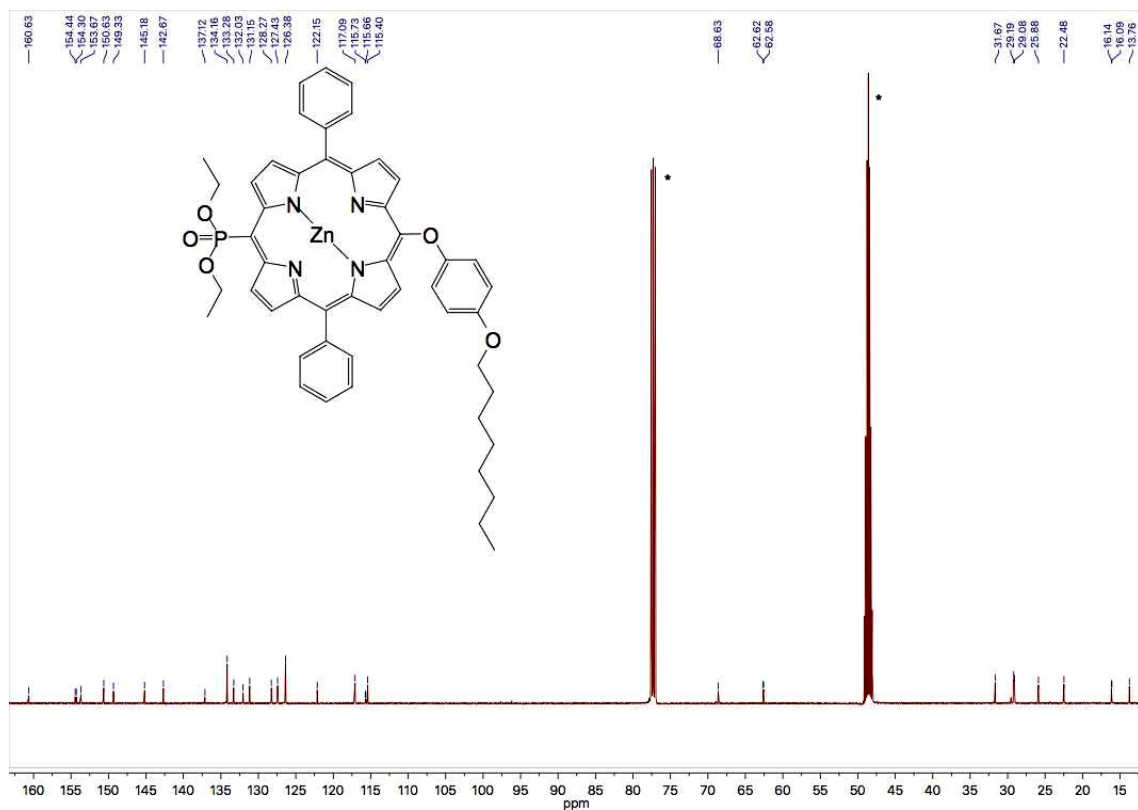
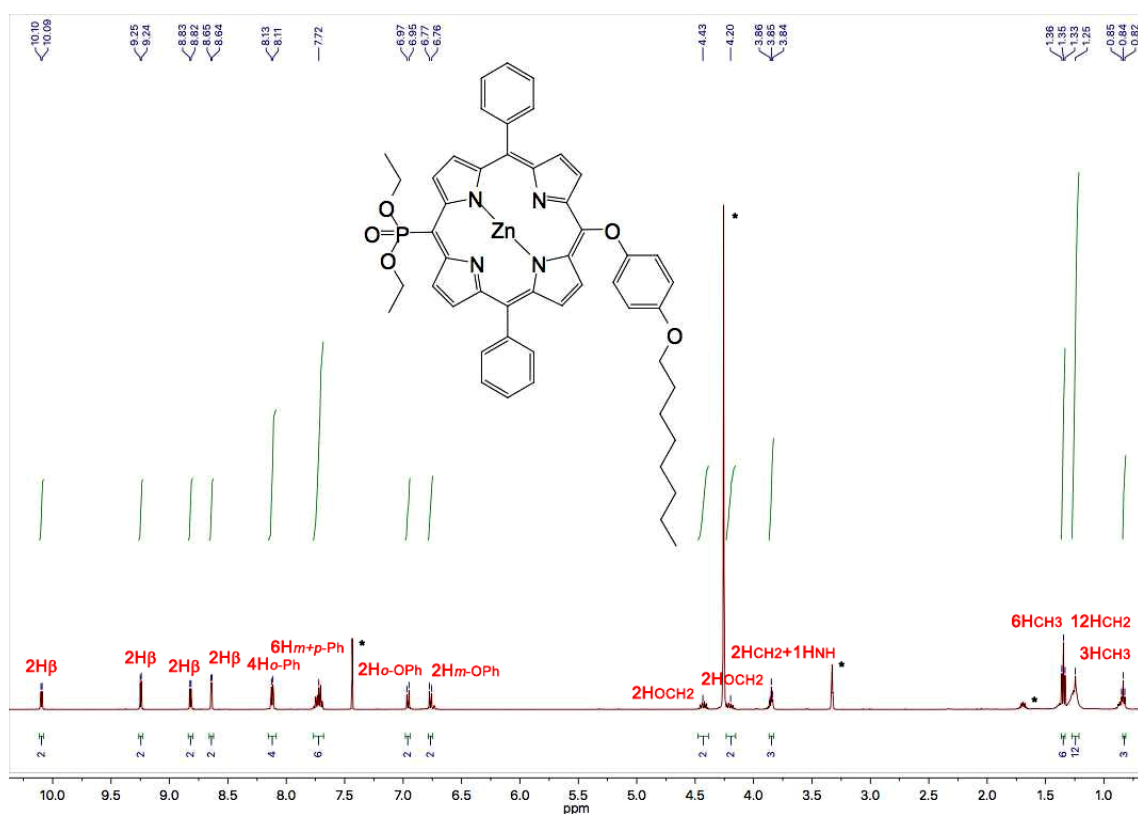


Supporting Information

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1. Spectral data for compounds



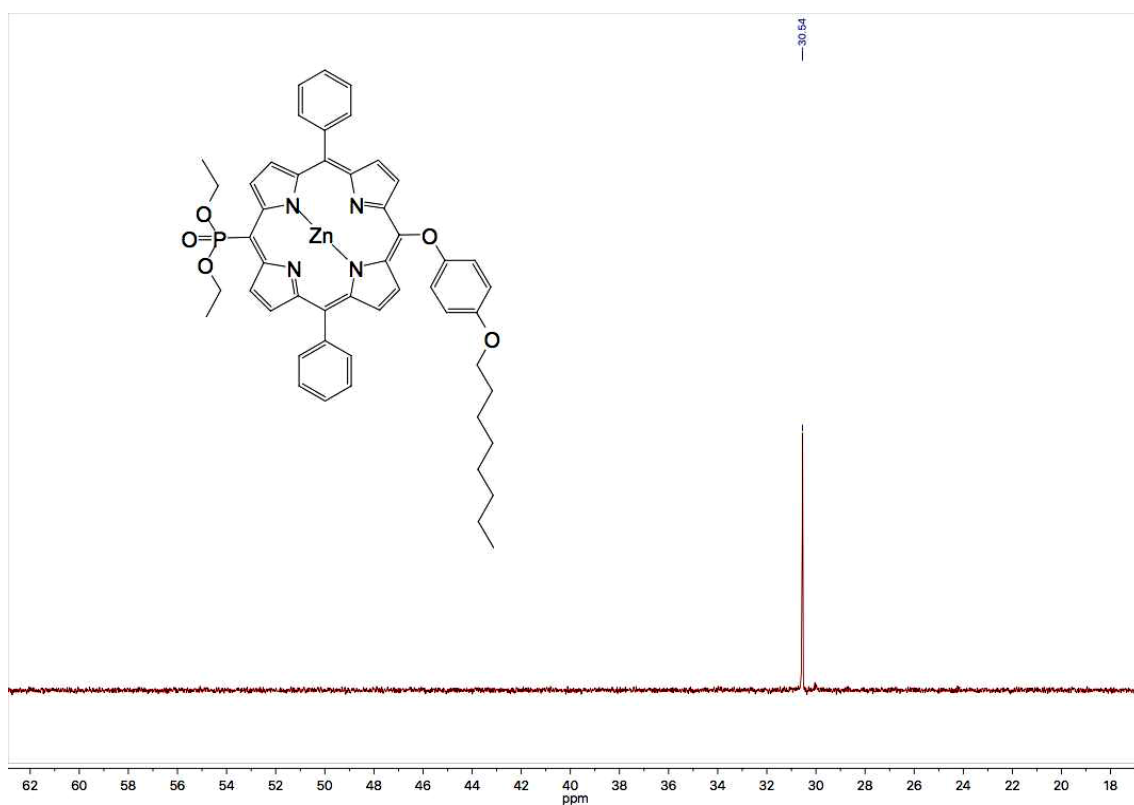


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3a** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

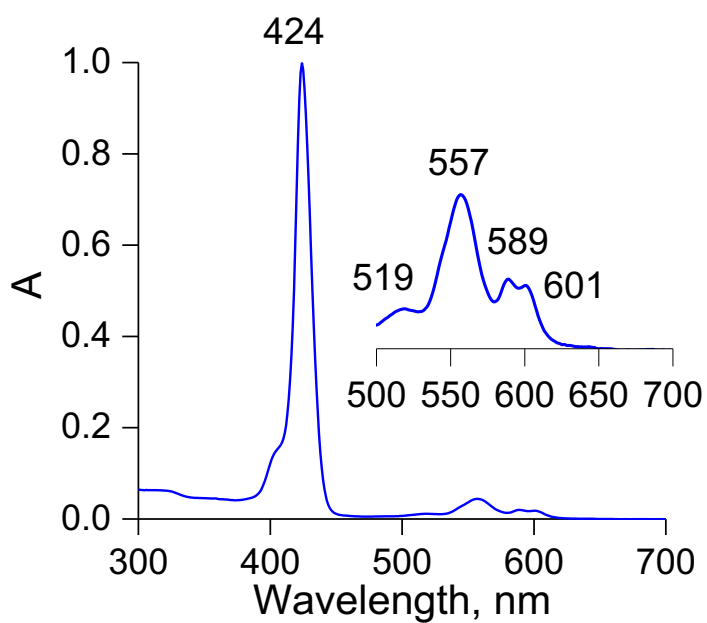


Figure S4. Normalized electronic absorption spectra of **3a** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

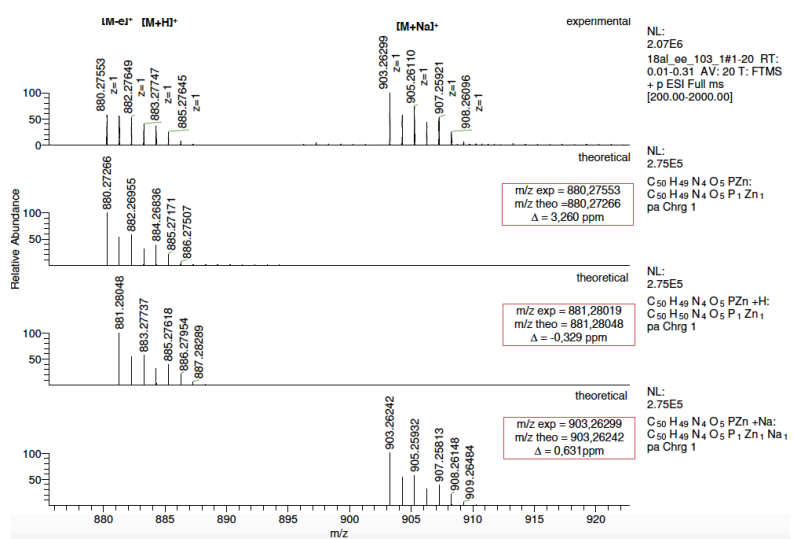
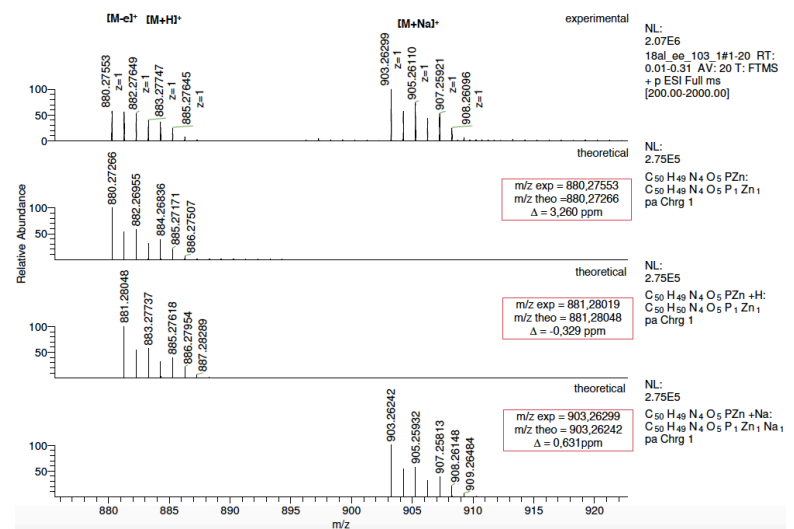
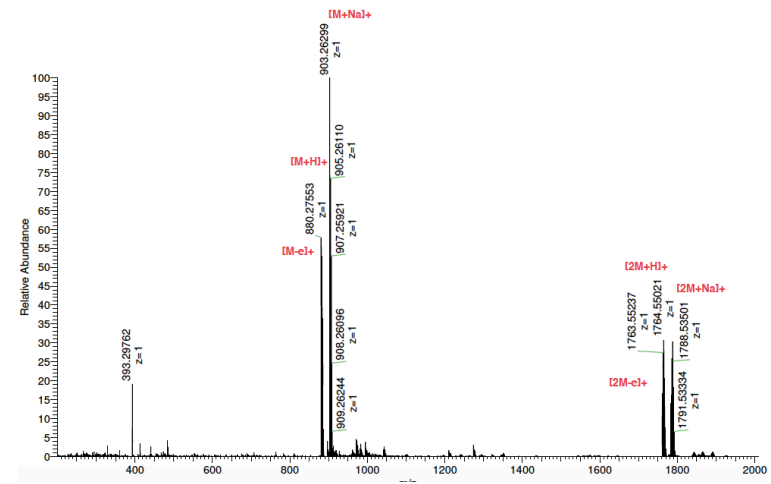


Figure S5. HRMS (ESI) spectrum of 3a.

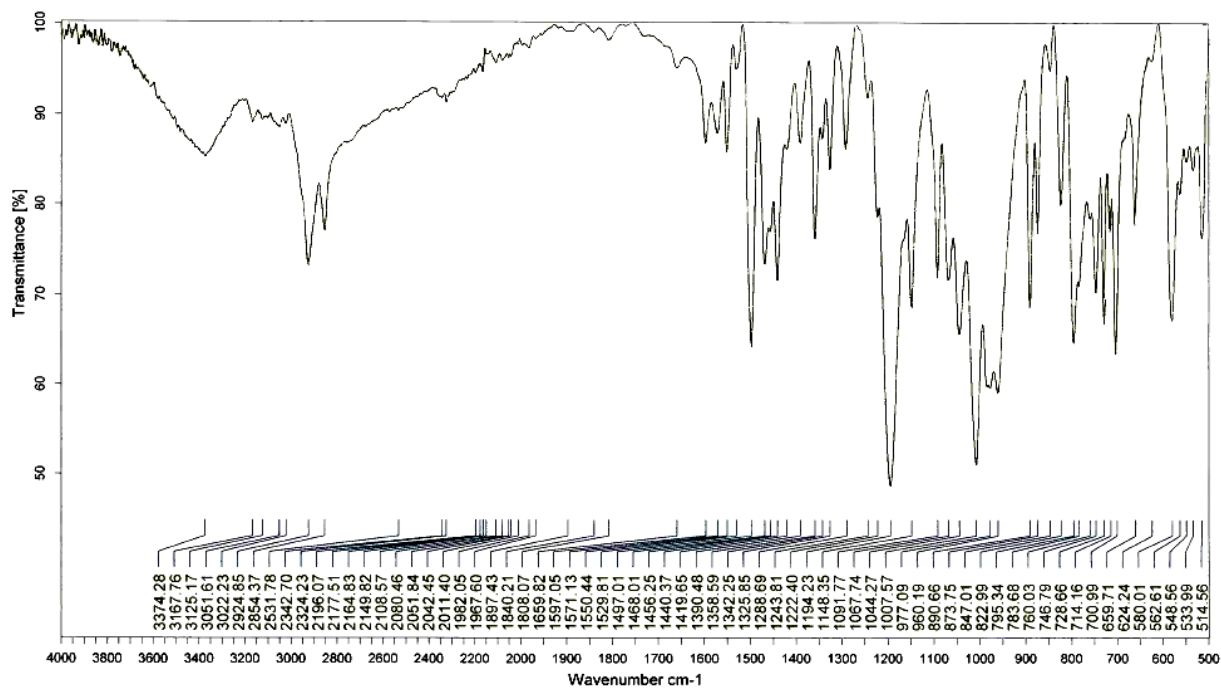


Figure S6. IR (neat) spectrum of **3a**.

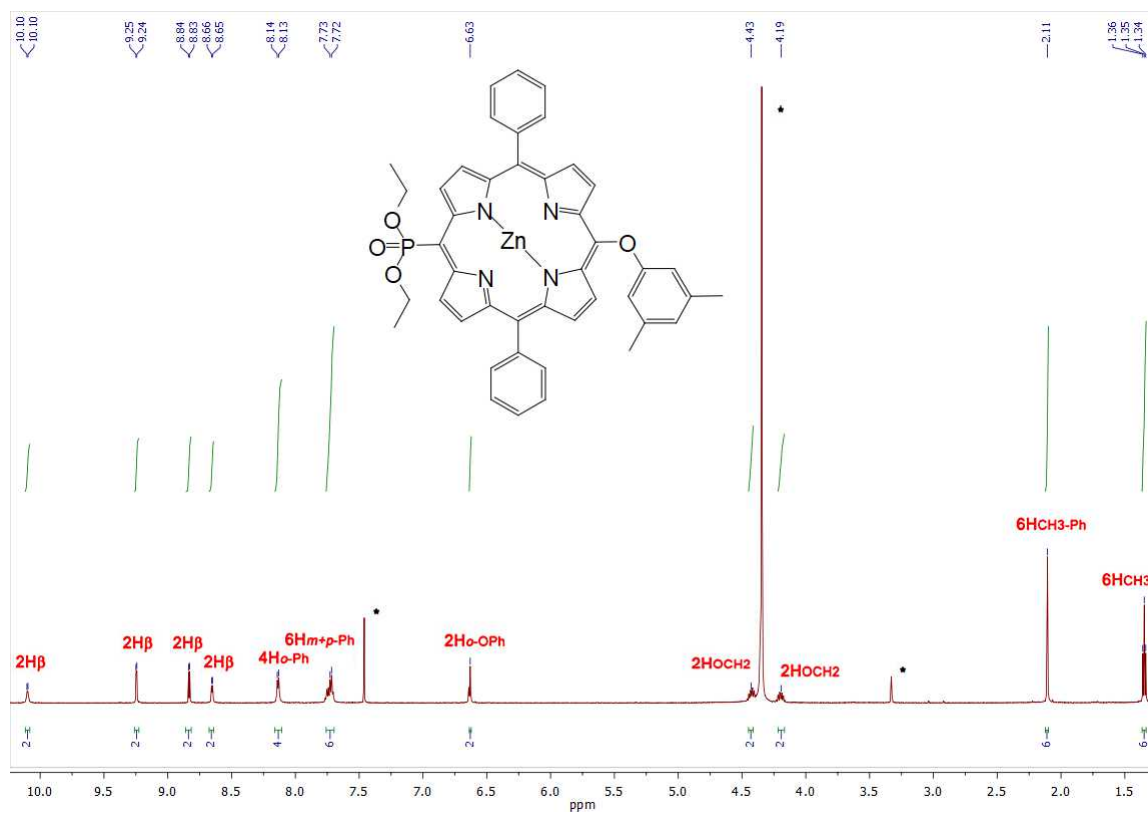


Figure S7. ^1H NMR spectrum of **3b** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.46 ppm – CHCl_3 , δ_{H} 4.34 ppm – DOH and H_2O , δ_{H} 3.33 ppm – CHD_2OD).

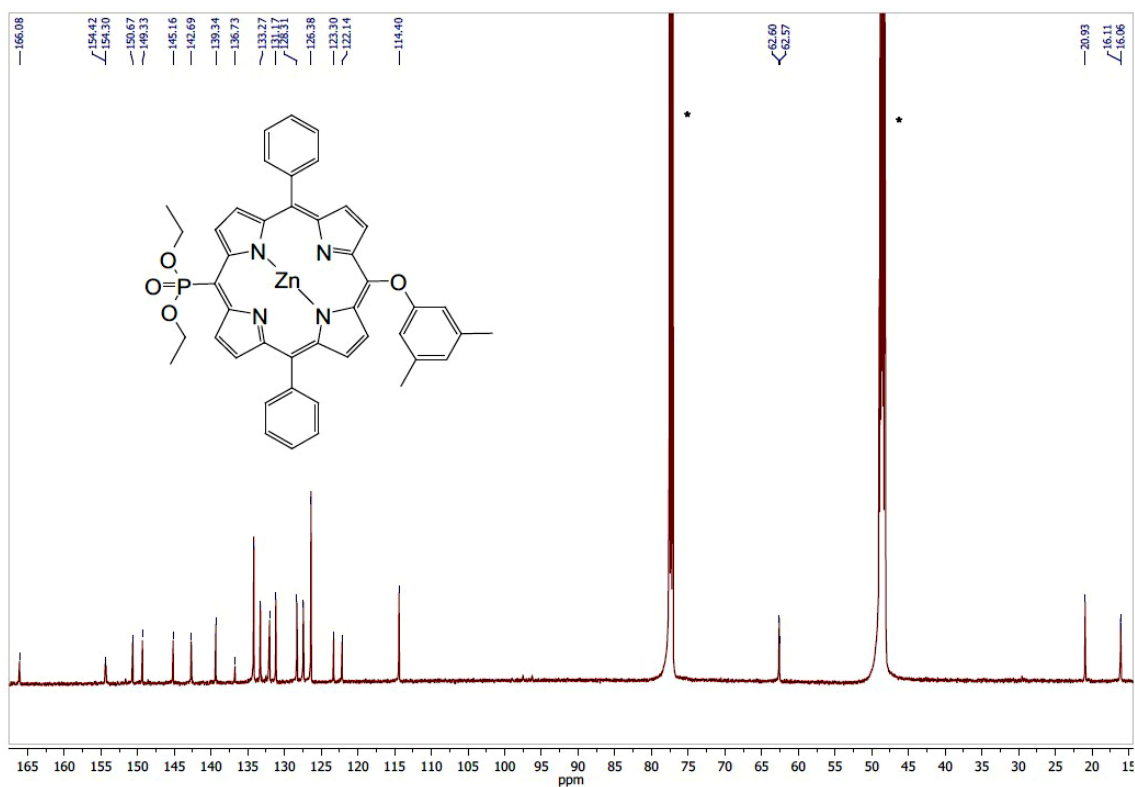


Figure S8. ^{13}C NMR spectrum of **3b** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{C} 77.31 ppm – CDCl_3 , δ_{C} 48.55 ppm – CD_3OD).

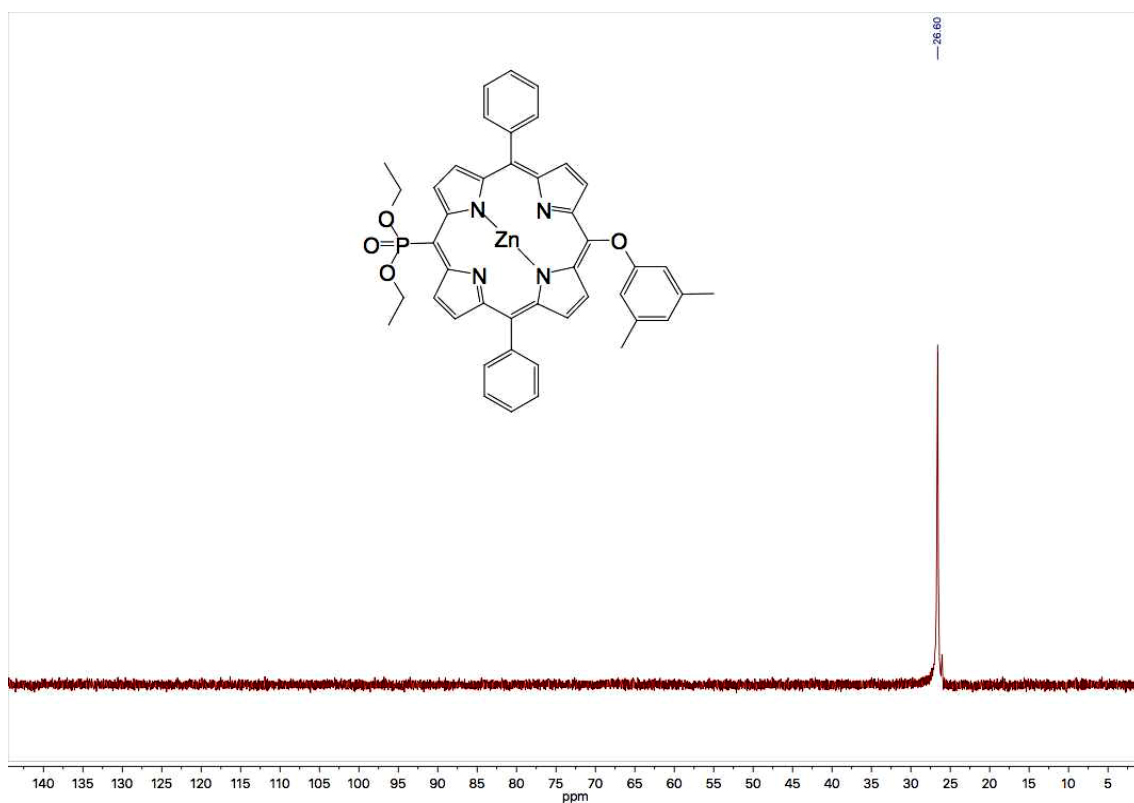


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3b** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

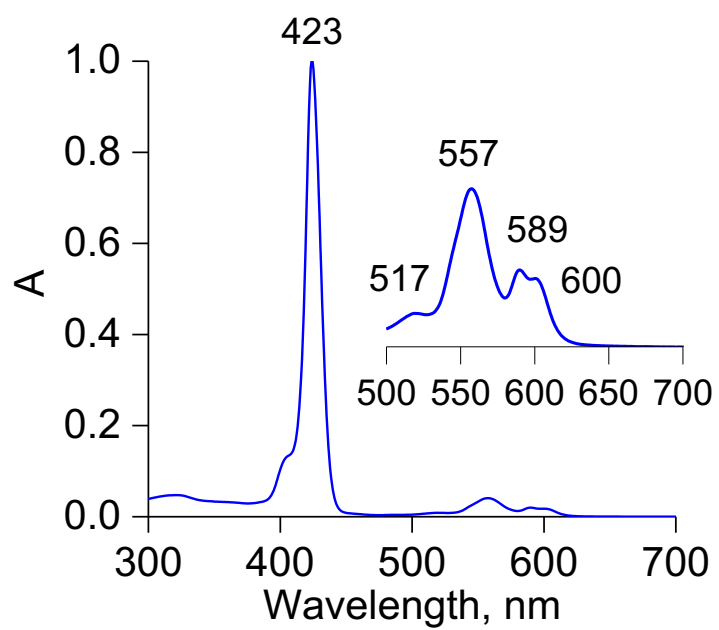


Figure S10. Normalized electronic absorption spectra of **3b** in CHCl₃/MeOH (2:1, v/v) solution (c = 6.25 μM).

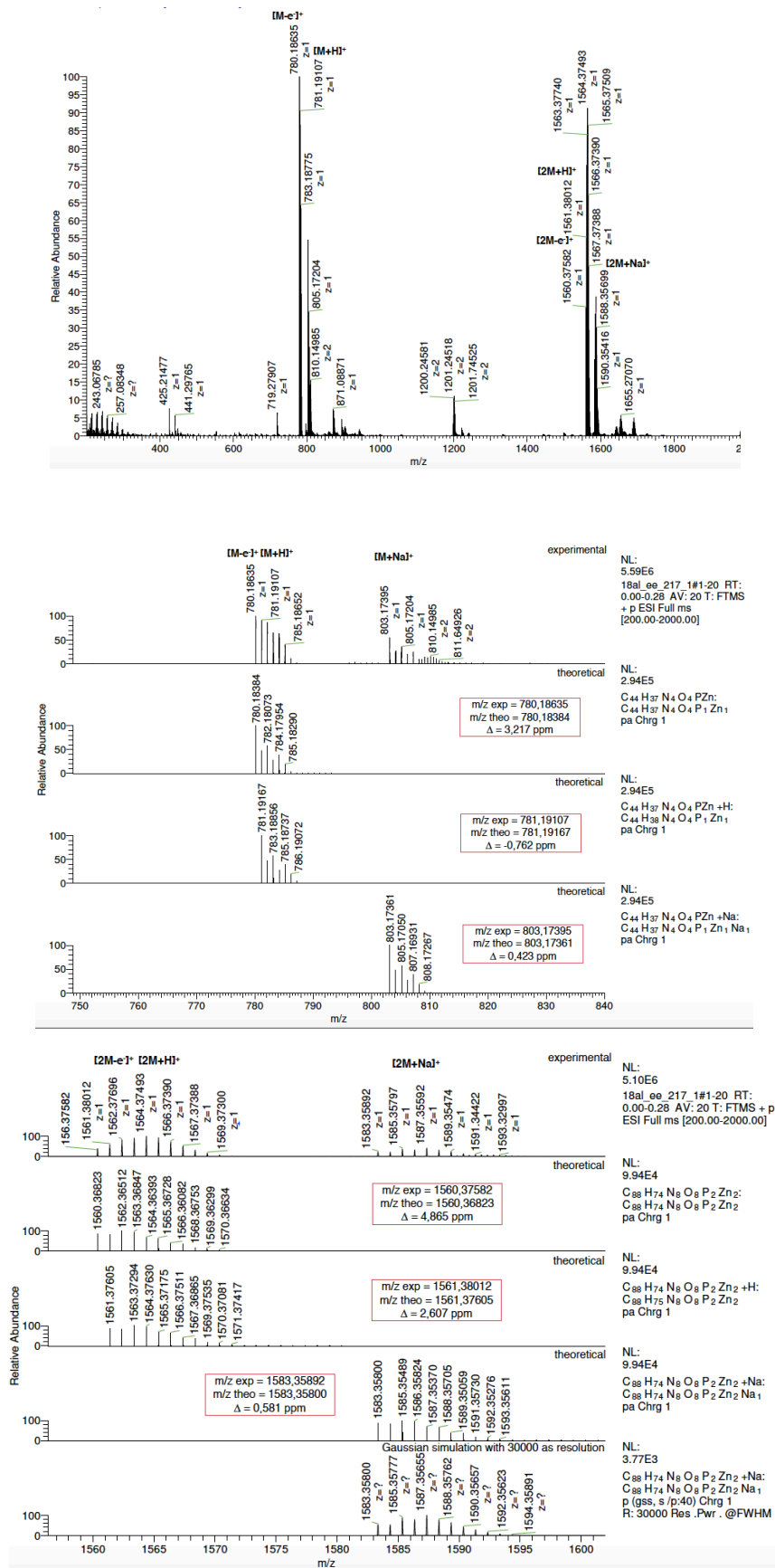


Figure S11. HRMS (ESI) spectrum of 3b.

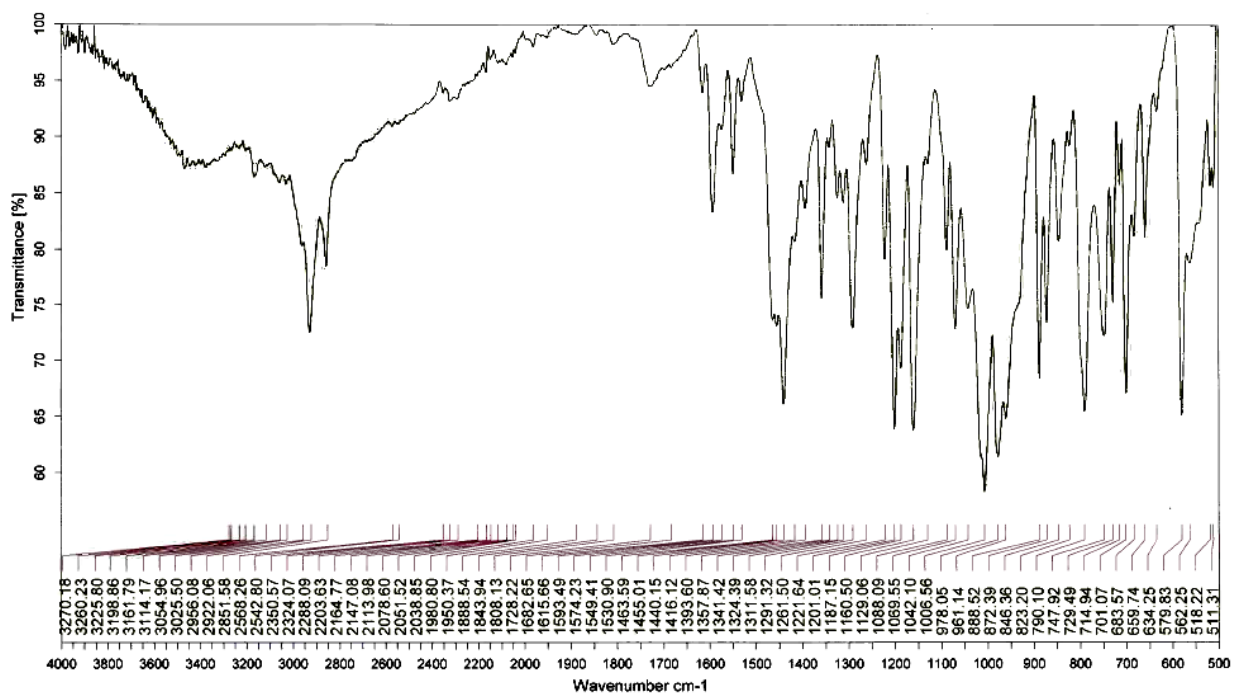


Figure S12. IR (neat) spectrum of **3b**.

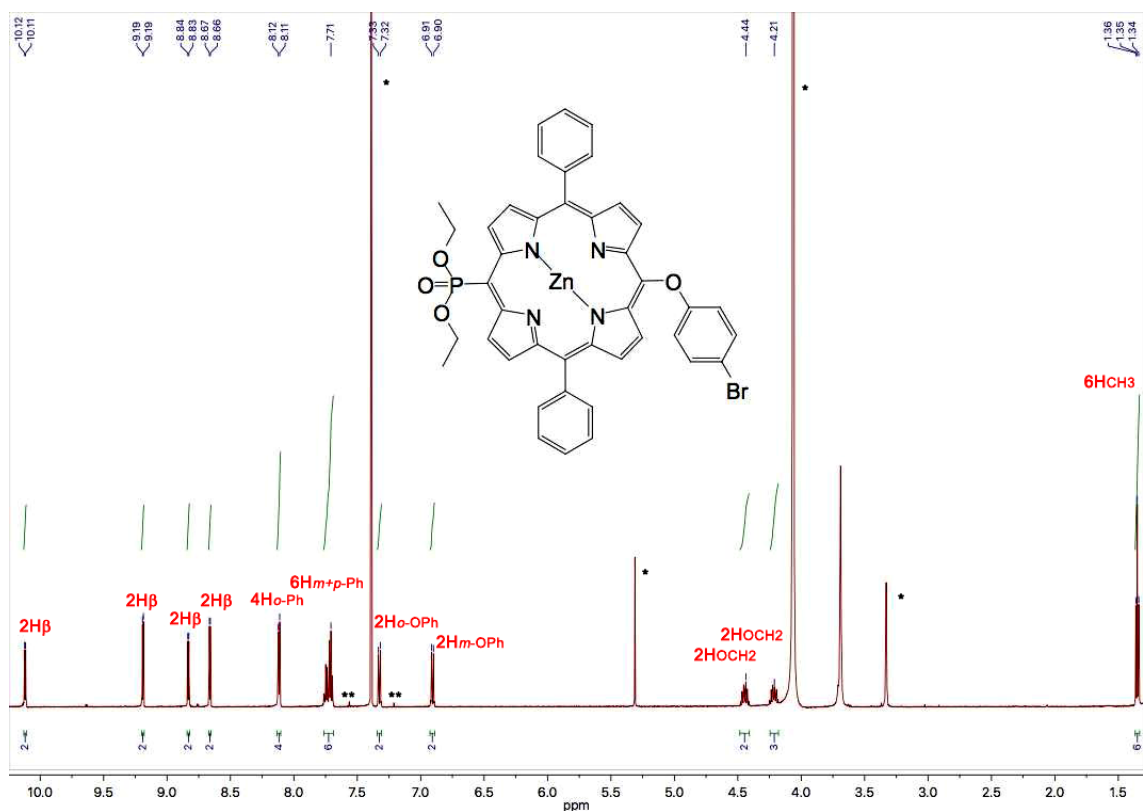


Figure S13. ^1H NMR spectrum of **3c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.38 ppm – CHCl_3 , δ_{H} 5.31 ppm – CH_2Cl_2 , δ_{H} 4.06 ppm – DOH and H_2O , δ_{H} 3.33 ppm – CHD_2OD). Solvent satellite peaks are indicated with **.

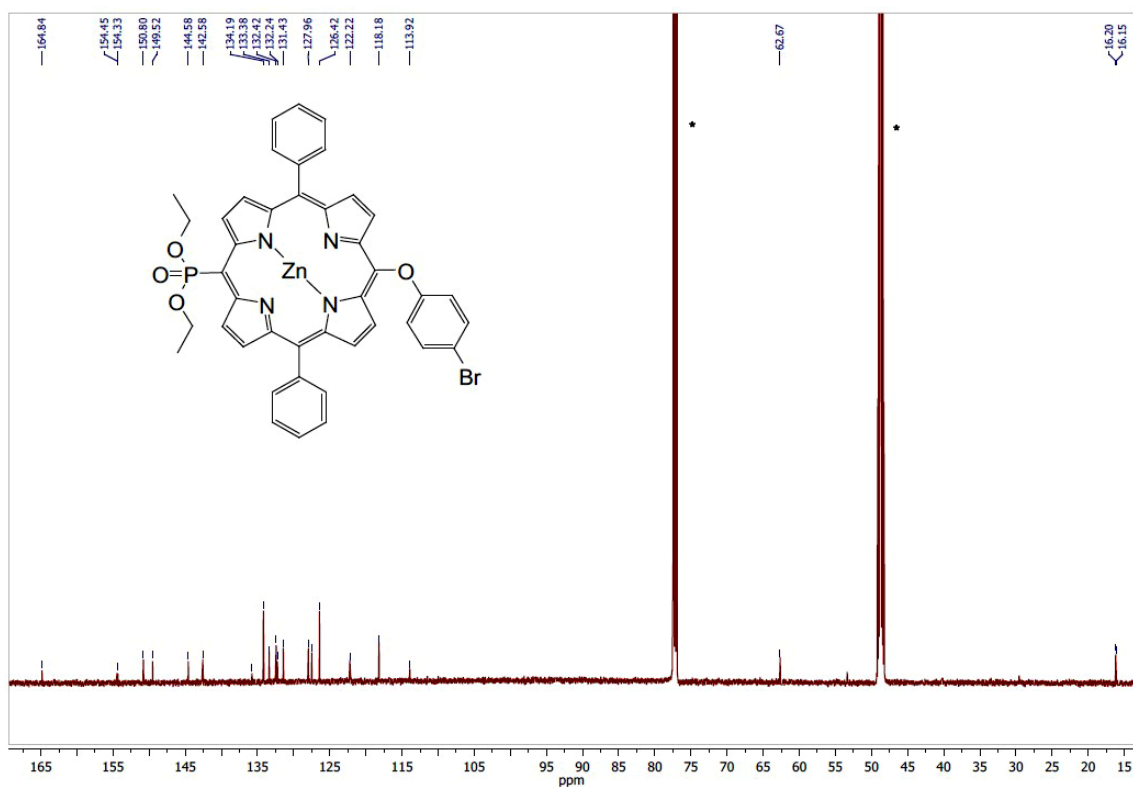


Figure S14. ^{13}C NMR spectrum of **3c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * ($\delta_{\text{C}} 77.21$ ppm – CDCl_3 , $\delta_{\text{C}} 48.71$ ppm – CD_3OD).

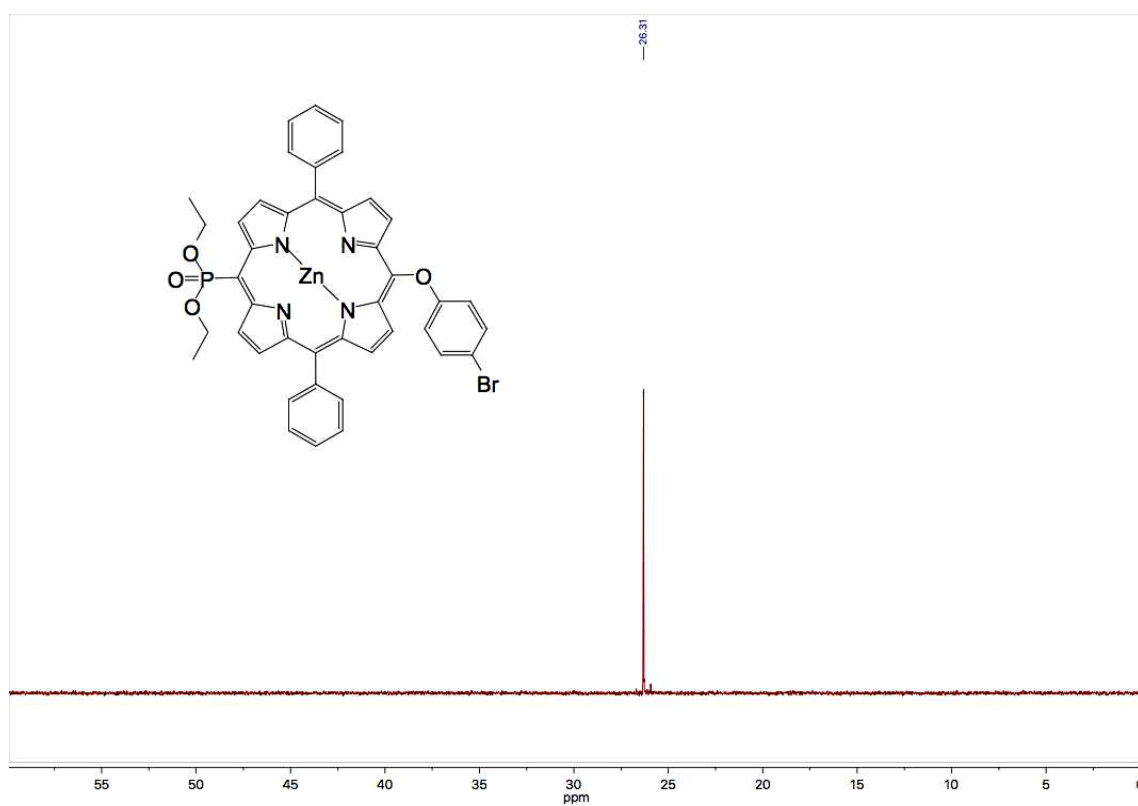


Figure S15. ^{31}P $\{^1\text{H}\}$ NMR spectrum of **3c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

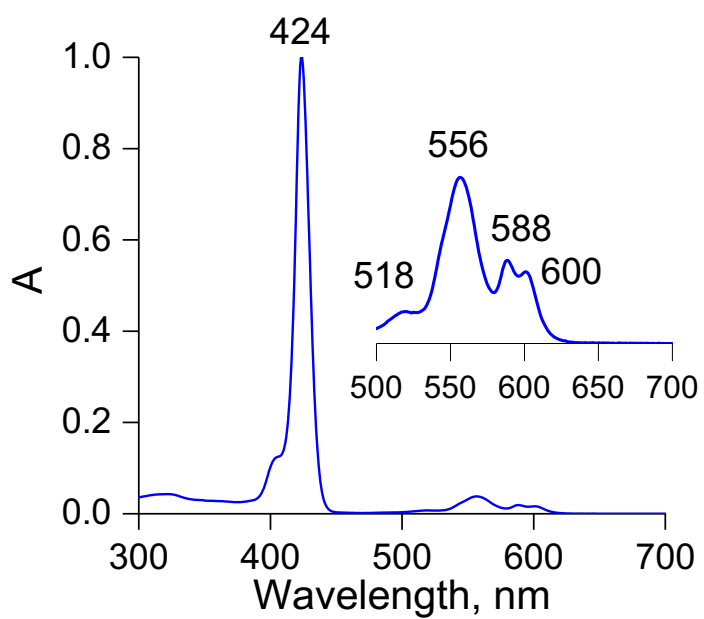


Figure S16. Normalized electronic absorption spectra of **3c** in $\text{CHCl}_3/\text{CD}_3\text{OD}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

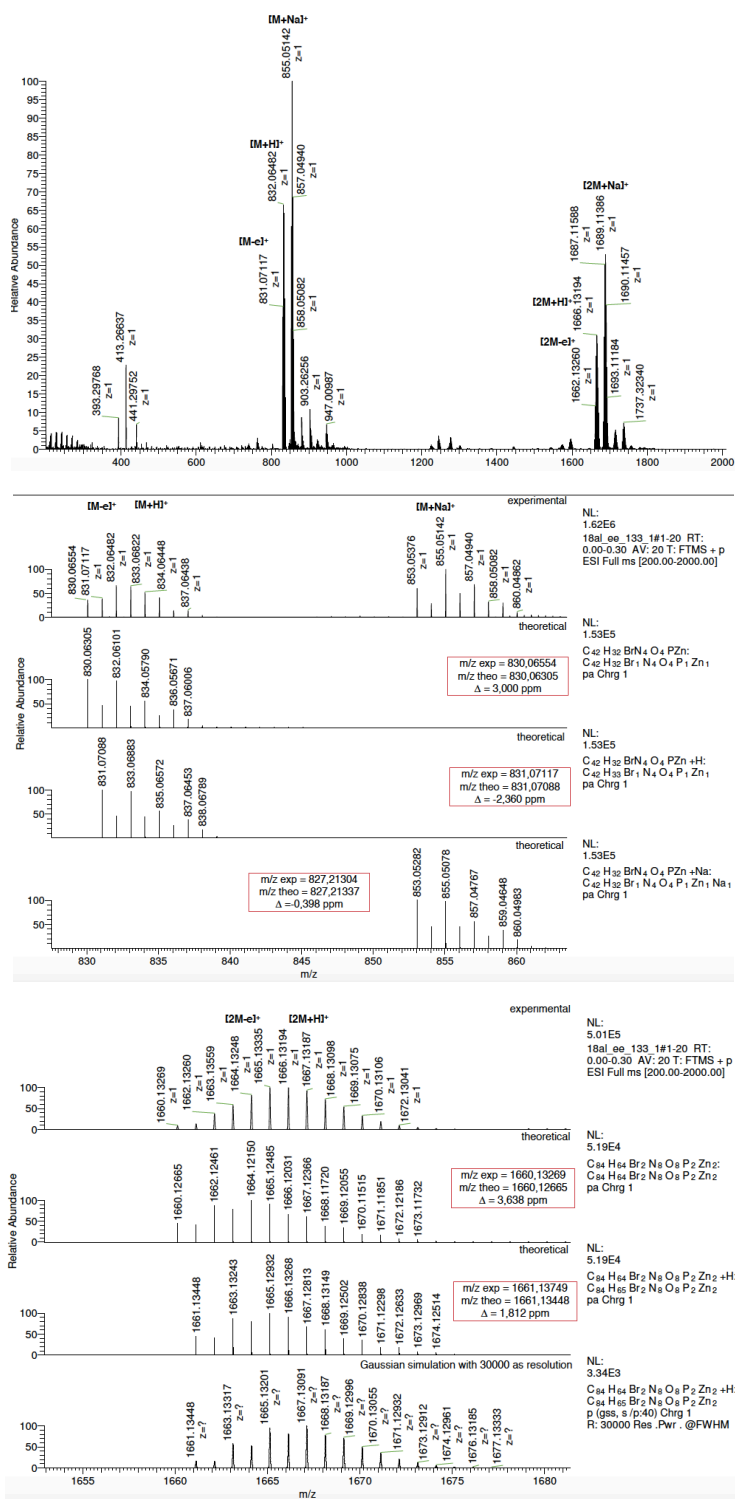


Figure S17. HRMS (ESI) spectrum of 3c.

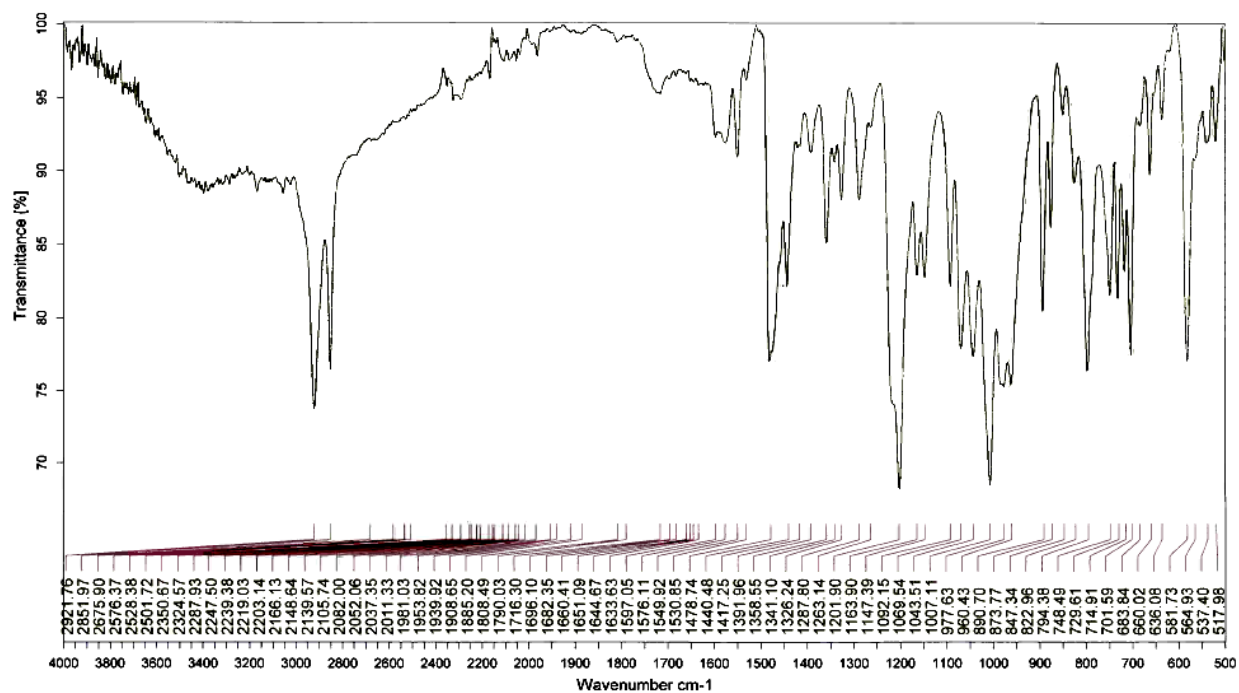


Figure S18. IR (neat) spectrum of **3c**.

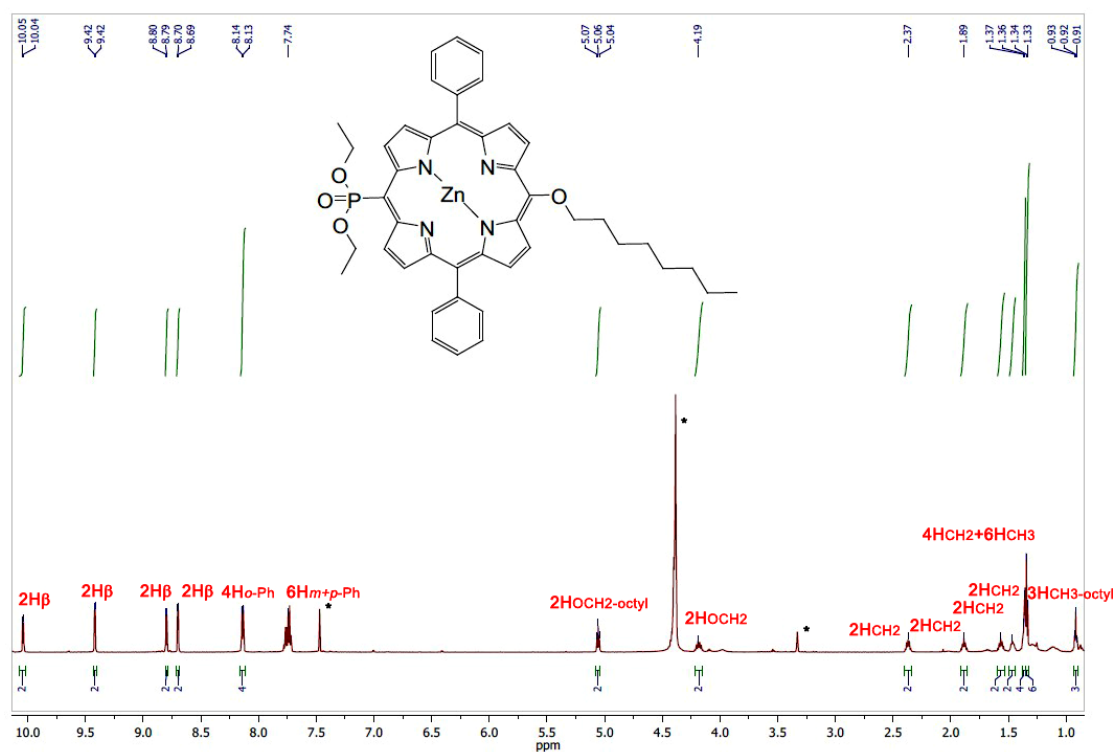


Figure S19. ^1H NMR spectrum of **3d** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.47 ppm – CHCl_3 , δ_{H} 4.39 ppm – DOH and H_2O , δ_{H} 3.32 ppm – CHD_2OD).

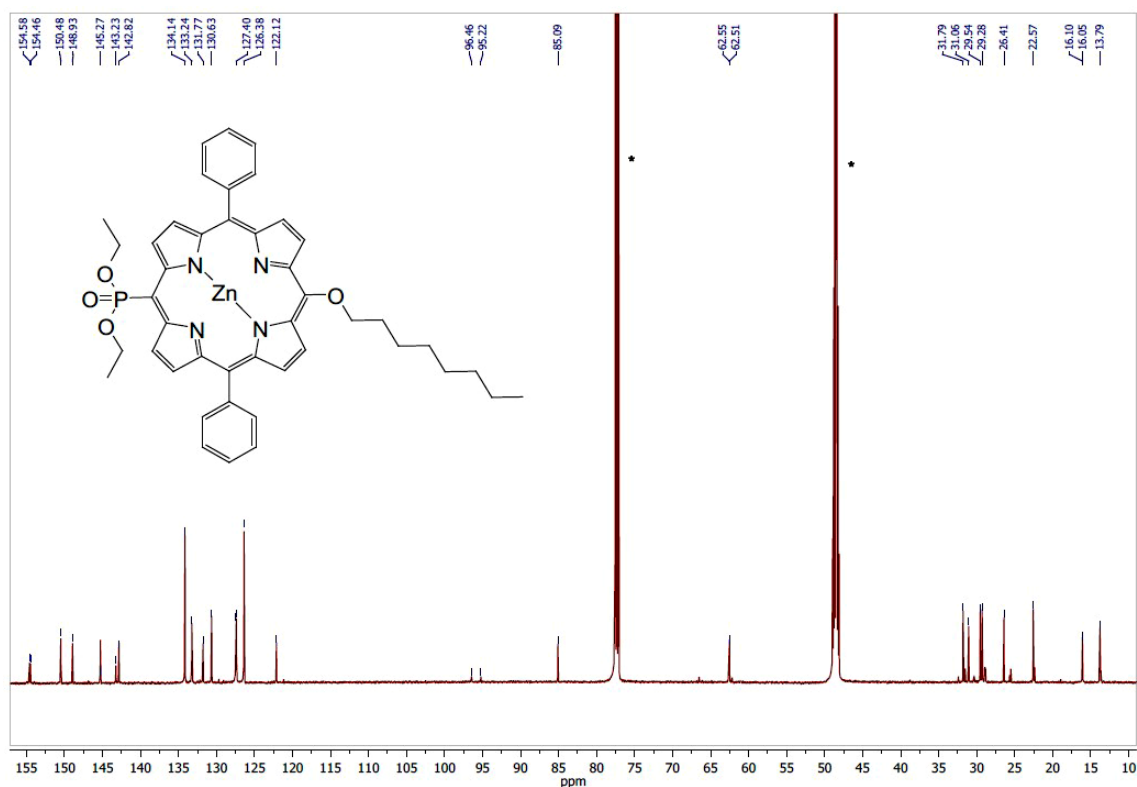


Figure S20. ¹³C NMR spectrum of **3d** (CDCl₃/CD₃OD 2:1, v/v). Solvent peaks are indicated with * (δ_c 77.33 ppm – CHCl₃, δ_c 48.52 ppm – CD₃OD).

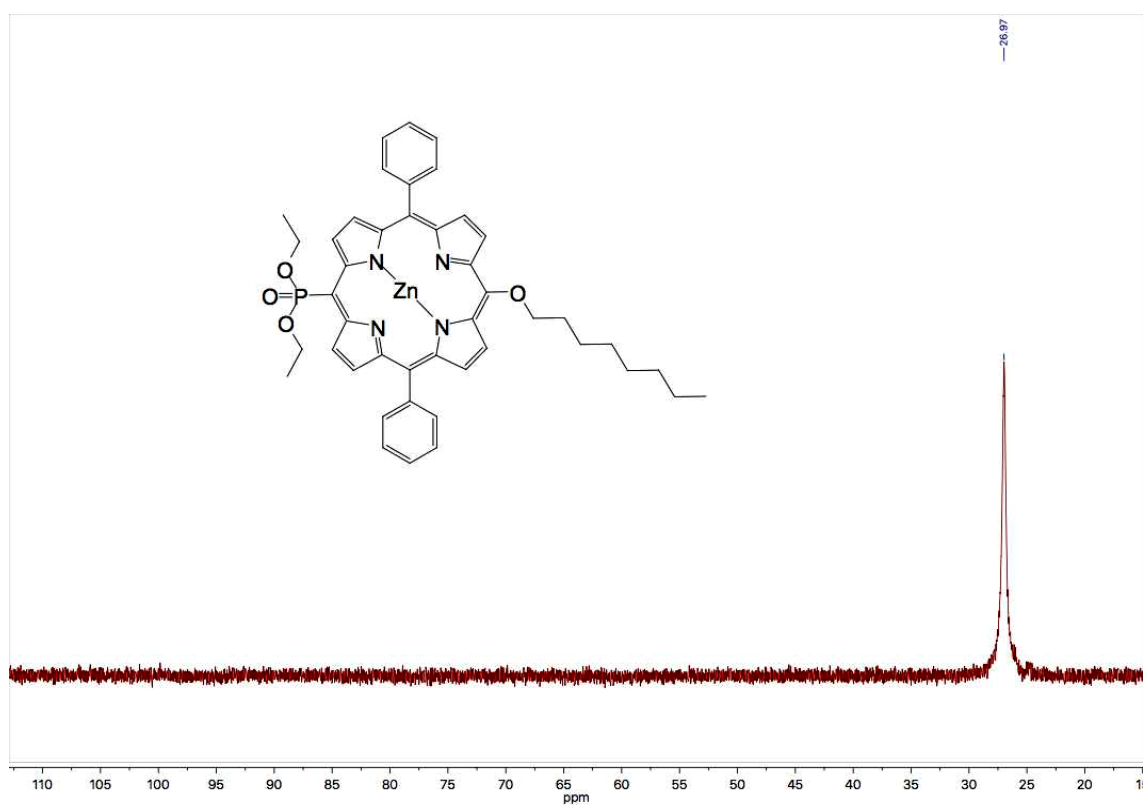


Figure S21. ³¹P {¹H} NMR spectrum of **3d** (CDCl₃/CD₃OD 2:1, v/v).

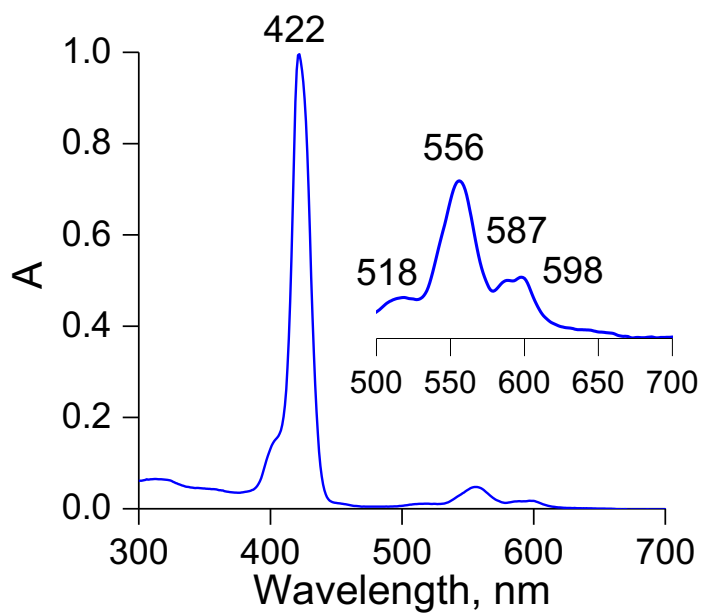


Figure S22. Normalized electronic absorption spectra of **3d** in CHCl₃/MeOH (2:1, v/v) solution (c = 6.25 μM).

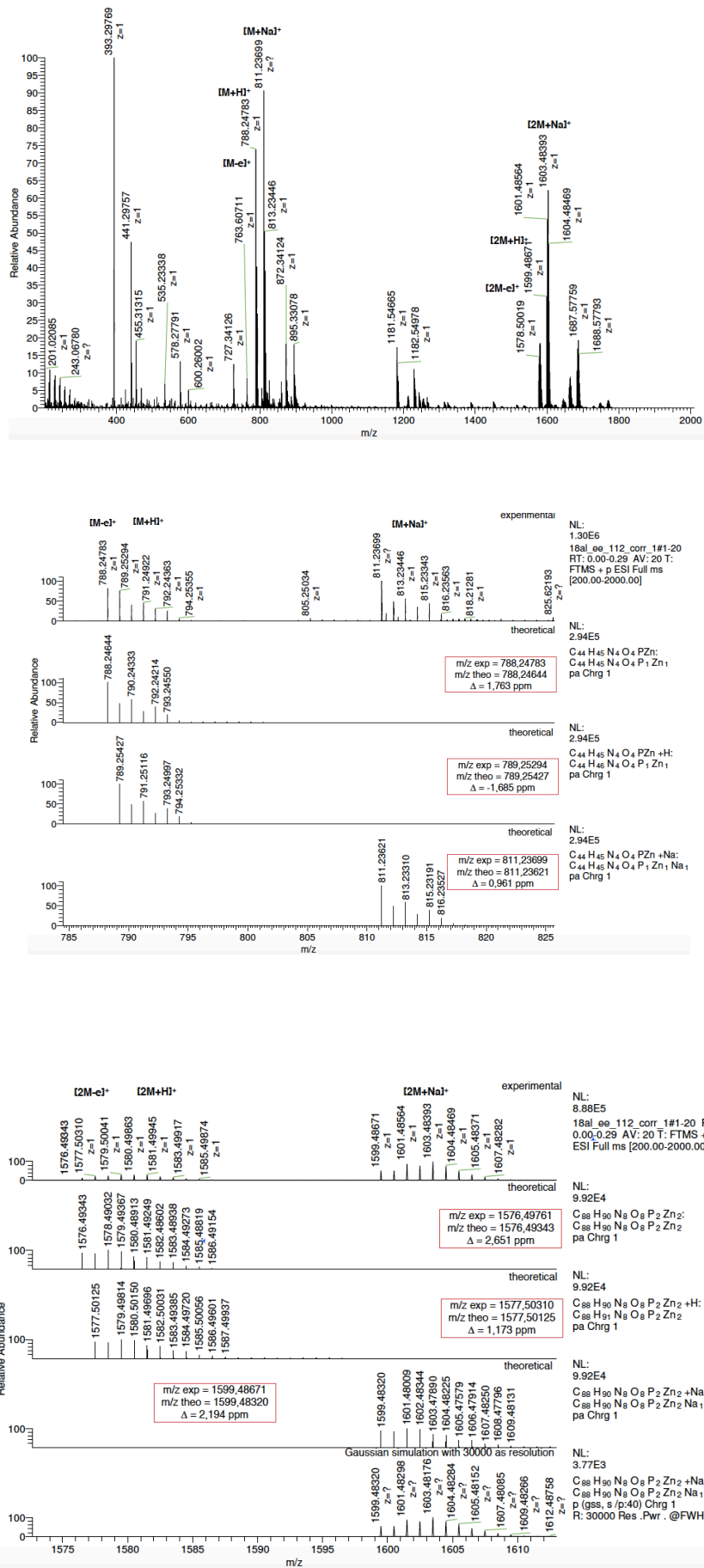


Figure S23. HRMS (ESI) spectrum of 3d.

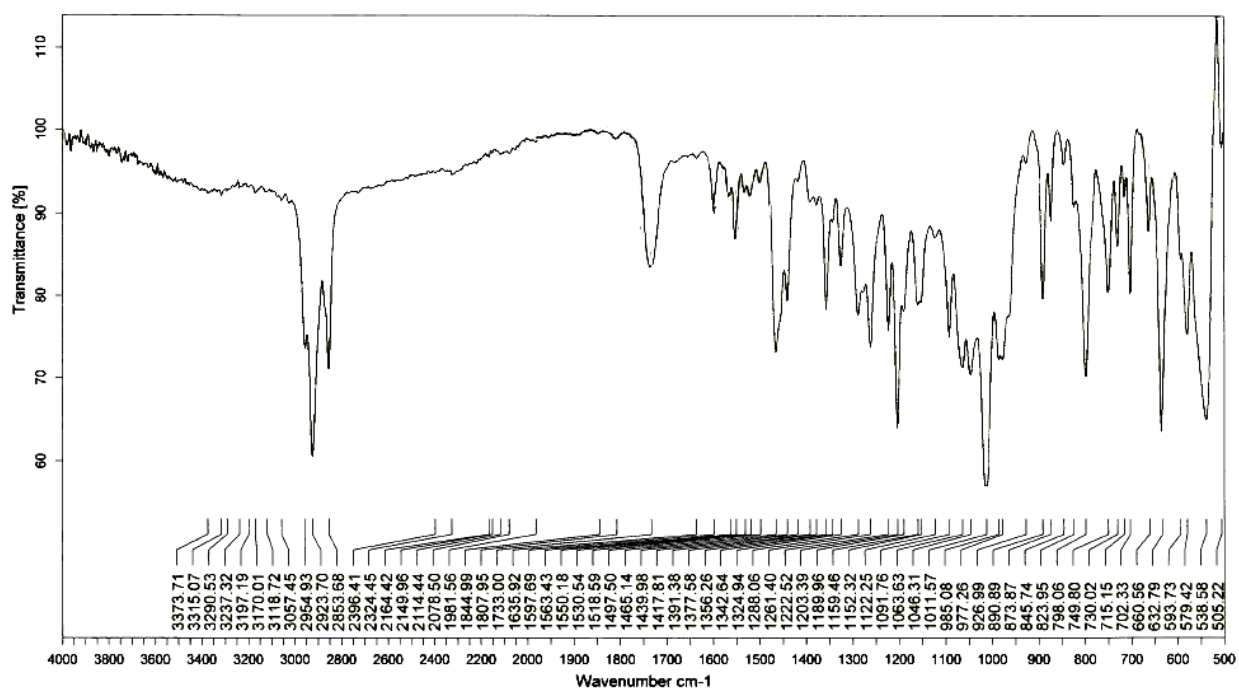


Figure S24. IR (neat) spectrum of **3d**.

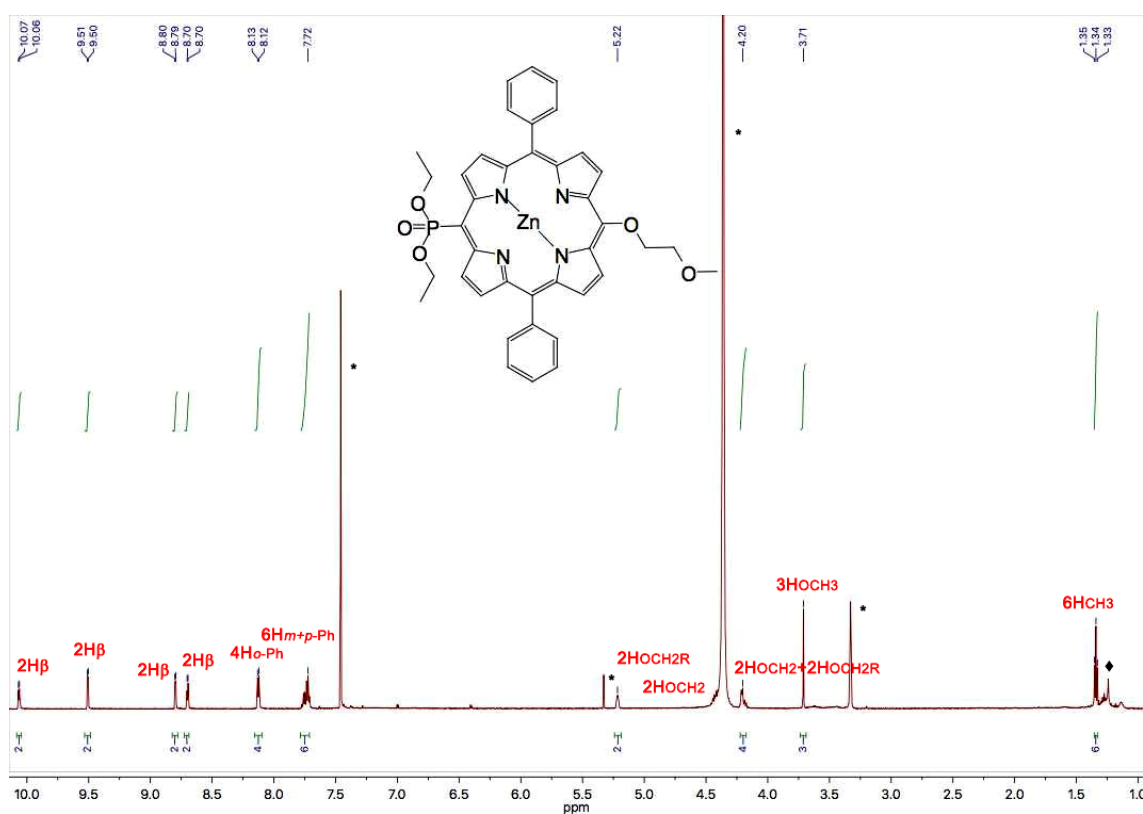


Figure S25. ^1H NMR spectrum of **3e** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.45 ppm – CHCl_3 , δ_{H} 4.35 ppm – DOH and H_2O , δ_{H} 3.33 ppm – CHD_2OD). Impurities in the $\text{CDCl}_3/\text{MeOD}$ mixture are indicated with ♦.

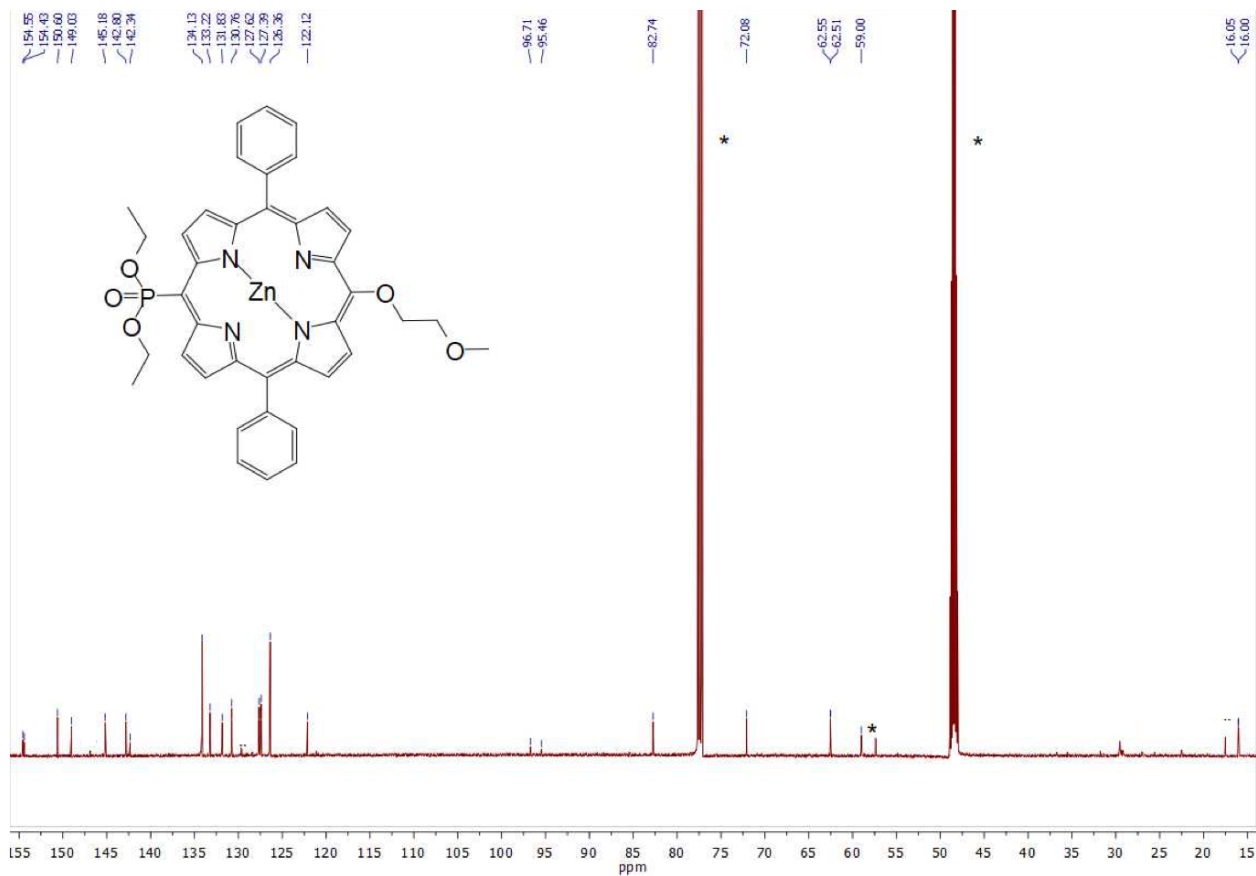


Figure S26. ^{13}C NMR spectrum of **3e** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks (δ_{C} 77.37 ppm – CDCl_3 , δ_{C} 59.00 ppm – CD_2Cl_2 , δ_{C} 48.45 ppm – CD_3OH) are indicated with *.

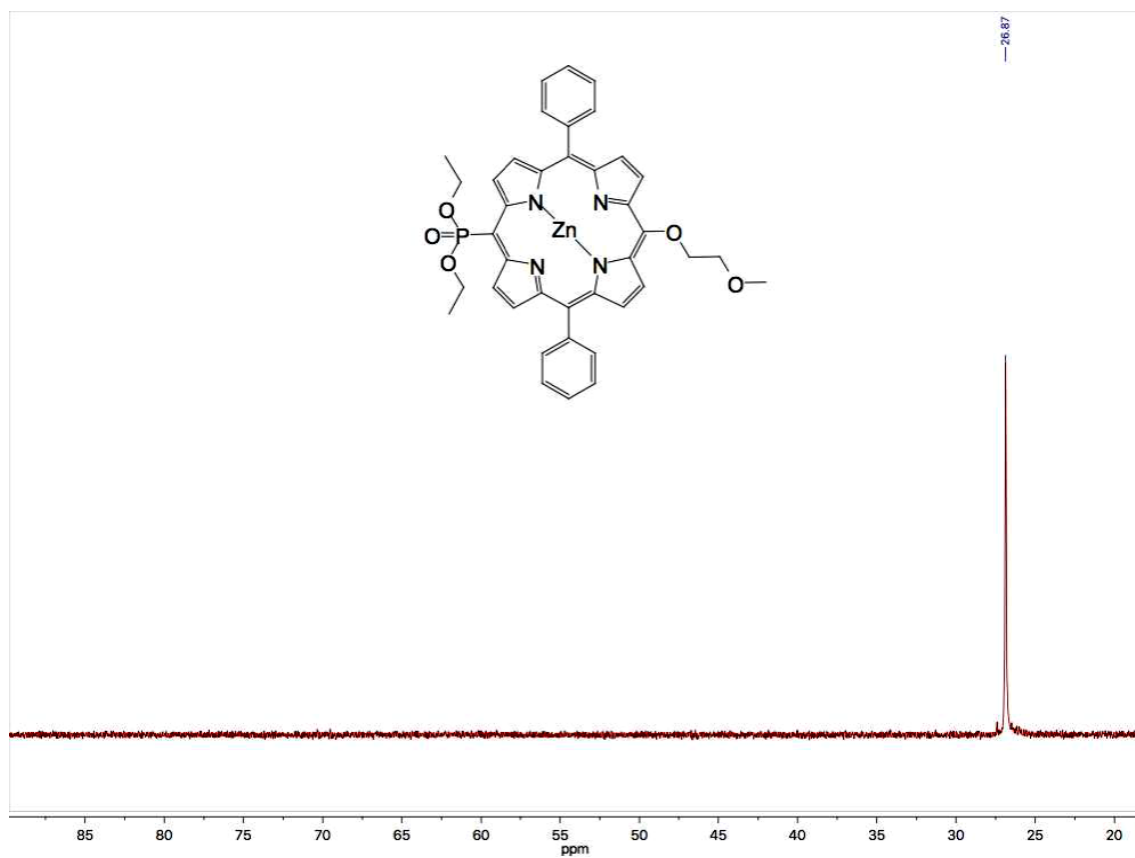


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3e** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

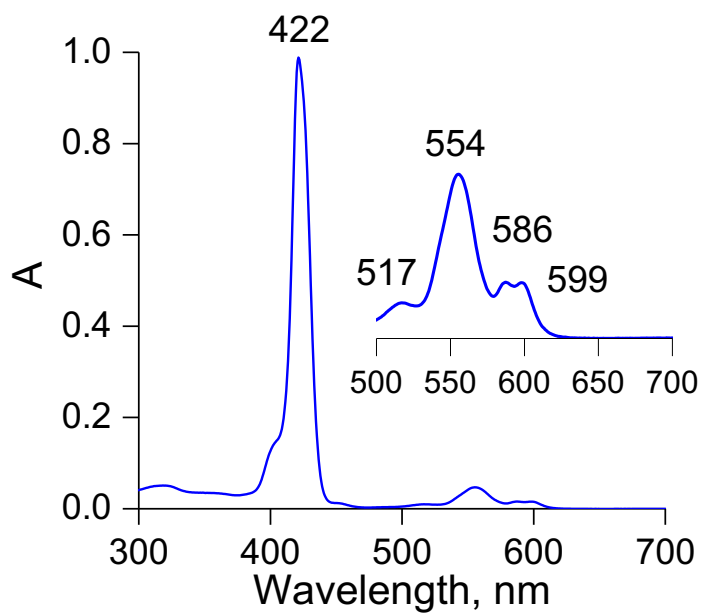


Figure S28. Normalized electronic absorption spectra of **3e** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

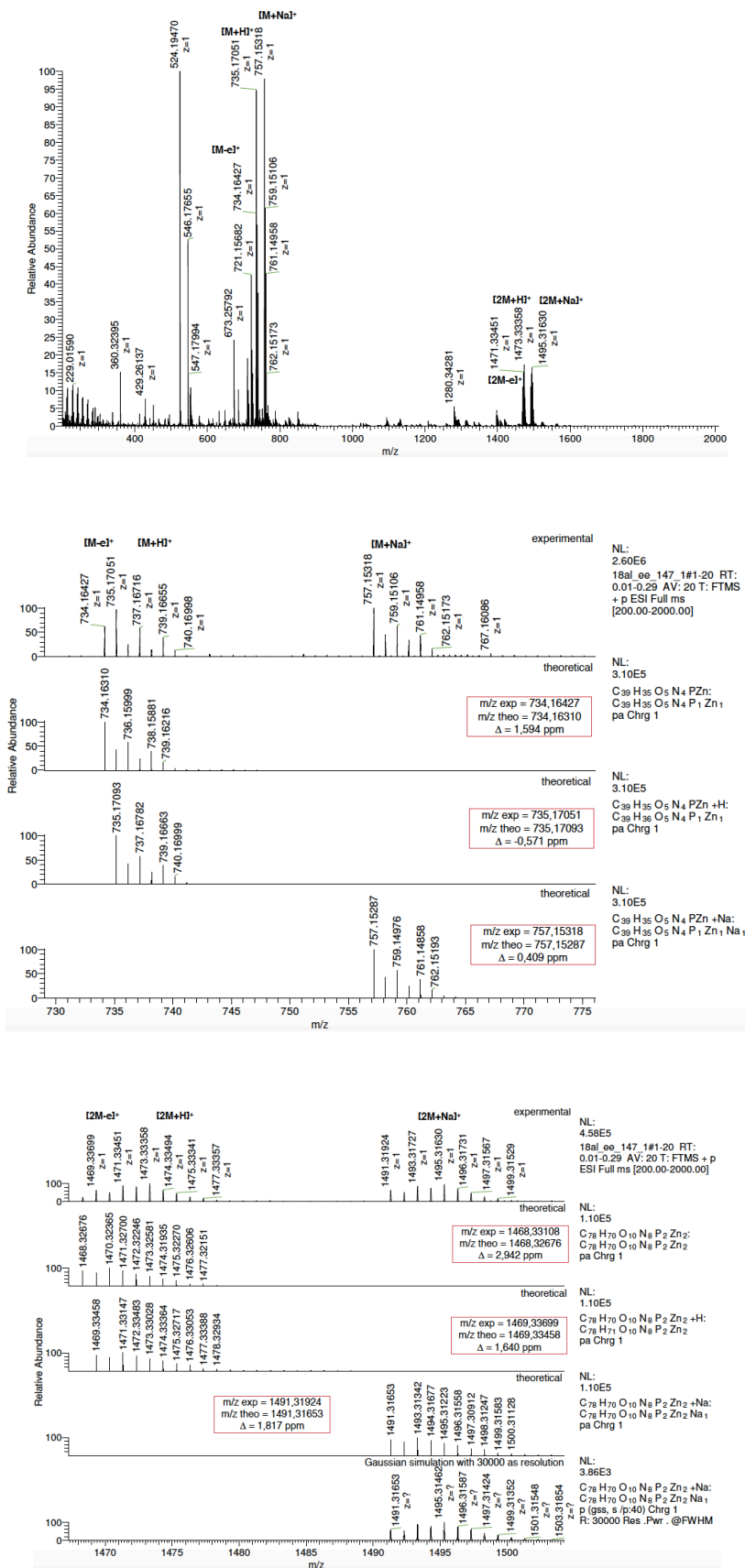


Figure S29. HRMS (ESI) spectrum of 3e.

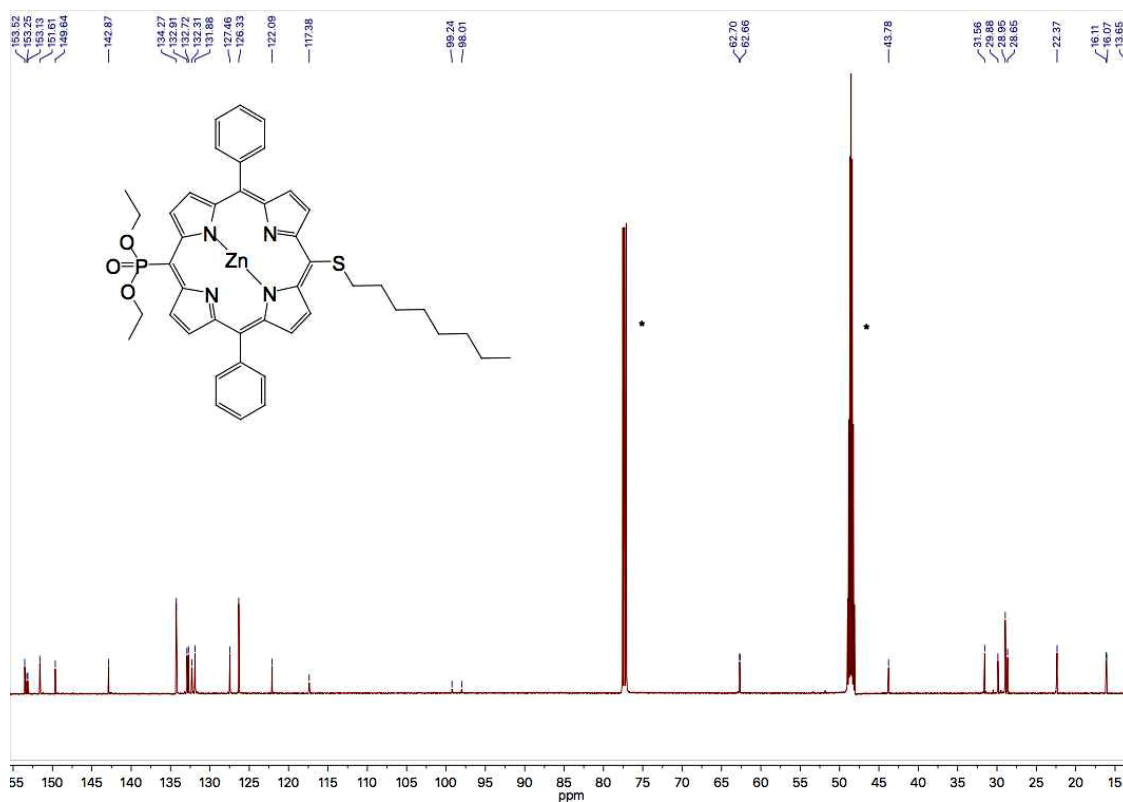


Figure S32. ^{13}C NMR spectrum of **4b** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * ($\delta_{\text{C}} 77.32$ ppm – CDCl_3 , $\delta_{\text{C}} 48.54$ ppm – CD_3OD).

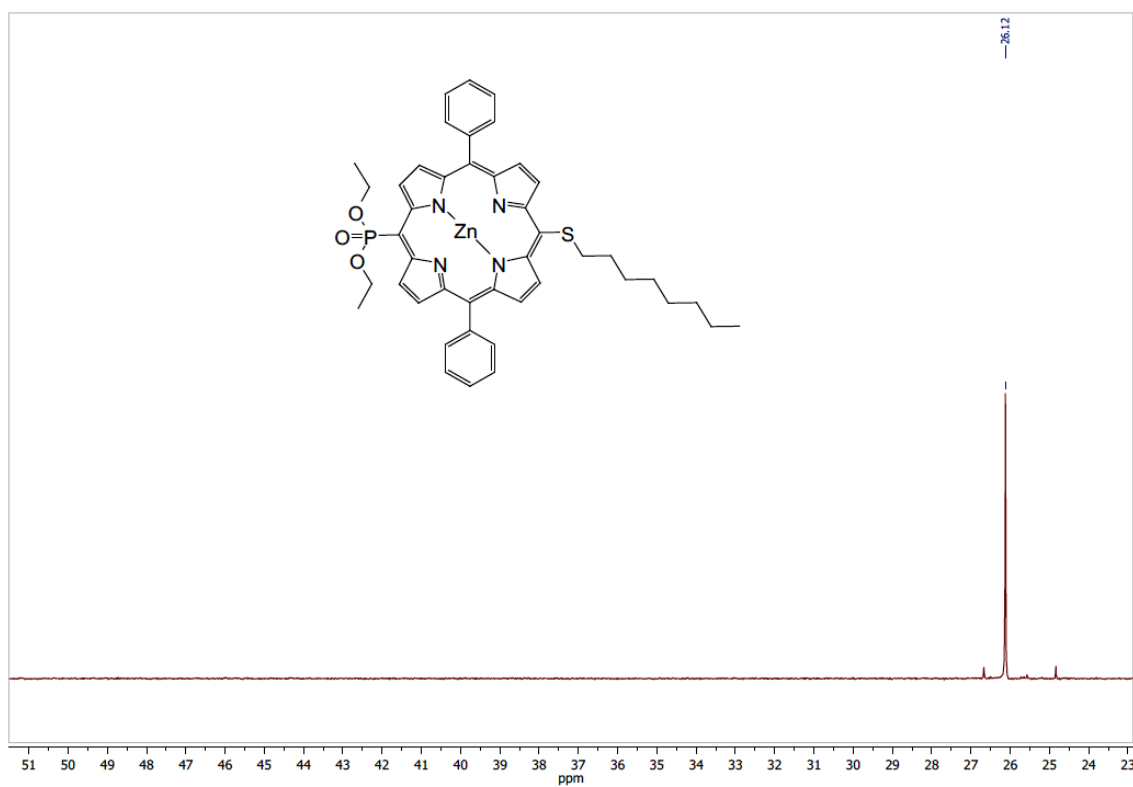


Figure S33. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4b** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

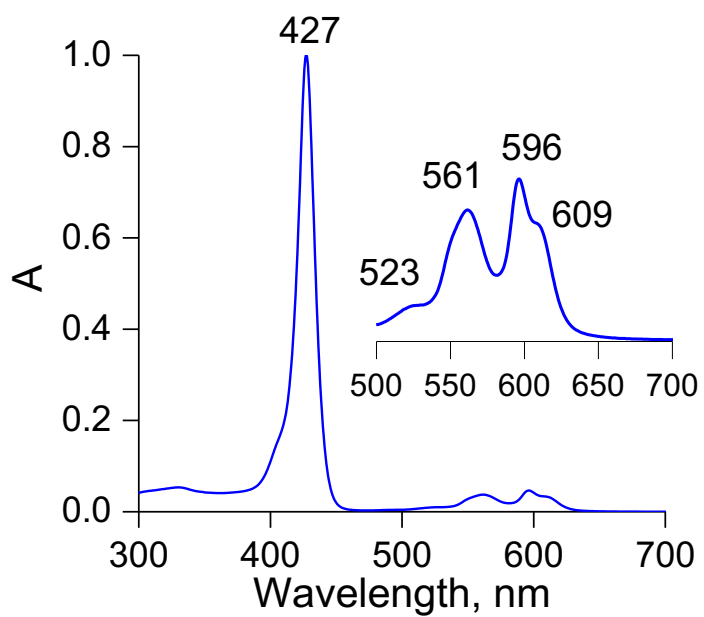


Figure S34. Normalized electronic absorption spectra of **4b** in $\text{CHCl}_3/\text{CD}_3\text{OD}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

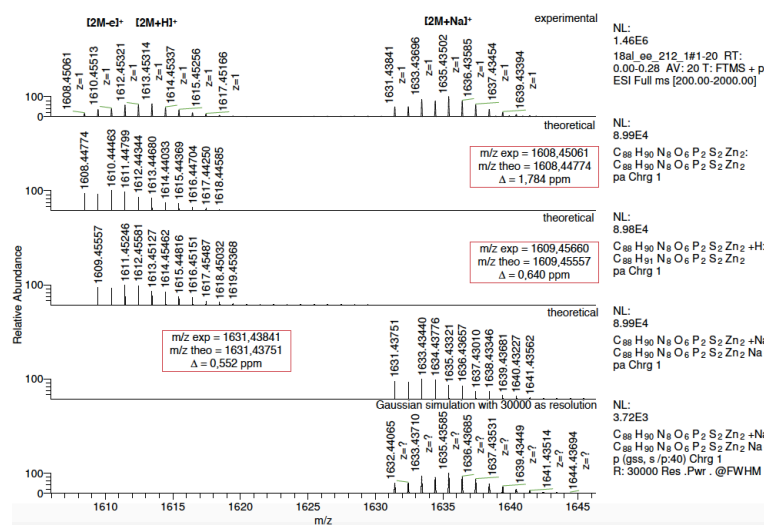
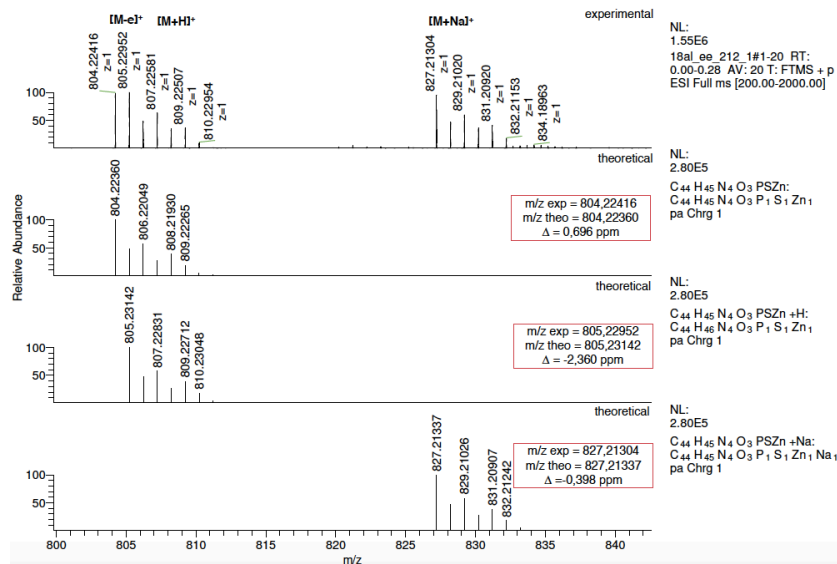
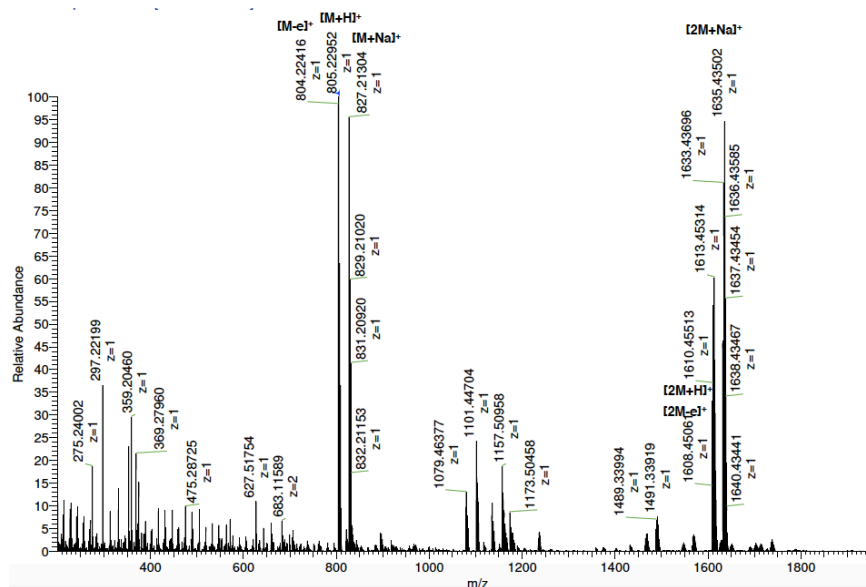


Figure S35. HRMS (ESI) spectrum of **4b**.

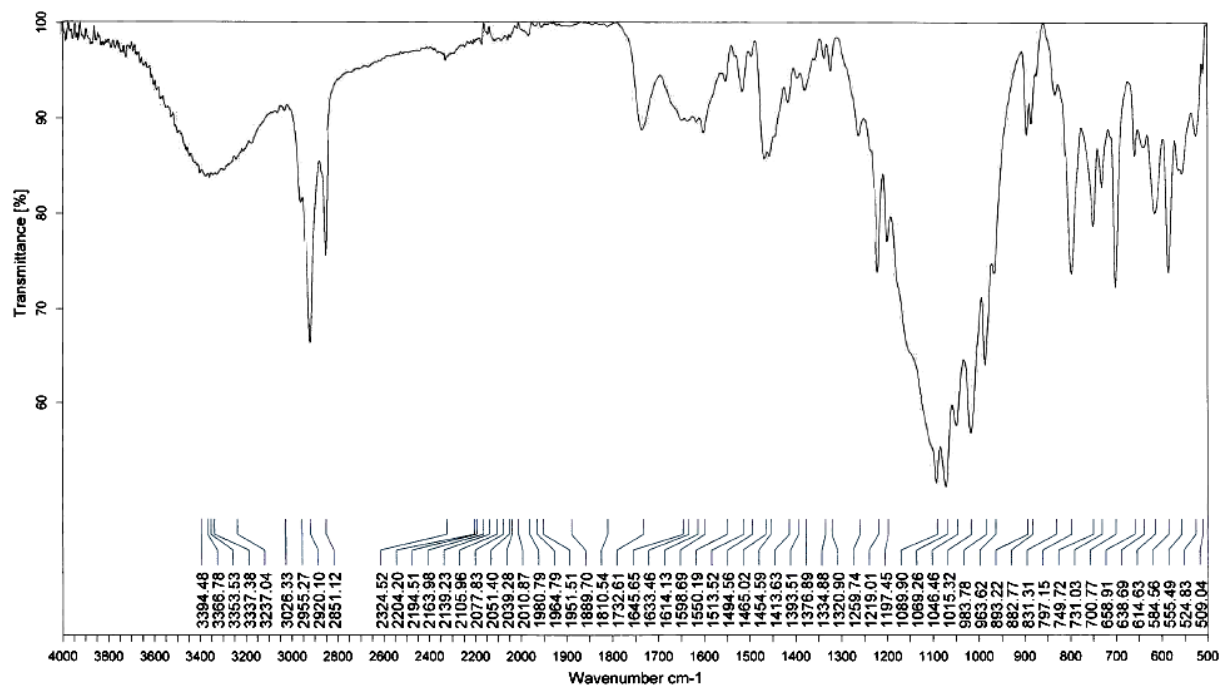


Figure S36. IR (neat) spectrum of **4b**.

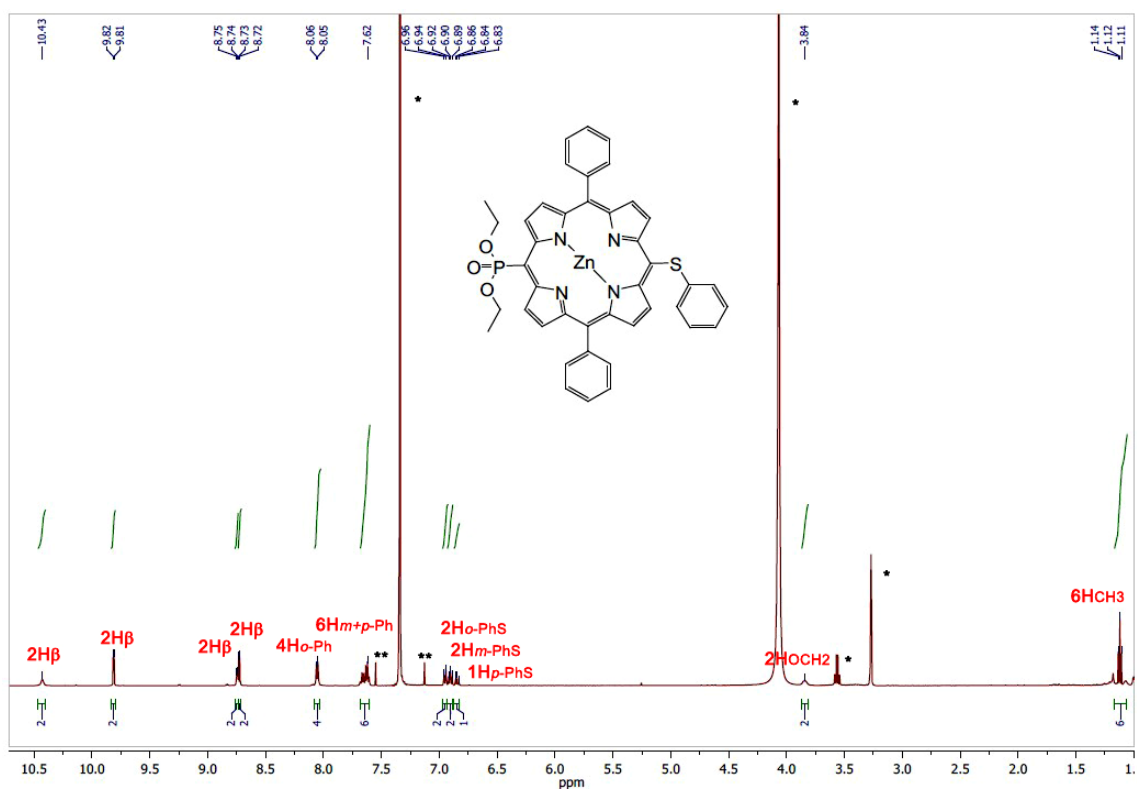


Figure S37. ^1H NMR spectrum of **4c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.34 ppm – CHCl_3 , δ_{H} 4.06 ppm – DOH and H_2O , 3.57 ppm – EtOH , δ_{H} 3.27 ppm – CHD_2OD). Solvent satellite peaks are indicated with **.

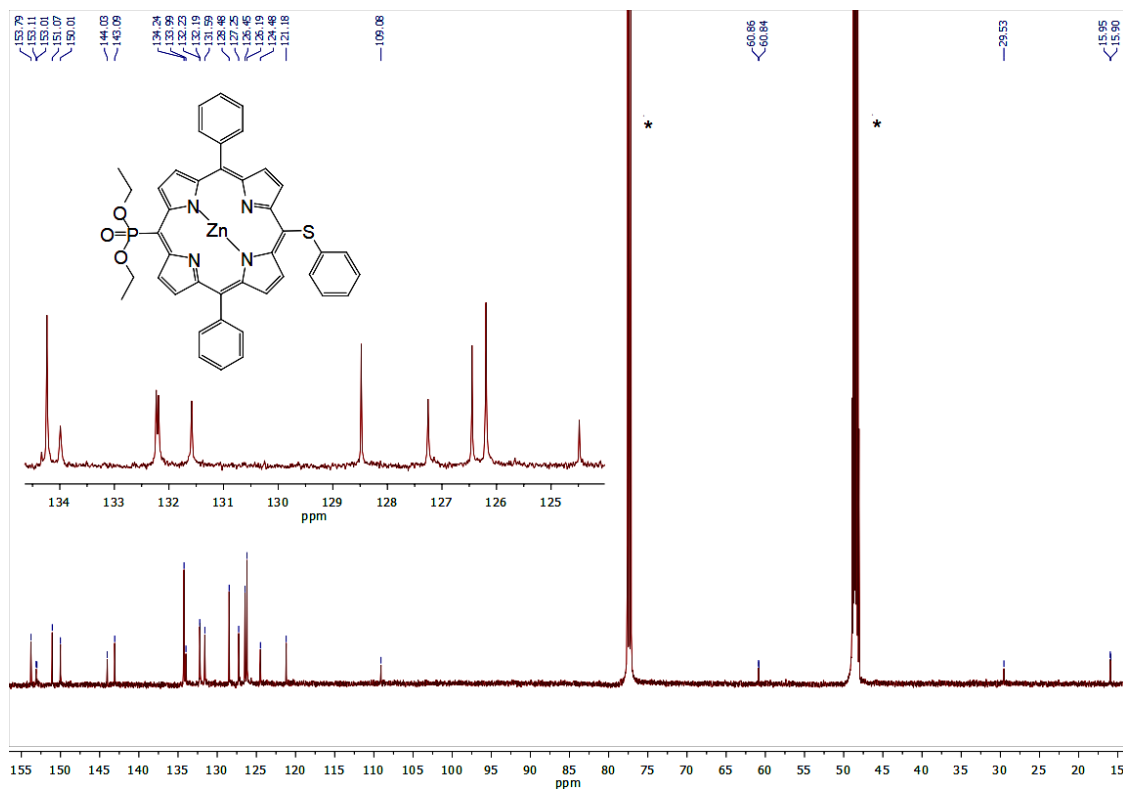


Figure S38. ^{13}C NMR spectrum of **4c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{C} 77.16 ppm – CDCl_3 , δ_{C} 48.47 ppm – CD_3OD).

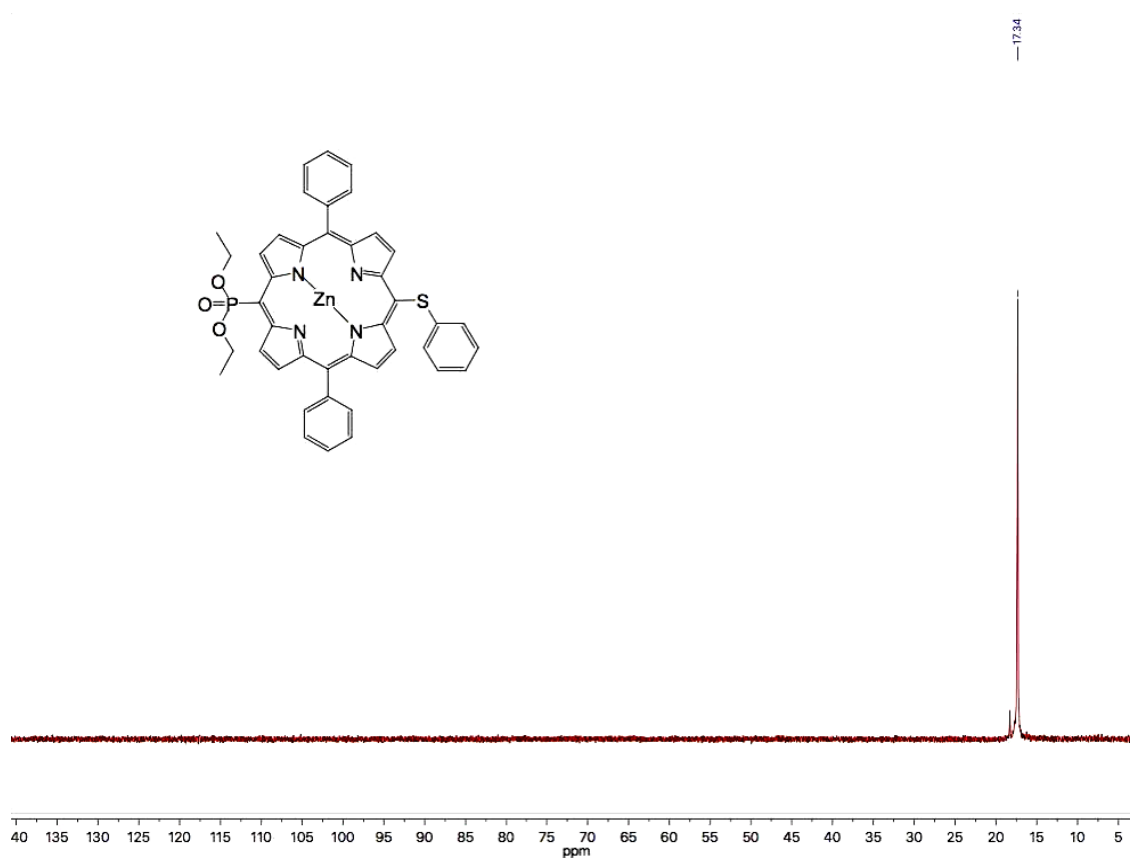


Figure S39. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

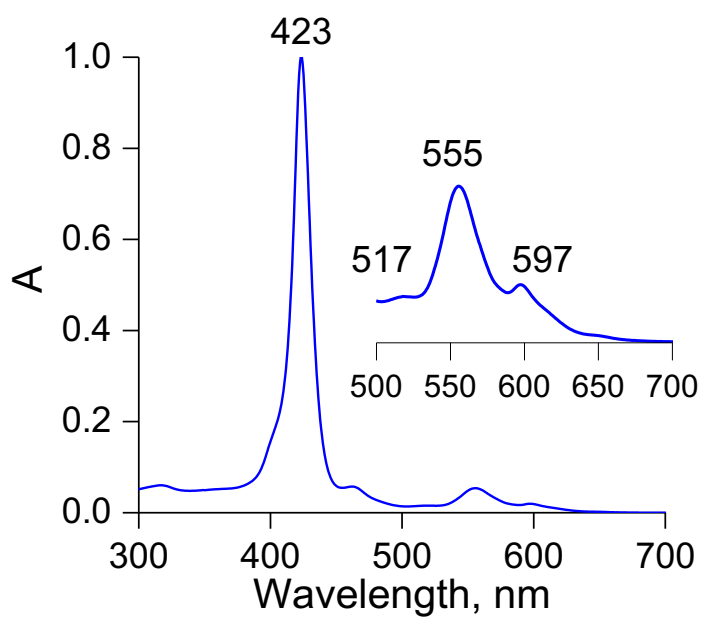
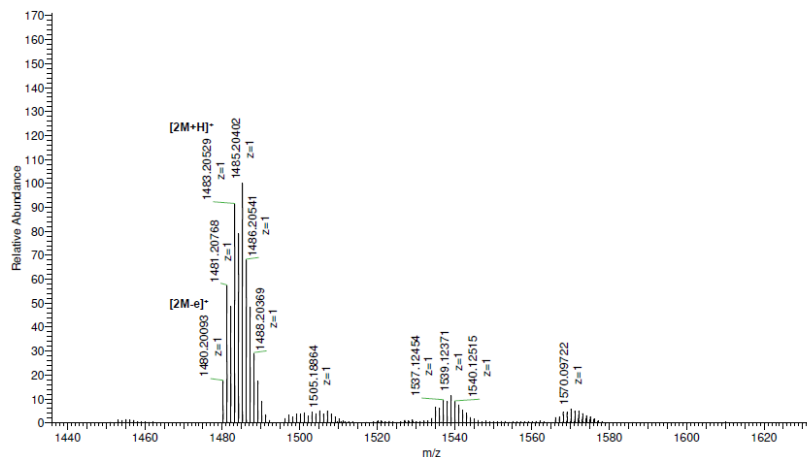
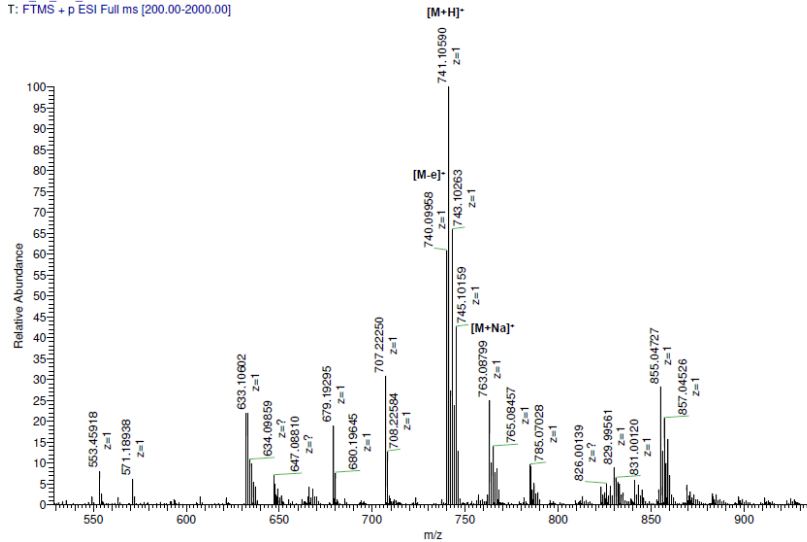
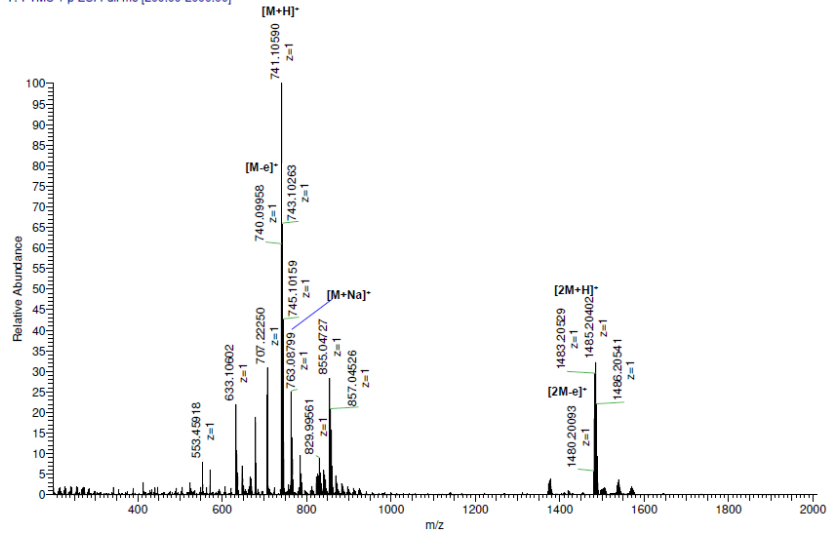


Figure S40. Normalized electronic absorption spectra of **4c** in CHCl₃/MeOH (2:1, v/v) solution (c = 6.25 μM).



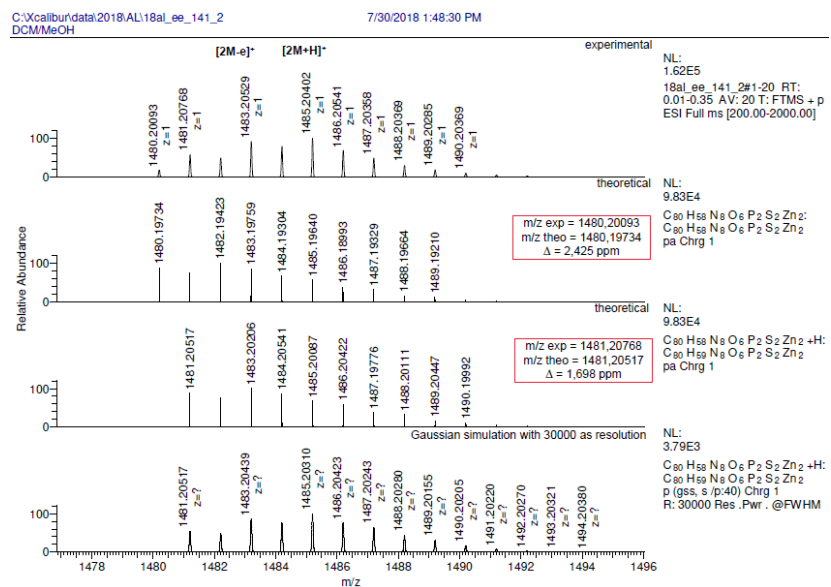
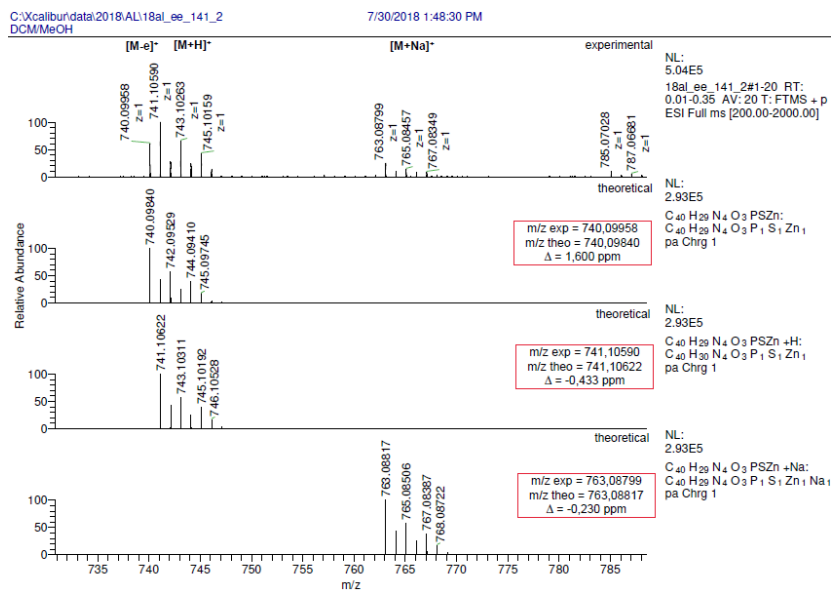


Figure S41. HRMS (ESI) spectrum of 4c.

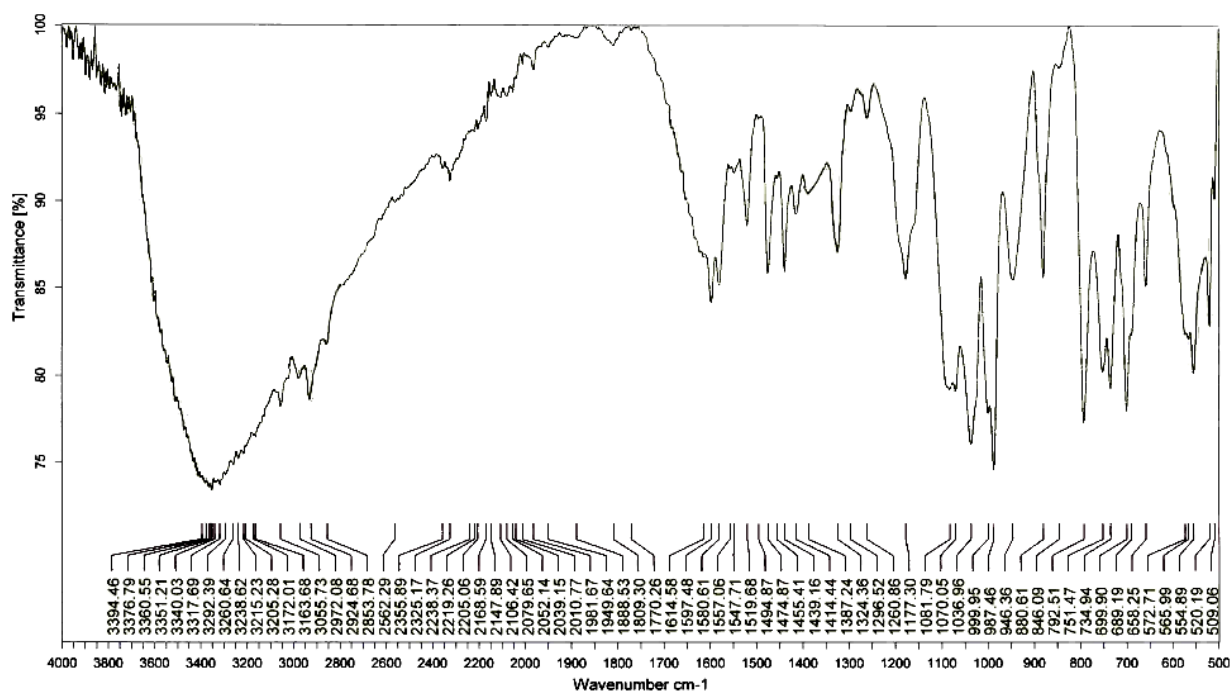


Figure S42. IR (neat) spectrum of 4c.

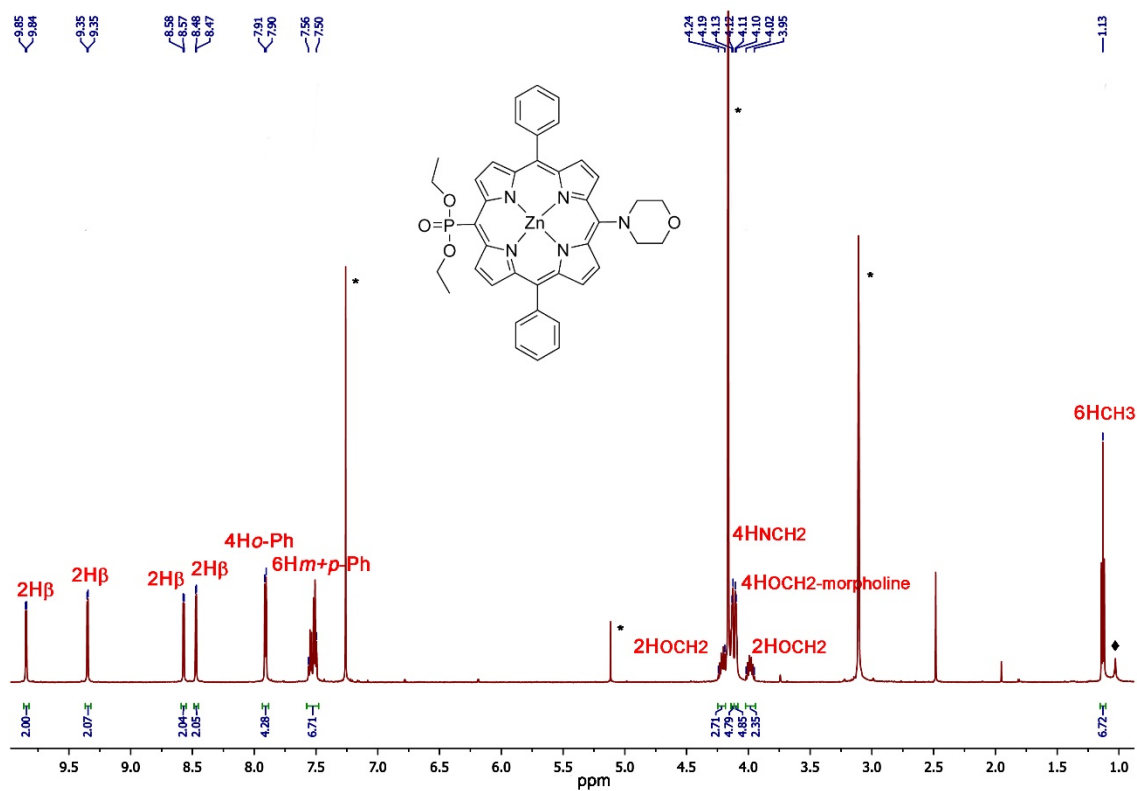


Figure S43. ^1H NMR spectrum of 5a ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.26 ppm – CHCl_3 , δ_{H} 5.12 ppm – CH_2Cl_2 , δ_{H} 4.13 ppm – DOH and H_2O , δ_{H} 3.11 ppm – CHD_2OD). Impurities in the $\text{CDCl}_3/\text{MeOD}$ mixture are indicated with ♦.

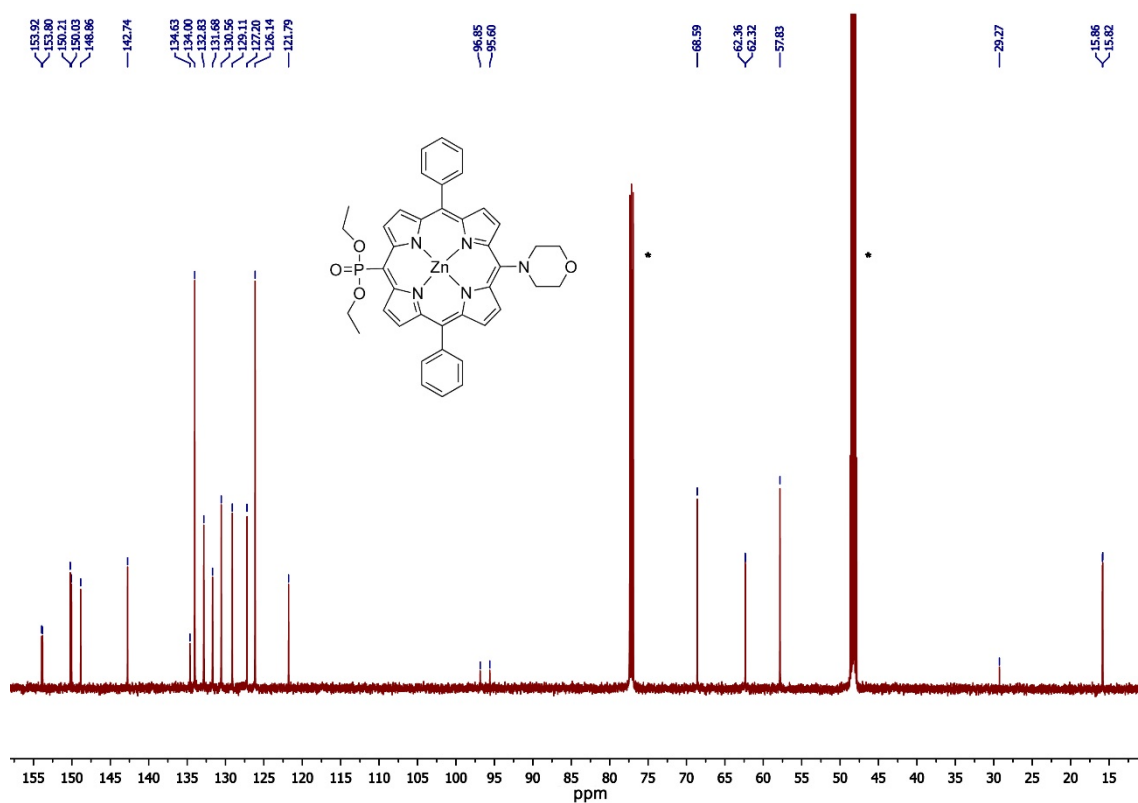


Figure S44. ¹³C NMR spectrum of **5a** (CDCl₃/CD₃OD 2:1, v/v). Solvent peaks are indicated with * (δ_c 77.16 ppm – CDCl₃, δ_c 49.00 ppm – CD₃OD).

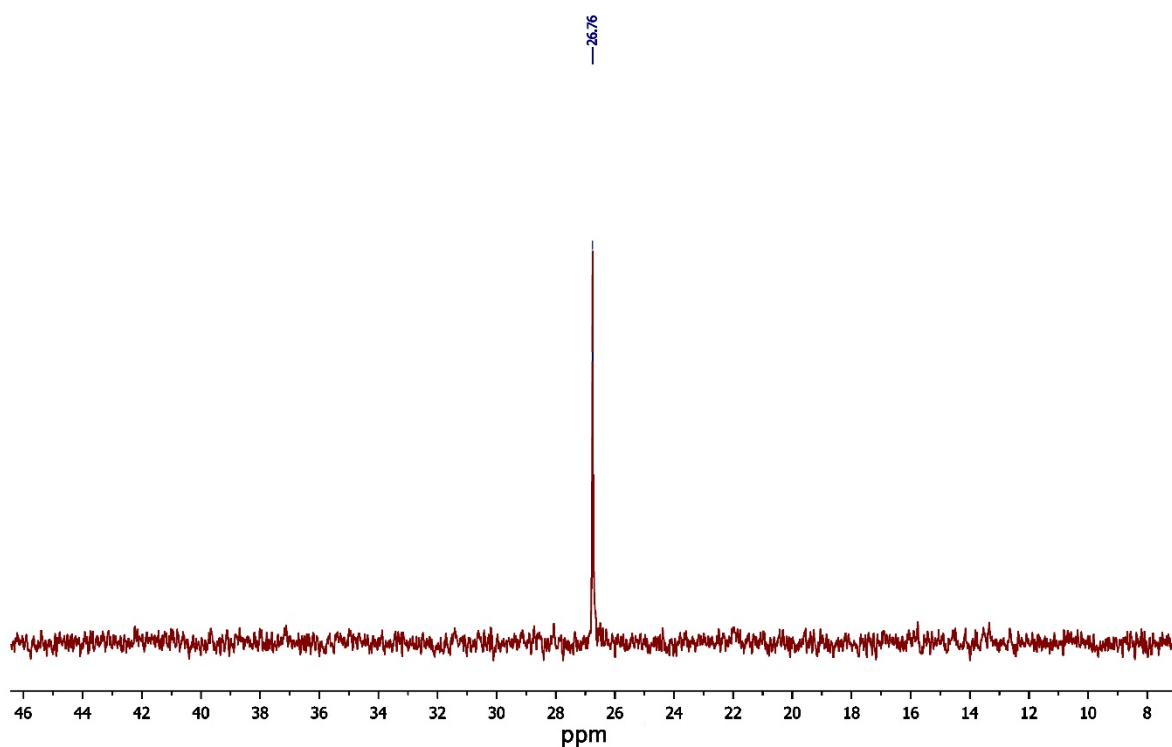


Figure S45. ³¹P {¹H} NMR spectrum of **5a** (CDCl₃/CD₃OD 2:1, v/v).

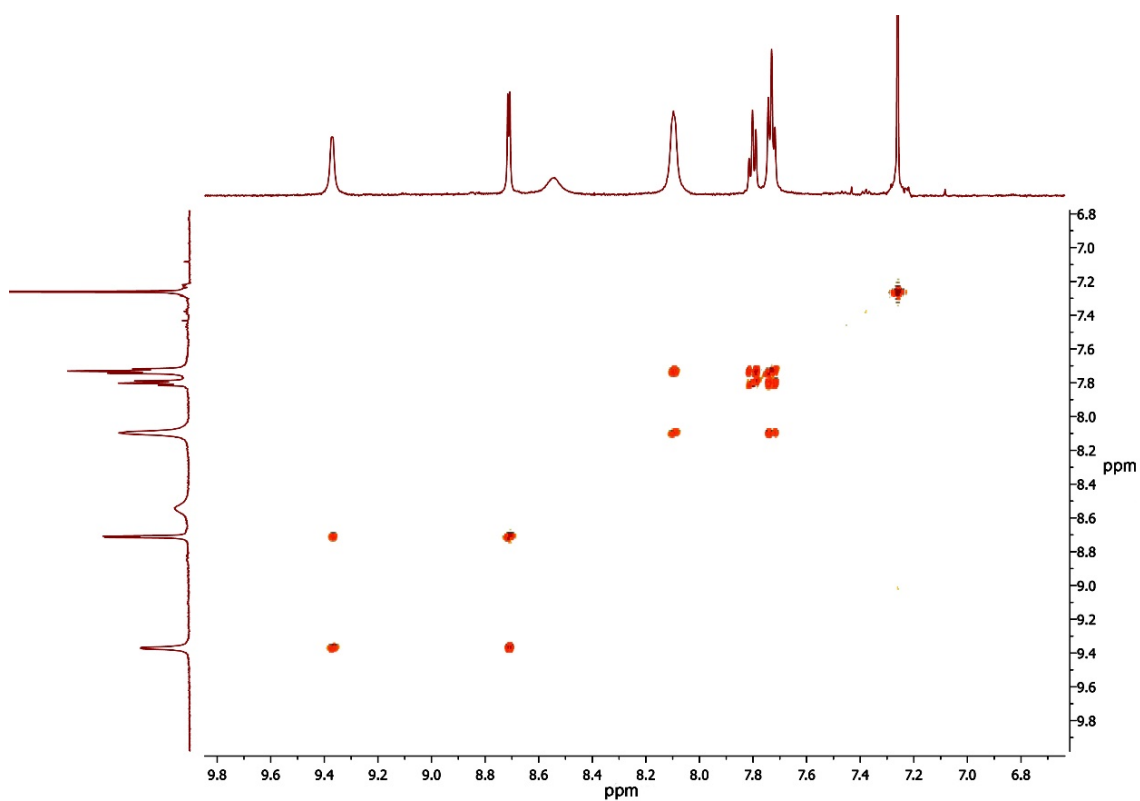


Figure S46. Aromatic region of ^1H , ^1H -COSY spectrum of **5a** in CDCl_3 .

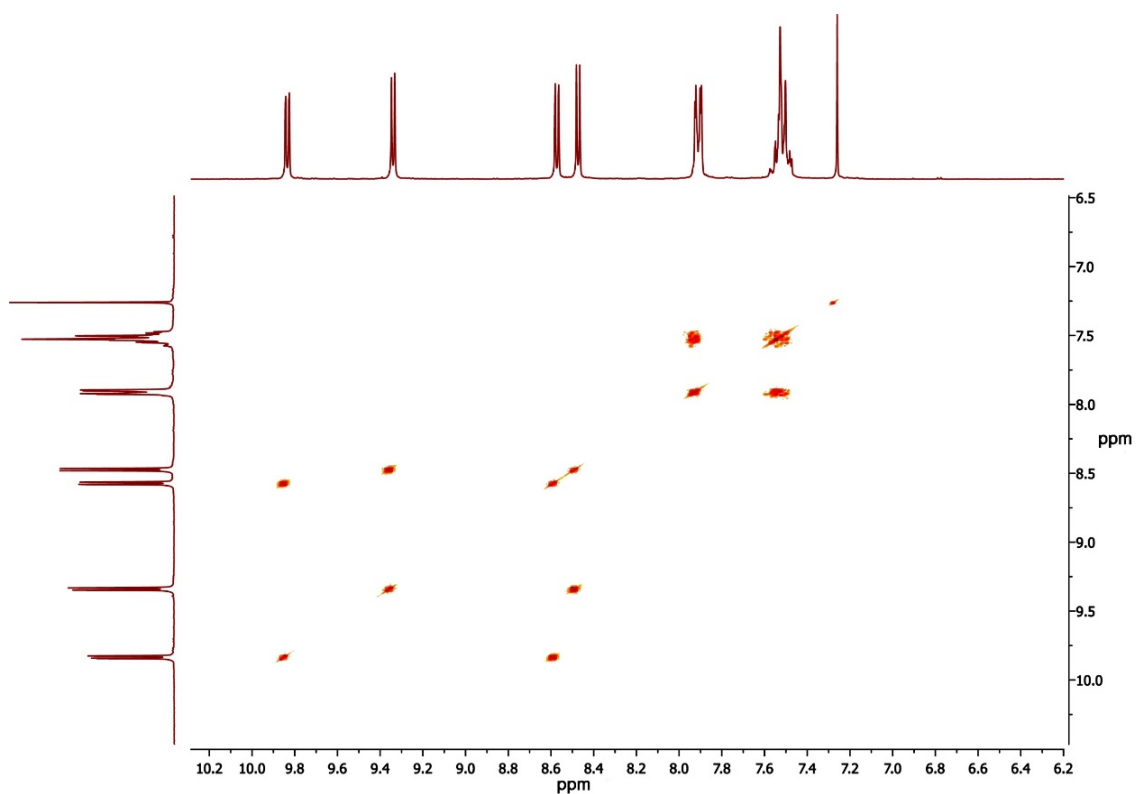


Figure S47. Aromatic region of ^1H , ^1H -COSY spectrum of **5a** in the mixture of $\text{CDCl}_3/\text{CD}_3\text{OD}$ (2:1, v/v).

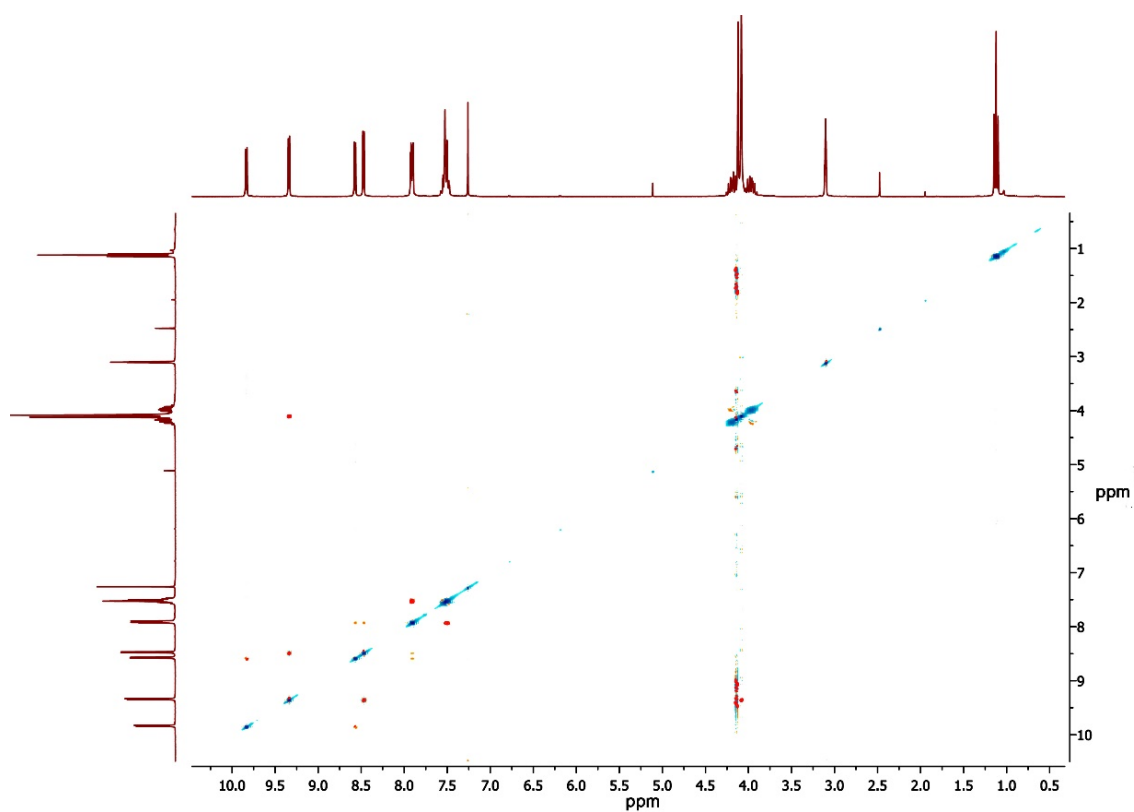


Figure S48. $^1\text{H}, ^1\text{H}$ -NOESY spectrum of **5a** in the mixture of $\text{CDCl}_3/\text{CD}_3\text{OD}$ (2:1, v/v).

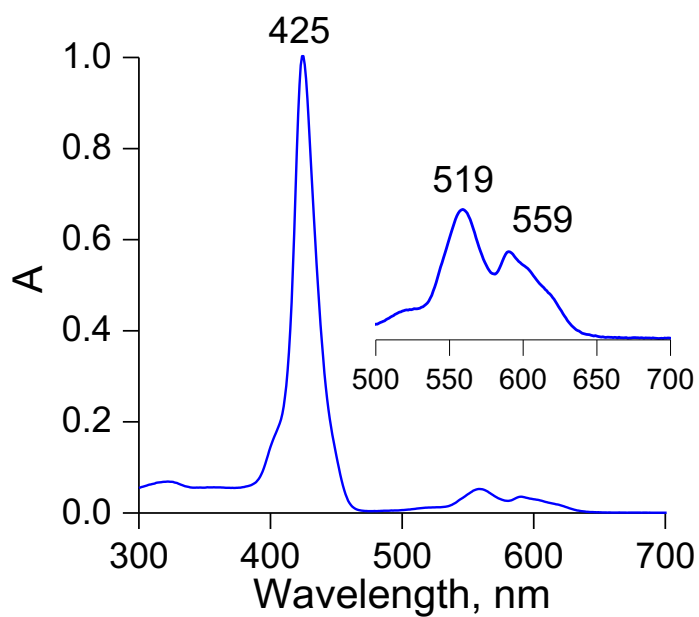


Figure S49. Normalized electronic absorption spectra of **5a** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12ye_1111_me_1 #3-29 RT: 0.02-0.24 AV: 27 NL: 7.79E6
T: FTMS + p ESI Full ms [70.00-2000.00]

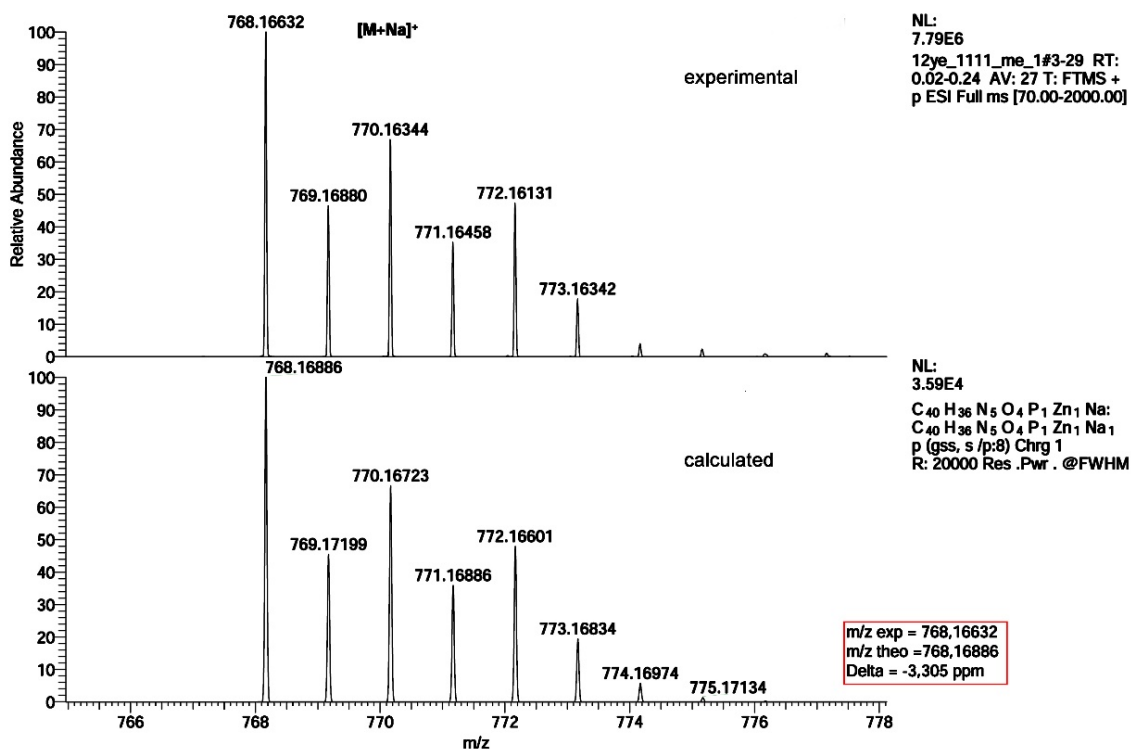
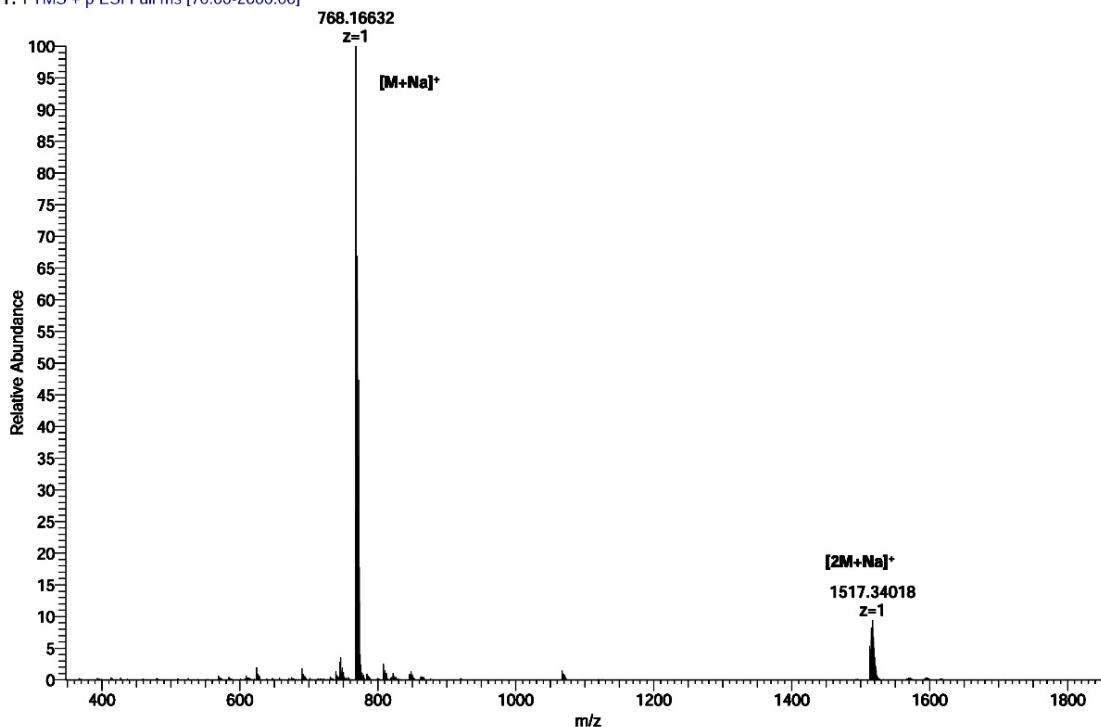


Figure S50. HRMS (ESI) spectrum of 5a.

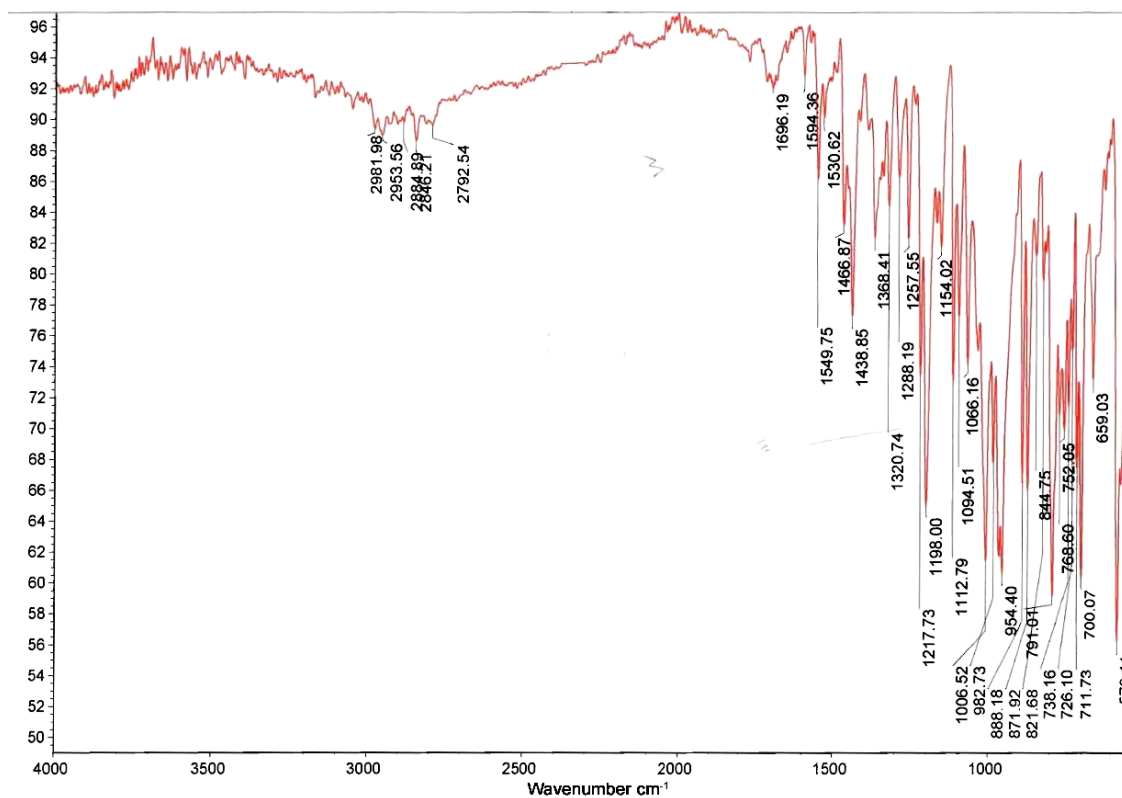


Figure S51. IR (neat) spectrum of **5a**.

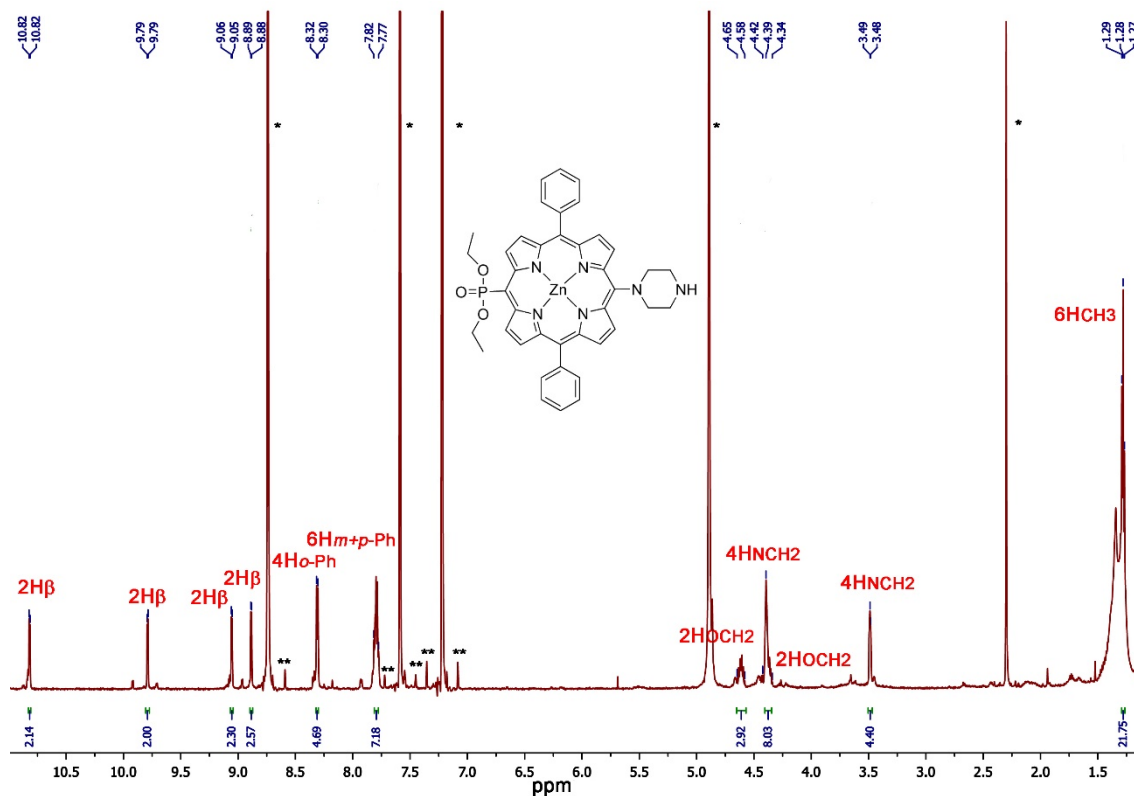


Figure S52. ^1H NMR spectrum of **5b** (Py-*d*5). Solvent peaks are indicated with * (δ_{H} 8.74, 7.58 and 7.22 ppm – Py, δ_{H} 4.89 ppm – DOH and H_2O , δ_{H} 2.30 ppm – acetone). Solvent satellite peaks are indicated with **.

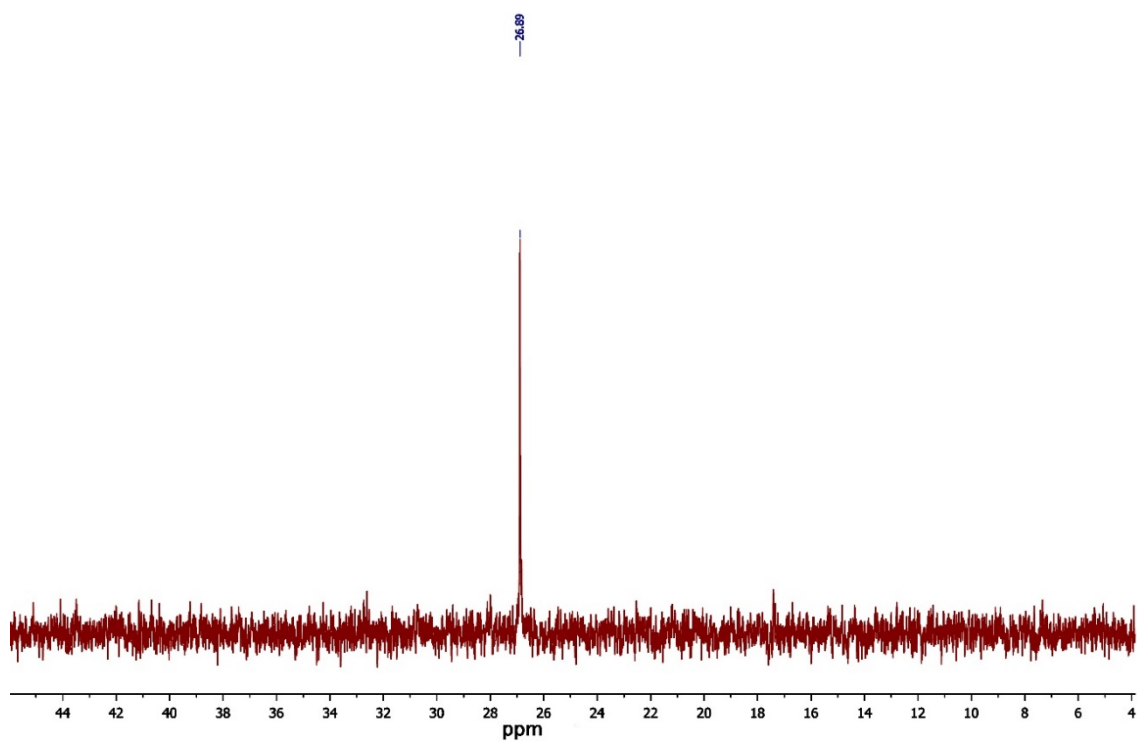


Figure S53. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5b** (Py-*d*5).

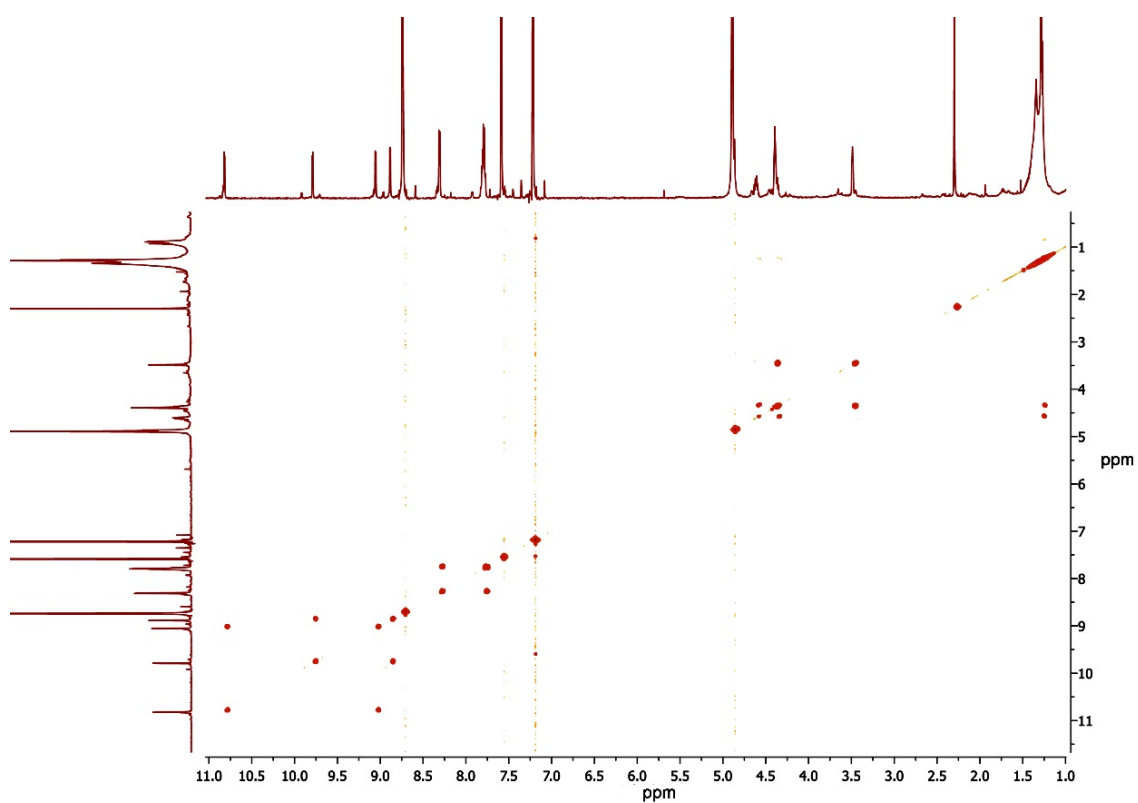


Figure S54. $^1\text{H},^1\text{H}$ -COSY spectrum of **5b** in Py-*d*5.

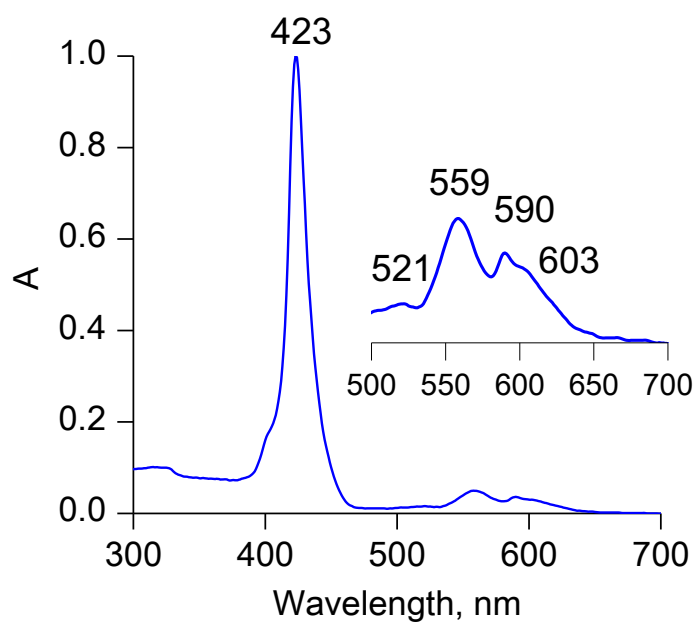


Figure S55. Normalized electronic absorption spectra of **5b** in CHCl₃/MeOH (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12ye_1001f2_2 #4-30 RT: 0.03-0.23 AV: 27 NL: 2.90E7
T: FTMS + p ESI Full ms [70.00-2000.00]

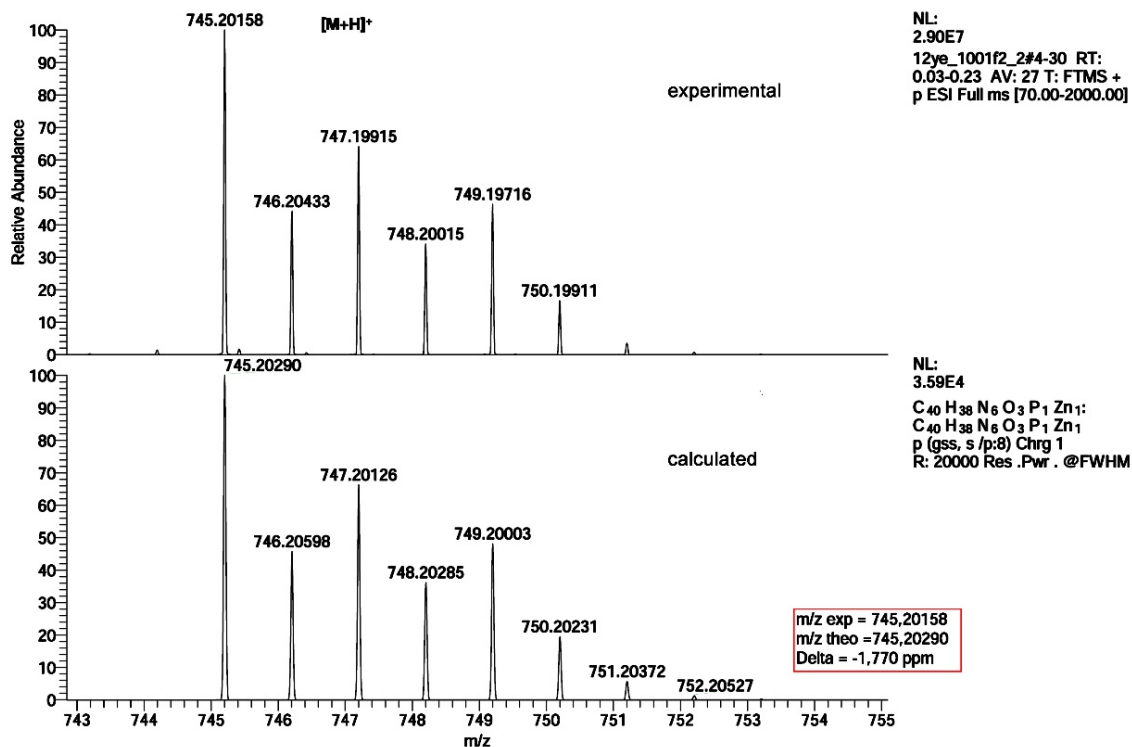
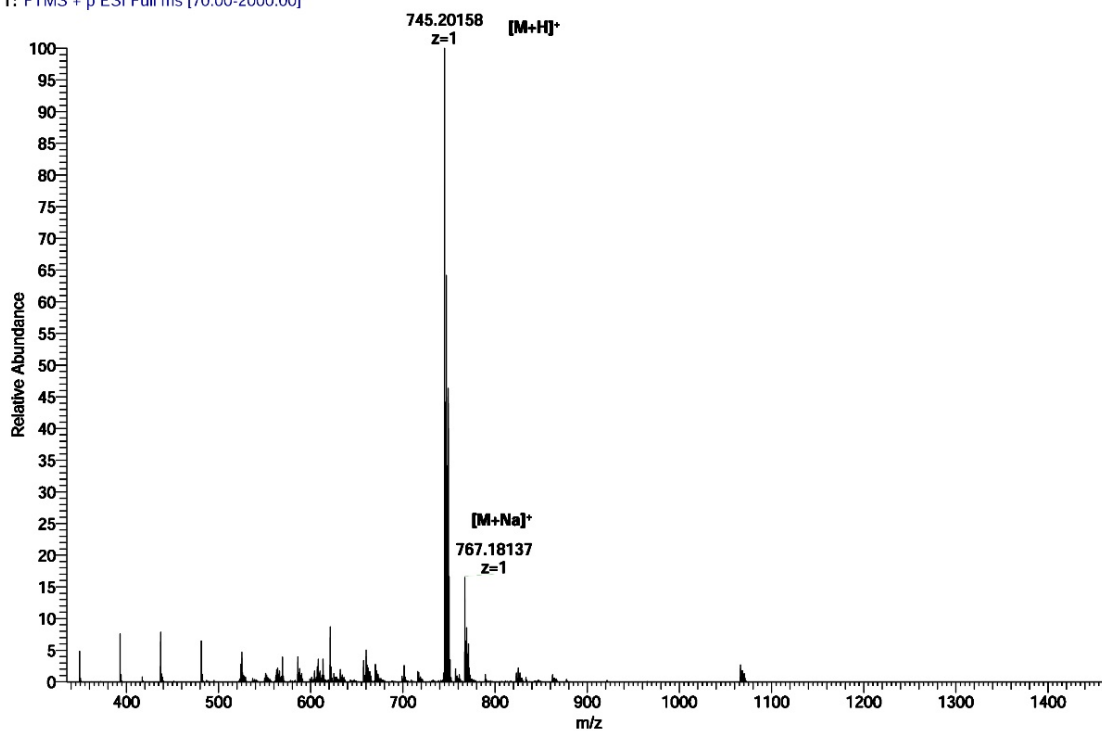


Figure S56. HRMS (ESI) spectrum of 5b.

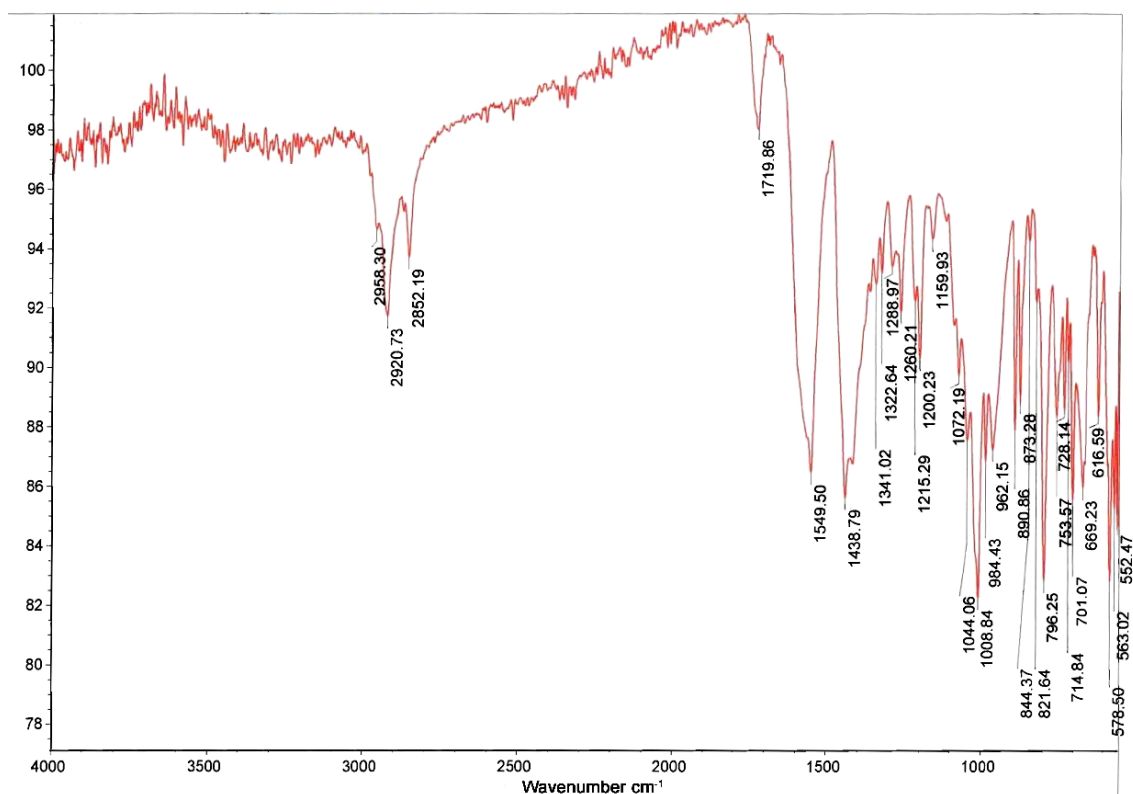


Figure S57. IR (neat) spectrum of **5b**.

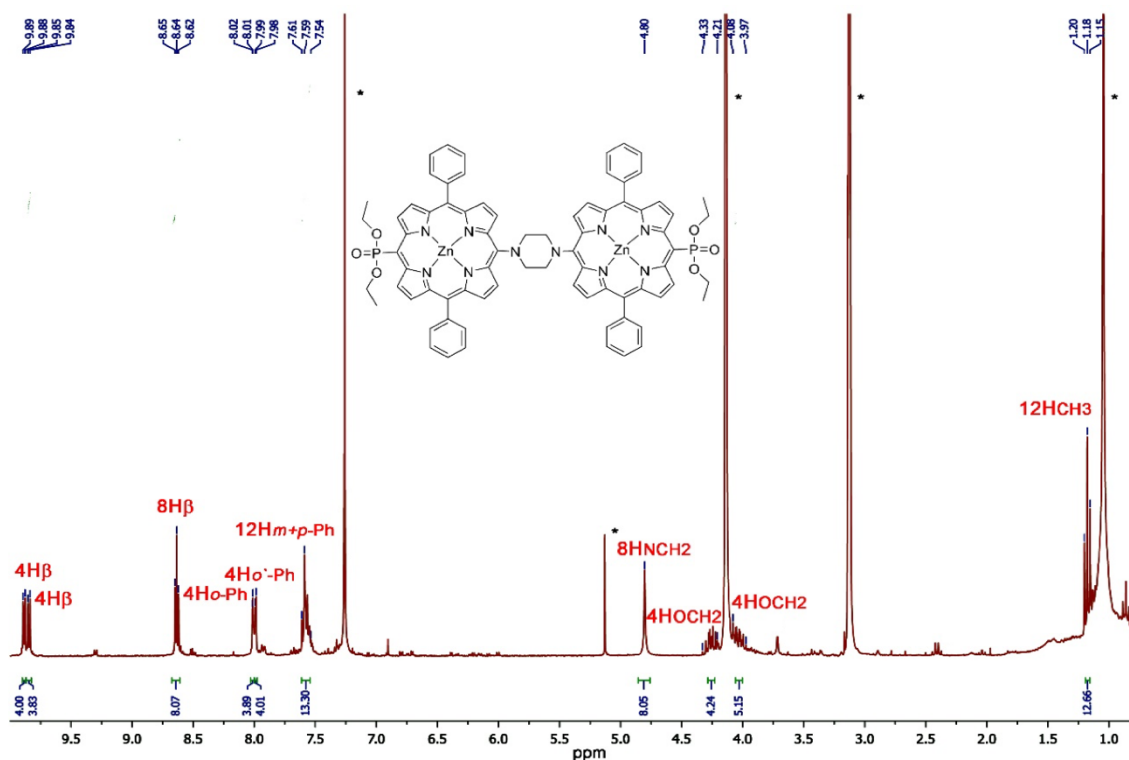


Figure S58. ^1H NMR spectrum of **11** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.26 ppm – CHCl_3 , δ_{H} 5.13 ppm – CH_2Cl_2 , δ_{H} 4.14 ppm – DOH and H_2O , δ_{H} 3.12 ppm – CHD_2OD).

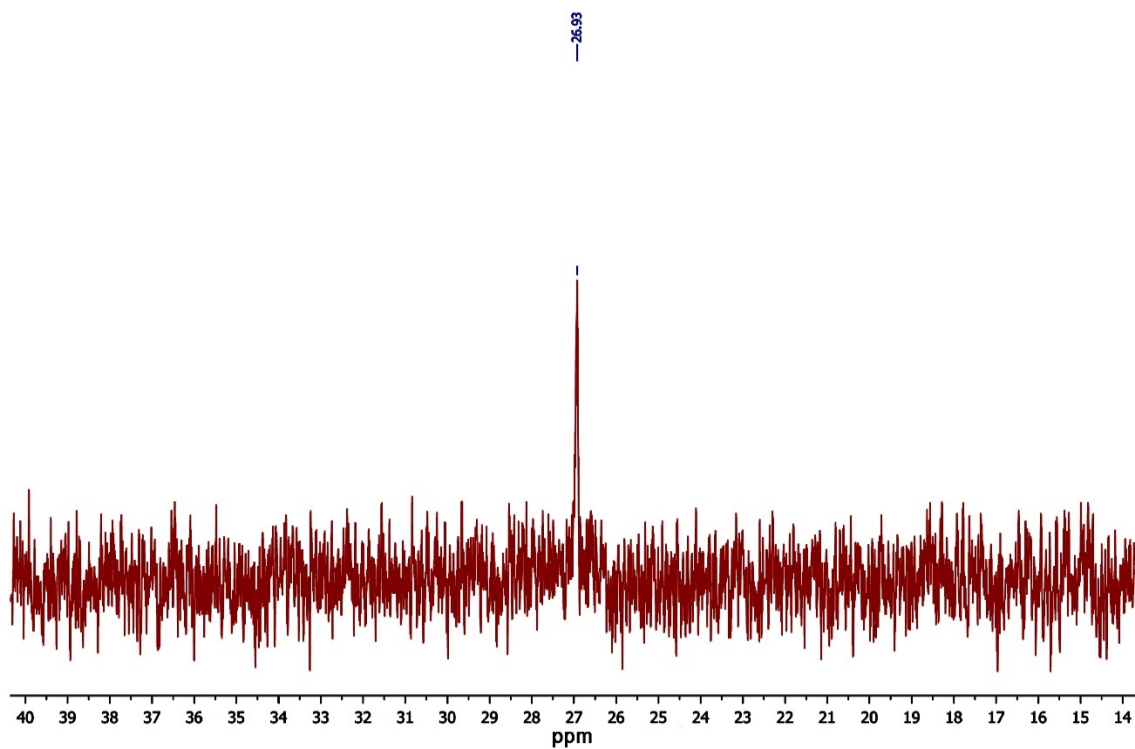


Figure S59. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

12ye_100_2 #4-29 RT: 0.03-0.23 AV: 26 NL: 9.32E6
T: FTMS + p ESI Full ms [500.00-2500.00]

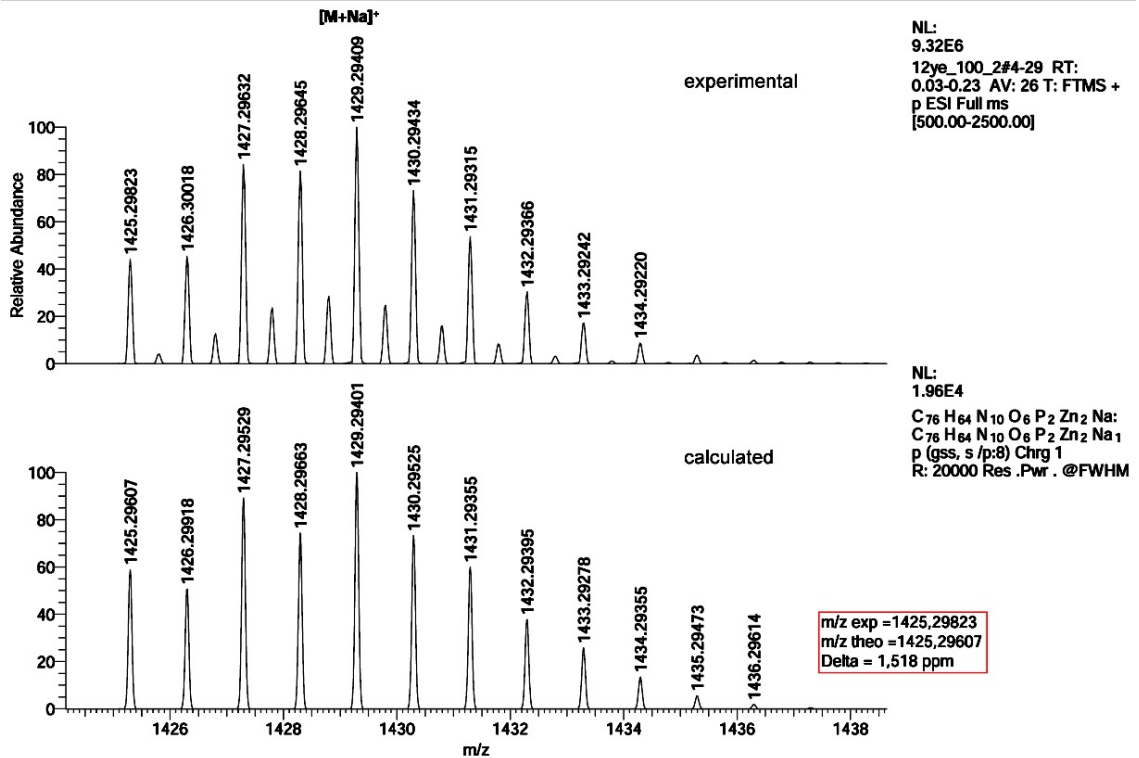
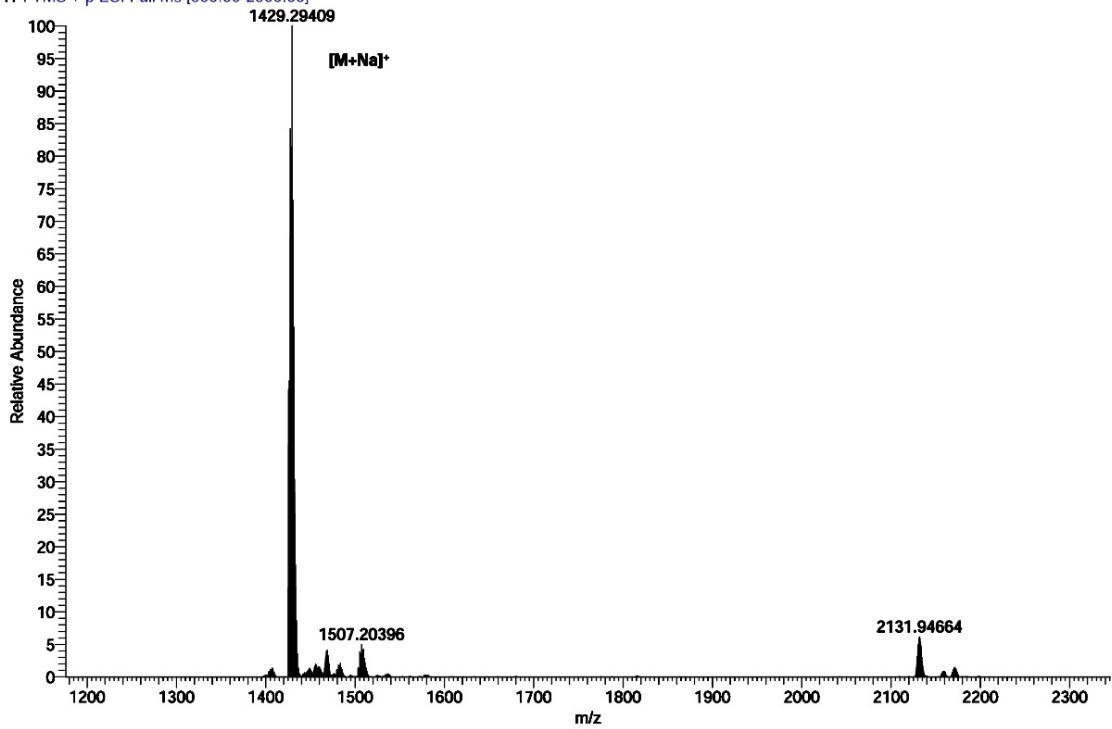


Figure S60. HRMS (ESI) spectrum of 11.

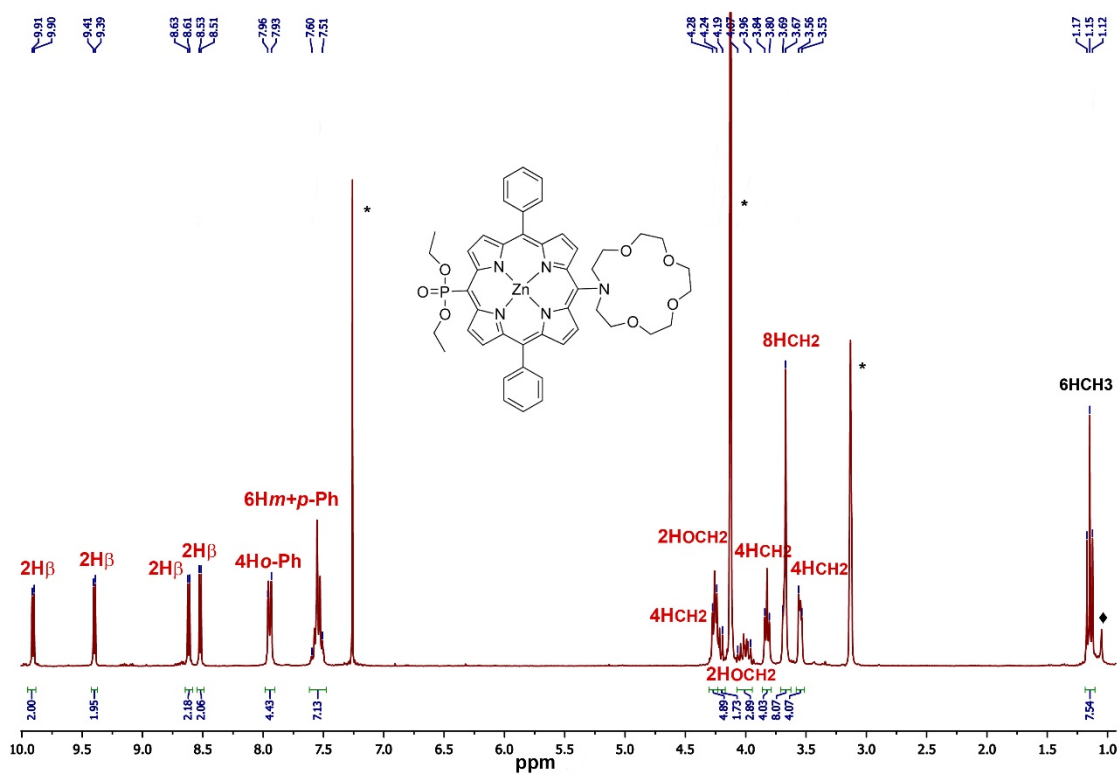


Figure S61. ^1H NMR spectrum of **5c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.26 ppm – CHCl_3 , δ_{H} 4.13 ppm – DOH and H_2O , δ_{H} 3.13 ppm – CHD_2OH). Impurities are indicated with \blacklozenge .

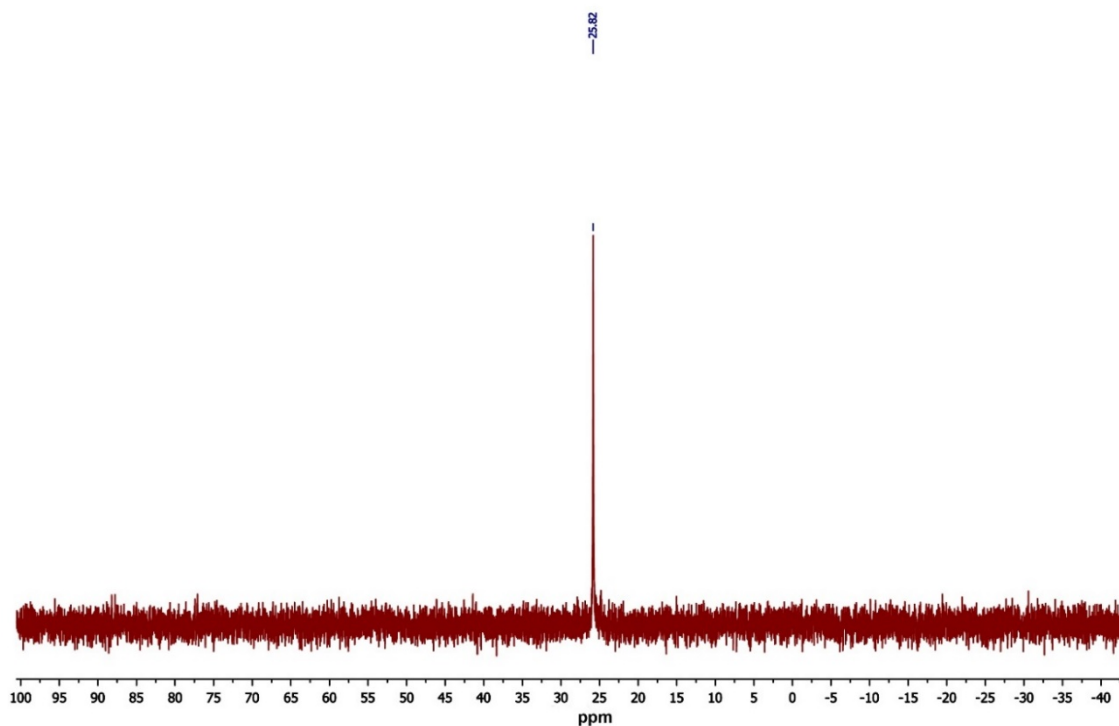


Figure S62. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5c** ($\text{CDCl}_3/\text{CD}_3\text{OD}$, 2:1, v/v).

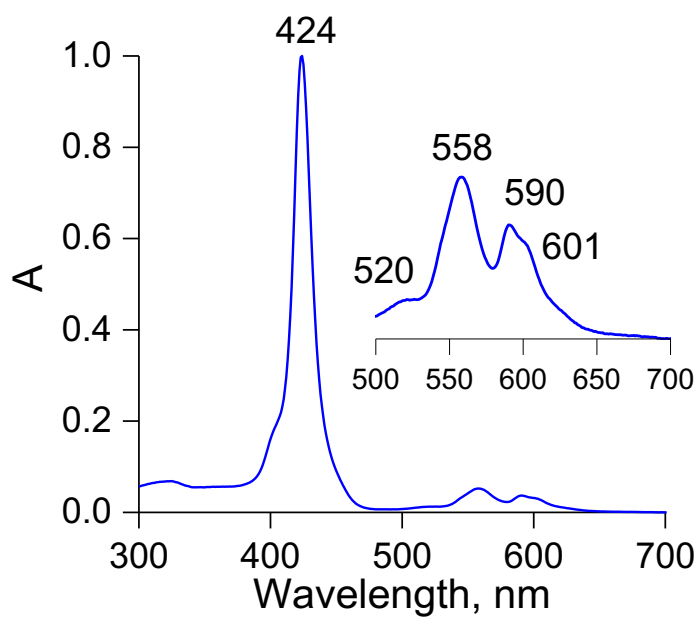
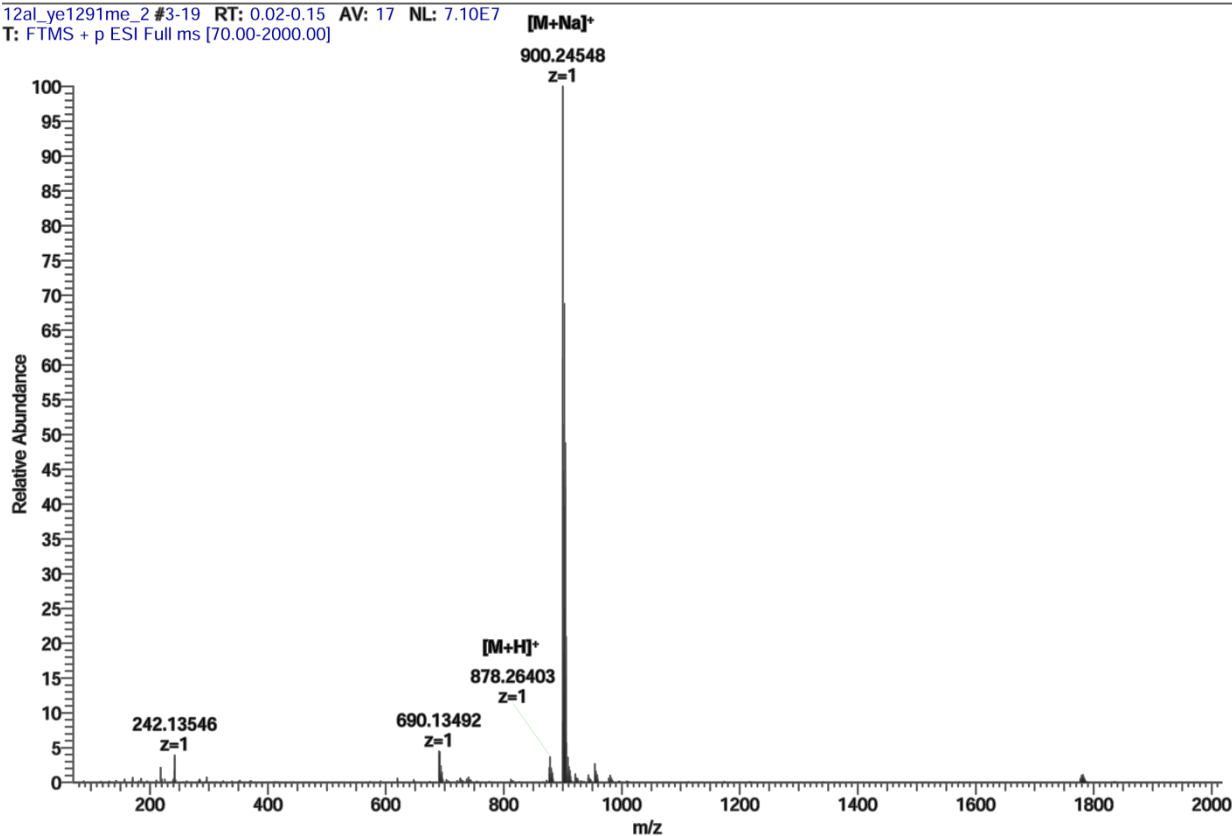


Figure S63. Normalized electronic absorption spectra of **5c** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12a_1291me_2 #3-19 RT: 0.02-0.15 AV: 17 NL: 7.10E7
T: FTMS + p ESI Full ms [70.00-2000.00]



C:\xcalibur\data\12a_1291me_2

7/20/2012 10:47:21 AM

12a_1291me

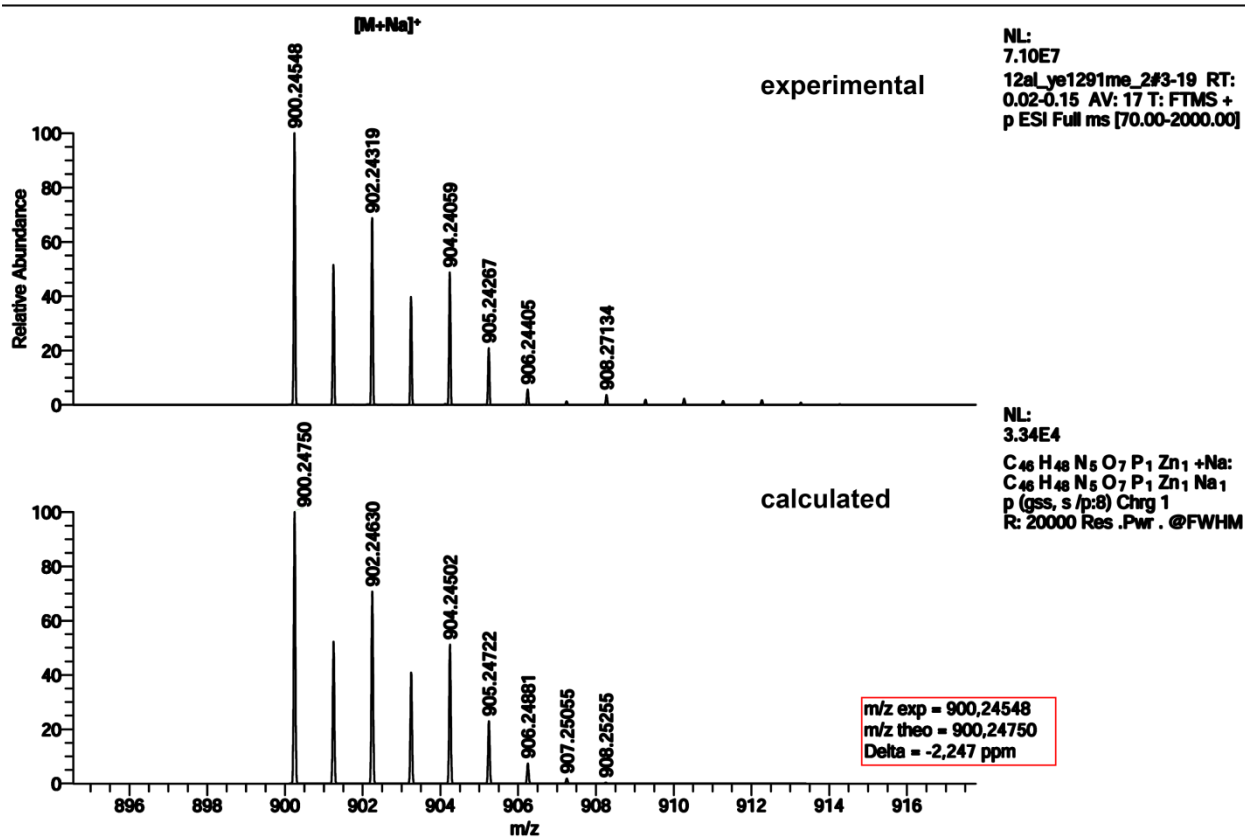


Figure S64. HRMS (ESI) spectrum of 5c.

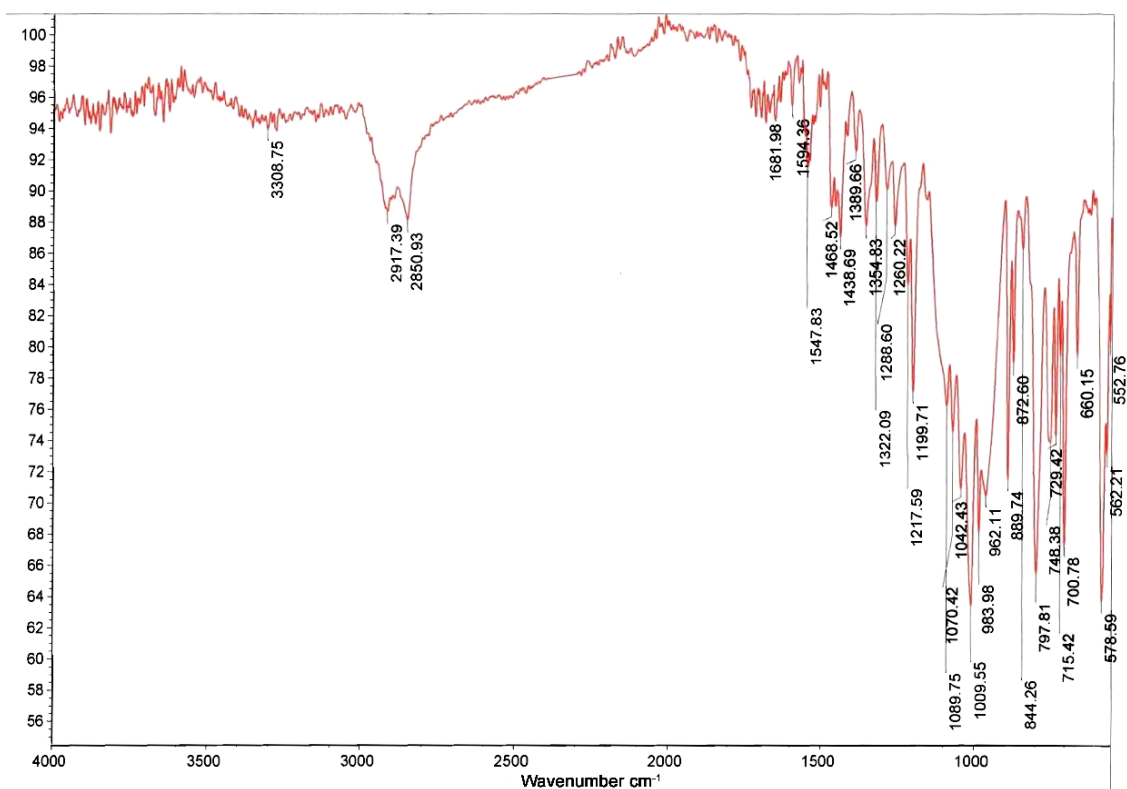


Figure S65. IR (neat) spectrum of **5c**.

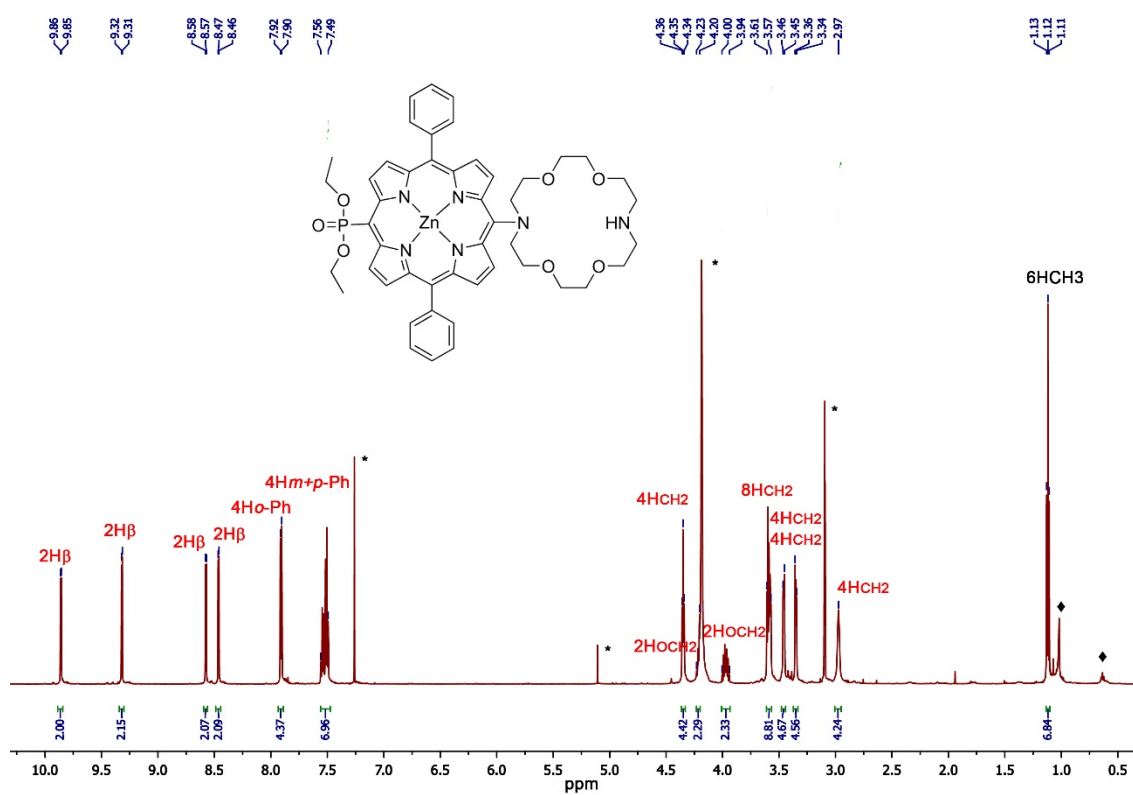


Figure S66. ¹H NMR spectrum of **5d** (CDCl₃/CD₃OD 2:1, v/v). Solvent peaks are indicated with * (δ_H 7.26 ppm – CHCl₃, δ_H 5.11 ppm – CH₂Cl₂, δ_H 4.19 ppm – DOH and H₂O, δ_H 3.09 ppm – CHD₂OD). Impurities are indicated with ♦.

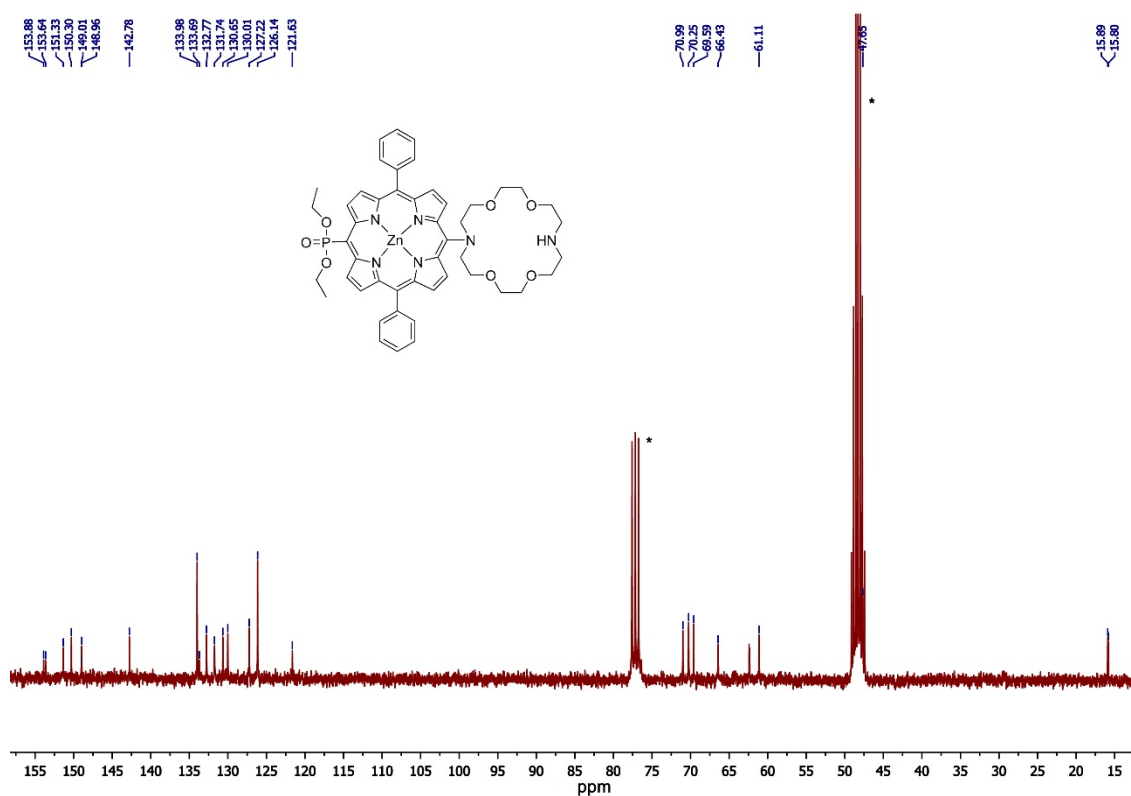


Figure S67. ^{13}C NMR spectrum of **5d** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * ($\delta_{\text{C}} 77.16$ ppm – CDCl_3 , $\delta_{\text{C}} 49.00$ ppm – CD_3OD).

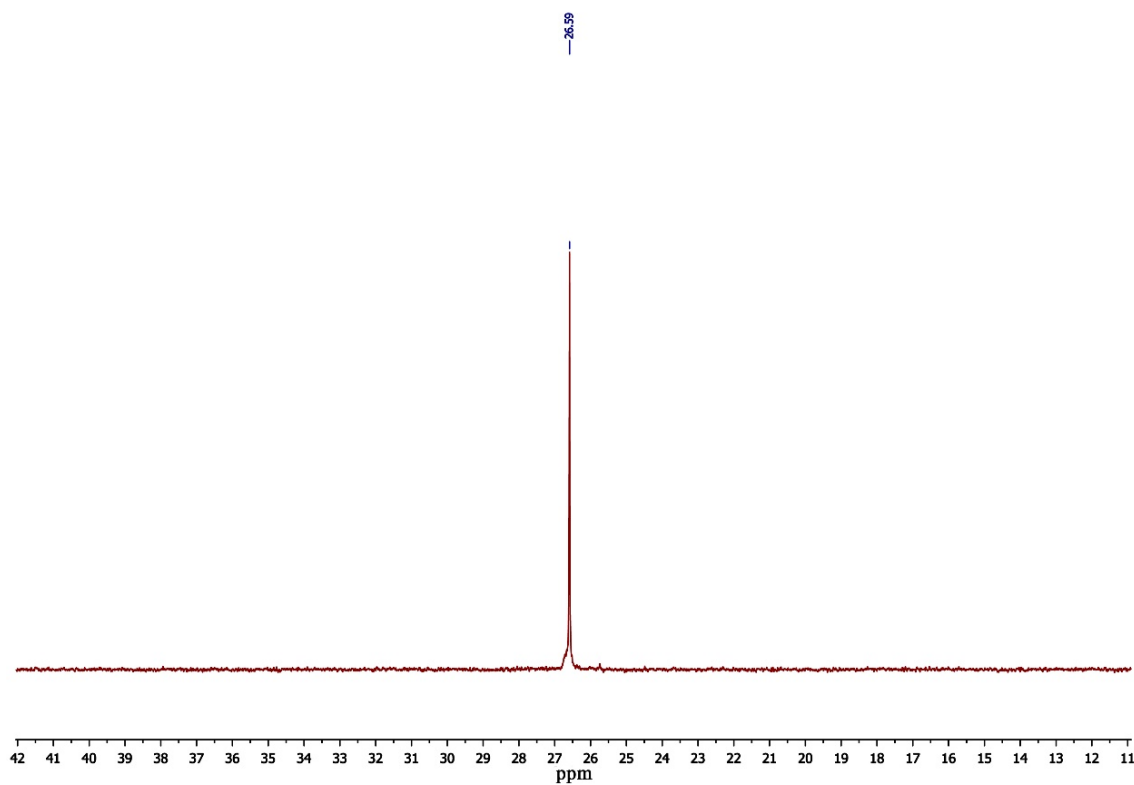


Figure S68. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5d** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

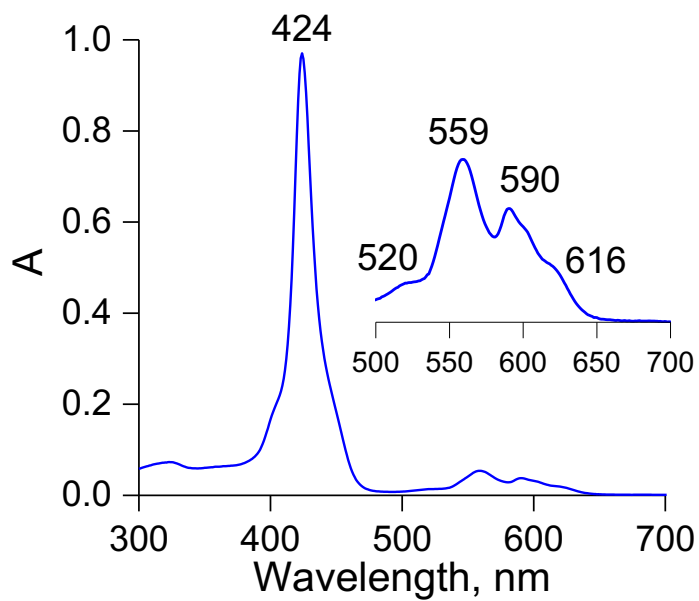


Figure S69. Normalized electronic absorption spectra of **5d** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12a_ye1202me_2 #3-19 RT: 0.02-0.15 AV: 17 NL: 3.89E7
T: FTMS + p ESI Full ms [70.00-2000.00]

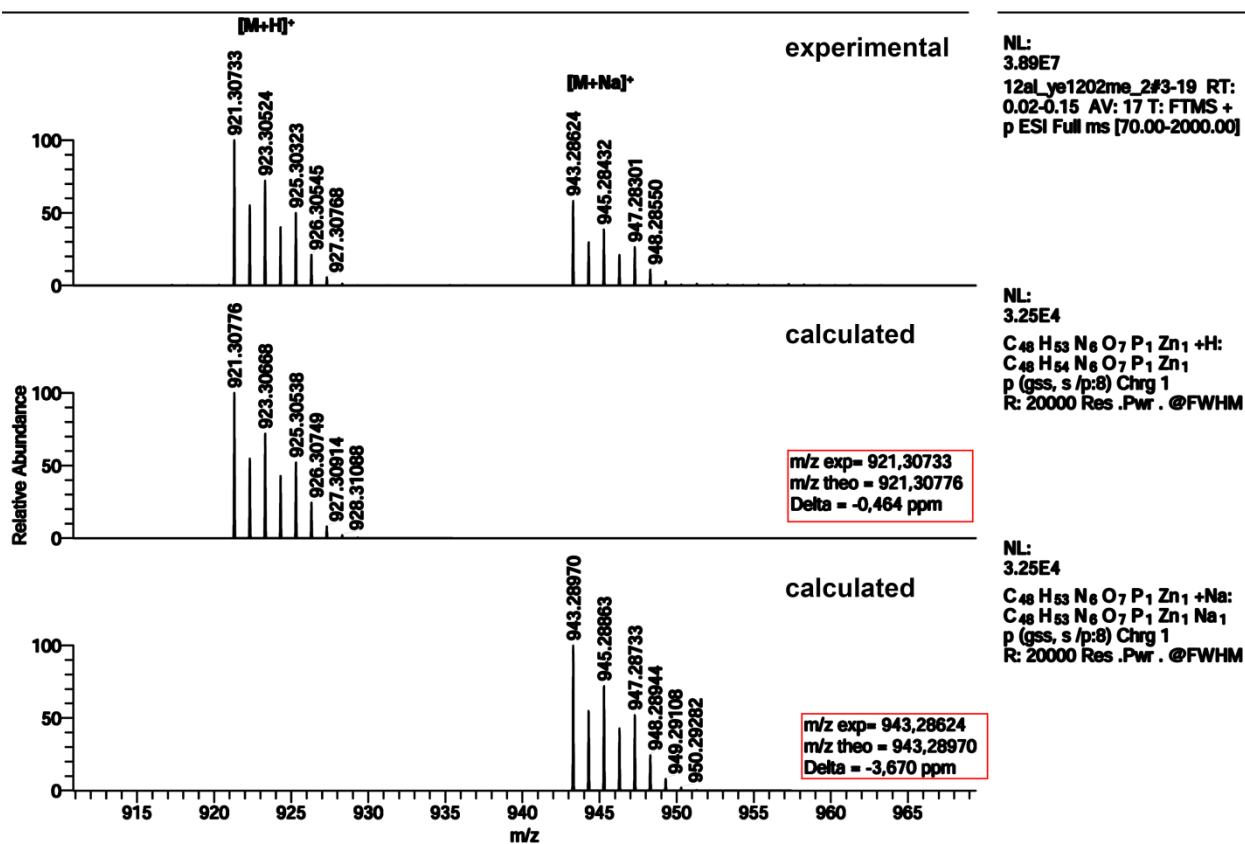
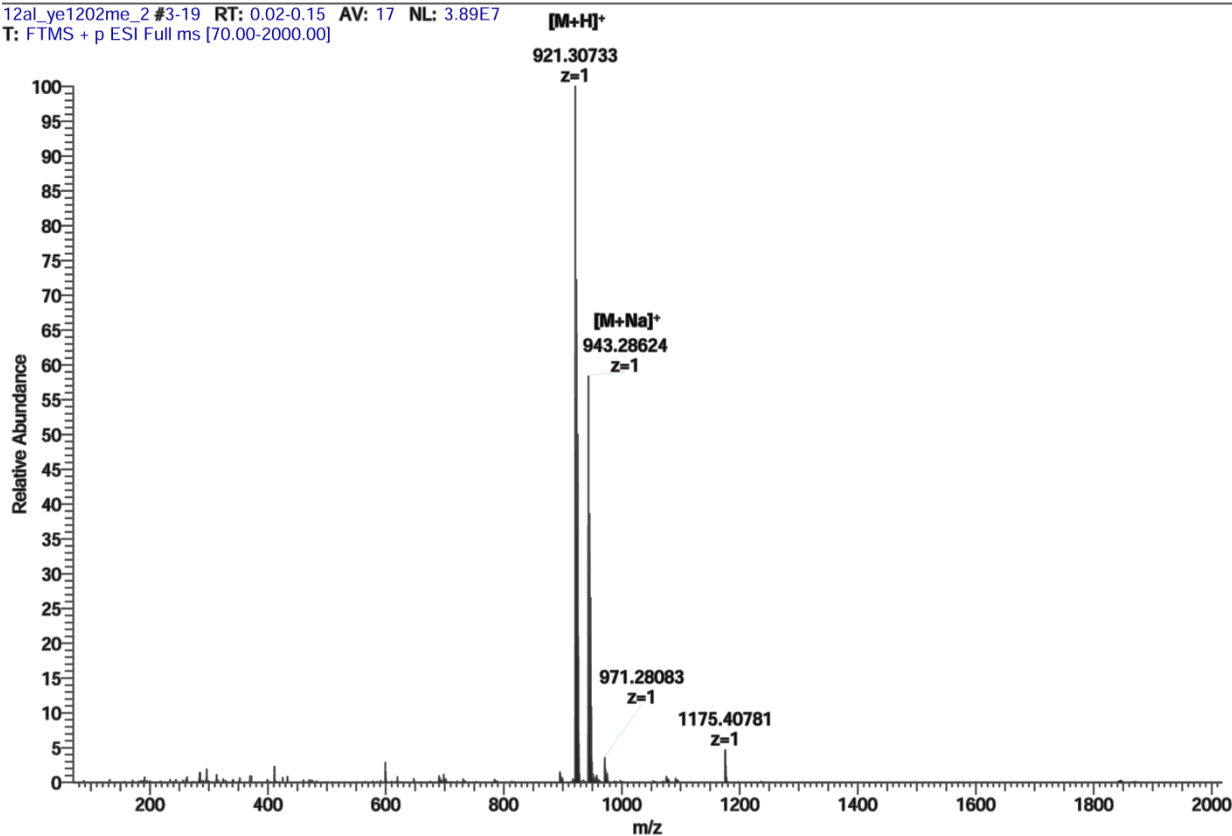


Figure S70. HRMS (ESI) spectrum of 5d.

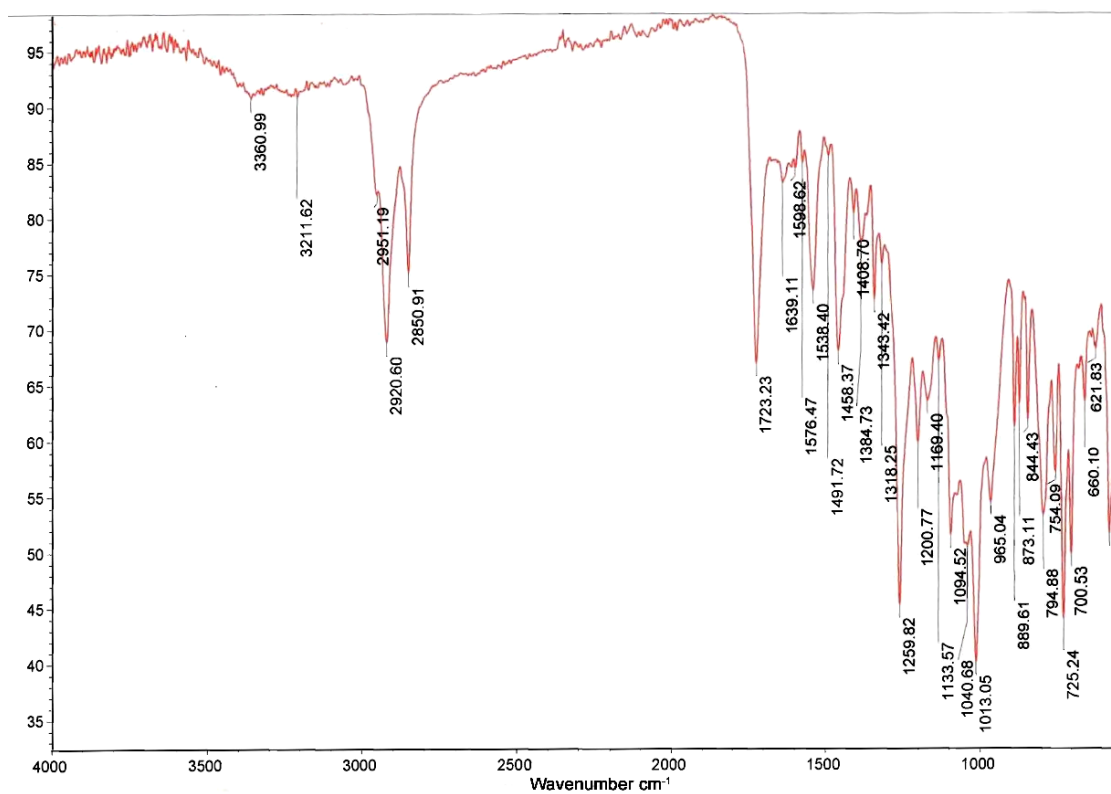


Figure S71. IR (neat) spectrum of **5d**.

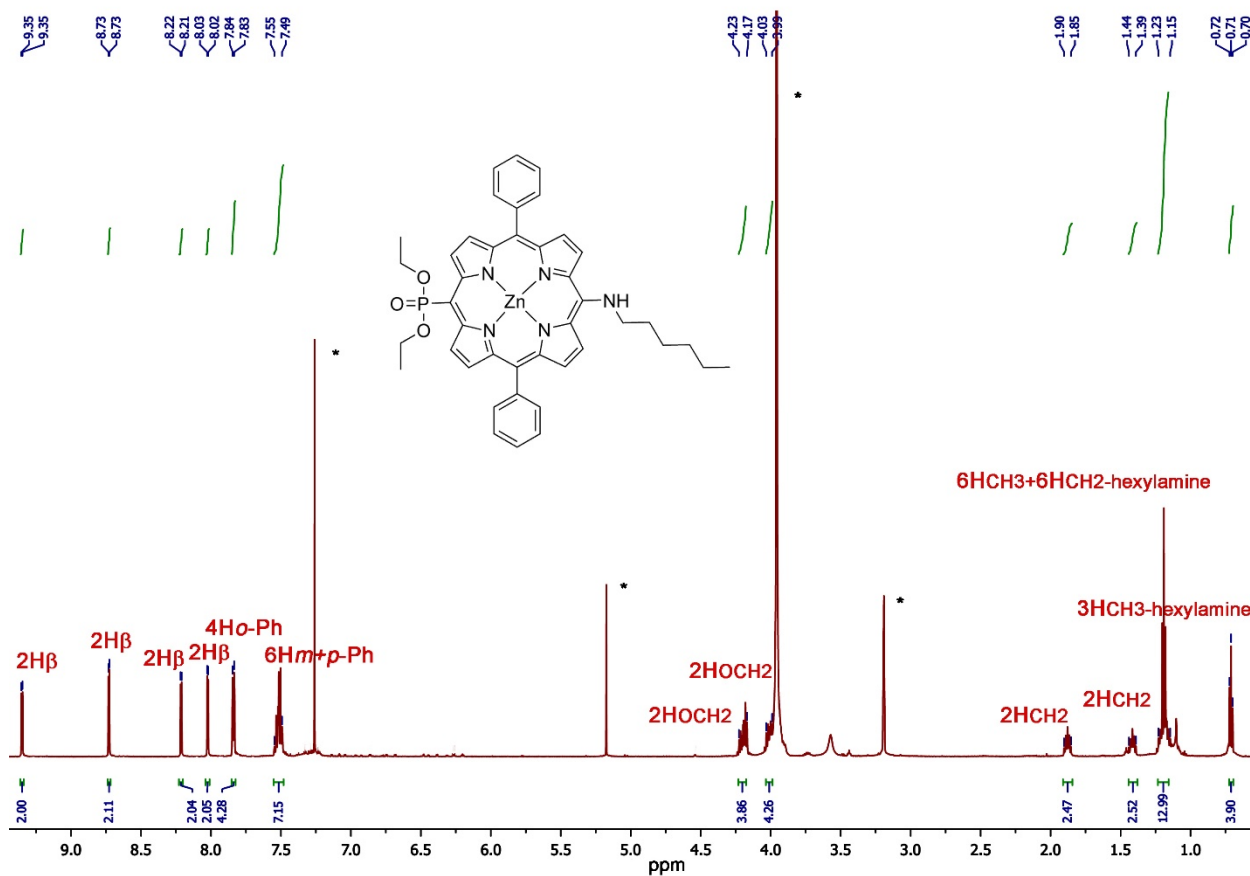


Figure S72. ^1H NMR spectrum of **5e** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.26 ppm – CHCl_3 , δ_{H} 5.17 ppm – CH_2Cl_2 , δ_{H} 3.99 ppm – DOH and H_2O , δ_{H} 3.19 ppm – CHD_2OD).

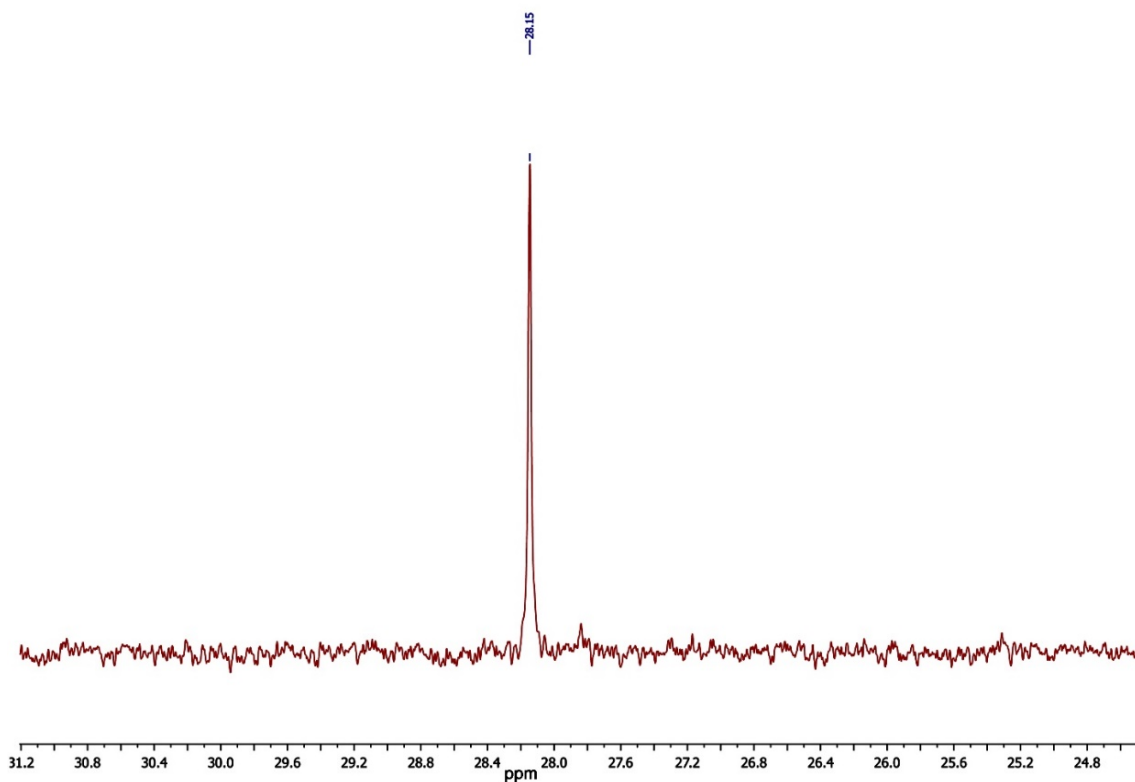


Figure S73. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5e** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

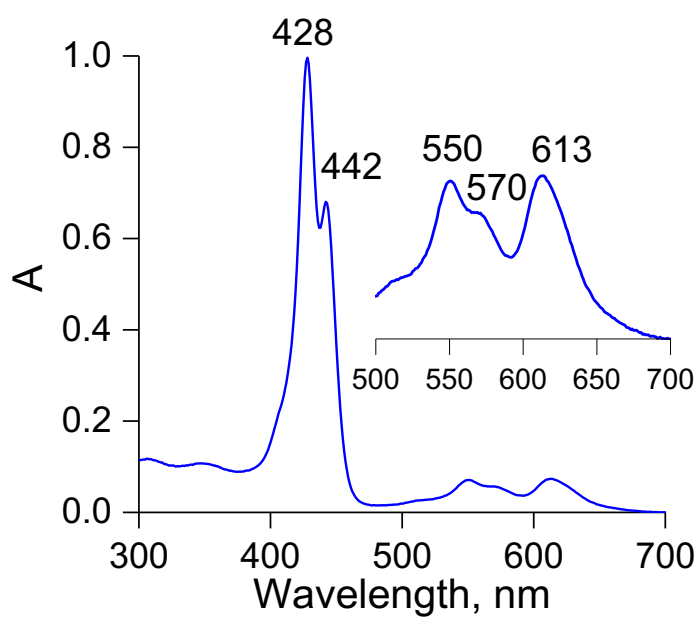


Figure S74. Normalized electronic absorption spectra of **5e** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12ye_1053f2_me_1 #4-29 RT: 0.03-0.25 AV: 26 NL: 4.68E6
T: FTMS + p ESI Full ms [70.00-2000.00]

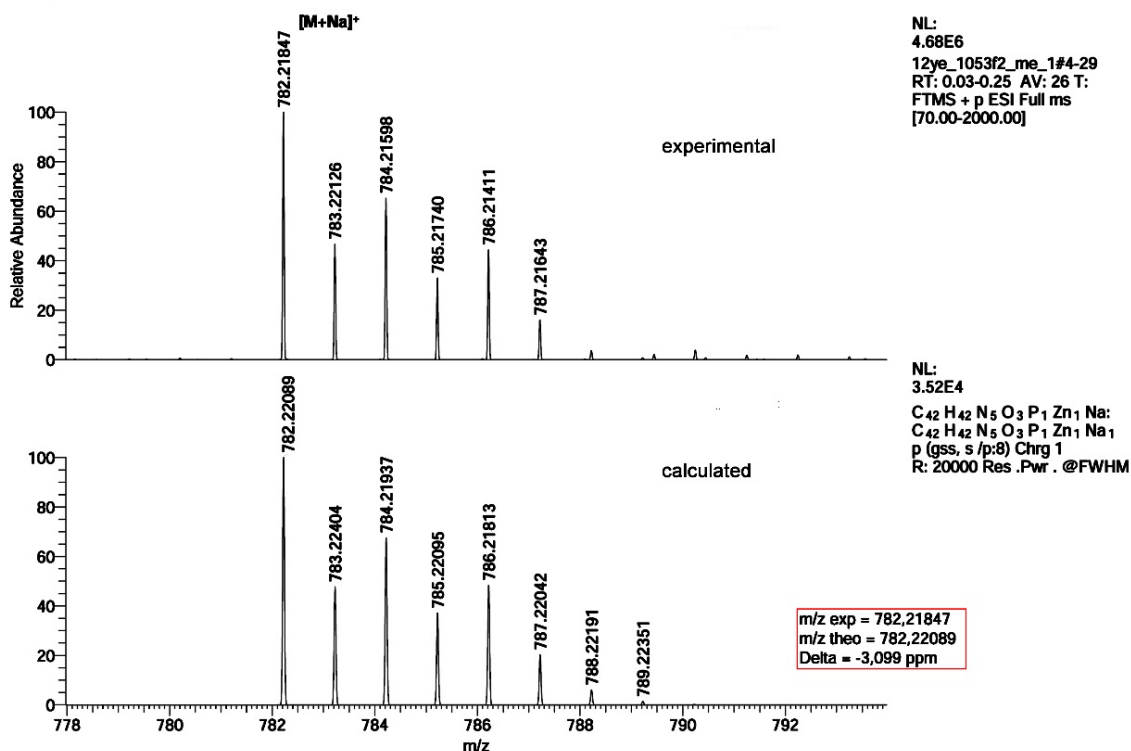
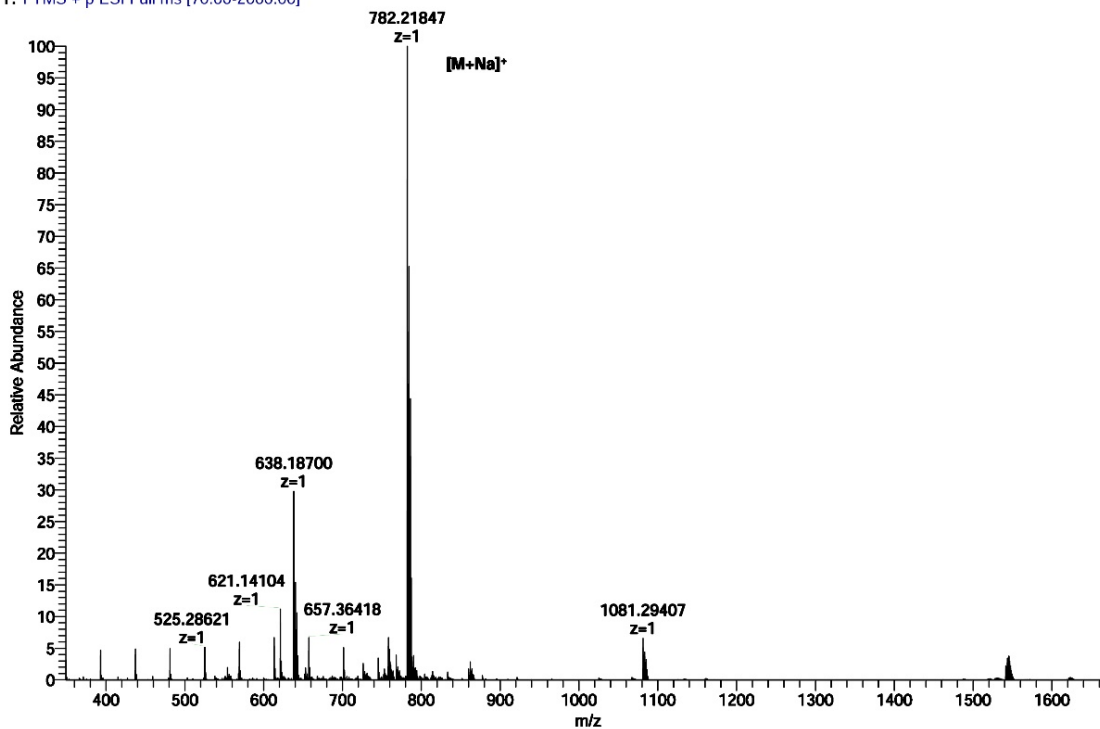


Figure S75. HRMS (ESI) spectrum of 5e.

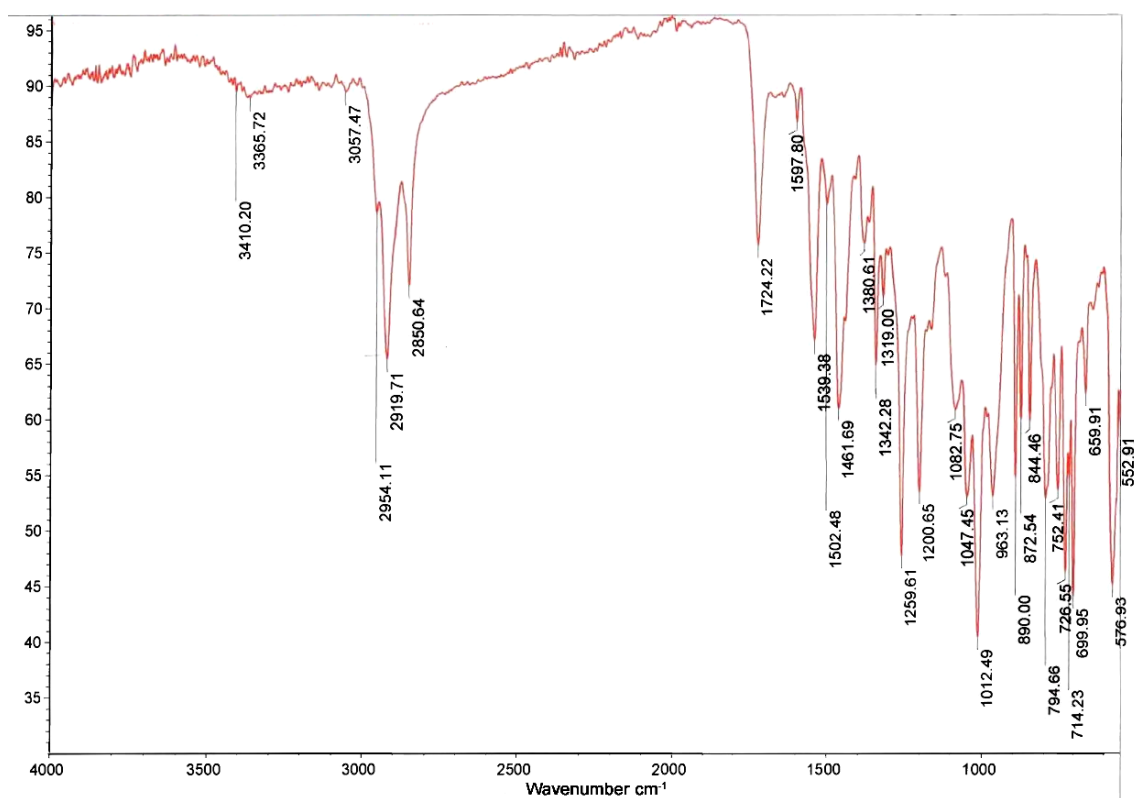


Figure S76. IR (neat) spectrum of **5e**.

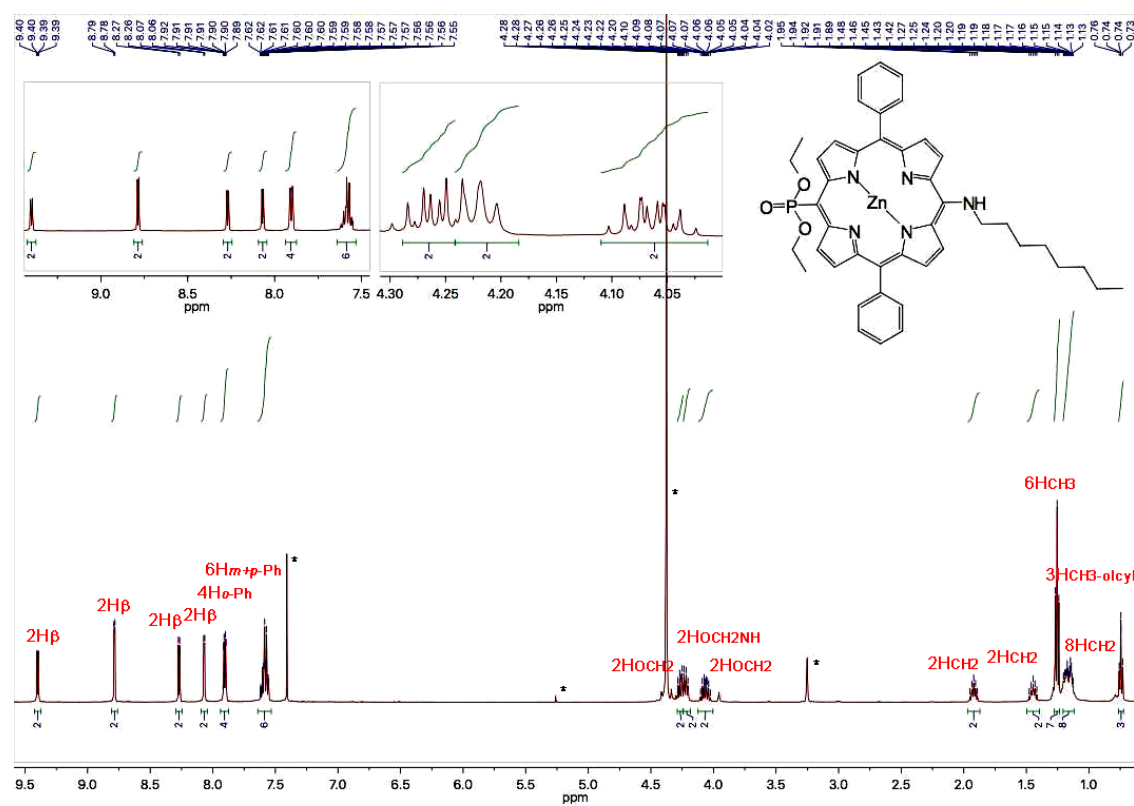


Figure S77. ^1H NMR spectrum of **5f** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.41 ppm – CHCl_3 , δ_{H} 5.26 ppm – CH_2Cl_2 , δ_{H} 4.37 ppm – DOH and H_2O , δ_{H} 3.26 ppm – CHD_2OD).

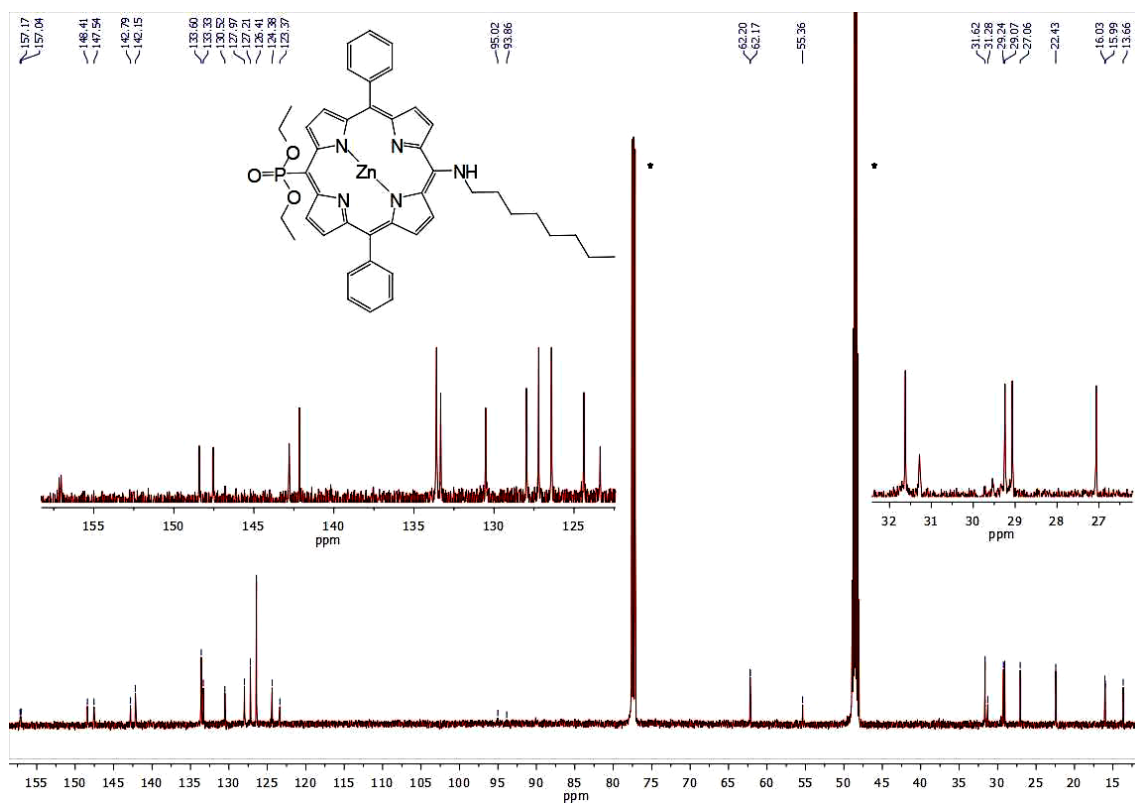


Figure S78. ¹³C NMR spectrum of **5f** (CDCl₃/CD₃OD 2:1, v/v). Solvent peaks are indicated with * (δ_C 77.36 ppm – CDCl₃, δ_C 48.48 ppm – CD₃OD).

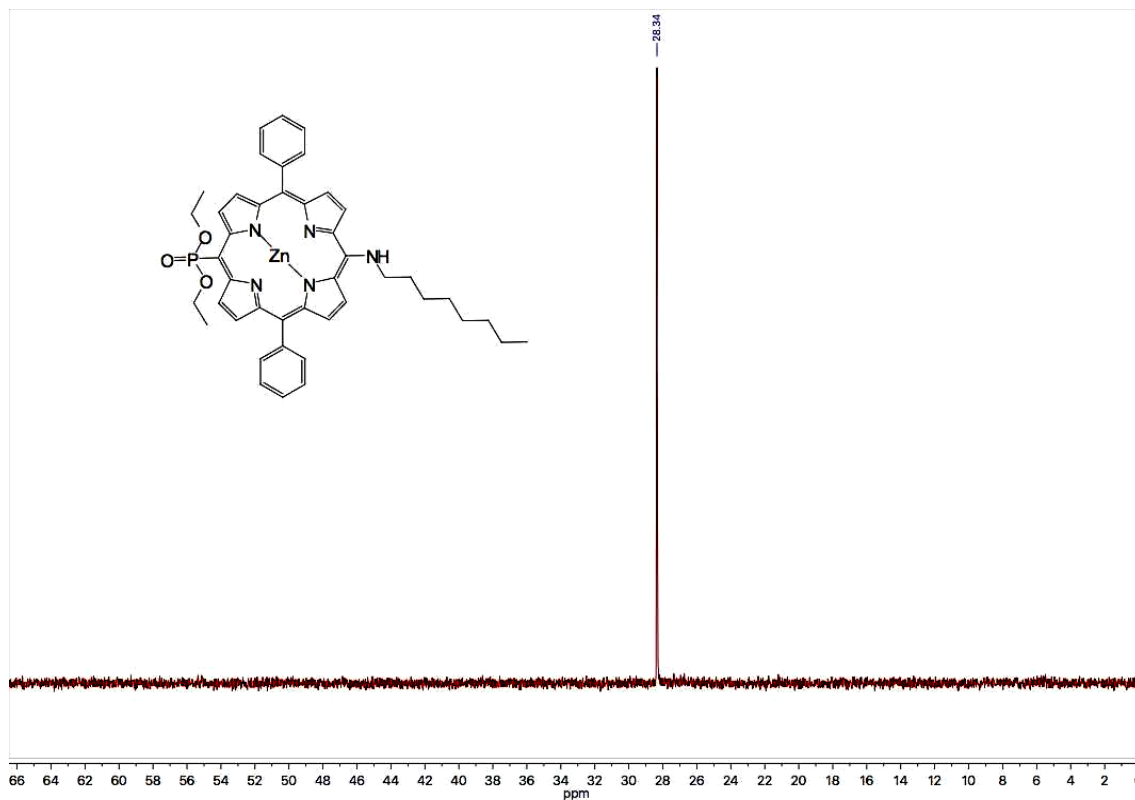


Figure S79. ³¹P {¹H} NMR spectrum of **5f** (CDCl₃/MeOD 2:1, v/v).

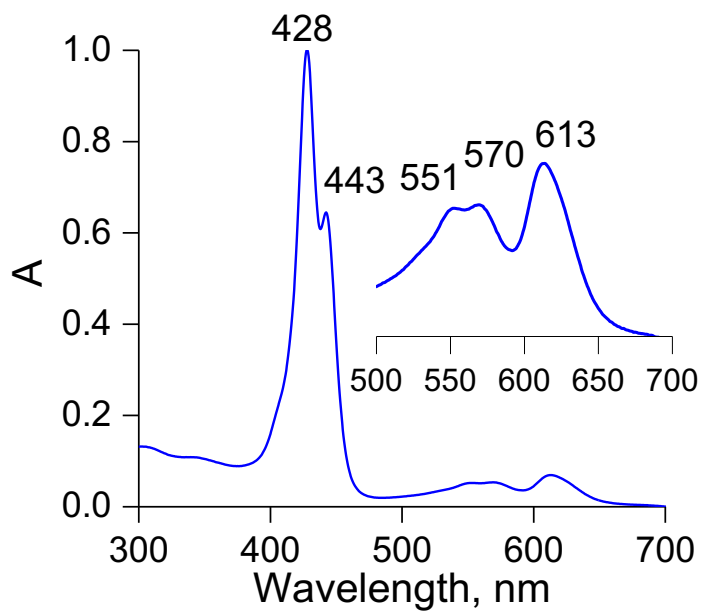


Figure S80. Normalized electronic absorption spectra of **5f** in CHCl₃/MeOH (2:1, v/v) solution (c = 6.25 μM).

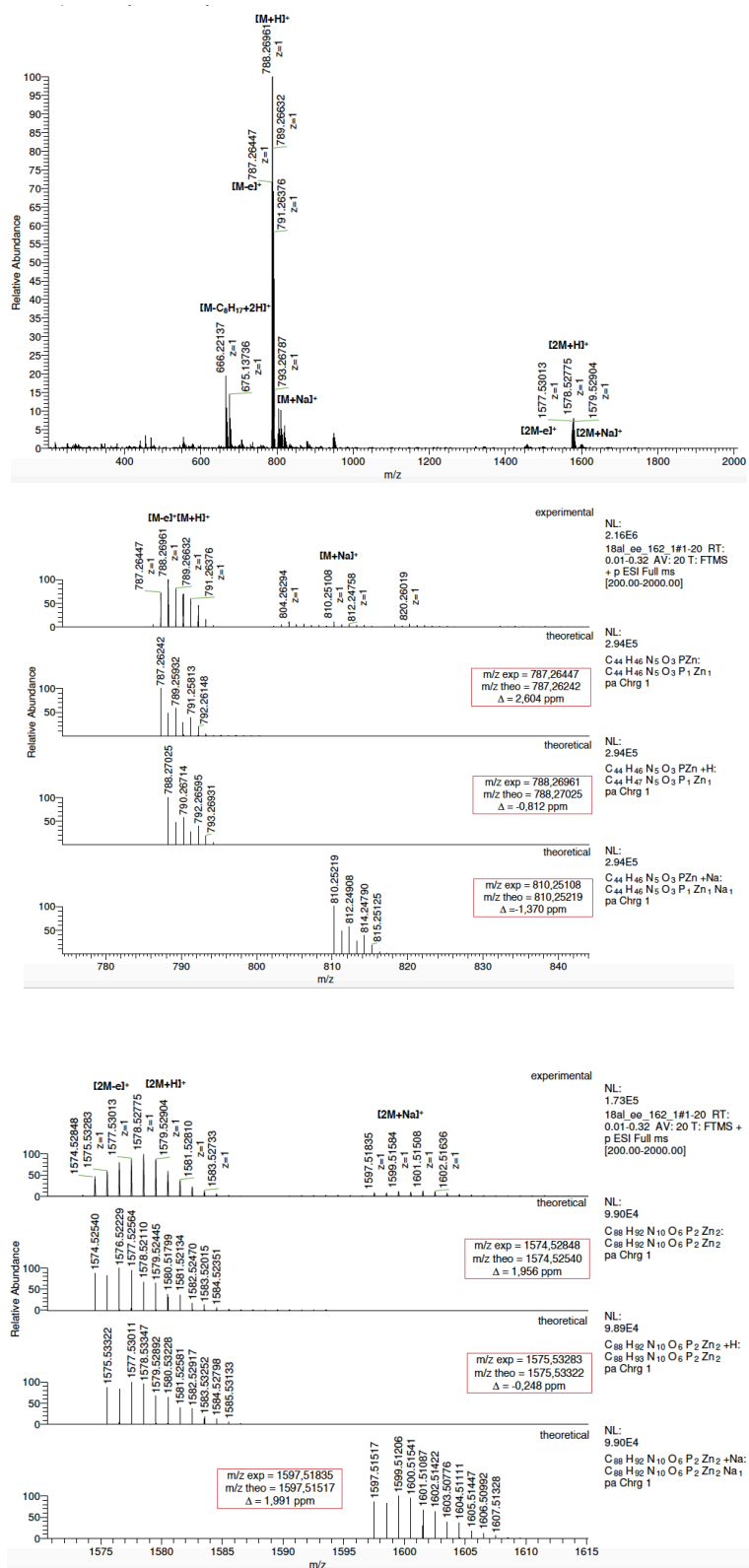


Figure S81. HRMS (ESI) spectrum of 5f.

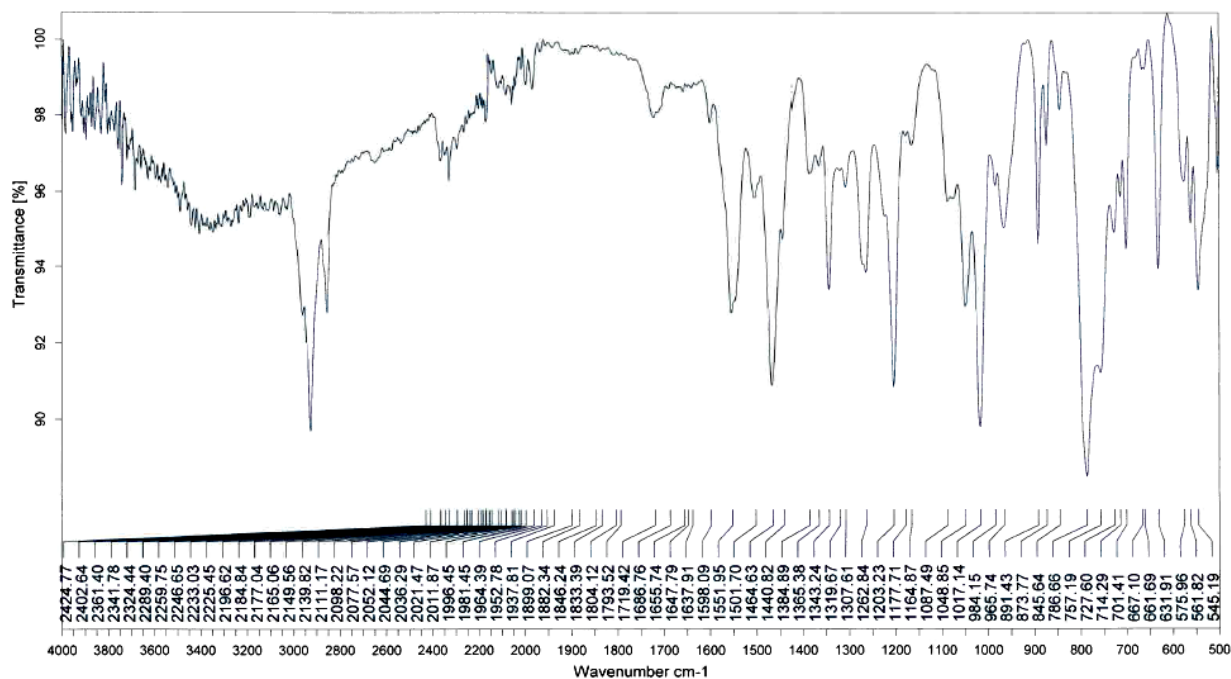


Figure S82. IR (neat) spectrum of **5f**.

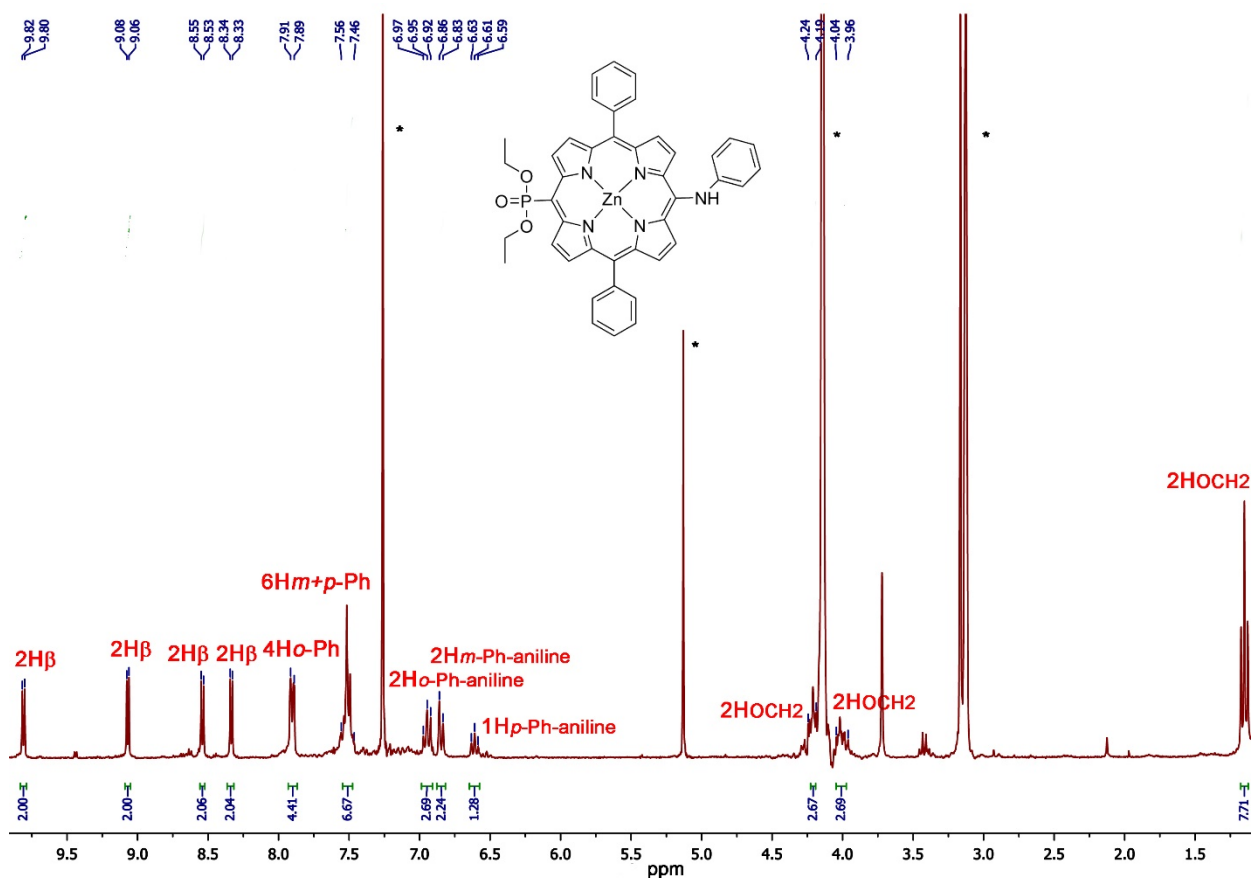


Figure S83. ¹H NMR spectrum of **5g** (CDCl₃/CD₃OD 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.26 ppm – CHCl₃, δ_{H} 5.13 ppm – CH₂Cl₂, δ_{H} 4.14 ppm – DOH and H₂O, δ_{H} 3.72 ppm – EtOH, δ_{H} 3.13 ppm – CHD₂OD).

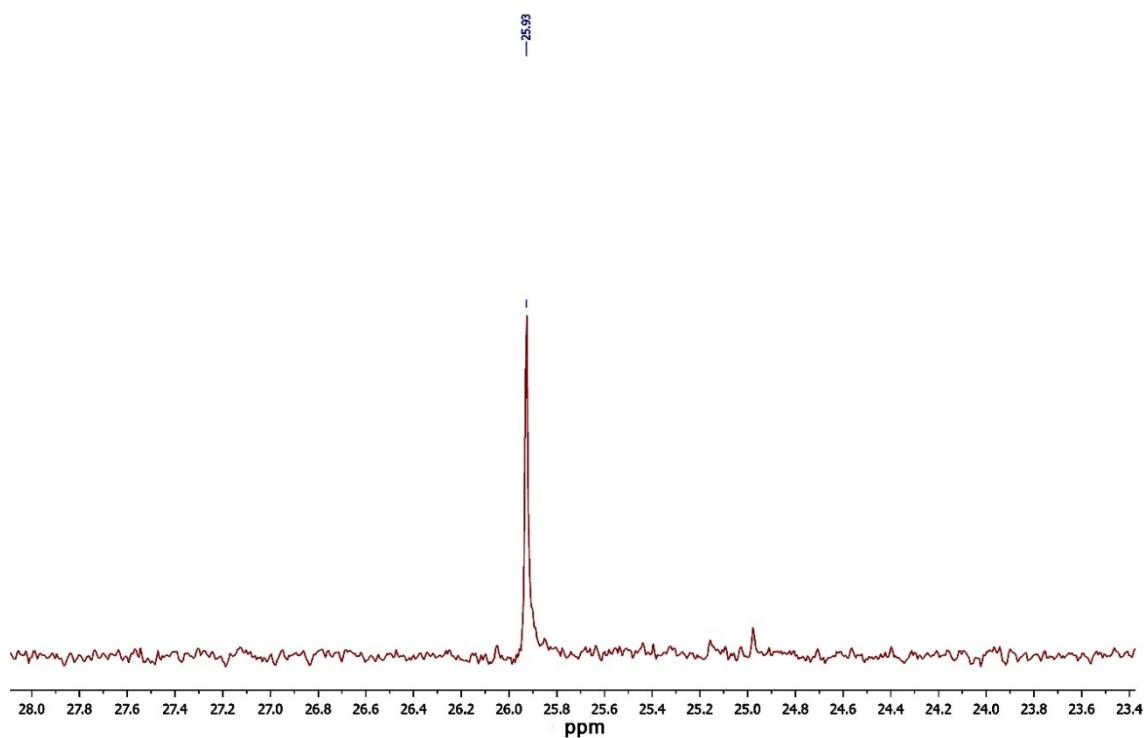


Figure S84. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5g** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

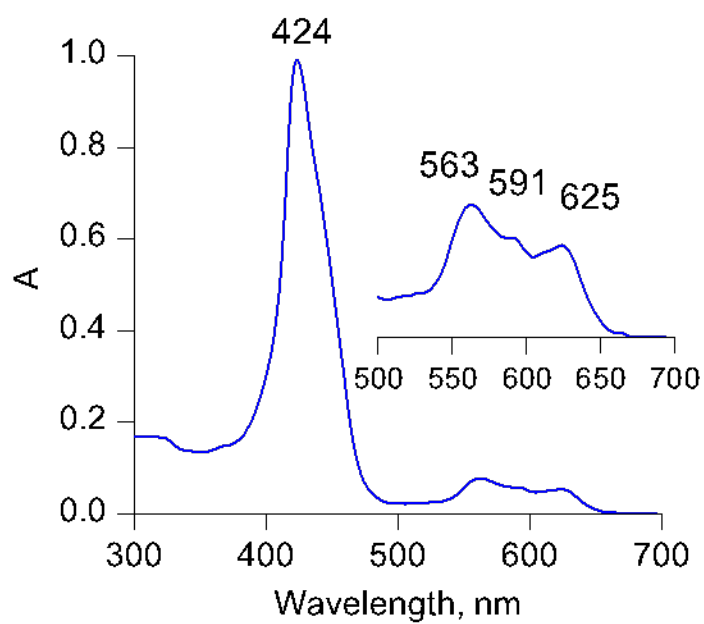


Figure S85. Normalized electronic absorption spectra of **5g** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12ye_1034_me_2 #6-30 RT: 0.06-0.30 AV: 25 NL: 7.26E5
T: FTMS + p ESI Full ms [70.00-2000.00]

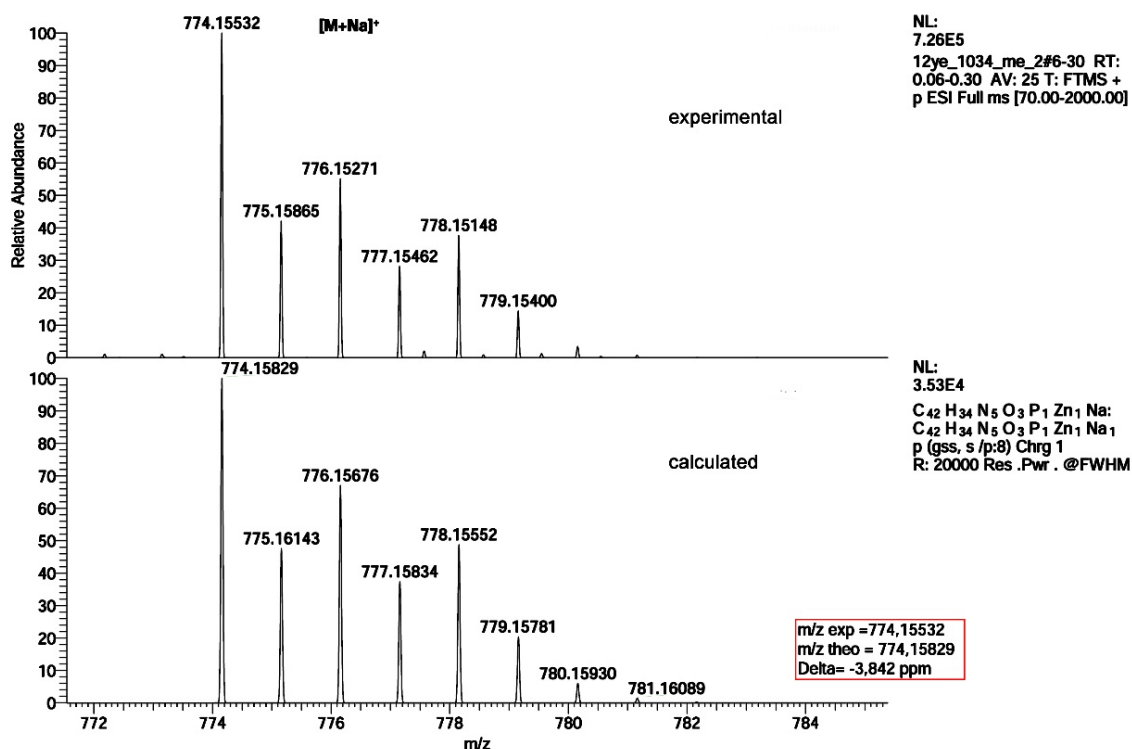
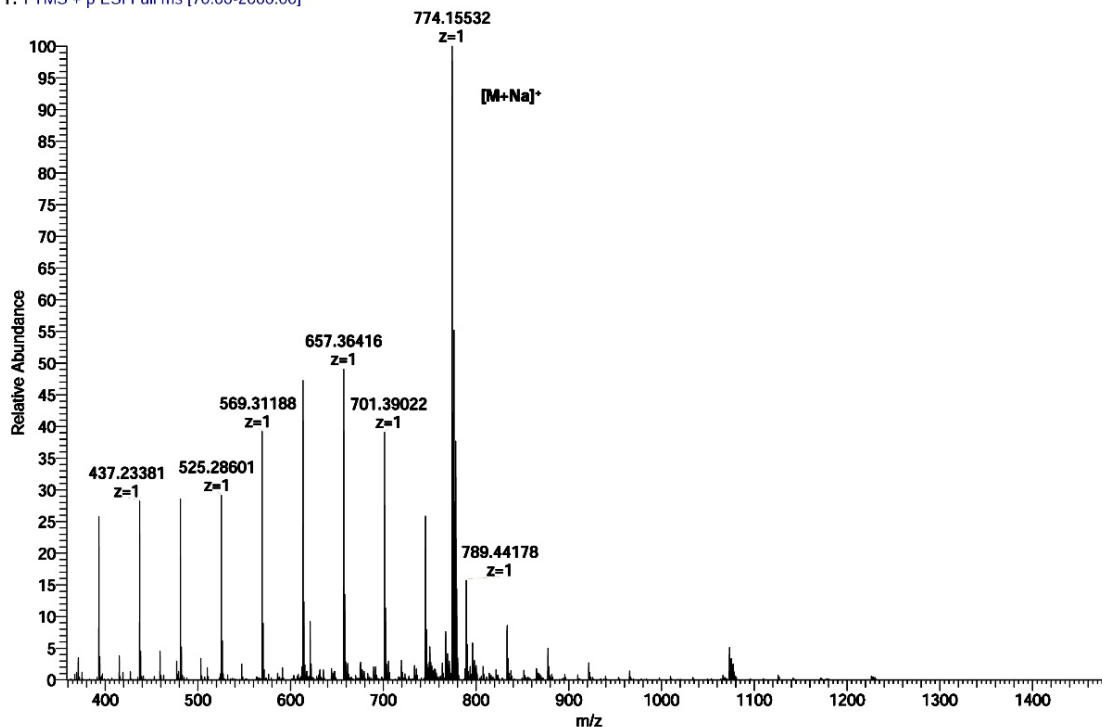


Figure S86. HRMS (ESI) spectrum of 5g.

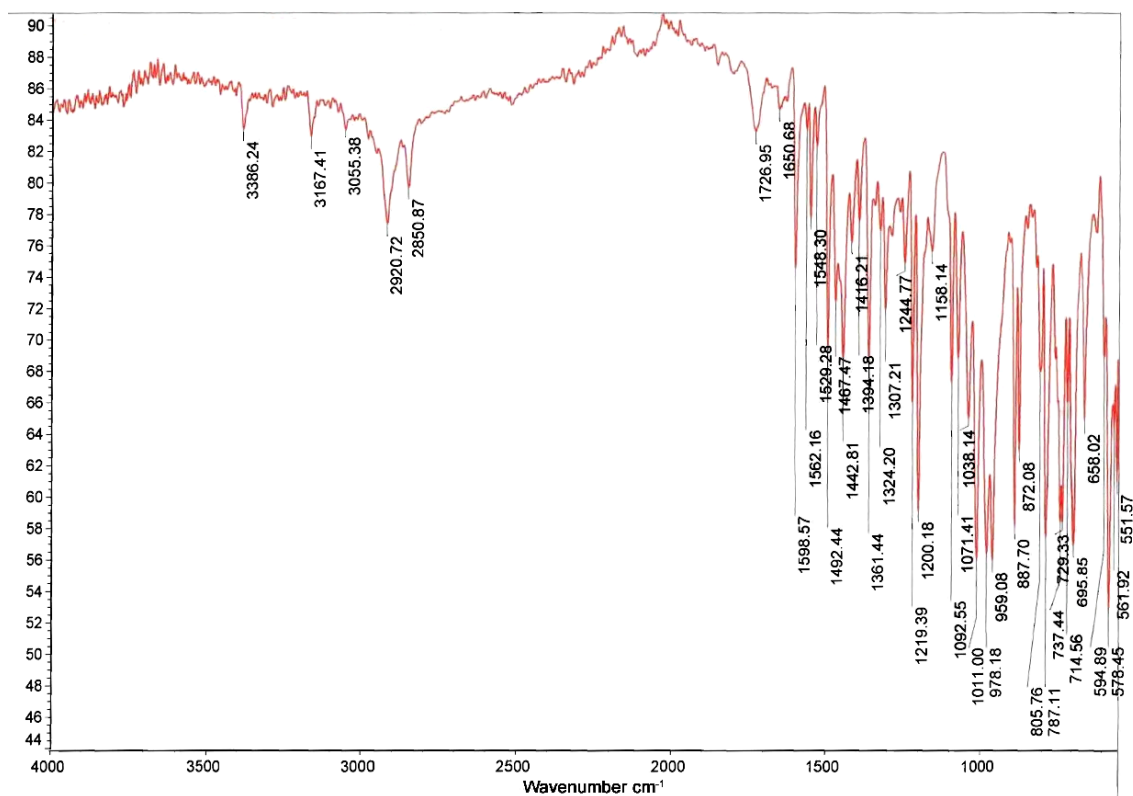


Figure S87. IR (neat) spectrum of **5g**.

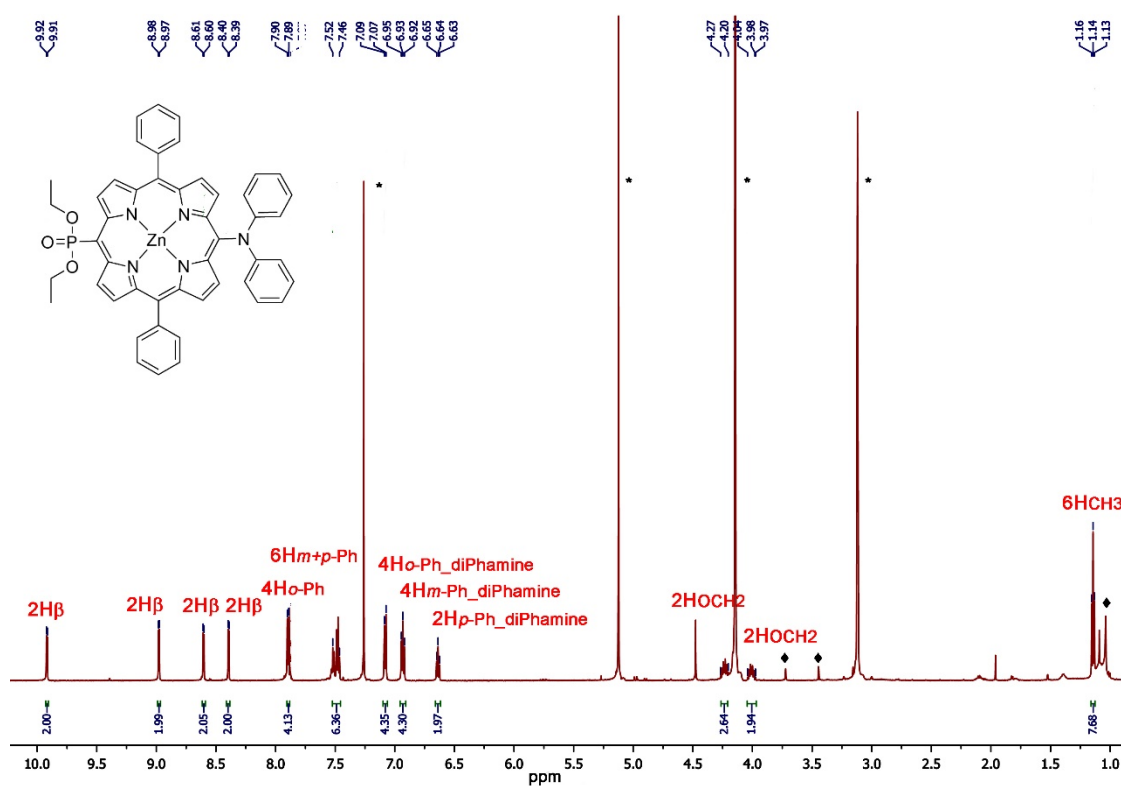


Figure S88. ^1H NMR spectrum of **5h** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v). Solvent peaks are indicated with * (δ_{H} 7.26 ppm – CHCl_3 , δ_{H} 5.12 ppm – CH_2Cl_2 , δ_{H} 4.14 ppm – DOH and H_2O , δ_{H} 3.12 ppm – CHD_2OD). Impurities are indicated with \diamond .

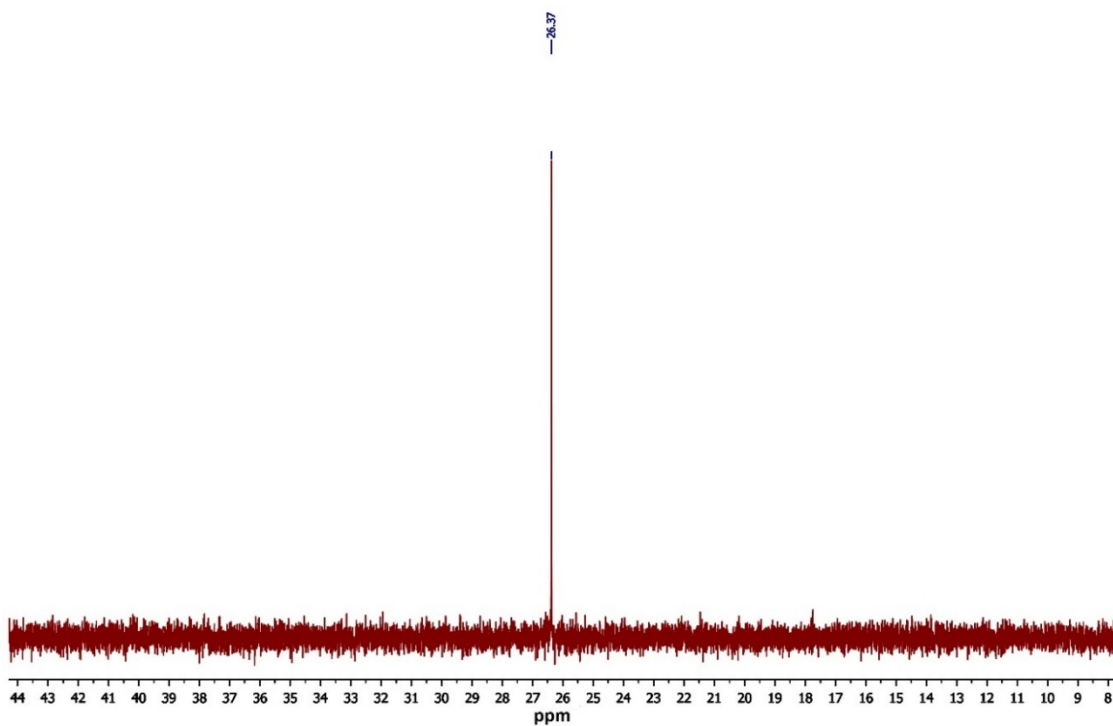


Figure S89. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5h** ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v).

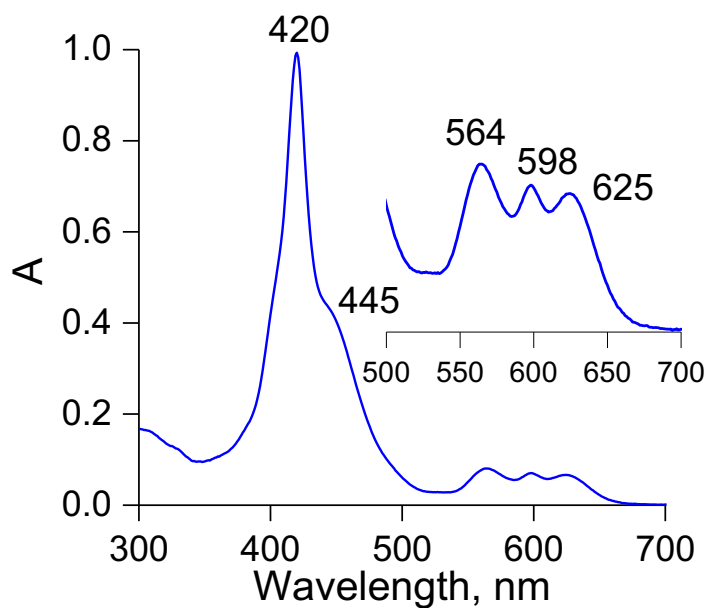


Figure S90. Normalized electronic absorption spectra of **5h** in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

12ye_1109_me_2 #4-29 RT: 0.04-0.25 AV: 26 NL: 5.86E6
T: FTMS + p ESI Full ms [70.00-2000.00]

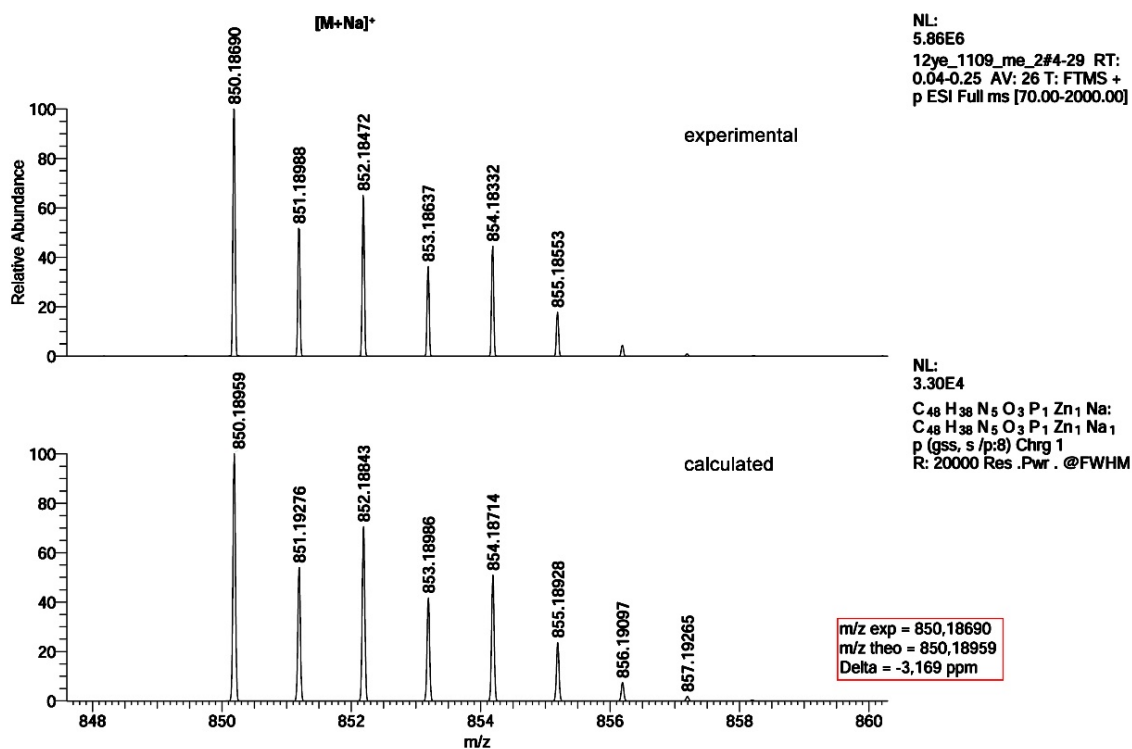
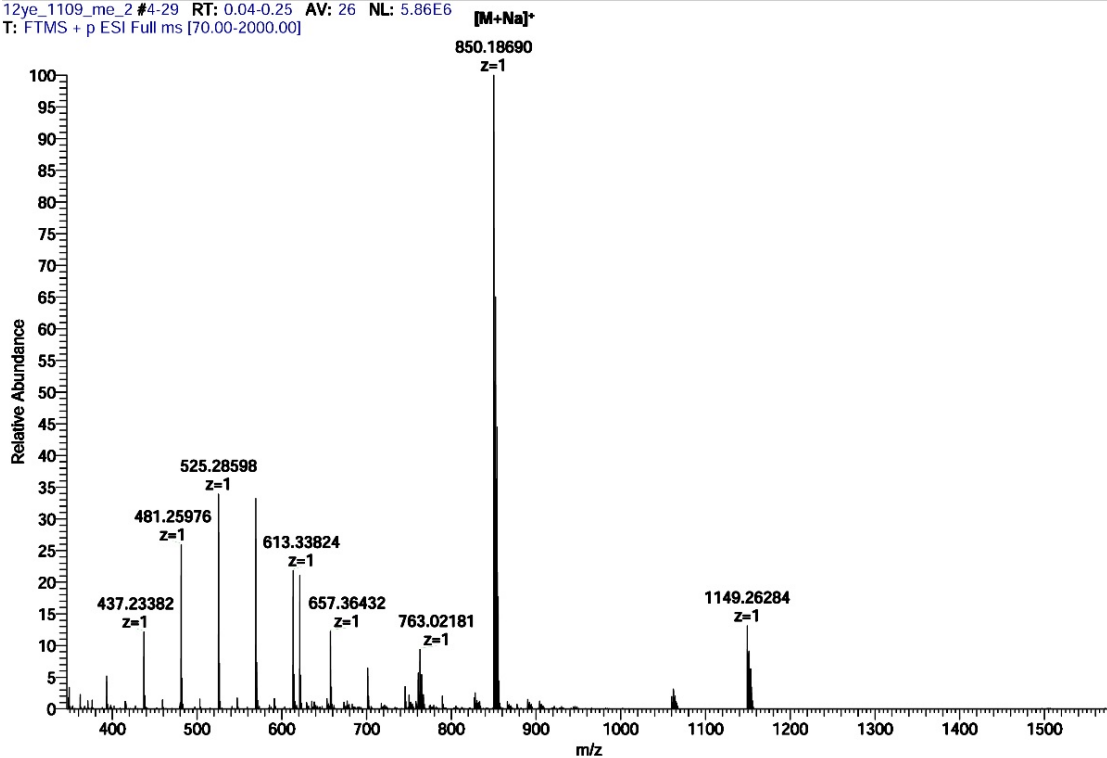


Figure S91. HRMS (ESI) spectrum of 5h.

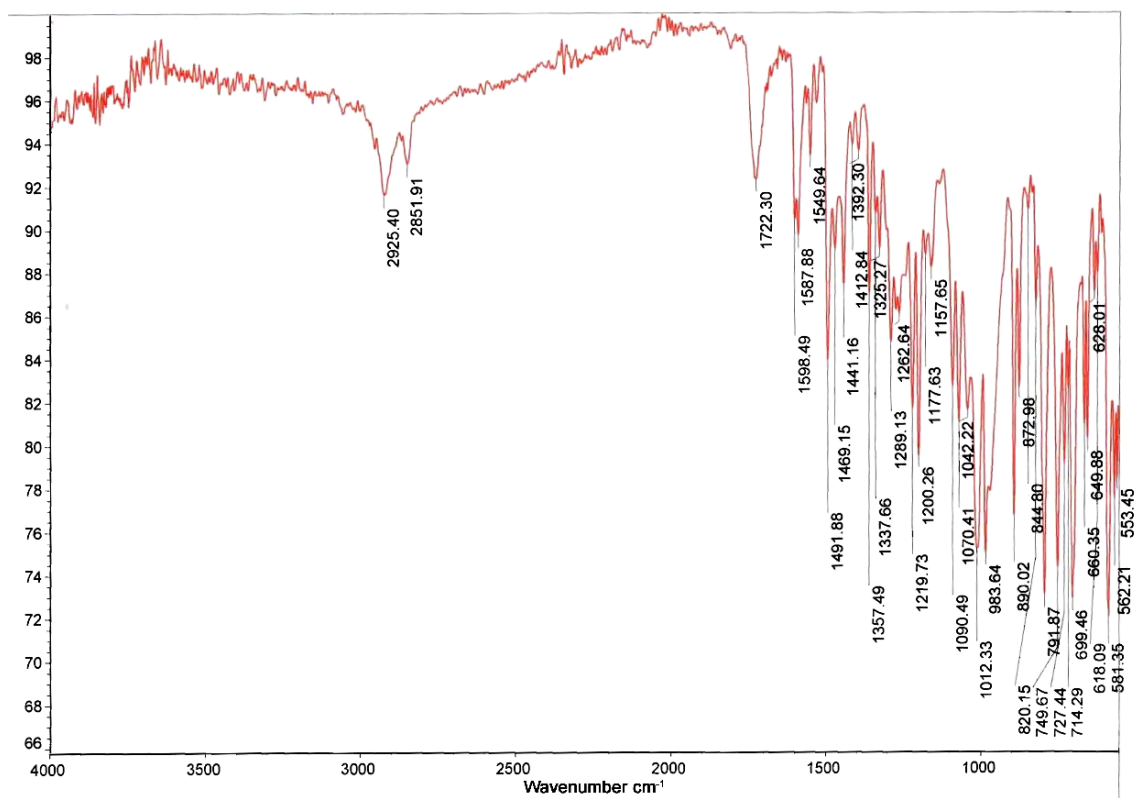


Figure S92. IR (neat) spectrum of 5h.

2. Summary of UV-vis data for porphyrins 3 (a-e), 4 (b-c) and 5 (a-h).

Table S1. UV-vis absorption bands and numbering of figures showing the spectra of porphyrins 3–5.

Compound	Absorption maximum, nm [$\log \epsilon$, ($M^{-1} \cdot cm^{-1}$)]	Figure showing the spectrum
3a	403 (5.43), 424 (6.33), 519 (4.26), 557 (4.92), 589 (4.57), 601 (4.53)	S4
3b	423 (5.63), 517 (3.65), 557 (4.33), 589 (4.02), 600 (3.97)	S10
3c	320 (4.18), 404 (4.64), 424 (5.31), 518 (3.44), 556 (4.12), 588 (3.83), 600 (3.76).	S16
3d	400 (5.09), 422 (5.98), 518 (3.99), 556 (4.65), 587 (4.1), 598 (4.20)	S22
3e	402 (4.71), 422 (5.51), 517 (3.61), 554 (4.23), 586 (3.77), 599 (3.78)	S28
4b	427 (5.45), 523 (3.42), 561 (4.03), 596 (4.12), 609 (4.18)	S34
4c	423 (5.46), 461 (4.21), 517 (3.72), 555 (4.19), 597 (3.91)	S40
5a	320 (4.26), 400 (4.59), 425 (5.45), 519 (3.47), 559 (4.14), 590 (3.97), 601 (3.89), 616 (3.69)	S49
5b^[a]	423, 521, 559, 590, 603	S55
5c	320 (4.28), 403 (4.72), 424 (5.45), 520 (3.56), 558 (4.18), 590 (4.02), 601 (3.95)	S63
5d	320 (4.23), 401 (4.88), 424 (5.77), 520 (3.47), 559 (4.10), 590 (3.94), 601 (3.86), 616 (3.67)	S69
5e	347 (4.29), 428 (5.27), 442 (5.09), 514 (3.71), 550 (4.13), 570 (4.03), 613 (4.14)	S74
5f	428 (5.97), 551 (4.76), 570 (4.78), 613 (4.89), 690 (4.01)	S80
5g^[a]	423, 521, 559, 590, 603	S85
5h	309 (4.22), 420 (5.02), 445 (4.64), 564 (3.92), 598 (3.85), 625 (3.81)	S90

[a] The self-assembly of compounds **5b** and **5g** in $CHCl_3$, CH_2Cl_2 and a $CHCl_3/MeOH$ mixture (2:1, v/v) was observed by 1H NMR spectroscopy. This aggregation also impedes the accurate determination of molar extinction coefficients (ϵ) of the dye.

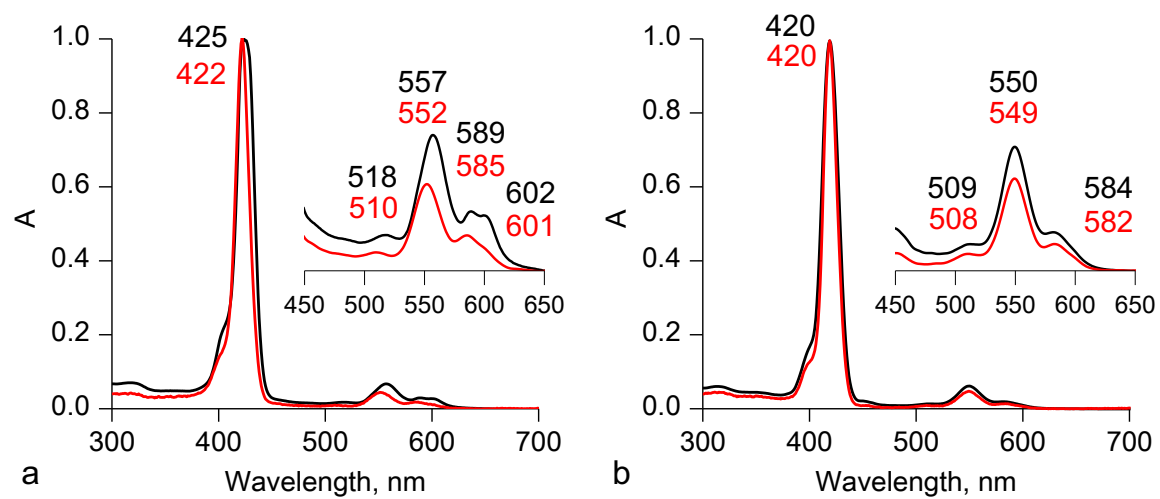


Figure S93. Normalized UV/vis spectra of porphyrins (a) **3a** and (b) **3d** in chloroform solutions: 10.00 μM (black line) and 0.63 μM (red line).

3. Summary of crystal data and structure refinement for porphyrin [5a]_n.

Single-crystal X-ray diffractive analysis of **5a** were performed using Bruker AXS SMART 1000, CCD-detector $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$, graphite monochromator, ω -scanning, $2\theta_{\text{max}} = 60^\circ$. Crystal data: $\text{C}_{40}\text{H}_{36}\text{N}_5\text{O}_4\text{PZn}$, $M = 747.08$, monoclinic, space group $\text{P2}(1)/n$, $a = 14.2619(18)\text{\AA}$, $b = 10.9968(14)\text{\AA}$, $c = 22.527(3)\text{\AA}$, $\beta = 91.998(2)^\circ$, $V = 3530.9(8)\text{\AA}^3$ (150 K), $Z = 4$, $D_{\text{calc}} = 1.405\text{ g cm}^{-3}$, 10257 measured reflections, 7956 independent reflections with $F^2 > 2\sigma(I)$, $\mu = 0.791\text{ mm}^{-1}$, $R_1 = 0.0514$, $wR_2 = 0.1312$. Corrections for absorption were made by SADABS [1]. The structure was solved by direct method and refined by the full-matrix least squares method for F^2 with anisotropic parameters for all non-hydrogen atoms. All calculations were performed using SAINT [2] and SHELXTL-97 [3] program packages.

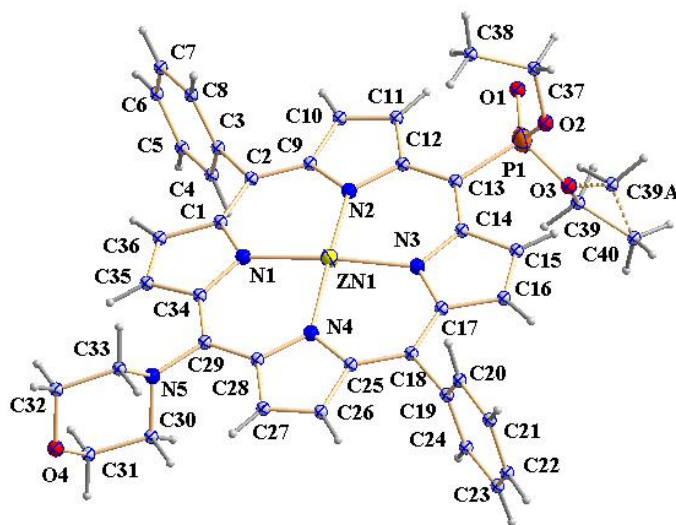


Figure S94. Independent part of coordination polymer [5a]_n (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

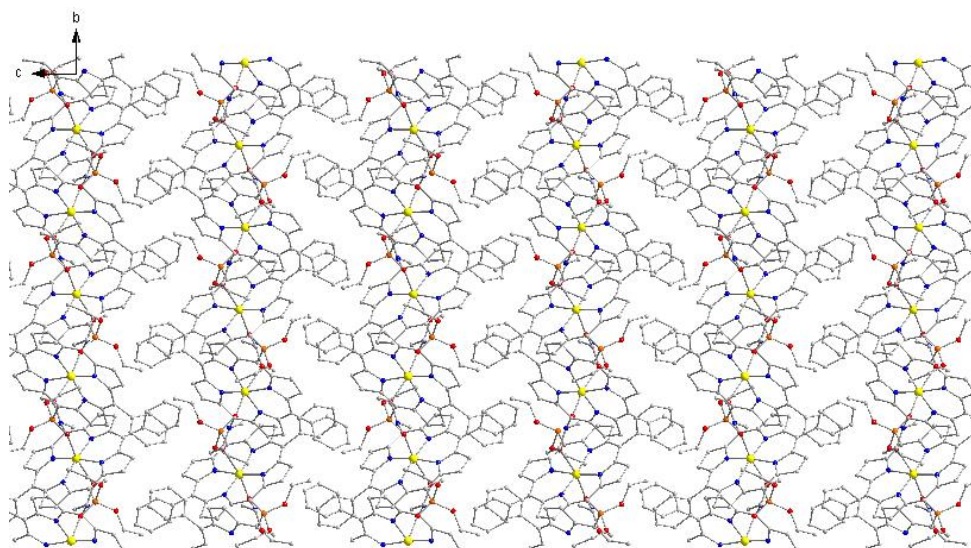


Figure S95. Crystal packing of coordination polymer [5a]_n (view along the crystallographic direction a). Hydrogen atoms are omitted for clarity.

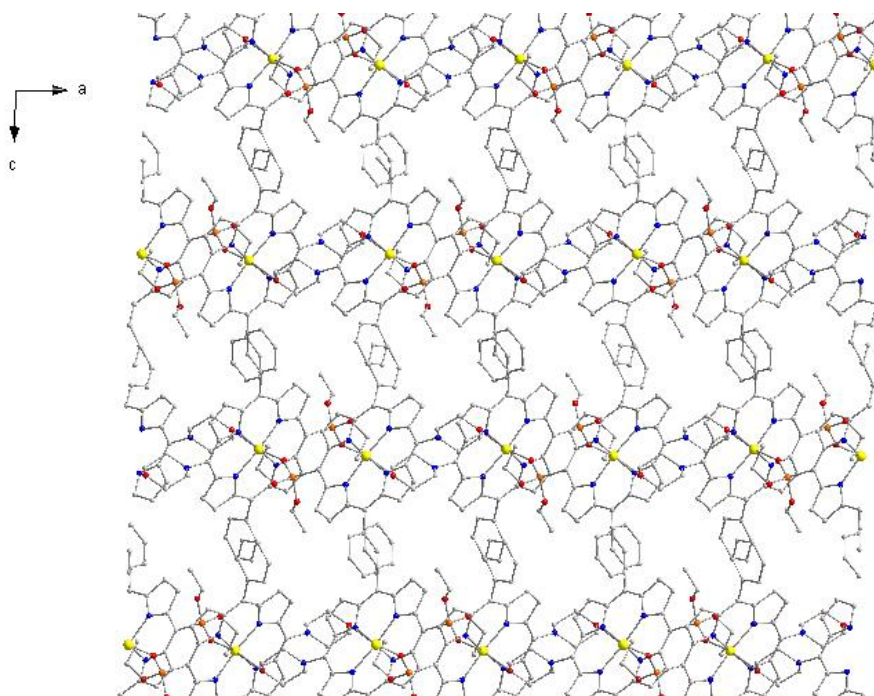


Figure S96. Crystal packing of coordination polymer $[5a]_n$ (view along the crystallographic direction b). Hydrogen atoms are omitted for clarity.

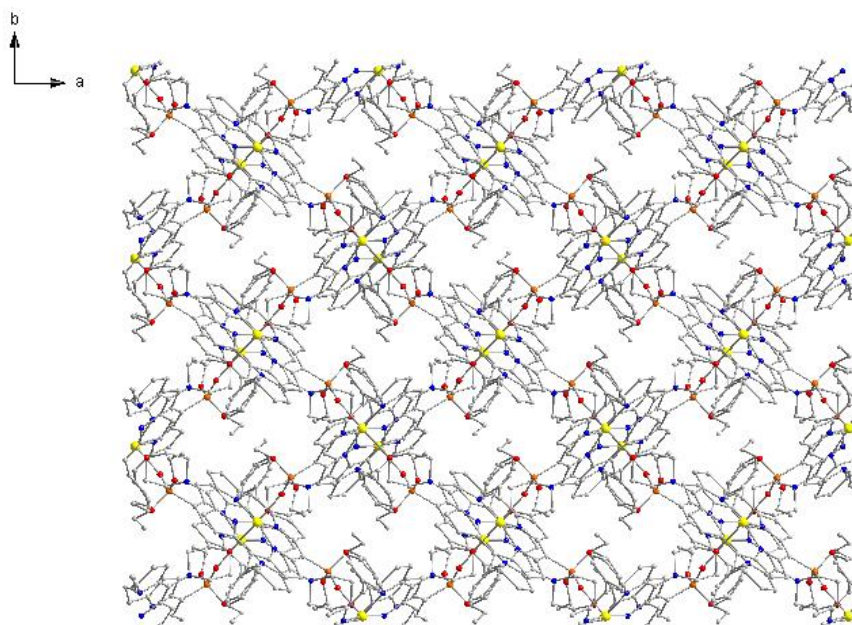


Figure S97. Crystal packing of coordination polymer $[5a]_n$ (view along the crystallographic direction b). Hydrogen atoms are omitted for clarity.

Table S2. Selected bond lengths [\AA] and angles [$^\circ$] for $[5a]_n$.

Zn1 N3 2.0451(18)	Zn1 N4 2.0603(19)
Zn1 N2 2.0649(19)	Zn1 N1 2.0701(19)
Zn1 O1 2.2675(17)	P1 O1 1.4677(19)
P1 O3 1.553(2) .	P1 O2 1.579(2) .

P1 C13 1.806(2) .	O2 C37 1.413(6) .
O3 C39A 1.294(7)	O3 C39 1.413(7) .
O4 C31 1.419(4) .	O4 C32 1.420(4) .
N1 C1 1.366(3) .	N1 C34 1.372(3) .
N2 C12 1.374(3) .	N2 C9 1.378(3) .
N3 C14 1.363(3) .	N3 C17 1.381(3) .
N4 C25 1.364(3) .	N4 C28 1.375(3) .
N5 C29 1.432(3) .	N5 C33 1.434(3) .
N5 C30 1.462(3) .	C1 C2 1.405(3) .
C1 C36 1.449(3) .	C2 C9 1.397(3) .
C2 C3 1.518(3) .	C3 C8 1.359(4) .
C3 C4 1.377(4) .	C4 C5 1.387(4) .
C5 C6 1.377(5) .	C6 C7 1.347(6) .
C7 C8 1.398(4) .	C9 C10 1.441(3) .
C10 C11 1.349(4)	C11 C12 1.456(3)
C12 C13 1.411(3)	C13 C12 1.411(3)
C13 C14 1.424(3)	C14 C13 1.424(3)
C14 C15 1.460(3)	C15 C16 1.337(3)
C16 C17 1.444(3)	C17 C18 1.397(3)
C18 C25 1.408(3)	C18 C19 1.505(3)
C19 C24 1.360(4)	C19 C20 1.368(4)
C20 C21 1.391(4)	C21 C22 1.353(6)
C22 C23 1.333(5)	C23 C24 1.396(4)
C25 C26 1.445(3)	C26 C27 1.352(4)
C27 C28 1.445(3)	C28 C29 1.402(3)
C29 C34 1.401(3)	C30 C31 1.501(4)
C32 C33 1.522(4)	C34 C35 1.447(3)
C35 C36 1.350(3)	C37 C38 1.491(10)
C39 C40 1.360(8)	C39A C40 1.515(8)
N3 Zn1 N4 91.30(7)	N3 Zn1 N2 88.81(7)
N4 Zn1 N2 171.14(8)	N3 Zn1 N1 171.01(8)
N4 Zn1 N1 88.81(7)	N2 Zn1 N1 89.71(7)
N3 Zn1 O1 87.96(7)	N4 Zn1 O1 91.31(8)

N2 Zn1 O1 97.55(8)	N1 Zn1 O1 101.02(7)
O1 P1 O3 113.61(12)	O1 P1 O2 113.44(12)
O3 P1 O2 100.20(16)	O1 P1 C13 116.97(11)
O3 P1 C13 105.45(14)	O2 P1 C13 105.47(11)
P1 O1 Zn1 152.09(11)	C37 O2 P1 123.9(3)
C39A O3 P1 124.5(4)	C39 O3 P1 131.0(4)
C31 O4 C32 111.3(2)	C1 N1 C34 106.56(18)
C1 N1 Zn1 126.60(15)	C34 N1 Zn1 126.46(15)
C12 N2 C9 106.63(18)	C12 N2 Zn1 127.38(15)
C9 N2 Zn1 125.99(15)	C14 N3 C17 107.13(18)
C14 N3 Zn1 127.91(15)	C17 N3 Zn1 124.74(15)
C25 N4 C28 106.67(19)	C25 N4 Zn1 125.55(15)
C28 N4 Zn1 127.68(15)	C29 N5 C33 118.9(2)
C29 N5 C30 118.4(2)	C33 N5 C30 112.3(2)
N1 C1 C2 125.6(2)	N1 C1 C36 109.7(2)
C2 C1 C36 124.6(2)	C9 C2 C1 125.9(2)
C9 C2 C3 117.3(2)	C1 C2 C3 116.7(2)
C8 C3 C4 118.3(3)	C8 C3 C2 122.0(3)
C4 C3 C2 119.7(2)	C3 C4 C5 121.3(3)
C6 C5 C4 119.3(3)	C7 C6 C5 119.8(3)
C6 C7 C8 120.5(3)	C3 C8 C7 120.7(3)
N2 C9 C2 126.1(2)	N2 C9 C10 109.8(2)
C2 C9 C10 124.0(2)	C11 C10 C9 107.1(2)
C10 C11 C12 107.4(2)	N2 C12 C13 124.9(2)
N2 C12 C11 109.07(19)	C13 C12 C11 126.0(2)
C12 C13 C14 125.1(2)	C12 C13 P1 119.71(16)
C14 C13 P1 115.17(16)	N3 C14 C13 125.09(19)
N3 C14 C15 108.77(19)	C13 C14 C15 126.1(2)
C16 C15 C14 107.6(2)	C15 C16 C17 107.3(2)
N3 C17 C18 126.2(2)	N3 C17 C16 109.18(19)
C18 C17 C16 124.6(2)	C17 C18 C25 126.5(2)
C17 C18 C19 117.2(2)	C25 C18 C19 116.3(2)
C24 C19 C20 118.2(3)	C24 C19 C18 121.5(2)
C20 C19 C18 120.2(2)	C19 C20 C21 119.9(3)

C22 C21 C20 120.9(4)	C23 C22 C21 119.6(3)
C22 C23 C24 120.3(3)	C19 C24 C23 121.0(3)
N4 C25 C18 125.3(2)	N4 C25 C26 109.8(2)
C18 C25 C26 125.0(2)	C27 C26 C25 107.2(2)
C26 C27 C28 106.9(2)	N4 C28 C29 125.0(2)
N4 C28 C27 109.5(2)	C29 C28 C27 125.5(2)
C34 C29 C28 125.3(2)	C34 C29 N5 114.3(2)
C28 C29 N5 120.3(2)	N5 C30 C31 108.6(3)
O4 C31 C30 110.9(2)	O4 C32 C33 111.0(2)
N5 C33 C32 109.1(2)	N1 C34 C29 126.4(2)
N1 C34 C35 109.76(19)	C29 C34 C35 123.7(2)
C36 C35 C34 106.8(2)	C35 C36 C1 107.1(2)
O2 C37 C38 113.7(4)	C40 C39 O3 113.4(6)
O3 C39A C40 111.0(5)	

4. Studies of porphyrins **3a**, **3d**, **2H-3a**, **2H-3d**, **TPyP** and **ZnTPyP** at the air/water interface and in LS films

Table S3. Soret band (nm) for the porphyrins **3a**, **2H-3a**, **3d** and **2H-3d** in chloroform solution and on liquid and solid surfaces

Porphyrin	Solution	Monolayer		LS film
	CHCl ₃	0 mN m ⁻¹	25 mN m ⁻¹	
3a	423	435	437	431
3d	420	431	433	430
2H-3a	419	431	435	428
2H-3d	416	425	430	424
TPyP	418	440	441	440
ZnTPyP	424	449	450	448

Table S4. Q bands (nm) for the porphyrins **3a**, **2H-3a**, **3d** and **2H-3d** in chloroform solutions and on liquid and solid surfaces

Porphyrin		3a			3d		2H-3a				2H-3d			
Solution	CHCl ₃	552	587	601	549	589	517	552	588	641	516	551	586	640
	0 mN m ⁻¹	567	589	604	559	602	519	558	595	648	519	552	592	643
Monolayer	25 mN m ⁻¹	567	591	606	561	602	522	558	595	648	523	557	594	644
	LS film	559	592	604	558	601	517	550	586	641	519	552	592	643

Table S5. Q bands (nm) for the porphyrins **TPyP** and **ZnTPyP** in chloroform solution and on liquid and solid surfaces

Porphyrin		TPyP				ZnTPyP	
Solution	CHCl ₃	514	546	590	650	555	595
	0 mN m ⁻¹	518	550	590	651	567	604
Monolayer	25 mN m ⁻¹	519	549	590	650	566	606
	LS film	521	554	590	655	565	605

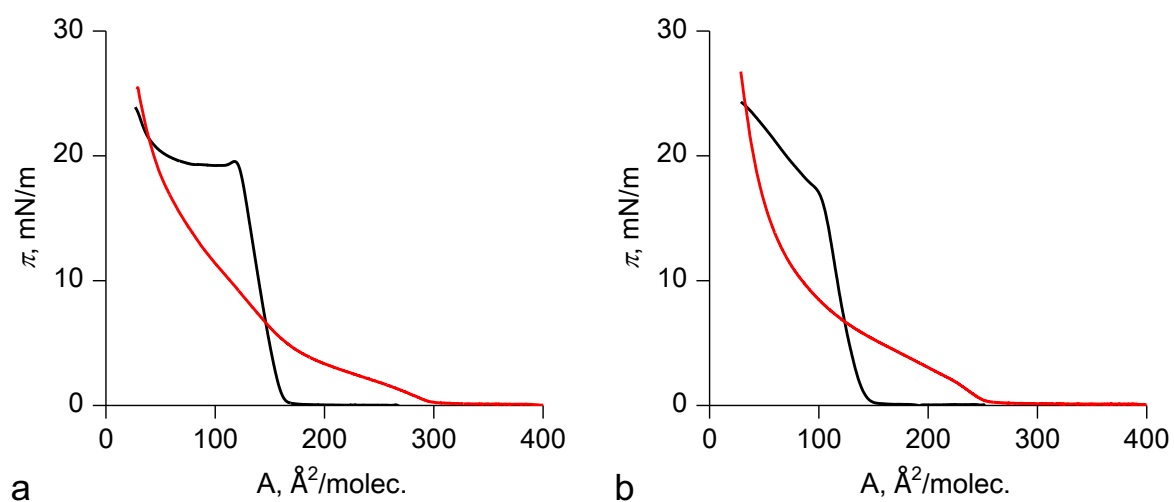


Figure S98. Surface pressure vs area isotherms (π - A curves) for the monolayer of (a) **3a** (red line) and **2H-3a** (black line), (b) **2H-3d** (red line) and **2H-3d** (black line) on the surface of deionized water.

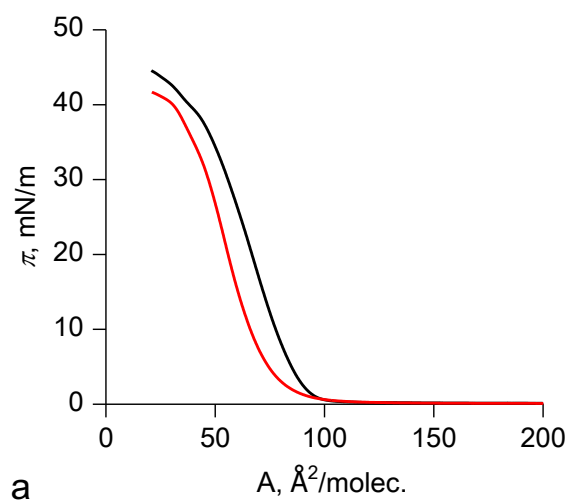


Figure S99. Surface pressure vs area isotherms (π - A curves) for the monolayer of **TPyP** (black line) and **ZnTPyP** (red line) on the surface of deionized water.

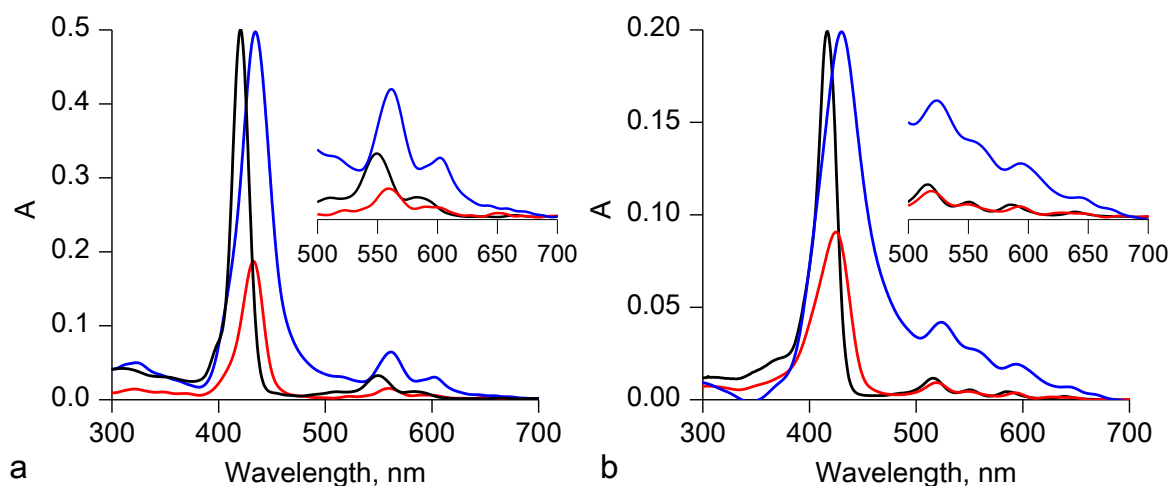


Figure S100. UV/vis spectra in CHCl_3 solution (black line) and *in situ* UV/vis spectra of the monolayer on the surface of deionized water at 0 mN m^{-1} (red line) and 25 mN m^{-1} (blue line) for (a) **3d** and (b) **2H-3d**.

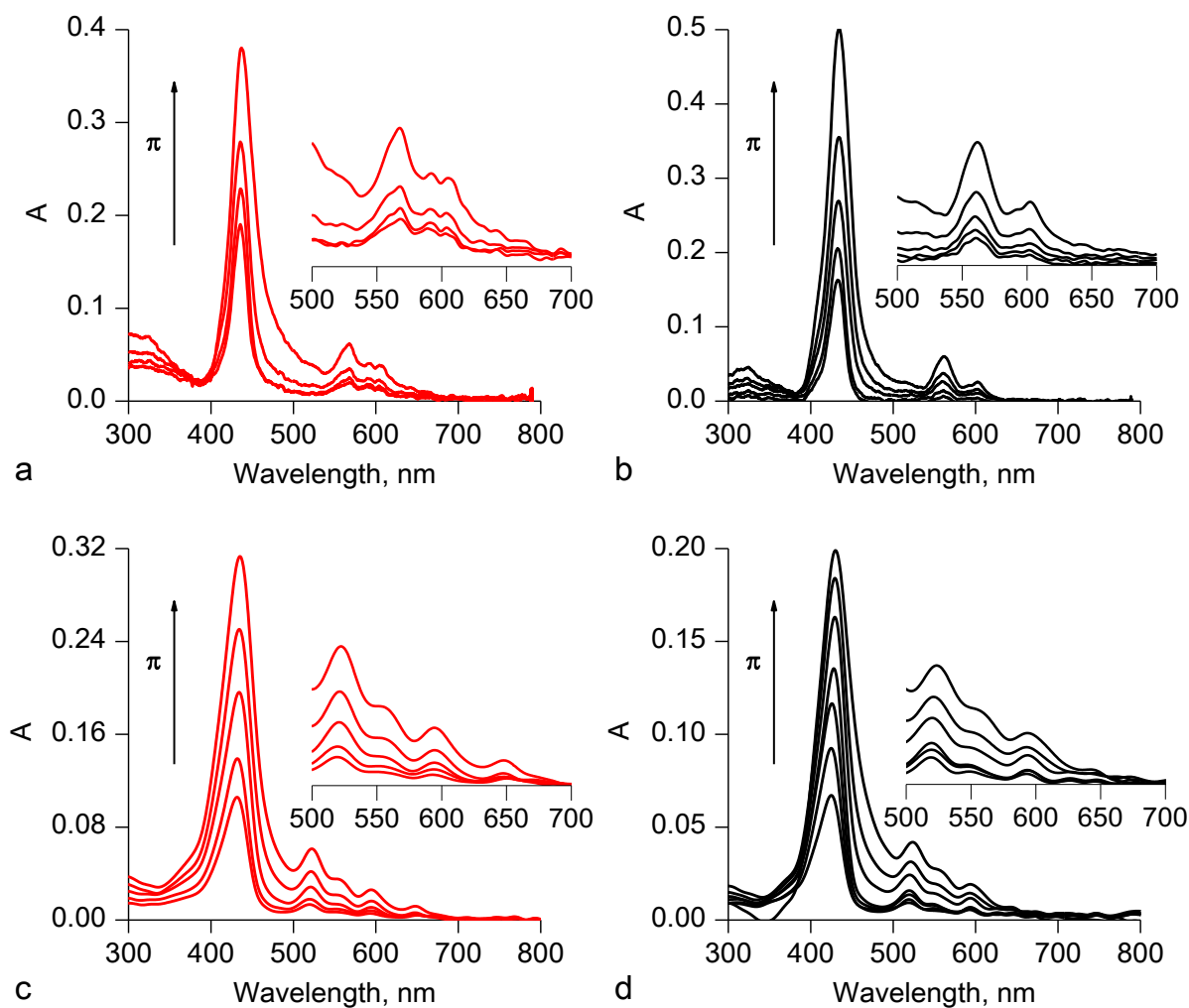


Figure S101. *In situ* UV/vis spectra for (a) **3a**, (b) **3d**, (c) **2H-3a** and (d) **2H-3d** monolayers on the surface of deionized water. The spectra were recorded during the compression of the monolayer.

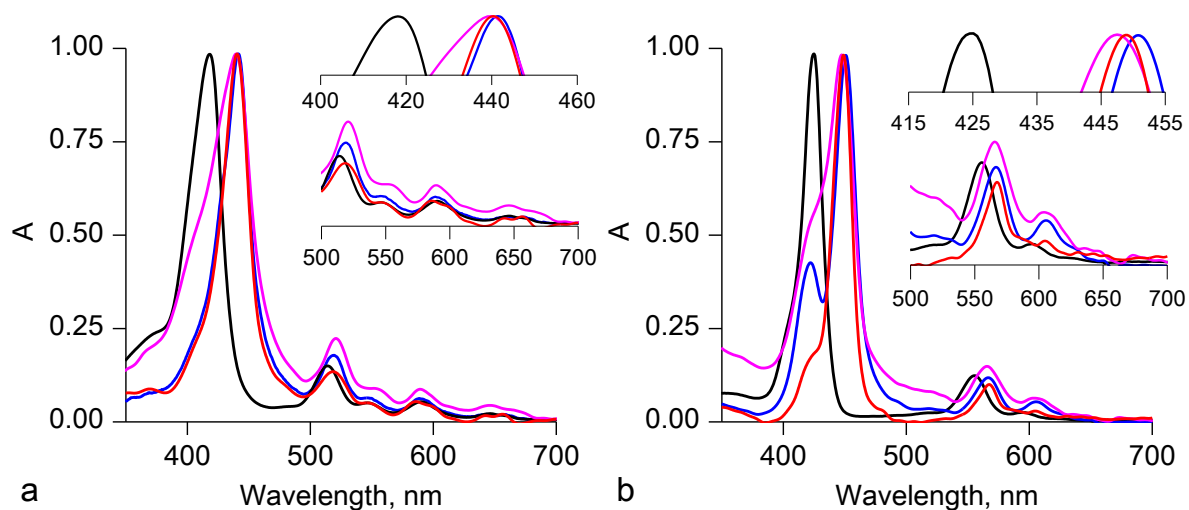


Figure S102. Normalized UV/vis spectra of porphyrins (a) **TPyP** and (b) **ZnTPyP** in chloroform solutions (black line), in the monolayer on the surface of deionized water at 0 mN m^{-1} (red line) and 25 mN m^{-1} (blue line), in 10-layered LS films (magenta line).

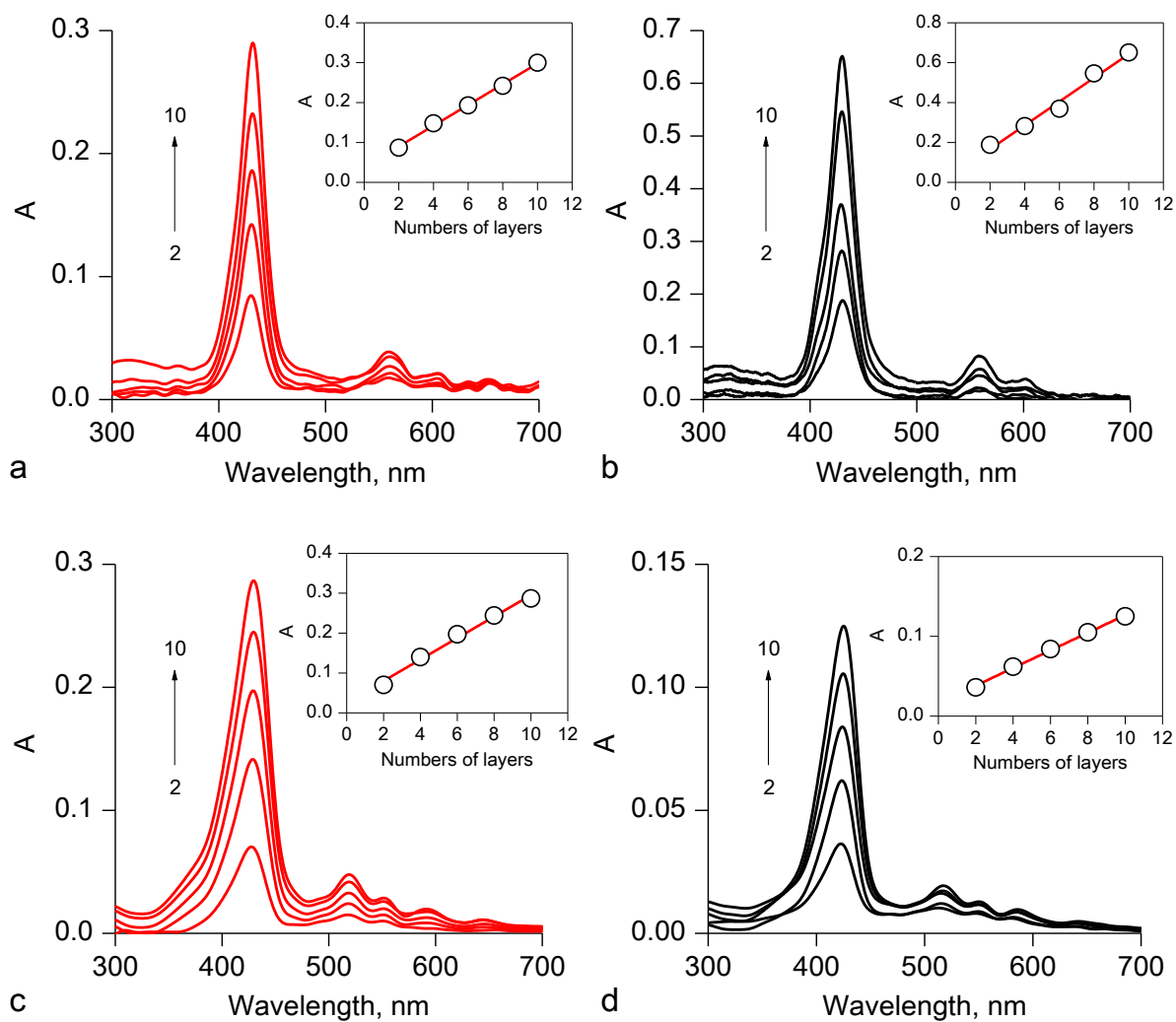


Figure S103. UV/vis spectra for LS films of (a) **3a**, (b) **3d**, (c) **2H-3a** and (d) **2H-3d**. Inset shows the dependence of the absorbance vs the number of layers in the LS films at $\lambda = 430 \text{ nm}$.

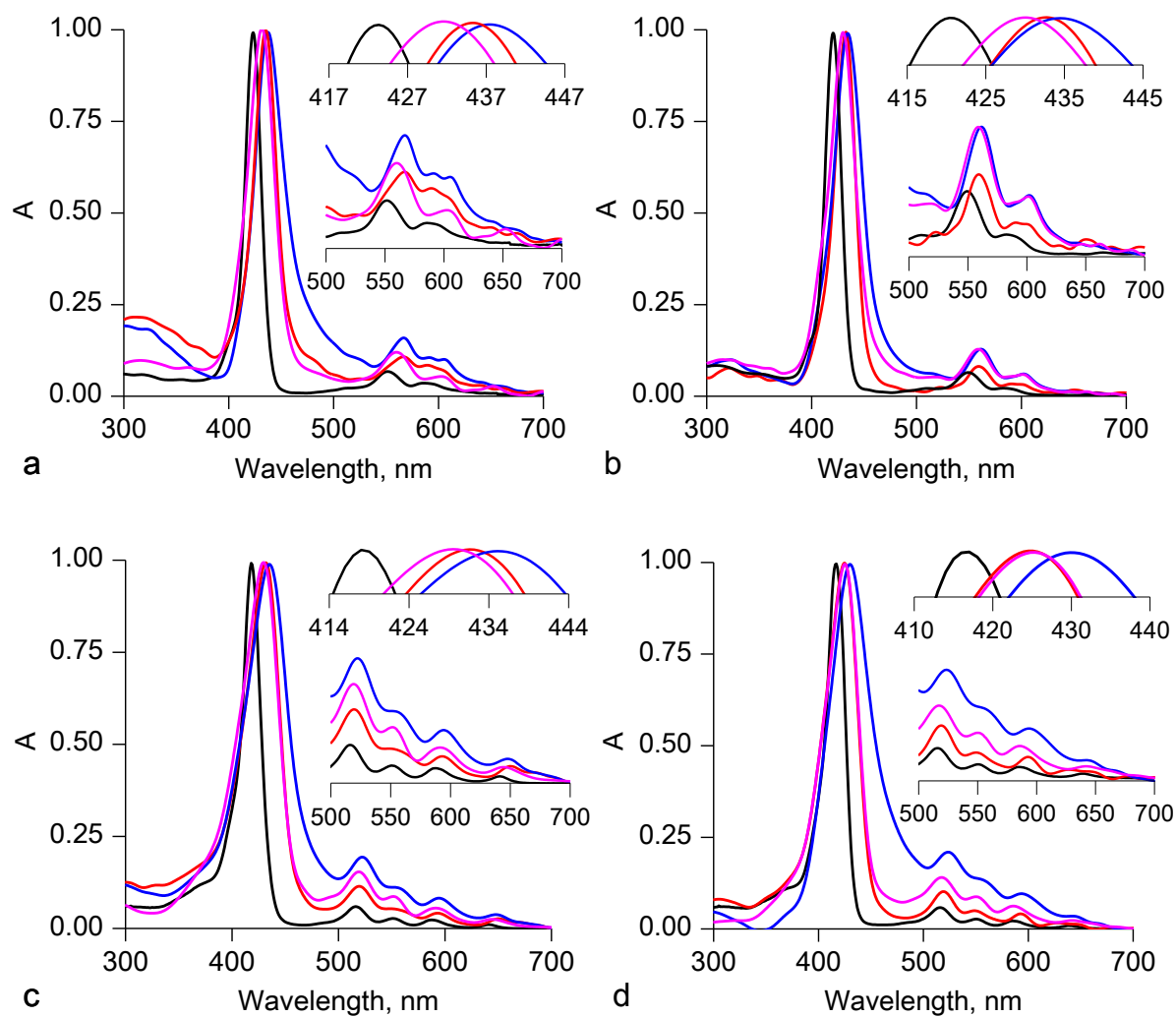


Figure S104. Normalized UV/vis spectra of porphyrins (a) **3a**, (b) **3d**, (c) **2H-3a** and (d) **2H-3d** in chloroform solutions (black line), in the monolayer on the surface of deionized water at 0 mN m⁻¹ (red line) and 25 mN m⁻¹ (blue line), in 10-layered LS films (magenta line).

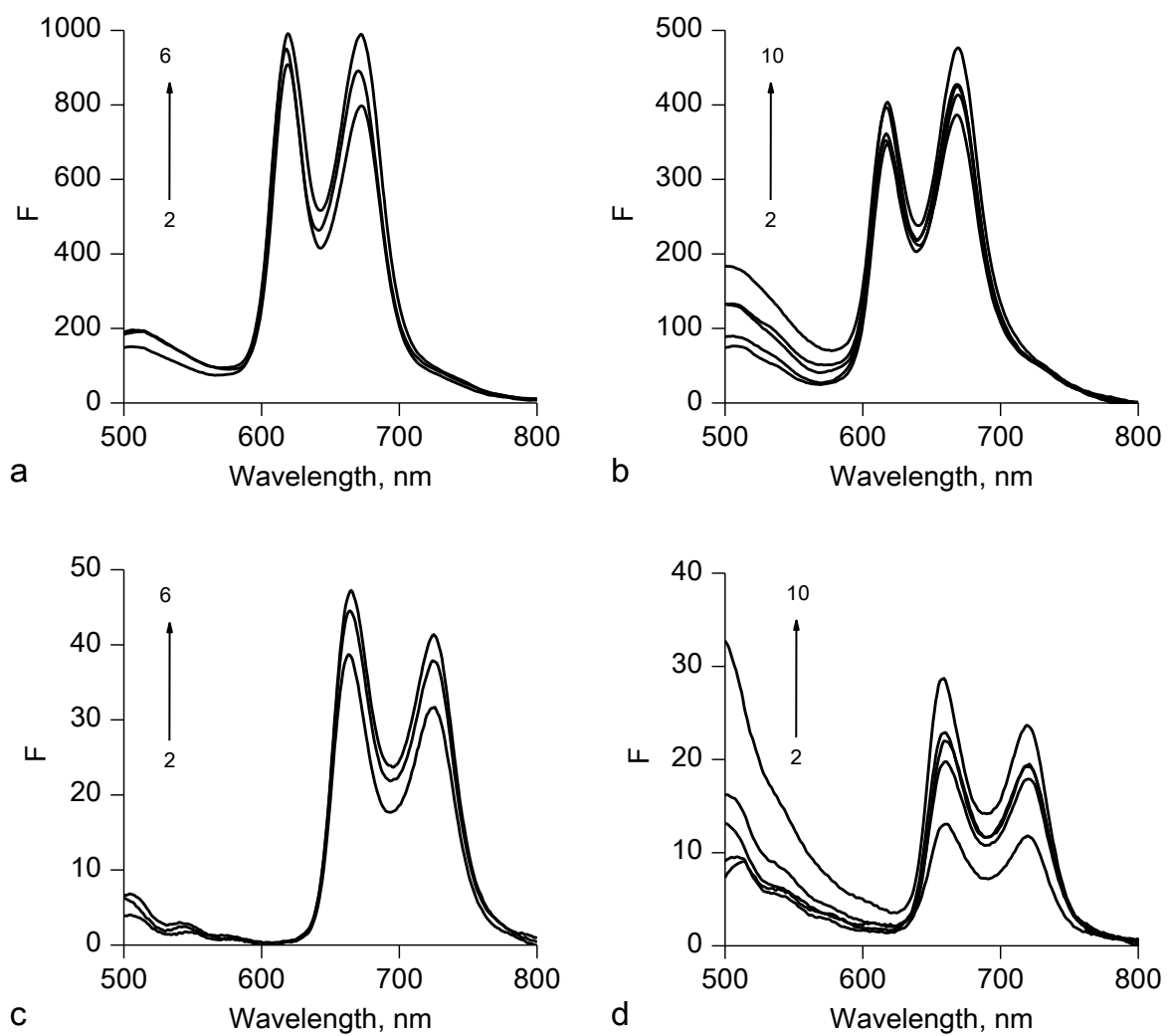


Figure S105. Fluorescence spectra for (a) **3a**, (b) **3d**, (c) **2H-3a** and (d) **2H-3d** LS films ($\lambda_{\text{ex}} = 420$ nm).

4. References

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