



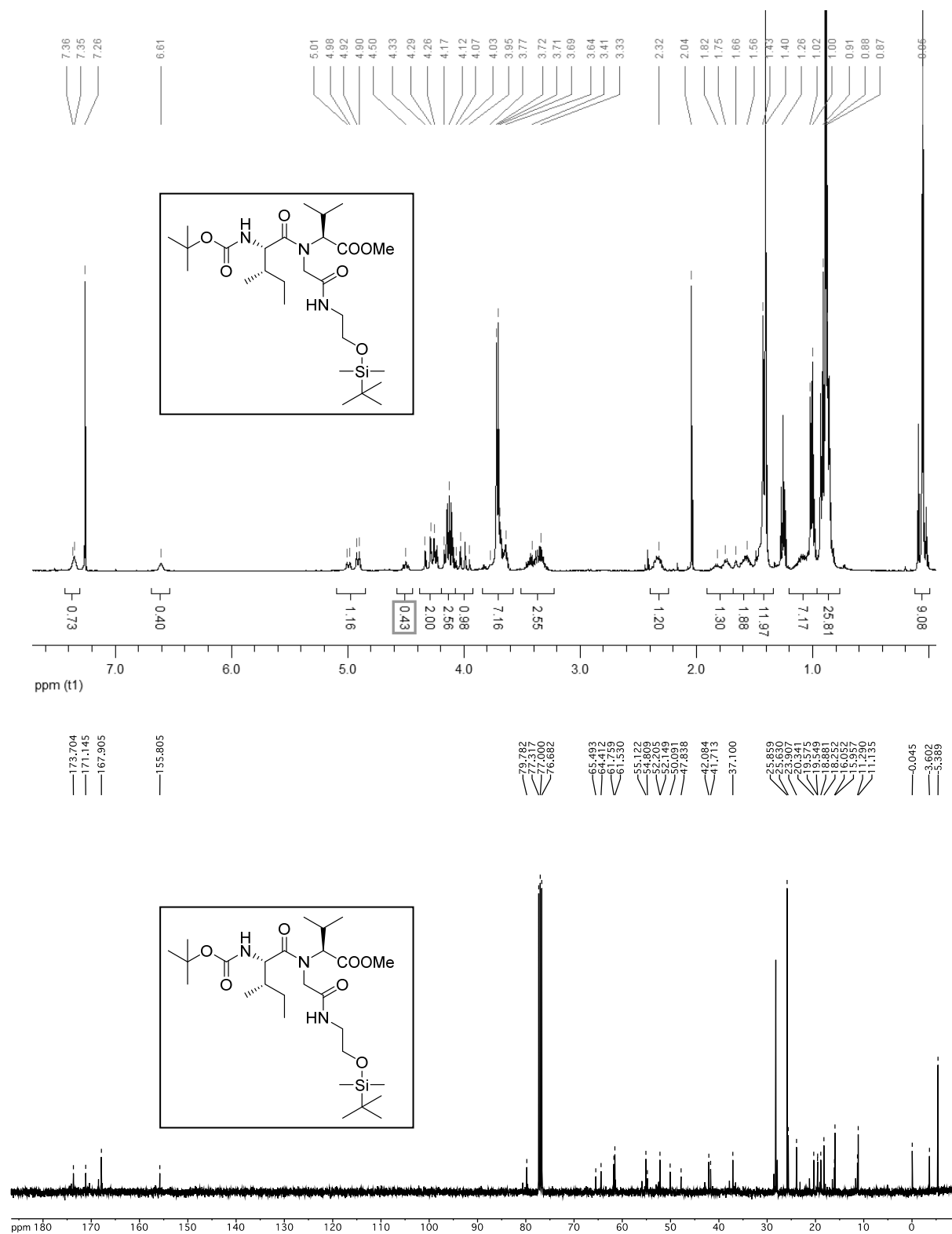
Synthesis of Pretubulysin-Derivatives *via* the TubUgi-Approach

Judith Hoffmann, Jan Gorges, Lukas Junk and Uli Kazmaier*

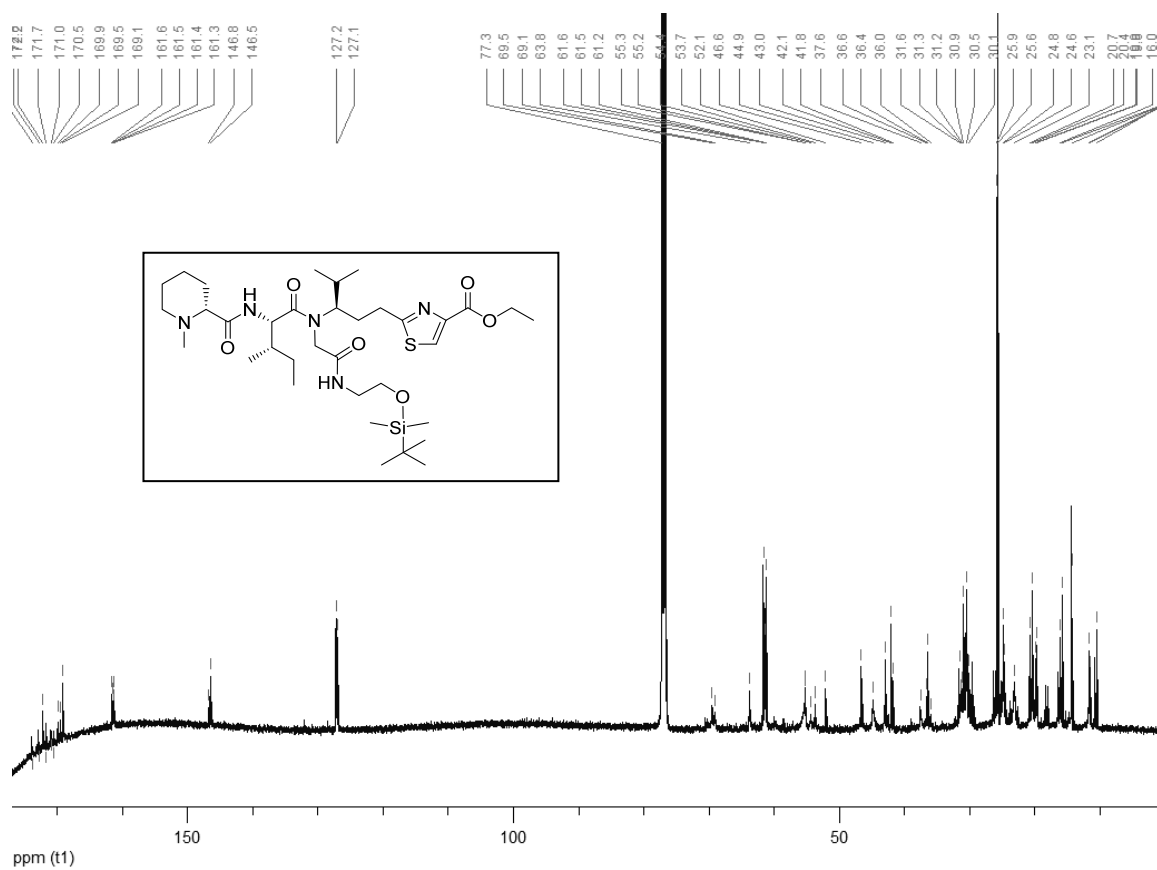
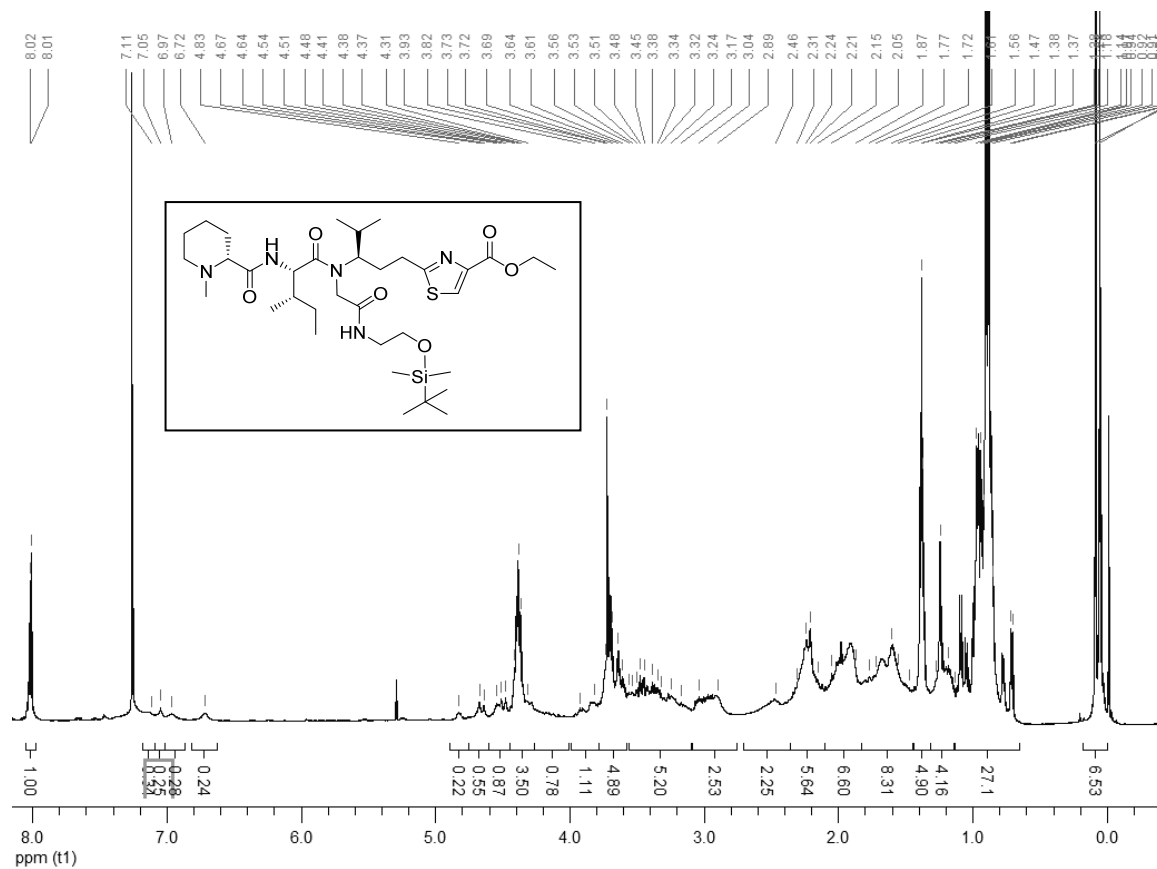
Supporting information

Copies of NMR spectra ($^1\text{H}/^{13}\text{C}$ NMR)

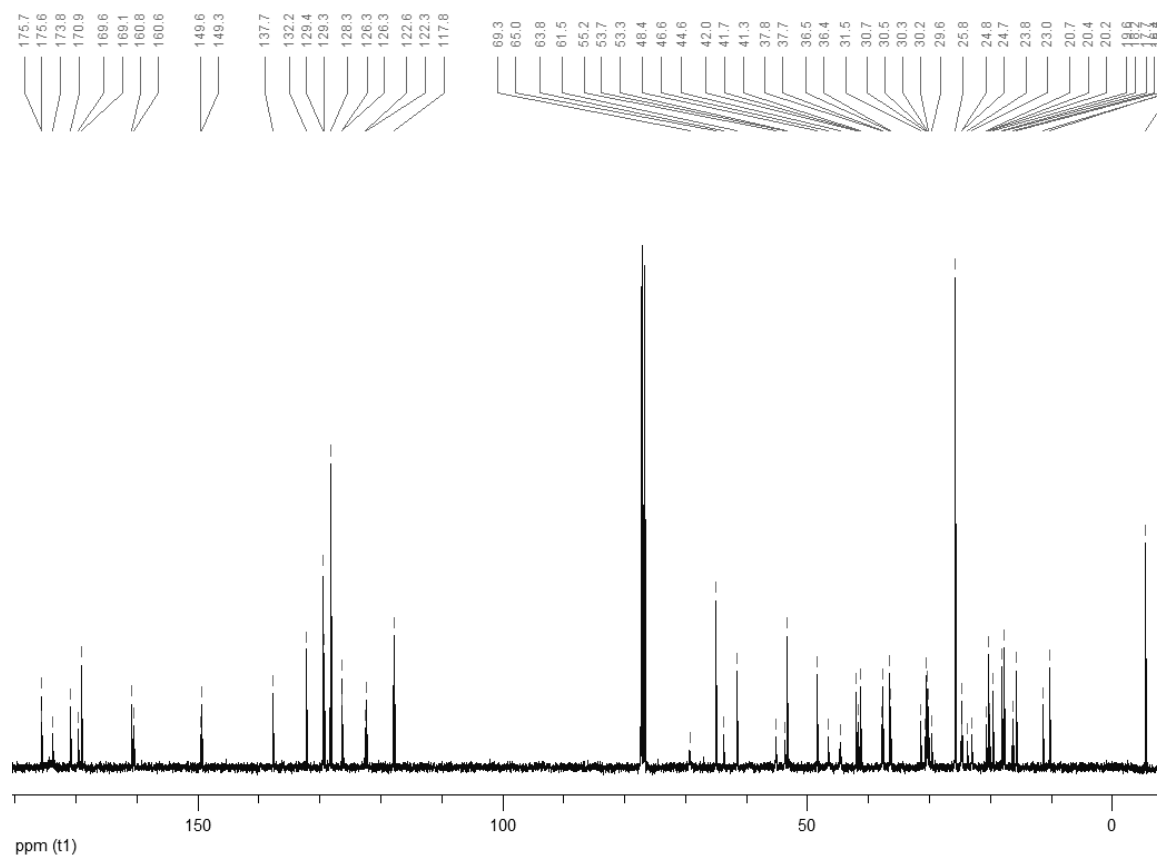
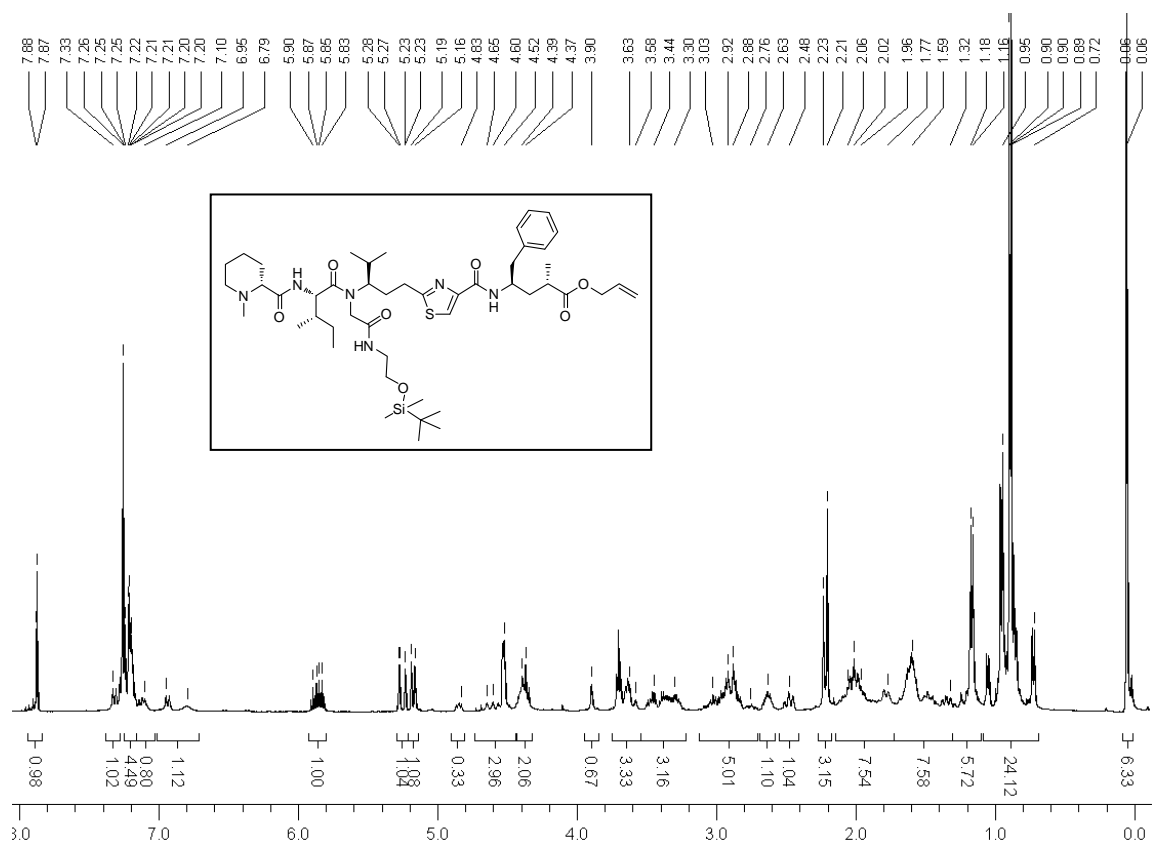
***N*-tert-Butyloxycarbonyl-(*S*)-isoleucyl-*N*-[*N'*-(2-*tert*-butyloxidimethylsilyloxyethyl)-aminocarbonylmethyl]-(*S*)-valin methylester (1).**



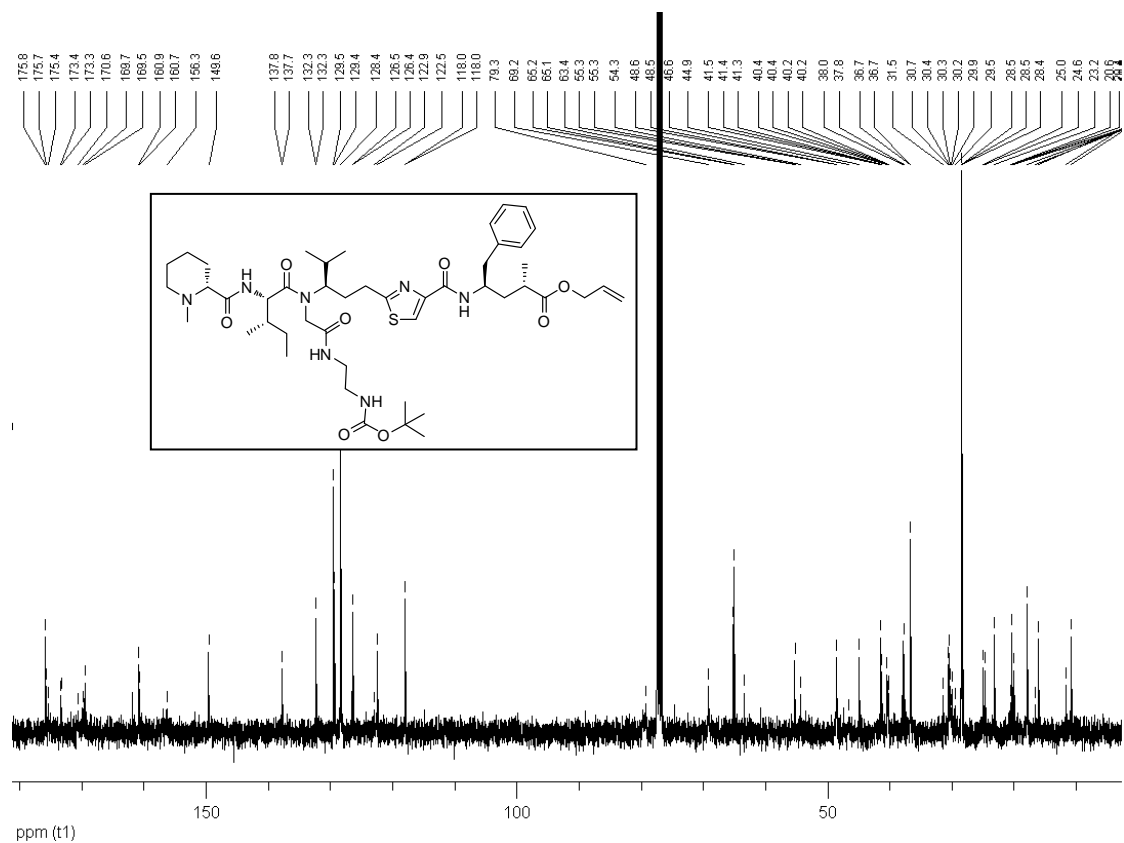
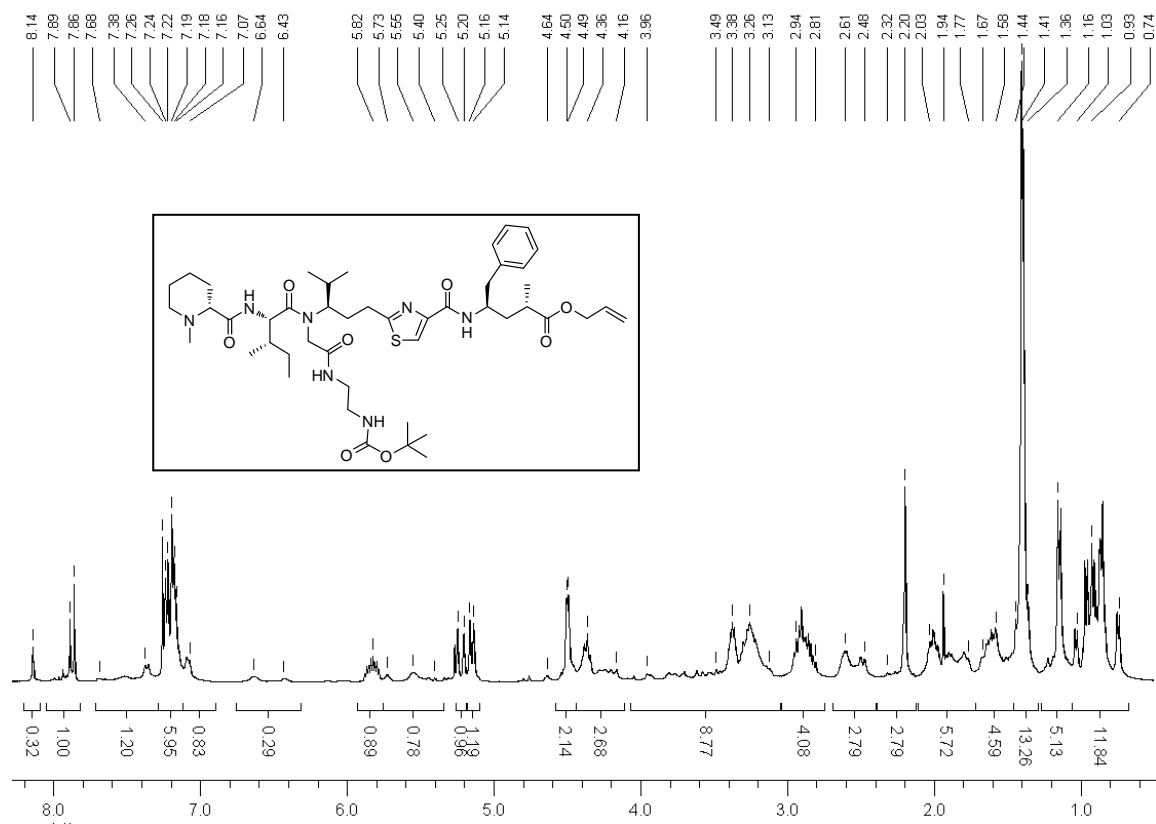
***N*-Methyl-*(R)*-pipocolyl-*(S)*-isoleucyl-*N*-[*N'*-(2-*tert*-butyloxydimethylsilyloxyethyl)amino-carbonylmethyl]-*des*acetoxy-*(S)*-tubuvalin methylester (3a).**



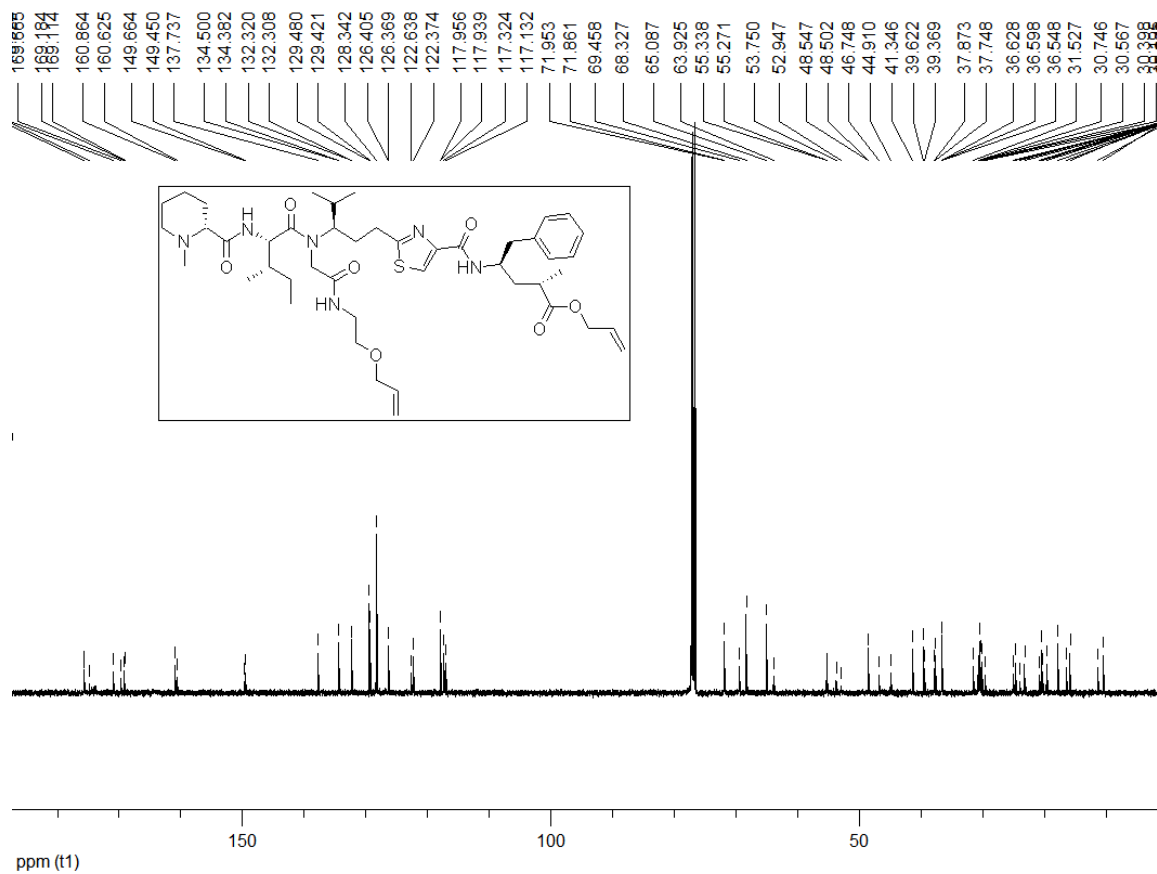
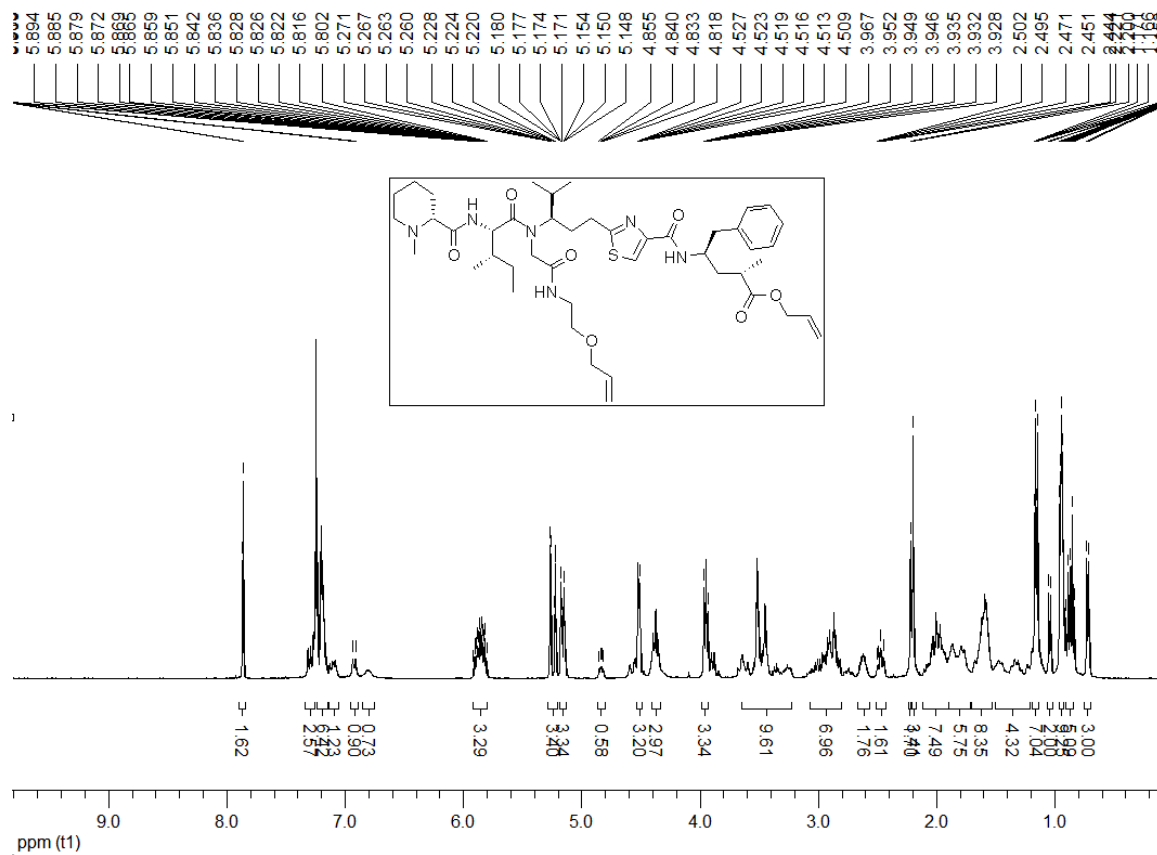
***N*-Methyl-(*R*)-piperocolyl-(*S*)-isoleucyl-*N*-[*N'*-(2-*tert*-butyloxydimethylsilyloxyethyl)amino-carbonylmethyl]-*des*acetoxy-(*S*)-tubuvalyl-(*S*)-tubuphenylalanin allylester (**4b**).**



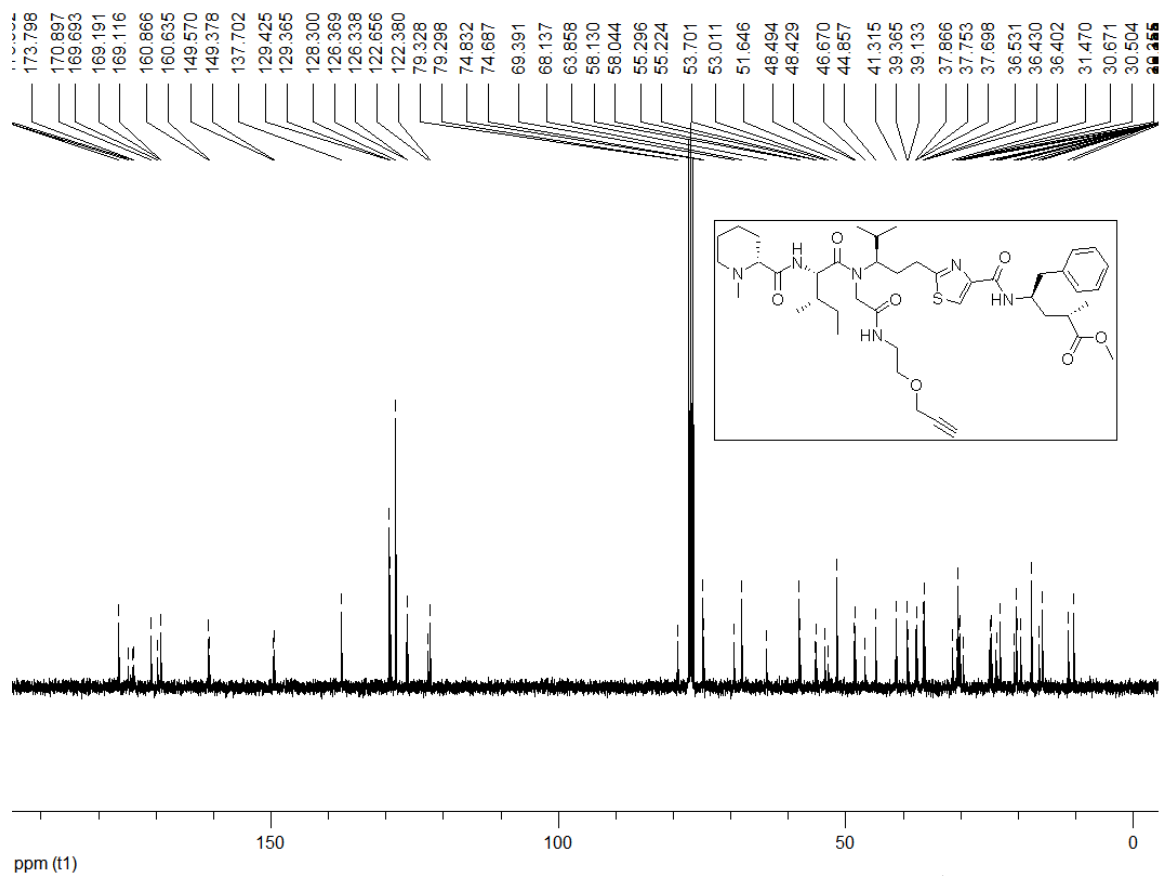
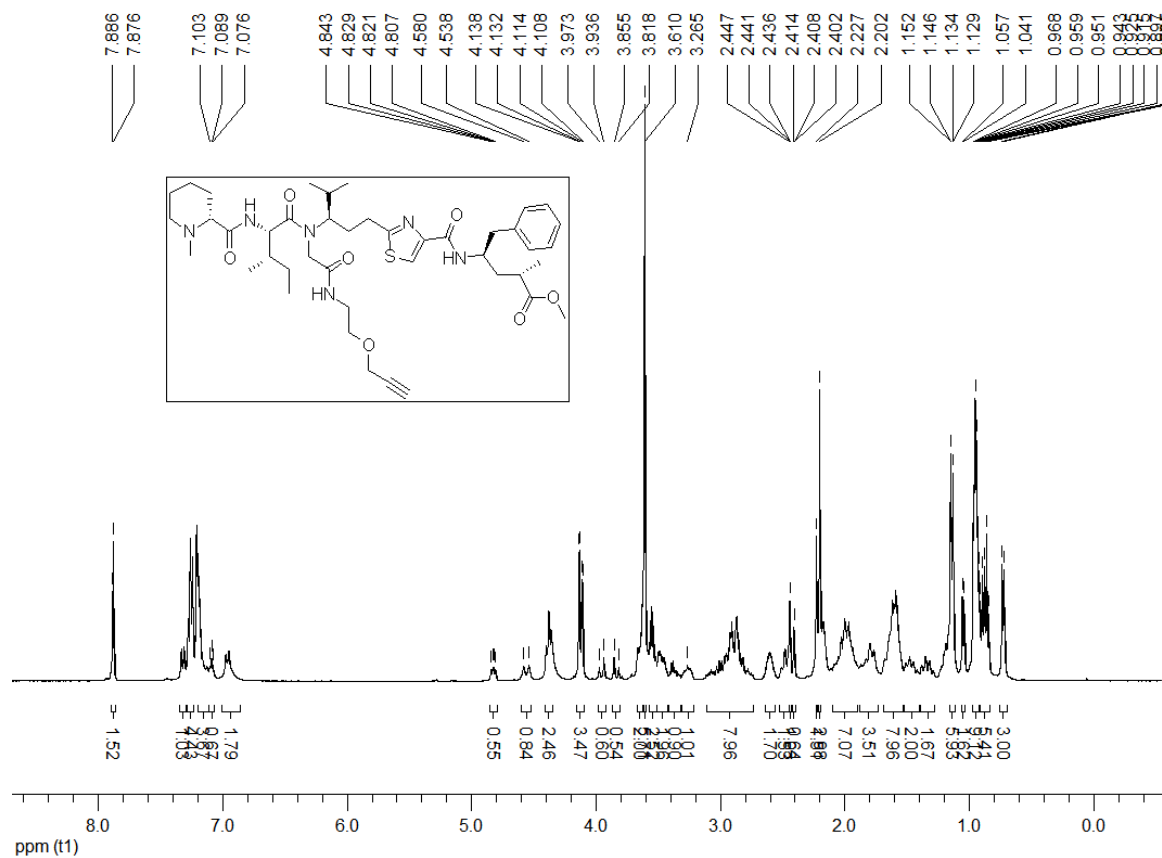
***N*-Methyl-(*R*)-pipecolyl-(*S*)-isoleucyl-*N*-[*N'*-(*tert*-butyloxycarbonylaminoethyl)amino-carbonylmethyl]-*des*acetoxy-(*S*)-tubuvalyl-(*S*)-tubuphenylalanin allylester (**6b**).**



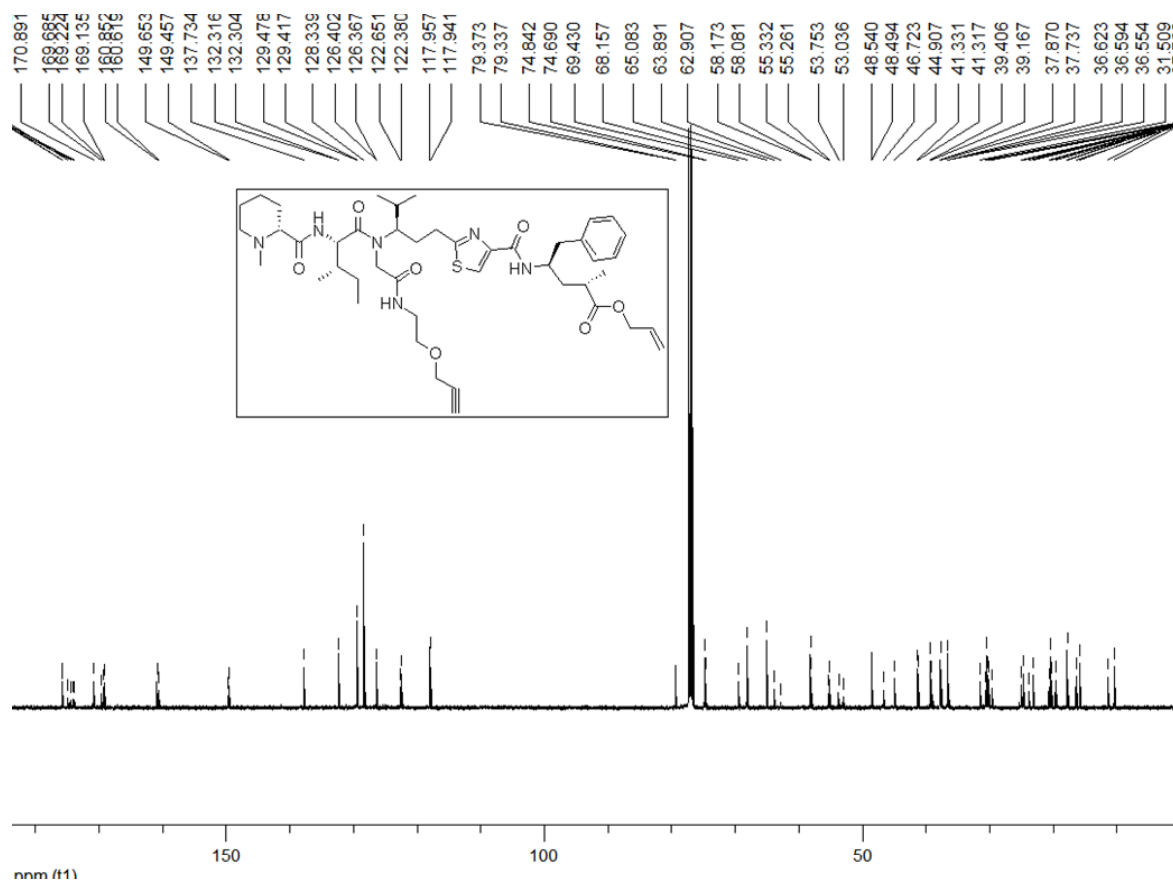
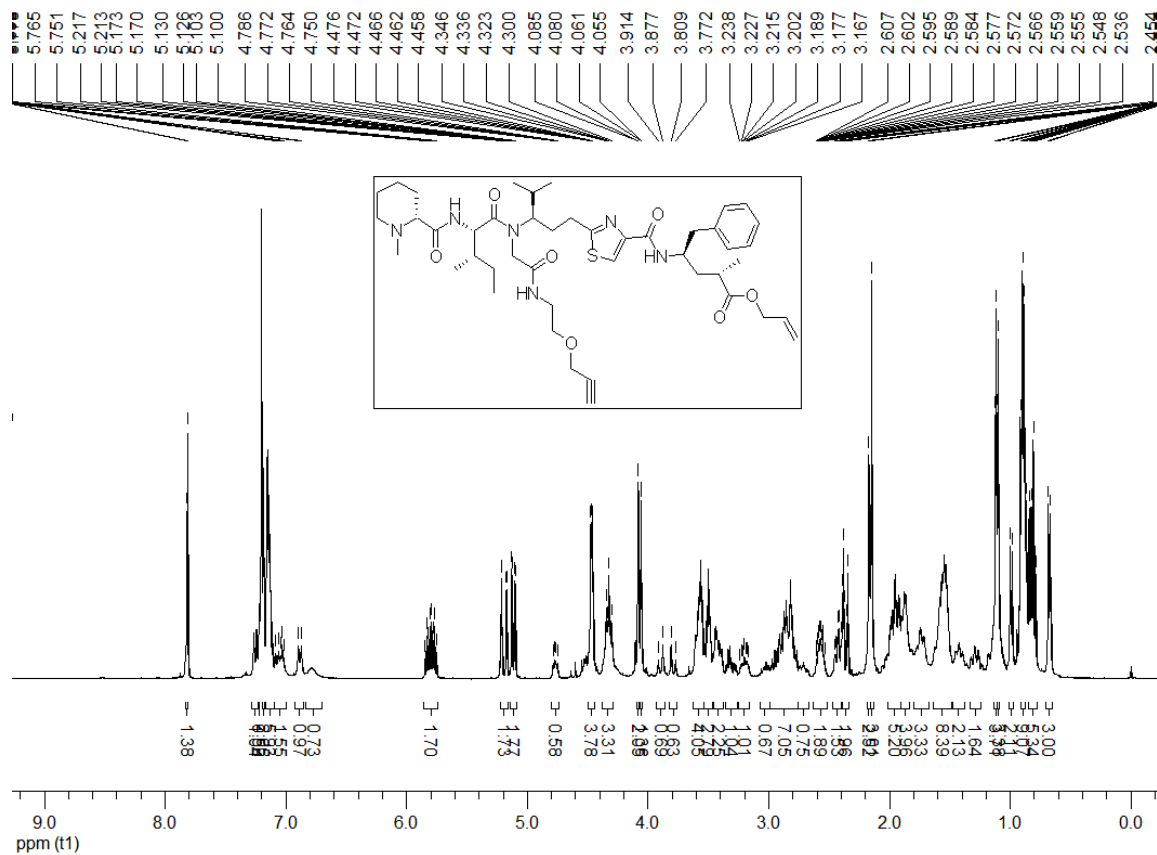
***N*-Methyl-*(R)*-pipocolyl-*(S)*-isoleucyl-*N*-[*N'*-(2-Allyloxyethyl)aminocarbonylmethyl]-*des*acetoxy-*(S)*-tubuvalyl-*(S)*-tubuphenylalanin allylester (**7b**).**



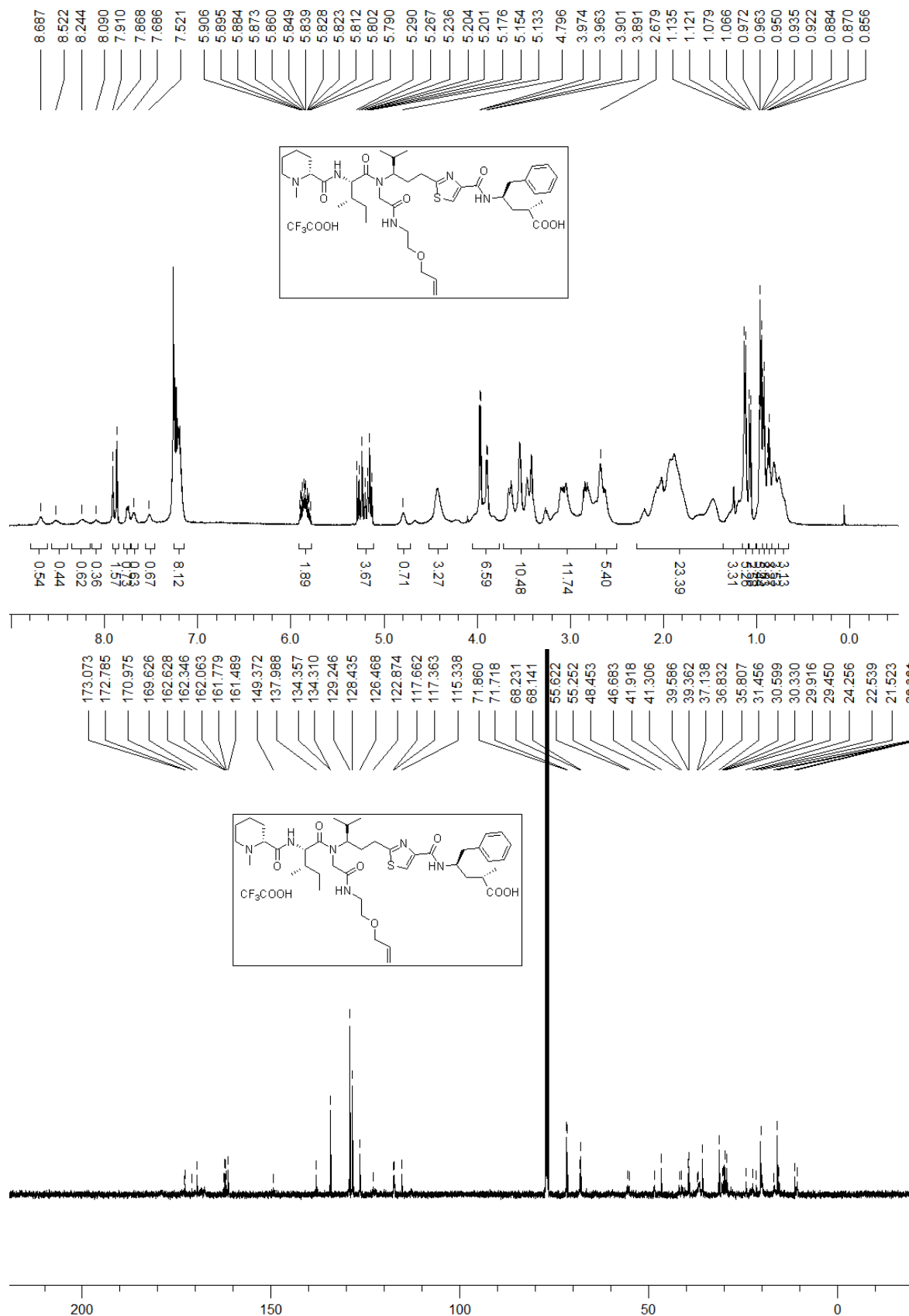
***N*-Methyl-*(R)*-pipecolyl-*(S)*-isoleucyl-*N*-[*N'*-(2-propargyloxyethyl)aminocarbonylmethyl]-desacetoxy-*(S)*-tubuvalyl-*(S)*-tubuphenylalanin methylester (**8c**).**



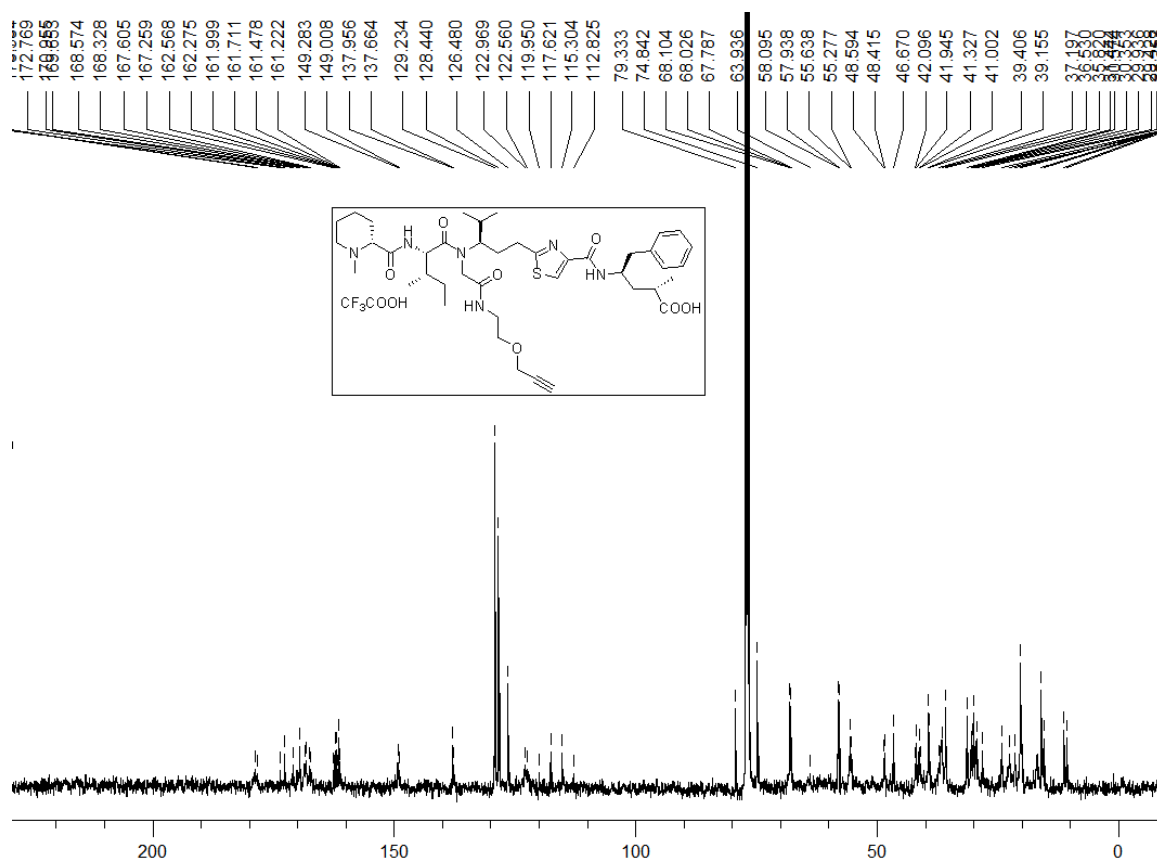
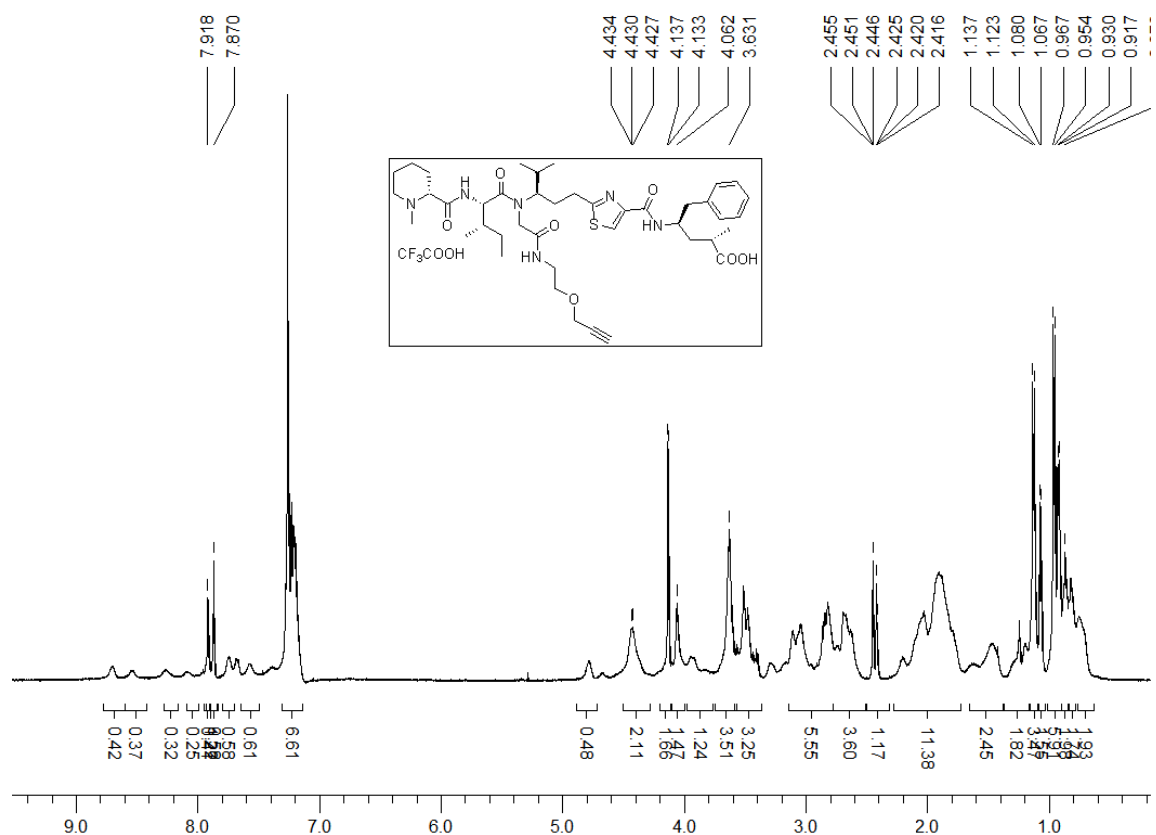
***N*-Methyl-*(R)*-pipecolyl-*(S)*-isoleucyl-*N*-[*N'*-(2-propargyloxyethyl)aminocarbonylmethyl]-desacetoxy-*(S)*-tubuvalyl-*(S)*-tubuphenylalanin allylester (8b).**



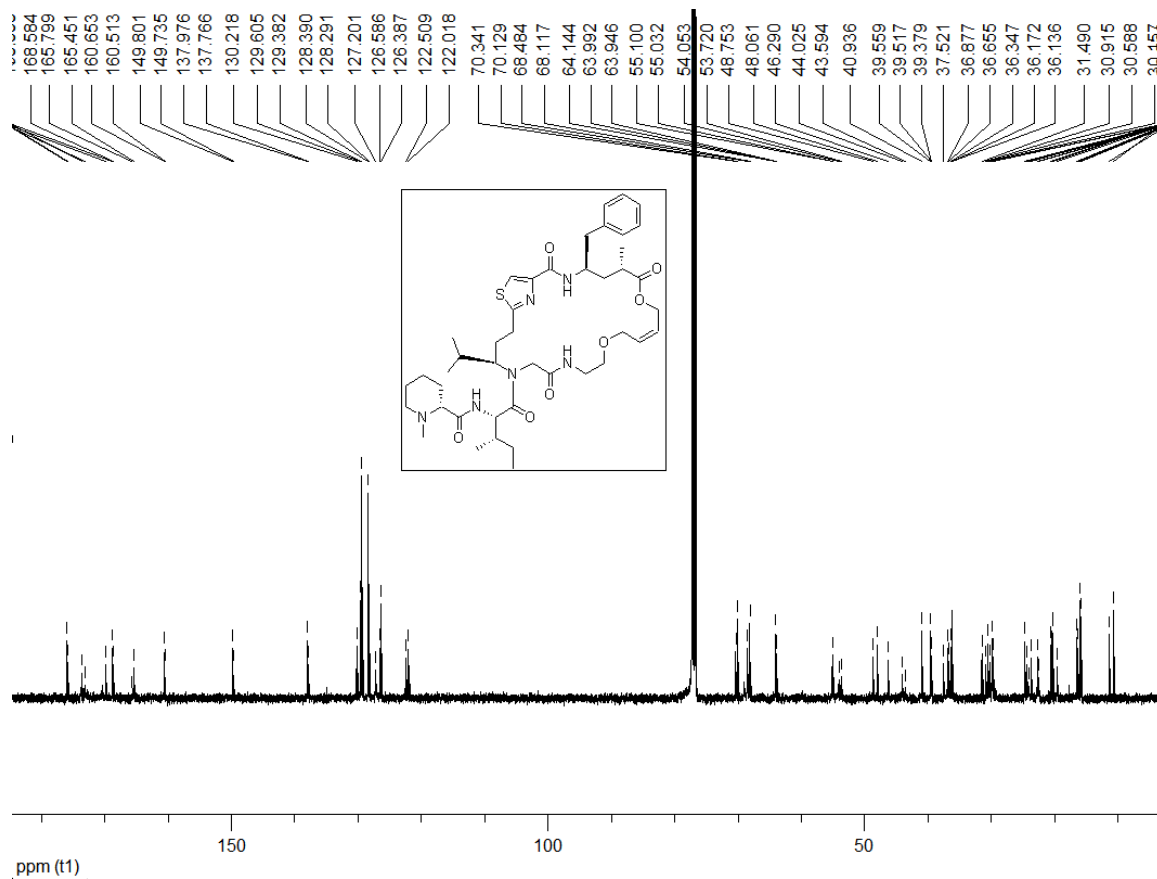
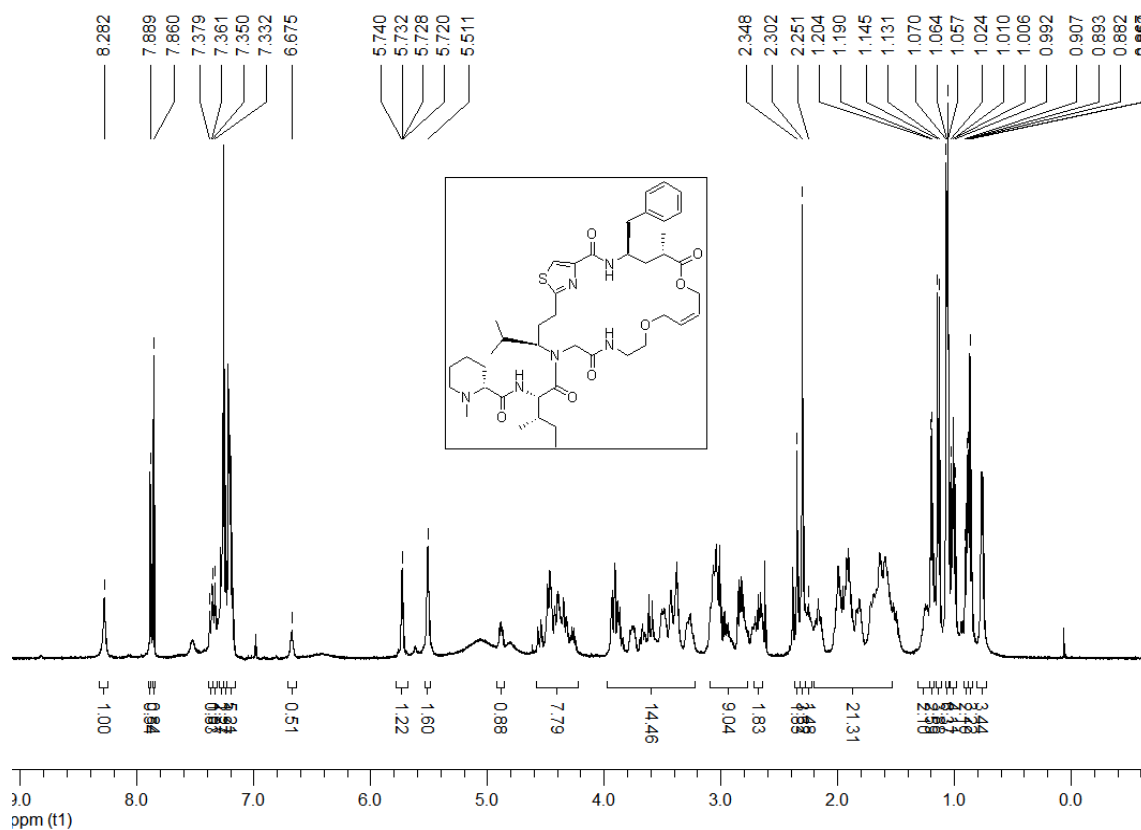
***N*-Methyl-*(R)*-pipecolyl-*(S)*-isoleucyl-*N*-[*N'*-(2-allyloxyethyl)aminocarbonylmethyl]-desacetoxy-*(S)*-tubuvalyl-*(S)*-tubuphenylalanin•CF₃COOH (7-OH).**



***N*-Methyl-*(R)*-pipecolyl-*(S)*-isoleucyl-*N*-[*N'*-(2-propargyloxyethyl)aminocarbonylmethyl]-desacetoxy-*(S)*-tubuvalyl-*(S)*-tubuphenylalanin•CF₃COOH (8-OH).**



Cyclopeptide 9.



***N*-Methyl-(*R*)-pipercolyl-(*S*)-isoleucyl-*N*'-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxyethyl]aminocarbonylmethyl]-desacetoxy-(*S*)-tubuvalyl-(*S*)-tubuphenylalanin methylester (10).**

