Supporting information

On the mechanism of the *aza*-Morita-Baylis-Hillman reaction: ESI-MS interception of a unique new intermediate

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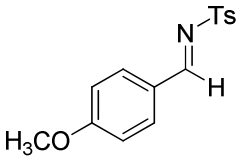
Experimental procedure for the preparation of *N*-[(*E*)-(4-methoxyphenyl)methylidene]-4-methylbenzenesulfonamide **(4)**



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To a solution of 4-Methoxy-benzaldeyde (*p*-anisaldehyde, 10g, 0.074 mol) in dry toluene was added *p*-toluenosulfonic acid (PTSA, 1 mol%, 0.13 g, 0.74 mmol) and *p*-toluenosulphonamide (12.6 g, 0.074 mol). The stirred resulting mixture was refluxed (Dean-Stark apparatus) overnight. Then, toluene was removed under reduced pressure and the residue was recrystallized from diethyl ether to provide the required imine as a solid in 99% yield.

^{1}H NMR (250 MHz, DMSO d_6) δ (ppm): 2.38 (s, 3H); 3.85 (s, 3H); 7.09 (d, *J*= 8.79, 2H); 7.42 (d, *J*= 8.13, 2H); 7,79 (d, *J*= 8.32, 2H), 7.98 (d, *J*=8.9, 2H); 9.02 (s, 1H); ^{13}C NMR (62.5 MHz, DMSO d_6) δ (ppm): 21.34 (CH_3); 21.51 (CH_3); 56.13 (CH_3); 56.28(CH_3); 114.95 (CH); 115.37(CH); 125.26 (CH); 127.86(CH); 129.73 (CH); 130.08 (CH); 130.44 (CH); 132.25 (CH); 134.26 (CH); 135.95 (CH); 141.86 (CH); 142.28 (CH); 144.69 (CH); 164.65 (C); 165.51 (C); 170.85 (C); 191.76 (CH); HRMS (ESI) Calcd. for $C_{15}H_{16}NO_3S$ 290.0851; Found 290.0909.

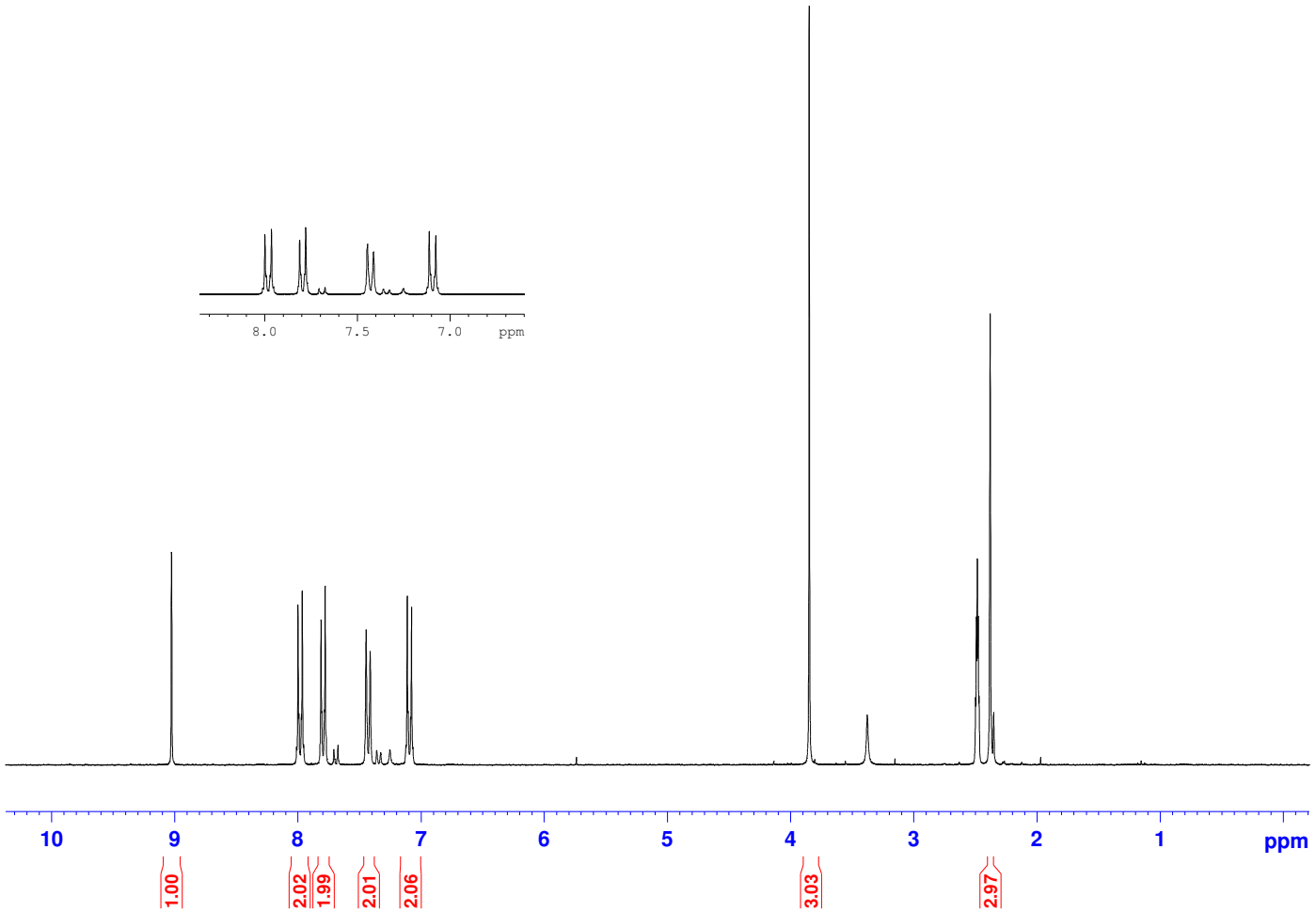


Fig. S1 ^{1}H NMR (250 MHz, DMSO d_6) spectrum of *p*-tosylimine **4**.

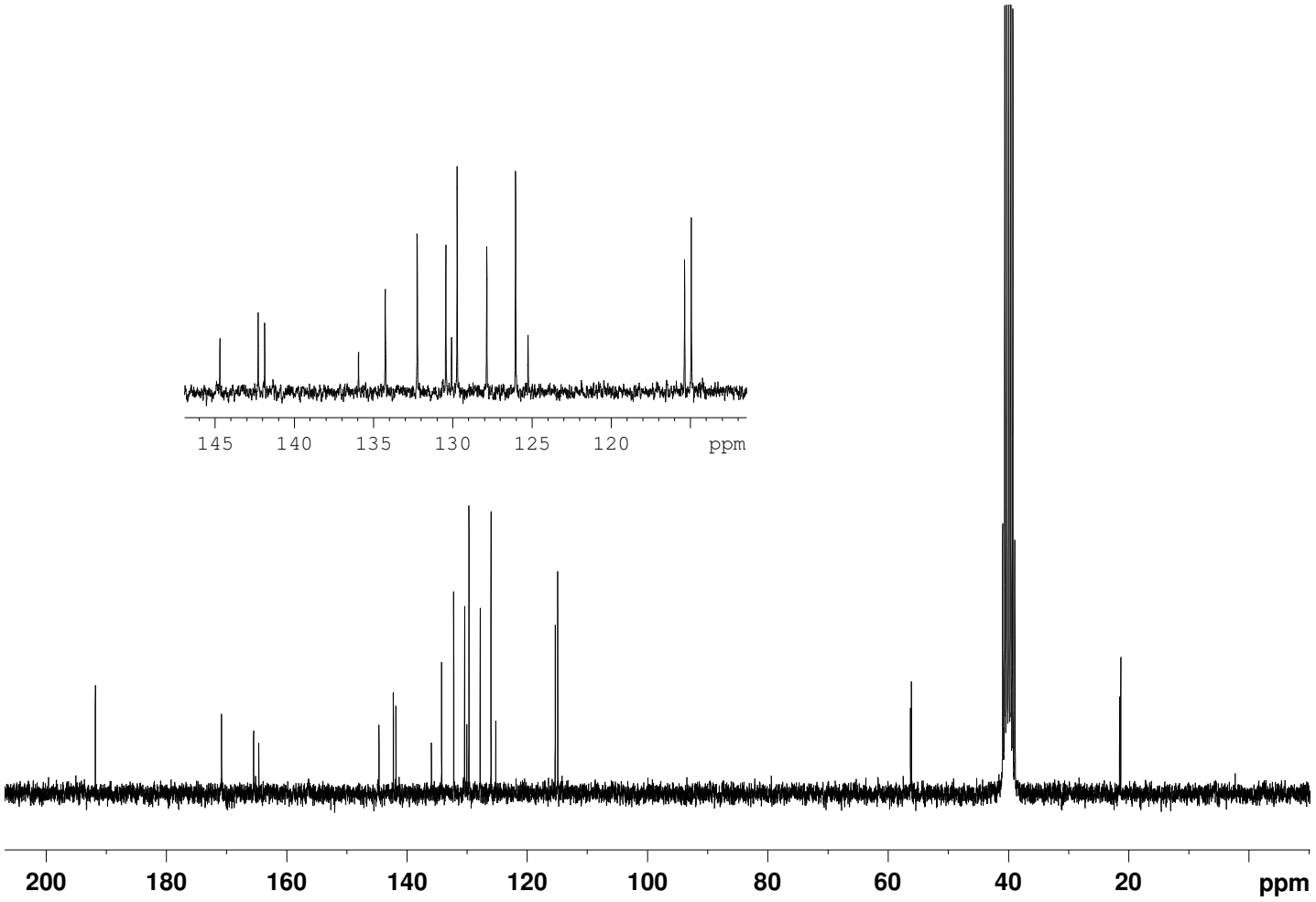


Fig. S2 ^{13}C NMR (62.5 MHz, DMSO d_6) spectrum of *p*-tosylimine **4**.

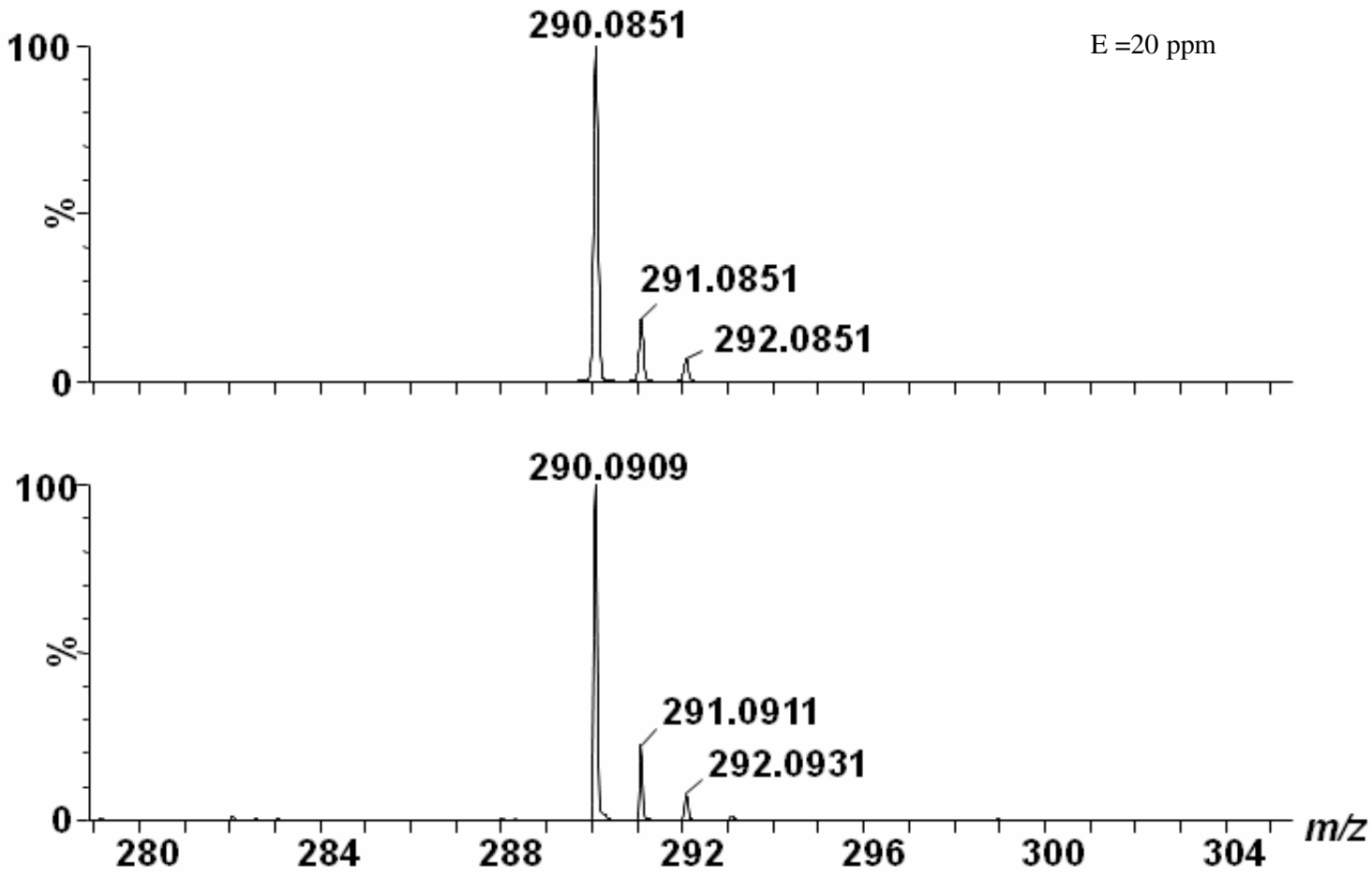


Fig. S3 HRMS ESI(+)-MS of *p*-tosylimine **4**.

ESI-MS or MS(/MS) spectra

Aza-MBH reaction using DABCO as base, monitored by ESI-MS

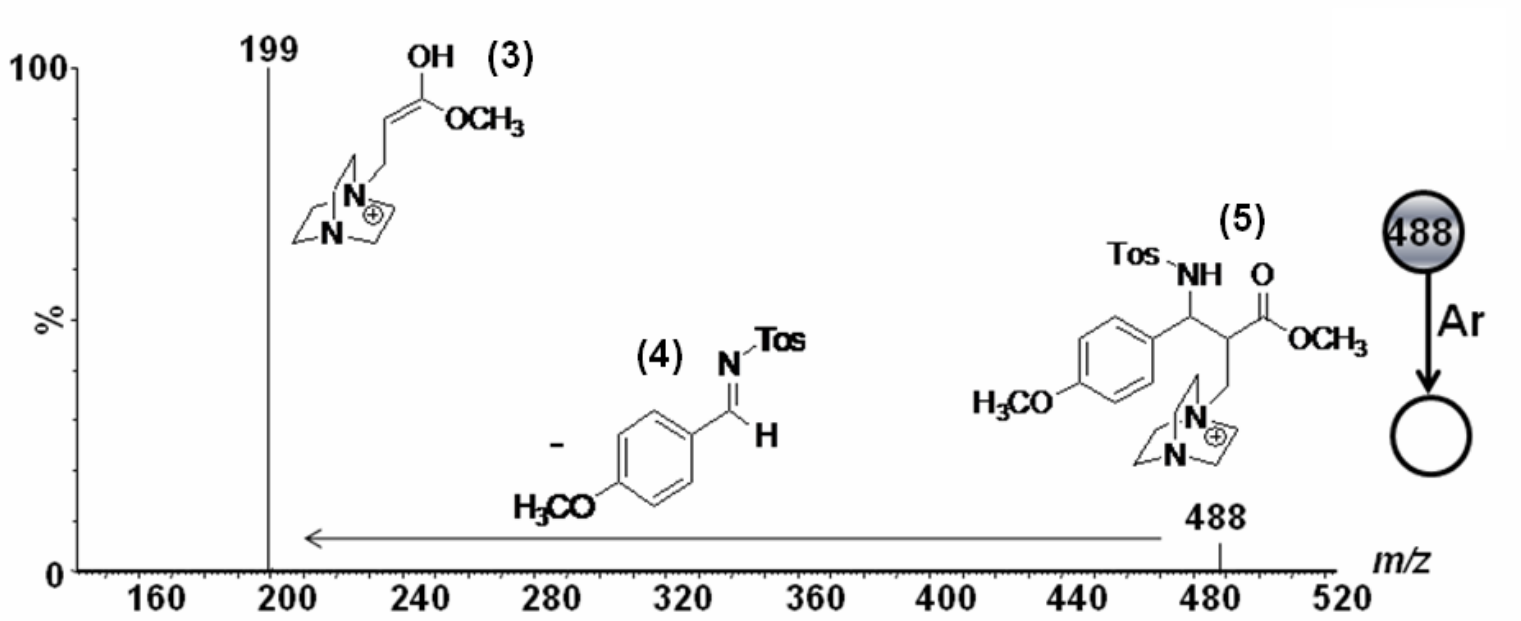


Fig. S4 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 488.

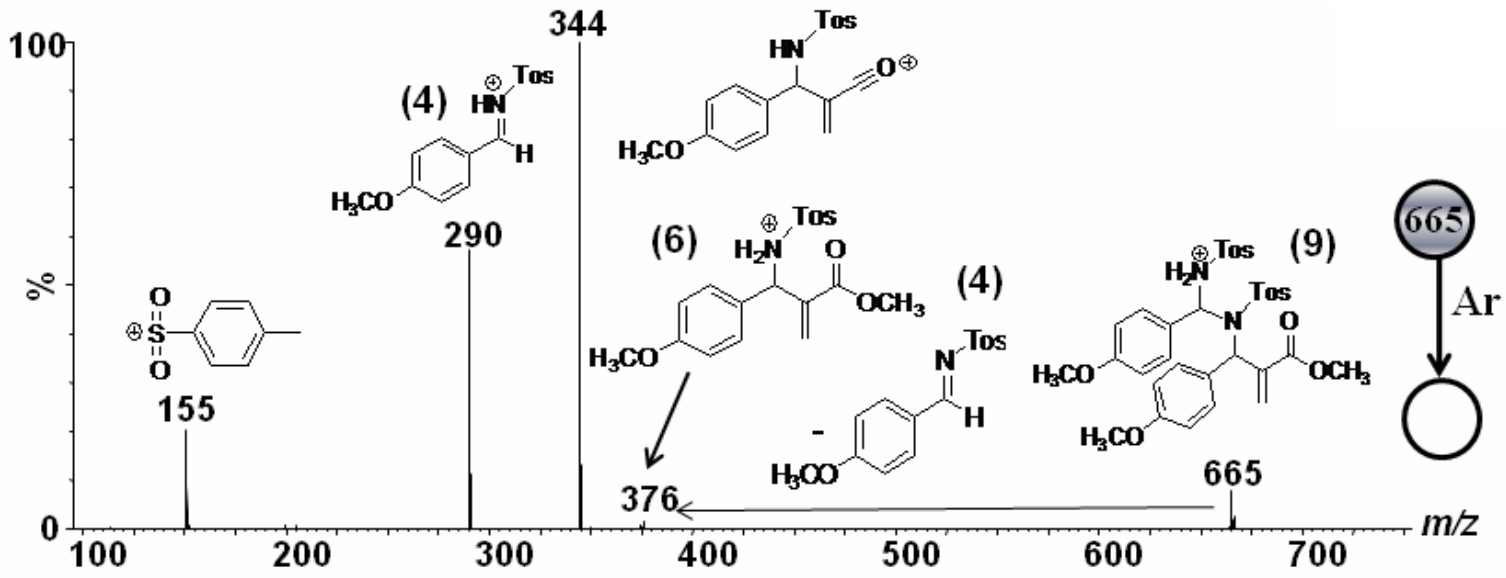


Fig. S5 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 665.

Aza-MBH reaction using quinuclidine as base monitored by ESI-MS

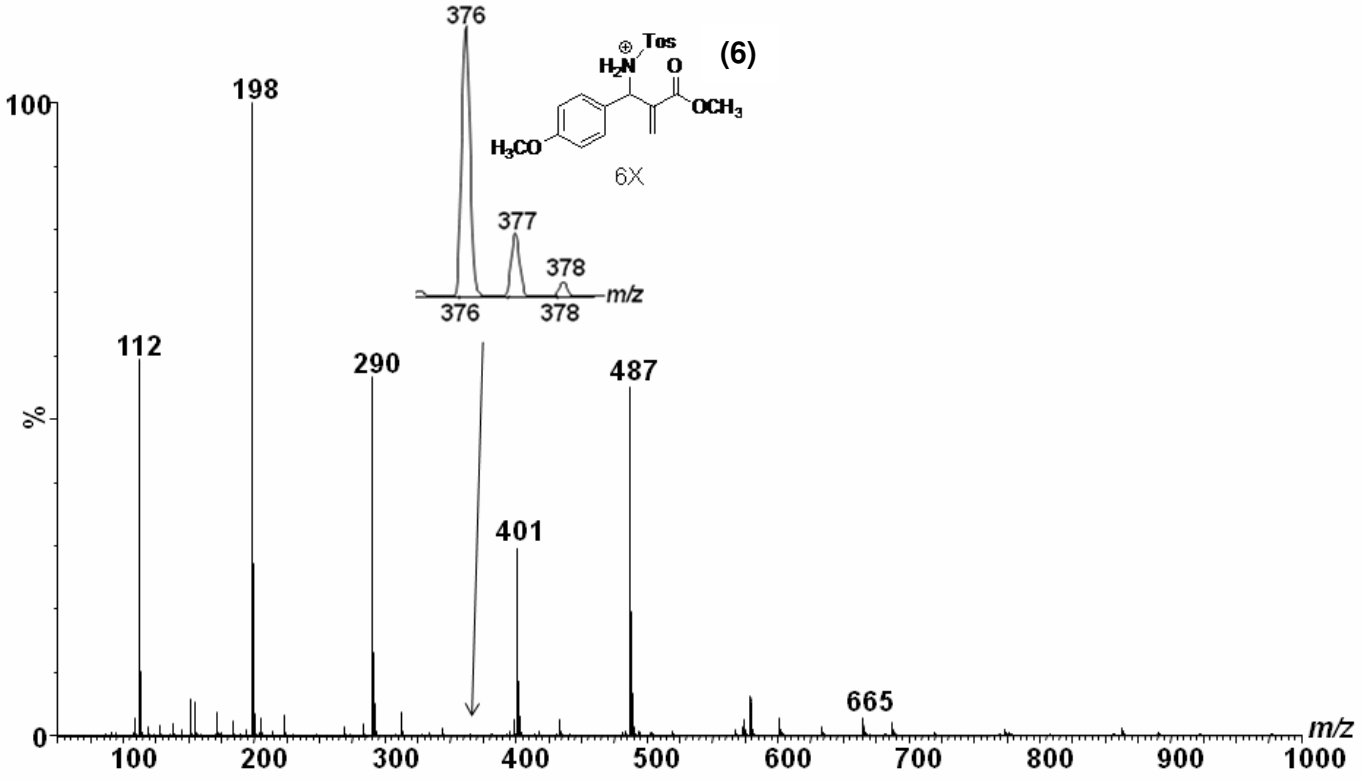


Fig. S6 ESI(+)-MS of the aza-MBH reaction between **4** and methyl acrylate (t = 30 min)

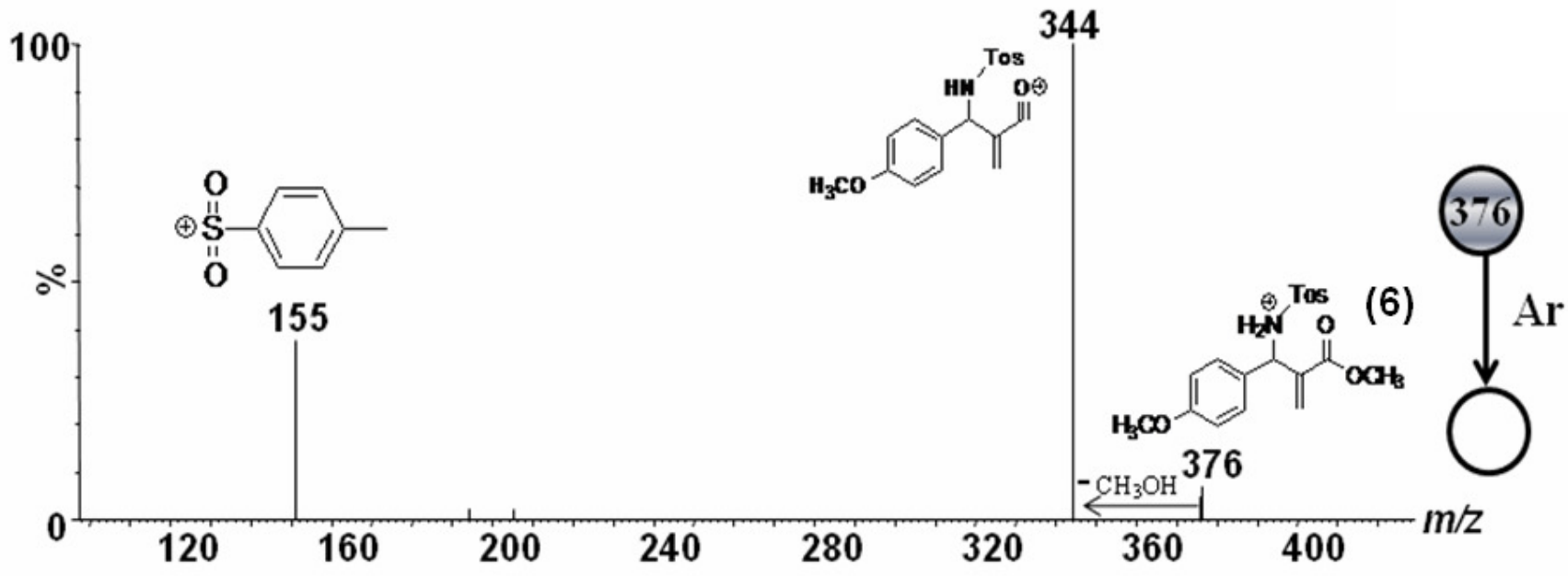


Fig. S7 ESI(+)-MS(/MS) spectrum of the *aza*-adduct of *m/z* 376.

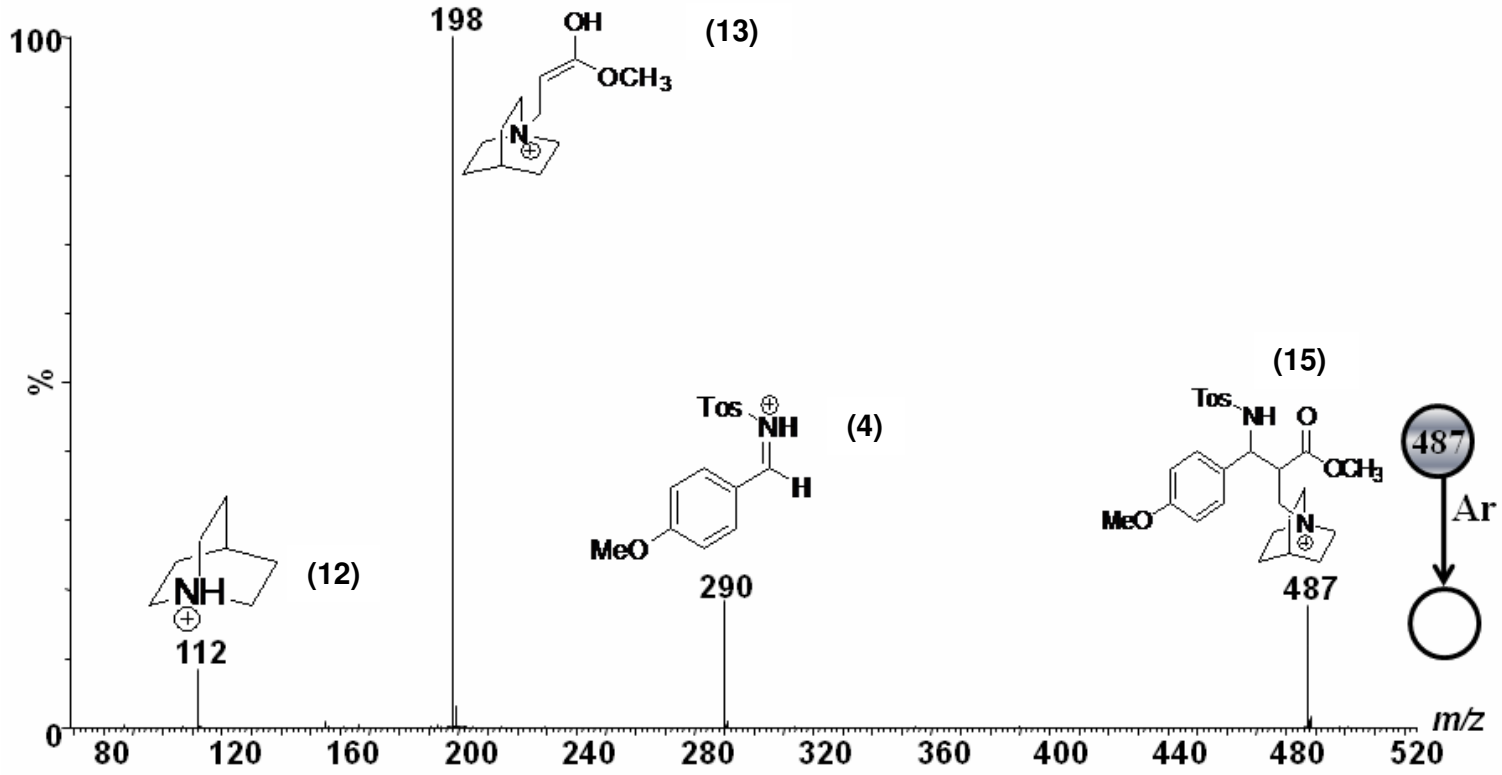


Fig. S8 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 487.

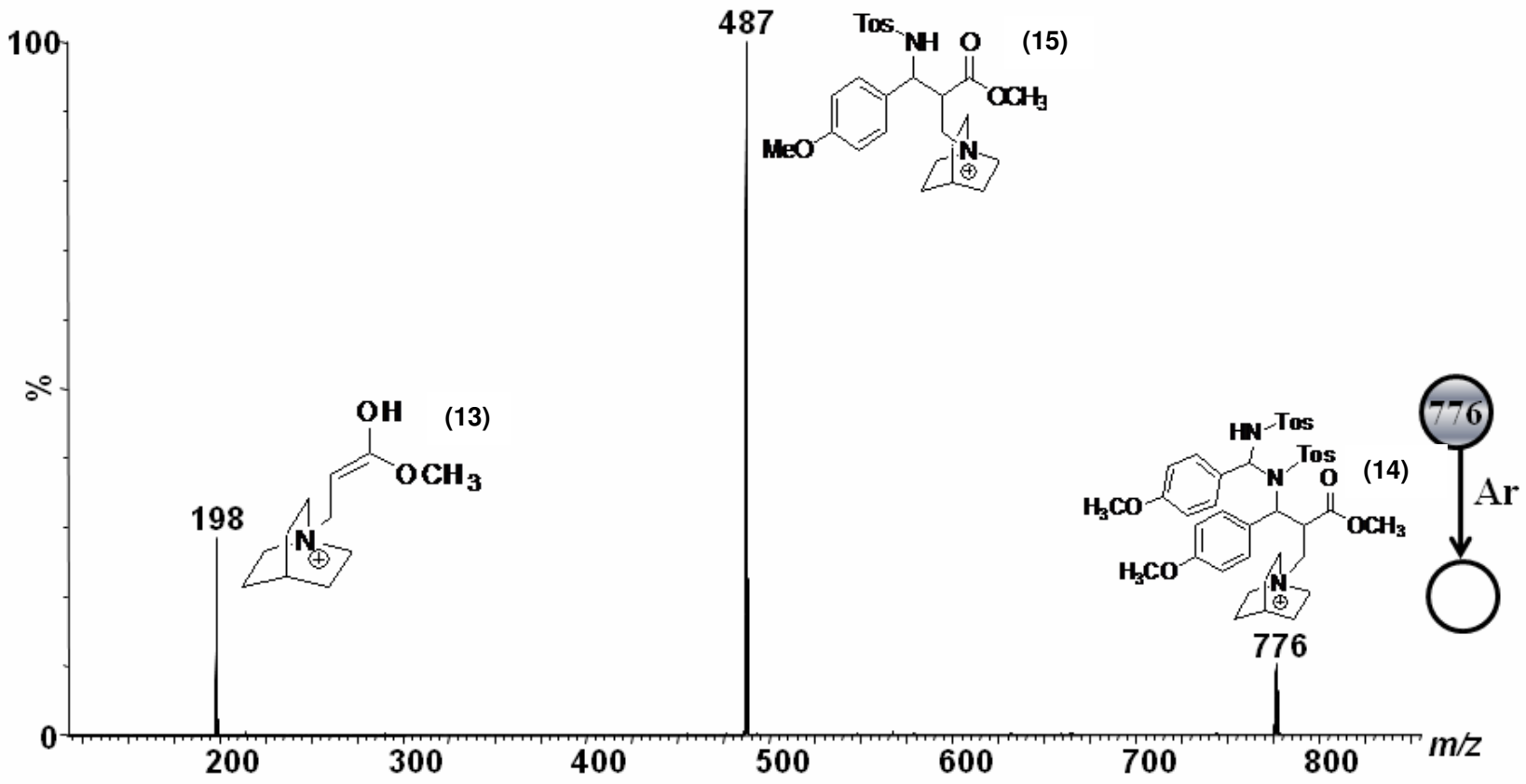
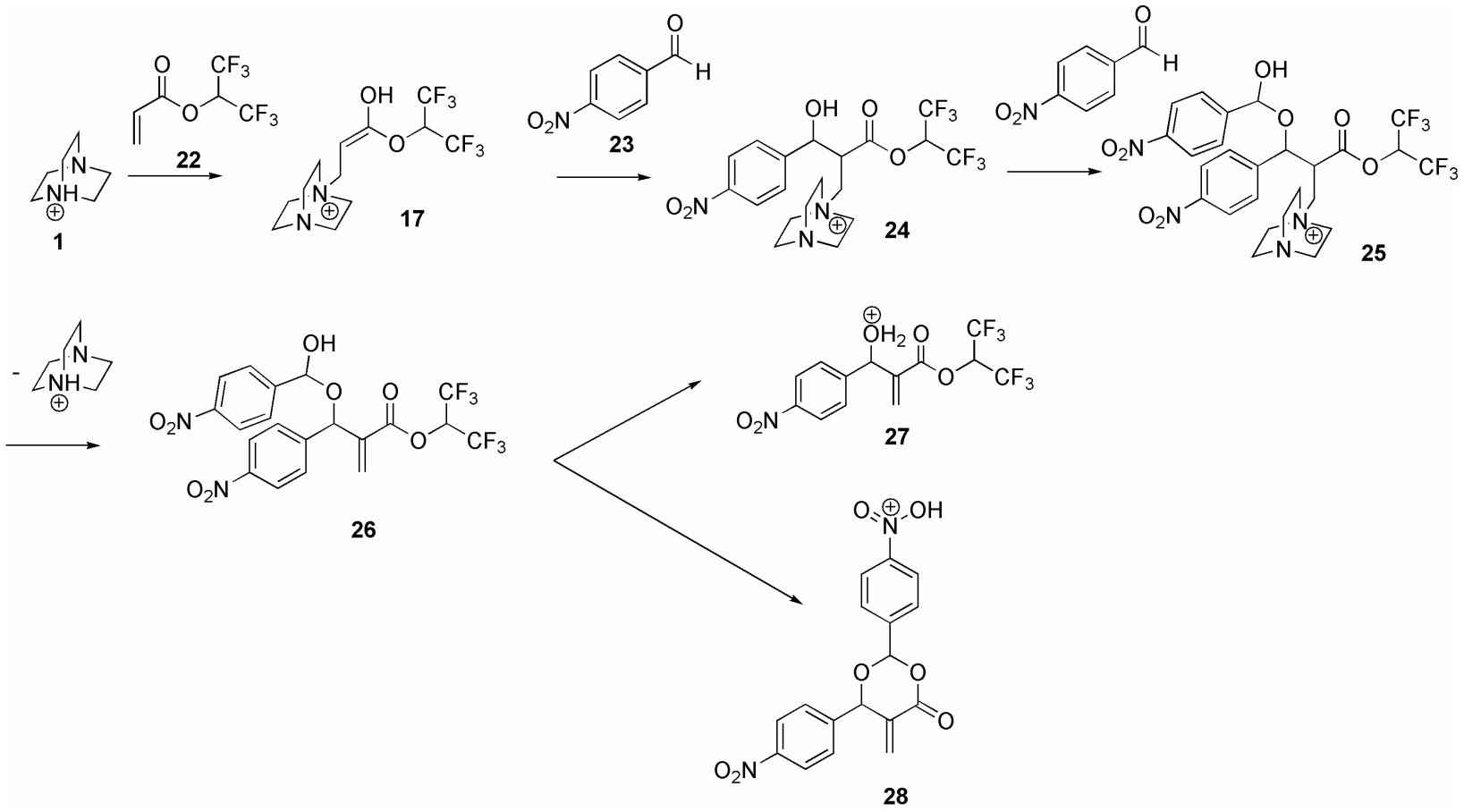


Fig. S9 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 776.



Scheme 1. Aza-MBH between tosylimine (4) and 1,1,1,3,3,3-hexafluoroisopropyl acrylate monitored by ESI-(+)-MS: General scheme

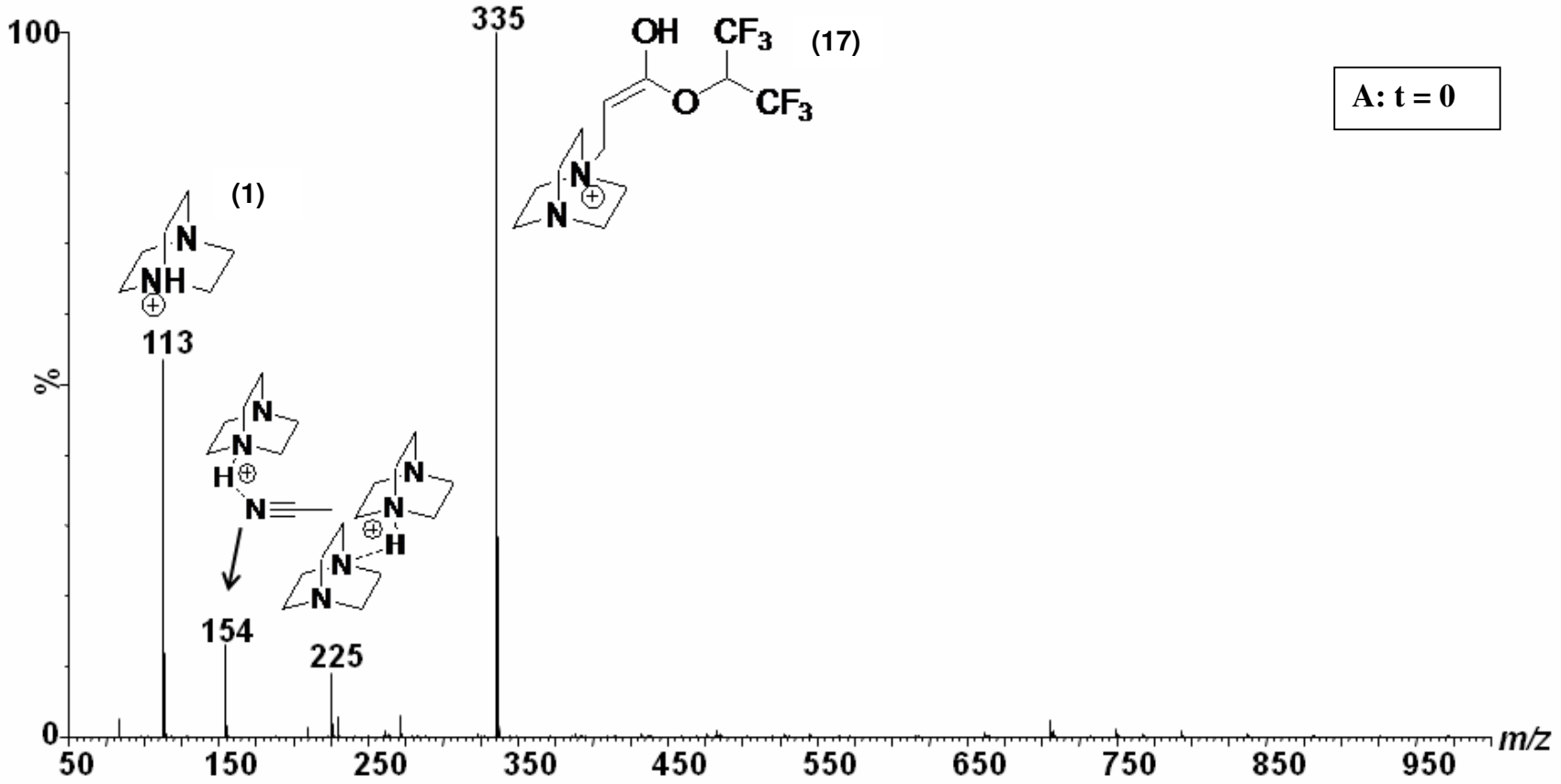


Fig. S10 (A): ESI(+)-MS spectrum of the MBH reaction between *p*-nitrobenzaldehyde and hexafluoroisopropyl acrylate in the presence of DABCO (*t* = 0 min).

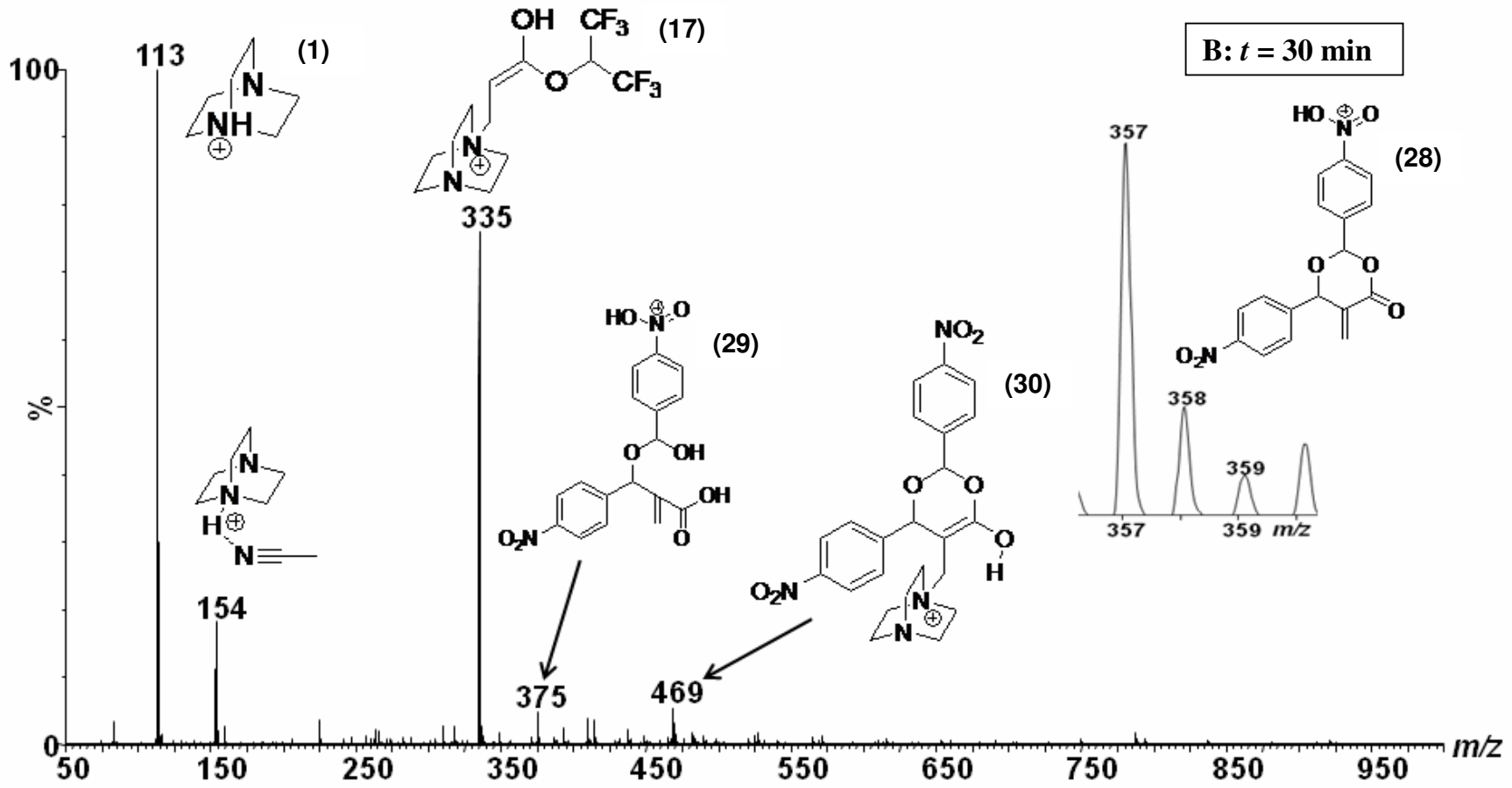


Fig. S10 (B): ESI(+)-MS spectrum of the MBH reaction between *p*-nitrobenzaldehyde and hexafluoroisopropyl acrylate in the presence of DABCO (*t* = 30 min).

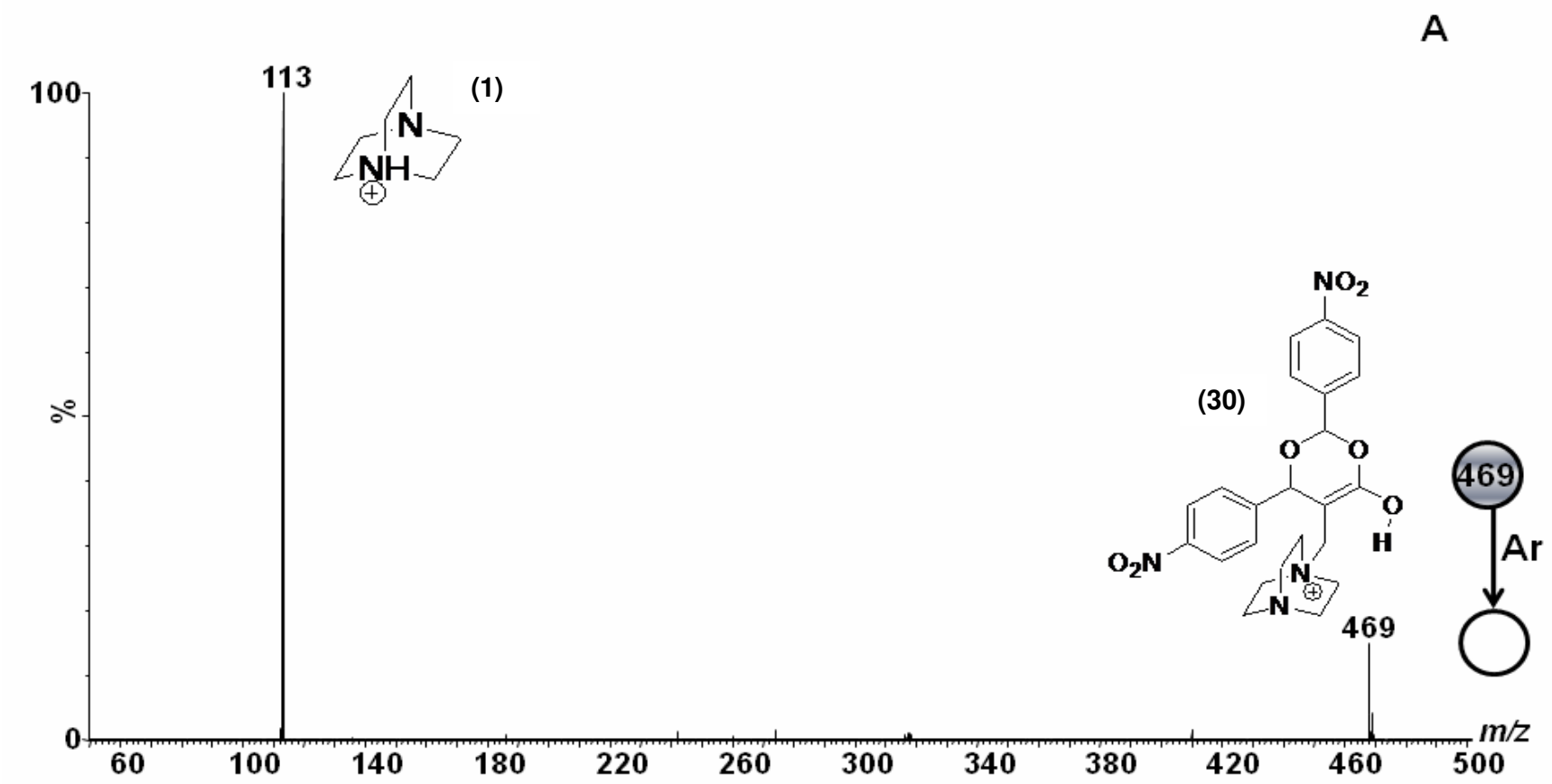


Fig. S11 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 469 (A).

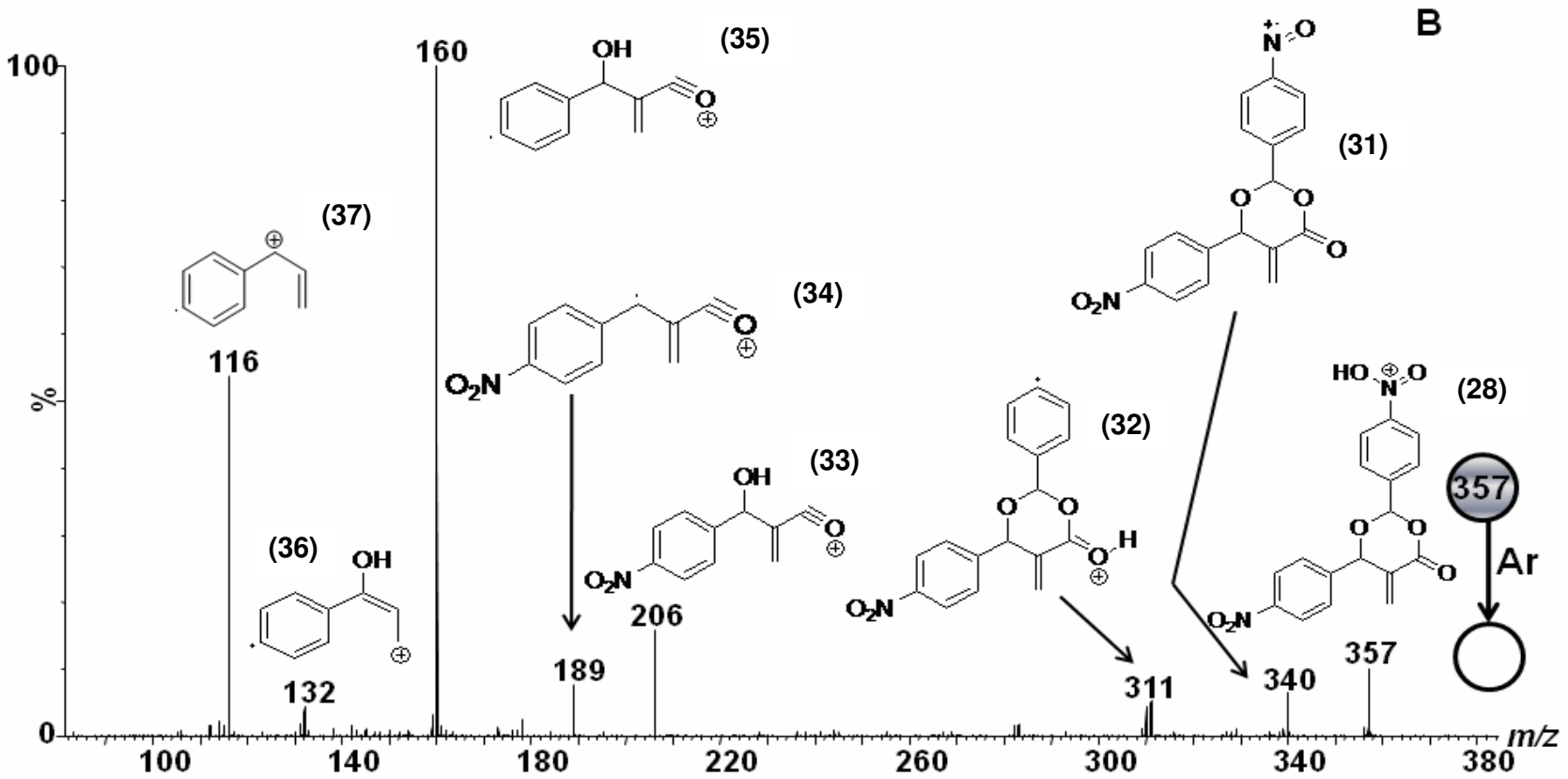


Fig. S12 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 357 (B).

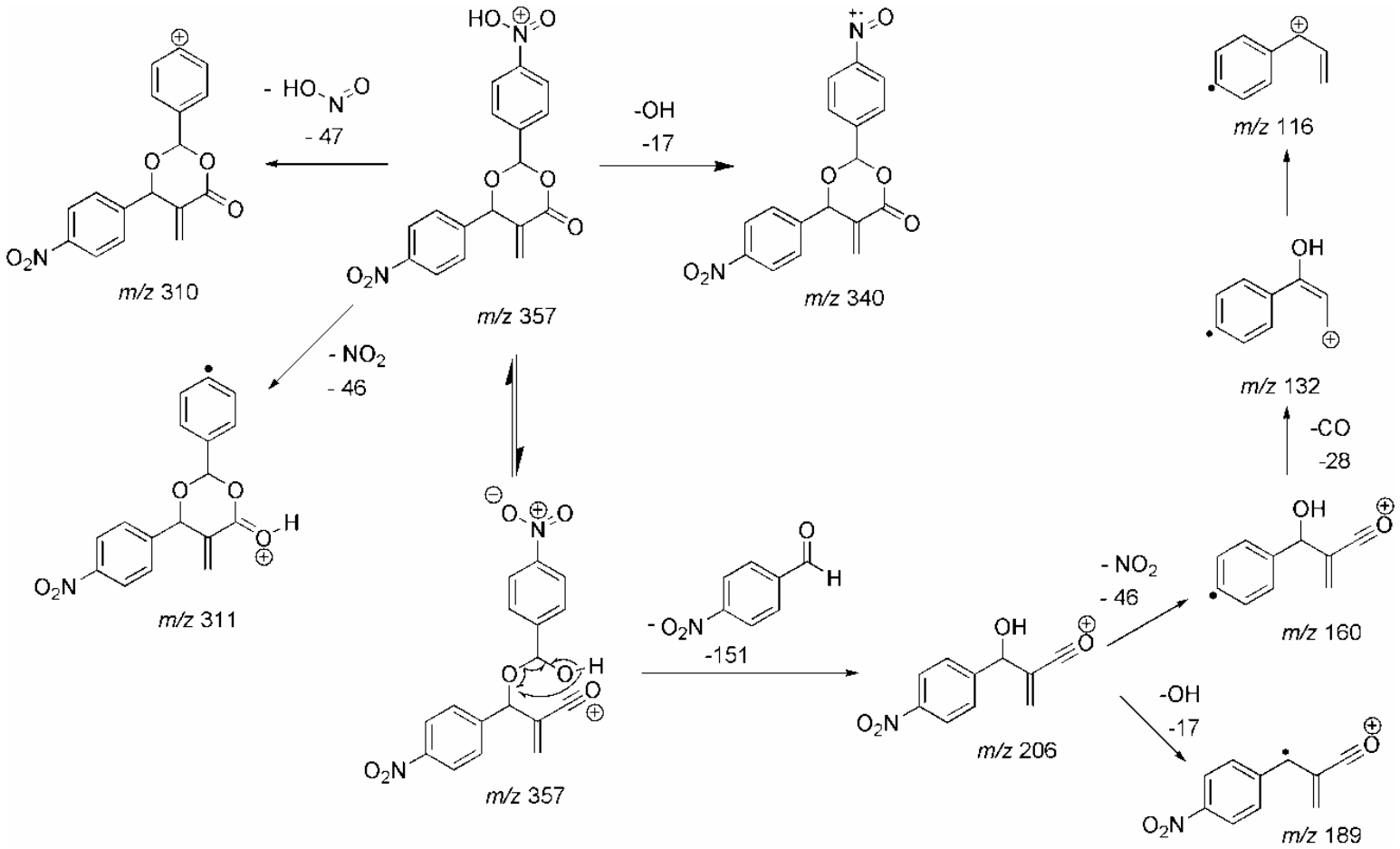


Fig. S13 Dioxanone (m/z 357) fragmentation chart

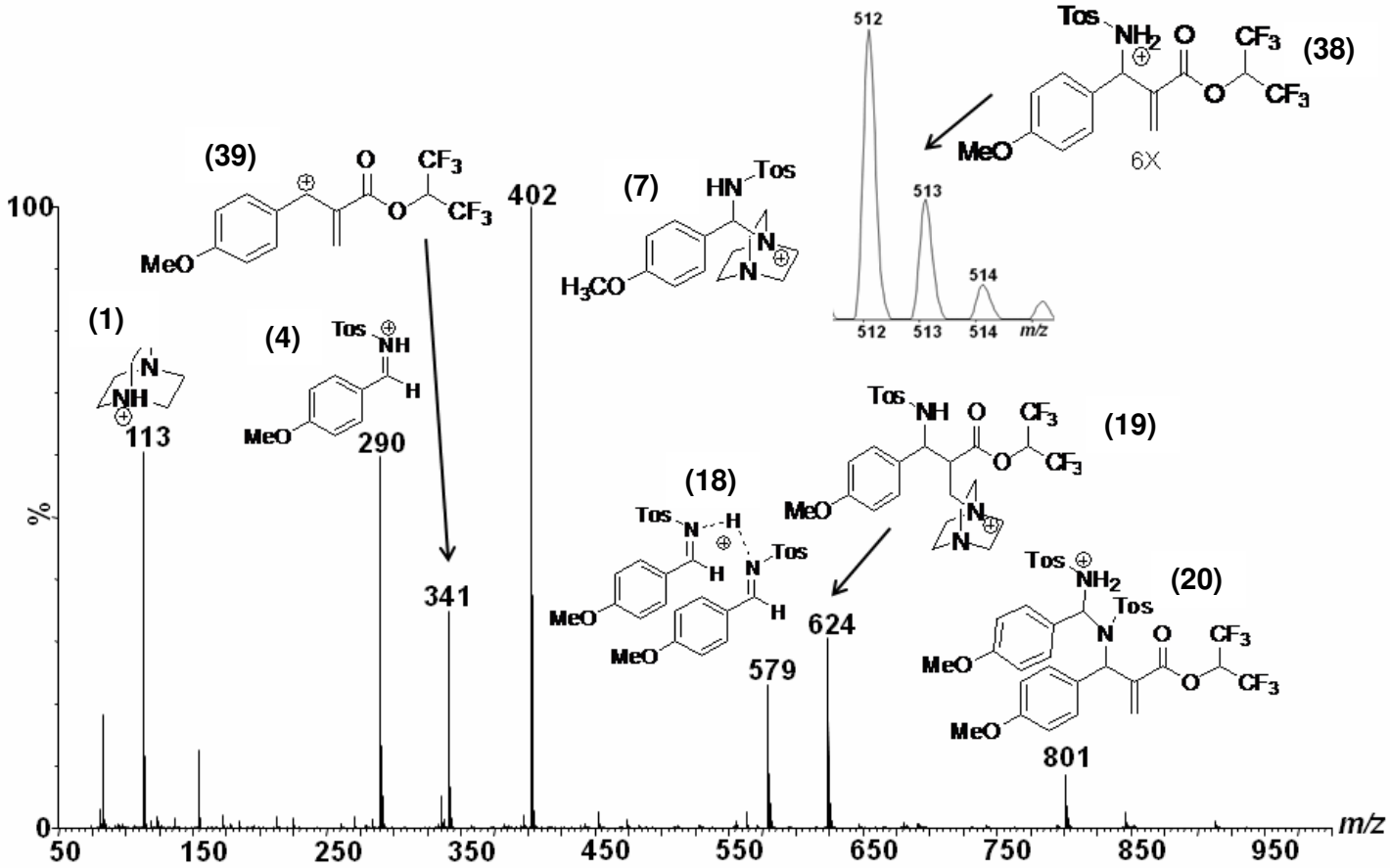


Fig.S14 ESI(+)-MS spectrum of the *aza*-MBH reaction between tosylimine (**4**) and hexafluoroisopropyl acrylate in the presence of DABCO (*t* = 30 min).

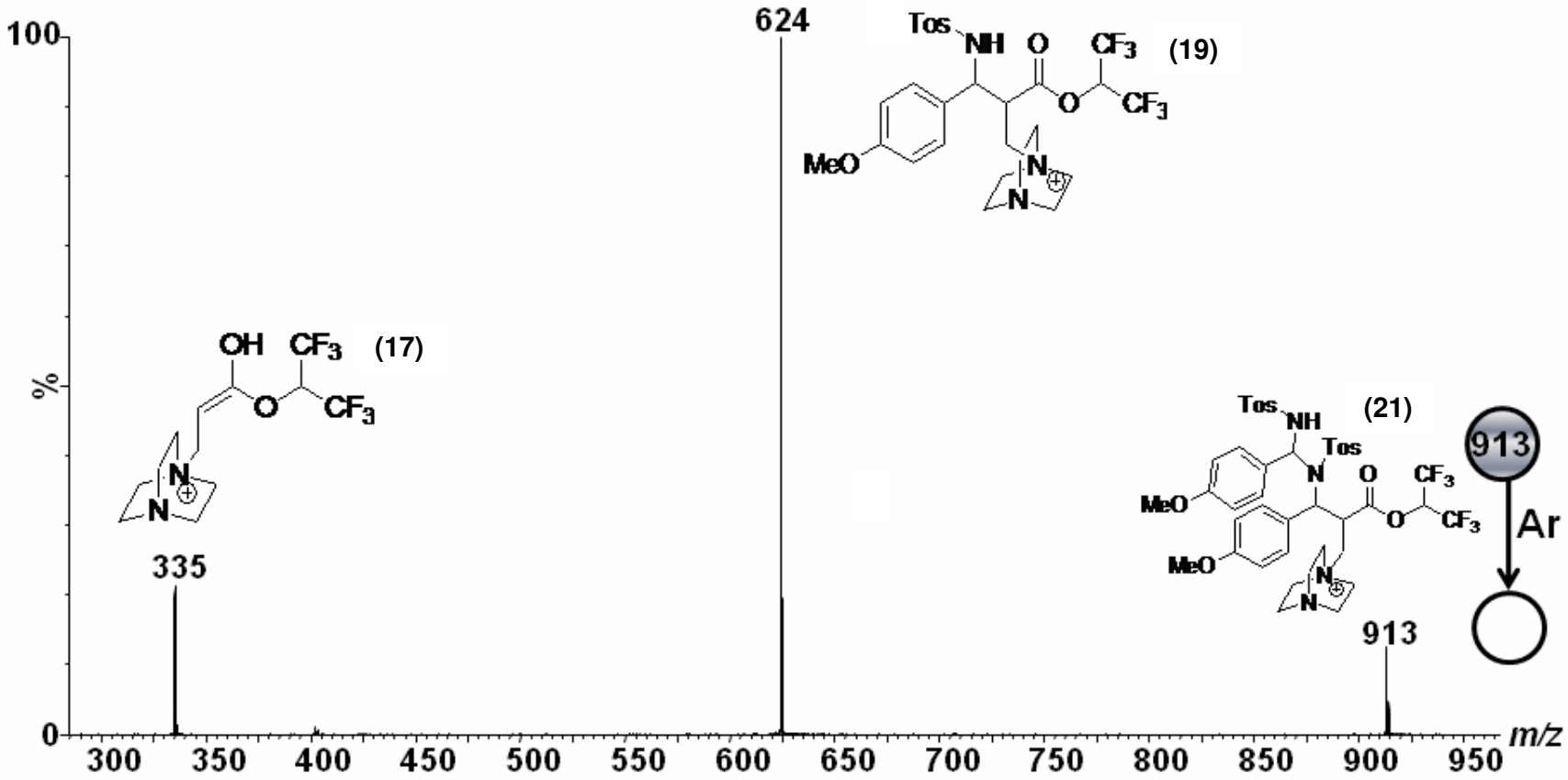


Fig. S15 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 913.

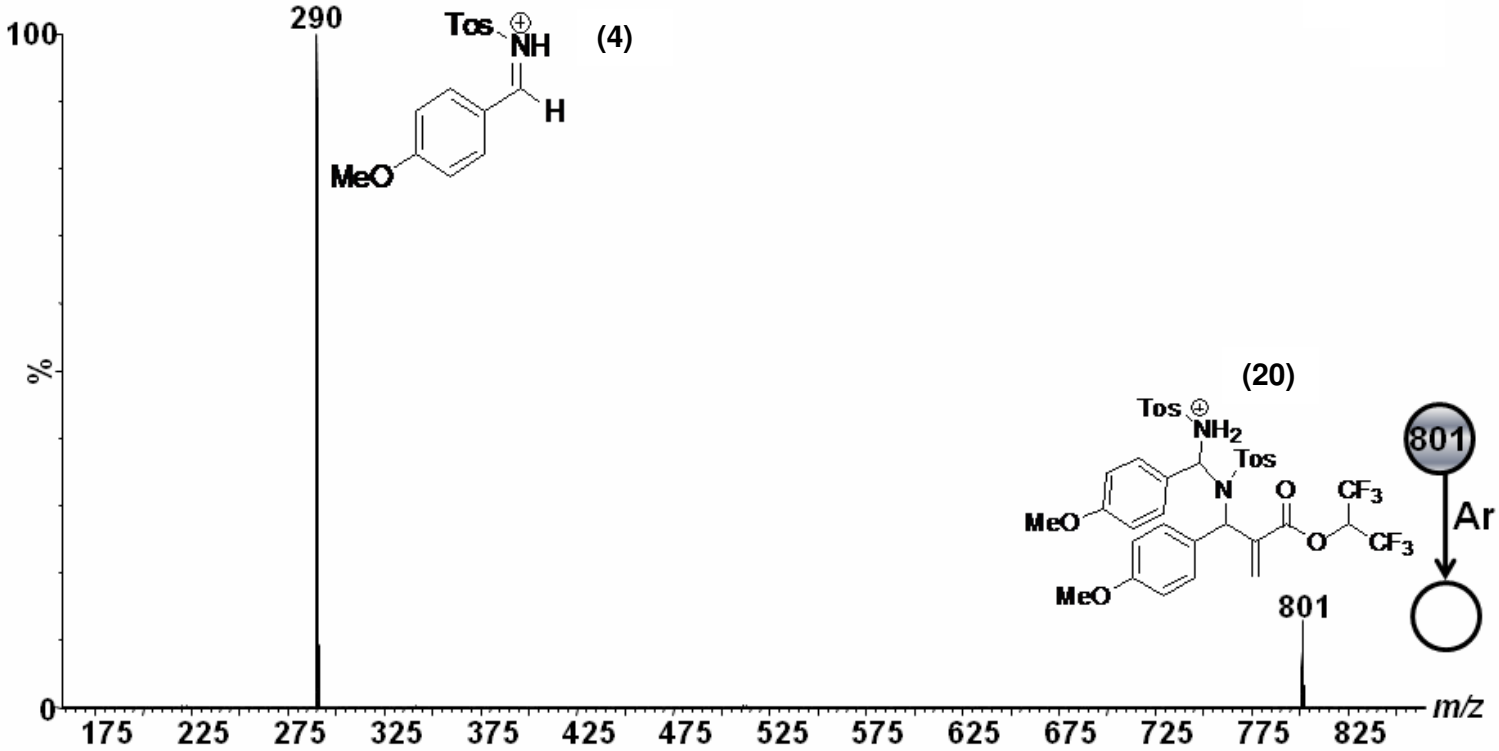


Fig. S16 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 801.

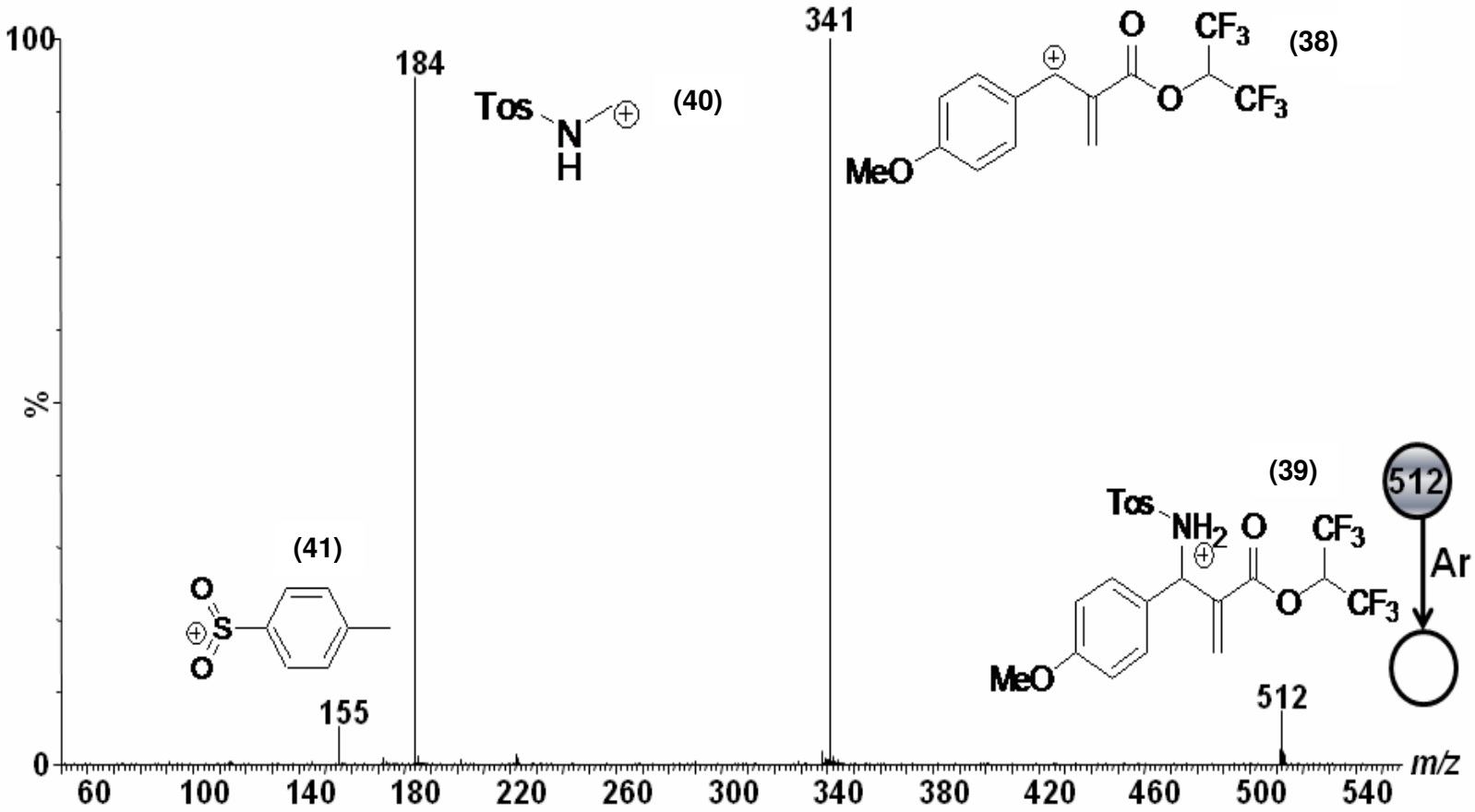


Fig. S17 ESI(+)-MS(/MS) spectrum of the ion of *m/z* 512.