

# Cross-bridging Reaction of 5,20-Diethynyl Substituted Hexaphyrins to Vinylene-bridged Hexaphyrins

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## **Acknowledgment**

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## **Supporting Information**

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### **I. General Information**

All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. <sup>1</sup>H NMR spectra were recorded on a JEOL ECA-600 spectrometer, (operating as 600.17 MHz for <sup>1</sup>H and 564.73 MHz for <sup>19</sup>F) using the residual solvent in CDCl<sub>3</sub> and THF-d<sub>8</sub> as the internal reference for <sup>1</sup>H ( $\delta = 7.26$  and 3.70 ppm, respectively) and hexafluorobenzene as external reference for <sup>19</sup>F ( $\delta = -162.9$  ppm). The spectroscopic grade CH<sub>2</sub>Cl<sub>2</sub> was used as solvents for all spectroscopic studies. UV/visible absorption was recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a BRUKER microTOF using positive mode ESI-TOF method of acetonitrile solutions. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-400).

## Experimental Section

### Compound 2:

To a solution of TIPS-propynal (105  $\mu\text{g}$ , 0.50 mmol) and 5,10-bis(pentafluorophenyl)tripyrrene (T) (278 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (22.2 mL) was added methanesulfonic acid (2.5 M diluted with  $\text{CH}_2\text{Cl}_2$ , 12.5  $\mu\text{L}$ ) at 0  $^\circ\text{C}$  under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then DDQ (500 mg) was added. After further stirring for 1 h at room temperature, the resulting solution was passed through a short basic-alumina column with  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  (1:9) as an eluent and the solvent was removed by a rotary evaporator. The residual mixture was purified by silica gel column chromatography with  $\text{CH}_2\text{Cl}_2$ /hexane (3:7) as an eluent. Appropriate fractions were collected and evaporated to dryness. Recrystallization from  $\text{CH}_2\text{Cl}_2$ /MeOH afforded **2** (43 mg, 12%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = -2.23 (s, 4H, inner  $\beta$ -H), -1.92 (br, 2H, NH), 1.51 (d,  $J$  = 7.3 Hz, 36H, TIPS-primary), 1.58 (m, 6H, TIPS-tertiary), 9.37 (d,  $J$  = 4.6 Hz, 4H, outer  $\beta$ -H), and 9.91 (d,  $J$  = 4.6 Hz, 4H, outer  $\beta$ -H) ppm;  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = -163.14 (m, 8F, *meta*-F), -153.14 (m, 4F, *para*-F), and -136.95 (d,  $J$  = 26.3 Hz, 8F, *ortho*-F) ppm; UV/vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$  [ $\text{M}^{-1}\text{cm}^{-1}$ ]): 1066 (25000), 925 (6200), 812 (22000), 744 (22000), 645 (46000) and 579 (260000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity):  $\text{C}_{76}\text{H}_{57}\text{F}_{20}\text{N}_6\text{Si}_2$  ( $[\text{M}+\text{H}]^+$ ), calcd: 1498.3858, found: 1498.3859 (100%); Crystal data:  $\text{C}_{76}\text{H}_{56}\text{F}_{20}\text{N}_6\text{Si}_2$  = 1489, triclinic, space group *P*-1 (No. 2),  $a$  = 8.390 (5),  $b$  = 13.865 (9),  $c$  = 15.169 (7)  $\text{\AA}$ ,  $\alpha$  = 95.39 (2),  $\beta$  = 103.75 (2),  $\gamma$  = 96.10 (2)  $^\circ$ ,  $V$  = 1691 (2)  $\text{\AA}^3$ ,  $Z$  = 1,  $D_{\text{calcd.}}$  = 1.462  $\text{g}/\text{cm}^3$ ,  $T$  = -150  $^\circ\text{C}$ ,  $R_1$  = 0.073 ( $I > 2\sigma(I)$ ),  $R_w$  = 0.222 (all data), GOF = 1.072. CCDC, 622031.

### Compound 3:

A solution of **2** (30 mg, 0.020 mmol) in AcOEt (5 mL) was heated at reflux for 1.5 d, followed by evaporation to dryness. The residue was purified by silica gel column chromatography with  $\text{CH}_2\text{Cl}_2$ /hexane (1:4) as an eluent to give **3** (27mg, 90%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = -2.63 (m, 3H, TIPS-tertiary), -1.67 (d, J = 7.3 Hz, 18H, TIPS-primary), -1.20 (s, 21H, TIPS), 8.56 (d, J = 4.6 Hz, 2H, outer β-H), 8.72 (m, 6H, outer β-H), 9.92 (d, J = 4.6 Hz, 2H, outer β-H), and 10.01 (d, J = 4.6 Hz, 2H, outer β-H) ppm; <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ = -161.14 (m, 8F, meta-F), -151.47 (m, 4F, para-F), -137.14 (d, J = 26.3 Hz, 2F, ortho-F), -136.96 (d, J = 26.3 Hz, 2F, ortho-F), -136.78 (d, J = 26.3 Hz, 2F, ortho-F), and -136.70 (d, J = 26.3 Hz, 4F, ortho-F) ppm; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε [M<sup>-1</sup>cm<sup>-1</sup>]): 974 (5600), 852 (5000), 753 (12000), 695 (29000), 586 (120000), and 556 (290000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C<sub>76</sub>H<sub>57</sub>F<sub>20</sub>N<sub>6</sub>Si<sub>2</sub> ([M+H]<sup>+</sup>), calcd: 1489.58, found: 1489.3859 (100%); Elemental analysis calcd for C<sub>76</sub>H<sub>56</sub>F<sub>20</sub>N<sub>6</sub>Si<sub>2</sub>: C 61.29, H 3.79, N 5.64, F 25.51; found: C 61.29, H 3.66, N 5.70, F 25.55.

#### Compound 4:

To a suspension of **3** and excess NaBH<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> was added MeOH. Resulting mixture was stirred for 1 h and quenched with water. The organic phase was successively washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent gave **4** in an almost quantitative yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.26 (d, J = 7.2 Hz, 18H, TIPS-primary), 3.19-3.74 (12H, β-H), 3.46 (m, 3H, TIPS-tertiary), 4.34 (d, J = 7.2 Hz, 18H, TIPS-primary), 5.33 (m, 3H, TIPS-tertiary), 26.96 (s, 2H, NH), and 27.32 (s, 2H, NH) ppm; <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ = -163.38 (s, 8F, meta-F), -154.40 (m, 2F, para-F), -154.23 (m, 2F, para-F), -139.63 (s, 2F, ortho-F), and -139.78 (m, 6F, ortho-F) ppm; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε [M<sup>-1</sup>cm<sup>-1</sup>]): 589 (37000), 506 (93000), and 308 (25000) nm; HR-ESI-TOF-Mass (negative-mode) (%intensity): C<sub>76</sub>H<sub>57</sub>F<sub>20</sub>N<sub>6</sub> ([M-H]<sup>-</sup>), calcd: 1489.3869, found: 1489.3860 (100%); Elemental analysis calcd for C<sub>76</sub>H<sub>58</sub>F<sub>20</sub>N<sub>6</sub>: C 61.20, H 3.92, N 5.63, F 25.48; found: C 61.35, H 3.82, N 5.56, F 25.52.

#### Compound 6:

To a solution of phenylpropynal (61 μl, 0.50 mmol) and

5,10-bis(pentafluorophenyl)tripyrane (**T**) (278 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (22 mL) was added methanesulfonic acid (2.5 M diluted with CH<sub>2</sub>Cl<sub>2</sub>, 12.5 μL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then DDQ (500 mg) was added. After further stirring for 1 h at room temperature, the resulting solution was passed through a short basic-alumina column with MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:9) and solvent was removed by a rotary evaporator. The residual mixture was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:4) as an eluent. Appropriate fractions were collected and evaporated to dryness. Recrystallization from hexane afforded **6** (15 mg, 4.5%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 1.17 (s, 2H, inner NH), 1.31 (d, *J* = 8.8 Hz, 2H, phenyl-*ortho*), 4.61 (t, *J* = 8.7 Hz, 2H, phenyl-*meta*), 4.71 (d, *J* = 8.7 Hz, 2H, phenyl-*ortho*), 5.25 (t, *J* = 7.3 Hz, 1H, phenyl-*para*), 6.09 (t, *J* = 8.7 Hz, 2H, phenyl-*meta*), 6.30 (d, *J* = 7.3 Hz, 1H, phenyl-*para*), 8.68 (d, *J* = 4.6 Hz, 2H, outer β-H), 8.74 (d, *J* = 4.1 Hz, 2H, outer β-H), 8.84 (s, 4H, outer β-H), 10.00 (d, *J* = 4.6 Hz, 2H, outer β-H), and 10.14 (d, *J* = 4.6 Hz, 2H, outer β-H) ppm; <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ = -160.88 (m, 8F, *meta*-F), -151.06 (s, 4F, *para*-F), -136.68 (d, *J* = 26.3 Hz, 2F, *ortho*-F), -136.42 (d, *J* = 17.6 Hz, 2F, *ortho*-F), -136.34 (d, *J* = 17.6 Hz, 2F, *ortho*-F), and -136.15 (d, *J* = 17.6 Hz, 2F, *ortho*-F) ppm; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε [M<sup>-1</sup>cm<sup>-1</sup>]): 962 (3700), 845 (5100), 743 (6000), 691 (30000), and 553 (320000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C<sub>70</sub>H<sub>25</sub>F<sub>20</sub>N<sub>6</sub> ([*M*+*H*]<sup>+</sup>), calcd: 1329.1816, found: 1329.1818 (100%); Elemental analysis calcd for C<sub>70</sub>H<sub>24</sub>F<sub>20</sub>N<sub>6</sub>: C 63.26, H 1.82, N 6.32, F 28.59; found: C 63.54, H 1.66, N 6.39, F 28.54.

#### Compound 7:

To a suspension of **6** and excess NaBH<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> was added MeOH. Resulting mixture was stirred for 1 h and quenched with water. The organic phase was successively washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent gave **7** in an almost quantitative yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.16-2.94 (12H, β-H), 8.71 (t, *J* = 7.2 Hz, 1H, phenyl-*para*), 9.06 (t, *J* = 7.2 Hz, 2H, phenyl-*meta*), 9.97 (t, *J*

= 7.8 Hz, 1H, phenyl-*para*) 10.78 (t,  $J = 7.2$  Hz, 2H, phenyl-*meta*), 11.71 (d,  $J = 6.6$  Hz, 2H, phenyl-*ortho*), 15.86 (d,  $J = 7.2$  Hz, 2H, phenyl-*ortho*), 31.61 (br, 4H, NH) ppm;  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = -160.26$  (m, 8F, *meta*-F),  $-154.09$  (m, 4F, *para*-F),  $-139.42$  (s, 2F, *ortho*-F),  $-138.64$  (s, 2F, *ortho*-F), and  $-138.48$  (s, 4F, *ortho*-F) ppm; UV/vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$  [ $\text{M}^{-1}\text{cm}^{-1}$ ]): 567 (5900, sh), 508 (120000), and 304 (48000) nm; HR-ESI-TOF-Mass (negative-mode) (%intensity):  $\text{C}_{70}\text{H}_{25}\text{F}_{20}\text{N}_6$  ( $[\text{M}-\text{H}]^-$ ), calcd: 1329.1827, found: 1329.1822 (100%); Elemental analysis calcd for  $\text{C}_{70}\text{H}_{26}\text{F}_{20}\text{N}_6$ : C 63.17, H 1.97, N 6.31, F 28.55; found: C 62.91, H 1.86, N 6.11, F 28.60.

#### Compound 8:

To a solution of **6** (20.5 mg, 0.0154 mmol) and  $\text{ZnCl}_2$  (1 g) in  $\text{CH}_2\text{Cl}_2$  (7 mL) was added MeOH (3 mL) and the resulting solution was stirred for 5 h at room temperature under nitrogen atmosphere. Reaction mixture was diluted with 20 mL of  $\text{CH}_2\text{Cl}_2$  and passed through silica gel column with MeOH in  $\text{CH}_2\text{Cl}_2$  (5%) as an eluent. After removal of solvent, the residual mixture was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  to get Zn-complex **8** (17.4 mg, 74%).  $^1\text{H}$ -NMR ( $\text{THF}-d_8$ ):  $\delta = 2.21$  (d,  $J = 8.7$  Hz, 2H, phenyl-*ortho*), 3.43 (d,  $J = 8.7$  Hz, 2H, phenyl-*ortho*), 4.58 (t,  $J = 8.7$  Hz, 2H, phenyl-*meta*), 5.08 (t,  $J = 7.3$  Hz, 1H, phenyl-*para*), 5.71 (t,  $J = 7.8$  Hz, 2H, phenyl-*meta*), 6.10 (d,  $J = 7.3$  Hz, 1H, phenyl-*para*), 9.22 (d,  $J = 4.6$  Hz, 1H, outer  $\beta$ -H), 9.26 (d,  $J = 4.6$  Hz, 1H, outer  $\beta$ -H), 9.28 (d,  $J = 4.1$  Hz, 1H, outer  $\beta$ -H), 9.33 (d,  $J = 4.6$  Hz, 1H, outer  $\beta$ -H), 9.54 (d,  $J = 4.6$  Hz, 1H, outer  $\beta$ -H), 9.75 (m, 2H, outer  $\beta$ -H), 9.87 (d,  $J = 4.6$  Hz, 2H, outer  $\beta$ -H), 11.18 (d,  $J = 5.0$  Hz, 1H, outer  $\beta$ -H) 11.24 (d,  $J = 4.6$  Hz, 1H, outer  $\beta$ -H) 11.28 (d,  $J = 4.6$  Hz, 1H, outer  $\beta$ -H) and 11.37 (d,  $J = 5.0$  Hz, 1H, outer  $\beta$ -H) ppm;  $^{19}\text{F}$ -NMR ( $\text{THF}-d_8$ ):  $\delta = -163.95$  (m, 8F, *meta*-F),  $-154.23$  (m, 4F, *para*-F),  $-139.50$  (d,  $J = 26.3$  Hz, 1F, *ortho*-F),  $-138.91$  (d,  $J = 26.3$  Hz, 1F, *ortho*-F),  $-138.70$  (d,  $J = 17.6$  Hz, 2F, *ortho*-F),  $-138.39$  (d,  $J = 17.5$  Hz, 1F, *ortho*-F),  $-138.25$  (d,  $J = 17.6$  Hz, 1F, *ortho*-F) and  $-138.07$  (s, 2F, *ortho*-F) ppm; UV/vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$  [ $\text{M}^{-1}\text{cm}^{-1}$ ]): 902 (4800), 821 (22000), 625 (72000), 581 (390000), and 399 (230000) nm;

HR-ESI-TOF-Mass (negative-mode) (%intensity):  $C_{70}H_{22}F_{20}N_6Zn_2Cl_2$  ( $[M]^-$ ), calcd: 1527.9520, found: 1527.9590 (100%); Elemental analysis calcd for  $C_{70}H_{22}F_{20}N_6Zn_2Cl_2 \cdot H_2O$ : C 54.36, H 1.56, N 5.43; found: C 54.25, H 1.65, N 5.35.

#### Compound 10:

To a solution of TIPS-propynal (210 mg, 1.0 mmol), phenylpropynal (122  $\mu$ l, 1.0 mmol) and 5,10-bis(pentafluorophenyl) tripyrrane (1.12 g, 2.0 mmol) in  $CH_2Cl_2$  (90 ml) was added methanesulfonic acid (2.5 M diluted with  $CH_2Cl_2$ , 50  $\mu$ L) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then DDQ (2.0 g) was added. After further stirring for 1 h at room temperature, the resulting solution was passed through a short basic-alumina column with MeOH/ $CH_2Cl_2$  (1:9) and the solvent was removed by a rotary evaporator. The residual mixture was purified by silica gel column chromatography with  $CH_2Cl_2$ /hexane (1:4) as an eluent. **10** (47 mg, 3.4%), **6** (41 mg, 3.1%), and **2** (25 mg, 1.7%) were obtained in this order.  $^1H$ -NMR ( $CDCl_3$ ): -1.00 (m, 21H, TIPS), 1.41 (s, 2H, NH), 1.53 (d,  $J = 8.3$  Hz, 2H, phenyl-*ortho*), 4.68 (t,  $J = 8.2$  Hz, 2H, phenyl-*meta*), 5.29 (t,  $J = 7.3$  Hz, 1H, phenyl-*para*), 8.62 (d,  $J = 4.6$  Hz, 2H, outer  $\beta$ -H), 8.68 (d,  $J = 4.6$  Hz, 2H, outer  $\beta$ -H), 8.81 (s, 4H, outer  $\beta$ -H), 9.89 (d,  $J = 4.1$  Hz, 2H, outer  $\beta$ -H), and 10.03 (d,  $J = 4.6$  Hz, 2H, outer  $\beta$ -H) ppm;  $^{19}F$ -NMR ( $CDCl_3$ ):  $\delta = -160.89$  (m, 8F, *meta*-F),  $-151.14$  (m, 4F, *para*-F),  $-136.71$  (m, 4F, *ortho*-F), and  $-136.50$  (m, 4F, *ortho*-F) ppm; UV/vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  ( $\epsilon$  [ $M^{-1}cm^{-1}$ ]): 962 (2900), 846 (4500), 737 (6300), 689 (21000), and 556 (290000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity):  $C_{73}H_{41}F_{20}N_6Si$  ( $[M+H]^+$ ), calcd: 1409.2837, found: 1409.2830 (100%).

#### Compound 11:

To a suspension of **10** and excess  $NaBH_4$  in  $CH_2Cl_2$  was added MeOH. Resulting mixture was stirred for 1 h and quenched with water. The organic phase was successively washed with water and brine, then dried over  $Na_2SO_4$ . Removal of

solvent gave **11** in an almost quantitative yield.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 3.26$  (d,  $J = 7.2$  Hz, 18H, TIPS-primary), 2.18-2.91 (12H,  $\beta$ -H), 4.06 (m, 3H, TIPS-tertiary), 9.99 (t,  $J = 7.8$  Hz, 1H, phenyl-*para*), 10.77 (t,  $J = 7.2$  Hz, 2H, phenyl-*meta*), 15.71 (d,  $J = 7.2$  Hz, 2H, phenyl-*ortho*), 31.89 (br, 2H, NH), and 31.97 (br, 2H, NH) ppm;  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = -160.38$  (s, 8F, *meta*-F), -154.40 (m, 2F, *para*-F), -154.23 (m, 2F, *para*-F), -139.63 (s, 2F, *ortho*-F), -138.87 (s, 2F, *ortho*-F) -138.78 (s, 2F, *ortho*-F) and -138.64 (s, 2F, *ortho*-F) ppm; UV/vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$  [ $\text{M}^{-1}\text{cm}^{-1}$ ]): 687 (18000), 552 (90000), and 508 (110000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity):  $\text{C}_{73}\text{H}_{42}\text{F}_{20}\text{N}_6$  ( $[\text{M}]^+$ ), calcd: 1410.2915, found: 1410.2918 (100%).

#### Compound **12**:

To a suspension of **2** and excess  $\text{NaBH}_4$  in  $\text{CH}_2\text{Cl}_2$  was added MeOH. Resulting mixture was stirred for 1 h and quenched with water. The organic phase was successively washed with water and brine, then dried over  $\text{Na}_2\text{SO}_4$ . Removal of solvent gave **12**, respectively, in an almost quantitative yield.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 2.08$  (br, 2H,  $\beta$ -H), 2.78 (br, 2H,  $\beta$ -H), 3.90 (s, 2H, NH), 7.61 (d,  $J = 4.6$  Hz, 2H,  $\beta$ -H), 7.84 (d,  $J = 4.6$  Hz, 2H,  $\beta$ -H), 7.91 (d,  $J = 5.0$  Hz, 2H,  $\beta$ -H), 8.05 (d,  $J = 4.6$  Hz, 2H,  $\beta$ -H), and 8.26 (br, 2H, NH) ppm;  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = -161.40$  (m, 4F, *meta*-F), -160.63 (m, 4F, *meta*-F), -152.88 (m, 2F, *para*-F), -151.73 (m, 2F, *para*-F), -137.70 (d,  $J = 26.3$  Hz, 4F, *ortho*-F), and -136.93 (d,  $J = 17.6$  Hz, 4F, *ortho*-F) ppm; UV/vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$  [ $\text{M}^{-1}\text{cm}^{-1}$ ]): 1052 (1800), 922 (6200), 869 (10000), 781 (16000), 617 (220000), 452 (29000), 403 (39000), and 314 (30000) nm; HR-ESI-TOF-Mass (negative-mode) (%intensity):  $\text{C}_{76}\text{H}_{57}\text{F}_{20}\text{N}_6$  ( $[\text{M-H}]^-$ ), calcd: 1489.3869, found: 1489.3875 (100%); Elemental analysis calcd for  $\text{C}_{76}\text{H}_{58}\text{F}_{20}\text{N}_6$ : C 61.20, H 3.92, N 5.63, F 25.48; found: C 61.39, H 4.06, N 5.57, F 25.75.

### III. Figures

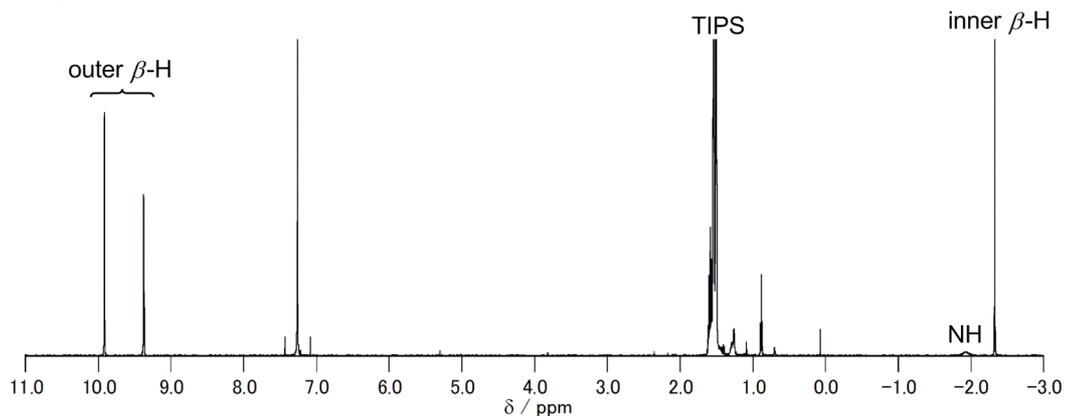


Figure S1.  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .

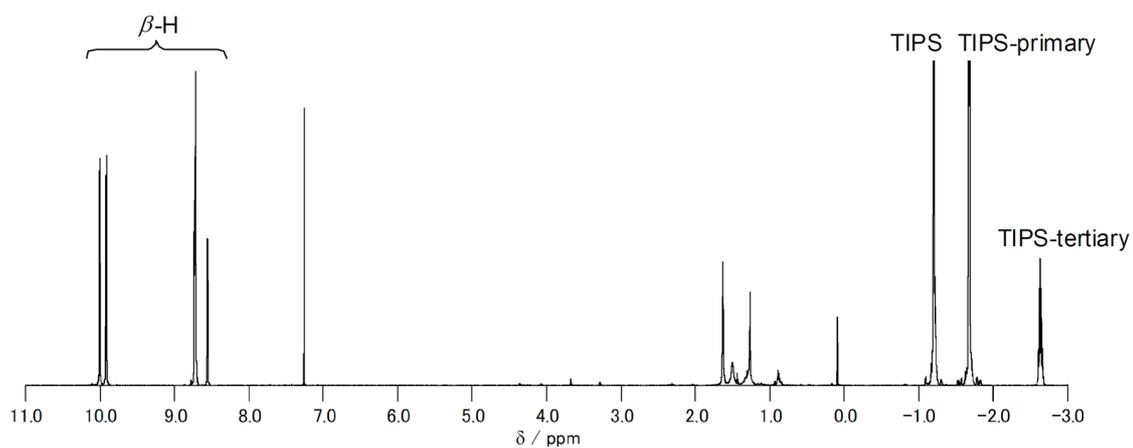


Figure S2.  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .

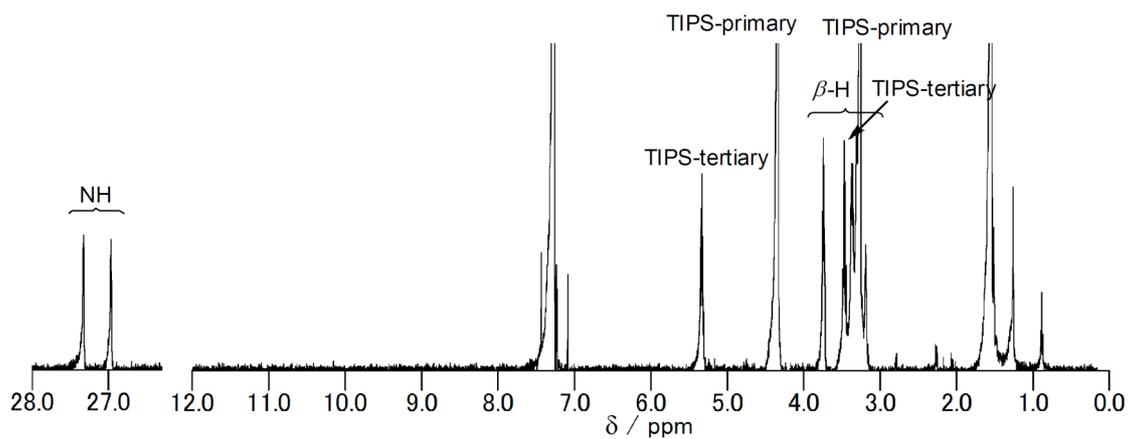


Figure S3.  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .

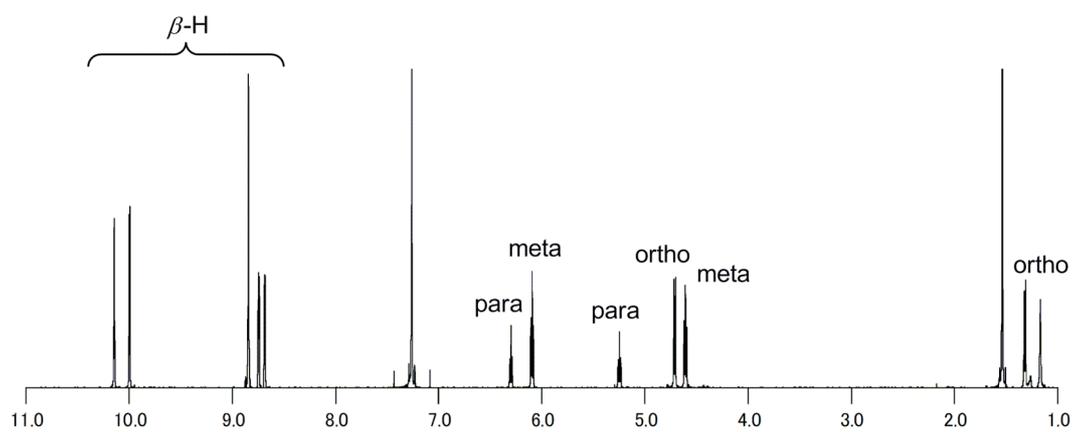


Figure S4.  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$ .

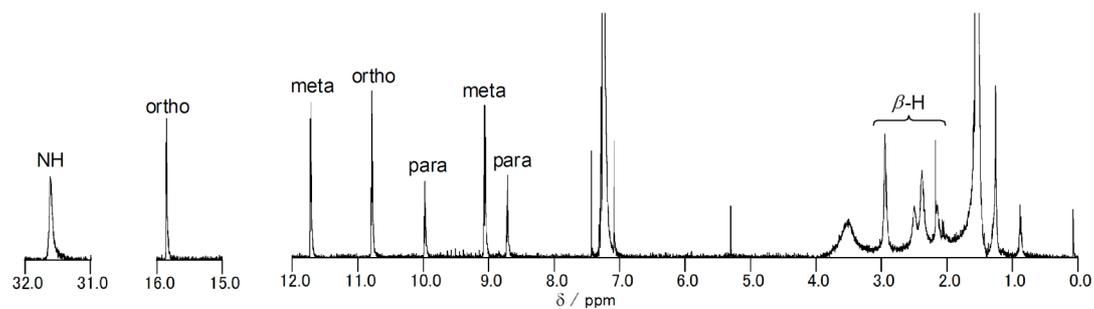


Figure S5.  $^1\text{H}$  NMR spectrum of **7** in  $\text{CDCl}_3$ .

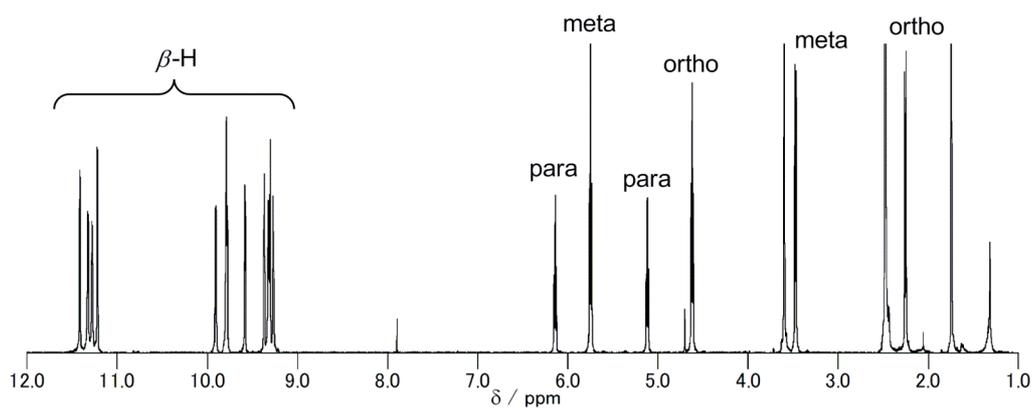


Figure S6.  $^1\text{H}$  NMR spectrum of **8** in  $\text{CDCl}_3$ .

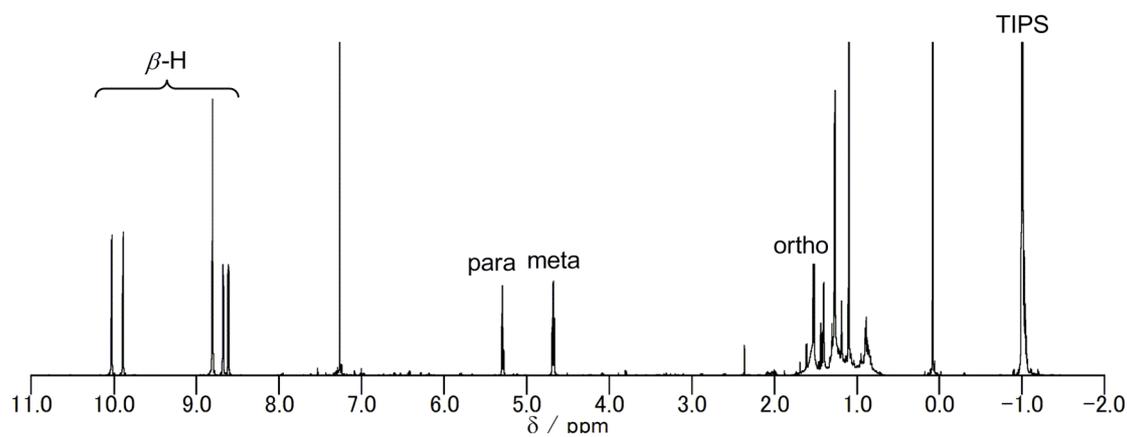


Figure S7.  $^1\text{H}$  NMR spectrum of **10** in  $\text{CDCl}_3$ .

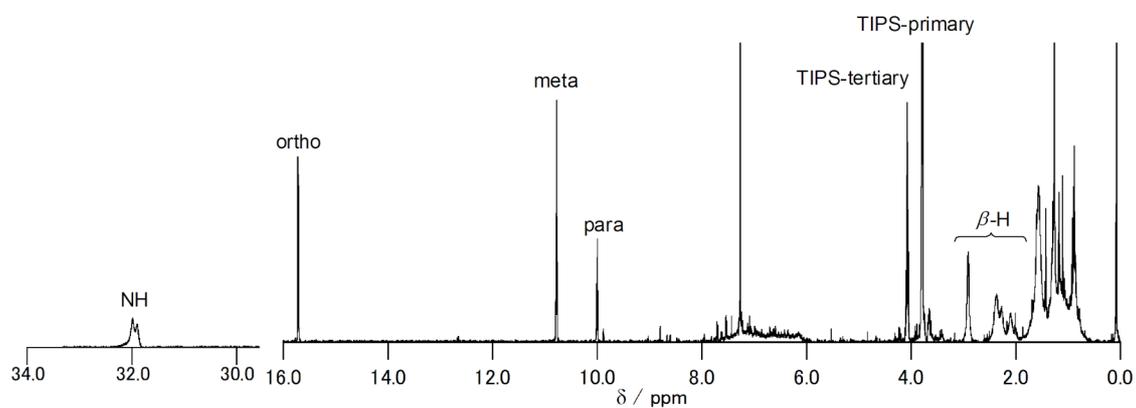


Figure S8.  $^1\text{H}$  NMR spectrum of **11** in  $\text{CDCl}_3$ .

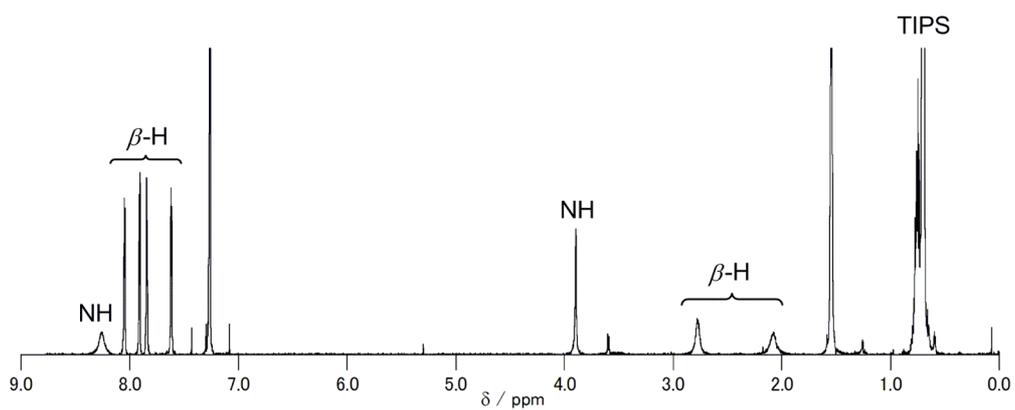
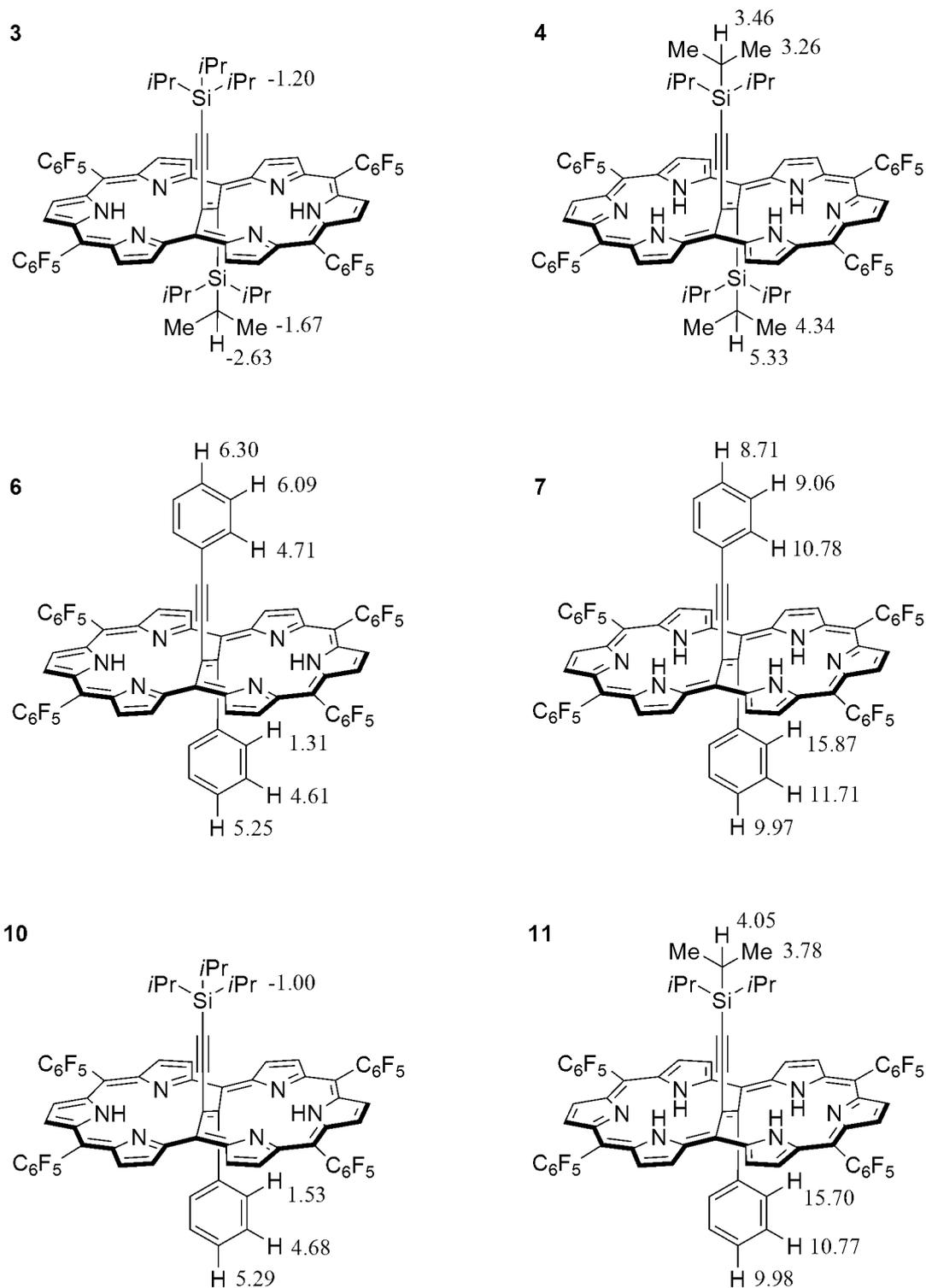


Figure S9.  $^1\text{H}$  NMR spectrum of **12** in  $\text{CDCl}_3$ .



**Figure S10.** Comparison of chemical shifts of [26]hexaphyrins **3**, **6**, and **10**, and [28]hexaphyrins **4**, **7**, and **11**. The former exhibit diatropic ring currents and the latter exhibit paratropic ring currents.

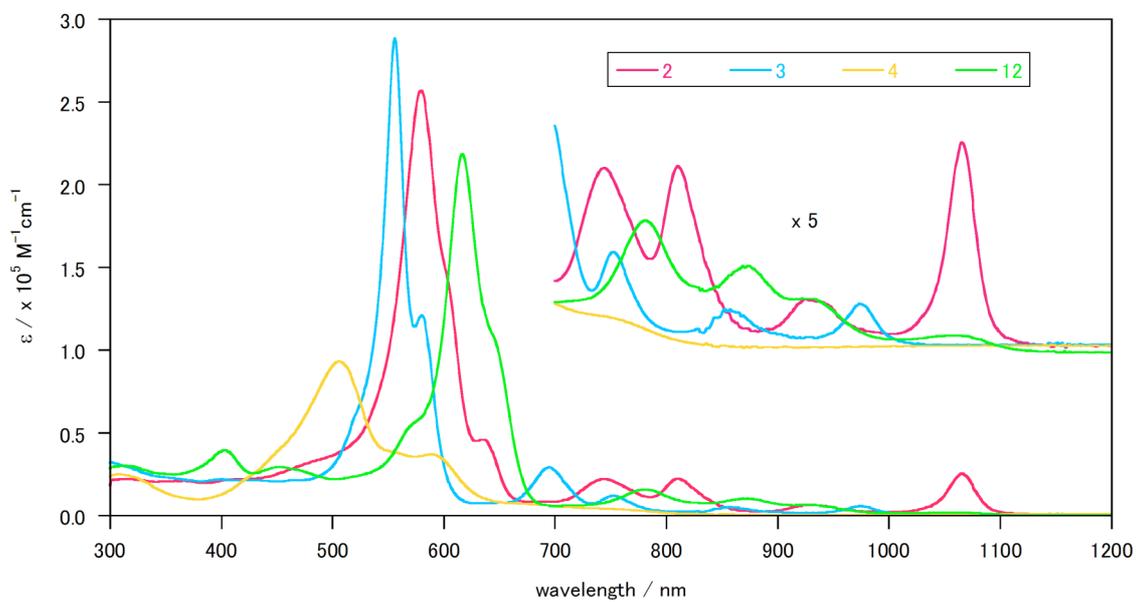


Figure S11. UV-visible absorption spectra of 2, 3, 4, and 12 in  $\text{CH}_2\text{Cl}_2$ .

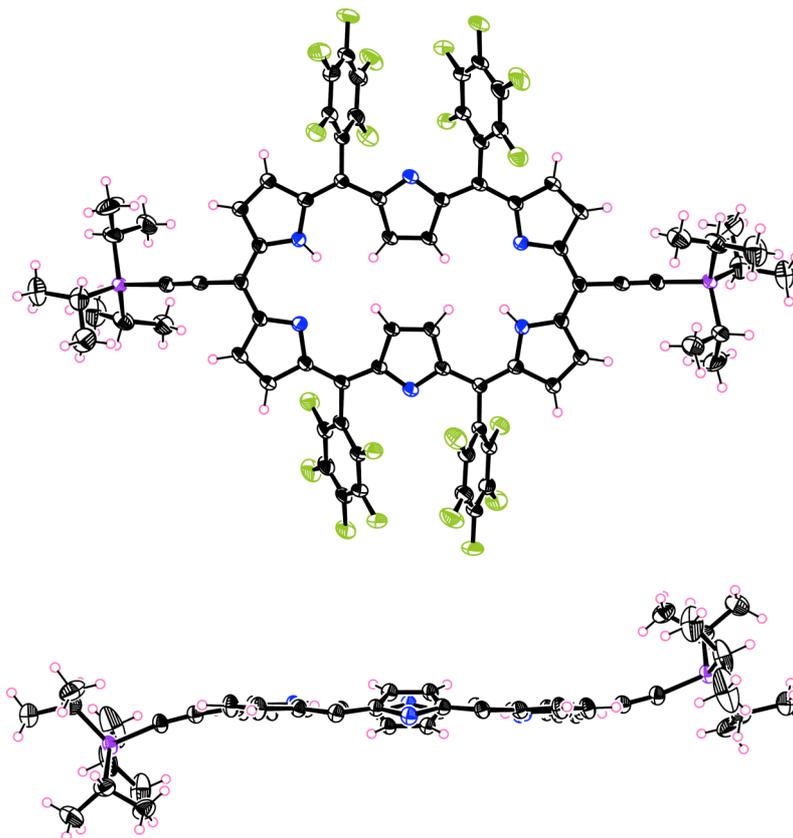


Figure S12. Crystal structures of 2. Upper: top view, lower: side view. Pentafluorophenyl groups and hydrogen atoms in the side view are omitted. Thermal ellipsoids are scaled to the 50% probability level.

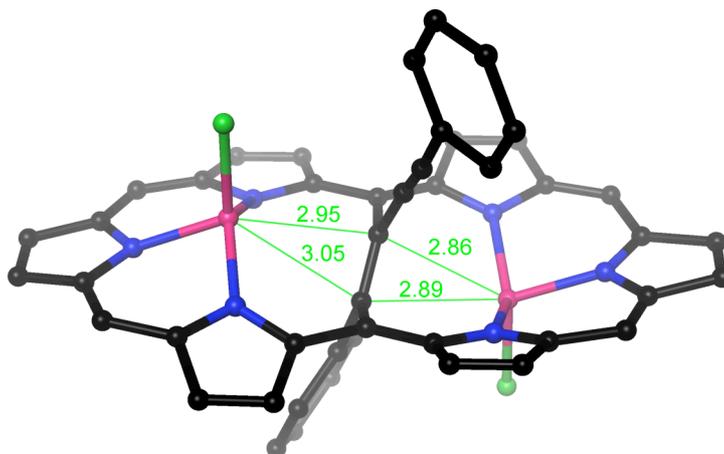


Figure S13. Distances between zinc(II) ions and vinylene bridge of **8**.

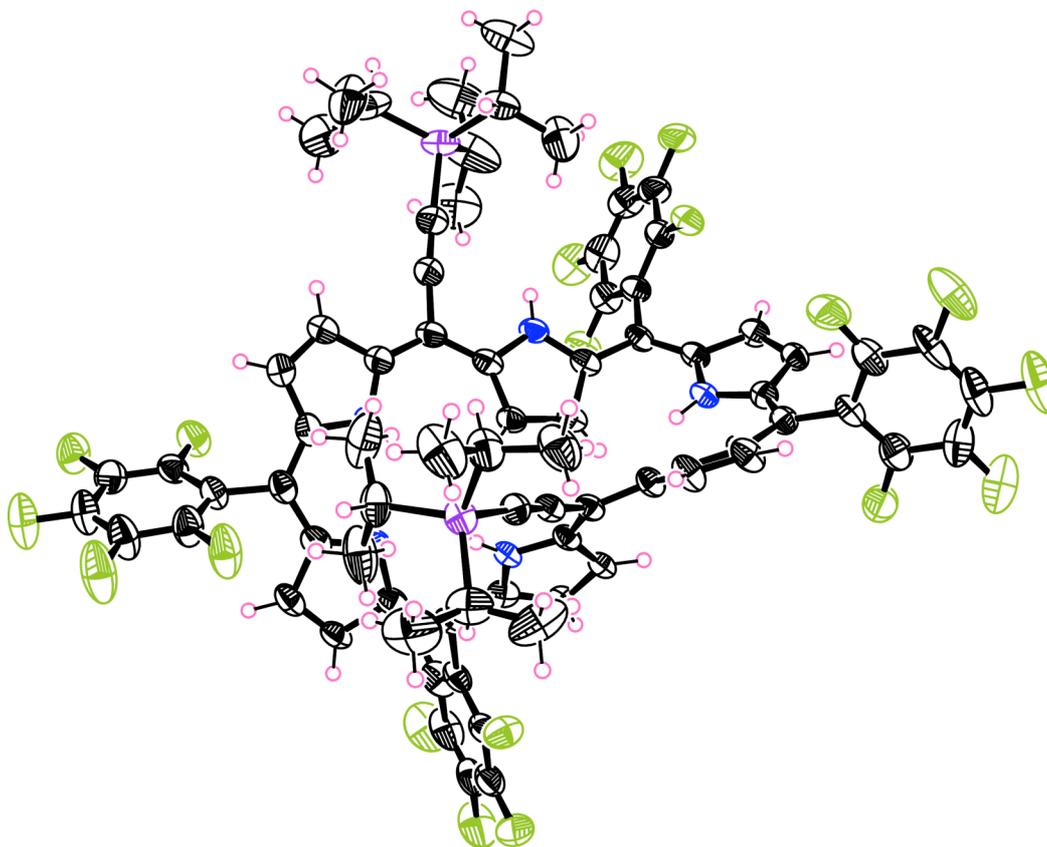


Figure S14. Preliminary crystal structure of **12**. Thermal ellipsoids are scaled to the 50% probability level. Crystal data: monoclinic, space group  $P2_1/n$  (No. 14),  $a = 16.210(4)$ ,  $b = 20.391(5)$ ,  $c = 23.229(6)$  Å,  $\beta = 98.095(12)^\circ$ ,  $Z = 4$ ,  $R_1 = 0.152$  ( $I > 2\sigma(I)$ ).

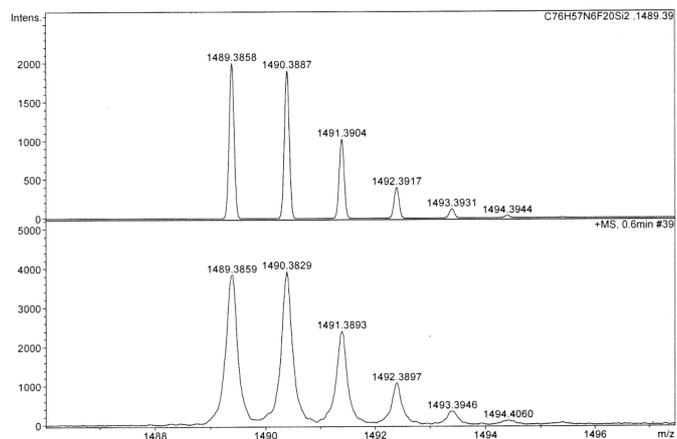


Figure S15. ESI TOS-mass spectrum of 2. Upper: calcd; lower: found.

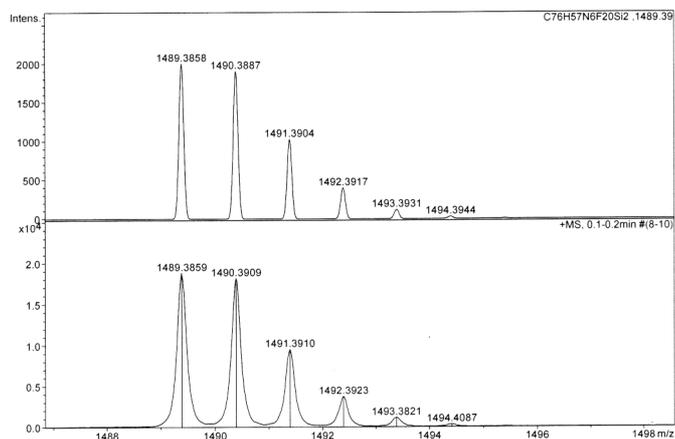


Figure S16. ESI TOS-mass spectrum of 3. Upper: calcd; lower: found.

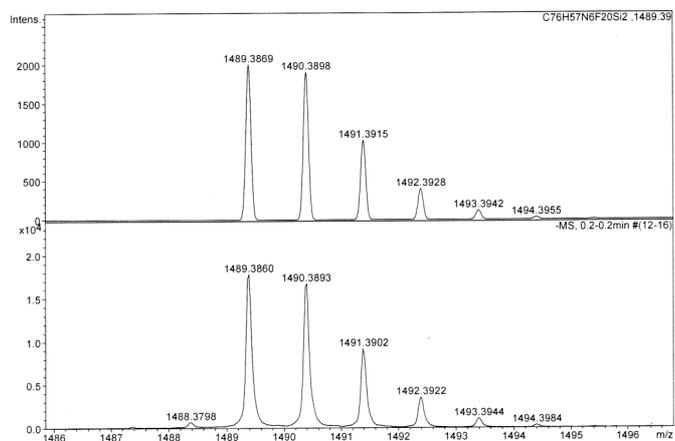


Figure S17. ESI TOS-mass spectrum of 4. Upper: calcd; lower: found.

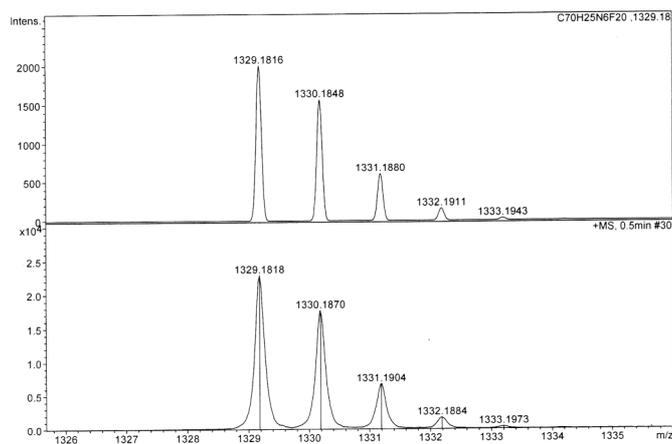


Figure S18. ESI TOS-mass spectrum of 6. Upper: calcd; lower: found.

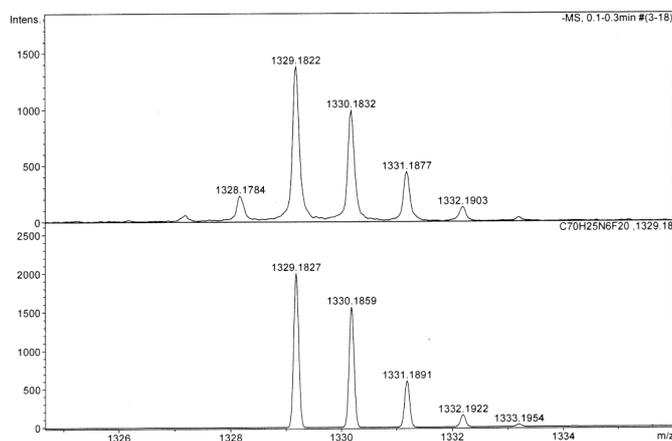


Figure S19. ESI TOS-mass spectrum of 7. Upper: found; lower: calcd.

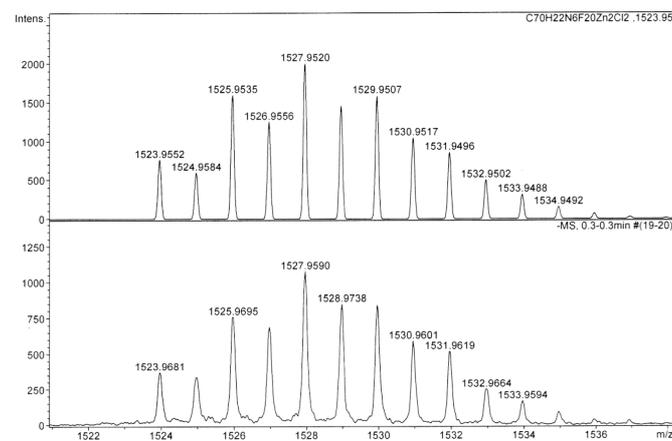


Figure S20. ESI TOS-mass spectrum of 8. Upper: calcd; lower: found.

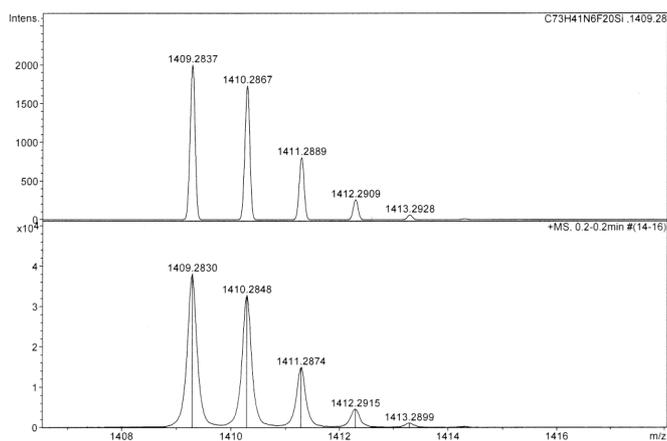


Figure S21. ESI TOS-mass spectrum of 10. Upper: calcd; lower: found.

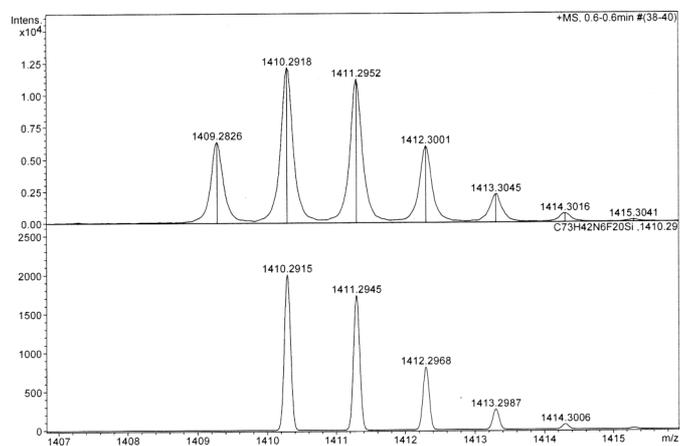


Figure S22. ESI TOS-mass spectrum of 11. Upper: found; lower: calcd.

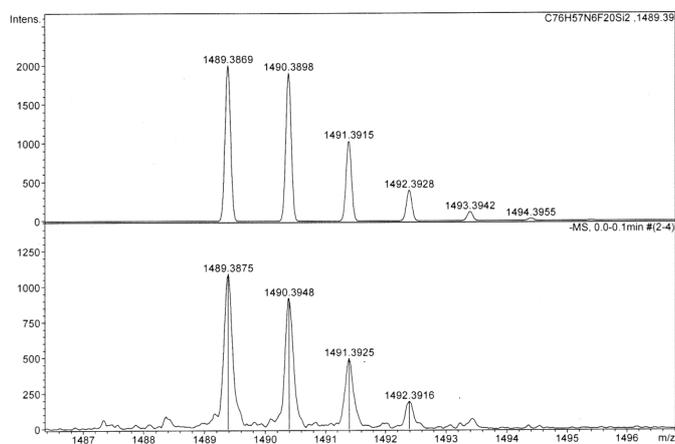
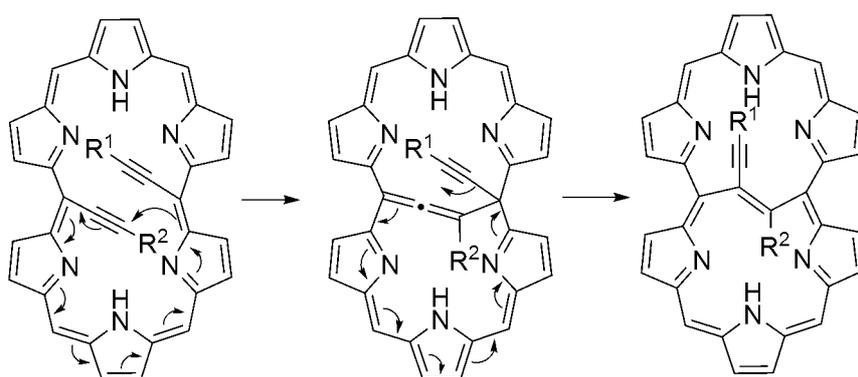


Figure S23. ESI TOS-mass spectrum of 12. Upper: calcd; lower: found.



*Scheme S1.* A possible reaction mechanism of the cross bridging reaction.