Electronic Supplementary Information

Design and Synthesis of *β*-Multi-Substituted Push-Pull Porphyrins

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1. General Procedures

^{1}H NMR spectra were recorded on Varian 300MHz or 400MHz spectrometers with TMS as an internal standard (negative for upfield). ^{19}F NMR spectra were recorded on a Varian 300MHz spectrometer. MALDI-MS and MALDI-HRMS were recorded on a Bruker APEX$_{III}$ FTICRMS mass spectrometer. UV-vis spectra were recorded on a Varian Cary 100 spectrometer. Elemental analyses were obtained on a Perkin-Elmer 2400 Series II Elemental Analyzer. Cyclic voltammetry measurements were carried out in a 0.1 M Bu$_4$NPF$_6$ solution in CH$_2$Cl$_2$ at room temperature using a scan rate of 100 mV s^{-1} under nitrogen on a CHI610D Instrument, with a platinum-carbon working electrode, a saturated calomel electrode, and a platinum wire as the auxiliary electrode. Column chromatography was performed using silica gel (mesh 300-400).

2. Experimental Procedures

Preparation of 7,8-dibromo-17,18-dihydroxy-5,10,15,20-tetraphenylchlorin (6)

7,8-dihydroxy-5,10,15,20-tetraphenylchlorin (**5**) (100 mg, 0.15 mmol), NBS (61 mg, 0.31 mmol) was added to a 100 mL flask. The flask was then evacuated and backfilled with nitrogen (three cycles). CH_2Cl_2 (20 mL) was added with a syringe. The resulting solution was stirred for 4 hours in an ice-water bath under nitrogen. Et_3N (1 mL) was added and then quickly filtered through a short silica plug (300-400 mesh, eluting with CH_2Cl_2). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, PE-CH_2Cl_2 as eluent) to yield products **6** (118 mg, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.57 (d, J = 4.7 Hz, 2 H, β-H), 8.22 (d , J = 4.7 Hz, 2 H, β-H), 8.19-7.65 (m, 20 H, Ph-H), 6.35 (s, 2 H, β-H, OH), 3.02 (s, 2 H), -1.72 (s, 2 H, NH); UV–vis (CH_2Cl_2) λ_{max} (relative intensity) 408(0.84), 516(0.07), 545(0.07), 592 (0.03), 644(0.13) nm; HRMS (MALDI) calc'd for $C_{44}H_{31}N_4O_2Br_2$ $[M+H]^+$ 805.0809, found 805.0808.

Preparation of 7,8-dibromo-17,18-dimethoxy-5,10,15,20-tetraphenylchlorin (7)

6 (95 mg, 0.12 mmol) was added to a 100 mL flask. The flask was then evacuated and backfilled with nitrogen (three cycles). THF (20 mL) was added with a syringe. NaH (35 mg, 1.2 mmol) was added in several portions. The reaction mixture was stirred for 30 min. Then 183 μL CH_3I was added with a syringe. The resulting solution continued to be stirred for 3h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were quickly filtered through a short silica plug (300-400 mesh, eluting with CH_2Cl_2). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, PE-CH_2Cl_2 as eluent) to yield the products **7** (87 mg, 88% yield) ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.56 (d, J = 5.7 Hz, 2 H, β-H), 8.19 -7.61 (m, 22 H, β-,Ph-H), 6.00 (s, 2 H, β-H, OH), 2.98 (s, 6 H, OCH_3), -1.81 (s, 2 H, NH); UV– vis (CH_2Cl_2) $\lambda_{max}(\varepsilon)$ 426 (8.7×10^4), 528 (9.4×10^3), 594 (6.9×10^3), 644 (7.2×10^3) nm; HRMS (MALDI) calc'd for $C_{46}H_{35}Br_2N_4O_2$ $[M+H]^+$ 833.1097, found 833.1121.

Preparation of 7,8-dibromo-17,18-dimethoxy-5,10,15,20-tetraphenylporphyrin (1)

7 (28 mg , 0.12 mmol), DDQ (30 mg, 0.13 mmol), and 10 ml $CHCl_3$ was added to a 50 mL flask. The resulting solution was stirred and heated under reflux for 10 h. The reaction mixture was quickly filtered through a short silica plug (300-400 mesh, eluting with CH_2Cl_2). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, PE-CH_2Cl_2 as eluent) to yield the products **1** (28 mg, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.78 (d, J = 4.6 Hz , 2 H , β-H), 8.63 (d, J = 4.6 Hz, 2 H, β-H), 8.18 (d, J = 6.4 Hz, 8 H, o-Ph-H), 7.80-7.75 (m, 12 H, m,p-Ph-H), 3.76 (s, 6 H, OCH_3), -2.97 (s, 2 H, NH). UV–vis (CH_2Cl_2) λ_{max} (ε) 425 (6.8×10^5), 524 (7.0×10^4), 596 (3.3×10^4), 663 (3.3×10^4) nm; HRMS (MALDI) calc'd for $C_{46}H_{33}Br_2N_4O_2$ $[M+H]^+$ 831.0967, found 831.0965.

Preparation of Nickel (II) 7,8-dibromo-17,18-dimethoxy-5,10,15,20-tetraphenylporphyrin (8)

yield 100%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.65 (d, J = 5.1 Hz, 2 H , $β$-H), 8.53 (d, J = 5.0 Hz, 2 H , $β$-H), 7.90-7.84 (m, 8 H, o-Ph-H), 7.65-7.62 (m, 12 H, m,p-Ph-H), 3.71 (s, 6 H, OCH$_3$); HRMS (MALDI) calc'd for C$_{46}$H$_{30}$Br$_2$N$_4$O$_2$Ni [M]$^+$ 886.0079, found 886.0084.

Preparation of Copper(Ⅱ) 7,8-dibromo-17, 18-dimethoxyl-5, 10, 15, 20-tetraphenylporphyrin (9)

1 (37 mg , 0.044 mmol), copper acetate tetrahydrate (5 mg, 0.44 mmol), and 10 ml DMF was added to a 50 mL flask. The resulting solution was stirred and heated under reflux for 1 h. To the cooled reaction mixture, CH$_2$Cl$_2$ (20 mL) and H$_2$O (20 mL) were added. The organic layer was washed with water and then quickly filtered through a short silica plug (300-400 mesh, eluting with CH$_2$Cl$_2$). The filtrate was concentrate to give the products **9** (39 mg, 100% yield). UV–vis (CH$_2$Cl$_2$): λ$_{max}$ (ε) 421 (1.4×10^5), 522 (4.8×10^3), 545 (1.1×10^4), 594 (3.4×10^3), 662 (2.6×10^3) nm HRMS (MALDI) calc'd for C$_{46}$H$_{30}$N$_4$O$_2$Br$_2$Cu [M]$^+$ 891.0032, found 891.0026.

Preparation of Copper(Ⅱ) 7,8-dimethoxy-17,18-ditrifluoromethyl-5,10,15,20-tetraphenylporphyrin (10)

9 (22 mg , 0.025 mmol), Pd$_2$(dba)$_3$ (2 mg, 0.002 mmol), and CuI (47 mg, 0.25 mmol) was added to a 50 mL flask. The flask was then evacuated and backfilled with nitrogen (three cycles). DMF (20 mL) and FSO$_2$CF$_2$COOMe (31 μl, 0.25 mmol) were added with a syringe. The resulting solution was stirred and heated under 100 ℃ for 10 h. To the cooled reaction mixture, CH$_2$Cl$_2$ (40 mL) and H$_2$O (40 mL) were added. The organic layer was washed with water and then quickly filtered through a short silica plug (300-400 mesh, eluting with CH$_2$Cl$_2$). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, PE- CH$_2$Cl$_2$ as eluent) to yield the products **10** (21 mg, 98% yield). HRMS (MALDI) calc'd for C$_{48}$H$_{30}$N$_4$O$_2$F$_2$Cu [M]$^+$ 871.1554, found 871.1564.

Preparation of 7,8-dimethoxy-17,18-ditrifluoromethyl-5,10,15,20-tetraphenylporphyrin (2)

10 (21 mg , 0.024 mmol) and CH$_2$Cl$_2$ (10 mL) was added to a 50 mL flask. Then the admixed acids (H$_2$SO$_4$:CF$_3$COOH = 4:1, 2 mL) was slowly added in the solution. The reaction was monitored by TLC. The reaction was quenched with water when **10** disappeared. The aqueous layer was extracted with CH$_2$Cl$_2$. The organic layer was washed with water and then quickly filtered through a short silica plug (300-400 mesh, eluting with CH$_2$Cl$_2$). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, PE-CH$_2$Cl$_2$ as eluent) to yield the products **2** (10 mg, 51% yield). ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 8.61 (d, J = 4.6 Hz, 2 H, $β$-H), 8.32 (d, J = 4.6 Hz, 2 H, $β$-H), 8.22 (d, J = 6.8 Hz, 4 H, o-Ph-H), 8.15 (d, J = 6.9 Hz, 4 H, o-Ph-H), 7.77-7.69 (m, 12 H, m,p-Ph-H), 3.67 (s, 6 H, OCH$_3$), -1.44 (s, 2 H, NH); ^{19}F NMR (282 MHz, CDCl$_3$) δ -48.9 (s, 6 F, CF$_3$); UV–vis (CH$_2$Cl$_2$): λ$_{max}$ (ε) 446 (3.4×10^5), 551 (3.5×10^4), 718 (4.1×10^4) nm; HRMS (MALDI) calc'd for C$_{48}$H$_{33}$N$_4$O$_2$ F$_6$[M+H]$^+$ 811.2502, found 811.2525.

Preparation of Nickel (Ⅱ) 7,8-dimethoxy-17-(4'-chlorooctofluorobutyl)-5,10,15,20–tetraphenylporphyrin (11)

8 (50 mg , 0.056 mmol), $Pd_2(dba)_3$ (5 mg, 0.005 mmol), and Cu (71 mg, 1.125 mmol) was added to a 50 mL flask. The flask was then evacuated and backfilled with nitrogen (three cycles). DMF (20 mL) and ClF_8C_4I (203 mg, 0.56 mmol) were added with a syringe. The resulting solution was stirred and heated under 100 $^{\circ}$C for 0.5 h. To the cooled reaction mixture, CH_2Cl_2 (40 mL) and H_2O (40 mL) were added. The organic layer was washed with water and then quickly filtered through a short silica plug (300-400 mesh, eluting with CH_2Cl_2). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, $PE-CH_2Cl_2$ as eluent) to yield the products **11** (40 mg, 74 % yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 9.02 (s, 1 H, β-H), 8.66-8.58 (m, 3 H, β-H), 8.49 (d, 1 H, β-H), 8.06-7.53 (m, 20 H, Ph-H), 3.75 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ -68.3 (m, 2 F, CF_2Cl), -97.5 (m, 2 F), -117.3 (m, 2 F), -119.5 (m, 2 F); HRMS (MALDI) calc'd for $C_{50}H_{31}N_4O_2F_8ClNi$ $[M]^+$ 964.1344, found 964.1356.

Preparation of Nickel (Ⅱ) 7,8-dimethoxy-17,18-tetrafluorobenzo-5,10,15,20–tetraphenylporphyrin (12)

11 (90 mg, 0.093mmol), $Na_2S_2O_4$ (162 mg, 0.93 mmol), and K_2CO_3 (129 mg, 0.93 mmol) was added to a 50 mL flask. The flask was then evacuated and backfilled with nitrogen (three cycles). DMF (15 mL) was added with a syringe. The resulting solution was stirred and heated under 100 $^{\circ}$C for 2 h. To the cooled reaction mixture, CH_2Cl_2 (30 mL) and H_2O (30 mL) were added. The organic layer was washed with water and then quickly filtered through a short silica plug (300-400 mesh, eluting with CH_2Cl_2). The filtrate was purified by flash chromatography (silica gel, 300-400 mesh, $PE-CH_2Cl_2$ as eluent) to yield the products **12** (67 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.52 (d, $J = 5.2$ Hz, 2 H, β-H), 8.38 (d, $J = 5.2$ Hz, 2 H, β-H), 8.08-7.97 (m, 8 H, o-Ph-H), 7.75-7.63 (m, 12 H, m,p-Ph-H), 3.64 (s, 6 H, OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ -131.3 (m, 2 F), -157.7 (m, 2 F); HRMS (MALDI) calc'd for $C_{50}H_{30}N_4O_2F_4Ni$ $[M]^+$ 852.1640, found 852.1653.

Preparation of 7,8-dimethoxy-17,18-tetrafluorobenzo-5,10,15,20–tetraphenylporphyrin (3)

12 (40 mg, 0.047 mmol) was dissolved in a 50 mL flask. A mixture of H_2SO_4 and CF_3COOH (2 mL, 4:1) was dropped into the flask slowly. The product was obtained in 40% yield (15 mg). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.73 (d , $J = 4.8$ Hz, 2 H , β-H), 8.51 (d , $J = 4.8$ Hz , 2 H, β-H), 8.35-8.23 (m, 8 H, o-Ph-H), 7.81-7.74 (m, 12 H, m,p-Ph-H), 3.70 (s, 6 H, OCH_3), -2.45 (s, 2 H, NH); ^{19}F NMR (282 MHz, $CDCl_3$) δ -132.2 (m, 2 F), -157.3 (m, 2 F); UV– vis (CH_2Cl_2): λ_{max} (ε) 431 (1.8×10^5), 527 (1.3×10^4), 561 (3.1×10^3), 607 (3.1×10^3), 669 (4.8×10^3) nm; HRMS (MALDI) calc'd for $C_{50}H_{33}N_4O_2F_4$ $[M+H]^+$ 797.2517, found 797.2534.

3. Figure S1 ^{1}H NMR of porphyrin **1** and **3** at 0 °C, -33 °C, and -60 °C.
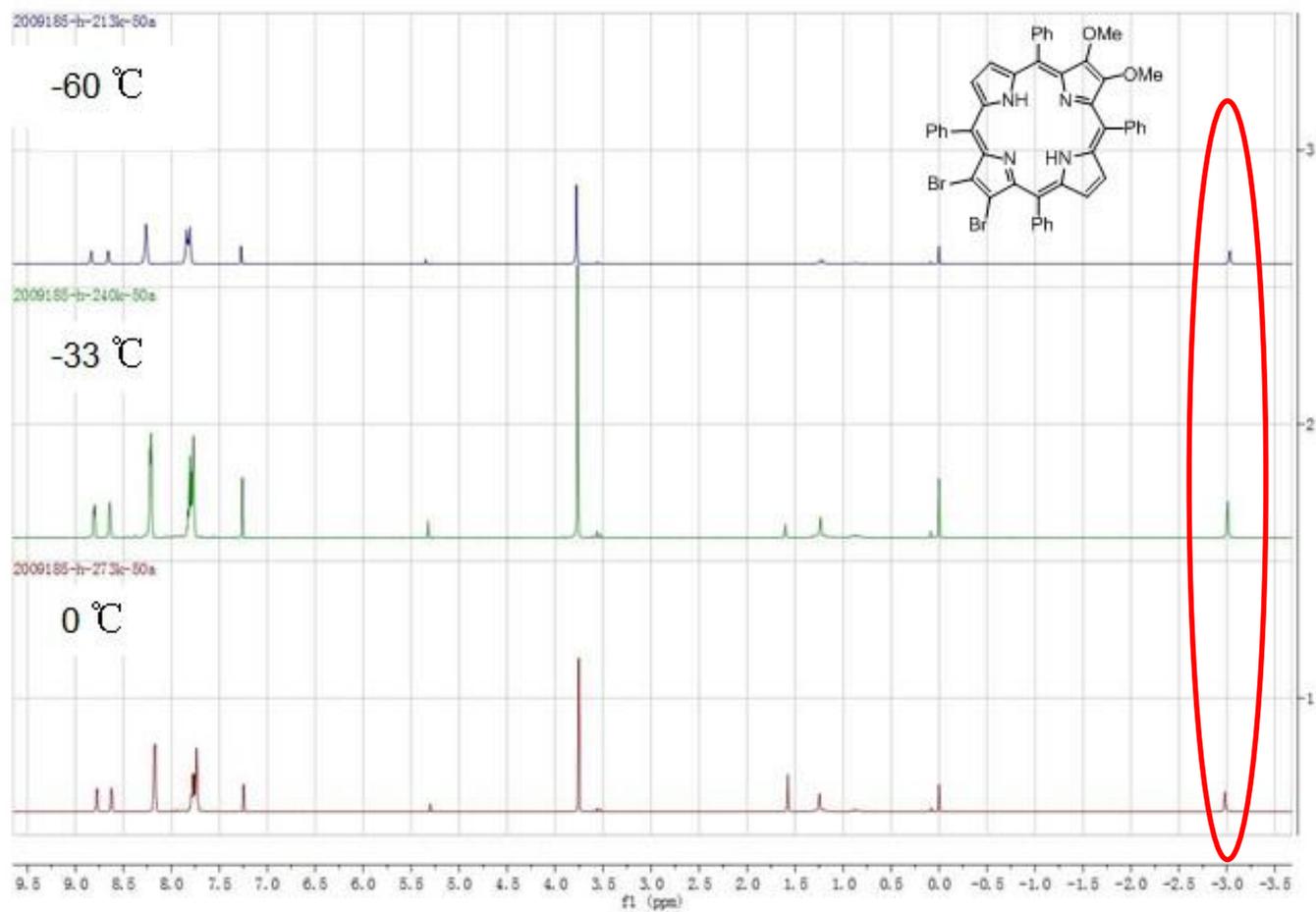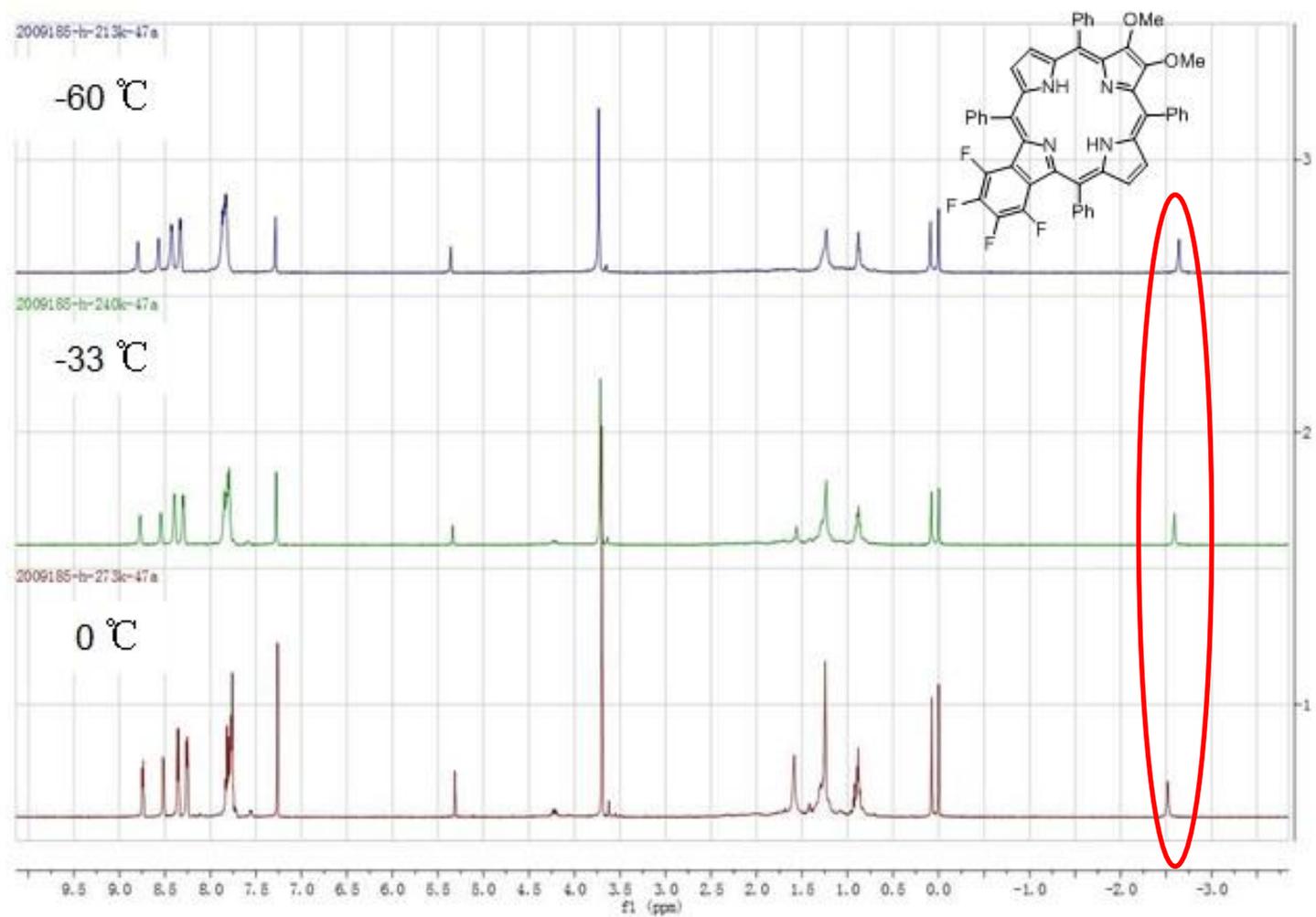
4. Figure S2. UV/Vis absorption spectra of the porphyrins **TPP**, **1**, **2** and **3** measured in dichloromethane.
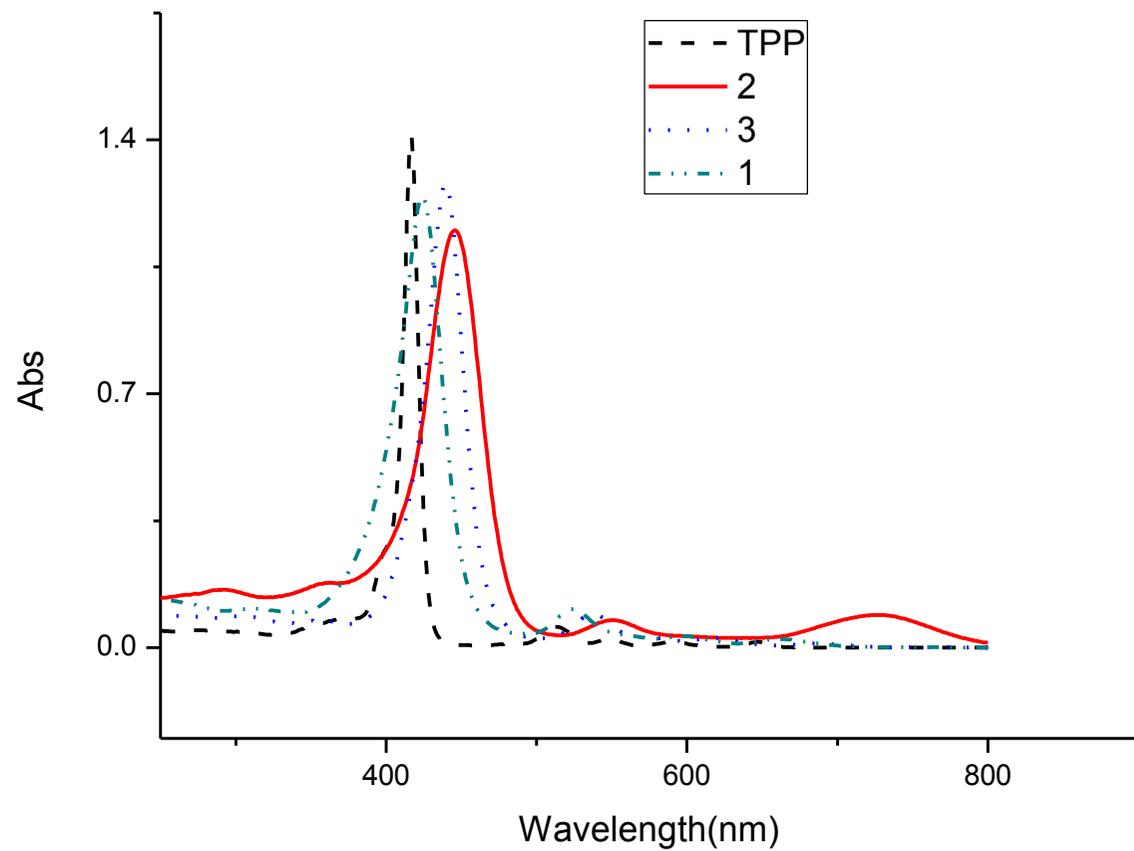
5. Figure S3 Cyclic voltammograms of porphyrins **1, 2** and **3** in CH_2Cl_2 with 0.1 M Bu_4NPF_6 at 25 ^oC
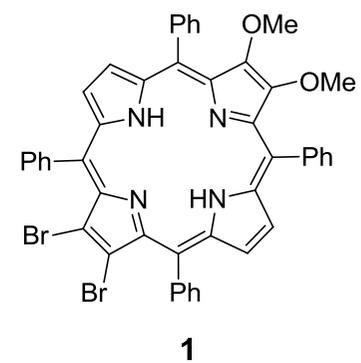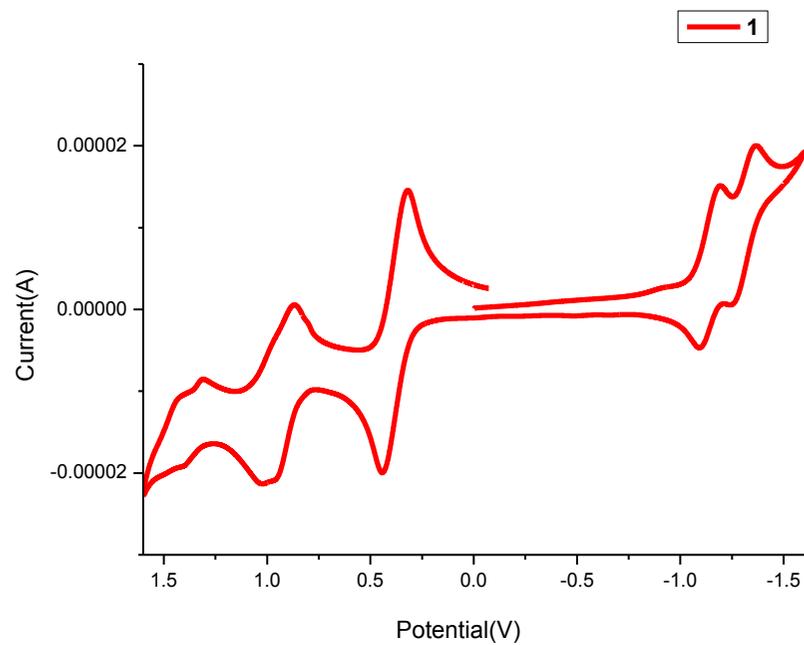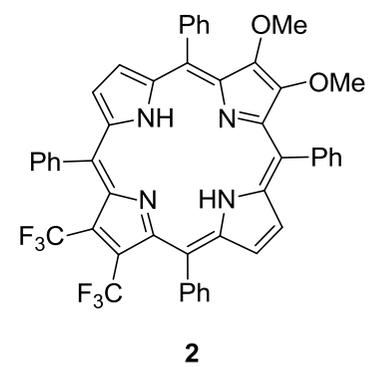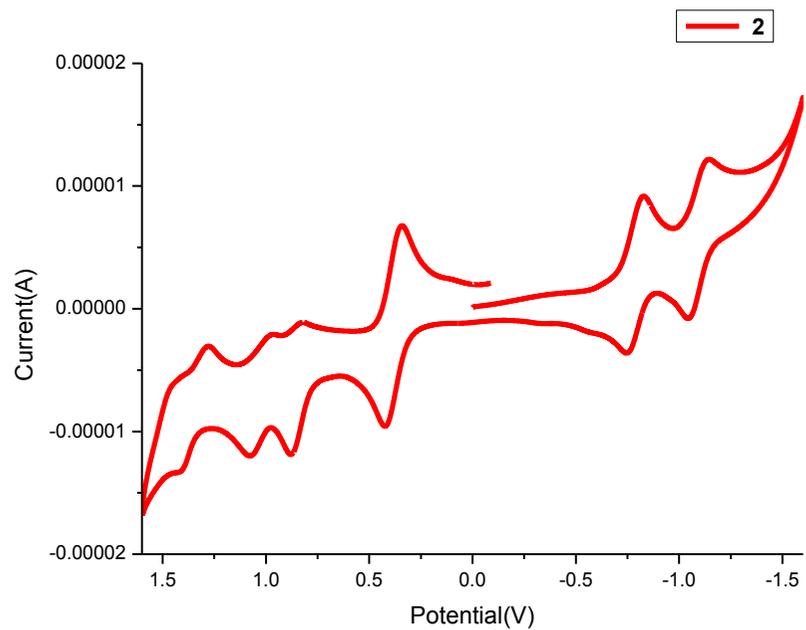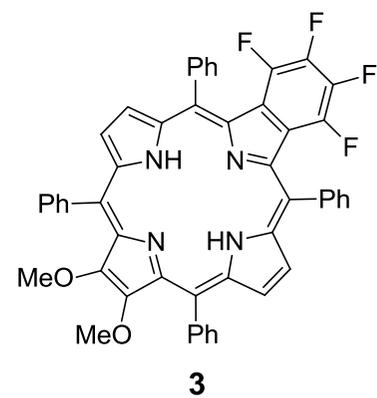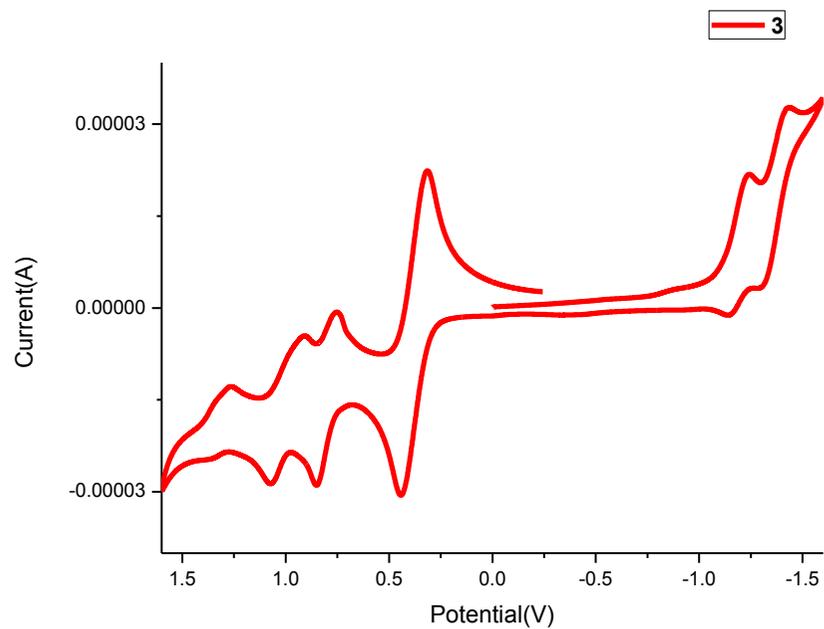
6. NMR spectra for target compounds **1**, **2** and **3**

8.619
8.603
8.327
8.309
8.228
8.215
8.156
8.149
8.136
7.774
7.762
7.734
7.722
7.260

3.665

1.280

0.024

2.002 3.998 1.89 5.83

0   8   6   4   2   0

S13

-48.904

0   -50   -100   -150   PPM

S14

S15

-132.162
-132.184
-132.216
-132.233

-157.253
-157.269
-157.301
-157.323

-120   -130   -140   -150   -160   -170   PPM
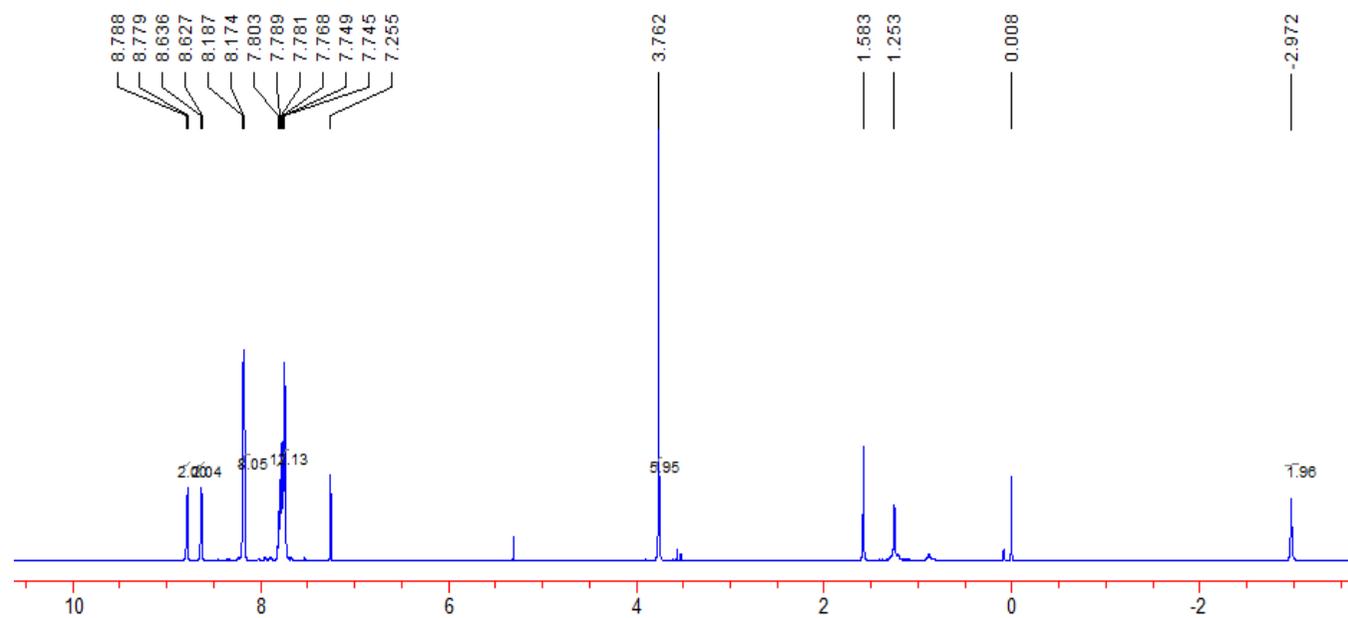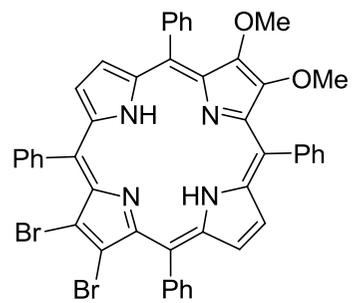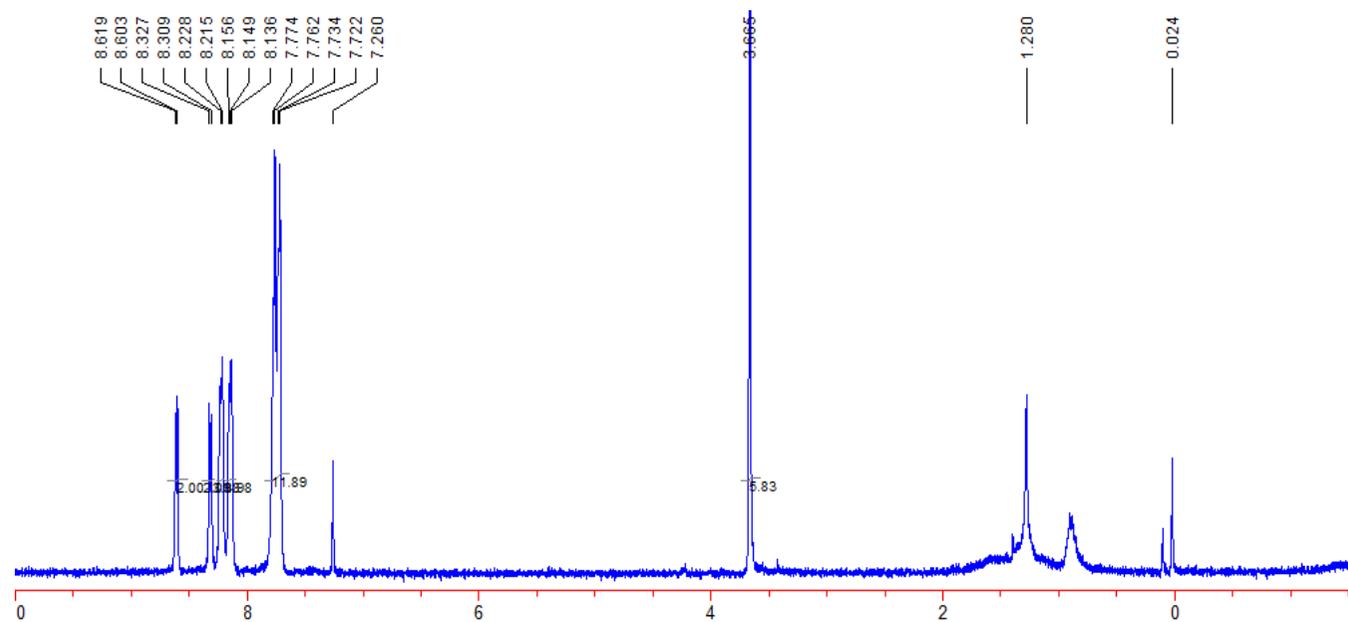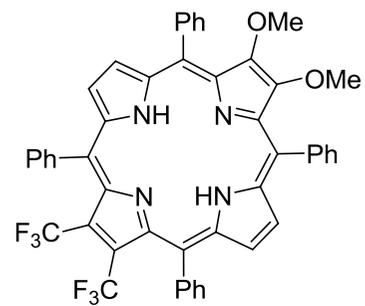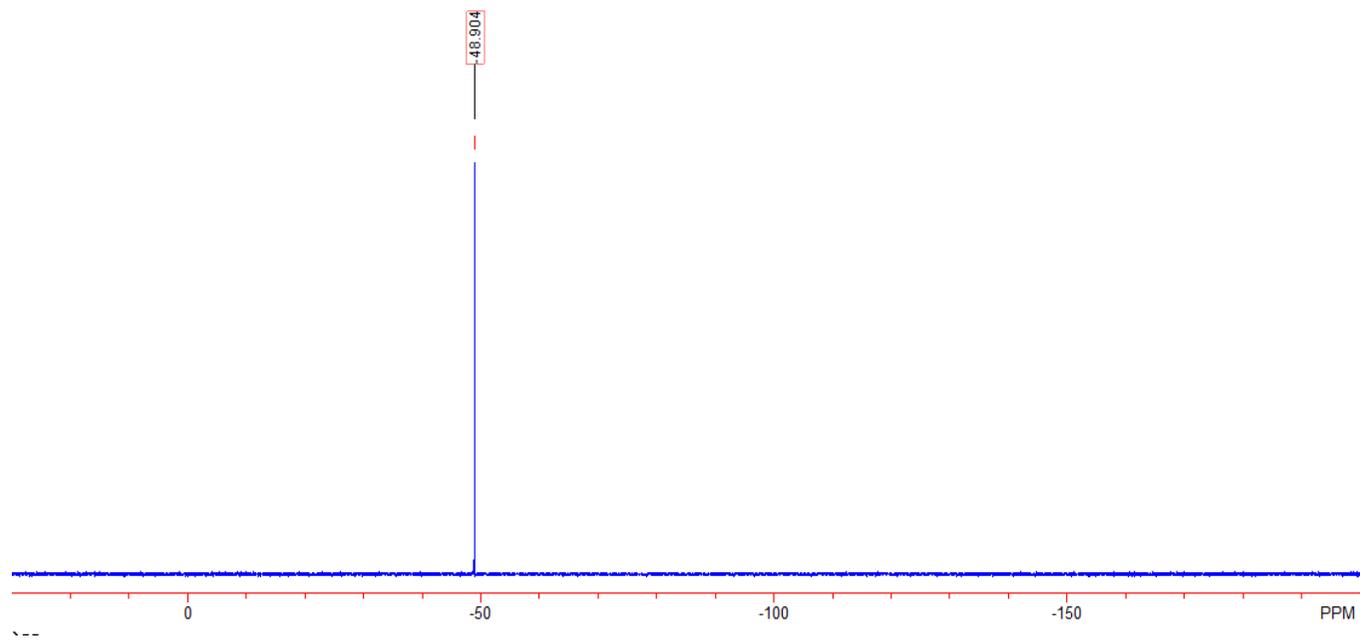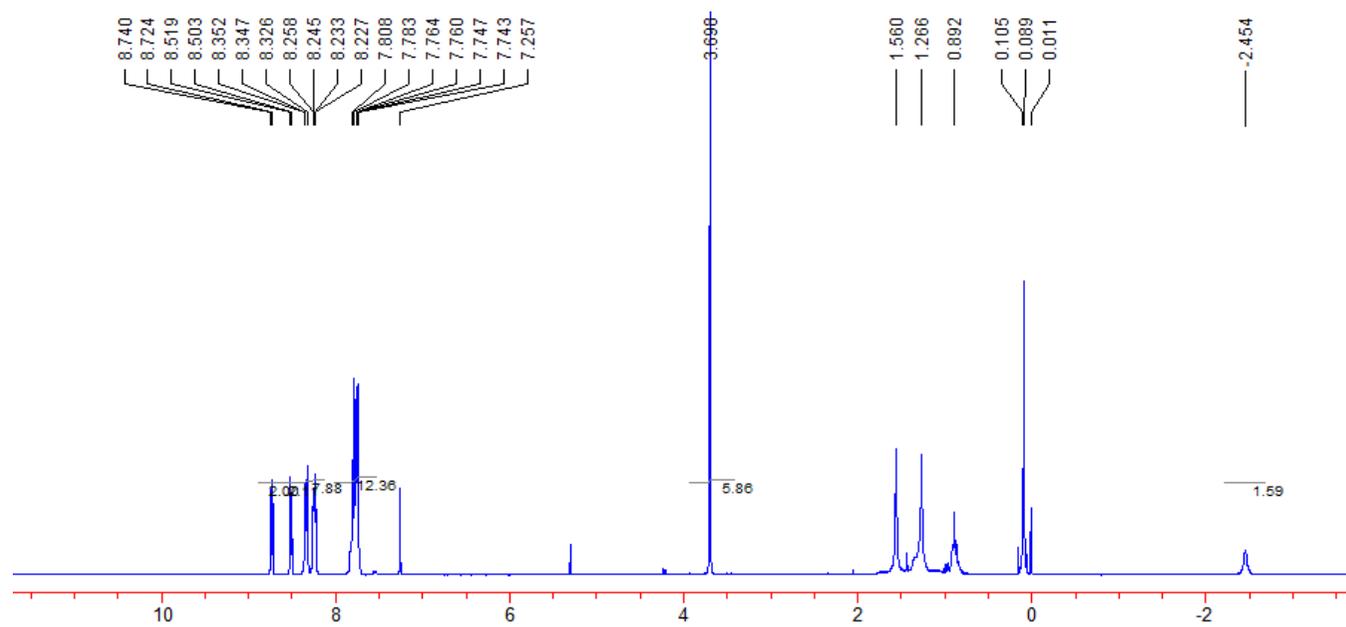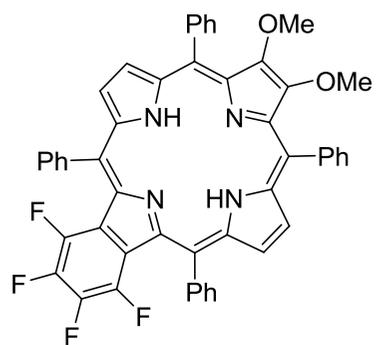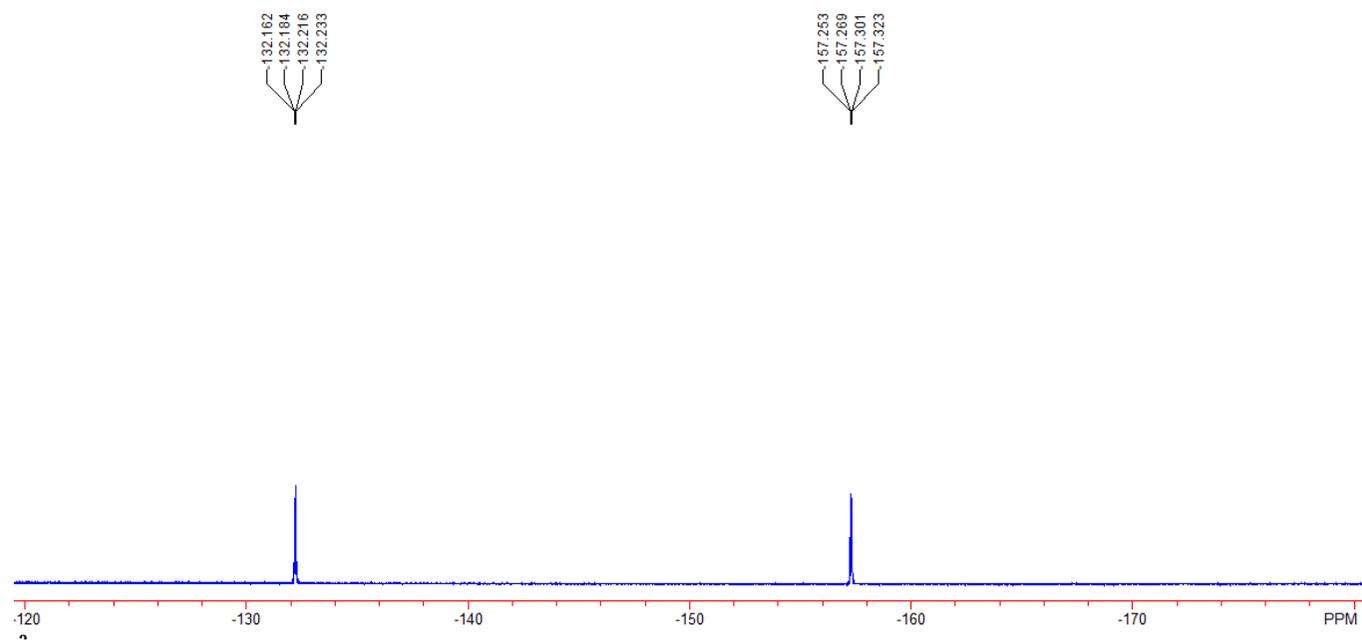
7. Geometry for target compounds **1, 2** and **3** by using the density functional theory (DFT) with the B3LYP/6-31G(d) basic set implemented in the Gaussian 09 program package