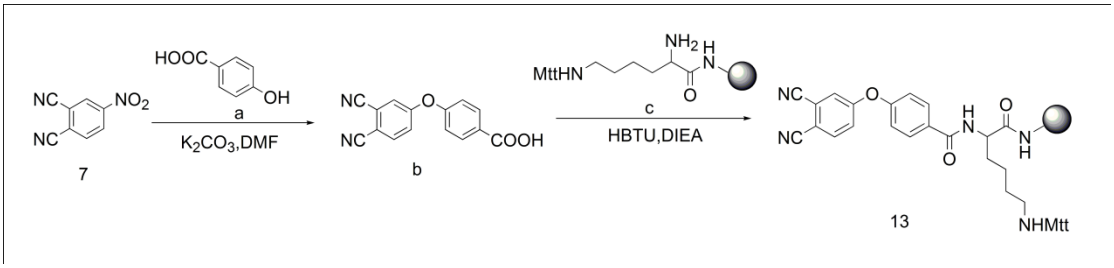
Supporting information

1. The synthesis procedure for resin-bound phthalonitrile 13.



Scheme S1. The procedure for the synthesis of resin-bound phthalonitrile **13.**

1.1. Chemicals and materials

Rink Amide MBHA Resin, Fmoc-lys(Mtt)-OH, 1-hydroxybenzotriazole (HOBt) and O-(benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) were obtained from GL Biochem Ltd. (Shanghai, China). Other chemical agents were from Alfa Aesar (Tianjin, China).

1.2. Synthesis procedure

Preparation of compound b. To a solution of 4-hydroxybenzoic acid (0.83 g, 6.0 mmol) in anhydrous DMSO (10 mL), 4- nitrophthalonitrile (1.0 g, 6.0 mmol) and finely ground K_2CO_3 (1.8 g, 12 mmol) were added. The mixture was stirred at room temperature for 18 h. As the reaction proceeded, a light yellow precipitate formed. The crude mixture was solidified by pouring into 400 mL of ice-water and the precipitate was collected by filtration. The crude mixture was dissolved in CH_3OH (~10 mL) and neutralized by a 1 N HCl solution. The light yellow colored precipitate was collected by filtration and was further washed with water to produce the product (1.26 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.18 (m, 2H, Ar-H), 7.79 (d, J = 8.7 Hz, 1H, Ar-H), 7.38 (d, J = 2.5 Hz, 1H, Ar-H), 7.33 (dd, J = 8.7, 2.5 Hz, 1H, Ar-H), 7.20 - 7.13 (m, 2H, Ar-H).

Preparation of resin c. Rink Amide MBHA resin (0.50 g) with 0.5 mmol/g loading capacity was swelled in DCM (20 mL) for 30 min. The solvent was filtered off and Fmoc was removed with 20% piperidine in DMF (10 mL) by agitating for 30 min. The resin was then washed with DMF (5 × 8.0 mL). Fmoc-Lys(Mtt)-OH (0.038 mmol, 23 mg), HOBt (0.038 mmol, 5.0 mg), HBTU (0.038 mmol, 14 mg) and diisopropylethyl amine (DIEA) (0.075 mmol, 13 μL) were dissolved in DMF/DCM (10 mL, 1:9) and added to the resin. The reaction mixture was shaken at room temperature for 1 h and then washed with DMF (3 × 10 mL). The non-reacted amine group was blocked with Ac_2O (1 mL) in 10 mL of DMF, and the Fmoc group was removed with 20% piperidine in DMF (10 mL) for 30 min to afford resin **c** after washing with DMF (5 × 8.0 mL).

Preparation of resin-bound phthalonitrile 13. Resin **c** (0.50 g) with 0.075 mmol/g Fmoc-Lys-(Mtt)-OH loading was suspended in DMF (10 mL). HOBt (0.19 mmol, 25 mg), HBTU (0.19 mmol, 71 mg), DIEA (0.38 mmol, 64 μL) and carboxylated phthalonitrile b (0.19 mmol, 47 mg) were dissolved in DMF (1.0 mL) and added to the resin **c.** The reaction mixture was shaken at room temperature for 2 h, followed by washing with DMF to afford resin-bound phthalonitrile **13**.

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) - 80% H_2O (0.14% TFA). The concentration of CH_3CN was ramped to 60% in 10 min and then to 80% in 40 min. The column was washed with 95% CH_3CN for 15 min and allowed to equilibrate at the initial mobile phase conditions for 60 min before the next injection.

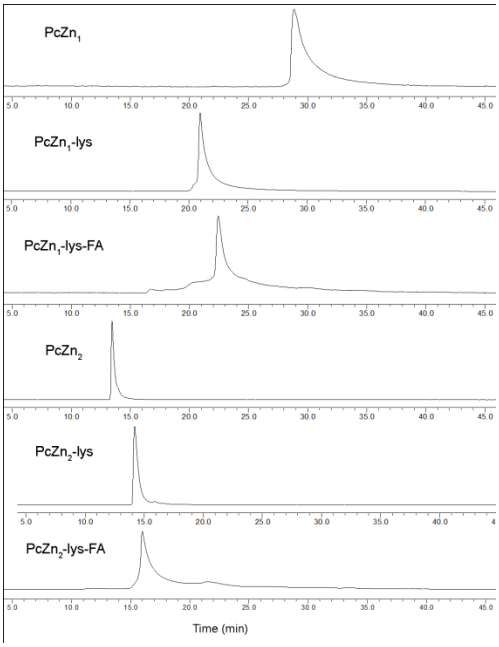


Fig. S1. HPLC trace of Pc **1-6**. Wavelength for detection: 680 nm. $PcZn_1$ (t_R=28.8 min), $PcZn_1$-lys (t_R =20.9 min), $PcZn_1$-lys-FA (t_R = 22.6 min), $PcZn_2$ (t_R =13.4 min), $PcZn_2$-lys (t_R =14.2 min), $PcZn_2$-lys-FA (t_R = 16.1 min).

3. Fluorescence spectra in DMSO

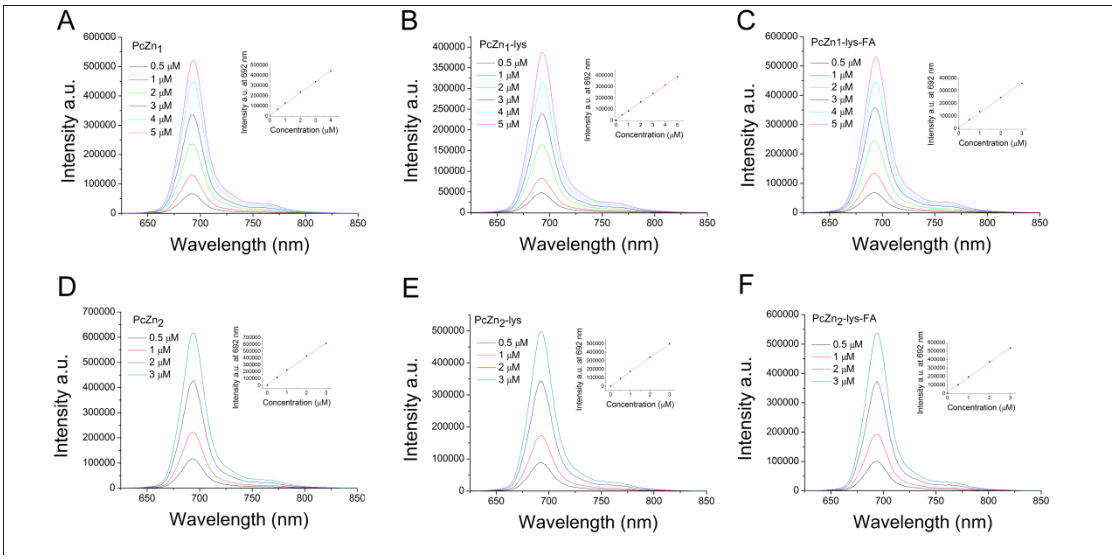


Fig. S2. Fluorescence emission spectra of $PcZn_1$ (A), $PcZn_1$-lys (B), $PcZn_1$-lys-FA (C), $PcZn_2$ (D), $PcZn_2$-lys (E) and $PcZn_2$-lys-FA (F) at various concentrations in DMSO. The inset plots the intensity at 692 nm versus the concentration of the corresponding compound.

4. Fluorescence lifetimes：

Fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before returning to the 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 lifetime of Pc **1-6** in DMSO was measured directly by fluorescence spectrometer.

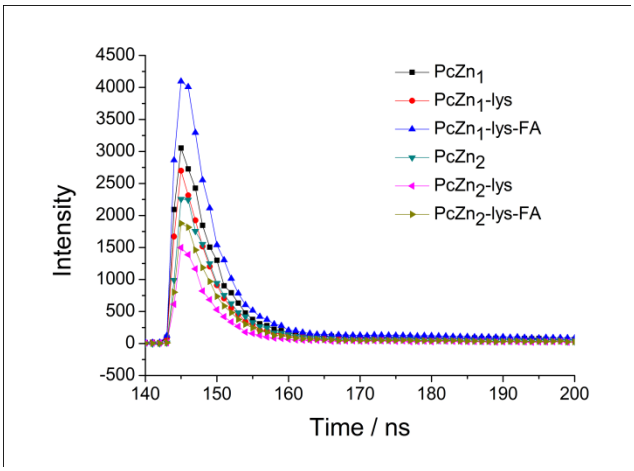


Fig. S3. Fluorescence decay curve of compound **1-6**. $PcZn_1$: 3.33 ns, $PcZn_1$-lys: 3.20 ns, $PcZn_1$-lys-FA: 3.06 ns, $PcZn_2$: 3.73 ns, $PcZn_2$-lys: 3.19 ns, $PcZn_2$-lys-FA: 3.49 ns.

5. Singlet oxygen quantum yields

The singlet oxygen quantum yields (Φ_Δ) give an indication of the efficiency of the 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.

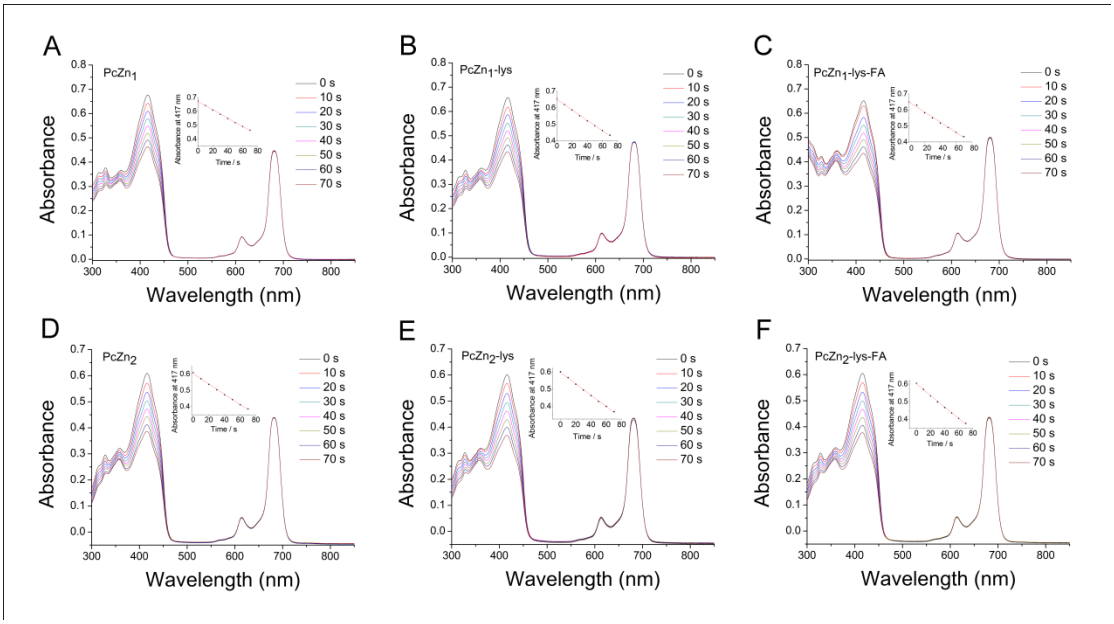


Fig. S4. A typical spectrum for the determination of the singlet oxygen quantum yield of $PcZn_1$ (A), $PcZn_1$-lys (B), $PcZn_1$-lys-FA (C), $PcZn_2$ (D), $PcZn_2$-lys (E) and $PcZn_2$-lys-FA (F) in DMSO using DPBF as a singlet oxygen quencher. Concentration = 4×10^{-6} M. Inset: Plots of DPBF absorbance vs. time.

Table S2. The absorbance and consumption rate of DPBF for $PcZn_1$ (1), $PcZn_1$-lys (2), $PcZn_1$-lys-FA (3), $PcZn_2$ (4), $PcZn_2$-lys (5) and $PcZn_2$-lys-FA (6) in DMSO. Non-substituted PcZn was used for reference. $A_{680\ nm}$: absorbance at 680 nm; R_{DPBF}/s^{-1}: the consumption rate of DPBF (Initial concentration: 2.5×10^{-5} mol/L).

	PcZn	**1**	**2**	**3**	**4**	**5**	**6**
$A_{680\ nm}$	0.26	0.45	0.44	0.47	0.43	0.50	0.43
R_{DPBF}/s^{-1} (10^{-3})	-2.86	-3.04	-3.18	-3.17	-3.34	-3.18	-3.26

7. Absorption and fluorescence spectra of non-substituted PcZn

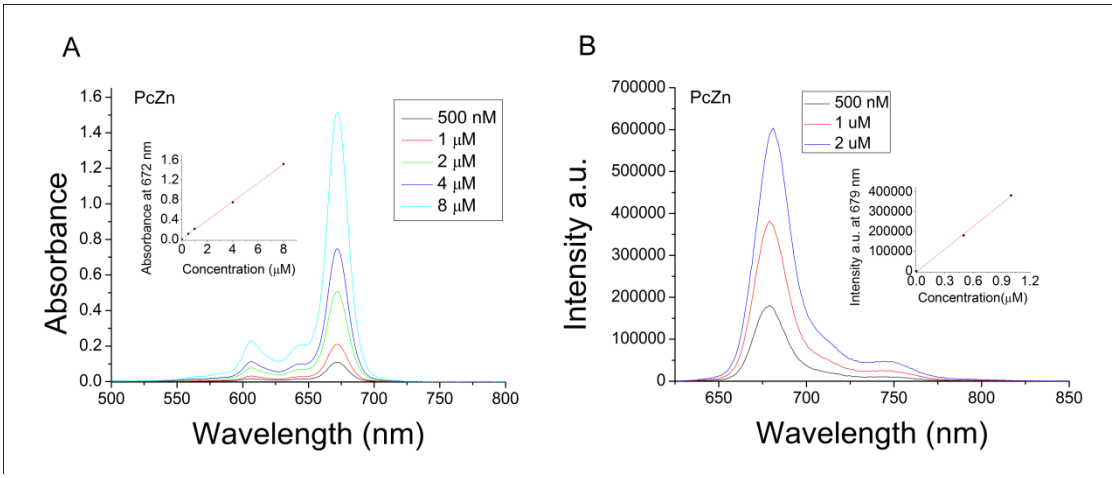


Fig. S5. Absorption spectra (A) and fluorescence spectra (B) of PcZn at various concentrations in DMSO. The inset plots Q-band absorbance (A) and fluorescence intensities (B) versus the concentration of the corresponding compounds.

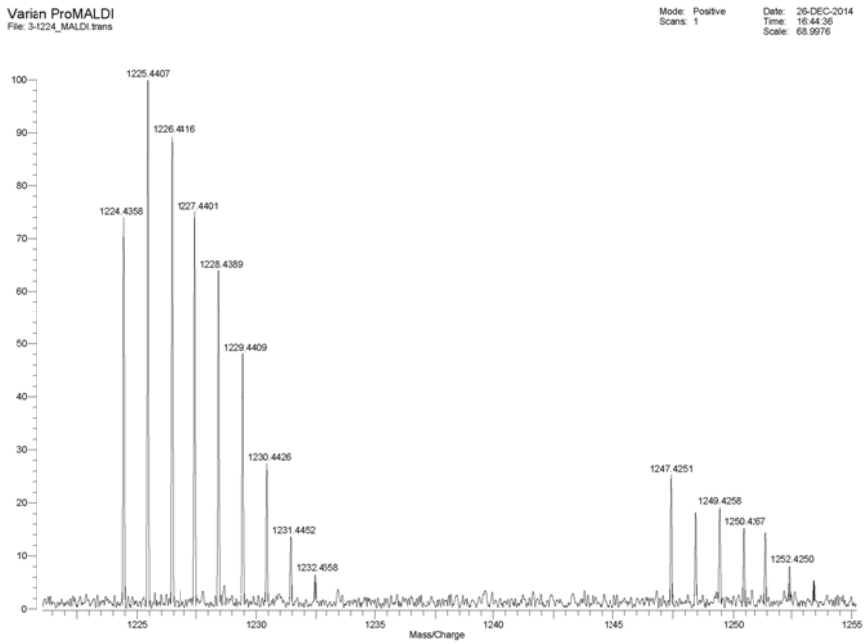


Fig. S6. $PcZn_1$ (ESI-HRMS calcd for $C_{60}H_{72}N_8NaO_{16}Zn$ $[M+Na]^+$ 1247.4250, found: m/z 1247.4251; calcd for $C_{60}H_{73}N_8O_{16}Zn$ $[M+H]^+$ 1225.4431, found: m/z 1225.4407).

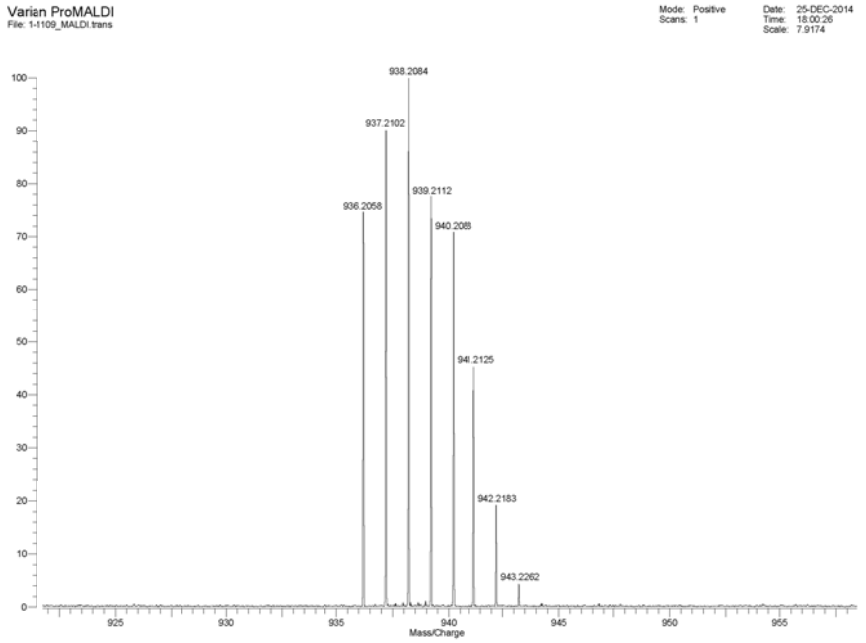


Fig. S7. $PcZn_2$ (ESI-HRMS calcd for $C_{44}H_{41}N_8O_{12}Zn$ $[M+H]^+$ 937.2130, found 937.2102).

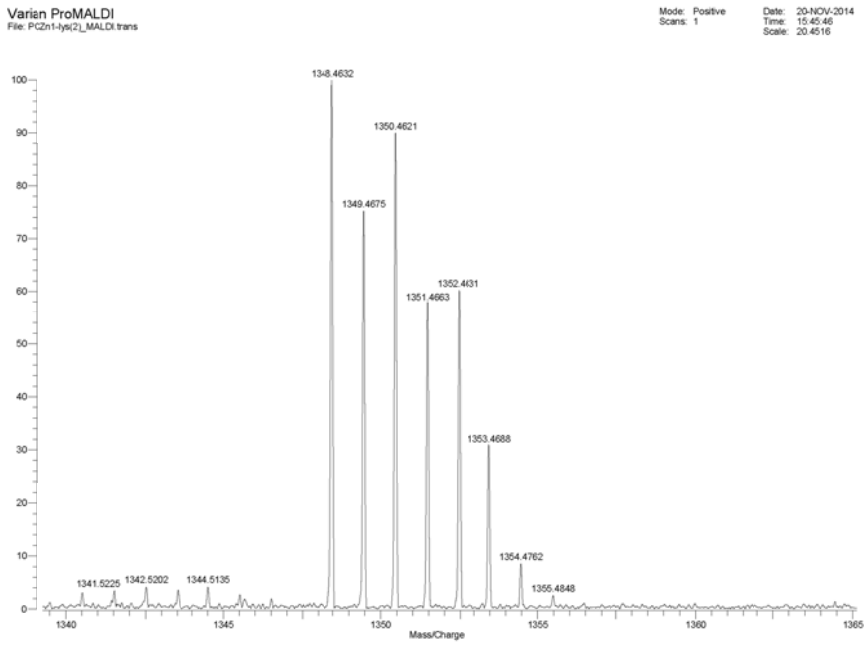


Fig. S8. $PcZn_1$-lys (ESI-HRMS calcd for $C_{66}H_{75}N_{11}NaO_{15}Zn$ $[M+Na]^+$ 1348.4628, found 1348.4632).

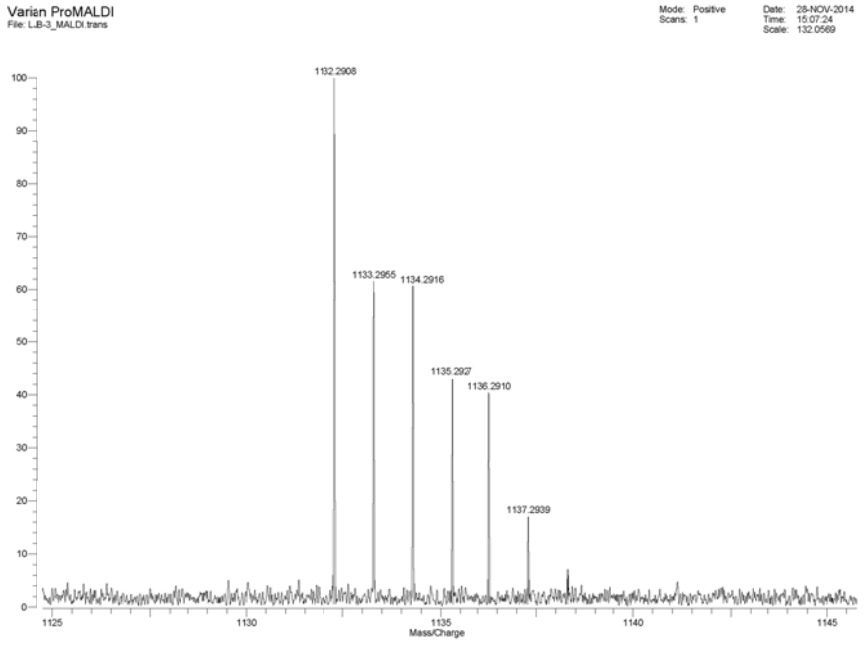


Fig. S9. $PcZn_2$-lys (ESI-HRMS calcd for $C_{54}H_{51}N_{11}NaO_{12}Zn^+$ $[M+Na]^+$ 1132.2902, found 1132.2908).

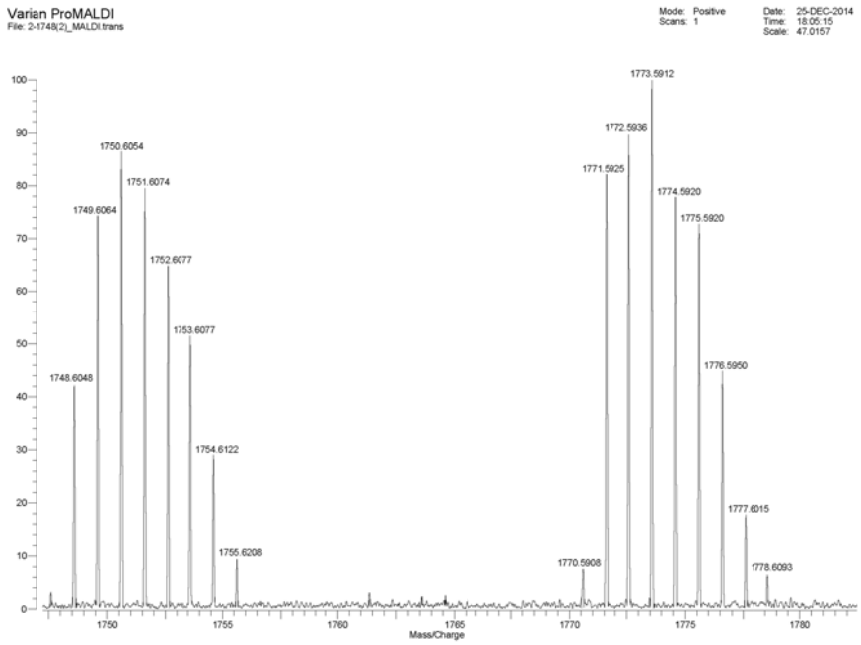


Fig. S10. $PcZn_1$-lys-FA (ESI-HRMS calcd for $C_{85}H_{92}N_{18}NaO_{20}Zn^+$ $[M+Na]^+$ 1771.5919, found 1771.5925).

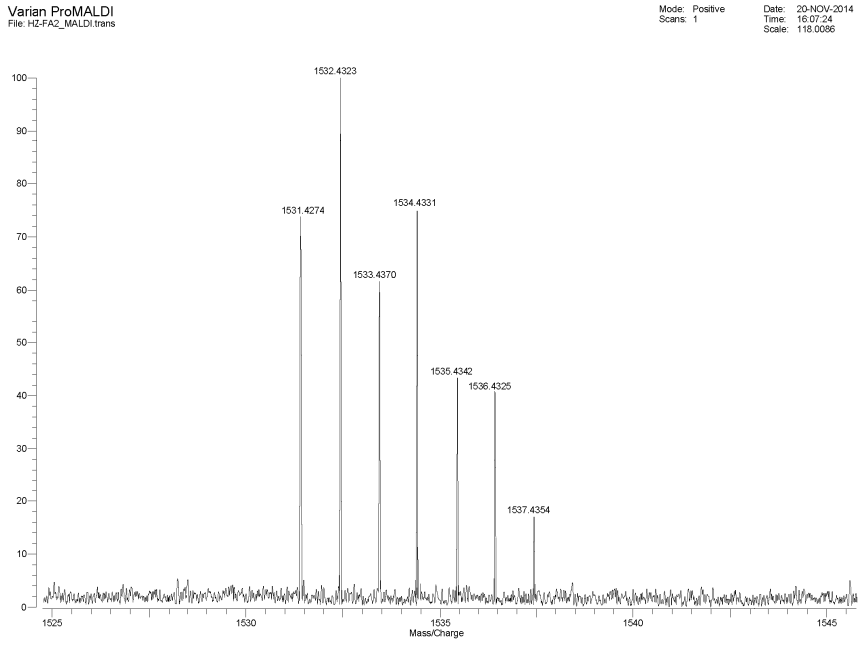
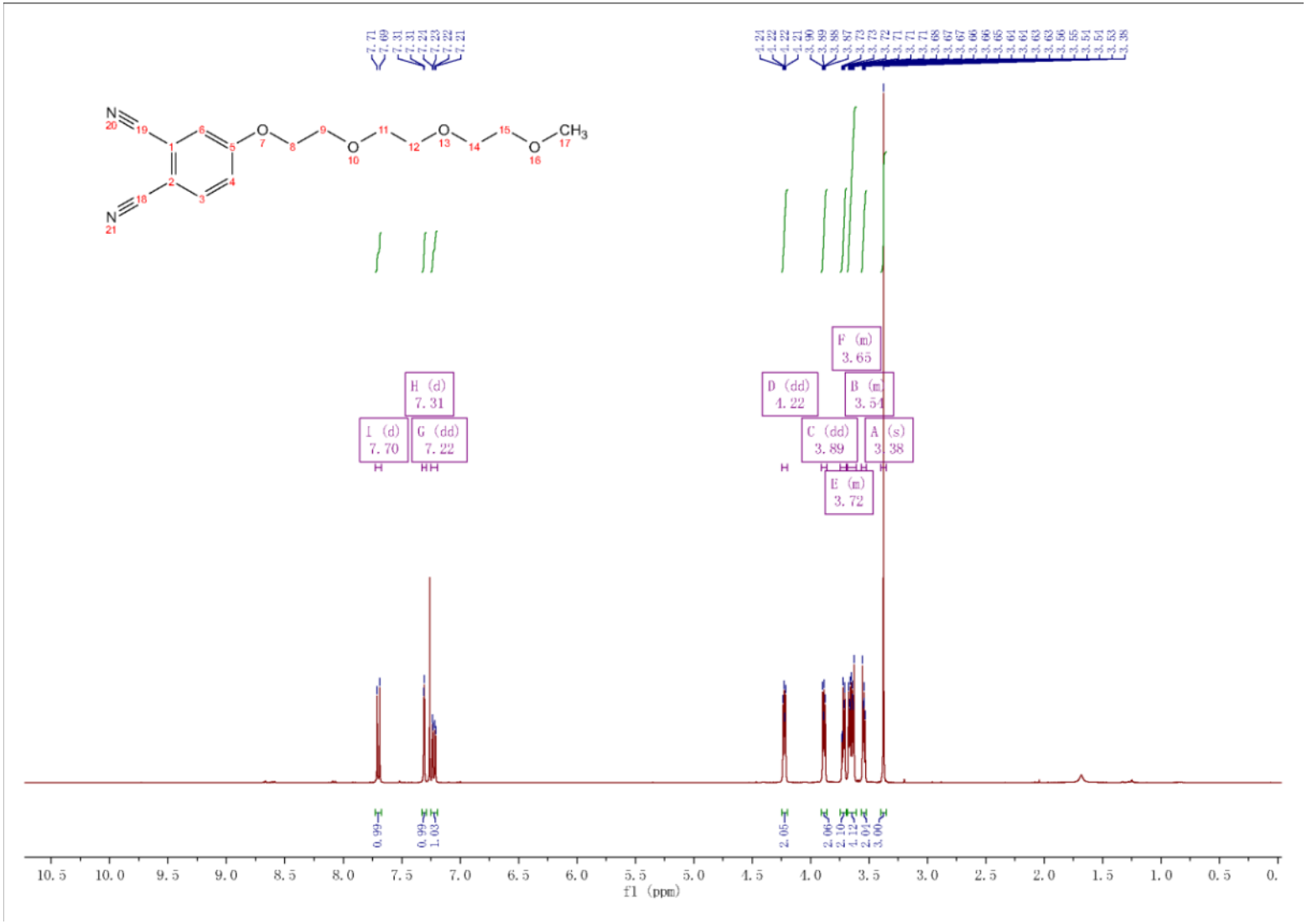


Fig. S11. $PcZn_2$-lys-FA (ESI-HRMS calcd for $C_{73}H_{69}N_{18}O_{17}Zn^+$ $[M+H]^+$ 1533.4374, found 1533.4370).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F (m)
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D (dd)
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E (m)
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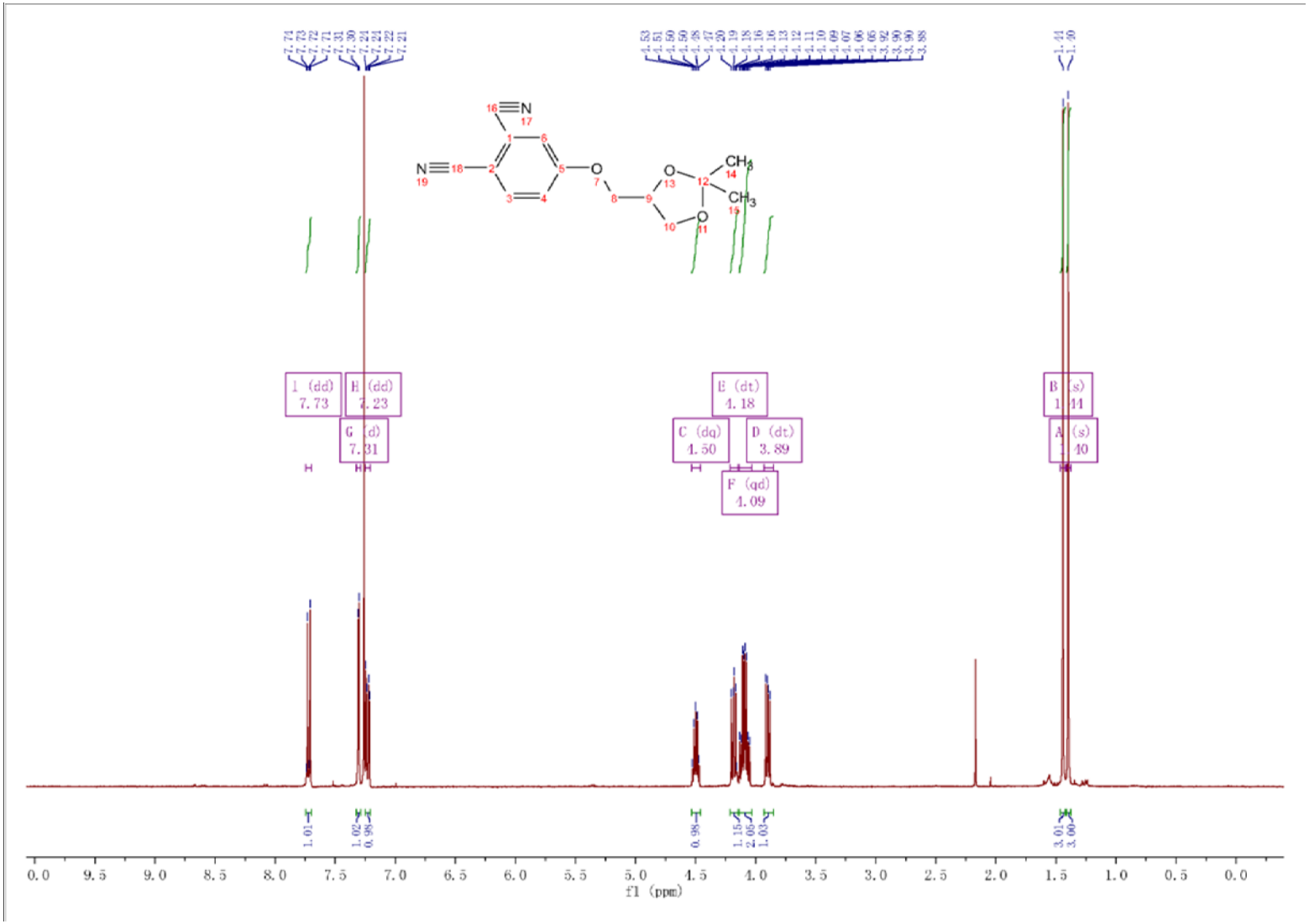
f1 (ppm)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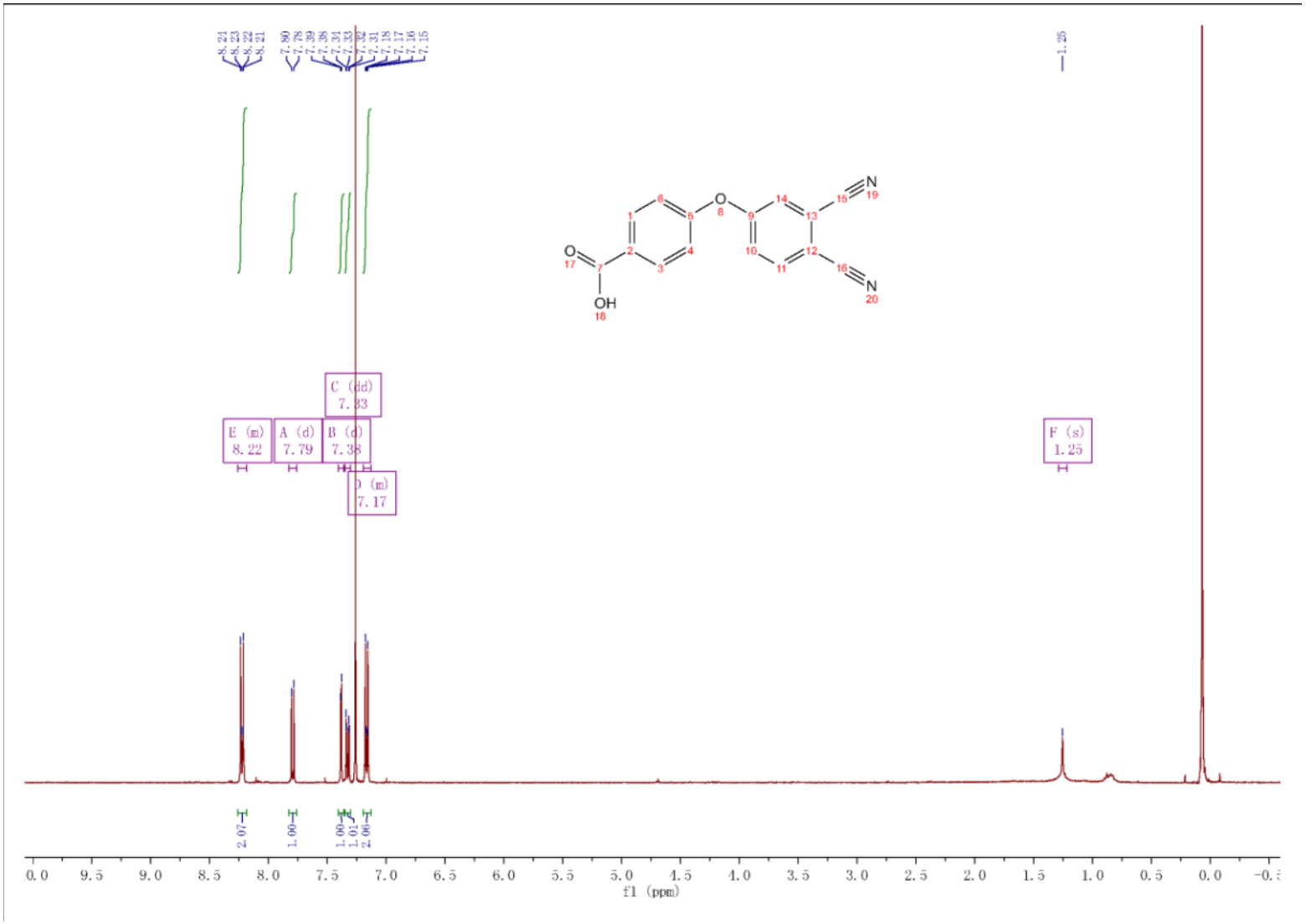
f1 (ppm)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7.33
7.32
7.31
7.18
7.17
7.16
7.15
1.25
C (dd)
7.33
E (m)
8.22
A (d)
7.79
B (d)
7.38
D (m)
7.17
F (s)
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1.00
1.01
2.06
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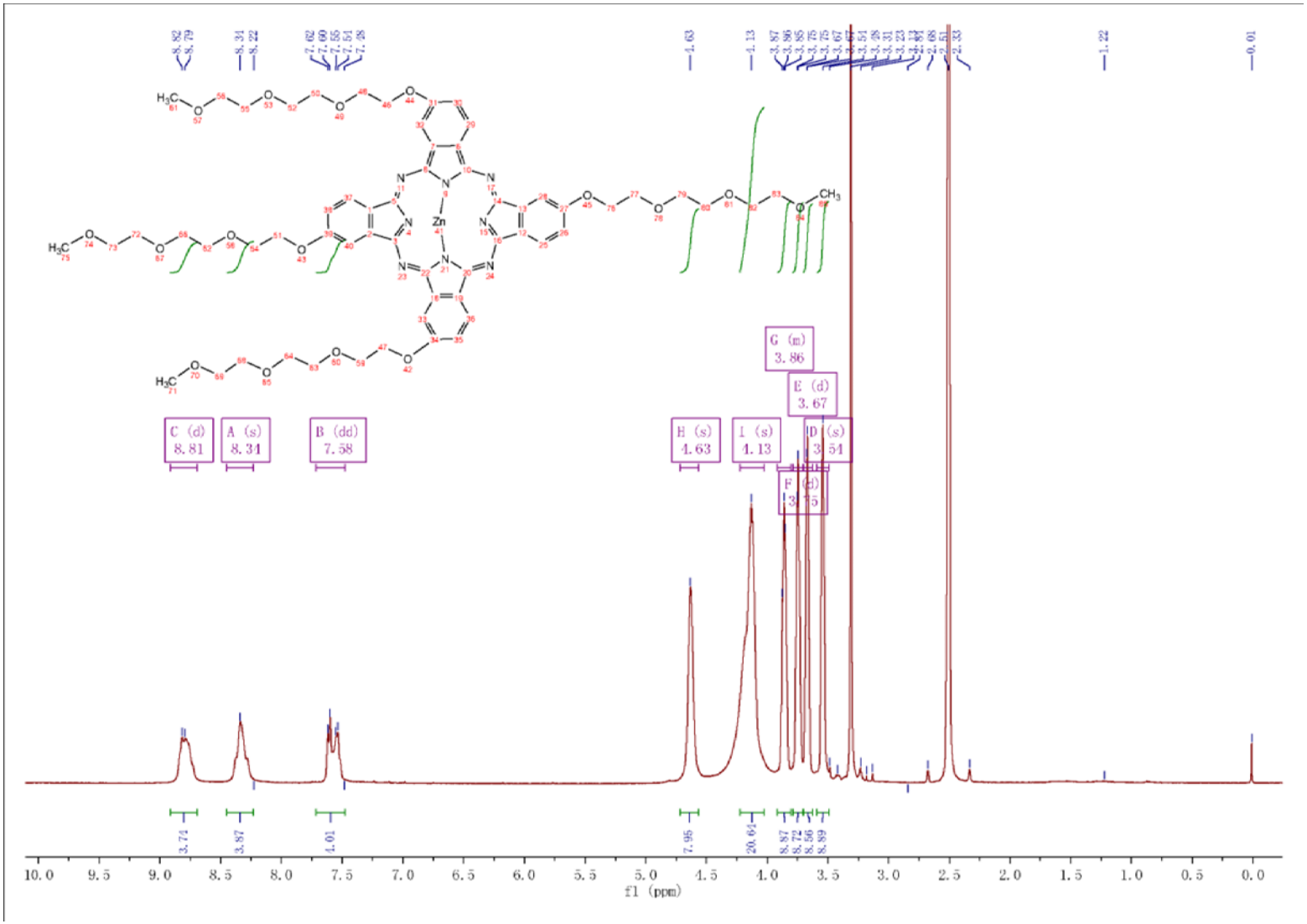
f1 (ppm)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B (dd)
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H (s)
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I (s)
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G (m)
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E (d)
3.67
D (s)
3.54
F (d)
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4.01
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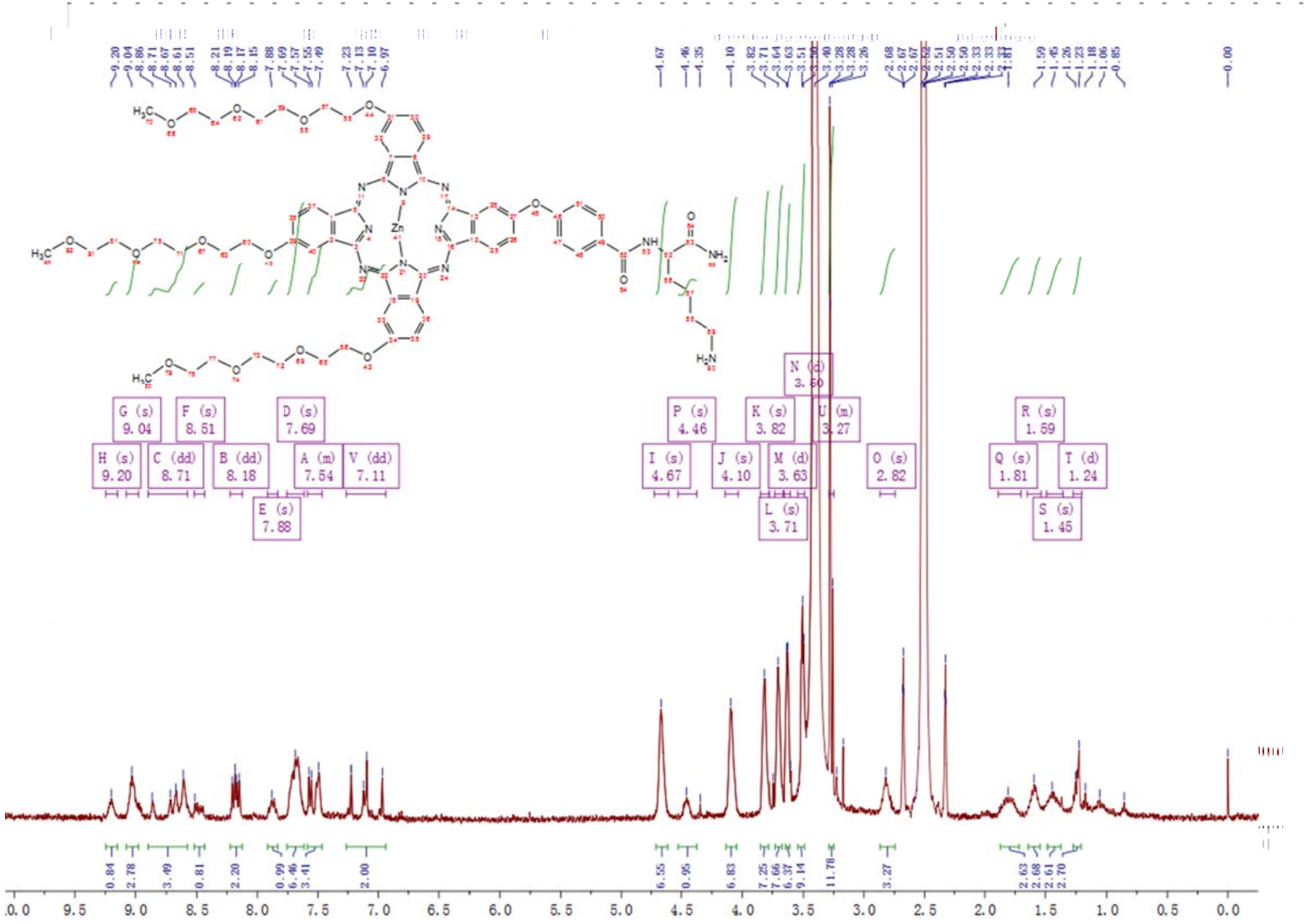
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V (dd) 7.11
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P (s) 4.46
K (s) 3.82
U (m) 3.27
R (s) 1.59
I (s) 4.67
J (s) 4.10
M (d) 3.63
O (s) 2.82
Q (s) 1.81
T (d) 1.24
L (s) 3.71
S (s) 1.45
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H2N
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3.49
0.81
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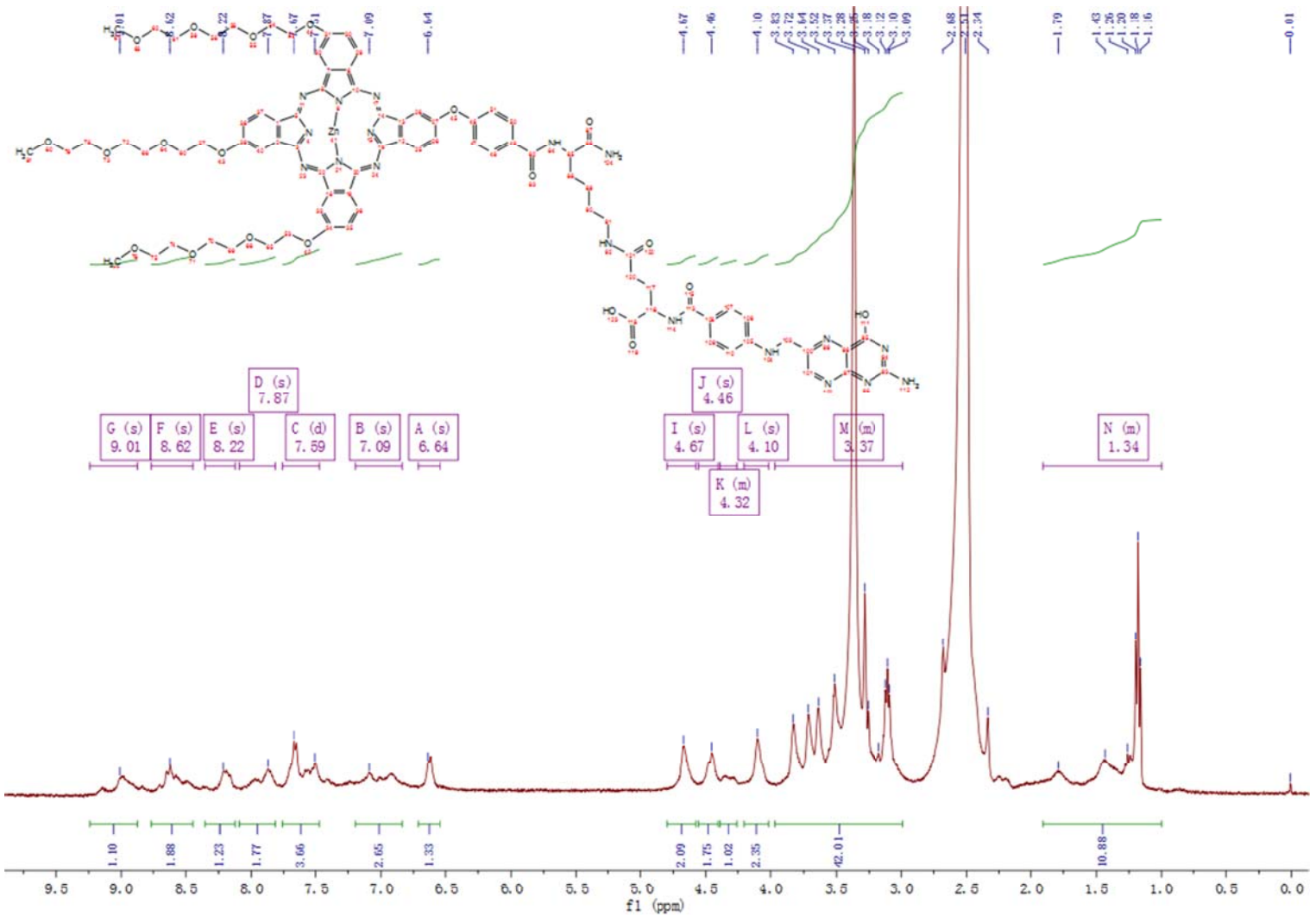
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K (m) 4.32
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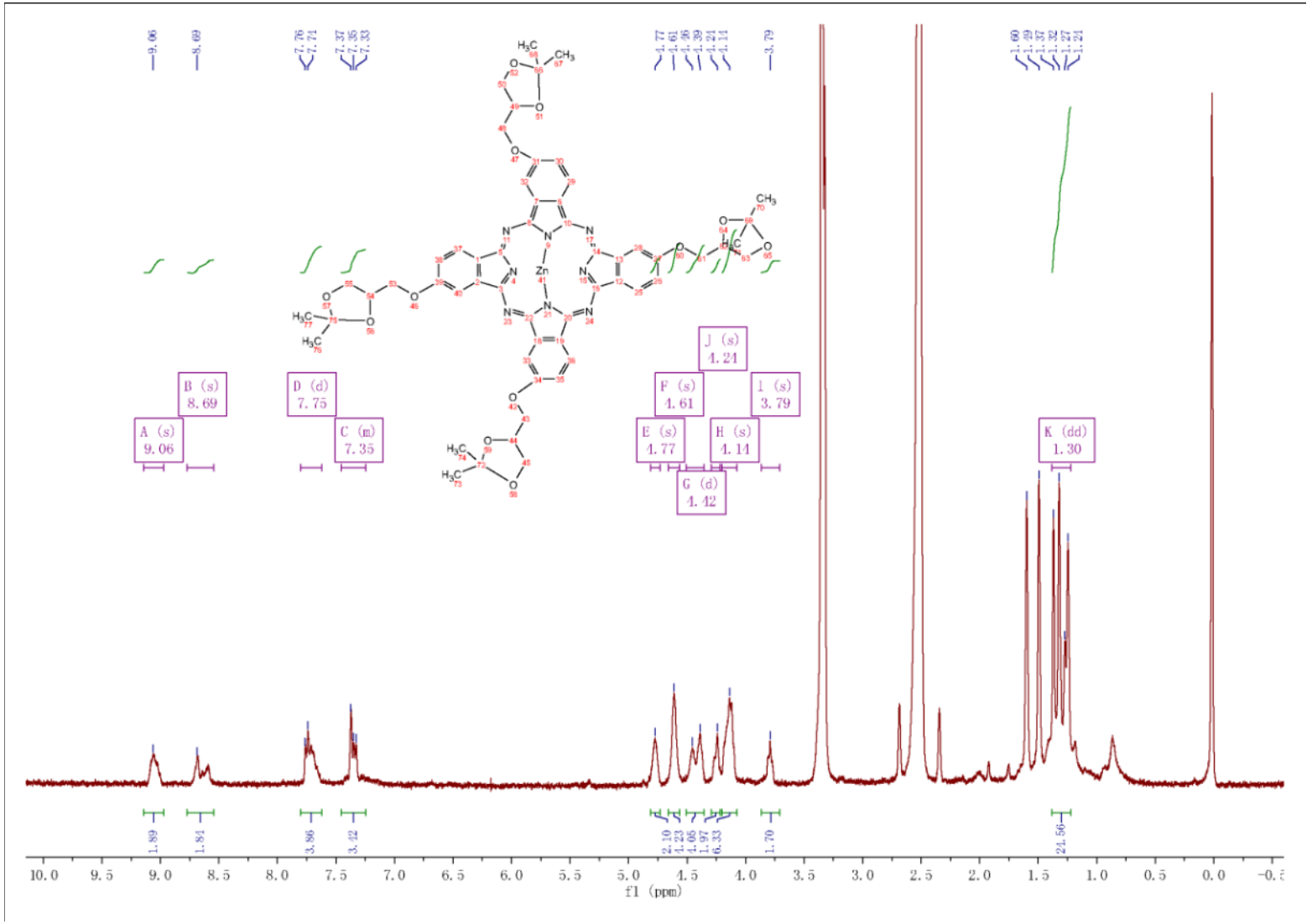
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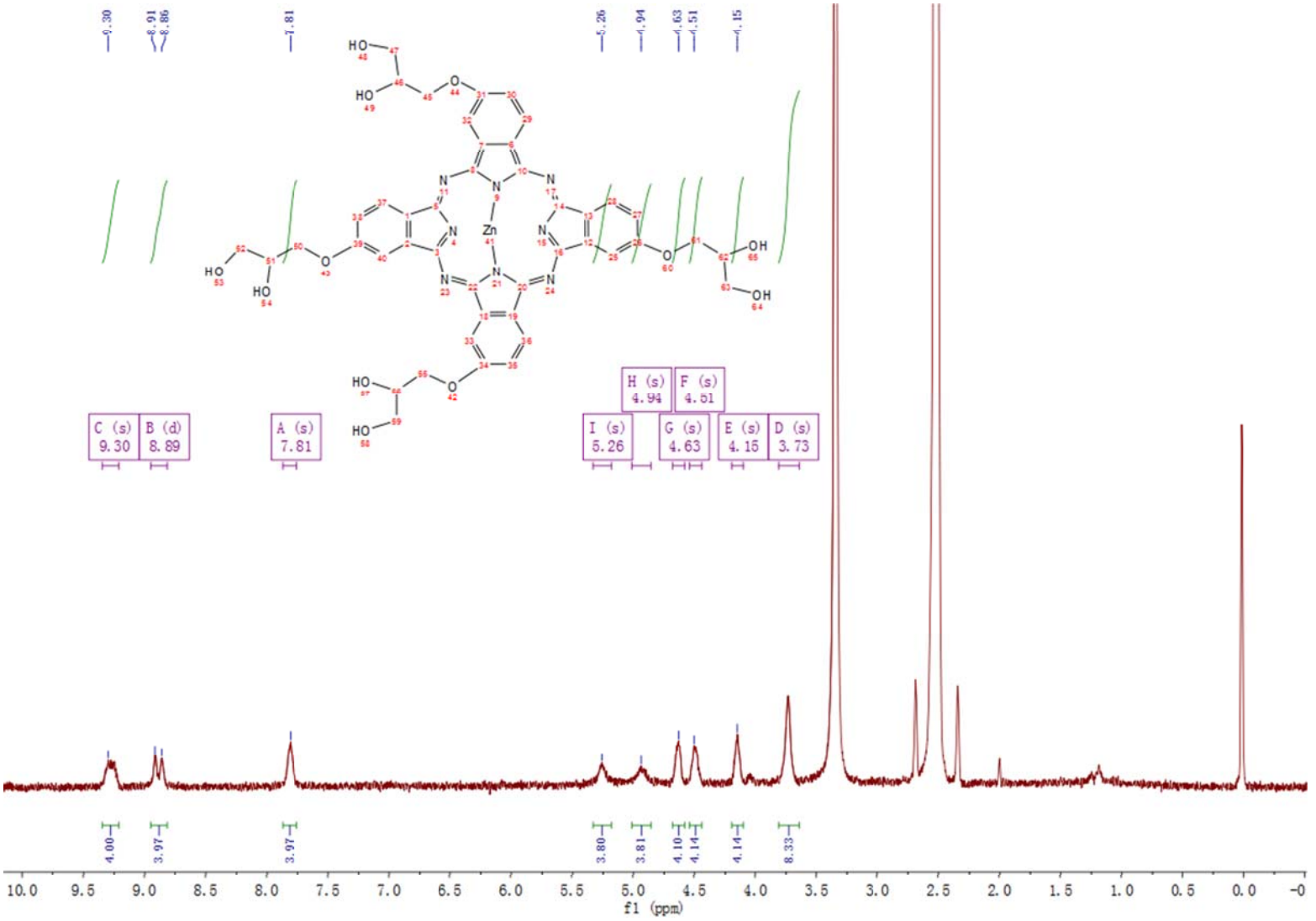
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A (s) 7.81
H (s) 4.94
F (s) 4.51
I (s) 5.26
G (s) 4.63
E (s) 4.15
D (s) 3.73
4.00
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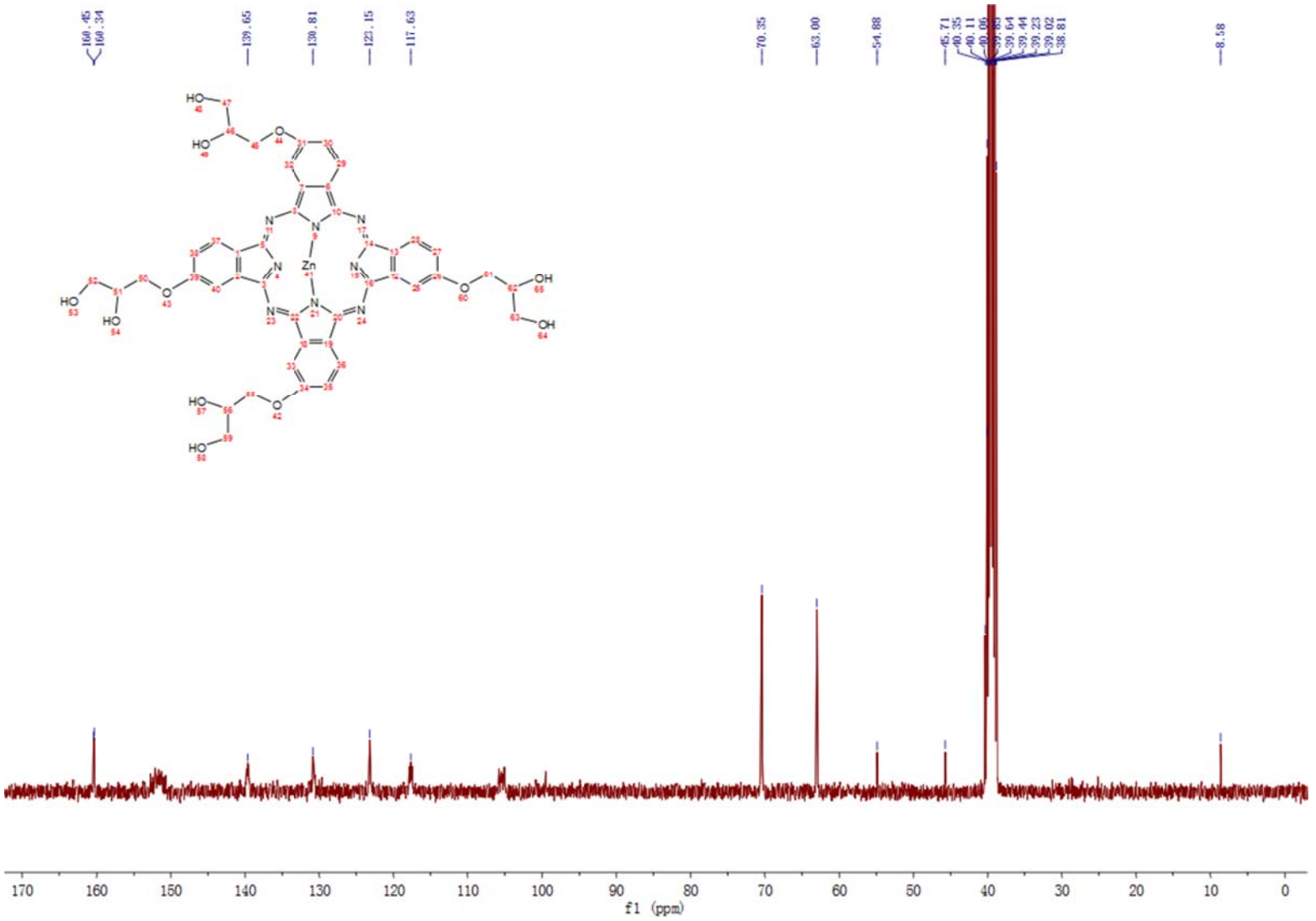
3.97
3.80
3.81
4.10
4.14
4.14
8.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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38.81
8.58
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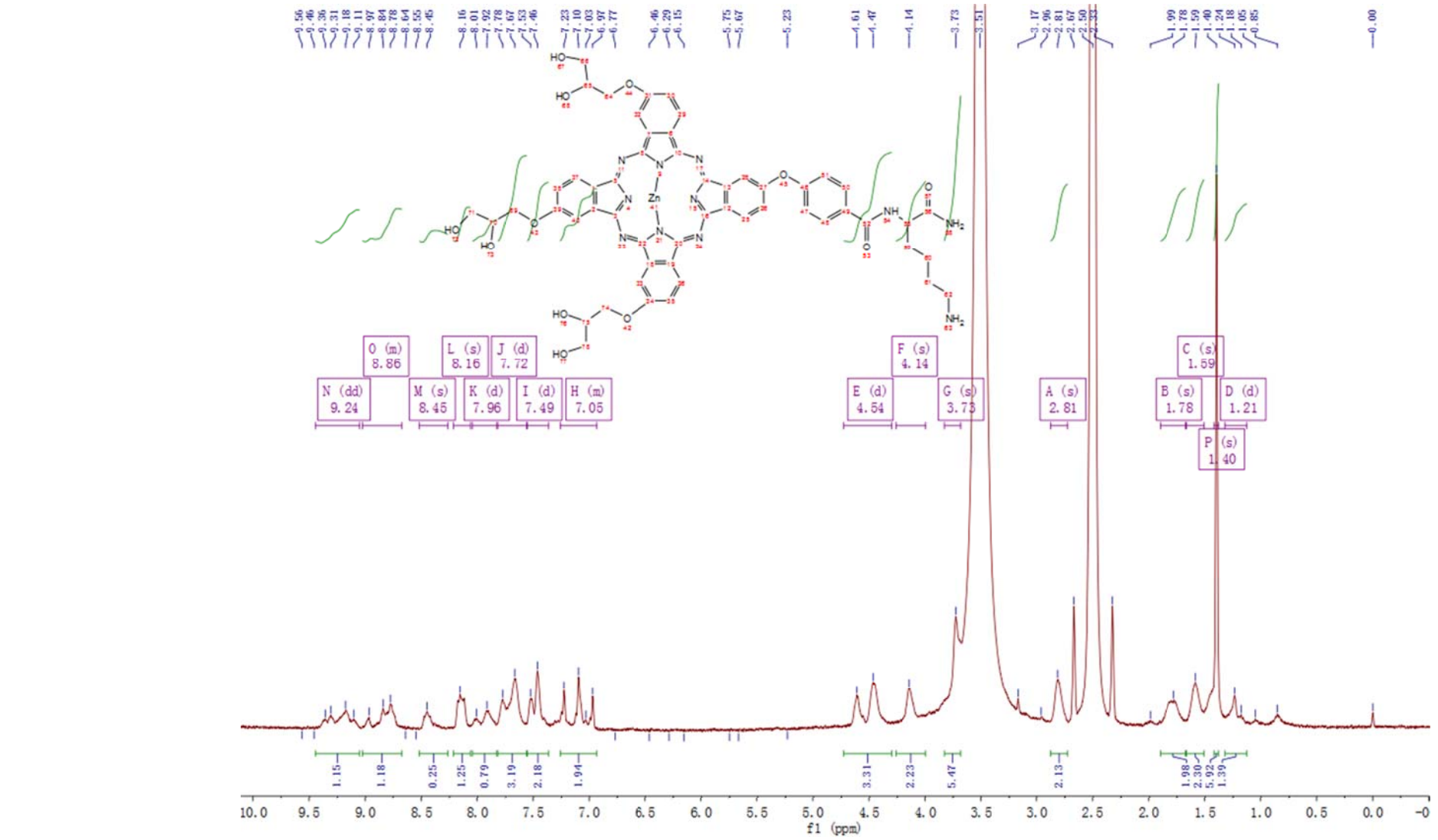
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6.46 6.29 6.15
5.75 5.67
5.23
4.61 4.47
4.14
3.73
3.51
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O (m) 8.86
M (s) 8.45
L (s) 8.16
K (d) 7.96
J (d) 7.72
I (d) 7.49
H (m) 7.05
E (d) 4.54
F (s) 4.14
G (s) 3.73
A (s) 2.81
B (s) 1.78
C (s) 1.59
D (d) 1.21
P (s) 1.40
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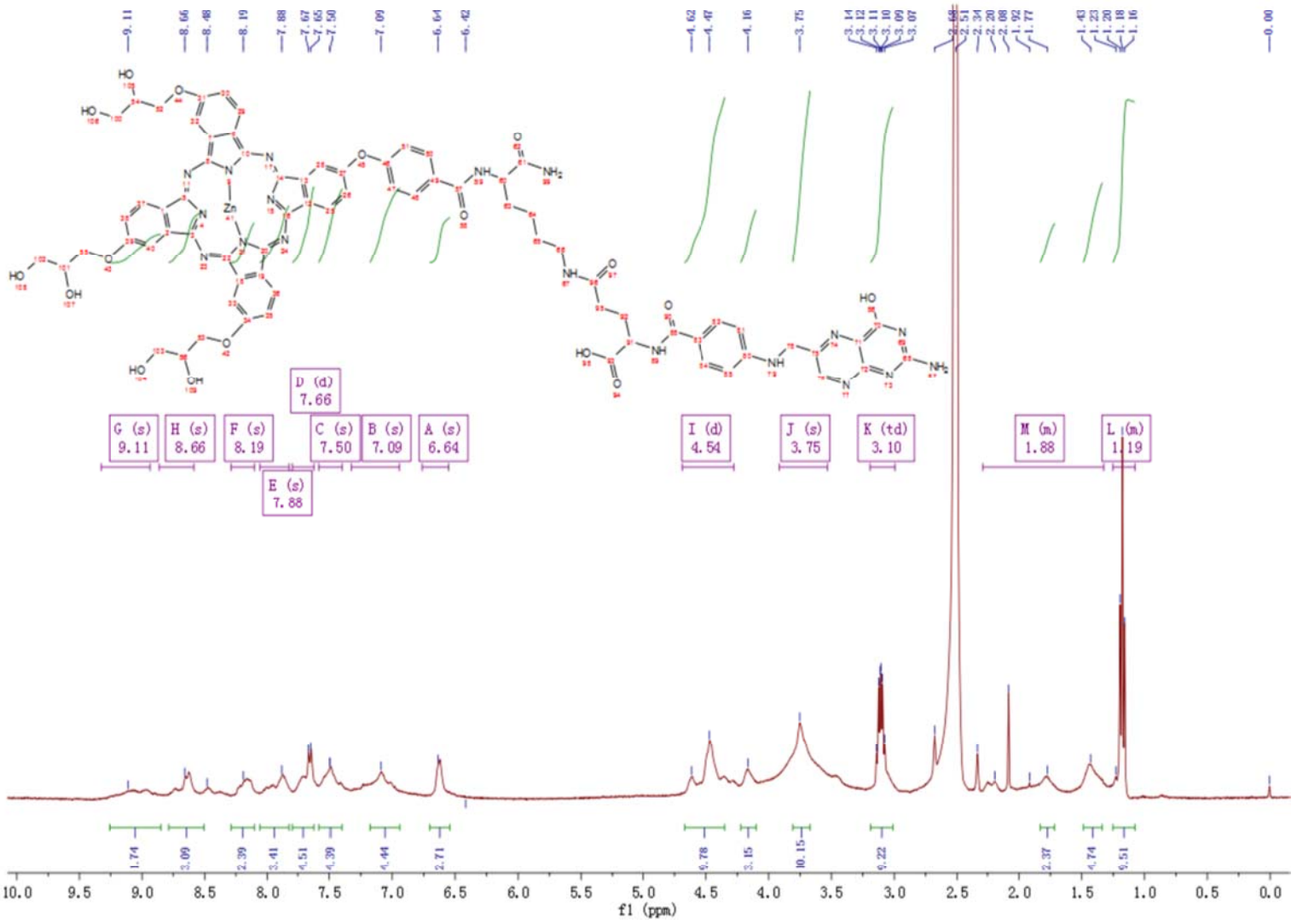
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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3.10
3.09
3.07
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2.20
2.08
1.92
1.77
1.43
1.23
1.20
1.18
1.16
0.00
G (s) 9.11
H (s) 8.66
F (s) 8.19
D (d) 7.66
C (s) 7.50
B (s) 7.09
A (s) 6.64
E (s) 7.88
I (d) 4.54
J (s) 3.75
K (td) 3.10
M (m) 1.88
L (m) 1.19
1.74
3.09
2.39
3.41
1.51
1.39
1.44
2.71
6.78
3.15
10.15
6.22
2.37
4.74
9.51
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)