Supporting Information for

Selective α-Deuteration of Amines and Amino Acids Using D_2O

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Index:

General experimental: All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBraun glove box. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar, Spectrochem and used without further purification. ^{1}H, ^{13}C, and DEPT spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz, ^{2}H: 61 MHz). ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, Singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet. Assignment of spectra was done based on one dimensional (dept-135) NMR technique.

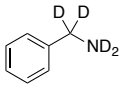
Preparation of [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] 1: Complex **1** is prepared by following our previous reports.[1] The stock solution of **1** is prepared by dissolving 145 mg of [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] in 2 ml of 1,4-dioxane. The prepared stock solution then stored in glove-box freezer and further used as catalyst (solution standard concentration: 1.45 mg/20 µl = 0.0025 mmol = 0.5 mol% of **1**).

General procedure for the deuteration of primary amines: To a screw cap scintillation vial primary amine (0.5 mmol), catalyst **1** (0.0025 mmol, 20 µl stock solution), and D_2O (0.4 ml, 20 mmol) were added under nitrogen atmosphere. The reaction vial was sealed and immersed into a pre-heated oil bath of 135 ºC and the reaction mixture was stirred for 24 h. If the reaction mixture is not homogeneous, the solvent was evaporated under reduced pressure and the resulted residue was extracted with dichloromethane. The combined organic phase is dried over sodium sulphate. Removal of solvent under reduced pressure provided pure products.

Precaution: Owing to the thin walled nature of the scintillation vial this is potentially a hazardous operation and must be conducted in a fume hood behind a blast shield.

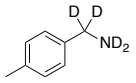
Spectral data of the deuterated primary amines:

Benzylamine-d4 (3a):[2] Colorless oil. Yield 45 mg (81%). ^{1}H NMR (D_2O, 400 MHz) δ 7.17-7.03



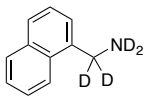
(m, 5H, ArC*H*), 4.46 (0.1H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.85 (quat-*C*), 128.49 (Ar*C*H), 128.27 (Ar*C*H), 127.06 (Ar*C*H), 52.95 (m, α-*C*H_2).

***p*-tolylmethanamine-d4 (3b):**[3] Colorless oil. Yield 49 mg (79%). ^{1}H NMR ($CDCl_3$, 400 MHz)



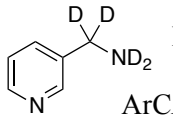
δ 7.24-7.13 (m, 4H, ArC*H*), 3.76 (s, 0.53H, α-CH_2), 2.34 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.42 (quat-*C*), 129.27 (Ar*C*H), 129.16 (quat-*C*), 127.10 (Ar*C*H), 46.00 (m, *C*H_2), 21.09 (*C*H_3).

Naphthalen-1-ylmethanamine-d4 (3c): Dark yellow liquid. Yield 71 mg (89%). ^{1}H NMR (D_2O,



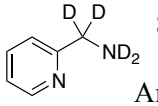
400 MHz) δ 8.04 (d, 1H, *J* = 8 Hz, ArC*H*), 7.86 (t, 1H, *J* = 8 Hz, ArC*H*), 7.76 (d, 1H, *J* = 8 Hz, ArC*H*), 7.51 (m, 3H, ArC*H*), 7.43 (d, 1H, *J* = 8 Hz, ArC*H*), 3.81 (0.37H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.63 (quat-*C*), 133.81 (quat-*C*), 131.10 (quat-*C*), 128.80 (Ar*C*H), 127.51 (Ar*C*H), 126.14 (Ar*C*H), 125.65 (Ar*C*H), 125.56 (Ar*C*H), 124.40 (Ar*C*H), 123.10 (Ar*C*H), 43.61 (m, *C*H_2). HRMS (ESI): m/z calcd for $C_{11}H_7ND_4$ $(M+H)^+$ 162.1221, found: 162.1216.

Pyridin-3-ylmethanamine-d4 (3d): Brown liquid. Yield 39 mg (69%). ^{1}H NMR ($CDCl_3$, 400



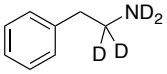
MHz) δ 8.47 (s, 1H, ArC*H*), 8.40 (d, 1H, *J* = 4 Hz, ArC*H*), 7.58 (d, 1H, *J* = 8 Hz, ArC*H*), 7.18 (d, 1H, *J* = 4 Hz, ArC*H*), 3.60 (t, 0.07H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.64 (Ar*C*H), 147.12 (Ar*C*H), 137.48 (quat-*C*), 136.49 (Ar*C*H), 124.17 (Ar*C*H), 42.02 (m, *C*H_2). HRMS (ESI): m/z calcd for $C_6H_5N_2D_4$ $(M+H)^+$ 113.1017, found: 113.1011.

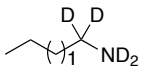
Pyridin-2-ylmethanamine-d4 (3e): Brown liquid. Yield 35 mg (62%). ^{1}H NMR (D_2O, 400 MHz) δ

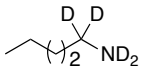


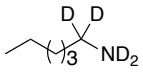
8.27 (d, 1H, *J* = 4 Hz, ArC*H*), 7.67 (t, 1H, *J* = 8 Hz, ArC*H*), 7.26 (d, 1H, *J* = 8 Hz, ArC*H*), 7.16 (t, 1H, *J* = 8 Hz, ArC*H*), 3.41 (t, 0.07H, α-CH_2). ^{13}C NMR (101 MHz,

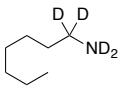
$CDCl_3$) δ 160.31 (quat-*C*), 148.18 (Ar*C*H), 138.17 (Ar*C*H), 122.61 (Ar*C*H), 121.84 (Ar*C*H), 45.35 (m, *C*H_2). HRMS (ESI): m/z calcd for $C_6H_5N_2D_4$ $(M+H)^+$ 113.1017, found: 113.1012.

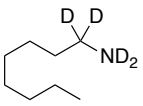
2-phenylethanamine-d4 (3f):[2] Yellow liquid. Yield 45 mg (72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ  7.05 (m, 5H, ArC*H*), 2.71 (t, 0.39H, α-CH_2), 2.52 (s, 1.92H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.72 (quat-*C*), 128.76 (Ar*C*H), 128.40 (Ar*C*H), 126.10 (Ar*C*H), 42.81 (m, α-*C*H_2), 39.77 (t, *C*H_2).

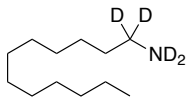
Butan-1-amine-d4 (3g):[4] Light yellow liquid. Yield 20 mg (51%). ^{1}H NMR (D_2O, 400 MHz) δ  2.57 (t, 0.87H, α-CH_2), 1.31 (m, 4H, CH_2), 0.83 (t, 3H, CH_3).

Pentan-1-amine-d4 (3h): Light yellow liquid. Yield 29 mg (64%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ  2.64 (t, 0.19H, α-CH_2), 1.31 (m, 4H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 29.78 (m, α-*C*H_2), 22.74 (*C*H_2), 22.66 (*C*H_2), 22.57 (*C*H_2), 14.16 (*C*H_3). HRMS (ESI): m/z calcd for $C_7H_{13}ND_4Na$ $(M+Na)^+$ 142.1510, found: 142.1504.

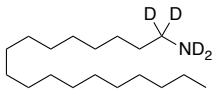
Hexan-1-amine-d4 (3i):[5] Yellow liquid. Yield 36 mg (68%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.58  (0.17H, α-CH_2), 1.26 (m, 8H, CH_2), 0.83 (t, 3H, *J* = 8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 41.44 (m, α-*C*H_2), 33.53 (*C*H_2), 31.76 (*C*H_2), 26.58 (*C*H_2), 22.69 (*C*H_2), 14.07 (*C*H_3).

Heptan-1-amine-d4 (3j): Yellow liquid. Yield 40 mg (67%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.50  (0.15H, α-CH_2), 1.51-1.18 (m, 8H, CH_2), 0.82 (t, 3H, *J* = 8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 49.63 (m, α-*C*H_2), 31.91 (*C*H_2), 29.33 (*C*H_2), 29.25 (*C*H_2), 27.22 (*C*H_2), 22.69 (*C*H_2), 14.13 (*C*H_3). HRMS (ESI): m/z calcd for $C_7H_{14}ND_4$ $(M+H)^+$ 120.1960, found: 120.1965.

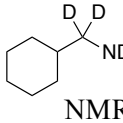
Octan-1-amine-d4 (3k):[6] Yellow liquid. Yield 46 mg (70%). ^{1}H NMR ($CDCl_3$, 400  MHz) δ 2.64 (0.18H, α-CH_2), 1.49-1.22 (br s, 10H, CH_2), 0.87 (t, 3H, *J* = 8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 49.51 (m, α-*C*H_2), 33.49 (*C*H_2), 31.81 (*C*H_2), 29.44 (*C*H_2), 29.27 (*C*H_2), 26.84 (*C*H_2), 22.63 (*C*H_2), 14.06 (*C*H_3).

Dodecan-1-amine-d4 (3l): White solid. Yield 74 mg (78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.54 (t, 

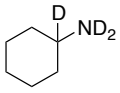
0.39H, α-CH_2), 1.26 (m, 20H, CH_2), 0.86 (t, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 49.55 (m, α-*C*H_2), 32.05 (*C*H_2), 29.80 (*C*H_2), 29.77 (4 *C*H_2), 29.76 (*C*H_2), 29.71 (*C*H_2), 29.48 (*C*H_2), 22.81 (*C*H_2), 14.23 (*C*H_3). HRMS (ESI): m/z calcd for $C_{12}H_{24}ND_4$ $(M+H)^+$ 190.2473, found: 190.2467.

Octadecan-1-amine-d4 (3m): White solid. Yield 112 mg (82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 

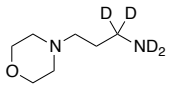
2.64 (t, 0.18H, α-CH_2), 1.25 (m, 32H, CH_2), 0.87 (t, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 49.65 (m, α-*C*H_2), 32.07 (*C*H_2), 29.84 (11*C*H_2), 29.80 (*C*H_2), 29.68 (*C*H_2), 29.51 (*C*H_2), 22.83 (*C*H_2), 14.25 (*C*H_3). HRMS (ESI): m/z calcd for $C_{18}H_{36}ND_4$ $(M+H)^+$ 274.3412, found: 274.3406.

Cyclohexylmethanamine-d4 (3n): Yellow liquid. Yield 43 mg (73%). ^{1}H NMR ($CDCl_3$, 400 MHz) 

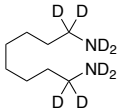
δ 2.49 (d, 0.46H, α-CH_2), 1.68 (m, 4H, CH_2), 1.21 (m, 5H, CH_2), 0.88 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 48.25 (m, *C*H_2), 41.01 (*C*H), 30.70 (*C*H_2), 26.61 (*C*H_2), 25.98 (*C*H_2). HRMS (ESI): m/z calcd for $C_7H_{12}ND_4$ $(M+H)^+$ 118.1528, found: 118.1525.

Cyclohexanamine-d4 (3o):[7] Yellow liquid. Yield 32 mg (62%). H NMR ($CDCl_3$, 400 MHz) δ 2.54 

(m, 0.30H, α-CH_2), 1.64 (m, 4H, CH_2), 1.07 (m, 6H, CH_2).

3-morpholinopropan-1-amine-d4 (3p): Brown liquid. Yield 38 mg (52%). ^{1}H NMR (D_2O, 400 

MHz) δ 3.64 (t, 4H, *J* = 8 Hz, OCH_2), 2.75 (t, 0.29 H, α-CH_2), 2.47 (m, 6H, NCH_2), 1.59 (m, 2H, CH_2). ^{13}C NMR (101 MHz, D_2O) δ 66.15 (O*C*H_2), 55.73 (*C*H_2), 52.59 (*C*H_2), 38.68 (m, α-*C*H_2), 27.86 (t, *C*H_2). HRMS (ESI): m/z calcd for $C_7H_{12}ON_2D_4Na$ $(M+Na)^+$ 171.1411, found: 171.1406.

Octane-1,8-diamine-d8 (3q): Yellow liquid. Yield 37 mg (49%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 

2.34 (0.73H, α-CH_2), 1.12-1.01 (m, 12H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 40.76 (m, α-*C*H_2), 32.84 (*C*H_2), 28.95 (*C*H_2), 26.30 (*C*H_2). HRMS (ESI): m/z calcd for $C_8H_{13}N_2D_8$ $(M+H)^+$ 153.2201, found: 153.2209.

General procedure for the deuteration of secondary amines:

To a screw cap scintillation vial secondary amine (0.5 mmol), catalyst **1** (0.005 mmol, 40 µl stock solution), and D_2O (0.4 ml, 20 mmol) were added under nitrogen atmosphere. The reaction vial was sealed and immersed into a pre-heated oil bath of 135 ºC and the reaction mixture was allowed to stirr for 24 h. The resultant reaction mixtures were characterized by NMR spectroscopy. If the reaction mixture is not homogeneous, the solvent was evaporated under reduced pressure and the residue was extracted with dichloromethane. Combined organic phase is dried over sodium sulphate. Removal of solvent under reduced pressure provided pure products.

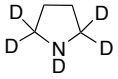
Precaution: Owing to the thin walled nature of the scintillation vial this is potentially a hazardous operation and must be conducted in a fume hood behind a blast shield.

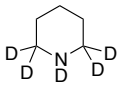
Spectral data of the deuterated secondary amines:

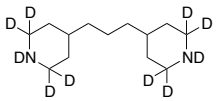
***N*-Methyl-1-phenylmethanamine-d4 (4a):** Yellow liquid. Yield 46 mg (73%). ^{1}H NMR (D_2O, 400 MHz) δ 7.29-7.22 (m, 5H, ArC*H*), 3.58 (s, 2H, NCH_2), 2.36 (m, 0.14 H, α-NCH_3). ^{13}C NMR (101 MHz, D_2O) δ 137.84 (quat-*C*), 128.70 (Ar*C*H), 128.59 (Ar*C*H), 127.61 (quat-*C*), 53.88 (*C*H_2), 33.22 (m, α-*C*H_3). HRMS (ESI): m/z calcd for $C_8H_8ND_4$ $(M+H)^+$ 126.1220, found: 126.1215.

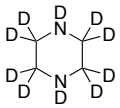
Dibutylamine-d5 (4b):[8] Yellow liquid. Yield 45 mg (67%). ^{1}H NMR (D_2O, 400 MHz) δ 2.87 (m, 1.15 H, α-CH_2), 1.55 (t, 4H, *J* = 8Hz, CH_2), 1.32 (m, 4H, CH_2), 0.88 (t, 6H, *J* = 8Hz, CH_3). ^{13}C NMR (101 MHz, D_2O) δ 47.22 (m, α-*C*H_2), 27.56 (*C*H_2), 19.19 (*C*H_2), 12.85 (*C*H_3).

Dihexylamine-d5 (4c):[6] Yellow liquid. Yield 71 mg (75%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.52 (t, 0.43H, α-CH_2), 1.22 (m, 16H, CH_2), 0.82 (t, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 48.61 (m, α-*C*H_2), 31.62 (*C*H_2), 28.60 (*C*H_2), 26.80 (*C*H_2), 22.54 (*C*H_2), 13.96 (*C*H_3).

Pyrrolidine-d5 (4d):[9] Yellow liquid. Yield 23 mg (61%). ^{1}H NMR (D_2O, 400 MHz) δ 2.77 (t, 1H,  α-CH_2), 1.65 (s, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 45.21 (m, α-*C*H_2), 24.39 (*C*H_2).

Piperidine-d5 (4e):[5,8] Yellow liquid. Yield 29 mg (64%). ^{1}H NMR (D_2O, 400 MHz) δ 2.79 (0.84H,  α-CH_2), 1.51 (br s, 6H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.20 (m, α-*C*H_2), 23.81 (*C*H_2), 22.78 (*C*H_2).

1,3-Di(piperidin-4-yl)propane-d10 (4f): Yellow liquid. Yield 78 mg (71%). ^{1}H NMR ($CDCl_3$, 400  MHz) δ 2.82 (0.31H, α-CH_2), 2.34 (0.34H, α-CH_2), 2.04 (0.70H, α-CH_2), 1.45-0.84 (m, 14H, CH_2). ^{13}C NMR (101 MHz, D_2O) δ 46.19 (m, α-*C*H_2), 37.84 (*C*H_2), 35.65 (*C*H_2), 35.45 (*C*H_2), 31.38 (*C*H_2), 25.01 (*C*H_2). HRMS (ESI): m/z calcd for $C_{13}H_{17}N_2D_{10}$ $(M+H)^+$ 221.2803, found: 221.2796.

Piperazine-d10 (4g): Yellow liquid. Yield 26 mg (54%). ^{1}H NMR (D_2O, 400 MHz) δ 2.73 (br s,  1.35H, α-CH_2). ^{13}C NMR (101 MHz, D_2O) δ 44.61 (m, α-*C*H_2). HRMS (ESI): m/z calcd for $C_4N_2D_{10}$ $(M+Na)^+$ 119.1364, found: 119.1372.

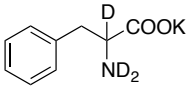
General procedure for the deuteration of amino acids:

In a screw cap scintillation vial amino acid (0.5 mmol) and KOH (0.5 mmol, 28 mg) were dissolved in D_2O (0.6 ml, 30 mmol) and stirred at room temperature for 30 minutes. Then the catalyst **1** (0.005 mmol, 40 µl stock solution) is added to the vial under nitrogen atmosphere sealed and immersed into a pre-heated oil-bath of 135 ºC and the reaction mixture was allowed to stirr for 36 h. The cooled reaction mixture is transferred to a NMR tube and analyzed by NMR spectroscopy.

Precaution: Owing to the thin walled nature of the scintillation vial this is potentially a hazardous operation and must be conducted in a fume hood behind a blast shield.

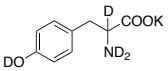
Spectral data of the deuterated amino acids:

Phenylalanine-d3 (5a):[10] ^{1}H NMR (D_2O, 400 MHz) δ 7.29 (m, 5H, ArC*H*), 3.44 (m, 0.16H, α-C*H*),



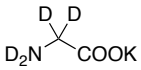
2.97 (d, 1H, J = 8 Hz, CH_2), 2.75 (d, 1H, *J* = 8 Hz, CH_2). ^{13}C NMR (101 MHz, D_2O) δ 181.96 (*C*OOK), 138.43 (quat-*C*), 129.51 (Ar*C*H), 128.68 (Ar*C*H), 126.70 (Ar*C*H), 57.36 (m, α-*C*H), 40.90 (d, *C*H_2).

Tyrosine-d4 (5b):[11] ^{1}H NMR (D_2O, 400 MHz) δ 7.07-6.57 (m, 4H, ArC*H*), 3.39 (m, 0.60H, α-C*H*),



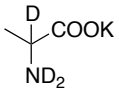
2.82 (d, 1H, J = 8 Hz, CH_2), 2.64 (d, 1H, *J* = 8 Hz, CH_2).

Glycine-d4 (5c):[12] ^{1}H NMR (D_2O, 400 MHz) δ 3.08 (0.21 H, α-*C*H_2). ^{13}C NMR (101 MHz, D_2O) δ



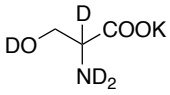
181.31 (*C*OOH), 44.11 (m, α-*C*H_2).

Alanine-d3 (5d):[7,13] ^{1}H NMR (D_2O, 400 MHz) δ 3.33 (m, 0.32 H, α-*CH*), 1.20 (s, 3H, CH_3). ^{13}C



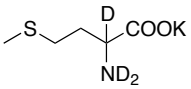
NMR (101 MHz, D_2O) δ 182.55 (*C*OOK), 50.84 (m, α-*C*H), 19.32 (*C*H_3).

Serine-d4 (5e):[10] ^{1}H NMR (D_2O, 400 MHz) δ 3.68 (m, 2H, OC*H*$_2$), 3.33 (m, 0.14H, α-*C*H) . ^{13}C



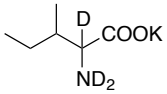
NMR (101 MHz, D_2O) δ 180.34 (*C*OOK), 64.51 (O*C*H_2), 57.12 (t, α-*C*H).

Methionine-d3 (5f):[12] ^{1}H NMR (D_2O, 400 MHz) δ 3.31 (m, 0.3H, α-C*H*), 2.54 (t, 2H, *J* = 8 Hz,



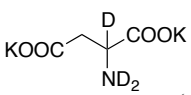
CH_2), 2.09 (s, 3H, CH_3), 1.84 (m, 2H, CH_2). ^{13}C NMR (101 MHz, D_2O) δ 182.55 (*C*OOK), 54.88 (m, α-*C*H), 34.02 (*C*H_2), 29.74 (*C*H_2), 14.20 (*C*H_3).

Isoleucine-d3 (5g):[14] ^{1}H NMR (D_2O, 400 MHz) δ 3.09 (d, 0.5H, α-C*H*), 1.63 (m, 1H, C*H*), 1.36 (m,

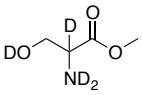


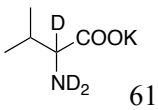
1H, C*H*), 1.10 (m, 1H, C*H*), 0.85 (m, 6H, CH_3). ^{13}C NMR (101 MHz, D_2O) δ 182.27 (*C*OOK), 37.95 (m, α-*C*H), 24.13 (*C*H), 15.54 (*C*H), 11.12 (*C*H_3).

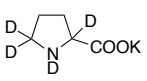
Aspartic acid-d3 (5h):[10,13] ^{1}H NMR (D_2O, 400 MHz) δ 3.53 (m, 0.27H, α-C*H*), 2.59 (d, 1H, *J* = 16



Hz, C*H*), 2.30 (d, 1H, *J* = 16 Hz, C*H*). ^{13}C NMR (101 MHz, D_2O) δ 181.38 (*C*OOK), 179.92 (*C*OOK), 53.38 (m, α-*C*H), 42.33 (*C*H_2).

Methyl 2-amino-3-hydroxypropanoate-d4 (5i): ^{1}H NMR (D_2O, 400 MHz) δ 3.70 (m, 2H, OCH_2),  3.34 (s, 3H, OCOCH_3). ^{13}C NMR (101 MHz, D_2O) δ 180.53 (*C*OOMe), 64.77 (O*C*H_2), 57.25 (t, α-*C*H), 49.08 (O*C*H_3). HRMS (ESI): m/z calcd for $C_4H_5NO_3D_4Na$ $(M+Na)^+$ 146.0731, found: 146.0726.

Valine-d3 (5j):[7,13] ^{1}H NMR (D_2O, 400 MHz) δ 3.02 (d, 0.2H, α-C*H*), 1.90 (sept, 1H, ^{i}PrC*H*), 0.88  (dd, 6H, J_1 = 28 Hz, J_2 = 8 Hz, ^{i}PrCH_3). ^{13}C NMR (101 MHz, D_2O) δ 182.73 (*C*OOK), 61.48 (m, α-*C*H), 31.72 (^{i}Pr*C*H), 19.21(^{i}Pr*C*H_3), 16.86 (^{i}Pr*C*H_3).

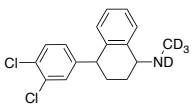
Proline-d4 (5k):[13] ^{1}H NMR (D_2O, 400 MHz) δ 3.43 (0.20H, α-C*H*), 2.98 (m, 0.64 H, α-CH_2), 2.70  (m, 0.37 H, α-CH_2), 2.05 (t, J = 8 Hz, 1H, CH_2), 1.69-1.64 (m, 3H, CH_2). ^{13}C NMR (101 MHz, D_2O) δ 179.51 (*C*OOK), 61.05 (m, α-*C*H), 46.02 (α-*C*H_2), 30.02 (*C*H_2), 24.67 (*C*H_2).

General procedure for selective deuteration of pharmaceuticals:

To a screw cap scintillation vial commercial drugs (0.5 mmol) and KOH (0.5 mmol, 28 mg) were dissolved in D_2O (0.6 ml, 30 mmol) and stirred at room temperature for 30 minutes. Excipients were removed by centrifuge. The clear supernatant liquid was transferred into another scintillation vial and catalyst (0.01 mmol, 80 µl stock solution) is added under nitrogen atmosphere, sealed and immersed into a pre-heated oil-bath of 150 ºC and the reaction mixture stirred for 24 h. The cooled reaction mixture is transferred to a NMR tube and analyzed by NMR spectroscopy.

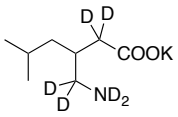
Precaution: Owing to the thin walled nature of the scintillation vial this is potentially a hazardous operation and must be conducted in a fume hood behind a blast shield.

Spectral data of the deuterated pharmaceuticals:

Sertraline-d4 (6):[15] ^{1}H NMR (D_2O, 400 MHz) δ 8.81 (d, 1H, J = 8Hz, ArC*H*), 8.46 (s, 1H, ArC*H*),  8.39 (d, 2H, J = 8Hz, ArC*H*), 8.23 (t, 3H, J = 8Hz, ArC*H*), 7.92 (d, 1H, J = 8Hz,

ArC*H*), 5.42 (t, 1H, *J* = 6Hz, C*H*), 5.05 (t, 1H, *J* = 8Hz, C*H*), 3.35 (0.16H, α-CH_2), 3.32-3.12 (m, 4H, CH_2).

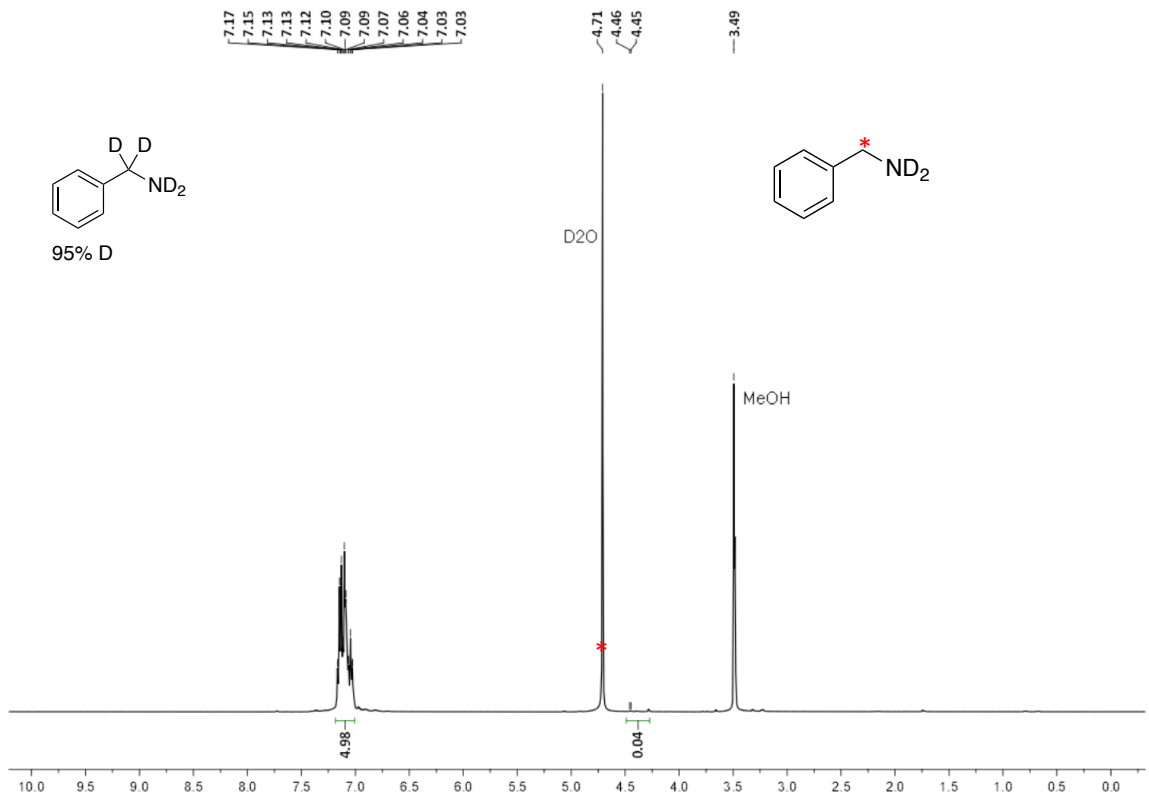
Pregabalin-d4 (7): ^{1}H NMR (D_2O, 400 MHz) δ 3.54-3.49 (m, 0.55H, α-CH_2 to COOK), 3.02-3.04



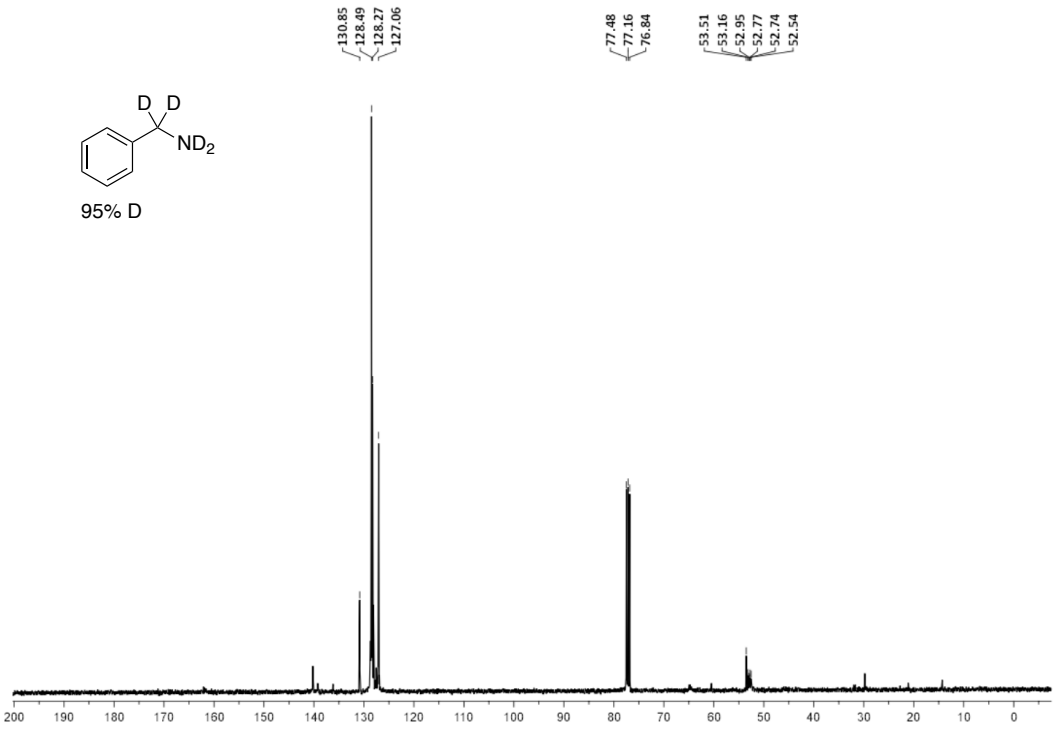
(m, 0.55H, α-CH_2 to COOK), 2.56 (m, 0.64H, α-CH_2 to NH_2), 1.57 (m, 1H, ^{i}PrC*H*), 1.36-1.24 (m, 2H, CH_2), 0.90 (d, 6H, *J* = 8 Hz, ^{i}PrCH_3). ^{13}C NMR (101 MHz, D_2O) δ 180.86 (*C*OOK), 48.24 (m, α-*C*H_2 to NH_2), 43.19 (*C*H_2), 32.26 (α-*C*H_2 to COOK), 25.77 (*C*H), 24.72 (^{i}Pr*C*H), 22.27 (^{i}Pr*C*H_3). HRMS (ESI): m/z calcd for $C_8H_{12}D_4KNO_2$ $(M)^+$ 201.1069, found: 201.1061.

NMR spectra of deuterated amines and amino acids: (Residual signals are marked as *)

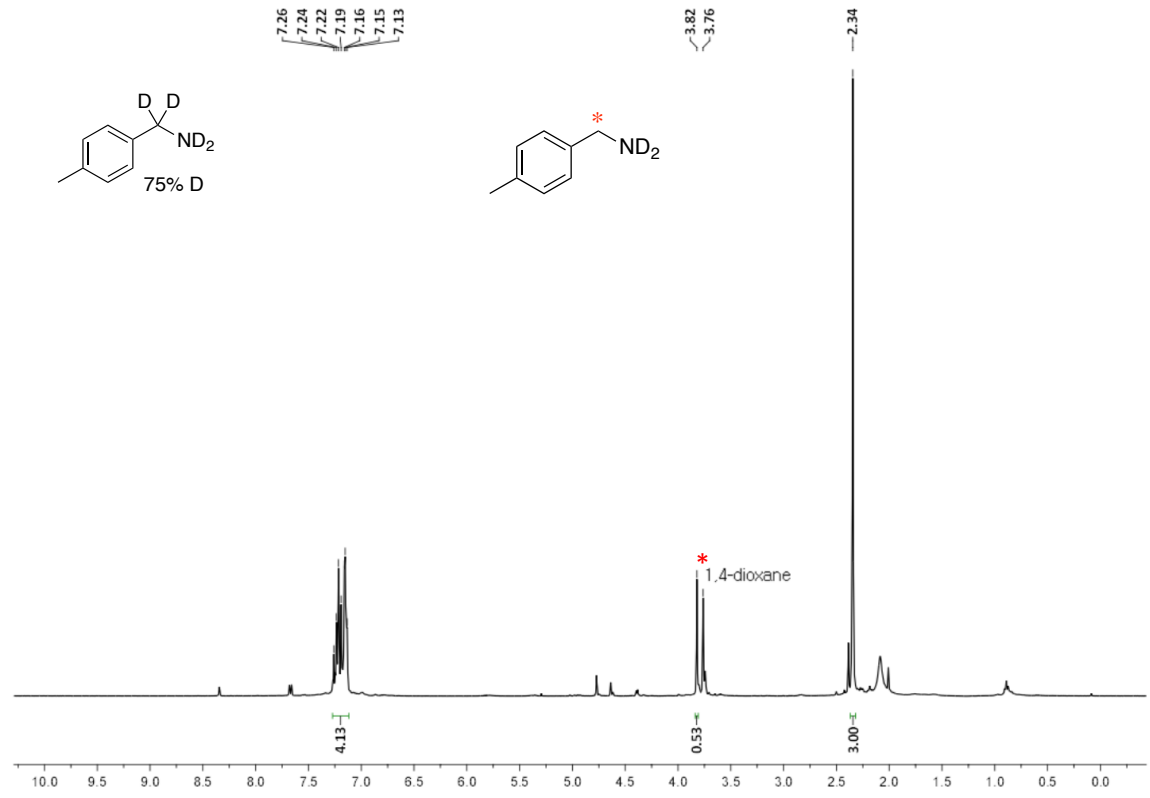
^{1}H NMR spectrum of benzylamine-d4 (**3a**) (400 MHz, D_2O):



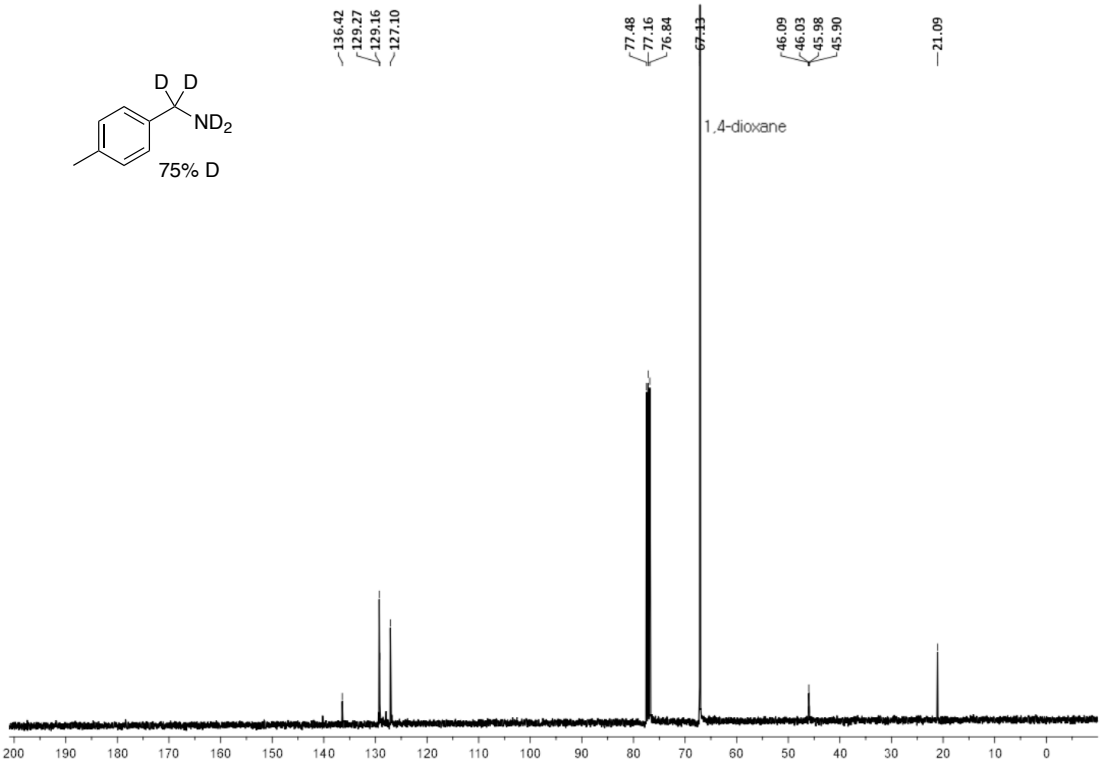
^{13}C NMR spectrum of benzylamine-d4 (**3a**) (101 MHz, $CDCl_3$):



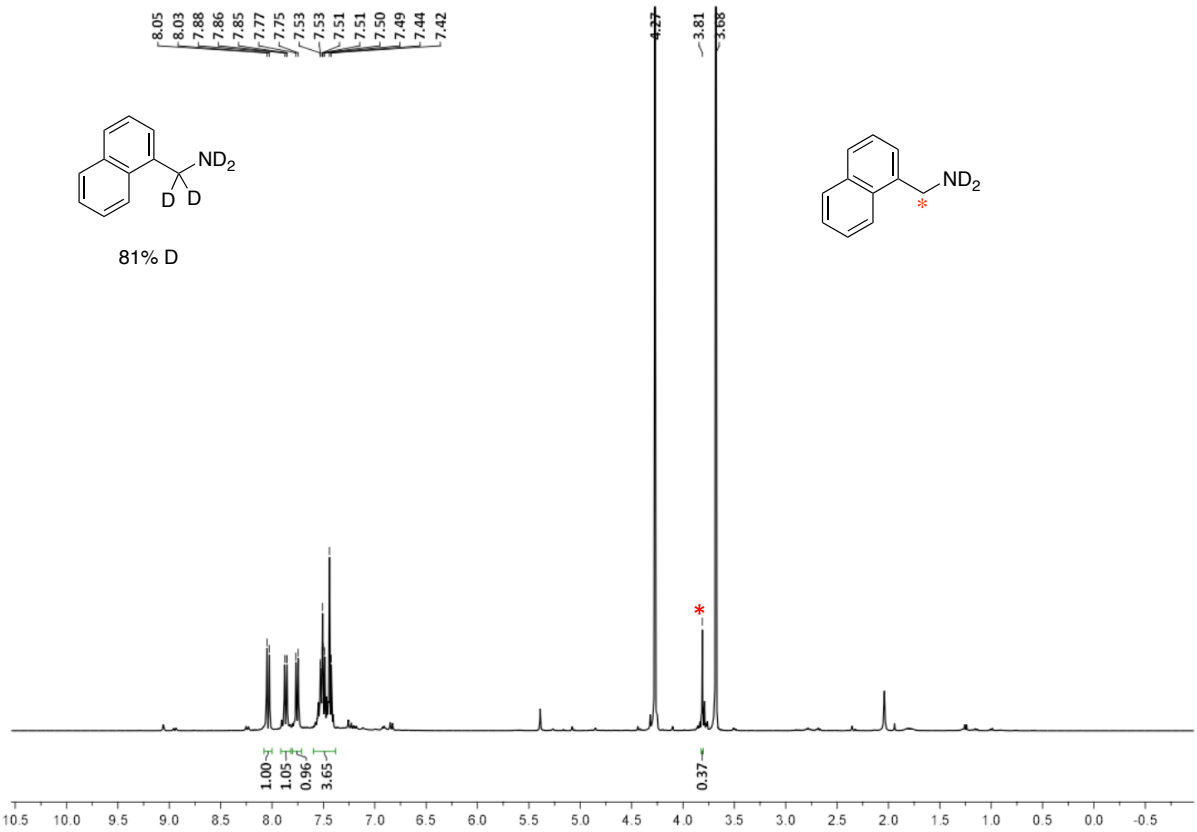
^{1}H NMR spectrum of *p*-tolylmethanamine-d4 (**3b**) (400 MHz, $CDCl_3$):



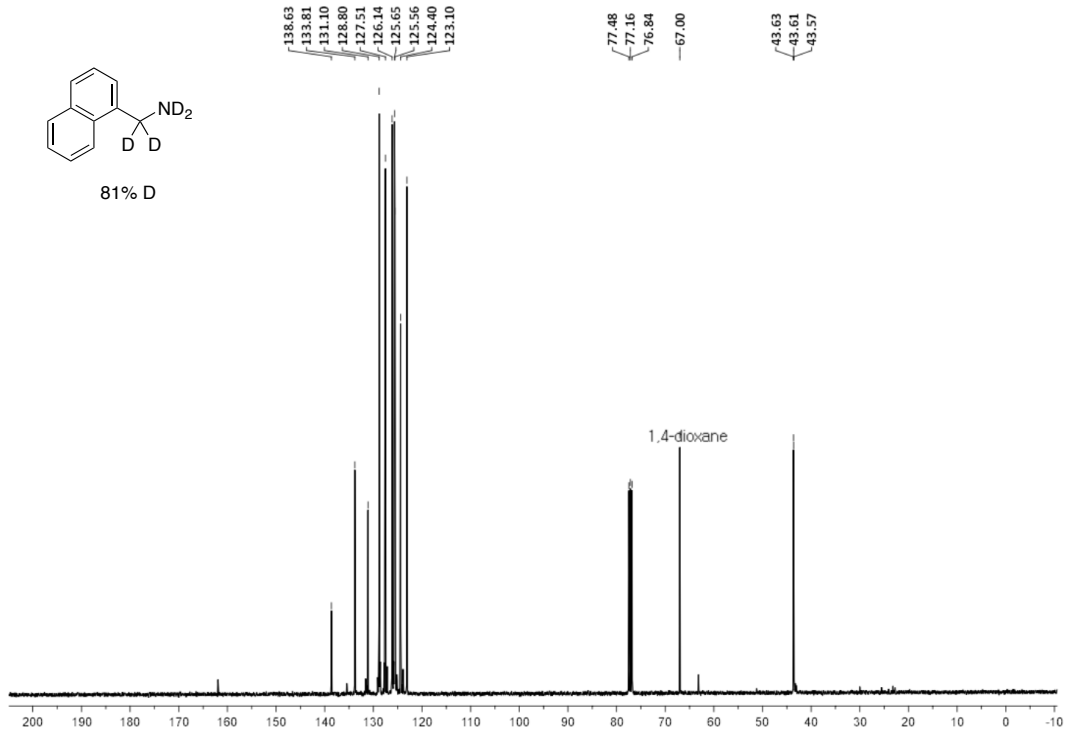
^{13}C NMR spectrum of *p*-tolylmethanamine-d4 (**3b**) (101 MHz, D_2O):



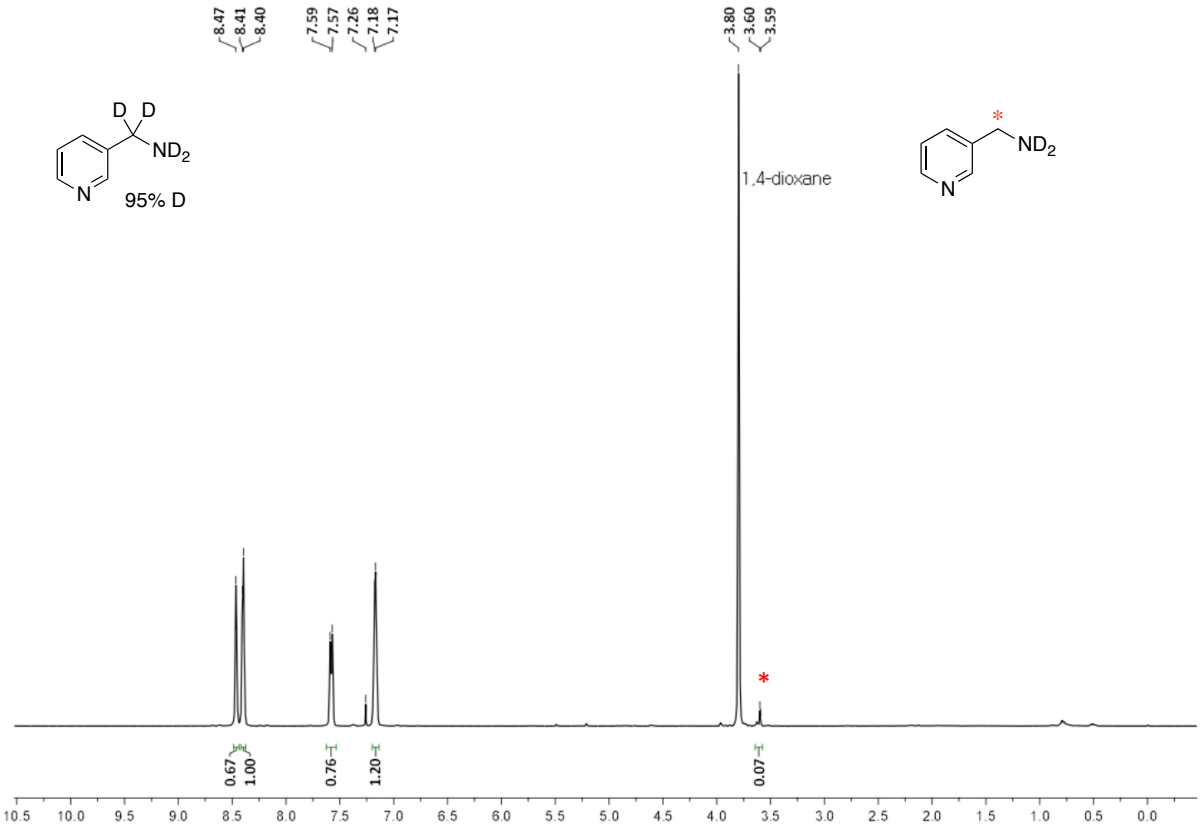
^{1}H NMR spectrum of naphthalen-1-ylmethanamine-d4 (**3c**) (400 MHz, D_2O):



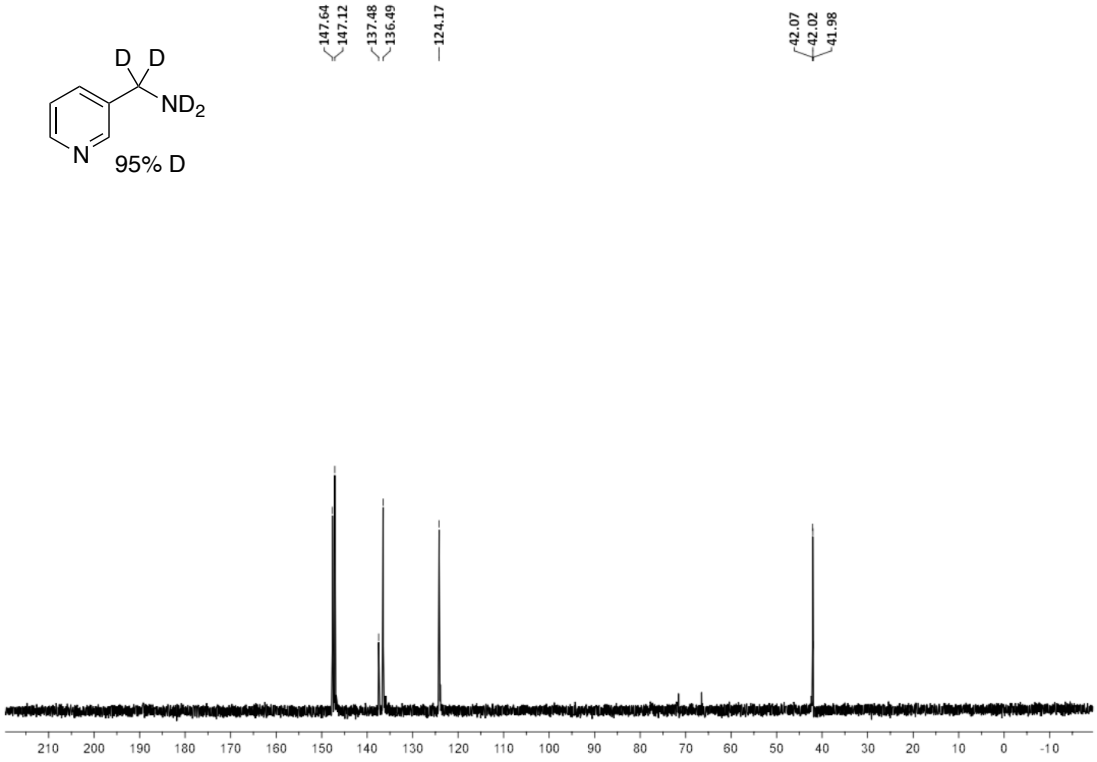
^{13}C NMR spectrum of naphthalen-1-ylmethanamine-d4 (**3c**) (101 MHz, D_2O):



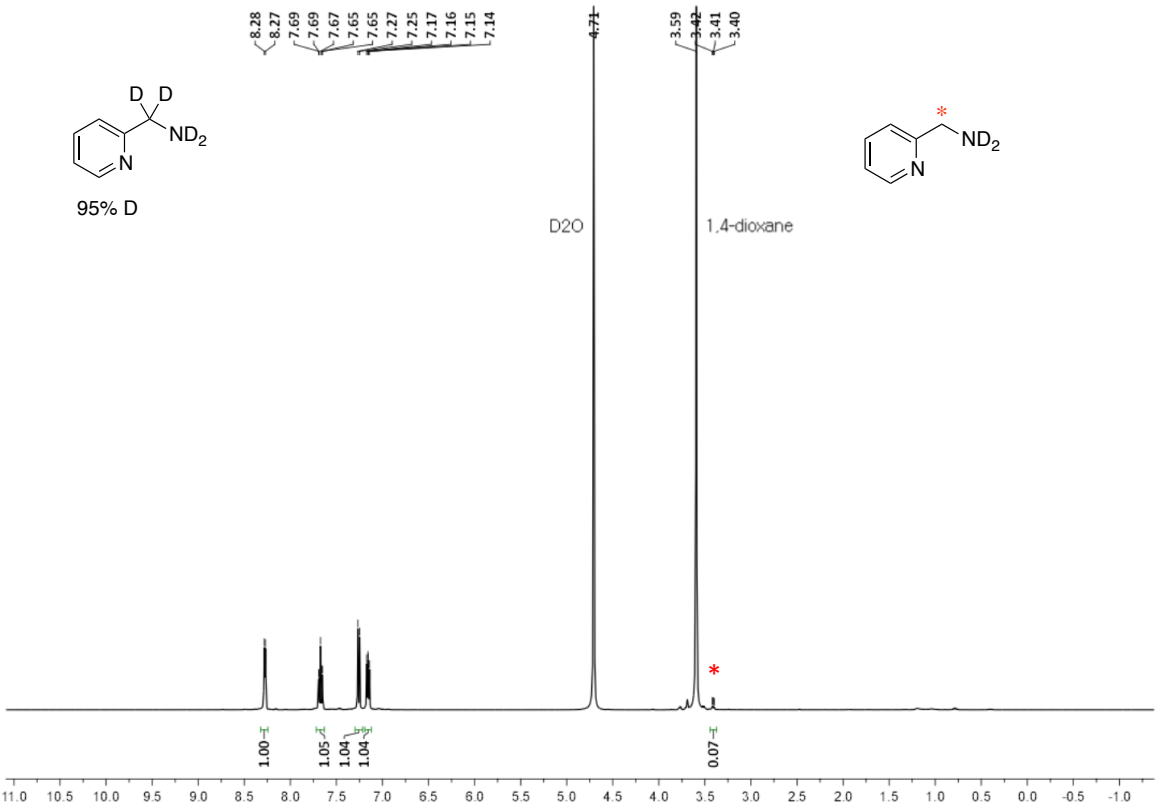
^{1}H NMR spectrum of pyridin-3-ylmethanamine-d4 (**3d**) (400 MHz, $CDCl_3$):



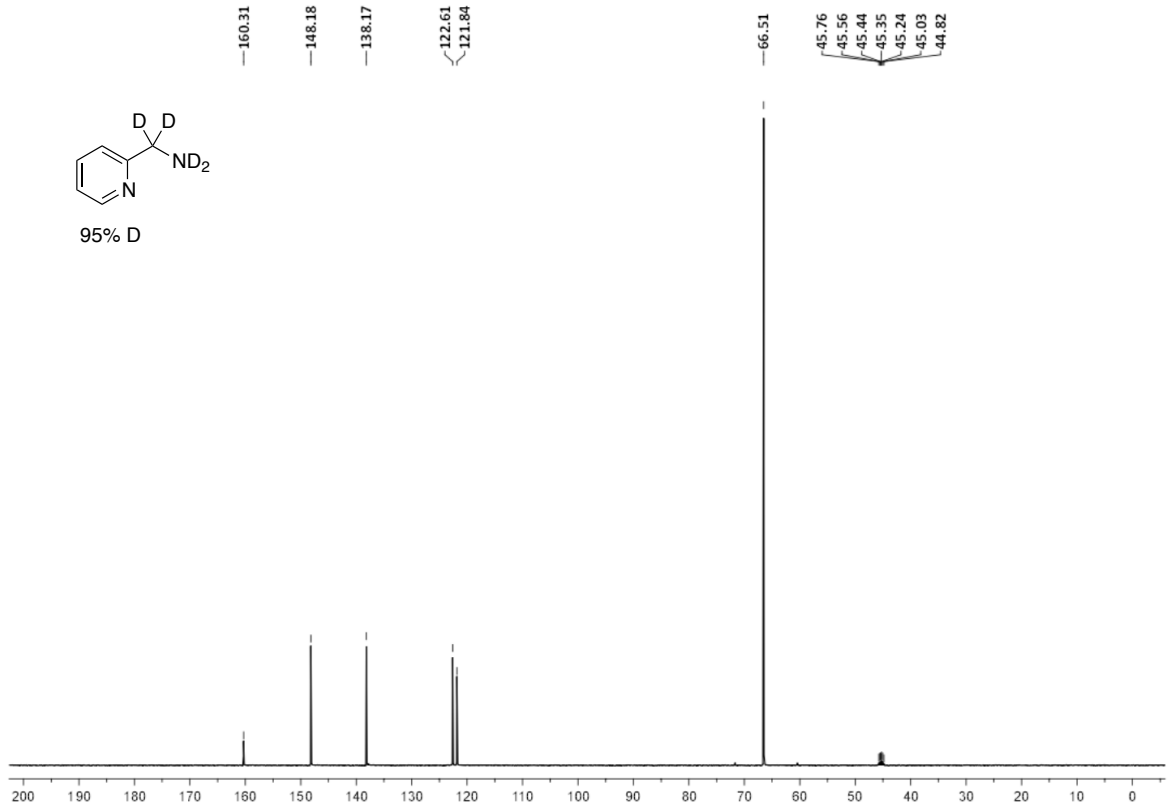
^{13}C NMR spectrum of pyridin-3-ylmethanamine-d4 (**3d**) (101 MHz, D_2O):



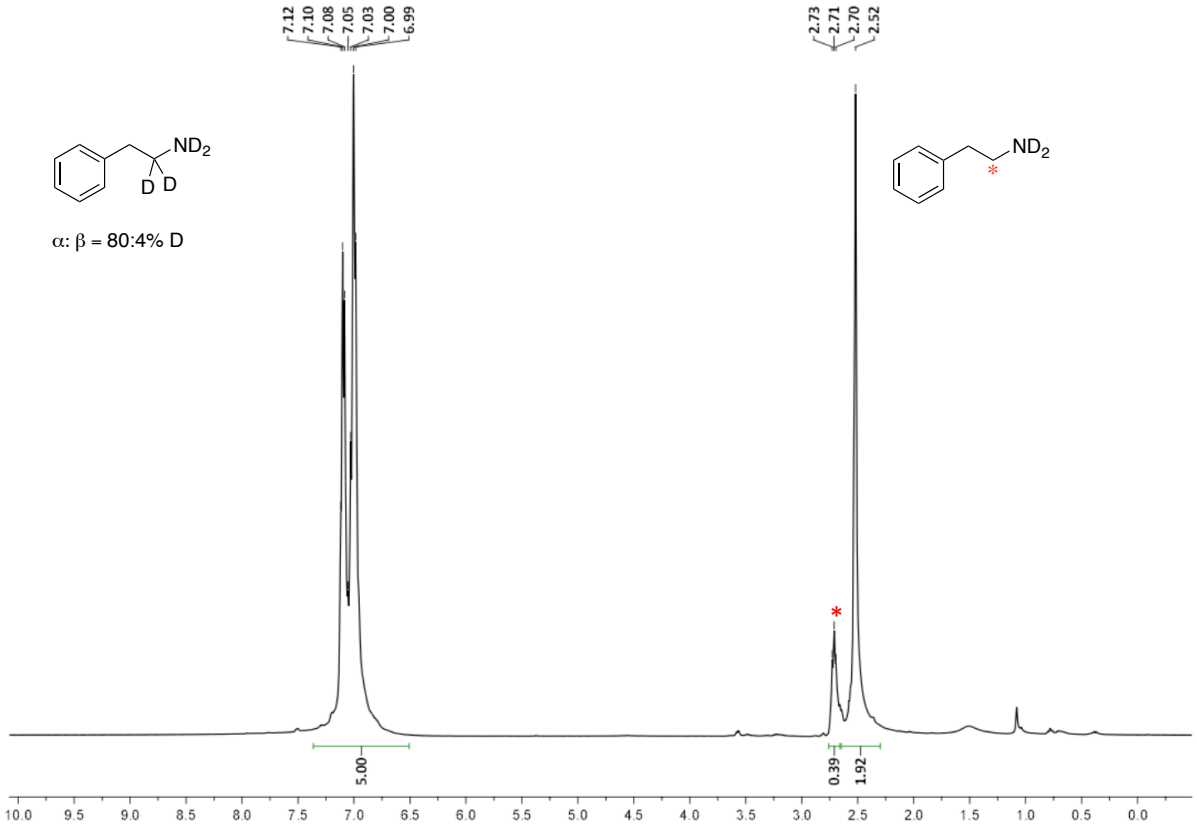
^{1}H NMR spectrum of pyridin-2-ylmethanamine-d4 (**3e**) (400 MHz, D_2O):



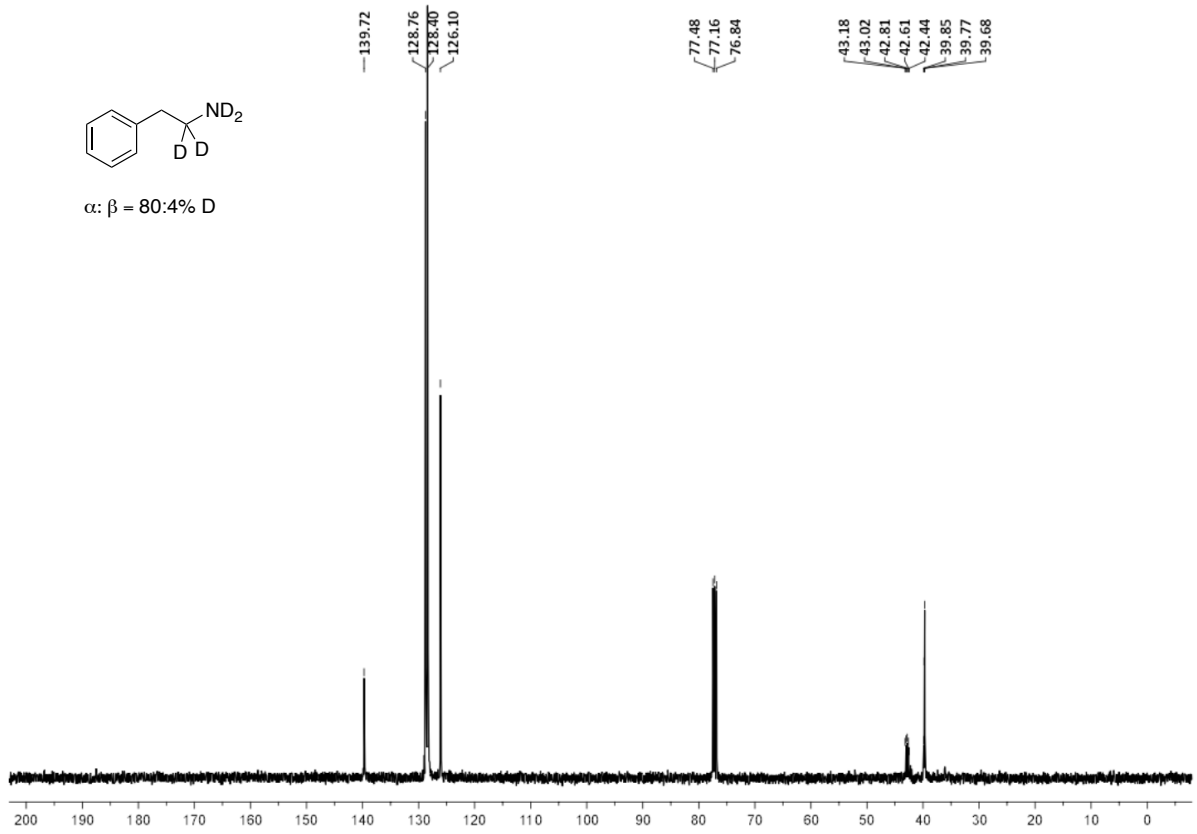
^{13}C NMR spectrum of pyridin-2-ylmethanamine-d4 (**3e**) (101 MHz, D_2O):



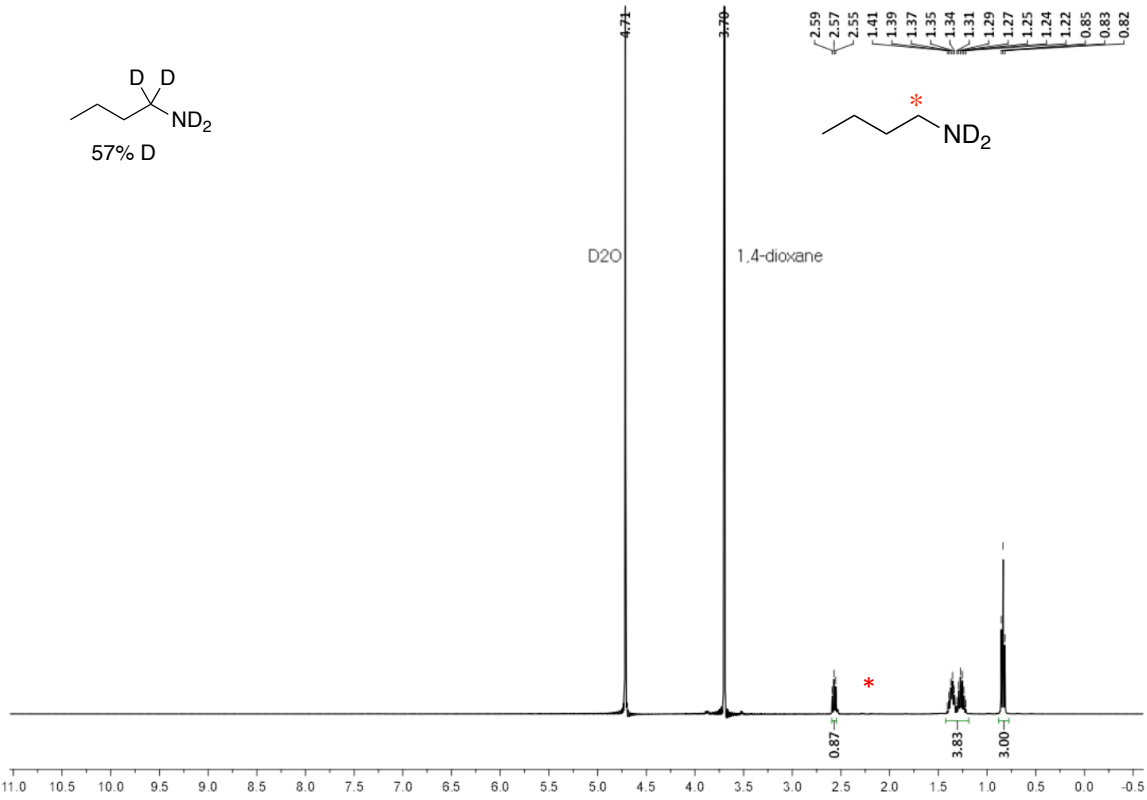
^{1}H NMR spectrum of 2-phenylethanamine-d4 (**3f**) (400 MHz, $CDCl_3$):



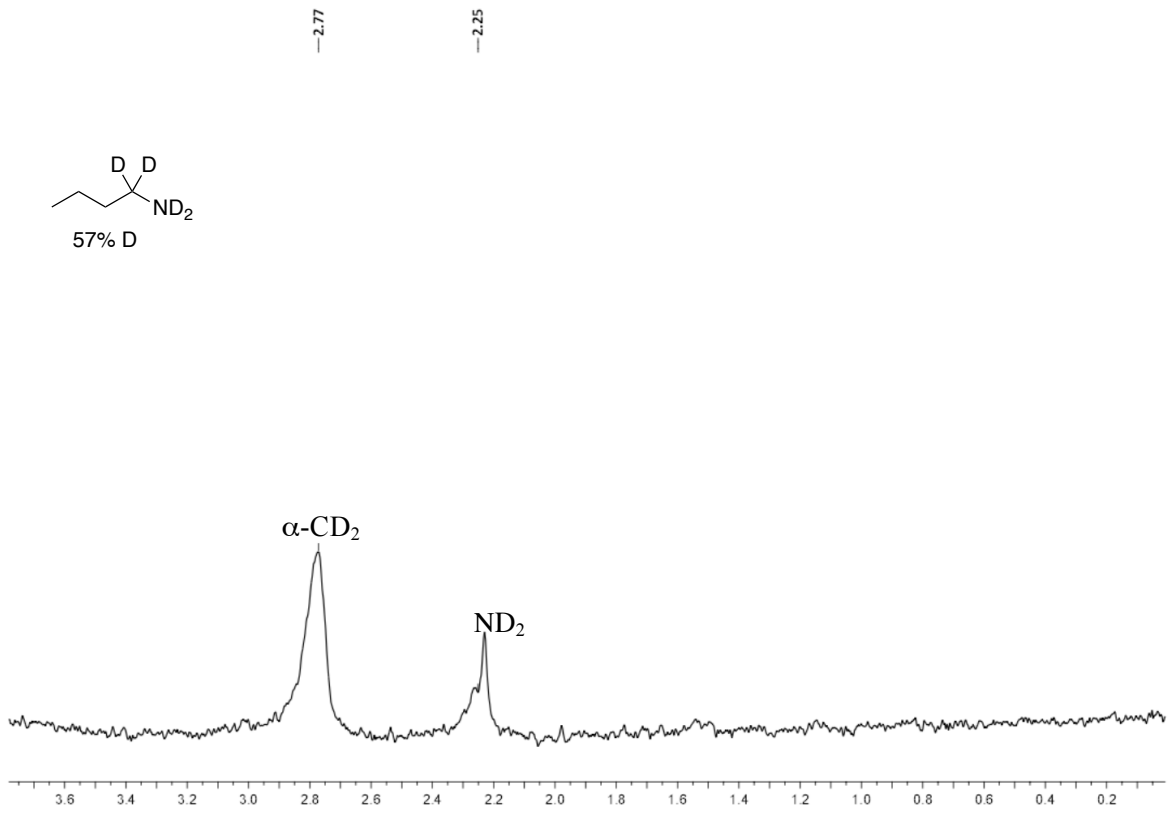
^{13}C NMR spectrum of 2-phenylethanamine-d4 (**3f**) (101 MHz, $CDCl_3$):



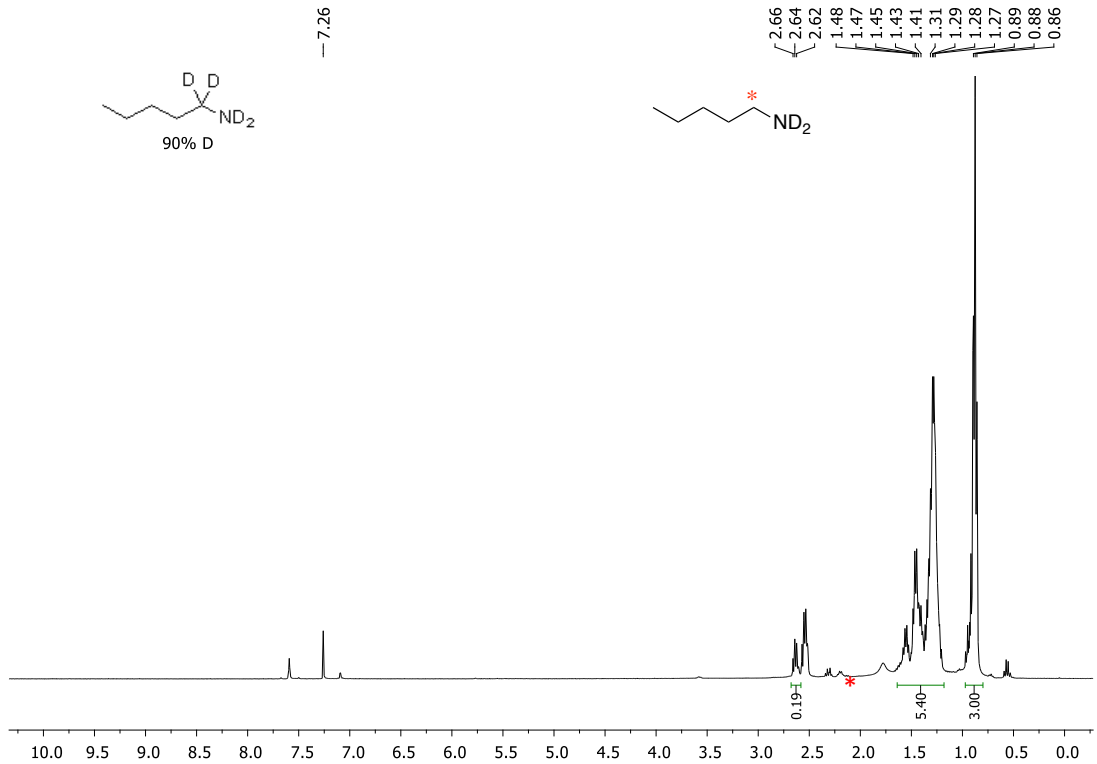
^{1}H NMR spectrum of butan-1-amine-d4 (**3g**) (400 MHz, D_2O):



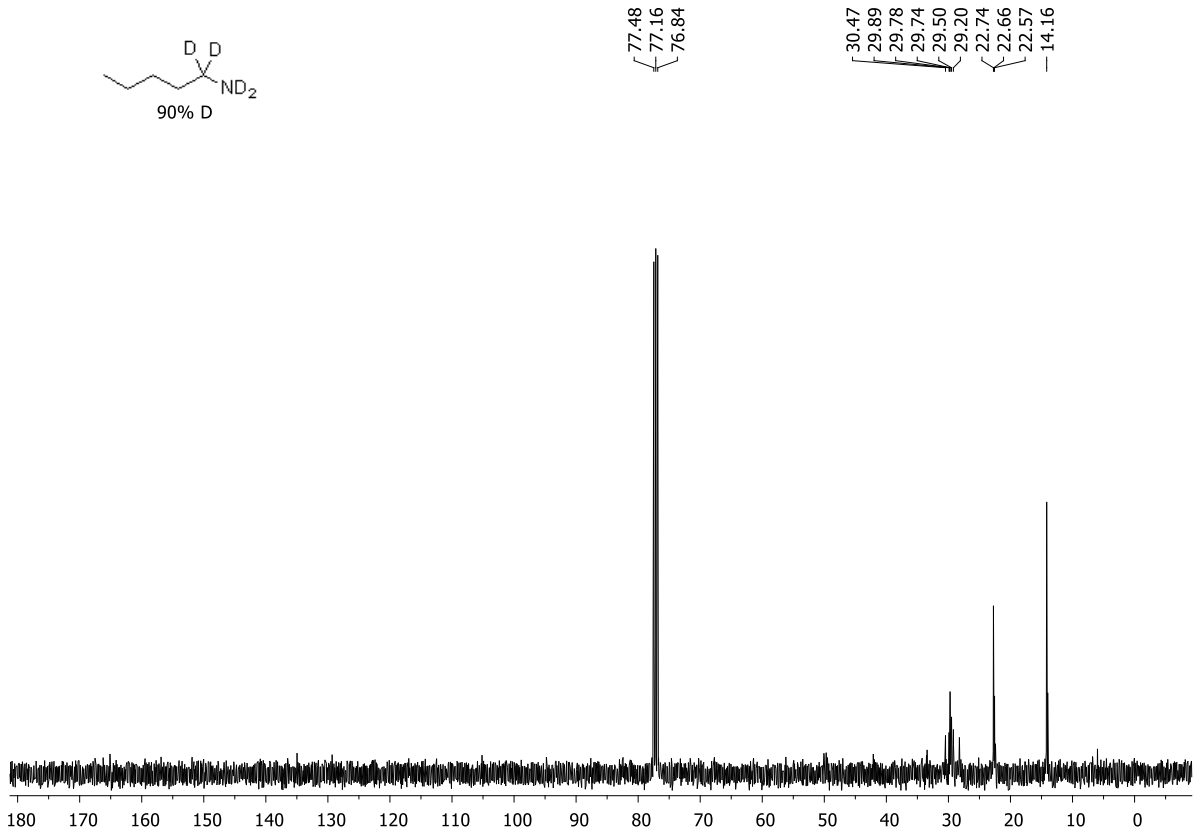
^{2}H NMR spectrum of butan-1-amine-d4 (**3g**) (61 MHz, D_2O): D_2O peak is omitted for clarity



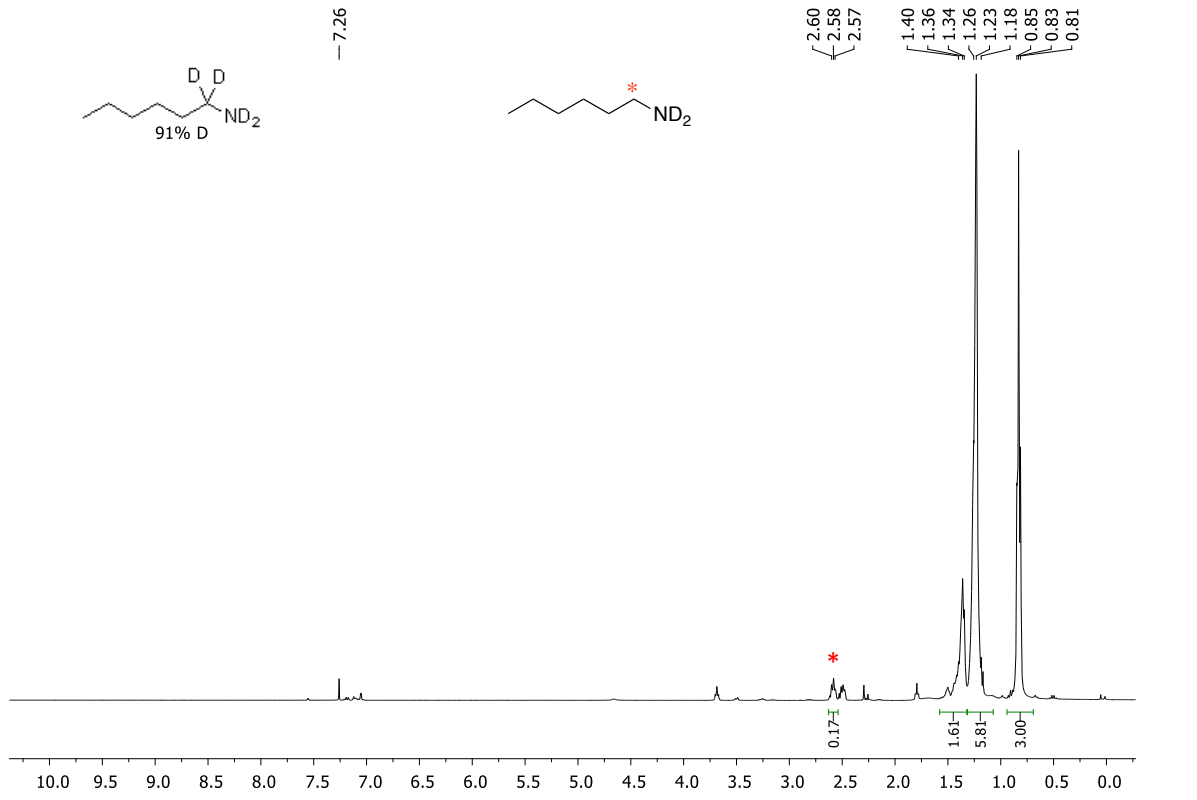
^{1}H NMR spectrum of pentan-1-amine-d4 (**3h**) (400 MHz, $CDCl_3$):



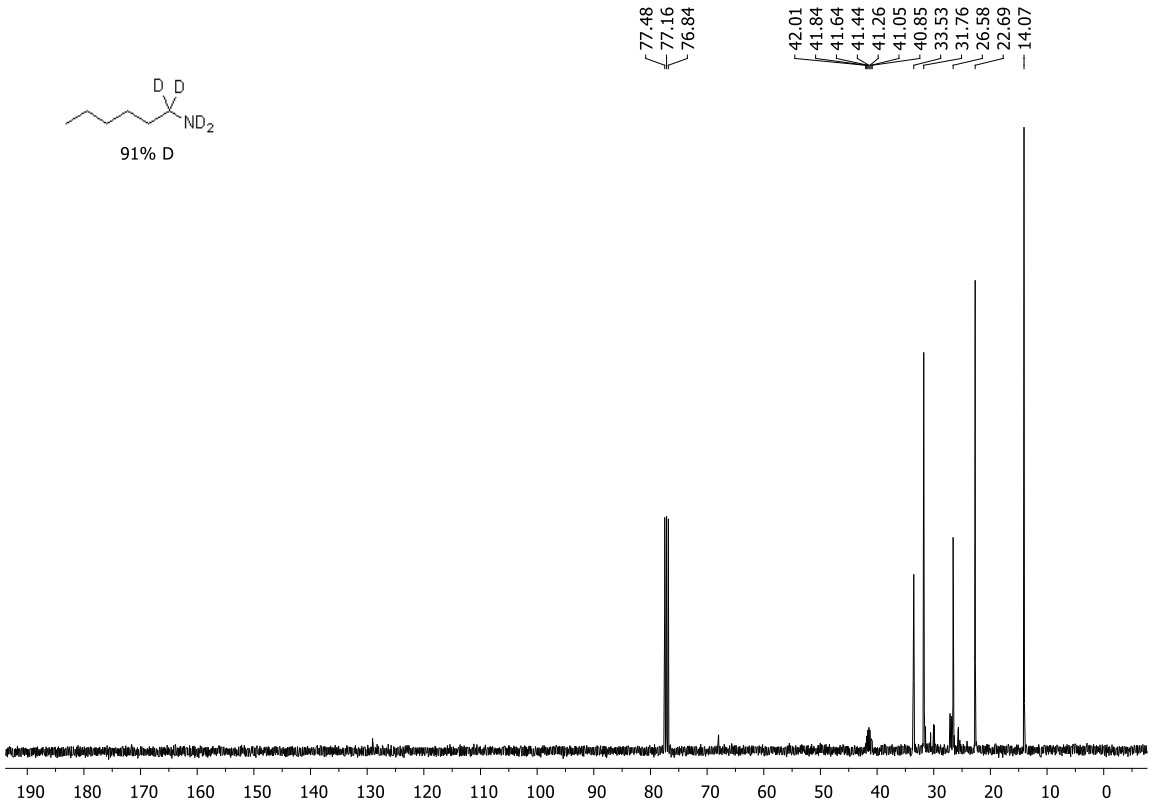
^{13}C NMR spectrum of pentan-1-amine-d4 (**3h**) (101 MHz, $CDCl_3$):



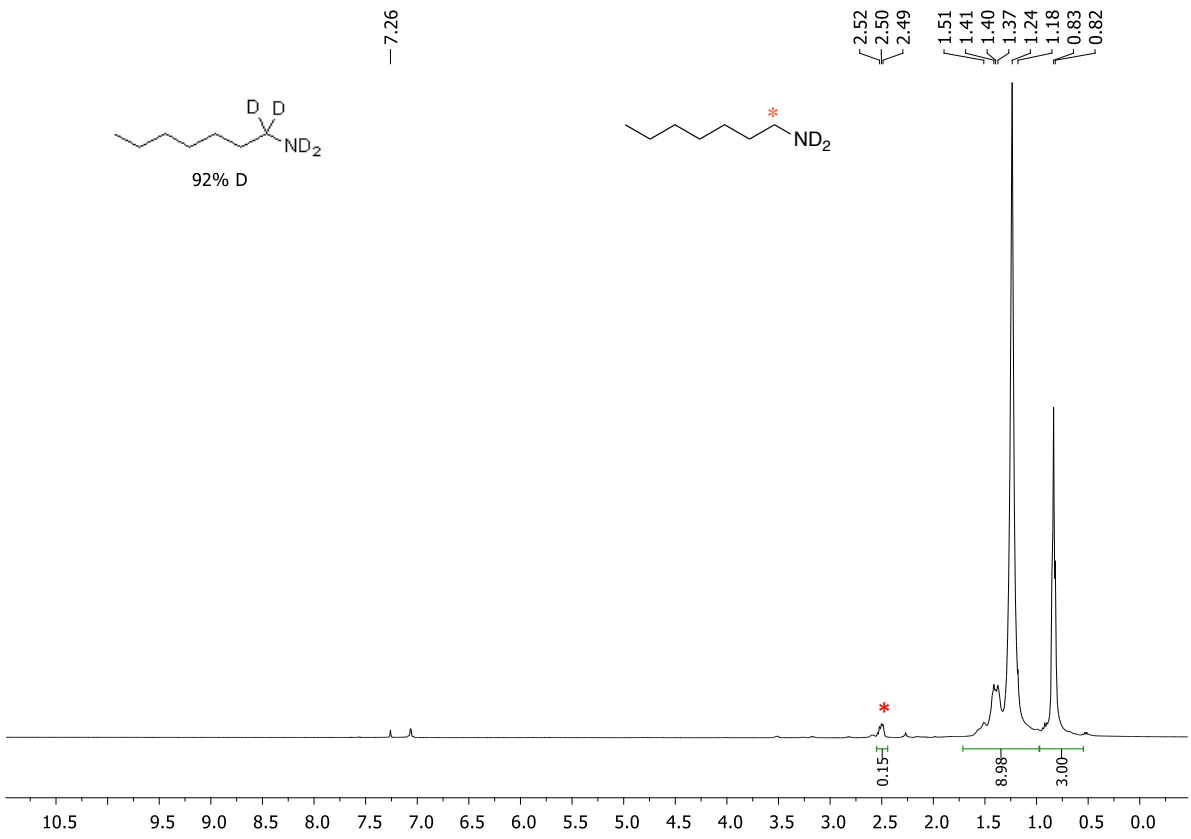
^{1}H NMR spectrum of hexan-1-amine-d4 (**3i**) (400 MHz, $CDCl_3$):



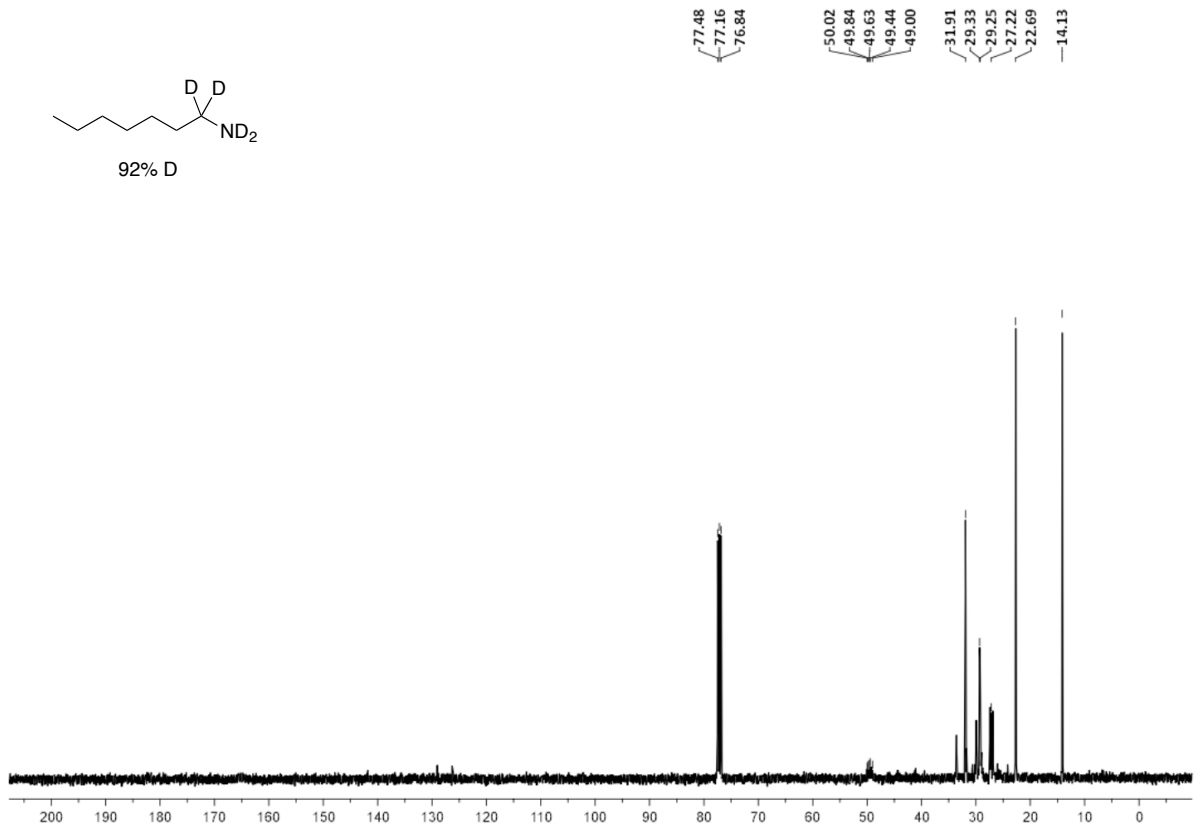
^{13}C NMR spectrum of hexan-1-amine-d4 (**3i**) (101 MHz, $CDCl_3$):



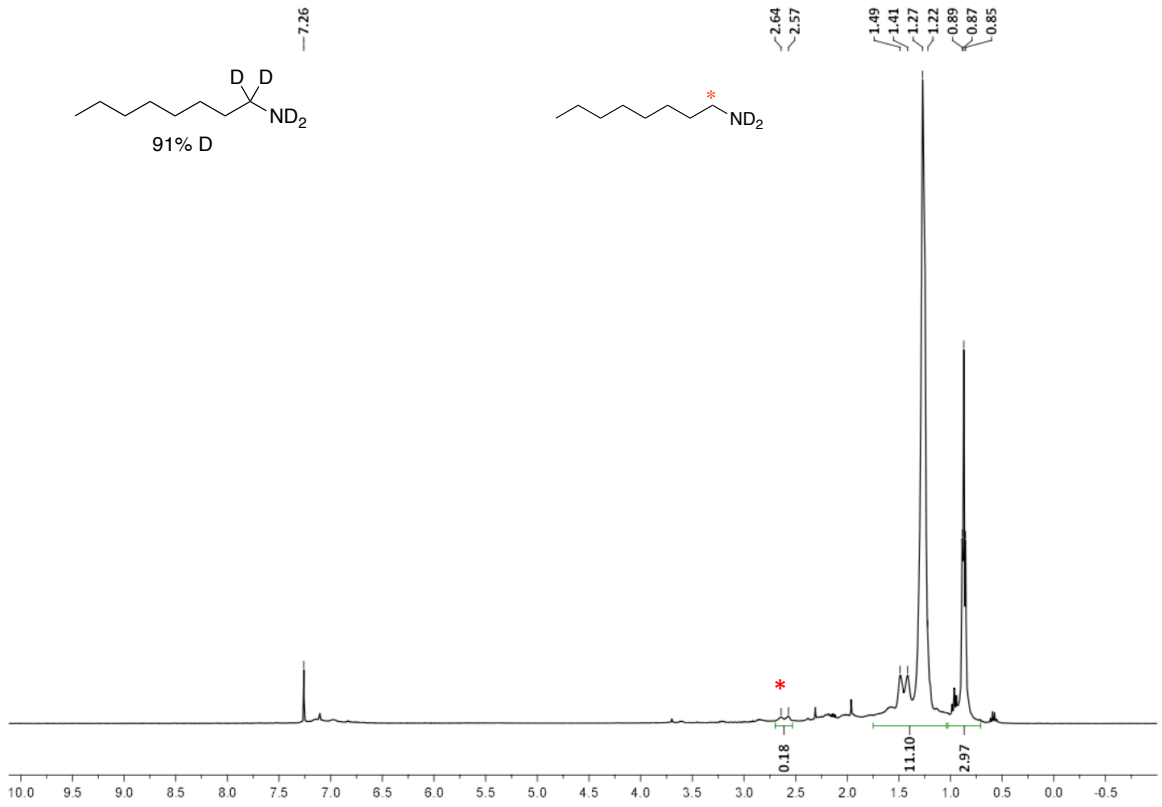
^{1}H NMR spectrum of heptan-1-amine-d4 (**3j**) (400 MHz, $CDCl_3$):



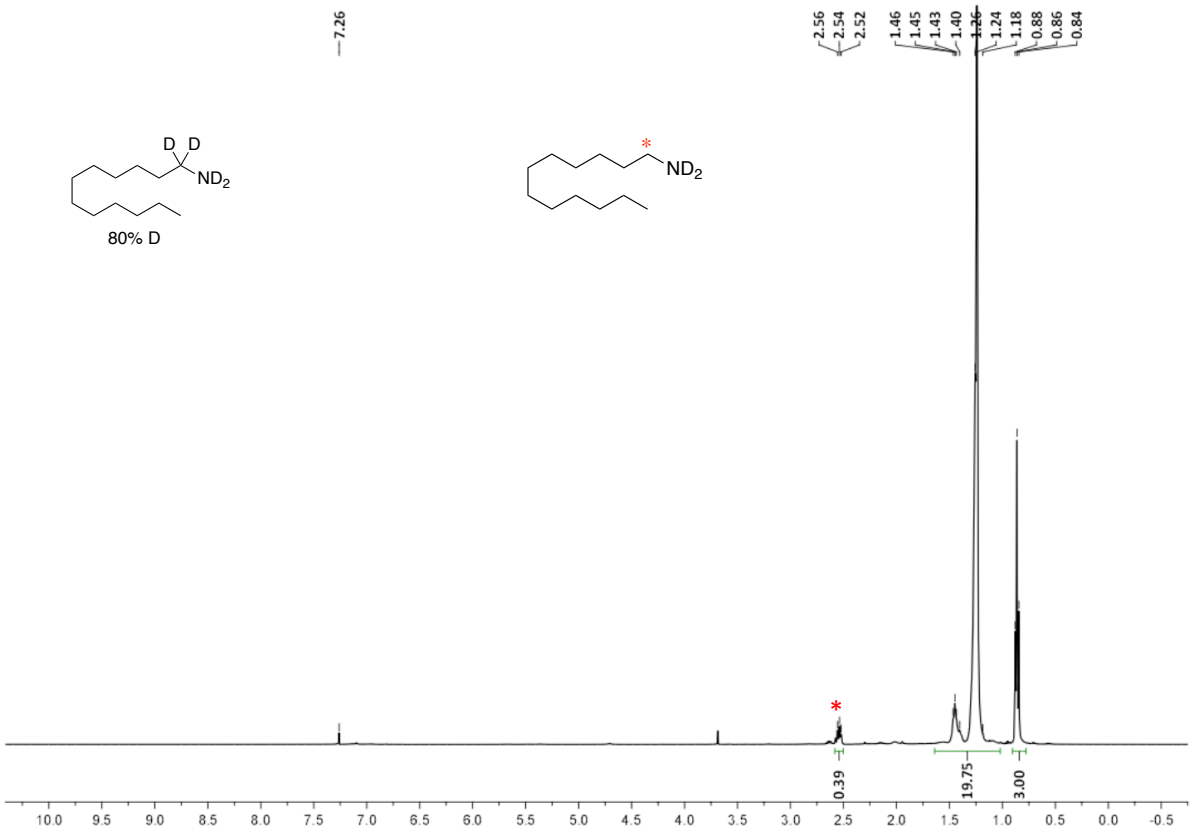
^{13}C NMR spectrum of heptan-1-amine-d4 (**3j**) (101 MHz, $CDCl_3$):



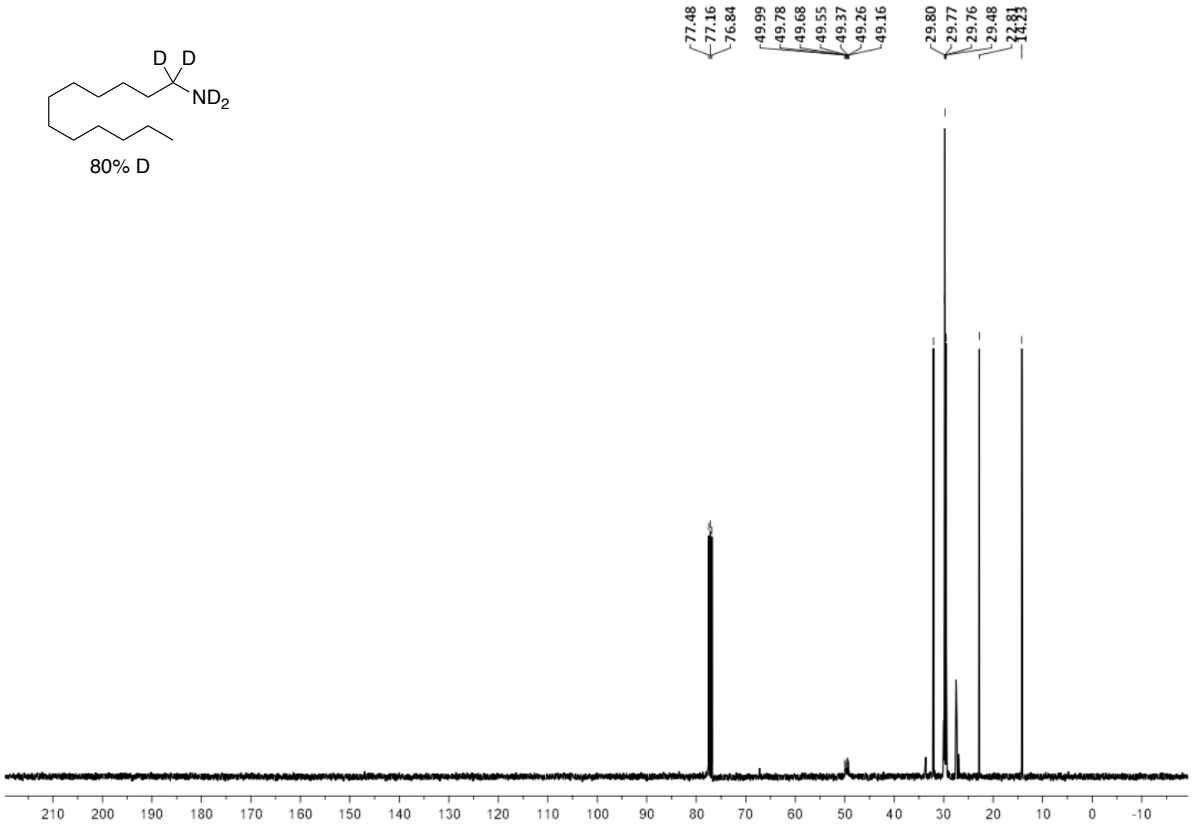
^{1}H NMR spectrum of octan-1-amine-d4 (**3k**) (400 MHz, $CDCl_3$):



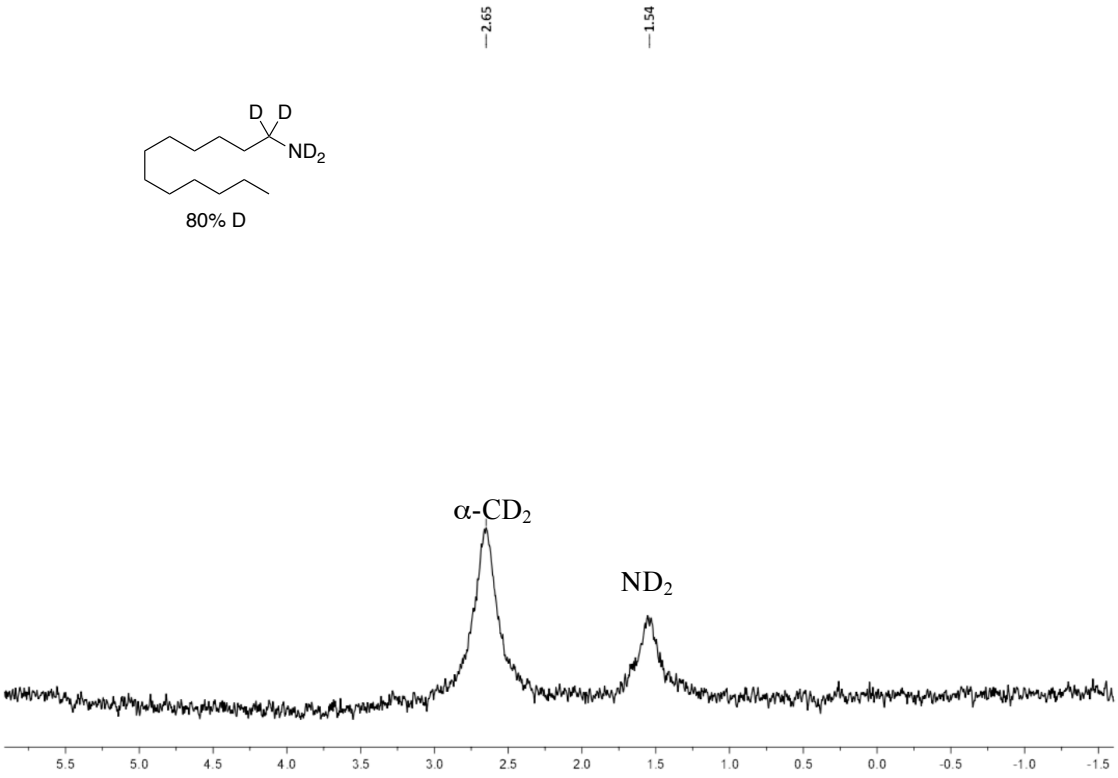
^{1}H NMR spectrum of dodecan-1-amine-d4 (**3l**) (400 MHz, $CDCl_3$):



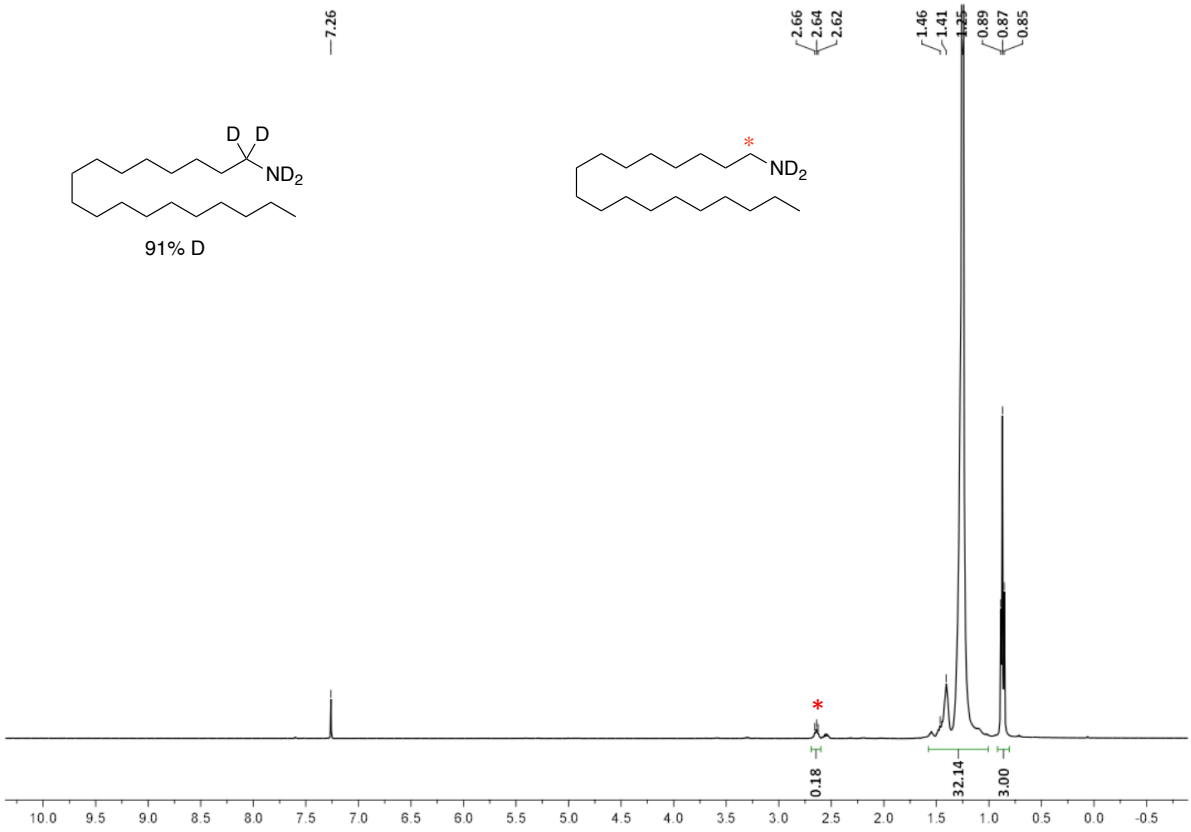
^{13}C NMR spectrum of dodecan-1-amine-d4 (**3l**) (101 MHz, $CDCl_3$):



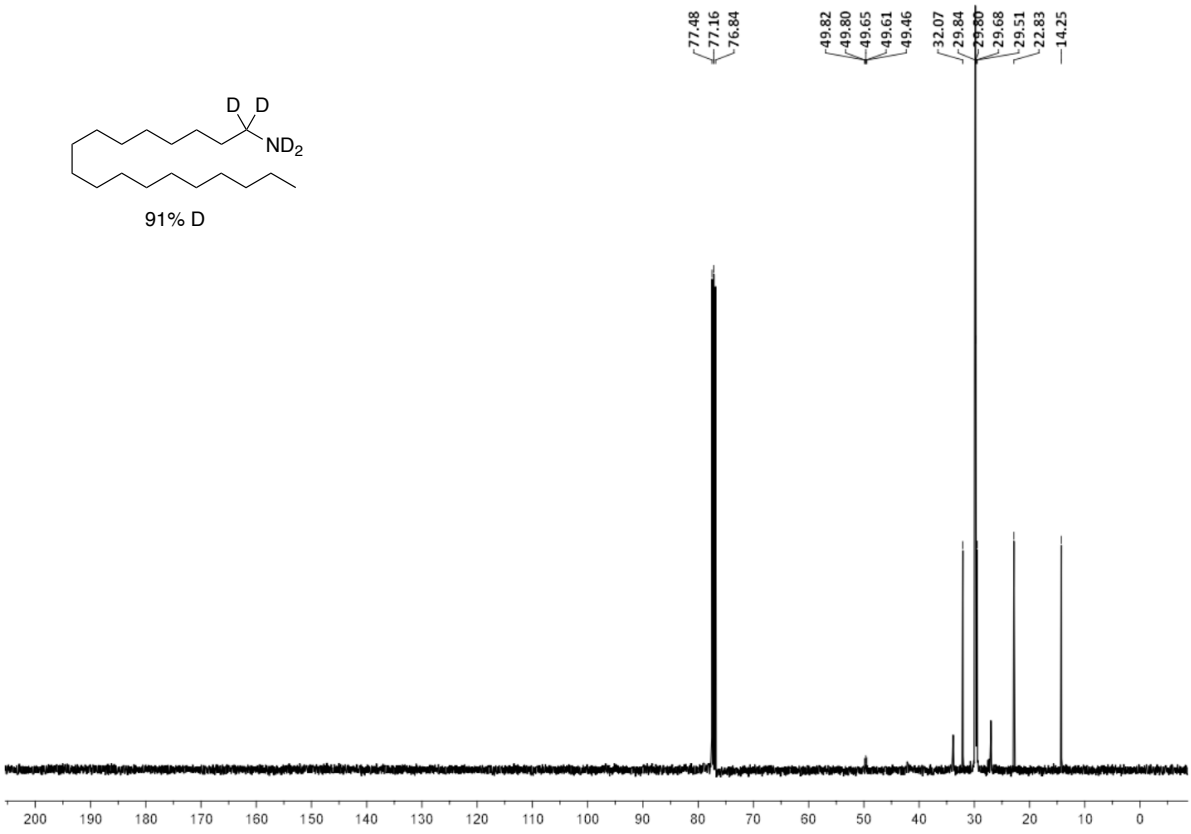
^{2}H NMR spectrum of dodecan-1-amine-d4 (**3l**) (61 MHz, $CDCl_3$): $CDCl_3$ peak is omitted for clarity



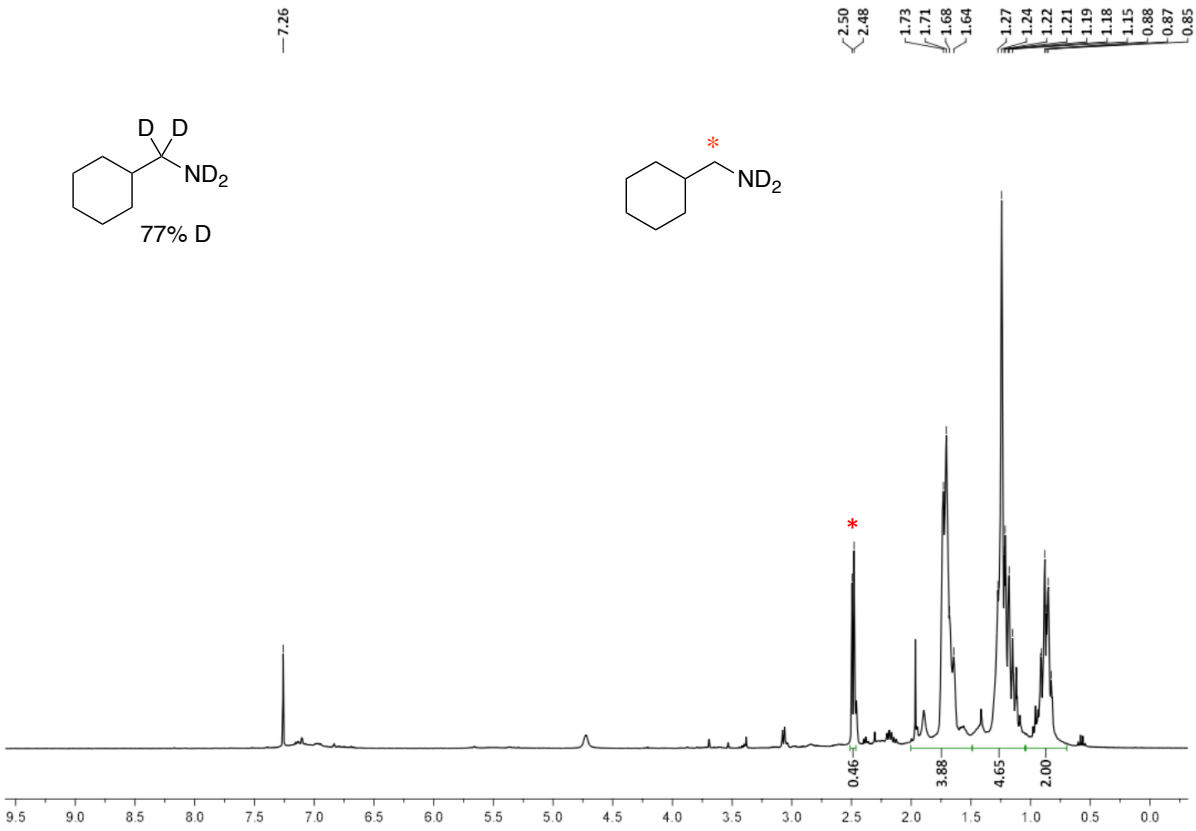
^{1}H NMR spectrum of octadecan-1-amine-d4 (**3m**) (400 MHz, $CDCl_3$):



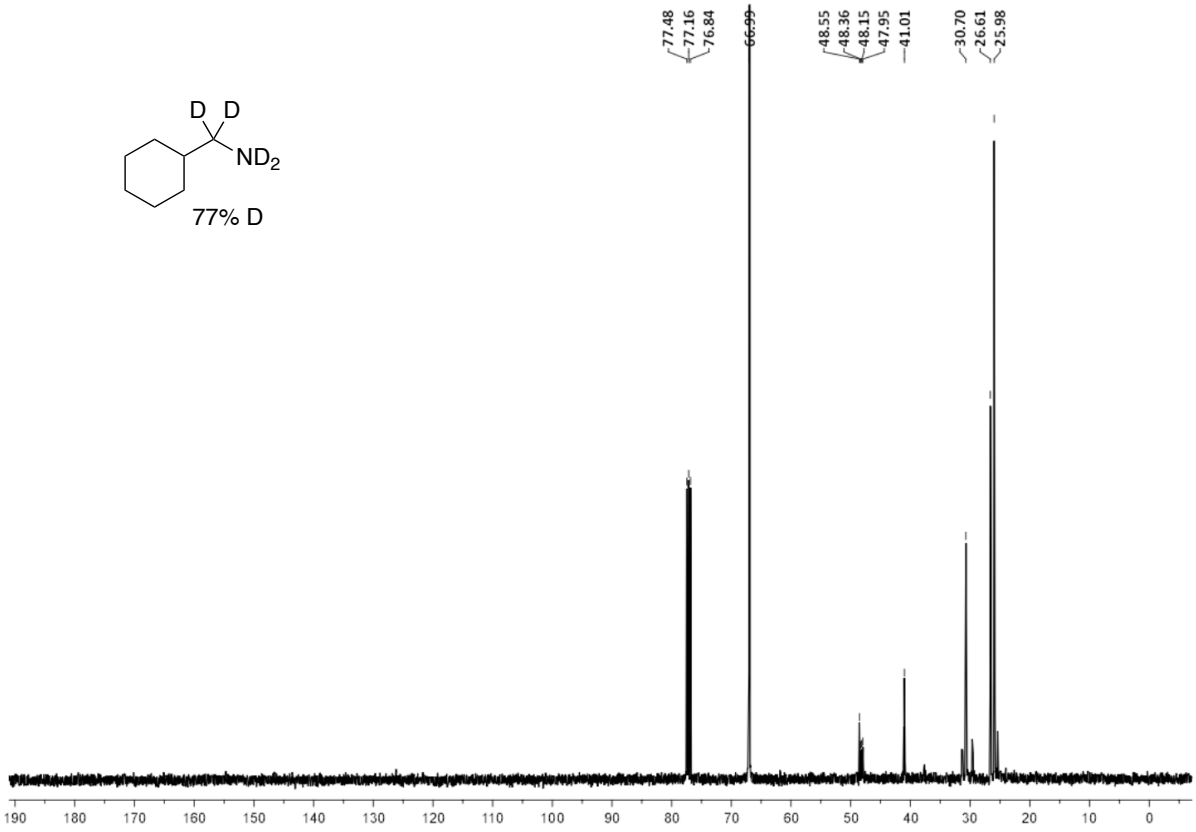
^{13}C NMR spectrum of octadecan-1-amine-d4 (**3m**) (101 MHz, $CDCl_3$):



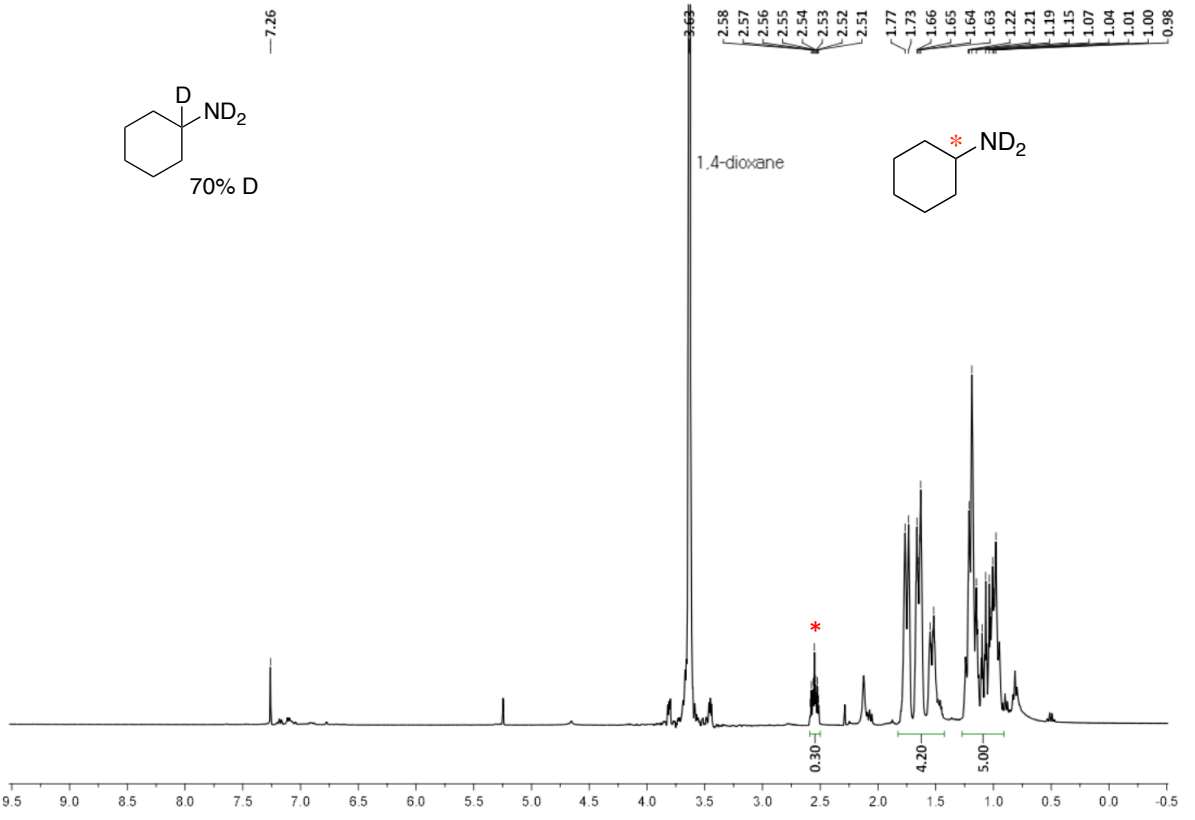
^{1}H NMR spectrum of cyclohexylmethanamine-d4 (**3n**) (400 MHz, $CDCl_3$):



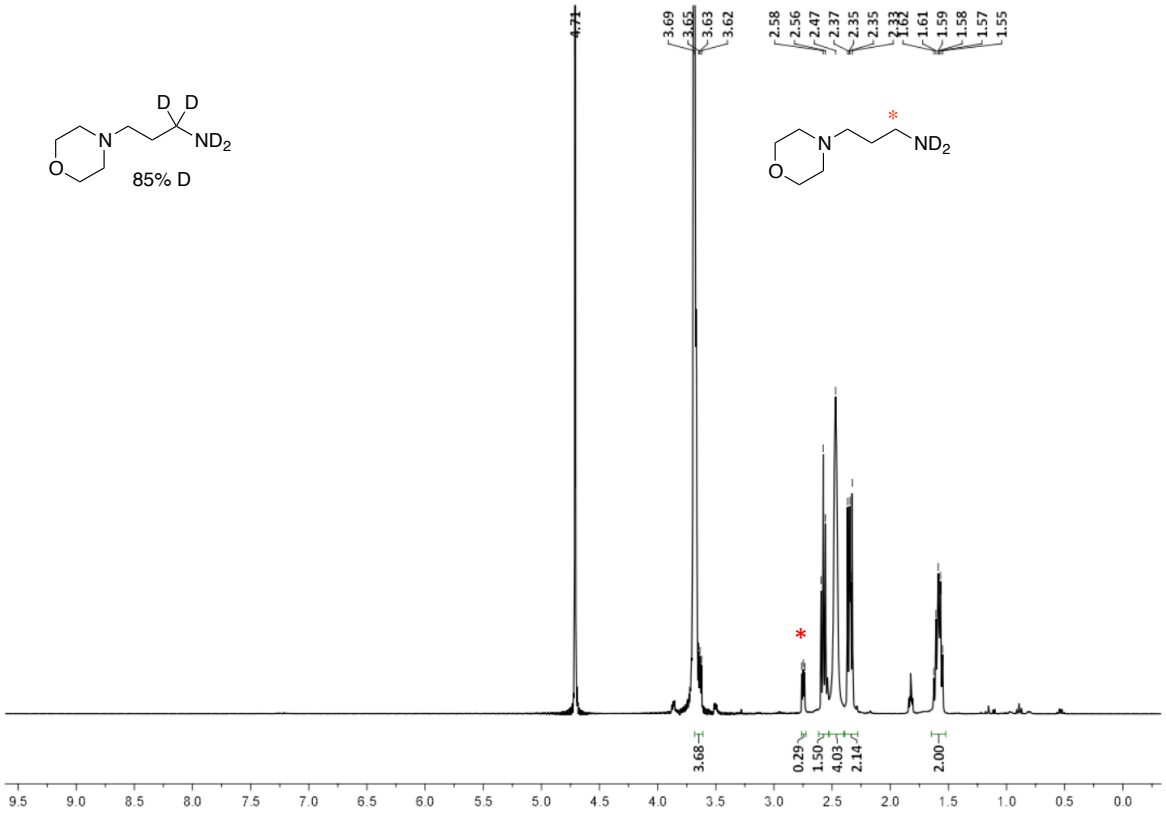
^{13}C NMR spectrum of cyclohexylmethanamine-d4 (**3n**) (101 MHz, $CDCl_3$):



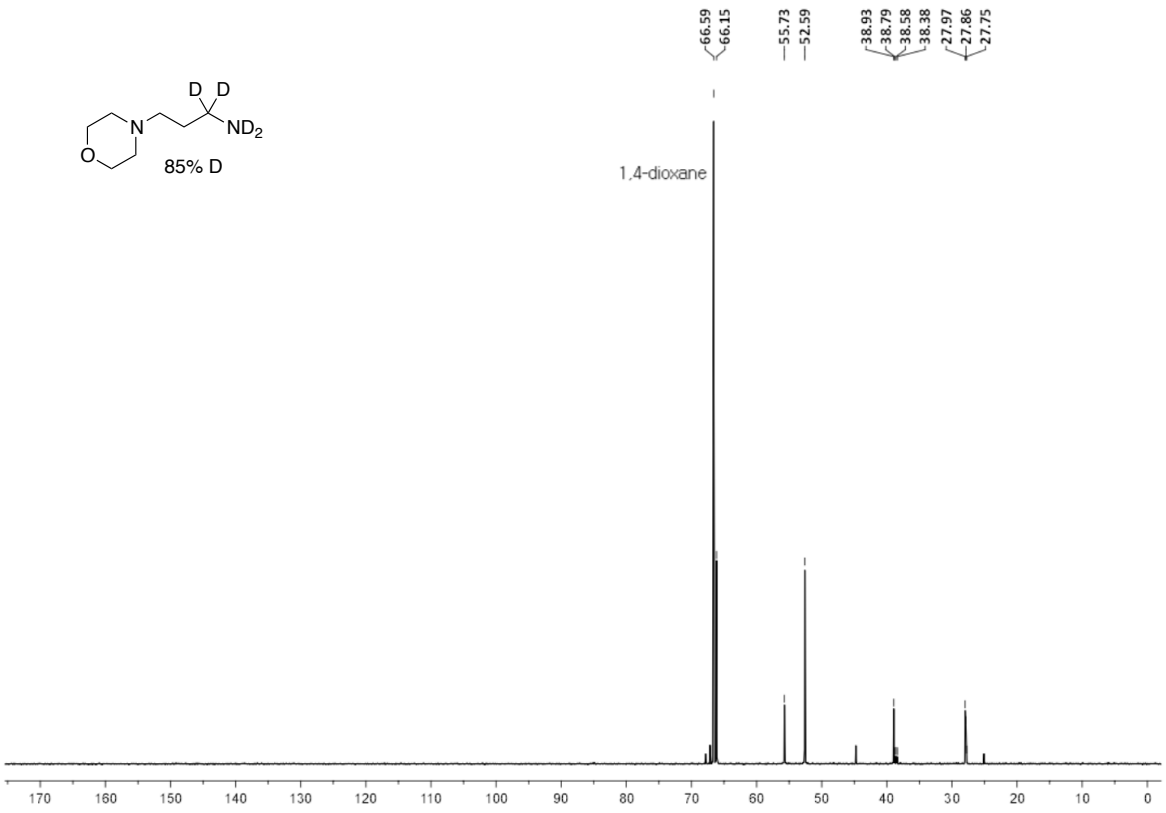
^{1}H NMR spectrum of cyclohexanamine –d3 (**3o**) (400 MHz, $CDCl_3$):



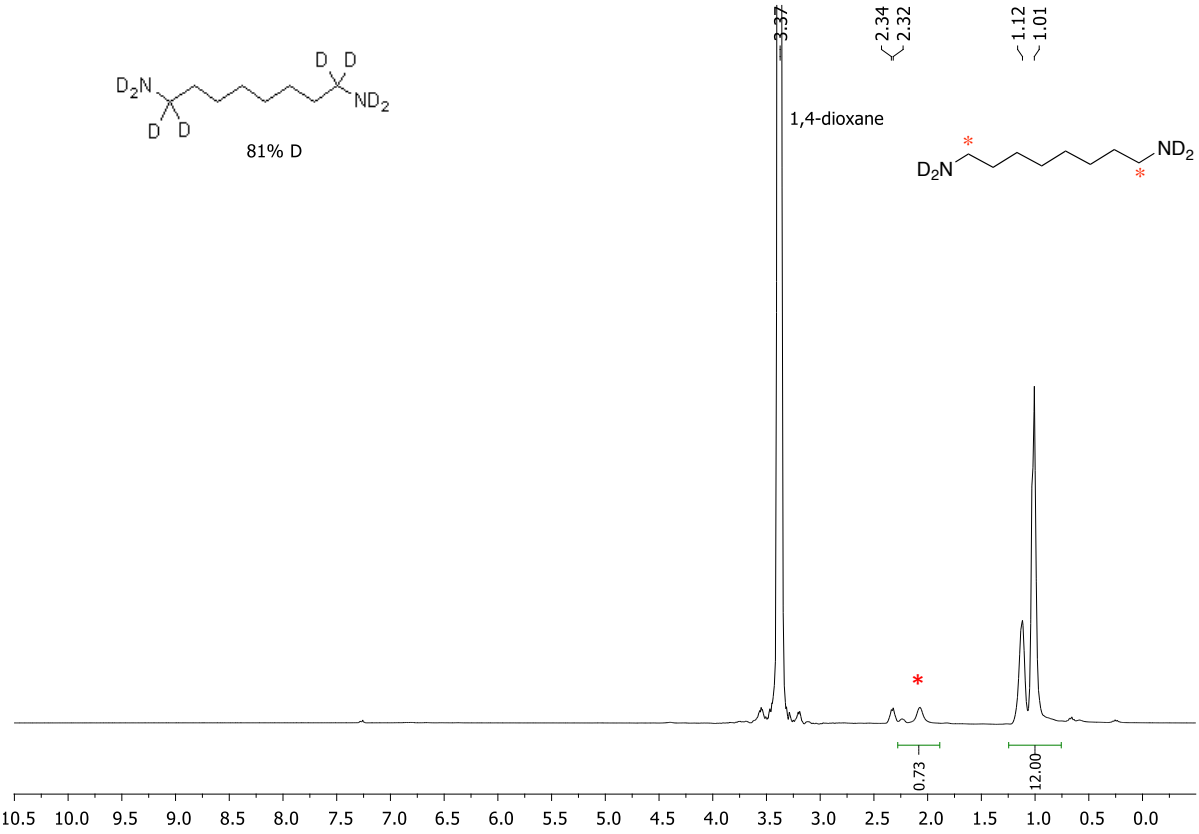
^{1}H NMR spectrum of 3-morpholinopropan-1-amine-d4 (**3p**) (400 MHz, D_2O):



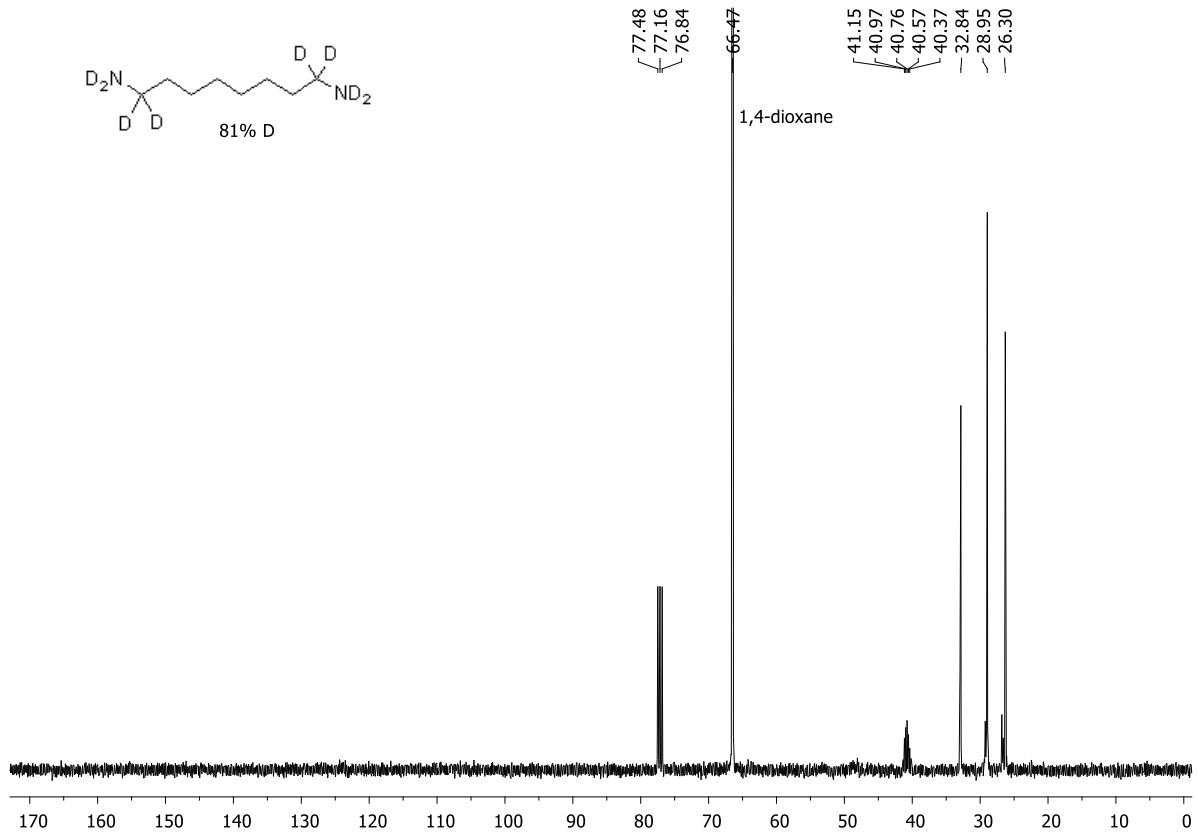
^{13}C NMR spectrum of 3-morpholinopropan-1-amine-d4 (**3p**) (101 MHz, D_2O):



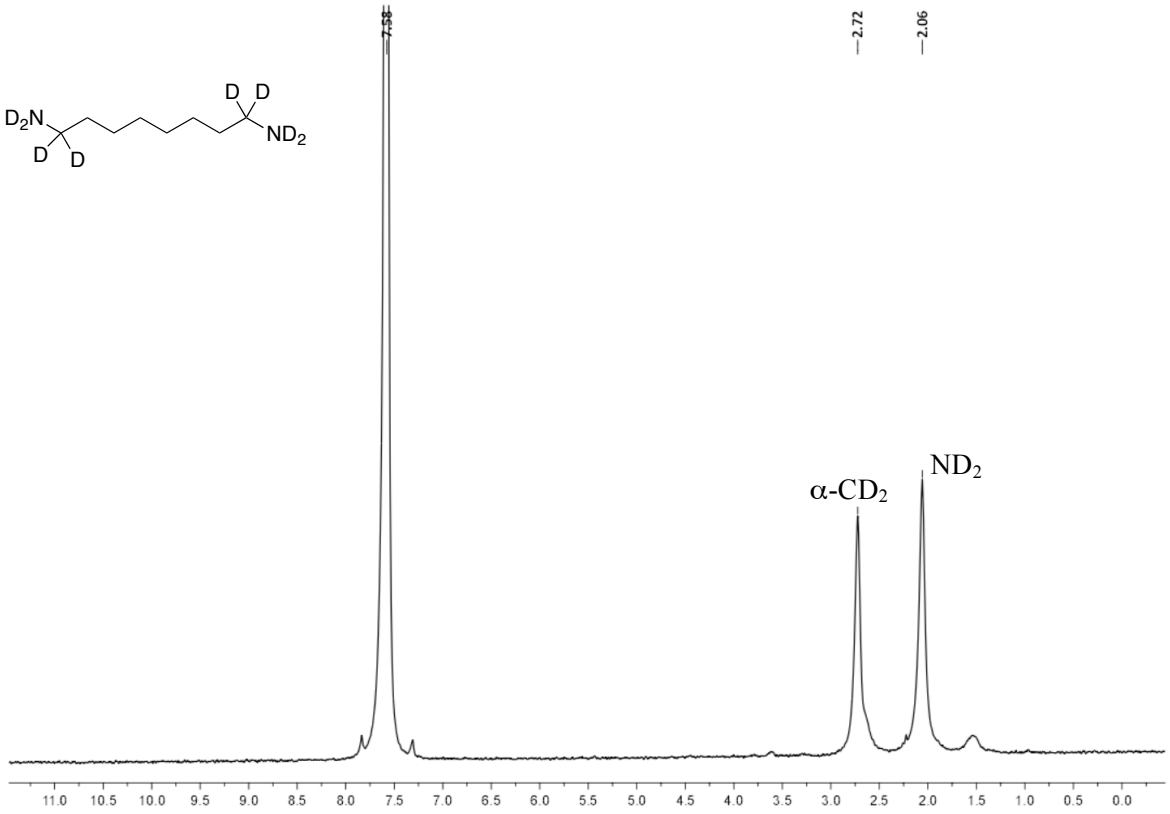
^{1}H NMR spectrum of octane-1,8-diamine-d8 (**3q**) (400 MHz, $CDCl_3$):



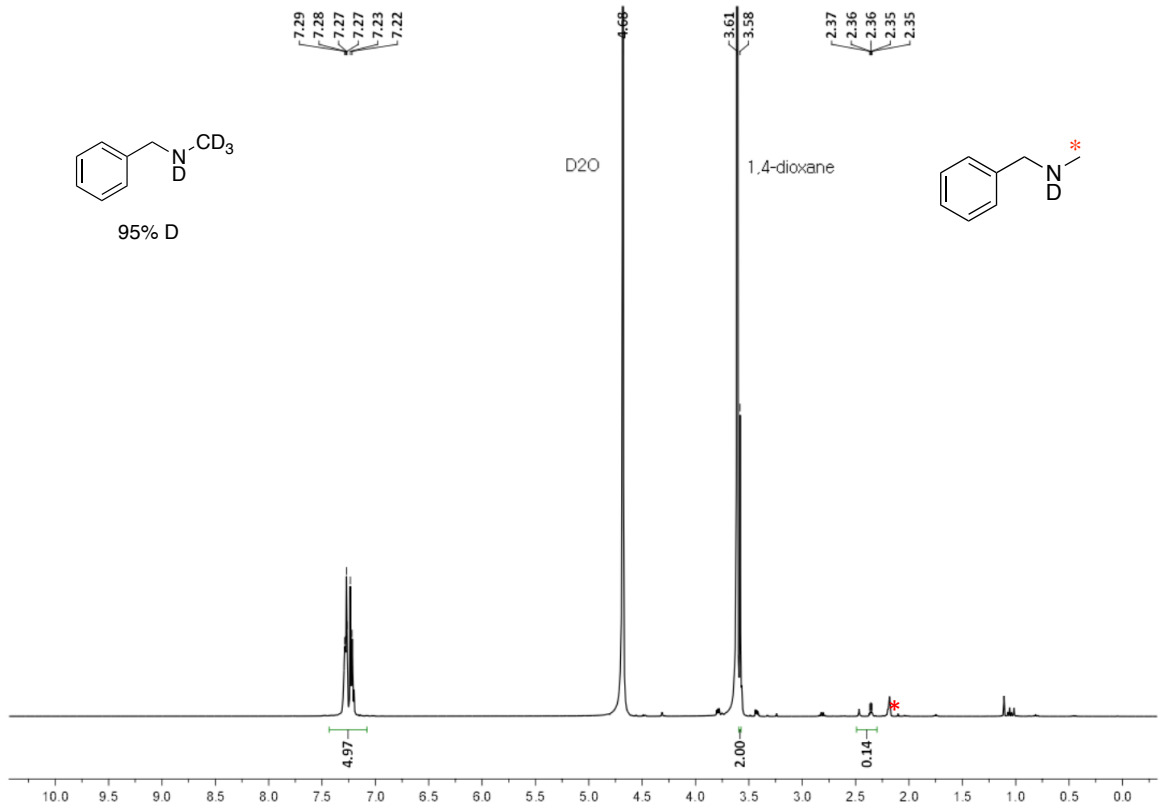
^{13}C NMR spectrum of octane-1,8-diamine-d8 (**3q**) (101 MHz, $CDCl_3$):



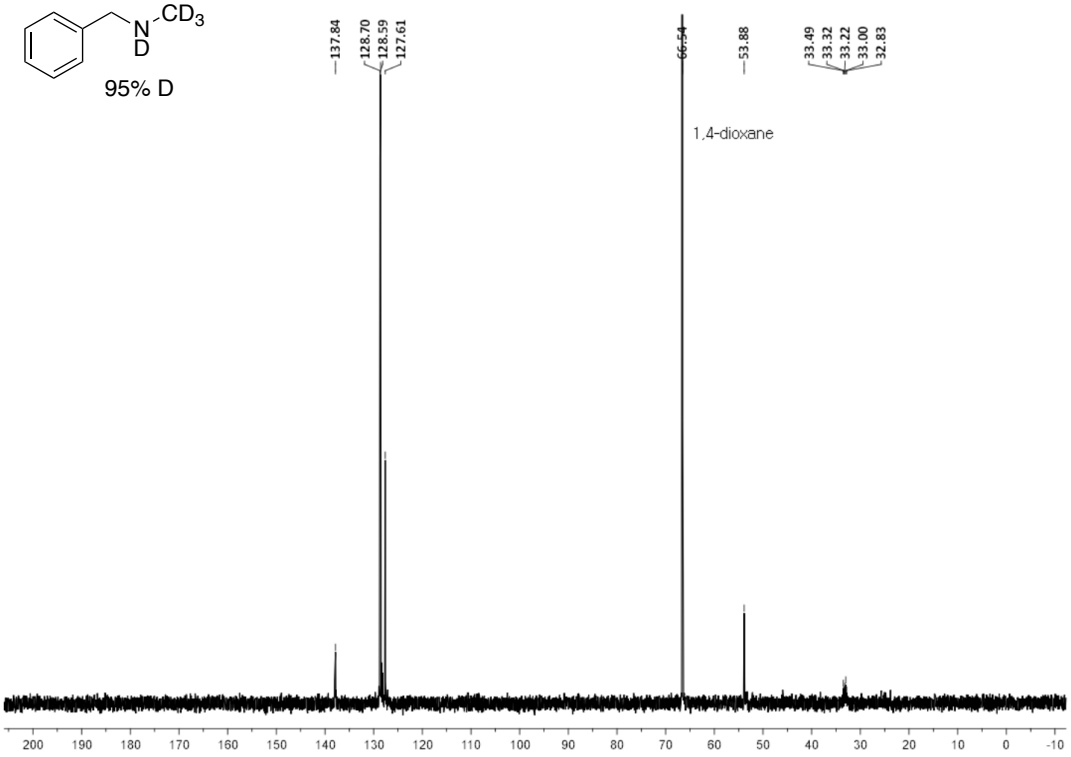
^{2}H NMR spectrum of octane-1,8-diamine-d8 (**3q**) (61 MHz, $CDCl_3$):



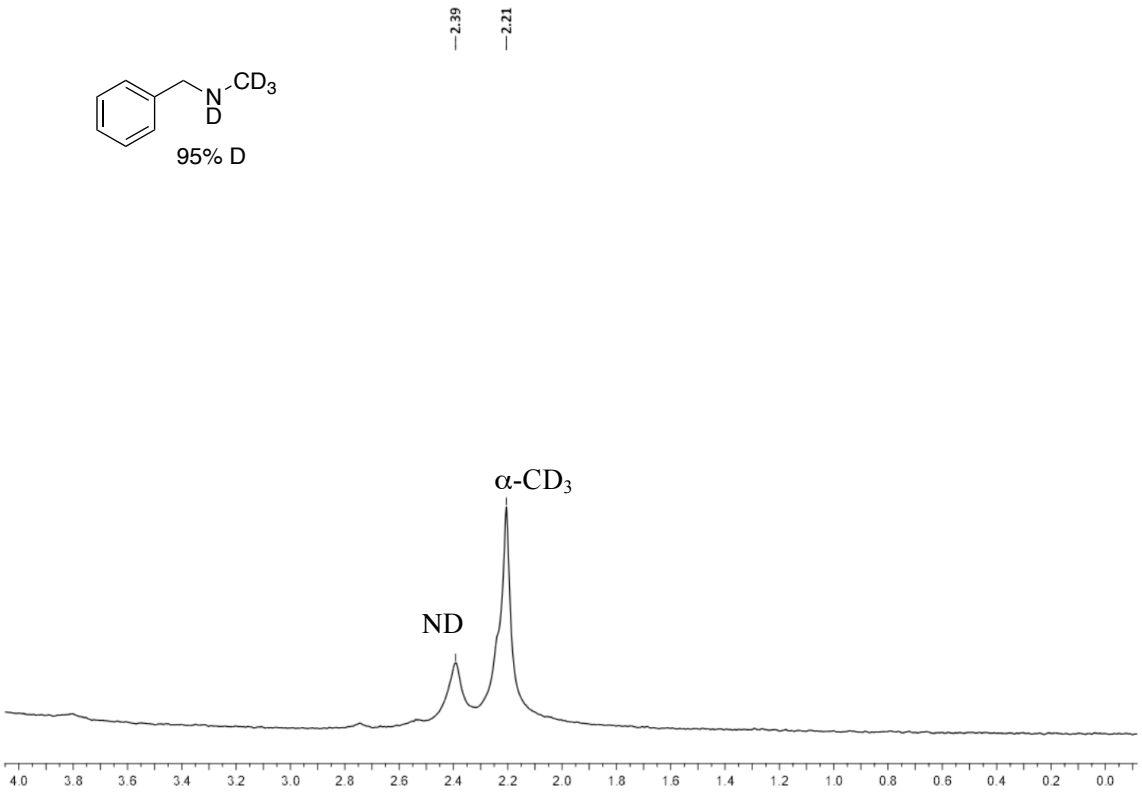
^{1}H NMR spectrum of N-methyl-1-phenylmethanamine-d4 (**4a**) (400 MHz, D_2O):



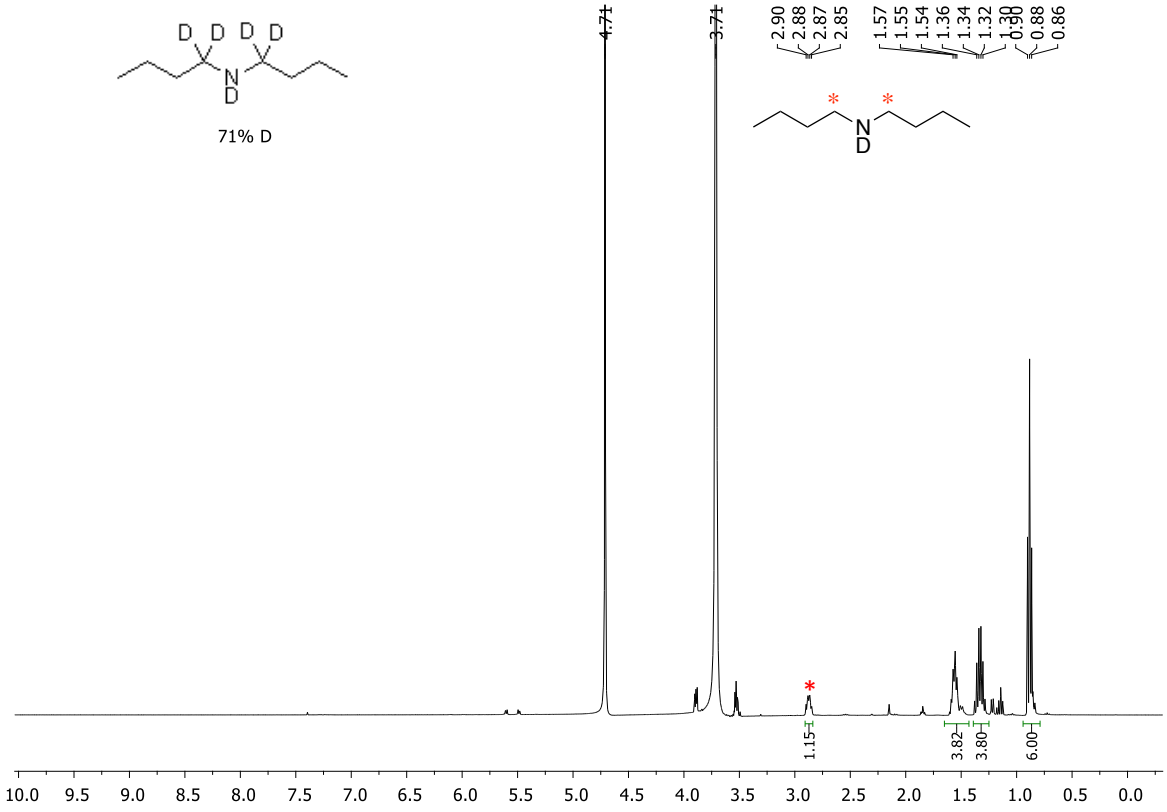
^{13}C NMR spectrum of N-methyl-1-phenylmethanamine-d4 (**4a**) (101 MHz, D_2O):



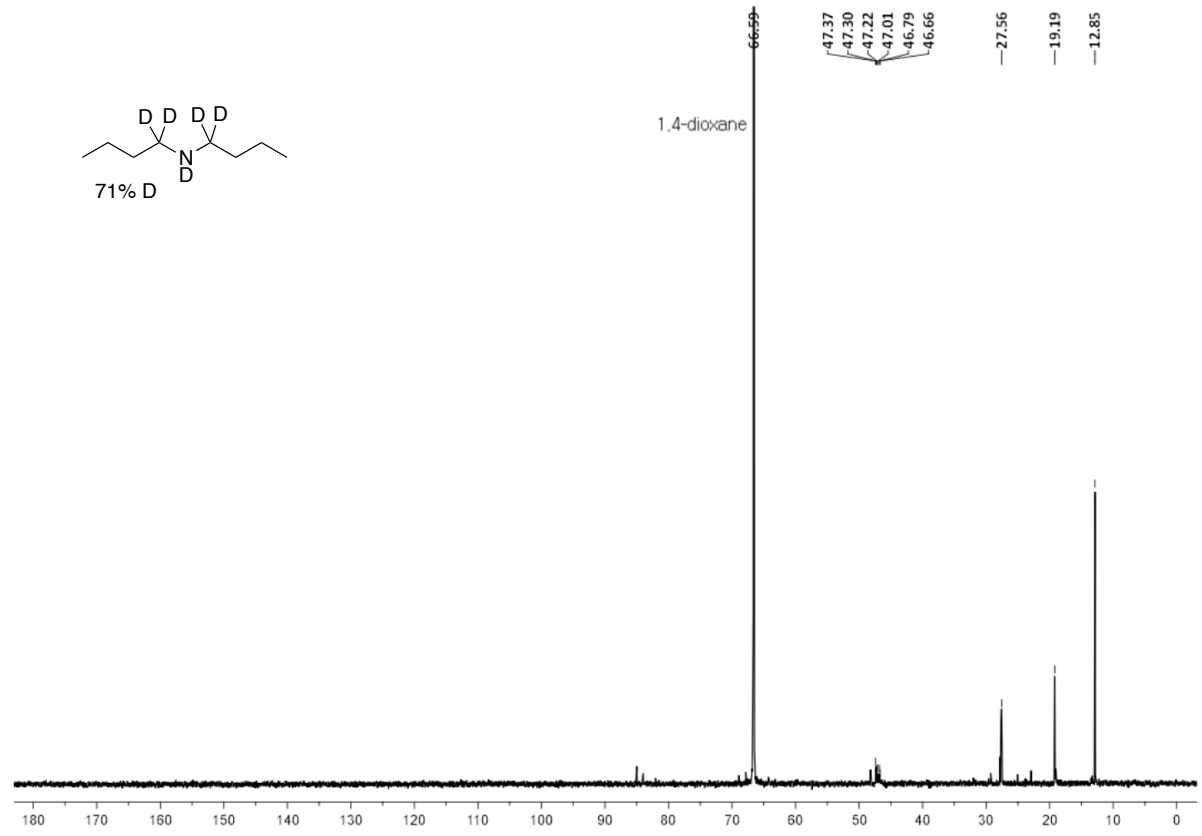
^{2}H NMR spectrum of N-methyl-1-phenylmethanamine-d4 (**4a**) (61 MHz, D_2O): D_2O peak is omitted for clarity.



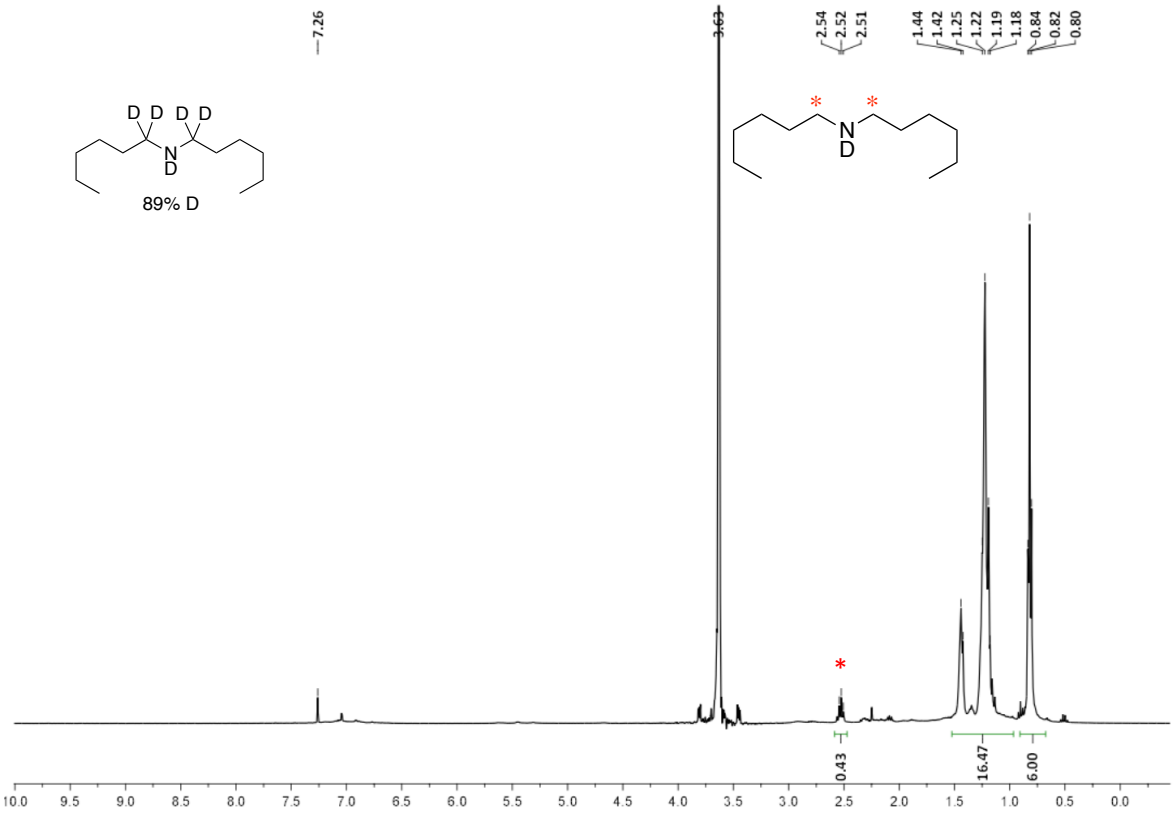
^{1}H NMR spectrum of dibutylamine-d5 (**4b**) (400 MHz, D_2O):



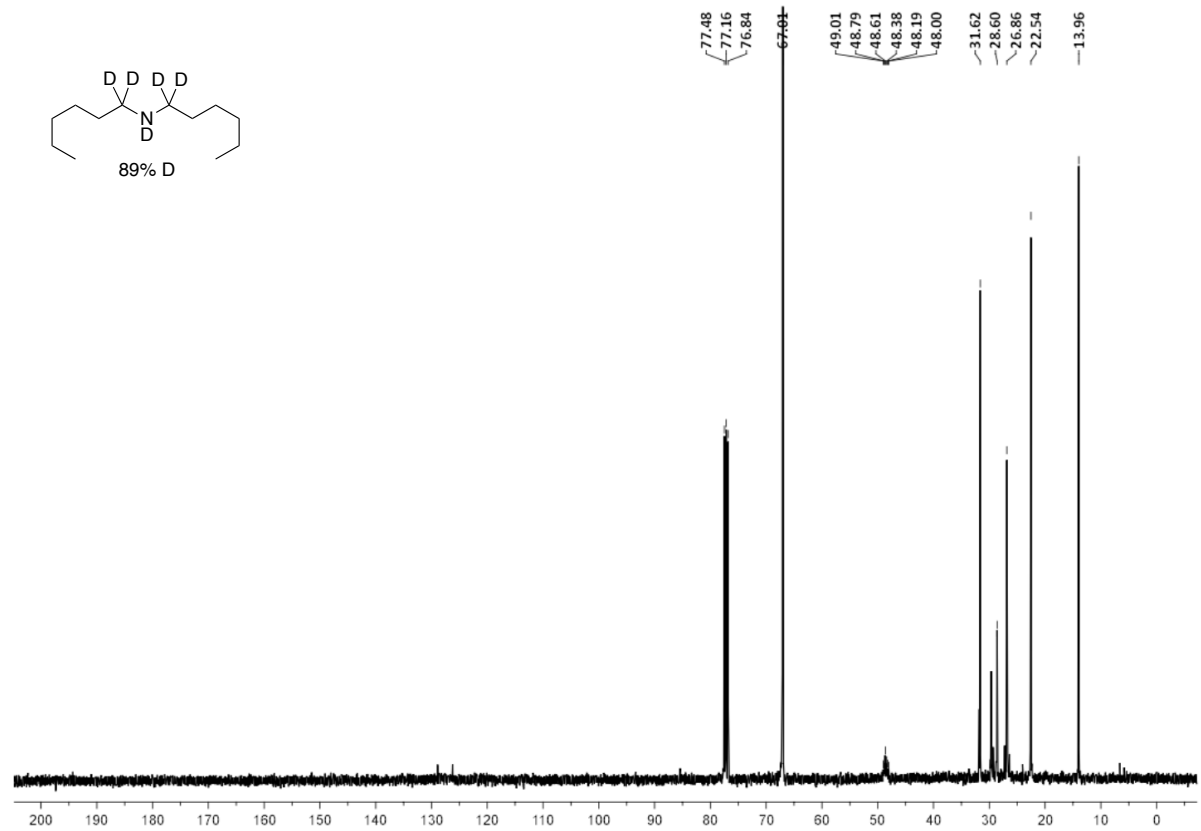
^{13}C NMR spectrum of dibutylamine-d5 (**4b**) (101 MHz, D_2O):



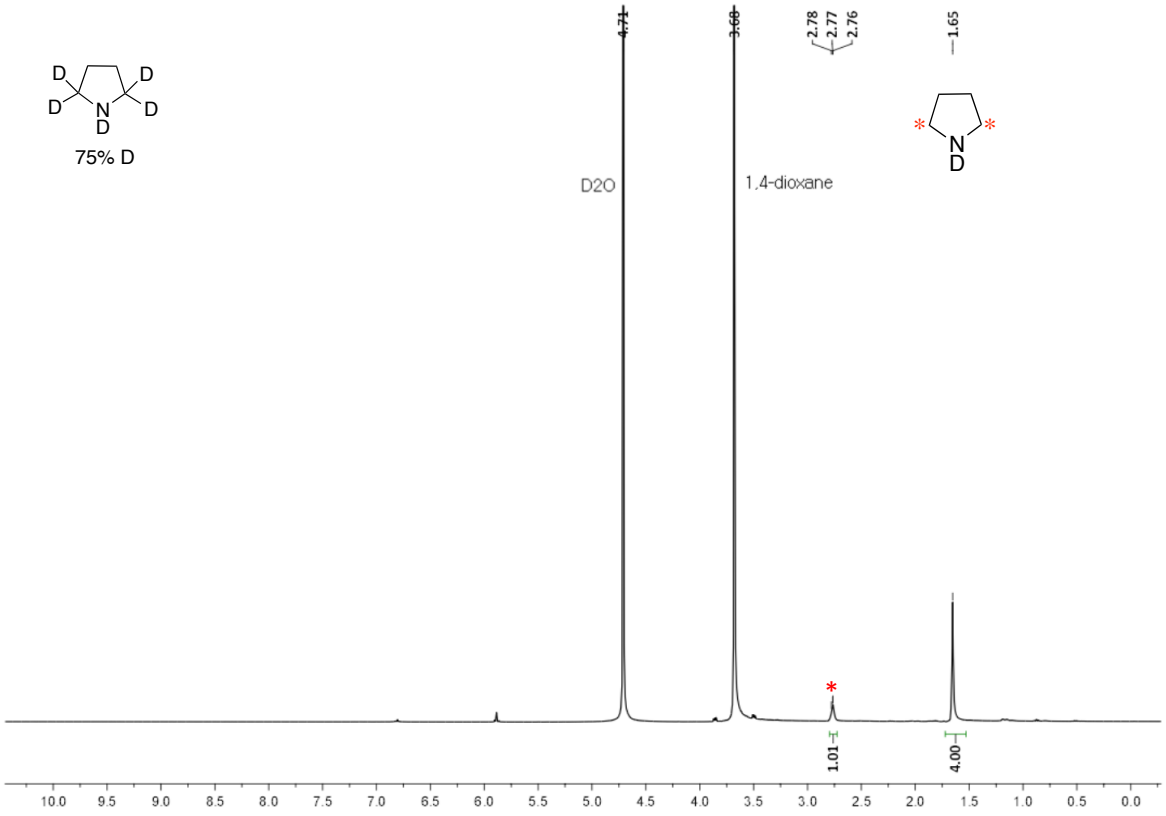
^{1}H NMR spectrum of dihexylamine-d5 (**4c**) (400 MHz, $CDCl_3$):



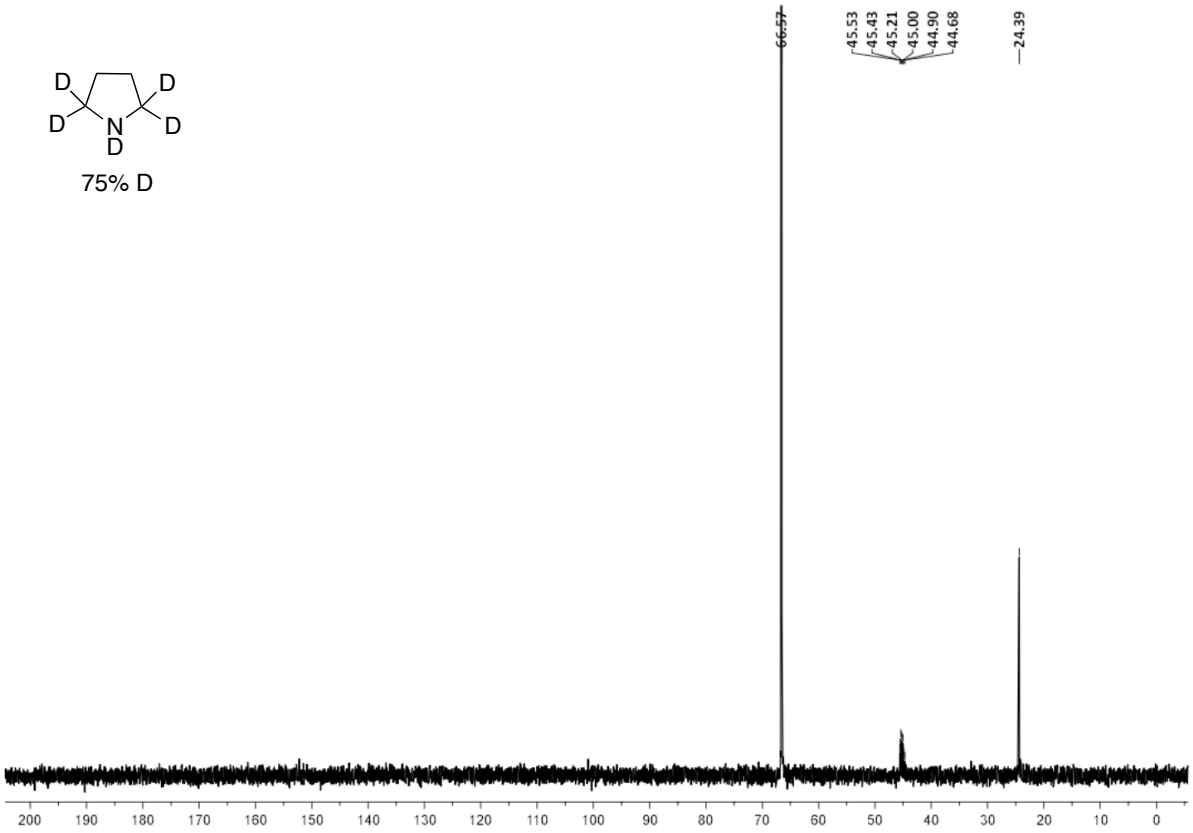
^{13}C NMR spectrum of dihexylamine-d5 (**4c**) (101 MHz, $CDCl_3$):



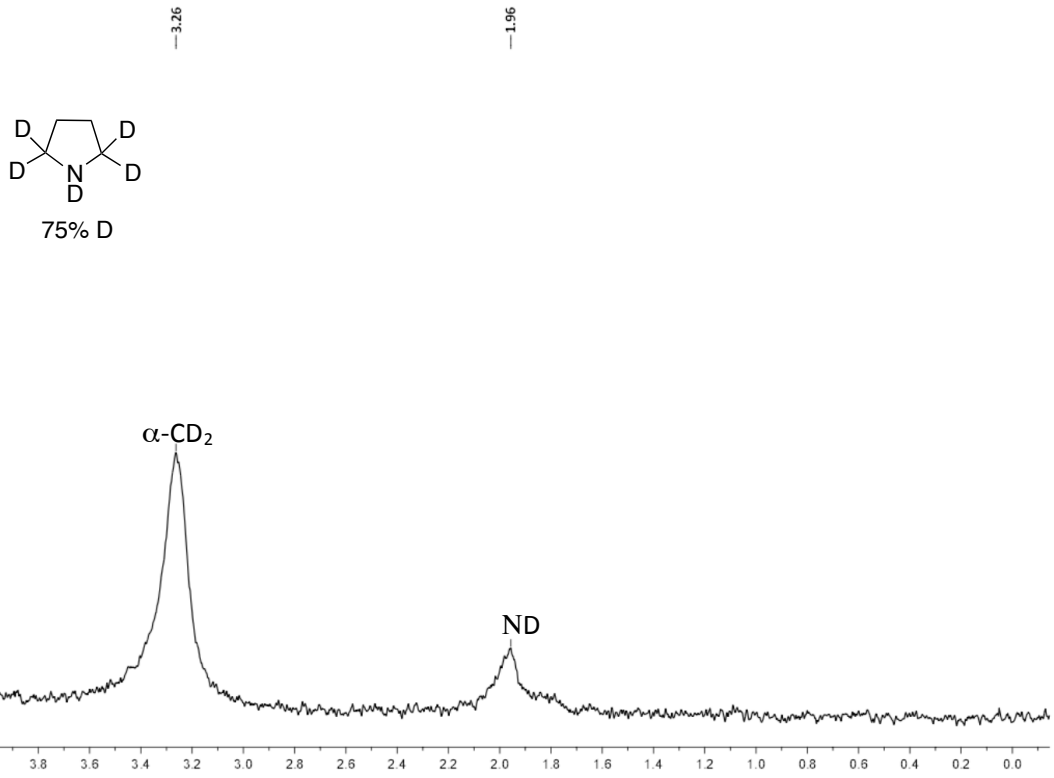
^{1}H NMR spectrum of pyrrolidine-d5 (**4d**) (400 MHz, D_2O):



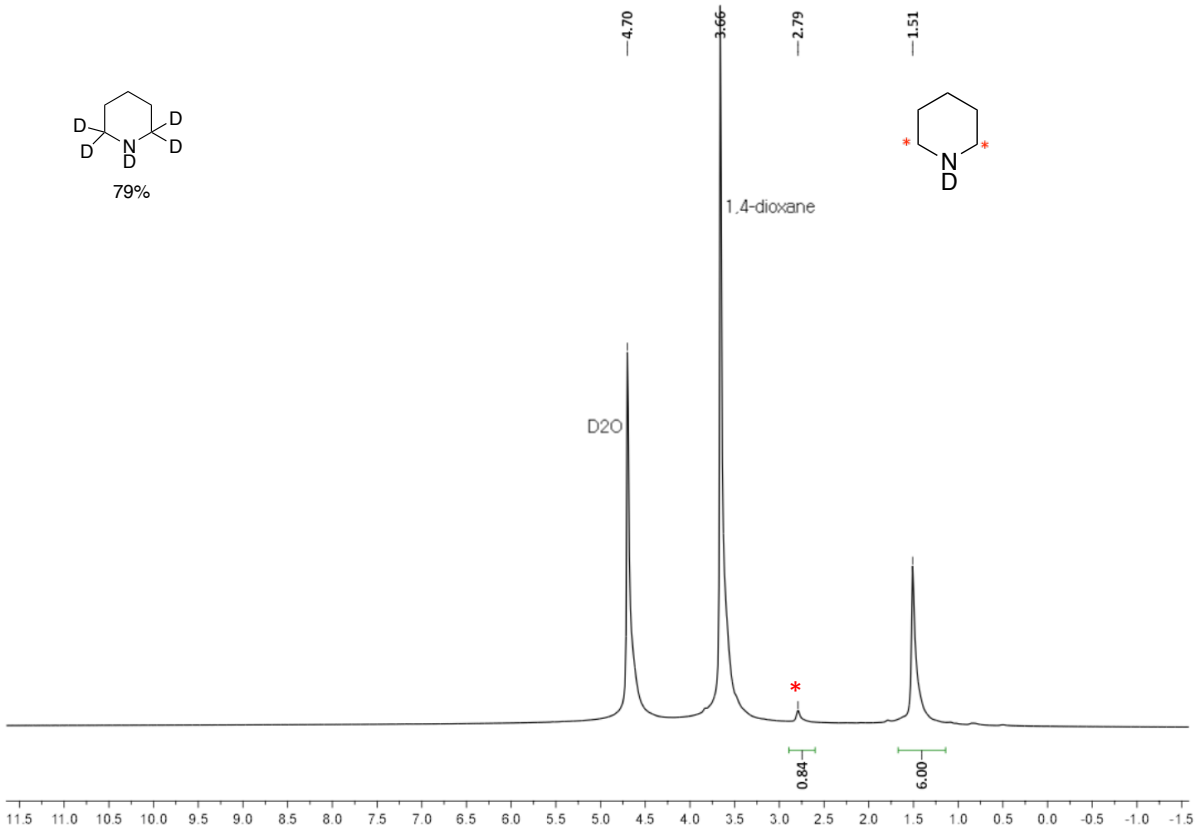
^{13}C NMR spectrum of pyrrolidine-d5 (**4d**) (101 MHz, D_2O):



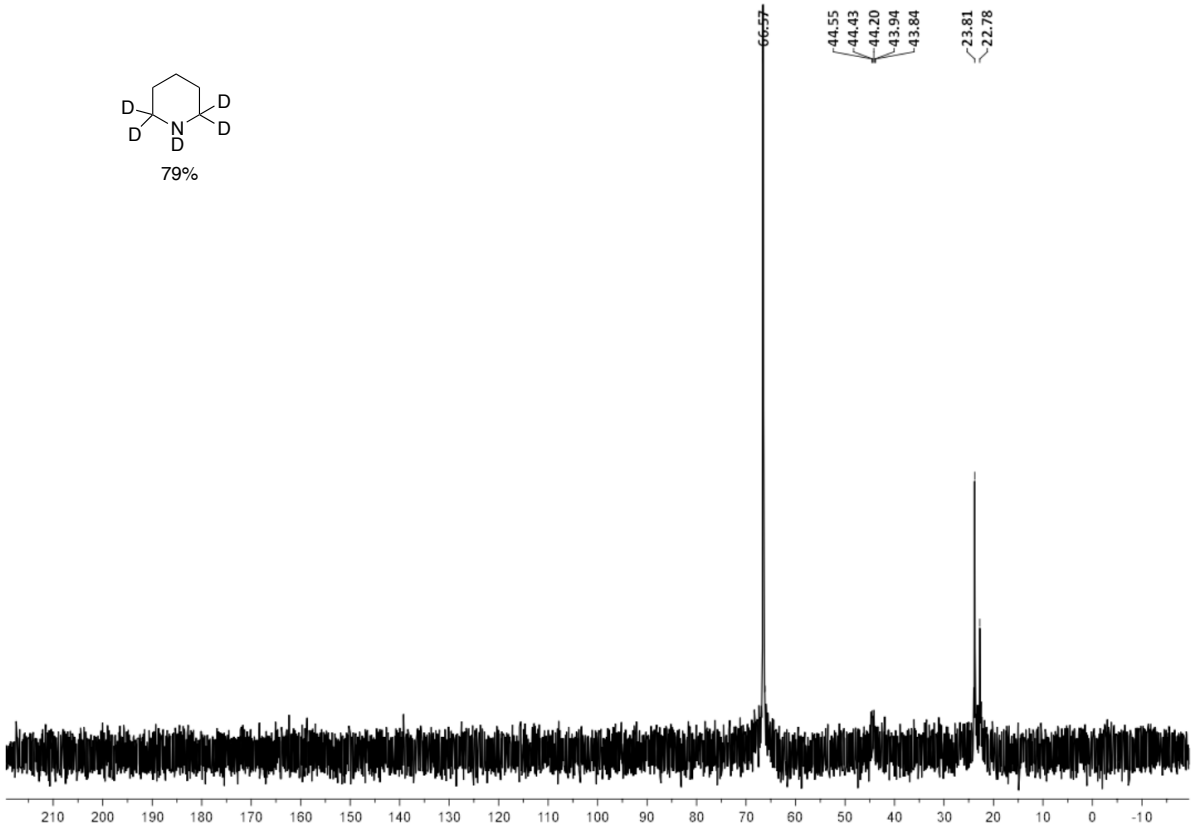
^{2}H NMR spectrum of pyrrolidine-d5 (**4d**) (61 MHz, D_2O): D_2O peak is omitted for clarity



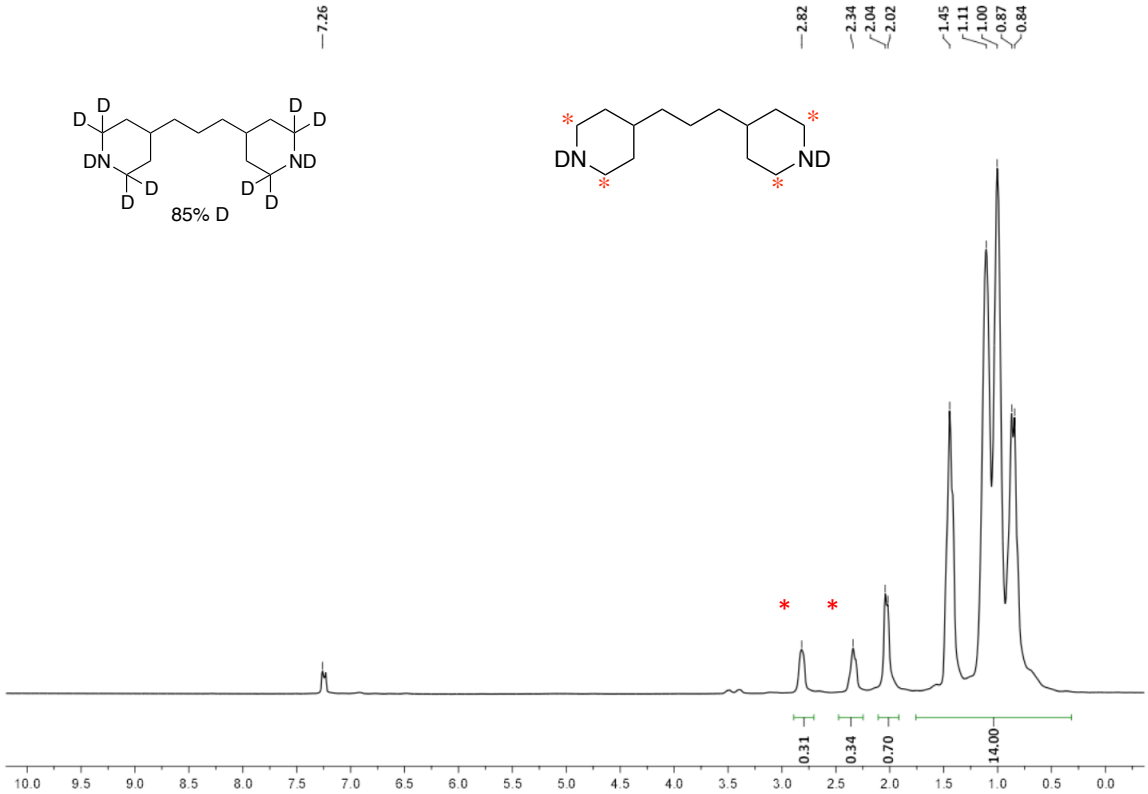
^{1}H NMR spectrum of piperidine-d5 (**4e**) (400 MHz, D_2O):



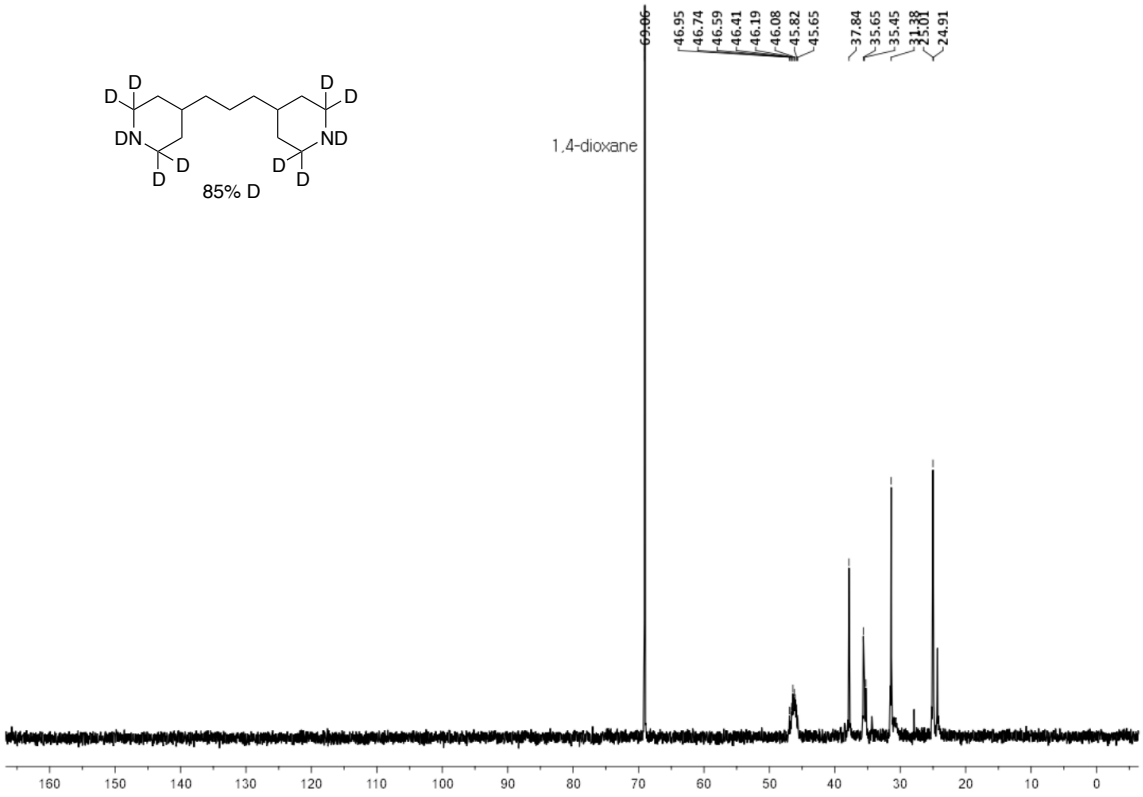
^{13}C NMR spectrum of piperidine-d5 (**4e**) (101 MHz, D_2O):



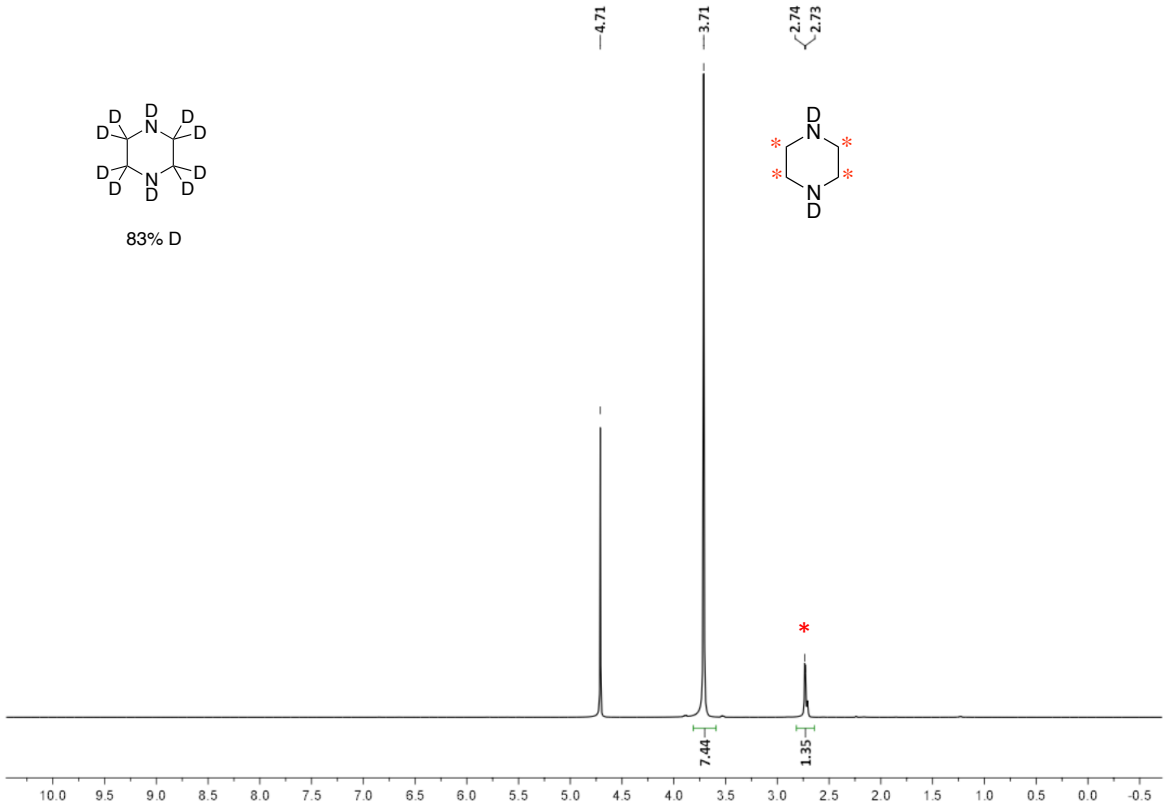
^{1}H NMR spectrum of 1,3-di(piperidin-4-yl)propane-d10 (**4f**) (400 MHz, $CDCl_3$):



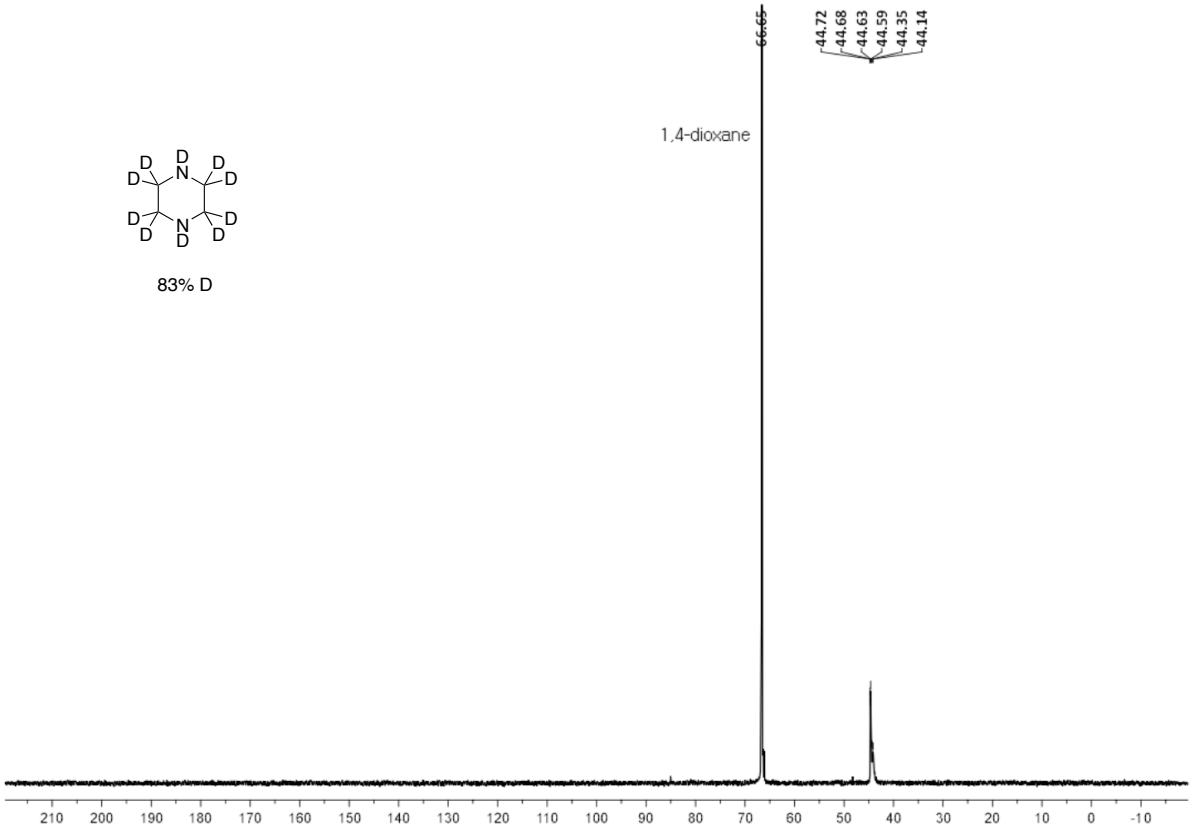
^{13}C NMR spectrum of 1,3-di(piperidin-4-yl)propane-d-10 (**4f**) (101 MHz, D_2O):



^{1}H NMR spectrum of piperazine-d10 (**4g**) (400 MHz, D_2O): (80 µl of 1,4-dioxane used as internal standard)

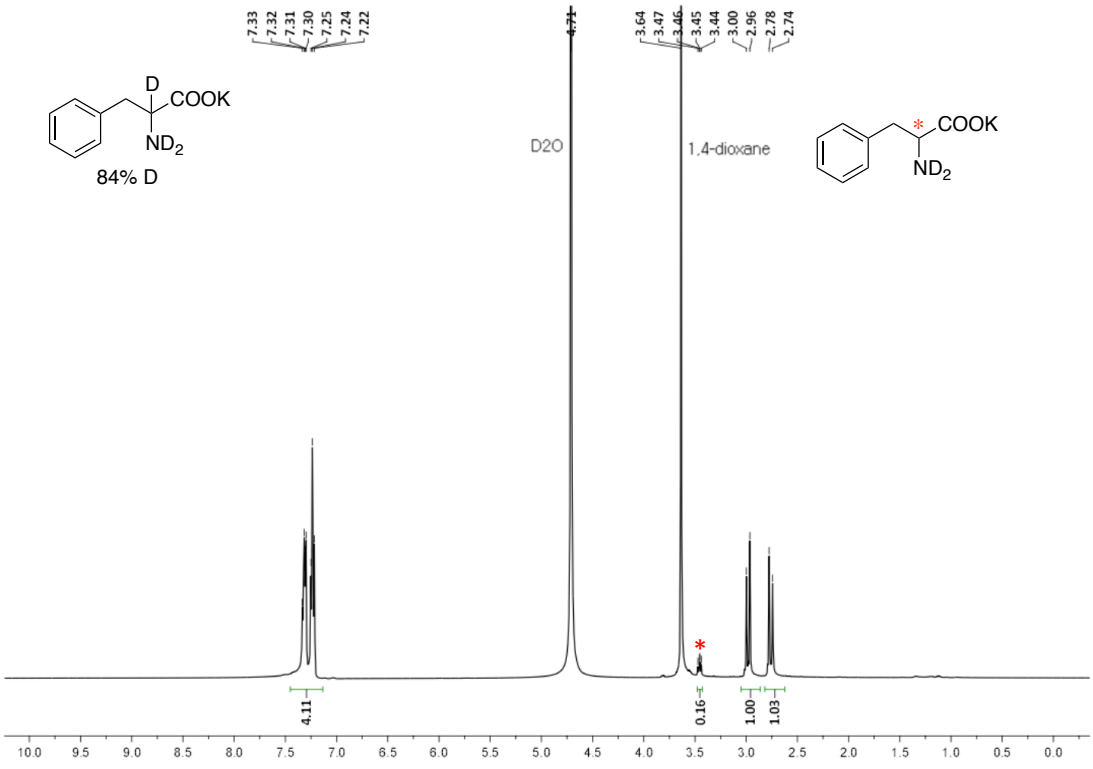


^{13}C NMR spectrum of piperazine-d10 (**4g**) (101 MHz, D_2O):

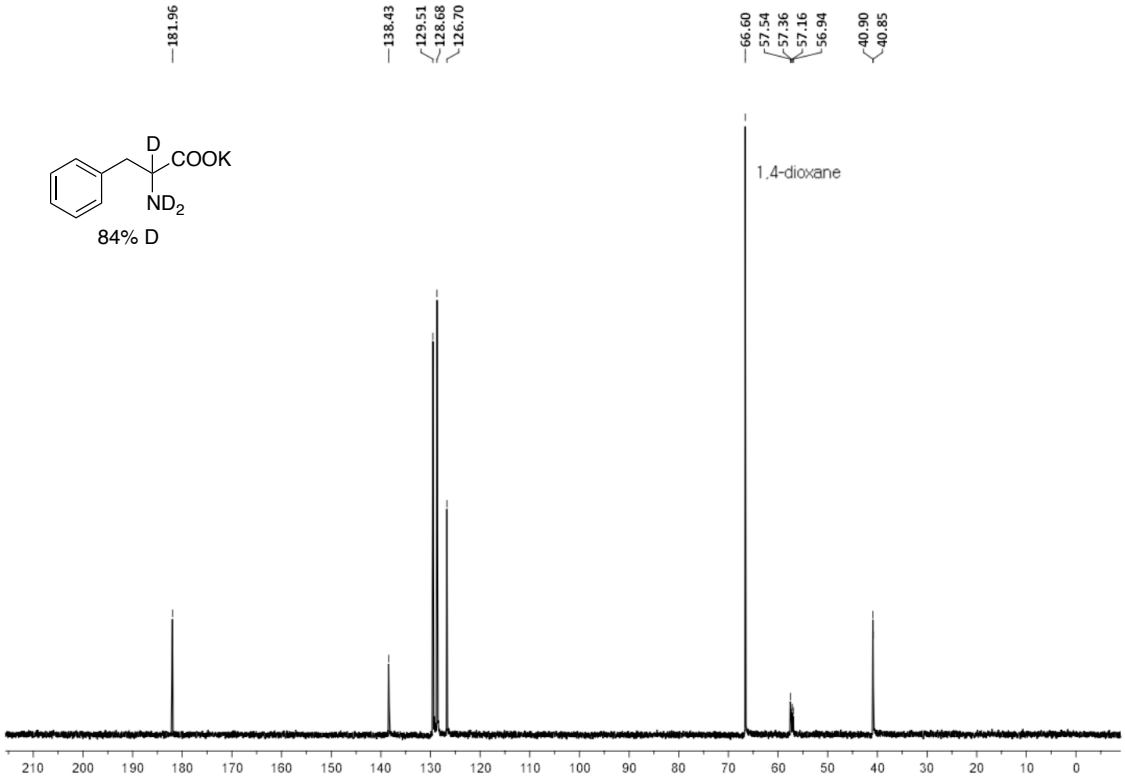


NMR spectra of deuterated amino acids:

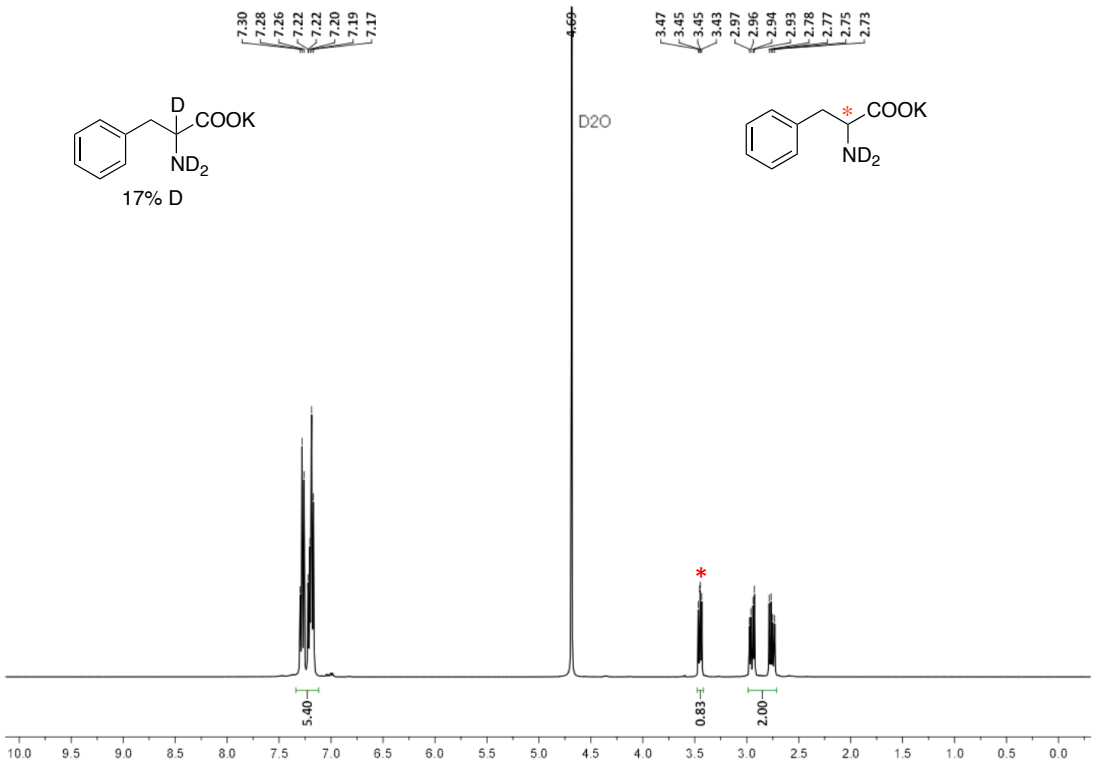
^{1}H NMR spectrum for potassium salt of L-phenylalanine-d3 (**5a**) (400 MHz, D_2O):



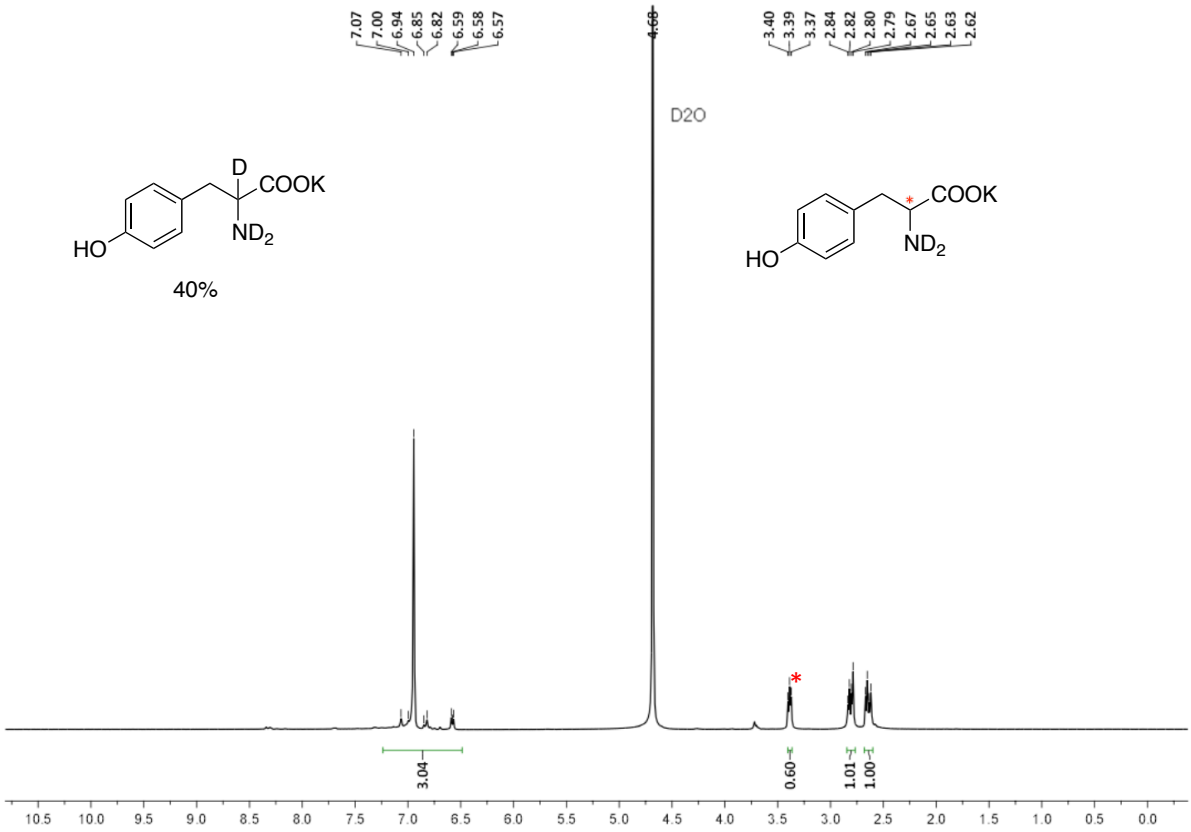
^{13}C NMR spectrum for potassium salt of L-phenylalanine-d3 (**5a**) (101 MHz, D_2O):



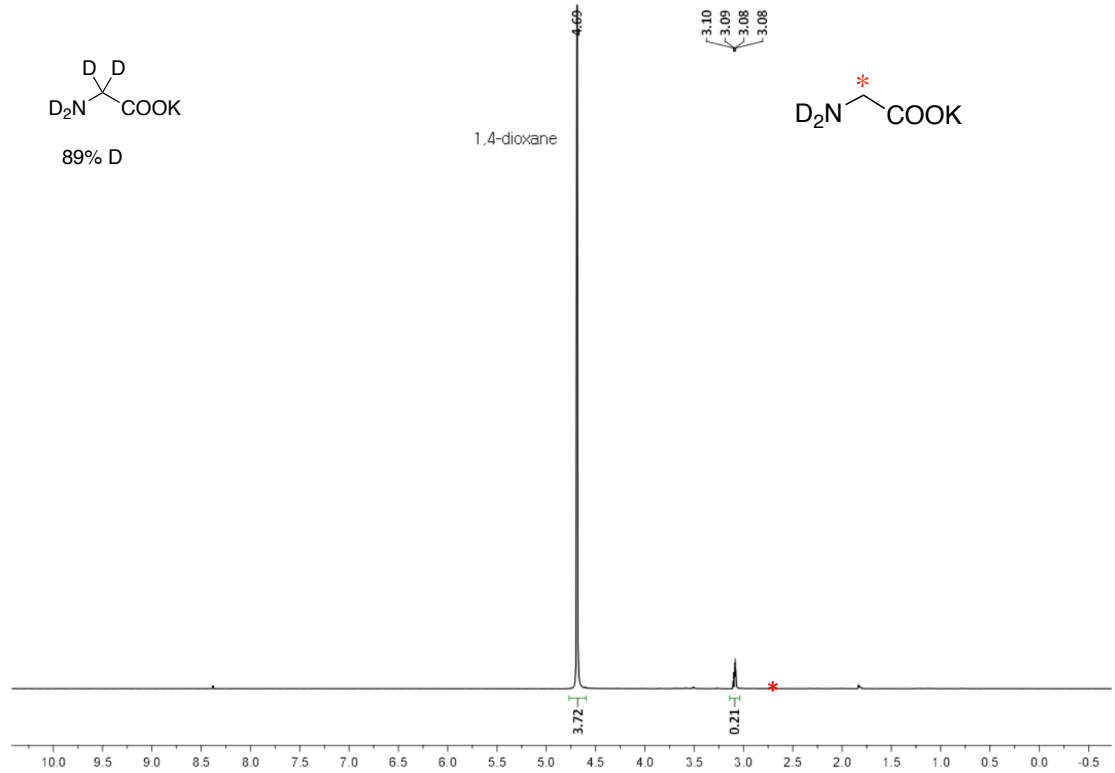
^{1}H NMR spectrum for the controlled experiment with potassium salt of L-phenylalanine-d3 (**5a**) (400 MHz, D_2O):



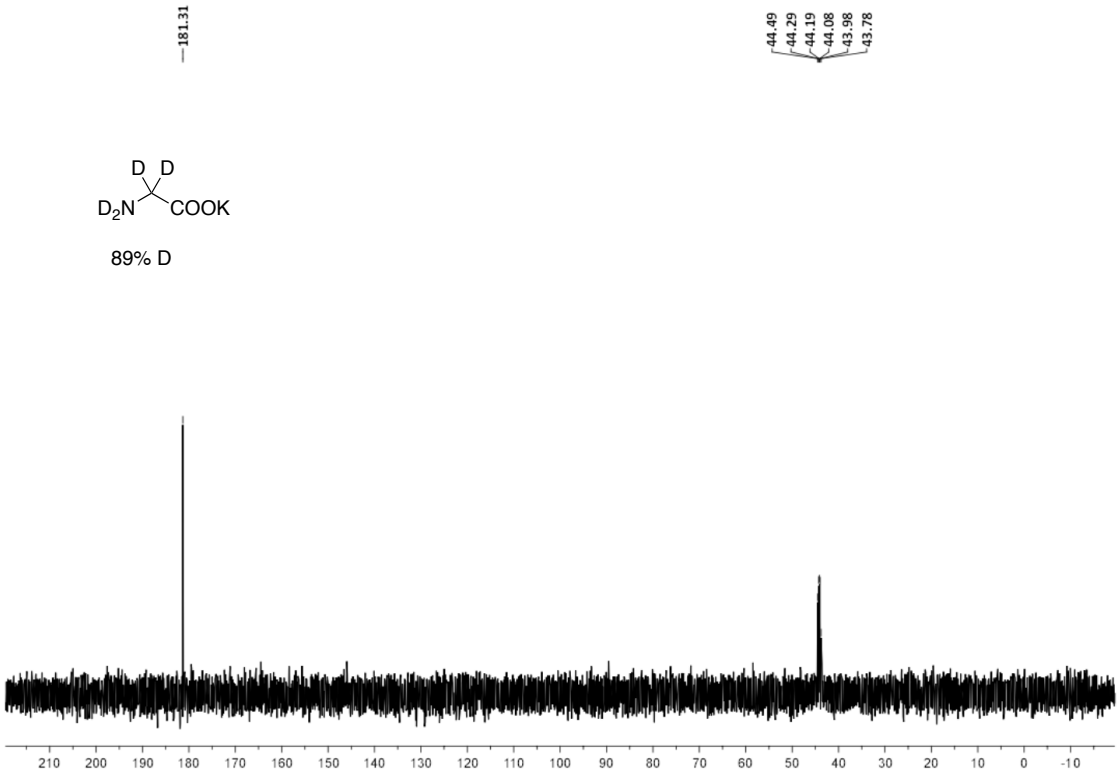
^{1}H NMR spectrum for potassium salt of L-tyrosine-d3 (**5b**) (400 MHz, D_2O):



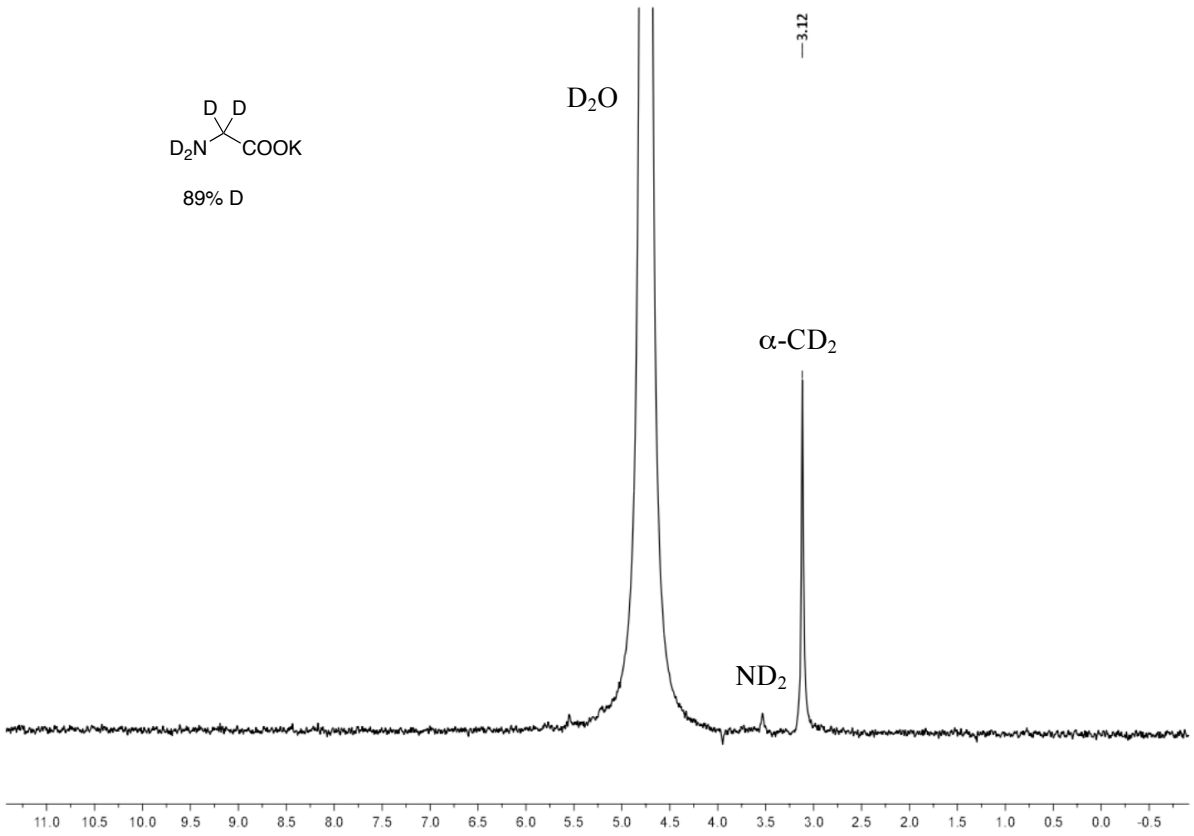
^{1}H NMR spectrum for potassium salt of glycine-d4 (**5c**) (400 MHz, D_2O): (40 µl of 1,4-dioxane used as internal standard)



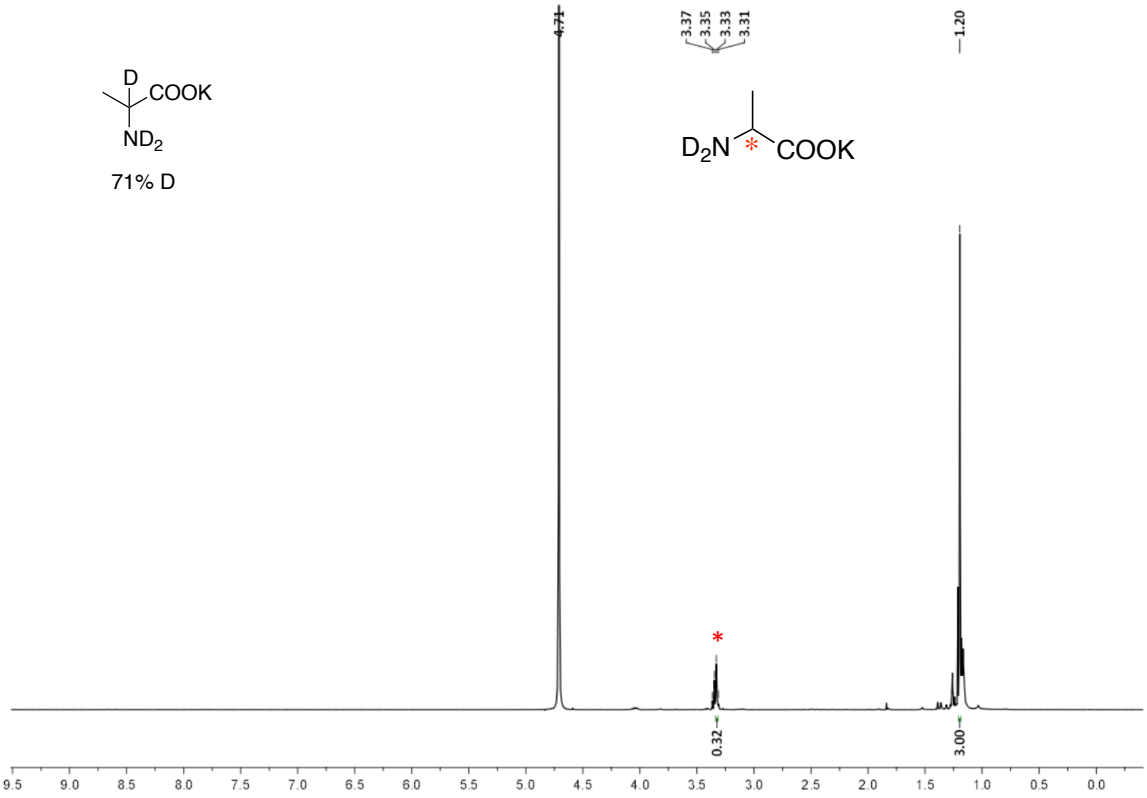
^{13}C NMR spectrum for potassium salt of glycine-d4 (**5c**) (101 MHz, D_2O):



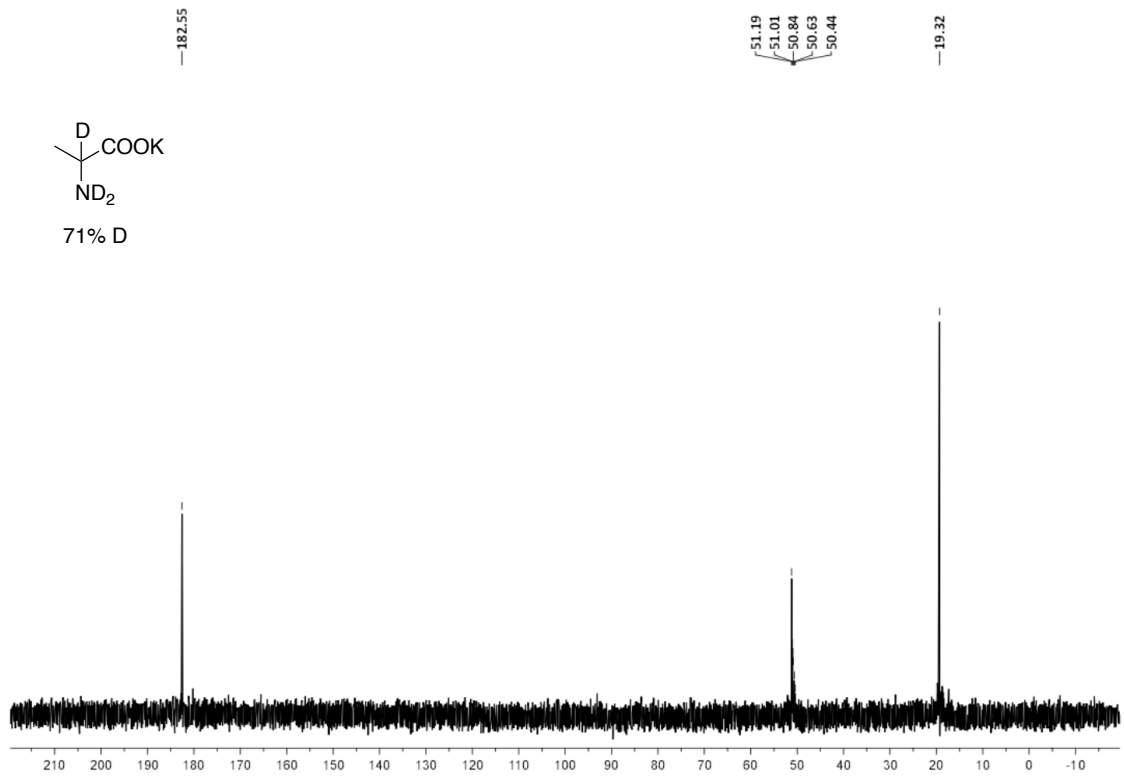
^{2}H NMR spectrum for potassium salt of glycine-d4 (**5c**) (61 MHz, D_2O):



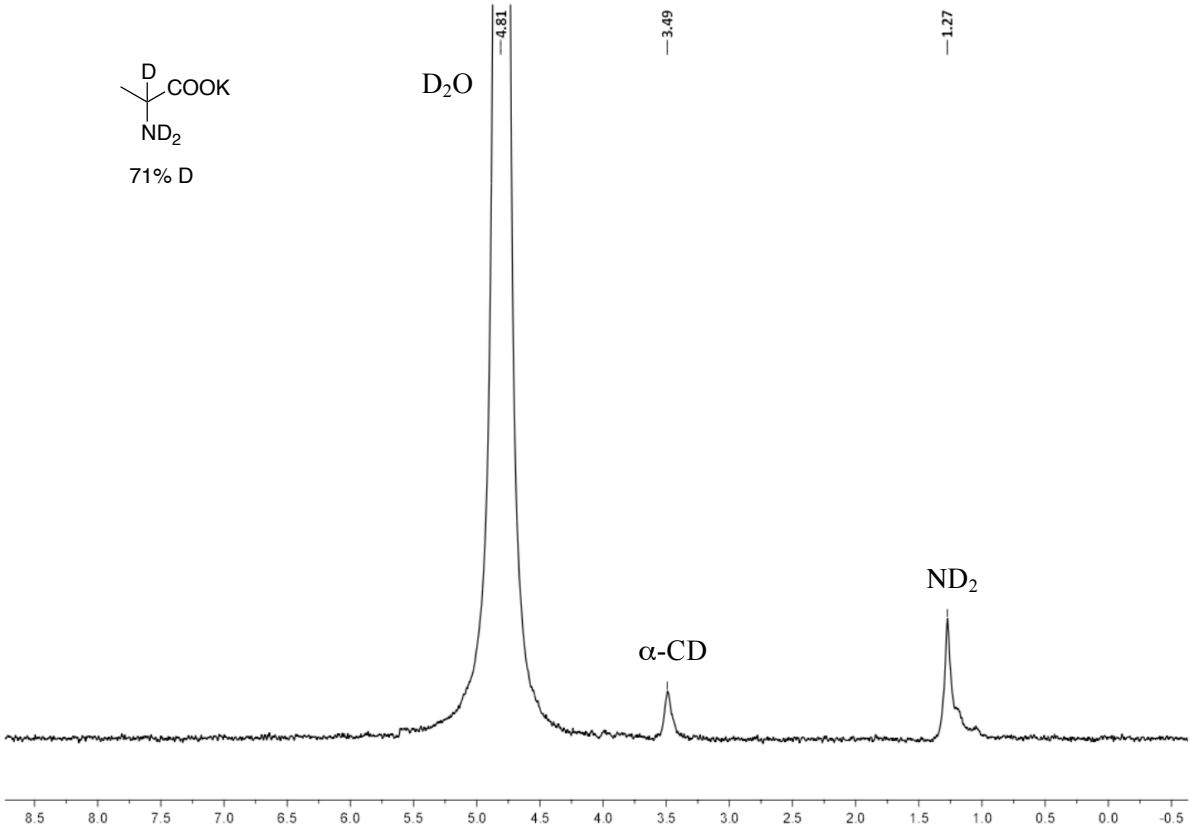
^{1}H NMR spectrum for potassium salt of alanine-d3 (**5d**) (400 MHz, D_2O):



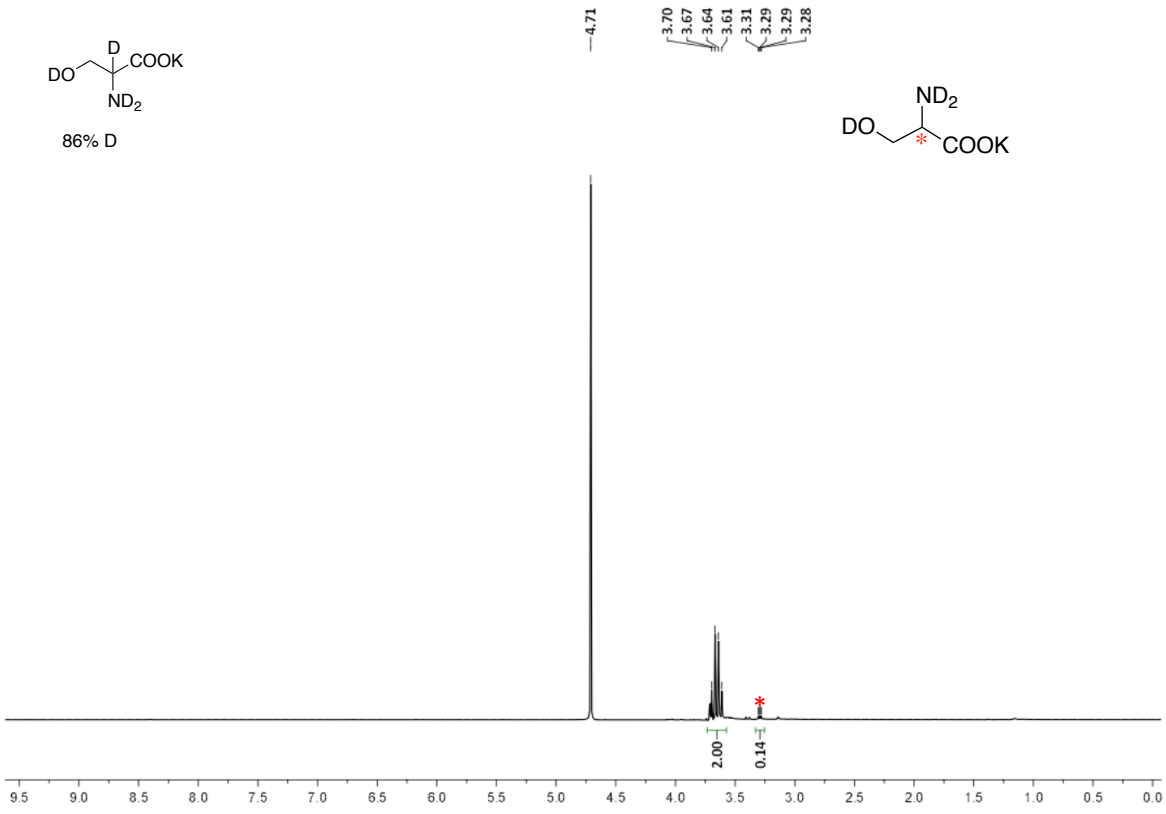
^{13}C NMR spectrum for potassium salt of alanine-d3 (**5d**) (101 MHz, D_2O):



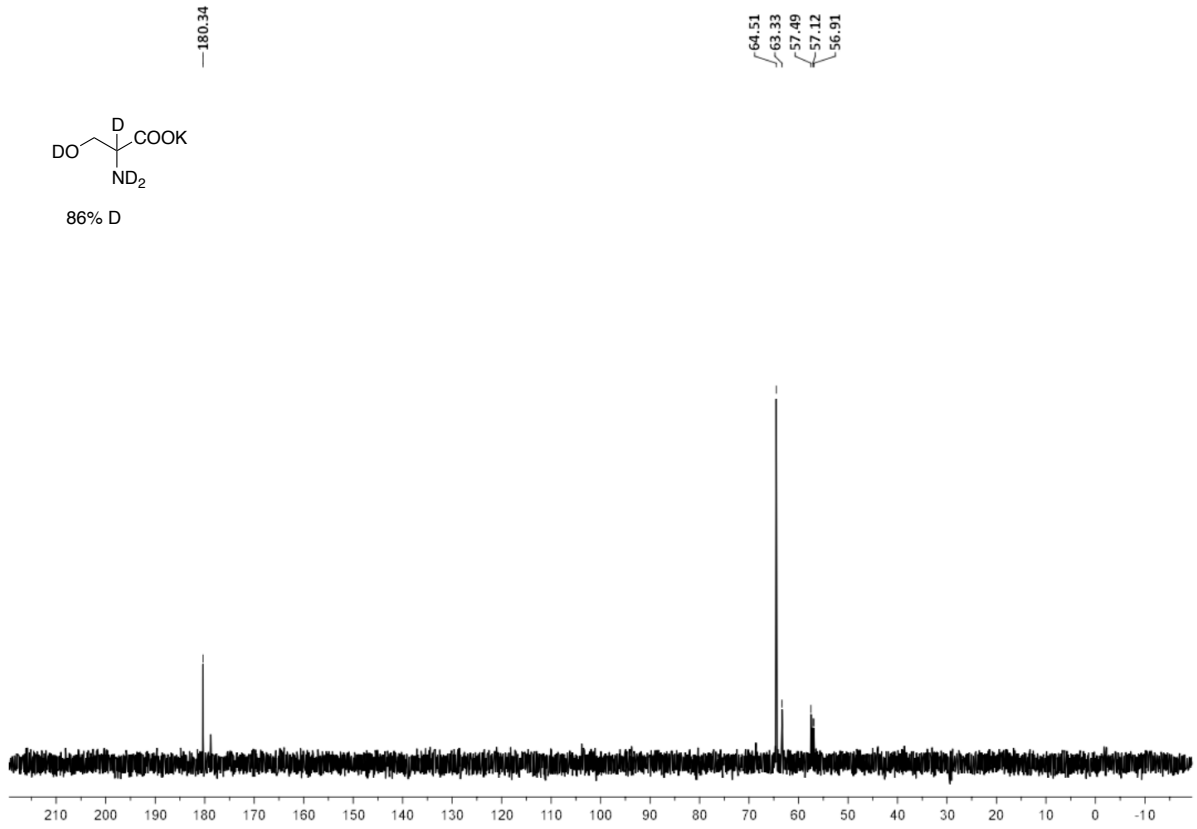
^{2}H NMR spectrum for potassium salt of alanine-d3 (**5d**) (61 MHz, D_2O):



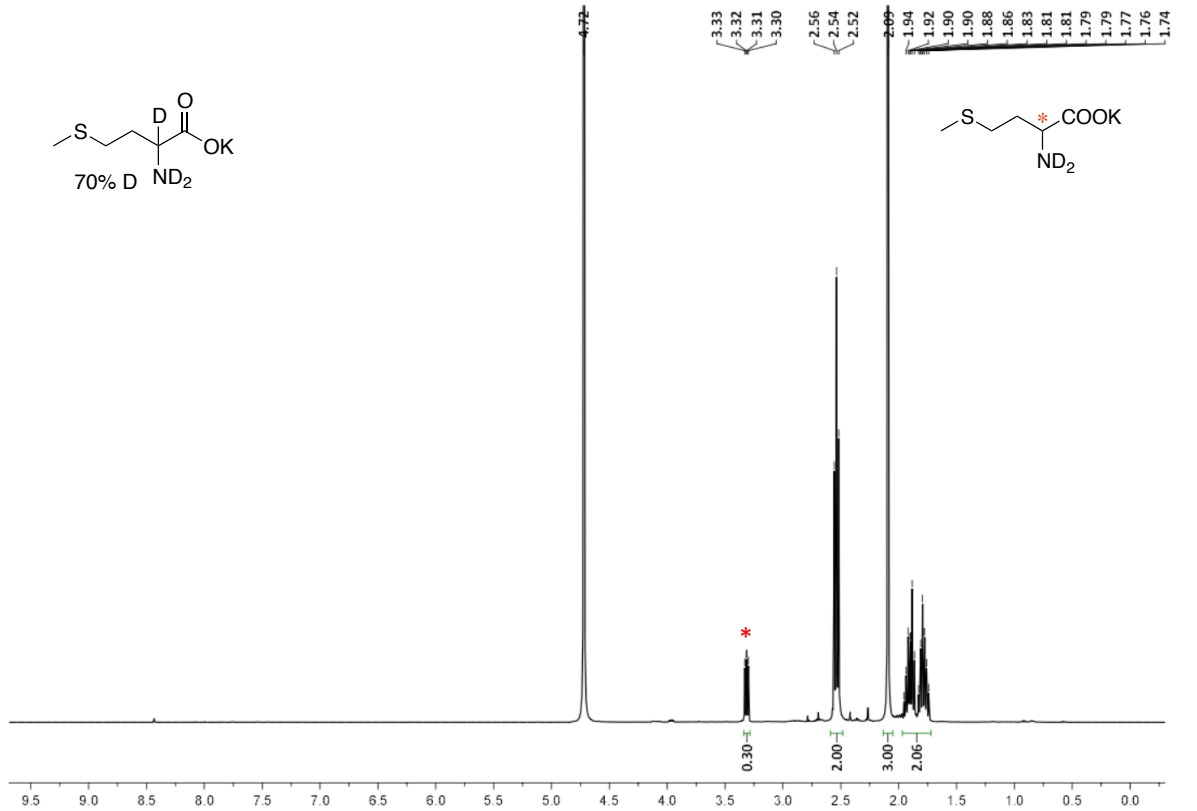
^{1}H NMR spectrum for potassium salt of serine-d4 (**5e**) (400 MHz, D_2O):



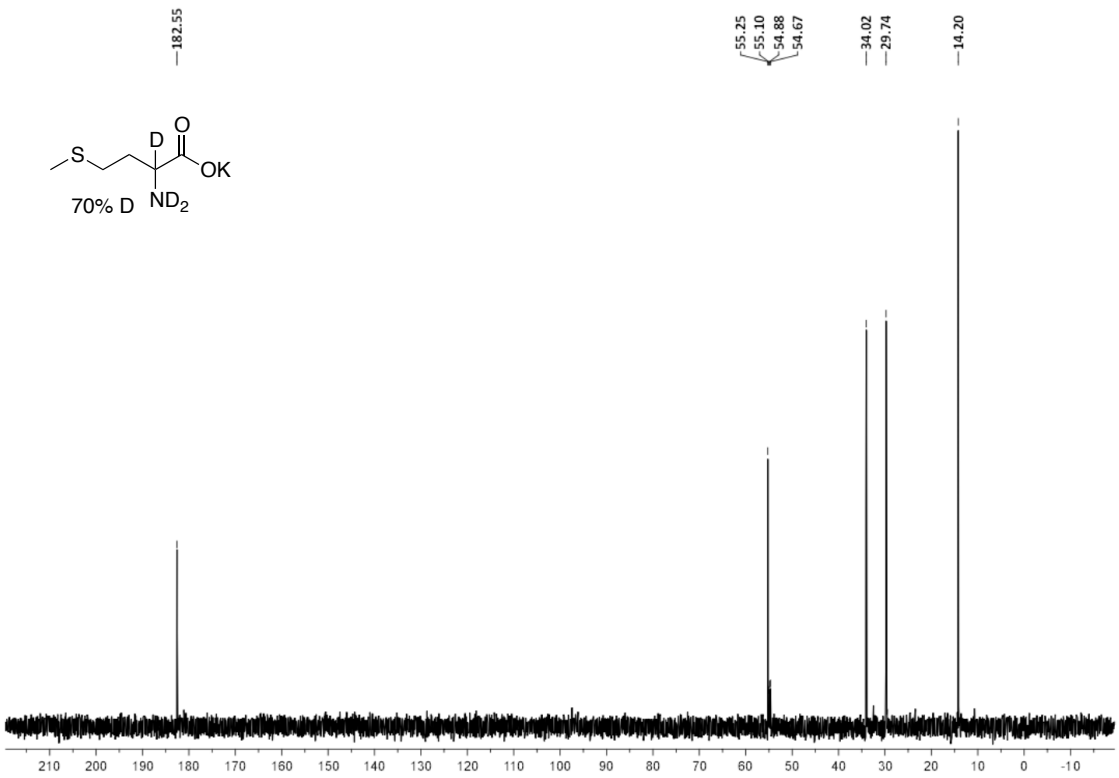
^{13}C NMR spectrum for potassium salt of serine-d4 (**5e**) (101 MHz, D_2O):



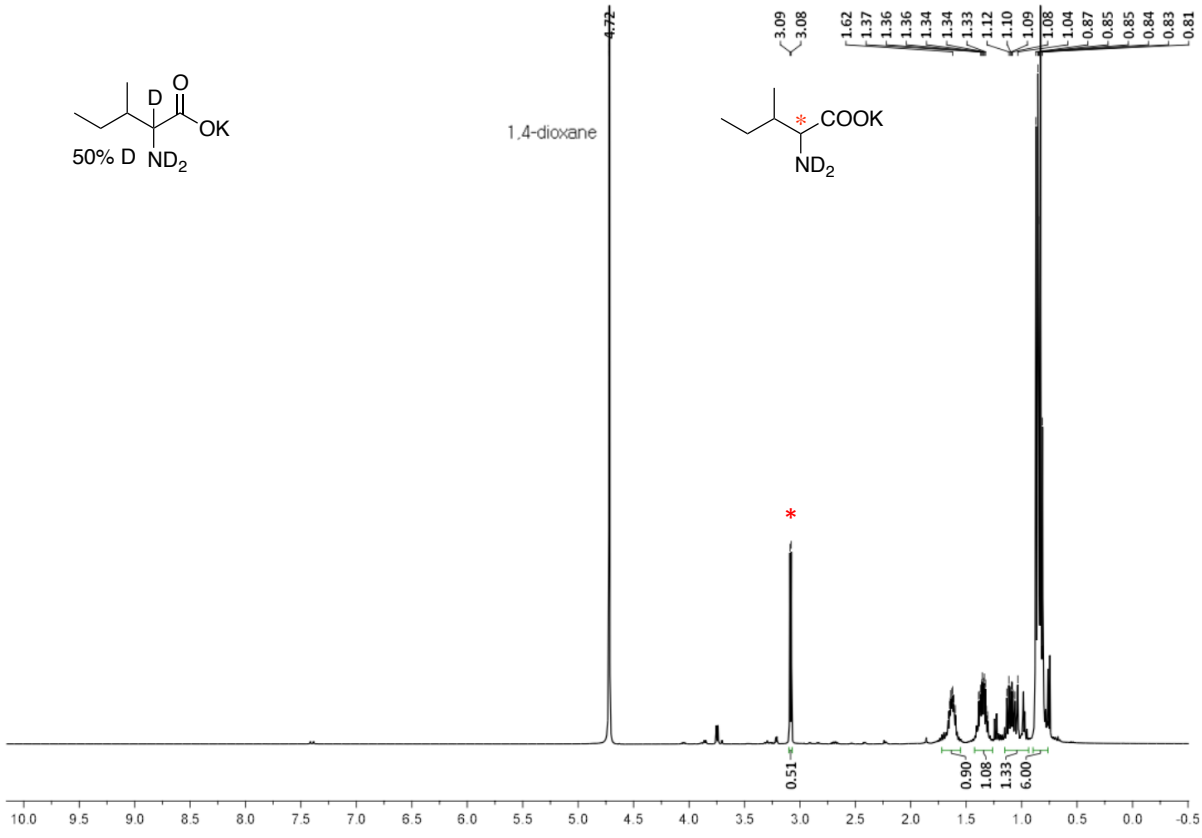
^{1}H NMR spectrum for potassium salt of methionine-d3 (**5f**) (400 MHz, D_2O):



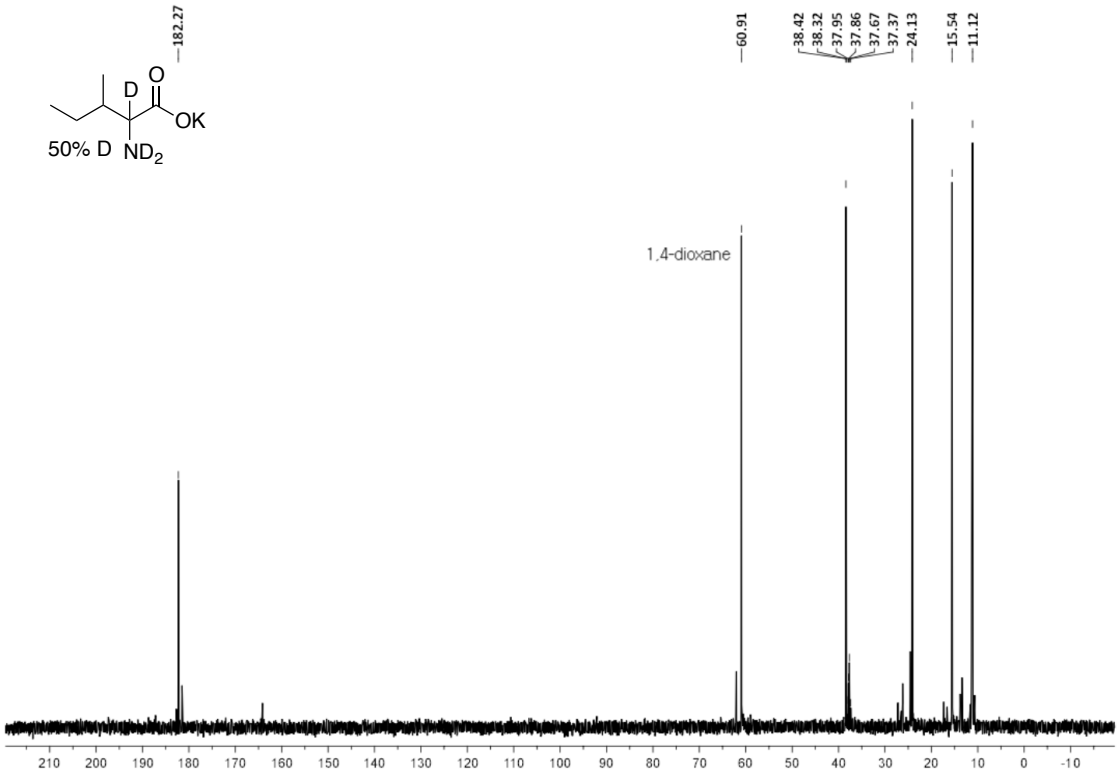
^{13}C NMR spectrum for potassium salt of methionine-d3 (**5f**) (101 MHz, D_2O):



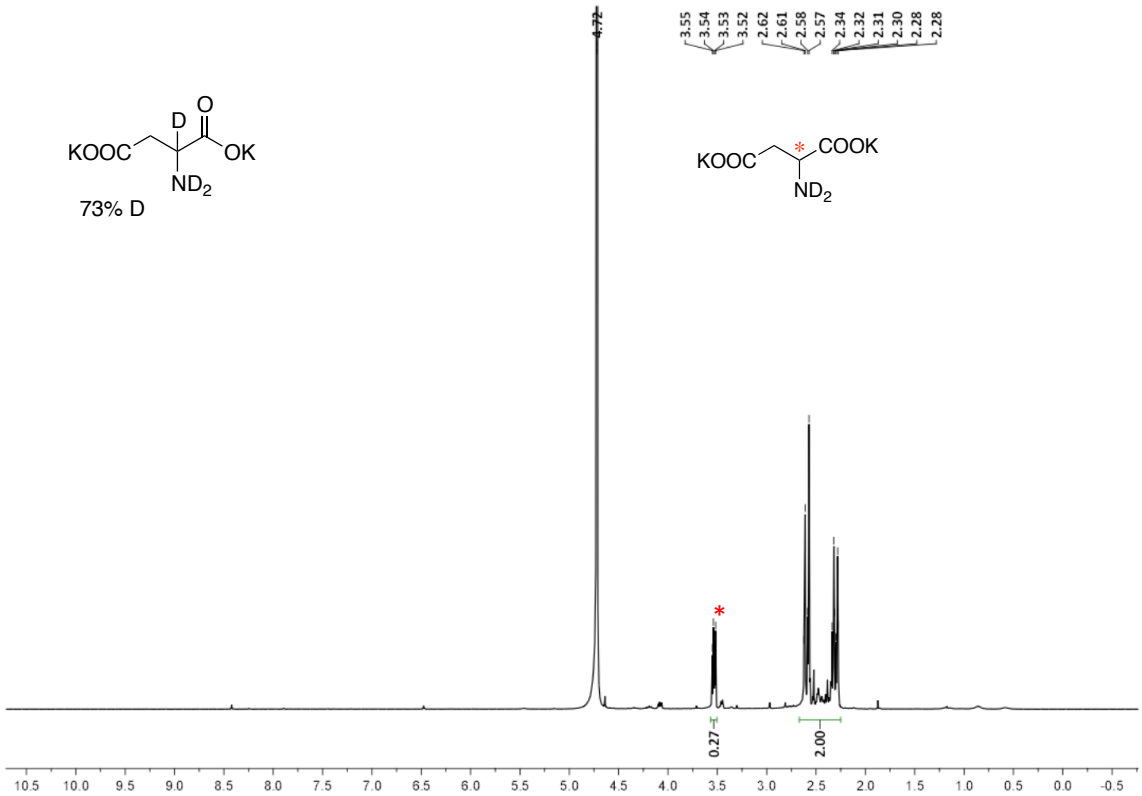
^{1}H NMR spectrum for potassium salt of isoleucine-d3 (**5g**) (400 MHz, D_2O):



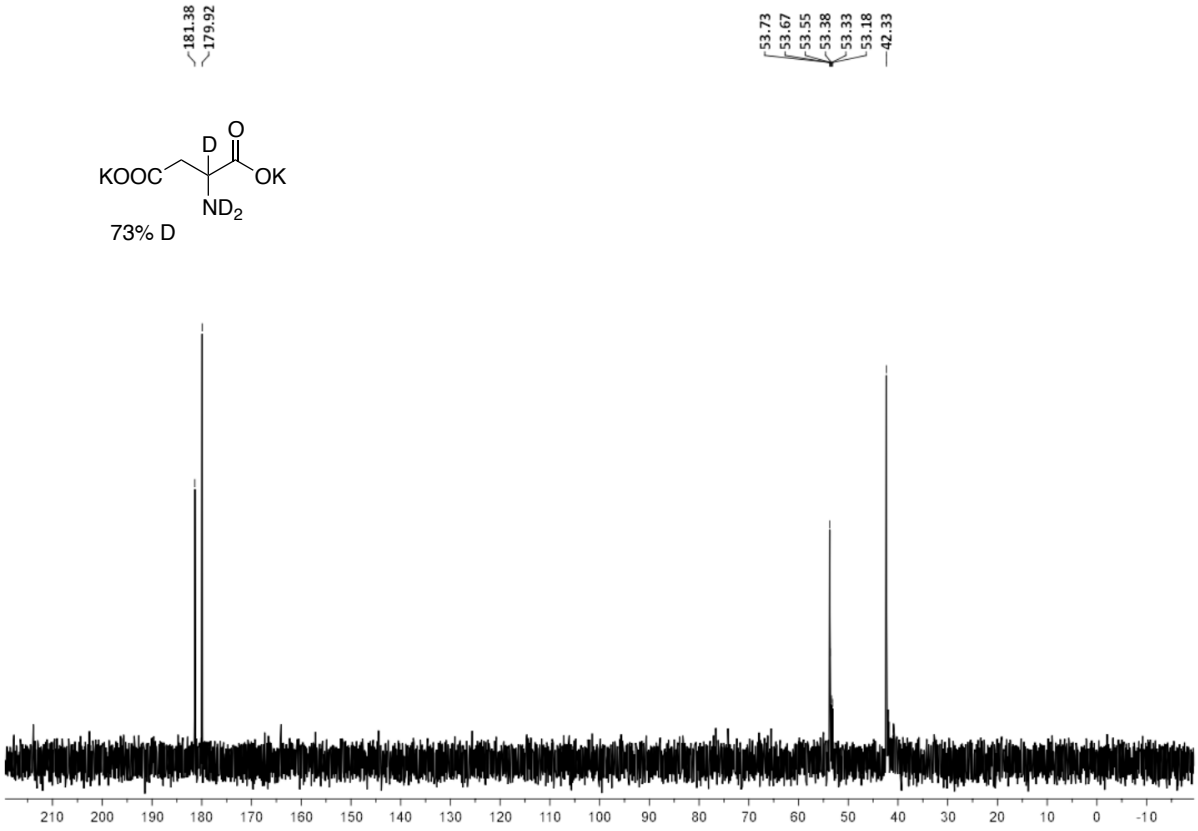
^{13}C NMR spectrum for potassium salt of isoleucine-d3 (**5g**) (101 MHz, D_2O):



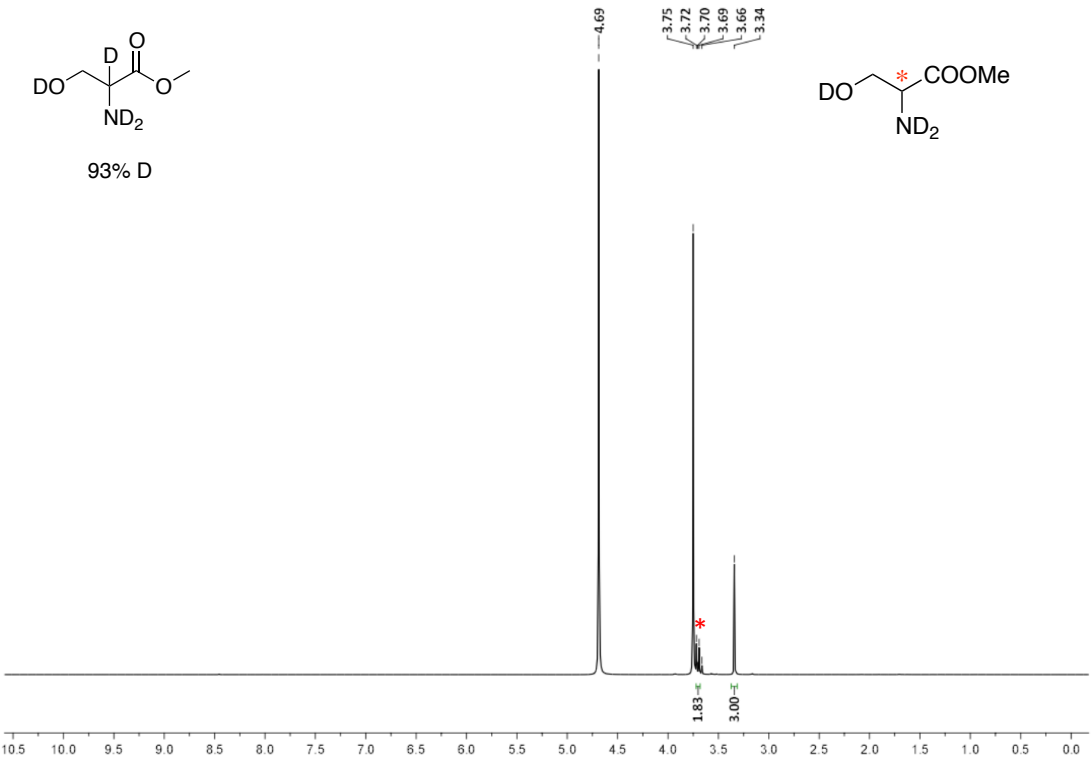
^{1}H NMR spectrum for potassium salt of aspartic acid-d3 (**5h**) (400 MHz, D_2O):



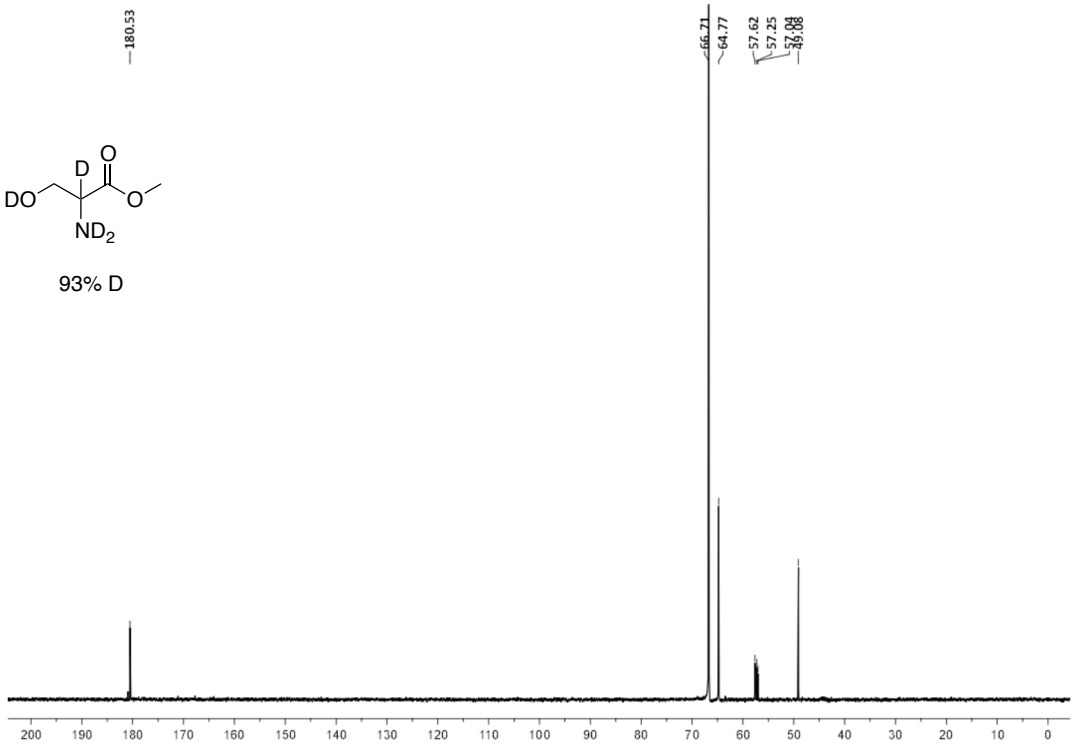
^{13}C NMR spectrum for potassium salt of aspartic acid-d3 (**5h**) (101 MHz, D_2O):



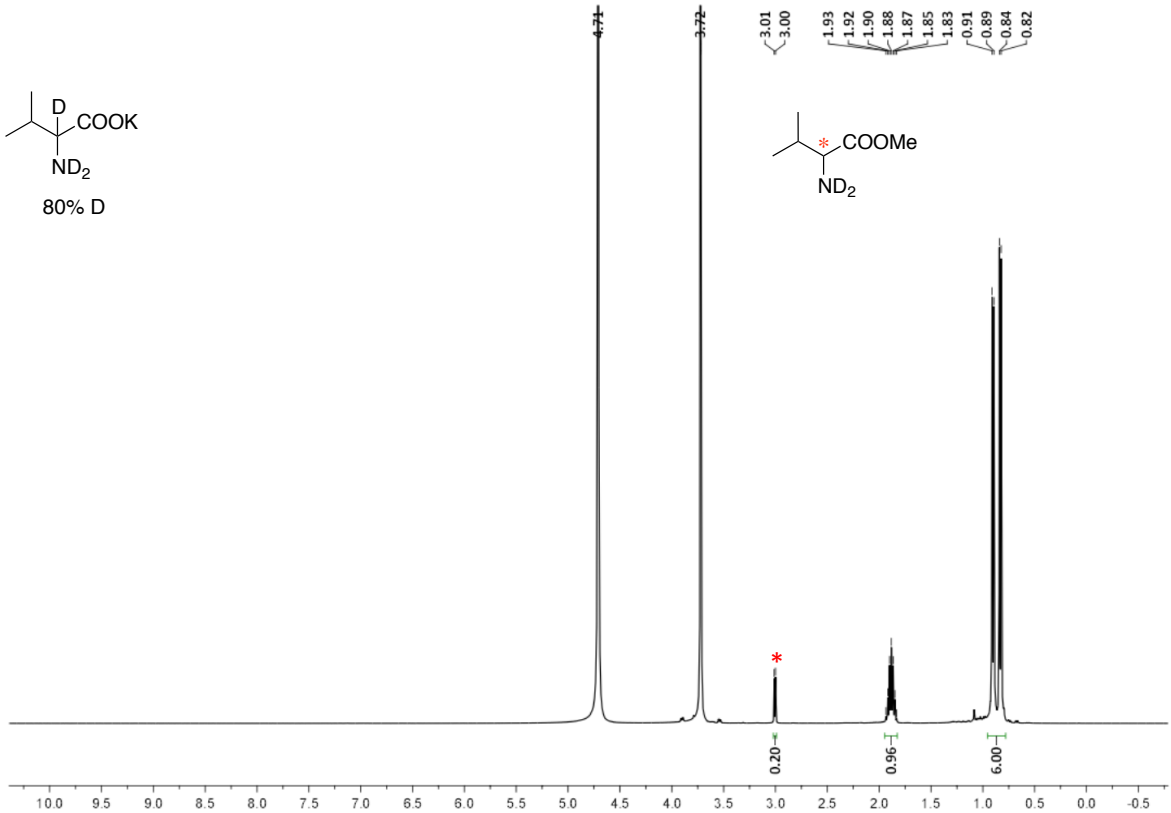
^{1}H NMR spectrum for methyl 2-amino-3-hydroxypropanoate-d4 (**5i**) (400 MHz, D_2O):



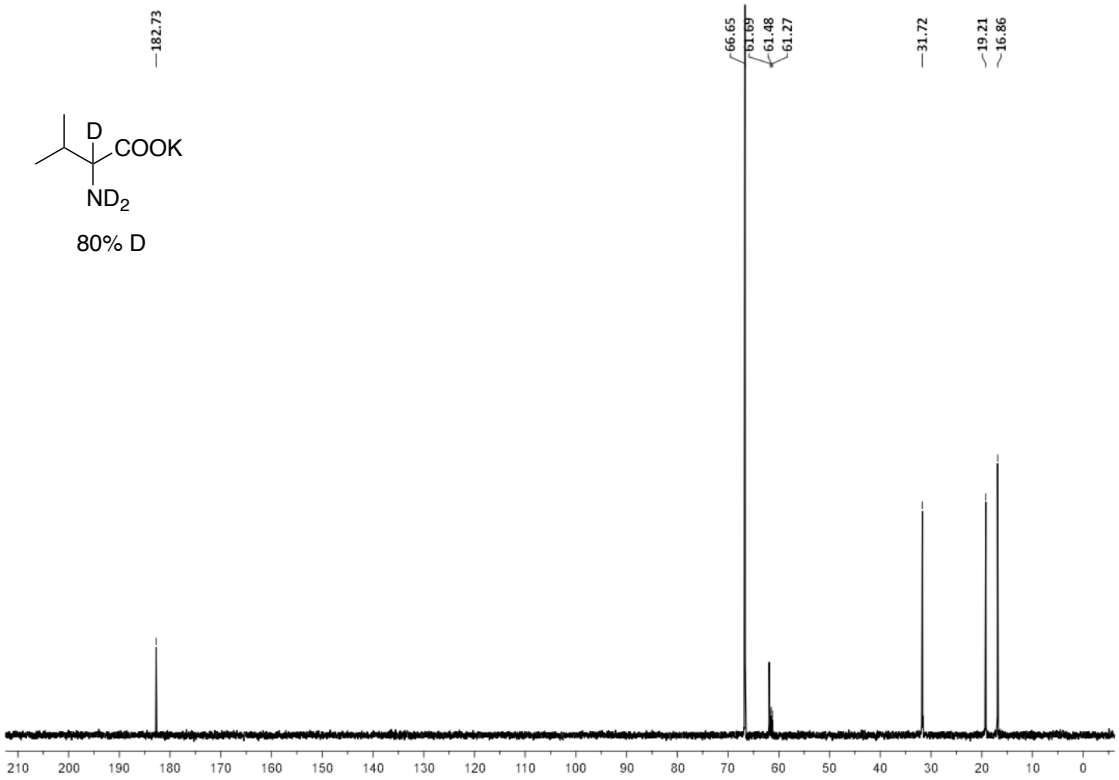
^{13}C NMR spectrum for methyl 2-amino-3-hydroxypropanoate-d4 (**5i**) (101 MHz, D_2O):



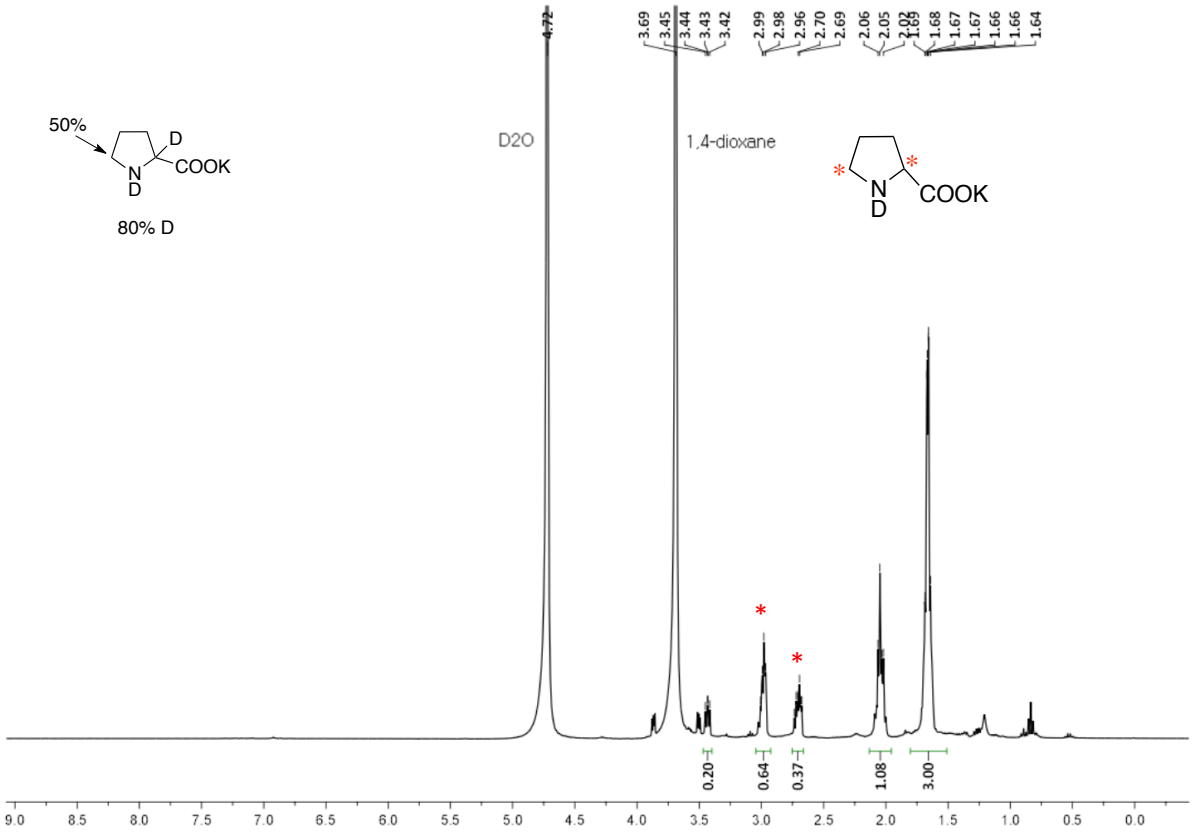
^{1}H NMR spectrum for potassium salt of valine-d3 (**5j**) (400 MHz, D_2O):



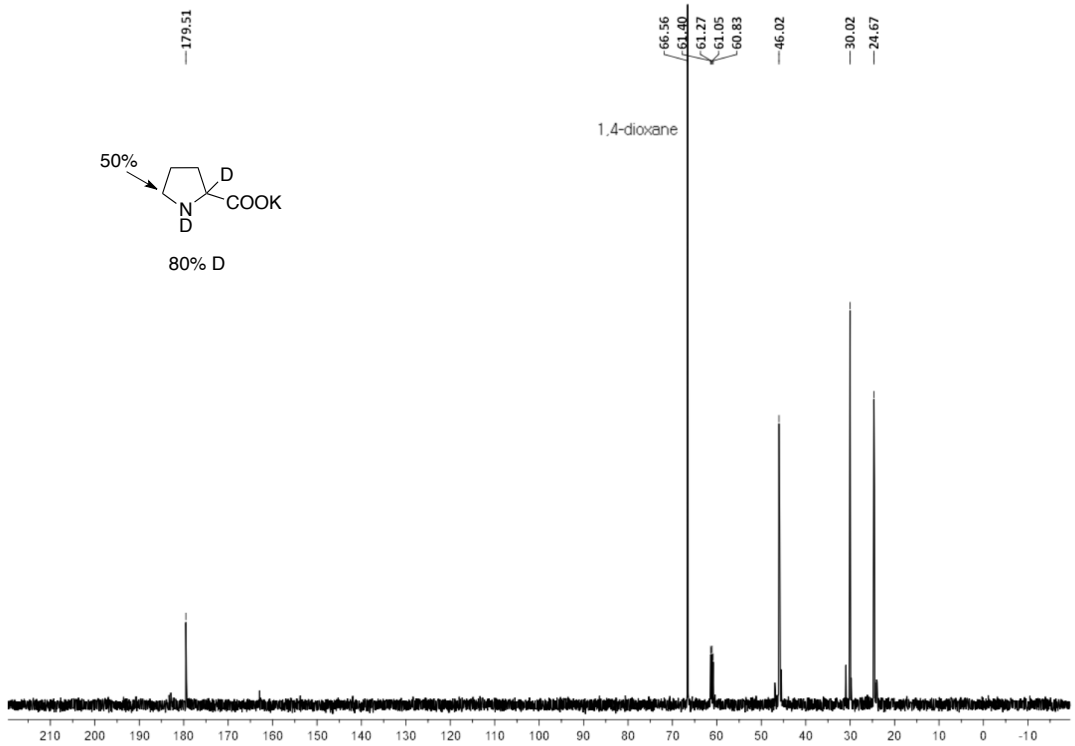
^{13}C NMR spectrum for potassium salt of valine-d3 (**5j**) (101 MHz, D_2O):



^{1}H NMR spectrum for potassium salt of L-proline-d4 (**5k**) (400 MHz, D_2O):

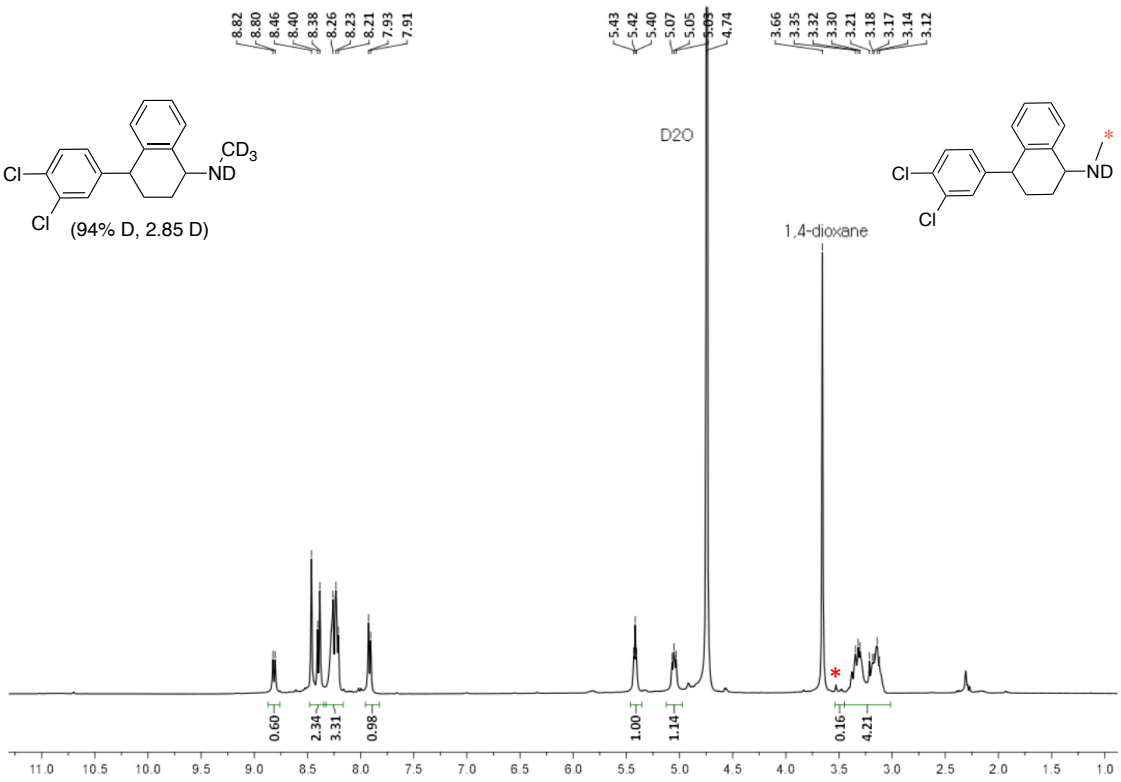


^{13}C NMR spectrum for potassium salt of L-proline-d4 (**5k**) (101 MHz, D_2O):

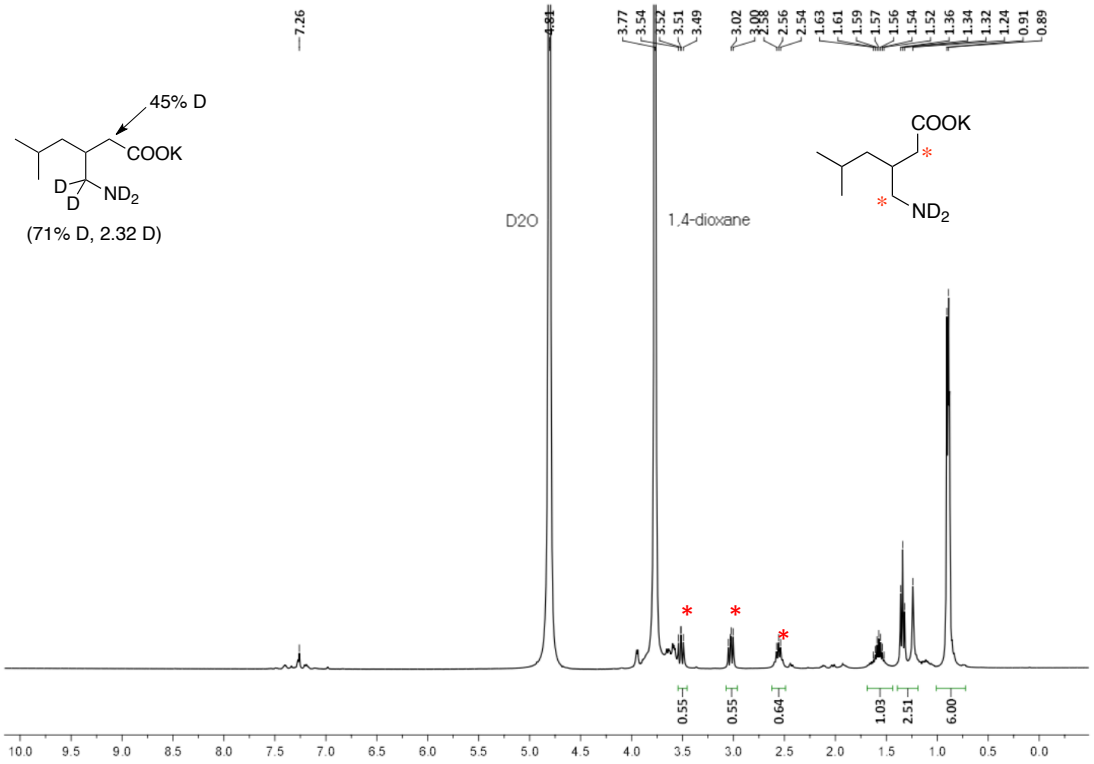


^{1}H NMR spectra of pharmaceuticals:

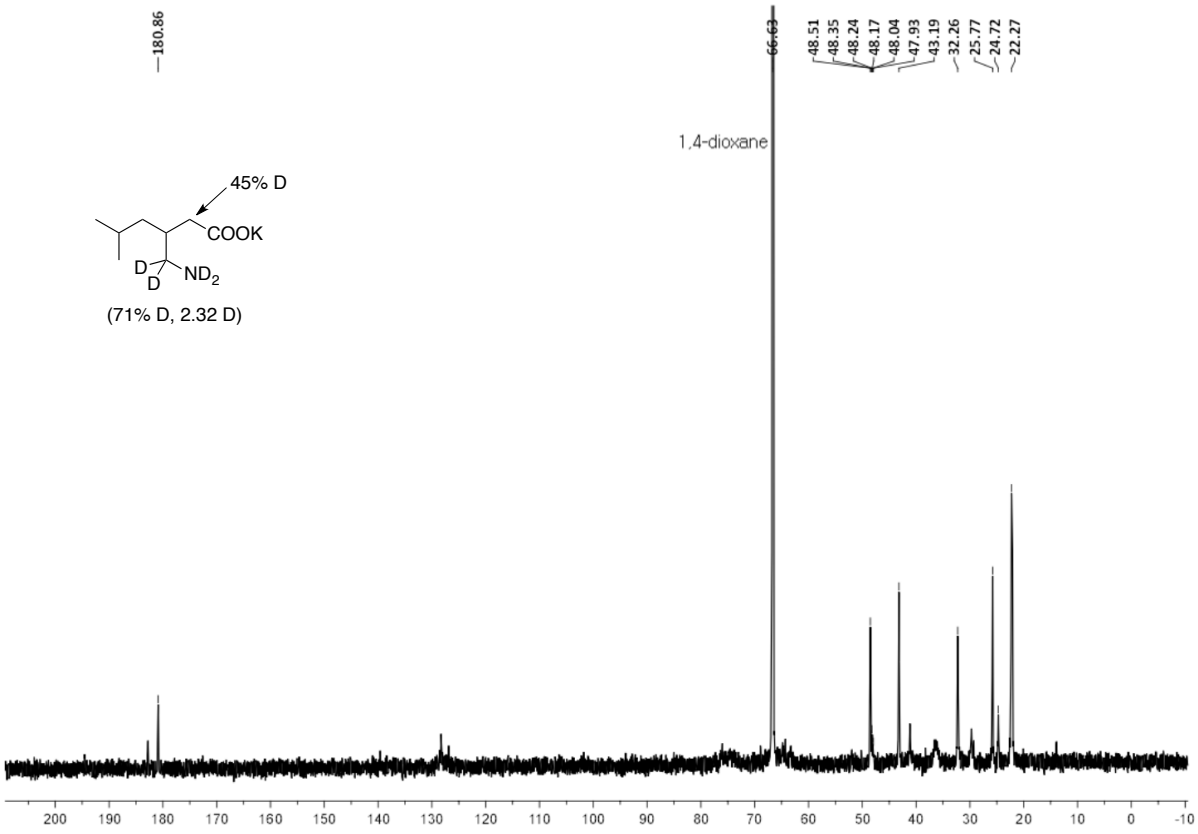
^{1}H NMR spectrum for potassium salt of sertraline-d4 (**6**)(400 MHz, D_2O):



^{1}H NMR spectrum for potassium salt of pregabalin-d4 (**7**) (400 MHz, D_2O):



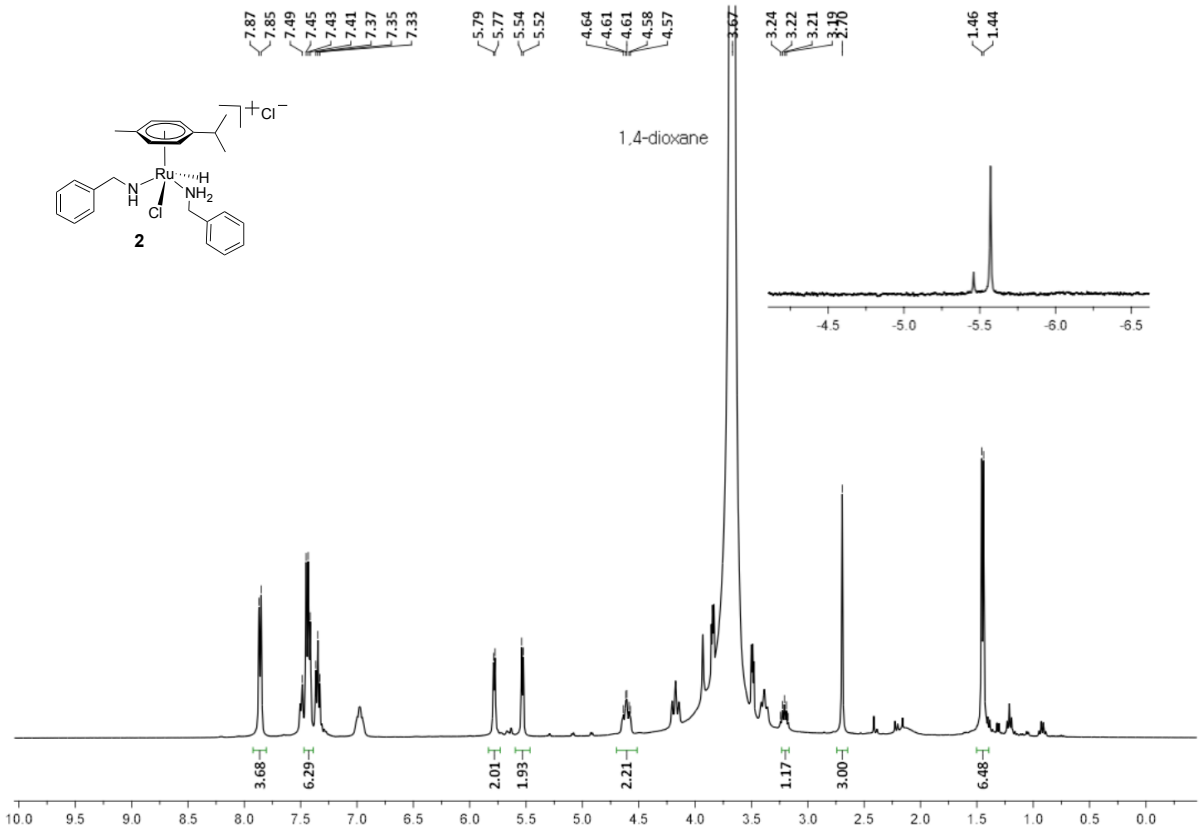
^{13}C NMR spectrum for potassium salt of pregabalin-d4 (**7**) (101 MHz, D_2O):



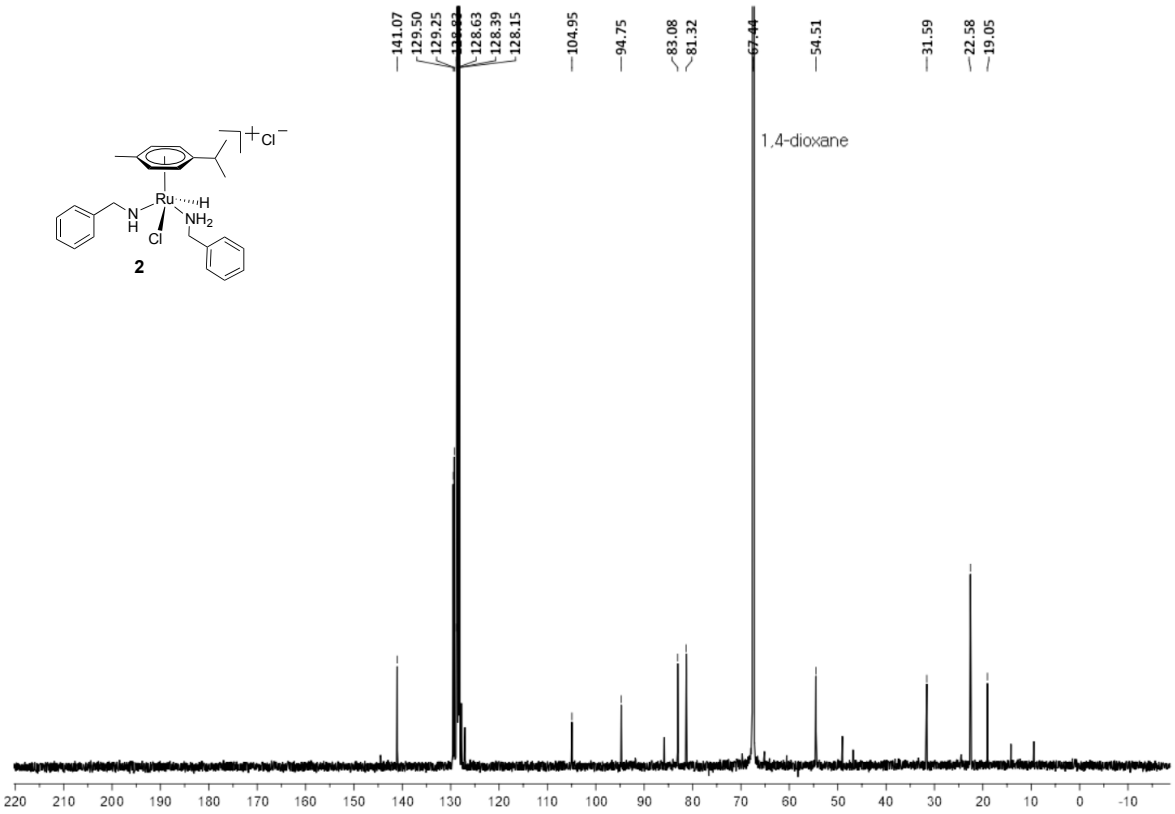
Synthesis of [{(η^6-*p*-cymene)RuHCl}($NHCH_2Ph$)(NH_2CH_2Ph)]Cl 2:

In a screw cap scintillation vial [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] **1** (0.017 mmol, 10 mg), benzylamine (5 equiv, 0.086 mmol, 9 µl) and 1,4-dioxane (0.5 ml) were added and the resulting mixture was allowed to stir at room temperature for 2 h. The volume of reddish-brown solution was reduced under vaccum and kept at -30 ºC for 24 h, which provided reddish-brown precipitate. The solution decanted and the precipitate was characterised by NMR and IR spectroscopy. IR (C_6D_6) 3427 (N-H), 2934, 2756, 2100, 2011 (Ru-H), 1552, 1431, 1328, 1187, 971, 823, 677 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz) δ 7.86 (d, 4H, *J* = 8Hz, ArC*H*), 7.49-7.33 (m, 6H, ArC*H*), 5.78 (d, 2H, *J* = 8Hz, ArC*H*), 5.53 (d, 2H, *J* = 8Hz, ArC*H*), 4.61 (br m, 2H, NH_2), 3.22 (m, 1H, ^{i}PrC*H*), 2.70 (s, 3H, CH_3), 1.45 (d, 6H, *J* = 8Hz, ^{i}PrCH_3), -5.56 (1H, Ru-*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.07 (quat-*C*), 129.50 (Ar*C*H), 129.25 (Ar*C*H), 128.83 (Ar*C*H), 104.95 (quat-*C*), 94.75 (quat-*C*), 83.08 (Ar*C*H), 81.32 (Ar*C*H), 54.51 (*C*H$_2$), 31.59 (*C*H), 22.58 (^{i}Pr*C*H$_3$), 19.05 (*C*H$_3$).

^{1}H NMR spectrum of precipitated **2** (C_6D_6, 400 MHz):



^{13}C NMR spectrum of precipitated **2** (C_6D_6, 101 MHz):



Determination of the molecular structure of 2 in the solid state by X-ray single crystal diffraction: A suitable single crystals of complex **2** for X-ray analysis was obtained from a solution of toluene. A suitable crystal was mounted on a glass fibre. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an Incoatec microsource (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+[16] and corrected for absorption with SADABS.[17] The structure was solved by direct methods and refined on F^2 with SHELXL-97.[18,19]

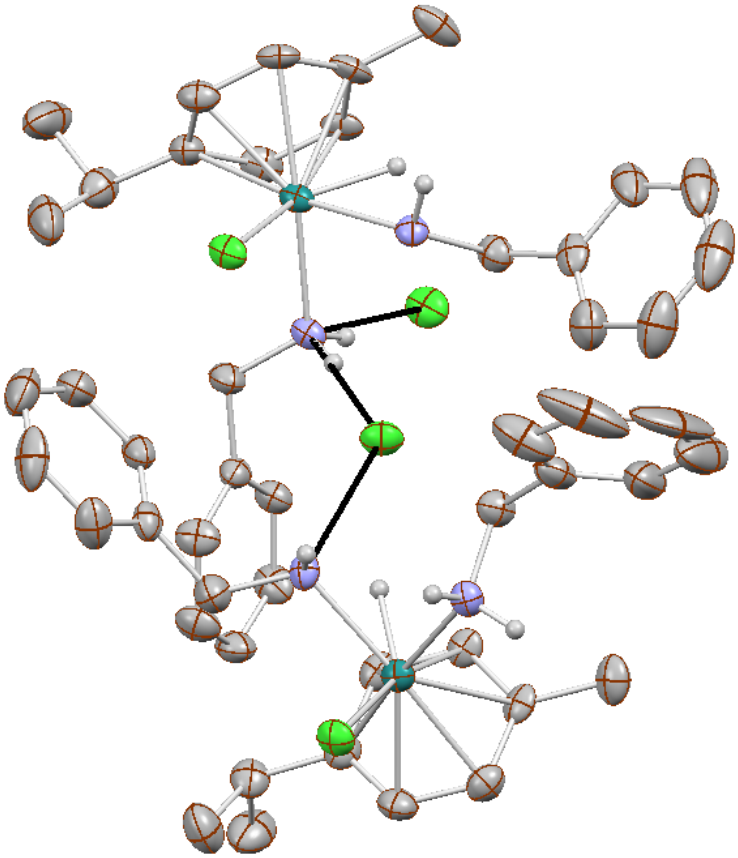


Figure S1. ORTEP structure of complex **2** with two molecules in unit cell showing hydrogen bond between $PhCH_2NH_2\cdots Cl\cdots NHCH_2Ph$. Elipsoids drawn with 50% probability.

Crystal data of Ru-complex 2: $C_{48}H_{64}Cl_4N_4Ru_2$, crystal dimensions: 0.19 × 0.15 × 0.12, triclinic with space group P-1 a = 11.418 (12)Å, b = 13.809 (15) Å, c = 15.565 (17) Å, α = 71.93 (14)°, β = 89.77 (14)°, γ = 86.05 (14)°, V = 2327 (4)Å^3, Z = 2, T = 100 K, $2\theta_{max}$ = 24.03, ρ_{calcd} = 1.485 g/cm^3, μ (MoKα) = 0.916 mm$^{-1.}$ min/max transmission factors = 0.5402/0.7457, 11856 Reflections collected, 6483 unique ($R1$ = 0.058), $WR2$ = 0.1374 (all data). The structure has been deposited at the CCDC data center and can be retrieved by using the number **CCDC 1481309**.

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