

Table S1. The relative intensities of $[M]^+$ and $[M-H]^+$ ions for compound 1-7

Compound	Isotope Ratio(m+1)%	$I_{[M-H]^+}$ %	$I^*_{[M]^+}$ %	$I_{[M]^+}$ %	$I_{[M]^+}/I_{[M-H]^+}$
1	22.67	36	100	92	2.56
2	23.834	77	100	84	1.09
3	21.306	100	97	73	0.73
4	24.9	100	41	16	0.16
5	24.428	100	26	2	0.02
6	24.428	100	24	0	0
7	25.533	100	25	0	0

Both $I_{[M-H]^+}$ % and $I^*_{[M]^+}$ % are the observed values. $I_{[M]^+}$ % was got by the observed value ($I^*_{[M]^+}$ %) minus the isotope of $I_{[M-H]^+}$ %. $I_{[M]^+}$ % = $I^*_{[M]^+}$ % (observed) - $I_{[M-H]^+}$ % (observed) × Isotope Ratio_(m+1)% (theory)

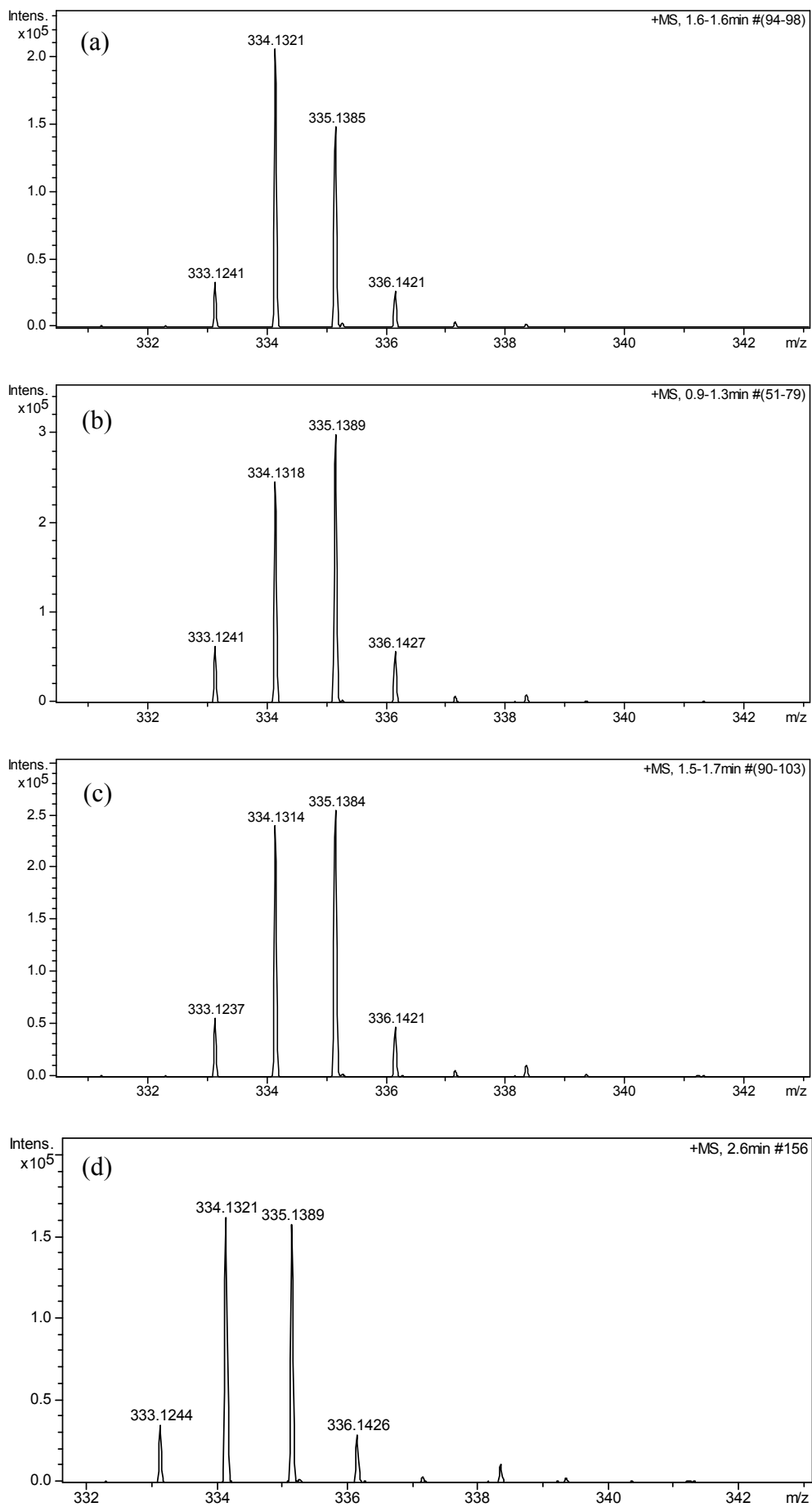


Figure S1. Effect of methanol solution of HCOOH (5×10^{-7} mol/L) addition on the intensities of $[M]^{+\bullet}$ and $[M-H]^+$ ions for compound 1 in positive-ion mode. (a) : the mass spectrum of compound 1 (10^{-6} mol/L); (b): after added with 10 μL HCOOH solution; (c): after added with 20 μL HCOOH solution; (d): after added with 30 μL HCOOH solution.

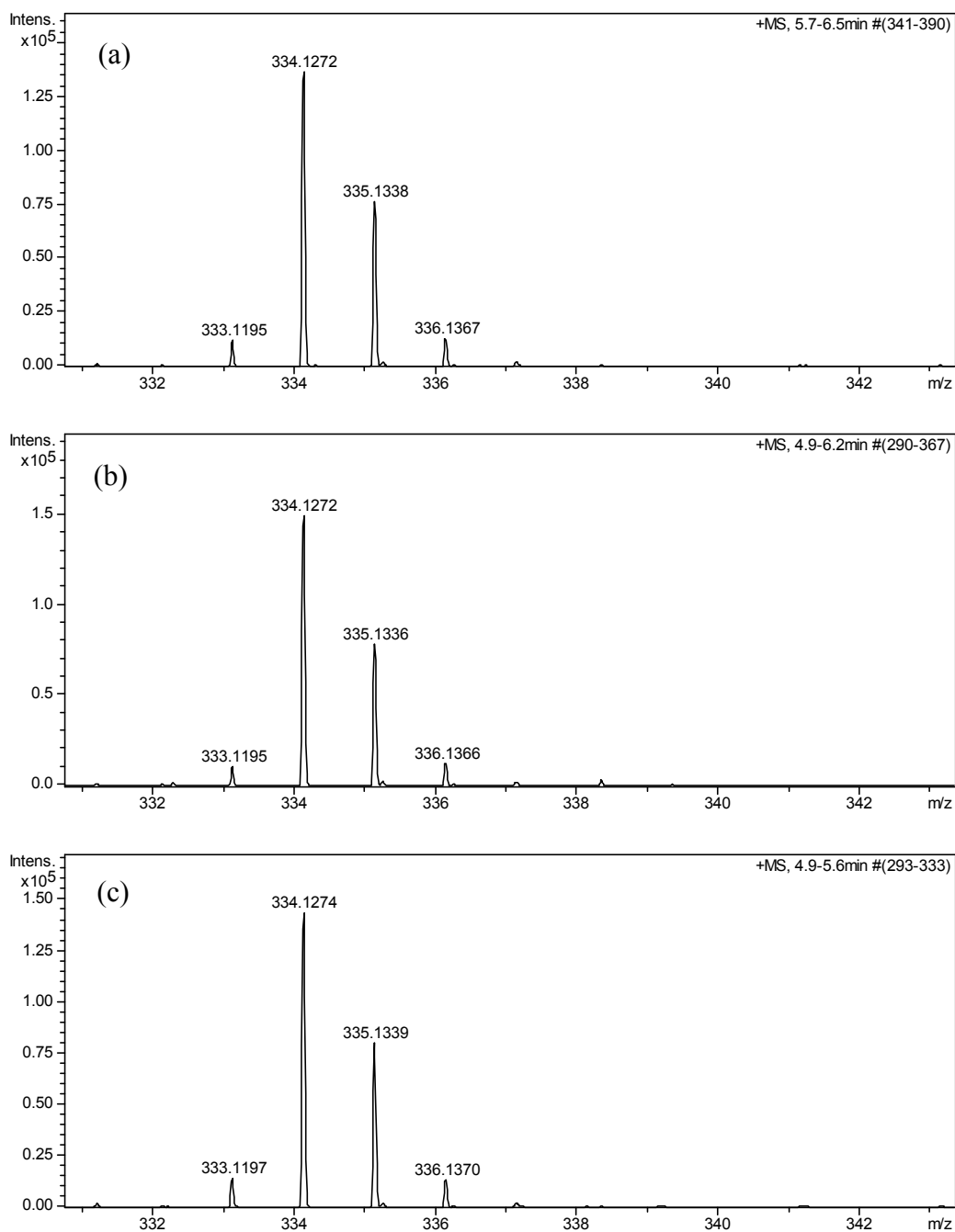


Figure S2. Effect of H₂O solution of NaOH (10^{-6} mol/L) addition on the intensities of $[M]^+$ and $[M-H]^+$ ions for compound **1** (10^{-6} mol/L) in positive-ion mode. (a): after added with 5 μ L NaOH solution; (c): after added with 10 μ L NaOH solution; (d): after added with 15 μ L NaOH solution.

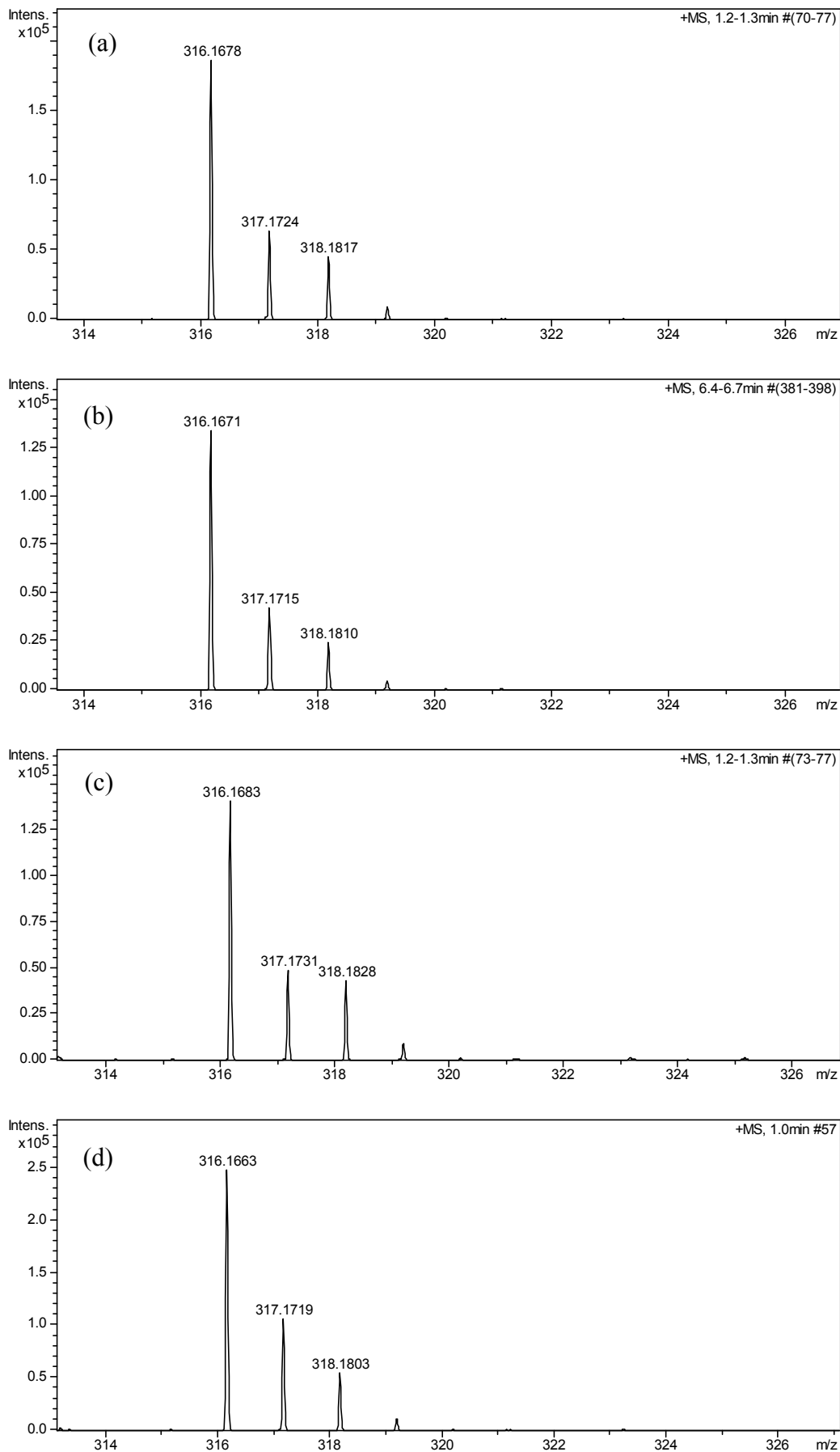


Figure S3. Effect of HCOOH solution (5×10^{-7} mol/L), H₂O, and NaOH solution (10^{-6} mol/L) addition on the intensities of [M]^{+•} and [M-H]⁺ ions for compound **5** (10^{-6} mol/L) in positive-ion mode, respectively. (a): the mass spectrum of compound **5** (10^{-6} mol/L); (b) after added with 20 μL HCOOH solution; (c): after added with 50 μL H₂O; (d): after added with 10 μL NaOH solution.

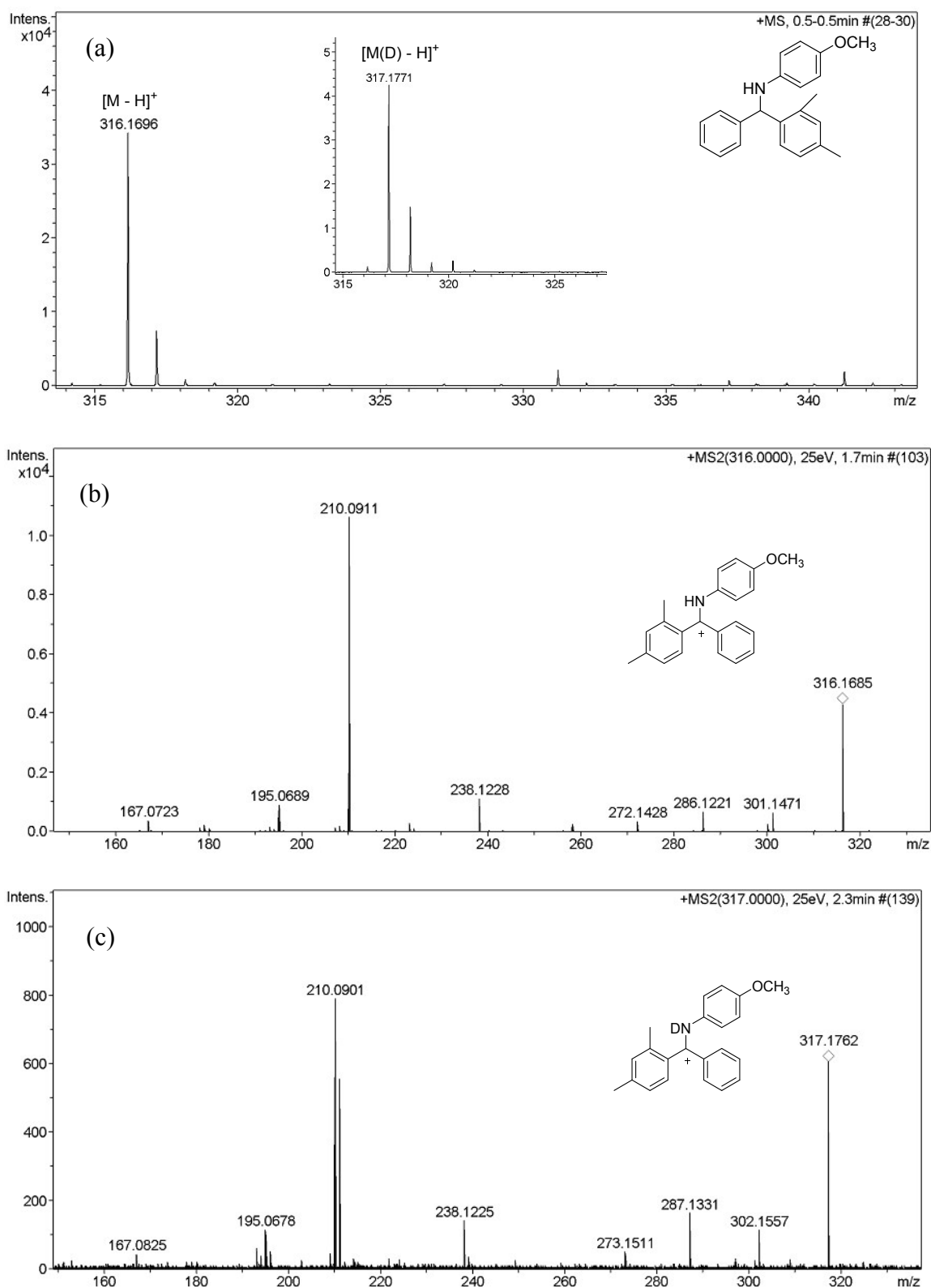


Figure S4. (a) The ESI-MS spectrum of compound **5** and D-labeling spectrum shown in the insert; (b) CID mass spectrum of $[5-H]^+$ ion at m/z 316 (collision energy: 25 eV); (c) CID mass spectrum of $[5(D)-H]^+$ ion at m/z 317 ion (collision energy: 25 eV).

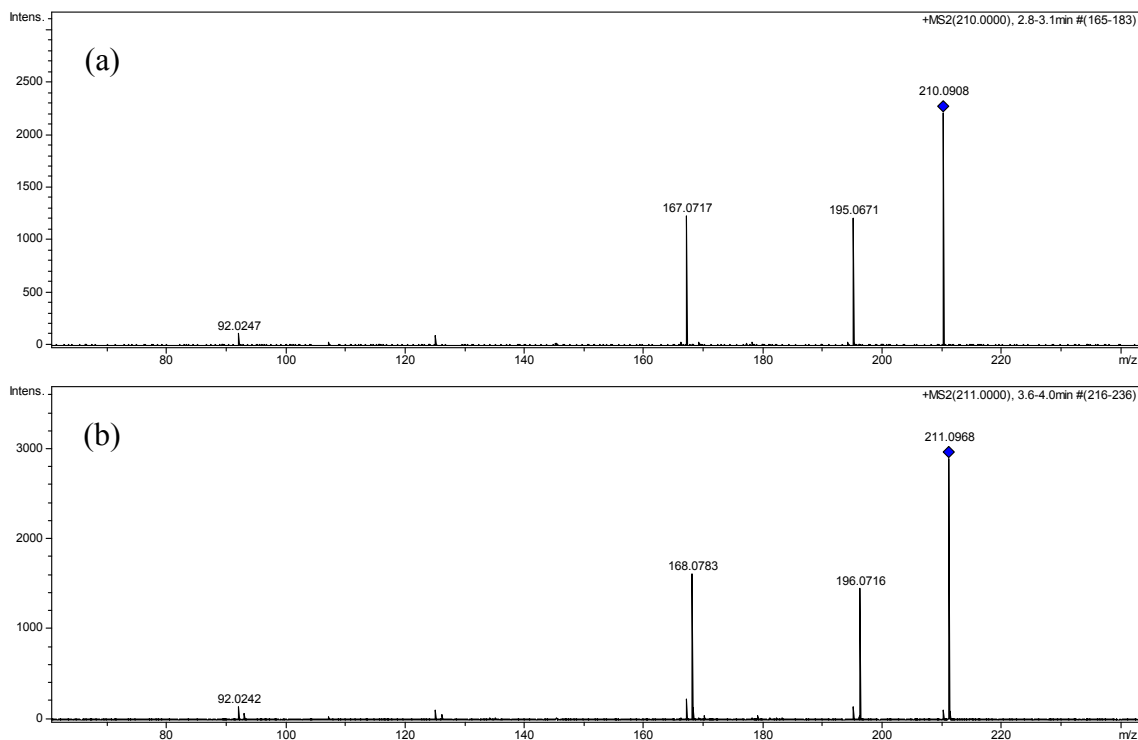
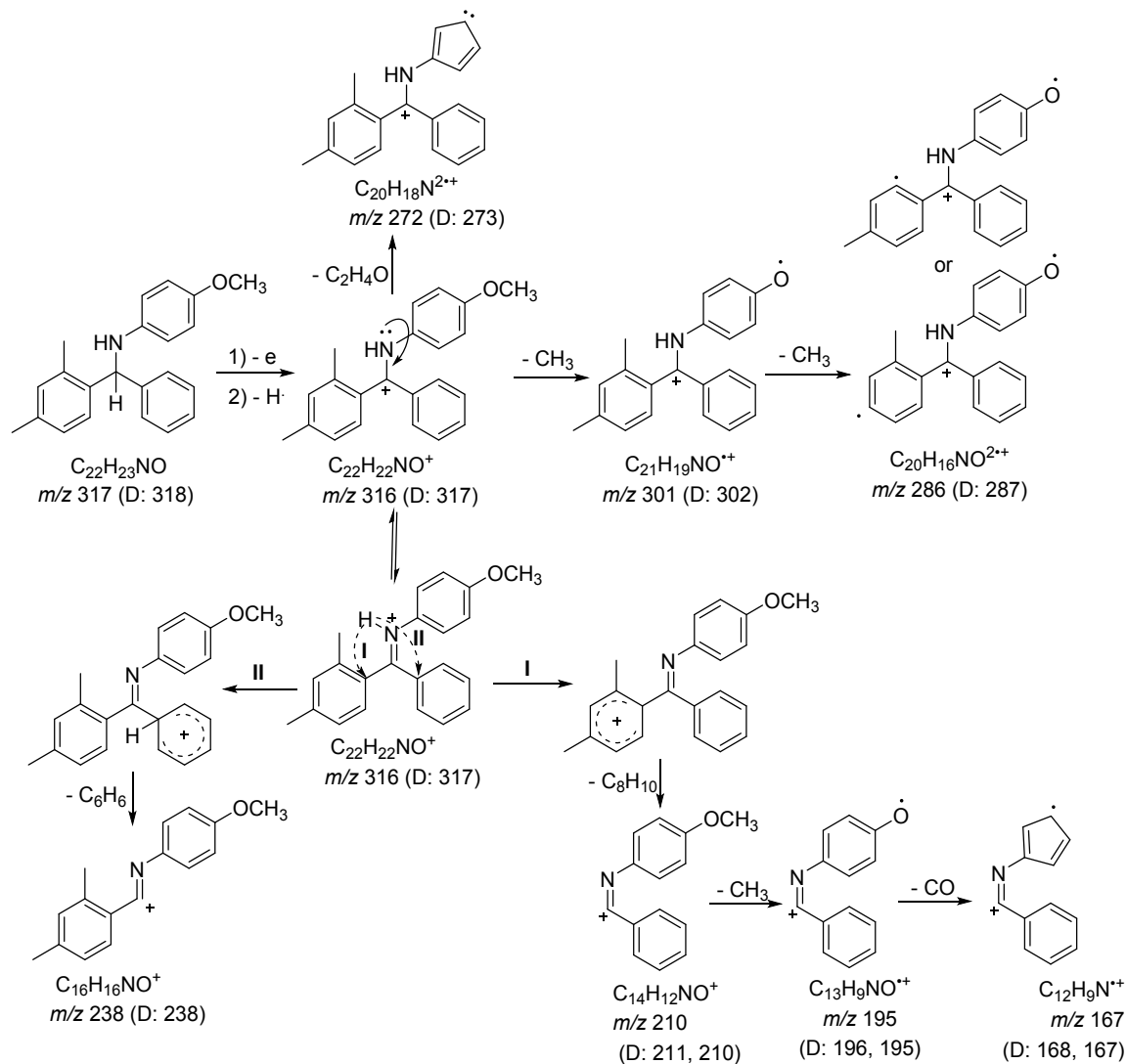


Figure S5. ESI-MS/MS/MS spectra of the selected precursor ions (collision energy: 20 eV) : (a) the m/z 210 ion from [5-H] (m/z 316); (b) the m/z 211 ion from [5(D)-H] (m/z 317).

Table S2. Elemental constituents of major product ions from [M-H]⁺ for compound 5.

Ions	Formula	Calculated	Observed	Error(ppm)
[M-H] ⁺	C ₂₂ H ₂₂ NO	316.1696	316.1685	3.5
[M-H-CH ₃] ⁺	C ₂₁ H ₁₉ NO	301.1461	301.1471	-3.2
[M-H-CH ₃ -CH ₃] ⁺	C ₂₀ H ₁₆ NO	286.1226	286.1221	2.0
[M-H-C ₂ H ₄ O] ⁺	C ₂₀ H ₁₈ N	272.1434	272.1428	2.1
[M-H-C ₆ H ₆] ⁺	C ₁₆ H ₁₆ NO	238.1226	238.1228	-0.9
[M-H-C ₈ H ₁₀] ⁺	C ₁₄ H ₁₂ NO	210.0913	210.0911	1.0
[M-H-C ₈ H ₆ -CH ₃] ⁺	C ₁₃ H ₉ NO	195.0679	195.0689	-5.1
[M-H-C ₈ H ₆ -CH ₃ -CO] ⁺	C ₁₂ H ₉ N	167.0730	167.0723	3.7



Scheme S1. Major fragmentation patterns of $[M-H]^+$ for compound **5**. Corresponding peaks in D-labelled spectrum were provided.

The corresponding fragment ions and their exact masses are listed in Table S2. A radical product ion at m/z 301 results from $[M-H]^+$ ion via the loss of a CH_3 radical,^[1] which produced a diradical cations at m/z 286 by the loss of a CH_3 radical once again. The m/z 272 ion was formed from $[M-H]^+$ ion by the loss of a C_2H_2O . $[M-H]^+$ ion can change to an imine compound through electron resonance, which generated m/z 210 ion and m/z 238 ion by losing a phenyl group or a 2,4-dimethylphenyl group respectively, through a process of hydrogen migration^[2]. Because electron donating groups can help stabilize the positive ions, the fragmentation process tend to the I process to produce more abundance of m/z 210 ions. The m/z 210 ion lost a CH_3 radical to form the m/z 195 ion, then lost a CO to generate the m/z 167 ion. The D-labelled spectrum (Figure S5(c)) supported the proposed pathways and corresponding peaks were provided in Scheme S1. The product ion at m/z 210 in MS/MS spectrum of m/z 316 corresponds to the ions at m/z 210 ($C_{14}H_{12}NO$) and m/z 211 ($C_{14}H_{11}DNO$) in D-labelled spectrum. The phenomenon may result from H/D scrambling.^[3] CID experiments for the two precursor ions were carried out respectively (Figure S5), and it is clear that corresponding profiles of spectra are very similar. This indicates that the structures of the two ions at m/z 210 and m/z 211 in D-labelled spectrum were very similar and were formed by H/D scrambling.

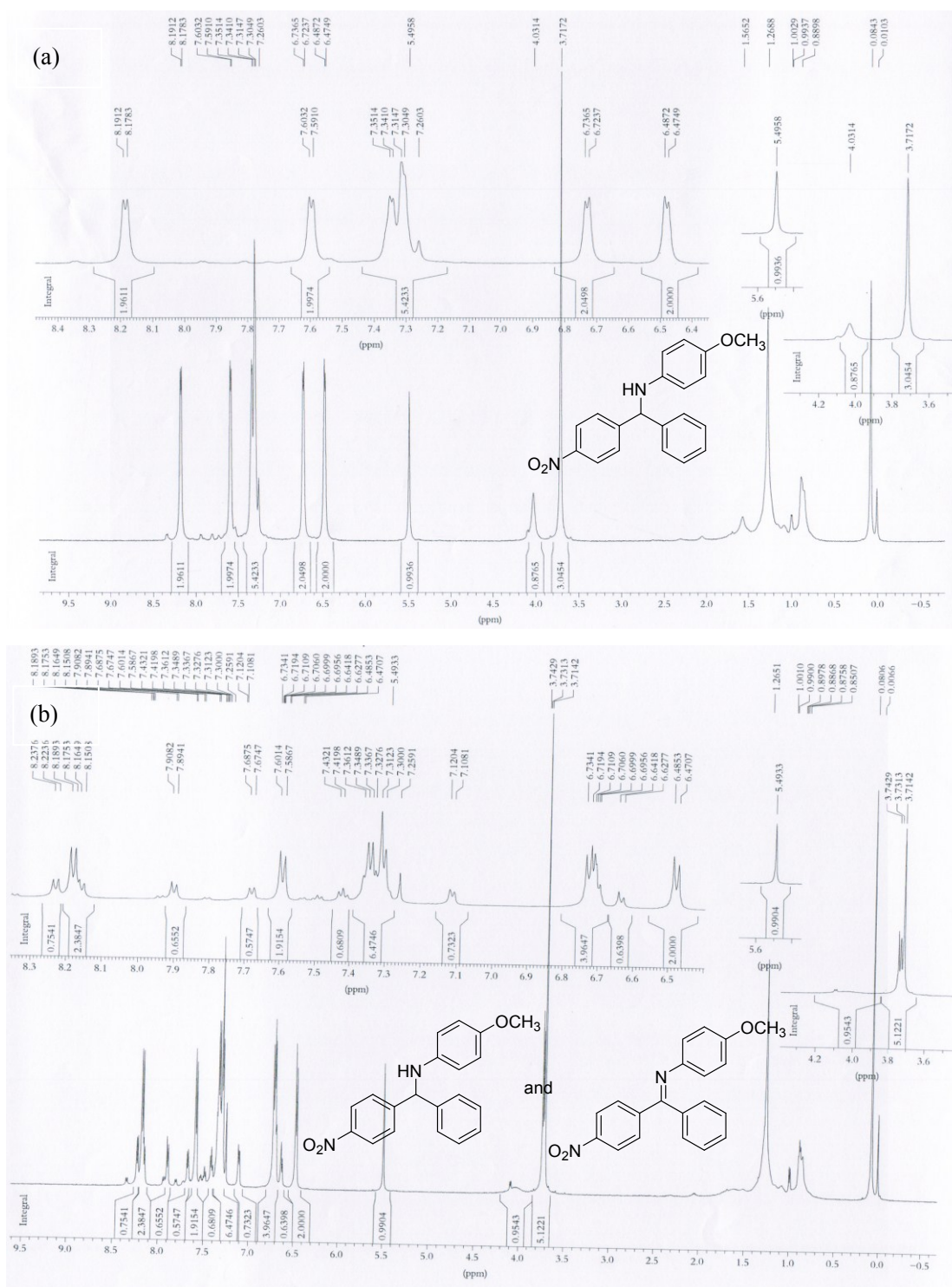


Figure S6. ¹H NMR spectra: (a) compound **1**; (b) add 0.5 equiv. oxidant (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) into compound **1**.

The peaks between 0.5 and 2 ppm are from the solvent (light petroleum). The chemical shifts of 1-C-H and N-H are at 5.5 ppm and 4 ppm, respectively. And the chemical shift of protons on OCH₃ group is at 3.7 ppm. In Figure S6(a), the ratio of these three protons was 1:1:3. After the oxidant was added into D-CHCl₃ solution of compound **1** (Figure S6(b)), the ratio of these three protons become 1:1:5. This indicates that part of C-N was oxidized to C=N.

References

- [1] Z. J. Wu, D. Han, X. Z. Chen, D. M. Fang, H. Y. Qi and G. L. Zhang, Analysis of benzofuran derivatives using electrospray ionization ion trap and electrospray ionization quadrupole time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* 2010; 24, 1211–1215.
- [2] N. Hu, Y. P. Tu, Y. Q. Liu, K. Z. Jiang and Y. J. Pan, Dissociative protonation and proton transfers: fragmentation of α , β -unsaturated aromatic ketones in mass spectrometry. *J. Org. Chem.* 2008, 73, 3369-3376.
- [3] T. Cai, D. Wang, X. Y. Xu, D. M. Fang, H. Y. Qi, Y. Jiang and Z. J. Wu, New evidence for H/D scrambling of tryptophan and its analogues in the gas phase. *Int. J. Mass Spectrom.*, 2015, 385, 26-31.