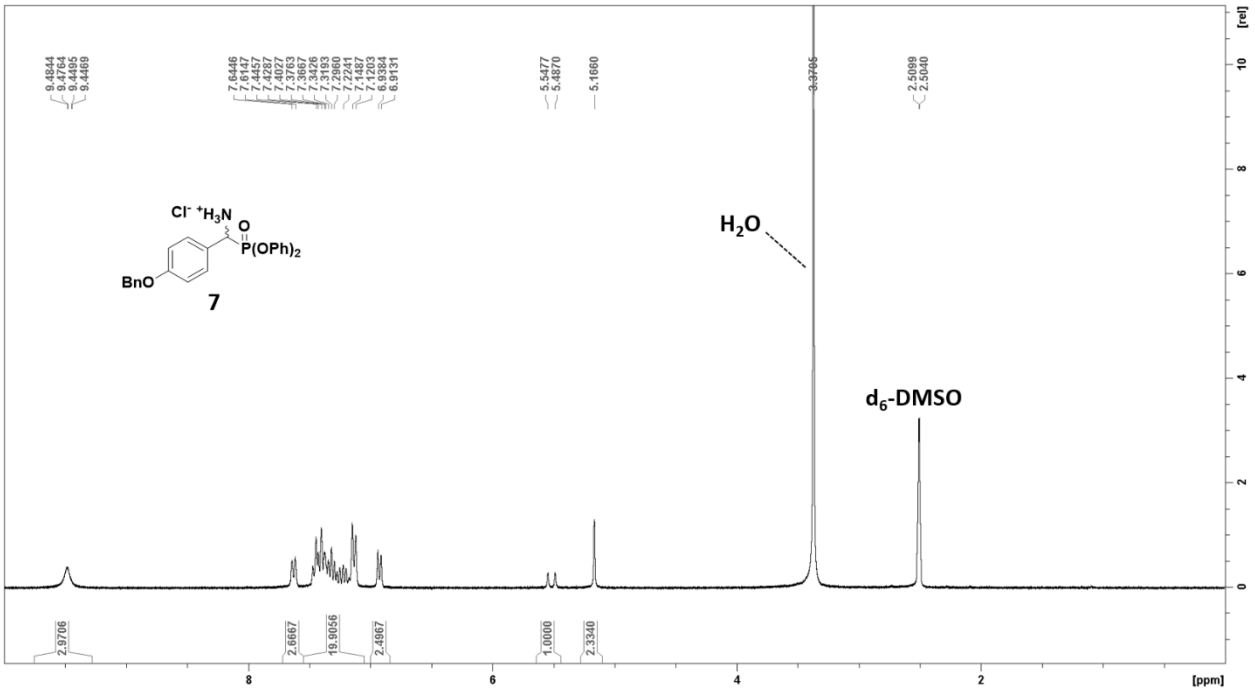
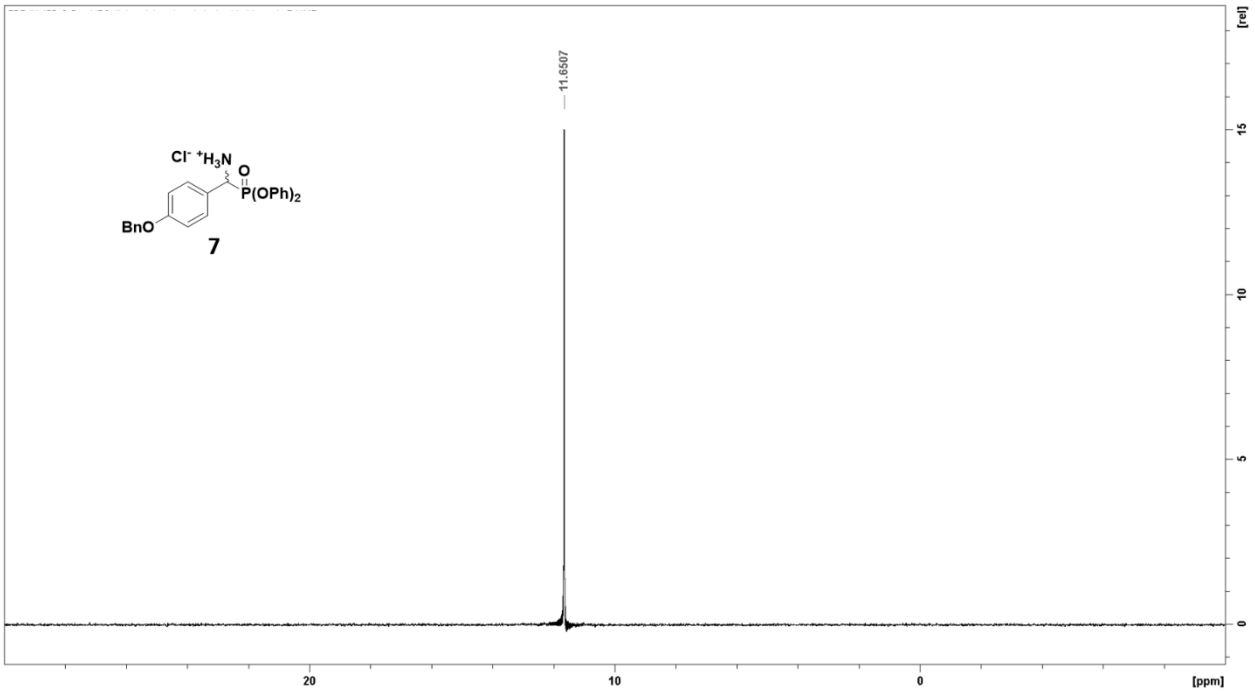
Supplemental Data: Related to "Synthesis of DPP and FP Substrate Analogue Inhibitors"

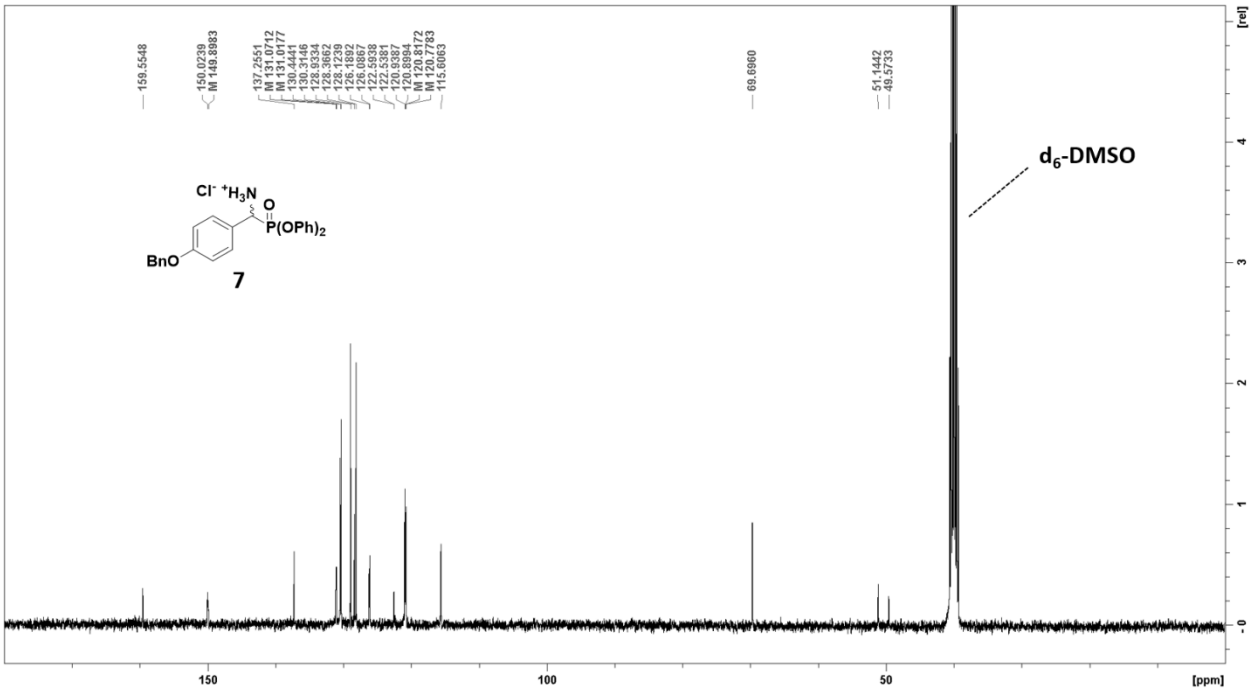
Spectroscopic and Spectrometric Characterization of Compounds



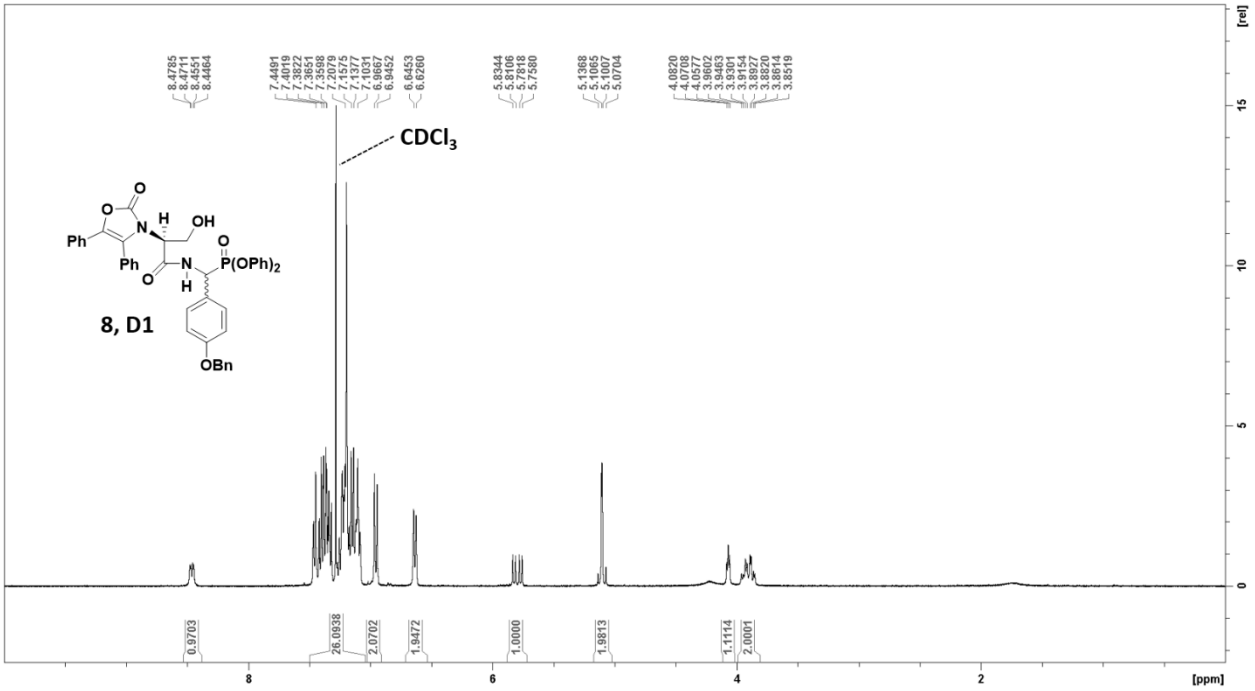
^{1}H NMR spectrum of **7** in d_6-DMSO.



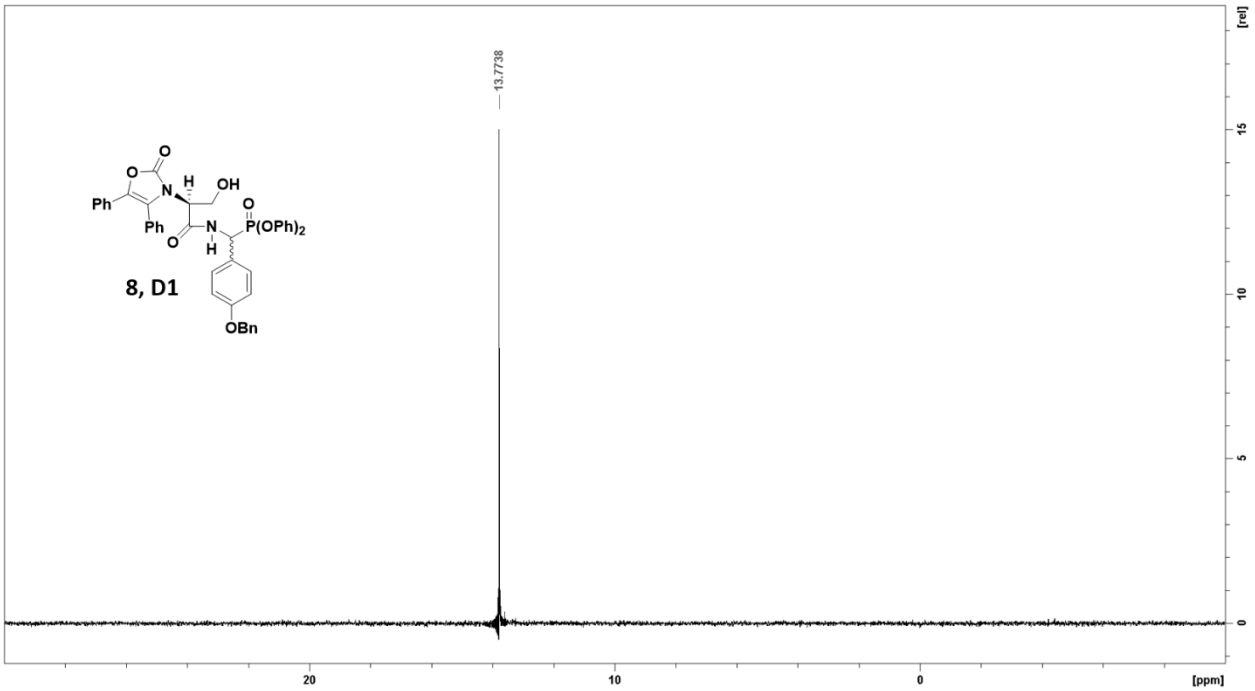
^{31}P NMR spectrum of **7** in d_6-DMSO.



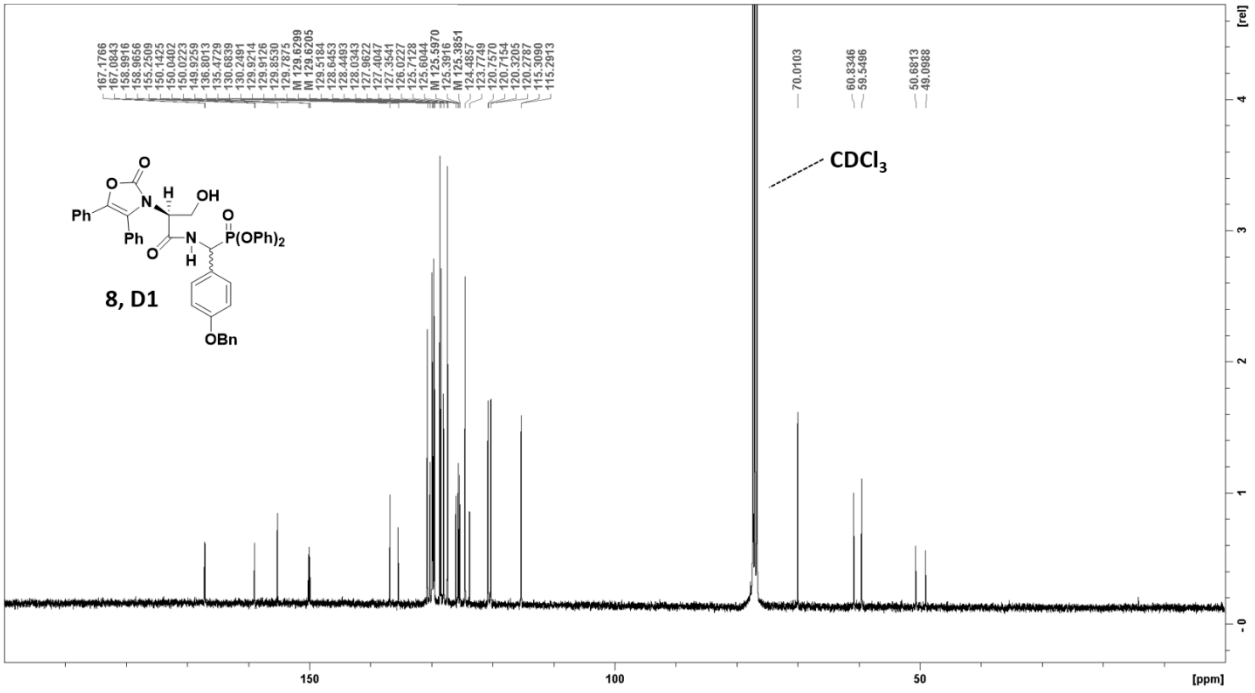
^{13}C NMR of **7** in d_6-DMSO.



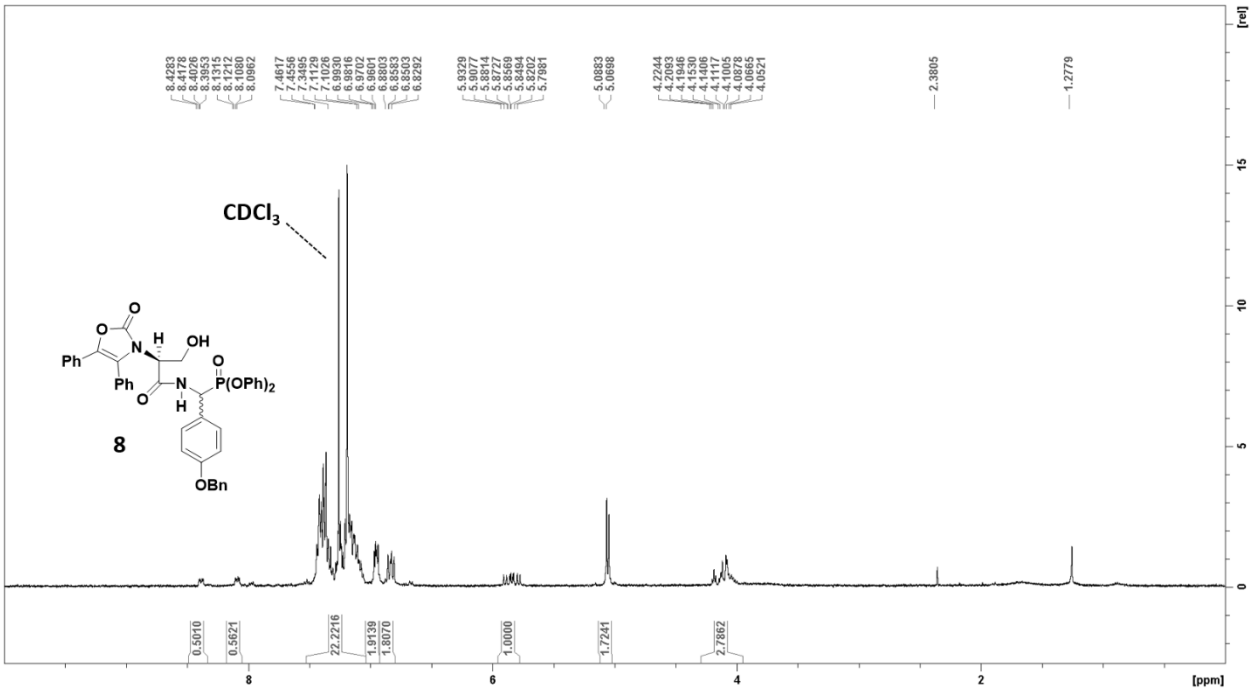
^{1}H NMR of **8**, diastereomer 1 (D1) in $CDCl_3$.



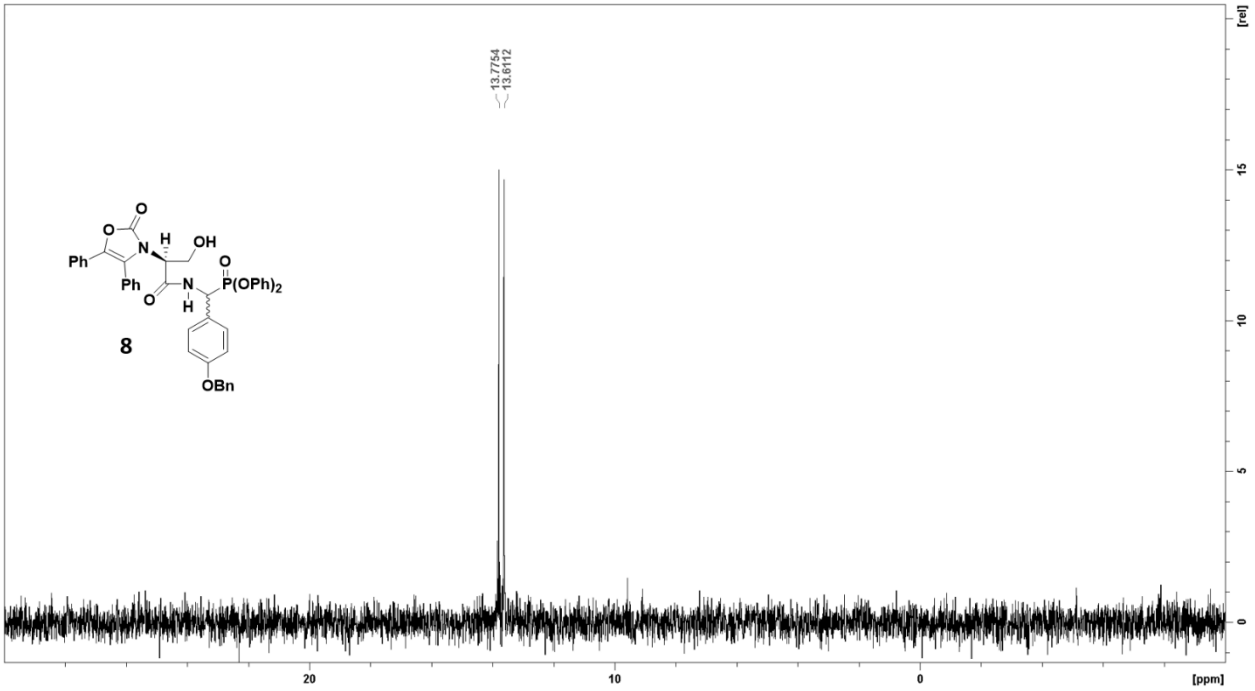
^{31}P NMR of **8**, diastereomer 1 (D1) in $CDCl_3$.



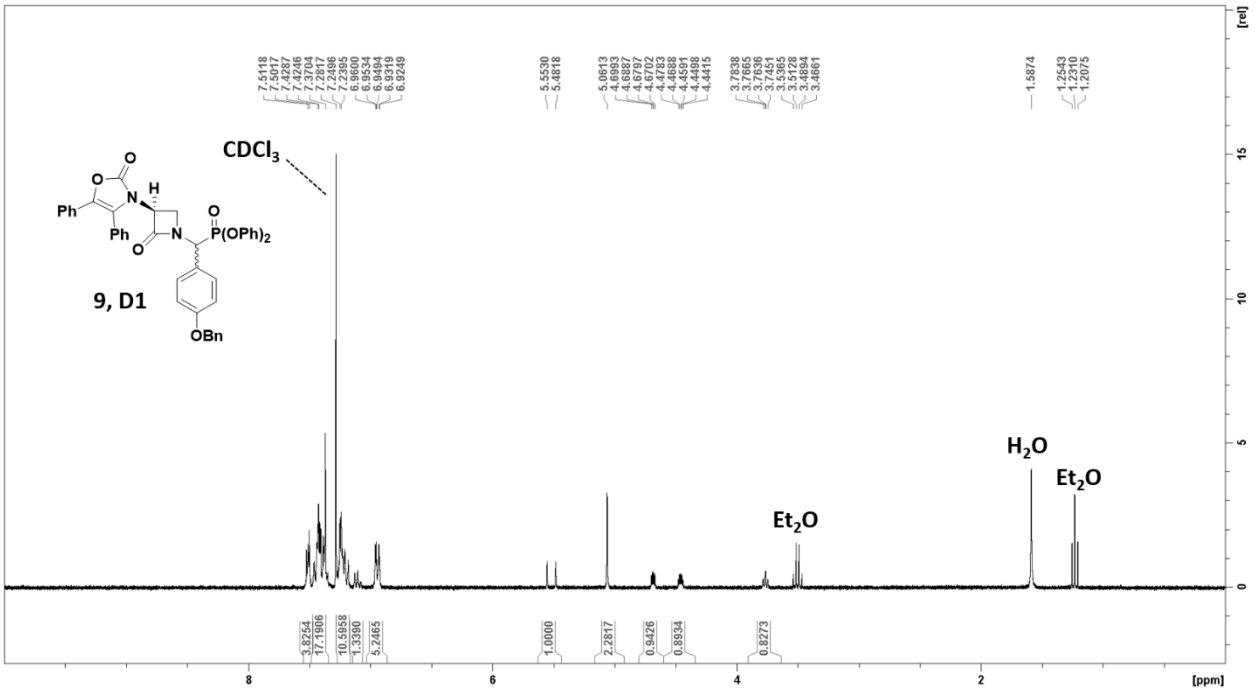
^{13}C NMR of **8**, diastereomer 1 (D1) in $CDCl_3$.



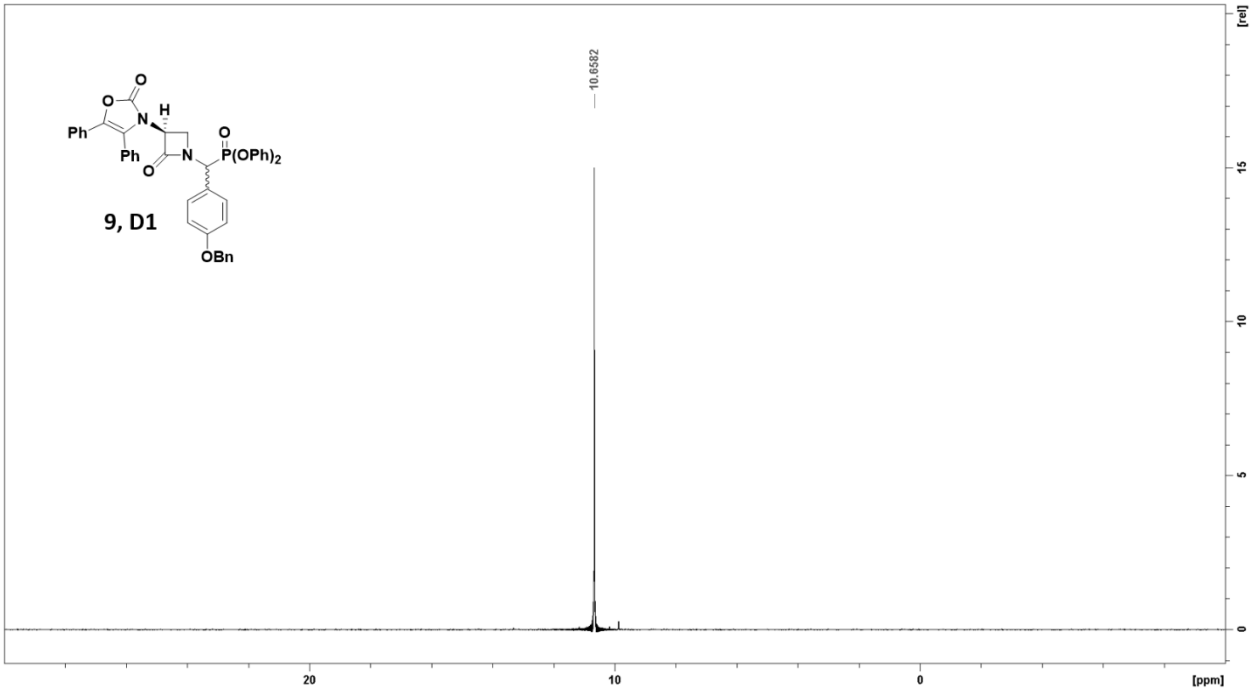
^{1}H NMR of **8** (~1:1 mixture of diastereomers 1 and 2) in $CDCl_3$.



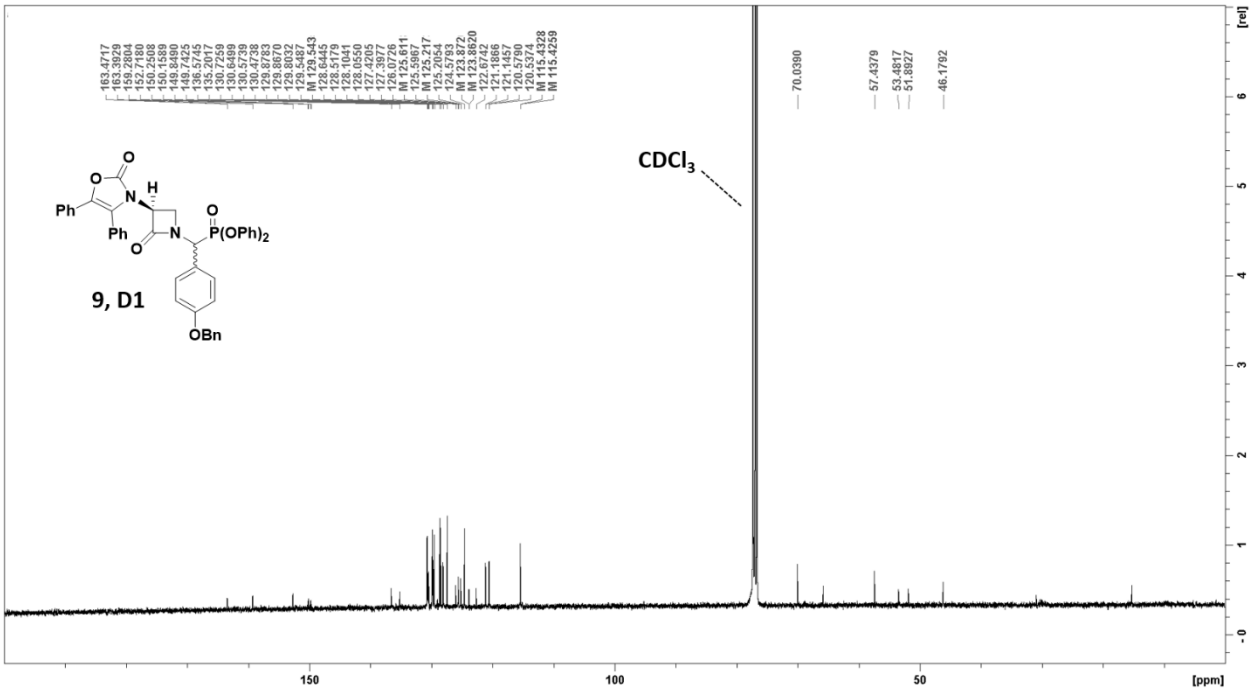
^{31}P NMR of **8** (~1:1 mixture of diastereomers 1 and 2) in $CDCl_3$.



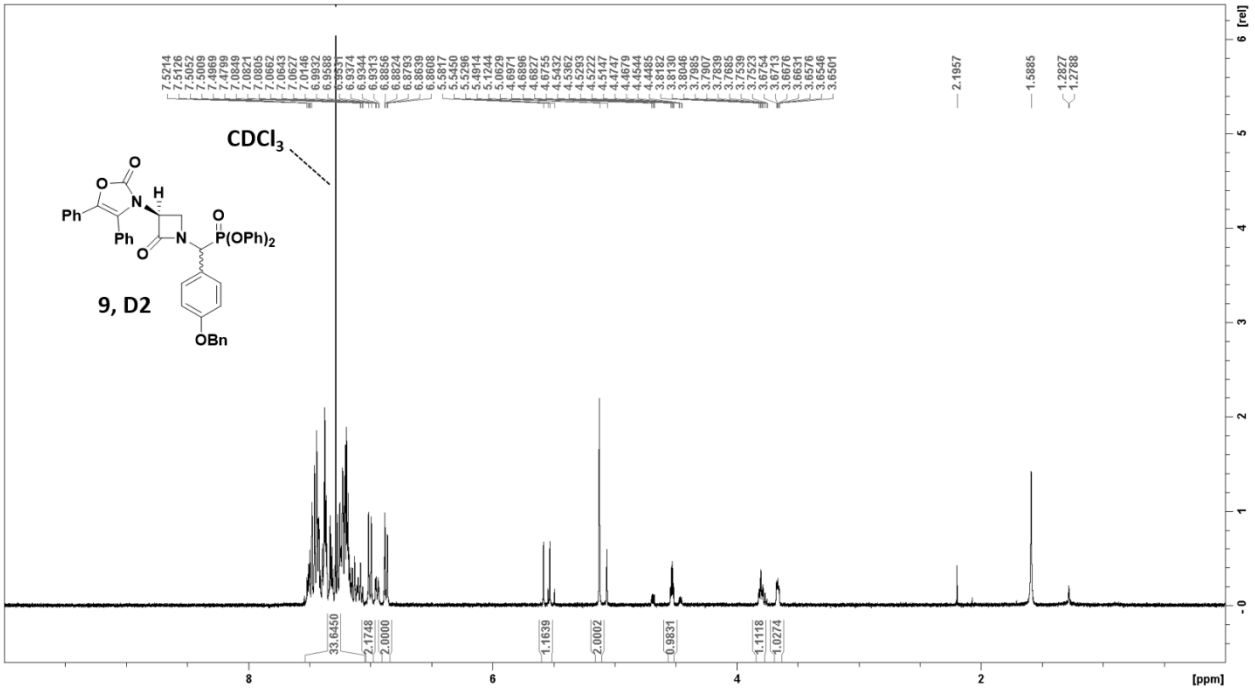
^{1}H NMR of **9**, diastereomer 1 (D1) in $CDCl_3$.



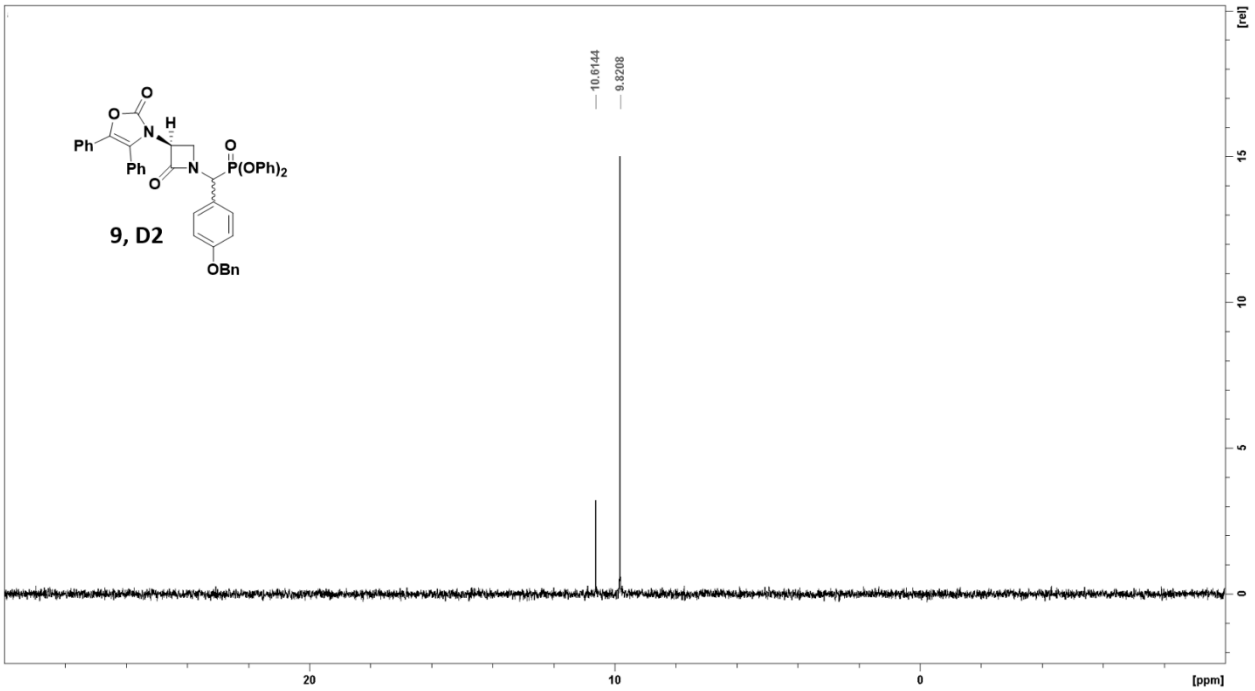
^{31}P NMR of **9**, diastereomer 1 (D1) in $CDCl_3$.



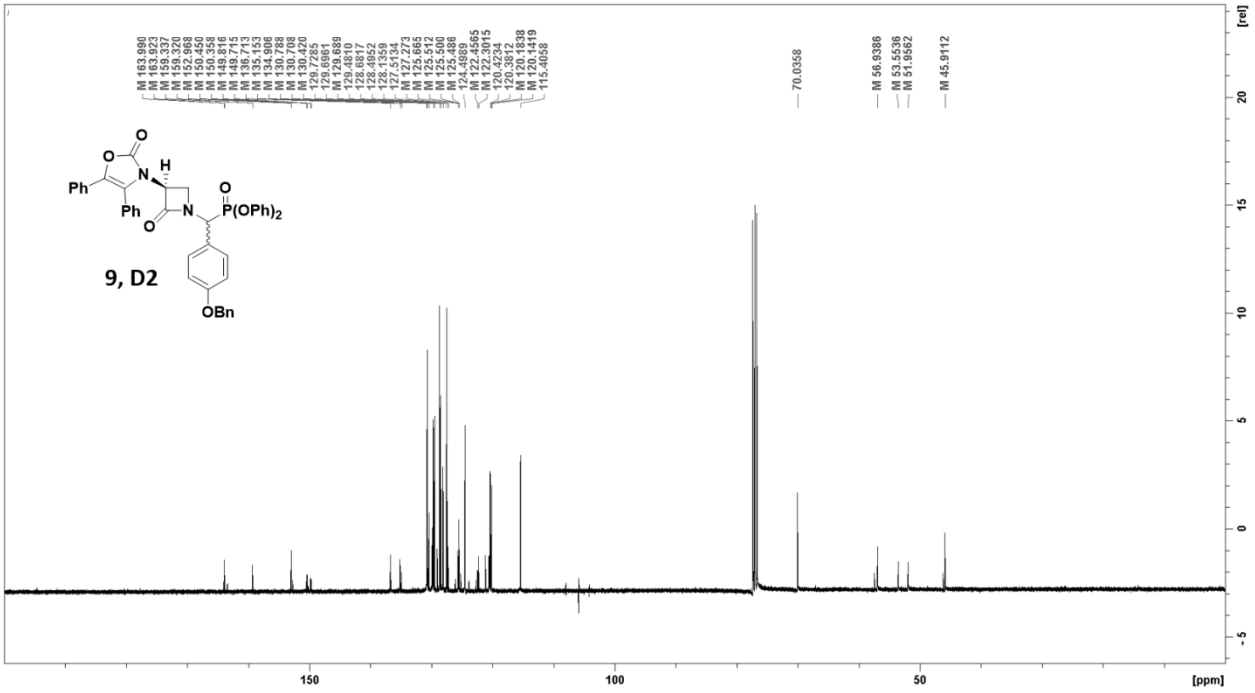
^{13}C NMR of **9**, diastereomer 1 (D1) in $CDCl_3$.



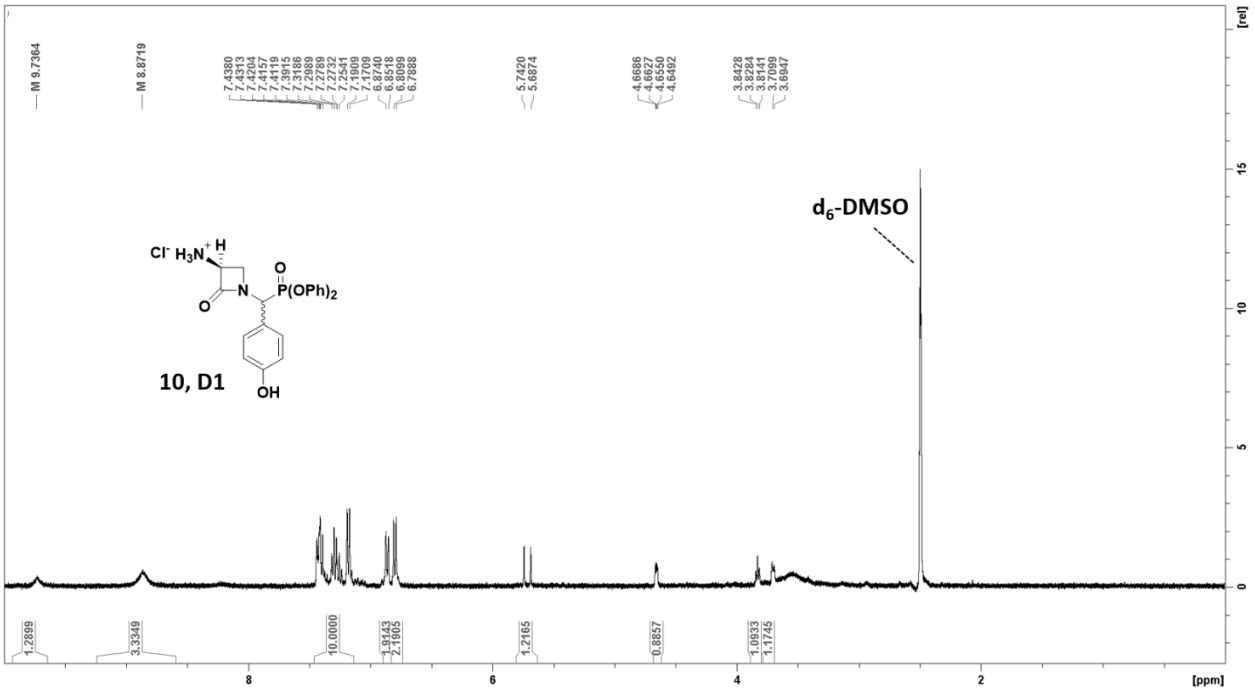
^{1}H NMR of **9**, diastereomer 2 (D2) enriched ~5:1 in $CDCl_3$.



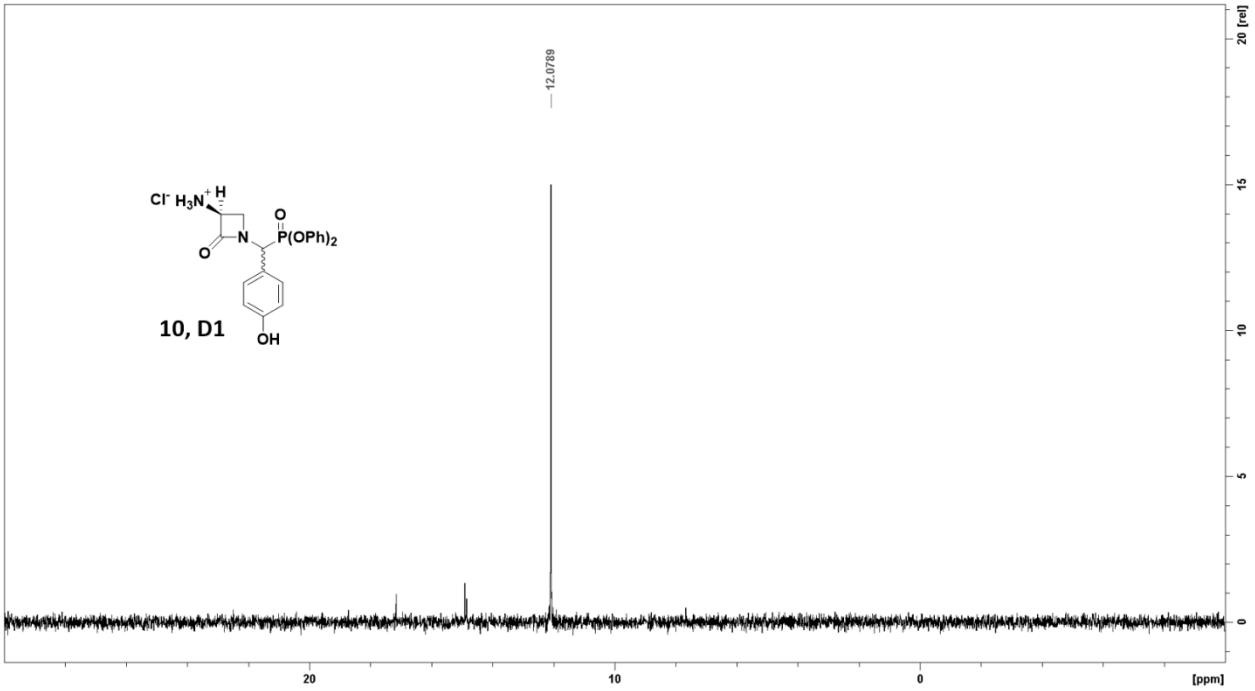
^{31}P NMR of **9**, diastereomer 2 (D2) enriched ~5:1 in $CDCl_3$.



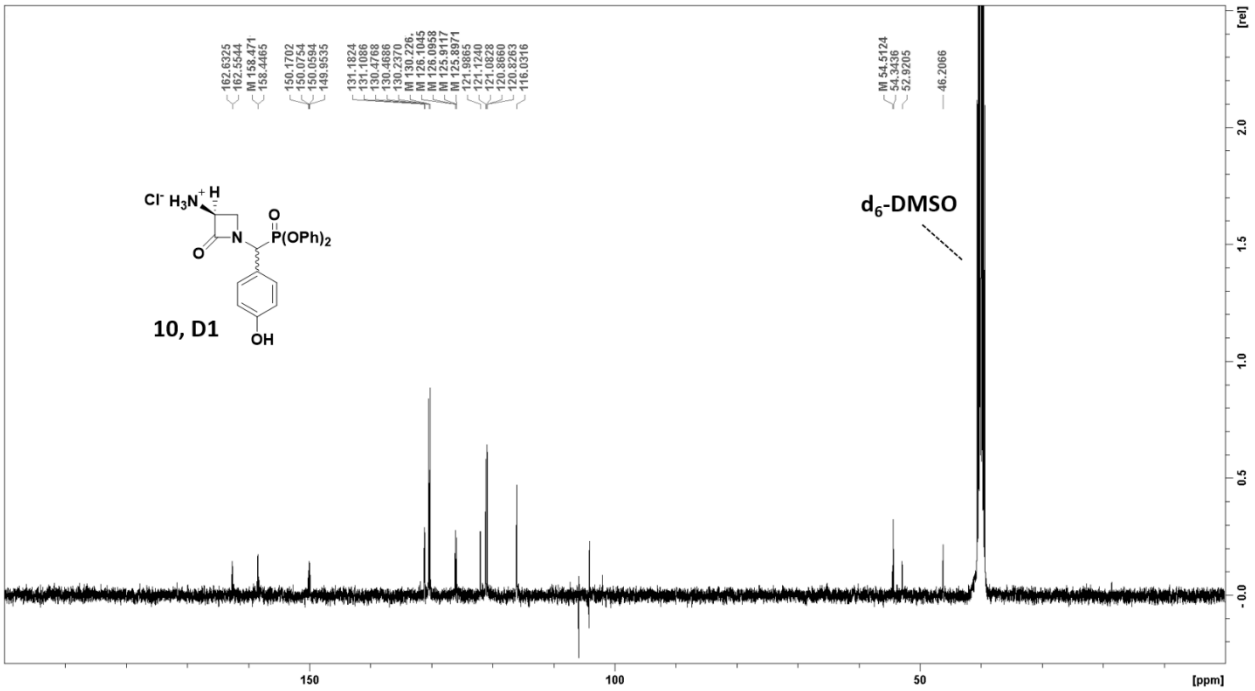
^{13}C NMR of **9**, diastereomer 2 (D2) enriched ~5:1 in $CDCl_3$.



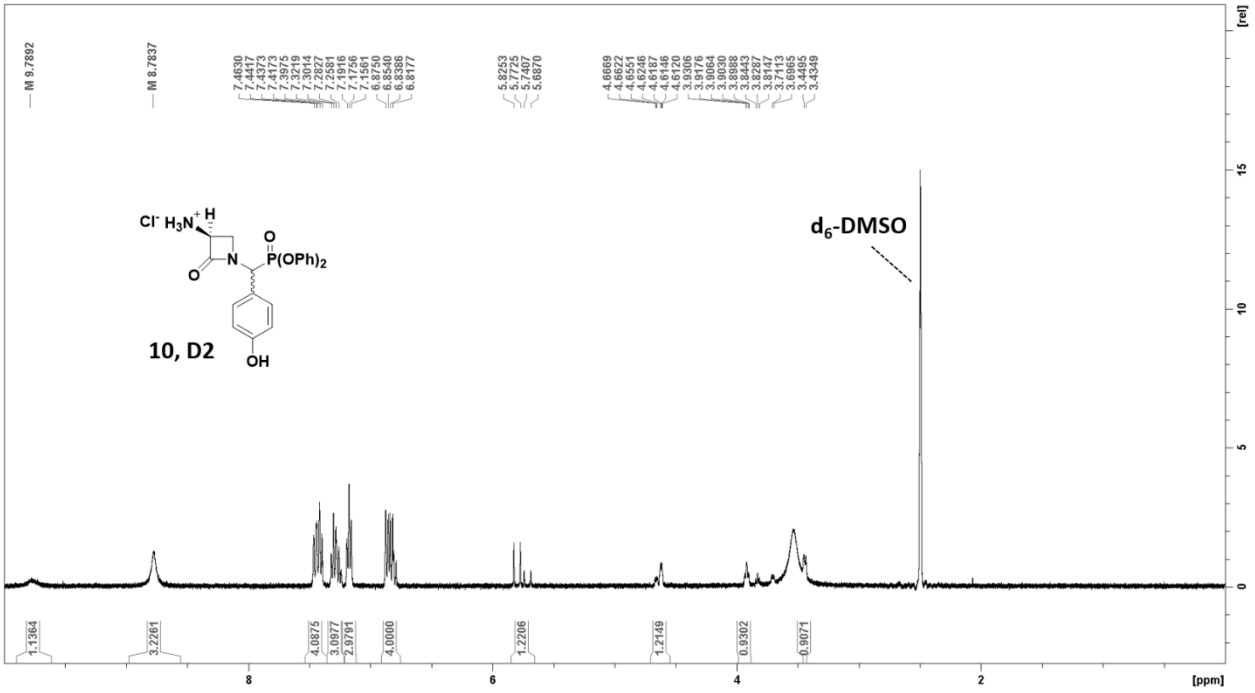
^{1}H NMR of **10**, diastereomer 1 (D1) in d_6-DMSO.



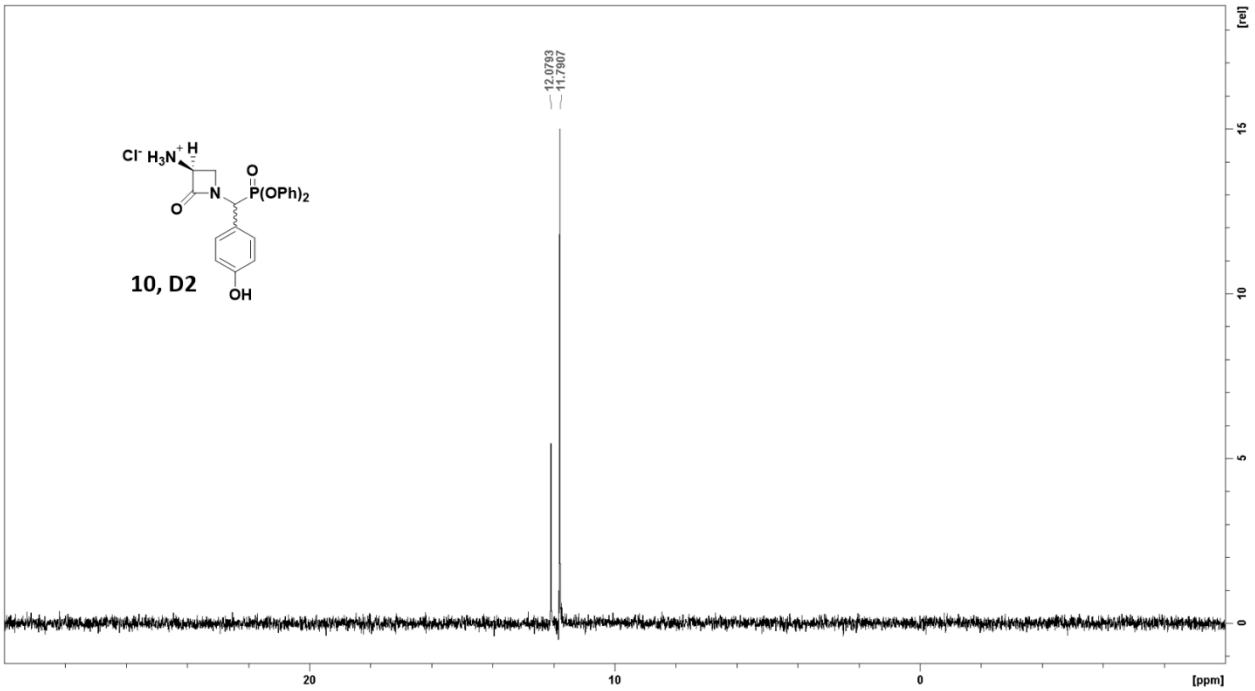
^{31}P NMR of **10**, diastereomer 1 (D1) in d_6-DMSO.



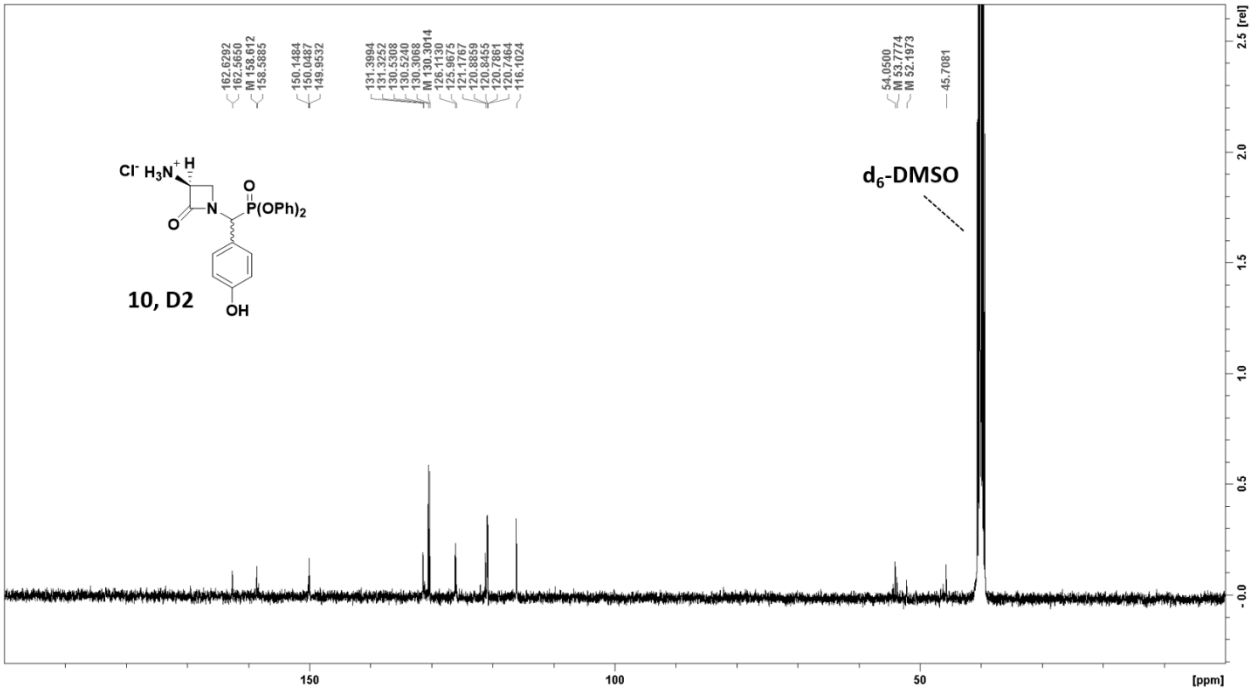
^{13}C NMR of **10**, diastereomer 1 (D1) in d_6-DMSO.



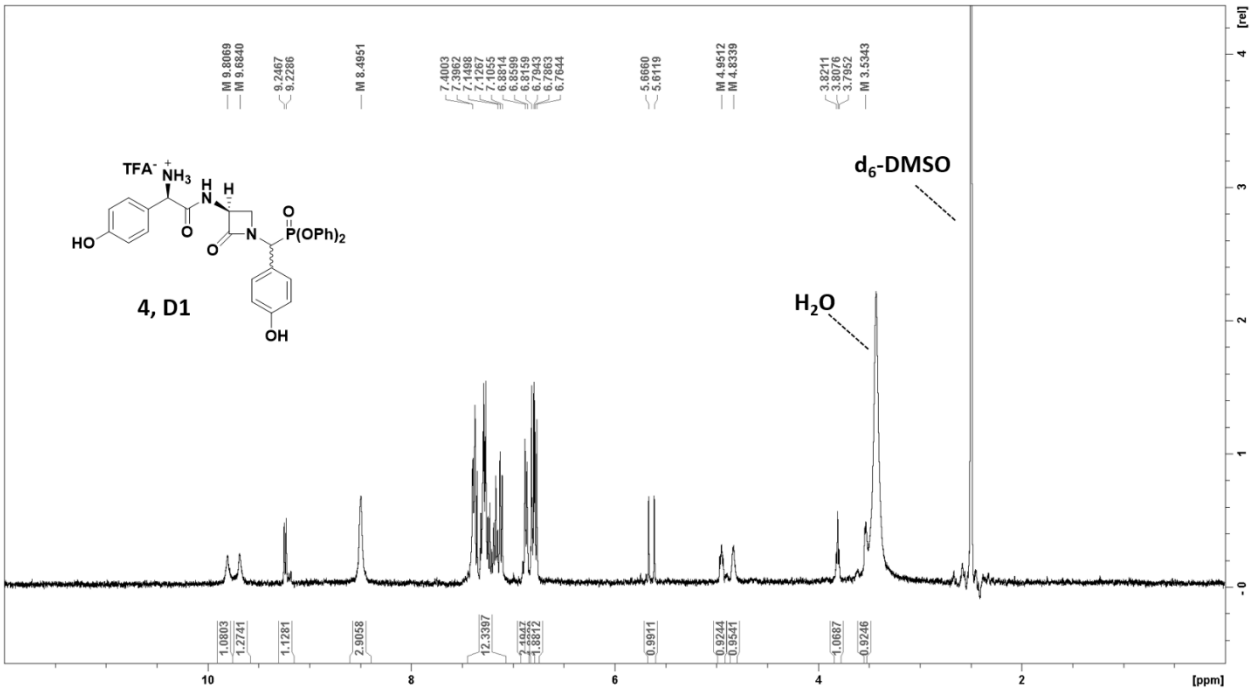
^{1}H NMR of **10**, diastereomer 2 (D2) enriched ~3:1 in d_6-DMSO.



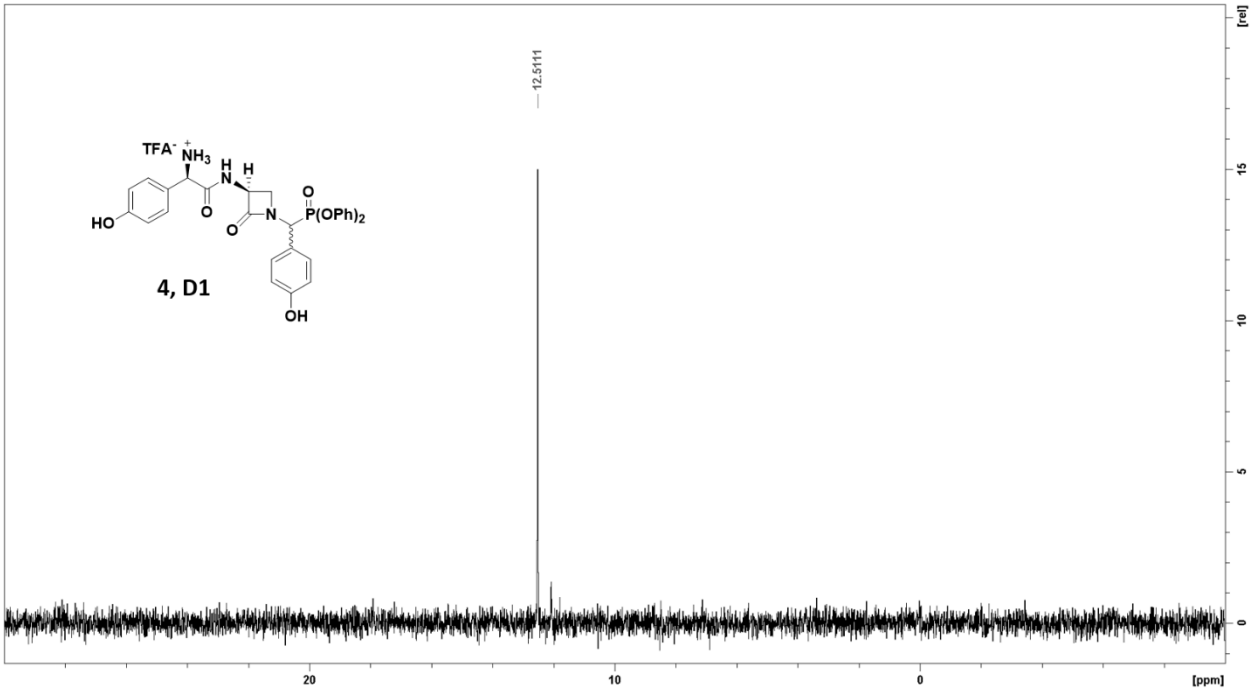
^{31}P NMR of **10**, diastereomer 2 (D2) enriched ~3:1 in d_6-DMSO.



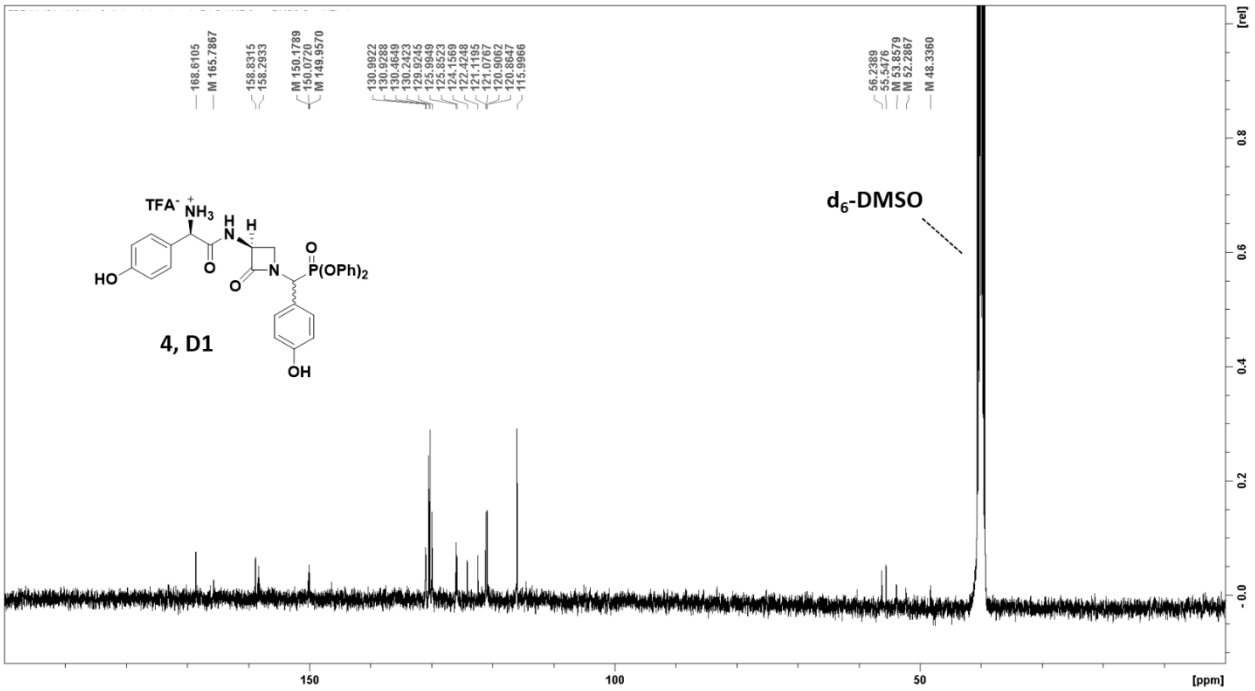
^{13}C NMR of **10**, diastereomer 2 (D2) enriched ~3:1 in d_6-DMSO.



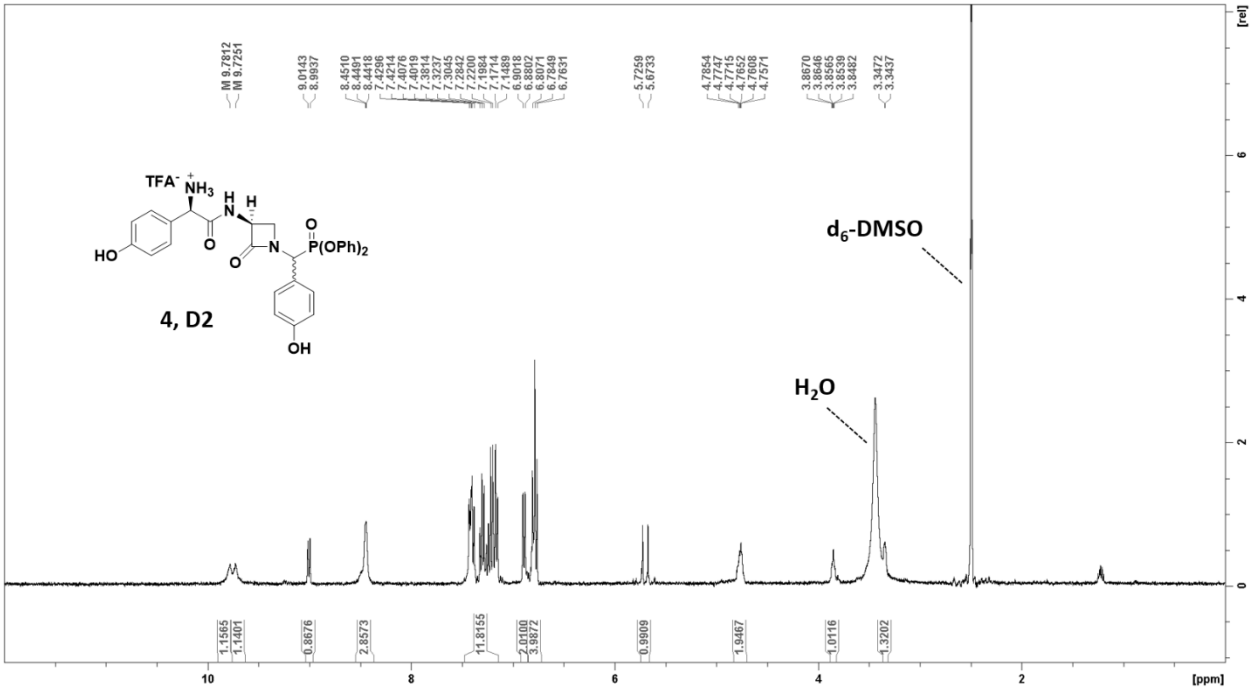
^{1}H NMR of **4**, diastereomer 1 (D1) in d_6-DMSO.



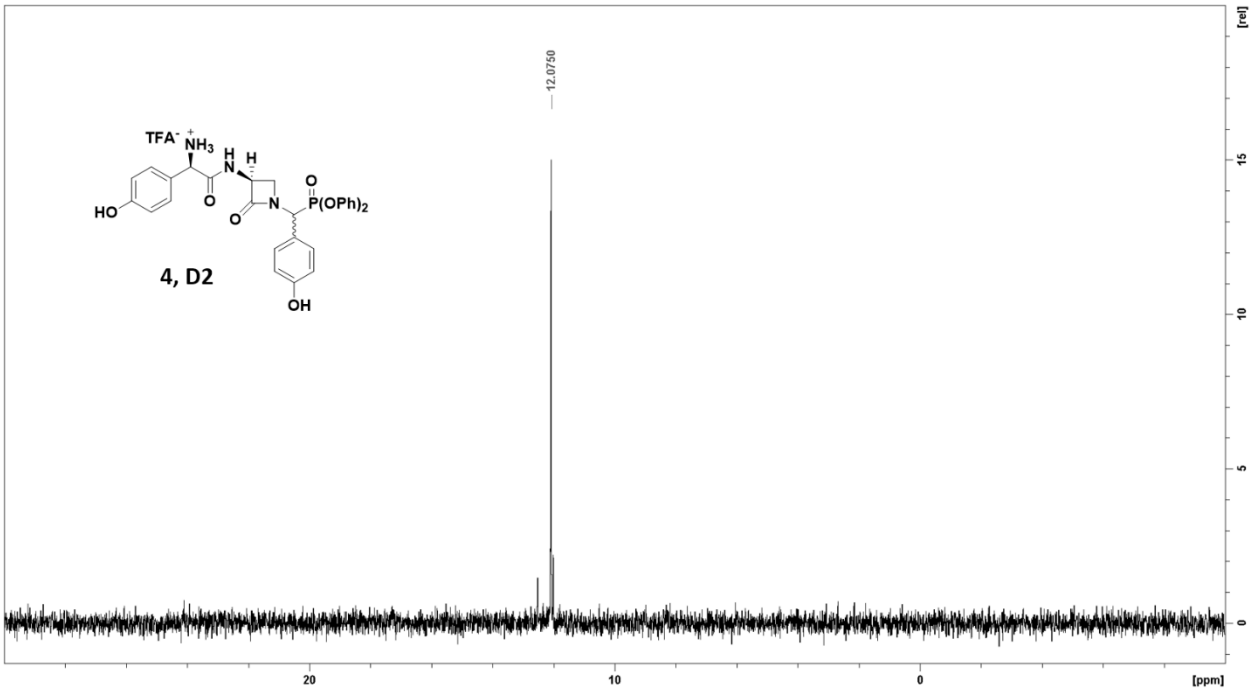
^{31}P NMR of **4**, diastereomer 1 (D1) in d_6-DMSO.



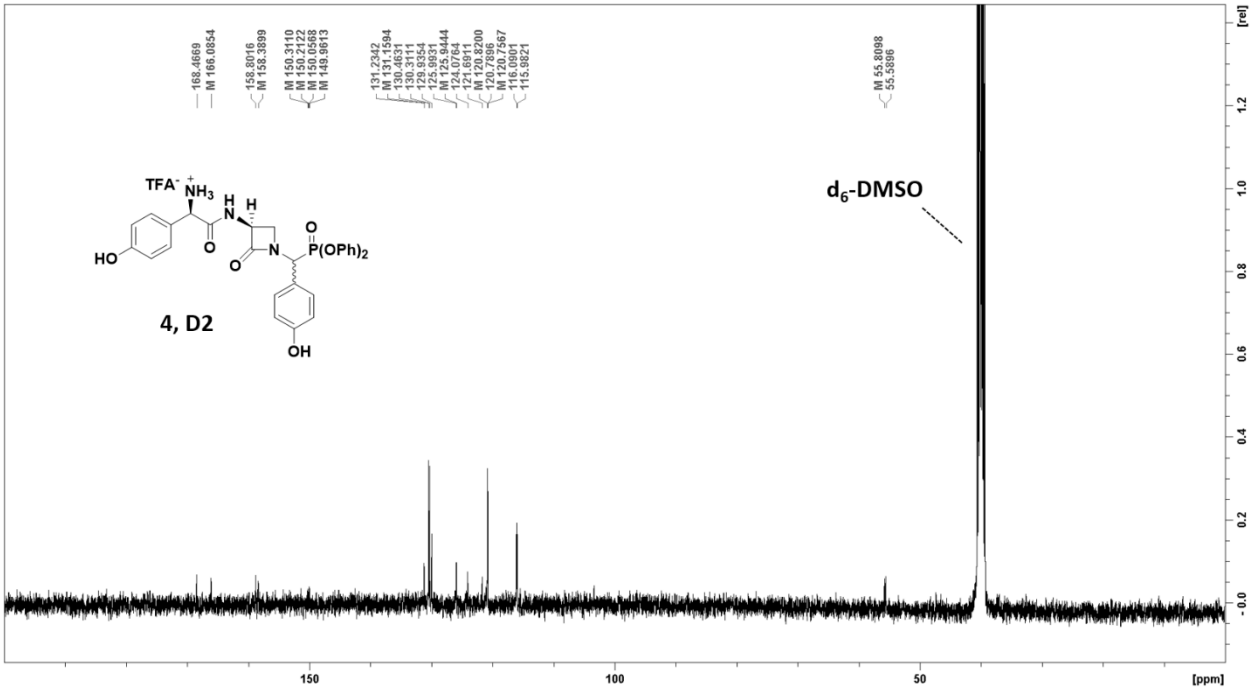
^{13}C NMR of **4**, diastereomer 1 (D1) in d_6-DMSO.



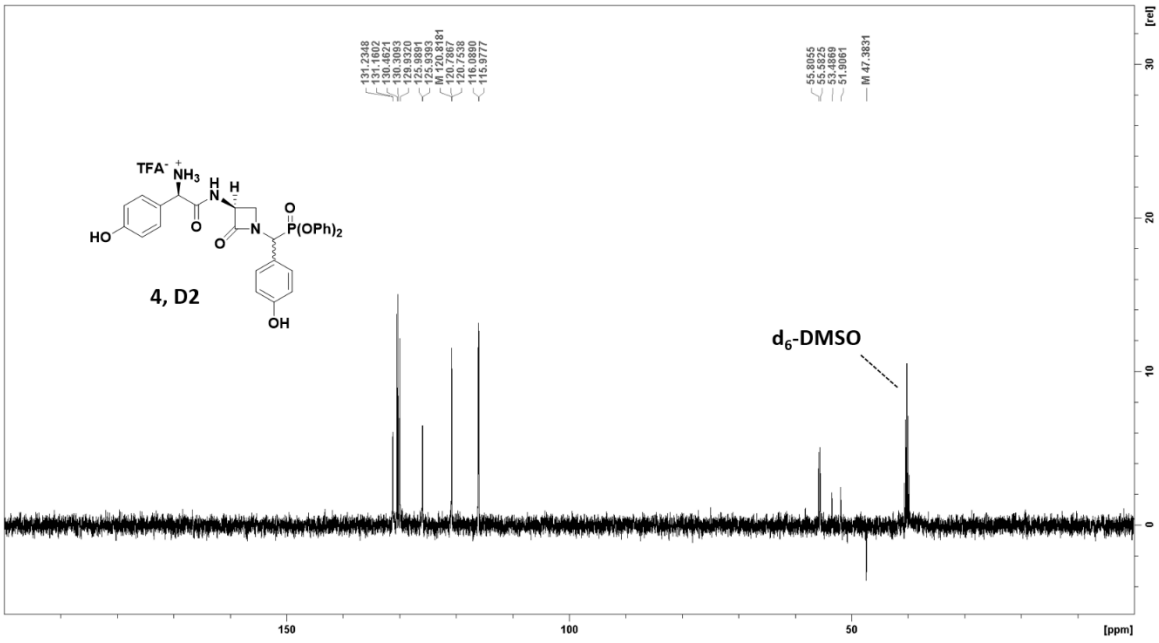
^{1}H NMR of **4**, diastereomer 2 (D2) in d_6-DMSO.



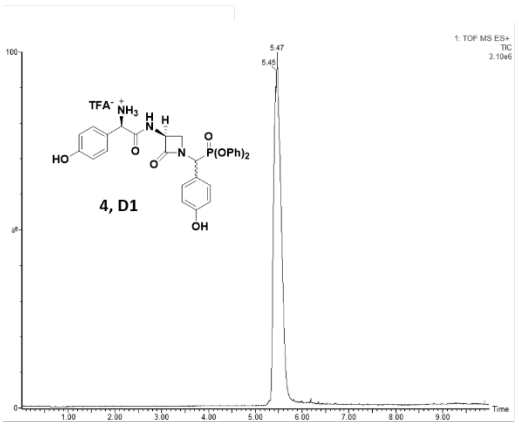
^{31}P NMR of **4**, diastereomer 2 (D2) in d_6-DMSO.

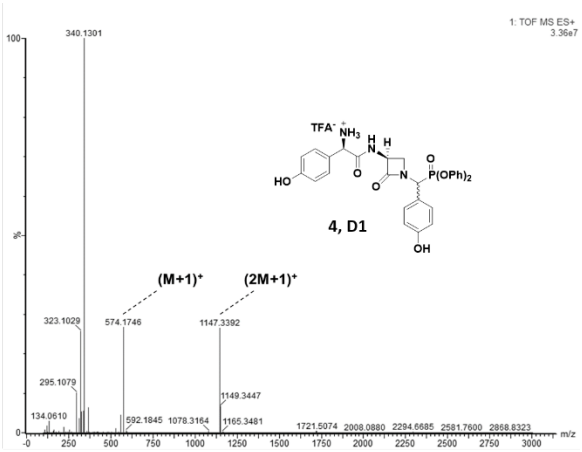


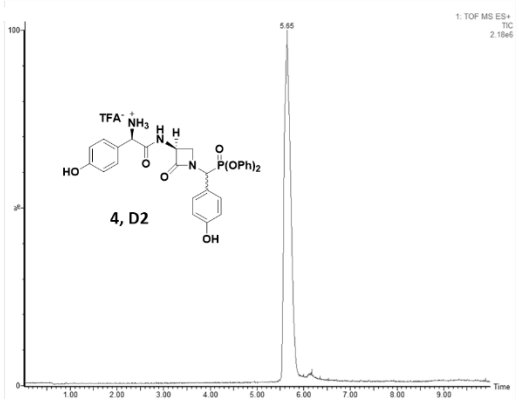
^{13}C NMR of **4**, diastereomer 2 (D2) in d_6-DMSO. Unaccounted for ^{13}C-signals were acquired with a DEPT-135 experiment (see Figure S34).

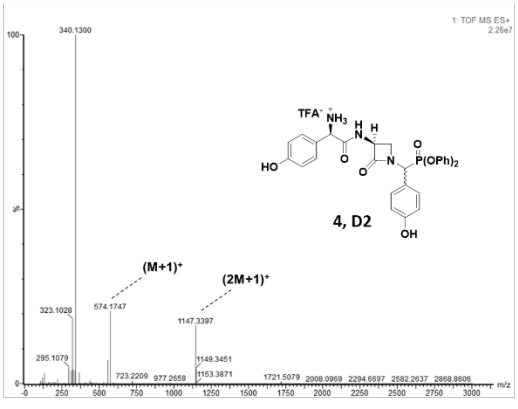


^{13}C DEPT-135 of **4**, diastereomer 2 (D2) in d_6-DMSO.

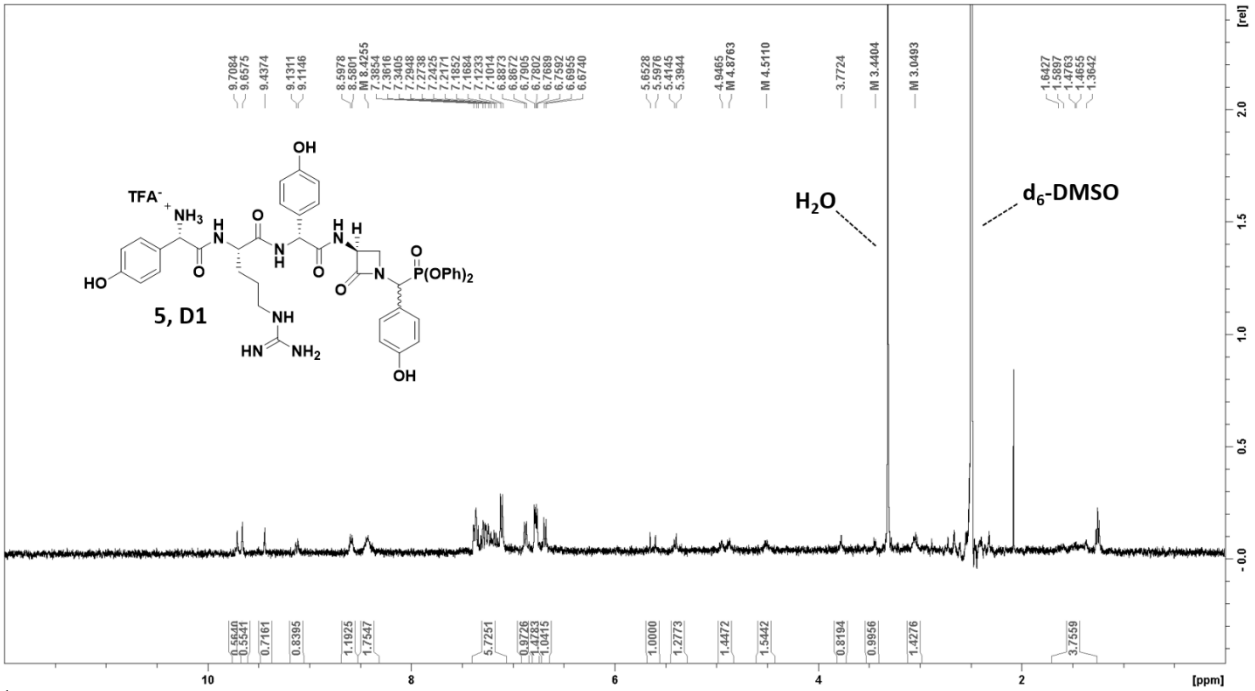




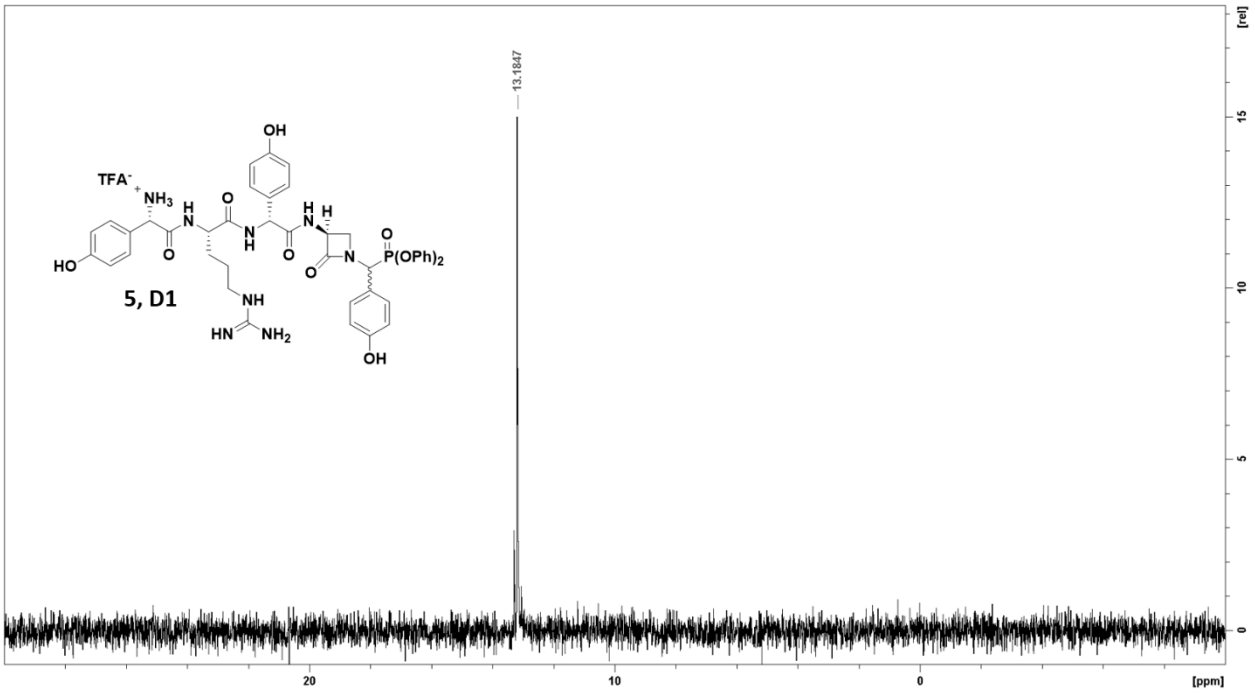




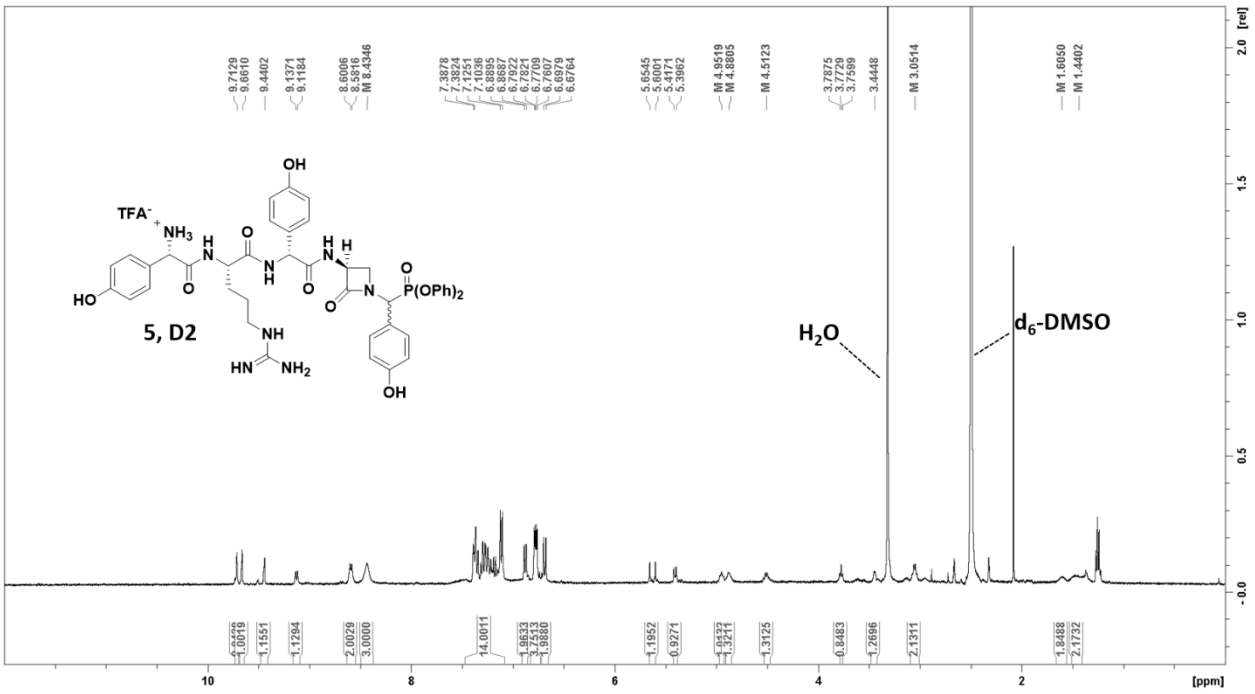
UPLC-HRMS analysis of **4**. (Left) UPLC trace of **4**, diastereomers 1 and 2 (D1 and D2). (Right) Mass spectra of **4**, diastereomers 1 and 2 (D1 and D2).



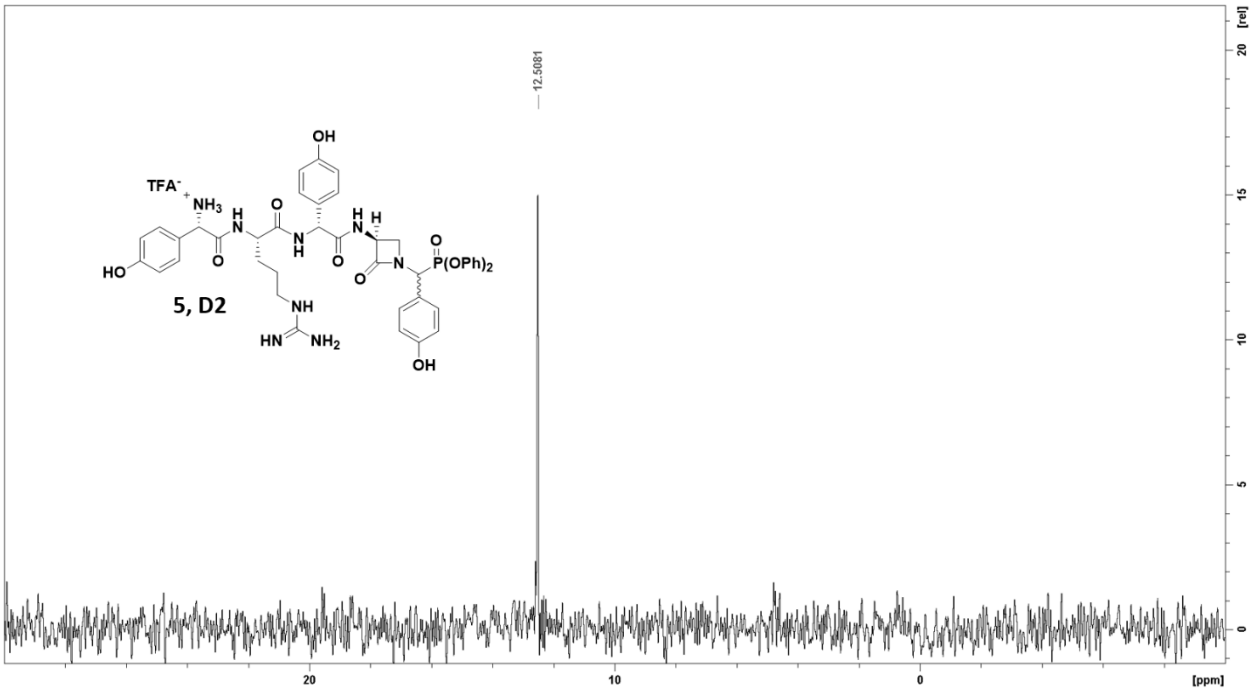
^{1}H NMR of **5**, diastereomer 1 (D1) in d_6-DMSO.



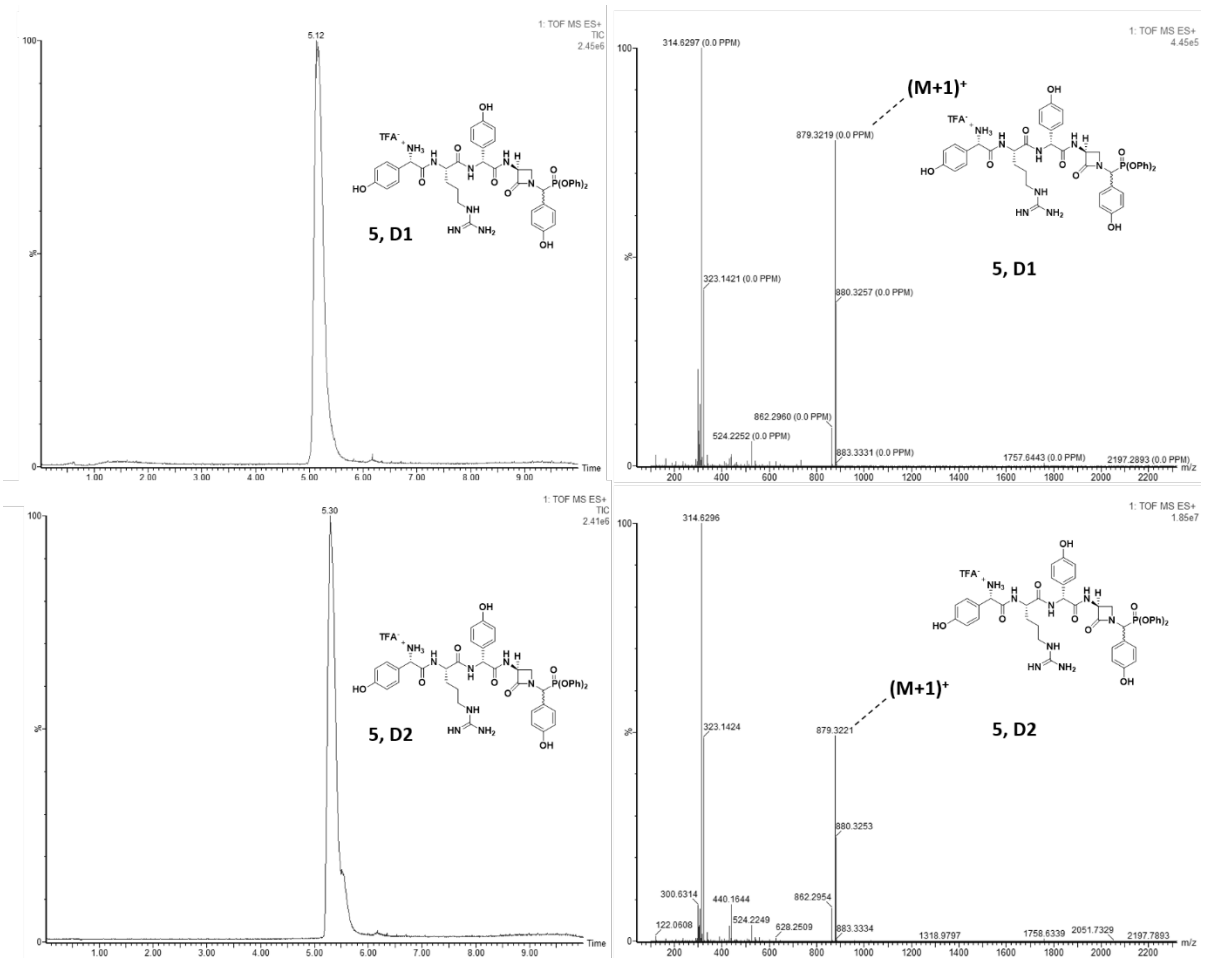
^{31}P NMR of **5**, diastereomer 1 (D1) in d_6-DMSO.



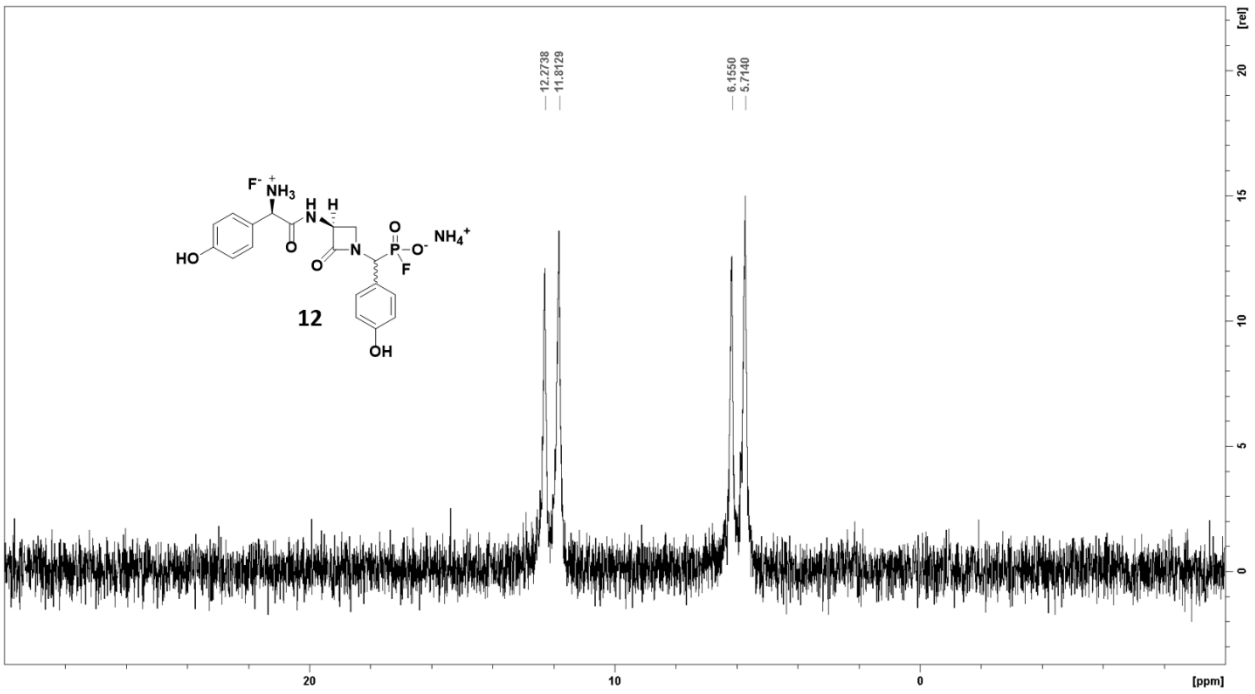
^{1}H NMR of **5**, diastereomer 2 (D2) in d_6-DMSO.



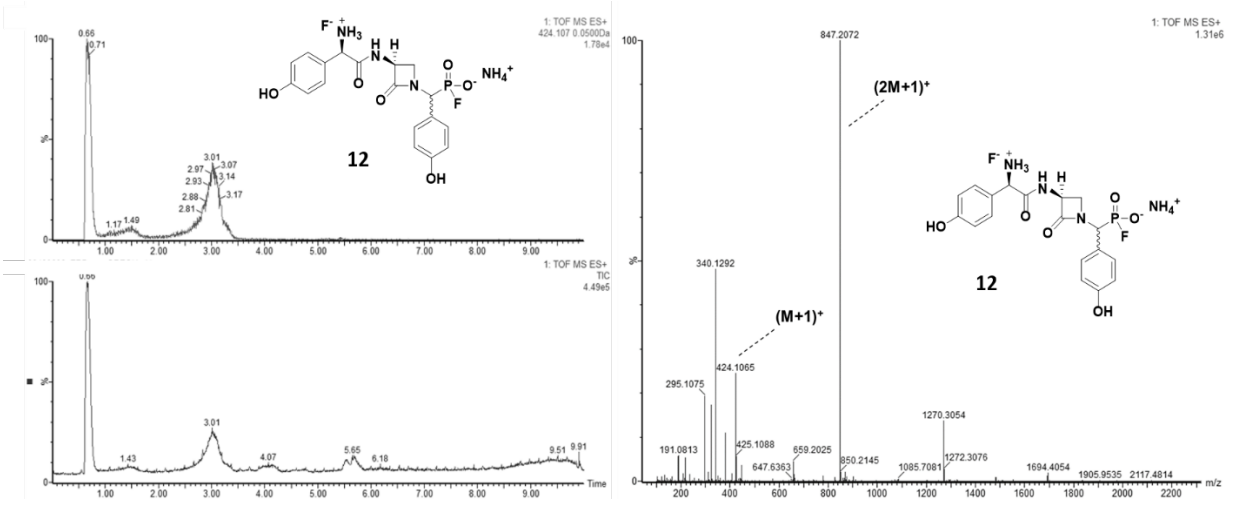
^{31}P NMR of **5**, diastereomer 2 (D2) in d_6-DMSO.



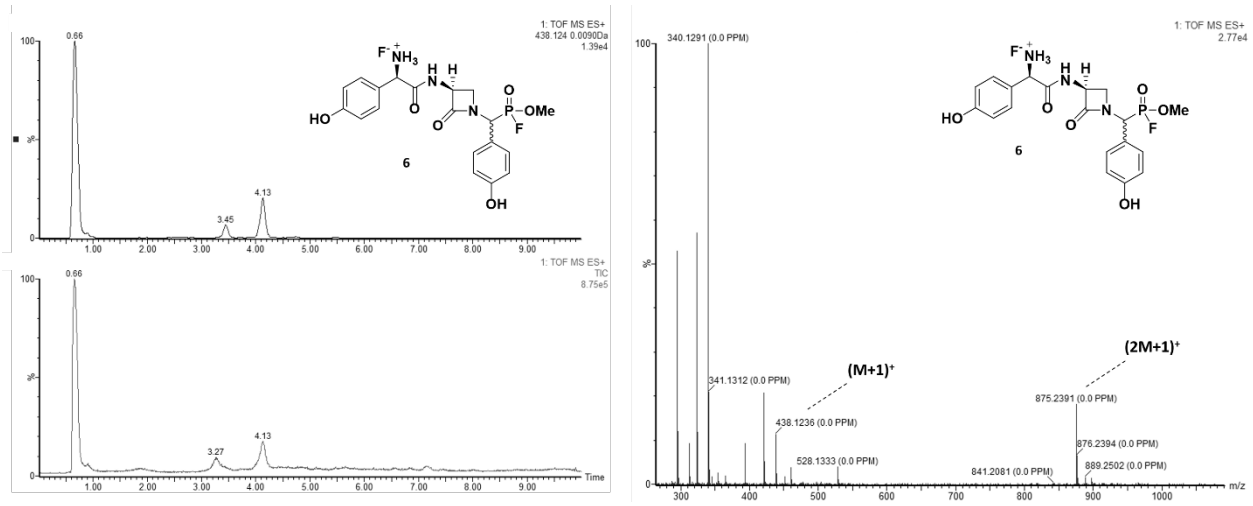
UPLC-HRMS analysis of **5**. (Left) UPLC trace of **5**, diastereomers 1 and 2 (D1 and D2). (Right) Mass spectra of **5**, diastereomers 1 and 2 (D1 and D2).



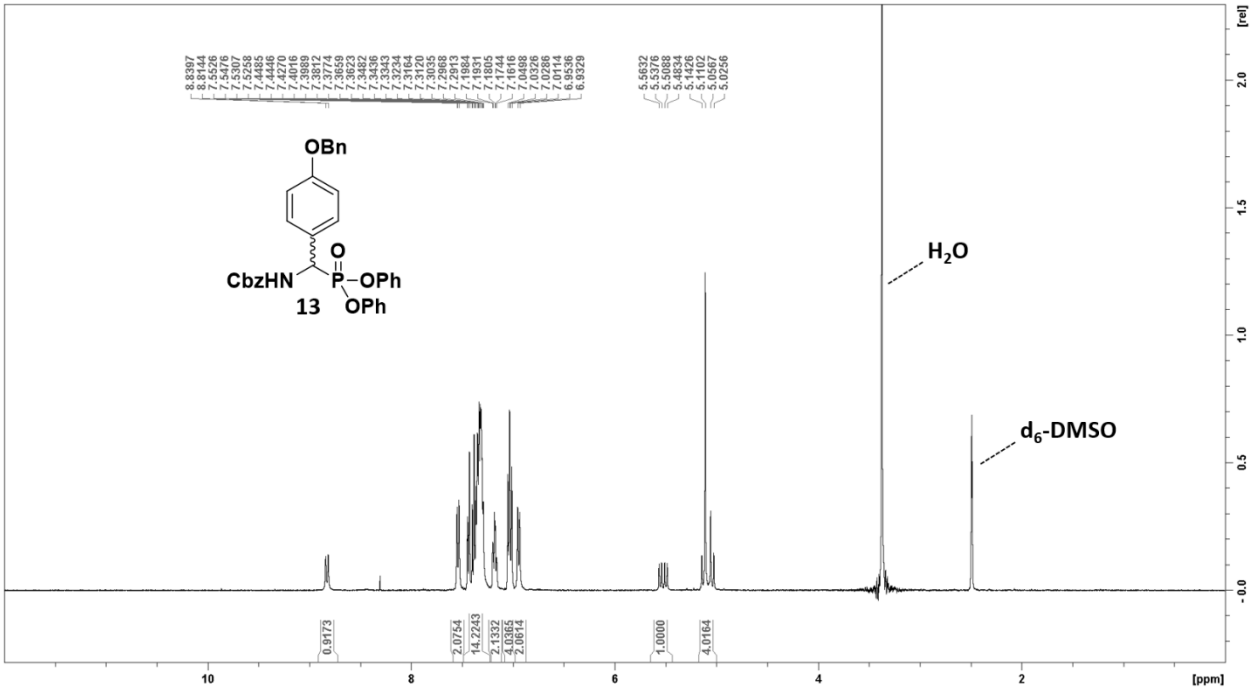
^{31}P NMR of **12** as a ~1:1 diastereomeric mixture. Characterization by ^{1}H and ^{19}F NMR was impeded by dramatic line broadening likely due to multiple charge-states and slow ion-pair exchange.



UPLC-HRMS analysis of **12** (~1:1 diastereomeric mixture). (Left, Bottom) UPLC trace of **12.** (Left, Top) Extracted ion chromatogram (EIC) of **12**, m/z = 424.107 ± 0.05, indicating that the free fluorophosphonate elutes at different retention times, likely due to differences between diastereomers and different protonation-states. (Right) Mass spectrum of **12**.



UPLC-HRMS analysis of **6**. (Left, Bottom) UPLC trace of **6**. (Left, Top) Extracted ion chromatogram (EIC) of **6**, m/z = 438.1225 ± 0.009, indicating elution of **6** at different retention times, likely due to the differences between diastereomers and different protonation-states. (Right) Mass spectrum of **6**.



^{1}H NMR of racemic **13** in d_6-DMSO.

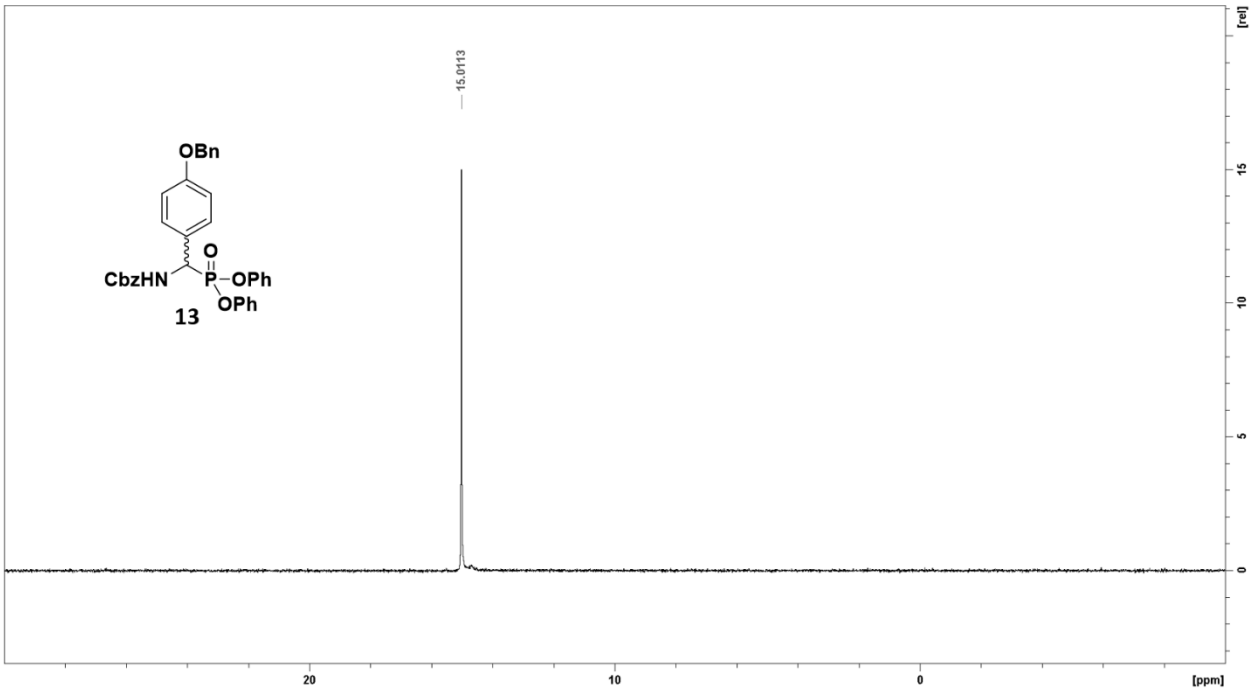


Figure 38. ^{31}P NMR of racemic **13** in d_6-DMSO.

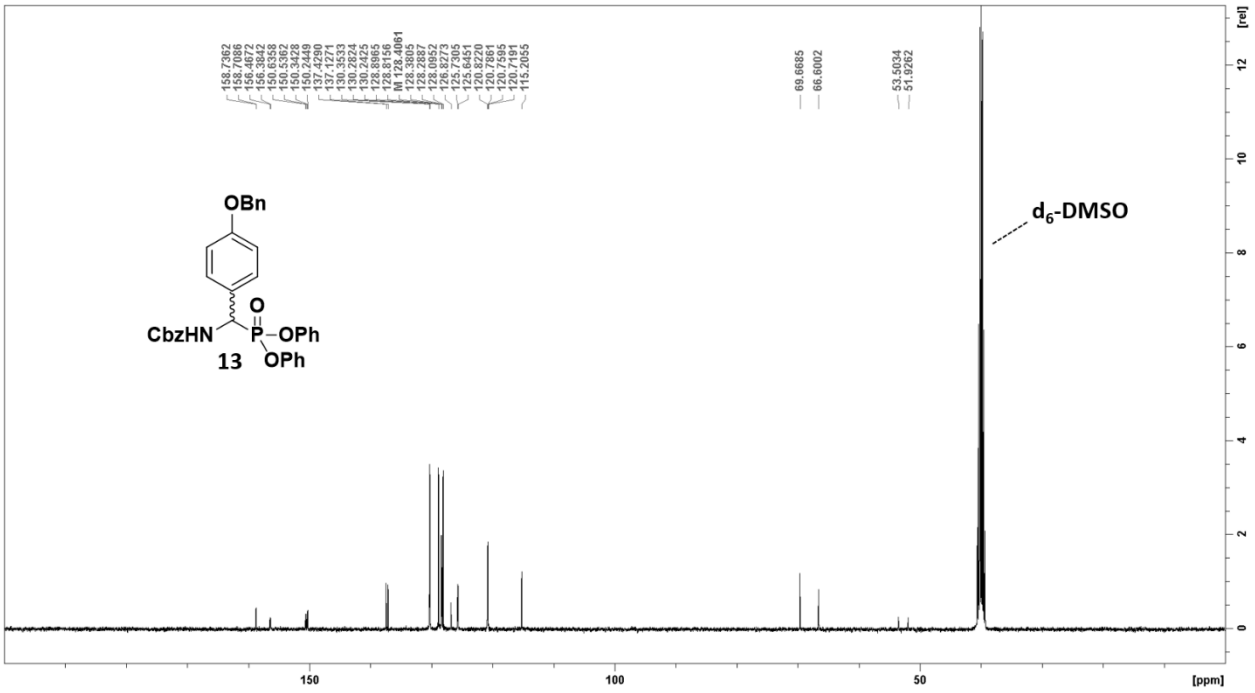


Figure 39. ^{13}C NMR of racemic **13** in d_6-DMSO.