

**Supplemental Table 1:** Calculated (C) and measured (M)  $m/z$  values of the precursor ions and of identified fragment ions for peptides in Figures 1 – 5.

*av* = average mass; *mono* = monoisotopic mass; ▼ - loss of  $H_2O$ ; ■ - loss of  $NH_3$ .

<b>Fig.1:</b> $^{1543}KAS^P GSENEG DYNPGRK^{1558}$									
$MH_3^{+3}$ (av)		$[M+3H]^{+3} - H_3PO_4$ (mono)				$[M+3H]^{+3} - H_3PO_4$ (mono)			
C	M	C	M	C	M	C	M	C	M
597.3	597.7	564.6	564.9	558.6	559.0				
b- $H_3PO_4$ (mono)		b ions (mono)		Peptide Sequence	y ions (mono)		y- $H_3PO_4$ (mono)		
M	C	M	C		C	M	C	M	
---		---		1 <b>K</b> 16				---	
		199.5	200.1	2 <b>A</b> 15			781.8 <sup>2+</sup>	782.3 <sup>2+</sup>	
269.2	269.2	■350.1	■350.1	3 <b>S<sup>P</sup></b> 14	795.3 <sup>2+</sup> ▼786.3 <sup>2+</sup>	795.9 <sup>2+</sup> ▼786.9 <sup>2+</sup>	746.3	746.9 <sup>2+</sup>	
				4 <b>G</b> 13	711.8 <sup>2+</sup> ■703.3 <sup>2+</sup>	712.4 <sup>2+</sup> ■703.8 <sup>2+</sup>			
				5 <b>S</b> 12					
				6 <b>E</b> 11					
656.8	656.3			7 <b>N</b> 10	575.3 <sup>2+</sup>	575.4 <sup>2+</sup>			
				8 <b>E</b> 9					
				9 <b>G</b> 8	906.4 453.7 <sup>2+</sup>	906.5 453.8 <sup>2+</sup>			
957.5	957.4	1055.5	1055.4	10 <b>D</b> 7	849.4 ▼831.4	849.7 ▼831.8			
				11 <b>Y</b> 6	734.4 367.7 <sup>2+</sup>	734.6 368.3 <sup>+2</sup>			
				12 <b>N</b> 5	571.3 ■554.3 ■277.6 <sup>2+</sup>	571.4 ■554.5 ■277.8 <sup>+2</sup>			
				13 <b>P</b> 4	457.3 ■220.6 <sup>+2</sup>	457.5 ■221.7 <sup>+2</sup>			
				14 <b>G</b> 3					
				15 <b>R</b> 2					
				16 <b>K</b> 1					

Fig.2A: <sup>1392</sup> VKAS <sup>P</sup> PITNDGEDEFVPSDGLDKDEYTFSPGK <sup>1422</sup>						
MH <sub>3</sub> <sup>+3</sup> (av)		[M+3H] <sup>+3</sup> - H <sub>3</sub> PO <sub>4</sub> (mono)		[M+3H] <sup>▼+3</sup> - H <sub>3</sub> PO <sub>4</sub> (mono)		
C	M	C	M	C	M	
1147.2	<b>1147.4</b>	1114.5	<b>1114.7</b>	1108.5	<b>1108.4</b>	
b-H <sub>3</sub> PO <sub>4</sub> (mono)		b ions (mono)		Peptide Sequence	y ions (mono)	
M	C	M	C		C	M
---				1 V 31	---	
---				2 K 30		
---				3 A 29		
---				4 S <sup>P</sup> 28	1570.2 <sup>+2</sup> ▼1561.1 <sup>+2</sup>	<b>1570.2<sup>+2</sup></b> ▼ <b>1561.2<sup>+2</sup></b>
---				5 P 27	1486.7 <sup>+2</sup> ■1478.2 <sup>+2</sup>	<b>1486.8<sup>+2</sup></b> ■ <b>1478.4<sup>+2</sup></b>
<b>578.9</b>	578.4	<b>676.6</b>	676.3	6 I 26		
				7 T 25	1381.6 <sup>+2</sup>	<b>1382.3<sup>+2</sup></b>
				8 N 24		
		<b>1006.7</b>	1006.5	9 D 23	1274.1 <sup>+2</sup>	<b>1274.8<sup>+2</sup></b>
				10 G 22	1216.5 <sup>+2</sup>	<b>1217.2<sup>+2</sup></b>
				11 E 21		
		<b>1308.0</b>	1307.6	12 D 20		
				13 E 19	1066.0 <sup>+2</sup>	<b>1066.2<sup>+2</sup></b>
				14 F 18		
<b>1584.7</b> <b>793.1<sup>+2</sup></b>	1584.7 792.9 <sup>+2</sup>	<b>1682.7</b> ■ <b>1665.7</b>	1682.7 ■1665.7	15 V 17	1854.9	<b>1855.1</b>
				16 P 16	1755.8 ▼1737.8 878.4 <sup>+2</sup> ▼869.4 <sup>+2</sup>	<b>1755.8</b> ▼ <b>1737.7</b> <b>878.9<sup>+2</sup></b> ▼ <b>869.8<sup>+2</sup></b>
				17 S 15		
		<b>1981.8</b>	1981.8	18 D 14		
				19 G 13	1456.7 728.9 <sup>+2</sup>	<b>1456.7</b> <b>729.6<sup>+2</sup></b>

		20	<b>L</b>	12		
		21	<b>D</b>	11		
		22	<b>K</b>	10	1171.6	<b>1171.7</b>
		23	<b>D</b>	9	1043.5	<b>1043.8</b>
		24	<b>E</b>	8	928.4	<b>928.7</b>
		25	<b>Y</b>	7		
		26	<b>T</b>	6		
		27	<b>F</b>	5	535.3	<b>535.4</b>
		28	<b>S</b>	4	▼370.2	<b>▼370.4</b>
		29	<b>P</b>	3		
		30	<b>G</b>	2		
31	<b>K</b>	1				

<b>Fig.2B:</b> $^{1423}\text{SKAT}^{\text{P}}\text{PEKSLHDKK}^{1435}$							
$\text{MH}_3^{+3}$ (av)		$[\text{M}+3\text{H}]^{+3} - \text{H}_3\text{PO}_4$ (mono)		$[\text{M}+3\text{H}]^{\nabla+3}$ (mono)		$[\text{M}+3\text{H}]^{\nabla+3} - \text{H}_3\text{PO}_4$ (mono)	
C	M	C	M	C	M	C	M
517.2	<b>517.9</b>	484.3	<b>484.9</b>	510.9	<b>511.5</b>	478.3	<b>479.2</b>

<b>b-H<sub>3</sub>PO<sub>4</sub></b> (mono)		<b>b ions (mono)</b>		<b>Peptide Sequence</b>	<b>y ions (mono)</b>		<b>y-H<sub>3</sub>PO<sub>4</sub> (mono)</b>	
M	C	M	C		C	M	C	M
			---	1 S 13				---
		<b>216.4</b>	216.1	2 K 12				
				3 A 11	667.3 <sup>+2</sup>	<b>667.7<sup>+2</sup></b>	618.3 <sup>+2</sup> ▼603.7 <sup>+2</sup>	<b>618.7<sup>+2</sup></b> ▼609.7 <sup>+2</sup>
<b>370.6</b>	370.2	<b>468.4</b>	468.2	4 T <sup>P</sup> 10				
				5 P 9	541.3 <sup>+2</sup> ■532.8 <sup>+2</sup>	<b>541.9<sup>+2</sup></b> ■533.2 <sup>+2</sup>		
		<b>694.4</b>	694.3	6 E 8				
				7 K 7				
				8 S 6	■710.4	<b>■711.0</b>		
				9 L 5				
				10 H 4				
<b>589.5<sup>+2</sup></b>	588.8 <sup>+2</sup>	<b>638.3<sup>+2</sup></b>	637.8 <sup>+2</sup>	11 D 3				
		<b>702.3<sup>+2</sup></b>	701.8 <sup>+2</sup>	12 K 2	275.2	<b>275.5</b>		
				13 K 1				

<b>Fig.3A: <math>^{656}\text{YAGPEDDAAITLAFSK}^{671}</math></b>				
<b><math>\text{MH}_2^{+2}</math> (av)</b>		<b><math>[\text{M}+2\text{H}]^{\nabla+2}</math> (mono)</b>		
<b>C</b>	<b>M</b>	<b>C</b>	<b>M</b>	
835.4	<b>835.8</b>	825.9	<b>826.0</b>	
<b>b ions (mono)</b>		<b>Peptide Sequence</b>	<b>y ions (mono)</b>	
<b>M</b>	<b>C</b>		<b>C</b>	<b>M</b>
---		1 <b>Y</b> 16	---	
		2 <b>A</b> 15		
		3 <b>G</b> 14	$717.9^{+2}$ $\nabla 708.9^{+2}$	$718.2^{+2}$ $\nabla 709.2^{+2}$
		4 <b>P</b> 13	$689.3^{+2}$	<b><math>689.7^{+2}</math></b>
		5 <b>E</b> 12		
		6 <b>D</b> 11	1151.6	<b>1151.7</b>
		7 <b>D</b> 10	1036.6	<b>1036.6</b>
		8 <b>A</b> 9	921.5	<b>921.7</b>
<b>890.5</b>	890.4	9 <b>A</b> 8	850.5	<b>850.7</b>
		10 <b>I</b> 7	779.5	<b>779.6</b>
		11 <b>T</b> 6	666.4	<b>666.5</b>
$1217.5$ $\nabla 1199.6$	$1217.6$ $\nabla 1199.5$	12 <b>L</b> 5	565.3	<b>565.6</b>
$\nabla 1417.5$	$\nabla 1417.6$	13 <b>A</b> 4	452.3	<b>452.4</b>
		14 <b>F</b> 3	381.2	<b>381.2</b>
		15 <b>S</b> 2		
		16 <b>K</b> 1		

<b>Fig.3B: <math>^{656}\text{Y}^* \text{AGPEDDAITLAFSK}^{671}</math></b>				
<b><math>\text{MH}_2^{+2}</math> (av)</b>				
<b>C</b>			<b>M</b>	
875.4			875.2	
<b>b ions (mono)</b>		<b>Peptide Sequence</b>	<b>y ions (mono)</b>	
<b>M</b>	<b>C</b>		<b>C</b>	<b>M</b>
---		1 <b>Y</b> 16	---	
		2 <b>A</b> 15		
		3 <b>G</b> 14	1434.7 717.9 <sup>+2</sup> ▼708.9 <sup>+2</sup>	1434.8 718.3 <sup>+2</sup> ▼708.9 <sup>+2</sup>
		4 <b>P</b> 13	1377.7 689.3 <sup>+2</sup>	1377.7 689.5 <sup>+2</sup>
		5 <b>E</b> 12		
		6 <b>D</b> 11	1151.6	1151.7
		7 <b>D</b> 10	1036.6	1036.6
		8 <b>A</b> 9	921.5	921.6
971.2	970.3	9 <b>A</b> 8	850.5	850.7
		10 <b>I</b> 7	779.5	779.4
		11 <b>T</b> 6	666.4	666.5
		12 <b>L</b> 5		
		13 <b>A</b> 4	452.3	452.4
		14 <b>F</b> 3		
		15 <b>S</b> 2		
		16 <b>K</b> 1		

<b>Fig.4: <math>^{656}\text{Y}^* \text{AGPEDDAAITLAFSK}^{671}</math></b>				
<b><math>\text{MH}_2^{+2}</math> (av)</b>				
<b>C</b>			<b>M</b>	
875.4			875.2	
<b>b ions (mono)</b> [+80 / +78 doublets]		<b>Peptide Sequence</b>	<b>y ions (mono)</b>	
<b>M</b>	<b>C</b>		<b>C</b>	<b>M</b>
---		1 <b>Y</b> 16	---	
		2 <b>A</b> 15		
		3 <b>G</b> 14		
		4 <b>P</b> 13	689.3 <sup>+2</sup>	689.8 <sup>+2</sup>
		5 <b>E</b> 12	1280.6	1280.6
		6 <b>D</b> 11	1151.6	1151.8
		7 <b>D</b> 10	1036.6	1036.8
		8 <b>A</b> 9	921.5	921.7
[970.3 / 968.3]	[970.3 / -2]	9 <b>A</b> 8	850.5	850.6
		10 <b>I</b> 7	779.5	779.6
[1184.6 / 1182.6] (+80/+78 doublet, low intensity)	[1184.5 / -2]	11 <b>T</b> 6	666.4	666.6
		12 <b>L</b> 5	565.3	565.6
		13 <b>A</b> 4	452.3	452.5
		14 <b>F</b> 3	381.2	381.4
		15 <b>S</b> 2		
		16 <b>K</b> 1		

<b>Fig.5A:</b> <sup>708</sup> HLTYNDFINK <sup>717</sup>				
<b>MH<sub>2</sub><sup>+2</sup> (av)</b>		<b>[M+2H]<sup>▼+2</sup> (mono)</b>		
<b>C</b>	<b>M</b>	<b>C</b>	<b>M</b>	
633.2	<b>633.7</b>	623.8	<b>624.5</b>	
<b>b ions (mono)</b>		<b>Peptide Sequence</b>	<b>y ions (mono)</b>	
<b>M</b>	<b>C</b>		<b>C</b>	<b>M</b>
---		1 <b>H</b> 10	---	
<b>251.4</b> 223.4 (a <sub>2</sub> ion)	251.1 223.2 (a <sub>2</sub> ion)	2 <b>L</b> 9	1127.6	<b>1127.7</b>
<b>352.4</b>	352.2	3 <b>T</b> 8	1014.5 ▼996.5	<b>1014.7</b> ▼996.8
		4 <b>Y</b> 7	913.4	<b>913.7</b>
		5 <b>N</b> 6	750.4	<b>750.7</b>
<b>744.6</b> ▼726.7	744.3 ▼726.3	6 <b>D</b> 5		
<b>891.7</b> ▼873.7	891.4 ▼873.4	7 <b>F</b> 4	521.3	<b>521.6</b>
<b>1004.7</b> ▼986.7	1004.5 ▼986.5	8 <b>I</b> 3	374.2	<b>374.4</b>
<b>1118.7</b>	1118.5	9 <b>N</b> 2	261.2	<b>261.4</b>
		10 <b>K</b> 1		



<b>Fig.5B:</b>				<b><sup>708</sup>HLTY*<sup>717</sup>NDFINK</b>			
<b>MH<sub>2</sub><sup>+2</sup> (av)</b>				<b>[M+2H]<sup>▼+2</sup> (mono)</b>			
<b>C</b>	<b>M</b>	<b>C</b>	<b>M</b>	<b>C</b>	<b>M</b>	<b>C</b>	<b>M</b>
673.2	<b>672.4</b>	663.8	<b>663.6</b>				
<b>b ions (mono)</b> [+80 / +78 doublets]		<b>Peptide Sequence</b>	<b>y ions (mono)</b> [+80 / +78 doublets]				
<b>M</b>	<b>C</b>		<b>C</b>	<b>M</b>			
	---	1 <b>H</b> 10		---			
<b>251.4</b> <b>223.4 (a<sub>2</sub> ion)</b>	251.1 223.2 (a <sub>2</sub> ion)	2 <b>L</b> 9	[1207.5 /-2]	<b>[1207.6 / 1205.6]</b>			
<b>352.4</b>	352.2	3 <b>T</b> 8	[1094.5 /-2] [▼1076.4 /-2]	<b>[1094.6 / 1092.7]</b> <b>[▼1076.7 / 1074.7]</b>			
		4 <b>Y*</b> 7	[993.4 /-2]	<b>[993.7 / 991.7]</b>			
		5 <b>N</b> 6	750.4	<b>750.8</b>			
<b>[824.6 / 822.6]</b> <b>[▼806.7 / 804.6]</b>	[824.3 /-2] [▼806.3 /-2]	6 <b>D</b> 5					
<b>[971.7 / 969.7]</b> <b>[▼953.6 / 951.4]</b>	[971.4 /-2] [▼953.4 /-2]	7 <b>F</b> 4	521.3	<b>521.6</b>			
<b>[1084.7 / 1082.8]</b> <b>[▼1066.7 / 1064.7]</b>	[1084.4 /-2] [▼1066.4 /-2]	8 <b>I</b> 3	374.2	<b>374.4</b>			
		9 <b>N</b> 2	261.2	<b>261.4</b>			
		10 <b>K</b> 1					