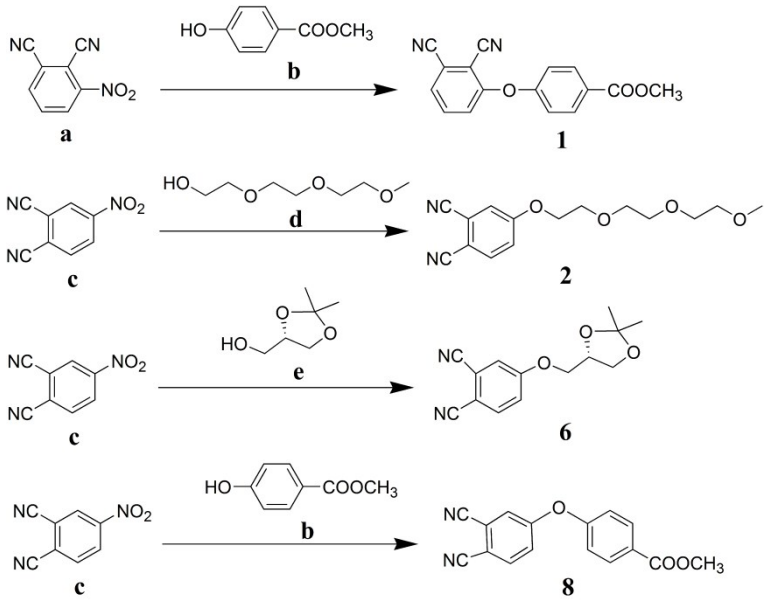
Supporting information

1. The synthesis procedure for phthalonitrile 1, 2, 6, 8 and Fmoc-Lys(tBu)-Ala-Arg(pbf)-Leu-Leu -Thr(tBu)-resin.



Scheme S1 The procedure for the synthesis of phthalonitrile 1, 2, 6, and 8.

1.1. Chemicals and materials

3-nitrophthalonitrile **a**, 4-hydroxybenzoic acid methyl ester **b**, 4-nitrophthalonitrile **c**, triethyleneglycol monomethyl ether **d** and S-(+)-2,2-dimethyl-1,3-dioxolane-4-methanol **e** were purchased from Alfa Aesar (Tianjin, China). Rink amide MBHA resin, Fmoc-Lys(tBu)-OH, Fmoc-Ala-OH, Fmoc-Arg(pbf)-OH, Fmoc-Leu-OH, Fmoc-Leu-OH, Fmoc-Thr(tBu)-OH, 1-hydroxybenzotriazole (HOBt) and O-(benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) were obtained from GL Biochem Ltd. (Shanghai, China). Solvents was purchased from J&K (Beijing, China) and used as received.

1.2. Synthesis procedure

Preparation of phthalonitrile 1. A mixture of 3-nitrophthalonitrile **a** (1.50 g, 8.66

mmol), methyl 4-hydroxybenzoate **b** (1.32 g, 8.66 mmol) and finely ground K_2CO_3 (1.80 g, 12.99 mmol) in DMF (5 mL) was stirred at room temperature for 24 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with distilled water (3 × 5 mL). The organic layer was dried over $NaSO_4$ and concentrated. The white solid was purified over a silica gel column using ethyl acetate-petroleum ether (1:1) as the eluent to afford phthalonitrile **1** (2.17 g, 90%).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 2H), 7.64 (t, J = 8.1 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.16 (dd, J = 14.9, 8.5 Hz, 3H), and 3.94 (s, 3H).

Preparation of phthalonitrile 2. A mixture of 4-nitrophthalonitrile **c** (1.5 g, 8.66 mmol), triethyleneglycol monomethyl ether **d** (2.13 g, 12.99 mmol) and finely ground K_2CO_3 (3.59 g, 25.98 mmol) in DMF (5 mL) was stirred at room temperature for 24 h. After pouring into 100 mL ice water, the resulting precipitate was isolated by filtration and purified by silica gel column with ethyl acetate–petroleum ether (1 : 1) as the eluent to afford phthalonitrile **2** (1.88 g, 75%).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.8, 4.4 Hz, 1H), 7.32 (d, J = 2.6 Hz, 1H), 7.24 (dd, J = 8.8, 2.6 Hz, 1H), 4.24 (dd, J = 5.2, 3.9 Hz, 2H), 3.90 (dd, J = 5.2, 3.9 Hz, 2H), 3.75 – 3.71 (m, 2H), 3.69 – 3.63 (m, 4H), 3.58 – 3.53 (m, 2H) and 3.39 (d, J = 2.8 Hz, 3H).

Preparation of phthalonitrile 6. A mixture of 4-nitrophthalonitrile **c** (1.5 g, 8.66 mmol), S-(+)-2,2-dimethyl-1,3-dioxolane-4-methanol **e** (1.14 mL, 8.66 mmol) and finely ground K_2CO_3 (3.59 g, 25.98 mmol) in DMF (5 mL) was stirred at 50 °C for 4 h. After pouring into 100 mL ice water, the resulting precipitate was isolated by filtration and purified by silica gel column with ethyl acetate–petroleum ether (1 : 3) as the eluent to afford phthalonitrile **6** (1.63 g, 73%).[3] ^{1}H NMR (400 MHz, CDCl3) δ 7.76 – 7.70 (m, 1H), 7.31 (d, J = 2.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 4.51 (dq, J = 11.0, 5.4 Hz, 1H), 4.19 (dd, J = 8.6, 6.5 Hz, 1H), 4.10 (qd, J = 9.7, 5.3 Hz, 2H), 3.91 (dd, J = 8.6, 5.6 Hz, 1H), 1.45 (s, 3H) and 1.40 (s, 3H).

Preparation of phthalonitrile 8. A mixture of 4-nitrophthalonitrile **c** (1.50 g, 8.66 mmol), methyl 4-hydroxybenzoate **b** (1.32 g, 8.66 mmol) and finely ground K_2CO_3 (1.80 g, 12.99 mmol) in DMF (5 mL) was stirred at room temperature for 24 h. The

reaction mixture was diluted with ethyl acetate (50 mL) and washed with distilled water (3 × 5 mL). The organic layer was dried over $NaSO_4$ and concentrated. The white solid was purified over a silica gel column using ethyl acetate-petroleum ether (1:1) as the eluent to afford phthalonitrile **8** (2.22 g, 92%).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 8.6 Hz, 1H), 7.35 (s, 1H), 7.30 (d, J = 8.7 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H) and 3.95 (s, 3H).

Synthesis of Fmoc-Lys(tBu)-Ala-Arg(pbf)-Leu-Leu-Thr(tBu)-resin. The peptide Leu-Ala-Arg-Leu-Leu-Thr with side chain protected was synthesized manually using a solid-phase peptide synthesis (SPPS) protocol. The Rink amide MBHA resin was immersed in DMF for 2 h to be activated. The first amino acid was coupled on the resin by adding HBTU (3 eq) and DIEA (4 eq) for 4 h in room temperature. Then, the resin was washed with DMF three times. A solution of 20% piperidine in DMF was added to remove the Fmoc protecting groups and HBTU was used to activate the carboxyl groups. Every amino acid was coupled on the resin in this way. After the final coupling, the Fmoc groups were retained, and the resin was washed with DMF and dried under vacuum. The dried resin containing the protected peptide sequence was used in the coupling reaction to the Pcs.

(1) H. Wang, D. Zhang, D. Sun, Y. Chen, L.-F Zhang, L. Tian, J. Jiang and Z.-H. Ni, *Crystal Growth Design Article*, 2009, **9**, 5273-5282.

(2) A. C. H. Ng, X. Y. Li, D. K. P. Ng, *Macromolecules*, 1999, **32**, 5292–5298.

(3) F. B. Nascimento, T. M. Manieri, G. Cerchiaro, A. O. Ribeiro, *Dyes Pigments*, 2013, **99**, 316-322.

2. HPLC chromatogram for the synthesized Pcs

HPLC was performed using a 150 × 4.6 mm, C-18 column, with a 0.6 mL/min flow rate at λ= 680 nm. The column was initially held at 20% CH_3CN (0.14% TFA) - 100% H_2O (0.14% TFA). The concentration of CH_3CN was ramped to 60% in 10 min and then to 100% in 35 min; this was maintained 5 min. The column was washed with 95% CH_3CN for 15 min and allowed to equilibrate at the initial mobile phase conditions for 15 min before the next injection.

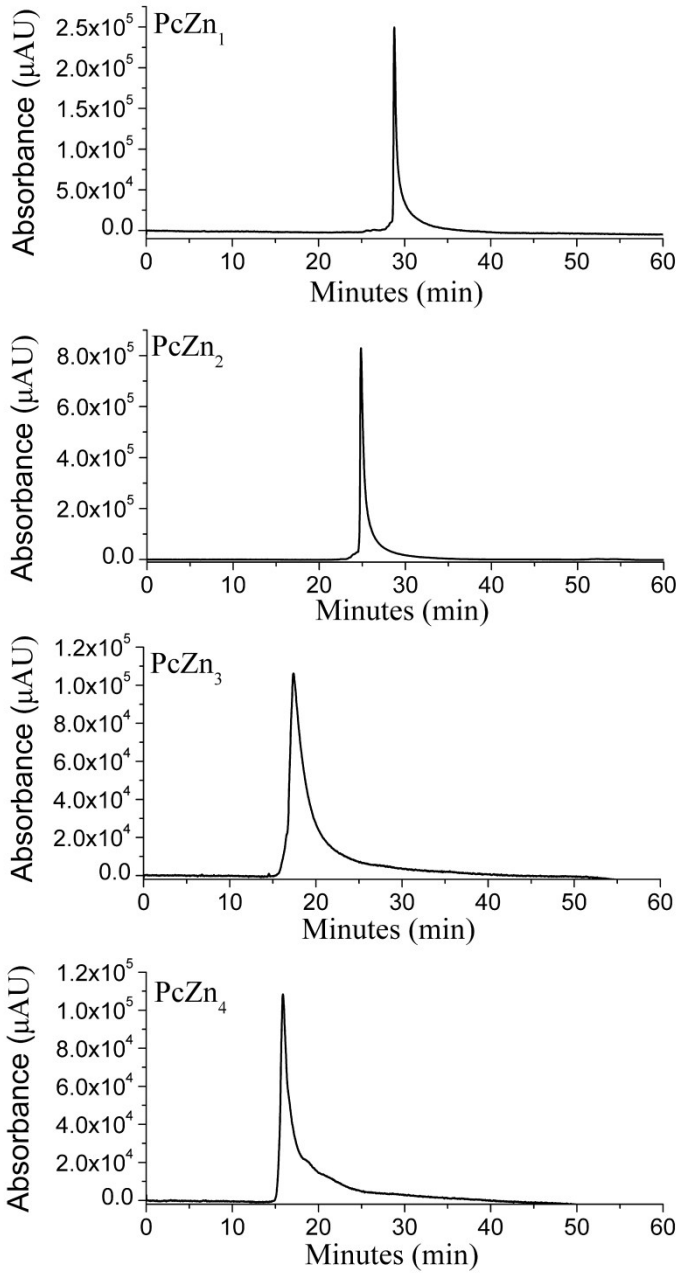


Fig. S1 HPLC trace of the Pcs. Wavelength for detection: 680 nm. $PcZn_1$ (t_R = 28.8 min), $PcZn_2$ (t_R = 24.8 min), $PcZn_3$ (t_R = 17.4 min) and $PcZn_4$ (t_R = 15.9 min).

3. Absorbance spectra in DMSO

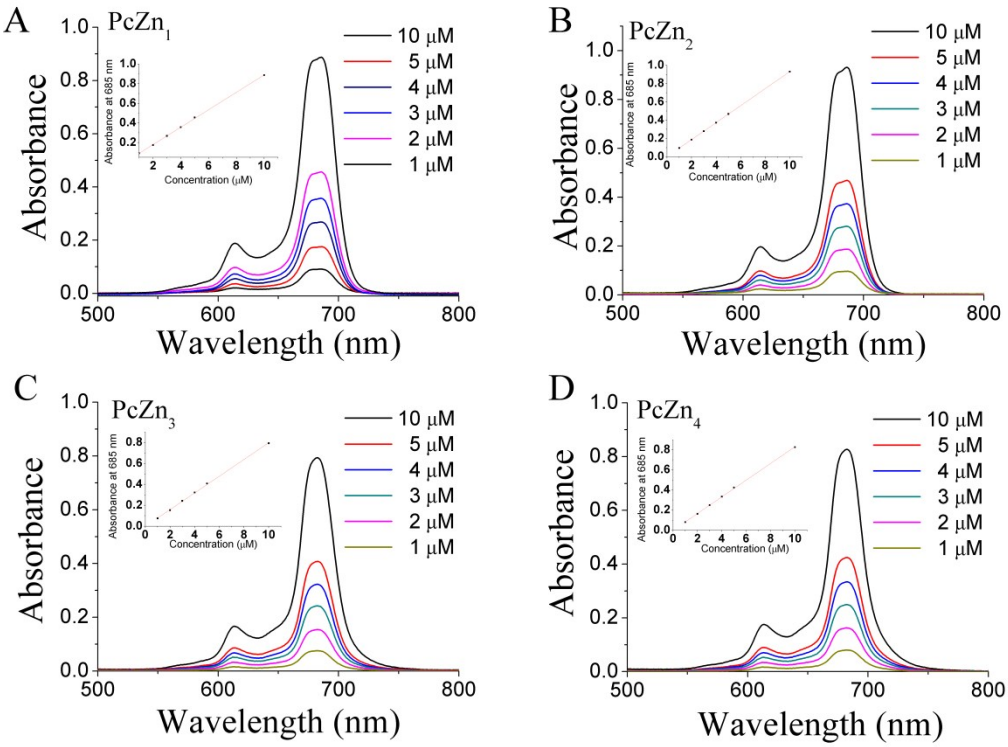


Fig. S2 Absorbance spectra of $PcZn_1$ (A), $PcZn_2$ (B), $PcZn_3$ (C), and $PcZn_4$ (D) at various concentrations in DMSO. The insets show plots of the intensity at 685 nm versus the concentration of the corresponding compound.

4. Fluorescence spectra in DMSO

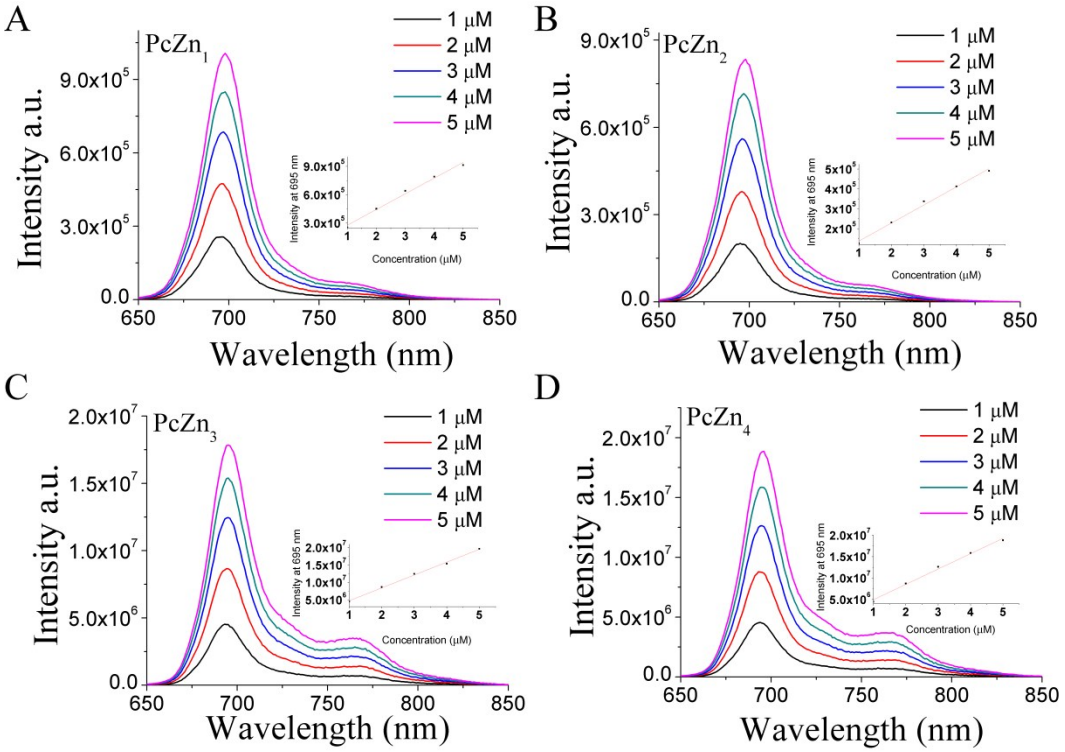


Fig. S3 Fluorescence emission spectra of $PcZn_1$ (A), $PcZn_2$ (B), $PcZn_3$ (C), and $PcZn_4$ (D) at various concentrations in DMSO. The insets show plots of the intensity at 695 nm versus the concentration of the corresponding compound.

5. Fluorescence lifetimes

Fluorescence lifetime (τ_F) refers to the average time a molecule remains in its excited state before returning to its ground state, and its value is directly related to that of Φ_F. The longer the lifetime, the higher the quantum yield of fluorescence. The fluorescence lifetimes of the Pcs in DMSO were measured directly using a fluorescence spectrometer.

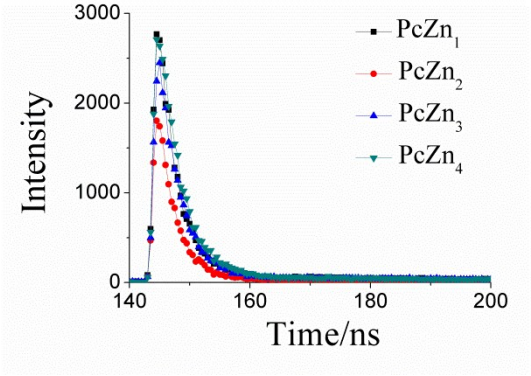


Fig. S4 Fluorescence decay curves of the Pcs. $PcZn_1$: 3.12 ns, $PcZn_2$: 3.87 ns, $PcZn_3$: 3.05 ns, and $PcZn_4$: 3.13 ns.

6. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) give an indication of the efficiency of potential photosensitizers in applications where singlet oxygen is required. The Φ_Δ values were determined using a chemical method (1,3-diphenylisobenzofuran (DPBF) in DMSO). The disappearance of DPBF was monitored using a UV-vis spectrophotometer.

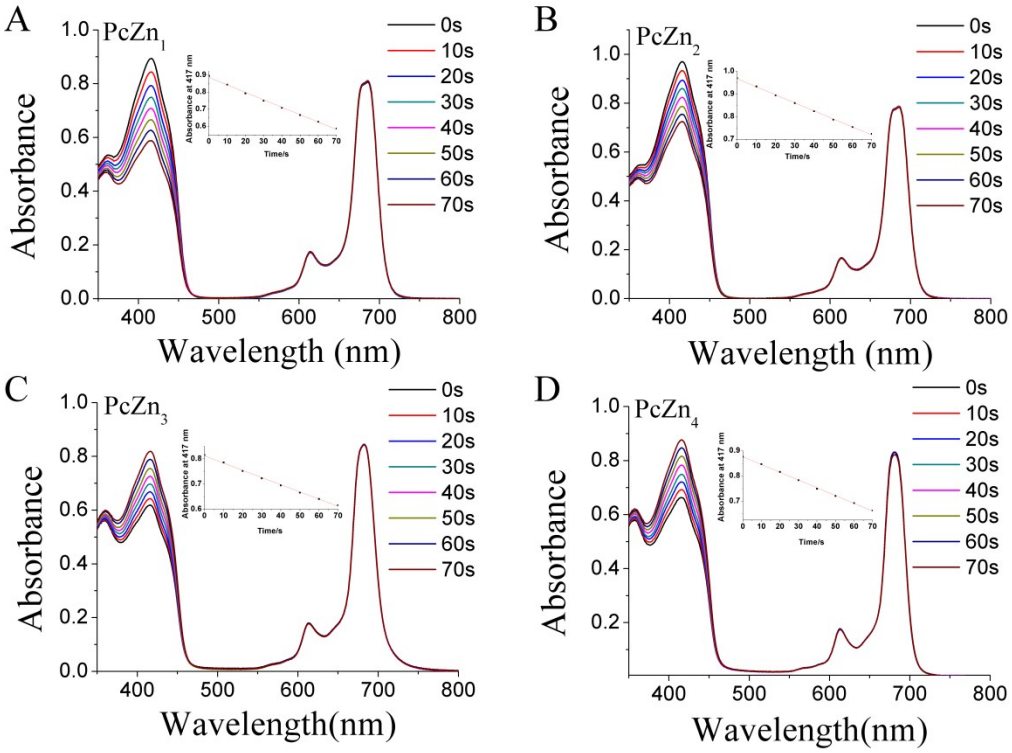


Fig. S5. A typical spectra for the determination of the singlet oxygen quantum yield of $PcZn_1$ (A), $PcZn_2$ (B), $PcZn_3$ (C) and $PcZn_4$ (D) in DMSO using DPBF as a singlet oxygen quencher. Concentration = 10 μM. The insets show plots of DPBF absorbance vs. time.

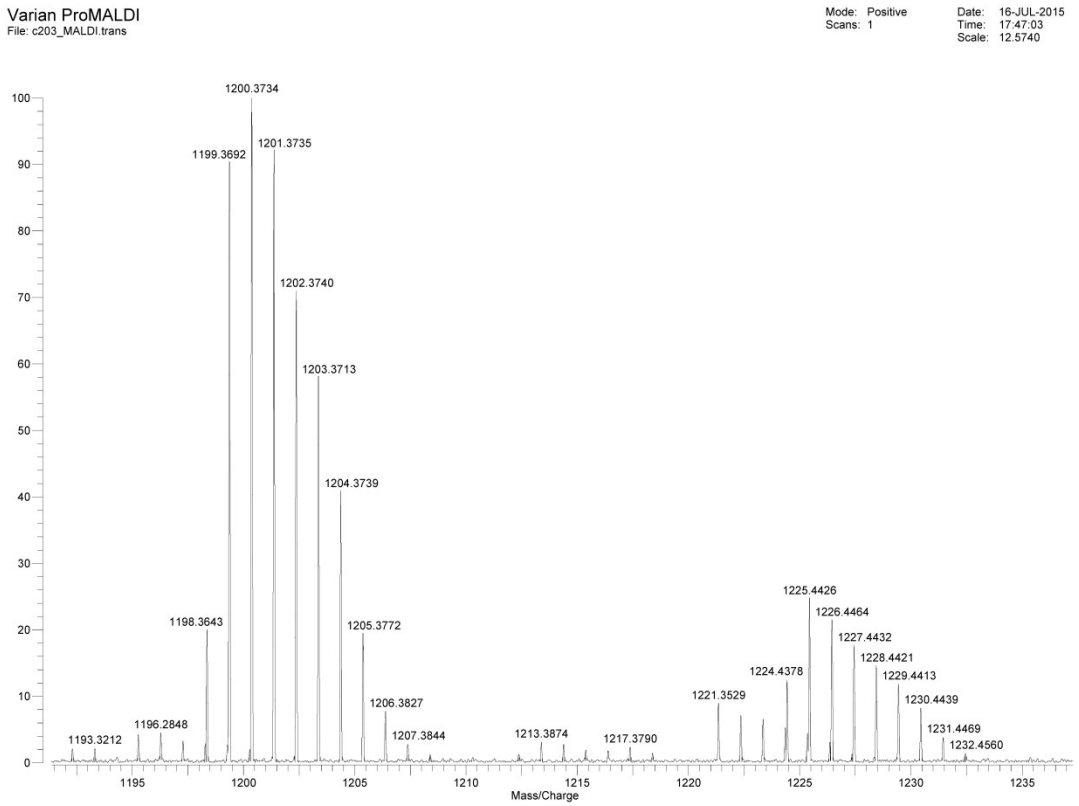


Fig. S6 $PcZn_1$ (ESI-HRMS calcd for $C_{60}H_{62}N_8O_{15}Zn$ $[M+H]^+$ 1199.3699, found 1199.3692; calcd for $C_{60}H_{62}N_8NaO_{15}Zn$ $[M+Na]^+$ 1221.3518, found: 1221.3529).

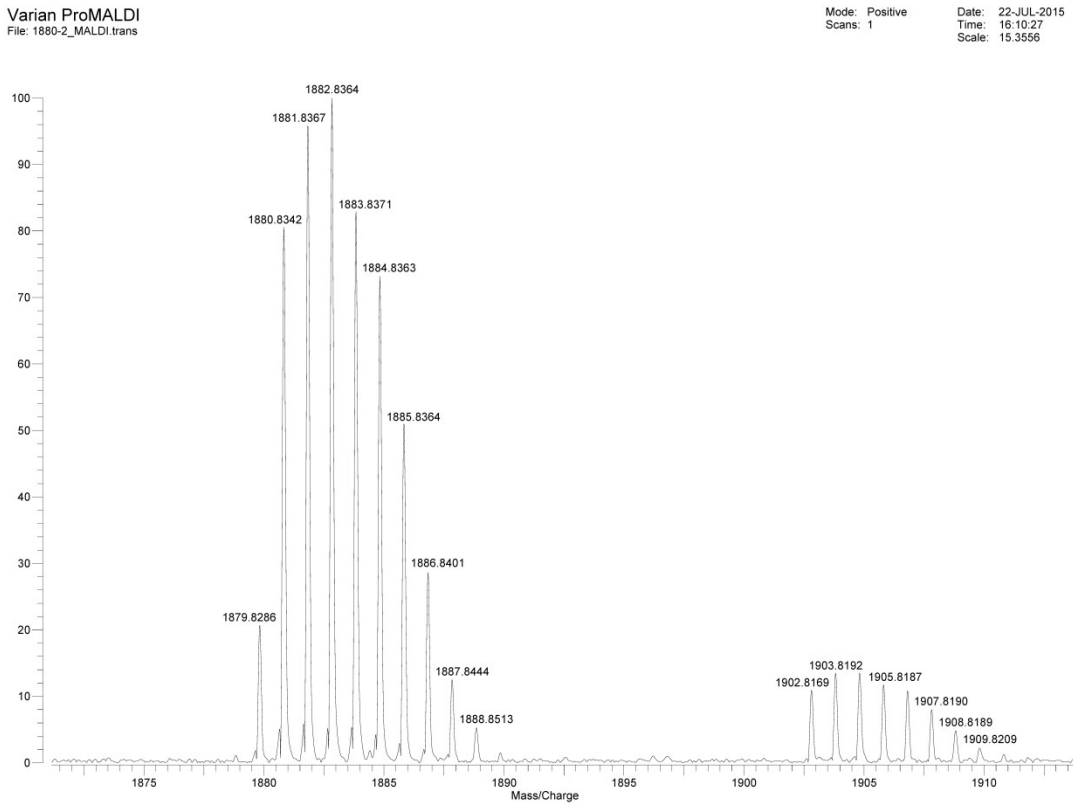


Fig. S7 $PcZn_2$ (ESI-HRMS calcd for $C_{91}H_{121}N_{19}O_{21}Zn$ $[M+H]^+$1880.8349, found 1880.8342, calcd for $C_{91}H_{121}N_{19}NaO_{21}Zn^+$ $[M+Na]^+$1902.8168, found: 1902.8169).

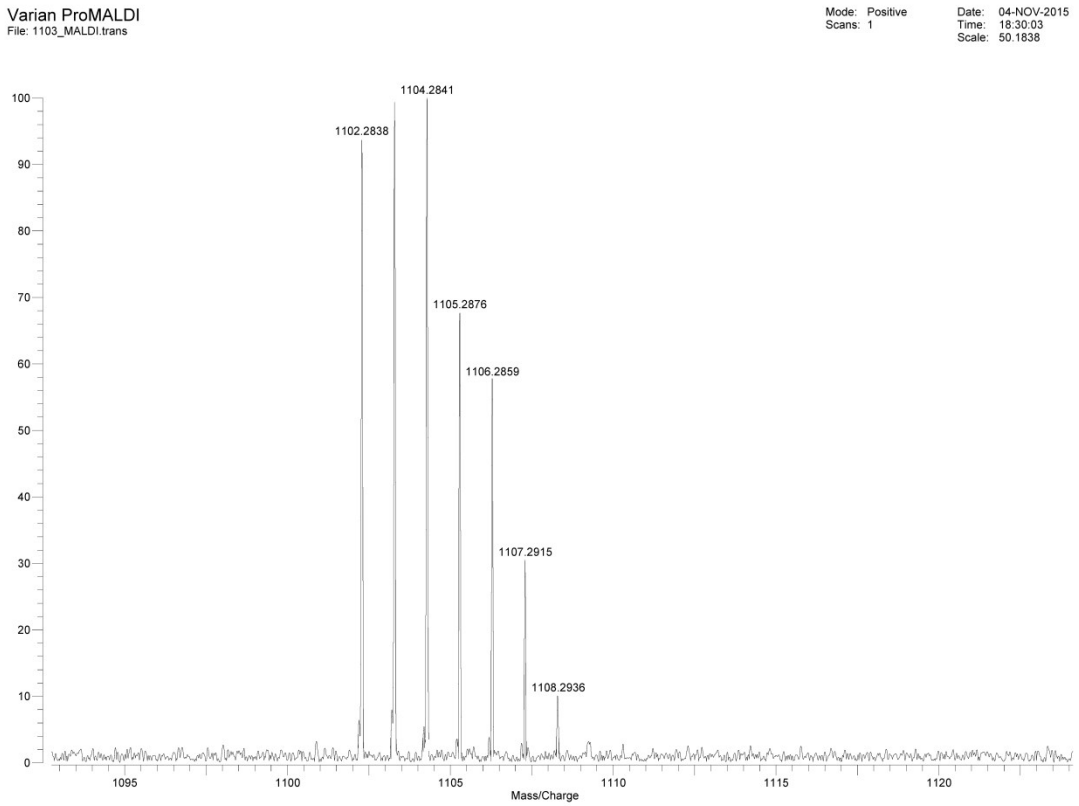


Fig. S8 Compound **9** (ESI-HRMS calcd for $C_{57}H_{50}N_8O_{12}Zn$ 1102.2840, found 1102.2838).

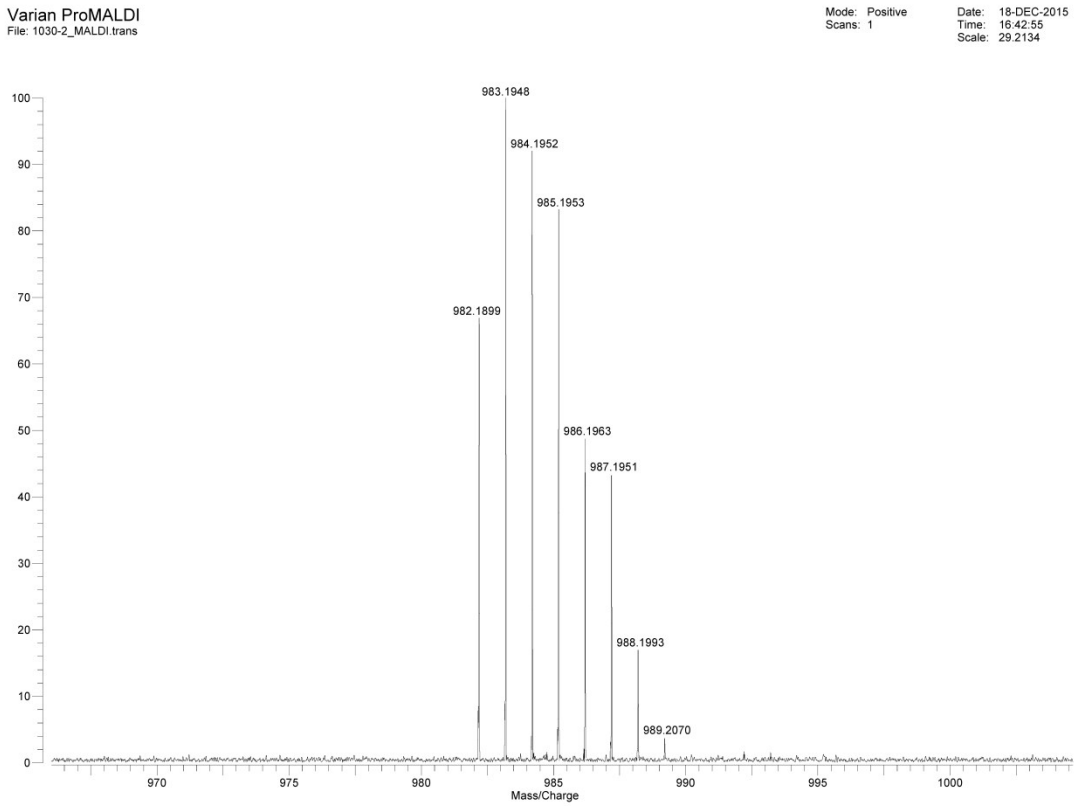


Fig. S9 $PcZn_3$ (ESI-HRMS calcd for $C_{48}H_{38}N_8O_{12}Zn$ $[M+H]^+$ 983.1973, found 983.1948).

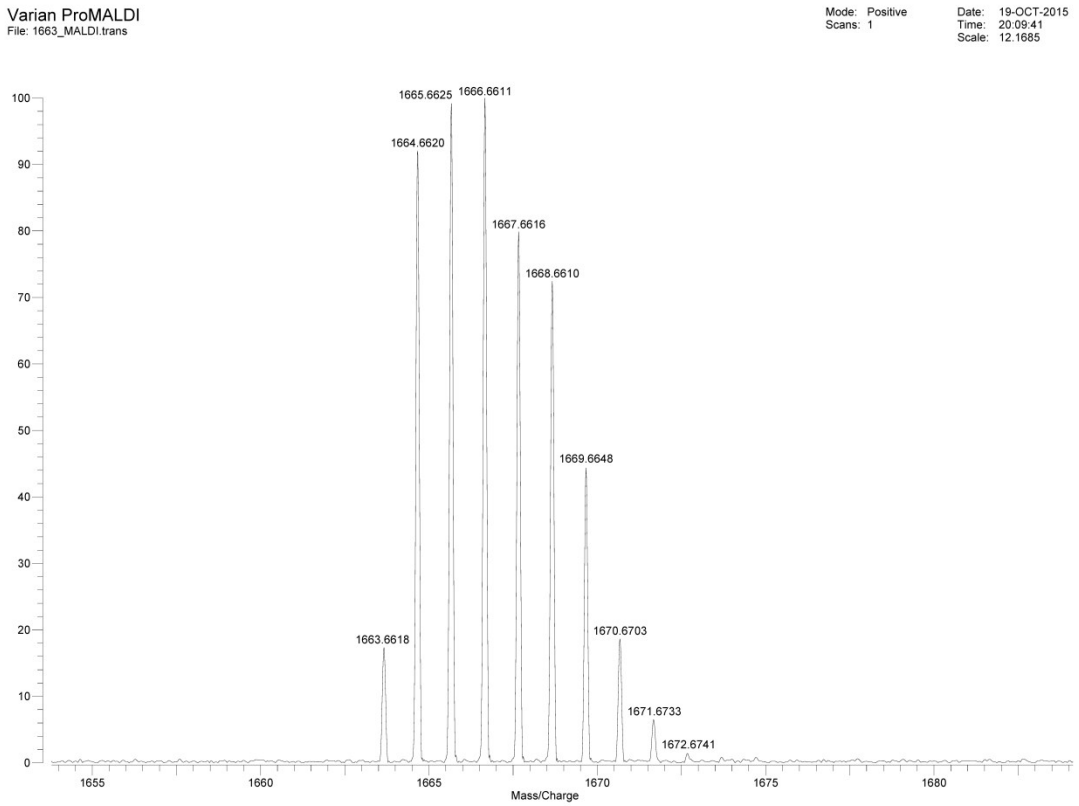
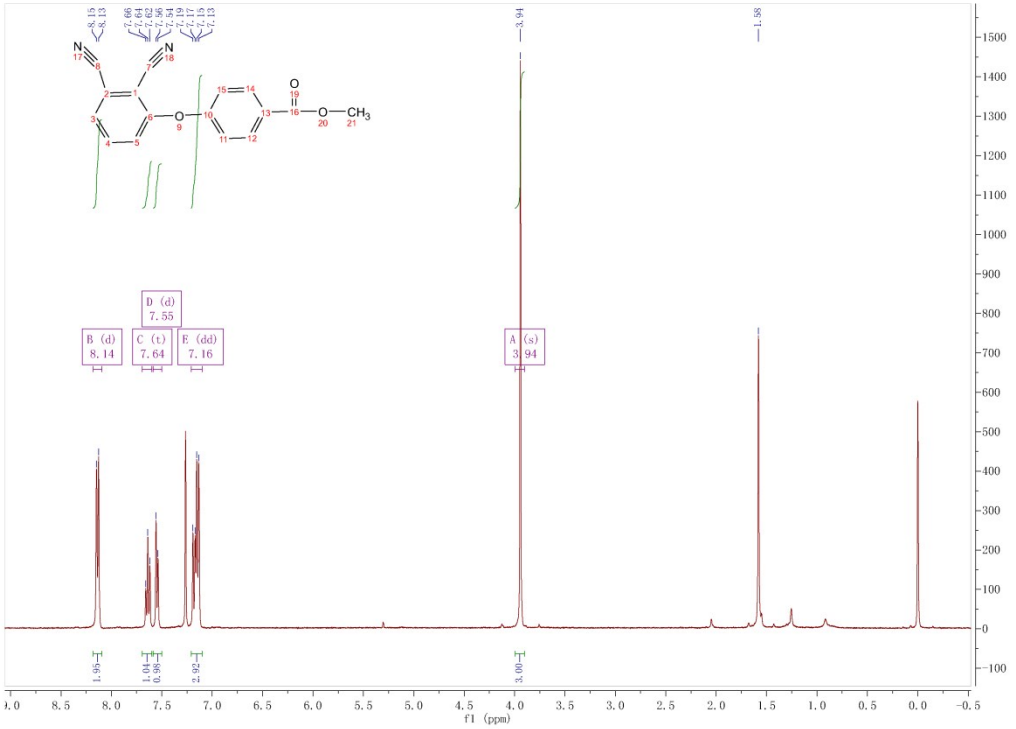
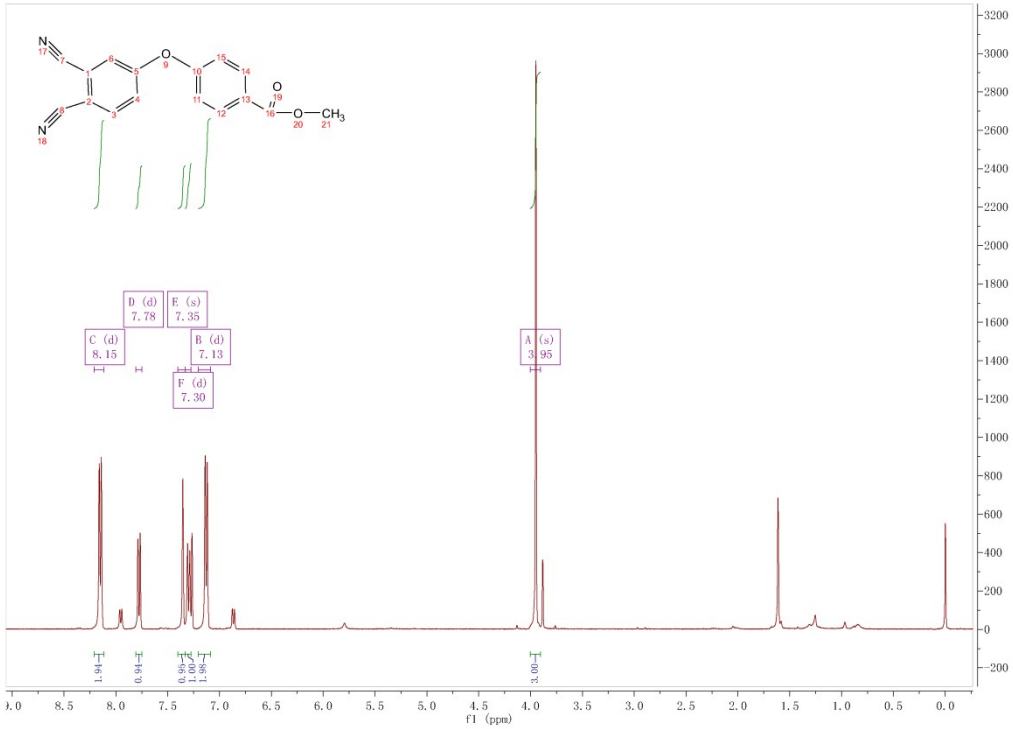
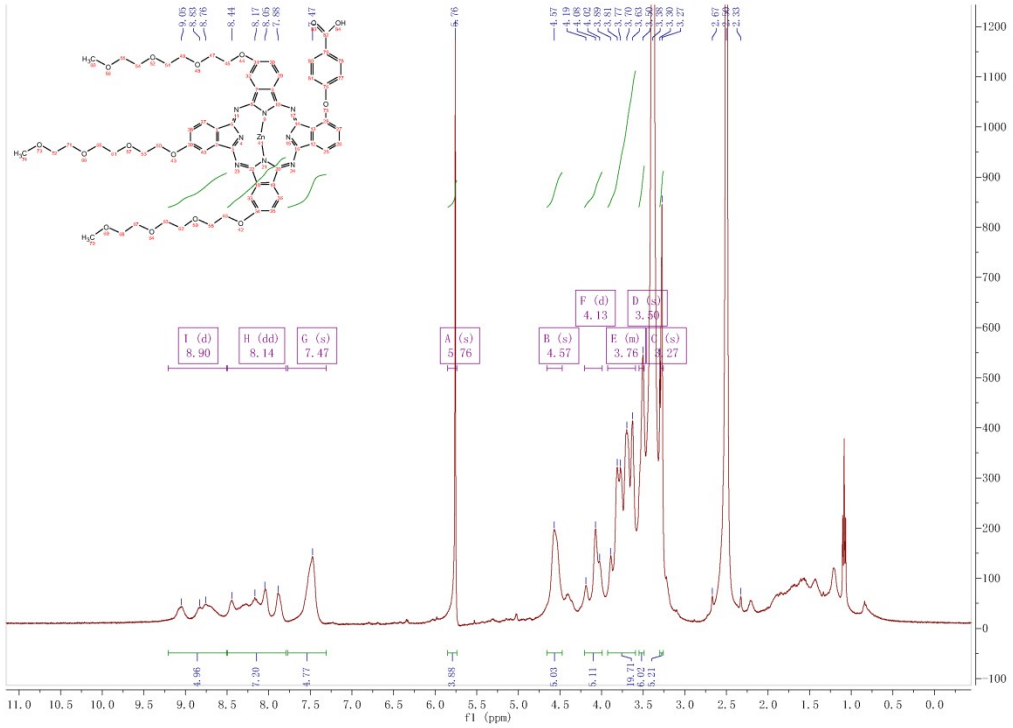
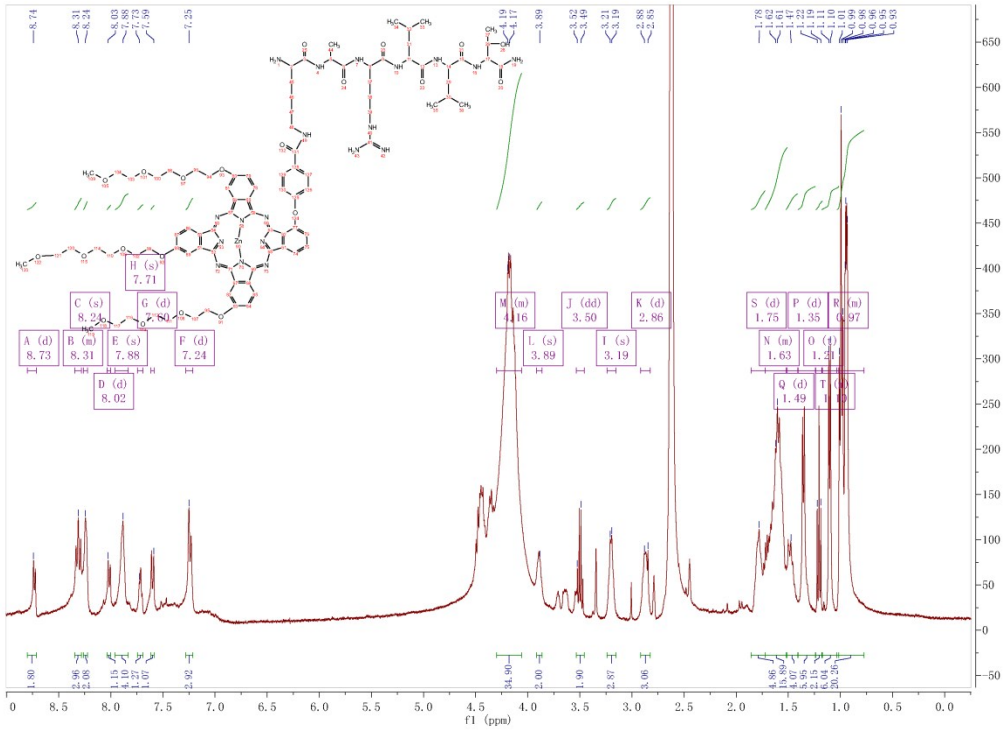


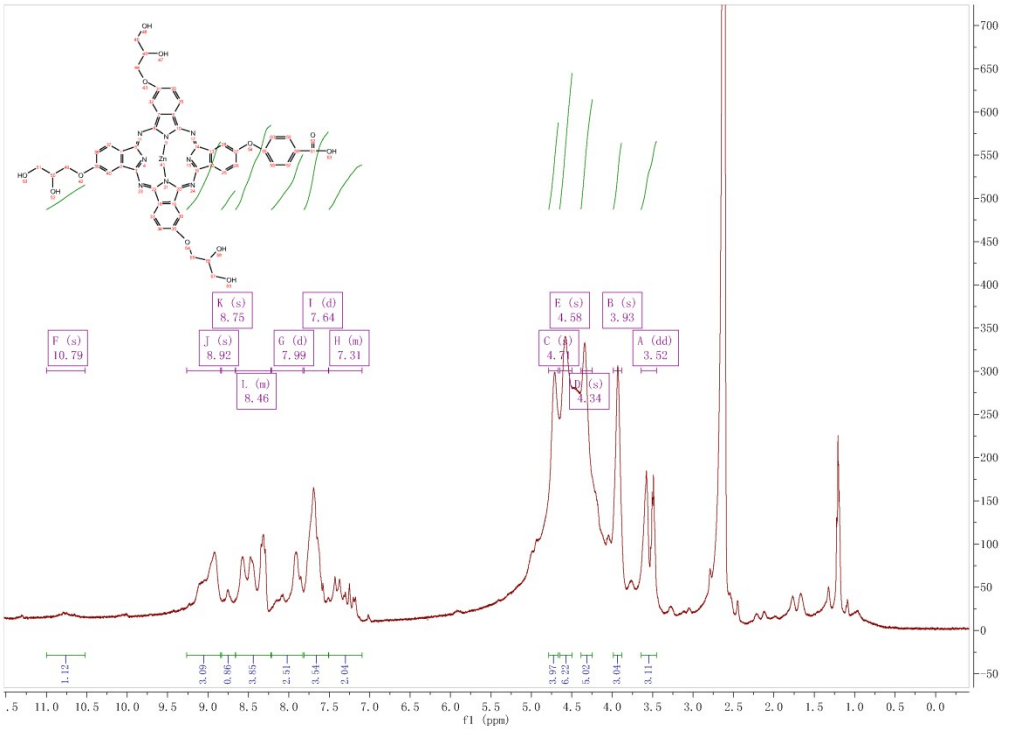
Fig. S10 $PcZn_4$ (ESI-HRMS calcd for $C_{79}H_{97}N_{19}O_{18}Zn$ $[M+H]^+$ 1664.6623, found 1664.6620).

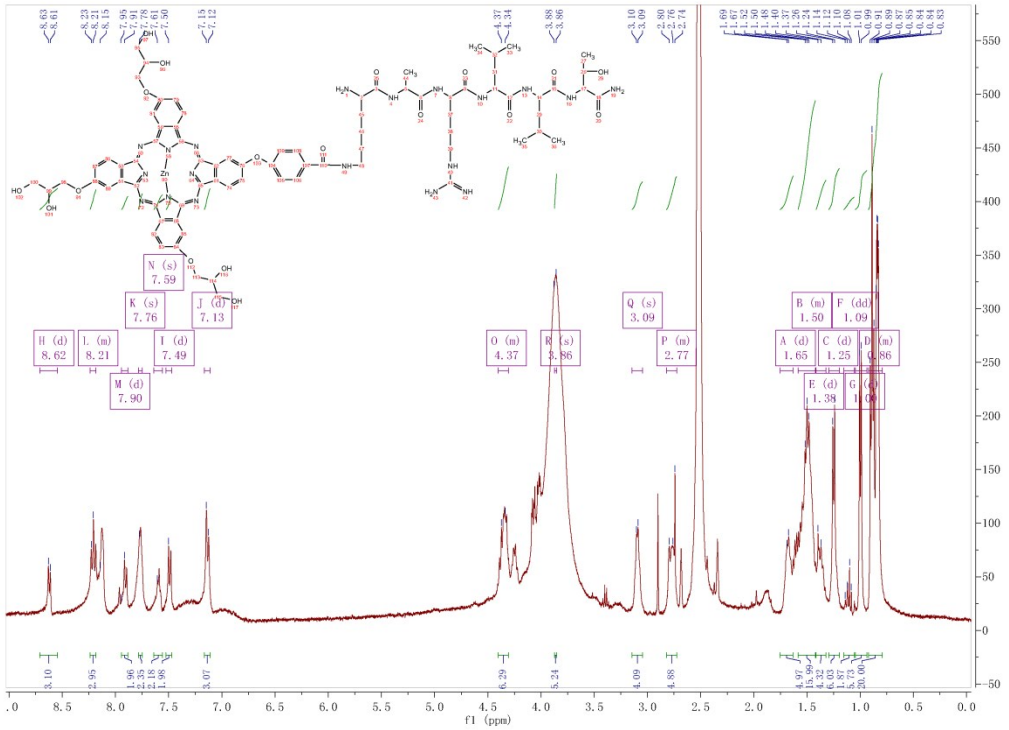

8.15
8.13
7.66
7.64
7.62
7.56
7.54
7.19
7.17
7.15
7.13
3.94
1.58
N
N
O
O
O
CH3
D (d)
7.55
B (d)
8.14
C (t)
7.64
E (dd)
7.16
A (s)
3.94
1.99
1.04
0.98
2.92
3.00
f1 (ppm)


D (d)
7.78
E (s)
7.35
C (d)
8.15
B (d)
7.13
F (d)
7.30
A (s)
3.95
1.94
0.94
0.95
1.00
1.98
3.00
f1 (ppm)


I (d) 8.90
H (dd) 8.14
G (s) 7.47
A (s) 5.76
B (s) 4.57
F (d) 4.13
E (m) 3.76
D (s) 3.50
C (s) 3.27
f1 (ppm)


A (d) 8.73
B (m) 8.31
C (s) 8.24
D (d) 8.02
E (s) 7.88
F (d) 7.24
G (d) 7.80
H (s) 7.71
I (s) 3.19
J (dd) 3.50
K (d) 2.86
L (s) 3.89
M (m) 4.16
N (m) 1.63
O (t) 1.24
P (d) 1.35
Q (d) 1.49
R (m) 0.97
f1 (ppm)


F (s) 10.79
K (s) 8.75
J (s) 8.92
L (m) 8.46
I (d) 7.64
G (d) 7.99
H (m) 7.31
E (s) 4.58
B (s) 3.93
C (d) 4.71
D (s) 4.34
A (dd) 3.52
1.12
3.09
0.86
3.85
2.51
3.94
2.04
3.97
6.22
5.02
3.04
3.11
f1 (ppm)


f1 (ppm)