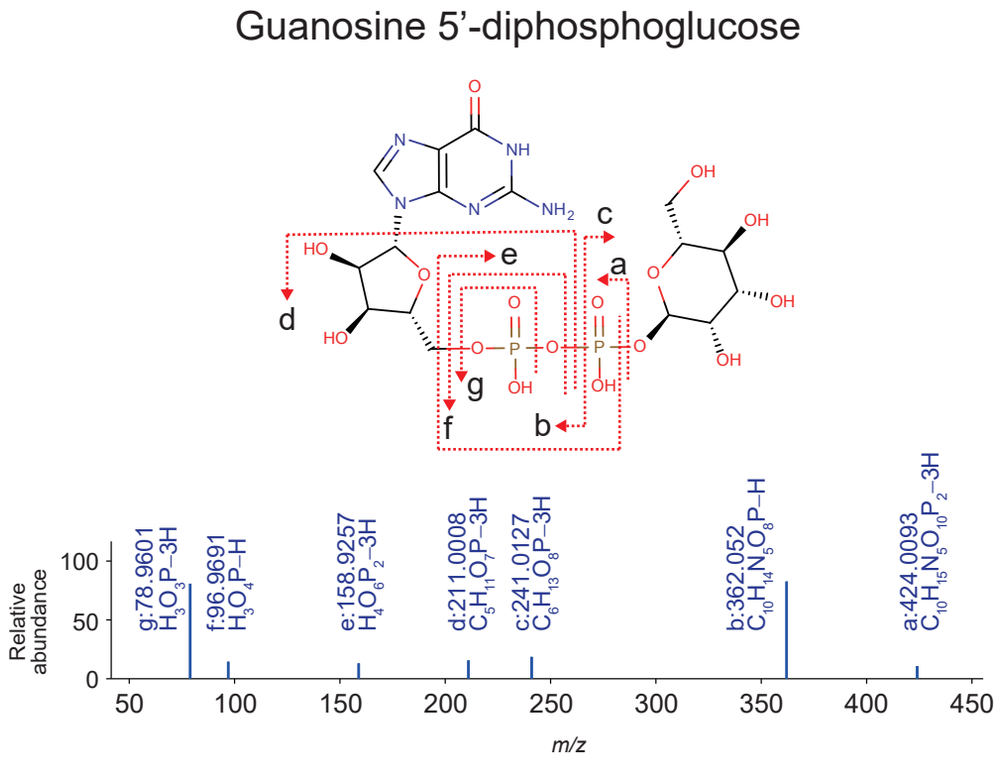
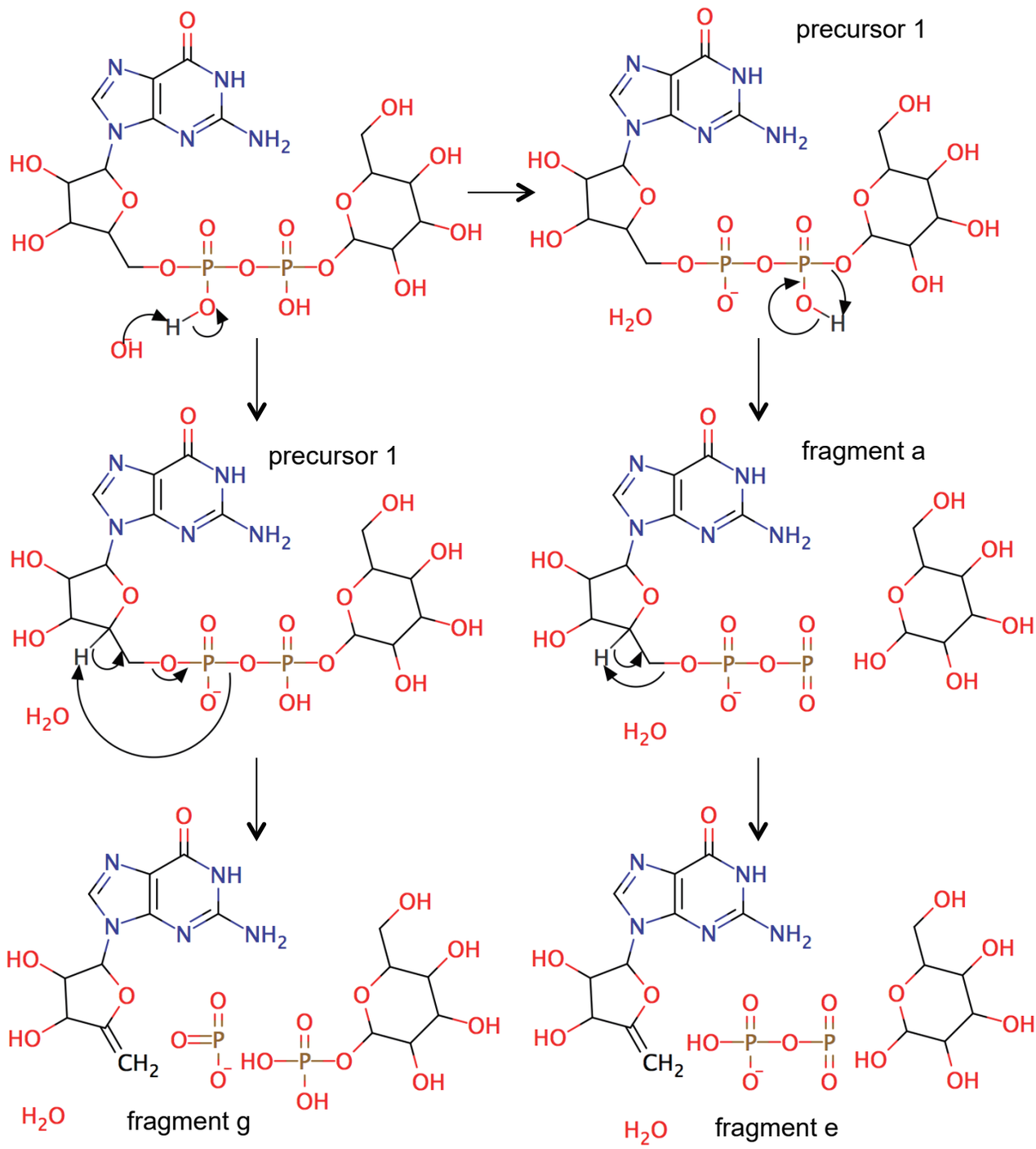
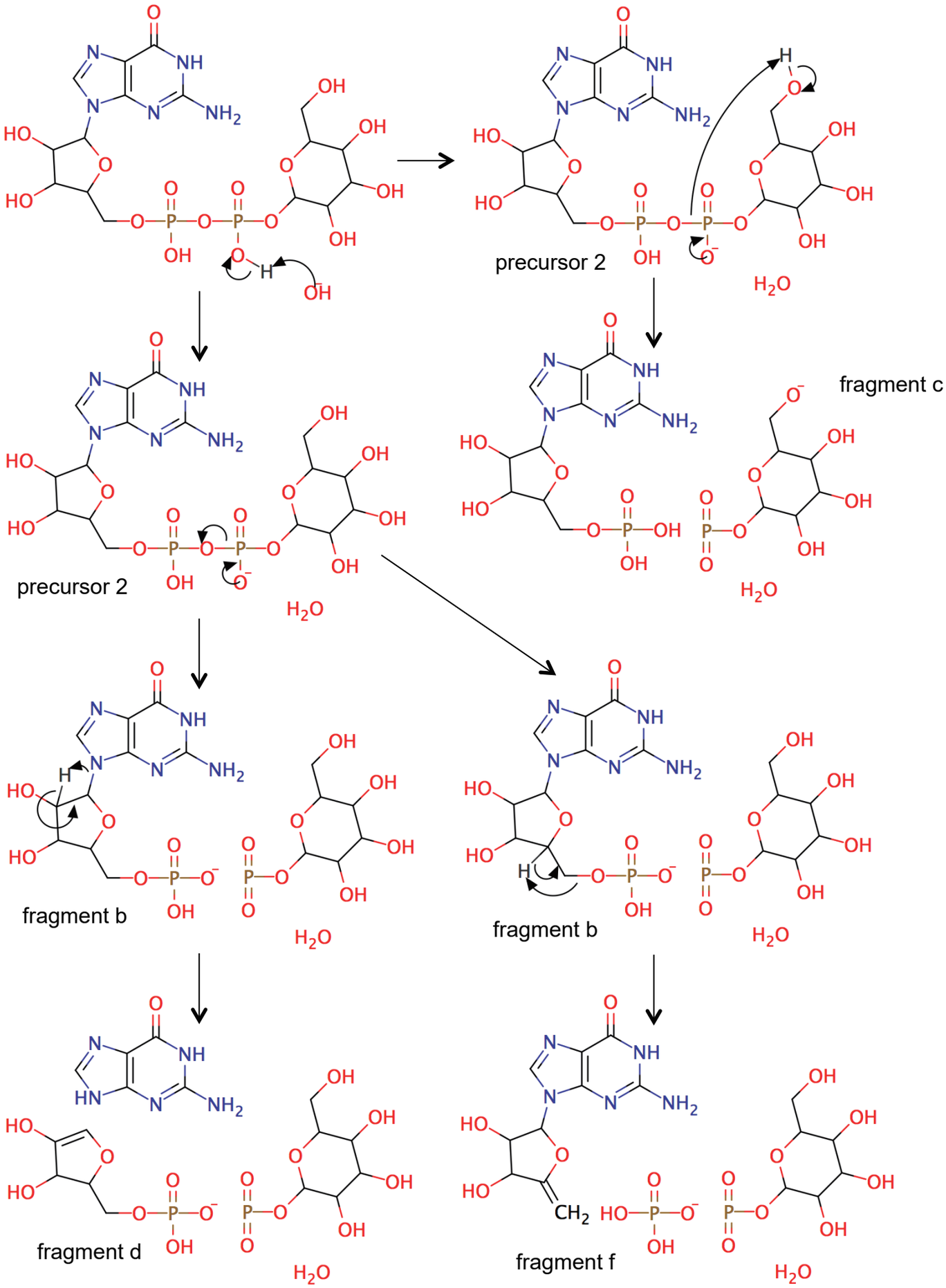
Figure S2. Peak annotation result of guanosine 5'-diphosphoglucose MS/MS spectra, and the putative fragmentation scheme



Fragment	Hydrogen rearrangement	Rule	Annotation	Theoretical *m/z*	Error (mDa)	Enthalpy change (kcal/mol)
a	P -2	N2	[M-3H]-	424.0059	3.36	-57.7
b	O 0	N1	[M-H]-	362.0502	1.83	-49.1
c	P -2	N2	[M-3H]-	241.0113	1.37	12.2
d	C -2, O 1	N2, N4	[M-3H]-	211.0008	1.04	-15.0
e	P -2, O 1 or O 0, P -1	N2, N4 or N1, N5	[M-3H]-	158.9248	0.86	-33.8
f	O 0, O -1	N1, N5	[M-H]-	96.9691	1.03	-20.1
g	P -2, O 1 or O 0, P -1	N2, N4 or N1, N5	[M-3H]-	78.9585	1.59	-32.1

Putative fragmentation scheme of Guanosine 5’-diphosphoglucose




precursor 2
fragment c
precursor 2
fragment b
fragment b
fragment d
fragment f