SUPPORTING INFORMATION

Use of Deuterium Labeling Studies to Determine the Stereochemical Outcome of Pd Migrations during an Asymmetric Intermolecular Heck Reaction

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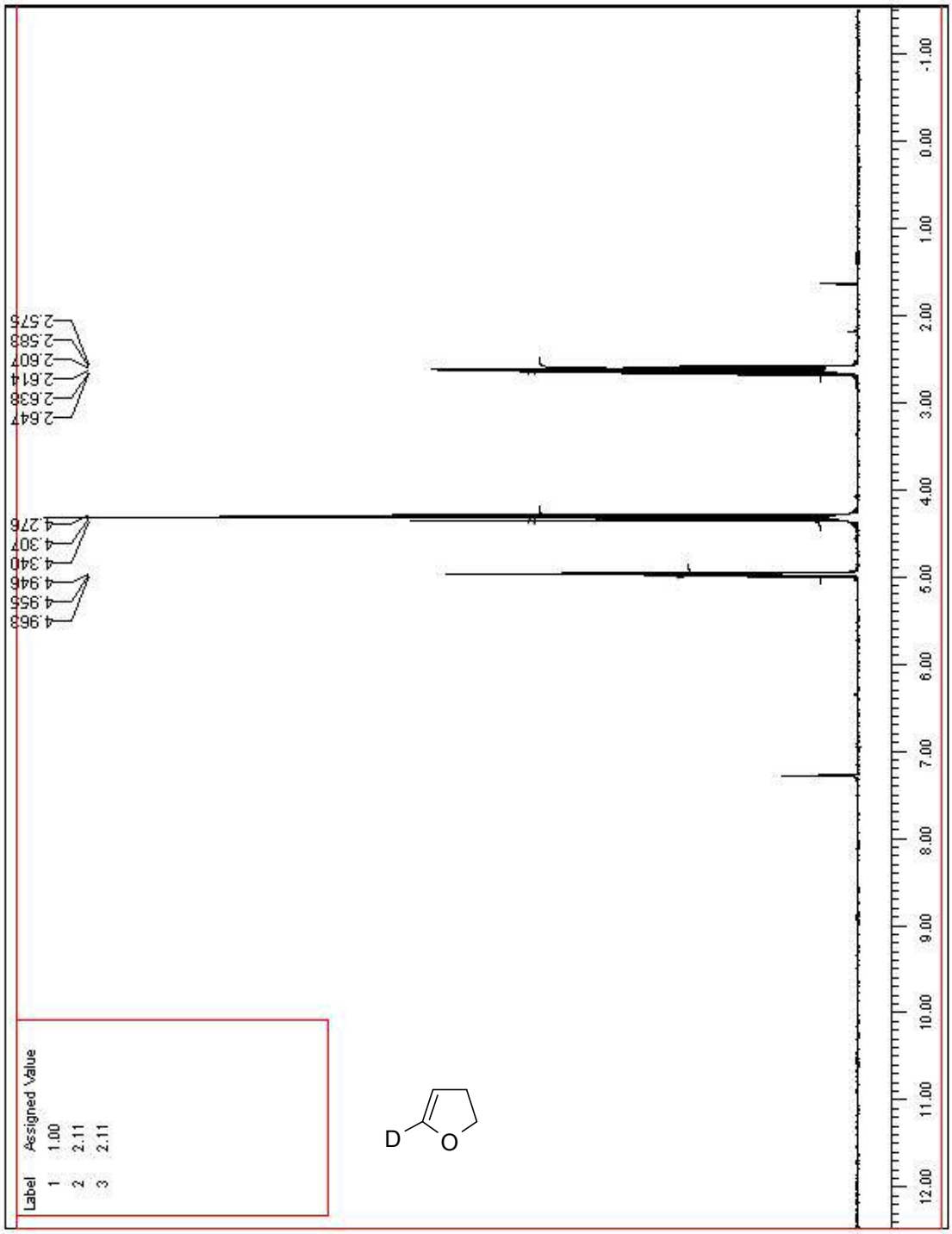
General Procedure 1: for the conversion of a lactone to a lactol: A solution of freshly distilled lactone (2.6 M, 1 equiv) in dichloromethane (DCM) was cooled in a dry ice/acetone bath for 75-120 min. A fridge-cold solution of DIBAL in DCM (1.2 equiv) was added slowly down the walls of the flask over 25 min. The reaction was stirred in the cold bath for 90-95 min and then MeOH or MeOD (78 mL/mol lactone) and saturated aqueous Rochelle salt solution (78 mL/mol lactone) were added dropwise. The reaction was then removed from the cold bath and stirred until a precipitate formed that stopped all stirring (usually after 20 min). DCM (~100 mL) was added and the reaction was stirred vigourously to suspend the solid material. This was then filtered and the filtrate was concentrated in vacuo to give the crude lactol while the solid was subjected to Soxhlet extraction overnight in DCM. Both the crude lactol as well as the lactol recovered from the continuous extraction were found to be unstable and were used immediately, without further purification.

General Procedure 2: for the conversion of a lactol to a dihydrofuran: A solution of TsOH in quinoline (45 mM) was placed in a 50 mL 3-necked round-bottom flask. An aqueous solution of NaOH (2 M, 1.7 mL/mL quinoline solution), was frozen in a ring around the bottom of a round-bottom receiver flask. A short-path distillation tube was used to connect the two flasks, and a glass stopper was used to stopper one of the three necks, with a Teflon stopper in the third neck. The assembled apparatus was placed such that the quinoline solution was in a preheated 190 ºC wax bath and the NaOH flask was in a dry ice/acetone bath. The lactol isolated from the reduction of the lactone was added dropwise, neat, via syringe through the Teflon stopper. Once all lactol was added, the Teflon stopper was quickly exchanged for a new stopper, and the quinoline solution was

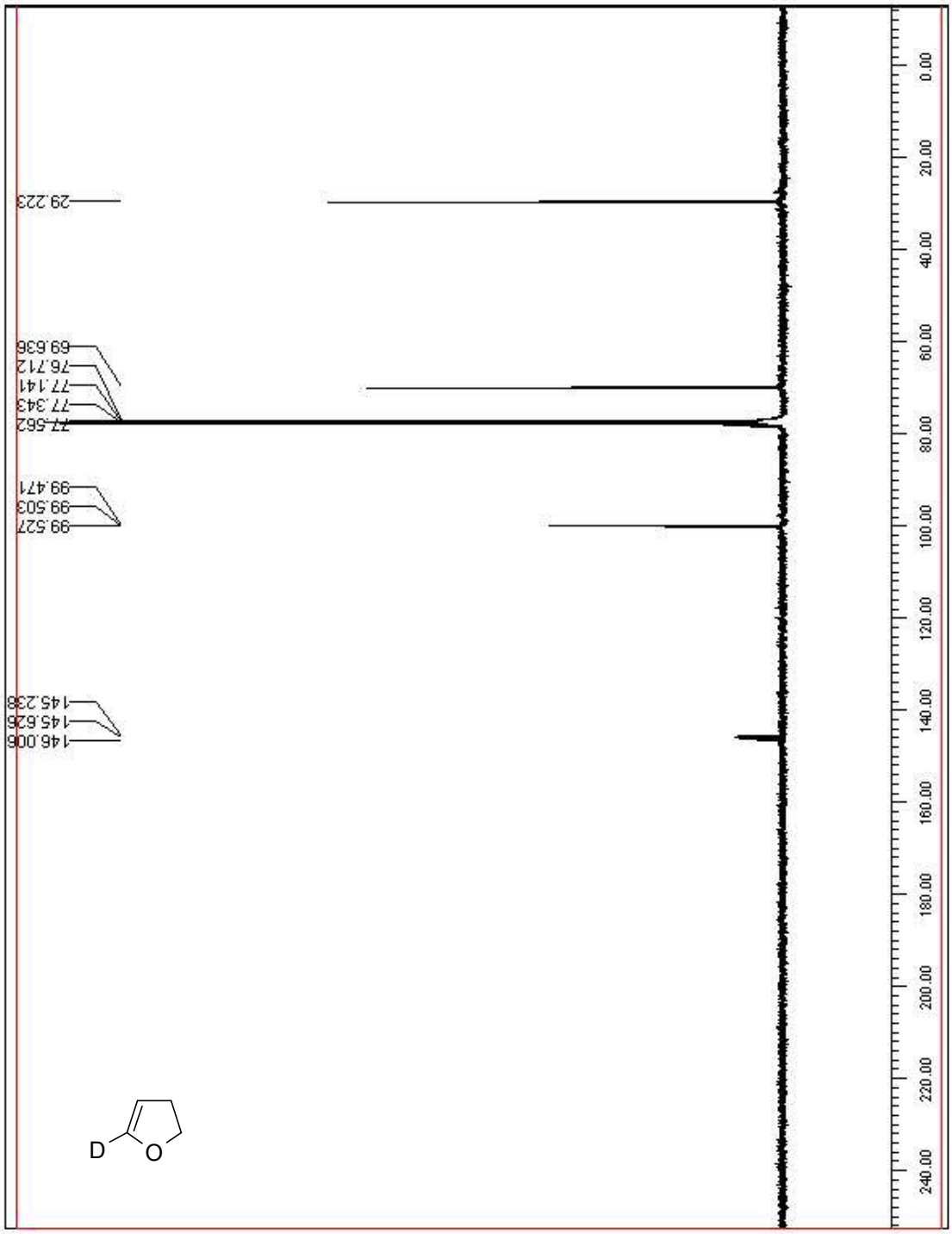
heated to 210 ºC for 60 min. The distillation apparatus was then removed from both baths and the receiver flask was removed from the apparatus. The liquid in it was quickly removed by pipette, before the NaOH solution could melt. The liquid was distilled by short-path distillation to give the dihydrofuran; traces of low-boiling solvents, such as Et_2O and DCM, were sometimes present as they cannot be separated from 2,3-dihydrofuran by fractional distillation.

General Procedure 3: for the asymmetric Heck reaction: $Pd(OAc)_2$ (9 mg, 0.04 mmol) and (*R*)-BINAP (50 mg, 0.081 mmol) were dissolved in benzene (2 mL) and stirred at room temperature for 10 min. PhOTf (0.196 mL, 1.21 mmol), *i*-Pr_2NEt (0.697 mL, 4.10 mmol), and the appropriate 2,3-dihydrofuran (0.513 mL, 6.77 mmol) were added, and the reaction vial was sealed and stirred in a pre-heated 40 ºC oil bath for 24 h. The reaction was then diluted with hexanes (10 mL) and filtered through a Pasteur pipette silica gel column (~ 1/8" tall). The solution was analyzed by chiral GC, and then concentrated *in vacuo*; pentane (10 mL) was added to this mixture, causing impurities to precipitate out, and these were filtered off. The pentane was removed *in vacuo* and NMR data for the reaction mixture was obtained. The products were then separated by flash column chromatography (19:1 pentane:diethyl ether) and characterized by NMR.

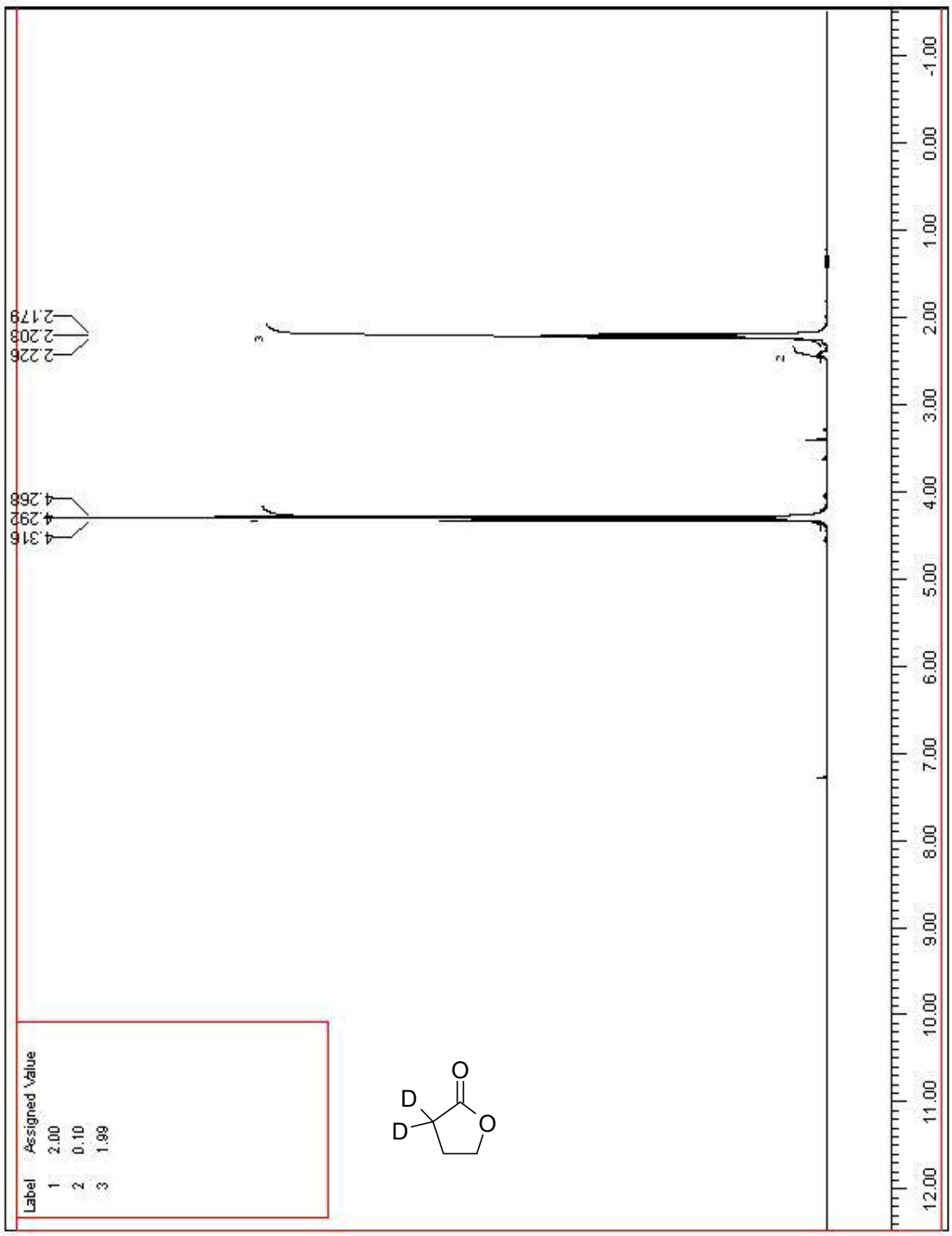
^{1}H NMR of 5-deuterio-2,3-dihydrofuran (**2b**)



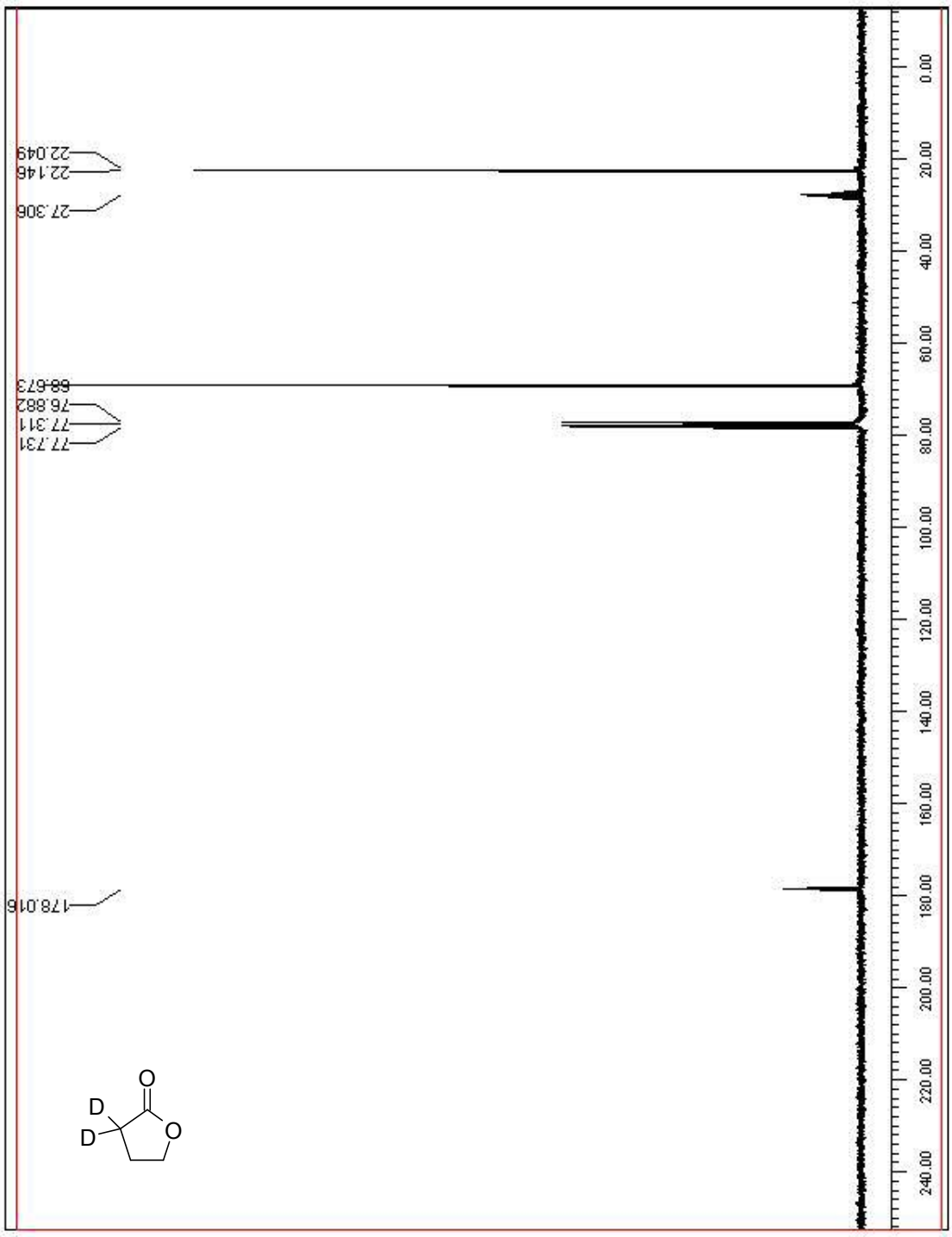
^{13}C NMR of 5-deuterio-2,3-dihydrofuran (**2b**)



^{1}H NMR of 2,2-dideuterio-γ-butyrolactone (**17c**)



^{13}C NMR of 2,2-dideuterio-γ-butyrolactone (**17c**)



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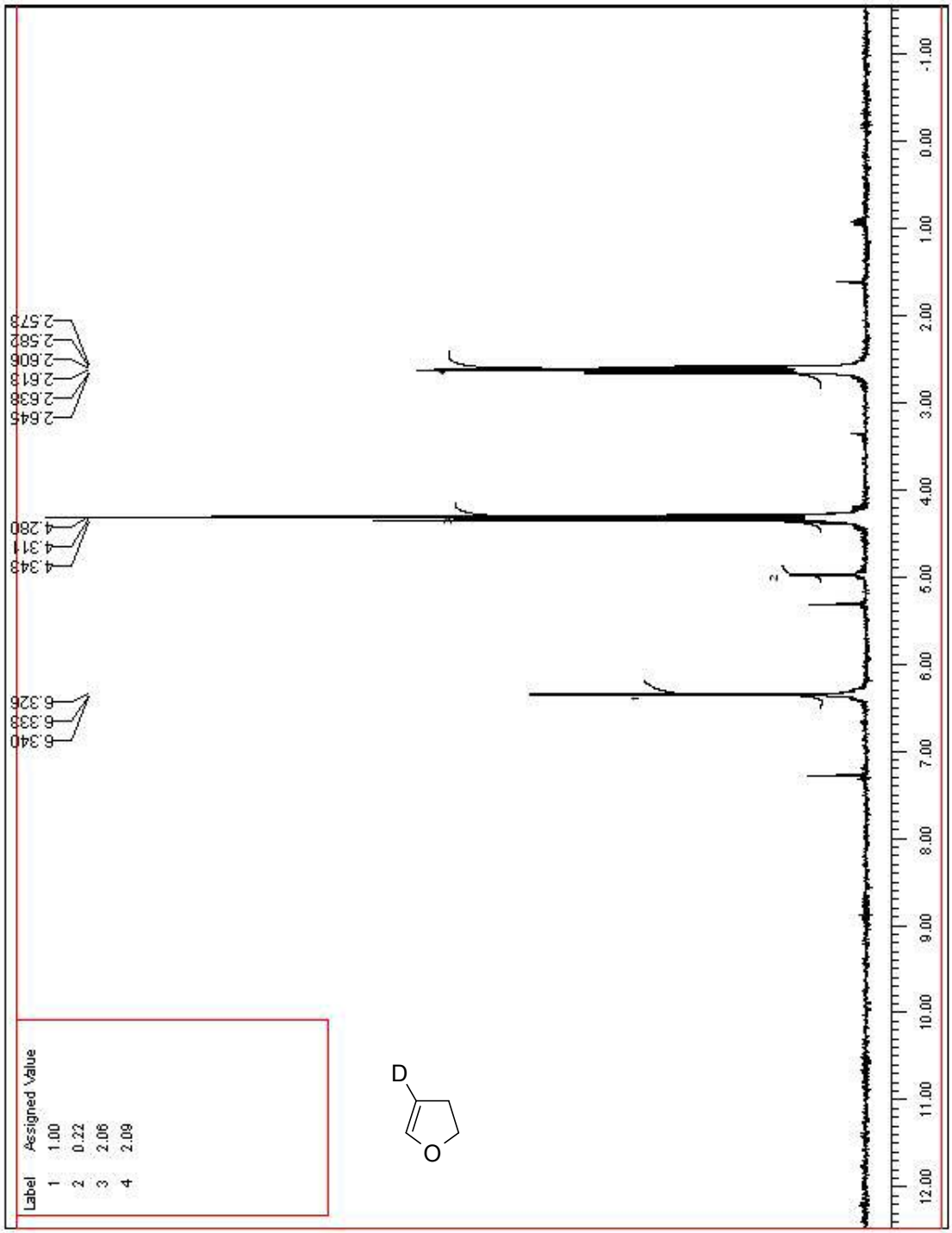

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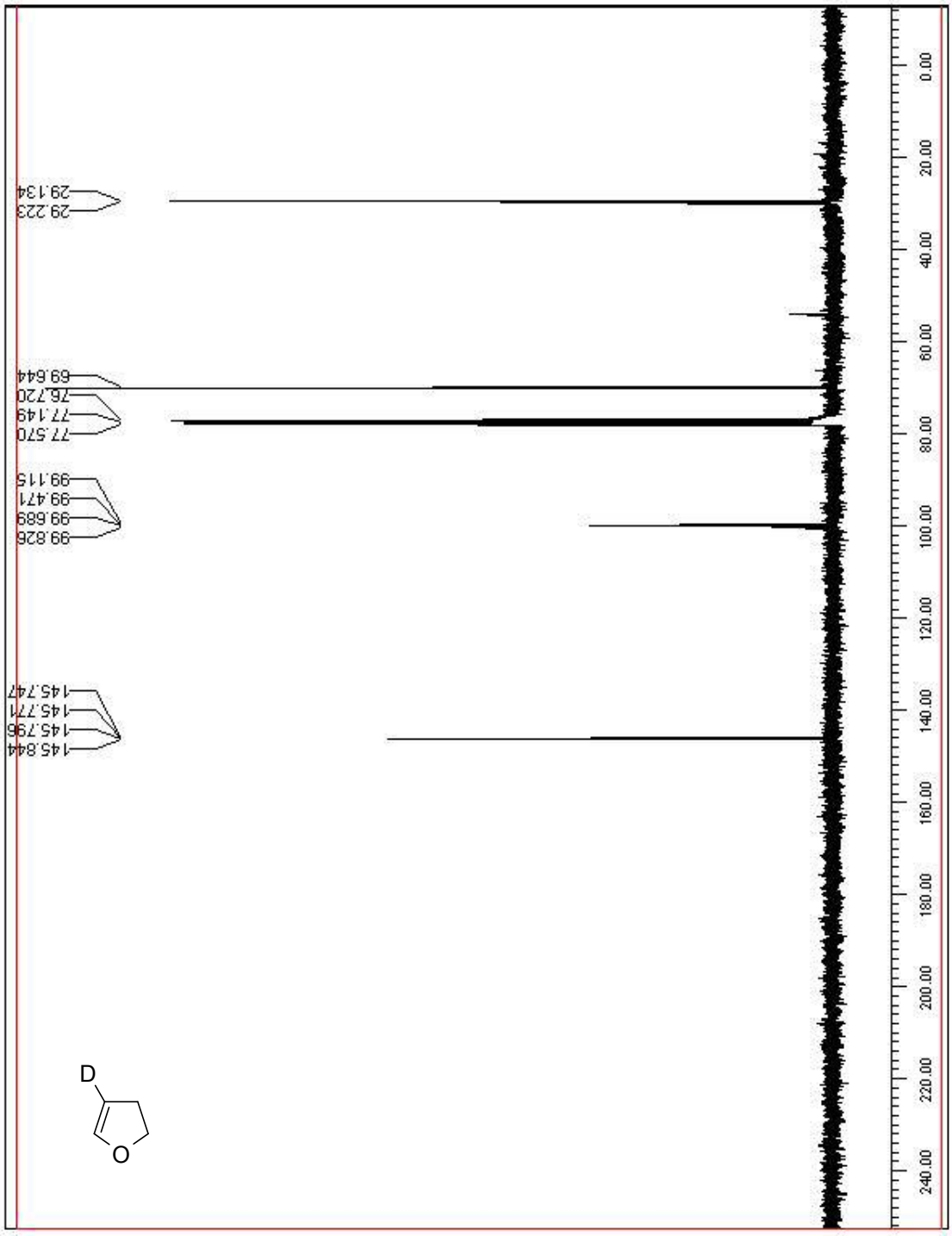

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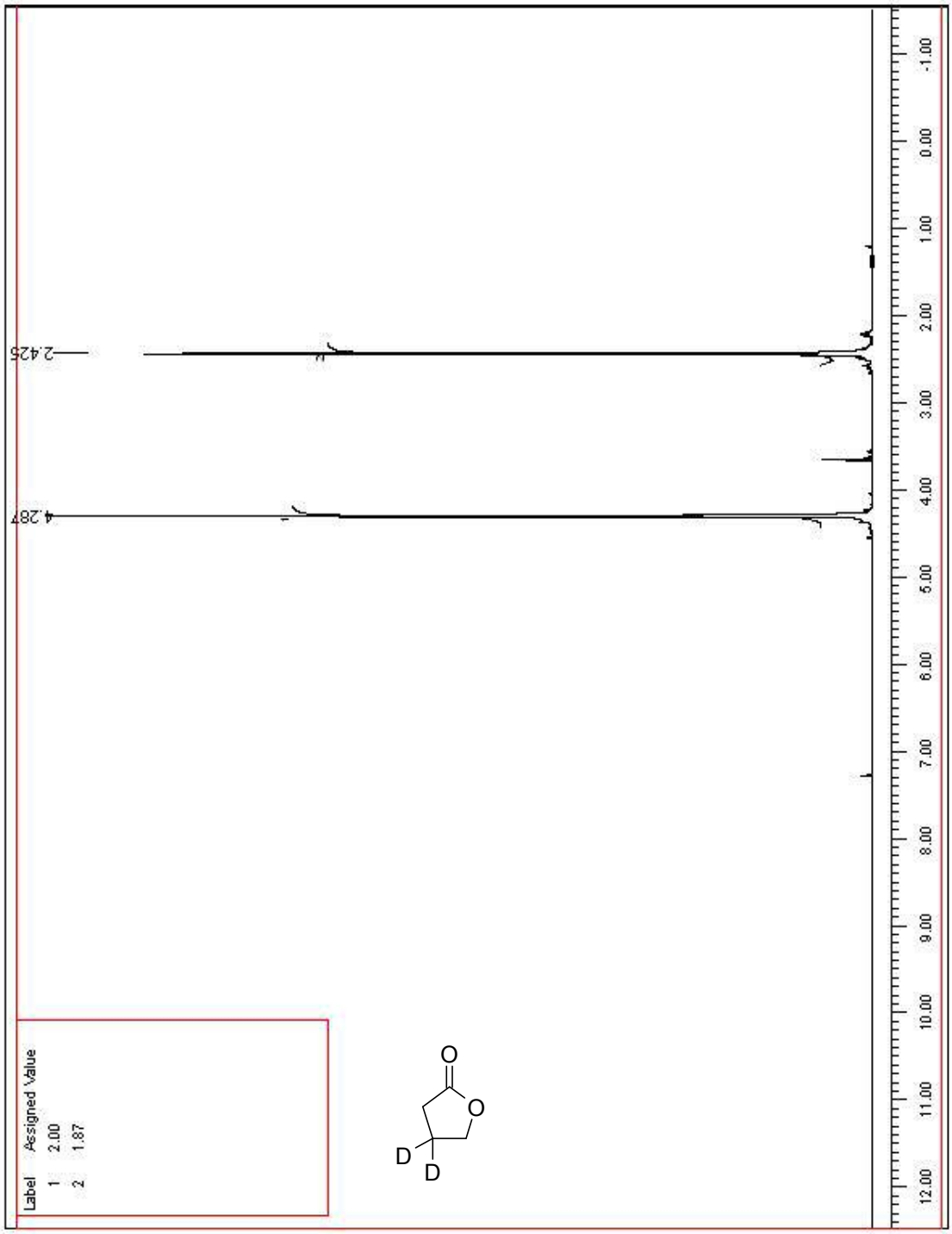
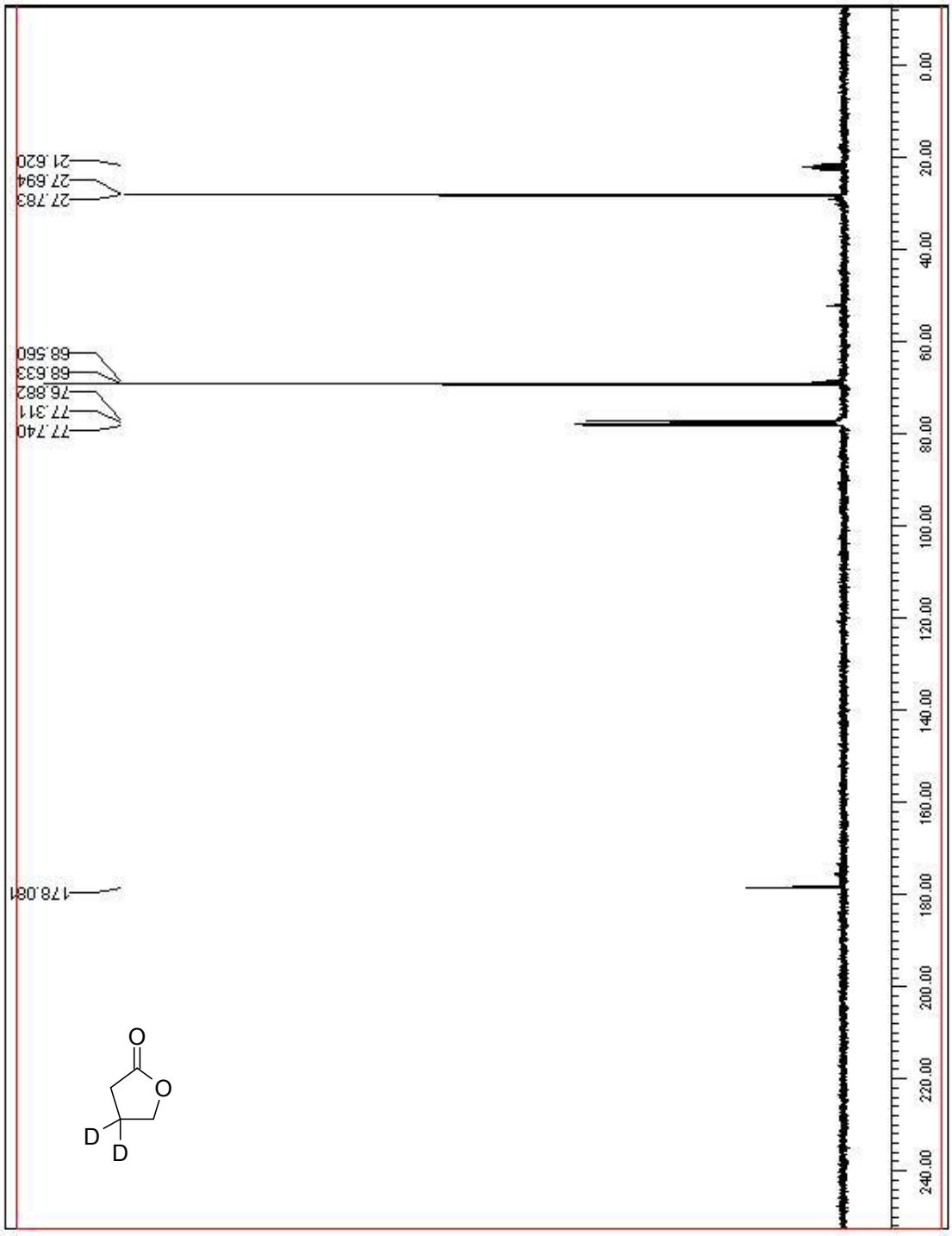


^{13}C NMR of 3,3-dideutero-γ-butyrolactone (**17d**)



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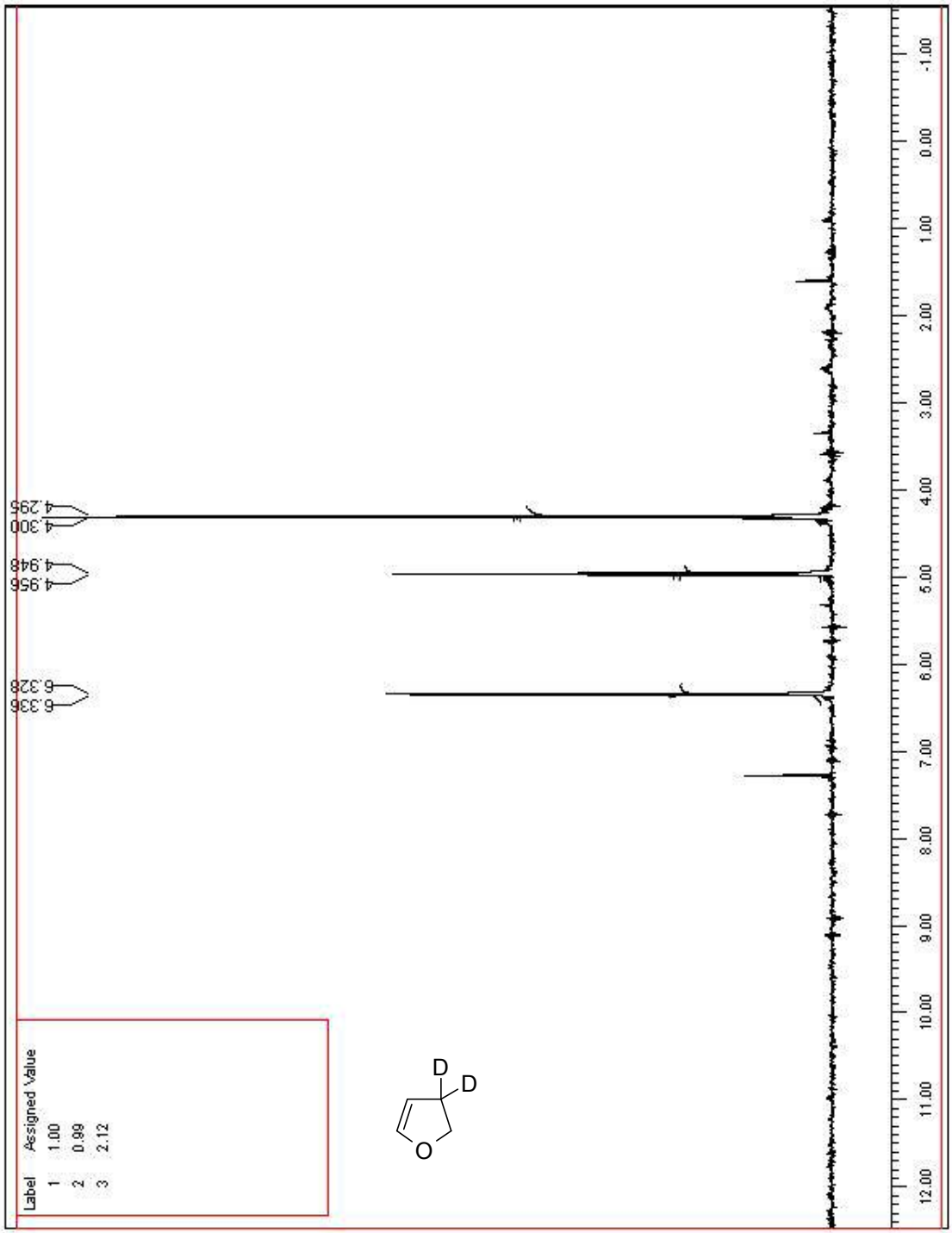

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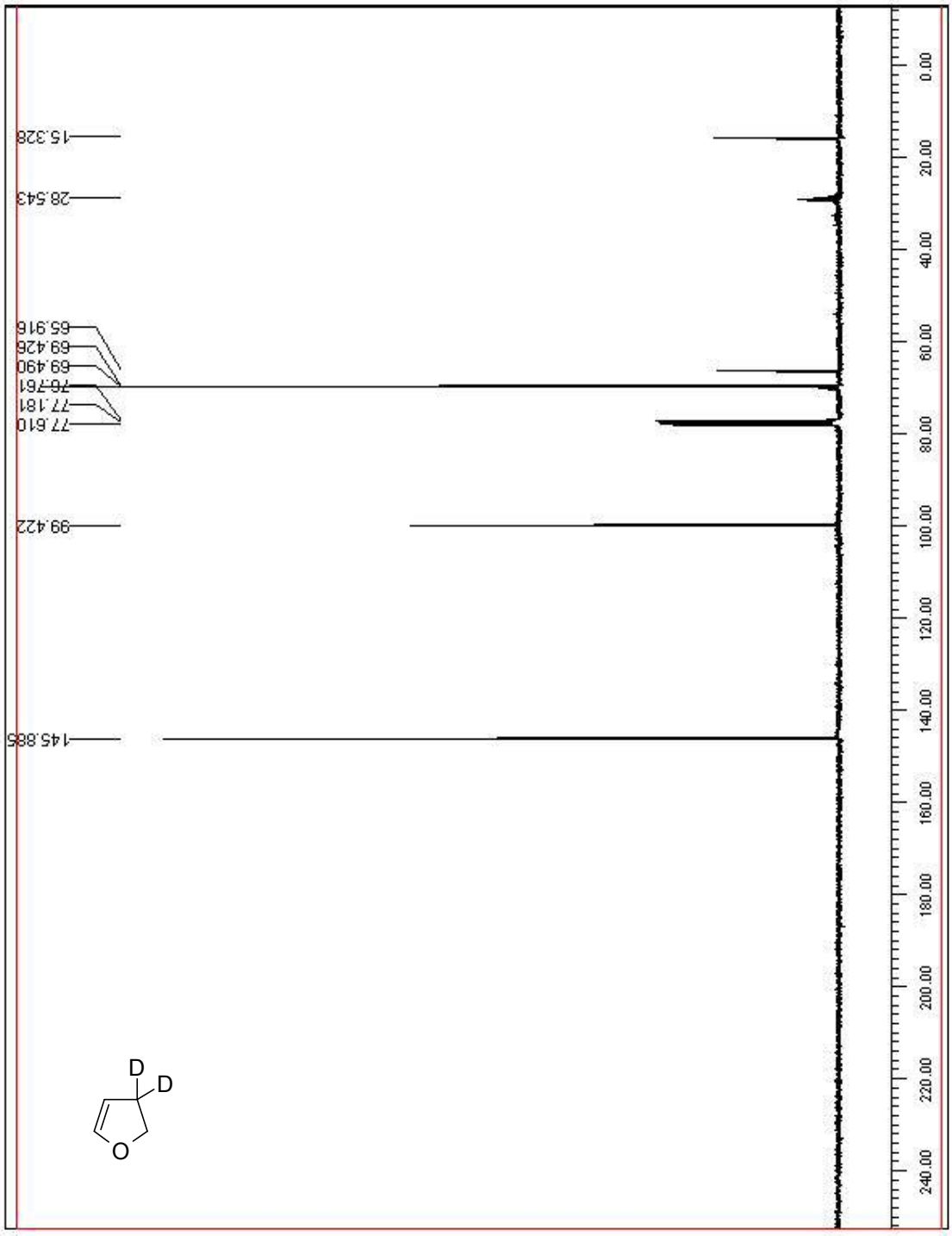
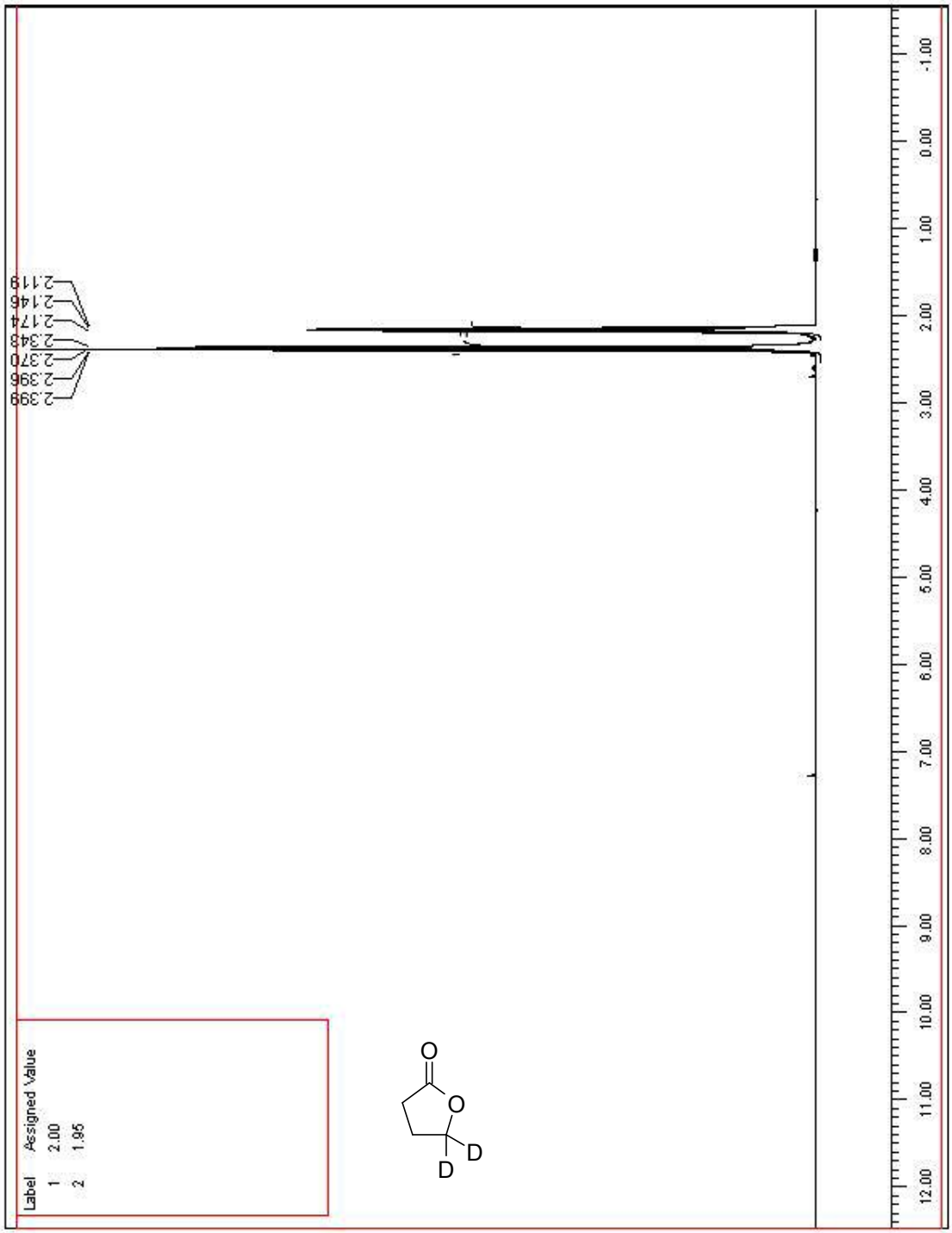
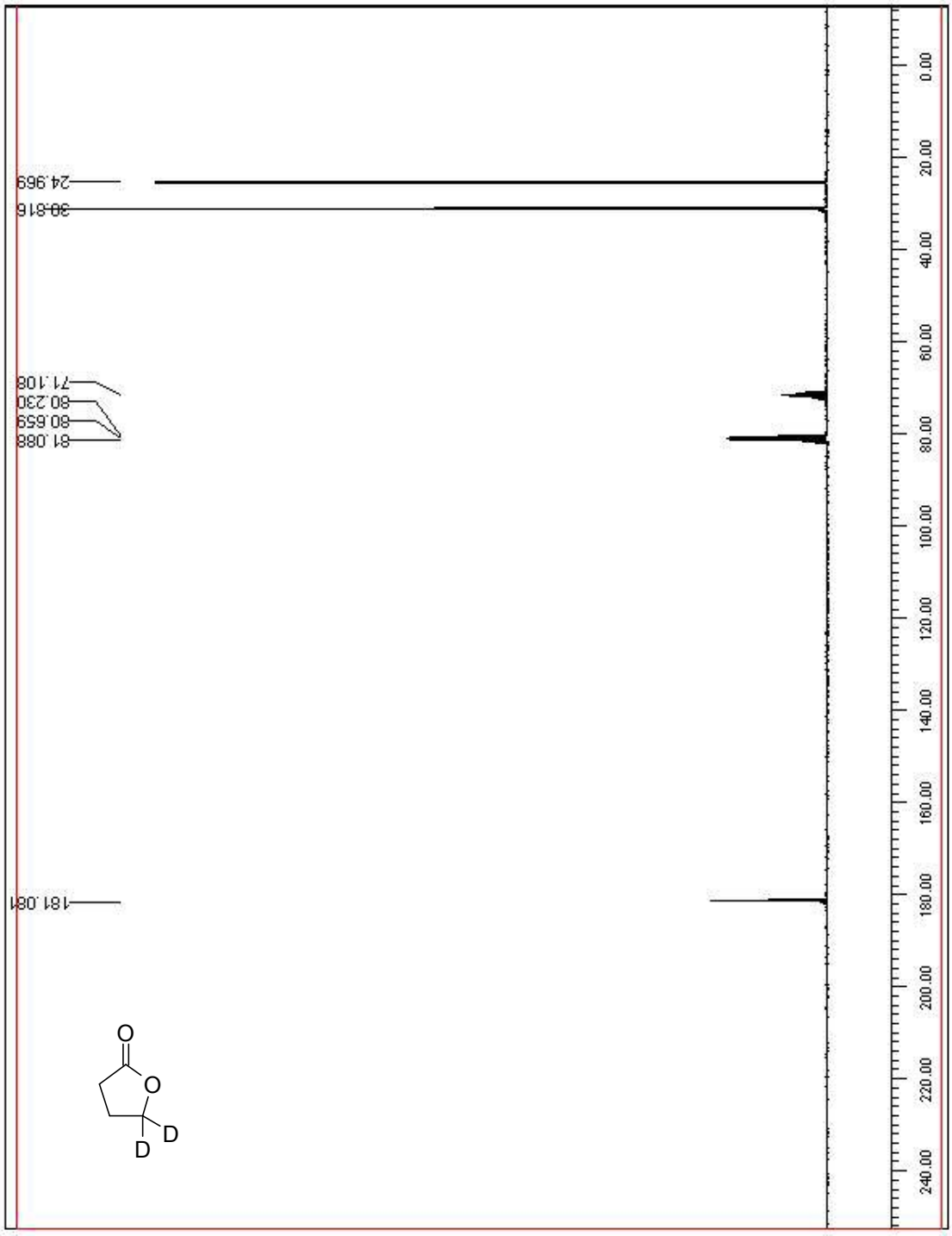


^{1}H NMR of 4,4-dideutero-γ-butyrolactone (**17e**)



^{13}C NMR of 4,4-dideutero-γ-butyrolactone (**17e**)



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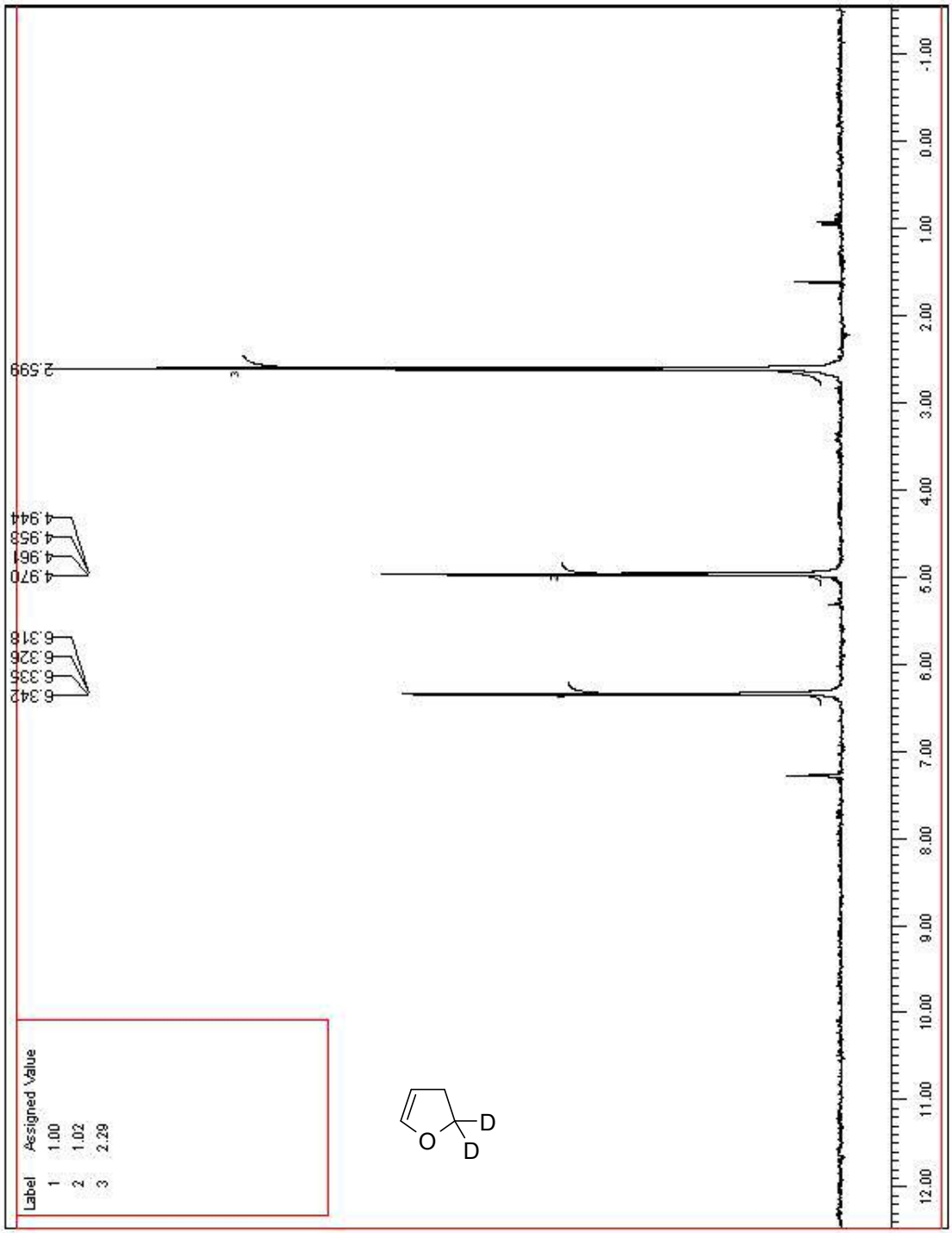

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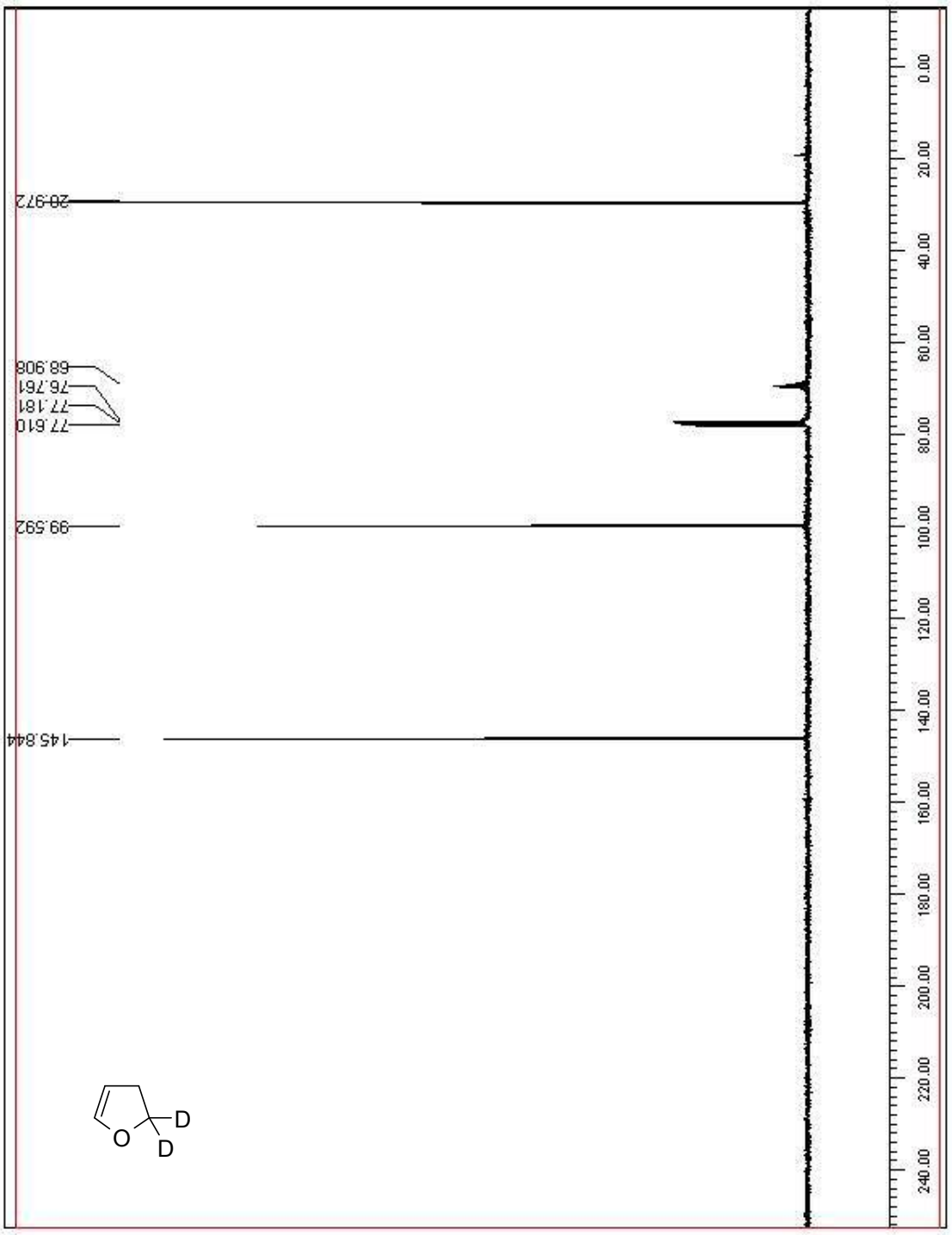
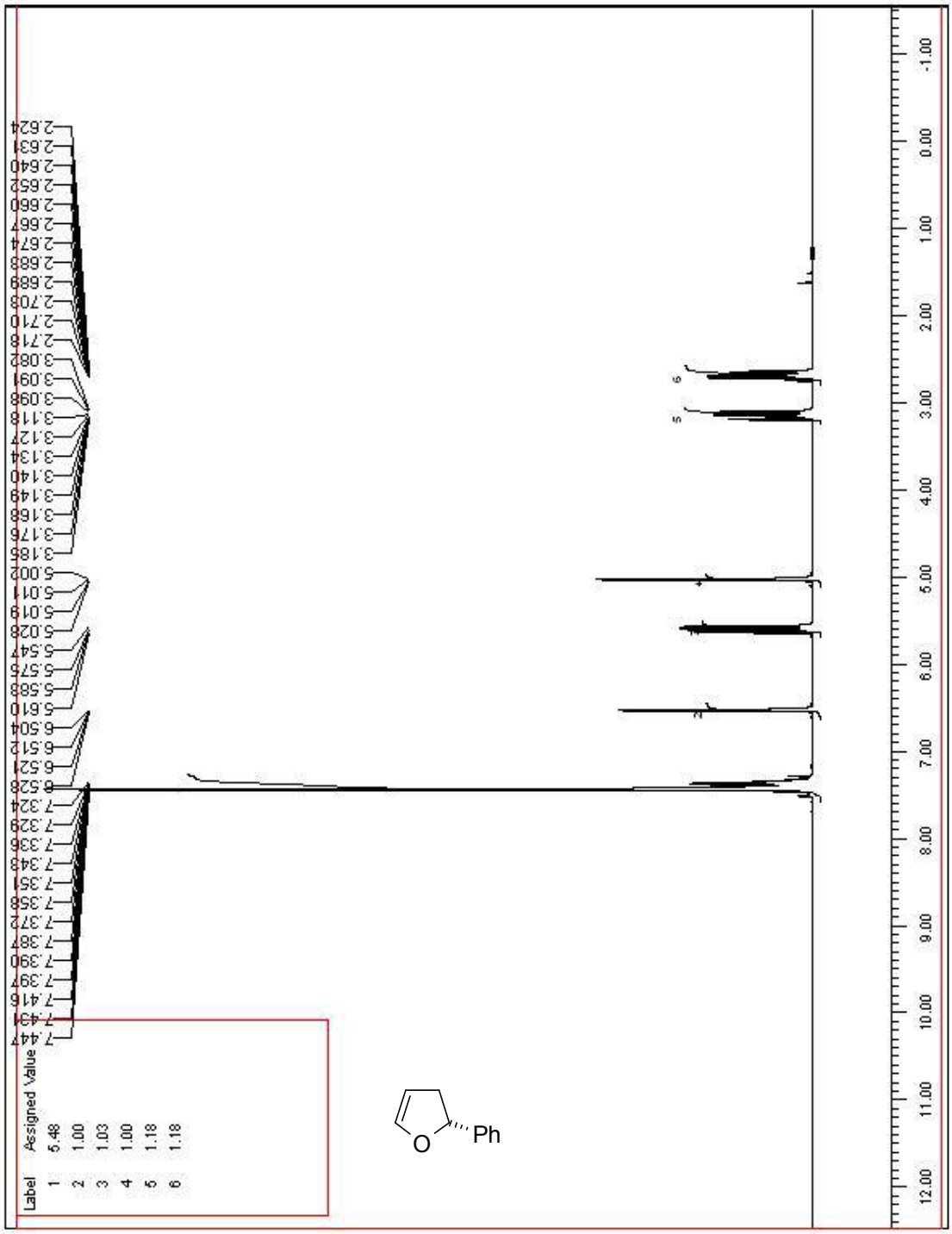


^{1}H NMR of 2-phenyl-2,3-dihydrofuran (**6a**)



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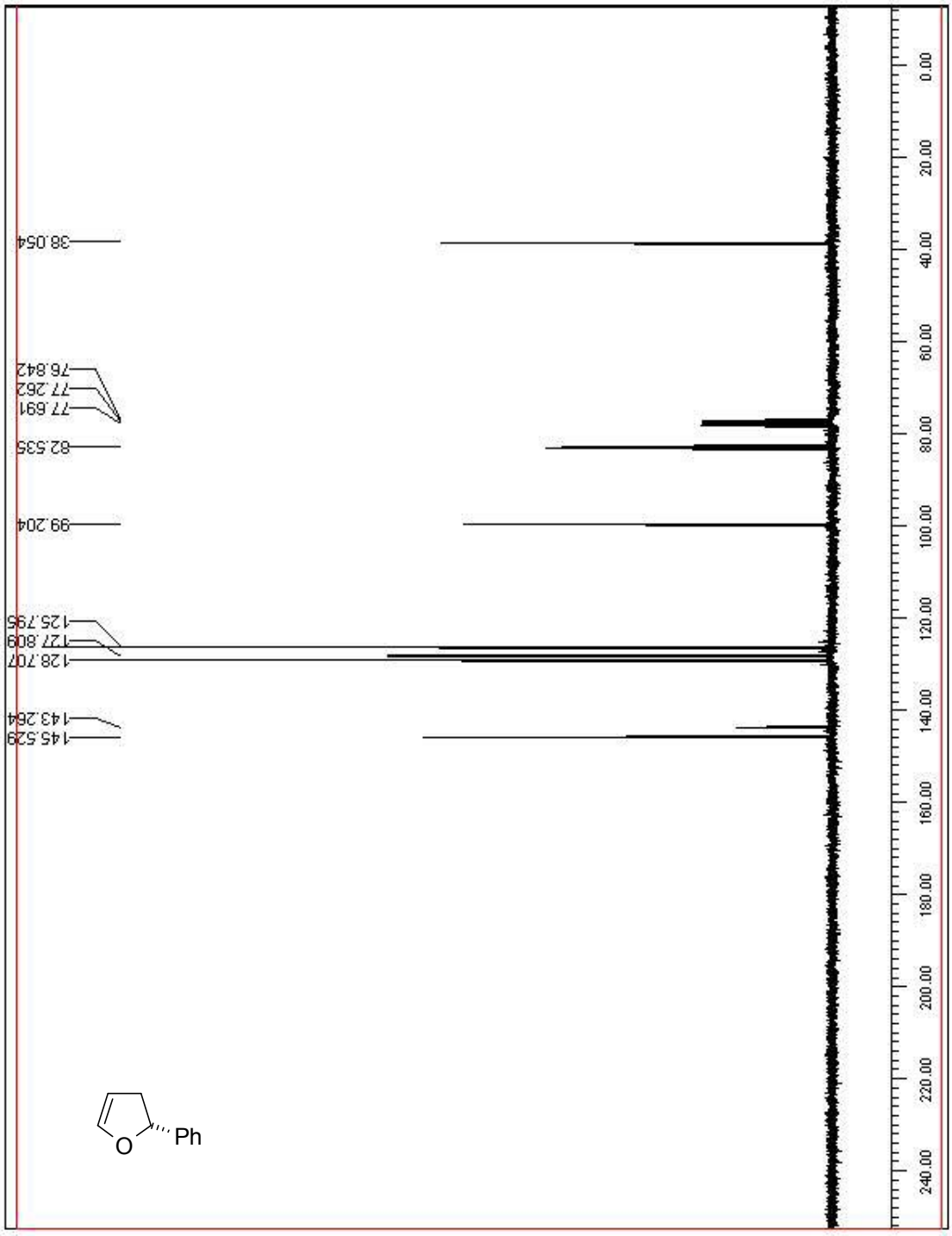
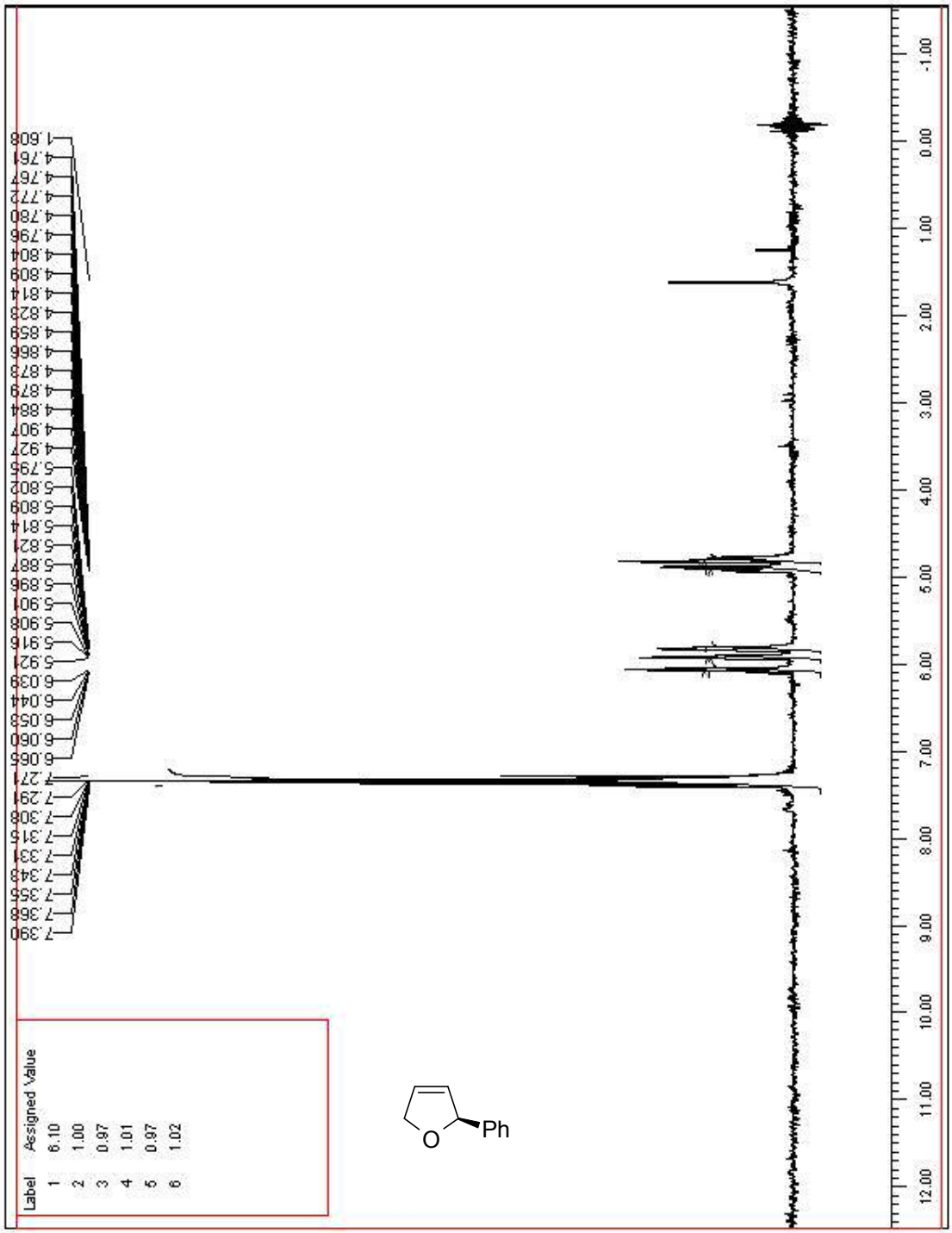
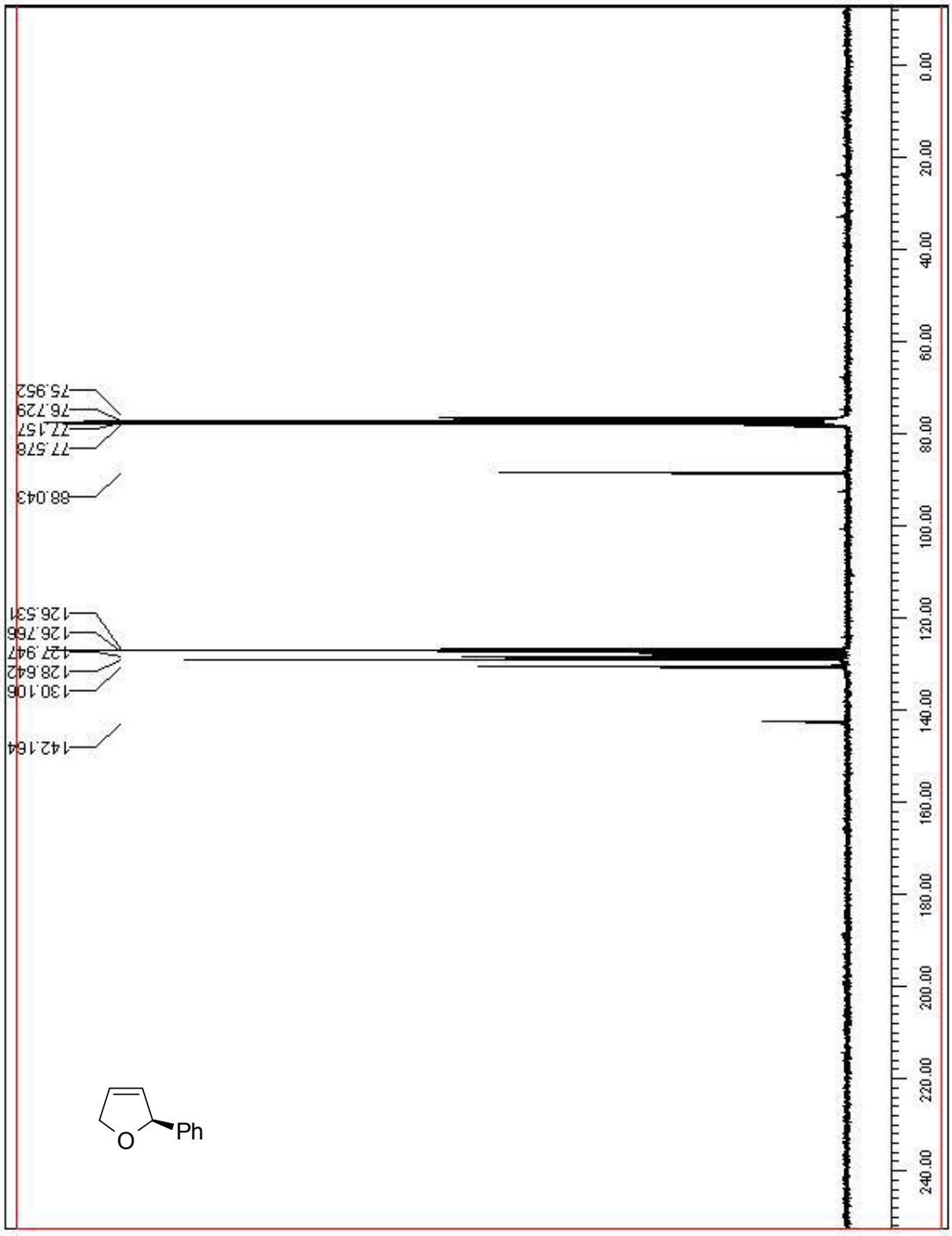


^{1}H NMR of 2-phenyl-2,5-dihydrofuran (**7a**)



^{13}C NMR of 2-phenyl-2,5-dihydrofuran (**7a**)



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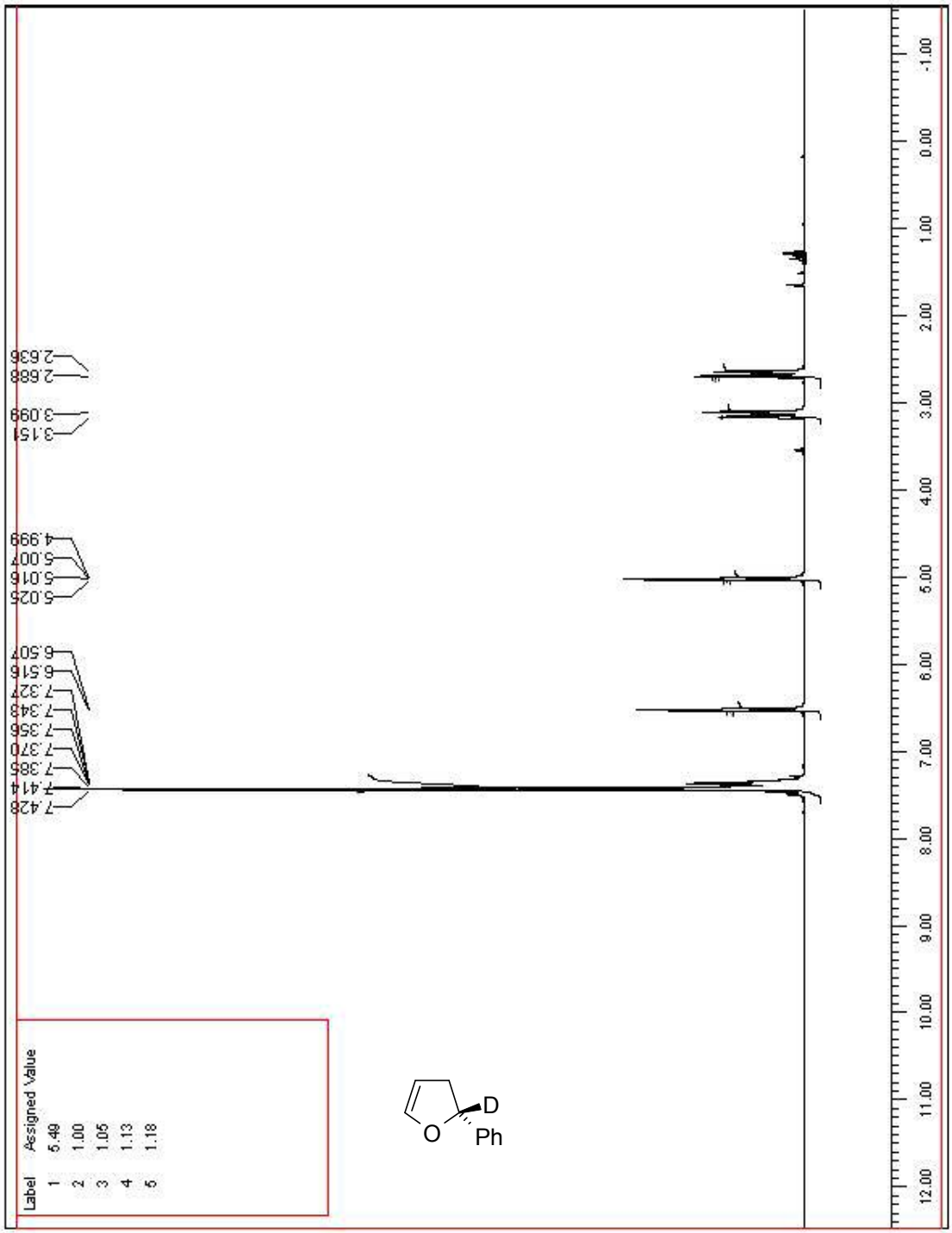

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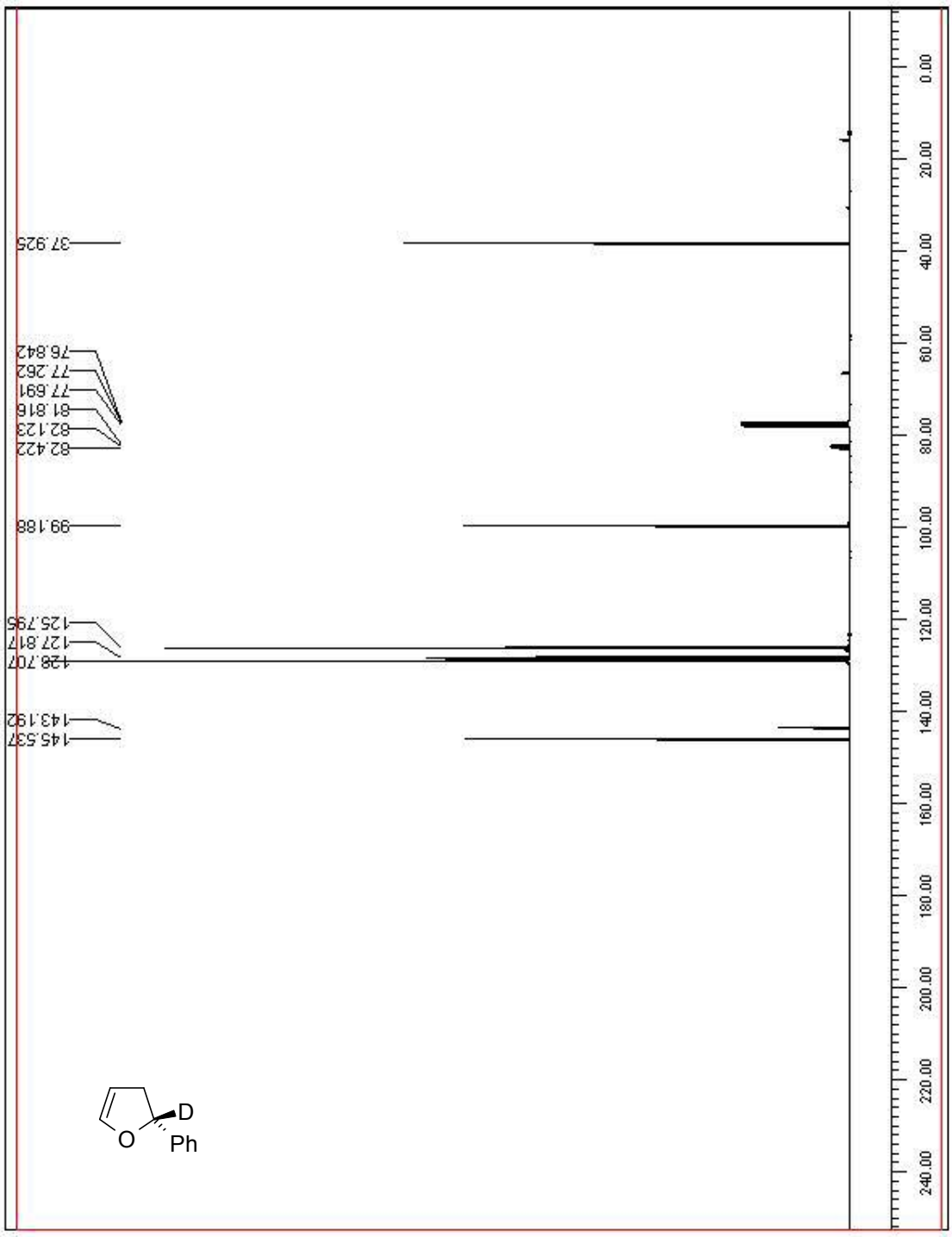

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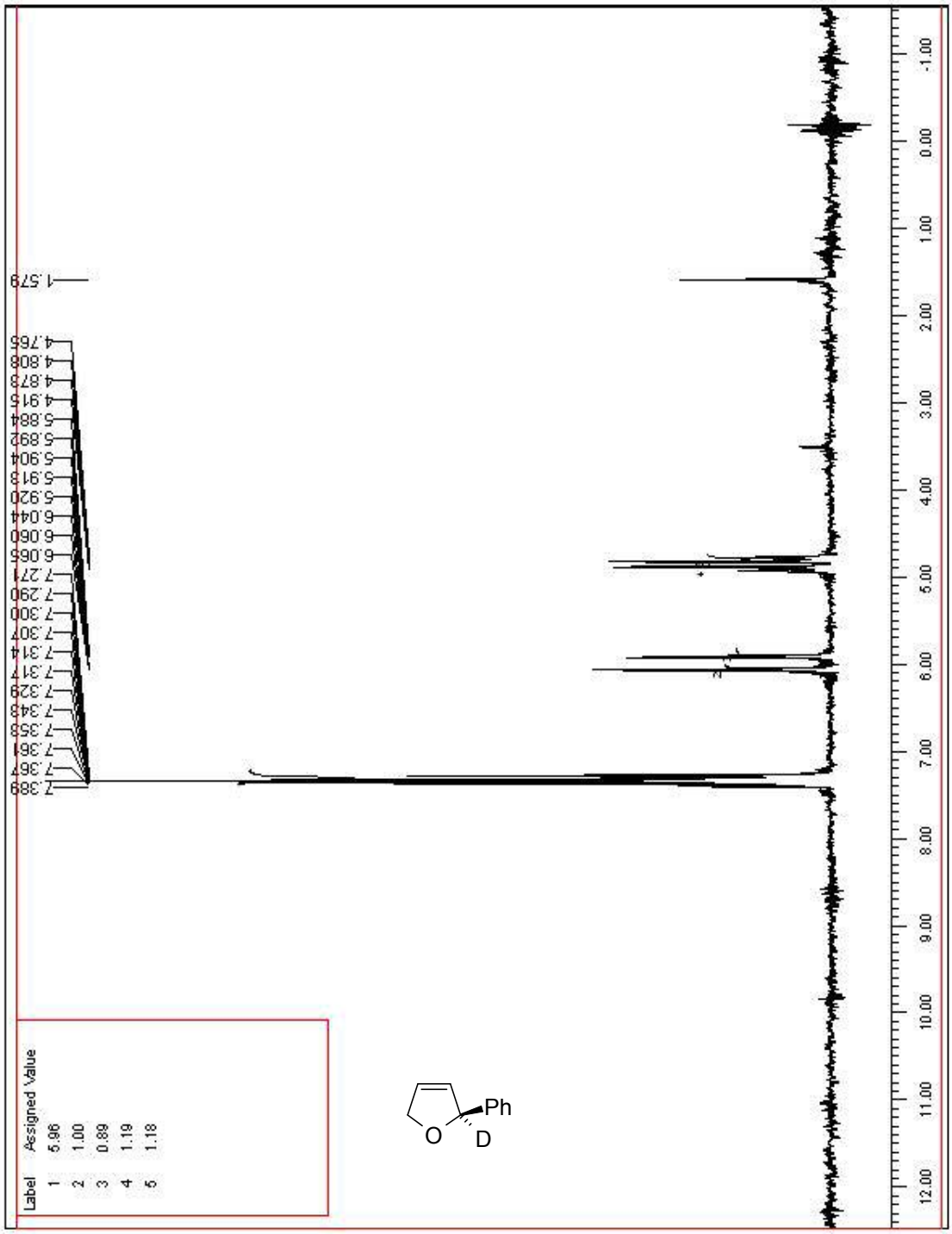

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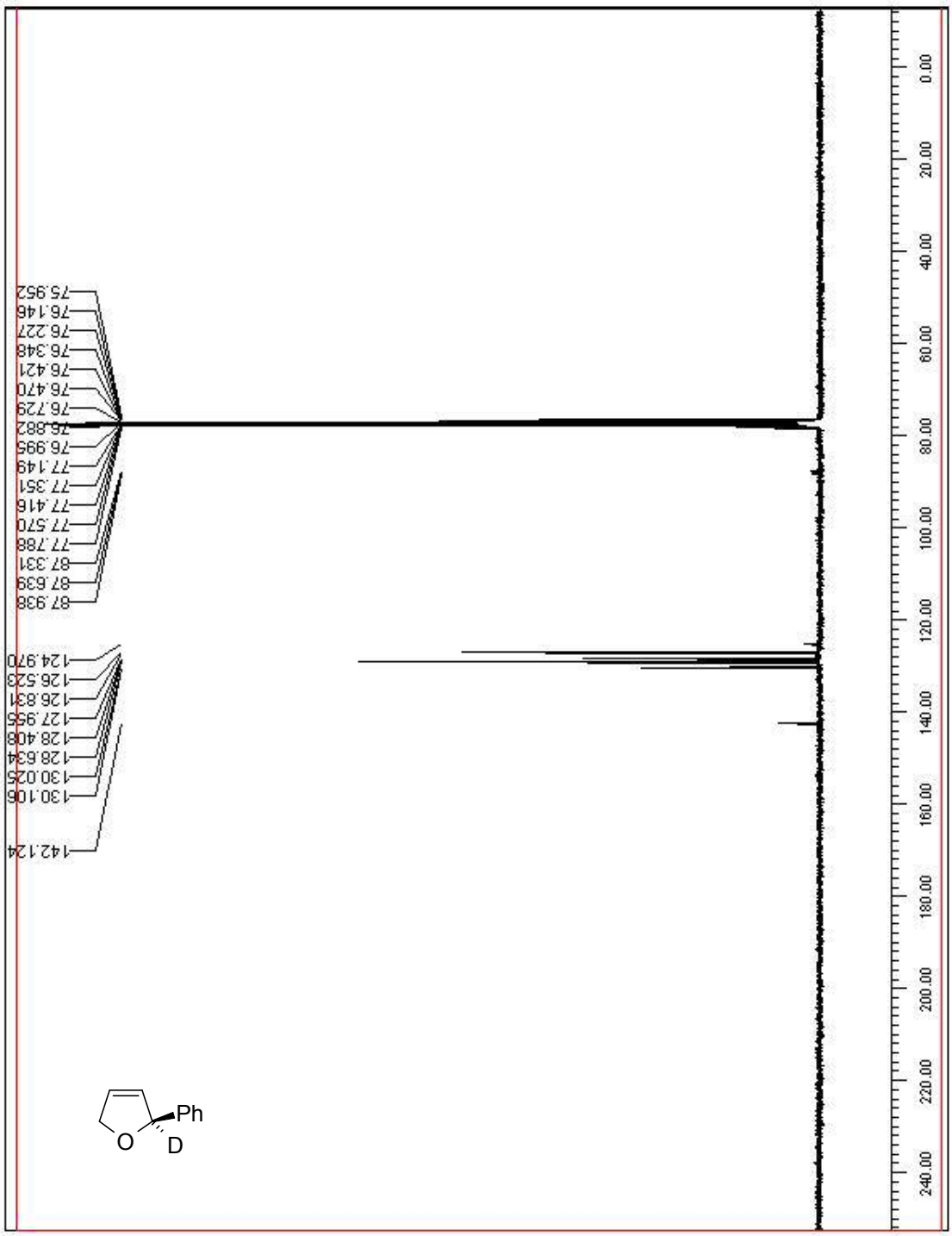
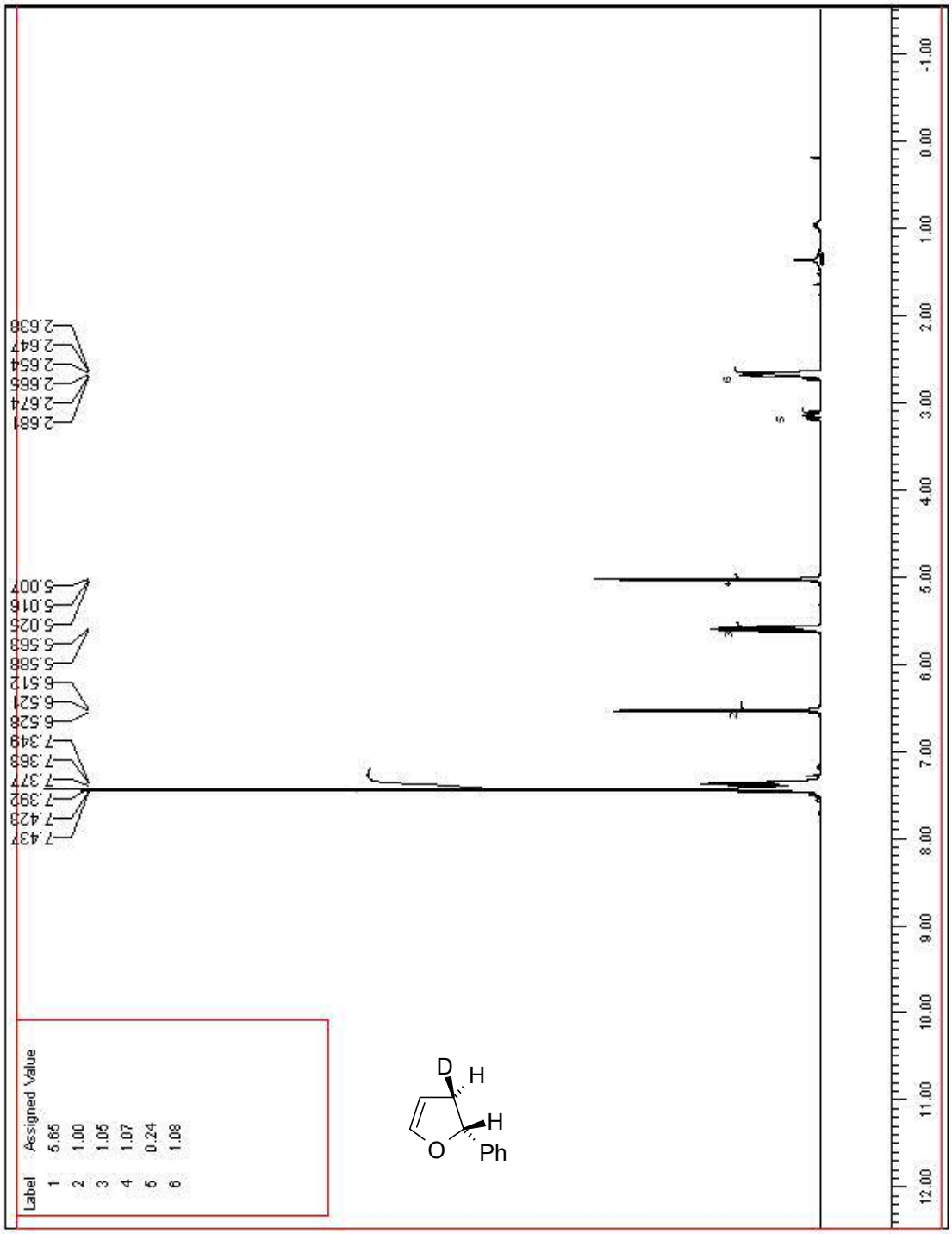


^{1}H NMR of (2*R*,3*R*)-3-deutero-2-phenyl-2,3-dihydrofuran (**6c**)



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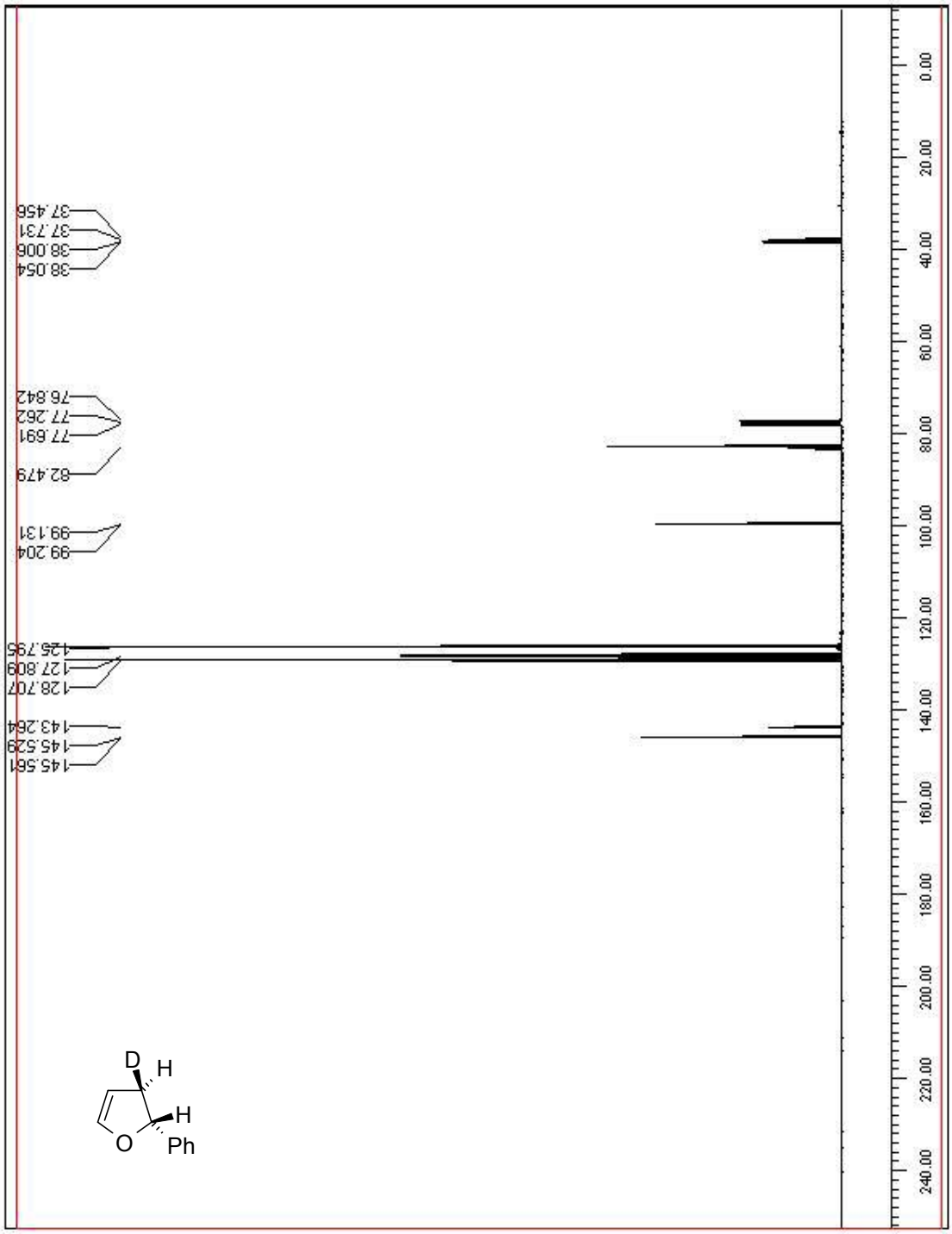

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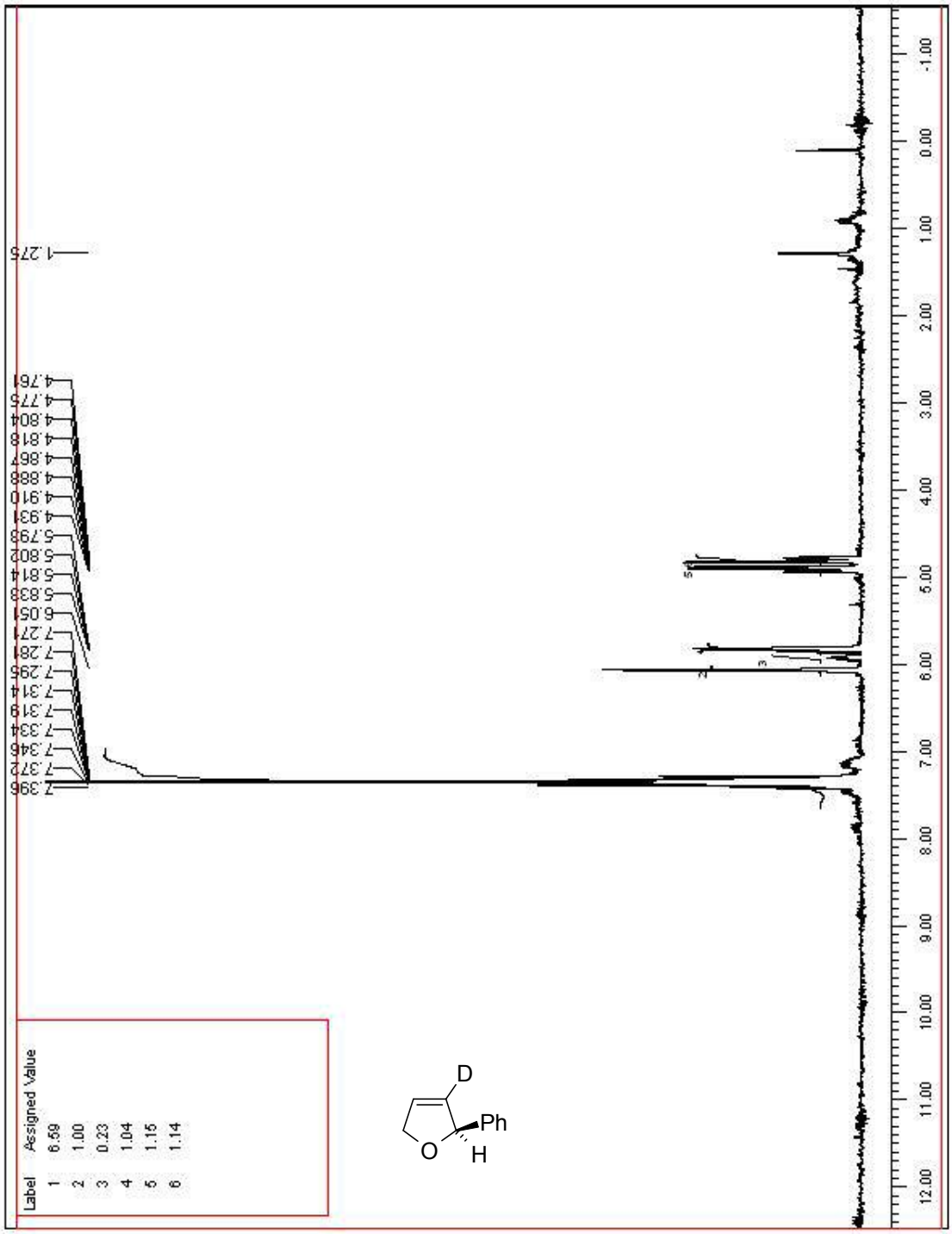

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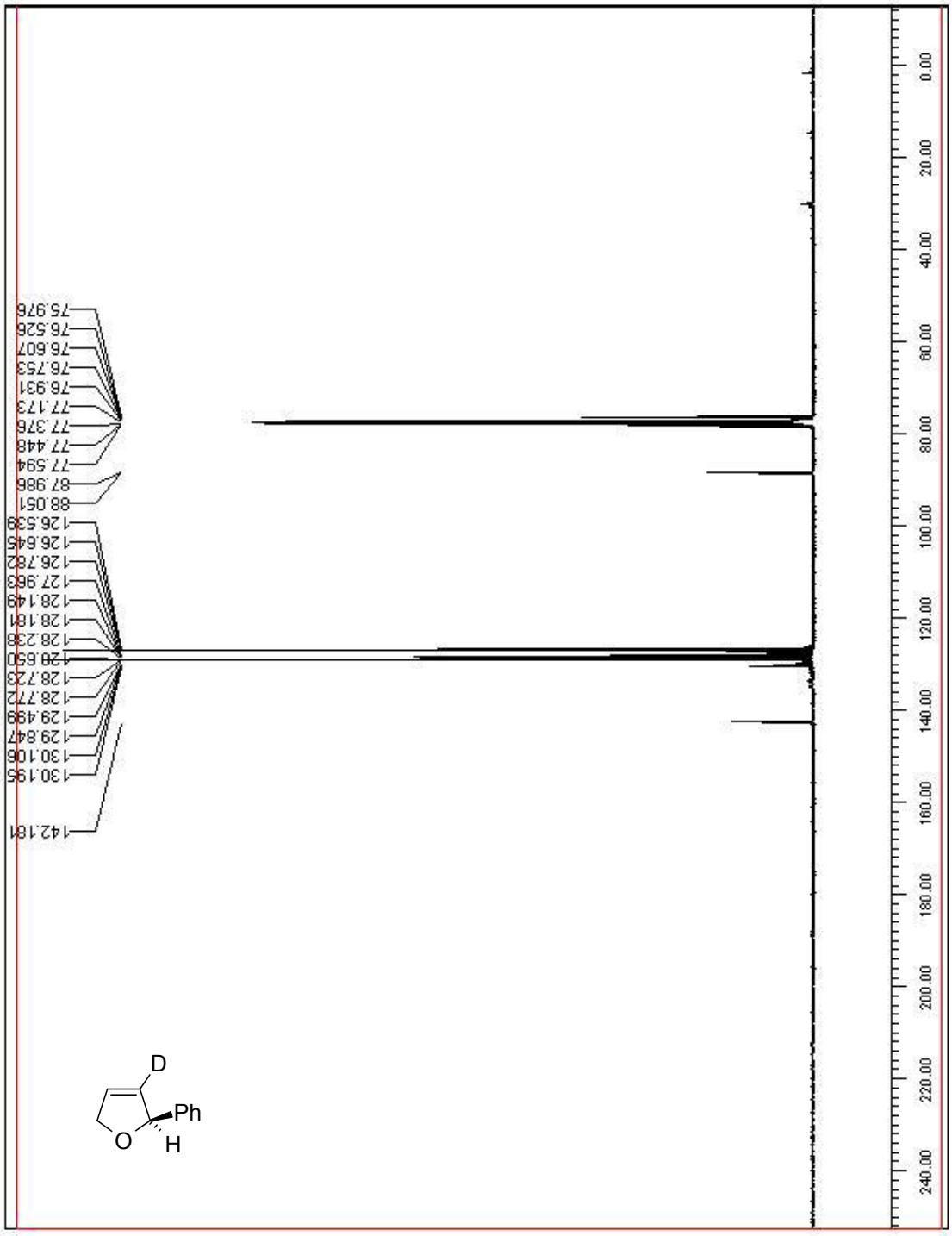

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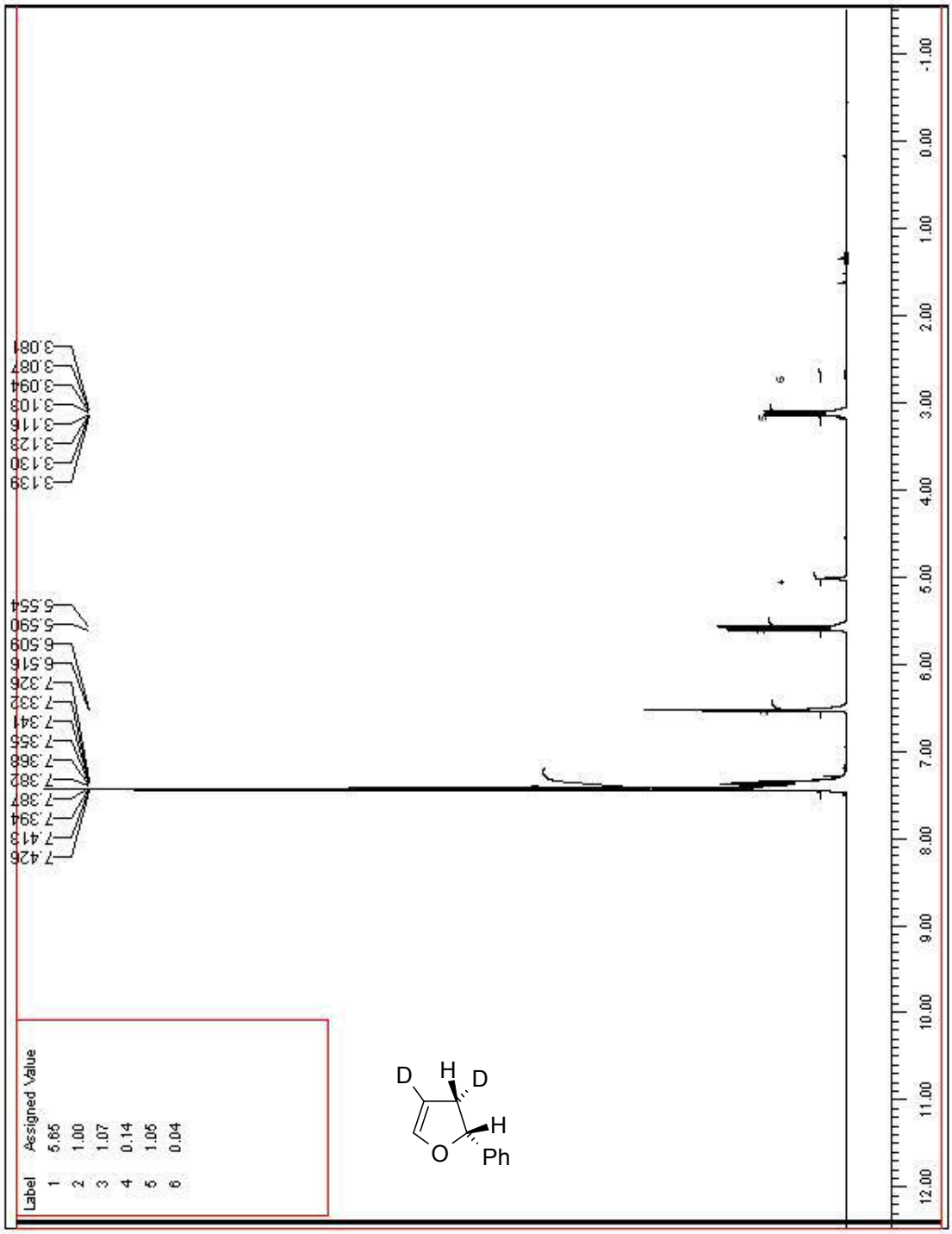

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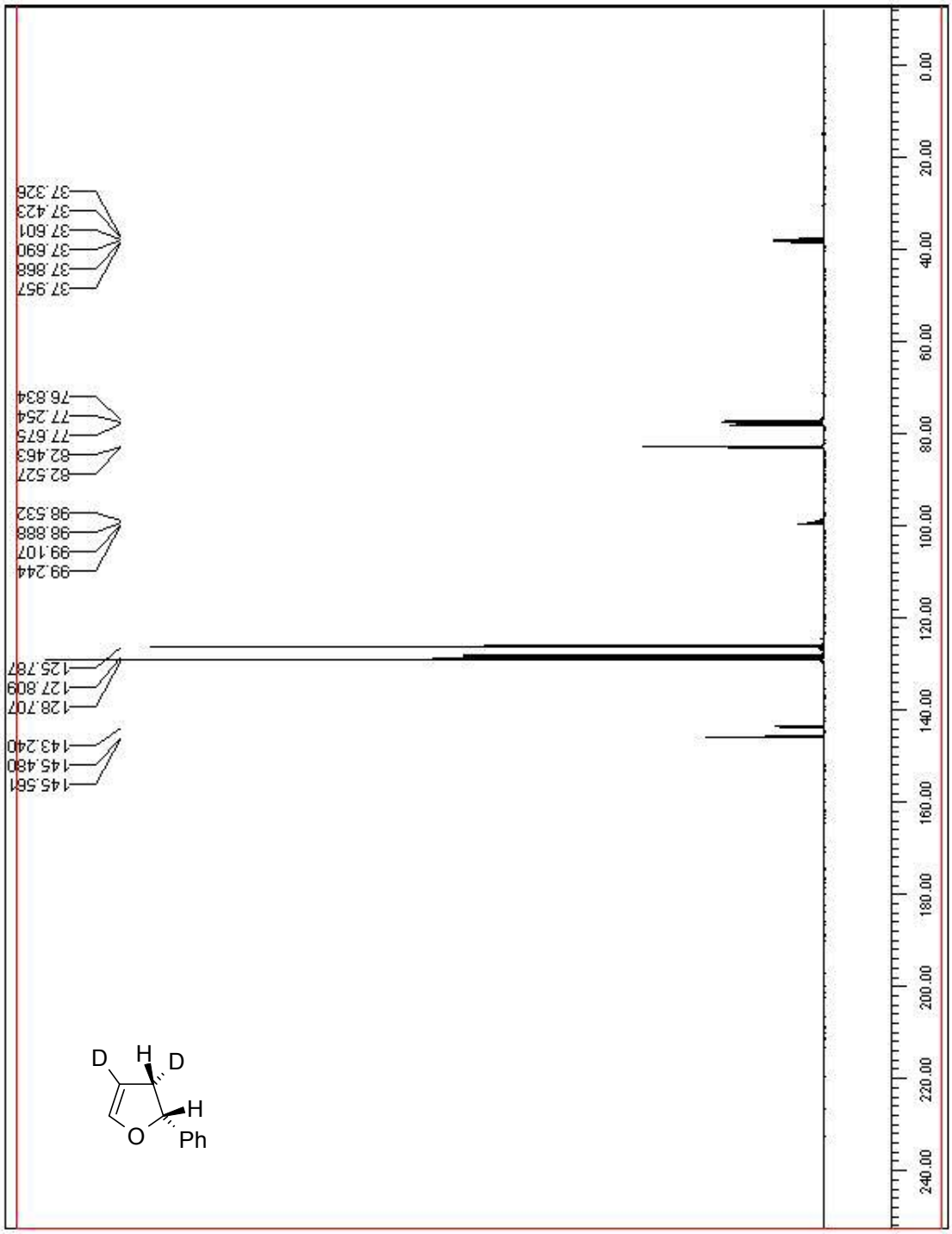

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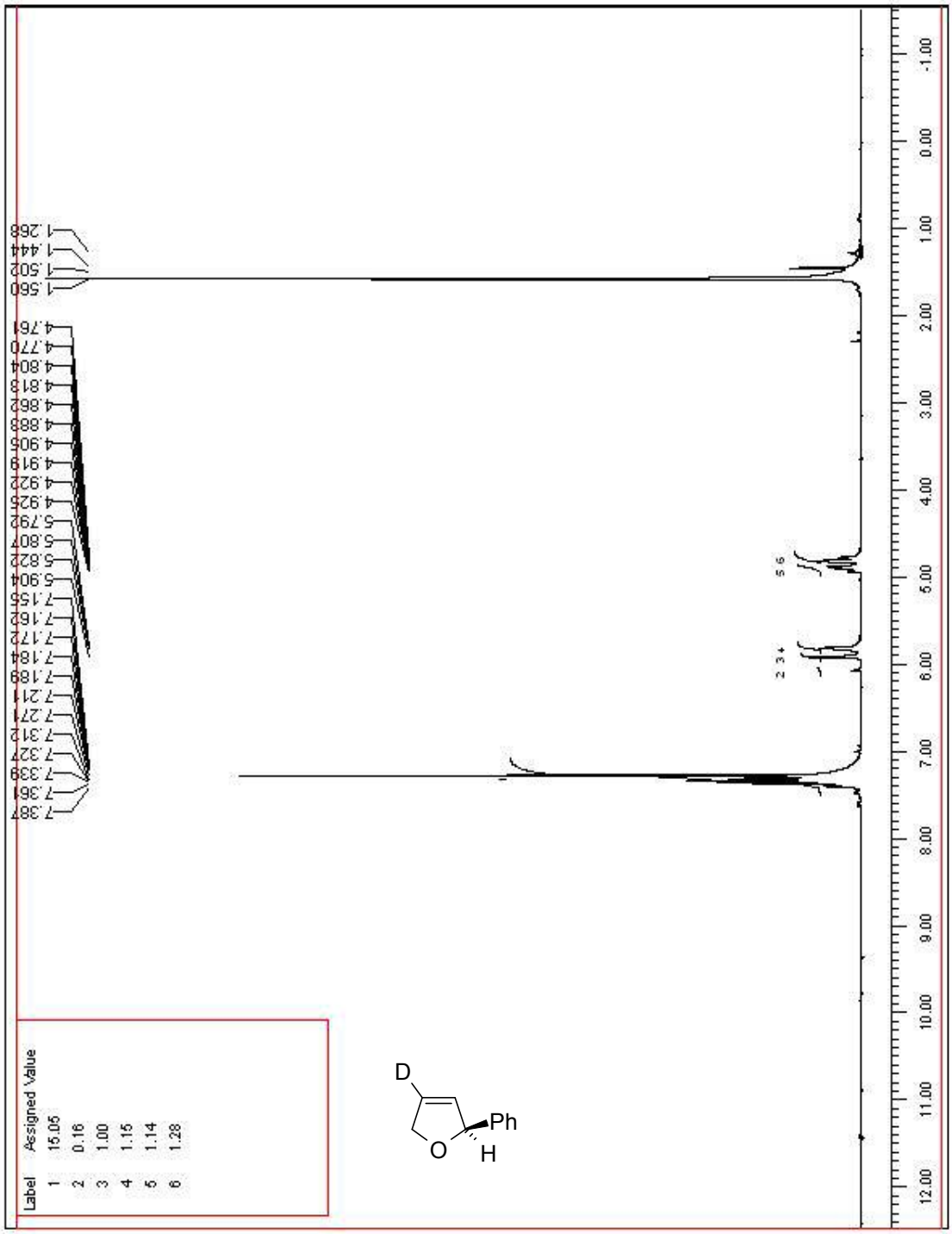

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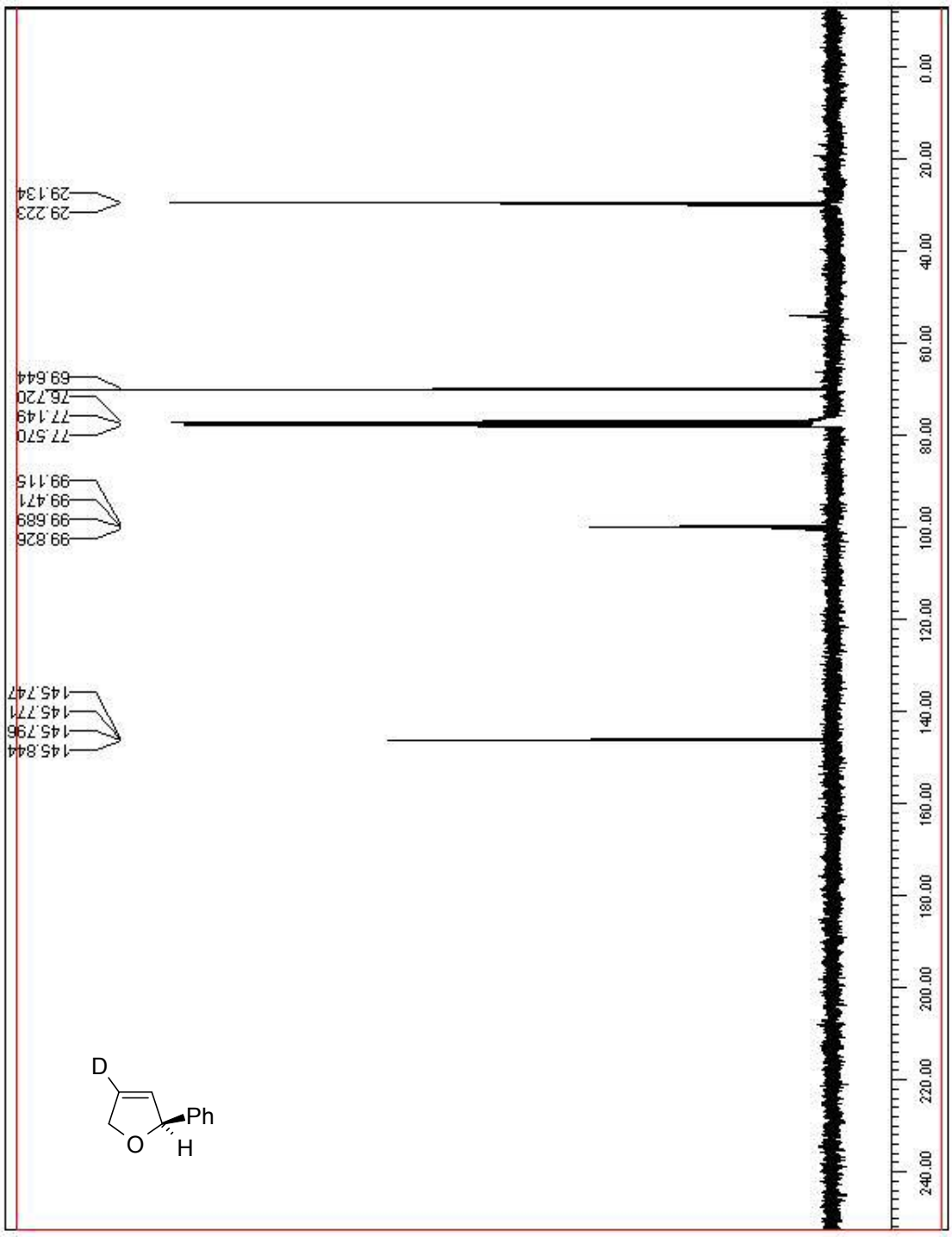

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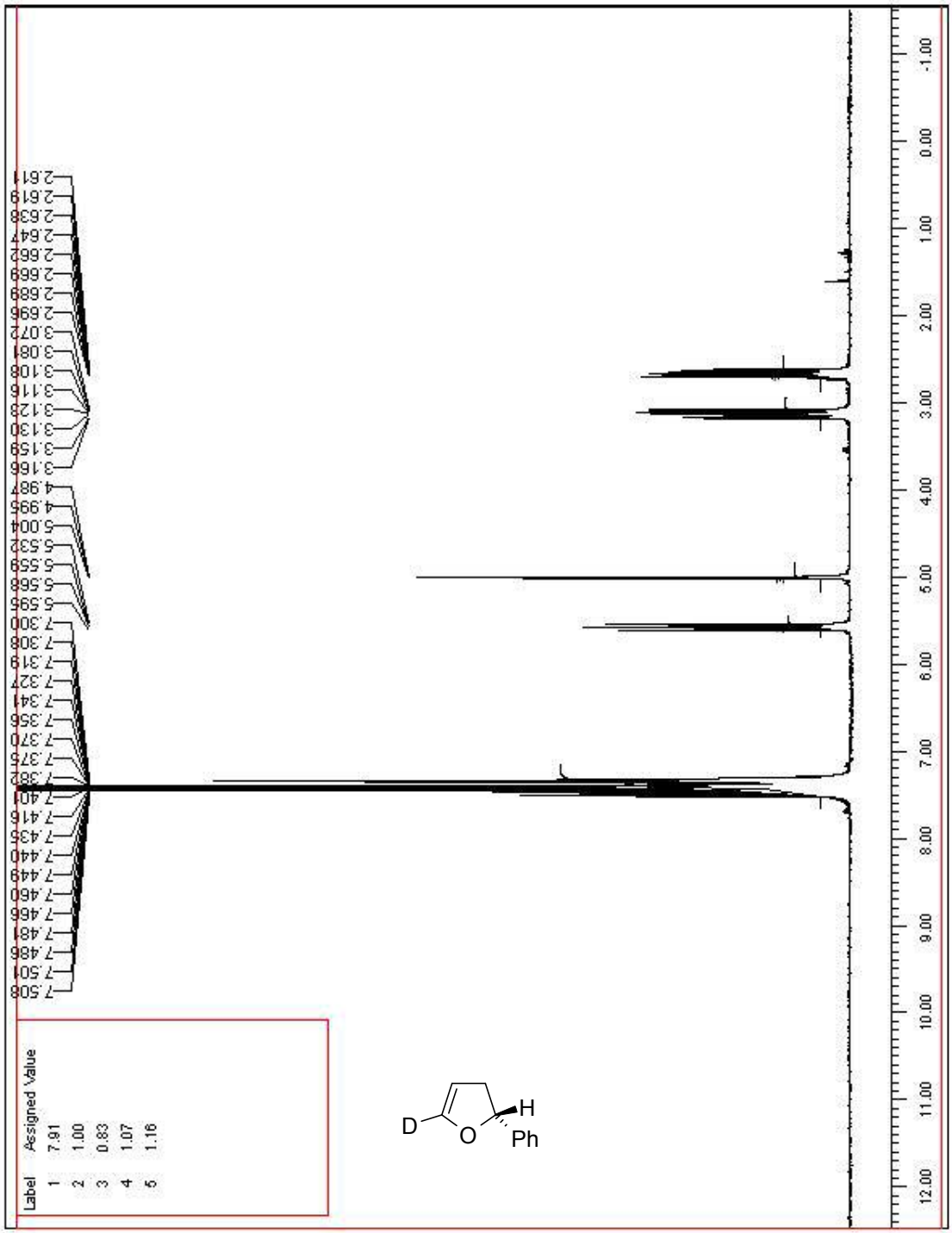
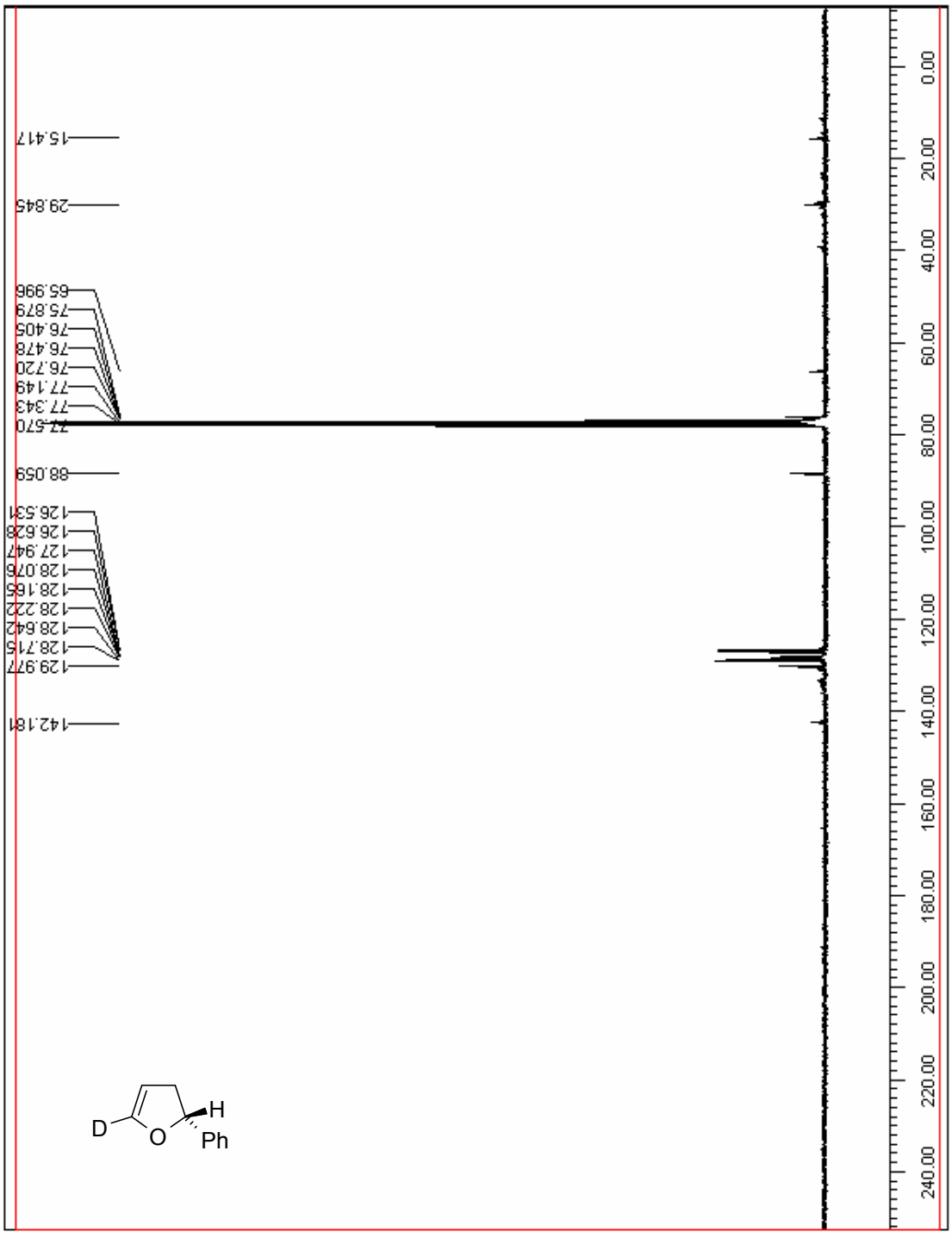


^{13}C NMR of (*R*)-5-deutero-2-phenyl-2,3-dihydrofuran (**6e**)



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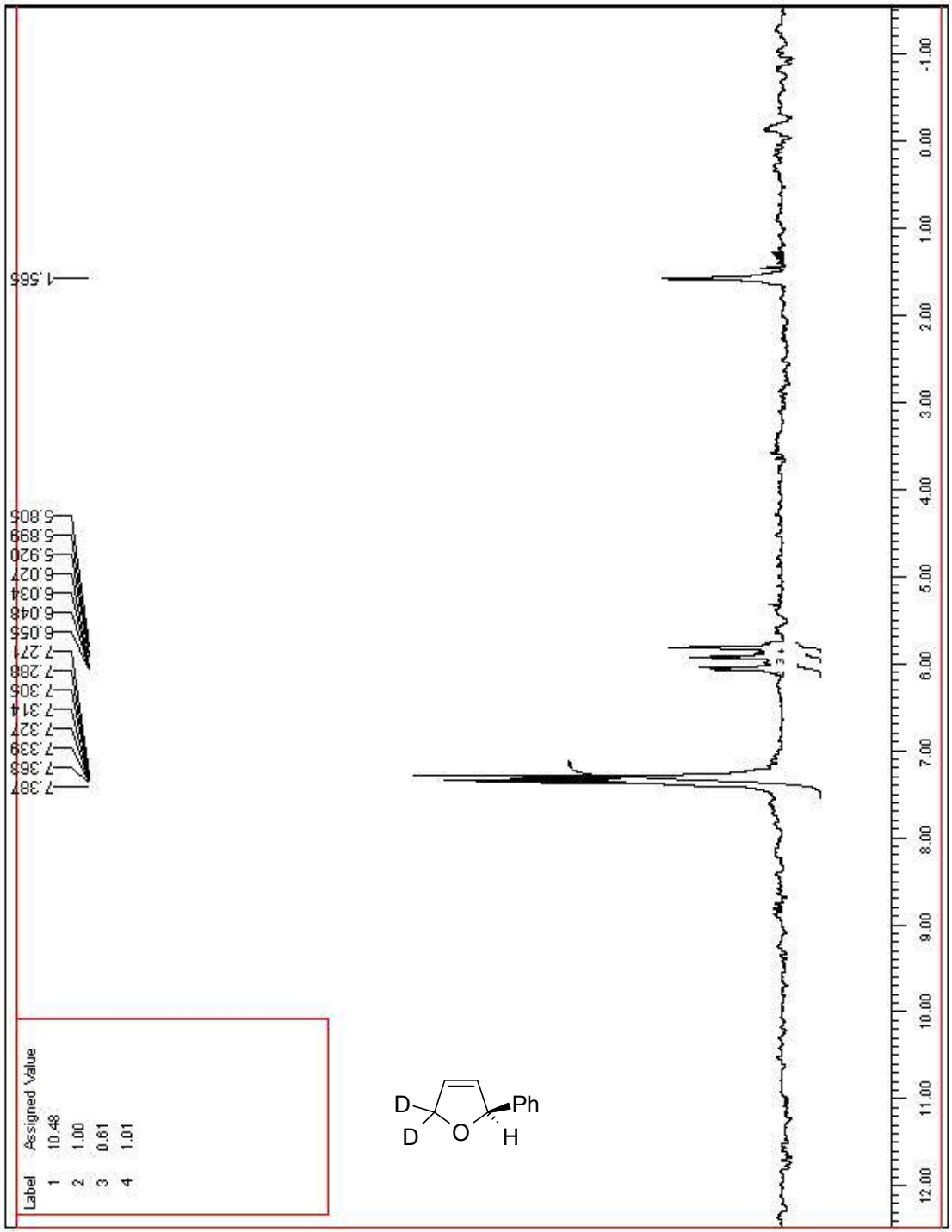

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