Supplemental FIGURE S3. Distribution of hexoses on AGP31 P2 *O*-glycopeptides using ETD MS/MS.

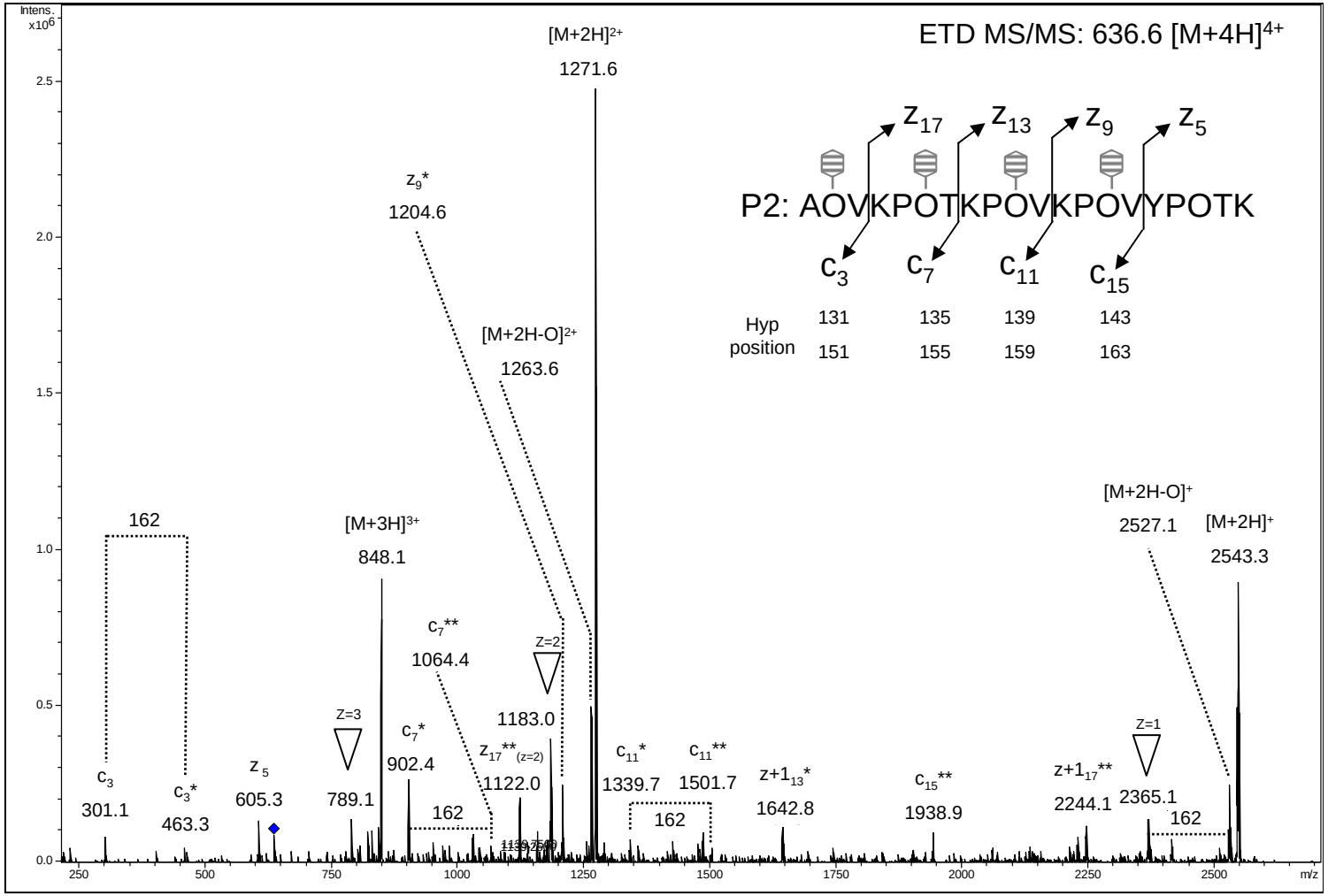


Figure S3A. ETD MS/MS analysis of the P2 glycopeptide containing 2 hexoses (636.6 [M+4H]$^{4+}$).
For simplification, Hyp residues (O) of the P2 peptide were located according to our experimental results and literature data. Fragmentation was carried out on the P2 *O*-glycopeptide containing 2 hexoses obtained following gel excision of an AGP31 enriched fraction in the 50-60 kDa mass range (see Figs. 2, 3A and 4). Sites of *O*-glycosylation were identified from c and z series of differentially glycosylated fragment ions. The number of hexose residues (⬭) found on each fragment is indicated by stars (*). Fragmentation pattern showed that different glycoforms exist with possible sites of *O*-glycosylation on Hyp131/151, Hyp135/155, Hyp139/159 and Hyp143/163 of the AGP31 Pro-rich domain. Peaks corresponding to the loss of one hexose and one hydroxyl moiety were found (▽). Parent ion fragmented is labeled with ◆ .

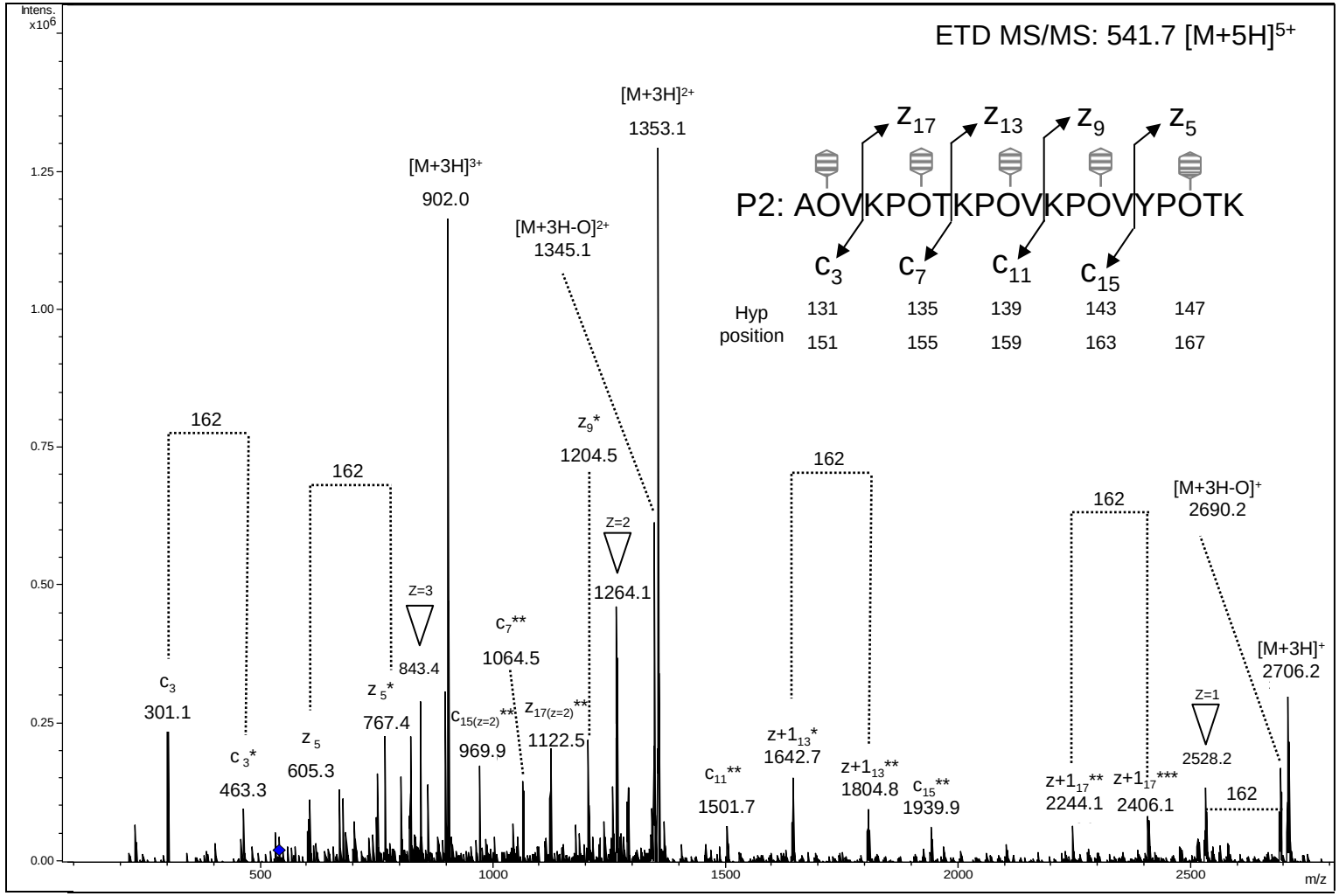


Figure S3B. ETD MS/MS analysis of the P2 glycopeptide containing 3 hexoses (541.7 [M+5H]$^{5+}$).
For simplification, Hyp residues (O) of the P2 peptide were located according to our experimental results and literature data. Fragmentation was carried out on the P2 *O*-glycopeptide containing 3 hexoses obtained following gel excision of an AGP31 enriched fraction in the 50-60 kDa mass range (see Figs. 2, 3A and 4). Sites of *O*-glycosylation were identified from c and z series of differentially glycosylated fragment ions. The number of hexose residues (hexagon) found on each fragment is indicated by stars (*). Fragmentation pattern showed that different glycoforms exist with possible sites of *O*-glycosylation on Hyp131/151, Hyp135/155, Hyp139/159, Hyp143/163 and Hyp147/167 of the AGP31 Pro-rich domain. Peaks corresponding to the loss of one hexose and one hydroxyl moiety were found (▽). Parent ion fragmented is labeled with ◆ .

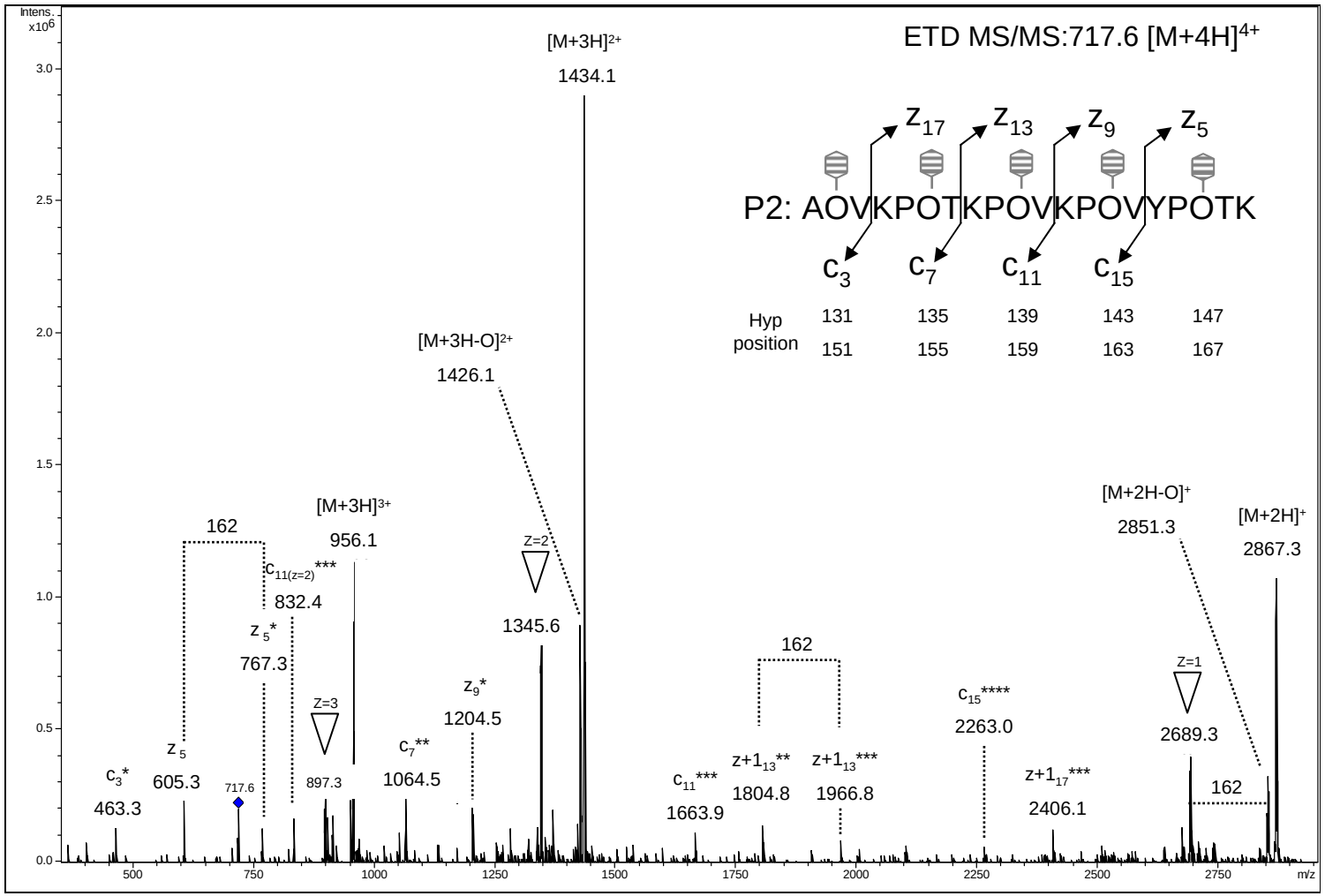


Figure S3C. ETD MS/MS analysis of the P2 glycopeptide containing 4 hexoses (717.6 [M+4H]$^{4+}$).
For simplification, Hyp residues (O) of the P2 peptide were located according to our experimental results and literature data. Fragmentation was carried out on the P2 *O*-glycopeptide containing 4 hexoses obtained following gel excision of an AGP31 enriched fraction in the 50-60 kDa mass range (see Figs. 2, 3A and 4). Sites of *O*-glycosylation were identified from c and z series of differentially glycosylated fragment ions. The number of hexose residues (⬭) found on each fragment is indicated by stars (*). Fragmentation pattern showed that different glycoforms exist with possible sites of *O*-glycosylation on Hyp131/151, Hyp135/155, Hyp139/159, Hyp143/163 and Hyp147/167 of the AGP31 Pro-rich domain. Peaks corresponding to the loss of one hexose and one hydroxyl moiety were found (▽). Parent ion fragmented is labeled with ◆.

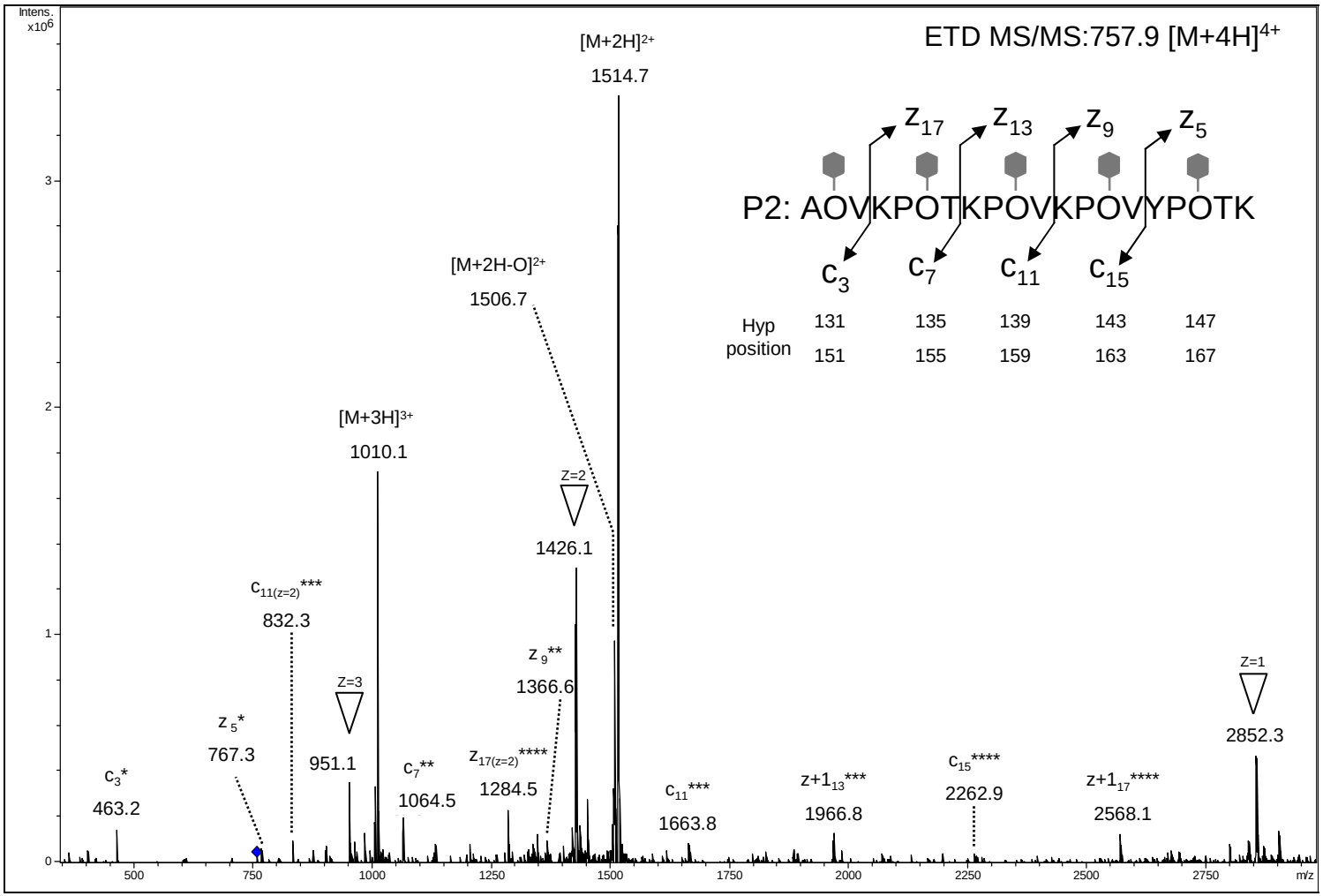
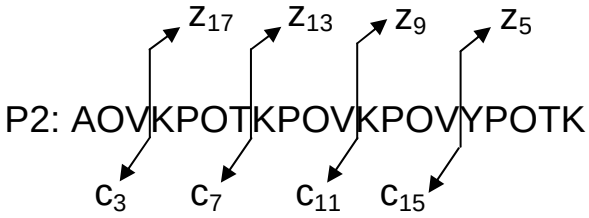


Figure S3D. ETD MS/MS analysis of the P2 glycopeptide containing 5 hexoses (757.9 $[M+4H]^{4+}$).
For simplification, Hyp residues (O) of the P2 peptide were located according to our experimental results and literature data. Fragmentation was carried out on the P2 *O*-glycopeptide containing 5 hexoses obtained following gel excision of an AGP31 enriched fraction in the 50-60 kDa mass range (see Figs. 2, 3A and 4). Sites of *O*-glycosylation were identified from c and z series of glycosylated fragment ions. The number of hexose residues (⬢) found on each fragment is indicated by stars (*). Fragmentation pattern showed that each Hyp residue of the P2 peptide of the AGP31 Pro-rich domain carries only one hexose. Peaks corresponding to the loss of one hexose and one hydroxyl moiety were found (▽). Parent ion fragmented is labeled with ◆.

Figure S3E. Number of hexose residues found on c and z fragment ions obtained by ETD MS/MS of the P2 *O*-glycopeptide containing 2, 3, 4 or 5 hexoses.
Fragmentations were carried out on P2 *O*-glycopeptides obtained following gel excision of an AGP31 enriched fraction in the 50-60 kDa mass range (see Figs. 2, 3A and 4). For simplification, Hyp residues (O) of the P2 peptide were located according to our experimental results and literature data.



	c series				**z / z+1 series**			
	3	7	11	15	5	9	13	17
P2 + 2 hexoses	0 1 -	- 1 2	- 1 2	- - 2	0 - -	- 1 -	- 1 -	- - 2
P2 + 3 hexoses	0 1 - -	- - 2 -	- - 2 -	- - 2 -	0 1 - -	- 1 - -	- 1 2 -	- - 2 3
P2 + 4 hexoses	- 1 - - -	- - 2 - -	- - - 3 -	- - - - 4	0 1 - - -	- 1 - - -	- - 2 3 -	- - - 3 -
P2 + 5 hexoses	- 1 - - - -	- - 2 - - -	- - - 3 - -	- - - - 4 -	- 1 - - - -	- - 2 - - -	- - - 3 - -	- - - - 4 -