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Triazole linked ruthenium(II) porphyrin: influence of connectivity pattern on photophysical and electrochemical properties

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Supporting Information

Materials Used

Pyrrole was distilled prior to use. All other reagents (Propionic acid- Spectrochem, 2-ethynyl pyridine - Alfa Aesar, 2-bromo pyridine – Spectrochem, LiCl – Spectrochem, $RuCl_3.xH_2O$ – Alfa Aesar, Solvents – Analytical grade) were of analytical grade and used without further purification. cis-$Ru(bpy)_2Cl_2$ was synthesized according to literature procedure.[1] Solvents for the electrochemical measurements were distilled from calcium hydride under argon. The compounds were purified using silica gel (60-120 mesh), neutral alumina chromatography.

Experimental

Synthesis

***5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin* (1)**

To a solution of pyrrole (0.8 ml, 12.1 mmol) in $CHCl_3$ (1.2 L), 3,5-di-*tert*-butylbenzaldehyde (2 g, 9.17 mmol), 4-[(trimethylsilyl)ethynyl]benzaldehyde (0.617 g, 3.04 mmol) and BF_3OEt_2 (1.19 ml) were added. After stirring the reaction mixture for 1 h at rt, DDQ (2.07 g, 9.11 mmol) was added and the mixture again stirred for 1 h. In order to neutralize the acid catalyst, Et_3N (0.5 ml) was added and the solution stirred for 10 min. The solvent was evaporated and residue was chromatographed on silica gel with 1:9 ratio chloroform/petroleum ether mixture as eluent. The second band was collected in 17% yield. The compound (528 mg, 0.516 mmol) was then

dissolved in MeOH–CH_2Cl_2 (20 ml) solution and K_2CO_3 (91 mg, 1.63 mmol) was added. After stirring at rt for 2 h, the solution was quenched with H_2O, the organic phase was washed with $CHCl_3$ and brine, dried with Na_2SO_4 anhydrous, and the solvent was removed in vacuum affording the deprotected porphyrin derivative (311 mg, 62%) as a pure red solid.

R_f : 0.6 (1:9 $CHCl_3$/Petroleum Ether); **UV−visible ($CHCl_3$), λ_{abs}/nm (log ε):** 422 (5.18), 517 (3.80), 554 (3.55), 592 (3.25), 648 (3.02); **^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm:** 8.90 (m, 6H, βH), 8.80 (d, *J*=4.56 Hz, 2H, βH), 8.18 (d, *J*=8 Hz, 2H, ArH), 8.08 (m, 6H, ArH), 7.87 (d, *J*=8 Hz, 2H, ArH), 7.79 (m, 3H), 3.31 (s, 1H), 1.51 (s, 54H, *t*-butyl), -2.59 (br.s., 2H, -NH); **^{13}C NMR (100 MHz, Chloroform-*d*) δ ppm:** 148.8, 148.1, 146.5, 146.5, 139.4, 134.5, 129.9, 129.8, 121.1, 114.2, 83.8, 78.2, 31.8, 29.9; **ESI-MS:** calculated 974.6226 ($C_{70}H_{78}N_4$), observed 975.6260 $(M+H)^+$.

***5-(4-acetamidophenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin* (4)**

3,5-di-*tert*-butylbenzaldehyde (2.99 g, 13.6 mmoles) and 4-acetamidobenzaldehyde (0.74 g, 4.5 mmoles) in propionic acid (240 ml) were refluxed with freshly distilled pyrrole (1.25 ml, 18 mmoles) for 2 h. The reaction mixture was cooled to room temperature, poured in ice cold water and left overnight. The black residue so formed was filtered and chromatographed on silica gel with 8:2 ratio chloroform/petroleum ether mixture as eluent. The second band was collected in 17% yield (0.771 g).

R_f : 0.3 ($CHCl_3$); **UV−visible ($CHCl_3$), λ_{abs}/nm (log ε):** 422 (5.02), 518 (4.66), 554 (4.65), 591 (4.61), 648 (4.61); **^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm:** 8.91 (s, 4H, βH), 8.89 (d, *J*=4.56 Hz, 2H, βH), 8.85 (d, *J*=5.04 Hz, 2H, βH), 8.13 (d, *J*=8.28 Hz, 2H, ArH), 8.09 (m, 6H, ArH), 7.80 (m, 5 H, ArH), 7.52 (br.s., 1H, -NH), 2.28 (s, 3H, $-CH_3$), 1.53 (s, 54H, *t*-butyl), -2.76 (br.s., 2H, -NH); **^{13}C NMR (100 MHz, Chloroform-*d*) δ ppm:** 168.6, 148.7, 141.3, 138.2, 137.4, 134.9, 129.9, 129.7, 123.6, 123.4, 121.5, 121.0, 117.9, 35.1, 31.8, 31.3, 29.8; **ESI-MS:** calculated 1007.6441 ($C_{70}H_{81}N_5O$), observed 1008.6519 $(M+H)^+$, 504.8278 $(M+2H)^{2+}$.

***5-(4-aminophenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin* (5)**

Porphyrin (**1**) (0.234 g, 0.232 mmoles) in a mixture of dry EtOH (120 mL) and conc. HCl (80 mL) was vigorously stirred in a preheated oil bath at 80 °C for 24 h under N_2. After completion of reaction, the solution was cooled to room temperature and then neutralized with 5% aq. NaOH solution to p*H* 8-9. The mixture was extracted with $CHCl_3$ (2×100 ml). The residue was dissolved in a minimum amount of $CHCl_3$ and chromatographed on silica gel with 1:1 ratio chloroform/petroleum ether mixture as eluent. The compound was collected in 92 % yield (0.206 g).

R_f : 0.7 ($CHCl_3$); **UV−visible ($CHCl_3$), λ_{abs}/nm (log ε):** 422 (5.27), 518 (4.78), 556 (4.76), 592 (4.74), 649 (4.74); **^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm:** 8.85 (d, *J*=4.6 Hz, 2H, βH), 8.80 (m, 6H, βH), 8.01 (m, 6H, ArH), 7.93 (d, *J*=7.8 Hz, 2H, ArH), 7.71 (m, 3H, ArH), 6.97 (d, *J*=7.8 Hz, 2H, ArH), 1.44 (s, 54H, *t*-butyl), -2.76 (br.s., 2H, -NH); **^{13}C NMR (100 MHz, Chloroform-*d*) δ ppm:** 148.7, 141.4, 137.2, 135.6, 129.8, 129.7, 126.8, 121.0, 120.9, 113.5, 110.1, 35.1, 31.8; **ESI-MS:** calculated 965.6335 ($C_{67}H_{77}N_5$), observed 966.6408 $(M+H)^+$.

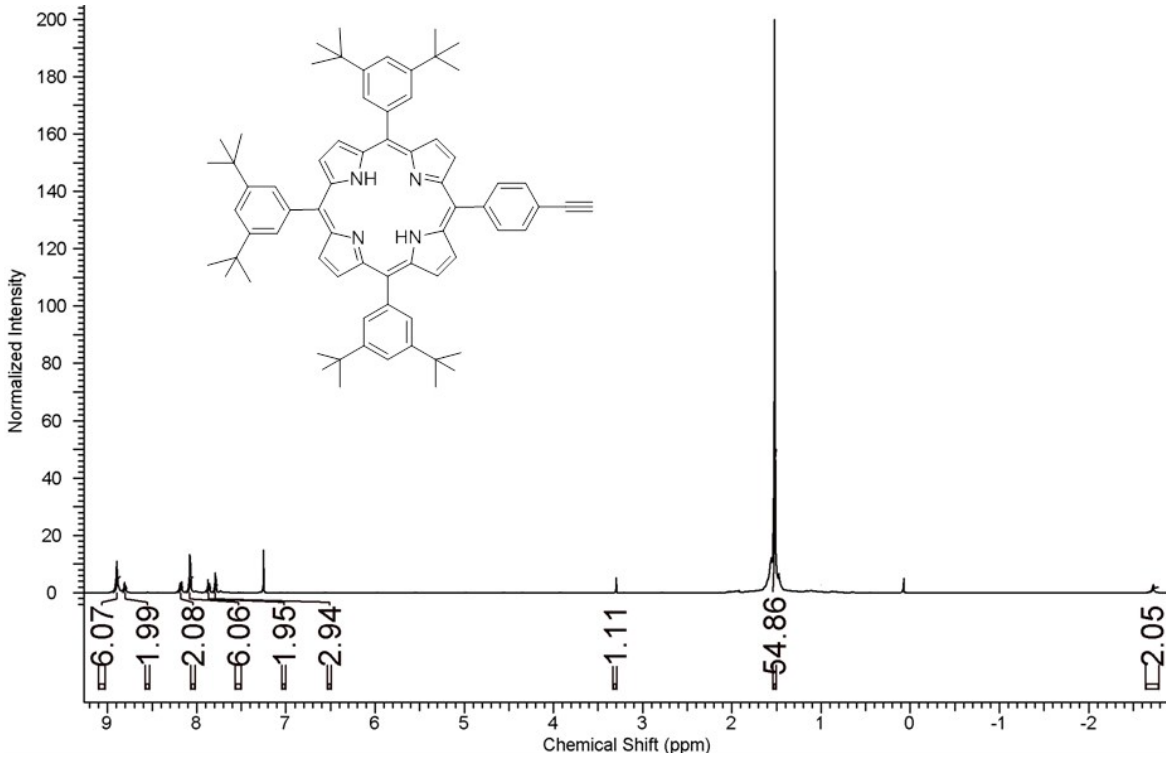
***5-(4-azidophenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin* (6)**

Porphyrin **2** (0.206 g, 0.21 mmoles) was dissolved in TFA (3.36 ml) and cooled to 0 °C in ice bath. Sodium nitrite (29.44 mg, 0.48 mmoles) was dissolved in 1 ml of water and added to the mixture, which was then stirred for 30 min at 0 °C. Sodium azide (36.71 mg, 0.64 mmoles) was dissolved in 1 ml of water and added to the reaction mixture. After the reaction was stirred in ice for 1 h, cold water was added to the flask. The crude mixture was extracted with CH_2Cl_2 and the organic layer was washed with water until it turned purple. The organic phase was dried over Na_2SO_4, filtered and dried. The residue was chromatographed on silica gel using with 3:7 ratio chloroform/petroleum ether as eluent, and the desired product was obtained after evaporation in 92 % yield (0.194 g).

R_f : 0.6 (60% Pet. Ether : $CHCl_3$); **UV−visible ($CHCl_3$), λ_{abs}/nm (log ε):** 422 (5.37), 518 (4.61), 554 (4.43), 592 (4.20), 647 (4.11); **^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm:** 8.82-8.75 (m, 8H, βH), 8.14 (d, *J*=7.48 Hz, 2H, ArH), 8.00 (m, 6H, ArH), 7.72 (m, 3H, ArH), 7.45 (d, *J*=7.6Hz, 2H, ArH), 1.45 (s, 54H, *t*-butyl), -2.78 (br.s., 2H, -NH); **^{13}C NMR (100 MHz, Chloroform-*d*) δ ppm:** 148.7, 141.1, 138.1, 135.8, 129.8, 129.5, 126.8, 121.6, 120.5, 113.6,

109.6., 35.2, 31.7; **ESI-MS:** calculated: 991.6240 ($C_{68}H_{77}N_7$), observed 992.6313 $(M+H)^+$; **FT IR (cm^{-1})**: 2120 (azide).

Characterization of synthesized compounds



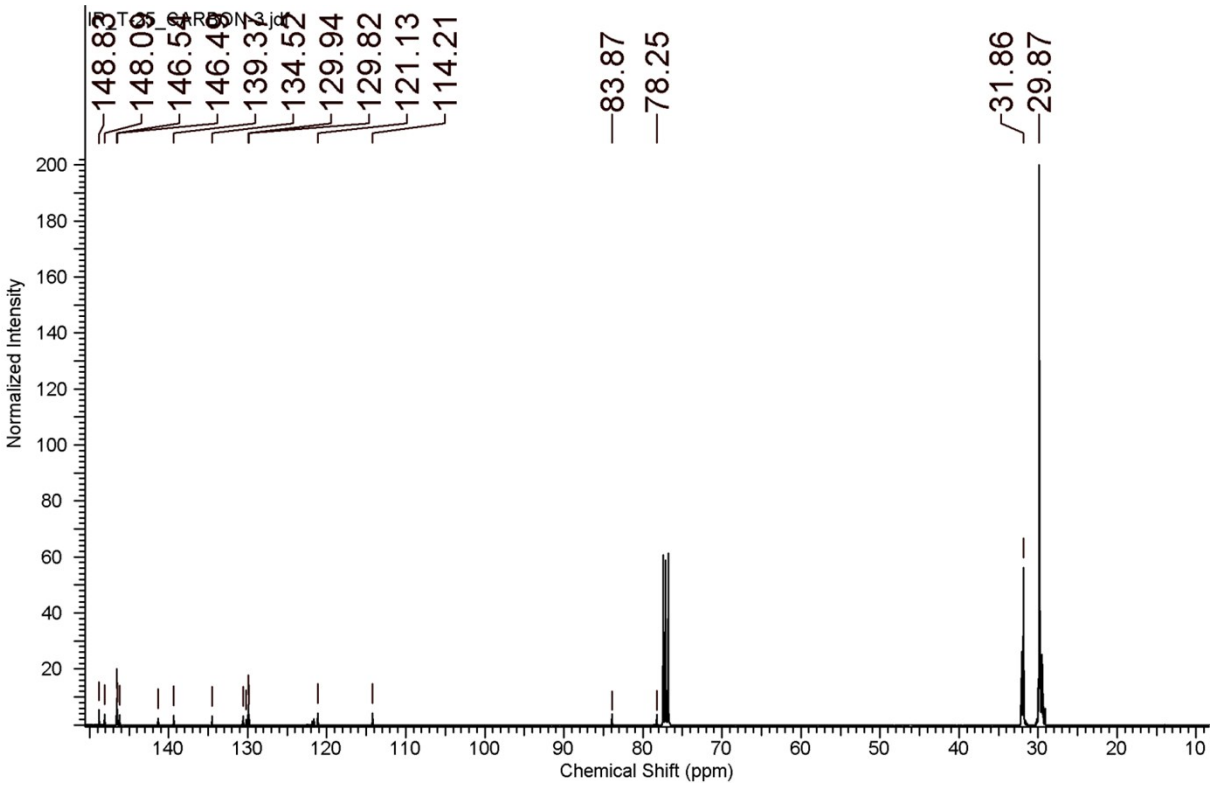
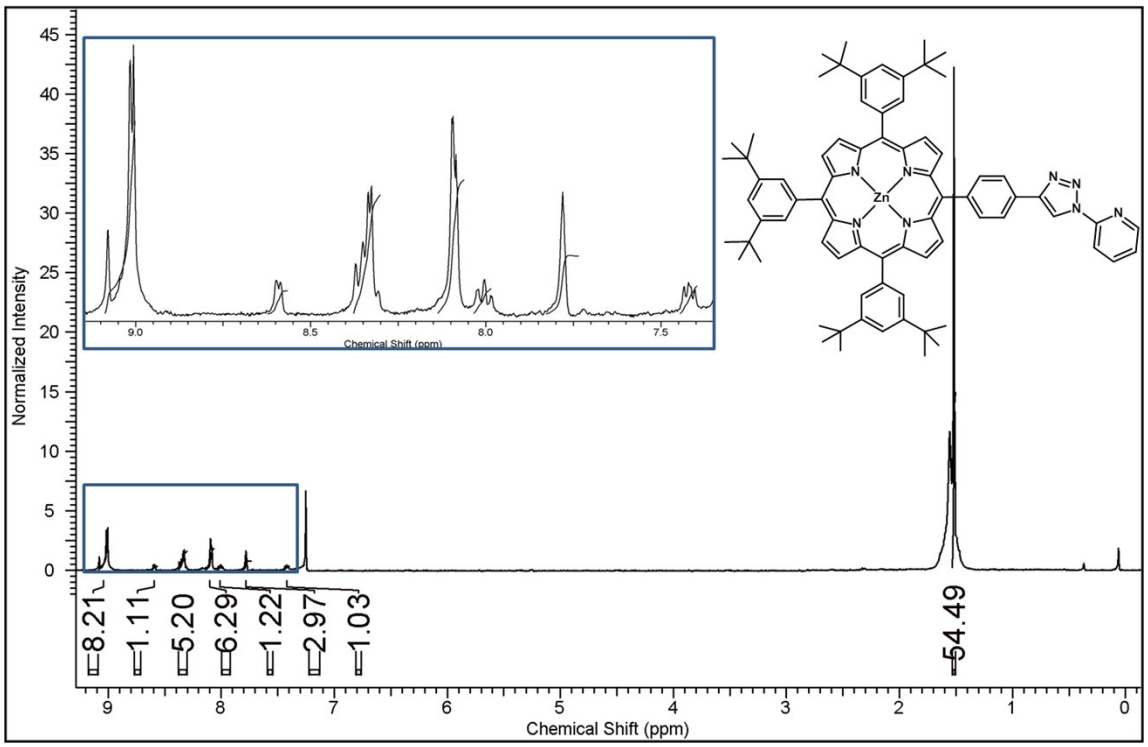


Figure S1: ^{1}H NMR and ^{13}C NMR spectrum of *5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin* (1) in Chloroform-*d*.



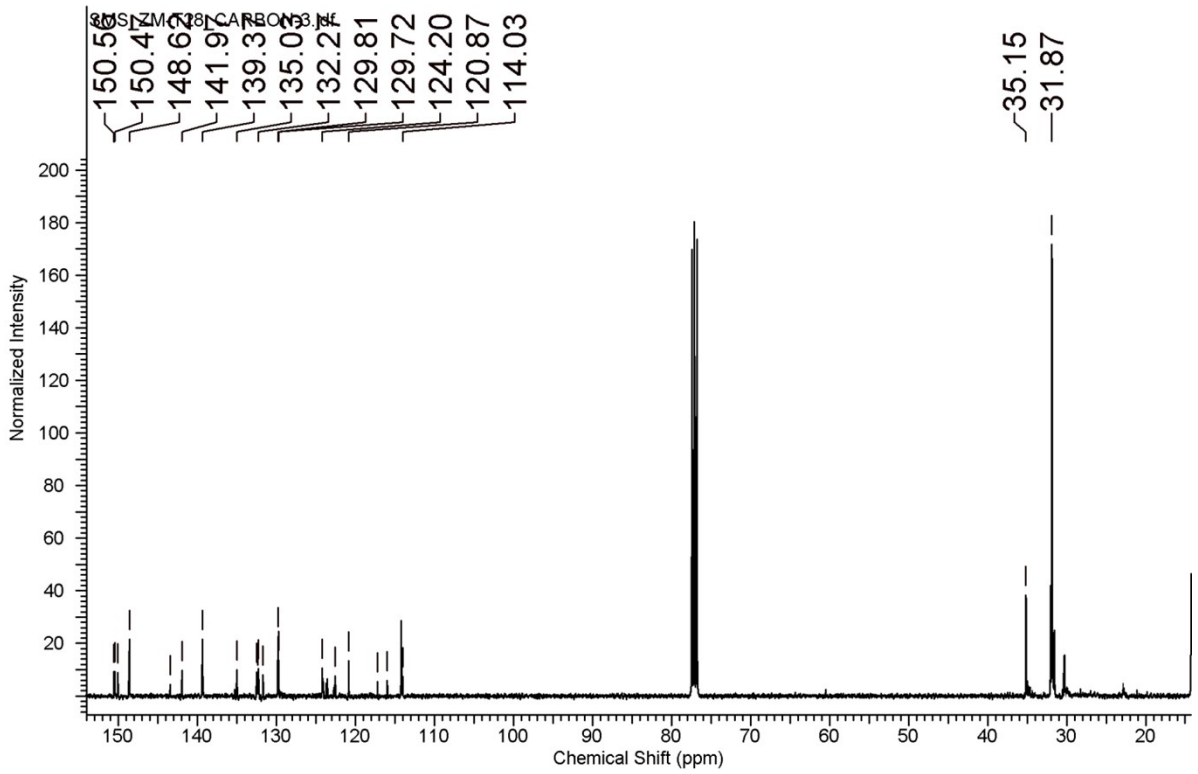


Figure S2: ^{1}H and ^{13}C NMR spectrum of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-4-(1'-pyridyl)-1,2,3-triazole (2-Zn)* in Chloroform-*d*.

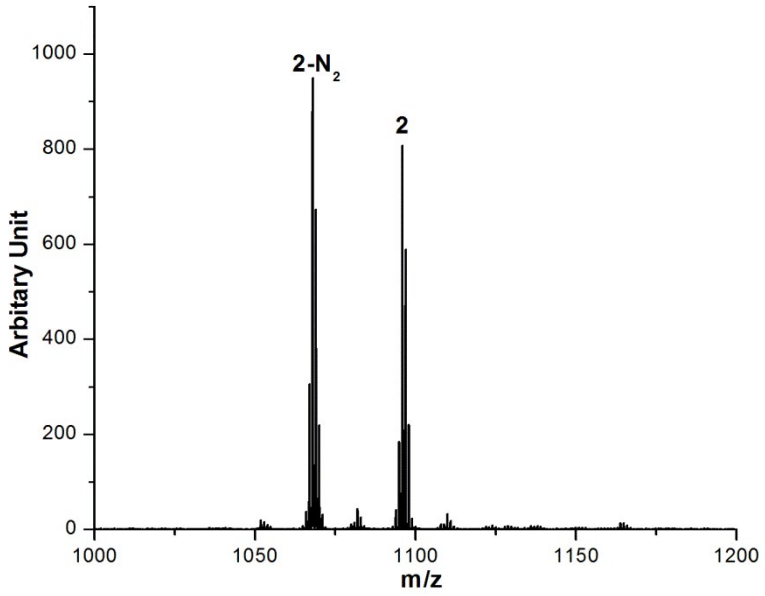
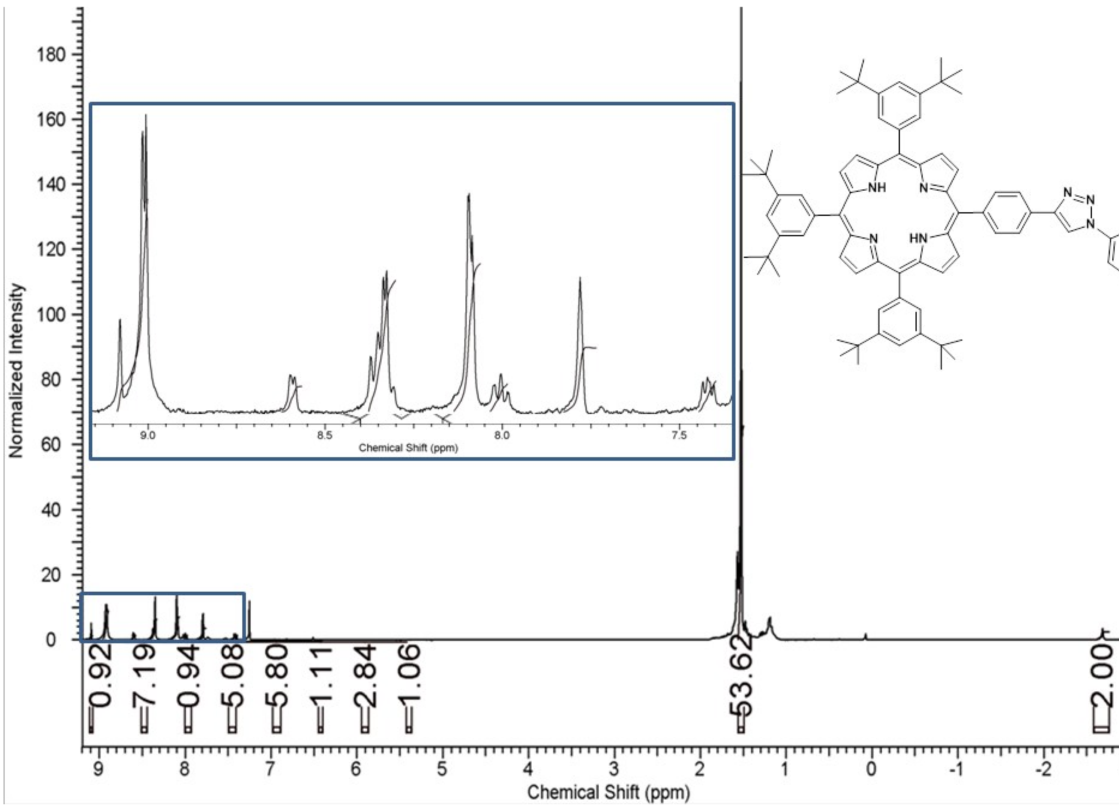


Figure S3: MALDI of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-4-(1'-pyridyl)-1,2,3-triazole (2-Zn)*


Normalized Intensity
Chemical Shift (ppm)
0.92
7.19
0.94
5.08
5.80
1.11
2.84
1.06
53.62
2.00
NH
N
HN
N
N
N
N
N

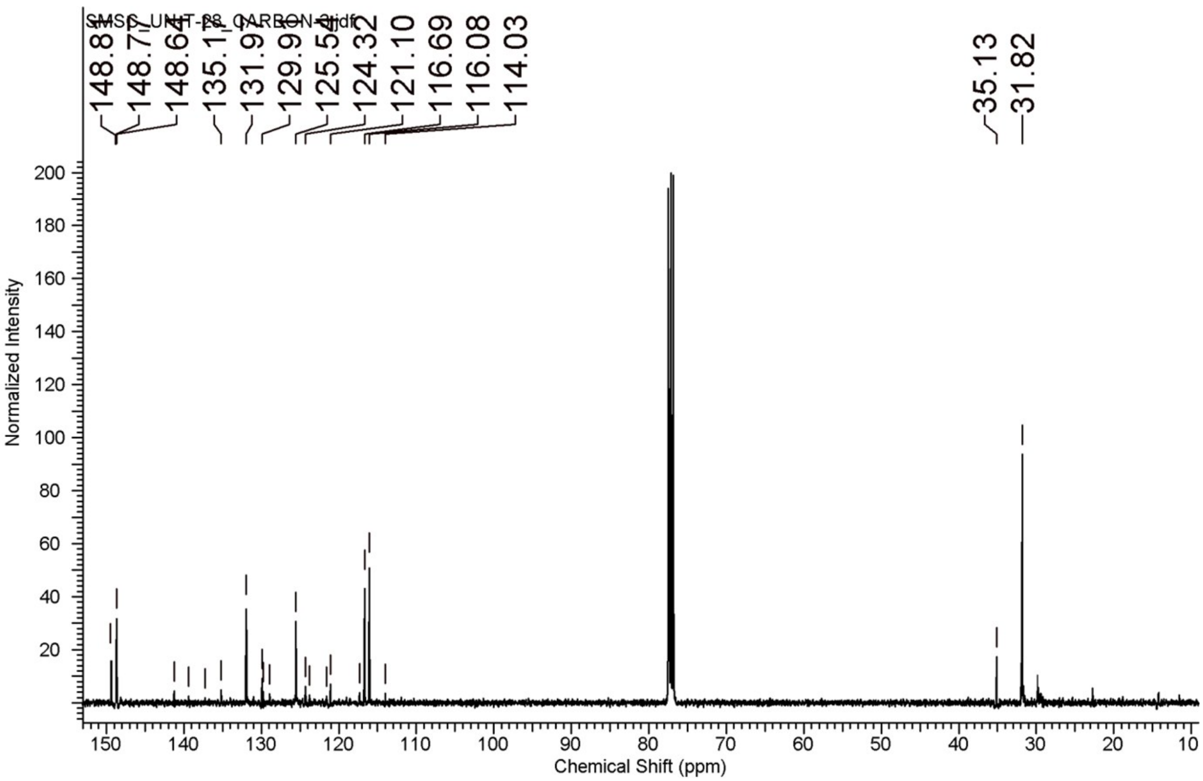

148.8
148.7
148.64
135.1
131.9
129.9
125.54
124.32
121.10
116.69
116.08
114.03
35.13
31.82
Normalized Intensity
Chemical Shift (ppm)

Figure S4: ^{1}H NMR and ^{13}C NMR spectrum of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin]-4-(1'-pyridyl)-1,2,3-triazole (2)* in Chloroform-*d*.

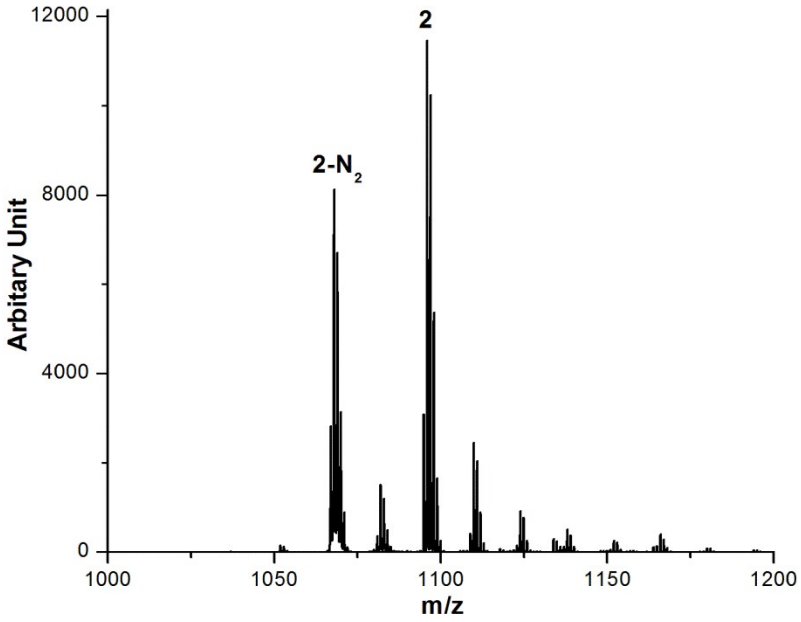


Figure S5: MALDI of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin]-4-(1'-pyridyl)-1,2,3-triazole (2)*.

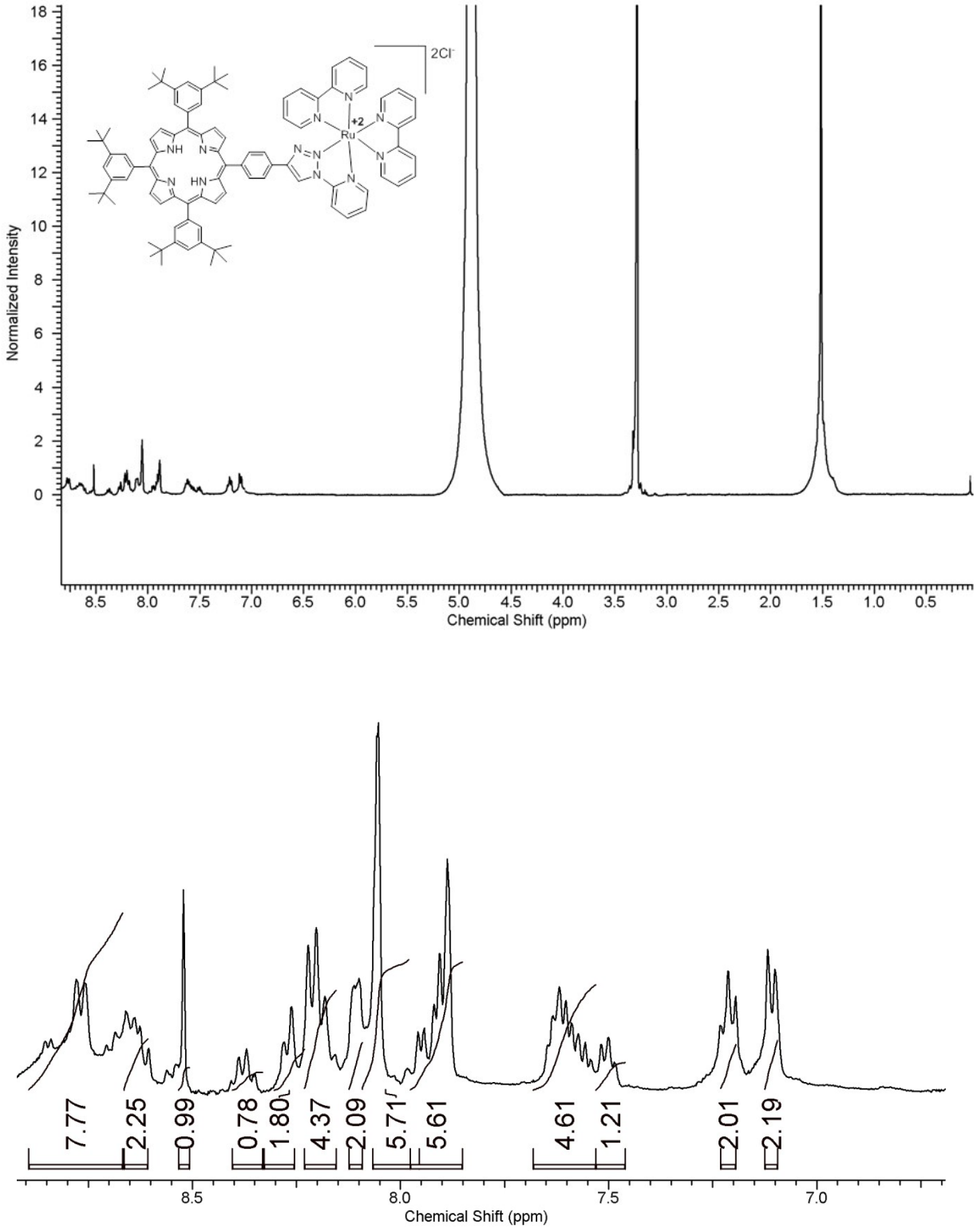
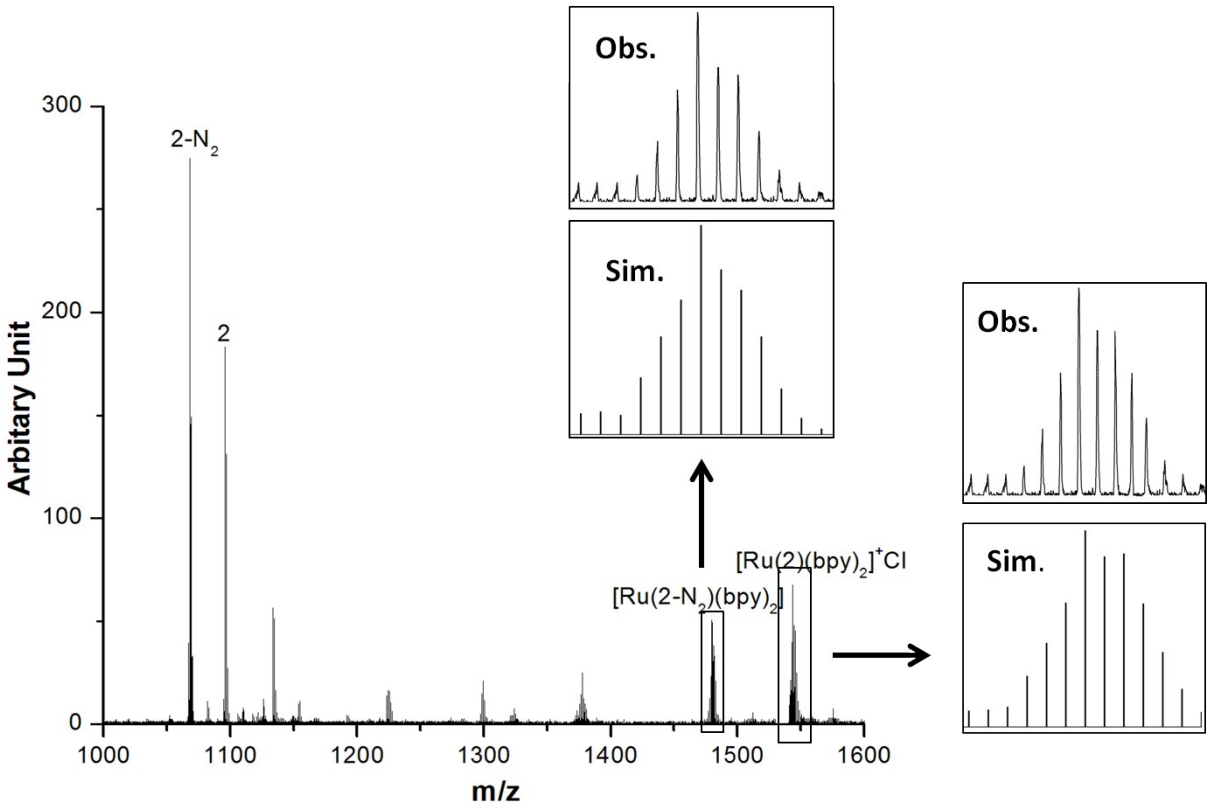


Figure S6: ^{1}H NMR spectrum of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinyl]-1H-1,2,3-triazol-1-yl-pyridine-2,2'-bispyridine ruthenium (II) chloride (3)* in Methanol-*d*.



Fgure S7: MALDI of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinyl]-1H-1,2,3-triazol-1-yl-pyridine-2,2'-bispyridine ruthenium (II) chloride (3)*

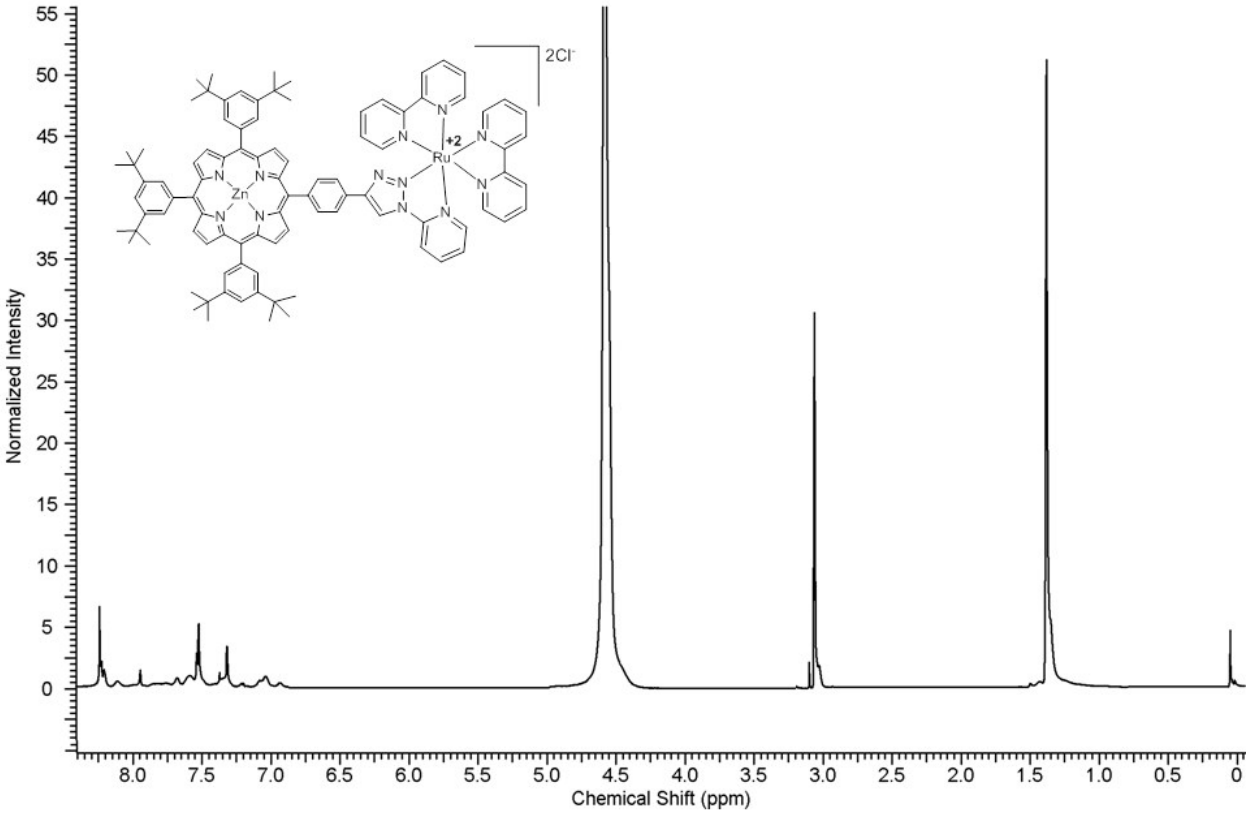


Figure S8: ^{1}H NMR spectrum of *2-[5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-1H-1,2,3-triazol-1-yl-pyridine-2,2'-bispyridine ruthenium (II) chloride (3-Zn)* in Methanol-*d*.

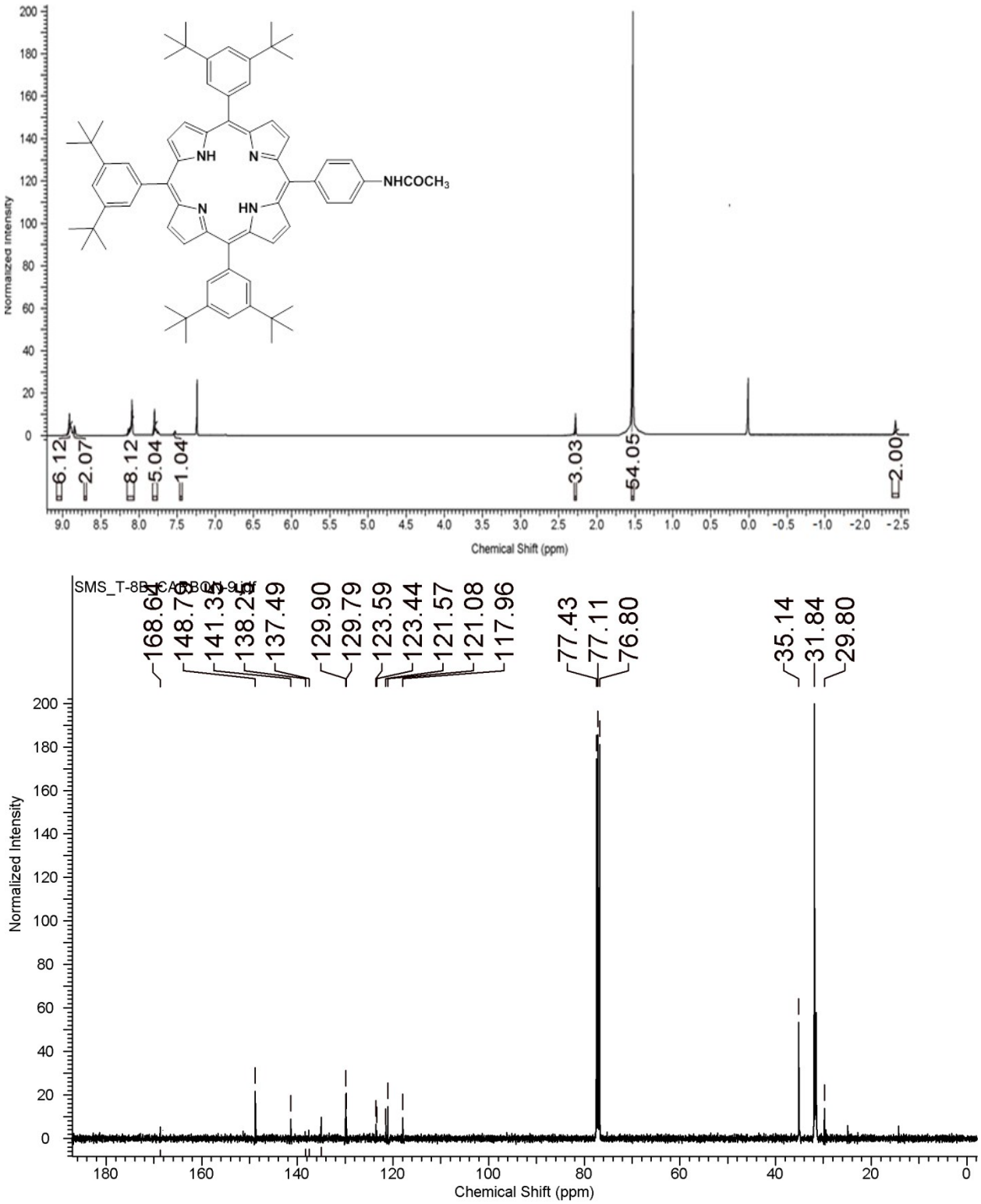


Figure S9: ^{1}H NMR and ^{13}C NMR spectrum of 5-(4-acetamidophenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (4) in Chloroform-*d*.

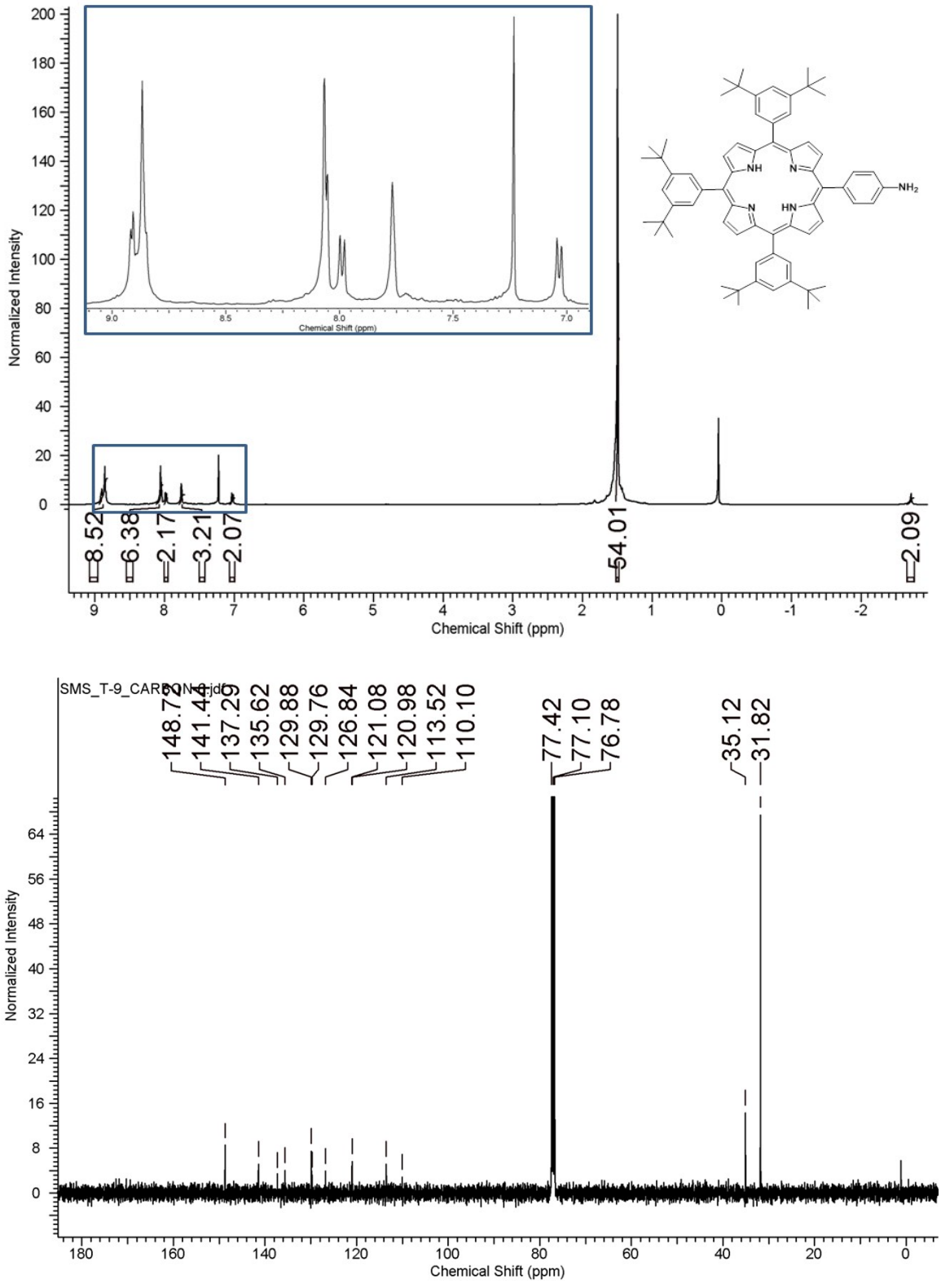


Figure S10: ^{1}H NMR and ^{13}C NMR spectrum of 5-(4-aminophenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (5) in Chloroform-*d*.

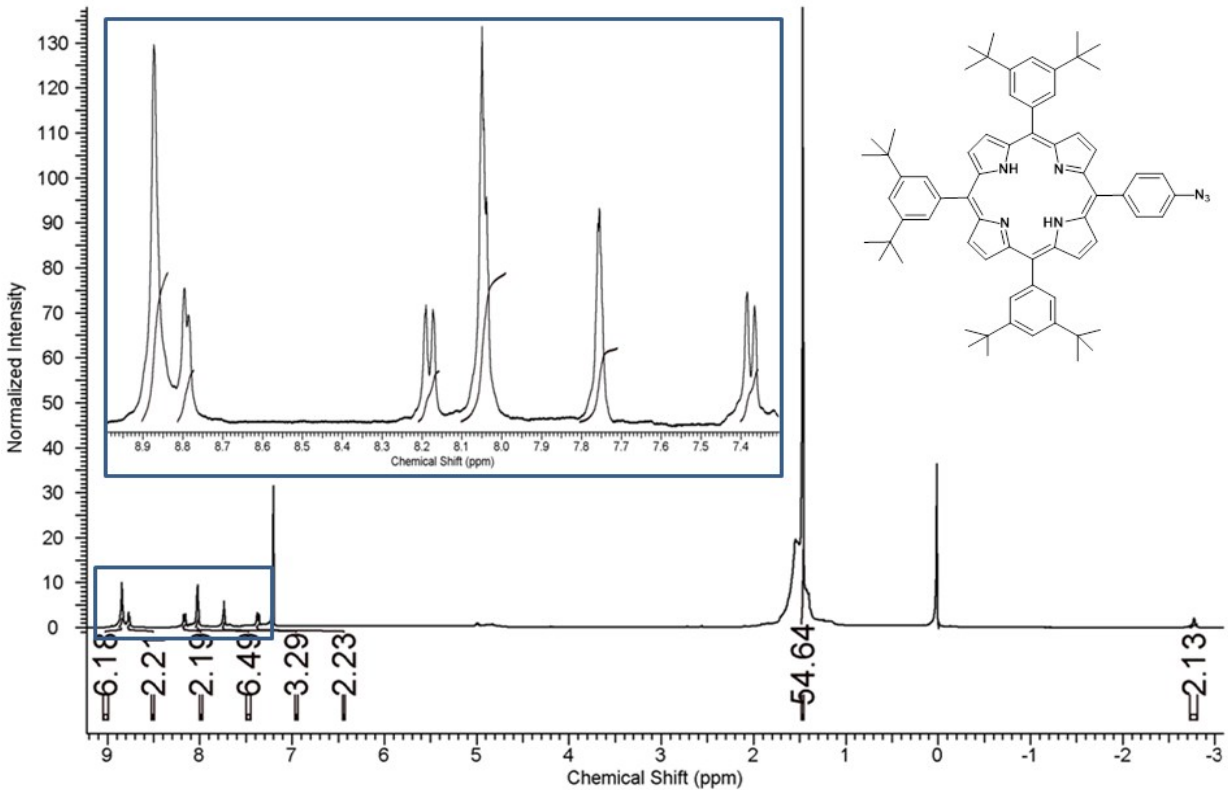


Figure S11: ^{1}H NMR spectrum of 5-(4-azidophenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (6) in Chloroform-*d*.

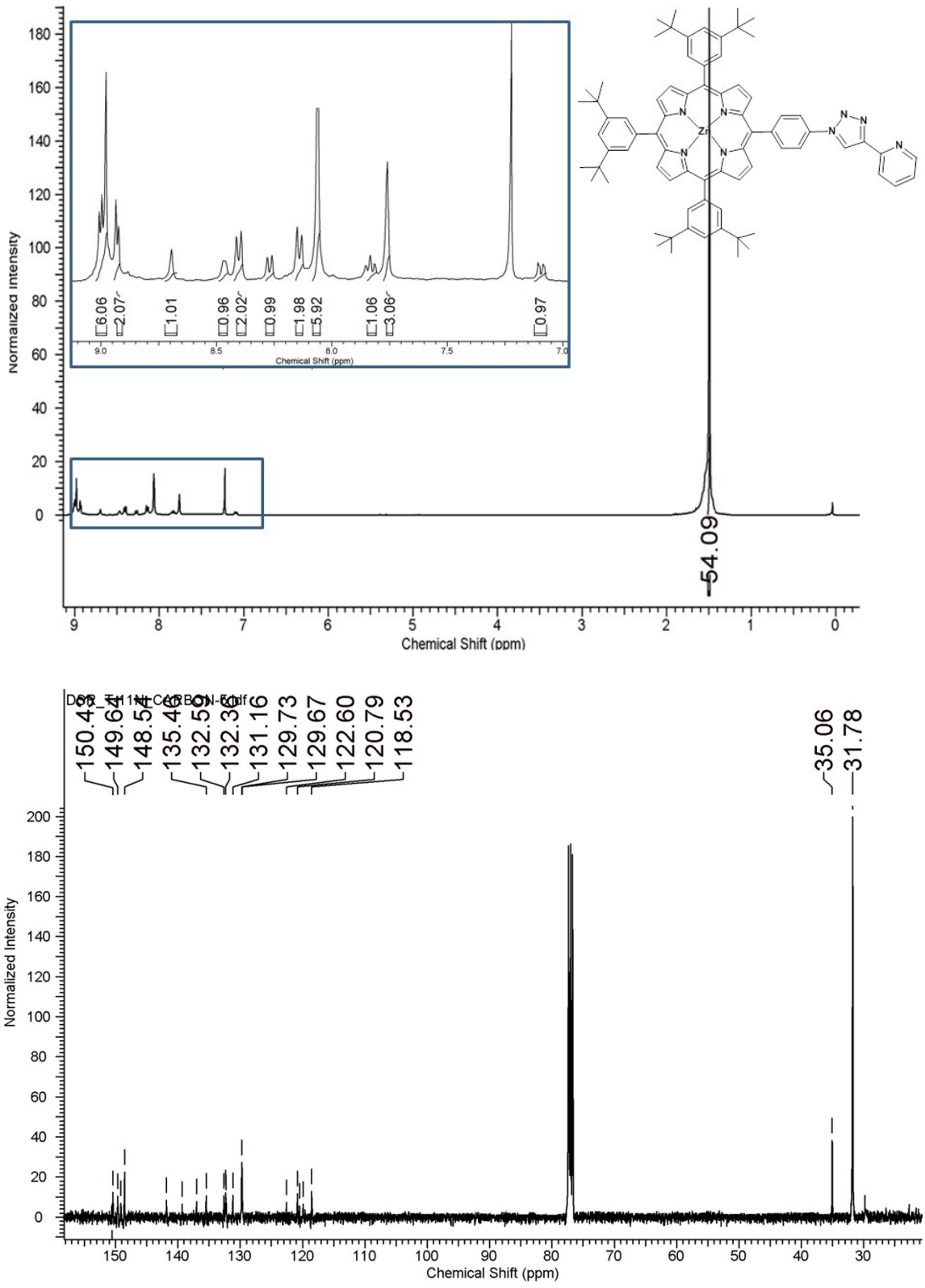


Figure S12: ^{1}H NMR spectrum of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-1,2,3-triazol-4-yl pyridine* (7-Zn) in Chloroform-*d*.

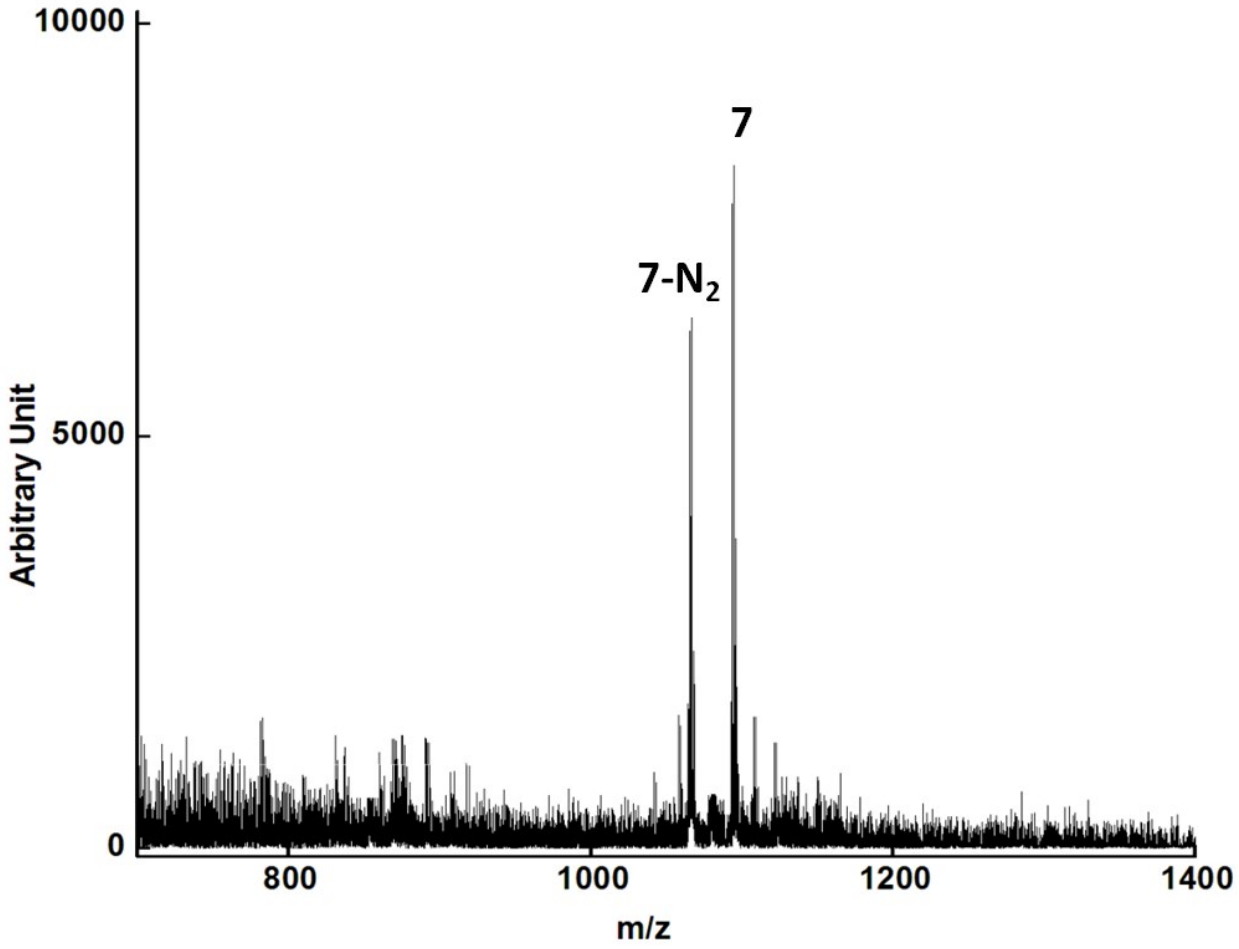


Figure S13: MALDI TOF spectrum of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-1,2,3-triazol-4-yl pyridine* (7-Zn)

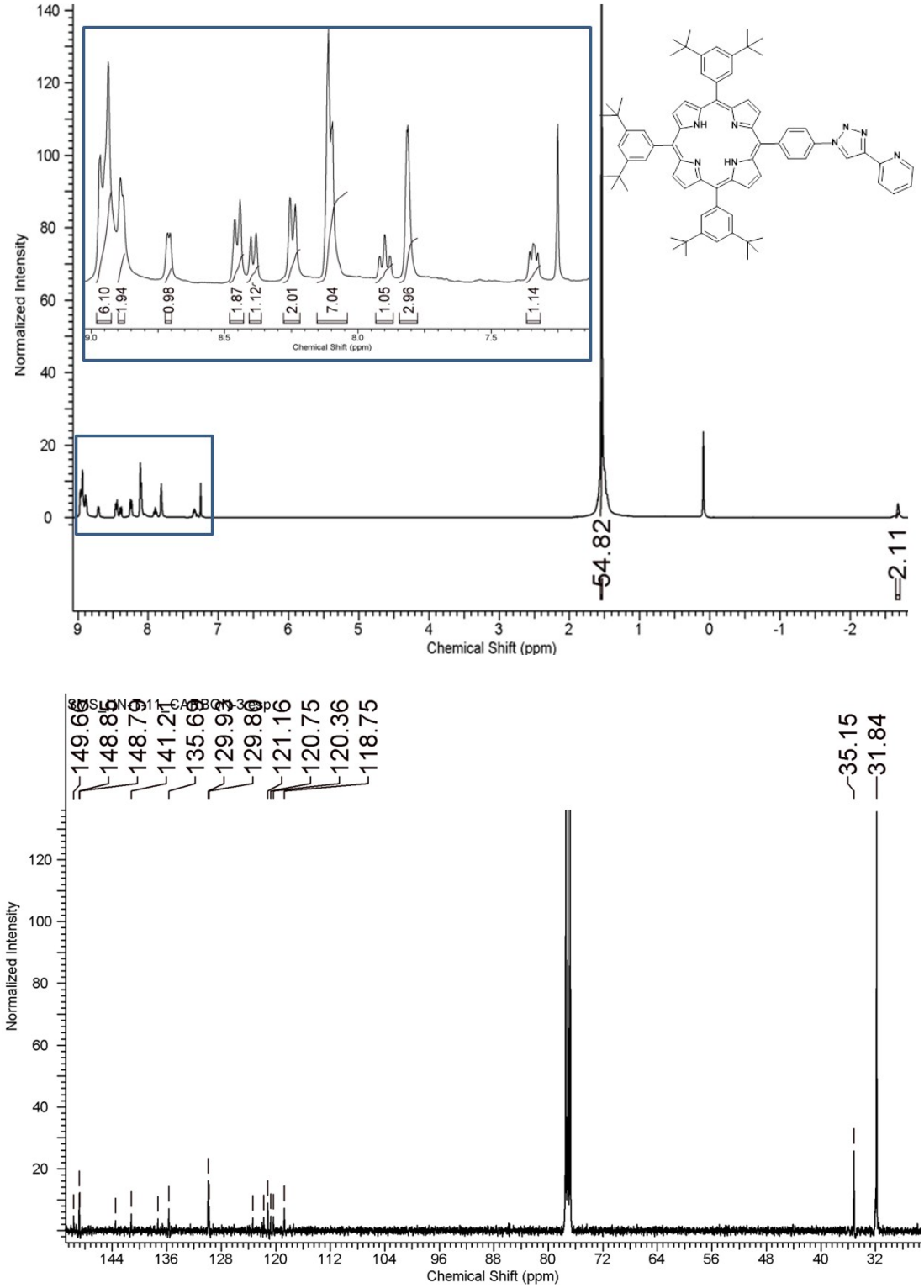
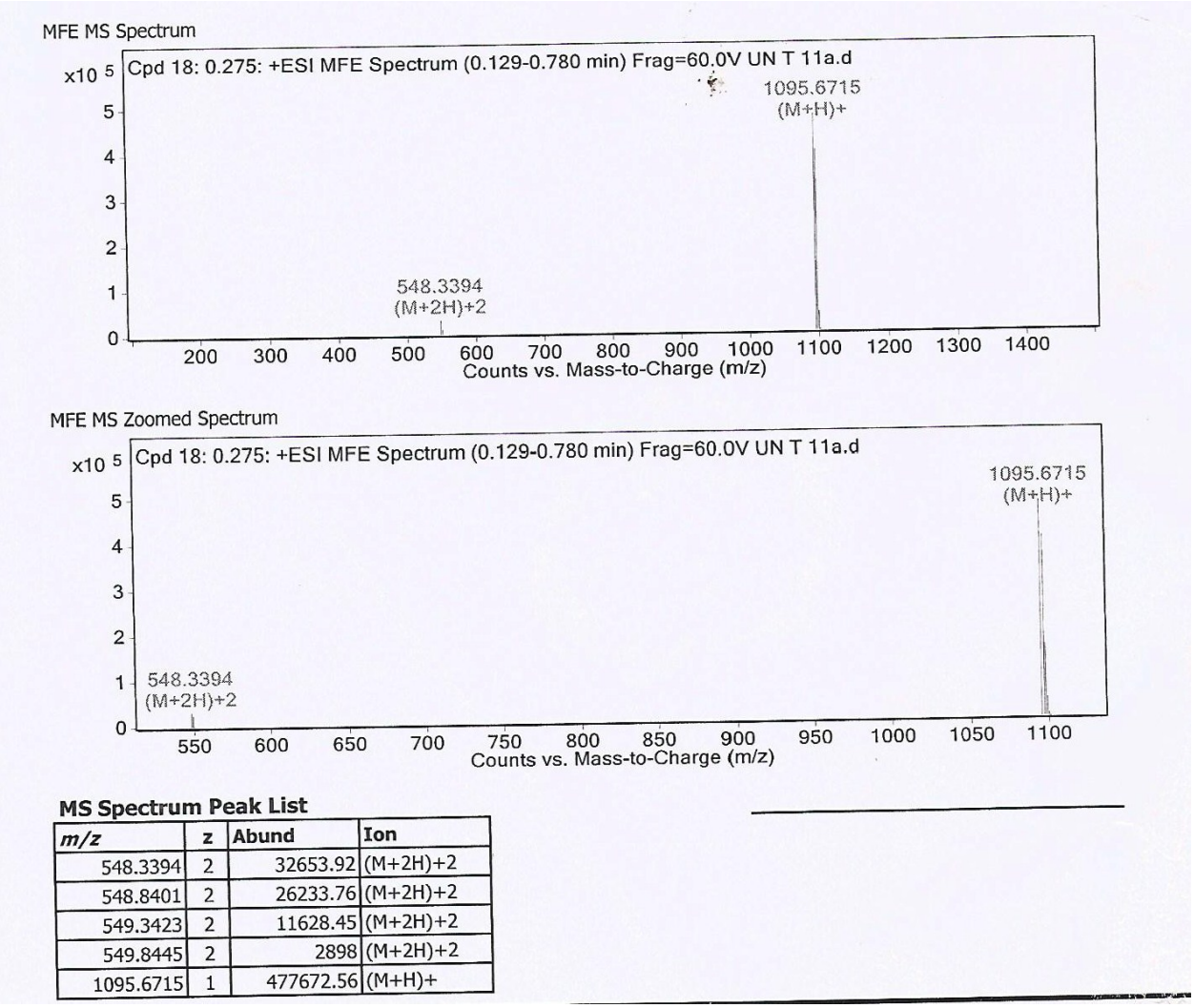


Figure S14: ^{1}H NMR and ^{13}C NMR spectrum of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butyl)phenylporphyrinato zinc]-1,2,3-triazol-4-yl pyridine* (7) in Chloroform-*d*.



MS Spectrum Peak List

m/z	z	Abund	Ion
548.3394	2	32653.92	(M+2H)+2
548.8401	2	26233.76	(M+2H)+2
549.3423	2	11628.45	(M+2H)+2
549.8445	2	2898	(M+2H)+2
1095.6715	1	477672.56	(M+H)+

Figure S15: ESI-MS spectrum of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butyl)phenylporphyrinato zinc]-1,2,3-triazol-4-yl pyridine* (7)

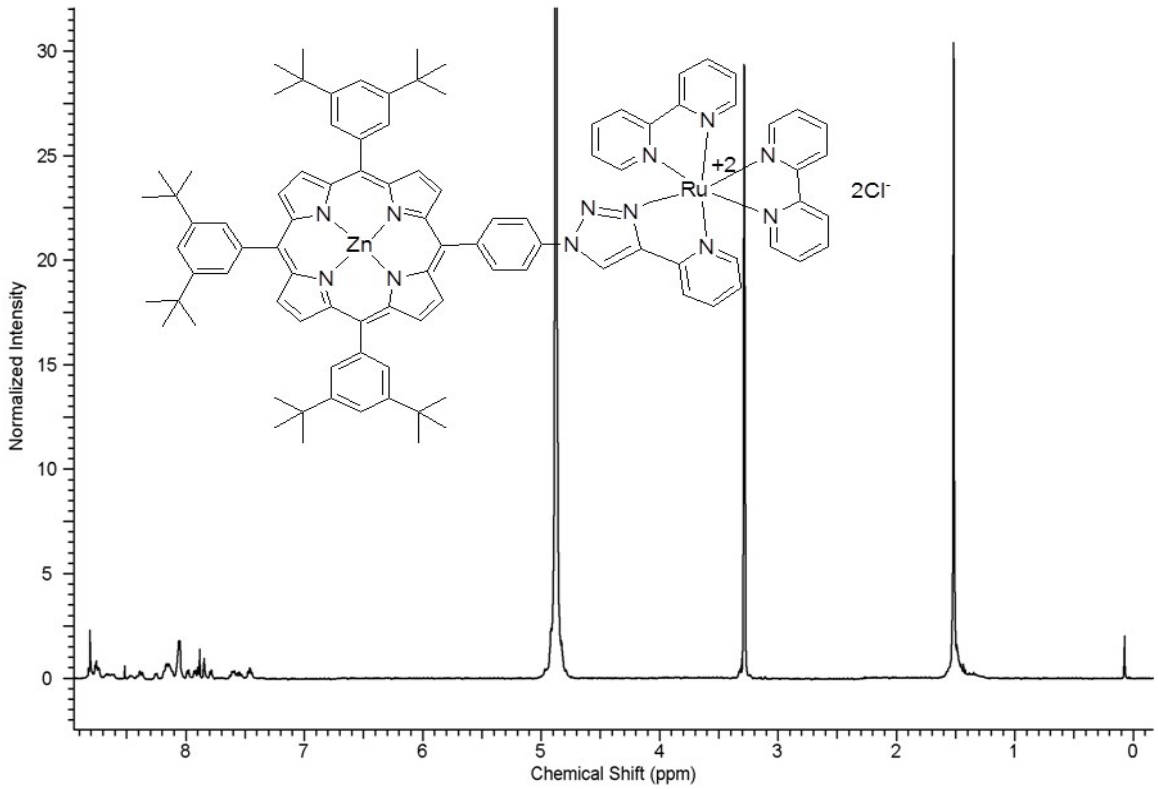


Figure S16: ^{1}H NMR spectrum of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-1H-1,2,3-triazol-4-yl-pyridine 2,2'-bispyridine ruthenium(II) chloride* (8-Zn) in Methanol-*d*.

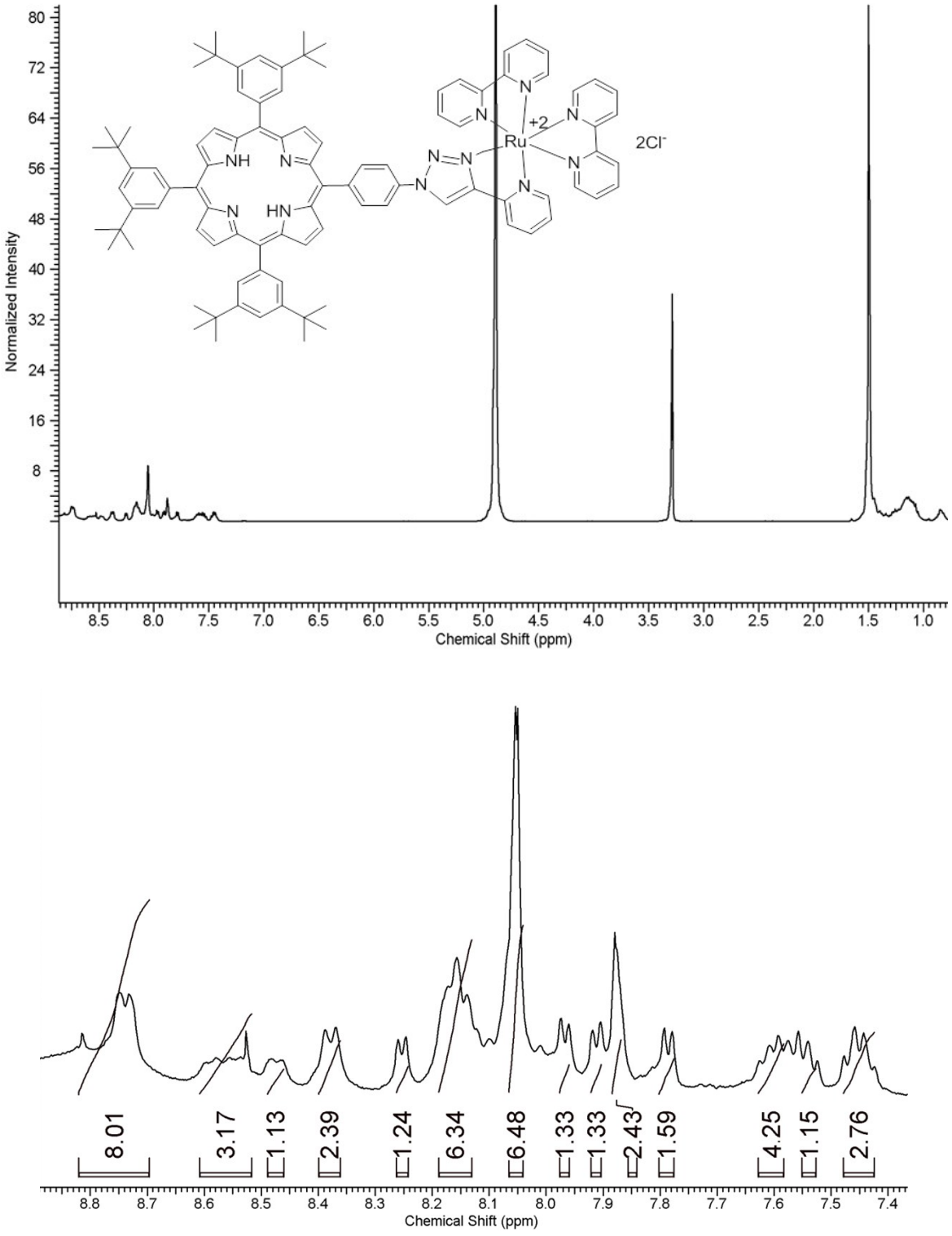


Figure S17: ^{1}H NMR spectrum of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butyl)phenylporphyrinyl]-1H-1,2,3-triazol-4-yl-pyridine 2,2'-bispyridine ruthenium (II) chloride* 8 in Methanol-*d*.

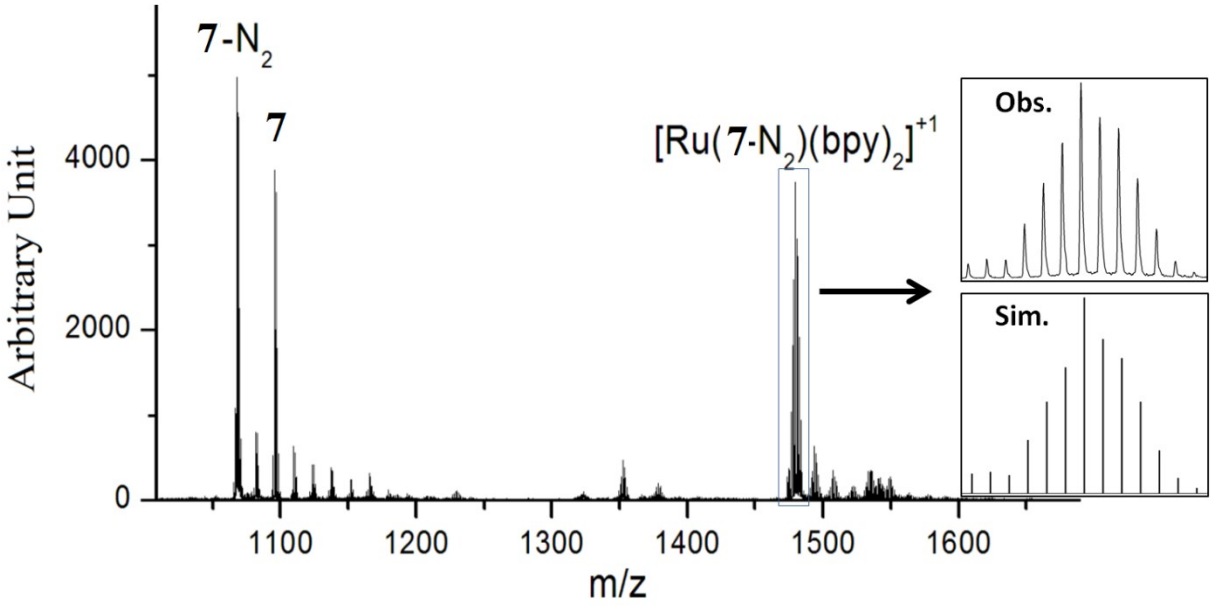


Figure S18: MALDI TOF and simulation pattern **of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butyl)phenylporphyrinyl]-1H-1,2,3-triazol-4-yl-pyridine 2,2'-bispyridine ruthenium (II) chloride* (8)**

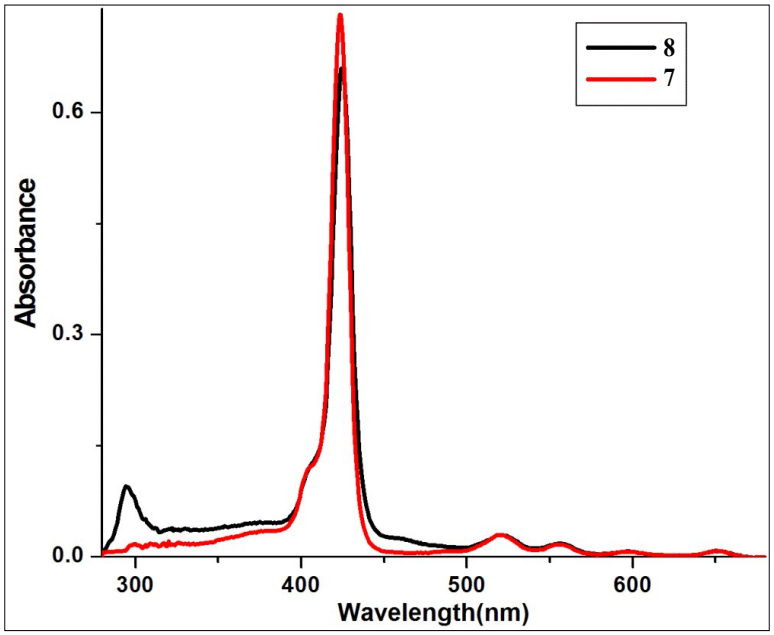


Figure S19: UV-visible spectra of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butyl)phenylporphyrinato zinc]-1,2,3-triazol-4-yl pyridine* (7) and its ruthenium complex (8)

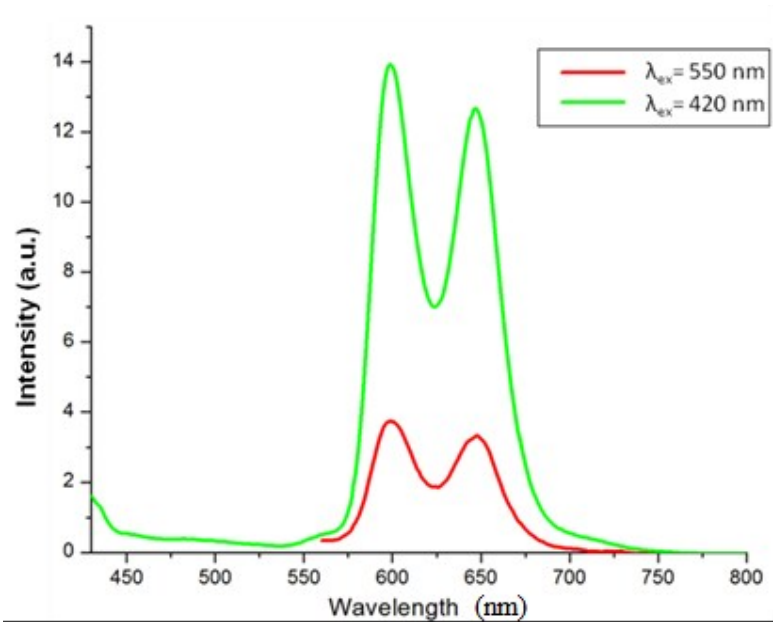


Figure S20: Steady state emission of 8-Zn with excitation of Soret band and Q band in $CHCl_3$ (5×10^{-6} M).

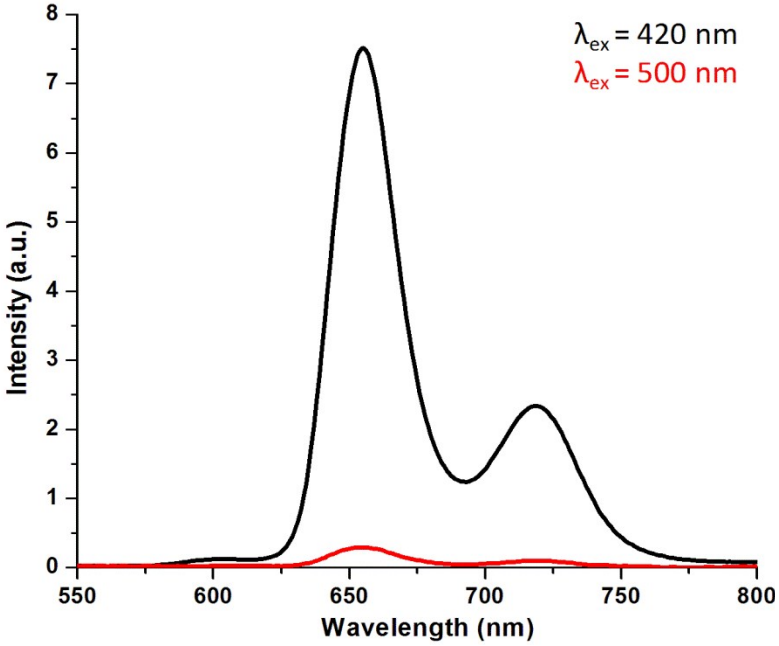


Figure S21: Steady state emission of 8 with excitation of Soret band and Q band in $CHCl_3$ (1.7×10^{-6} M).

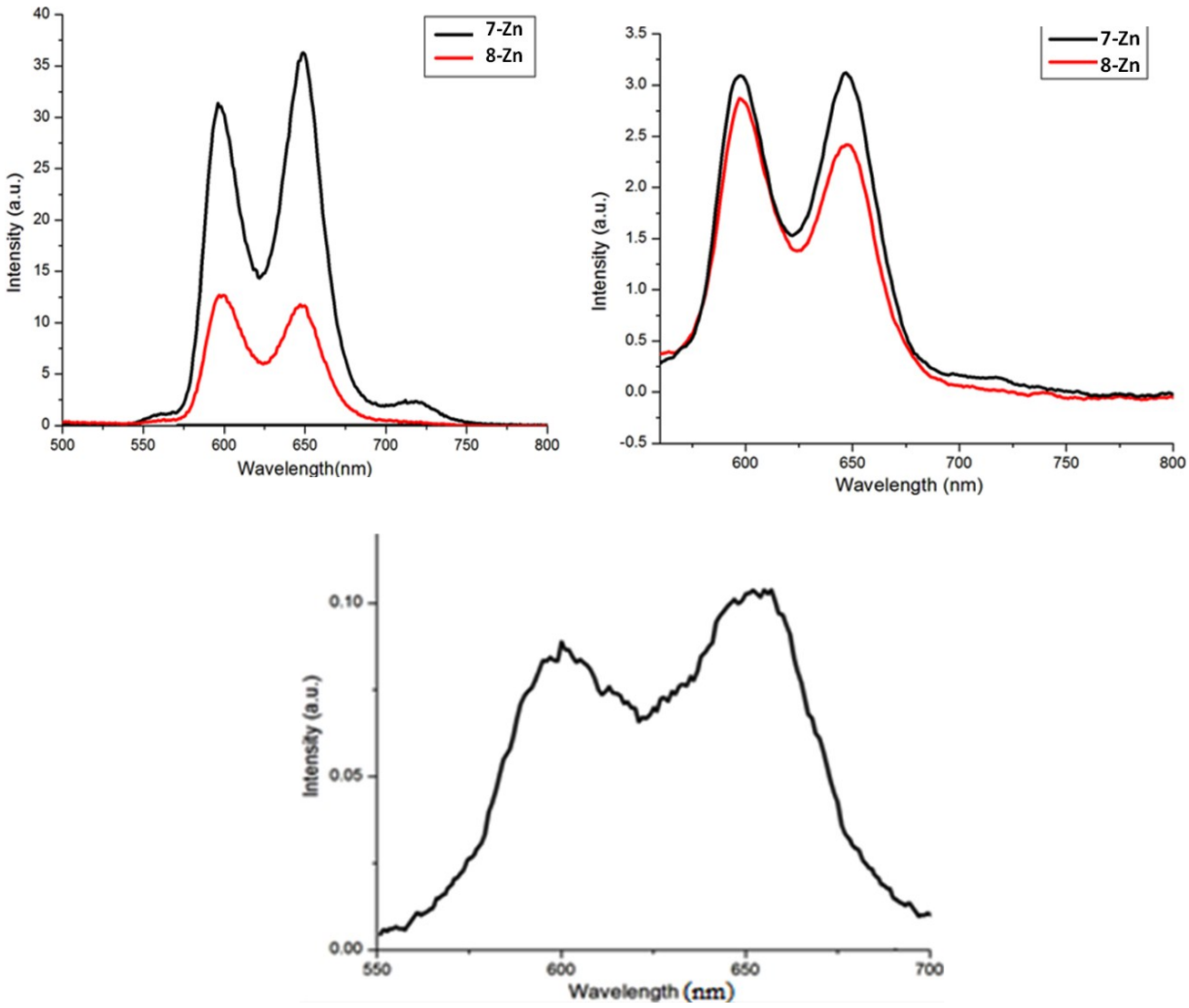


Figure S22: Steady state emission of 8-Zn with excitation of i) Soret band, ii) Q band, iii) MLCT band in $CHCl_3$ (5×10^{-6} M)

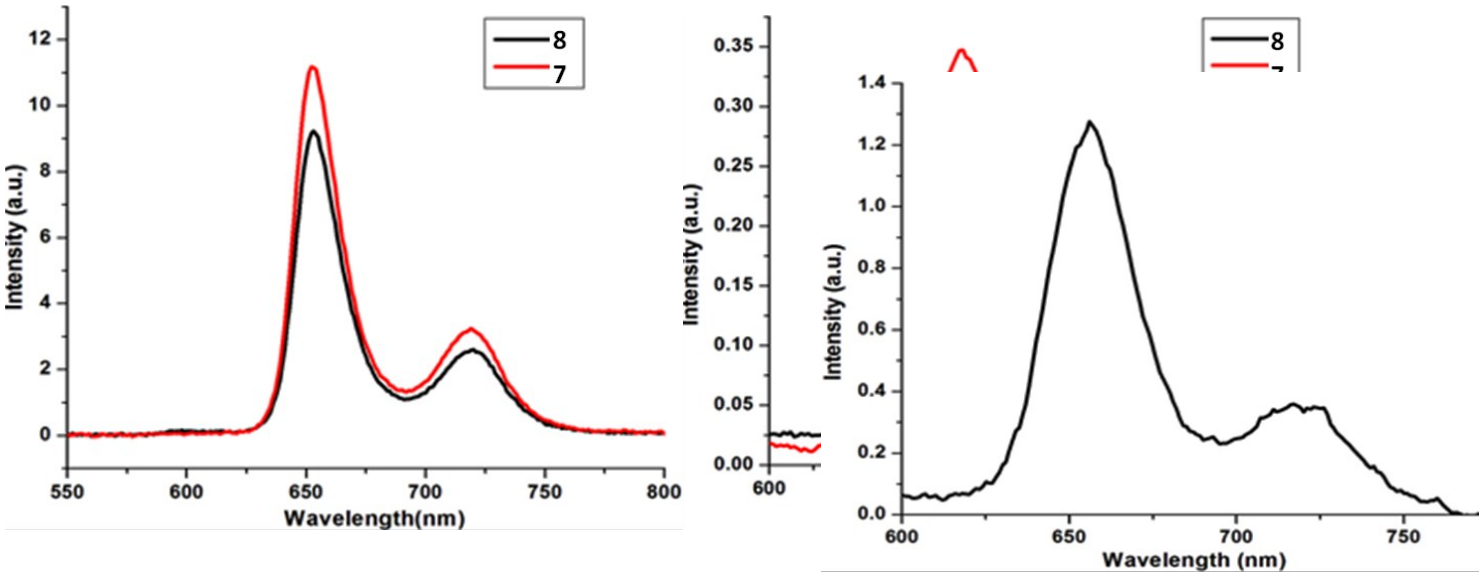


Figure S23: Steady state emission of 8 with excitation of i) Soret band, ii) Q band, iii) MLCT band in $CHCl_3$ (5×10^{-6} M)

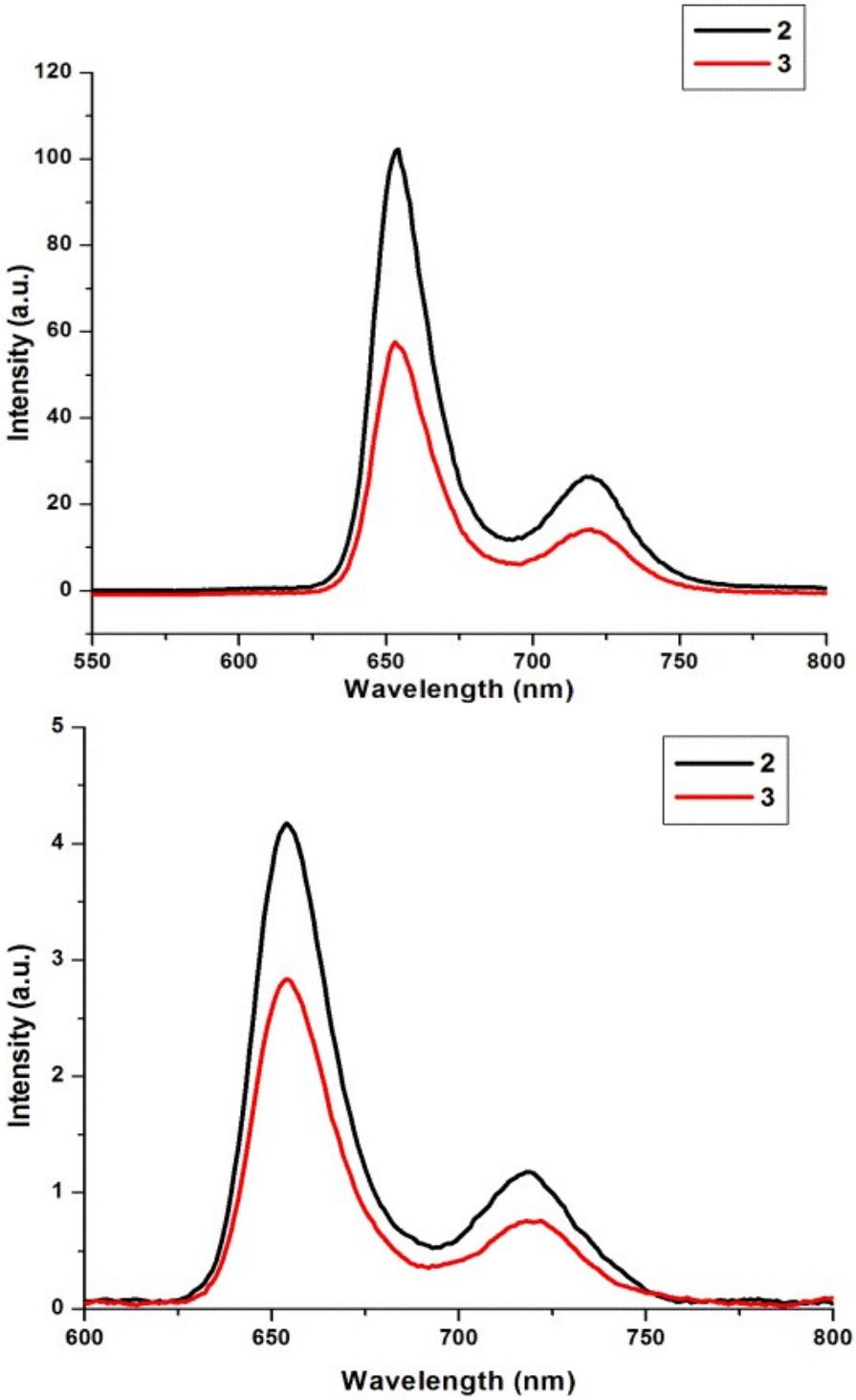


Figure S24: Steady state emission of 2, 3 with excitation of a) Soret band and b) Q band in $CHCl_3$ (5×10^{-6} M)

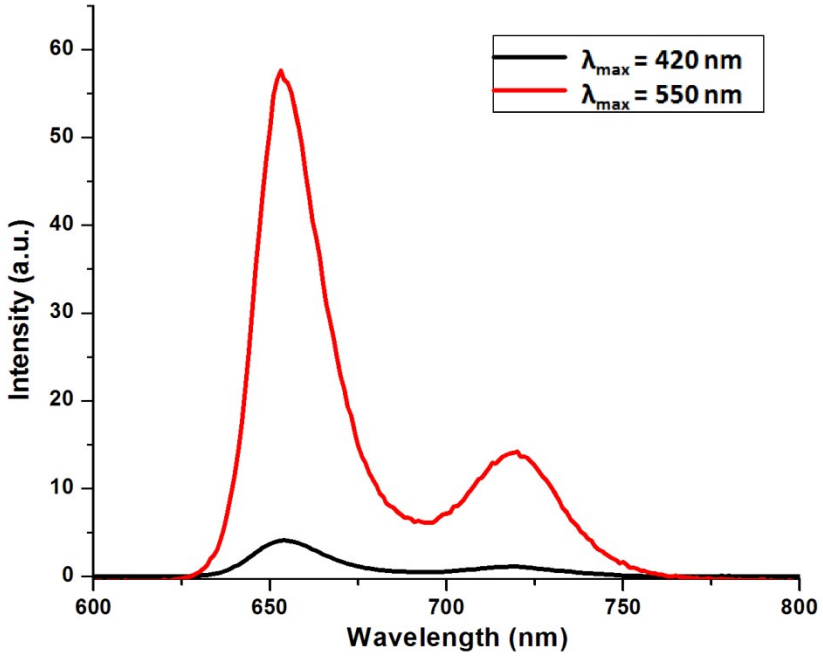


Figure S25: Steady state emission of 3 with excitation of Q band in $CHCl_3$ (5×10^{-6} M)

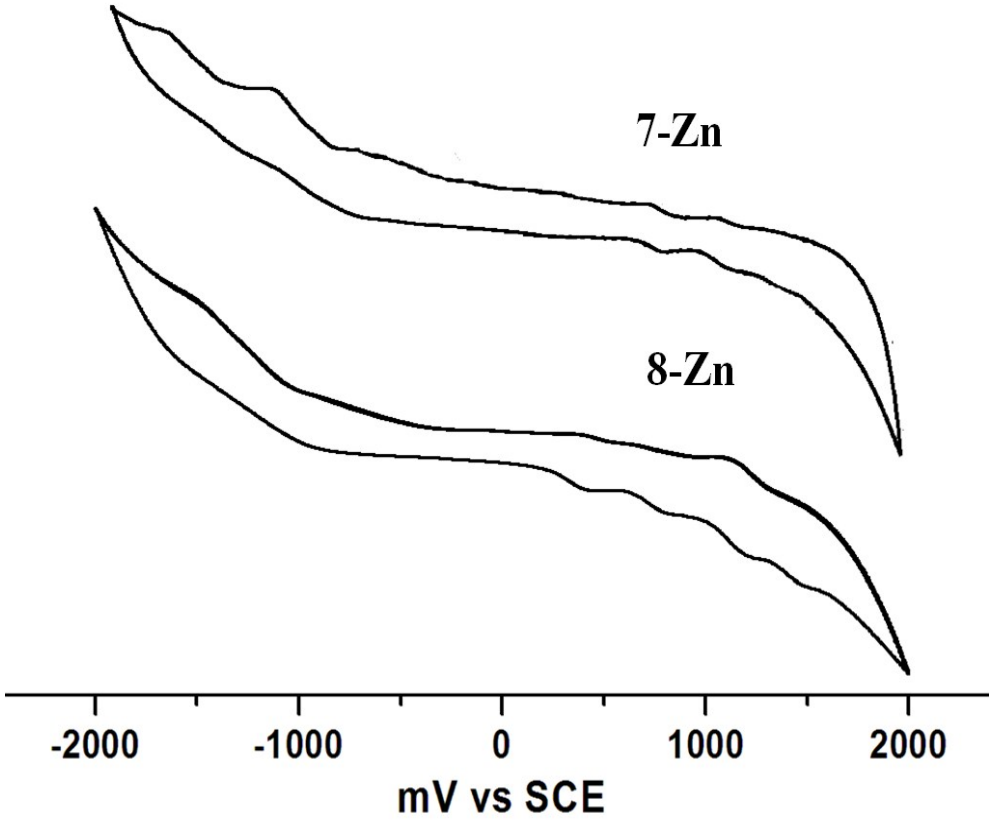


Figure S26: Cyclic voltammogram (CV) of 7-Zn, 8-Zn in CH_2Cl_2 with a scan rate of 50 mV/s (0.1 M $TBAPF_6$).

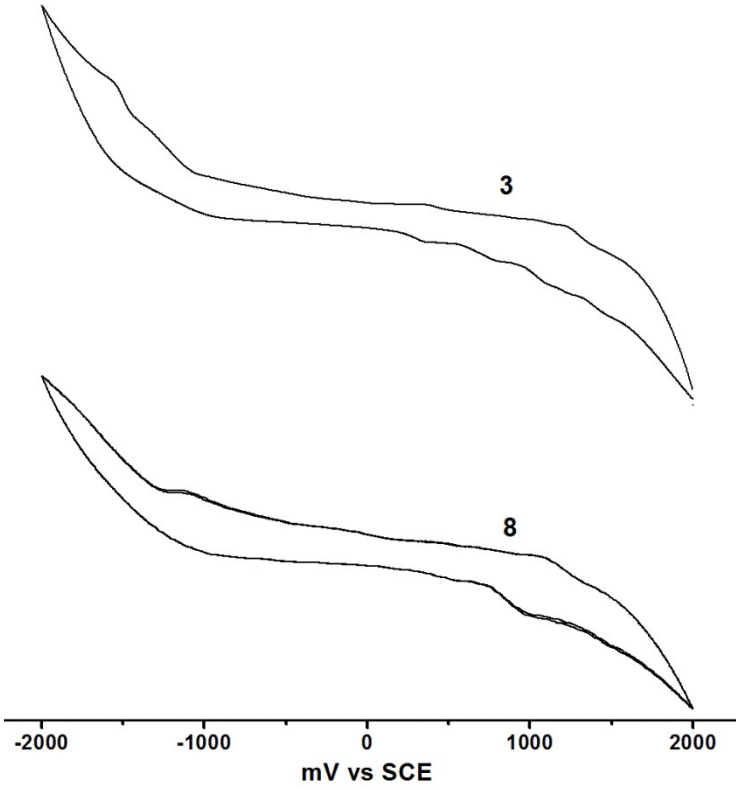


Figure S27: Cyclic voltammogram (CV) of 8, 3 in CH_2Cl_2 with a scan rate of 50 mV/s (0.1 M $TBAPF_6$).

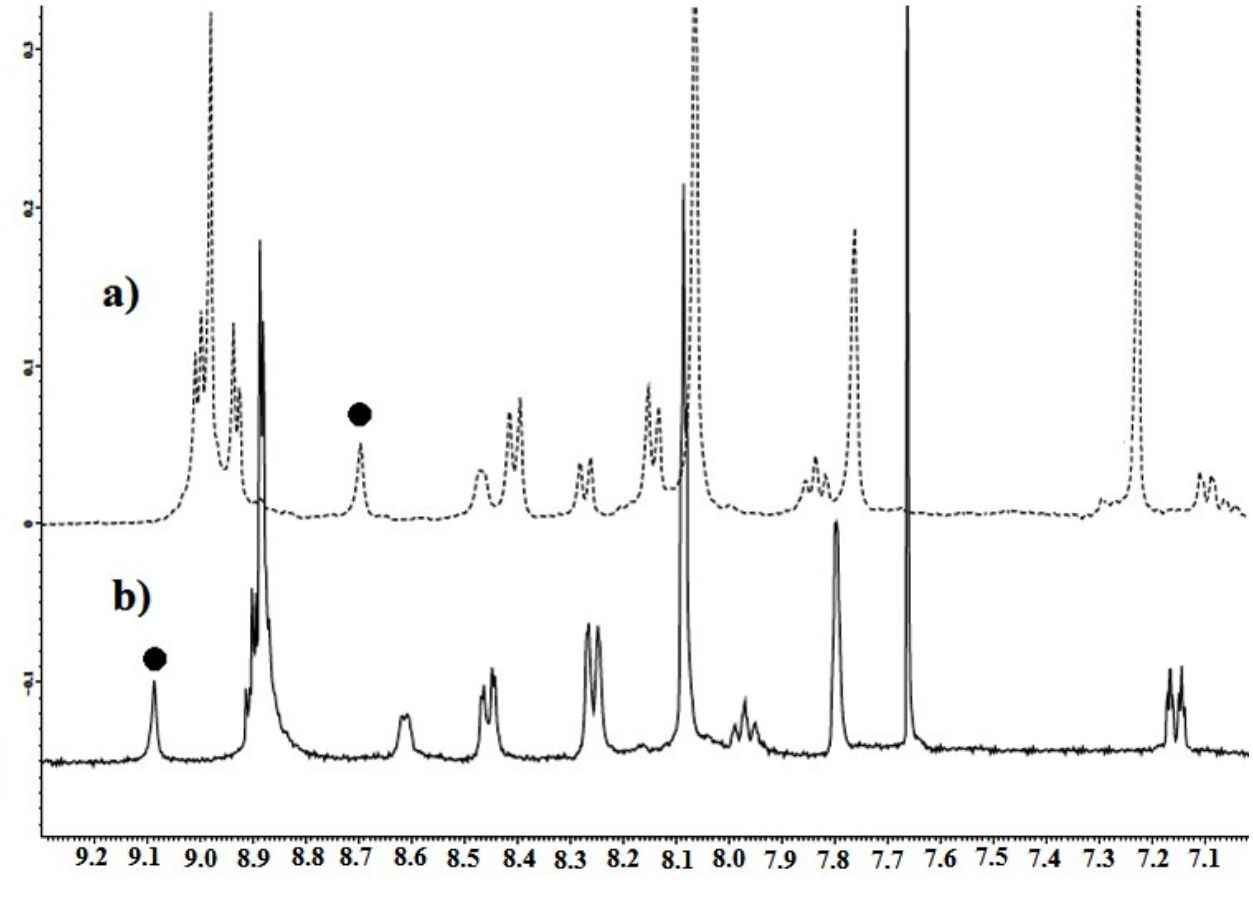


Figure S28: [1]H NMR spectral changes of *2-[5-(1-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrinato zinc]-1,2,3-triazol-4-yl)pyridine* (7-Zn) a) in $CDCl_3$ b) in Chloroform-*d*: Methanol-*d* (1:1).

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[1] Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. Mixed phosphine 2,2′-bipyridine complexes of ruthenium, *Inorg. Chem*., **1978**, *17*, 3334−3341.