

**STRUCTURAL ANALYSIS OF ACRIDINEDIONES AND CONDENSED ACRIDINES DERIVATIVES BY MASS SPECTROMETRY****PERIYASAMY MURUGAN***Department of Chemistry, Vel Tech University, Avadi, Chennai 600 062, India.***ABSTRACT**

Several series of acridinediones and pyrazoloacridines derivatives have been investigated by EI mass spectrometry because of their versatile wide applications such as laser dyes¹, OLED properties², solar cell³ and biological activities⁴. For all acridinediones compounds the electron ionization (EI) spectra are very clean, being dominated by loss of atoms or radicals such as CO, CH₃, ketene, isobutylene. In the case of pyrazoloacridine derivatives, loss of H and HCN was observed from the compounds derived from dihydroresorcinol and loss of H, CH₃ due to presence of methyl groups was observed from the compounds derived from dimedone. In this paper, we would like to report the mass spectral fragmentation of 9- mono substituted acridinediones (1a-g, 2a-h) and 10,10'-bisacridinediones (3a-c), 9,9'-bisacridinediones (4a-b) and mono, bis-pyrazoloacridine derivatives (5 a-d, 6 e-g, 7).

KEY WORDS: Acridinedione, pyrazoloacridine, dihydroresorcinol, dimedone, ketene, isobutylene, methyl group.

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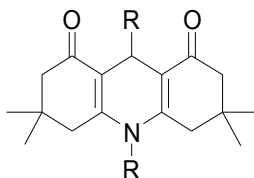
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INTRODUCTION

Mass spectrometry (MS) is unequivocally a powerful tool of characterization of organic compounds. The mass spectra of 9-substituted acridinediones in general show very weak molecular ion. The base peak is invariably due to the ion obtained by loss of 9- substituents (Scheme – I, Table –I). Signal due to cleavages at α -bond and β -bond of the N-alkyl substituent have been observed (b,c) from the molecular ion. The fragmentations due to loss of CO and isobutylene from (a) have been observed (d,e,f). Another common fragment at m/z 272(or273) has also been recognized from acridinediones, by loss of the substituents at

9, 10 and gaining one H^+ . In case of 9,9'-bisacridinedione fragmented into the mono acridinediones followed by the further general pattern characteristic of 9-substituted acridinediones (4 a-b). For mono, bis-pyrazoloacridines systems we have observed that the molecular ion as a base peak for compounds 5a-d derived from dihydroresocinol. Whereas, for dimedone derived compounds 6a-c, 7, the base peak was the ion obtained from the molecular ion by loss of a methyl group from that gem-dimethyl groups. Loss of H and HCN was observed from compounds 5a-d from the molecular ion. For the compounds 6a-c and 7, these were a loss of H, CH_3 due to presence of methyl groups.

Experimental



1 a-h

Compound	R	Compound	R
1a	$C_6H_5CH_2-$	1e	$CH_3CH_2CH_2-$
1b	$CH_2=CH-CH_2-$	1f	$CH_3CH_2CH_2CH_2-$
1c	$CH_3COOCH_2CH_2-$	1g	Furfuryl
1d	$CH_3OCH_2CH_2CH_2-$	1h	$P-NH_2SO_2-C_6H_4-$

Common fragments (m/z 272 or 273) in most of the compounds observed was given below

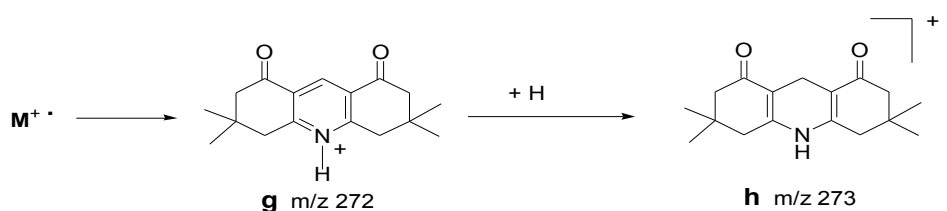
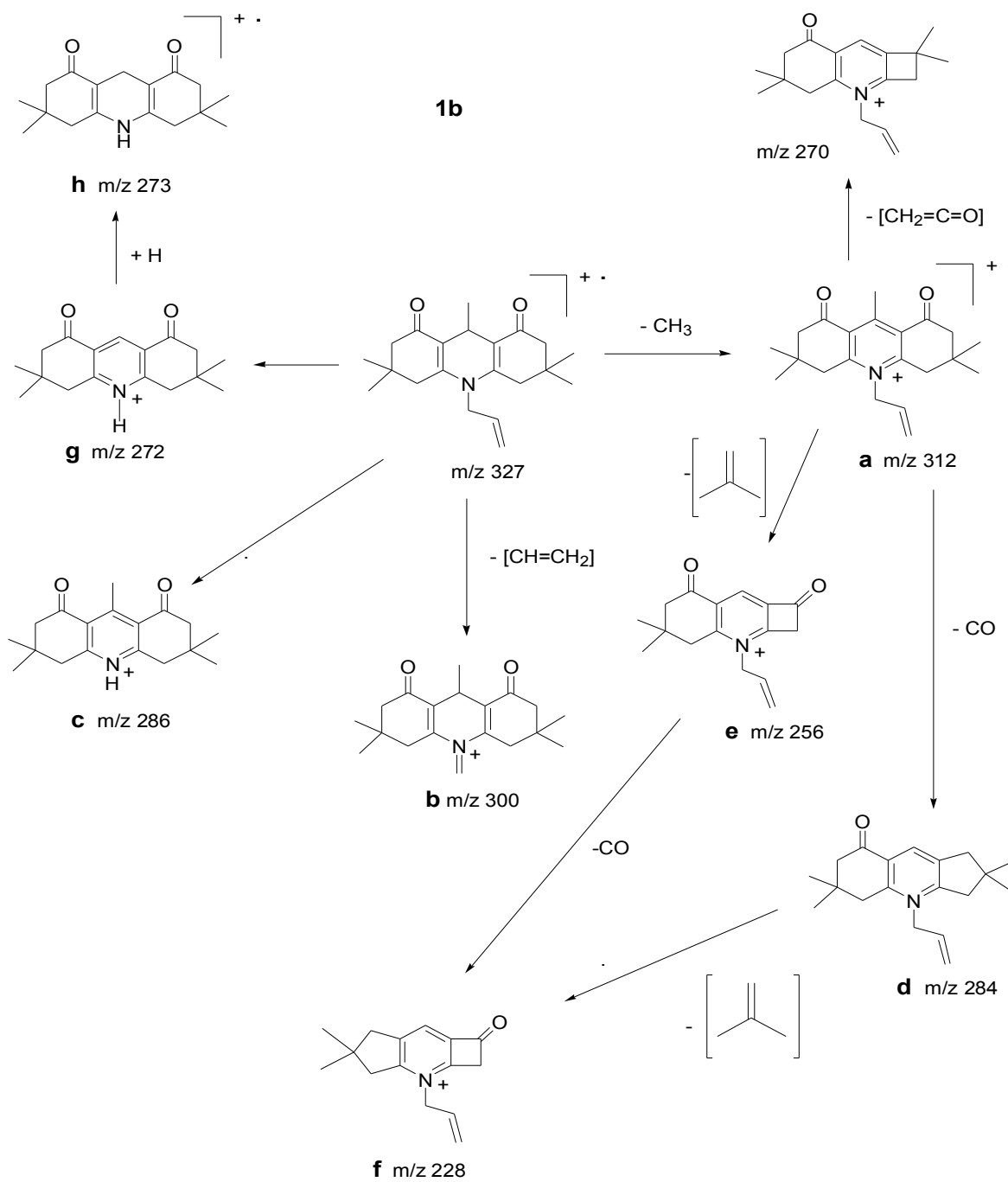


Table I

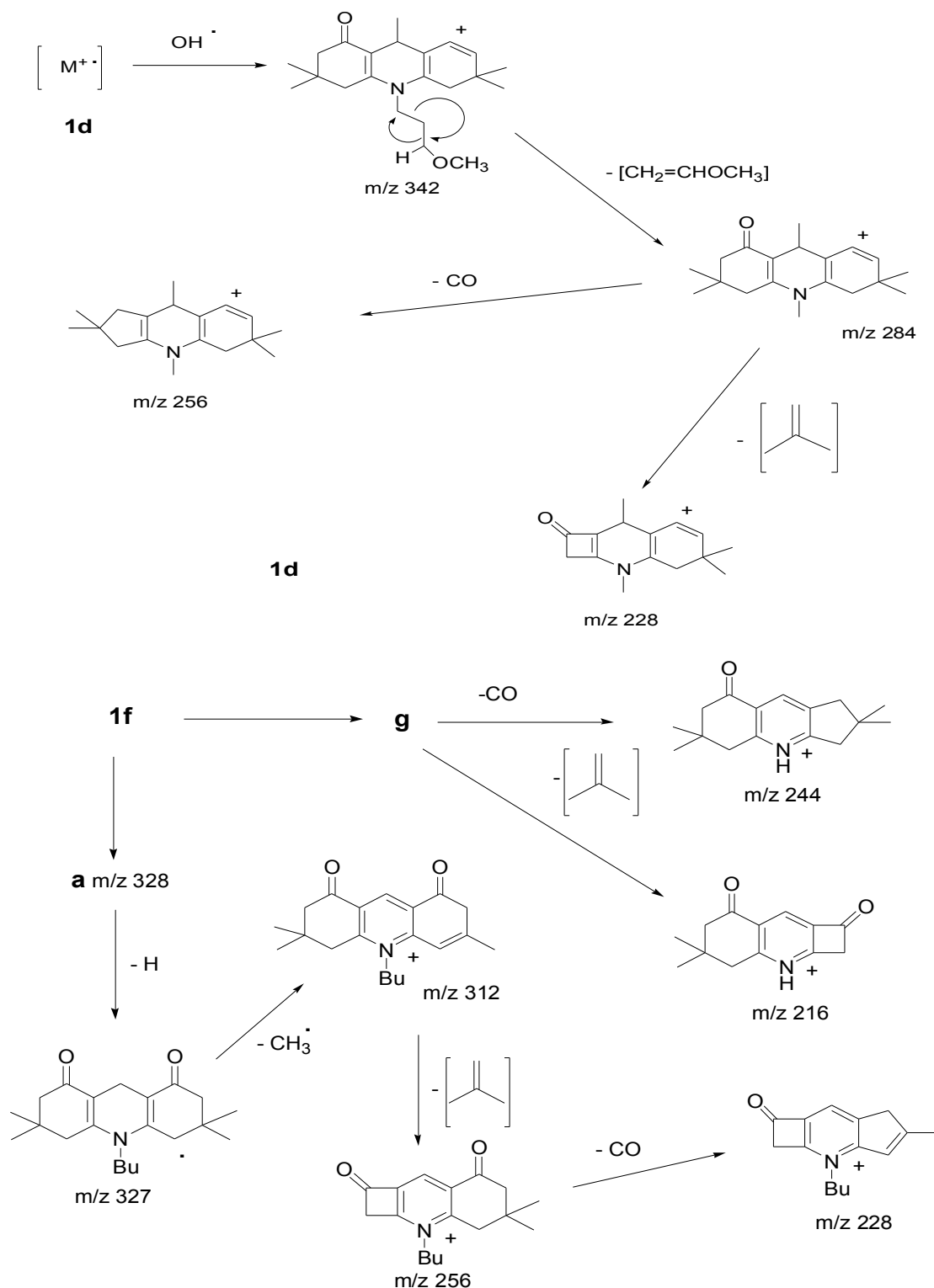
COMPOUNDS							
Compound	Fragment	1a	1b	1c	1d	1f	1g
M ⁺		377 (0.1)	327 (0.5)	374 (M+1, 0.1)	359 (1.5)	343 (25)	368 (M+1, 20) 367(20) 366(35)
a		362 (17.6)	312 (100)	358 (34.3)	344 (100)	328 (100)	352 (70)
b		-	300 (0.3)	300 (0.5)	300 (1.9)	300 (10.0)	-
c		286 (1.5)	286 (2.5)	-	286 (1.5)	286 (20)	286 (10)
d		-	284 (3.4)	-	284 (1.2)	284 (1.2)	-
e		-	256 (1.3)	-	256 (1.7)		
f		-	228 (1.9)	-	-	-	-
g		-	272 (2.1)	272 (1.2)	272 (1.9)	272 (90)	272 (1)
h		273 (1)	273 (17.7)	-	-	-	-

Compound 1b shows loss of 9-substituted CH₃ group at m/z 312 and followed by loss of ketene at m/z 270, other major signals at m/z 300,284,256,228 may arise from fragment of ethylene, CO, isobutylene respectively



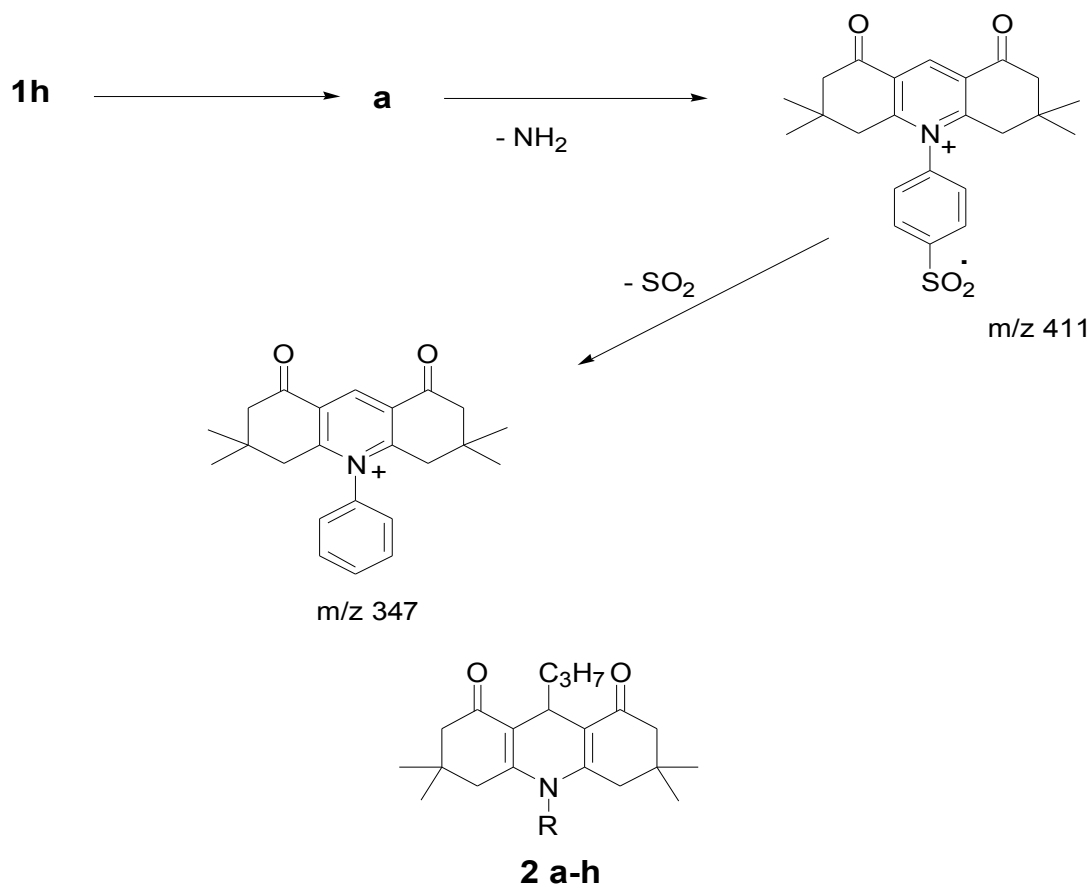
Scheme - I

Other signals arising from the specific structural features have been recognized. Compound 1c show the loss of ketene from the acetoxy group followed by CO.



Compound (1g) shows a strong M-1 signal in addition to many common fragments. The base peak is due to furyl ion (m/z 81). Compound 1a also shows the base peak due to tropylium ion (m/z 91). This is in line with the general observation reported in the literature¹. Further the absence of signal at m/z 300 (fragment b) due to the cleavage of the β – bond of the N-substituents resulting in the loss of unstable phenyl and furyl radical is notice for compounds 1a and 1g, supporting the fragmentation pathway.

Compound 1h shows the loss of NH₂ and SO₂ from sulfonamide group.



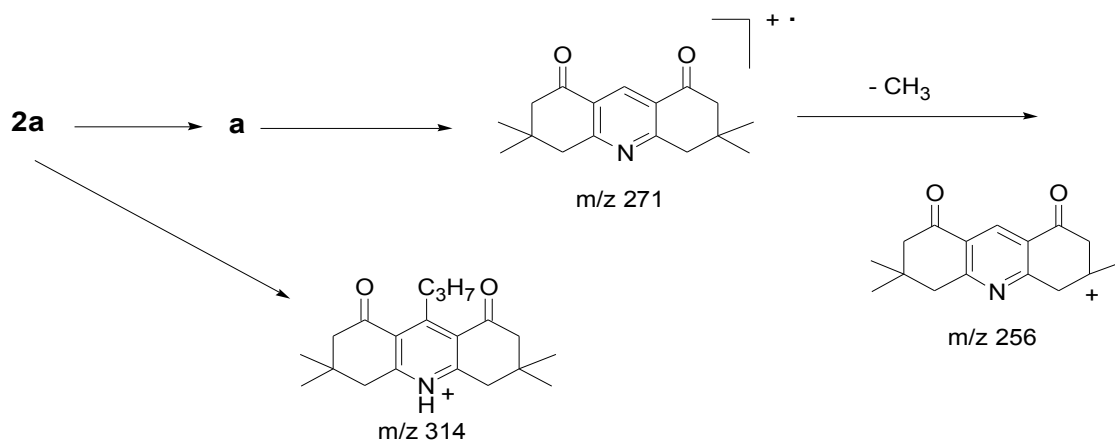
Compound	R	Compound	R
2a	C ₆ H ₅ CH ₂ -	2e	CH ₃ CH ₂ CH ₂ -
2b	CH ₂ =CH-CH ₂ -	2f	CH ₃ CH ₂ CH ₂ CH ₂ -
2c	CH ₃ COOCH ₂ CH ₂ -	2g	P - CH ₃ O-C ₆ H ₄ -
2d	CH ₃ OCH ₂ CH ₂ CH ₂ -	2h	H

The mass spectra of 9-propyl acridinediones in general show very weak molecular ion signals. The propyl group loss is highly facile to give the respective fragment a, as the base peak. Fragmentation, in general takes same mode as is observed in the 9-methyl analog. A detailed fragmentation is depicted for compound 2c (Scheme – II ; Table- II).

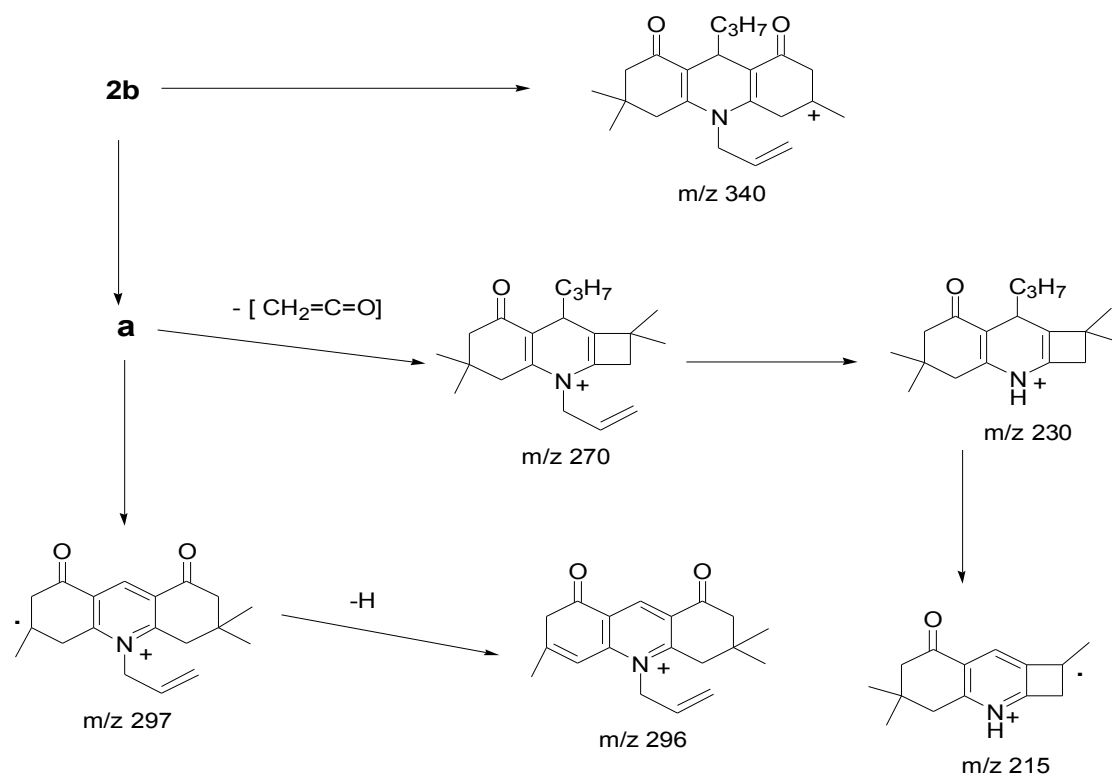
Table II
COMPOUNDS

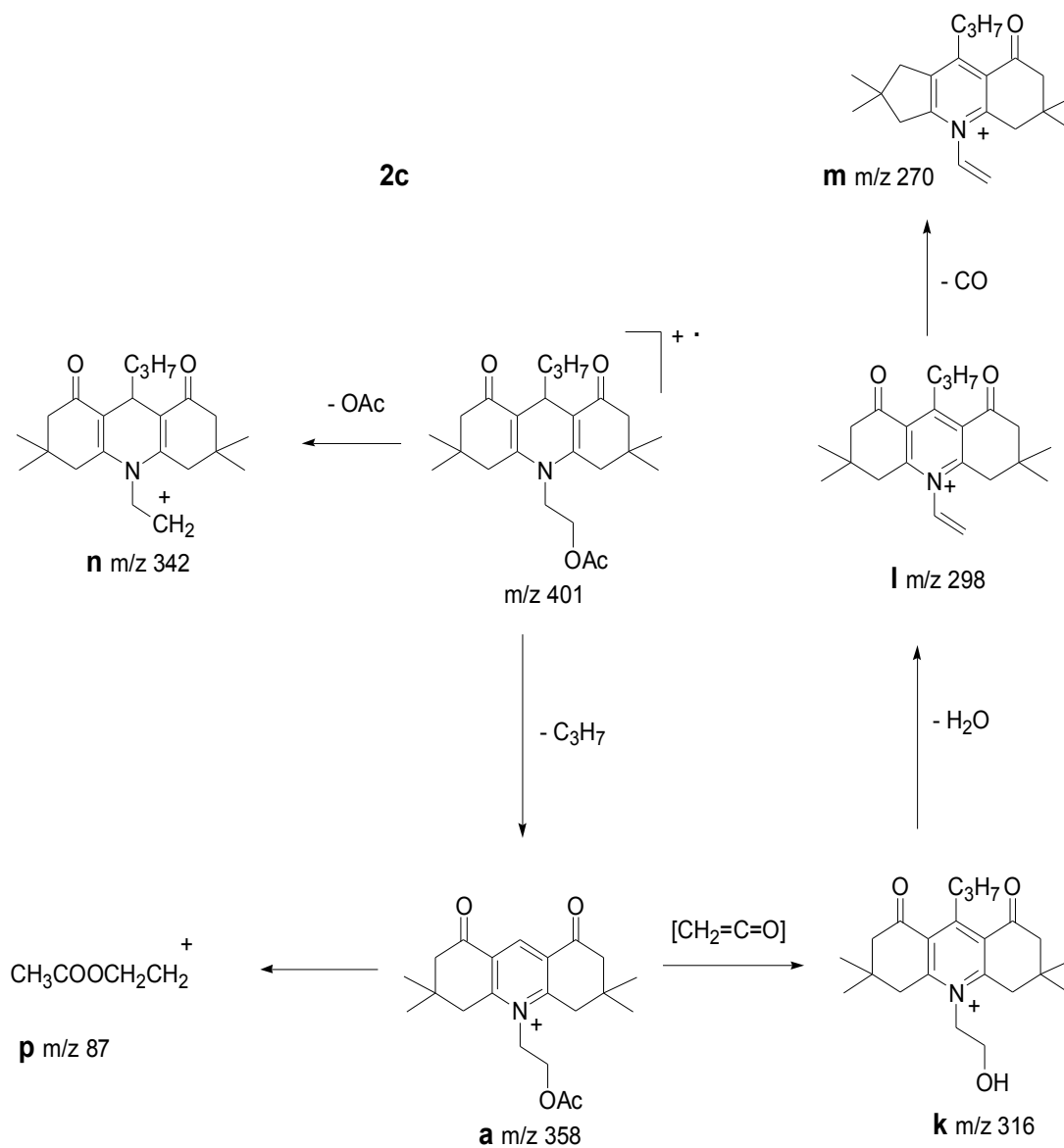
COMPOUND Fragment	2a	2b	2c	2e	2f	2g	2h
M⁺	405 (0.12)	-	401 (0.07)	-	371 (0.06)	422 (M+1,10.9)	314 (M-1,1.2)
a	362 (79.8)	312 (100)	358 (100)	314 (100)	328 (100)	378 (100)	272 (100)
b	-	284 (0.6)	328 (0.45)	-	-	-	-
c	-	-	300 (2.5)	-	-	-	-
d	-	-	284 (1.8)	-	-	-	-
e	-	-	256 (0.8)	-	-	-	-
f	-	-	228 (0.8)	-	-	-	-
g	272 (4.8)	272 (2.6)	272 (2.9)	-	272 (8.8)	272 (100)	-
h	273 (6.0)	273 (6.0)	273 (2.3)	-	273 (5.1)	-	-
i	-	-	-	-	216 (1.6)	-	216 (4.1)
j	-	-	-	-	215 (1.0)	-	215 (2.2)

Signals characteristic of the N-substituents are also observed. Compound 2a gives tropylium ion as the base peak at m/z 91. Benzyl group loss from M^+ as well as from fragment **a** give signals at m/z 314 and m/z 271 respectively.



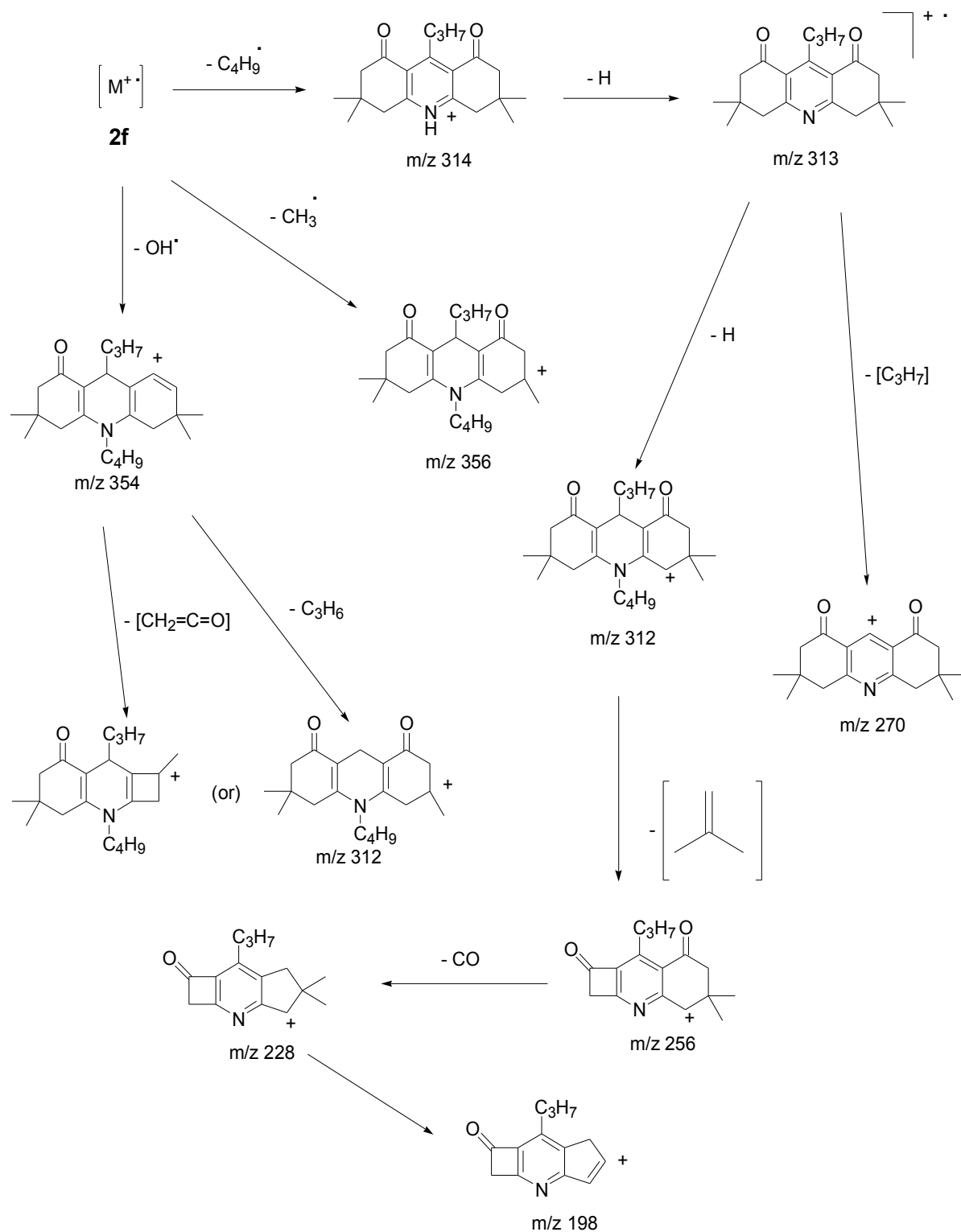
Compound 2b shows also loss of CH_3 at m/z 340; other signals at m/z 297, 296, 270, 230, 215 may arise from fragmenta as depicted.



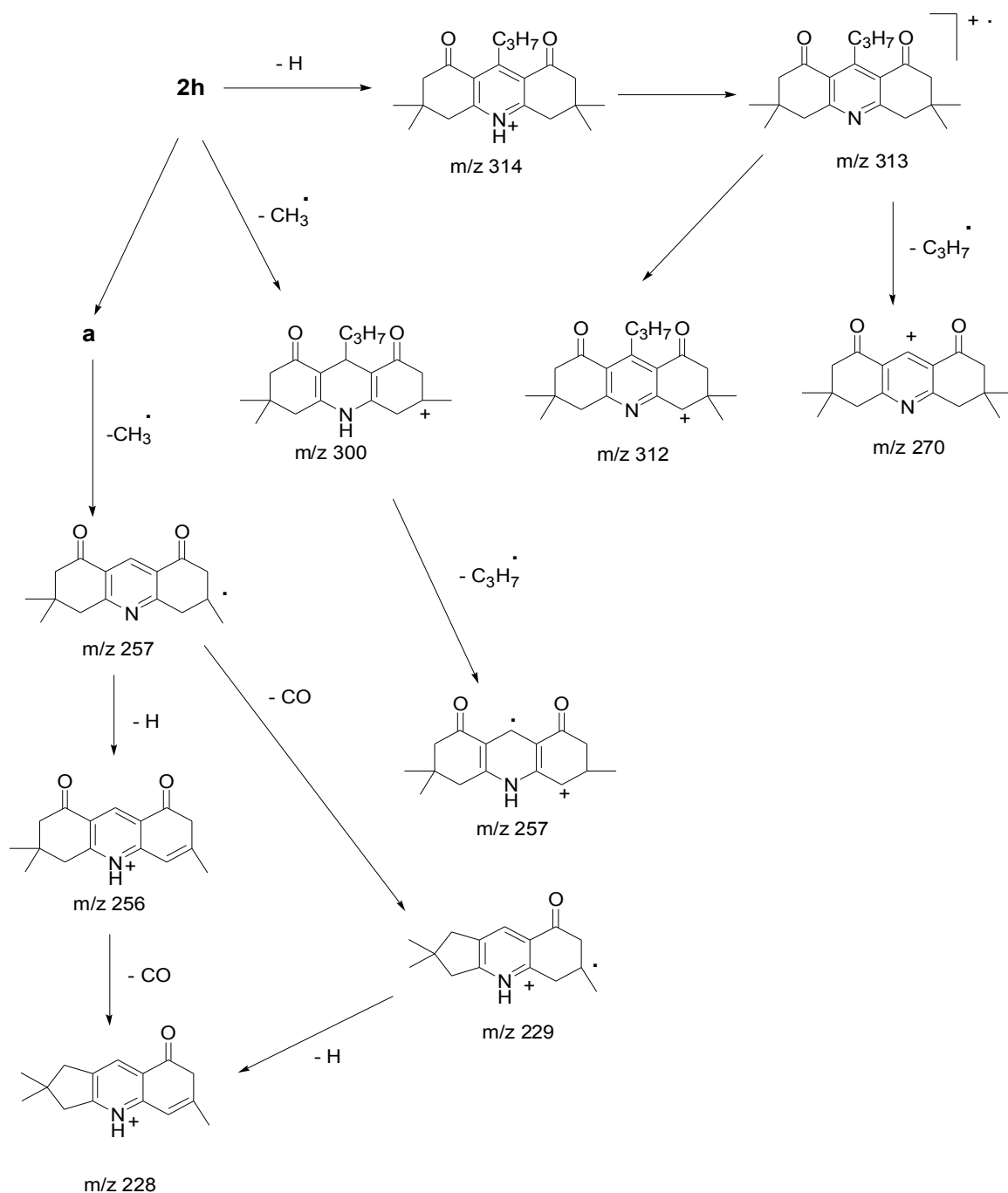


Scheme- II

Compound 2f shows (M-CH₃)⁺, (M-OH)⁺, (M-C₄H₉)⁺ and other derived signals as follows



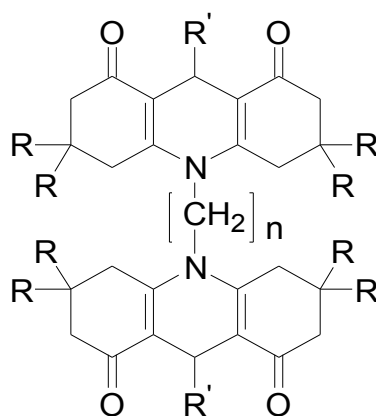
Compound 2g shows many peaks arising from fragments and through the loss of CH_2O from a.



Next we discuss the mass spectral fragmentation of bisacridinediones. The fragmentations of 10,10'-bisacridinediones 3a, 3b, 3c were depicted (Table -III, Scheme -III). In general, the molecular ion was not detected (except 3a). The fragmentations occur so as to

give acridinedione moieties, followed by the loss of CO as observed in the mono system. The 9,9'-bisacridinedione fragmented into the monoacridinediones followed by further general pattern characteristic of 9-substituted acridinediones.

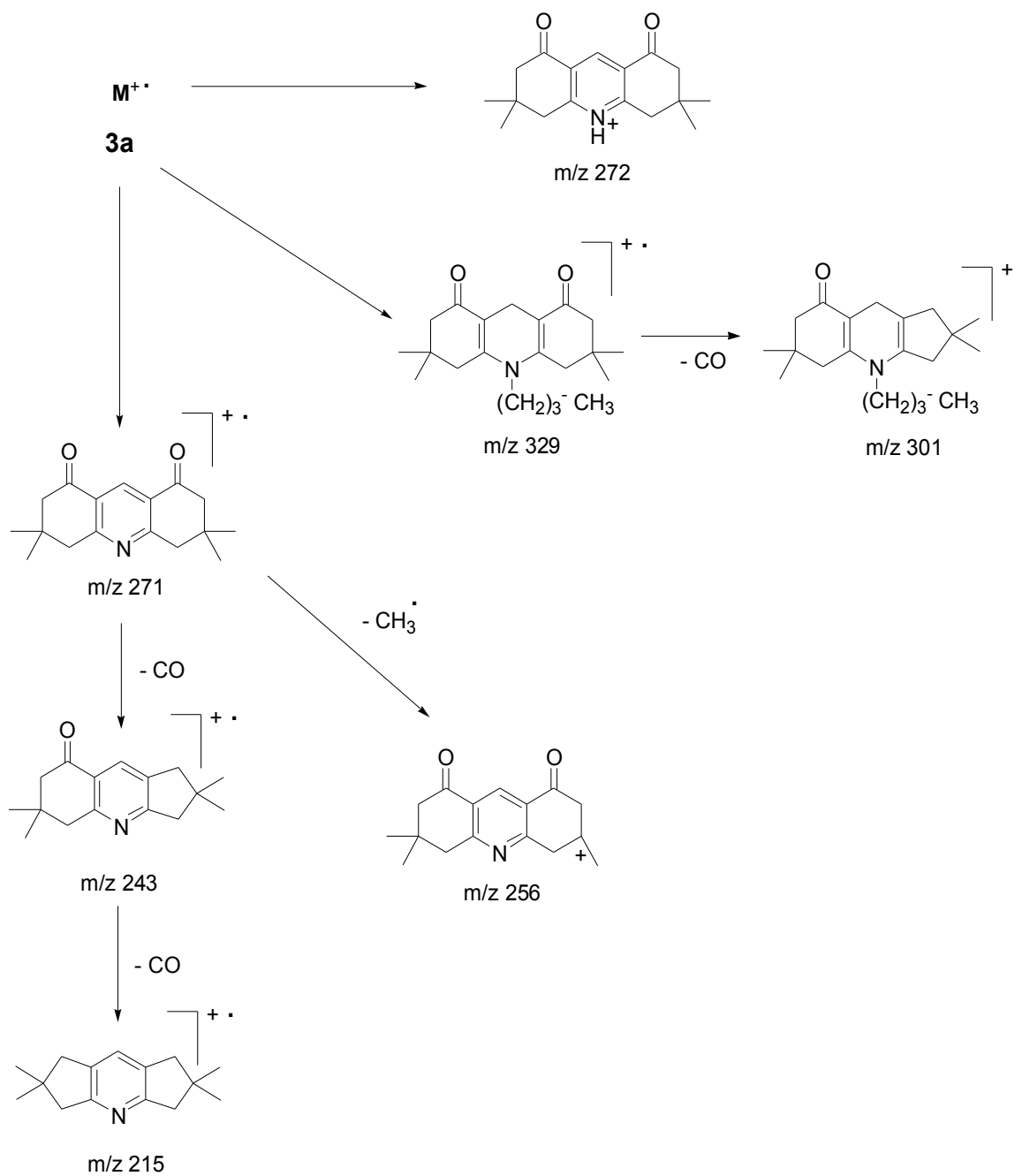
10,10'- Bisacridinediones



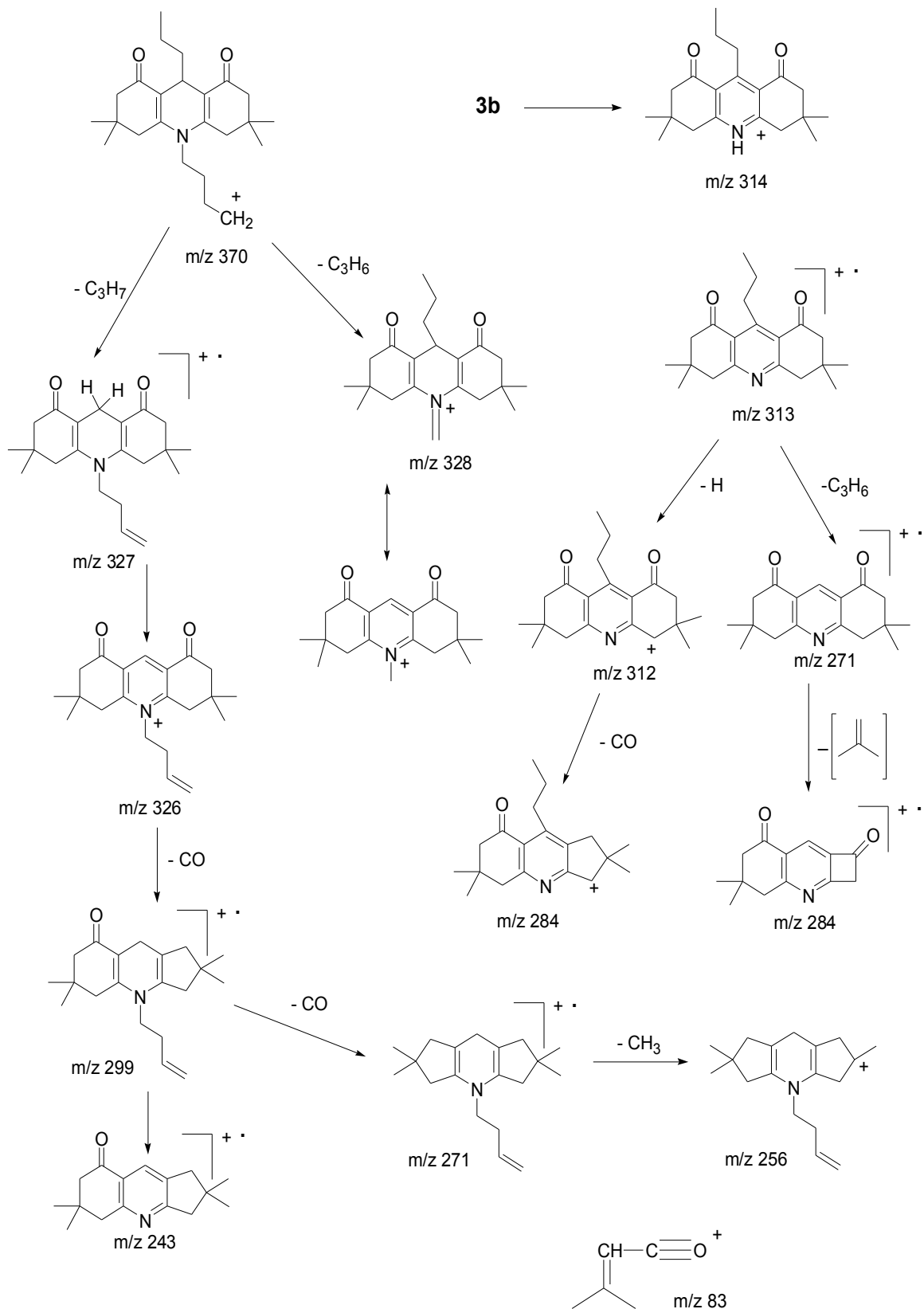
3 a - c

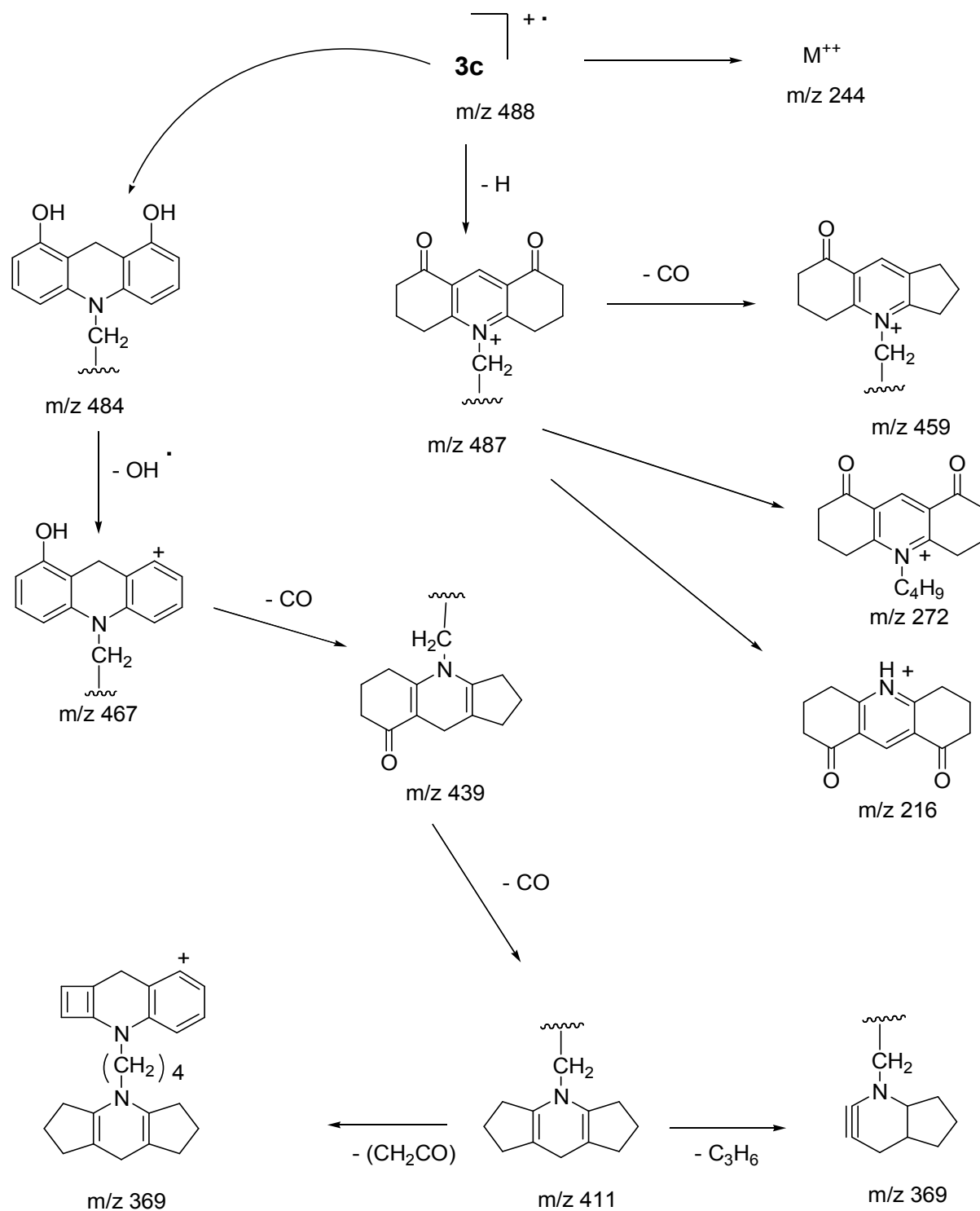
Table III

COMPOUND	R	R'	n
3a	CH ₃	H	4
3b	CH ₃	C ₃ H ₇	4
3c	H	H	4



Scheme III





The 9,9' - bisacridinedione fragmentations are explained as given below, for compounds 4a, 4b. Here again, the initial fragmentation occurs to result in two acridinedione units followed by the general pattern (Table – IV , Scheme-IV).

9,9' - Bisacridinediones

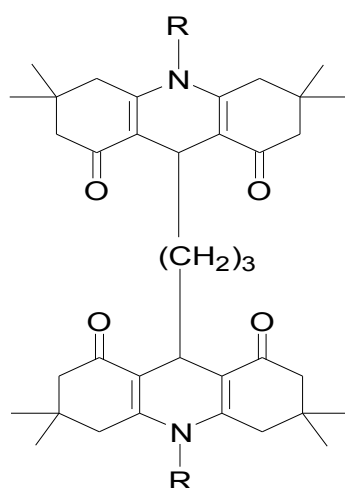
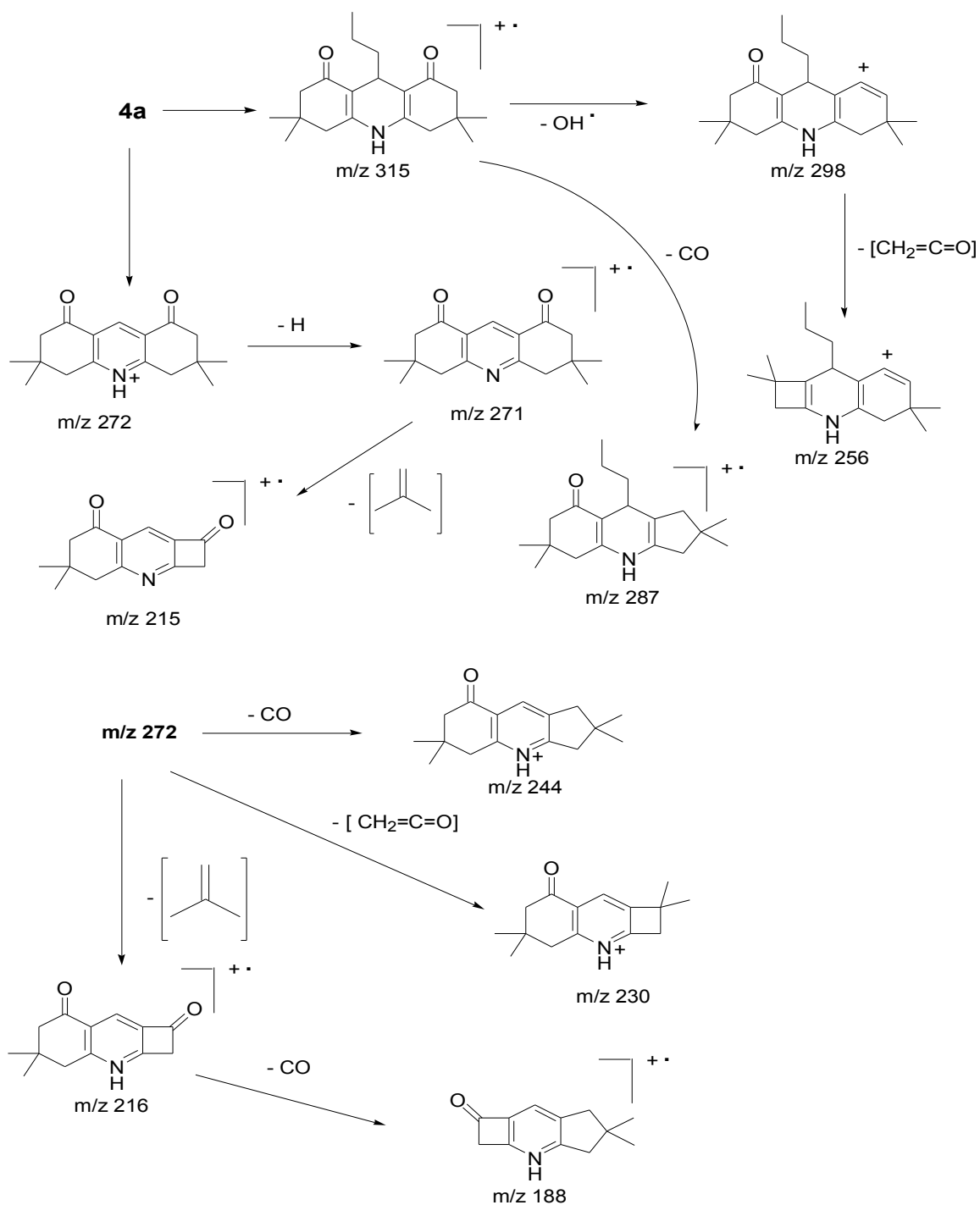
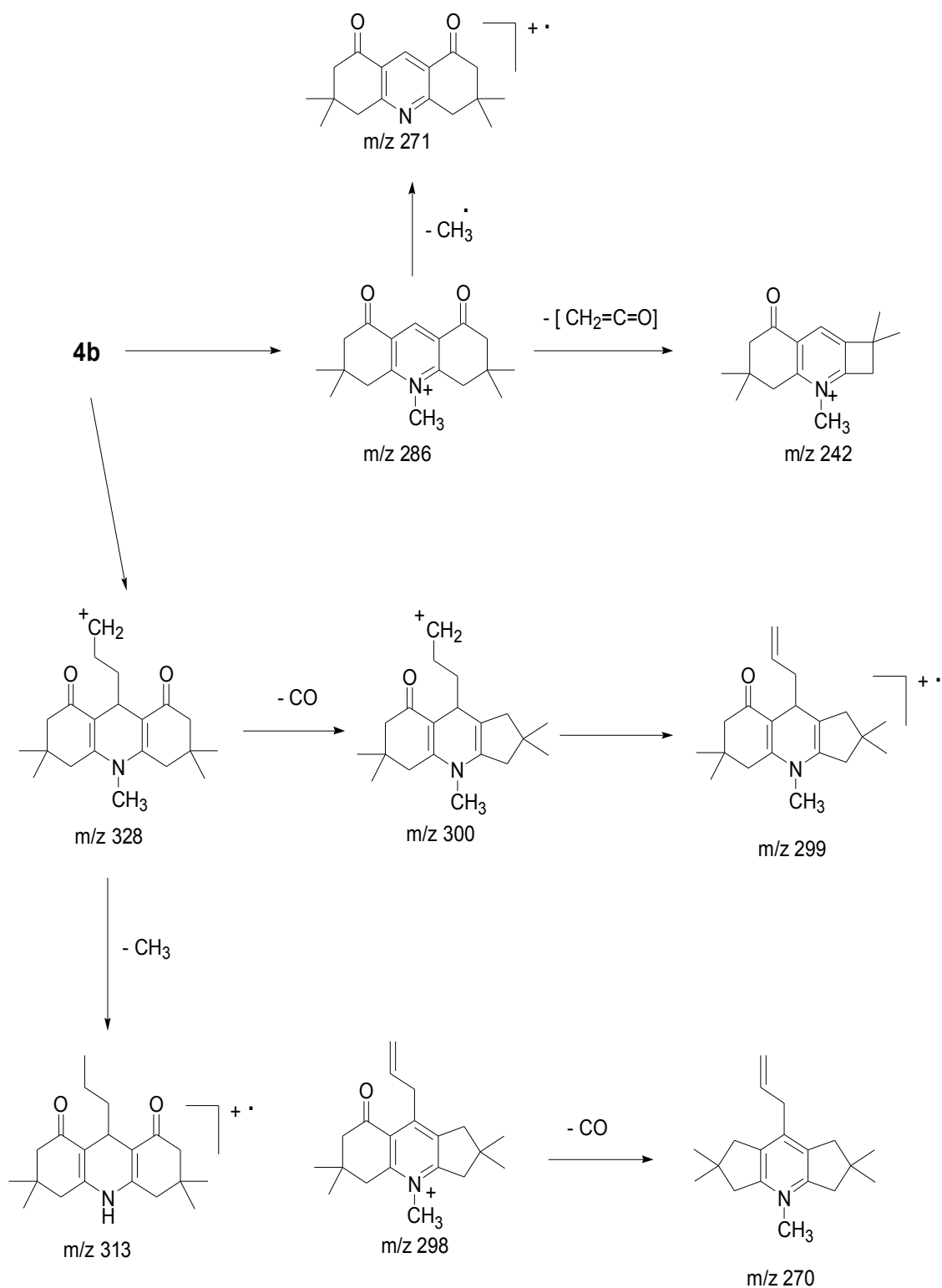


Table IV

COMPOUND	R
4a	H
4b	CH ₃



Scheme IV

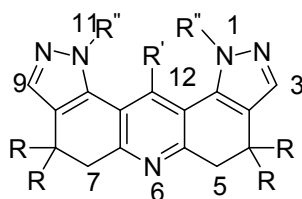


Mass spectra for mono and bis-pyrazoloacridines were studied (Table V, VI, Scheme- V,VI) . It has been observed that the molecular ion was the base peak for compounds 5a-d derived from dihydroresocinol. Whereas, for dimedone derived compounds

6a-c,7, base peak was obtained from molecular ion by loss of a methyl group from that gem-dimethyl groups. Loss of H and HCN was observed from the compounds 5a-d from the molecular ion. For the compounds 6a-c and 7, these were a loss of H, CH₃ due to presence

of methyl groups. As commonly observed in acridinedione systems that the mass spectral fragmentations of 7 shows loss of isobutylene

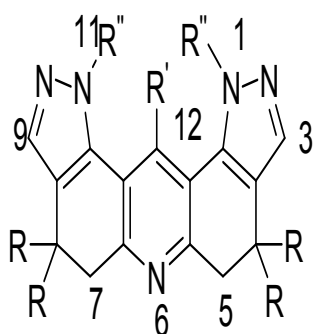
and ketene, due to presence gem-dimethyl groups and carbonyl group (Scheme- VII).



5 a-d

Table V

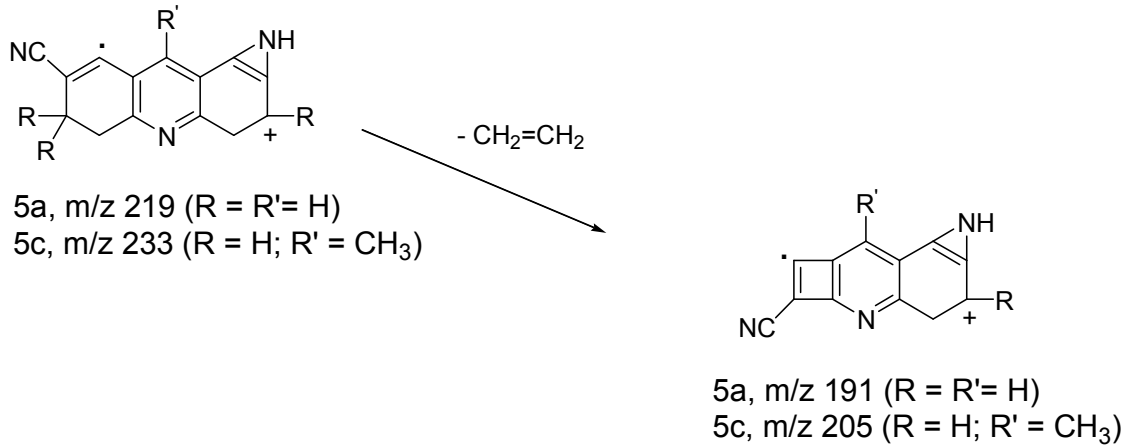
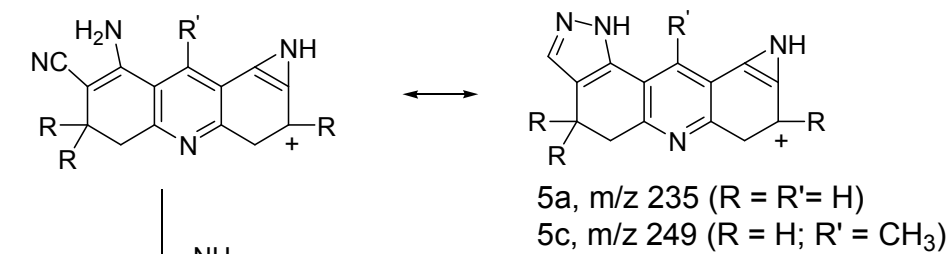
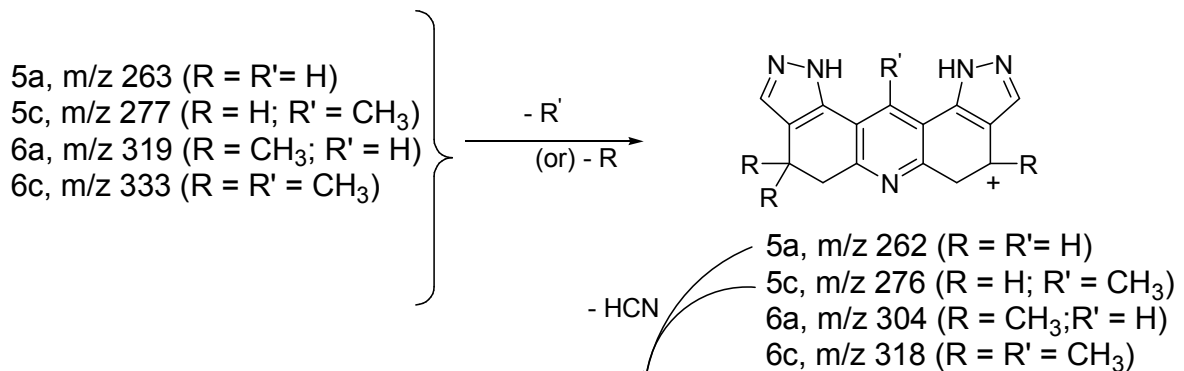
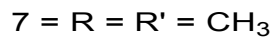
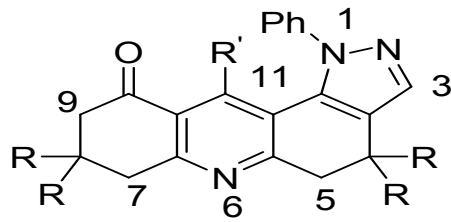
COMPOUND	R	R'	R''
5a	H	H	H
5b	H	H	C ₆ H ₅
5c	H	CH ₃	H
5d	H	CH ₃	C ₆ H ₅



6 a-c

Table VI

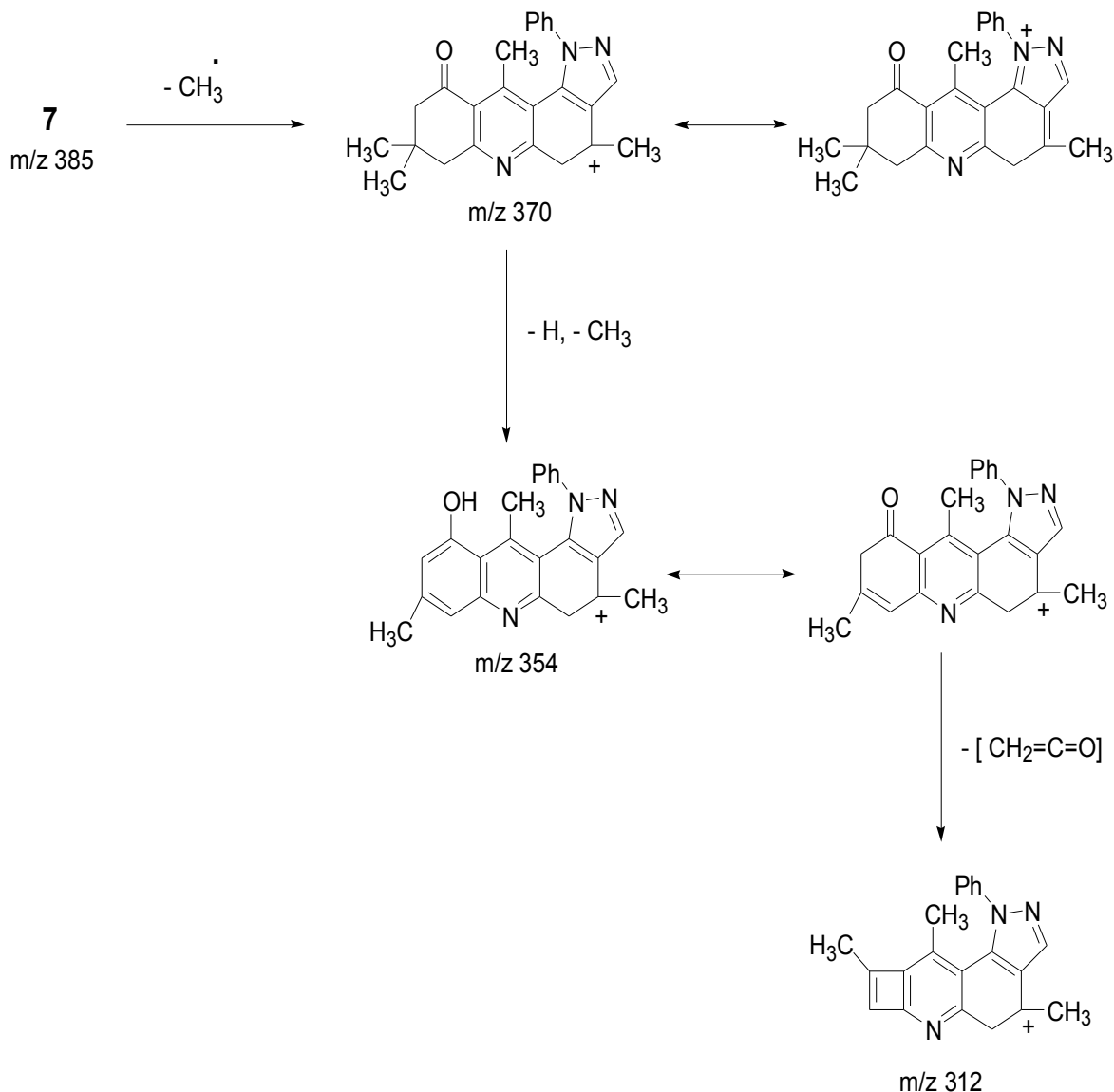
COMPOUND	R	R'	R''
6a	CH ₃	H	H
6b	CH ₃	H	C ₆ H ₅
6c	CH ₃	CH ₃	H



Scheme – V, VI

For compound 5c (m/z 277 M^+) the loss of H gives rise to m/z 276 peak, which on further fragmentation gives rise to m/z 249 signal (by the loss of HCN), which then leads to m/z 205 signal, similar to compound 5a.

The methyl radical loss from the gem-dimethyl group but 12-methyl group fragmentation does not occur from compound 6c.



Scheme VII

CONCLUSION

Totally 28 acridinediones and pyrozoloacridines derivatives were studied for their mass spectral fragmentations. Molecular mass information and fragmentation pattern are easily obtained under the electron

ionization (EI) condition. Common fragment at m/z 272 (or 273) has also been recognized from most of the acridinediones, by loss of the substituents at 9, 10 and gaining one H^+ . In the case of 10, 10-bisacridinediones, the molecular ion was not detected (except 3a). The 9,9'-bisacridinedione fragmented into mono acridinediones followed by the further

general pattern characteristic of 9-substituted acridinediones. In the case of dimedone derived compounds pyrazoloacridines 6a-c, 7, base peak was obtained from molecular ion by loss of a methyl group from those gem-dimethyl groups.

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