Electronic Supplementary Material (ESI) for RSC Advances.

Gram-scale synthesis of porphycenes through acid-catalyzed oxidative macrocyclizations of *E/Z*-mixed 5,6-diaryldipyrroethenes

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Materials and measurements.

All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. ^{1}H NMR, and ^{13}C NMR spectra were recorded using a Bruker Avance 500 NMR spectrometer. ^{19}F NMR spectra were recorded using a JEOL JNM-ECZ400 NMR spectrometer. Chemical shifts were referenced against tetramethylsilane or residual solvent peak as an internal standard. ESI-MS was performed using a Bruker micrOTOF II instrument. MALDI-TOF mass spectra were performed using a Bruker MALDI-TOF-MS Autoflex III. UV–vis absorption spectra were recorded using a Hitachi U-3310 spectrophotometer. Fluorescence excitation and emission spectra were collected at room temperature on a Hitachi F-7000 fluorescence spectrometer. Emission spectra were collected in the range between 420-820 nm, with a scan speed of 240 nm/min, and the slits were set at 5.0 nm (excitation slit) and 5.0 nm (emission slit). The absolute photoluminescence quantum yields (Φ_{PL}) were determined as a solution state using absolute PL quantum yields measurement system C9920-02 (Hamamatsu photonics) after excitation at 380 nm. Time-resolved photoluminescence lifetimes were curried out by using time-correlated single photon counting lifetime spectroscopy system, Quantaurus-Tau C11367-02 (Hamamatsu photonics). The decay constants and fitting parameters (τ_1,A_1) for transient decays were determined using the embedded software of Quantaurus-Tau. Electrochemical studies were performed on Bioanalytical Systems CV-50W electrochemical workstations with a platinum wire as a counter electrode. A saturated calomel electrode or Ag/AgCl (saturated NaCl) electrode obtained from BAS was used as the reference electrode. Working electrode was a polished disk involving platinum material. All solvents were dried and distilled prior to use under N_2. Elemental analysis was performed at the Service Center of Elementary Analysis of Organic Compounds at Kyushu University.

X-ray crystal structural analysis.

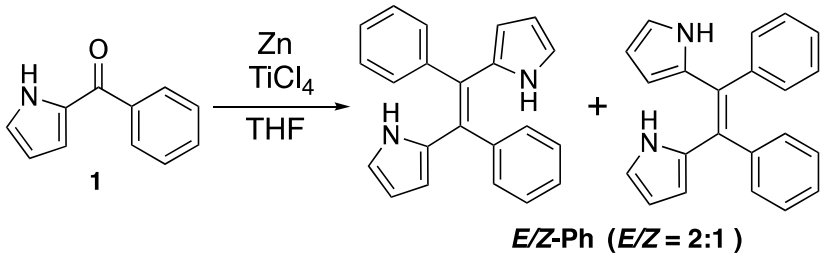
PhPc: A single crystal of **PhPc** was mounted on a loop. X-ray diffraction patterns were recorded at −173 ºC using a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromator and a Mo Kα radiation source (λ = 0.71073 Å).

CF_3Pc, **FPc**, **CH_3Pc**: A single crystal of **2** was mounted on a loop. X-ray diffraction patterns were recorded at −170 ºC using a Bruker D8 Venture diffractometer equipped with a multilayered confocal mirror monochromator and a Mo Kα radiation source (λ = 0.71073 Å).

The data frames were integrated using SAINT[1] and merged to give a unique data set for structure determination. Absorption corrections were performed using SADABS.[2] The structures were refined using SHELXT (Sheldrick, 2015) and SHELXL (Sheldrick, 2015).[3] All non-hydrogen atoms were anisotropically refined. Inner N–H hydrogen atoms were placed according to the Q-peaks. Other hydrogen atoms were placed using geometrically idealized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-1868296 for **PhPc**, CCDC-1868292 for **CF_3Pc,** CCDC-1868294 for **FPc,** CCDC-1868293 for **CH_3Pc**. The data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

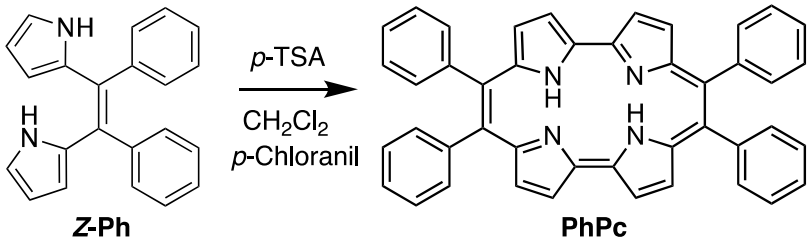
Organic Synthesis.

Synthesis of *E/Z*-Ph.



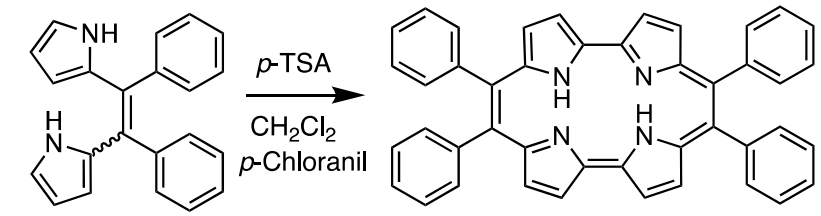
$TiCl_4$ (18.2 g, 96.0 mmol) was added dropwise to a dry THF (320 mL) solution of activated Zn powder (12.6 g, 192 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was refluxed for 3 h an d then **1** (TCI, 98%) (4.11 g, 24.0 mmol) in THF (25 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous $NaHCO_3$ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield ***E/Z*-Ph** as a yellow solid (1.65 g, 44.3%). The *E* :*Z* ratio of the isomers in the *E/Z* mixture was determined as 2:1 by integration of the pyrroles α-H proton signals in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (brs, $2H_Z$, NH), 7.47 (m,$10H_E$, Ph), 7.29 (brs, $2H_E$, NH), 7.10 (m,$10H_Z$, Ph), 6.70 (m, $2H_Z$, Py), 6.41 (m, $2H_E$, Py), 6.14 (m, $2H_Z$, Py), 5.89 (m, $4H_{Z/E}$, Py), 5.32 (m, $2H_E$, Py). Elemental analysis calcd (%) for $C_{22}H_{18}N_2$: C 85.13, H 5.85, N 9.03; found: C 85.16, H 5.90, N 9.05.

Synthesis of PhPc using *Z*-Ph as a precursor.



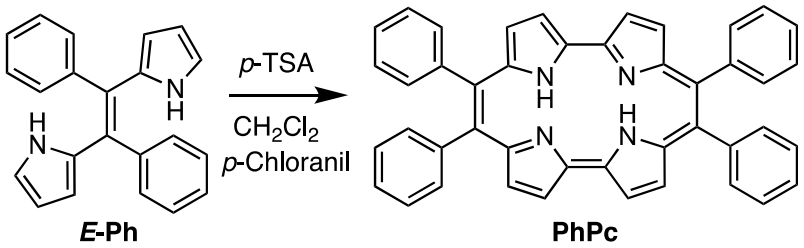
To a 500 mL flask containing *Z*-Ph (100 mg, 0.322 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O 30.6 mg, 0.161 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (237 mg, 0.966 mmol) was added and stirred further 3 hours under air at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield Ph-Pc as a purple solid (45.0 mg, 45.8%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.43 (d, 4H, Py), 8.43 (d, 4H, Py), 7.71 (m, 8H, Ph), 7.38 (m, 12H, Ph), 5.98 (brs, 2H, NH). HRMS (FAB): *m/z* calcd for $C_{48}H_{38}N_4$ $[M]^+$ 614.2470; found: 614.2469.

Synthesis of PhPc using *E/Z*-Ph as a precursor.



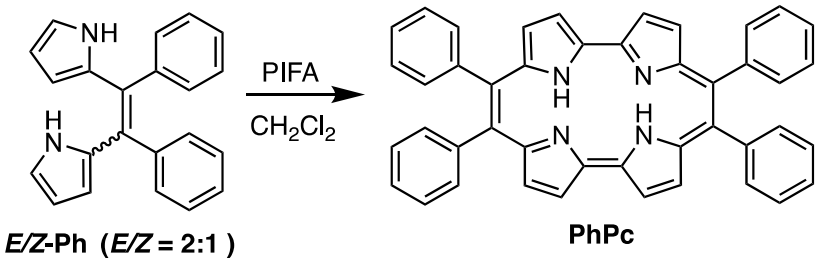
To a 500 mL flask containing ***E/Z*-Ph** (200 mg, 0.644 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (61.2 mg, 0.322 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (475 mg, 1.93 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **PhPc** as a purple solid (70.0 mg, 35.5%).

Synthesis of PhPc using *E*-Ph as a precursor.



To a 500 mL flask containing ***E*-Ph** (100 mg, 0.322 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (30.6 mg, 0.161 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (237 mg, 0.966 mmol) was added and stirred further 3 hours under air at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **PhPc** as a purple solid (29.0 mg, 29.5%).

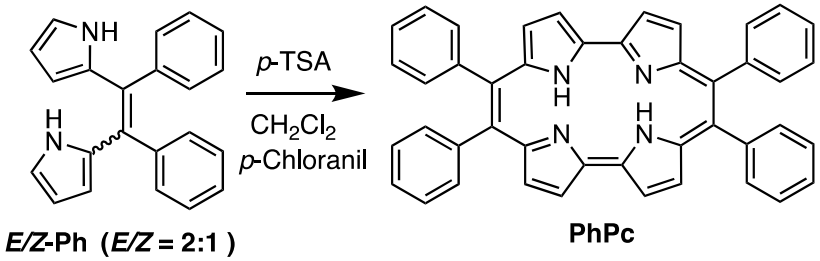
Synthesis of PhPc using *E/Z*-Ph as a precursor by hypervalent iodine.



***E/Z*-Ph (*E/Z* = 2:1)** **PhPc**

[bis(trifluoroacetoxyiodo)]benzene (PIFA) (138 mg, 0.322 mmol) in dry dichloromethane (5 mL) was quickly added to a stirred solution of ***E/Z*-Ph** (100 mg, 0.322 mmol) in dry dichloromethane (25 mL) in an ice bath. The solution was stirred for 1.5 h and the reaction was quenched with silica gel 60N (15 mL) and methanol (15 mL). The mixture was stirred overnight under air and evaporated to dryness. The resultant silica-gel mixture was charged on fresh silica gel 60N and eluted with dichloromethane to yield **PhPc** as a purple solid (1 mg, 1 %).

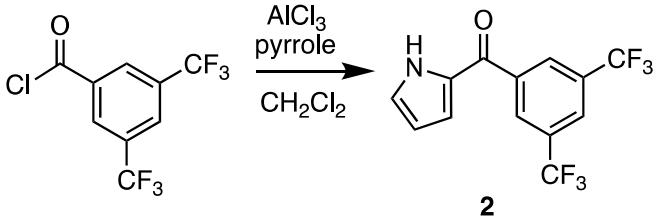
Synthesis of PhPc using *E/Z*-Ph as a precursor. （Large Scale）



***E/Z*-Ph (*E/Z* = 2:1)** **PhPc**

To a 3 L flask containing ***E/Z*-Ph** (1.50 g, 4.83 mmol), 3 L of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (1.84 g, 9.66 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (3.56 g, 14.5 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **PhPc** as a purple solid (0.903 g, 60.8%).

Synthesis of 2.



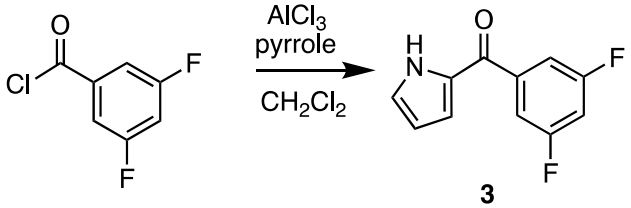
2

Aluminum(Ⅲ) chloride (9.60 g, 72.0 mmol) was mixed with dry dichloromethane (600 mL) in a two-necked flask under nitrogen atmosphere. 3,5-Bis(trifluoromethyl)benzoyl chloride (10.8 mL, 60.0 mmol) was added dropwise to the solution under stirring. After stirring for several minutes, pyrrole (4.58 mL, 66.0 mmol) was added and the solution was stirred overnight at room temperature. The reaction was quenched with 1 M aqueous HCl under cooling. The mixture was extracted with dichloromethane; the organic layer was washed with distilled water and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product

was purified using silica-gel column chromatography (dichloromethane 100%) to yield **2** as a white solid (9.96 g, 54.0%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.62 (brs, 1H, NH), 8.34 (s, 2H, Ar), 8.07 (s, 1H, Ar), 7.24 (m, 1H, Py), 6.86 (m, 1H, Py), 6.42 (m, 1H, Py). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.14, 140.02, 132.21, 130.22, 128.95, 126.53, 125.12, 124.10, 121.93, 119.93, 111.95ppm. Elemental analysis calcd (%) for $C_{13}H_7F_6NO$: C 50.83, H 2.30, N 4.56; found: C 50.61, H 2.22, N 4.55. HRMS (EI, *m/z*): Calcd for $C_{13}H_7F_6NO$ $[M]^+$ 307.0432; found: 307.0429.

Synthesis of 3.

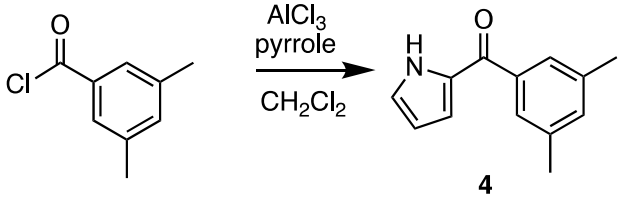


3

Aluminium(Ⅲ) chloride (9.60 g, 72.0 mmol) was mixed with dry dichloromethane (600 mL) in a two-necked flask under nitrogen atmosphere. 3,5-Difluorobenzoyl chloride (7.51 mL, 60.0 mmol) was added dropwise to the solution under stirring. After stirring for several minutes, pyrrole (4.58 mL, 66.0 mmol) was added and the solution was stirred overnight at room temperature. The reaction was quenched with 1 M aqueous HCl under cooling. The mixture was extracted with dichloromethane; the organic layer was washed with distilled water and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane 100%) to yield **3** as white solid (6.94 g, 55.8%).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 9.63 (brs, 1H, NH), 7.42 (m, 2H, Ar), 7.20(m, 1H, Ar), 7.01 (m, 1H, Py), 6.91(m, 1H, Py), 6.38 (m, 1H, Py). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.68, 163.81, 161.72, 141.19, 130.35, 126.04, 119.67, 111.54, 107.07 ppm. Elemental analysis calcd (%) for $C_{11}H_7F_2NO$: C 63.77, H 3.41, N 6.76; found: C 63.79, H 3.34, N 6.78. HRMS (EI, *m/z*): Calcd for $C_{11}H_7F_2NO$ $[M]^+$ 207.0496; found for 207.0495.

Synthesis of 4.

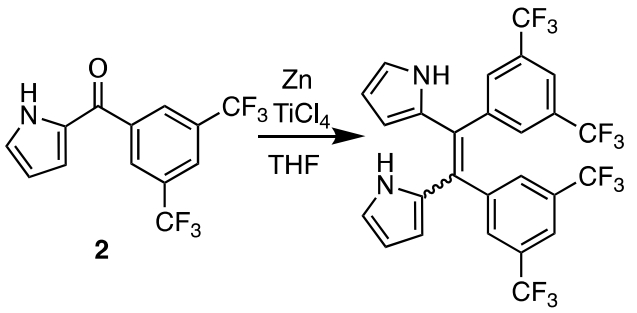


4

Aluminum(Ⅲ) chloride (8.00 g, 60.0 mmol) was mixed with dry dichloromethane (500 mL) in a two-necked flask under nitrogen atmosphere. 3,5-Dimethylbenzoyl chloride (7.40 mL, 50.0 mmol) was added dropwise to the solution under stirring. After stirring for several minutes, pyrrole (3.82 mL, 55.0 mmol) was added and the solution was stirred overnight at room temperature. The reaction was quenched with 1 M aqueous HCl under cooling. The mixture was extracted with dichloromethane; the organic layer was washed with distilled water and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane 100%) to yield **4** as a white solid (6.82 g, 68.4%). ^{1}H NMR (500

MHz, $CDCl_3$): δ = 9.68 (brs, 1H, NH), 7.51 (s, 2H, Ar), 7.20(s, 1H, Ar), 7.13 (m, 1H, Py), 6.89 (m, 1H, Py), 6.35 (m, 1H, Py), 2.39 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 185.17, 138.41, 137.96, 133.49, 131.36, 126.71, 124.83, 119.14, 110.90, 21.26 ppm. Elemental analysis calcd (%) for $C_{13}H_{13}NO$: C 78.36, H 6.58, N 7.03; found: C 78.31, H 6.51, N 6.80. HRMS (EI, *m/z*): Calcd for $C_{13}H_{13}NO$ $[M]^+$ 199.0997; found: 199.0995.

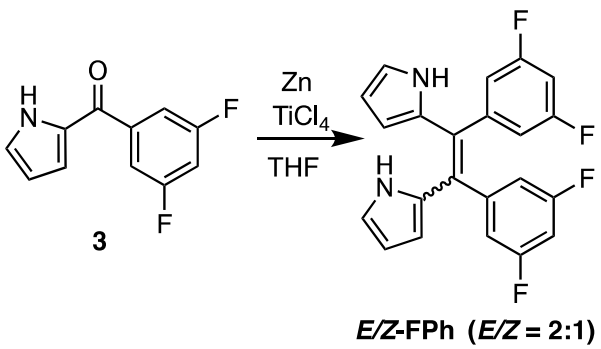
Synthesis of *E/Z*-CF_3.



$TiCl_4$ (21.6 g, 114 mmol) was added dropwise to a dry THF (400 mL) solution of activated Zn powder (15.0 g, 229 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then **2** (8.80 g, 28.6 mmol) in THF (50 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous $NaHCO_3$ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield *E/Z*- CF_3 as a yellow solid (3.50 g, 42.0%). The *E* : *Z* ratio of the isomers in the *E/Z* mixture was determined as 3:2 by integration of the pyrroles α-H proton signals in the ^{1}H NMR spectrum.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (brs, $2H_Z$, NH), 7.81 (s, $2H_E$, Ar), 7.76 (s, $4H_E$, Ar), 7.62 (s, $2H_Z$, Ar), 7.49 (s, $4H_Z$, Ar), 7.39 (brs, $2H_E$, NH), 6.82 (m, $2H_Z$, Py), 6.62 (m, $2H_E$, Py), 6.25 (m, $2H_Z$, Py), 6.08 (m, $2H_E$, Py), 6.03 (m, $2H_Z$, Py), 5.64 (m, $2H_E$, Py). Elemental analysis calcd (%) for $C_{26}H_{14}F_{12}N_2$: C 53.62, H 2.42, N 4.81; found: C 53.87, H 2.37, N 4.83. HRMS (EI, *m/z*): Cald for $C_{26}H_{14}F_{12}N_2$ $[M]^+$ 582.0965; found: 582.0966.

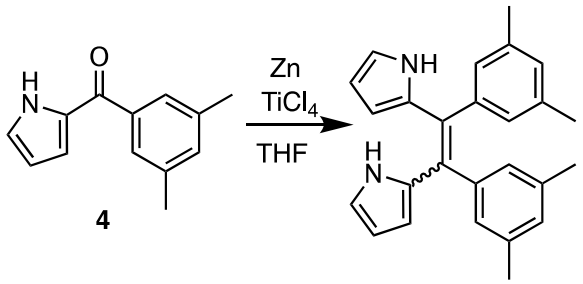
Synthesis of *E/Z*-F.



$TiCl_4$ (21.2 g, 112 mmol) was added dropwise to a dry THF (450 mL) solution of activated Zn powder (14.6

g, 224 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then **3** (5.80 g, 28.0 mmol) in THF (50 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous $NaHCO_3$ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield ***E/Z-* F** as a yellow solid (3.58 g, 66.9%). The *E* : *Z* ratio of the isomers in the *E/Z* mixture was determined as 2:1 by integration of the pyrroles α-H proton signals in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (brs, $2H_Z$, NH), 7.40 (brs, $2H_E$, NH), 6.94 (m, $4H_E$, Ar), 6.86 (m, $2H_E$, Ar), 6.74 (m, $4H_Z$, Ar), 6.65-6.61 (m, $2H_Z$, Ar /2Hz, Py), 6.58 (m, $2H_E$, Py), 6.19 (m, $2H_Z$, Py), 6.04 (m, $2H_E$, Py), 5.99 (m, $2H_Z$, Py), 5.57 (m, $2H_E$, Py). Elemental analysis calcd (%) for $C_{22}H_{14}F_4N_2$: C 69.11, H 3.69, N 7.33; found: C 69.06, H 3.72, N 7.25. HRMS (EI, *m/z*): Calcd for $C_{22}H_{14}F_4N_2$ $[M]^+$ 382.1093; found: 382.1090.

Synthesis of *E/Z*-CH_3.

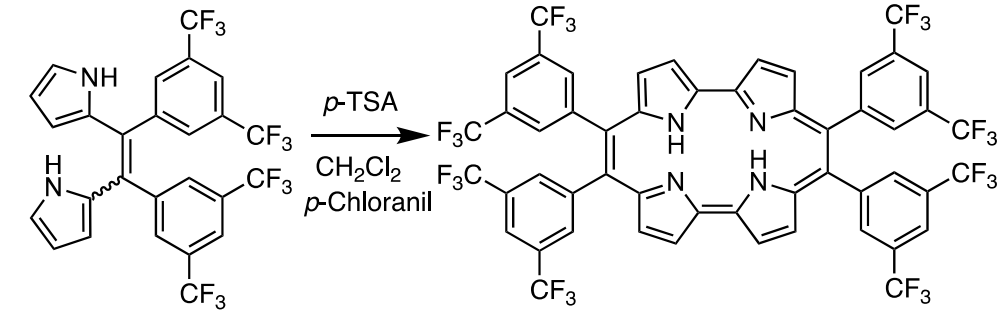


***E/Z*-CH_3Ph (*E/Z* = 9:5)**

$TiCl_4$ (4.55 g, 24.0 mmol) was added dropwise to a dry THF (80 mL) solution of activated Zn powder (3.14 g, 48.0 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then **4** (1.20 g, 6.00 mmol) in THF (25 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous $NaHCO_3$ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield (*E/Z*)-CH_3 as a yellow solid (460 mg, 41.8%). The *E* : *Z* ratio of the isomers in the *E/Z* mixture was determined as 9:5 by integration of the pyrroles α-H proton signals in the ^{1}H NMR spectrum.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (brs, $2H_Z$, NH), 7.30 (brs, $2H_E$, NH), 7.10 (s, $6H_E$, Ar), 6.70 (m,$6H_Z$, Ar / $2H_Z$, Py), 6.45 (m, $2H_E$, Py), 6.17 (m, $2H_Z$, Py), 5.96 (m, $4H_{Z/E}$, Py), 5.38 (m, $2H_E$, Py), 2.37 (s, $12H_E$, CH_3), 2.12 (s, $12H_Z$, CH_3). Elemental analysis calcd (%) for $C_{26}H_{26}N_2$: C 85.21, H 7.15, N 7.64; found: C 85.29, H 7.20, N 7.59. HRMS (EI, *m/z*): Calcd for $C_{26}H_{26}N_2$ $[M]^+$ 366.2096; found: 366.2095.

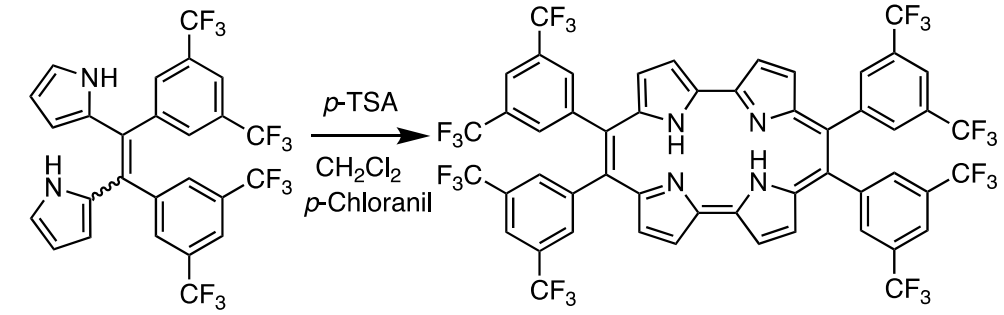
Synthesis of CF_3Pc.



***E/Z*-CF_3Ph (*E/Z* = 3:2)** **CF_3Pc**

To a 500 mL flask containing ***E/Z*-CF_3** (200 mg, 0.343 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (32.5 mg, 0.171 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (253 mg, 1.03 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **CF_3Pc** as a purple solid (160 mg, 80.5%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.61 (d, 4H, Py), 8.47 (d, 4H, Py), 8.14 (s, 8H, Ar), 7.97 (s, 4H, Ar), 5.68 (brs, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.72, 145.12, 137.16, 132.46, 131.68, 130.74, 127.35, 124.16, 121.99, 121.07 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.24. HRMS (FAB): *m/z* calcd for $C_{52}H_{22}F_{24}N_4$ $[M]^+$ 1158.1461; found for 1158.1460.

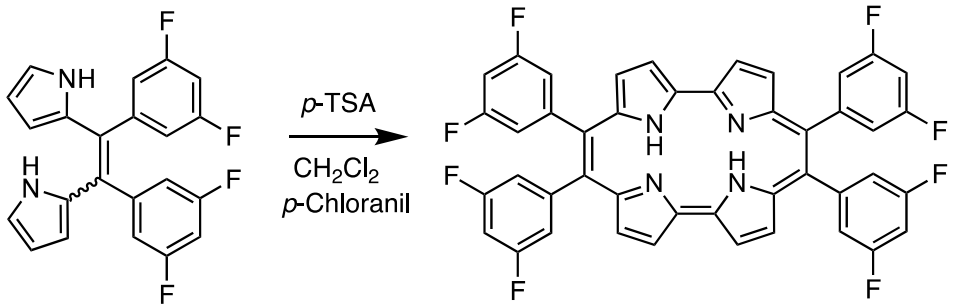
Synthesis of CF_3Pc. (Large Scale)



***E/Z*-CF_3Ph (*E/Z* = 3:2)** **CF_3Pc**

To a 3 L flask containing ***E/Z*-CF_3** (1.50 g, 2.58 mmol), 1.5 L of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (245 mg, 1.29 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (1.97 g, 7.74 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **CF_3Pc** as a purple solid (1.06 g, 70.9%).

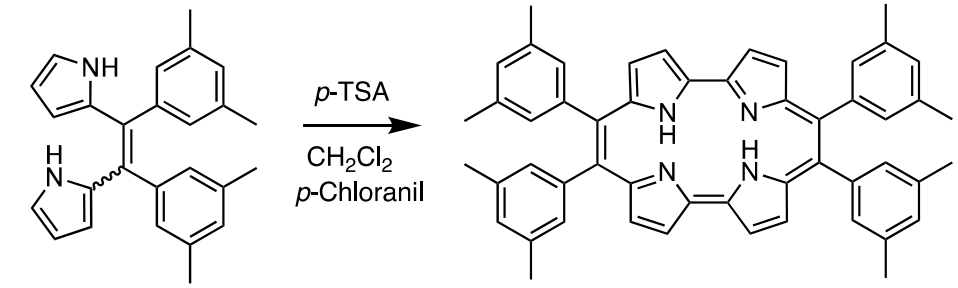
Synthesis of FPc. (Large Scale)



E/Z*-FPh** (E/Z* = 2:1**) **FPc**

To a 3 L flask containing ***E/Z*-F** (2 g, 5.23 mmol), 3 L of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (497 mg, 2.61 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (3.86 g, 15.7 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **FPc** as a purple solid (1.42 g, 71.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.51 (d, 4H, Py), 8.49 (d, 4H, Py), 7.28 (m, 8H, Ar), 6.99 (m, 4H, Ar), 5.66 (brs, 2H, NH). ^{13}C NMR (125 MHz, THF-d_8): δ = 148.41, 146.26, 140.98, 137.74, 132.33, 128.41, 127.50, 117.61, 103.36 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -112.58. HRMS (FAB): *m/z* calcd for $C_{44}H_{22}F_8N_4$ $[M]^+$ 758.1716; found for 758.1715.

Synthesis of CH_3Pc.



E/Z*-CH_3Ph** (E/Z* = 9:5**) **CH_3Pc**

To a 500 mL flask containing ***E/Z*-CH_3** (100 mg, 0.273 mmol), 160 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. *p*-TSA·H_2O (259 mg, 1.36 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (201 mg, 0.819 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield **CH_3Pc** as a purple solid (46.0 mg, 46.4%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.41 (d, 4H, Py), 8.52 (d, 4H, Py), 7.30 (s, 8H, Ar), 6.99 (s, 4H, Ar), 5.94 (brs, 2H, NH), 2.36 (s, 24H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.80, 144.27, 136.06, 134.91, 131.85, 131.73, 130.86, 127.58, 124.83, 21.21 ppm. HRMS (FAB): *m/z* calcd for $C_{52}H_{46}N_4$ $[M]^+$ 726.3722; found for 726.3723.

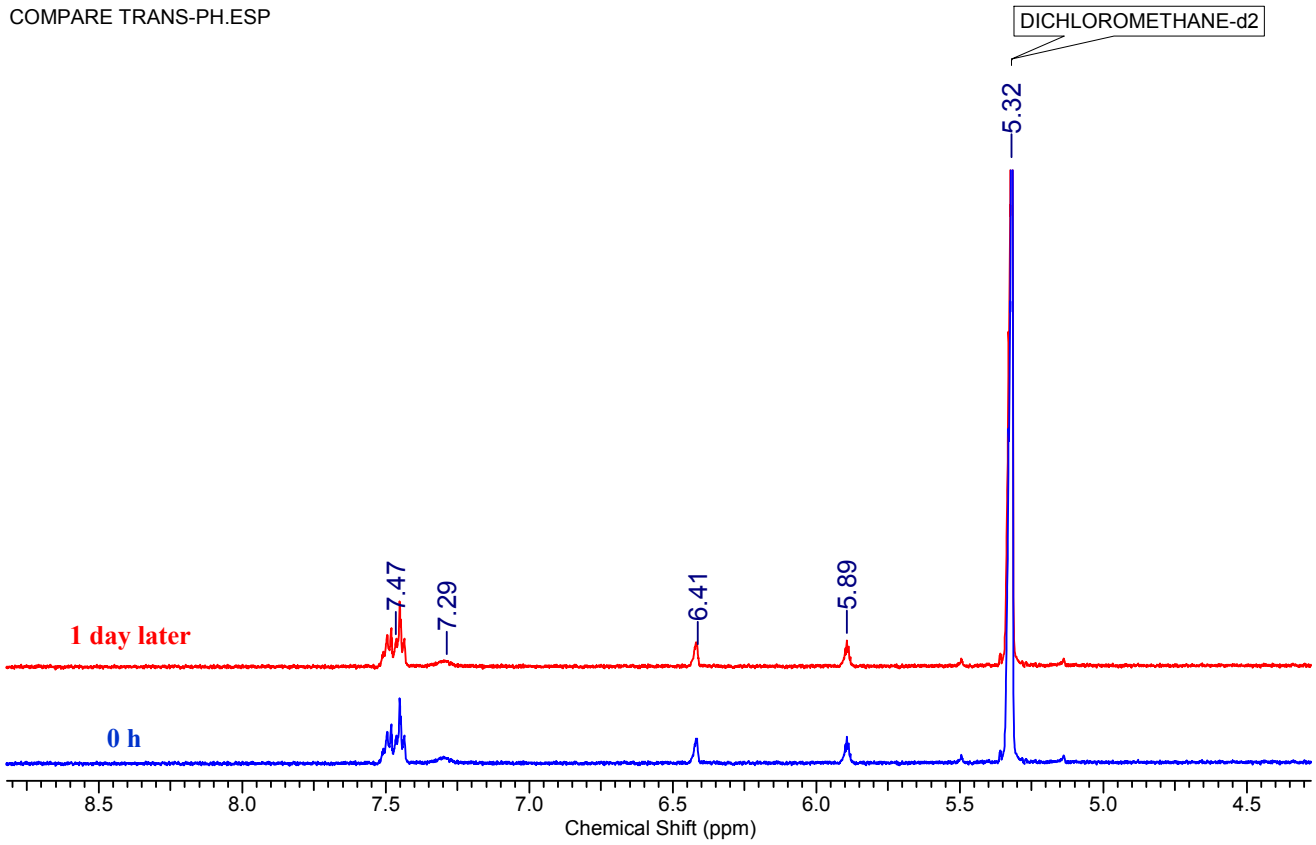


Fig. S1. ^{1}H NMR spectrum of ***E*-Ph** in CD_2Cl_2 at different times.

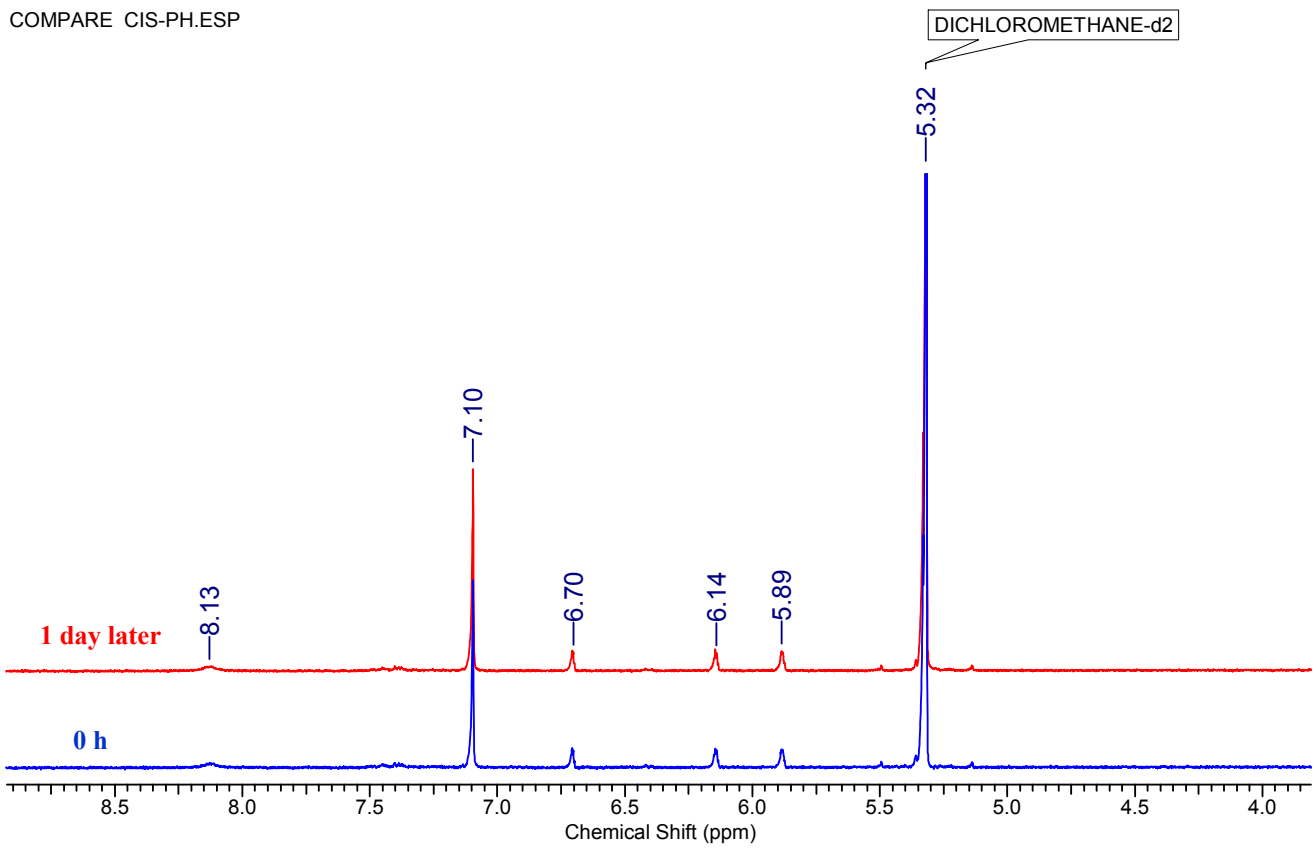


Fig. S2 ^{1}H NMR spectrum of ***Z*-Ph** in CD_2Cl_2 at different times.

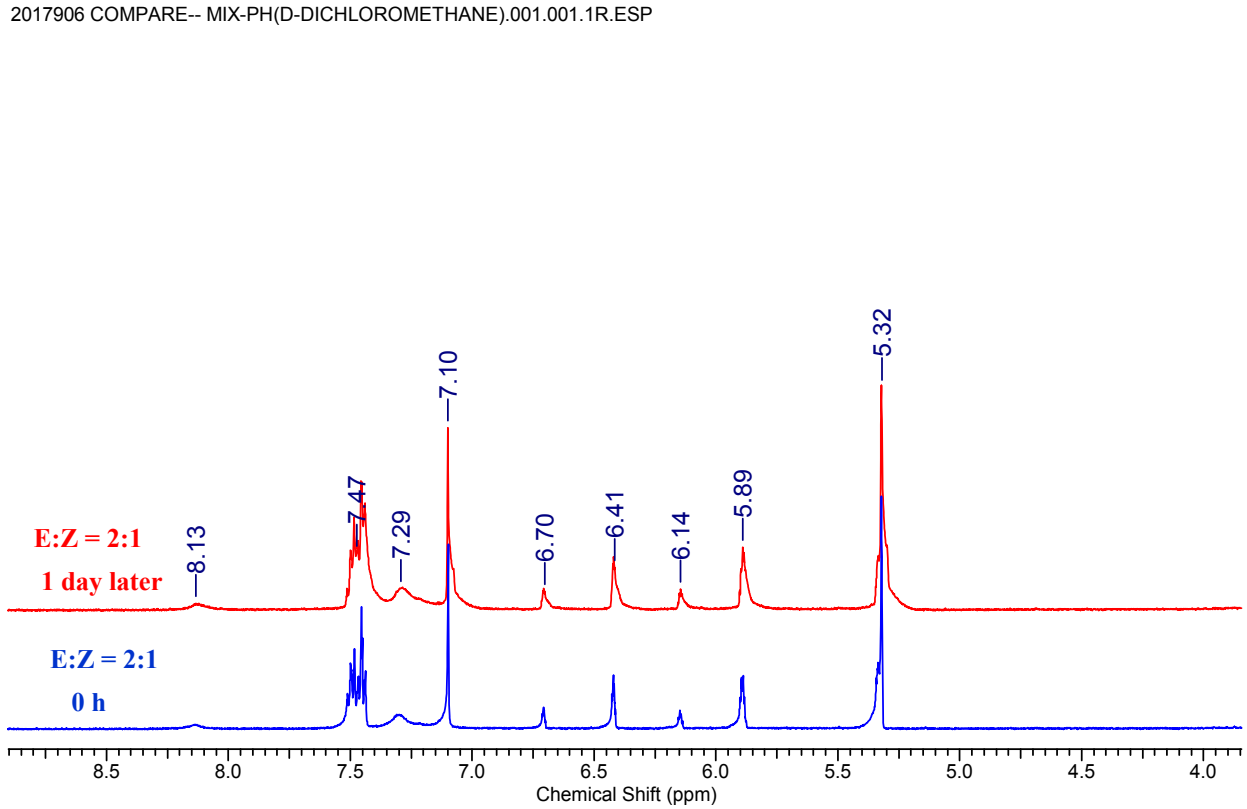


Fig. S3 ^{1}H NMR spectrum of ***E/Z*-Ph** in CD_2Cl_2 at different times.

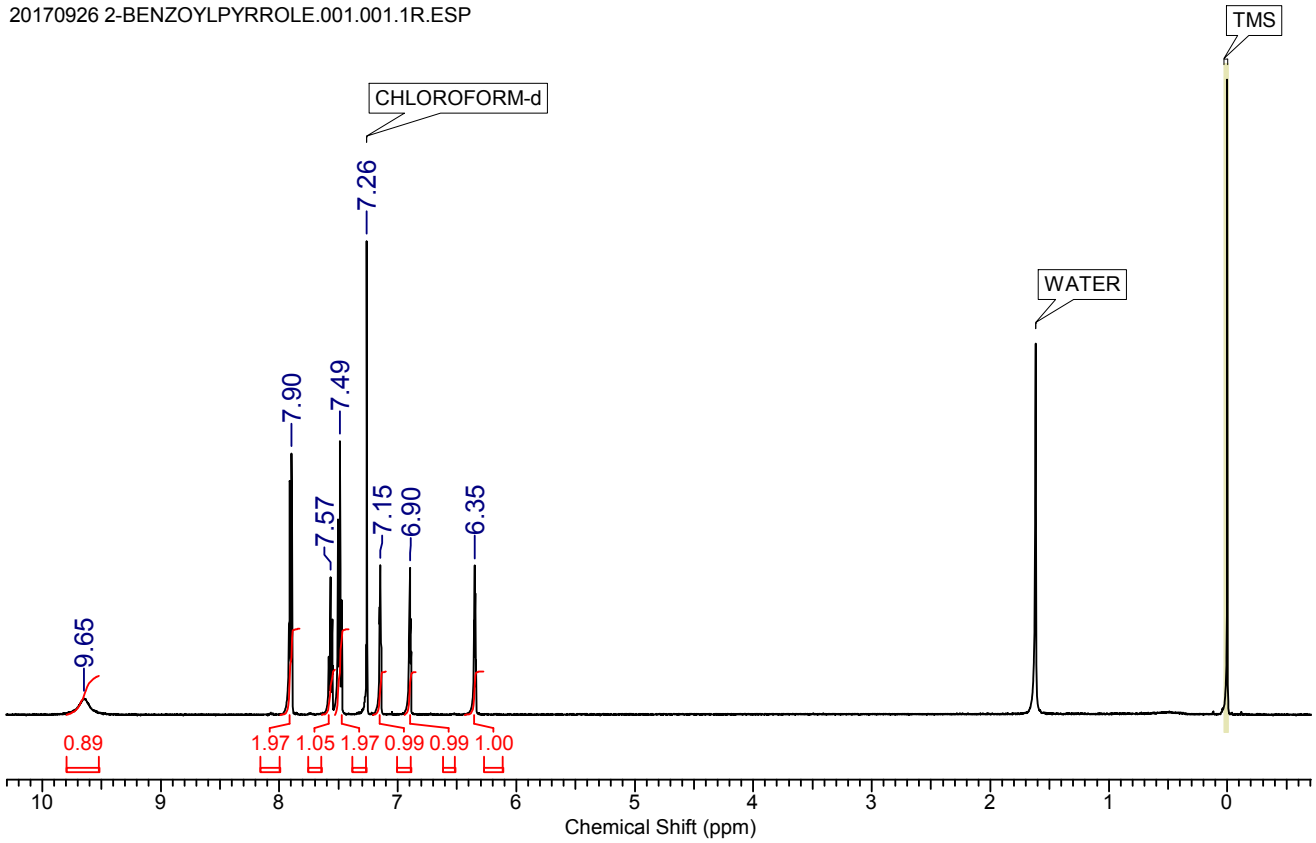


Fig. S4 ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at room temperature.

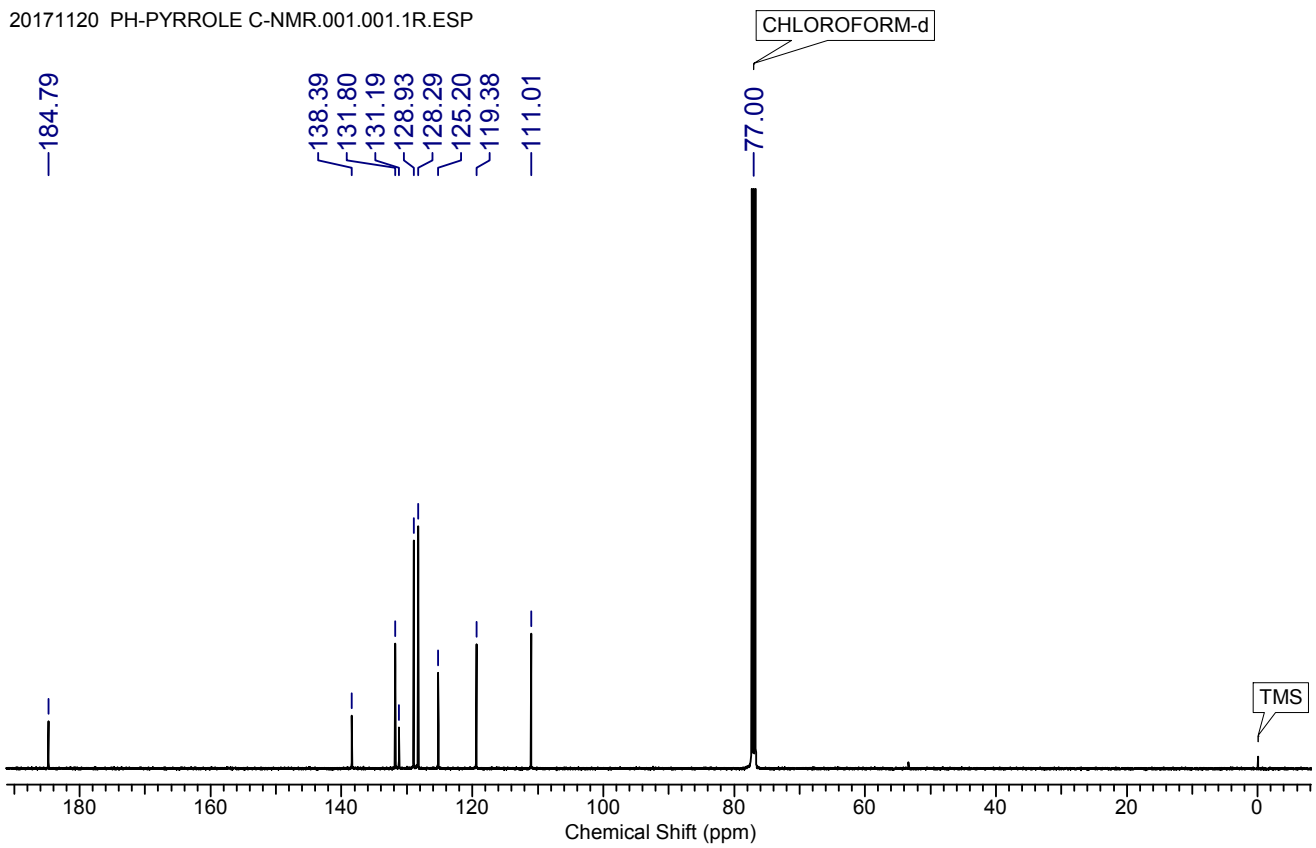


Fig. S5 ^{13}C NMR spectrum of compound **1** in $CDCl_3$ at room temperature.

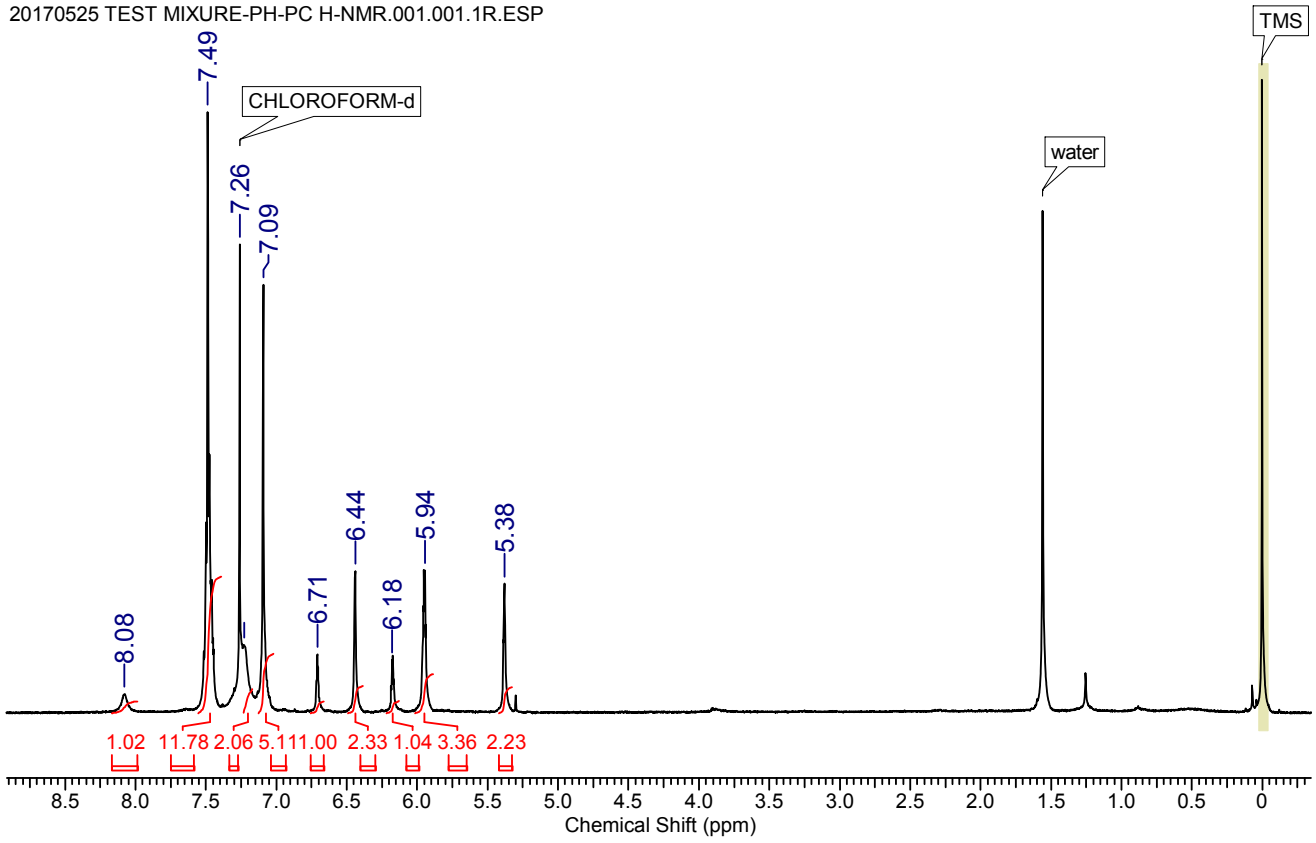


Fig. S6 ^{1}H NMR spectrum of ***E/Z* -Ph** in $CDCl_3$ at room temperature.

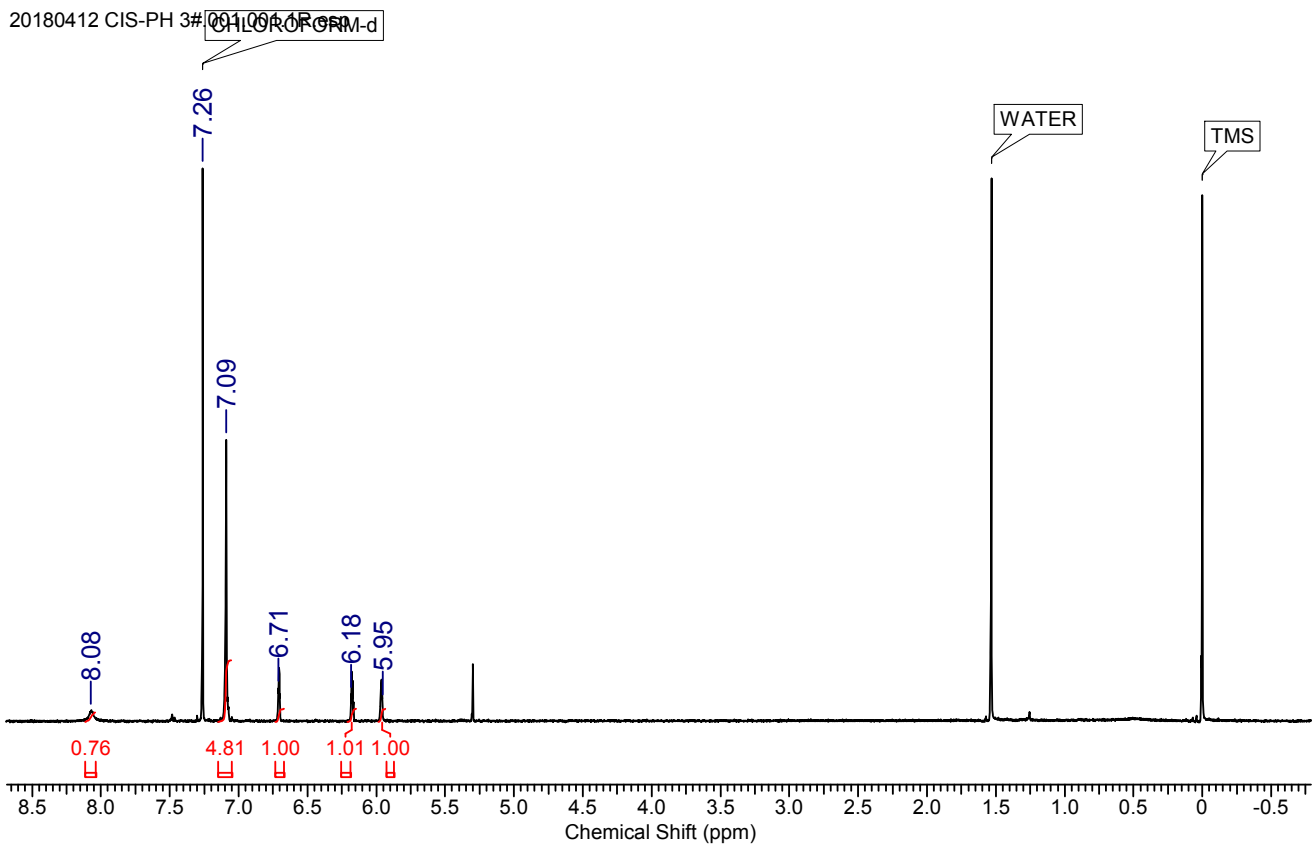


Fig. S7 ^{1}H NMR spectrum of ***Z* -Ph** in $CDCl_3$ at room temperature.

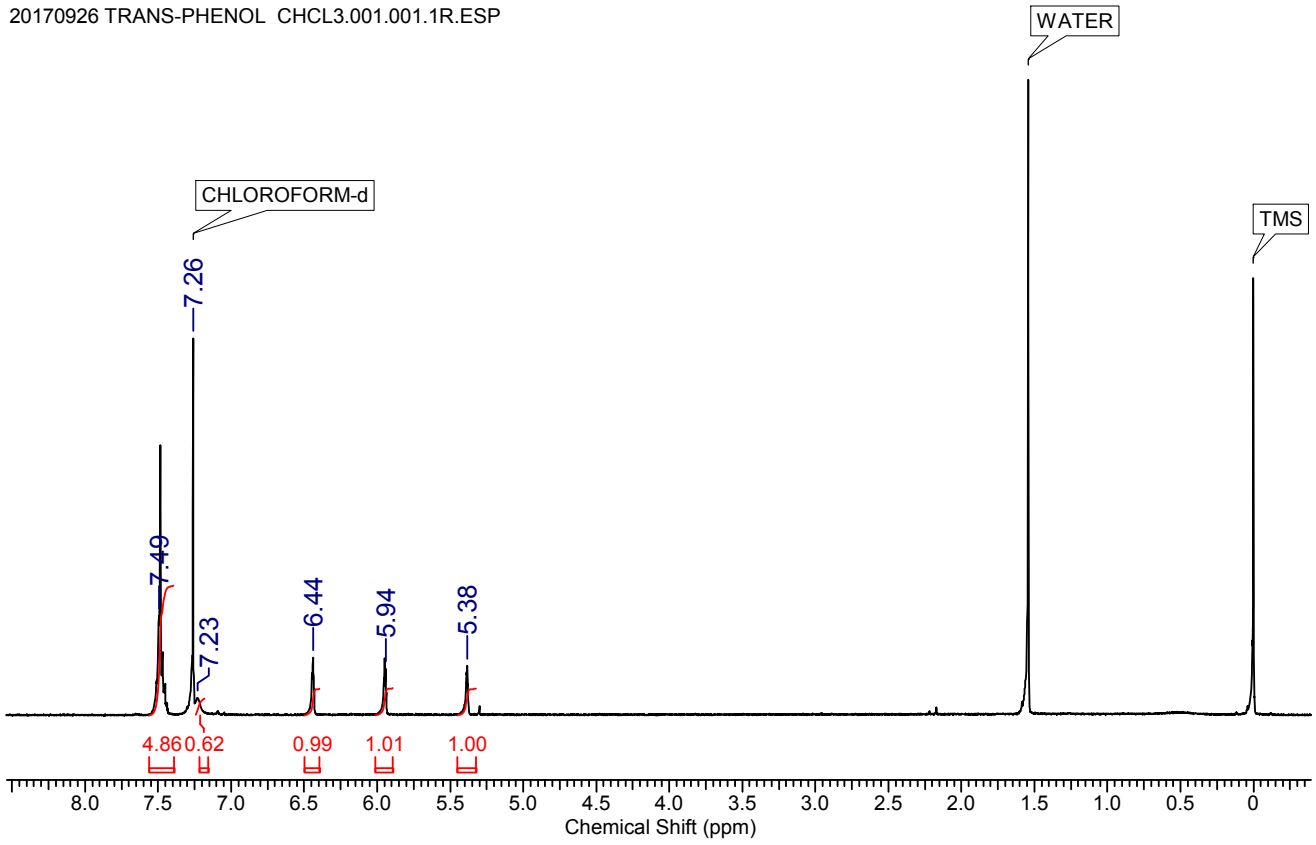


Fig. S8 ^{1}H NMR spectrum of ***E* -Ph** in $CDCl_3$ at room temperature.

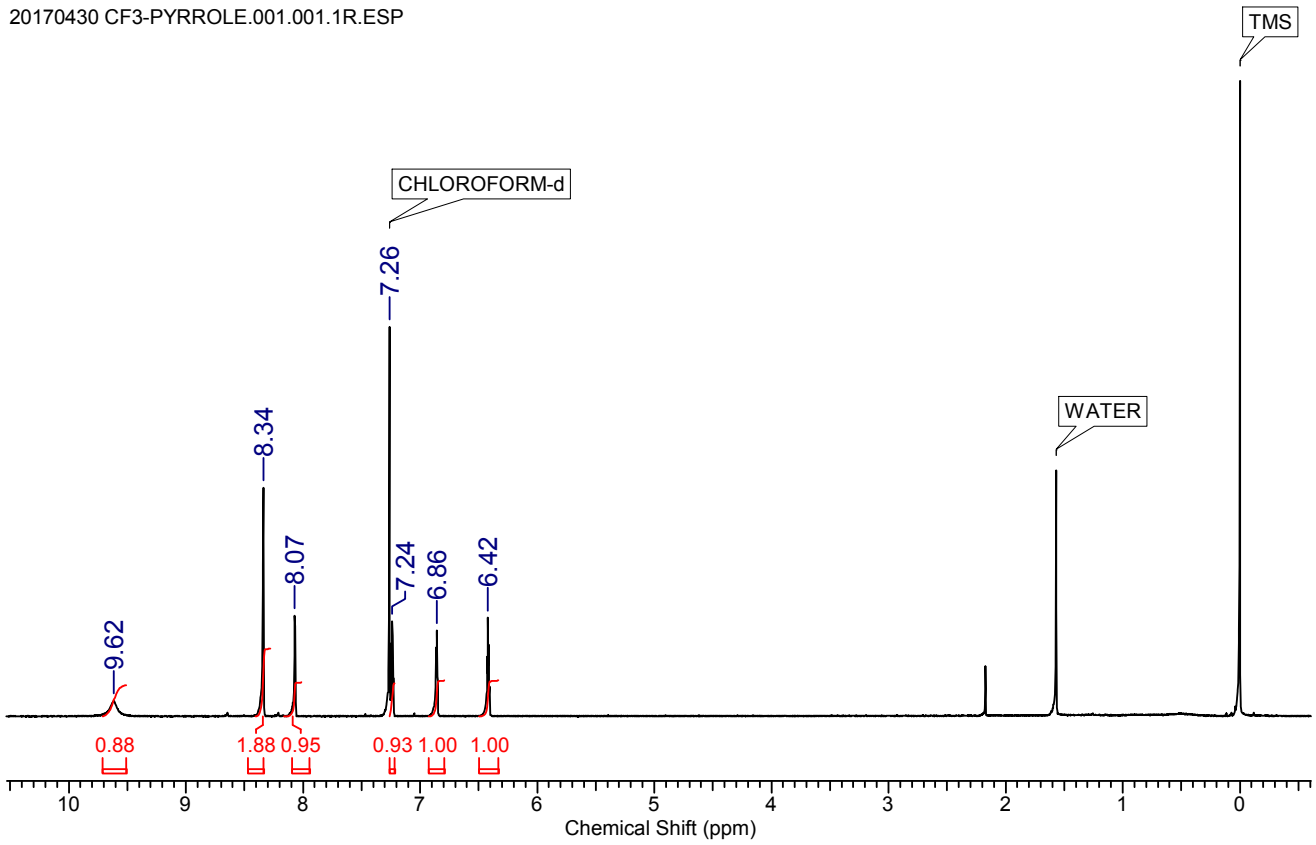


Fig. S9 ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature.

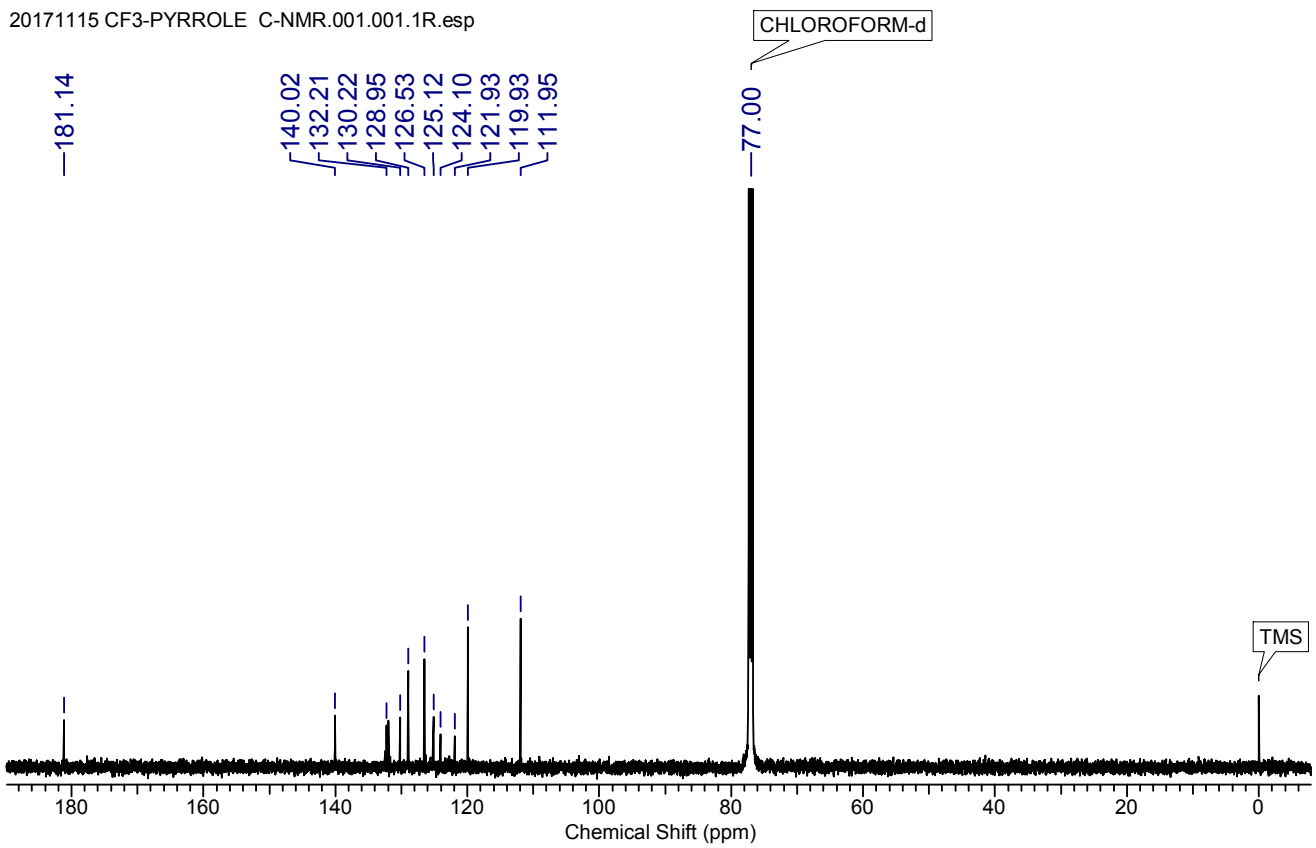


Fig. S10 ^{13}C NMR spectrum of compound **2** in $CDCl_3$ at room temperature.

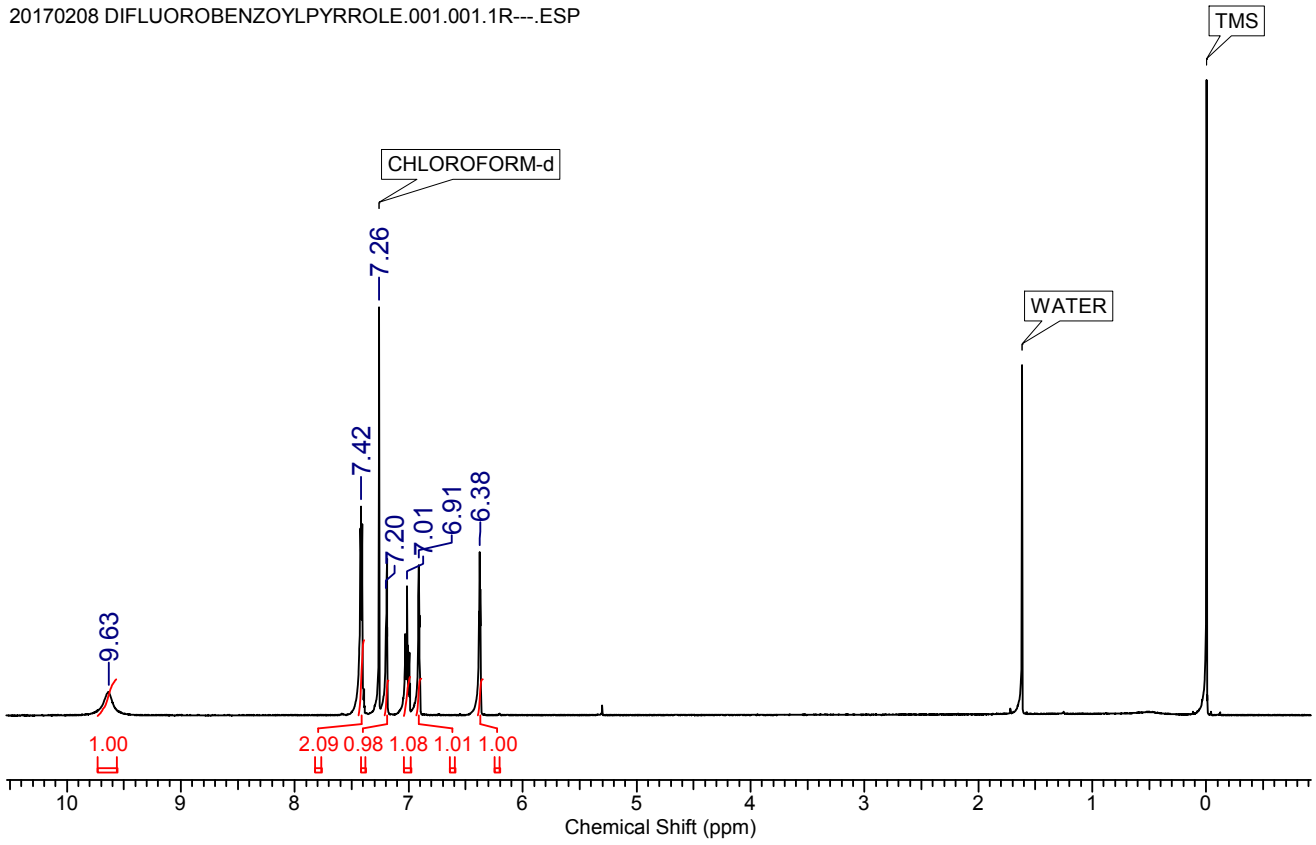


Fig. S11 ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature.

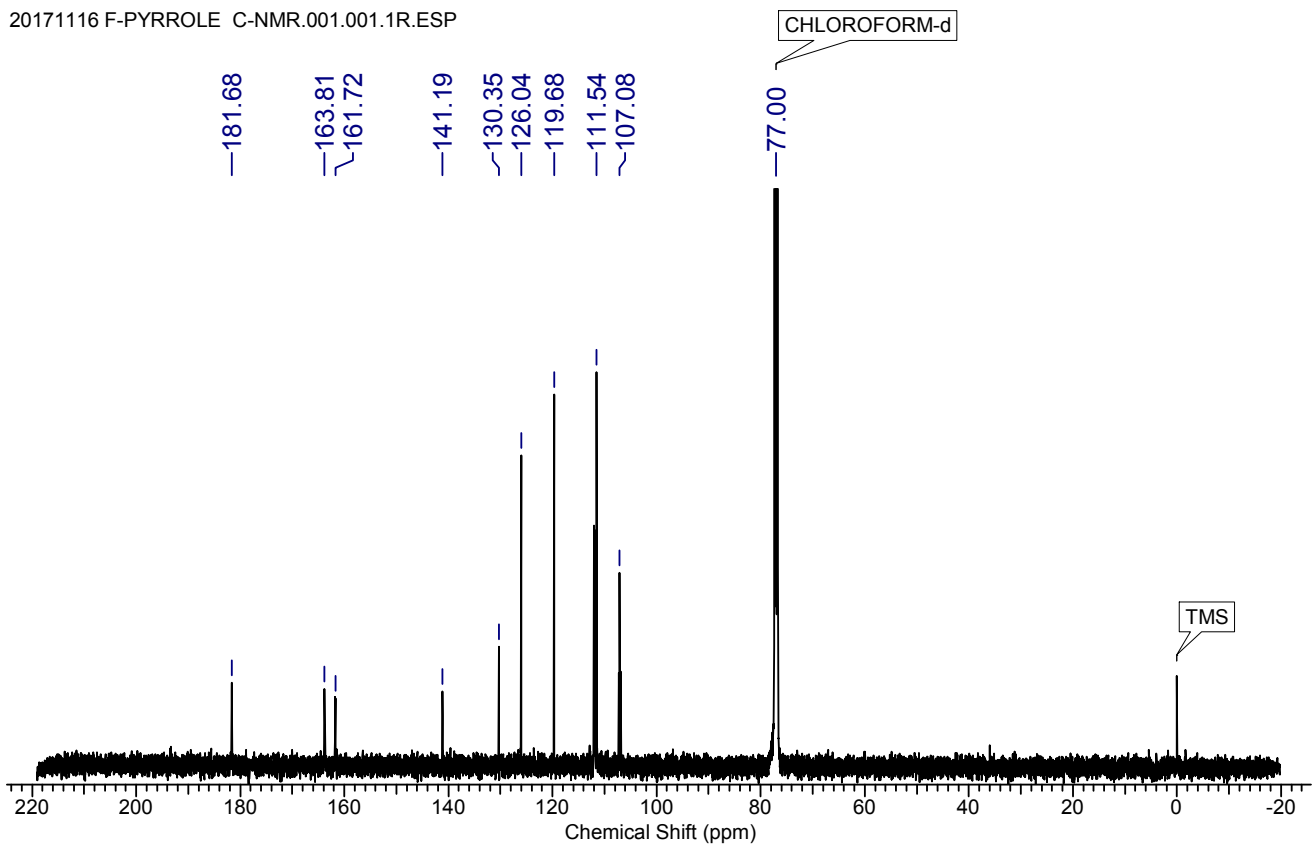


Fig. S12 ^{13}C NMR spectrum of **3** in $CDCl_3$ at room temperature.

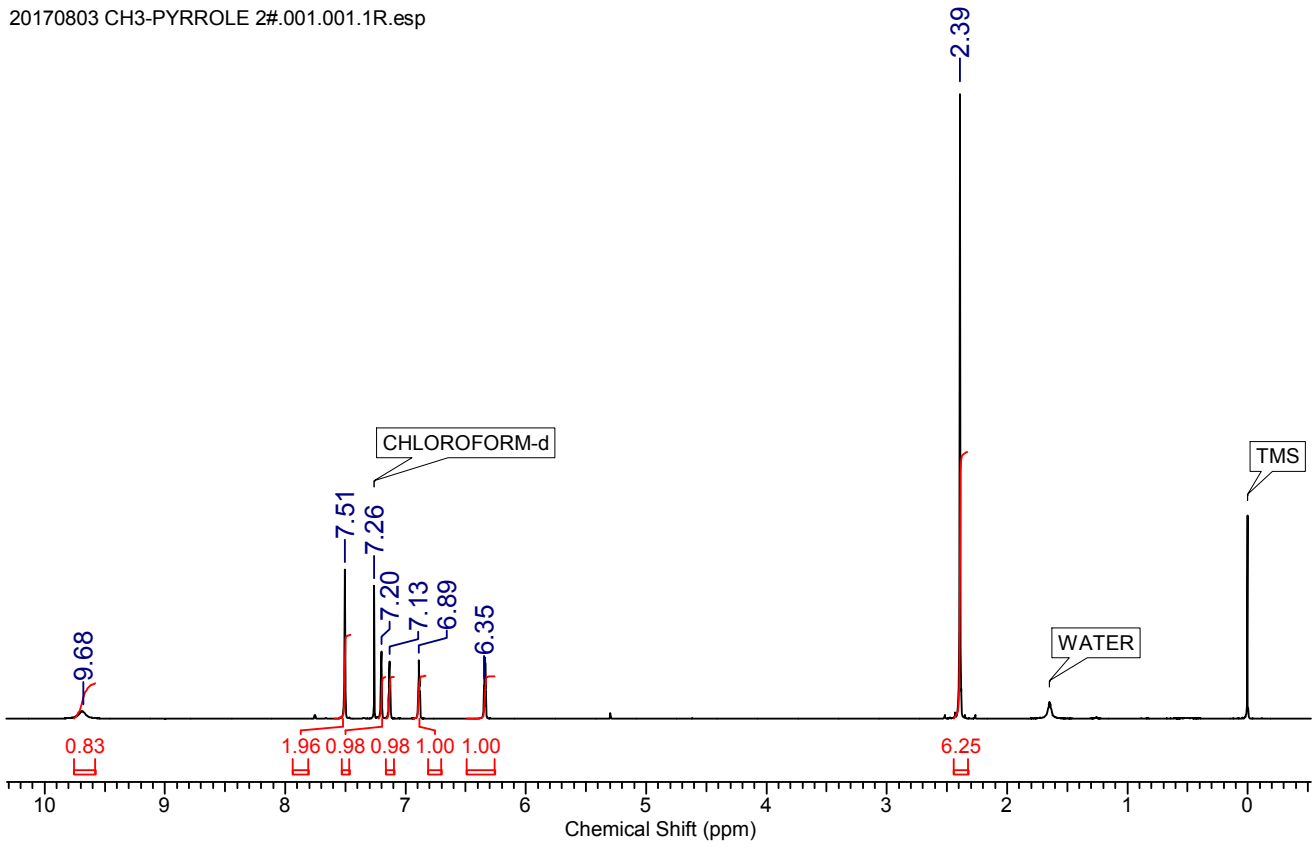


Fig. S13 ^{1}H NMR spectrum of **4** in $CDCl_3$ at room temperature.

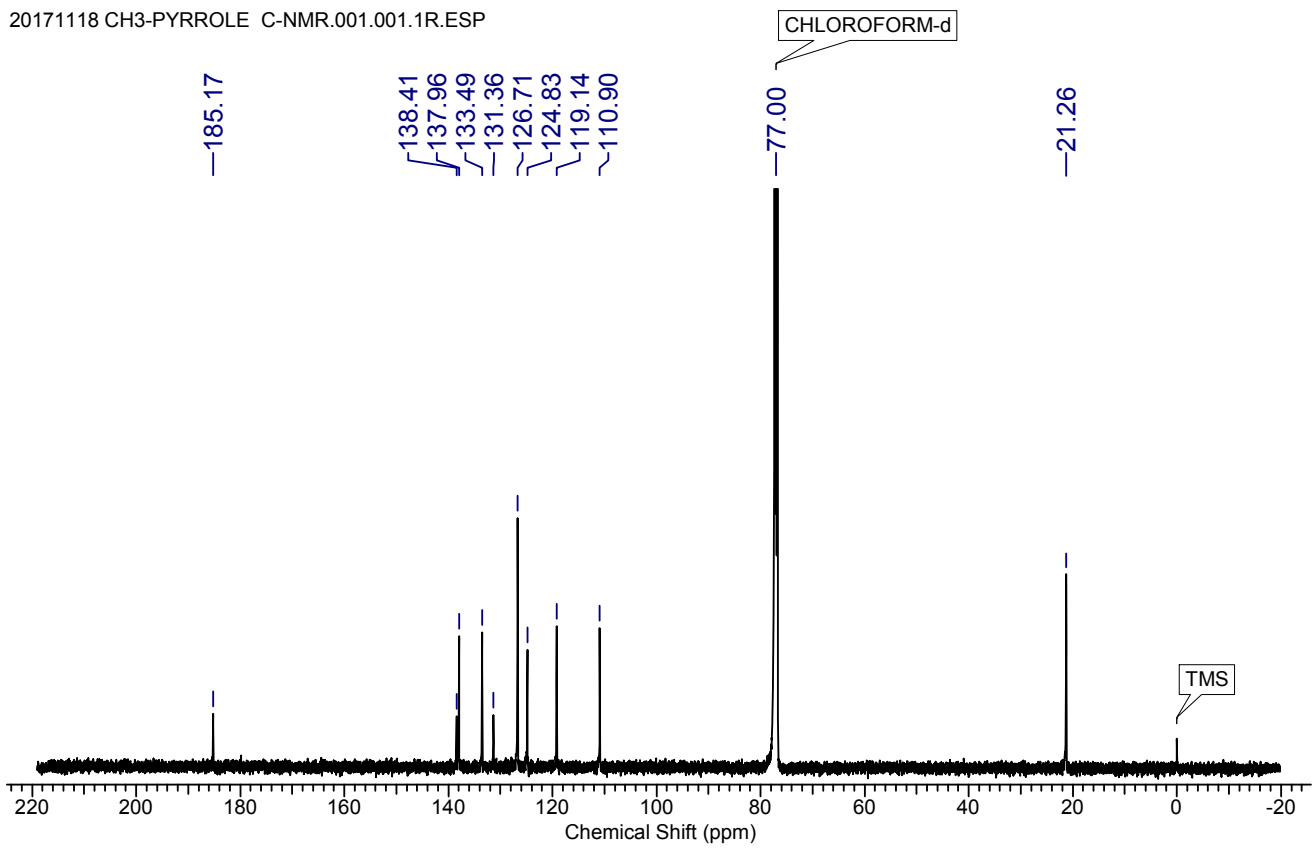


Fig. S14 ^{13}C NMR spectrum of **4** in $CDCl_3$ at room temperature.

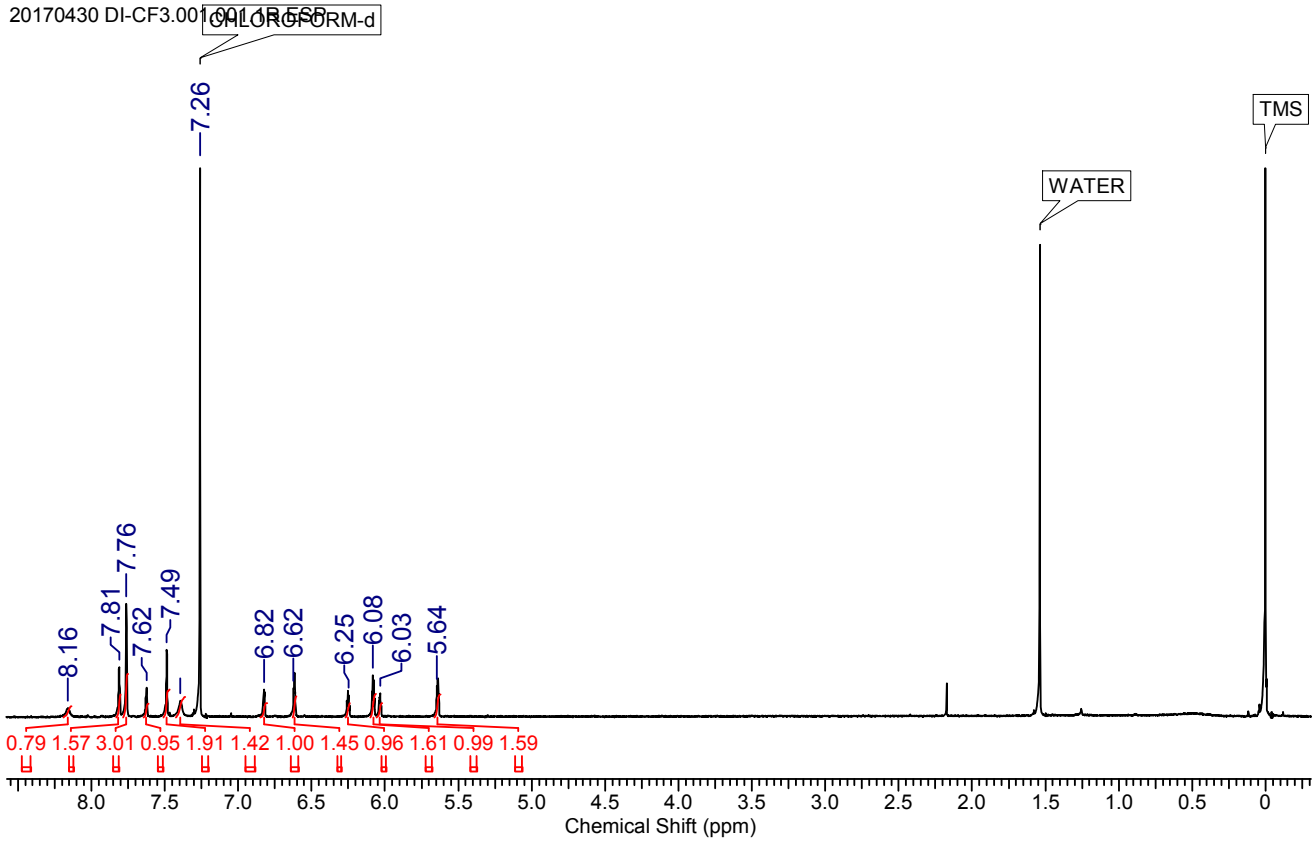


Fig. S15 ^{1}H NMR spectrum of ***E/Z*-CF_3** in $CDCl_3$ at room temperature.

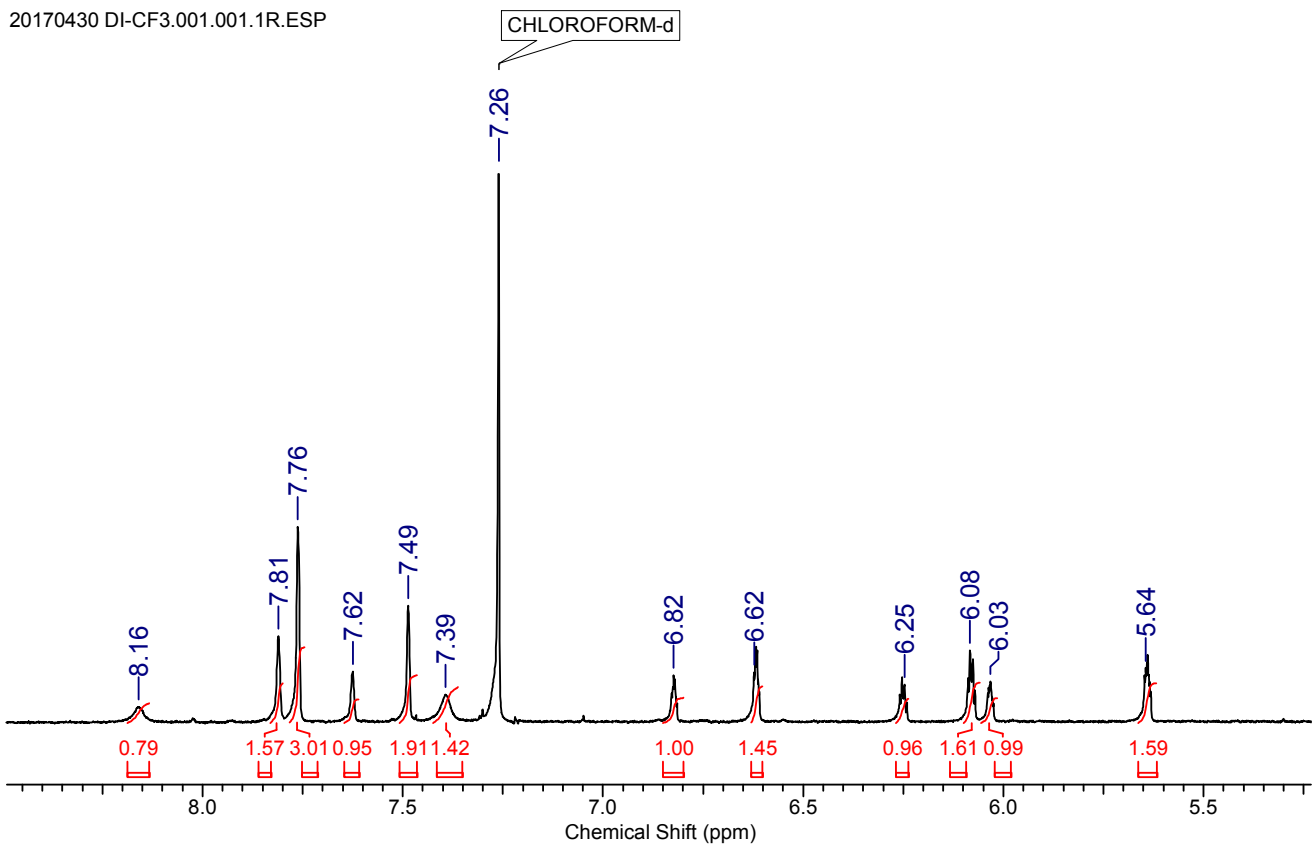


Fig. S16 ^{1}H NMR spectrum of ***E/Z*-CF_3** in $CDCl_3$ at room temperature

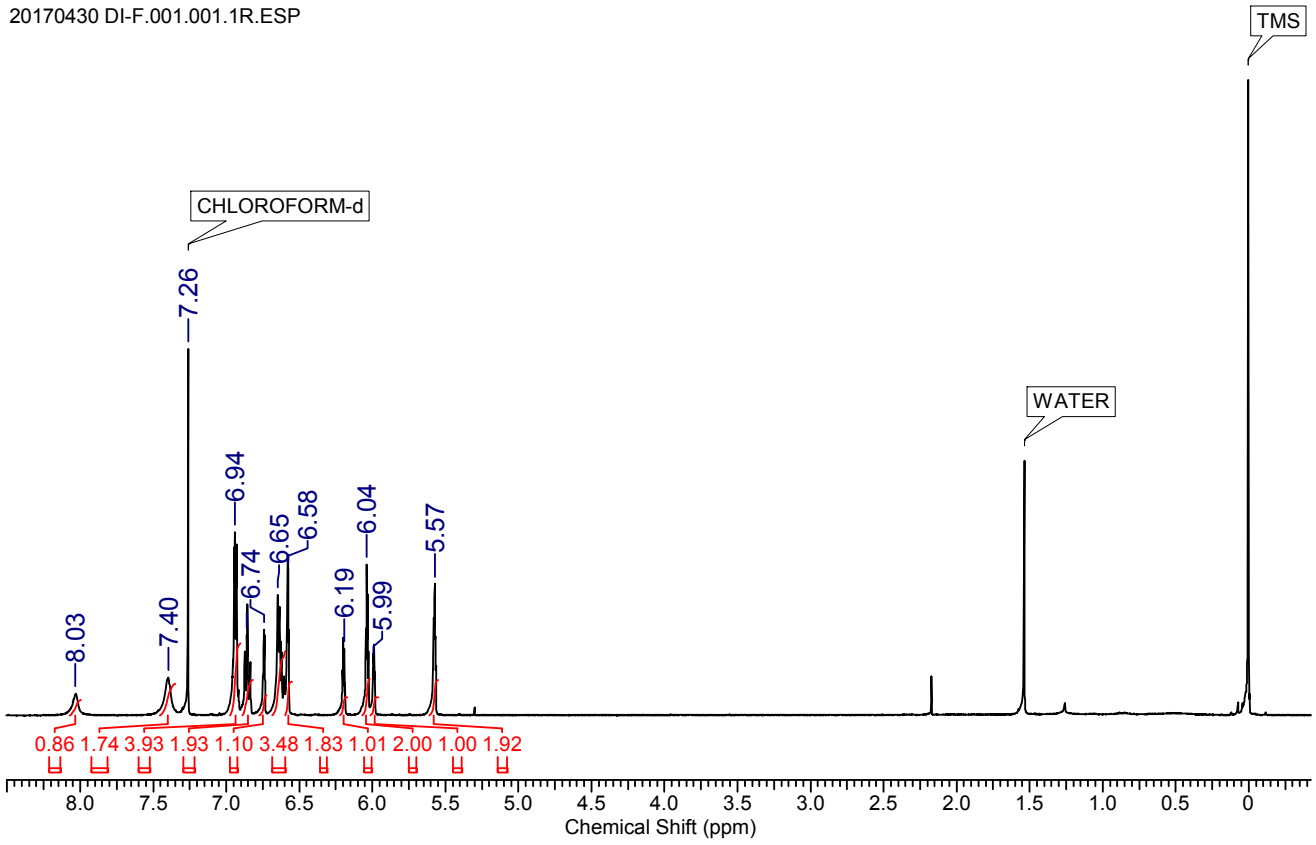


Fig. S17 ^{1}H NMR spectrum of ***E/Z*-F** in $CDCl_3$ at room temperature

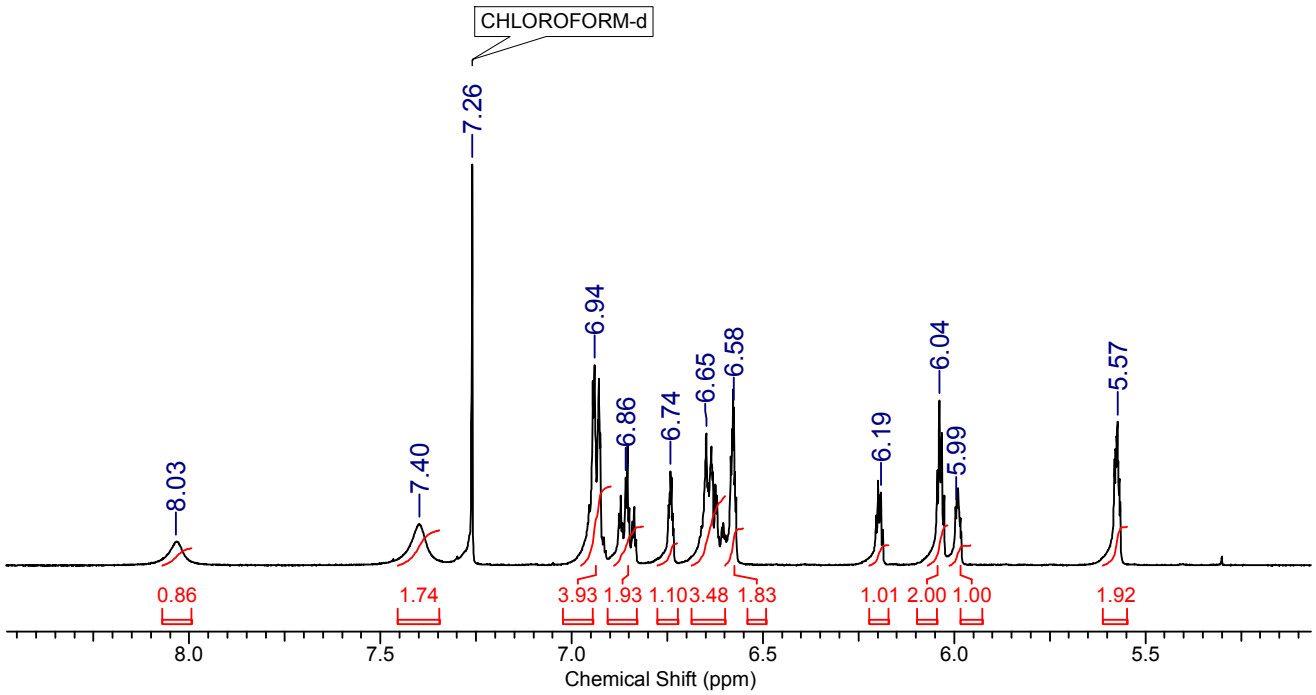


Fig. S18 ^{1}H NMR spectrum of ***E/Z*-F** in $CDCl_3$ at room temperature

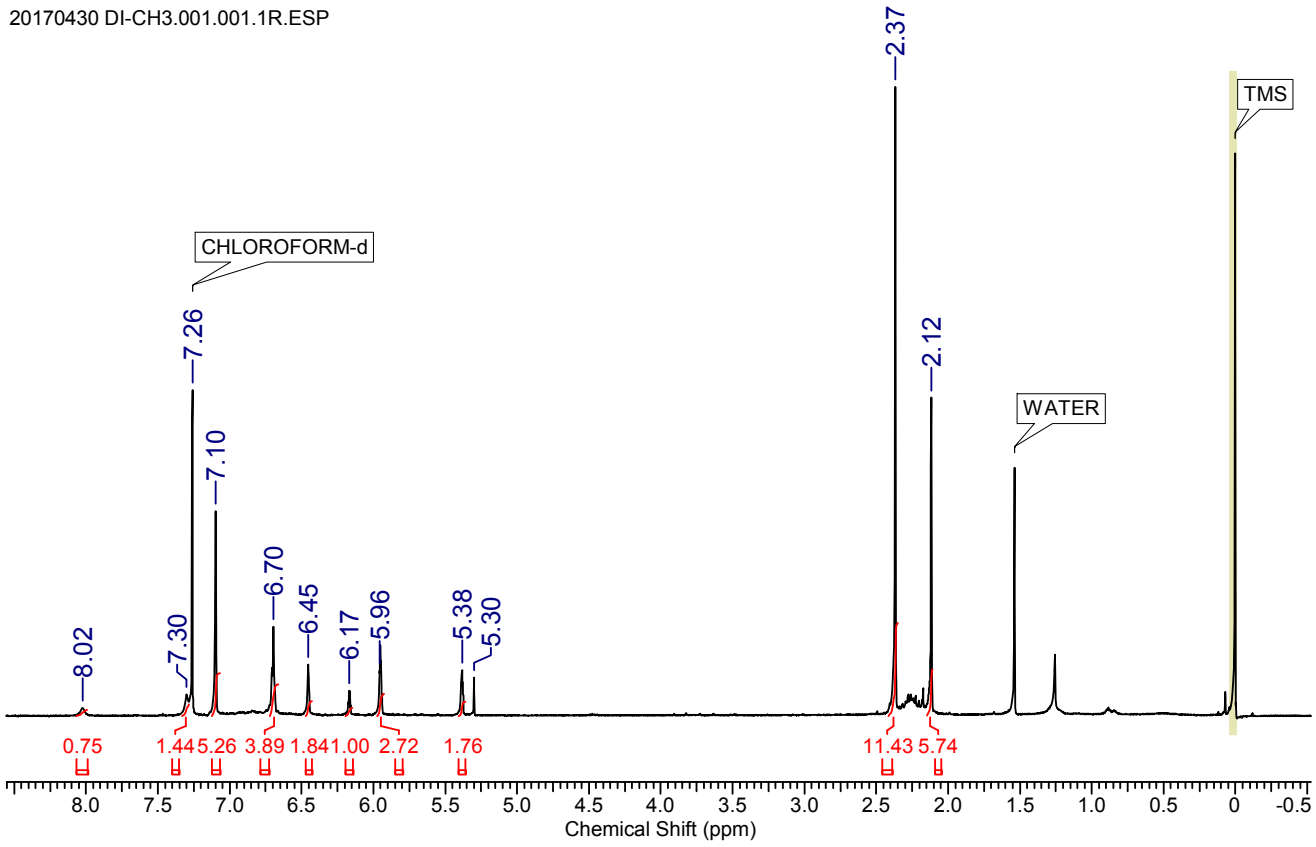


Fig. S19 ^{1}H NMR spectrum of ***E/Z*-CH_3** in $CDCl_3$ at room temperature

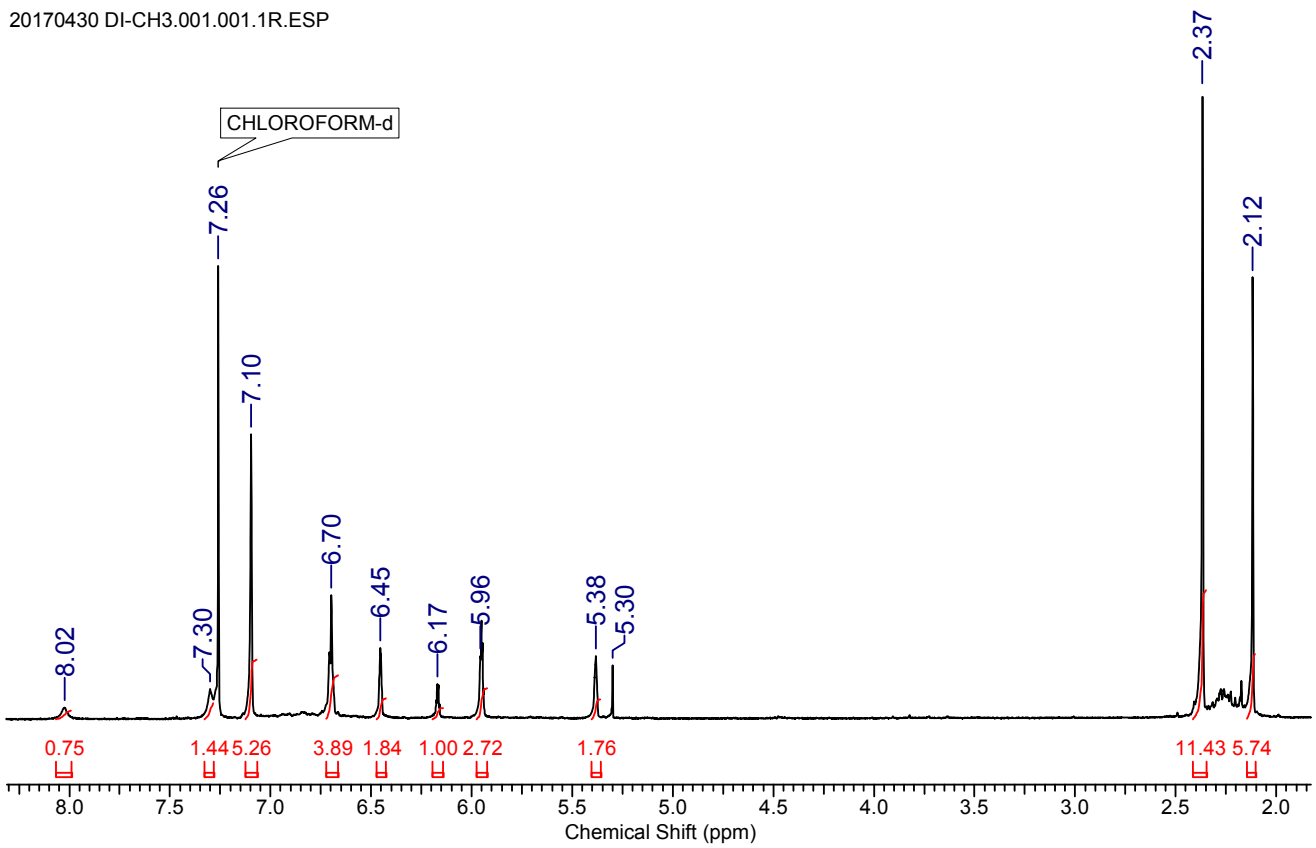


Fig. S20 ^{1}H NMR spectrum of ***E/Z*-CH_3** in $CDCl_3$ at room temperature

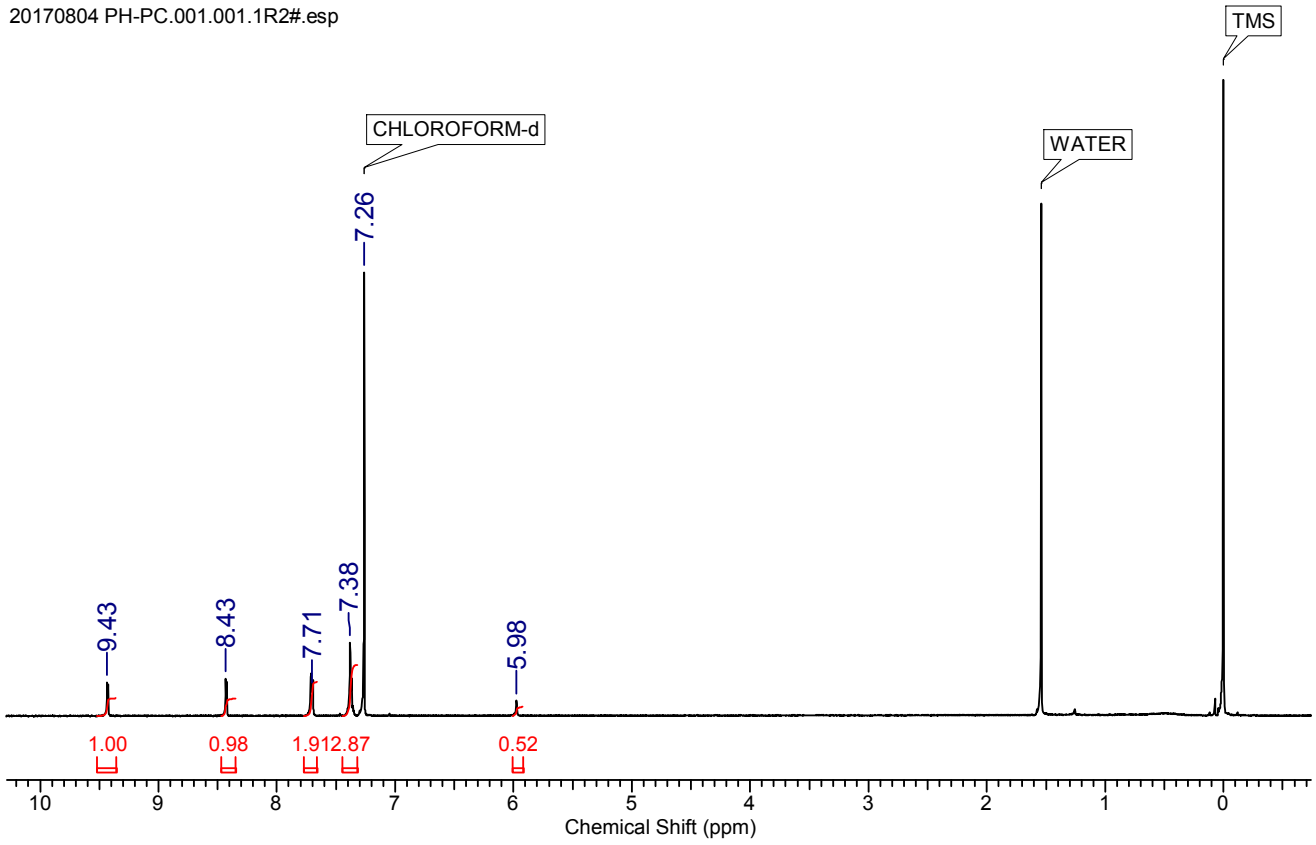


Fig. S21 ^{1}H NMR spectrum of **PhPc** in $CDCl_3$ at room temperature.

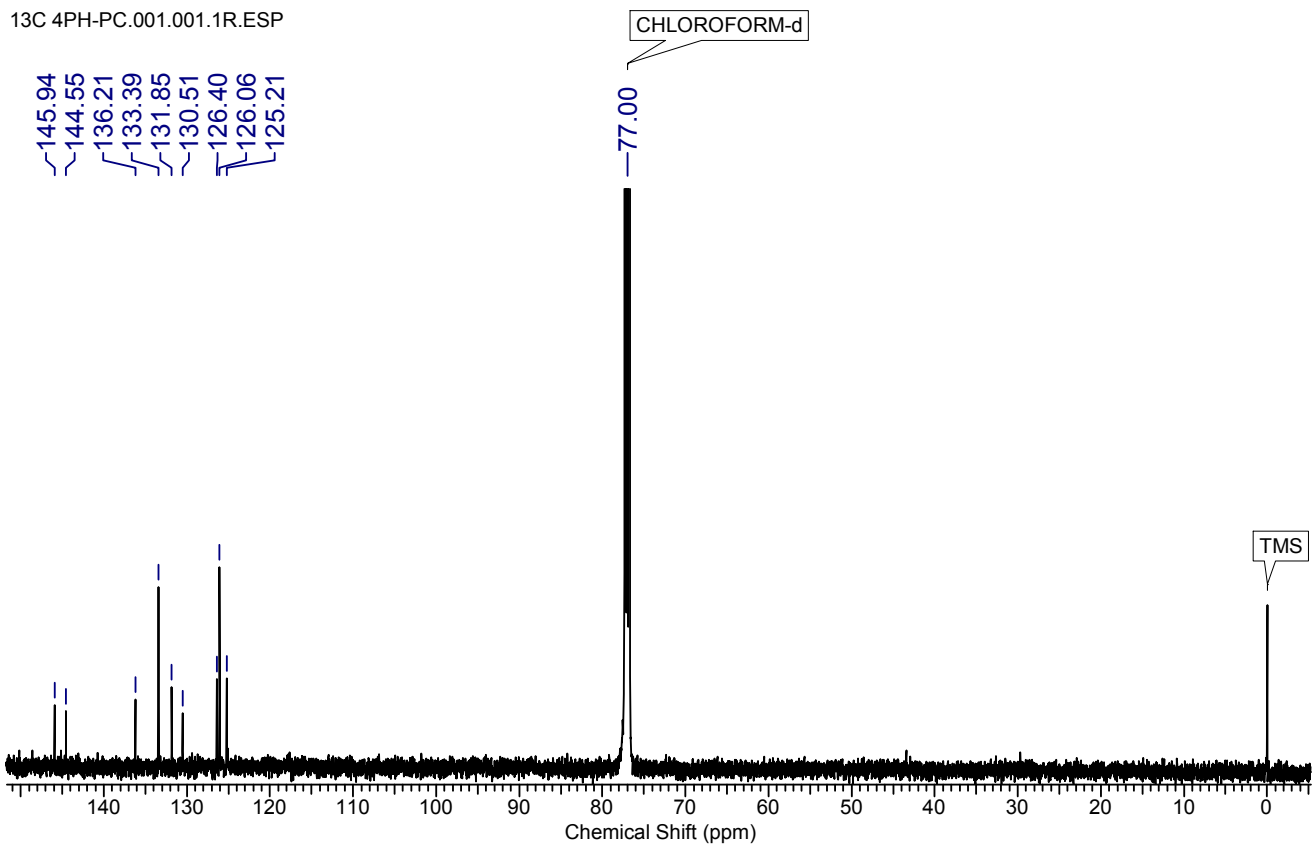


Fig. S22 ^{13}C NMR spectrum of **PhPc** in $CDCl_3$ at room temperature.

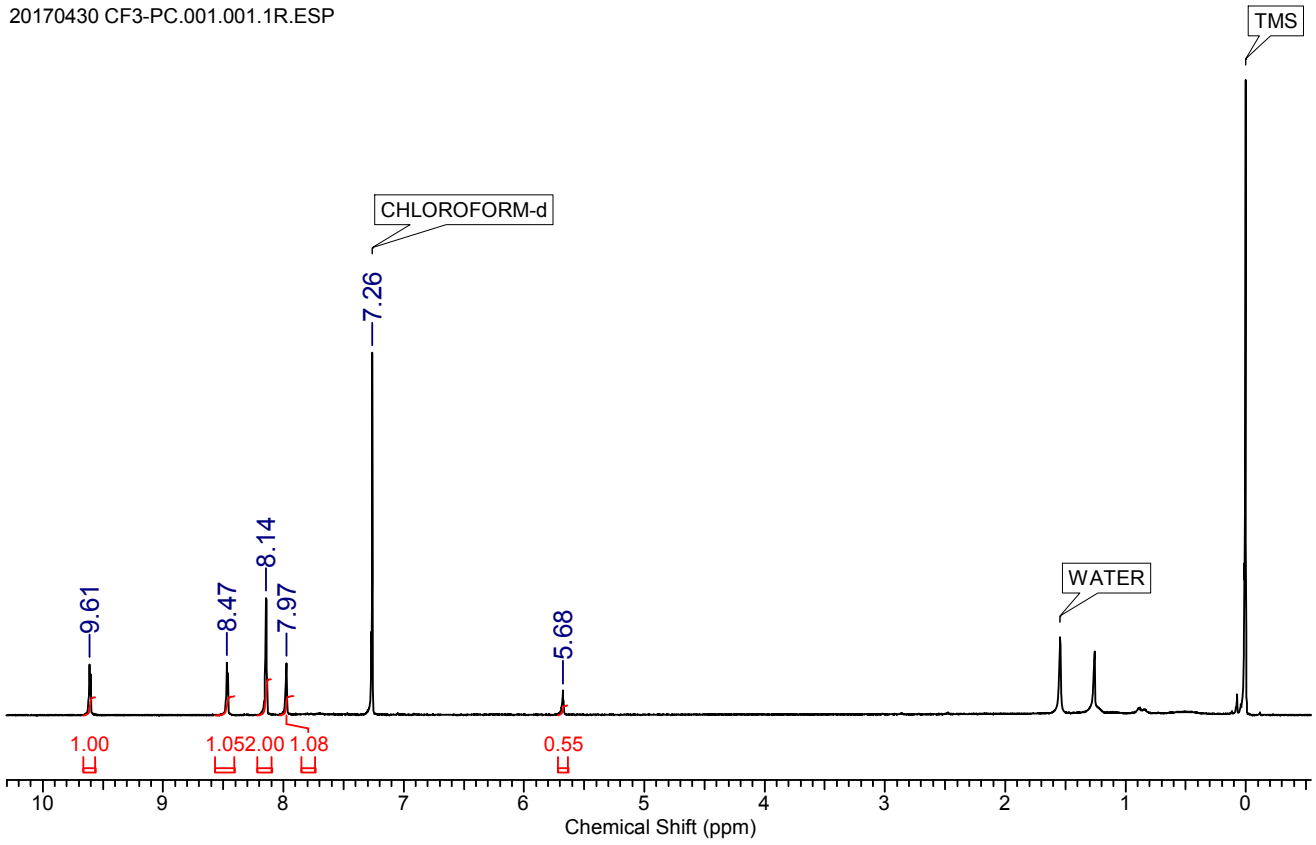


Fig. S23 ^{1}H NMR spectrum of **CF_3Pc** in $CDCl_3$ at room temperature

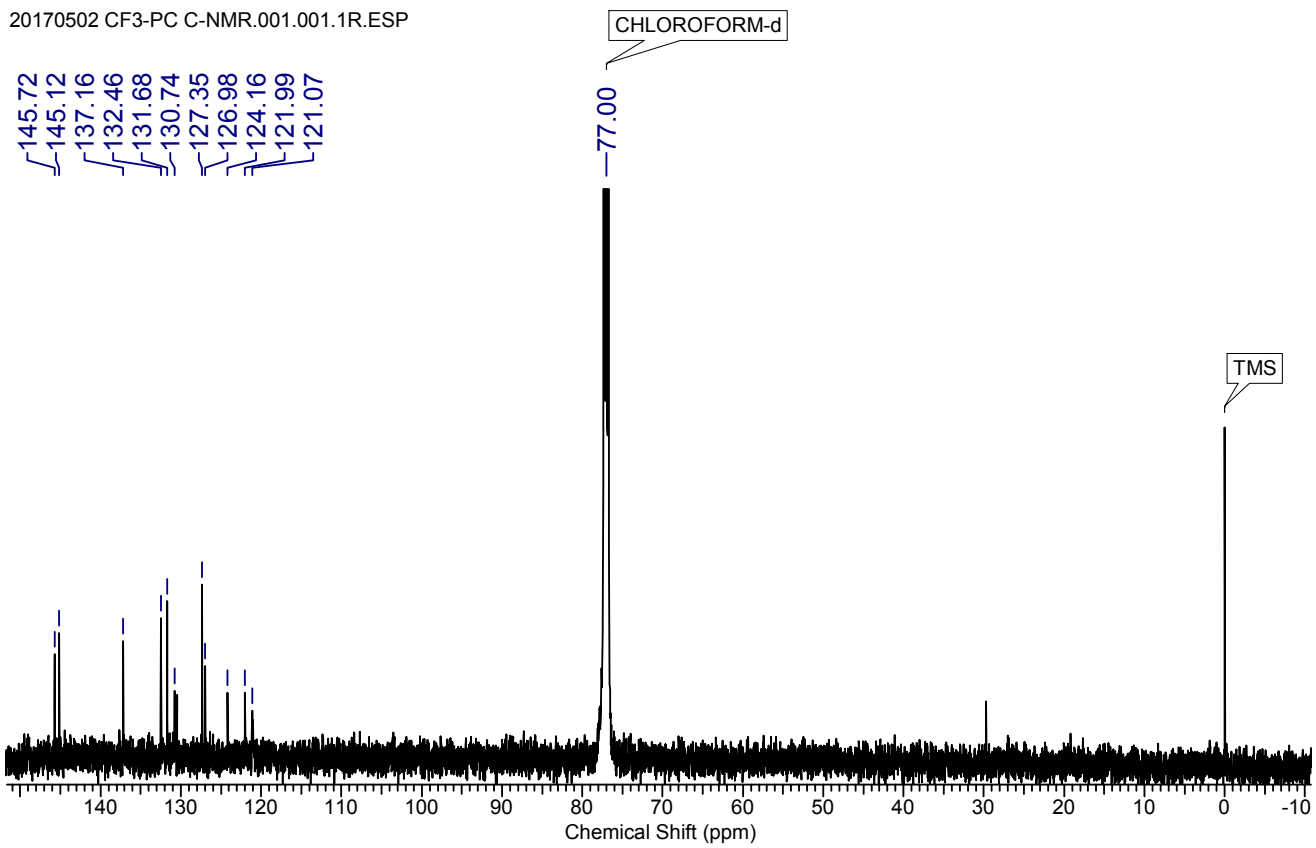


Fig. S24 ^{13}C NMR spectrum of **CF_3Pc** in $CDCl_3$ at room temperature

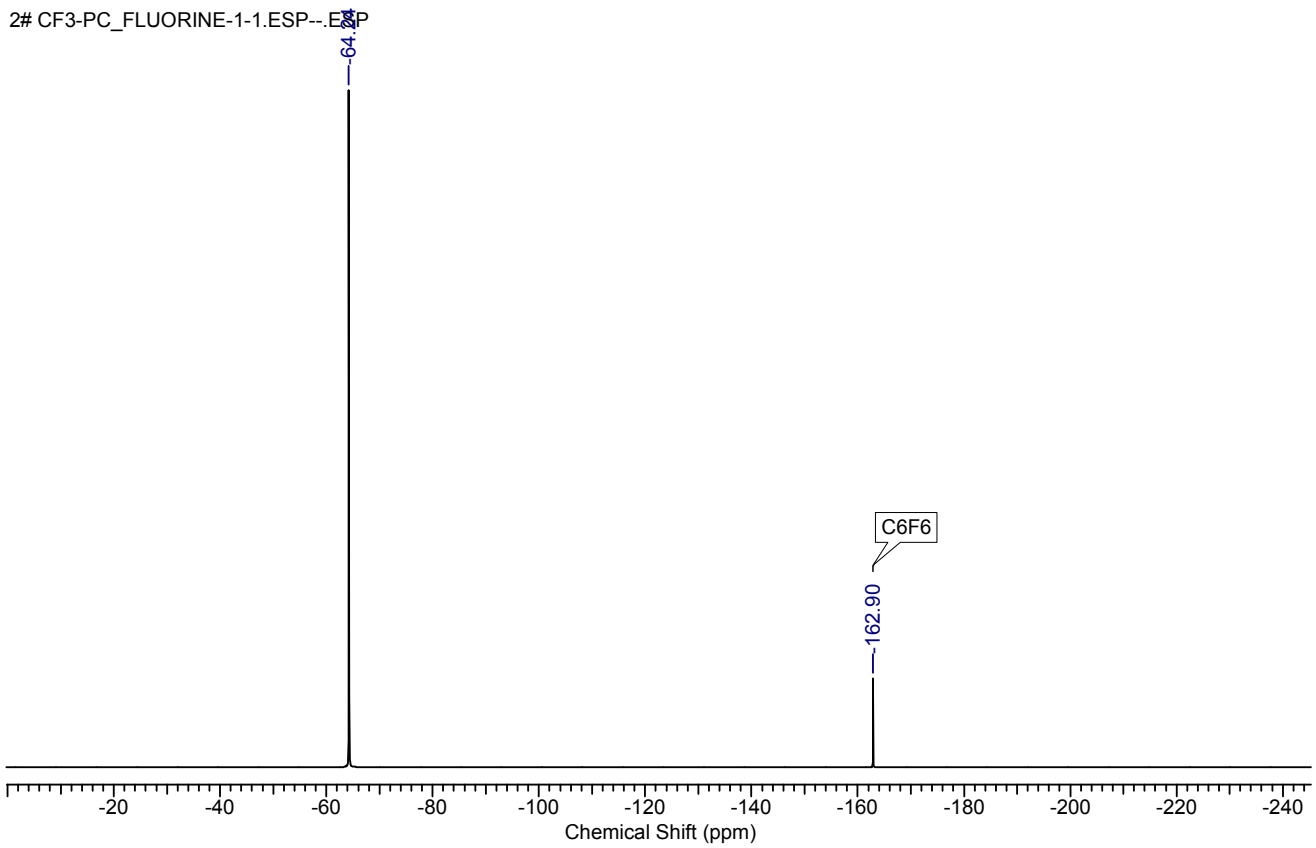


Fig. S25 ^{19}F NMR spectrum of **CF_3Pc** in $CDCl_3$ at room temperature.

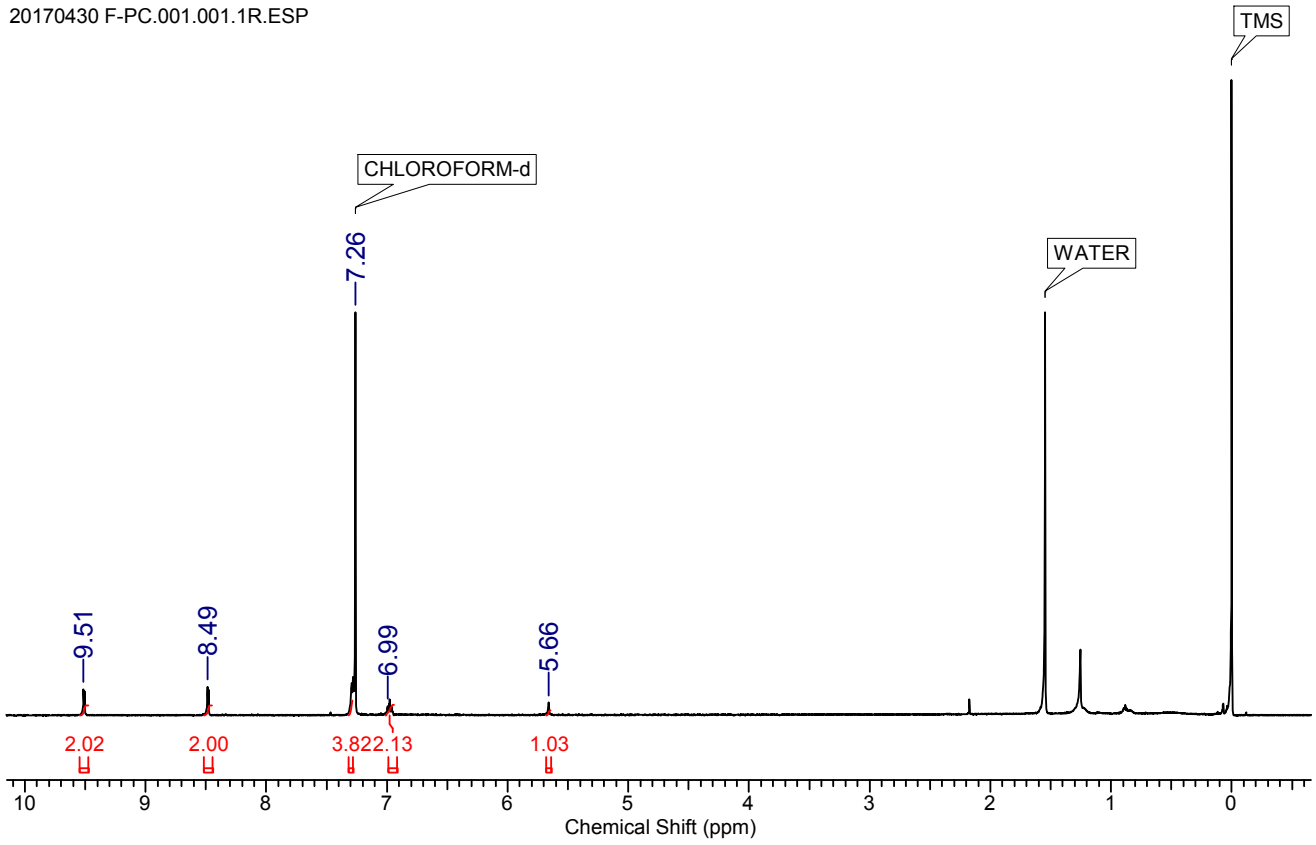


Fig. S26 ^{1}H NMR spectrum of **FPc** in $CDCl_3$ at room temperature

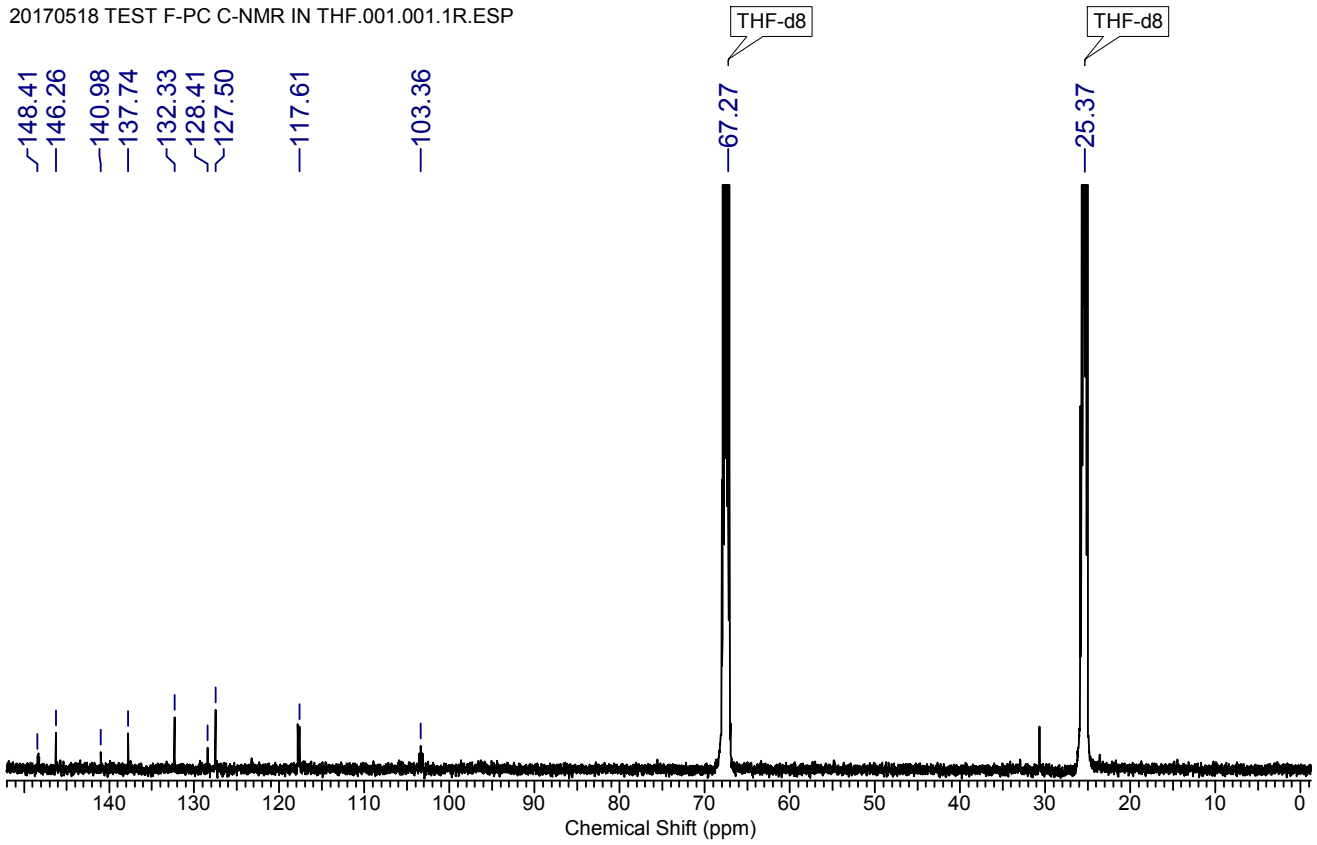


Fig. S27 ^{13}C NMR spectrum of **FPc** in THF-d_8 at room temperature

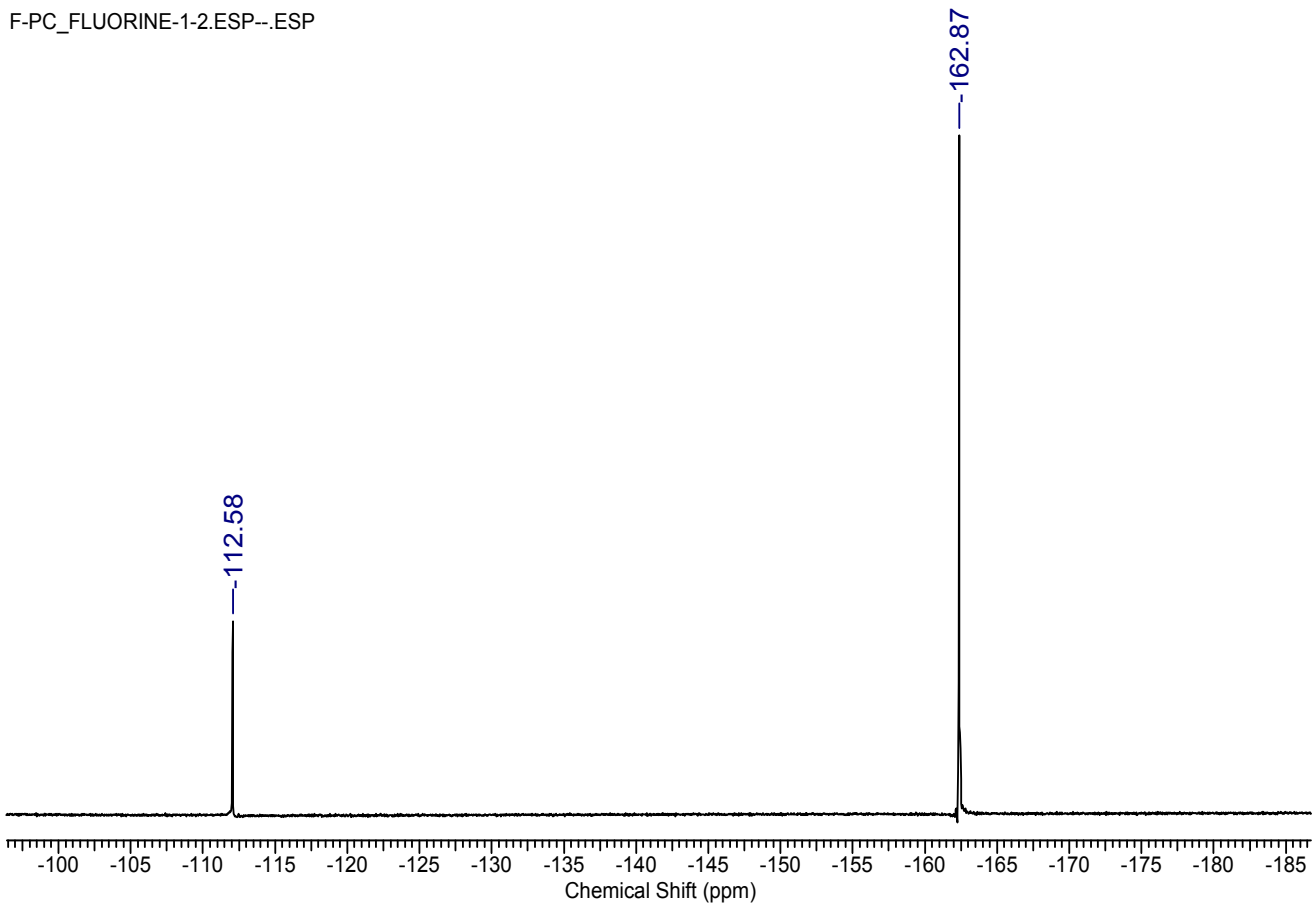


Fig. S28 ^{19}F NMR spectrum **FPc** in $CDCl_3$ at room temperature

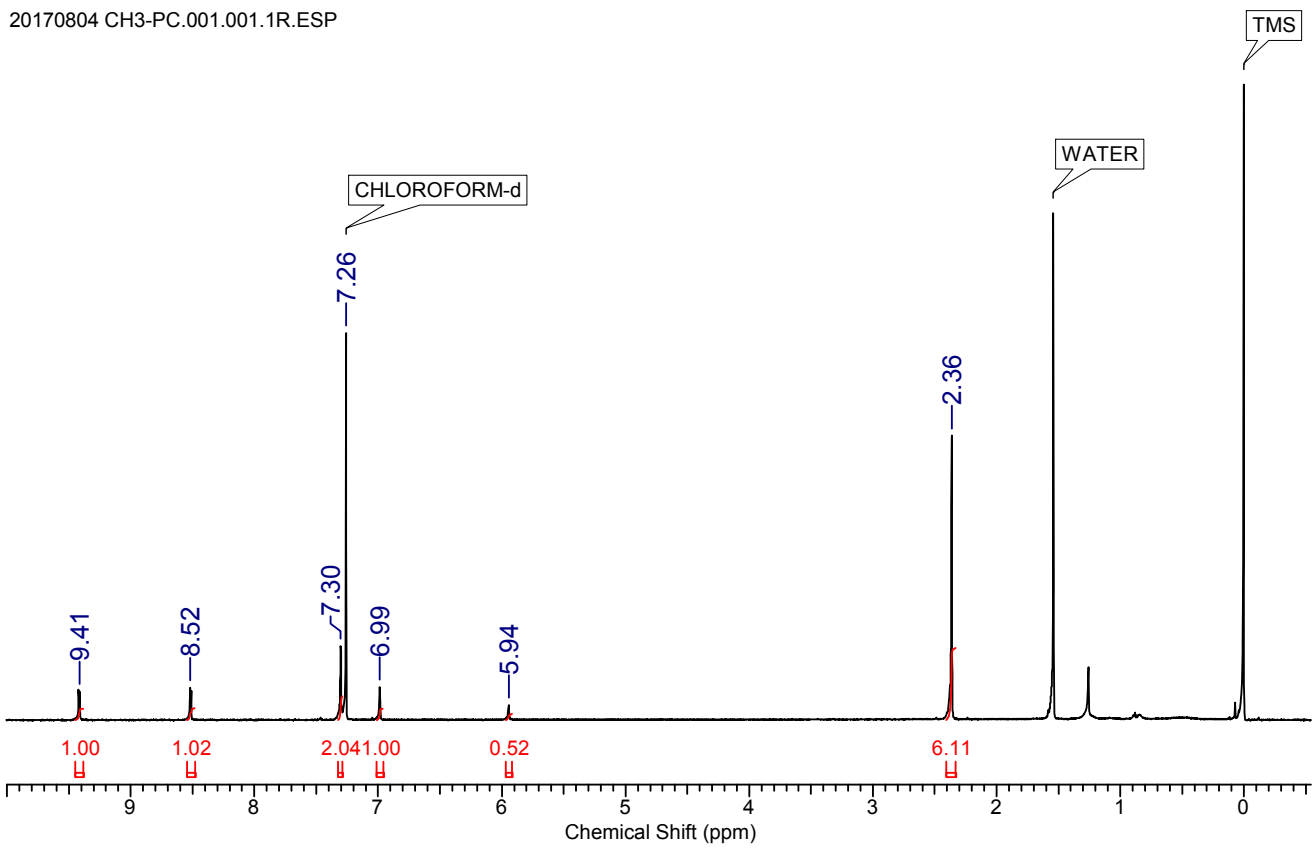


Fig. S29 ^{1}H NMR spectrum of **CH_3Pc** in $CDCl_3$ at room temperature

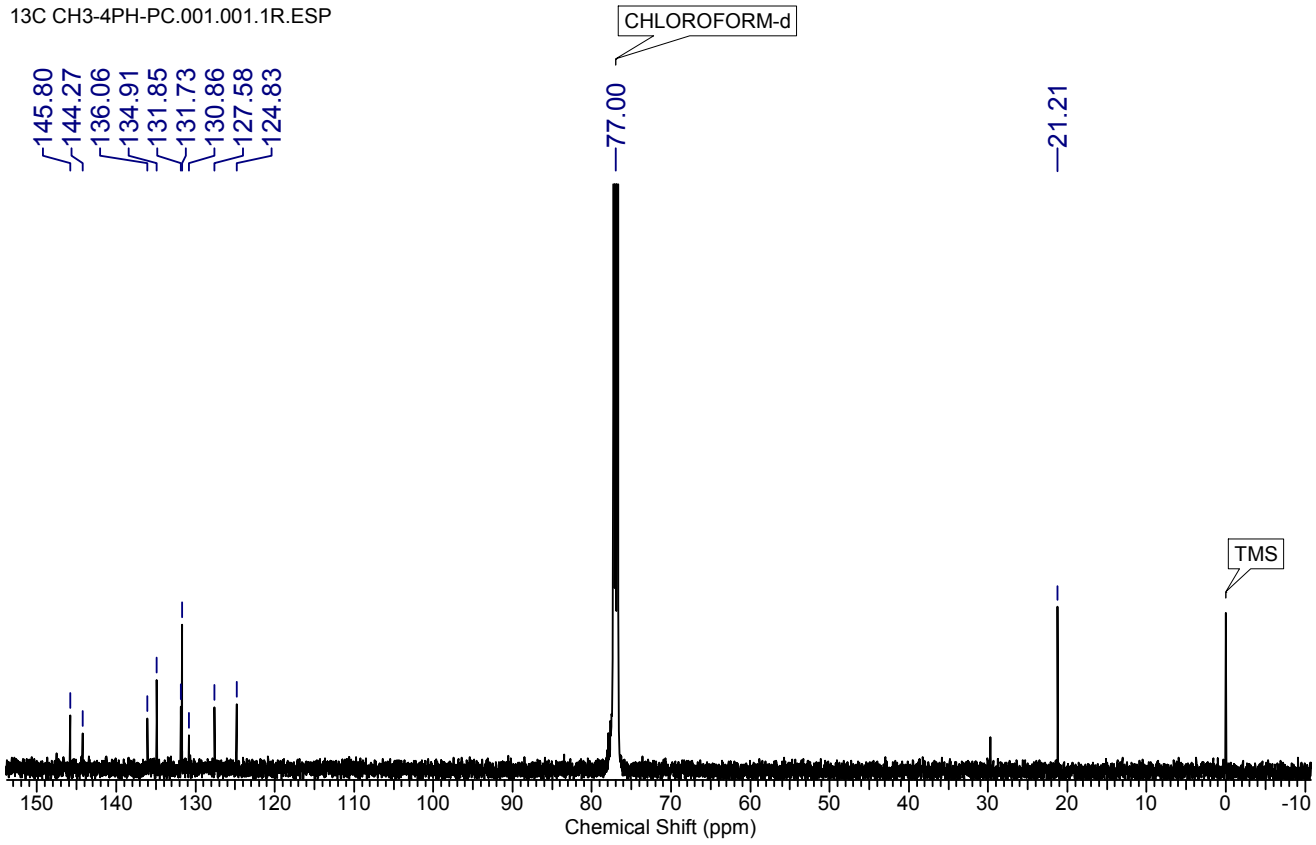


Fig. S30 ^{13}C NMR spectrum of **CH_3Pc** in $CDCl_3$ at room temperature

Table S1 Crystallographic data for **PhPc**

Compound	**PhPc**
CCDC No.	1868296
empirical formula	$C_{44}H_{30}N_4$, 2($CHCl_3$)
formula weight	853.46
temperature [K]	100
wavelength [Å]	0.71073
crystal system	triclinic
space group	P -1
a [Å]	9.235(16)
b [Å]	9.638(17)
c [Å]	11.86(2)
α [°]	78.93
β [°]	76.86(5)
γ [°]	73.21(4)
Volume [Å^3]	975(3)
Z	1
Density (calculated) [g/cm^3]	1.454
Absorption coefficient [mm^{-1}]	0.482
F(000)	438.0
θ [°]	1.78 to 28.70
Reflections collected	6705
Independent reflections	4940 [$R_{(int)}$ = 0.0.347]
Data / restraints / parameters	4940 / 0 / 257
Goodness-of-fit on F^2	1.107
$R1^a$ [$I>2\sigma(I)$]	0.0618
$wR2^b$ (all data)	0.1604
Largest diff. peak and hole [e.Å^{-3}]	0.545 and −0.550

Table S2 Crystallographic data for **CF_3Pc**

Compound	**CF_3Pc**
CCDC No.	1868292
empirical formula	$C_{52}H_{22}F_{24}N_4$
formula weight	1158.74
temperature [K]	103
wavelength [Å]	0.71073
crystal system	monoclinic
space group	C 2/c
a [Å]	35.48(3)
b [Å]	14.931(11)
c [Å]	8.852(6)
α [°]	90
β [°]	99.42(2)
γ [°]	90
Volume [Å^3]	4626(6)
Z	4
Density (calculated) [g/cm^3]	1.664
Absorption coefficient [mm^{-1}]	0.167
F(000)	2312
θ [°]	2.21 to 23.25
Reflections collected	20383
Independent reflections	3322 [$R_{(int)}$ = 0.2320]
Data / restraints / parameters	3322 / 0 / 365
Goodness-of-fit on F^2	1.031
*R*1 [$I>2\sigma(I)$]	0.0988
*wR*2 (all data)	0.2659
Largest diff. peak and hole [e.Å^{-3}]	0.406 and −0.363

Table S3 Crystallographic data for **FPc**

Compound	**FPc**
CCDC No.	1868294
empirical formula	$C_{24}H_{22}F_8N_4$, $0.793(C_2H_4Cl_2)$
formula weight	837.12
temperature [K]	103
wavelength [Å]	0.71073
crystal system	monoclinic
space group	P 21/n
a [Å]	8.4081(6)
b [Å]	13.0237(9)
c [Å]	17.9996(12)
α [°]	90
β [°]	103.022(2)
γ [°]	90
Volume [Å^3]	1920.4(2)
Z	2
Density (calculated) [g/cm^3]	1.448
Absorption coefficient [mm^{-1}]	0.219
F(000)	851.3
θ [°]	2.94 to 25.20
Reflections collected	86147
Independent reflections	3444 [$R_{(int)}$ = 0.0751]
Data / restraints / parameters	3444 / 0 / 272
Goodness-of-fit on F^2	1.073
*R*1 [$I>2\sigma(I)$]	0.0566
*wR*2 (all data)	0.1716
Largest diff. peak and hole [e.Å^{-3}]	0.992 and −0.507

Table S4 Crystallographic data for **CH_3Pc**

Compound	**CH_3Pc**
CCDC No.	1868293
empirical formula	$C_{52}H_{46}N_4$
formula weight	726.93
temperature [K]	103
wavelength [Å]	0.71073
crystal system	monoclinic
space group	P 21/n
a [Å]	8.7406(11)
b [Å]	15.369(2)
c [Å]	16.406(2)
α [°]	90
β [°]	103.303(4)
γ [°]	90
Volume [Å^3]	2144.8(5)
Z	2
Density (calculated) [g/cm^3]	1.126
Absorption coefficient [mm^{-1}]	0.066
F(000)	772.0
θ [°]	1.84 to 27.51
Reflections collected	32049
Independent reflections	4877 [$R_{(int)}$ = 0.0509]
Data / restraints / parameters	4877 / 168 / 262
Goodness-of-fit on F^2	1.095
*R*1 [$I>2\sigma(I)$]	0.0611
*wR*2 (all data)	0.1848
Largest diff. peak and hole [e.Å^{-3}]	0.983 and −0.467

Optical properties:

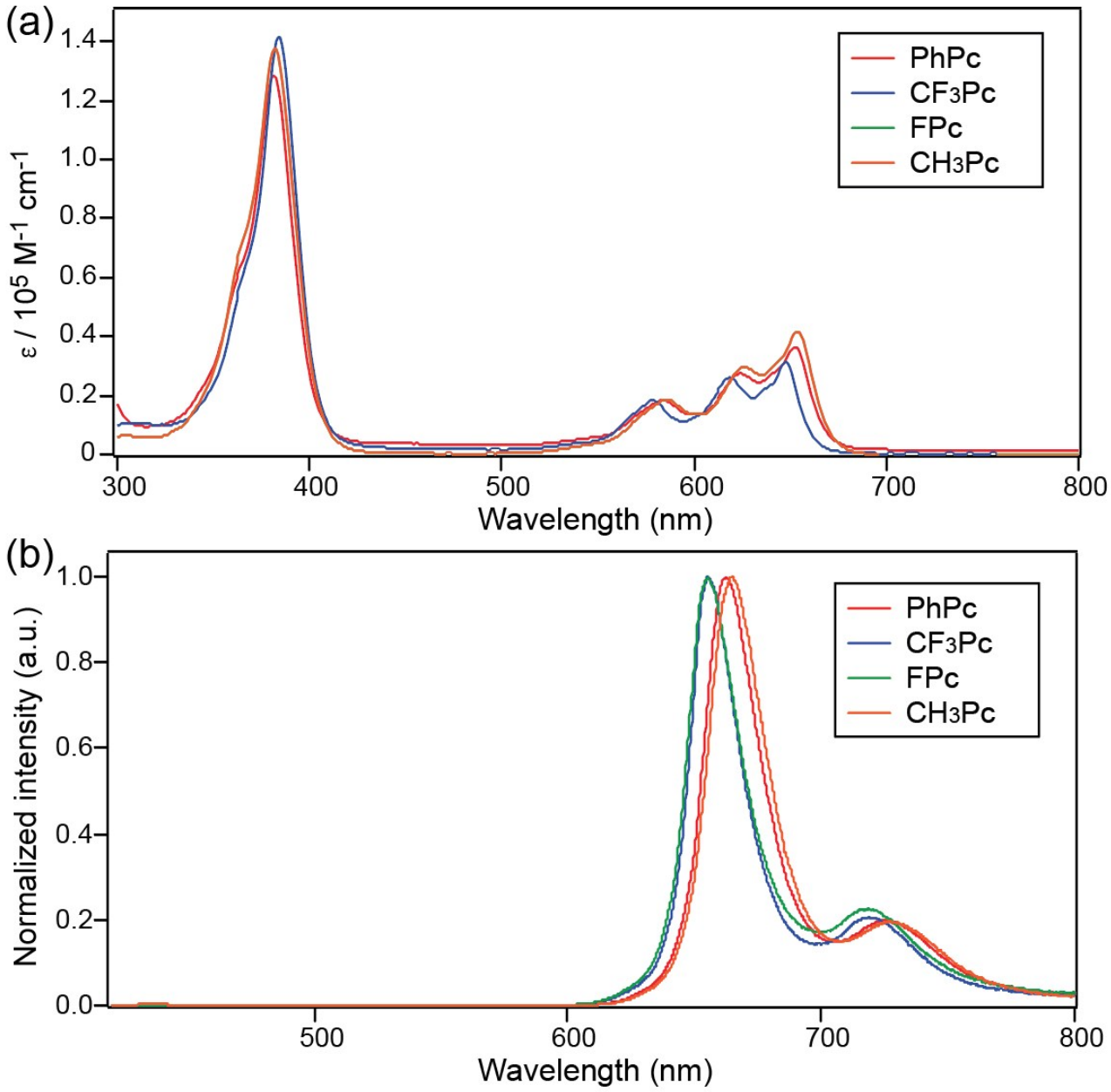


Fig. S31 (a)Absorption spectra of **PhPc**, **CF_3Pc**, **FPc**, and **CH_3Pc** in CH_2Cl_2. (b) Emission spectra of **PhPc**, **CF_3Pc**, **FPc**, and **CH_3Pc** in CH_2Cl_2 (1×10^{-6} M). Excitation at their Soret band.

Lifetime measurements:

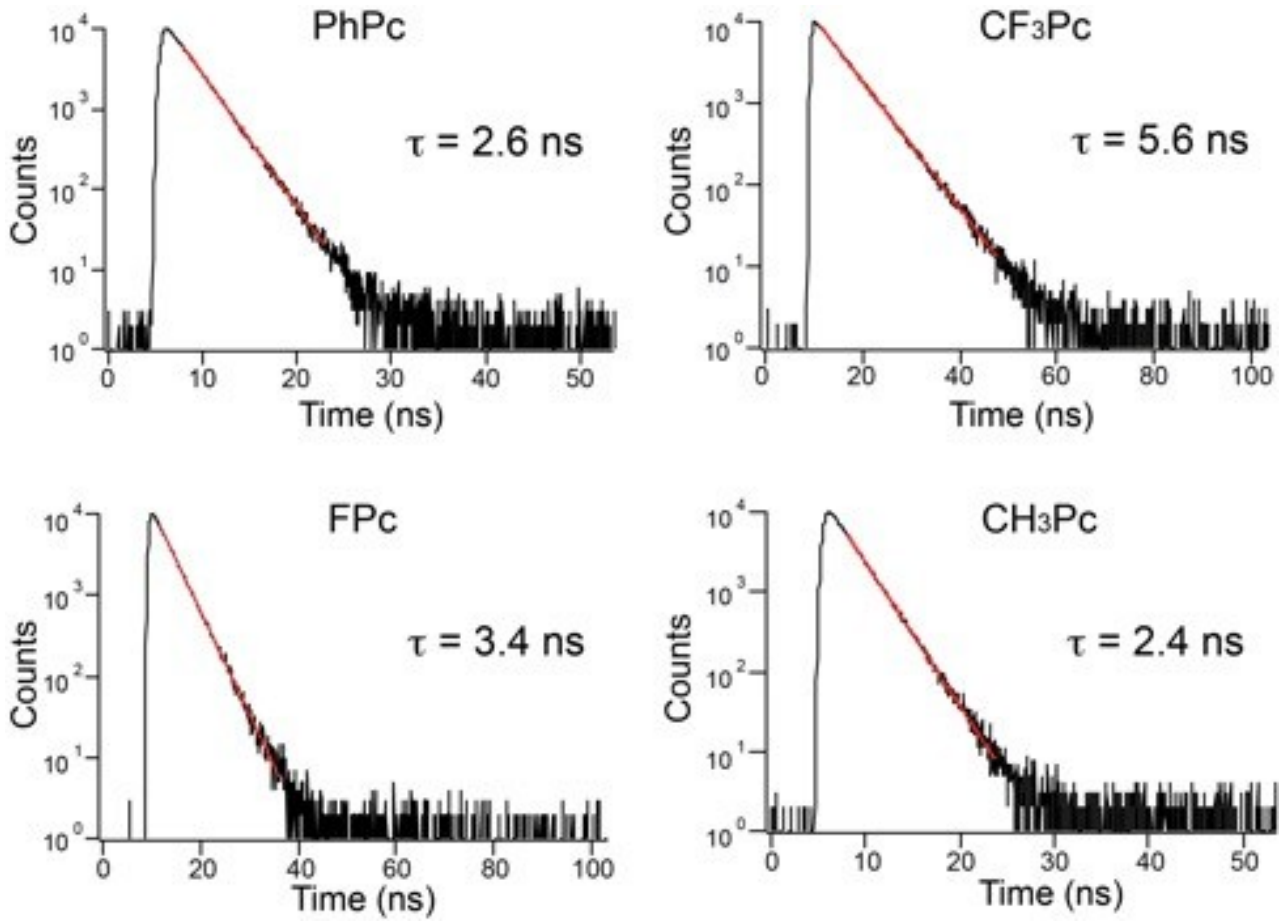


Fig. S32 Fluorescence-decay profile of porphycene derivatives in CH_2Cl_2.

Electrochemical Data:

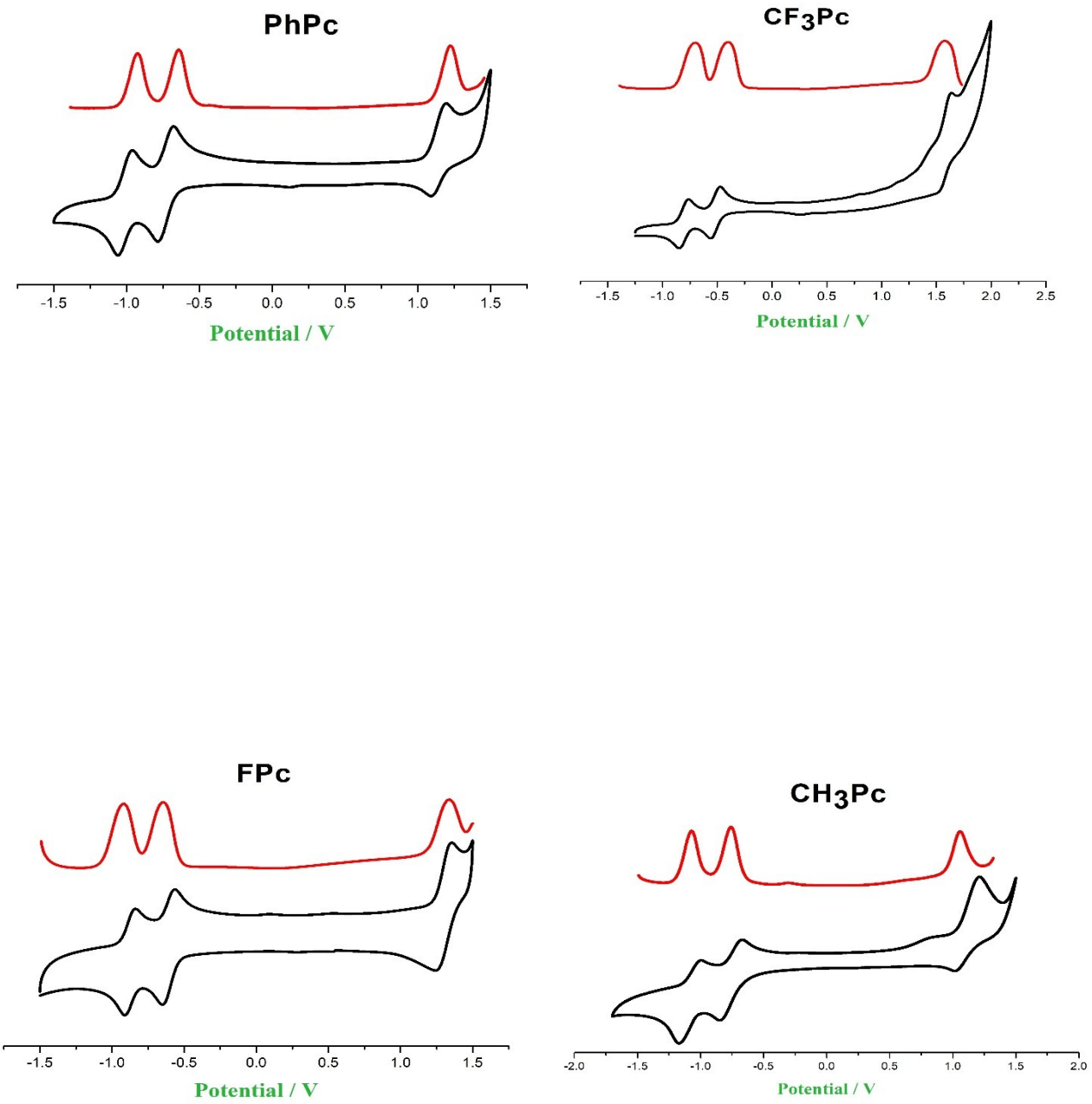


Fig. S33 Cyclic voltammogram (black line) and differential pulse voltammogram (red line) of porphycene derivatives in CH_2Cl_2.

Computational Studies

The potential energy curves (PECs) for the rotation around the C=C bond shown in Fig. S34 were calculated using the DFT(ωB97XD)/6-31G(d,p) method because intramolecular van der Waals interaction could be expected. The rotation was controlled by changing the pyrrole-C=C-pyrrole dihedral angle (ϕ). In the calculations, we firstly located the energy minima corresponding to the E- and Z-forms. Then, ϕ was modulated at the 5º increment. At the curve crossing regions, the increment was set to 1º. The other degree of freedom except for ϕ was fully optimized. Because of the relative orientations of the pyrrole and phenyl groups, we obtained some PECs in each system. Fig. 2 (b) and (c) show the PECs connecting the lowest-energy points at each configuration. The transition state was located through polynomial fitting (up to the 6-th order) at around the two local minima corresponding to the *E*- and *Z*-forms.

Results and Discussion

To understand the *E/Z*-isomerization, we conducted a computational investigation of the potential energy curve (PEC) along the reaction coordinate for the *E/Z*-isomerization of **Ph** and its protonated form (**Ph+H**) using DFT. For comparison, compounds with Me groups in place of the phenyl groups in **Ph**, hereafter denoted as **Me** and **Me+H**, were also calculated. The dihedral angle (ϕ), defined in Fig. 34(a), was manually modulated and other degrees of freedom were optimized at each point (each value of ϕ).

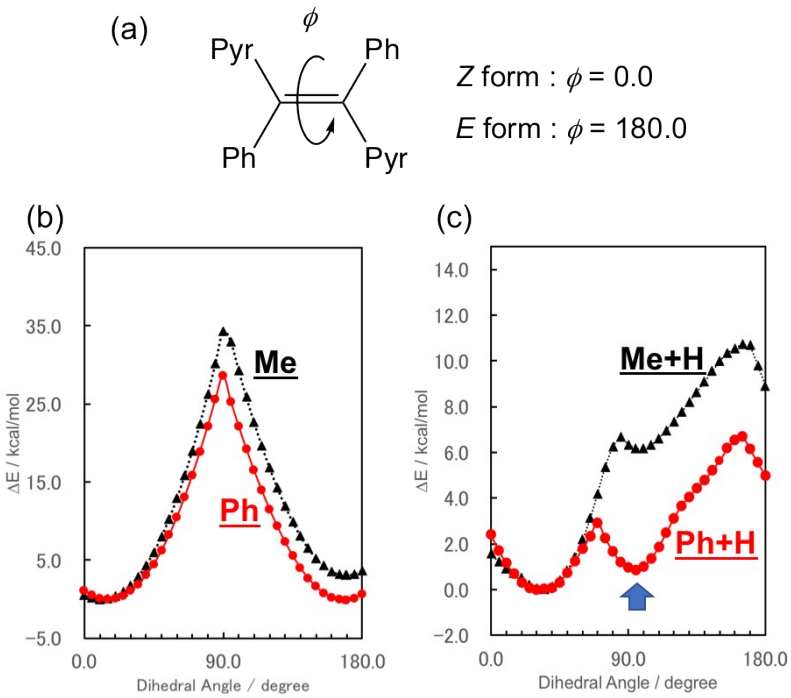


Fig. S34 (a) The pyrrole(Pyr)-C=C-pyrrole dihedral angle (ϕ) taken as a reaction coordinate in the *E/Z* isomerization, and the potential energy curves (b) before and (c) after protonation of **Ph** and **Me** (denoted as **Ph+H** and **Me+H**, respectively) calculated by using the DFT(□B97xd)/6-31G(d,p) method. Arrow indicates the important reaction intermediate.

Table S5 Summary of energy minima and transition state (TS) on the potential curves of **Ph**, **Me**, and their protonated forms. The reaction coordinate is ϕ (unit in degree) defined in Fig. S34(a). The relative energy (ΔE) from the *Z*-type conformation is tabulated in kcal/mol unit.

Molecule	Z-type		TS		E-type	
	ϕ	ΔE	ϕ	ΔE	ϕ	ΔE
Ph	15.0	0.0	88.8	31.4	167.3	-0.1
Ph+H	30.0	0.0	70.6	3.0	95.0	0.9
Me	10.0	0.0	91.5	35.6	169.5	3.0
Me+H	33.6	0.0	82.3	7.1	95.0	6.2

The obtained PECs highlighted the essential differences between **Ph** and **Me**. Before protonation, the both systems had two energy minima corresponding to the *E* and *Z* forms. Starting from the *E* form, the dihedral distortion resulted in system destabilization of the system. When ϕ was nearly 90º (see Table S5), the PEC had a maximum corresponding to the transition state. In the unprotonated form, the activation energies of **Ph** and **Me** were 31.5 and 32.6 kcal/mol, respectively. These energies indicate that the isomerization is very difficult.

In contrast, protonation at the ethylene moiety drastically changes the PECs. In this case, two energy minima appear at around 30° and 95°, with the transition states located at 71º and 82º in **Ph+H** and **Me+H**, respectively. The lower energy conformation is now the ***Z***-type form rather than the ***E***-type form. The barrier heights from the ***E***-type forms of **Ph+H** and **Me+H** are 2.1 and 0.9 kcal/mol, respectively. These values are consistent with the decrease in the bond order of the C–C bonds (from double bond to single bond) after protonation. The lowering of the barrier heights clearly indicates that rotation along the C–C bond easily occur to predominantly yield the *Z*-type form. Another interesting feature is the shallow barrier height of *Z*-type **Me** and an energy difference between the two minima of 6.0 kcal/mol. These features suggest that the *Z*-type form is the major conformation in **Me+H** due to both thermodynamic and kinetic stabilities. In contrast, the PEC for **Ph+H** shows a bistable character around the TS, with an energy difference between the *E*- and *Z*-type forms of only 0.9 kcal/mol. This indicates that these two forms may exist thermodynamically. The relative conversion between these forms is less favorable than in **Me+H**, both thermodynamically and kinetically. Such features were unchanged, even when the solvent effect of CH_2Cl_2 was accounted for using the polarizable continuum model (PCM).

The computational results suggest that gram-scale synthesis from **Ph** should have become possible due to the enhanced (relative) stability of the *Z*-type form of the protonated species. Therefore, we can conclude that the reactive intermediate might be trapped owing to the phenyl group in **Ph**. As the optimized geometries show that buckling of the phenyl group occurred at the TS, steric repulsion would be a factor in the larger activation energy compared with that of **Me**.

Quantum mechanical calculations were performed with Gaussian 09 Program.[4] All calculations were done by Density functional theory (DFT) with restricted Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) was used. The 6-31G(d,p) basis set was used for all atoms. The initial geometry was taken from the X-ray crystallographic structures. The molecular orbitals were visualized using ChemCraft.

Table S6 Selected orbital energies of optimized structures of **PhPc**, **CF_3Pc.**

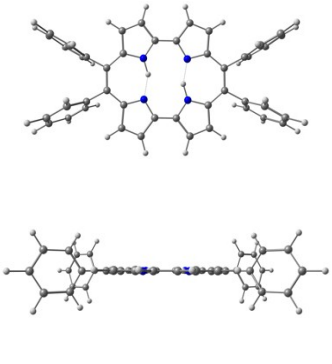
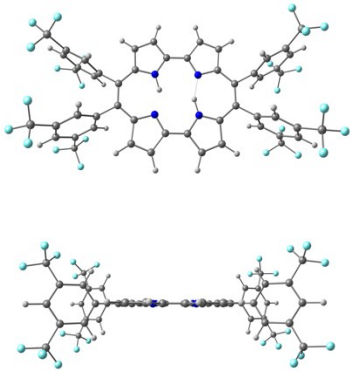
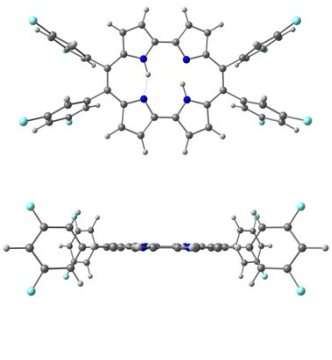
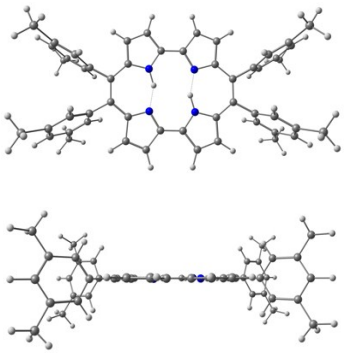
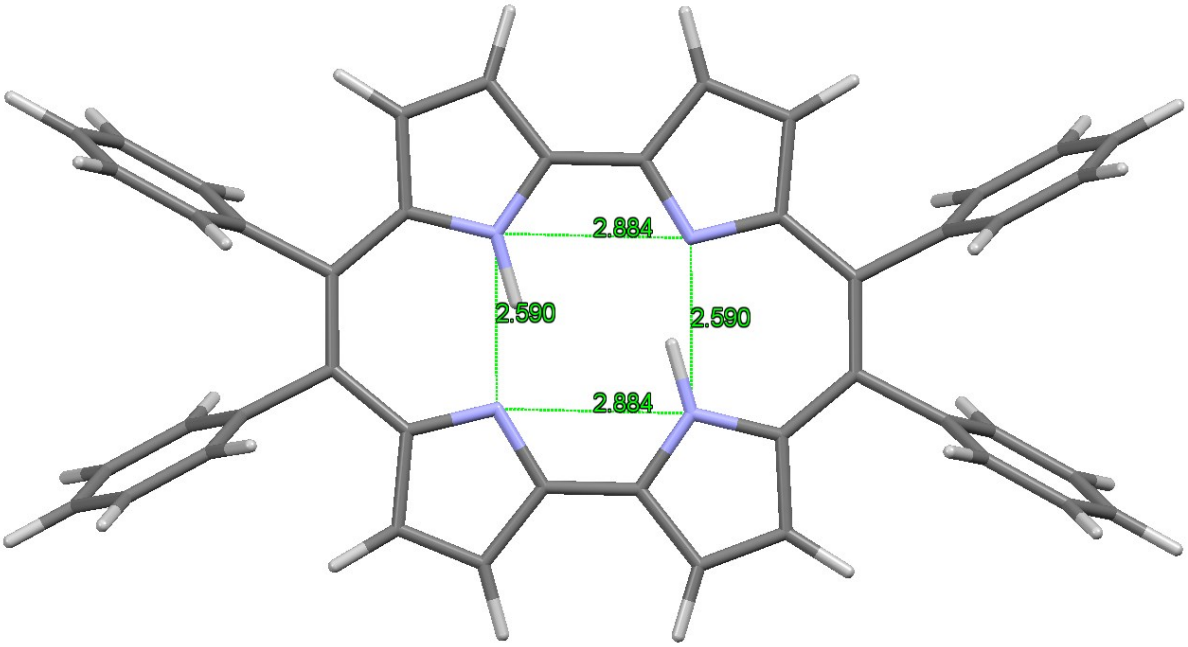
Optimized structure of porphycene			
LUMO+1	-1.50	-2.34	
LUMO	-2.78	-3.53	
HOMO	-5.15	-5.93	
HOMO-1	-5.21	-6.00	

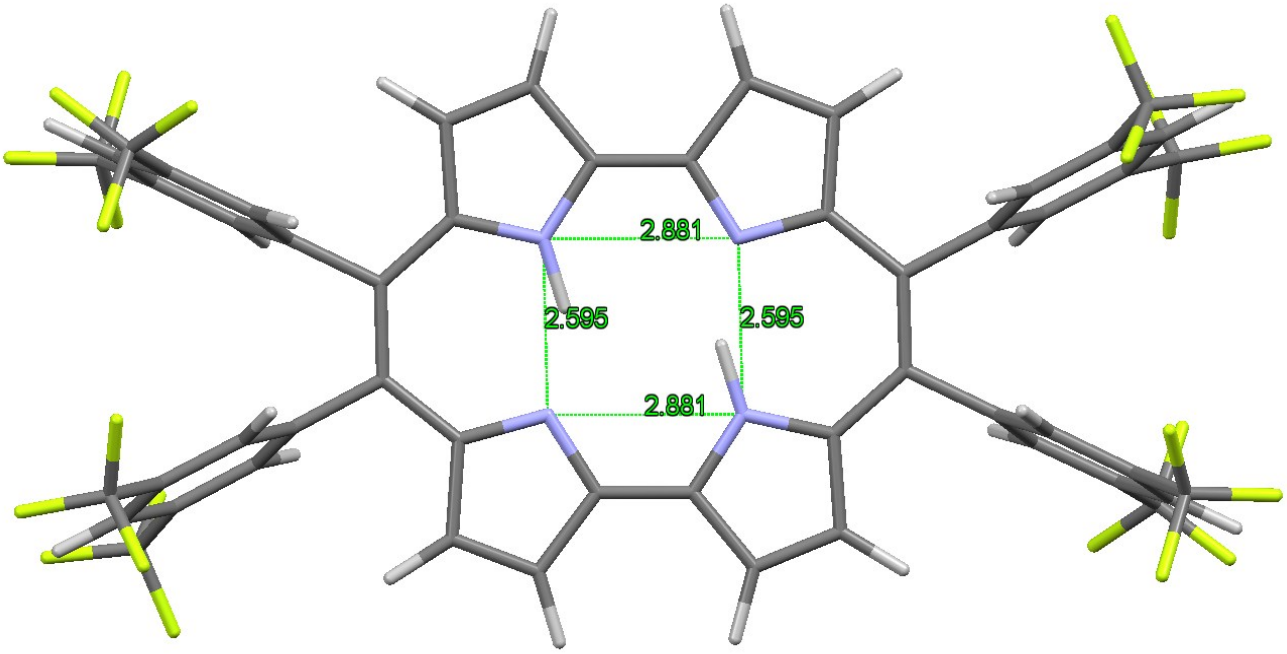
Table S7 Selected orbital energies of optimized structures of **FPc**, and **CH_3Pc.**

Optimized structure of porphycene			
LUMO+1	-1.97	-1.38	
LUMO	-3.19	-2.66	
HOMO	-5.58	-5.02	
HOMO-1	-5.65	-5.08	

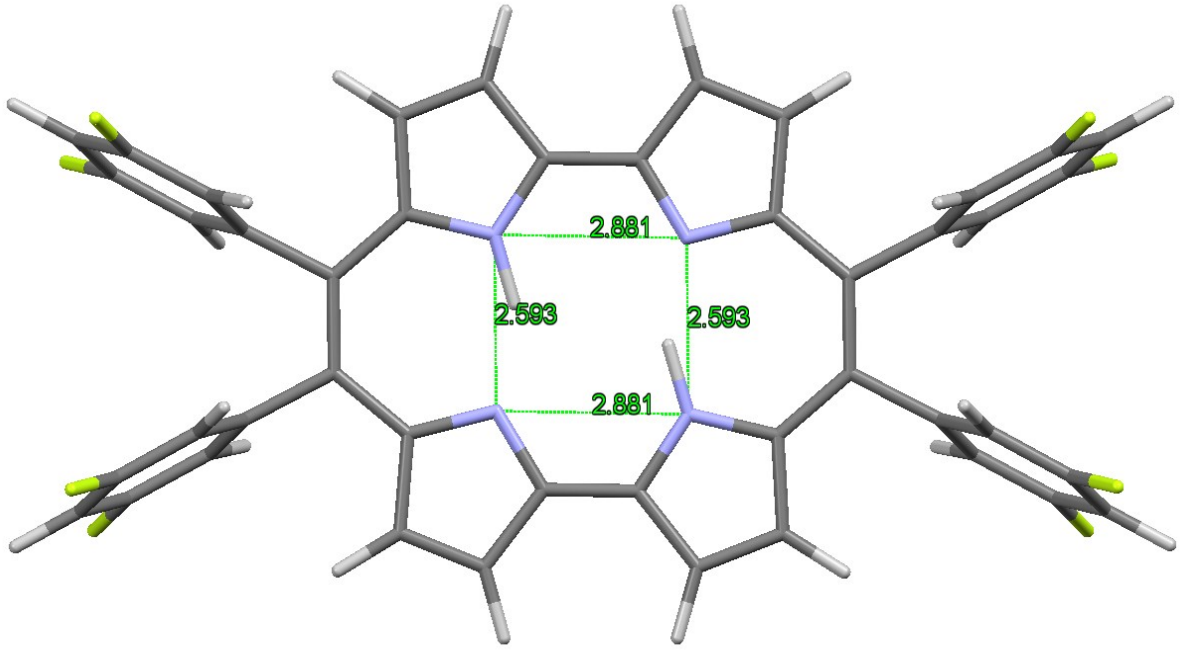
(a)



(b)



(c)



(d)

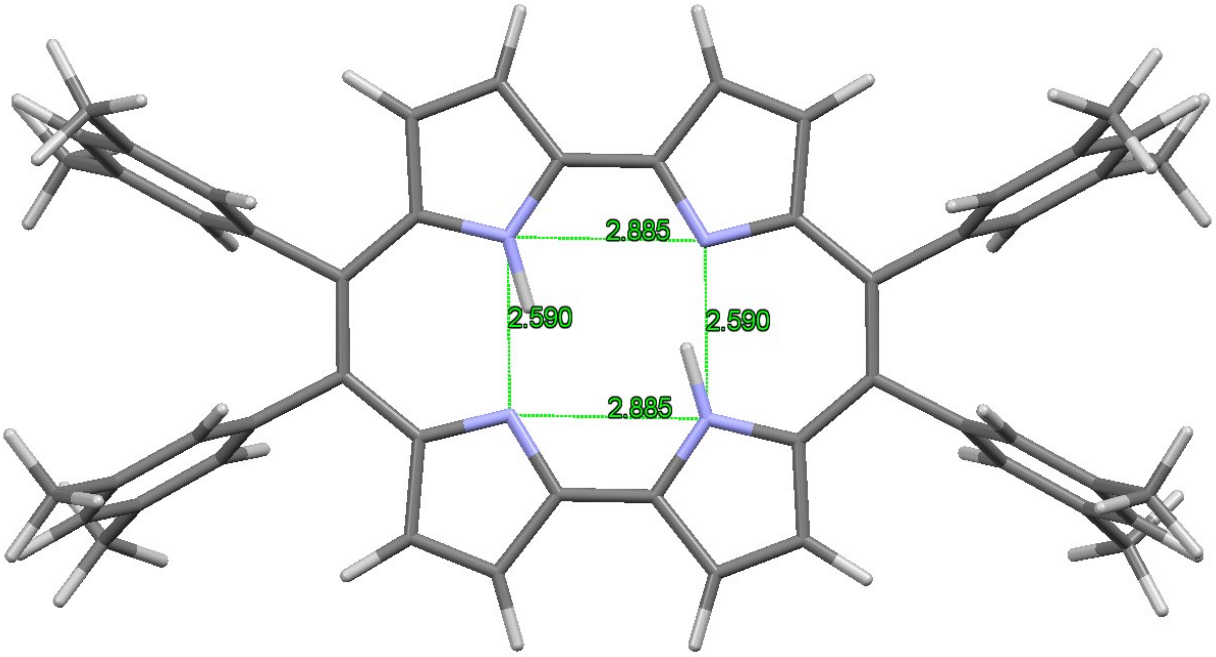


Table S8 Comparison between crystal structures and optimized structures of porphycene derivatives.

□	N1–N2 (Å)	N1–N3 (Å)
DFT optimized **PhPc**	2.884	2.590
Crystal structure **PhPc**	2.874	2.547
DFT optimized **CF_3Pc**	2.881	2.595
Crystal structure **CF_3Pc**	2.894	2.552
DFT optimized **FPc**	2.881	2.593
Crystal structure **FPc**	2.866	2.562
DFT optimized **CH_3Pc**	2.885	2.590
Crystal structure **CH_3Pc**	2.873	2.568

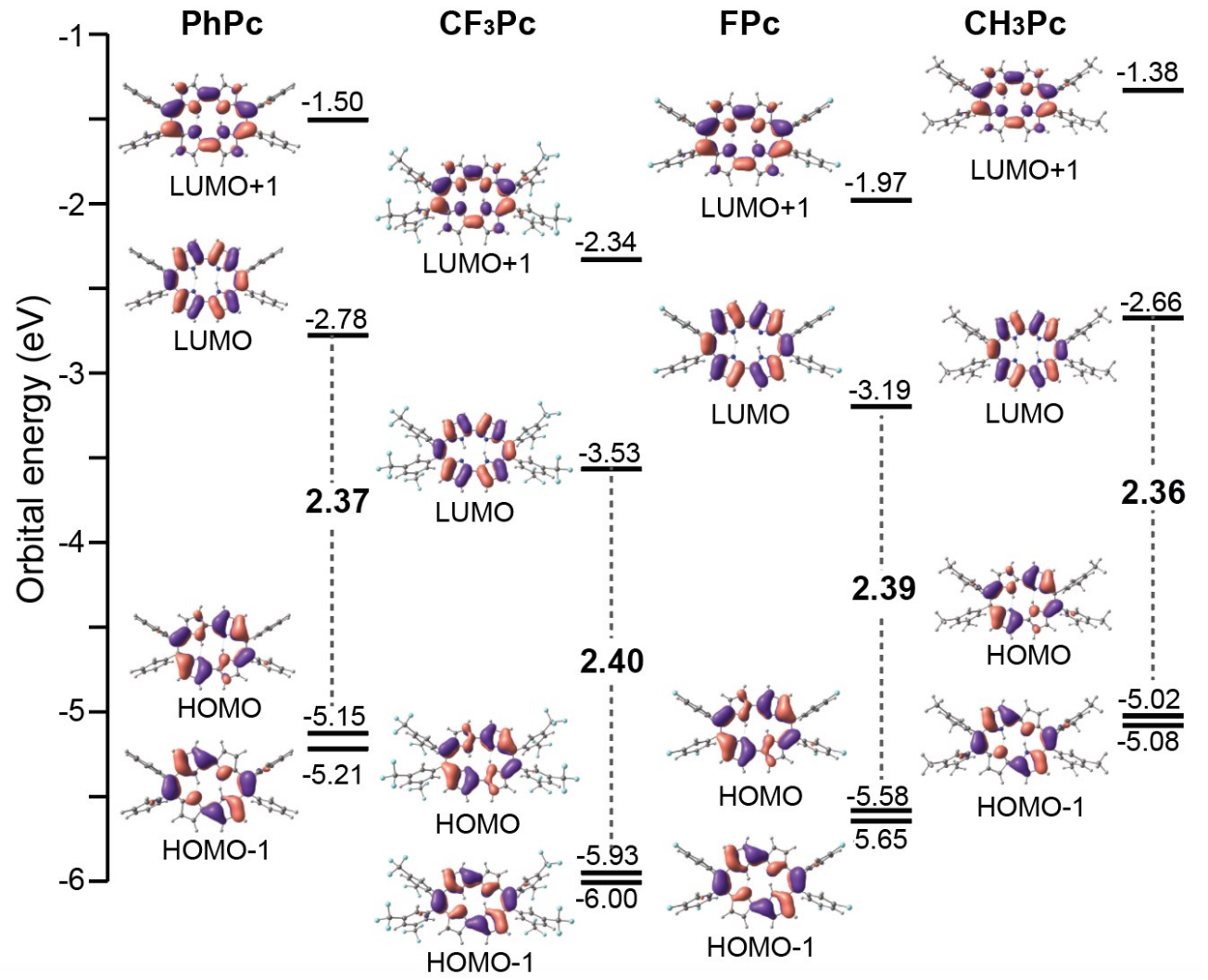


Fig. S35 Frontier molecular orbitals of *meso*-tetraarylporphycene derivatives based on DFT/B3LYP/6-31G(d,p) calculations. Energy levels of the HOMO-1, HOMO, LUMO, LUMO+1 molecular orbital of the *meso*-tetraarylporphycene derivatives were depicted.

Coordinates of the optimized structure of PhPc:

C	2.791727833	1.628598574	0.019968358
C	2.871820160	3.065849041	0.073257221
H	3.789275092	3.632678093	0.101306529
C	1.589917024	3.561512812	0.085849130
H	1.290929735	4.599452869	0.123916420
C	0.696281809	2.445574976	0.044149234
C	-0.716123146	2.423828422	0.047988456
C	-1.603194849	3.564244695	0.101296968
H	-1.306970373	4.603620172	0.144767066
C	-2.869704721	3.058852127	0.092498184
H	-3.794902199	3.613285837	0.130027084
C	-2.748421259	1.605563663	0.029610691
C	-3.857303945	0.706346041	0.012172114
C	-3.877141821	-0.710008953	-0.005472510
C	-5.196327065	1.404221086	0.023656862
C	-5.923035650	1.548718490	1.213006713
H	-5.525388793	1.132236739	2.133468923
C	-7.143743422	2.223994794	1.224717432
H	-7.692248817	2.327599957	2.156605690
C	-7.657071759	2.767877254	0.046333738
H	-8.607724346	3.293022003	0.055683181
C	-6.939163921	2.635735472	-1.142966135
H	-7.327862602	3.059055157	-2.064818536
C	-5.716962917	1.962304552	-1.152224954
H	-5.155823637	1.868892814	-2.077545223
C	-5.221754540	-1.395754483	-0.021558384
C	-5.747695944	-1.956036199	1.151022589
H	-5.189049423	-1.867753844	2.078375296
C	-6.973602406	-2.622690845	1.136431696
H	-7.366959646	-3.046988794	2.055824756
C	-7.689497572	-2.745912784	-0.054974753
H	-8.643200125	-3.265384028	-0.068425114
C	-7.170672882	-2.200268528	-1.230197152
H	-7.717907246	-2.296933569	-2.163540627
C	-5.946089522	-1.532346921	-1.213447581
H	-5.544169770	-1.114063739	-2.131160747
N	-1.425061314	1.272695028	0.007364862

N	1.458628307	1.317505456	0.004407178
H	1.156489641	0.302493904	-0.005686874
C	-2.791728357	-1.628597680	-0.019972210
C	-2.871821139	-3.065848210	-0.073253259
H	-3.789276140	-3.632677114	-0.101298831
C	-1.589918363	-3.561512579	-0.085842594
H	-1.290931429	-4.599452943	-0.123904001
C	-0.696282815	-2.445574871	-0.044148325
C	0.716122141	-2.423828797	-0.047987486
C	1.603193827	-3.564245245	-0.101292766
H	1.306969288	-4.603620838	-0.144760051
C	2.869703927	-3.058852656	-0.092498188
H	3.794901469	-3.613286456	-0.130027715
C	2.748420613	-1.605563853	-0.029614074
C	3.857303495	-0.706345744	-0.012179176
C	3.877141456	0.710009545	0.005465956
C	5.196327113	-1.404220419	-0.023661674
C	5.923035068	-1.548723295	-1.213011550
H	5.525387206	-1.132246269	-2.133475591
C	7.143743104	-2.223999318	-1.224719792
H	7.692247759	-2.327608906	-2.156608013
C	7.657072500	-2.767875756	-0.046333779
H	8.607725352	-3.293020172	-0.055681395
C	6.939165720	-2.635728328	1.142966077
H	7.327865407	-3.059043208	2.064820304
C	5.716964346	-1.962297848	1.152222668
H	5.155825781	-1.868881511	2.077543037
C	5.221754741	1.395754393	0.021557300
C	5.747698431	1.956042020	-1.151020097
H	5.189053010	1.867765142	-2.078374121
C	6.973605475	2.622695587	-1.136423732
H	7.366964356	3.046998250	-2.055813945
C	7.689499159	2.745910291	0.054984403
H	8.643202136	3.265380593	0.068438899
C	7.170672511	2.200259950	1.230203122
H	7.717905764	2.296919234	2.163547855
C	5.946088464	1.532339534	1.213448359
H	5.544167124	1.114051351	2.131158694

N	1.425060419	-1.272695346	-0.007364733
N	-1.458628900	-1.317504747	-0.004417169
H	-1.156489572	-0.302493460	0.005663412

Coordinates of the optimized structure of CF_3Pc:

F	6.807340047	4.998335805	0.635144183
F	5.777431790	6.712081422	-0.215007575
F	2.889865887	8.284996129	4.237247277
F	3.867676962	2.171306568	7.605520370
F	6.792963783	6.902781768	1.697178866
F	3.439229581	4.097542647	6.697910108
F	5.460118167	3.634937833	7.373720097
F	2.519486824	6.521779758	5.458943552
F	1.025791465	7.174222338	4.024422988
F	7.897160377	1.374421274	2.165088031
F	8.574541335	1.845098052	4.183659529
F	7.800053335	-0.134070334	3.724597382
N	1.385442919	-0.231321545	1.298191619
N	-0.492879914	-1.897961446	-0.114341340
C	2.354565835	0.248036151	2.129449621
C	-0.844222638	-4.116101560	0.032117461
H	-1.259618841	-5.096393841	-0.142974643
C	2.295533345	2.767863776	1.593387104
C	0.382350222	-2.382057837	0.809885533
C	4.168403005	4.449105569	1.333304286
H	4.640728430	3.783506060	0.619386862
C	2.772265599	1.606516235	2.250892873
C	2.958962233	4.080111792	1.934505765
C	1.298921693	-1.564863852	1.506478880
C	2.366554303	4.960777349	2.844839973
H	1.419917679	4.700736590	3.307119348
C	-1.267768589	-2.904483244	-0.623033486
C	2.902884658	-0.858404874	2.909628271
H	3.676072463	-0.786271702	3.659226174
C	2.245602111	-1.985344289	2.516020322
H	2.387848957	-2.993176500	2.881212140
C	0.165250095	-3.793130815	0.905771641

H	0.706248143	-4.466156295	1.555358823
C	6.045310997	6.068976597	0.944367025
C	5.203909641	1.446660302	2.918591734
H	5.419542813	1.022973395	1.943662410
C	2.986792368	6.169006549	3.172838870
C	3.891290671	1.808960739	3.243358602
C	6.241263480	1.636987790	3.833822429
C	4.680966539	2.548230050	5.418131286
C	2.356842265	7.046290457	4.224215256
C	4.777329255	5.663422615	1.651840404
C	3.640642200	2.350219379	4.508842912
H	2.630143158	2.631921533	4.783014249
C	7.634235168	1.185593506	3.476106430
C	4.365760338	3.117994781	6.777959385
C	4.194676492	6.527868577	2.579685954
H	4.675054782	7.463493218	2.836867669
C	5.987928127	2.193823742	5.086879779
H	6.796416559	2.360510691	5.787486739
H	-0.648789320	-0.901833880	-0.435598038
F	-6.807340047	-4.998335805	-0.635144183
F	-5.777431790	-6.712081422	0.215007575
F	-2.889865887	-8.284996129	-4.237247277
F	-3.867676962	-2.171306568	-7.605520370
F	-6.792963783	-6.902781768	-1.697178866
F	-3.439229581	-4.097542647	-6.697910108
F	-5.460118167	-3.634937833	-7.373720097
F	-2.519486824	-6.521779758	-5.458943552
F	-1.025791465	-7.174222338	-4.024422988
F	-7.897160377	-1.374421274	-2.165088031
F	-8.574541335	-1.845098052	-4.183659529
F	-7.800053335	0.134070334	-3.724597382
N	-1.385442919	0.231321545	-1.298191619
N	0.492879914	1.897961446	0.114341340
C	-2.354565835	-0.248036151	-2.129449621
C	0.844222638	4.116101560	-0.032117461
H	1.259618841	5.096393841	0.142974643
C	-2.295533345	-2.767863776	-1.593387104
C	-0.382350222	2.382057837	-0.809885533

C	-4.168403005	-4.449105569	-1.333304286
H	-4.640728430	-3.783506060	-0.619386862
C	-2.772265599	-1.606516235	-2.250892873
C	-2.958962233	-4.080111792	-1.934505765
C	-1.298921693	1.564863852	-1.506478880
C	-2.366554303	-4.960777349	-2.844839973
H	-1.419917679	-4.700736590	-3.307119348
C	1.267768589	2.904483244	0.623033486
C	-2.902884658	0.858404874	-2.909628271
H	-3.676072463	0.786271702	-3.659226174
C	-2.245602111	1.985344289	-2.516020322
H	-2.387848957	2.993176500	-2.881212140
C	-0.165250095	3.793130815	-0.905771641
H	-0.706248143	4.466156295	-1.555358823
C	-6.045310997	-6.068976597	-0.944367025
C	-5.203909641	-1.446660302	-2.918591734
H	-5.419542813	-1.022973395	-1.943662410
C	-2.986792368	-6.169006549	-3.172838870
C	-3.891290671	-1.808960739	-3.243358602
C	-6.241263480	-1.636987790	-3.833822429
C	-4.680966539	-2.548230050	-5.418131286
C	-2.356842265	-7.046290457	-4.224215256
C	-4.777329255	-5.663422615	-1.651840404
C	-3.640642200	-2.350219379	-4.508842912
H	-2.630143158	-2.631921533	-4.783014249
C	-7.634235168	-1.185593506	-3.476106430
C	-4.365760338	-3.117994781	-6.777959385
C	-4.194676492	-6.527868577	-2.579685954
H	-4.675054782	-7.463493218	-2.836867669
C	-5.987928127	-2.193823742	-5.086879779
H	-6.796416559	-2.360510691	-5.787486739
H	0.648789320	0.901833880	0.435598038

Coordinates of the optimized structure of FPc:

F	-5.061082653	5.480898110	4.088678304
F	-3.964613439	2.049203389	7.110595918
F	0.810874629	4.713222977	7.017550894
F	-0.109223907	7.622961682	3.440303446
N	-0.745068321	-1.496512996	-0.926065620
N	-1.571882092	0.349676547	1.125940212
H	-0.584580996	0.607438362	0.844627570
C	-1.975723963	-1.536948149	-0.366672828
C	-2.379826719	-0.633667546	0.640505945
C	-0.686248862	-2.494195517	-1.854453043
C	-2.217797758	1.080251673	2.086129113
C	-3.629549285	-0.537583526	1.330163265
H	-4.483147028	-1.180468959	1.169100644
C	-3.534778354	0.510278244	2.213626587
H	-4.299226469	0.861235364	2.889149079
C	-1.691741898	2.192367155	2.797604855
C	-2.764174357	-2.600616645	-0.948494369
H	-3.783046941	-2.856369486	-0.691480251
C	-1.965339791	-3.198074407	-1.877327132
H	-2.218388351	-4.030180897	-2.516438774
C	-0.423712762	2.813126973	2.691844691
C	-2.671826366	2.764397966	3.793331622
C	-3.425932622	3.900486967	3.474122979
H	-3.311640554	4.404716874	2.522198847
C	-0.170812751	3.995272662	3.597263472
C	-4.339055191	4.387881672	4.402085085
C	-2.863590300	2.132199226	5.029272761
H	-2.304921129	1.244009457	5.300338758
C	-0.269297919	5.298382549	3.090975578
H	-0.540921359	5.482541153	2.058107299
C	-3.789133114	2.659645282	5.922669619
C	-4.545592791	3.790468911	5.639840254
H	-5.261859143	4.186461184	6.348696622
C	0.201764075	3.800156442	4.933022050
H	0.300895527	2.806093281	5.352170664
C	0.451715573	4.908574400	5.734004541
C	-0.009255032	6.373215997	3.933400543

C	0.354204933	6.213194225	5.265099173
H	0.553655666	7.063090618	5.905557773
F	5.061082653	-5.480898110	-4.088678304
F	3.964613439	-2.049203389	-7.110595918
F	-0.810874629	-4.713222977	-7.017550894
F	0.109223907	-7.622961682	-3.440303446
N	0.745068321	1.496512996	0.926065620
N	1.571882092	-0.349676547	-1.125940212
H	0.584580996	-0.607438362	-0.844627570
C	1.975723963	1.536948149	0.366672828
C	2.379826719	0.633667546	-0.640505945
C	0.686248862	2.494195517	1.854453043
C	2.217797758	-1.080251673	-2.086129113
C	3.629549285	0.537583526	-1.330163265
H	4.483147028	1.180468959	-1.169100644
C	3.534778354	-0.510278244	-2.213626587
H	4.299226469	-0.861235364	-2.889149079
C	1.691741898	-2.192367155	-2.797604855
C	2.764174357	2.600616645	0.948494369
H	3.783046941	2.856369486	0.691480251
C	1.965339791	3.198074407	1.877327132
H	2.218388351	4.030180897	2.516438774
C	0.423712762	-2.813126973	-2.691844691
C	2.671826366	-2.764397966	-3.793331622
C	3.425932622	-3.900486967	-3.474122979
H	3.311640554	-4.404716874	-2.522198847
C	0.170812751	-3.995272662	-3.597263472
C	4.339055191	-4.387881672	-4.402085085
C	2.863590300	-2.132199226	-5.029272761
H	2.304921129	-1.244009457	-5.300338758
C	0.269297919	-5.298382549	-3.090975578
H	0.540921359	-5.482541153	-2.058107299
C	3.789133114	-2.659645282	-5.922669619
C	4.545592791	-3.790468911	-5.639840254
H	5.261859143	-4.186461184	-6.348696622
C	-0.201764075	-3.800156442	-4.933022050
H	-0.300895527	-2.806093281	-5.352170664
C	-0.451715573	-4.908574400	-5.734004541

C	0.009255032	-6.373215997	-3.933400543
C	-0.354204933	-6.213194225	-5.265099173
H	-0.553655666	-7.063090618	-5.905557773

Coordinates of the optimized structure of CH_3Pc:

N	-0.786761636	-1.401304383	-1.034772635
N	-1.626966131	0.462745258	1.001038088
C	-2.061857049	-1.338076851	-0.588324623
C	-0.734794874	-2.372653791	-1.992196500
C	-2.289361175	1.227630039	1.923567820
C	-0.411194170	2.773191046	2.744061119
C	-0.130882138	3.899390269	3.710325276
C	0.070131008	3.641619214	5.070603520
H	-0.001626442	2.619845692	5.432787008
C	-2.066847905	-2.947252159	-2.154711802
H	-2.334376717	-3.730373976	-2.847455759
C	-2.888625929	-2.302980869	-1.277515404
H	-3.946668525	-2.465533045	-1.122184032
C	-1.734832806	2.268434099	2.719032374
C	-2.472441602	-0.427025108	0.410229530
C	-0.015385590	5.215490134	3.246605147
H	-0.150974887	5.417233960	2.187174328
C	-3.766529467	-0.230273340	0.986321462
H	-4.656766967	-0.785077503	0.725686162
C	-3.659038401	0.782053392	1.909938124
H	-4.446265840	1.189607051	2.524685134
C	-2.746030071	2.896516597	3.647021844
C	0.370515560	4.673186522	5.967098229
C	0.475034553	5.978611539	5.474090086
H	0.717910971	6.787436368	6.160488701
C	0.282270474	6.268710158	4.118748007
C	-3.339913727	4.123512079	3.336923230
H	-3.047282122	4.639774133	2.426954981
C	-3.144136592	2.226805847	4.812061730
H	-2.697700794	1.264339224	5.048179375
C	0.559338431	4.383982699	7.438031273
H	1.211140263	5.123924827	7.912017187

H	0.996672756	3.393944111	7.598880942
H	-0.399765976	4.405141634	7.970639178
C	0.375431121	7.688590615	3.609606536
H	1.050578233	8.291260265	4.224512928
H	-0.604929528	8.181340096	3.625404382
H	0.736833985	7.721140995	2.577358156
C	-4.307218967	4.692990594	4.174047713
C	-4.106119515	2.770850166	5.668927170
C	-4.679257788	4.003293391	5.332154641
H	-5.436676355	4.432732471	5.985155450
C	-4.919233633	6.032855858	3.837676840
H	-5.084315672	6.139517406	2.760906566
H	-4.261851384	6.855112793	4.146570507
H	-5.878965663	6.173771314	4.343088119
C	-4.506011999	2.055705591	6.938683269
H	-3.961744208	2.451411389	7.805336429
H	-4.290512079	0.984975944	6.880183042
H	-5.573873336	2.175809787	7.147112799
H	-0.599386163	0.638394649	0.814309307
N	0.786761636	1.401304383	1.034772635
N	1.626966131	-0.462745258	-1.001038088
C	2.061857049	1.338076851	0.588324623
C	0.734794874	2.372653791	1.992196500
C	2.289361175	-1.227630039	-1.923567820
C	0.411194170	-2.773191046	-2.744061119
C	0.130882138	-3.899390269	-3.710325276
C	-0.070131008	-3.641619214	-5.070603520
H	0.001626442	-2.619845692	-5.432787008
C	2.066847905	2.947252159	2.154711802
H	2.334376717	3.730373976	2.847455759
C	2.888625929	2.302980869	1.277515404
H	3.946668525	2.465533045	1.122184032
C	1.734832806	-2.268434099	-2.719032374
C	2.472441602	0.427025108	-0.410229530
C	0.015385590	-5.215490134	-3.246605147
H	0.150974887	-5.417233960	-2.187174328
C	3.766529467	0.230273340	-0.986321462
H	4.656766967	0.785077503	-0.725686162

C	3.659038401	-0.782053392	-1.909938124
H	4.446265840	-1.189607051	-2.524685134
C	2.746030071	-2.896516597	-3.647021844
C	-0.370515560	-4.673186522	-5.967098229
C	-0.475034553	-5.978611539	-5.474090086
H	-0.717910971	-6.787436368	-6.160488701
C	-0.282270474	-6.268710158	-4.118748007
C	3.339913727	-4.123512079	-3.336923230
H	3.047282122	-4.639774133	-2.426954981
C	3.144136592	-2.226805847	-4.812061730
H	2.697700794	-1.264339224	-5.048179375
C	-0.559338431	-4.383982699	-7.438031273
H	-1.211140263	-5.123924827	-7.912017187
H	-0.996672756	-3.393944111	-7.598880942
H	0.399765976	-4.405141634	-7.970639178
C	-0.375431121	-7.688590615	-3.609606536
H	-1.050578233	-8.291260265	-4.224512928
H	0.604929528	-8.181340096	-3.625404382
H	-0.736833985	-7.721140995	-2.577358156
C	4.307218967	-4.692990594	-4.174047713
C	4.106119515	-2.770850166	-5.668927170
C	4.679257788	-4.003293391	-5.332154641
H	5.436676355	-4.432732471	-5.985155450
C	4.919233633	-6.032855858	-3.837676840
H	5.084315672	-6.139517406	-2.760906566
H	4.261851384	-6.855112793	-4.146570507
H	5.878965663	-6.173771314	-4.343088119
C	4.506011999	-2.055705591	-6.938683269
H	3.961744208	-2.451411389	-7.805336429
H	4.290512079	-0.984975944	-6.880183042
H	5.573873336	-2.175809787	-7.147112799
H	0.599386163	-0.638394649	-0.814309307

Coordinates of the optimized structure of $PhCF_3Pc$:

N	3.700135116	1.271297222	0.103274385
N	3.732791882	-1.312448569	-0.098199840
H	3.430253946	-0.301530377	-0.013345106
N	0.851615620	-1.267948038	-0.103359166
N	0.819590797	1.319293212	0.110222600
H	1.121366544	0.308929315	0.020743496
C	-5.494779118	2.570683062	0.263611619
H	-6.477823279	3.021690946	0.309627846
C	-0.511790840	1.630030919	0.151660629
C	6.132100987	0.705847016	0.063122089
C	-5.644811134	2.026504638	2.724025896
C	2.972056470	-2.434737818	-0.221354939
C	-5.378971958	-3.079675390	2.198590603
C	-1.572767760	-0.698378483	-0.067014044
C	-0.469659500	-1.599621071	-0.150672025
C	5.148222858	3.045854354	0.321235884
H	6.074522004	3.593818930	0.400335987
C	2.994671309	2.416957722	0.231388054
C	-0.593772603	-3.043388277	-0.314798931
H	-1.517489084	-3.597128362	-0.390827368
C	0.673073074	-3.547607426	-0.358428313
H	0.967906745	-4.581768654	-0.473183246
C	5.066537232	-1.621047495	-0.137414344
C	-2.945218669	1.374850860	0.140316153
C	5.024838547	1.599941017	0.148396047
C	5.146944160	-3.051877217	-0.298049710
H	6.064878225	-3.613947208	-0.369595055
C	6.151322610	-0.708181878	-0.056731993
C	-3.491677682	-1.957421818	0.995529379
H	-2.950581959	-1.943230681	1.935546885
C	3.866610987	-3.545400445	-0.346196149
H	3.567786103	-4.577560076	-0.461608195
C	8.010534644	-2.050275338	1.004104474
H	7.444247359	-2.041281172	1.930988711
C	1.560140580	-2.414328071	-0.224764766
C	-4.753961942	-2.549700707	0.934111861
C	9.454527645	-2.088945855	-1.377461841

H	10.009892712	-2.105190220	-2.310742825
C	0.689651694	3.551204244	0.357446068
H	0.987927637	4.583708359	0.470685646
C	-4.920919518	2.009676563	1.402358118
C	-0.593243347	3.057933640	0.310259820
H	-1.508679484	3.624931657	0.381179014
C	3.883729273	3.550415960	0.369433172
H	3.588601893	4.583642249	0.492000122
C	1.582287955	2.441686873	0.232115610
C	-2.920491872	-1.375081438	-0.142237475
C	-1.592168366	0.710262339	0.066287296
C	8.230679894	-1.422792683	-1.313685002
H	7.837937346	-0.924503637	-2.194599363
C	-4.783036765	2.542587914	-0.936046533
C	7.471623656	1.400071389	0.120670739
C	7.496014811	-1.390485634	-0.120799770
C	-3.628942239	-1.427544700	-1.346131564
H	-3.198577660	-0.991303962	-2.241463236
C	-3.655760116	1.420356828	1.343449603
H	-3.225024785	0.982852843	2.237924453
C	-5.463766738	-2.584941049	-0.266598933
H	-6.444110190	-3.041690872	-0.313098543
C	9.236242717	-2.714483143	0.942248051
H	9.621461688	-3.217106309	1.824763845
C	8.209036280	1.444587520	1.311297312
H	7.821009125	0.950730572	2.196887462
C	9.201930600	2.726480369	-0.955464412
H	9.581941249	3.225664592	-1.842209871
C	-3.517286956	1.957600653	-0.996845909
H	-2.975244598	1.947718591	-1.936376201
C	-5.408898201	3.072402335	-2.200276201
C	7.980217921	2.054437841	-1.009969690
H	7.411080328	2.037065296	-1.934974325
C	9.428805820	2.119060893	1.368058362
H	9.985769955	2.145600629	2.300190581
C	9.930292600	2.760451966	0.234338341
H	10.880232385	3.284906694	0.278768827
C	9.962212095	-2.735271384	-0.249236852

H	10.915440611	-3.253192779	-0.299224127
C	-5.613758536	-2.043746487	-2.727721067
C	-4.890834611	-2.023953480	-1.405726400
F	-5.715953300	0.786698516	3.257005199
F	-5.002132133	2.803063006	3.626356536
F	-6.903631573	2.496849791	2.610657307
F	-4.490514716	3.657389146	-3.001109925
F	-6.369061955	3.986014827	-1.943853163
F	-5.981682248	2.079810022	-2.917061100
F	-4.459587888	-3.659228122	3.001998975
F	-5.956738844	-2.087694091	2.912838302
F	-6.335494655	-3.997433769	1.943179668
F	-4.955637466	-2.798657208	-3.637047250
F	-5.709738430	-0.800405863	-3.249500000
F	-6.863203120	-2.539648589	-2.619523576

References

1. Bruker AXS, *SAINT*, Bruker AXS Inc., Madison, WI, USA. 2017.

2. Bruker AXS, *SADABS*, Bruker AXS Inc., Madison, WI, USA. 2016.

3. a) G. M. Sheldrich, *Acta Cryst.* 2015, **A71**, 3–8; b) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.

4. 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, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.