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SUPPLEMENTARY MATERIAL

Oxidative Degradation of Ranitidine Induced by UV and Ultrasound: Identification of Transformation Products using LC-Q-ToF-MS

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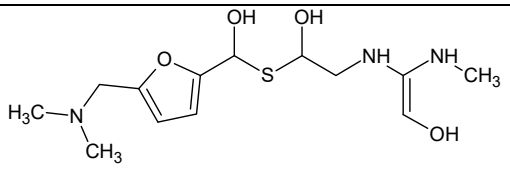
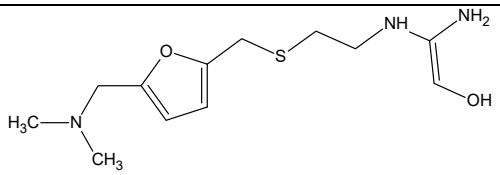
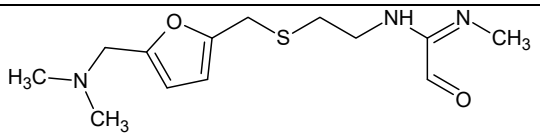
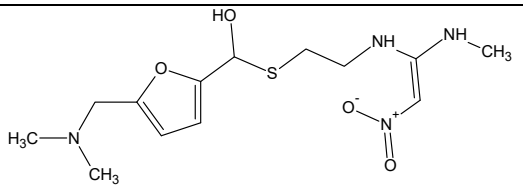
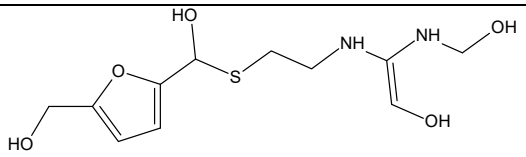
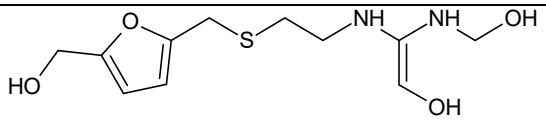
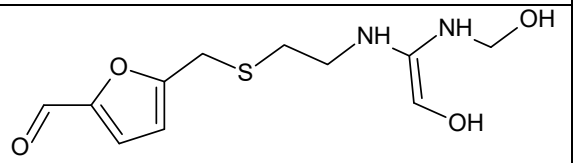
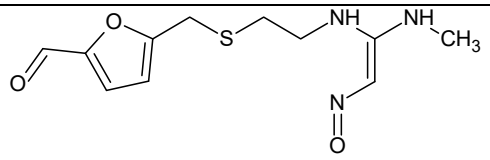
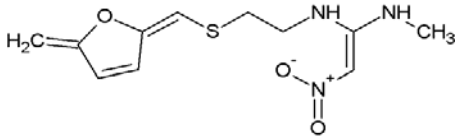
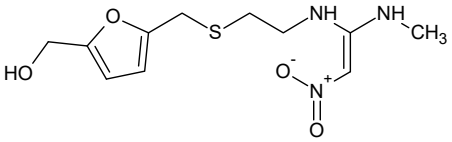
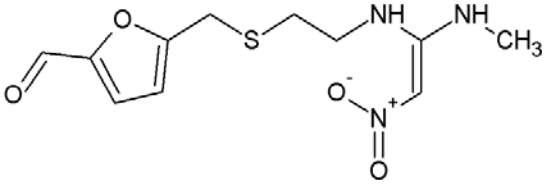
Table S1.Elemental composition and measured mass error.

Sl. No.	R_t	Fragment ions		Error (ppm)	Structure of the TP
		m/z	Elemental composition		
TP-1	2.7	318.1488*	$C_{13}H_{24}N_3O_4S$	3.5	
		300.1382#	$C_{13}H_{22}N_3O_3S$	0	
		282.1276	$C_{13}H_{20}N_3O_2S$	3.5	
		277.0647	$C_{13}H_{13}N_2O_3S$	1.1	
		255.0803	$C_{11}H_{15}N_2O_3S$	3.5	
		237.0698	$C_{11}H_{13}N_2O_2S$	6.3	
		231.0803	$C_9H_{15}N_2O_3S$	6.5	
		227.0854	$C_{10}H_{15}N_2O_2S$	5.3	
		217.0647	$C_8H_{13}N_2O_3S$	1.4	
		186.0589	$C_8H_{12}NO_2S$	1.1	
		145.0436	$C_5H_9N_2OS$	2.5	
		138.0919	$C_8H_{12}NO$	3.6	
TP-2	2.7	272.1433*	$C_{12}H_{22}N_3O_2S$	3.3	
		227.0854	$C_{10}H_{15}N_2O_2S$	2.4	
		207.0749	$C_{10}H_{13}N_2OS$	2.7	
		186.0589	$C_8H_{12}NO_2S$	2.7	
		138.0919	$C_8H_{12}NO$	3.8	
		117.0486#	$C_4H_9N_2S$	2.6	
TP-3	2.9	284.1433*	$C_{13}H_{22}N_3O_2S$	4.2	
		266.1327	$C_{13}H_{20}N_3OS$	3.4	
		264.1120	$C_{12}H_{18}N_3O_2S$	4.8	
		256.1484	$C_{12}H_{22}N_3OS$	2.7	
		239.0854	$C_{11}H_{15}N_2O_2S$	3.8	
		211.0905	$C_{10}H_{15}N_2OS$	1.9	
		198.0589	$C_9H_{12}NO_2S$	2.5	
		170.0640	$C_8H_{12}NOS$	1.2	
		153.0374	C_8H_9OS	3.3	
		145.0436 #	$C_5H_9N_2OS$	1.4	
		138.0919	$C_8H_{12}NO$	3.6	
		124.0762	$C_7H_{10}NO$	2.4	
		117.0486	$C_4H_9N_2S$	4.3	
		113.0715	$C_5H_9N_2O$	1.8	

		88.0221	C_3H_6NS	1.1	
		158.0388	$C_5H_8N_3OS$	3.8	
TP-4	3.4	331.1440*	$C_{13}H_{23}N_4O_4S$	2.1	
		313.1334	$C_{13}H_{21}N_4O_3S$	1.3	
		286.0862	$C_{11}H_{16}N_3O_4S$	3.5	
		268.0790	$C_{13}H_{16}N_3O_4S$	0.4	
		222.0827	$C_{11}H_{14}N_2OS$	3.6	
		188.0745	$C_8H_{14}NO_2S$	1.6	
		156.1031	$C_8H_{14}NO_2$	0.6	
		138.0919#	$C_8H_{12}NO$	4.3	
TP-5	4.3	291.1015*	$C_{11}H_{19}N_2O_5S$	0.7	
		273.0909	$C_{11}H_{17}N_2O_4S$	2.9	
		255.0803	$C_{11}H_{15}N_2O_3S$	3.7	
		243.0803	$C_{10}H_{15}N_2O_3S$	2.2	
		241.1011	$C_{11}H_{17}N_2O_2S$	0	
		231.0798	$C_9H_{15}N_2O_3S$	6.4	
		209.1086	$C_8H_{19}NO_3S$	1.2	
		187.0423	$C_8H_{11}O_3S$	2.1	
		163.0550#	$C_5H_{11}N_2O_2S$	1.6	
TP-6	6.2	275.1066*	$C_{11}H_{19}N_2O_4S$	0.4	
		257.0960	$C_{11}H_{17}N_2O_3S$	1.9	
		163.0541	$C_5H_{11}N_2O_2S$	1.8	
		147.0592	$C_5H_{11}N_2OS$	5.4	
		111.0446#	$C_6H_7N_2O_2$	1.8	
		105.0664	$C_3H_9N_2O_2$	5.7	
		95.0497	C_6H_7O	4.2	
		83.0497	C_5H_7O	1.2	
TP-7	6.4	273.0909*	$C_{11}H_{17}N_2O_4S$	3.7	
		255.0803	$C_{11}H_{15}N_2O_3S$	3.5	
		227.0854	$C_{10}H_{15}N_2O_2S$	4.8	
		109.0290#	$C_5H_5O_2$	0.9	
		196.0432	$C_9H_{10}NO_2S$	2.6	
		186.0589	$C_8H_{12}NO_2S$	1.1	
		169.0323	$C_8H_9O_2S$	0	
		117.0486	$C_4H_9N_2S$	6.8	

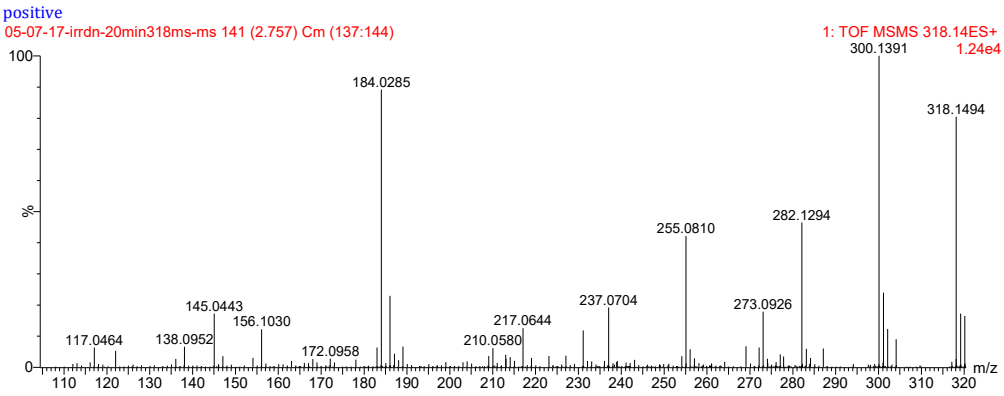
TP-8	7.3	270.012*	$C_{11}H_{16}N_3O_3S$	0.4	
		239.0490	$C_{10}H_{11}N_2O_3S$	2.1	
		186.0589	$C_8H_{12}NO_2S$	1.1	
		169.0310	$C_8H_9O_2S$	3	
		160.0545	$C_5H_{10}N_3OS$	0	
		144	$C_7H_{12}OS$	2.1	
		125.0048	$C_4H_3N_3S$	4	
		109.0290#	$C_6H_5O_2$	1.8	
		85.0402	$C_3H_5N_2O$	1.2	
		81	$C_3H_3N_3$	4.9	
TP-9	7.5	270.0912*	$C_{11}H_{16}N_3O_3S$	2.6	
		253.0885	$C_{11}H_{15}N_3O_2S$	2	
		236.0858	$C_{11}H_{14}N_3OS$	2.1	
		224.0983#	$C_{11}H_{16}N_2OS$	0	
		181.0799	$C_9H_{13}N_2S$	1.7	
		141.0010	$C_6H_5O_2S$	2.8	
		130.0565	$C_5H_{10}N_2S$	2.3	
		117.0486	$C_4H_9N_2S$	1.7	
		98.0844	$C_5H_{10}N_2$	1	
TP-10	8.5	288.097*	$C_{11}H_{18}N_3O_4S$	0	
		270.0912	$C_{11}H_{16}N_3O_3S$	4.4	
		241.099	$C_{11}H_{17}N_2O_2S$	5	
		191.1218	$C_8H_{19}N_2OS$	5.2	
		176.0480	$C_5H_{10}N_3O_2S$	8	
		159.0440	$C_2H_{11}N_2O_4S$	3.8	
		131.0643	$C_5H_{11}N_2S$	3.1	
		111.0446#	$C_6H_7O_2$	0.9	
		100.1	$C_5H_{11}N_2$	4	
TP-11	9.1	286.0862*	$C_{11}H_{16}N_3O_4S$	0.3	
		252.0807	$C_{11}H_{14}N_3O_2S$	0	
		240.0932	$C_{11}H_{16}N_2O_2S$	1.7	
		225.0698	$C_{10}H_{13}N_2O_2S$	3.1	
		186.0589	$C_8H_{12}NO_2S$	3.2	
		176.0494	$C_5H_{10}N_3O_2S$	0.6	
		169.0323	$C_8H_9O_2S$	0.6	
		147.0592	$C_5H_{11}N_2OS$	3.4	
		131.0632#	$C_5H_{11}N_2S$	0.8	
		109.0290	$C_6H_5O_2$	0.9	

		100.1	$C_5H_{12}N_2$	2	

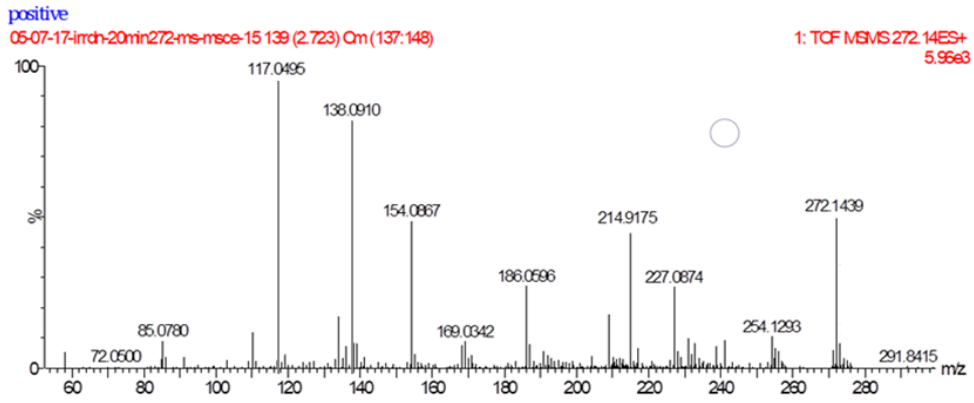
***[M+H]$^+$ ion of the transformation products**

$^{\#}$ Base peak.

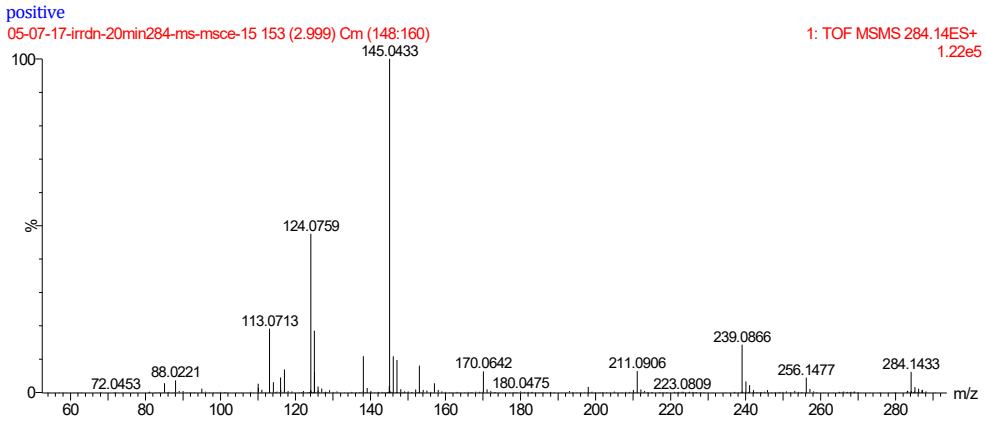
TP-1(m/z=318)



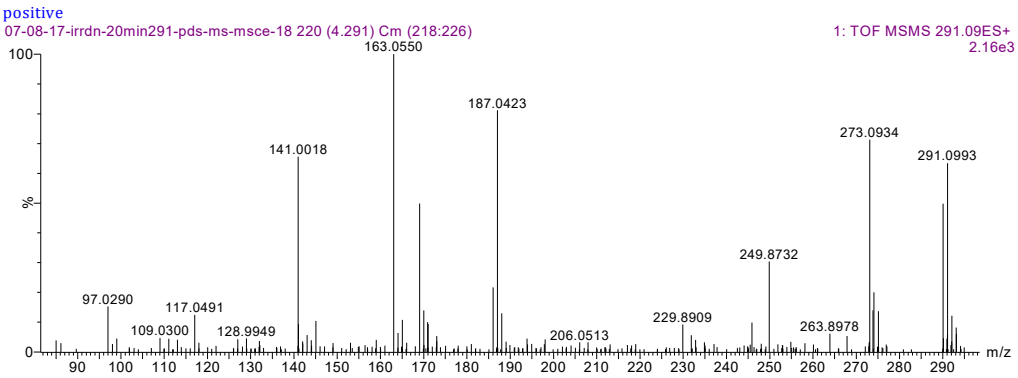
TP-2(m/z=272)



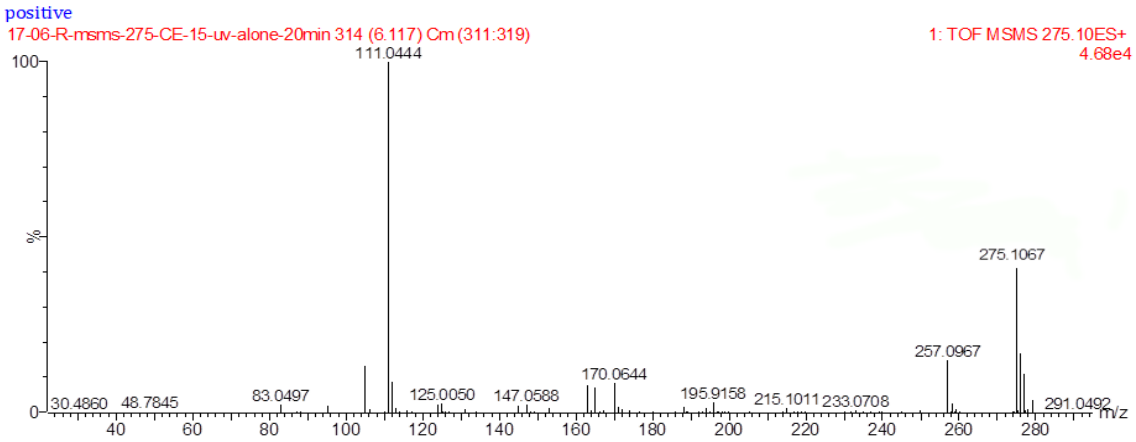
TP-3(m/z=284)



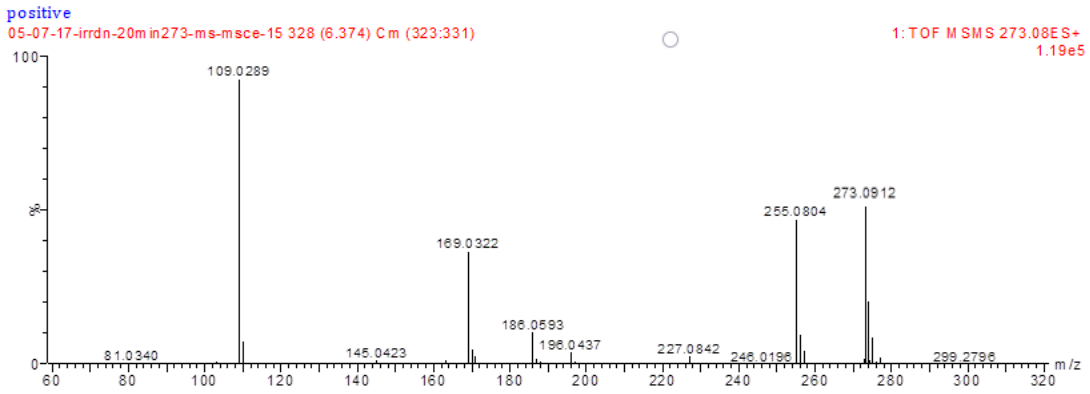
TP-5(m/z=291)



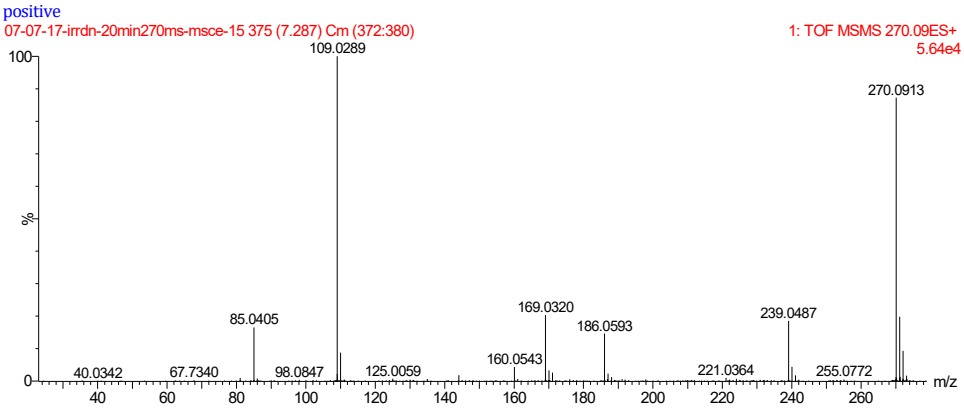
TP-6(m/z=275)



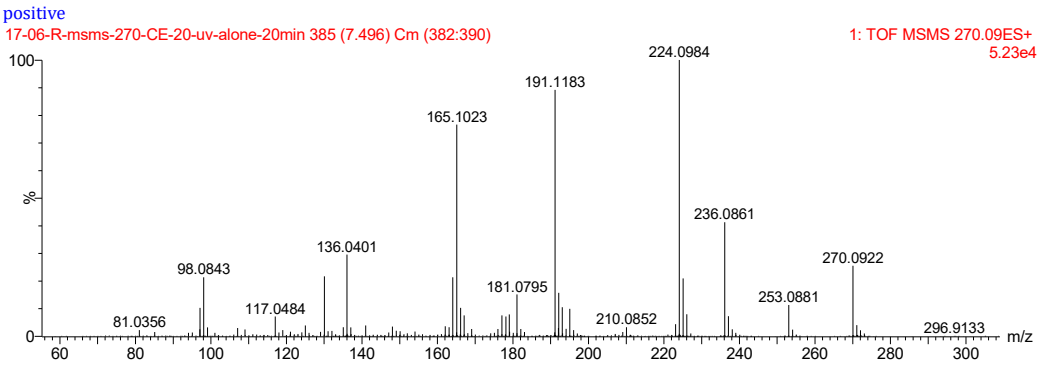
TP-7(m/z=273)



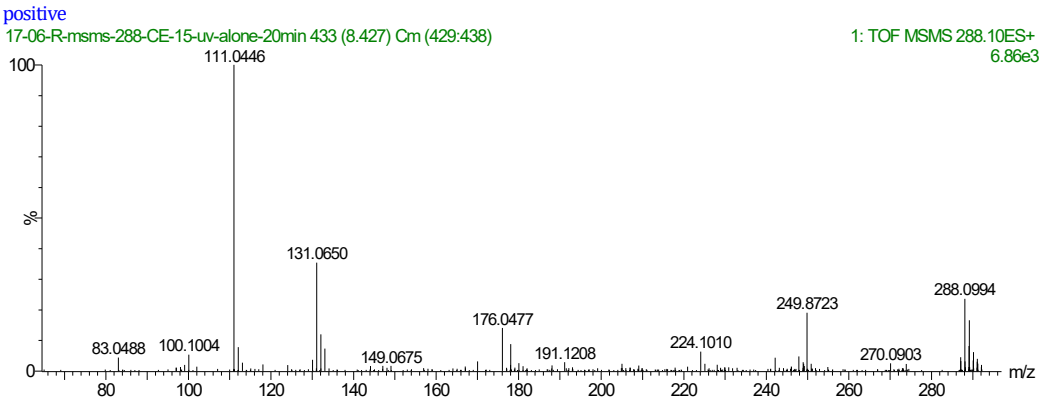
TP-8(m/z=270)



TP-9(m/z=270)



TP-10(m/z=288)



TP-11(m/z=286)

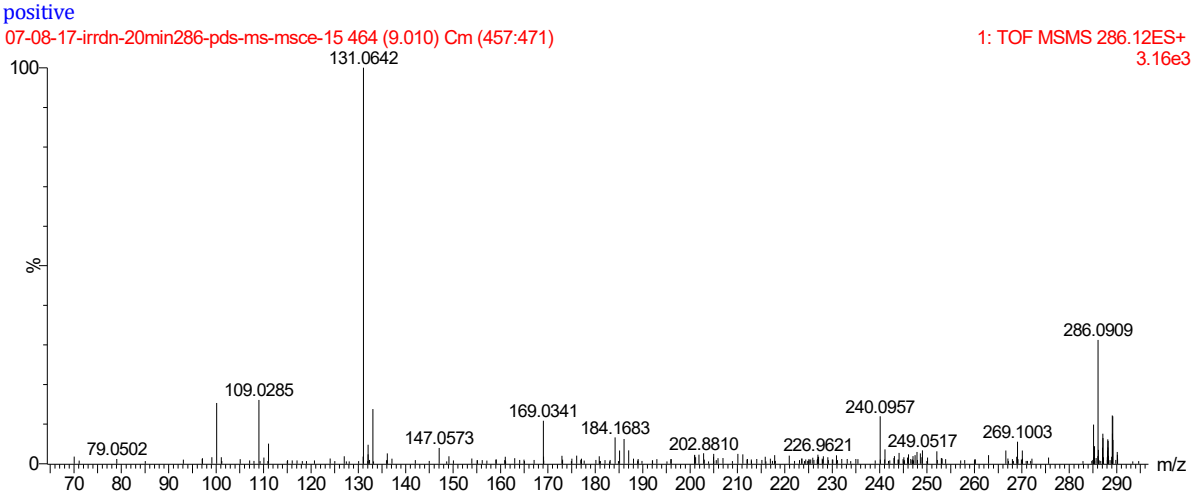
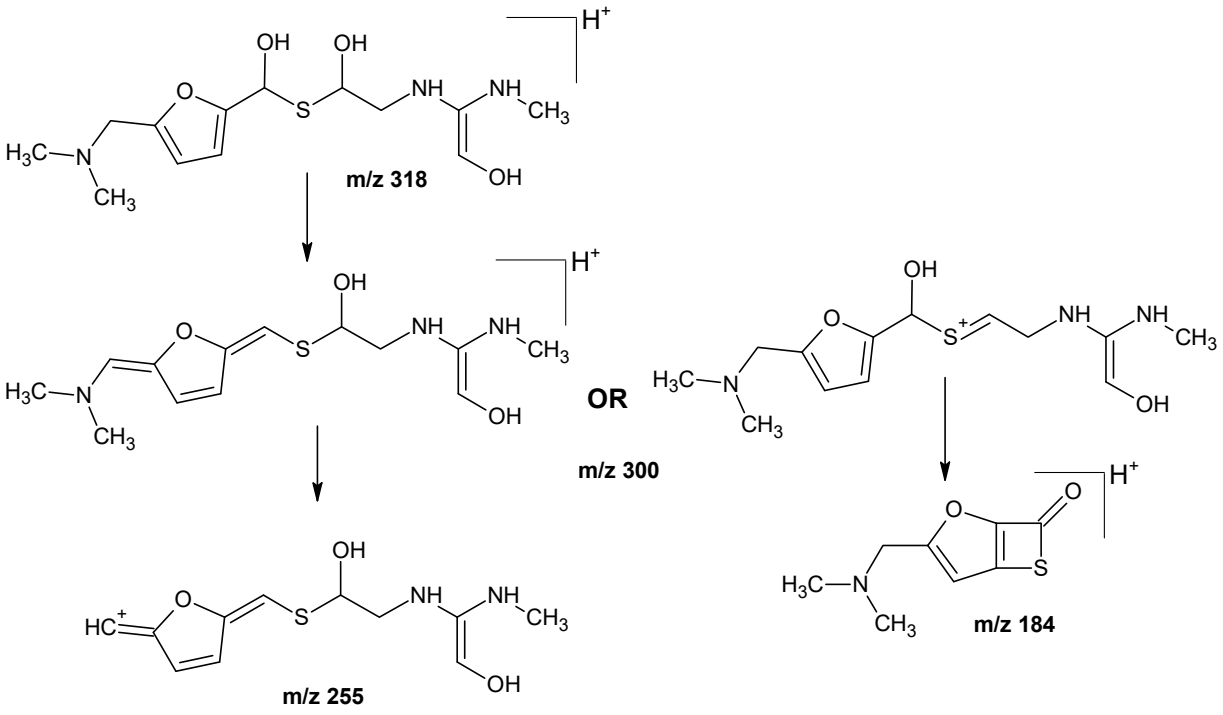


Fig.S1.Mass spectral data (MS^2) of TPs of Ranitidine (RNTD)

ESI-CID

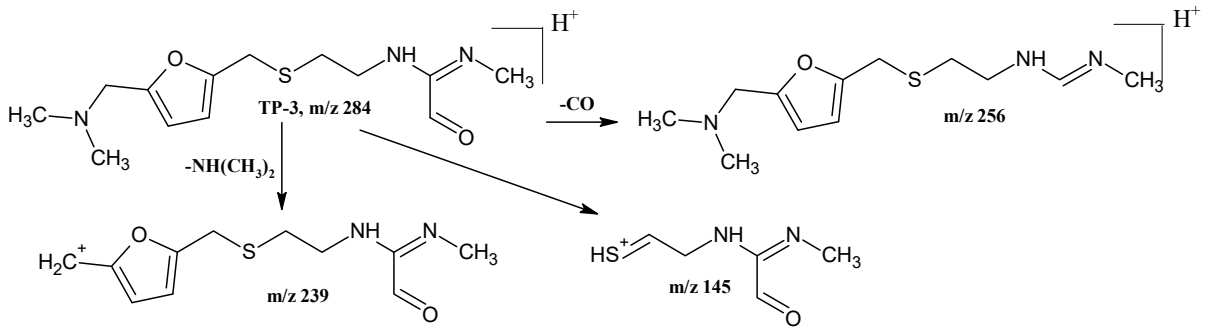
TP-1 was eluted from the mixture with m/z 318 and elemental composition $C_{13}H_{24}N_3O_4S$.A comparison of the elemental composition with that of RNTD shows that the lost N is in the form of NO_2 and three O-atoms are added to the structure as -OH groups. The two consecutive water losses, also indicates the presence of -OH groups. The peak at m/z 138 as in the case of RNTD gives the evidence for unmodified furan part. It is proposed that the -OH groups are situated at the C10, C12 and C19 , which was confirmed from the analysis of the CID spectrum as follows. A prominent peak was found in the spectrum with m/z 184 ($C_8H_{10}NO_2S$) which could be formed,

only if an -OH group is attached to C10, by the breakage of S11-C12 bond. The third -OH group must have come to the structure as an ipso attack at the C19 eliminating the NO_2. The proposed structure of this compound and the proposed CID mechanism are given in the scheme S1.



Scheme S1. Proposed ESI-CID mechanism of TP-1

TP-3 is eluted at t_r=2.9 minutes at an m/z 284 with elemental composition, $C_{13}H_{22}N_3O_2S$. It contains the same number of carbon atoms as RNTD but lacks one atom each of H, N and O. It is obvious that the $–NO_2$ group is lost from RNTD. Moreover, there was a peak corresponding to a CO loss. The plausible structure consistent with the elemental composition and the observed CO loss is given in the scheme S2.



SchemeS2. Proposed ESI-CID mechanism of TP-3

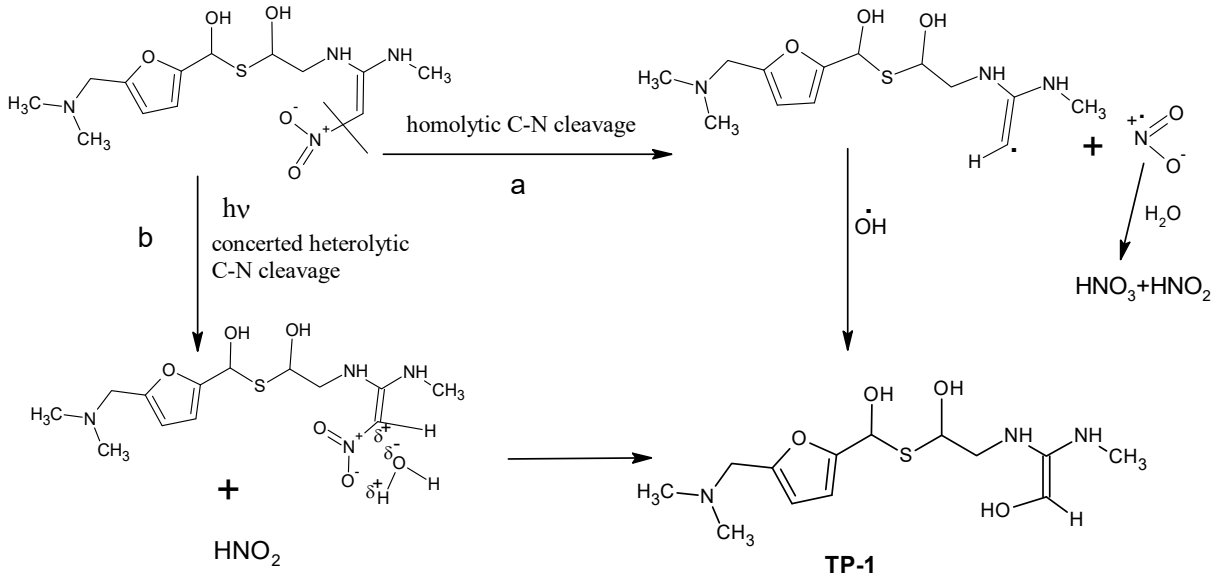


Fig.S2. Proposed reaction pathway for the denitration.

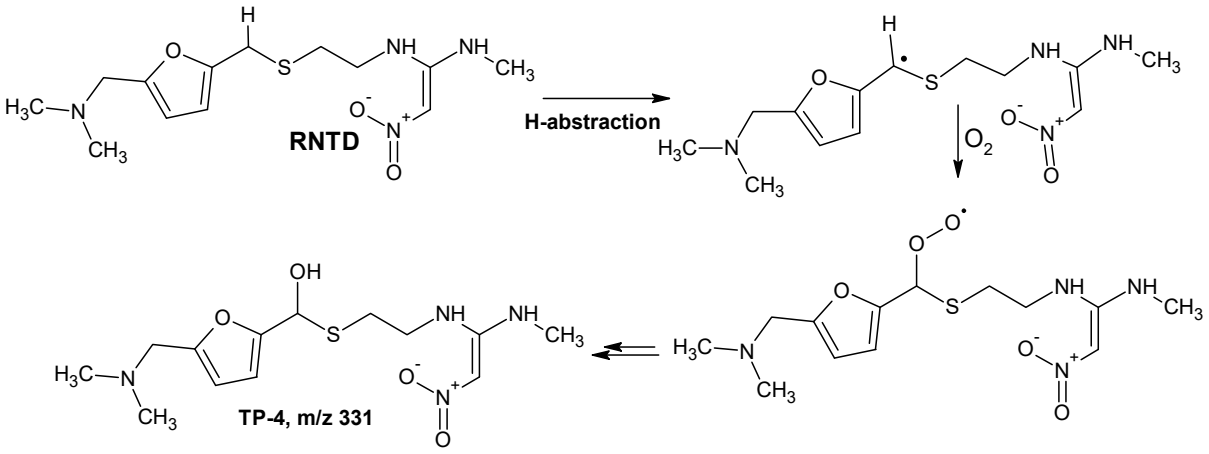


Fig.S3. Proposed transformation pathway for the formation of TP-4

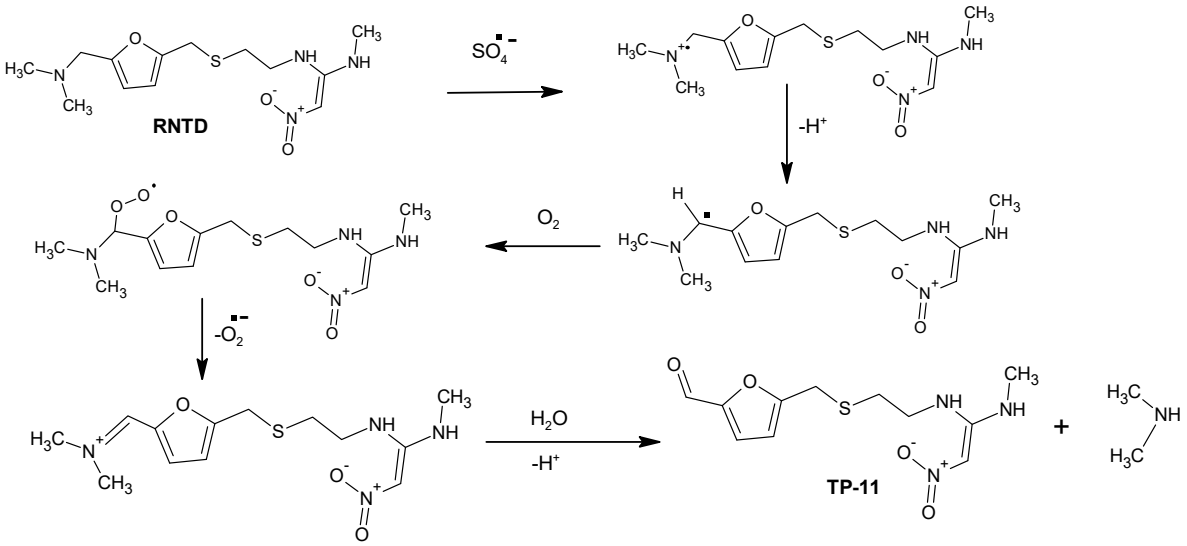


Fig.S4. Proposed transformation pathway for the formation of TP-11 by UV/PDS

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