Supporting Information

Orthogonal Construction of ZnSalen/Salophen Library as a Colour Palette for One- and Two-Photon Live Cell Imaging

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1 General experimental information

All solvents and chemicals were purchased from Alfa Aesar and J&K and used without further purification, unless specifically mentioned. Cellular imaging trackers were purchased from Invitrogen (Life Technologies). The ^{1}H NMR spectroscopic measurements were carried out using a Varian-300 NMR or a Bruker-400 NMR spectrometer, at 300 MHz or 400 MHz, respectively. Tetramethysilane (TMS) is used as the internal reference. The ^{19}F NMR spectroscopic measurements were carried out using a Varian-300 NMR and CF_3COOH was selected as the external reference. Electrospray ionization (ESI) mass spectra were performed on a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR, Bruker, USA). FT-IR spectra were taken on a Nicolet iN10 MX Fourier Transform Infrared Spectrometer. The steady-state absorption spectra were attained on an Agilent 8453 UV-*vis* spectrophotometer in 1cm path length quartz cells. Single-photon luminescence spectra were recorded using fluorescence lifetime and steady state spectrophotometer (Edinburgh Instrument FLS920). Quantum yields of one photon emission of all the synthesized compounds were measured relative to the fluorescence of Rhodamine B in ethanol or fluorescein in 1M NaOH aqueous solution. The two-photon absorption cross section of the probes was calculated at each wavelength relative to Rhodamine B as standard. The two photon fluorescence data was acquired using a Tsunami femtosecond Ti: Sapphire laser (pulse width ≤100fs, 80 MHz repetition rate, tuning range 740-880 nm, Spectra Physics Inc., USA). Cyclic voltammetry experiments were recorded on a Shanghai Chenhua CHI660C electrochemical workstation. A glassy carbon electrode was selected as working electrode while SCE (saturated calomel electrode) served as reference electrode; the auxiliary electrode was a platinum wire. Confocal fluorescent images of living cells were performed using Nikon A1R-si Laser Scanning Confocal Microscope (Japan), equipped with lasers of 405/488/543/638 nm. Several lasers and channels were used to obtain images. Two photon fluorescence microscopy images were performed on a modified Olympus Fluoview FV1000MPE microscope system equipped with an excitation light laser provided by a modelocked Ti: sapphire laser, (Mai Tai, Spectra-Physics Inc., USA).

2 Synthesis and characterization

All the reactions were carried out under nitrogen. To monitor the reactions, thin-layer chromatography was performed and visualized by 254 nm UV-illumination.

2.1 Structure of salicylaldehydes and diamines used in this work:

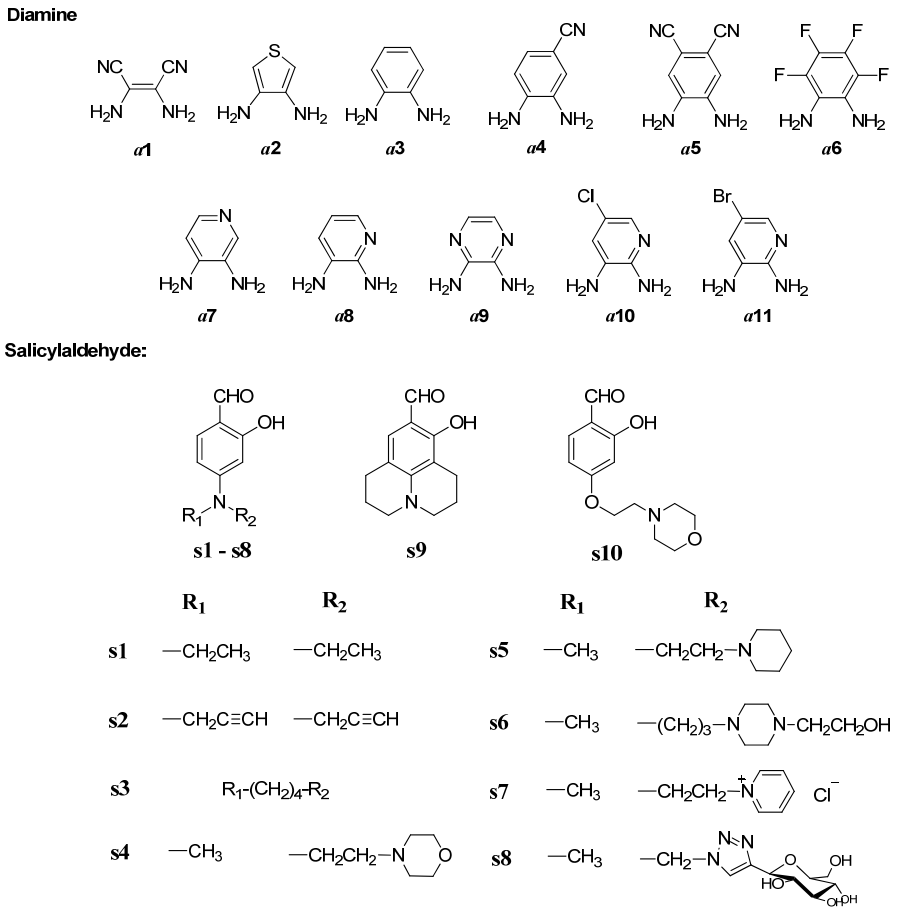


Figure S1 Summary of the structures of salicylaldehydes and diamines used in this work

2.2 Synthesis and characterization of diamine

All diamines except ***a*6** are commercially available. Thiophene-3,4-diamine (a10) was used in the form of dihydrochloride.

Synthesis of *a*6

Diamine ***a*6** was prepared according to the reported literature[1]. Light gray solid was obtained.

^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 3.40 (4H, s, NH_2).

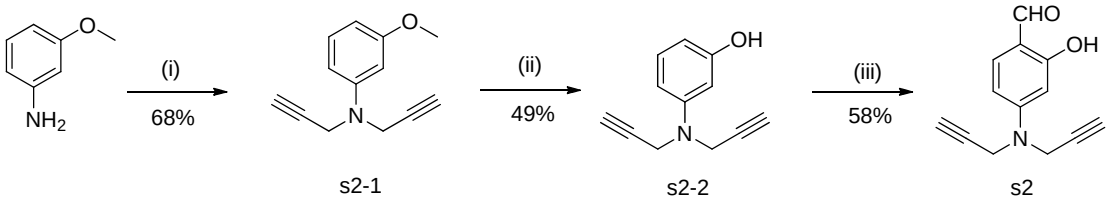
^{19}F NMR (282MHz, CH_2Cl_2): δ (ppm) -95.82 (2F, m), -85.54 (2F, m).

FT-IR (KBr pellete, cm^{-1}): 3441 (s, N-H), 3341 (s, N-H).

2.3 Synthesis of salicylaldehyde derivatives

Salicylaldehyde **s1** and **s9** are commercially available. Salicylaldehyde **s6, s7, s8** were prepared according to the reported literature.[2,3]

2.3.1 Synthesis of **s2**



Scheme S1. Synthetic route for preparation of **s2:** (i) 3-bromoprop-1-yne, K_2CO_3, CH_3CN, reflux, 12h; (ii) BBr_3, DCM, -78 °C to r.t., 16h; (iii-1) $POCl_3$, DMF, 0°C to r.t., 12h; (iii-2) icy H_2O.

s2-1 3-methoxy-N,N-di(prop-2-ynyl)aniline

A reaction mixture of 3-methoxyaniline (2.0 g, 15.0 mmol), 3-bromoprop-1-yne (3.6 g, 30.0 mmol) and K_2CO_3 (2.0g, 15.0 mmol) in acetonitrile (50 mL) was refluxed under nitrogen for 12 h. After filtration and evaporation, the remaining liquid residue was purified by column chromatography to give **s2-1** as yellow oil (2.0g, 68%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.20 (1H, t, J = 16.2 Hz, ArH), 6.56 (1H, dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, ArH), 6.52 (1H, t, J = 4.8 Hz, ArH), 6.45 (1H, dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, ArH), 4.12 (4H, d, J = 2.4 Hz, 2× CH_2), 3.8 (3H, s, OCH_3), 2.26 (2H, t, J = 4.8 Hz, 2× C≡CH).

s2-2 3-(diprop-2-ynylamino)phenol

Compound **s2-1** (2.0 g, 10.0 mmol) was dissolved in 10 mL redistilled CH_2Cl_2, and boron tribromide (1.2 mL, 12.0 mmol) was added at -78°C. The mixture was warmed slowly to room temperature and stirred for 16 h. Cold methanol was added to quench extra boron tribromide. After evaporation and extraction (using CH_2Cl_2 and H_2O), the residue was purified by column chromatography to give **s2-2** as yellow oil (0.9 g, 49%).

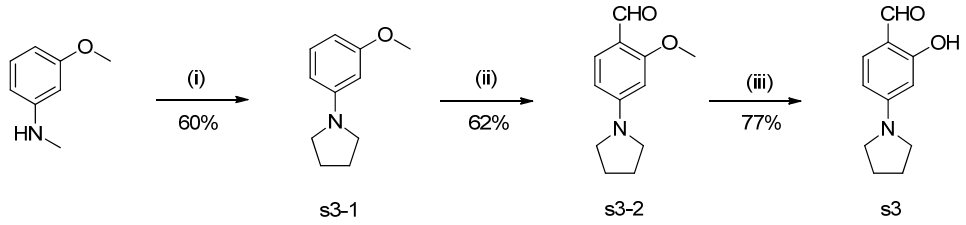
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.11 (1H, t, J = 5.4 Hz, ArH), 6.50 (1H, dd, J_1 = 7.8 Hz, J_2 = 2.4 Hz, ArH), 6.45 (1H, t, J = 4.5 Hz, ArH), 6.37 (1H, dd, J_1 = 7.8 Hz, J_2 = 2.4 Hz, ArH), 4.05 (4H, d, J = 2.4 Hz, 2× CH_2), 2.24 (2H, t, J = 4.8 Hz, 2× C≡CH).

s2 4-(diprop-2-ynylamino)-2-hydroxybenzaldehyde

$POCl_3$ (0.8 mL, 5.0 mM) was added slowly in anhydrous DMF (5 mL) in the ice-water bath and stirred for 30 min. Then compound **s2-2** (0.9 g, 5.0 mmol) dissolved in DMF was added in drops. The mixture was slowly warmed to room temperature and stirred overnight. The reaction solution was poured into ice, stirred for a few minutes, and filtered to give **s2** as brown solid (610.0 mg, 58%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.48 (1H, s, OH), 9.63 (1H, s, CHO), 7.40 (1H, d, J = 8.4 Hz, ArH), 6.50 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.7 Hz, ArH), 6.36 (1H, d, J = 2.4 Hz, ArH), 4.03 (4H, d, J = 2.4 Hz, 2× CH_2), 2.24 (2H, t, J = 2.4 Hz, 2× C≡CH).

2.3.2 Synthesis of **s3**



Scheme S2. Synthetic route for preparation of **s3:** (i) $Br(CH_2)_4Br$, KOH, CH_3CN, reflux, 12h; (ii-1) $POCl_3$, DMF, 0°C to r.t., 30min; (ii-2) icy H_2O, 30min. (iii) BBr_3, DCM, -78°C to r.t., 16h.

s3-1 1-(3-methoxyphenyl)pyrrolidine

3-methoxy-N-methylaniline (3 g, 21.9 mmol), 1,4-dibromobutane (5 g, 23.1 mmol) and KOH (3.1 g, 55.4 mmol) were mixed in 30 mL CH_3CN and the mixture was refluxed for 12 h. After filtration and evaporation, the remaining liquid residue was purified by column chromatography to give **s3-1** as yellow oil (2.33 g, 60%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.13 (1H, t, J = 8.1Hz, ArH), 6.22 (2H, m, ArH), 6.11 (1H, t, J = 2.4 Hz, ArH), 3.80 (3H, s, OCH_3), 3.26 (4H, m, 2× NCH_2), 1.99 (4H, m, 2× NCH_2CH_2).

s3-2 2-methoxy-4-(pyrrolidin-1-yl)benzaldehyde

$POCl_3$ (1.3 mL, 13.9 mmol) was slowly added into anhydrous DMF (1.5 mL) in ice-water bath and stirred for 30 minutes. Then **s3-1** (2.5g, 14.1 mmol) was added in drops. The mixture was slowly warmed to room temperature and stirred for additional 20 min. Then the reaction was quenched by 10 mL icy water with vigorous stirring and saturated aqueous $NaHCO_3$ solution was used to tune pH to 7~8. Ethyl acetate is used as extractant, each 20 mL. The organic phase containing only one solute (monitored by TLC, PE: EA 3:1) was merged and dried by anhydrous Na_2SO_4. After evaporation, product **s3-2** was obtained as a while solid (1.80 g, 62%).

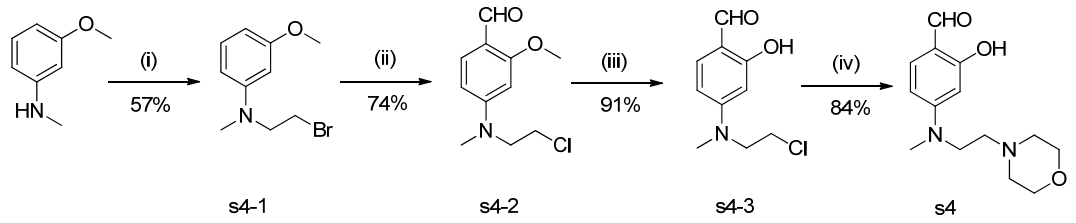
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.13 (1H, s, CHO), 7.70 (1H, d, J = 8.7 Hz, ArH), 6.18 (1H, dd, J_1 = 8.8 Hz, J_2 = 1.4 Hz, ArH), 5.91 (1H, d, J = 1.7 Hz, ArH), 3.89 (3H, s, OCH3), 3.44 (4H, m, NCH_2), 2.03 (4H, m, NCH_2CH_2).

s3 2-hydroxy-4-(pyrrolidin-1-yl)benzaldehyde

s3-2 (1.45 g, 7.1 mmol) was dissolved in 30 mL CH_2Cl_2 under N_2, and boron tribromide (1.6 mL, 17.2 mmol) was added at -78°C. The mixture was warmed slowly to room temperature and stirred for 16 hours. Cold methanol and icy water was added to quench reaction and saturated aqueous $NaHCO_3$ solution was used to tune pH to 7~8. After extracting three times by ethyl acetate, each

25 mL, the organic layer was merged and dried by anhydrous Na_2SO_4. It was then purified by column chromatography (eluent PE: EA 10:1) to give product **s3** as a yellow solid (1.04 g, 77%).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.69 (1H, s, OH), 9.50 (1H, s, CHO), 7.28 (1H, d, J = 8.9Hz, ArH), 6.17 (1H, dd, J_1 = 2.1Hz, J_2 = 8.7Hz, ArH), 5.97 (1H, d, J = 2.0Hz, ArH), 3.38 (4H, t, J = 6.6Hz, NCH_2), 2.04 (4H, m, NCH_2CH_2).

2.3.3 Synthesis of **s4**



Scheme S3. Synthetic route for preparation of **s4:** (i) $BrCH_2CH_2Br$, $KHCO_3$, CH_3CN, reflux, 12h; (ii-1) $POCl_3$, DMF, 0°C to r.t., 30min; (ii-2) icy H_2O, 30min. (iii) BBr_3, DCM, -78°C to r.t., 16h; (iv) morpholine, $KHCO_3$, KI, CH_3CN, reflux, 12h.

s4-1 N-(2-bromoethyl)-3-methoxy-N-methylaniline

A reaction mixture of 3-methoxy-N-methylaniline (2.0 g, 14 mmol), 1, 2-dibromoethane (27.5 g, 140 mmol) and $KHCO_3$ (1.7 g, 17 mmol) in acetonitrile (30 mL) was refluxed under nitrogen for 12 h. After filtration and evaporation, the remaining liquid residue was purified by column chromatography to give **s4-1** as yellow oil (2.04 g, 57%).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.01 (1H, m, ArH), 6.20 (3H, m, ArH), 4.91 (3H, s, OCH_3), 3.69 (2H, t, J = 15.3Hz, NCH_2), 3.49 (2H, t, J = 15.3Hz, CH_2Br), 2.96 (3H, s, NCH_3).

s4-2 4-((2-chloroethyl)(methyl)amino)-2-methoxybenzaldehyde

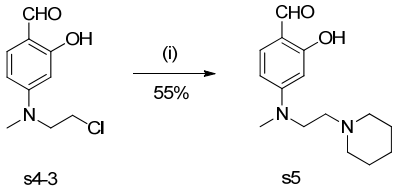
$POCl_3$ (1.0 mL, 10.7 mmol) was slowly added into anhydrous DMF (1.2 mL) in ice-water bath and stirred for 30 minutes. Then **s4-1** (3.0 g, 12.3 mmol) was added in drops. The mixture was slowly warmed to room temperature and stirred for additional 20 minutes. Then the reaction was quenched by 10mL icy water with vigorous stirring and saturated aqueous $NaHCO_3$ solution was used to tune pH to 7~8. Ethyl acetate is used as extractant, each 20 mL. The organic phase containing only one solute (monitored by TLC, PE: EA 3:1) was merged and dried by anhydrous Na_2SO_4. After evaporation, product **s4-2** was obtained as a while solid (2.15 g, 74%).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.18 (1H, s, CHO), 7.44 (1H, d, J = 8.9Hz, ArH), 6.32 (1H, dd, J_1 = 2.2Hz, J_2 = 8.8Hz, ArH), 6.09 (1H, d, J = 2.2Hz, ArH), 3.91 (3H, s, OCH_3), 3.78 (2H, t, J = 6.8Hz, NCH_2), 3.67 (2H, t, J = 6.5Hz, CH_2Br), 3.14 (3H, s, NCH_3).

s4-3 4-((2-chloroethyl)(methyl)amino)-2-hydroxybenzaldehyde

s4-2 (1.2 g, 5.3 mmol) was dissolved in 30mL CH_2Cl_2 under N_2, and boron tribromide (1.2 mL, 12.9 mmol) was added at -78°C. The mixture was warmed slowly to room temperature and stirred for 16 hours. Cold methanol and icy water was added to quench reaction and saturated aqueous $NaHCO_3$ solution was used to tune pH to 7~8. After extracting three times by ethyl acetate, each 25 mL, the organic layer was merged and dried by anhydrous Na_2SO_4. It was then purified by column chromatography (eluent PE: EA 10:1) to give product **s4-3** as yellow solid (1.02 g, 91%).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.58 (1H, s, OH), 9.58 (1H, s, CHO), 7.35 (1H, d, J = 8.7 Hz, ArH), 6.33 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, ArH), 6.14 (1H, d, J = 2.4 Hz, ArH), 3.77 (2H, t, J = 13.2 Hz, NCH_2), 3.67 (2H, t, J = 13.2 Hz, CH_2Br), 3.14 (3H, s, NCH_3),.

s4 2-hydroxy-4-(methyl(2-morpholinoethyl)amino)benzaldehyde
s4-3 (1.4 g, 6.6 mmol)**,** $KHCO_3$ (1.32 g, 13.2 mmol), KI (3.3 g, 19.9 mmol) was mixed by 40 mL CH_3CN under N_2 and morpholine (5 mL, excess) was then added dropwise. The mixture was refluxed for 12 hours, and after filtration, excess morpholine and solvent of the filtrate was removed under reduced pressure. The brown residue was dissolved in CH_2Cl_2, and was then purified by column chromatography to give **s4** as orange oil (1.45 g, 84%).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.60 (1H, s, OH), 9.53 (1H, s, CHO), 7.29 (1H, d, J = 8.9Hz, ArH), 6.30 (1H, dd, J_1 = 2.3Hz, J_2 = 8.9Hz, ArH), 6.10 (1H, d, J = 2.1Hz, ArH), 3.71 (4H, m, CH_2OCH_2), 3.54 (2H, t, J = 7.2Hz, $N(CH_3)CH_2$), 3.07 (3H, s, NCH_3), 2.56 (2H, t, J = 7.2Hz, $N(CH_3)CH_2CH_2$), 2.50 (4H, m, $CH_2CH_2OCH_2CH_2$).

2.3.4 Synthesis of **s5**



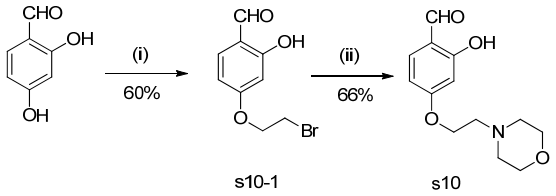
s4-3 s5

Scheme S4. Synthetic route for preparation of **s5:** (i) piperidine, $KHCO_3$, KI, CH_3CN, reflux, 12h.

s5 2-hydroxy-4-(methyl(2-(piperidin-1-yl)ethyl)amino)benzaldehyde
s4-3 (0.25 g, 0.95 mmol)**,** $KHCO_3$ (0.15 g, 1.5 mmol), KI (0.24g, 1.5 mmol) was mixed with 20 mL CH_3CN under N_2 and piperidine (0.5 mL, excess) was then added dropwise. The mixture was refluxed for 12h, and after filtration, excess piperidine and solvent of the filtrate was removed under reduced pressure. The brown residue was dissolved in CH_2Cl_2, which was purified by column chromatography to give **s5** as red solid (0.14 g, 55%).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.61 (1H, s, OH), 9.52 (1H, s, CHO), 7.28 (1H, d, J = 8.9 Hz, ArH), 6.31 (1H, m, ArH), 6.09 (1H, d, J = 2.3 Hz, ArH), 3.55 (2H, m, $N(CH_3)CH_2$), 3.06 (3H,

s, NCH_3), 2.52 (2H, m, $N(CH_3)CH_2CH_2$), 2.46 (4H, m, 2× CH_2), 1.61 (4H, m, 2× CH_2), 1.47 (2H, m, CH_2).

2.3.5 Synthesis of **s10**



Scheme S5. Synthetic route for preparation of **s10:** (i) $BrCH_2CH_2Br$, $KHCO_3$, CH_3CN, reflux, 12h; (ii) morpholine, $KHCO_3$, KI, CH_3CN, reflux, 12h.

s10-1 4-(2-bromoethoxy)-2-hydroxybenzaldehyde

A reaction mixture of 2,4-dihydroxybenzaldehyde, 1,2-dibromoethane and $KHCO_3$ in acetonitrile was refluxed under nitrogen for 12 h. After filtration and evaporation, the remaining liquid residue was purified by column chromatography to give **s10-1** as white solid (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.46 (1H, s, OH), 9.74 (1H, s, CHO), 7.46 (1H, d, J = 8.7 Hz, ArH), 6.57 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, ArH), 6.43 (1H, d, J = 2.3 Hz, ArH), 4.34 (2H, t, J = 6.2 Hz, CH_2Br), 3.65 (2H, t, J = 6.2 Hz, OCH_2).

s10 2-hydroxy-4-(2-morpholinoethoxy)benzaldehyde

s10-1 (0.8 g, 3.3 mmol)**,** $KHCO_3$ (0.65g, 6.5 mmol), KI (1.63 g, 9.8 mmol) was mixed with 40 mL CH_3CN under N_2 and morpholine (5 mL, excess) was then added dropwise. The mixture was refluxed for 12h, and after filtration, excess morpholine and solvent of the filtrate was removed under reduced pressure. The brown residue was dissolved in CH_2Cl_2, which was purified by column chromatography to give **s10**as orange oil (0.54 g, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.46 (1H, s, OH), 9.72 (1H, s, CHO), 7.43 (1H, d, J = 8.7 Hz, ArH), 6.55 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.3 Hz, ArH), 6.43 (1H, d, J = 2.3 Hz, ArH), 4.16 (2H, t, J = 6.2 Hz, CH_2Br), 3.73 (4H, m, $CH_2CH_2OCH_2CH_2$), 2.82 (2H, t, J = 6.2 Hz, OCH_2), 2.57 (4H, m, CH_2OCH_2).

2.4 Synthesis and characterization of ZnSalen/Salophen complexes

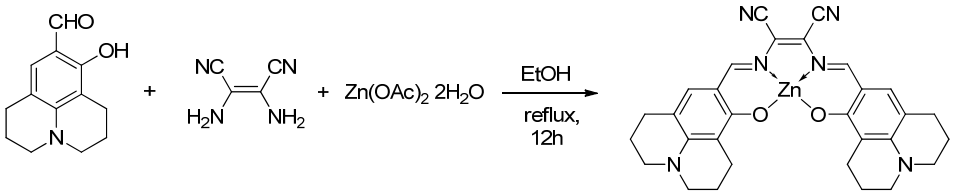
2.4.1 Synthetic Procedures:

Unless specially mentioned, ZnSalen/Salophens are synthesized according to the following general methods.

Two equivalents of salicylaldehyde derivative and one equivalent of diamine were dissolved in ethanol. After stirring at room temperature for 1h, 1.05 equiv. of $Zn(OAc)_2 \cdot H_2O$ was added and the mixture was kept stirring and refluxing for additional 16h, during which some precipitate formed. After cooling to the room temperature, the mixture was filtered and the solid was washed

in turn by water, methanol, ethyl acetate (or dichloromethane, acetone), and petroleum ether, 1mL each time, to remove the extra zinc salt, diamine and salicylaldehyde derivatives. After dried under reduced pressure, the product was obtained as powder or sheet-like solid.

A typical synthetic procedure of ZnSalen (synthesis of **a1s9)**:

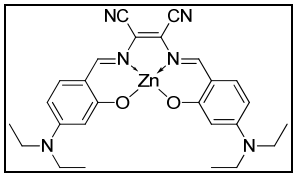


Scheme S6. Synthetic route for preparation of **a1s9.**

s9 (50.0 mg, 0.23 mmol) and **a1** (12.4 mg, 0.12 mmol) were dissolved in 10mL ethanol. After stirring at room temperature for 1h, $Zn(OAc)_2 \cdot H_2O$ (25.3mg, 0.12 mmol) was added and the mixture was kept stirring and refluxing for additional 16h. After cooling to the room temperature, the mixture was filtered and the brown solid was washed in turn by water, methanol, ethyl acetate and petroleum ether, 1mL each time. After drying under reduced pressure, the product **a1s9** was obtained as red-brown powder.

2.4.2 Characterization of ZnSalen/Salophens

a1s1



Dark green solid, yield 75%.

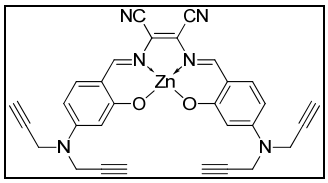
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.12 (2H, s, 2× CH=N), 7.18 (2H, d, J = 9.1Hz, ArH), 6.23 (2H, d, J = 9.1Hz, ArH), 5.83 (2H, s, ArH), 3.41 (8H, m, 4× CH_2), 1.15 (12H, t, J = 6.3Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{26}H_{29}N_6O_2Zn$ ($[M+H]^+$) 521.16380, found 521.16324.

FT-IR (KBr pellete, cm^{-1}): 2974 (C-H), 2930 (C-H), 2210 (C≡N), 1616 (C=N), 1568 (Ar C=C), 1489 (Ar C=C), 1443 (Ar C=C), 1180 (C-O).

UV-vis (DMSO) λ_{max}, nm (log ε): 387 (4.79), 439 (4.39), 593 (4.93)

a1s2



Brown solid, yield 77%.

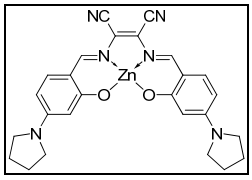
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.27 (2H, s, 2× CH=N), 7.30 (2H, d, J = 9.2Hz, ArH), 6.37 (2H, dd, J_1 = 9.1Hz, J_2 = 2.4Hz, ArH), 6.10 (2H, d, J = 2.4Hz, ArH), 4.27 (8H, d, J = 1.9Hz, 4× CH_2), 3.26 (4H, t, J = 2.2Hz, 4× C≡CH).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{30}H_{21}N_6O_2Zn$ ([M+H]$^+$) 561.10120, found 561.10172.

FT-IR (KBr pellete, cm^{-1}): 3283 (C≡C), 2214 (C≡N), 1614 (C=N), 1574 (Ar C=C), 1499 (Ar C=C), 1452 (Ar C=C), 1180 (C-O).

UV-vis (DMSO) λ_{max}, nm (log ε): 377 (4.69), 420 (4.33), 578 (4.78).

a1s3



Brown solid, yield 69%.

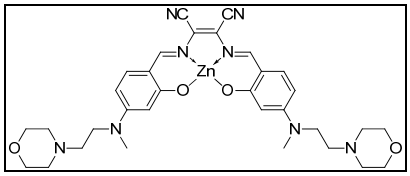
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.13 (2H, s, 2× CH=N), 7.18 (2H, d, J = 9.0Hz, ArH), 6.15 (2H, dd, J_1 = 1.9Hz, J_2 = 9.0Hz, ArH), 5.71 (2H, d, J = 1.7Hz, ArH), 3.36 (8H, m, 4× NCH_2), 1.96 (8H, m, 4× NCH_2CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{26}H_{35}N_6NaO_2Zn$ ([M+Na]$^+$) 549.19324, found 549.19400.

FT-IR (KBr pellete, cm^{-1}): 2970 (C-H), 2860 (C-H), 2205 (C≡N), 1620 (C=N), 1577 (Ar C=C), 1516 (Ar C=C), 1495 (Ar C=C), 1447 (Ar C=C), 1188 (C-O).

UV-vis (DMSO) λ_{max}, nm (log ε): 387 (4.70), 439 (4.33), 593 (4.81)

a1s4



Black solid, yield 50%.

^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.14 (2H, s, 2× CH=N), 7.17 (2H, d, J = 9.2 Hz, ArH), 6.31 (2H, d, J = 9.1 Hz, ArH), 5.84 (2H, s, ArH), 3.59 (8H, s, 2× CH_2OCH_2), 3.45 (4H, m, 2× $N(CH_3)CH_2$),

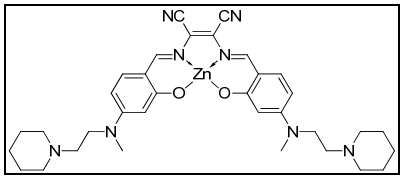
3.01 (6H, s, 2× CH_3), 2.35 (8H, s, 2× $CH_2CH_2OCH_2CH_2$), 2.30 (4H, t, J = 6.8Hz, 2× $N(CH_3)CH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{32}H_{39}N_8O_4Zn$ ($[M+H]^+$) 663.23852, found 663.23832.

FT-IR (KBr pellete, cm^{-1}): 2949(C-H), 2208 (C≡N), 1614 (C=N), 1568 (Ar C=C), 1516 (Ar C=C), 1493 (Ar C=C), 1441 (Ar C=C), 1180 (O-H).

UV-vis (DMSO) λ_{max}, nm (log ε): 387 (4.75), 437 (4.45), 593 (4.82).

a1s5



Viridis solid, yield 49%.

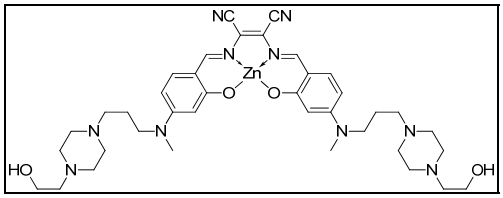
^1H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.14 (2H, s, 2× CH=N), 7.16 (2H, d, J = 9.3Hz, ArH), 6.26 (2H, dd, J_1 = 9.2Hz, J_2 = 2.4Hz, ArH), 5.83 (2H, d, J = 2.3Hz, ArH), 3.51 (4H, m, 2× $N(CH_3)CH_2$), 3.02 (6H, s, 2× CH_3), 2.43 (4H, m, 2× $N(CH_3)CH_2CH_2$), 2.39 (8H, m, 4× CH_2), 1.49 (8H, m, 4× CH_2), 1.38 (4H, m, 2× CH_2).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{34}H_{43}N_8O_2Zn$ ($[M+H]^+$) 659.27950, found 659.27968.

FT-IR (KBr pellete, cm^{-1}): 2930 (C-H), 2853 (C-H), 2808 (C-H), 2210 (C≡N), 1614 (C=N), 1568 (Ar C=C), 1514 (Ar C=C), 1493 (Ar C=C), 1443 (Ar C=C).

UV-vis (DMSO) λ_{max}, nm (log ε): 387 (4.74), 439 (4.37), 594 (4.89).

a1s6



Black solid, yield 41%.

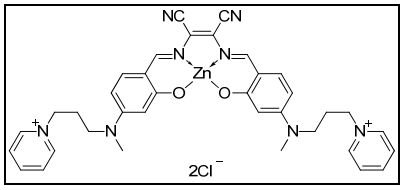
^1H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.14 (s, 2H, 2× CH=N), 7.17 (d, 2H, J = 9.3 Hz, ArH), 6.31 (2H, dd, J_1= 2.2 Hz, J_2 = 9.2 Hz, ArH), 5.84 (2H, d, J = 2.1 Hz, ArH), 4.39 (2H, s, 2× OH), 3.49 (4H, t, J = 5.9 Hz, 2× CH_2OH), 3.43 (4H, m, 2× $N(CH_3)CH_2$), 3.01 (6H, s, 2× CH_3), 2.3-2.5 (20H, m, 10× CH_2), 2.28 (4H, t, J = 6.6Hz, CH_2), 1.70 (4H, m, 2× $CH_2CH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{38}H_{53}N_{10}O_4Zn$ ($[M+H]^+$) 777.35372, found 777.35141.

FT-IR (KBr pellete, cm^{-1}): 3418 (O-H), 2940 (C-H), 2827 (C-H), 2208 (C≡N), 1616 (C=N), 1568 (Ar C=C), 1518 (Ar C=C), 1493 (Ar C=C), 1458 (Ar C=C).

UV-vis (DMSO) λ_{max}, nm (log ε): 387 (4.67), 439 (4.30), 595 (4.78).

a1s7



Red solid, yield 56%.

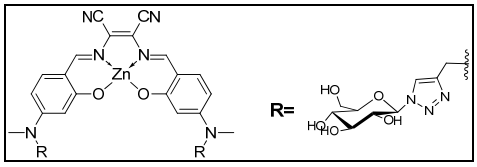
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.10 (4H, d, J = 5.6 Hz, pyH), 8.61 (2H, t, J = 7.8 Hz, pyH), 8.17 (4H, t, J = 6.7 Hz, pyH), 8.14 (2H, s, 2× CH=N), 7.18 (2H, d, J = 9.3 Hz, ArH), 6.26 (2H, dd, J_1 = 2.4 Hz, J_2 = 9.1 Hz, ArH), 5.80 (2H, d, J = 2.2 Hz, ArH), 4.68 (4H, m, 2× py-CH_2), 3.53 (4H, m, 2× N(CH_3)CH_2), 2.99 (6H, s, 2× CH_3), 2.24 (4H, m, 2× pyCH_2CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{36}H_{36}ClN_8O_2Zn$ ([M-Cl]$^+$) 711.19357, found 711.19157.

FT-IR (KBr pellete, cm^{-1}): 2920 (C-H), 2851 (C-H), 2208 (C≡N), 1616 (C=N), 1564 (Ar C=C), 1539 (Ar C=C), 1516 (Ar C=C), 1497 (Ar C=C), 1466 (Ar C=C).

UV-vis (DMSO) λ_{max}, nm (log ε): 387 (3.03), 413 (3.08), 593 (2.97).

a1s8



Dark brown solid, yield 78%.

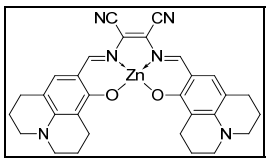
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.24 (s, 2H), 8.06 (s, 2H), 7.19 (d, 2H, J = 7.6 Hz), 6.40 (d, 2H, J = 7.6 Hz), 5.96 (s, 2H), 5.51 (d, 2H, J = 8.8 Hz), 5.36 (s, 2H), 5.26 (s, 2H), 5.14 (s, 2H), 4.66 (m, 6H), 3.75 (s, 2H), 3.41 (s, 4H), 3.14 (s, 6H), 3.37 (s, 2H).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{38}H_{43}N_{12}O_{12}Zn$ ([M+H]$^+$), 923.24094; found 923.24361.

IR (KBr pellete, cm^{-1}): 3334 (C-H), 2218 (C≡N), 1612 (C=N), 1574 (Ar C=C), 1512 (Ar C=C), 1431 (Ar C=C).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 384 (4.40), 589 (4.44).

a1s9



Red brown solid, yield 70%.

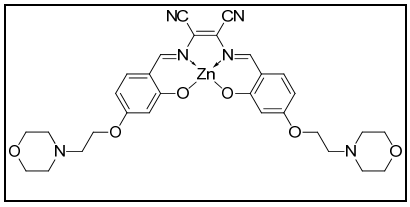
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 7.95 (2H, s, 2× CH=N), 6.71 (2H, s, ArH), 3.27 (8H, m, 4× CH_2), 2.65 (4H, t, J = 6.0 Hz, 2× CH_2), 2.58 (4H, m, 2× CH_2), 1.84 (8H, m, 4× CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{30}H_{29}N_6O_2Zn$ ([M+H]$^+$) 569.16380; found 569.16433.

IR (KBr pellete, cm^{-1}): 2934 (C-H), 2846 (C-H), 2205 (C≡N), 1624 (C=N), 1574 (Ar C=C), 1503 (Ar C=C), 1423 (Ar C=C).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 400 (4.95), 458 (4.44), 621 (5.04).

a1s10



Dark red solid, yield 77%.

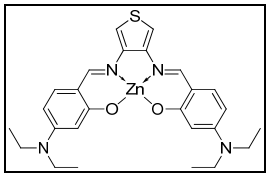
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.39 (2H, s, 2× CH=N), 7.36 (2H, d, J = 9.3Hz, ArH), 6.25 (2H, d, J = 2.4Hz, ArH), 6.23 (2H, s, ArH), 4.13 (4H, t, J = 5.6Hz, 2× $PhOCH_2$), 3.58 (8H, m, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.61Hz, 2× $PhOCH_2CH_2$), 2.47 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for$C_{30}H_{33}N_6O_6Zn$ ([M+H]$^+$), 637.17476; found 637.17312.

IR (KBr pellete, cm^{-1}): 2949 (C-H), 2922 (C-H), 2864 (C-H), 2822 (C-H), 2218 (C≡N), 1614 (C=N), 1582 (Ar C=C), 1512 (Ar C=C), 1487 (Ar C=C), 1441 (Ar C=C), 1202 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 341 (4.50), 367 (4.40), 383 (4.43), 445 (4.11), 553 (4.57).

a2s1



Two equivalents of salicylaldehyde derivative (**s1,** 50mg, 0.26 mmol), one equivalent of diamine (**a2**, in the form of dihydrochloride, 24.2 mg, 0.13 mmol) and two equivalents of $NaHCO_3$ (26mg, 0.26 mmol) were mixed in 6mL ethanol. After stirring at room temperature for 1h, 1.5 equiv. of $Zn(OAc)_2 \cdot H_2O$ was added and the mixture was kept stirring and refluxing for additional 16h. After cooling to the room temperature, solvent of the mixture was evaporated under reduced pressure and 3mL methanol was added. The mixture was filtered and the yellow filtrate was set to volatilize at room temperature for about 20h, during which some yellow precipitate formed. After filtering and washed with 0.5mL ethanol, a2s1 was obtained as a yellow powder (15.6 mg, yield 23%).

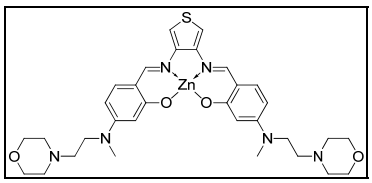
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.63 (2H, s, 2× CH=N), 7.48 (2H, s, thiophene H), 7.04 (2H, d, J = 9.0 Hz, ArH), 6.07 (2H, dd, J_1 = 8.9 Hz, J_2 = 2.4 Hz, ArH), 5.83 (2H, d, J = 2.4 Hz, ArH), 3.37 (8H, m, 4× CH_2), 1.14 (12H, t, J = 7.0 Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{52}H_{61}N_8O_4S_2Zn_2$ ([2M+H]$^+$) 1053.28346, found 1053.28161.

FT-IR (KBr pellette, cm^{-1}): 2972 (C-H), 2928 (C-H), 1593 (C=N), 1510 (Ar C=C), 1431(Ar C=C), 1178 (Ar C=C).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 413 (4.57), 445 (4.48).

a2s4



Two equivalents of salicylaldehyde derivative (**s3**, 60mg, 0.23 mmol), one equivalent of diamine (**a2**, in the form of dihydrochloride, 21.5 mg, 0.12mmol) and two equivalents of $NaHCO_3$ (23mg, 0.23 mmol) were mixed in 6mL ethanol. After stirring at room temperature for 1h, 1.5 equiv. of $Zn(OAc)_2{\cdot}H_2O$ was added and the mixture was kept stirring and refluxing for additional 16h. After cooling to the room temperature, solvent of the mixture was evaporated under reduced pressure and 3mL methanol was added. The mixture was filtered and the yellow filtrate was set to volatilize at room temperature for about 20h, during which some brown precipitate formed. After filtering and washed with 0.5mL ethanol, a2s5 was obtained as a light brown powder (54mg, yield 71%).

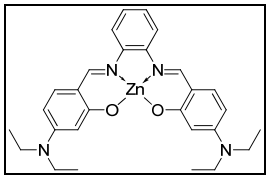
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.65 (2H, s, 2× CH=N), 7.50 (2H, s, thiophene H), 7.05 (2H, d, J = 8.8Hz, ArH), 6.10 (2H, d, J = 8.9Hz, ArH), 5.85 (2H, s, ArH), 3.58 (8H, m, CH_2OCH_2), 3.48 (4H, t, J = 6.8Hz, 2× N(CH_3)CH_2), 2.97 (6H, s, 2× CH_3), 2.48 (4H, s, 2× N(CH_3)CH_2CH_2), 2.45 (8H, s, 2× C$H_2$$CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{32}H_{41}N_6O_4SZn$ ([M+H]$^+$) 669.21960, found 669.22128.

FT-IR (KBr pellete, cm^{-1}): 2957 (C-H), 2864 (C-H), 2831 (C-H), 1584 (C=N), 1520 (Ar C=C), 1454 (Ar C=C), 1431 (Ar C=C), 1148 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 413 (4.51), 444 (4.40).

a3s1



Yellow solid, yield 69%.

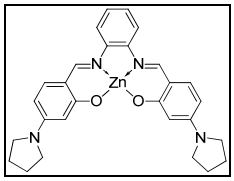
^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) 8.66 (2H, s, 2× CH=N), 7.69 (2H, m, ArH), 7.17 (2H, m, ArH), 7.13 (2H, d, J = 8.94Hz, ArH), 6.07 (2H, d, J = 8.42Hz, ArH), 5.85 (2H, s, ArH), 3.36 (8H, m, 4× CH_2), 1.14 (12H, t, J = 6.74Hz, 4× CH_3).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{28}H_{33}N_4O_2Zn$ ($[M+H]^+$) 521.18895, found 521.19134.

FT-IR (KBr pellete, cm^{-1}): 2970 (C-H), 2922 (C-H), 1605 (C=N), 1568 (Ar C=C), 1506 (Ar C=C), 1429 (Ar C=C), 1190 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 390 (4.65), 449 (4.48).

a3s3



Yellow solid, yield 68%.

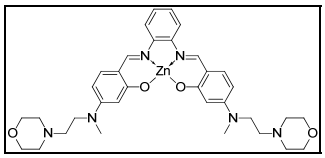
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.66 (2H, s, 2× CH=N), 7.68 (2H, m, ArH), 7.17 (2H, m, ArH), 7.14 (2H, d, J = 9.0 Hz, ArH), 5.98 (2H, dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, ArH), 5.71 (2H, d, J = 2.1 Hz, ArH), 3.30 (8H, m, 4× NCH_2), 1.96 (8H, m, 4× NCH_2CH_2).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{28}H_{29}N_4O_2Zn$ ($[M+H]^+$) 517.15765, found 517.15899.

FT-IR (KBr pellette, cm^{-1}): 2974 (C-H), 2918 (C-H), 2860 (C-H), 1620 (C=N), 1578 (Ar C=C), 1516 (Ar C=C), 1495 (Ar C=C), 1447 (Ar C=C), 1188 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 390 (4.63), 448 (4.56).

a3s4



Yellow solid, yield 40%.

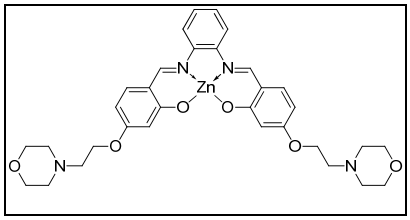
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.68 (2H, s, 2× CH=N), 7.70 (2H, m, ArH), 7.18 (2H, m, ArH), 7.14 (2H, d, J = 9.0 Hz, ArH), 6.10 (2H, dd, J_1 = 8.9 Hz, J_2 = 1.9 Hz, ArH), 5.84 (2H, s, ArH), 3.58 (8H, m, 2× CH_2OCH_2), 3.49 (4H, t, J = 6.8 Hz, 2× $N(CH_3)CH_2$), 2.98 (6H, s, 2× CH_3), 2.47 (8H, s, 2× $CH_2CH_2OCH_2CH_2$), 2.45 (4H, d, J = 4.3 Hz, 2× $N(CH_3)CH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{32}H_{43}N_6O_4Zn$ ($[M+H]^+$) 663.26318, found 663.26532.

FT-IR (KBr pellete, cm^{-1}): 2949 (C-H), 2862 (C-H), 2816 (C-H), 1616 (C=N), 1568 (Ar C=C), 1516 (Ar C=C), 1493 (Ar C=C), 1443 (Ar C=C), 1180 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 391 (4.64), 446 (4.47).

a3s10



Yellow solid, yield 72%.

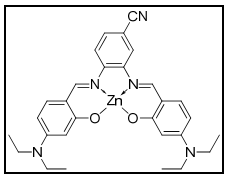
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.87 (2H, s, 2× CH=N), 7.80 (2H, dd, J_1 = 6.2Hz, J_2 = 3.5 Hz, ArH), 7.29 (4H, m, ArH), 6.17 (4H, m, ArH), 4.09 (4H, t, J = 5.7Hz, 2× $PhOCH_2$), 3.59 (8H, m, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.7Hz, 2× $PhOCH_2CH_2$), 2.48 (8H, d, J = 4.5Hz, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for$C_{32}H_{37}N_4O_6Zn$ ([M+H]$^+$) 637.19991, found 637.19884.

FT-IR (KBr pellete, cm^{-1}): 2922 (C-H), 2855 (C-H), 1609 (C=N), 1584 (Ar C=C), 1526(Ar C=C), 1431(Ar C=C), 1194 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 311 (4.47), 389 (4.55), 429 (4.33).

a4s1



Yellow solid, yield 57%.

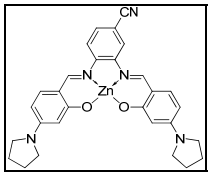
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.74 (1H, s, CH=N), 8.71 (1H, s, CH=N), 8.15 (1H, d, J = 1.6 Hz, ArH), 7.82 (1H, d, J = 8.7 Hz, ArH), 7.53 (1H, dd, J_1 = 8.4Hz, J_2 = 1.7 Hz, ArH), 7.15 (1H, d, J = 9.1 Hz, ArH), 7.14 (1H, d, J = 9.1 Hz, ArH), 6.13 (2H, m, ArH), 5.82 (2H, t, J = 2.0 Hz, ArH), 3.37 (8H, m, CH_2), 1.15 (12H, t, J = 7.0 Hz, CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{29}H_{32}N_5O_2Zn$ ([M+H]$^+$) 546.18420, found 546.18320.

FT-IR (KBr pellete, cm^{-1}): 2974 (C-H), 2930 (C-H), 2905 (C-H), 2222 (C≡N), 1609 (C=N), 1568 (Ar C=C), 1503 (Ar C=C), 1435 (Ar C=C), 1204 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 403 (4.70), 466 (4.60).

a4s3



Yellow solid, yield 60%.

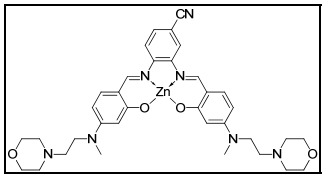
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.74 (1H, s, CH=N), 8.71 (1H, s, CH=N), 8.14 (1H, d, J = 1.3 Hz, ArH), 7.82 (1H, d, J = 8.6 Hz, ArH), 7.53 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, ArH), 7.16 (1H, d, J = 9.0 Hz, ArH), 7.15 (1H, d, J = 8.9 Hz, ArH), 6.03 (2H, m, ArH), 5.70 (2H, t, J = 2.0Hz, ArH), 3.30 (8H, m, 4× NCH_2), 1.96 (8H, m, 4× NCH_2CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{29}H_{28}N_5O_2Zn$ ([M+H]$^+$) 542.15290, found 542.15309.

FT-IR (KBr pellete, cm^{-1}): 2959 (C-H), 2920 (C-H), 2847 (C-H), 2218 (C≡N), 1611 (C=N), 1572 (Ar C=C), 1516 (Ar C=C), 1483 (Ar C=C), 1441 (Ar C=C), 1205 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 402 (4.71), 468 (4.60).

a4s4



Orange solid, yield 50%.

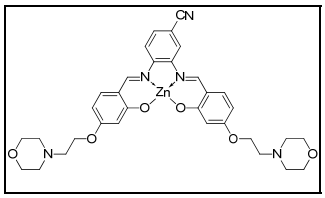
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.76 (1H, s, CH=N), 8.73 (1H, s, CH=N), 8.16 (1H, d, J = 1.5 Hz, ArH), 7.83 (1H, d, J = 8.7 Hz, ArH), 7.55 (1H, dd, J_1 = 8.5 Hz, J_2 = 1.6 Hz, ArH), 7.16 (1H, d, J = 9.1 Hz, ArH), 7.15 (1H, d, J = 9.1 Hz, ArH), 6.16 (2H, m, ArH), 5.83 (2H, t, J = 2.0Hz, ArH), 3.58 (8H, m, 2× CH_2OCH_2), 3.51 (4H, m, 2× $N(CH_3)CH_2$), 3.00 (3H, s, CH_3), 2.99 (3H, s, CH_3), 2.48 (4H, s, 2× $CH_2CH_2OCH_2CH_2$), 2.44 (8H, m, 2× $N(CH_3)CH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{35}H_{42}N_7O_4Zn$ ([M+H]$^+$) 688.25843, found 688.25907.

FT-IR (KBr pellete, cm^{-1}): 2954 (C-H), 2916 (C-H), 2855 (C-H), 2818 (C-H), 2222 (C≡N), 1604 (C=N), 1564 (Ar C=C), 1512 (Ar C=C), 1431 (Ar C=C), 1205 (Ar C=C).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 403 (4.67), 467 (4.56).

a4s10



Yellow solid, yield 79%.

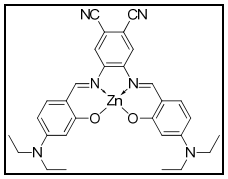
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.95 (2H, m, 2× CH=N), 8.30 (1H, s, ArH), 7.96 (1H, d, J = 8.5Hz, ArH), 7.70 (1H, d, J = 8.5Hz, ArH), 7.29 (2H, t, J = 8.6Hz, ArH), 6.20 (4H, d, J = 7.1Hz, ArH), 4.11 (4 H, t, J = 5.5Hz, 2× $PhOCH_2$), 3.59 (8H, m, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.6Hz, 2× $PhOCH_2CH_2$), 2.45 (4H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{33}H_{36}N_5O_6Zn$ ([M+H]$^+$) 662.19516, found 662.19514.

FT-IR (KBr pellete, cm^{-1}): 2955 (C-H), 2923 (C-H), 2861 (C-H), 2821 (C-H), 2226 (C≡N), 1612 (C=N), 1582 (Ar C=C), 1522 (Ar C=C), 1435 (Ar C=C), 1200 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 320 (4.51), 404 (4.58), 445 (4.40).

a5s1



Orange red solid, yield 81%.

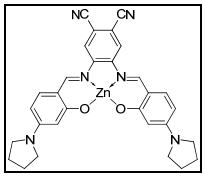
^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.78 (2H, s, 2× CH=N), 8.36 (2H, s, ArH), 7.14 (2H, d, J = 9.2 Hz, ArH), 6.20 (2H, dd, J_1 = 9.1Hz, J_2 = 2.2 Hz, ArH), 5.81 (2H, d, J = 2.1 Hz, ArH), 3.40 (8H, m, 4× CH_2), 1.15 (12H, t, J = 6.9 Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{30}H_{31}N_6O_2$ Zn ([M+H]$^+$) 571.17945, found 571.17919.

FT-IR (KBr pellete, cm^{-1}): 2972 (C-H), 2924 (C-H), 2222 (C≡N), 1607 (C=N), 1560 (Ar C=C), 1493 (Ar C=C), 1437 (Ar C=C), 1186 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 428 (4.68), 504 (4.51).

a5s3



Orange red solid, yield 91%.

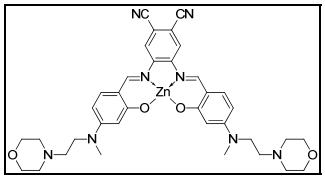
^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.79 (2H, s, 2× CH=N), 8.35 (2H, s, ArH), 7.15 (2H, d, J = 9.0 Hz, ArH), 6.10 (2H, dd, J_1 = 8.9Hz, J_2 = 2.1 Hz, ArH), 5.69 (2H, d, J = 2.0 Hz, ArH), 3.32 (8H, m, 4× NCH_2), 1.95 (8H, m, 4× NCH_2CH_2).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. For $C_{60}H_{53}N_{12}O_4Zn_2$ ($[2M+H]^+$) 1133.28902, found 1133.28503.

FT-IR (KBr pellete, cm^{-1}): 2959 (C-H), 2920 (C-H), 2847 (C-H), 2218 (C≡N), 1611 (C=N), 1572 (Ar C=C), 1516 (Ar C=C), 1483 (Ar C=C), 1441 (Ar C=C), 1205 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 427 (4.68), 509 (4.52).

a5s4



Orange solid, yield 70%.

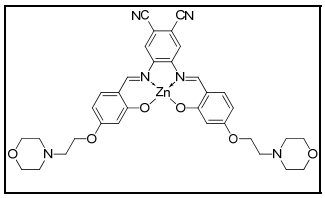
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.80 (2H, s, 2× CH=N), 8.37 (2H, s, ArH), 7.15 (2H, d, J = 9.2 Hz, ArH), 6.23 (2H, dd, J_1 = 9.1Hz, J_2 = 2.2 Hz, ArH), 5.82 (2H, d, J = 2.1 Hz, ArH), 3.58 (8H, m, 2× CH_2OCH_2), 3.52 (4H, t, J = 6.8 Hz, 2× $N(CH_3)CH_2$), 3.01 (6H, s, 2× CH_3), 2.48 (8H, s, 2× $CH_2CH_2OCH_2CH_2$), 2.44 (4H, m, 2× $N(CH_3)CH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{36}H_{41}N_8O_4Zn$ ($[M+H]^+$) 713.25367, found 713.25365.

FT-IR (KBr pellete, cm^{-1}): 2949 (C-H), 2918 (C-H), 2858 (C-H), 2814 (C-H), 2224 (C≡N), 1603 (C=N), 1562 (Ar C=C), 1514 (Ar C=C), 1497 (Ar C=C), 1443 (Ar C=C), 1219 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 428 (4.67), 508 (4.52).

a5s10



Orange solid, yield 48%.

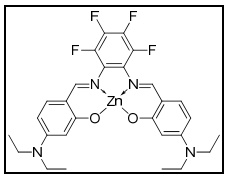
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.01 (2H, s, 2× CH=N), 8.53 (2H, s, ArH), 7.28 (2H, d, J = 8.5Hz, ArH), 6.23 (4H, m, ArH), 4.12 (4H, t, J = 5.2Hz, 2× PhO-CH_2), 3.59 (8H, d, J = 4.0Hz, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.2Hz, 2× $PhOCH_2CH_2$), 2.47 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{34}H_{35}N_6O_6Zn$ ($[M+H]^+$) 687.19041, found 687.18950.

FT-IR (KBr pellete, cm^{-1}): 2931 (C-H), 2856 (C-H), 2830 (C-H), 2228 (C≡N), 1612 (C=N), 1574 (Ar C=C), 1514 (Ar C=C), 1439 (Ar C=C), 1215 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 333 (4.52), 422 (4.62), 470 (4.42).

a6s1



Yellow solid, yield 33%.

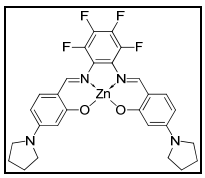
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.58 (2H, s, CH=N), 7.00 (2H, d, J = 9.1 Hz, ArH), 6.09 (2H, dd, J_1 = 9.0Hz, J_2 = 2.4 Hz, ArH), 5.79 (2H, d, J = 2.1 Hz, ArH), 3.37 (8H, m, 4× CH_2), 1.13 (12H, t, J = 7.0 Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{56}H_{57}N_8O_4F_8Zn_2$ ([2M+H]$^+$) 1185.29525 found 1185.29194.

FT-IR (KBr pellete, cm^{-1}): 2974 (C-H), 2928 (C-H), 1614 (C=N), 1566 (Ar C=C), 1487 (Ar C=C), 1429 (Ar C=C), 1186 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 389 (4.85), 452 (4.51).

a6s3



Orange solid, yield 36%.

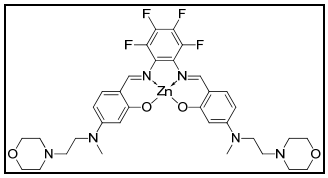
^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 8.91 (2H, s, 2× CH=N), 7.25 (2H, d, J = 8.9 Hz, ArH), 6.31 (2H, d, J = 2.2 Hz, ArH), 6.15 (2H, dd, J_1 = 8.8Hz, J_2 = 2.3 Hz, ArH), 3.14 (8H, t, J = 6.5 Hz, 4× NCH_2), 1.59 (8H, m, 4× $NCH_2C\mathit{H}_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{28}H_{25}F_4N_4O_2Zn$ ([M+H]$^+$) 589.11996, found 589.12052.

FT-IR (KBr pellete, cm^{-1}): 2961 (C-H), 2858 (C-H), 1614 (C=N), 1560 (Ar C=C), 1516 (Ar C=C), 1483 (Ar C=C), 1449 (Ar C=C), 1225 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 390 (4.80), 451 (4.47).

a6s4



Orange solid, yield 30%.

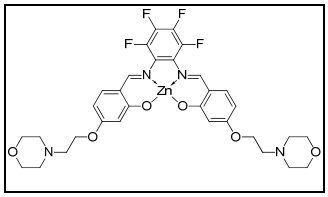
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.60 (2H, s, 2× CH=N), 7.02 (2H, d, J = 9.1 Hz, ArH), 6.12 (2H, dd, J_1 = 9.0Hz, J_2 = 2.3Hz, ArH), 5.80 (2H, d, J = 2.0 Hz, ArH), 3.57 (8H, m, 2× CH_2OCH_2), 3.49 (4H, t, J = 7.0 Hz, 2× $N(CH_3)CH_2$), 2.98 (6H, s, 2× CH_3), 2.46 (4H, m, 2× $CH_2CH_2OCH_2CH_2$), 2.43 (8H, m, 2× $N(CH_3)CH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{68}H_{77}N_{12}O_8F_8Zn_2$ ([2M+H]$^+$) 1469.44370, found 1469.44221.

FT-IR (KBr pellete, cm^{-1}): 2957 (C-H), 2918 (C-H), 2854 (C-H), 2820 (C-H), 1616 (C=N), 1568 (Ar C=C), 1514 (Ar C=C), 1487 (Ar C=C), 1443 (Ar C=C), 1205 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 388 (4.82), 450 (4.49).

a6s10



Yellow solid, yield 79%.

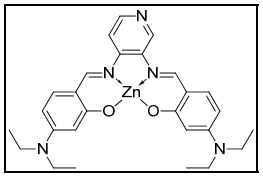
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.77 (2H, s, 2× CH=N), 7.18 (2H, d, J = 8.8Hz, ArH), 6.16 (4H, m, ArH), 4.10 (4H, t, J = 5.7Hz, 2× PhO-CH_2), 3.58 (8H, m, 4× CH_2OCH_2), 2.69 (4H, t, J = 5.7Hz, 2× $PhOCH_2CH_2$), 2.47 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{32}H_{33}F_4N_4O_6Zn$ ([M+H]$^+$) 709.16222, found 709.16168.

FT-IR (KBr pellete, cm^{-1}): 2959 (C-H), 2860 (C-H), 2820 (C-H), 1614 (C=N), 1585 (Ar C=C), 1526 (Ar C=C), 1445 (Ar C=C), 1217 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 312 (4.51), 386 (4.47), 426 (4.26).

a7s1



Orange solid, yield 54%.

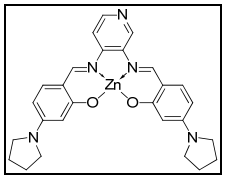
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.88 (1H, s, pyH), 8.80 (1H, s, CH=N), 8.73 (1H, s, CH=N), 8.24 (1H,d, J = 5.4 Hz, pyH), 7.62 (1H, d, J = 5.6 Hz, pyH), 7.14 (2H, t, J = 9.0 Hz, ArH), 6.14 (1H, dd, J_1 = 9.1Hz, J_2 = 2.0Hz, ArH), 6.09 (1H, dd, J_1 = 8.6Hz, J_2 = 1.9Hz, ArH), 5.83 (1H, d, J = 2.1 Hz, ArH), 5.82 (1H, d, J = 2.0 Hz, ArH), 3.38 (8H, m, 4× CH_2), 1.17 (12H, t, J = 6.7Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{32}N_5O_2Zn$ ([M+H]$^+$) 522.18420, found 522.18299.

FT-IR (KBr pellete, cm^{-1}): 2972 (C-H), 2926 (C-H), 2904 (C-H), 1605 (C=N), 1562 (Ar C=C), 1487 (Ar C=C), 1437 (Ar C=C), 1200 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 395 (4.67), 458 (4.48).

a7s3



Brown solid, yield 59%.

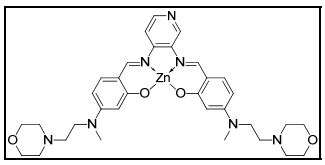
^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 9.14 (1H, s, pyH), 9.03 (1H, s, CH=N), 8.90 (1H, s, CH=N), 8.48 (1H, d, J = 5.4 Hz, pyH), 7.50 (1H, d, J = 5.4 Hz, pyH), 7.36 (1H, s, ArH), 7.34 (1H, s, ArH), 6.41 (1H, s, ArH), 6.36 (1H, s, ArH), 6.15 (1H, s, ArH), 6.13 (1H, s, ArH), 3.17 (8H, m, 4× NCH_2), 1.60 (8H, m, 4× NCH_2CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{28}N_5O_2Zn$ ([M+H]$^+$) 518.15290, found 518.15307.

FT-IR (KBr pellete, cm^{-1}): 2965 (C-H), 2927 (C-H), 2858 (C-H), 1616 (C=N), 1597 (Ar C=C), 1560 (Ar C=C), 1518 (Ar C=C), 1481 (Ar C=C), 1443 (Ar C=C), 1207 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 396 (4.64), 456 (4.46).

a7s4



Orange solid, yield 50%.

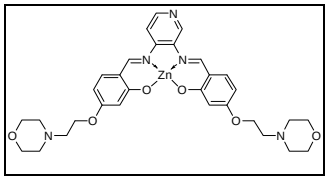
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.87 (1H, s, pyH), 8.80 (1H, s, CH=N), 8.76 (1H, s, CH=N), 8.24 (1H, d, J = 5.4 Hz, pyH), 7.63 (1H, d, J = 5.6 Hz, pyH), 7.16 (1H, d, J = 9.3Hz, ArH), 7.13 (1H, d, J = 9.4Hz, ArH), 6.18 (1H, dd, J_1 = 9.0Hz, J_2 = 1.6Hz, ArH), 6.13 (1H, dd, J_1 = 8.9Hz, J_2 = 1.6Hz, ArH), 5.84 (1H, d, J = 1.4 Hz, ArH), 5.83 (1H, d, J = 1.4 Hz, ArH), 3.58 (8H, s, 2× CH_2OCH_2), 3.50 (4H, d, J = 6.4 Hz, 2× $N(CH_3)CH_2$), 3.00 (3H, s, CH_3), 2.98 (3H, s, CH_3), 2.48 (4H, s, 2× $N(CH_3)CH_2CH_2$), 2.44 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{33}H_{42}N_7O_4Zn$ ([M+H]$^+$) 664.25843, found 664.25834.

FT-IR (KBr pellete, cm^{-1}): 2955 (C-H), 2858 (C-H), 2822 (C-H), 2198 (C-H), 1612 (CH=N), 1593 (Ar C=C), 1562 (Ar C=C), 1514 (Ar C=C), 1493 (Ar C=C), 1441 (Ar C=C), 1202 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 396 (4.65), 457 (4.46).

a7s10



Yellow solid, yield 85%.

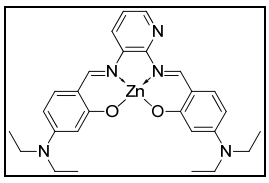
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.02 (1H, s, pyH), 9.02 (1H, s, CH=N), 8.98 (1H, s, CH=N), 8.40 (1H, d, J = 5.5Hz, pyH), 7.75 (1H, d, J = 5.6Hz, pyH), 7.30 (2H, dd, J_1 = 12.5Hz, J_2 =5.6 Hz, ArH), 6.19 (4H, m, ArH), 4.11 (4H, m, 2× $PhOCH_2$), 3.59 (8H, m, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.6Hz, 2× $PhOCH_2CH_2$), 2.47 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{31}H_{36}N_5O_6Zn$ ([M+H]$^+$) 638.19516, found 638.19529.

FT-IR (KBr pellete, cm^{-1}): 2957 (C-H), 2918 (C-H), 2858 (C-H), 2816 (C-H), 1609 (C=N), 1574 (Ar C=C), 1520 (Ar C=C), 1433 (Ar C=C), 1205 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 316 (4.49), 395 (4.53) , 436 (4.32).

a8s1



Yellow solid, yield 54%.

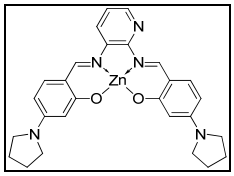
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.10 (1H, s, CH=N), 8.71 (1H, s, CH=N), 8.13 (1H, d, J = 4.6 Hz, pyH), 8.06 (1H, d, J = 8.1 Hz, pyH), 7.16 (1H, d, J = 8.5Hz, pyH), 7.14 (2H, m, ArH), 6.11 (2H t, J = 7.6 Hz, ArH), 5.85 (2H, s, ArH), 3.37 (8H, m, 4× CH_2), 1.15 (12H, t, J = 6.8 Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{32}N_5O_2Zn$ ([M+H]$^+$) 522.18420, found 522.18415.

FT-IR (KBr pellete, cm^{-1}): 2970 (C-H), 2924 (C-H), 1593 (Ar C=C), 1553 (Ar C=C), 1504 (Ar C=C), 1431 (Ar C=C), 1196 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 382 (4.46), 432 (4.60).

a8s3



Yellow solid, yield 60%.

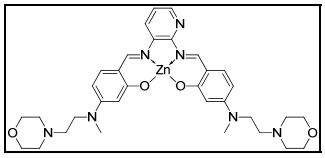
^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 9.78 (1H, s, CH=N), 8.90 (1H, s, CH=N), 8.31 (1H, dd, J_1 = 4.6 Hz, J_2 = 1.5 Hz, pyH), 7.91 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, pyH), 7.38 (2H, t, J = 8.9 Hz, ArH), 7.06 (1H, dd, J_1 = 8.0 Hz, J_2 = 4.7Hz, pyH), 6.46 (1H, d, J = 2.2Hz, ArH), 6.40 (1H, d, J = 2.2Hz, ArH), 6.17 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz, ArH), 6.13 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz, ArH), 3.19 (8H, m, 4× NCH_2), 1.62 (8H, m, 4× NCH_2CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{28}N_5O_2Zn$ ([M+H]$^+$) 518.15290, found 518.15376.

FT-IR (KBr pellete, cm^{-1}): 2965 (C-H), 2858 (C-H), 1616 (C=N), 1597 (Ar C=C), 1560 (Ar C=C), 1517 (Ar C=C), 1481 (Ar C=C), 1444 (Ar C=C), 1207 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 385 (4.46), 433 (4.61).

a8s4



Yellow solid, yield 40%.

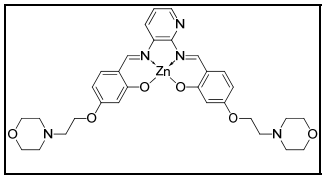
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.12 (1H, s, CH=N), 8.73 (1H, s, CH=N), 8.15 (1H, dd, J_1 = 4.6, J_2 = 1.4 Hz, pyH), 8.08 (1H, m, pyH), 7.19 (2H, m, ArH), 7.14 (1H, d, J = 9.0 Hz, pyH), 6.17 (2H, m, ArH), 5.89 (2H, m, ArH), 3.59 (8H, m, 2× CH_2OCH_2), 3.50 (4H, m, 2× $N(CH_3)CH_2$), 3.00 (3H, s, CH_3), 2.99 (3H, s, CH_3), 2.46 (12H, m, 2× $CH_2CH_2OCH_2CH_2$ and 2× $N(CH_3)CH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{33}H_{42}N_7O_4Zn$ ([M+H]$^+$) 664.25843, found 664.25847.

FT-IR (KBr pellete, cm^{-1}): 2974 (C-H), 2870 (C-H), 2765 (C-H), 1614 (C=N), 1591 (Ar C=C), 1557 (Ar C=C), 1516 (Ar C=C), 1437 (Ar C=C), 1202 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 385 (4.46), 429 (4.58).

a8s10



Yellow solid, yield 67%.

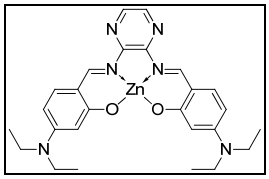
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.31 (1H, s, CH=N), 8.95 (1H, s, CH=N), 8.29 (1H, dd, J_1 = 4.6Hz, J_2 = 1.4 Hz, pyH), 8.23 (1H, m, pyH), 7.34 (2H, m, ArH), 7.28 (1H, d, J = 8.8Hz, pyH), 6.20 (4H, m, ArH), 4.11 (4H, m, 2× $PhOCH_2$), 3.59 (8H, m, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.6Hz, 2× $PhOCH_2CH_2$), 2.47 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{31}H_{36}N_5O_6Zn$ ([M+H]$^+$) 638.19516, found 638.19463.

FT-IR (KBr pellete, cm^{-1}): 2961 (C-H), 2924 (C-H), 2860 (C-H), 2810 (C-H), 1607 (C=N), 1566 (Ar C=C), 1524 (Ar C=C), 1439 (Ar C=C), 1209 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 317 (4.38), 407 (4.52), 449 (4.33).

a9s1



Orange solid, yield 61%.

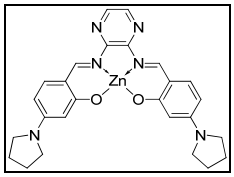
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.02 (2H, s, 2× CH=N), 8.07 (2H, s, pzH), 7.18 (2H, d, J = 9.1 Hz, ArH), 6.16 (2H, d, J = 9.2 Hz, ArH), 5.85 (2H, s, ArH), 3.43 (8H, m, 4× CH_2), 1.14 (12H, t, J = 6.8Hz, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{26}H_{31}N_6O_2Zn$ ([M+H]$^+$) 523.17945, found 523.17841.

FT-IR (KBr pellete, cm^{-1}): 2970 (C-H), 2926 (C-H), 1605 (C=N), 1578 (Ar C=C), 1491 (Ar C=C), 1427 (Ar C=C), 1198 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 383 (4.39), 466 (4.75), 483 (4.77).

a9s3



Orange solid, yield 37%.

^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 9.03 (2H, s, 2× CH=N), 8.07 (2H, s, pzH), 7.19 (2H, d, J = 9.0 Hz, ArH), 6.08 (2H, dd, J_1 = 2.1 Hz, J_2 = 8.8 Hz, ArH), 5.73 (2H, d, J = 2.1 Hz, ArH), 3.34 (8H, m, 4× NCH_2), 1.97 (8H, m, 4× NCH_2CH_2).

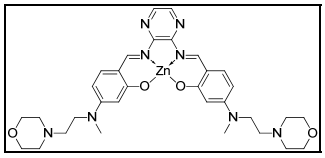
HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{26}H_{27}N_6O_2Zn$ ([M+H]$^+$) 519.14815, found 519.14849.

FT-IR (KBr pellete, cm^{-1}): 2966 (C-H), 2855 (C-H), 1616 (C=N), 1576 (Ar C=C), 1506 (Ar C=C),

1477 (Ar C=C), 1456 (Ar C=C), 1434 (Ar C=C), 1200 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 384 (4.40), 469 (4.78), 483 (4.80).

a9s4



Orange solid, yield 24%.

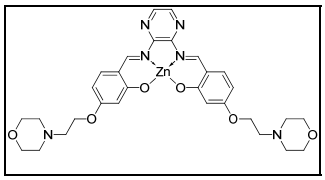
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.05 (2H, s, 2× CH=N), 8.09 (2H, s, pzH), 7.19 (2H, d, J = 9.1 Hz, ArH), 6.20 (2H, dd, J_1 = 8.9Hz, J_2 = 1.6Hz, ArH), 5.85 (2H, s, ArH), 3.58 (8H, m, ArH), 3.52 (4H, t, J = 6.7 Hz, ArH), 3.02 (6H, s, 2× CH_3), 2.46 (12H, m, 2× N(CH_3)$CH_2C\mathit{H}_2$ and 2× $C\mathit{H}_2CH_2OCH_2C\mathit{H}_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{32}H_{41}N_8O_4Zn$ ([M+H]$^+$) 665.25637, found 665.25402.

FT-IR (KBr pellete, cm^{-1}): 2974 (C-H), 2870 (C-H), 2765 (C-H), 1591 (Ar C=C), 1557 (Ar C=C), 1516 (Ar C=C), 1437 (Ar C=C), 1202 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 384 (4.46), 467 (4.82), 482 (4.83).

a9s10



Yellow solid, yield 70%.

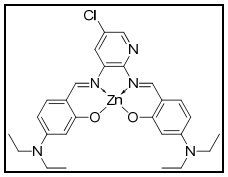
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.26 (2H, s, 2× CH=N), 8.30 (2H, s, pzH), 7.37 (2H, d, J = 8.9Hz, ArH), 6.22 (4H, m, ArH), 4.13 (4H, t, J = 5.7Hz, 2× $PhOCH_2$), 3.59 (8H, m, 4× CH_2OCH_2), 2.70 (4H, dd, J_1 =11.2Hz, J_2 = 5.5 Hz, 2× $PhOCH_2C\mathit{H}_2$), 2.52 (8H, m, 2× $C\mathit{H}_2CH_2OCH_2C\mathit{H}_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{30}H_{35}N_6O_6Zn$ ([M+H]$^+$) 639.19041, found 639.19107.

FT-IR (KBr pellete, cm^{-1}): 2961 (C-H), 2930(C-H), 2860(C-H), 2808(C-H), 1597 (Ar C=C), 1503 (Ar C=C), 1431 (Ar C=C), 1215 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 333 (4.38), 443 (4.57), 457 (4.55).

a10s1



Yellow solid, yield 53%.

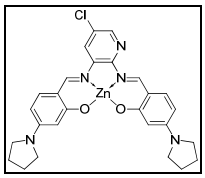
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.90 (1H, s, CH=N), 8.70 (1H, s, CH=N), 8.10 (1H, d, J = 8.4 Hz, pyH), 7.20 (2H, m, ArH and pyH), 7.11 (1H, d, J = 9.0 Hz, ArH), 6.15 (1H, dd, J_1 = 9.1Hz, J_2 = 2.0 Hz, ArH), 6.11 (1H, dd, J_1 = 9.0Hz, J_2 = 2.0 Hz, ArH), 5.84 (2H, s, ArH), 3.38 (8H, m, 4× CH_2), 1.15 (12H, t, 4× CH_3).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{31}ClN_5O_2Zn$ ([M+H]$^+$) 556.14523, found 556.14502.

FT-IR (KBr pellete, cm^{-1}): 2930 (C-H), 2903 (C-H), 2794 (C-H), 1597 (Ar C=C), 1553 (Ar C=C), 1504 (Ar C=C), 1433 (Ar C=C), 1209 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 388 (4.50), 457 (4.68).

a10s3



Orange solid, yield 60%.

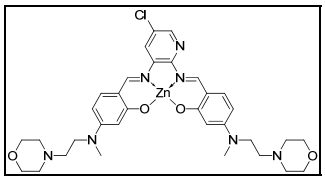
^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 8.91 (1H, s, CH=N), 8.71 (1H, s, CH=N), 8.10 (1H, d, J = 8.6 Hz, pyH), 7.20 (2H, m, ArH and pyH), 7.12 (1H, d, J = 8.9 Hz, ArH), 6.07 (1H, dd, J_1 = 8.9Hz, J_2 = 2.2 Hz, ArH), 6.02 (1H, dd, J_1 = 8.8Hz, J_2 = 2.2 Hz, ArH), 5.72 (1H, d, J = 2.2 Hz, ArH), 5.71 (1H, d, J = 2.1 Hz, ArH), 3.33 (8H, m, 4× NCH_2), 1.97 (8H, t, J = 5.8 Hz, 4× $NCH_2C\mathit{H}_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{54}H_{53}Cl_2N_{10}O_4Zn_2$ ([2M+H]$^+$) 1103.22058, found 1103.22240.

FT-IR (KBr pellete, cm^{-1}): 2966 (C-H), 2930 (C-H), 2858 (C-H), 1585 (Ar C=C), 1549 (Ar C=C), 1514 (Ar C=C), 1479 (Ar C=C), 1437 (Ar C=C).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 389 (4.52), 451 (4.70).

a10s4



Orange solid, yield 17%.

^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 9.52 (1H, s, CH=N), 8.84 (1H, s, CH=N), 7.87 (1H, d, J = 8.2 Hz, pyH), 7.36 (1H, d, J = 8.9 Hz, ArH), 7.31 (1H, d, J = 8.9 Hz, ArH), 7.09 (1H, d, J = 8.3 Hz, pyH), 6.57 (1H, d, J = 1.5 Hz, ArH), 6.49 (1H, d, J = 1.4 Hz, ArH), 6.35 (2H, m, ArH), 3.65(8H, m,

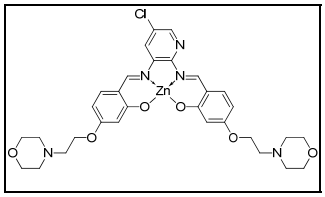
2× CH_2OCH_2), 3.46 (4H, m, 2× $N(CH_3)CH_2$), 2.96 (3H, s, CH_3), 2.93 (3H, s, CH_3), 2.43 (4H, m, 2× $N(CH_3)CH_2CH_2$), 2.32 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{33}H_{41}ClN_7O_4Zn$ ($[M+H]^+$) 698.21945, found 698.22025.

FT-IR (KBr pellete, cm^{-1}): 2953 (C-H), 2922 (C-H), 2857 (C-H), 1589 (Ar C=C), 1551 (Ar C=C), 1514 (Ar C=C), 1435 (Ar C=C), 1204 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 390 (4.50), 445 (4.66).

a10s10



Yellow solid, yield 94%.

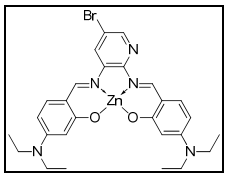
^1H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.13 (1H, s, CH=N), 8.94 (1H, s, CH=N), 8.28 (1H, d, J = 8.7 Hz, pyH), 7.39 (2 H, t, J = 8.5 Hz, ArH and pyH), 7.27 (1H, d, J = 8.7 Hz, ArH), 6.20 (4H, m, ArH), 4.11 (4H, m, 2× $PhOCH_2$), 3.59 (8H, m, 4× CH_2OCH_2), 2.70 (4H, m, 2× $PhOCH_2CH_2$), 2.48 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{31}H_{35}ClN_5O_6Zn$ ($[M+H]^+$) 672.15618, found 672.15638.

FT-IR(KBr, cm^{-1}): 2955, 2928, 2862, 1605, 1558, 1518, 1441, 1200.

UV-vis (DMSO) λ_{max}, nm (log ε): 321 (4.43), 416 (4.58) , 451 (4.45).

a11s1



Dark yellow solid, yield 68%.

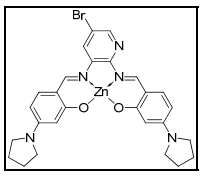
^1H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.04 (1H, s, CH=N), 8.74 (1H, s, CH=N), 8.30 (1H, d, J = 2.1 Hz, pyH), 8.16 (1H, d, J = 2.1 Hz, pyH), 7.14 (2H, m, ArH), 6.15 (1H, d, J = 2.4 Hz, ArH), 6.12 (1H, d, J = 2.4 Hz, ArH), 5.83 (2H, s, ArH), 3.39 (8H, m, 2× CH_2), 1.15 (12H, t, J = 7.0 Hz, 2× CH_3)..

HR MS (ESI^+, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{31}BrN_5O_2Zn$ ($[M+H]^+$) 600.09471, found 600.09507.

FT-IR(KBr, cm^{-1}): 2970 (C-H), 2924 (C-H), 1593 (Ar C=C), 1545 (Ar C=C), 1503 (Ar C=C), 1435 (Ar C=C), 1200 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 387 (4.42), 456 (4.64).

a11s3



Yellow solid, yield 63%.

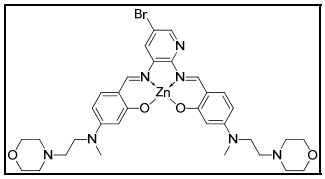
^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 9.05 (1H, s, CH=N), 8.74 (1H, s, CH=N), 8.29 (1H, d, J = 1.9 Hz, pyH), 8.17 (1H, d, J = 2.0 Hz, pyH), 7.15 (2H, t, J = 8.6 Hz, ArH), 6.05 (2H, d, J = 8.7Hz, ArH), 5.71 (2H, s, ArH), 3.26 (8H, m, 4× NCH_2), 1.98 (8H, m, 4× NCH_2CH_2).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{27}H_{27}BrN_5O_2Zn$ ($[M+H]^+$) 596.06341, found 596.06307.

FT-IR (KBr pellete, cm^{-1}): 2945 (C-H), 2914 (C-H), 2857 (C-H), 2814 (C-H), 1585 (Ar C=C), 1545 (Ar C=C), 1499 (Ar C=C), 1491 (Ar C=C), 1443 (Ar C=C), 1433 (Ar C=C), 1198 (C-O).

UV-*vis* (DMSO) λ_{max}, nm: 385 (4.44), 457 (4.67).

a11s4



Dark yellow solid, yield 63%.

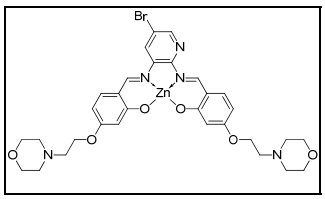
^{1}H NMR (400 MHz, d^5-Pyr): δ (ppm) 9.61 (1H, s, CH=N), 8.86 (1H, s, CH=N), 8.35 (1H, d, J = 2.0 Hz, pyH), 8.16 (1H, d, J = 2.0 Hz, pyH), 7.41 (1H, d, J = 9.0 Hz, ArH), 7.36 (1H, d, J = 9.1 Hz, ArH), 6.56 (1H, d, J = 2.2 Hz, ArH), 6.52 (1H, d, J = 2.2 Hz, ArH), 6.37 (1H, dd, J_1 = 9.0, J_2 = 2.3 Hz, ArH), 6.33 (1H, dd, J_1 = 9.0, J_2 = 2.3 Hz, ArH), 3.64 (8H, m, 2× CH_2OCH_2), 3.47 (4H, m, 2× $N(CH_3)CH_2$), 2.96 (3H, s, CH_3), 2.94 (3H, s, CH_3), 2.43 (4H, m, 2× $N(CH_3)CH_2CH_2$), 2.33 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{33}H_{41}BrN_7O_4Zn$ ($[M+H]^+$) 742.16894, found 742.16900.

FT-IR (KBr pellete, cm^{-1}): 2958 (C-H), 2929 (C-H), 2855 (C-H), 1587 (Ar C=C), 1548 (Ar C=C), 1512 (Ar C=C), 1200 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 391 (4.43), 450 (4.65).

a11s10



Yellow solid, yield 80%.

^{1}H NMR (400 MHz, d^6-DMSO): δ (ppm) 9.26 (1H, s, CH=N), 8.99 (1H, s, CH=N), 8.51 (1H, d, J = 2.1Hz, pyH), 8.35 (1 H, d, J = 2.1Hz, pyH), 7.34 (1H, d, J = 8.9Hz, ArH), 7.28 (1H, d, J = 9.1Hz, ArH), 6.19 (4H, m, ArH), 4.11 (4H, t, J = 5.4Hz, 2× $PhOCH_2$), 3.59 (8 H, m, 4× CH_2OCH_2), 2.70 (4H, t, J = 5.7Hz, 2× $PhOCH_2CH_2$), 2.45 (8H, m, 2× $CH_2CH_2OCH_2CH_2$).

HR MS (ESI$^+$, DMSO, FT-ICR): *m/z* calcd. for $C_{31}H_{35}BrN_5O_6Zn$ ($[M+H]^+$) 716.10567, found 716.10520.

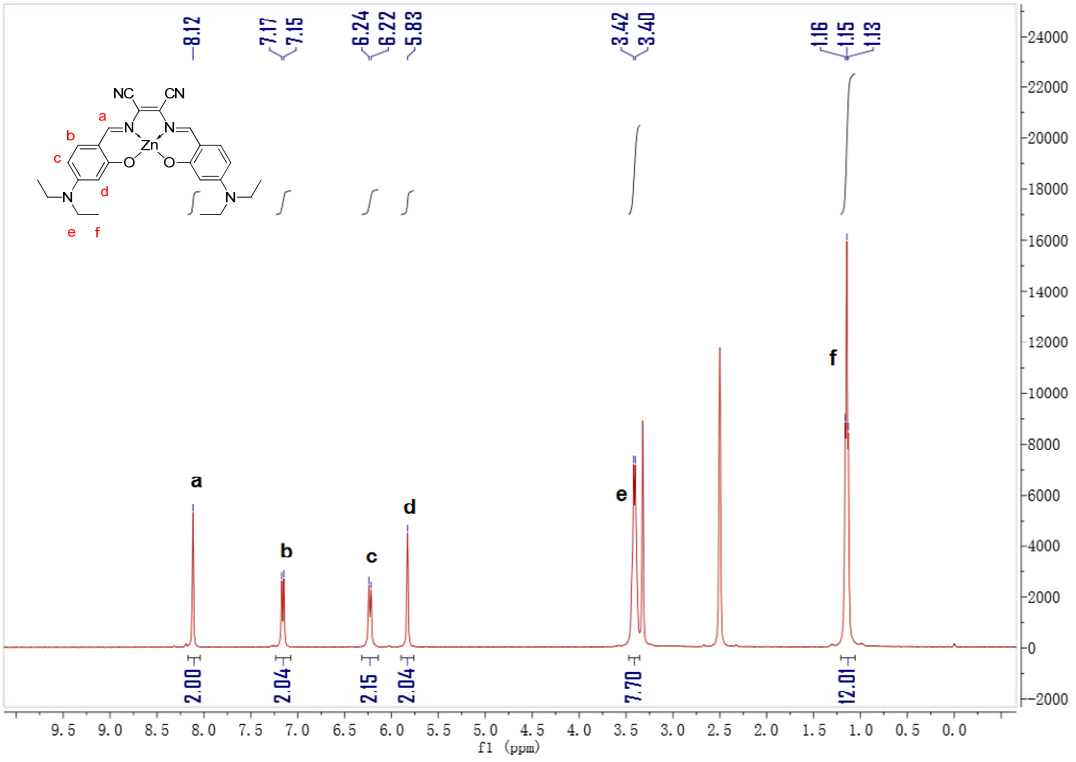
FT-IR (KBr pellete, cm^{-1}): 2953 (C-H), 2928 (C-H), 2862 (C-H), 2826 (C-H), 1605 (C=N), 1553 (Ar C=C), 1518 (Ar C=C), 1439 (Ar C=C), 1209 (C-O).

UV-*vis* (DMSO) λ_{max}, nm (log ε): 323 (4.45), 421 (4.58), 454 (4.46).

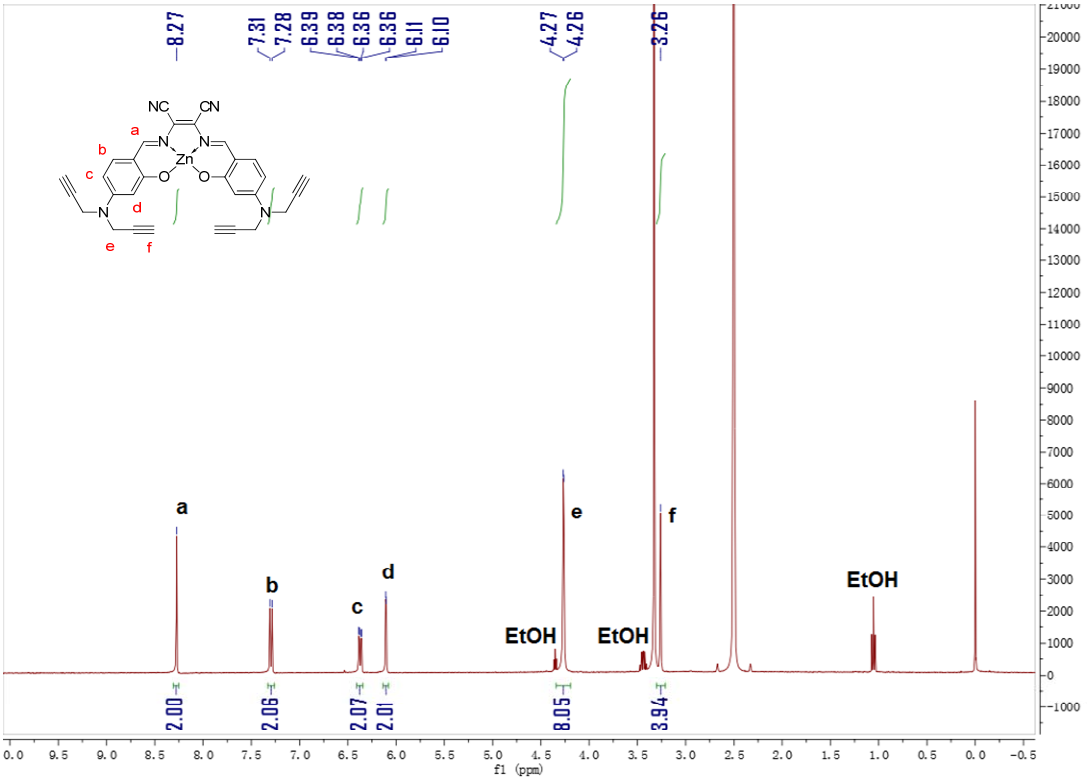
2.4.3 ^{1}H NMR Spectra of ZnSalen/Salophens

Unless specially mentioned, the ^{1}H NMR spectra were recorded in d^6-DMSO and the peaks for residue solvent (DMSO, δ = 3.33 ppm), water (δ = 2.50 ppm) and TMS (δ = 0 ppm) were omitted for clarity.

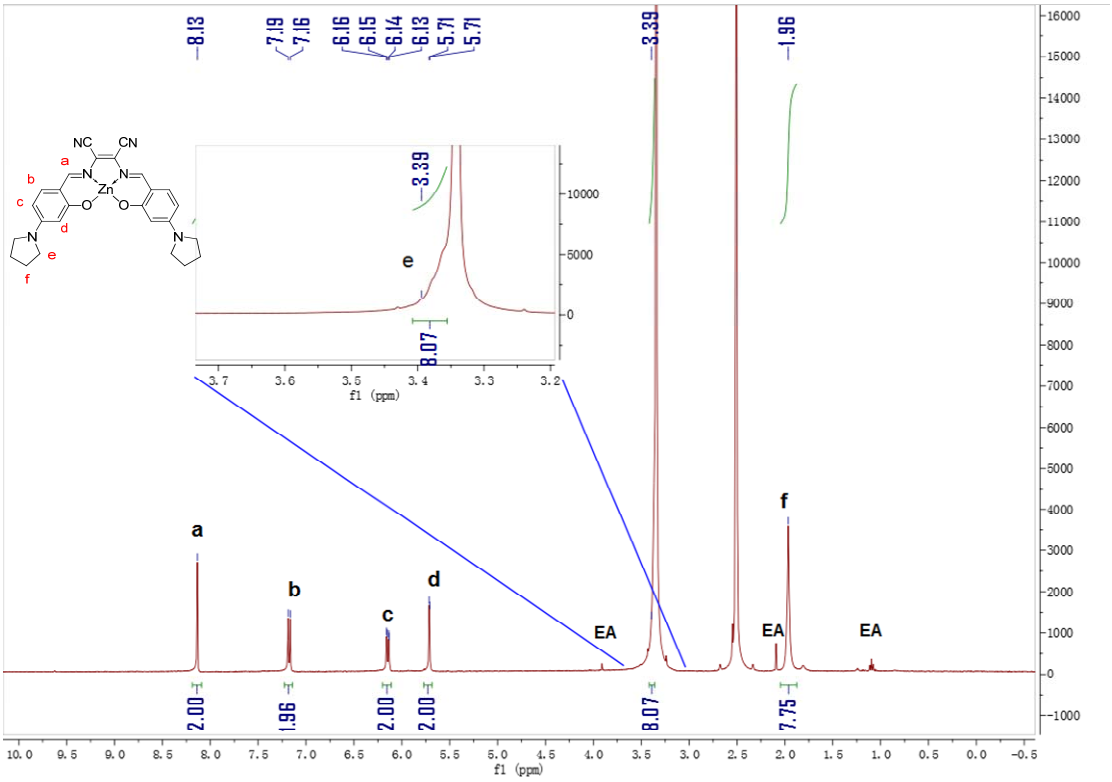
a1s1



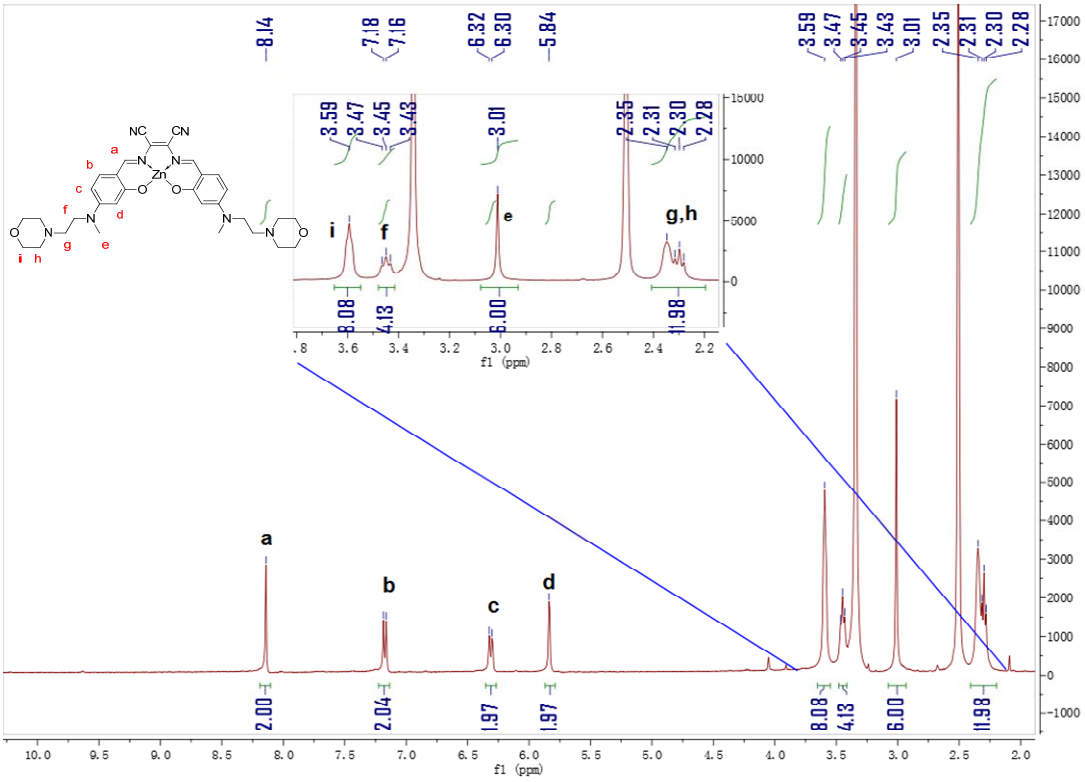
a1s2


8.27
7.31
7.28
6.39
6.38
6.36
6.36
6.11
6.10
4.27
4.26
3.26
NC
CN
Zn
a
b
c
d
e
f
EtOH
EtOH
EtOH
2.00
2.06
2.07
2.01
8.05
3.94
f1 (ppm)

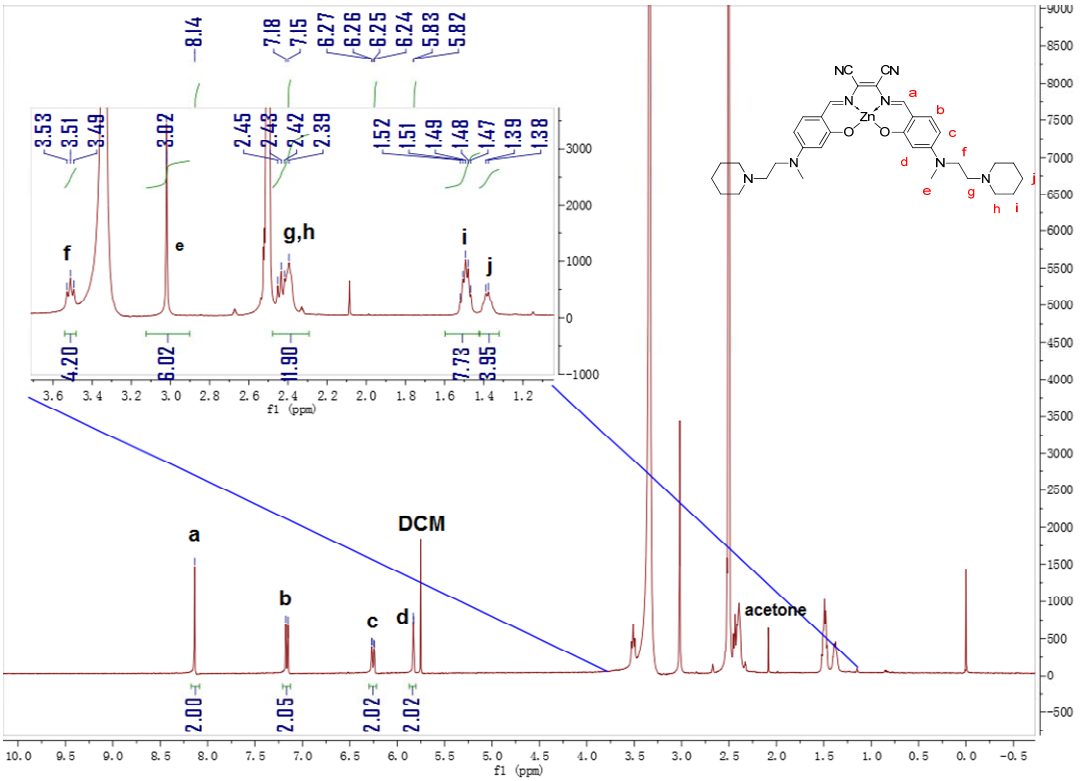
a1s3


8.13
7.19
7.16
6.16
6.15
6.14
6.13
5.71
5.71
3.39
1.96
NC
CN
Zn
a
b
c
d
e
f
EA
EA
EA
2.00
1.96
2.00
2.00
8.07
7.75
8.07
f1 (ppm)

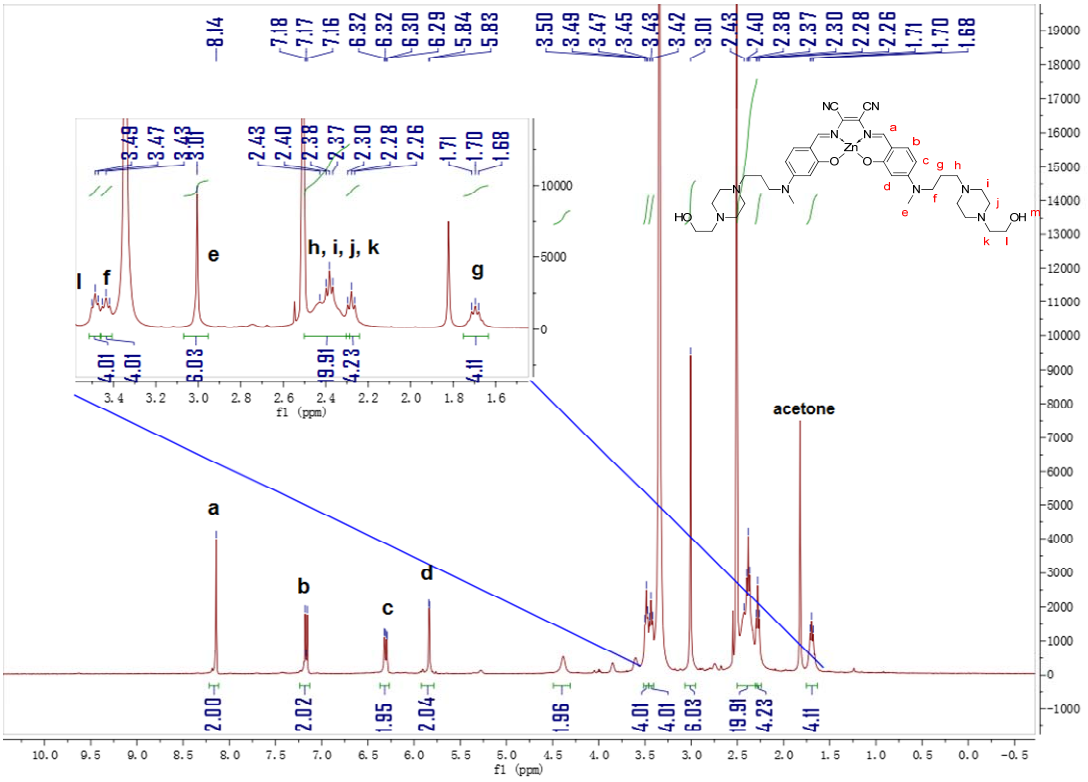
a1s4


8.14
7.18
7.16
6.32
6.30
5.84
3.59
3.47
3.45
3.43
3.01
2.35
2.31
2.30
2.28
a
b
c
d
e
f
g,h
i
2.00
2.04
1.97
1.97
8.08
4.13
6.00
11.98
f1 (ppm)

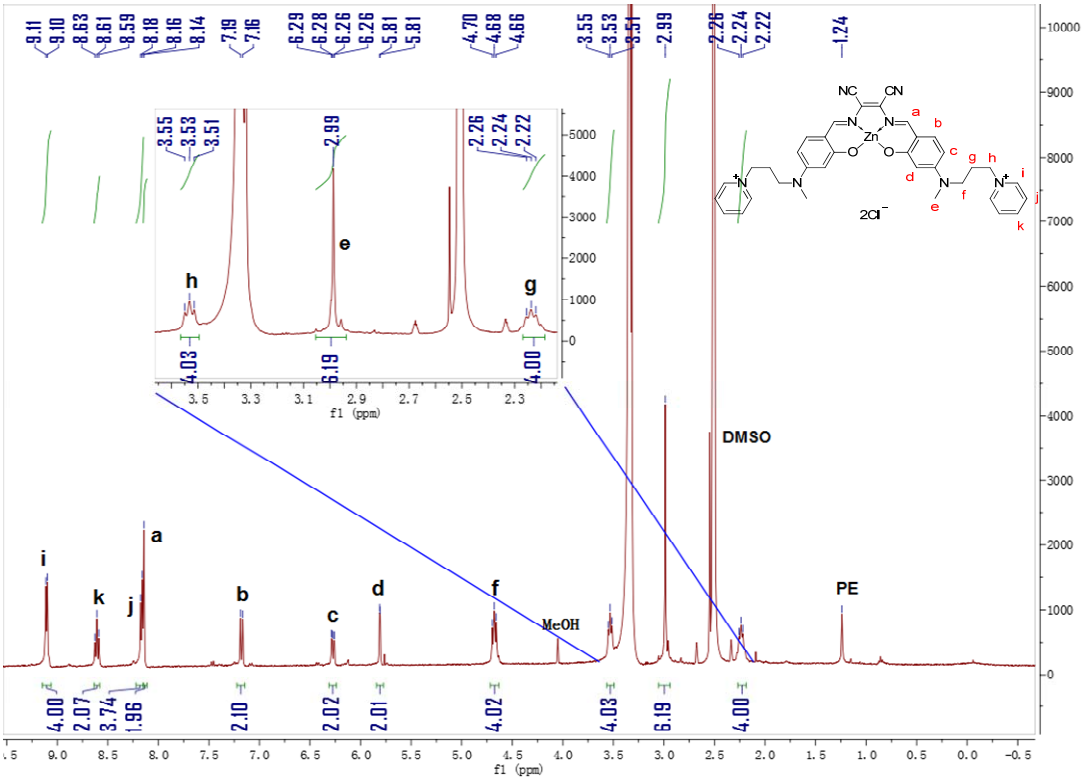
a1s5


8.14
7.18
7.15
6.27
6.26
6.25
6.24
5.83
5.82
3.53
3.51
3.49
3.02
2.45
2.43
2.42
2.39
1.52
1.51
1.49
1.48
1.47
1.39
1.38
a
b
c
d
e
f
g,h
i
j
DCM
acetone
2.00
2.05
2.02
2.02
4.20
6.02
11.90
7.73
3.95
f1 (ppm)

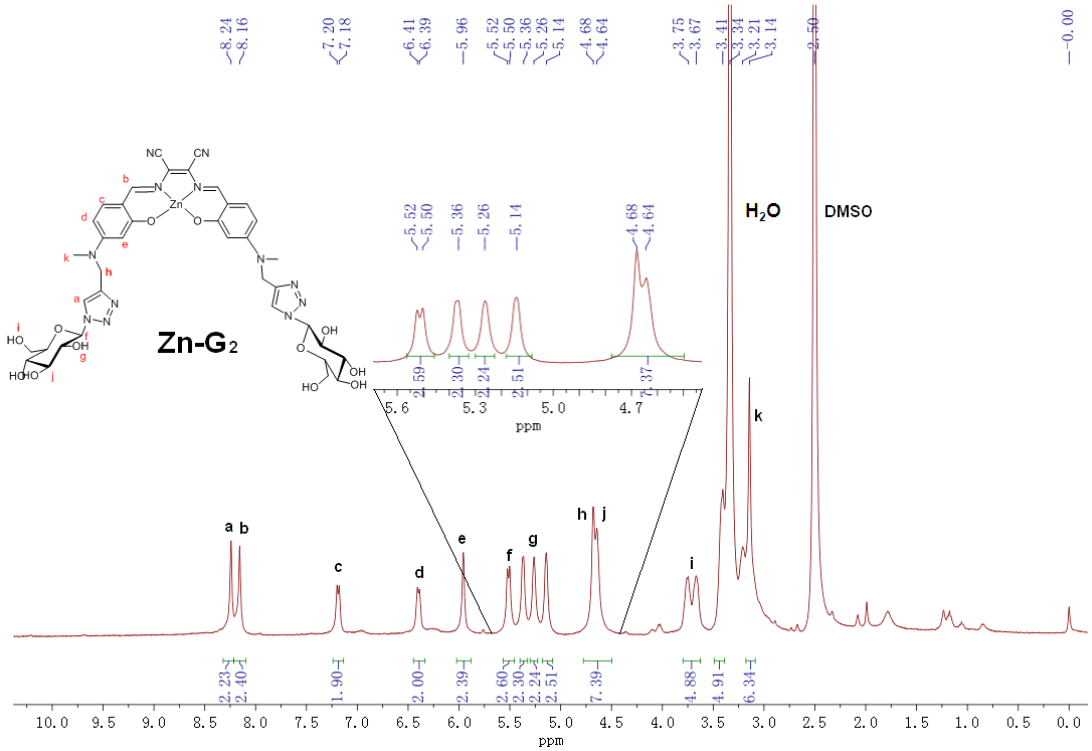
a1s6


acetone
a
b
c
d
e
f
g
h, i, j, k
l
f1 (ppm)

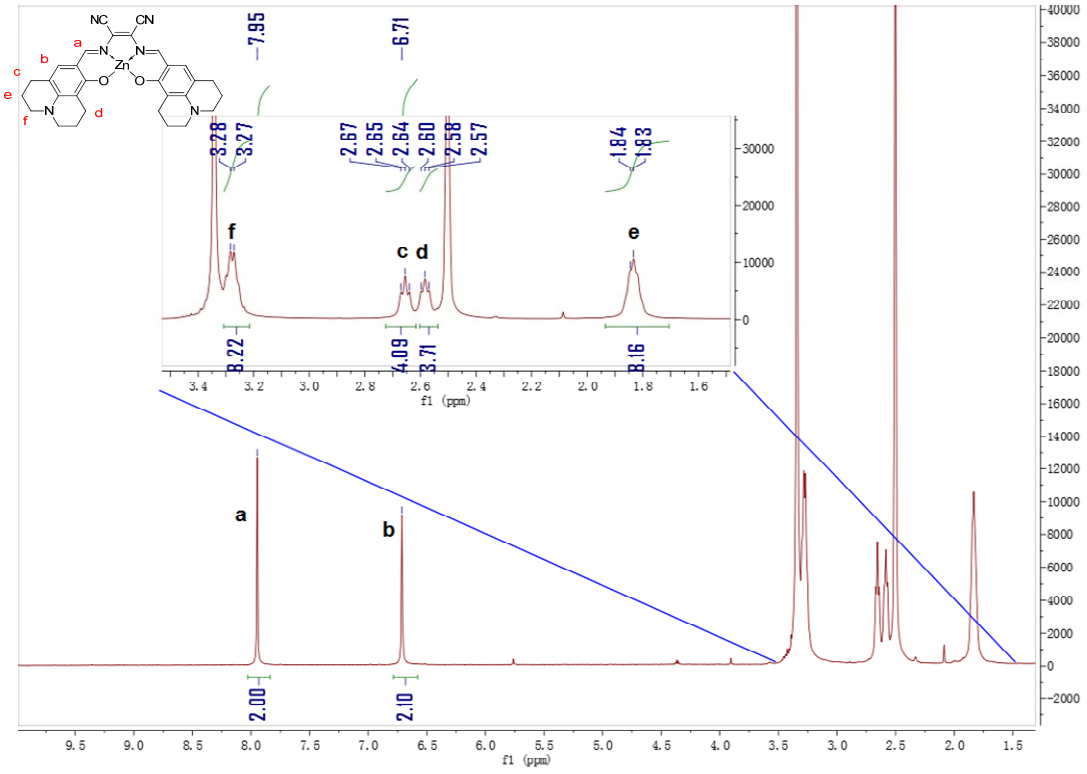
a1s7


DMSO
MeOH
PE
a
b
c
d
e
f
g
h
i
j
k
f1 (ppm)

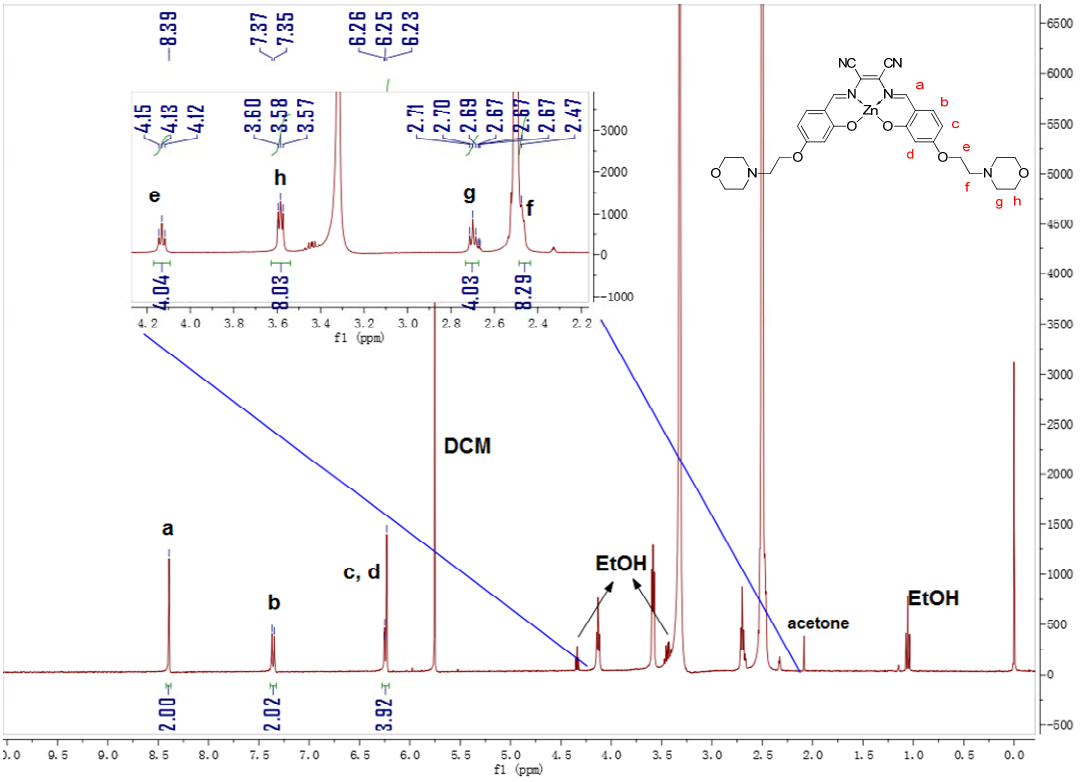
a1s8



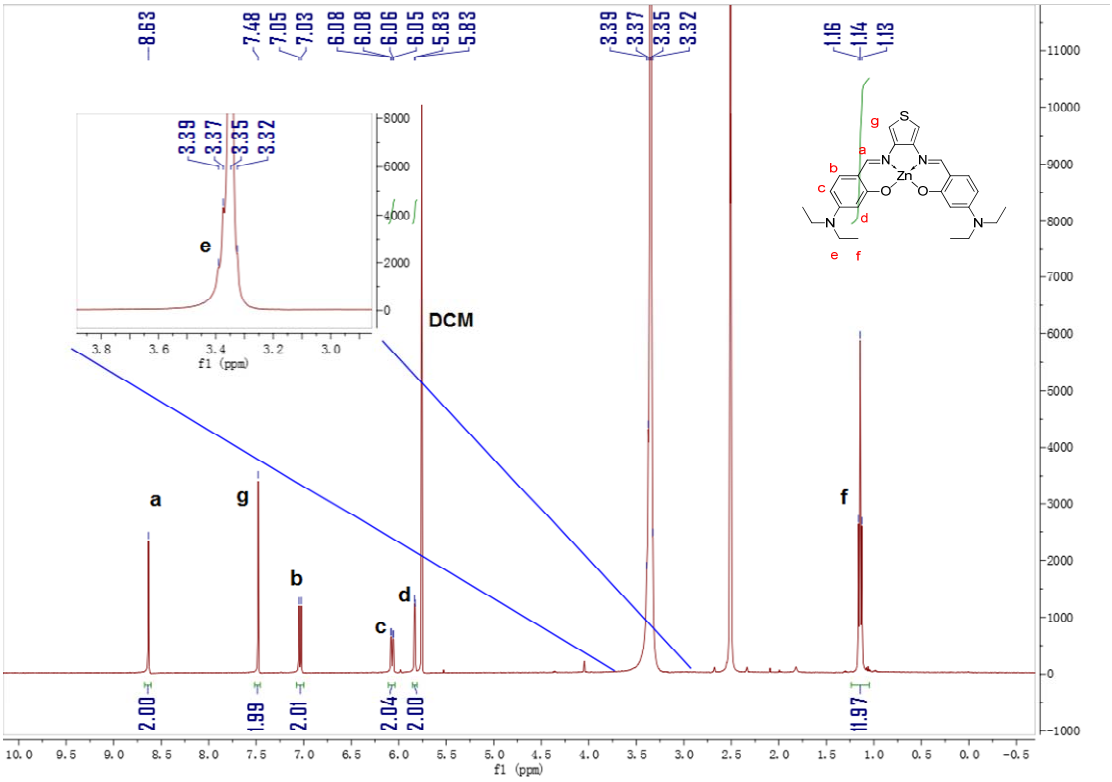
a1s9



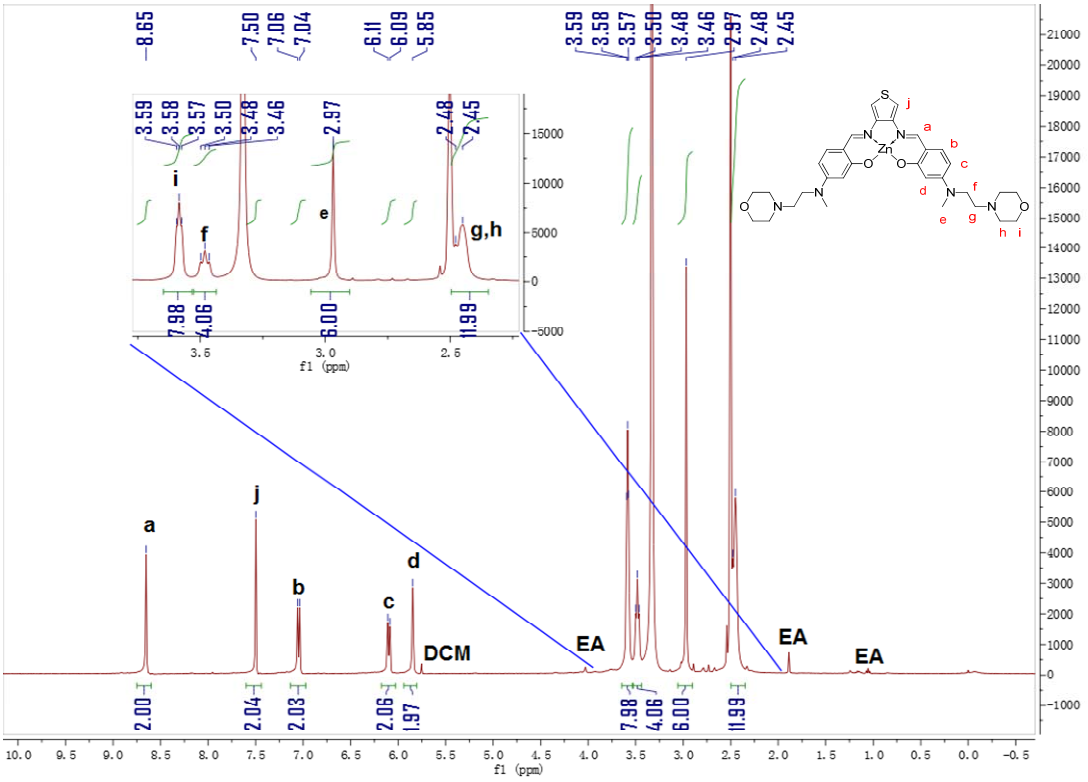
a1s10



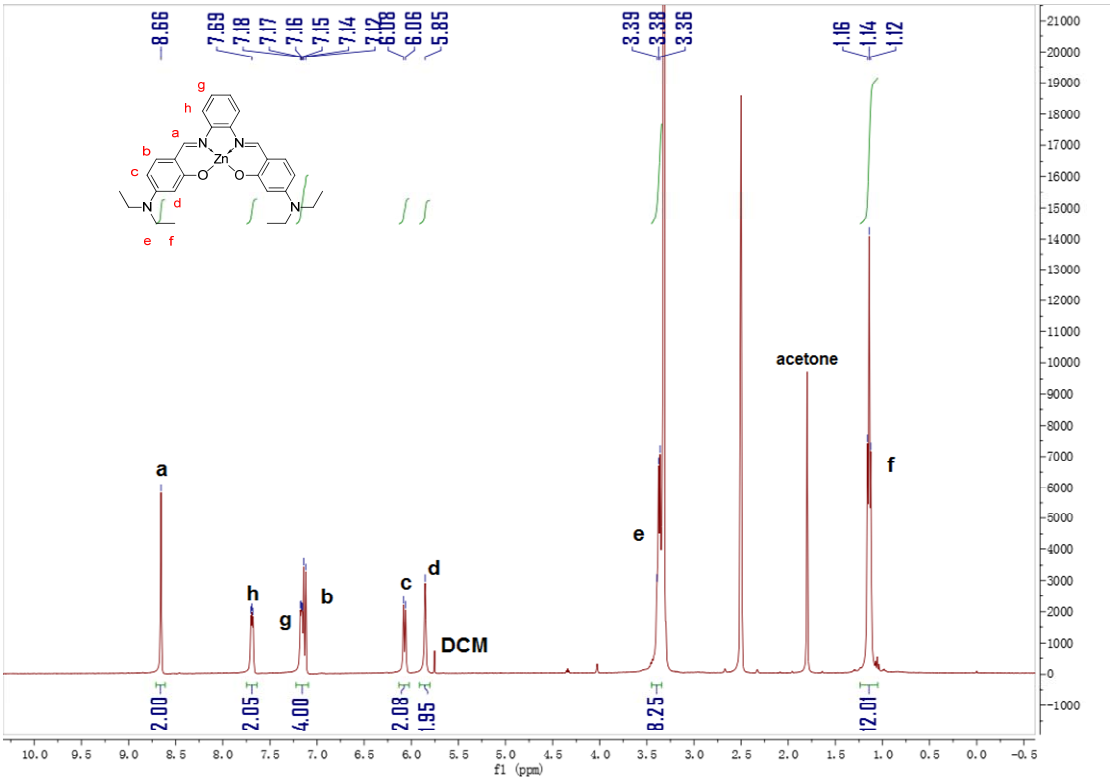
a2s1



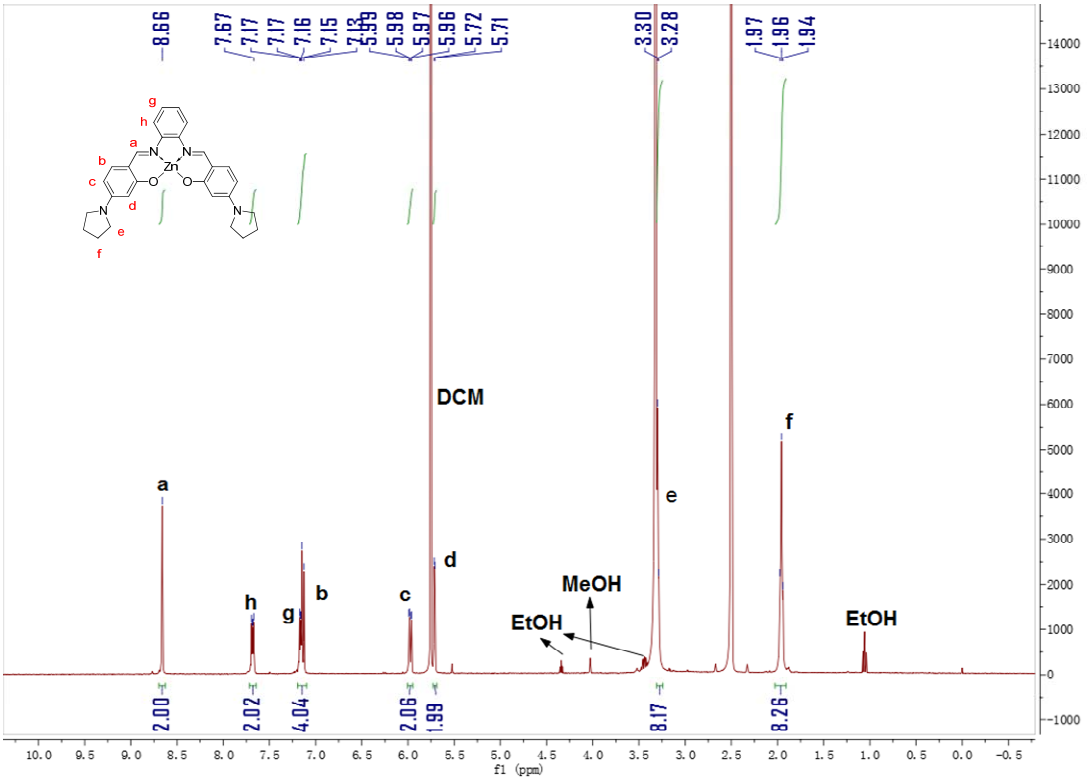
a2s3


8.65
7.50
7.06
7.04
6.11
6.09
5.85
3.59
3.58
3.57
3.50
3.48
3.46
2.97
2.48
2.45
i
f
e
g,h
7.98
4.06
6.00
11.99
a
j
b
c
d
DCM
EA
EA
EA
2.00
2.04
2.03
2.06
1.97
7.98
4.06
6.00
11.99
f1 (ppm)

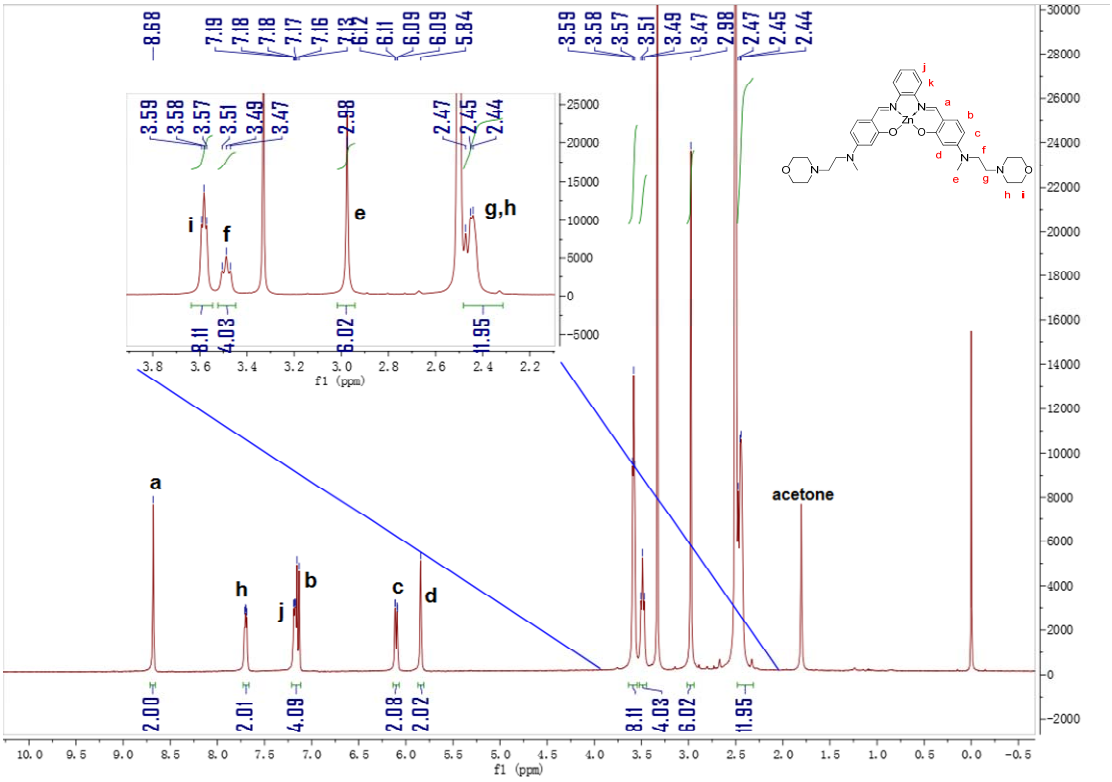
a3s1


8.66
7.69
7.18
7.17
7.16
7.15
7.14
7.12
6.08
6.06
5.85
3.39
3.38
3.36
1.16
1.14
1.12
acetone
a
h
g
b
c
d
DCM
e
f
2.00
2.05
4.00
2.08
1.95
8.25
12.01
f1 (ppm)

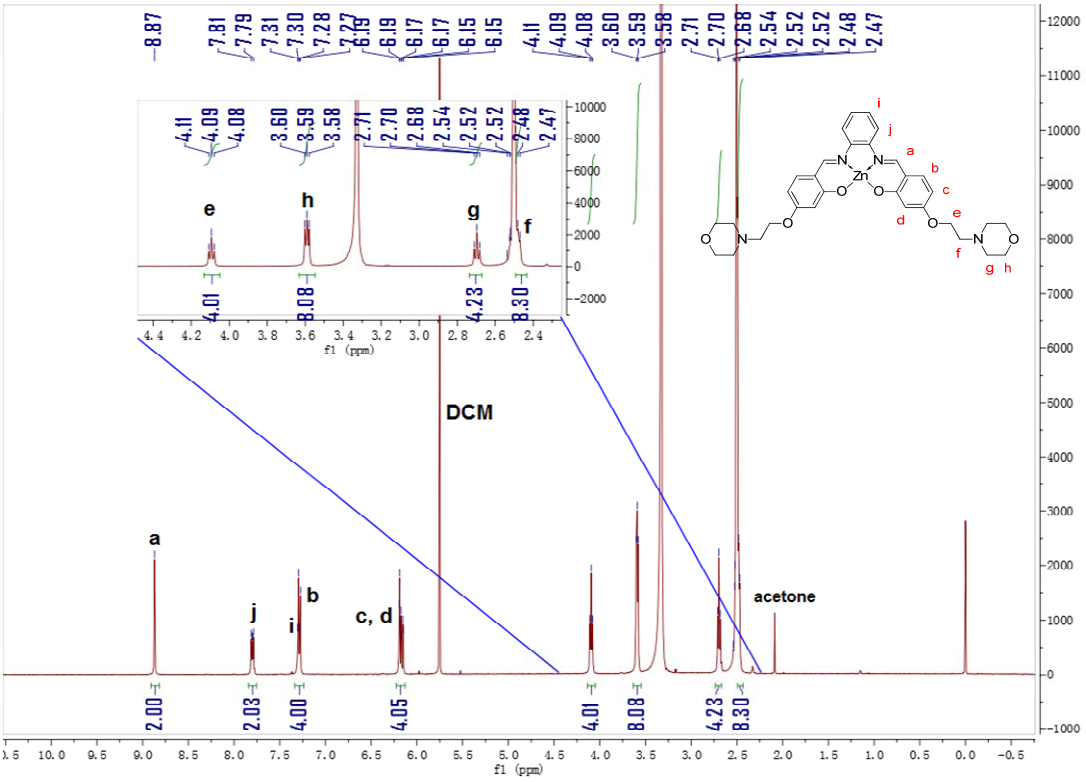
a3s3


DCM
MeOH
EtOH
EtOH
a
h
g
b
c
d
e
f
f1 (ppm)

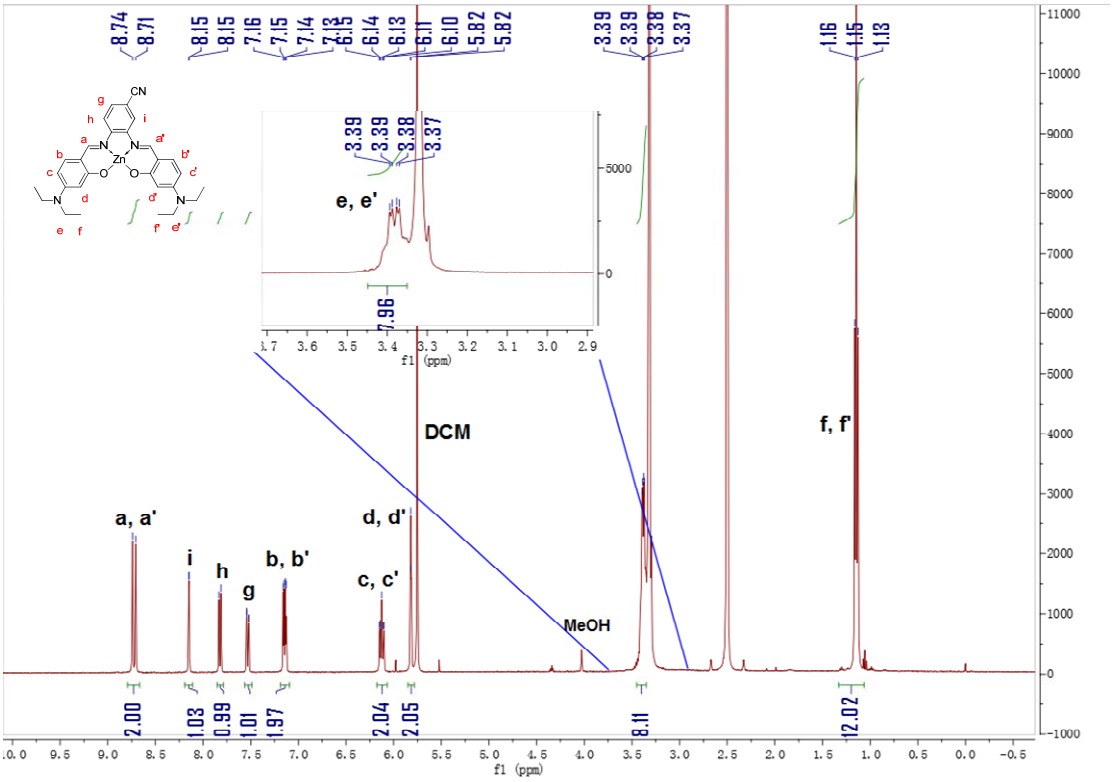
a3s4


acetone
a
h
j
b
c
d
i
f
e
g,h
f1 (ppm)

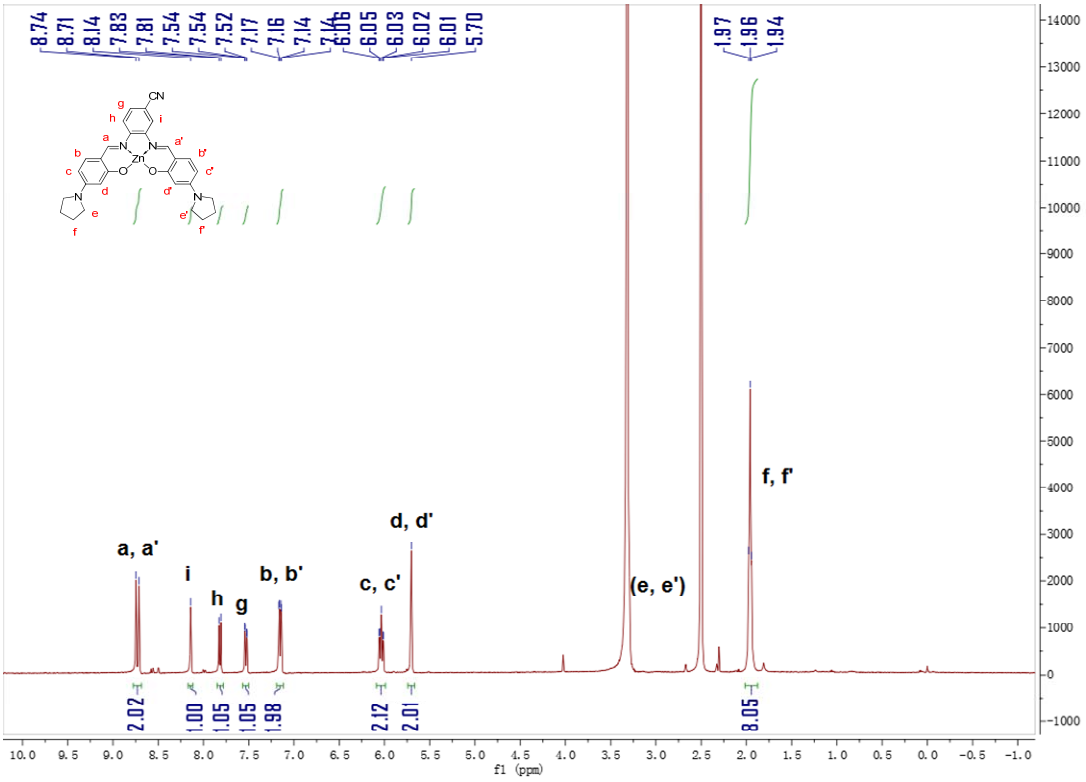
a3s10



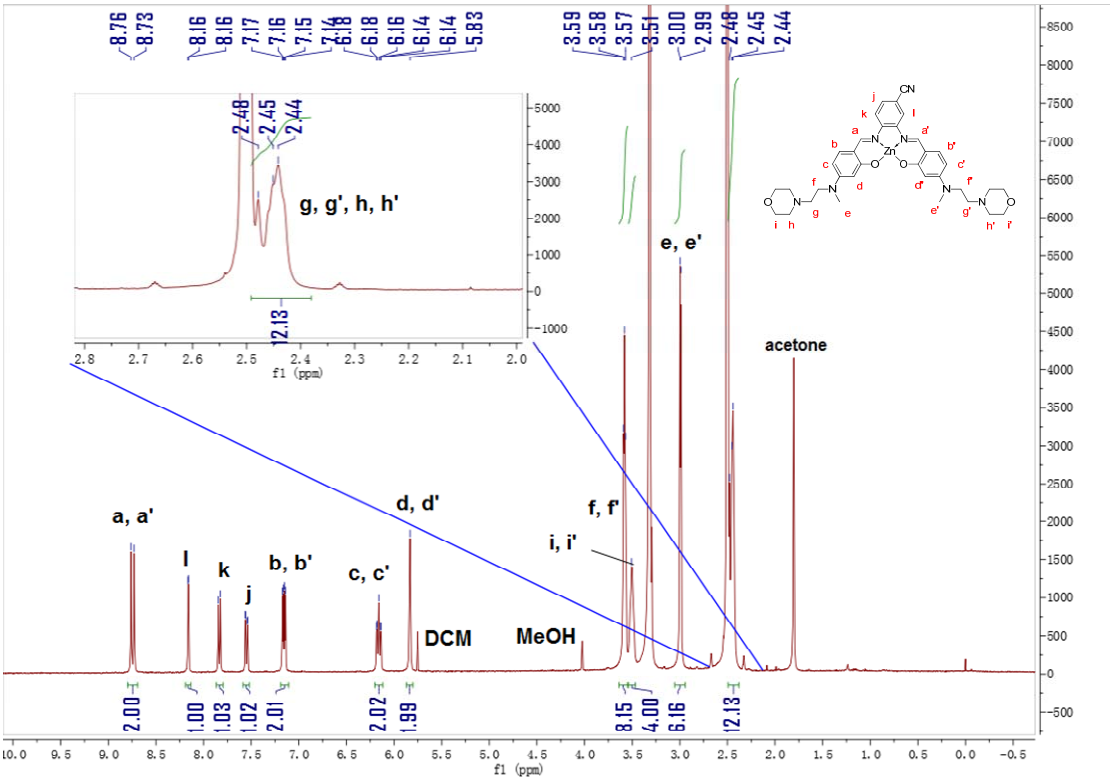
a4s1



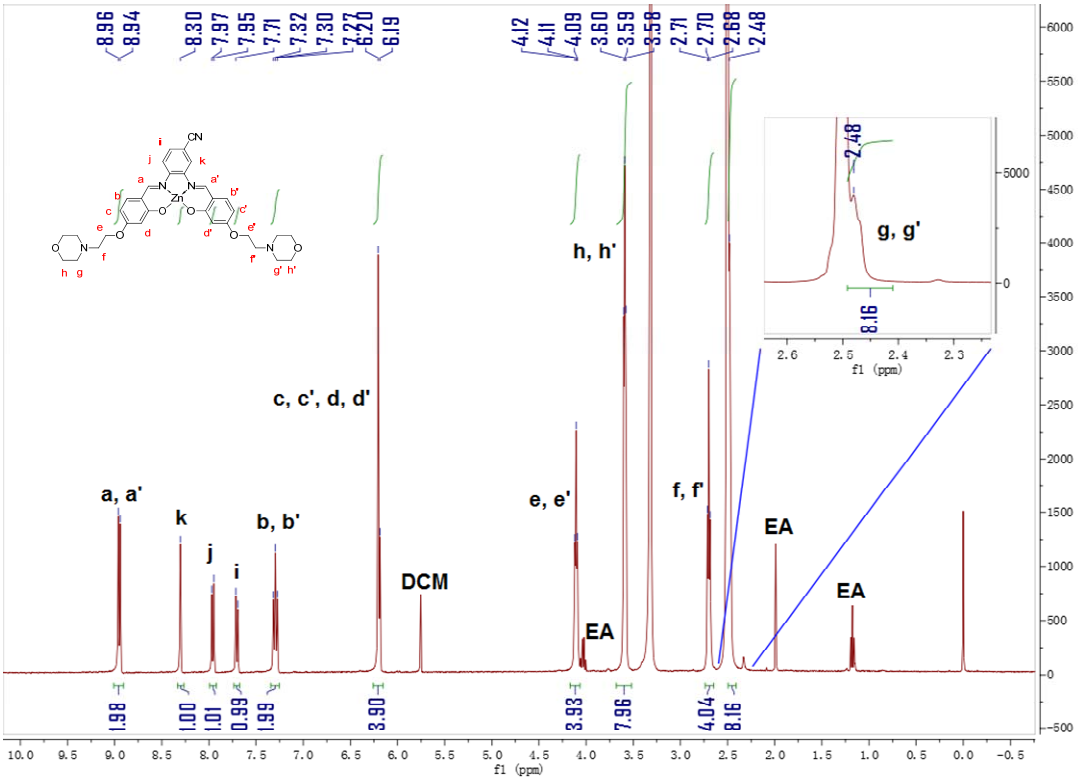
a4s3


8.74
8.71
8.14
7.83
7.81
7.54
7.54
7.52
7.17
7.16
7.14
6.06
6.05
6.03
6.02
6.01
5.70
1.97
1.96
1.94
a, a'
i
h
g
b, b'
c, c'
d, d'
(e, e')
f, f'
2.02
1.00
1.05
1.05
1.98
2.12
2.01
8.05
f1 (ppm)

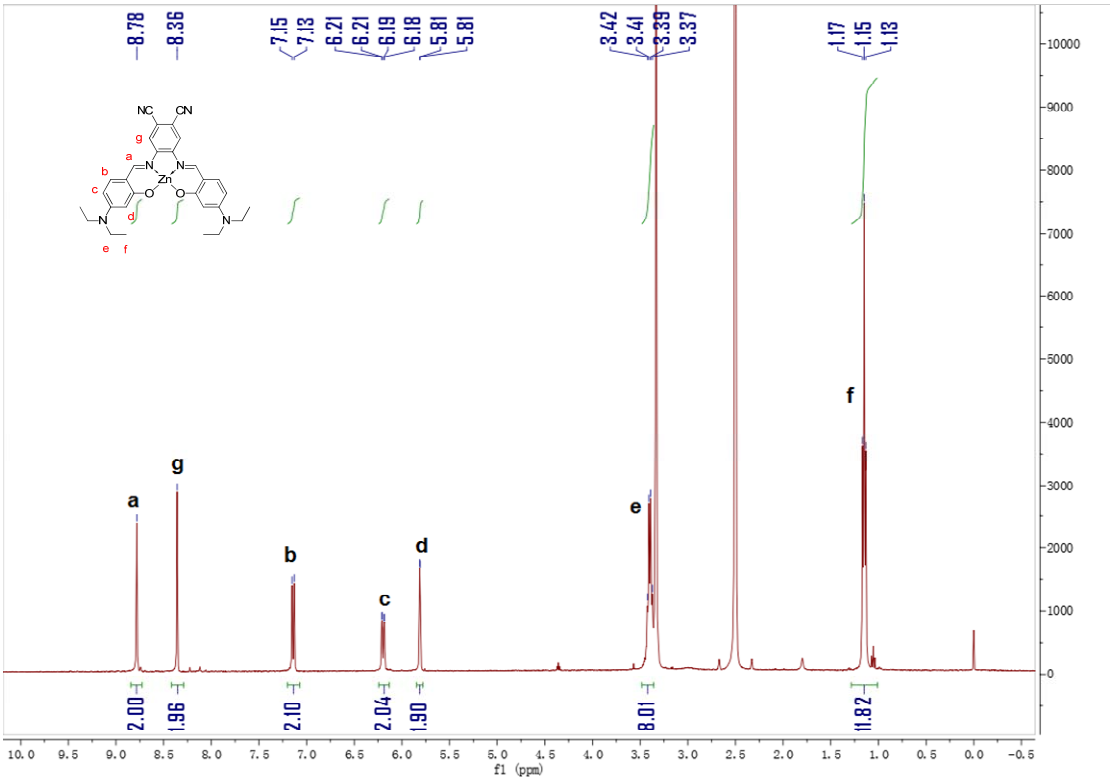
a4s4


8.76
8.73
8.16
8.16
7.17
7.16
7.15
6.18
6.18
6.16
6.14
6.14
5.83
3.59
3.58
3.57
3.51
3.00
2.99
2.48
2.45
2.44
g, g', h, h'
12.13
e, e'
acetone
a, a'
l
k
j
b, b'
c, c'
d, d'
DCM
MeOH
f, f'
i, i'
2.00
1.00
1.03
1.02
2.01
2.02
1.99
8.15
4.00
6.16
12.13
f1 (ppm)

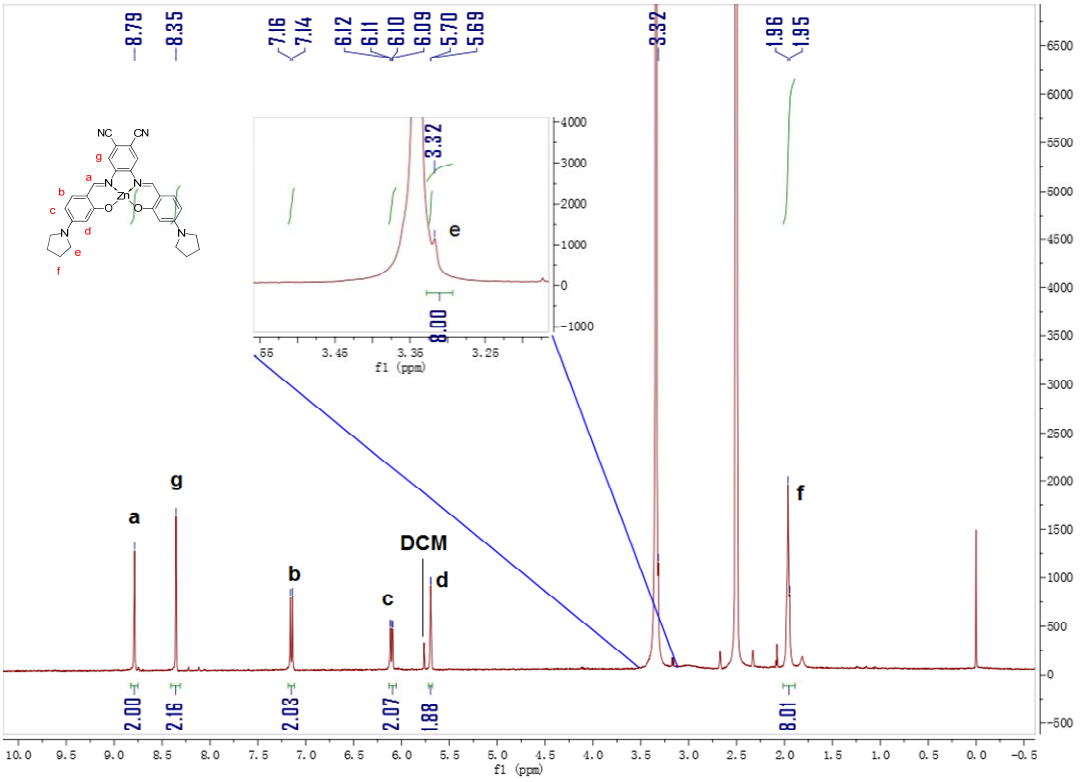
a4s10


8.96
8.94
8.30
7.97
7.95
7.71
7.32
7.30
7.27
6.20
6.19
4.12
4.11
4.09
3.60
3.59
3.58
2.71
2.70
2.68
2.48
a, a'
k
j
i
b, b'
c, c', d, d'
DCM
e, e'
EA
h, h'
f, f'
EA
EA
g, g'
8.16
1.98
1.00
1.01
0.99
1.99
3.90
3.93
7.96
4.04
8.16
f1 (ppm)

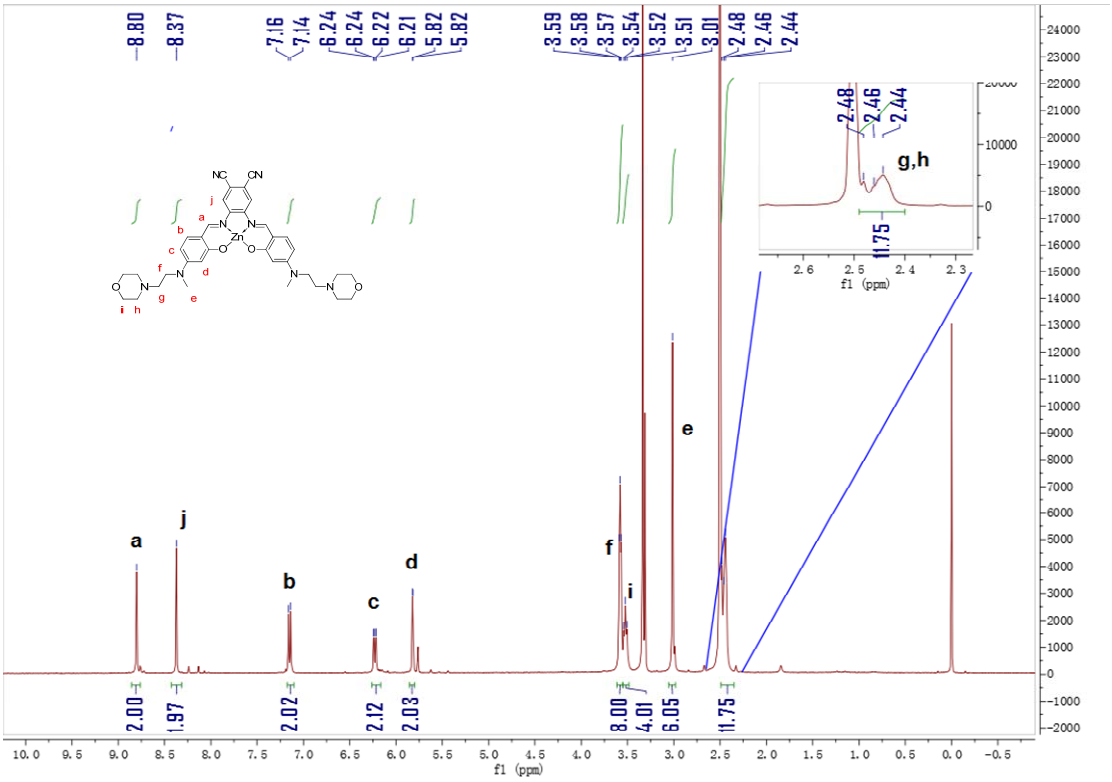
a5s1


8.78
8.36
7.15
7.13
6.21
6.21
6.19
6.18
5.81
5.81
3.42
3.41
3.39
3.37
1.17
1.15
1.13
a
g
b
c
d
e
f
2.00
1.96
2.10
2.04
1.90
8.01
11.82
f1 (ppm)

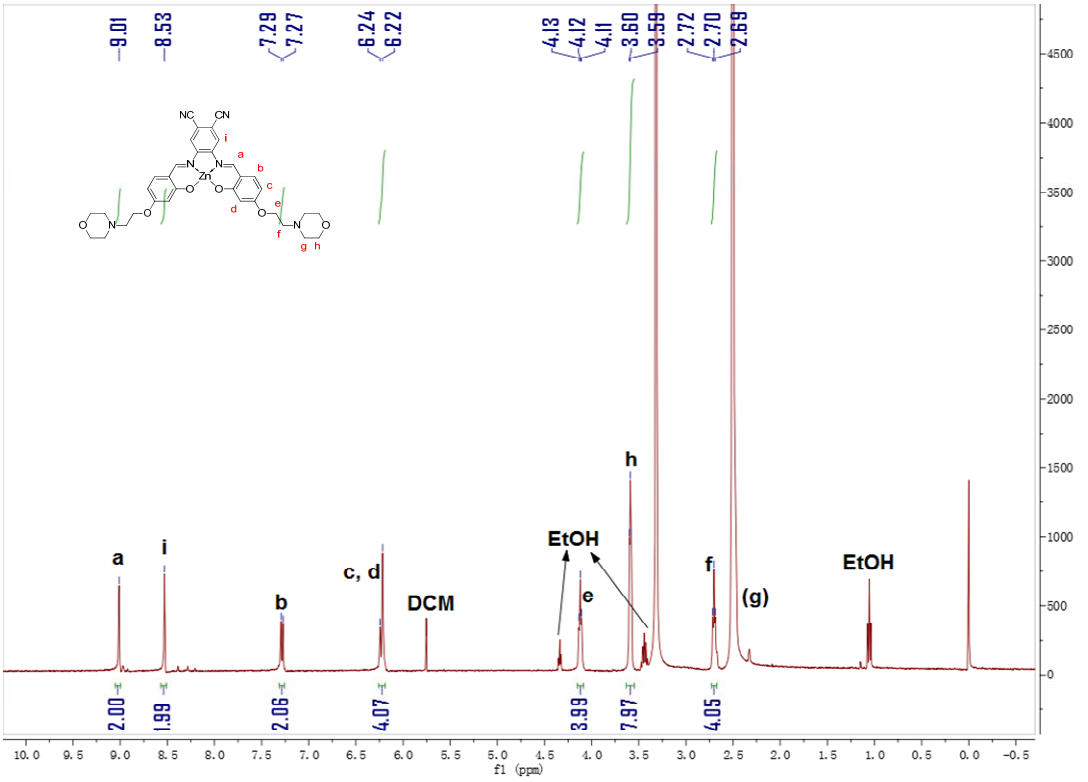
a5s3


8.79
8.35
7.16
7.14
6.12
6.11
6.10
6.09
5.70
5.69
3.32
1.96
1.95
NC
CN
Zn
a
b
c
d
e
f
g
DCM
2.00
2.16
2.03
2.07
1.88
8.01
8.00
f1 (ppm)

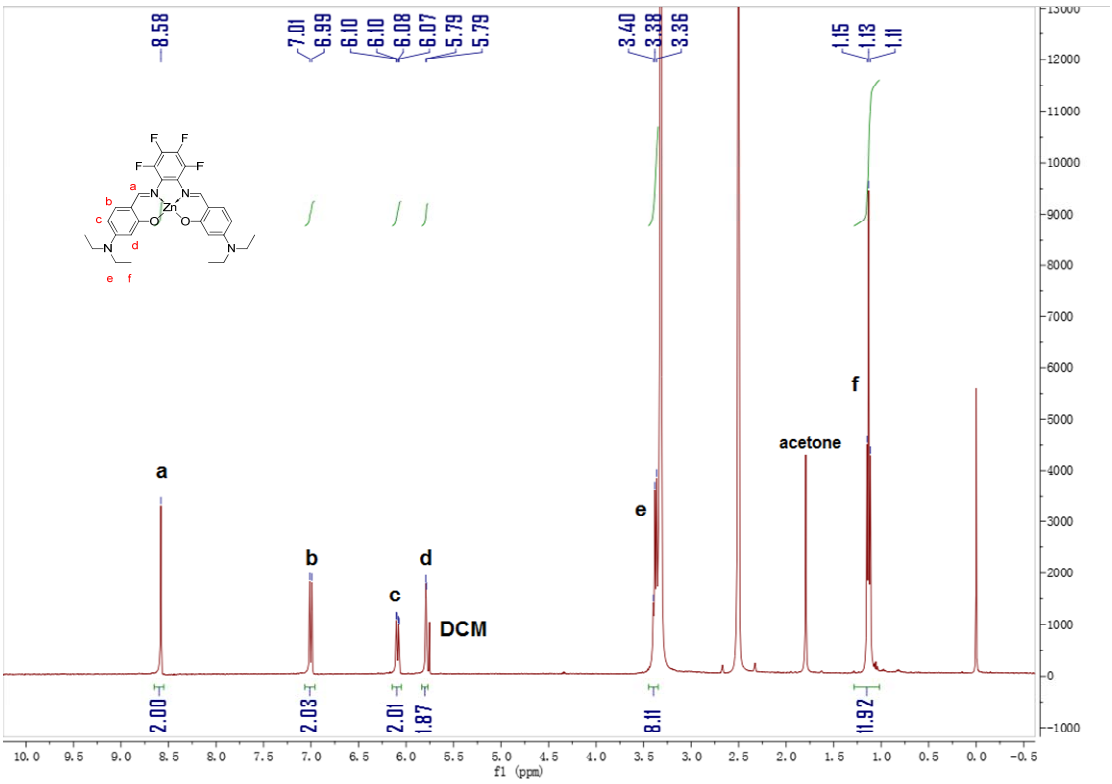
a5s4


8.80
8.37
7.16
7.14
6.24
6.24
6.22
6.21
5.82
5.82
3.59
3.58
3.57
3.54
3.52
3.51
3.01
2.48
2.46
2.44
NC
CN
Zn
a
b
c
d
e
f
g
h
i
j
g,h
2.00
1.97
2.02
2.12
2.03
8.00
4.01
6.05
11.75
f1 (ppm)

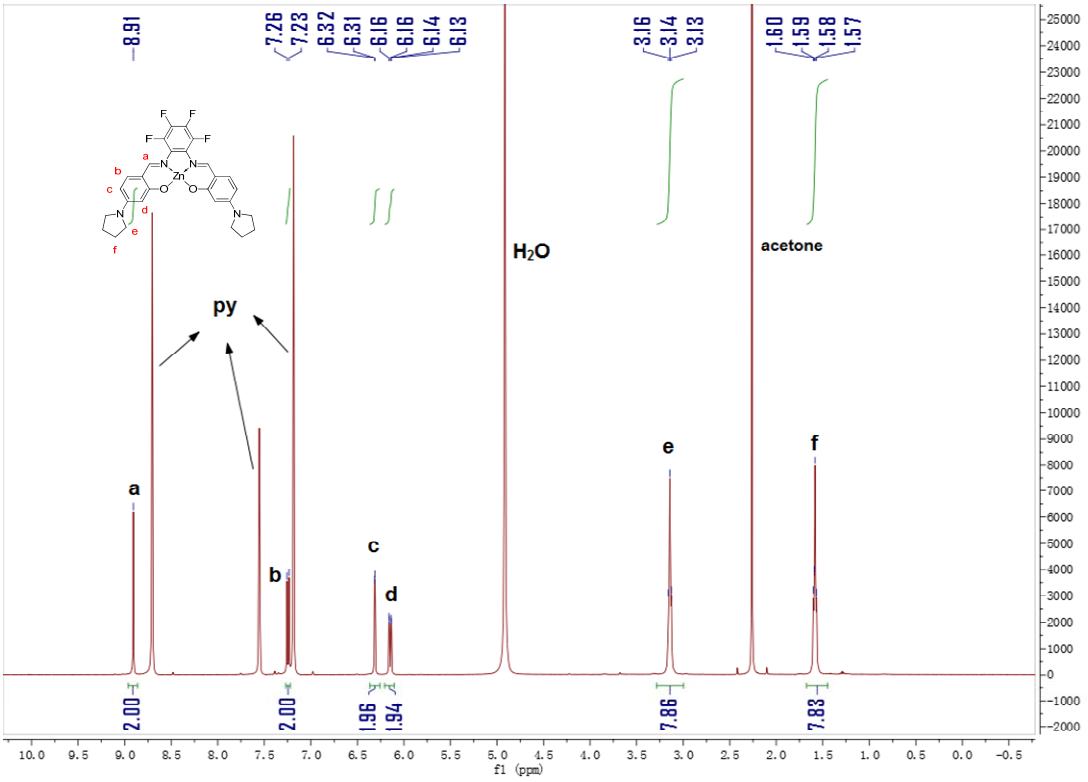
a5s10


9.01
8.53
7.29
7.27
6.24
6.22
4.13
4.12
4.11
3.60
3.59
2.72
2.70
2.69
a
i
b
c, d
DCM
EtOH
e
h
f
(g)
EtOH
2.00
1.99
2.06
4.07
3.99
7.97
4.05
f1 (ppm)

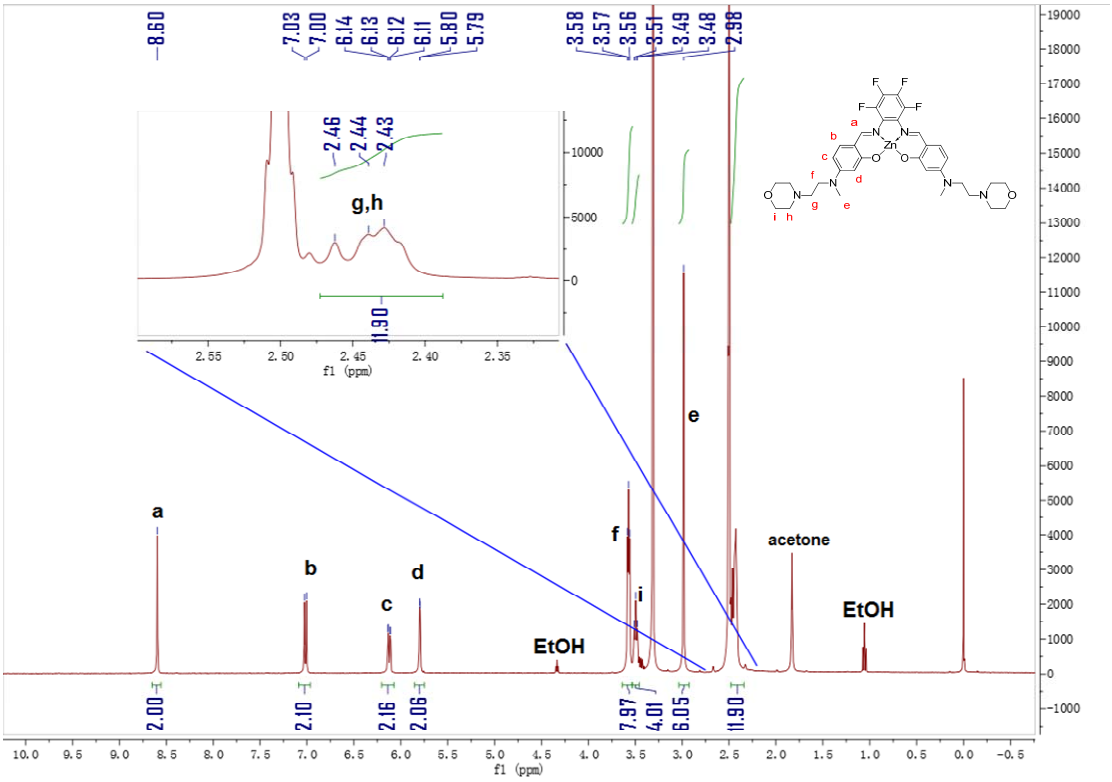
a6s1


8.58
7.01
6.99
6.10
6.10
6.08
6.07
5.79
5.79
3.40
3.38
3.36
1.15
1.13
1.11
a
b
c
d
DCM
e
acetone
f
2.00
2.03
2.01
1.87
8.11
11.92
f1 (ppm)

a6s3


8.91
7.26
7.23
6.32
6.31
6.16
6.16
6.14
6.13
3.16
3.14
3.13
1.60
1.59
1.58
1.57
H2O
acetone
py
a
b
c
d
e
f
2.00
2.00
1.96
1.94
7.86
7.83
f1 (ppm)

a6s4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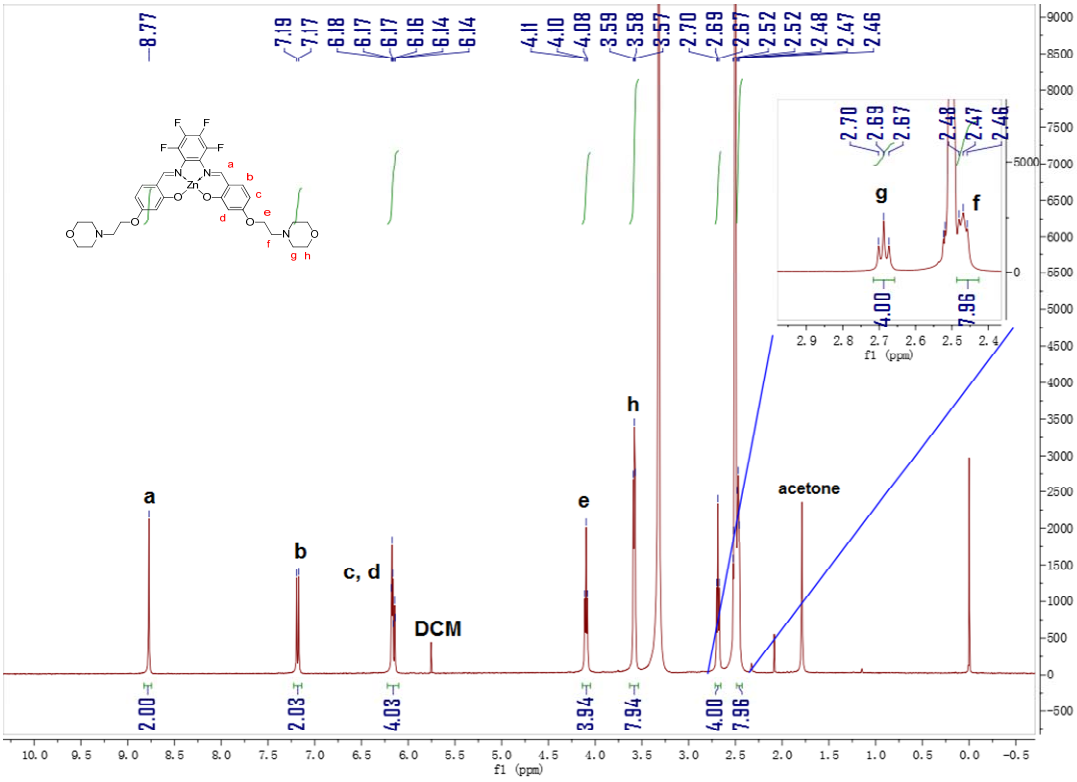
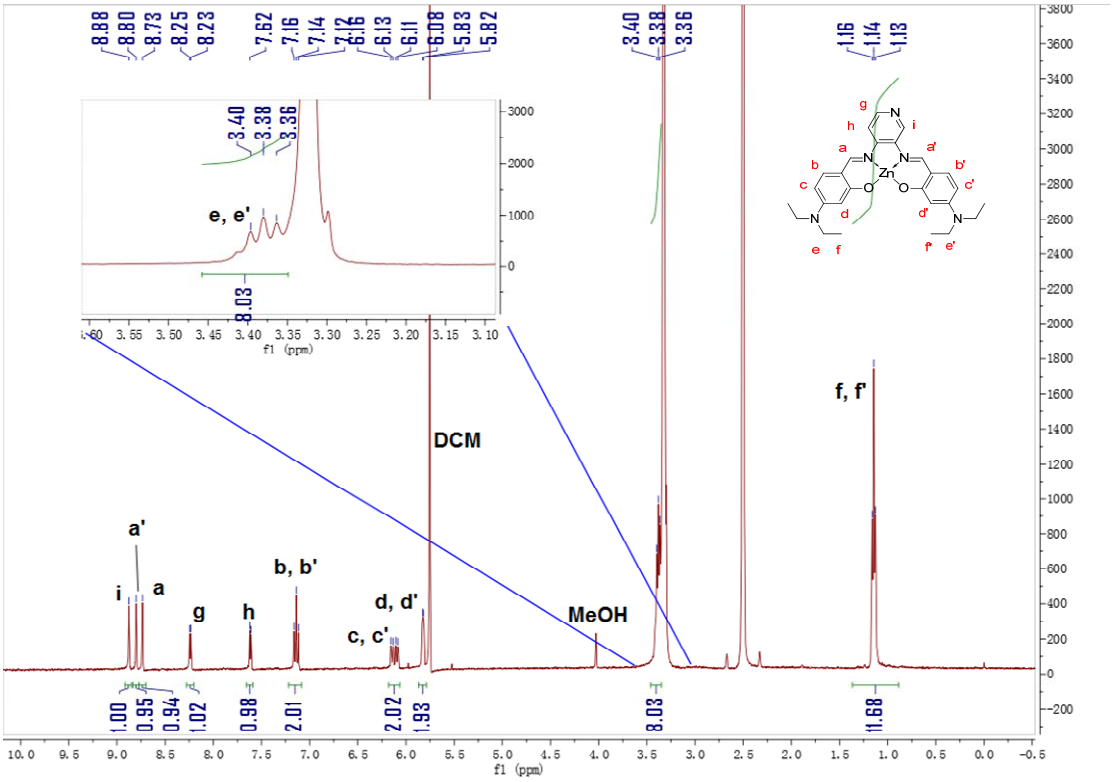
7.03
7.00
6.14
6.13
6.12
6.11
5.80
5.79
3.58
3.57
3.56
3.51
3.49
3.48
2.98
2.46
2.44
2.43
g,h
11.90
a
b
c
d
e
f
i
EtOH
EtOH
acetone
2.00
2.10
2.16
2.06
7.97
4.01
6.05
11.90
f1 (ppm)

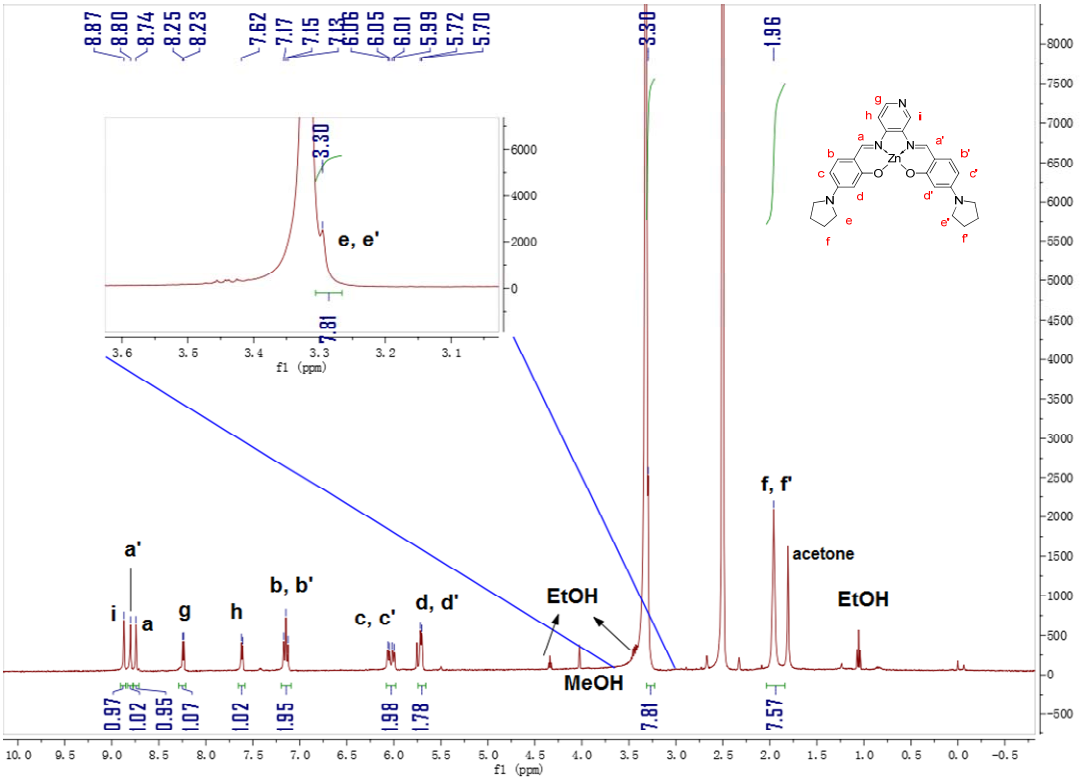
a6s10


a
b
c, d
DCM
e
h
acetone
g
f
f1 (ppm)

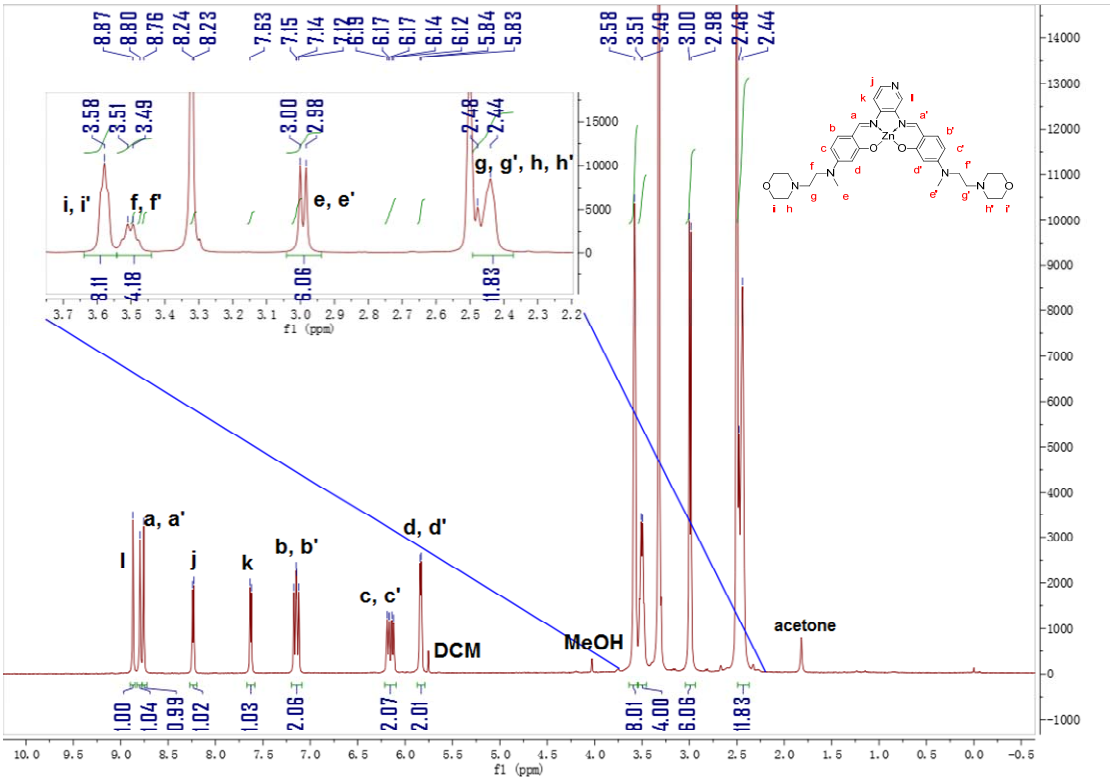
a7s1


e, e'
a'
i
a
g
h
b, b'
d, d'
c, c'
DCM
MeOH
f, f'
f1 (ppm)

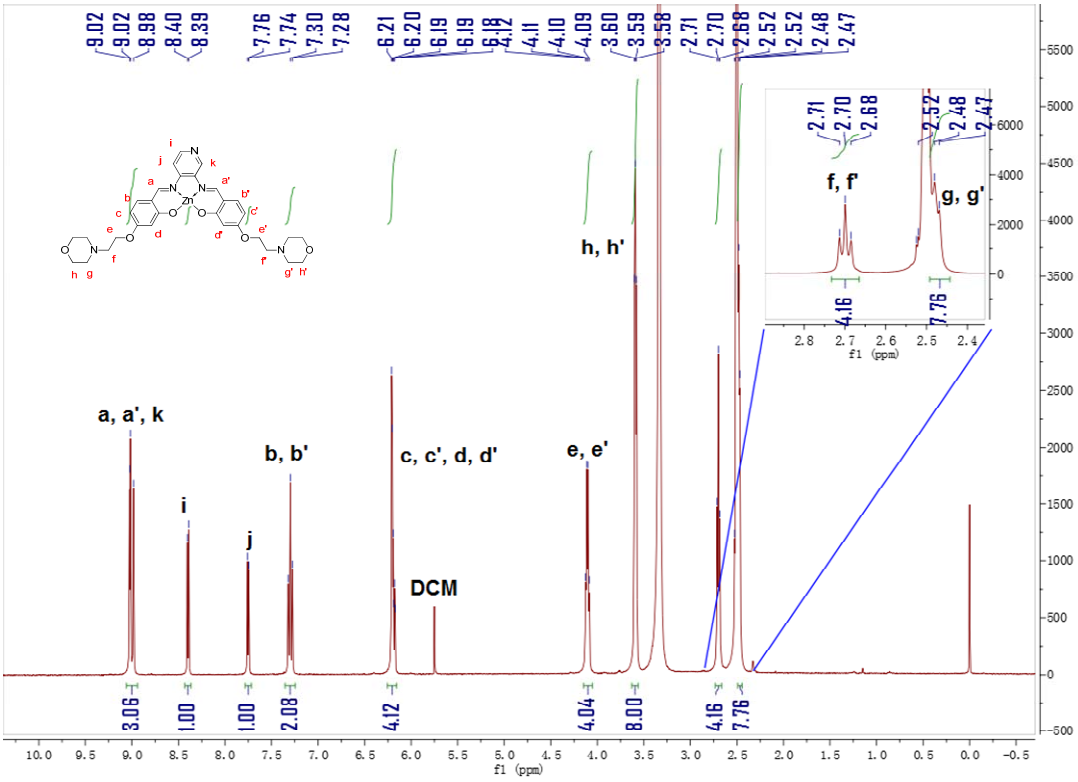
a7s3


e, e'
a'
i
a
g
h
b, b'
c, c'
d, d'
EtOH
MeOH
f, f'
acetone
EtOH

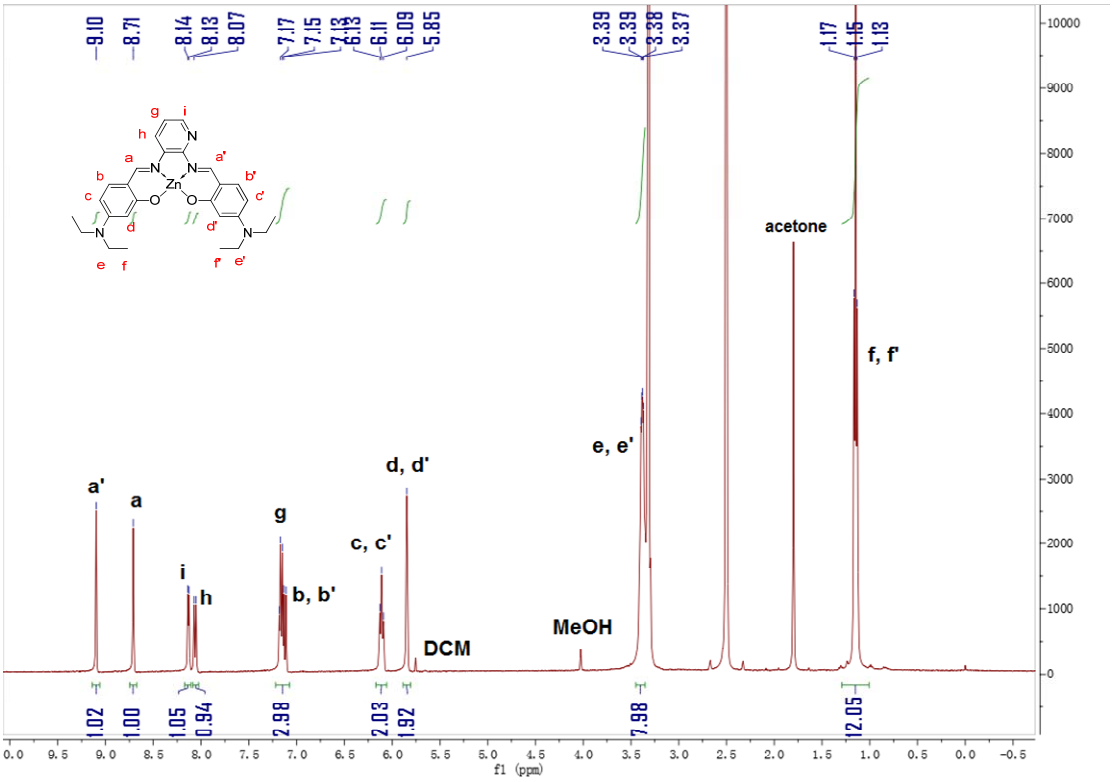
a7s4


i, i'
f, f'
e, e'
g, g', h, h'
a, a'
l
j
k
b, b'
c, c'
d, d'
DCM
MeOH
acetone

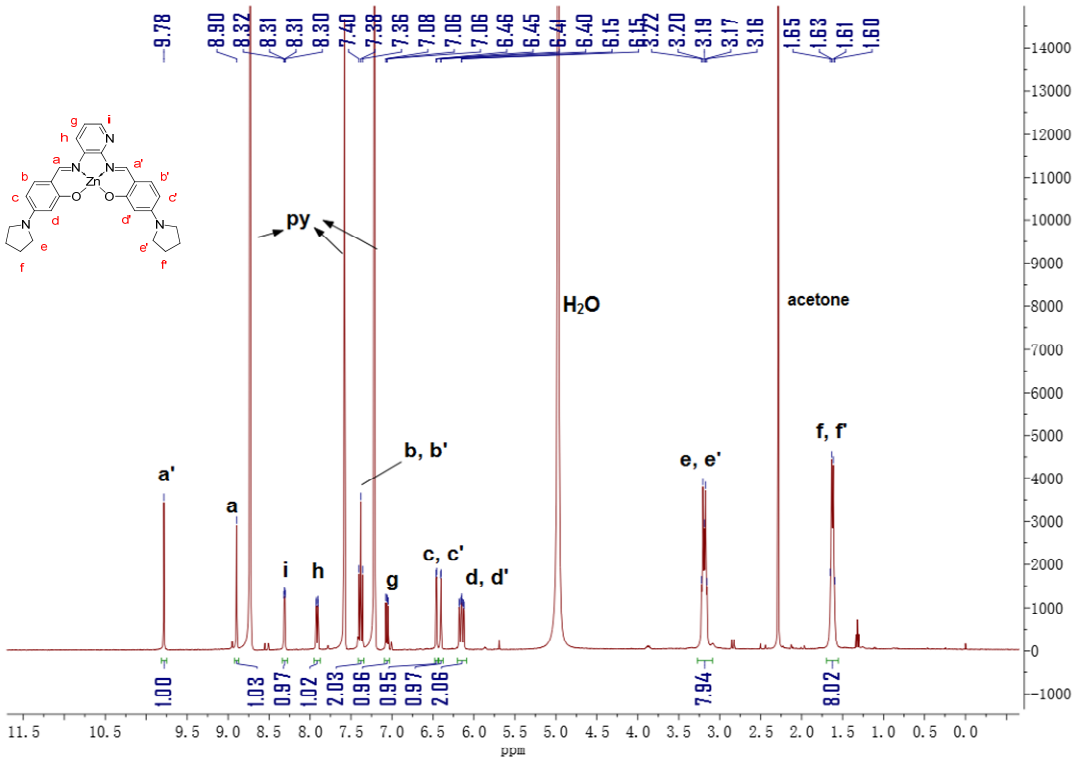
a7s10


a, a', k
i
j
b, b'
c, c', d, d'
DCM
e, e'
h, h'
f, f'
g, g'
f1 (ppm)

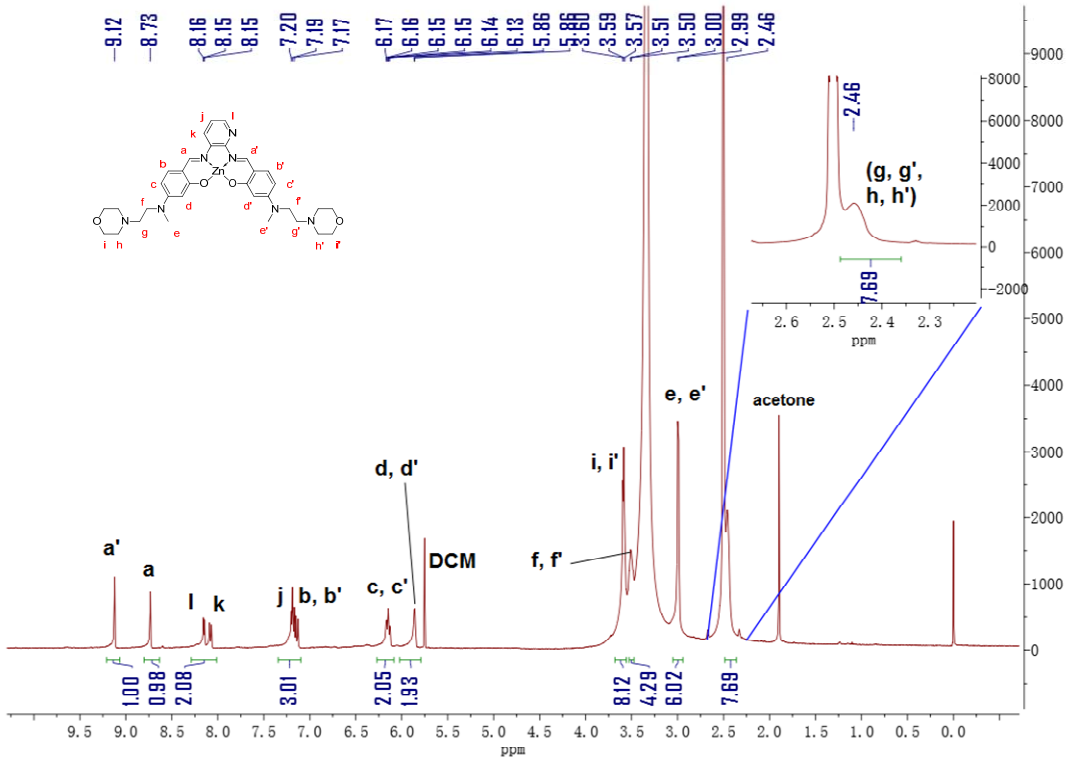
a8s1


a'
a
i
h
g
b, b'
c, c'
d, d'
DCM
MeOH
e, e'
acetone
f, f'
f1 (ppm)

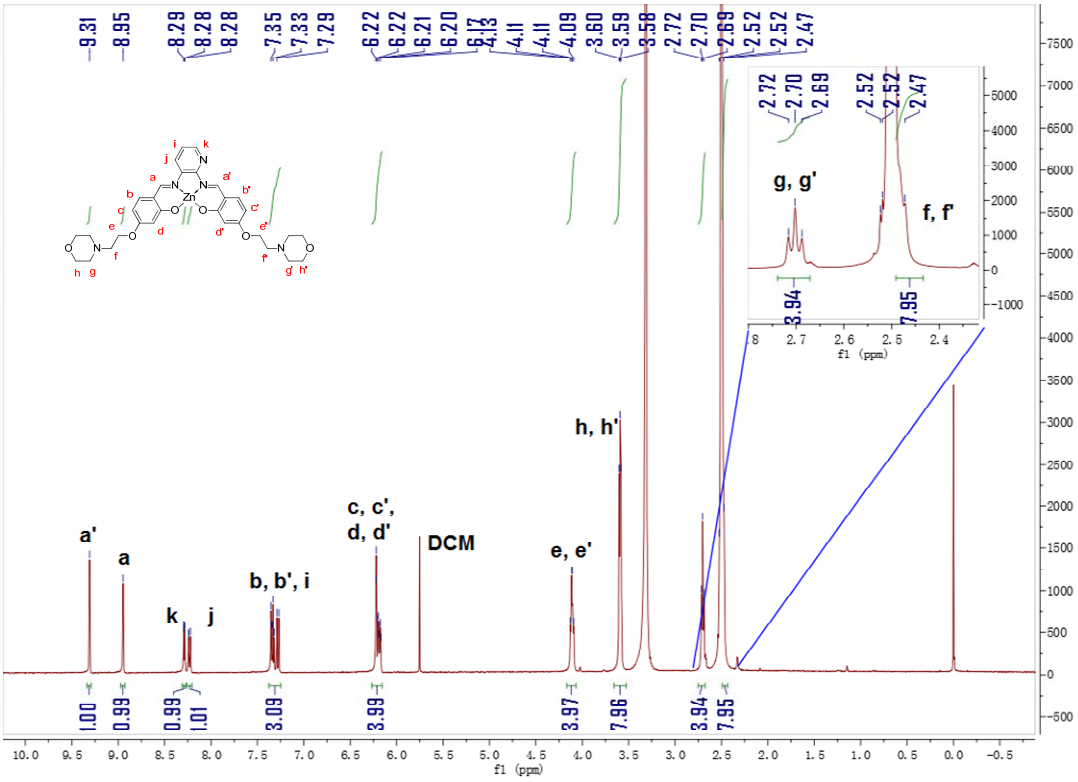
a8s3


py
H2O
acetone
a'
a
i
h
g
b, b'
c, c'
d, d'
e, e'
f, f'
ppm

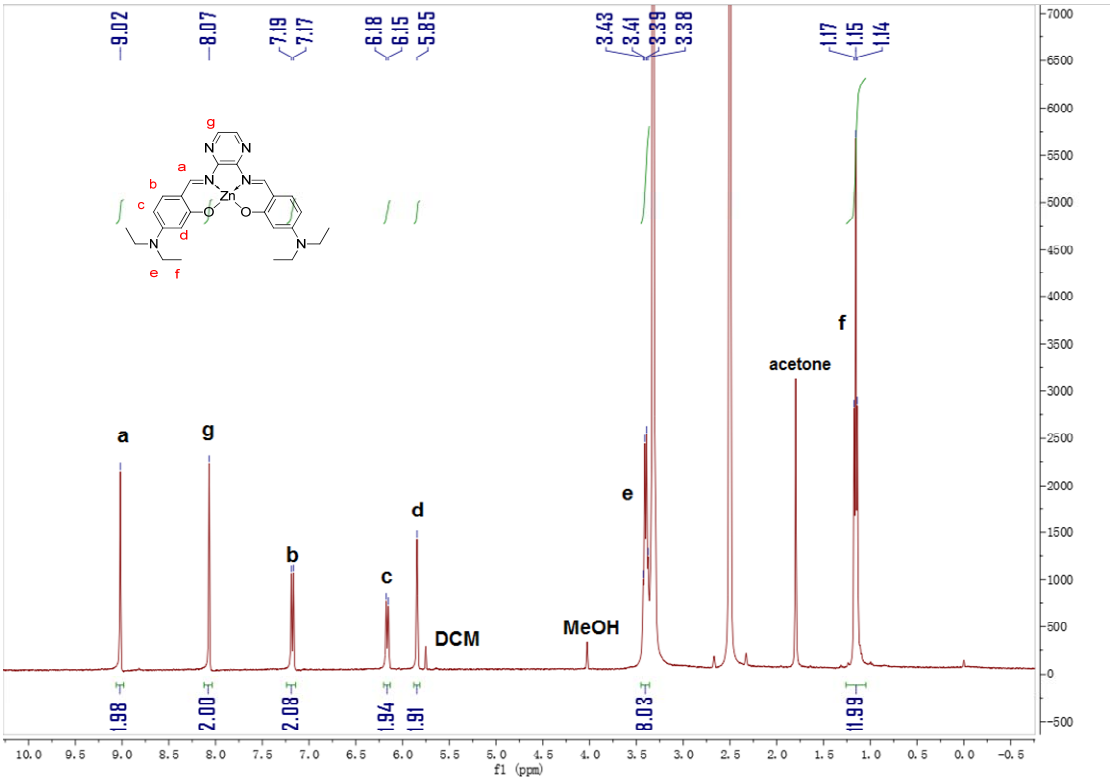
a8s4


a'
a
l
k
j
b, b'
c, c'
d, d'
DCM
f, f'
i, i'
e, e'
acetone
(g, g', h, h')
ppm

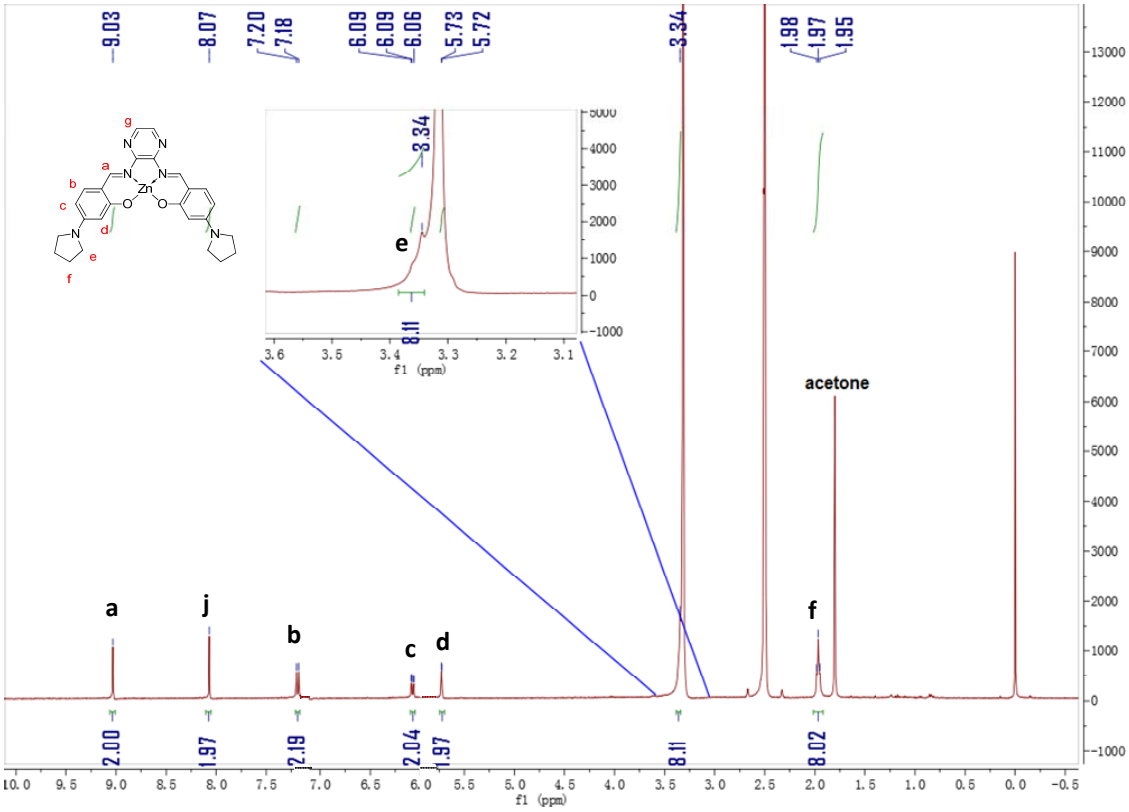
a8s10


a'
a
k
j
b, b', i
c, c',
d, d'
DCM
e, e'
h, h'
g, g'
f, f'
f1 (ppm)

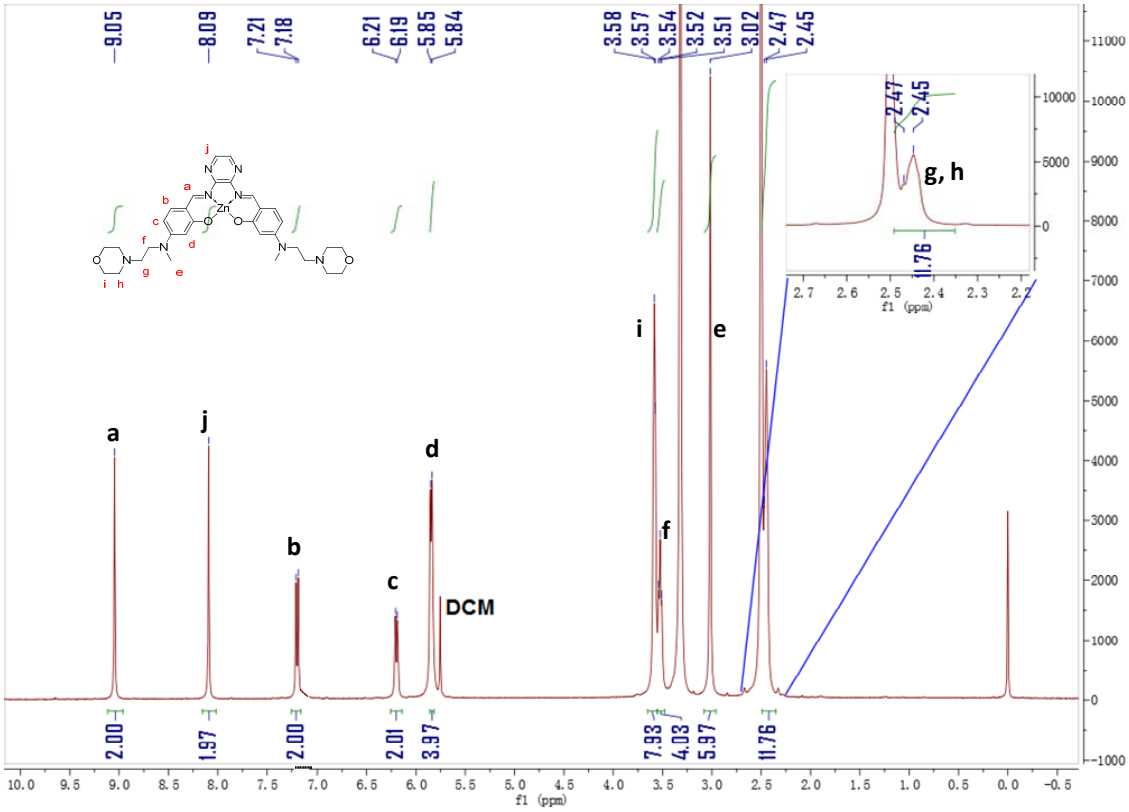
a9s1


a
g
b
c
d
DCM
MeOH
e
acetone
f
f1 (ppm)

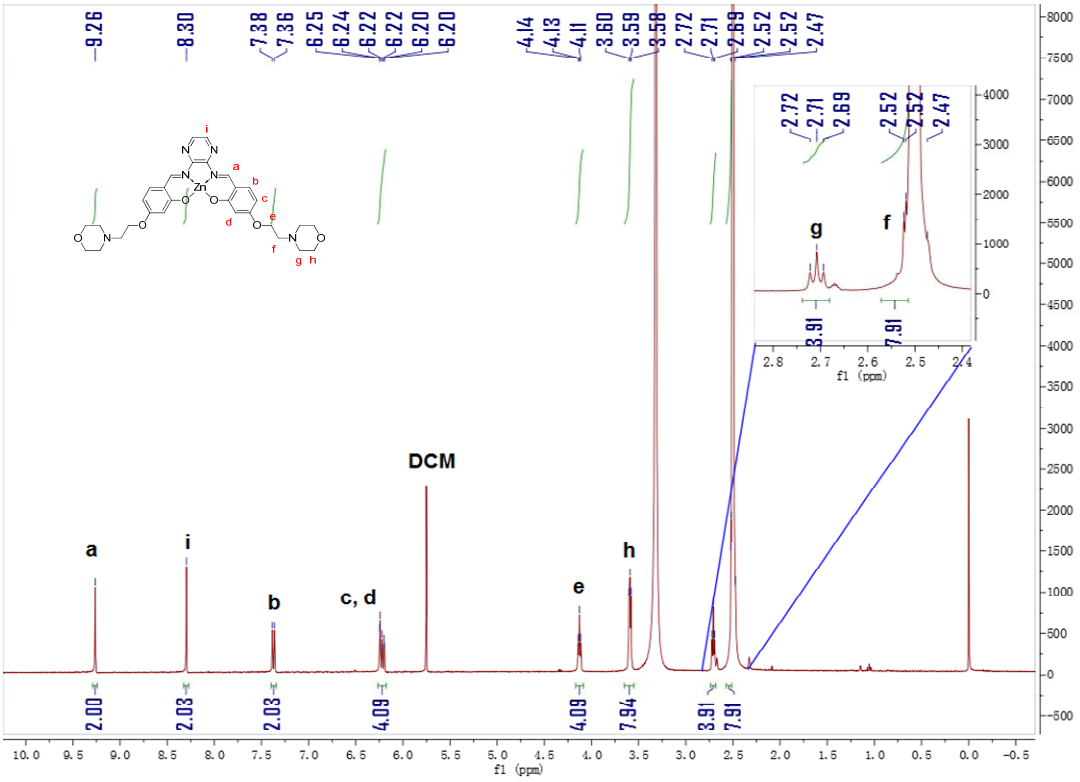
a9s3


9.03
8.07
7.20
7.18
6.09
6.09
6.06
5.73
5.72
3.34
1.98
1.97
1.95
acetone
a
j
b
c
d
f
2.00
1.97
2.19
2.04
1.97
8.11
8.02
f1 (ppm)

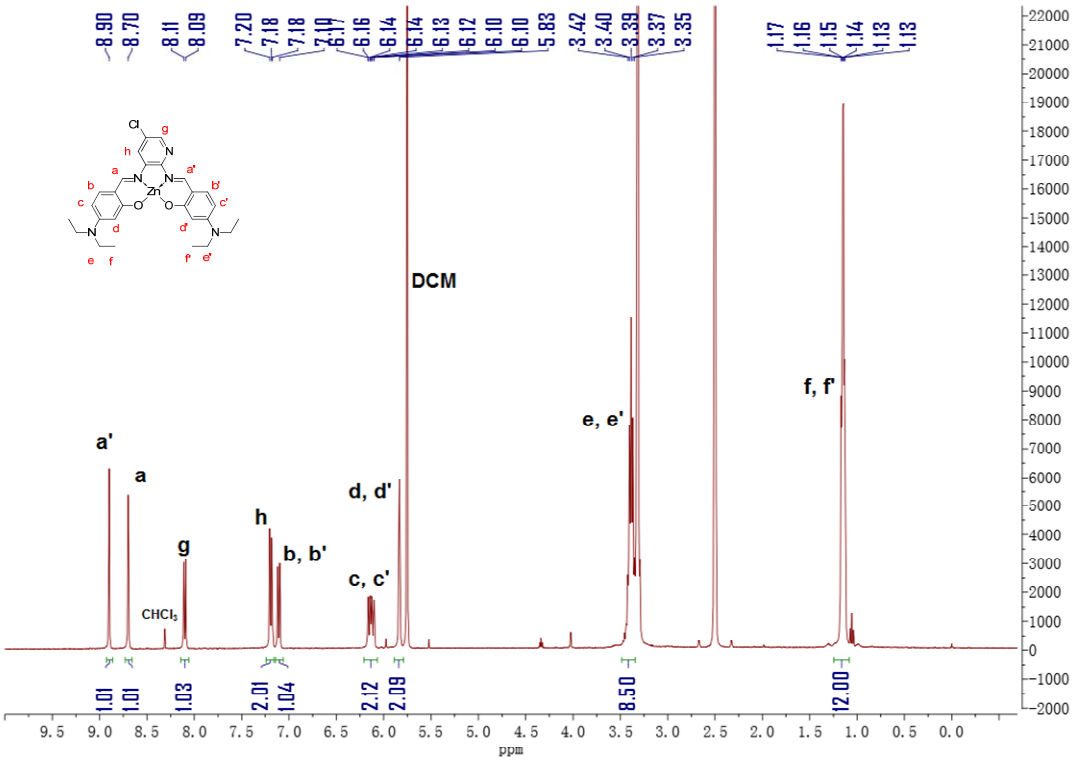
a9s4


9.05
8.09
7.21
7.18
6.21
6.19
5.85
5.84
3.58
3.57
3.54
3.52
3.51
3.02
2.47
2.45
g, h
i
e
a
j
d
f
b
c
DCM
2.00
1.97
2.00
2.01
3.97
7.93
4.03
5.97
11.76
f1 (ppm)

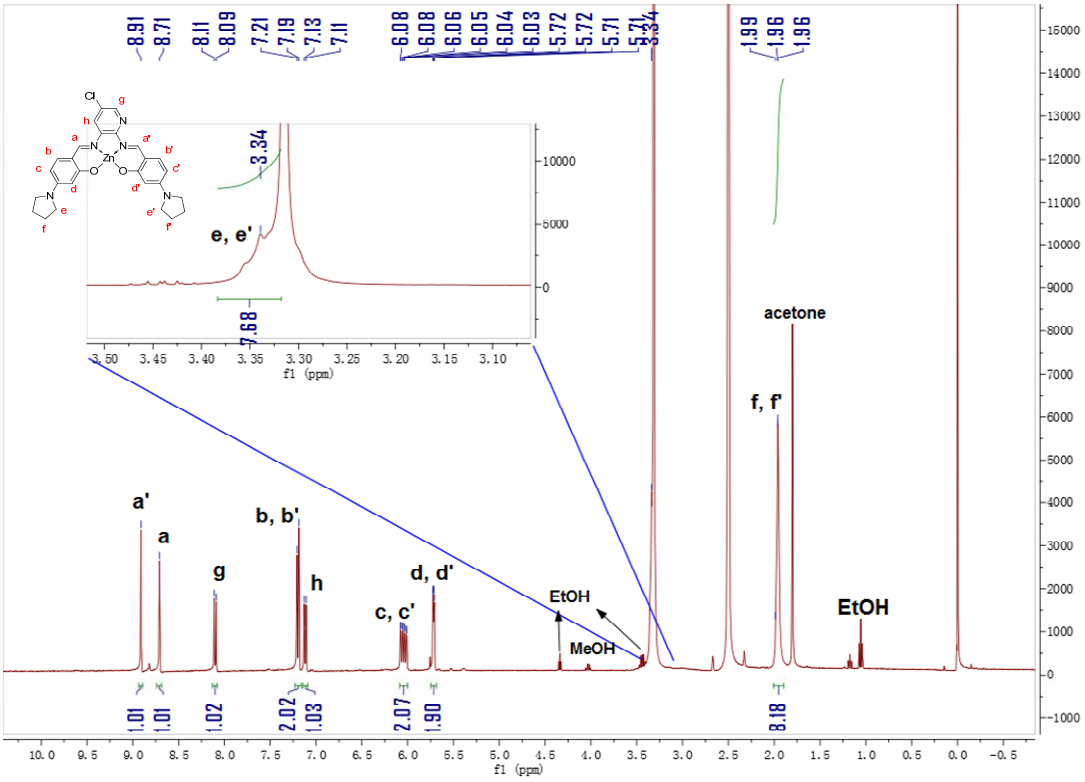
a9s10



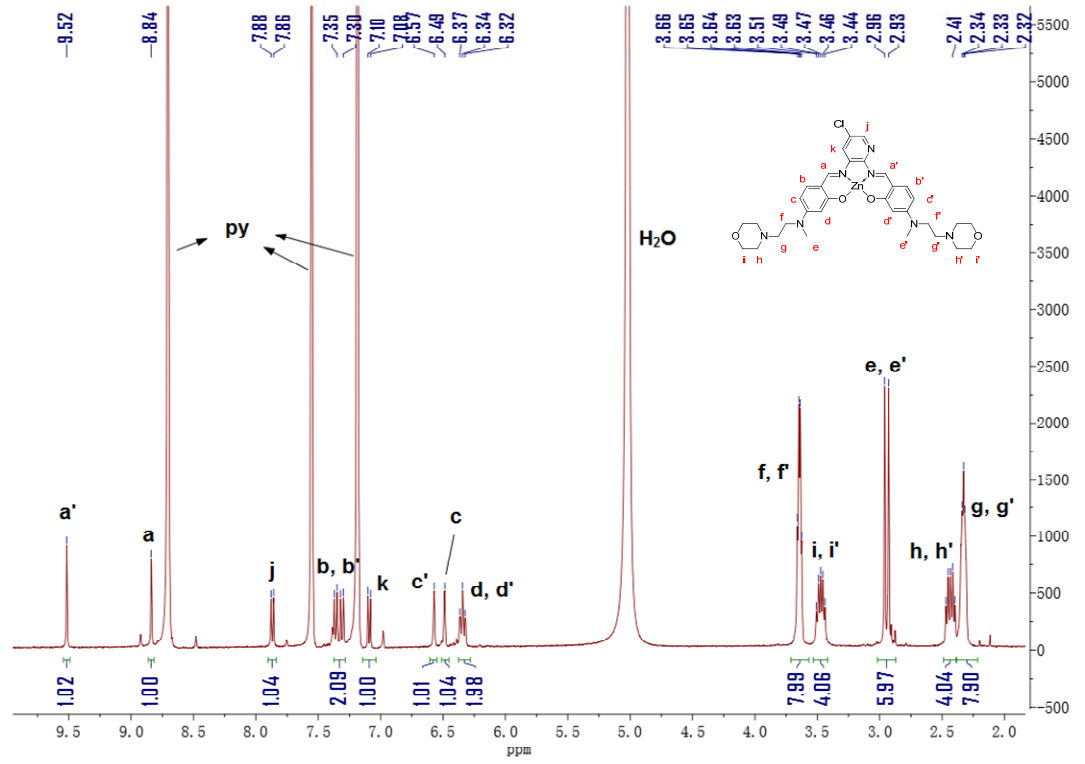
a10s1



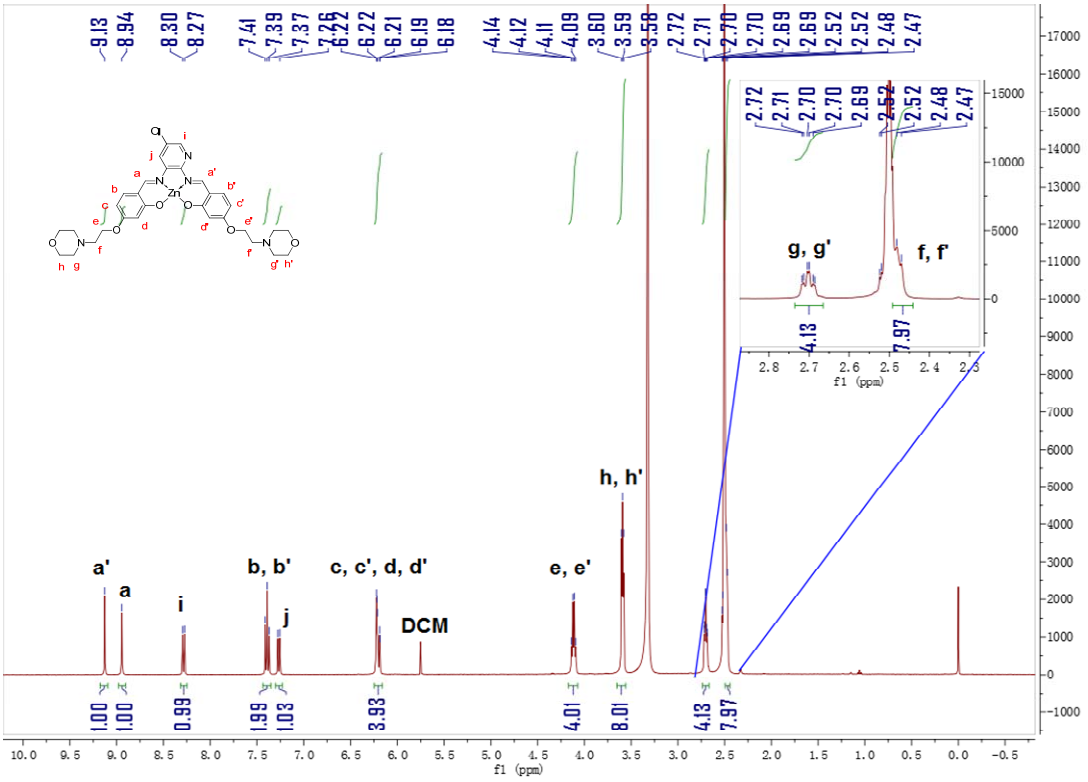
a10s3


8.91
8.71
8.11
8.09
7.21
7.19
7.13
7.11
6.08
6.08
6.06
6.05
6.04
6.03
5.72
5.72
5.71
5.71
5.34
1.99
1.96
1.96
3.34
e, e'
7.68
acetone
f, f'
a'
a
g
b, b'
h
c, c'
d, d'
EtOH
MeOH
EtOH
1.01
1.01
1.02
2.02
1.03
2.07
1.90
8.18
f1 (ppm)

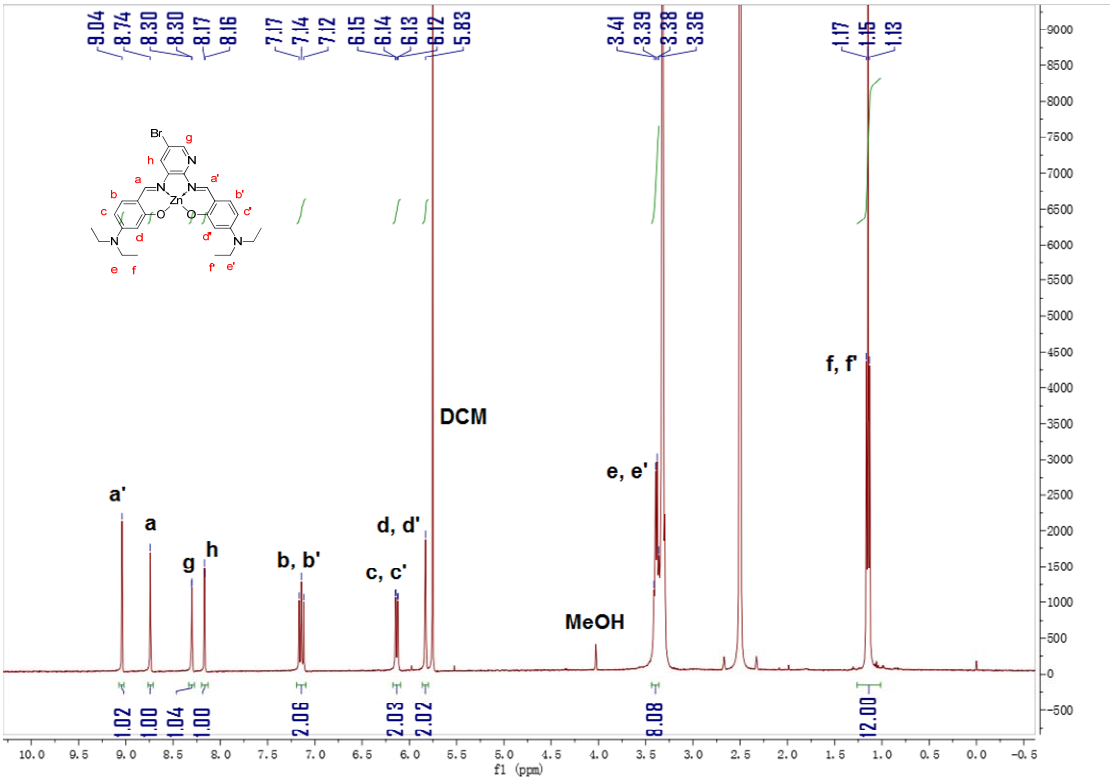
a10s4


9.52
8.84
7.88
7.86
7.35
7.30
7.10
7.08
6.57
6.48
6.37
6.34
6.32
3.66
3.65
3.64
3.63
3.51
3.49
3.47
3.46
3.44
2.96
2.93
2.41
2.34
2.33
2.32
py
H2O
a'
a
j
b, b'
k
c'
c
d, d'
f, f'
e, e'
i, i'
h, h'
g, g'
1.02
1.00
1.04
2.09
1.00
1.01
1.04
1.98
7.99
4.06
5.97
4.04
7.90
ppm

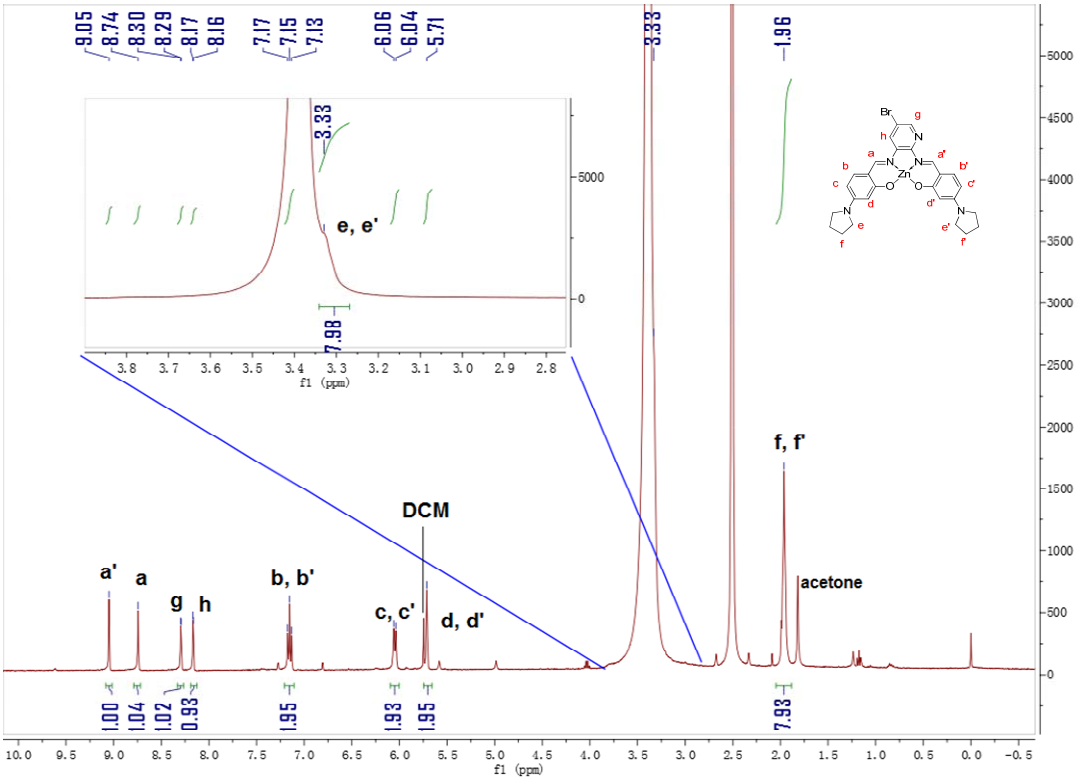
a10s10



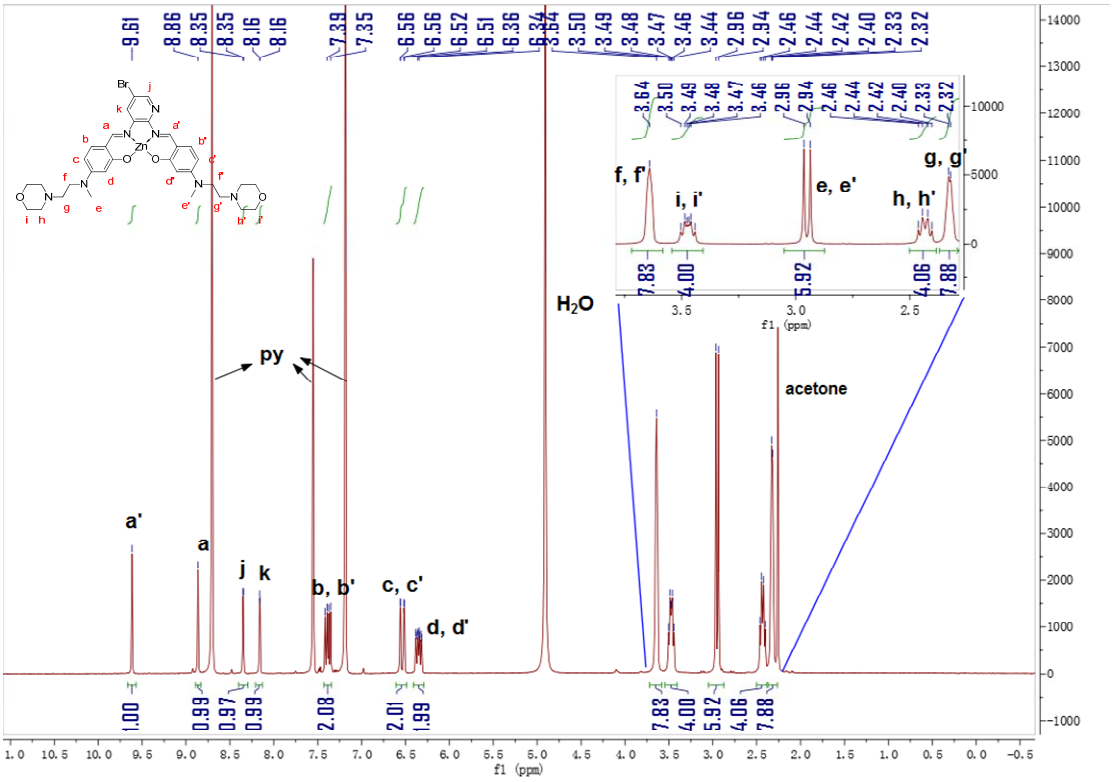
a11s1



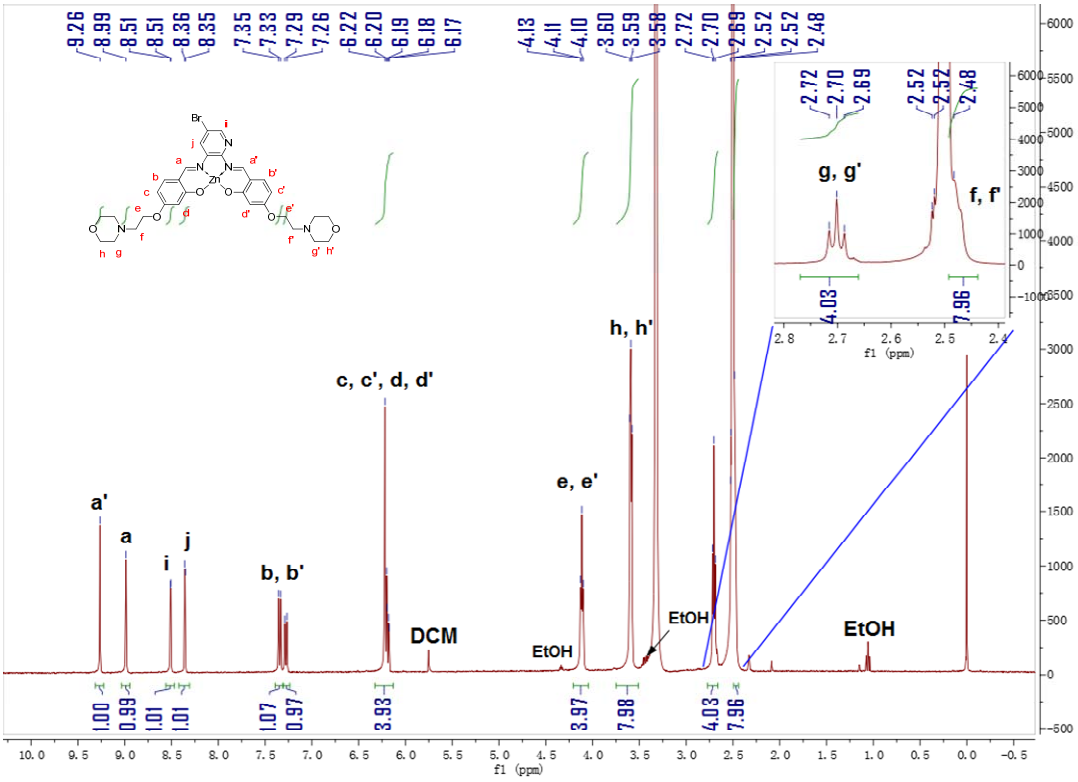
a11s3


9.05
8.74
8.30
8.29
8.17
8.16
7.17
7.15
7.13
6.06
6.04
5.71
3.33
1.96
e, e'
7.98
f, f'
DCM
a'
a
g
h
b, b'
c, c'
d, d'
acetone
1.00
1.04
1.02
0.93
1.95
1.93
1.95
7.93
f1 (ppm)

a11s4

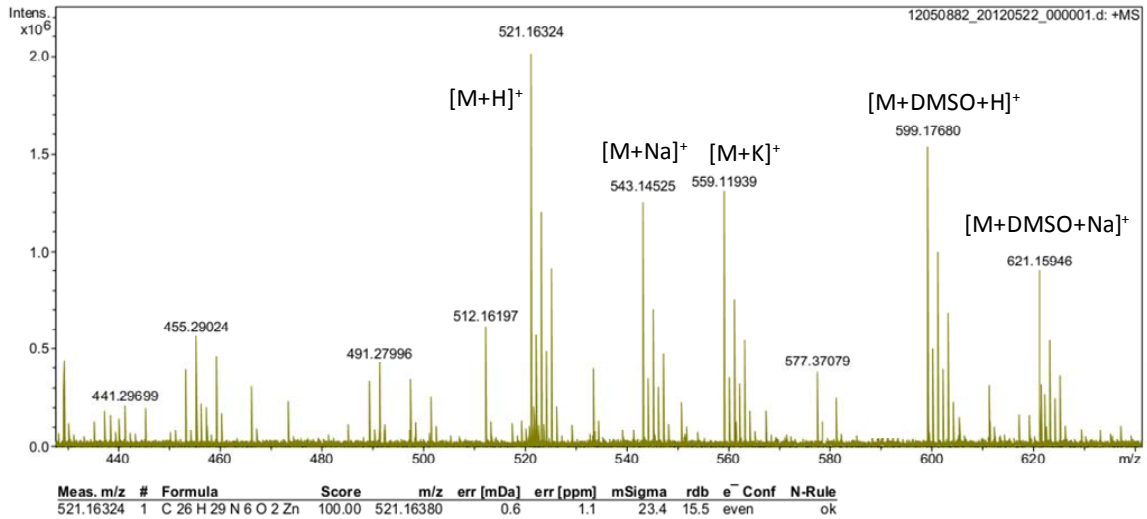

9.61
8.86
8.35
8.35
8.16
8.16
7.39
7.35
6.56
6.56
6.52
6.51
6.36
6.34
3.64
3.50
3.49
3.48
3.47
3.46
3.44
2.96
2.94
2.46
2.44
2.42
2.40
2.33
2.32
f, f'
i, i'
e, e'
h, h'
g, g'
7.83
4.00
5.92
4.06
7.88
H2O
py
acetone
a'
a
j
k
b, b'
c, c'
d, d'
1.00
0.99
0.97
0.99
2.08
2.01
1.99
7.83
4.00
5.92
4.06
7.88
f1 (ppm)

a11s10



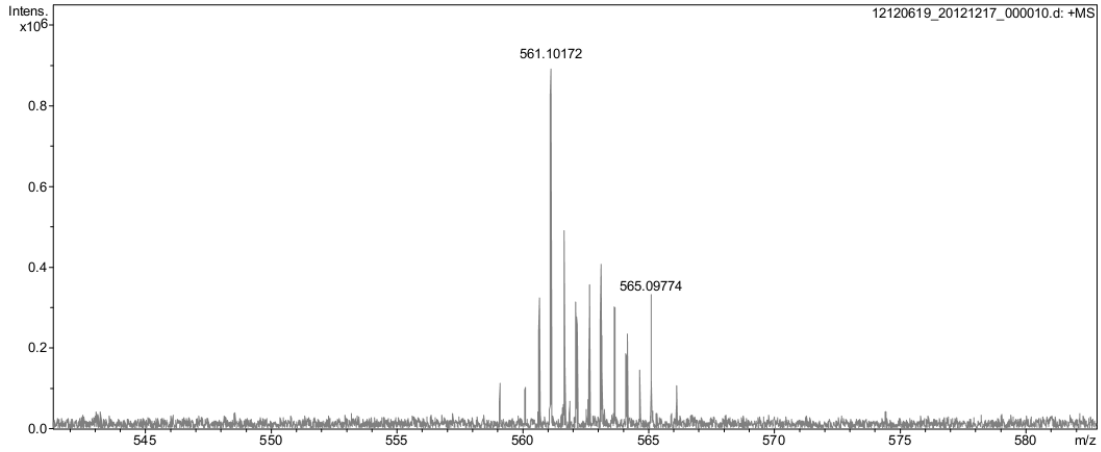
2.4.4 HR ESI MS Spectra of ZnSalen/Salophens

a1s1



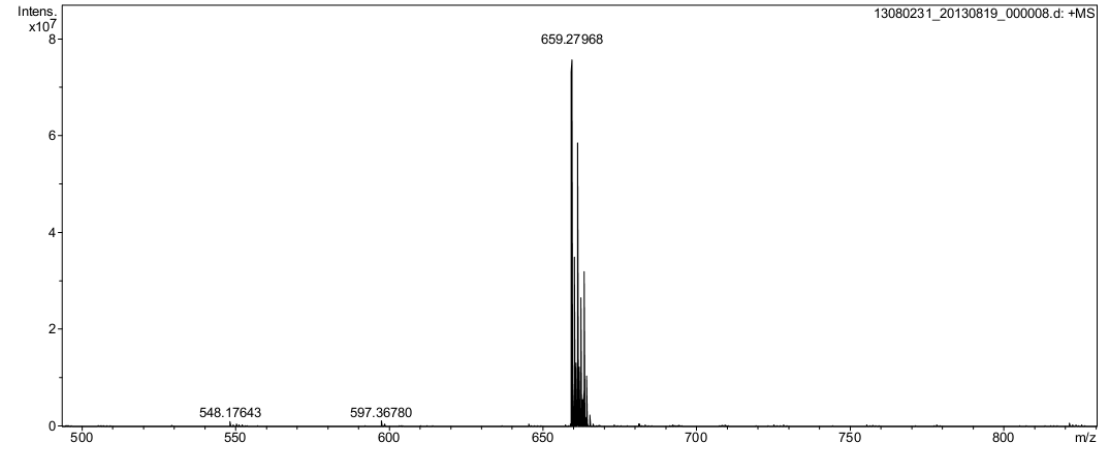
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
521.16324	1	C 26 H 29 N 6 O 2 Zn	100.00	521.16380	0.6	1.1	23.4	15.5	even	ok

a1s2



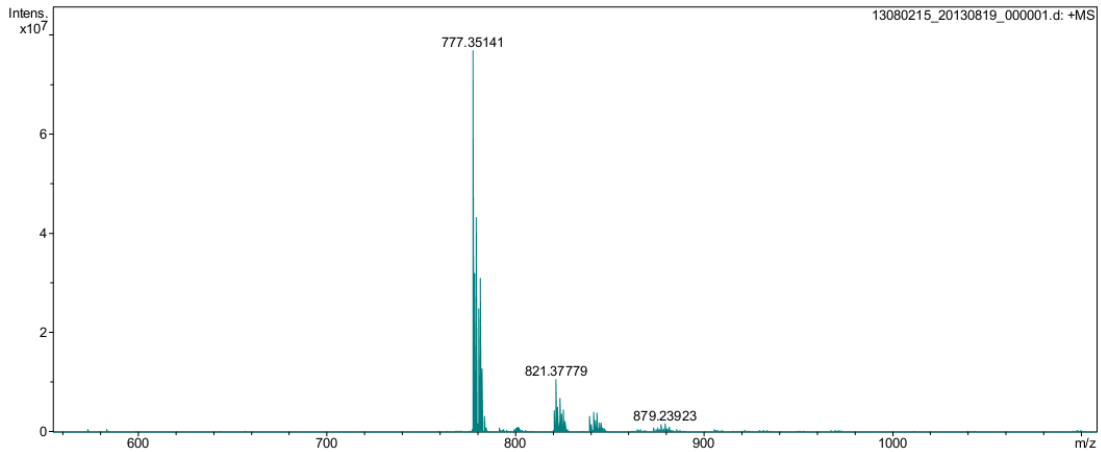
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
561.10172	1	C 30 H 21 N 6 O 2 Zn	100.00	561.10120	-0.5	-0.9	77.6	23.5	even	ok

a1s5



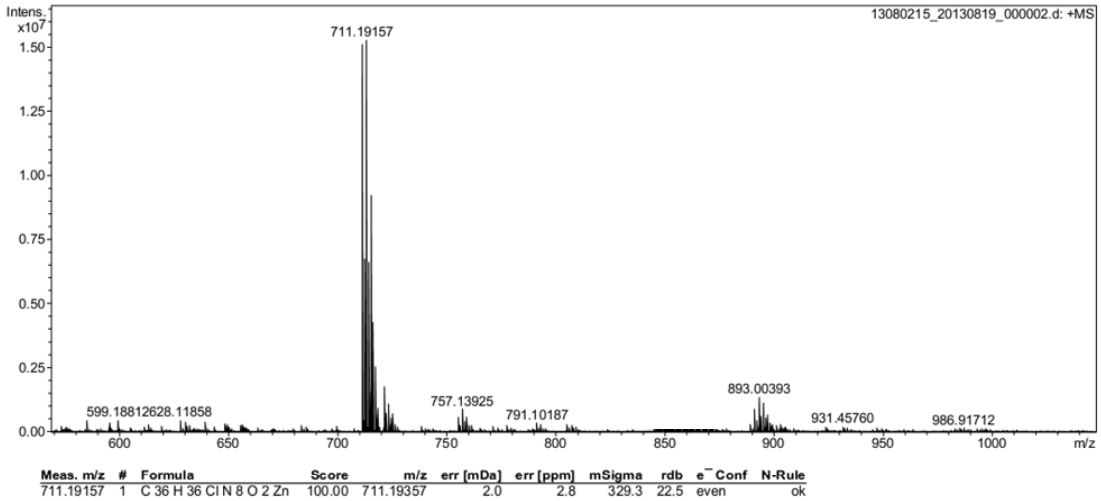
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
659.27968	1	C 34 H 43 N 8 O 2 Zn	100.00	659.27950	-0.2	-0.3	44.6	17.5	even	ok

a1s6



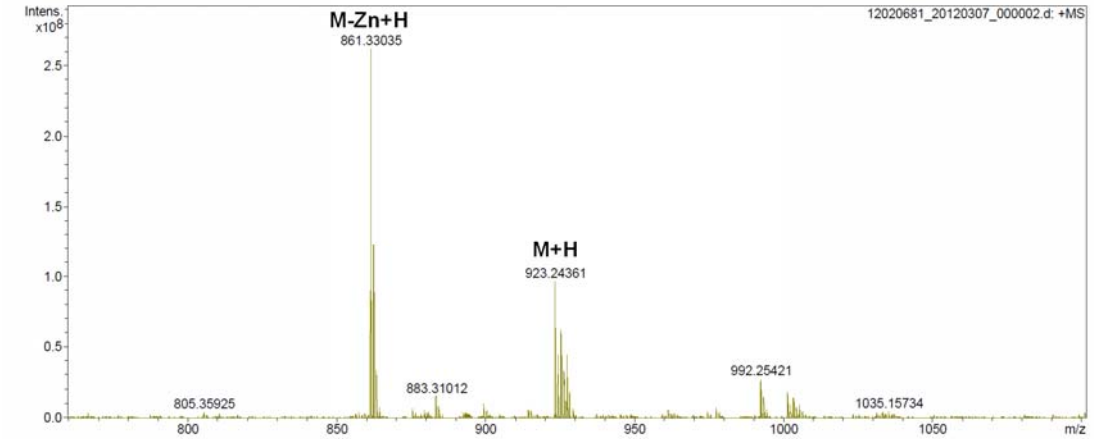
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
777.35141	1	C 38 H 53 N 10 O 4 Zn	100.00	777.35372	2.3	3.0	49.6	17.5	even	ok

a1s7



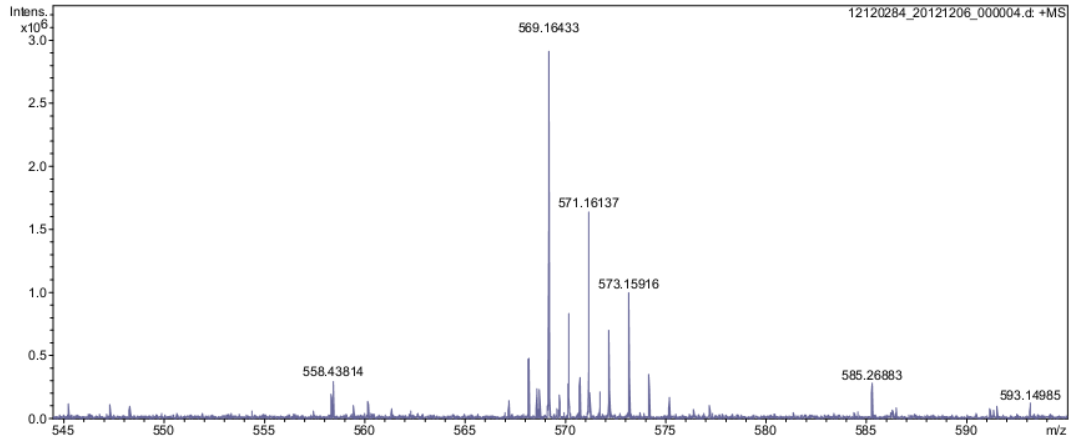
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
711.19157	1	C 36 H 36 Cl N 8 O 2 Zn	100.00	711.19357	2.0	2.8	329.3	22.5	even	ok

a1s8



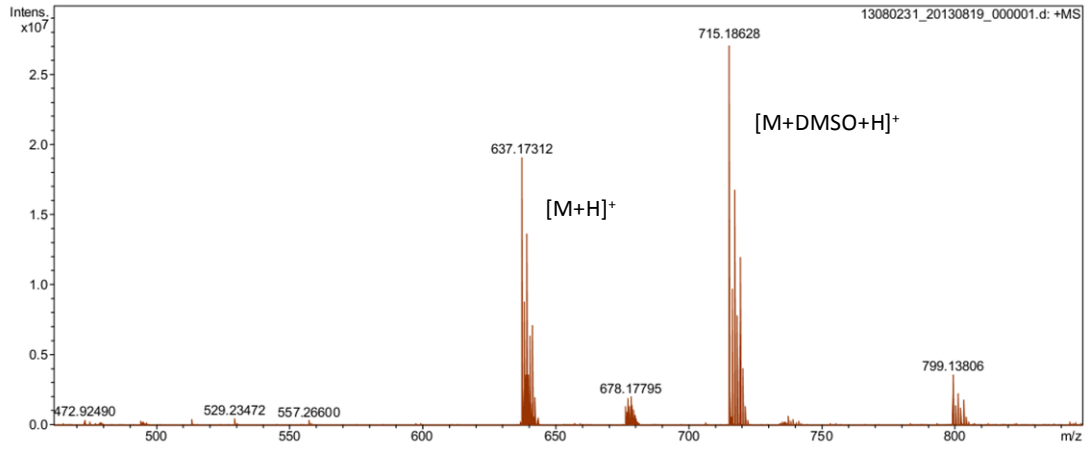
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
923.24361	1	C 38 H 43 N 12 O 12 Zn	100.00	923.24094	-2.7	-2.9	29.2	23.5	even	ok

a1s9



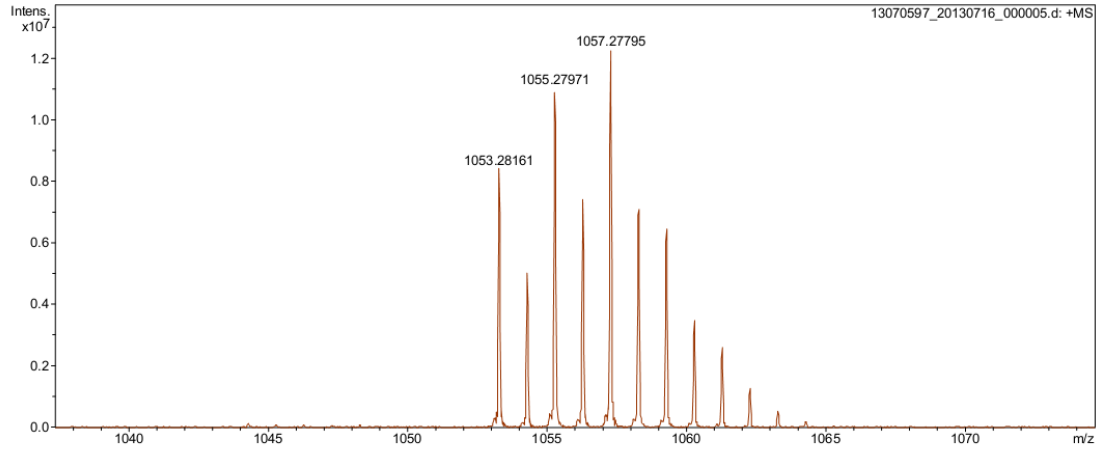
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
569.16433	1	C 30 H 29 N 6 O 2 Zn	100.00	569.16380	-0.5	-0.9	62.8	19.5	even	ok

a1s10



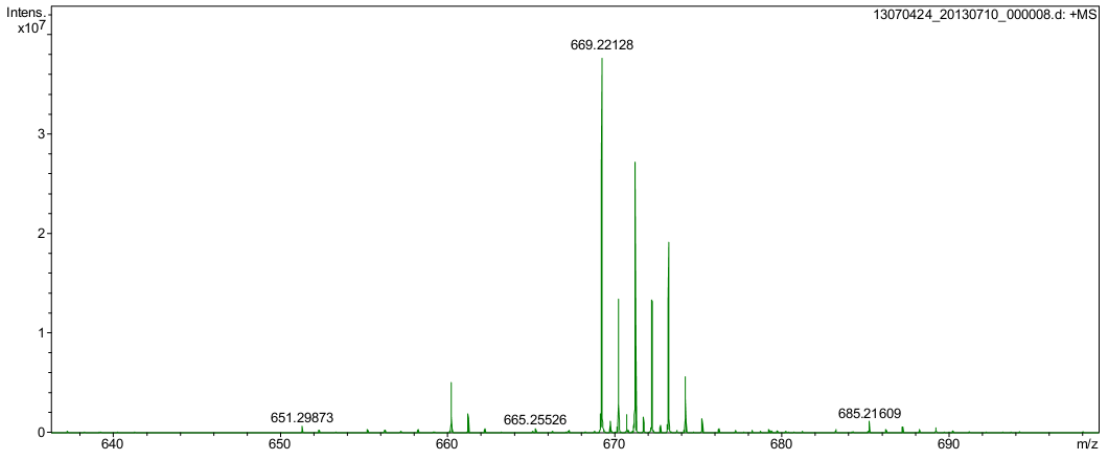
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
637.17312	1	C 30 H 33 N 6 O 6 Zn	100.00	637.17476	1.6	2.6	60.3	17.5	even	ok

a2s1



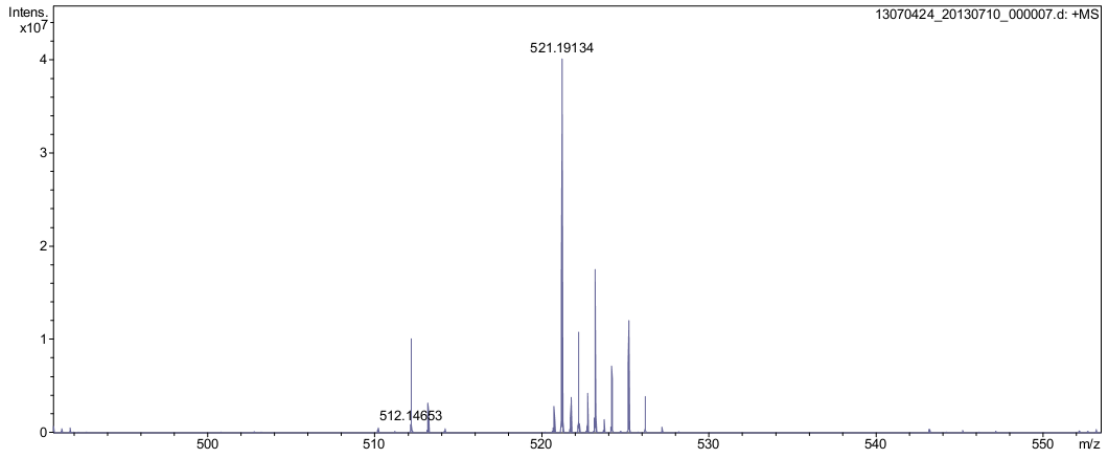
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1053.28161	1	C 52 H 61 N 8 O 4 S 2 Zn 2	100.00	1053.28346	1.9	1.8	22.8	26.5	even	ok

a2s3



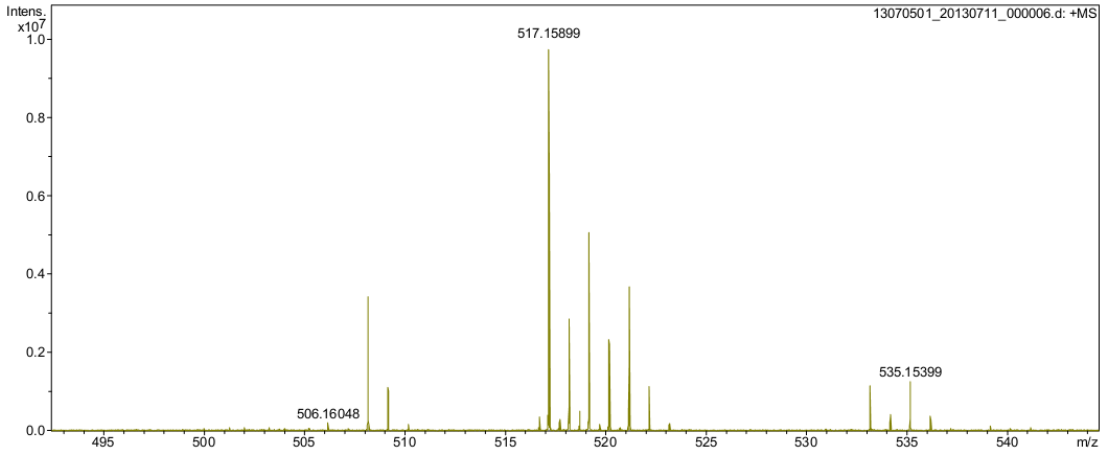
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
669.22128	1	C 32 H 41 N 6 O 4 S Zn	100.00	669.21960	-1.7	-2.5	20.6	15.5	even	ok

a3s1



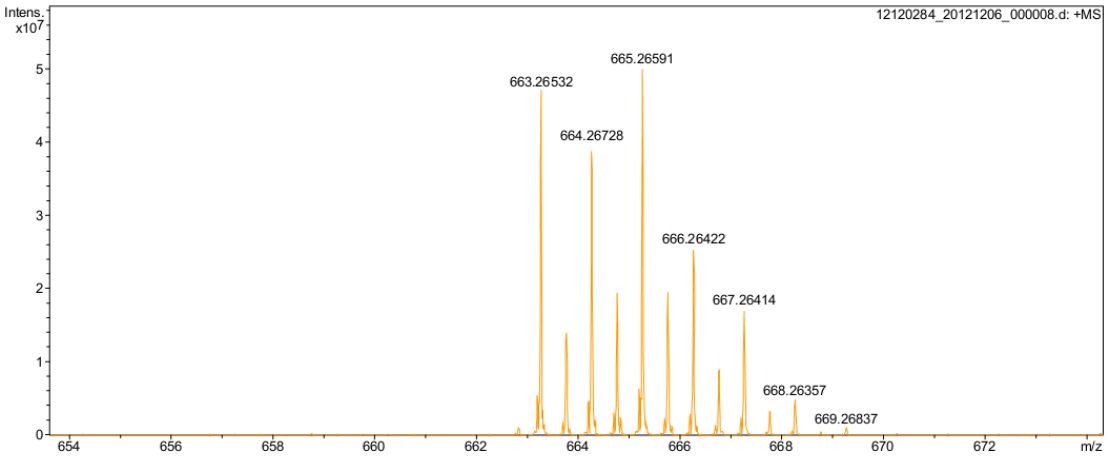
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
521.19134	1	C 28 H 33 N 4 O 2 Zn	100.00	521.18895	-2.4	-4.6	91.3	14.5	even	ok

a3s3



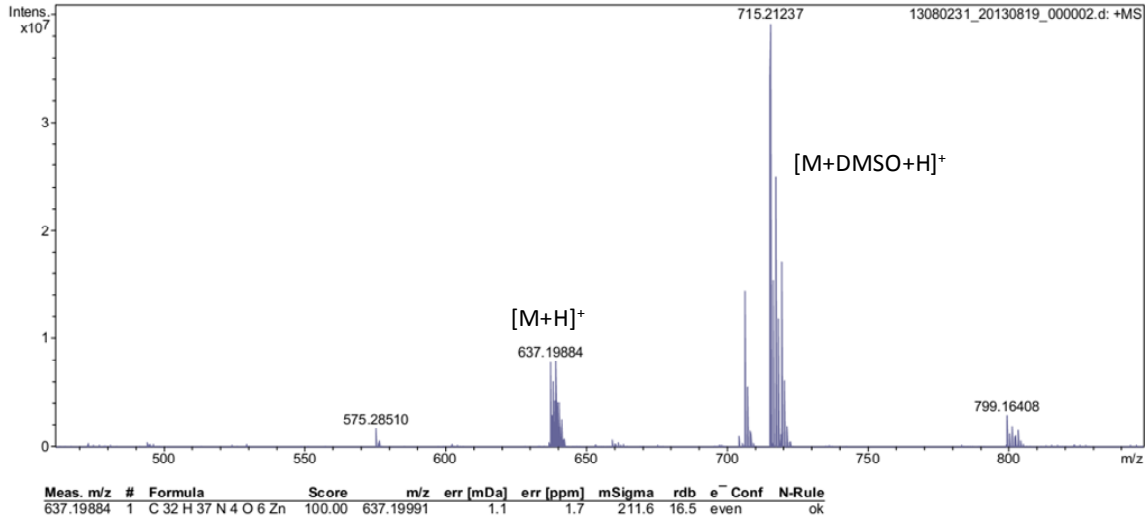
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
517.15899	1	C 28 H 29 N 4 O 2 Zn	100.00	517.15765	-1.3	-2.6	50.0	16.5	even	ok

a3s4



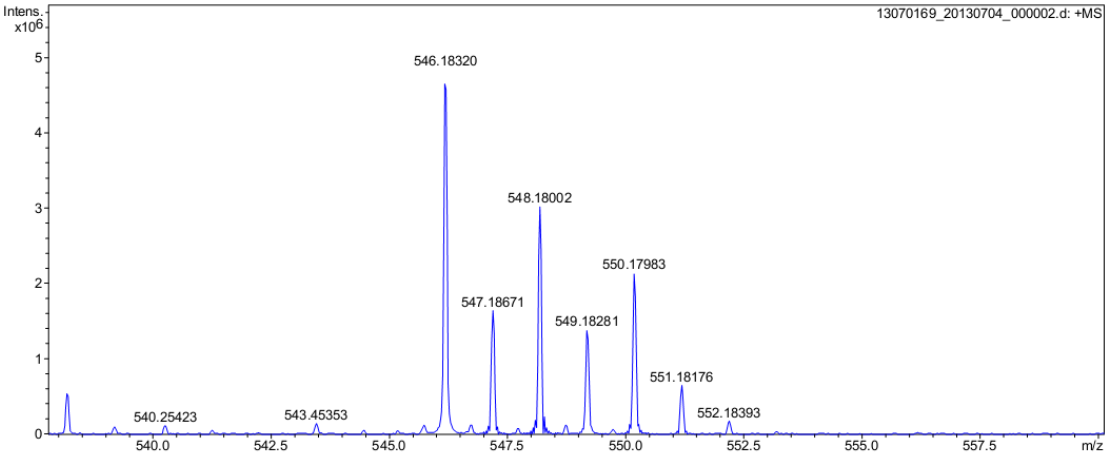
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
663.26532	1	C 34 H 43 N 6 O 4 Zn	100.00	663.26318	-2.1	-3.2	204.6	16.5	even	ok

a3s10



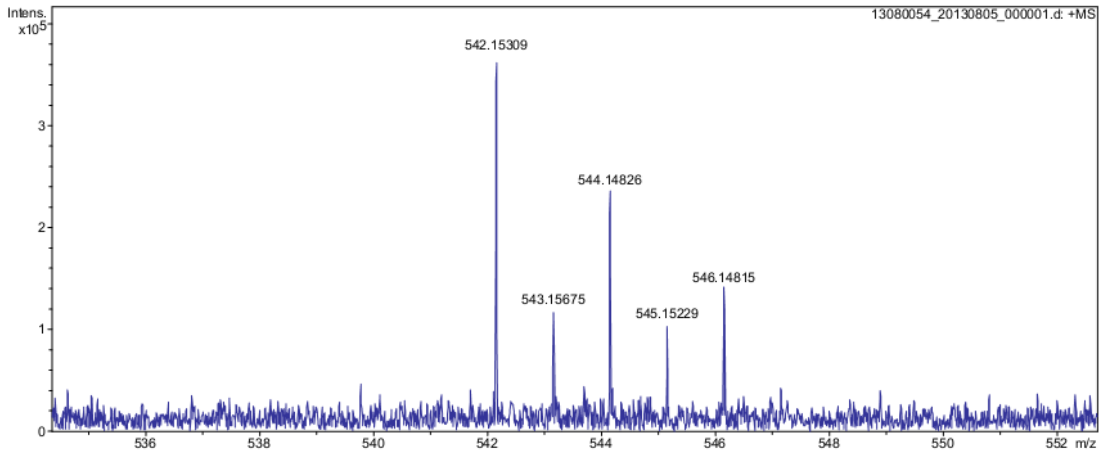
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
637.19884	1	C 32 H 37 N 4 O 6 Zn	100.00	637.19991	1.1	1.7	211.6	16.5	even	ok

a4s1



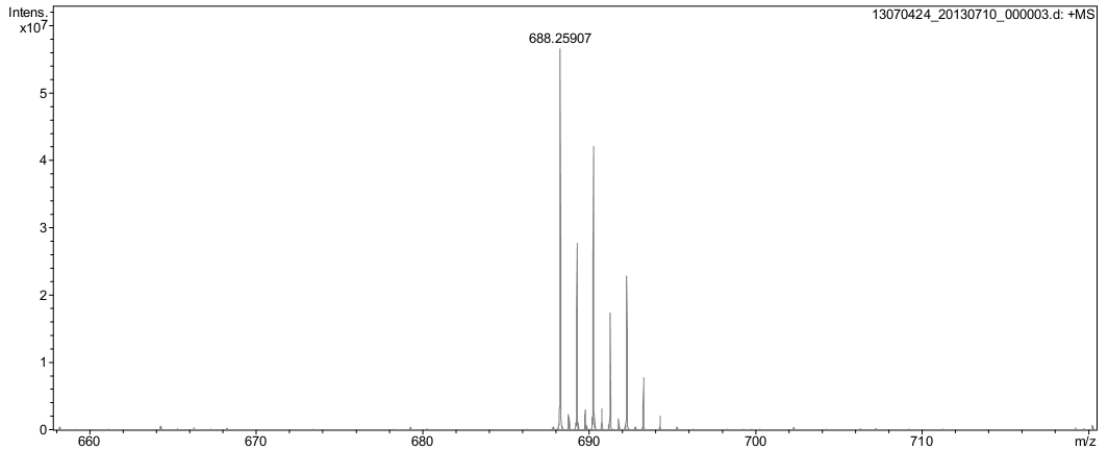
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
546.18320	1	C 29 H 32 N 5 O 2 Zn	100.00	546.18420	1.0	1.8	5.0	16.5	even	ok

a4s3



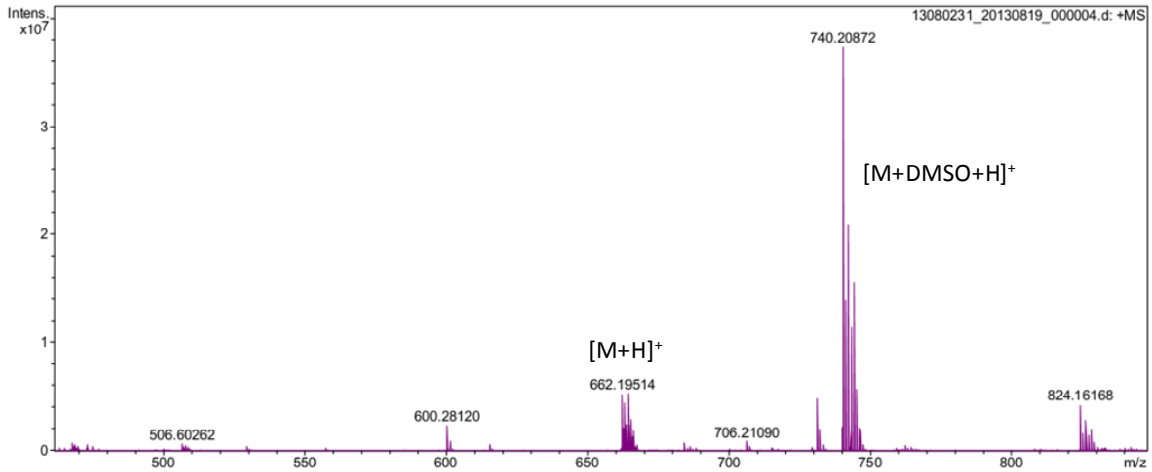
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
542.15309	1	C 29 H 28 N 5 O 2 Zn	100.00	542.15290	-0.2	-0.3	55.0	18.5	even	ok

a4s4



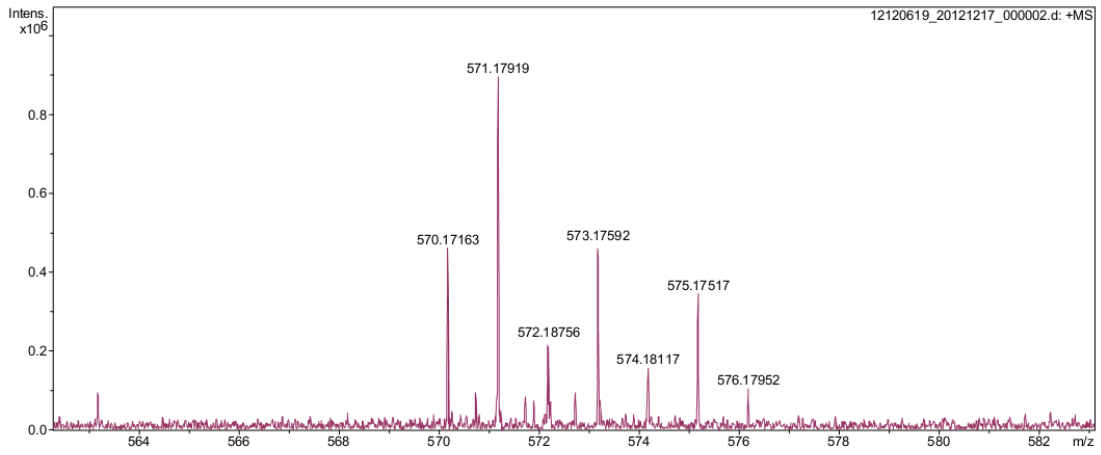
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
688.25907	1	C 35 H 42 N 7 O 4 Zn	100.00	688.25843	-0.6	-0.9	57.0	18.5	even	ok

a4s10



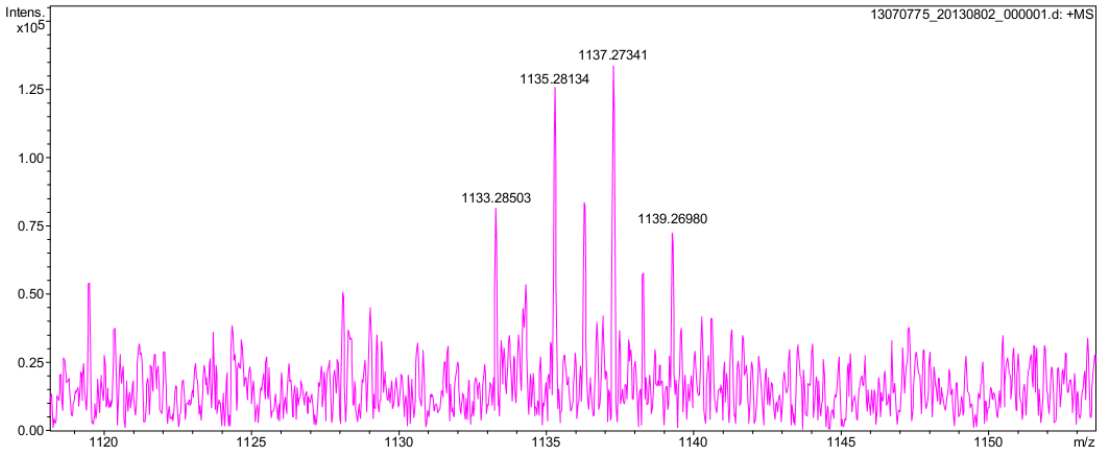
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
662.19514	1	C 33 H 36 N 5 O 6 Zn	100.00	662.19516	0.0	0.0	218.8	18.5	even	ok

a5s1



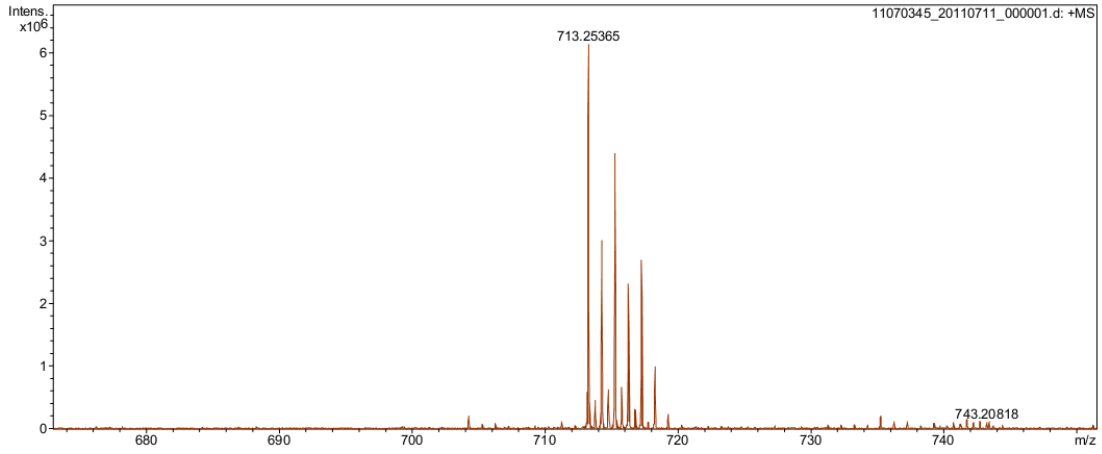
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
571.17919	1	C 30 H 31 N 6 O 2 Zn	100.00	571.17945	0.3	0.5	70.9	18.5	even	ok

a5s3



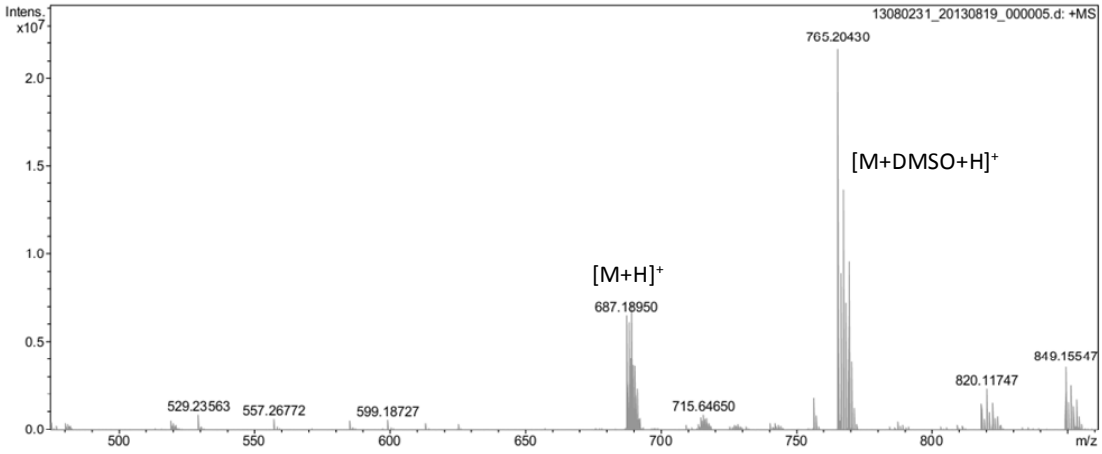
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1133.28503	1	C 60 H 53 N 12 O 4 Zn 2	100.00	1133.28902	4.0	3.5	258.8	40.5	even	ok

a5s4



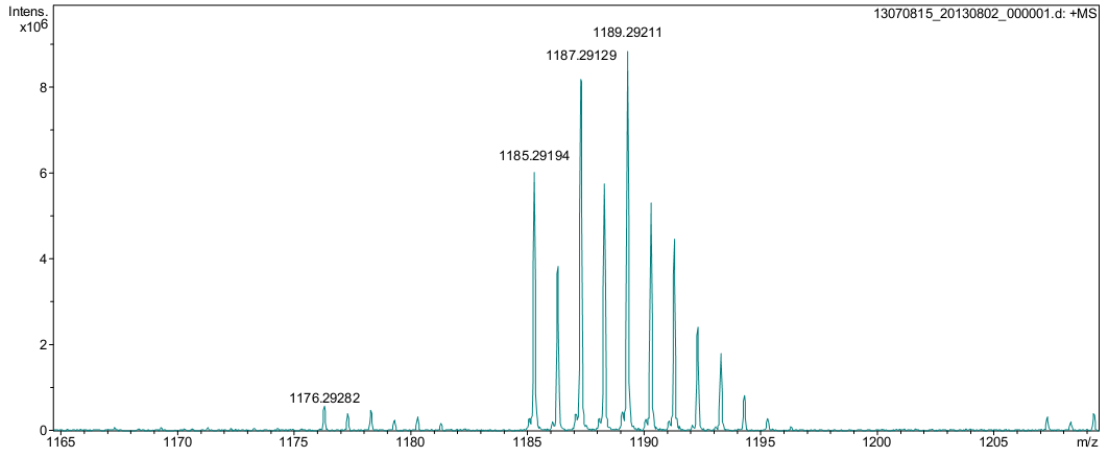
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
713.25365	1	C 36 H 41 N 8 O 4 Zn	100.00	713.25367	0.0	0.0	38.0	20.5	even	ok

a5s10



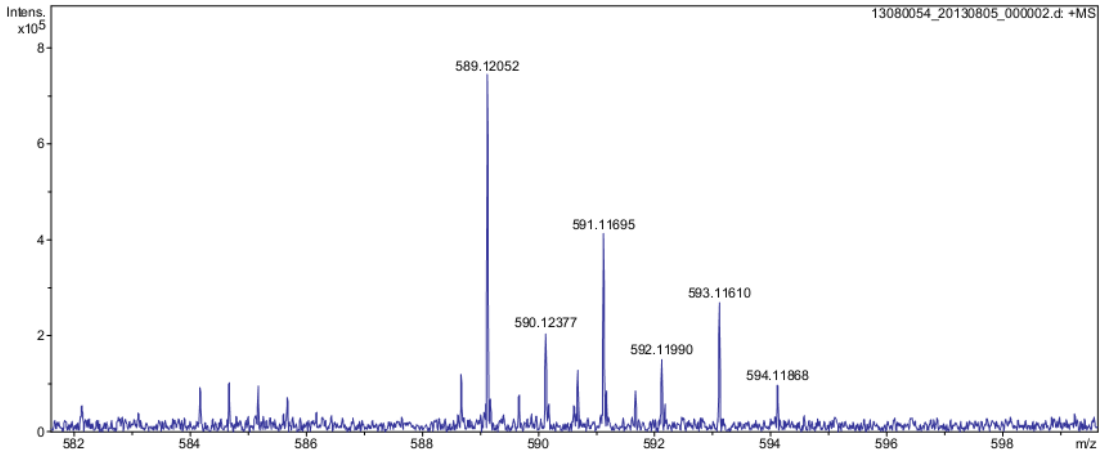
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
687.18950	1	C 34 H 35 N 6 O 6 Zn	100.00	687.19041	0.9	1.3	321.3	20.5	even	ok

a6s1



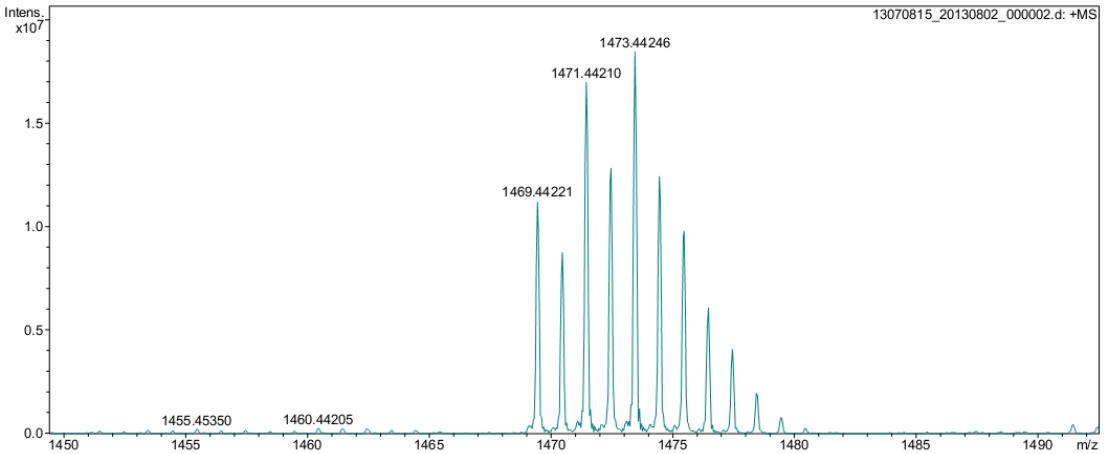
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1185.29194	1	C 56 H 57 F 8 N 8 O 4 Zn 2	100.00	1185.29525	3.3	2.8	18.6	28.5	even	ok

a6s3



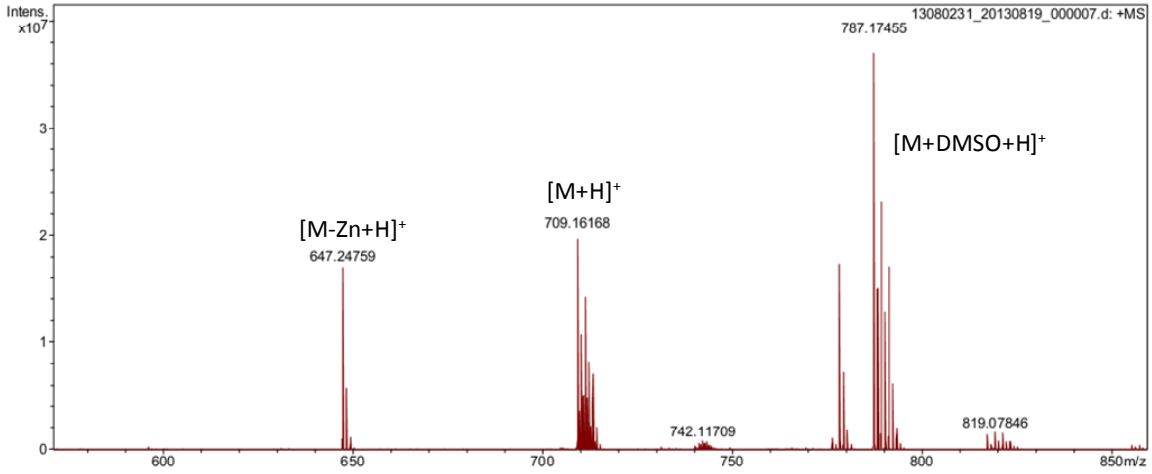
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
589.12052	1	C 28 H 25 F 4 N 4 O 2 Zn	100.00	589.11996	-0.6	-0.9	46.9	16.5	even	ok

a6s4



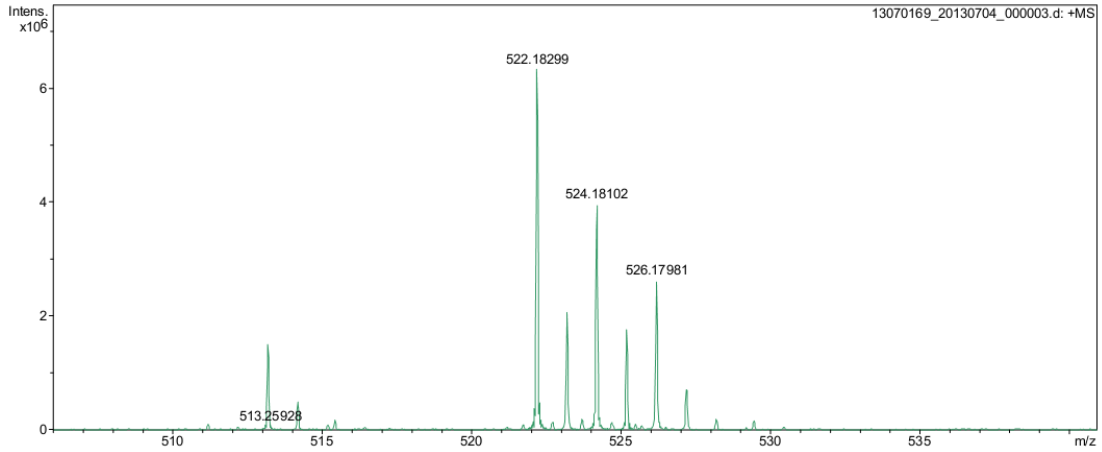
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1469.44221	1	C 68 H 77 F 8 N 12 O 8 Zn 2	100.00	1469.44370	1.5	1.0	16.2	32.5	even	ok

a6s10



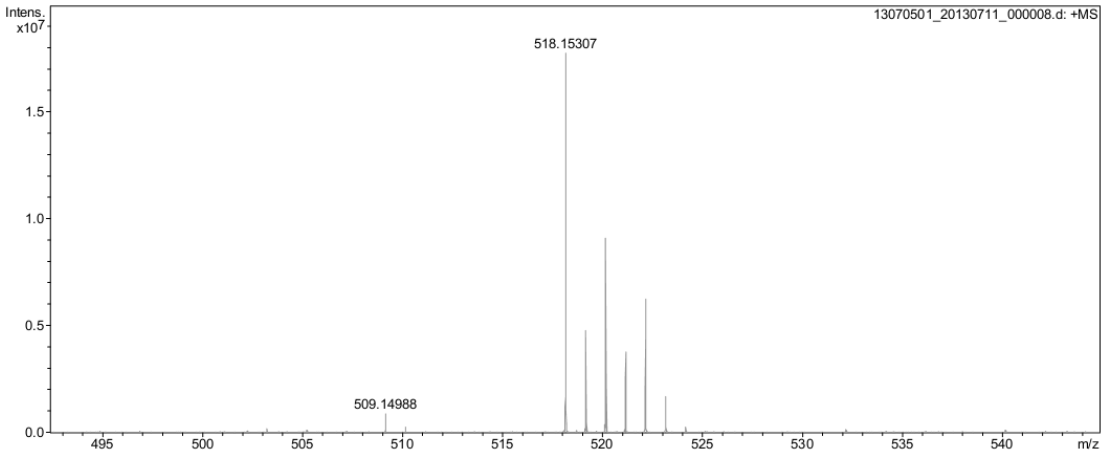
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
709.16168	1	C 32 H 33 F 4 N 4 O 6 Zn	100.00	709.16222	0.5	0.8	84.4	16.5	even	ok

a7s1



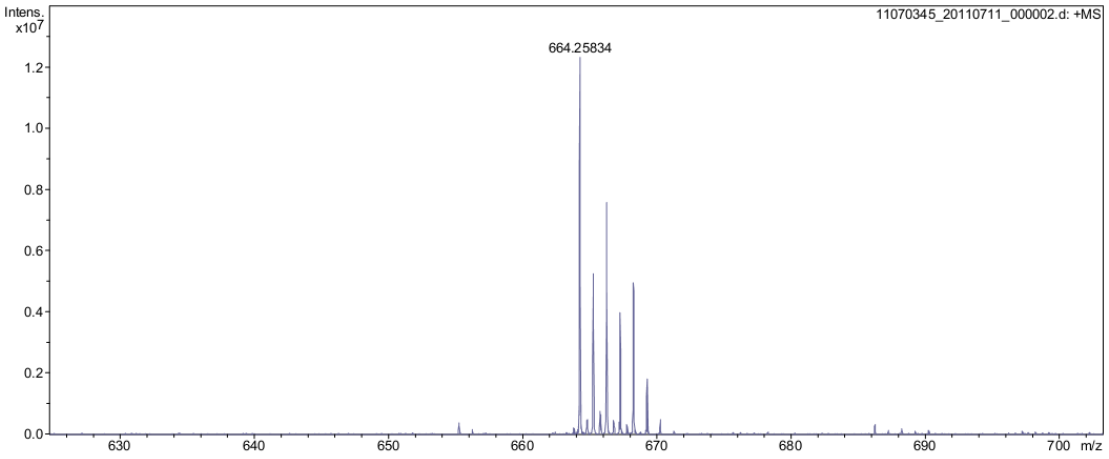
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
522.18299	1	C 27 H 32 N 5 O 2 Zn	100.00	522.18420	1.2	2.3	11.6	14.5	even	ok

a7s3



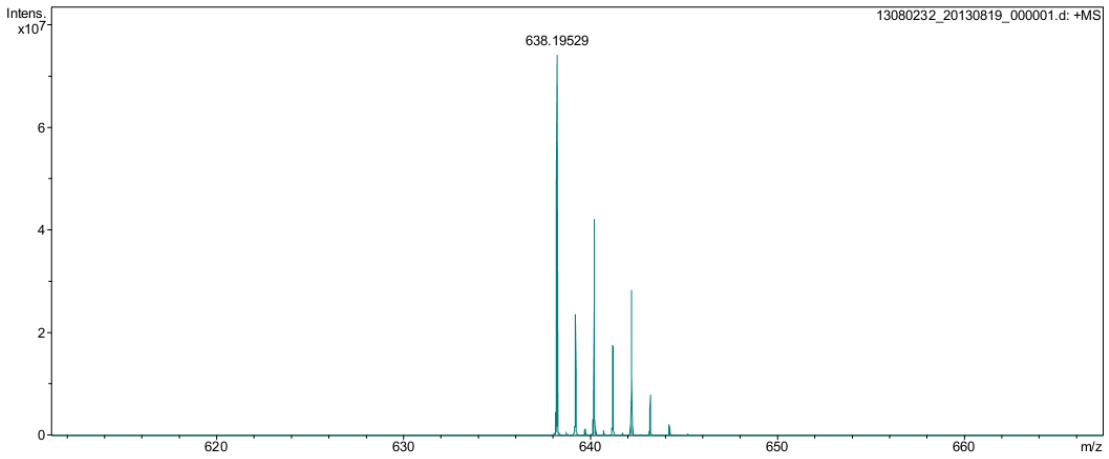
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
518.15307	1	C 27 H 28 N 5 O 2 Zn	100.00	518.15290	-0.2	-0.3	55.6	16.5	even	ok

a7s4



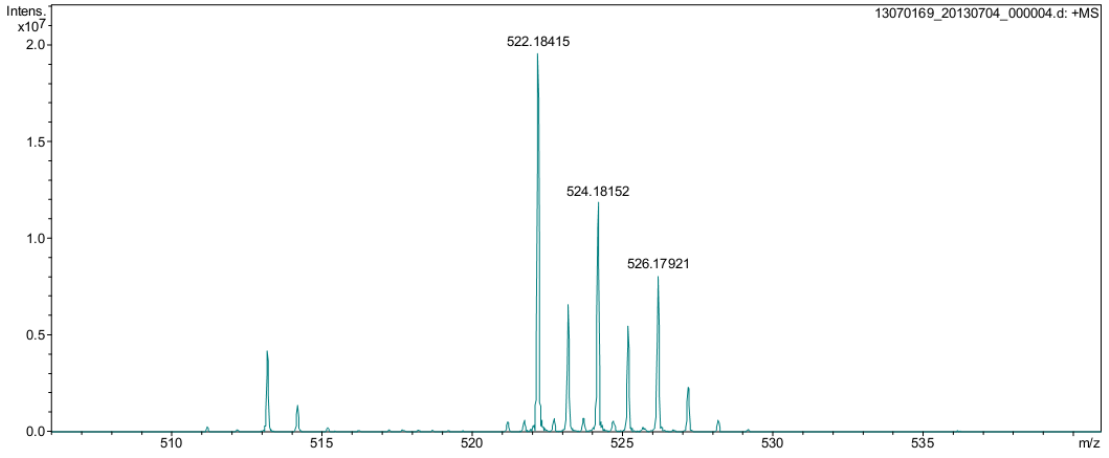
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
664.25834	1	C 33 H 42 N 7 O 4 Zn	100.00	664.25843	0.1	0.1	26.6	16.5	even	ok

a7s10



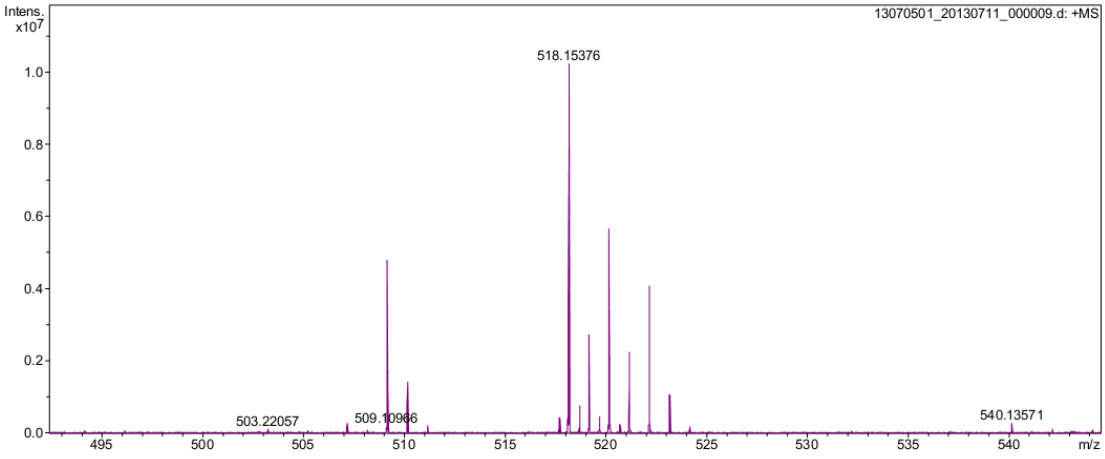
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
638.19529	1	C 31 H 36 N 5 O 6 Zn	100.00	638.19516	-0.1	-0.2	48.4	16.5	even	ok

a8s1



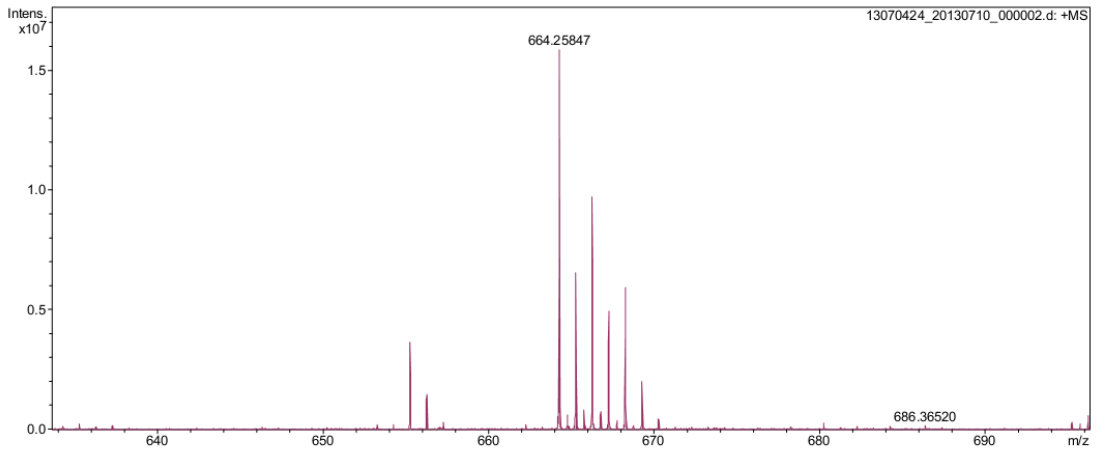
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
522.18415	1	C 27 H 32 N 5 O 2 Zn	100.00	522.18420	0.0	0.1	13.4	14.5	even	ok

a8s3



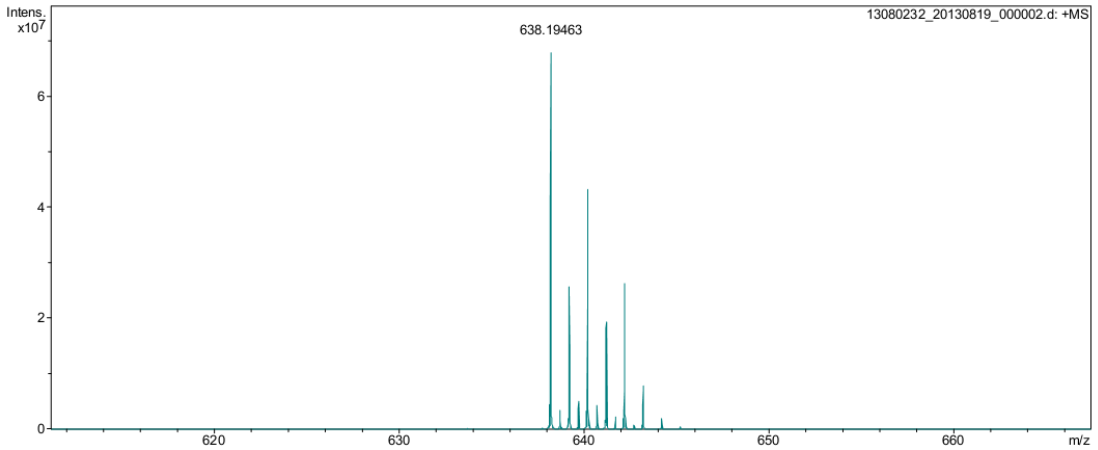
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
518.15376	1	C 27 H 28 N 5 O 2 Zn	100.00	518.15290	-0.9	-1.7	35.5	16.5	even	ok

a8s4



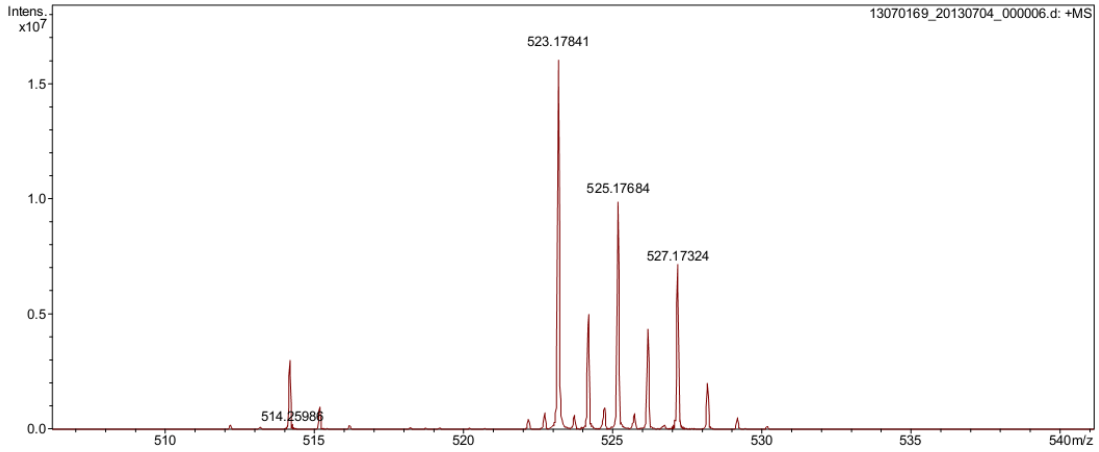
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
664.25847	1	C 33 H 42 N 7 O 4 Zn	100.00	664.25843	-0.0	-0.1	36.1	16.5	even	ok

a8s10



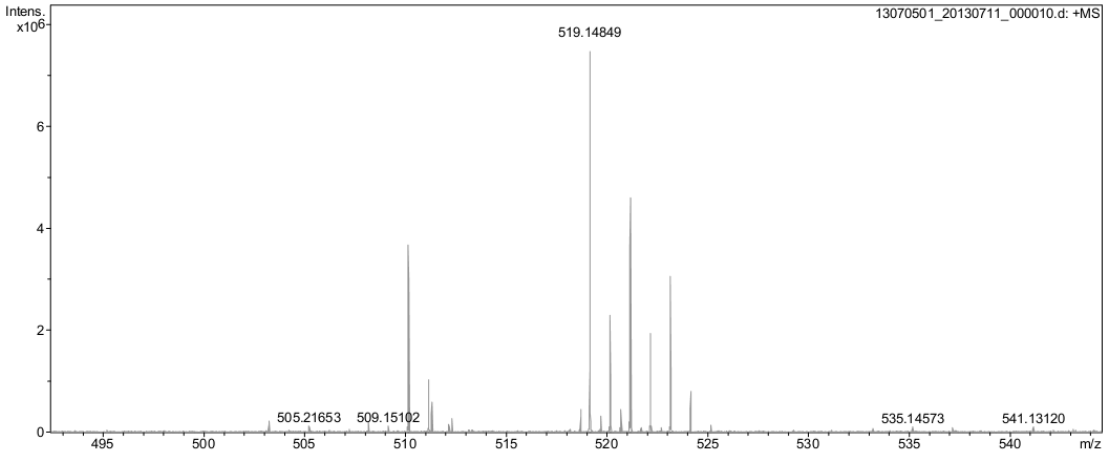
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
638.19463	1	C 31 H 36 N 5 O 6 Zn	100.00	638.19516	0.5	0.8	34.2	16.5	even	ok

a9s1



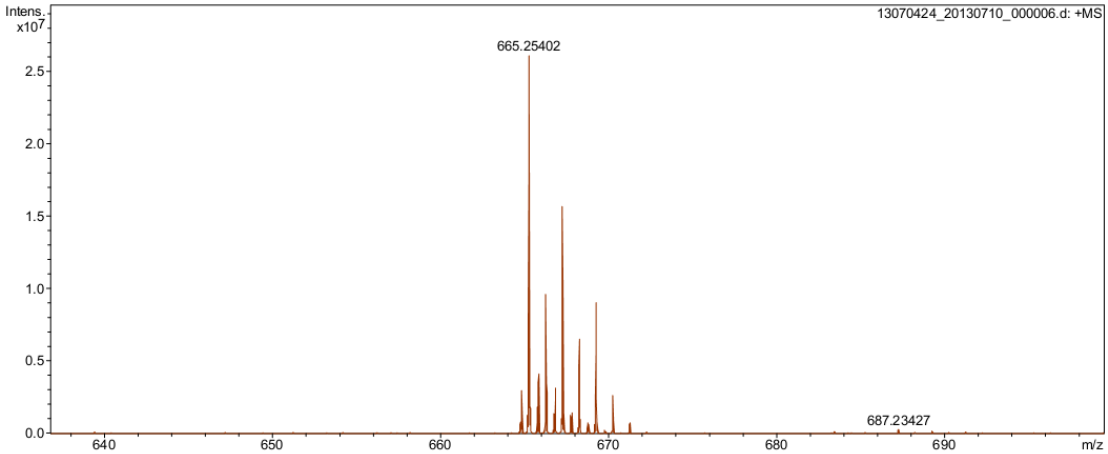
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
523.17841	1	C 26 H 31 N 6 O 2 Zn	100.00	523.17945	1.0	2.0	4.9	14.5	even	ok

a9s3



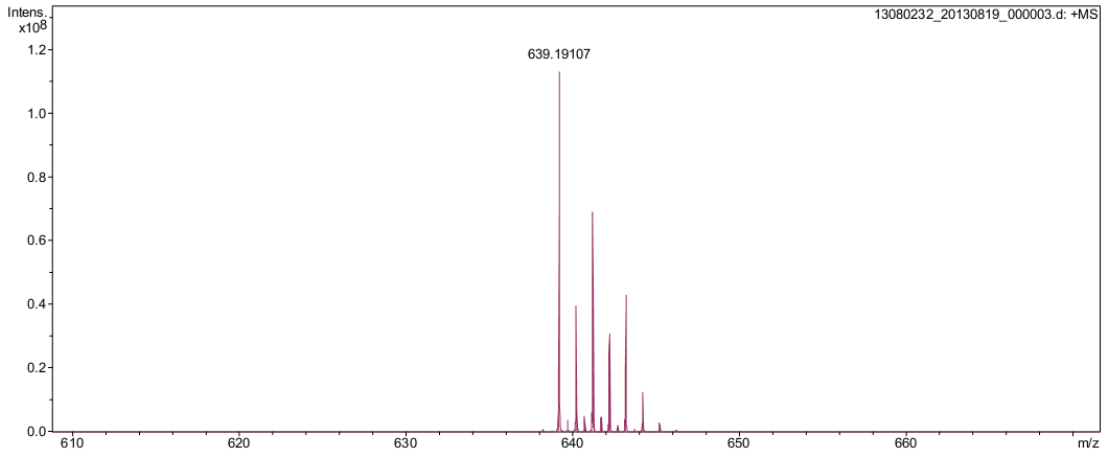
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
519.14849	1	C 26 H 27 N 6 O 2 Zn	100.00	519.14815	-0.3	-0.7	17.6	16.5	even	ok

a9s4



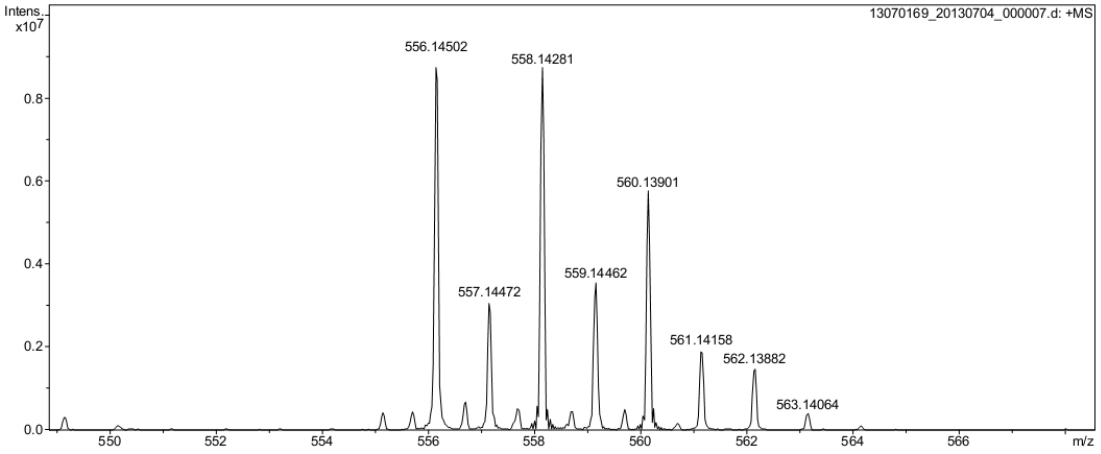
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
665.25402	1	C 32 H 41 N 8 O 4 Zn	100.00	665.25367	-0.3	-0.5	50.4	16.5	even	ok

a9s10



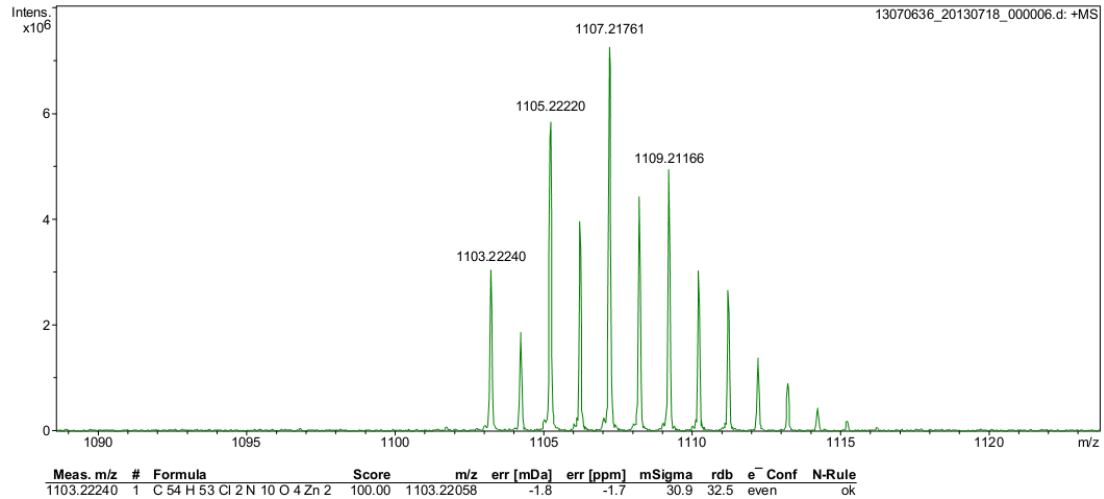
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
639.19107	1	C 30 H 35 N 6 O 6 Zn	100.00	639.19041	-0.7	-1.0	36.6	16.5	even	ok

a10s1



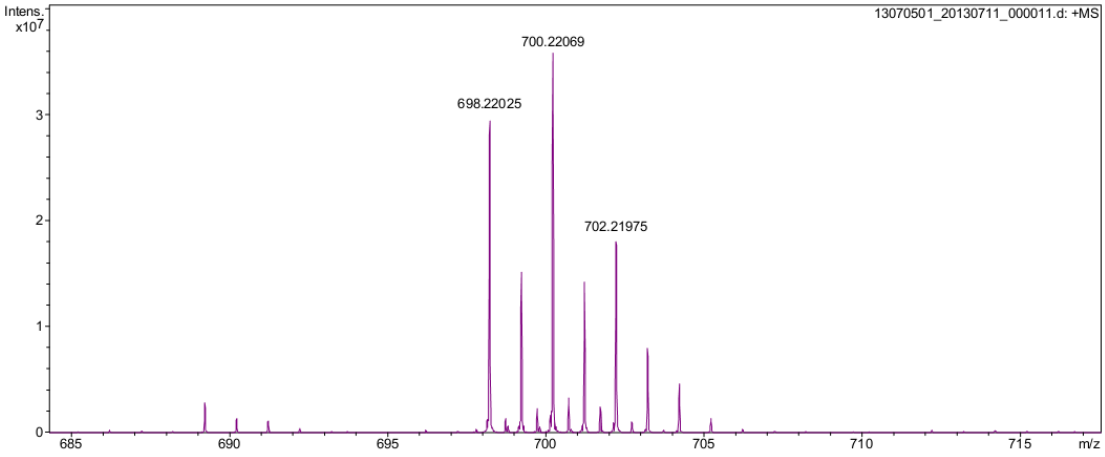
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
556.14502	1	C 27 H 31 Cl N 5 O 2 Zn	100.00	556.14523	0.2	0.4	15.9	14.5	even	ok

a10s3



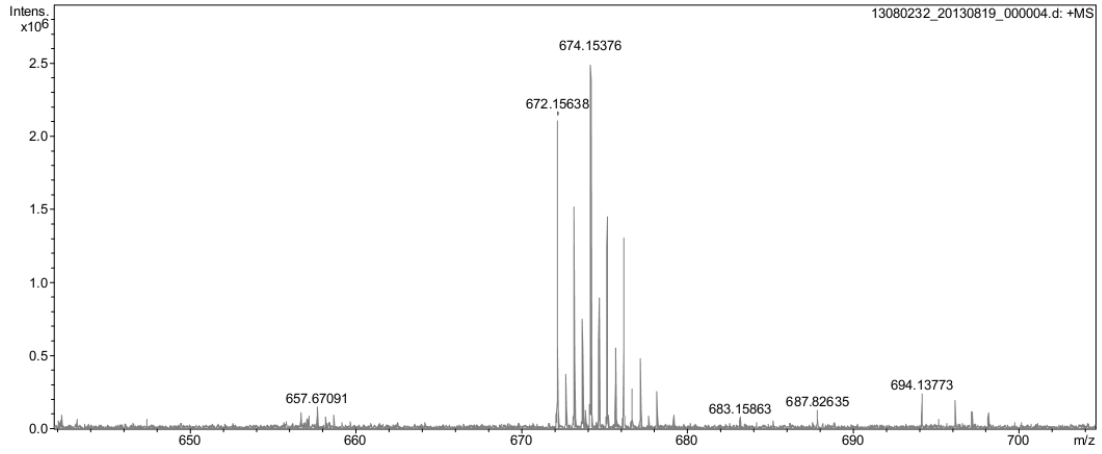
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1103.22240	1	C 54 H 53 Cl 2 N 10 O 4 Zn 2	100.00	1103.22058	-1.8	-1.7	30.9	32.5	even	ok

a10s4



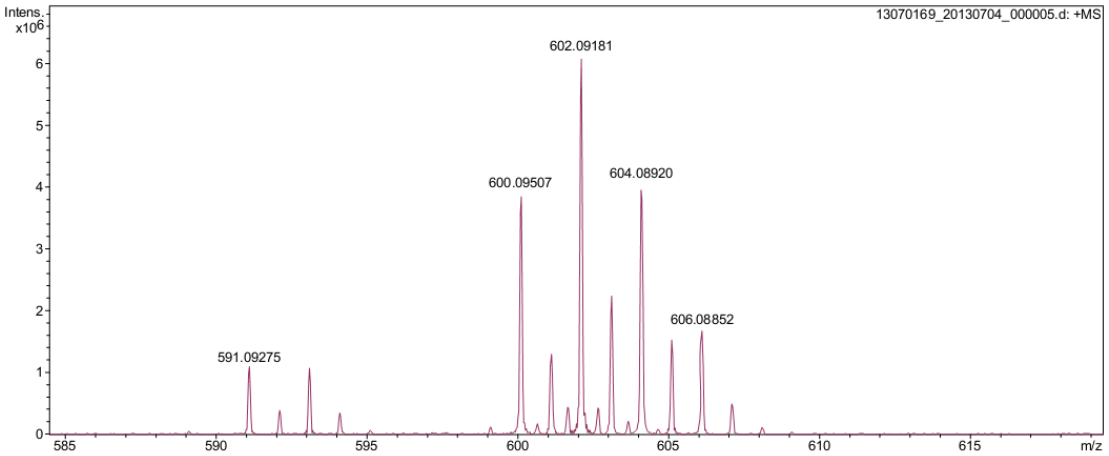
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
698.22025	1	C 33 H 41 Cl N 7 O 4 Zn	100.00	698.21945	-0.8	-1.1	82.1	16.5	even	ok

a10s10



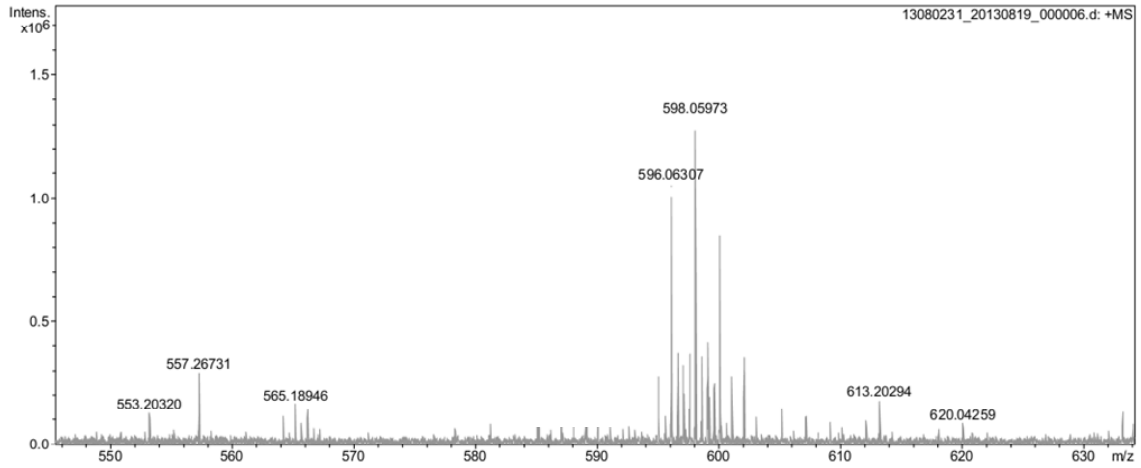
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
672.15638	1	C 31 H 35 Cl N 5 O 6 Zn	100.00	672.15618	-0.2	-0.3	127.0	16.5	even	ok

a11s1



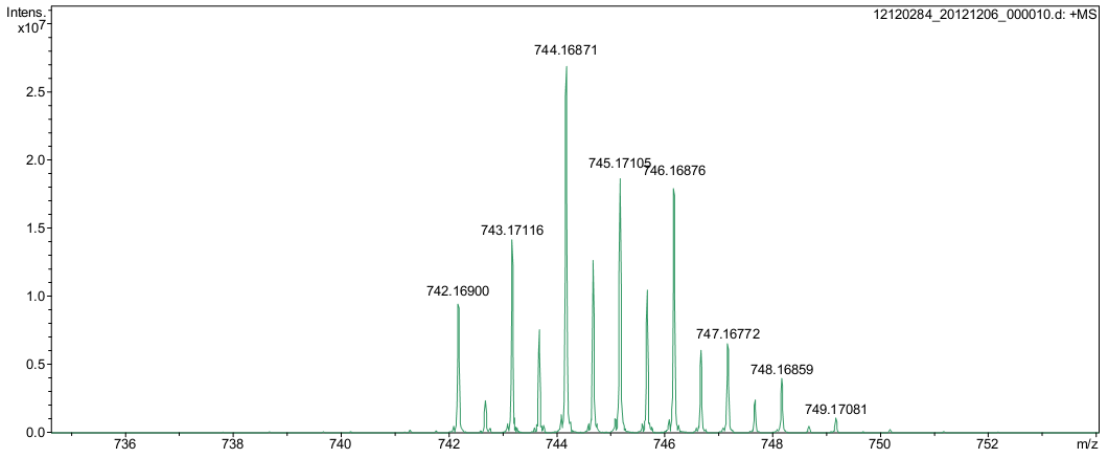
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
600.09507	1	C 27 H 31 Br N 5 O 2 Zn	100.00	600.09471	-0.4	-0.6	8.3	14.5	even	ok

a11s3



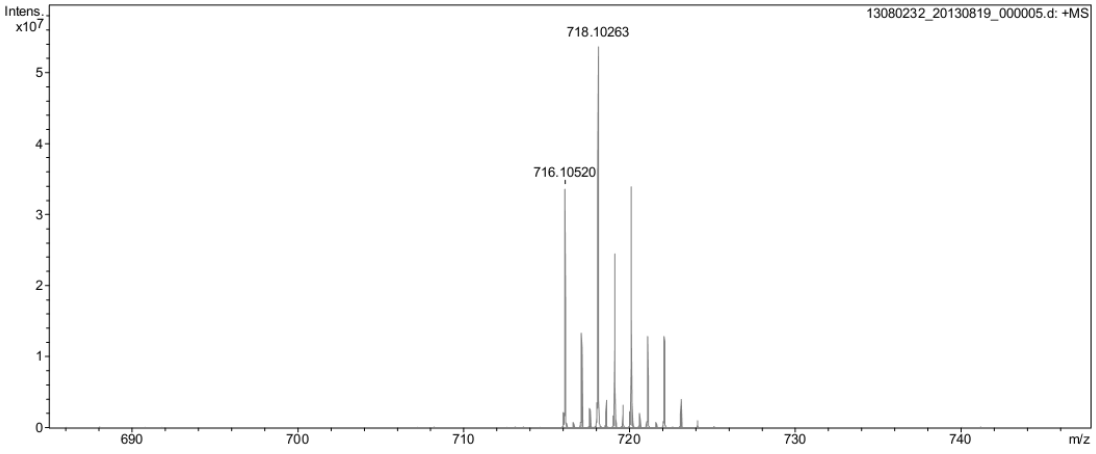
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
596.06307	1	C 27 H 27 Br N 5 O 2 Zn	100.00	596.06341	0.3	0.6	52.1	16.5	even	ok

a11s4



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
742.16900	1	C 33 H 41 Br N 7 O 4 Zn	100.00	742.16894	-0.1	-0.1	158.9	16.5	even	ok

a11s10



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
716.10520	1	C 31 H 35 Br N 5 O 6 Zn	100.00	716.10567	0.5	0.7	33.1	16.5	even	ok

3 Photophysical properties

3.1 Determination of the fluorescence quantum yield of ZnSalen/Salophens

Quantum yields of one-photon emission of synthesized ZnSalen/Salophens were measured with Rhodamine B (RhB, dissolved in ethanol, for λ_{emi} of ZnSalen/Salophen above 600nm) or fluorescein (FLS, dissolved in 0.1M NaOH aqueous solution, for λ_{emi} of ZnSalen/Salophen from 490nm to 560nm) as reference. The one photon fluorescence measurements were performed in 1cm quartz cells with 1 μM compound in DMSO or DCM on a fluorescence lifetime and steady state spectrophotometer (Edinburgh Instrument FLS920) equipped 450 W Xenon light, slits 2.5×2.5. The values of fluorescence quantum yield, Φ (sample), were calculated according to equation as following[4]:

$$\Phi_{sample} = \Phi_{ref} \cdot \frac{OD_{ref} \cdot I_{sample} \cdot d^2_{sample}}{OD_{sample} \cdot I_{ref} \cdot d^2_{ref}} \quad (1)$$

Φ_{ref} : The values of fluorescence quantum yield of the reference. Φ_{RhB} =0.65, Φ_{FLS} =0.92.[5]

I: integrated emission intensity.
OD: optical density at the excitation wavelength.

d: the refractive index of solvents. d_{DMSO} = 1.478, d_{DCM} = 1.444, d_{H_2O} =1.333, d_{EtOH} = 1.361.

3.2 Determination of the two-photon absorption cross section of a1s1, a3s1-a11s1 and a1s10.

The two-photon absorption spectra of **a1s1, a3s1-a11s1** and **a1s10** were determined over a broad spectral region (740nm to 860nm) by the typical two-photon induced fluorescence method relative to Rhodamine B as standard. The two-photon fluorescence data were acquired using a Tsunami femtosecond Ti: Sapphire laser (pulse width ≤100fs, 80 MHz repetition rate, tuning range 710–880 nm Spectra Physics Inc., USA). The two-photon fluorescence measurements were performed in a 1cm quartz cell with 1×10^{-4} mol/L sample dissolved in DMSO and the excitation power density is set to be 100 mW. The two-photon absorption cross section of **a1s1, a3s1-a11s1** and **a1s10** (δ_{sample}) was calculated at every 10nm wavelength from 740nm to 860nm according to equation as following:

$$\delta_{sample} = \delta_{ref} \cdot \frac{\Phi_{ref} \cdot C_{ref} \cdot I_{sample} \cdot d_{sample}}{\Phi_{sample} \cdot C_{sample} \cdot I_{ref} \cdot d_{ref}} \quad (2)$$

δ_{ref} : Two-photon absorption cross section of the reference (Rhodamine B), which was read out from the previous literature[6].

Φ : Quantum yield of sample and reference.
I: Integrated emission intensity.
C: Concentration of each sample.
d: The refractive index of solvents. d_{DMSO}= 1.478, d_{EtOH} = 1.361.

3.3 Simulation of the two-photon absorption cross section according to the two-state model

3.3.1 Estimation the transition dipole moment, $\mu_{g\text{-}e}$[7]

The transition dipole moment, $\mu_{g\text{-}e}$, was calculated from the area under the UV–*vis* absorption band through equation

$$S = \int \varepsilon M d\omega = \frac{2\pi\omega_{ge} n N_0 \mu_{g-e}^2 M}{3(2.303)\varepsilon_0 ch} \quad (3)$$

where M is the concentration of the chromophore, n is the refractive index of the solvent, ε is the molar absorption coefficient, N_0 is Avogadro's constant, ε_0 is the permittivity of a vacuum, c is speed of light in a vacuum, h is Planck's constant, and ω_{ge} can be found simply from the band maximum of the UV–*vis* absorption spectrum of the chromophore. The UV-*vis* spectra for the selected ZnSalen/Salophens were recorded in DMSO.

3.3.2 Determination of the magnitude of the change in the dipole moment on excitation from the ground state to the excited state, $\Delta\mu_{ge}$.[8-11]

$\Delta\mu_{ge}$ was determined *via* Lippert-Mataga plot using the equation:

$$\Delta\tilde{\nu} = \frac{2\Delta\mu_{ge}^2}{4\pi\varepsilon_0 hca^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right]$$

where $\Delta\tilde{\nu}$ refers to the Stokes shift (in cm^{-1}), n and ε are refractive index and dielectric constant of the solvent, respectively. The other terms in Equation (2) are Planck's constant (h), speed of light (c), Onsager cavity radius of the solute molecule (a) and the permittivity of a vacuum (ε_0). $\Delta\mu_{ge}$ can be obtained from the slope of the plot of $\Delta\tilde{\nu}$ *v.s.* $\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right]$.

In our experiment, the absorptive and emissive wavelengths were respectively recorded in the following solvent: (1) toluene, (2) dichloromethane, (3) chloroform, (4) 1, 2-dichloroethane, (5) tertiary butanol, (6) isopropanol, (7) ethanol and (8) acetonitrile. Linear fit were carried out after precluding the obviously deviating points. The Onsager cavity radius of the ZnSalen/Salophens are approximated from the optimized ground state geometry and set as 40% of the long axis of transition arm of one side of ZnSalen/Salophen molecule, as suggested by Lippert[8] for elongated nonspherical molecules.

3.3.3 Fitting the dipole moment properties to the two-state model[12]

The two-state model can be expressed as following:

$$\delta \propto \frac{\Delta\mu_{ge}^2 \mu_{g-e}^2}{E_{ge}^2 \Gamma}$$

where E_{ge} corresponds to the vertical transition energy, Γ refers to the damping which we assumed to be identical for all exited states of selected ZnSalen/Salophens and δ at 790nm was chosen for comparison among the six ZnSalen/Salophen complexes. Therefore, the simulation was carried out on

$$\delta_{790nm} \propto \frac{\Delta\mu_{ge}^2 \mu_{g-e}^2}{E_{ge}^2}$$

3.4 Cyclic voltammetry of a1s1-a11s1 and a1s10

Cyclic voltammetry experiments were recorded on a Shanghai Chenhua CHI660C electrochemical workstation at room temperature under N_2 atmosphere. A glassy carbon electrode was selected as working electrode while SCE (saturated calomel electrode) served as reference electrode; the auxiliary electrode was a platinum wire. All samples were 10 mM in complex with 0.1 M tetrabutylammonium fluoroborate (Bu_4NBF_4) supporting electrolyte in dry dimethyl formamide solution. The scan rate was set to be 20 mV/s and the reduction potential calibration was performed at the end of each data collection cycle using the ferrocene/ferrocenium couple $[(C_5H_5)_2Fe]^{+/0}$ as an internal standard.

3.5 Computational studies of a1s1-a11s1 and a1s10.

For the theoretical study of excited state photophysics of **a1s1-a11s1** and **a1s10**, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods[13,14] were performed and the Becke's three–parameter hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation (B3LYP functional[15]) was used with Lanl2dz pseudopotential[16,17] basis set for Zn, 6-31G** for main group elements, as implemented in the Gaussian 09 package. Geometries for **a1s1-a11s1** and **a1s10** were fully optimized without symmetry constraints. The solvent effect was involved through the PCM approach[18] (DMSO, ε=46.826). The vibration frequency calculations at the same level were carried out to confirm each stationary point to be either a minimum. Then we calculated the vertical excitation energies based on the optimized geometries of the ZnSalen/Salophen molecules.

3.6 Supporting Tables and Figures

Table S1. Absorptive and emissive properties of ZnSalen/Salophens [a]

ZnSalen/Salophen	λ_{abs}, nm(log ε) [b]	λ_{emi}, nm(λ_{ex}, nm) [c]	Φ_{lum} [d]
a1s1	387 (4.79), 439 (4.39), 593(4.93)	632 (593)	0.65
a1s2	377 (4.69), 420 (4.33), 578 (4.78)	621 (578)	0.52
a1s3	387 (4.70), 439 (4.33), 593 (4.81)	635 (593)	0.60
a1s4	387 (4.75), 437 (4.45), 593 (4.82)	633 (593)	0.69
a1s5	387(4.74), 439(4.37), 594(4.89)	637 (594)	0.68
a1s6	387(4.67), 439(4.30), 595(4.78)	634 (595)	0.67
a1s7	387(3.03), 413(3.08), 593(2.97)	630 (593)	0.34
a1s8	384(4.40),589 (4.44)	626 (589)	0.23
a1s9	400(4.95), 458(4.44), 621 (5.04)	659 (621)	0.29
a1s10	341(4.50), 367(4.40), 383 (4.43), 445 (4.11),553(4.57)	619 (553)	0.074
a1s1	387 (4.79), 439 (4.39), 593(4.93)	632 (593)	0.65
a2s1	413 (4.57), 445 (4.48)	478, 499 (445)	<0.001
a3s1	390 (4.65), 449 (4.48)	501, 520 (449)	0.021
a4s1	403 (4.70), 466 (4.60)	524 (466)	0.054
a5s1	428 (4.68), 504 (4.51)	553 (504)	0.089
a6s1	389 (4.85), 452 (4.51)	511 (452)	0.090
a7s1	395 (4.67), 458 (4.48)	544 (458)	0.032
a8s1	382 (4.46), 432 (4.60)	507, 525 (432)	0.069
a9s1	383 (4.39), 466 (4.75), 483 (4.77)	518 (483)	0.036
a10s1	388 (4.50), 457 (4.68)	540 (457)	0.059
a11s1	387 (4.42), 456 (4.64)	515 (456)	0.029
a1s3	387 (4.70), 439 (4.33), 593 (4.81)	635 (593)	0.60
a3s3	390 (4.63), 448 (4.56)	502, 524 (448)	0.017
a4s3	402 (4.71), 468 (4.60)	529 (468)	0.053
a5s3	427 (4.68), 509 (4.52)	552 (509)	0.060
a6s3	390 (4.80), 451 (4.47)	510 (451)	0.083
a7s3	396 (4.64), 456 (4.46)	542 (456)	0.033
a8s3	385 (4.46), 433 (4.61)	508, 530 (433)	0.062
a9s3	384 (4.40), 469 (4.78), 483 (4.80)	515 (483)	0.023
a10s3	389 (4.52), 451 (4.70)	524 (451)	0.053
a11s3	385 (4.44), 457 (4.67)	516, 542 (457)	0.027
a1s4	387 (4.75), 437 (4.45), 593 (4.82)	633 (593)	0.69
a2s4	413 (4.51), 444 (4.40)	471, 498 (444)	<0.001

a3s4	391 (4.64), 446 (4.47)	501, 519 (446)	0.017
a4s4	403 (4.67), 467 (4.56)	529 (467)	0.048
a5s4	428 (4.67), 508 (4.52)	554 (508)	0.045
a6s4	388 (4.82), 450 (4.49)	512 (450)	0.075
a7s4	396 (4.65), 457 (4.46)	511, 528 (457)	0.036
a8s4	385 (4.46), 429 (4.58)	505, 532 (429)	0.051
a9s4	384 (4.46), 467 (4.82), 482 (4.83)	517, 539 (482)	0.021
a10s4	390 (4.50), 445 (4.66)	531 (445)	0.054
a11s4	391 (4.43), 450 (4.65)	514, 543 (450)	0.030
a1s10	341 (4.50), 367(4.40), 383 (4.43), 445 (4.11),553(4.57)	619 (553)	0.074
a3s10	311 (4.47), 389 (4.55), 429 (4.33)	489 (429)	0.002
a4s10	320 (4.51), 404 (4.58), 445 (4.40)	514 (445)	0.014
a5s10	333 (4.52), 422 (4.62) ,470 (4.42)	540 (470)	0.015
a6s10	312 (4.51), 386 (4.47) , 426 (4.26)	502 (426)	0.011
a7s10	316 (4.49), 395 (4.53) , 436 (4.32)	512 (436)	0.006
a8s10	317 (4.38), 407 (4.52) , 449 (4.33)	493, 510 (449)	0.005
a9s10	333 (4.38), 443 (4.57), 457 (4.55)	510 (457)	0.004
a10s10	321 (4.43), 416 (4.58) , 451 (4.45)	506, 528 (451)	0.009
a11s10	323 (4.45), 421 (4.58) , 454 (4.46)	500 (454)	0.002

[a]: All data was determined in DMSO at a concentration of 20 μM

[b]: Wavelength of absorptive peaks and the corresponding extinction coefficient.

[c]: Wavelength of emissive peaks and the related excitation wavelength.

[d]: Fluorescence quantum yield, the uncertainty is ±15%.

Table S2. Fluorescence lifetime (τ_{fl}), radiative (k_{fl}) and nonradiative rate constant (k_{nr}) of **a1s1-a1s10** and **a3s1-a11s1**[a]

ZnSalen/Salophens	τ_{fl} (*ns*) (λ_{emi})	k_{fl} (ns^{-1})	k_{nr} (ns^{-1})
a1s1	3.8 (632)	1.6×10^{8}	1.1×10^{8}
a1s2	4.1 (621)	1.3×10^{8}	1.2×10^{8}
a1s3	3.8 (635)	1.6×10^{8}	1.1×10^{8}
a1s4	3.6 (633)	1.9×10^{8}	8.6×10^{7}
a1s5	4.1 (637)	1.7×10^{8}	7.8×10^{7}
a1s6	3.6 (634)	1.9×10^{8}	9.2×10^{7}
a1s7	3.9 (630)	8.7×10^{7}	1.7×10^{8}
a1s8	4.1 (626)	5.6×10^{7}	1.9×10^{8}
a1s9	4.0 (659)	7.3×10^{7}	1.8×10^{8}

a1s10	1.4 (619)	4.6×10^{8}	2.5×10^{8}
a2s1	0.82 (478), 0.91(499)	/	/
a3s1	0.16 (501), 0.21 (520)	1.3×10^{8}, 9.9×10^{7}	6.1×10^{9}, 4.6×10^{9}
a4s1	0.72 (524)	7.5×10^{7}	1.3×10^{9}
a5s1	0.85 (533)	1.0×10^{8}	1.1×10^{9}
a6s1	0.36 (511)	2.5×10^{8}	2.5×10^{9}
a7s1	0.49 (544)	6.5×10^{7}	2.0×10^{9}
a8s1	0.47 (507), 0.84 (525)	1.5×10^{8}, 8.4×10^{7}	2.0×10^{9}, 1.1×10^{9}
a9s1	0.61 (518)	5.9×10^{7}	1.6×10^{9}
a10s1	0.81 (540)	7.3×10^{7}	1.2×10^{9}
a11s1	0.28 (515)	1.0×10^{8}	3.5×10^{9}

[a]: The data was all determined in DMSO. The uncertainty for the lifetime is ±15%.

Table S3. Two-photon absorption cross-section (GM) of **a1s1**, **a3s1-a11s1** and **a1s10** at different wavelength (nm)

Wavelength (nm)	**a1s1**	**a3s1**	**a4s1**	**a5s1**	**a6s1**	**a7s1**	**a8s1**	**a9s1**	**a10s1**	**a11s1**	**a1s10**
740	61	104	117	94	39	173	61	41	54	43	87
750	55	95	177	92	46	165	65	87	70	51	110
760	56	100	163	36	18	60	25	31	67	53	102
770	61	83	163	87	43	165	41	86	65	47	91
780	68	56	167	78	28	95	23	50	52	37	66
790	82	56	157	105	27	116	33	81	43	36	47
800	105	38	138	134	20	91	25	59	29	29	30
810	130	30	151	113	17	87	24	31	29	34	23
820	146	30	118	158	13	59	19	48	24	26	20
830	173	26	88	171	12	52	20	39	21	23	18
840	215	27	72	191	11	39	22	41	18	28	27
850	161	14	40	139	5	26	14	32	12	19	23
860	122	13	3	81	4	15	9	17	7	12	14

Table S4. Estimation of the $\mu_{g\text{-}e}$ and $\Delta\mu_{ge}$ of **a1s1**, **a3s1**, **a5s1**, **a6s1**, **a9s1** and **a1s10**.

ZnSalen/ Salophens	Band area (cm^{-1})	$\mu_{g\text{-}e}$ (D)	a (Å)	$\frac{2\Delta\mu_{ge}^2}{4\pi\varepsilon_0 hca^3}$ (cm^{-1})	$\Delta\mu_{ge}$ (D)
a1s1	108735579.5	35.5	9.027	1736	0.285
a3s1	103944301	30.2	9.962	1470	0.304
a5s1	51754770	22.8	11.42	2032	0.439
a6s1	91218790	28.4	10.72	1211	0.308
a9s1	90081373	29.2	9.768	1629	0.311
a1s10	52953992.0	23.9	8.973	2589	0.345

Table S5. Experimental HOMO and LUMO energy level of **a1s1-a11s1** and **a1s10**

ZnSalen/Salophen	E_{onset}^{red} (V)	LUMO (eV)	E_g (eV) [b]	HOMO (eV)[c]
a1s1	-1.10	-3.16	1.84	-5.00
a1s10	-0.89	-3.37	1.94	-5.31
a2s1	—	—	2.26	—
a3s1	—	—	2.37	—
a4s1	-1.57	-2.69	2.20	-4.89
a5s1	-1.48	-2.78	2.17	-4.95
a6s1	-1.67	-2.59	2.30	-4.89
a7s1	-1.68	-2.58	2.25	-4.83
a8s1	-1.84	-2.42	2.33	-4.75
a9s1	-1.55	-2.71	2.17	-4.88
a10s1	-1.66	-2.60	2.20	-4.80
a11s1	-1.65	-2.61	2.19	-4.80

[a] Determined from the onset of the reduction voltages.

[b] Calculated from the edges of the absorption spectra.

[c] Determined from the onset of the reduction voltages.

Table S6. Calculated HOMO and LUMO energy level of **a1s1-a11s1** and **a1s10**

ZnSalen/Salophen	LUMO (*eV*)	HOMO (*eV*) [b]	E_g (*eV*) [c]
a1s1	-2.59	-5.08	2.49
a1s10	-2.86	-5.56	2.70
a2s1	-1.57	-4.99	3.42
a3s1	-1.59	-4.93	3.34
a4s1	-1.95	-5.06	3.11
a5s1	-2.28	-5.18	2.90
a6s1	-1.74	-5.07	3.33
a7s1	-1.80	-5.06	3.26
a8s1	-1.69	-4.99	3.30
a9s1	-1.93	-5.08	3.15
a10s1	-1.80	-5.04	3.24
a11s1	-1.80	-5.04	3.24

Table S7. Distributions of HOMO and LUMO levels on the phenoixde and diamine-imine units of **a1s1-a11s1** and **a1s10**

ZnSalen/	**HOMO Distributions (%)**		**LOMO Distributions (%)**	
Salophen	**Phenoixde**	**Diamine-imine**	**Phenoixde**	**Diamine-imine**
a1s1	58	28	30	67
a2s1	55	36	26	70
a3s1	57	34	36	59
a4s1	58	32	28	69
a5s1	58	32	21	76
a6s1	58	32	34	62
a7s1	59	30	34	61
a8s1	57	33	37	58
a9s1	57	34	22	75
a10s1	56	34	33	62
a11s1	56	34	32	60
a1s10	60	37	29	70

Table S8. Calculated electronic transitions properties for **a1s1-a11s1** and **a1s10** obtained from TD-DFT calculations with PCM solvation model.

ZnSalen/Salophen	Transitions	λ_{calcd} (nm)	λ_{exptl} (nm)	f	Major contribution
a1s1	S_0–S_1	556	593	1.0948	HOMO→LUMO (100%)
a2s1	S_0–S_1	406	445	0.4599	HOMO→LUMO (36%) HOMO→$LUMO_{+1}$ (57%)
a3s1	S_0–S_1	434	449	0.7970	HOMO→LUMO (100%)
a4s1	S_0–S_1	460	466	0.6611	HOMO→LUMO (100%)
a5s1	S_0–S_1	493	504	0.7005	HOMO→LUMO (100%)
a6s1	S_0–S_1	434	452	0.7489	HOMO→LUMO (100%)
a7s1	S_0–S_1	442	458	0.6871	HOMO→LUMO (100%)
a8s1	S_0–S_1	438	432	0.8259	HOMO→LUMO (100%)
a9s1	S_0–S_1	438	483	0.3745	HOMO→LUMO (87%)
a10s1	S_0–S_1	444	457	0.8486	HOMO→LUMO (88%)
a11s1	S_0–S_1	444	456	0.8556	HOMO→LUMO (96%)
a1s10	S_0–S_1	521	553	0.7028	HOMO→LUMO (97%)

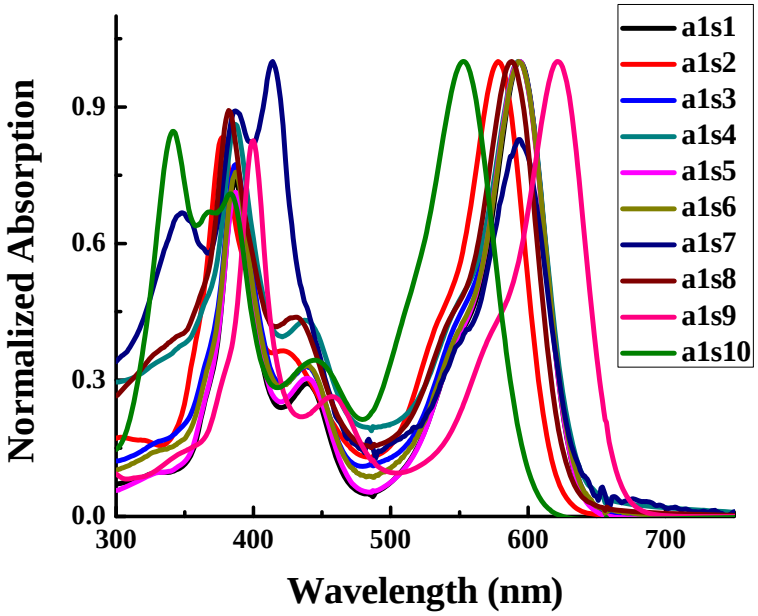


Figure S2 (a) Normalized UV-*vis* spectra of **a1s1-a1s10** in DMSO at 298K

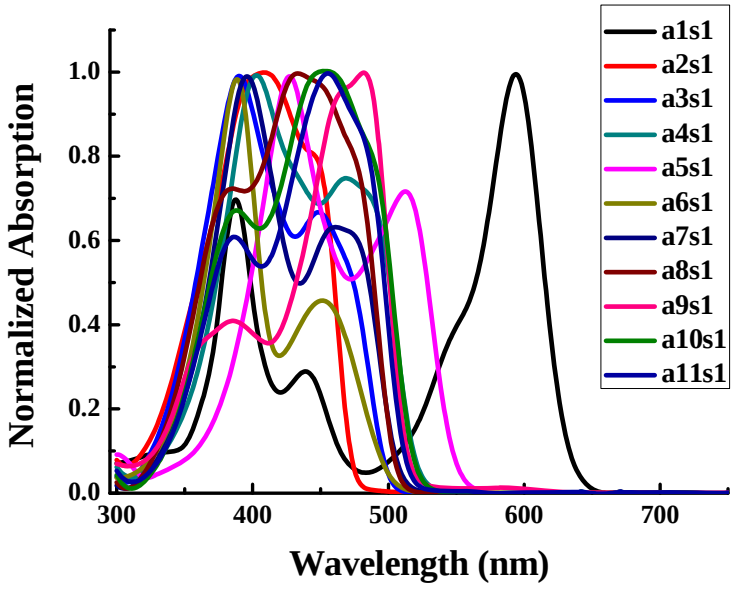


Figure S2 (b) Normalized UV-*vis* spectra of **a1s1-a11s1** in DMSO at 298K

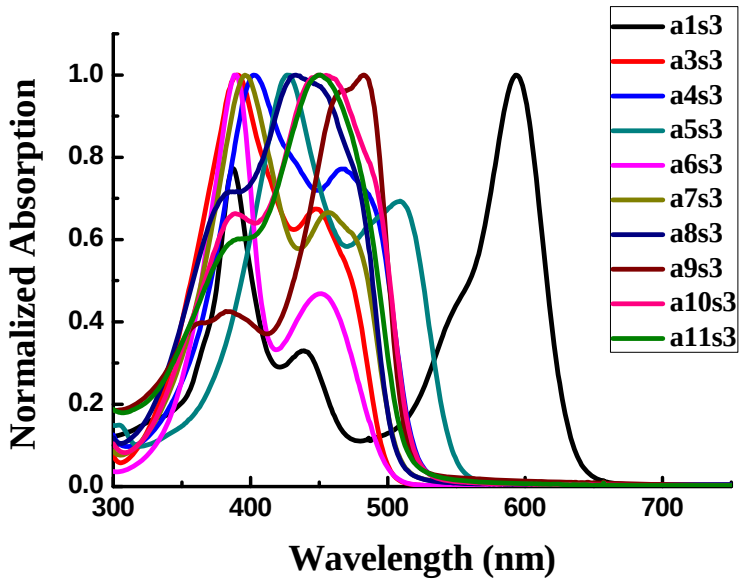


Figure S2 (c) Normalized UV-*vis* spectra of **a1s3-a11s3** in DMSO at 298K

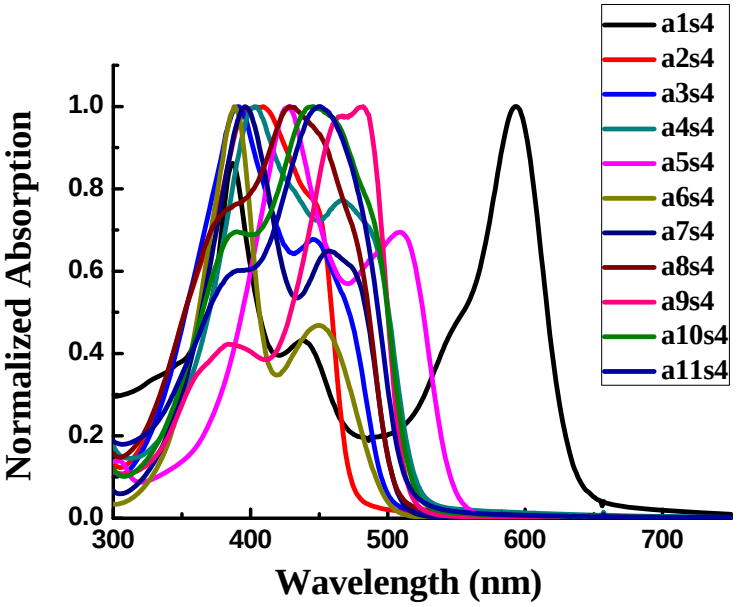


Figure S2 (d) Normalized UV-*vis* spectra of **a1s4-a11s4** in DMSO at 298K

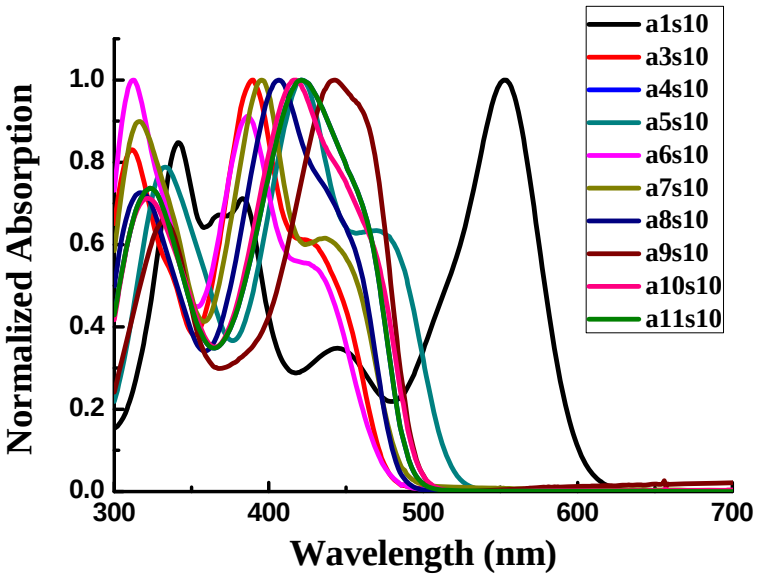


Figure S2 (e) Normalized UV-*vis* spectra of **a1s10-a11s10** in DMSO at 298K

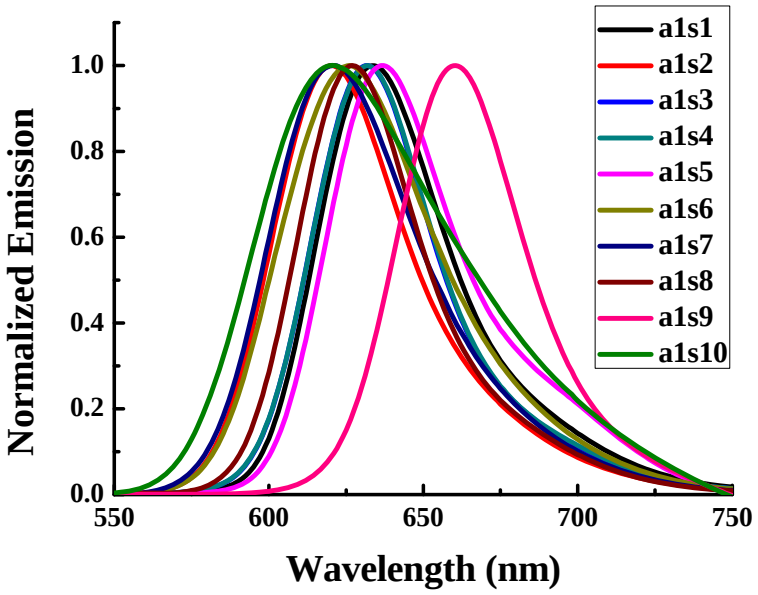


Figure S3 (a) Normalized emission spectra of **a1s1-a1s10** in DMSO at 298K. The excitation wavelength for each complex is referred to **Table S1**.

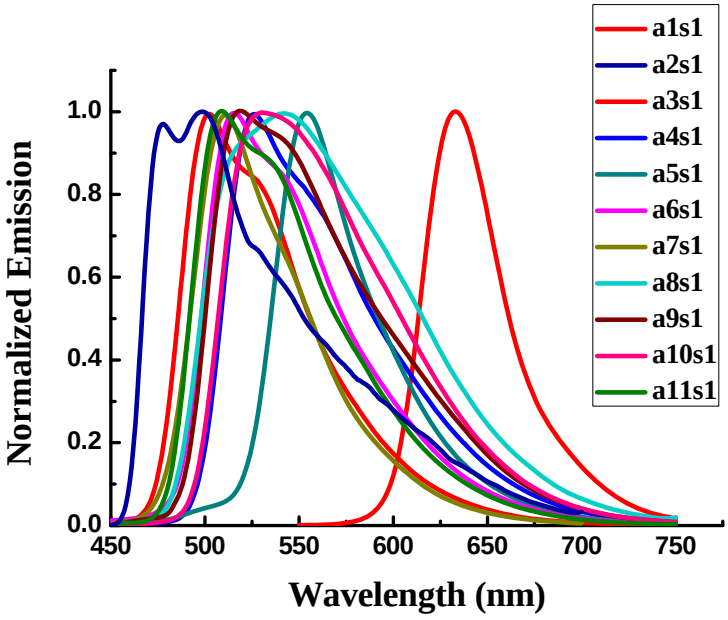


Figure S3 (b) Normalized emission spectra of **a1s1-a11s1** in DMSO at 298K. The excitation wavelength for each complex is referred to **Table S1**.

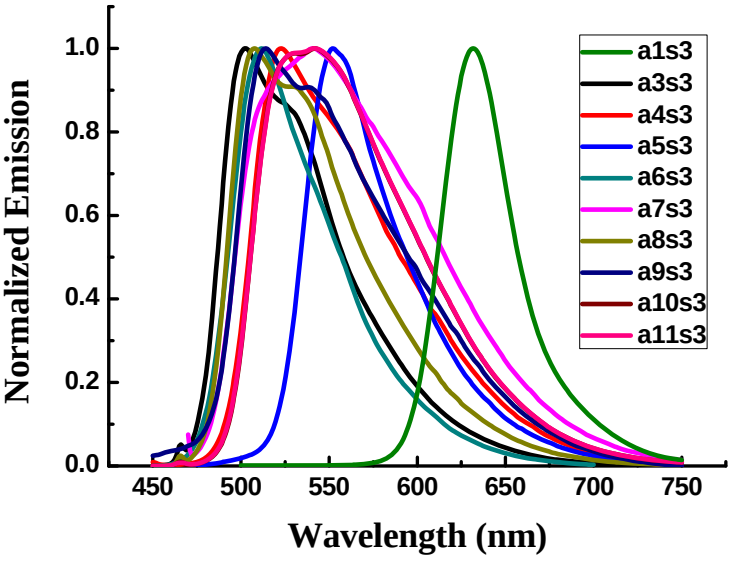


Figure S3 (c) Normalized emission spectra of **a3s3-a11s3** in DMSO at 298K. The excitation wavelength for each complex is referred to **Table S1**.

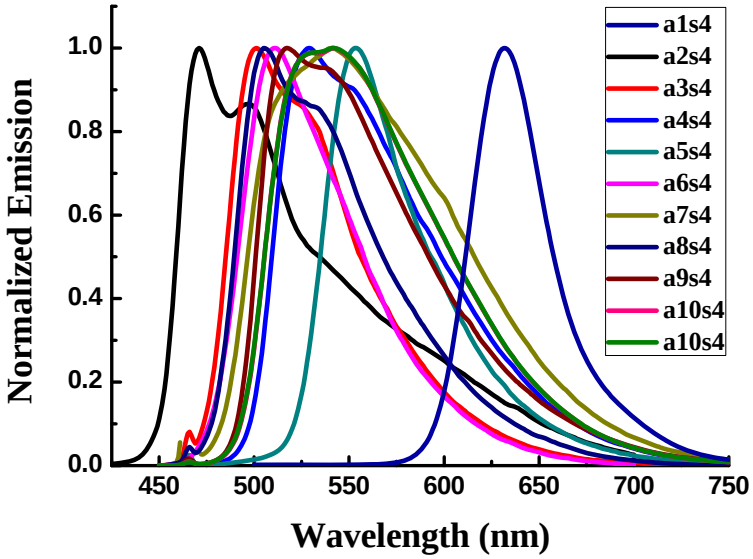


Figure S3 (d) Normalized emission spectra of **a2s4-a11s4** in DMSO at 298K. The excitation wavelength for each complex is referred to **Table S1**.

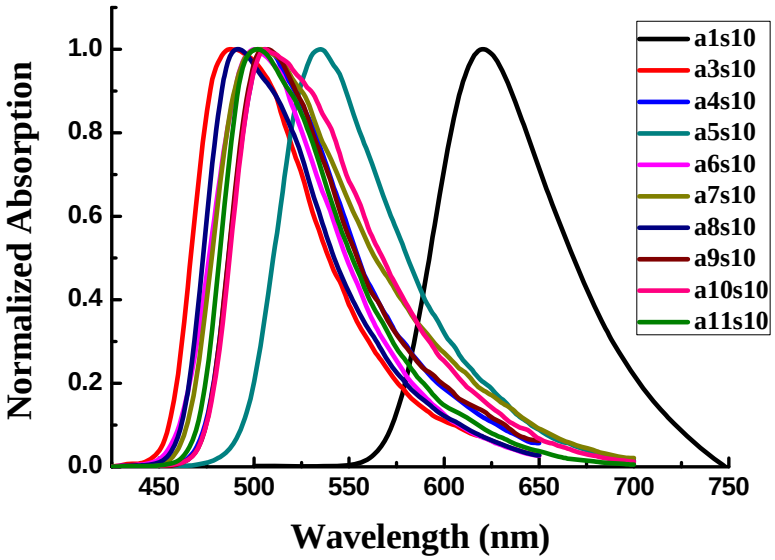


Figure S3 (e) Normalized emission spectra of **a3s10-a11s10** in DMSO at 298K. The excitation wavelength for each complex is referred to **Table S1**.

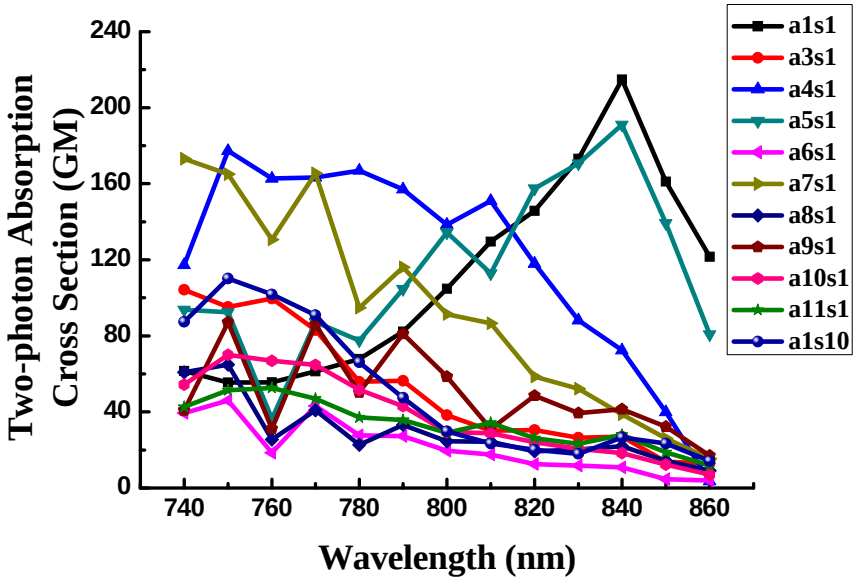


Figure S4 Two-photon induced absorption cross section of **a1s1-a11s1** and **a1s10** from 740nm to 860nm with Rhodamine B as reference.

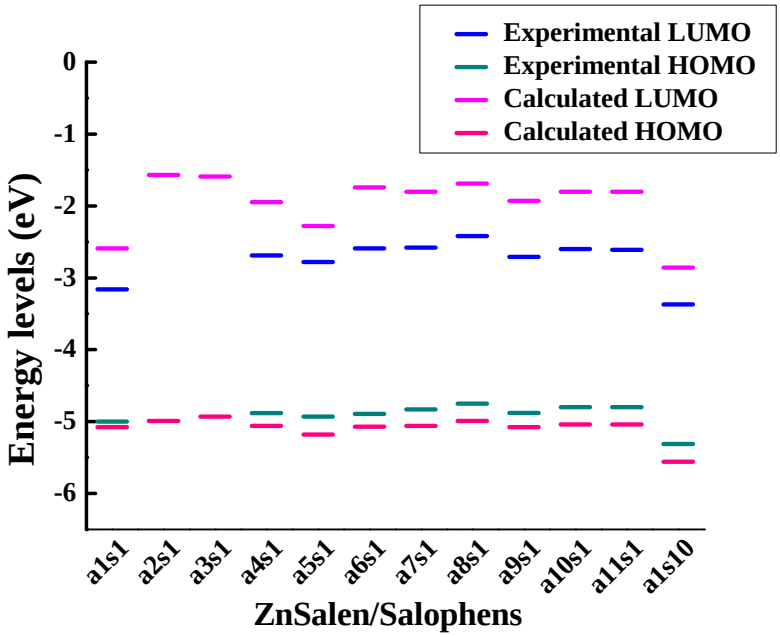
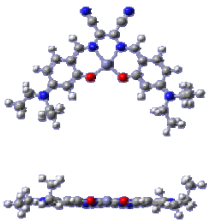
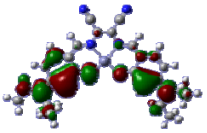
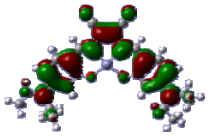
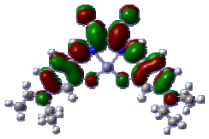
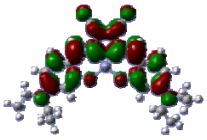
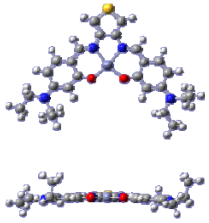
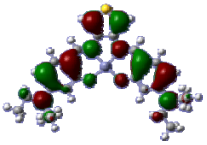
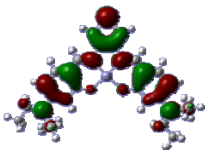
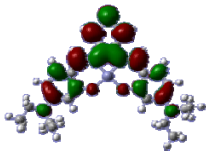
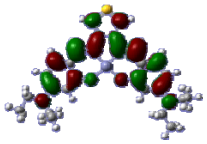
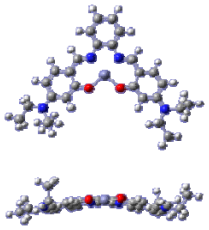
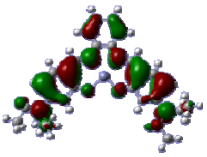
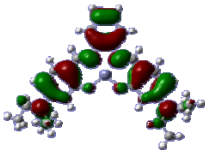
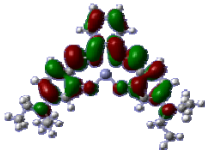
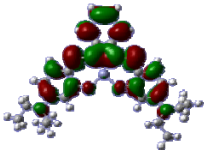
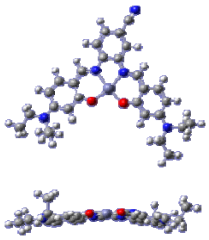
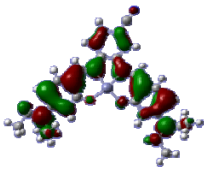
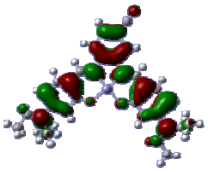
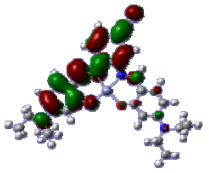
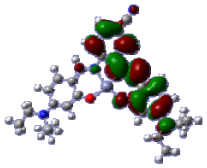
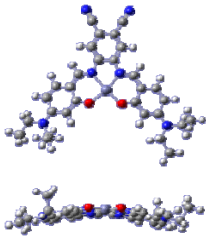
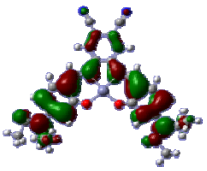
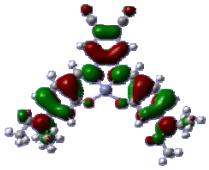
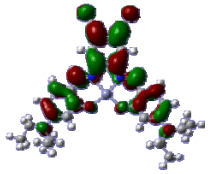
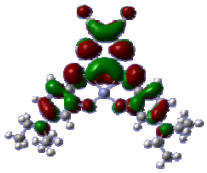
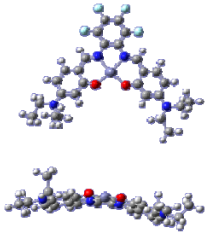
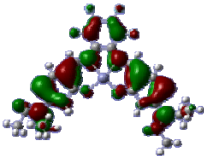
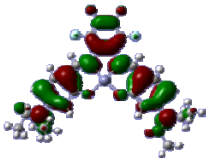
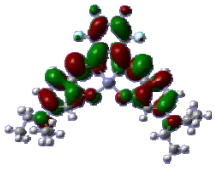
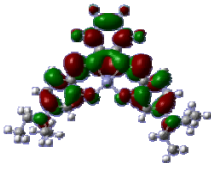
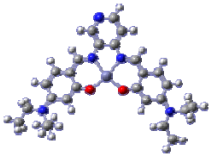
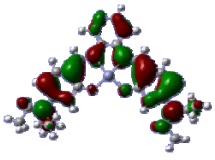
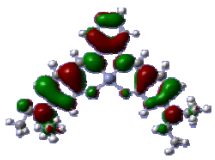
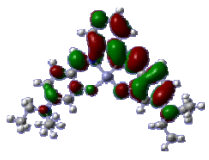
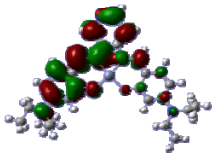


Figure S5 Comparison of the calculated and experimental FOMO energy levels of **a1s1-a1s11** and **a1s10**

ZnSalen/ Salophens	Optimized Structures	FOMOs of ZnSalen/Salophens			
		HOMO-1	HOMO	LUMO	LUMO+1
a1s1		 -5.60 eV	 -5.07 eV	 -2.59 eV	 -1.35 eV
a2s1		 -5.16 eV	 -4.99 eV	 -1.56 eV	 -1.44 eV
a3s1		 -5.28 eV	 -4.93 eV	 -1.59 eV	 -1.38 eV
a4s1		 -5.40 eV	 -5.06 eV	 -1.95 eV	 -1.63 eV
a5s1		 -5.49 eV	 -5.18 eV	 -2.27 eV	 -1.93 eV
a6s1		 -5.35 eV	 -5.07 eV	 -1.74 eV	 -1.46 eV
a7s1					

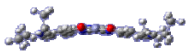
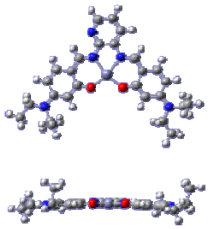
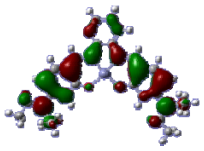
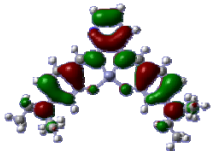
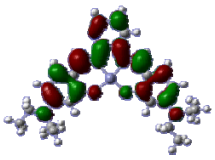
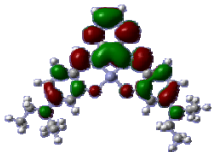
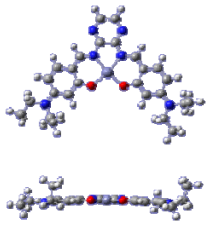
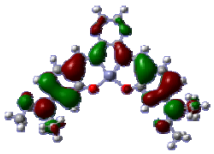
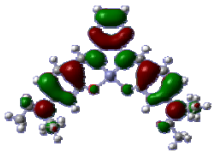
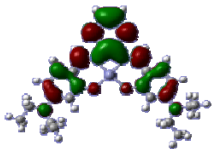
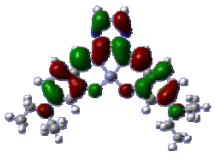
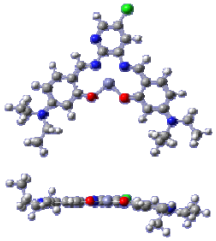
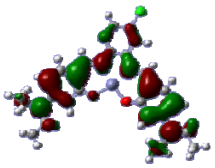
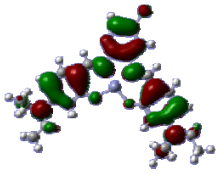
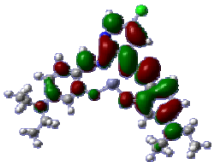
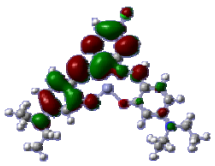
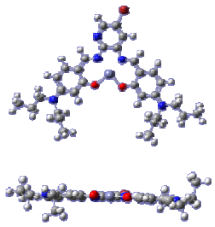
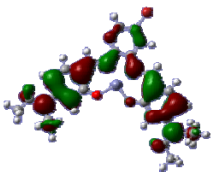
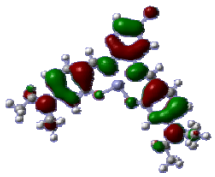
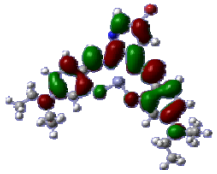
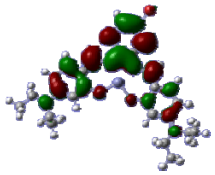
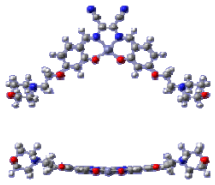
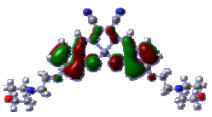
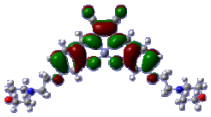
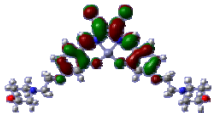
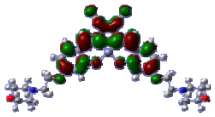
		-5.39 eV	-5.06 eV	-1.80 eV	-1.54 eV
a8s1		 -5.37 eV	 -4.99 eV	 -1.69 eV	 -1.62 eV
a9s1		 -5.44 eV	 -5.08 eV	 -1.93 eV	 -1.77 eV
a10s1		 -5.41 eV	 -5.04 eV	 -1.80 eV	 -1.76 eV
a11s1		 -5.41 eV	 -5.04 eV	 -1.80 eV	 -1.77 eV
a1s10		 -5.89 eV	 -5.56 eV	 -2.85 eV	 -1.59 eV

Figure S6 Optimized structures, FOMOs and energy levels of **a1s1-a11s1** and **a1s10**

4 Determination of the octanol-water partition coefficients (log P)

4.1 Methods

Equal volume (2000mL) of n-octanol and water were thoroughly mixed by an oscillator and separated after 24 h. **a1s1-a1s10** and **a2s4-a11s4** (0.50mg each) was then dissolved in 40mL of the separated n-octanol and the solution was allowed to equilibrate for further 24 h. The extinction coefficient was then calculated and 40mL of water (previously separated from the mixture) was added. The new water-octanol system was allowed to equilibrate for additional 24h. After separating, both fractions were analyzed by UV-*vis* spectra. The log *P* values were calculated by the following equation

$$\log P = \log \frac{C_{octanol}}{C_{water}}$$

where $C_{octanol}$ and C_{water} refer to the concentration of ZnSalen/Salophen compound in the n-octanol and water, respectively.

5 Live Cell imaging

5.1 Cell culture

All cells were incubated in complete medium (Dulbecco's modified Eagle's Medium, supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin) at 37 °C in atmosphere containing 5% CO_2.For imaging, HeLa cells were grown in poly-D-lysine-coated dishes and incubated in 2mL of complete medium for 24 h. Cells were washed with PBS, and stocked dyes (2 mM in DMSO) were added to obtain a final concentration of 2 μM. The treated cells were incubated for another hour in dark at 37 °C. A few minutes prior to confocal imaging cells were washed twice with PBS. A confocal laser scanning microscope (A1R-si, Nikon, Japan) was used to obtain images. Cells were imaged via the fluorescence mode with a 60× immersion lens with the following parameters: laser power 100%, pinhole 1.0 A.U., excitation wavelength 405nm or 488nm or 543 nm, detector slit 552-617 nm, resolution 1024×1024, and a scan speed 0.5 frames per second.

5.2 CCK-8 assay

The cytotoxicity assays were conducted according to the literature[19]. HeLa cells were seeded in flat-bottomed 96-well plates, 10^4 cells per well, with 200 μL complete culture media in the dark for 24h. After washed with PBS for three times (200μL*3), the cells were incubated with appropriate concentrations of ZnSalen/Salophens (5μM for **a9s3, a10s3, a7s4**, 10 μM for **a8s1**, and 20 μM for the rest). All stock solutions were prepared in DMSO and diluted with complete media, and the final DMSO concentrations were less than 0.1%. After cultured for 24 h, the cells were washed with PBS three times (200μL*3). 10 μL Cell Counting Kit-8 (CCK-8) solution and 90μL PBS were added per well simultaneously. After 2 hours, the absorbance at 450nm was read by 96-well plate reader. The viability of HeLa cells was calculated by the following equation:

$$CV = (As-Ab) / (Ac-Ab) \times 100\%$$

where CV stands for the viability of cells，As, Ac and Ab stand for the absorbance of cells containing ZnSalen/Salophens, cell control (0 μM ZnSalen/Salophens) and blank control (wells containing no cells or ZnSalen/Salophens).

5.3 Colocalization assay

HeLa cells were placed onto 0.1mM poly-D-lysine coated glasses in complete media and the cells were incubated for 24 h. A stock solution of ZnSalen/Salophens in chromatographic grade, anhydrous DMSO was prepared as 2 mM. The solution was diluted to a final concentration of 2 μM by complete growth medium. Stock solutions of Lyso Tracker Green DND-26, Lyso Tracker Red DND-99, ER Tracker Blue-White DPX, ER Tracker Green dye, Hoechst 33528 were prepared as 1mM, and the stock solution was diluted to the working concentrations in complete medium (For Lyso Tracker Green DND-26: 72nM; for others: 1 μM). After incubating for an hour, cells were washed with PBS buffer twice before confocal experiments. Images were taken under conditions as follows: 60× immersion lens with a resolution of 1024×1024 and a speed of 0.5 frame per second, suitable excitation wavelength and detector slit for ZnSalen/Salophens in respect to their fluorescence wavelength, 100% laser power for ZnSalen/Salophen samples, and 80% laser power for Lyso Tracker, ER Tracker and Hoechst 33528. Differential interference contrast (DIC) and fluorescent images were processed and analyzed using Image J. The Pearson's Coefficient was calculated by Image J.

5.4 Emission spectra in living cells

The emission spectra of ZnSalen/Salophens in living cells were recorded by Laser Scanning Confocal Microscope (A1R-si, Nikon, Japan) at three channels. For the channel No.1, the excitation wavelength was set to be 405nm and detector slit 425-460nm. For the channel No.2, the excitation wavelength and the detector slit were 488nm and 505-560nm, respectively. And for channel No.3, the excitation wavelength was 543nm and detector slit 552 to 617 nm. Camera settings were the same as described above with the exception of spectral detector mode with a scan resolution of 2.5 nm.

5.5 One-photon multicolour imaging

HeLa cells were placed onto 0.1mM poly-D-lysine coated glasses in complete media and the cells were incubated for 24 h. A stock solution of ZnSalen in chromatographic grade, anhydrous DMSO was prepared as 2 mM. The solution was diluted to a final concentration of 2 μM by complete growth medium. Stock solution of Hoechst 33528 (a commercial nucleus tracker) was prepared as 1mM, and was diluted to the working concentrations, 1μM, in complete medium. After incubated for an hour, cells were washed with PBS buffer twice before confocal experiments. Images were taken under conditions as follows: 60× immersion lens with a resolution of 1024×1024 and a speed of 0.5 frame per second, 100% laser power for ZnSalen/Salophens, and 80% laser power for the nucleus tracker. To obtain multicolour images, lasers and detector slits of different wavelengths are used. For the channel No.1, the excitation wavelength was set to be 405 nm and detector slit 425-460 nm. For the channel No.2, the excitation wavelength and the detector slit were 488 nm and 505-560 nm, respectively. And for the channel No.3, the excitation wavelength was 543 nm and detector slit 552 to 617 nm. Differential interference contrast (DIC) and fluorescent images were processed and analyzed using Image J.

5.6 Two-photon confocal microscopy imaging

Two photon fluorescence microscopy images were performed on a modified Olympus Fluoview FV1000MPE microscope system equipped with an excitation light laser provided by a

modelocked Ti: sapphire laser, (Mai Tai, Spectra-Physics Inc., USA). The microscopy settings were as follows: 60× immersion water objective, a resolution of 512×512, 840 nm excitation wavelength, red slit for **a1s2**, yellow silt for **a5s4**, green slit for **a10s4**, blue slit for **a4s4**, 30 % laser power (10 mW). HeLa cells were treated with 5 μM of ZnSalen/Salophens for 24 h and washed with prewarmed PBS buffer before photoirradiation at 840 nm.

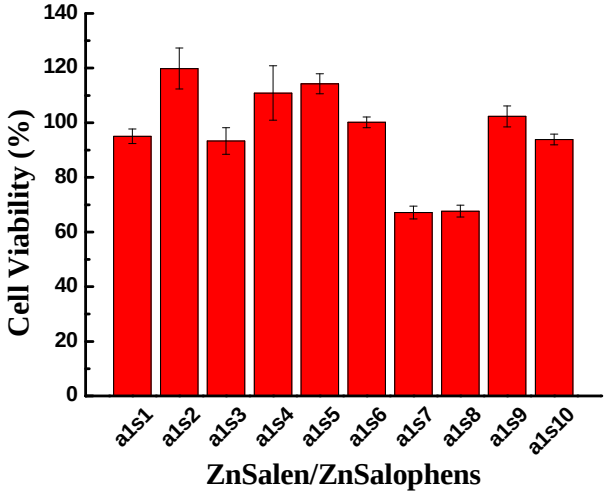
5.7 Multicolour two-photon confocal microscopy imaging

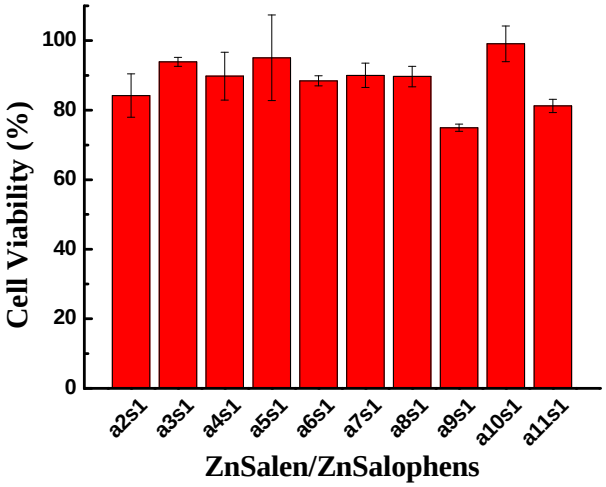
HeLa cells were placed onto 0.1mM poly-D-lysine coated glasses in complete media and the cells were incubated for 24 h. A stock solution of ZnSalen in chromatographic grade, anhydrous DMSO was prepared as 2 mM. The solution was diluted to a final concentration of 2 μM by complete growth medium. After incubated for an hour, cells were washed with PBS buffer twice before confocal experiments. Images were taken under conditions as follows: 60× immersion lens with a resolution of 1024×1024 and a speed of 0.5 frames per second, 100% laser power for ZnSalen/Salophens. To obtain multi-colour images, lasers and detector slits of different wavelengths are used. For both channels, the excitation wavelength was set to be 800nm. For channel No.1, red slit was used. For the channel No.2, green slit was used. Differential interference contrast (DIC) and fluorescent images were processed and analyzed using Image J.

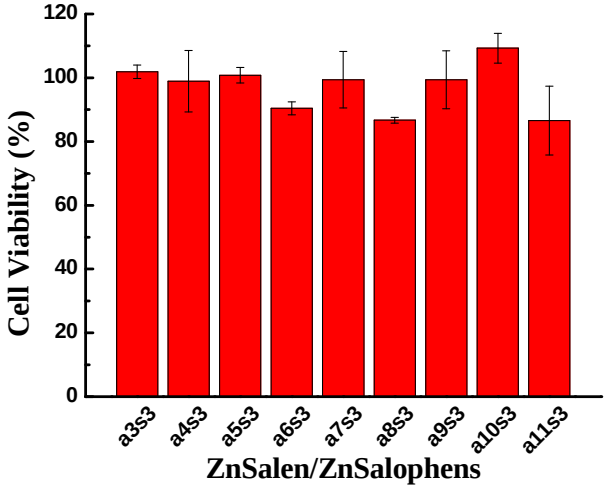
5.8 Supporting Tables and Figures

Table S9. Colocalized Organelles and the corresponding Pearson's coefficient of selected ZnSalen/Salophens (ER stands for endoplasmic reticulum)

ZnSalen/Salophens	Colocalized Organelle	Pearson's coefficient
a1s1	Lysosome	0.52
a1s2	ER	0.89
a1s3	ER	0.74
a1s4	Lysosome	0.71
a1s5	Lysosome	0.77
a1s6	Lysosome	0.54
a1s7	Lysosome (Endosome)	0.66
a1s8	Lysosome	0.73
a1s9	ER	0.82
a1s10	Lysosome	0.91
a4s3	ER	0.92
a5s3	ER	0.61
a6s3	ER	0.51
a8s3	ER	0.52
a10s3	ER	0.92
a4s4	Lysosome	0.32
a5s4	Lysosome	0.71
a6s4	Lysosome	0.69
a8s4	Lysosome	0.85
a10s4	Lysosome	0.78


Cell Viability (%)
140
120
100
80
60
40
20
0
a1s1
a1s2
a1s3
a1s4
a1s5
a1s6
a1s7
a1s8
a1s9
a1s10
ZnSalen/ZnSalophens


Cell Viability (%)
100
80
60
40
20
0
a2s1
a3s1
a4s1
a5s1
a6s1
a7s1
a8s1
a9s1
a10s1
a11s1
ZnSalen/ZnSalophens


Cell Viability (%)
120
100
80
60
40
20
0
a3s3
a4s3
a5s3
a6s3
a7s3
a8s3
a9s3
a10s3
a11s3
ZnSalen/ZnSalophens

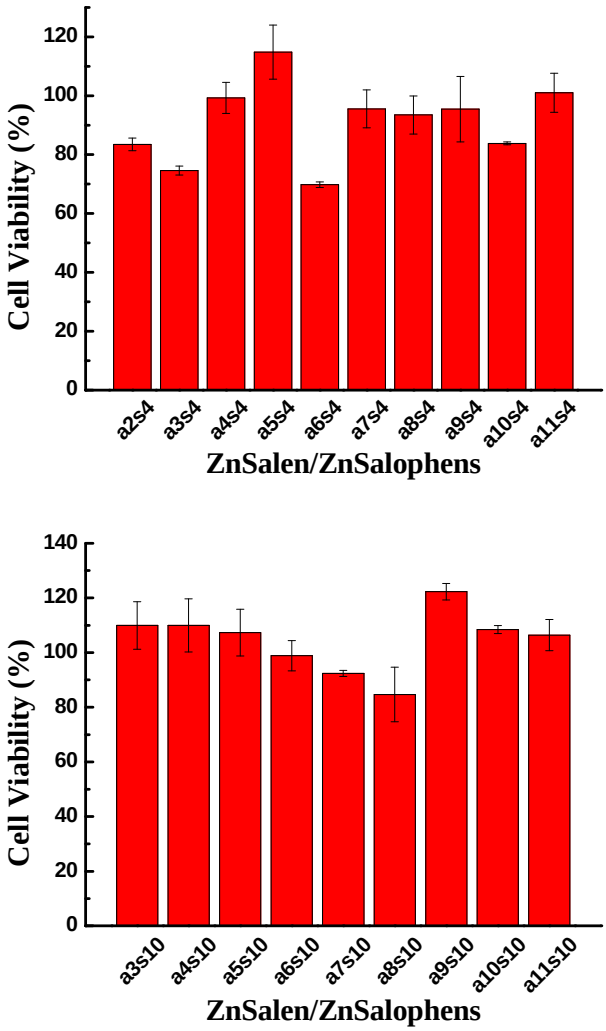


Figure S7 CCK-8 assay result of ZnSalen/Salophens. Cells were incubated with 20 μM of ZnSalen/Salophens under dark. Exceptionally for **a9s3, a10s3, a7s4**, the incubating concentration is 5 μM and for **a8s1**, the incubating concentration is 10 μM.

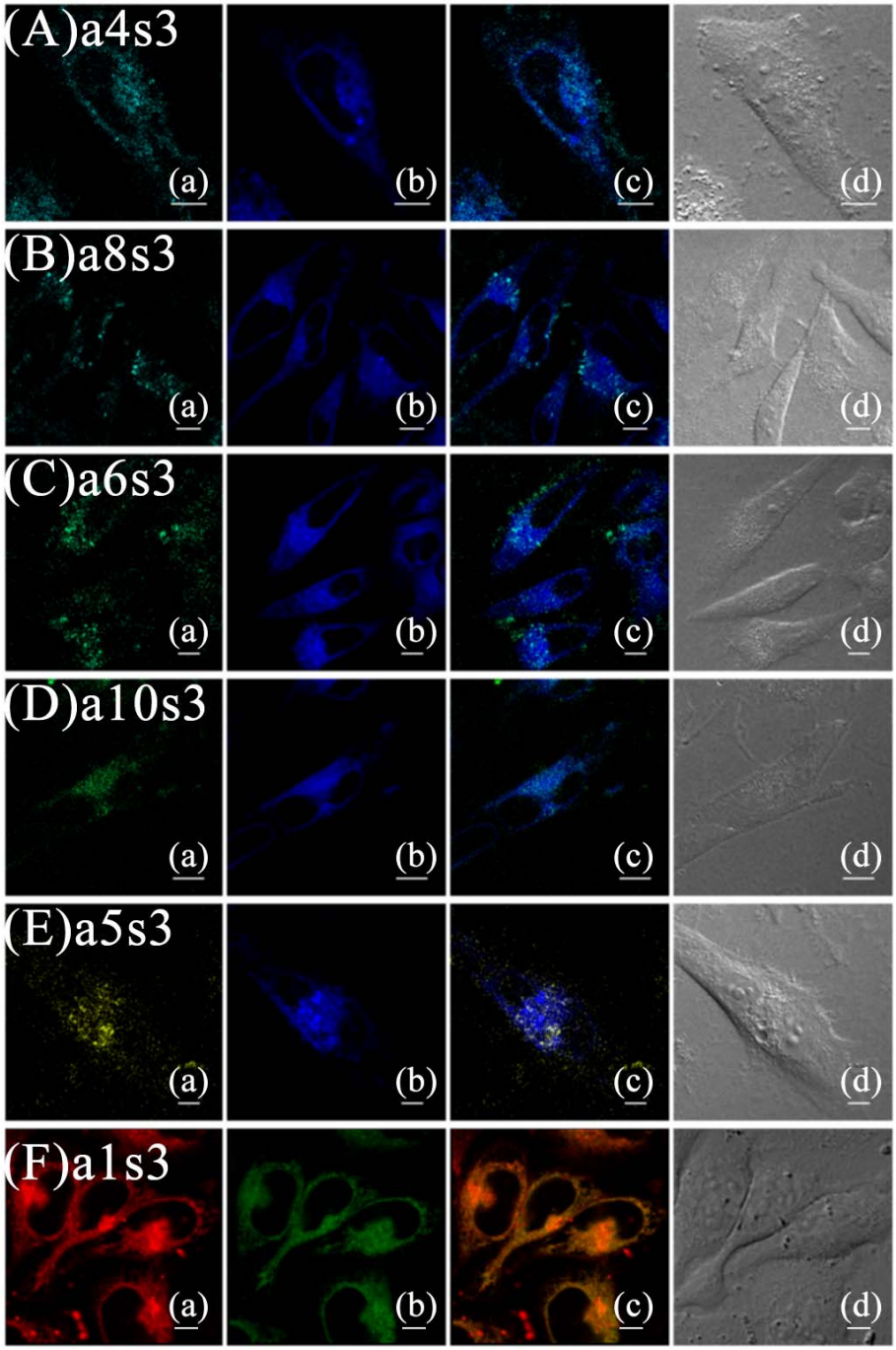


Figure S8 One-photon fluorescence colocalization images of HeLa cells incubated with 2μM probes and commercial dyes. (a) Image of ZnSalen/Salophens; (b) image of ER Tracker Blue (for Row A-E) and ER Tracker Green (for Row F); (c) merged images of (a) and (b); (d) differential interference contrast (DIC) image. Row A-F: colocalization study of (A) **a4s3**; (B) **a8s3**; (C) **a6s3;** (D) **a10s3**; (E) **a5s3** and (F) **a1s3**.

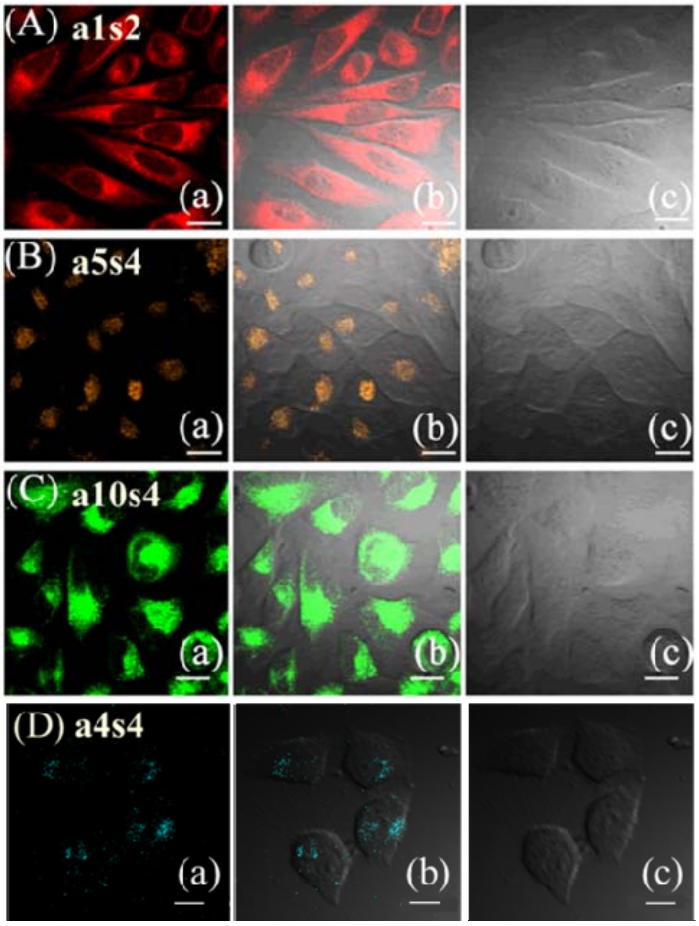


Fig. S9 Two-photon images of HeLa cells incubated with 5μM probes. (a) Image of ZnSalen/Salophens; (b) merged images of ZnSalen/Salophens and differential interference contrast (DIC); (c) DIC image. Row A-D: two-photon live cell image of (A) **a1s2** for ER, red; (B) **a5s4** for lysosome, orange; (C) **a10s4** for lysosome, green and (D) **a4s4** for lysosome, cyan.

6 Reference

1 A. Heaton, M. Hill and F. Drakesmith, *J. Fluorine Chem.*, 1997, **81**, 133-138.
2 Y. Hai, J.-J. Chen, P. Zhao, H. Lv, Y. Yu, P. Xu and J.-L. Zhang, *Chem. Commun.*, 2011, **47**, 2435-2437.
3 J.-J. Chen, J. Jing, H. Chang, Y. Rong, Y. Hai, J. Tang, J.-L. Zhang and P. Xu, *Autophagy*, 2013, **9**, 894-904.
4 T. Karstens and K. Kobs, *J. Phys. Chem.*, 1980, **84**, 1871-1872.
5 G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991-1024.
6 C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481-491.
7 M. S. Paley, J. M. Harris, H. Looser, J. C. Baumert, G. C. Bjorklund, D. Jundt and R. J. Twieg, *J. Org. Chem.*, 1989, **54**, 3774-3778.
8 E. Lippert, *Z. Naturforsch., A: Phys. Sci.*, 1955, **10**, 541-545.
9 E. Lippert, *Zeitschrift Fur Elektrochemie*, 1957, **61**, 962-975.
10 N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 1955, **28**, 690-691.
11 N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 1956, **29**, 465-470.
12 D. Q. Li, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1988, **110**, 1707-1715.
13 A. D. Laurent and D. Jacquemin, *Int. J. Quantum Chem*, 2013, **113**, 2019-2039.
14 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997-1000.
15 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
16 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283.
17 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310.
18 G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, -.
19 M. Ishiyama, Y. Miyazono, K. Sasamoto, Y. Ohkura and K. Ueno, *Talanta*, 1997, **44**, 1299-1305.