

Table S1. Statistics of hydrogen rearrangements for CNOPS elements in GNPS

Positive ion mode				Negative ion mode			
C 79305, N 7444, O 17296 S 606, P 63				C 2582, N 38, O 909, S 11, P 3			
Cleavage	Element	Hydrogen rearrangement	Count	Cleavage	Element	Hydrogen rearrangement	Count
First bond cleavage (ionized element behavior)	C	0	3729		C	0	40
	C	+1	1115		C	-1	17
	C	+2	410		C	-2	54
	N	0	289		N	0	2
	N	+1	153		N	-1	1
	N	+2	470		N	-2	0
	O	0	109		O	0	42
	O	+1	163		O	-1	44
	O	+2	418		O	-2	0
	S	0	72		S	0	2
	S	+1	13		S	-1	1
	S	+2	18		S	-2	0
	P	0	9		P	0	0
P	+1	0		P	-1	0	
P	+2	0		P	-2	0	
Second and later bond cleavage (neutralized element behavior)	C	-1	20367		C	+1	51
	C	0	1233		C	0	21
	C	+1	4445		C	-1	245
	N	-1	535		N	+1	0
	N	0	84		N	0	0
	N	+1	1156		N	-1	1
	O	-1	258		O	+1	29
	O	0	28		O	0	2
	O	+1	1034		O	-1	8
	S	-1	102		S	+1	0
	S	0	12		S	0	0
	S	+1	39		S	-1	1
	P	-1	6		P	+1	0
P	0	1		P	0	0	
P	+1	1		P	-1	0	

A total 35,738 (positive) and 632 (negative) MS/MS peaks within 50-mDa mass accuracy were classified as the same way as the statistics of MassBank.