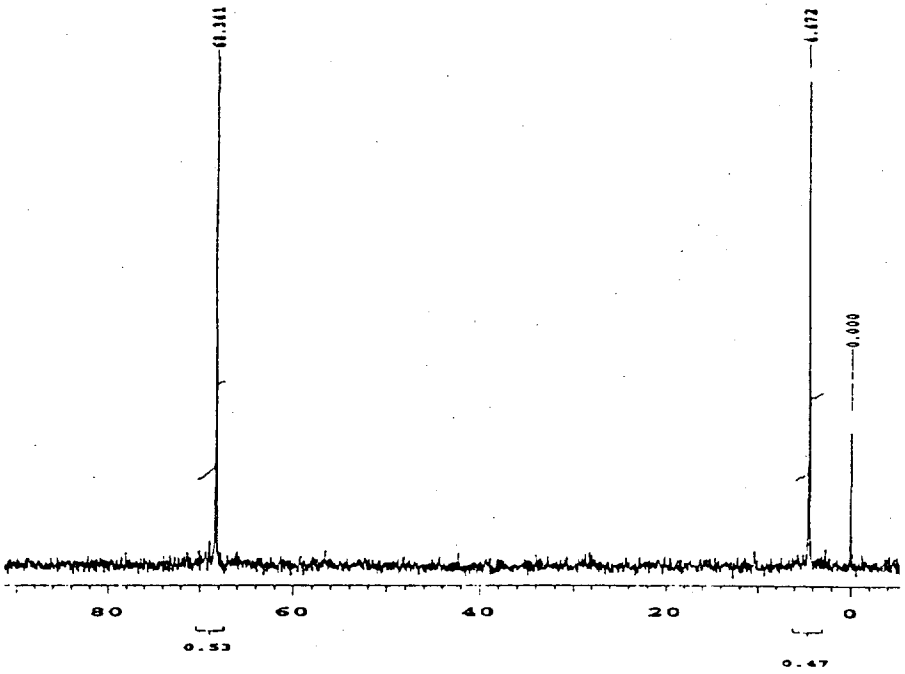
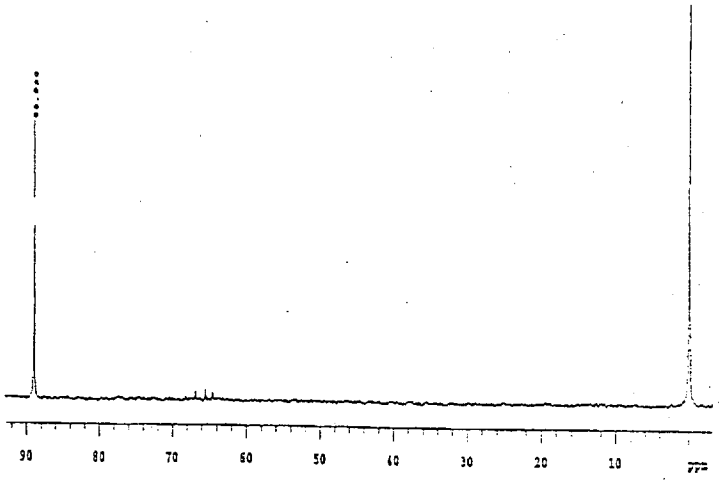
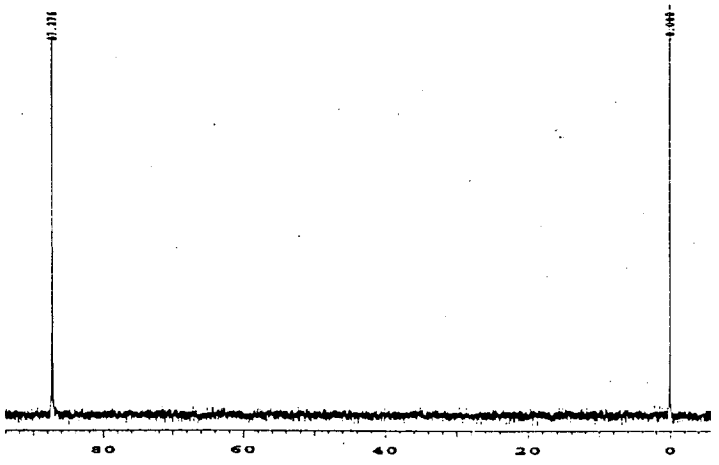



**Figure 1.** $^{31}P$ NMR of H-phosphonothioate condensed to the tyrosylpeptide-resin using DPCP. Both the desired H-phosphonothioate diester ($\delta$ = 68.3) and the H-phosphonate diester side product ($\delta$ = 4.5) are present.

Panel A




Panel B




Panel C

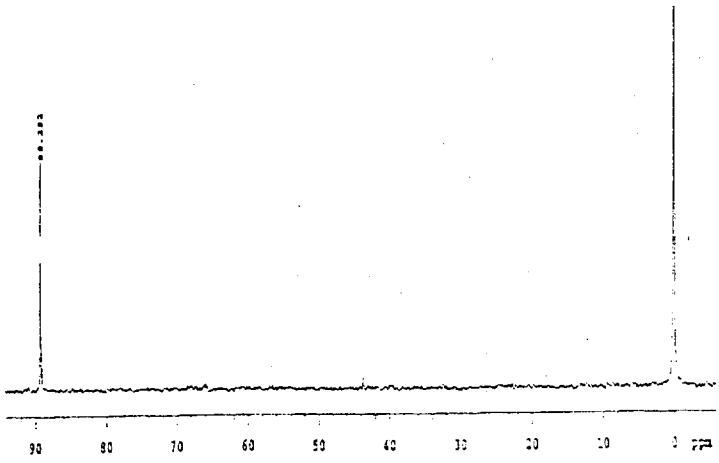



**Figure 2.** $^{31}P$ NMRs of HPLC purified dithio-phosphoeptides. Panel A: Ac-T($POS_2$)IIPLPG-$NH_2$, 89.0 ppm; Panel B: Ac-Y($POS_2$)IIPLPG-$NH_2$, 87.3 ppm; Panel C: Ac-S($POS_2$)IIPLPG-$NH_2$, 89.3.

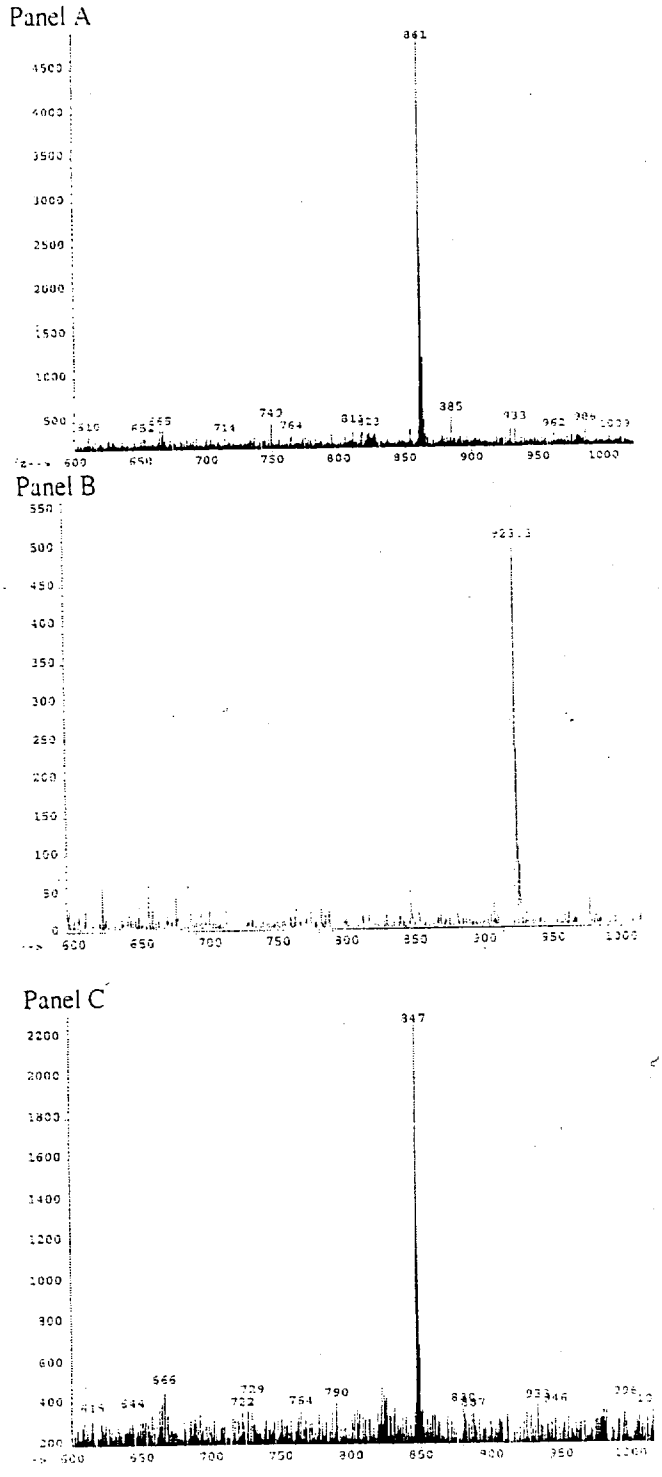



**Figure 3.** ESI-MS of reverse phase HPLC purified dithiophosphopeptides. Panel A: Ac-T($POS_2$)IIPLPG-$NH_2$ (861 AMU); Panel B: Ac-Y($POS_2$)IIPLPG-$NH_2$ (923 AMU); Panel C: Ac-S($POS_2$)IIPLPG-$NH_2$ (847 AMU).

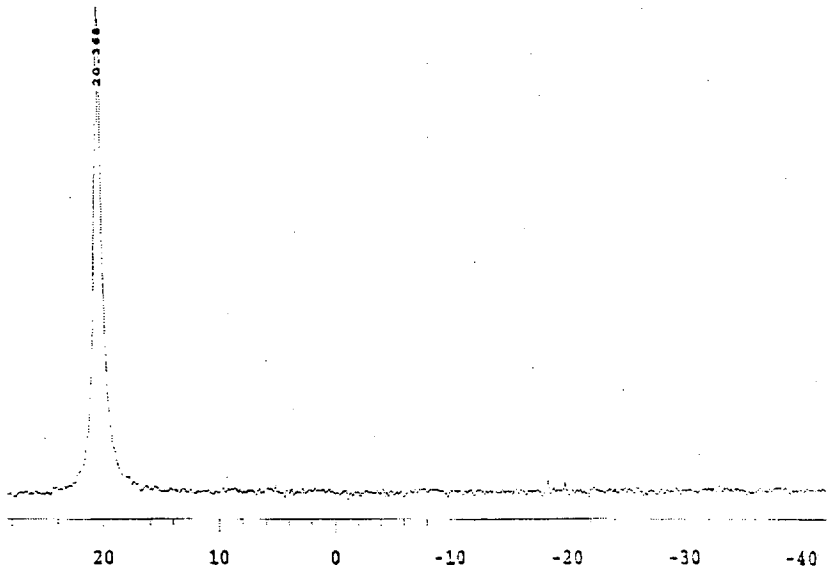
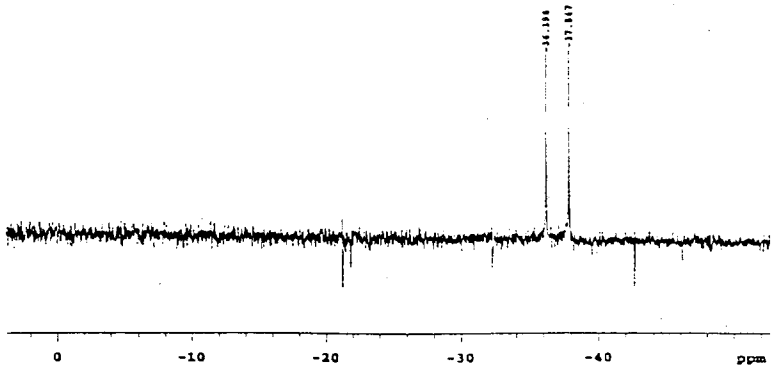



**Figure 4.** Boron NMR of acetylated-resin after treatment with borane and ammonium hydroxide showing the boric-acid like product at 20 ppm.

Panel A




Panel B

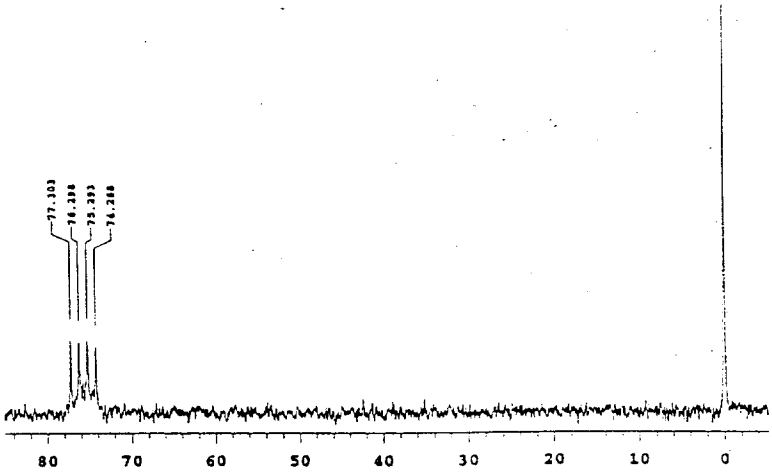
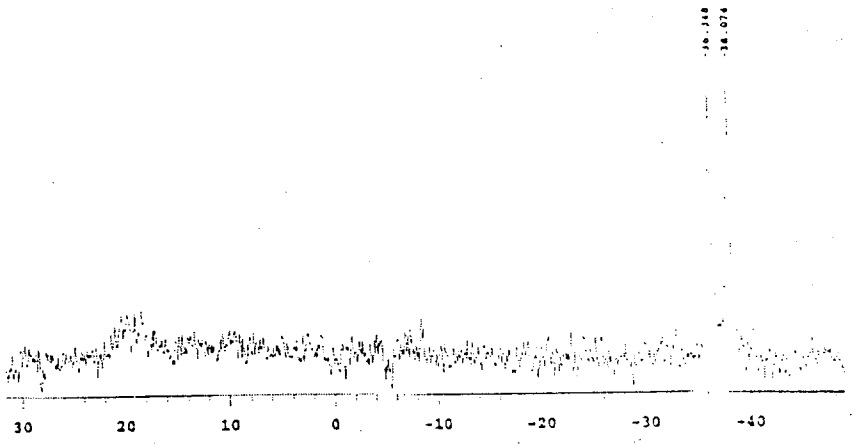



**Figure 5.** NMR spectra of reverse phase HPLC purified Ac-Y($PO_2BH_3$)IIPLPG-$NH_2$. Panel A: $^{11}B$ NMR (-36.2, -37.8); Panel B: $^{31}P$ NMR (77.3, 76.3, 75.3, 74.3).

Panel A




Panel B

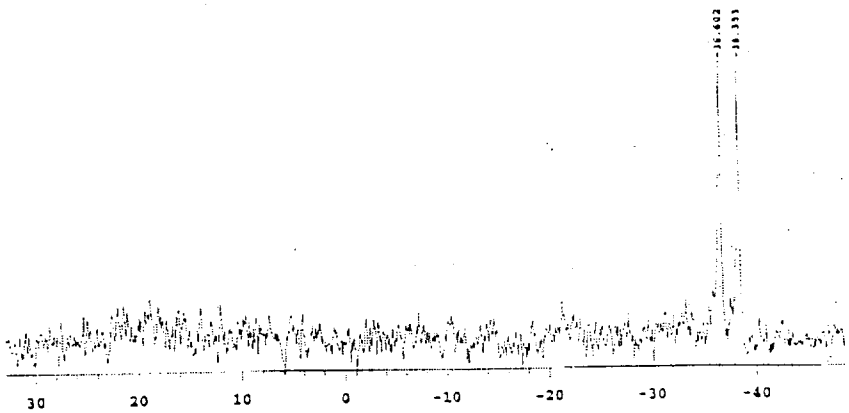
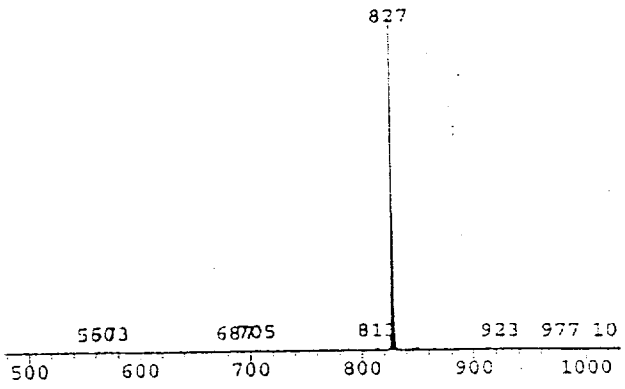
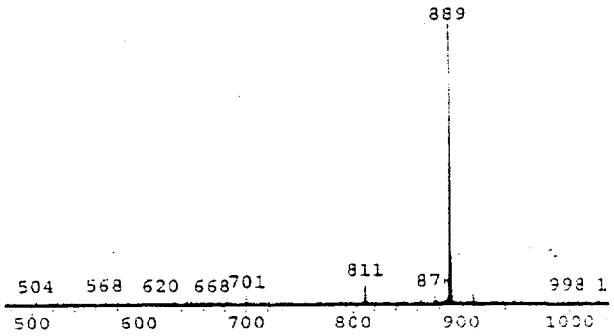



**Figure 6.** $^{11}B$ NMR of HPLC purified boranophosphopeptides. Panel A: Ac-T($PO_2BH_3$)IIPLPG-NH2 ($\delta$ = -36.3, -38.1); Panel B: Ac-S($PO_2BH_3$)IIPLPG-NH2 ($\delta$ = -36.6, -38.4)

Panel A




Panel B




Panel C

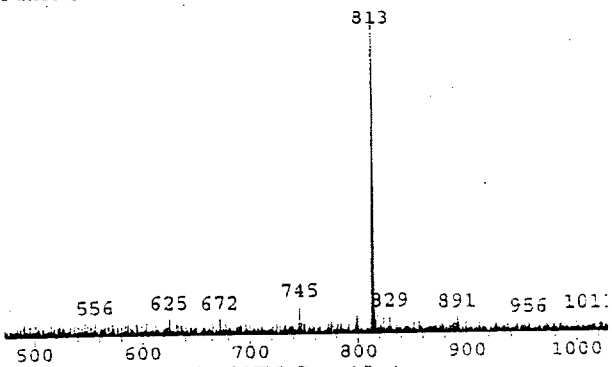



**Figure 7.** ESI-MS of HPLC purified boranophosphopeptides. Panel A: Ac-T($PO_2BH_3$)IIPLPG-$NH_2$ (826 AMU); Ac-Y($PO_2BH_3$)IIPLPG-$NH_2$ (889 AMU); Ac-S($PO_2BH_3$)IIPLPG-$NH_2$ (813 AMU).

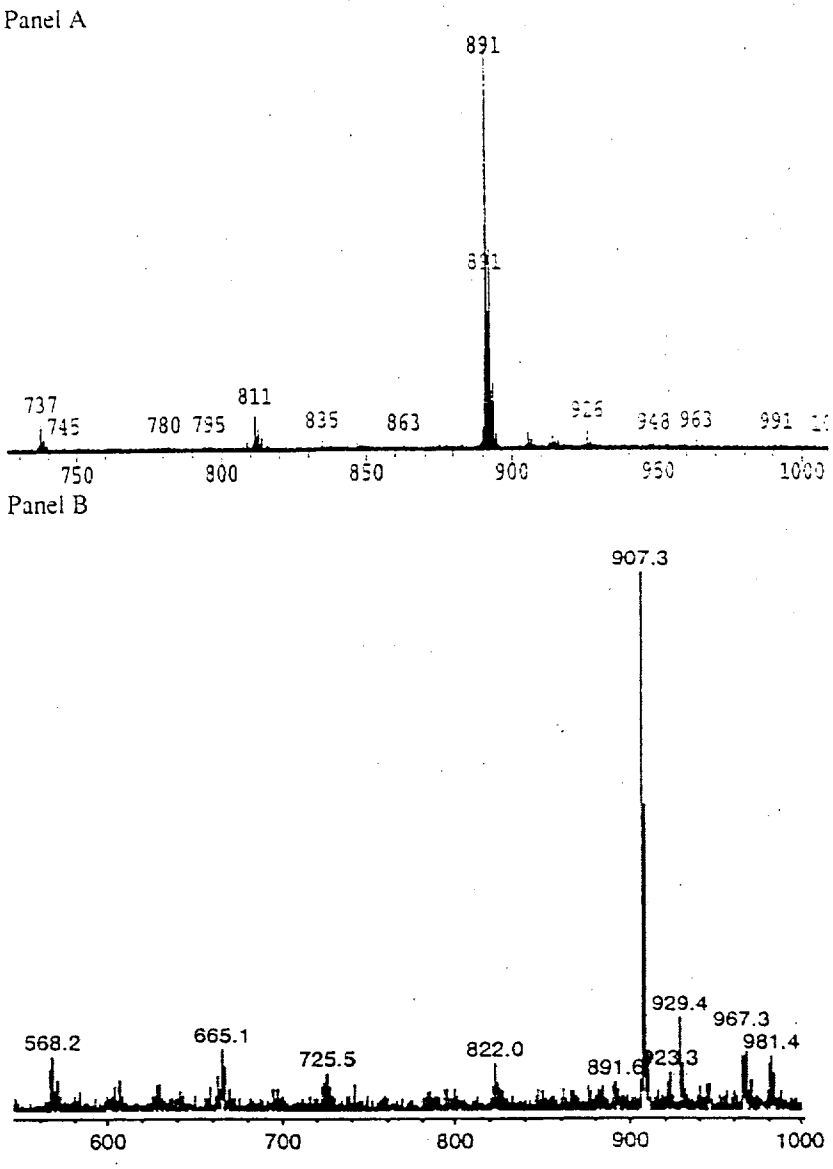



**Figure 8.** ESI-MS of reaction mixtures following the synthesis of phospho and thiophosphopeptides. Panel A. Ac-Y(PO3)IIPLPG-NH2 (891 AMU); Panel B. Ac-Y(PO2S)IIPLPG-NH2 (907 AMU).

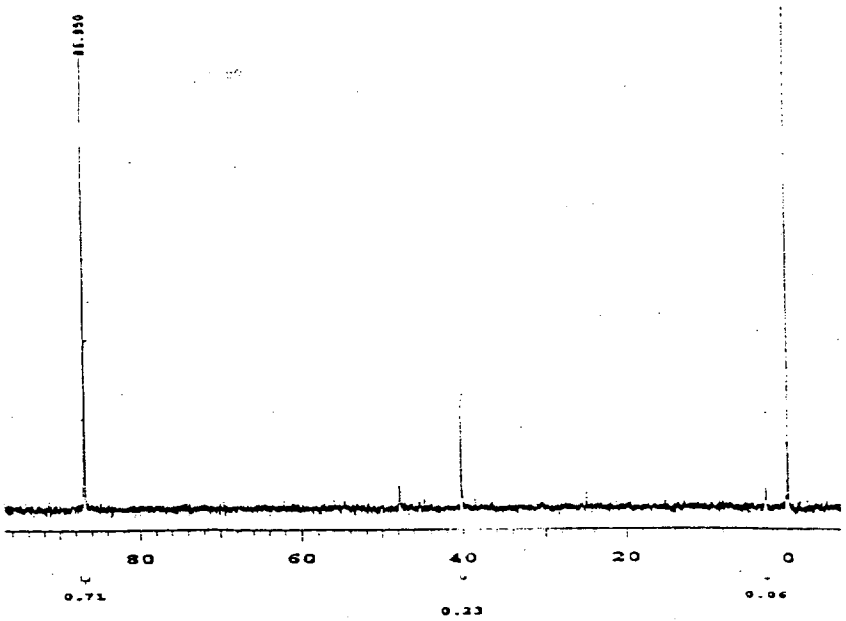



**Figure 9.** $^{31}P$ NMR of the reaction mixture from the synthesis of Ac-GNDY($POS_2$)IIPL-$NH_2$ following purification by reverse phase HPLC. Ac-GNDY($POS_2$)IIPL-$NH_2$ (87 ppm); Ac-GNDY($PO_2S$)IIPL-$NH_2$ (40 ppm).

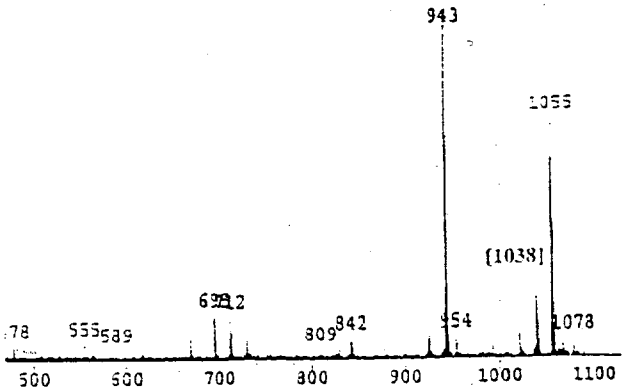
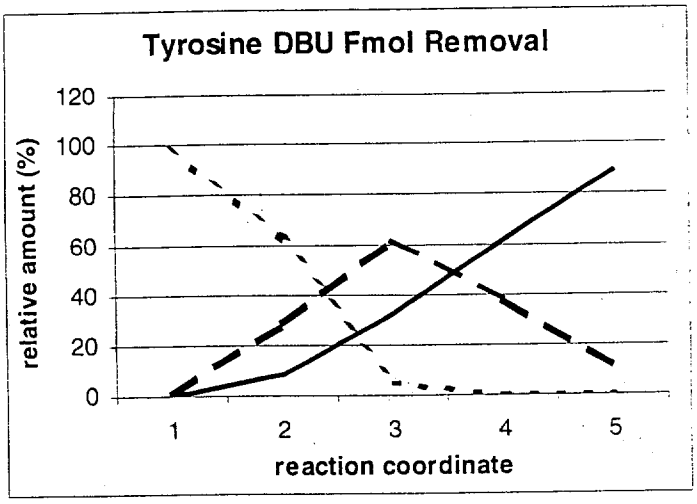
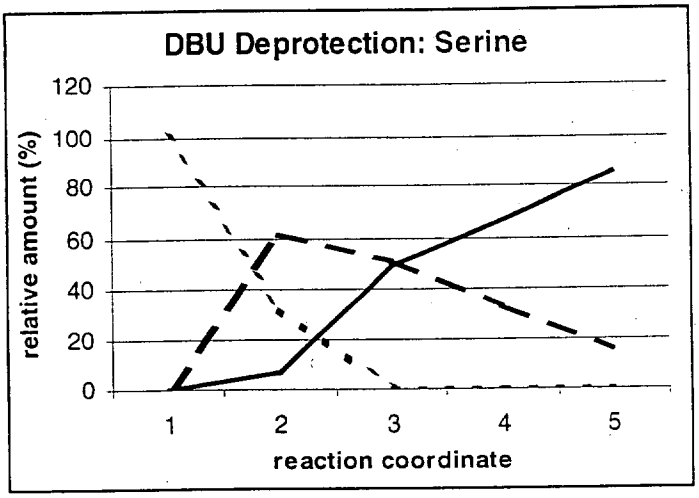



Figure 10. ESI-MS of the reaction mixture obtained following the synthesis of Ac-GNDY($POS_2$)IIPL-$NH_2$. Ac-GNDY($POS_2$)IIPL-$NH_2$ (1055); Ac-GNDY($PO_2S$)IIPL-$NH_2$ (1038, number inserted); GNDYIIPL-$NH_2$ (943.)



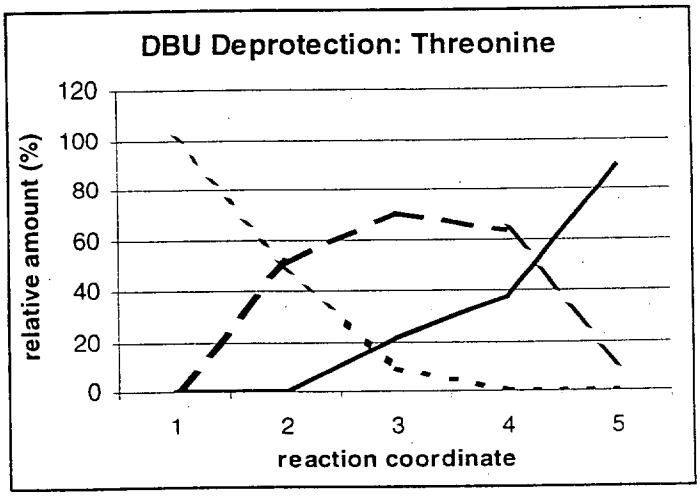




**Figure 11.** DBU deprotection studies with PS-PEG linked Fmol-dithiophosphoryl derivatives of threonine, serine, and tyrosine. ---- Fmol-dithiophosphoryl amino acid; — — — dithiophosphoryl amino acid: —— side product formation at 65 ppm. The results were obtained over 60 min by integrating appropriate peaks obtained by $^{31}P$ Gel Phase NMR (see experimental section).

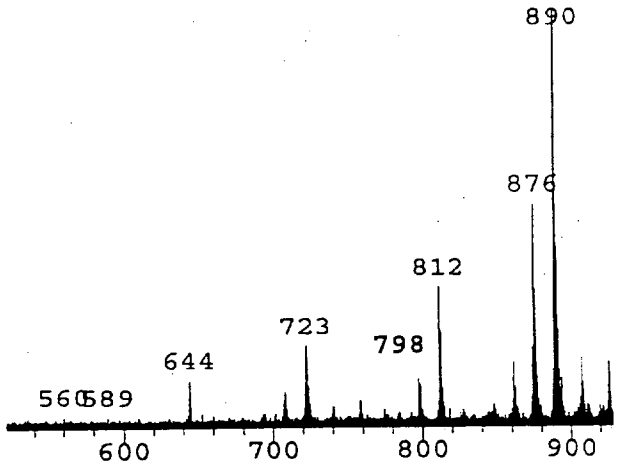



**Figure 12.** ESI-MS of the reaction mixture obtained during synthesis of **12a**. Peaks at 890 and 812 reflect the boranylphosphoryl peptide and unphosphorylated peptide, respectively. The corresponding peaks at 876 and 798 represent peptides having one reduced amide linkage. Additional peaks corresponding to further reductions in amide linkages can also be detected.

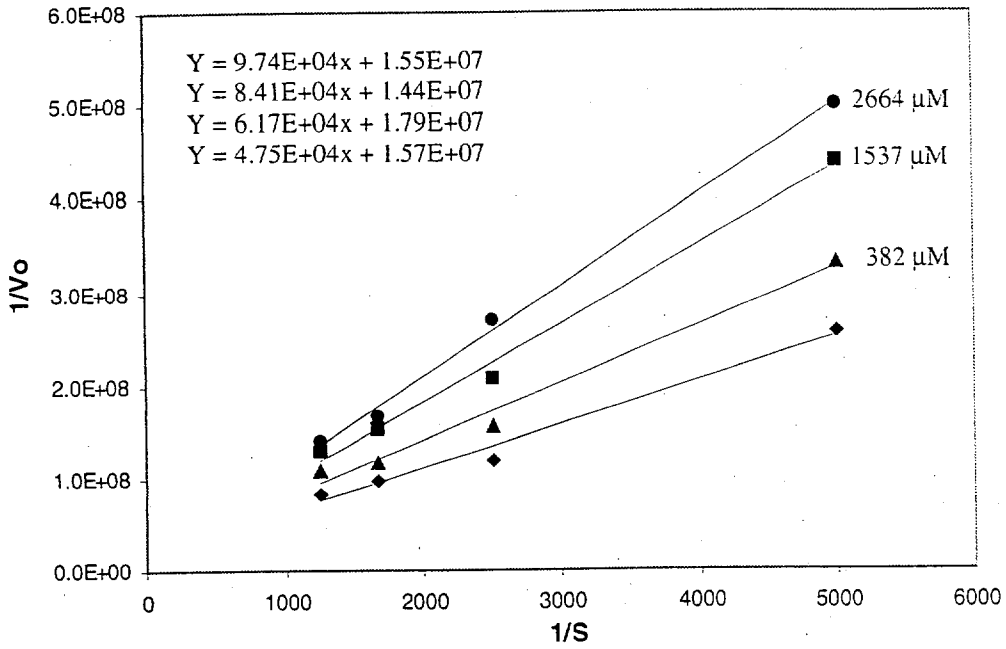



**Figure 13.** Inhibition of *Yersinia* PTP by Ac-Y($PO_2S$)IIPLPG-$NH_2$. Inhibitor concentrations are shown adjacent to the corresponding double reciprocal plot line. The unlabeled line represents enzymic hydrolysis of *p*-nitrophenylphosphate without inhibitor present (1/S, $M^{-1}$), ($1/V_o$, s/M).

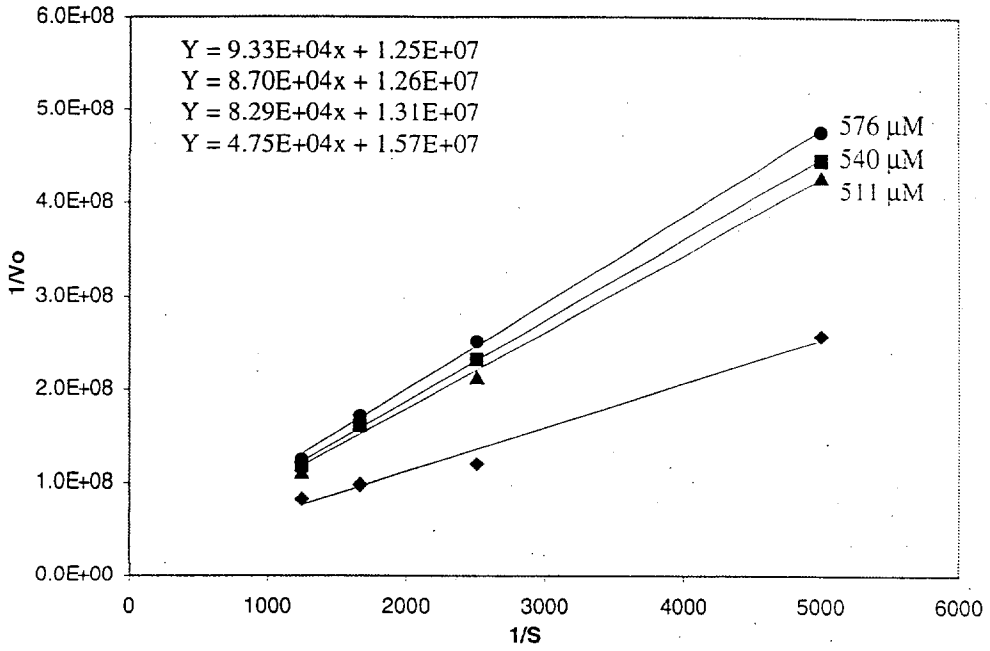



**Figure 14.** Inhibition of *Yersinia* PTP by Ac-Y($POS_2$)IIPLPG-$NH_2$. Inhibitor concentrations are shown adjacent to the corresponding double reciprocal plot line. The unlabeled line represents enzymic hydrolysis of *p*-nitrophenylphosphate without inhibitor present(1/S, $M^{-1}$), ($1/V_o$, s/M).

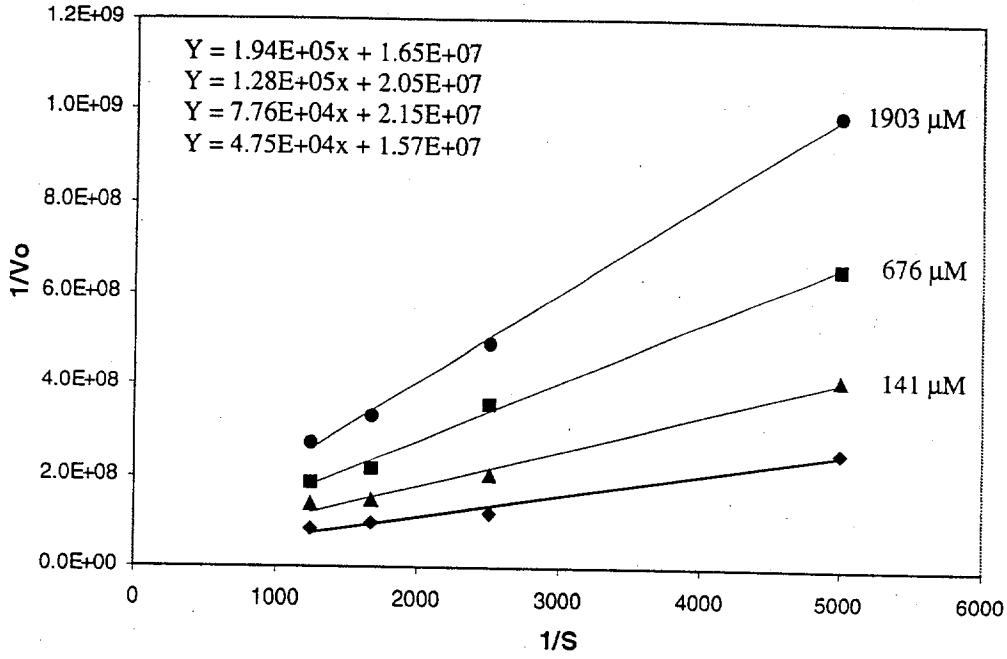



**Figure 15.** Inhibition of *Yersinia* PTP by Ac-Y($PO_2BH_3$)IIPLPG-$NH_2$. Inhibitor concentrations are shown adjacent to the corresponding double reciprocal plot line. The unlabeled line represents enzymic hydrolysis of *p*-nitrophenylphosphate without inhibitor present(1/S, $M^{-1}$), ($1/V_o$, s/M).