

Supporting Information

Preparation of deuterium labeled compounds by Pd/C-Al-D₂O facilitated
selective H-D exchange reactions

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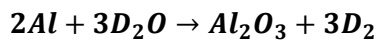
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D₂ gas production experiment



Amount of Al (mmol)

- 100mg: $n(Al) = \frac{m(Al)}{M(Al)} = \frac{100mg}{\frac{27g}{mol}} = 3.7mmol$
- 50mg: $n(Al) = \frac{m(Al)}{M(Al)} = \frac{50mg}{\frac{27g}{mol}} = 1.9mmol$
- 25mg: $n(Al) = \frac{m(Al)}{M(Al)} = \frac{25mg}{\frac{27g}{mol}} = 0.92mmol$

According to the above equation, the maximum amount of gas that can be produced is:

- 100mg: $n(D_2) = \frac{3}{2} \times 3.7mmol = 5.6mmol$
- 50mg: $n(D_2) = \frac{3}{2} \times 1.9mmol = 2.9mmol$
- 25mg: $n(D_2) = \frac{3}{2} \times 0.92mmol = 1.38mmol$

➤ Measurements of volume of gas produced under conventional heating

The volume of gas produced was measured over 6h at 80°C using various amount of Al in 1.5mL of D₂O:

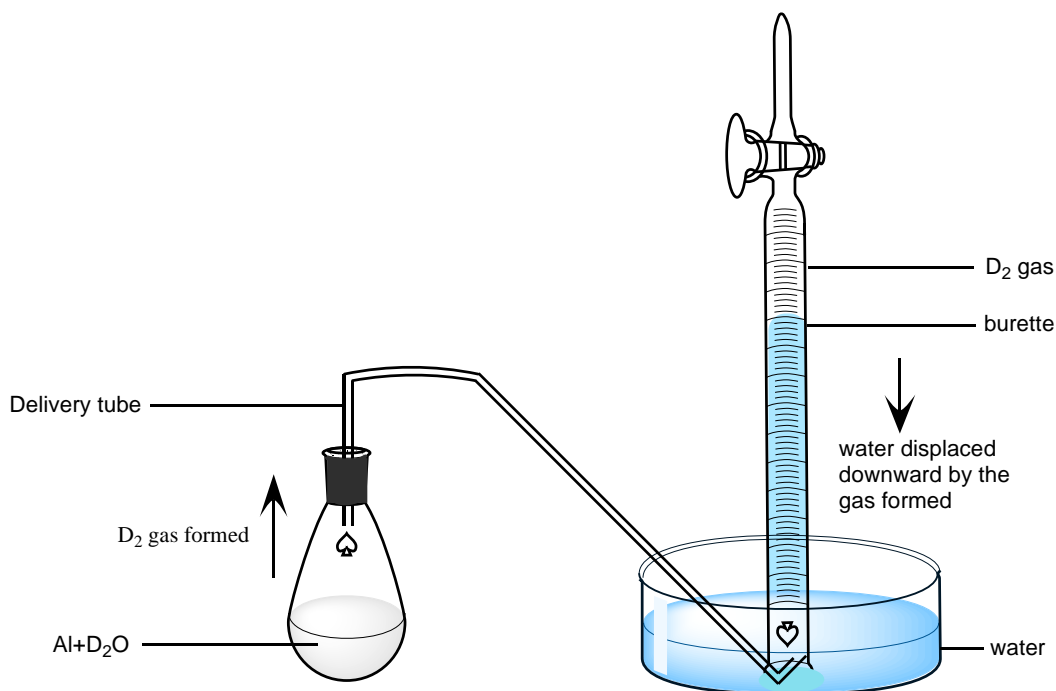


Figure S1. Measurement of the volume of D₂ gas formed at 80°C

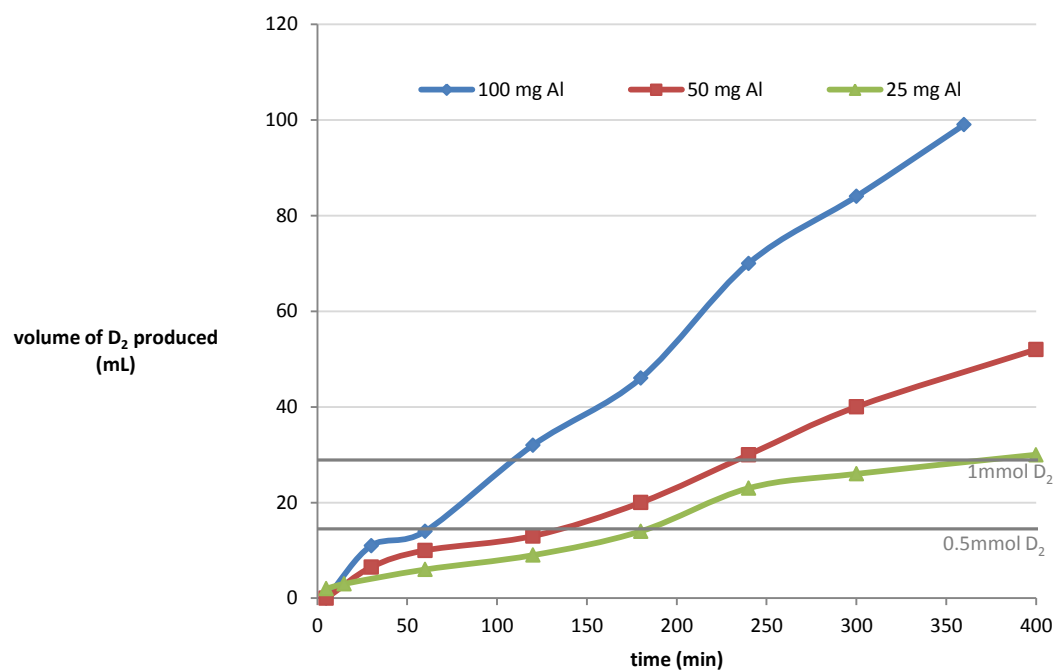


Figure 1 (from article): Volume of D₂ produced over time using various amount of Al at 80°C (oil bath).

Assuming that D₂ gas follows the ideal gas Law

After 6h using 25mg of Al, about 30mL of gas was produced.

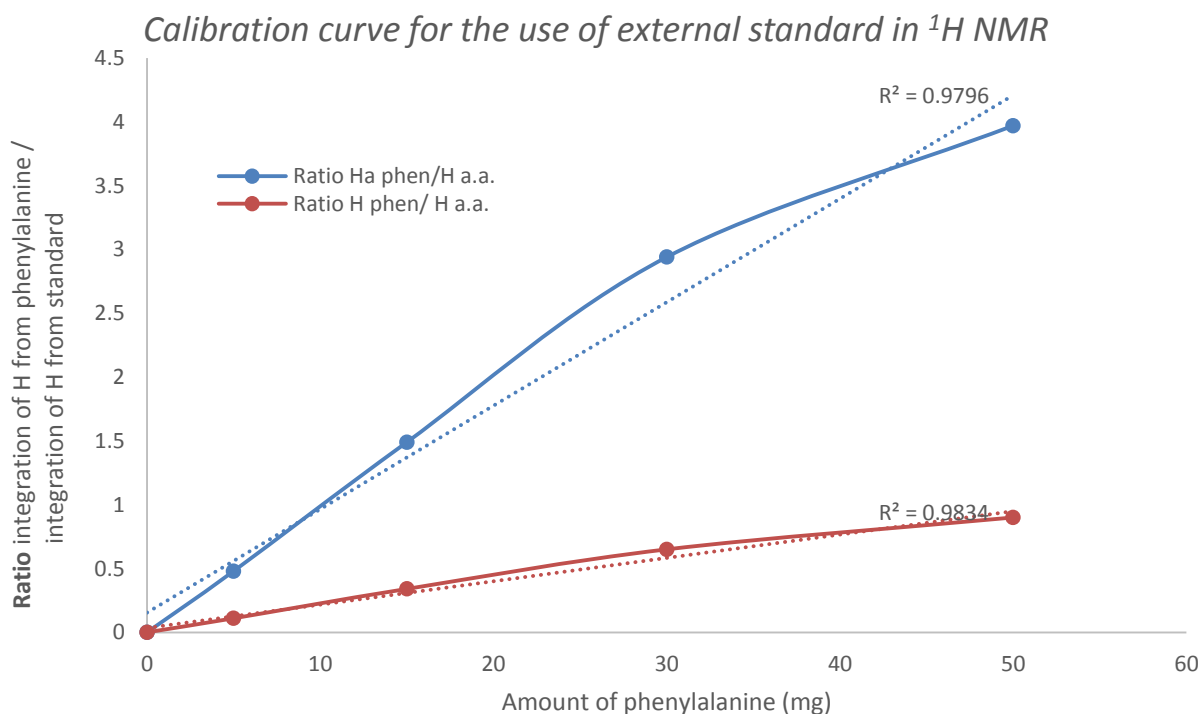
$$PV = nRT$$

$$n(D_2) = \frac{P \times V}{R \times T} \text{ with } R = 0.08206 \text{ L atm mol}^{-1}K^{-1}$$

$$n(D_2) = \frac{1 \text{ atm} \times 0.030 \text{ L}}{0.08206 \text{ L atm mol}^{-1}K^{-1} \times 353K} = 1.0 \text{ mmol}$$

Figure S2. Calibration of the quantitative determination of hydrogen content method in ^1H NMR

40 μL of acetic acid (the external standard) was added to 10 mL of D_2O . 1 mL of this stock solution was added to 1 mL of phenylalanine solution in a vial and stirred up for 2 min. 0.7 mL of this mixture was taken for NMR analysis. For each substrate, a reference spectrum was generated and used as a comparison to any spectrum obtained after H-D exchange reaction. The deuterium content was calculated based on the ratio of the integration of hydrogen before H-D exchange to the integration of hydrogen after H-D exchange, both standardized with the acetic acid signal. Note that a new reference spectrum had to be taken when using a different standard stock solution to reduce additional errors.



Amount of phenylalanine (mg)	Ratio H_a /H a.a.	Ratio H/H a.a.
0	0	0
5	0.48	0.11
15	1.49	0.34
30	2.94	0.65
50	3.97	0.9

$H=H_B, H_C, H_D$; a.a.=acetic acid (standard)

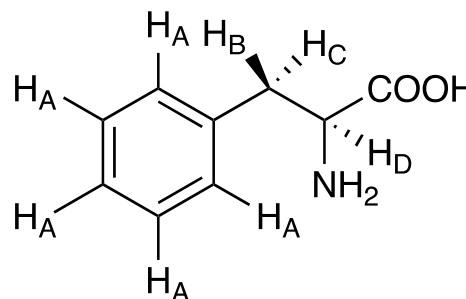


Figure S3. ^1H NMR spectra for the calibration of the quantitative determination of hydrogen content method using acetic acid as the external standard and phenylalanine

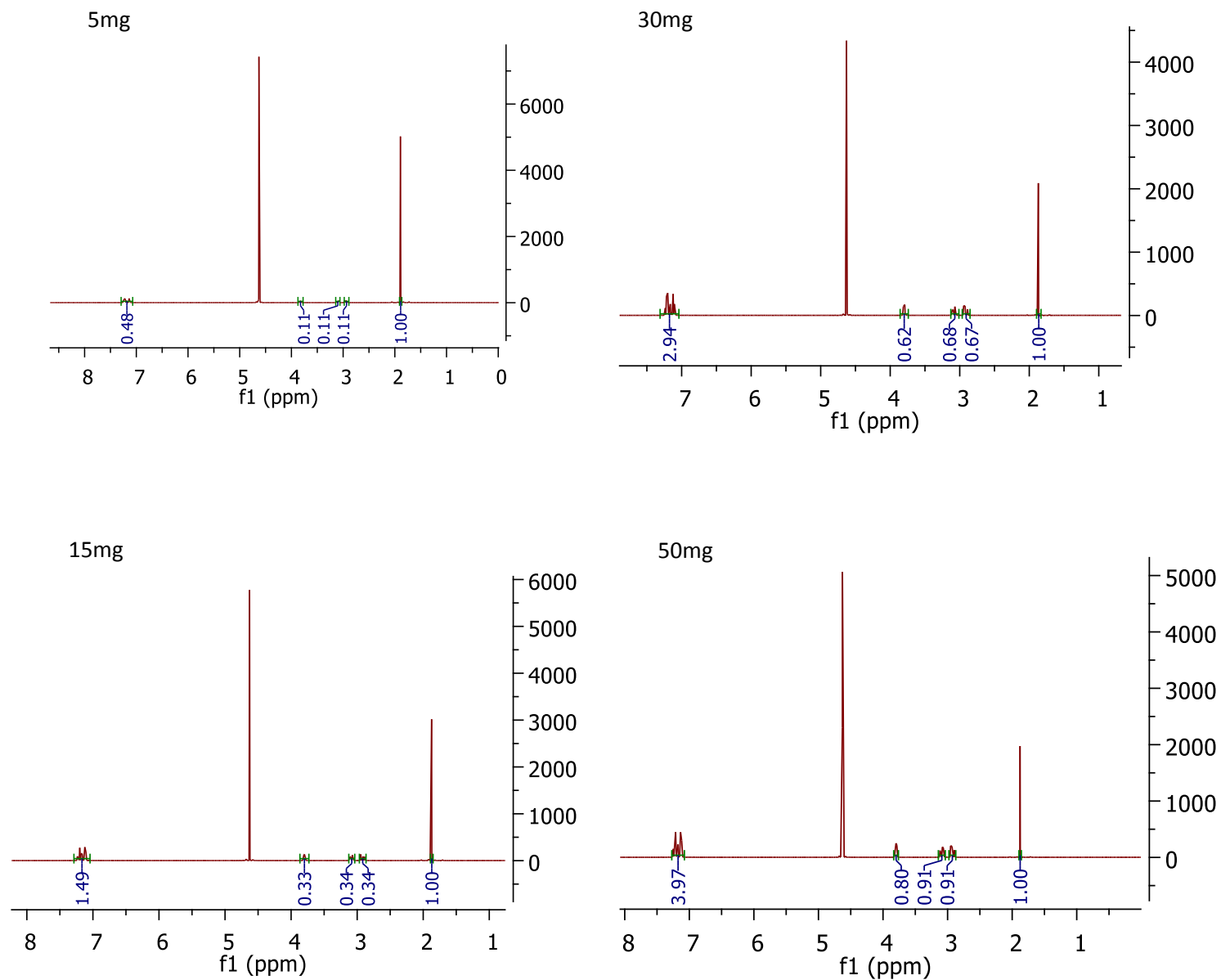


Figure S4. H-D exchange reaction of phenylalanine for 24h at 80°C under conventional heating

(20mg of Pd/C, 100mg of Al)

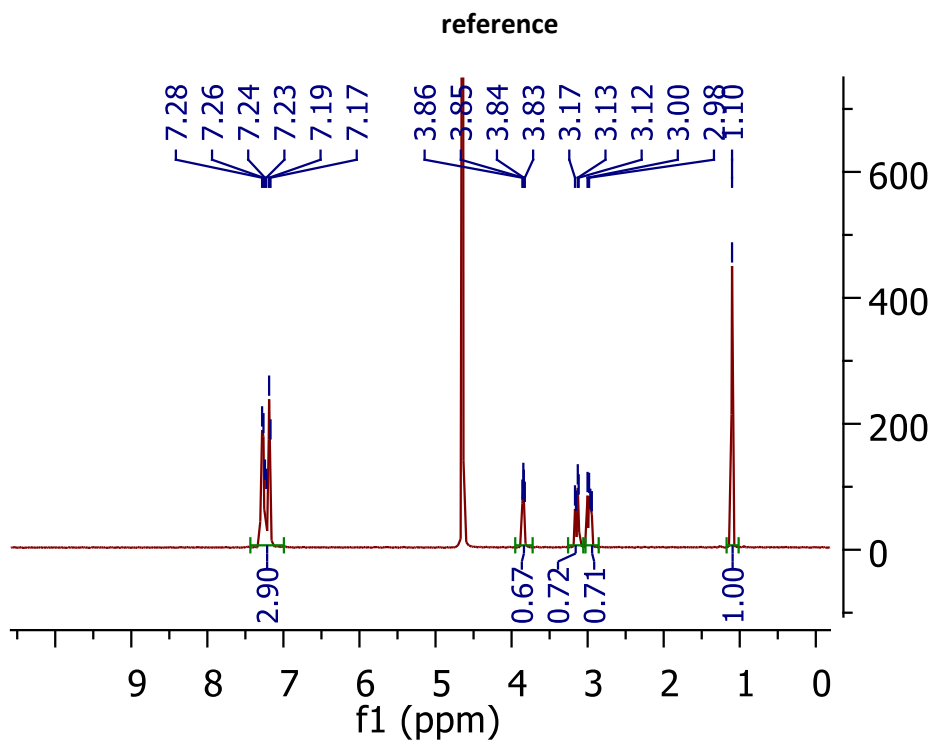
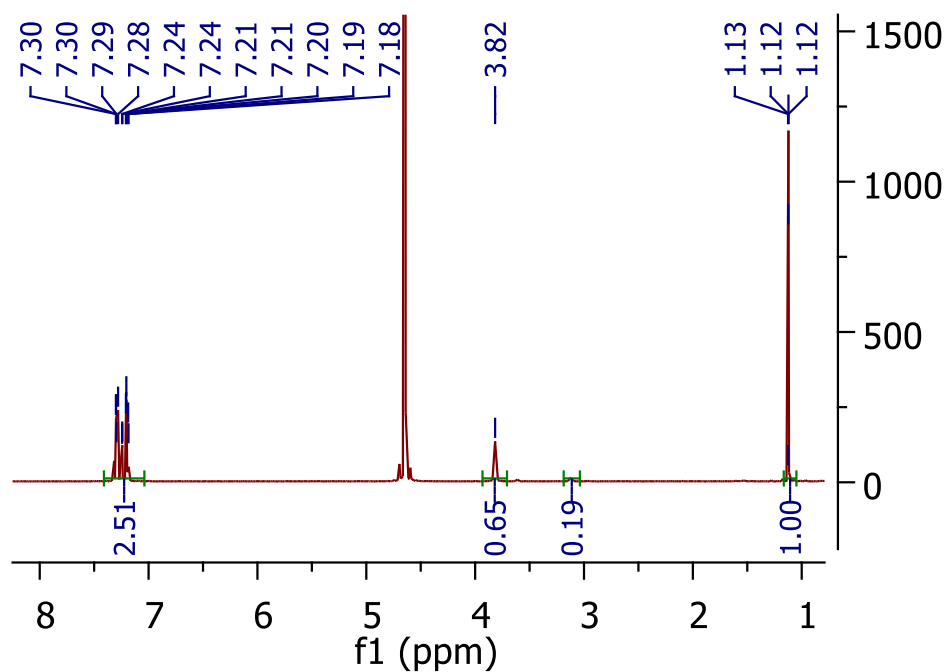


Figure S5. H-D exchange reaction of phenylalanine for 1h under MW at 80°C

(20mg of Pd/C, 100mg of Al)

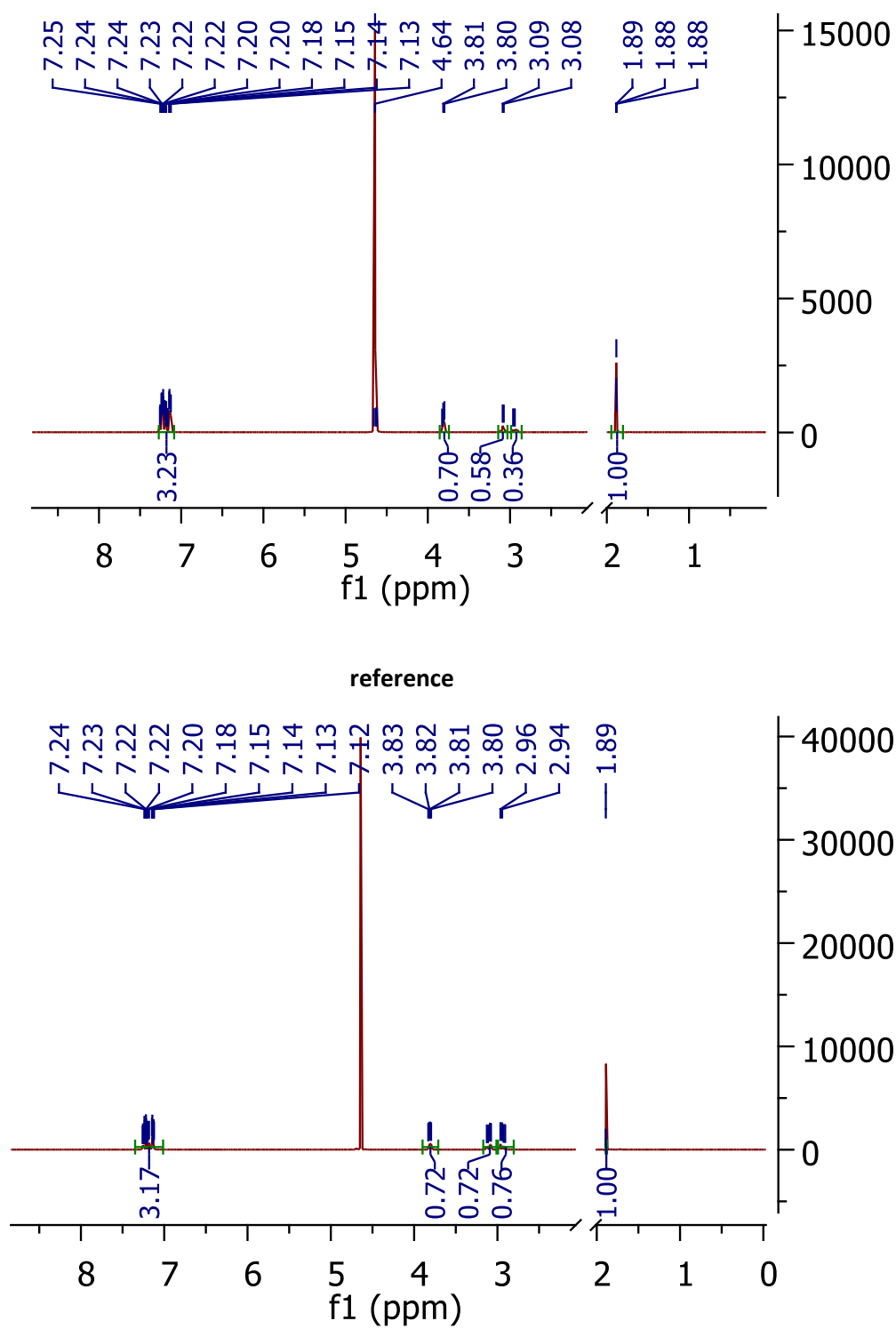
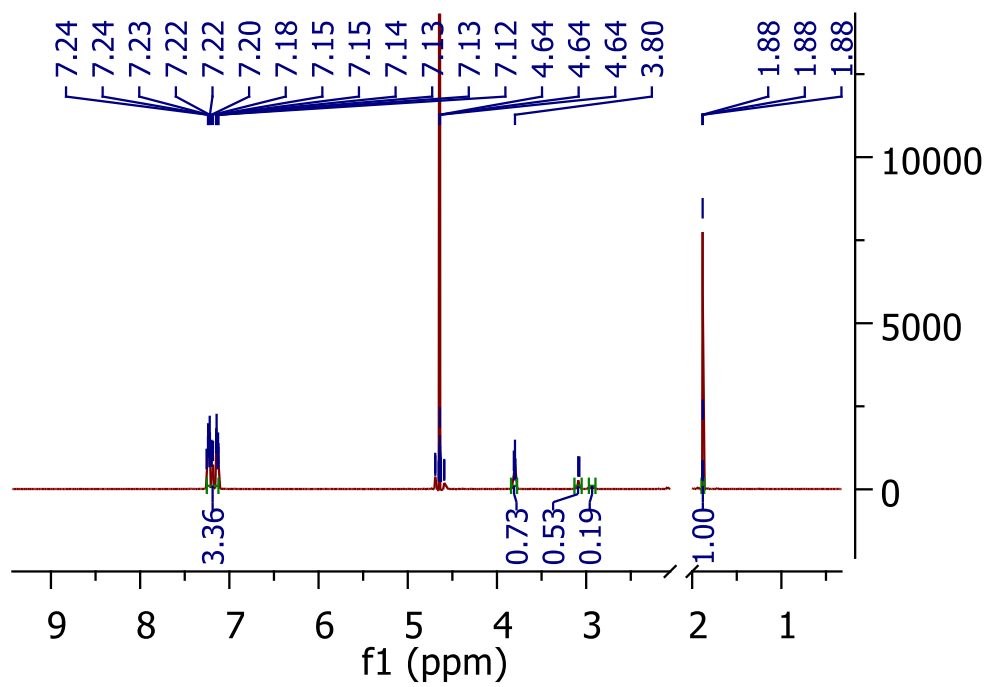


Figure S6. H-D exchange reaction of phenylalanine for 1h under MW at 100°C

(20mg of Pd/C, 100mg of Al)



reference

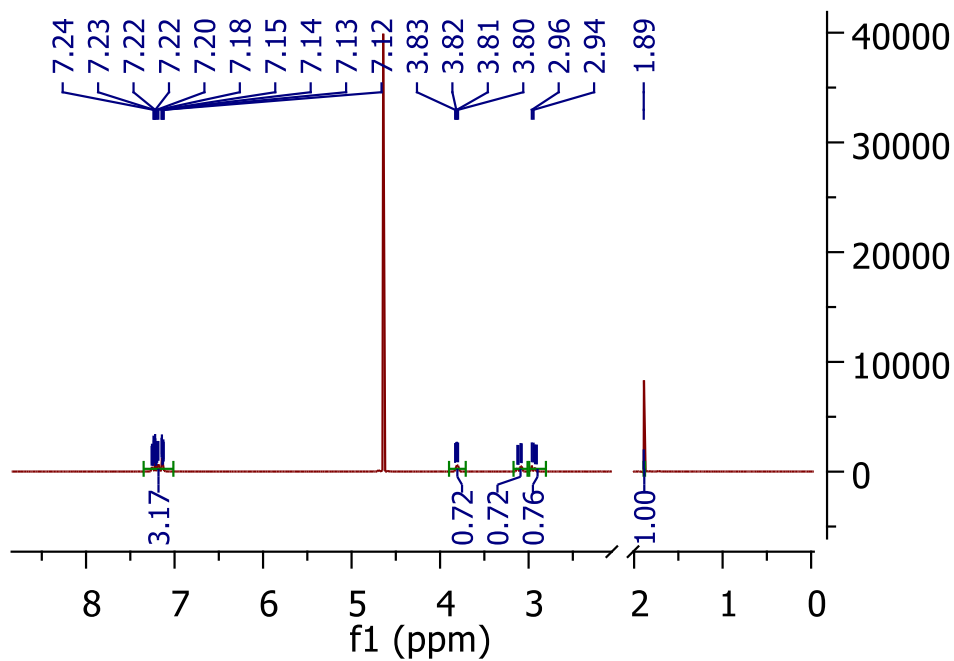
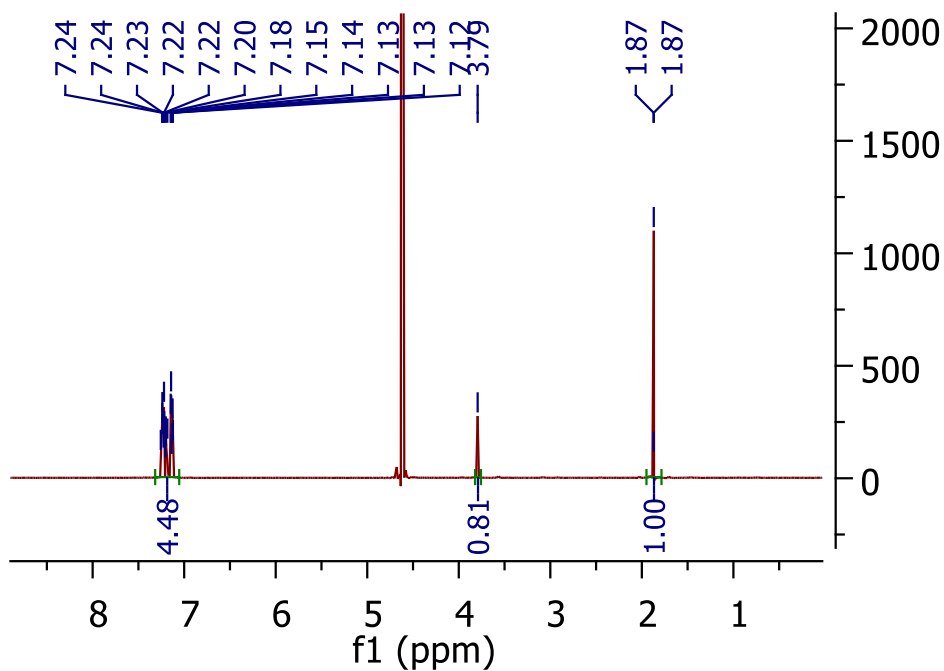


Figure S7. H-D exchange reaction of phenylalanine for 1h under MW at 120°C

(20mg of Pd/C, 100mg of Al)



reference

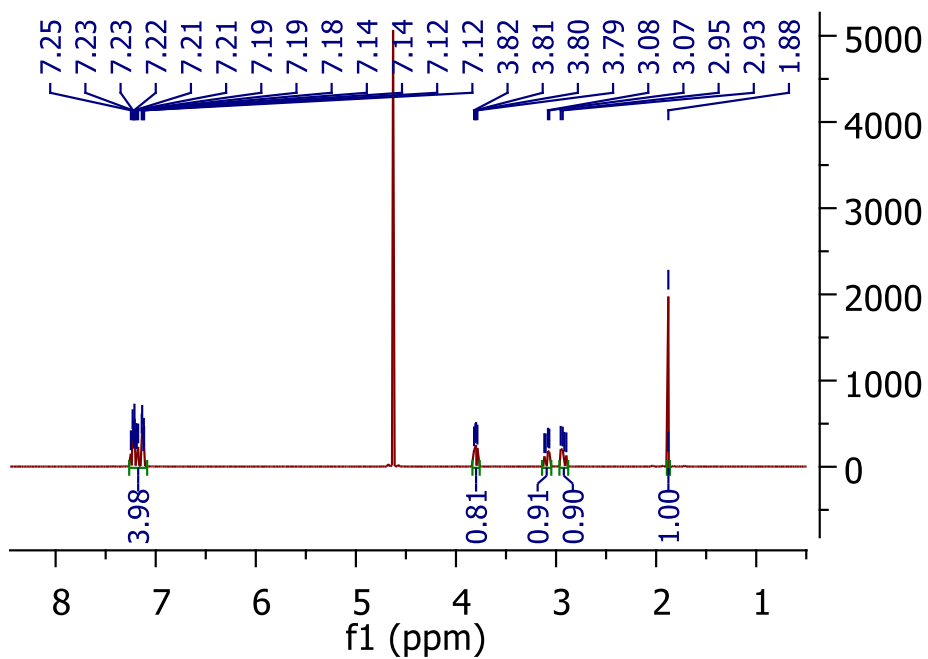


Figure S8. H-D exchange reaction of phenylalanine for 20 min under MW at 120°C

(20mg of Pd/C, 100mg of Al)

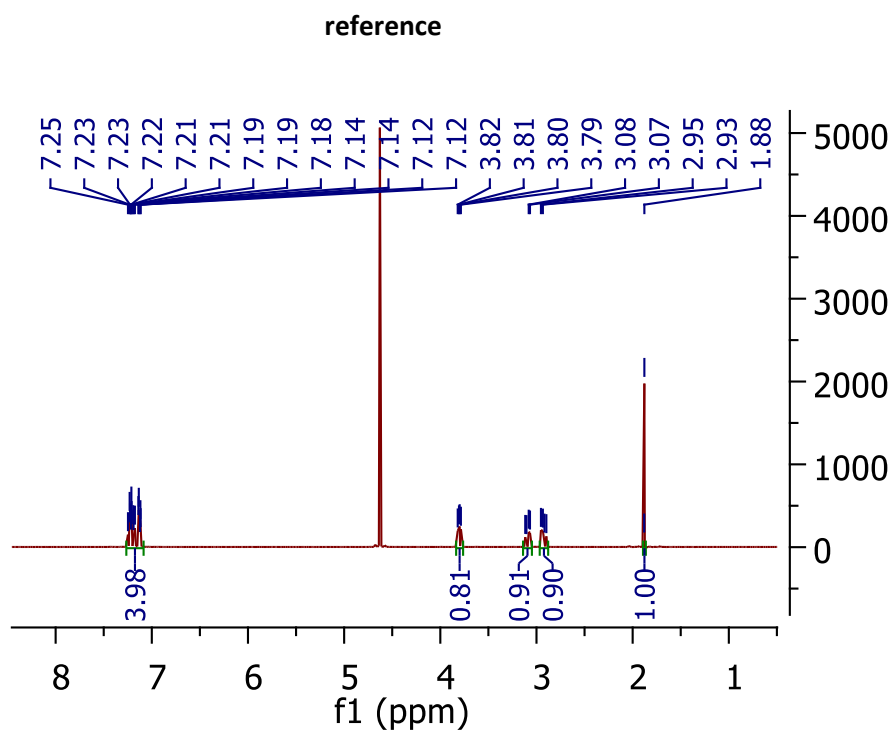
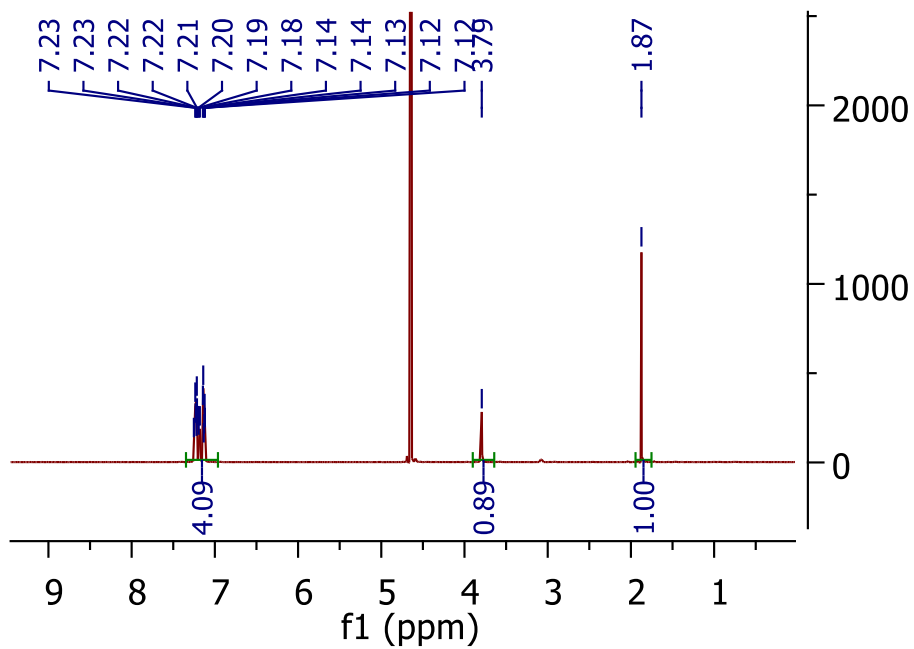


Figure S9. H-D exchange reaction of phenylalanine with 10mg of catalyst and 100mg of Al

(1h, MW, 120 °C)

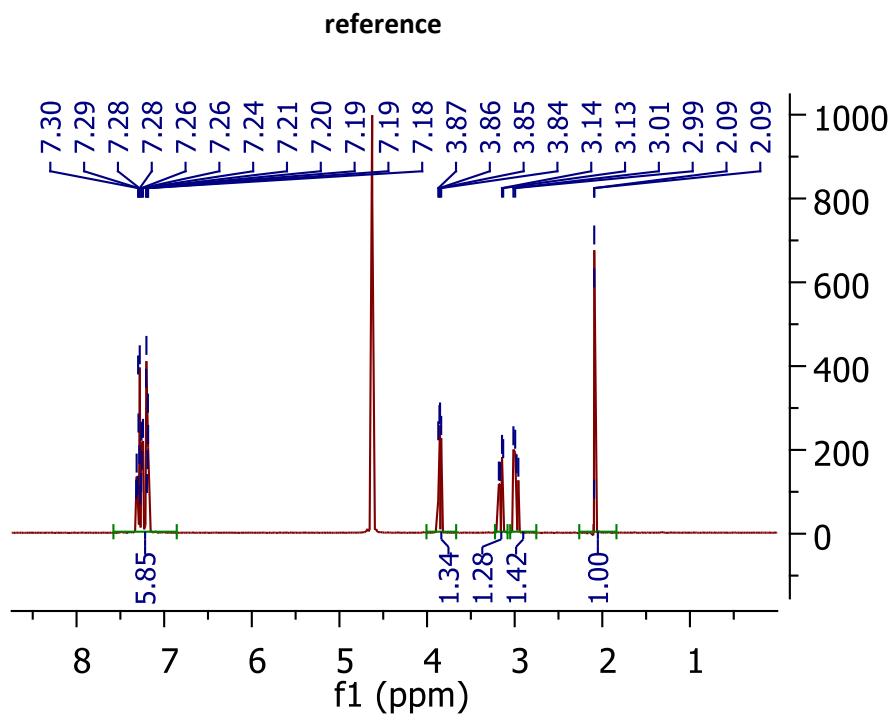
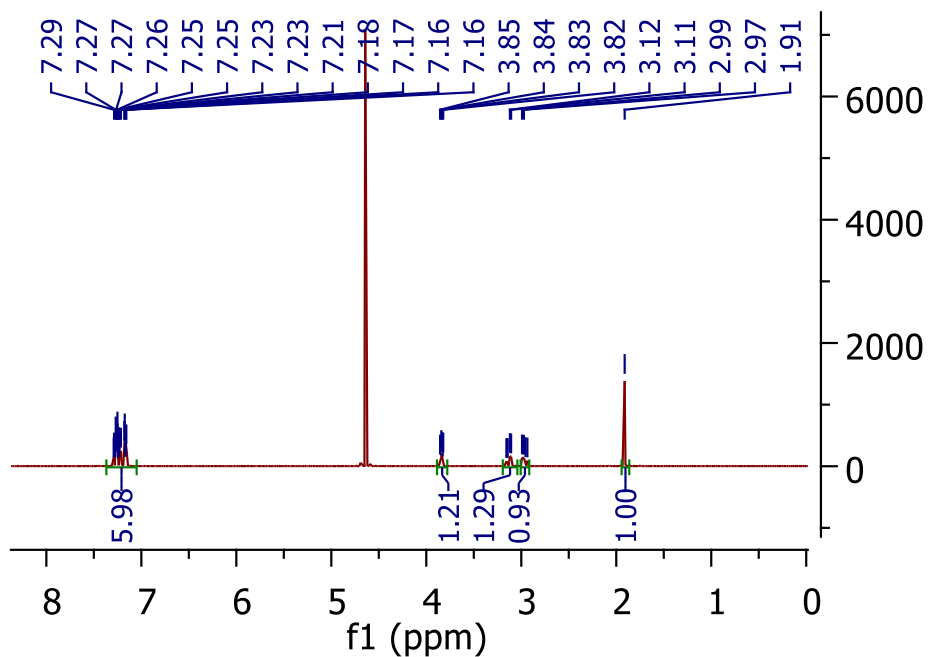
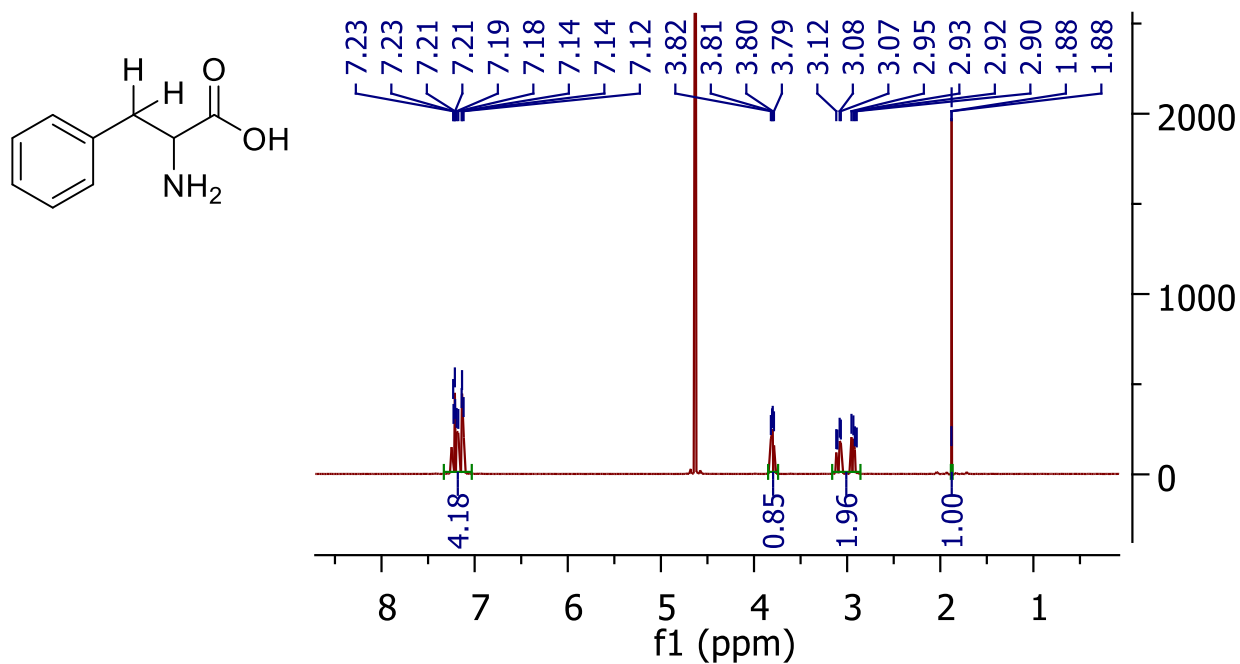


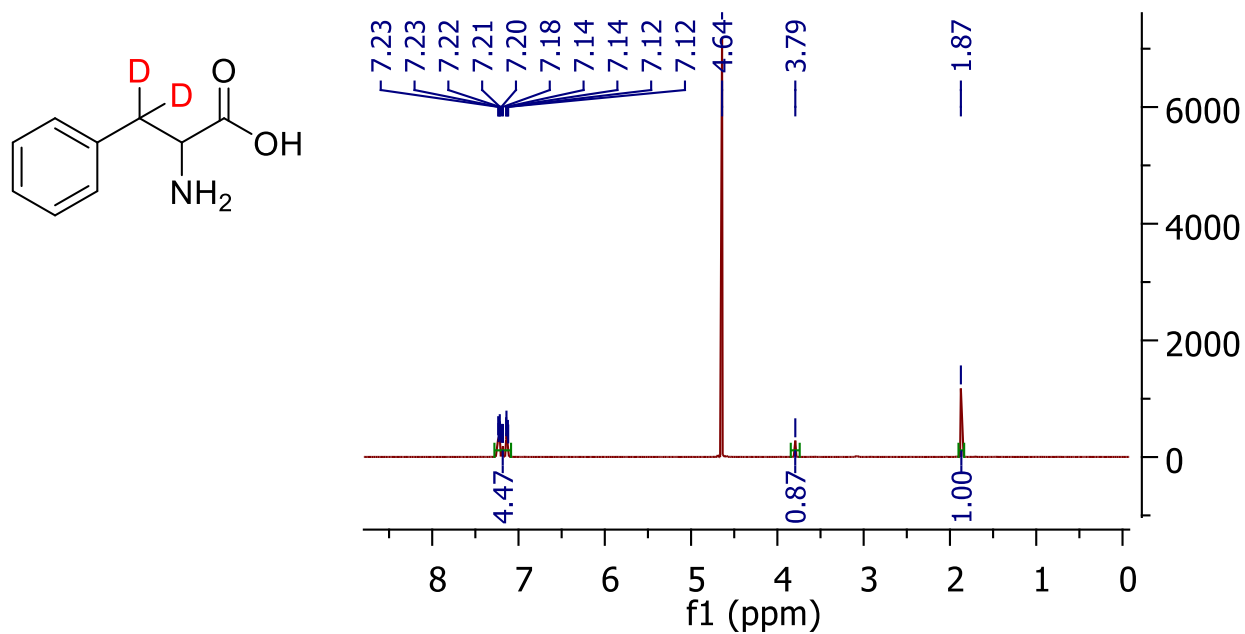
Figure S10. H-D exchange reaction of phenylalanine

(20mg of Pd/C, MW, 120 °C)

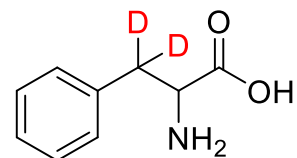
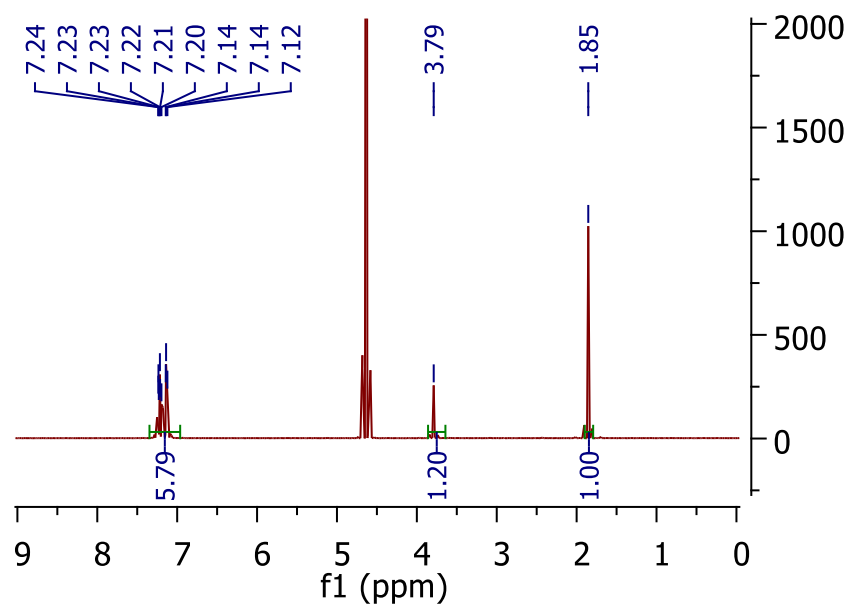
a. ^1H NMR



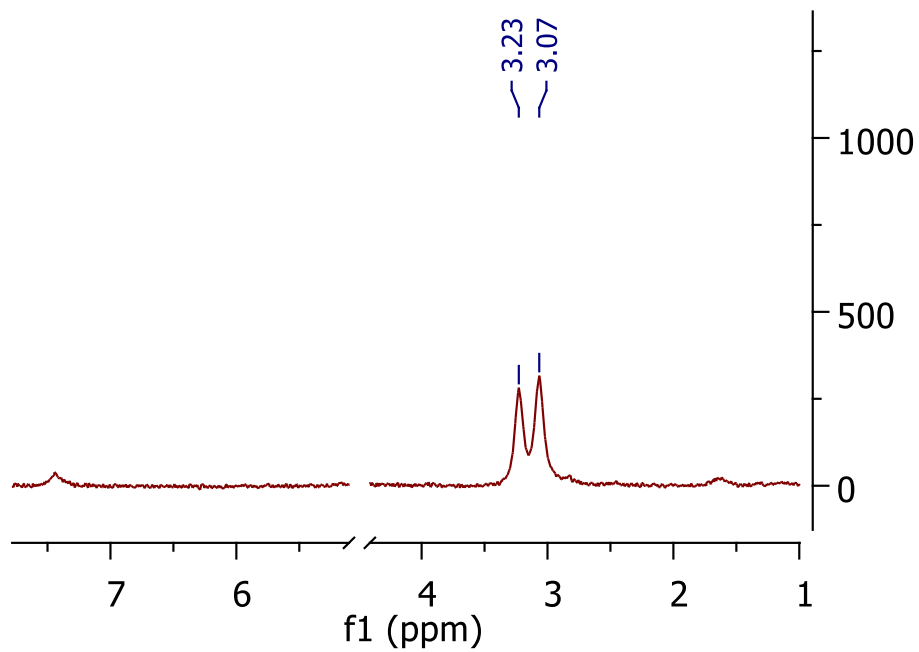
100mg of Al, 20min reaction



25mg Al, 60min reaction



b. ²H NMR



c. Mass Spectrum

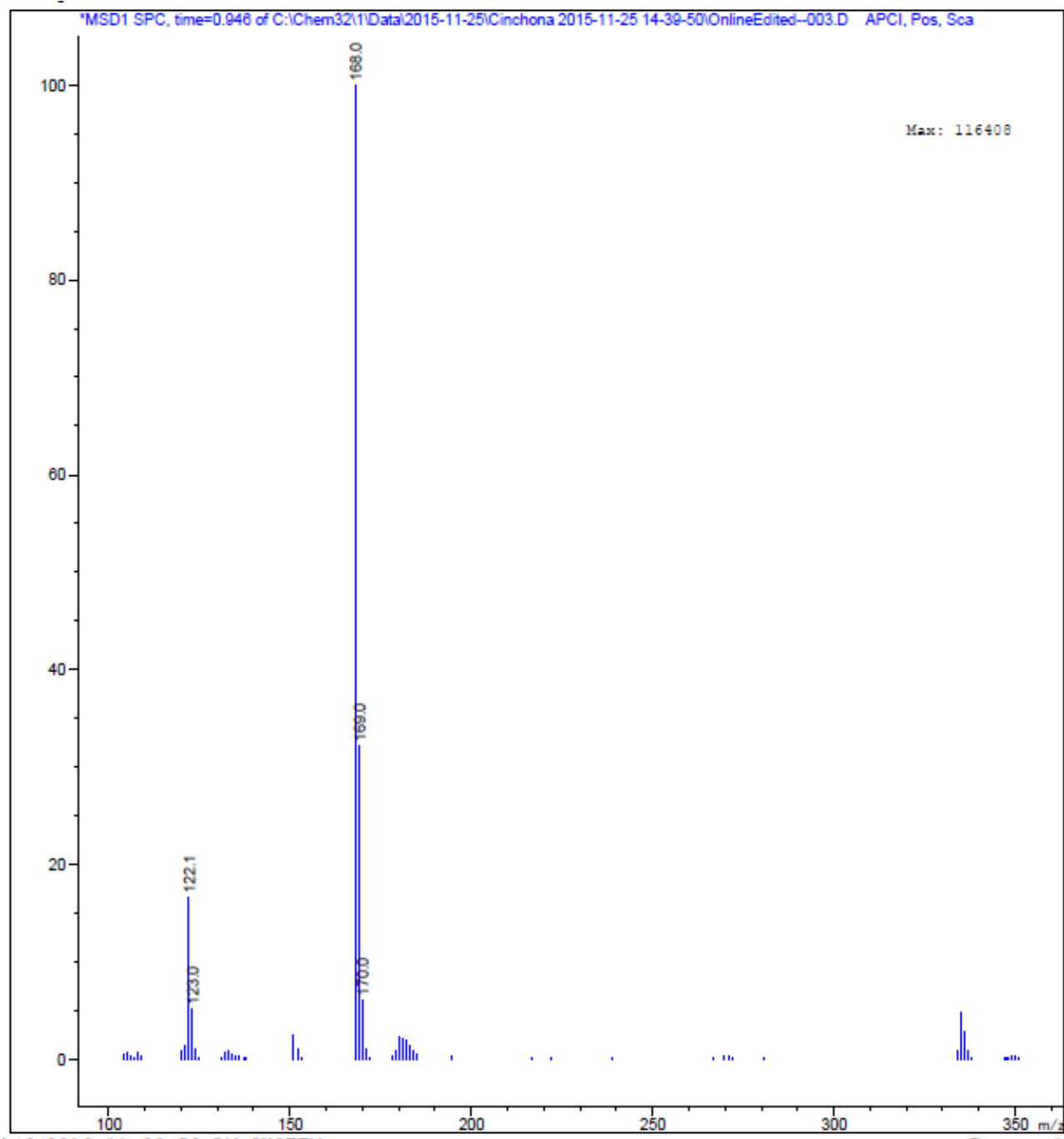
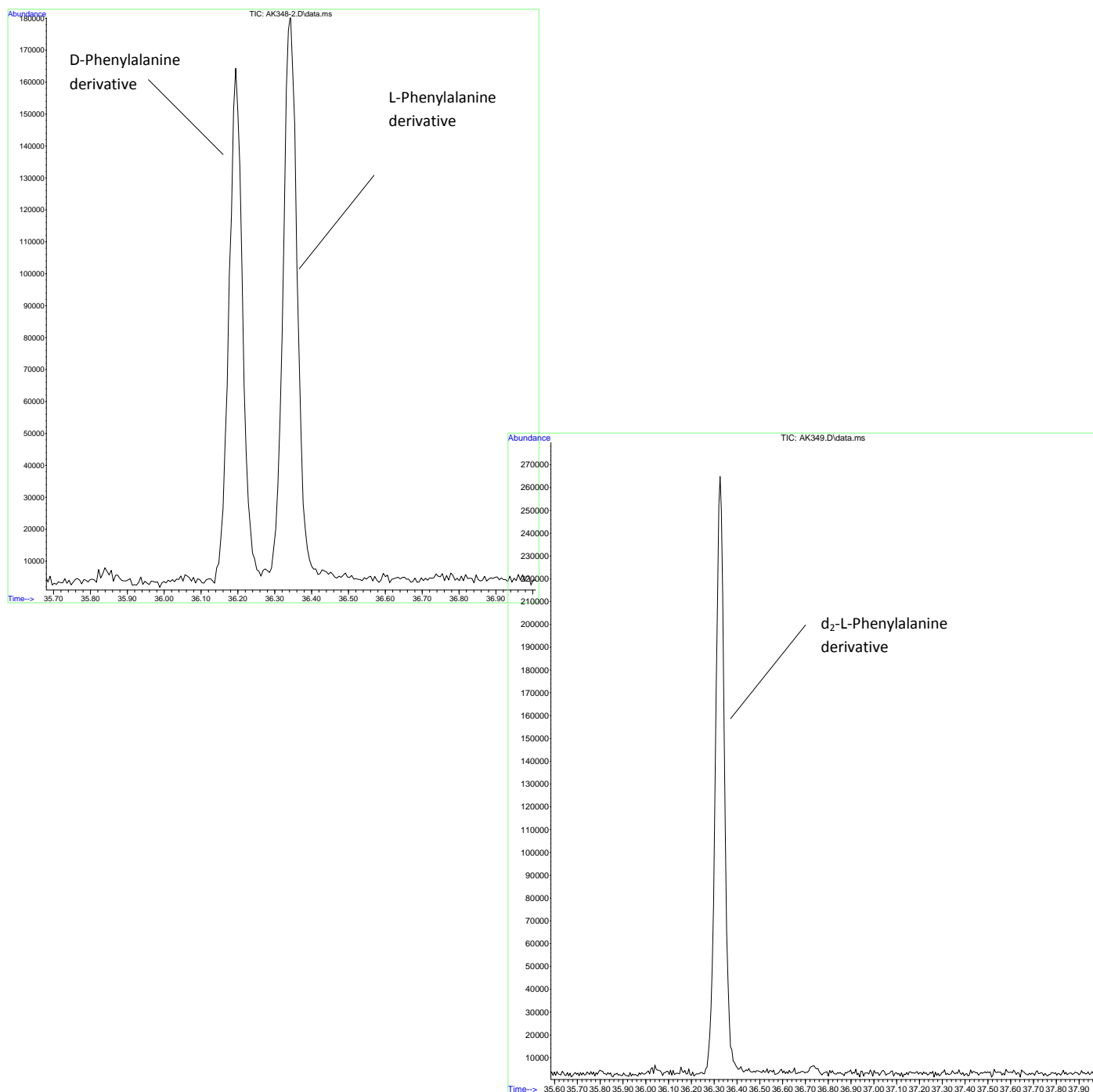
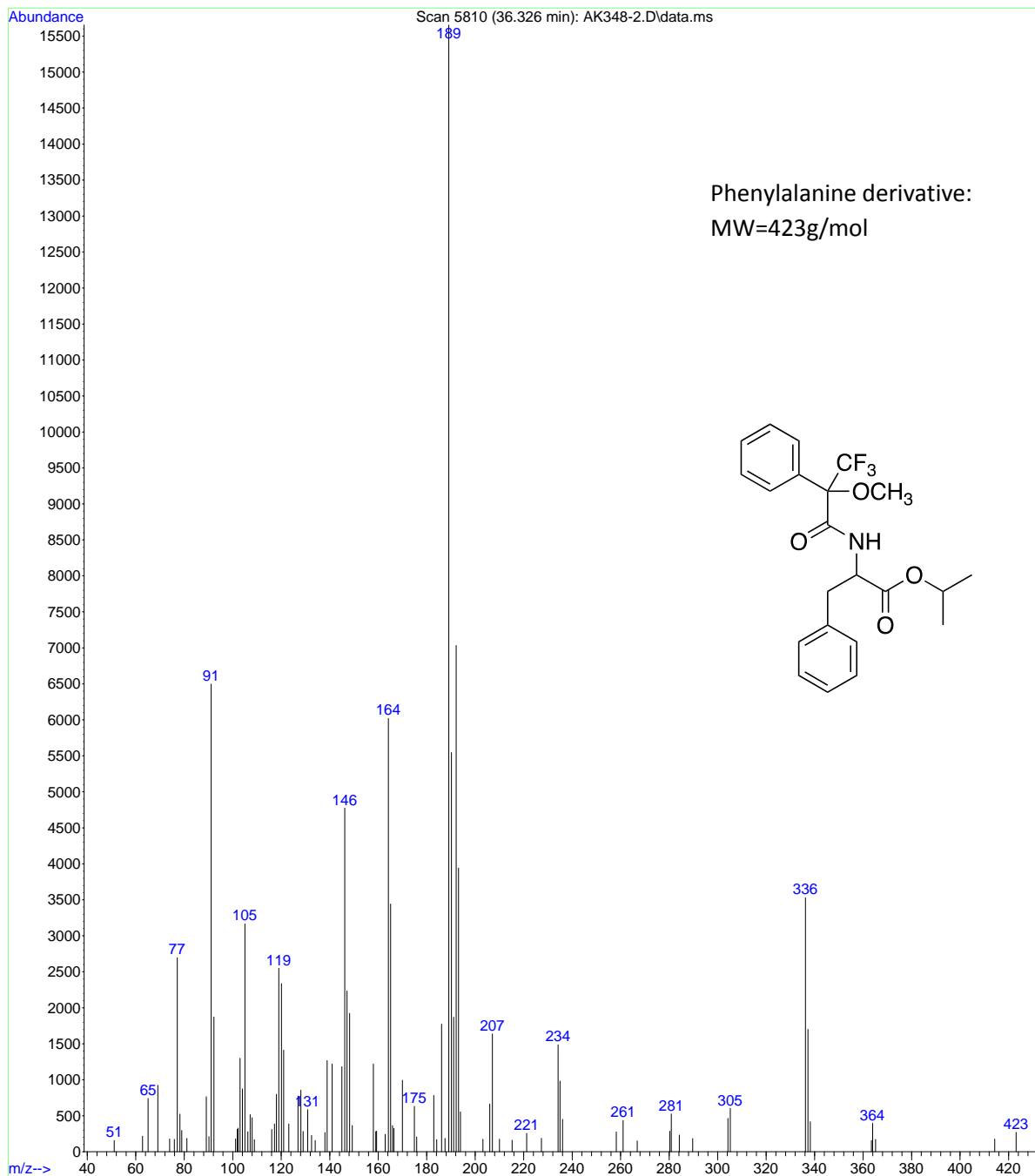


Figure S11. Determination of the chirality of deuterated phenylalanine

Phenylalanine was derivatized using isopropyl alcohol to form an amino acid ester first and then it was reacted with Mosher's chloride to functionalize the amino group; before it was injected in the GC-MS. The first chromatogram shows the separation of a pseudo racemic mixture of phenylalanine. The mass spectrum of both products was identical. The second chromatogram corresponds to the derivatized d₂-phenylalanine.





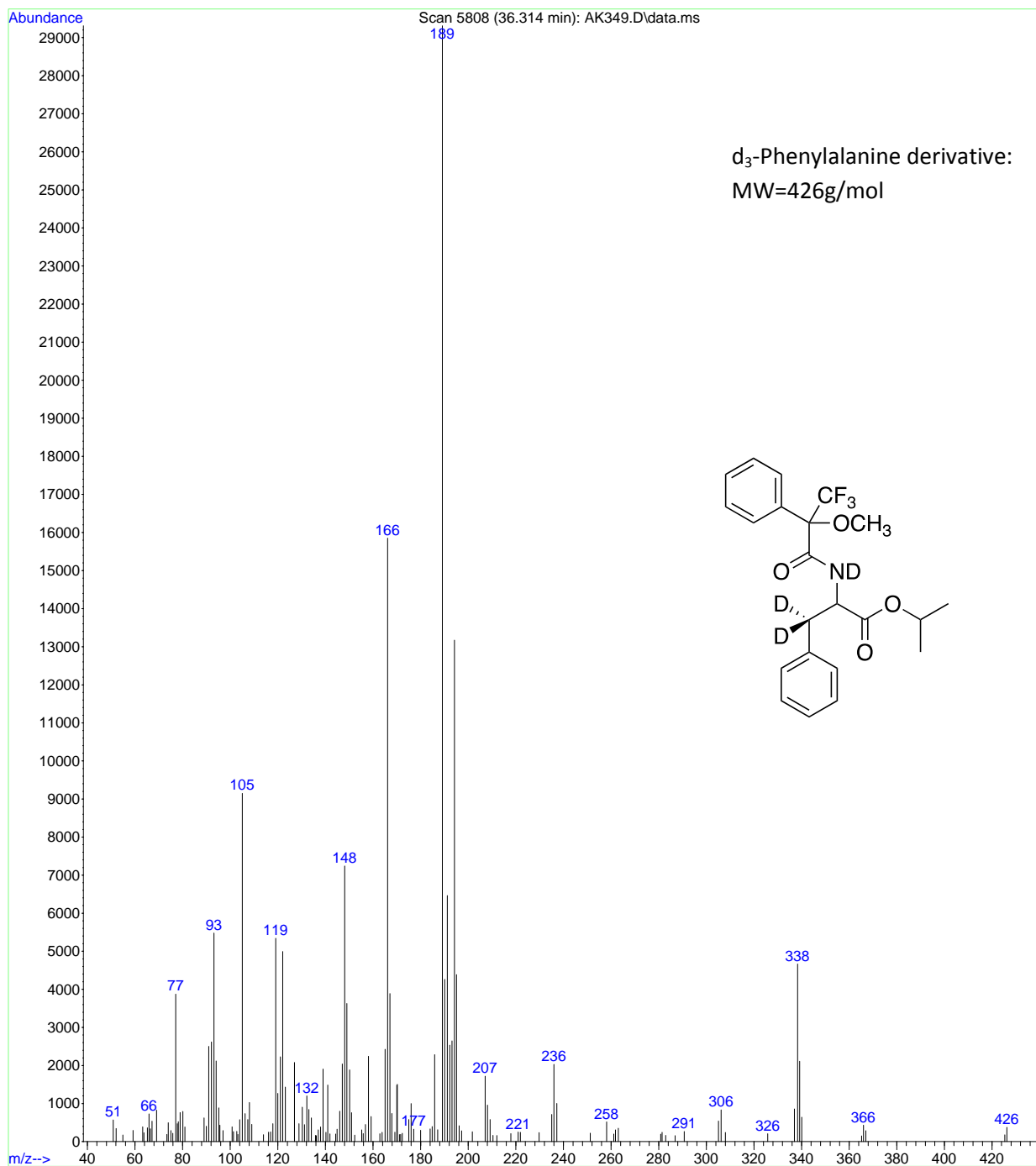
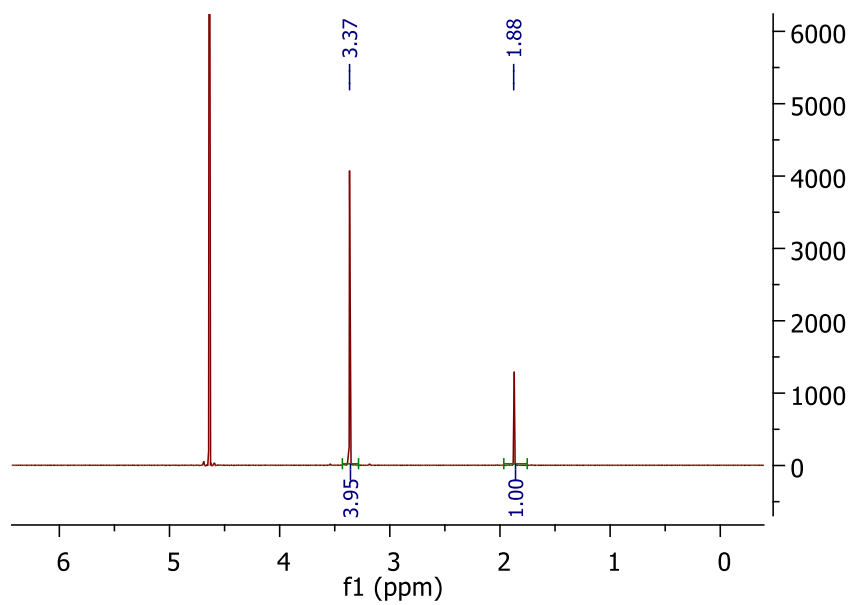
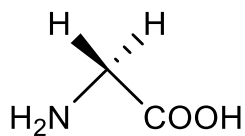


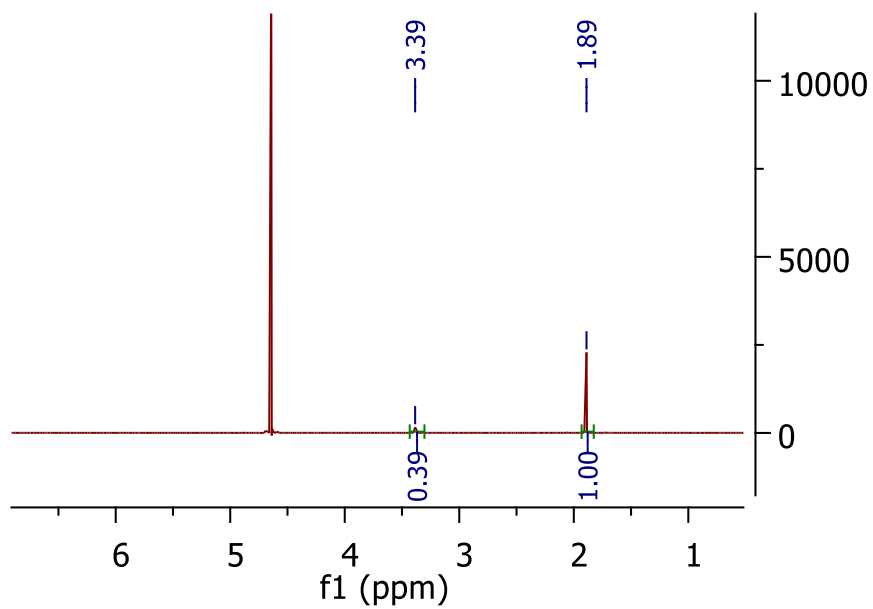
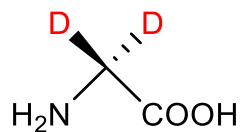
Figure S12. H-D exchange reaction of glycine

(20mg of Pd/C, MW, 170 °C, 60min))

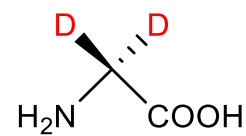
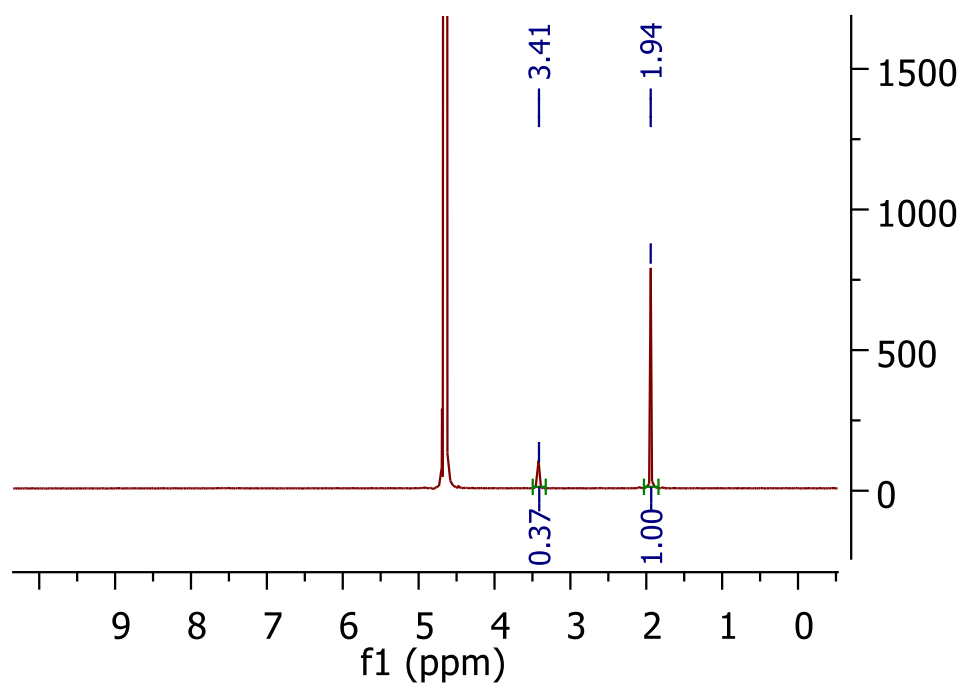
a. ^1H NMR



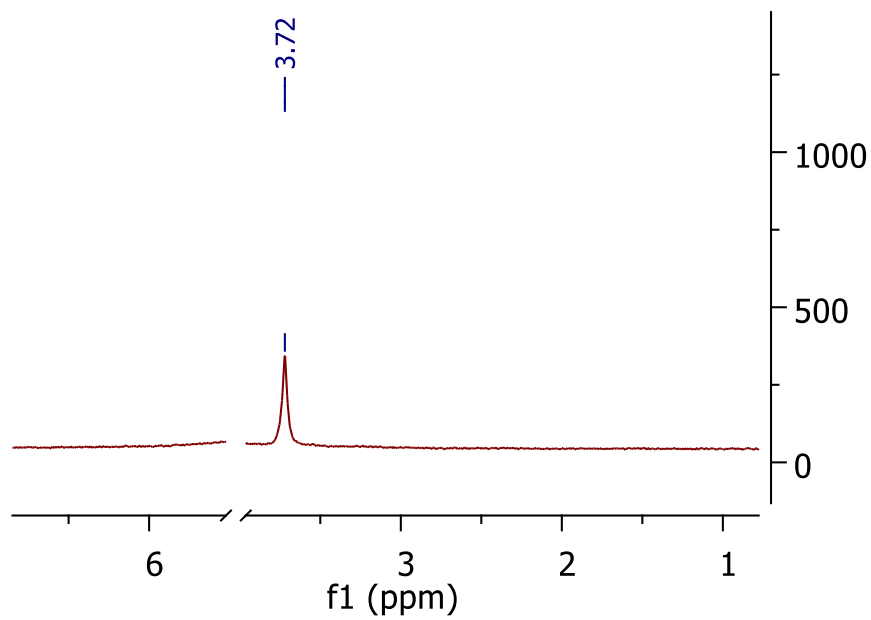
100mg Al



25mg Al



b. ^2H NMR



c. Mass Spectrum

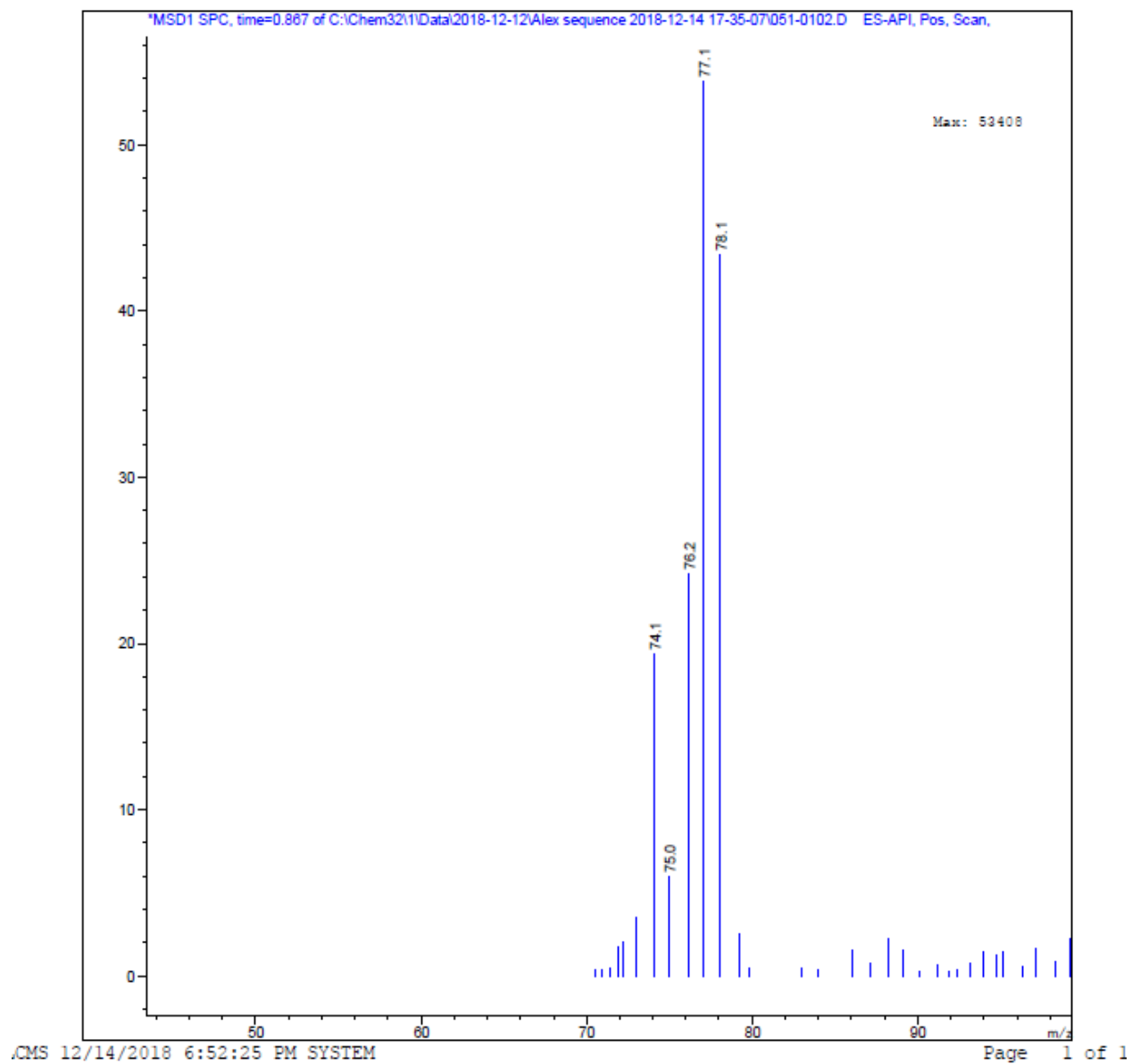
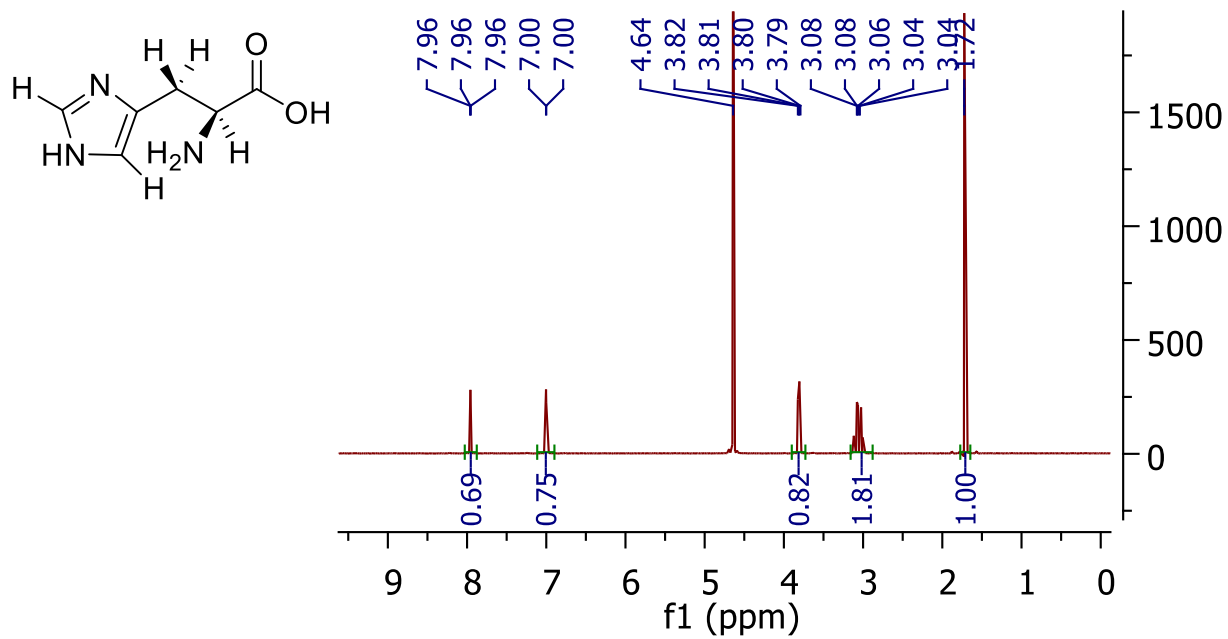


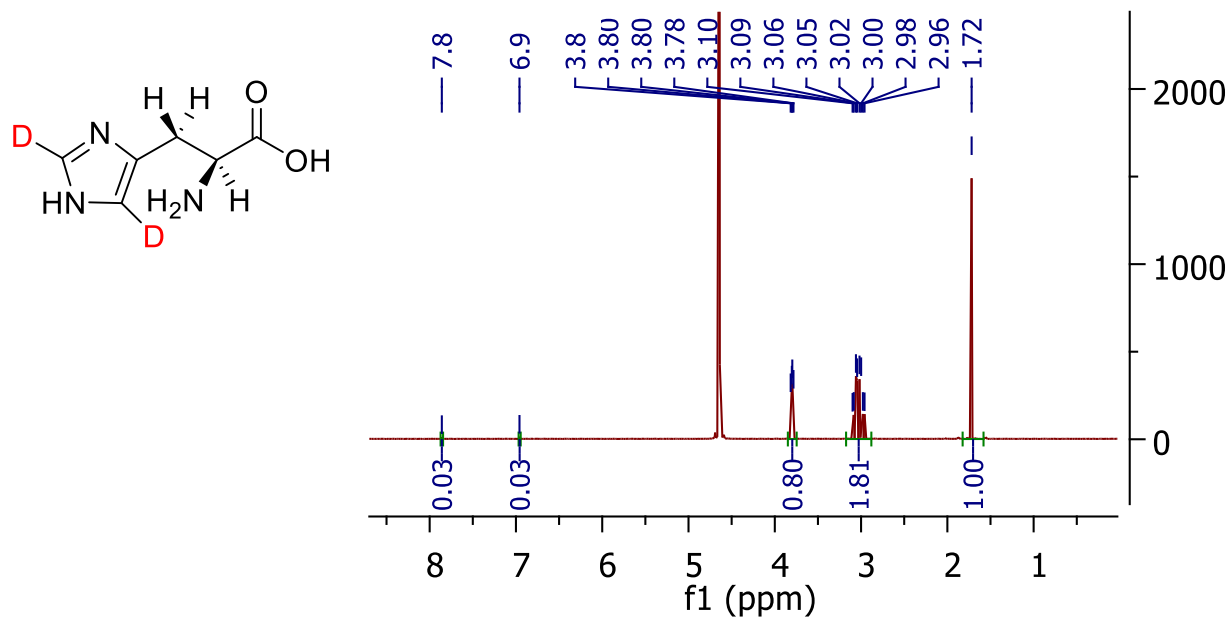
Figure S13. H-D exchange reaction of histidine

(20mg of Pd/C, MW, 120 °C, 60min)

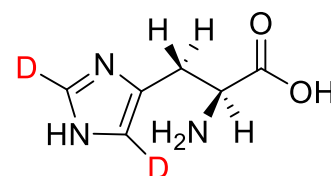
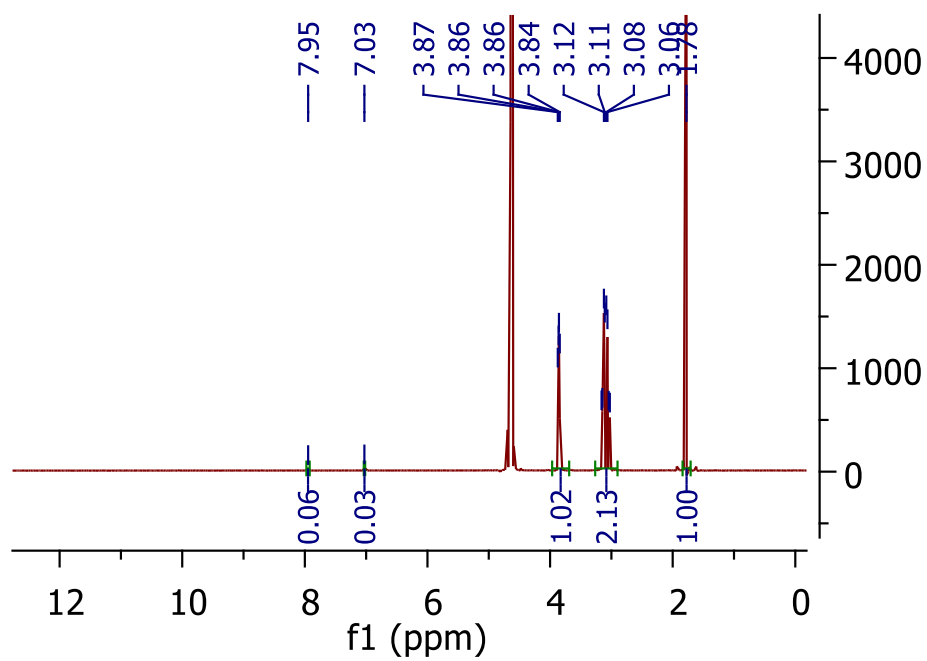
a. ^1H NMR



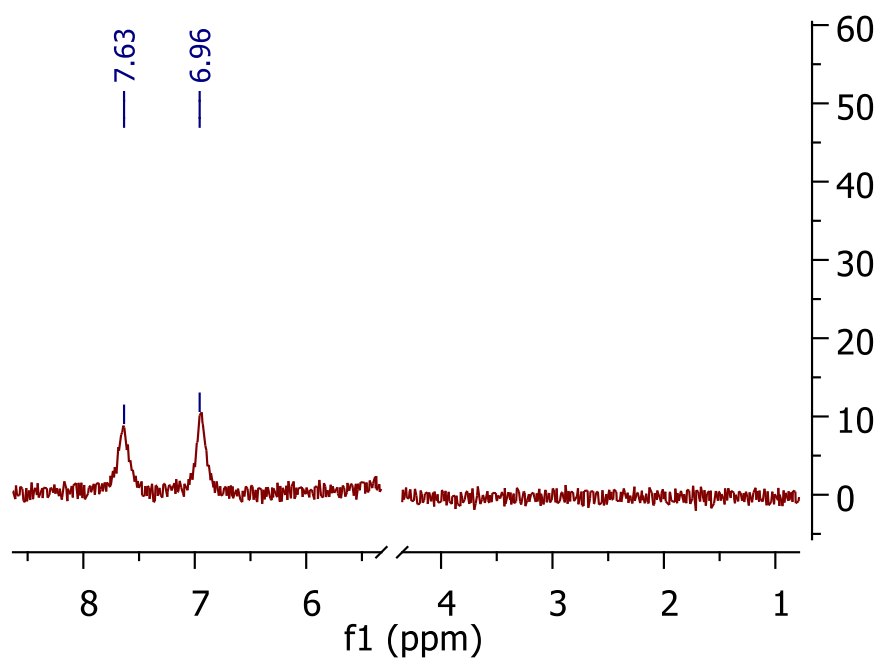
100mg Al



25mg Al



b. ²H NMR



c. Mass spectrum

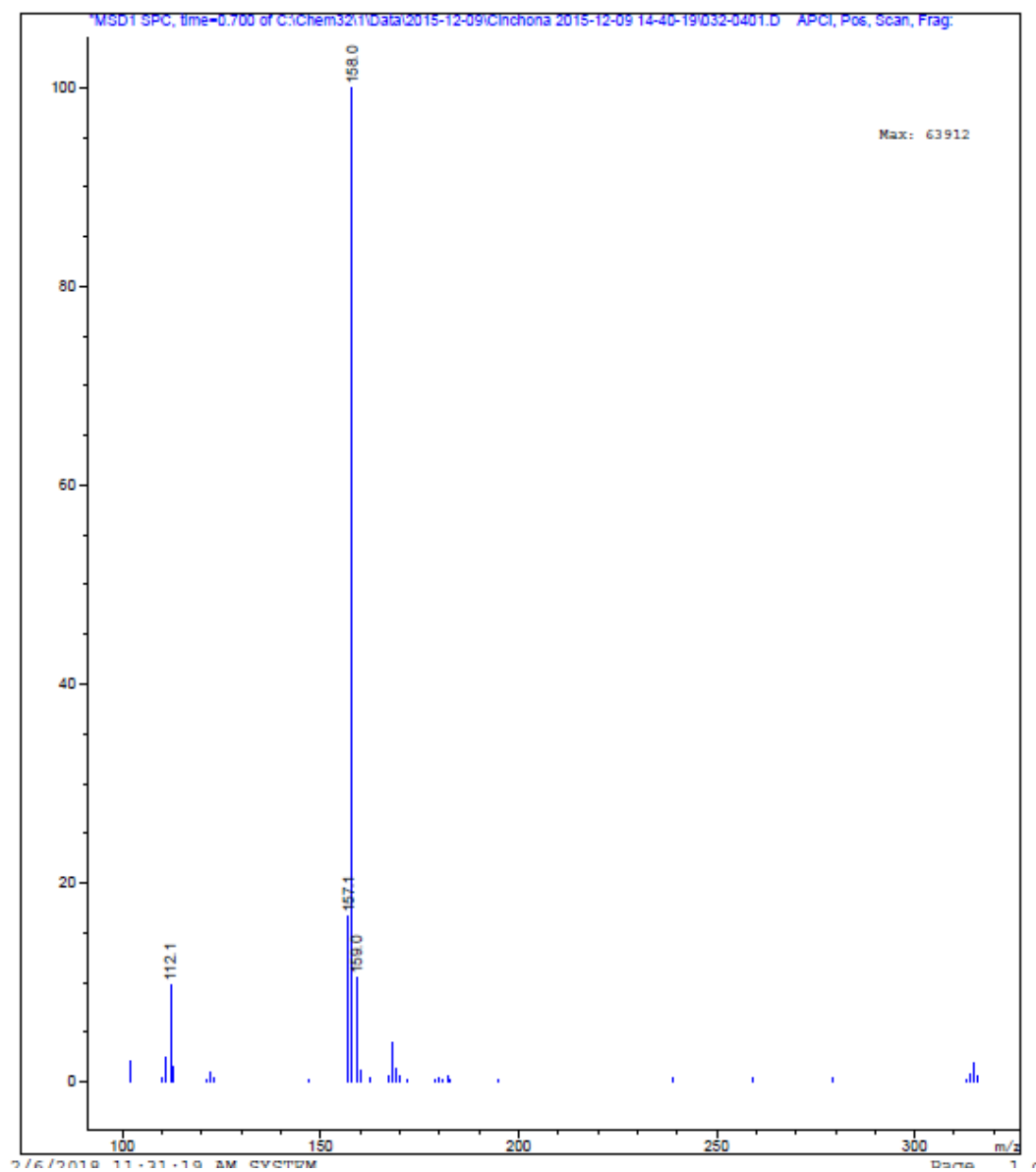
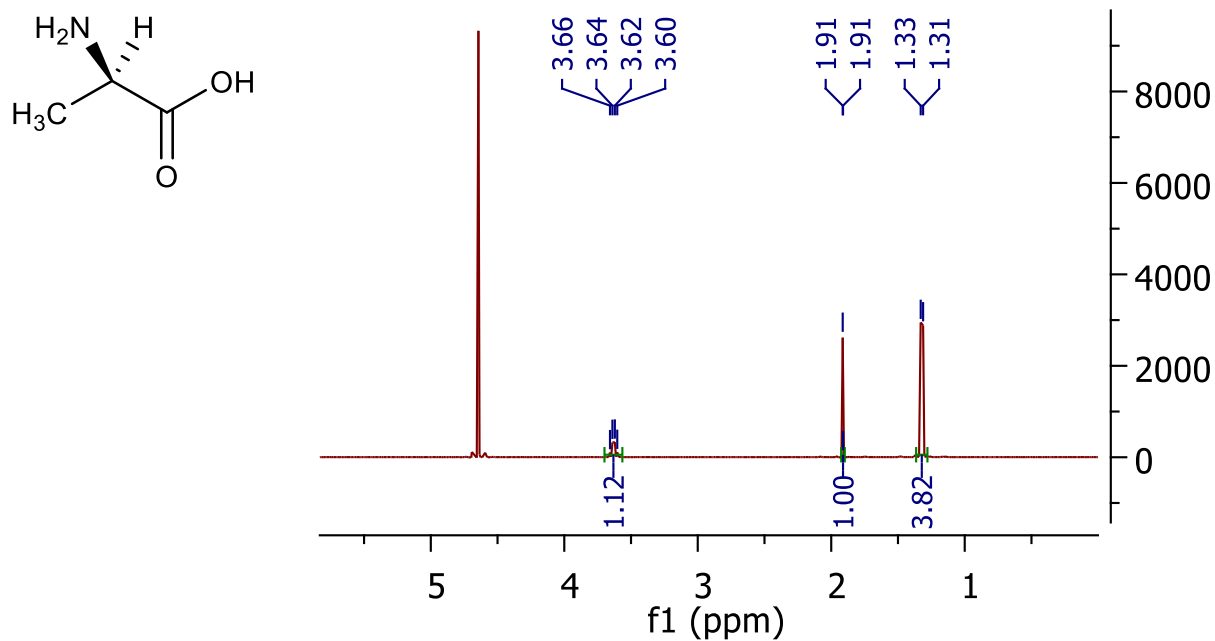


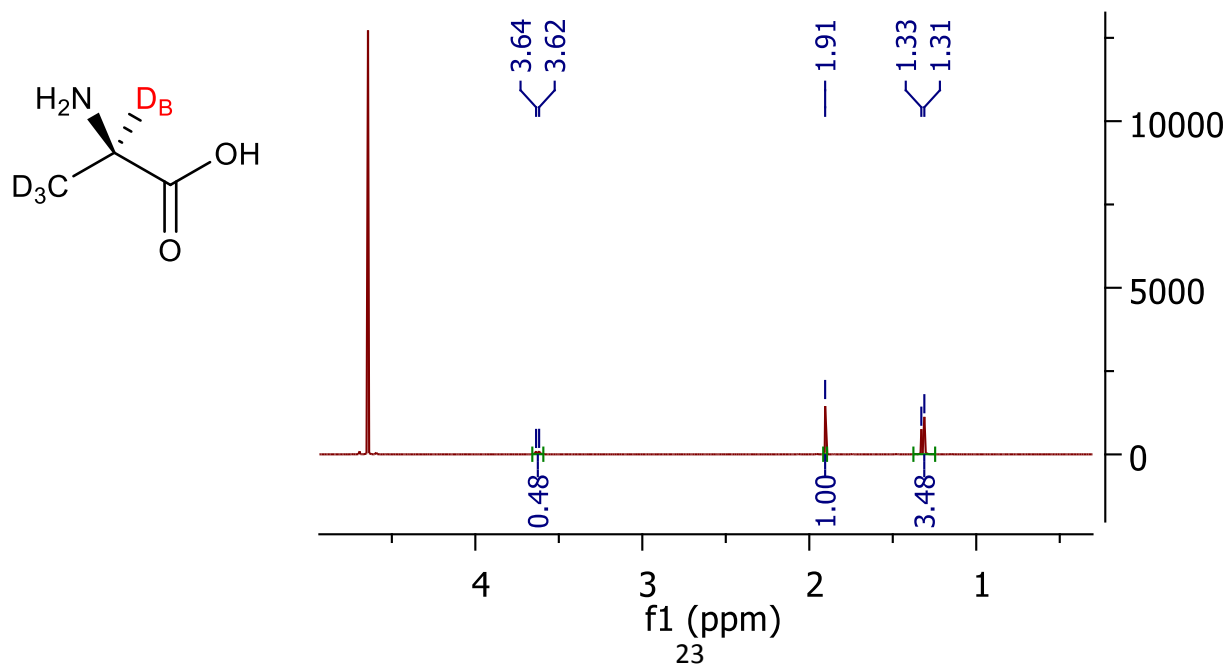
Figure S14. H-D exchange reaction of alanine

(20mg of Pd/C, MW, 120 °C, 60min)

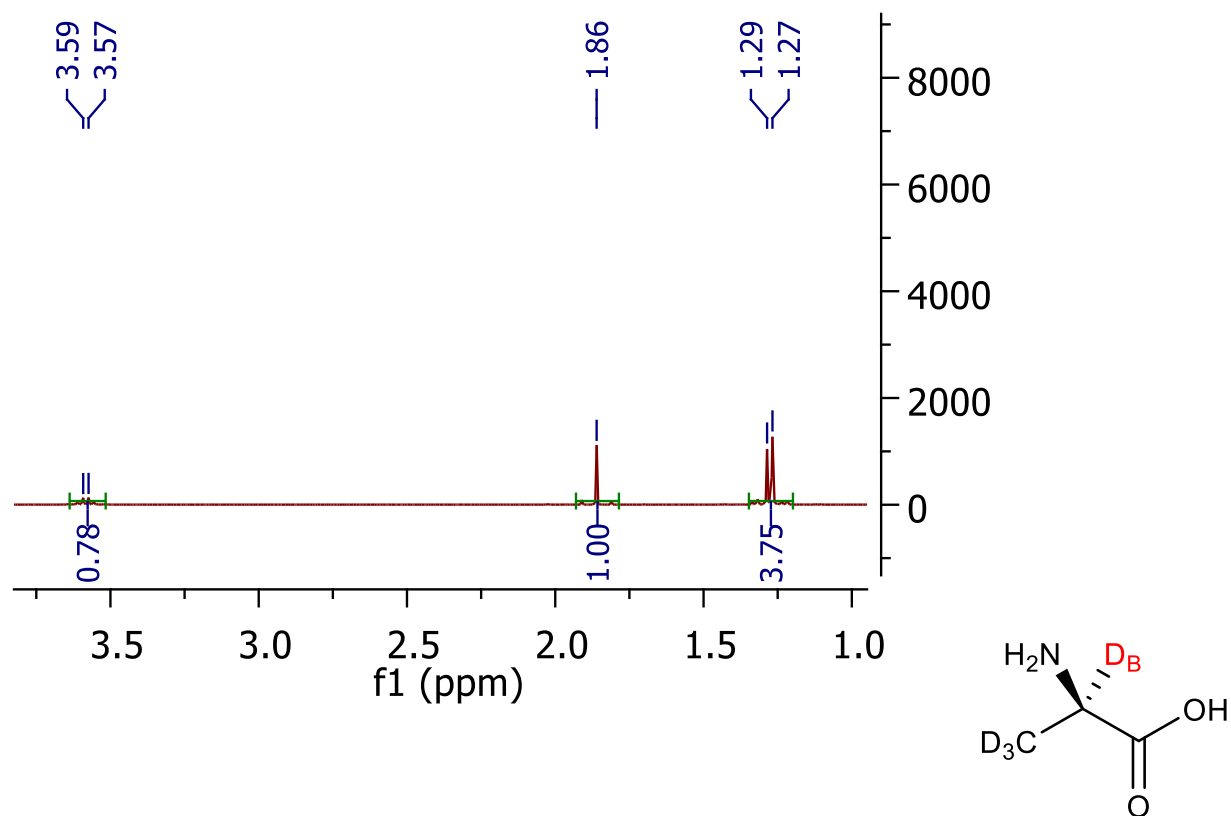
a. ^1H NMR



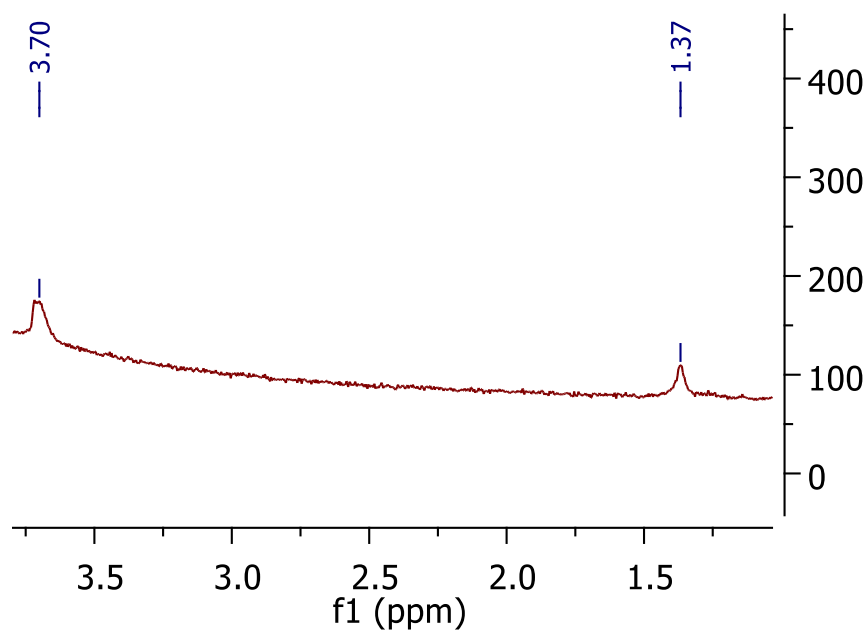
100mg Al



25mg AI (40% yield)

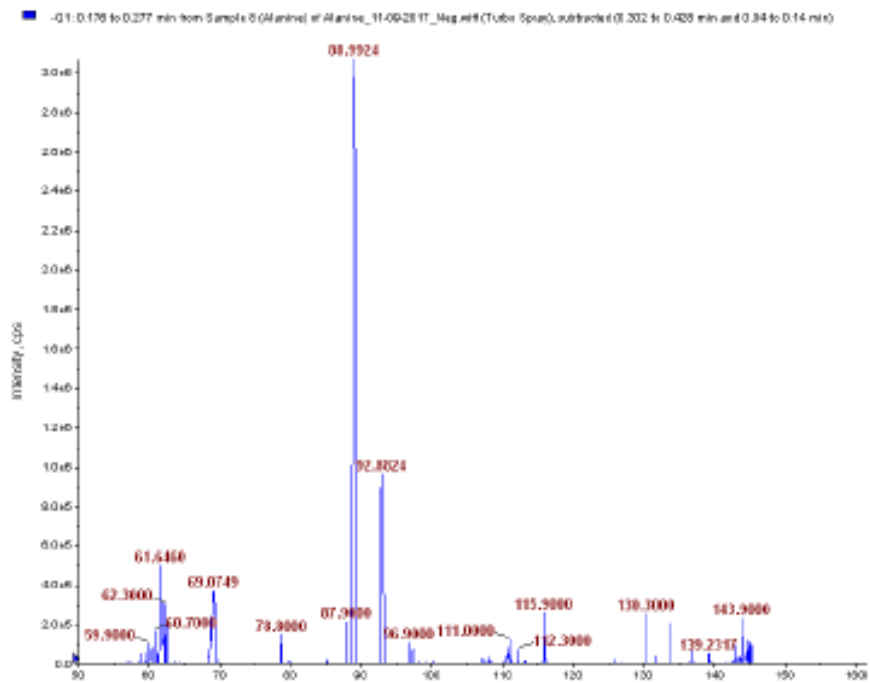


b. ^2H NMR



c. Mass spectrum

d_1 -L-alanine/ d_4 -L-alanine



Non-deuterated L-alanine

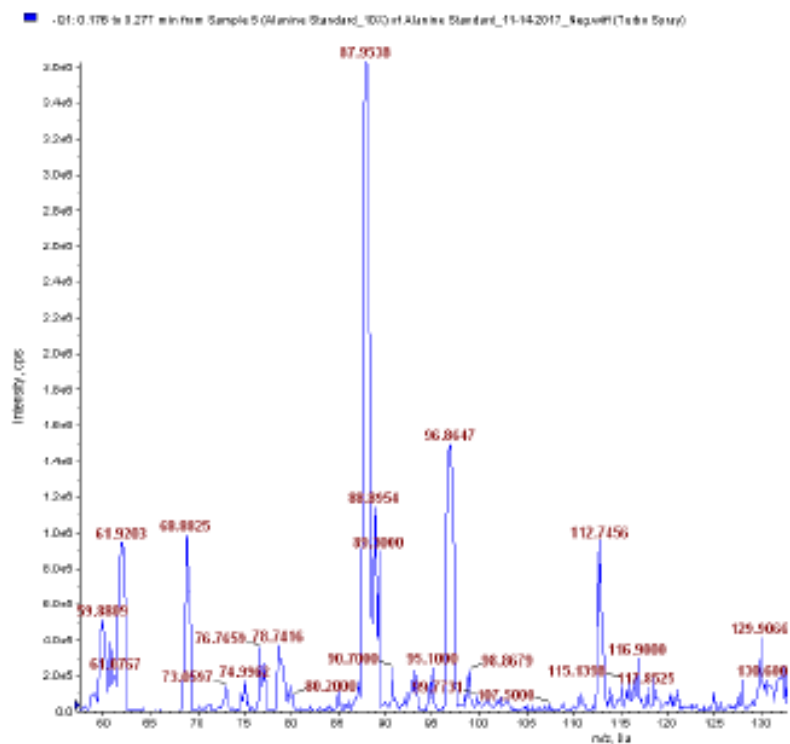
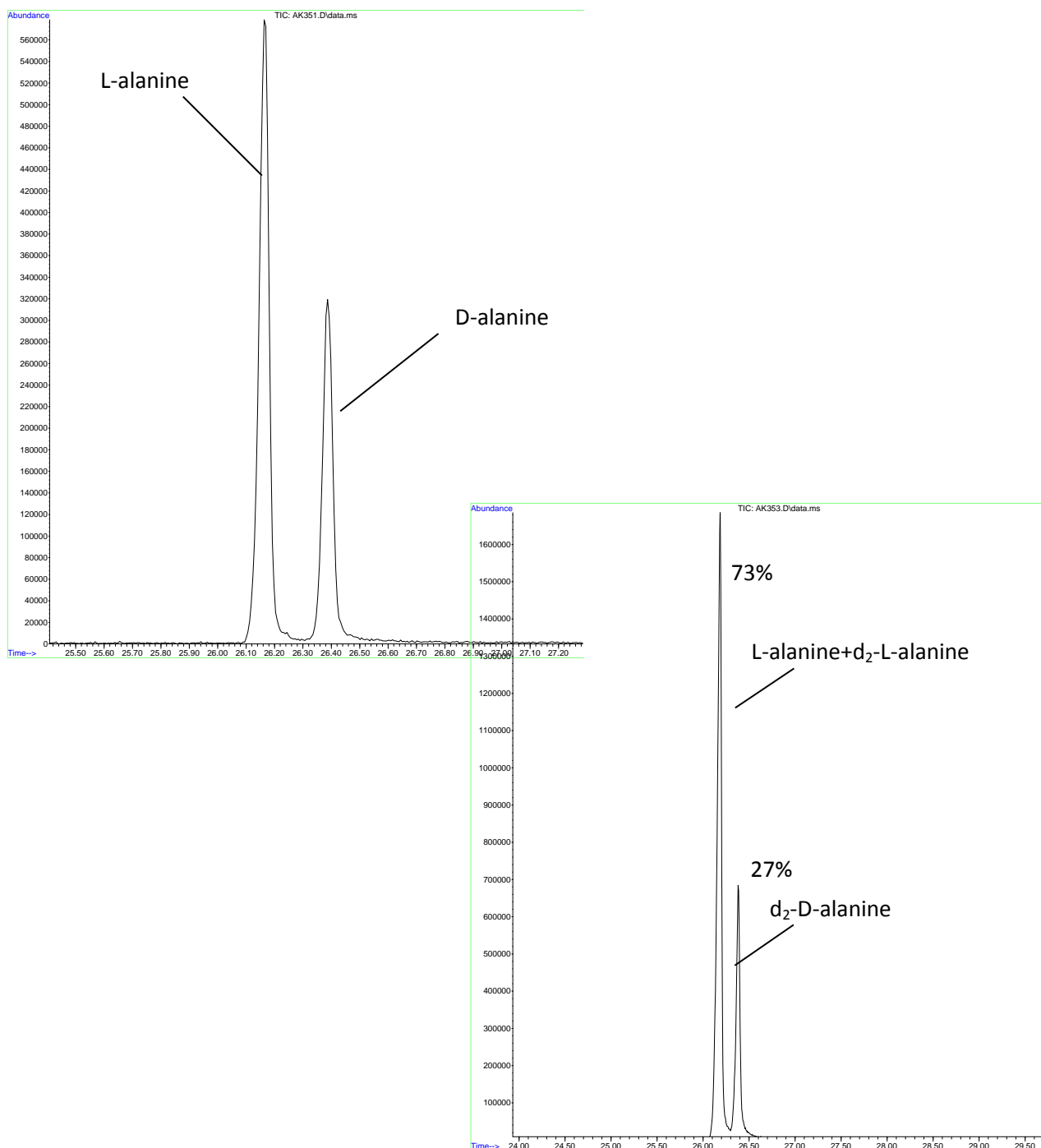
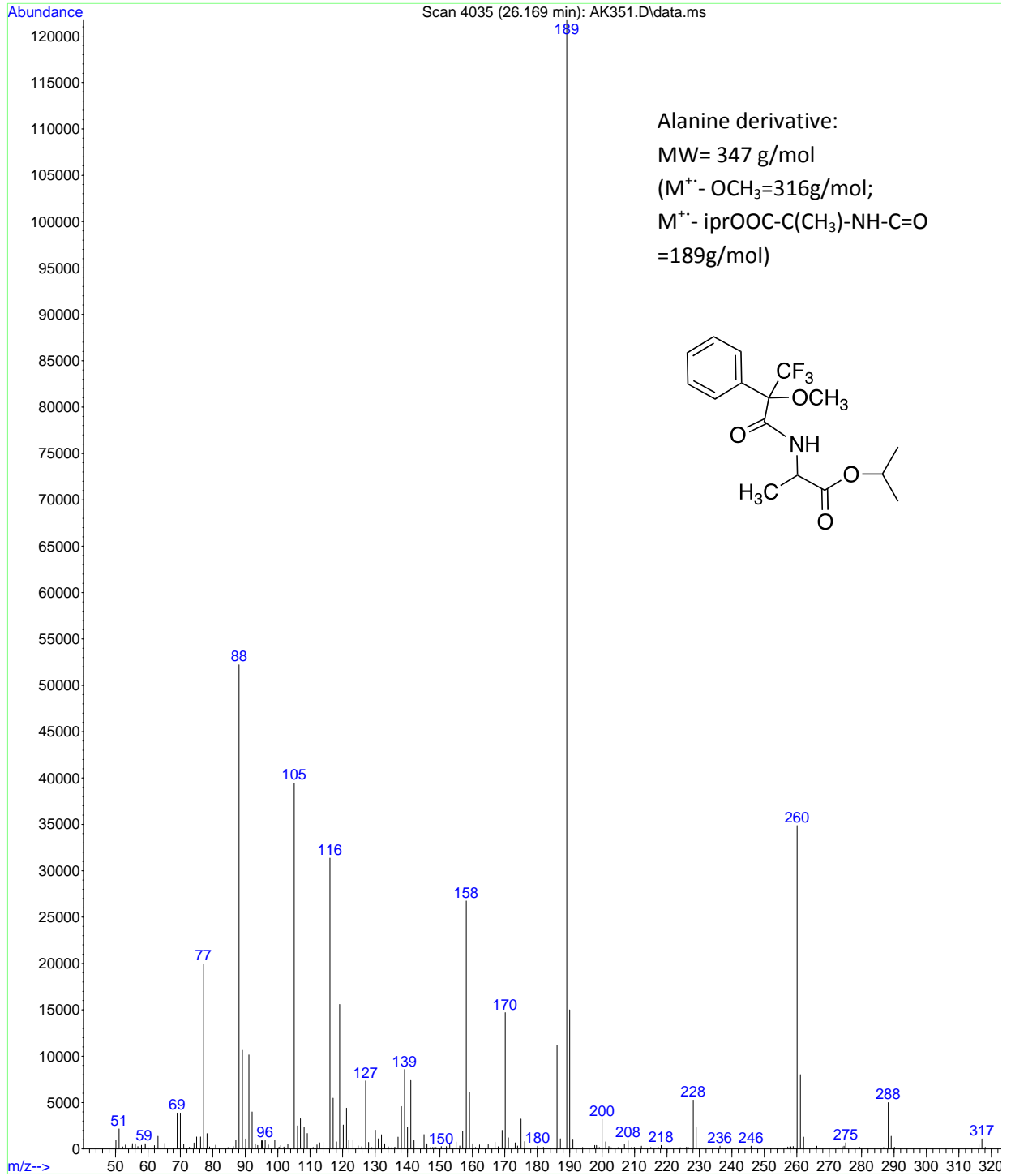


Figure S15. Determination of the chirality of deuterated alanine

Alanine was derivatized using isopropyl alcohol to form an amino acid ester first and then it was reacted with Mosher's chloride to functionalize the amino group; before it was injected in the GC-MS. The first chromatogram shows the separation of a pseudo racemic mixture of alanine. The mass spectrum of both products was identical. The second chromatogram corresponds to the derivatized d₂-alanine.





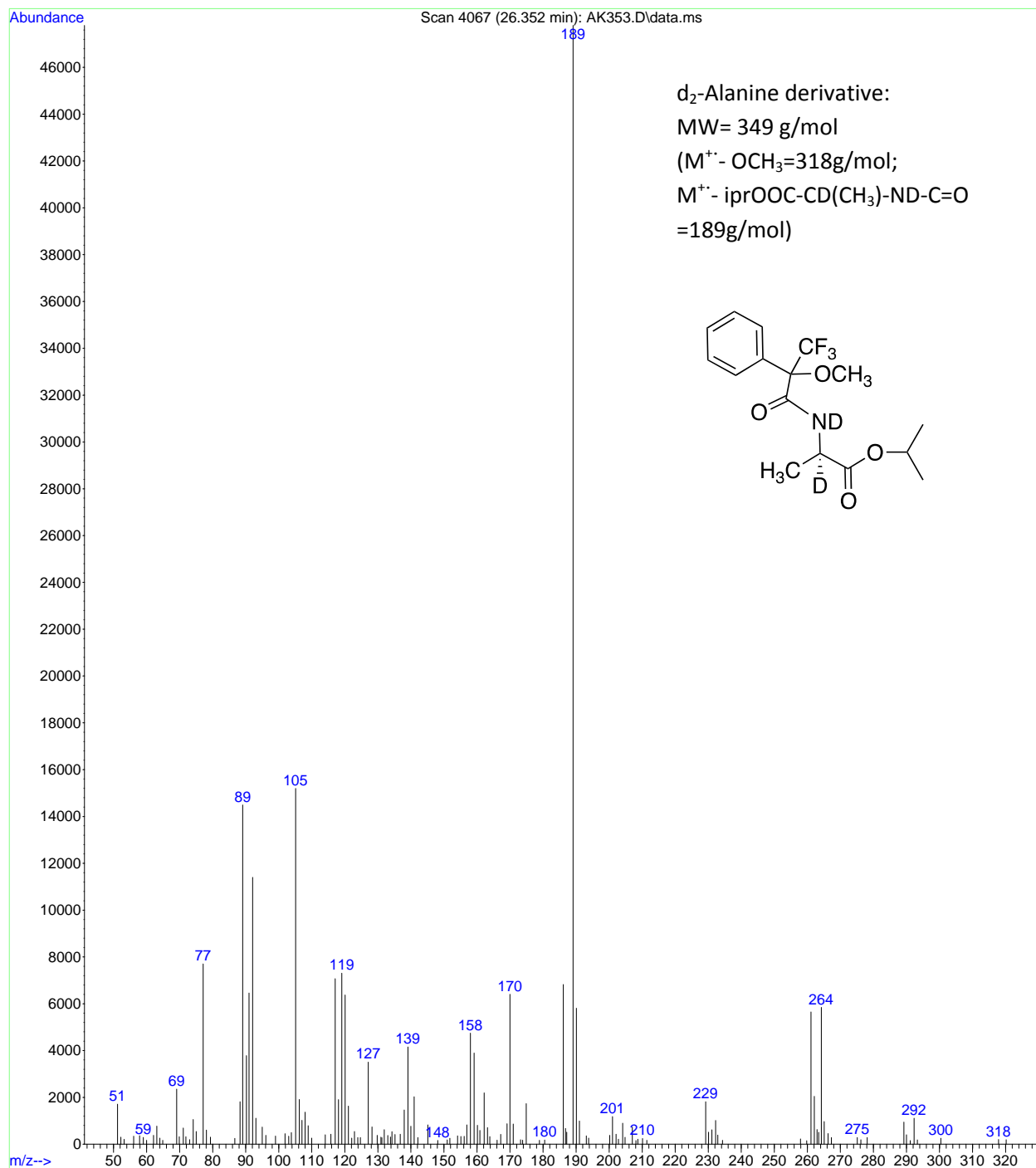
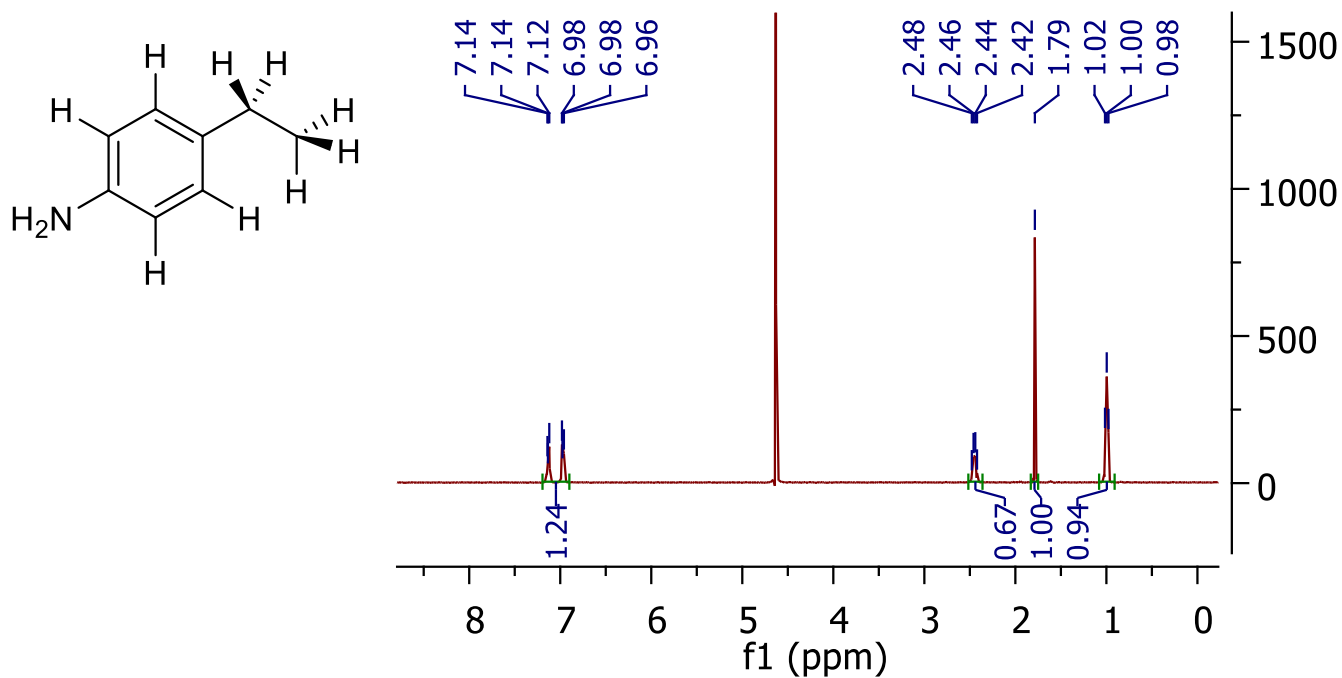


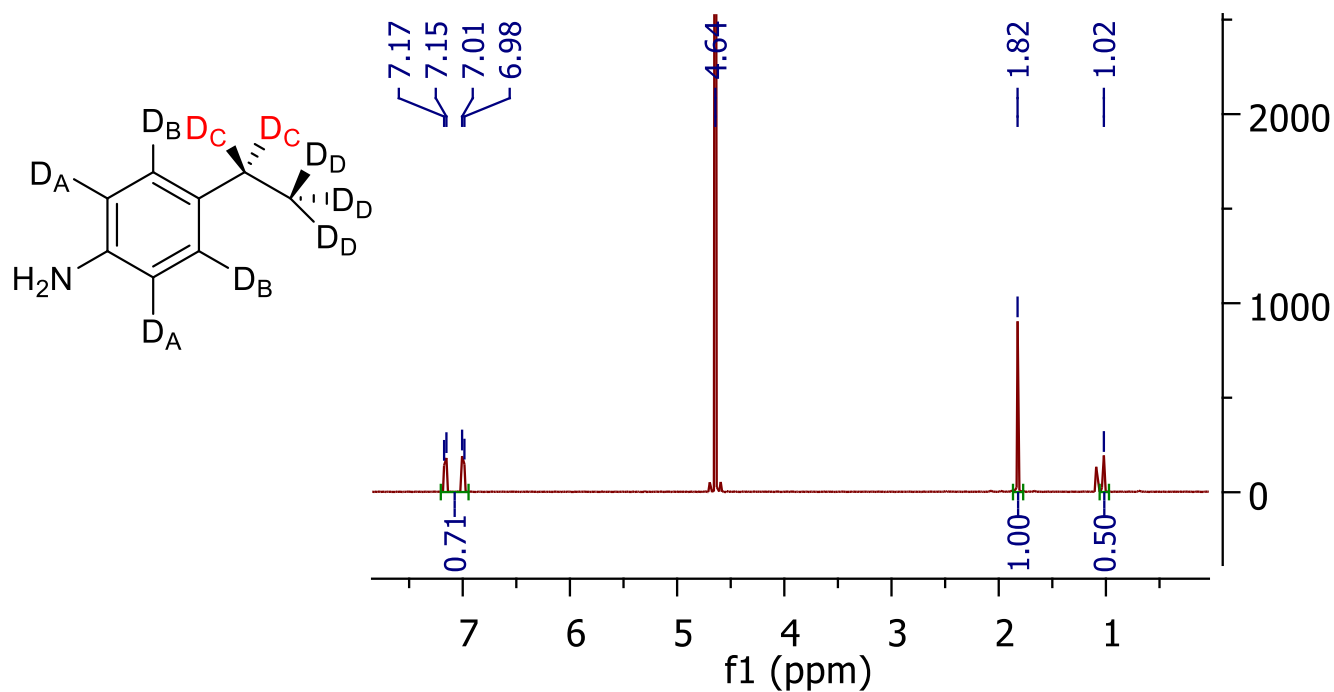
Figure S16. H-D exchange reaction of ethylaniline

(20mg of Pd/C, MW, 60 °C)

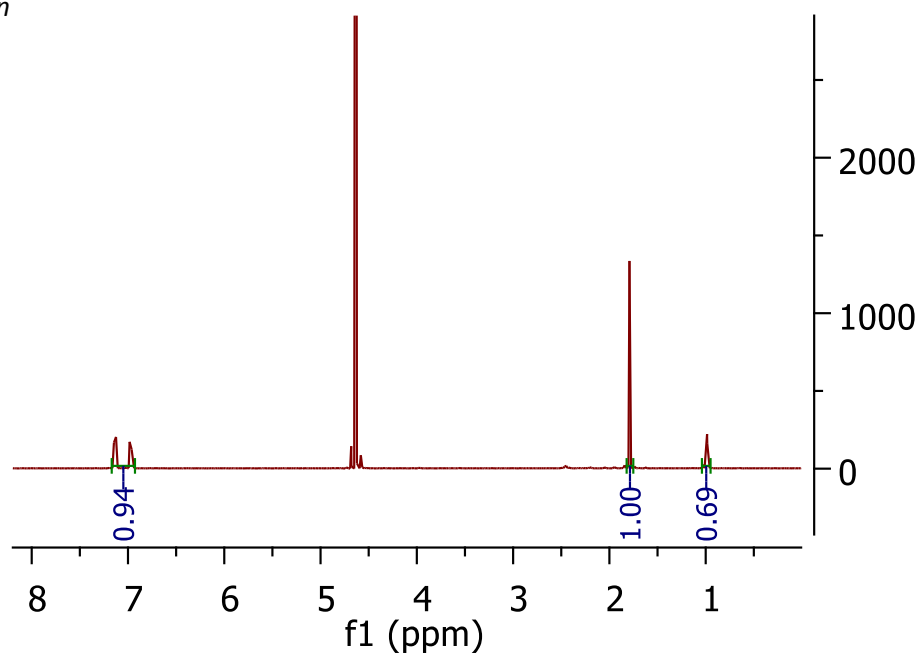
a. ^1H NMR



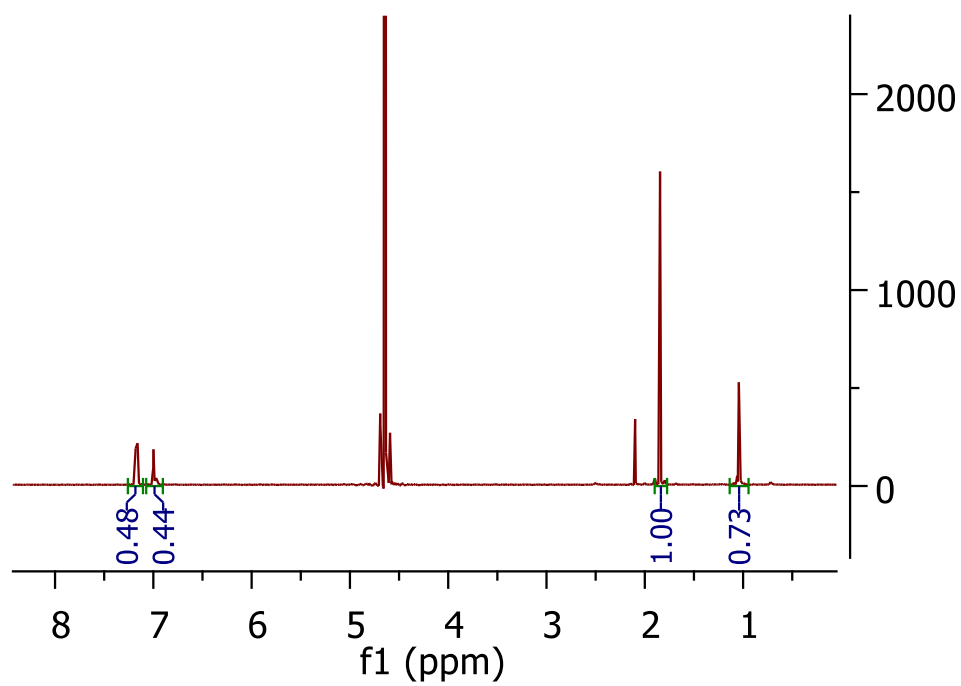
100mg Al, 60min



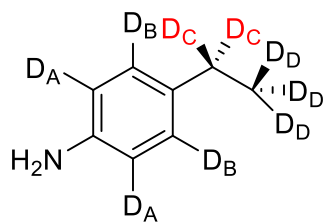
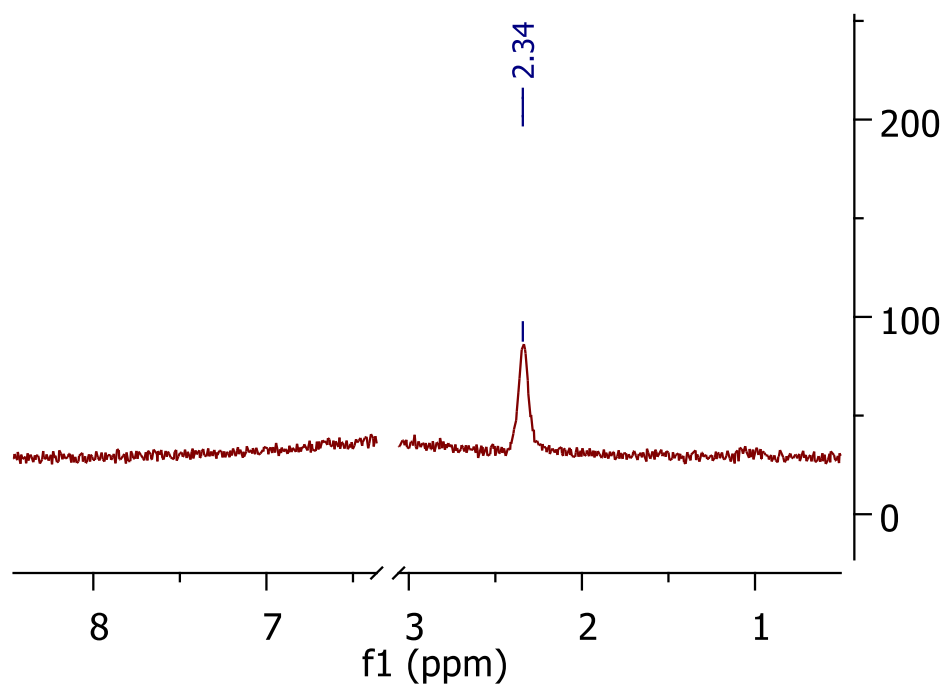
100mg Al, 20min



25mg Al, 20min



b. ^2H NMR



c. Mass spectrum

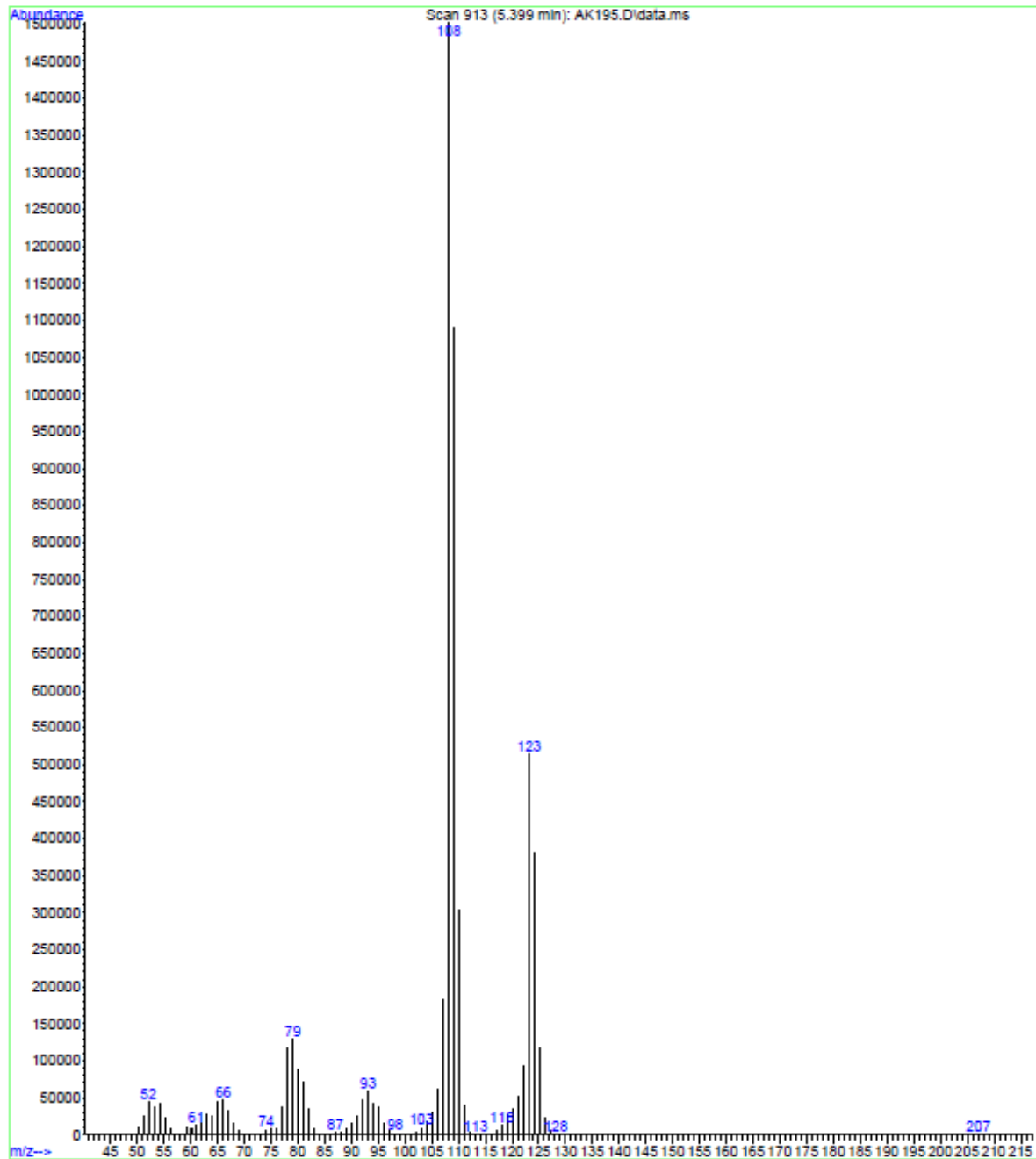
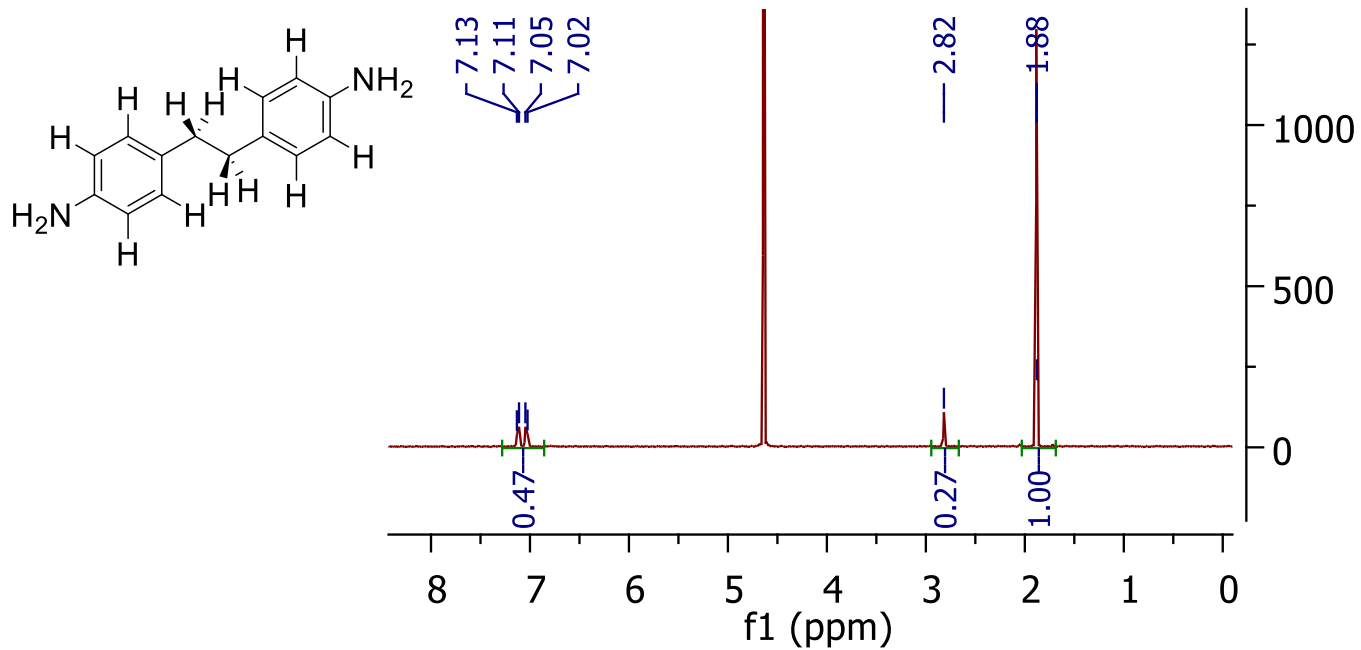


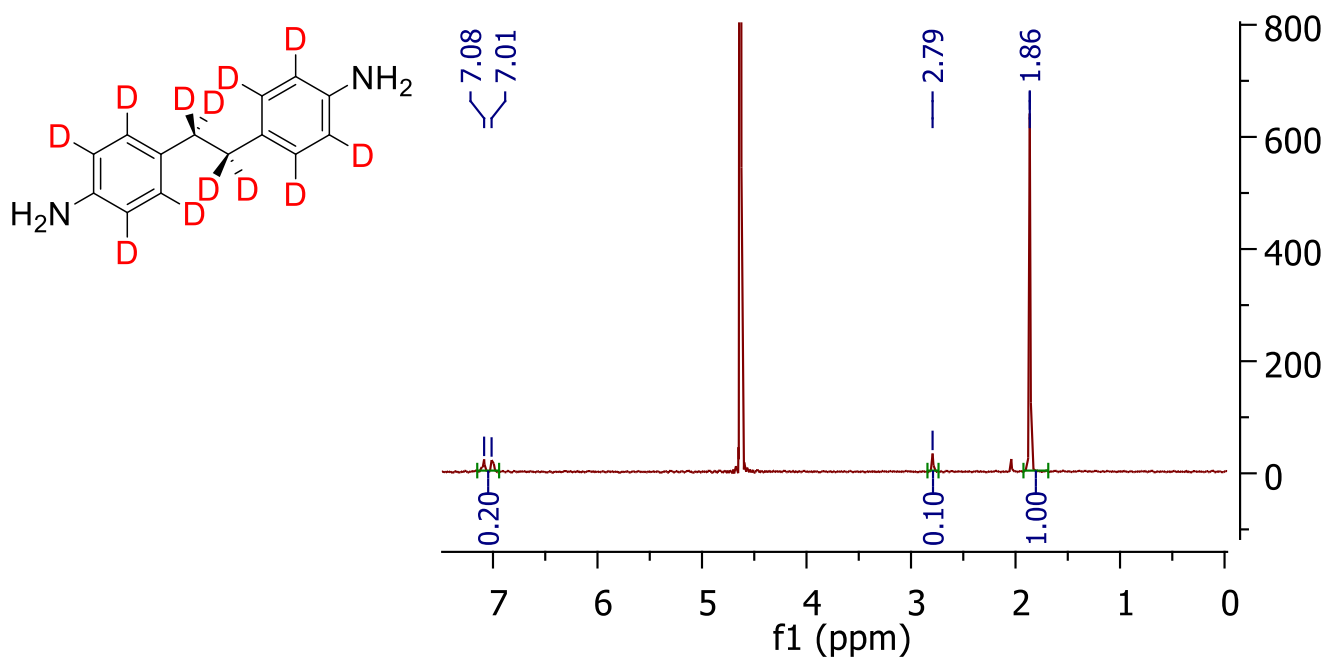
Figure S17. H-D exchange reaction of ethylenedianiline

(20mg of Pd/C, MW, 60min)

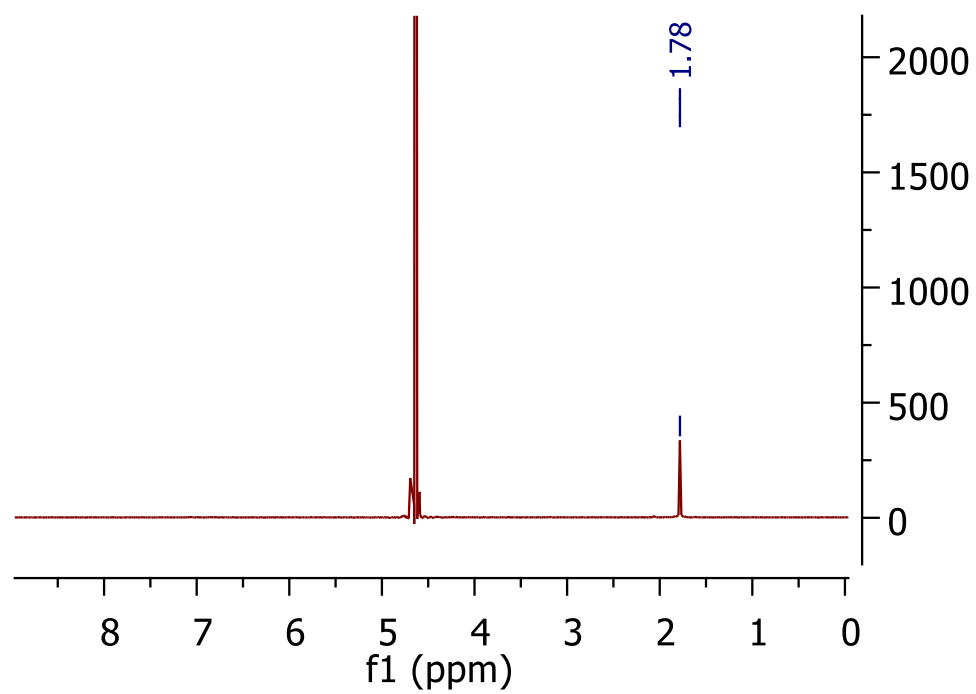
a. ^1H NMR



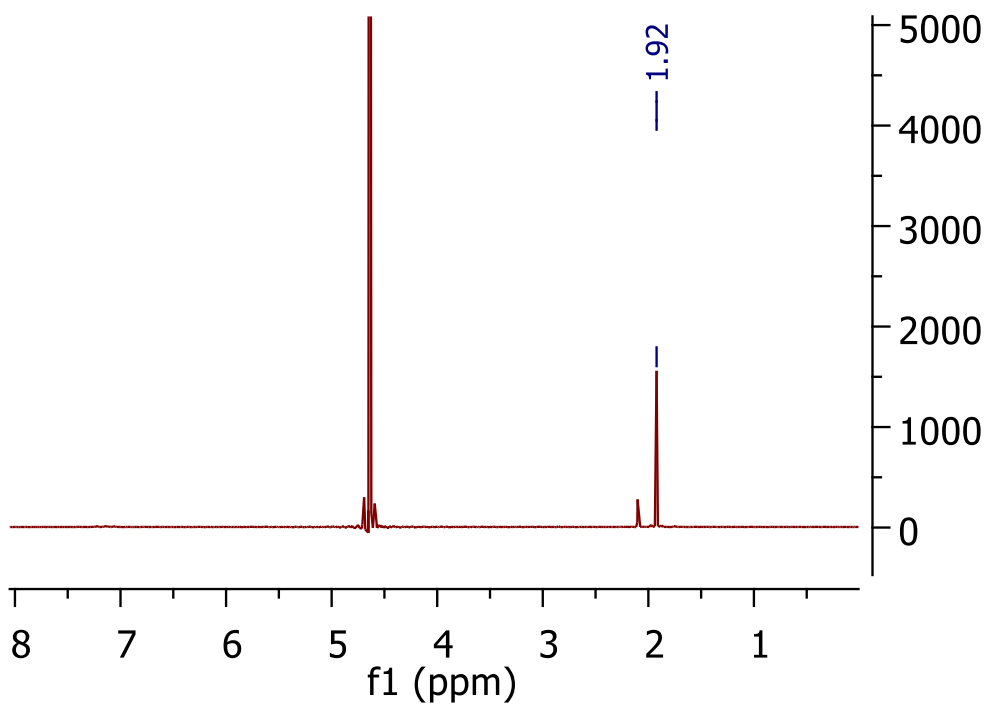
100mg Al, 80°C



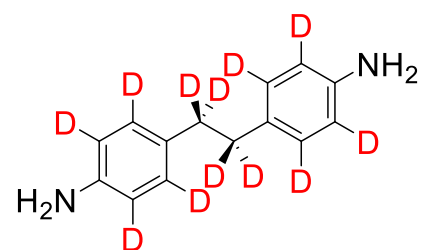
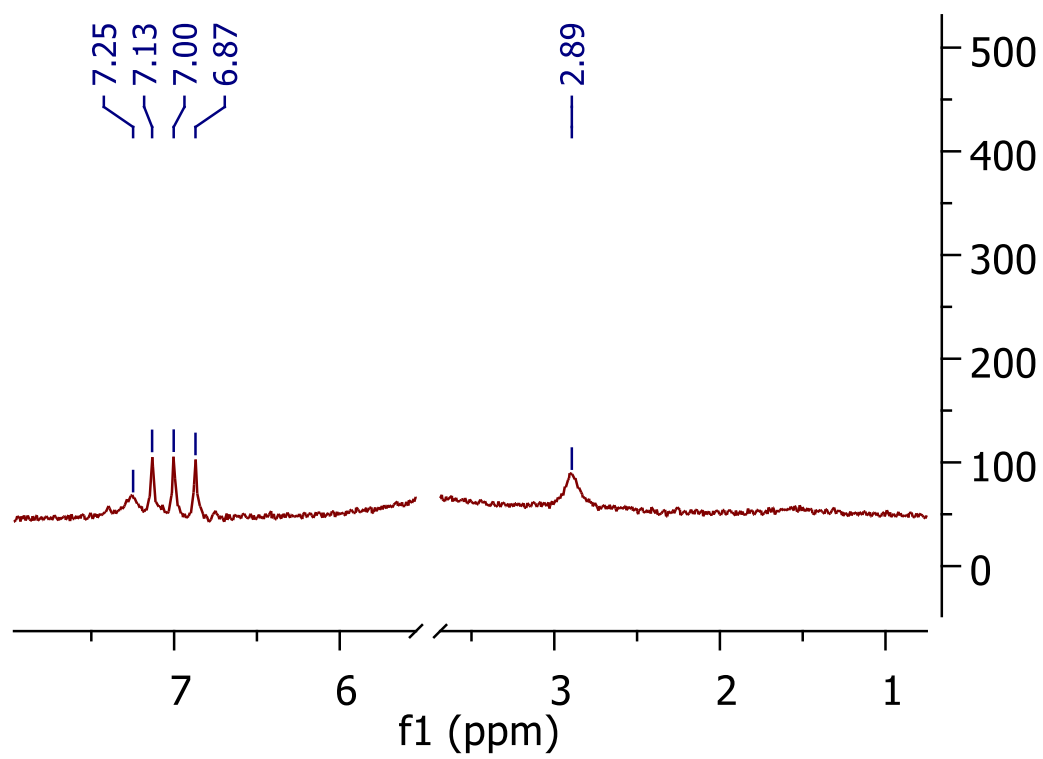
100mg of Al, 120 °C



25mg Al, 120 °C



b. ^2H NMR



c. Mass spectrum

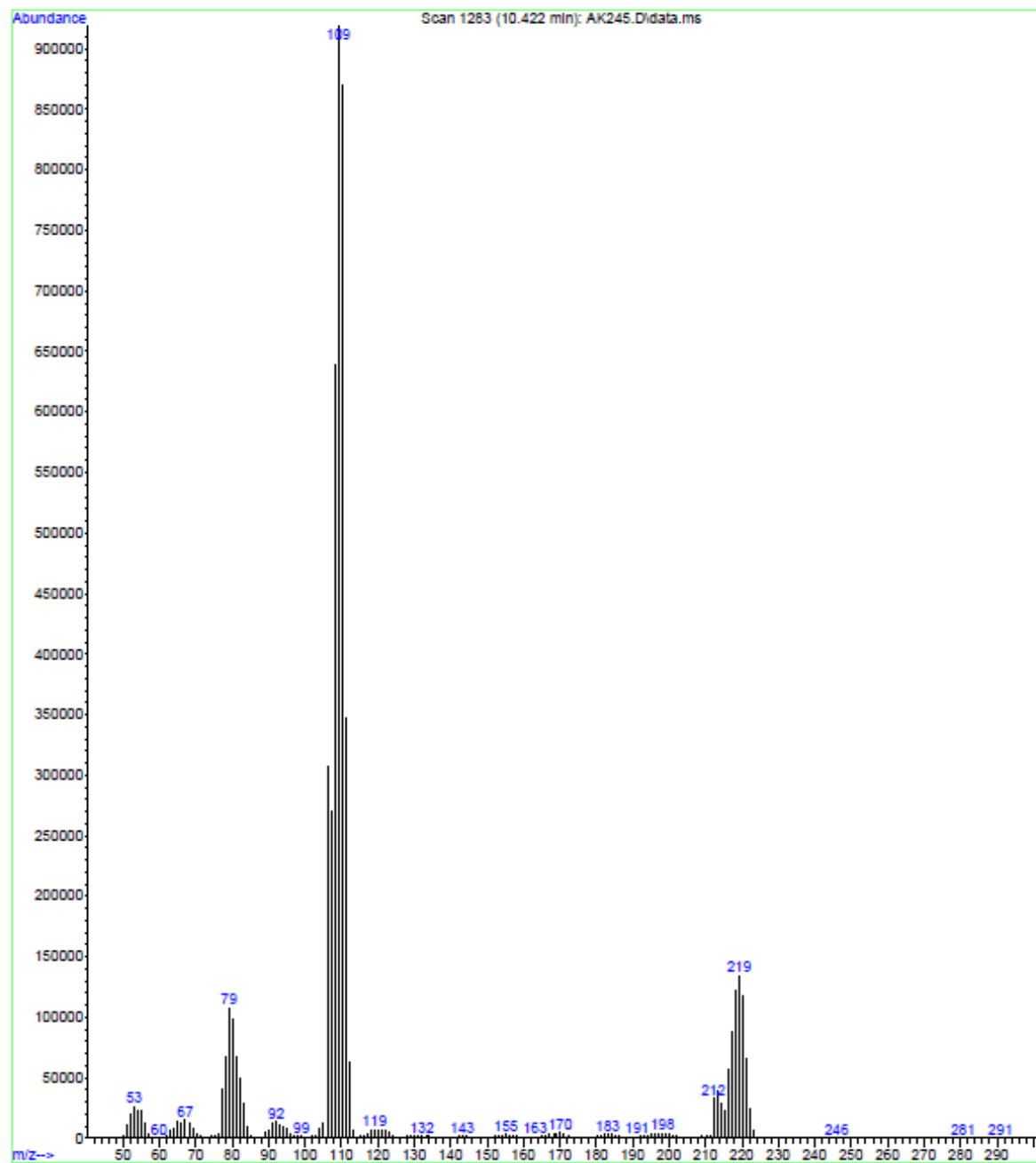
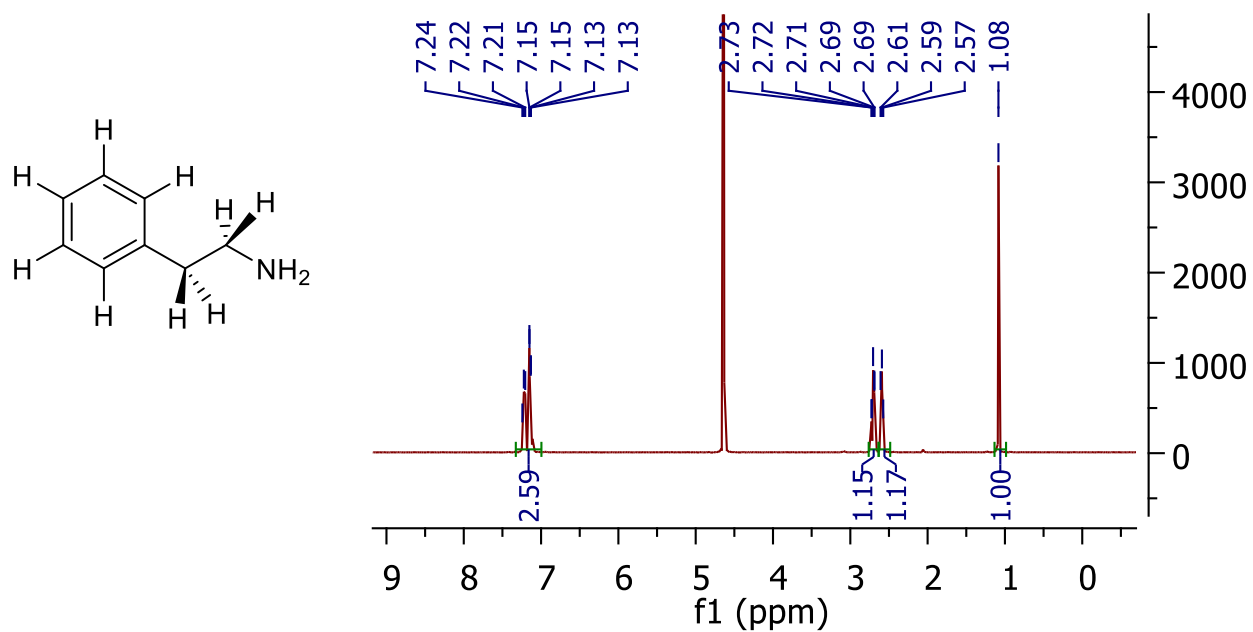


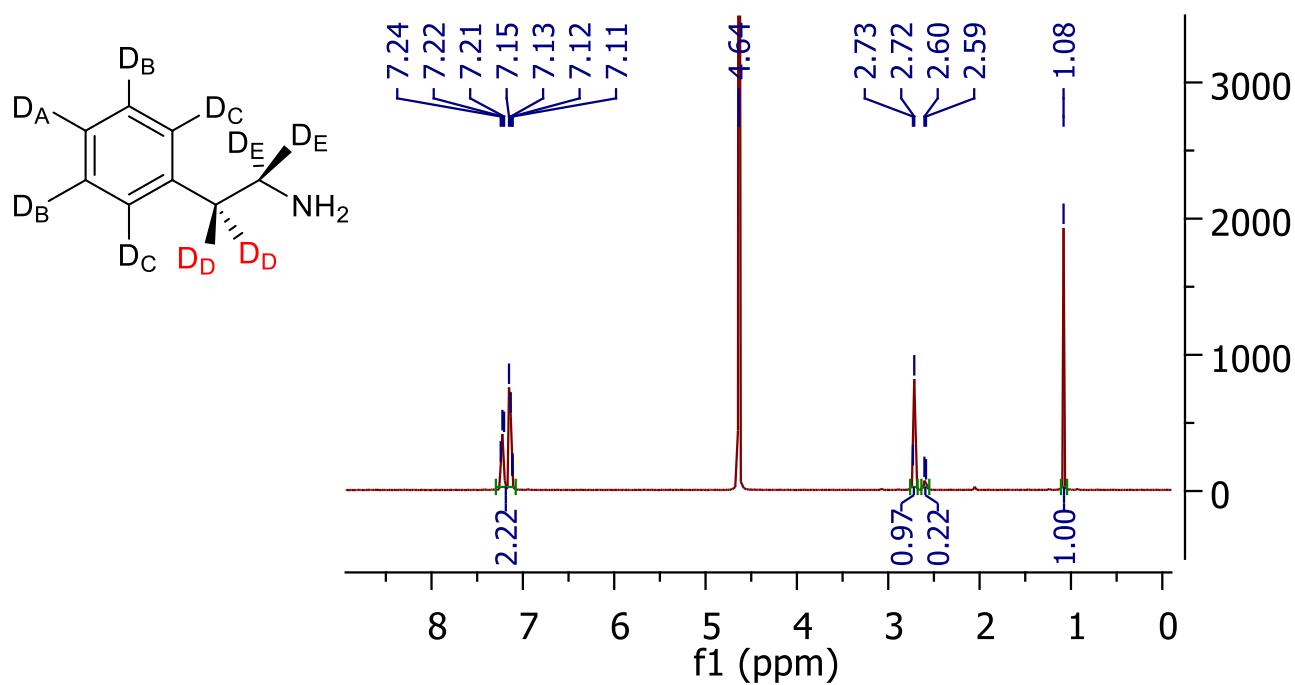
Figure S18. H-D exchange reaction of 2-phenylethylamine

(20mg of Pd/C, MW, 60min, 80°C)

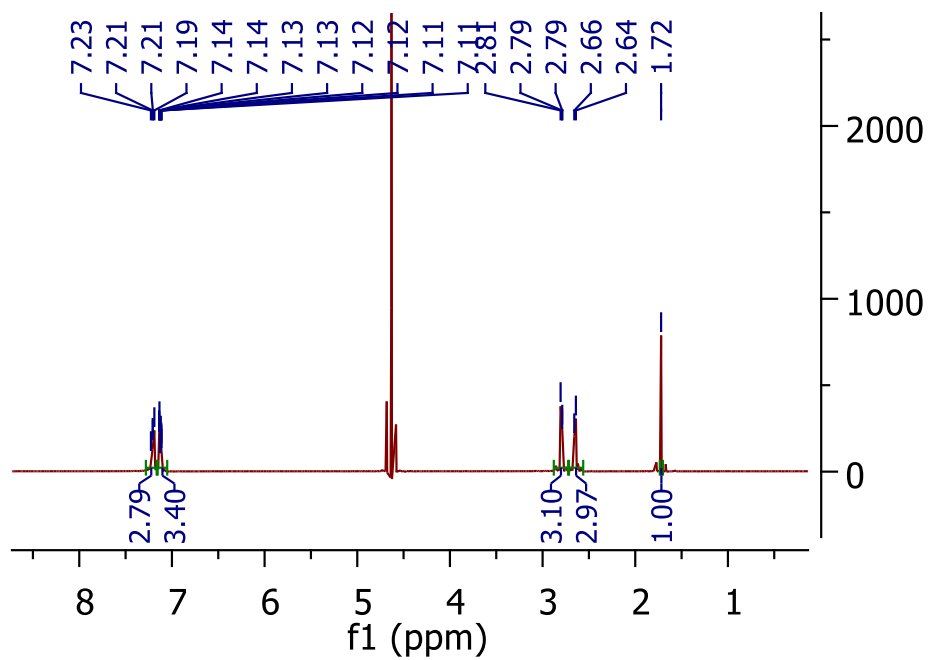
a. ^1H NMR



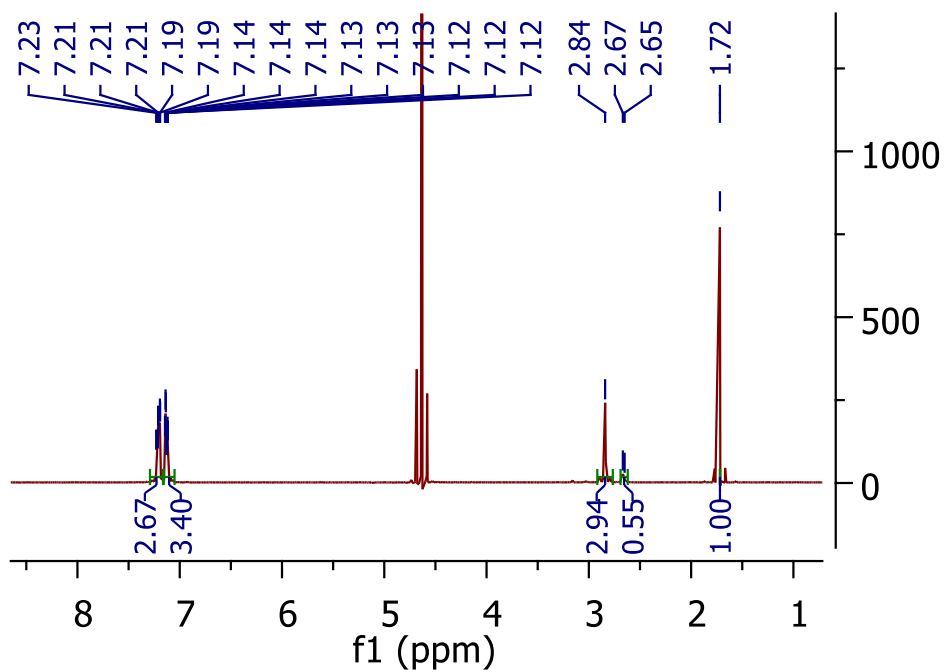
100mg Al



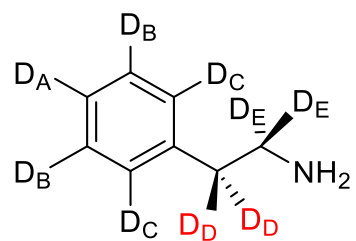
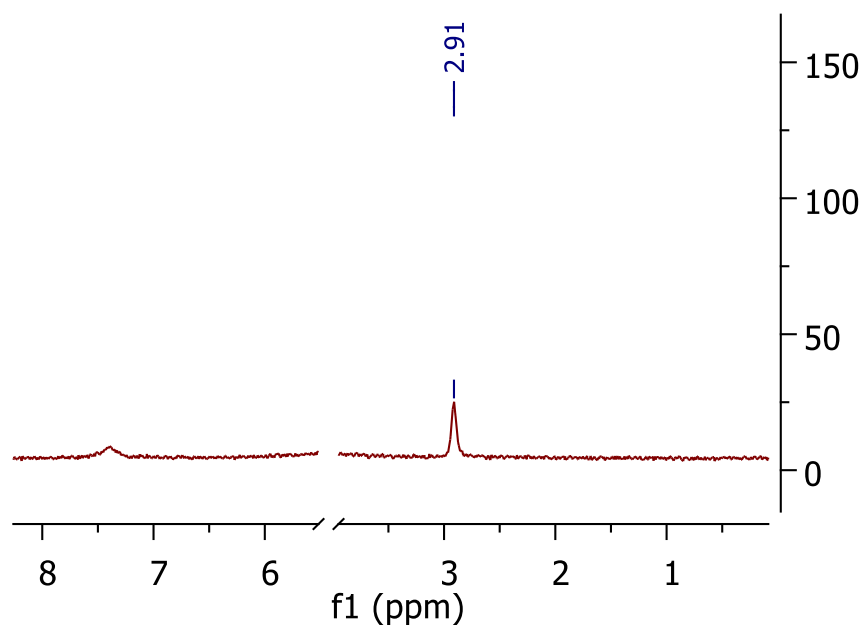
25mg Al



Reference



b. ^2H NMR



c. Mass spectrum

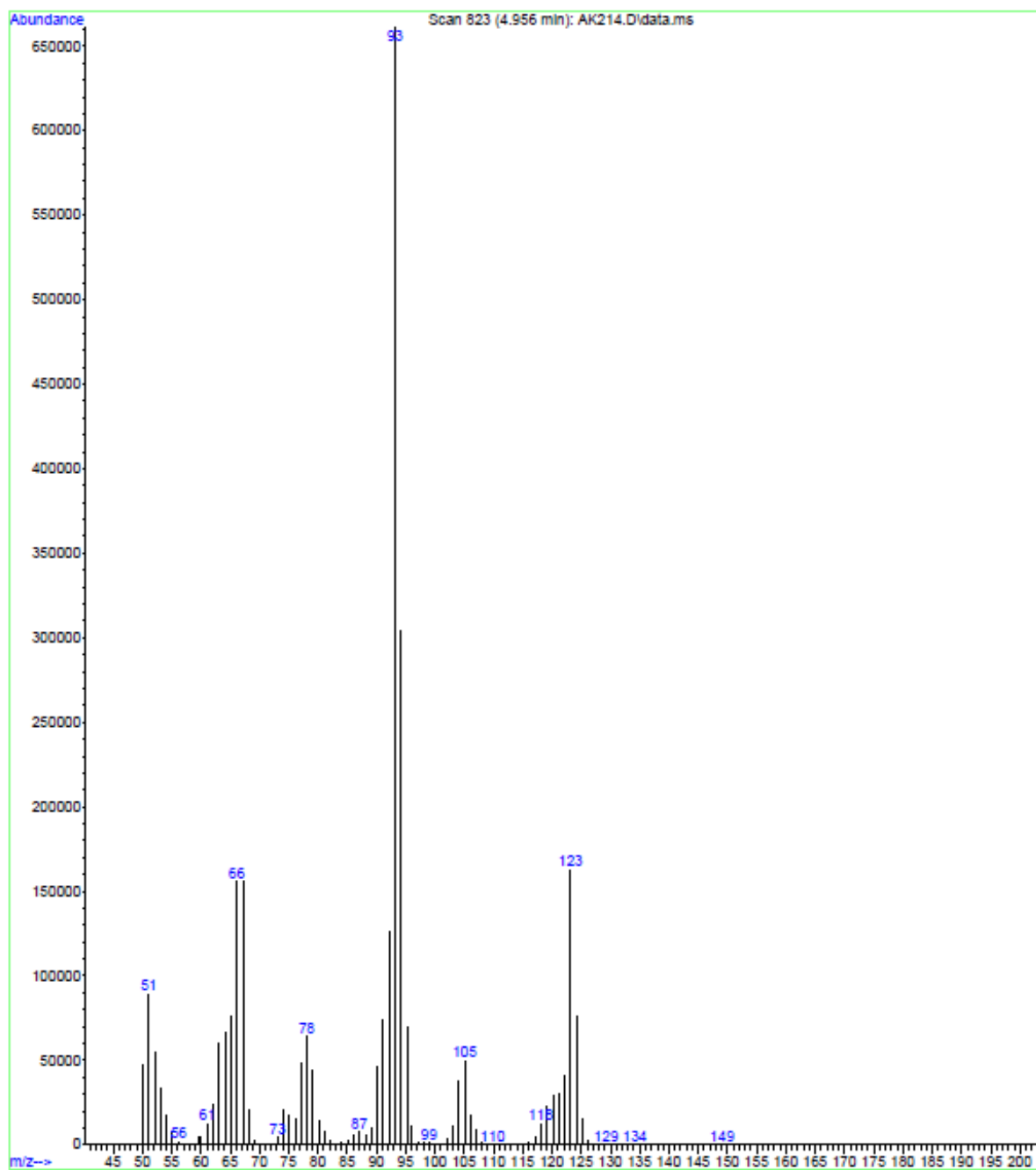
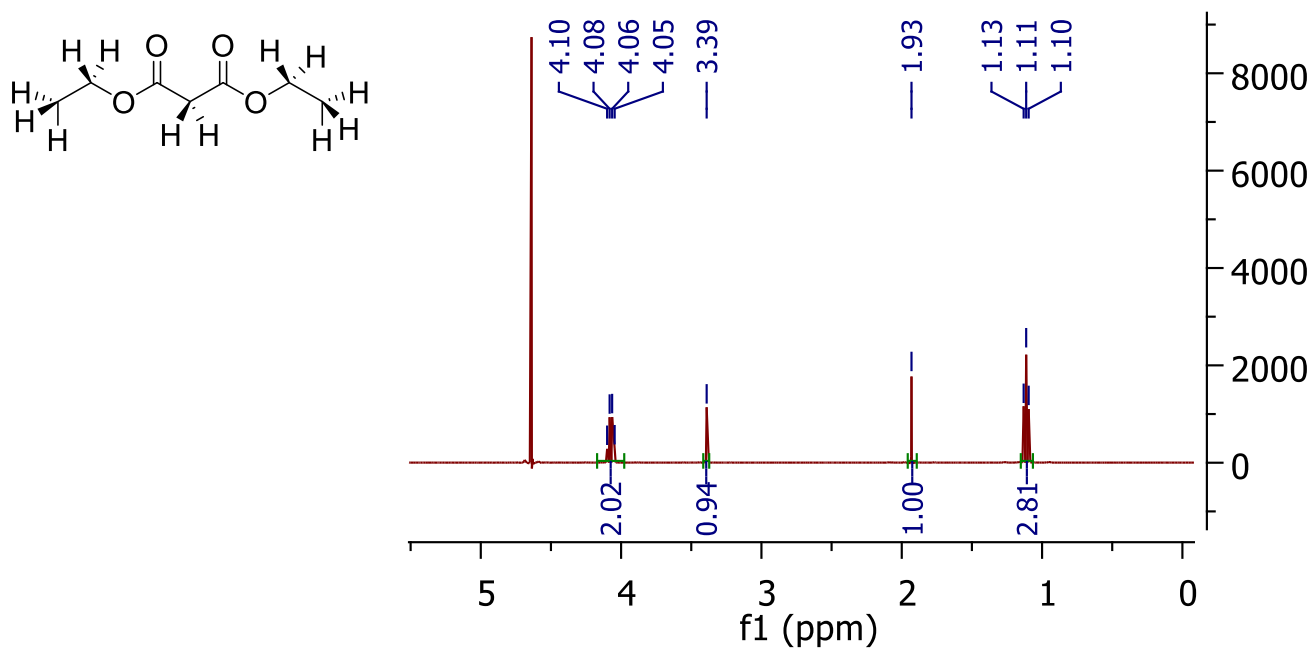


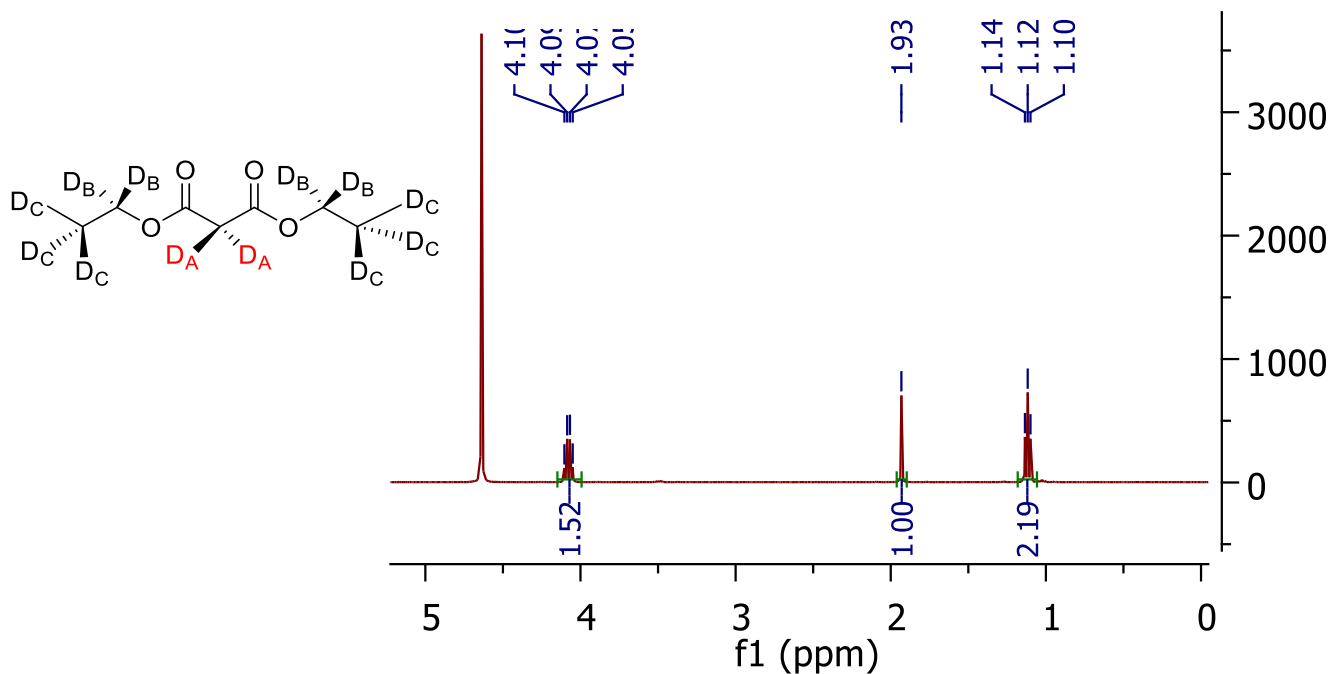
Figure S19. H-D exchange reaction of diethyl malonate

(20mg of Pd/C, MW, 60min, 100°C)

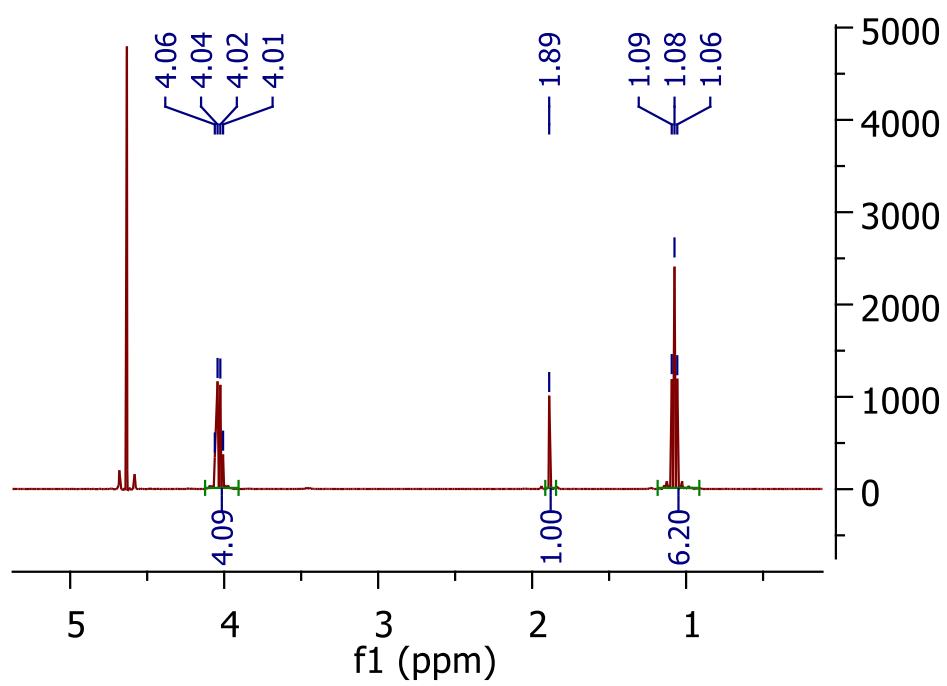
a. ^1H NMR



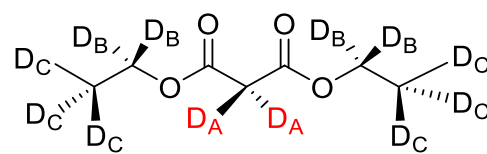
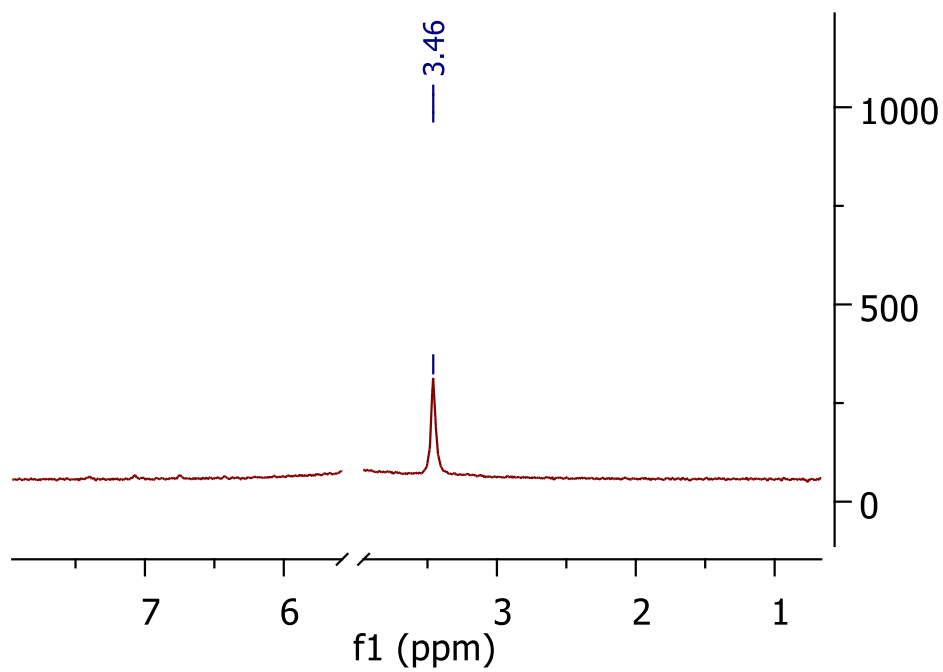
100mg Al



25mg Al (same yield)



b. ^2H NMR



c. Mass spectrum

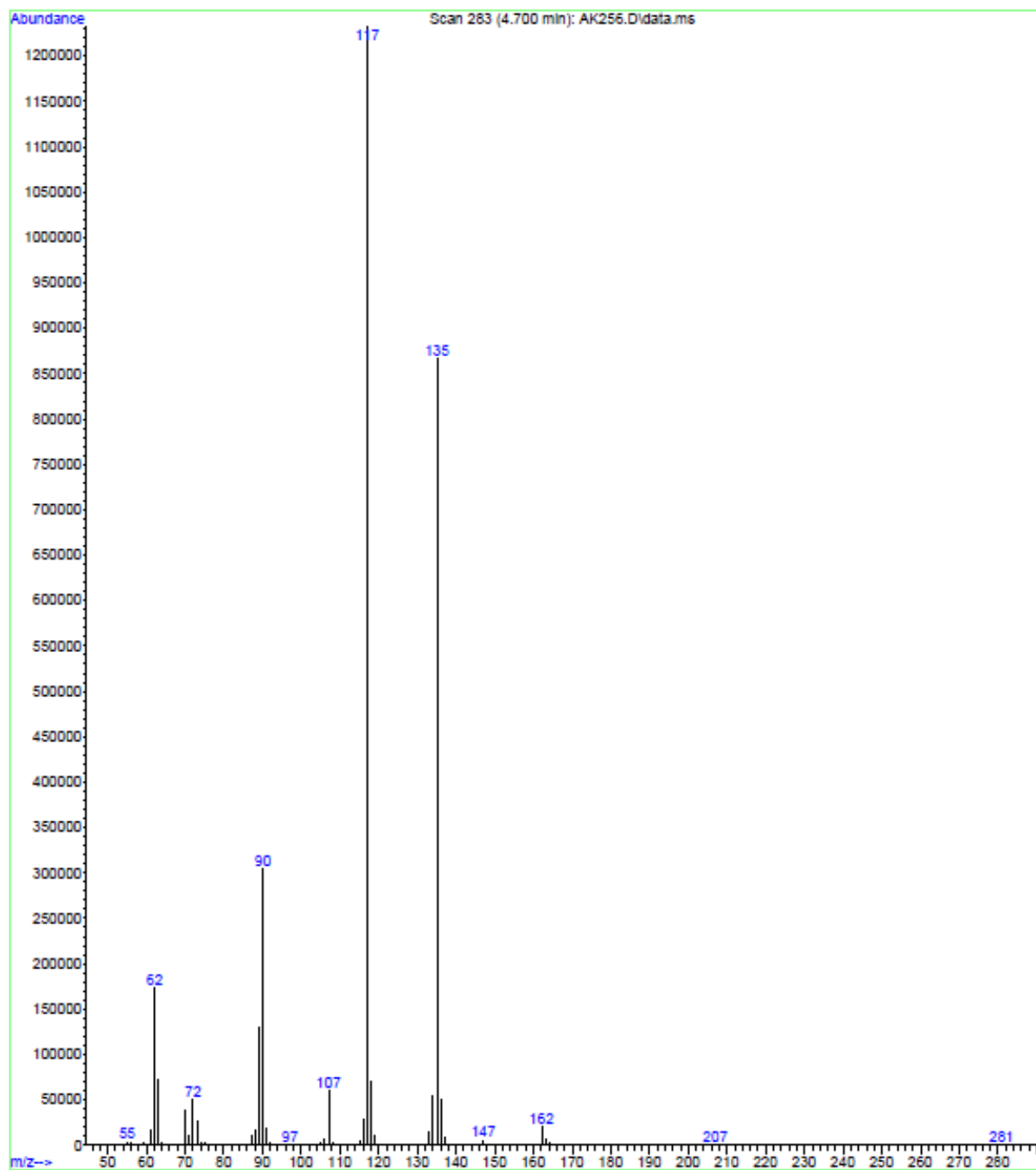
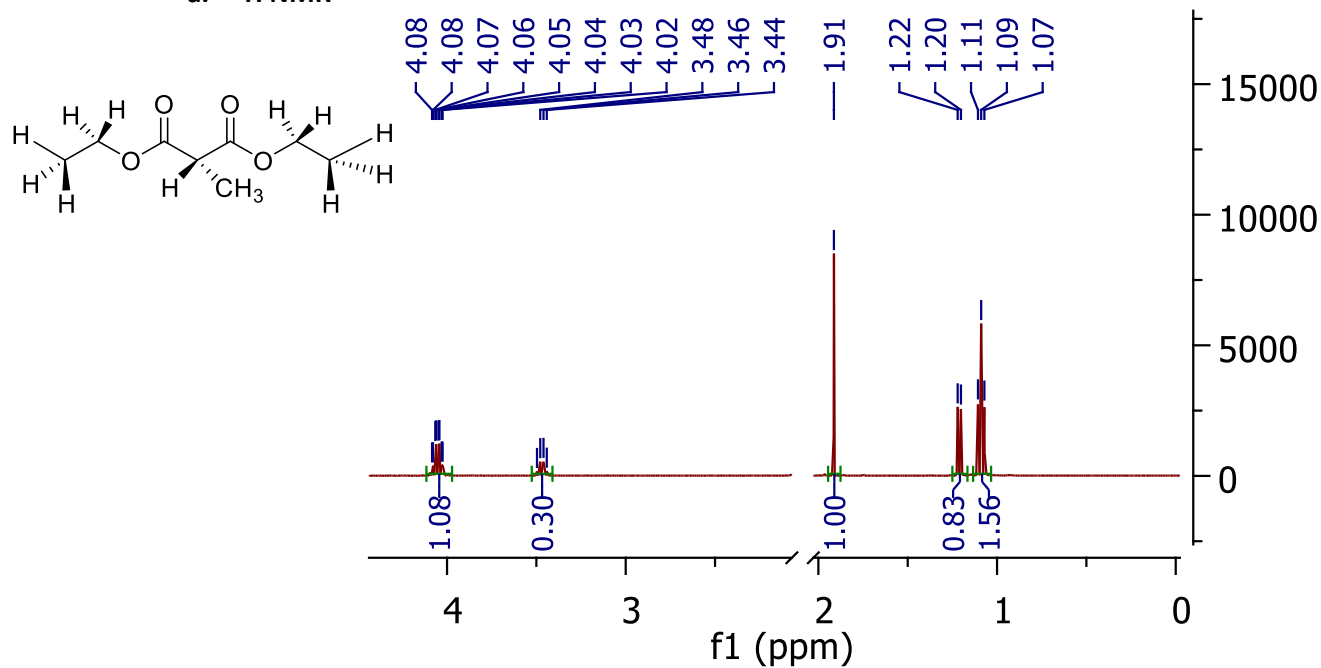


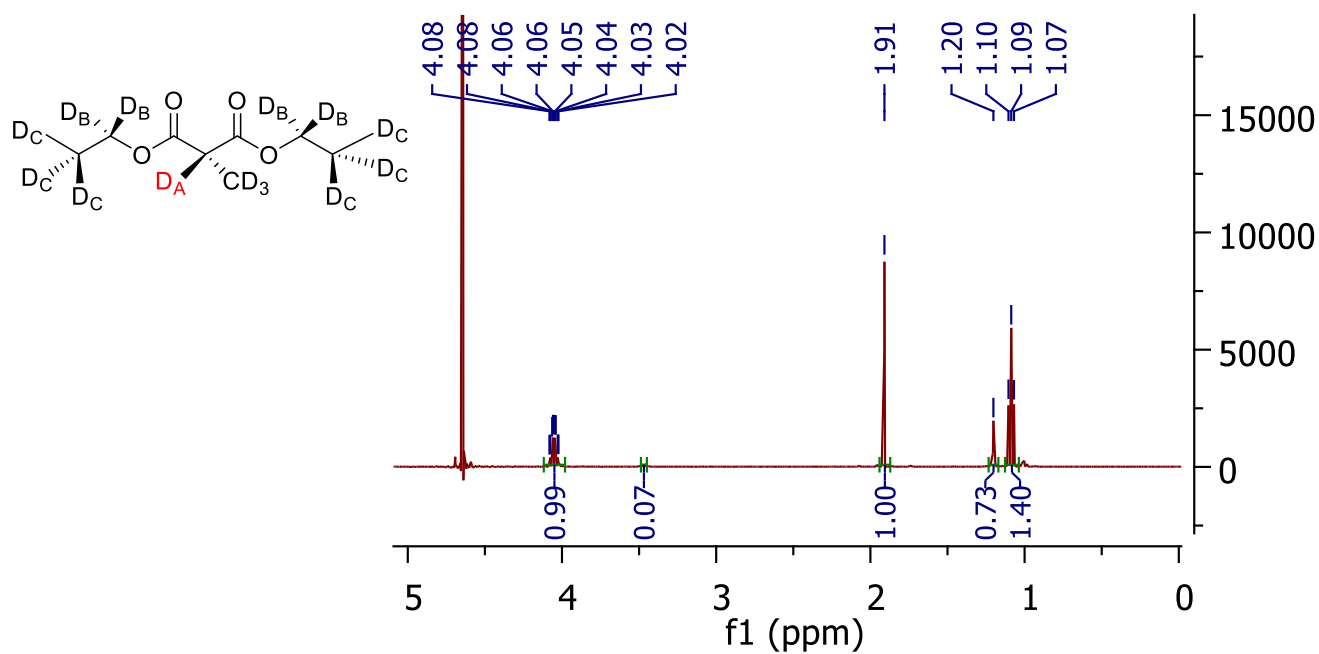
Figure S20. H-D exchange reaction of diethylmethyl malonate

(20mg of Pd/C, MW, 60min, 80°C)

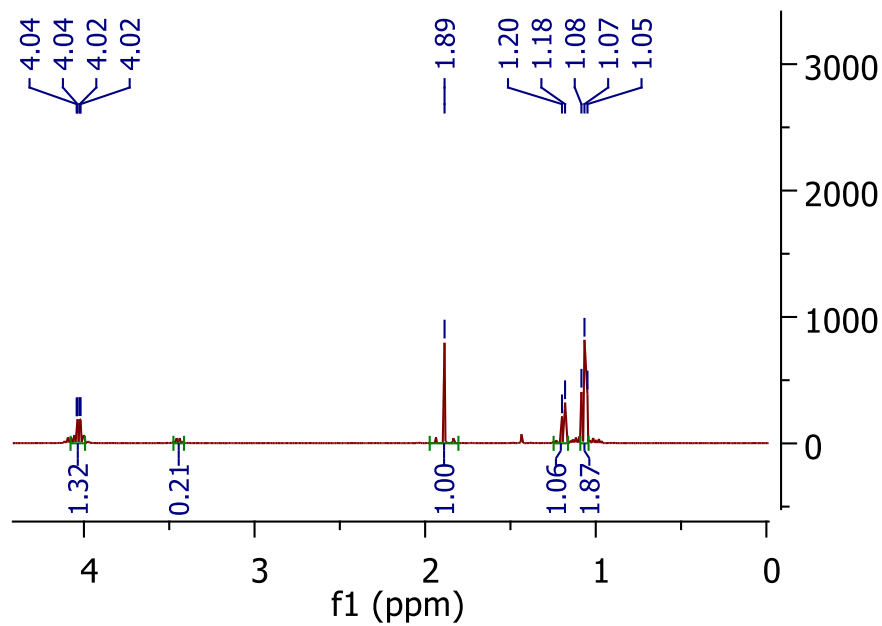
a. ^1H NMR



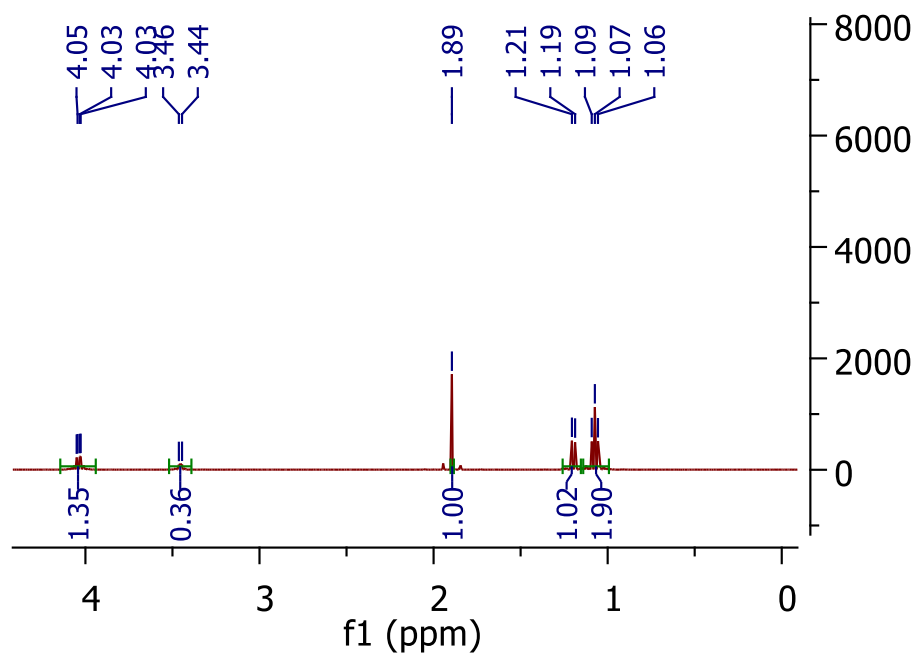
100mg Al



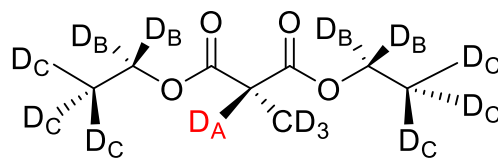
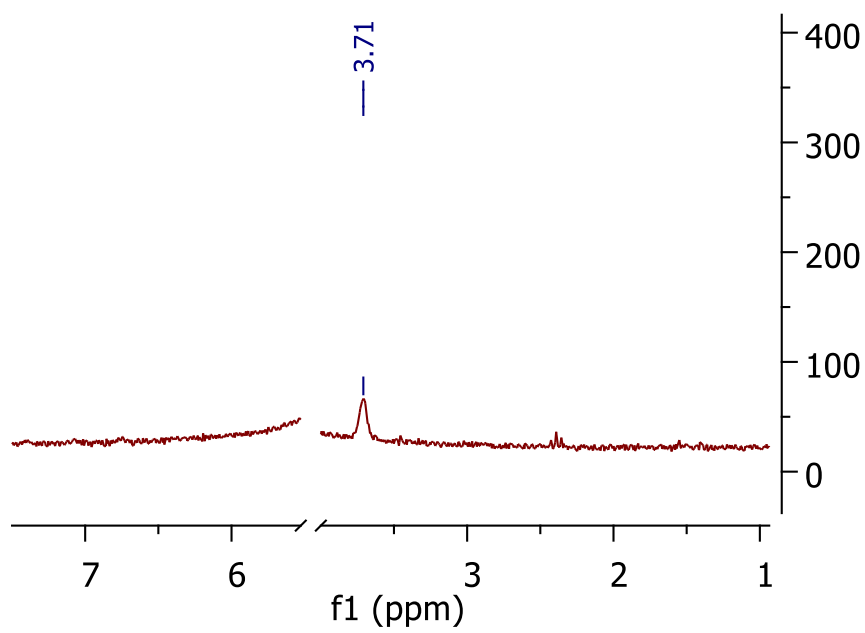
25mg Al (45% yield)



reference



b. ^2H NMR



c. Mass spectrum

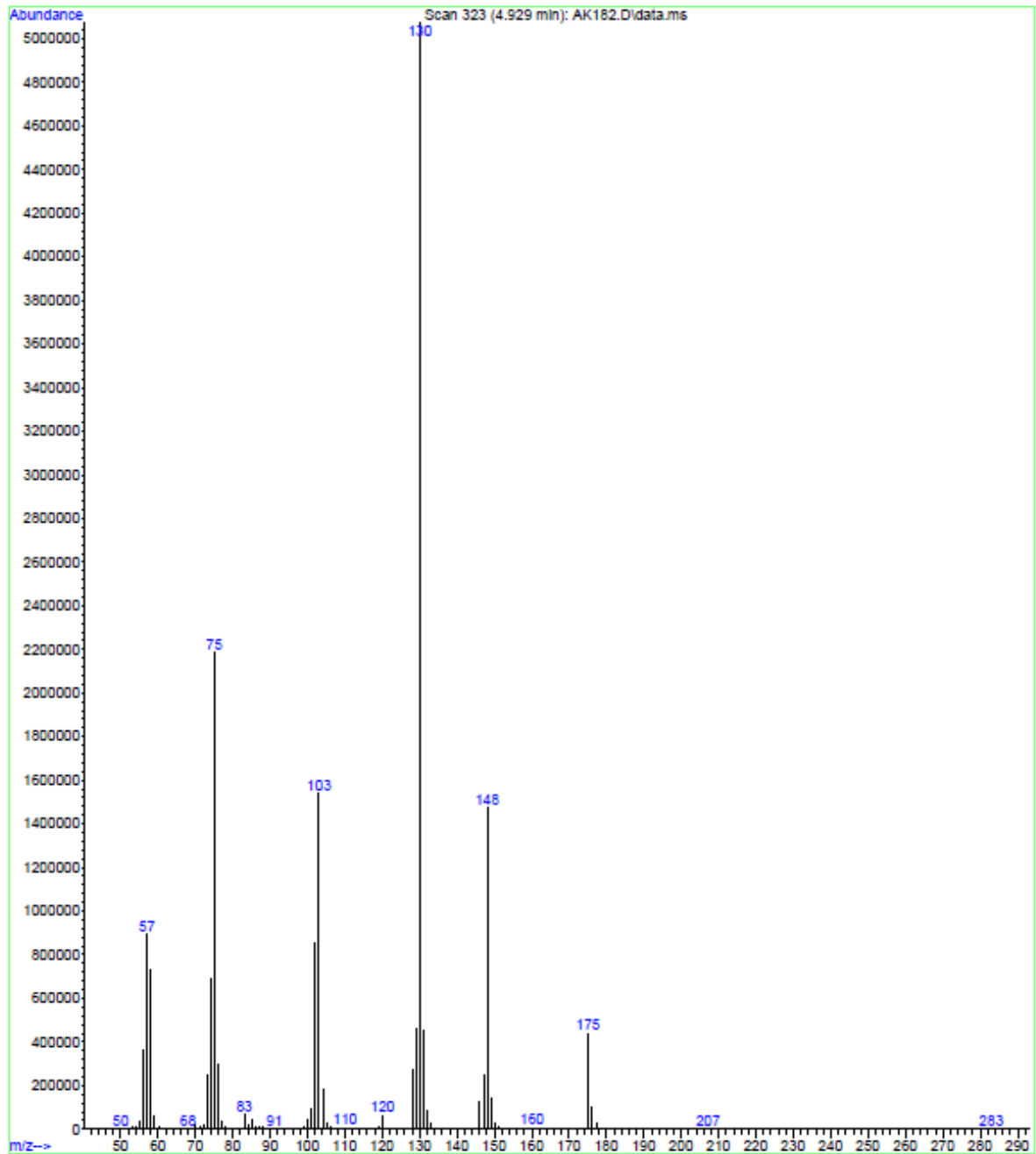
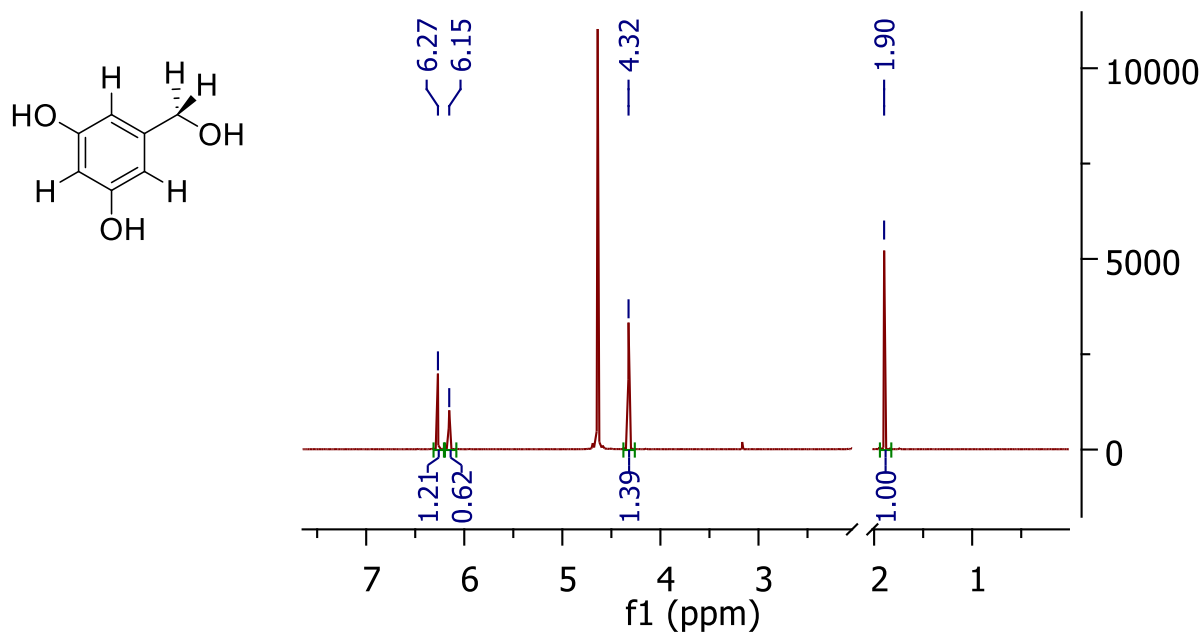


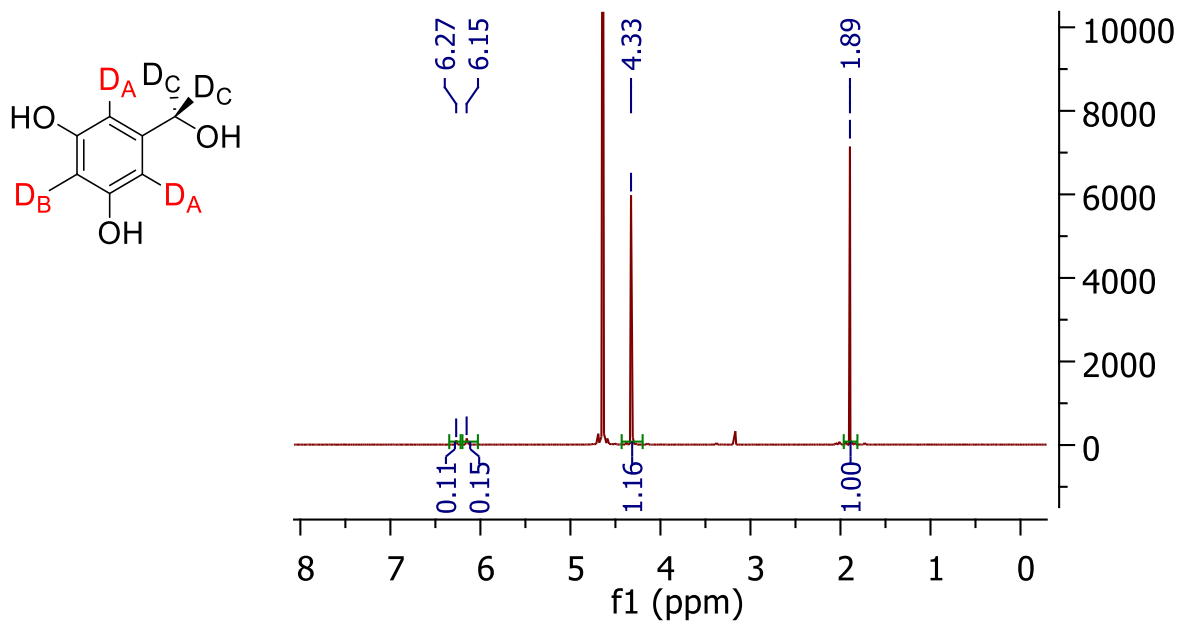
Figure S21. H-D exchange reaction of 3,5-dihydroxybenzyl alcohol

(20mg of Pd/C, MW, 60min, 120°C)

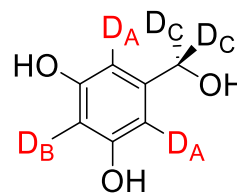
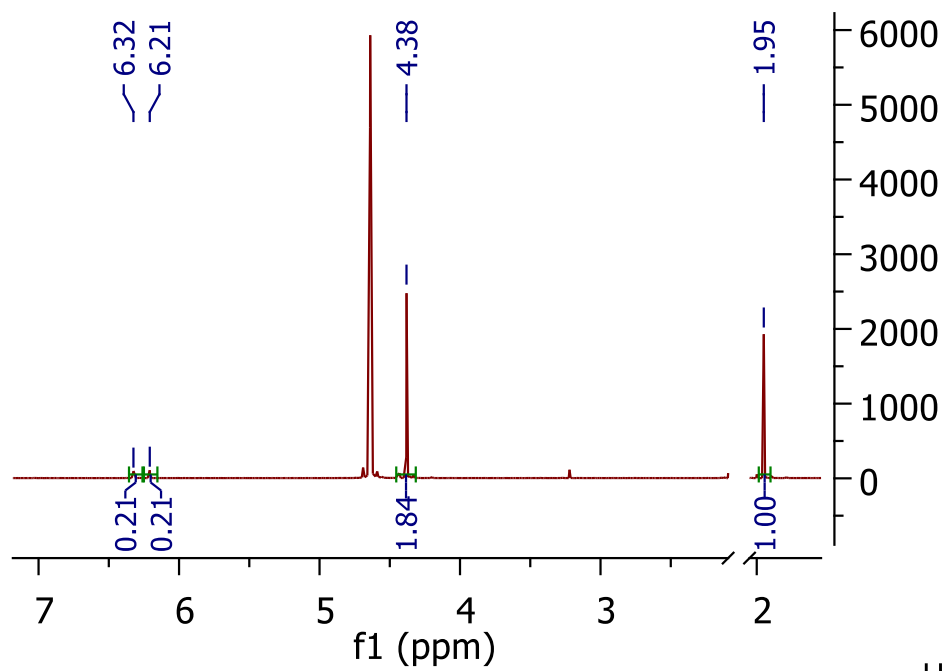
a. ^1H NMR



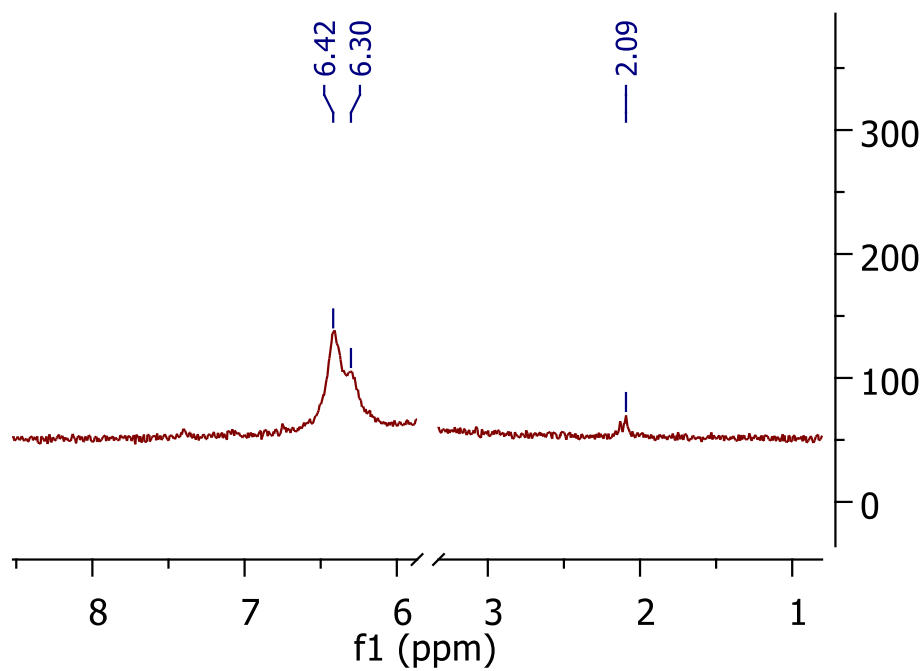
100mg Al



25mg Al (same yield)



b. ²H NMR



c. Mass spectrum

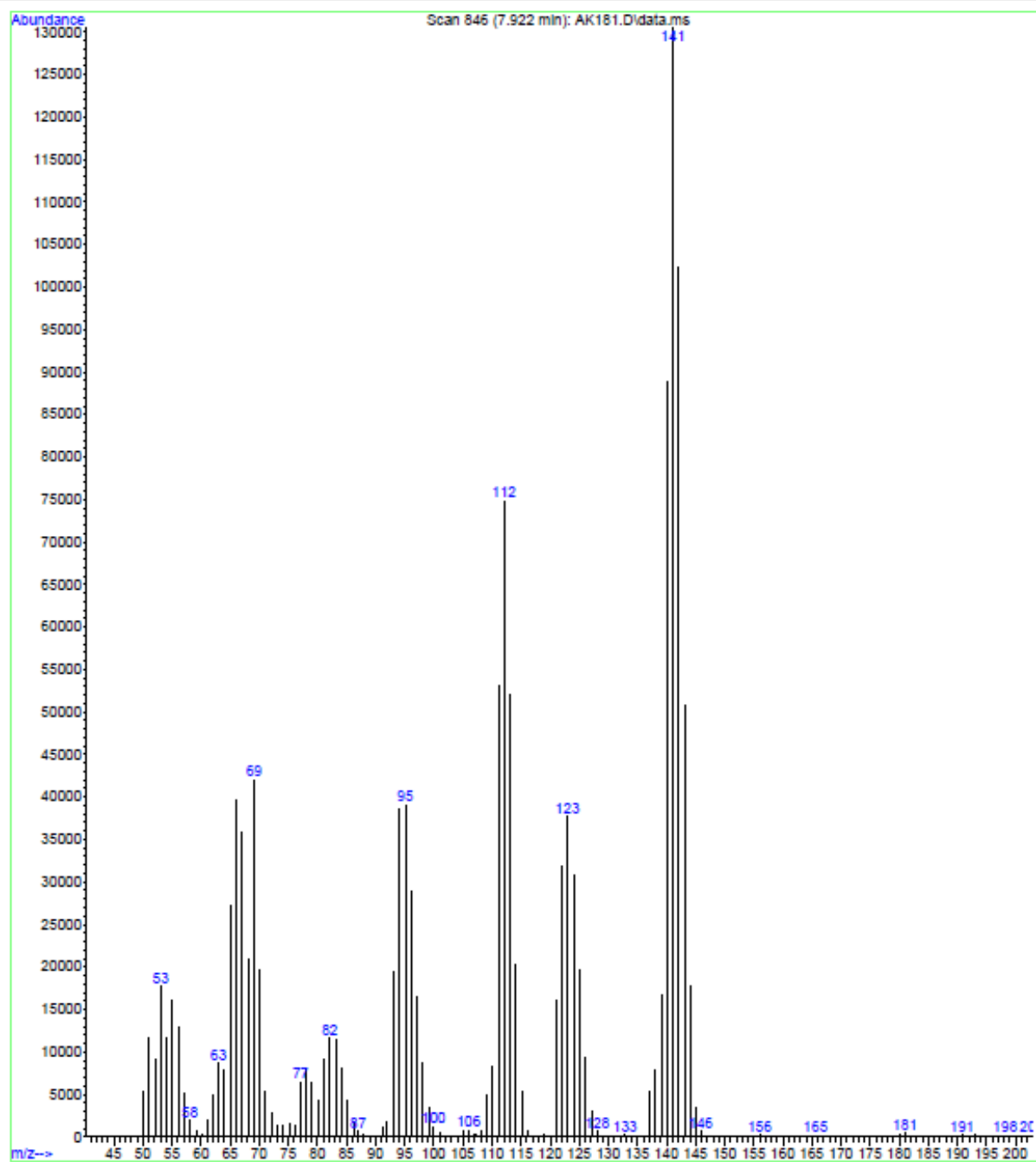
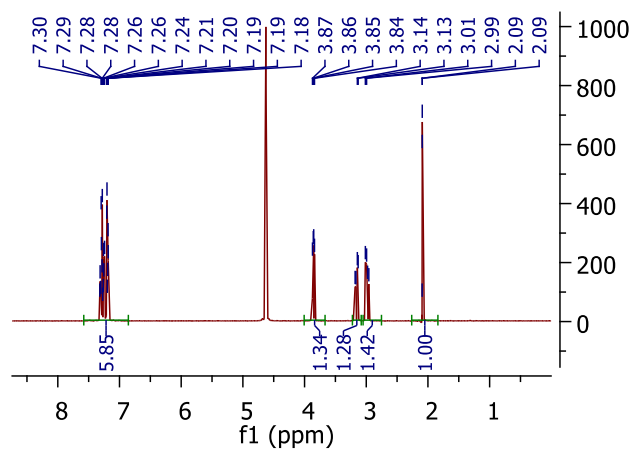
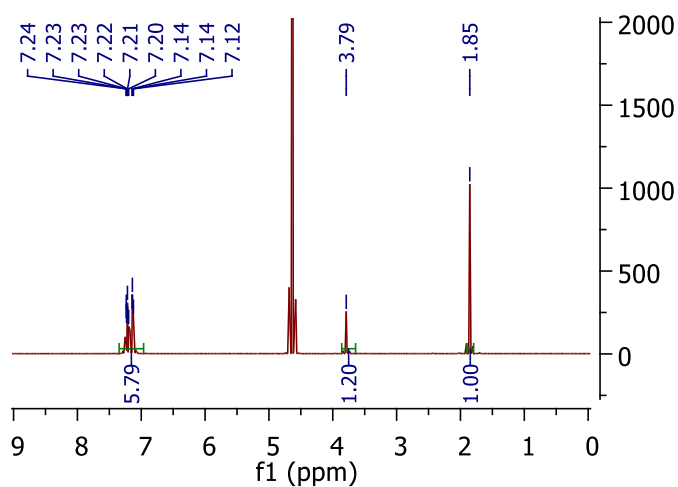


Figure S22. Recycling of the catalytic system

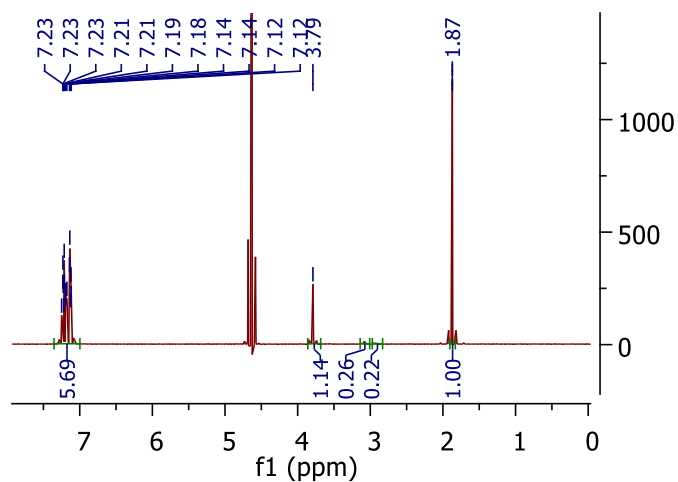
Reference



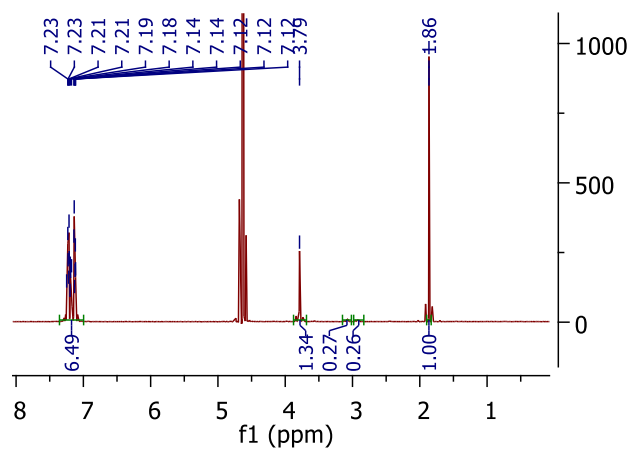
First cycle



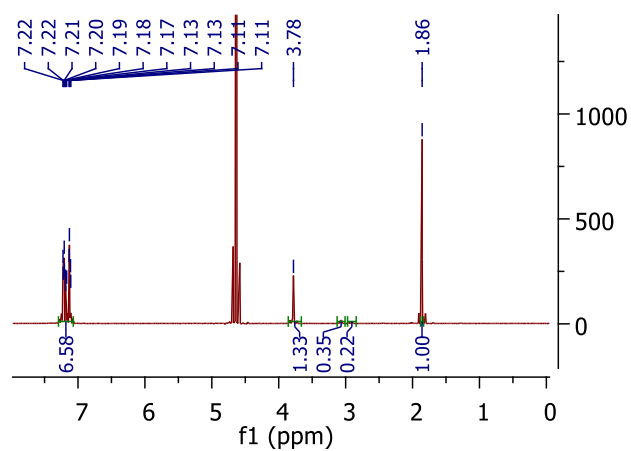
Second cycle



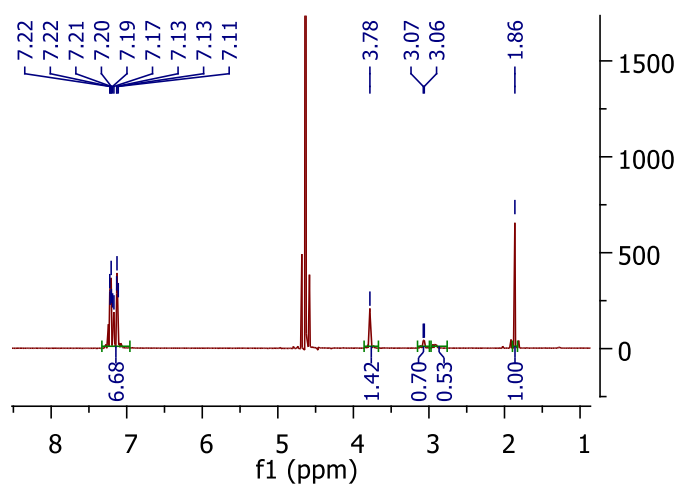
Third cycle



Fourth cycle



Fifth cycle



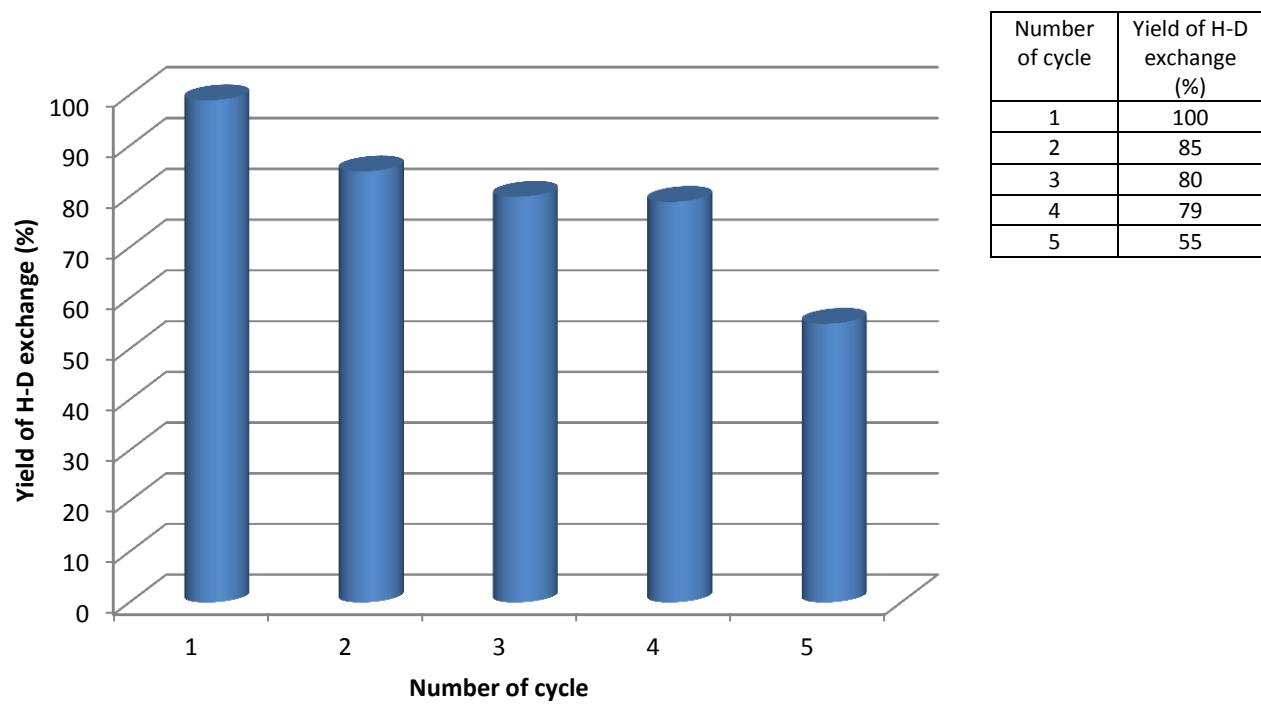


Figure S23. %yield of H-D exchange for five consecutive reaction cycles