Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Molecular Engineering for Efficient and Selective Iron Porphyrin Catalysts for Electrochemical Reduction of CO_2 to CO

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Experimental Section:

Materials.

Dimethylformamide (anhydrous 99.8%) and deionized water used in electrochemical measurements were purchased from Sigma Aldrich. All of the chemicals used in synthesis were purchased from Acros Organics, Alfa Aesar, or Sigma Aldrich and used without further purification. Synthesized porphyrins were characterized by UV-Vis spectroscopy, ATR-FTIR, NMR spectroscopy, Elemental analysis, and HRMS. Analytical TLC was performed on silica-gel plates (Merck) and flash chromatography was performed on silica gel (40-63 μm, Merck). ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer in $CDCl_3$ (δ = 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ = 77.0 ppm). Chemical shifts and Coupling constants (*J*) are reported in ppm and Hz respectively. HRMS measurements were performed on a Finnigan LCQ Advantage MAX mass spectrometer. UV-Vis absorption spectra of synthesized porphyrins were recorded on a Lambda 750 UV-Vis spectrophotometer in CH_2Cl_2 as solvent. Fourier transform infrared (FT-IR) spectra were measured with a Nicolet™ iS™10 FT-IR Spectrometer, with an attenuated total reflection (ATR) system equipped with a diamond glass.

Cyclic Voltammetry.

The CV measurements were performed on Autolab potential station with a GPES electrochemical interface 4.9 (Eco Chemie) in dry DMF containing 1 mM of catalyst and 0.1 M recrystallized tetrabutylammoniunhexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. The cell assembly consists of a glassy carbon (diameter 3mm) as a working electrode, $Ag/AgNO_3$ (0.01 M in CH_3CN) as a reference electrode, and platinum wire as a counter electrode, respectively. A ferrocene/ferrocenium redox couple was used as an internal reference. The cyclovoltammetric scan rates was fixed at 100 mV/s. The electrolysis solution was purged with argon or CO_2 for 10 minutes, prior to measurement. All potentials reported herein are converted to their corresponding values versus NHE using an internal reference of ferrocene/ferrocenium (0.71 V vs. NHE in DMF).

Electrolysis.

Electrolysis were performed on Autolab potential station with a GPES electrochemical interface 4.9 (Eco Chemie). The experiments were carried out in H cell (Figure S1) with a glassy carbon (area 1 cm^2) as working electrode, $Ag/AgNO_3$ (0.01 M in CH_3CN) as the reference electrode, and platinum mesh as counter electrode, respectively. The working compartment contains 1 mM catalyst dissolved in 10 ml electrolyte (0.1 M $TBAPF_6$ in DMF) and 2 M H_2O as proton source whereas the counter compartment contains 2 M Tetrabutylammonium acetate dissolved in 10 ml electrolyte. The working and counter compartment is separated by glass frit. The electrolysis solution was purged with CO_2 for 10 minutes, prior to electrolysis measurement and stirring is contentiously on during 2 h of electrolysis experiment.

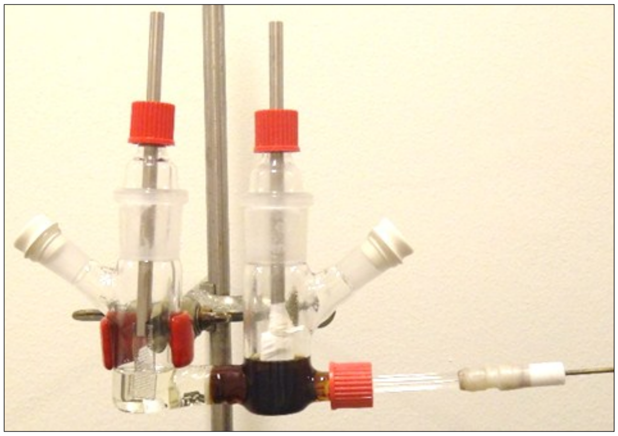


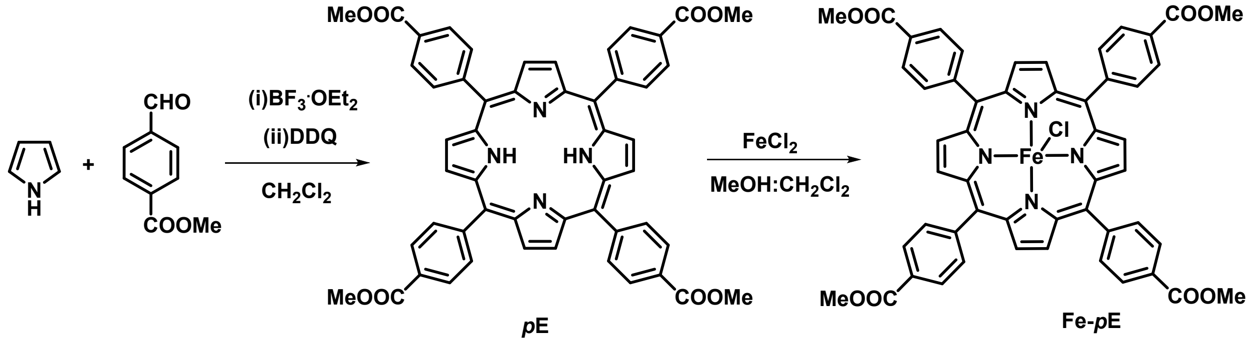
Figure S1. Bulk electrolysis H cell.

Gas detection.

Gas chromatography analysis of evolved gases in the bulk electrolysis was performed with a Shimadzu GC 2014 equipped with a thermal conductivity detector. The quantification of the gas products CO and H_2 was performed by the chromatography analysis of the gas evolved in the headspace. The calibration curves for CO and H_2 were determined separately by injecting known quantities of the gas. The carrier gas was helium flowing at constant pressure with a flow of 30 mL/min. Injection of gaseous sample (250 μL) was performed by using gas-tight Hamilton syringe. The retention time for H_2 and CO is 0.8 minutes and 5.2 minutes respectively.

Synthesis of Fe-*p*E, Fe-*m*E, and Fe-*o*E:

Synthesis of *p*E and Fe-*p*E.

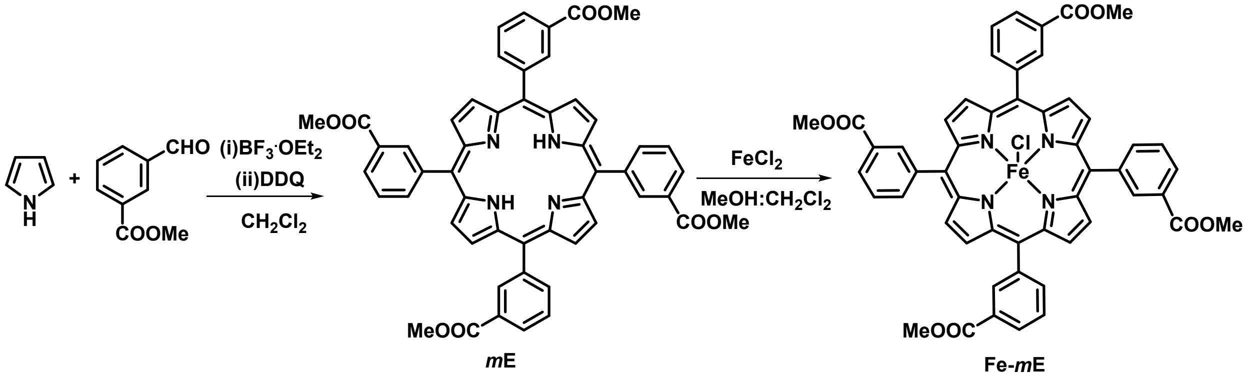


Scheme S1: Synthesis of *p*E and Fe-*p*E. column by using 1% methanol in CH_2Cl_2. The obtained solid was again purified by silica

5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)-21H,23H-porphyrin (*p*E). In 500 mL dichloromethane (CH_2Cl_2), methyl 4-formylbenzoate (0.820 gm, 5 mmol), and pyrrole (0.345 mL, 5 mmol) added and degassed with nitrogen for 20 minutes, then $BF_3.OEt_2$ (0.617 mL, 0.5 mmol) was added via syringe (Scheme S1). The solution was stirred under inert atmosphere in the dark for 1 hour. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.135 gm, 5 mmol) was added to the reaction mixture and stirred for an additional 1 h. The excess solvent was removed under reduced pressure and the resulting black solid was filtered by short silica gel column by using 1% methanol in CH_2Cl_2. The obtained solid was again purified by silica gel column chromatography by using CH_2Cl_2 as eluent affording *p*E porphyrin as solid powder in 17% yield (0.719 gm). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.83 (s, 8H), 8.45 (d, J = 8.1 Hz, 8H), 8.30 (d, J = 8.1 Hz, 8H), 4.12 (s, 12H), -2.79 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ =167.2, 146.6, 134.5, 131.7, 131.1, 129.7, 127.9, 119.3, 52.43; IR (Neat, cm^{-1}): 3316, 1717, 1606, 1434, 1402, 1309, 1274, 1223, 1110, 1021, 965, 798; λ_{abs} (CH_2Cl_2): 420, 516, 550, 590, 646; HRMS-ESI calcd for $C_{52}H_{38}N_4O_8$ $[M]^+$:846.2690, found 846.2960; EA calcd for $C_{52}H_{38}N_4O_8$: C 73.75%, H 4.52%, N 6.62%; found C 73.47%, H 4.46%, N 6.59%.

5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin-Fe(III) chloride (Fe-*p*E). In mixture of CH_2Cl_2 and methanol (70 mL:30 mL) *p*E porphyrin (0.253 gm, 0.3 mmol) was mixed with iron (II) chloride (0.381 gm, 3 mmol) and 50 µL 2,6-lutidine was added and refluxed at 50°C for 12 h. After completion, reaction mixture cooled down and excess solvent was evaporated. The resulted solid dissolved in CH_2Cl_2, washed with aqueous 1 M HCl solution and water. Organic layer was separated, dried and purified by silica gel column chromatography by using 1% methanol in CH_2Cl_2 as eluent affording Fe-*p*E in 92% yield (0.258 gm). IR (Neat, cm^{-1}): 1722, 1607, 1565, 1434, 1401, 1309, 1273, 1203, 1112, 998, 821; λ_{abs}/nm (CH_2Cl_2), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 413 (104), 512 (11), 570 (6); HRMS-ESI calcd for $C_{52}H_{36}FeN_4O_8$ $[M]^+$:900.1883, found 900.1873; EA calcd for $C_{52}H_{36}FeN_4O_8$: C 66.72%, H 3.88%, N 5.98%; found C 67.09%, H 4.27%, N 5.98%.

Synthesis of *m*E and Fe-*m*E.



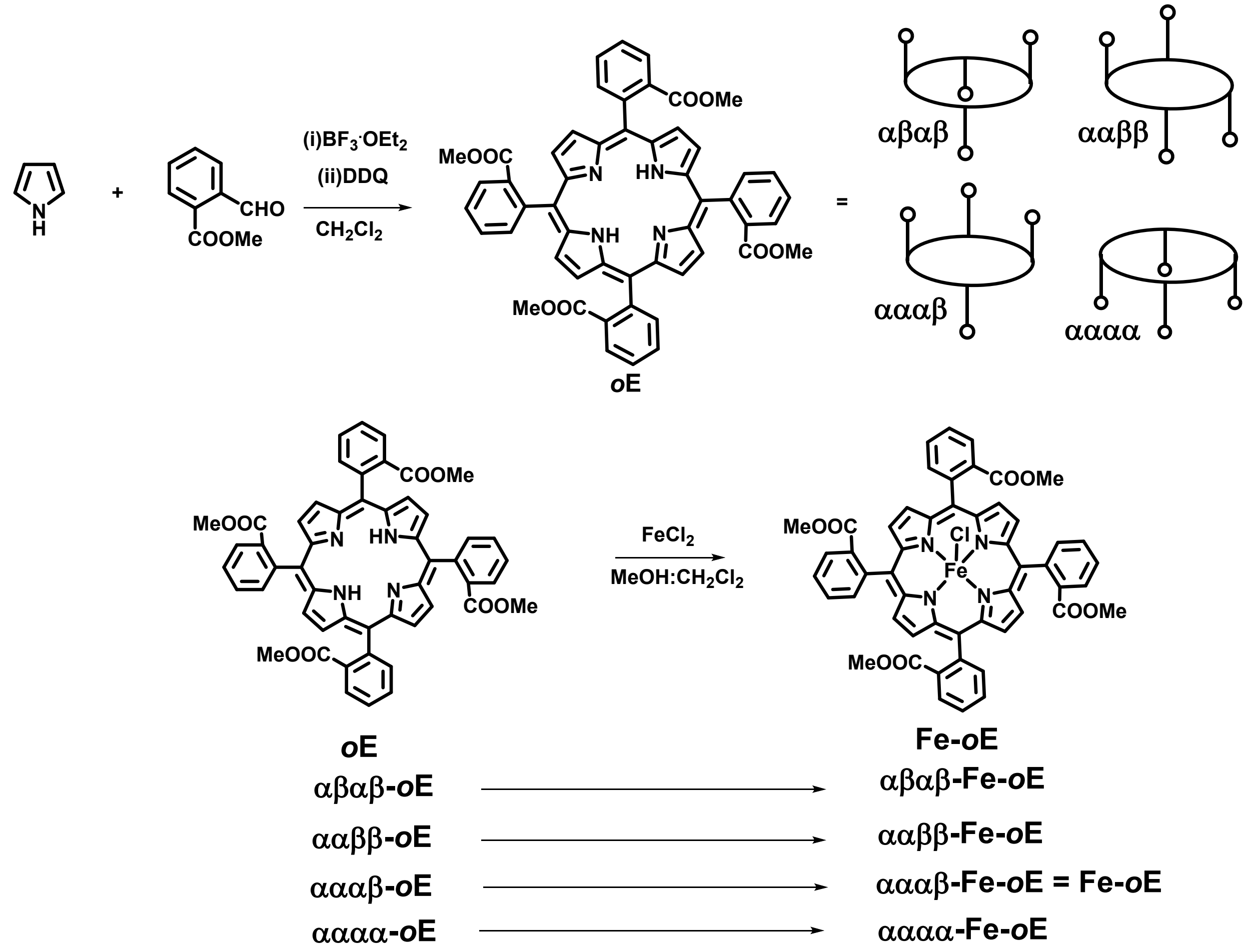
Scheme S2: *Synthesis of mE and Fe-mE.*

Synthesis of *5,10,15,20-Tetrakis(3-methoxycarbonylphenyl)-21H,23H-porphyrin* (*m*E). In 500 mL CH_2Cl_2, methyl 3-formylbenzoate (0.820 gm, 5mmol) and pyrrole (0.345mL, 5 mmol) added and degassed with nitrogen for 20 minutes, then $BF_3.OEt_2$ (0.617 mL, 0.5 mmol) was added via a syringe (Scheme 2). The solution was stirred under inert atmosphere in the dark for 1 h. Then DDQ (1.135 gm, 5 mmol) was added to the reaction mixture and stirred for an additional 1 h. The excess solvent was removed under reduced pressure and the resulting black solid was filtered by short silica gel column by using 1% methanol in CH_2Cl_2. The obtained solid was again purified by silica gel column chromatography by using CH_2Cl_2 as eluent affording *m*E porphyrin as solid powder in 15% yield (0.635 gm). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.90 (s, 4H), 8.81 (s, 8H), 8.49 (d, J = 7.9 Hz, 4H), 8.41 (d, J = 7.5 Hz, 4H), 7.86 (t, J = 7.6 Hz, 4H), 3.99 (s, 12H), -2.78 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 167.2, 142.2, 138.4, 134.9, 129.1, 128.9, 126.9, 119.2, 114.2, 52.3; IR (Neat, cm^{-1}): 3323, 1728, 1604, 1582, 1435, 1402, 1286, 1267, 1236, 1105, 964, 802, 756; λ_{abs} (CH_2Cl_2): 419, 515, 549, 593, 650; HRMS-ESI calcd for

$C_{52}H_{38}FeN_4O_8$ $[M]^+$:846.2690, found 846.2708; EA calcd for $C_{52}H_{38}N_4O_8$: C 73.75%, H 4.52%, N 6.62%; found C 73.65%, H 4.30%, N 6.53%.

5,10,15,20-Tetrakis(3-methoxycarbonylphenyl)porphyrin-Fe(III) chloride (Fe-*m*E). In mixture of CH_2Cl_2 and methanol (70 mL:30 mL) *m*E porphyrin (0.253 gm, 0.3 mmol) was mixed with iron (II) chloride (0.381 gm, 3 mmol) and 50 µL 2,6-lutidine was added and refluxed at 50°C and for 12 h. After completion reaction mixture cooled down and excess solved was evaporated. The resulted solid was dissolved in CH_2Cl_2 and washed with aqueous 1 M HCl solution and water. Organic layer separated, dried and purified by silica gel column chromatography by using 1% methanol in CH_2Cl_2 as eluent affording Fe-*m*E in 87% yield (0.244 gm). IR (Neat, cm^{-1}): 1722, 1601, 1435, 1282, 1238, 1215, 1108, 1003, 973, 801; λ_{abs}/nm (CH_2Cl_2), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 414 (108), 510 (12), 570 (7); HRMS-ESI calcd for $C_{52}H_{36}FeN_4O_8$ $[M]^+$:900.1883, found 900.1891; EA calcd for $C_{52}H_{36}FeN_4O_8$: C 66.98%, H 3.80%, N 5.98%; found C 66.72%, H 3.88%, N 6.19%.

Synthesis of oE and Fe-oE.



Scheme S3: Synthesis of *o*E and Fe-*o*E.

Synthesis of *5,10,15,20-Tetrakis(2-methoxycarbonylphenyl)-21H,23H-porphyrin (oE).* In 500 mL CH_2Cl_2, methyl 2-formylbenzoate (0.820 gm, 5mmol) and pyrrole (0.345mL, 5 mmol) added and degassed with nitrogen for 20 minutes, then $BF_3.OEt_2$ (0.617 mL, 0.5 mmol) was added via a syringe. The solution was stirred under inert atmosphere in the dark for 1 h. Then DDQ (1.135 gm, 5 mmol) was added to the reaction and reaction mixture and stirred for an additional 1 h. The excess solvent was removed under reduced pressure and resulted black solid was filtered by short silica gel column by using 1% methanol in CH_2Cl_2. The obtained solid was again purified by silica gel column chromatography by using Hexane:CH_2Cl_2 (1:1/v:v) to CH_2Cl_2 as eluent afforded four atropisomers. In an order of elution they were named as αβαβ-*o*E, ααββ-*o*E αααβ-*o*E and αααα-*o*E (Scheme S3).

αβαβ-*o*E: Yield 3.4% (0.142 gm), ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.58 (s, 8H), 8.38-8.36 (m, 4H), 8.21-8.36 (m, 4H), 8.21-8.19 (m, 4H), 7.87-7.80 (m, 8H), 2.88 (s, 12H), -2.42 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 167.8, 142.7, 136.0, 134.0, 130.8, 129.6, 129.5, 128.2, 118.7, 114.2, 51.6; IR (Neat, cm^{-1}): 3317, 1725, 1595, 1432, 1289, 1255, 1186, 1128, 1082, 983, 797, 733; λ_{abs} (CH_2Cl_2):422, 518, 552, 598, 653; HRMS-ESI calcd for $C_{52}H_{38}N_4O_8$ $[M]^+$:846.2690, found 846.2700; EA calcd for $C_{52}H_{38}N_4O_8$: C 73.75%, H 4.52%, N 6.62%; found C 73.52%, H 4.44%, N 6.54%.

ααββ-*o*E: Yield 4.0% (0.168 gm), ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.63 (s, 8H), 8.58 (s, 4H), 8.38-8.36 (m, 4H), 8.17-8.15 (m, 4H), 7.88-7.80 (m, 8H), 2.71 (s, 12H), -2.44 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 167. 8, 142.2, 138.6, 135.8, 134.1, 130.2, 129.4, 128.1, 118.7, 51.2; IR (Neat, cm^{-1}): 3317, 1718, 1596, 1572, 1467, 1437, 1287, 1262, 1157, 1086, 984, 800; λ_{abs} (CH_2Cl_2): 422, 518, 554, 599, 656; HRMS-ESI calcd for $C_{52}H_{38}N_4O_8$ $[M]^+$:846.2690, found 846.2666; EA calcd for $C_{52}H_{38}N_4O_8$: C 73.75%, H 4.52%, N 6.62%; found C 73.63%, H 4.67%, N 6.59%.

αααβ-*o*E: Yield 6.4% (0.640 gm), ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.65-8.63 (m, 8H), 8.42-8.39 (m, 4H), 8.19-8.17 (m, 4H), 7.90-7.82 (m, 8H), 2.92 (s, 6H), 2.81 (s, 3H), 2.64 (s, 3H), -2.39 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 167.8, 142.2, 138.6, 135.8, 134.1, 130.2, 129.5, 129.4, 128.1, 118.7, 51.2; IR (Neat, cm^{-1}): 3317, 1728, 1716, 1595, 1445, 12889 1255, 1128, 1082, 969, 797, 738; λ_{abs} (CH_2Cl_2): 422, 518, 554, 599, 653; HRMS-ESI calcd for $C_{52}H_{38}N_4O_8$ $[M]^+$:846.2690, found 846.2676; EA calcd for $C_{52}H_{38}N_4O_8$: C 73.75%, H 4.52%, N 6.62%; found C 73.92%, H 4.30%, N 6.90%.

αααα-*o*E: Yield 2.8% (0.118 gm), ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.64 (m, 8H), 8.43-8.41 (m, 4H), 8.12-8.10 (m, 4H), 7.89-7.85 (m, 4H), 7.83-7.79 (m, 4H), 2.91 (s, 12H), -2.34 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 167.9, 142.2, 136.3, 134.2, 130.8, 129.6, 129.5, 128.7, 128.1, 118.8, 51.5; IR (Neat, cm^{-1}): 3319, 1727, 1595, 1572, 1472, 1445, 1433, 1348, 1289, 1257, 1161, 1133, 1085, 968, 797; λ_{abs} (CH_2Cl_2): 422, 518, 554, 599, 653; HRMS-ESI calcd for $C_{52}H_{38}N_4O_8$ $[M]^+$:846.2690, found 846.2665; EA calcd for $C_{52}H_{38}N_4O_8$: C 73.75%, H 4.52%, N 6.62%; found C 73.56%, H 4.55%, N 6.78%.

5,10,15,20-Tetrakis(3-methoxycarbonylphenyl)porphyrin-Fe(III) chloride (Fe-*o*E). In mixture of CH_2Cl_2 and methanol (70 mL:30 mL) the respective porphyrin αβαβ-*o*E, ααββ-*o*E αααβ-*o*E, or αααα-*o*E (0.253 gm, 0.3 mmol) was mixed with iron (II) chloride (0.381 gm, 3 mmol) and 50 µL 2,6-lutidine was added and refluxed at 50°C and for 12 h. After completion reaction mixture cooled down and excess solved was evaporated. The resulted solid was dissolved in CH_2Cl_2 and washed with aqueous 1 M HCl solution and water. Organic layer was separated, dried and purified by silica gel column chromatography by using 1% methanol in CH_2Cl_2 as eluent afforded αβαβ-Fe-*o*E, ααββ-Fe-*o*E, αααβ-Fe-*o*E, or αααα-Fe-*o*E. The free base porphyrin αααβ-*o*E was obtained in highest yield of all derivatives.

αβαβ-Fe-*o*E: Yield 87% (0.244 gm), IR (Neat, cm^{-1}): 1716, 1596, 1432, 1333, 1292, 1257, 1204, 1127, 1086, 998, 799; λ_{abs}/nm (CH_2Cl_2), ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 421 (104), 512 (13), 578 (6); HRMS-ESI calcd for $C_{52}H_{36}FeN_4O_8$ $[M]^+$:900.1883, found 900.1902; EA calcd for $C_{52}H_{36}FeN_4O_8$: C 66.72%, H 3.88%, N 5.98%; found C 66.72%, H 4.01%, N 5.90%.

ααββ-Fe-*o*E: Yield 92% (0.257 gm), IR (Neat, cm^{-1}): 1727, 1677, 1596, 1481, 1332, 1293, 1255, 1204, 1132, 1085, 998, 800; λ_{abs}/nm (CH_2Cl_2), ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 421 (111), 513 (14), 577 (6); HRMS-ESI calcd for $C_{52}H_{36}FeN_4O_8$ $[M]^+$:900.1883, found 900.1902; EA calcd for $C_{52}H_{36}FeN_4O_8$: C 66.72%, H 3.88%, N 5.98%; found C 67.18%, H 4.07%, N 5.88%.

αααβ-Fe-*o*E: Yield 89% (0.249 gm) IR (Neat, cm^{-1}): 1716, 1596, 1572, 1455, 1333, 1293, 1255, 1204, 1128, 1204, 1128, 1086, 998, 799; λ_{abs}/nm (CH_2Cl_2), ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 421 (84), 512 (12), 578 (5); HRMS-ESI calcd for $C_{52}H_{36}FeN_4O_8$ $[M]^+$:900.1883, found 900.1874; EA calcd for $C_{52}H_{36}FeN_4O_8$: C 66.72%, H 3.88%, N 5.98%; found C 67.08%, H 3.90, N 5.92%.

αααα-Fe-*o*E: Yield 90% (0.252), IR (Neat, cm^{-1}): 1718, 1597, 1446, 1332, 1294, 1257, 1204, 1128, 1087, 997, 801; λ_{abs}/nm (CH_2Cl_2), ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 421 (101), 512 (13), 578 (6); HRMS-ESI calcd for $C_{52}H_{36}FeN_4O_8$ $[M]^+$:900.1883, found 900.1879. EA calcd for $C_{52}H_{36}FeN_4O_8$: C 66.72%, H 3.88%, N 5.98%; found C 66.72%, H 3.97%, N 5.82%.

The CV of **αβαβ-Fe-*o*E**, **ααββ-Fe-*o*E**, **αααβ-Fe-*o*E**, and **αααα-Fe-*o*E** measured in CO_2 saturated electrolyte gives similar catalytic activity however αααβ-Fe-*o*E gave slightly higher performance compared to remaining three atropisomers (Figure S2). As all of the four atropisomers gave similar performance we have not tried to explore them in more details. ***The third derivative αααβ-Fe-oE is used as Fe-oE and used with same name in the manuscript.***

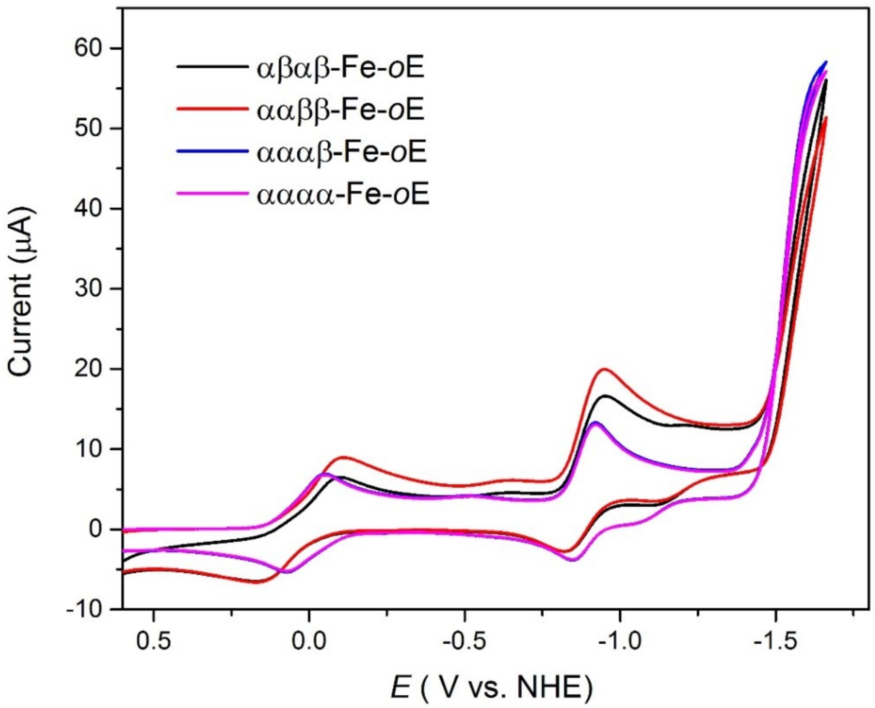


Figure S2. CVs of **αβαβ-Fe-*o*E**, **ααββ-Fe-*o*E**, **αααβ-Fe-*o*E**, and **αααα-Fe-*o*E** in CO_2 saturated electrolyte.

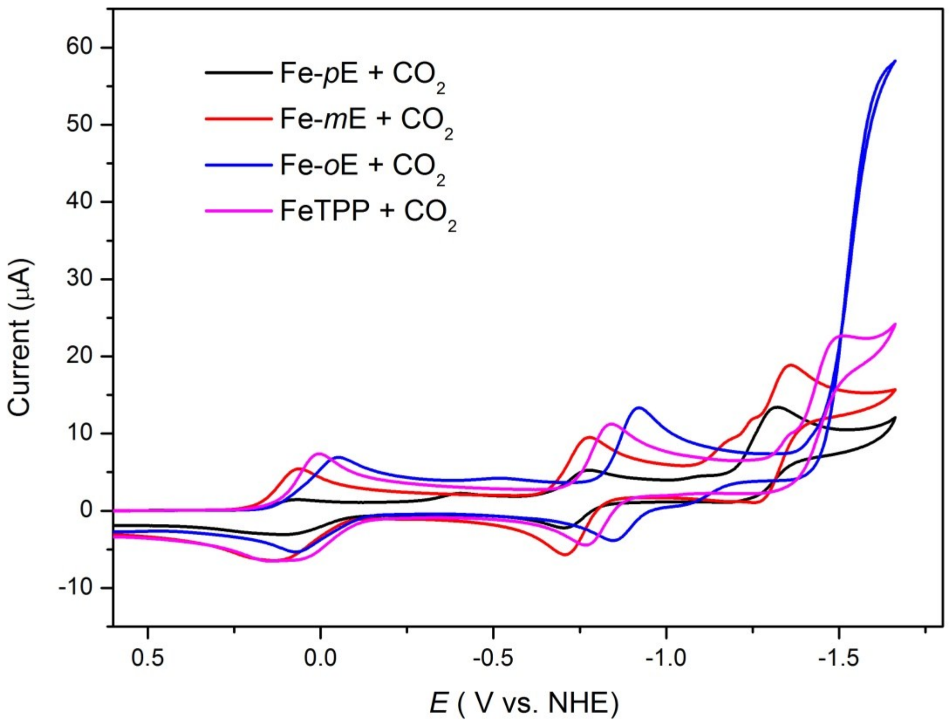


Figure S3. CVs of **Fe-*p*E**, **Fe-*m*E**, **Fe-*o*E** and **FeTPP** in CO_2 saturated electrolyte.

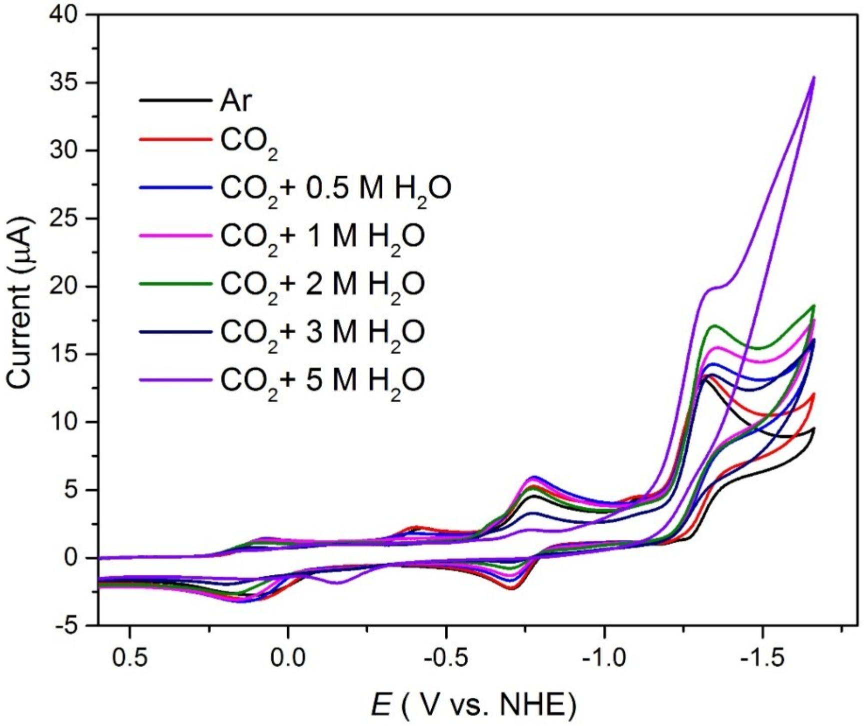


Figure S4. CVs of **Fe-*p*E** in argon, CO_2, 0.5 M, 1 M, 2 M, 3 M, and 5 M H_2O added in CO_2 saturated electrolyte.

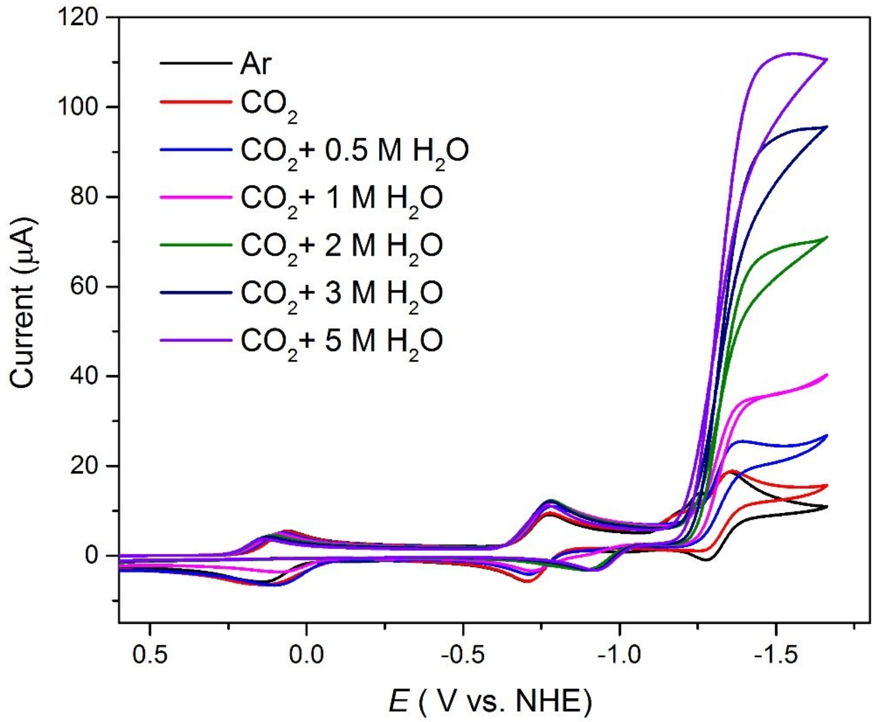


Figure S5. CVs of **Fe-*m*E** in argon, CO_2, 0.5 M, 1 M, 2 M, 3 M, and 5 M H_2O added in CO_2 saturated electrolyte.

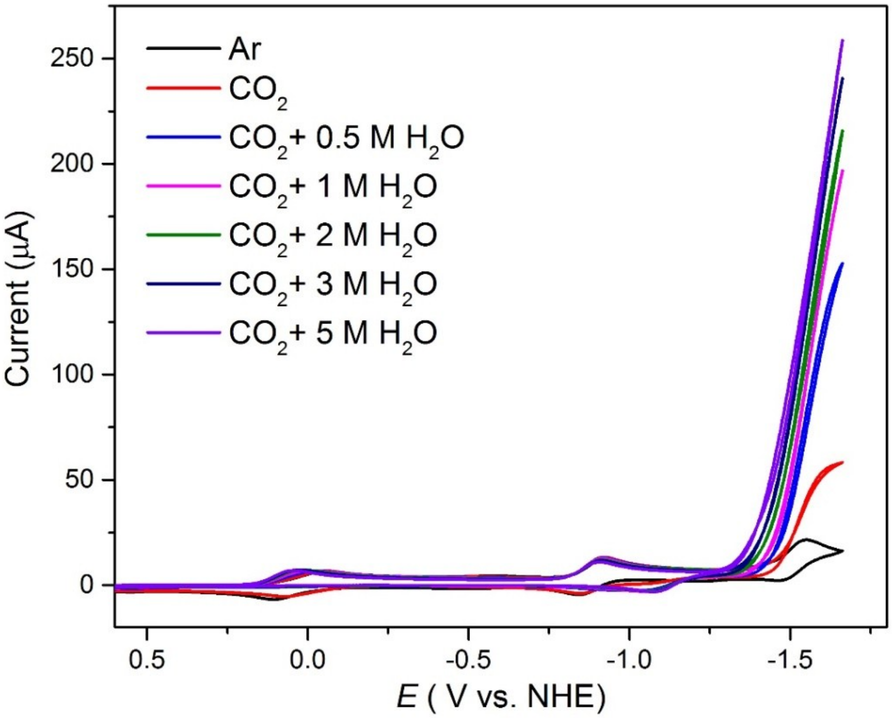


Figure S6. CVs of **Fe-*o*E** in argon, CO_2, 0.5 M, 1 M, 2 M, 3 M, and 5 M H_2O added in CO_2 saturated electrolyte.

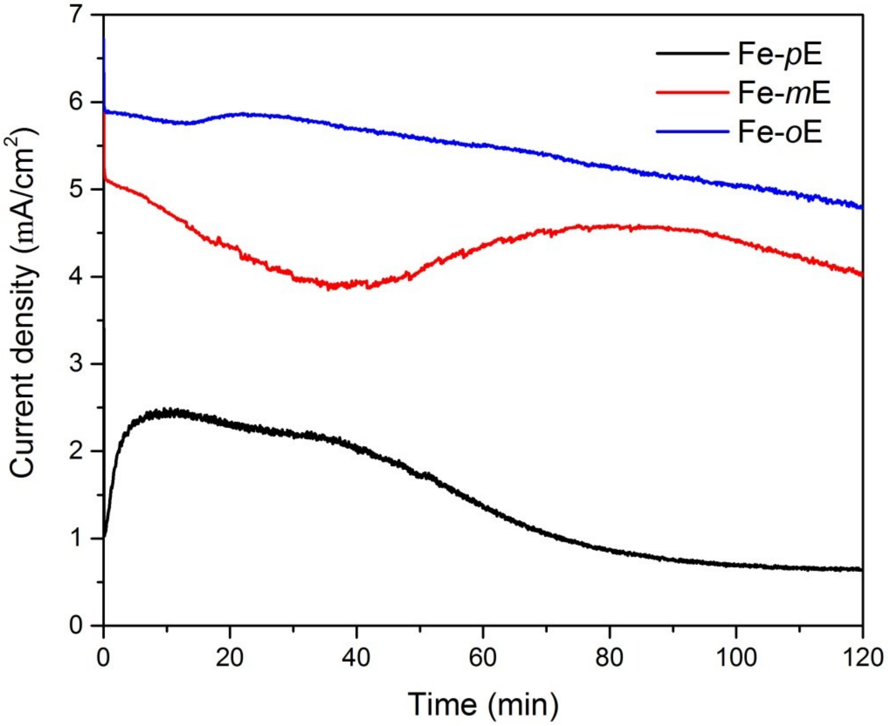


Figure S7. Current-time profile of **Fe-*p*E**, **Fe-*m*E**, and **Fe-*o*E** during 2 h of bulk electrolysis.

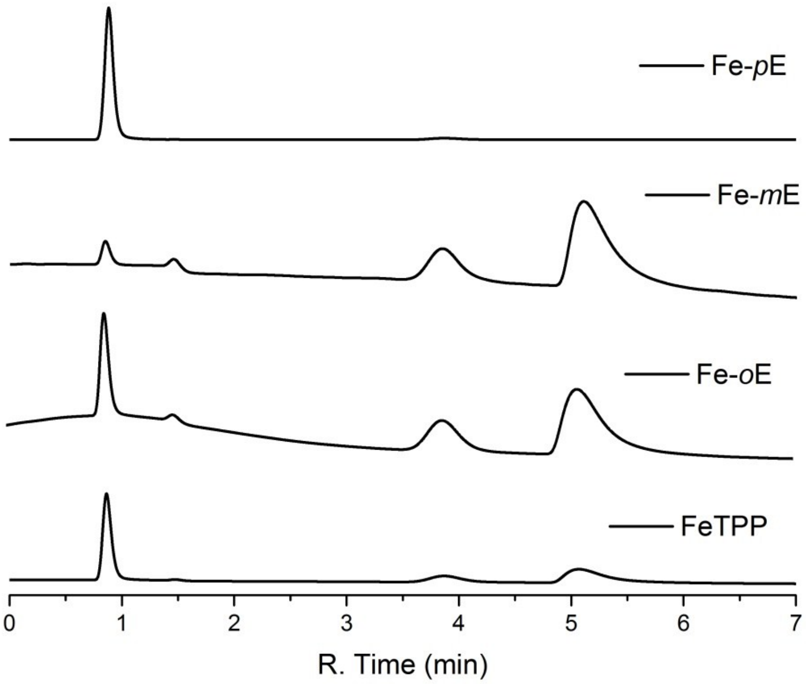


Figure S8. GC traces of **Fe-*p*E**, **Fe-*m*E**, **Fe-*o*E**, and **FeTPP**. The retention time for H_2 and CO is 0.8 and 5.2 minutes respectively.

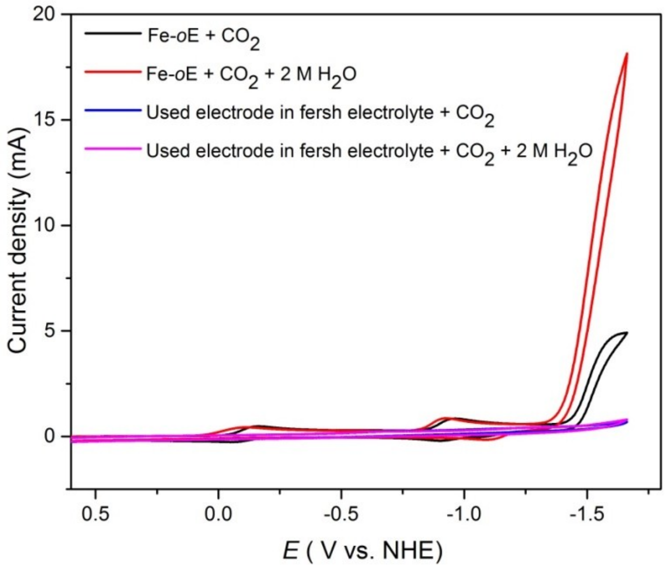


Figure S9. CVs of **Fe-*o*E** in CO_2 saturated electrolyte, CO_2 saturated electrolyte + 2 M H_2O, used electrode + CO_2 saturated fresh electrolyte (no catalyst), and used electrode + CO_2 saturated fresh electrolyte (no catalyst) + 2 M H_2O.

Table S1. Standard redox potentials of **Fe-*p*E**, **Fe-*m*E**, **Fe-*o*E**, and **FeTPP** determined by CVs (V vs NHE).

Catalyst	Fe(III)/Fe(II)	Fe(II)/Fe(I)	Fe(I)/Fe(0)
Fe-*p*E	0.09	-0.74	-1.28
Fe-*m*E	0.10	-0.74	-1.31
Fe-*o*E	0.07	-0.88	-1.50
FeTPP	0.07	-0.80	-1.43

Table S2. Faradaic efficiency, TON and TOF of **Fe-*p*E**, ***Fe-mE***, **Fe-*o*E**, and **FeTPP** based on CVs and 2 h bulk electrolysis in CO_2 saturated electrolyte + 2 M H_2O added in it.

Catalyst	Charge (C)	FE CO (%)	FE H_2 (%)	TON CO	TON H_2	log TOF_0 (S^{-1}) CO
Fe-*p*E	30.11	0.00	82.90	0.00	13.06	NA[a]
Fe-*m*E	31.32	65.36	0.19	10.61	0.03	-7.73
Fe-*o*E	39.19	97.49	1.77	19.80	0.36	-10.73
FeTPP	39.76	84.83	7.12	17.48	2.04	-9.76

[a] Data is not included as CO production is not observed.

Computational Section:

All geometries were fully optimized by the DFT calculations using OPBE method with the Gaussian09 software package. The 6-31g* basis set was used for C, H, O and N atoms, while LANL2DZ basis set with effective core potentials (ECP) were used for Fe atom. In addition, polarization functions were added for Fe ($\zeta_f = 2.462$).

TS of $\mathrm{Fe^{II}}$–COOH

Fe	-0.03156	0.10764	-0.34928
N	-0.68564	1.92314	-0.71769
N	-1.87172	-0.57024	-0.32404
N	0.60941	-1.74313	-0.35367
N	1.79893	0.72699	-0.75589
C	2.2566	2.02752	-0.74739
C	3.66664	2.07909	-1.02401
H	4.26562	2.98266	-1.05601
C	4.06088	0.79975	-1.27637
H	5.05029	0.44829	-1.54767
C	2.90667	-0.03511	-1.06996
C	2.93351	-1.43312	-1.1336
C	1.85212	-2.21606	-0.71859
C	1.93278	-3.64132	-0.53441
H	2.80604	-4.24717	-0.74953
C	0.74527	-4.0326	0.00292
H	0.43362	-5.03092	0.28869
C	-0.07975	-2.85609	0.07581
C	-1.44088	-2.8911	0.3903
C	-2.2847	-1.80476	0.13816
C	-3.7186	-1.86008	0.2239
H	-4.29239	-2.71012	0.57598
C	-4.18575	-0.66737	-0.24113
H	-5.21655	-0.34189	-0.33093
C	-3.03412	0.13973	-0.5407

C	-3.10936	1.4908	-0.89249
C	-1.98885	2.32663	-0.92853
C	-2.05762	3.75249	-1.10259
H	-2.95846	4.31718	-1.31702
C	-0.79466	4.23116	-0.92027
H	-0.45918	5.26157	-0.96393
C	0.05401	3.09	-0.70572
C	1.4495	3.16367	-0.63863
C	6.16853	-3.27255	-3.33583
C	6.39552	-2.89983	-2.01354
C	5.37868	-2.34142	-1.21605
C	4.10229	-2.10996	-1.78444
C	3.89742	-2.48545	-3.12731
C	4.90453	-3.06934	-3.8958
H	7.37615	-3.03791	-1.55902
H	2.91771	-2.30042	-3.56917
H	4.70237	-3.35164	-4.93074
C	3.16071	7.12213	-0.97341
C	2.88532	6.60631	0.29075
C	2.08577	4.51971	-0.67992
H	3.06668	7.19972	1.18649
C	-6.9086	3.07314	-2.22324
C	-6.46682	3.3831	-0.93953
C	-5.25558	2.87513	-0.43424
C	-4.44715	2.05251	-1.25941
C	-4.9105	1.75827	-2.55586
C	-6.12462	2.2503	-3.03667
H	-7.05483	4.03012	-0.28924
H	-4.28688	1.13198	-3.1946
H	-6.45006	1.9978	-4.04764
C	-3.08185	-6.39127	2.30918
C	-2.29942	-5.47072	3.01066
C	-1.77153	-4.34912	2.36422

C	-2.00729	-4.13633	0.99415
C	-2.79603	-5.07365	0.27882
C	-3.33358	-6.18585	0.953
H	-2.09208	-5.60675	4.0734
H	-3.93968	-6.89895	0.39558
H	6.97292	-3.7176	-3.92422
H	-3.49619	-7.26756	2.81176
H	-7.85708	3.47261	-2.58624
H	3.57418	8.12701	-1.07583
C	2.36022	5.06384	-1.94925
H	2.13232	4.46116	-2.82908
C	2.36726	5.30966	0.46157
C	2.90023	6.34175	-2.10313
H	3.10562	6.72733	-3.10364
C	-0.17909	0.37832	1.31185
O	-0.58715	0.63952	2.37425
C	-4.94003	3.29144	0.97536
O	-4.09405	2.45118	1.589
C	-3.72619	2.80691	2.92473
H	-3.27208	3.80575	2.94692
H	-4.6052	2.79657	3.58304
H	-3.00011	2.05001	3.23135
O	-5.43585	4.2744	1.50674
H	0.80285	-2.58481	4.27046
O	-0.18727	-2.59818	4.57034
H	-0.44705	-1.69025	4.35344
C	5.7962	-2.04676	0.20211
O	6.93986	-1.72306	0.49039
O	4.81254	-2.25531	1.08033
C	5.15661	-2.09128	2.47362
H	5.96956	-2.78415	2.73099
H	5.49256	-1.0624	2.6543
H	4.22602	-2.30664	3.02934

C	2.15776	4.89522	1.89498
O	1.97762	5.70279	2.79562
O	2.25086	3.57367	2.05735
C	2.11277	3.07541	3.40038
H	2.21679	1.98586	3.31321
H	2.89164	3.51362	4.0392
H	1.12783	3.34776	3.80101
H	2.19519	-1.13974	3.10891
O	2.24142	-2.4507	3.61787
H	2.0498	-2.96319	2.81662
O	2.20751	-0.12874	2.68555
H	2.74105	-0.22668	1.88713
C	-3.02503	-4.93517	-1.19141
O	-2.24634	-4.46895	-2.00153
O	-4.24899	-5.43	-1.54421
C	-4.52833	-5.36462	-2.93954
H	-5.53069	-5.79185	-3.05717
H	-4.51347	-4.3251	-3.29421
H	-3.79687	-5.94347	-3.52047
H	-1.17674	-3.63498	2.95442

TS of Fe^{I}–COOH

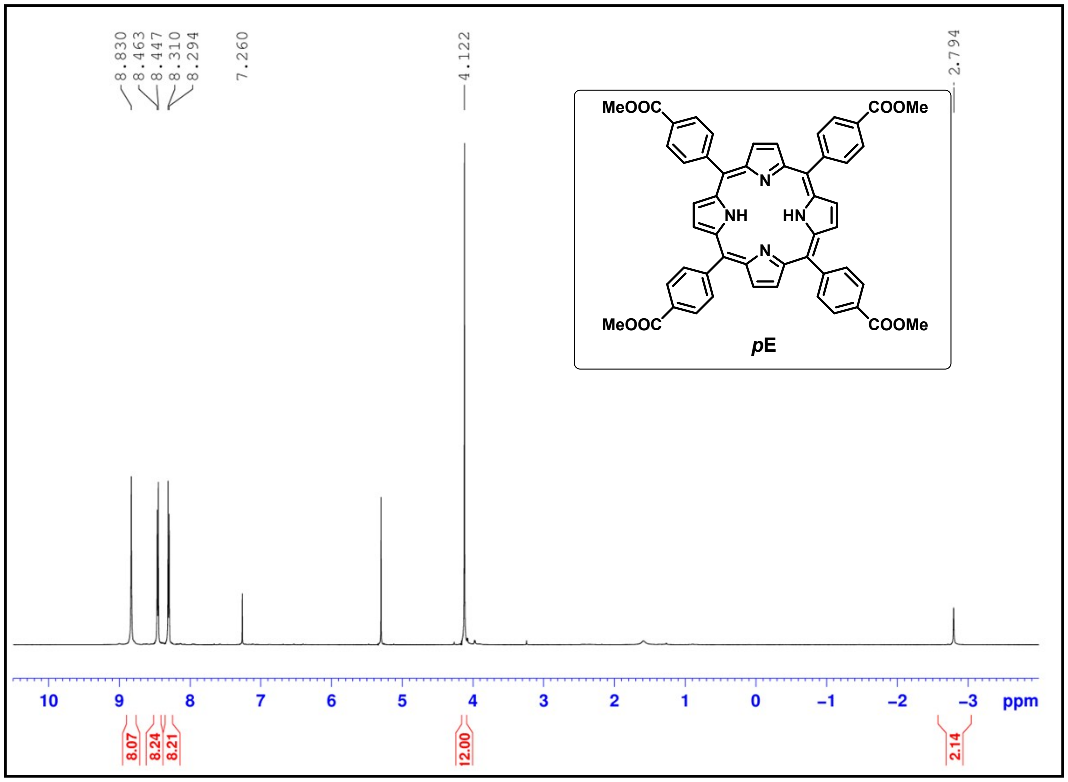
Fe	-0.1236	-0.0646	-0.34864
N	-2.05814	-0.1976	-0.72735
N	0.01562	-2.02836	-0.36467
N	1.84669	0.03898	-0.38914
N	-0.19767	1.89073	-0.73322
C	-1.3336	2.68491	-0.72675
C	-0.99736	4.05708	-0.96754
H	-1.70436	4.87974	-0.99977
C	0.34986	4.09705	-1.18955
H	0.95795	4.9617	-1.43237
C	0.84022	2.75683	-1.00785
C	2.19502	2.39121	-1.09128

C	2.64468	1.11135	-0.71944
C	4.03201	0.79474	-0.52092
H	4.85613	1.47984	-0.69029
C	4.07838	-0.47392	-0.01167
H	4.95187	-1.04743	0.28112
C	2.72642	-0.94275	0.03658
C	2.36619	-2.25517	0.35547
C	1.09098	-2.7655	0.11332
C	0.74758	-4.1514	0.21375
H	1.41546	-4.9359	0.55371
C	-0.53407	-4.27181	-0.24188
H	-1.13711	-5.17105	-0.31126
C	-0.98822	-2.94658	-0.57267
C	-2.31373	-2.65358	-0.93911
C	-2.80834	-1.3324	-0.95515
C	-4.18469	-0.98848	-1.16834
H	-4.97734	-1.6879	-1.41132
C	-4.29192	0.36341	-0.98619
H	-5.18416	0.97648	-1.05877
C	-2.96995	0.8504	-0.73469
C	-2.64336	2.21049	-0.66314
C	4.87464	5.09218	-3.15255
C	4.46405	5.41615	-1.86277
C	3.65339	4.55091	-1.10087
C	3.18246	3.34065	-1.68051
C	3.63174	3.02815	-2.98211
C	4.46598	3.87428	-3.71138
H	4.77401	6.3529	-1.39899
H	3.27778	2.09828	-3.42896
H	4.77417	3.59523	-4.72178
C	-5.97905	4.9257	-1.15085
C	-5.59691	4.54921	0.1335
C	-3.77228	3.19104	-0.75231
H	-6.14542	4.90319	1.00632
C	-4.86176	-5.85241	-2.35986

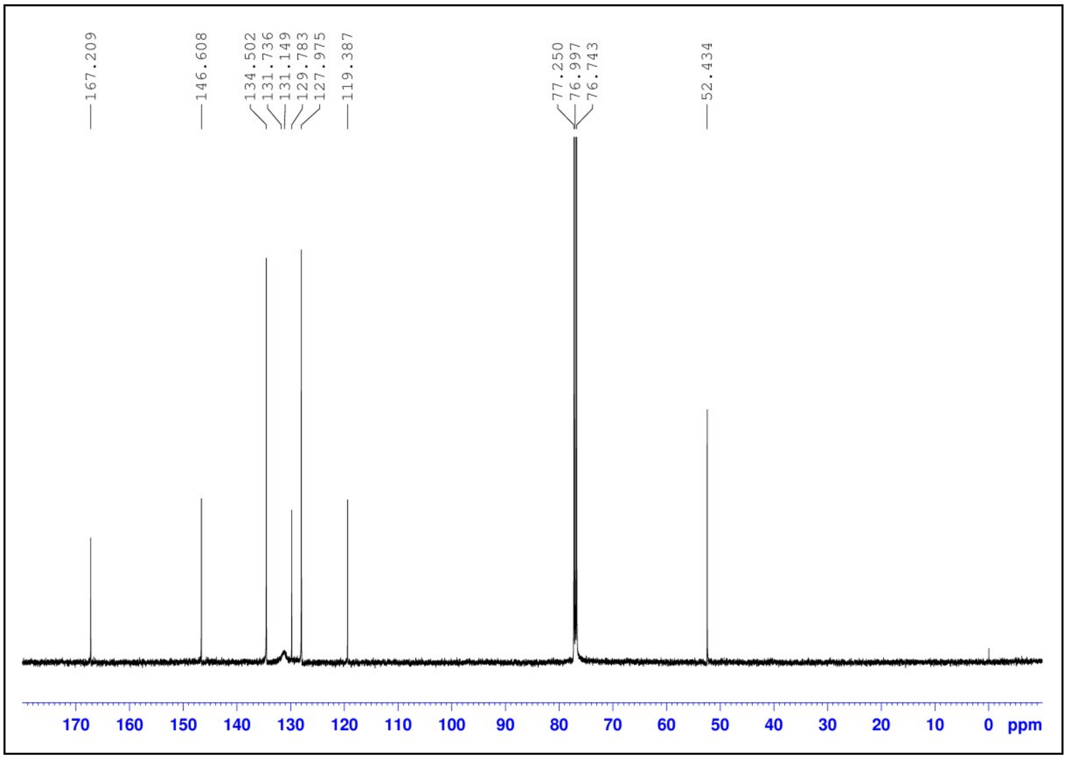
C	-5.18474	-5.22242	-1.16477
C	-4.36426	-4.22091	-0.60126
C	-3.19761	-3.78967	-1.30801
C	-2.87699	-4.47686	-2.49963
C	-3.68009	-5.48733	-3.02613
H	-6.08256	-5.50095	-0.61249
H	-1.98122	-4.16165	-3.03654
H	-3.40079	-5.96814	-3.96661
C	5.25628	-4.62735	2.52309
C	4.36216	-3.77186	3.17572
C	3.44448	-3.02291	2.43378
C	3.38483	-3.1168	1.03187
C	4.31695	-3.96063	0.366
C	5.24112	-4.70596	1.13345
H	4.37143	-3.66576	4.26179
H	5.9485	-5.35509	0.61931
H	5.51062	5.77937	-3.71517
H	5.97424	-5.22265	3.09254
H	-5.51623	-6.62577	-2.76838
H	-6.83246	5.59251	-1.29421
C	-4.18302	3.57798	-2.04193
H	-3.63462	3.17459	-2.89366
C	-4.49263	3.7016	0.35824
C	-5.26188	4.44126	-2.25053
H	-5.54551	4.72267	-3.26719
C	-0.43602	-0.17839	1.31096
O	-0.83943	-0.58108	2.33522
C	-4.80019	-3.75535	0.74761
O	-3.82134	-3.1278	1.42633
C	-4.1716	-2.63376	2.71406
H	-5.03665	-1.95994	2.65288
H	-4.41184	-3.45962	3.39979
H	-3.28791	-2.08951	3.05904
O	-5.91638	-3.96485	1.21739
H	2.36166	0.00559	4.52786

O	2.03475	-0.90625	4.87072
H	1.15201	-0.92495	4.47146
C	3.41016	5.01238	0.3097
O	3.41183	6.19616	0.63071
O	3.28947	3.99374	1.16639
C	3.13793	4.33525	2.55619
H	3.9915	4.94789	2.88115
H	2.21311	4.90955	2.69915
H	3.08697	3.37107	3.09434
C	-4.19489	3.41707	1.80376
O	-5.03216	3.53418	2.69265
O	-2.91799	3.08198	2.00004
C	-2.51418	2.78479	3.34394
H	-1.44803	2.53229	3.26823
H	-2.68639	3.65863	3.98855
H	-3.09367	1.93628	3.73194
H	1.51183	1.62604	3.1305
O	2.7327	1.40768	3.78904
H	3.24283	1.0186	3.06021
O	0.56962	1.83861	2.60726
H	0.84476	2.25857	1.78264
C	4.36154	-4.06376	-1.11785
O	3.46289	-3.8429	-1.90888
O	5.61144	-4.46835	-1.54251
C	5.72253	-4.60251	-2.95024
H	6.75747	-4.91724	-3.13516
H	5.02255	-5.35537	-3.3421
H	5.52099	-3.64915	-3.45932
H	2.784	-2.33228	2.96482

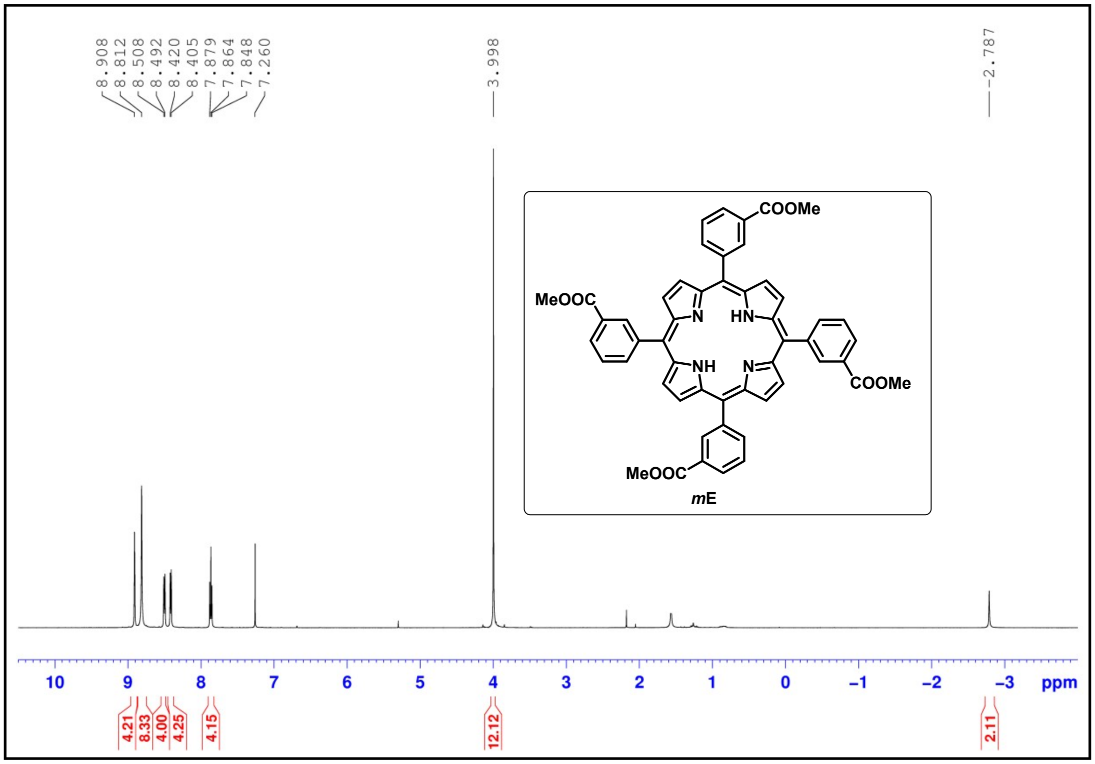
^{1}H NMR (500 MHz, CDCl$_3$) spectra of *p*E



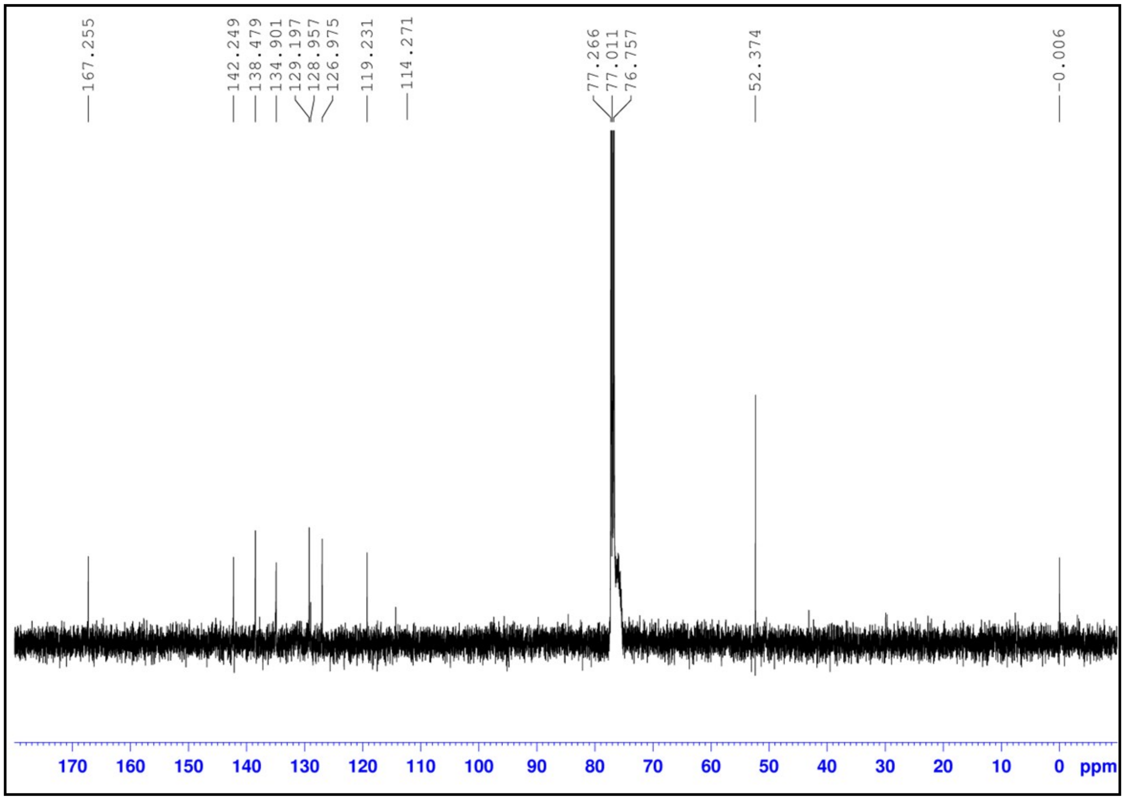
^{13}C NMR (500 MHz, CDCl$_3$) spectra of *p*E



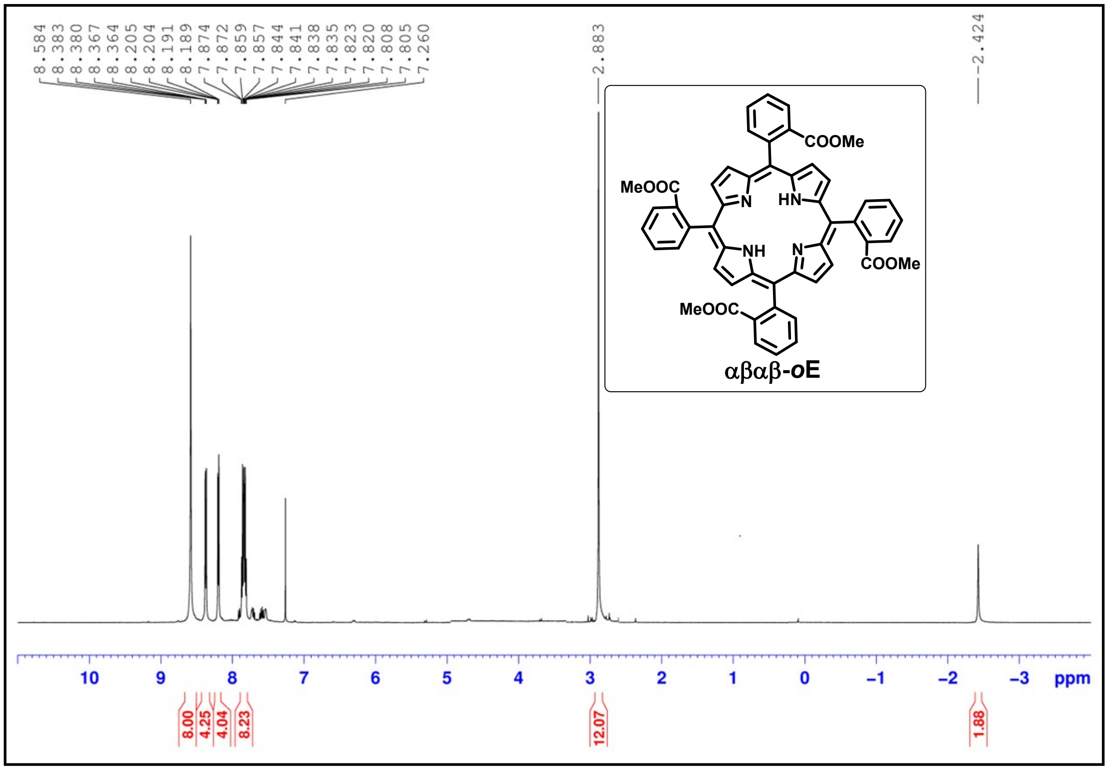
^{1}H NMR (500 MHz, $CDCl_3$) spectra of *m*E



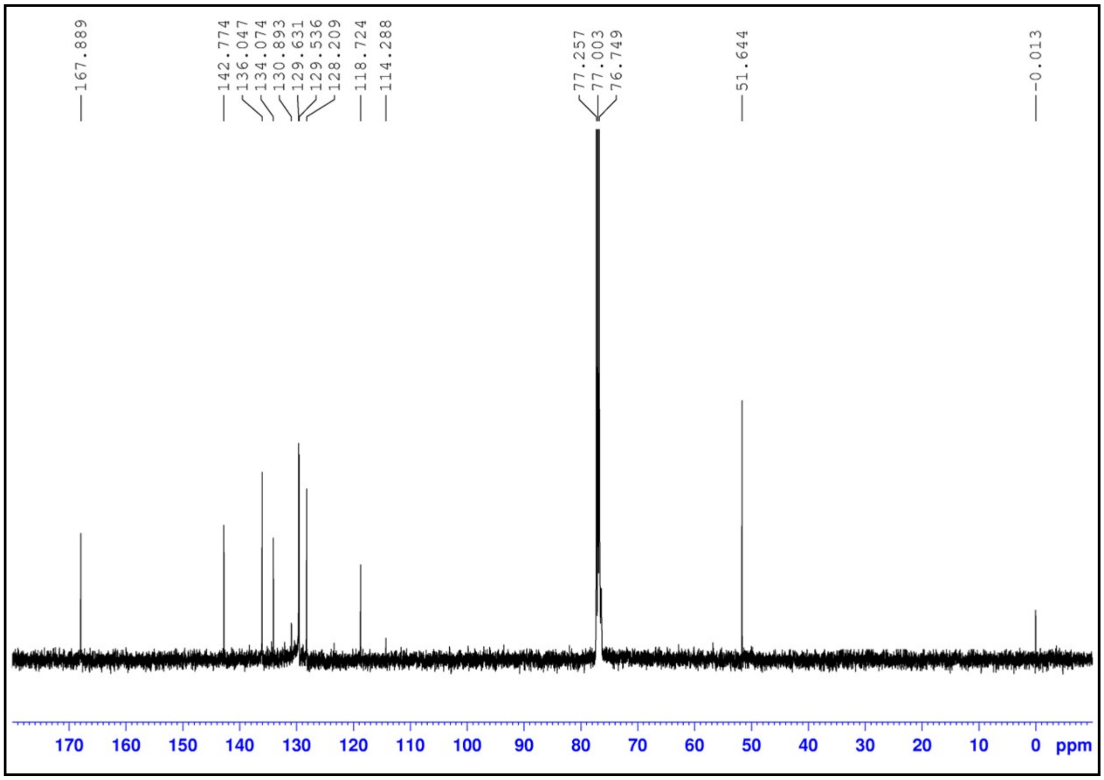
^{13}C NMR (500 MHz, $CDCl_3$) spectra of *m*E



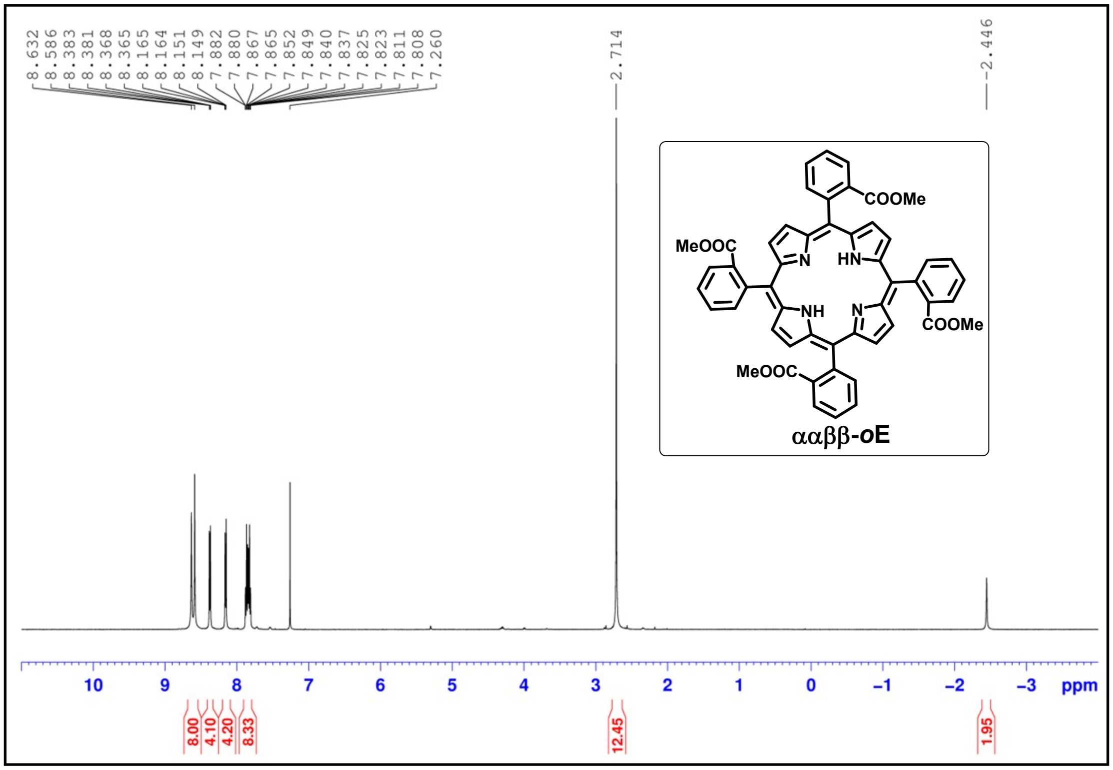
^{1}H NMR (500 MHz, CDCl$_3$) spectra of αβαβ-*o*E



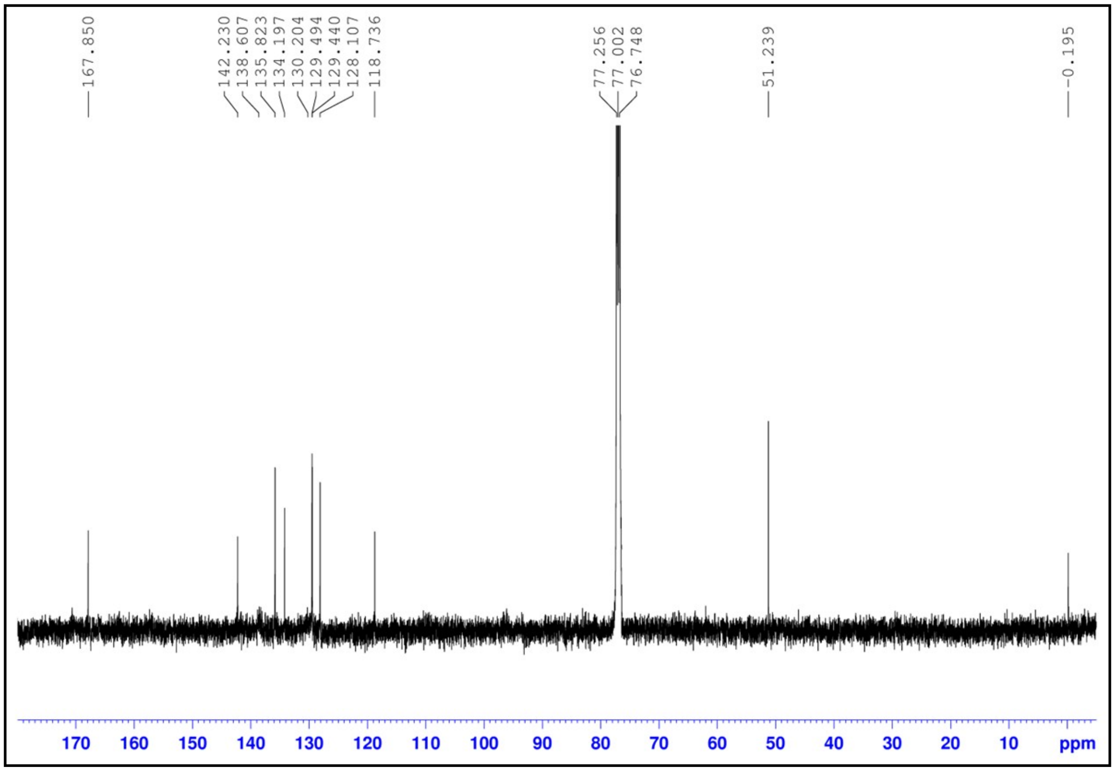
^{13}C NMR (500 MHz, CDCl$_3$) spectra of αβαβ-*o*E



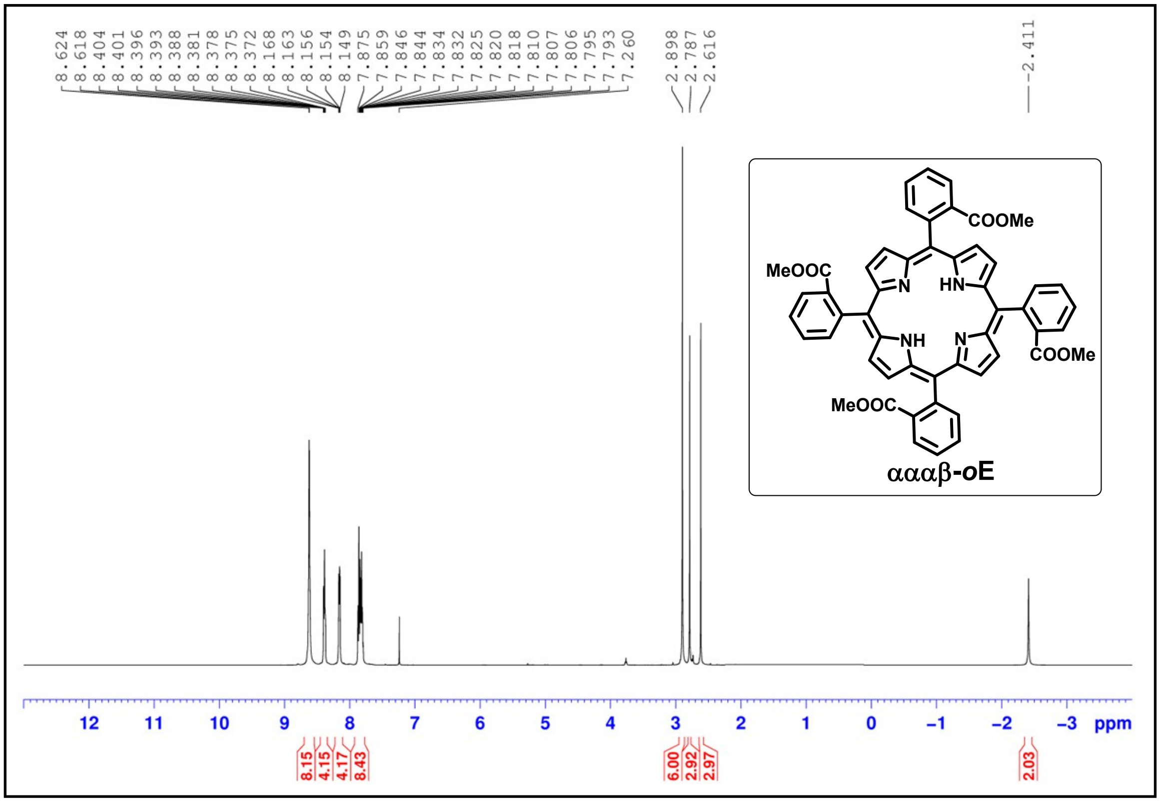
^{1}H NMR (500 MHz, $CDCl_3$) spectra ααββ-*o*E



^{13}C NMR (500 MHz, $CDCl_3$) spectra ααββ-*o*E



^{1}H NMR (500 MHz, $CDCl_3$) spectra αααβ-*o*E



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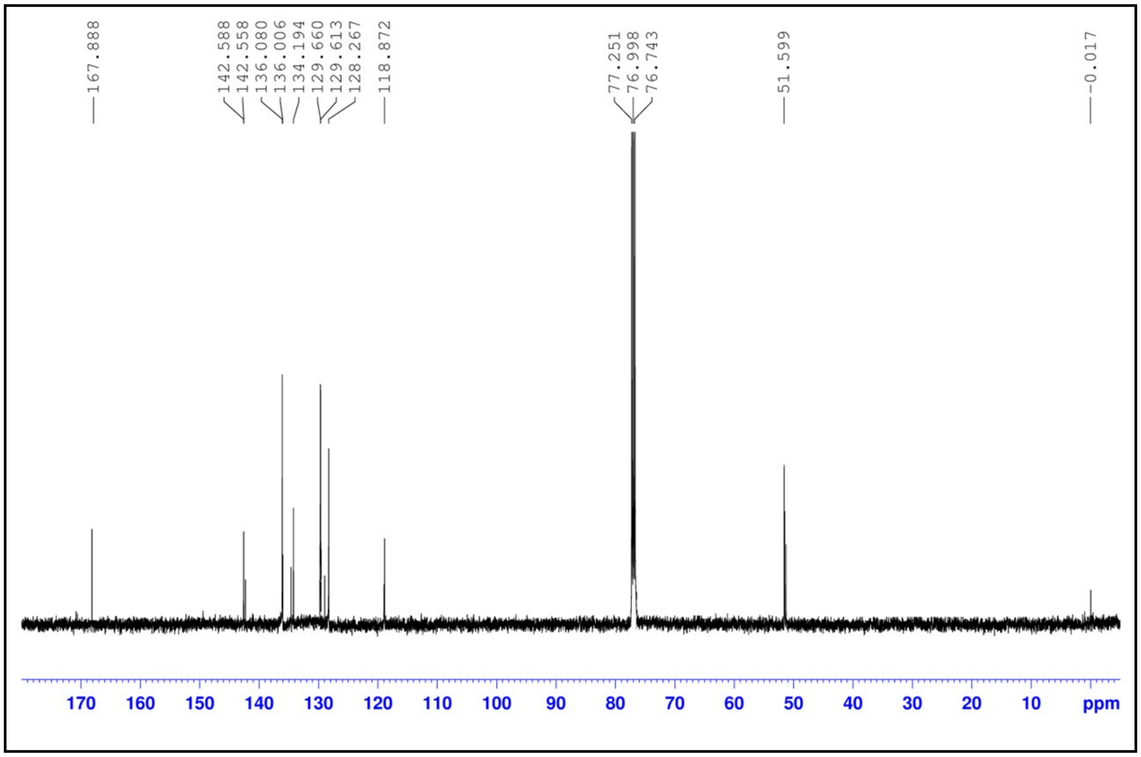
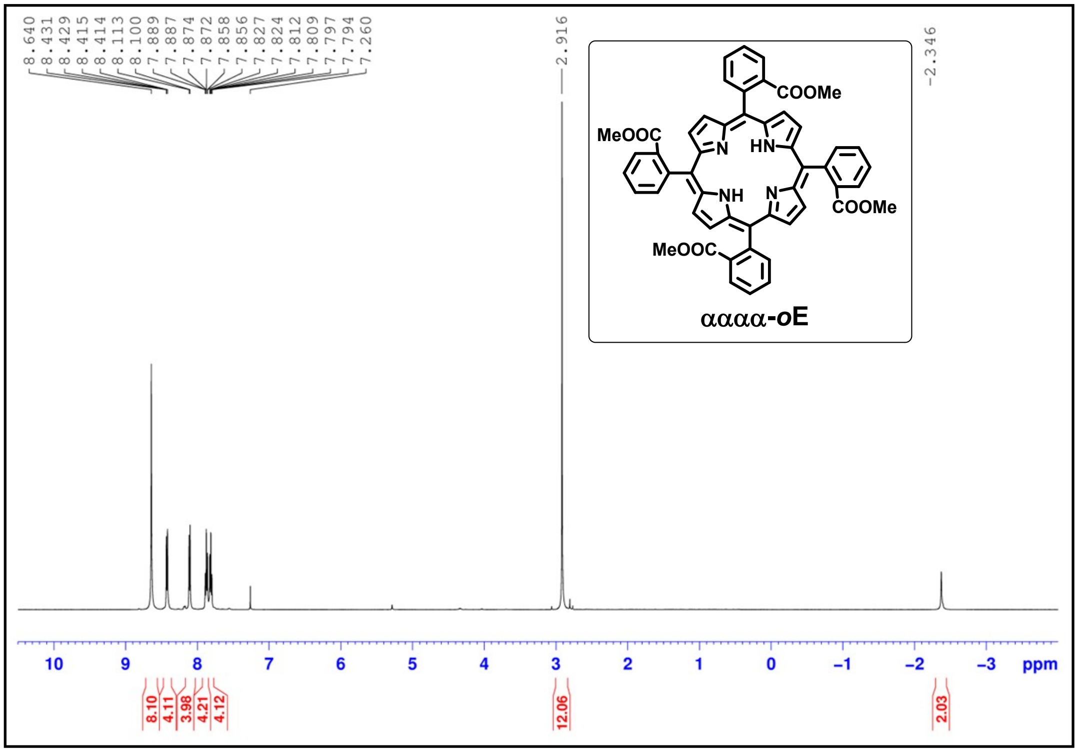


^{1}H NMR (500 MHz, CDCl$_3$) spectra αααα-*o*E



^{13}C NMR (500 MHz, CDCl$_3$) spectra αααα-*o*E