Supplementary Information

Keggin type heteropolyacid-mediated novel green protocol for the synthesis of porphyrins

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1. Supplementary Figure

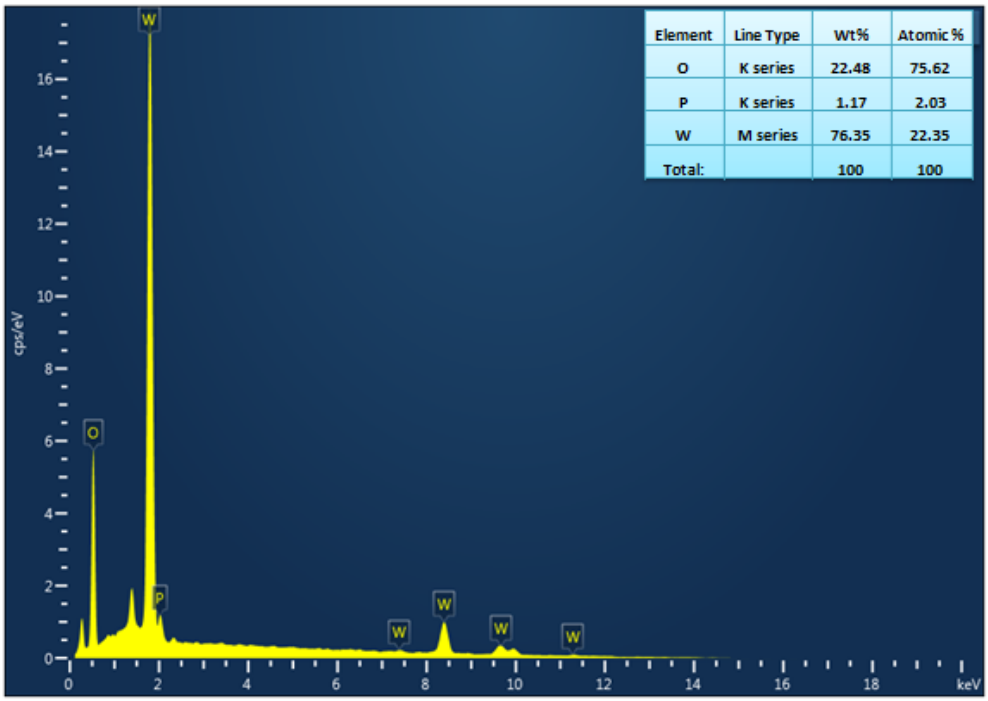


Fig. S1 (a) EDX of Heteropolyacid, HPW

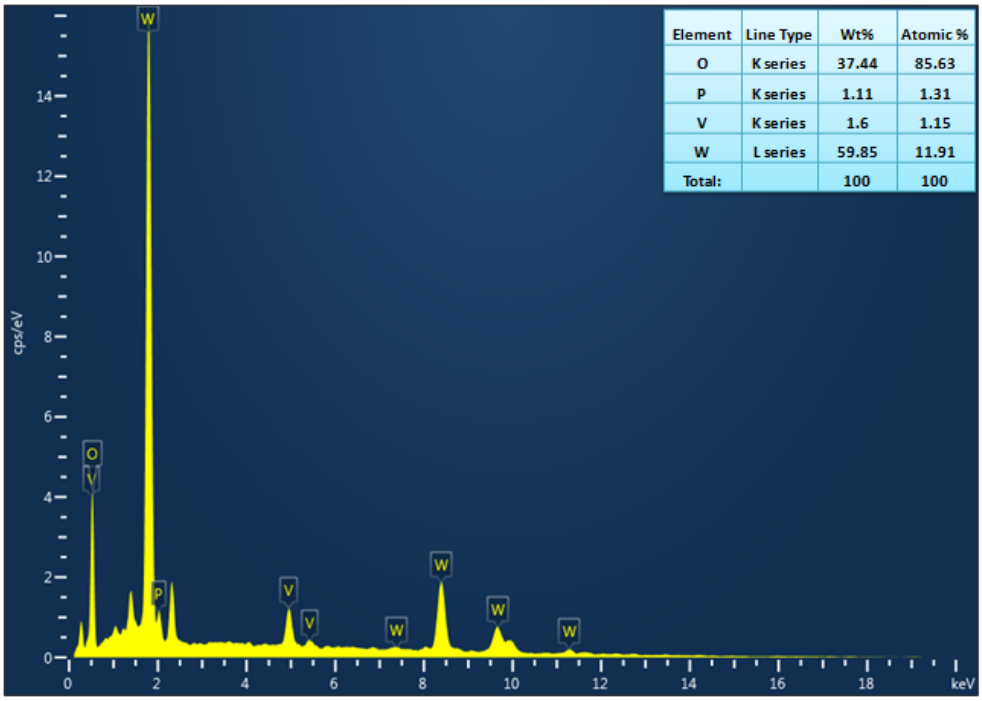


Fig. S1 (b) EDX of Heteropolyacid, HPV_1W

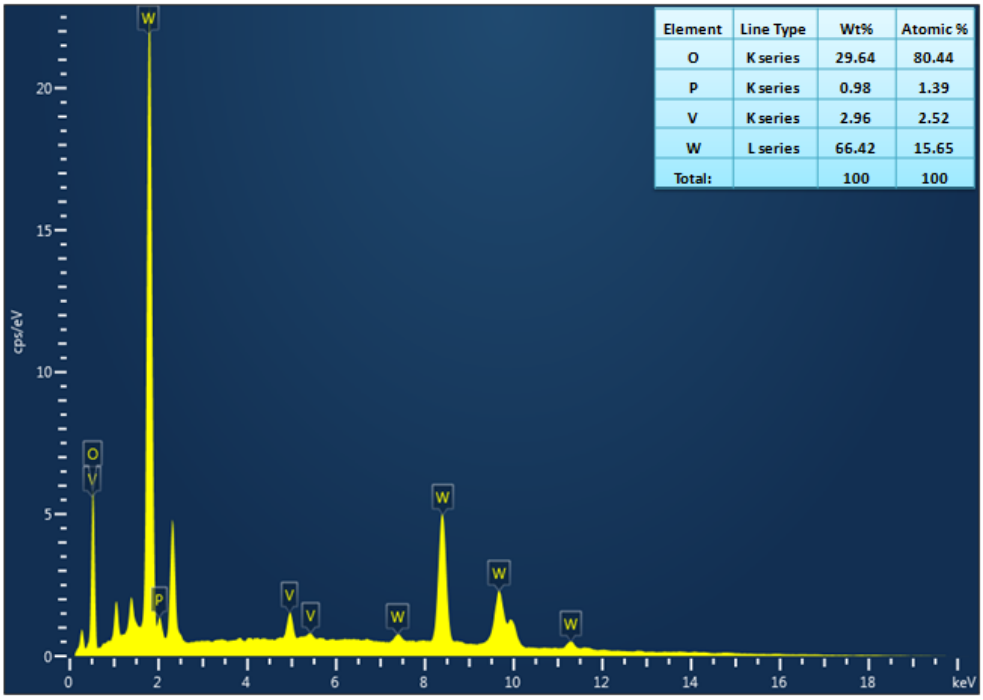


Fig. S1 (c) EDX of Heteropolyacid, HPV_2W

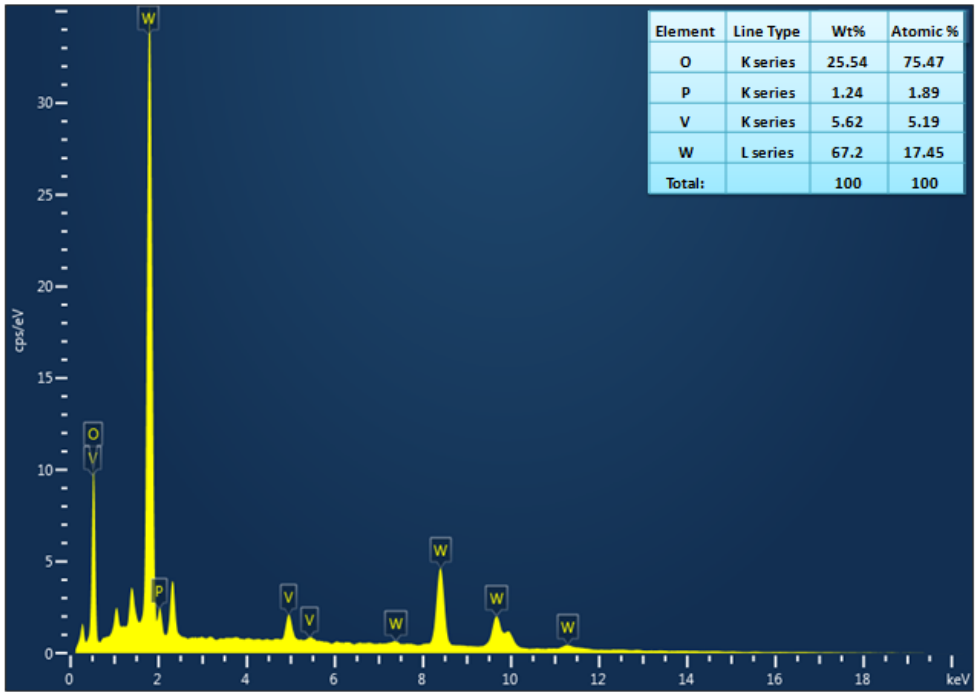


Fig. S1 (d) EDX of Heteropolyacid, HPV_3W

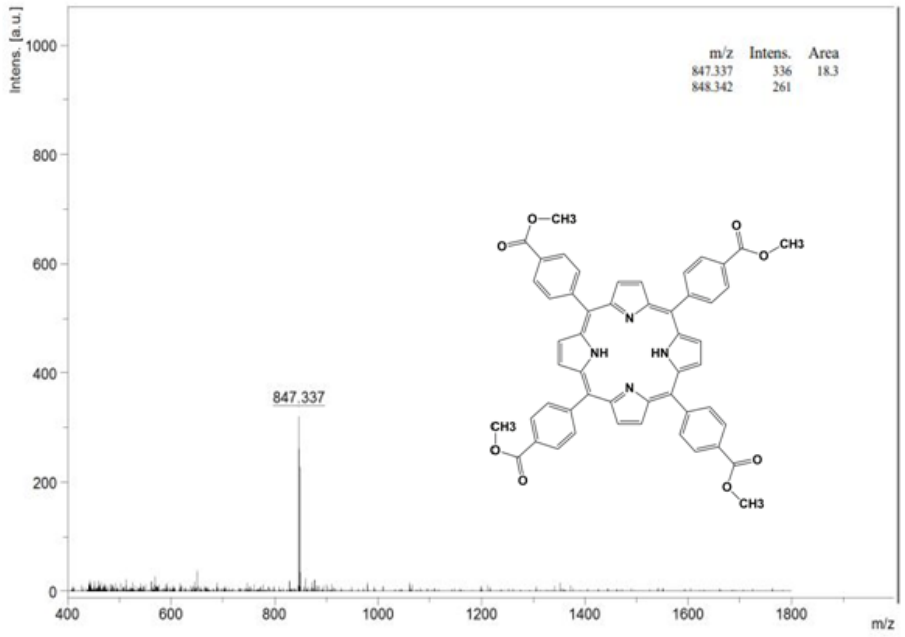


Fig. S2 (a) MALDI-TOF Mass spectrum of meso-Tetrakis(4-methoxycarbonylphenyl)porphyrin

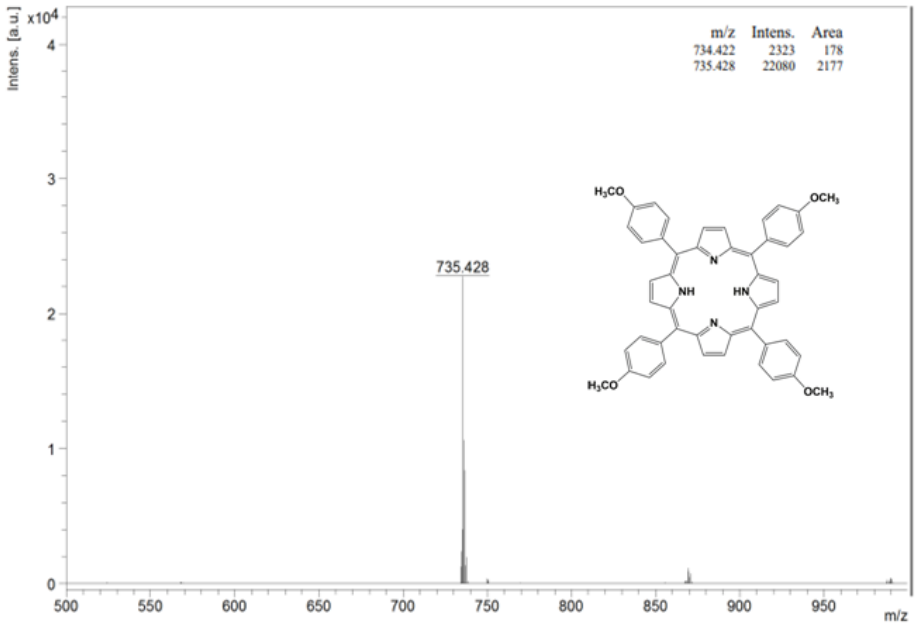


Fig. S2 (b) MALDI-TOF Mass spectrum of meso-Tetrakis(4-methoxyphenyl)porphyrin

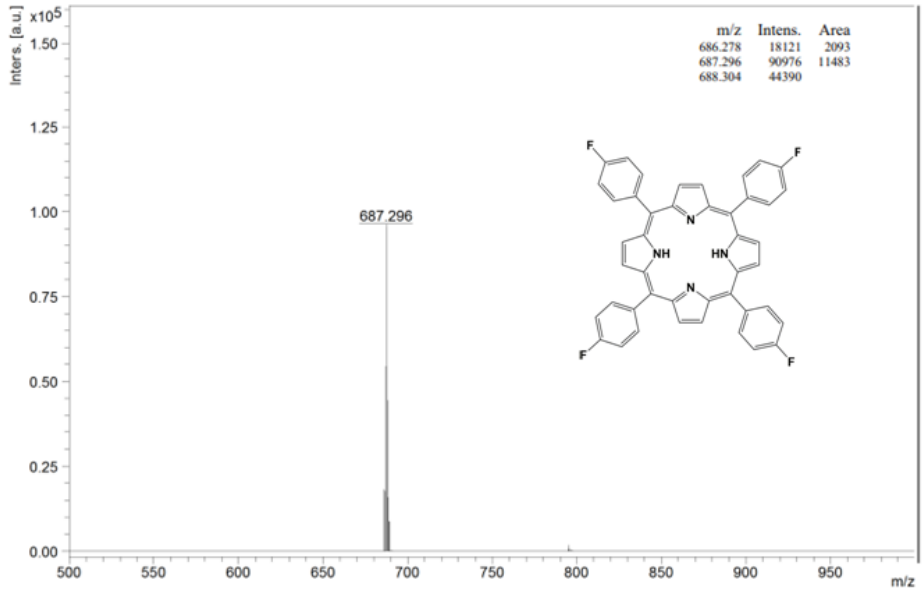


Fig. S2 (c) MALDI-TOF Mass spectrum of meso-tetra(4-fluorophenyl)porphyrin

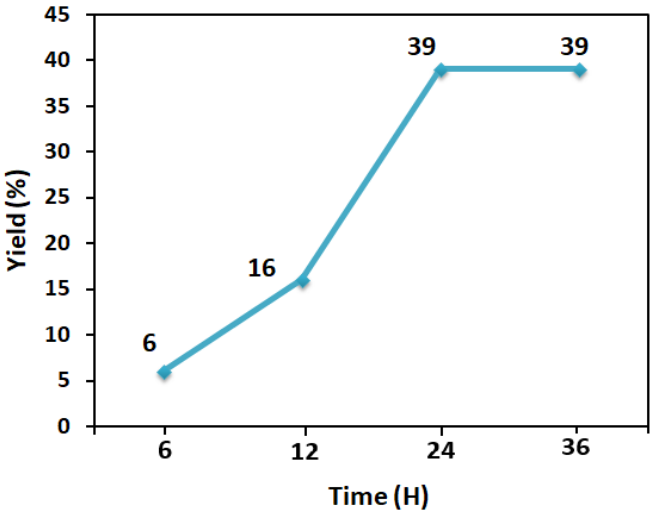


Fig. S3 Porphyrin yield monitored as a function of time

Reaction conditions: 1 mmol methyl 4-formylbenzoate, 1 mmol pyrrole, 10 mL CH_3CN, 0.5 mol% catalyst, 70 °C, Autoclave.

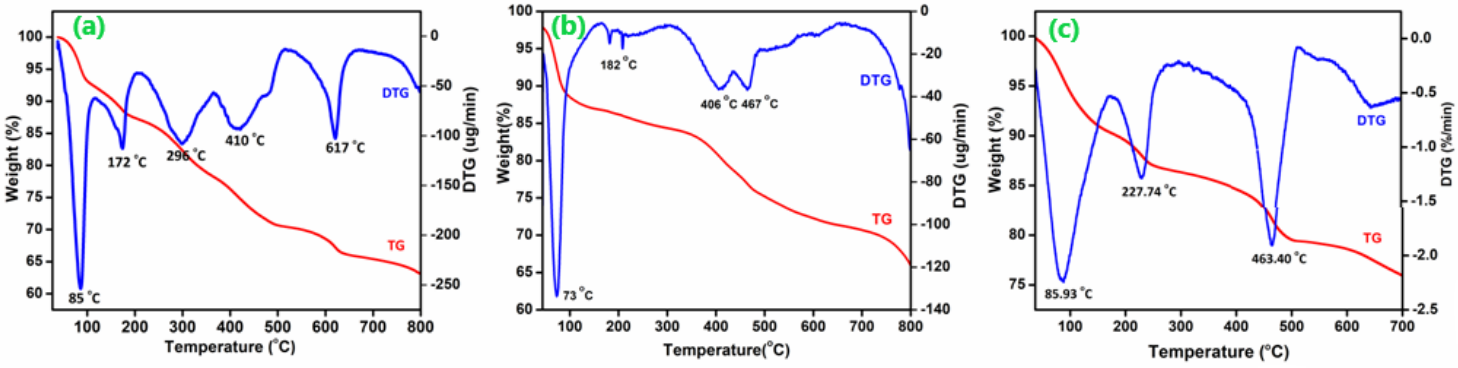


Fig. S4. TG-DTG Curves of (a) HPV_1W (b) HPV_2W (c) HPV_3W

2. Supplementary Table

Table S1 : Comparative evaluation of catalytic activity

Si. No.	Aldehyde	Solvent	Reaction Conditions	Yield (%)	Ref
1		Pyridine	Solvent: Sealed tubes at 220 °C for 48 Hr.	10%	[2]
2			Catalyst: BF_3-etherate (0.3Mm), Co catalyst: TFA (15 mM) Oxidant: DDQ in toluene, Time: 4 Hr	50-55%	[9]

3	Benzaldehyde	Dichloromethane	Catalyst: 10^{-2} M BF_3-$O(Et)_3$ 0.1 eqv. NaCl or 0.0031 eqv .$Bu_3BzlNCl$,	50%	[10]
4		Dichloromethane	Acid: BF_3-etherate/NaCl (1/250) mM, Oxidant-DDQ, Time-1 Hr.	58%	[11]
5		Dichloromethane	Catalyst: CF_3SO_2Cl, N_2 atmosphere, Aerated at 39 ^{o}C for 4 Hr.	62%	[13]
7			Acid: Toluenesulfonic acid, 1:1 molar ratio of pyrrole and benzaldehyde (3.73 mmol) and Toluenesulfonic acidground in Retsch MM 200 MILL at a frequency of 25 Hz. Pink solid dissolved in 50 mL $CHCl_3$, Oxidant: DDQ, 2 Hr stirring.	28%	[16]
8			High temperature gas phase conditions: Temperature controlled sand bath, 200 ^{o}C, Dioxygen as Oxidant	23%	[18]
9			High temperature gas phase conditions: Gas tight rubber septem, Temperature controlled sand bath, Dioxygen as Oxidant, Catalyst: Benzoic acid, 200 ^{o}C	32%	[19]
10		Propionic acid	Nitrobenzene oxidant, Microwave irradiation-650W, 200 ^{o}C, 3 bar internal pressure, 5-10 min.	35%	[23]
11			Catalyst: 0.2 eqv.of I_2, Reagent concentration: 10^{-2} mol/L, Microwave irradiation, Solvent: CH_2Cl_2, Oxidant: *p*-Chloranil (0.75 eqv).	35-47%	[25]
12		Propionic aicd	Nitrobenzene oxidant, Microwave irradiation, 5 min, 640 W.	20%	[26]
13		Dichloromethane	Acid ionic liquid (R-SO_3H- 3 mL), Oxidant: DDQ (14.5 mM), Quencher: Triethylamine, RT.	43%	[28]
14		Ionic liquid: $[HC_4im][CF_3CO_2]$	Reactants: 280 mM, 120 ^{o}C, 1 Hr	15%	[30]
15		Ionic liquid: $[HC_1im][CF_3CO_2]$	Reactants: 280 mM ,120 ^{o}C, 1 Hr.	8%	[31]
16		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving at 70 ^{o}C.	20%	**This Work**
17		Dichloromethane	Catalyst: CF_3SO_2Cl, N_2 atmosphere, Aerated at 39 ^{o}C for 3 Hr.	56%	[13]
18		Propionic acid: glacial acetic acid	Nitrobenzene oxidant, Reflux for 2 Hr.	50%	[14]
19			Acid: Toluenesulfonic acid, 1:1 molar ratio of pyrrole and 4-chloro Benzaldehyde (3.73 mmol) and Toluenesulfonic acidground in Retsch MM		

	4-Chlorobenzaldehyde		200 MILL at a frequency of 25 Hz. Pink solid dissolved in 50 mL $CHCl_3$, Oxidant: DDQ, 2 Hr stirring.	20%	[16]
20			High temperature gas phase conditions: Temperature controlled sand bath, 200 ^{o}C, Dioxygen as Oxidant	10%	[18]
21			High-temperature gas-phase conditions: Gas-tight rubber septum, Temperature controlled sand bath, Dioxygen as Oxidant, Catalyst: Benzoic acid, 200 ^{o}C.	25%	[19]
22		Propionic acid	Microwave irradiation 3 -5 min, extraction with CH_2Cl_2 (100 mL).	7%	[22]
23		propionic acid	10 mmol pyrrole (3.5 mL)+ Nitrobenzene (1.5 mL), microwave irradiation, 5 min, 640 W	21%	[26]
24		Dichloromethane	Catalyst: activated FSM-16, N_2 atmosphere, Oxidant- *p*-chloranil, Reflux 1-2 Hr.	7%	[34]
25		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving 70 ^{o}C.	27%	**This Work**
26	4-Fluorobenzaldehyde		Acid: Toluenesulfonic acid, 1:1 molar ratio of pyrrole and 4-Fluoro benzaldehyde (3.73 mmol) and Toluenesulfonic acid ground in Retsch MM 200 MILL at a frequency of 25 Hz. Pink solid dissolved in 50 mL $CHCl_3$, Oxidant: DDQ, 2 Hr stirring.	9.7%	[16]
27		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving 70 ^{o}C.	29%	**This Work**
28	4-Methoxybenzaldehyde	Dichloromethane	Catalyst: 10^{-2} M BF_3-O(Et)$_3$ 0.1 eqv. NaCl or 0.0031 eqv. $Bu_3BzlNCl$,	22%	[10]
29		Propionic acid	Oxidizing agent : Nitrobenzene (15 ml), 120 ^{o}C, 1 Hr	45%	[12]
30			High temperature gas phase conditions: Temperature controlled sand bath, 200 ^{o}C, Dioxygen as Oxidant	20%	[18]
31			High temperature gas phase conditions: Gas tight rubber septem, Temperature controlled sand bath, Dioxygen as Oxidant, Catalyst: Benzoic acid, 200 ^{o}C	25%	[19]
32			Catalyst: Activated charcoal treated with conc. nitric acid (68%), Temperature Controlled Sand Bath, 200 ^{o}C, 1 Hr.	33%	[20]
			Reactants: 0.1 mol pyrrole, Microwave irradiation		

33		Propionic acid	3 -5 min, Extraction with CH_2Cl_2 (100 mL).	15%	[22]
34		Ionic liquid: $[HC_4im][CF_3CO_2]$	Reactants : 280 mM, 120 °C, 1 Hr.	6.7%	[30]
35		Dichloromethane	Catalyst: activated FSM-16, N_2 atmosphere, Oxidant- *p*-chloranil, Reflux 1-2 Hr.	Trace amount	[34]
36		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving at 70 °C.	12%	**This Work**
37	4-Formylbenzoic acid	Propionic acid	Reactants: 0.24 M Pyrrole, Methanol/Pyridine, Refluxing Condition, 2 Hr.	34%	[5]
38		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving at 70 °C.	26%	**This Work**
39	Methyl 4-formylbenzoate		High temperature gas phase conditions: Gas tight rubber septum, Temperature controlled sand bath, Dioxygen as Oxidant, Catalyst: Benzoic acid, 200 °C.	19%	[19]
40		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving 70 °C.	39%	**This Work**
41	1-Naphthaldehyde		Acid: Toluenesulfonic acid, 1:1 molar ratio of pyrrole and 1-Naphthaldehyde (3.73 mmol) and Toluenesulfonic acid ground in Retsch MM 200 MILL at a frequency of 25 Hz. Pink solid dissolved in 50 mL $CHCl_3$, Oxidant: DDQ, 2 Hr stirring.	9.7%	[16]
42		Acetonitrile	Catalyst: $H_4PVW_{11}O_{40}$, Autoclaving 70 °C.	14%	**This Work**

Table S2 Influence of temperature on porphyrin yield

Entry	Temperature (°C)	Yield (%)
1.	50	15
2.	60	23
3.	70	39
4.	80	27

Reaction conditions: 1 mmol methyl 4-formylbenzoate, 1 mmol pyrrole, 10 mL CH_3CN, 0.5 mol% catalyst, Autoclave

Table S3 Screening the catalytic activity of various HPAs

Entry	HPA	Yield (%)
1.	HPW	10
2.	HPV_1W	39
3.	HPV_2W	15
4.	HPV_3W	18

Reaction conditions: 1 mmol methyl 4-formylbenzoate, 1 mmol pyrrole, 10 mL CH_3CN, 0.5 mol% catalyst, 70 °C, Autoclave

3. Supplementary Data

S1 : ^1H & ^{13}C NMR of synthesized porphyrins

Tetraphenylporphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (s, 8H), 8.22 (m, 8H), 7.77 (m, 12H),-2.75 (s, 2H, NH); ^{13}C NMR (101 MHz, $CDCl_3$: δ (ppm) 142.28, 134.61, 127.82, 126.80, 120.25. [1, 2, 3]

meso-Tetra(4-chlorophenyl)porphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.83 (s, 8H), 8.13 (d, 8H), 7.73 (d, 8H), -2.88 (s, 2H, NH); ^{13}C NMR (101 MHz, $CDCl_3$: δ (ppm) 140.44, 135.58, 134.48, 127.13, 119.07. [1]

meso-Tetrakis(4-carboxyphenyl)porphyrin: ^1H NMR (400 MHz, DMSO): 10.03 (s, 4H, COOH), 8.83 (s, 8H), 8.38 (d, 8H), 8.32 (d, 8H), -2.93 (s, 2H, NH); ^{13}C NMR (101 MHz, DMSO: δ (ppm) 173.06, 151.52, 140.33, 136.58, 133.72, 125.42. [4]

meso-Tetrakis(4-methoxycarbonylphenyl)porphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.81 (s, 8H), 8.43 (d, 8H), 8.27 (d, 8H), 4.10 (s, 12H), -2.83 (s, 2H, NH); ^{13}C NMR (101 MHz, $CDCl_3$: δ (ppm) 167.34, 146.70, 134.61, 129.84, 128.09, 119.48, 52.59, 29.80, 27.34. [1]

meso-Tetrakis(4-methoxyphenyl)porphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.82 (s, 8H), 8.13 (d, *J = 8.0 Hz*, 8H), 7.27 (d, *J = 8.0 Hz*, 8H), 4.11 (s, 12H), -2.77 (s, 2H, NH) [1]

meso-Tetra(4-fluorophenyl)porphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.84 (s, 8H), 8.17 (s, 8H), 7.47 (s, 8H), -2.81 (s, 2H, NH).[5]

meso-Tetrakis(2,5-dimethylphenyl)porphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (s, 8H), 7.47 (d, 8H), 7.25 (s, 4H), 2.53 (s, 12 H), 1.98 (s, 12H), -2.66 (s, 2H, NH); ^{13}C NMR (101 MHz, $CDCl_3$: δ (ppm) 141.42, 139.39, 136.64, 135.12, 133.35, 128.81, 119.01, 114.23, 29.47, 22.80, 14.29

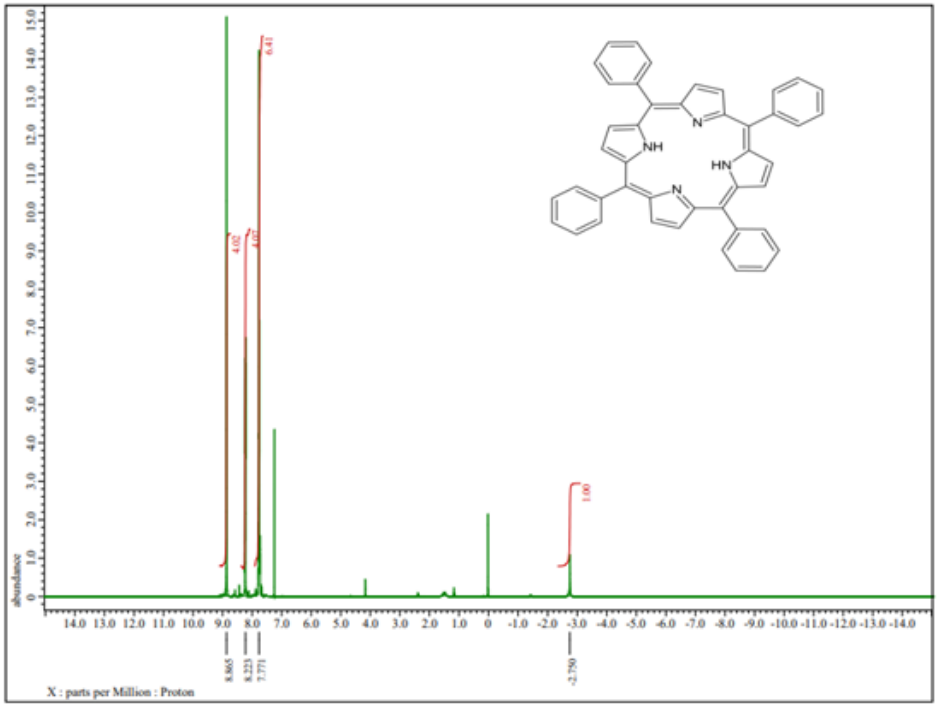
meso-Tetrakis(4-ethynylphenyl)porphyrin: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.88 (s, 8H), 8.19 (d, 8H), 7.91 (d, 8H), 3.35 (s, 4H), -2.82 (s, 2H, NH); ^{13}C NMR (101 MHz, $CDCl_3$: δ (ppm) 148.16, 139.87, 136.14, 134.57, 77.41

meso-Tetrakis(2-hydroxy-3,5-dichlorophenyl)porphyrin: ^1H NMR (400 MHz, DMSO): 9.87 (s, 4H, OH), 8.88 (s, 8H), 8.31 (s, 4H), 7.88 (s, 4H), -2.86 (s, 2H, NH); ^{13}C NMR (101 MHz, DMSO: δ (ppm) 197.01, 169.83, 137.77, 137.19, 135.46, 120.68, 119.34, 62.89, 61.19, 43

meso-Tetrakis(1-naphthyl)porphyrin: ^1H NMR (400 MHz, DMSO): 8.47 (s, 8H), 8.24 (m, 8H), 8.09 (d, 4H), 7.82 (m, 4H), 7.46 (m, 4H), 7.10 (m, 8H), -2.26 (s, 2H, NH).[6]

Tetraphenylporphyrin:

^{1}H NMR Spectrum



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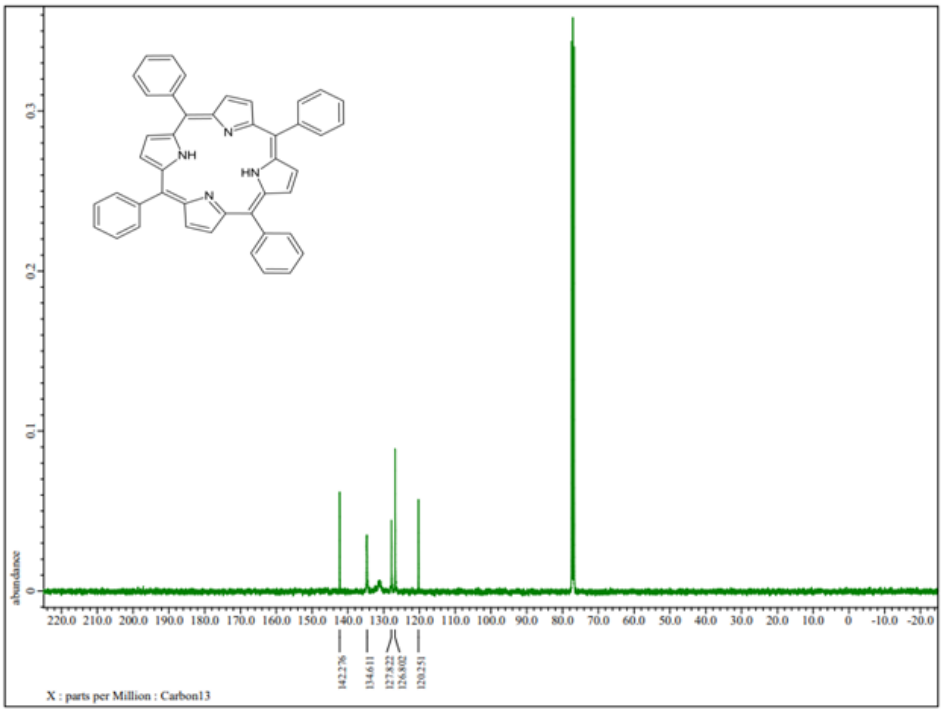
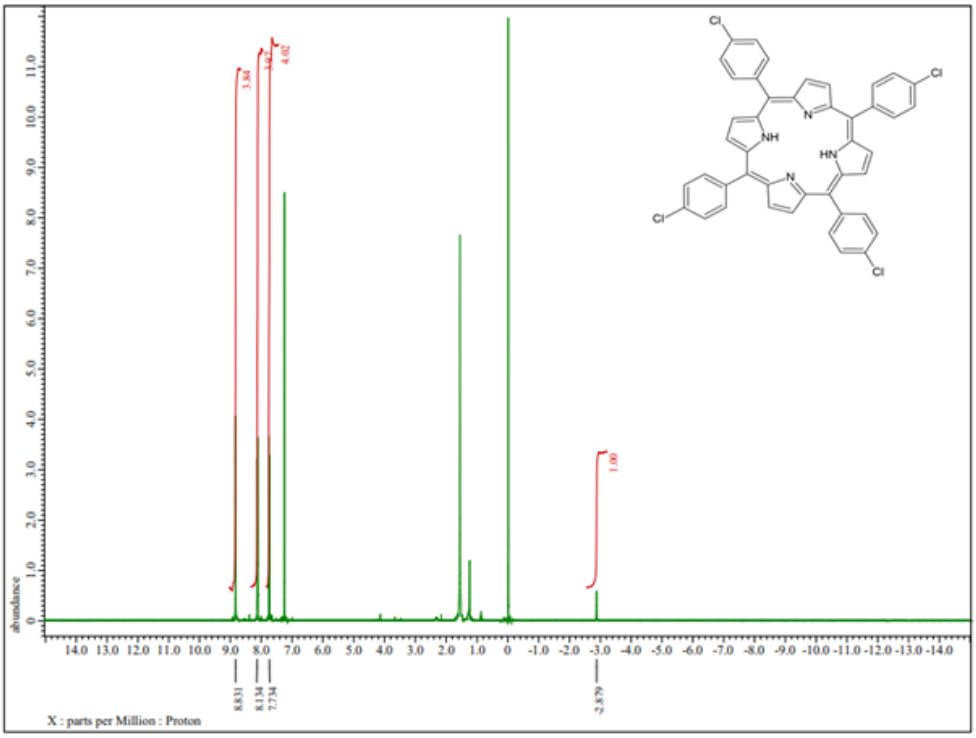


meso-Tetra(4-chlorophenyl)porphyrin:

^{1}H NMR Spectrum



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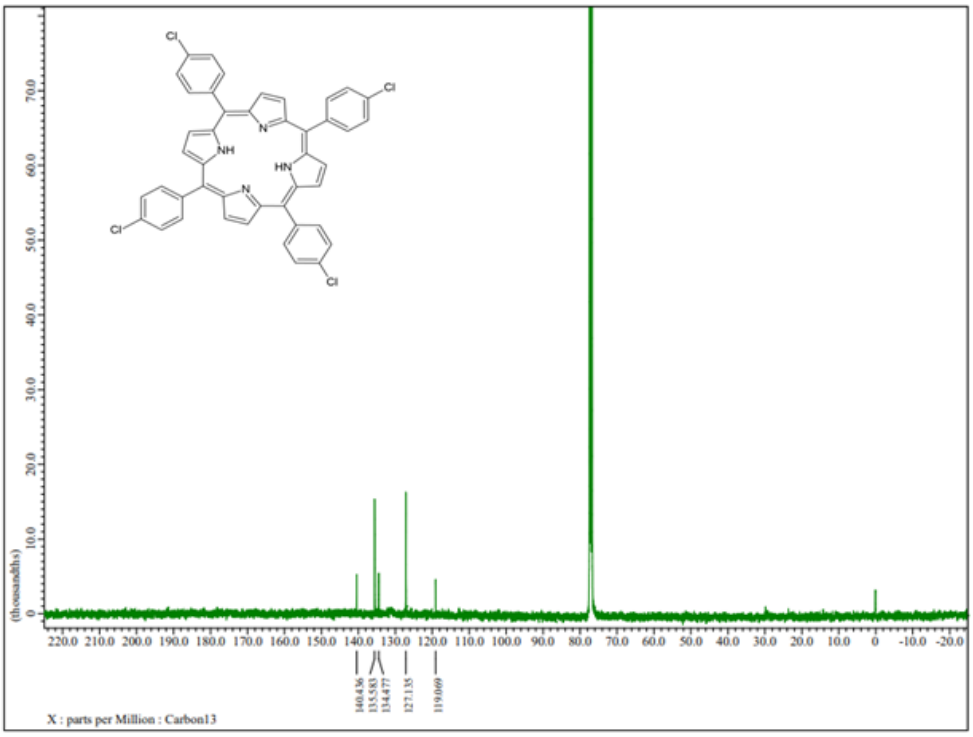

meso-Tetrakis(4-carboxyphenyl)porphyrin:

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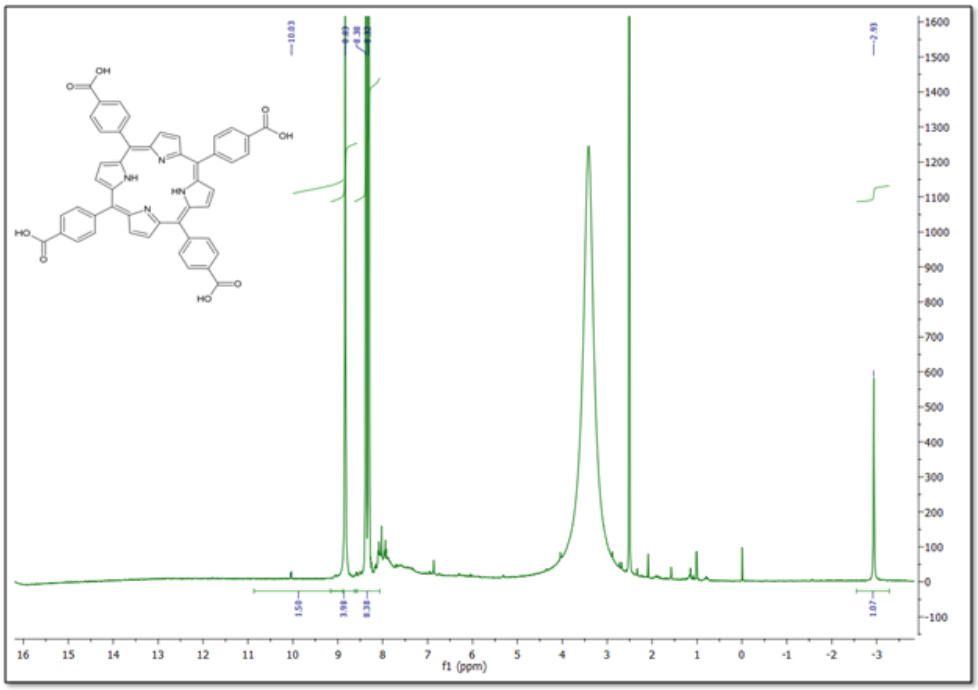

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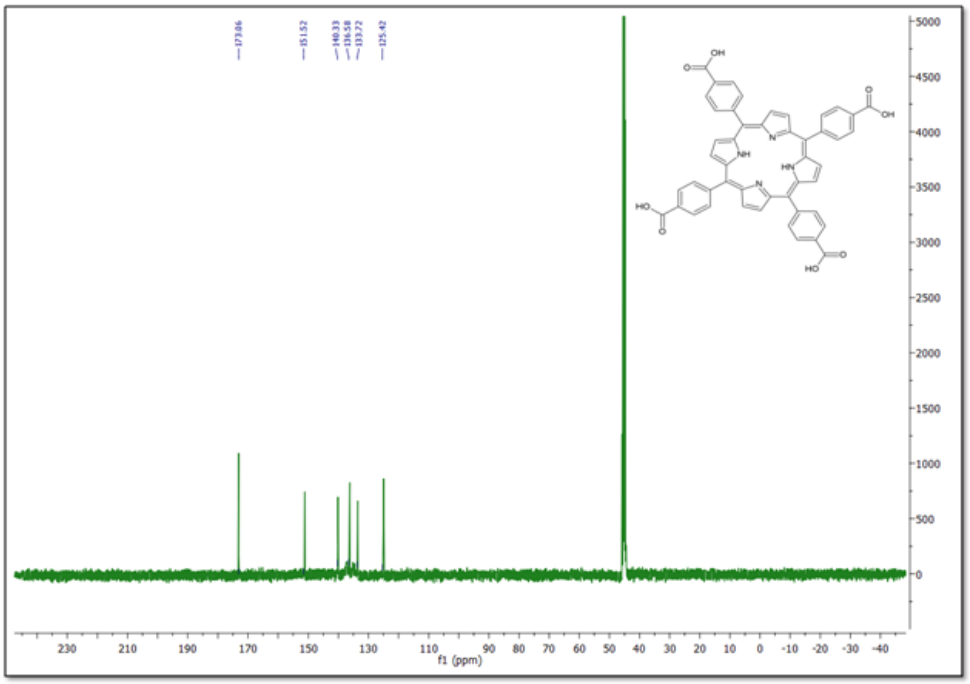

meso-Tetrakis(4-methoxycarbonylphenyl)porphyrin:

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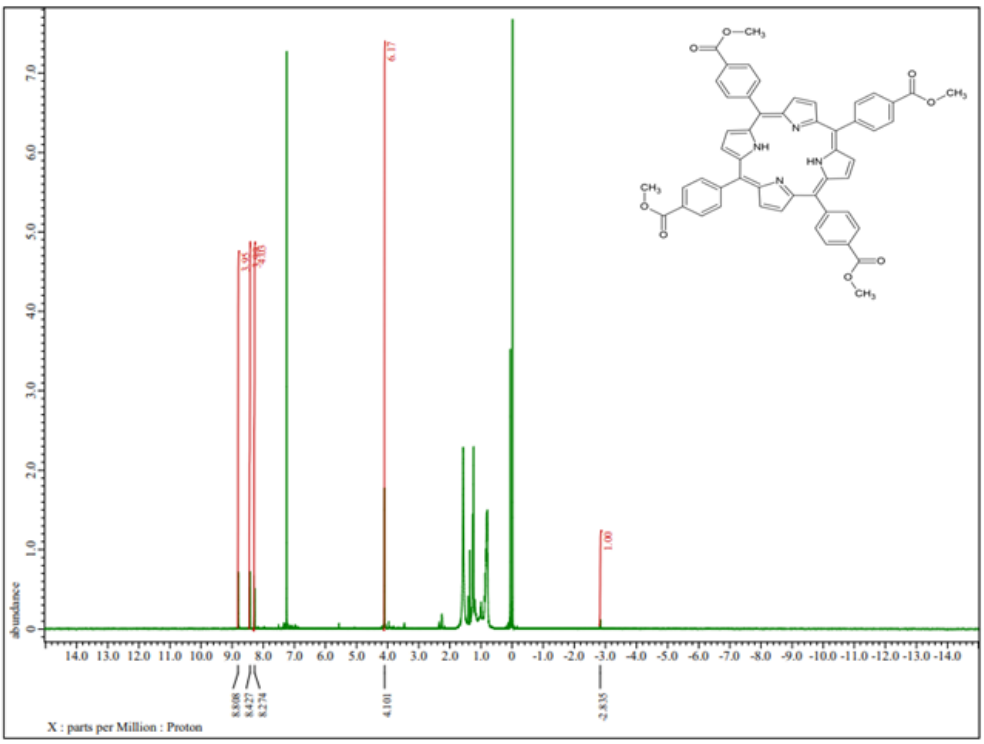

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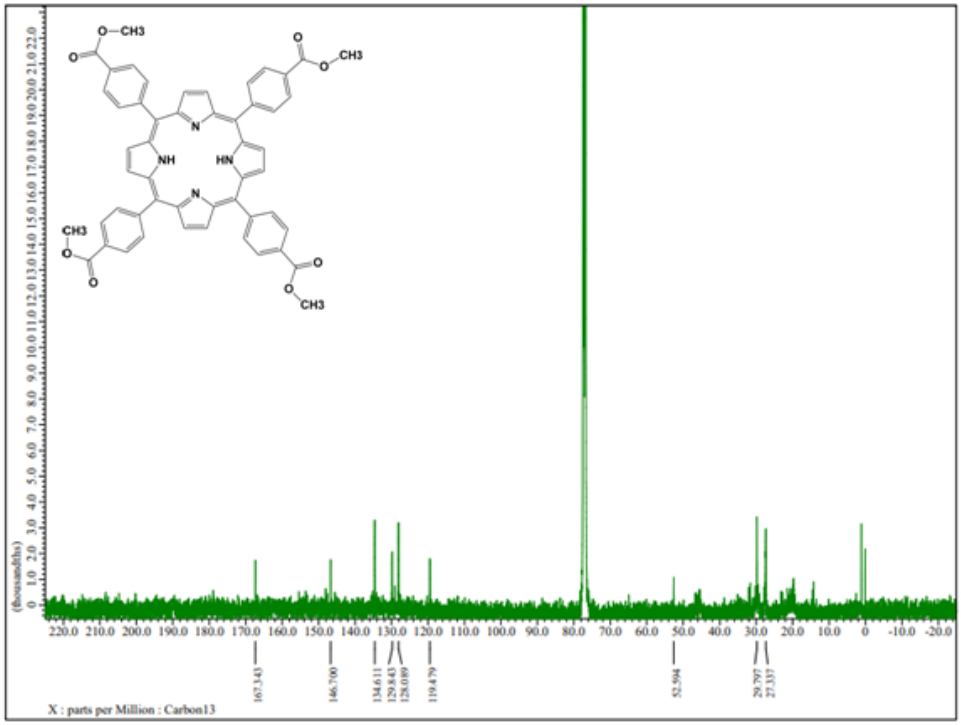

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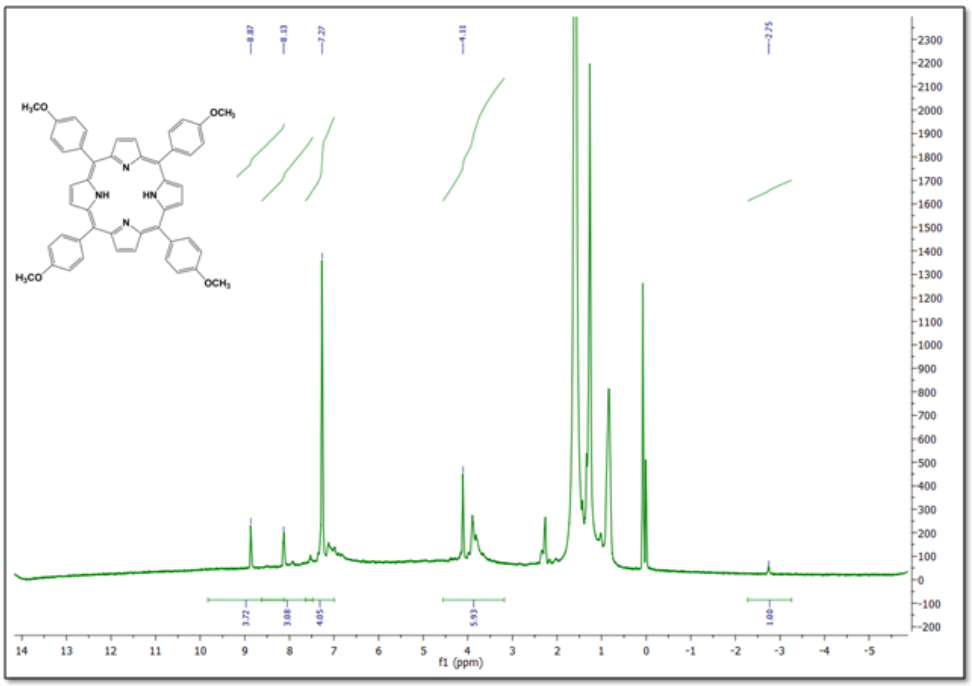

meso-Tetra(4-fluorophenyl)porphyrin:

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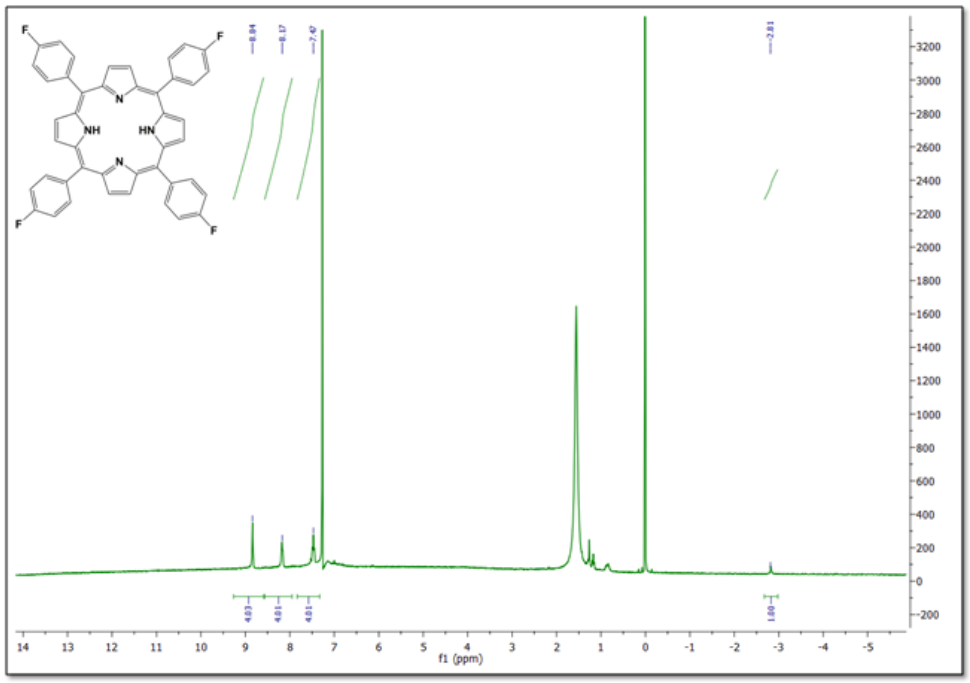

meso-Tetrakis(2,5-dimethylphenyl)porphyrin:

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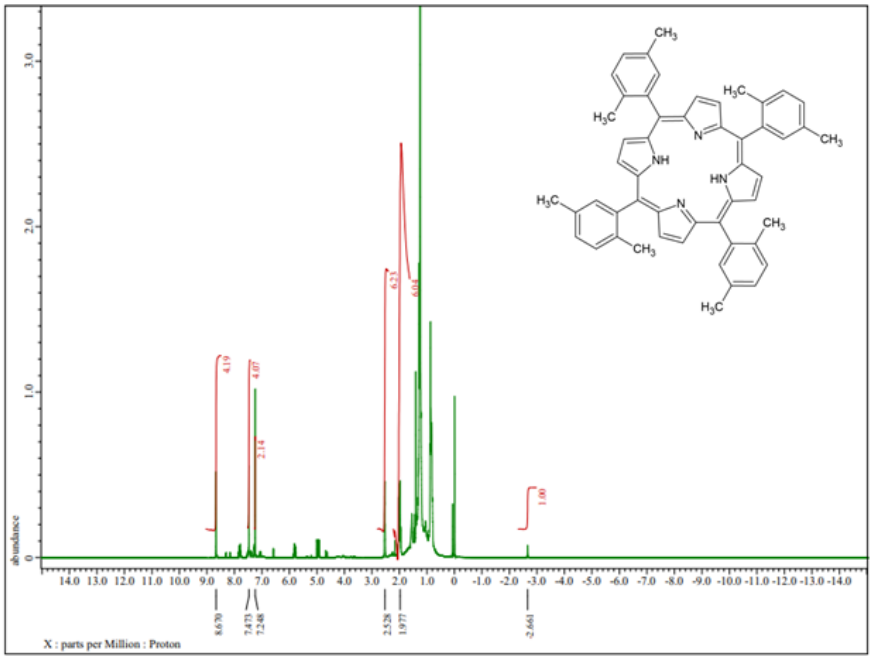
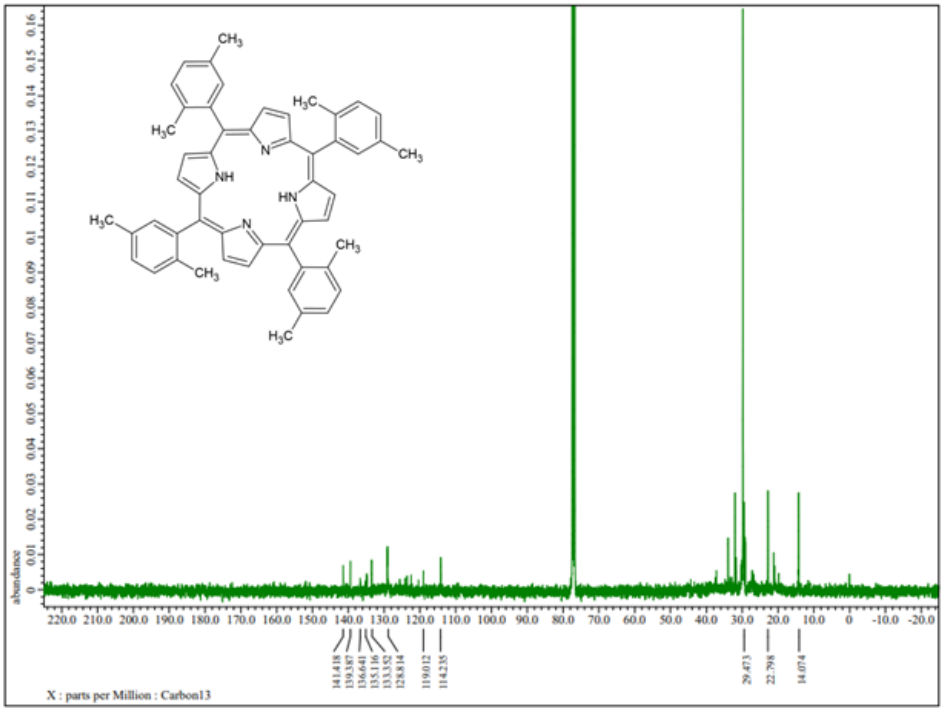
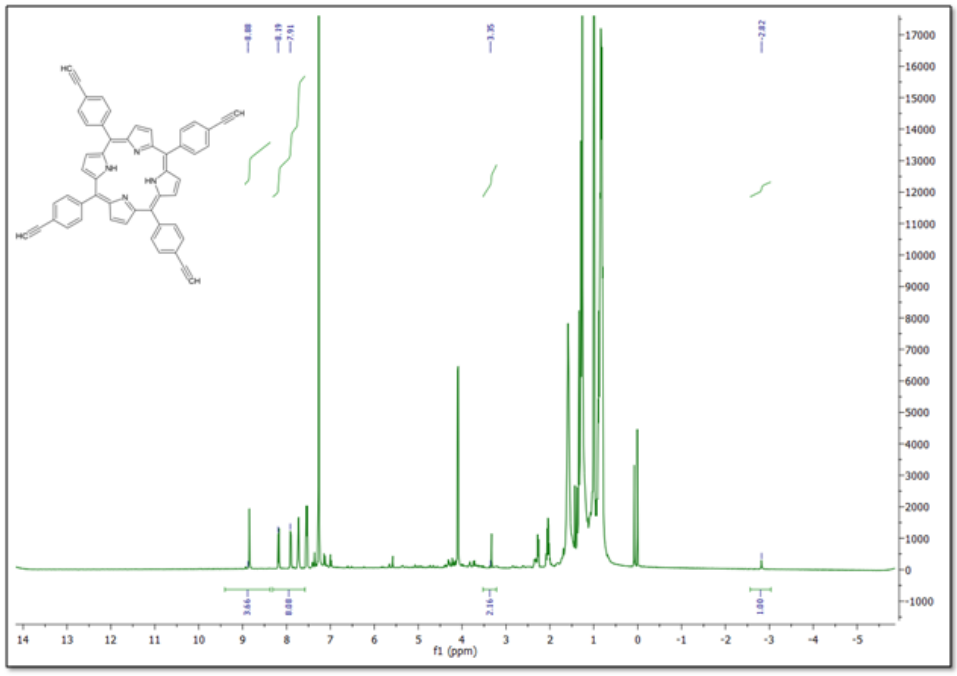


^{13}C NMR Spectrum

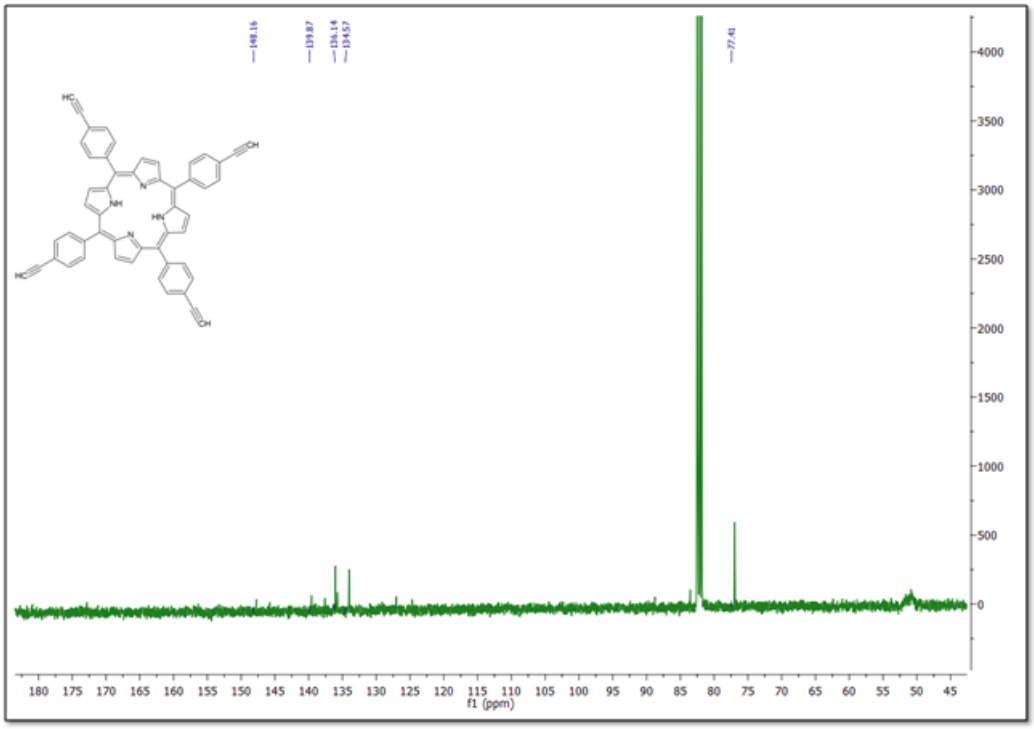


meso-Tetrakis(4-ethynylphenyl)porphyrin

^{1}H NMR Spectrum

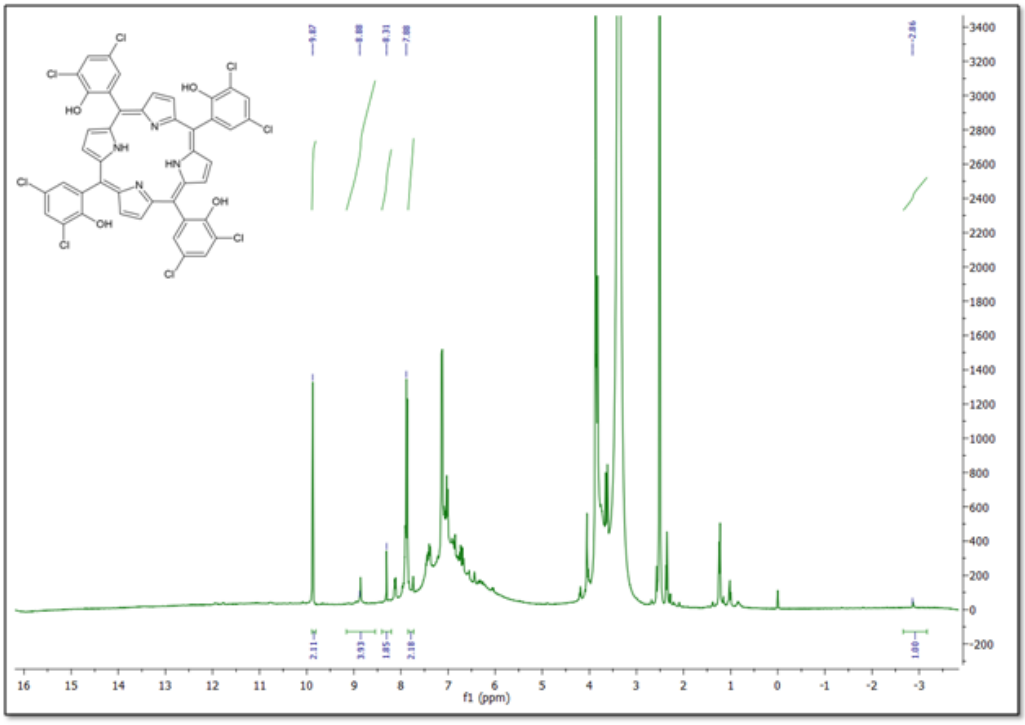


^{13}C NMR Spectrum



meso-Tetrakis(2-hydroxy-3,5-dichlorophenyl)porphyrin:

^{1}H NMR Spectrum



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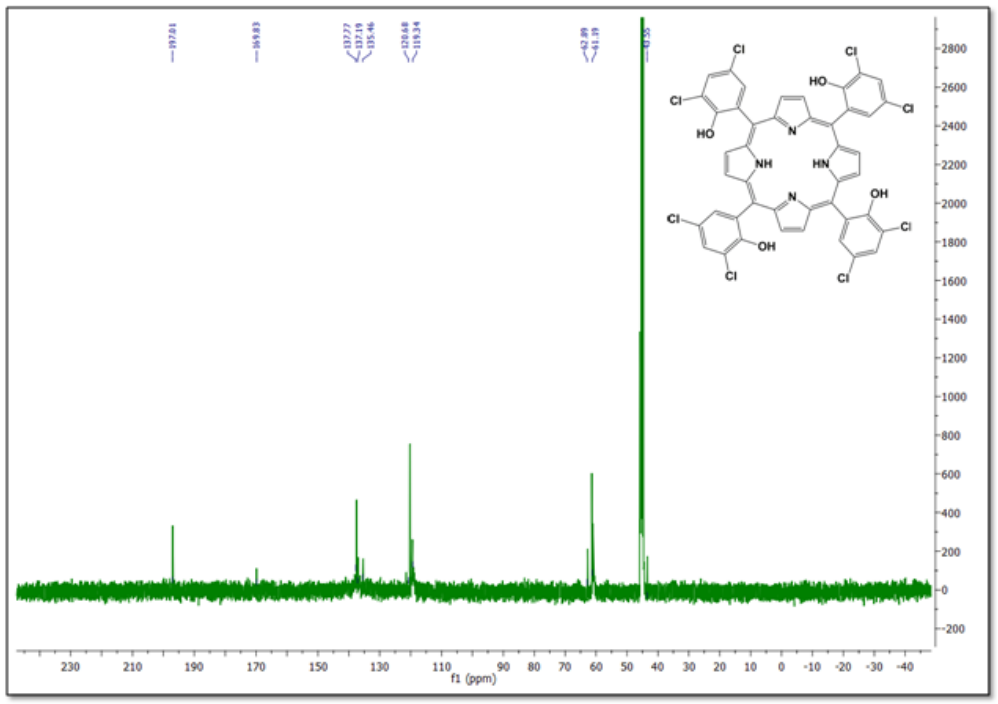
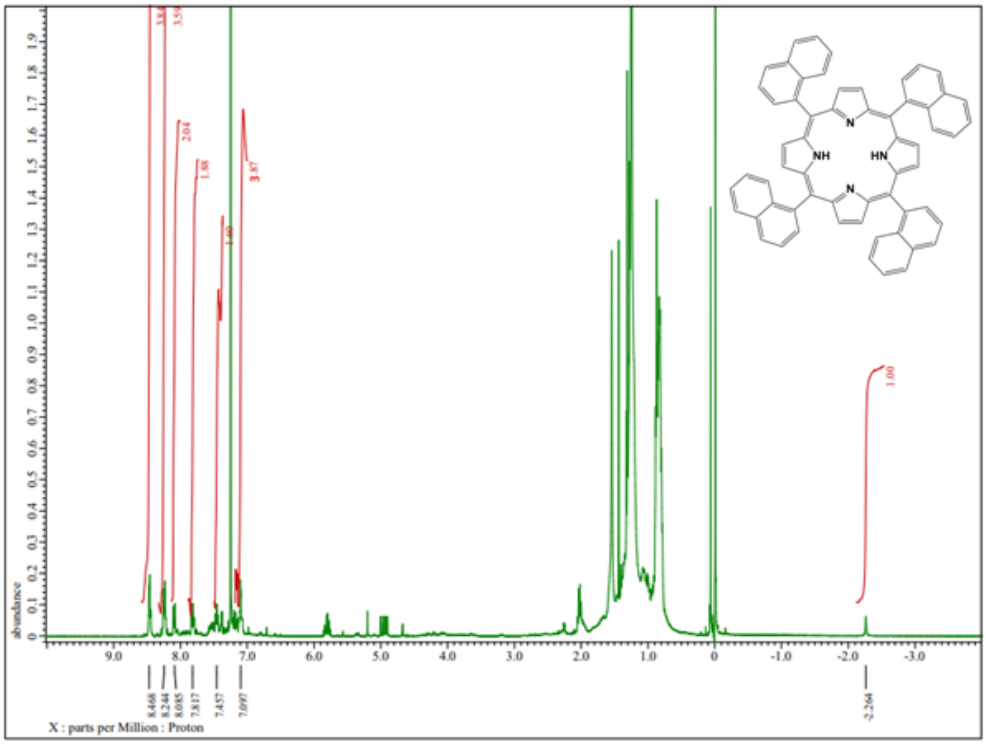


meso-Tetrakis(1-naphthyl)porphyrin:

^{1}H NMR Spectrum



Reference for supplementary information

1. S. Mondal, T. Pain, K. Sahu and S. Kar, *ACS Omega*, 2021, **6**, 22922−22936

2. D. Mohajer, S. Zakavi, S. Rayati, M. Zahedi, N. Safari, H. R. Khavasi and S. Shahbazian, *New J. Chem.,* 2004, **28** , 1600–1607

3. H. Shy, P. Mackin, A. S. Orvieto, D. Gharbharan, G. R. Peterson, N. Bampos and T. D. Hamilton, *Faraday Discuss.***,** 2014, **170**, 59-69.

4. F. E.-Almeida, C. D.-Uribe, W. Vallejo, O. Peña, D. G.-Camargo, A. R. R.Bohórquez, X. Zarate and E. Schott, *Chemical Papers*, 2021, **75**, 4817-4829.

5. H. Yaman and A. Kayan, *J Porphyr Phthalocyanines*, 2017, **21**, 231-237.

6. C. H. da Silveira, E. Garoforo, O. A. Chaves, P. F. B. Gonçalves, L. Streit and B. A. Iglesias, *Inorganica Chimica Acta*, 2018, **482**, 542-553.