

Supporting Information

Stereocontrolled Syntheses of Peptide Thioesters Containing Modified Seryl Residues as Probes of Antibiotic Biosynthesis

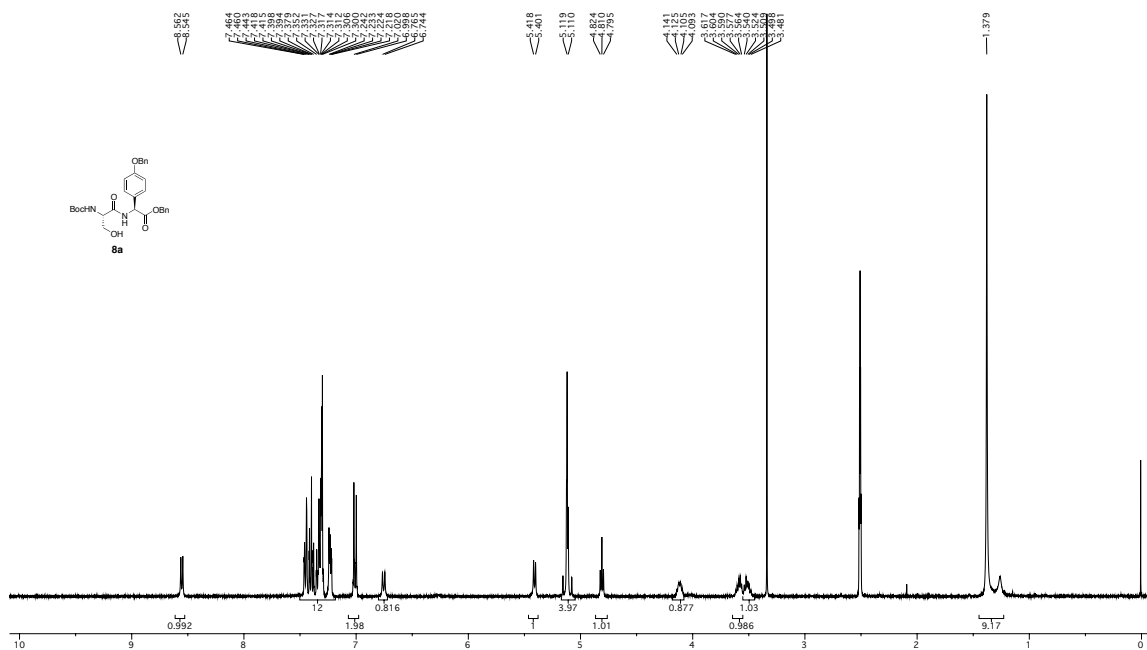
Nicole M. Gaudelli and Craig A. Townsend*, Department of Chemistry, Johns
Hopkins University, 3400 N. Charles Street, Baltimore, MD 21218

*ctownsend@jhu.edu

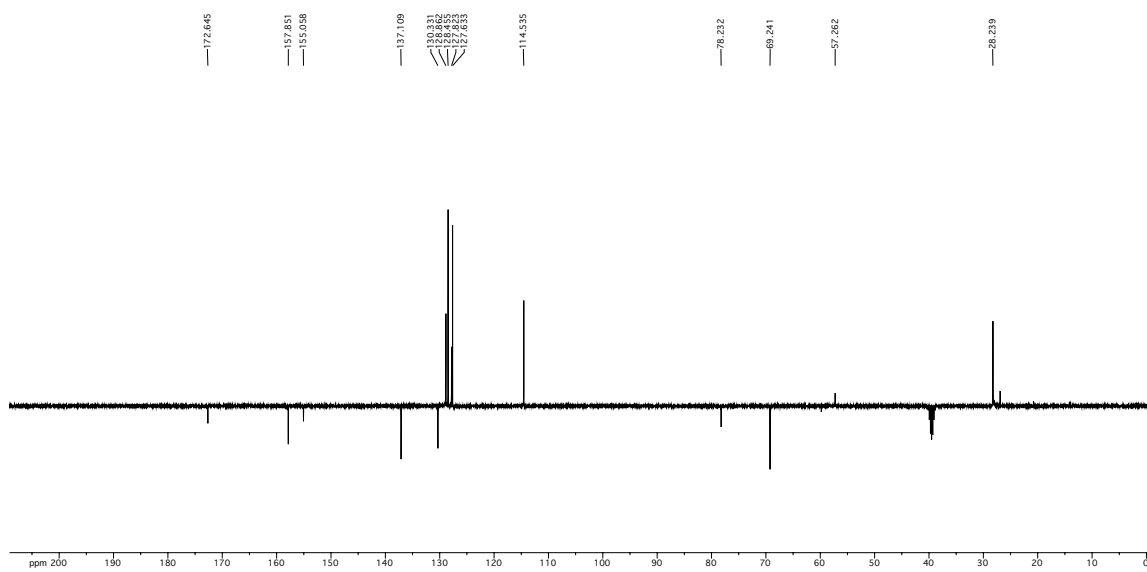
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NMR Spectra of New Compounds.....S2

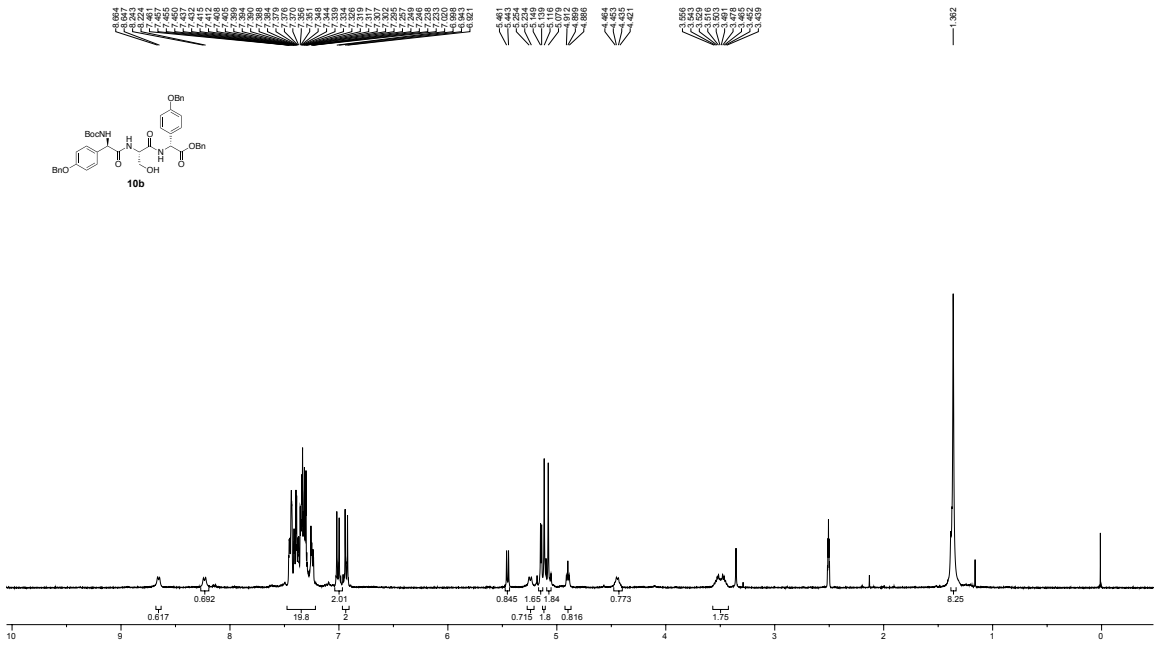
HPLC Chromatographs of Chemical Epimerization of ThioestersS36



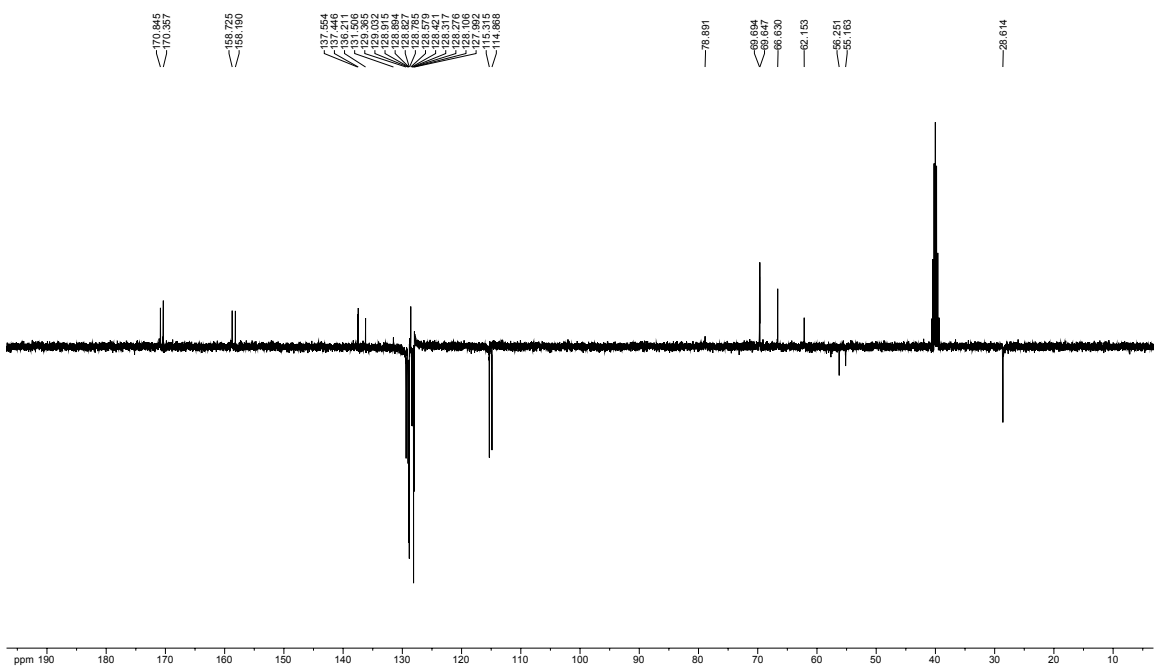
400 MHz ¹H-NMR Compound 8a – d₆-DMSO with TMS



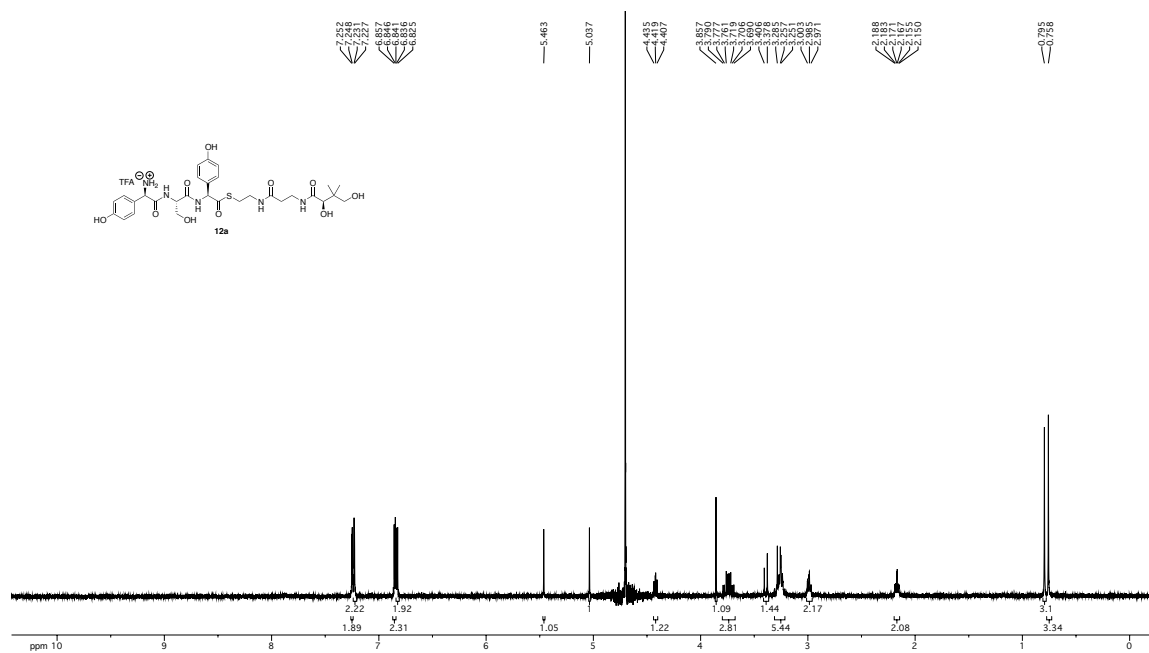
101 MHz ¹³C-NMR Compound 8a – d₆-DMSO with TMS



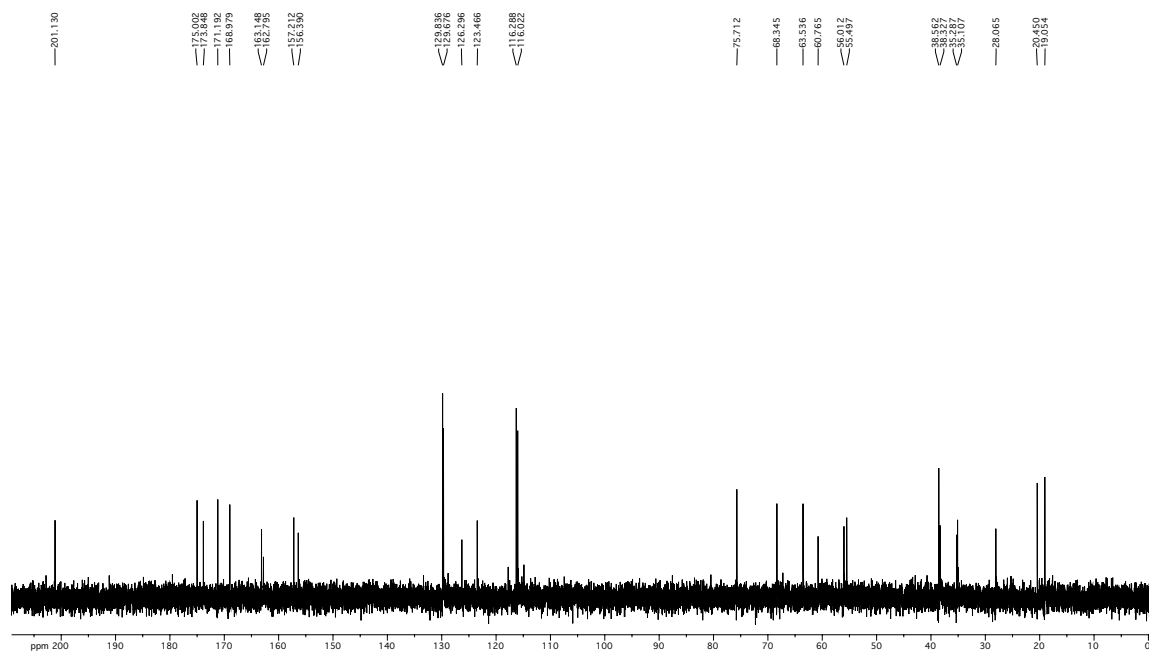
400 MHz ¹H-NMR Compound 10b – d₆DMSO with TMS



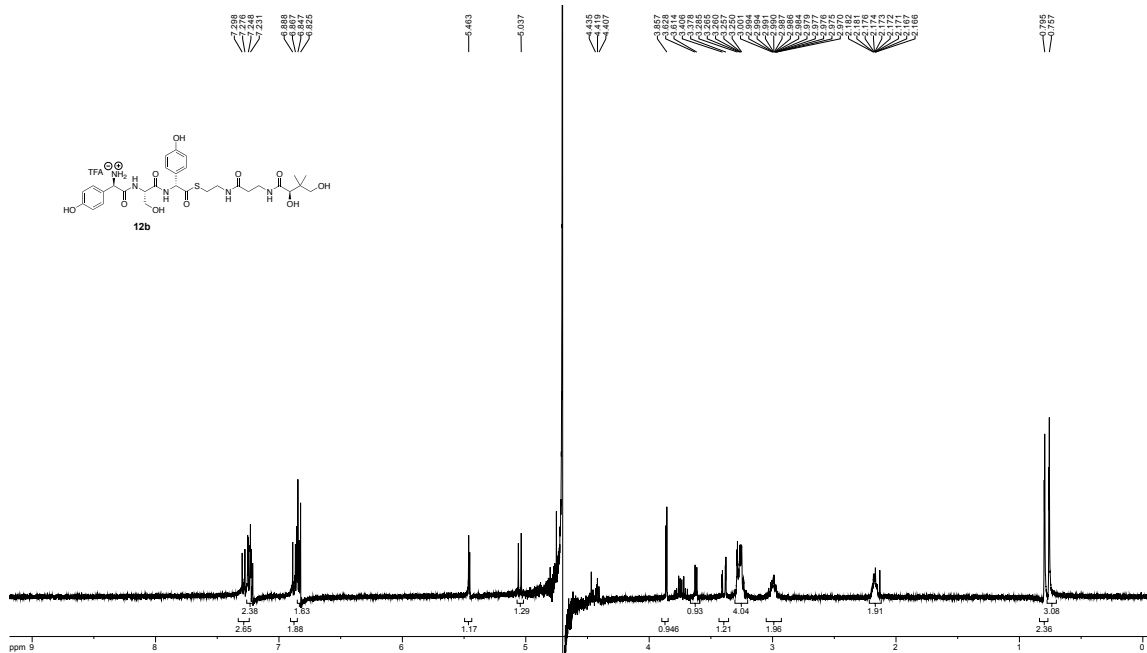
101 MHz ¹³C-NMR Compound 10b – d₆DMSO with TMS



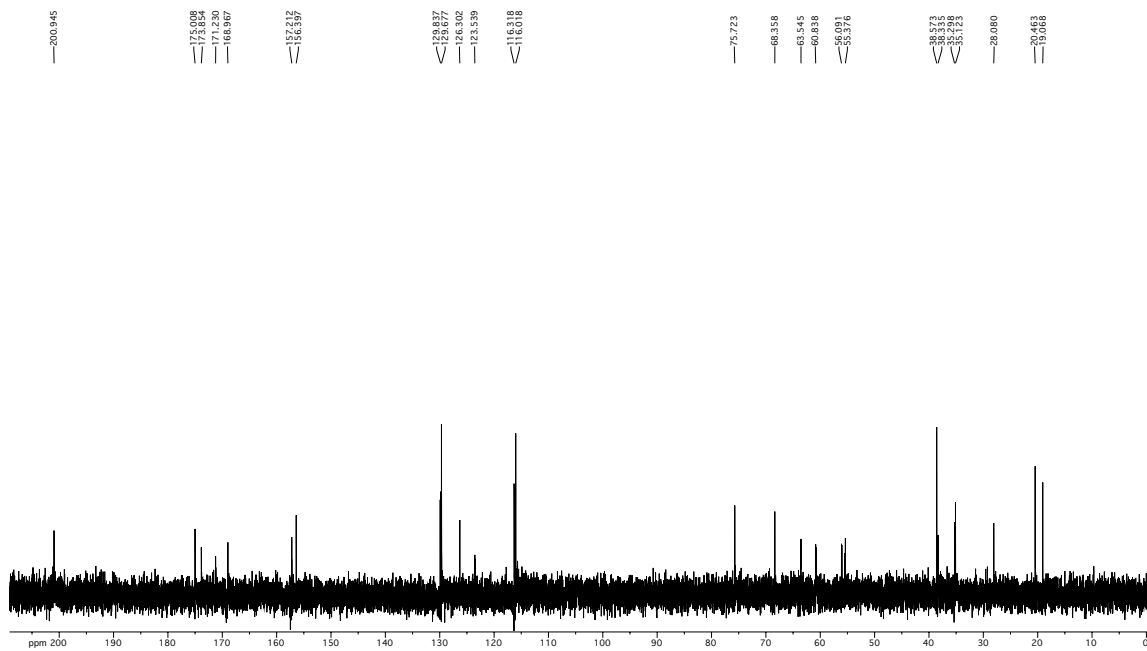
400 MHz ¹H-NMR Compound 12a – D₂O



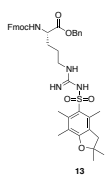
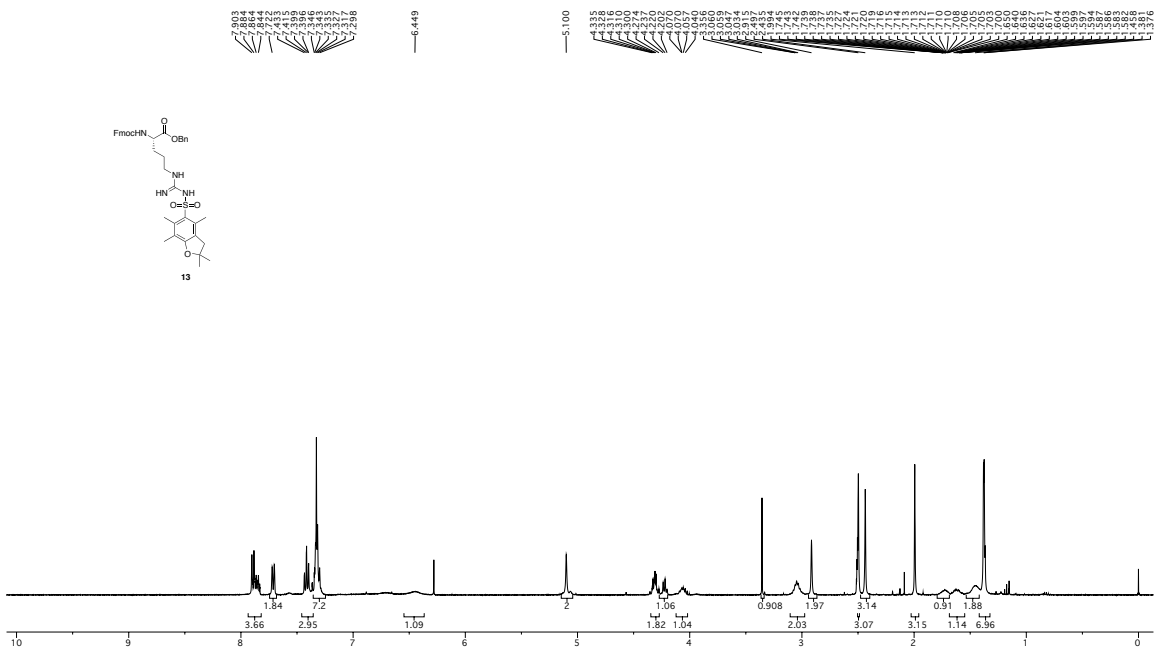
101 MHz ¹³C-NMR Compound 12a – D₂O



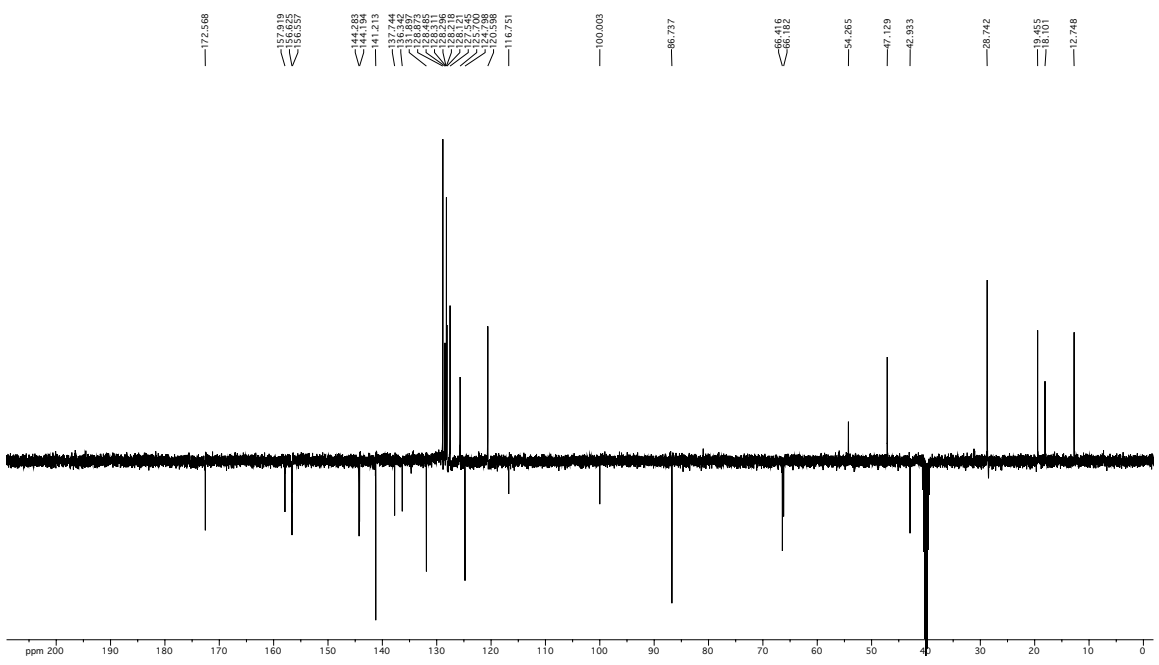
400 MHz ¹H-NMR Compound 12b – D₂O



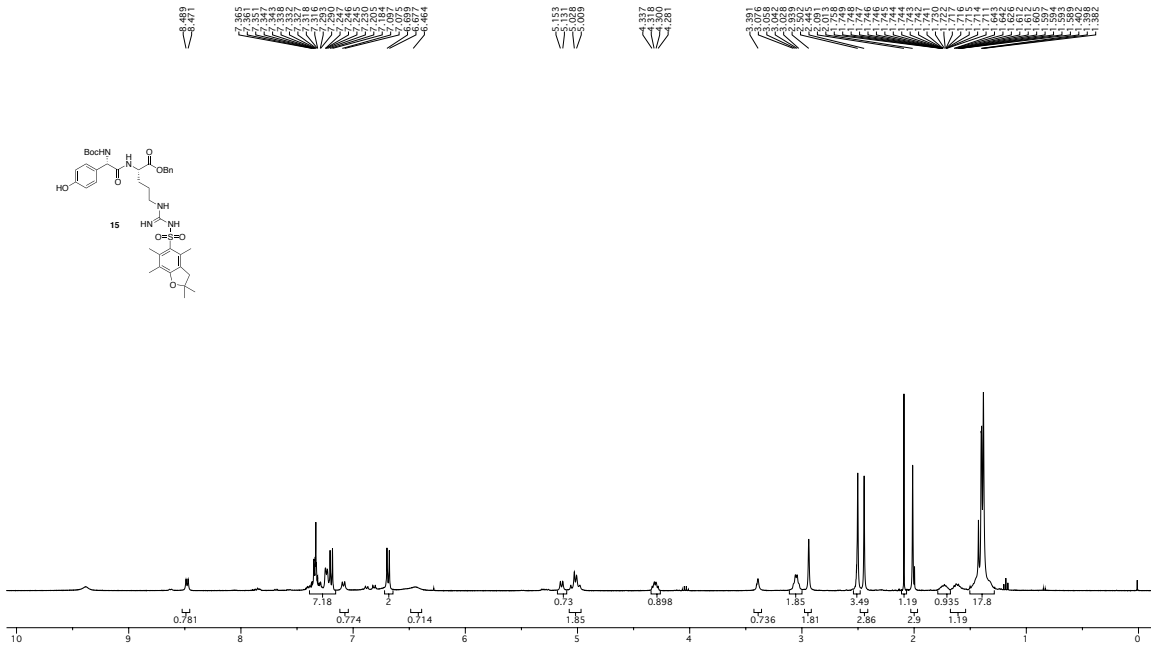
101 MHz ¹³C-NMR Compound 12b – D₂O



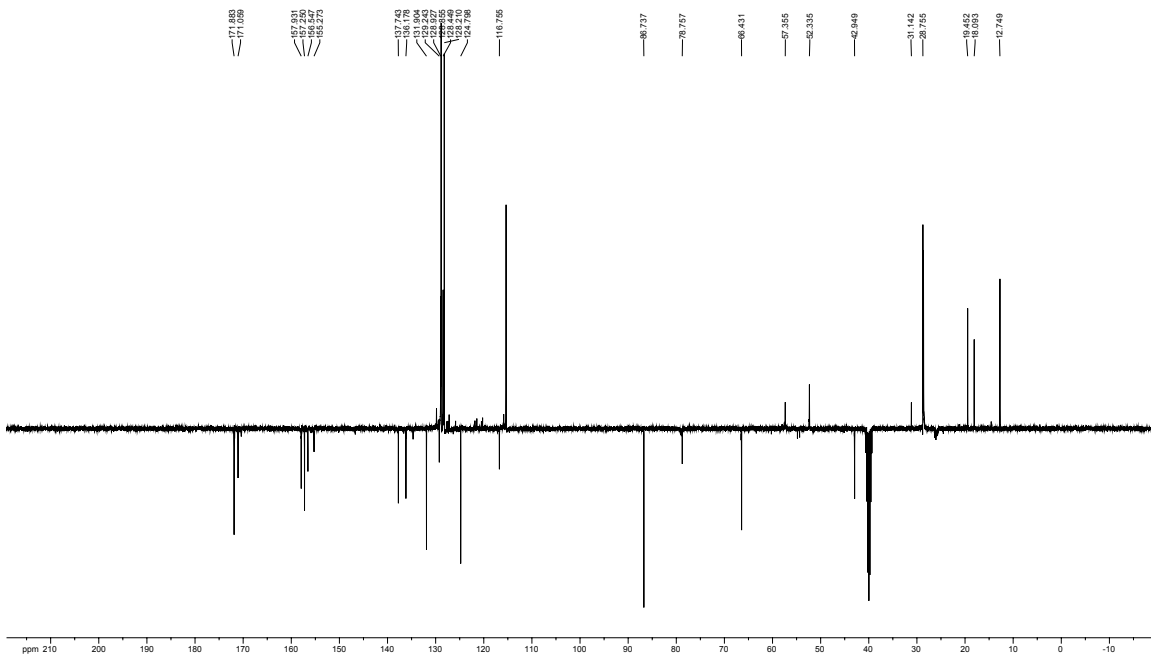
400 MHz $^1\text{H-NMR}$ Compound 13 – $\text{d}_6\text{-DMSO}$ with TMS



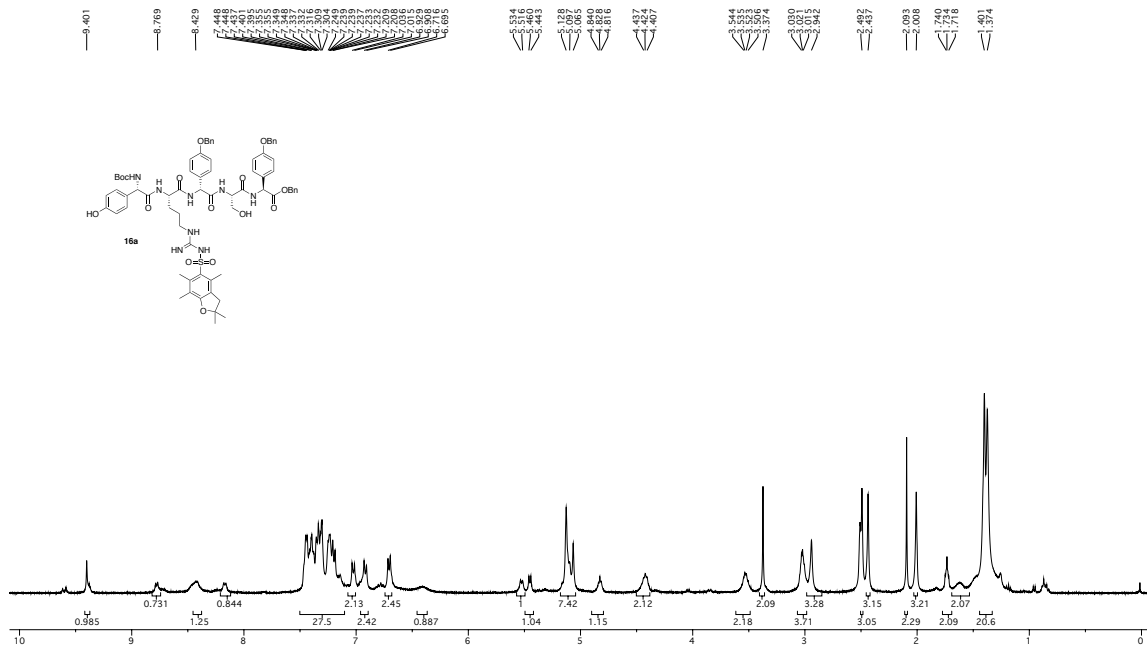
101 MHz $^{13}\text{C-NMR}$ Compound 13 – $\text{d}_6\text{-DMSO}$ with TMS



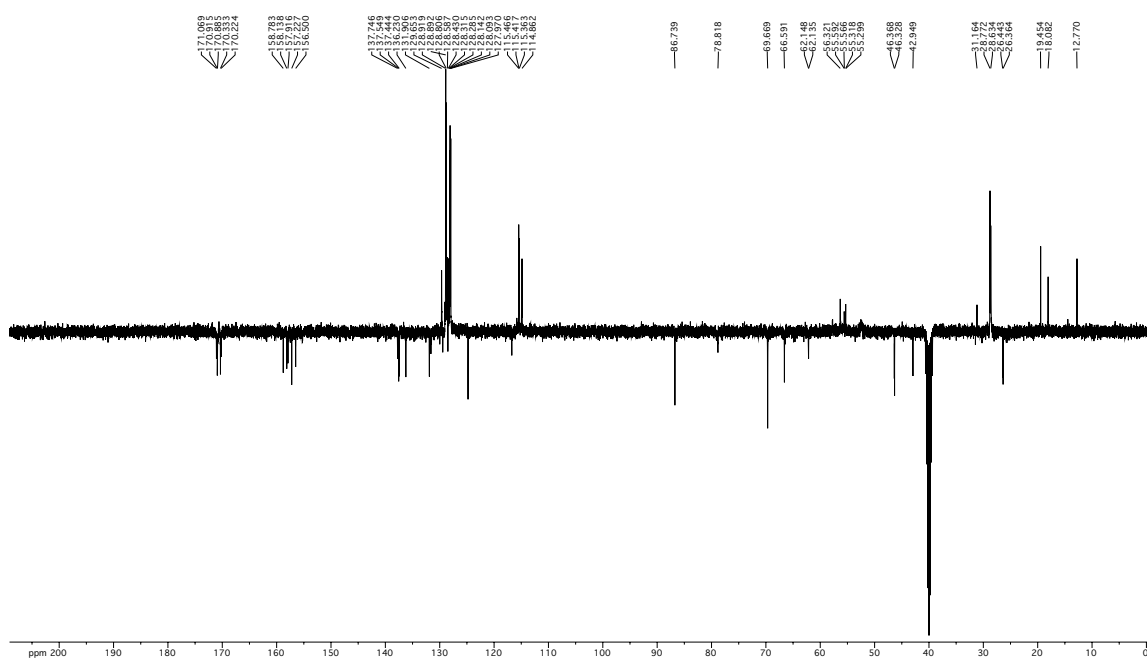
400 MHz ¹H-NMR Compound 15 – d₆-DMSO with TMS



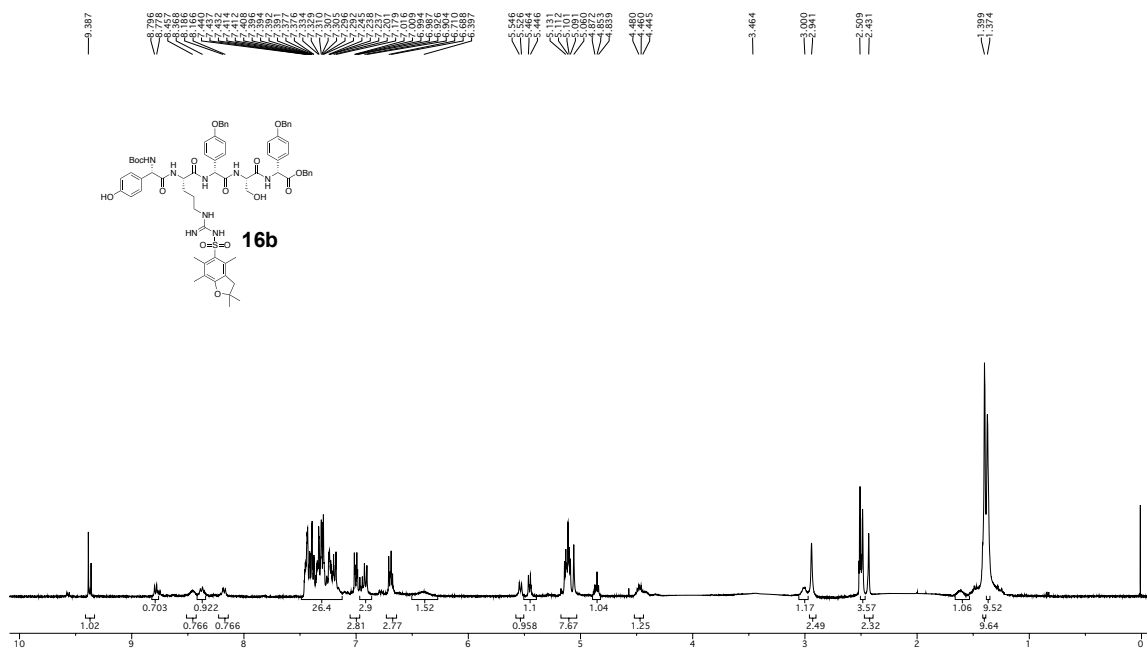
101 MHz ¹³C-NMR Compound 15 – d₆-DMSO with TMS



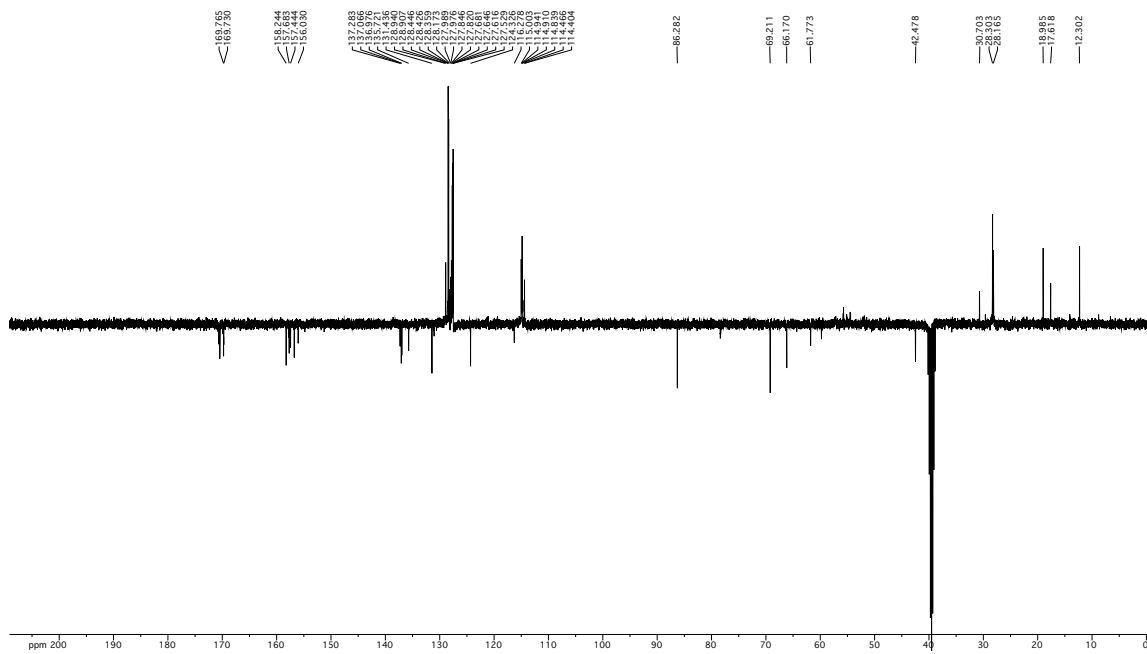
400 MHz ¹H-NMR Compound 16a – d₆-DMSO with TMS



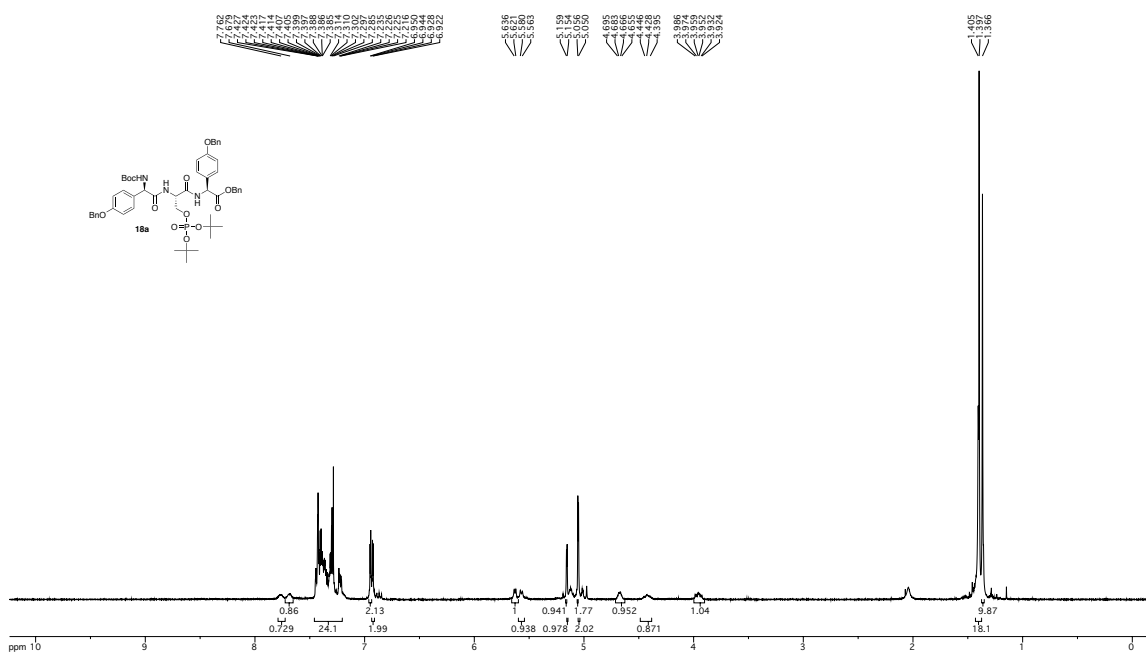
101 MHz ¹³C-NMR Compound 16a – d₆-DMSO with TMS



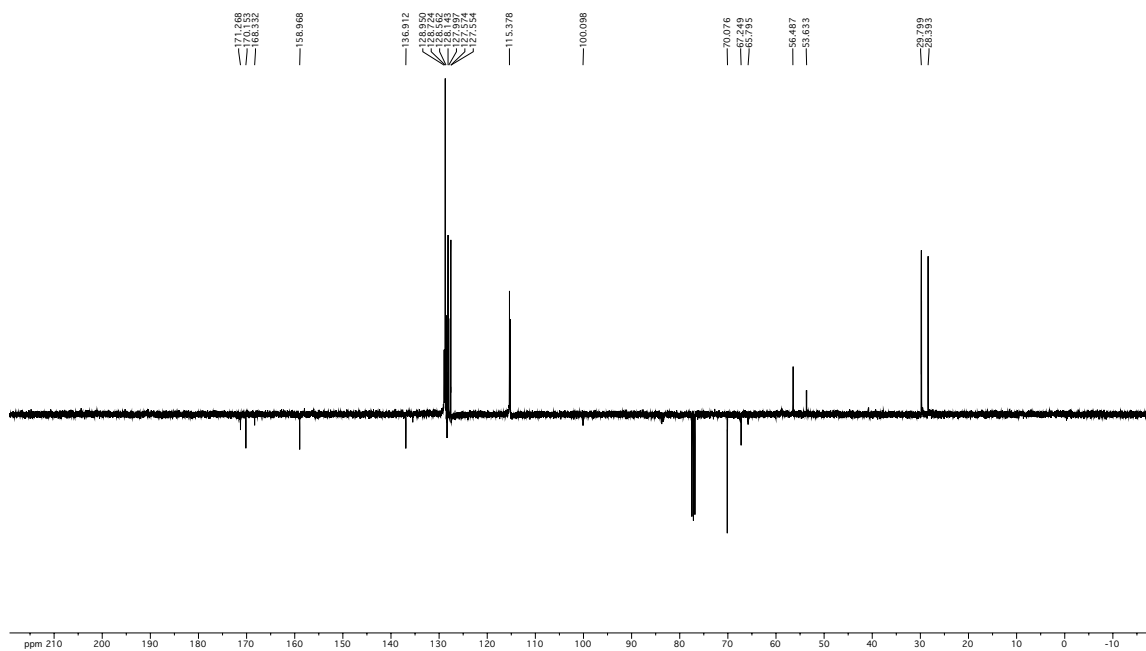
400 MHz ¹H-NMR Compound 16b – d₆-DMSO with TMS



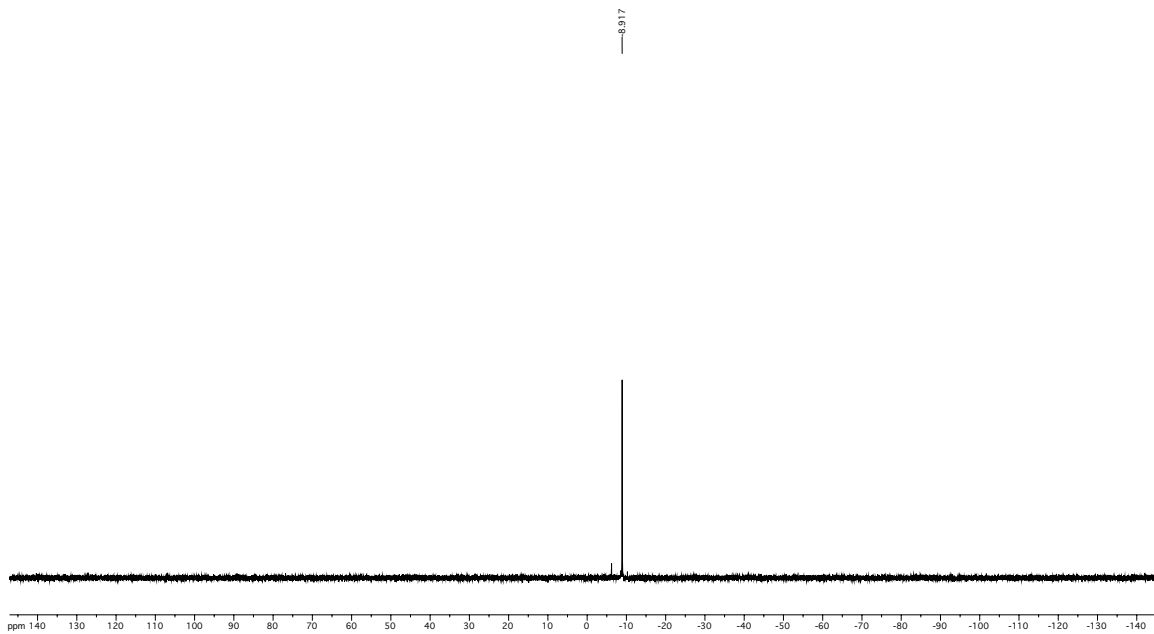
101 MHz ¹³C-NMR Compound 16b – d₆-DMSO with TMS



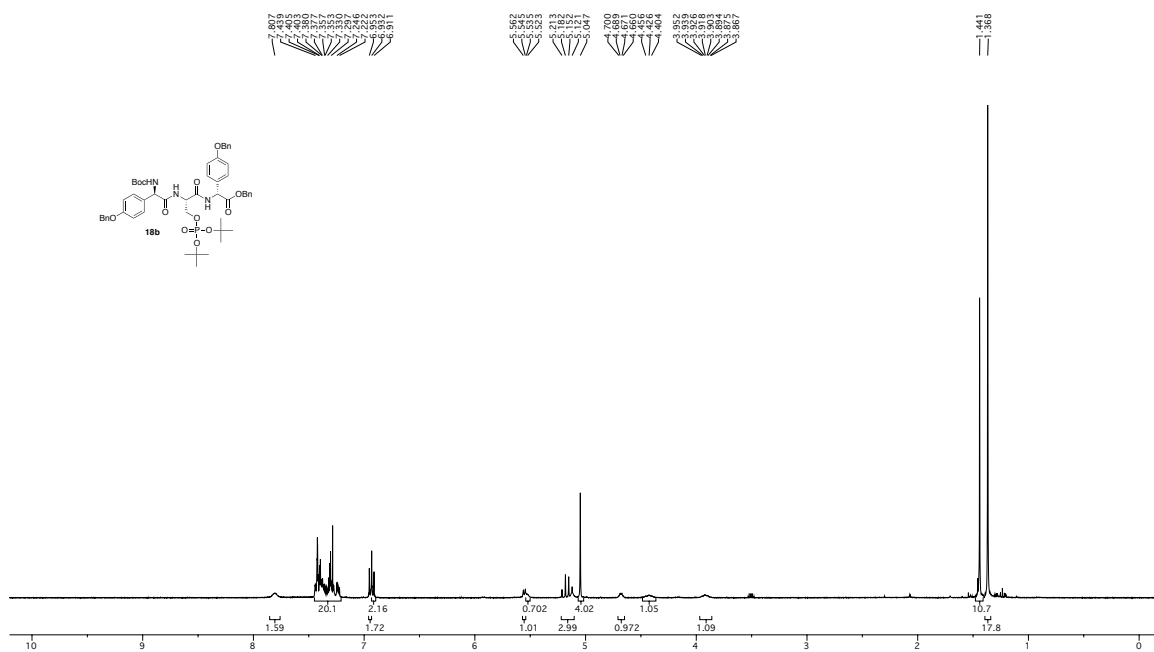
400 MHz $^1\text{H-NMR}$ Compound 18a – CDCl_3



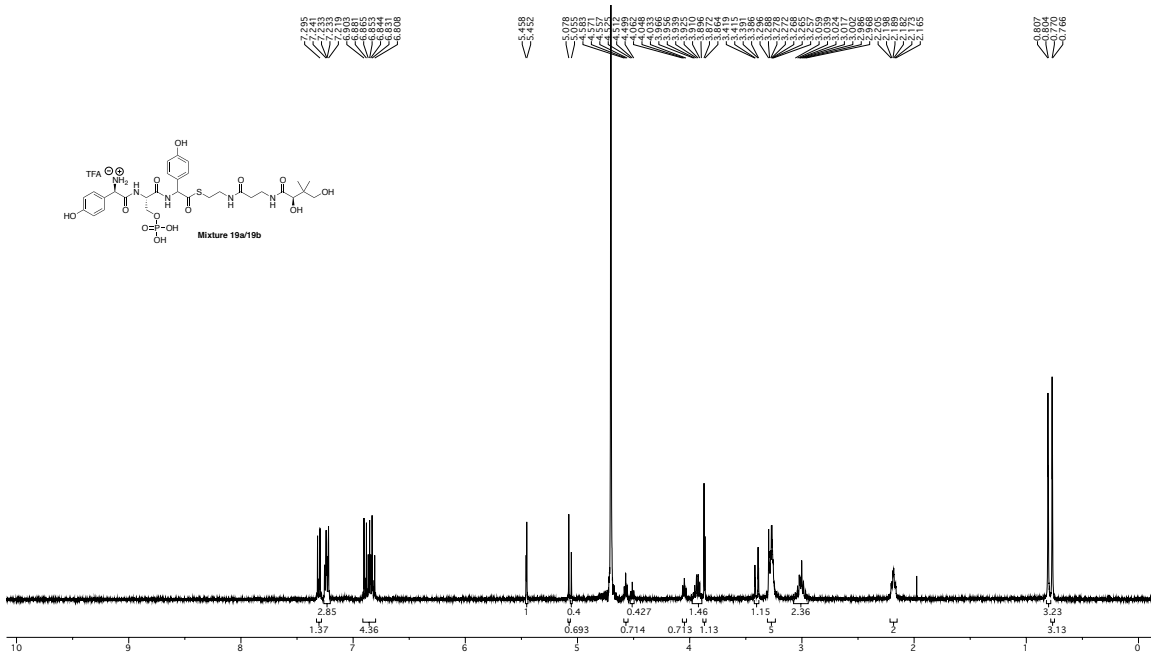
101 MHz $^{13}\text{C-NMR}$ Compound 18a – CDCl_3



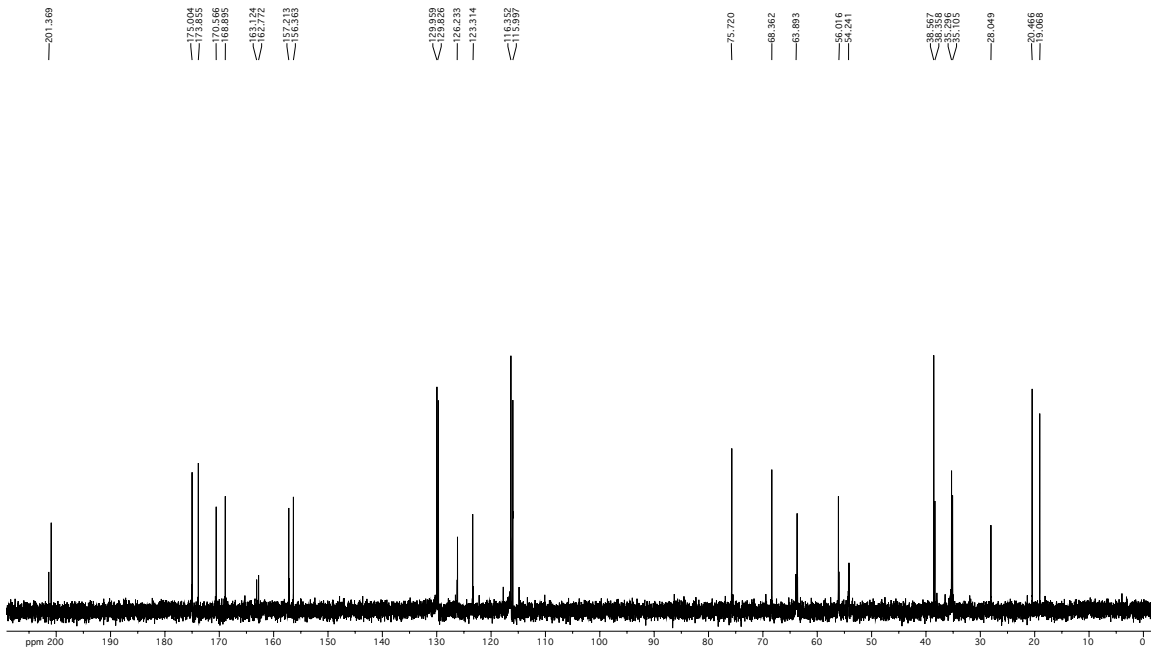
162 MHz ^{31}P -NMR Compound 18a – CDCl_3



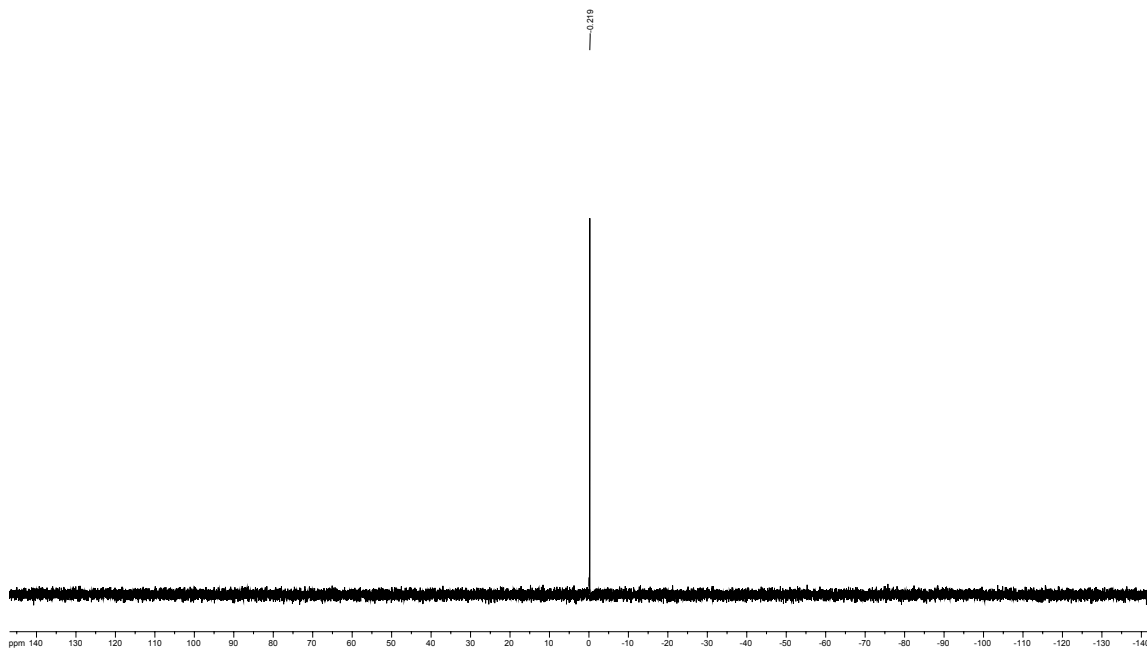
400 MHz ^1H -NMR Compound 18b – CDCl_3



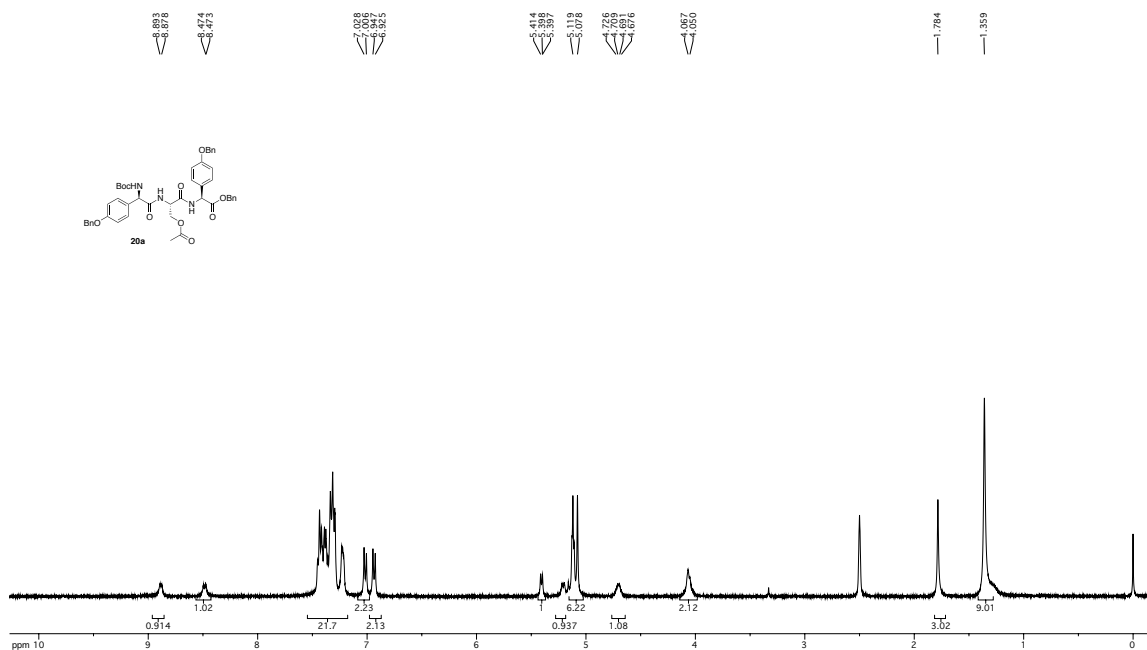
400 MHz ^1H -NMR Compound 19a/b Mixture- D_2O



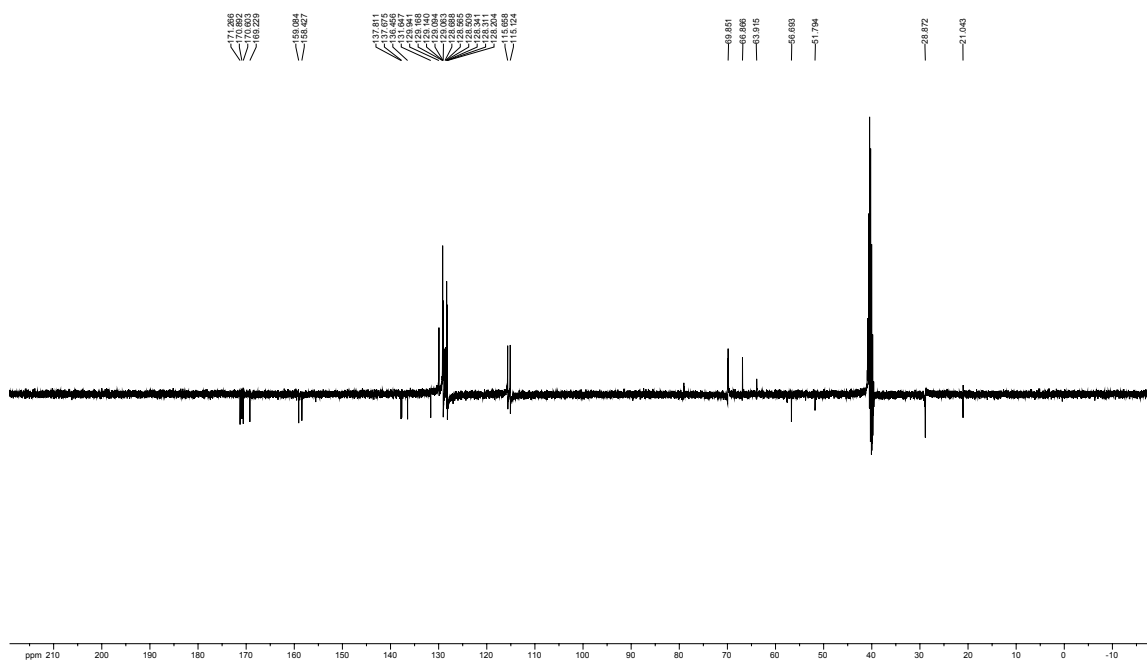
101 MHz ^{13}C -NMR Compound 19a/b Mixture - D_2O



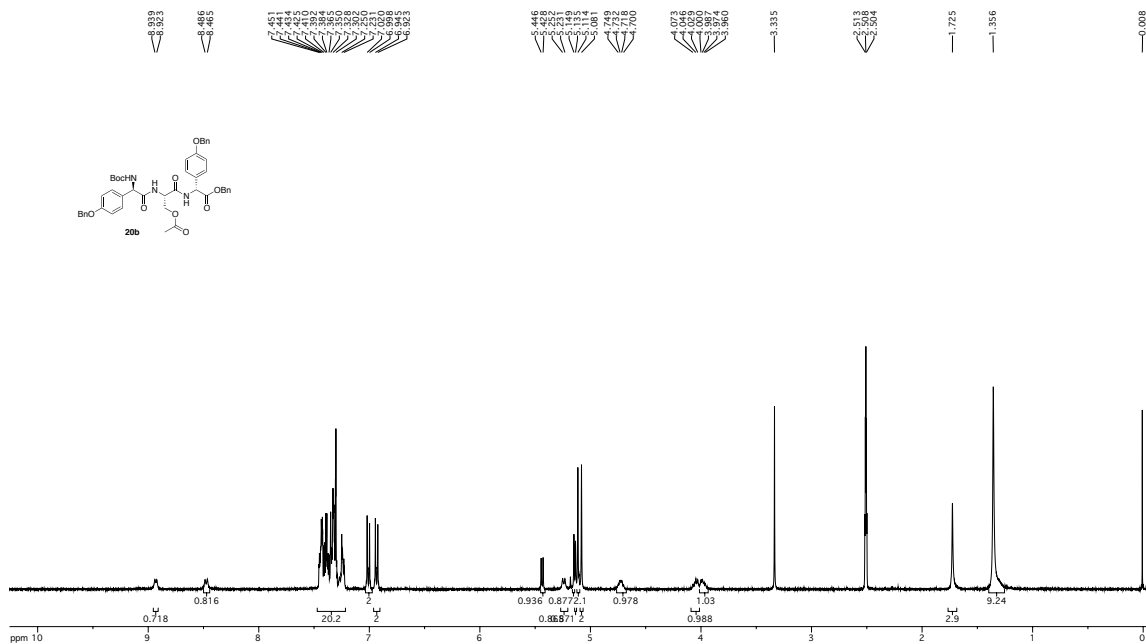
162 MHz ^{31}P -NMR Compound 19a/b Mixture – D_2O



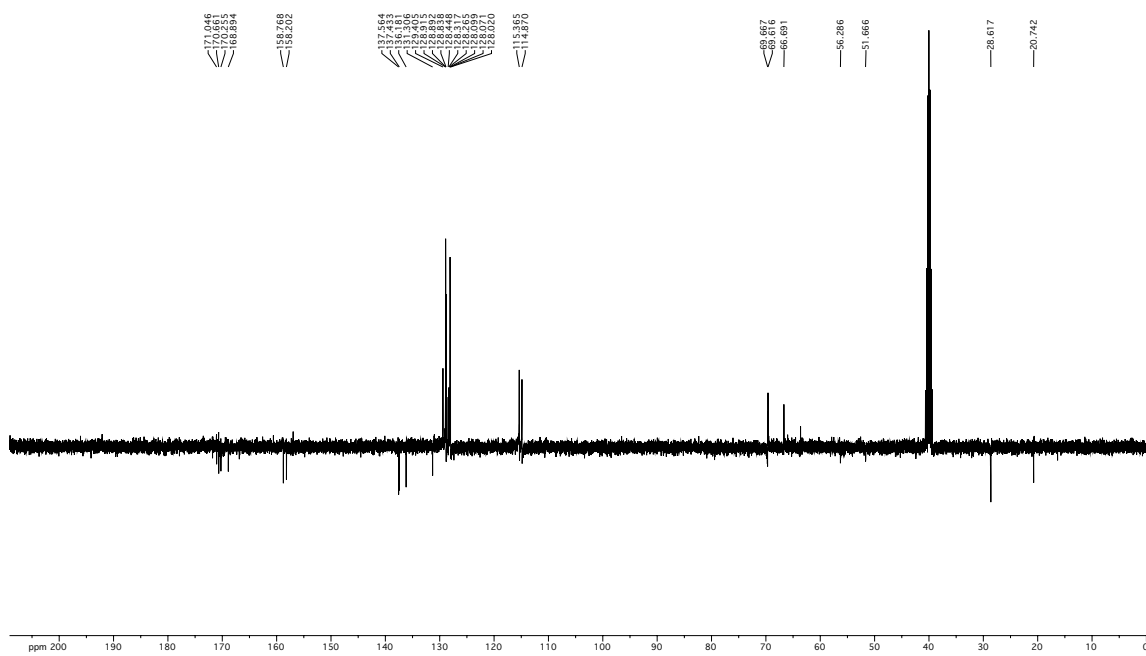
400 MHz ¹H-NMR Compound 20a – d₆DMSO with TMS

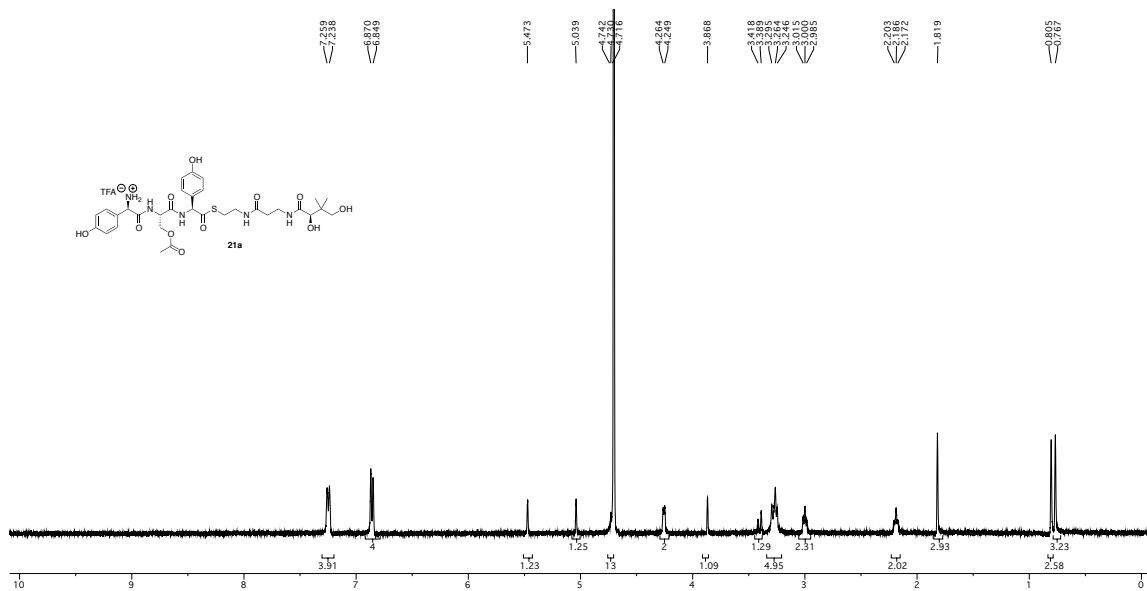


101 MHz ¹³C-NMR Compound 20a – d₆DMSO with TMS

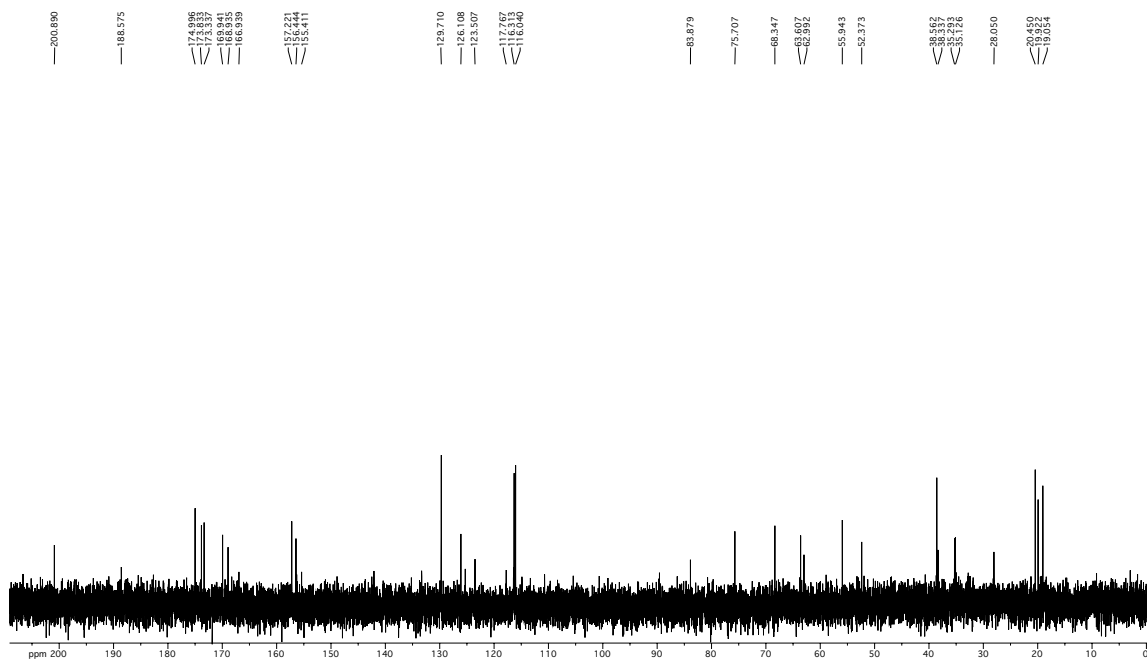


400 MHz ¹H-NMR Compound 20b – d₆-DMSO with TMS

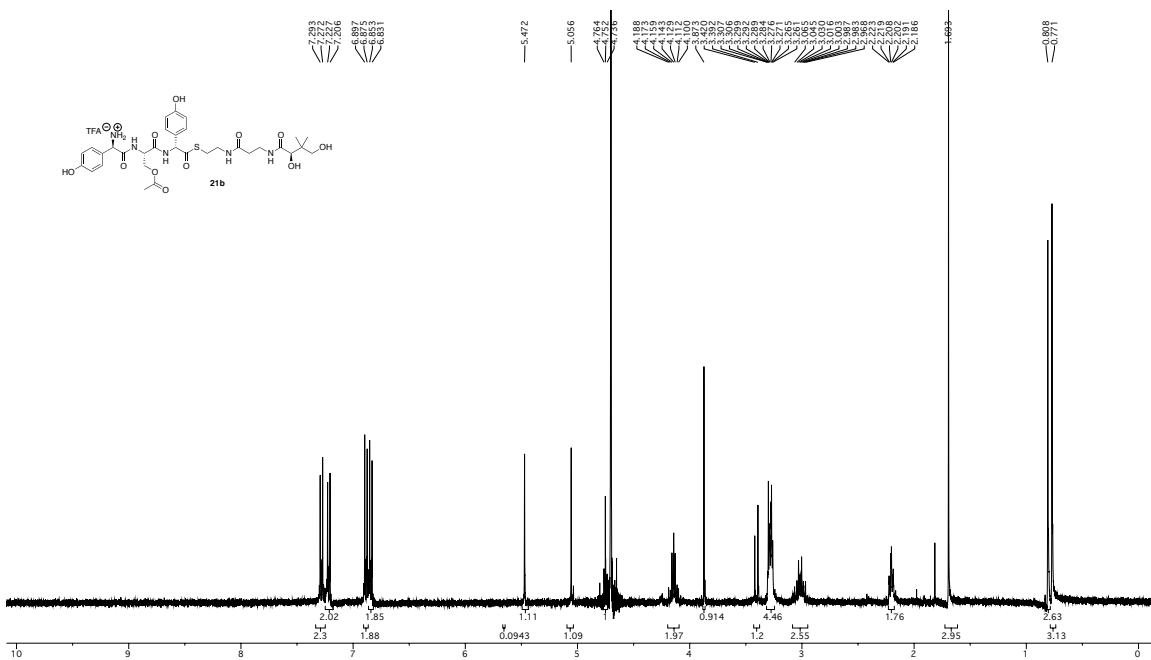




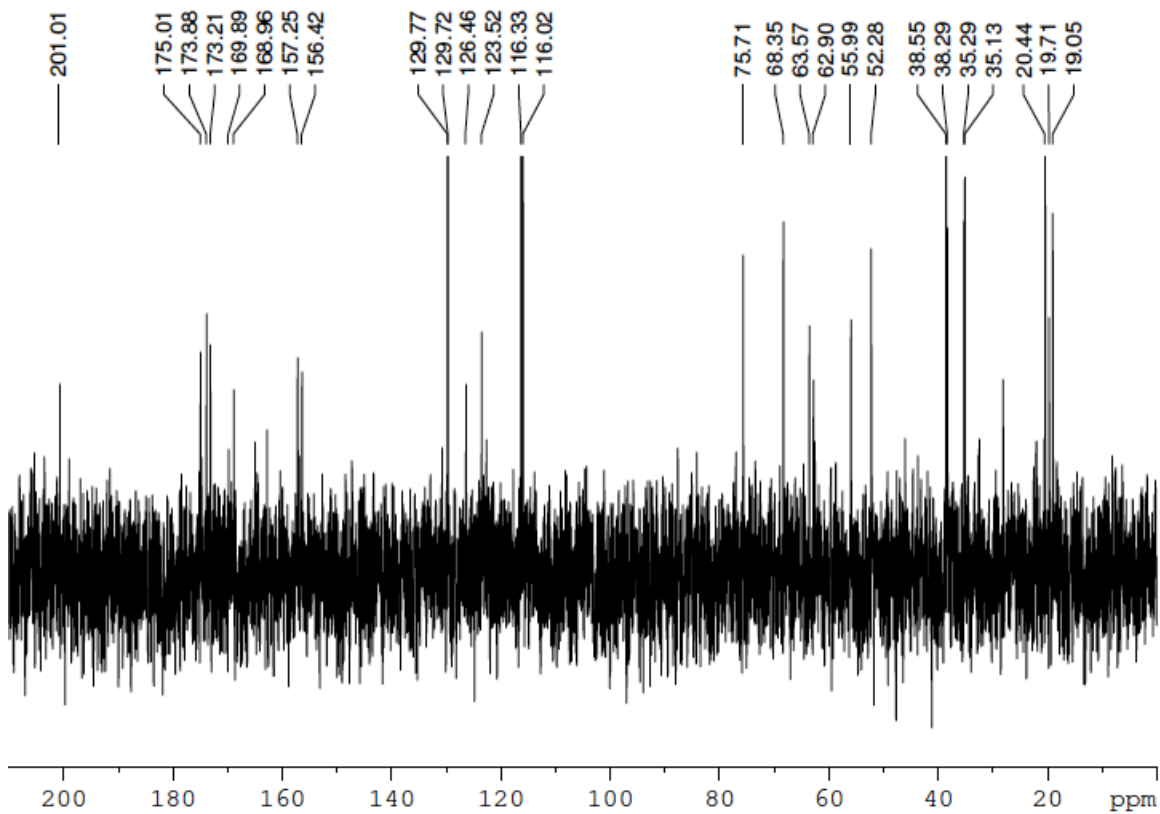
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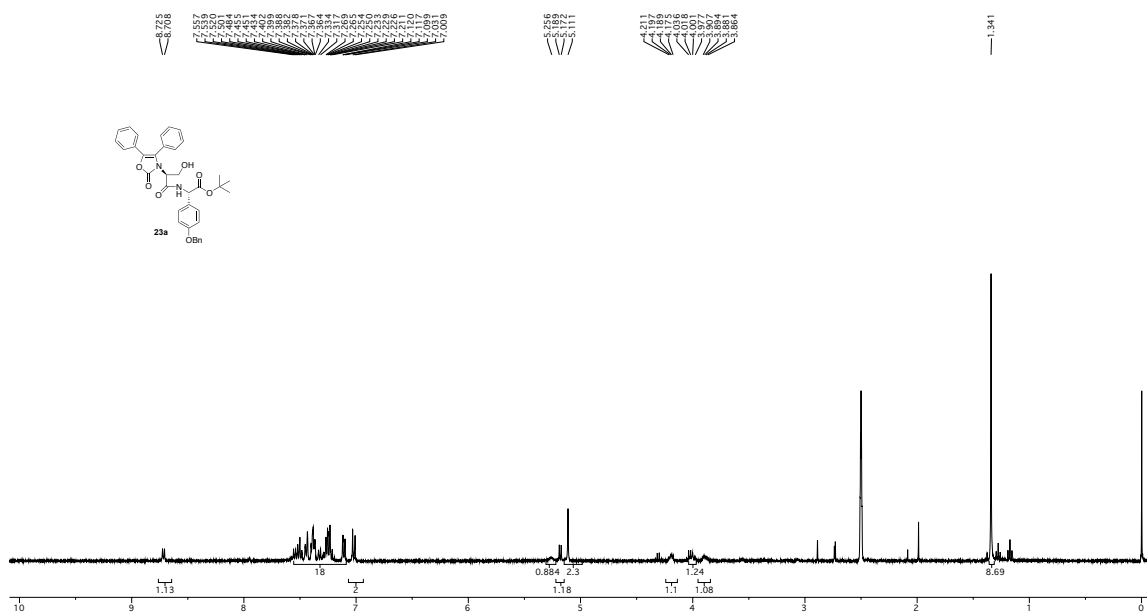
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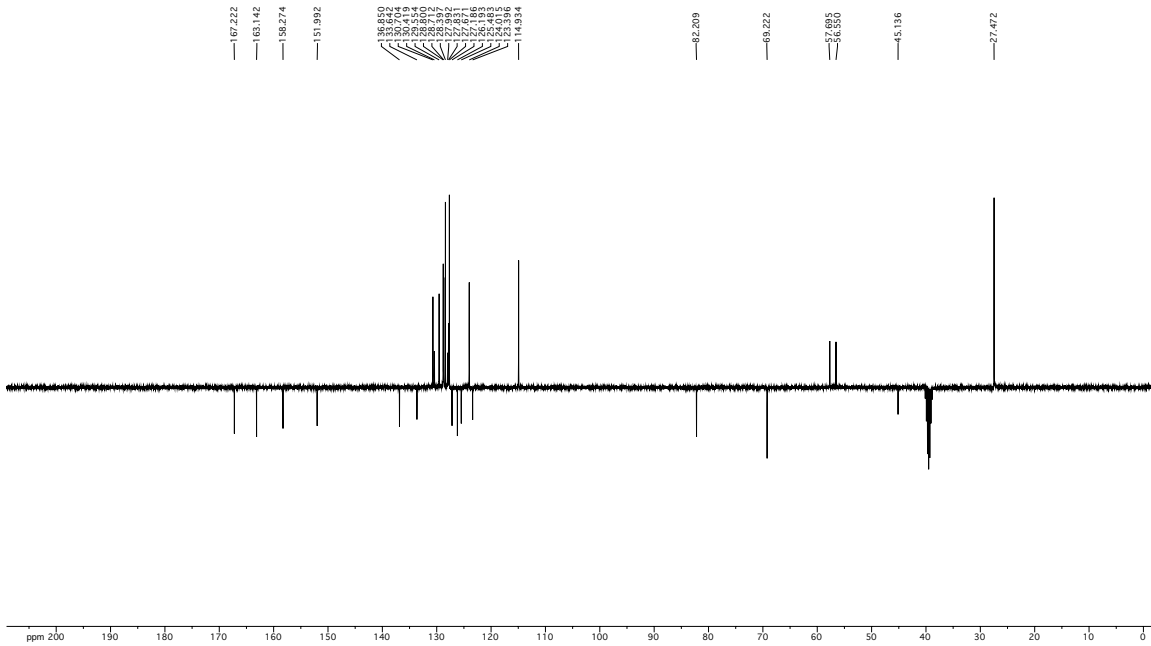
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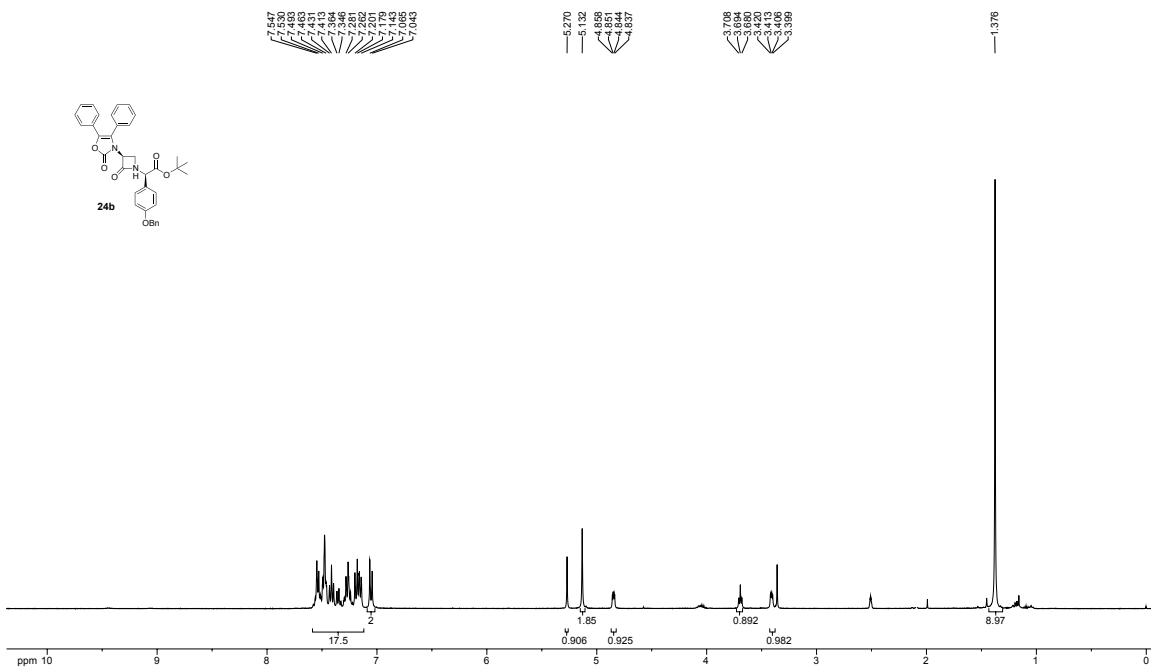
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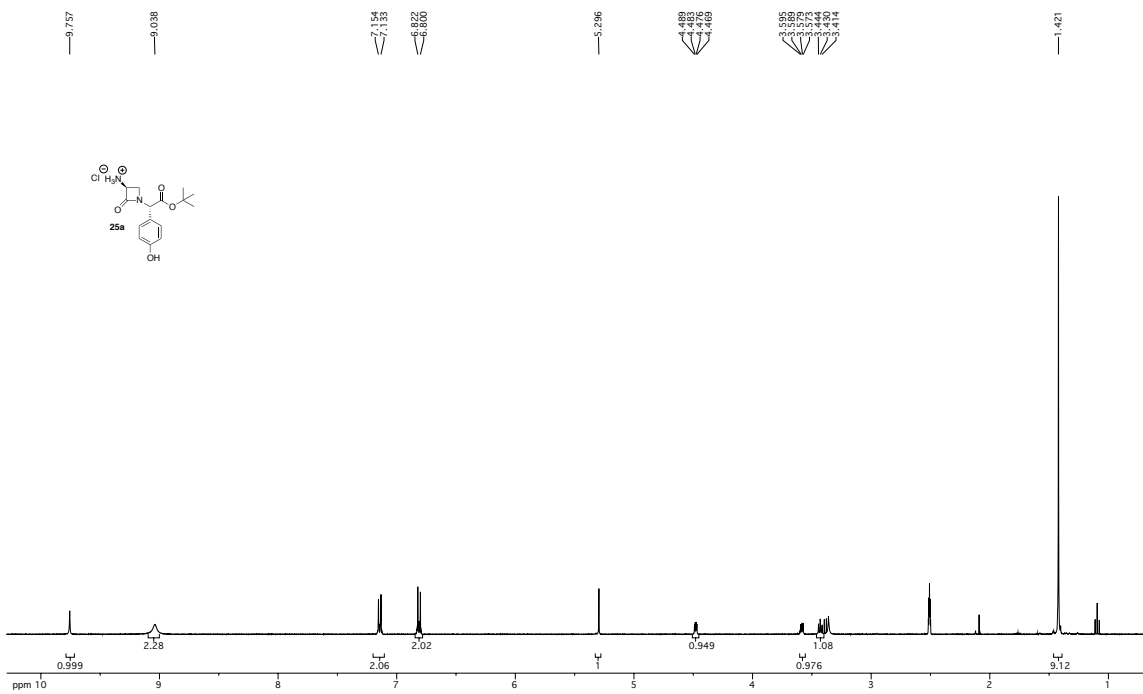
400 MHz ¹H-NMR Compound 23a – d₆-DMSO with TMS



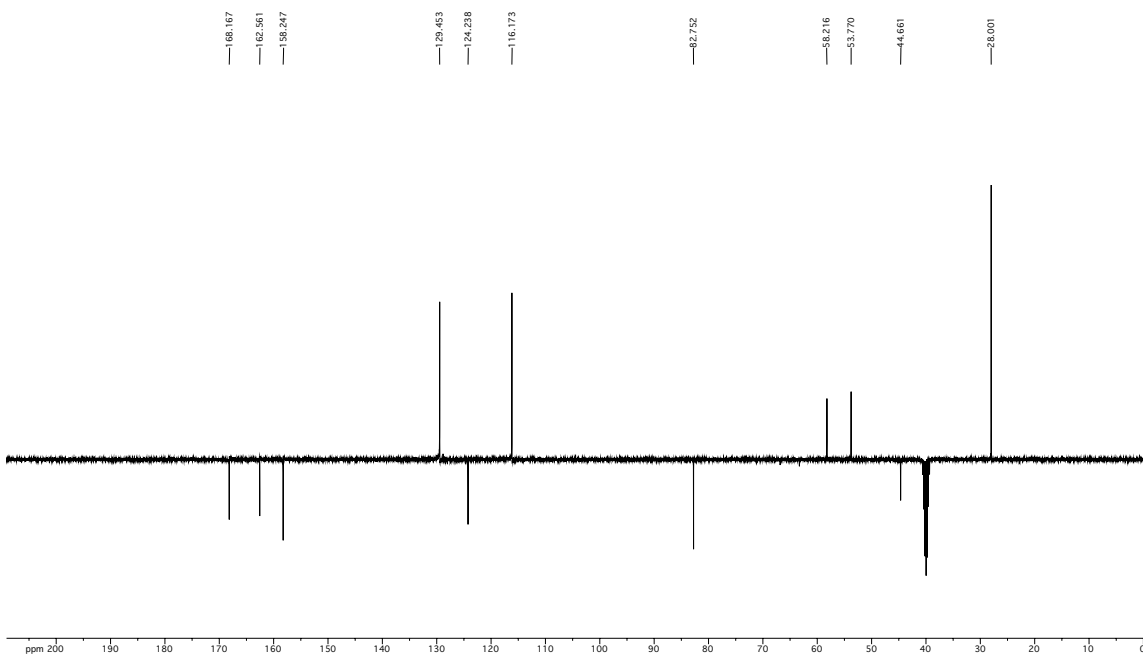
101 MHz ^{13}C -NMR Compound 24a – d_6 -DMSO with TMS



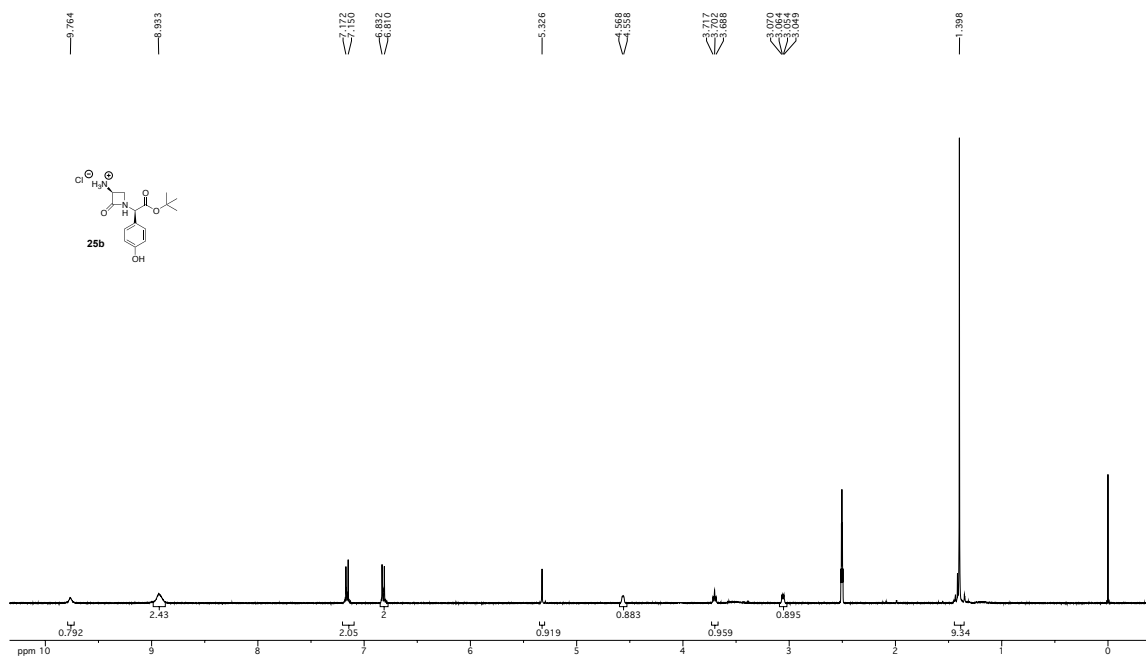
400 MHz ^1H -NMR Compound 24b – d_6 -DMSO with TMS



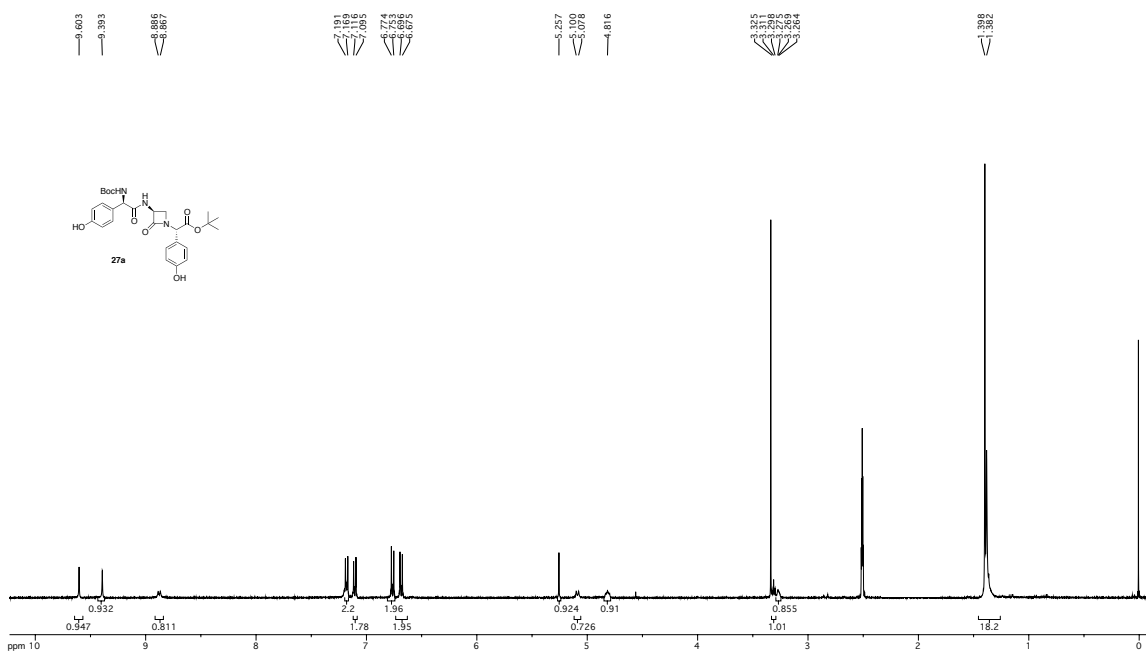
400 MHz ¹H-NMR Compound 25a – d₆-DMSO with TMS



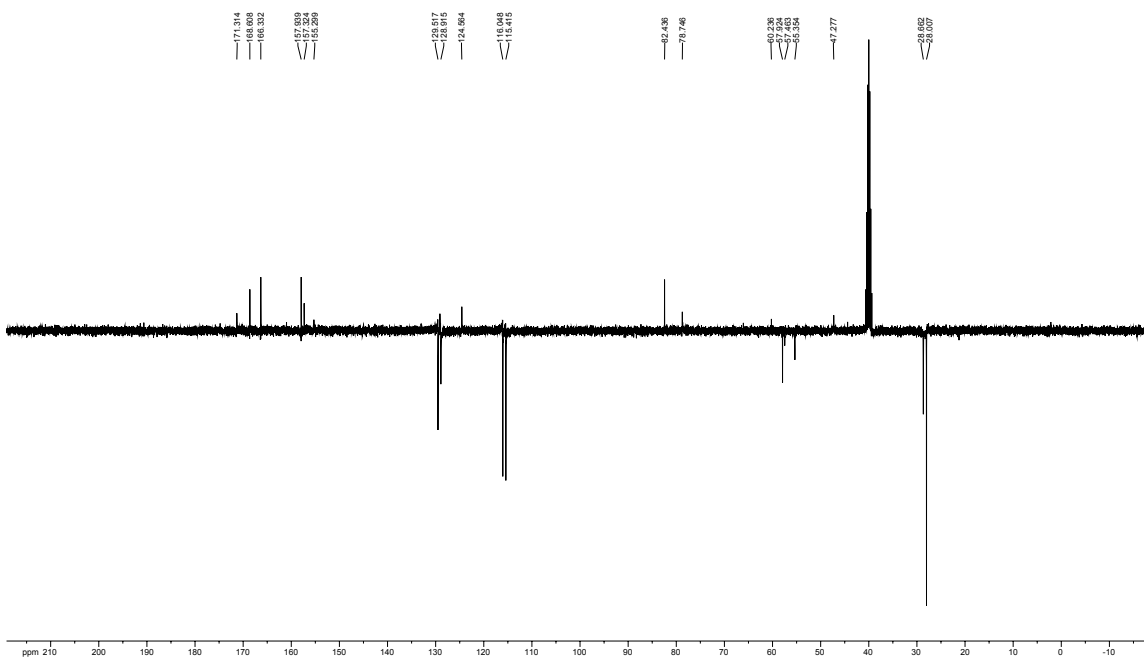
101 MHz ¹³C-NMR Compound 25a – d₆-DMSO with TMS



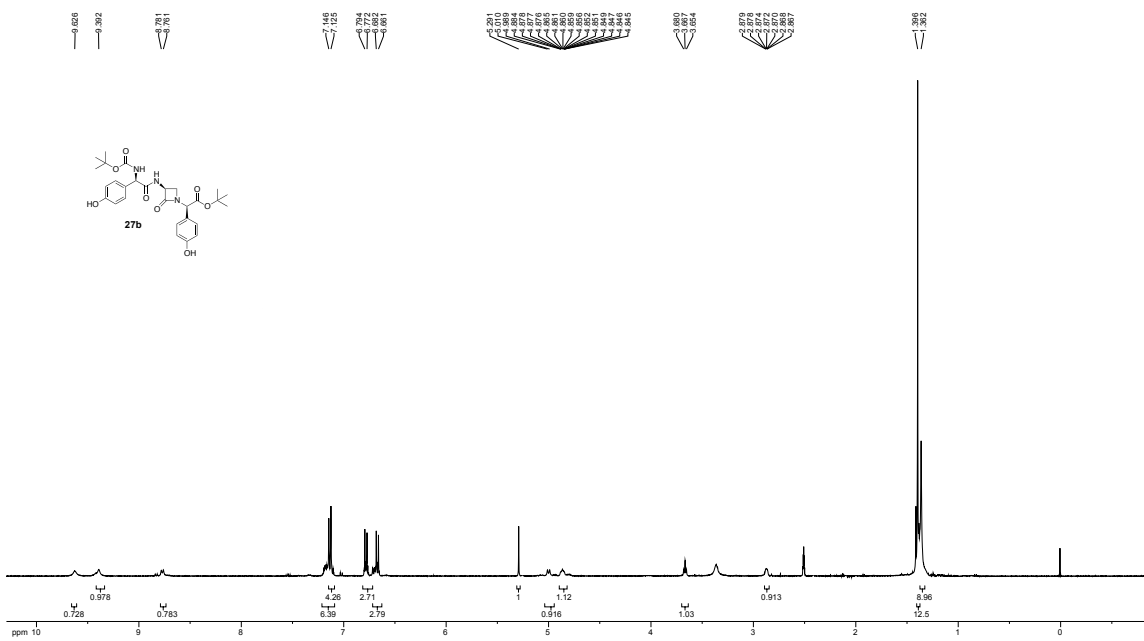
400 MHz ¹H-NMR Compound 25b – d₆-DMSO with TMS



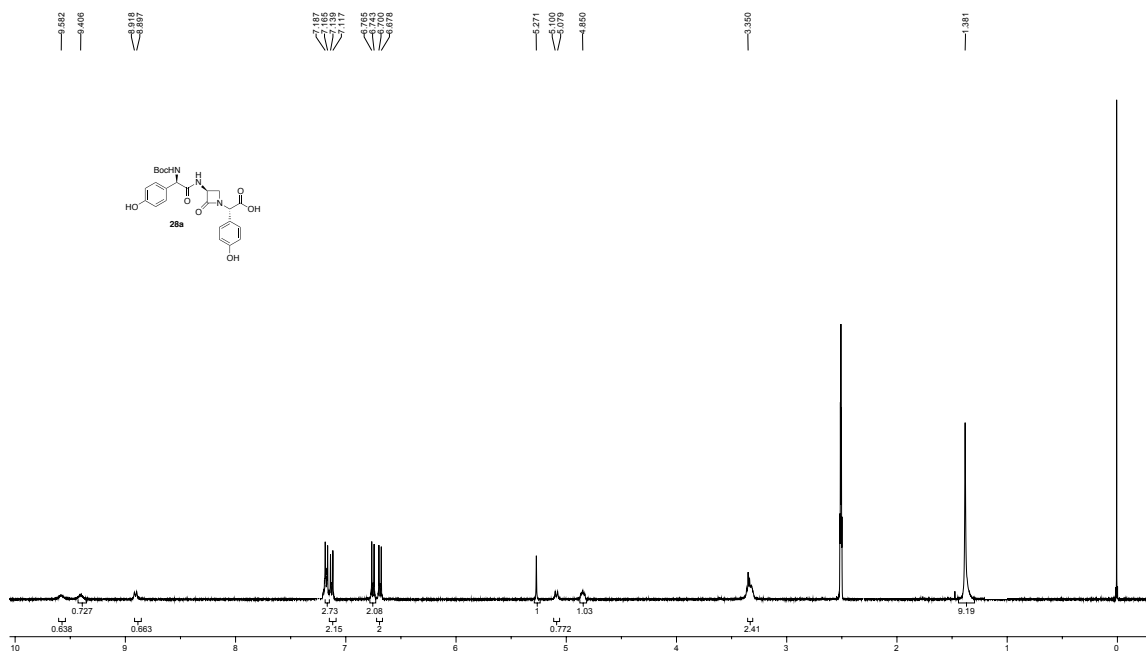
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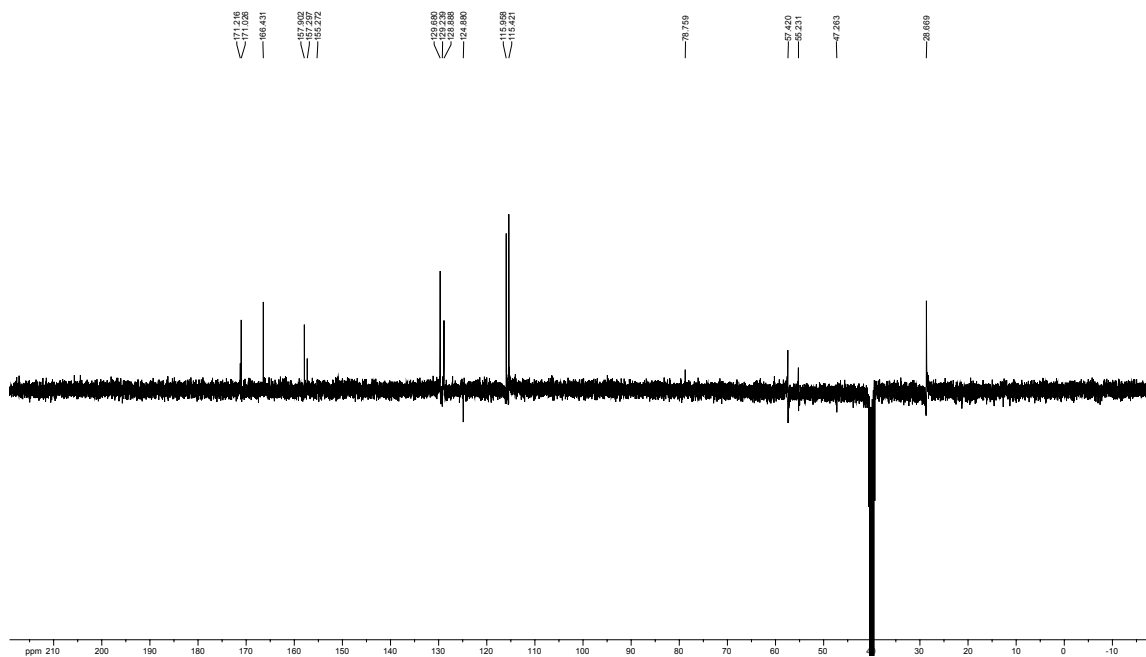
101 MHz ¹³C-NMR Compound 27a – d₆-DMSO with TMS



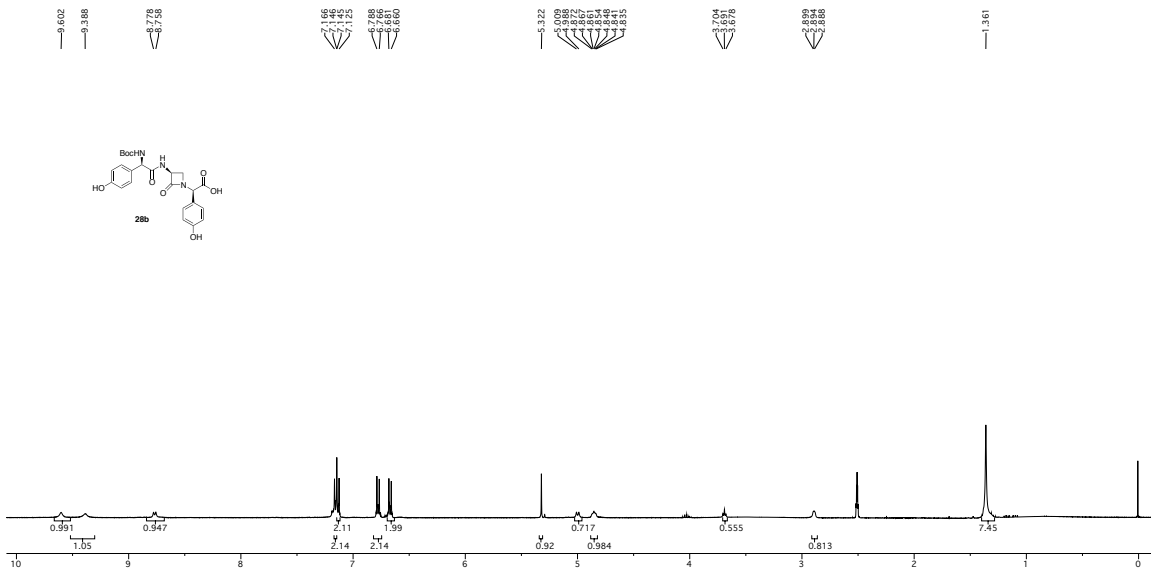
400 MHz ¹H-NMR Compound 27b – d₆-DMSO with TMS



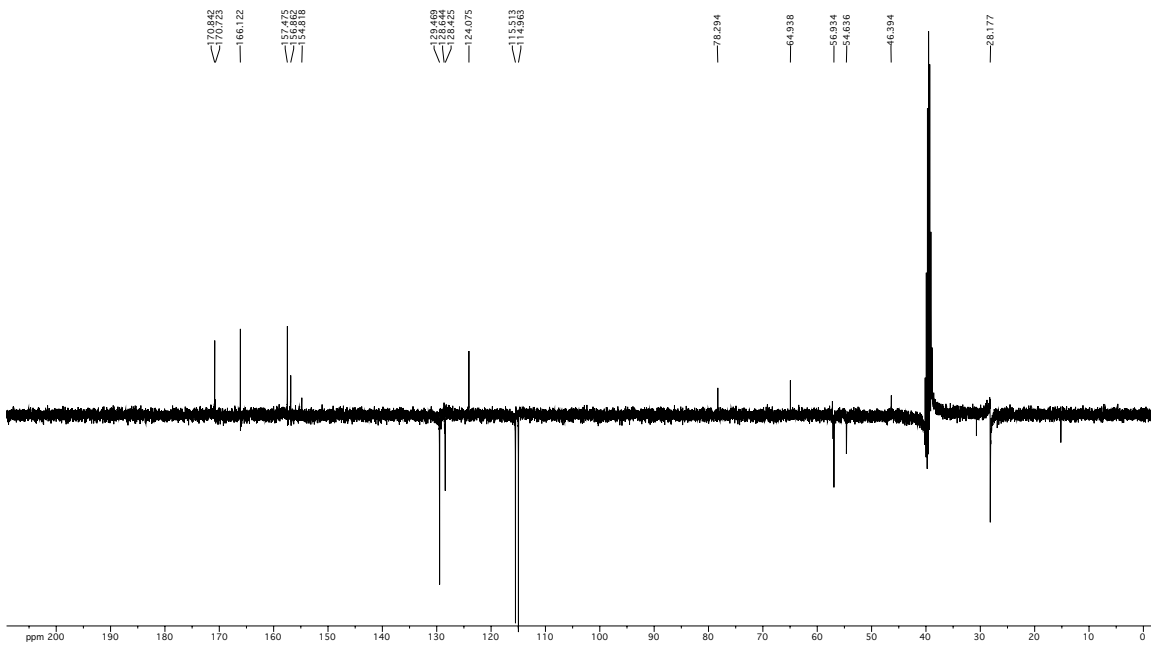
400 MHz ¹H-NMR Compound 28a – d₆-DMSO with TMS



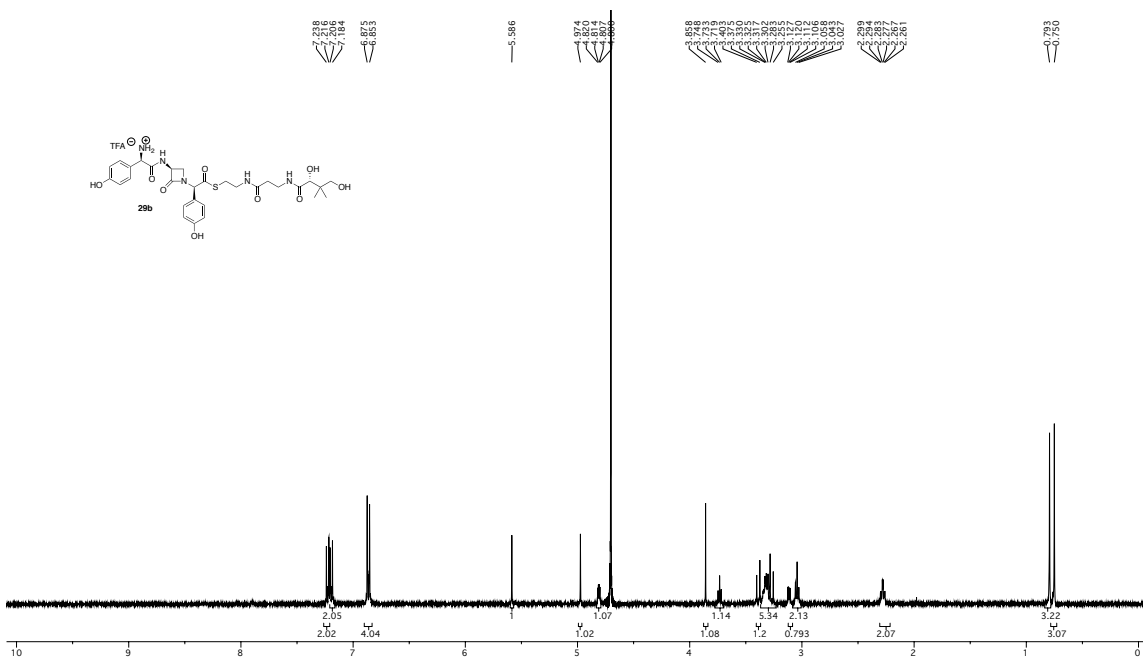
101 MHz ¹³C-NMR Compound 28a – d₆-DMSO with TMS



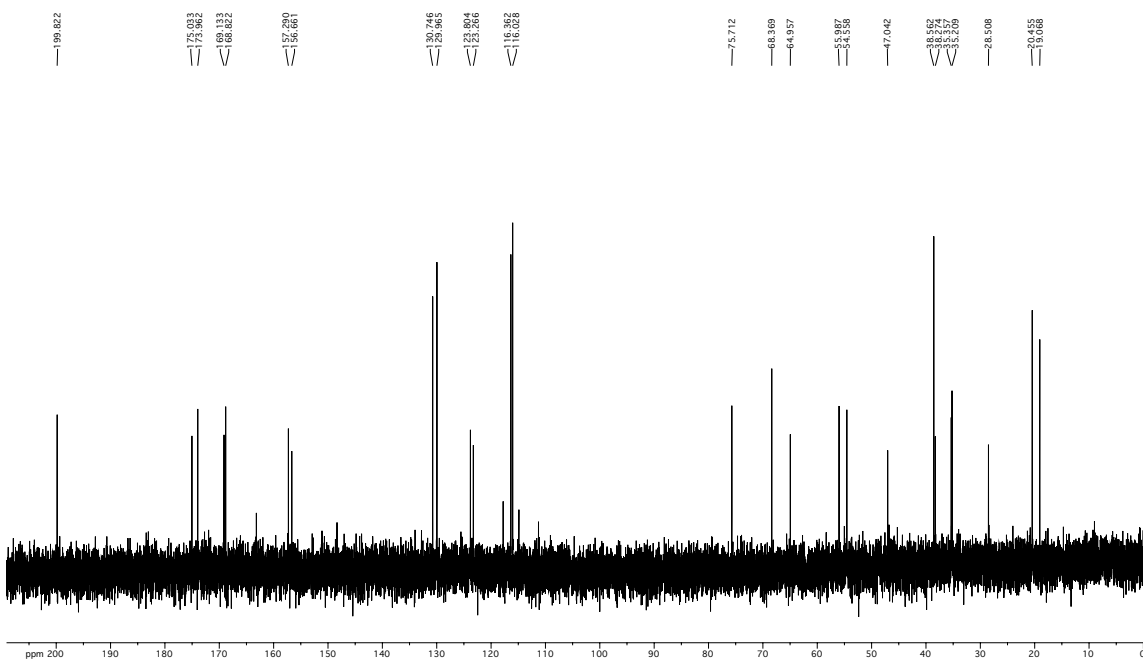
400 MHz ¹H-NMR Compound 28b – d₆-DMSO with TMS



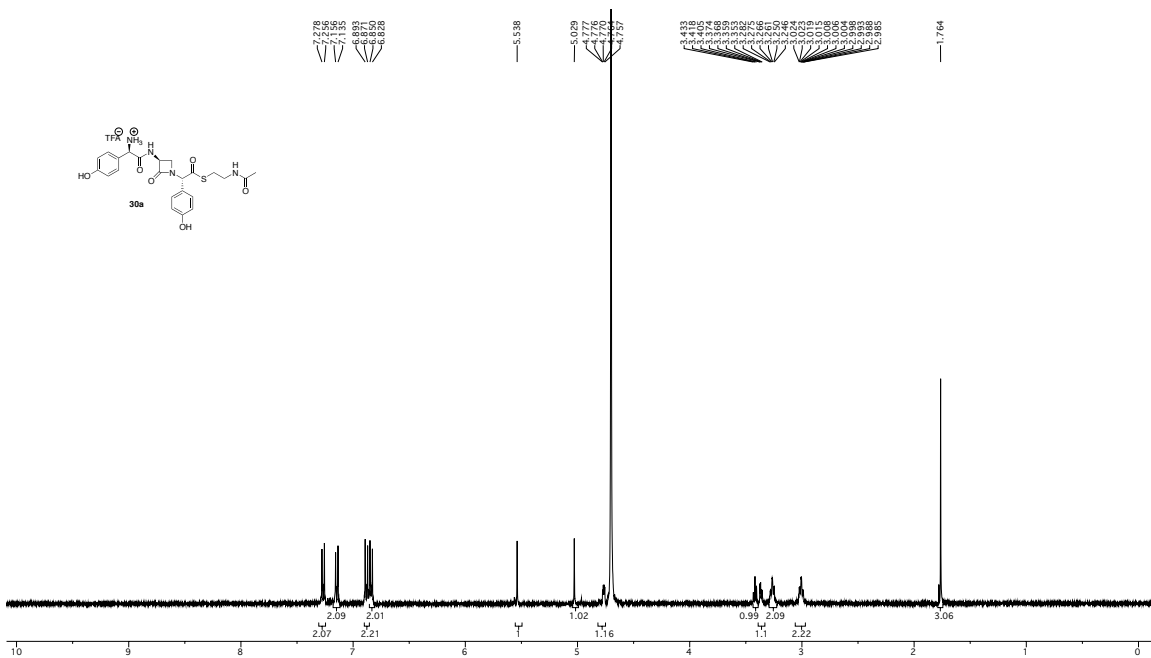
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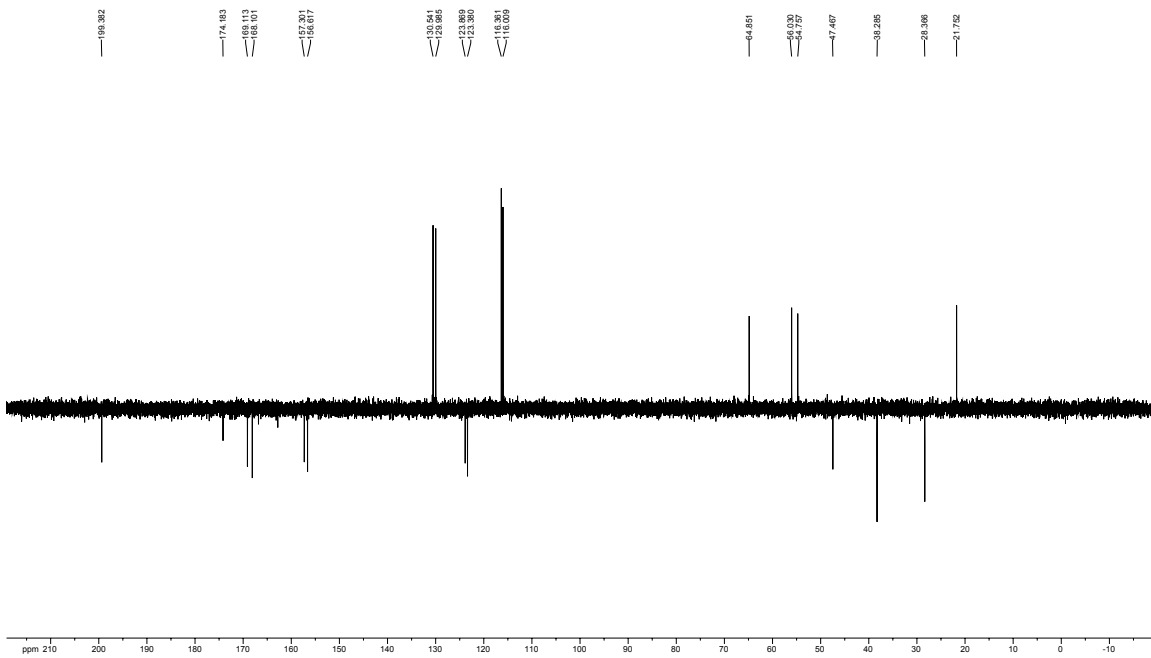
400 MHz ¹H-NMR Compound 29b – D₂O



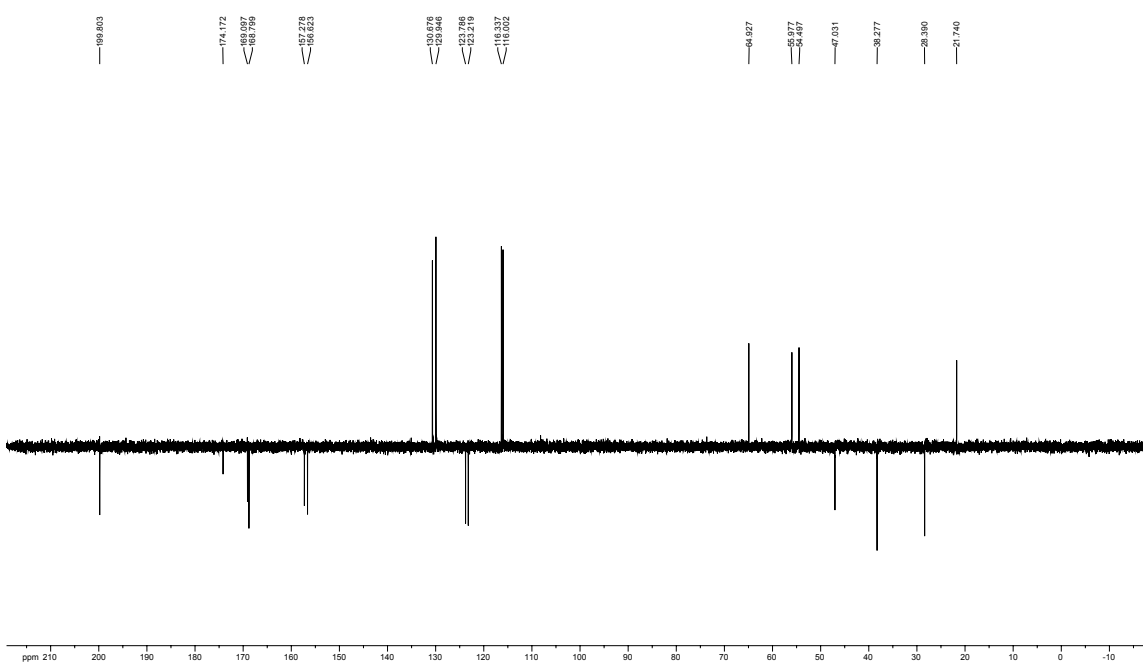
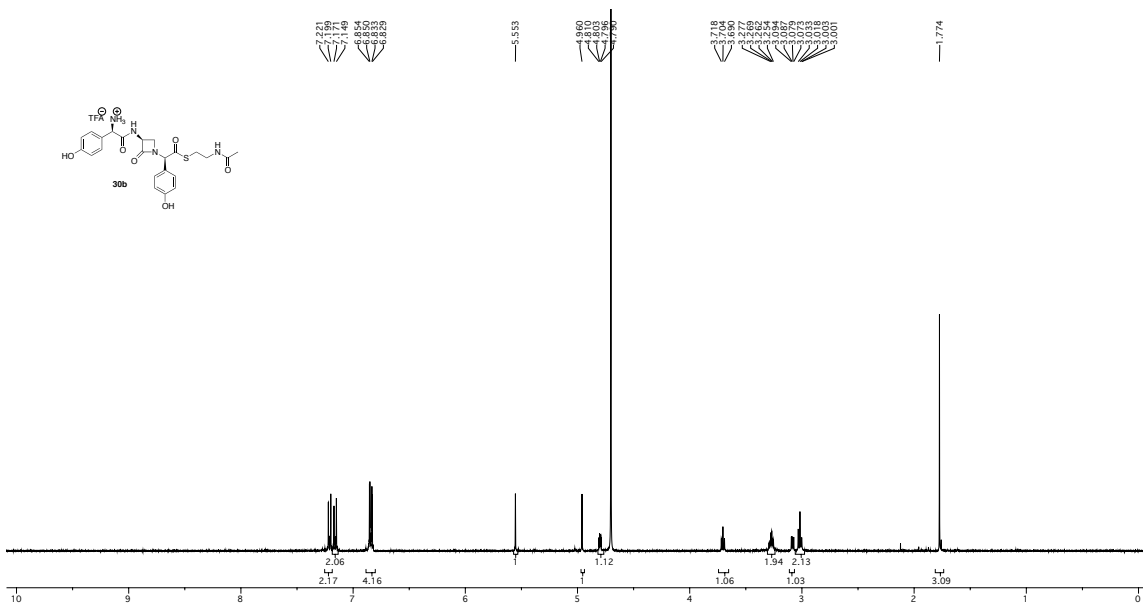
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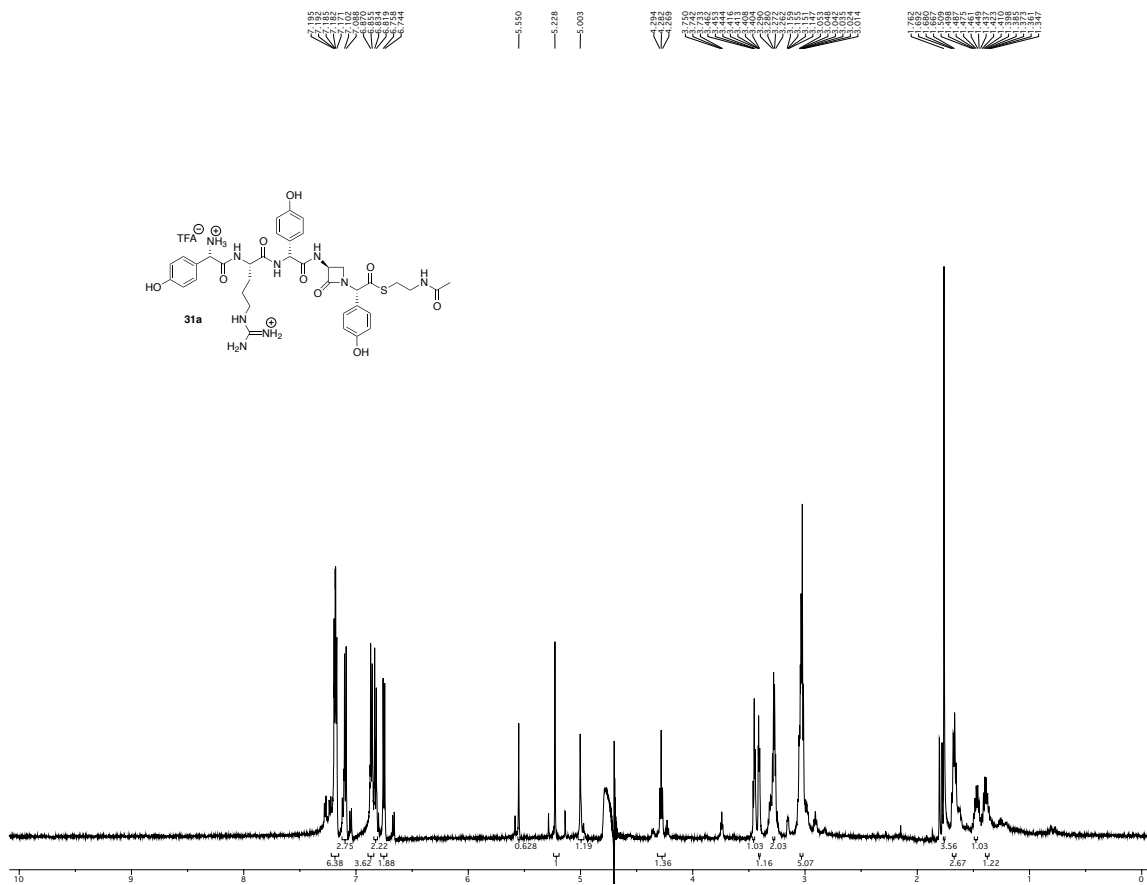


400 MHz ¹H-NMR Compound 30a – D₂O

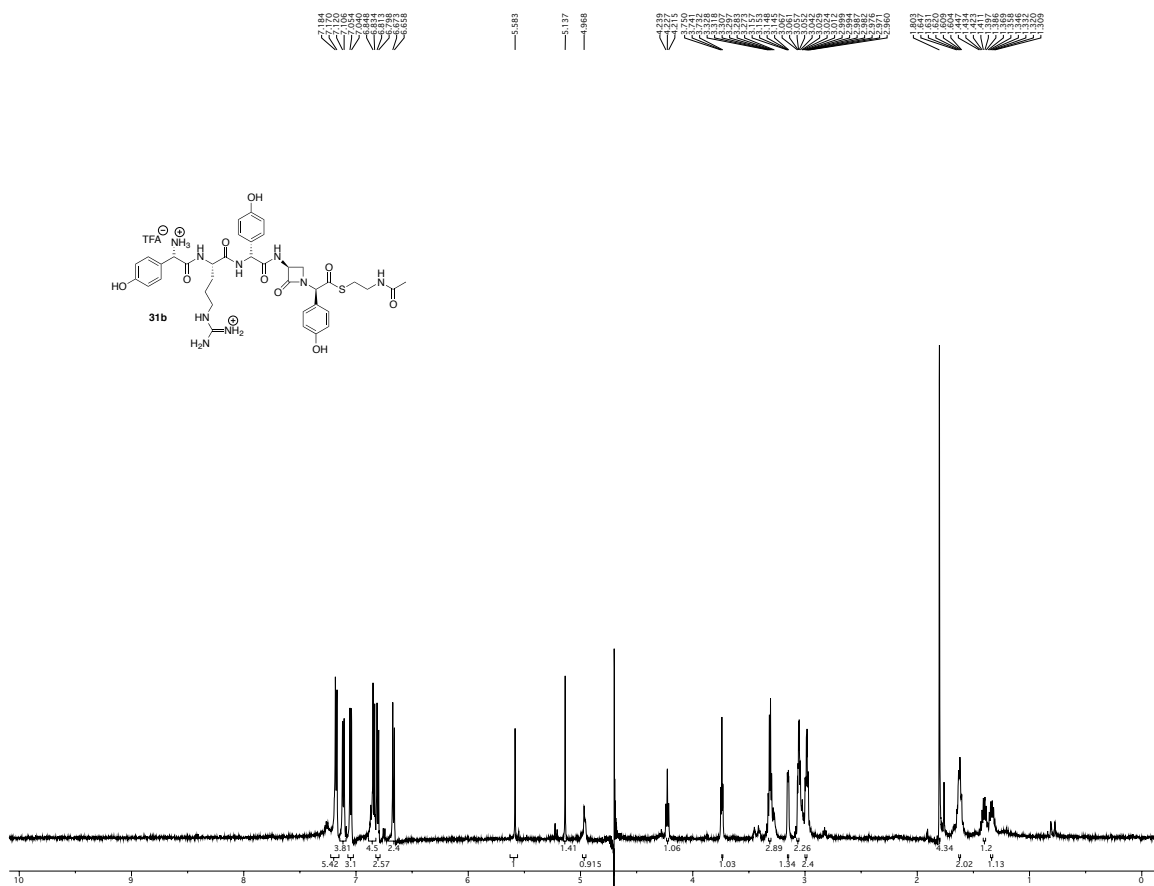


101 MHz ¹³C-NMR Compound 30a – D₂O





600 MHz ¹H-NMR Compound 31a – D₂O

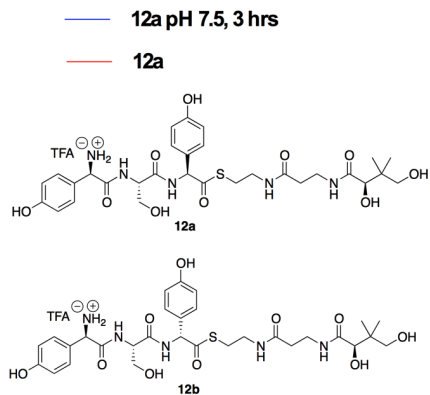
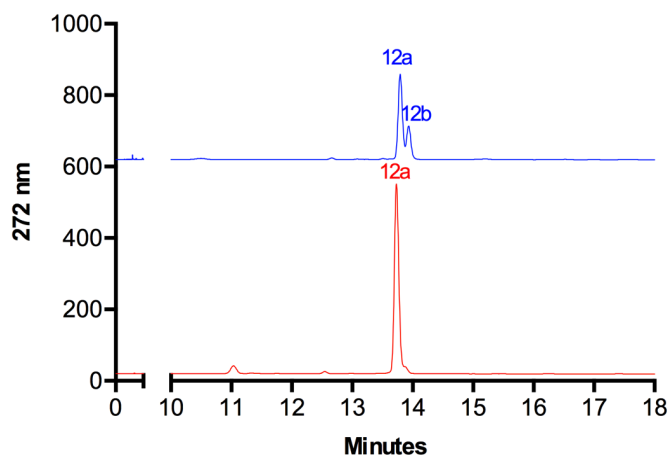


600 MHz ¹H-NMR Compound 31b – D₂O

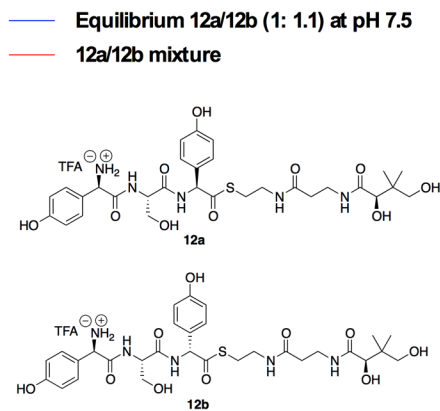
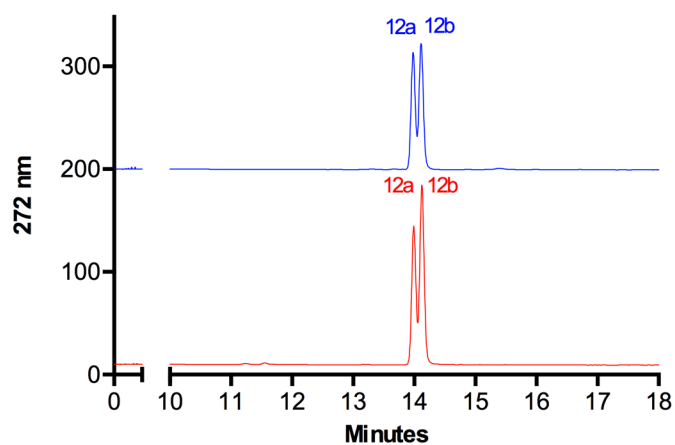
HPLC Analysis of the Effect of 50 mM K_iPO_4 , pH 7.5 on Epimerization of the C-terminal pHPG α -Hydrogen of Synthesized Thioester Substrates.

Analytical HPLC purifications were performed on an Agilent 1200 instrument multi-wavelength UV-Vis detector in conjunction with a reverse phase Luna 5u phenyl hexyl analytical column (250 x 4.60mm ID) using Analytical Method A as described previously.

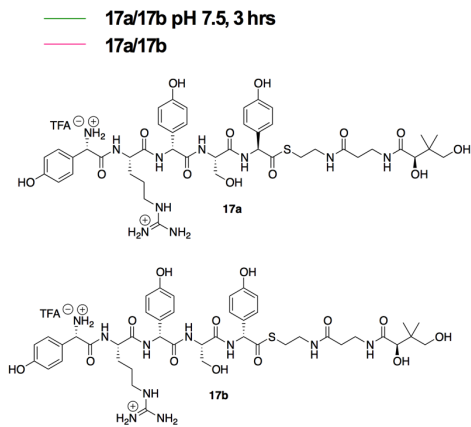
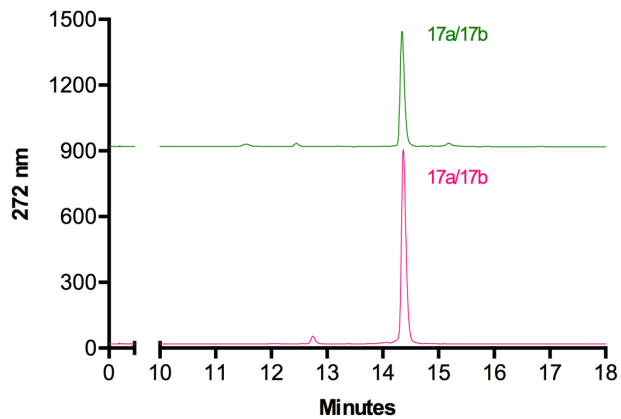
Chemical Epimerization of 12a to 12b at pH 7.5



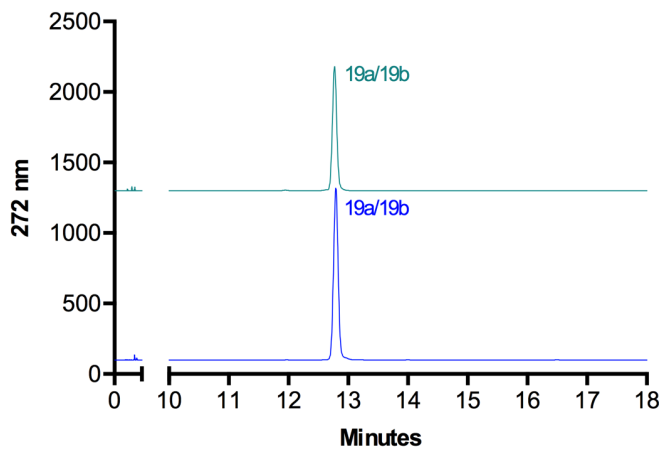
Chemical Epimerization of 12b to 12a at pH 7.5



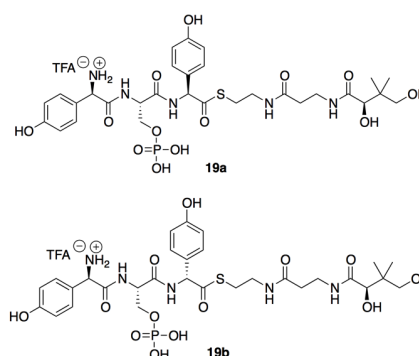
Chemical Epimerization of 17a/17b Mixture at pH 7.5



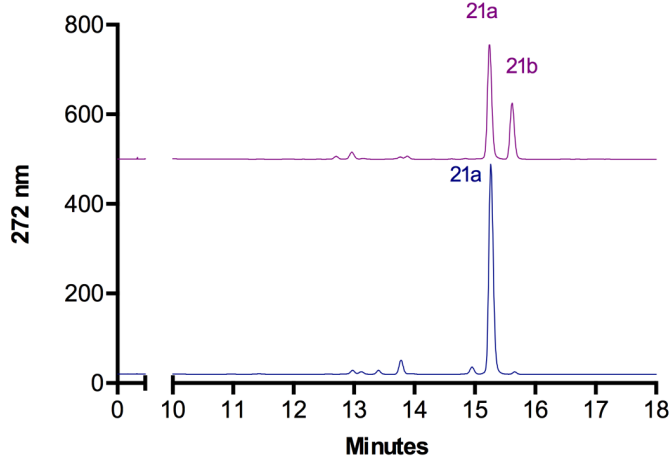
Chemical Epimerization of 19a/19b Mixture at pH 7.5



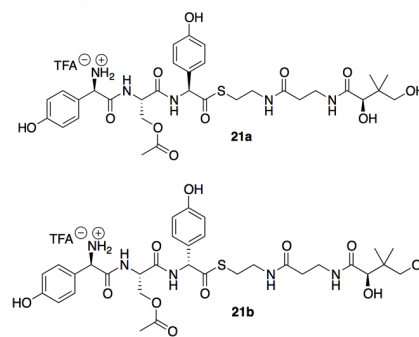
— 19a/19b pH 7.5, 3 hrs
— 19a/19b



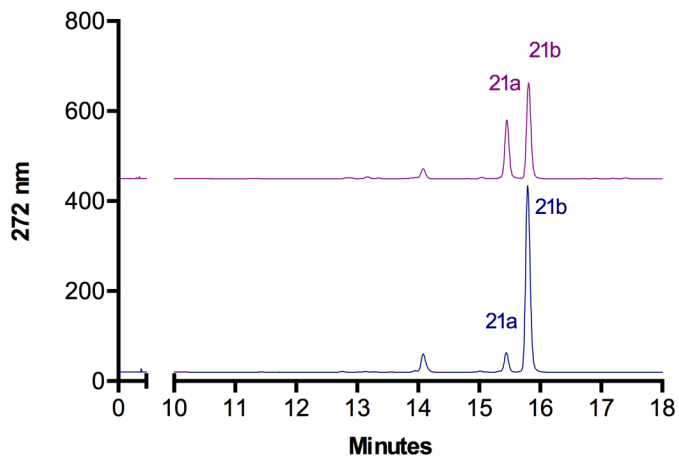
Chemical Epimerization of 21a to 21b at pH 7.5



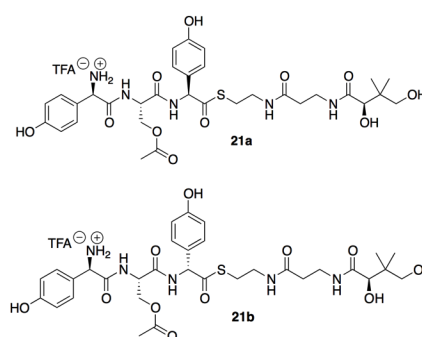
— 21a pH 7.5, 3hrs
— 21a



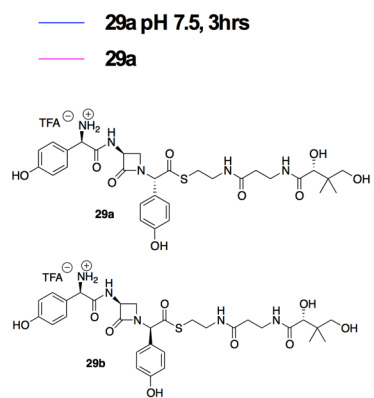
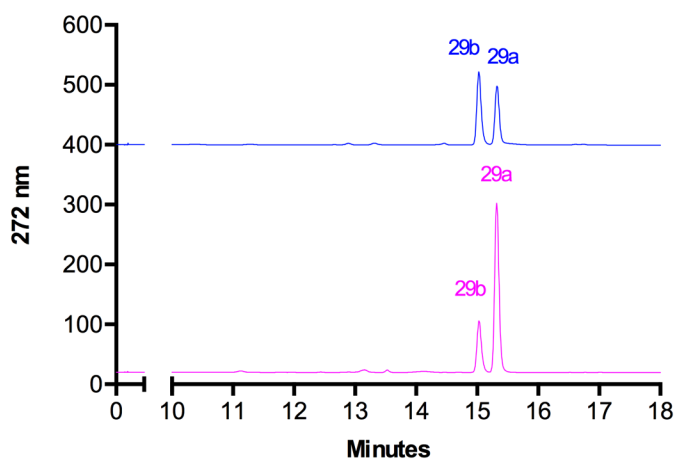
Chemical Epimerization of 21b to 21a at pH 7.5



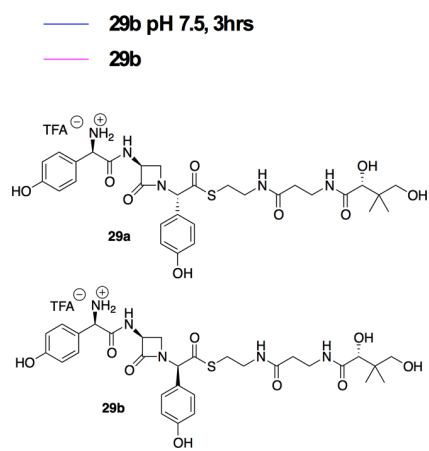
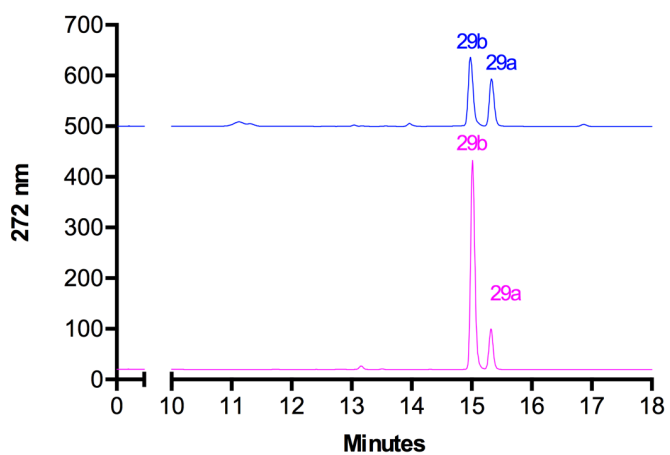
— 21b pH 7.5, 3hrs
— 21b



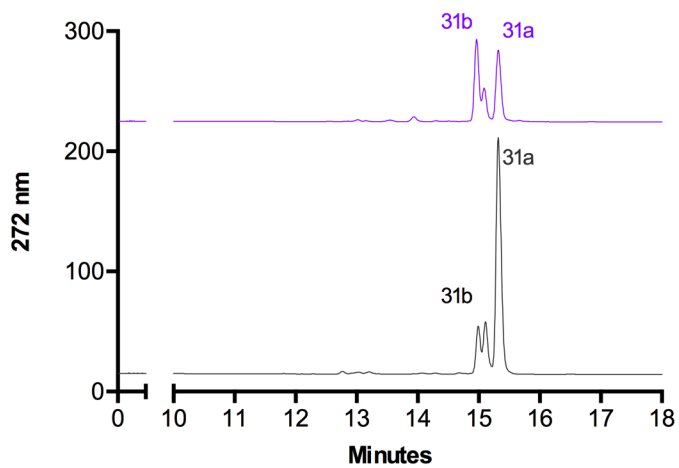
Chemical Epimerization of 29a to 29b at pH 7.5



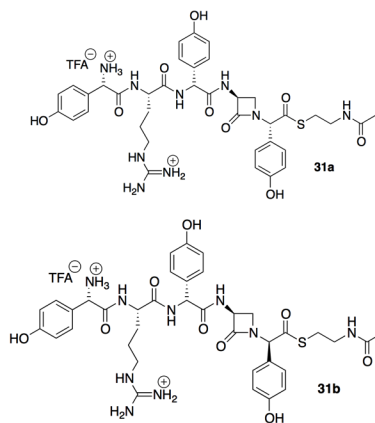
Chemical Epimerization of 29b to 29a at pH 7.5



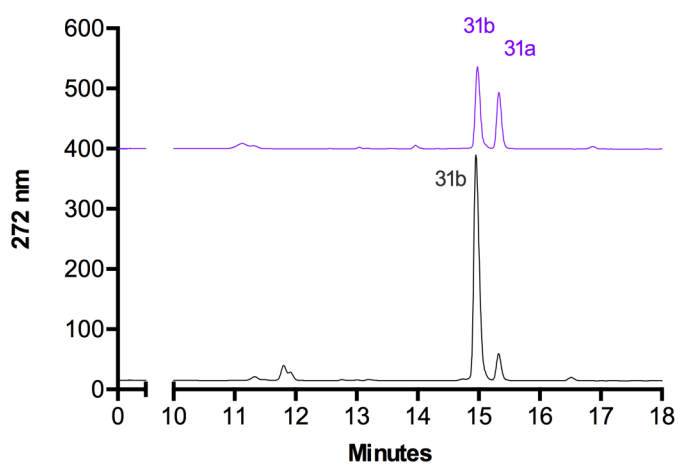
Chemical Epimerization of 31a to 31b at pH 7.5



— 31a pH 7.5, 3hrs
— 31a



Chemical Epimerization of 31b to 31a at pH 7.5



— 31b pH 7.5, 3hrs
— 31b

