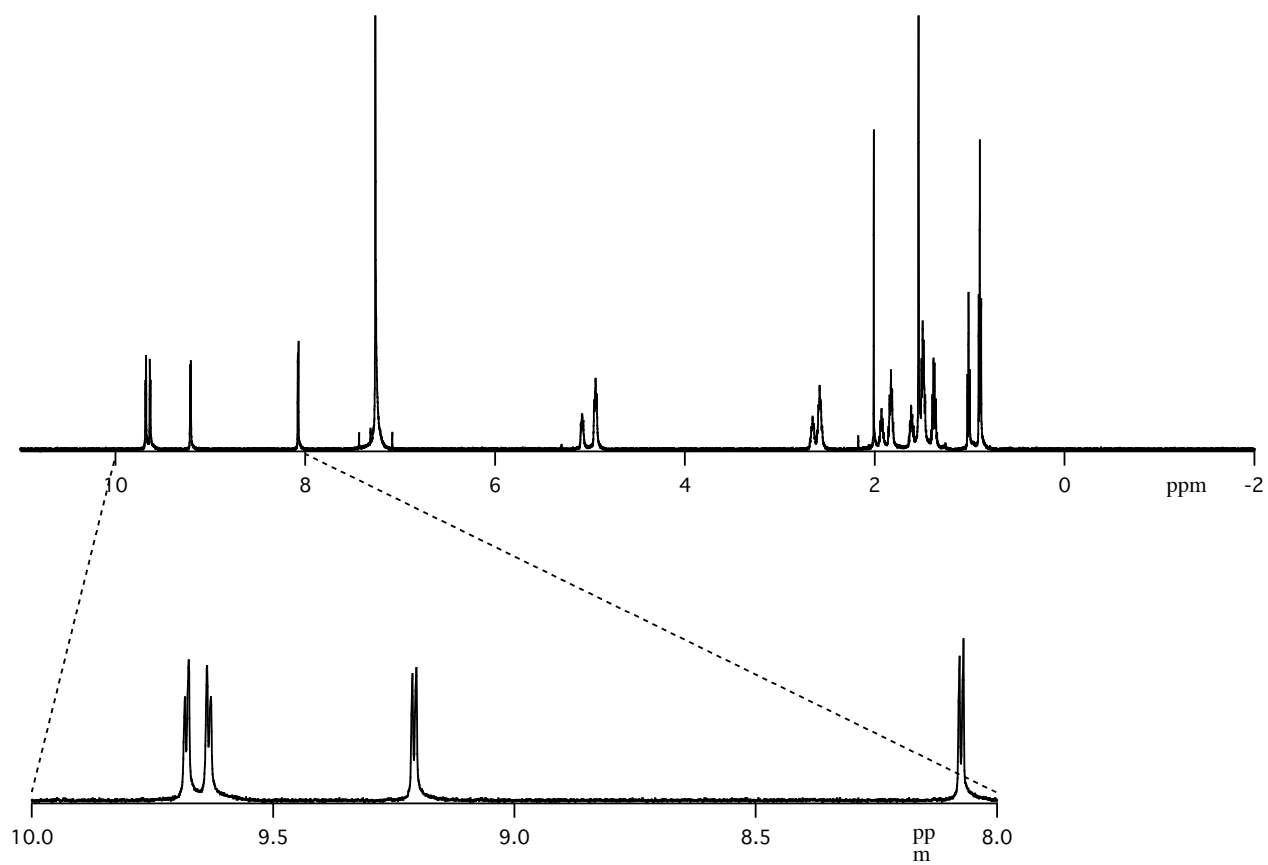


Figure S6. ^1H NMR spectrum of **5** in CDCl_3 .

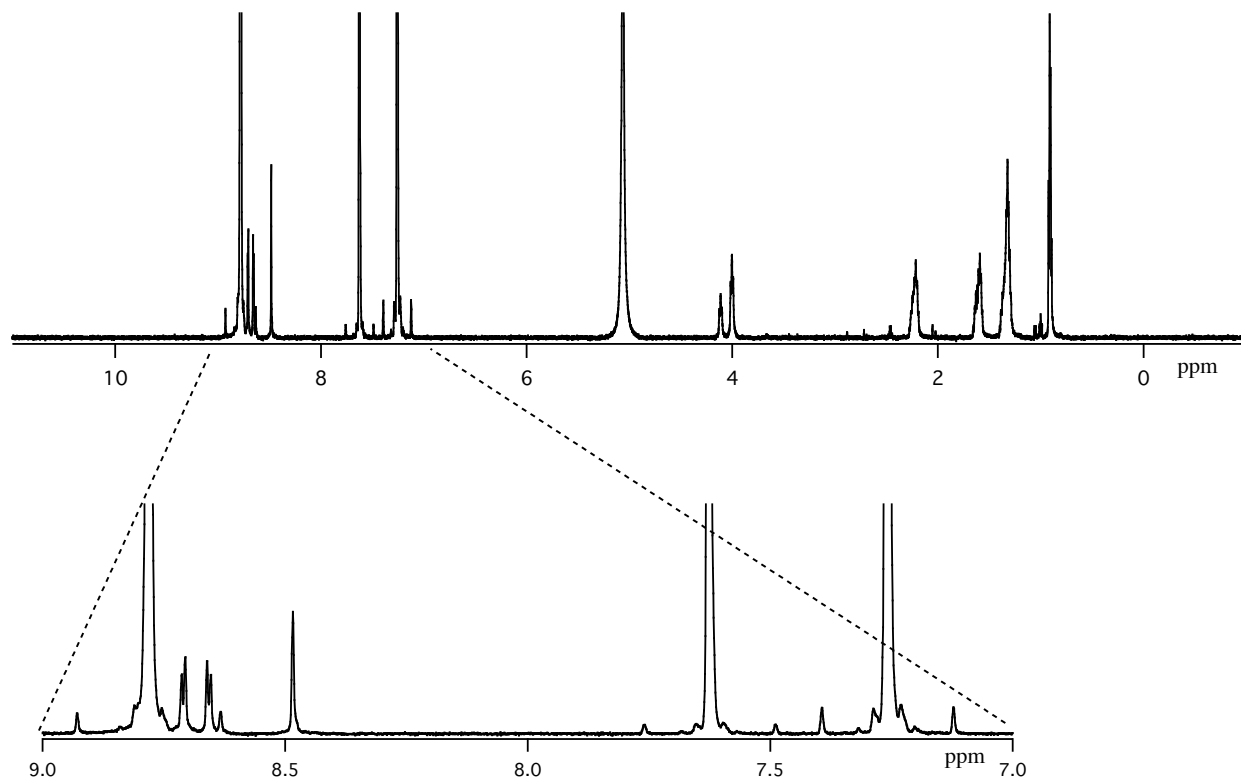


Figure S7. ^1H NMR spectrum of **6** in $\text{pyridine-}d_5$.

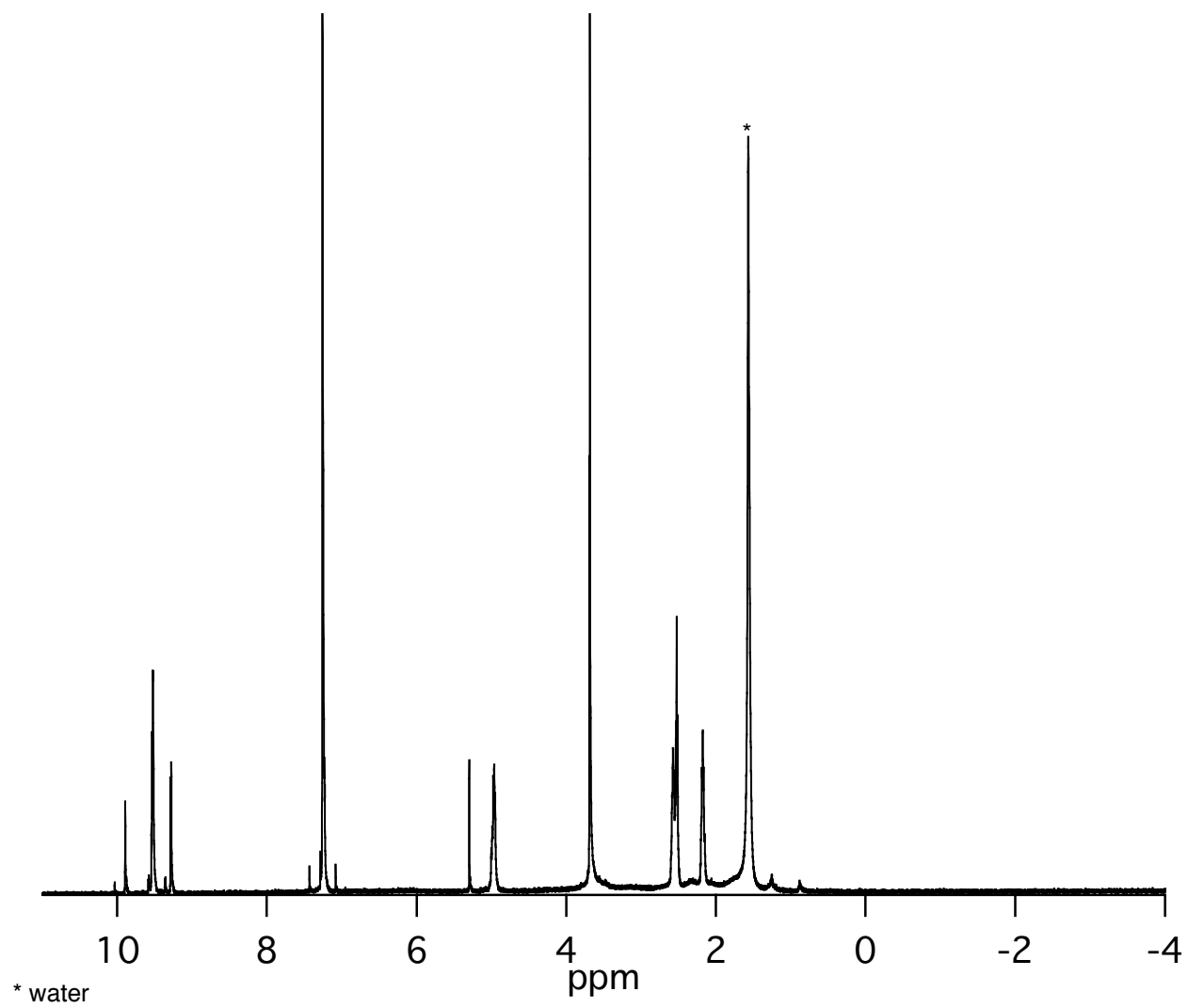


Figure S8. ^1H NMR spectrum of **Zn-7** in CDCl_3 .

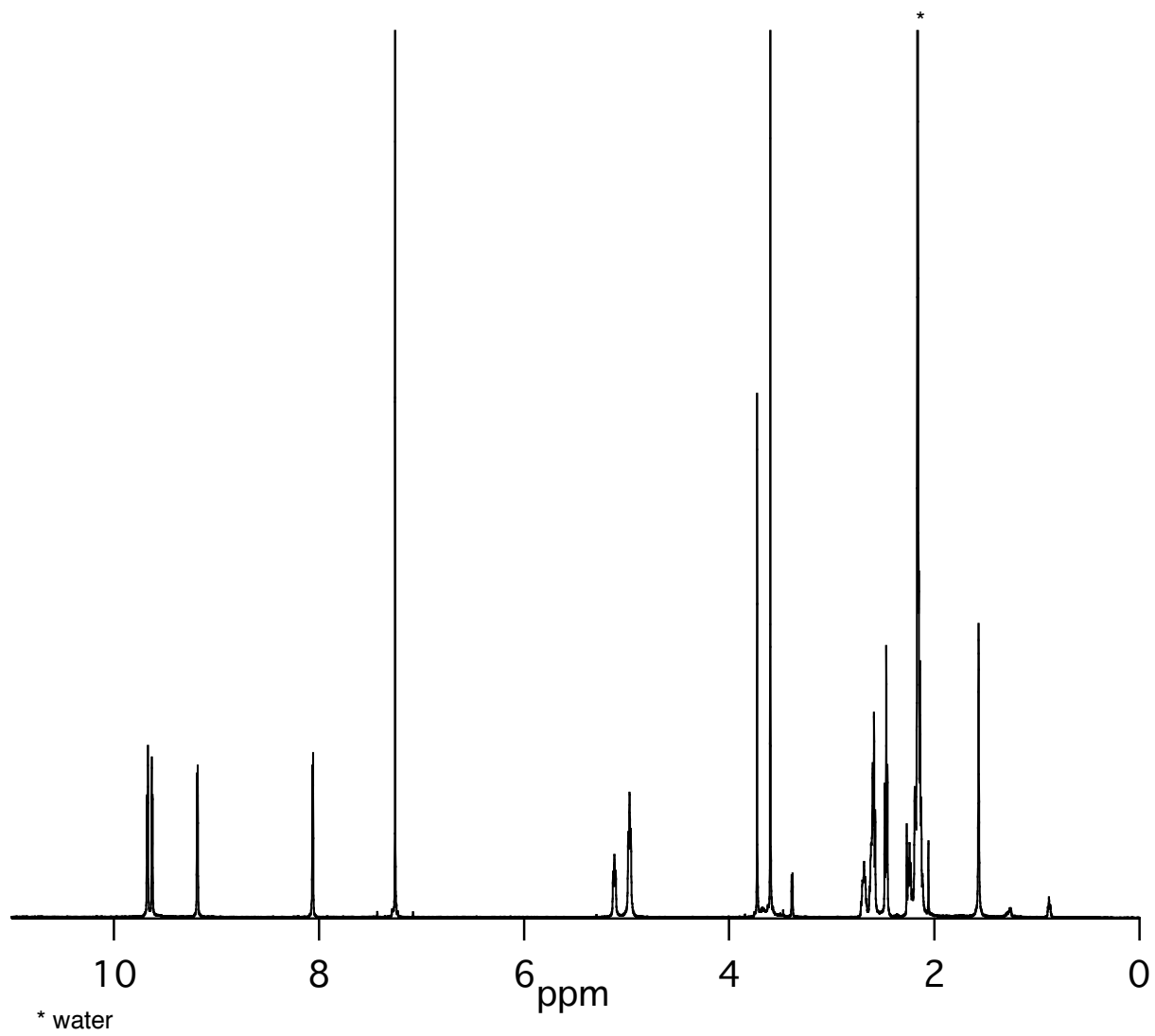


Figure S9. ^1H NMR spectrum of **8** in CDCl_3 .

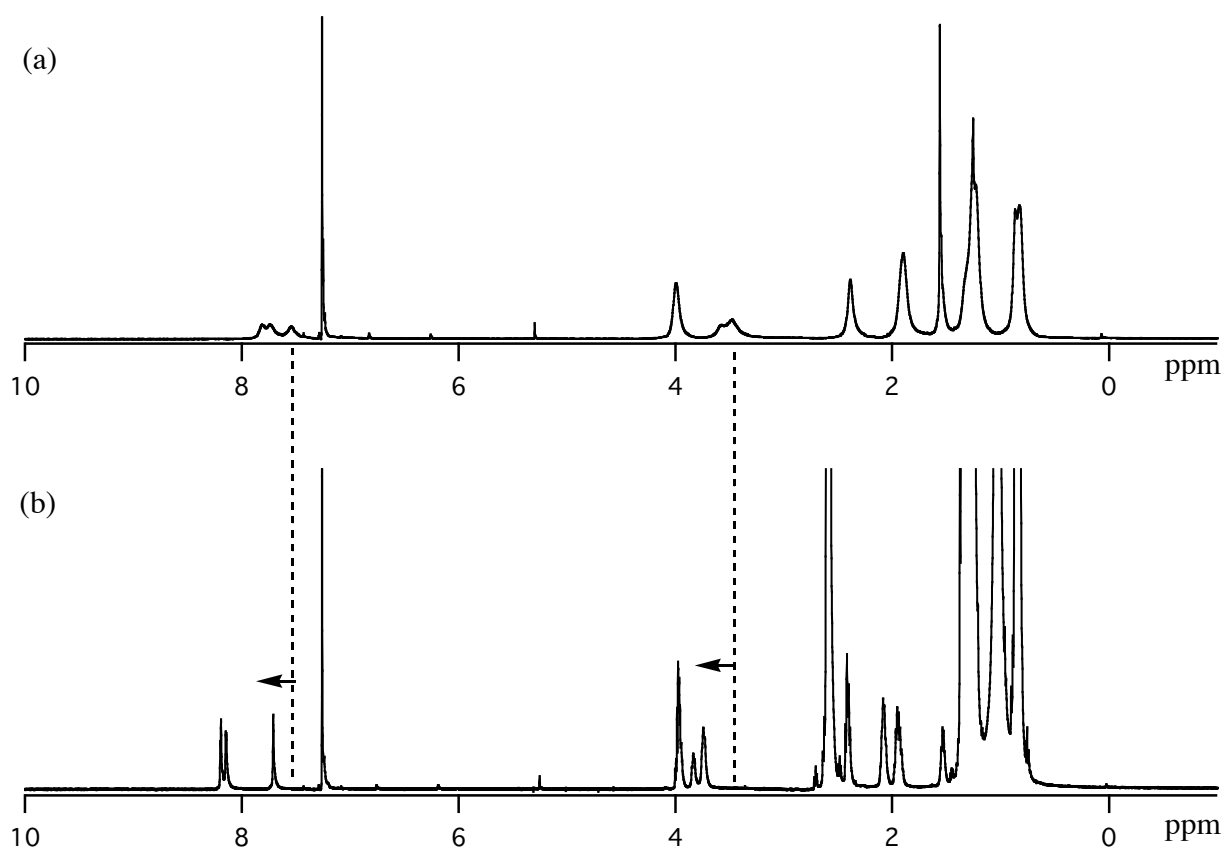


Figure S10. ^1H NMR spectra of **10** (a) in CDCl_3 and (b) in CDCl_3 containing butylamine.