**Supporting Information**

# PIFA-promoted intramolecular oxidative cyclization of pyrrolo- and indolo[1,2-*a*]quinoxaline-appended porphyrins: An efficient synthesis of *meso,β*-pyrrolo- and indolo[1,2-a]quinoxalino-fused porphyrins

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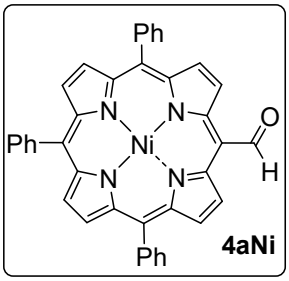
# I. Experimental Section

## (a) Materials and methods

Unless otherwise noted, chemicals and reagents were purchased from commercially available sources like Merck, Sigma-Aldrich and Spectrochem. Reactions were monitored by thin layer chromatography (TLC) performed using silica pre-coated alumina sheet ordered from Merck and crude products were purified by column chromatography using silica gel 100-200 mesh. All NMR spectra were recorded on a 400 MHz Bruker AVANCE II spectrometer at 400 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR) in deuterated solvent, $CDCl_3$. HRMS spectra were obtained on a 6200 series TOF (Q-TOF, B.06.01 (B6172 SP1). The UV-Vis spectra of the synthesized porphyrins were recorded by using Steady State Absorption Spectrophotometer (Jasco V-650 UV spectrophotometer) in spectroscopy grade dichloromethane. The fluorescence spectra were measured on a Fluoromax-4 spectrometer, quartz cuvette size (optical path length 10 mm) received from Perkin-Elmer. For fluorescence emission, the porphyrinoids were excited at 430 nm.

## II. Procedure and characterization data of the synthesized compounds



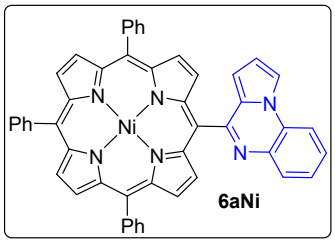

**Synthesis of [5-formyl-10,15,20-*tri*-phenylporphyrinato]nickel(II)[1, 2] (4aNi):** In a dry two neck round bottom flask containing dry DMF (10 mmol) purged with nitrogen and cooled to 0 °C. Freshly distilled $POCl_3$ (10 mmol) was added *via* syringe at the same temperature and allowed to stir the contents at room temperature for 20 min. The solution of [5,10,15-triphenylporphyrinato]nickel(II) (0.3 g, 0.5 mmol) in dichloroethane (75 mL) was slowly added. Further, the reaction mixture was refluxed for 6 h. After completion, the reaction mixture was cooled to room temperature, then a saturated solution of sodium acetate was added and stirred for overnight. The organic layer was separated and extracted with chloroform (3 × 100 mL). The combined organic layer was dried over anhydrous sodium sulphate and the solvent was evaporated under reduced pressure. The crude product thus obtained was purified by column chromatography over silica gel. Upon elution with hexane/chloroform (9:1, *v/v*) gave pure fractions which were evaporated under reduced pressure to obtain product **4aNi** as green solid (0.25 g, 80% yield).

Similarly, other compounds were prepared and isolated.[1]

**Preparation of 2-(1*H*-pyrrolo-1-yl)aniline (5a)**

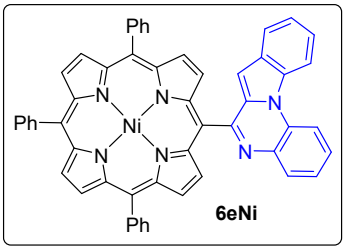
A mixture of 1-fluoronitrobenzene (1.5 g, 5.0 mmol) and pyrrole (5.0 mmol) in DMSO (10 mL) was refluxed for 1 h. The reaction mixture was cooled to 5 °C and slowly poured into the saturated sodium bicarbonate solution. Extracted the reaction mixture with ethyl acetate (50 mL) and washed the organic layer with water (100 mL), dried organic layer over anhydrous sodium sulphate and distilled off the excess of solvent at reduced pressure. The crude residue was filtered through silica gel using hexane/ethyl acetate as solvent system to afford 1-(2-nitrophenyl)-1*H*-pyrrole, which was used directly in the next step without any further purification. To a solution of 1-(2-nitrophenyl)-1*H*-pyrrole (10 mmol) in methanol (25 mL) was added 10% Pd/C (1g) and cooled the reaction contents to 0 °C. To the mixture, $NaBH_4$ was added (20 mmol) portion-wise and the contents were allowed to stir at 20 °C for 30 min. The reaction mixture was filtered over a celite bed and washed with ethyl acetate. The filtrate was evaporated in *vacuo* and the residue thus obtained was purified using column chromatography (hexane/ethyl acetate) to afford pure product **5a** as light yellow solid (2.0 g, 75% yield), exp. mp 93-95 °C (lit. mp 94-96 °C).[2]

Similarly **5b** was prepared and isolated as a yellow semi-solid (1.8 g, 72% yield).

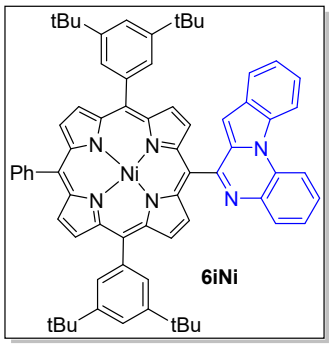



**Synthesis of *meso*-pyrrolo[1,2-a]quinoxalino-10,15,20-triphenylporphyrin (6aNi):** To a stirred solution of **4aNi** (0.20 g, 0.32 mmol) and **5a** (0.32 mmol) in dry toluene (10 mL), TFA (50 µL, 0.64 mmol) was added dropwise at 0 °C. The reaction mixture was refluxed at 110 ˚C for 2 h and added solid $KMnO_4$ (1.6 mmol). Continued the heating for another 1 h. Removed the excess of solvent and obtained the solid residue was taken into water (100 mL) and extracted with dichloromethane (3 × 25 mL) and dried over anhydrous sodium sulphate. Removed the organic solvent under reduced pressure and the crude product was purified by column chromatography using hexane/chloroform (70:30, *v/v*) as an eluent to obtain **6aNi** as purple solid (210 mg, 85% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm) 410, 534, 565; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, $J$ = 4.9 Hz, 2H), 8.8-8.7 (m, 6H), 8.35 (d, $J$ = 7.9 Hz, 1H), 8.14 – 8.05 (m, 7H), 7.76-7.74 (m, 12H), 6.74 – 6.71 (m, 1H), 5.91 (d, $J$ = 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.2, 142.8, 142.5, 142.4, 140.1, 140.1, 136.5, 133.8, 133.7, 133.0, 132.3, 132.0, 131.4, 130.9, 130.3, 128.3, 127.8, 127.8, 126.9, 125.6, 120.1, 119.3, 114.4, 114.2, 114.0, 112.9, 110.7; ESI-HRMS *m/z* calcd. for $C_{49}H_{31}N_6Ni$ $[M+H]^+$: 761.1964 found 761.1944.

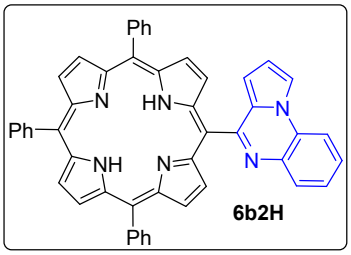
Similarly, compounds **6eNi** and **6iNi** were prepared and isolated




**6eNi:** Purple solid (180 mg, 69% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 411, 528; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 5.0 Hz, 2H), 8.11-8.77 (m, 7H), 8.67 (d, *J* = 8.7 Hz, 1H), 8.40 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.07 (br, 6H), 7.87 (td, *J* = 7.2, 1.5 Hz, 1H), 7.76 – 7.67 (m, 9H), 7.66 – 7.55 (m, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.12 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.9, 143.3, 142.8, 142.5, 142.2, 140.9, 140.8, 136.8, 133.7, 133.7, 133.2, 132.8, 132.4, 132.1, 131.3, 131.2, 130.9, 129.2, 129.2, 127.8, 127.8, 126.9, 124.7, 124.5, 122.9, 122.7, 120.2, 119.4, 115.0, 114.6, 112.5, 104.9; ESI-HRMS *m/z* calcd. for $C_{53}H_{33}N_6Ni[M+H]^+$ 811.2120, found 811.2101.



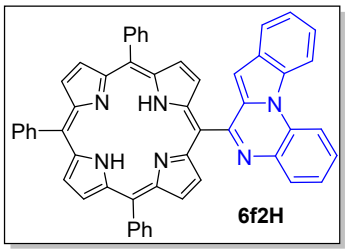

**6iNi:** Purple solid (190 mg, 78% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 414, 528; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 4.4 Hz, 2H), 8.82 (q, J = 7.5 Hz, 7H), 8.67 (d, J = 8.8 Hz, 1H), 8.41 (d, J = 7.9 Hz, 1H), 8.08 (br, 4H), 7.88 (t, J = 7.8 Hz, 1H), 7.78 – 7.54 (m, 10H), 7.36 (t, J = 7.5 Hz, 1H), 6.12 (d, J = 2.6 Hz, 1H), 1.76 (d, J = 15.2 Hz, 36H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.1, 149.0, 143.5, 143.0, 142.5, 142.1, 141.1, 139.8, 136.81, 133.73, 133.68, 133.50, 132.78, 132.35, 132.20, 131.33, 130.9, 130.9, 129.2, 129.0, 127.8, 126.9, 124.6, 124.5, 122.9, 122.7, 121.2, 120.7, 119.9, 115.0, 114.6, 112.2, 104.9, 35.0, 31.7; ESI-HRMS *m/z* calcd. for $C_{69}H_{65}N_6Ni[M+H]^+$ 1035.4624 found 1035.4569.



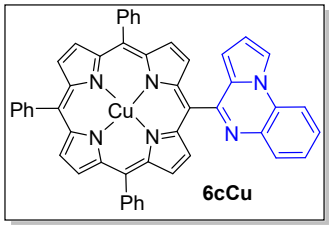

**Synthesis of free-base *meso*-pyrrolo[1,2-a]quinoxalino-10,15,20-*tri*-phenylporphyrin (6b2H):** To as solution of **6aNi** (100 mg, 0.13 mmol) in trifluoroacetic acid (1 mL), and sulfuric acid (45 µL, 2.5 eq.) was added and the reaction mixture was stirred at 0 ˚C for 1 h. After completion of the reaction, the contents were diluted with chloroform (20 mL) and washed with aqueous solution of sodium bicarbonate (3 × 30 mL). The organic phase was dried and evaporated. The residue thus obtained was subjected to a silica gel column chromatography using chloroform as an eluent to afford pure **6b2H** as purple solid (54 mg, 58% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 454, 665; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J*

= 4.9 Hz, 2H), 8.02 – 8.84 (m, 6H), 8.36 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.31-8.190 (m, 8H), 7.83 – 7.74 (m, 10H), 7.69 (td, *J* = 7.8, 1.4 Hz, 1H), 6.78 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.04 (dd, *J* = 4.1, 1.3 Hz, 1H), -2.63 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.2, 142.2, 142.0, 136.6, 134.6, 131.3, 130.9, 128.3, 127.8, 127.7, 126.7, 125.7, 121.4, 120.4, 114.5, 114.1, 113.6, 111.2; ESI-HRMS *m/z* calcd. for $C_{49}H_{33}N_6[M+H]^+$ 705.2767 found 705.2749.

Similarly **6f2H** was prepared and isolated

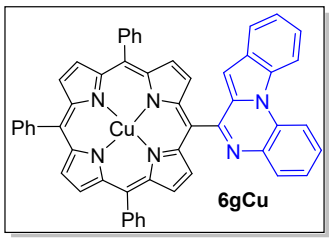



**6f2H:** Red solid (55 mg, 59% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 446, 545, 657; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 4.8 Hz, 2H), 8.92 – 8.86 (m, 7H), 8.73 (d, *J* = 8.8 Hz, 1H), 8.42 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.32 – 8.21 (m, 6H), 7.91 (td, *J* = 7.4, 1.6 Hz, 1H), 7.78 (m, 10H), 7.71 – 7.57 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.28 (s, 1H), -2.57 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.1, 142.2, 141.9, 136.9, 134.7, 134.6, 134.5, 132.8, 131.3, 131.0, 129.3, 129.2, 127.8, 127.8, 126.8, 126.7, 124.7, 124.5, 123.0, 122.8, 121.6, 120.5, 115.1, 114.7, 113.1, 105.4; ESI-HRMS *m/z* calcd. for $C_{53}H_{35}N_6$ $[M+H]^+$ 755.2923 found 755.2878.



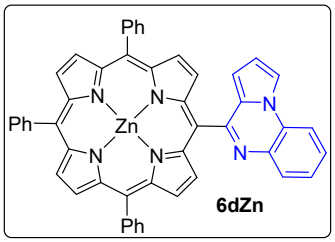

**Synthesis of *meso*-pyrrolo[1,2-a]quinoxalino-10,15,20-*tri*-phenyl-porphyrin (6cCu):** To solution of **6b2H** (30 mg,0.04 mmol) in a mixture of chloroform and methanol (20 mL, 1:1), copper acetate (0.4 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. After completion of the reaction, the contents were diluted with chloroform (20 mL) and washed with distilled water (3 × 30 mL). The organic phase was dried and evaporated. The residue thus obtained was subjected to column chromatography (silica gel) using chloroform as an eluent to afford pure **6cCu** as purple solid (22 mg, 67% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 413, 542; ESI-HRMS *m/z* calcd. for $C_{49}H_{31}N_6Cu$ $[M+H]^+$ 766.1906 found 766.1893.

Similarly compound **6gCu** was prepared and isolated



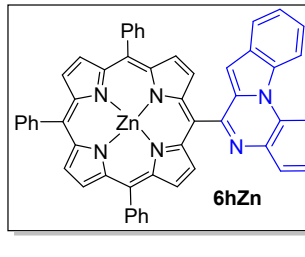

**6gCu:** Purple solid (24 mg, 74% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 414, 542; ESI-HRMS *m/z* calcd. for $C_{53}H_{33}N_6Cu$ $[M+H]^+$ 816.2063, found 816.2103.

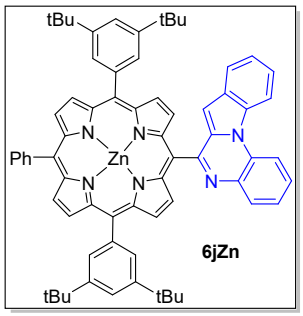
**Synthesis of *meso*-pyrrolo[1,2-a]quinoxalino-10,15,20-triphenylporphyrin (6dZn):** To a solution of **6bZn** (30 mg, 0.04 mmol) in a mixture of chloroform and methanol (20 mL, 1:1), $Zn(OAc)_2 \cdot H_2O$ (0.4 mmol) was added and stirred the contents at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with chloroform (20 mL) and washed with distilled water (3 × 30 mL). The organic phase was dried over anhydrous sodium sulfate and evaporated under vacuum. The residue thus obtained was subjected to column chromatography (silica gel) using chloroform as an eluent to afford pure **6dZn** as purple solid (26 mg, 79% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 456, 669; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.01 – 8.96 (m, 8H), 8.31 – 8.24 (m, 4H), 8.18 – 8.15 (m, 4H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.77 (m, 10H), 7.64 (td, *J* = 7.7, 1.3 Hz, 1H), 6.76 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.05 (d, *J* = 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.8, 150.6, 150.3, 149.9, 149.8, 142.3, 134.6, 134.1, 132.8, 132.2, 131.9, 130.9, 130.7, 128.1, 127.6, 127.5, 126.6, 126.5, 126.5, 125.7, 121.3, 114.4, 114.1, 114.1, 111.3; ESI-HRMS *m/z* calcd. for $C_{49}H_{31}N_6Zn[M+H]^+$ 766.1902 found 766.1897.




Similarly conpounds **6hZn** and **6jZn** were prepared and isolated

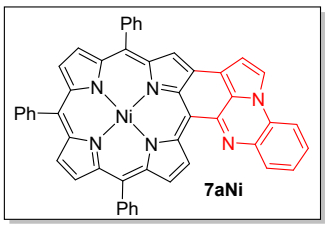
**6hZn:** Purple solid (26 mg, 80% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm):446, 604, 659; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 4.7 Hz, 2H), 9.00 (q, *J* = 4.7 Hz, 4H), 8.94 (d, *J* = 4.7 Hz, 2H), 8.86 (d, *J* = 8.3 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.30-8.26 (m, 4H), 8.22 – 8.20 (m, 2H), 7.90 – 7.86 (td, J = 5.8 Hz, J = 1.4 Hz, 1H), 7.83 – 7.73 (m, 10H), 7.67 – 7.54 (m, 3H), 7.34 (t, J = 7.4 Hz, J = 7.5 Hz, 1H), 6.31 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.8, 150.7, 150.3, 149.9, 149.7, 142.8, 142.7, 136.8, 134.8, 134.5, 134.4, 134.4, 133.0, 132.8, 132.3, 131.9, 131.2, 130.9, 130.7, 129.3, 129.1, 127.6, 127.5, 126.6, 126.5, 124.7, 124.5, 122.9, 122.7, 122.5, 121.4, 115.1, 114.7, 113.9, 105.5; ESI-HRMS *m/z* calcd. for $C_{53}H_{33}N_6Zn$ $[M+H]^+$ 817.2058 found 817.2033.



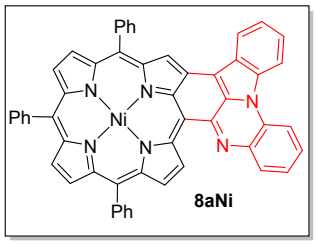

**6jZn:** Purple solid (24 mg, 75% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 448, 605, 660; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.07 – 8.98 (m, 8H), 8.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.75 (dd, J = 8.9, 1.0 Hz, 1H), 8.29 (m, 3H), 8.16 (t, *J* = 1.7 Hz, 2H), 8.08 (t, *J* = 1.7 Hz, 2H), 7.90 (td, *J* = 7.2, 1.6 Hz, 1H), 7.83 – 7.77 (m, 5H), 7.69 – 7.59 (m, 3H), 7.43 – 7.35 (td, *J* = 7

.0, 1.0 Hz, 1H), 6.35 (s, 1H), 1.55 (d, *J* = 15.2 Hz, 36H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.1, 149.0, 143.5, 143.0, 142.5, 142.1, 141.1, 139.8, 136.8, 133.7, 133.7, 133.5, 132.8, 132.3, 132.2, 131.3, 130.9, 130.9, 129.2, 129.0, 127.8, 126.9, 124.6, 124.5, 122.9, 122.7, 121.2, 120.7, 119.9, 115.0, 114.6, 112.2, 104.9, 35.0, 31.7; ESI-HRMS *m/z* calcd. for $C_{69}H_{65}N_6Zn[M+H]^+$ 1041.4562 found 1041.4522.



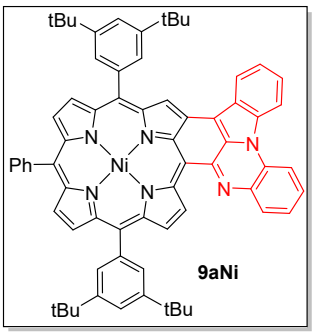

**Synthesis of *meso,β*-pyrrolo[1,2-*a*]quinoxalino-10,15,20-triphenylporphyrin (7aNi):** To a cooled (-78 °C) solution of **6aNi** (25 mg, 0.032 mmol) in dry dichloromethane (10 mL) was added very carefully $BF_3$.OEt2 (0.020 mmol) solution in dichloromethane (2 mL). The reaction mixture was stirred at -78 °C for 10 min and then added PIFA (0.040 mmol) solution in dry DCM (10 mL) very slowly over a period of 15 min. Progress of the reaction was monitored by TLC. After 10 min, the mixture was treated with sodium bicarbonate (10% aqueous solution) and the organic phase was extracted with dichloromethane (3× 50 mL) and washed with water (50 mL). Excess of solvent was distilled off and the crude product so obtained was purified by column chromatography using dichloromethane/hexane (30:70) as an eluent to afford **7aNi** as dark blackish solid (11 mg, 44% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 430, 456, 535, 579, 665; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, J = 8.6 Hz, 1H), 8.80 – 8.73 (m, 6H), 8.67 (d, J = 4.6 Hz, 1H), 8.03 (d, J = 6.9 Hz, 1H), 7.98 (d, J = 7.0 Hz, 4H), 7.76-7.62 (m, 12H), 6.95 (d, J = 4.5 Hz, 1H), 6.55 (d, J = 4.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.2, 142.7, 142.5, 142.3, 140.8, 140.7, 139.3, 137.6, 133.7, 133.7, 133.1, 132.4, 132.1, 131.2, 130.9, 130.2, 128.8, 127.8, 127.8, 127.5, 126.9, 126.2, 125.5, 124.0, 123.9, 123.4, 122.8, 120.2, 119.3, 116.2, 115.9, 115.9, 115.2, 114.1, 111.9, 110.5; ESI-HRMS *m/z* calcd. for $C_{49}H_{28}N_6NiK[M+K]^+$ 797.1366, found.797.1446.

Similarly, compounds **8aNi** and **9aNi** were prepared and isolated.



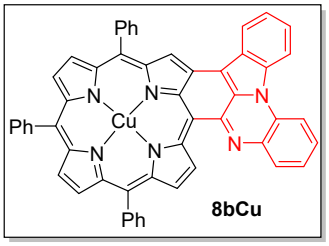

**8aNi:** Brown solid (14 mg, 56% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 393, 512, 710; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.15 (d, J = 5.0 Hz, 1H), 8.59 (d, J = 5.0 Hz, 1H), 8.48 (dd, J = 4.8, 4.8 Hz, 2H), 8.39 (s, 1H), 8.36 (t, J = 4.5 Hz, 2H), 8.28 – 8.24 (m, 2H), 8.17 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.99 (dd, J = 5.6, 1.6 Hz, 2H), 7.92 – 7.87 (m, 4H), 7.73 – 7.64 (m, 9H), 7.49 – 7.33 (m, 5H);$^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.2, 144.6, 144.5,

143.9, 143.5, 143.1, 142.1, 141.9, 140.4, 140.3, 140.2, 140.1, 139.3, 138.8, 136.9, 136.8, 135.5, 135.0, 133.3, 133.3, 133.3, 132.5, 131.8, 131.2, 131.0, 130.8, 128.5, 127.9, 127.9, 127.8, 127.8, 127.2, 127.0, 126.9, 126.3, 124.5, 124.4, 123.8, 123.8, 123.6, 122.4, 122.1, 121.2, 120.5, 119.2, 115.3, 114.5, 107.2, 104.5; ESI-HRMS *m/z* calcd. for $C_{53}H_{31}N_6Ni[M+H]^+$ 809.1964, found 809.1971.



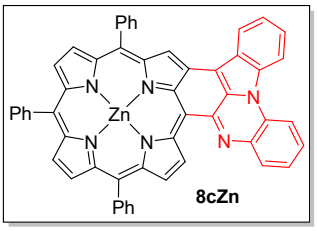

**9aNi:** Brown solid (15 mg, 60% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 400, 513, 711; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.22 (d, J = 5.0 Hz, 1H), 8.76 (d, J = 5.0 Hz, 1H), 8.62 (s, 1H), 8.43 – 8.37 (m, 3H), 8.33 – 8.31 (m, 2H), 8.28 – 8.26 (m, 1H), 8.21 – 8.15 (m, 2H), 7.91 – 7.89 (m, 2H), 7.81 (d, J = 1.8 Hz, 2H), 7.76 (d, J = 1.9 Hz, 2H), 7.70 (t, J = 1.8 Hz, 1H), 7.65 (t, J = 1.8 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.47 – 7.32 (m, 5H), 1.45 (d, J = 15.1 Hz, 36H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.5, 149.4, 149.2, 144.8, 144.6, 144.0, 143.9, 143.0, 142.0, 141.8, 140.3, 139.5, 139.4, 138.9, 136.8, 136.7, 136.0, 135.1, 133.2, 132.4, 131.7, 131.2, 130.9, 128.7, 128.5, 128.3, 127.9, 127.8, 127.0, 126.4, 124.5, 124.3, 123.9, 123.7, 122.7, 122.2, 121.9, 121.3, 121.2, 120.9, 120.6, 115.3, 114.4, 107.3, 104.5, 46.0, 35.1, 35.0, 31.7; ESI-HRMS *m/z* calcd. for $C_{69}H_{63}N_6Ni[M+H]^+$ 1033.4468, found 1033.4448.

**Synthesis of *meso,β*-indolo[1,2-*a*]quinoxalino-10,15,20-triphenylporphyrin (8bCu):** To a




cooled (-78 °C) solution of **6gCu** (25 mg, 0.032 mmol) in dry dichloromethane (10 mL) was added very carefully $BF_3$.OEt2 (0.020 mmol) solution in dichloromethane (2 mL). The reaction mixture was stirred at -78 °C for 10 min and then added PIFA (0.040 mmol) solution in dry DCM (10 mL) very slowly over a period of 15 min. Progress of the reaction was monitored by TLC. After 10 min, the mixture was treated with sodium bicarbonate (10% aqueous solution) and the organic phase was extracted with dichloromethane (3× 50 mL) and washed with water (50 mL). Excess of solvent was distilled off and the crude product so obtained was purified by column chromatography using dichloromethane/hexane (30:70) as an eluent to afford **8bCu** brown solid (10 mg, 40% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 413, 512, 643, 705; ESI-HRMS *m/z* calcd. for $C_{53}H_{30}N_6Cu[M+K]^+$ 852.1465, found 852.2546.

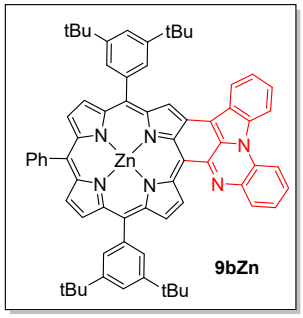
**Synthesis of *meso,β*-indolo[1,2-*a*]quinoxalino-10,15,20-*tri*-phenylporphyrin (8cZn):** To a




cooled (-78 °C) solution of **6gZn** (25 mg, 0.032 mmol) in dry

dichloromethane (10 mL) was added very carefully $BF_3.OEt_2$ (0.020 mmol) solution in dichloromethane (2 mL). The reaction mixture continued to stir at -78 °C for 10 min and then added PIFA (0.040 mmol) solution in dry DCM (10 mL) very slowly over a period of 15 min. Progress of the reaction was monitored by TLC. After 10 min, the mixture was treated with sodium bicarbonate (10% aqueous solution) and the organic phase was extracted with dichloromethane (3× 50 mL) and washed with water (50 mL). Excess of solvent was distilled off and obtained the crude product was demetalated in the presence of trifluoroacetic acid and sulphuric acid (0.85 mmol) to afford the appropriate free-base porphyrin. Next, the complexation of free-base porphyrin with zinc acetate using the protocol described for **6dZn** delivered the corresponding product **8cZn** as brown solid (08 mg, 33% yield); UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 454, 520, 560, 674, 742; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.67 (d, J = 4.9 Hz, 1H), 8.66 (dd, J = 4.5, 2.9 Hz, 2H), 8.59 – 8.54 (m, 3H), 8.40 (s, 1H), 8.25 – 8.21 (m, 2H), 8.19-8.17 (m, 2H), 8.13 – 8.10 (m, 2H), 8.01 (d, J = 7.1 Hz, 2H), 7.86-7.77 (m, 9H), 7.71 – 7.68 (m, 2H), 7.16 – 7.08 (m, 3H), 6.92 – 6.86 (m, 2H); ESI-HRMS *m/z* calcd. for $C_{53}H_{34}N_7Zn[M+NH_4]^+$ 832.2167 found 832.2367

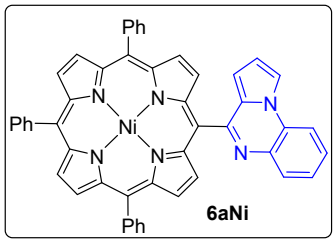
Similarly, compound **9bZn** was prepared and isolated.

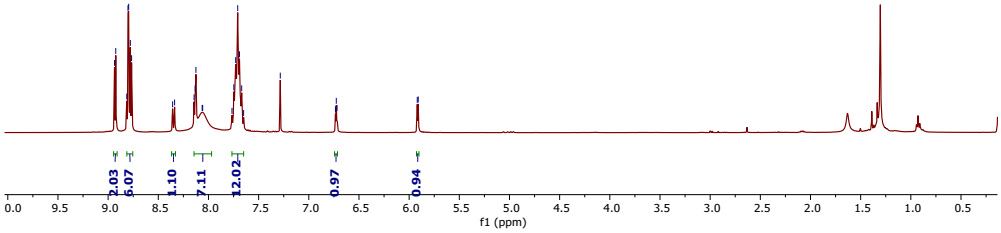



**9bZn:** Brown solid (12 mg, 47% yield); Normalized UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (nm): 453, 521, 558, 674, 779; $^1$H NMR (400 MHz, $CDCl_3$) δ 11.00 (d, J = 4.8 Hz, 1H), 8.90 (d, J = 4.9 Hz, 1H), 8.81 – 8.57 (m, 5H), 8.29 – 7.94 (m, 9H), 7.93 – 7.84 (m, 2H), 7.84 – 7.65 (m, 4H), 7.38 (t, J = 7.4 Hz, 2H), 6.98 – 6.84 (m, 2H), 1.68 – 1.51 (d, J = 15.2 Hz, 36H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.8, 149.4, 149.3, 149.0, 148.8, 148.7, 142.5, 141.7, 141.6, 138.4, 135.2, 135.1, 134.6, 134.0, 133.8, 132.4, 131.4, 131.3, 131.1, 130.6, 129.9, 129.4, 127.6, 127.5, 127.5, 126.7, 124.7, 124.3, 123.8, 123.8, 122.0, 121.0, 120.9, 120.7, 115.8, 115.1, 113.9, 107.7, 106.2, 35.2, 35.1, 31.8; ESI-HRMS *m/z* calcd. for $C_{69}H_{63}N_6Zn[M+H]^+$ 1039.4406, found 1039.4366.

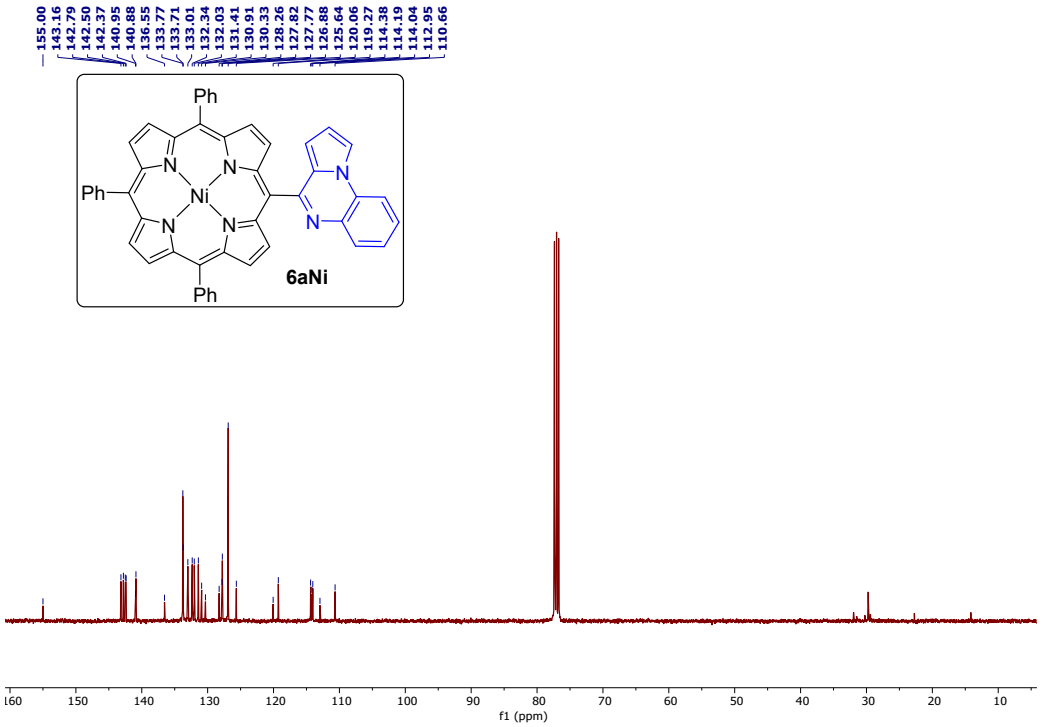
**Actual NMR ($^1$H, $^{13}$C, COSY, DEPT 135) and HRMS spectra of the synthesized compounds**

**$^1$H NMR spectrum of 6aNi**

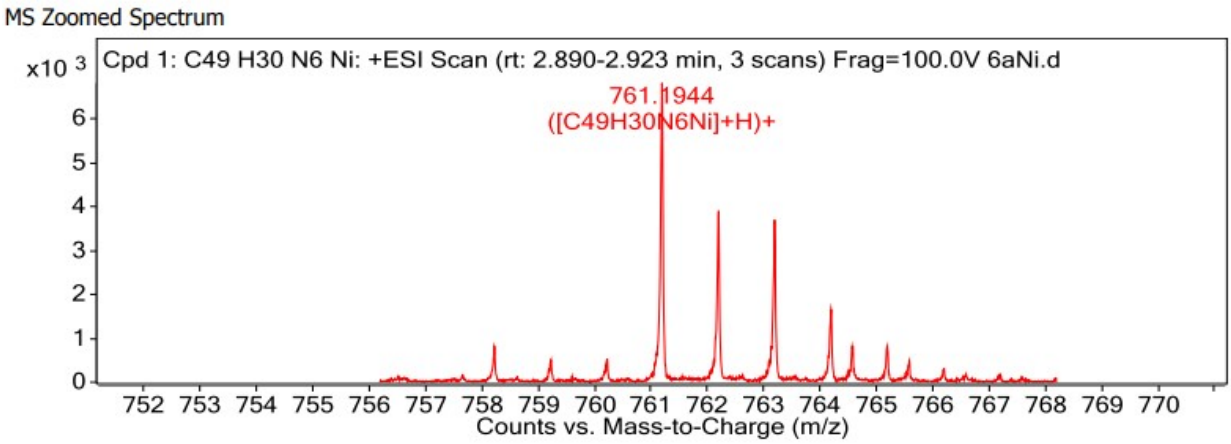



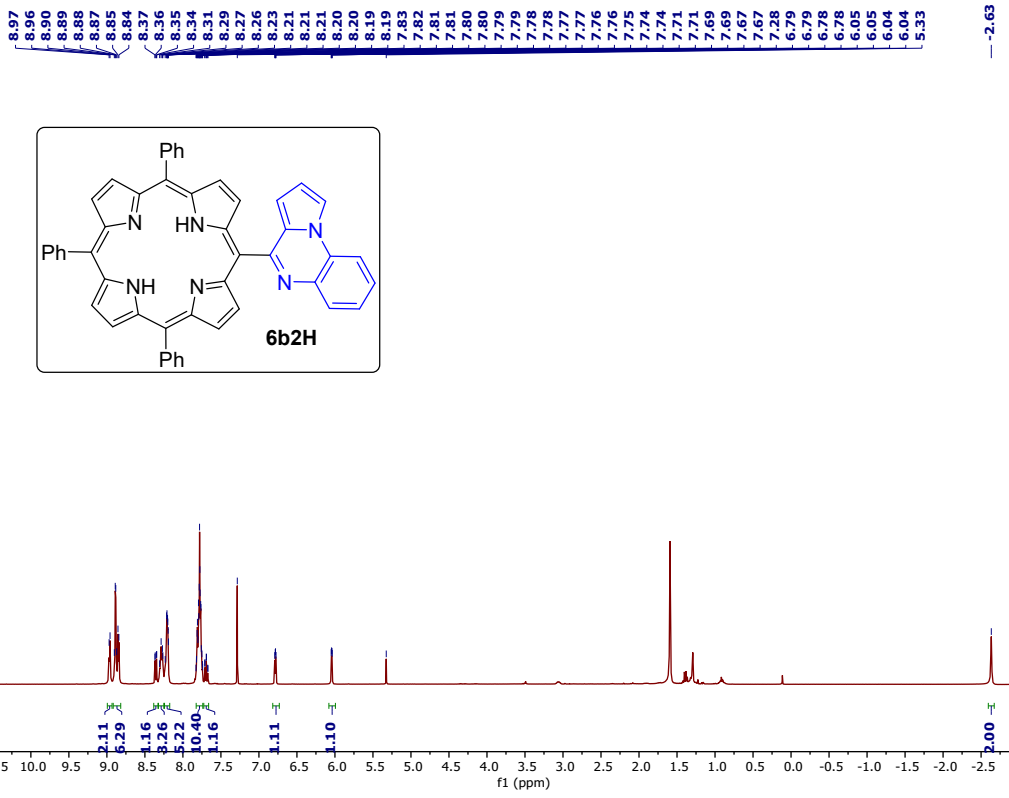

**$^{13}$C NMR spectrum of 6aNi**



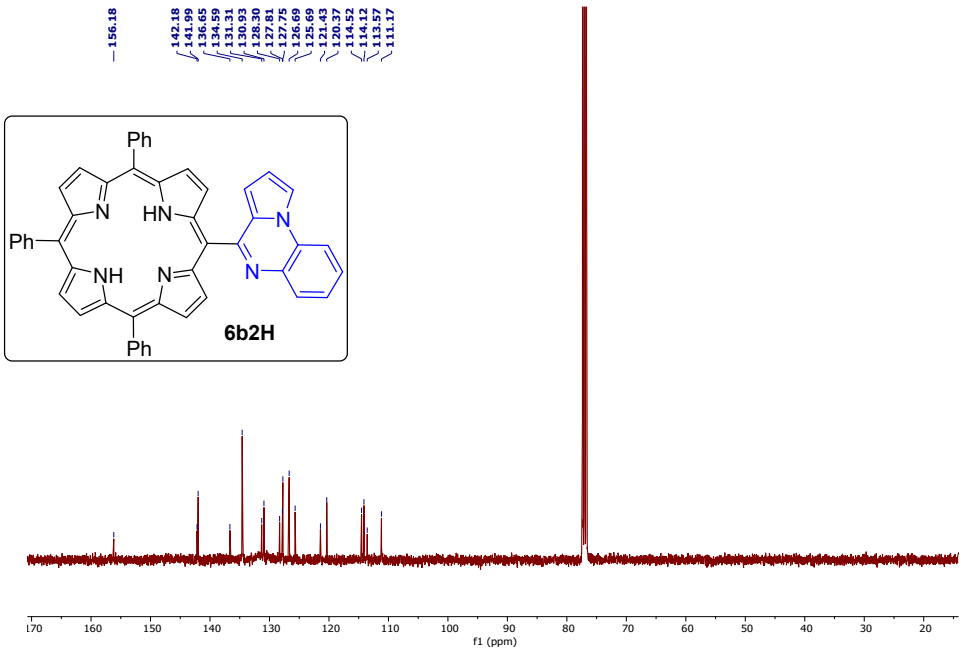

**HRMS spectrum of 6aNi**



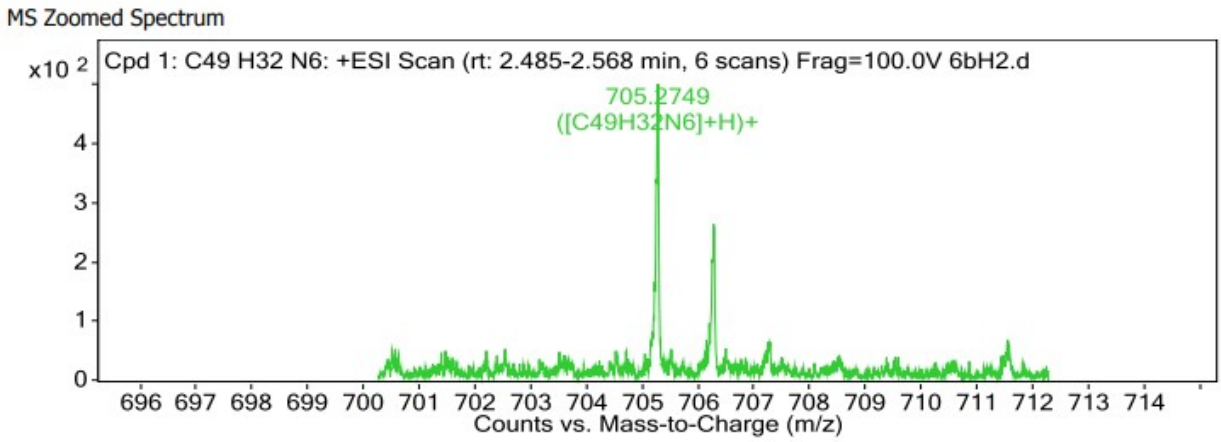

**$^{1}$H NMR spectrum of 6b2H**



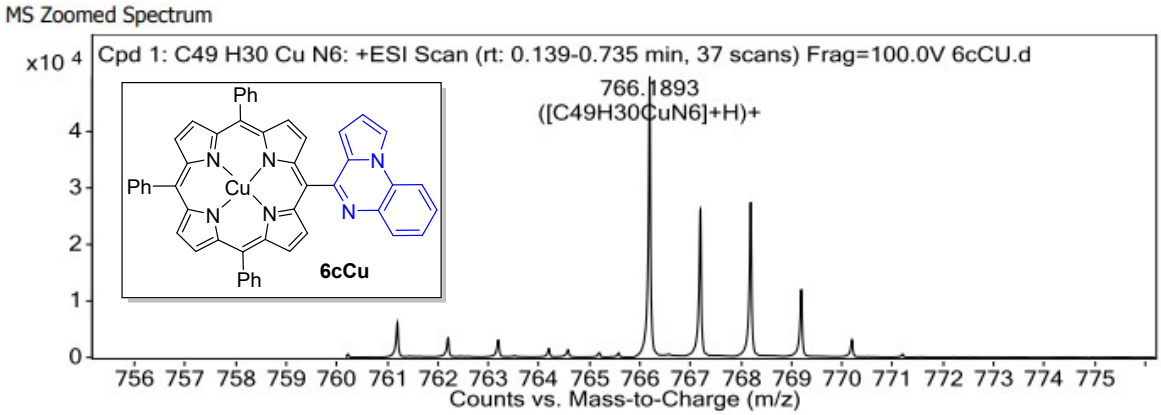

## $^{13}$C NMR spectrum of 6b2H



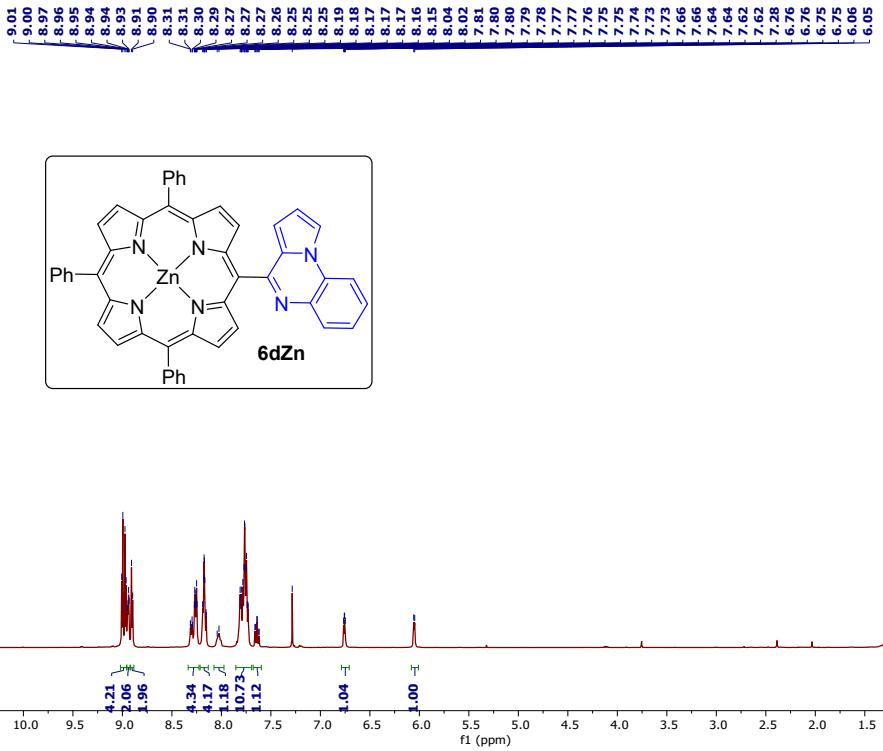

## HRMS spectrum of 6b2H



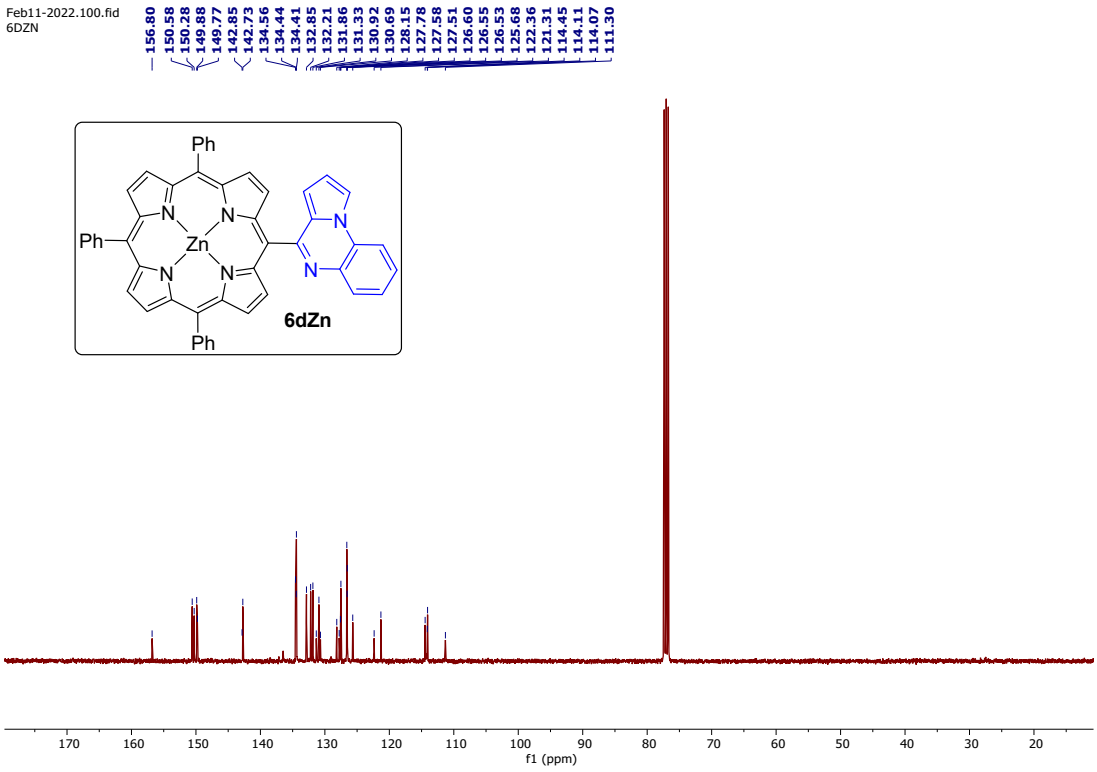

**HRMS spectrum of 6cCu**



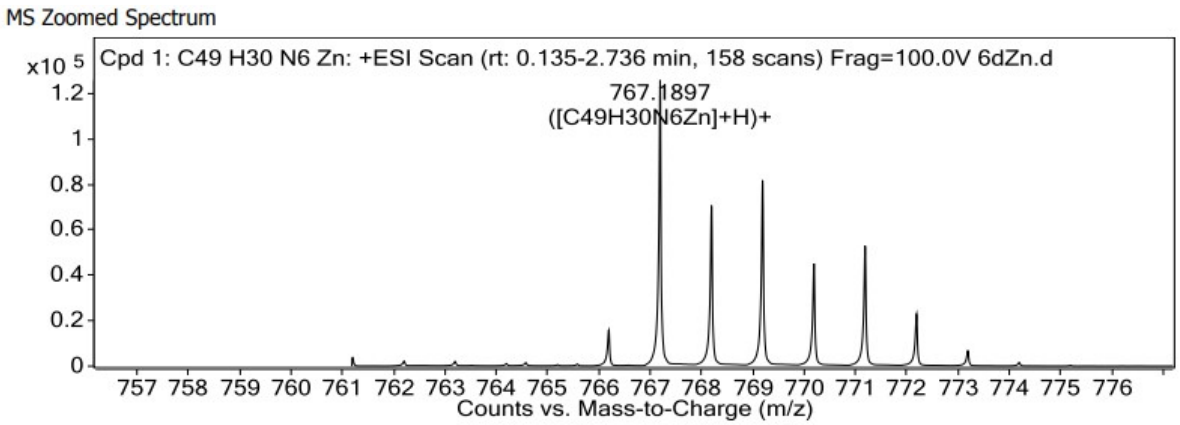

**$^{1}$H NMR spectrum of 6dZn**



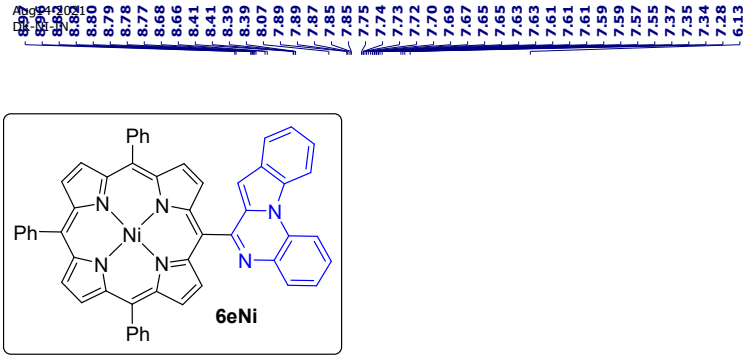

## $^{13}$C NMR spectrum of 6dZn

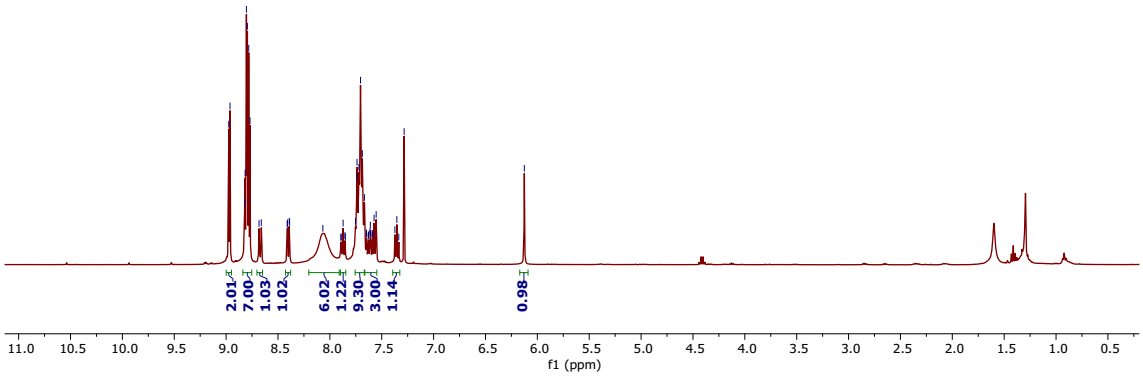



## HRMS spectrum of 6dZn

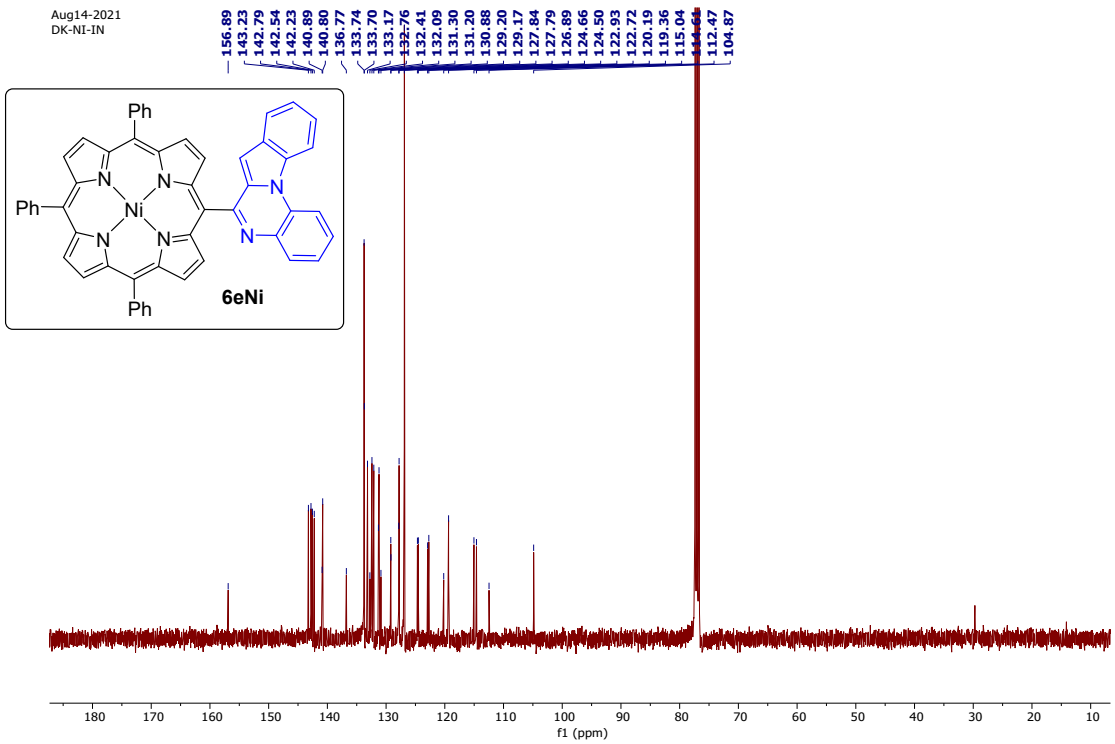



## $^{1}$H NMR spectrum of 6eNi

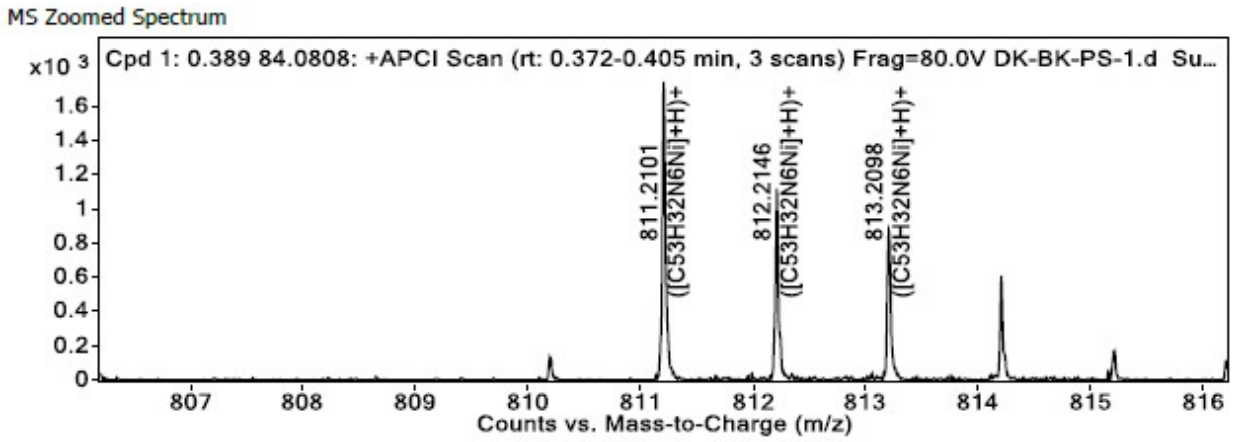


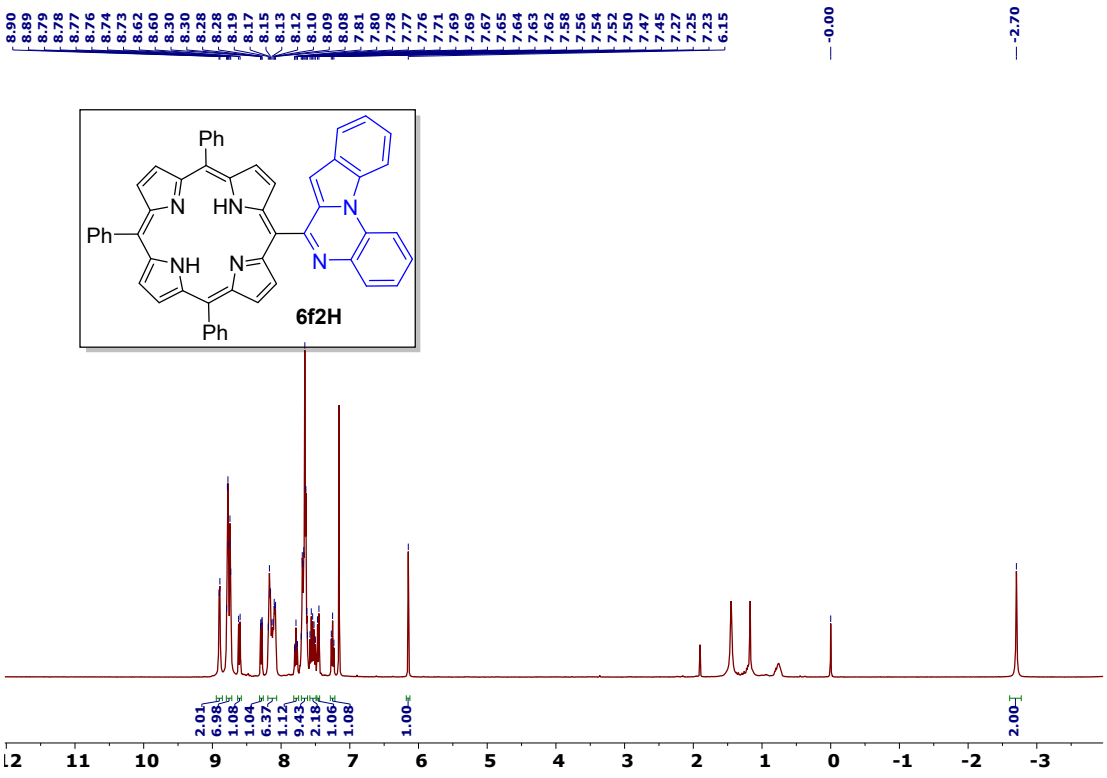

## $^{13}$C NMR spectrum of 6eNi



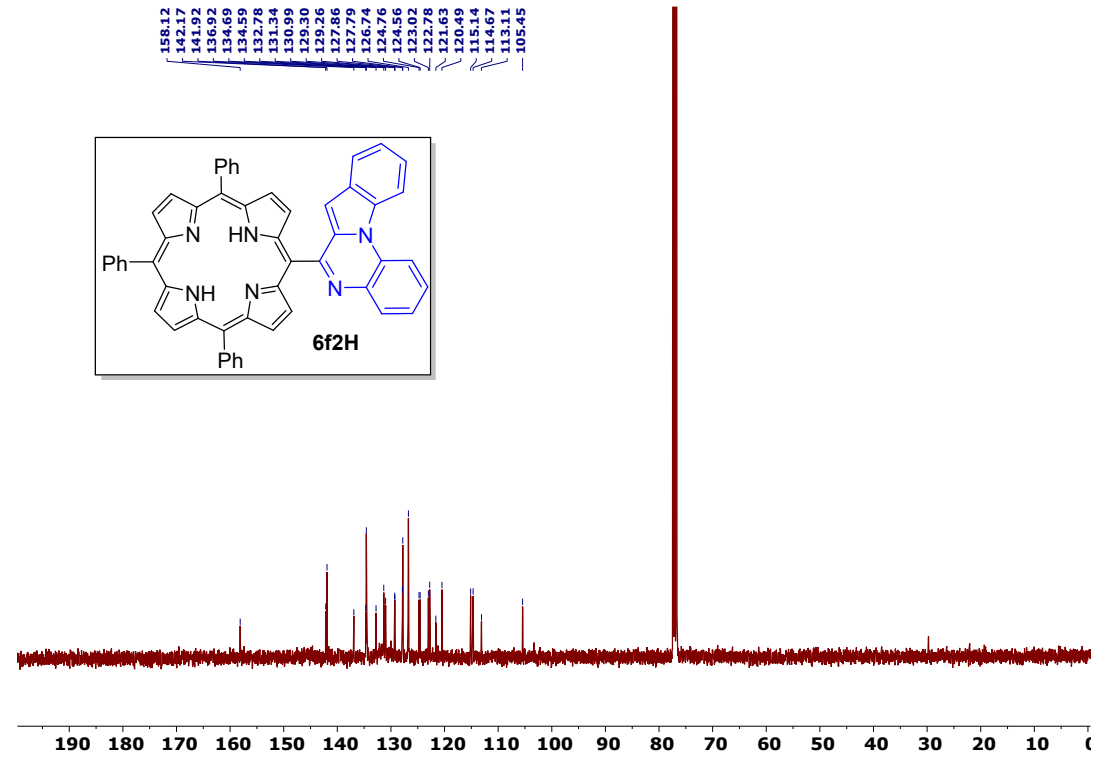

**HRMS spectrum of 6eNi**



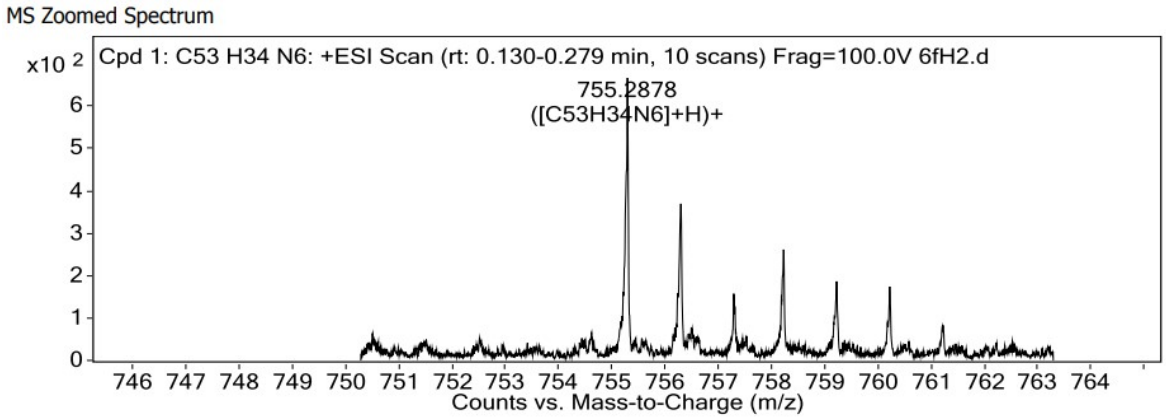

**$^{1}$H NMR spectrum of 6f2H**



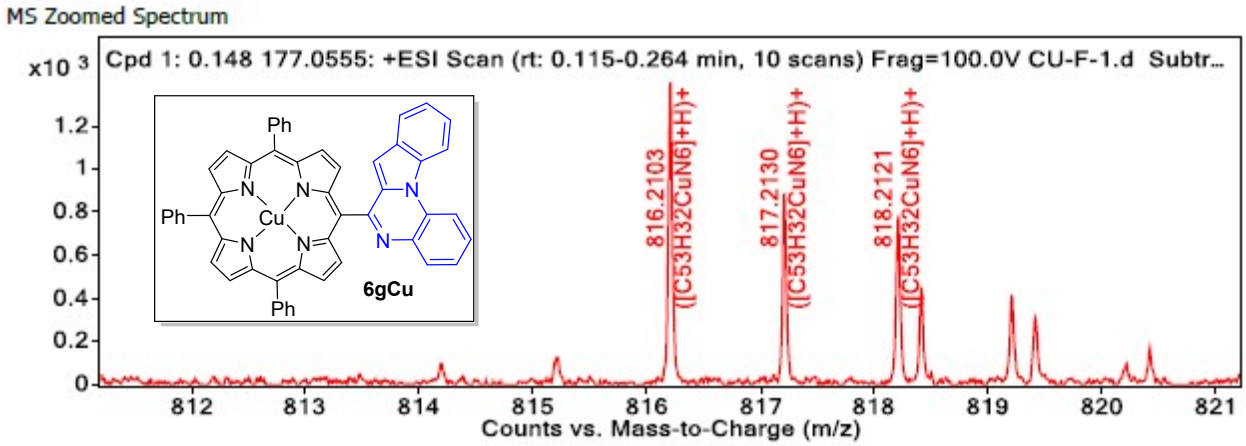

## $^{13}$C NMR spectrum of 6f2H



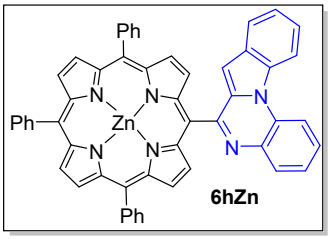
## HRMS spectrum of 6f2H

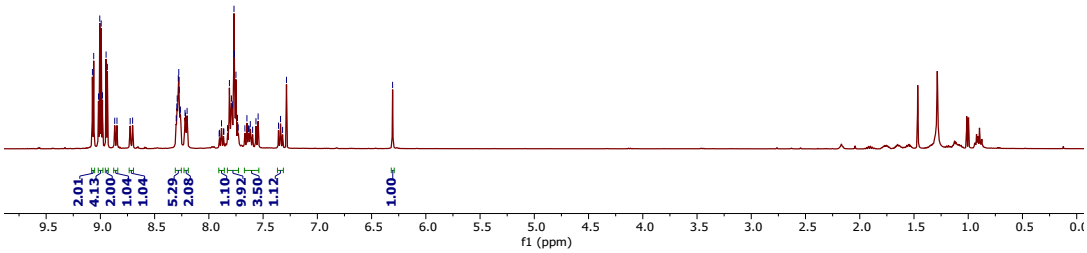



## HRMS spectrum of 6gCu

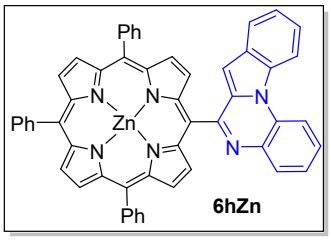


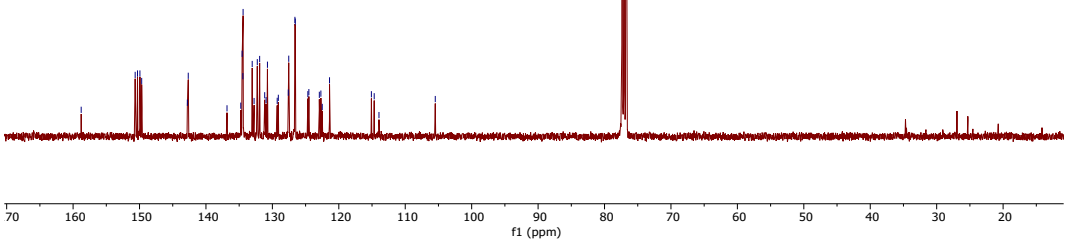
## $^{1}$H NMR spectrum of 6hZn



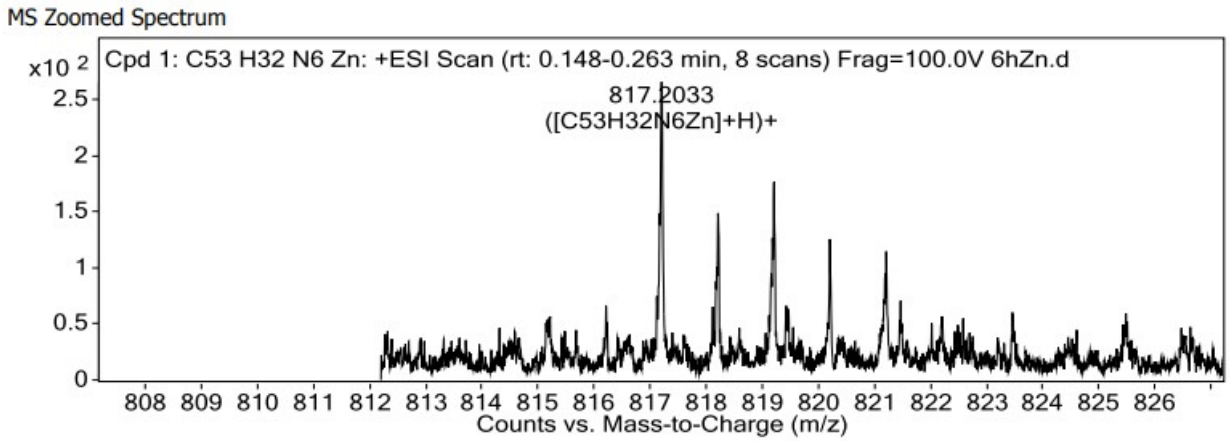




## $^{13}$C NMR spectrum of 6hZn

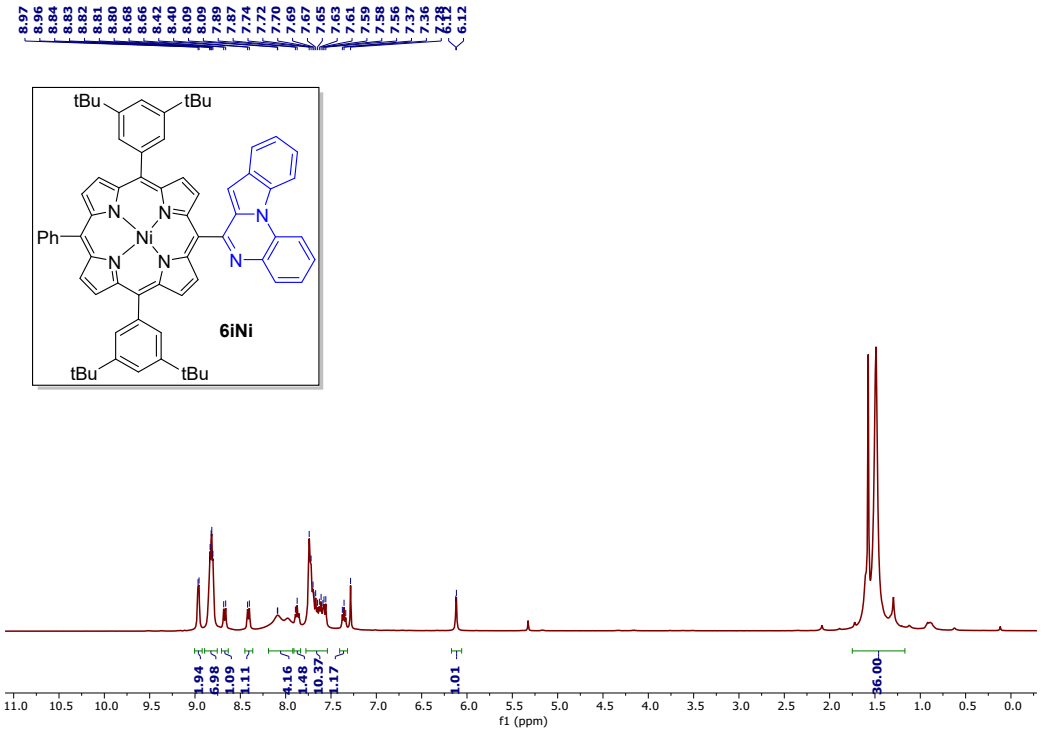



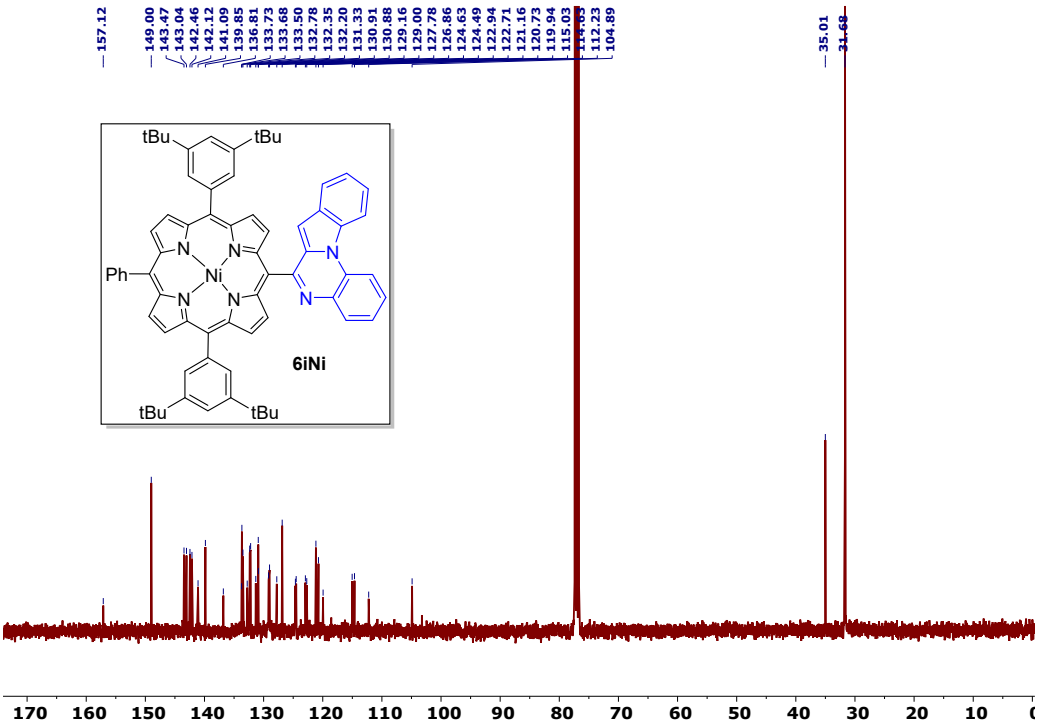
## HRMS spectrum of 6hZn



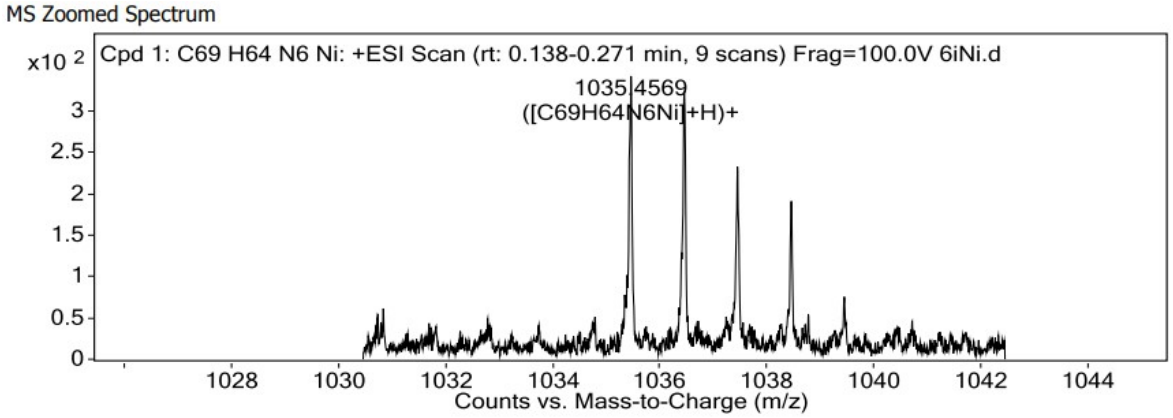

## $^1$H NMR spectrum of 6iNi



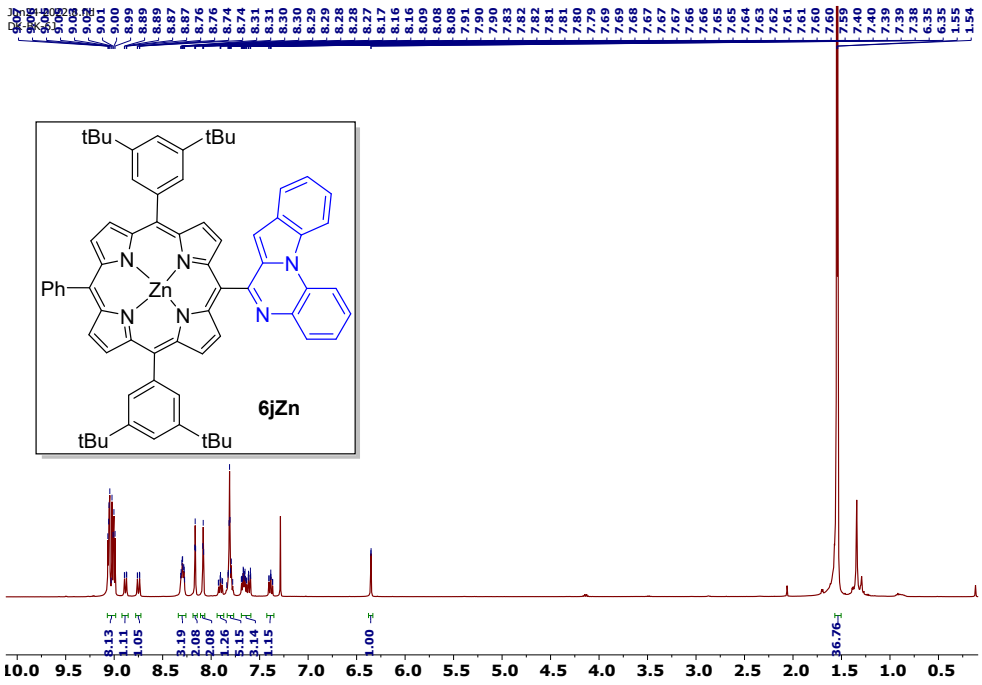
## $^{13}$C NMR spectrum of 6iNi



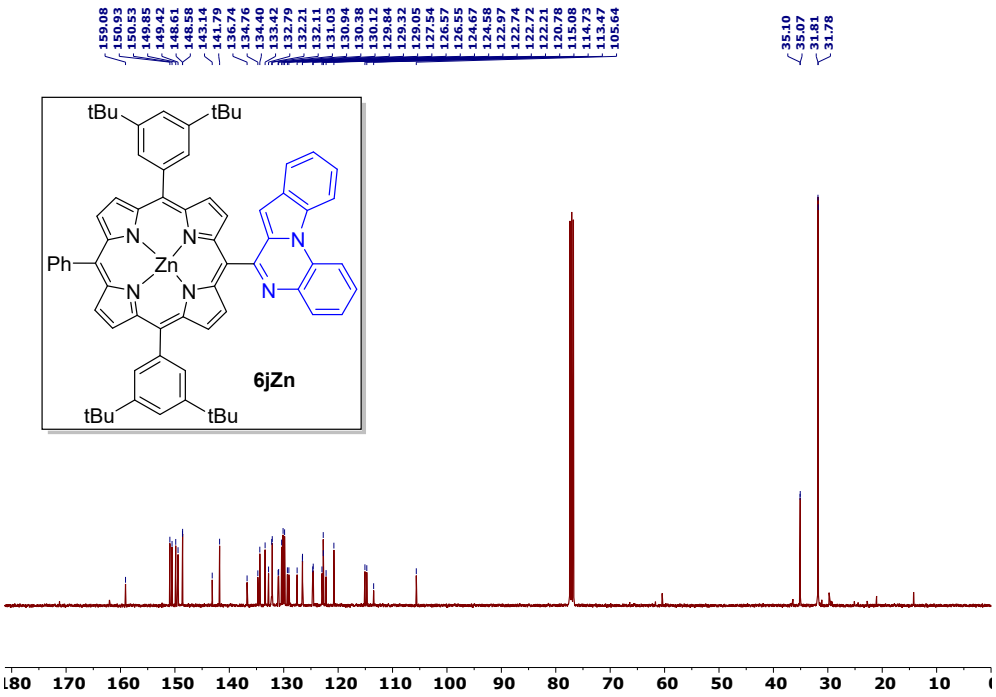

## HRMS spectrum of 6iNi



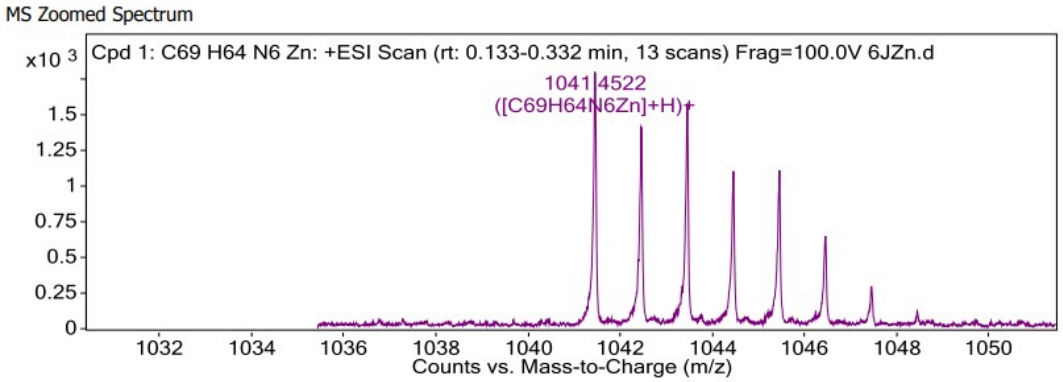
## $^{1}$H NMR spectrum of 6jZn



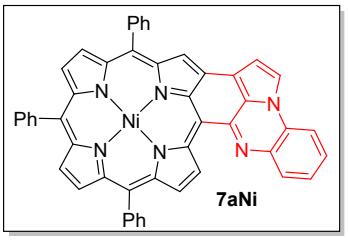

## $^{13}$C NMR spectrum of 6jZn

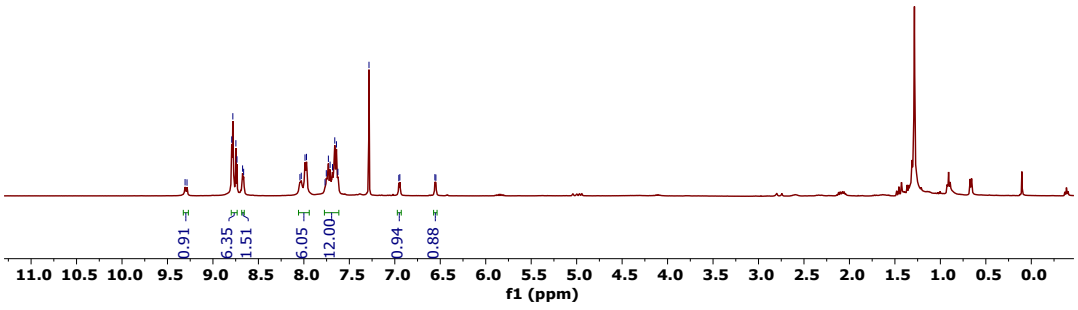


## HRMS spectrum of 6jZn

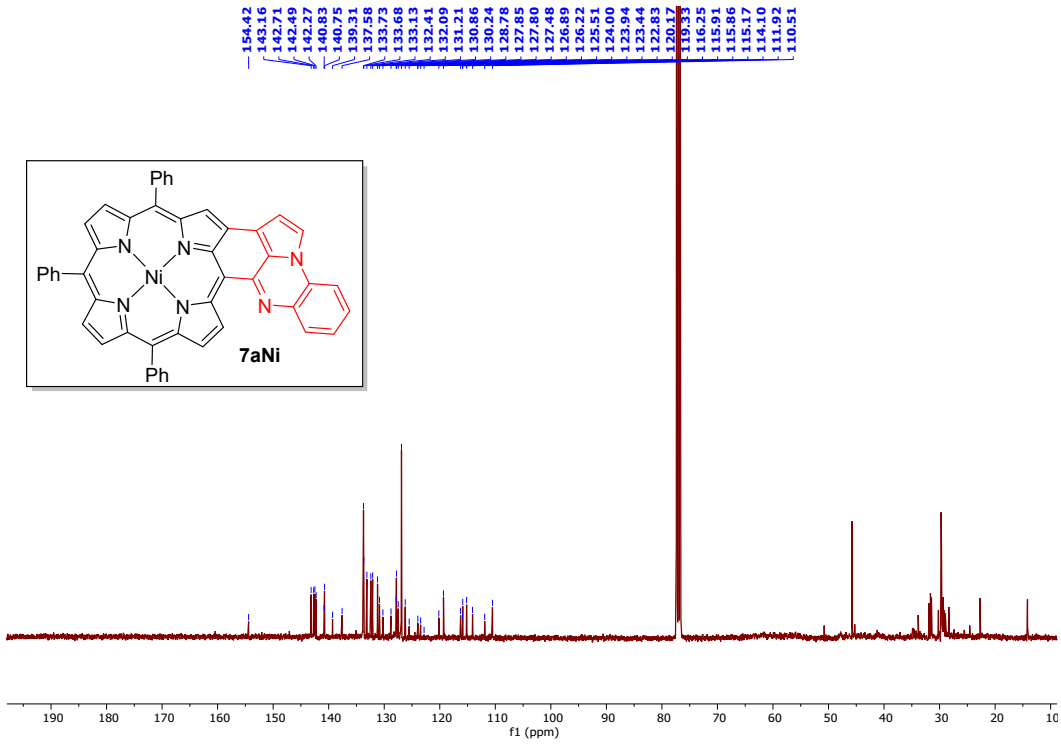



## $^{1}$H NMR spectrum of 7aNi

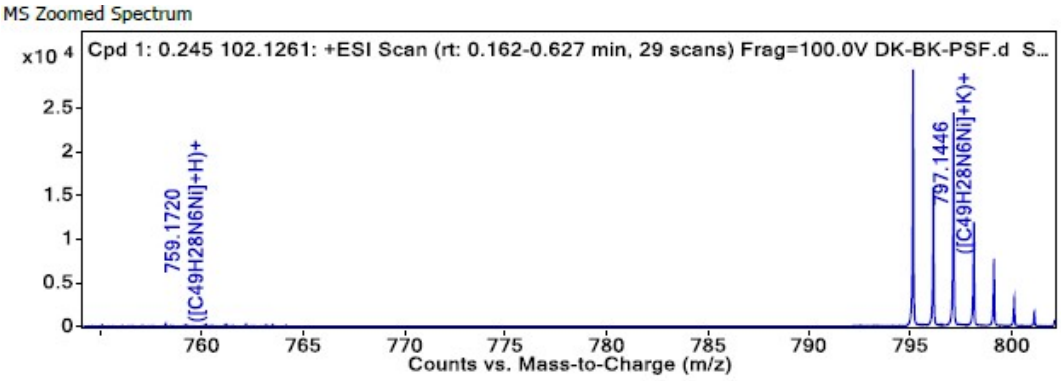



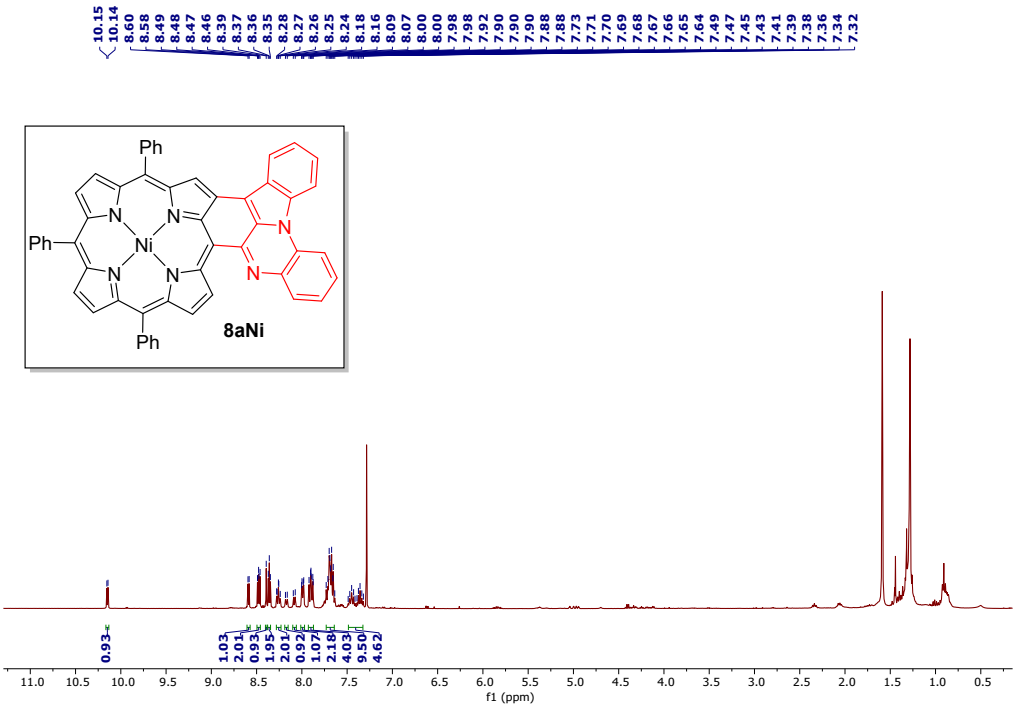
## $^{13}$C NMR spectrum of 7aNi



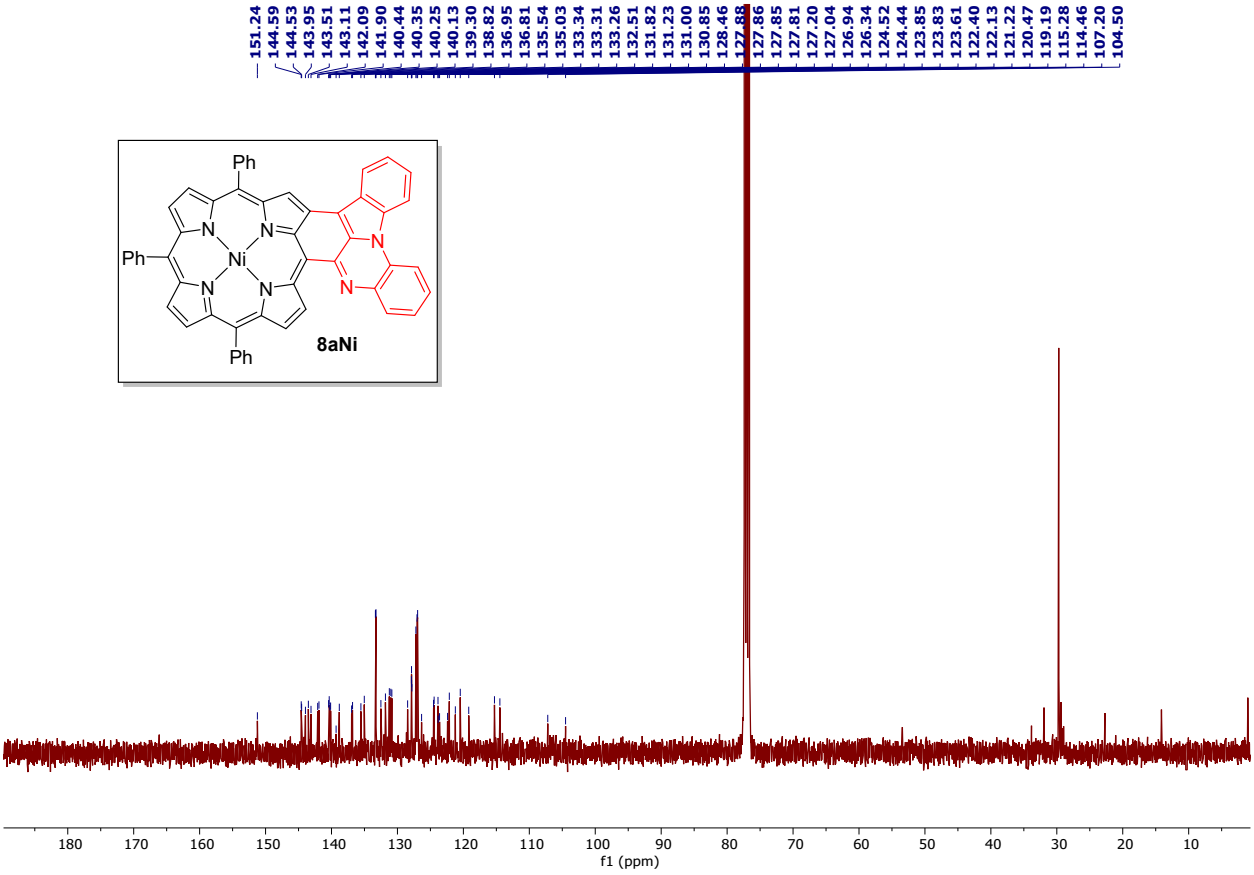

## HRMS spectrum of 7aNi



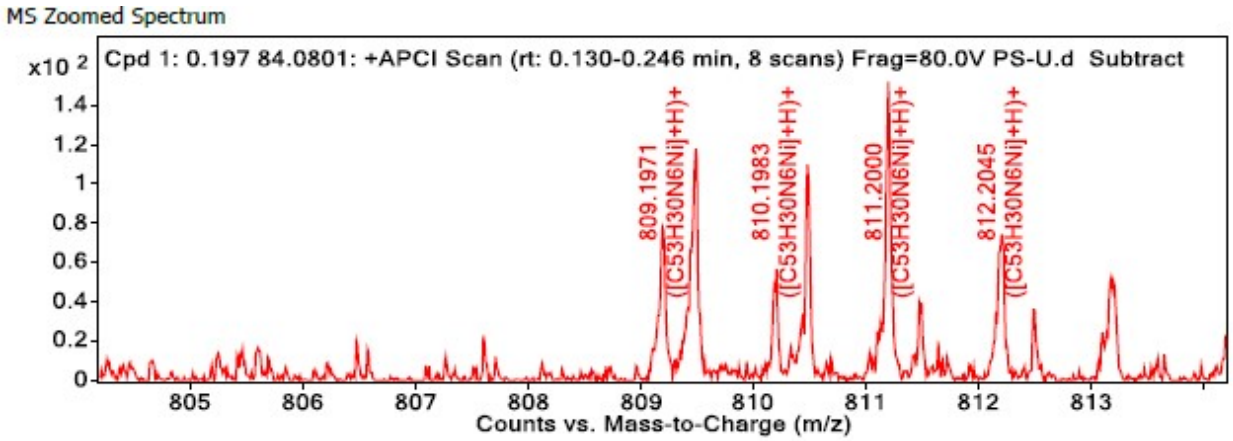
## $^{1}$H NMR spectrum of 8aNi



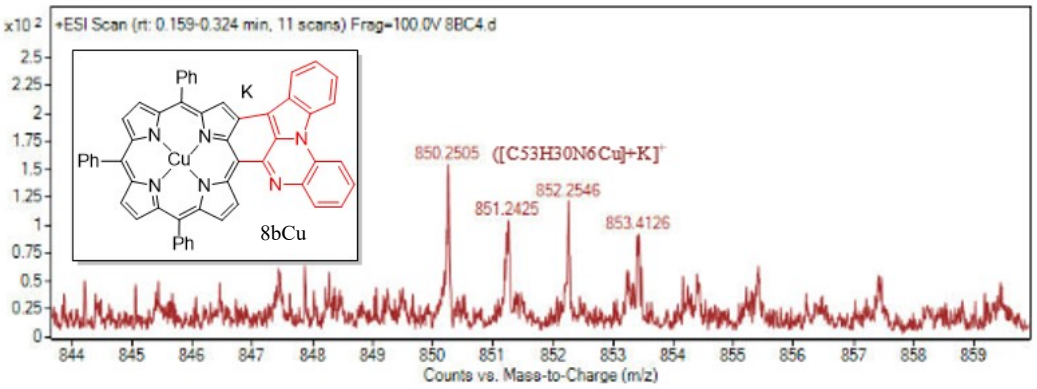
## $^{13}$C NMR spectrum of 8aNi



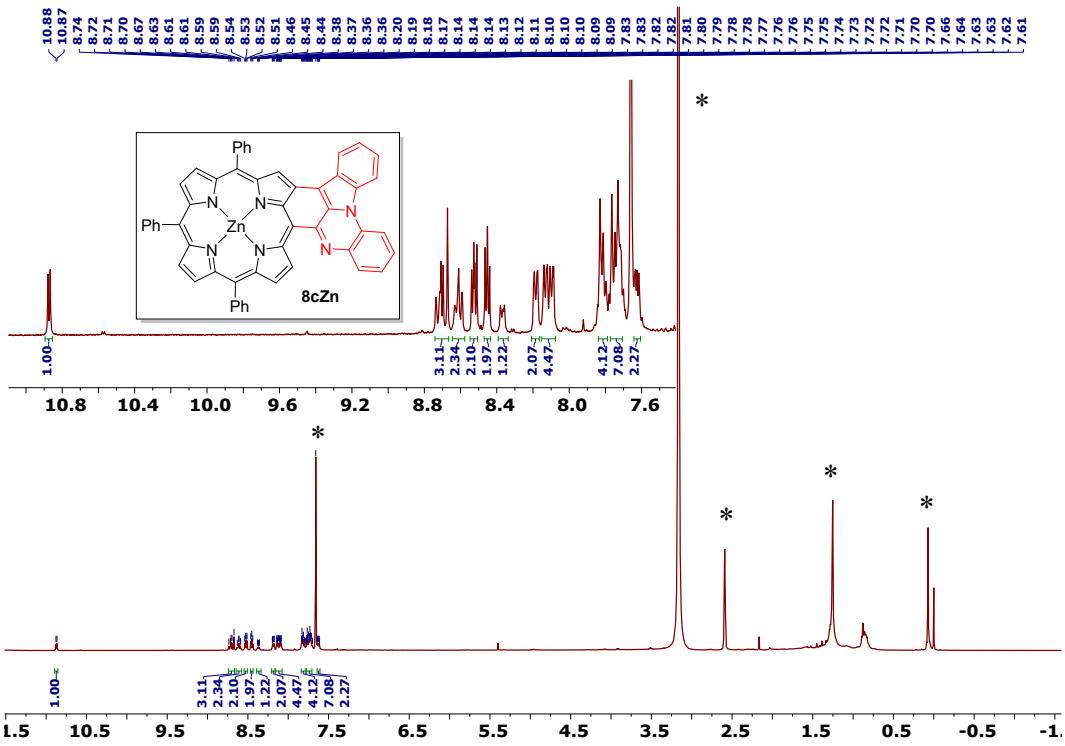

## HRMS spectrum of 8aNi



**HRMS spectrum of 8bCu**

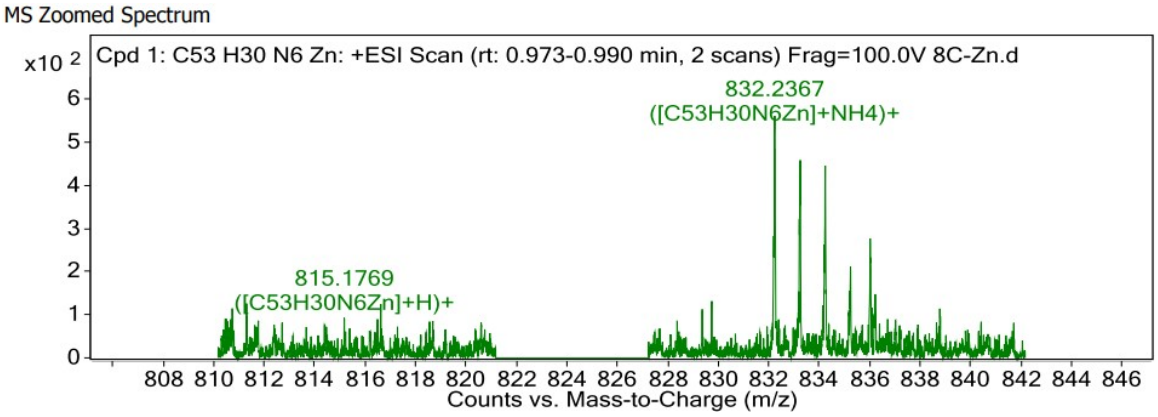



**$^{1}$H NMR spectrum of 8cZn**

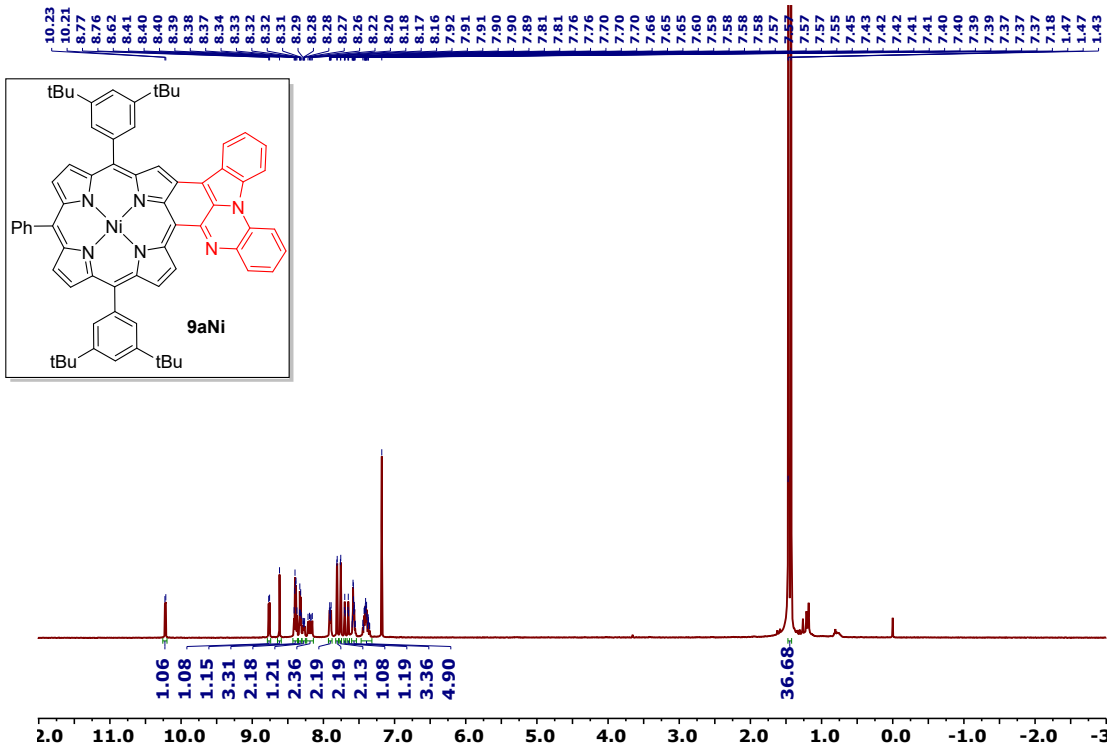



* Solvent impurities

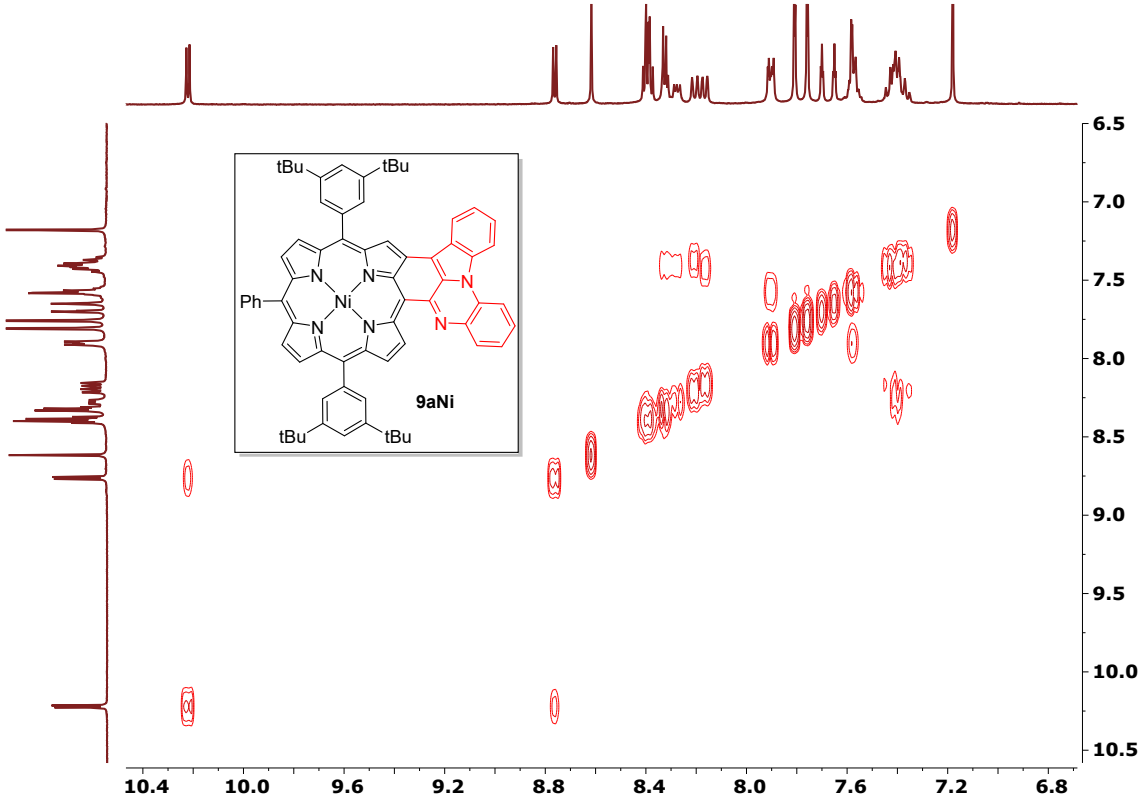
## HRMS spectrum of 8cZn



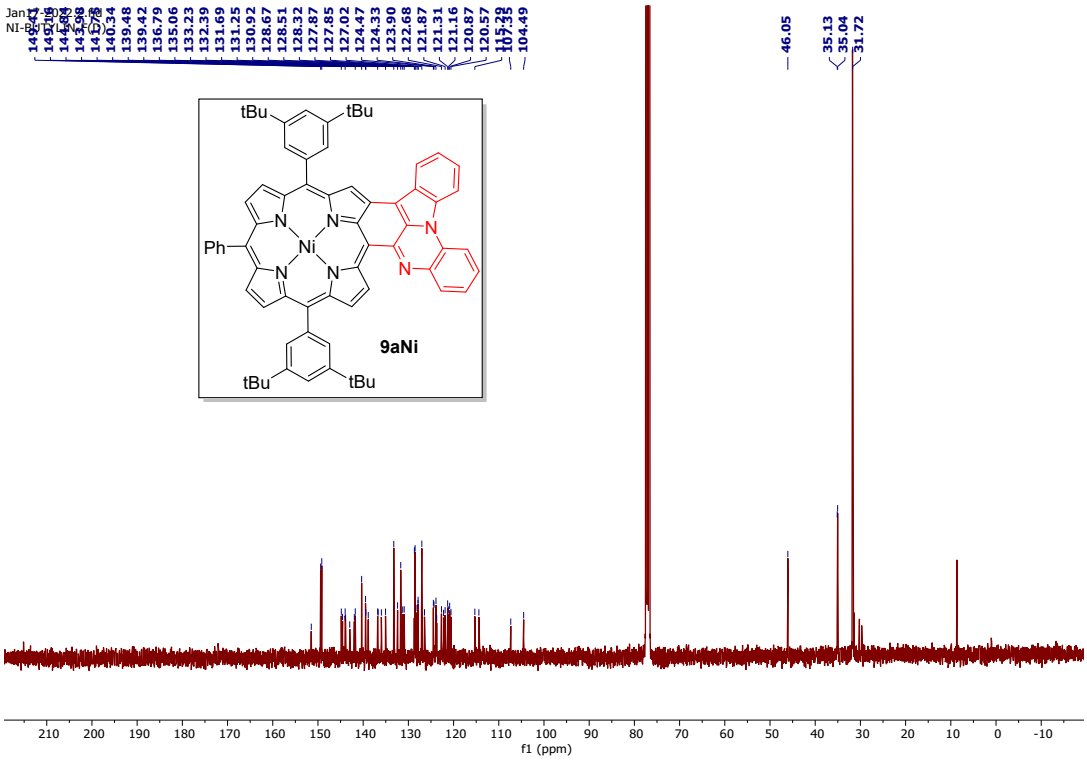

## $^1$H NMR spectrum of 9aNi



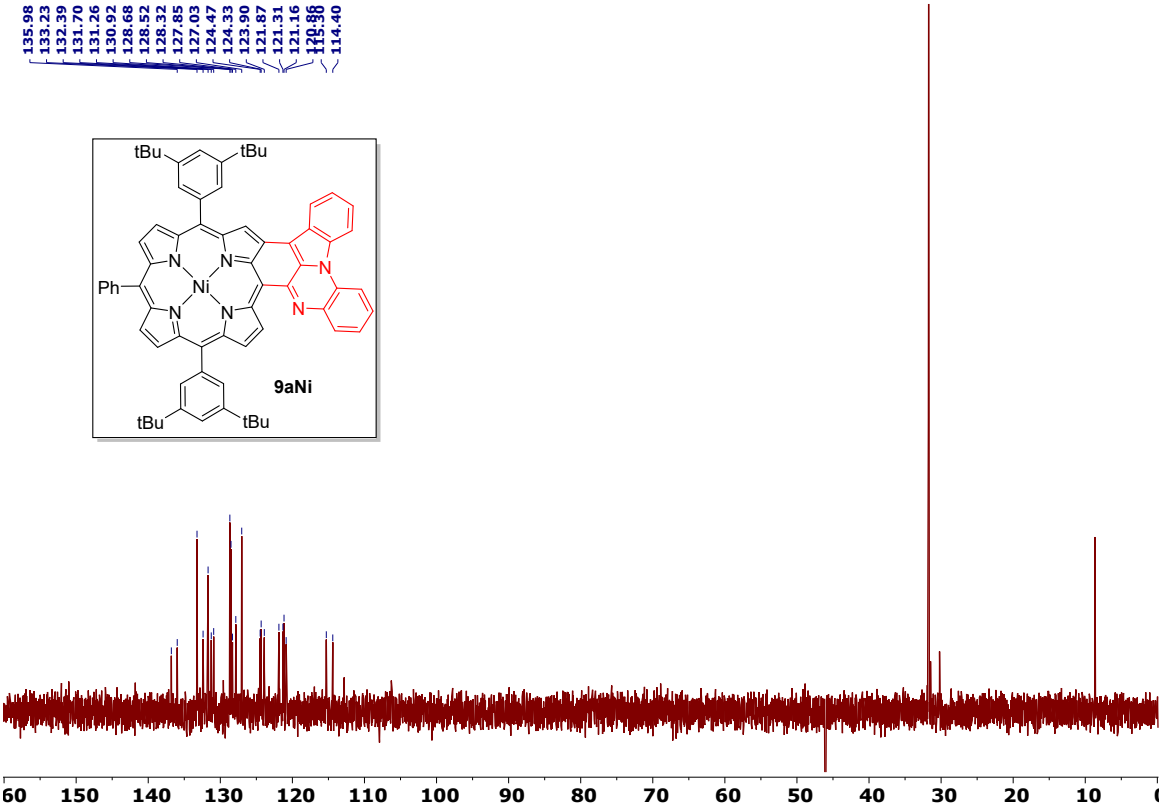
## COSY spectrum of 9aNi



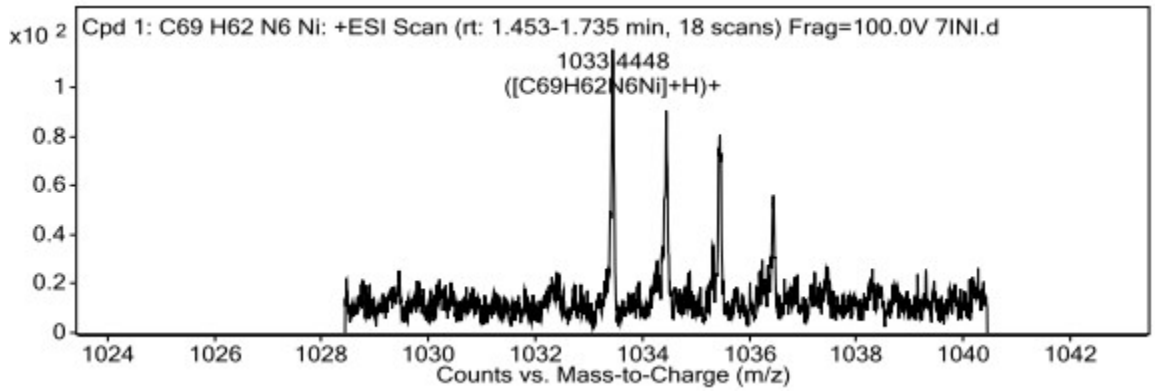

## $^{13}$C NMR spectrum of 9aNi



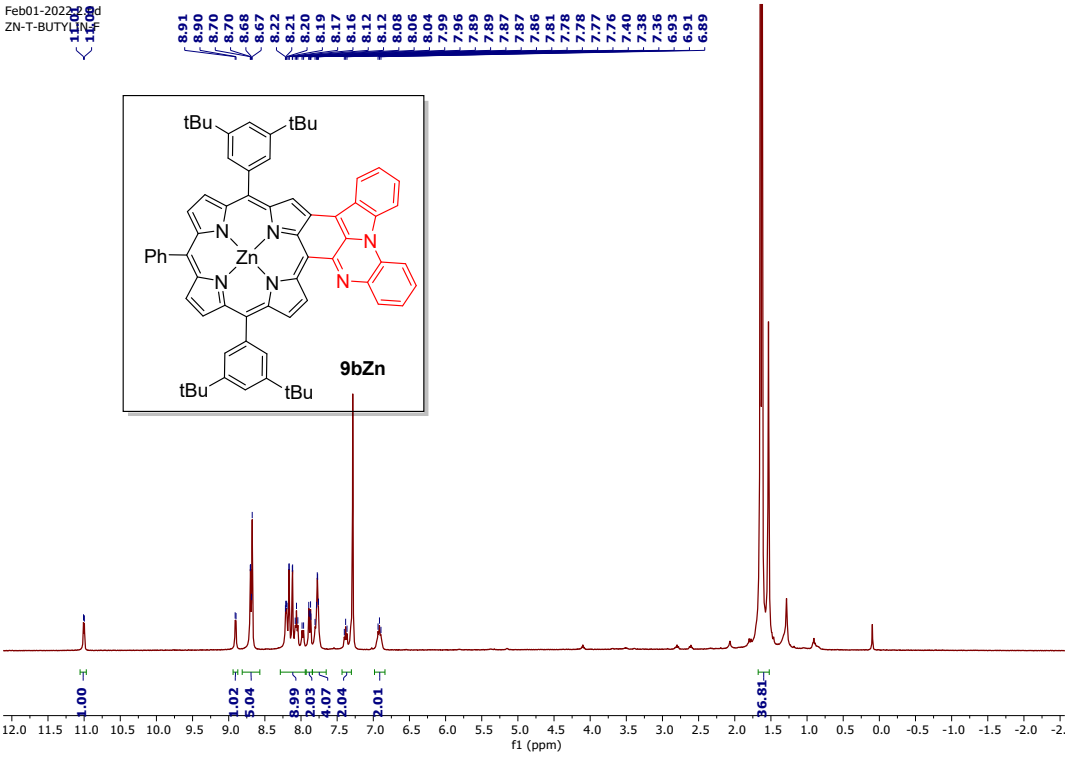
## DEPT 135 NMR spectrum of 9aNi



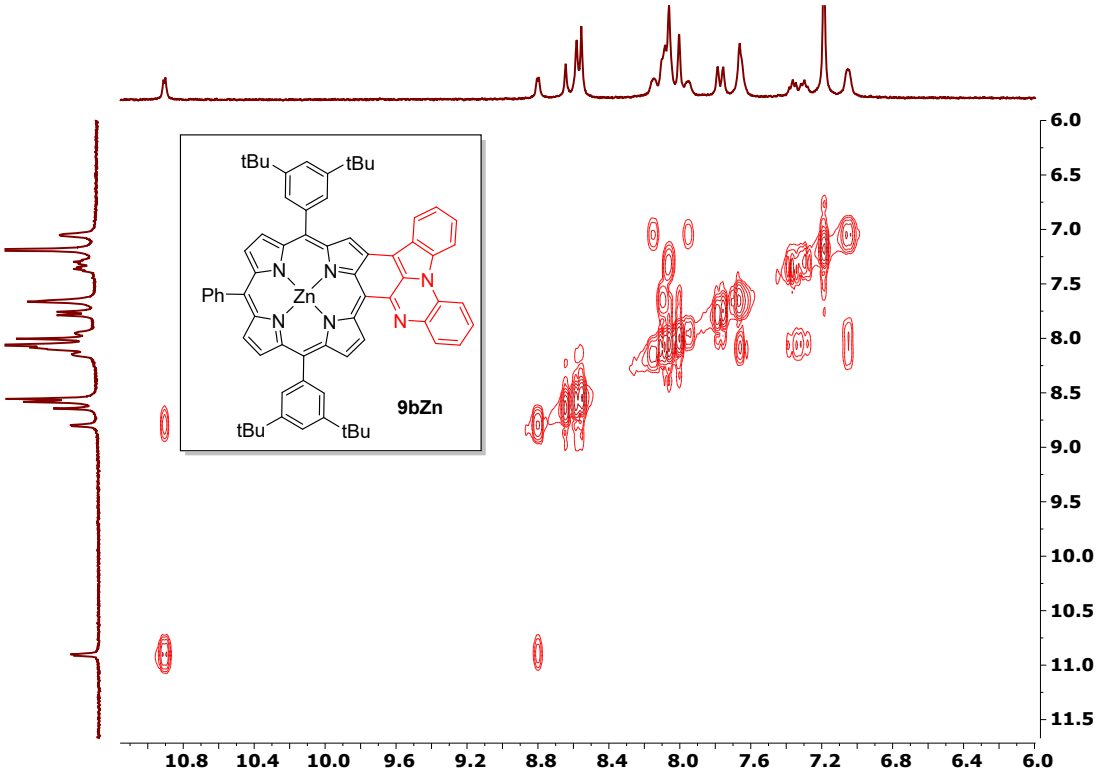

## HRMS spectrum of 9aNi



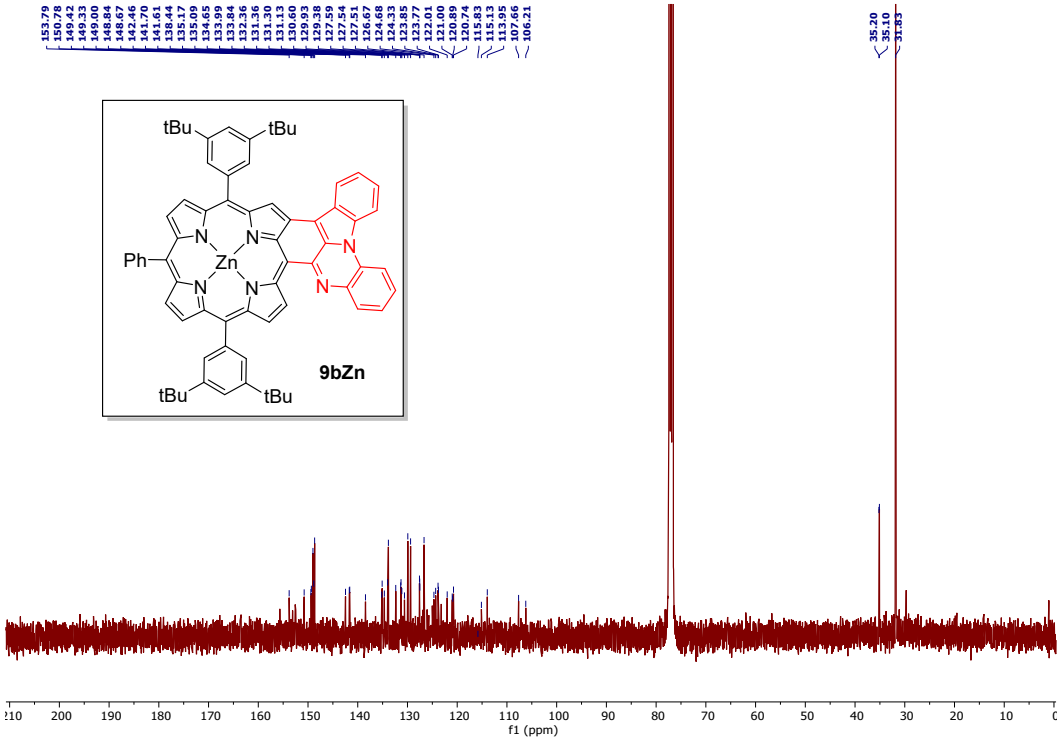
## $^{1}$H NMR spectrum of 9bZn



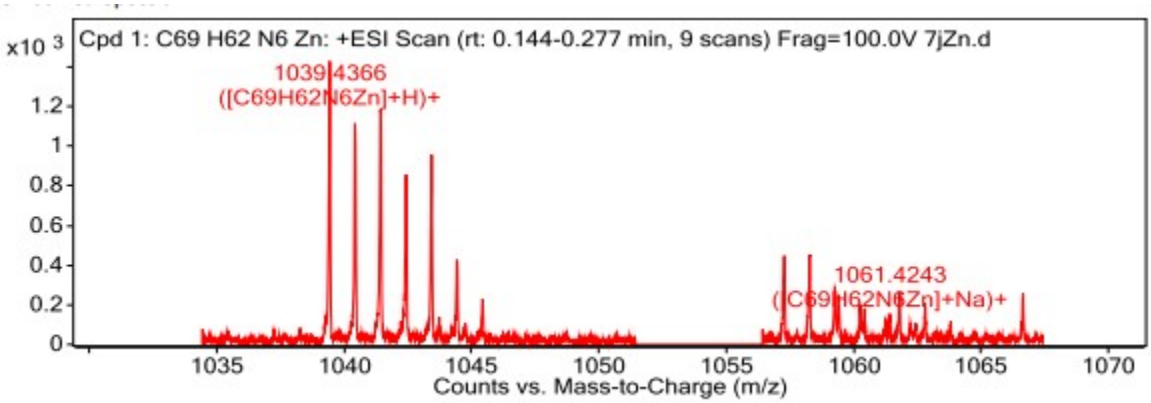

## COSY spectrum of 9bZn



## $^{13}$C NMR spectrum of 9bZn




## HRMS spectrum of 9bZn



# III. Photophysical Study and other related data

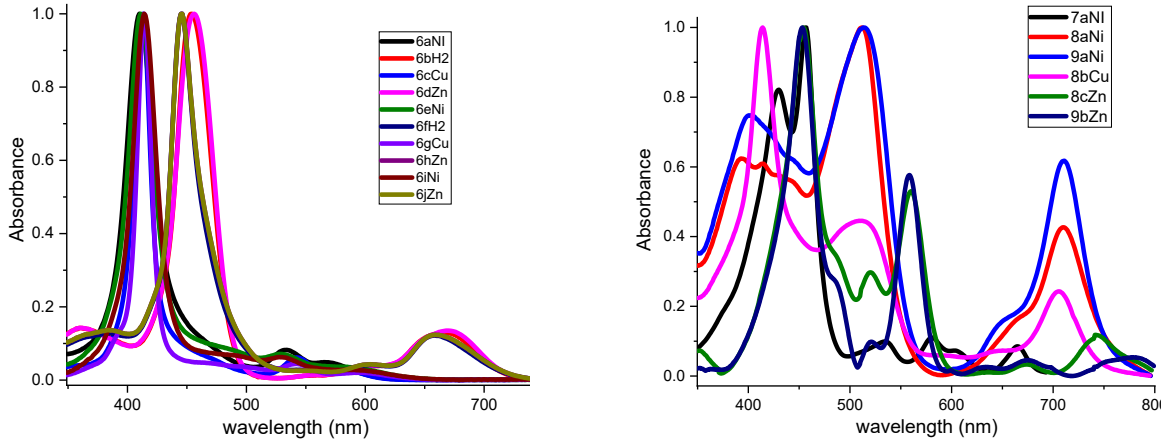



**Fig. S1** Normalized absorption spectra of *meso*,-pyrrolo- and indolo[1,2-a]quinoxalino appended/fused porphyrin derivatives in dichloromethane

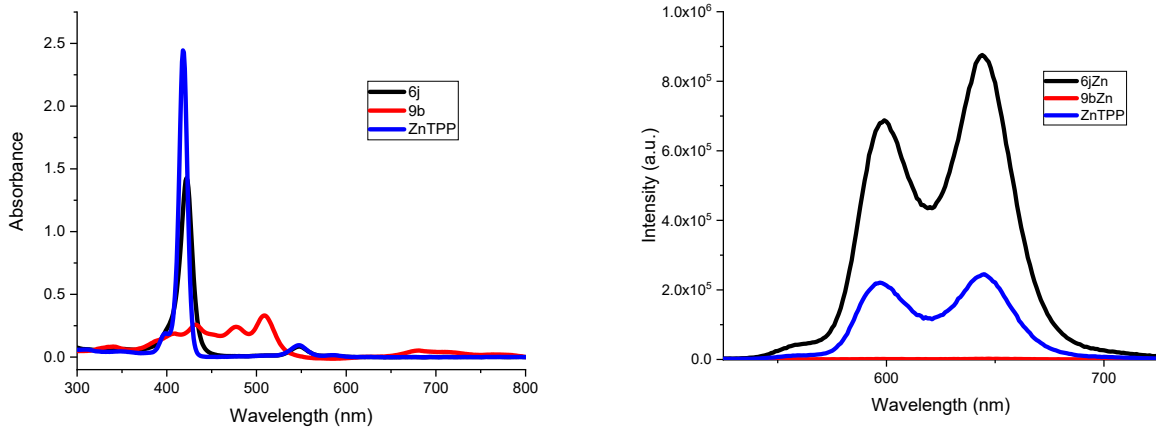



**Fig. S2** UV-Visible absorption and emission spectra of **ZnTPP**, **6jZn** and **9bZn** in dichloromethane

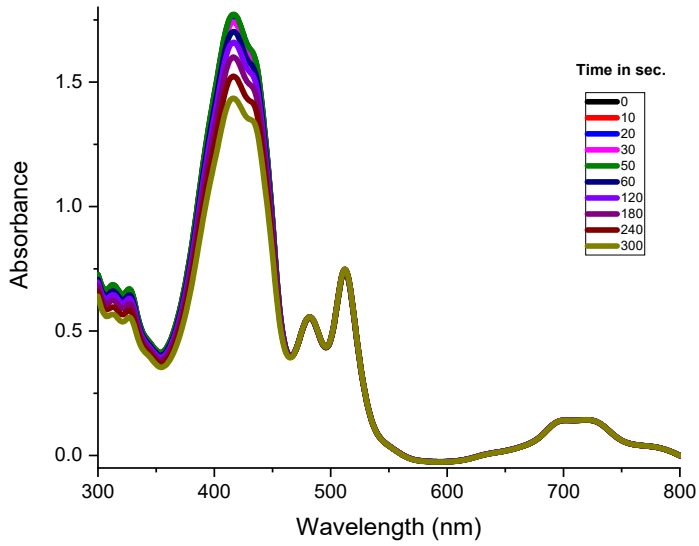



**Fig. S3** Photodecomposition of DPBF by singlet oxygen ($\lambda_{abs}$ : 416 nm) after irradiation of **9bZn** (2μM) in dichloromethane.

**Table S1** The theoretical and experimental calculations for energy gap of *meso*,-pyrrolo- and indolo[1,2-a]quinoxalino appended/fused porphyrin derivatives

| Compounds | Band gap (eV) computational level 1 | Band gap using absorption spectrum |
|---|---|---|
| **6aNi** | 2.85 | 2.90 |
| **6cCu** | 2.83 | 2.94 |
| **6dZn** | 2.80 | 2.58 |
| **6eNi** | 2.85 | 2.90 |
| **6f2H** | 2.65 | 2.68 |
| **6gCu** | 2.85 | 2.92 |
| **6hZn** | 2.80 | 2.67 |
| **6iNi** | 2.92 | 2.88 |
| **6jZn** | 2.78 | 2.67 |
| **7aNi** | 2.21 | 2.60 |
| **8aNi** | 2.03 | 2.30 |
| **8bCu** | 2.02 | 2.27 |
| **8cZn** | 2.00 | 2.14 |
| **9aNi** | 2.04 | 2.26 |
| **9bZn** | 2.01 | 2.16 |

**9aNi Coordinates**

| | | | |
|---|---|---|---|
| N | 3.17209281825753 | 0.69141408928393 | -0.01491175809950 |
| N | 5.42505628210091 | 1.92949630292462 | 0.82152174512167 |
| N | 4.29446272406800 | -1.72517643123474 | 0.46555971766724 |
| N | 6.56926763893381 | -0.49936914975170 | 1.27979724764513 |
| C | 5.09218881452755 | -2.85613312378903 | 0.44612869503483 |
| C | 7.51087508407884 | 0.24793817269010 | 1.95824727926695 |
| C | 4.86609722679980 | 3.05368222534758 | 0.25321638523648 |
| C | 1.98961340055993 | -0.03645831040479 | -0.09363541550723 |
| C | 7.15486011958429 | -1.74151551104928 | 1.08137119061060 |
| C | 6.41984915335742 | 2.39943666711525 | 1.67496017510351 |
| C | 2.99182723159046 | -2.18943490705428 | 0.41304736294374 |
| C | 2.89171116626616 | 1.91149795408357 | -0.57816591696187 |
| C | 3.72796652024287 | 3.04005048317208 | -0.58019573817331 |
| C | 1.86002676505853 | -1.39075261425258 | 0.21333162382593 |
| C | 7.40010144639551 | 1.61143469224260 | 2.26792007363848 |
| C | 6.47839674768804 | -2.87531601018352 | 0.62400945910290 |
| C | 0.95366070290444 | 0.74712467594570 | -0.70174904461742 |
| C | 5.48606826216298 | 4.24298037232321 | 0.77935622047700 |
| C | 4.27631043730643 | -4.03965949162617 | 0.39035243597822 |
| C | 8.70457433468054 | -0.52403507706933 | 2.17070939068737 |
| C | 1.51588215064262 | 1.94962543811062 | -1.05728883525833 |
| C | 6.40907888554795 | 3.83785402335123 | 1.69559006156637 |
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| C | 8.44090279369567 | 2.22907266636977 | 3.14256301173109 |
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| H | 0.76540124505559 | 7.52128929584343 | -3.96295629446238 |
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| | | | |
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| H | 8.40533716254378 | 0.21864261691896 | 6.78857327106711 |
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| H | 11.71319263649721 | 2.05506158104056 | 6.90629771876955 |
| H | 8.46589928230477 | 3.94457119173555 | 7.49062794926156 |
| H | 10.23354233595581 | 4.11935151617434 | 7.44266969380907 |
| H | 9.47214923430847 | 3.20118517999401 | 8.75923338248787 |
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| H | 10.34333626608254 | 6.44955562877619 | 3.43863489633010 |
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| H | 12.09613072089632 | 5.57664770703181 | 1.04224352770975 |
| H | 10.34120785491433 | 5.32962948187830 | 1.12545812164124 |
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| H | 13.04642999568352 | 3.89457975086464 | 4.22556725598694 |
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## 9bZn Coordinates

| | | | |
|---|---|---|---|
| N | 2.93323168092273 | 0.72177988807569 | 0.30187970442831 |
| N | 5.35920150529371 | 1.99469845661883 | 1.19242472771297 |
| N | 4.01496552668602 | -1.88887486381561 | 0.98592627162441 |
| N | 6.42933236537390 | -0.62462000189218 | 1.95174371518405 |
| C | 4.69238094248331 | -3.02793661378627 | 1.37437392042077 |
| C | 7.49855812120402 | 0.15236966509608 | 2.33777889975008 |
| C | 4.69246817791963 | 3.13965997702073 | 0.81957262794942 |
| C | 1.82991548103062 | -0.05385783479628 | -0.02939086065809 |
| C | 6.81625567481950 | -1.94010429577464 | 2.11530102614235 |
| C | 6.51821646158587 | 2.40048916567870 | 1.83985065430875 |
| C | 2.75404834312358 | -2.28964588519934 | 0.60560495079141 |
| C | 2.63679393788121 | 2.00963573273794 | -0.06006371528000 |
| C | 3.45275594020251 | 3.16082922152883 | 0.11010795819057 |
| C | 1.72735364739491 | -1.44643885535294 | 0.12846920837579 |
| C | 7.53046259589668 | 1.56619022754048 | 2.33738229994679 |
| C | 6.01065164916210 | -3.07175313801976 | 1.86701381747963 |
| C | 0.80609115515900 | 0.76984704324828 | -0.60929454320476 |
| C | 5.42118460022885 | 4.29746611466494 | 1.29144432466696 |
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