# *Supporting Information*

## Bis(zinc porphyrin) as a Bidentate CD-Sensitive Host Molecule: Direct Determination of Absolute Configuration of Mono-alcohols

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## Table of Contents:

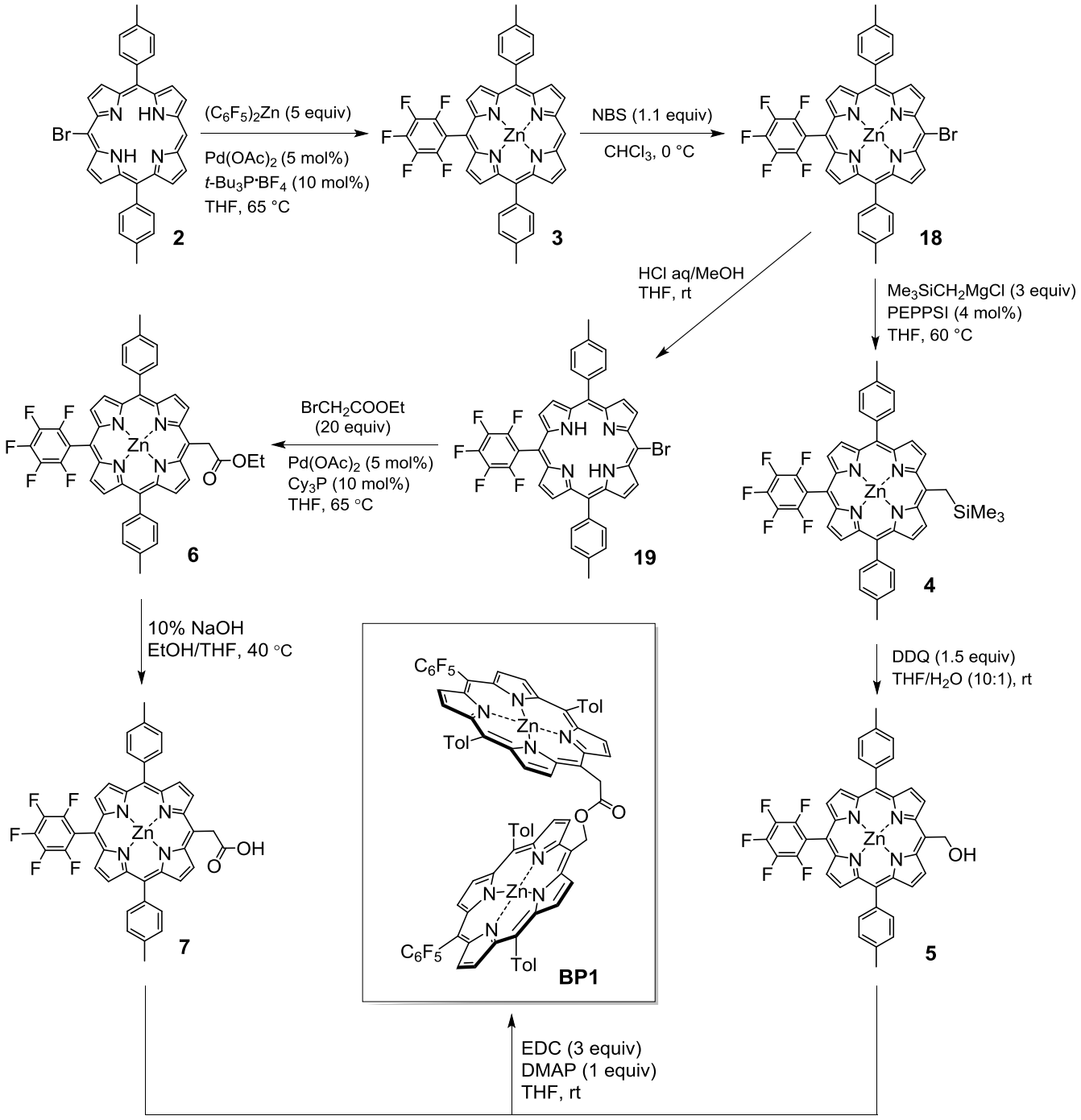
## 1. General Information

$^{1}$H and $^{13}$C-NMR spectra were recorded at rt on a JEOL JNM-LA500 spectrometer using perdeuterated solvents as internal standards. Chemical shifts of $^{1}$H and $^{13}$C spectra are given in ppm relative to residual protiated solvent and relative to the solvent respectively: $CHCl_3$ ($\delta$ = 7.26) for $^{1}$H-NMR and relative to the central resonance of $CDCl_3$ ($\delta$ = 77.0) for $^{13}$C-NMR. $^{19}$F-NMR spectra were recorded at rt on a on a JEOL JNM-ECA500 spectrometer using benzotrifluoride as an external standard. The chemical shift values are expressed as $\delta$ values (ppm) and the couple constants values (J) are in Hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. UV−Visible spectra were recorded on a JASCO V-660 dual-beam grating spectrophotometer with a 1 cm cell. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on JEOL JNM-DX302 spectrometer. The CD spectra were recorded on a JASCO J-820 spectrophotometer with a 1 cm cell at 25 °C in 1% $CH_2Cl_2$/hexane (scan speed: 50 nm/min, scan number: 5–15, bandwidth: 2 nm).

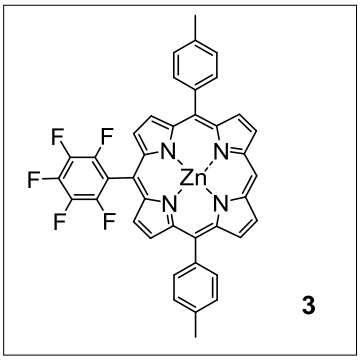
Reactions involving moisture sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques and glassware that was flame-dried and cooled under argon before use. Dry THF was purchased for the reactions and used without further desiccation. $CH_2Cl_2$ and *n*-hexane were distilled over $CaH_2$, and used immediately. 10-Bromo-5,15-di(p-tolyl)porphyrin **2** was prepared as described in the literature.[1] Other chemicals were purchased from commercial sources and used as received unless stated otherwise.

[1] Takanami, T.; Hayashi, M.; Chijimatsu, H.; Inoue, W.; Inoue, N.; Suda, K. *Org. Lett.* **2005**, *7*, 3937.

## 2. Synthesis of Bis(zinc porphyrin) BP1



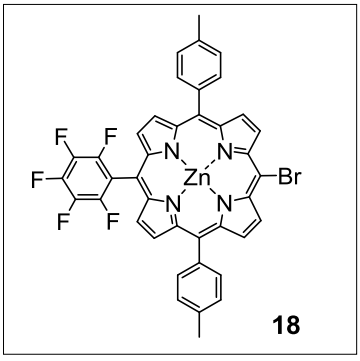
**Preparation of [5,15-di(*p*-tolyl)-10-pentafluorophenylporphyrinato]zinc(II) 3.**[2] An oven-dried



**3**

100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with a free base bromoporphyrin **2** (105 mg, 0.185 mmol), bis(pentafluorophenyl)zinc (370 mg, 0.9 mmol, 5 equiv), $Pd(OAc)_2$ (2.1 mg, 9.3 μmol, 5 mol%), and *t*-$Bu_3P{\cdot}HBF_4$ (5.4 mg, 18.5 μmol, 10 mol%). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (25 mL) was added. The mixture was stirred at 60 °C for 1 h, having been monitored by TLC (hexane/toluene 1:1). Upon completion of the reaction, the mixture was allowed to reach room temperature. The reaction mixture was diluted with $CH_2Cl_2$ (50 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/toluene, 1:1). The first red purple band eluted was collected, and taken to dryness. Recrystallization from hexane/$CH_2Cl_2$ gave the pure product; red-purple solid; 128.0 mg, 95% yield; $R_f$ = 0.61 (hexane/toluene, 1:1); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.76 (1H, s), 9.10 (2H, d, $J$ = 4.6 Hz), 9.03 (2H, d, $J$ = 4.6 Hz), 8.91 (4H, d, $J$ = 4.6 Hz), 8.05 (4H, d, $J$ = 7.6 Hz), 7.57 (4H, d, $J$ = 7.6 Hz), 2.74 (6H, s); $^{13}$C-NMR ($CDCl_3$, 125 MHz) $\delta$ 150.6, 150.3, 149.2, 148.9, 146.6 (2C, d, $J_{CF}$ = 245.2 Hz), 141.7 (1C, d, $J_{CF}$ = 255.5 Hz), 139.3, 137.4 (2C, d, $J_{CF}$ = 252.4 Hz), 137.3, 134.5, 133.4, 132.5, 131.8, 129.5, 127.4, 121.2, 117.6, 106.9, 101.2, 21.5; $^{19}$F-NMR ($CDCl_3$, 466 MHz) $\delta$ −138.7 (2F, dd, $J_{FF}$ = 24.5, 8.5 Hz), −155.7 (1F, t, $J_{FF}$ = 21.0 Hz), −164.2 (2F, td, $J_{FF}$ =23.6, 8.5 Hz); IR (KBr) 3113, 3086, 3024, 2920, 2873, 2804, 1724, 1489, 1319, 1180, 1065, 995, 791 cm$^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 418.0 (5.6), 547.0 (4.2) nm; HRMS (EI) [$M^+$] calcd for $C_{40}H_{23}F_5N_4Zn$: 718.1134, found 718.1138.

**Preparation of [10-bromo-5,15-di(*p*-tolyl)-20-pentafluorophenylporphyrinato]zinc(II) 18.** To a



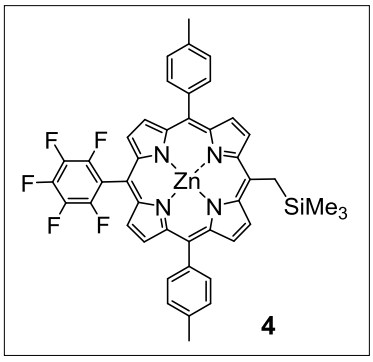
**18**

solution of a porphyrin **3** (340 mg, 0.47 mmol) in $CHCl_3$ (100 mL) was added NBS (*N*-bromosuccinamide) (93 mg, 0.52 mmol) at 0 °C. The reaction mixture was stirred for 2 h and quenched with acetone (10 mL). The solvent was evaporated to dryness. Column chromatography on silica gel (hexane/toluene 1:1) followed by recrystallization from hexane/$CH_2Cl_2$ gave the pure compound; purple solid; 362 mg, 97% yield; $R_f$ = 0.44 (hexane/toluene, 1:1); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.70 (2H, d, $J$ = 4.9 Hz), 8.98 (2H, d, $J$ = 4.6 Hz), 8.97 (2H, d,

[2] Sugita, N.; Hayashi, S.; Ishii, S.; Takanami, T. *Catalysis*, **2013**, *3*, 839.

$J$ = 4.9 Hz), 8.78 (2H, d, $J$ = 4.6 Hz), 8.04 (4H, d, $J$ = 7.6 Hz), 7.56 (4H, d, $J$ = 7.6 Hz), 5.83 (2H, s), 2.71 (6H, s); $^{13}$C-NMR ($CDCl_3$, 125 MHz) $\delta$ 150.4, 150.8, 149.9, 149.6, 146.5 (2C, d, $J_{CF}$ = 252.4 Hz), 141.8 (1C, d, $J_{CF}$ = 249.3 Hz), 139.1, 137.6, 137.5 (2C, d, $J_{CF}$ = 259.7 Hz), 134.4, 134.0, 133.4, 133.3, 129.9, 127.4, 122.5, 117.1, 106.3, 101.8, 21.5; $^{19}$F-NMR ($CDCl_3$, 466 MHz) $\delta$ −138.8 (2F, dd, $J_{FF}$ = 23.5, 7.5 Hz), −154.7 (1F, t, $J_{FF}$ = 21.4 Hz), −163.9 (2F, td, $J_{FF}$ =23.5, 8.6 Hz); IR (KBr) 3019, 2920, 2862, 1489, 1331, 1207, 1176, 1111, 1068, 991, 944 cm$^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 425.0 (5.7), 558.0 (4.3) nm; HRMS (EI) [$M^+$] calcd for $C_{40}H_{22}F_5BrN_4Zn$: 796.0239, found 796.0238.

**Preparation of [5,15-di(*p*-tolyl)-10-pentafluorophenyl-20-(trimethylsilyl)methylporphyrinato] zinc(II) 4.** Prepared according to a literature precedent with slight modification.[3] An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with *meso*-bromoporphyrin **18** (200 mg, 0.25 mmol) and PEPPSI ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl) palladium(II) dichloride, 10 mg, 7.8 μmol, 4 mol %). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (35 mL) was added. To the solution was added a 1.0 M THF solution of $Me_3SiCH_2MgCl$ (0.75 mL, 0.75 mmol, 3 equiv) at rt. The mixture was stirred at 60 °C for 1 h, having been monitored by TLC (hexane/THF, 2:1). Upon completion of the reaction, the mixture was allowed to reach room temperature. The reaction mixture was diluted with $CH_2Cl_2$ (500 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was charged on the top of a silica gel column packed with hexane/$CH_2Cl_2$/$Et_3N$ (10:1:0.5), and the column was eluted with hexane/$CH_2Cl_2$ (5:1 to 2:1). The fractions containing product were collected and concentrated under a reduced pressure. The resulting crude product was recrystallized from $CH_2Cl_2$/hexane to give the pure product; purple solid; 210 mg, 99% yield; $R_f$ = 0.54 (hexane/THF, 2:1); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.35 (2H, d, $J$ = 4.6 Hz), 8.94 (2H, d, $J$ = 4.6 Hz), 8.88 (2H, d, $J$ = 4.6 Hz), 8.71 (2H, d, $J$ = 4.6 Hz), 8.06 (4H, d, $J$ = 7.6 Hz), 7.55 (4H, d, $J$ = 7.6 Hz), 4.55 (2H, s), 2.71 (6H, s), -0.01 (9H, s); $^{13}$C-NMR ($CDCl_3$, 125 MHz) $\delta$ 150.4, 150.3, 150.0, 149.6, 146.8 (2C, d, $J_{CF}$ = 240.0 Hz), 141.8 (1C, d, $J_{CF}$ = 251.4 Hz), 139.9, 137.7 (2C, d, $J_{CF}$ = 253.5 Hz), 137.5, 134.6, 133.9, 131.8, 129.9, 129.3, 127.6, 124.4, 121.7, 117.8, 99.5, 27.4, 21.8, -0.5; $^{19}$F-NMR ($CDCl_3$, 466 MHz) $\delta$ −138.8 (2F, dd, $J_{FF}$ = 24.2, 8.5 Hz), −155.5 (1F, t, $J_{FF}$ = 21.3 Hz), −164.3 (2F, td, $J_{FF}$ =24.2, 8.5 Hz); IR (KBr) 3020, 2954, 2866, 1338, 1250, 1211, 1149, 1072, 760, cm$^{-1}$;

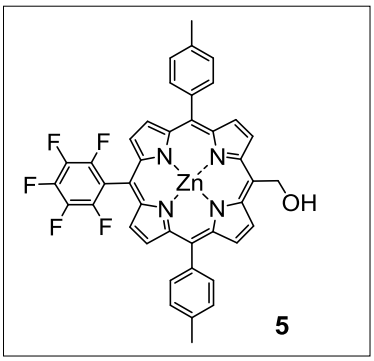


**4**

[3] Sugita, N.; Hayashi, S.; Hino, F.; Takanami, T. *J. Org. Chem.* **2012**, *77*, 10488.

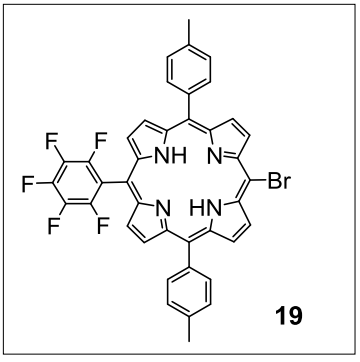
UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 426.0 (4.9), 558.0 (3.5) nm; HRMS (EI) [$M^+$] calcd for $C_{44}H_{33}F_5N_4SiZn$: 804.1686, found 804.1682.

**Preparation of [5,15-di(*p*-tolyl)-10-hydroxymethyl-20-pentafluorophenylporphyrinato]zinc(II) 5.**[3] To a solution of silylmethylporphyrin **4** (105 mg, 0.13 mmol) in a mixed solution of $H_2O$/THF (1:10, 110 mL) was added DDQ (45 mg, 0.2 mmol, 1.5 equiv.) at rt. After being stirred at rt for 0.5 h, the reaction was quenched with $Et_3N$ (2 mL). Then, the mixture was diluted with $CH_2Cl_2$ (200 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel ($CH_2Cl_2$) followed by recrystallization from $CH_2Cl_2$/hexane gave the pure product; red-purple solid; 97 mg, 99% yield; $R_f$ = 0.15 (2:1 hexane/THF); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.65 (2H, d, $J$ = 4.6 Hz), 9.01 (2H, d, $J$ = 4.6 Hz), 8.93 (2H, d, $J$ = 4.6 Hz), 8.73 (2H, d, $J$ = 4.6 Hz), 8.04 (4H, d, $J$ = 7.6 Hz), 7.53 (4H, d, $J$ = 7.6 Hz), 6.97 (2H, d, $J$ = 6.1 Hz), 3.16 (1H, t, $J$ = 6.0 Hz), 2.69 (6H, s); $^{13}$C-NMR ($CDCl_3$+THF-8d, 125 MHz) $\delta$ 150.7, 150.4, 150.3, 149.0, 146.6 (2C, d, $J_{CF}$ = 245.2 Hz), 141.6 (1C, d, $J_{CF}$ = 263.8 Hz), 139.9, 137.3 (2C, d, $J_{CF}$ = 249.3 Hz), 137.1, 134.4, 133.1, 132.9, 129.3, 128.8, 127.1, 121.3, 117.8, 117.3, 100.9, 64.7, 21.4; $^{19}$F-NMR ($CDCl_3$+THF-8d, 466 MHz) $\delta$ −138.7 (2F, dd, $J_{FF}$ = 24.6, 8.6 Hz), −154.9 (1F, t, $J_{FF}$ = 21.4 Hz), −164.1 (2F, td, $J_{FF}$ =24.6, 8.6 Hz); IR (KBr) 3521, 3105, 3024, 2924, 2858, 1493, 1335, 1342, 1207, 1148, 1072, 995, cm$^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 422.0 (5.7), 553.0 (4.5) nm; HRMS (EI) [$M^+$] m/z calcd for $C_{41}H_{25}F_5N_8OZn$: 748.1240, found 748.1237.



**5**

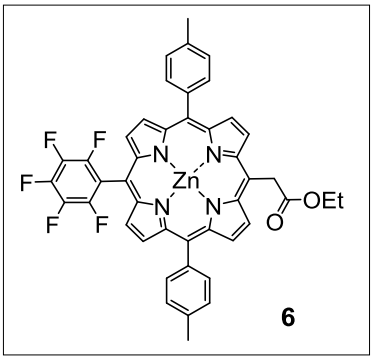
**Preparation of 10-bromo-5,15-di(*p*-tolyl)-10-pentafluorophenylporphyrin 19.** A mixture of MeOH (65 mL) and conc. HCl (7.5 mL) was added dropwise to a partially dissolved solution of a zincated *meso*-bromoporphyrin **18** (200 mg, 0.25 mmol) in THF (ca. 50 μL) at rt. The mixture was stirred at rt for 10 min, diluted with THF/$Et_2O$ (2:1, 50 mL), and then neutralized with saturated sodium bicarbonate. The solution was washed with brine, and the organic layer was dried over $MgSO_4$ and concentrated in vacuo. The resulting solid was purified by recrystallization from hexane/$CH_2Cl_2$ to give the pure free base **19** as a purple solid; 175 mg, 95% yield; $R_f$ = 0.44 (hexane/$CH_2Cl_2$, 1:1); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.66 (2H, d, $J$ = 4.6 Hz), 8.90 (2H, d, $J$ = 4.6 Hz), 8.89 (2H, d, $J$ = 4.6 Hz), 8.69 (2H, d, $J$ = 4.6 Hz), 8.05 (4H, d, $J$ = 7.6 Hz), 7.56 (4H, d, $J$ = 7.6 Hz), 2.71 (6H, s) , -2.75 (2H, s); $^{13}$C-NMR ($CDCl_3$, 125 MHz) $\delta$ 146.5 (2C, d,



**19**

$J_{CF}$ = 249.3 Hz), 142.3 (1C, d, $J_{CF}$ = 248.3 Hz), 138.7, 138.6, 138.1, 137.7 (2C, d, $J_{CF}$ = 254.5 Hz), 134.8, 132.9 (8C, br), 129.3, 127.9, 121.9, 116.8, 105.3, 101.1, 21.8; $^{19}$F-NMR ($CDCl_3$, 466 MHz) $\delta$ −138.4 (2F, dd, $J_{FF}$ = 24.6, 6.1 Hz), −154.2 (1F, t, $J_{FF}$ = 21.0 Hz), −163.7 (2F, td, $J_{FF}$ =24.7, 7.4 Hz); IR (KBr) 3321, 3024, 2916, 1493, 1346, 1218, 1180, 1133, 1030, 980, 925 cm$^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 419 (5.6), 516.0 (4.2), 551.0 (3.9), 595.0 (3.7), 650.0 (3.6) nm; HRMS (FAB) $[M+H]^+$ calcd for $C_{40}H_{22}F_5BrN_4$: 735.1183, found 735.1185.

**Preparation of [5,15-di(*p*-tolyl)-10-(2-ethoxycarbonylethyl)-20-pentafluorophenylrinato] zinc(II) 6.**[4] An oven-dried 200 ml sealable Schlenk flask equipped with a magnetic stirring bar was charged with Zn dust (2.1 g, 32 mmol) and CuCl (318 mg, 3.2 mmol). The reaction vessel was evacuated and flushed with argon (three times), and dry THF (8 mL) was added. The Zn(Cu) couple suspension was refluxed for 1.5 h using an oil-bath. During this activation period, another oven-dried 10 mL sealable flask was evacuated and flushed with argon (three times) and then charged dry THF (6 mL) and ethyl bromoacetate (700 μL, 6.7 mmol). The reaction vessel containing Zn(Cu) couple was removed from the oil-bath. To initiate the reaction, ca. 1/10 of the THF solution of ethyl bromoacetate was added via a syringe to the stirred Zn(Cu) couple suspension while the suspension was still hot. The rest of the solution was added in such a rate as to maintain a gentle reflux (ca. 5 min). The reaction mixture was stirred and refluxed until its color to black (ca. 2 h). To the resulting ca. 0.5 M THF solution of the zinc enolate was added dropwise a mixture of bromoporphyrin **19** (210 mg, 0.28 mmol), $Pd(OAc)_2$ (7 mg 10 mol%), and $PCy_3$ (17 mg, 20 mol%) in THF (80 mL) over a period of 5 min. The reaction mixture was heated under argon at 65 °C for 10 h, and then allowed to reach rt. The reaction mixture was filtered through a filter paper, diluted with THF/$Et_2O$ (2:1, 20 mL), and washed with aqueous $NH_4Cl$ and brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. Column chromatography on silica gel ($CH_2Cl_2$) followed by recrystallization from $CH_2Cl_2$/hexane to give the pure compound; purple solid; 212 mg, 94% yield; $R_f$ = 0.48 ($CH_2Cl_2$); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.45 (2H, d, $J$ = 4.6 Hz), 9.01 (2H, d, $J$ = 4.6 Hz), 8.98 (2H, d, $J$ = 4.6 Hz), 8.80 (2H, d, $J$ = 4.6 Hz), 8.05 (4H, d, $J$ = 7.9 Hz), 7.56 (4H, d, $J$ = 7.9 Hz), 5.83 (2H, s), 4.12 (2H, q, $J$ = 7.0 Hz), 2.72 (6H, s), 1.14 (3H, t, $J$ = 7.0 Hz); $^{13}$C-NMR ($CDCl_3$, 125 MHz) $\delta$ 172.3, 150.4, 150.2, 150.1, 149.2, 146.6 (2C, d, $J_{CF}$ = 244.1 Hz), 141.4 (1C, d, $J_{CF}$ = 257.6 Hz), 139.1, 137.2 (2C, d, $J_{CF}$ = 253.5 Hz), 137.1, 134.1, 133.4, 132.8,

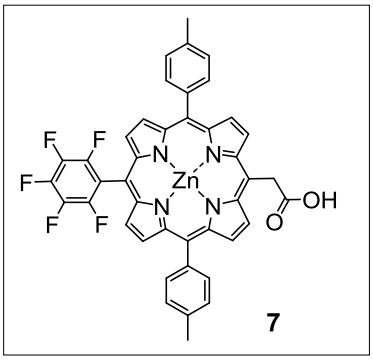


**6**

[4] Takanami, T.; Yotsukura, M.; Inoue, W.; Inoue, N.; Hino, F.; Suda, K. *Heterocycles*, **2008**, *76*, 439.

129.3, 129.2, 127.1, 121.5, 117.1, 112.3, 101.0, 61.0, 40.6, 21.3, 13.9; $^{19}$F-NMR ($CDCl_3$, 466 MHz) $\delta$ −138.7 (2F, dd, $J_{FF}$ = 22.8, 7.5 Hz), −155.0 (1F, t, $J_{FF}$ = 21.0 Hz), −164.1 (2F, td, $J_{FF}$ =24.7, 7.5 Hz); IR (KBr) 3113, 3024, 2981, 2927, 2866, 1732, 1497, 1446, 1338, 1300, 1257, 1211, 1149, 1076, 1037, 995, cm$^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 424.0 (5.7), 555.0 (4.3) nm; HRMS (EI) [$M^+$] calcd for $C_{44}H_{29}F_5N_4O_2Zn$: 804.1502, found 804.1507.

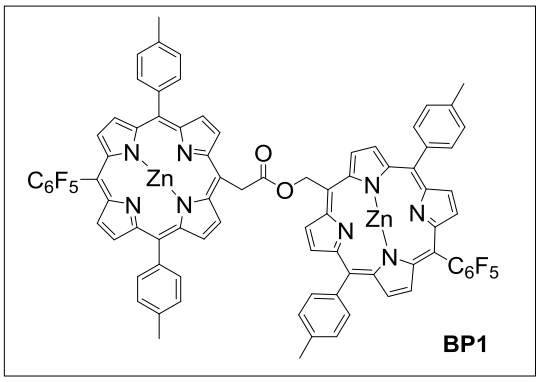
**Preparation of [5,15-di(*p*-tolyl)-10-carboxymethyl-20-pentafluorophenylporphyrinato]zinc(II)**



**7**

**7.** To a solution of [5,15-di(*p*-tolyl)-10-(2-ethoxycarbonylethyl)-20-pentafluorophenylporphyrinato] zinc(II) **6** (205 mg, 0.25 mmol) in EtOH/THF (2:1 vol/vol, 30 mL) was added 10% NaOHaq (10 mL). The suspension was stirred at 40 °C for 1.5 h, and then allowed to reach rt. The solution was diluted with THF/$Et_2O$ (2:1, 30 mL), and washed with aqueous $NH_4Cl$ and brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting soild was purified by recrystallization from $CH_2Cl_2$/hexane to give the pure compound; purple solid; 193 mg, 99% yield; $R_f$ = 0.15 (hexane/THF, 1:1); $^1$H-NMR ($CDCl_3$+THF-8d, 500 MHz) $\delta$ 9.54 (2H, d, $J$ = 4.9 Hz), 8.96 (2H, d, $J$ = 4.6 Hz), 8.90 (2H, d, $J$ = 4.9 Hz), 8.69 (2H, d, $J$ = 4.6 Hz), 8.03 (4H, d, $J$ = 7.6 Hz), 7.50 (4H, d, $J$ = 7.6 Hz), 6.05 (2H, s), 2.68 (6H, s); $^{13}$C-NMR ($CDCl_3$+THF-8d, 125 MHz) $\delta$ 174.3, 150.2, 150.1, 149.9, 149.0, 146.3 (2C, d, $J_{CF}$ = 246.2 Hz), 141.2 (1C, d, $J_{CF}$ = 252.4 Hz), 139.7, 137.0 (2C, d, $J_{CF}$ = 253.5 Hz), 136.7, 134.1, 132.9, 132.5, 128.89, 128.85, 126.8, 120.9, 117.6, 112.3, 99.9, 40.6, 21.2; $^{19}$F-NMR ($CDCl_3$+THF-8d, 466 MHz) $\delta$ −137.3 (2F, dd, $J_{FF}$ = 25.8, 7.9 Hz), −150.1 (1F, t, $J_{FF}$ = 19.8 Hz), −163.0 (2F, td, $J_{FF}$ =23.9, 8.0 Hz); IR (KBr) 3625, 3386, 3113, 3020, 2981, 2923, 2873, 1705, 1647, 1612, 1492, 1442, 1338, 1307, 1211, 1180, 1072, 995, cm$^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 424.0 (4.9), 555.0 (3.5) nm; HRMS (EI) [$M^+$] calcd for $C_{42}H_{25}F_5N_4O_2Zn$: 776.1189, found 776.1194.

**Preparation of bis(zinc porphyrin) BP1.** To a solution of carboxymethyl-substituted porphyrin **7** (75 mg, 0.096 mmol) and EDC (1-ethyl-3-(3-dimethyl-aminopropyl)carbodiimide hydrochloride, 54 mg, 0.3 mmol) in THF (30 mL) was added hydroxymethyl-substituted porphyrin **5** (60 mg, 0.08 mmol) at rt. The solution was stirred for 5 min, and then DMAP (*N*,*N*-dimethyl-4-aminopyridine, 10 mg, 0.08 mmol) was added. After stirring for 48 h at rt, the solution was diluted with THF/$Et_2O$ (2:1, 60 mL), and washed with brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. Column chromatography on silica gel (hexane/THF, 10:1 to 5:1) followed by recrystallization from $CH_2Cl_2$/hexane to give the pure compound; purple solid; 84 mg, 70% yield (based on **5**); $R_f$ = 0.4 (hexane/THF, 3:1); $^1$H-NMR ($CDCl_3$, 500 MHz) $\delta$ 9.38 (2H, d, $J$ = 4.9 Hz), 9.27 (2H, d, $J$ = 4.9 Hz), 8.94 (2H, d, $J$ = 4.6 Hz), 8.91 (2H, d, $J$ = 4.6 Hz), 8.81 (2H, d, $J$ = 4.6 Hz), 8.77 (2H, d, $J$ = 4.6 Hz), 8.54 (2H, d, $J$ = 4.6 Hz), 8.54 (2H, d, $J$ = 4.6 Hz), 7.73 (4H, d, $J$ = 7.6 Hz), 7.66 (4H, d, $J$ = 7.6 Hz), 7.51 (2H, s), 7.36 (4H, d, $J$ = 7.6 Hz), 7.25 (4H, d, $J$ = 7.6 Hz), 6.05 (2H, s), 2.65 (6H, s), 2.60 (6H, s); $^{13}$C-NMR ($CDCl_3$, 125 MHz) $\delta$ 171.3, 150.7, 150.5, 150.4, 150.3, 150.17, 150.16, 149.3, 149.0, 146.6 (2C, d, $J_{CF}$ = 248.3 Hz), 141.7 (1C, d, $J_{CF}$ = 257.6 Hz), 139.1, 139.0, 137.4 (2C, d, $J_{CF}$ = 254.5 Hz), 137.3, 137.1, 134.2, 134.1, 133.6, 133.5, 132.9, 132.6, 129.7, 129.5, 129.2, 129.0, 127.2, 127.1, 121.7, 121.5, 117.4, 117.3, 112.0, 111.3, 102.2, 101.3, 66.4, 41.0, 21.4, 21.3; $^{19}$F-NMR ($CDCl_3$, 466 MHz) $\delta$ −138.6 (2F, dd, $J_{FF}$ = 25.8, 8.0 Hz), −138.7 (2F, dd, $J_{FF}$ = 25.9, 8.0 Hz), −154.9 (1F, t, $J_{FF}$ = 20.8 Hz), −155.0 (1F, t, $J_{FF}$ = 21.3 Hz), −164.0 (2F, td, $J_{FF}$ =24.1, 8.0 Hz), −164.1 (2F, td, $J_{FF}$ =24.0, 8.0 Hz); IR (KBr) 3117, 3020, 2924, 2862, 2731, 1728, 1647, 1493, 1338, 1207, 1146, 1072, 991, 941 $cm^{-1}$; UV-Vis ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$) 422.0 (5.7), 426.0 (5.7), 554.0 (4.5) nm; HRMS (EI) [$M^+$] calcd for $C_{83}H_{48}F_{10}N_8O_2Zn_2$: 1506.2323, found 1506.2324.



## 3. Comparison of $^1$H NMR and UV-vis Spectra of Bis(zinc porphyrin) BP1 with Those of the Monomeric Counterparts 5 and 6

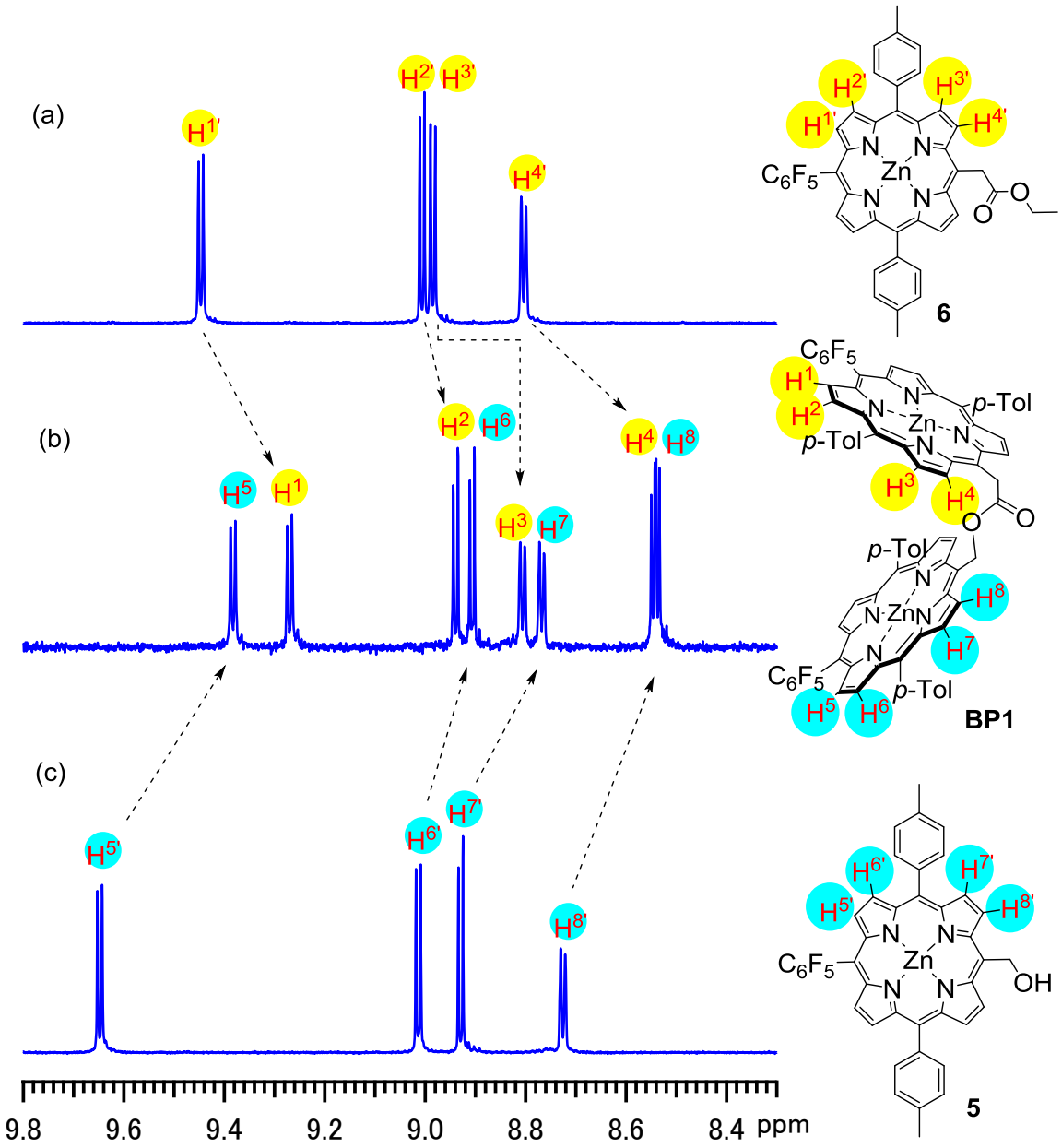



**Fig. S1** $^1$H NMR spectra ($CDCl_3$, rt) of (a) carboethoxymethyl-substituted zinc porphyrin **6**, (b) bis(zinc porphyrin) **BP1**, and (c) hydroxymethyl-substituted zinc porphyrin **5** in the region corresponding to the resonance of the β pyrrolic protons of the porphyrin rings.

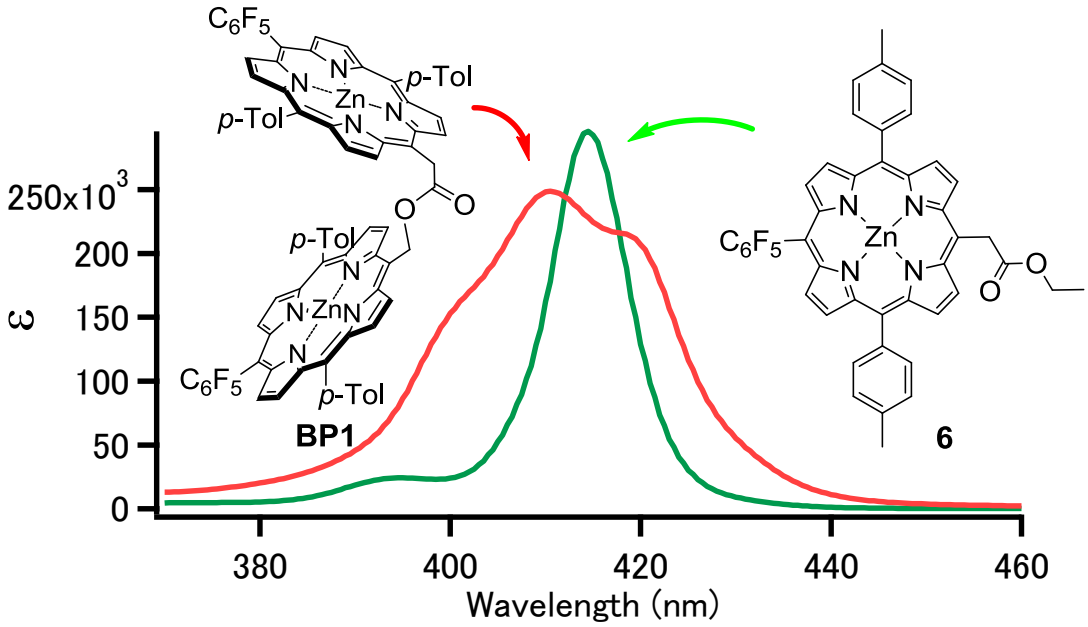



**Fig. S2** UV-vis specta of bis(zinc porphyrin) **BP1** (red-line) and carboethoxymethyl-substituted zinc porphyrin **6** (green-line) in 1% $CH_2Cl_2$/hexane at 25 °C.

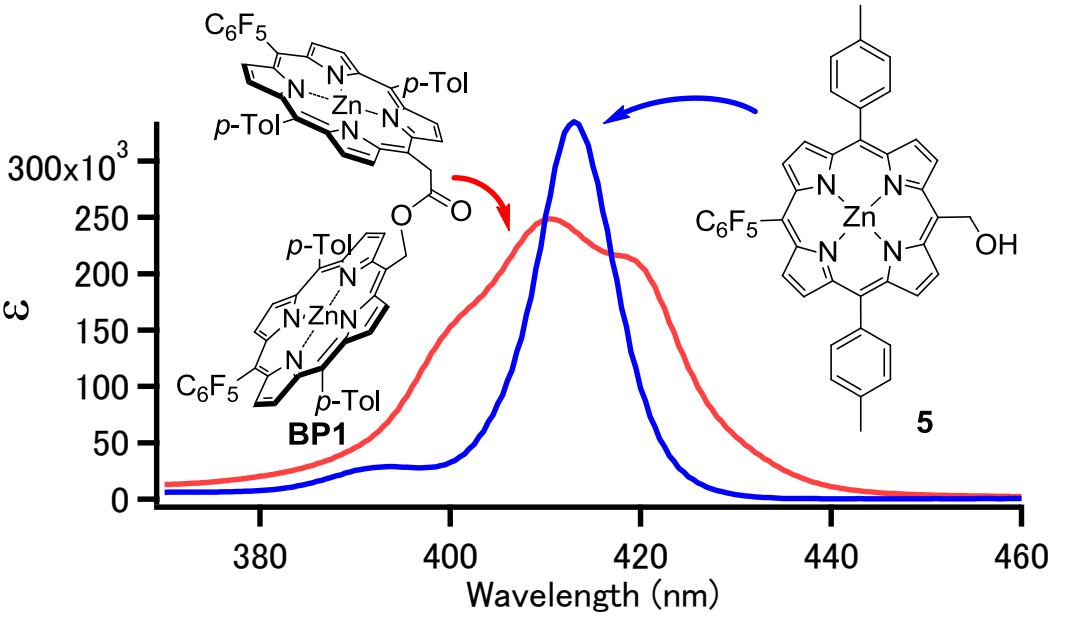



**Fig. S3** UV-vis specta of bis(zinc porphyrin) **BP1** (red-line) and hydroxymethyl-substituted zinc porphyrin **5** (blue-line) in 1% $CH_2Cl_2$/hexane at 25 °C.

## 4. $^{1}$H NMR Binding Experiments for Complexation of Bis(Zinc Porphyrin) BP1 With Ethanol

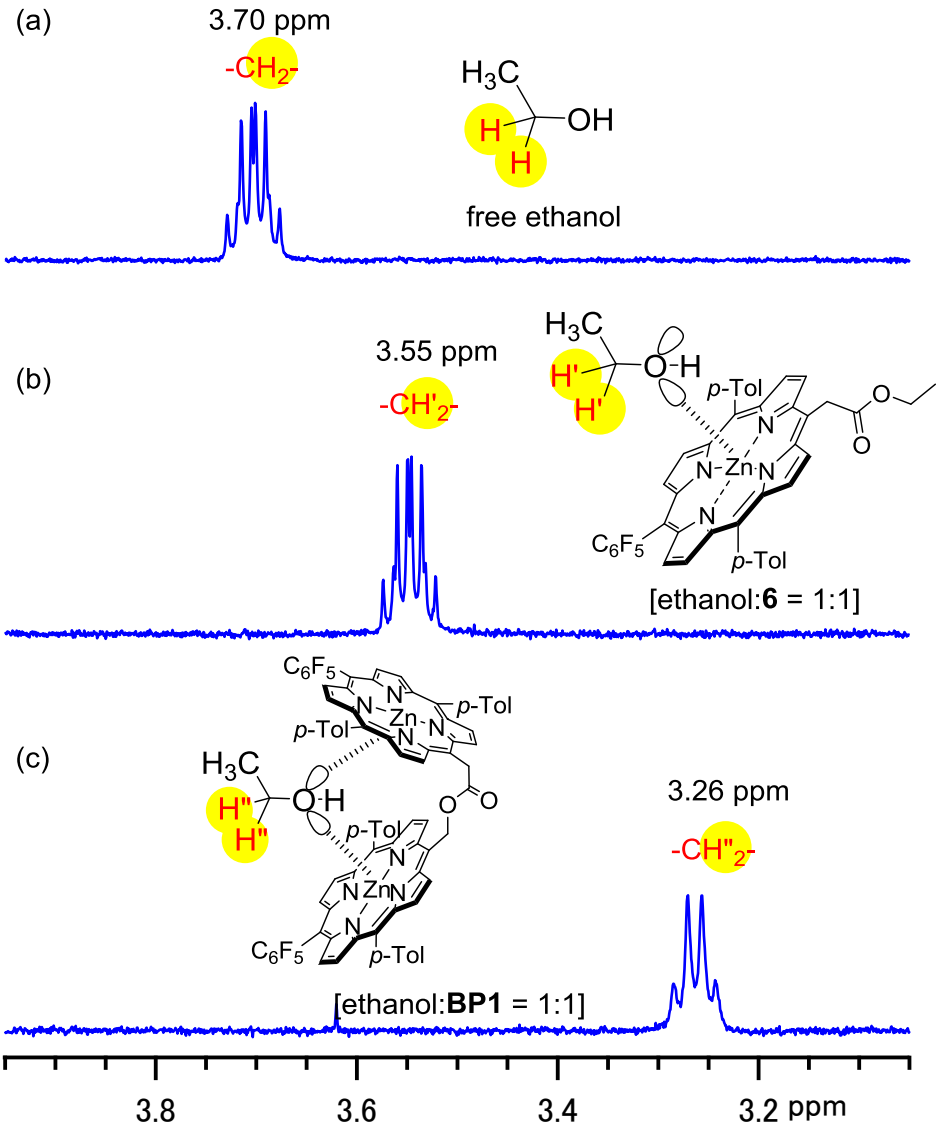



**Fig. S4** $^{1}$H NMR ($CDCl_3$, rt) spectra of ethanol (a) without zinc porphyrins and in the presence of (b) carboethoxymethyl-substituted zinc porphyrin **6** (ethanol/**6** = 1:1) and (c) bis(zinc porphyrin) **BP1** (ethanol/**BP1** = 1:1) in the region corresponding to the resonance of the methylene protons.

## 5. Spectroscopic Titrations for Evaluation of Association Constants

The association constants $K_{assoc}$ for host-guest complexes were determined through titration of the host molecules **BP1** and its monomeric counter part **6** with ethanol as the guest molecule. The UV-vis spectra of the titration of ethanol shown below (Figure S6 and S7) demonstrates the change in the Soret band absorption upon binding of ethanol to the host molecule. $K_{assoc}$ values were evaluated from the following equation by applying a nonlinear curve-fitting method to the changes in absorbance (ΔAbs) upon titration of host molecule **BP1** or **6** with guest molecule:

$$\Delta\mathrm{Abs} = \frac{\mathrm{L}\left[K_{\mathrm{assoc}}\cdot\mathrm{X} + K_{\mathrm{assoc}}\cdot\mathrm{A} + 1\right] - \sqrt{\mathrm{L}^2\left(K_{\mathrm{assoc}}\cdot\mathrm{X} + K_{\mathrm{assoc}}\cdot\mathrm{A} + 1\right)^2 - 4K_{\mathrm{assoc}}^2\cdot\mathrm{A}\cdot\mathrm{X}\cdot\mathrm{L}^2}}{2K_{\mathrm{assoc}}\cdot\mathrm{A}}$$

where X and A represent $[\mathrm{Guest}]_{total}$ and $[\mathrm{Host}]_{total}$, respectively; L denotes ΔAbs at 100% complexation; L and $K_{assoc}$ are parameters.[5] IGOR Pro (ver 6.22) software was used for curve-fitting analysis.

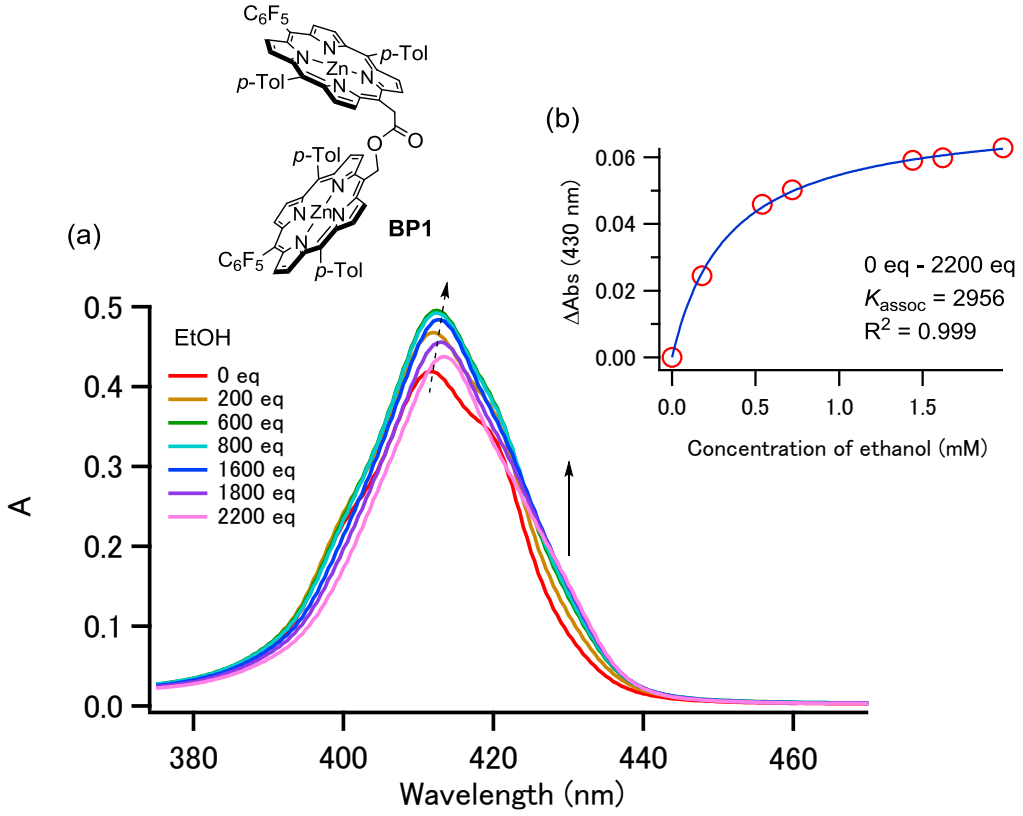



**Fig. S5** (a) Spectral change upon titration of **BP1** with ethanol in 1% $CH_2Cl_2$/hexane at 25 °C. (b) Changes in ΔAbs at 430 nm for evaluating $K_{assoc}$. [**BP1**] = 1.0 μM; [ethanol]/[**BP1**] = 0–2200.

[5] Shoji, Y.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2006,** *128*, 10690.

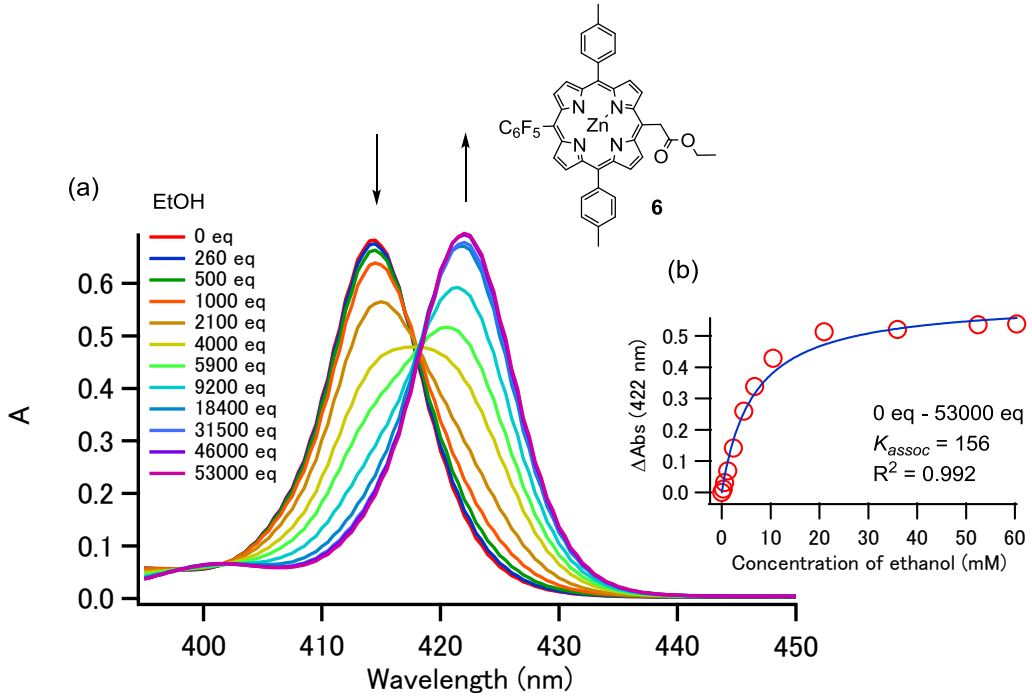



**Fig. S6** (a) Spectral change upon titration of **6** with ethanol in 1% $CH_2Cl_2$/hexane at 25 °C. (b) Changes in ΔAbs at 422 nm for evaluating $K_{assoc}$. [**6**] = 1.0 μM; [ethanol]/[**BP1**] = 0–53000.

## 6. Job's Continuous Plot Analysis to Determine Complex Stoichiometry

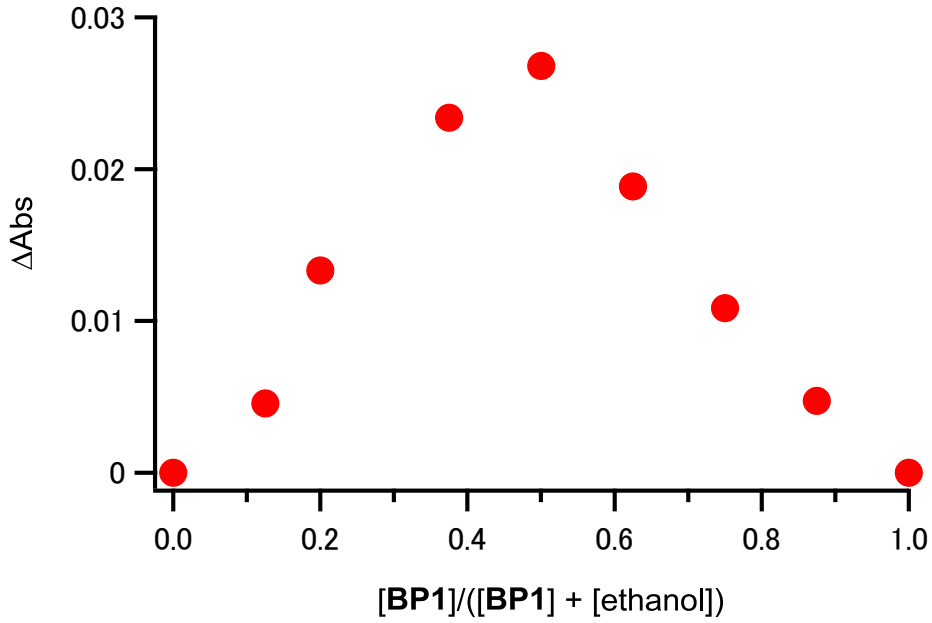



**Fig. S7** Job's diagram. Solutions of the bidentate host **BP1** and ethanol (guest) in 1% $CH_2Cl_2$/hexane were prepared with a fixed total concentration of host and guest (2 μM). The UV-vis spectra were recorded at 0 °C and ΔAbs was monitored at 414 nm. Peaking at 0.5 mol fraction corresponds to a 1:1 **BP1**:ethanol complex.

## 7. Computational Analysis

Density functional theory (DFT) calculations were run with Spartan'10 (Wavefunction, Inc., Irvine, CA). Geometry optimization was performed by the semiempirical method (AM1) followed by DFT calculation at the B3LYP/6-31G* level of theory.

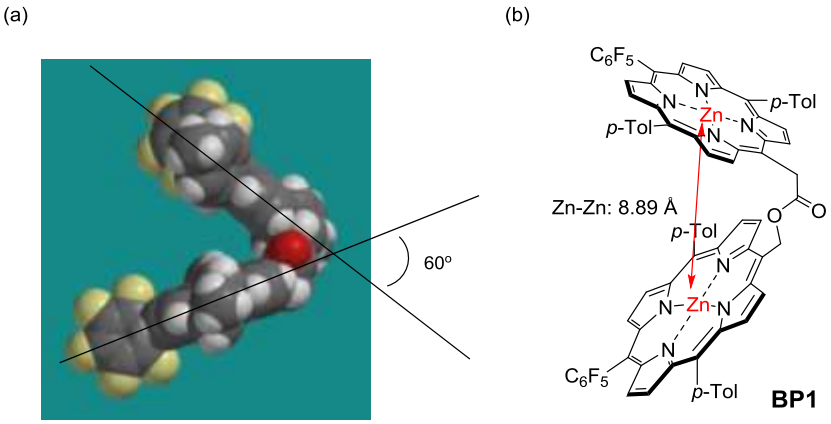



**Fig. S8** DFT calculation for bis(zinc porphyrin) **BP1:** (a) dihedral angle of the two porphyrin planes and (b) zinc-zinc distance.

## 8. CD Spectra and Proposed Working Model for Assigning the Absolute Configuration of Chiral Alcohols

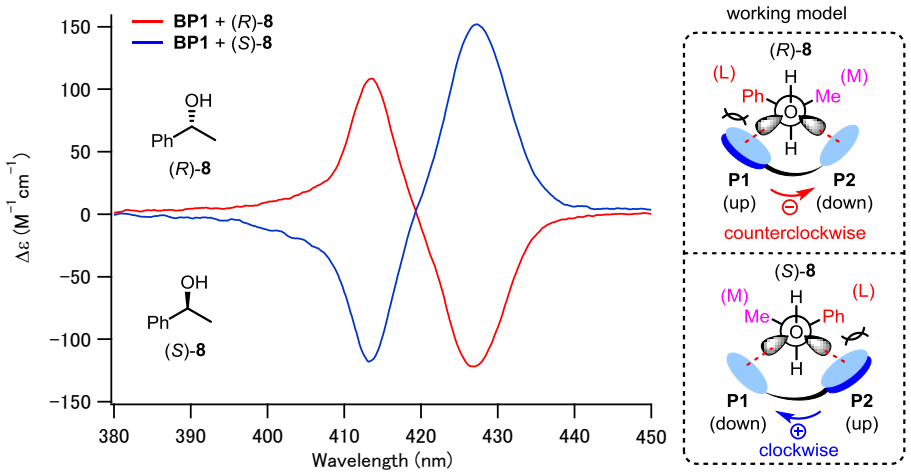



**Fig. S9** ECCD spectra of **8** ($1.7 \times 10^{-3}$ M) in the presence of **BP1** ($1.7 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignments of M, L groups are based on the conformational energies, *A* values: Ph, 2.8 kcal $mol^{-1}$; Me, 1.74 kcal $mol^{-1}$. [6]

[6] E. L. Eliel, S. H. Wilen and L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley: New York, **1994**, pp. 696-697, Table 11.7.

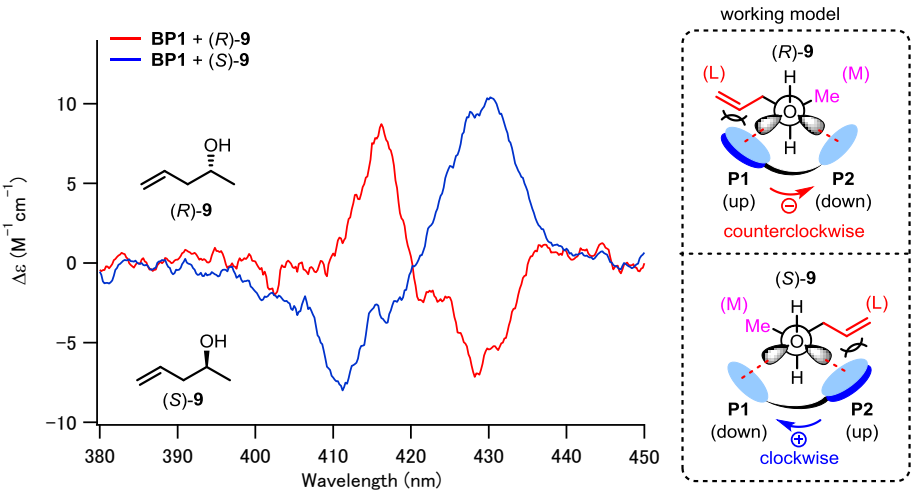
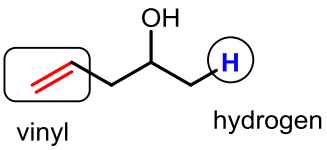



**Fig. S10** ECCD spectra of **9** ($1.6 \times 10^{-3}$ M) in the presence of **BP1** ($1.6 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. Neither the conformational energy, *A* value, nor the Taft's steric substituent constant, $E_s$, were not available for allylic substituent. Therefore, the *A* values of the substituents on the $\beta$ carbons, vinyl group and hydrogen, were compared as shown in the figure depicted below. The reported *A* value for vinyl group (1.49 or 1.68 kcal $mol^{-1}$) is larger than that for hydrogen (0.00 kcal $mol^{-1}$),[6] and thus the allylic and the Me substituents can be assigned to L and M groups, respectively.



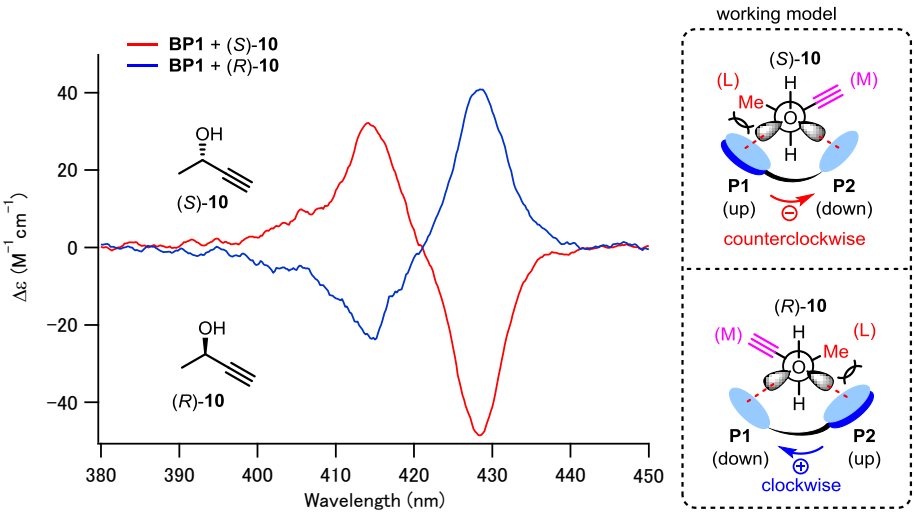



**Fig. S11** ECCD spectra of **10** ($1.7 \times 10^{-3}$ M) in the presence of **BP1** ($1.7 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignments of M, L groups are based on the conformational energies, *A* values: C≡CH, 0.41-0.52 kcal $mol^{-1}$; Me, 1.74 kcal $mol^{-1}$.[6]

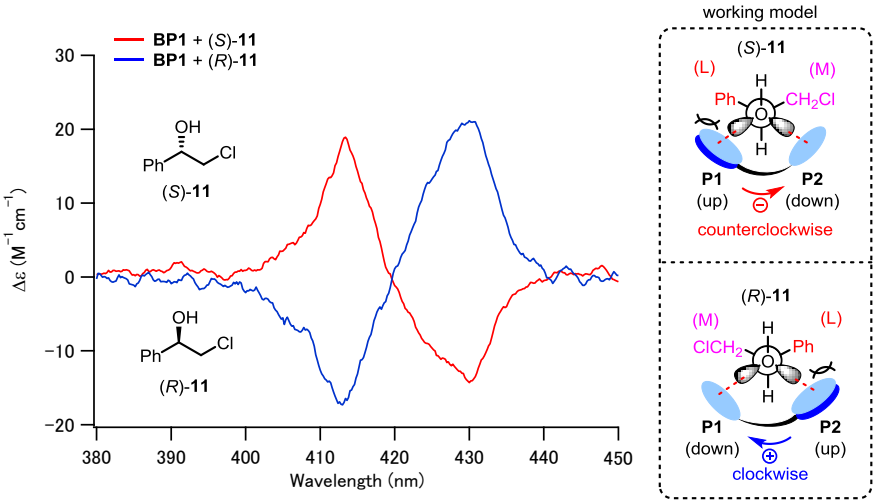



**Fig. S12** ECCD spectra of **11** ($1.7 \times 10^{-3}$ M) in the presence of **BP1** ($1.7 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignments of M, L groups are based on the Taft's steric substituent constants, $E_s$: Ph, -2.55 [7]; $CH_2Cl$, -0.24. [8]

[7] T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry, 3rd ed.*, Harper & Row, New York, 1987, p. 153, Table 2.5.

[8] D. Datta and D. Majumdar, *J. Phys. Org. Chem.*, 1991, **4**, 611.

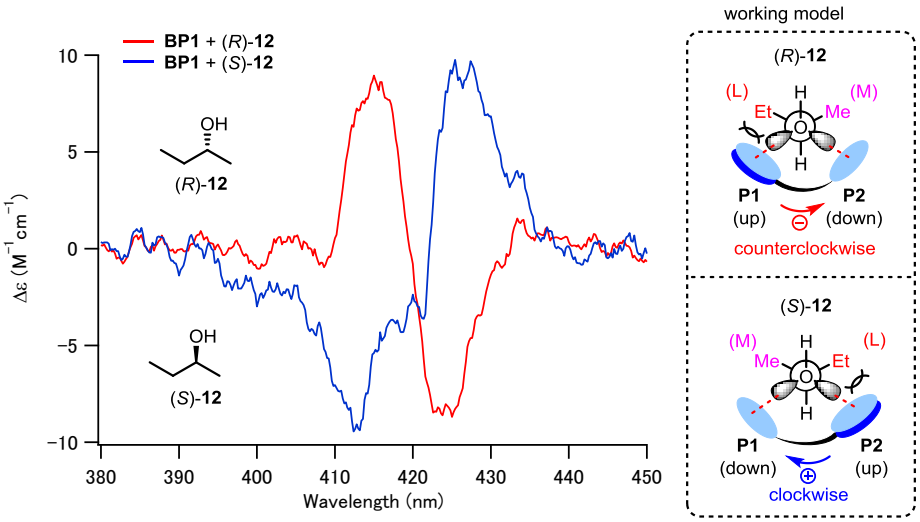



**Fig. S13** ECCD spectra of **12** ($1.5 \times 10^{-3}$ M) in the presence of **BP1** ($1.5 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignments of M, L groups are based on their conformational energies, *A* values: Et, 1.79 kcal mol$^{-1}$; Me, 1.74 kcal mol$^{-1}$.[6]

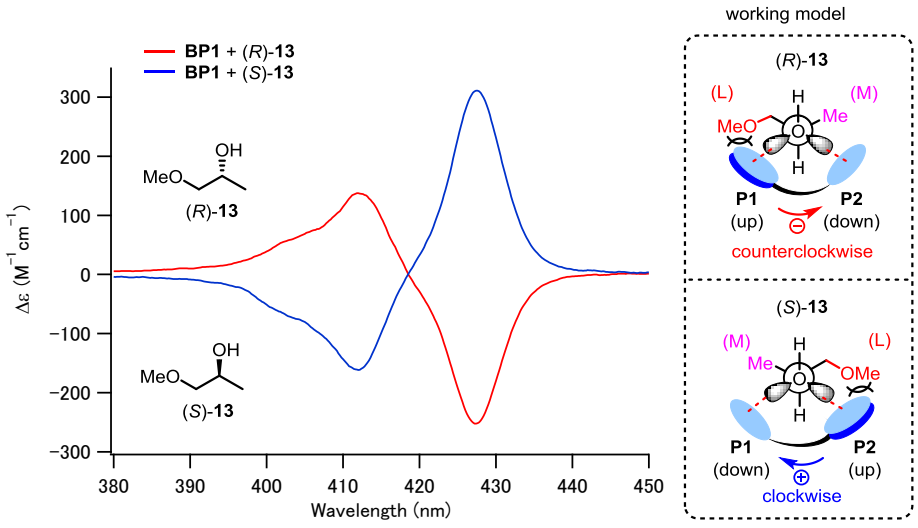



**Fig. S14** ECCD spectra of **13** ($1.5 \times 10^{-3}$ M) in the presence of **BP1** ($1.5 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignments of M, L groups are based on the Taft's steric substituent constants, $E_s$: Me, 0.00; $CH_3OCH_2$, -0.19.[7]

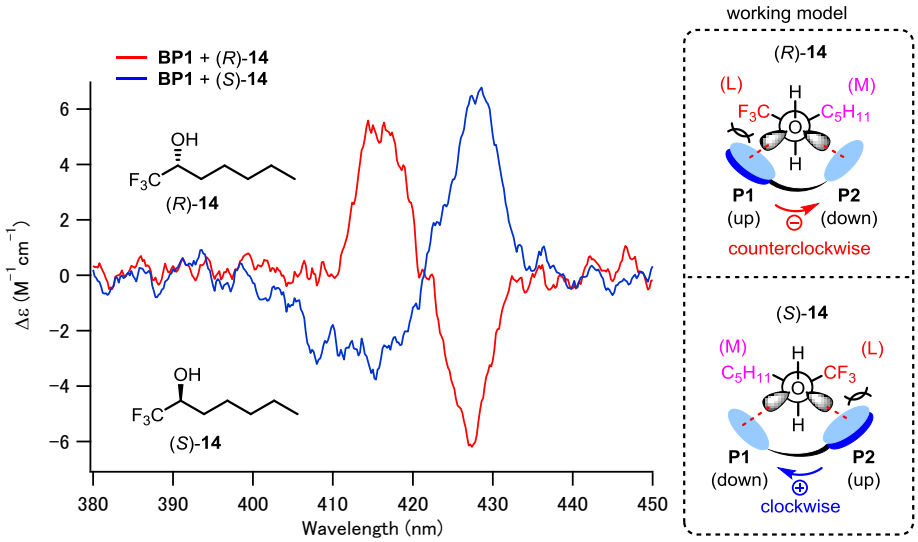



**Fig. S15** ECCD spectra of **14** ($1.6 \times 10^{-3}$ M) in the presence of **BP1** ($1.6 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignments of M, L groups are based on the Taft's steric substituent constants, $E_s$: $CF_3$, -1.16; $CH_2(CH_2)_3CH_3$, -0.40.[8]

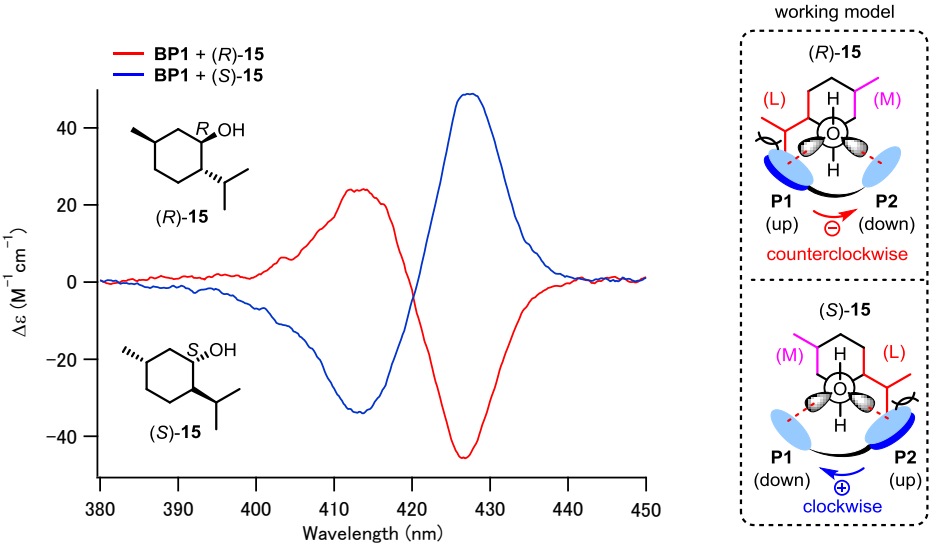
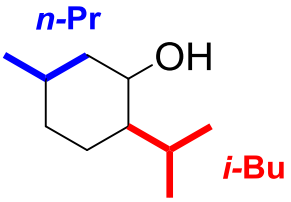



**Fig. S16** ECCD spectra of **15** ($1.5 \times 10^{-3}$ M) in the presence of **BP1** ($1.5 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. As shown in the figure depicted below, the substrate **15** consists of *i*-Bu (red line) and *n*-Pr (blue line) moieties. The reported Taft's steric substituent constants ($E_s$) for *i*-Bu and *n*-Pr are -0.93 and -0.36, respectively.[7] Therefore, the red colored *i*-Bu and the blue colored *n*-Pr moieties can be assigned to L and M groups, respectively.



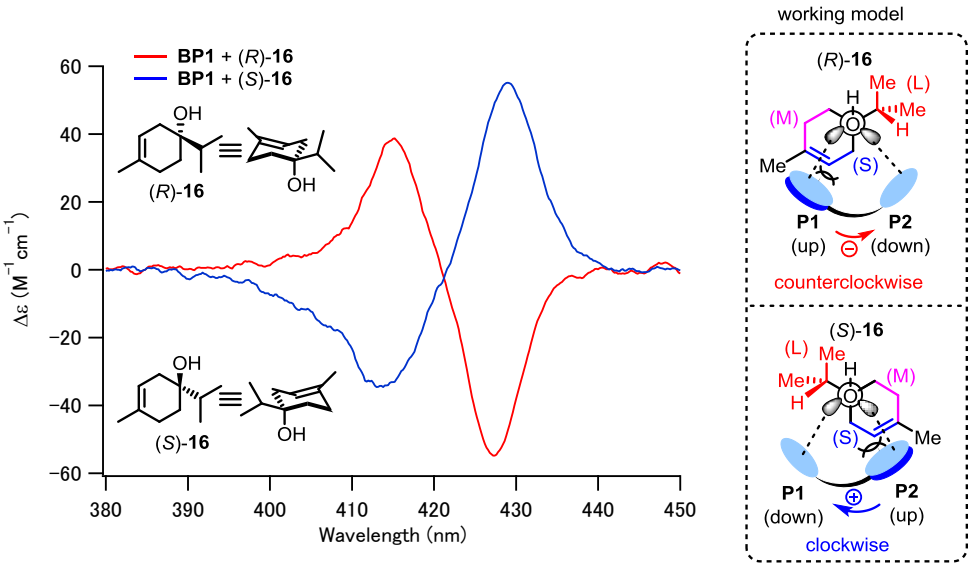
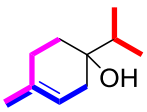



**Fig. S17** ECCD spectra of **16** ($1.5 \times 10^{-3}$ M) in the presence of **BP1** ($1.5 \times 10^{-6}$ M) in 1% $CH_2Cl_2$/hexane at 25 °C. Dashed box: proposed working model for assigning the absolute configuration of the chiral guest. The assignment of L, M, and S groups in the substrate **16** and the prediction of CD signs of the host-guest complexes of **BP1** with (*R*)-**16** and (*S*)-**16** can be achieved as follows.



As shown in the figure depicted on the right, the substrate **16** consists of *i*-Pr moiety (red line) and two C4 units (purple and blue lines). As for these C4 units, the blue colored C4 unit consists of two $sp^3$ and two $sp^2$ carbons, while the purple colored C4 unit contains three $sp^3$ and one $sp^2$ carbon. In general, $sp^2$ carbon-containing compounds tend to have smaller *A* values than those of the corresponding $sp^3$ carbon-containing compounds (e.g. $H_2C$=CH-, *A* = 1.49 or 1.68 kcal $mol^{-1}$; $CH_3CH_2$-, *A* = 1.79 kcal $mol^{-1}$).[6] Hence, the purple colored C4 unit should be larger than the blue colored C4 unit in the substrate. The purple colored C4 unit can be regarded as *n*-Bu substituent. Then, we compared the Taft's steric substituent constants ($E_s$) for *n*-Bu with that for *i*-Pr, as their *A* values were not available in the literature. The reported $E_s$ for *n*-Bu and *i*-Pr are -0.39 and -0.47, respectively.[8] Therefore, the red colored *i*-Pr should be larger than the purple colored C4 unit in the substrate. As a consequence, the red colored *i*-Pr moiety and the purple and blue colored C4 units can be assigned to L, M, and S groups, respectively, and the working models for the substrate **16** can be obtained as shown in the dashed box. In analogy with other monoalcoholic substrates examined, the host **BP1** approaches the hydroxyl group from the side of the S group of the substrate **16** to capture the hydroxyl lone pairs. When (*R*)-**16** is used as the substrate, porphyrin ring **P1** would rise above porphyrin ring **P2** because of the steric repulsion between **P1** and the cyclohexenyl moiety on the left side rather than the largest *i*-Pr substituent as shown in the dashed box upper half. As a result, **P1** adopts a counter clockwise helicity relative to **P2**, which would produce a negative ECCD spectrum.

## 9. NMR Spectra of New Compounds

**Fig. S18** $^{1}$H NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

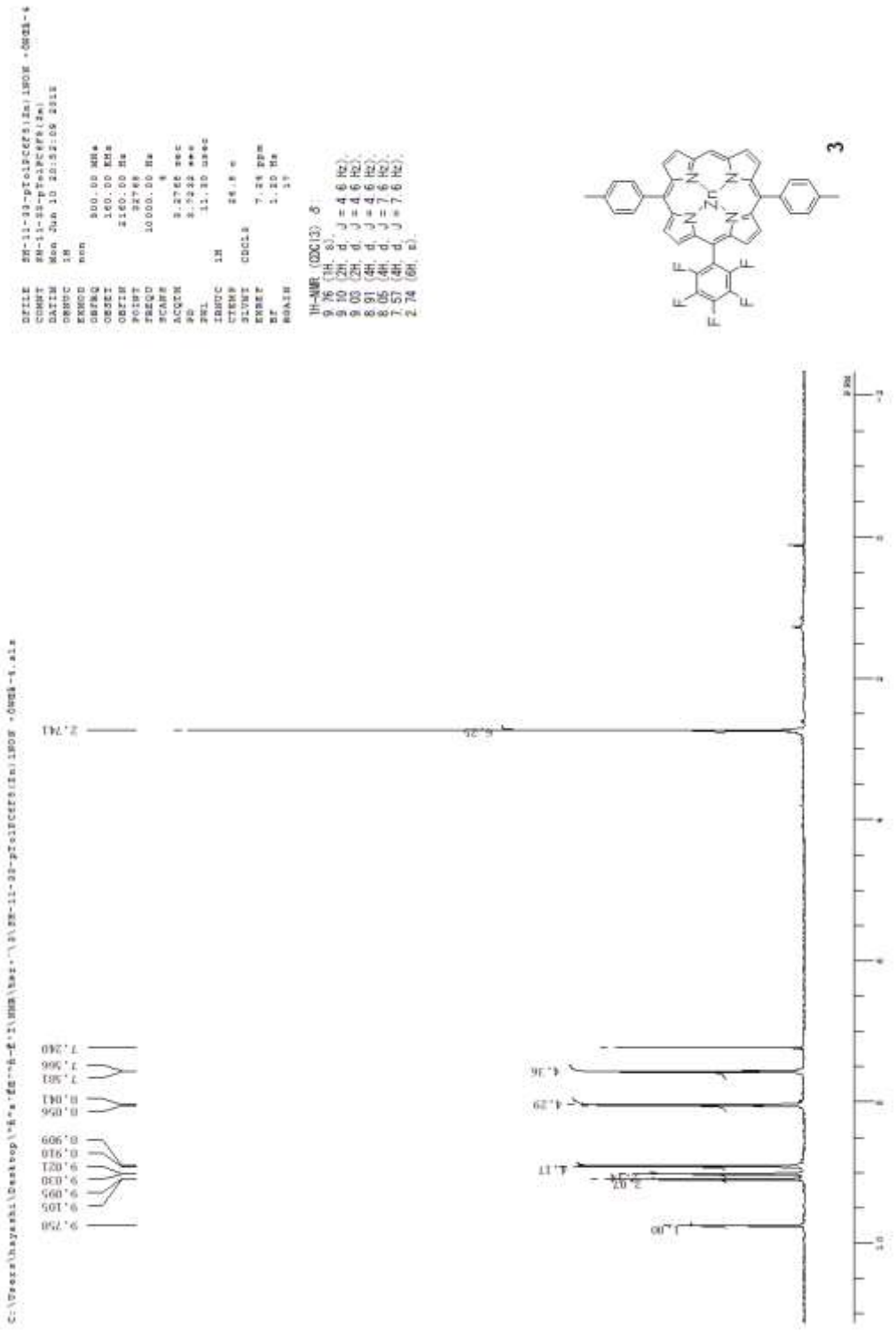


**Fig. S19** $^{13}C$ NMR spectrum of compound **3** (125 MHz, $CDCl_3$)

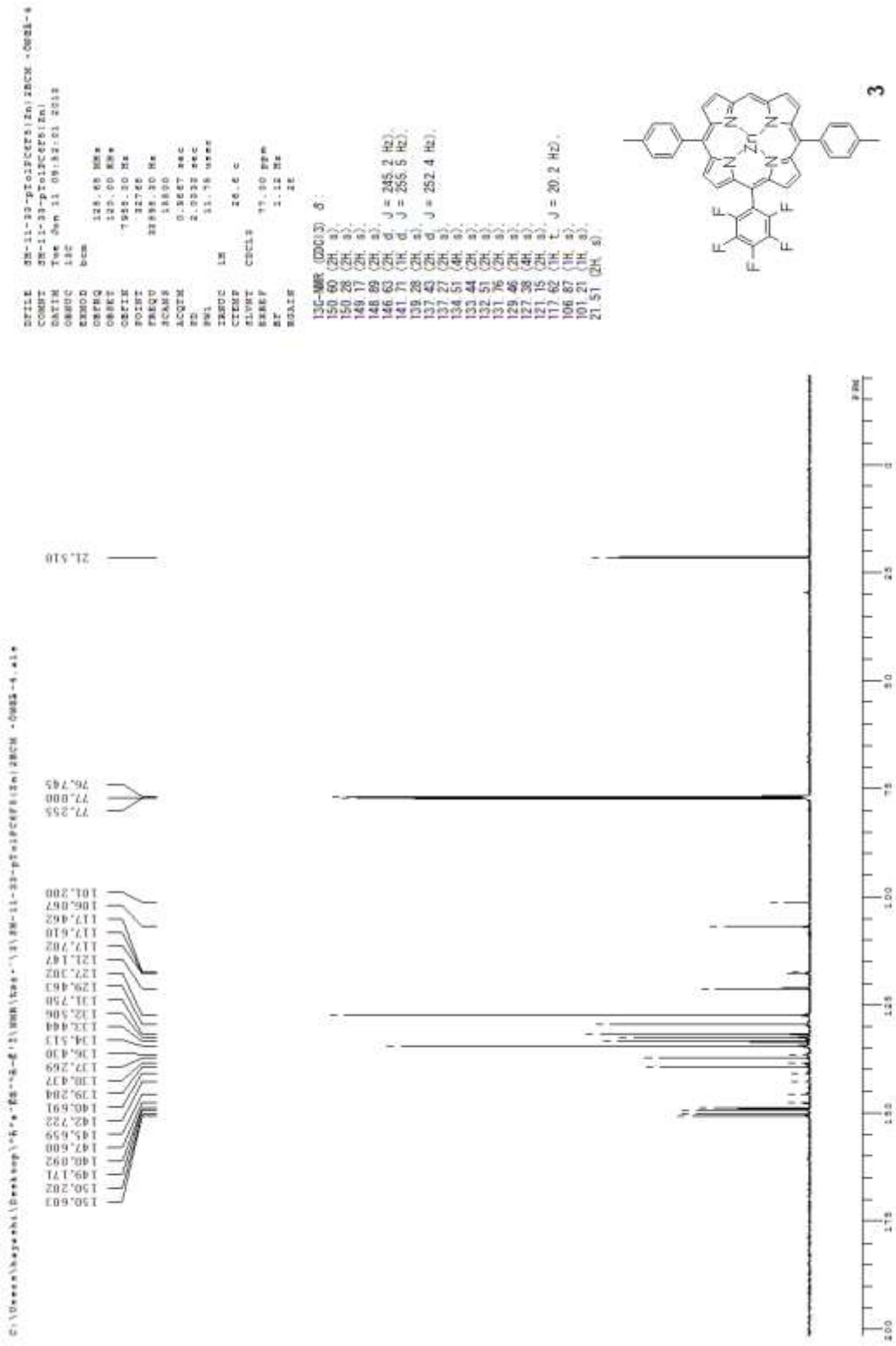


**Fig. S20** $^{19}$F NMR spectrum of compound **3** (466 MHz, $CDCl_3$)

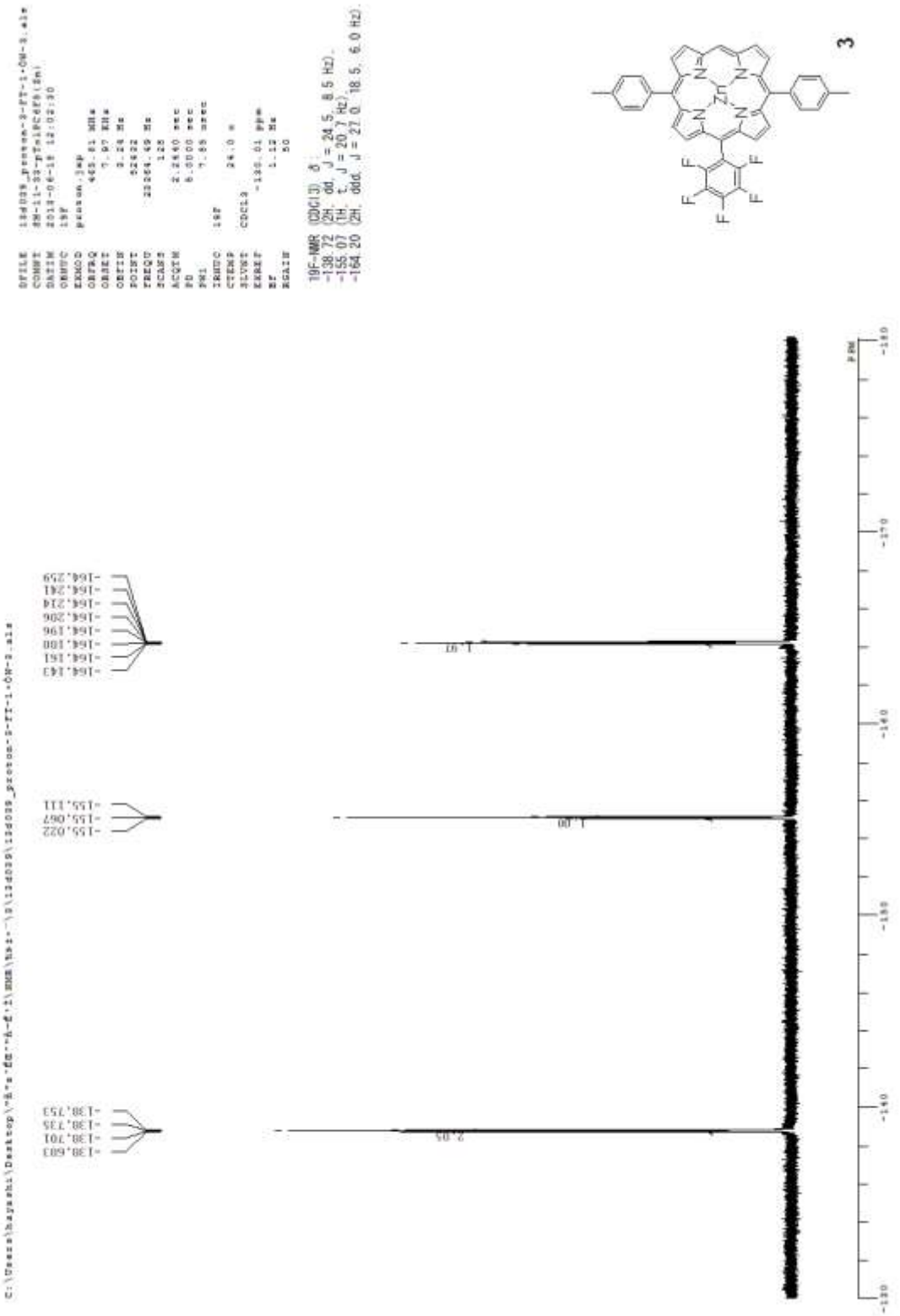


**Fig. S21** $^{1}$H NMR spectrum of compound **18** (500 MHz, $CDCl_3$)

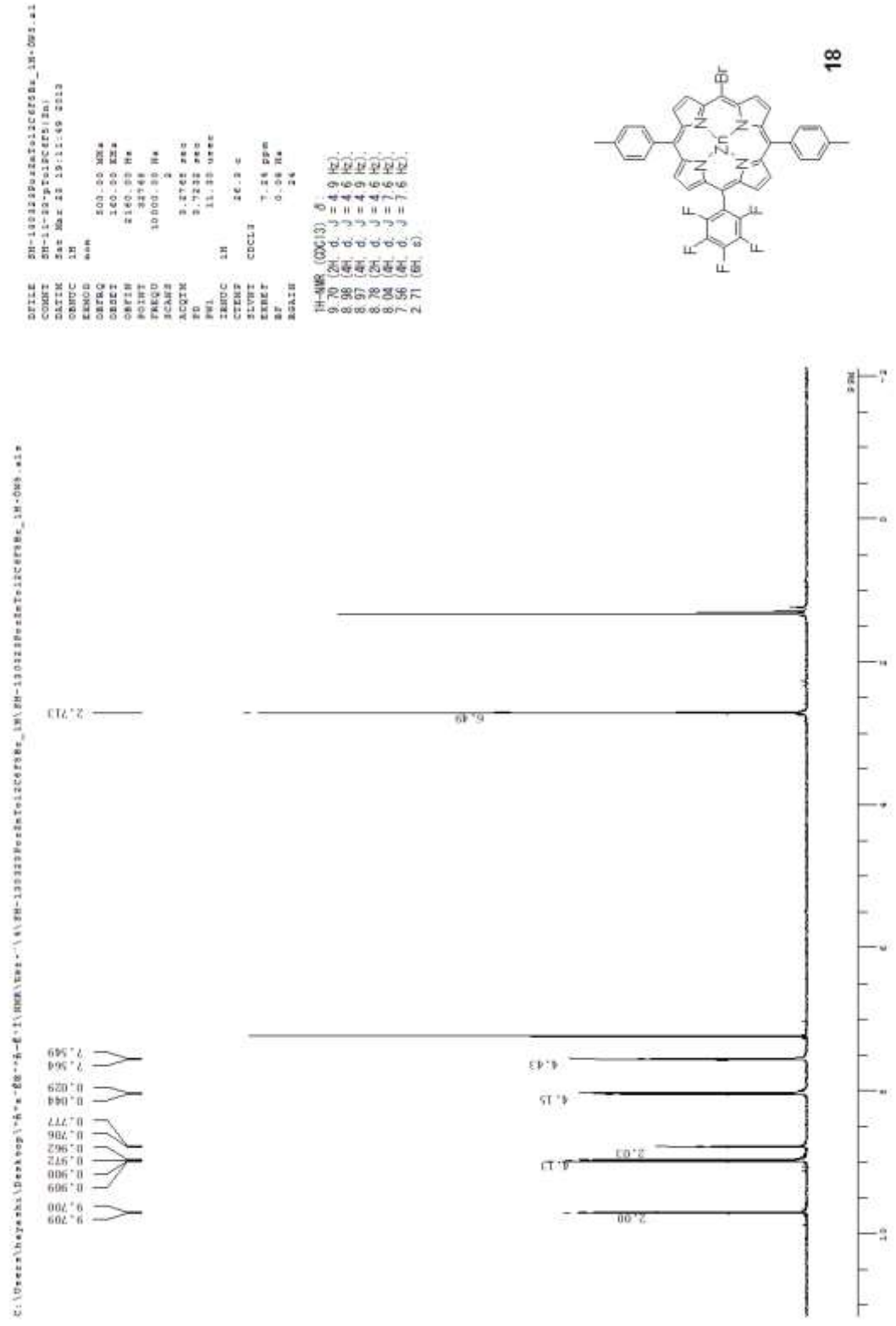


**Fig. S22** $^{13}$C NMR spectrum of compound **18** (125 MHz, $CDCl_3$)

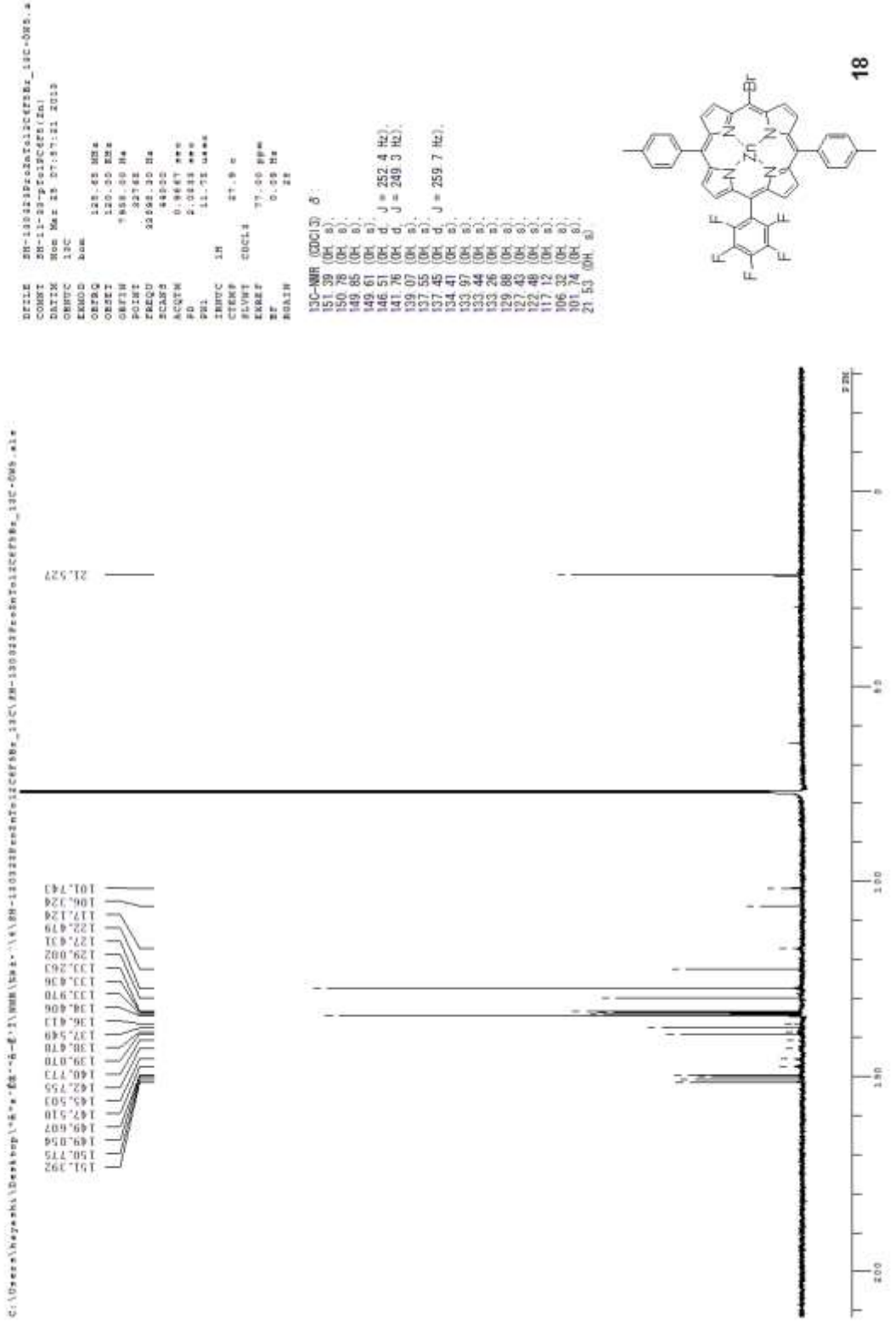


**Fig. S23** $^{19}$F NMR spectrum of compound **18** (466 MHz, $CDCl_3$)

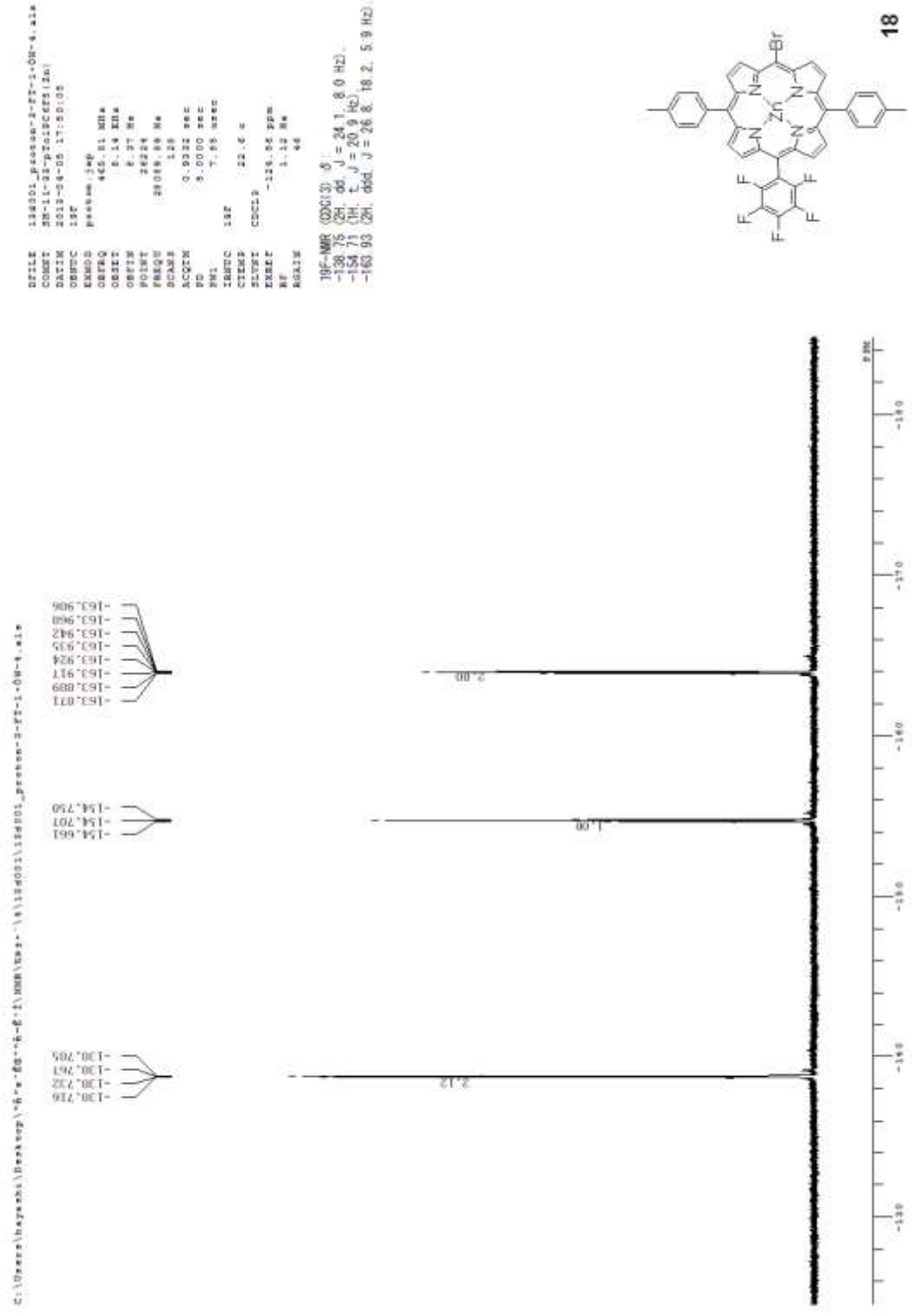


**Fig. S24** $^{1}$H NMR spectrum of compound **4** (500 MHz, $CDCl_3$)

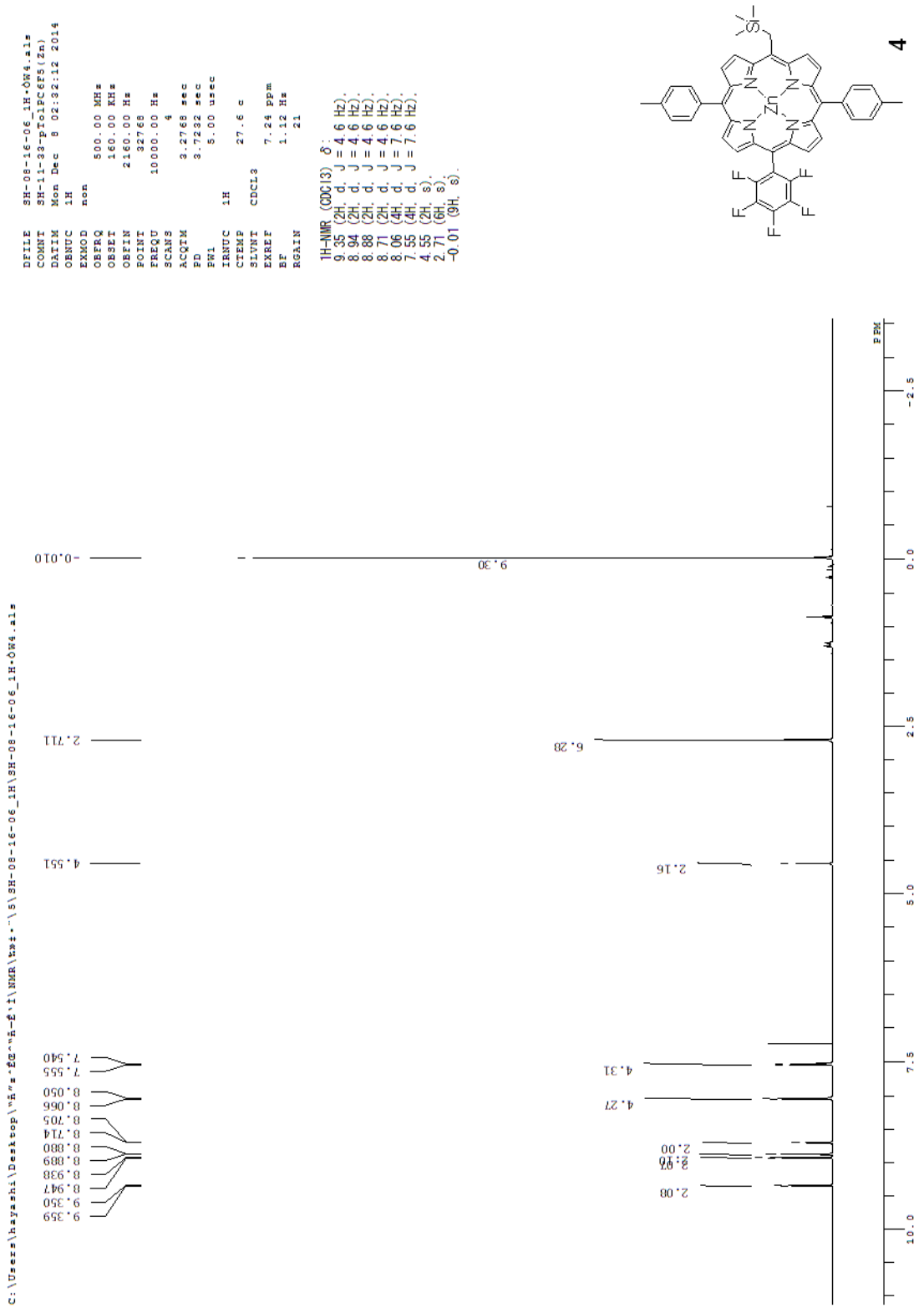


**Fig. S25** $^{13}$C NMR spectrum of compound **4** (125 MHz, $CDCl_3$)

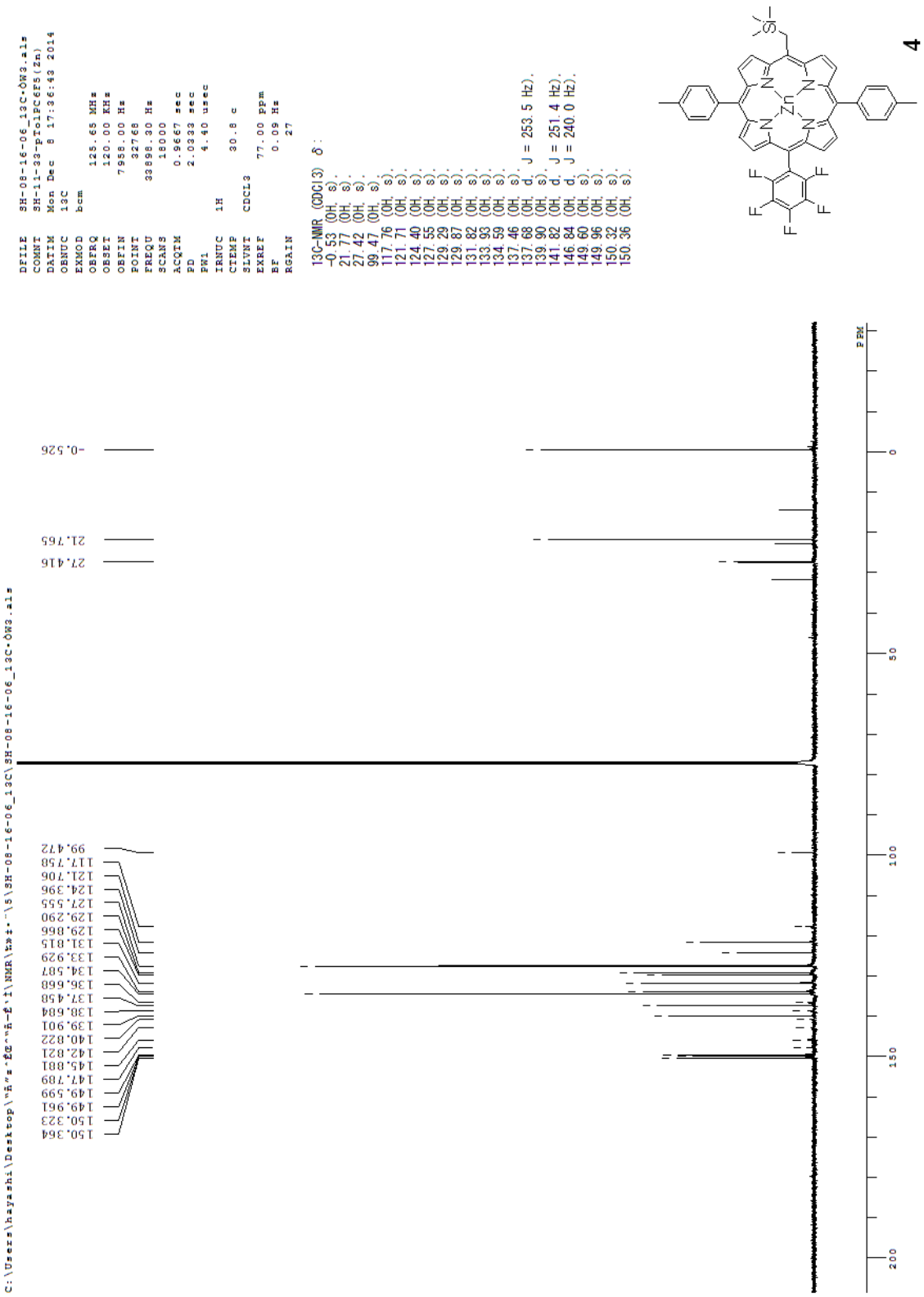


**Fig. S26** $^{19}F$ NMR spectrum of compound **4** (466 MHz, $CDCl_3$)

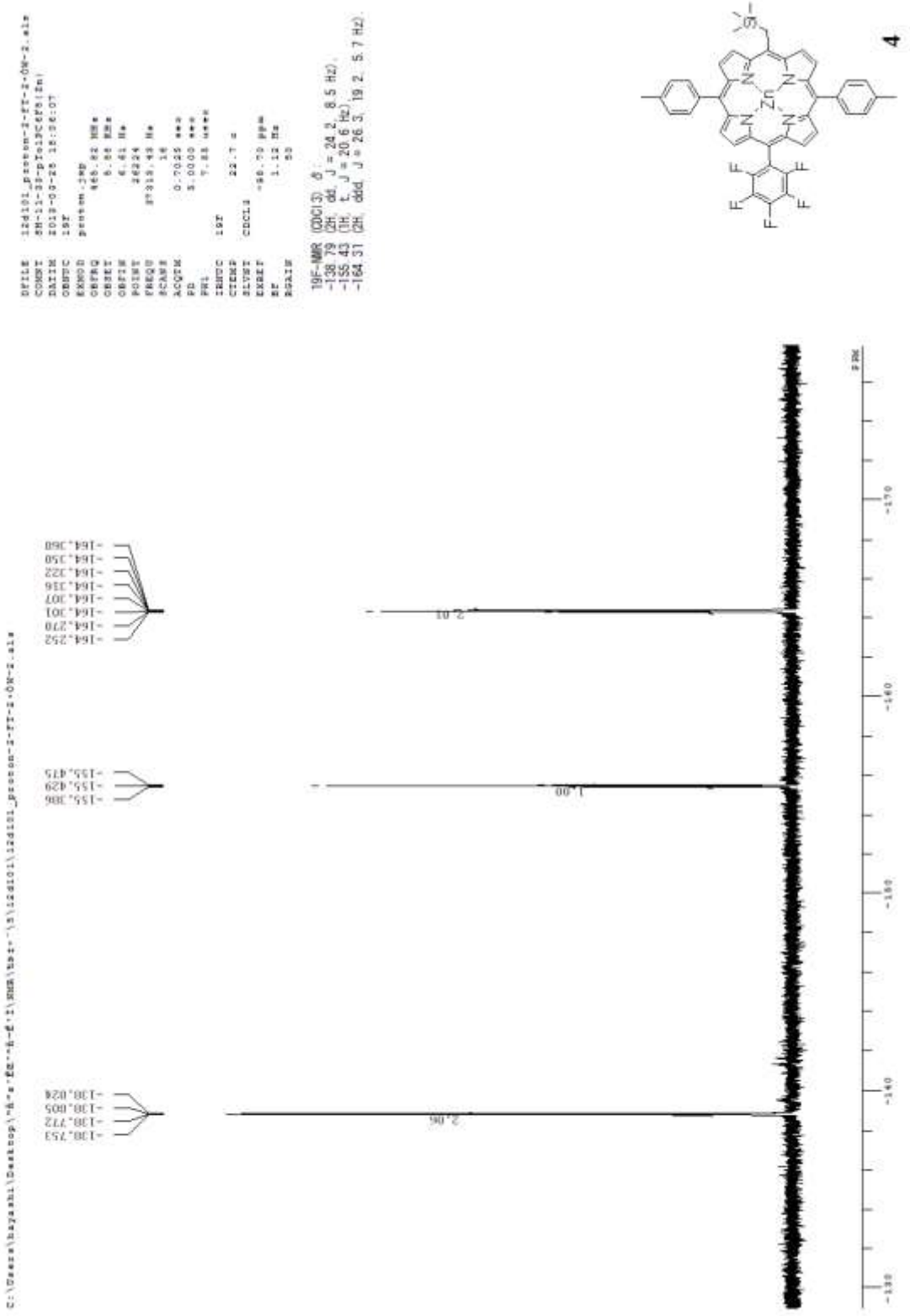


**Fig. S27** $^{1}$H NMR spectrum of compound **5** (500 MHz, $CDCl_3$)

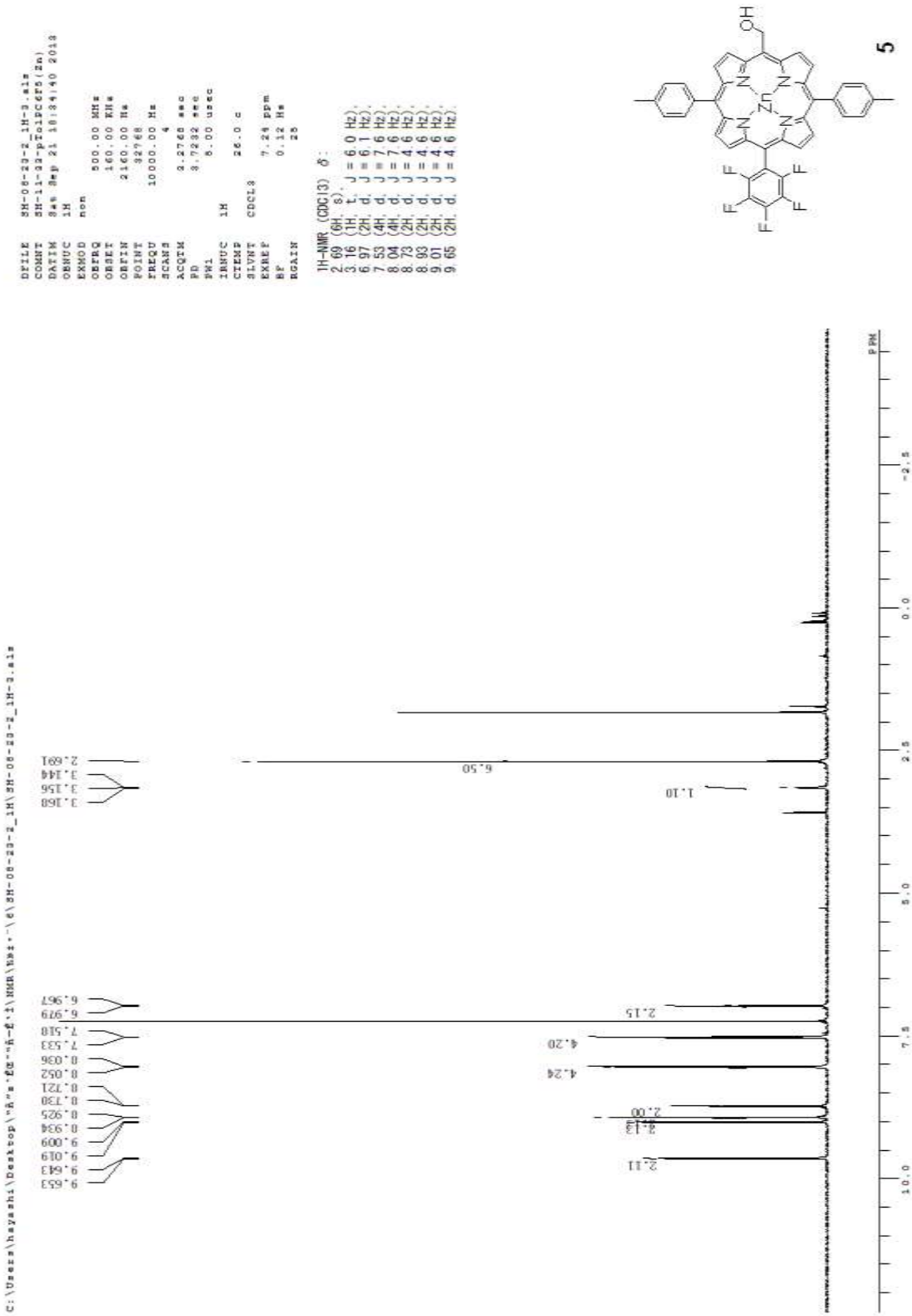


**Fig. S28** $^{13}C$ NMR spectrum of compound **5** (125 MHz, $CDCl_3$)

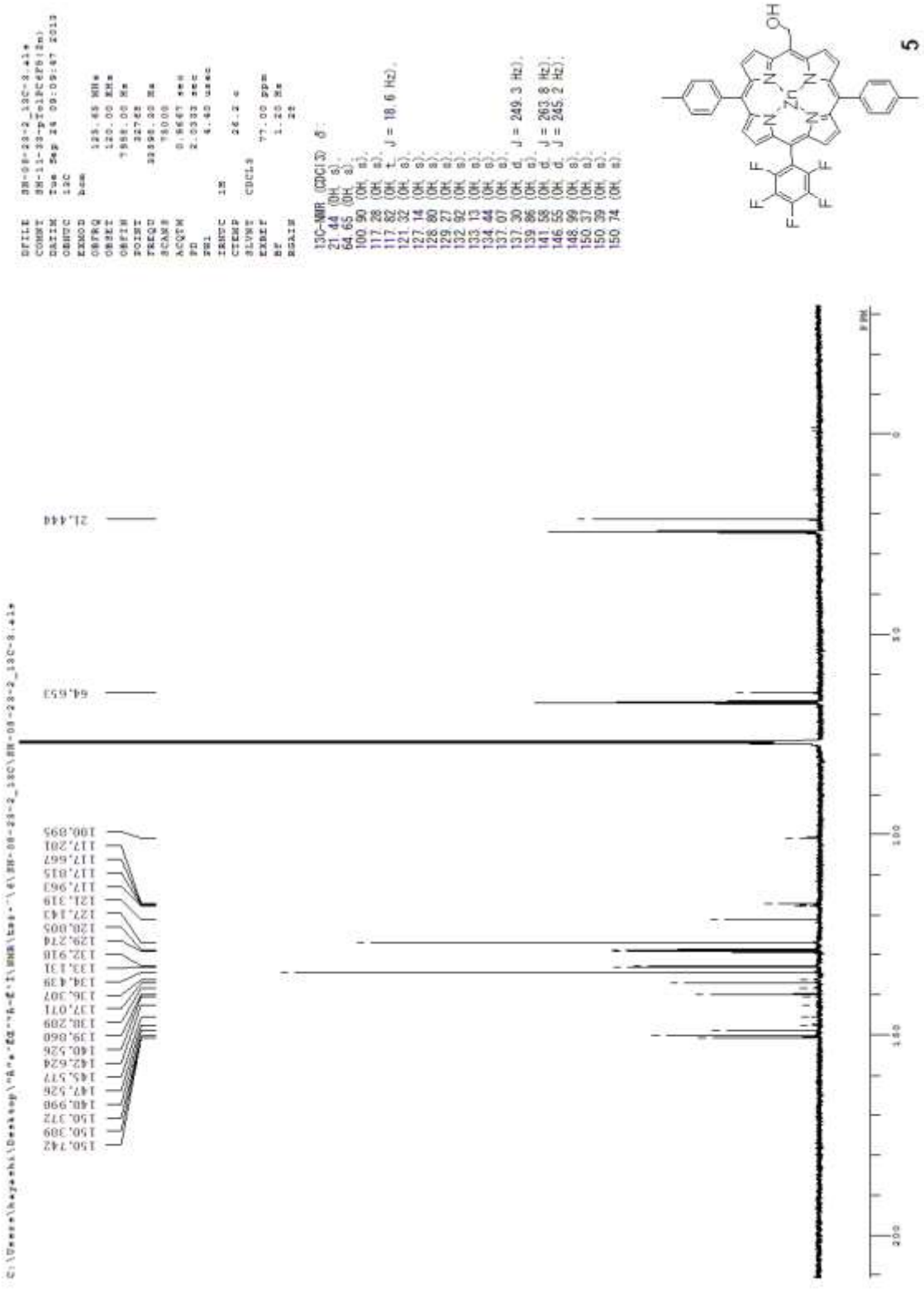


**Fig. S29** $^{19}$F NMR spectrum of compound **5** (466 MHz, $CDCl_3$)

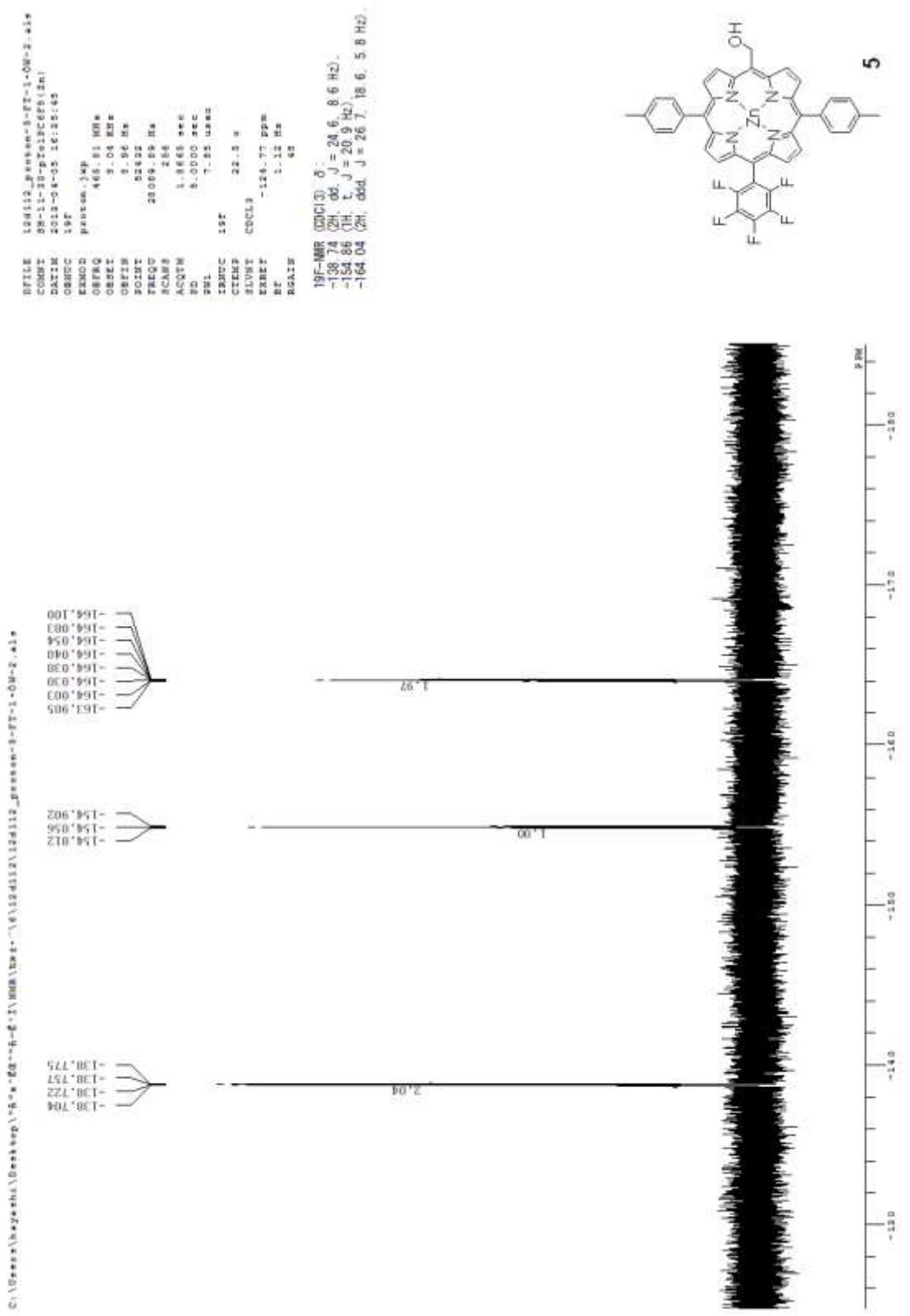


**Fig. S30** $^{1}$H NMR spectrum of compound **19** (500 MHz, $CDCl_3$)

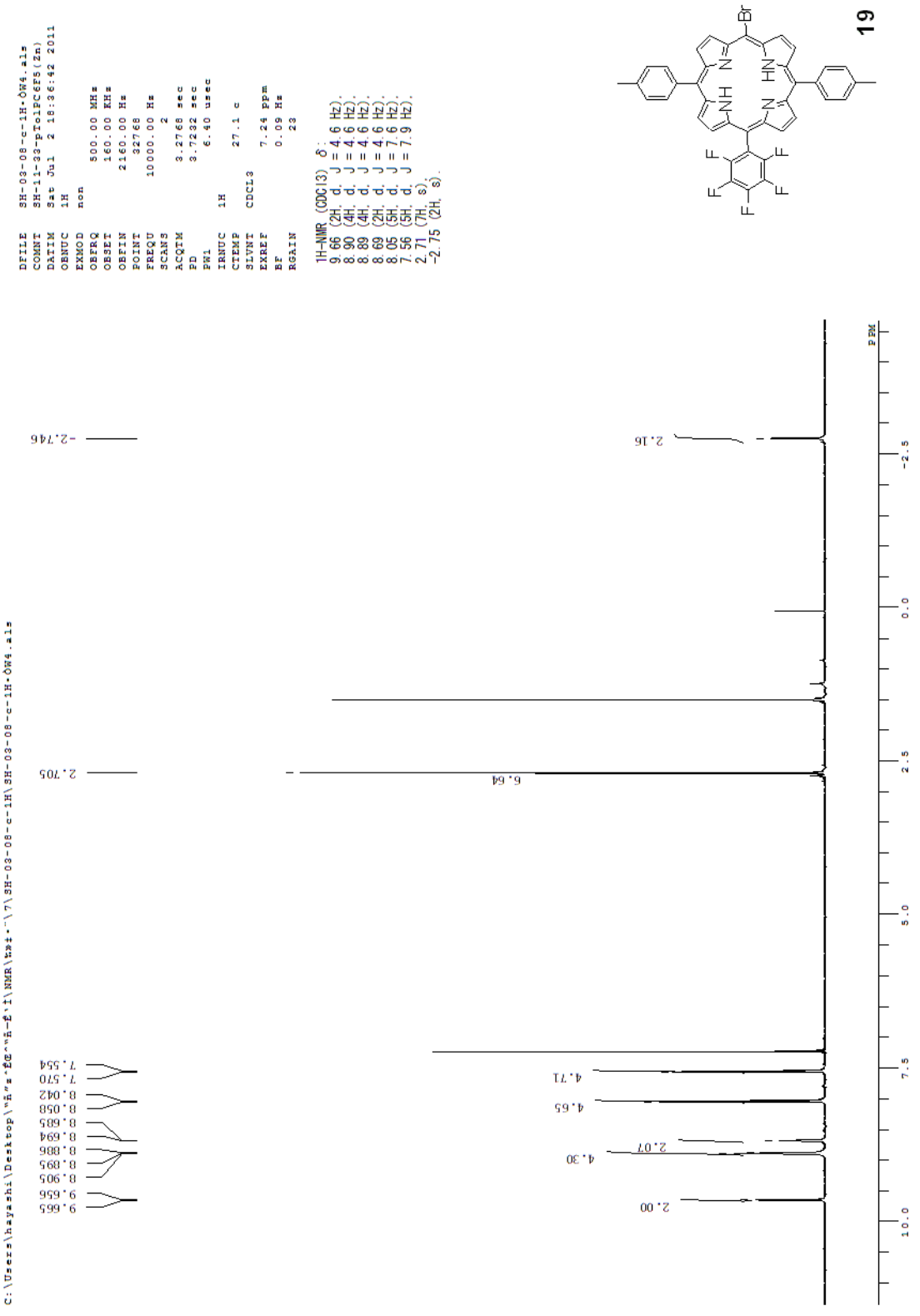


**Fig. S31** $^{13}C$ NMR spectrum of compound **19** (125 MHz, $CDCl_3$)

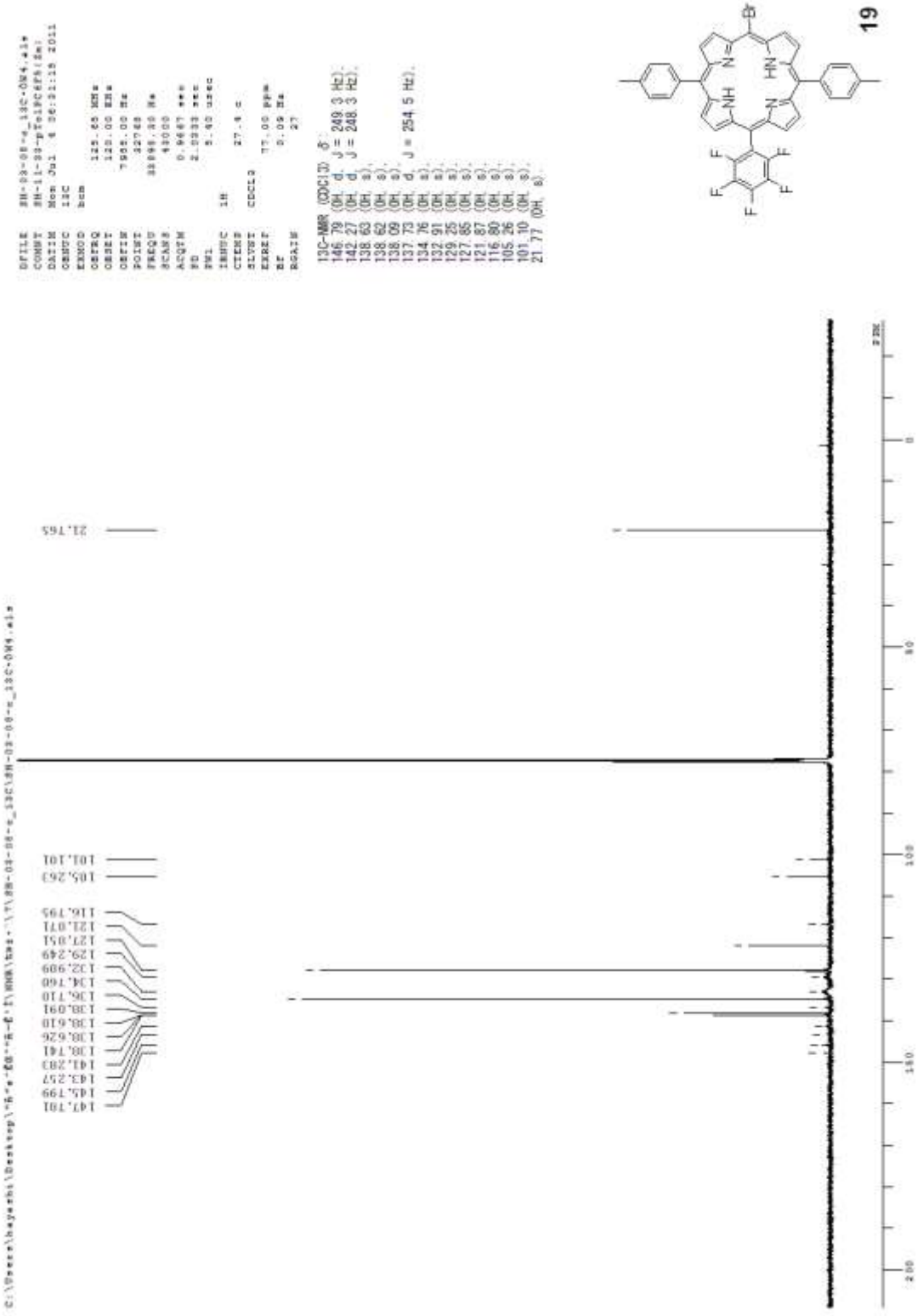


**Fig. S32** $^{19}$F NMR spectrum of compound **19** (466 MHz, $CDCl_3$)

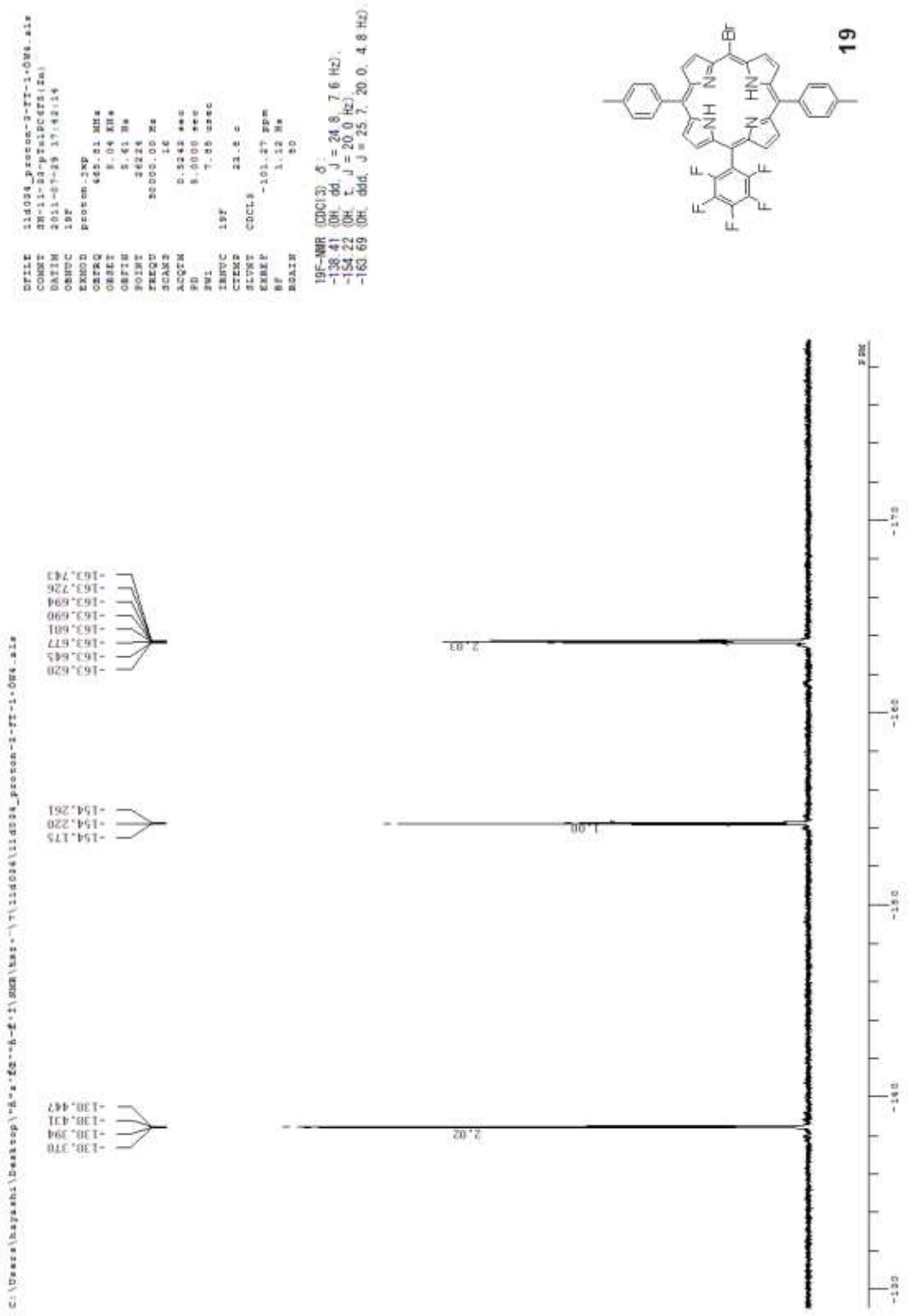


**Fig. S33** $^{1}$H NMR spectrum of compound **6** (500 MHz, $CDCl_3$)

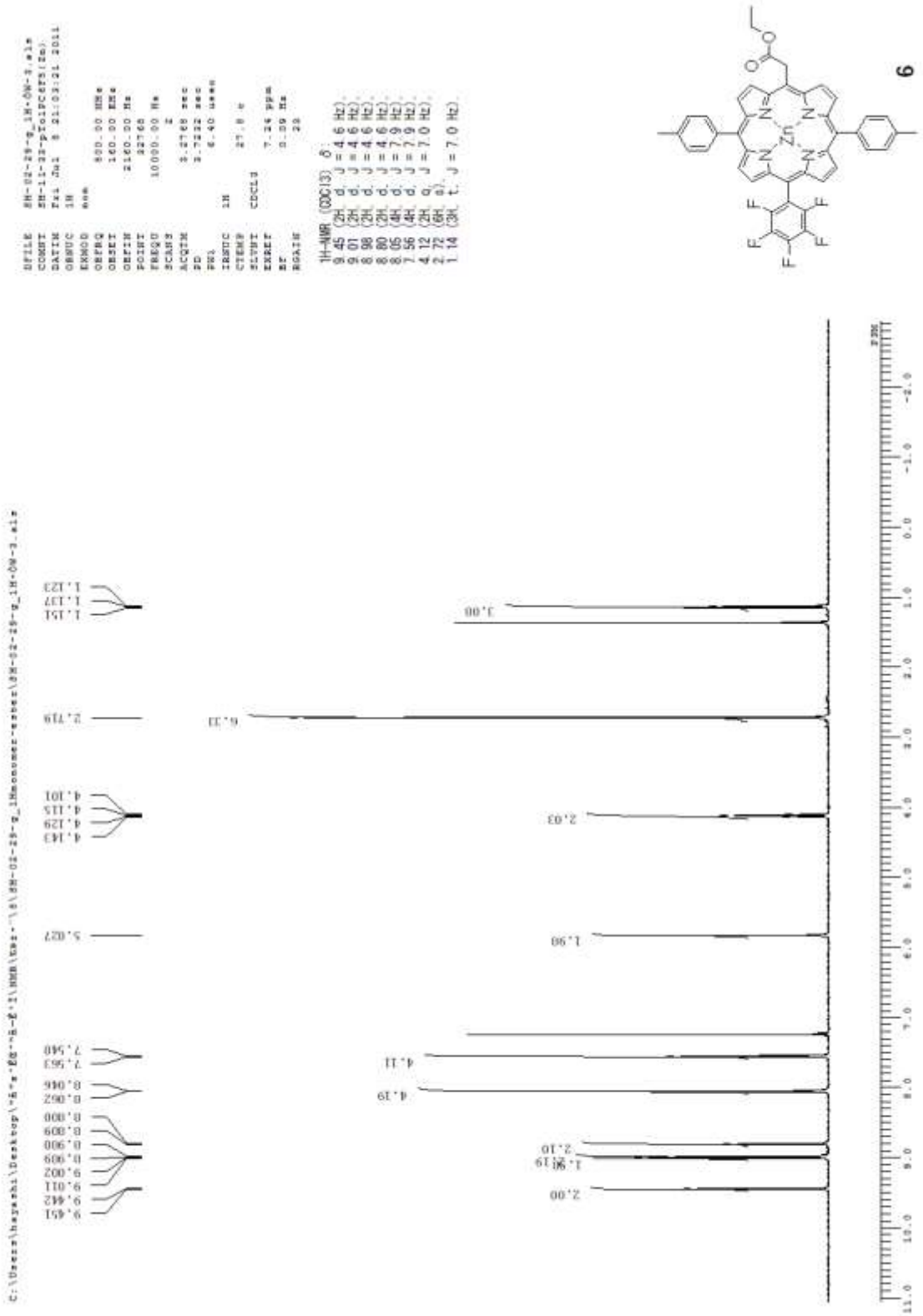


**Fig. S34** $^{13}$C NMR spectrum of compound **6** (125 MHz, $CDCl_3$)

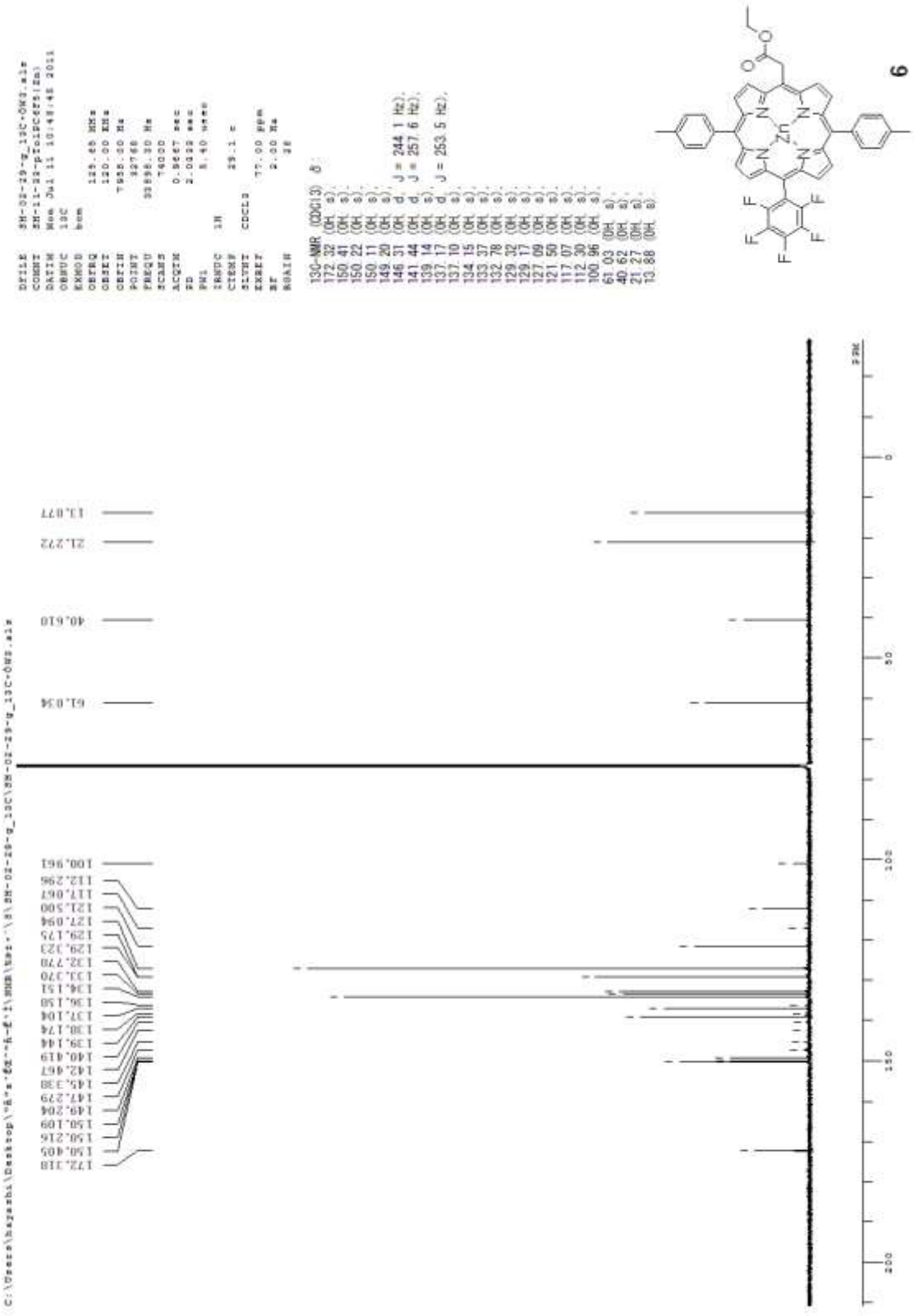


**Fig. S35** $^{19}F$ NMR spectrum of compound **6** (466 MHz, $CDCl_3$)

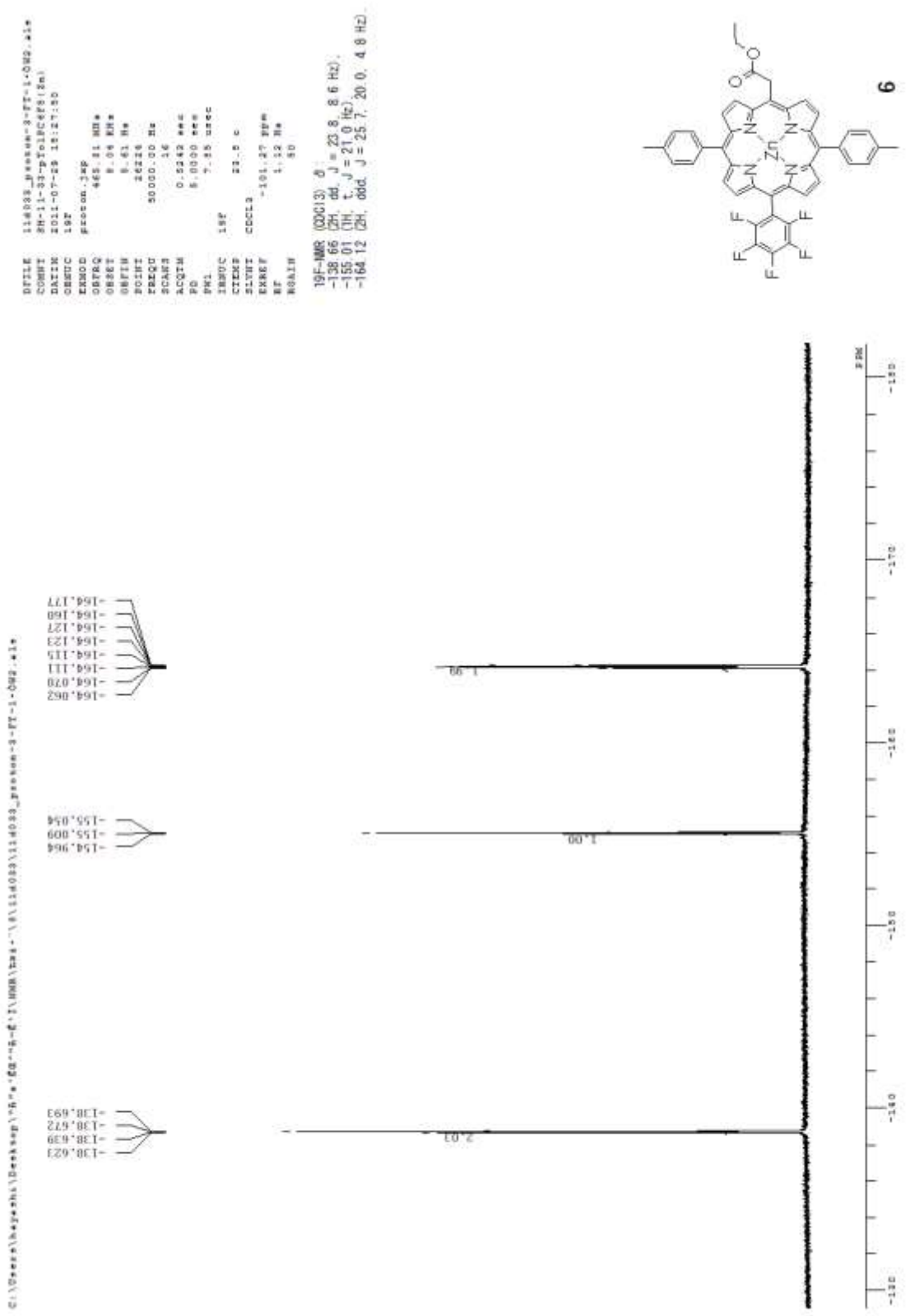


**Fig. S36** $^{1}$H NMR spectrum of compound **7** (500 MHz, $CDCl_3$)

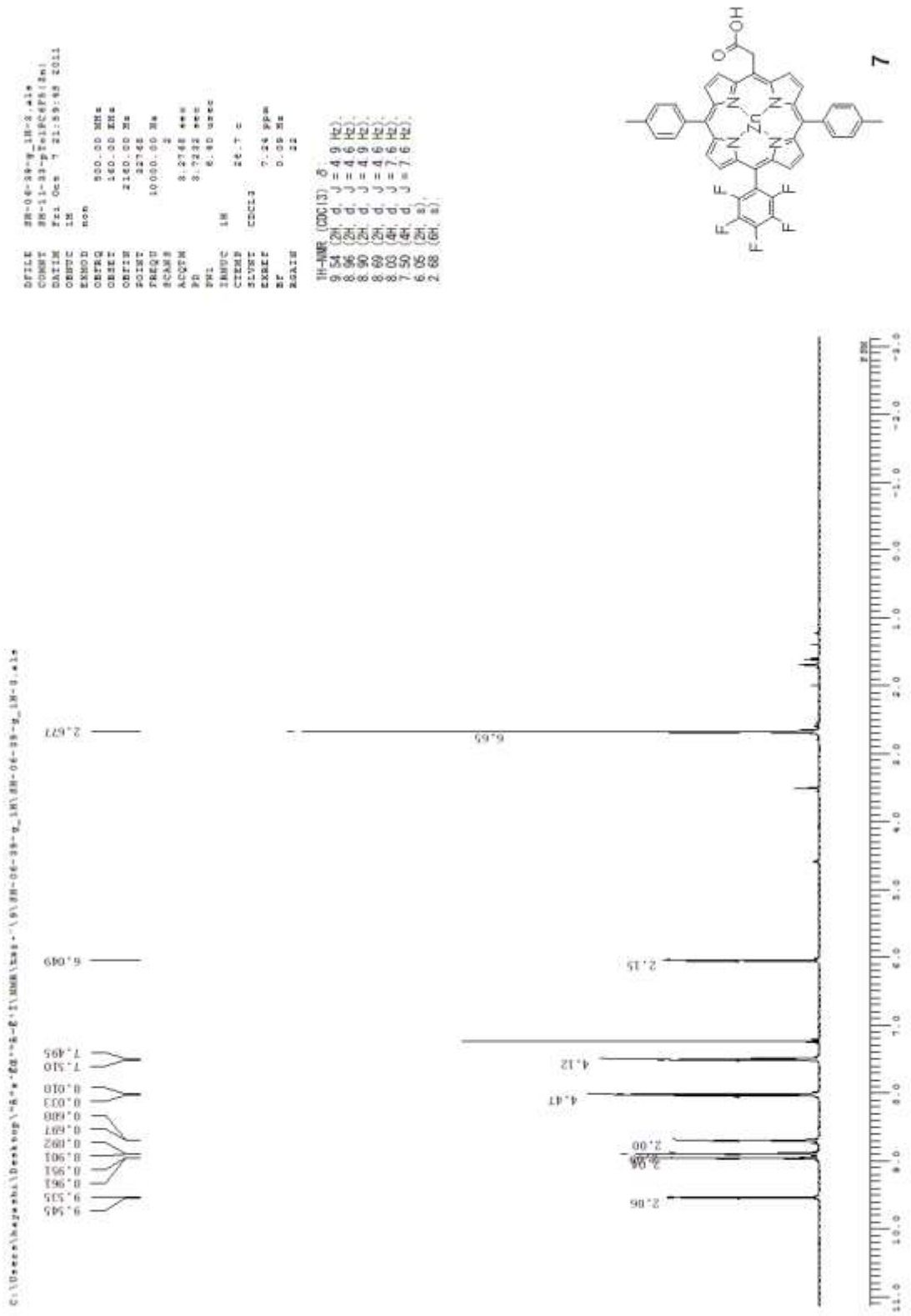


**Fig. S37** $^{13}C$ NMR spectrum of compound **7** (125 MHz, $CDCl_3$)

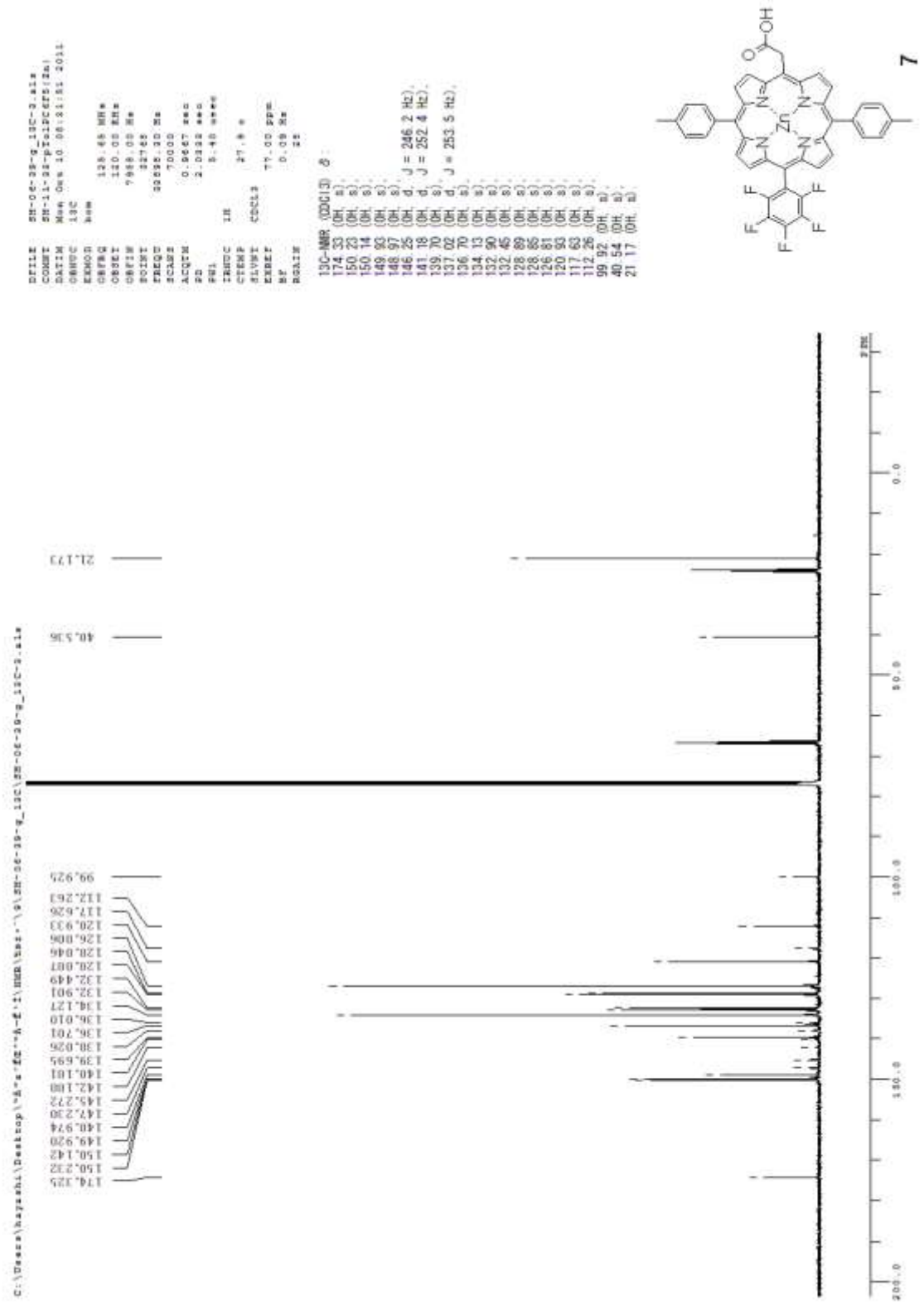


**Fig. S38** $^{19}$F NMR spectrum of compound **7** (466 MHz, $CDCl_3$)

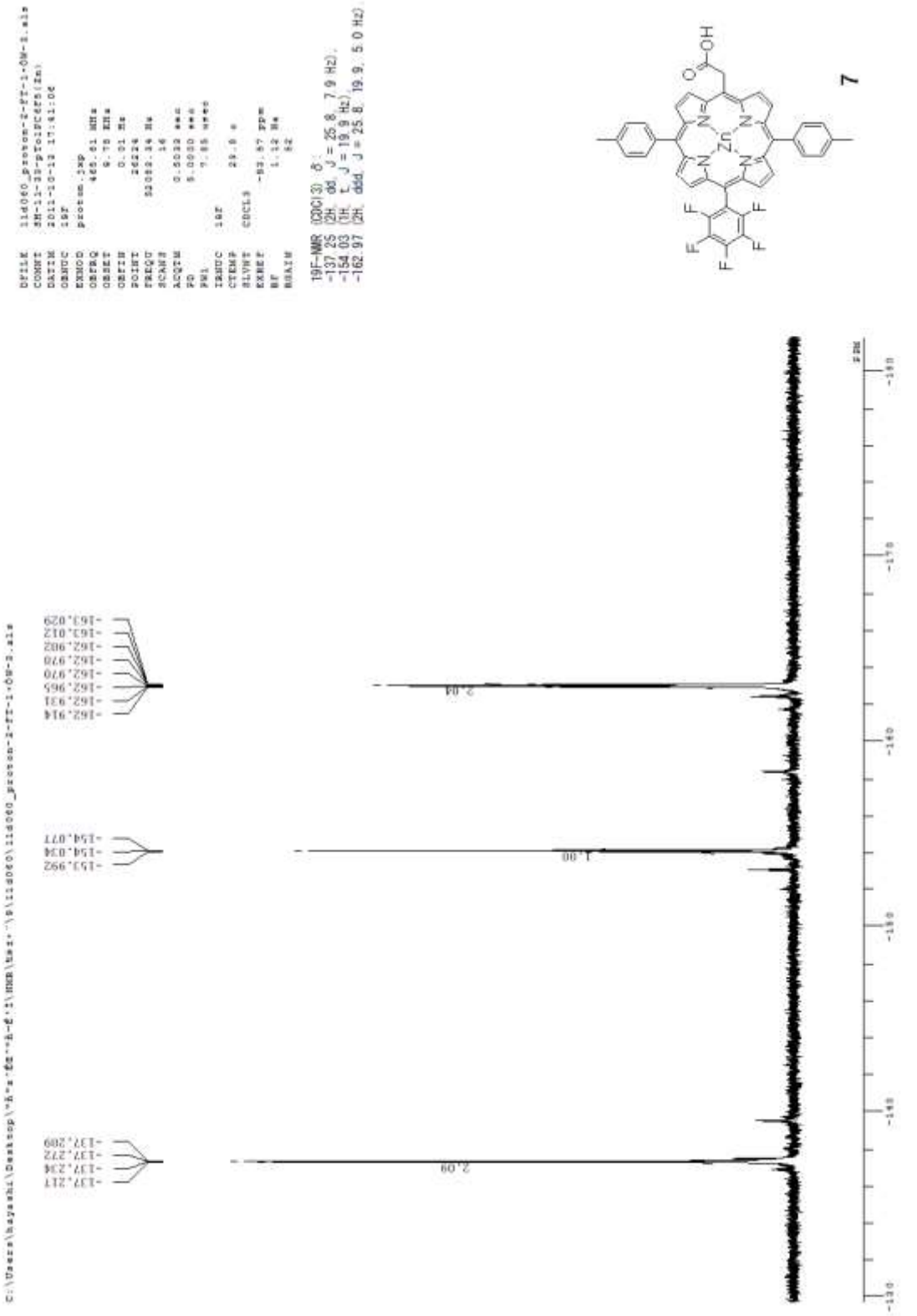


**Fig. S39** $^{1}$H NMR spectrum of compound **BP1** (500 MHz, $CDCl_3$)

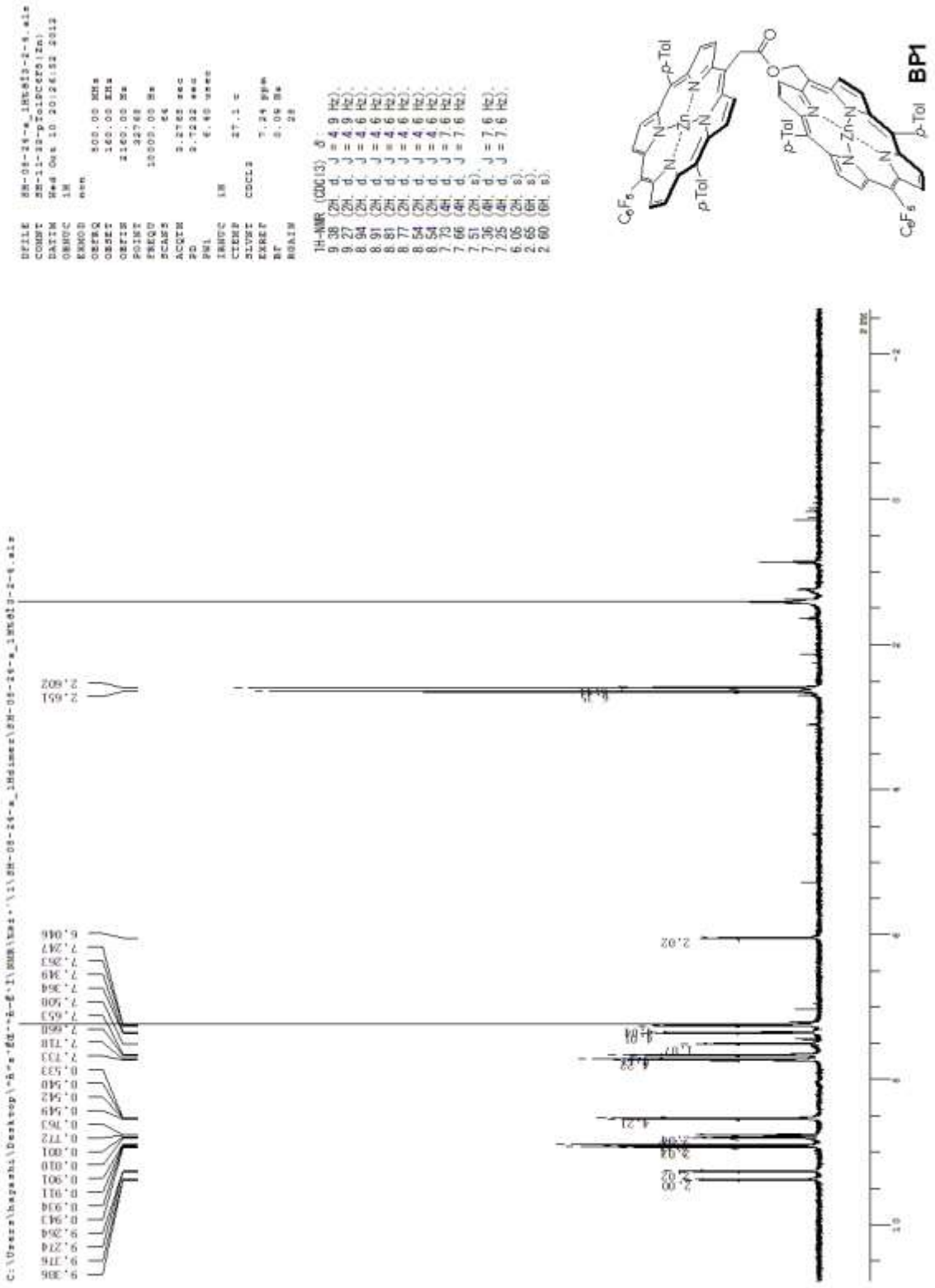


**Fig. S40** $^{13}C$ NMR spectrum of compound **BP1** (125 MHz, $CDCl_3$)

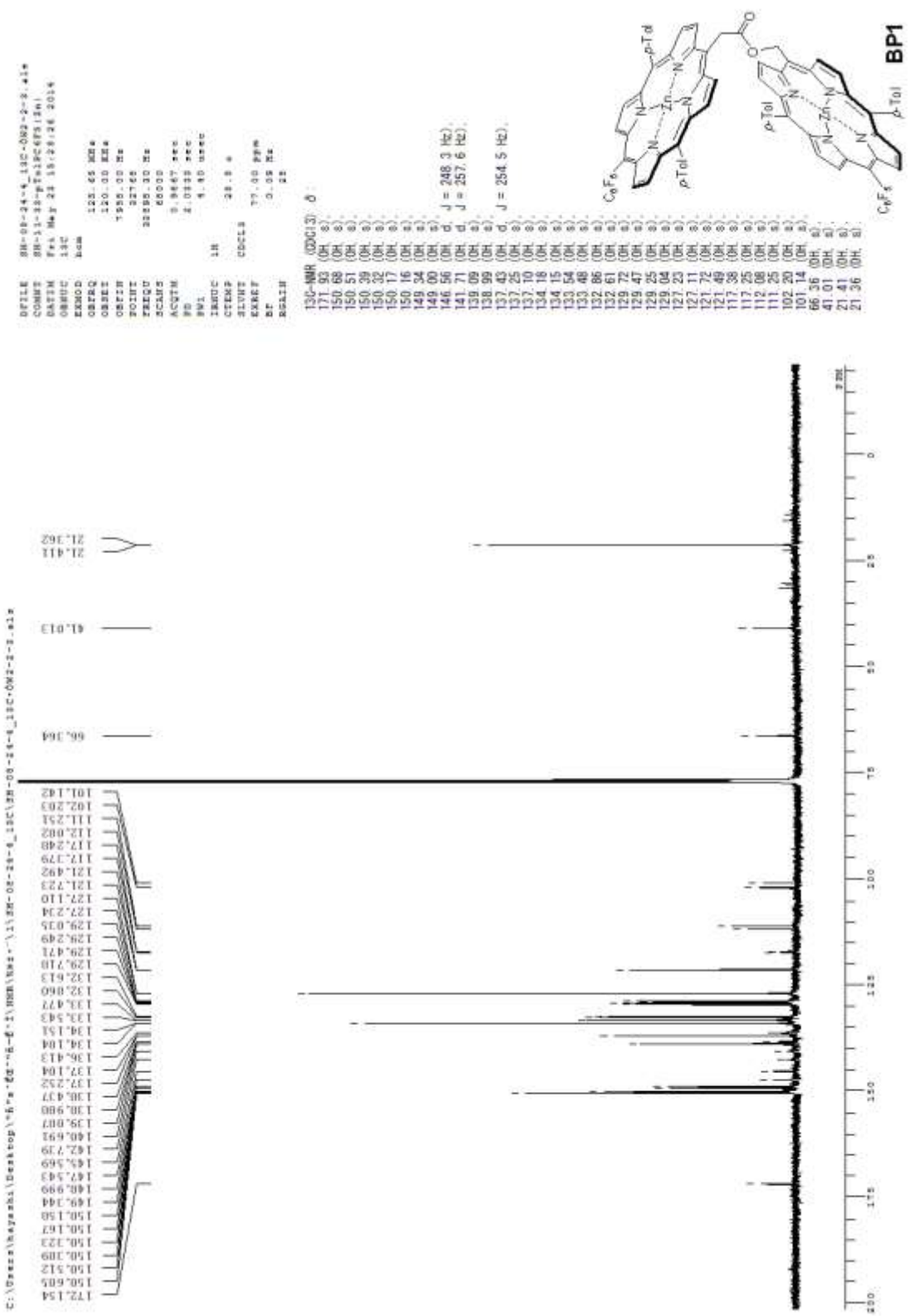


**Fig. S41** $^{19}$F NMR spectrum of compound **BP1** (466 MHz, $CDCl_3$)