

## Supporting Information

### Synthesis of three cisplatin-conjugated asymmetric porphyrin photosensitizers for photodynamic therapy

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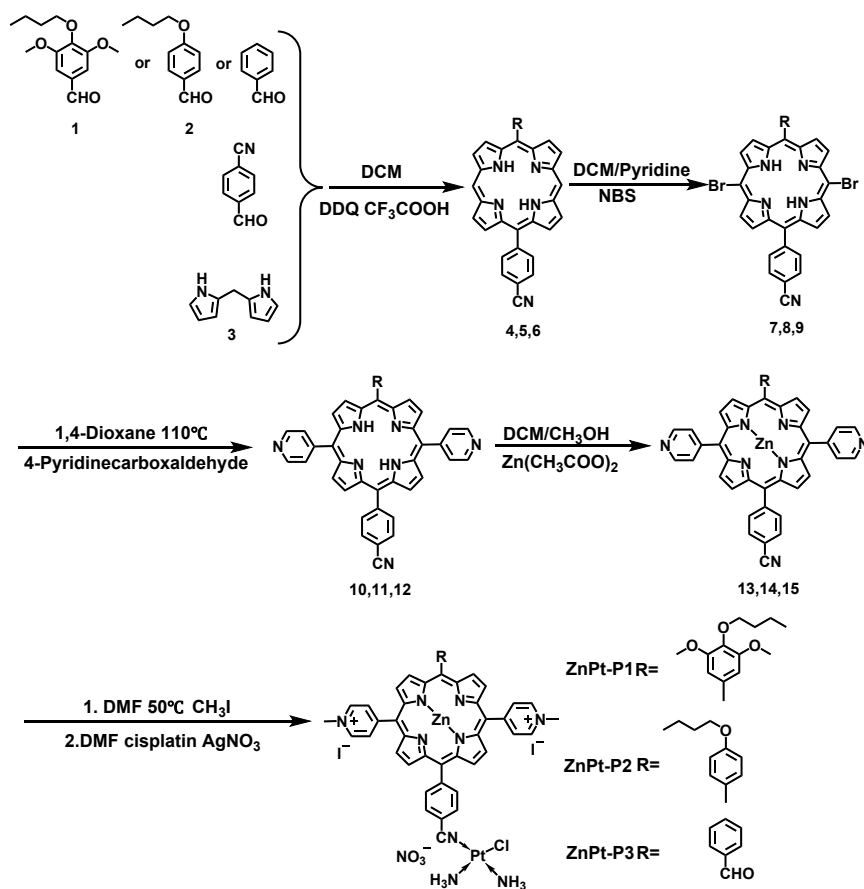
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## Experimental section

### Synthesis and Characterization



**Scheme S1.** The synthetic routes of target compounds ZnPt-P1~ZnPt-P3

The synthetic pathways for the target compounds ZnPt-P1~ZnPt-P3 are shown in **Scheme S1**, and compounds 1, 2, 3 were synthesized according to literature<sup>1-3</sup>.

### Synthesis of compounds 4,5,6.

Compound 1 (596 mg, 2.5 mmol) or compound 2 (432 mg, 2.5 mmol) or benzaldehyde (260  $\mu$ L, 2.5 mmol) was dissolved in 500 ml dichloromethane, and then 4-cyanobenzaldehyde (262 mg, 2 mmol) and compound 3 (584 mg, 4 mmol) were added under the protection of argon at room temperature. After 30 min of reaction, trifluoroacetic acid (183  $\mu$ L) was added to continue the reaction for 3 h, then add dichlorodicyanobenzoquinone (1.36 g, 6 mmol) to continue the reaction for 1 h, and add 5 ml triethylamine to stop the reaction. After the reaction, the solvent was removed under reduced pressure, and the volume ratio of dichloromethane to petroleum ether = 1:1 was used as the eluent. The residue was purified by column chromatography to obtain the purple product<sup>4</sup>.

**Compound 4** (20.5% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  (ppm) -2.89 (s, 2H, NH-H), 1.13 (d, 3H, CH<sub>3</sub>-H), 1.68 (dd, 2H, CH<sub>2</sub>-H), 1.98 (dt, 2H, CH<sub>2</sub>-H), 3.99 (s, 6H, OCH<sub>3</sub>-H), 4.33 (t, 2H, OCH<sub>2</sub>-H), 7.50 (s, 2H, Ph-H), 8.10 (d, 2H,

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Ph-H), 8.38 (d, 2H, Ph-H), 8.96 (d, 1H,  $\beta$ -H), 9.19 (d, 2H,  $\beta$ -H), 9.41 (dd, 4H,  $\beta$ -H), 10.33 (s, 2H, Po-meso-H), HRMS (ESI, positive ion mode, m/z):  $[M]^+$  calcd for  $[C_{39}H_{34}O_3N_5]^+$ , 620.2656; found, 620.2656.

**Compound 5 (19.3% yield):**  $^1H$  NMR ( $CDCl_3$ , 600MHz):  $\delta$  (ppm) -3.12 (s, 2H, NH-H), 0.92-1.01 (m, 3H,  $CH_3$ -H), 1.65-1.76 (m, 2H,  $CH_2$ -H), 1.96-2.04 (m, 2H,  $CH_2$ -H), 4.29 (t, 2H, OCH<sub>2</sub>-H), 7.32-7.37 (m, 2H, Ph-H), 8.08-8.13 (m, 2H, Ph-H), 8.14-8.19 (m, 2H, Ph-H), 8.36-8.40 (m, 2H, Ph-H), 8.95 (d, 2H,  $\beta$ -H), 9.14 (d, 2H,  $\beta$ -H), 9.41 (dd, 4H,  $\beta$ -H), 10.32 (s, 2H, Po-meso-H), HRMS (ESI, positive ion mode, m/z):  $[M]^+$  calcd for  $[C_{37}H_{30}ON_5]^+$ , 520.2445; found, 520.2446.

**Compound 6 (10.3% yield):**  $^1H$  NMR ( $CDCl_3$ , 600MHz):  $\delta$  (ppm) -3.16 (s, 2H, NH-H), 7.81 (dd, 3H, Ph-H), 8.11 (d, 2H, Ph-H), 8.39 (m, 2H, Ph-H), 8.97 (d, 2H,  $\beta$ -H), 9.10 (d, 2H,  $\beta$ -H), 9.42 (dd, 4H,  $\beta$ -H), 10.34 (s, 2H, Po-meso-H), HRMS (ESI, positive ion mode, m/z):  $[M]^+$  calcd for  $[C_{33}H_{22}N_5]^+$ , 488.1870; found, 488.1874.

#### **Synthesis of compounds 7,8,9.**

To the mixed solvent of dichloromethane (40 mL) and pyridine (0.4mL), add compound 4 (124 mg, 0.2 mmol) or compound 5 (104 mg, 0.2 mmol) or compound 6 (97.6mg, 2mmol) and N-bromosuccinimide (76.5 mg, 0.43 mmol). The reaction was carried out at 0 °C for 70 minutes, and then the reaction was terminated with 1 mL of acetone. At the end of the reaction, the solvent is evaporated by rotation. The crude product was purified by silica gel column chromatography, and the 1:2 volume ratio of dichloromethane to petroleum ether was used as eluent to obtain compounds 7, 8 and 9<sup>5,6</sup>.

**Compound 7 (69.5% yield):**  $^1H$  NMR ( $CDCl_3$ , 600MHz):  $\delta$  (ppm) -2.74 (s, 2H, NH-H), 1.11 (t, 3H,  $CH_3$ -H), 1.66-1.73 (m, 2H,  $CH_2$ -H), 2.21 (t, 2H,  $CH_2$ -H), 3.96 (s, 6H,  $OCH_3$ -H), 4.32 (t, 2H, OCH<sub>2</sub>-H), 7.39 (s, 2H, Ph-H), 8.09 (d, 2H, Ph-H), 8.29 (d, 2H, Ph-H), 8.71 (s, 2H,  $\beta$ -H), 8.95 (d, 2H,  $\beta$ -H), 9.63 (s, 4H,  $\beta$ -H), HRMS (ESI, positive ion mode, m/z):  $[M]^+$  calcd for  $[C_{39}H_{32}O_3N_5Br_2]^+$ , 776.0866; found, 776.0868.

**Compound 8 (71% yield):**  $^1H$  NMR ( $CDCl_3$ , 600MHz):  $\delta$  (ppm) -3.01 (s, 2H, NH-H), 0.92-1.01 (m, 3H,  $CH_3$ -H), 1.65-1.76 (m, 2H,  $CH_2$ -H), 1.96-2.04 (m, 2H,  $CH_2$ -H), 4.29 (t, 2H, OCH<sub>2</sub>-H), 7.32-7.37 (m, 2H, Ph-H), 8.08-8.13 (m, 2H, Ph-H), 8.14-8.19 (m, 2H, Ph-H), 8.36-8.40 (m, 2H, Ph-H), 8.95 (d, 2H,  $\beta$ -H), 9.14 (d, 2H,  $\beta$ -H), 9.41 (dd, 4H,  $\beta$ -H), HRMS (ESI, positive ion mode, m/z):  $[M]^+$  calcd for  $[C_{37}H_{28}ON_5Br_2]^+$ , 716.0655; found, 716.0649.

**Compound 9 (73% yield):**  $^1H$  NMR ( $CDCl_3$ , 600MHz):  $\delta$  (ppm) -3.13 (s, 2H, NH-H), 7.47 (dd, 3H, Ph-H), 7.87 (d, 2H, Ph-H), 8.09-8.05 (m, 2H, Ph-H), 9.01 (d, 2H,  $\beta$ -H), 9.20 (d, 2H,  $\beta$ -H), 9.29 (dd, 4H,  $\beta$ -H), HRMS (ESI, positive ion mode, m/z):  $[M]^+$  calcd for  $[C_{33}H_{20}N_5Br_2]^+$ , 644.0080; found, 644.0071.

#### **Synthesis of compounds 10,11,12.**

In a three-necked round-bottom flask, 200 mL of 1,4-dioxane solvent was added to compound 7 (194 mg, 0.25

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mmol) or compound 8 (179 mg, 0.25 mmol) or compound 9 (161 mg, 0.25 mmol) and 4-pyridineboronic acid (76 mg, 0.625 mmol), followed by tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol) and anhydrous potassium carbonate (240 mg, 1.8 mmol) and refluxed at 110 °C under argon protection after 6 h reaction time. After cooling to room temperature, the solvent was finished by rotary evaporation, and compounds 10,11,12 were purified by column chromatography on silica gel using a dichloromethane to methanol ratio of 200:1 v/v as eluent<sup>7,8</sup>.

**Compound 10** (81% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz): δ (ppm) -2.86 (s, 2H, NH-H), 1.11 (t, 3H, CH<sub>3</sub>-H), 1.60-1.72 (m, 2H, CH<sub>2</sub>-H), 1.94-2.03 (m, 2H, CH<sub>2</sub>-H), 3.96 (s, 6H, OCH<sub>3</sub>-H), 4.32 (t, 2H, OCH<sub>2</sub>-H), 8.08 (d, 2H, Ph-H), 8.14-8.18 (m, 4H, Py-H), 8.31-8.35 (m, 2H, Ph-H), 8.79 (d, 2H, β-H), 8.84 (dd, 4H, Py-H), 9.01-9.07 (m, 6H, β-H), HRMS (ESI, positive ion mode, m/z): [M]<sup>+</sup> calcd for [C<sub>49</sub>H<sub>40</sub>O<sub>3</sub>N<sub>7</sub>]<sup>+</sup>, 774.3187; found, 774.3170.

**Compound 11** (85% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz): δ (ppm) -3.12 (s, 2H, NH-H), 1.01-1.07 (m, 3H, CH<sub>3</sub>-H), 1.58-1.63 (m, 2H, CH<sub>2</sub>-H), 1.96-2.04 (m, 2H, CH<sub>2</sub>-H), 4.35 (t, 2H, OCH<sub>2</sub>-H), 7.32-7.37 (m, 2H, Ph-H), 8.08-8.13 (m, 2H, Ph-H), 8.14-8.19 (m, 6H, Py-H+Ph-H), 8.36-8.40 (m, 2H, Ph-H), 8.67 (d, 2H, β-H), 8.73 (dd, 4H, Py-H), 8.97-9.03 (m, 6H, β-H), HRMS (ESI, positive ion mode, m/z): [M]<sup>+</sup> calcd for [C<sub>47</sub>H<sub>36</sub>ON<sub>7</sub>]<sup>+</sup>, 714.2976; found, 714.2969

**Compound 12** (78% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz): δ (ppm) -2.95 (s, 2H, NH-H), 7.67-7.77 (m, 3H, Ph-H), 8.01-8.77 (m, 4H, Py-H), 8.11-8.15 (m, 2H, Ph-H), 8.24-8.28 (m, 2H, Ph-H), 8.71-8.79 (m, 6H, β-H+Py-H), 8.85 (d, 2H, β-H), 8.96-8.99 (m, 4H, β-H), HRMS (ESI, positive ion mode, m/z): [M]<sup>+</sup> calcd for [C<sub>43</sub>H<sub>28</sub>N<sub>7</sub>]<sup>+</sup>, 642.2401; found, 642.2394.

### **Synthesis of compounds 13,14,15**

In a 250 mL round bottom flask, 200 mg of compound 10 or compound 11 or compound 12 was added to a mixture of 80 mL of dichloromethane and 20 mL of methanol, and then 800 mg of zinc acetate was added and refluxed at 45°C overnight. At the end of the reaction, the solvent was rotary evaporated, dichloromethane was added to dissolve, and the organic phase was extracted with distilled water and dichloromethane, and the solvent was rotary evaporated to obtain compounds 13,14,15<sup>9,10</sup>.

**Compound 13**(95% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz): δ (ppm) 1.11 (t, 3H, CH<sub>3</sub>-H), 1.60-1.72 (m, 2H, CH<sub>2</sub>-H), 1.94-2.03 (m, 2H, CH<sub>2</sub>-H), 3.96 (s, 6H, OCH<sub>3</sub>-H), 4.32 (t, 2H, OCH<sub>2</sub>-H), 8.08 (d, 2H, Ph-H), 8.14-8.18 (m, 4H, Py-H), 8.31-8.35 (m, 2H, Ph-H), 8.79 (d, 2H, β-H), 8.84 (dd, 4H, Py-H), 9.01-9.07 (m, 6H, β-H), HRMS (ESI, positive ion mode, m/z): [M]<sup>+</sup> calcd for [C<sub>49</sub>H<sub>38</sub>O<sub>3</sub>N<sub>7</sub>Zn]<sup>+</sup>, 836.2322; found, 836.2332.

**Compound 14**(93% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz): δ (ppm) 1.01-1.07 (m, 3H, CH<sub>3</sub>-H), 1.58-1.63 (m, 2H, CH<sub>2</sub>-H), 1.96-2.04 (m, 2H, CH<sub>2</sub>-H), 4.35 (t, 2H, OCH<sub>2</sub>-H), 7.32-7.37 (m, 2H, Ph-H), 8.08-8.13 (m, 2H, Ph-H), 8.14-8.19 (m,

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6H, Py-H+Ph-H), 8.36-8.40 (m, 2H, Ph-H), 8.67 (d, 2H,β-H) 8.73 (dd, 4H, Py-H), 8.97-9.03 (m, 6H, β-H), HRMS (ESI, positive ion mode, m/z): [M]<sup>+</sup> calcd for [C<sub>47</sub>H<sub>34</sub>ON<sub>7</sub>Zn]<sup>+</sup>, 776.2111; found, 776.2099.

**Compound 15**(87% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz): δ (ppm) 7.67-7.77(m, 3H, Ph-H), 8.01-8.77 (m, 4H, Py-H), 8.11-8.15 (m, 2H, Ph-H), 8.24-8.28 (m, 2H, Ph-H), 8.71-8.79 (m, 6H, β-H+Py-H), 8.85 (d, 2H, β-H), 8.96-8.99 (m, 4H, β-H), HRMS (ESI, positive ion mode, m/z): [M]<sup>+</sup> calcd for [C<sub>43</sub>H<sub>26</sub>N<sub>7</sub>Zn]<sup>+</sup>, 704.1536; found, 704.1523.

### **Synthesis of porphyrins ZnPt-P1~ZnPt-P3**

Use 5 mL of DMF as solvent, add 100 mg of compound 13 or compound 14 or compound 15 to dissolve it, then add 1mL of iodomethane, under the protection of argon gas at 50 °C and avoid light reaction for 3 h, distillation under reduced pressure to remove DMF, add dichloromethane, at this time there will be purple solid precipitation, using centrifugation to collect the product, dried to obtain the product 16,17,18<sup>11,12</sup>.

Cis-platinum (53.6 mg, 0.178 mmol) and AgNO<sub>3</sub> (30.3 mg, 0.178 mmol) were weighed and dissolved in 2 mL of DMF solution and stirred at room temperature for 24 h under light-proof conditions. The resulting suspension was centrifuged to remove the gray AgCl precipitate, and then the resulting yellowish solution was added to 2 mL DMF solution, and then 0.178 mmol of compound 17 or compound 18 or compound 19 was added, and the reaction was carried out at 50°C for 24 h under light-proof conditions, cooled to room temperature, and the solvent DMF was rotary evaporated, then washed with methanol, dichloromethane and ether, and centrifuged A purple solid was obtained, and then dried under vacuum at 60°C to obtain porphyrins ZnPt-P1~ZnPt-P3<sup>13-16</sup>.

ZnPt-P1(81% yield): <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 600MHz): δ (ppm) 1.05 (t, 3H, CH<sub>3</sub>-H), 1.62 (m, 2H, CH<sub>2</sub>-H), 1.84 (p, 2H, CH<sub>2</sub>-H), 3.90 (s, 6H, OCH<sub>3</sub>-H), 4.21 (t, 2H, OCH<sub>2</sub>-H), 4.61(s, 6H, NH<sub>3</sub>-H), 4.70 (s, 6H, Py-CH<sub>3</sub>-H), 7.45 (s, 2H, Ph-H), 8.32 (d, 2H, Py-H), 8.38 (d, 2H, Py-H), 8.88 (dd, 2H, Ph-H), 8.91-8.98 (m, 8H, β-H+Py-H+Ph-H), 9.05 (d, 2H, β-H), 9.41 (d, 4H, β-H), <sup>13</sup>C NMR (151 MHz, DMSO) δ (ppm) 158.95, 151.66, 150.79, 150.14, 149.75, 148.37, 148.15, 147.51, 144.08, 137.65, 137.05, 135.27, 133.88, 133.04, 132.59, 132.27, 131.97, 131.24, 122.89, 120.12, 115.56, 113.45, 111.40, 72.86, 56.74, 54.90, 54.87, 54.84, 48.24, 40.52, 32.48, 19.28, 14.34. HRMS (ESI, positive ion mode, m/z): [M]<sup>3+</sup> calcd for [C<sub>51</sub>H<sub>49</sub>O<sub>3</sub>N<sub>9</sub>ZnClPt]<sup>3+</sup>, 376.4190; found, 376.4185.

ZnPt-P2(83% yield): <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 600MHz): δ (ppm) 1.06 (t, 3H, CH<sub>3</sub>-H), 1.62 (s, 2H, CH<sub>2</sub>-H), 1.91 (s, 2H, CH<sub>2</sub>-H), 4.08 (t, 2H, OCH<sub>2</sub>-H), 4.60(s, 6H, NH<sub>3</sub>-H), 4.69 (s, 6H, Py-CH<sub>3</sub>-H), 7.39 (s, 2H, Ph-H), 8.08(s, 2H, Ph-H), 8.32 (d, 2H, Ph-H), 8.35 (d, 4H, Py-H), 8.94 (t, 10H,β-H+Py-H+Ph-H), 9.40 (s, 4H, β-H), <sup>13</sup>C NMR (151 MHz, DMSO) δ 159.06, 158.96, 151.04, 149.85, 148.27, 148.12, 144.07, 135.78, 135.28, 133.76, 133.03, 132.62, 132.29, 131.88, 131.25, 122.99, 119.93, 115.54, 113.26, 67.96, 48.20, 40.53, 31.49, 19.43, 14.34. HRMS (ESI, positive ion mode, m/z): [M]<sup>3+</sup> calcd for [C<sub>49</sub>H<sub>45</sub>ON<sub>9</sub>ZnClPt]<sup>3+</sup>, 356.4119; found, 356.4120.

ZnPt-P3(80% yield): <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 600MHz): δ (ppm) 4.60(s, 6H, NH<sub>3</sub>-H), 4.70 (s, 6H, Py-CH<sub>3</sub>-H), 7.80-7.99(m, 5H, Ph-H), 8.21 (d, 2H, Ph-H), 8.38 (d, 4H, Py-H), 8.85-9.10 (m, 10H, β-H+Py-H+Ph-H), 9.44 (d, 4H, β-H), <sup>13</sup>C NMR (151 MHz, DMSO) δ 162.79, 158.92, 150.63, 149.86, 148.31, 148.20, 144.60, 144.08, 135.29, 134.61, 133.59, 133.09, 132.62, 132.34, 132.02, 131.25, 127.32, 122.89, 120.10, 115.62, 48.34, 48.22, 36.28, 34.84, 31.26.

HRMS (ESI, positive ion mode, m/z): [M]<sup>3+</sup> calcd for [C<sub>45</sub>H<sub>37</sub>N<sub>9</sub>ZnClPt]<sup>3+</sup>, 332.3928; found, 332.3928.

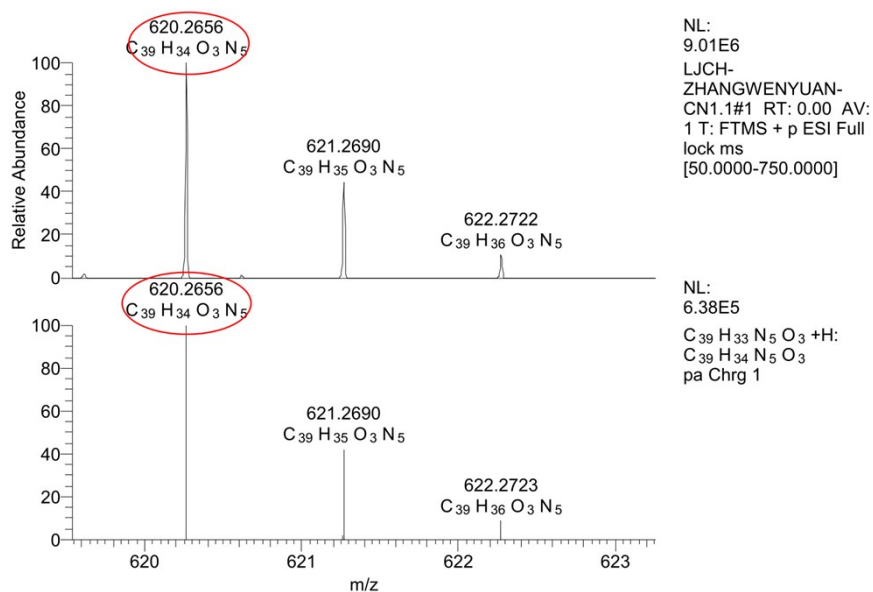


Figure S1. HRMS of compound 4.

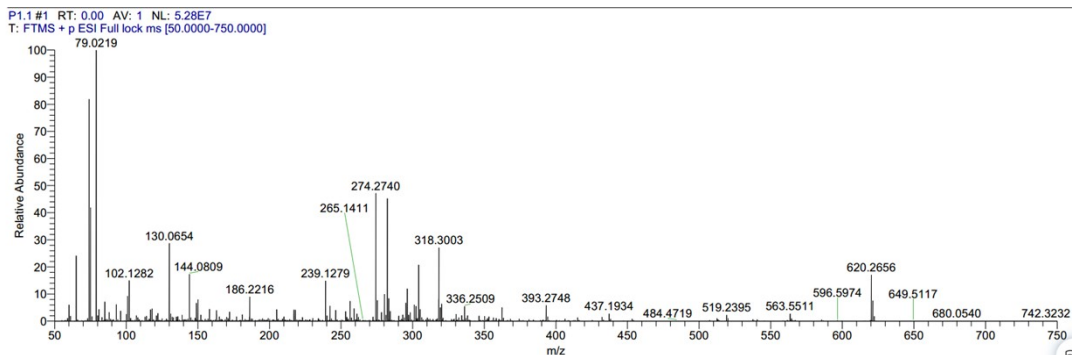


Figure S2. Full spectrum of compound 4 by HRMS

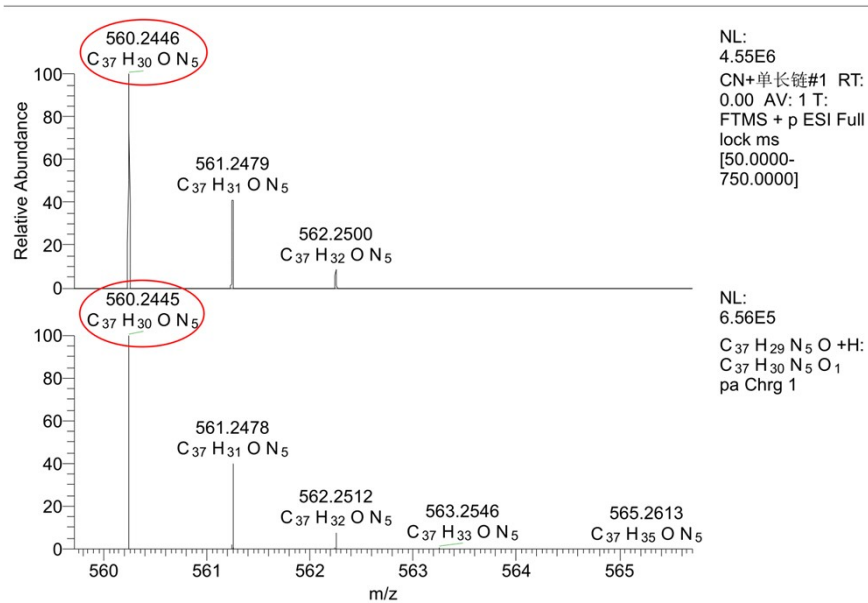


Figure S3. HRMS of compound 5.

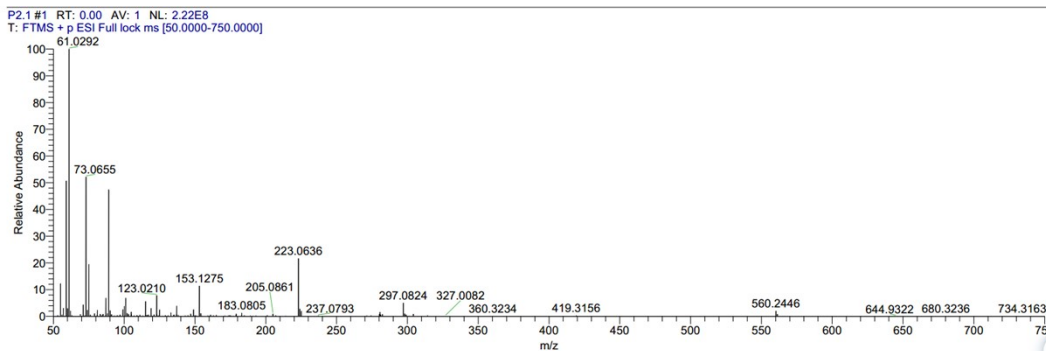


Figure S4. Full spectrum of compound 5 by HRMS

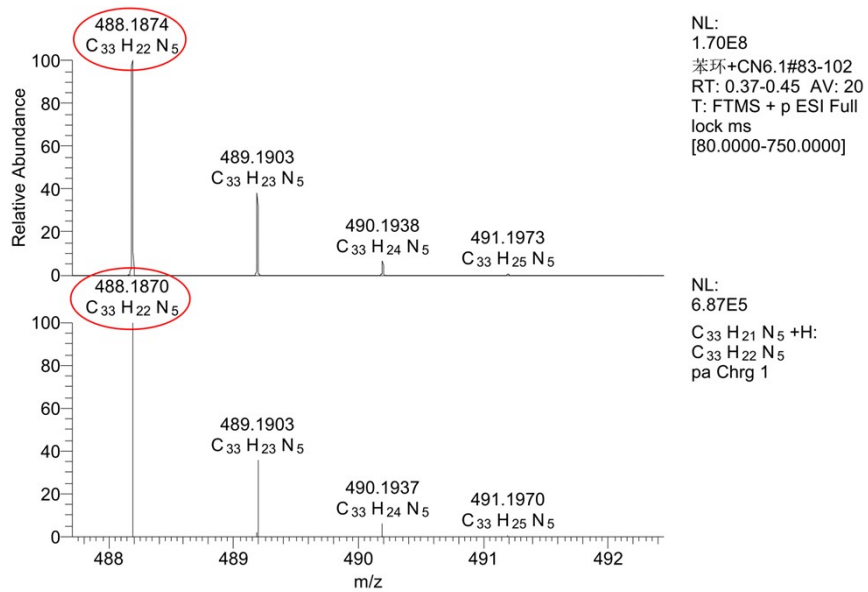


Figure S5. HRMS of compound 6.

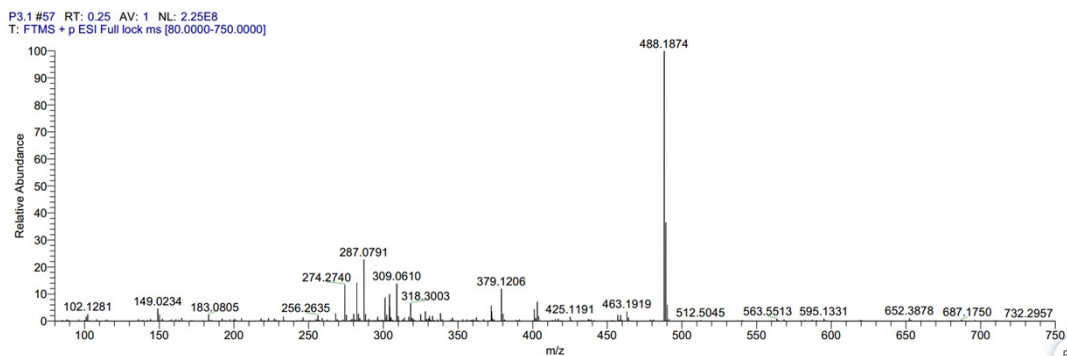


Figure S6. Full spectrum of compound 6 by HRMS

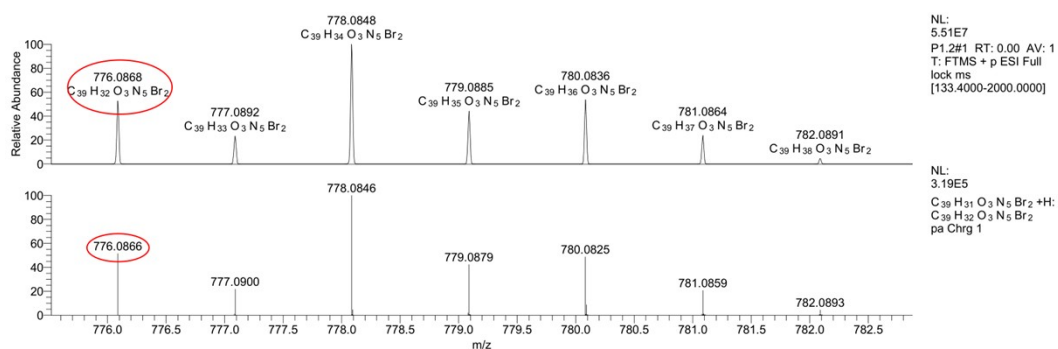


Figure S7. HRMS of compound 7.

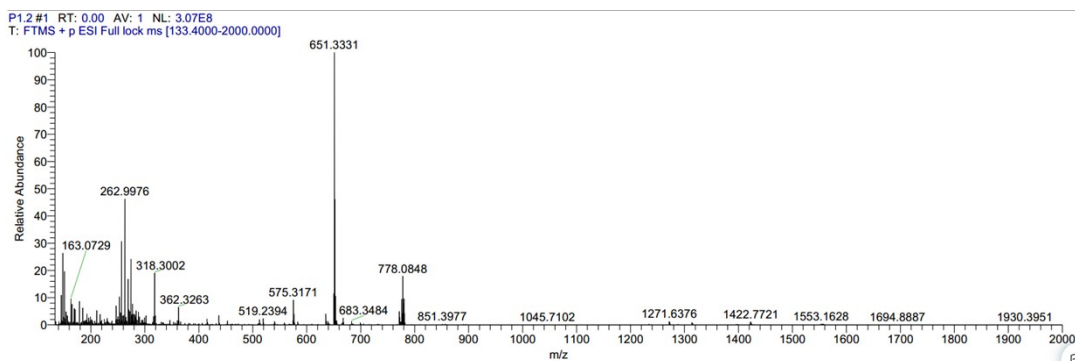


Figure S8. Full spectrum of compound 7 by HRMS

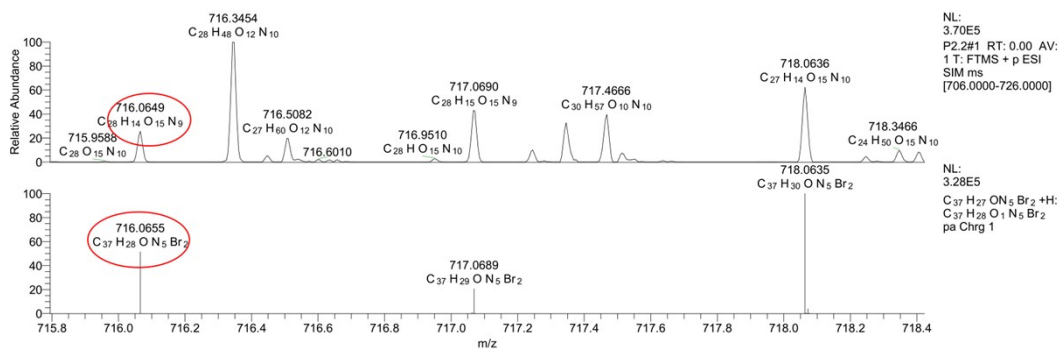




Figure S9. HRMS of compound 8.

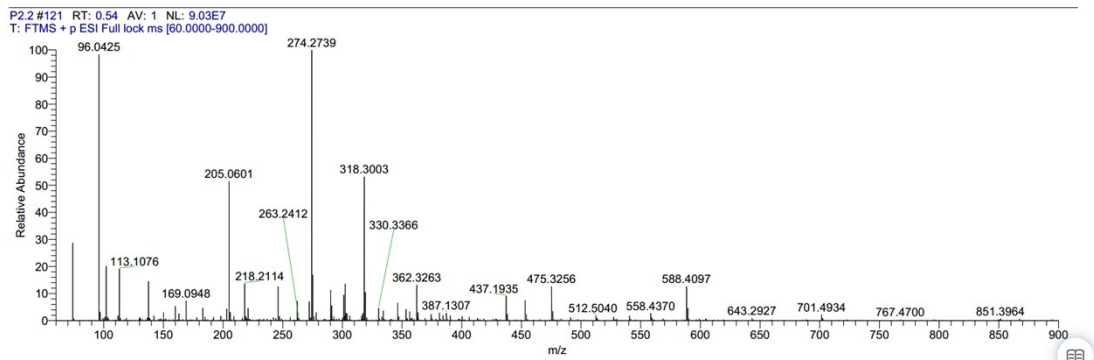


Figure S10. Full spectrum of compound 8 by HRMS

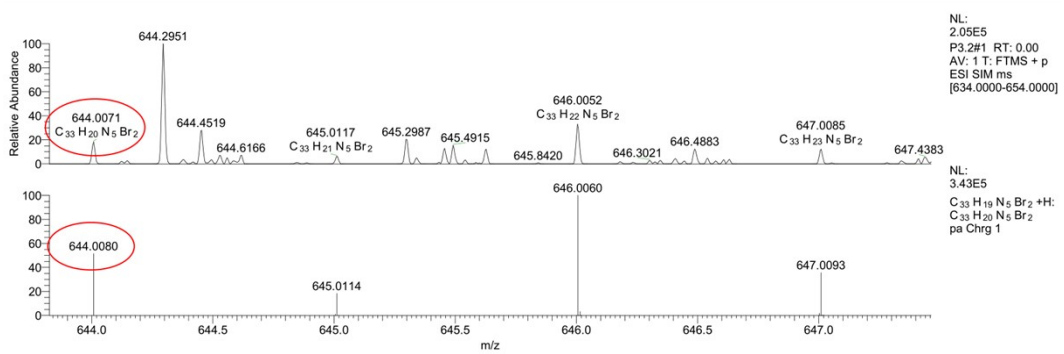


Figure S11. HRMS of compound 9.

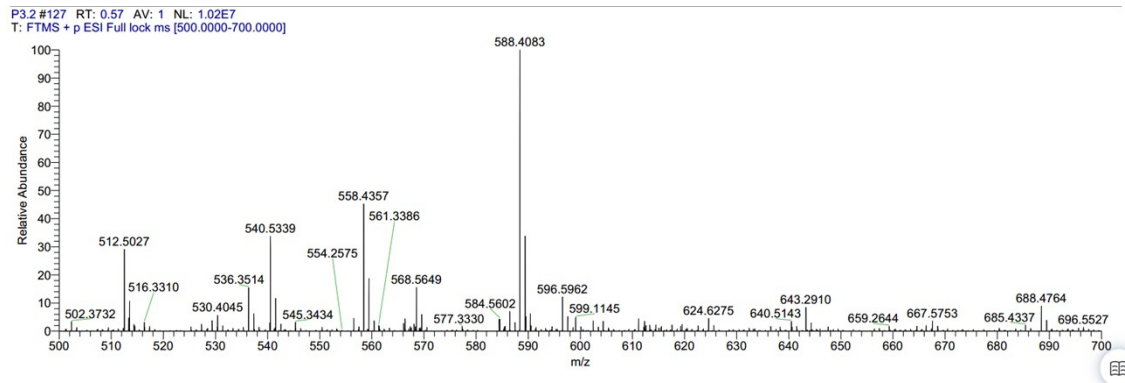


Figure S12. Full spectrum of compound 9 by HRMS

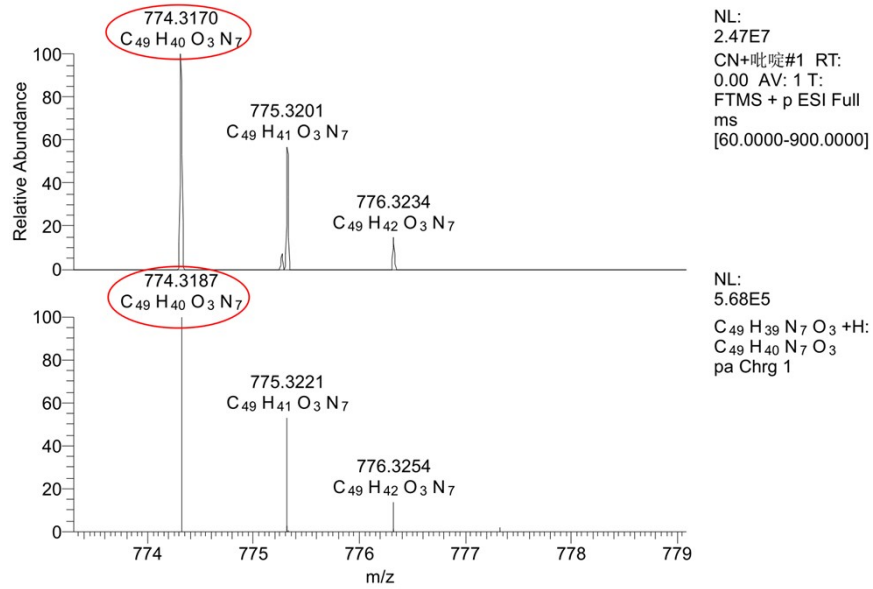


Figure S13. HRMS of compound 10.

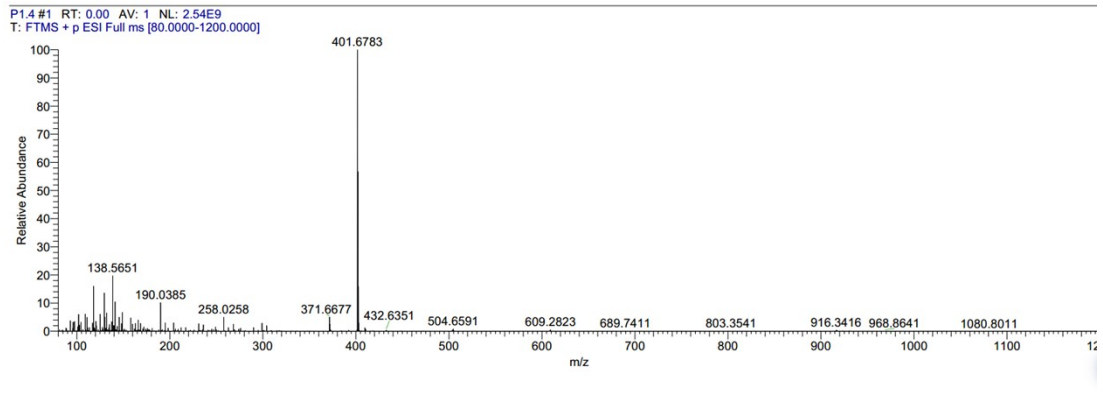


Figure S14. Full spectrum of compound 10 by HRMS

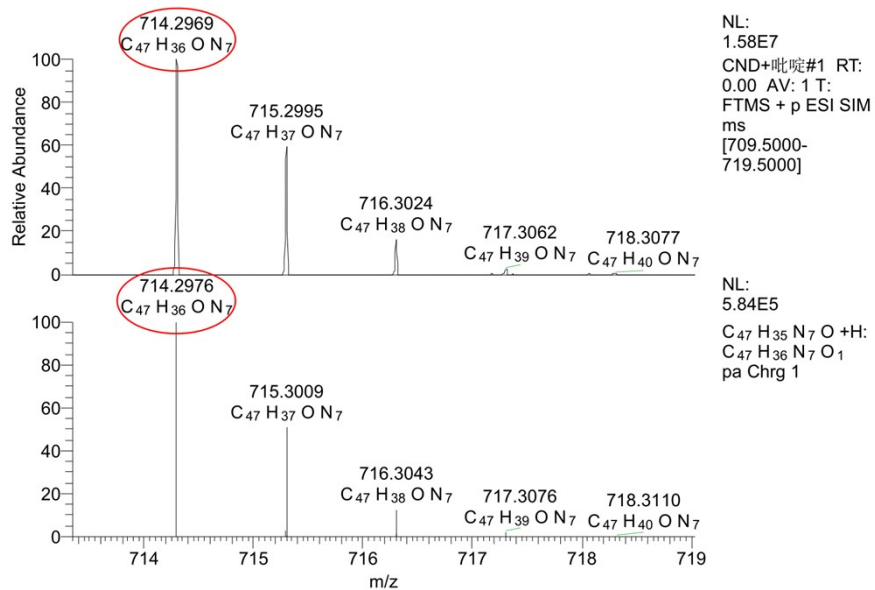


Figure S15. HRMS of compound 11.

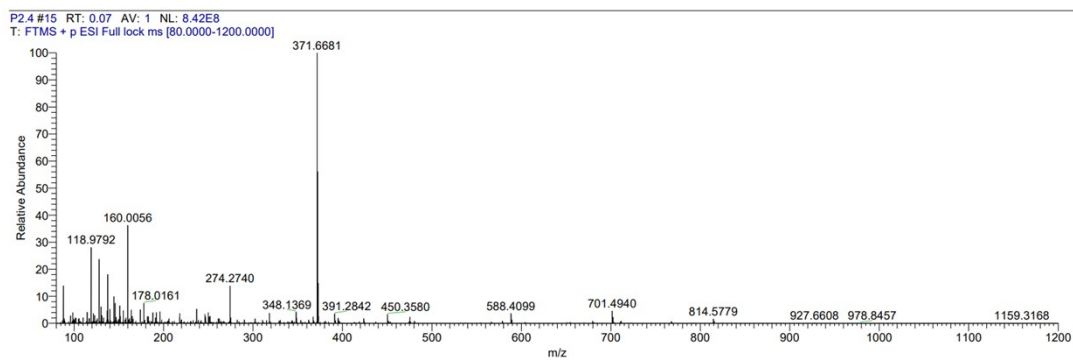


Figure S16. Full spectrum of compound 11 by HRMS

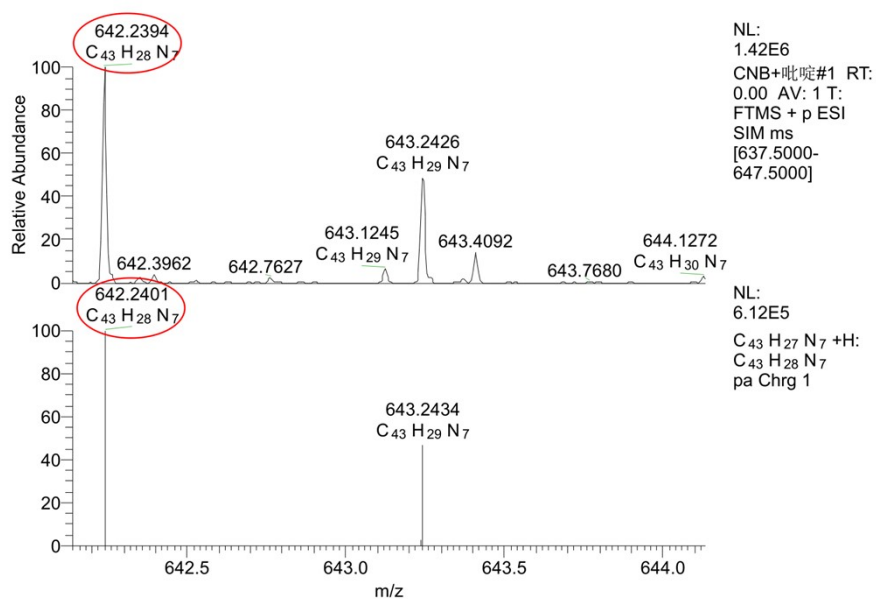


Figure S17. HRMS of compound 12.

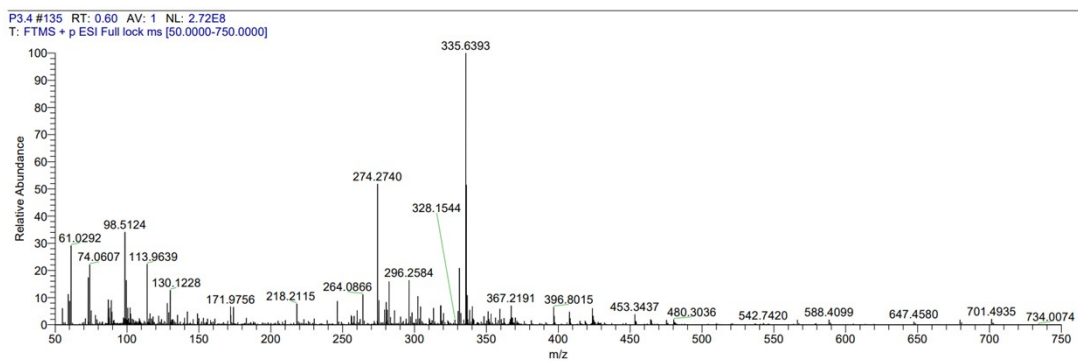


Figure S18. Full spectrum of compound 12 by HRMS

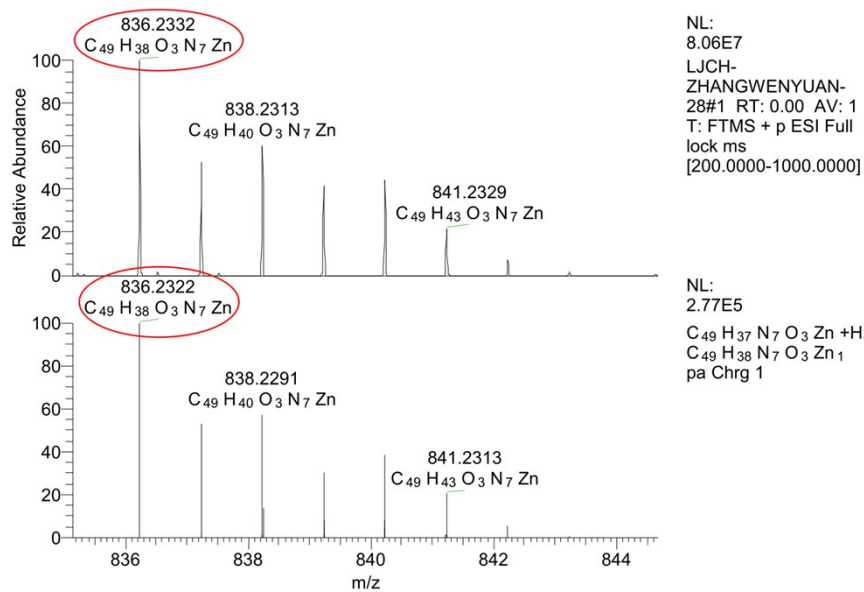


Figure S19. HRMS of compound 13.

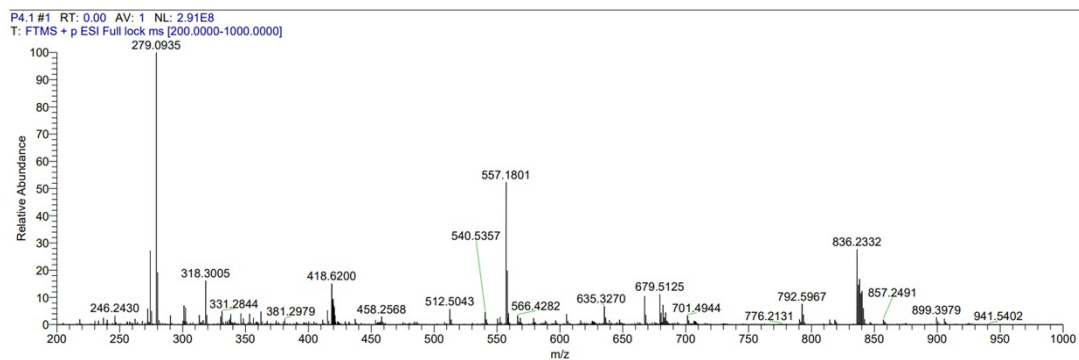


Figure S20. Full spectrum of compound 13 by HRMS

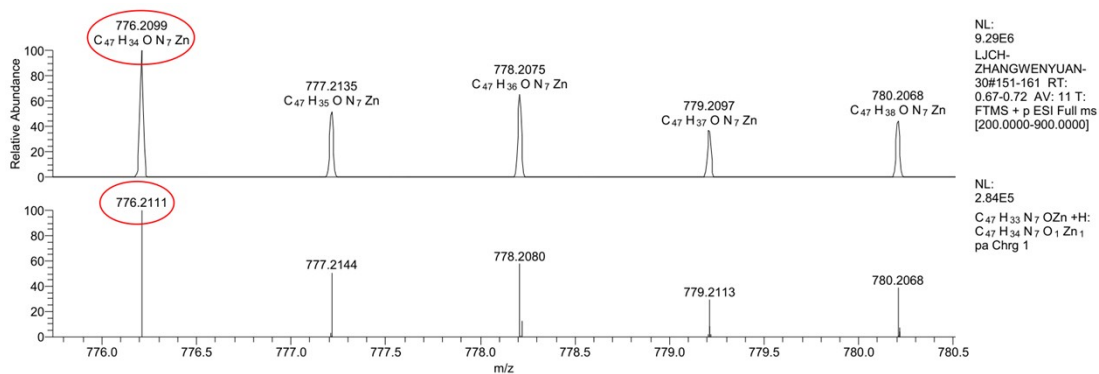


Figure S21. HRMS of compound 14

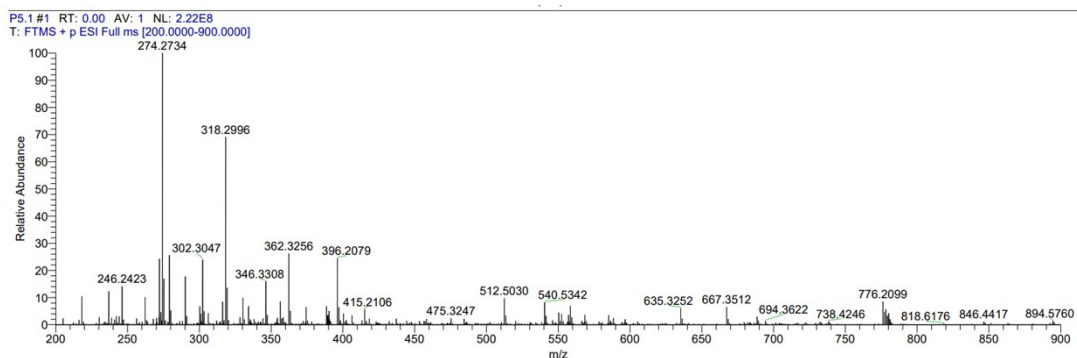


Figure S22. Full spectrum of compound 14 by HRMS

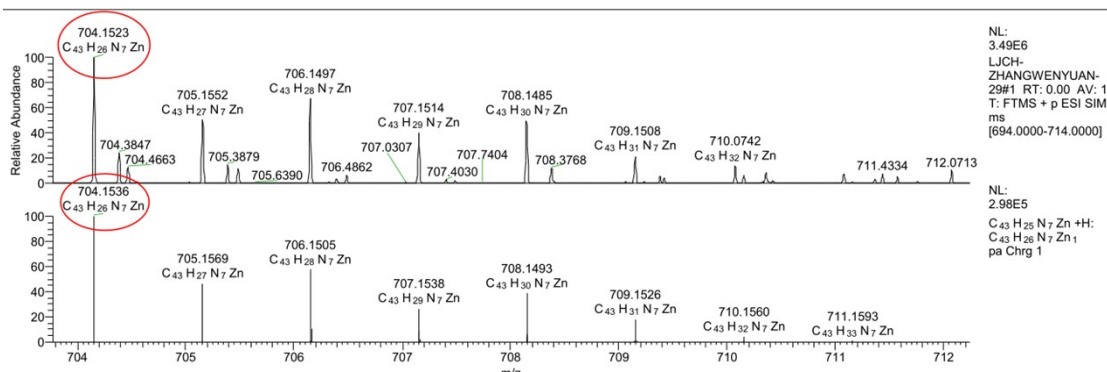


Figure S23. HRMS of compound 15

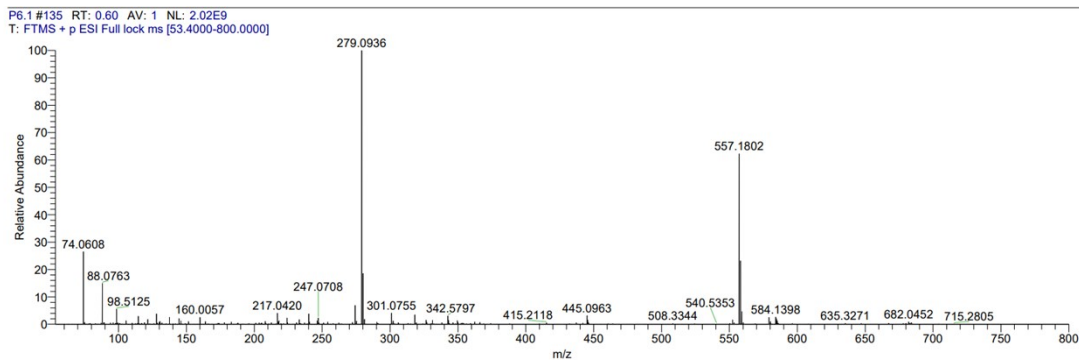


Figure S24. Full spectrum of compound 15 by HRMS

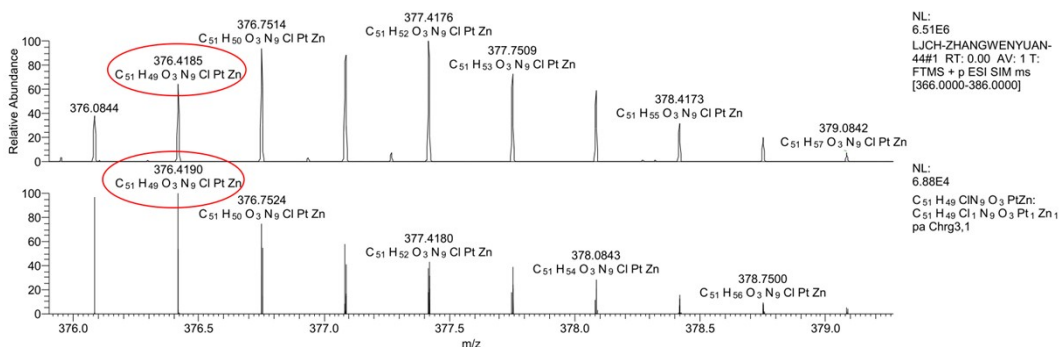


Figure S25. HRMS of ZnPt-P1

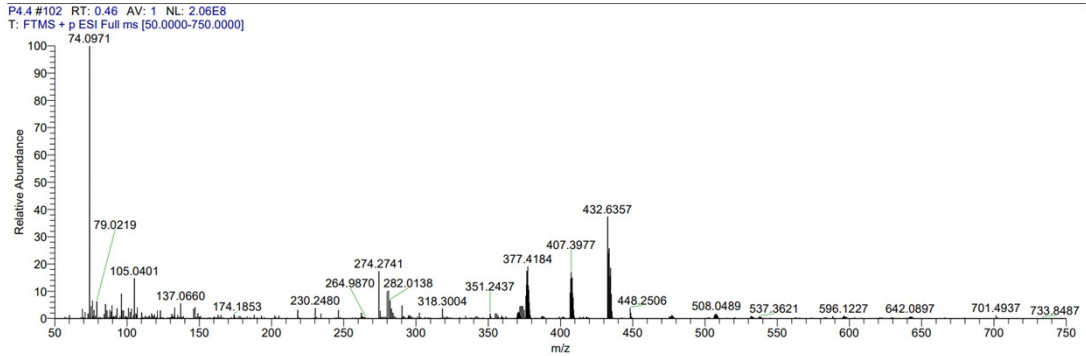


Figure S26. Full spectrum of ZnPt-P1 by HRMS

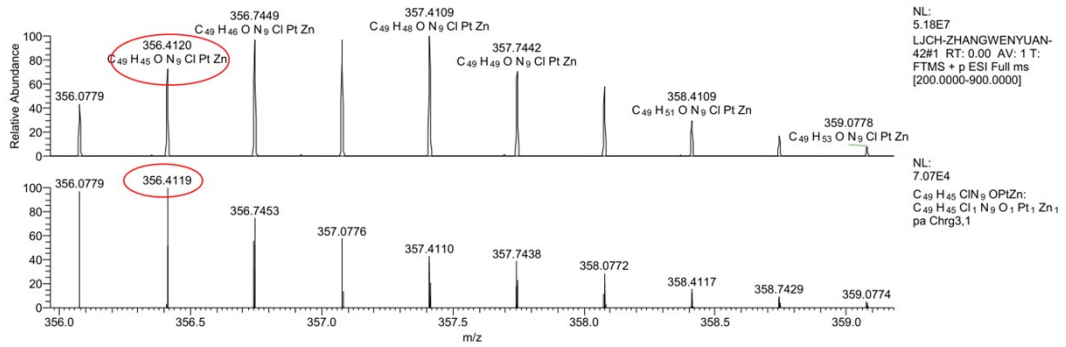


Figure S27. HRMS of ZnPt-P2

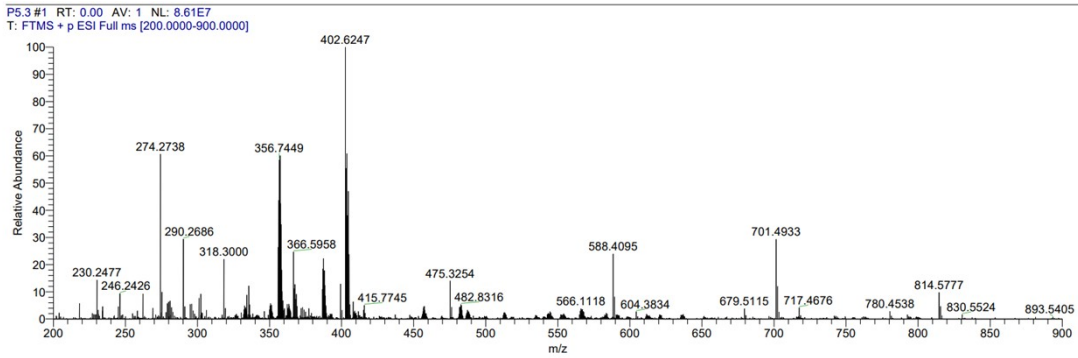


Figure S28. Full spectrum of ZnPt-P2 by HRMS

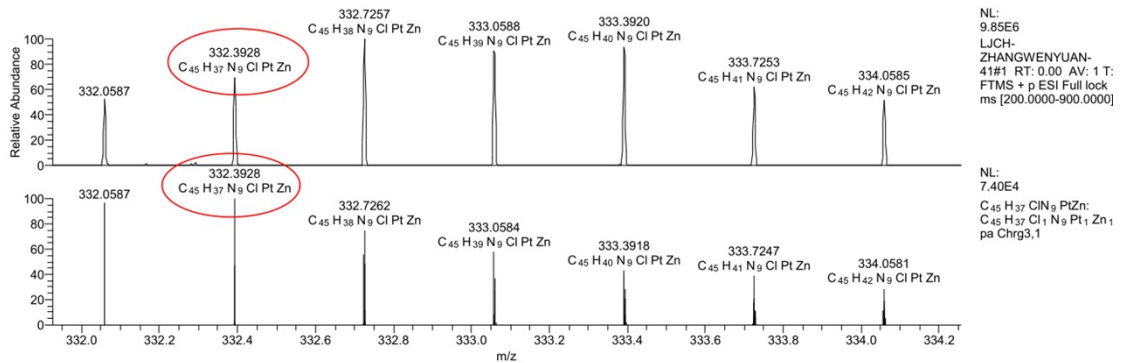


Figure S29. HRMS of ZnPt-P3

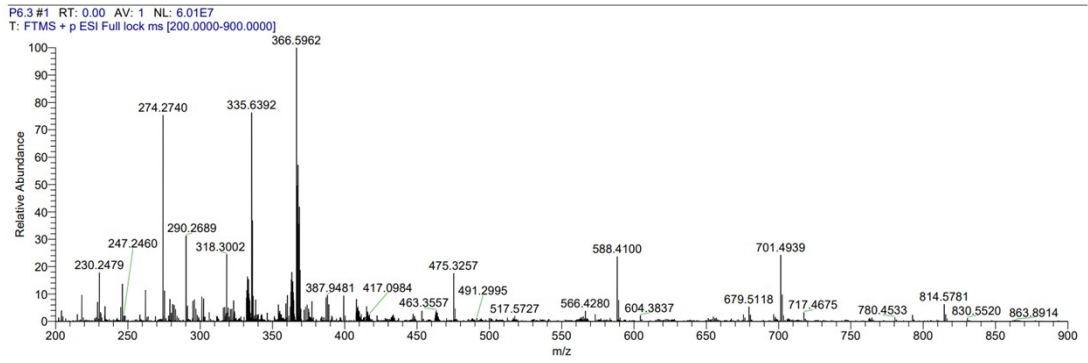


Figure S30. Full spectrum of ZnPt-P3 by HRMS

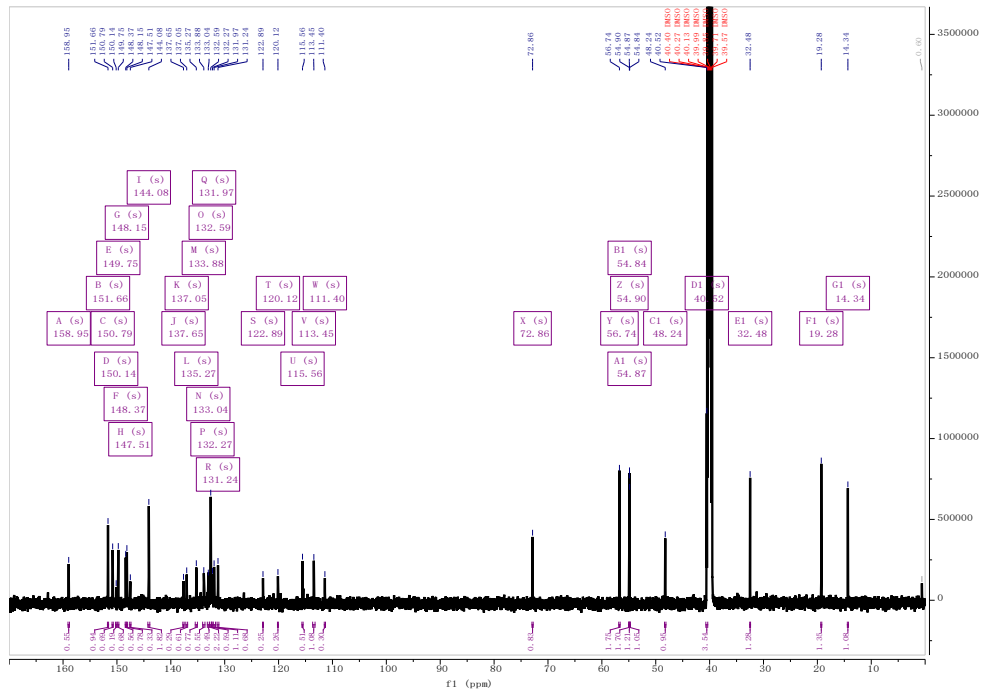


Figure S31. Spectrum of ZnPt-P1 by <sup>13</sup>C-NMR

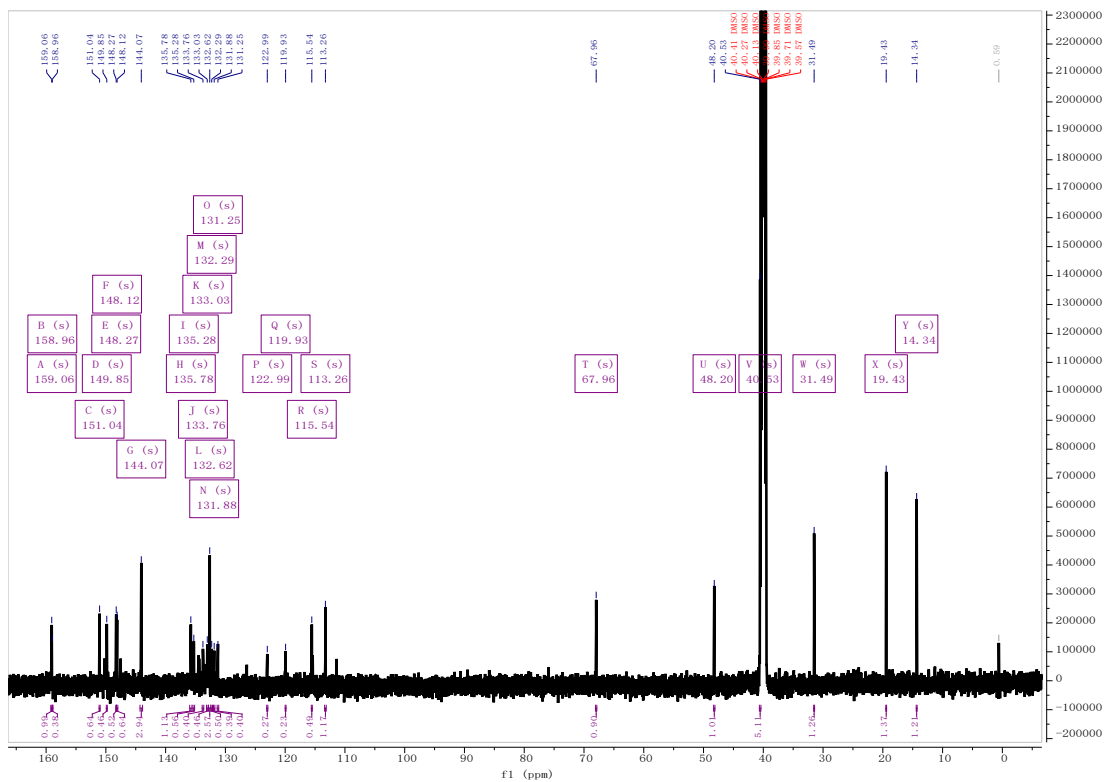


Figure S32. Spectrum of ZnPt-P2 by  $^{13}\text{C}$ -NMR

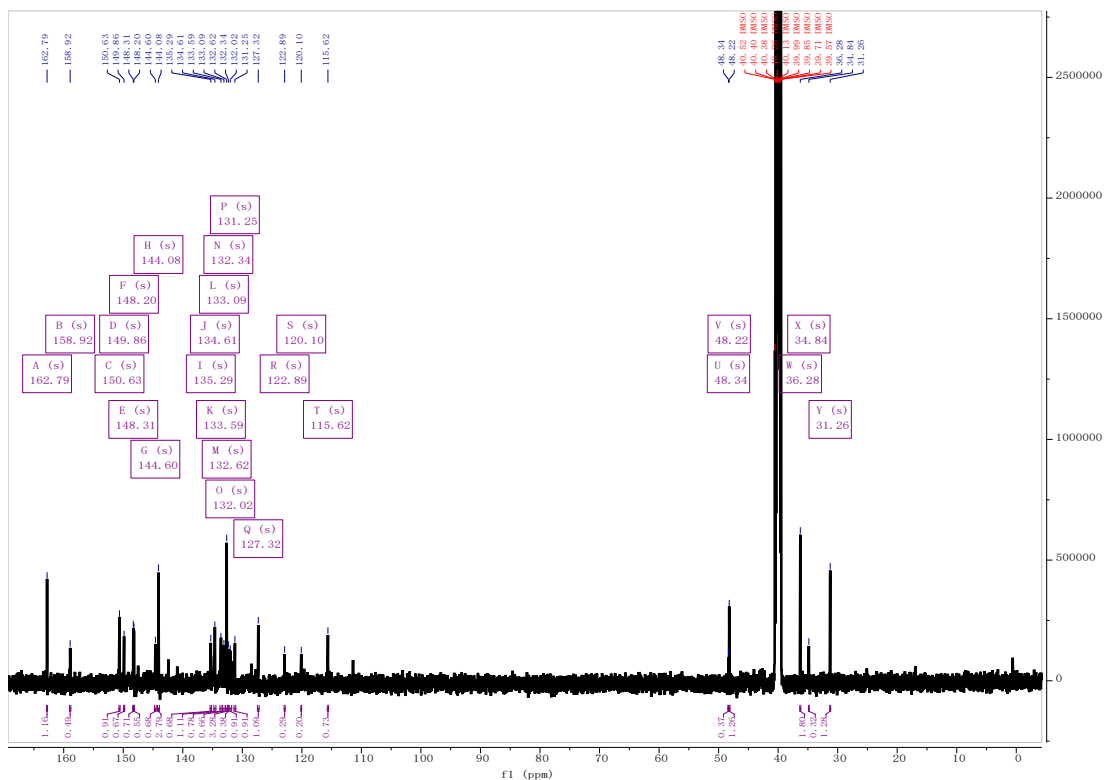
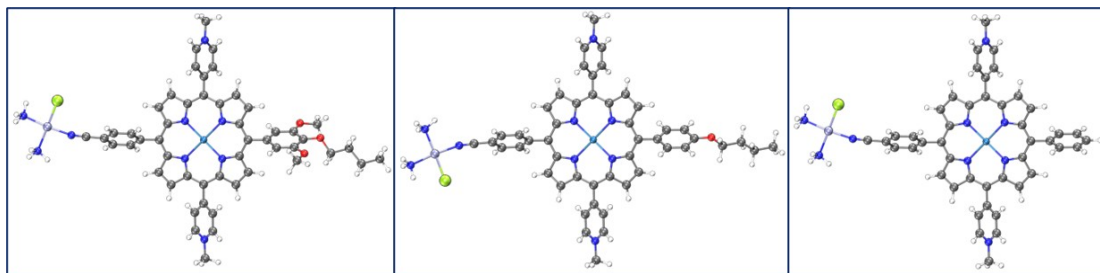


Figure S33. Spectrum of ZnPt-P3 by  $^{13}\text{C}$ -NMR



## Results and Discussion



**Figure S34.** Simulation molecular optimization diagram of ZnPt-P1~ZnPt-P3

**Table S1.** Vertical excitation energies ( $\Delta E_v$ , eV) of low-lying singlet and triplet states of ZnPt-P1 calculated at the minimum value of  $S_0$  optimized by PBE0-D3 (BJ)/6-31G(d,p) theory

State	$\Delta E_v$	Transition	% weight	f (L)
$S_0$				
$S_1$	1.2360	H $\rightarrow$ L	99.0	0.02910
$S_2$	1.3597	H-1 $\rightarrow$ L	98.3	0.02140
$S_3$	1.7863	H $\rightarrow$ L+1	98.3	0.00090
$S_4$	1.9041	H $\rightarrow$ L+2	64.3	
		H-1 $\rightarrow$ L+2	18	0.07250
$T_1$	1.0858	H $\rightarrow$ L	81.3	
		H-2 $\rightarrow$ L	6.6	
		H-3 $\rightarrow$ L	5.9	
$T_2$	1.2448	H-1 $\rightarrow$ L	68.5	
		H-3 $\rightarrow$ L	13.0	
		H-2 $\rightarrow$ L	7.7	
$T_3$	1.4454	H-2 $\rightarrow$ L	39.1	
		H-1 $\rightarrow$ L	20.7	
		H-3 $\rightarrow$ L	11.7	
		H $\rightarrow$ L+2	8.9	
$T_4$	1.5708	H-3 $\rightarrow$ L	41.5	
		H-2 $\rightarrow$ L	24.9	
		H $\rightarrow$ L	10.8	
		H-1 $\rightarrow$ L	6.0	

**Table S2.** Vertical excitation energies ( $\Delta E_v$ , eV) of low-lying singlet and triplet states of ZnPt-P2 calculated at the minimum value of  $S_0$  optimized by PBE0-D3 (BJ)/6-31G(d,p) theory

State	$\Delta E_v$	Transition	% weight	f (L)
$S_0$				
$S_1$	1.4304	H $\rightarrow$ L	98.1	0.08240

S <sub>2</sub>	1.9493	H-1→L	61.3	0.00450
		H→L+2	19.5	
		H→L+1	14.4	
S <sub>3</sub>	1.9722	H-1→L+1	83.4	0.00100
		H→L+	8.6	
		H-1→L	7.0	
S <sub>4</sub>	2.1365	H-2→L	84.6	0.21730
		H-1→L+2	10.6	
T <sub>1</sub>	1.1269	H → L	80.4	
T <sub>2</sub>	1.3617	H-2 → L	14.8	
		H-1→L	74.8	
		H→L+2	10.4	
T <sub>3</sub>	1.7095	H-1→L+3	6.7	
		H→L+2	44.0	
		H→L+1	23.9	
T <sub>4</sub>	1.7561	H-1→L	16.4	
		H-2→L+2	6.9	
		H-2→L	64.1	
		H→L	18.6	
		H-1→L+2	8.6	

**Table S3.** Vertical excitation energies ( $\Delta E_v$ , eV) of low-lying singlet and triplet states of ZnPt-P3 calculated at the minimum value of S<sub>0</sub> optimized by PBE0-D3 (BJ)/6-31G(d,p) theory

State	$\Delta E_v$	Transition	% weight	f (L)
S <sub>0</sub>				
S <sub>1</sub>	1.9377	H → L	87.8	0.26810
		H-1→L+2	9.1	
S <sub>2</sub>	2.0107	H-1→L	84.3	0.02330
		H→L+2	12.5	
S <sub>3</sub>	2.4218	H→L+1	95.2	0.02500
S <sub>4</sub>	2.4352	H-1→L+1	91.7	0.02130
		H-1→L+2	6.6	
T <sub>1</sub>	1.3595	H-1 → L	85.6	
		H → L+3	6.7	
T <sub>2</sub>	1.3932	H-1→L	78.6	
		H→L+2	10.6	
		H-1→L+3	7.5	
T <sub>3</sub>	1.8784	H→L+2	60.5	
		H→L+1	17.8	
		H-1→L	14.2	
T <sub>4</sub>	1.9893	H-1→L+2	69.1	
		H-1→L+1	18.8	

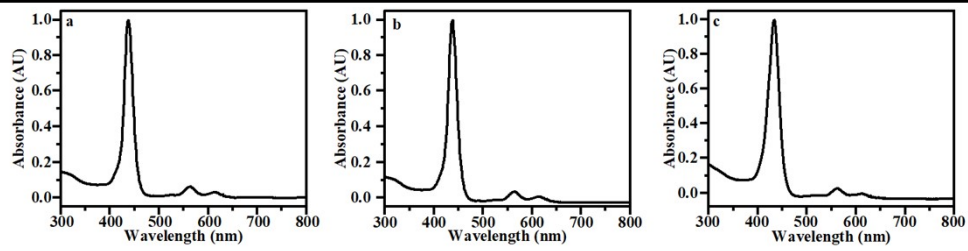


Figure S35. UV-Vis's absorption spectrums of ZnPt-P1(a), ZnPt-P2(b) and ZnPt-P3(c)

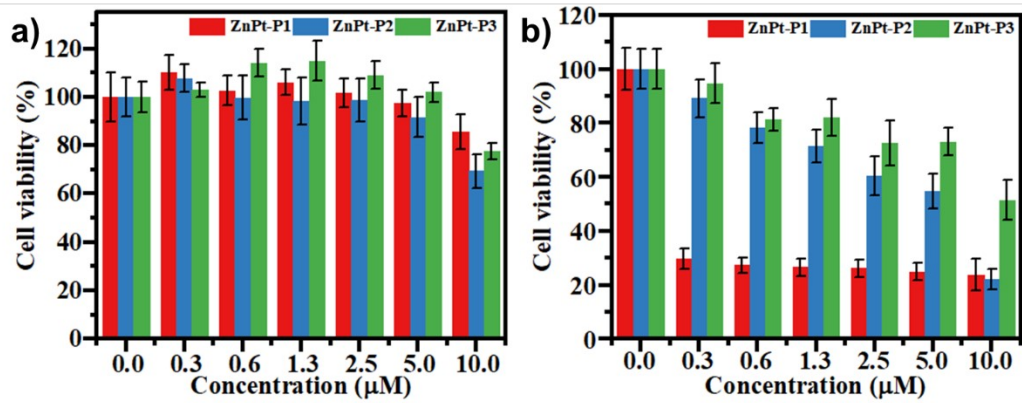
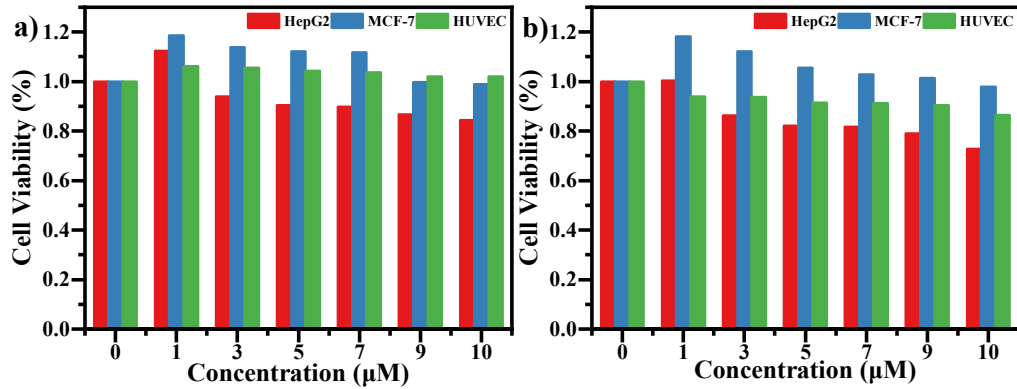
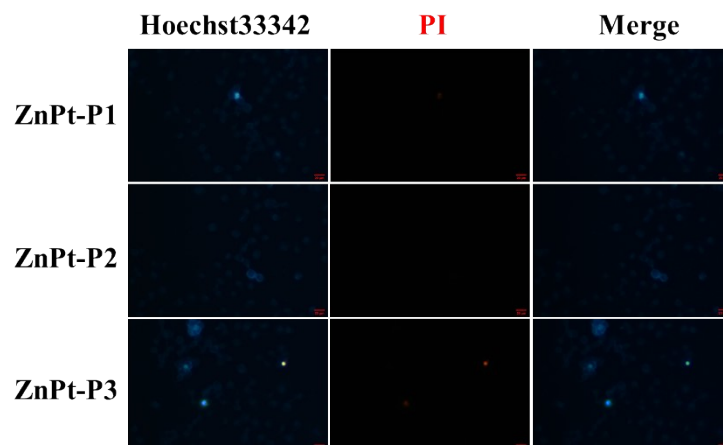


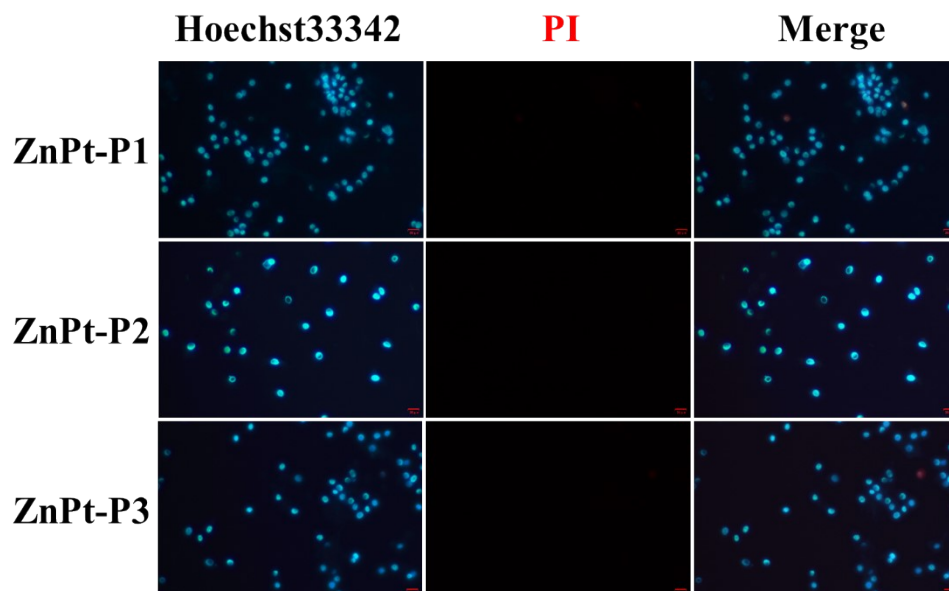
Figure S36. The in vitro cytotoxicity of ZnPt-P1, ZnPt-P2 and ZnPt-P3 on HepG2 cells in Dark (a) and Light (b) was detected by MTT assay.



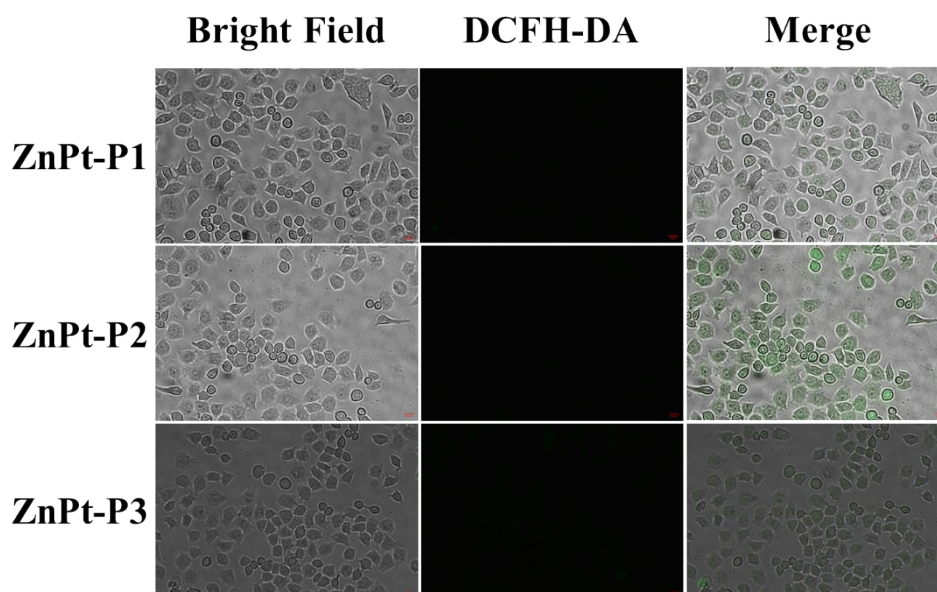
**Figure S37.** The in vitro cytotoxicity of H<sub>2</sub>TPyP on HepG2, MCF-7 and HUVEC cells in Dark (a) and Light (b) was detected by MTT assay.



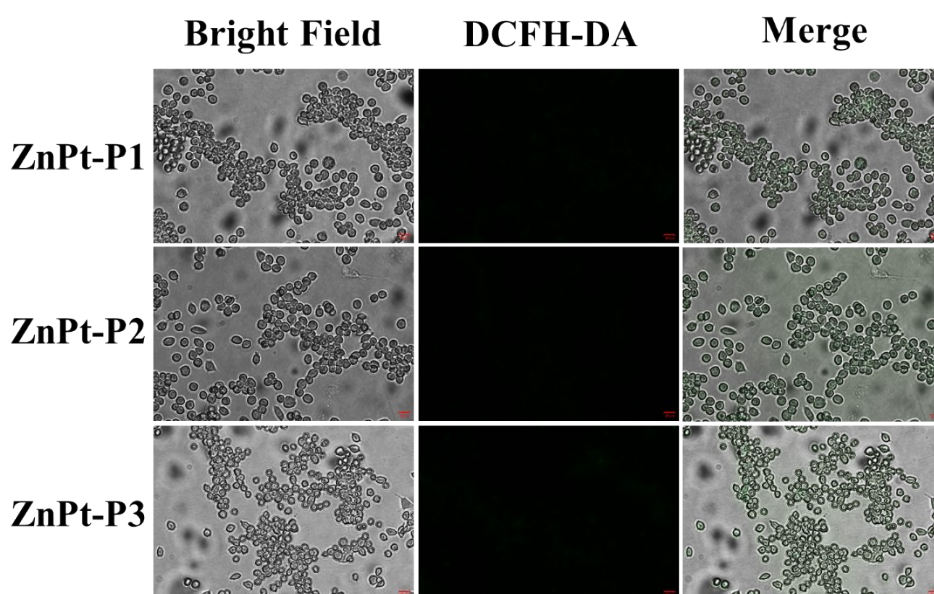
**Figure S38.** Fluorescence images of HepG2 cells in the ZnPt-P1~ZnPt-P3 groups stained with Hoechst 33342/PI for 24 hours under dark conditions



**Figure S39.** Fluorescence images of MCF-7 cells in the ZnPt-P1~ZnPt-P3 groups stained with Hoechst 33342/PI for 24 hours under dark conditions



**Figure S40.** HepG2 cells producing fluorescence microscope photos of ROS in ZnPT-P1 ~ ZnPT-P3 groups (dark)



**Figure S41.** MCF-7 cells producing fluorescence microscope photos of ROS in ZnPT-P1 ~ ZnPT-P3 groups (dark)

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