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Supporting Information

Magnesium tetrapyrazinoporphyrazines: tuning of the pK_a of red-fluorescent pH indicators

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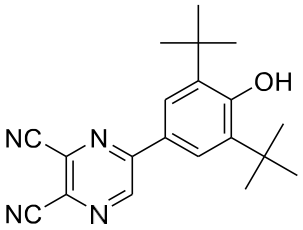
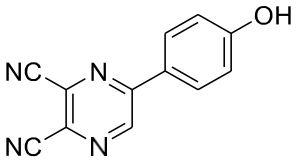


5-chloropyrazine-2,3-dicarbonitrile[1] (1.50 g, 9 mmol) and 2,6-di(*tert*-butyl)phenol (4.89 g, 24 mmol) were dissolved in anhydr. MeCN (30 mL) under argon atmosphere. Finely ground K_2CO_3 (6.57 g, 48 mmol) was added in several portions while the solution turned dark purple. The mixture was stirred under argon at rt for 3 days. After that, the reaction mixture was poured into a beaker with water (200 mL) and the solution was acidified with HCl. The solution changed the color from intense purple to yellow-brown after acidification. Product was extracted by ethylacetate (3 × 100 mL), the organic layer was separated and dried by Na_2SO_4. The product was purified by column chromatography on silica with toluene/hexane 2:1 as mobile phase (R_f = 0.15). The analytical sample was recrystallized from $CHCl_3$/hexane. Yield: 1.28 g (42%) of white-yellow solid. M.p. 238.3 – 239.0°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ=9.18 (s, 1H, ArH), 7.95 (s, 2H, ArH), 5.85 (s, 1H, OH), 1.51 (s, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ=158.65, 155.42, 143.51, 137.56, 133.15, 129.16, 125.53, 123.82, 113.53, 113.26, 34.61, 30.11 ppm; IR (ATR): ν = 3627 (OH), 2237 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{22}N_4O$: C 71.83, H 6.63, N 16.75; found C 70.34, H 6.54, N 16.85.

General method for synthesis of compounds 11-15

Appropriately substituted acetophenone (1 eq) was dissolved in dioxane/water mixture (9:1, v/v, approx. 4 mL per 1 mmol of acetophenone) and selenium dioxide (3 eq) was added. The mixture was refluxed overnight and then cooled down to rt. Diaminomaleonitrile (2 eq) and conc. HCl (0.2 mL per 1 mmol of acetophenone) were added and the mixture was refluxed again for next 1.5 h. The mixture was filtered through a filter paper, the solid on the filter was washed with THF and the solvents were evaporated. The crude product was then purified by column chromatography on silica (mobile phases are mentioned below) or by recrystallization.

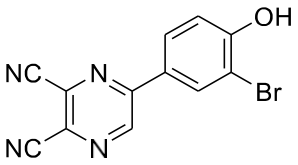
*Synthesis of 5-(4-hydroxyphenyl)pyrazine-2,3-dicarbonitrile (**11**).*



The synthesis was performed according to the general procedure for this compound starting from 4-hydroxyacetophenone (3 g, 22 mmol). Mobile phase: hexane/ethylacetate/acetic acid 20:6:1 (R_f = 0.22). Yield: 2.91 g (59%) of yellow solid. Analytical sample was recrystallized from EtOH/water. M.p. 159.2 – 160.1°C; ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ=10.48 (s, 1H, OH), 9.56 (s, 1H, ArH), 8.14 (d, J = 8.9 Hz, 1H, ArH), 6.95 (d, J = 8.9 Hz, 1H, ArH); ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=158.43, 152.37, 144.68, 133.06, 132.92, 130.05, 129.28, 125.28, 117.22, 114.72, 114.34, 110.84

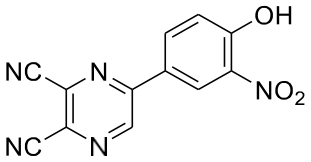
ppm; IR (ATR): ν = 3460 (OH), 2236 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{12}H_6N_4O$: C 64.86, H 2.72, N 25.21; found C 65.02, H 2.67, N 24.92.

*5-(3-bromo-4-hydroxyphenyl)pyrazine-2,3-dicarbonitrile (**12**).*



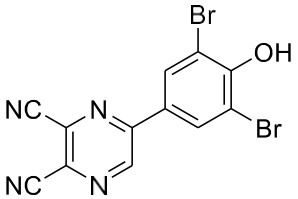
The synthesis was performed according to the general procedure for this compound starting from 3- bromo-4-hydroxyacetophenone (1.2 g, 5.6 mmol) – for synthesis see below. Mobile phase: toluene/ethylacetate/acetic acid 40:5:1 (R_f = 0.32). Yield: 776 mg (46%) of white-yellow solid. Analytical sample was recrystallized from EtOH/water. M.p. 189.1 – 190.0°C; ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ=11.37 (s, 1H, OH), 9.63 (s, 1H, ArH), 8.43 (d, J=2.2 Hz, 1H, ArH), 8.14 (dd, J= 8.6, 2.3 Hz, 1H, ArH), 7.13 (d, J= 8.7 Hz, 1H, ArH); ^{13}CNMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=162.06, 153.67, 144.40, 133.09, 130.36, 129.35, 123.72, 116.65, 114.82, 114.41 ppm; IR (ATR): ν = 3373 (OH), 2248 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{12}H_5BrN_4O$: C 47.87, H 1.67, N 18.61; found C 47.96, H 1.56, N 18.67.

*5-(4-hydroxy-3-nitrophenyl)pyrazine-2,3-dicarbonitrile (**13**).*



The synthesis was performed according to the general procedure for this compound starting from 4- hydroxy-3-nitroacetophenone (1.21 g, 6.7 mmol) – for synthesis see below. Mobile phase: hexane/ethylacetate/acetic acid 20:5:1. Yield: 998 mg (56%) of orange solid. Analytical sample was recrystallized from MeOH/water. M.p. 179 – 189°C; ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ=12.05 (s, 1H, OH), 9.70 (s, 1H, ArH), 8.76 (d, J = 2.4 Hz, 1H, ArH), 8.41 (dd, J = 8.9, 2.4 Hz, 1H, ArH), 7.31 (d, J = 8.9 Hz, 1H, ArH); ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=155.27, 151.82, 144.92, 138.16, 133.99, 133.06, 130.71, 125.39, 123.89, 120.29, 114.60, 114.25 ppm; IR (ATR): ν = 3236 (OH), 3089 (CH), 2243 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{12}H_5N_5O_3$: C 53.94, H 1.89, N 26.21; found C 53.86, H 1.78, N 26.21.

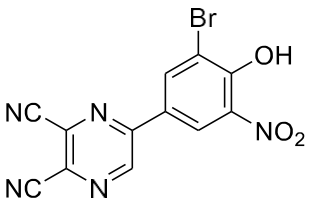
*5-(3,5-dibromo-4-hydroxyphenyl)pyrazine-2,3-dicarbonitrile (**14**).*



The synthesis was performed according to the general procedure for this compound starting from 3,5- dibromo-4-hydroxyacetophenone (3.43 g, 11.7 mmol) – for synthesis see below. Mobile phase: hexane/ethylacetate/acetic acid 20:10:1. Yield: 3.06 g (69%) of orange solid. Analytical sample was recrystallized from EtOH. M.p. 236 °C (dec.); ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ=11.02 (s, 1H, OH), 9.70 (s, 1H, ArH), 8.45 (s, 1H, ArH); ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=154.79, 151.02, 145.06, 132.98, 132.04, 130.77, 126.81, 114.57, 114.22, 112.79 ppm; IR (ATR): ν = 3333 (OH), 3085,

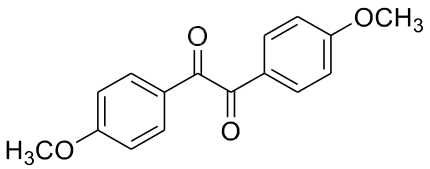
3062 (CH), 2244 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{12}H_4Br_2N_4O + 1H_2O$: C 37.93, H 1.06, N 14.74; found C 38.43, H 1.08, N 14.54.

*5-(3-bromo-4-hydroxy-5-nitrophenyl)pyrazine-2,3-dicarbonitrile (**15**).*



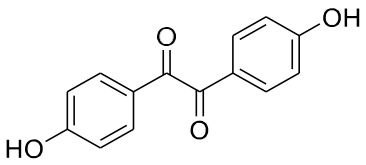
The synthesis was performed according to the general procedure for this compound starting from 3- bromo-4-hydroxy-5-nitroacetophenone (3 g, 11.6 mmol) – for synthesis see below. Mobile phase: hexane/ethylacetate/acetic acid 20:6:1 (R_f = 0.37). Yield: 2.54 g (63%) of orange solid. Analytical sample was recrystallized from EtOH. M.p. 215.2 – 215.9 °C; ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ=9.75 (s, 1H, ArH), 8.77 (s, 2H, ArH); ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=152.66, 150.66, 145.15, 138.47, 136.89, 133.01, 131.05, 124.62, 124.33, 115.81, 114.53, 114.18 ppm; IR (ATR): v = 3216 (OH), 3081 (CH), 2251 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{12}H_4BrN_5O_3$: C 41.64, H 1.16, N 20.24; found C 41.16, H 1.01, N 20.10.

*Synthesis of 1,2-bis(4-methoxyphenyl)ethan-1,2-dione (**16**)*



4-Anisaldehyde (3.00 g, 22 mmol), 1,8-diazabicyclo[5.4.0]undec-7-en (0.6 mL, 4.3 mmol) and 3,3'- (dodecane-1,12-diyl)bis(1-methyl-1*H*-benzo[*d*]imidazol-3-ium) dibromide[2] as catalyst (660 mg, 1.1 mmol) were mixed with water (22 mL)and stirred at rt for 24 h. After that, the product was extracted with ethylacetate (3 × 50 mL), the organic layer was separated, dried by Na_2SO_4 and the solvent was evaporated. The crude acyloin was converted to diketone without isolation. The product was dissolved in acetic acid (100 mL) and ammonium nitrate (2.2 g, 27.5 mmol) and copper(II) acetate (48 mg, 264 µmol) were added. The mixture was refluxed for 2 h, cooled down and the solvent was evaporated. The solid was extracted by THF and filtered. The product was purified by column chromatography on silica with hexane/ethylacetate 3:1 as the mobile phase. Yield: 2.02 g (67% based on 4-anisaldehyde) of white solid. M.p. 129.7 – 131.6 °C (lit.[3] 130-134°C) ; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ=7.95 (4H, d, J=8.9 Hz, ArH), 6.97 (4H, d, J=8.9 Hz, ArH), 3.89 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ=193.5, 164.8, 132.3, 126.3, 114.3, 55.6 ppm; IR (ATR): v = 3064 3031 (CH), 1655 (s, CO), 1596 (s), 1572 cm^{-1}.

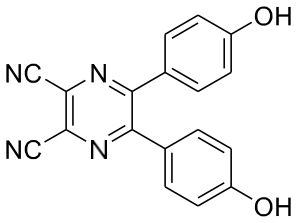
*Synthesis of 1,2-bis(4-hydroxyphenyl)ethan-1,2-dione (**17**)*



Diketone **16** (2.00 g, 7.4 mmol) was dissolved in acetic acid (4 mL) and hydrobromic acid was added (4 mL). The mixture was refluxed for 24 h, cooled down to rt and the solvents were evaporated. The solid was extracted with THF, the organic solvent was dried with Na_2SO_4, filtered and evaporated. The

product was purified by column chromatography on silica with hexane/ethylacetate/acetic acid 10:5:1 as the mobile phase (R_f = 0.32). Yield: 1.42 g (79%) of light yellow solid. M.p. 248.9 – 249.5.6 °C (lit.[4] 250-252°C); ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ= 10.88 (2H, bs, OH), 7.73 (4H, d, *J*=8.7 Hz, ArH), 6.91 (4H, d, *J*=8.7 Hz, ArH); ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=193.8, 164.3, 132.4, 124.3, 116.3 ppm; IR (ATR): *v* =3396 (OH), 1641 (CO), 1597 (s), 1567 cm^{-1}.

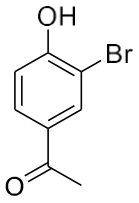
*Synthesis of 5,6-bis(4-hydroxyphenyl)pyrazine-2,3-dicarbonitrile (**18**)*



Diketone **17** (1.18 g, 4.84 mmol) was dissolved in warm acetic acid (100 mL) and diaminomaleonitrile (1.05 g, 9.7 mmol) was added. The mixture was refluxed for 3 days. The solvent was evaporated and the solid was extracted with THF and filtered. The THF extract was evaporated and purified by column chromatography on silica with with hexane/ethylacetate/acetic acid 10:5:1 as the mobile phase (R_f = 0.32). The product has exactly the same mobility on silica as the starting diketone in number of different mobile phases and its residues (always determined by ^{1}H NMR) cannot be removed by column chromatography. The pure product **18** was obtained only after careful crystallization from MeOH with addition of few drops of water. Yield: 0.54 g (35%) of yellow solid. The analytical data corresponded well to those published.[5] M.p. 245°C (dec); ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ=10.14 (s, 1H, OH), 7.38 (d, J = 8.7 Hz, 1H, ArH), 6.77 (d, J = 8.8 Hz, 1H, ArH); ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ=160.10, 154.08, 131.52, 128.70, 126.56, 115.75, 114.58 ppm; IR (ATR): *v* = 3407 (OH), 2252 (CN) cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{10}N_4O_2$: C 68.79, H 3.21, N 17.83; found C 68.55, H 3.53, N 16.62.

Synthesis of substituted acetophenones

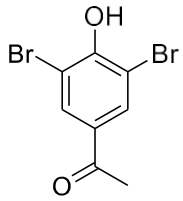
Synthesis of 3-bromo-4-hydroxyacetophenone



The literature reports number of selective monobrominations of 4-hydroxyacetophenone using various brominating agents with yields typically about 90%, *e.g.* using Br_2+DABCO,[6] HBr + H_2O_2,[7] hexamethylenetetramine-bromine.[8] Despite this, all tested procedures in our laboratory, gave always a mixture of mono- and dibrominated product as revealed by TLC monitoring. The analysis of TLC mixtures resulted in the one procedure that was selected as the most suitable. 4- Hydroxyacetophenone (4 g, 29.4 mmol) was dissolved in dichloromethane (80 mL) and cooled down by ice/NaCl to -5°C. Hexamethylenetetramine-bromine (8 g, 17.4 mmol) was added, the reaction was left to warm up slowly to room temperature and stirred for 24 h. The yellow suspension was filtered and the solid washed with dichloromethane. The filtrate was washed with solution of sodium thiosulfate and water. The organic phase was dried over sodium sulfate, filtered and purified by column chromatography on silica with toluene:ethylacetate:acetic acid 10:1:0.2. The first fraction was

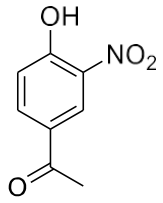
dibrominated compound (2.46 g, 29%), the second fraction was the required monobrominated derivative (1.51 g, 24%) and the starting material was also recovered (1.47 g, 37%). M.p. 102 – 104 °C (lit.[9] 112 – 117 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ=8.14 (d, J = 2.1 Hz, 1H, ArH), 7.86 (dd, J = 8.5, 2.1 Hz, 1H, ArH), 7.08 (d, J = 8.5 Hz, 1H, ArH), 6.43 (bs, 1H, OH), 2.57 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ=195.80, 156.52, 133.02, 131.39, 129.98, 115.89, 110.57, 26.27 ppm; IR (ATR): ν = 3124 (OH), 1650 (s, CO) cm^{-1}.

Synthesis of 3,5-dibromo-4-hydroxyacetophenone



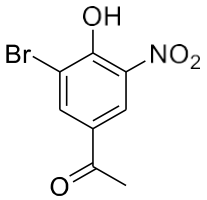
Procedure was adopted from the literature.[10] Bromine (1 mL, 19 mmol) was dissolved in acetic acid (3 mL) and added dropwise into the solution of 4-hydroxyacetophenone (1.22 g, 9 mmol) and sodium acetate (2.29 g, 28 mmol) in acetic acid (20 mL) at rt. The reaction mixture was stirred for 30 min, water (20 mL) was added, precipitate was collected and washed with water. The product was purified by chromatography on silica with hexane/ethylacetate/acetic acid 10:5:1 as the mobile phase and the pure product was recrystallized from ethanol. Yield 2.12 g (81%) of white crystals. M.p. 184–186 °C (lit.[9] 185–187 °C); ^{1}H NMR (500 MHz, CD_3COCD_3, 25°C, TMS): δ=9.38 (s, 1H, OH), 8.15 (s, 2H, ArH), 2.58 (s, 3H, CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 25°C, TMS): δ= 194.59, 155.44, 133.55, 132.62, 111.35, 26.36 ppm; IR (ATR): ν = 3176 (OH), 1661 (s, CO) cm^{-1}

Synthesis of 4-hydroxy-3-nitroacetophenone



4-Hydroxyacetophenone (2.72 g, 20 mmol) was dissolved in concentrated sulfuric acid (30 mL) and cooled down by external ice/NaCl bath. Potassium nitrate (2.16 g, 21.4 mmol) was added in several small portions paying the attention not to heat the reaction. After the last addition, the reaction was stirred for another 1 h in the ice bath and then poured on crushed ice and the solid was collected. TLC examination (hexane:ethylacetate: acetic acid 20:10:3) indicated just one product of sufficient purity for subsequent reactions. Yield 3.2 g (88 %) of yellow solid. M.p. 131.3–132.4 °C (lit.[11] 131 –132.6 ℃); ^{1}H NMR (500 MHz, CD_3COCD_3, 25°C, TMS): δ=10.82 (s, 1H, OH), 8.69 (d, J = 2.2 Hz, 1H, ArH), 8.27 (dd, J = 8.8, 2.2 Hz, 1H, ArH), 7.32 (d, J = 8.8 Hz, 1H, ArH), 2.64 (s, 3H, CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 25°C, TMS): δ= 195.18, 158.19, 136.98, 134.96, 130.59, 126.65, 120.99, 26.41 ppm; IR (ATR): ν = 3277 (OH), 3112 (CH), 1678 (s, CO) cm^{-1}

Synthesis of 3-bromo-4-hydroxy-5-nitroacetophenone



Synthesis of 4-hydroxy-3-nitroacetophenone (3 g, 17 mmol) and anhydr. sodium acetate (2 g, 24 mmol) were dissolved in acetic acid (100 mL). Bromine (0.85 mL, 2.65 g, 17 mmol) dissolved in acetic acid (10 mL) was added dropwise at rt and the reaction was stirred at rt for 24 h. Acetic acid was evaporated at reduced pressure, the residue was dissolved in ethylacetate and washed three times with water acidified with HCl and once with solution of sodium thiosulfate. The organic phase was dried over sodium sulfate, filtered and evaporated to dryness. The product was recrystallized from EtOH/water. TLC examination (hexane:ethylacetate: acetic acid 20:6:1) indicated just one product of sufficient purity for subsequent reactions. Yield 4.29 g (87 %) of white-yellow solid. M.p. 134.5–135.2 °C (lit.[12] 136 °C); ^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS): δ= 8.41 (d, J = 2.2 Hz, 1H, ArH), 8.38 (d, J = 2.2 Hz, 1H, ArH), 2.58 (s, 3H, CH_3). ^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS): δ= 194.63, 152.83, 137.72, 137.49, 128.80, 125.08, 114.48, 26.66 ppm; IR (ATR): ν = 3226 (OH), 3103 (CH), 1694 (s, CO) cm^{-1}

Absorption, emission and excitation spectra

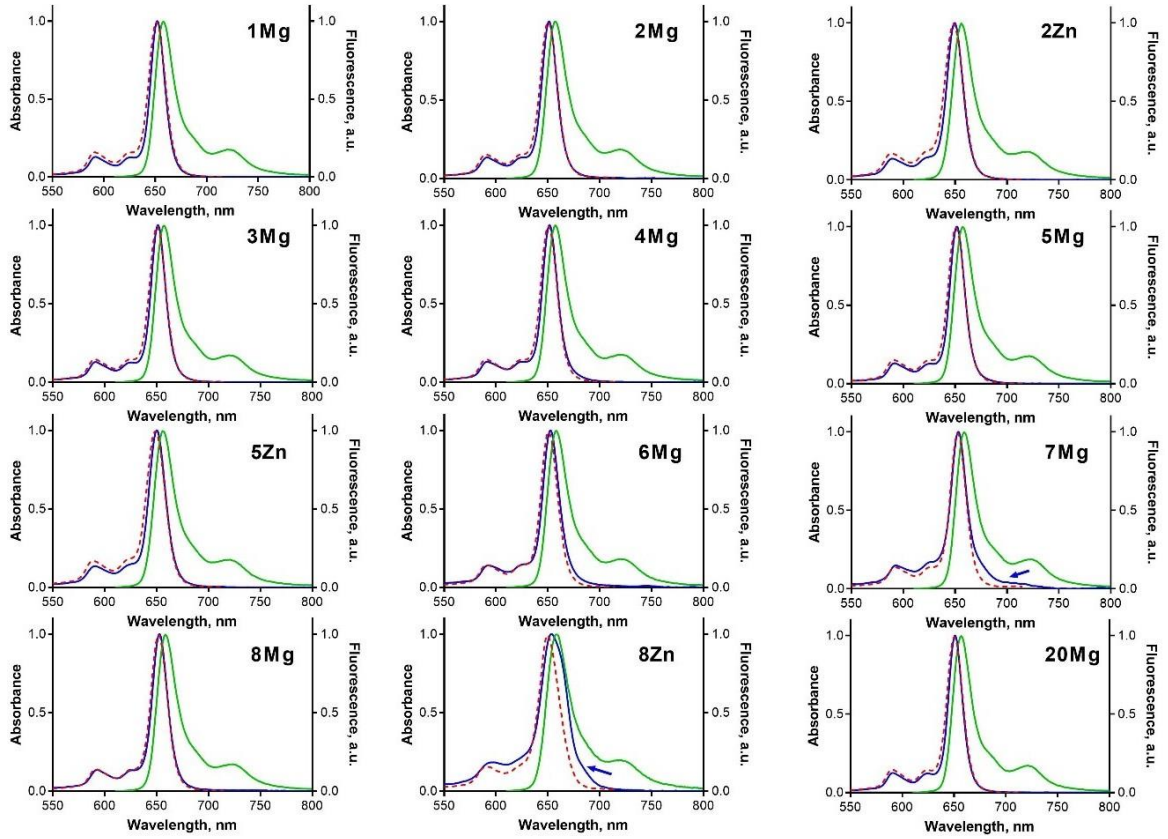


Fig. S1. Normalized absorption (blue), emission (green) and excitation (red dashed) spectra of TPyzPzs in THF. Arrows indicate bands corresponding to aggregates visible in absorption spectra.

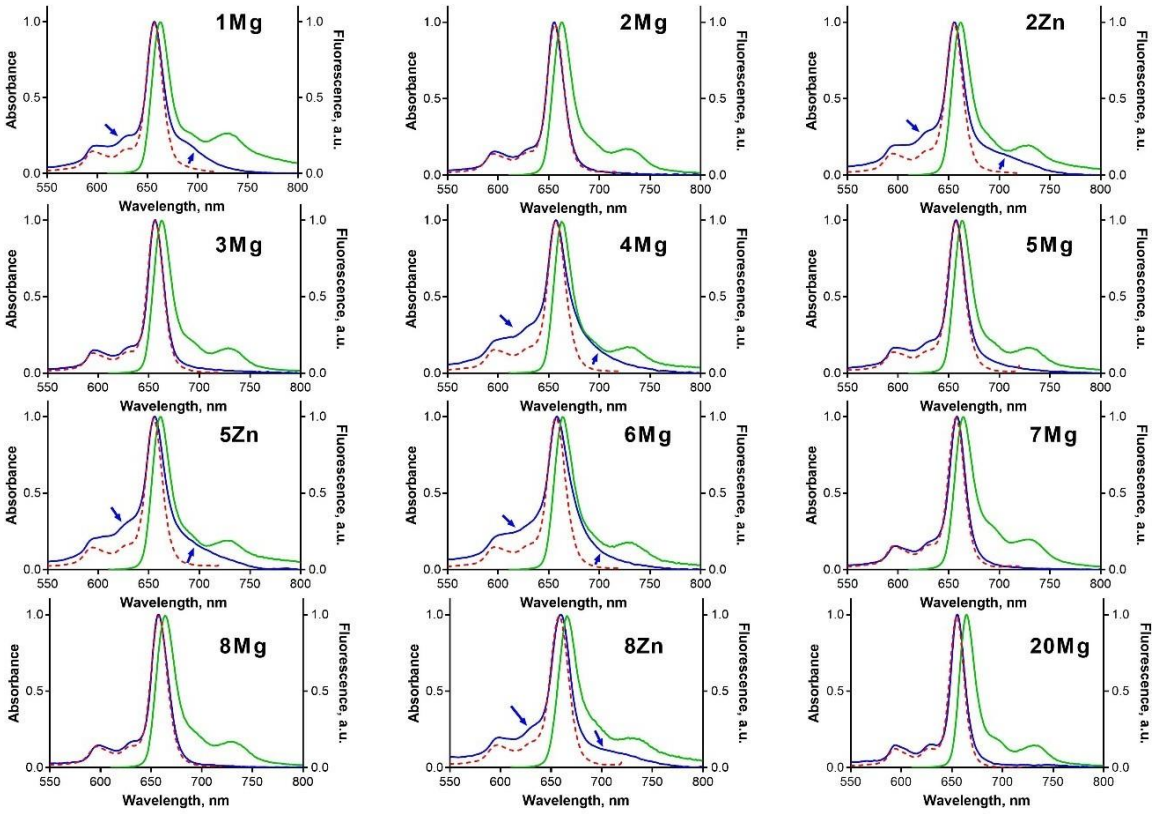


Fig. S2. Normalized absorption (blue), emission (green) and excitation (red dashed) spectra of TPyzPzs in microemulsions. Arrows indicate bands corresponding to aggregates visible in absorption spectra. The spectra were collected at pH of the buffer corresponding to fully protonated form.

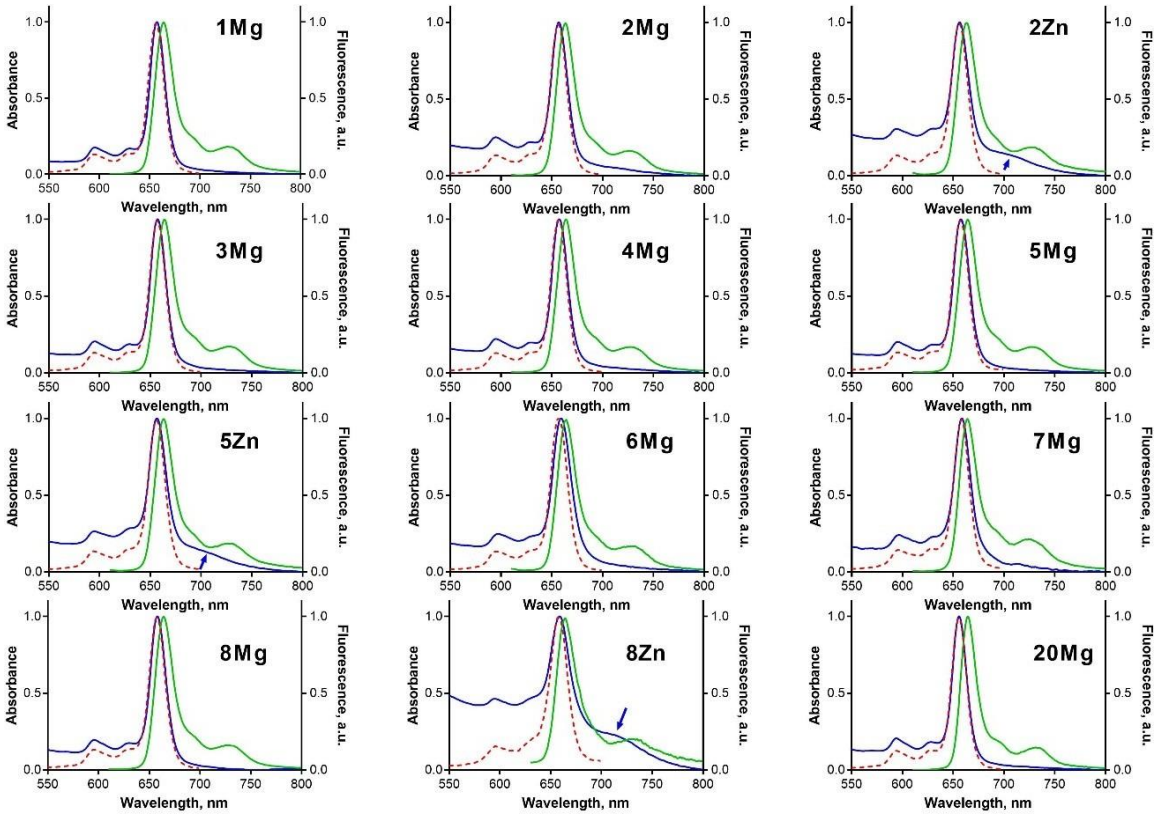


Fig. S3. Normalized absorption (blue), emission (green) and excitation (red dashed) spectra of TPyzPzs in liposomes. Arrows indicate bands corresponding to aggregates visible in absorption spectra. Increased background in absorption spectra is due to light-scattering in liposomal suspension. The spectra were collected at pH of the buffer corresponding to fully protonated form.

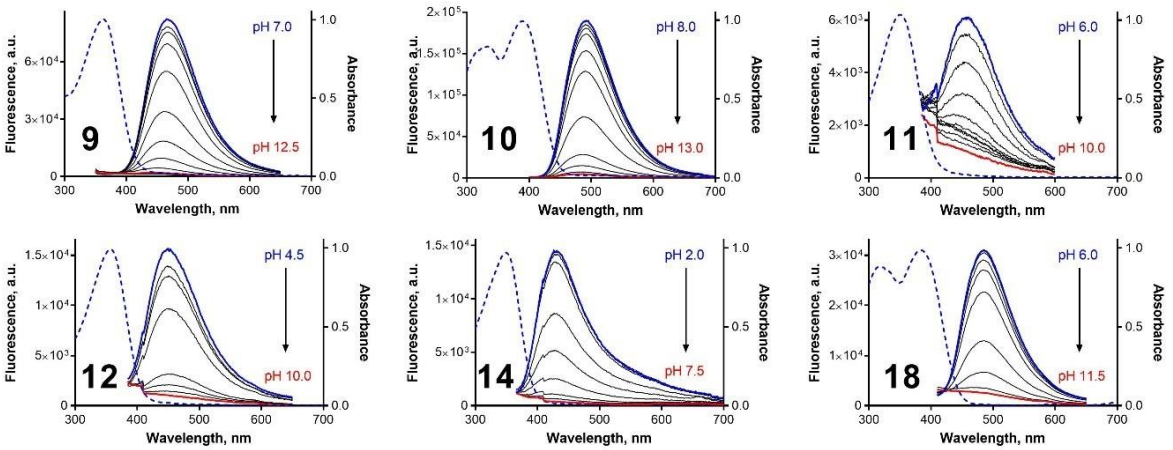


Fig. S4. Changes in fluorescence emission of pyrazinedicarbonitriles in microemulsions with the pH. Only the protonated form is fluorescent. Absorption spectra of protonated forms are shown as blue dashed line.

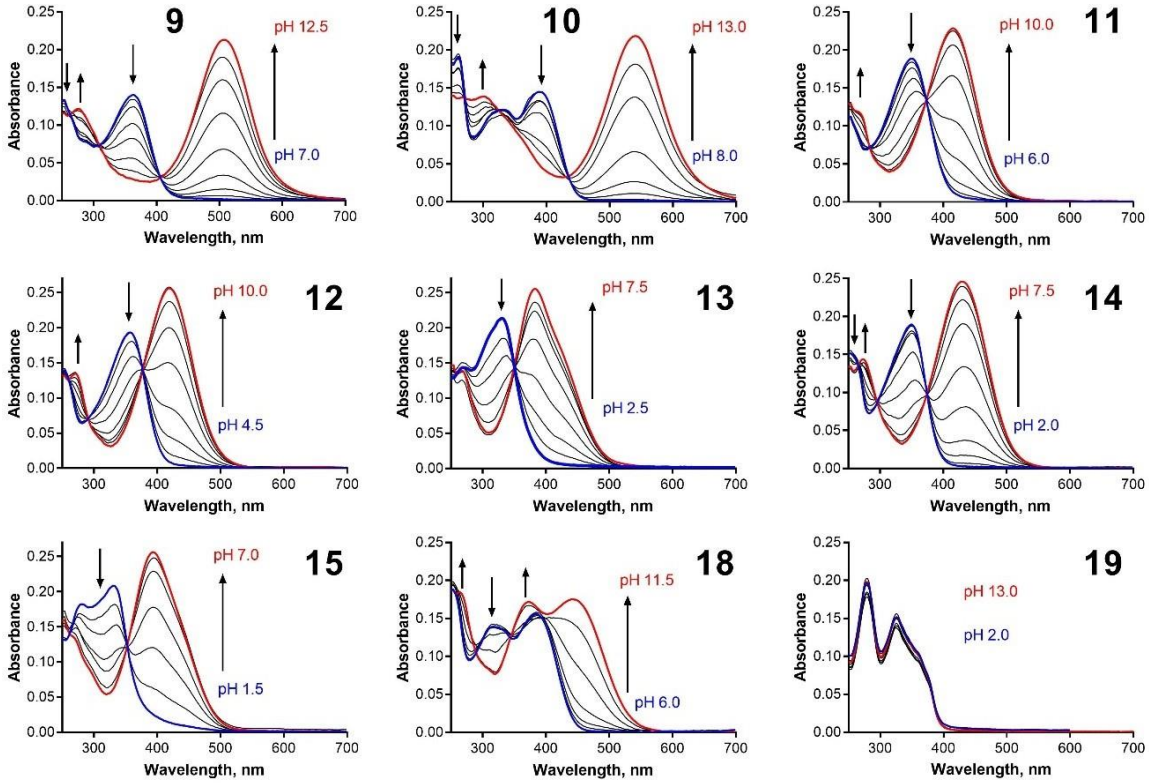


Fig. S5. Changes in absorption spectra of pyrazinedicarbonitriles in microemulsions with the pH.

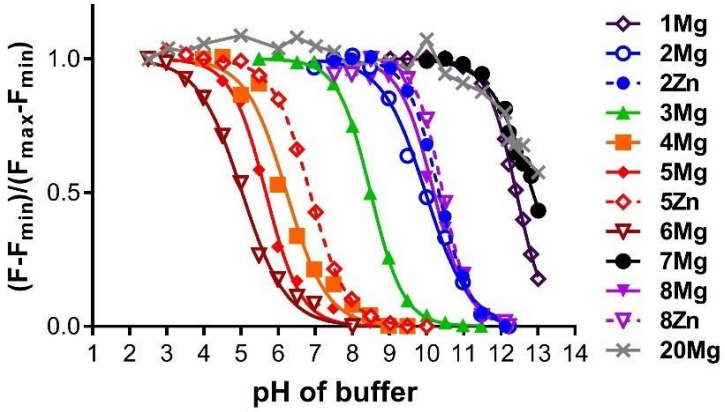


Fig. S6. Dependence of fluorescence changes in emission maximum of different TPyzPz indicators in microemulsion on pH. F_{min} was considered zero for **1Mg**, **7Mg** and **20Mg**.

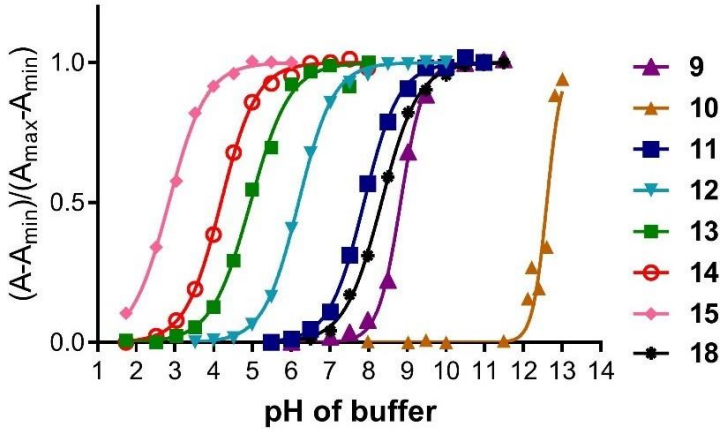


Fig. S7. Dependence of absorbance of deprotonated form of pyrazinedicarbonitriles in water (containing 5 % of DMSO) on pH.

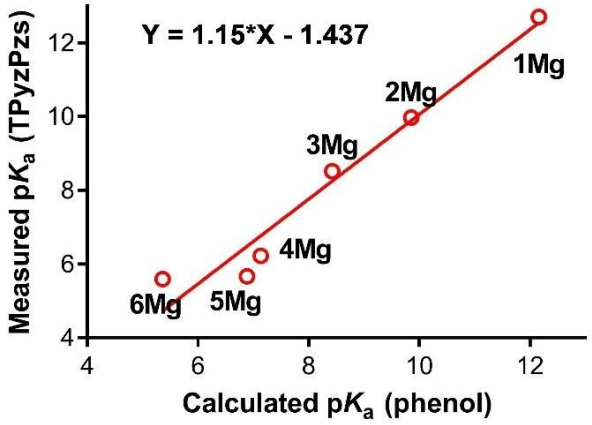


Fig. S8. Correlation between measured pK_a of TPyzPz indicators in liposomes and calculated pK_a values for *para* unsubstituted phenol with corresponding substituents (calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02).

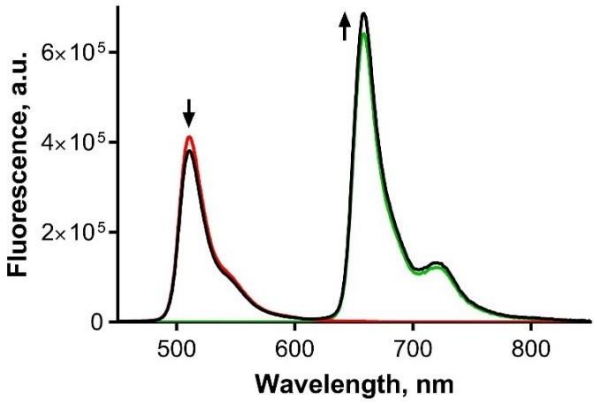


Fig. S9. Emission spectra of BODIPY (red, 1 μM) and **5Mg** (green, 1 μM) in THF (λ_{exc} = 445 nm). The emission spectra after mixing (black, 1 μM each dye) indicated only negligible resonance energy transfer not exceeding 5%.

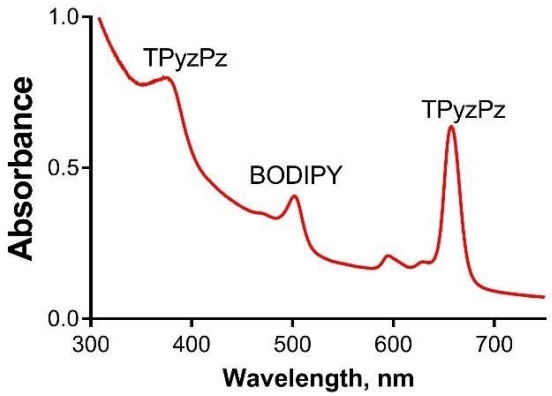


Fig. S10. Absorption spectra of TPyzPz **5Mg** and BODIPY in liposomes in buffer of pH=3.5. Concentration of the dyes was 1 μM each, concentration of DOPC lipids was 1000 μM. Increased background in absorption spectra is due to light-scattering in liposomal suspension.

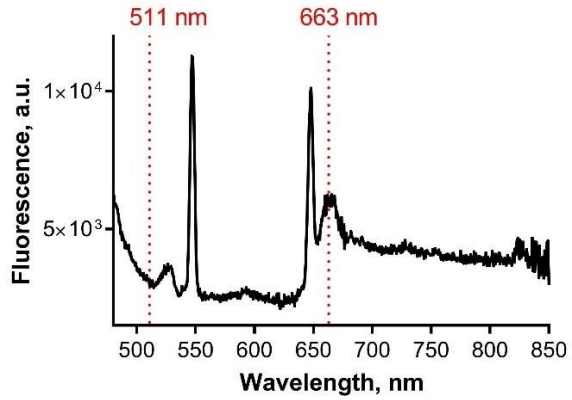


Fig. S11. Emission of the empty DOPC liposomes in buffer of pH = 3.5 (λ_{exc} = 445 nm). The peaks of scattered light at 547 nm and 648 nm, do not interfere with monitoring wavelength of 511 nm and 663 nm. Small signal at 663 nm is due to residual TPyzPz contamination from the extruder during preparation of empty DOPC liposomes.

Determination of singlet oxygen production in microemulsions

The stock solution (50 μM) of the corresponding zinc TPyzPzs in microemulsions were prepared as mentioned in the manuscript. The stock solution of 1,3-diphenylisobenzofuran (DPBF) was prepared in THF at concentration 250 mM. The stock solution of TPyzPzs in microemulsions (500 μL) was mixed with DPBF stock solution (30 μL) and vortexed for 1 min to allow incorporation of DPBF into oil droplets and kept strictly in the dark. This solution was diluted (50 μL into 2.5 mL) into buffer of corresponding pH, bubbled with oxygen for 1 min and the singlet oxygen production was measured following this procedure:

The solution was stirred and irradiated for defined times using a xenon lamp (100 W, ozone free XE DC short arc lamp, Newport,). Incident light was filtered through a water filter (6 cm) and cut-off filter OG530 to remove heat and light under 523 nm, respectively. Decrease of DPBF in solution with irradiation time was monitored at 417 nm. The rate of the DPBF decomposition was expressed as a slope (k) of the plot of the dependence of ln(A_0/A_t) on irradiation time t, with A_0 and A_t being the absorbances of the DPBF at 417 nm before irradiation and after irradiation time t. The slope k was corrected to the different light absorption of TPyzPzs by dividing it by a total amount of light absorbed by the TPyzPzs (I_{aT}). I_{aT} is calculated as a sum of intensities of the absorbed light I_a at wavelengths from 523 nm to 850 nm (step 0.5 nm). Light under 523 nm is completely filtered off by OG530 filter and light above 850 nm is not absorbed by the studied TPyzPzs. I_a at given wavelength is calculated using Beer's law (Equation 1):

$$I_a = I_0\left(1 - e^{-2.3A}\right) \qquad \text{Eq.1}$$

where I_0 is a transmittance of the filter at the given wavelength and A absorbance of the TPyzPz at this wavelength. The results are plotted in Figure S12 where steeper slope k indicate stronger singlet oxygen production.

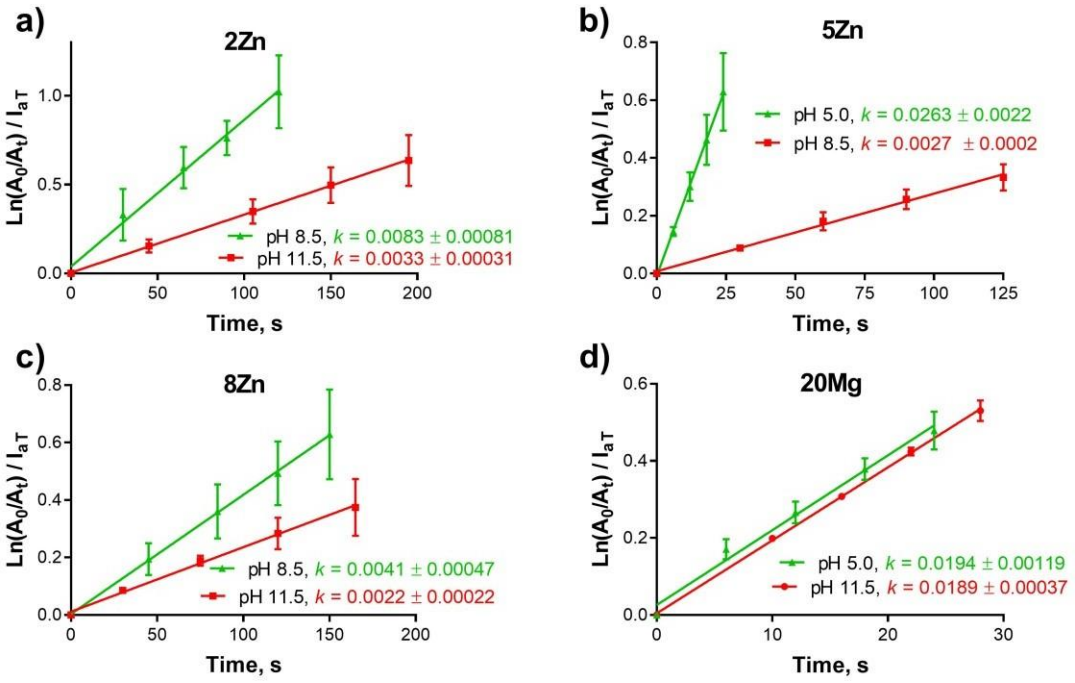
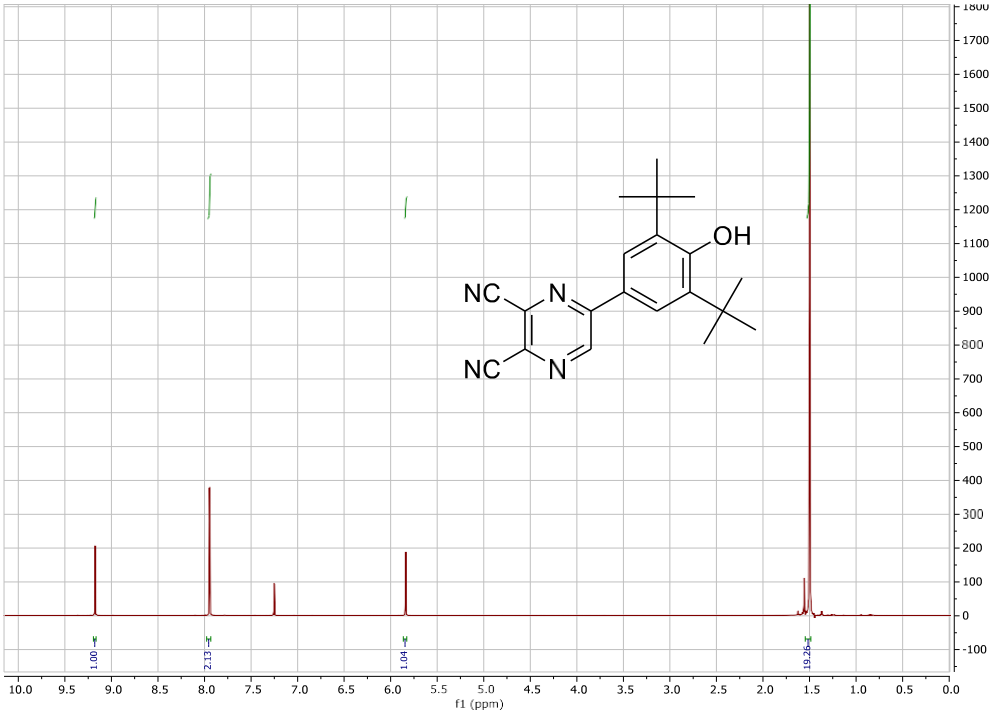
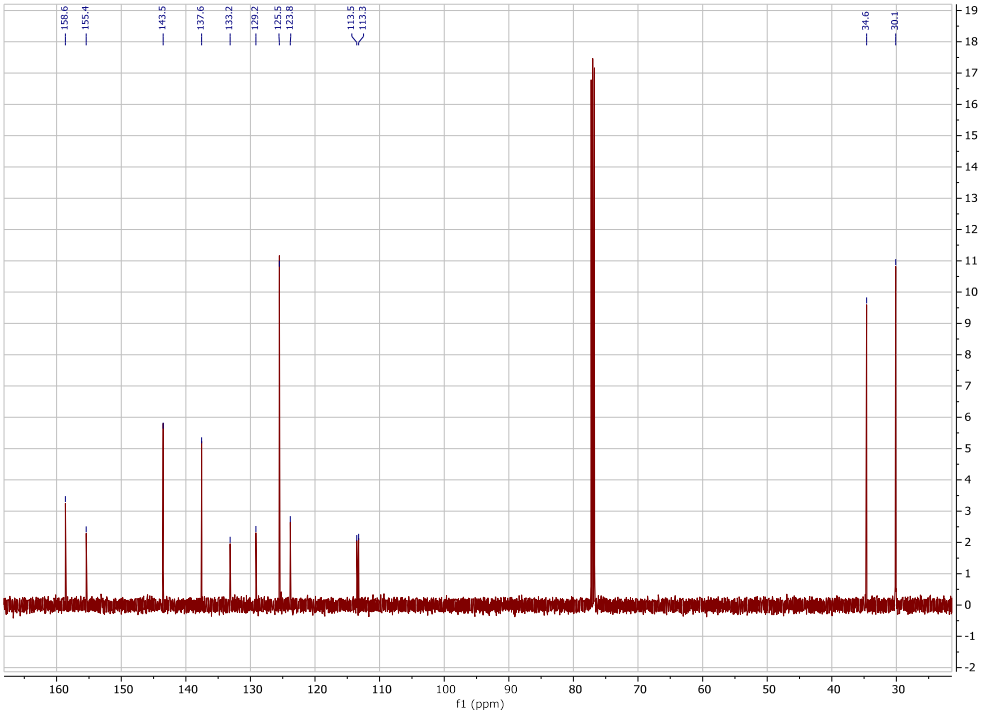


Fig. S12. Singlet oxygen production of compounds **2Zn** (a), **5Zn** (b), **8Zn** (c) and **20Mg** (d) in microemulsions at different pH expressed as decomposition of DPBF (monitored at the absorption maximum of DPBF λ_{max}=417 nm). The ON state is shown in green, the OFF state is shown in red (except **20Mg** that is always-ON). The stronger singlet oxygen production is exerted by the compound, the steeper is the slope (*k*) of the dependence. Mean of two independent experiments.

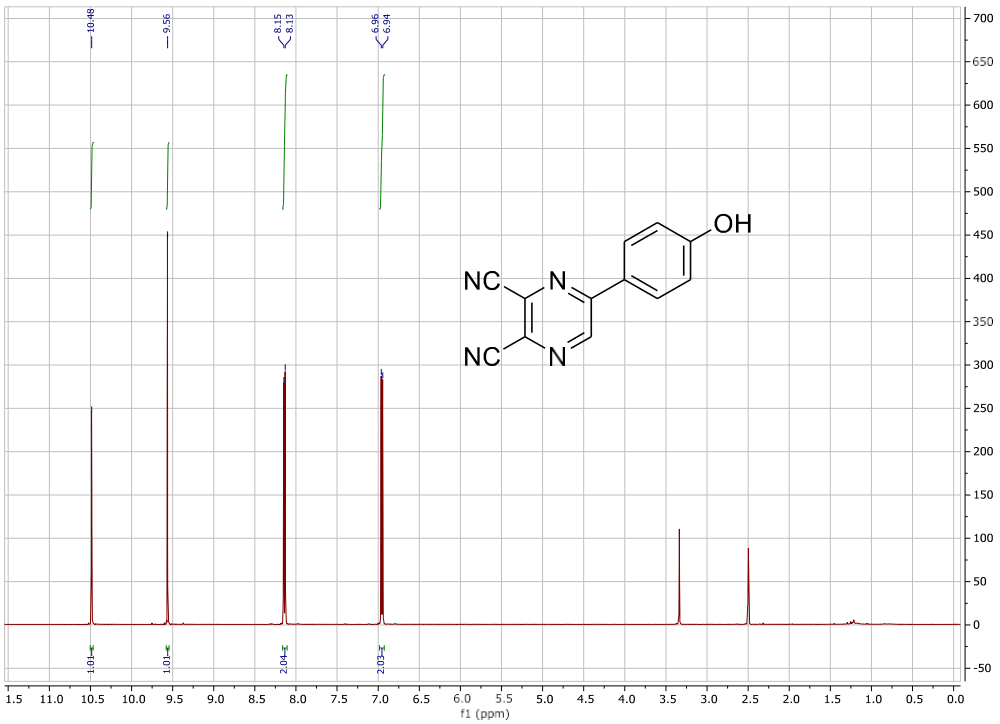
NMR spectra



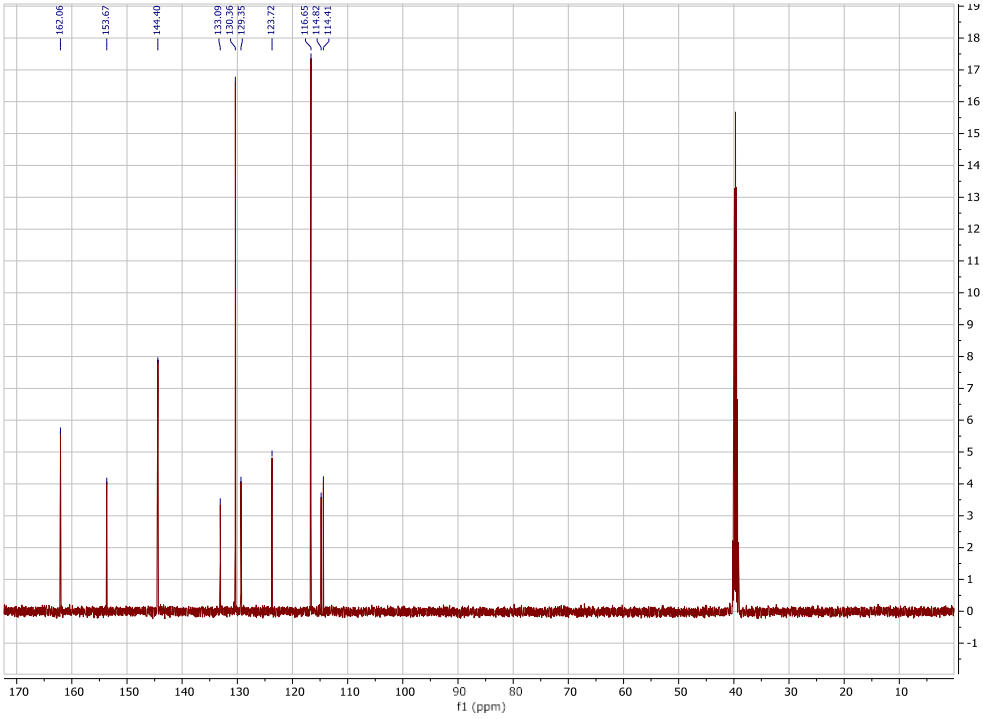
^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS), compound **9**



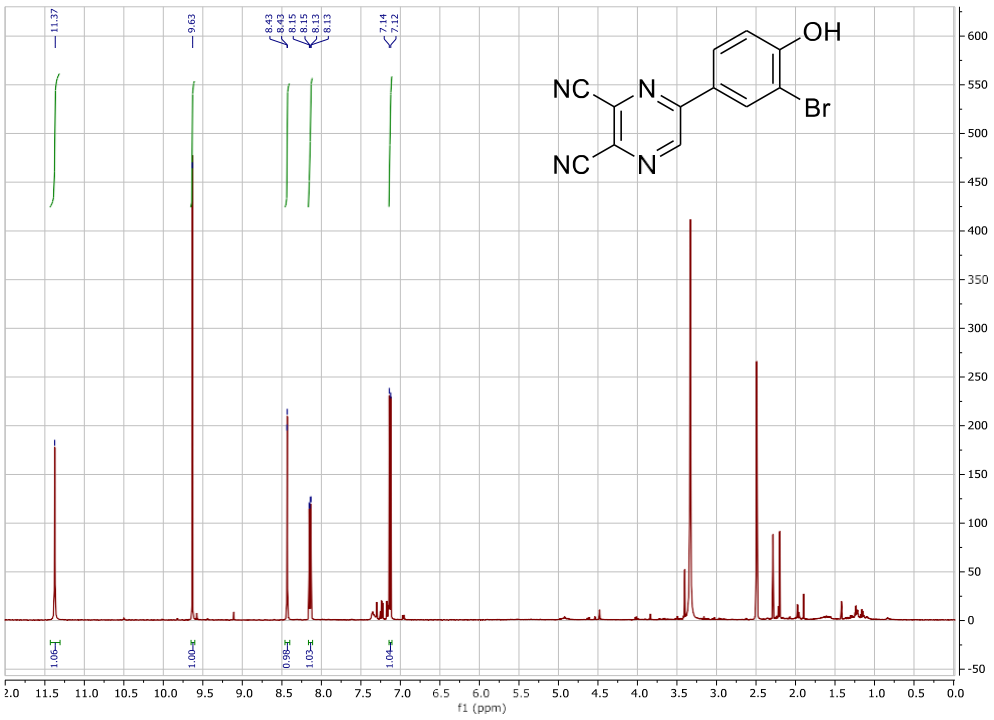
^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS), compound **9**



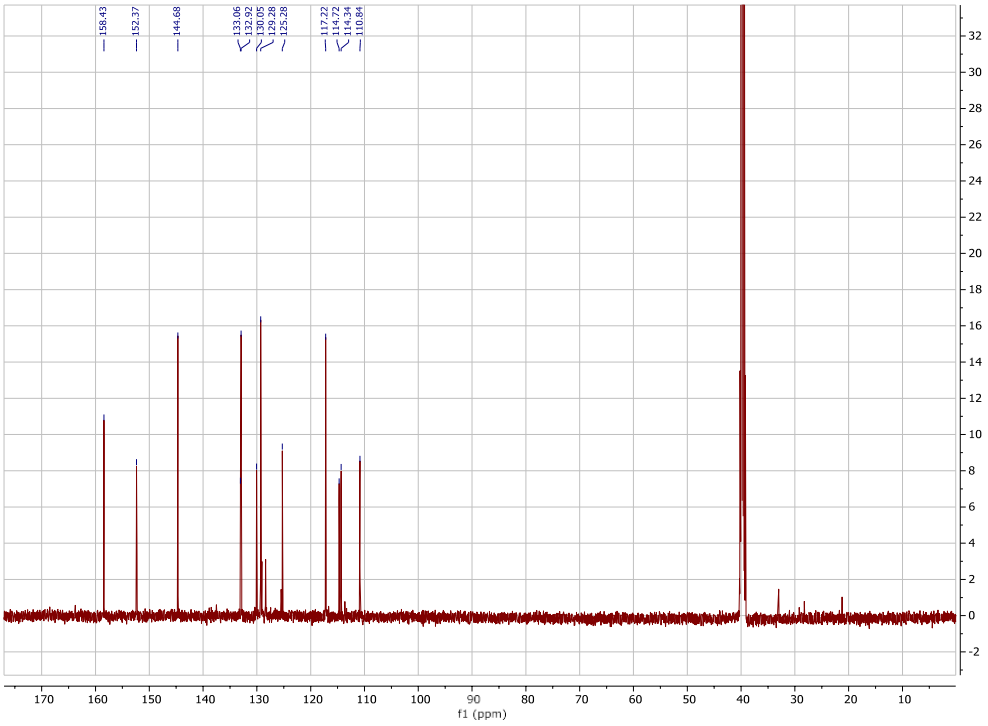
^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS, compound **11**



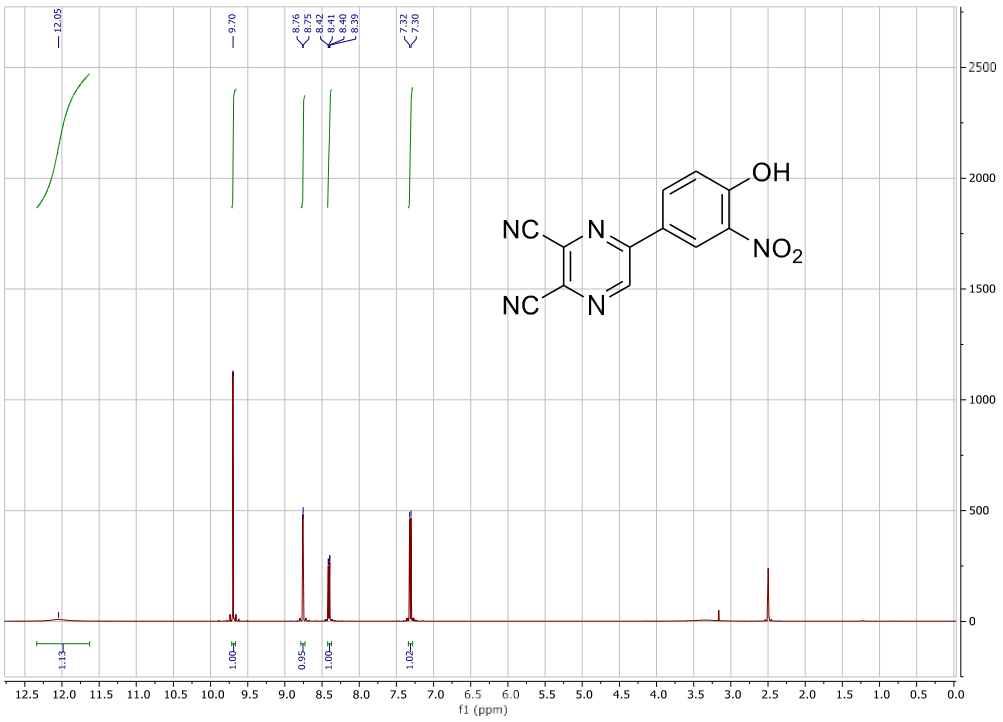
^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS), compound **11**



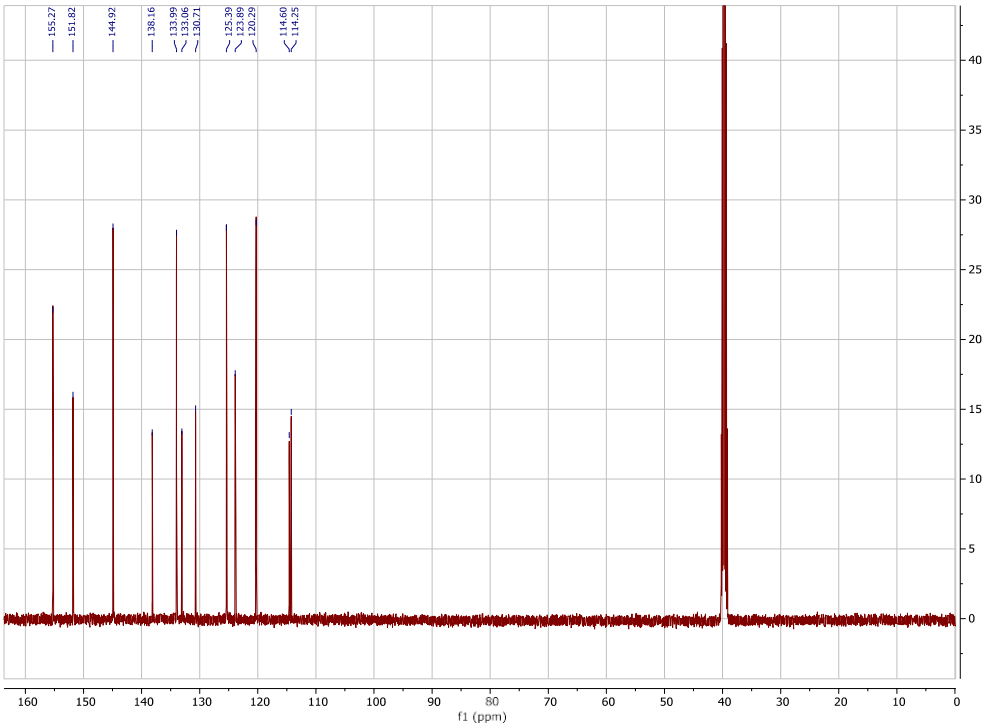
^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS, compound **12**



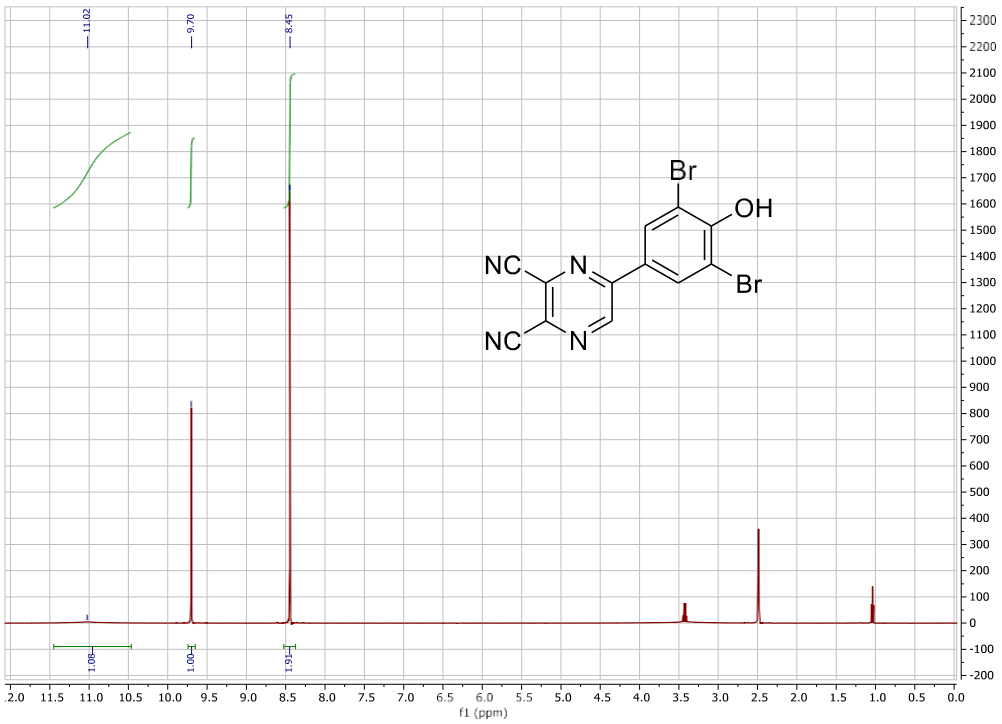
^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS), compound **12**



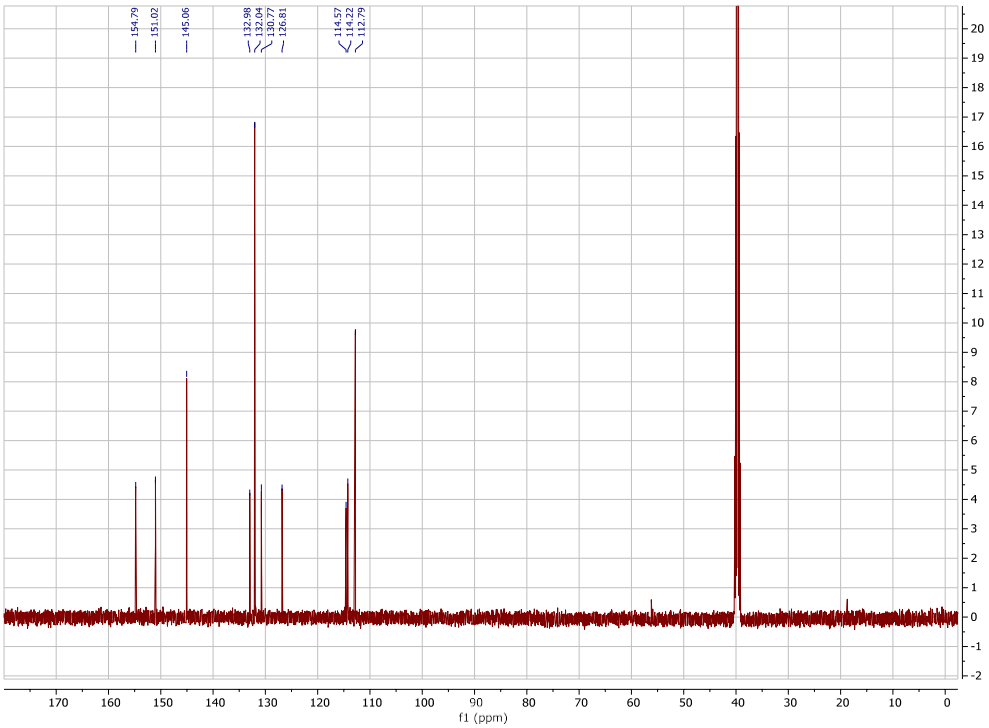
^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS, compound **13**



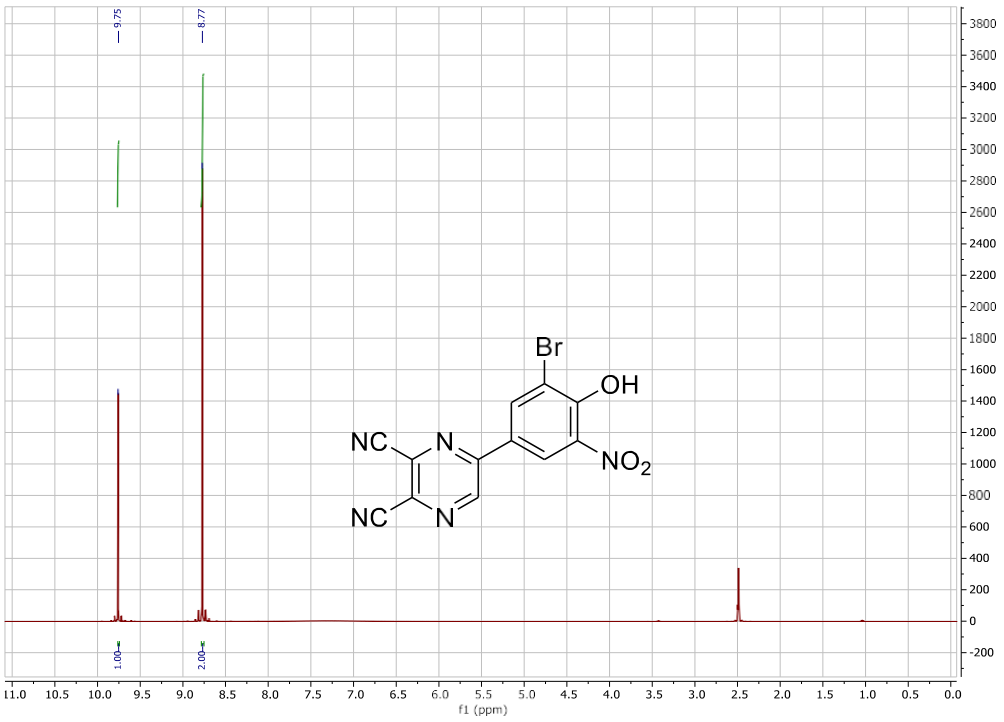
^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS), compound **13**



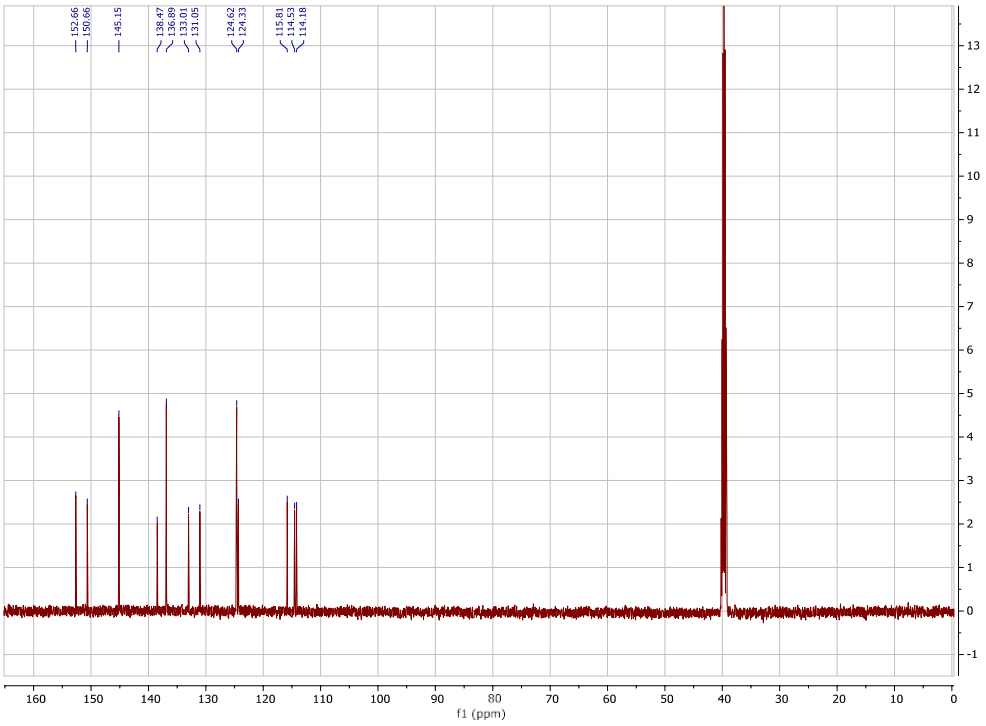
^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS, compound **14**



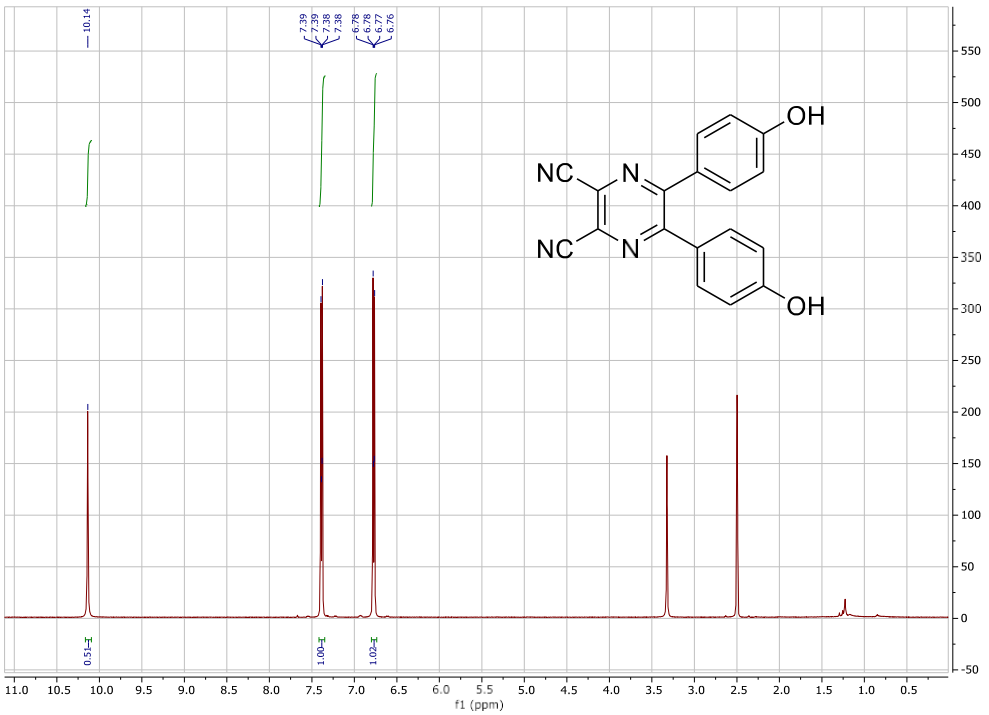
^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS), compound **14**



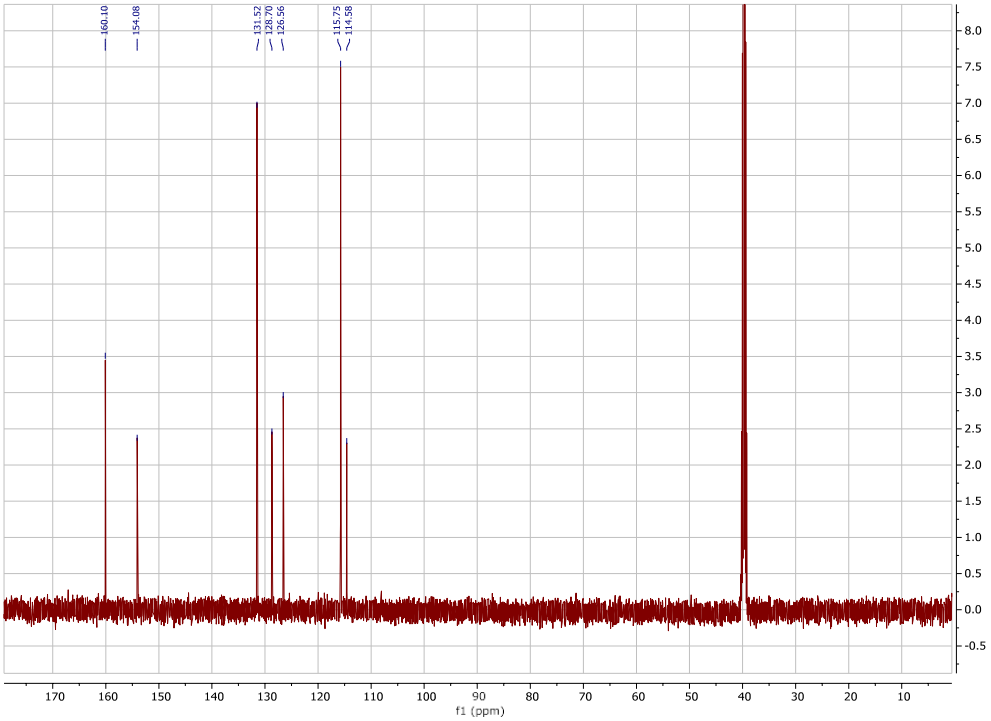
^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS, compound **15**



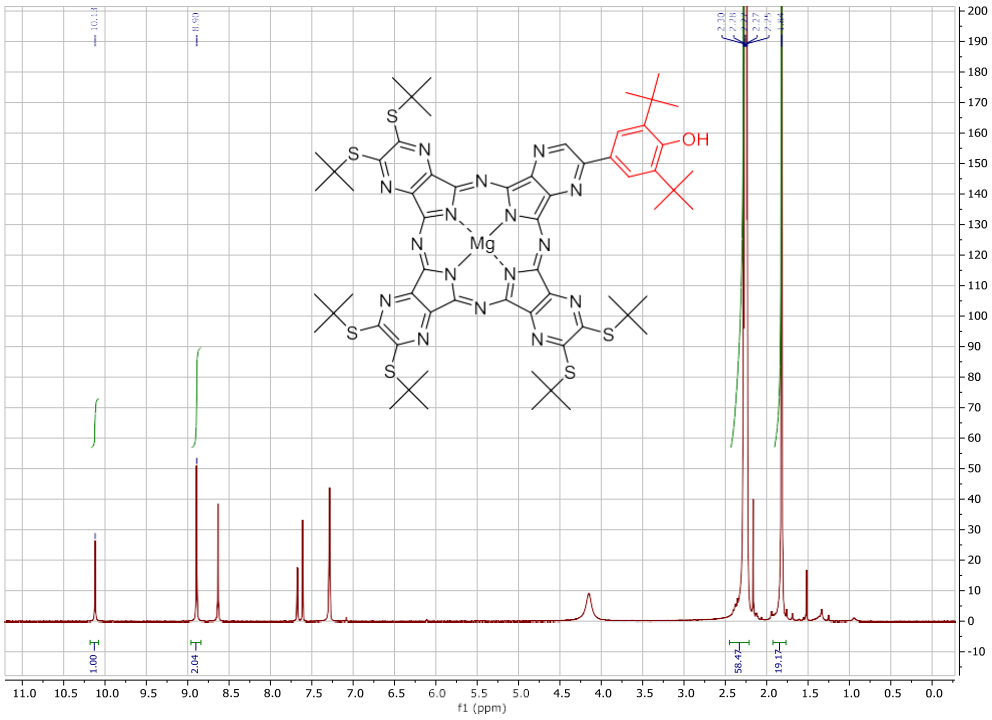
^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS), compound **15**



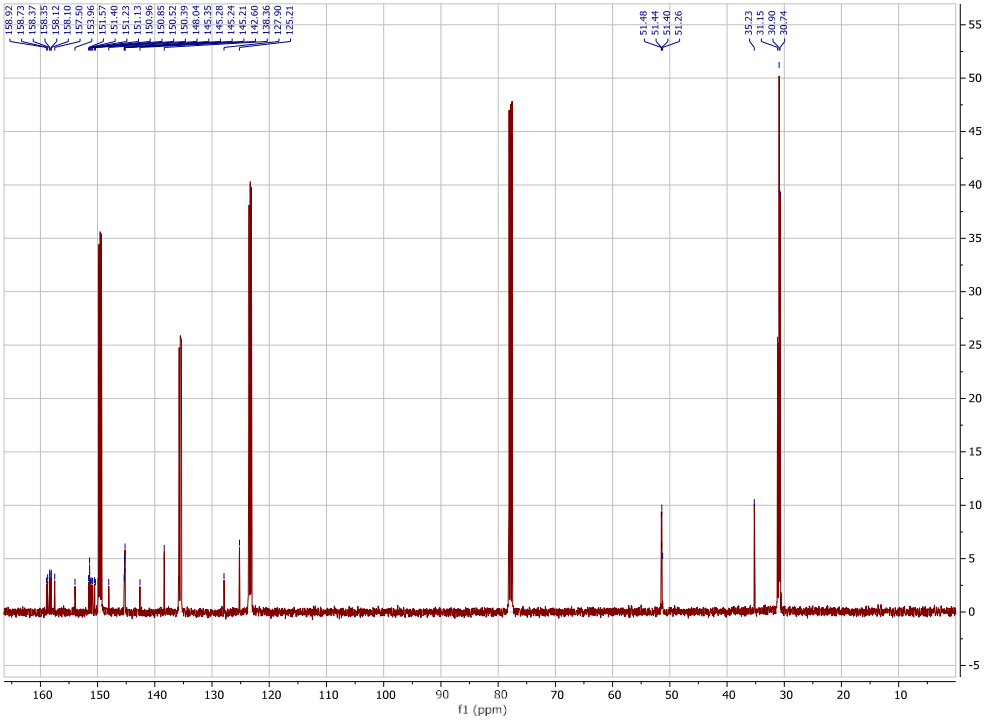
^{1}H NMR (500 MHz, CD_3SOCD_3, 25°C, TMS, compound **18**



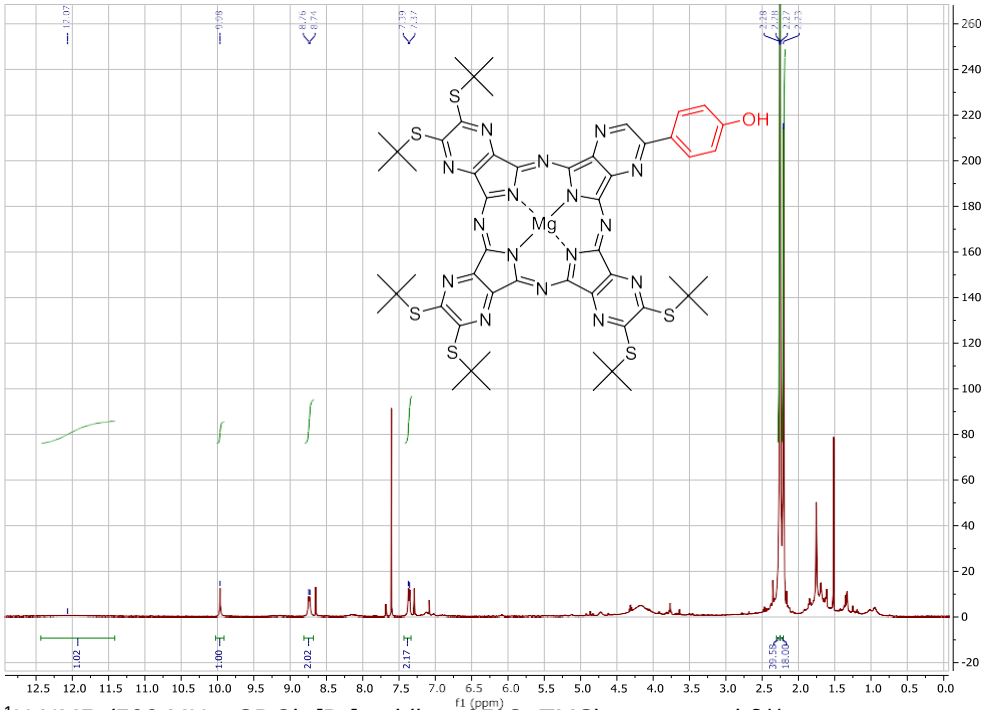
^{13}C NMR (125 MHz, CD_3SOCD_3, 25°C, TMS), compound **18**



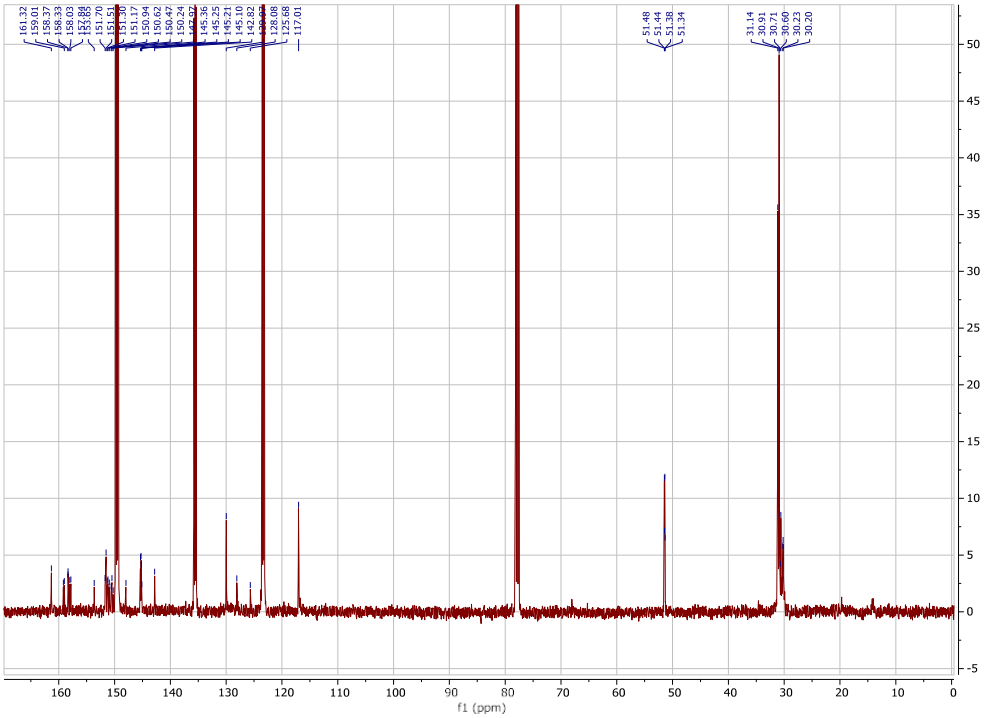
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **1Mg**



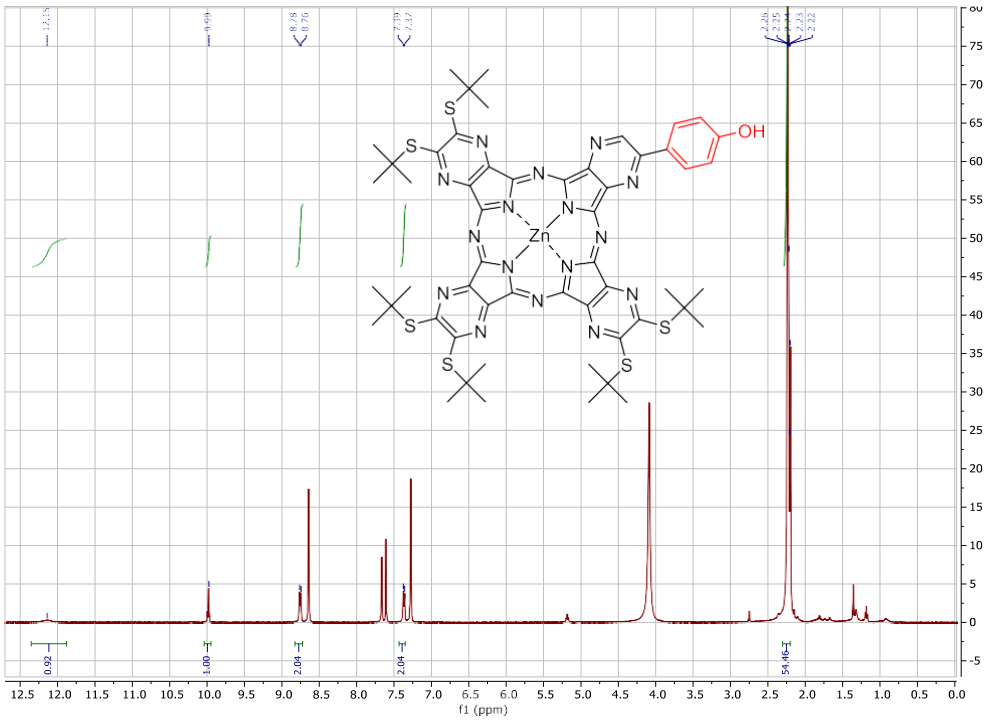
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **1Mg**



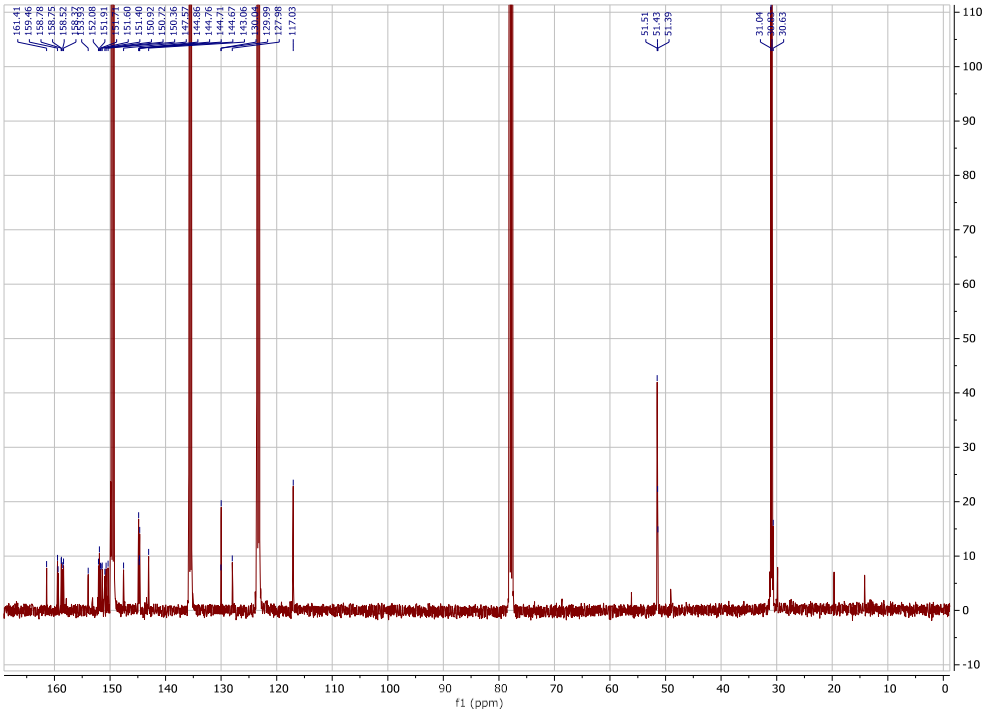
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **2Mg**



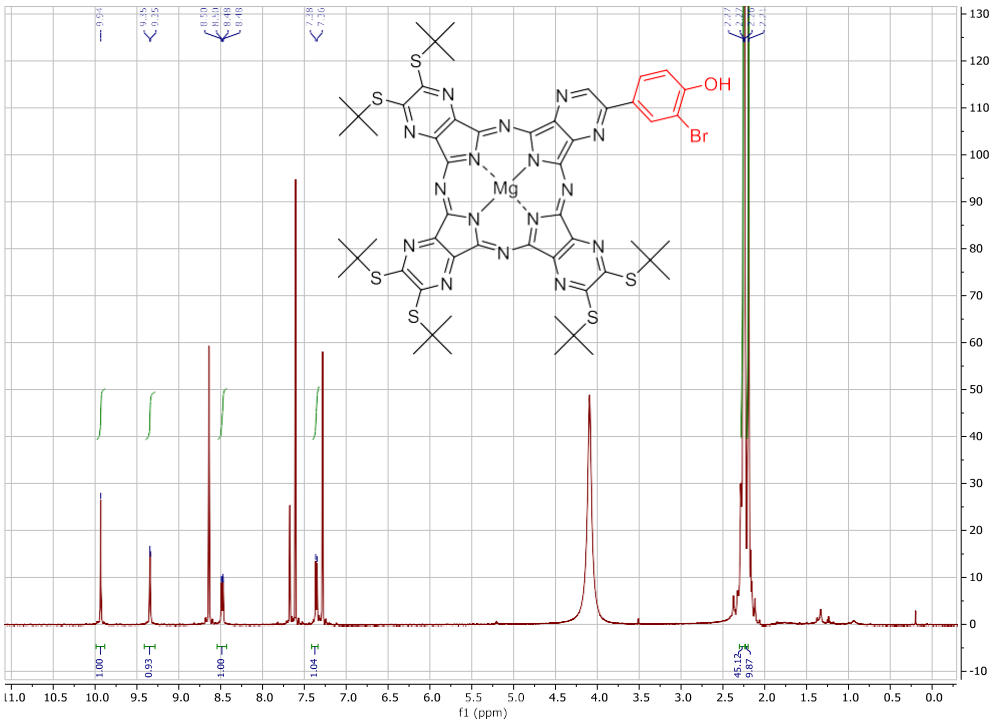
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **2Mg**



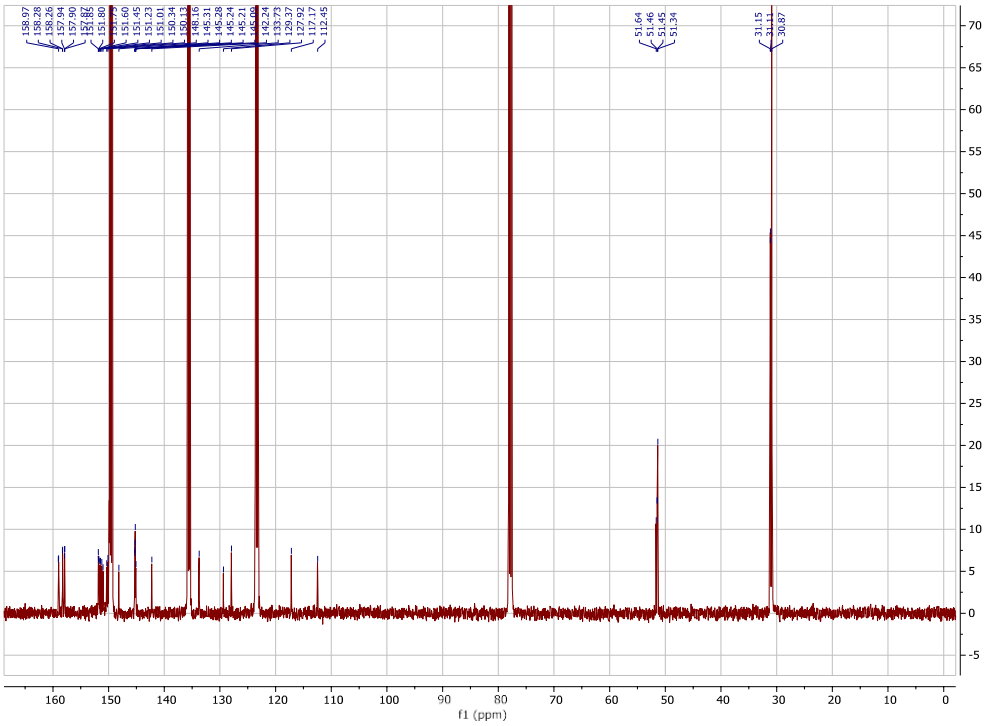
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **2Zn**



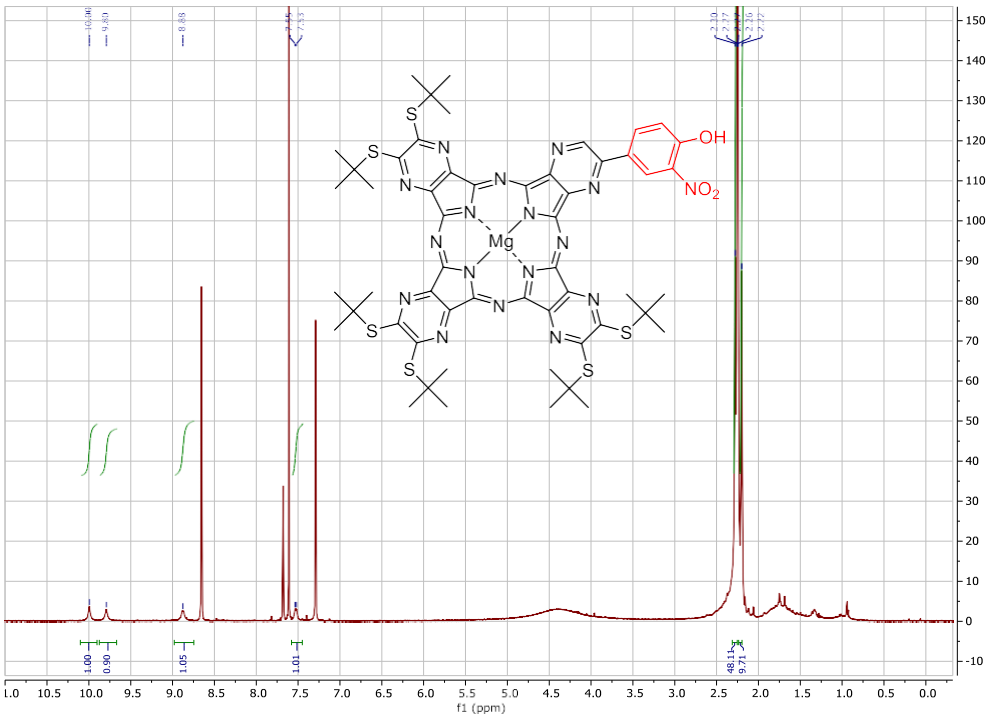
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **2Zn**



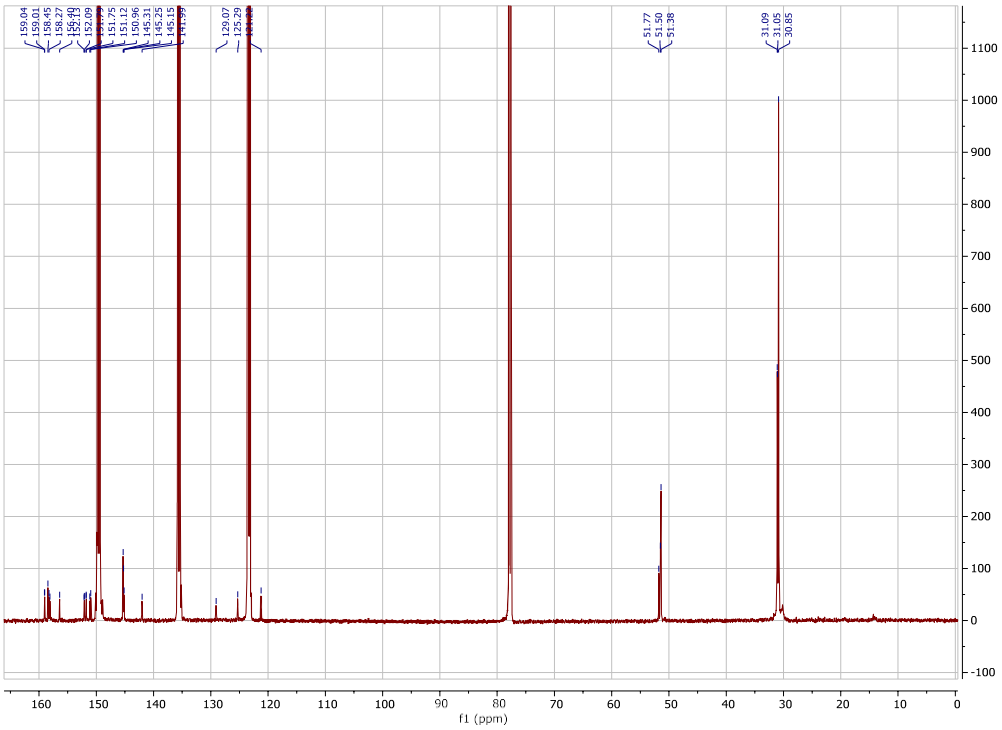
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **3Mg**



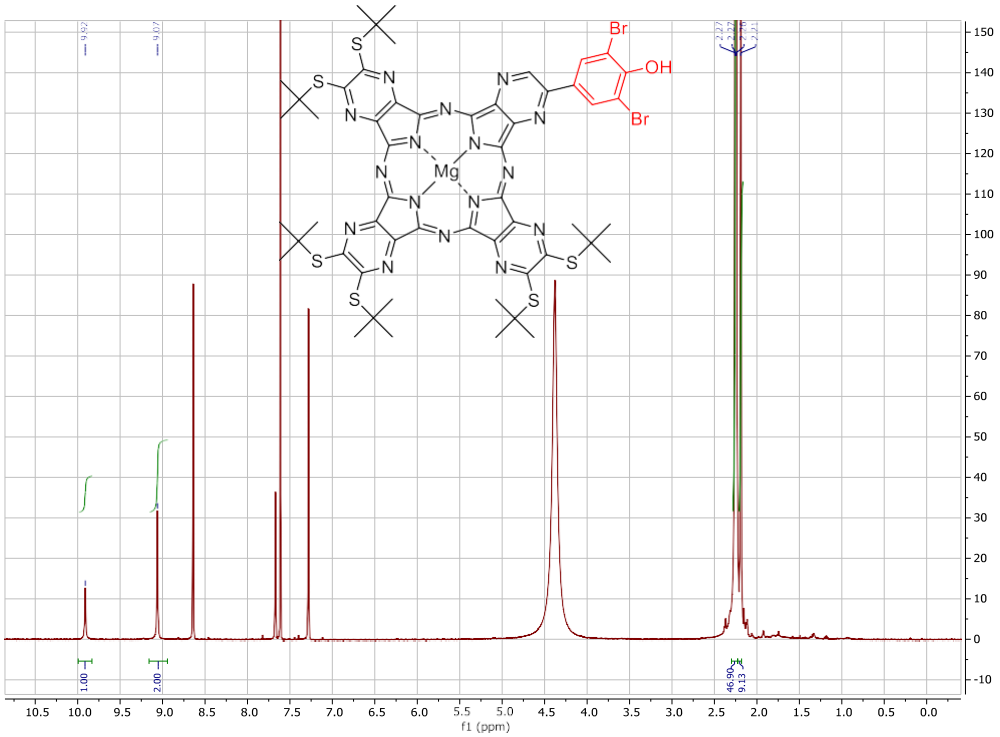
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **3Mg**



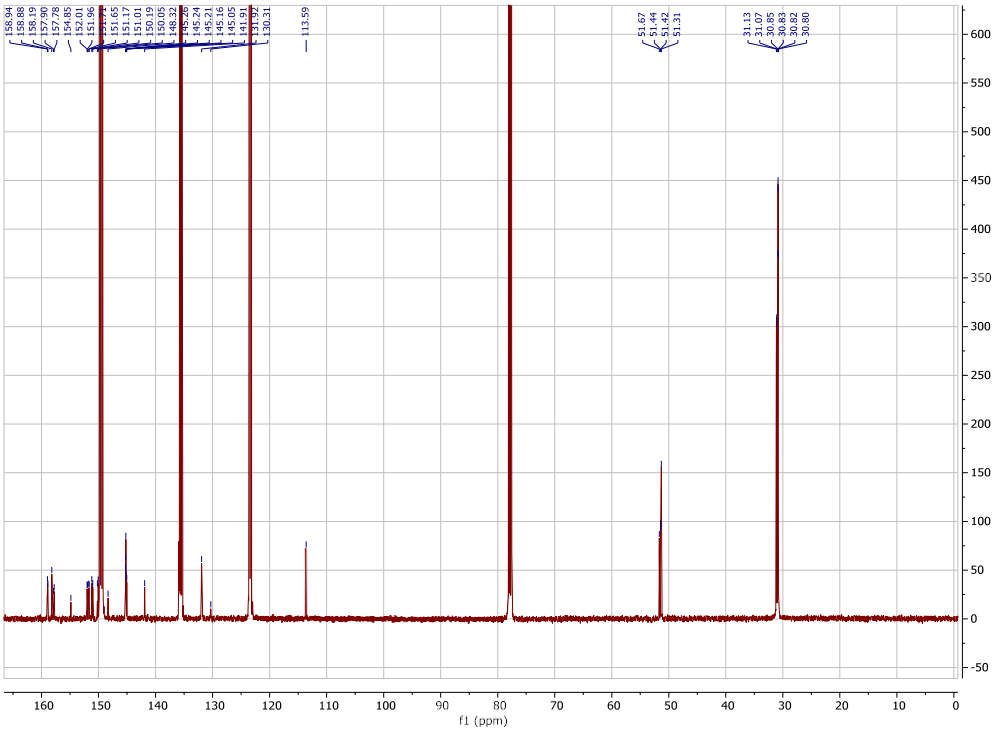
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **4Mg**



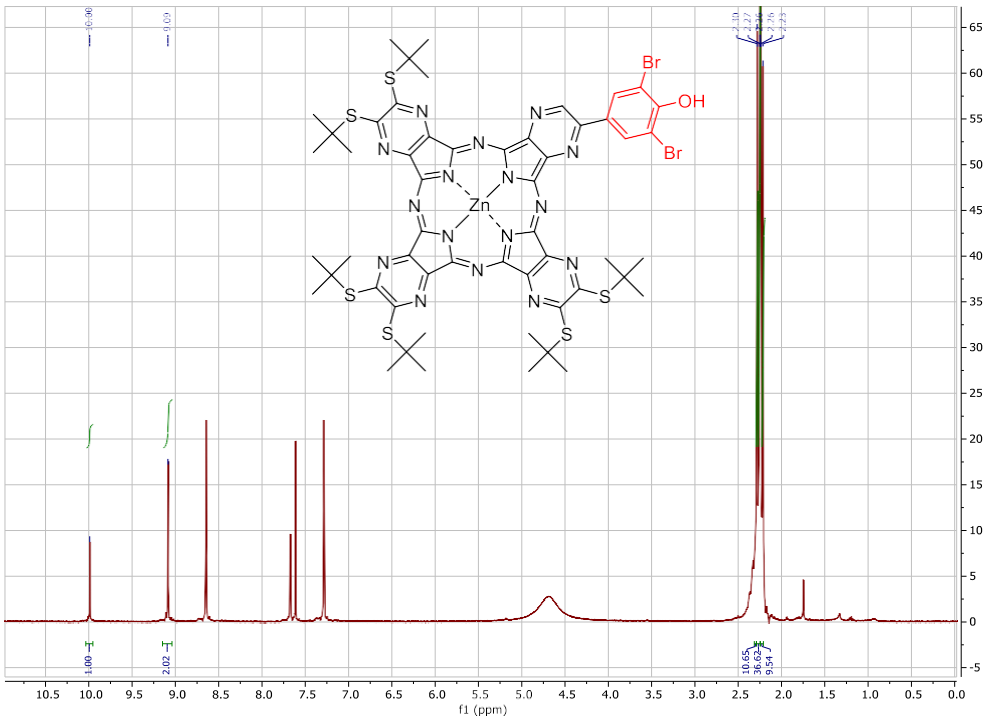
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **4Mg**



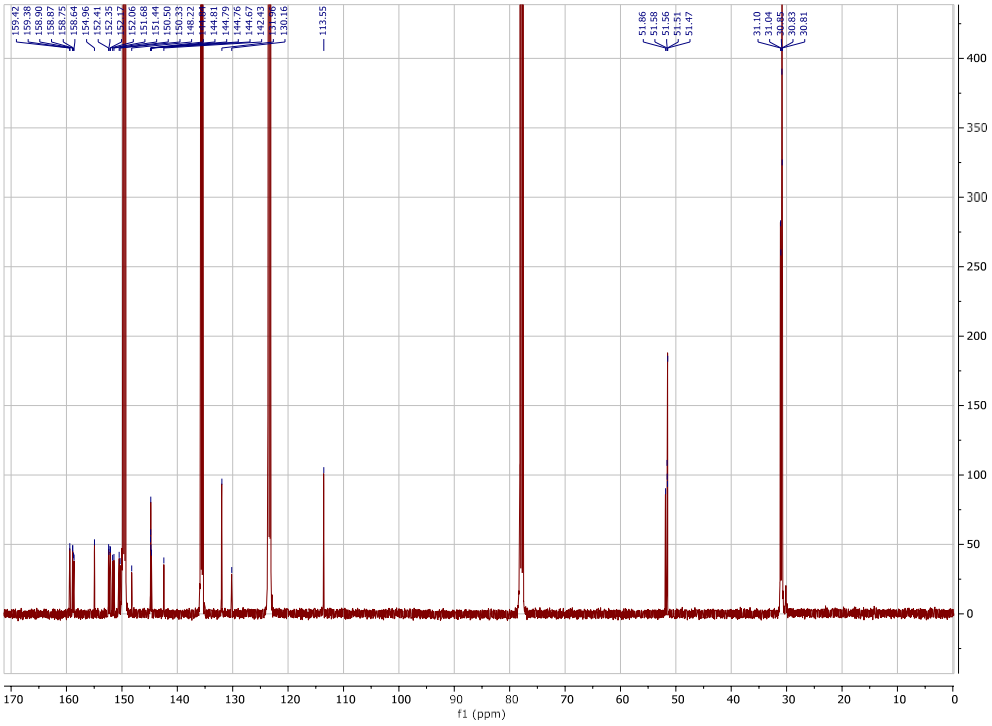
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **5Mg**



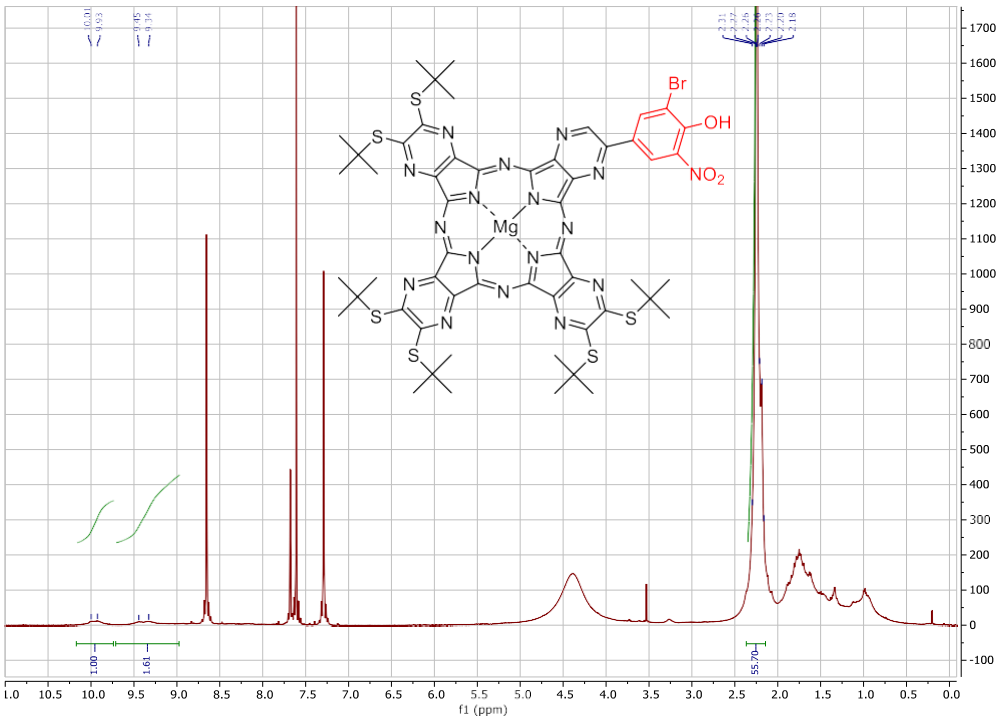
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **5Mg**



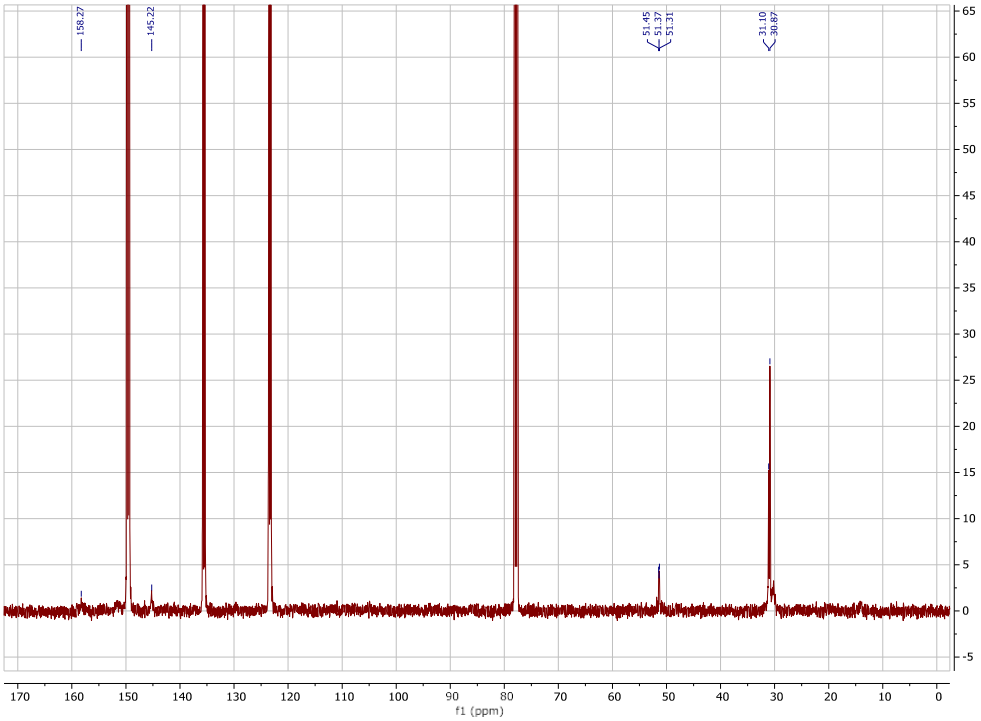
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **5Zn**



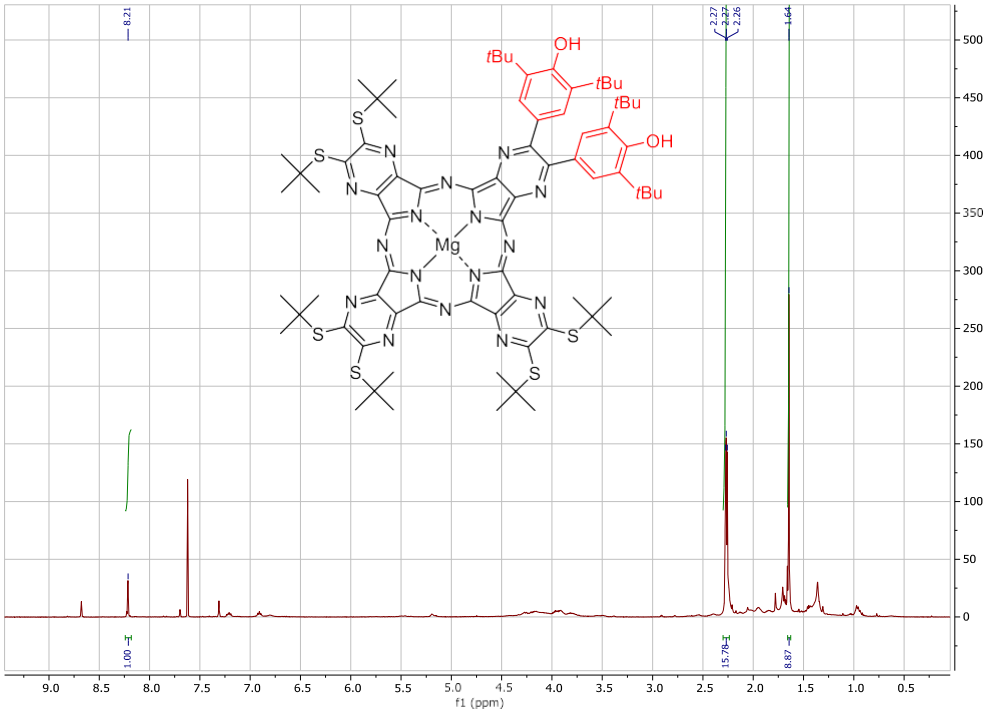
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **5Zn**



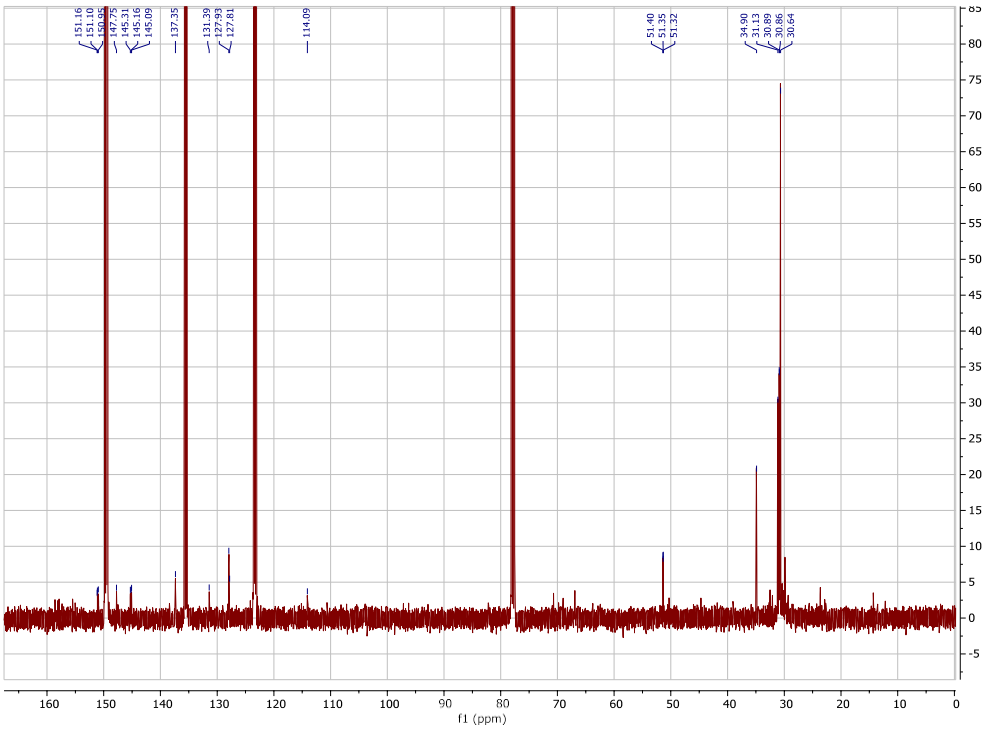
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **6Mg**



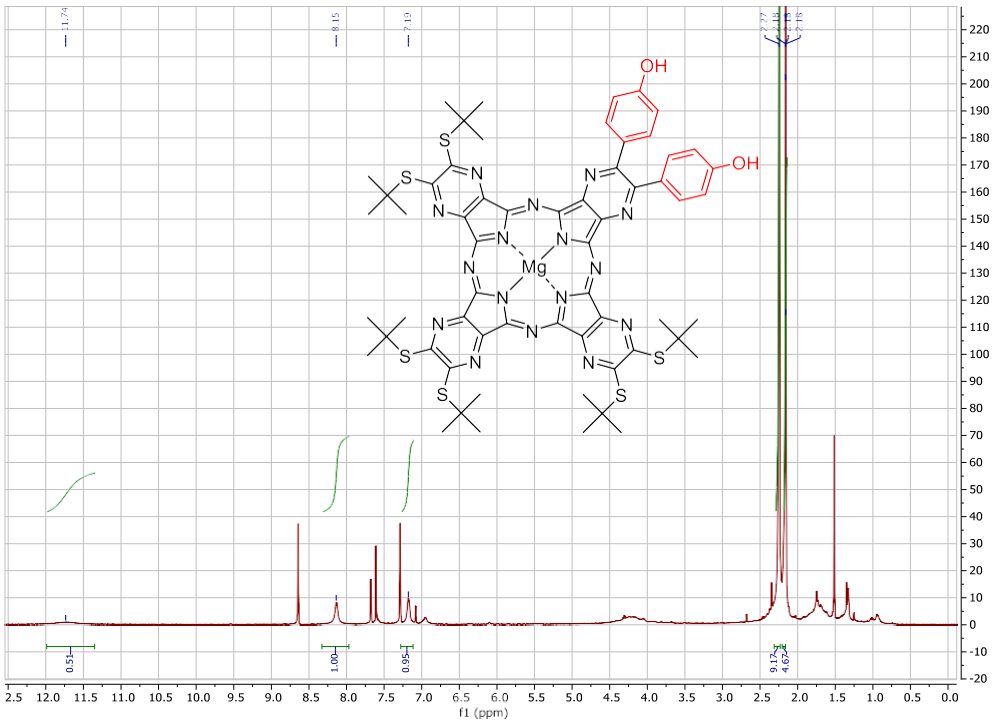
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **6Mg**



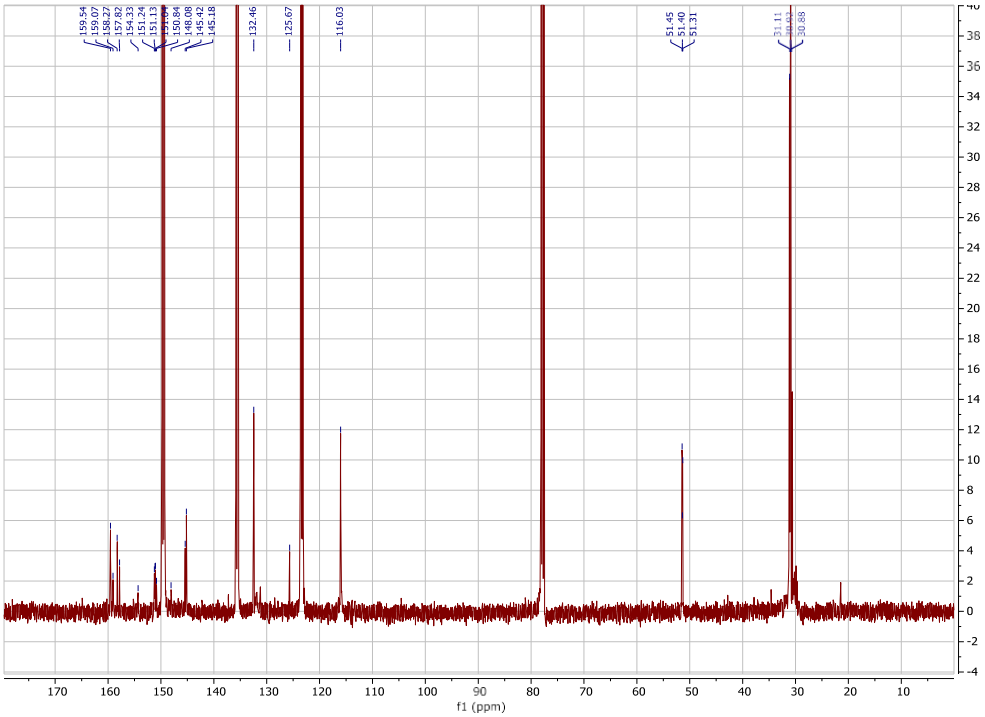
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **7Mg**



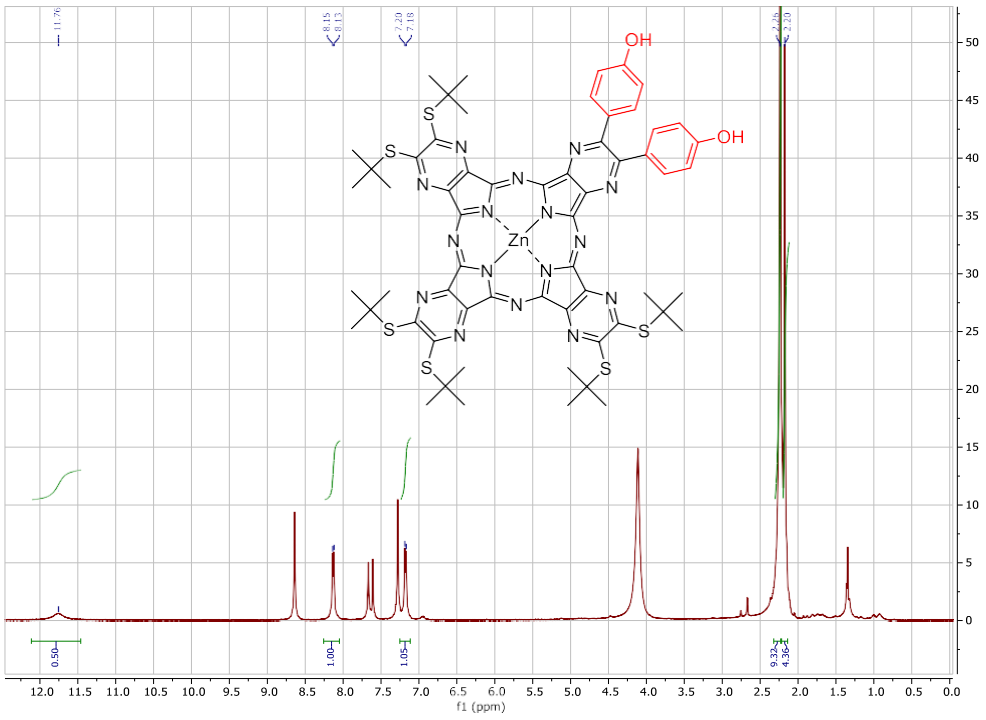
^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **7Mg**



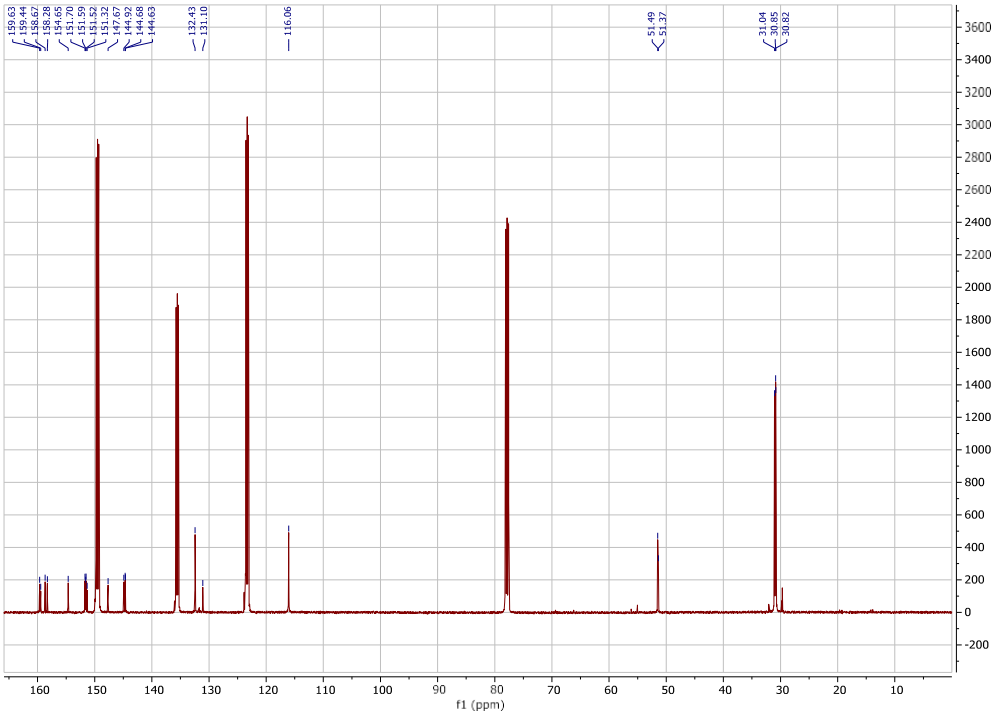
^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **8Mg**



^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **8Mg**



^{1}H NMR (500 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **8Zn**



^{13}C NMR (125 MHz, $CDCl_3$:[D_5]pyridine, 25°C, TMS), compound **8Zn**

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