

Supplementary Information

Application of non-polar solvents to extractive electrospray ionization of 1-hydroxypyrene

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1. Materials and methods

1-OHP was purchased from Sigma-Aldrich. Methanol (HPLC grade) was provided by Burdick & Jackson (Muskegon, MI, USA). Organic solvents of methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 1-butanol (BuOH), 1-pentanol (PeOH), 1-hexanol (HeOH), benzene (BeNE), *o*-xylene (*o*-XyNE), *m*-xylene (*m*-XyNE), *p*-xylene (*p*-XyNE), *n*-pentane (PeNE) and *n*-hexane (HeNE) were GC standards and obtained from Tianjin Guangfu Fine Chemical Research Institute. Toluene (analytical reagent grade) was bought from Sinopharm Chemical Reagent Co. Ltd. Ultrapure water (resistivity 18.2 M Ω • cm) was supplied by a Barnstead Nanopure ultrapure water purification system (Thermo Scientific, USA). All chemicals were directly used without further treatment.

Stock solution of 1-OHP (100 mg L⁻¹) was prepared by dissolving 10.0 mg of 1-OHP in 100 mL of methanol, and stored in 20-mL brown vials in the dark at 4 °C. 50 μ g L⁻¹ of 1-OHP in methanol was prepared through serial dilution of 1-OHP stock solution with methanol.

A homemade EESI source (**Fig. S1**) was set up as described previously,^{1,2} *i.e.*, the distance *a* between the end-tips of the two sprays and the distance *b* between the spray tips and the MS inlet were about 1 and 10 mm, respectively. The angle α between the two sprays and the angle β between individual sprays and the MS inlet were around 60° and 150°, respectively.

This homemade EESI source was coupled to a commercial LTQ-XL mass spectrometer (Finnigan, San Jose, USA). The ESI voltage was set at – 4 kV (the mass

spectrometer worked in the negative ion detection mode); the temperature of the ion-transport capillary was 400 °C. The injection rates of ESI solvent and sample solution were set at 1 $\mu\text{L min}^{-1}$ and 4 $\mu\text{L min}^{-1}$, respectively. High purity nitrogen gas (purity $\geq 99.999\%$) was supplied from a gas cylinder and used for nebulizing ESI solvent and sample solution; the gas pressure was 1.2 MPa as read from the downstream gauge of the pressure regulator attached to the cylinder. The maximum ion injection time was set at 200 ms and the Automatic Gain Control (AGC) was enabled to regulate the number of ions injected in the cell. Helium gas was used as collision gas, and the pressure in the collision cell ranged from $0.82\text{--}0.83 \times 10^{-5}$ Torr according to the ion gauge. Before individual experiments, 20 $\mu\text{g L}^{-1}$ of 1-OHP in methanol was analyzed by EESI-MS/MS to assure the homemade source has worked properly.

2. The homemade EESI source

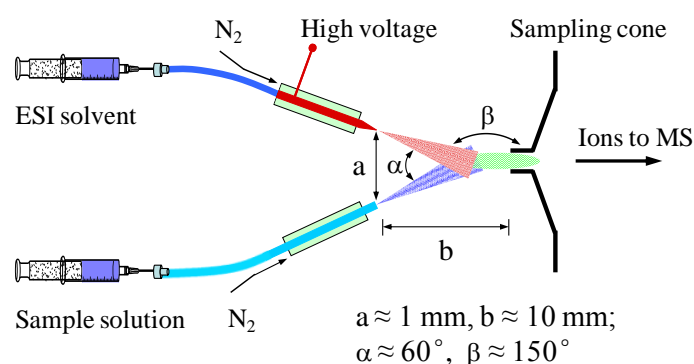
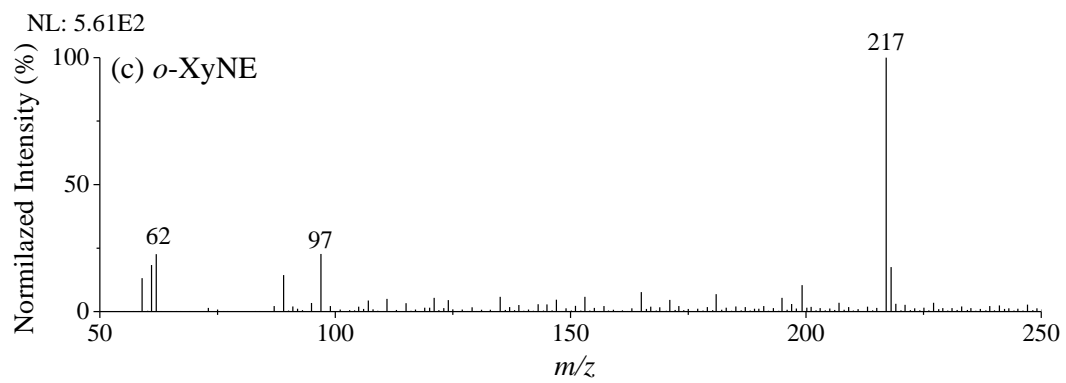
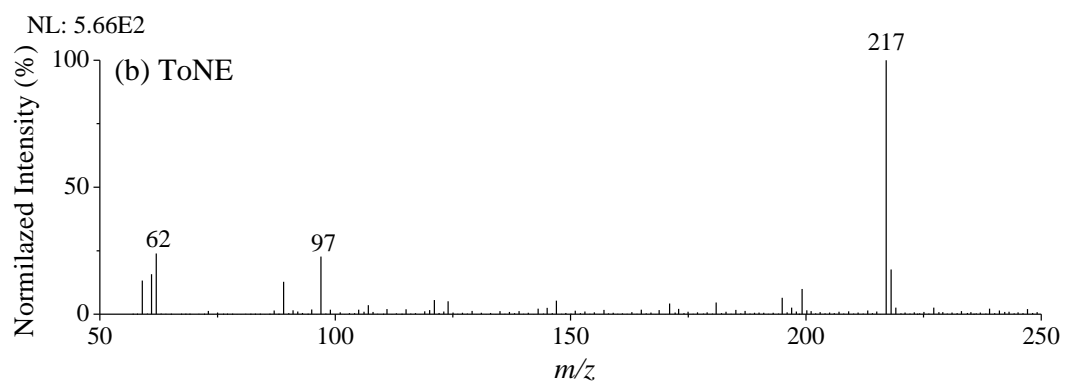
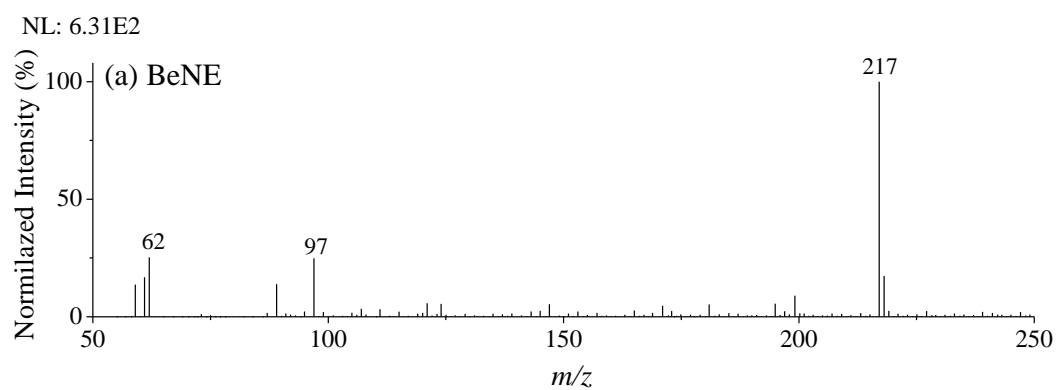


Fig. S1 Schematic diagram of the homemade EESI source.

3. EESI-MS spectra of 1-OHP water solution ($50 \mu\text{g L}^{-1}$) when six non-polar organic solvents were used as the primary ESI solvent, respectively.



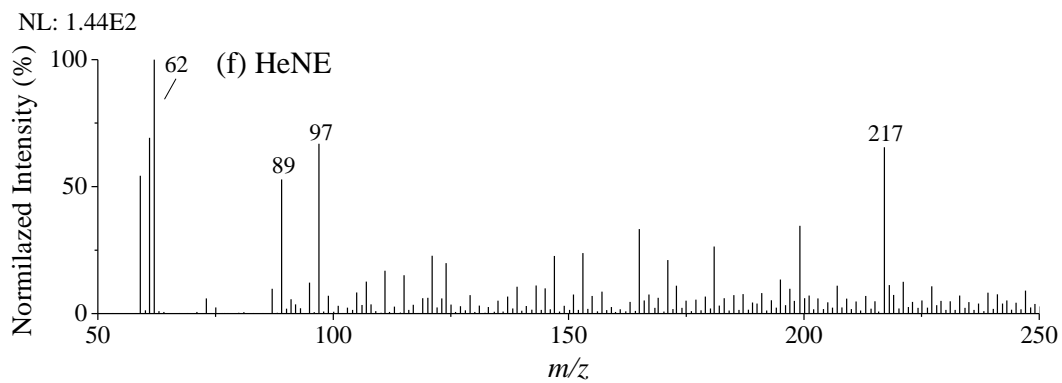
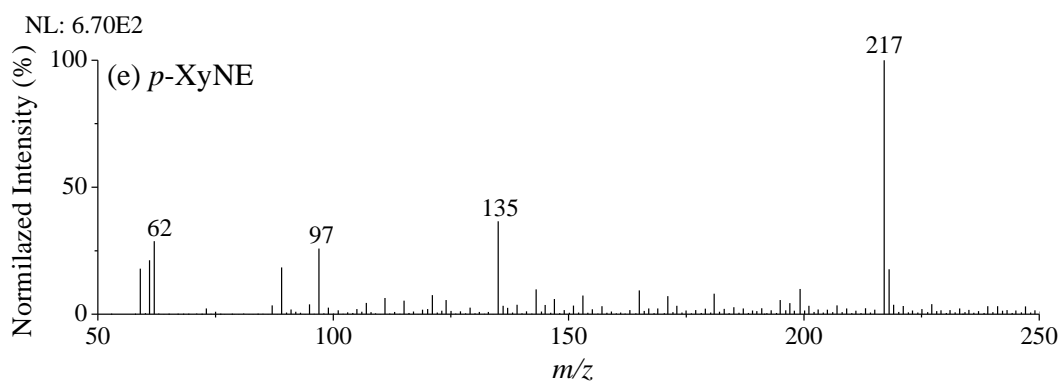
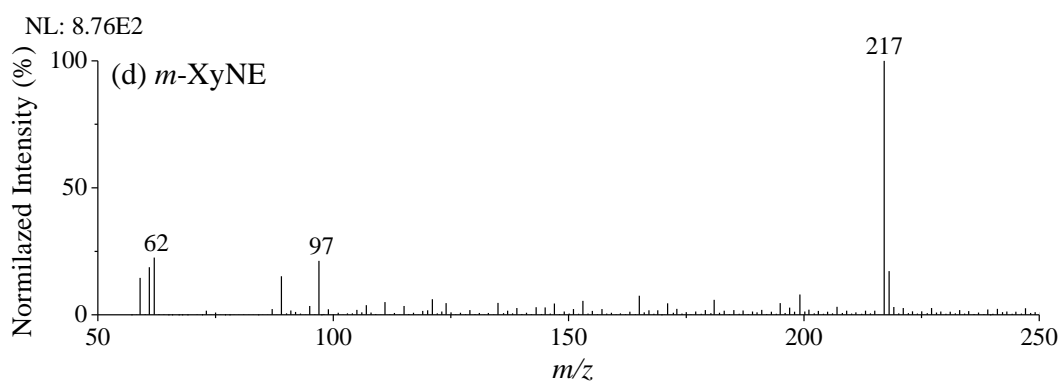


Fig. S2 EESI-MS spectra of 1-OHP water solution ($50 \mu\text{g L}^{-1}$) when BeNE (a), ToNE (b), *o*-XyNE (c), *m*-XyNE (d), *p*-XyNE (e) and HeNE (f) were used as the primary ESI solvent, respectively.

4. MS spectrum of 1-OHP water solution ($50 \mu\text{g L}^{-1}$) when only the water solution was introduced into the EESI source.

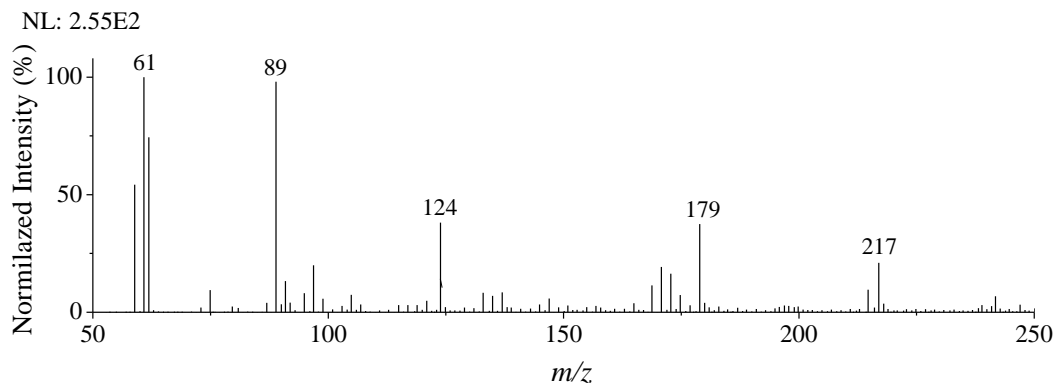
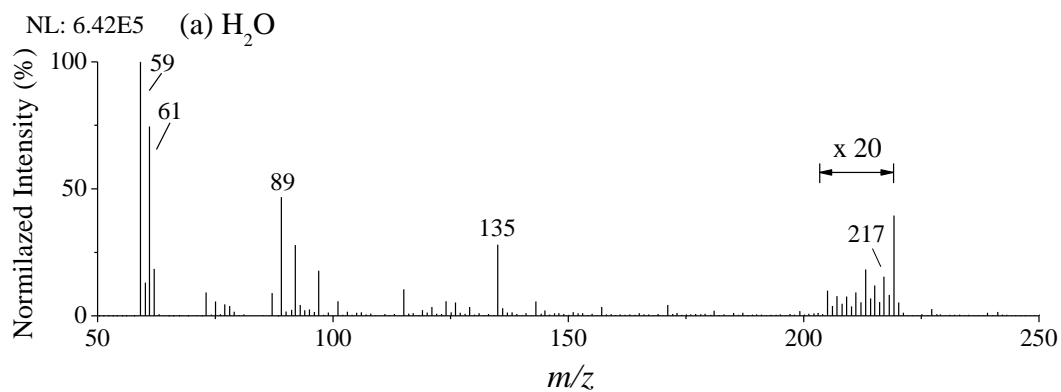
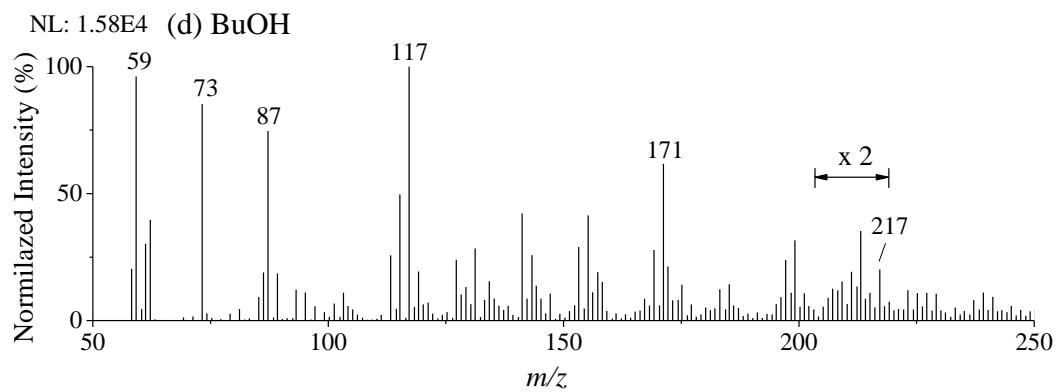
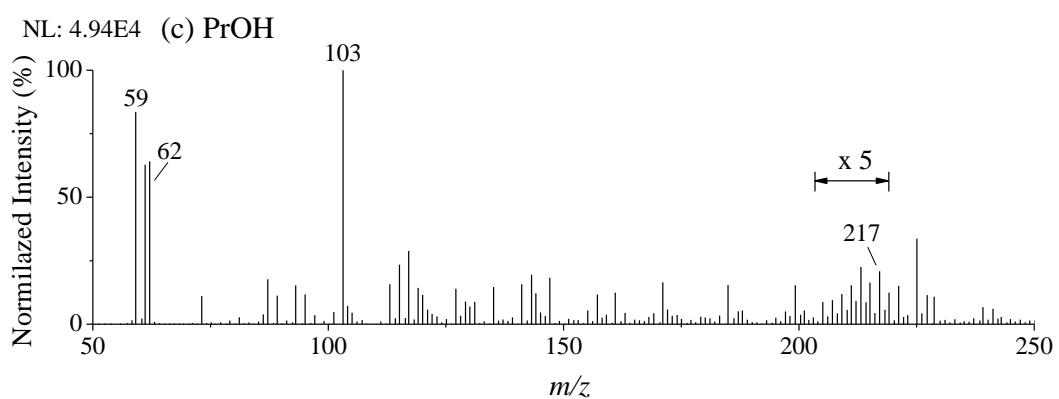
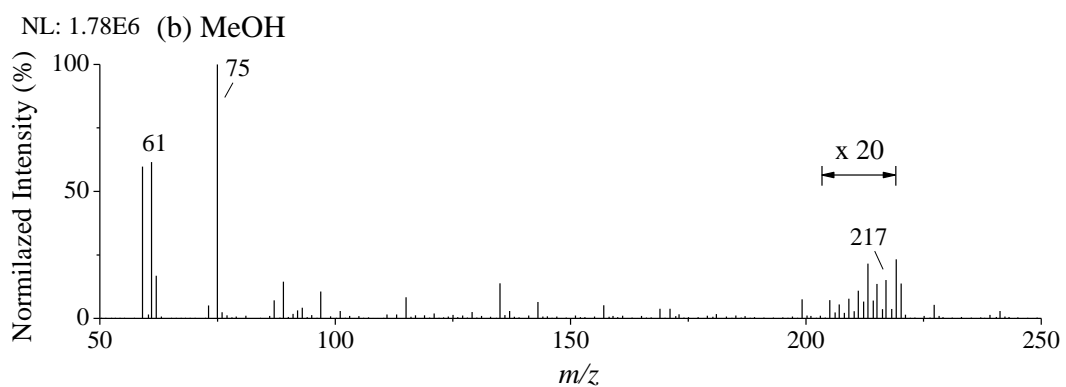


Fig. S3 MS spectrum of 1-OHP water solution ($50 \mu\text{g L}^{-1}$) when only the sample solution was introduced into the EESI source.

5. EESI-MS spectra of 1-OHP water solution ($50 \mu\text{g L}^{-1}$) when six polar solvents were used as the primary ESI solvent, respectively.





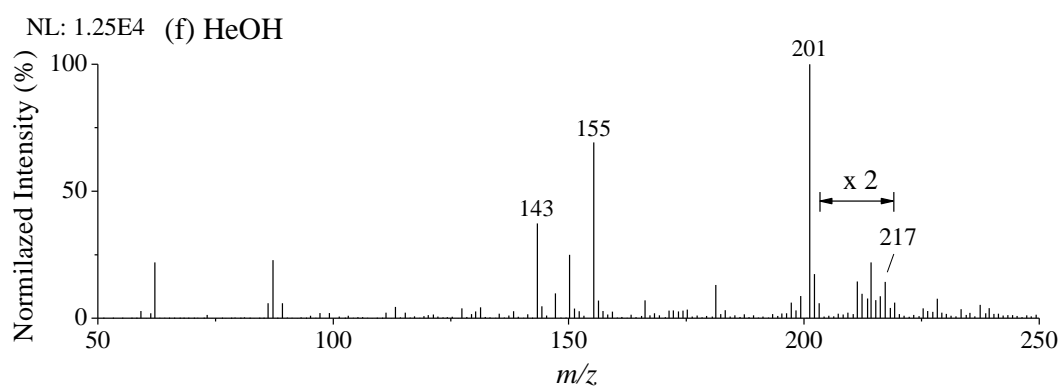
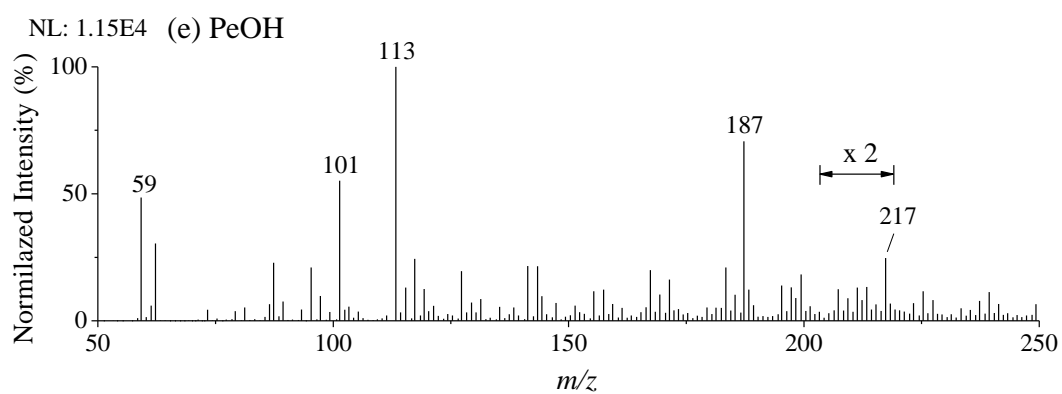
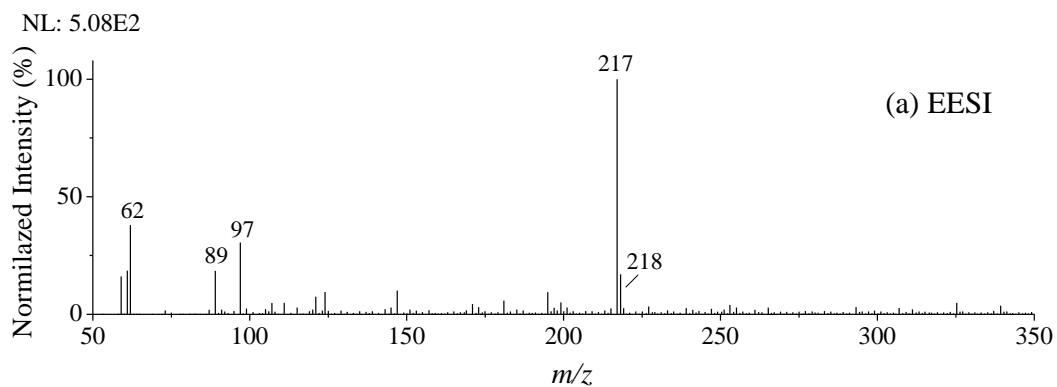


Fig. S4 EESI-MS spectra of 1-OHP water solution ($50 \mu\text{g L}^{-1}$) when water (a), MeOH (b), PrOH (c), BuOH (d), PeOH (e) and HeOH (f) were used as the primary ESI solvent, respectively.

6. EESI/ESI-MS spectra of different sample solutions ($50 \mu\text{g L}^{-1}$ of 1-OHP).



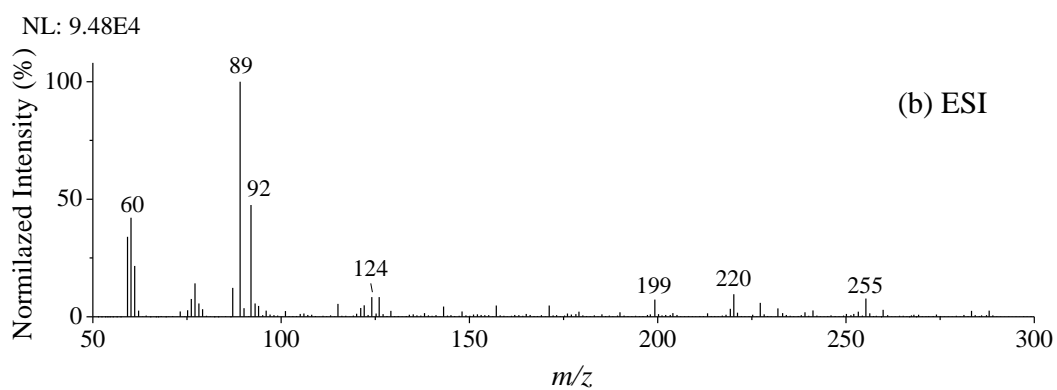


Fig. S5 EESI-MS (a) and ESI-MS (b) of 1-OHP water solution ($50 \mu\text{g L}^{-1}$); PeNE was used as the primary ESI solvent for EESI-MS analysis.

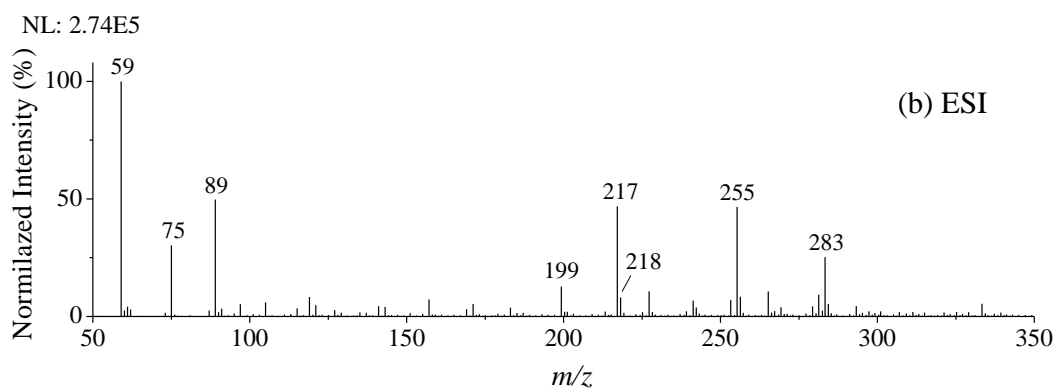
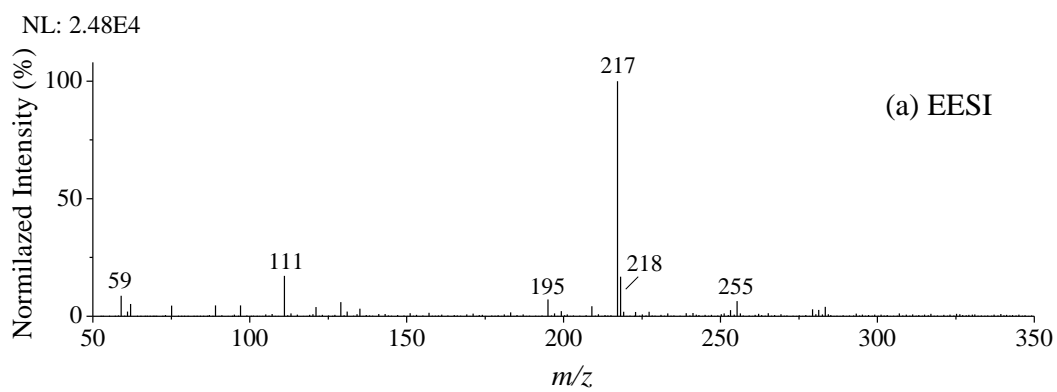


Fig. S6 EESI-MS (a) and ESI-MS (b) spectra of 1-OHP MeOH solution ($50 \mu\text{g L}^{-1}$);

PeNE was used as the primary ESI solvent for EESI-MS analysis.

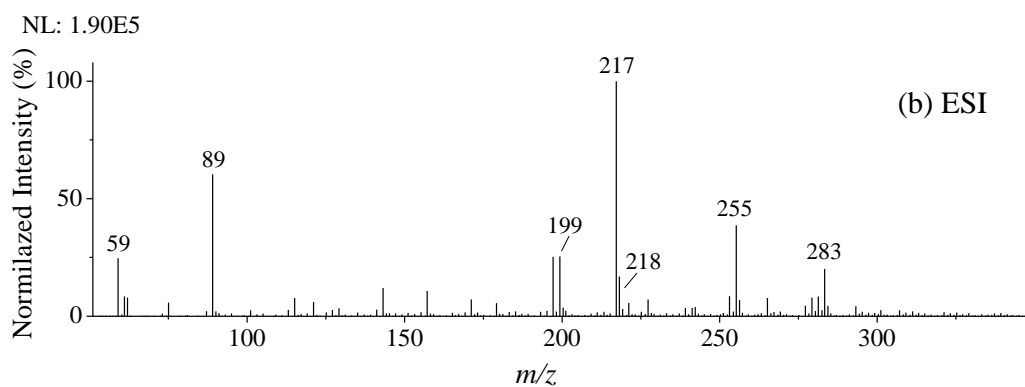
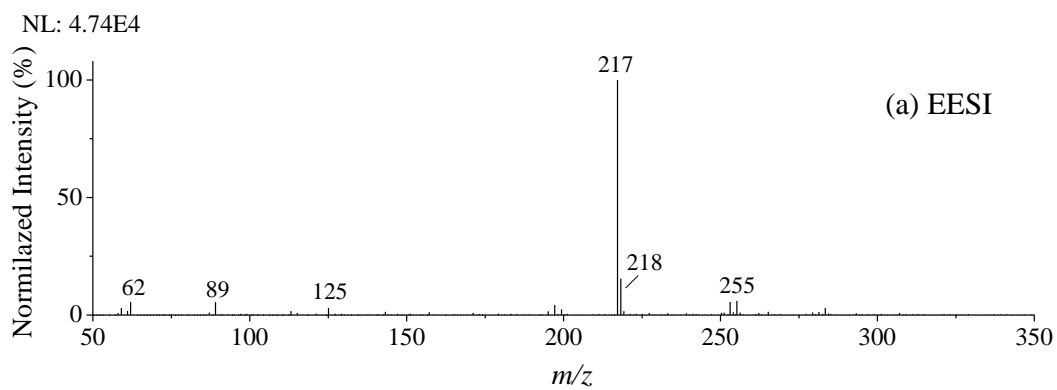


Fig. S7 EESI-MS (a) and ESI-MS (b) spectra of 1-OHP EtOH solution ($50 \mu\text{g L}^{-1}$);

PeNE was used as the primary ESI solvent for EESI-MS analysis.

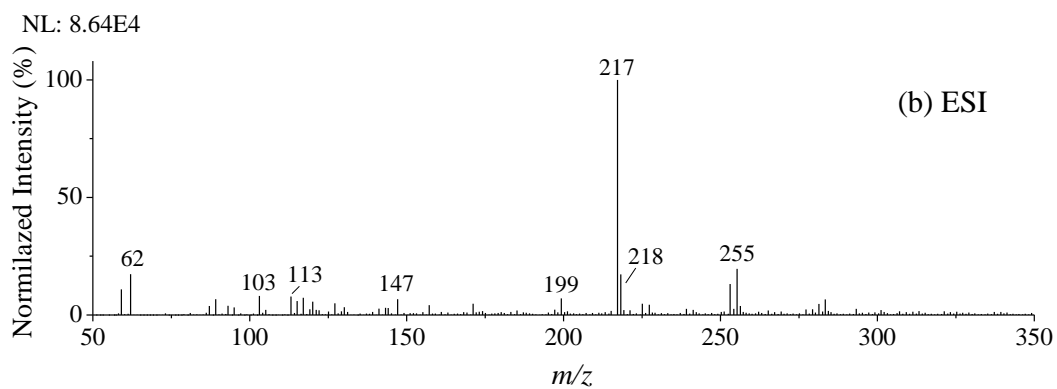
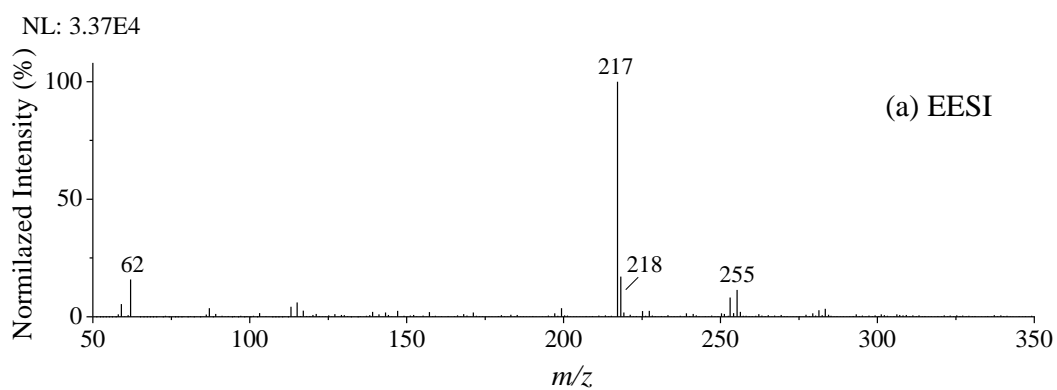
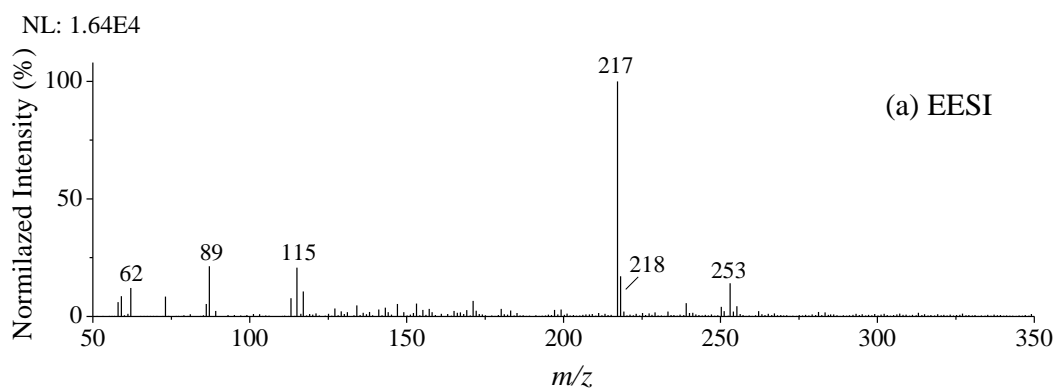


Fig. S8 EESI-MS (a) and ESI-MS (b) spectra of 1-OHP PrOH solution ($50 \mu\text{g L}^{-1}$);

PeNE was used as the primary ESI solvent for EESI-MS analysis.



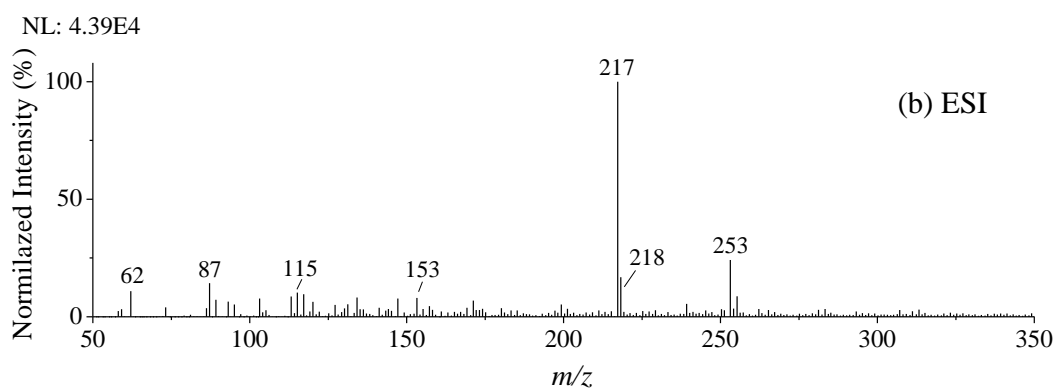


Fig. S9 EESI-MS (a) and ESI-MS (b) spectra of 1-OHP BuOH solution ($50 \mu\text{g L}^{-1}$);
PeNE was used as the primary ESI solvent for EESI-MS analysis.

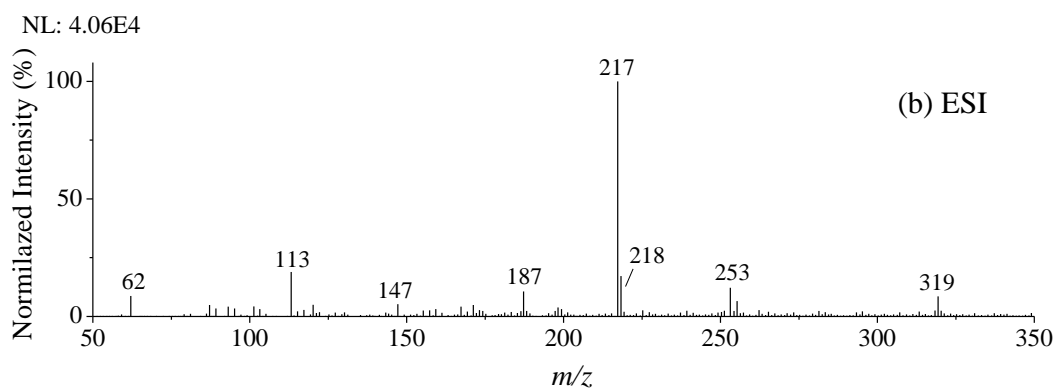
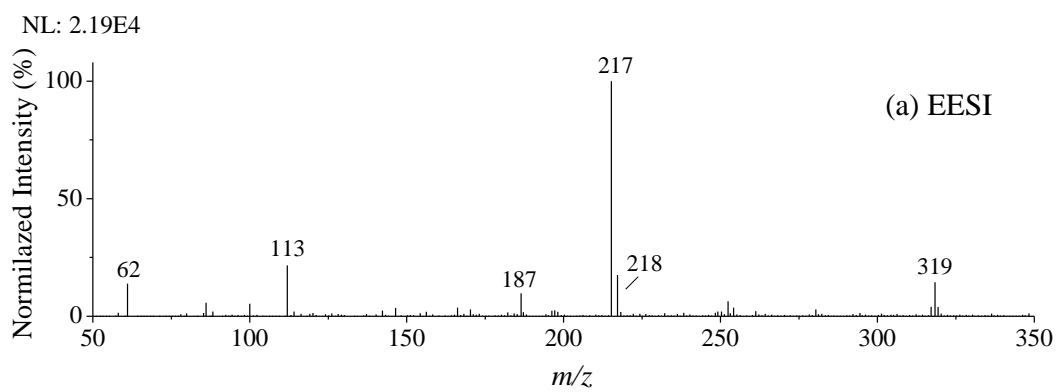


Fig. S10 EESI-MS (a) and ESI-MS (b) spectra of 1-OHP PeOH solution ($50 \mu\text{g L}^{-1}$);

PeNE was used as the primary ESI solvent for EESI-MS analysis.

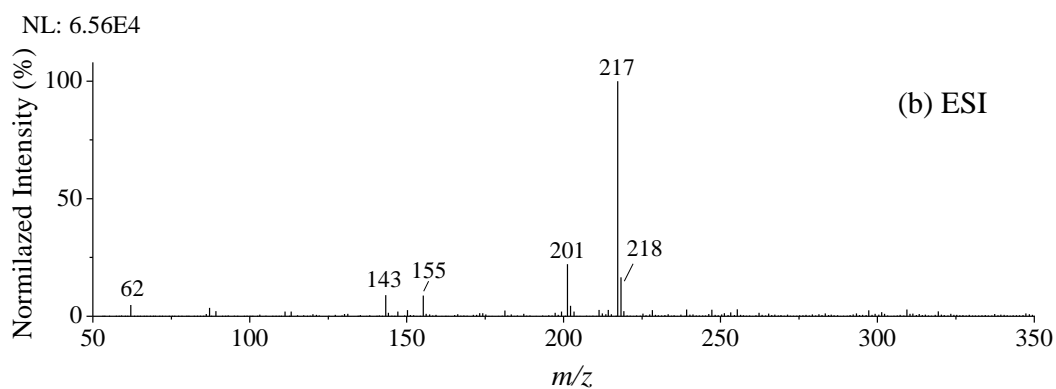
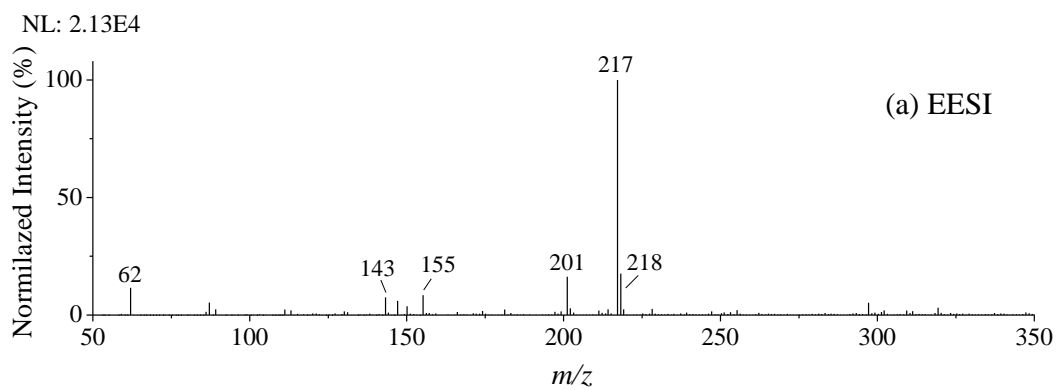


Fig. S11 EESI-MS (a) and ESI-MS (b) spectra of 1-OHP HeOH solution ($50 \mu\text{g L}^{-1}$);

PeNE was used as the primary ESI solvent for EESI-MS analysis.

7. Some chemical and physical properties of the solvents used in this study.

Table S1 Some chemical and physical properties of the solvents used in this study.^{3,4}

Solvents	MW^a (g mol ⁻¹)	RP^b	BP^c (°C)	S_w^d (g L ⁻¹ , 20 °C)
Water				
Ultrapure water	18.02	1.000	100 ^e	/
Alcohols				
Methanol (MeOH)	32.04	0.762	64.7	5.411×10^2 (NS ^f)
Ethanol (EtOH)	46.07	0.654	78 ^e	NA ^g
1-Propanol (PrOH)	60.10	0.617	97.2	1.882×10^2 (NS)
1-Butanol (BuOH)	74.12	0.586	117	$(4.671-7.709) \times 10^1$
1-Pentanol (PeOH)	88.15	0.568	138	$8.992 \times 10^{-1}-2.706 \times 10^1$
1-Hexanol (HeOH)	102.18	0.559	155–159 ^e	4.975–7.011
Arenes				
Benzene (BeNE)	78.11	0.111	80	$7.994 \times 10^{-1}-2.070$
Toluene (ToNE)	92.14	0.099	110.6	$(4.591-5.869) \times 10^{-1}$
<i>o</i> -Xylene (<i>o</i> -XyNE)	106.17	NA	144	$(1.704-2.399) \times 10^{-1}$
<i>m</i> -Xylene (<i>m</i> -XyNE)		NA	139.3	1.554×10^{-1}
<i>p</i> -Xylene (<i>p</i> -Xylene)		0.074	137	$(1.648-1.911) \times 10^{-1}$
Alkanes				
<i>n</i> -Pentane (PeNE)	72.15	0.009	36.1 ^e	$(1.750-3.928) \times 10^{-2}$
<i>n</i> -Hexane (HeNE)	86.18	0.009	65	$9.470 \times 10^{-3}-1.603 \times 10^{-1}$ (25 °C)

^a MW , molecular weight; ^b RP , relative polarity of E_T^N , the normalized solvent polarity parameter and derived from the empirical solvent polarity parameter $E_T(30)^3$; BP , boiling point; ^d S_w , solubility in water⁴; ^e, data are from Wikipedia (<http://en.wikipedia.org>); ^fNS, temperature not stated; ^gNA, not available.

1. J. Ding, H. Gu, S. Yang, M. Li, J. Li and H. Chen, *Anal. Chem.*, 2009, **81**, 8632–8638.
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3. C. Reichardt, in *Solvents and Solvent Effects in Organic Chemistry*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003, pp. 418–424.
4. S. H. Yalkowsky and Y. He, in *Handbook of Aqueous Solubility Data*, CRC Press LLC, Boca Raton.