

Supporting Information

Organophotocatalytic α -deuteration of unprotected primary amines via H/D exchange with D₂O

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1. General Information

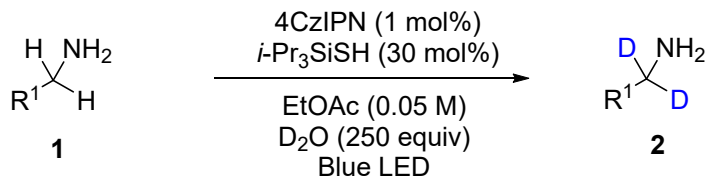
Commercially available reagents were purchased from Sigma Aldrich, Matrix Chemical, AK Sci, Alfa Aesar, TCI, and Chem Cruz, and used as received unless otherwise noted. Except Isatin, 6-Chloroisatin and 5-Bromoisatin are purchased from Sigma Aldrich. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with a fluorescence F254 indicator were used for thin-layer chromatography (TLC) analysis. ^1H and ^{13}C NMR spectra were recorded on Bruker Advance 400/500 or JEOL 400. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm) or dimethyl sulfoxide (2.50 ppm) as internal standards. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant in Hertz (Hz) and hydrogen numbers based on integration intensities. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of CDCl_3 (77.16 ppm) as internal standards.

2. General Procedures and Optimization of Reaction Conditions

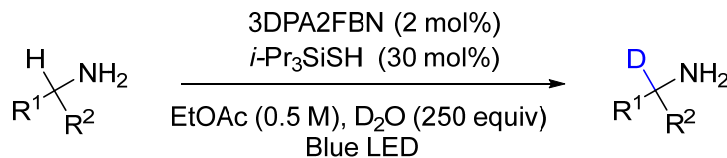


Figure S1. The Visible-Light Photoredox Catalysis Experimental Setup

2.1 General Procedures of Synthesis of α -Deuterated Amine:

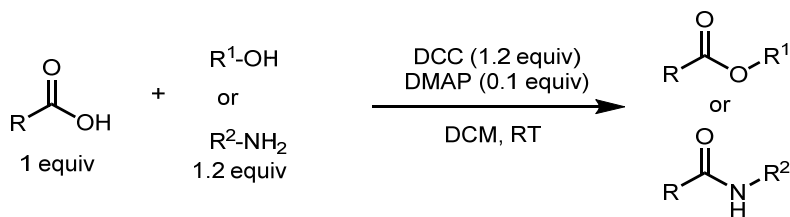


General Procedure A: To an oven-dried 10 mL-Schlenk tube equipped with a stir bar, was added amine (0.2 mmol, 1.0 equiv), photocatalyst 4CzIPN (1.6 mg, 1 mol%), triisopropylsilanethiol (12 μ L, 30 mol%) and the tube was evacuated and backfilled with N₂ (three times). Anhydrous EtOAc (4 mL), and 1 mL of D₂O were added by syringe under N₂. The solution was then stirred at room temperature under the irradiation of two 40 W Kessil Blue LEDs for 48 h. After completion of the reaction, the top layer EtOAc was concentrated and treated with a 2.0 M solution of HCl in diethyl ether and filtered. The solid was then washed with diethyl ether and dried under a vacuum to give the pure product. Alternatively, the top layer EtOAc was concentrated and diluted with CH₂Cl₂ (10 mL) and HCl (5 mL, 1.0 M, aq). The organic layer was disposed and the aqueous layer diluted with CH₂Cl₂ (10 mL) and Ammonium hydroxide solution (10 mL, 33%, aq). The aqueous layer was extracted with CH₂Cl₂ (3 \times 10 mL). Organic layers were combined, dried over Na₂SO₄, filtered, and concentrated. Percentages of exchanged protons are determined by ¹H NMR.



General Procedure B: To an oven-dried 10 mL-Schlenk tube equipped with a stir bar, was added amine (0.2 mmol, 1.0 equiv), photocatalyst 3DPA2FBN (2.6 mg, 2 mol%), triisopropylsilanethiol (12 μ L, 30 mol%) and the tube was evacuated and backfilled with N₂ (three times). 4 mL anhydrous EtOAc, and 1 mL D₂O were added by syringe under N₂. The solution was then stirred at room temperature under the irradiation of two 40 W Kessil Blue LEDs for 48h. After completion of the reaction, the top layer EtOAc was concentrated and treated with a 2.0 M solution of HCl in diethyl ether and filtered. The solid was then washed with diethyl ether and dried under a vacuum to give the pure product. Percentages of exchanged protons are determined by ¹H NMR.

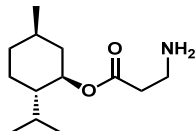
2.2 General Procedure for Synthesis of 1as-1au



To an oven-dried round-bottom flask with a magnetic stir bar was added acid (3 mmol, 1.0 equiv.), alcohol or amine (3.6 mmol, 1.2 equiv.), DCC (742 mg, 3.6 mmol, 1.2 equiv.) and DMAP (37m

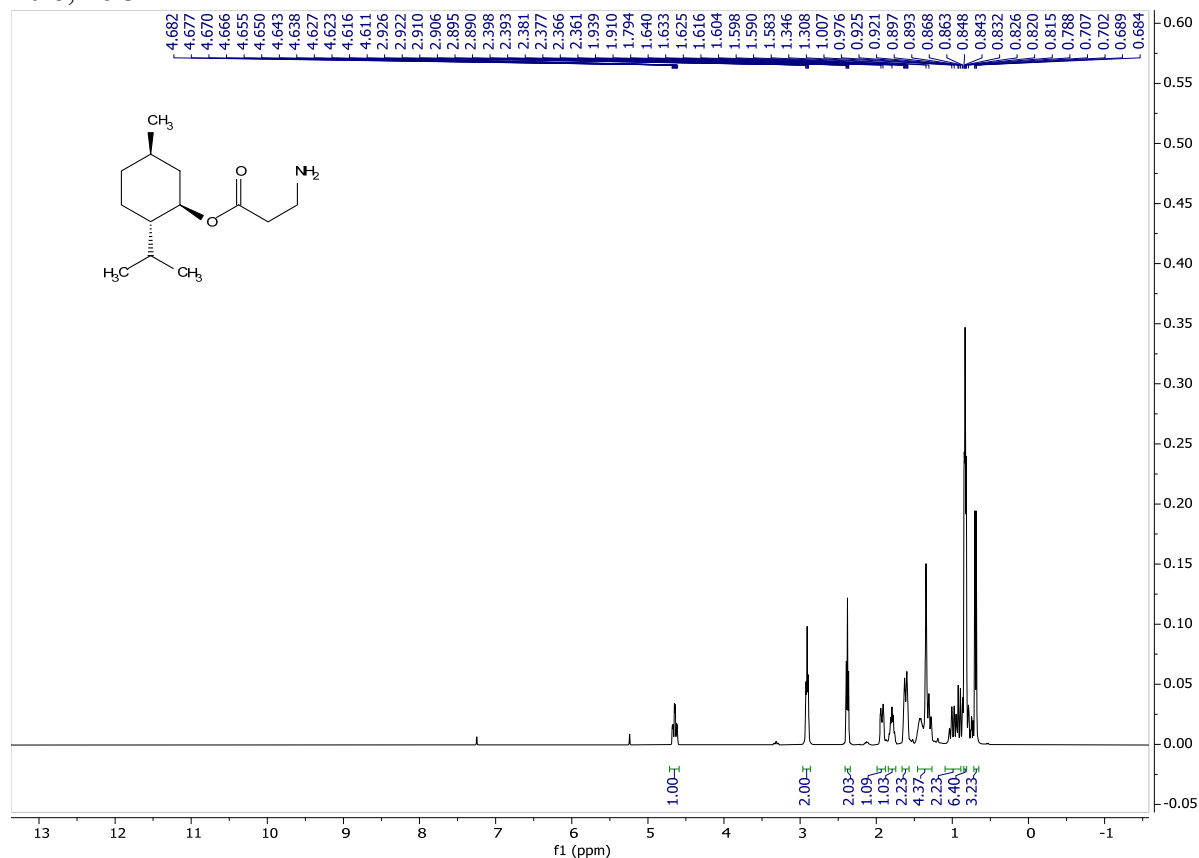
g, 0.30 mmol, 0.1 equiv.). Dry dichloromethane (20 mL) was added and the mixture was allowed to stir at room temperature until the acid was consumed (followed by TLC). Typical reaction times were between 12 h. The white precipitates were filtered off and the solvent was removed under reduced pressure. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel eluting with hexane/ethyl acetate.

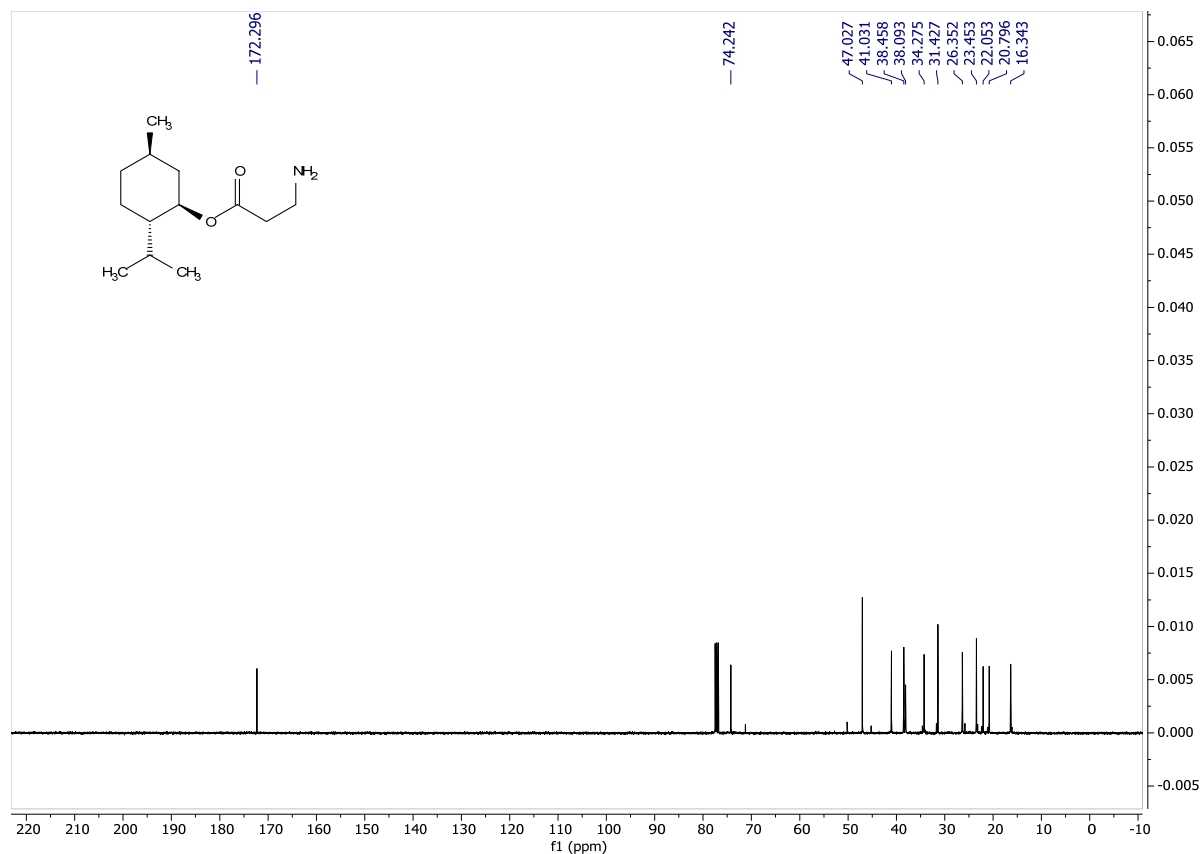
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-aminopropanoate (1a_s): The title product was prepared according to the general procedure and purified by column chromatography on silica gel eluting with hexane/ethyl acetate (8:1) as white solid about 500 mg (73%).



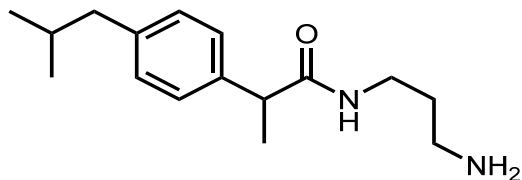
¹H NMR (400 MHz, CDCl₃) δ 4.65 (tdd, *J* = 10.9, 4.5, 1.8 Hz, 1H), 2.91 (td, *J* = 6.3, 1.9 Hz, 2H), 2.38 (td, *J* = 6.3, 1.9 Hz, 2H), 1.92 (d, *J* = 11.7 Hz, 1H), 1.79 (s, 1H), 1.61 (ddd, *J* = 13.2, 5.8, 2.9 Hz, 2H), 1.33 (d, *J* = 15.2 Hz, 4H), 1.09 – 0.89 (m, 2H), 0.83 (td, *J* = 5.4, 4.4, 2.0 Hz, 6H), 0.70 (dd, *J* = 7.1, 2.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.3, 74.2, 47.0, 41.0, 38.5, 38.1, 34.3, 31.4, 26.4, 23.5, 22.1, 20.8, 16.3.



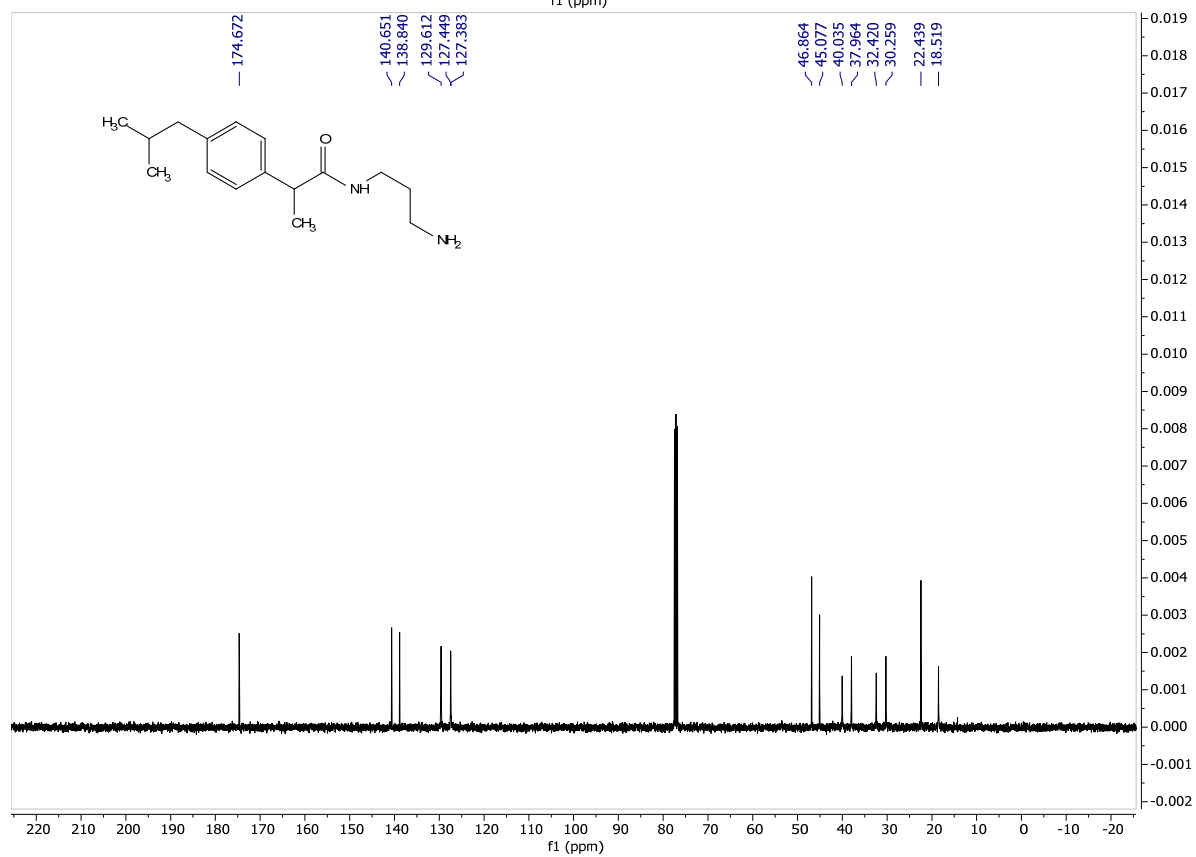
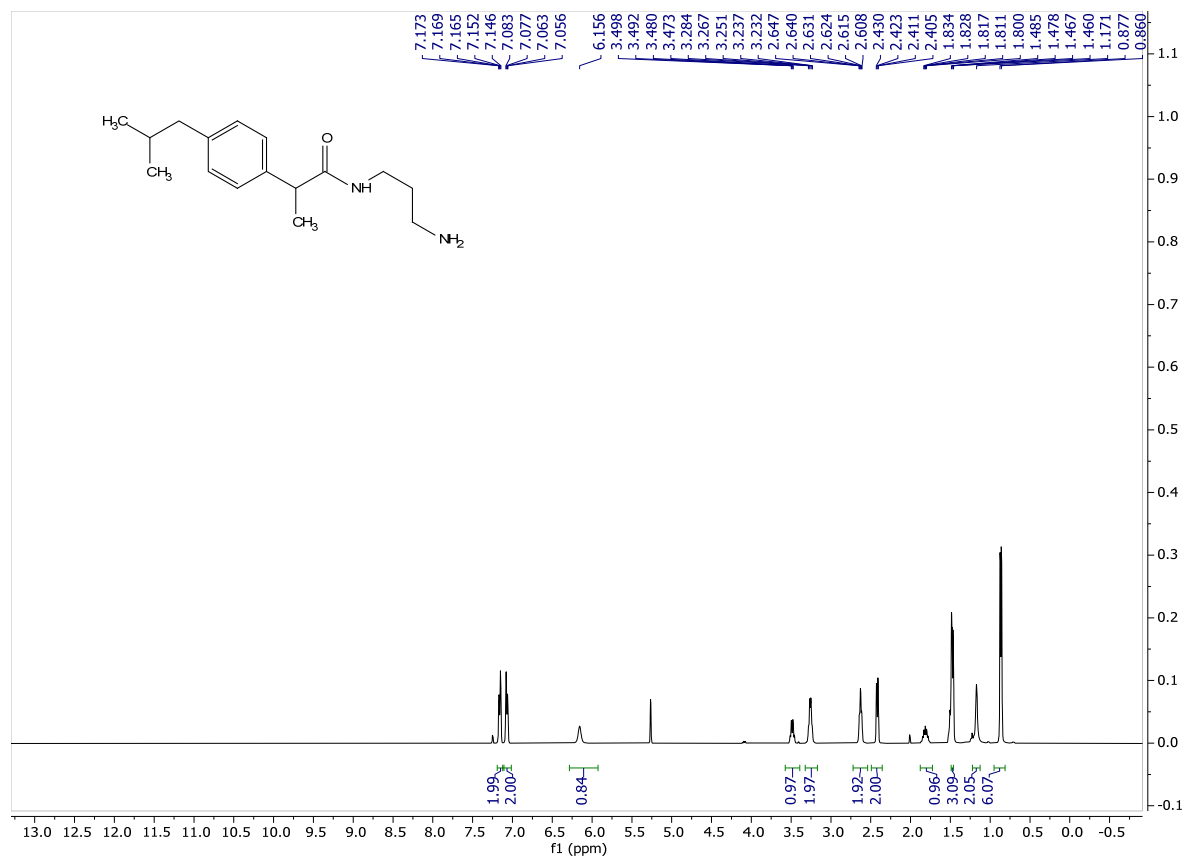


N-(3-Aminopropyl)-2-(4-isobutylphenyl)propanamide (1at): The title product was prepared according to the general procedure and purified by column chromatography on silica gel eluting with hexane/ethyl acetate (10:1) as white oil about 660 mg (83%).

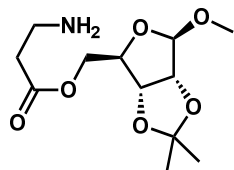


¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.11 (m, 2H), 7.07 (dd, *J* = 8.3, 2.7 Hz, 2H), 6.16 (s, 1H), 3.49 (dd, *J* = 7.4, 2.6 Hz, 1H), 3.26 (q, *J* = 7.0 Hz, 2H), 2.63 (td, *J* = 6.4, 2.6 Hz, 2H), 2.42 (dd, *J* = 7.4, 2.6 Hz, 2H), 1.81 (dtd, *J* = 13.6, 6.7, 2.3 Hz, 1H), 1.49 – 1.46 (m, 3H), 1.17 (s, 2H), 0.87 (d, *J* = 6.8 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 174.7, 140.7, 138.8, 129.6, 127.4, 127.4, 46.9, 45.1, 40.0, 38.0, 32.4, 30.3, 22.4, 18.5.

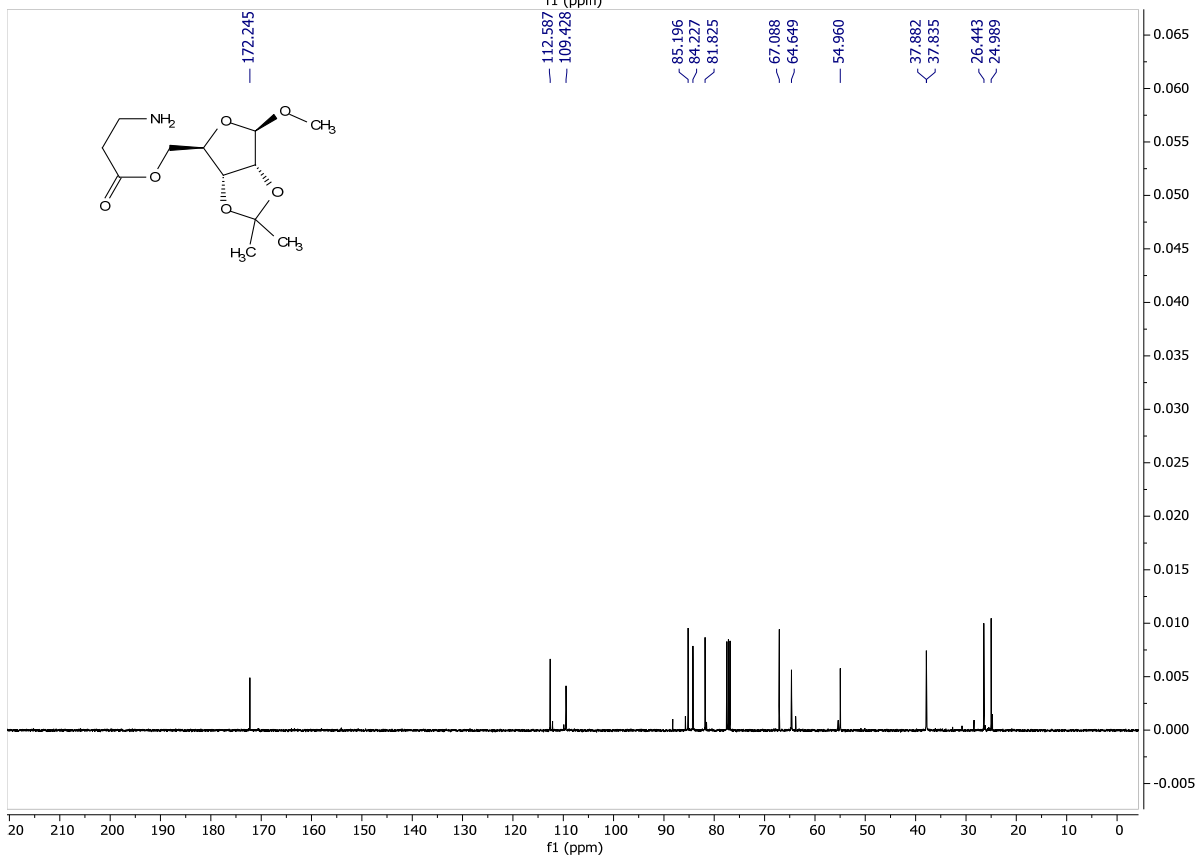
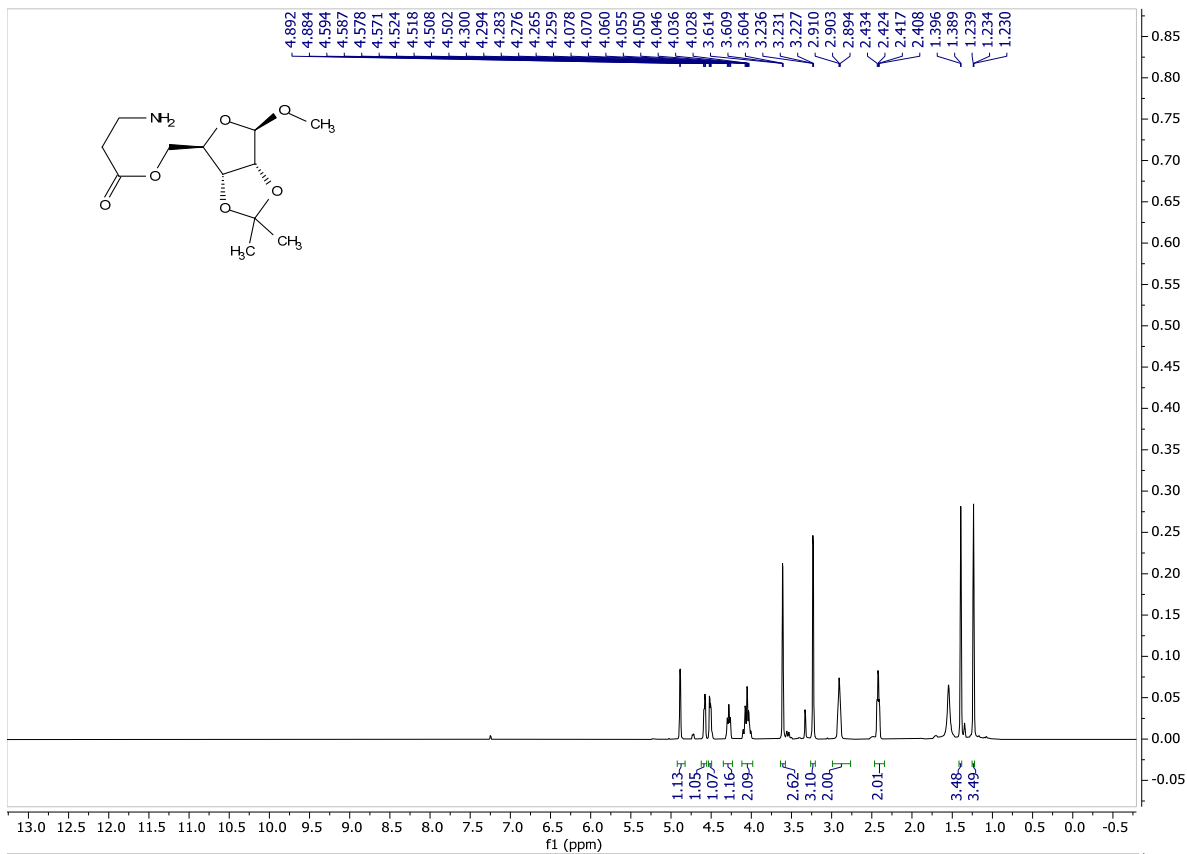


((3a*R*,4*R*,6*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl 3-aminopropanoate (1au): The title product was prepared according to the general procedure and purified by column chromatography on silica gel eluting with hexane/ethyl acetate (10:1) as white oil about 600 mg (73%).



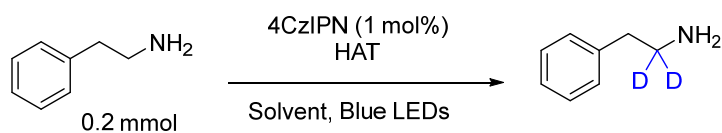
^1H NMR (400 MHz, CHLOROFORM-*D*) δ 4.89 (d, $J = 3.0$ Hz, 1H), 4.58 (dd, $J = 6.4, 2.6$ Hz, 1H), 4.51 (dd, $J = 6.4, 2.7$ Hz, 1H), 4.33 – 4.24 (m, 1H), 4.05 (ddd, $J = 10.8, 8.0, 3.1$ Hz, 2H), 3.66 – 3.49 (m, 3H), 3.27 – 3.18 (m, 3H), 2.91 (d, $J = 3.1$ Hz, 2H), 2.42 (d, $J = 2.9$ Hz, 2H), 1.40 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 172.2, 112.6, 109.4, 85.2, 84.2, 81.8, 64.6, 55.0, 37.9, 37.8, 26.4, 25.0.

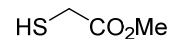
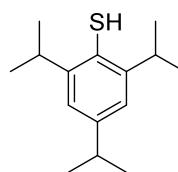
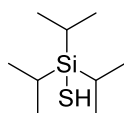
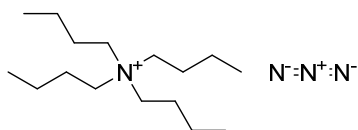


2.3 Reaction Conditions Optimization

Table S1. Optimization of reaction conditions for primary alkylamines

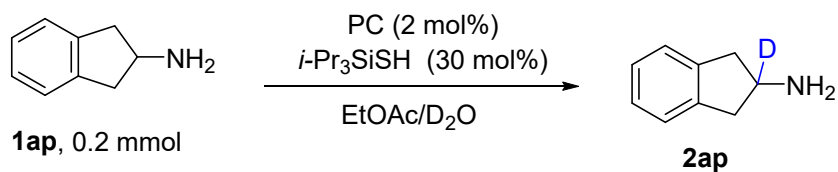


Entry	HAT-Cat	Solvent	D ₂ O	Times	D/%
1	HAT-1 (15 mol%), HAT-2 (30 mol%)	EA (0.1 M)	80 equiv.	16 h	45
2	HAT-1 (15 mol%), HAT-3 (30 mol%)	EA (0.1 M)	80 equiv.	16 h	32
3 ^a	HAT-1 (15 mol%), HAT-4 (30 mol%)	EA (0.1 M)	80 equiv.	16 h	49
4	HAT-1 (15 mol%), HAT-3 (30 mol%)	ACN (0.1 M)	80 equiv.	16 h	25
5	HAT-1 (15 mol%), HAT-3 (30 mol%)	MeOH (0.1M)	80 equiv.	16 h	0
6	HAT-1 (15 mol%), HAT-3 (30 mol%)	DCM (0.1 M)	80 equiv.	16 h	nd
7	HAT-1 (15 mol%), HAT-3 (30 mol%)	Acetone (0.1 M)	80 equiv.	16 h	0
8	HAT-1 (15 mol%)	EA (0.1 M)	80 equiv.	16 h	0
9	HAT-2 (30 mol%)	EA (0.1M)	80 equiv.	16 h	69
10	HAT-1 (15 mol%), HAT-2 (30 mol%)	D ₂ O (0.2M)		16 h	39
11	HAT-1 (15 mol%), HAT-2 (30 mol%)	THF (0.1 M)	80 equiv.	16 h	37
12	HAT-2 (50 mol%)	EA (0.1 M)	80 equiv.	16 h	85
13	HAT-4 (30 mol%)	EA (0.1 M)	80 equiv.	16 h	50
14	HAT-2 (30 mol%)	EA (0.05 M)	80 equiv.	16 h	75
15	HAT-2 (30 mol%)	EA (0.1 M)	250 equiv.	16 h	87
16	HAT-2 (100 mol%)	EA (0.1 M)	80 equiv.	16 h	94
17	HAT-2 (30 mol%)	EA (0.1M)	250 equiv.	36 h	95
18	HAT-2 (50 mol%)	EA (0.1M)	250 equiv.	16 h	83
19	HAT-2 (30 mol%)	EA (0.1M)	80 equiv.	36 h	90
20	HAT-2 (20 mol%)	EA (0.1 M)	80 equiv.	36 h	83
21	HAT-2 (30 mol%)	EA (0.05 M)	250 equiv.	36 h	100



^aThe crude NMR spectra is messy.

Table S2. Optimization of reaction conditions for secondary alkylamines



Entry	PC	Solvent	D ₂ O	Times	D/%
1	PC-1	EA (0.05 M)	250 equiv.	48 h	30
2	PC-2	EA (0.05 M)	250 equiv.	16 h	100
3	PC-3	EA (0.05 M)	250 equiv.	16 h	0
4	PC-4	EA (0.05 M)	250 equiv.	16 h	0

4CzIPN PC-1

$$[E_{1/2}(\text{PC}^*/\text{PC}^{\cdot-}) = +1.35 \text{ V vs SCE}]$$

$$[E_{1/2}(\text{PC}/\text{PC}^{\cdot-}) = -1.21 \text{ V vs SCE}]$$

[Ir(dFCF₃ppy)₂-(5,5'-dFbpy)]PF₆ PC-3

$$[E_{1/2}(\text{PC}^*/\text{PC}^{\cdot-}) = +1.61 \text{ V vs SCE}]$$

$$[E_{1/2}(\text{PC}/\text{PC}^{\cdot-}) = -1.54 \text{ V vs SCE}]$$

i-Pr₃SiSH

$$E_{1/2}^{\text{ox}} = +0.28 \text{ V vs. SCE}$$

$$E_{1/2}^{\text{red}} = -0.82 \text{ V vs. SCE}$$

3DPA2FBN PC-2

$$[E_{1/2}(\text{PC}^*/\text{PC}^{\cdot-}) = +0.92 \text{ V vs SCE}]$$

$$[E_{1/2}(\text{PC}/\text{PC}^{\cdot-}) = -1.92 \text{ V vs SCE}]$$

[Ir(dFCF₃ppy)₂-(5,5'-dCF₃bpy)]PF₆ PC-4

$$[E_{1/2}(\text{PC}^*/\text{PC}^{\cdot-}) = +1.68 \text{ V vs SCE}]$$

$$[E_{1/2}(\text{PC}/\text{PC}^{\cdot-}) = -1.07 \text{ V vs SCE}]$$

$$E_{1/2}^{\text{ox}}(\text{nBuNH}_2) = +1.40 \text{ V vs SCE}$$

3. Stern-Volmer Quenching Experiments

In a typical experiment, a solution of photocatalyst 4CzIPN in ethyl acetate (1.25×10^{-4} M) was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 520 nm was collected with excited wavelength of 360 nm.

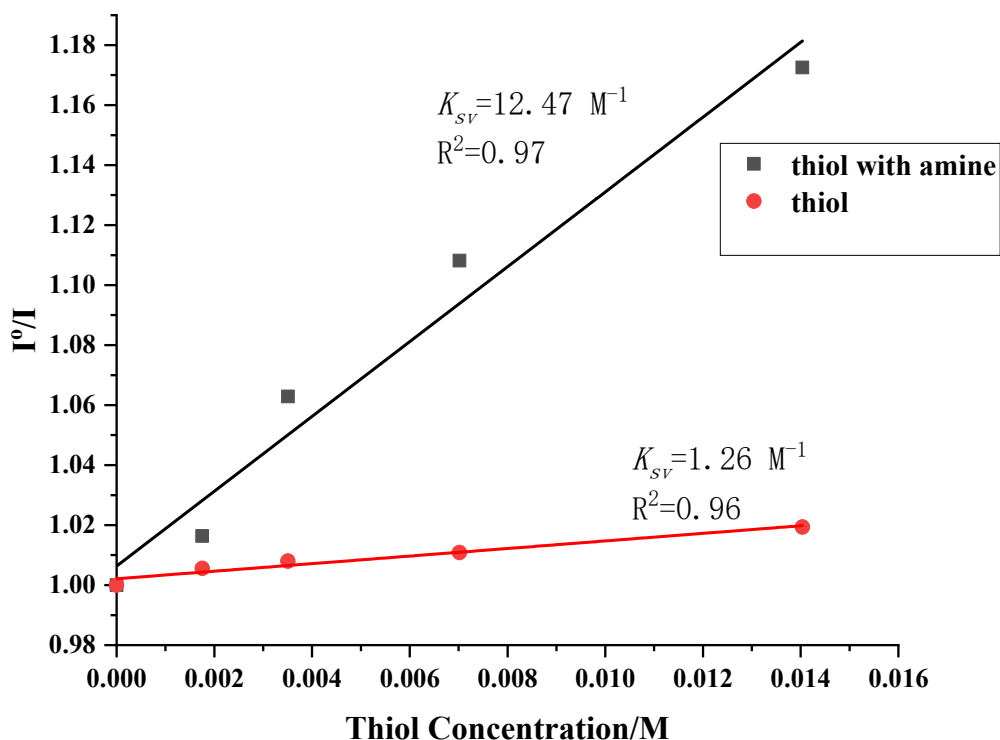


Figure S2. Stern-Volmer plot of 4CzIPN with varying reaction components. Dark Line: Stern-Volmer plot of 4CzIPN with constant phenylethylamine (0.3 M) and varying concentration of triisopropylsilanethiol. The Stern-Volmer constant (K_{SV}) for the quenching of Thiol in the presence of amine is $K_{SV} = 12.47 \text{ M}^{-1}$. Red line: Stern-Volmer plot of 4CzIPN with varying concentration of triisopropylsilanethiol. The Stern-Volmer constant (K_{SV}) for the quenching of Thiol is $K_{SV} = 1.26 \text{ M}^{-1}$. The deprotonated thiol showed enhanced quenching ability than thiol.

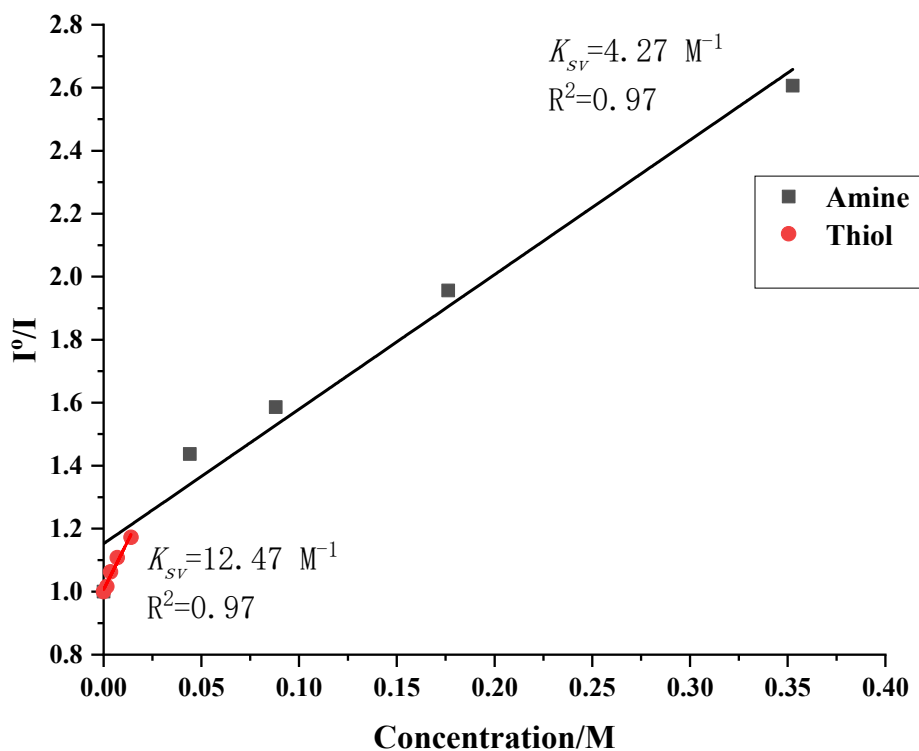
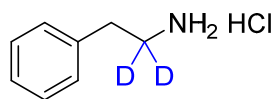


Figure S3. Stern-Volmer plot of 4CzIPN with varying reaction components. Dark Line: Stern-Volmer plot of 4CzIPN with varying concentration of phenylethylamine. The Stern-Volmer constant (K_{SV}) for the quenching of amine is $K_{SV} = 4.27 \text{ M}^{-1}$. Red Line: Stern-Volmer plot of 4CzIPN with constant phenylethylamine (0.3 M) and varying concentration of triisopropylsilanethiol. The Stern-Volmer constant (K_{SV}) for the quenching of Thiol in the presence of amine is $K_{SV} = 12.47 \text{ M}^{-1}$. The deprotonated thiol showed enhanced quenching ability than the phenylethylamine.

4. Compound Characterization Data

The compounds **2a**, **2r**, **2o**, **2y**, **2z**, **2ac**, **2ad**, **2ai**, **2an**, **2ao** and **2ap** are known compounds.¹⁻⁴

2-Phenylethan-1,1-*d*₂-1-amine hydrochloride (**2a**):

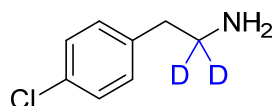


The title product was prepared according to the general procedure and isolated as white solid about 30.2 mg (95%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 8.05 (s, 3H), δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 3H), 2.84 (s, 2H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 137.9, 129.2, 129.2, 127.3, 33.3.

2-(4-Chlorophenyl)ethan-1,1-*d*₂-1-amine hydrochloride (**2b**):



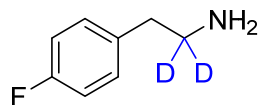
The title product was prepared according to the general procedure A and isolated as white solid about 37 mg (96%).

¹H NMR (500 MHz, DMSO) δ 8.45 – 7.99 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.90 (s, 2H).

¹³C NMR (126 MHz, DMSO) δ 136.9, 131.8, 131.1, 129.0, 32.5, 32.4, 32.4, 32.3.

HRMS (ESI-TOF) *m/z*: [C₈H₈D₂ClN + H]⁺ calcd for C₈H₉D₂ClN: 158.0706, found: 158.0700.

2-(4-Fluorophenyl)ethan-1,1-*d*₂-1-amine hydrochloride (**2c**):



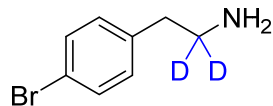
The title product was prepared according to the general procedure A and isolated as white solid about 33.6 mg (95%).

¹H NMR (500 MHz, DMSO) δ 8.16 (t, *J* = 20.1 Hz, 2H), 7.36 – 7.24 (m, 2H), 7.23 – 7.12 (m, 2H), 2.88 (s, 2H).

¹³C NMR (126 MHz, DMSO) δ 162.6, 160.7, 134.0, 131.1, 131.0, 115.9, 115.7, 32.4, 32.3, 32.2.

HRMS (ESI-TOF) m/z : $[C_8H_8D_2FN + H]^+$ calcd for $C_8H_9D_2FN$: 142.1001, found: 142.0996.

2-(4-Bromophenyl)ethan-1,1- d_2 -1-amine hydrochloride (2d):



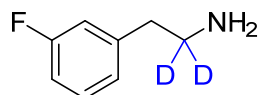
The title product was prepared according to the general procedure A and isolated as white solid about 45 mg (95%).

1H NMR (500 MHz, DMSO) δ 7.57 – 7.47 (m, 2H), 7.28 – 7.20 (m, 2H), 2.89 (s, 2H).

^{13}C NMR (126 MHz, DMSO) δ 137.4, 131.9, 131.5, 120.3, 32.5, 32.4, 32.4, 32.3.

HRMS (ESI-TOF) m/z : $[C_8H_8D_2BrN + H]^+$ calcd for $C_8H_9D_2BrN$: 202.0200, found: 202.0195.

3-(3-Fluorophenyl)ethan-1,1- d_2 -1-amine hydrochloride (2e):



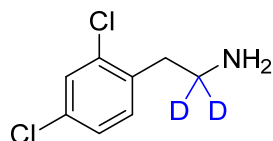
The title product was prepared according to the general procedure A and isolated as white solid about 33.3 mg (94%).

1H NMR (500 MHz, DMSO) δ 8.48 – 8.01 (m, 2H), 7.42 – 7.28 (m, 2H), 7.26 – 7.10 (m, 2H), 2.95 (s, 2H).

^{13}C NMR (126 MHz, DMSO) δ 162.0, 160.1, 131.6, 131.5, 129.5, 129.4, 125.1, 125.1, 124.6, 124.4, 115.9, 115.7, 26.7, 26.6, 26.6, 26.6.

HRMS (ESI-TOF) m/z : $[C_8H_8D_2FN + H]^+$ calcd for $C_8H_9D_2FN$: 142.1001, found: 142.0995.

2-(2,4-Dichlorophenyl)ethan-1,1- d_2 -1-amine hydrochloride (2f):



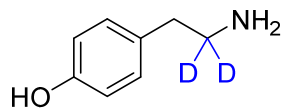
The title product was prepared according to the general procedure A and isolated as white solid about 43.5 mg (96%).

1H NMR (500 MHz, DMSO) δ 8.70 – 8.15 (m, 2H), 7.61 (d, J = 2.1 Hz, 1H), 7.49 – 7.35 (m, 2H), 3.04 (s, 2H).

^{13}C NMR (126 MHz, DMSO) δ 134.5, 132.8, 129.3, 128.1, 30.4, 30.3, 30.3.

HRMS (ESI-TOF) m/z : $[C_8H_7D_2Cl_2N + H]^+$ calcd for $C_8H_8D_2Cl_2N$: 192.0316, found: 192.0310.

4-(2-Aminoethyl-2,2- d_2)phenol hydrochloride (2g):



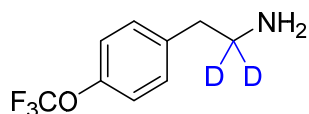
The title product was prepared according to the general procedure A and isolated as white solid about 33.2 mg (90%).

1H NMR (400 MHz, DMSO- D_6) δ 9.32 (s, 1H), 7.96 (s, 3H), 7.06 – 6.87 (m, 2H), 6.75 – 6.60 (m, 2H), 2.72 (d, J = 5.6 Hz, 2H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 156.7, 130.1, 127.8, 115.9, 32.5.

HRMS (ESI-TOF) m/z : $[C_8H_9D_2NO + H]^+$ calcd for $C_8H_{10}D_2NO$: 140.1044, found: 140.1039.

2-(4-(Trifluoromethoxy)phenyl)ethan-1,1- d_2 -1-amine hydrochloride (2h):



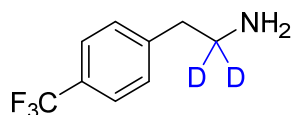
The title product was prepared according to the general procedure A and isolated as white solid about 47.1 mg (93%).

1H NMR (400 MHz, DMSO) δ 8.62 – 7.79 (m, 2H), 7.45 – 7.37 (m, 2H), 7.32 (dt, J = 7.7, 1.1 Hz, 2H), 2.95 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 147.6, 147.6, 137.5, 131.1, 124.4, 121.8, 121.6, 119.3, 116.7, 32.4, 32.4, 32.3.

HRMS (ESI-TOF) m/z : $[C_9H_8D_2F_3NO + H]^+$ calcd for $C_9H_9D_2F_3NO$: 208.0918, found: 208.0913.

2-(4-(Trifluoromethyl)phenyl)ethan-1,1- d_2 -1-amine hydrochloride (2i):



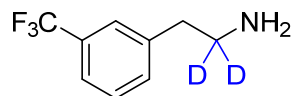
The title product was prepared according to the general procedure A and isolated as white solid about 43.1 mg (95%).

1H NMR (400 MHz, DMSO- D_6) δ 8.56 – 7.95 (m, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 2.97 (s, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 142.9, 130.2, 128.9, 128.5, 128.1, 127.8, 127.5, 126.2, 126.0, 125.9, 125.9, 125.9, 123.5, 120.8, 33.0, 32.9, 32.9.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_8\text{D}_2\text{F}_3\text{N} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_9\text{D}_2\text{F}_3\text{N}$: 192.0969, found: 192.0964.

2-(3-(Trifluoromethyl)phenyl)ethan-1,1- d_2 -1-amine hydrochloride (2j):



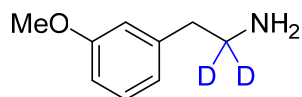
The title product was prepared according to the general procedure A and isolated as white solid about 43.1 mg (95%).

^1H NMR (500 MHz, DMSO) δ 8.10 (s, 3H), 7.65 (s, 1H), 7.64 – 7.55 (m, 3H), 2.99 (s, 2H).

^{13}C NMR (126 MHz, DMSO) δ 138.3, 132.4, 129.0, 129.0, 128.8, 128.5, 124.8, 124.8, 124.7, 124.7, 122.9, 122.9, 122.6, 31.8.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_8\text{D}_2\text{F}_3\text{N} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_9\text{D}_2\text{F}_3\text{N}$: 192.0969, found: 192.0964.

2-(3-Methoxyphenyl)ethan-1,1- d_2 -1-amine hydrochloride (2k):



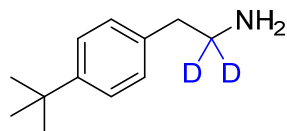
The title product was prepared according to the general procedure A and isolated as white solid about 35.9 mg (95%).

^1H NMR (500 MHz, DMSO) δ 8.06 (s, 2H), 7.24 (t, $J = 7.7$ Hz, 1H), 6.87 – 6.78 (m, 3H), 3.75 (s, 3H), 2.85 (s, 2H).

^{13}C NMR (126 MHz, DMSO) δ 158.8, 138.3, 129.0, 120.2, 113.7, 111.6, 54.4, 32.2.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_{11}\text{D}_2\text{NO} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{D}_2\text{NO}$: 154.1201, found: 154.1195.

2-(4-(*tert*-Butyl)phenyl)ethan-1,1- d_2 -1-amine hydrochloride (2l):



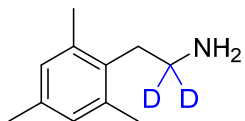
The title product was prepared according to the general procedure A and isolated as white solid about 41.2 mg (96%).

^1H NMR (500 MHz, DMSO) δ 7.43 – 7.26 (m, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 2.86 (d, $J = 7.1$ Hz, 2H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 149.5, 134.8, 128.8, 125.8, 34.6, 32.8, 32.8, 32.7, 32.7, 31.6.

HRMS (ESI-TOF) m/z : $[\text{C}_{12}\text{H}_{17}\text{D}_2\text{N} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{D}_2\text{N}$: 180.1721, found: 180.1715.

2-Mesitylethan-1,1- d_2 -1-amine hydrochloride (2m):



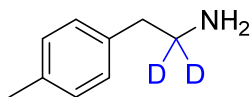
The title product was prepared according to the general procedure A and isolated as white solid about 39.4 mg (98%).

^1H NMR (400 MHz, DMSO- D_6) δ 6.73 (s, 2H), 2.57 (s, 2H), 2.19 (d, $J = 1.6$ Hz, 6H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 136.2, 134.6, 134.2, 129.1, 34.0, 21.0, 20.0.

HRMS (ESI-TOF) m/z : $[\text{C}_{11}\text{H}_{15}\text{D}_2\text{N} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{16}\text{D}_2\text{N}$: 166.1565, found: 166.1559.

2-(*p*-Tolyl)ethan-1,1- d_2 -1-amine hydrochloride (2n):



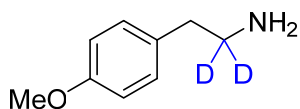
The title product was prepared according to the general procedure A and isolated as white solid about 33.5 mg (97%).

^1H NMR (400 MHz, DMSO- D_6) δ 8.40 – 7.99 (m, 2H), 7.09 (d, $J = 1.8$ Hz, 5H), 2.81 (s, 2H), 2.23 (d, $J = 1.7$ Hz, 3H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 136.2, 134.9, 129.7, 129.0, 32.9, 32.8, 32.8, 21.2.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_{11}\text{D}_2\text{N} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{D}_2\text{N}$: 138.1252, found: 138.1246.

2-Phenylethan-1,1- d_2 -1-amine hydrochloride (2o):



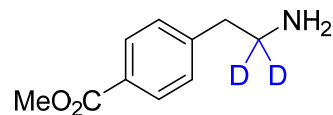
The title product was prepared according to the general procedure A and isolated as white solid about 36.2 mg (96%).

^1H NMR (400 MHz, DMSO- D_6) δ 8.05 (s, 3H), δ 7.29 (t, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 7.2$ Hz, 3H), 2.84 (s, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 137.9, 129.2, 129.2, 127.3, 33.3.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_{11}\text{D}_2\text{NO} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{D}_2\text{NO}$: 154.1201, found: 154.1195.

Methyl 4-(2-aminoethyl-2,2- d_2)benzoate hydrochloride (2p):



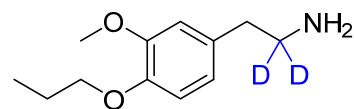
The title product was prepared according to the general procedure A and isolated as white solid about 43 mg (99%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 7.87 (dt, $J = 8.2, 2.0$ Hz, 2H), 7.38 (dd, $J = 8.3, 1.9$ Hz, 2H), 2.96 (s, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 166.6, 143.7, 130.0, 129.7, 128.6, 52.6, 33.1, 33.1, 33.0, 33.0.

HRMS (ESI-TOF) m/z : $[\text{C}_{10}\text{H}_{11}\text{D}_2\text{NO}_2 + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{D}_2\text{NO}_2$: 182.1150, found: 182.1145.

2-(3-Methoxy-4-propoxyphenyl)ethan-1,1- d_2 -1-amine hydrochloride (2q):



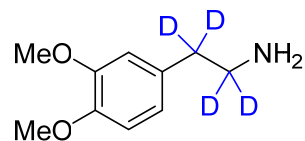
The title product was prepared according to the general procedure A and isolated as white solid about 46.4 mg (94%).

^1H NMR (500 MHz, DMSO) δ 8.33 – 7.84 (m, 2H), 6.88 (d, $J = 8.2$ Hz, 2H), 6.74 (dd, $J = 8.1, 2.0$ Hz, 1H), 3.87 (t, $J = 6.6$ Hz, 2H), 3.76 (s, 3H), 2.82 (s, 2H), 1.70 (q, $J = 7.1$ Hz, 2H), 0.96 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (126 MHz, DMSO) δ 149.5, 147.4, 130.2, 121.1, 113.8, 113.3, 70.2, 56.0, 32.8, 22.6, 10.9.

HRMS (ESI-TOF) m/z : $[\text{C}_{12}\text{H}_{17}\text{D}_2\text{NO}_2 + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{D}_2\text{NO}_2$: 212.1620, found: 212.1614.

2-(3,4-Dimethoxyphenyl)ethan-1,1,2,2- d_4 -1-amine (2r):

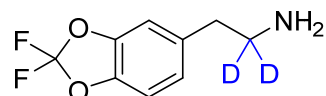


The title product was prepared according to the general procedure A and isolated as white solid about 42.4 mg (96%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 6.93 – 6.73 (m, 2H), 6.65 (d, $J = 7.7$ Hz, 1H), 3.69 (dd, $J = 11.5, 2.1$ Hz, 6H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 149.2, 147.6, 133.4, 120.9, 113.1, 112.4, 56.0, 55.9.

2-(2,2-Difluorobenzo[*d*][1,3]dioxol-5-yl)ethan-1,1-*d*₂-1-amine hydrochloride (2s):



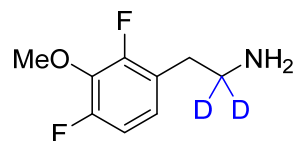
The title product was prepared according to the general procedure A and isolated as white solid about 43 mg (90%).

^1H NMR (500 MHz, DMSO) δ 7.98 (s, 3H), 7.44 – 7.29 (m, 2H), 7.11 (dd, $J = 8.3, 1.7$ Hz, 1H), 2.91 (d, $J = 6.8$ Hz, 2H).

^{13}C NMR (126 MHz, DMSO) δ 142.3, 141.0, 133.6, 130.6, 124.2, 110.0, 109.4, 31.8.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_7\text{D}_2\text{F}_2\text{NO}_2 + \text{H}]^+$ calcd for $\text{C}_9\text{H}_8\text{D}_2\text{F}_2\text{NO}_2$: 204.0805, found: 204.0800.

2-(2,4-Difluoro-3-methoxyphenyl)ethan-1,1-*d*₂-1-amine hydrochloride (2t):



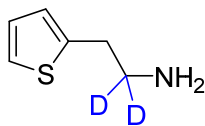
The title product was prepared according to the general procedure A and isolated as white solid about 40.5 mg (90%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 7.32 – 6.71 (m, 2H), 3.87 (s, 3H), 2.91 (q, $J = 8.7, 6.0$ Hz, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 155.9, 155.9, 155.6, 155.5, 153.5, 153.4, 153.1, 153.1, 136.5, 136.4, 136.2, 124.8, 124.7, 124.7, 124.6, 122.1, 122.0, 112.7, 112.7, 112.5, 112.5, 62.3, 62.3, 62.3, 26.4.

HRMS (ESI-TOF) m/z : $[\text{C}_9\text{H}_9\text{D}_2\text{F}_2\text{NO} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{10}\text{D}_2\text{F}_2\text{NO}$: 190.1012, found: 190.1007.

2-(Thiophen-2-yl)ethan-1,1-*d*₂-1-amine hydrochloride (2u):



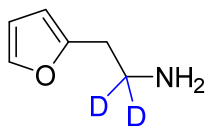
The title product was prepared according to the general procedure A and isolated as white solid about 30.3 mg (92%).

¹H NMR (500 MHz, D₂O) δ 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.95 (dq, *J* = 3.4, 1.0 Hz, 1H), 3.15 (s, 2H).

¹³C NMR (126 MHz, D₂O) δ 138.5, 127.6, 126.7, 125.4, 26.7.

HRMS (ESI-TOF) *m/z*: [C₆H₇D₂NS + H]⁺ calcd for C₆H₈D₂NS: 130.0659, found: 130.0654.

2-(Furan-2-yl)ethan-1,1-*d*₂-1-amine hydrochloride (2v):



The title product was prepared according to the general procedure A and isolated as white solid about 28.3 mg (95%).

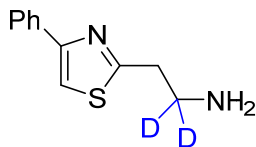
¹H NMR (400 MHz, DMSO-*D*₆) δ 8.07 (d, *J* = 48.8 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.36 (dt, *J* = 3.7, 1.9 Hz, 1H), 6.22 (t, *J* = 2.5 Hz, 1H), 2.92 (d, *J* = 5.9 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 151.4, 142.7, 111.1, 107.2, 26.1, 26.0, 25.9, 25.9.

HRMS (ESI-TOF) *m/z*: [C₆H₇D₂NO + H]⁺ calcd for C₆H₈D₂NO: 114.0888, found: 114.0882.

2-(4-Phenylthiazol-2-yl)ethan-1,1-*d*₂-1-amine hydrochloride (2w):

The title product was prepared according to the general procedure A and isolated as white solid about 46.46 mg (95%).

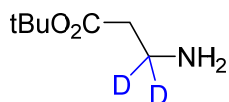


¹H NMR (400 MHz, DMSO-*D*₆) δ 7.95 – 7.84 (m, 3H), 7.39 (td, *J* = 7.7, 1.7 Hz, 2H), 7.29 (td, *J* = 7.2, 1.4 Hz, 1H), 3.03 (s, 2H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 169.5, 154.2, 134.8, 129.3, 128.4, 126.5, 114.1, 37.4.

HRMS (ESI-TOF) *m/z*: [C₁₁H₁₀D₂N₂S + H]⁺ calcd for C₁₁H₁₁D₂N₂S: 207.0925, found: 207.0920.

***tert*-Butyl 3-aminopropanoate-3,3-*d*₂ hydrochloride (2x):**



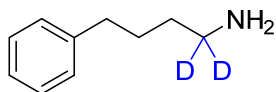
The title product was prepared according to the general procedure A and isolated as colorless oil about 30 mg (82%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 8.13 – 7.86 (m, 3H), 2.56 (s, 2H), 1.38 (s, 9H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 170.1, 81.3, 32.7, 28.3.

HRMS (ESI-TOF) *m/z*: [C₇H₁₃D₂NO₂ + H]⁺ calcd for C₇H₁₄D₂NO₂: 148.1307, found: 148.1301.

4-Phenylbutan-1,1-*d*₂-1-amine hydrochloride (2y):

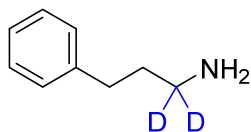


The title product was prepared according to the general procedure A and isolated as white solid about 35.5 mg (95%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 8.04 (d, *J* = 17.8 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.05 (m, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.64 – 1.47 (m, 3H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 142.3, 128.9, 128.8, 126.3, 35.1, 28.2, 26.9, 26.9, 26.8.

3-Phenylpropan-1,1-*d*₂-1-amine hydrochloride (2z):

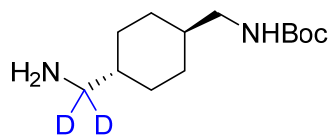


The title product was prepared according to the general procedure A and isolated as white solid about 35.5 mg (95%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 7.29 – 7.23 (m, 2H), 7.16 (dd, *J* = 12.1, 7.4 Hz, 3H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.95 – 1.75 (m, 2H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 141.5, 129.0, 128.8, 126.6, 32.3, 29.1, 29.0, 28.9.

***tert*-Butyl (((1*r*,4*r*)-4-(aminomethyl-*d*₂)cyclohexyl)methyl)carbamate hydrochloride (2aa):**



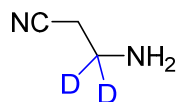
The title product was prepared according to the general procedure A and isolated as white solid about 50.4 mg (90%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 8.10 (t, *J* = 19.5 Hz, 2H), 2.71 (d, *J* = 6.3 Hz, 2H), 1.73 (d, *J* = 12.5 Hz, 2H), 1.64 (d, *J* = 11.8 Hz, 2H), 1.45 (t, *J* = 11.3 Hz, 1H), 1.39 – 1.25 (m, 9H), 1.23 (t, *J* = 6.4 Hz, 1H), 0.82 (dq, *J* = 21.1, 12.5, 11.7 Hz, 4H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 156.3, 77.8, 46.6, 46.4, 38.2, 35.9, 35.9, 35.8, 30.0, 29.8, 28.8.

HRMS (ESI-TOF) *m/z*: [C₁₃H₂₄D₂N₂O₂+ H]⁺ calcd for C₁₃H₂₅D₂N₂O₂: 245.2198, found: 245.2193.

3-Aminopropanenitrile-3,3-*d*₂ hydrochloride (2ab):



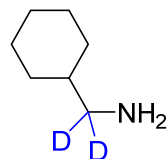
The title product was prepared according to the general procedure A and isolated as white solid about 19 mg (90%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 8.18 (s, 3H), 2.82 (s, 2H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 118.4, 16.0.

HRMS (ESI-TOF) *m/z*: [C₃H₄D₂N₂+ H]⁺ calcd for C₃H₅D₂N₂: 73.0735, found: 73.0729.

Cyclohexylmethan-*d*₂-amine hydrochloride (2ac):



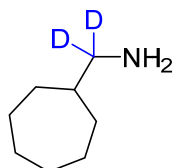
The title product was prepared according to the general procedure A and isolated as brown solid about 26.8 mg (89%).

¹H NMR (400 MHz, DMSO) δ 7.88 (s, 2H), 1.76 – 1.63 (m, 4H), 1.56 – 1.49 (m, 1H), 1.25 – 1.12 (m, 3H), 0.93 (td, *J* = 11.9, 3.1 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 35.7, 35.7, 30.1, 26.1, 25.5.

HRMS (ESI-TOF) m/z : $[\text{C}_7\text{H}_{13}\text{D}_2\text{N} + \text{H}]^+$ calcd for $\text{C}_7\text{H}_{14}\text{D}_2\text{N}$: 116.1408, found: 116.1403.

Cycloheptylmethan- d_2 -amine hydrochloride (2ad):

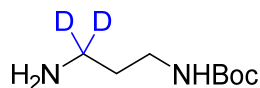


The title product was prepared according to the general procedure A and isolated as brown solid about 28 mg (85%).

^1H NMR (500 MHz, DMSO) δ 7.82 (s, 3H), 1.73 – 1.38 (m, 11H), 1.23 – 1.13 (m, 2H).

^{13}C NMR (126 MHz, DMSO) δ 39.3, 36.6, 31.9, 31.9, 27.8.

***tert*-Butyl (3-aminopropyl-3,3- d_2)carbamate hydrochloride (2ae):**



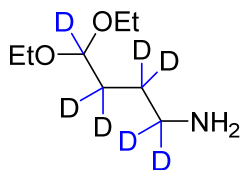
The title product was prepared according to the general procedure A and isolated as white solid about 34.7 mg (82%).

^1H NMR (500 MHz, DMSO) δ 2.98 (d, $J = 6.1$ Hz, 2H), 1.65 (t, $J = 6.8$ Hz, 2H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 156.2, 78.2, 37.3, 28.7, 28.0.

HRMS (ESI-TOF) m/z : $[\text{C}_8\text{H}_{16}\text{D}_2\text{N}_2\text{O}_2 + \text{H}]^+$ calcd for $\text{C}_8\text{H}_{17}\text{D}_2\text{N}_2\text{O}_2$: 177.1572, found: 177.1567.

4,4-Diethoxybutan-1,1,2,2,3,3,4- d_7 -1-amine hydrochloride (2af):



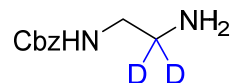
The title product was prepared according to the general procedure A and isolated as colorless oil about 28.5 mg (70%).

^1H NMR (500 MHz, DMSO) δ 3.39 (q, $J = 7.0$ Hz, 4H), 1.24 (s, 2H), 1.13 – 1.04 (m, 6H).

^{13}C NMR (126 MHz, DMSO) δ 65.4, 15.6.

HRMS (ESI-TOF) m/z : $[\text{C}_8\text{H}_{12}\text{D}_7\text{NO}_2 + \text{H}]^+$ calcd for $\text{C}_8\text{H}_{13}\text{D}_7\text{NO}_2$: 169.1933, found: 169.1928.

Benzyl (2-aminoethyl-2,2- d_2)carbamate hydrochloride (2ag):



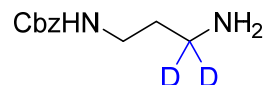
The title product was prepared according to the general procedure A and isolated as white solid about 42.6 mg (92%).

^1H NMR (400 MHz, DMSO- D_6) δ 8.37 – 8.05 (m, 2H), 7.38 – 7.25 (m, 5H), 4.99 (s, 2H), 3.23 (s, 2H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 156.8, 137.5, 128.9, 128.4, 128.3, 66.1, 38.4, 38.4, 38.3, 38.2.

HRMS (ESI-TOF) m/z : $[\text{C}_{10}\text{H}_{12}\text{D}_2\text{N}_2\text{O}_2 + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{D}_2\text{N}_2\text{O}_2$: 197.1259, found: 197.1254.

Benzyl (3-aminopropyl-3,3- d_2)carbamate hydrochloride (2ah):



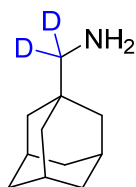
The title product was prepared according to the general procedure A and isolated as white solid about 45.7 mg (93%).

^1H NMR (400 MHz, DMSO- D_6) δ 8.11 (t, J = 18.7 Hz, 1H), 7.30 (q, J = 7.3 Hz, 5H), 4.98 (s, 2H), 3.02 (t, J = 6.4 Hz, 2H), 1.67 (t, J = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 156.7, 137.7, 128.9, 128.3, 128.3, 65.8, 37.9, 37.8, 27.9, 27.8, 27.8, 27.7.

HRMS (ESI-TOF) m/z : $[\text{C}_{11}\text{H}_{14}\text{D}_2\text{N}_2\text{O}_2 + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{15}\text{D}_2\text{N}_2\text{O}_2$: 211.1416, found: 211.1410.

Adamantan-1-ylmethan- d_2 -amine hydrochloride (2ai):

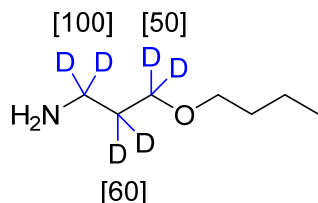


The title product was prepared according to the general procedure A and isolated as white solid about 36.5 mg (90%).

^1H NMR (500 MHz, DMSO) δ 8.16 – 7.74 (m, 2H), 1.96 (q, J = 3.3 Hz, 3H), 1.81 – 1.54 (m, 8H), 1.52 (d, J = 2.9 Hz, 4H).

^{13}C NMR (126 MHz, DMSO) δ 39.3, 36.6, 31.9, 27.8.

3-Butoxypropan-1,1,2,2,3,3- d_6 -1-amine hydrochloride (2aj):



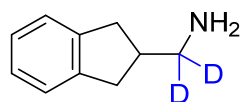
The title product was prepared according to the general procedure A and isolated as colorless oil about 28.3 mg (82%).

^1H NMR (400 MHz, CHLOROFORM- D) δ 3.56 (dd, J = 8.0, 3.2 Hz, 1H), 3.42 (tt, J = 9.6, 4.8 Hz, 2H), 2.03 (t, J = 5.8 Hz, 1H), 1.52 (q, J = 7.1 Hz, 2H), 1.39 – 1.30 (m, 2H), 1.25 (d, J = 7.0 Hz, 2H), 0.91 (td, J = 7.4, 1.6 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM- D) δ 71.4, 69.1, 31.7, 29.8, 19.4, 17.8, 14.0.

HRMS (ESI-TOF) m/z : [$\text{C}_7\text{H}_{11}\text{D}_6\text{NO} + \text{H}$] $^+$ calcd for $\text{C}_7\text{H}_{12}\text{D}_6\text{NO}$: 138.1765, found: 138.1760.

(2,3-Dihydro-1H-inden-2-yl)methan- d_2 -amine hydrochloride: (2ak):



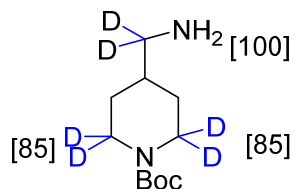
The title product was prepared according to the general procedure A and isolated as white solid about 33.3 mg (90%).

^1H NMR (400 MHz, DMSO- D_6) δ 8.25 (d, J = 18.8 Hz, 2H), 7.16 (p, J = 4.4 Hz, 2H), 7.08 (dq, J = 4.7, 2.9, 1.7 Hz, 2H), 2.98 (q, J = 9.8 Hz, 2H), 2.68 (dd, J = 9.1, 5.0 Hz, 3H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 142.5, 126.9, 124.9, 37.8, 36.8.

HRMS (ESI-TOF) m/z : [$\text{C}_{10}\text{H}_{11}\text{D}_2\text{N} + \text{H}$] $^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{D}_2\text{N}$: 150.1252, found: 150.1246.

***tert*-Butyl 4-(aminomethyl-*d*₂)piperidine-1-carboxylate-2,2,6,6-*d*₄ hydrochloride (2al):**



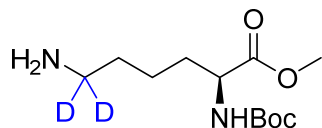
The title product was prepared according to the general procedure A and isolated as white solid about 45 mg (88%).

¹H NMR (400 MHz, DMSO-*D*₆) δ 8.08 (d, *J* = 40.5 Hz, 3H), 3.85 (s, 2H), 1.68 (ddd, *J* = 27.7, 12.0, 5.4 Hz, 3H), 1.35 (d, *J* = 1.6 Hz, 9H), 1.04 – 0.93 (m, 2H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 154.3, 79.1, 34.0, 29.2, 28.6.

HRMS (ESI-TOF) *m/z*: [C₁₁H₁₆D₆N₂O₂+ H]⁺ calcd for C₁₁H₁₇D₆N₂O₂: 211.2136, found: 211.2130.

Methyl (*tert*-butoxycarbonyl)-*L*-lysinate-6,6-*d*₂ hydrochloride (2am):



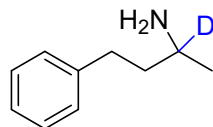
The title product was prepared according to the general procedure A and isolated as white solid about 47.7 mg (80%).

¹H NMR (400 MHz, CHLOROFORM-*D*) δ 5.06 (dd, *J* = 26.2, 7.9 Hz, 1H), 4.28 (d, *J* = 9.1 Hz, 1H), 3.72 (d, *J* = 1.5 Hz, 3H), 2.08 (s, 2H), 1.86 – 1.73 (m, 1H), 1.62 (dt, *J* = 13.6, 7.0 Hz, 1H), 1.43 (s, 9H), 1.36 (q, *J* = 7.6, 7.2 Hz, 2H).

¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 173.4, 155.5, 80.0, 53.4, 52.4, 32.7, 29.8, 28.0, 23.1, 22.6.

HRMS (ESI-TOF) *m/z*: [C₁₂H₂₂D₂N₂O₄+ H]⁺ calcd for C₁₂H₂₃D₂N₂O₄: 263.1940, found: 263.1934.

4-Phenylbutan-2-*d*₂-amine hydrochloride (2an):

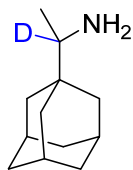


The title product was prepared according to the general procedure B and isolated as white solid about 35.7 mg (96%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 8.41 – 7.85 (m, 2H), 7.32 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 2.71 – 2.53 (m, 2H), 1.96 – 1.80 (m, 1H), 1.70 (dtd, $J = 13.9, 6.5, 3.1$ Hz, 1H), 1.19 (d, $J = 1.8$ Hz, 3H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 141.6, 129.0, 128.8, 126.5, 36.3, 36.2, 36.2, 31.3, 18.4, 18.4, 18.3.

1-(Adamantan-1-yl)ethan-1-*d*-1-amine hydrochloride (2ao):

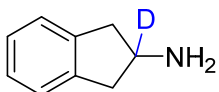


The title product was prepared according to the general procedure B and isolated as white solid about 38.9 mg (90%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 7.92 (d, $J = 20.0$ Hz, 2H), 1.97 – 1.87 (m, 3H), 1.63 (d, $J = 12.4$ Hz, 3H), 1.50 (dt, $J = 25.1, 12.1$ Hz, 9H), 1.06 (d, $J = 1.7$ Hz, 3H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 37.6, 36.7, 34.5, 34.5, 34.5, 28.0, 13.1, 13.1, 13.0.

2,3-Dihydro-1*H*-inden-2-*d*-2-amine hydrochloride (2ap):



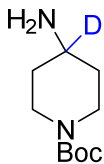
The title product was prepared according to the general procedure B and isolated as white solid about 32.6 mg (96%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 8.43 (s, 2H), 7.23 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.15 (dt, $J = 5.2, 2.1$ Hz, 2H), 3.21 (d, $J = 16.4$ Hz, 2H), 2.97 (d, $J = 16.3$ Hz, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 140.4, 127.4, 125.2, 37.7.

HRMS (ESI-TOF) m/z : $[\text{C}_{10}\text{H}_{11}\text{D}_2\text{N} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{D}_2\text{N}$: 150.1252, found: 150.1246.

***tert*-Butyl 4-aminopiperidine-1-carboxylate-4-*d* hydrochloride (2aq):**



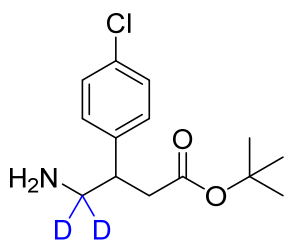
The title product was prepared according to the general procedure B and isolated as white solid about 43.1 mg (91%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 8.07 (s, 3H), 3.89 (d, $J = 13.7$ Hz, 2H), 2.74 (s, 2H), 1.83 (d, $J = 12.6$ Hz, 2H), 1.36 (d, $J = 1.7$ Hz, 10H), 1.31 (dd, $J = 12.8, 4.3$ Hz, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 154.3, 79.5, 41.5, 29.8, 28.6.

HRMS (ESI-TOF) m/z : $[\text{C}_{10}\text{H}_{19}\text{DN}_2\text{O}_2 + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{20}\text{DN}_2\text{O}_2$: 202.1666, found: 202.1660.

***tert*-Butyl 4-amino-3-(4-chlorophenyl)butanoate-4,4- d_2 hydrochloride (2ar):**



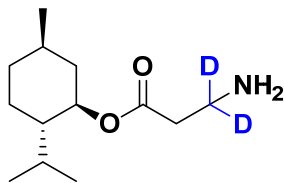
The title product was prepared according to the general procedure A and isolated as white solid about 55.2 mg (90%).

^1H NMR (400 MHz, $\text{DMSO-}D_6$) δ 8.05 (s, 3H), 7.36 (dd, $J = 8.5, 2.0$ Hz, 2H), 7.31 (dd, $J = 8.5, 2.0$ Hz, 2H), 3.33 – 3.26 (m, 1H), 2.79 (ddd, $J = 15.7, 5.3, 1.9$ Hz, 1H), 2.53 – 2.47 (m, 1H), 1.18 (d, $J = 1.9$ Hz, 9H).

^{13}C NMR (101 MHz, $\text{DMSO-}D_6$) δ 170.5, 139.4, 132.4, 130.6, 129.0, 80.5, 39.4, 39.3, 28.1.

HRMS (ESI-TOF) m/z : $[\text{C}_{14}\text{H}_{18}\text{D}_2\text{ClNO}_2 + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{D}_2\text{ClNO}_2$: 272.1386, found: 272.1381.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 3-aminopropanoate-3,3- d_2 (2as):



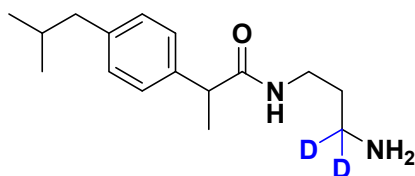
The title product was prepared according to the general procedure A and isolated as white solid about 46.6 mg (88%).

^1H NMR (400 MHz, CHLOROFORM- D) δ 4.71 – 4.67 (m, 1H), 2.52 (s, 2H), 1.95 (d, J = 6.9 Hz, 2H), 1.81 (q, J = 7.2 Hz, 1H), 1.71 – 1.62 (m, 2H), 1.46 (dtt, J = 12.0, 6.1, 3.1 Hz, 1H), 1.41 – 1.31 (m, 1H), 1.07 – 0.93 (m, 2H), 0.92 – 0.82 (m, 7H), 0.73 (dd, J = 7.0, 1.9 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM- D) δ 171.9, 74.8, 47.0, 41.0, 34.3, 31.5, 26.4, 23.5, 22.1, 20.8, 16.4.

HRMS (ESI-TOF) m/z : $[\text{C}_{13}\text{H}_{23}\text{D}_2\text{NO}_2 + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{24}\text{D}_2\text{NO}_2$: 230.2089, found: 230.2084.

***N*-(3-Aminopropyl-3,3- d_2)-2-(4-isobutylphenyl)propanamide (2at):**



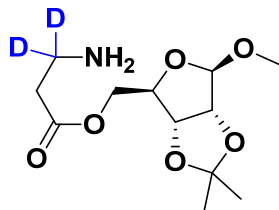
The title product was prepared according to the general procedure A and isolated as white solid about 55.2 mg (92%).

^1H NMR (400 MHz, DMSO- D_6) δ 7.84 (t, J = 6.0 Hz, 1H), 7.16 (dd, J = 8.1, 2.0 Hz, 2H), 7.02 (dd, J = 8.1, 2.1 Hz, 2H), 3.59 – 3.42 (m, 1H), 3.01 (p, J = 6.7 Hz, 2H), 2.35 (dd, J = 7.1, 2.1 Hz, 2H), 1.75 (dtt, J = 14.3, 7.7, 3.8 Hz, 1H), 1.36 (t, J = 7.0 Hz, 2H), 1.25 (dd, J = 7.0, 2.0 Hz, 3H), 0.81 (dd, J = 6.7, 2.0 Hz, 6H).

^{13}C NMR (101 MHz, DMSO- D_6) δ 173.8, 140.2, 139.7, 129.3, 127.4, 45.3, 44.8, 36.7, 33.3, 30.2, 22.7, 19.2.

HRMS (ESI-TOF) m/z : $[\text{C}_{16}\text{H}_{24}\text{D}_2\text{N}_2\text{O} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{25}\text{D}_2\text{N}_2\text{O}$: 265.2249, found: 265.2243.

((3*aR*,4*R*,6*R*,6*aR*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4- d][1,3]dioxol-4-yl)methyl 3-aminopropanoate-3,3- d_2 (2au):



The title product was prepared according to the general procedure A and isolated as white solid about 50 mg (80%).

^1H NMR (400 MHz, CHLOROFORM-*D*) δ 4.96 (d, J = 3.3 Hz, 1H), 4.87 – 4.75 (m, 1H), 4.63 – 4.53 (m, 1H), 4.43 (d, J = 3.3 Hz, 1H), 3.67 (s, 1H), 3.62 (d, J = 3.4 Hz, 1H), 3.43 (d, J = 3.2 Hz, 3H), 3.31 (d, J = 3.4 Hz, 1H), 1.47 (s, 3H), 1.31 (s, 3H).

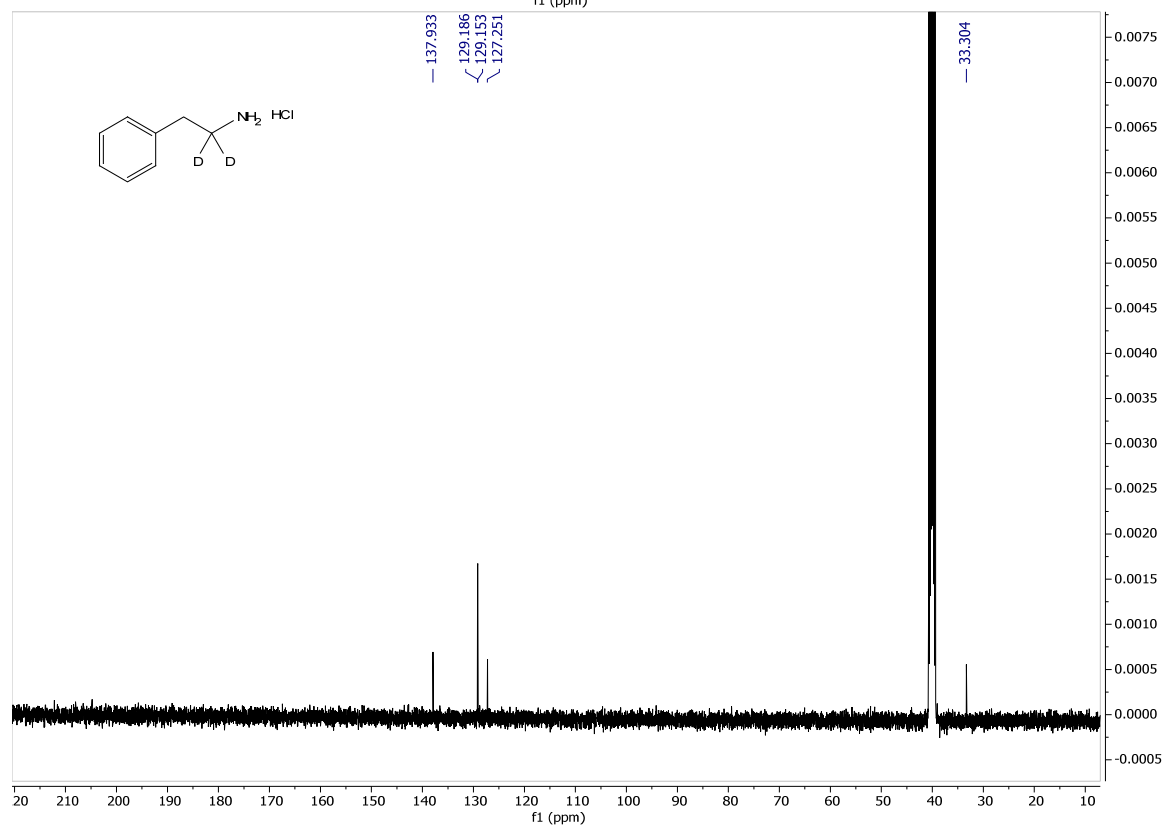
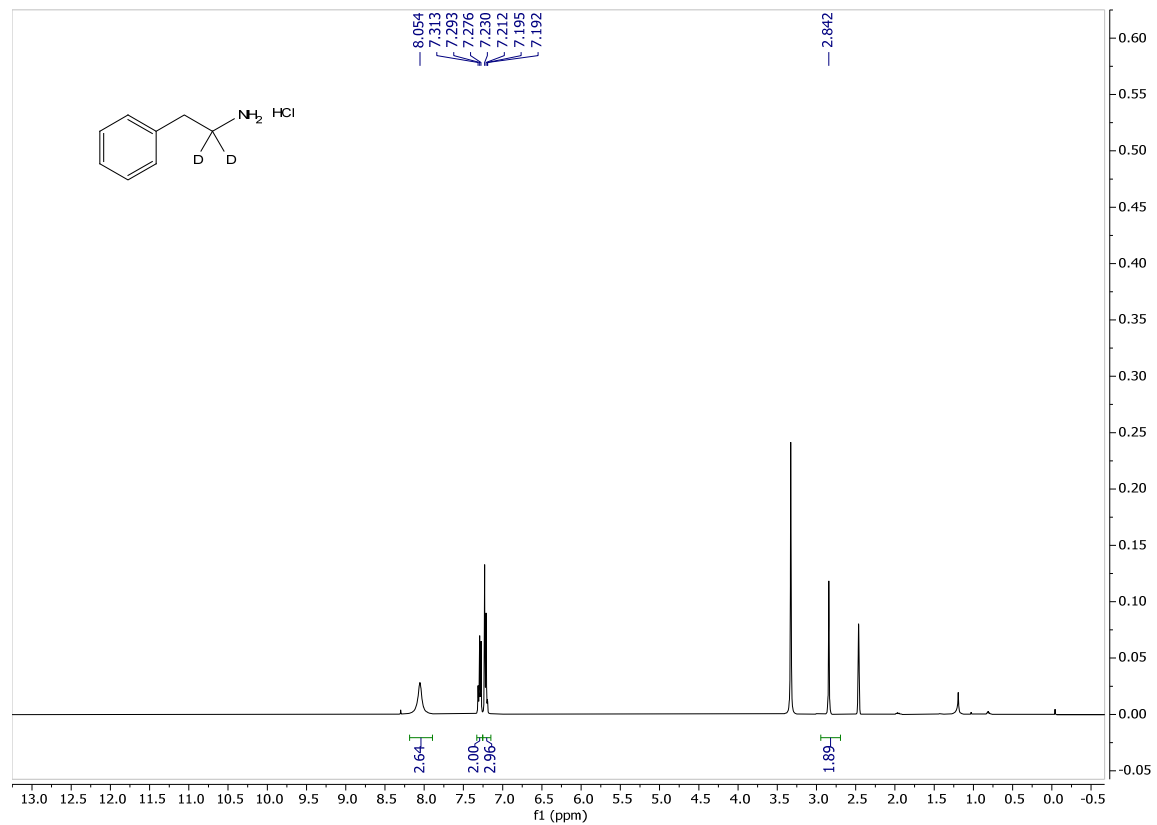
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 169.0, 110.1, 110.0, 88.5, 85.9, 81.6, 64.1, 55.6, 33.6, 26.4, 24.9, 24.8.

HRMS (ESI-TOF) m/z : $[\text{C}_{12}\text{H}_{19}\text{D}_2\text{NO}_6 + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{20}\text{D}_2\text{NO}_6$: 278.1573, found: 278.1567.

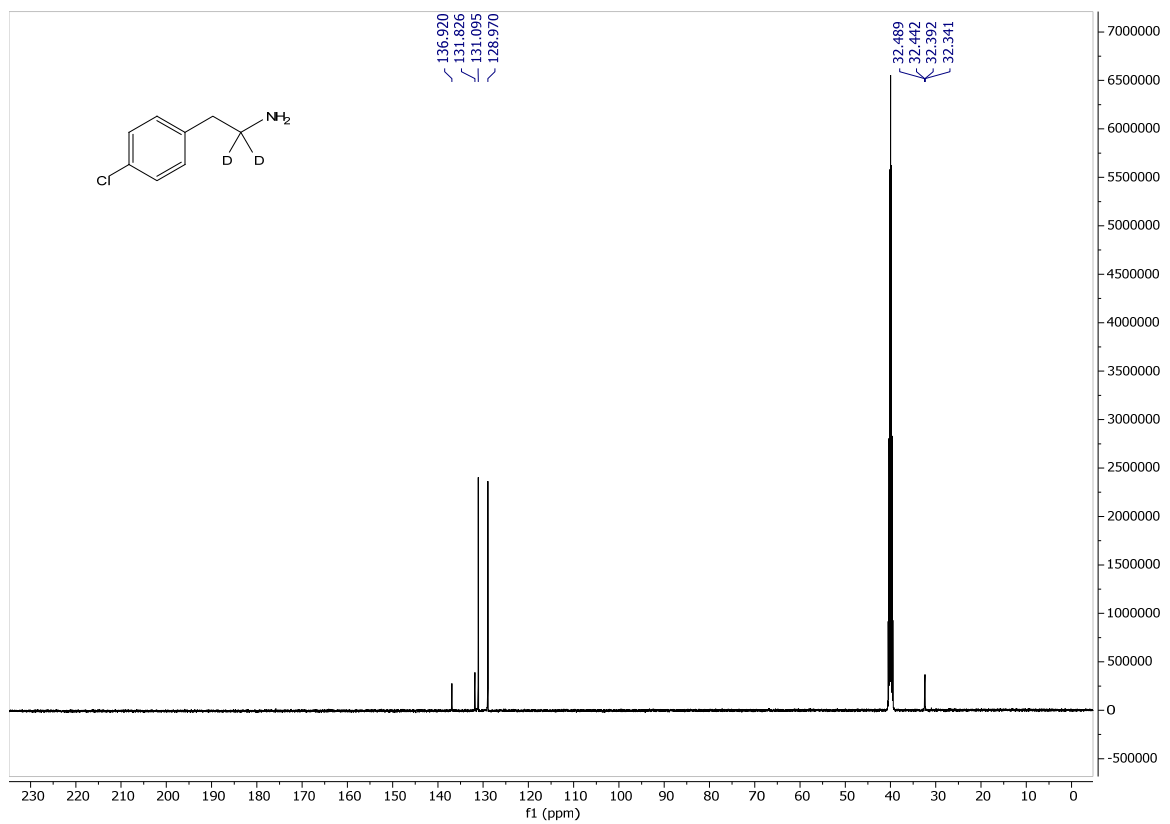
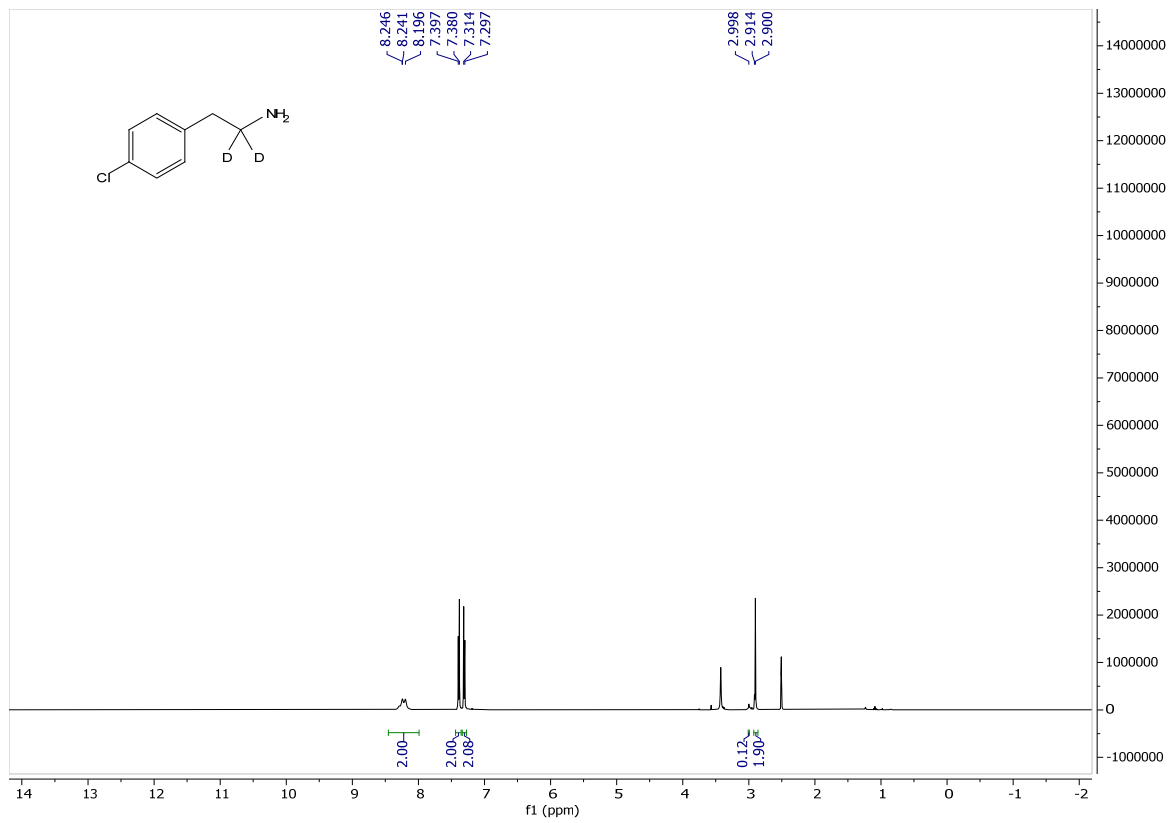
5. References

1. Y. Ding, S. Luo, A. Adijiang, H. Zhao and J. An, *J. Org. Chem.*, 2018, **83**, 12269-12274.
2. Y. Ding, S. Luo, C. Weng and J. An, *J. Org. Chem.*, 2019, **84**, 15098-15105.
3. L. Ning, H. Li, Z. Lai, M. Szostak, X. Chen, Y. Dong, S. Jin and J. An, *J. Org. Chem.*, 2021, **86**, 2907-2916.
4. S. Luo, C. Weng, Z. Qin, K. Li, T. Zhao, Y. Ding, C. Ling, Y. Ma and J. An, *J. Org. Chem.*, 2021, **86**, 11862-11870.

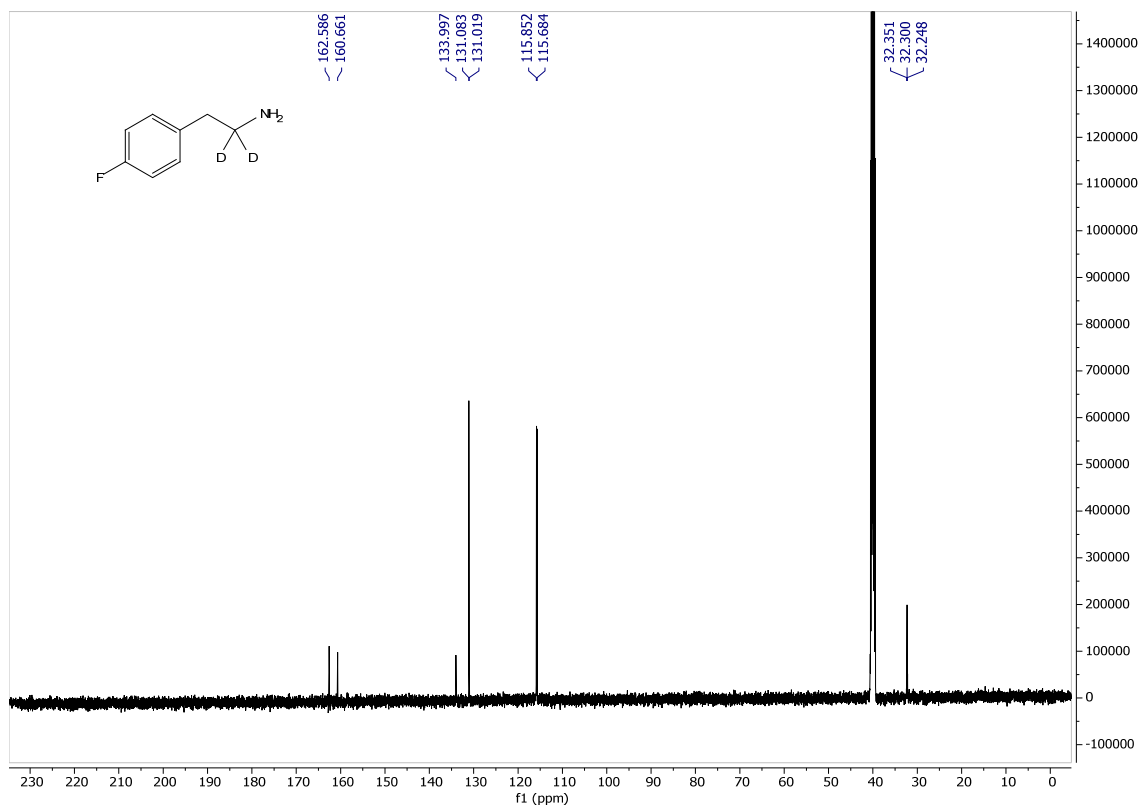
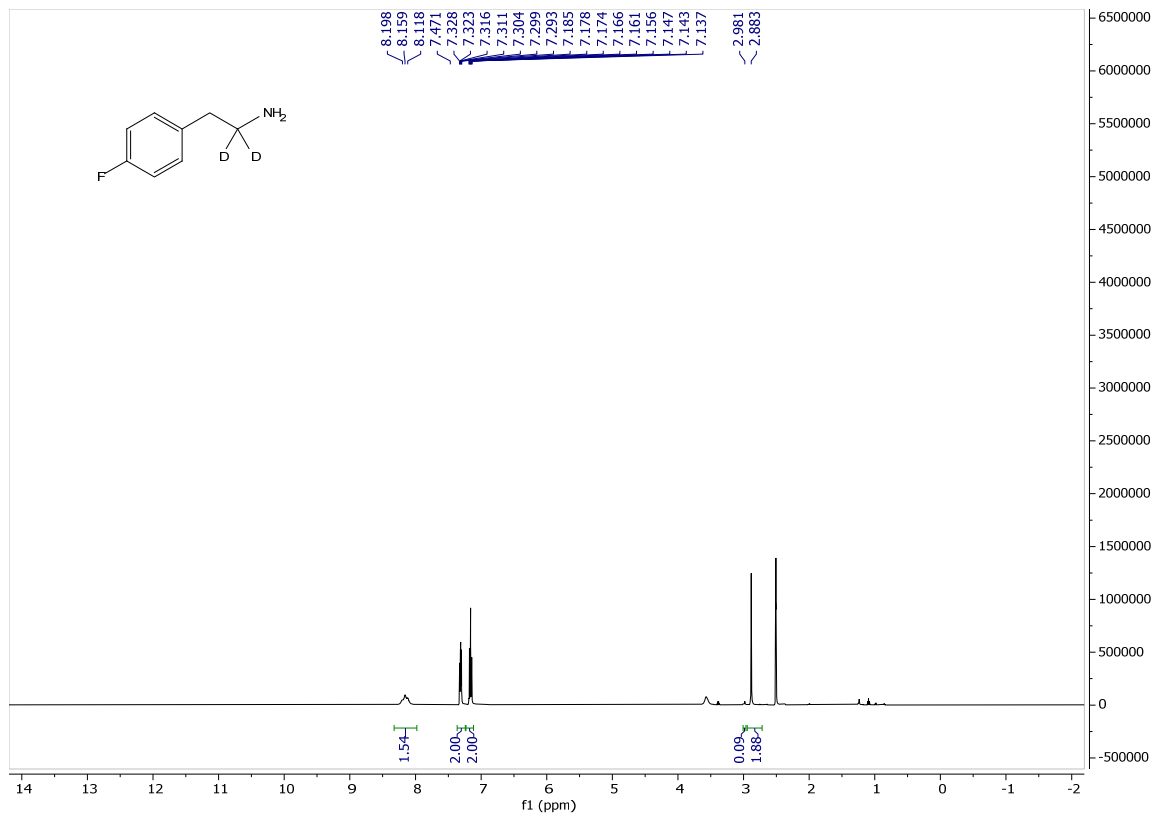
6. ^1H and ^{13}C NMR Spectra 2a



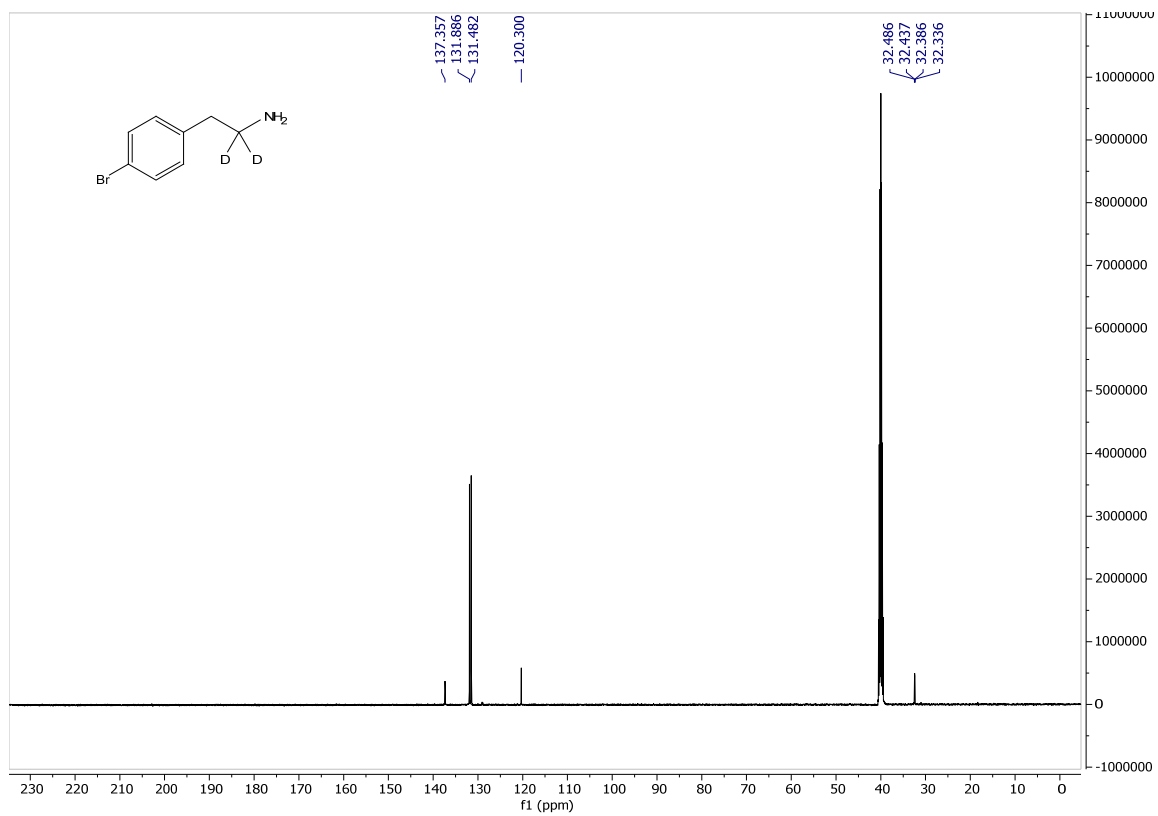
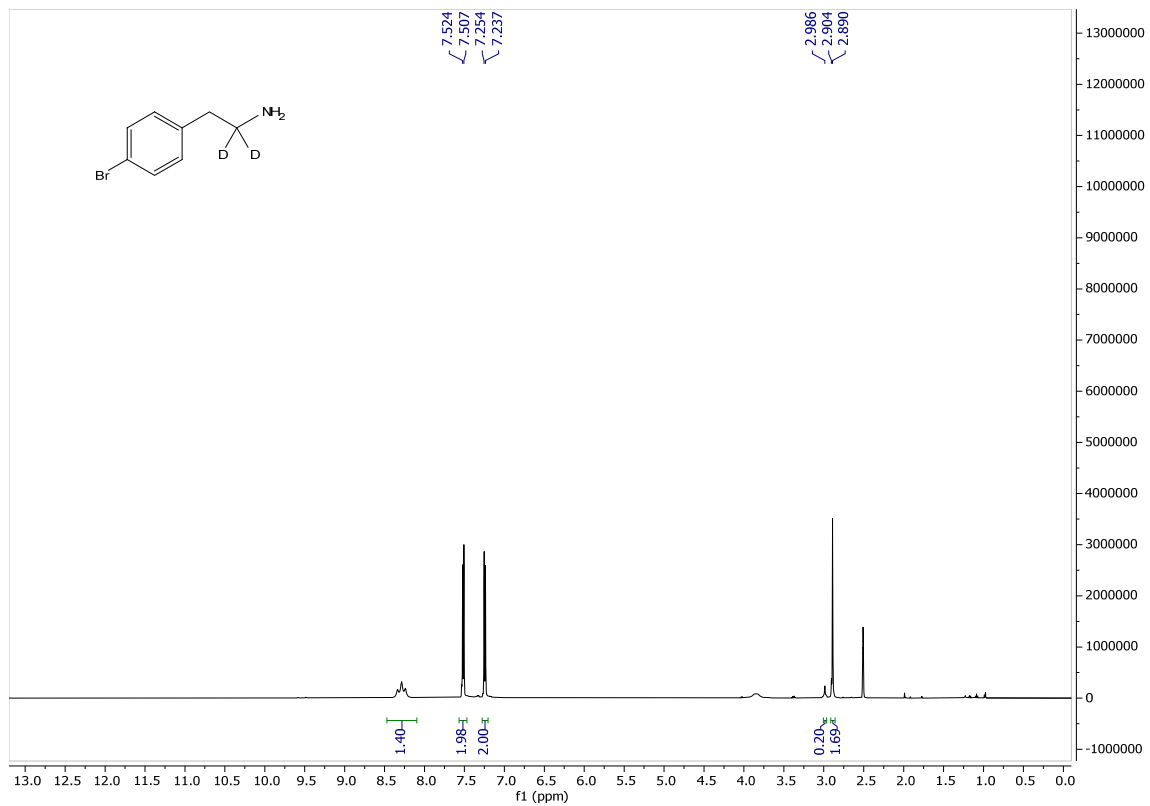
2b



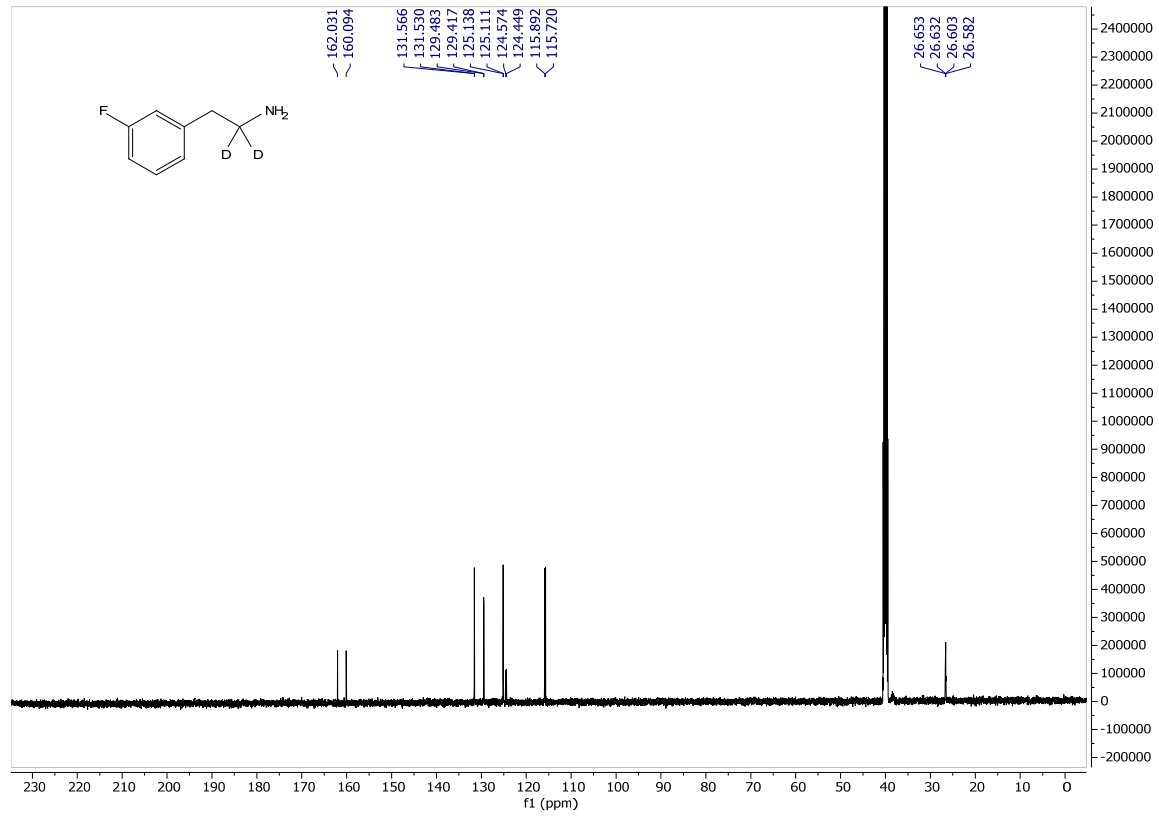
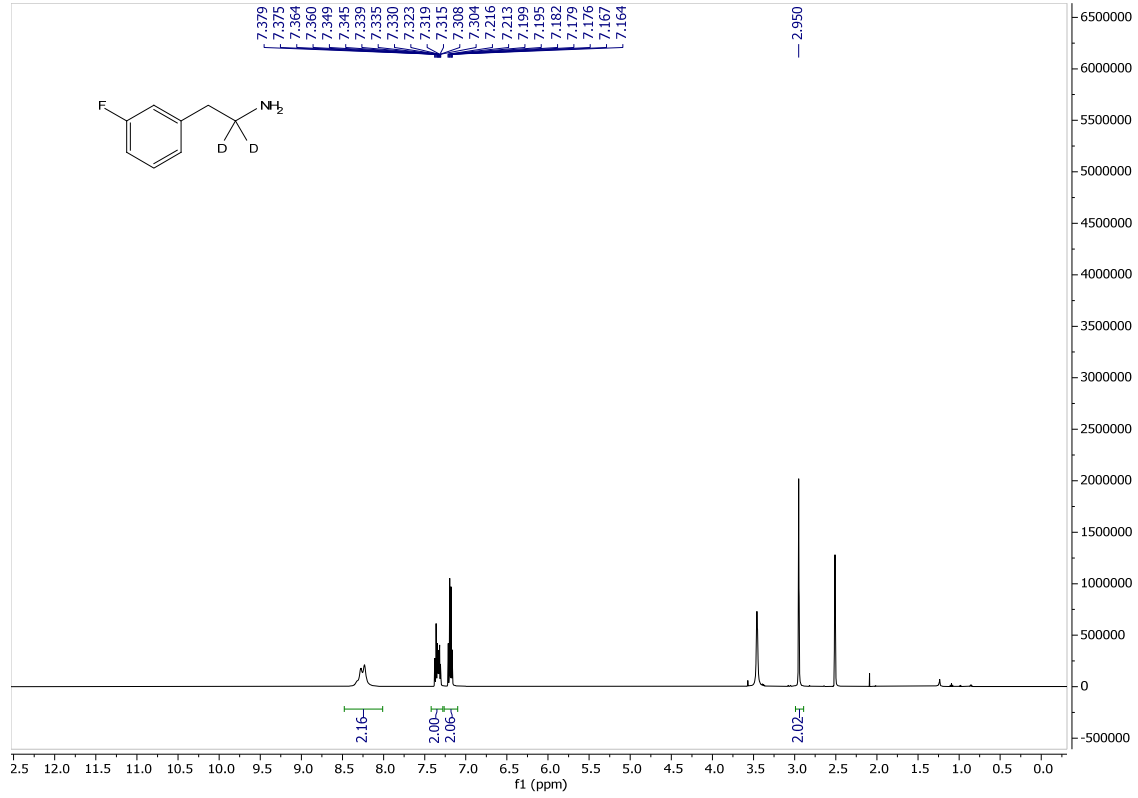
2c



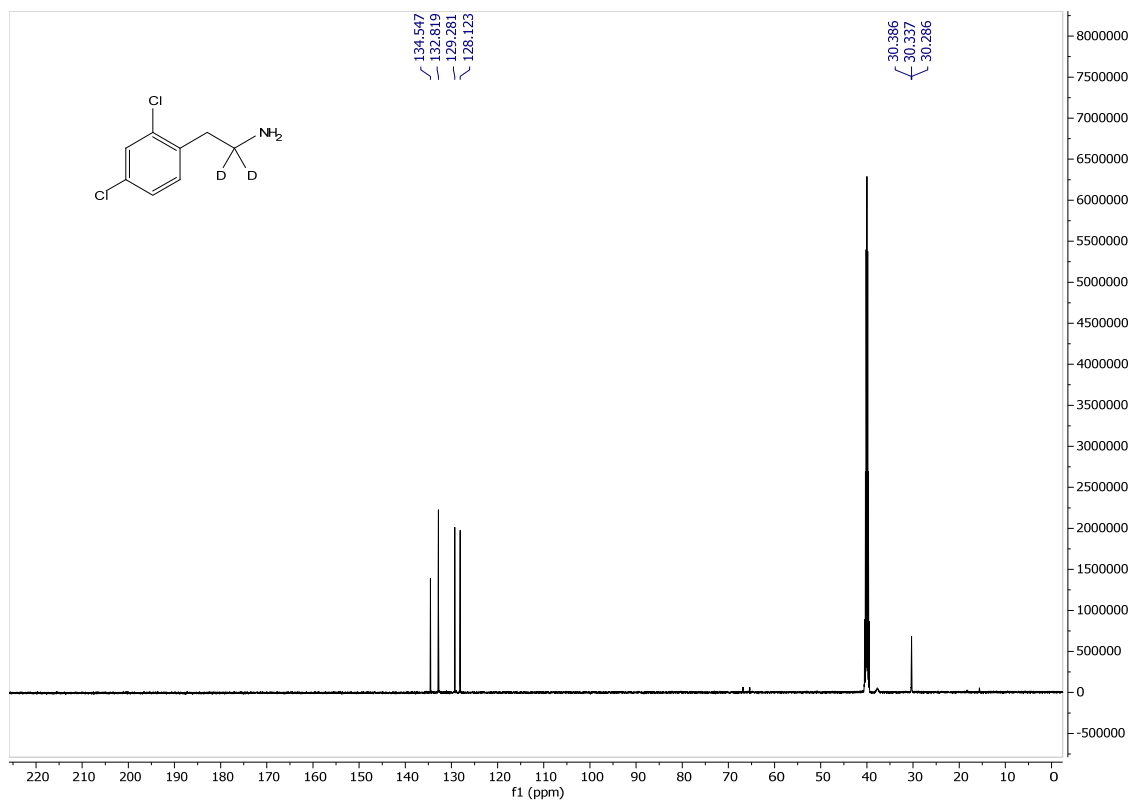
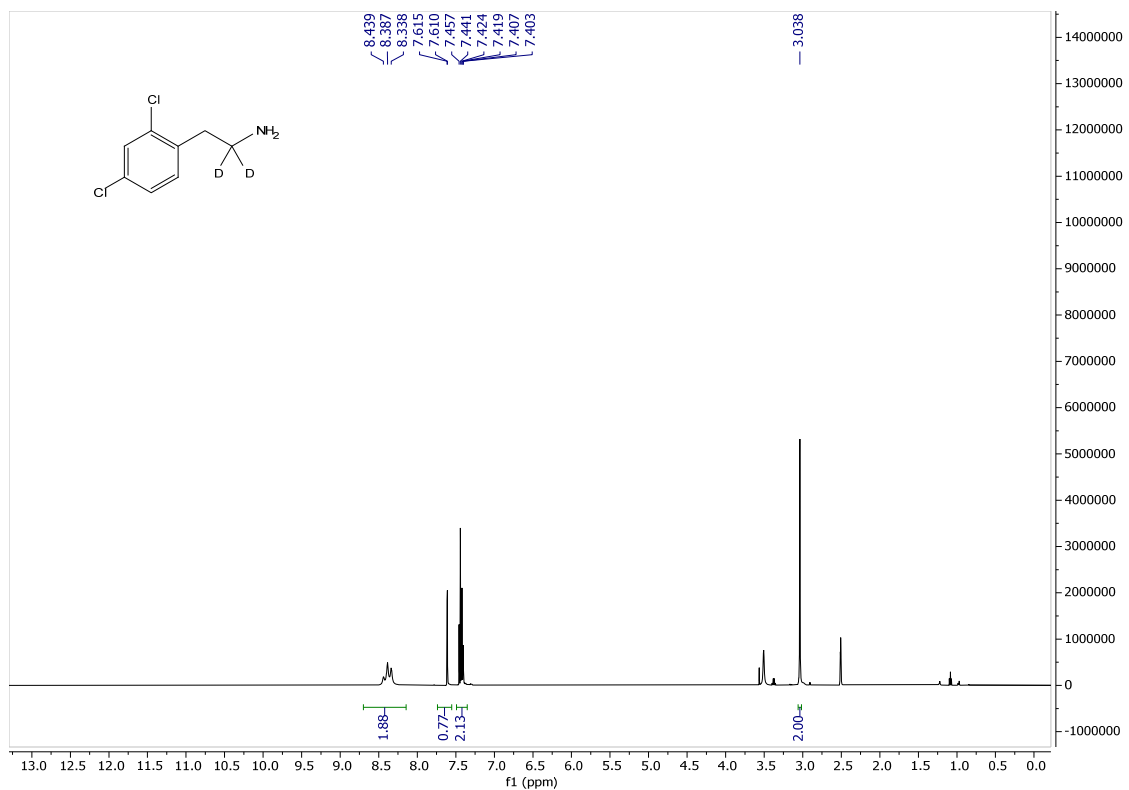
2d



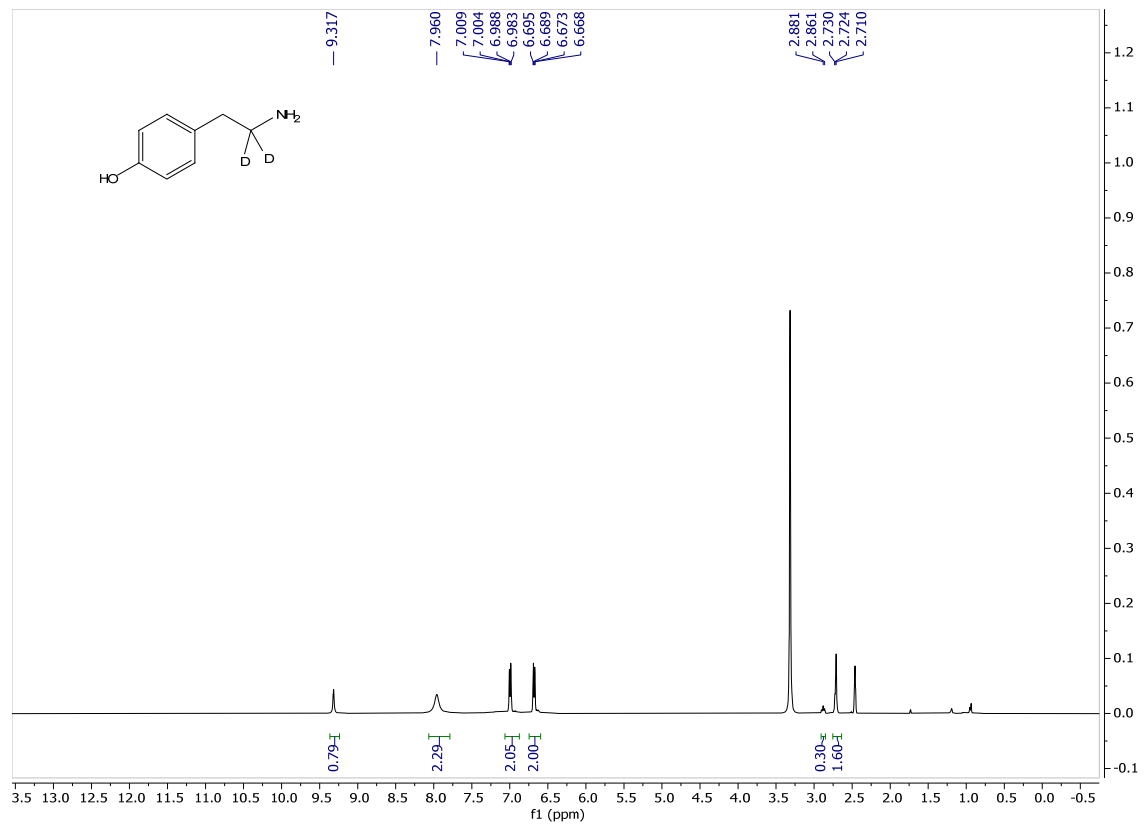
2e

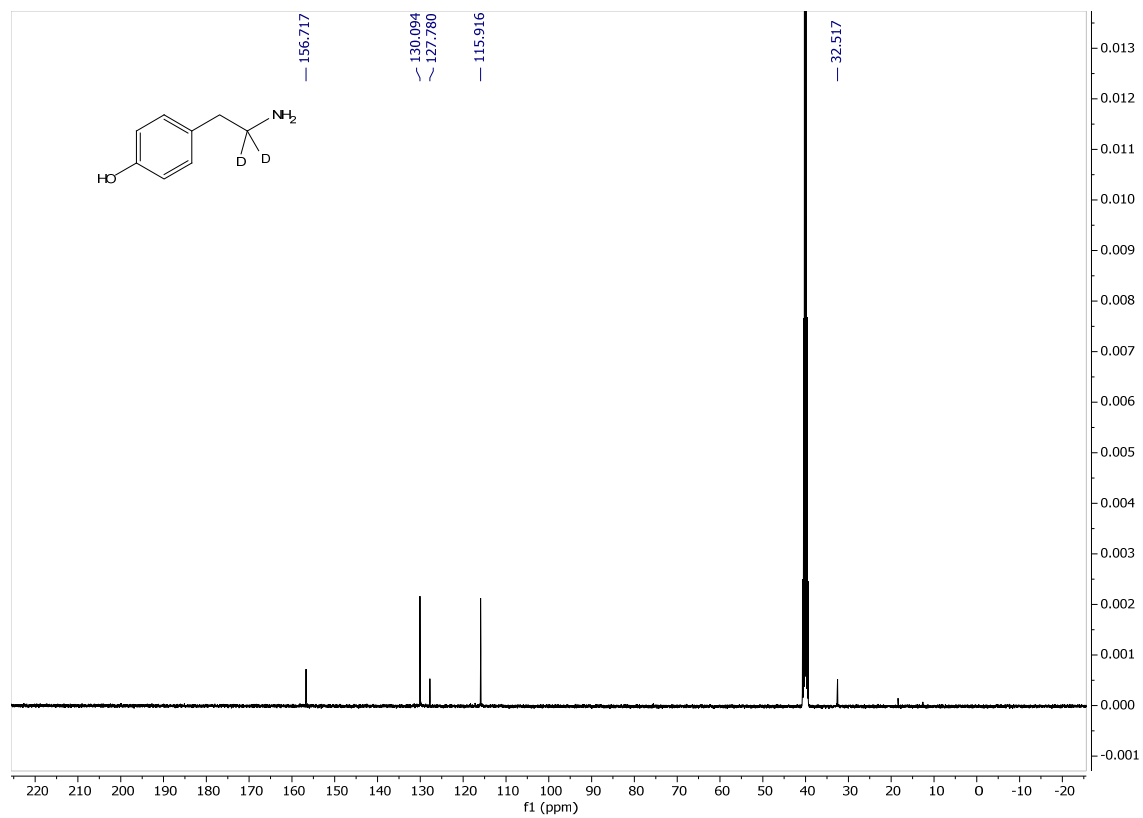


2f

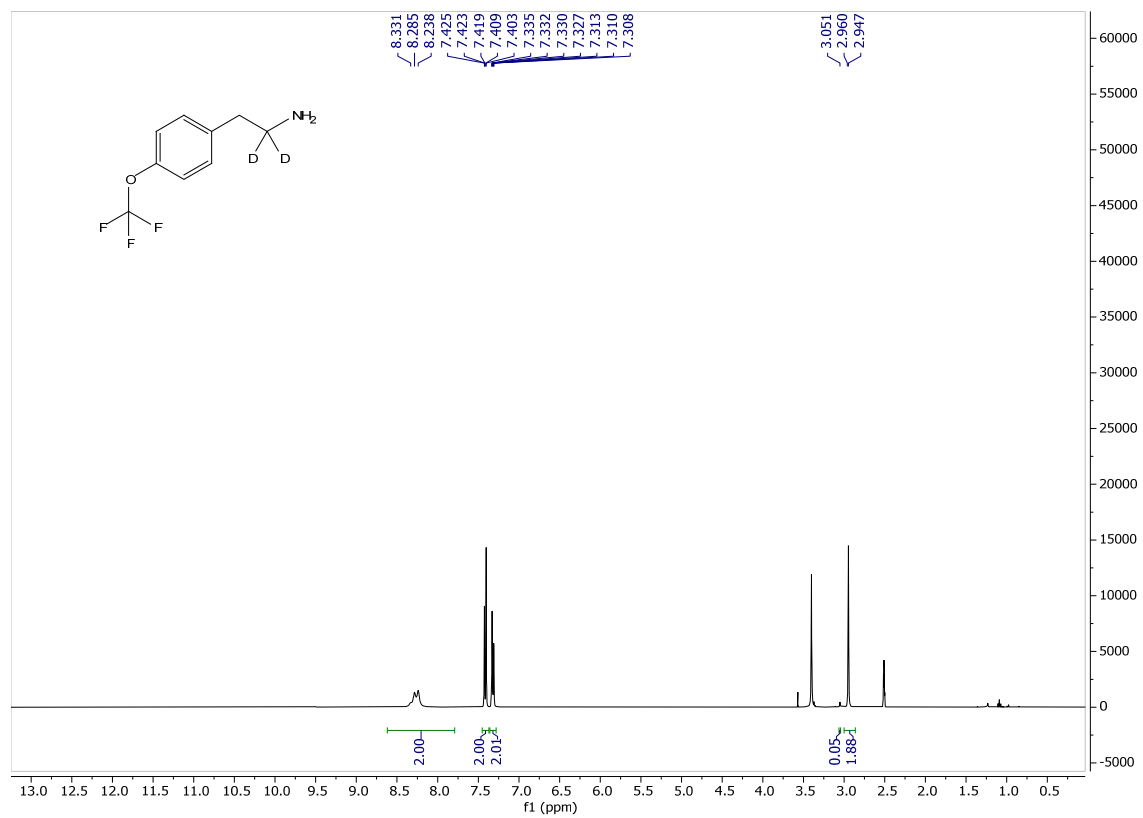


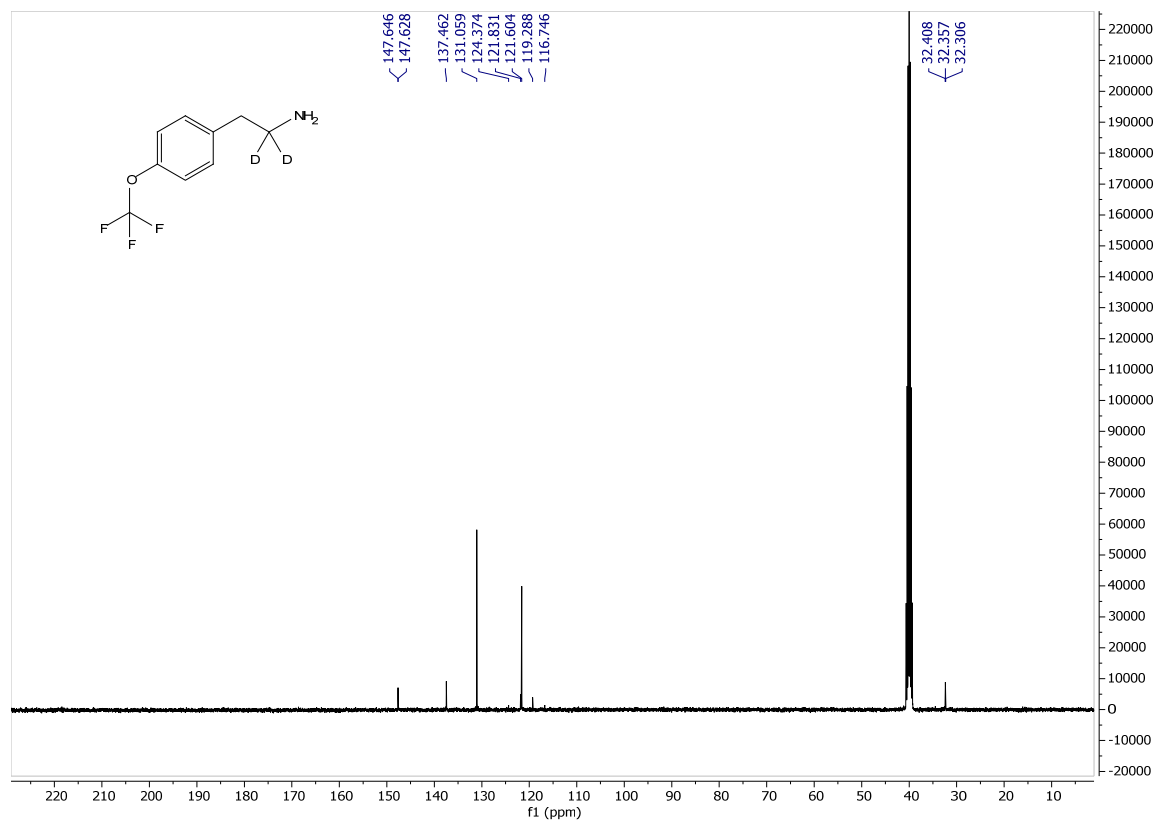
2g



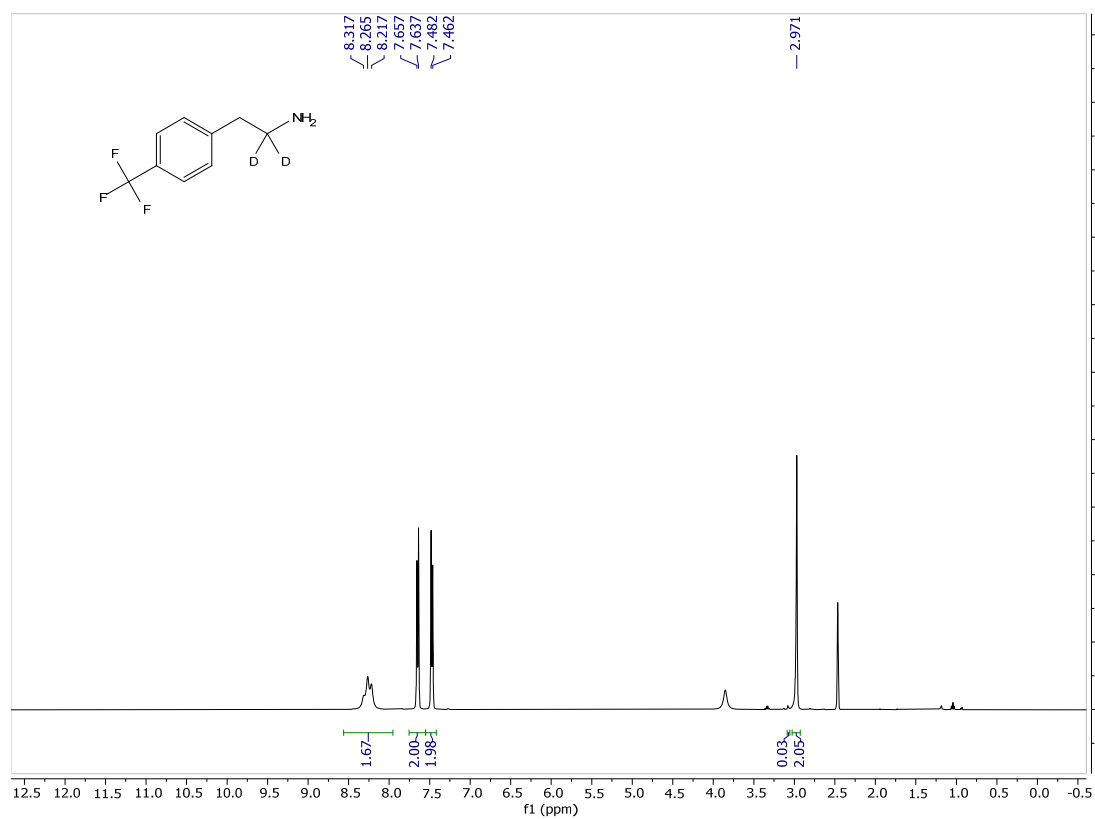


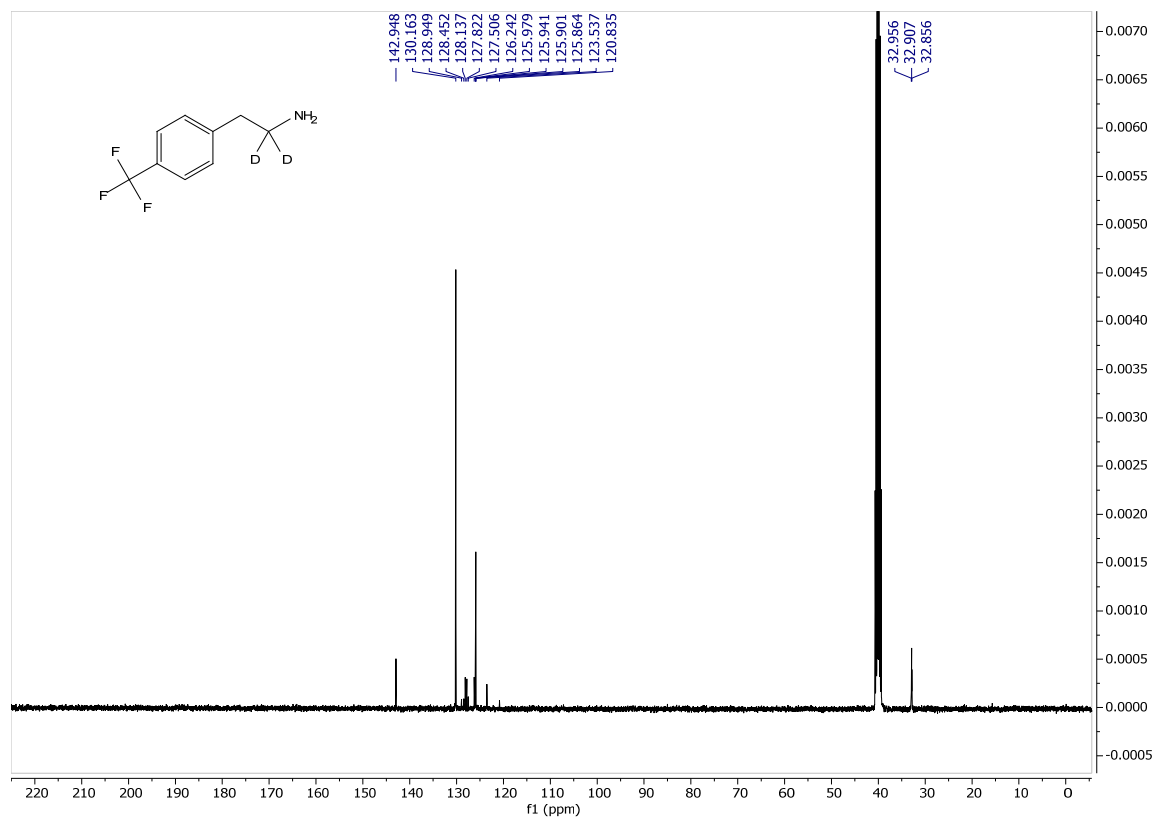
2h



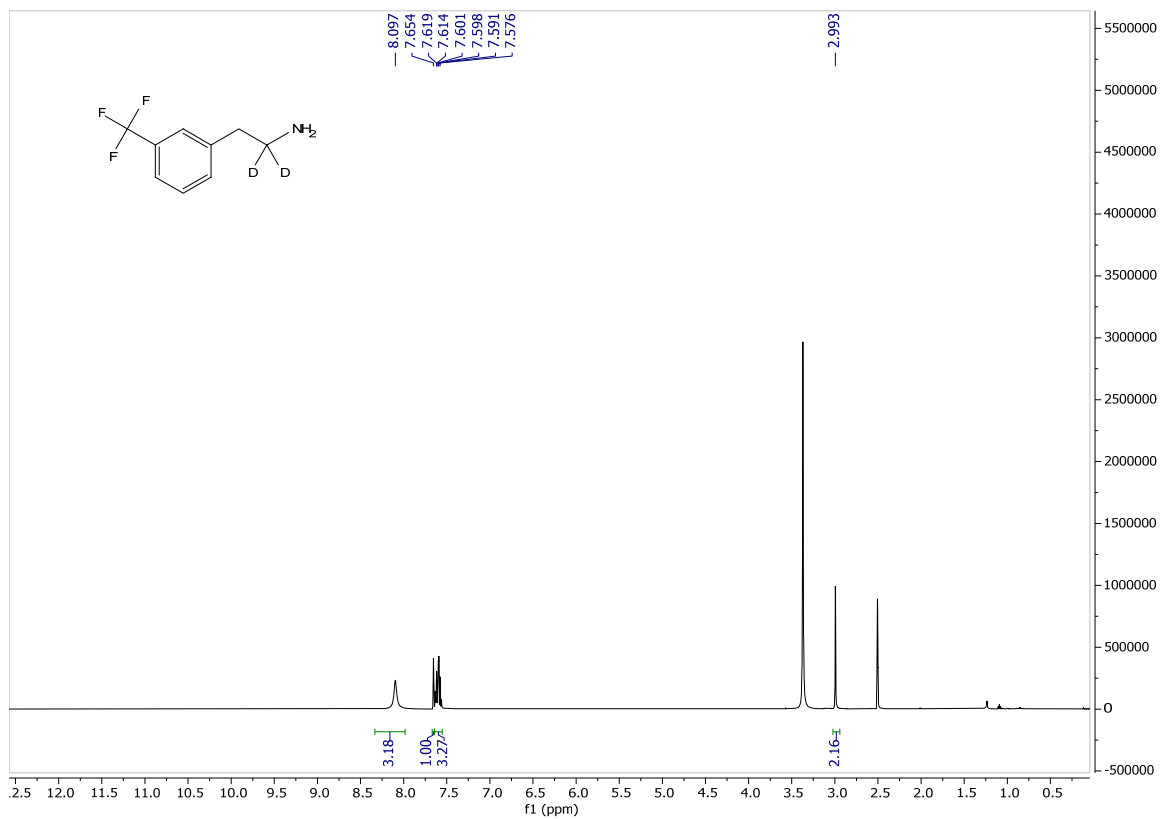


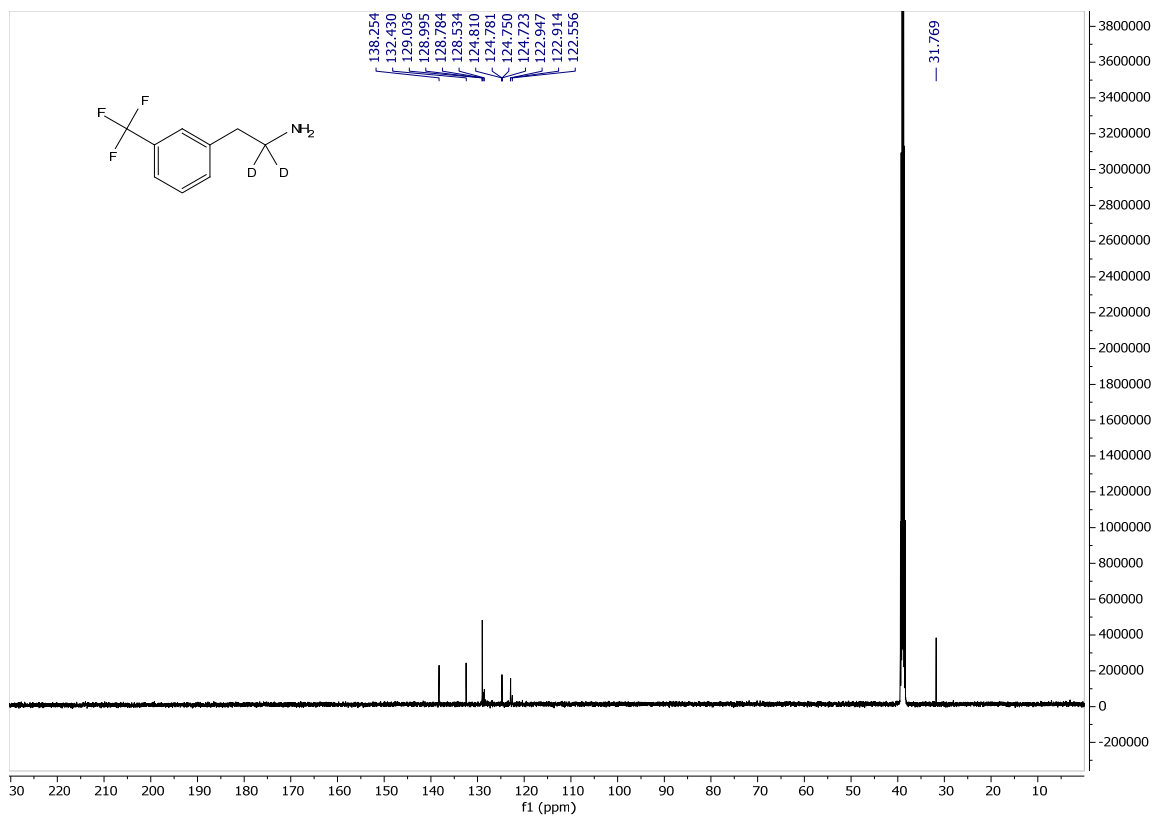
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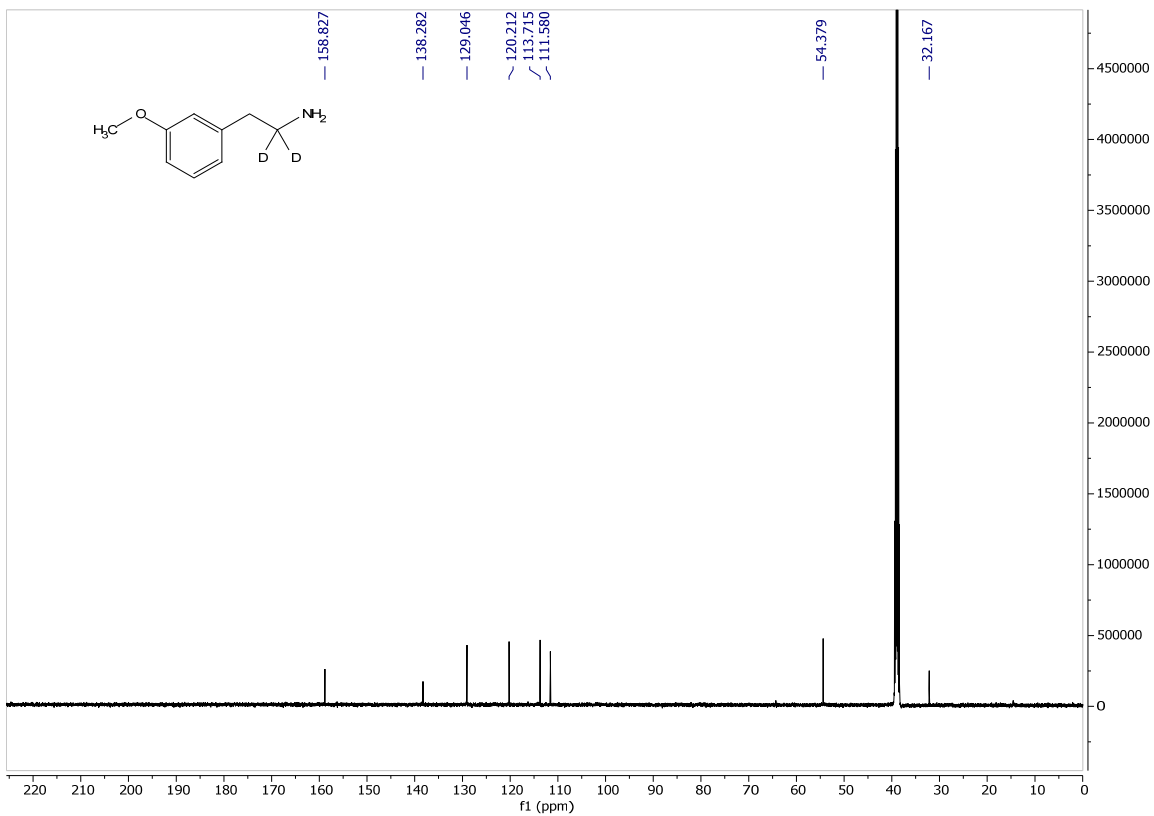
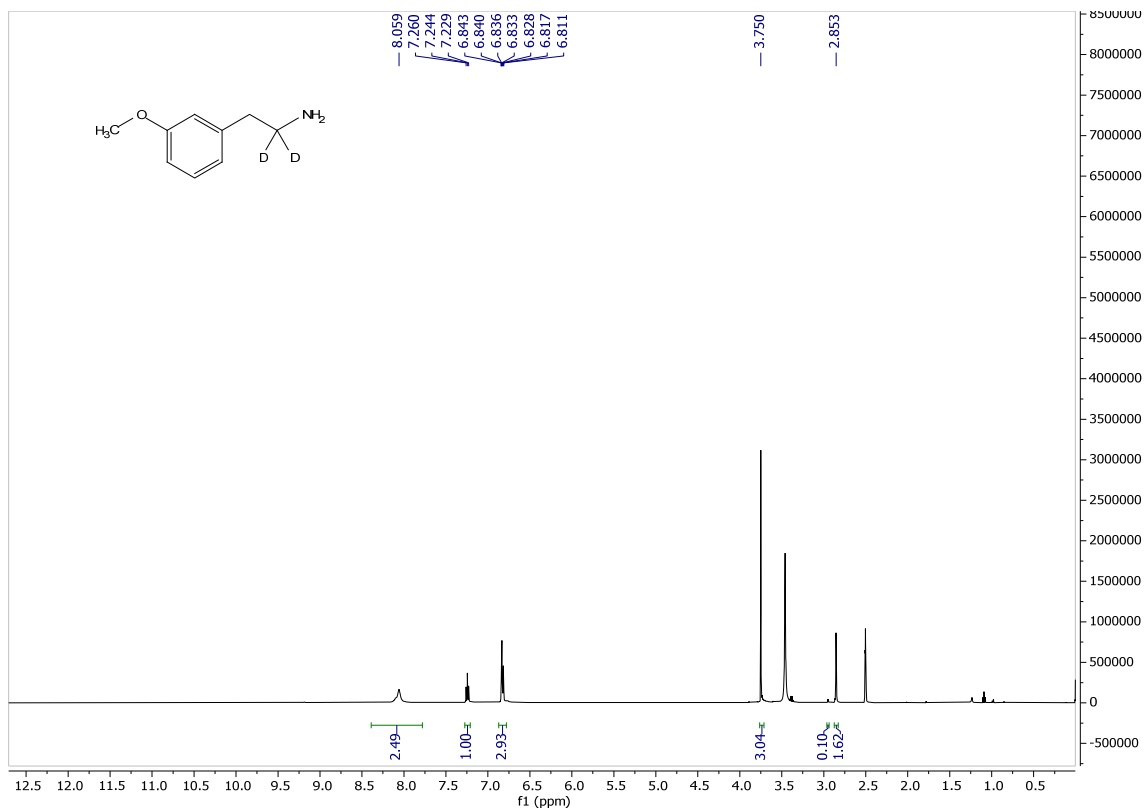


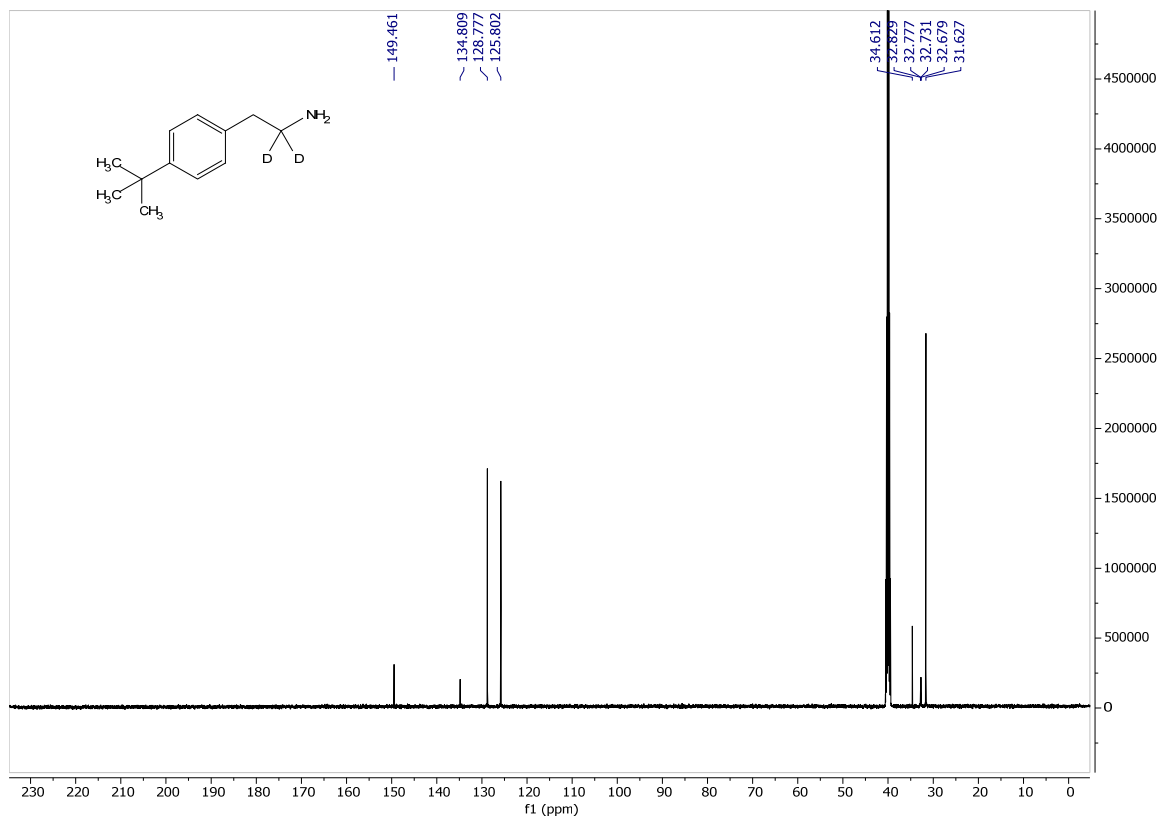
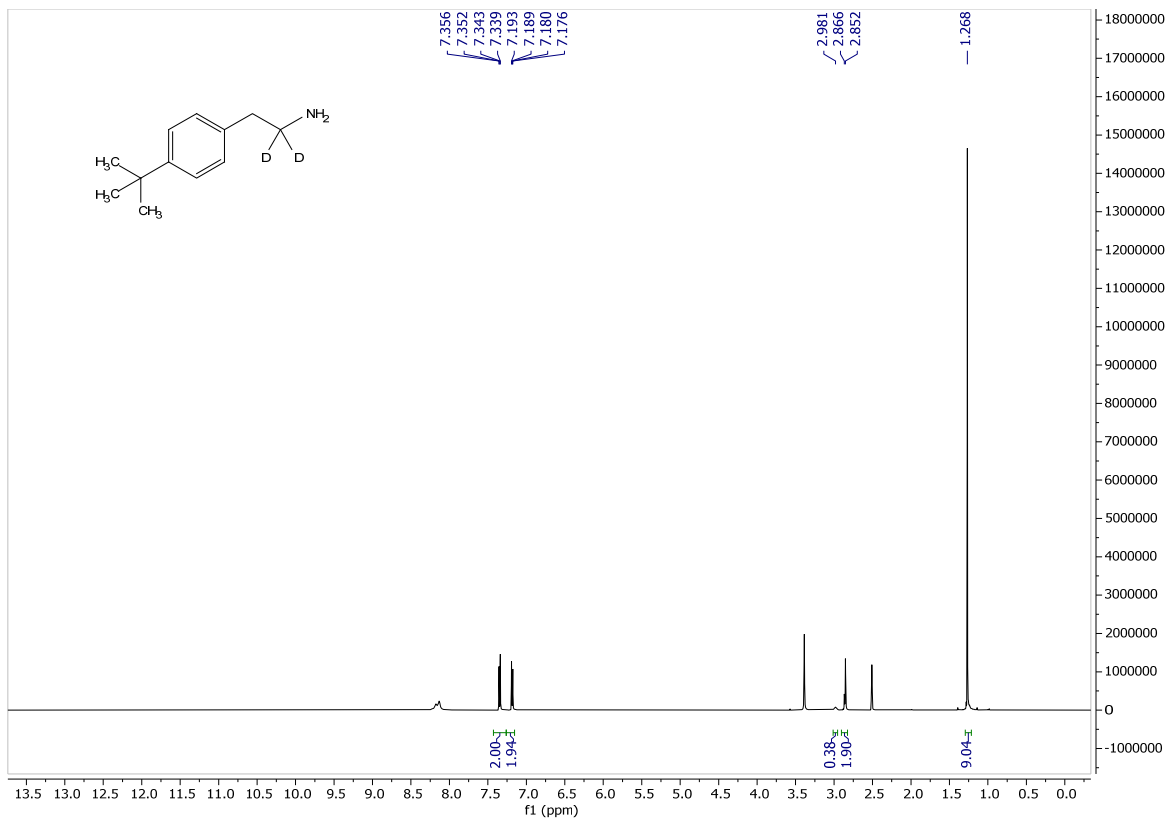
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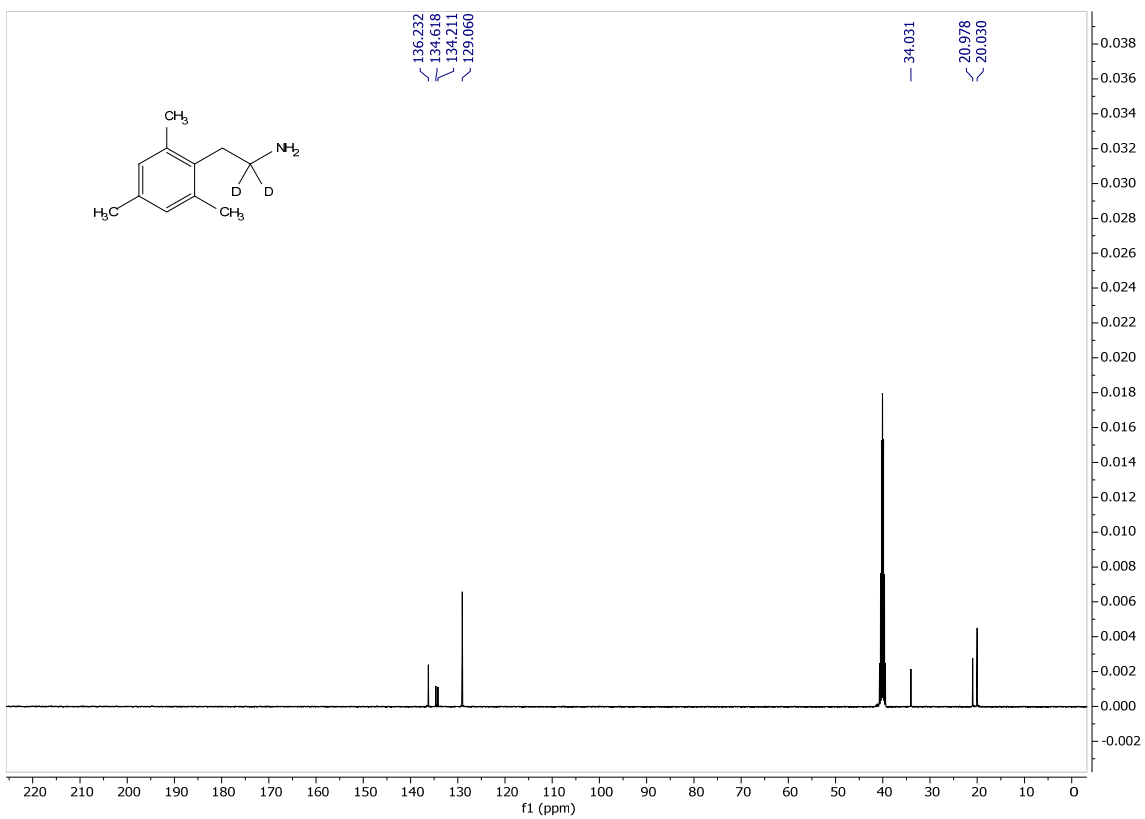
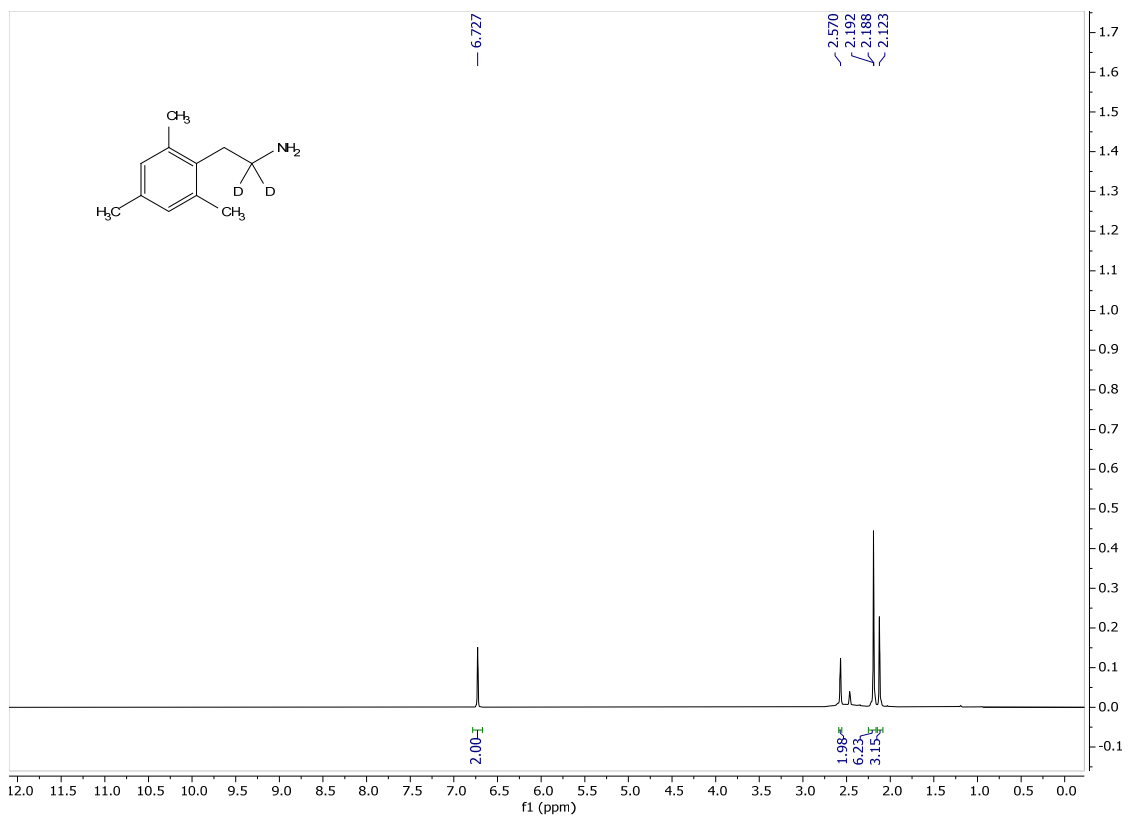


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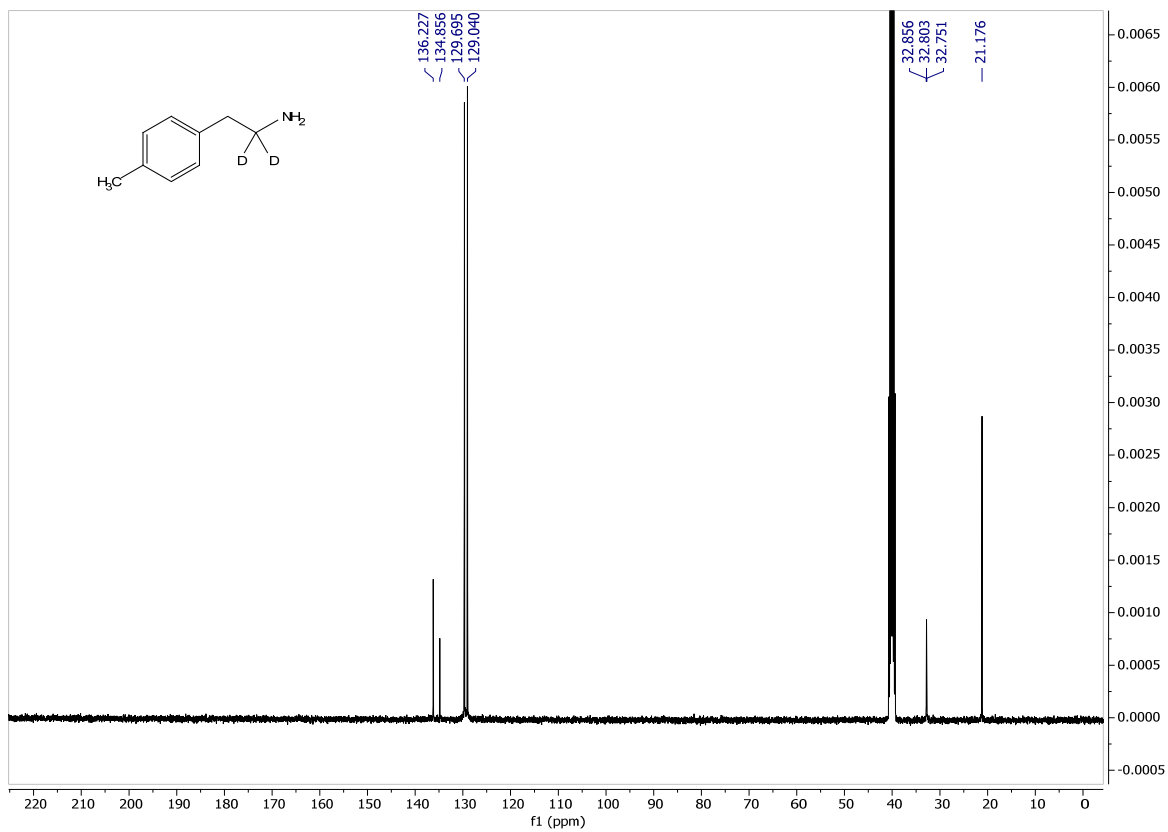
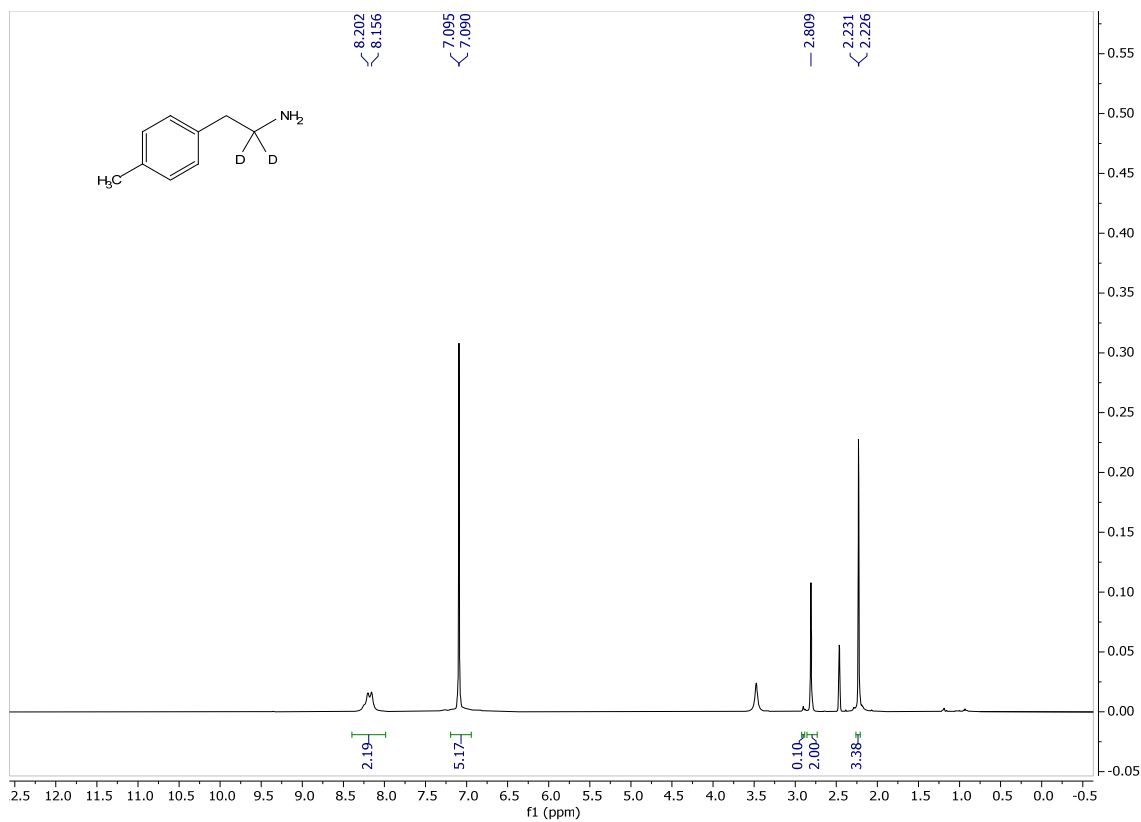


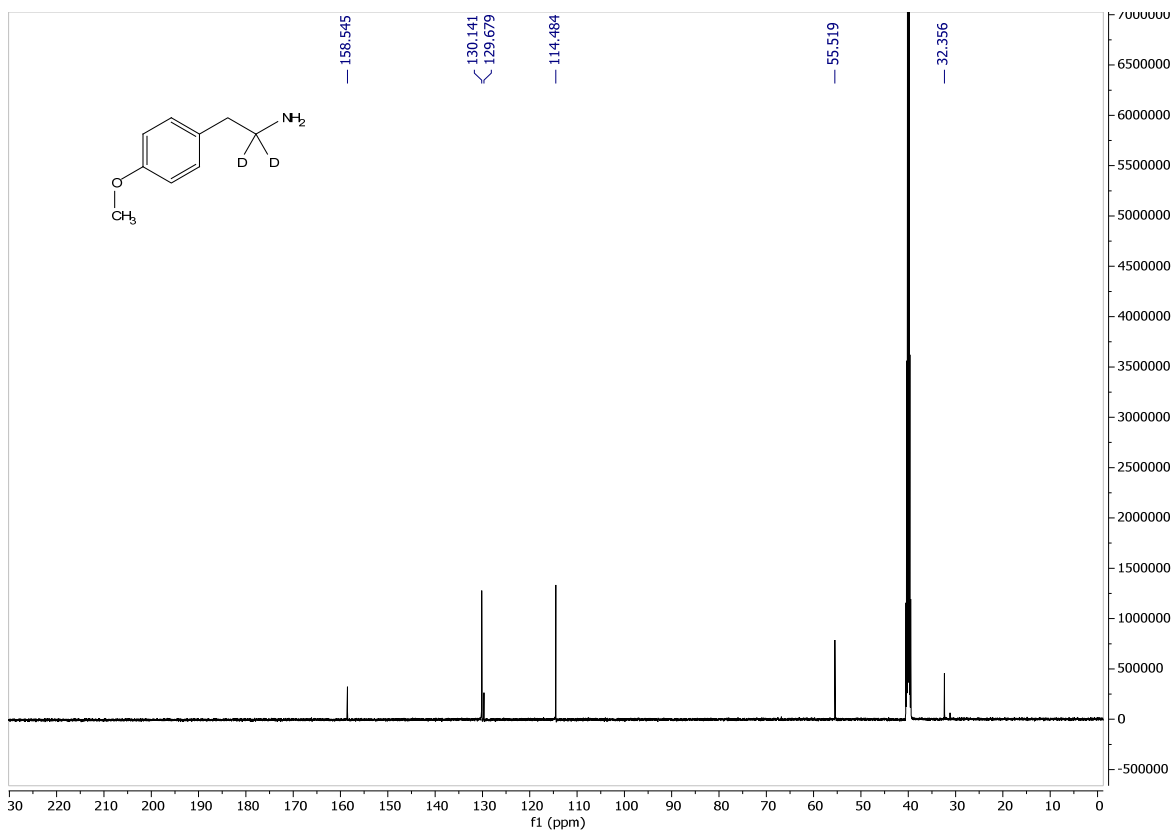
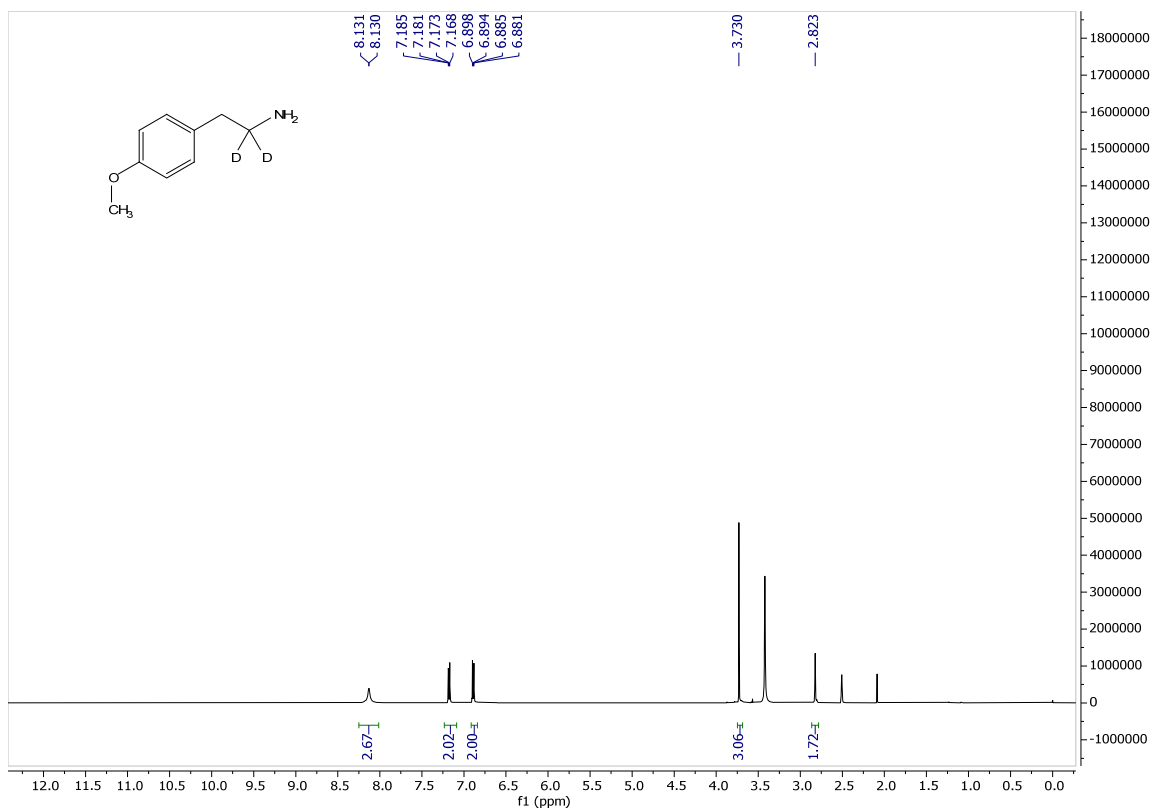


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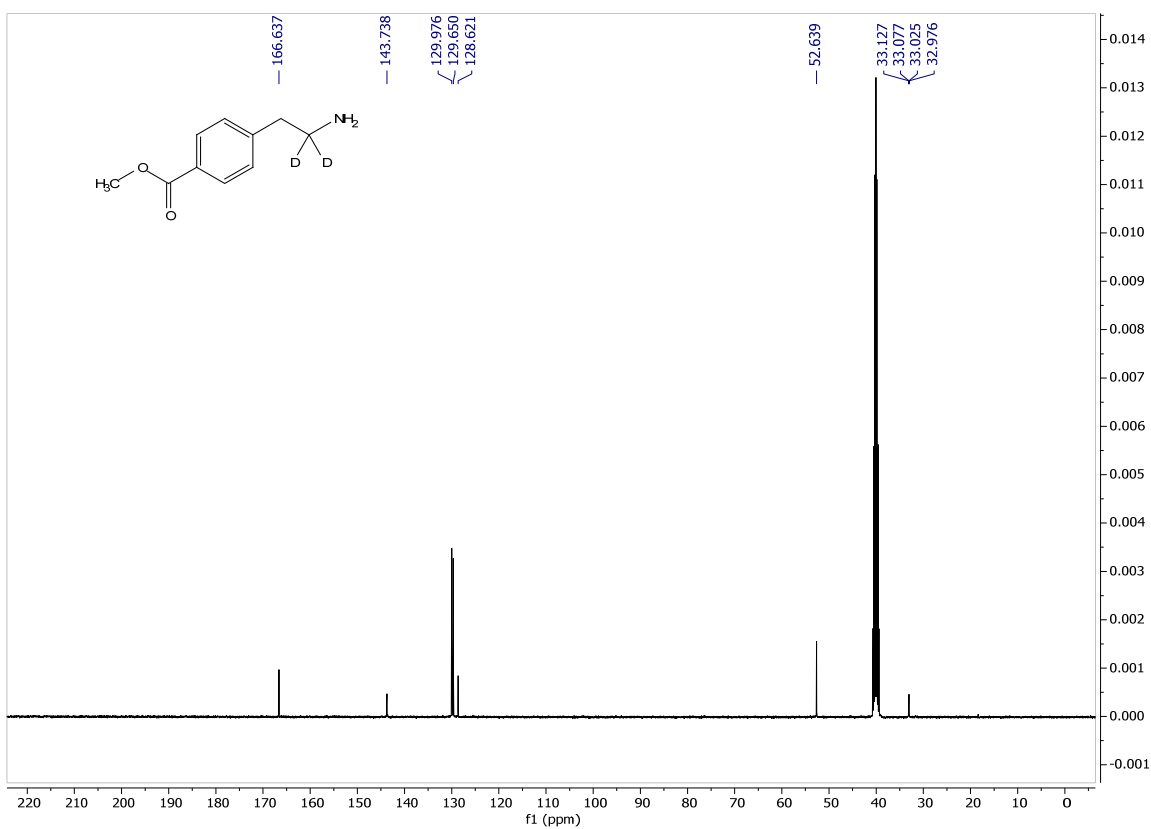
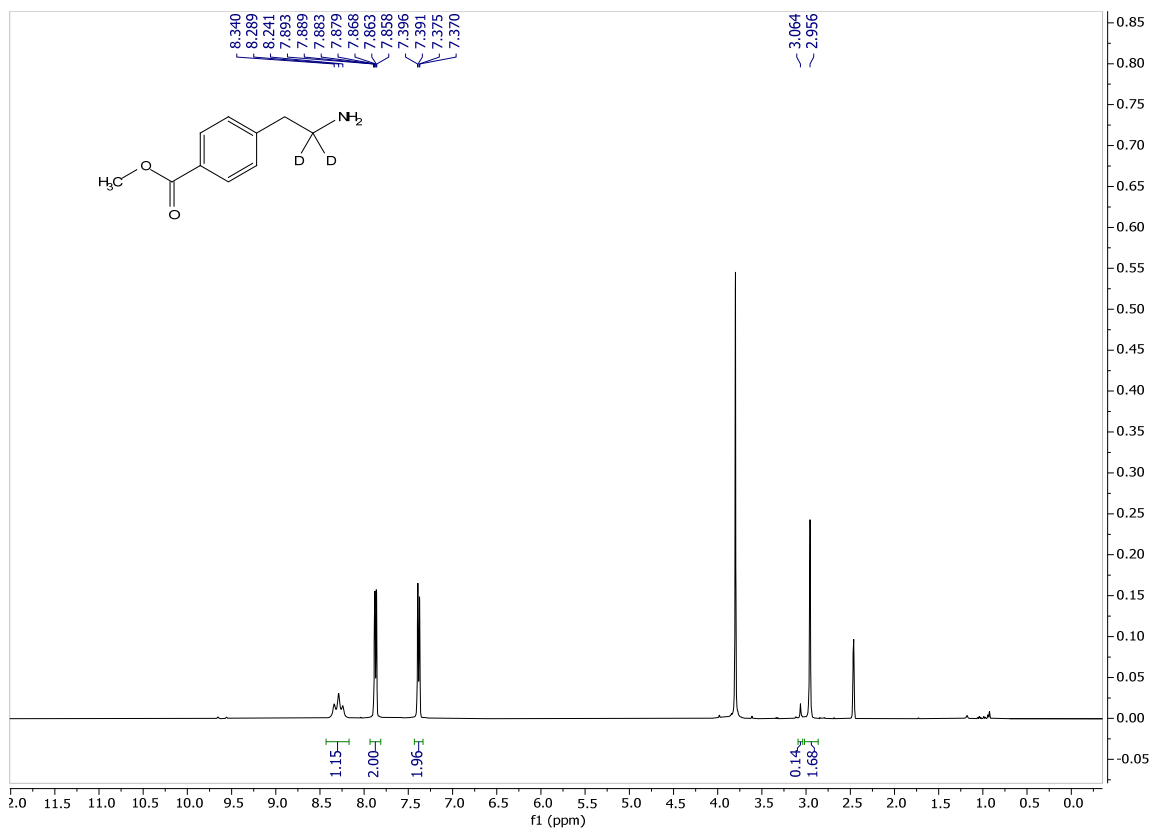


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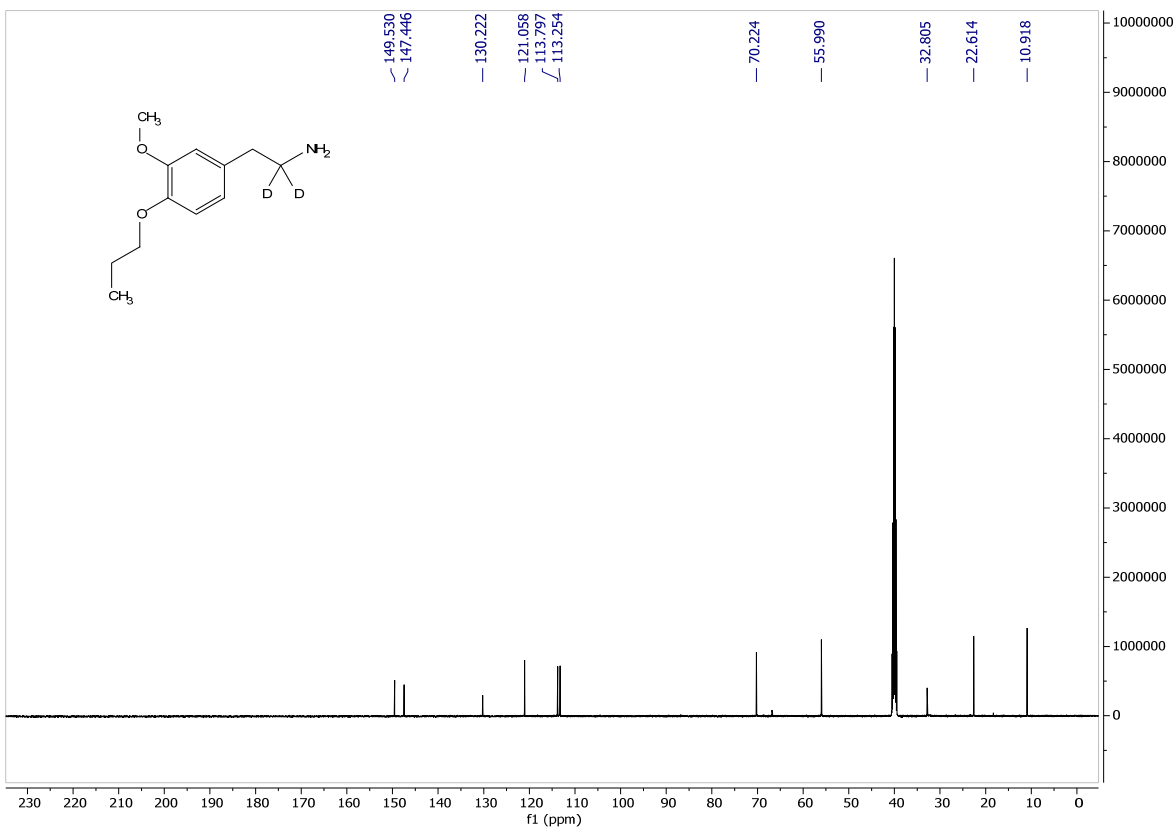
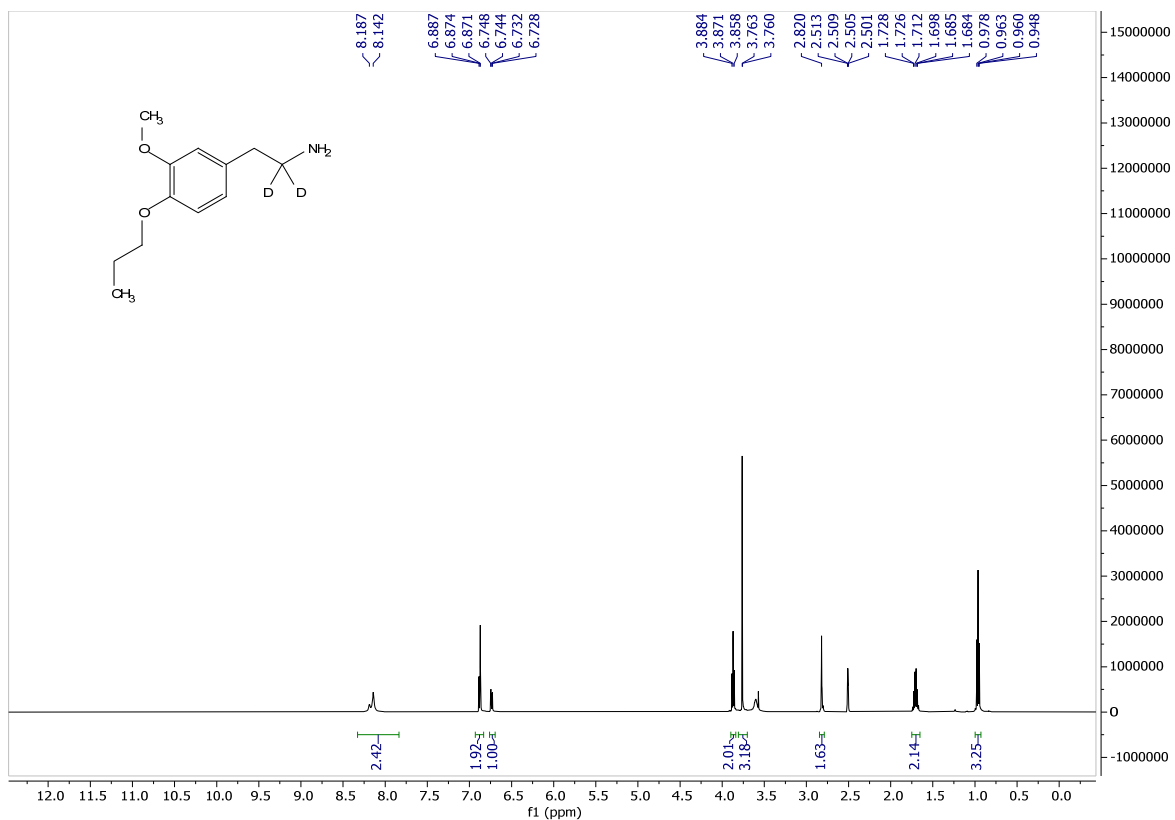




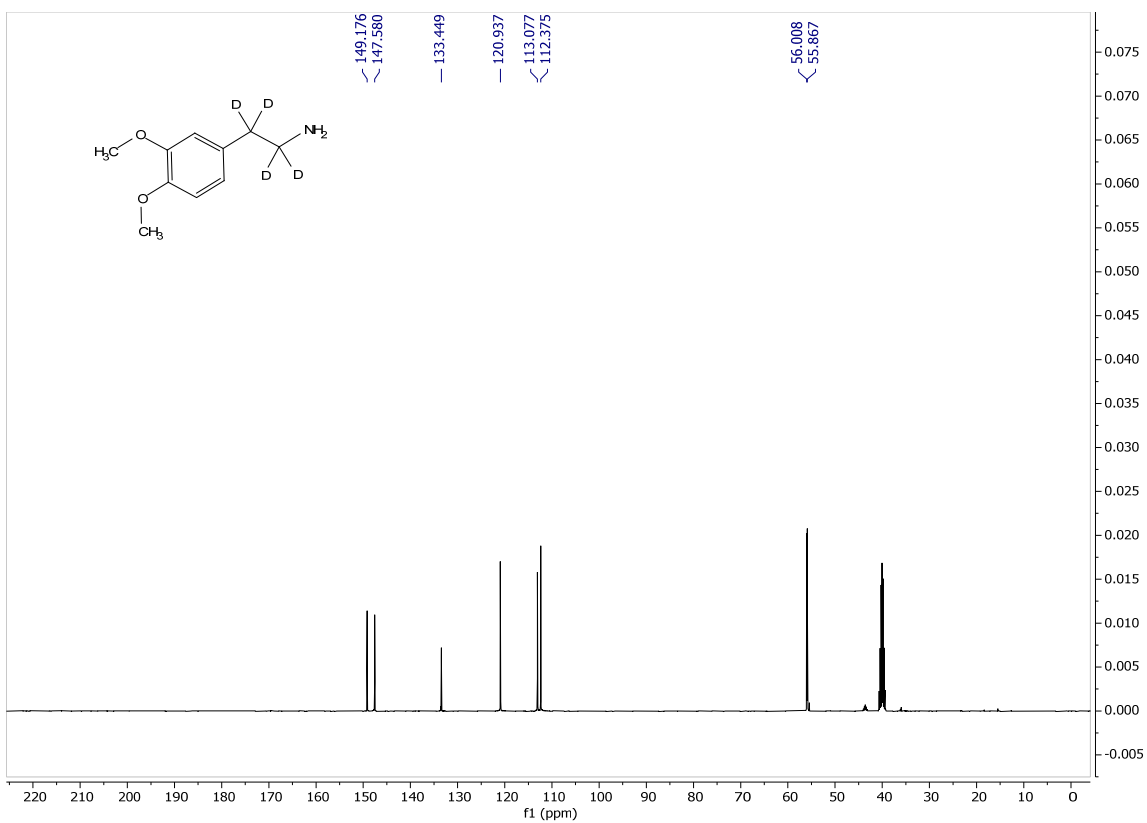
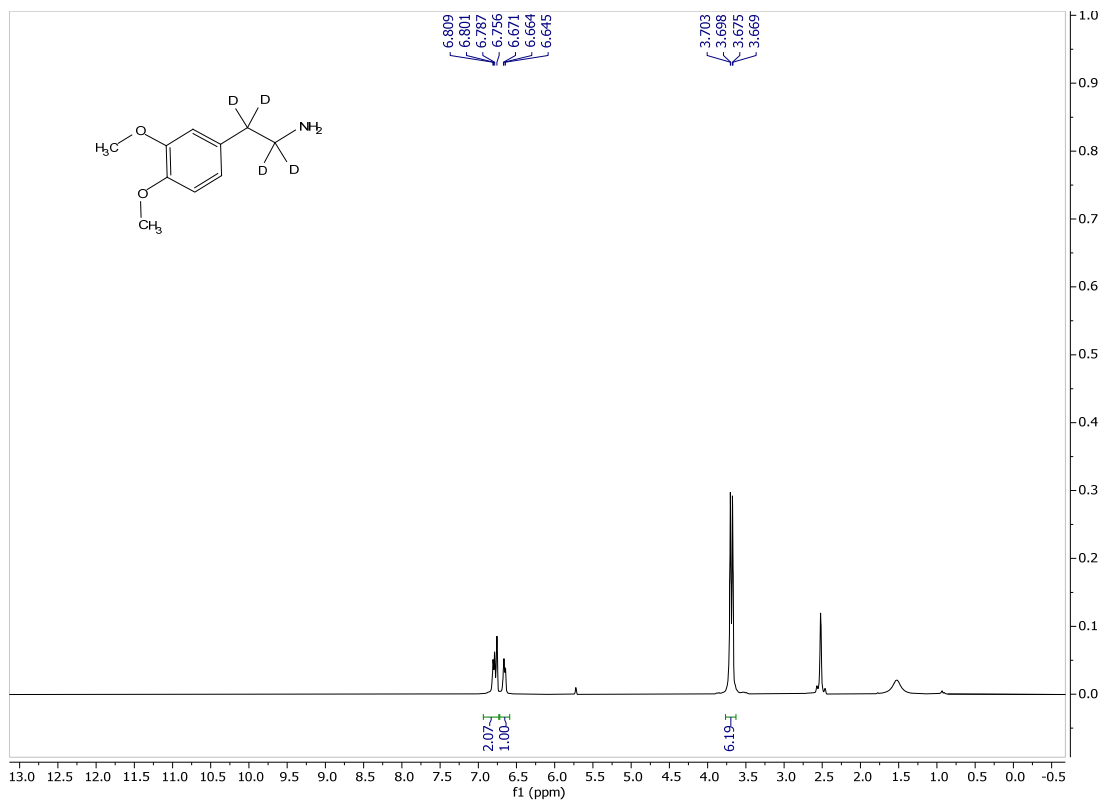
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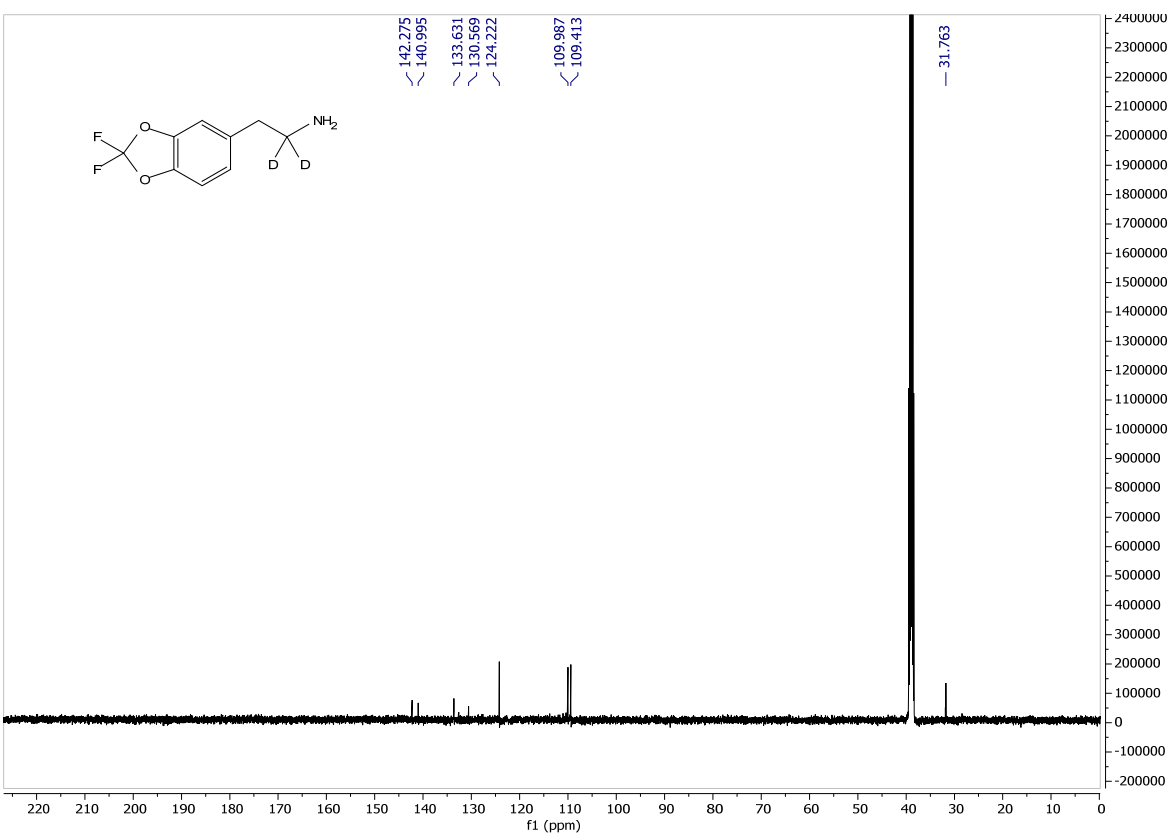
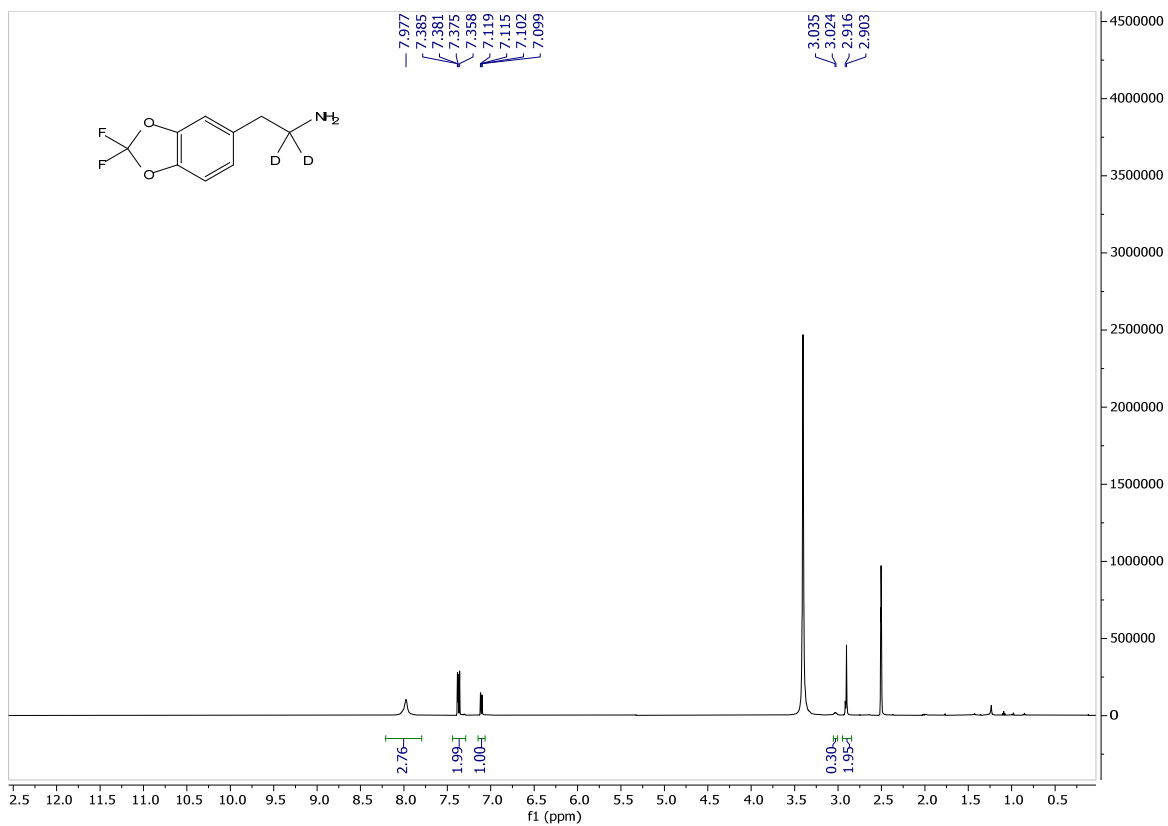
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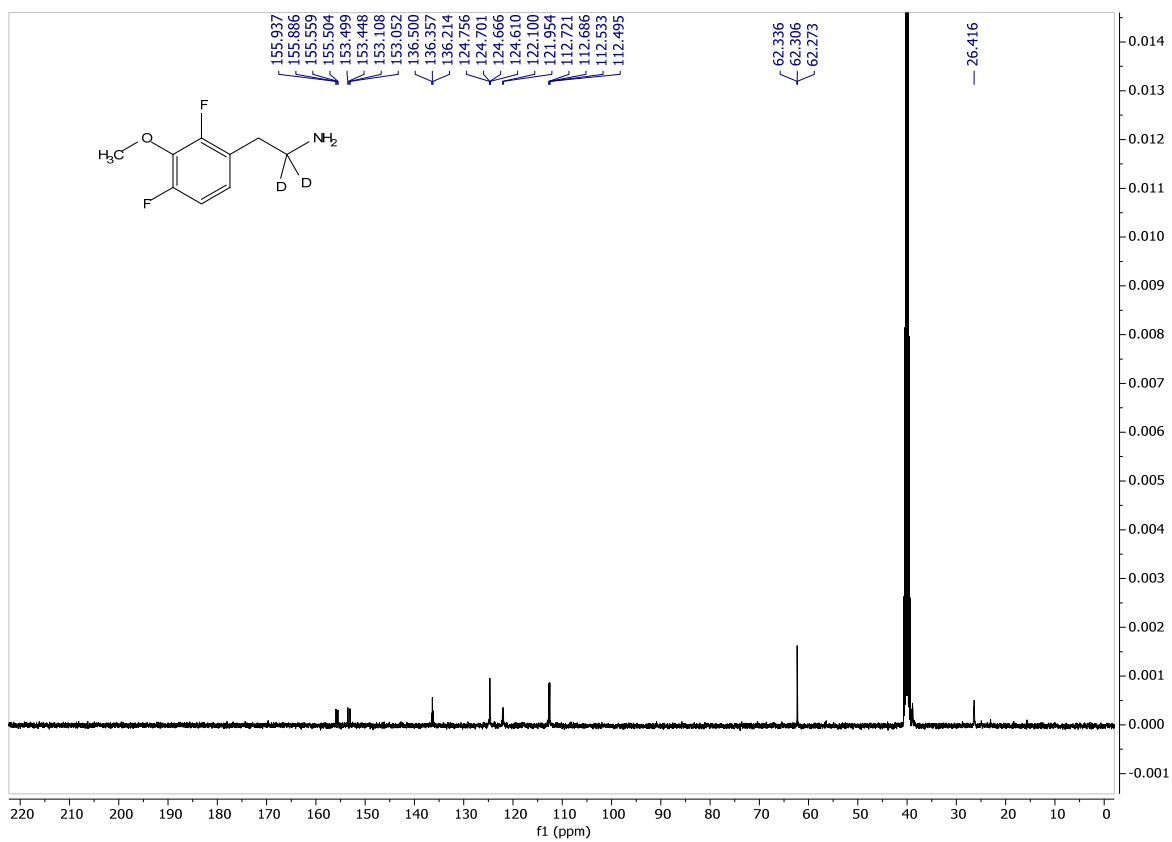
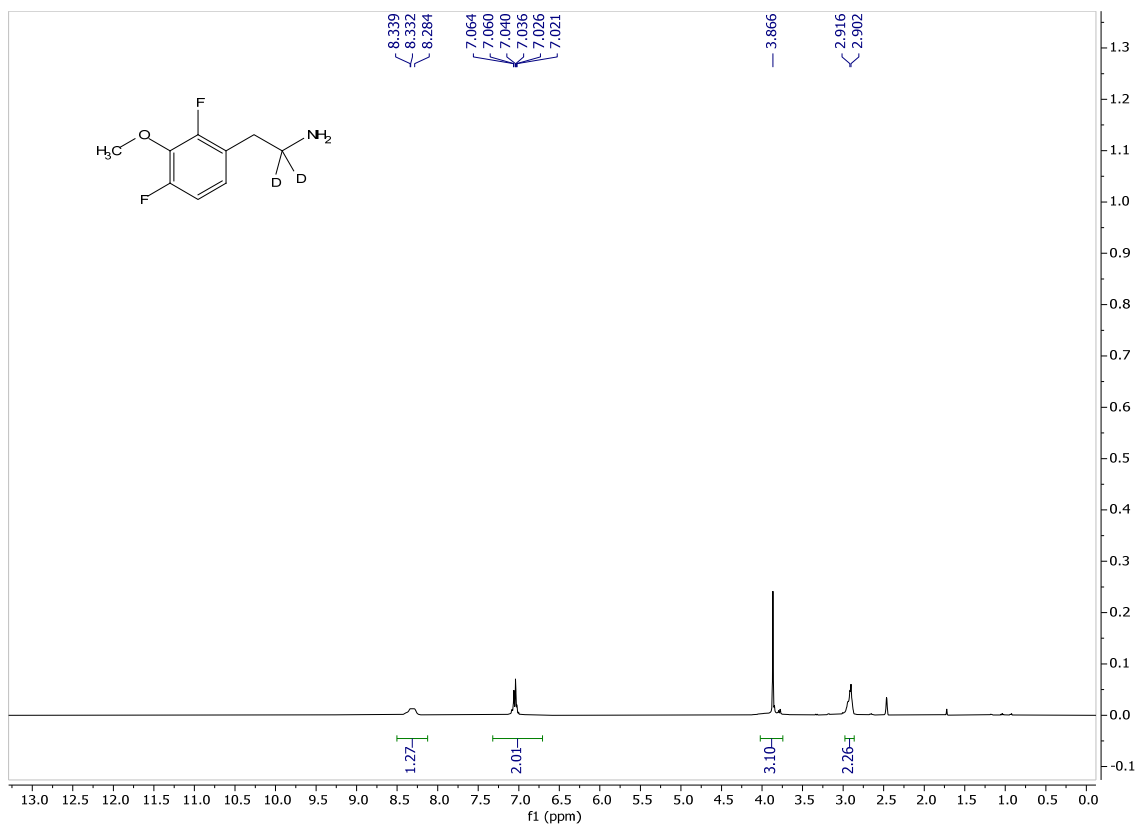
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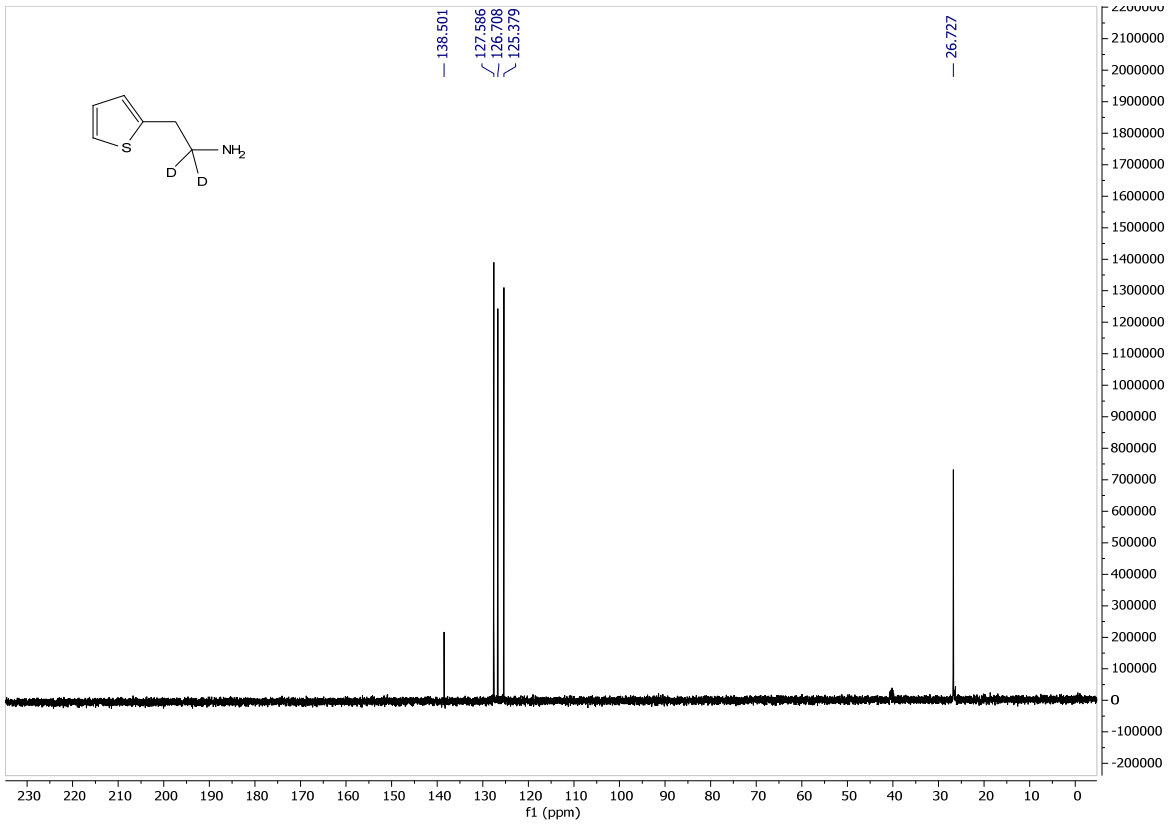
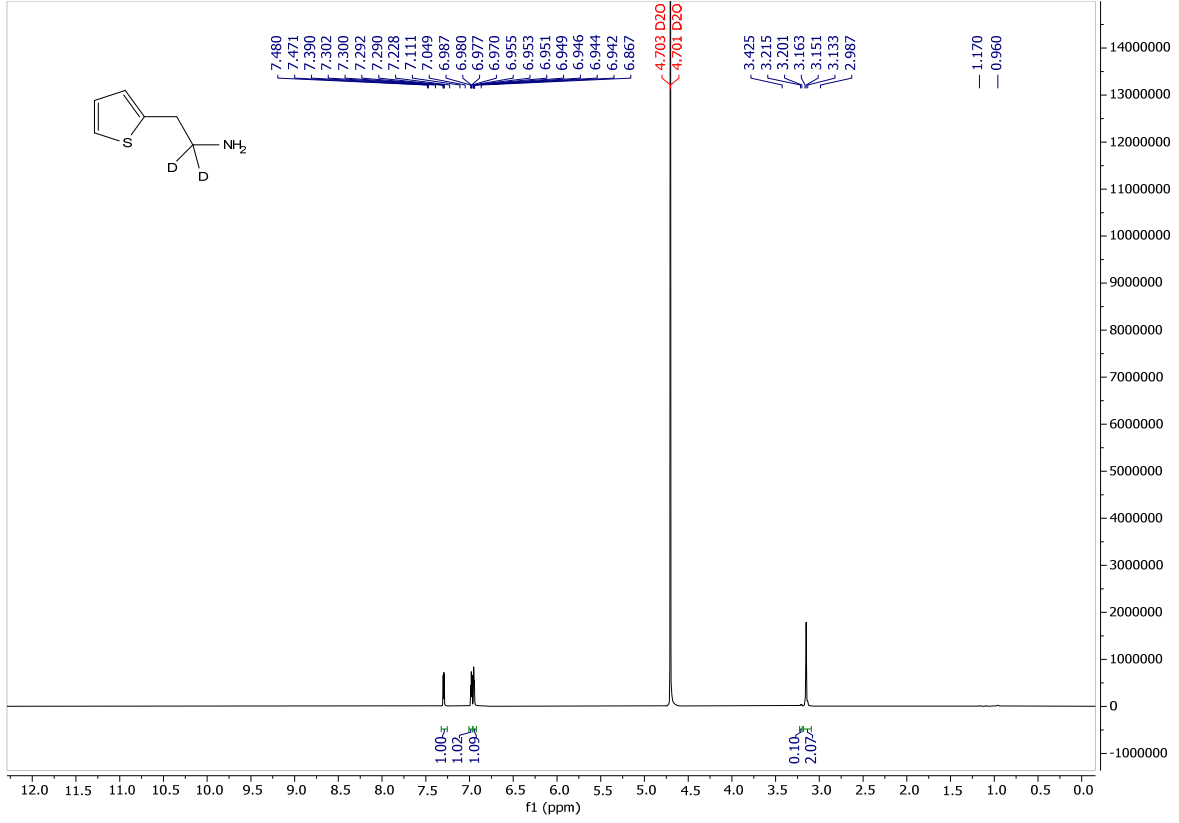
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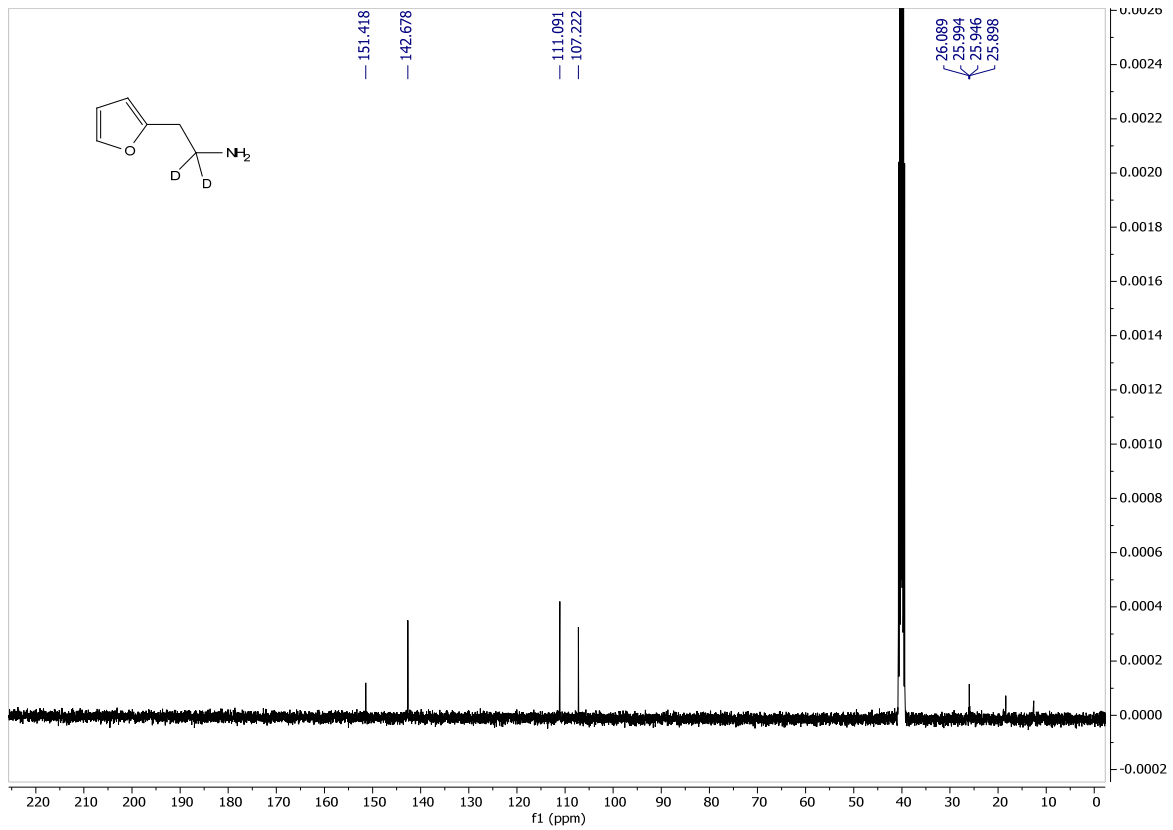
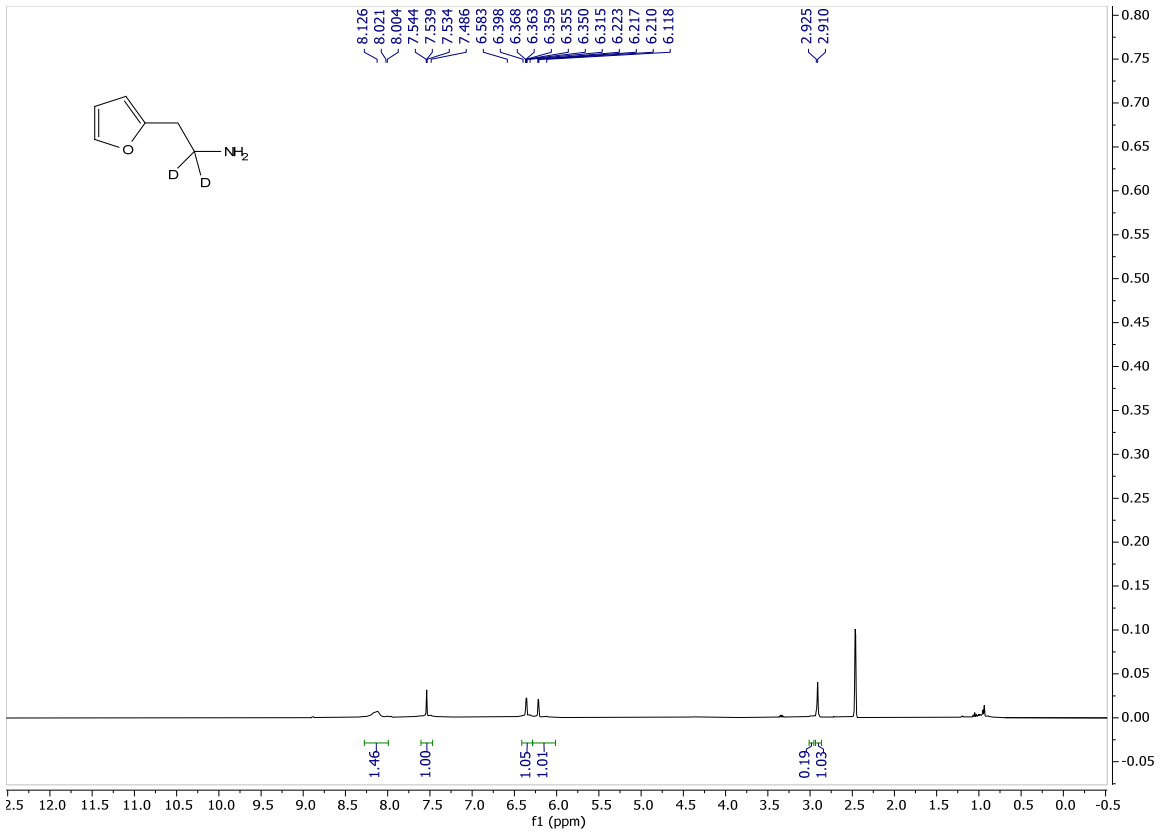
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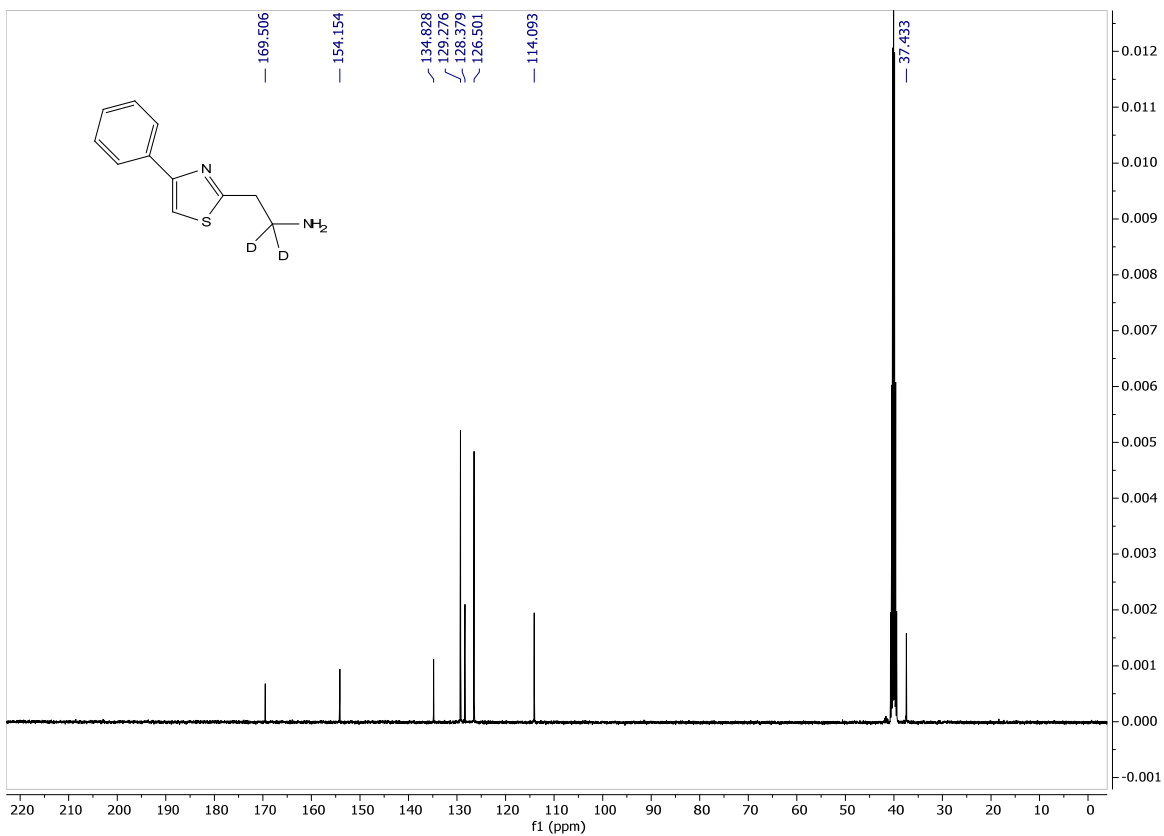
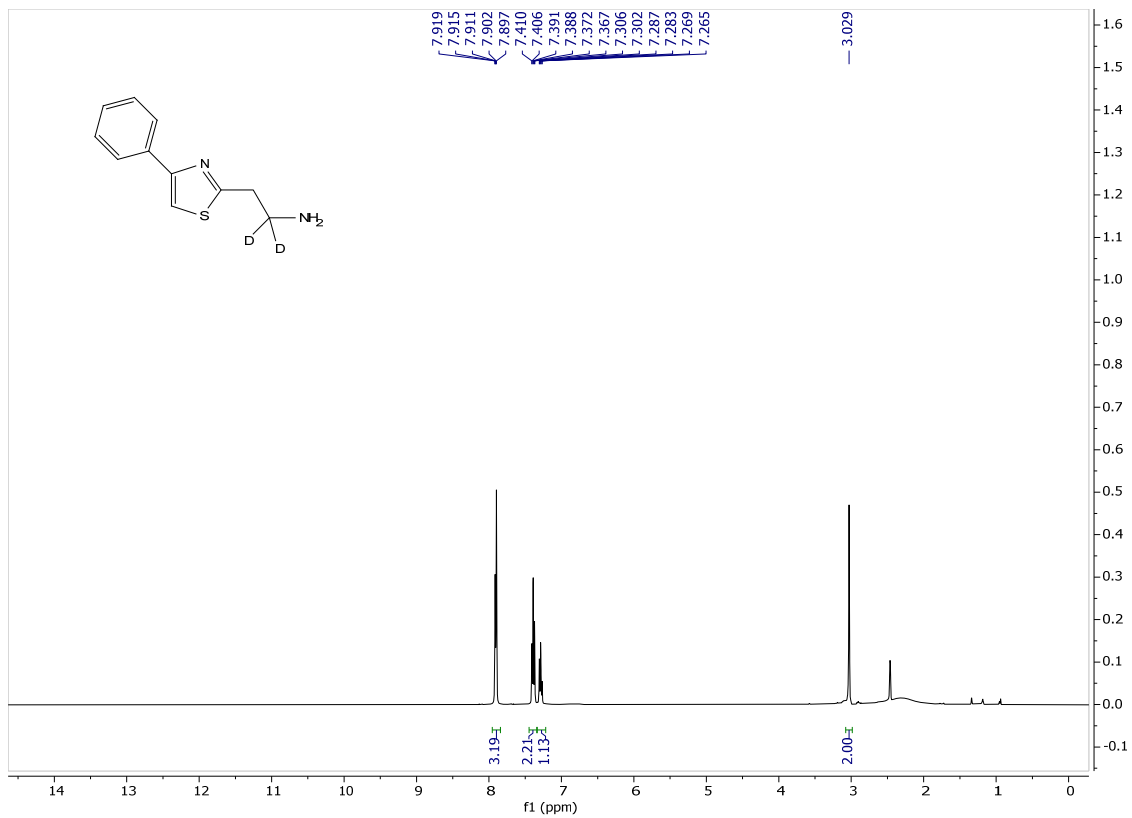
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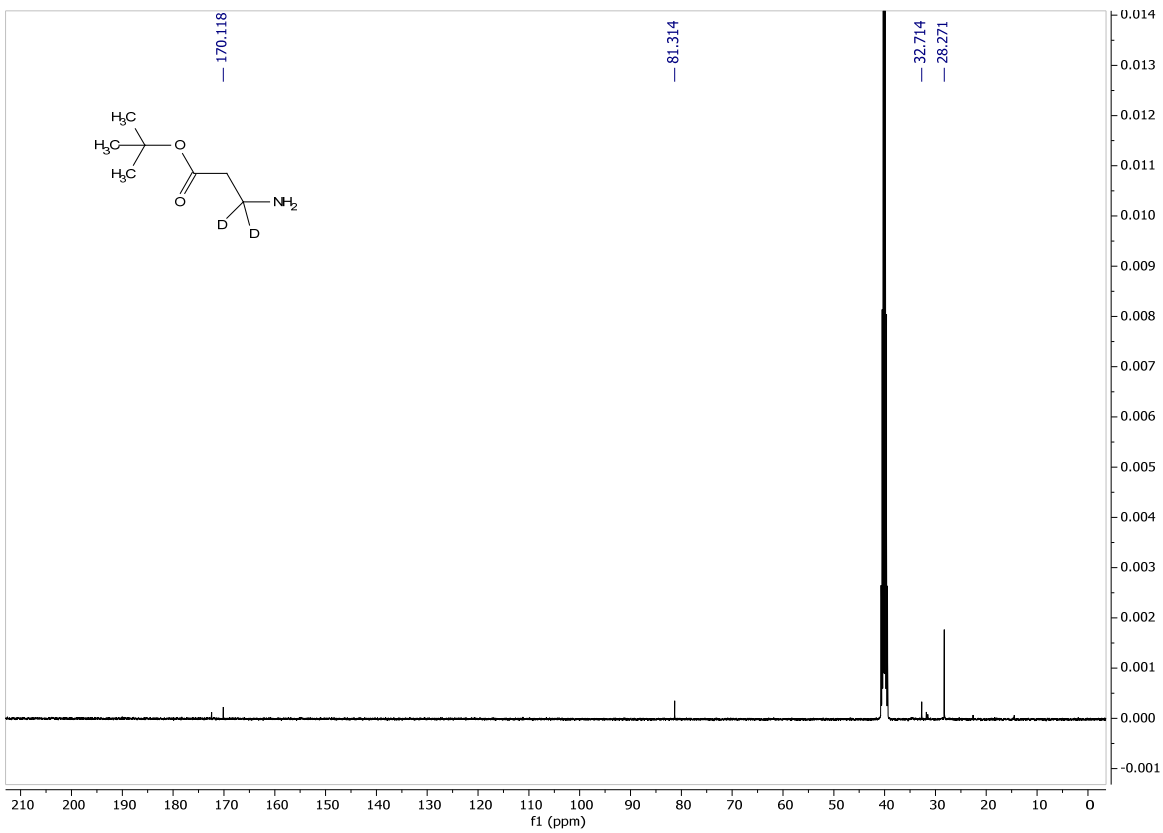
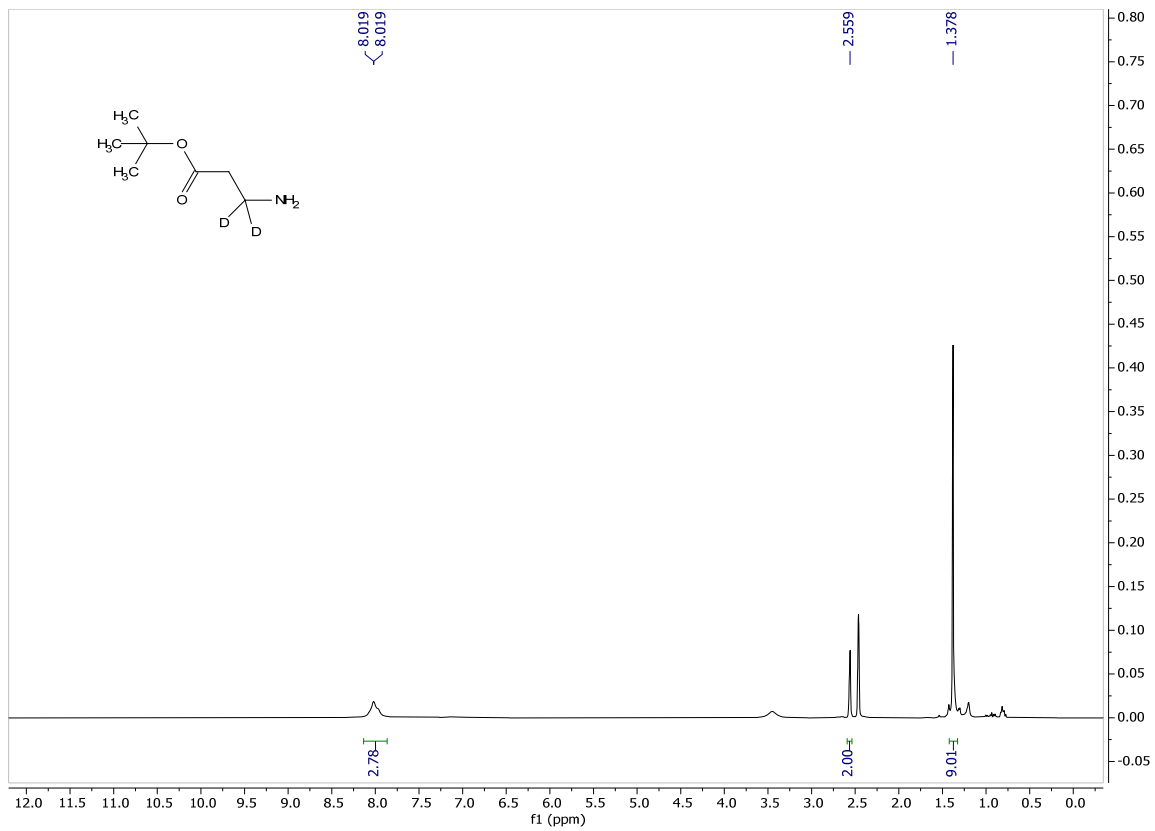
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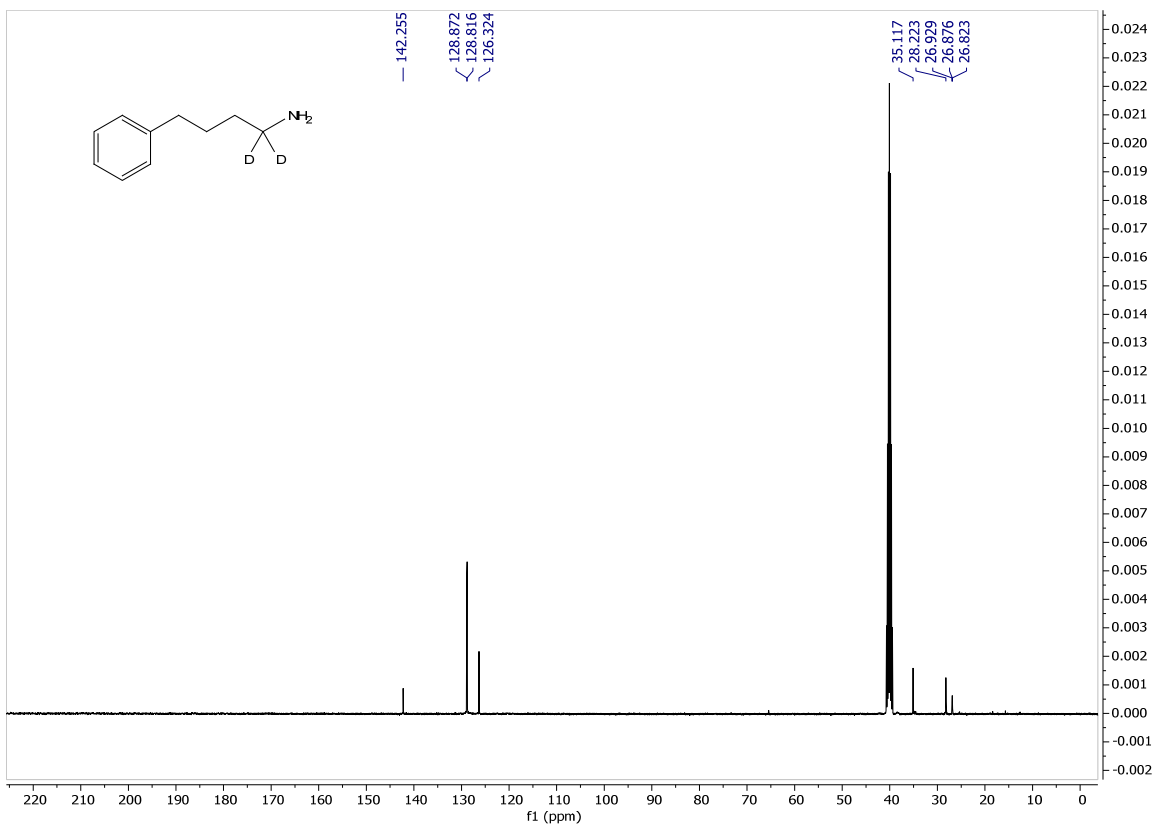
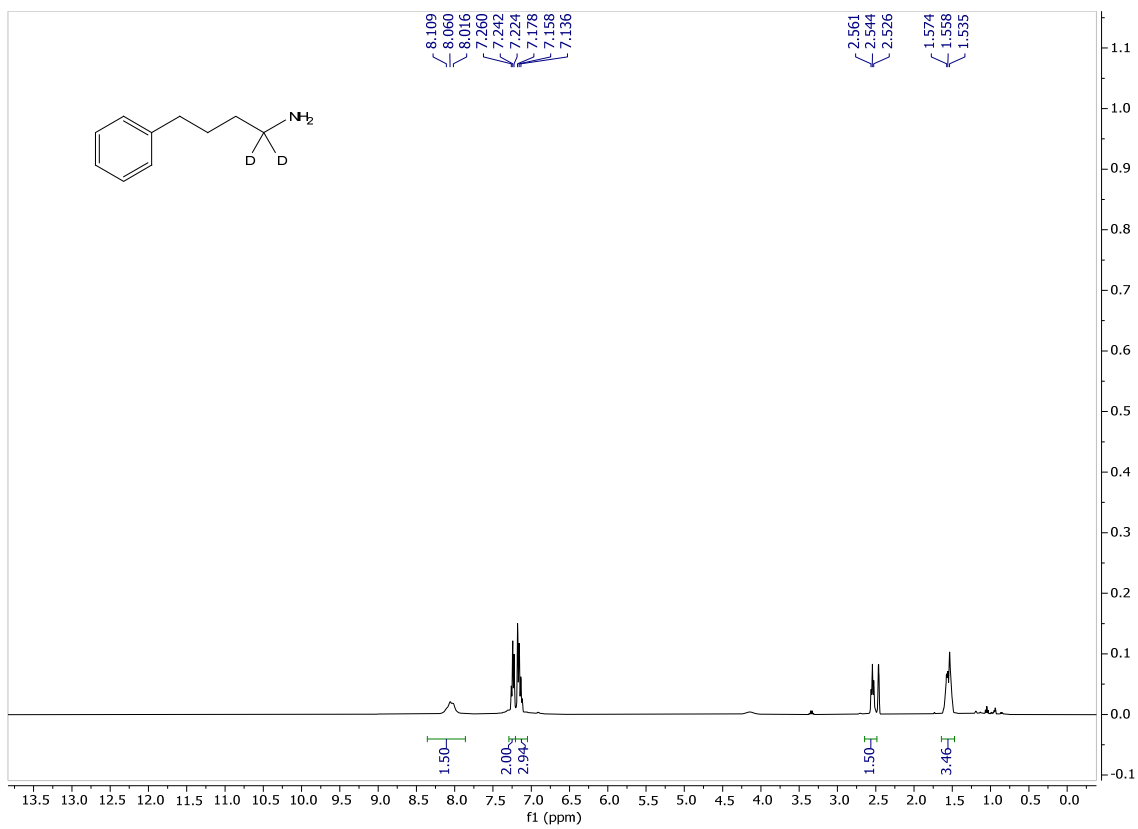
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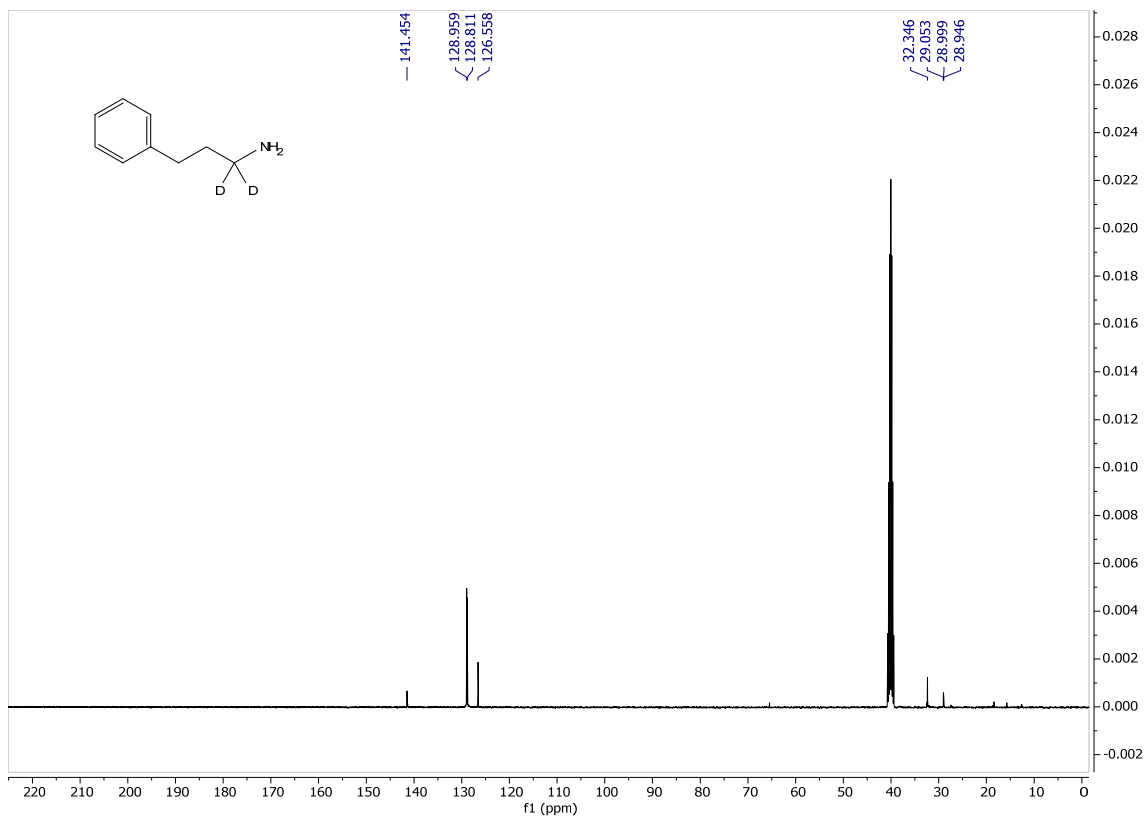
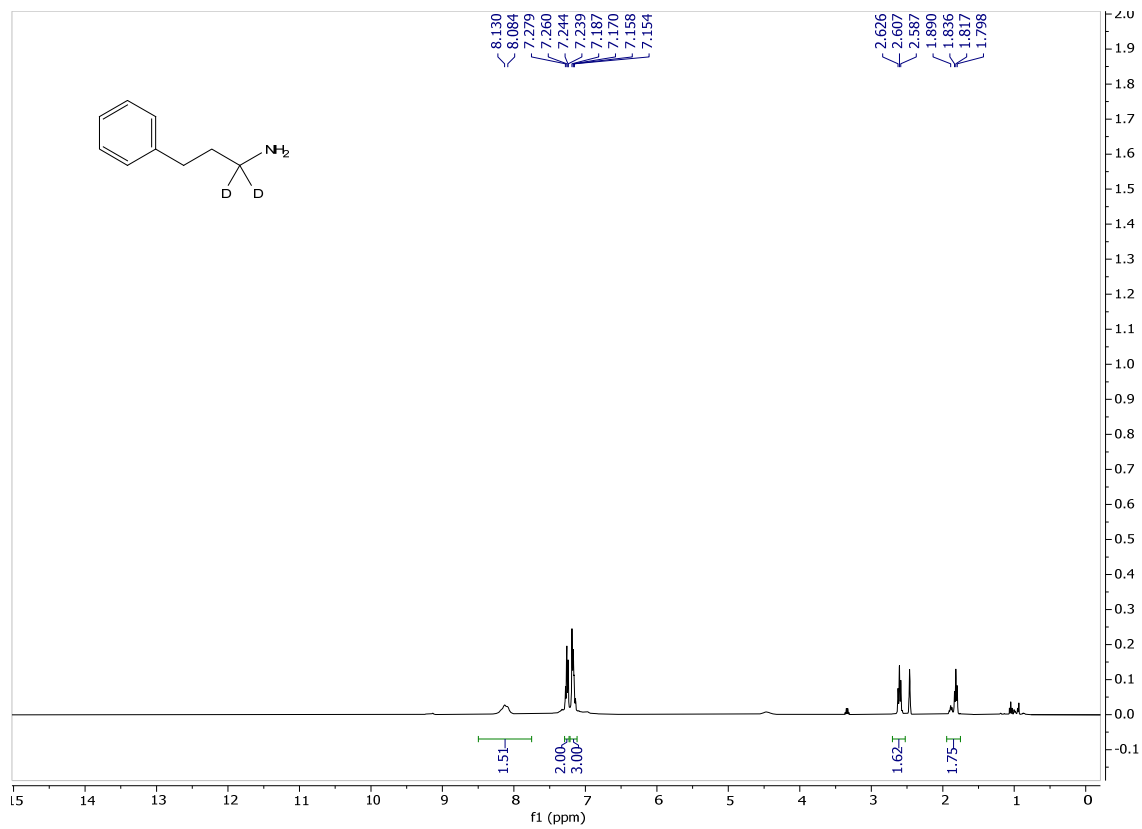
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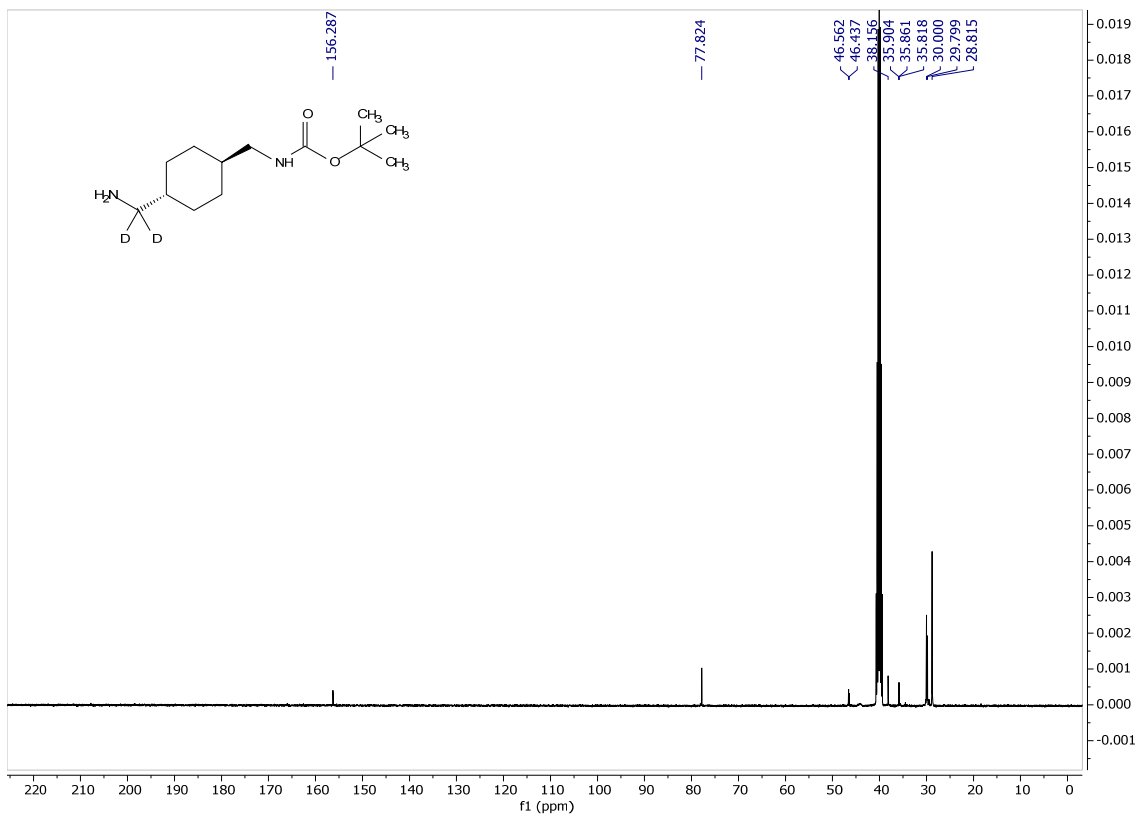
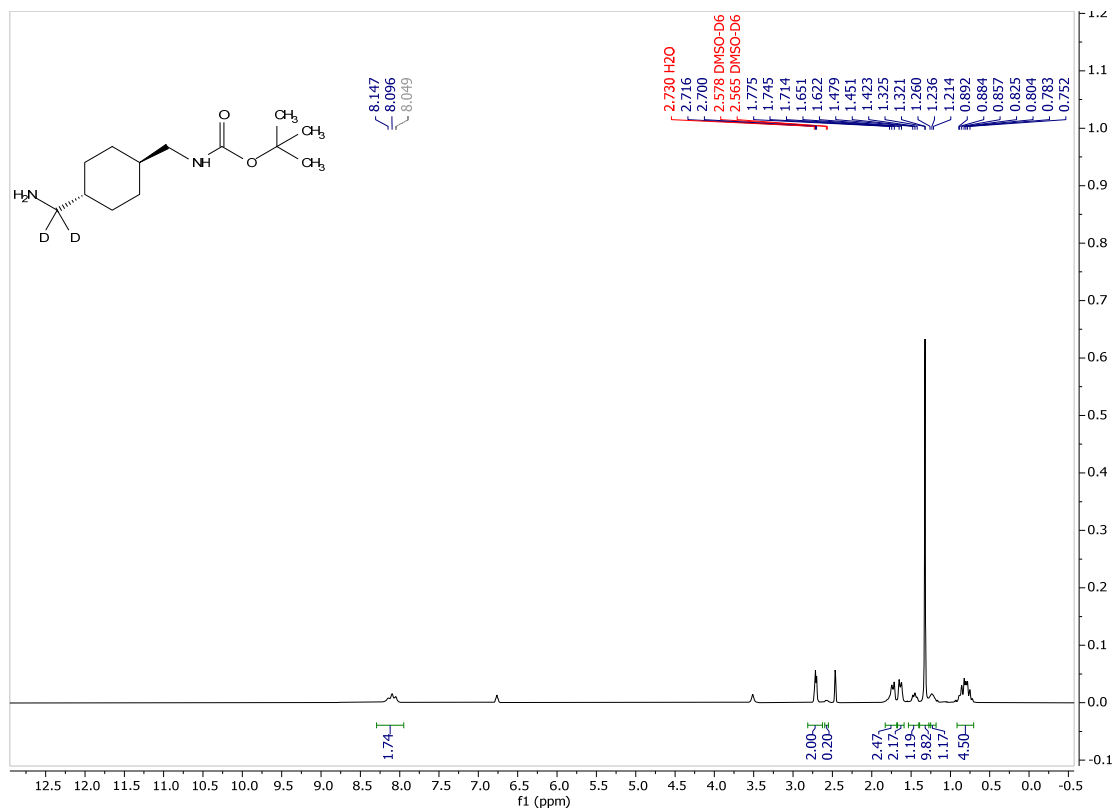
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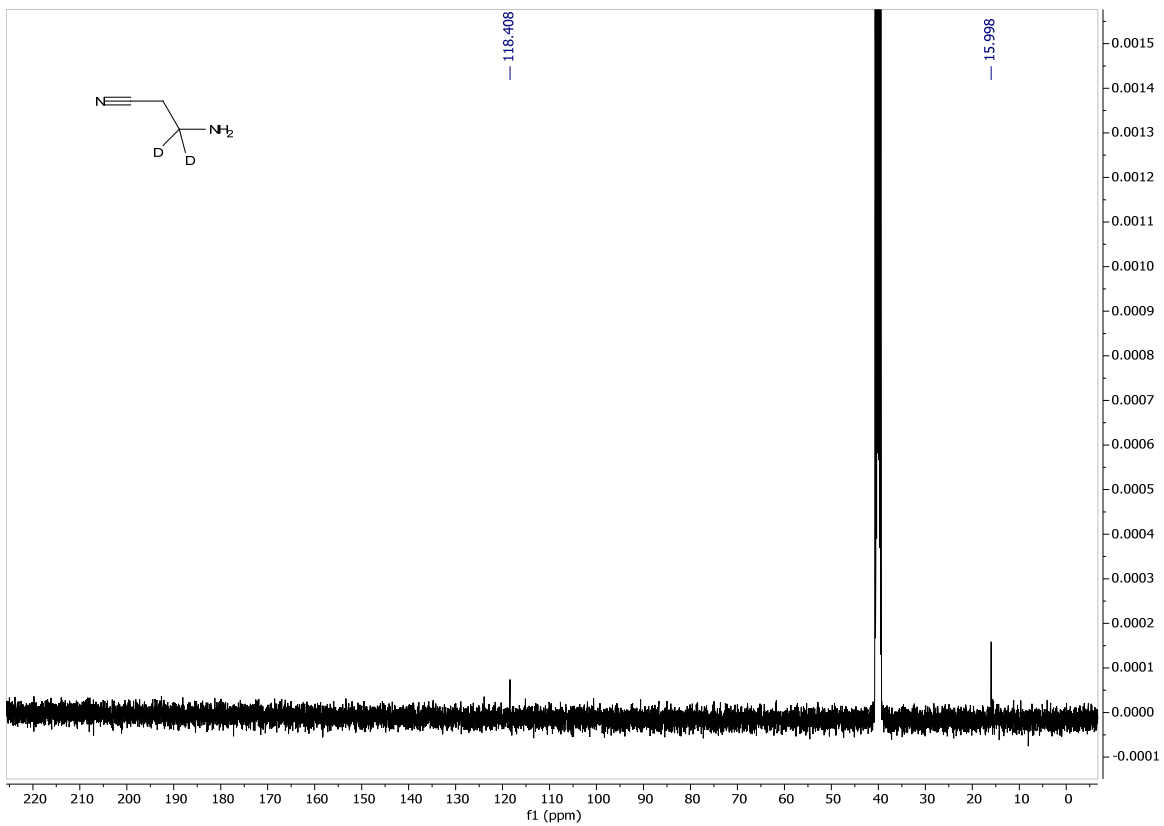
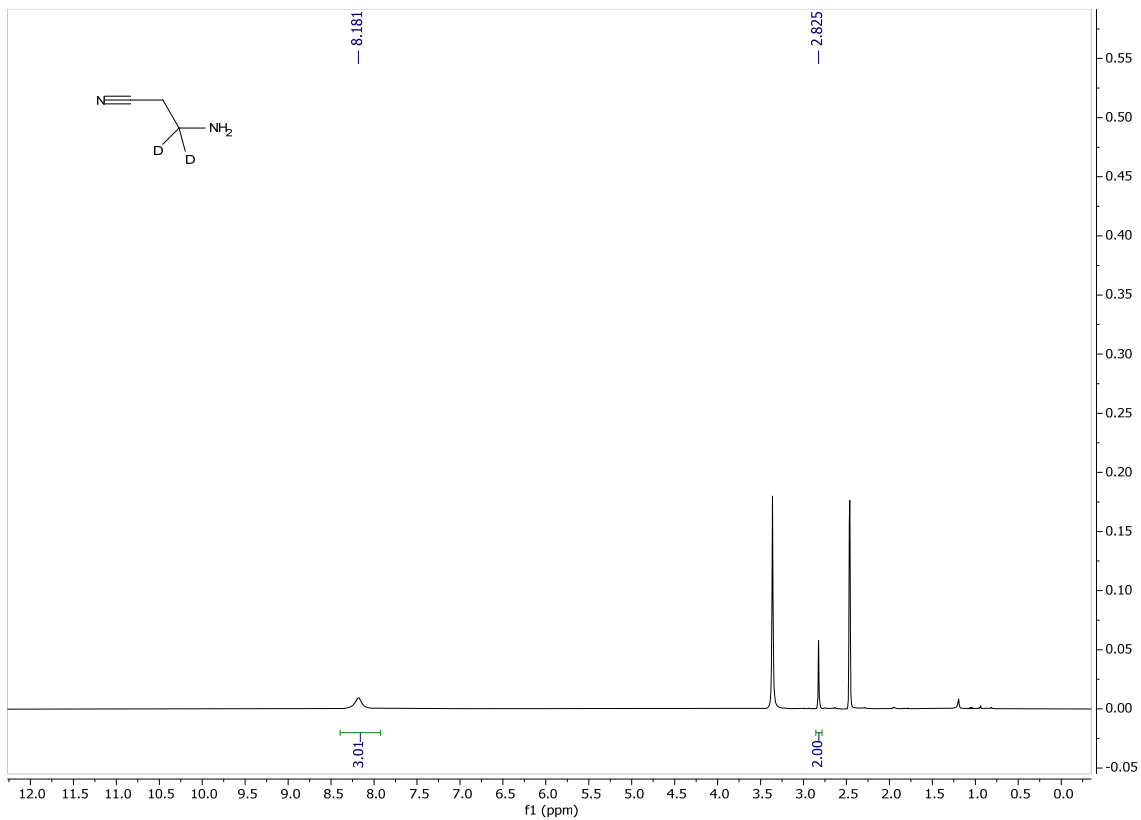
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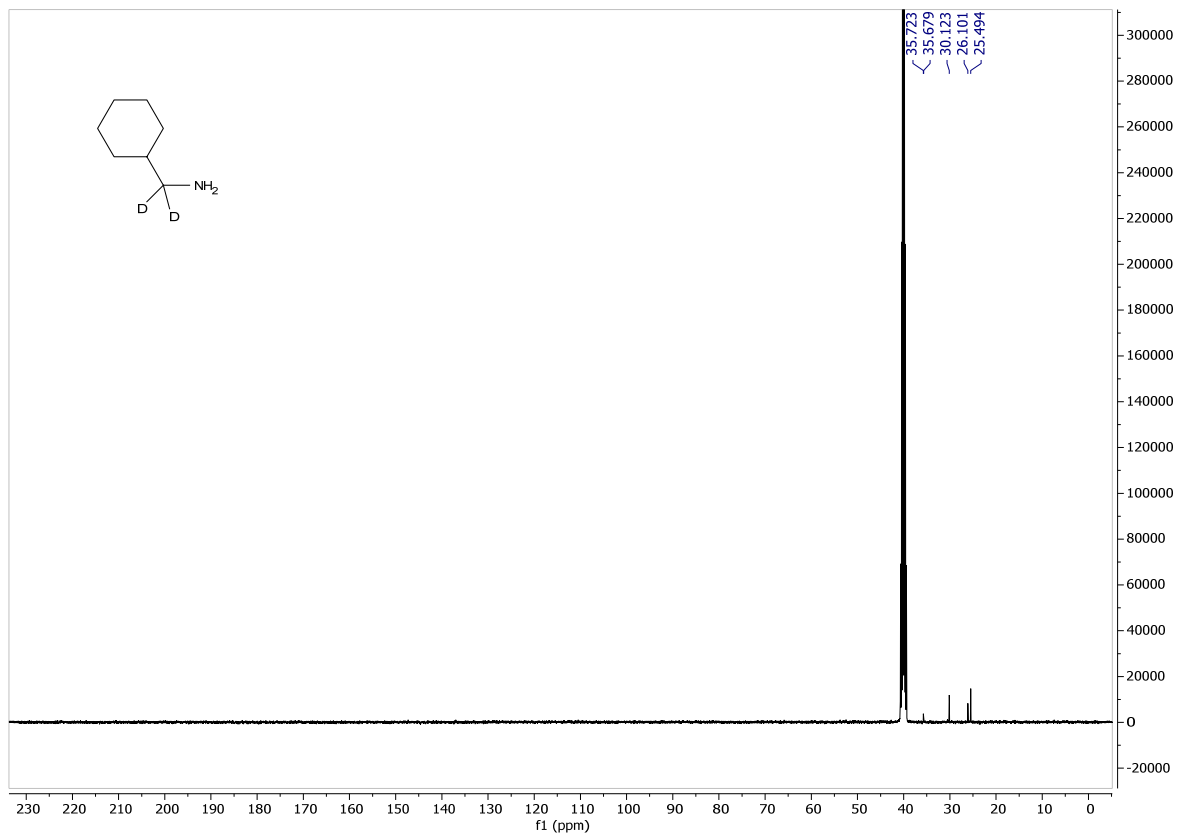
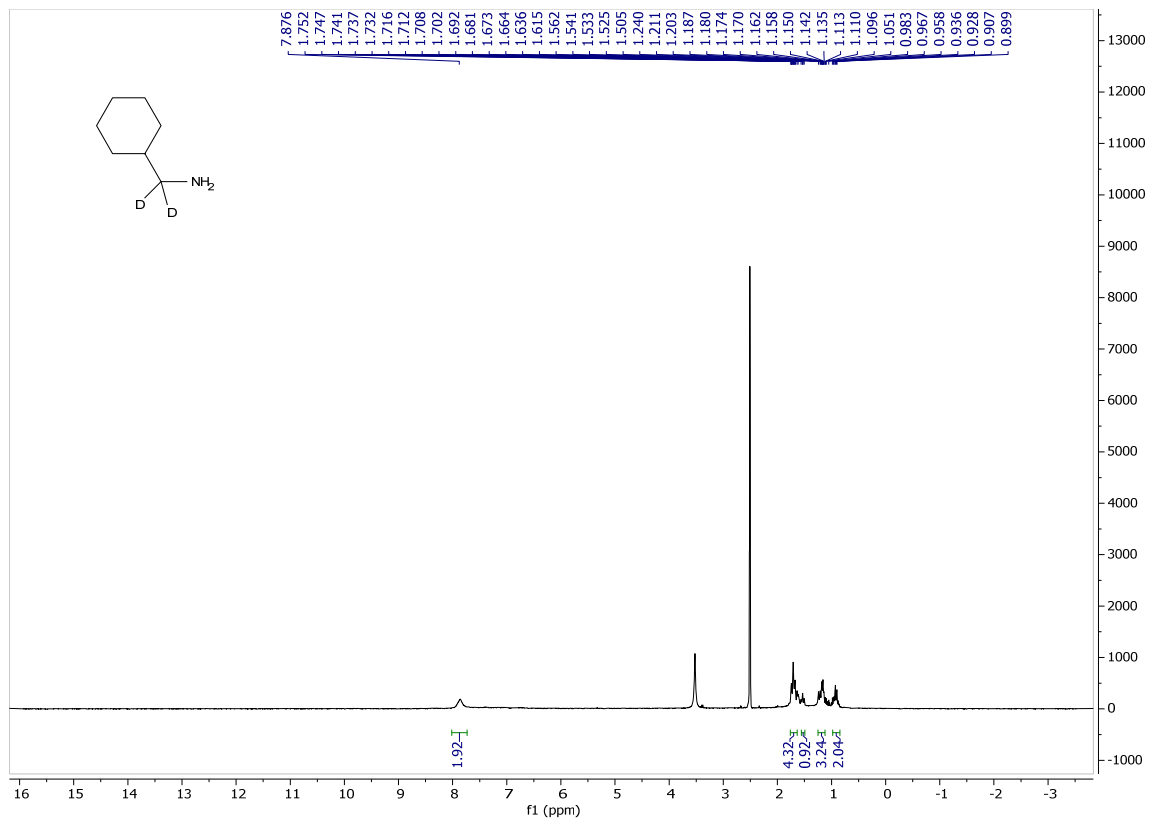
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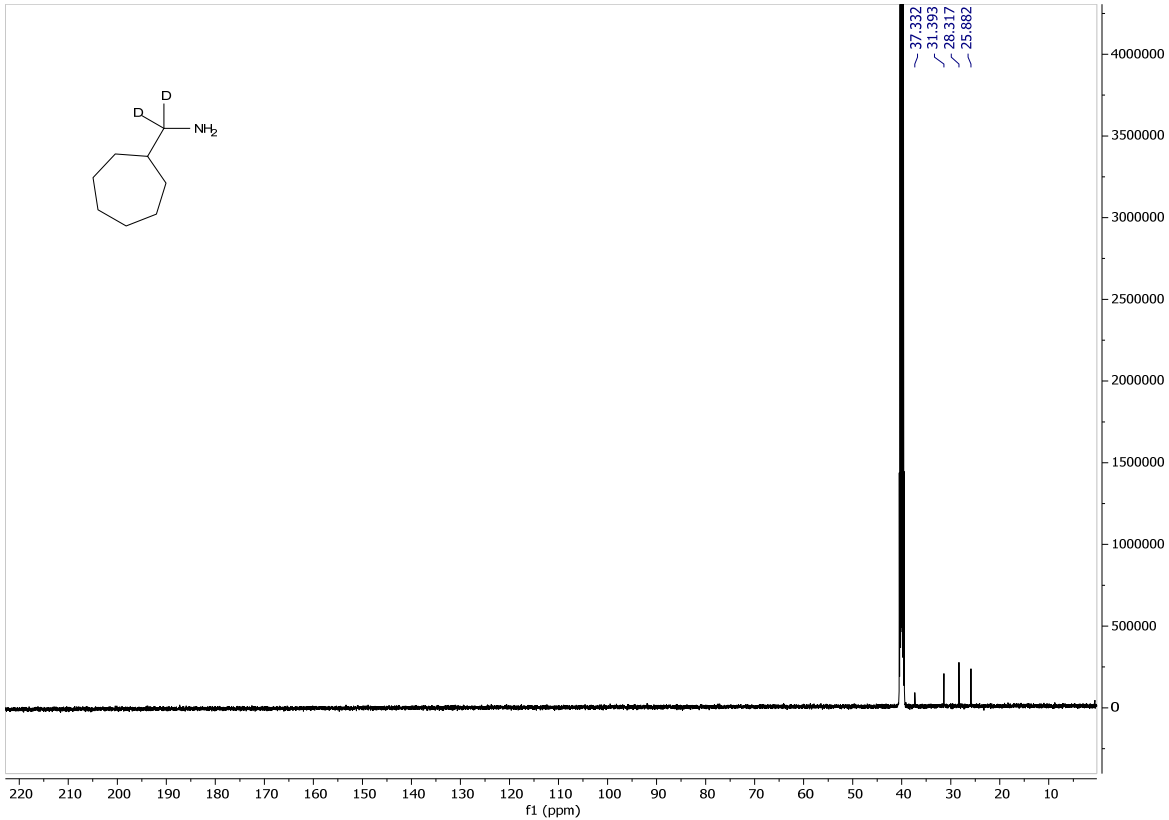
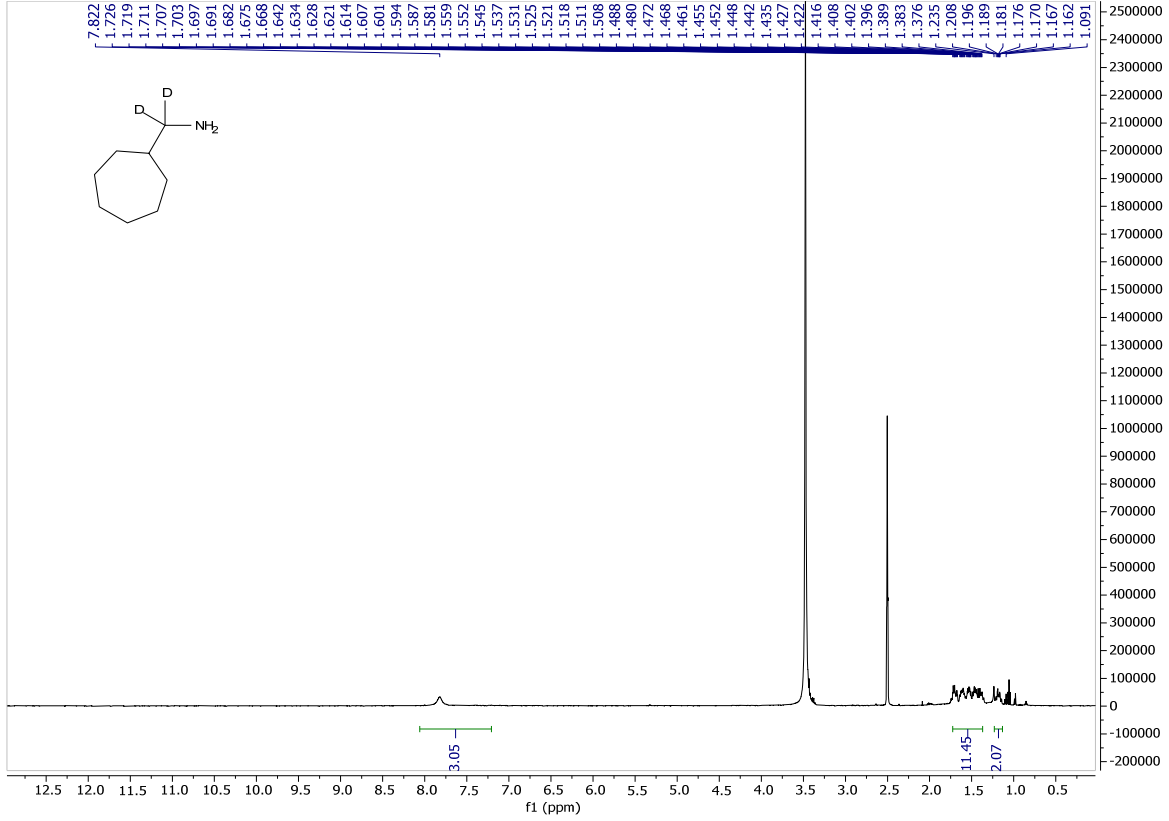
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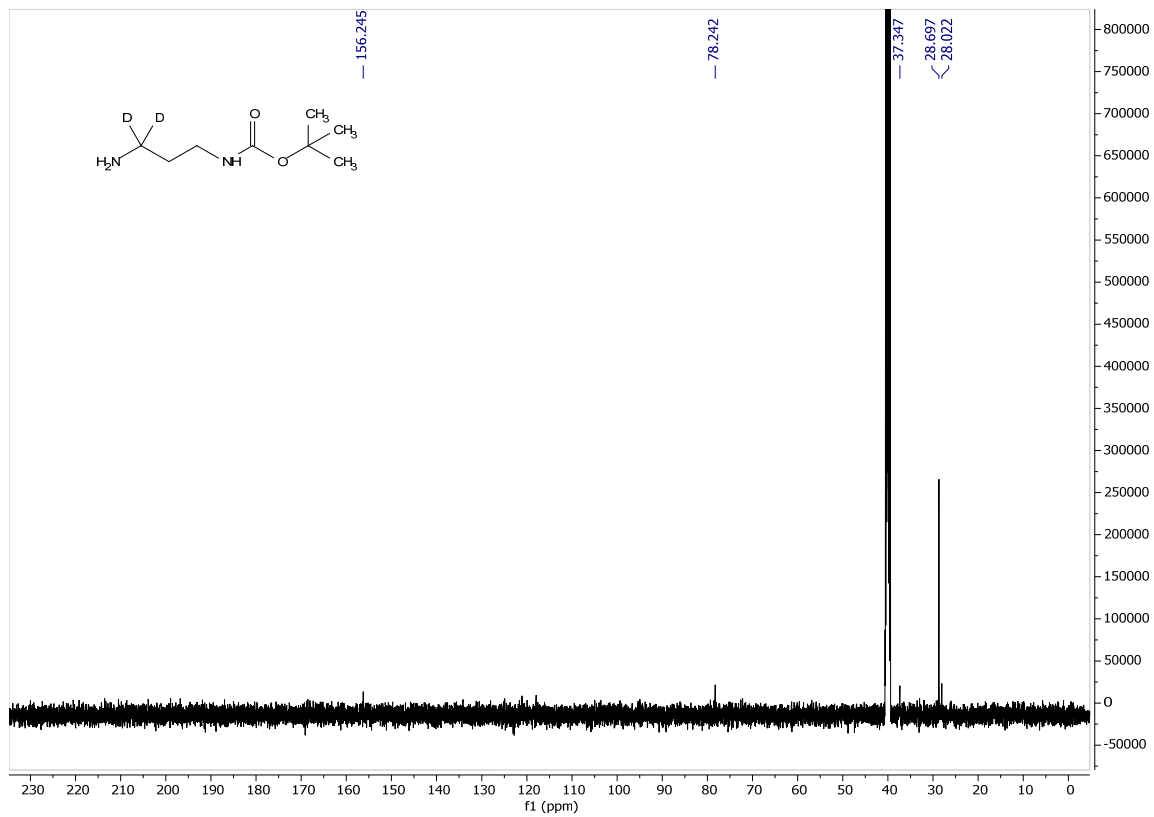
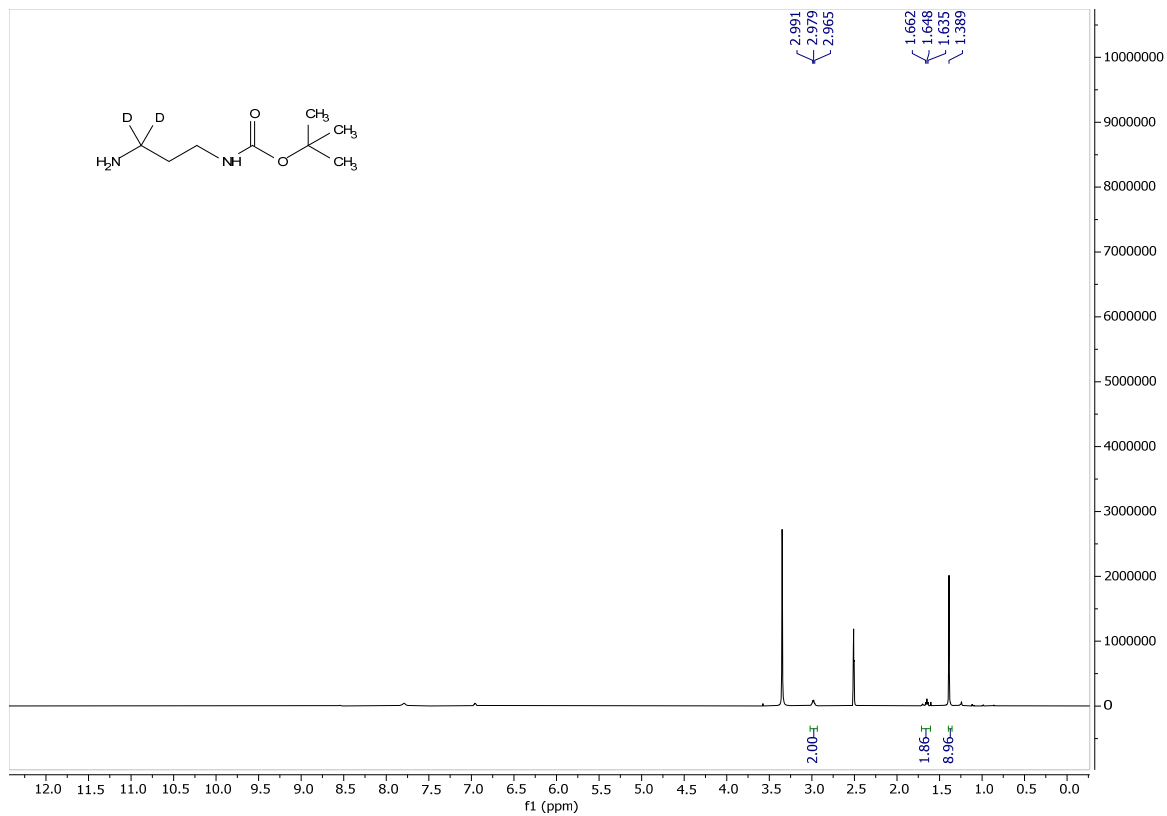
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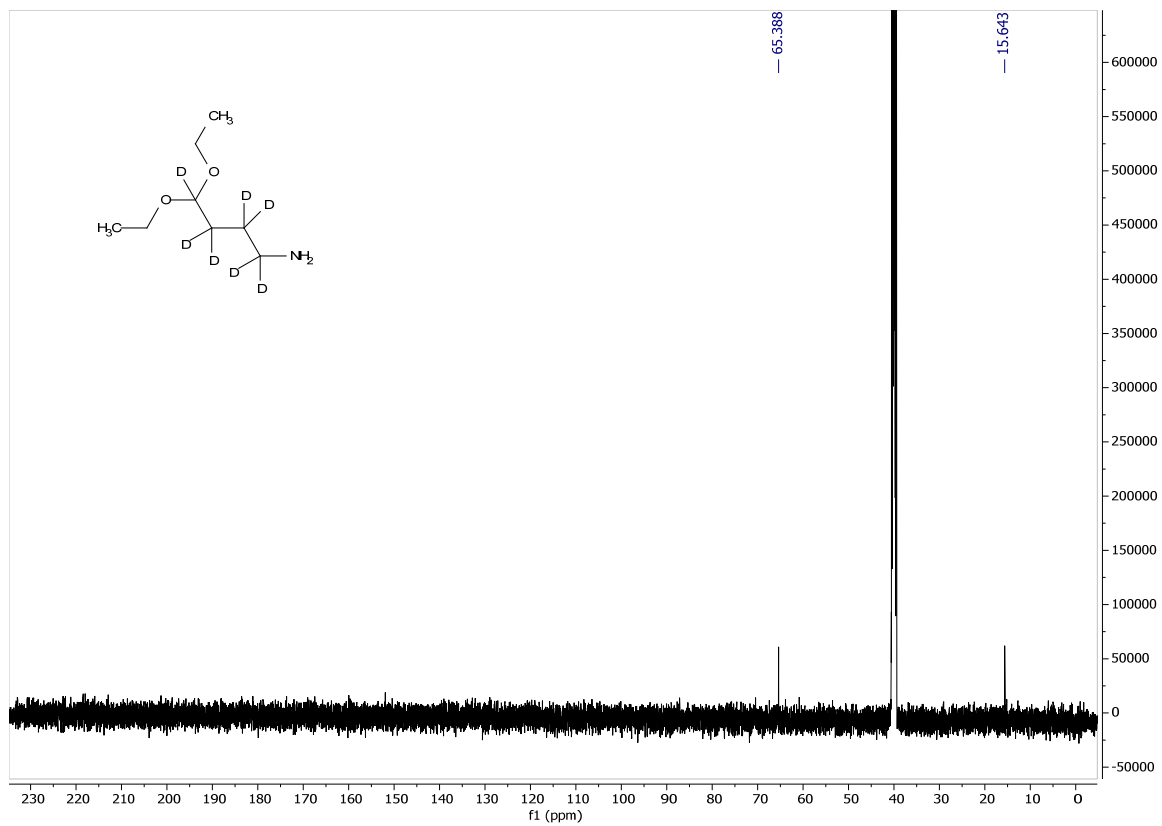
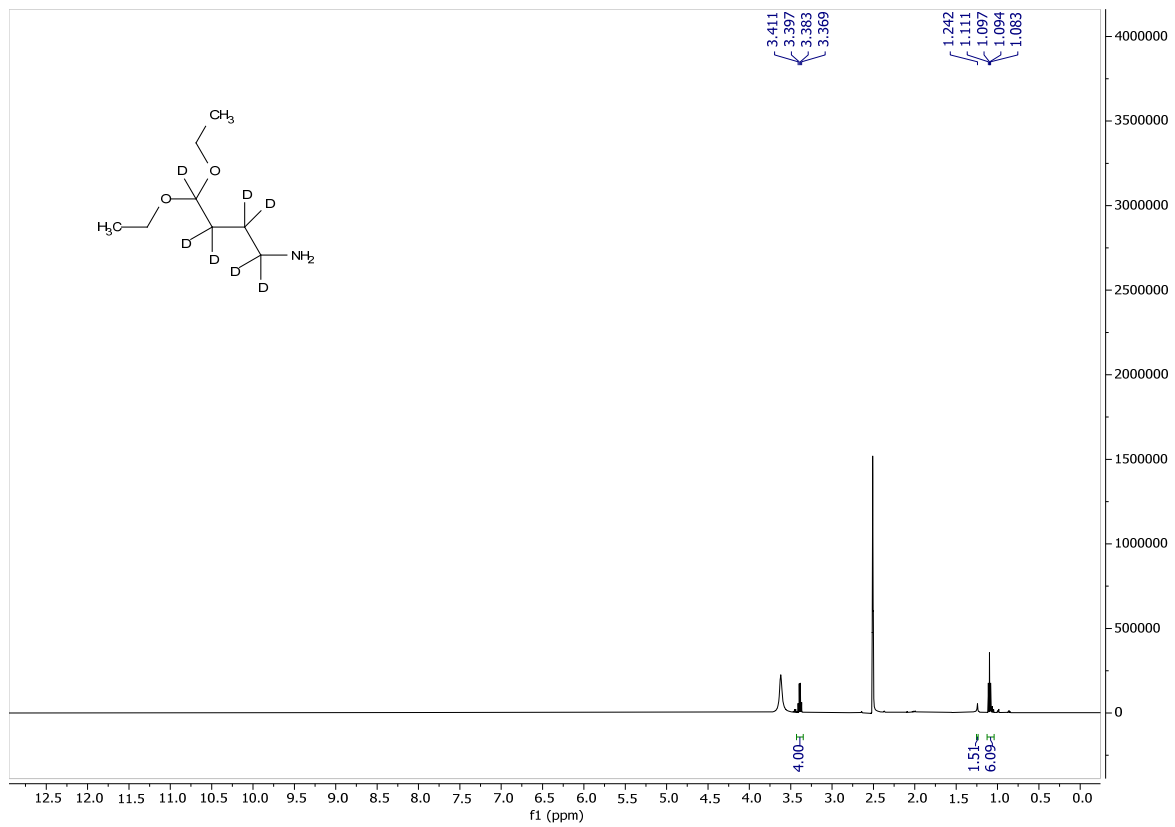
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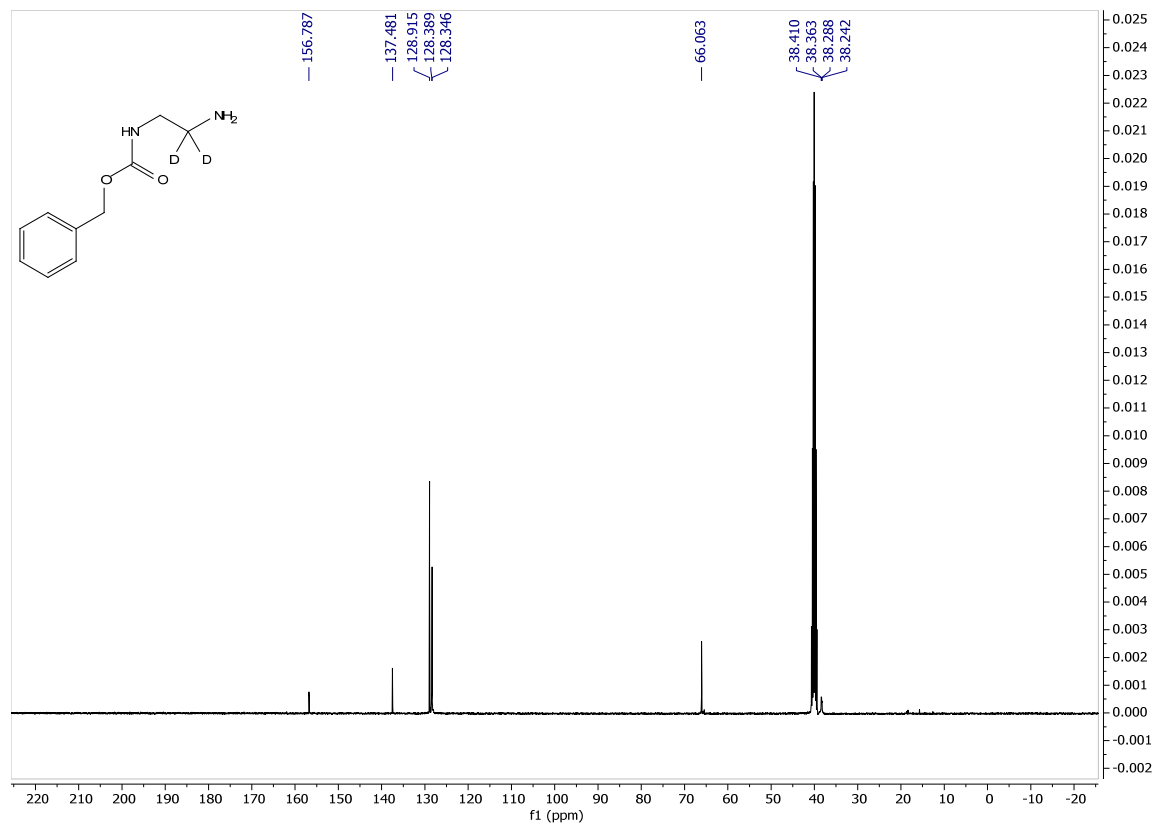
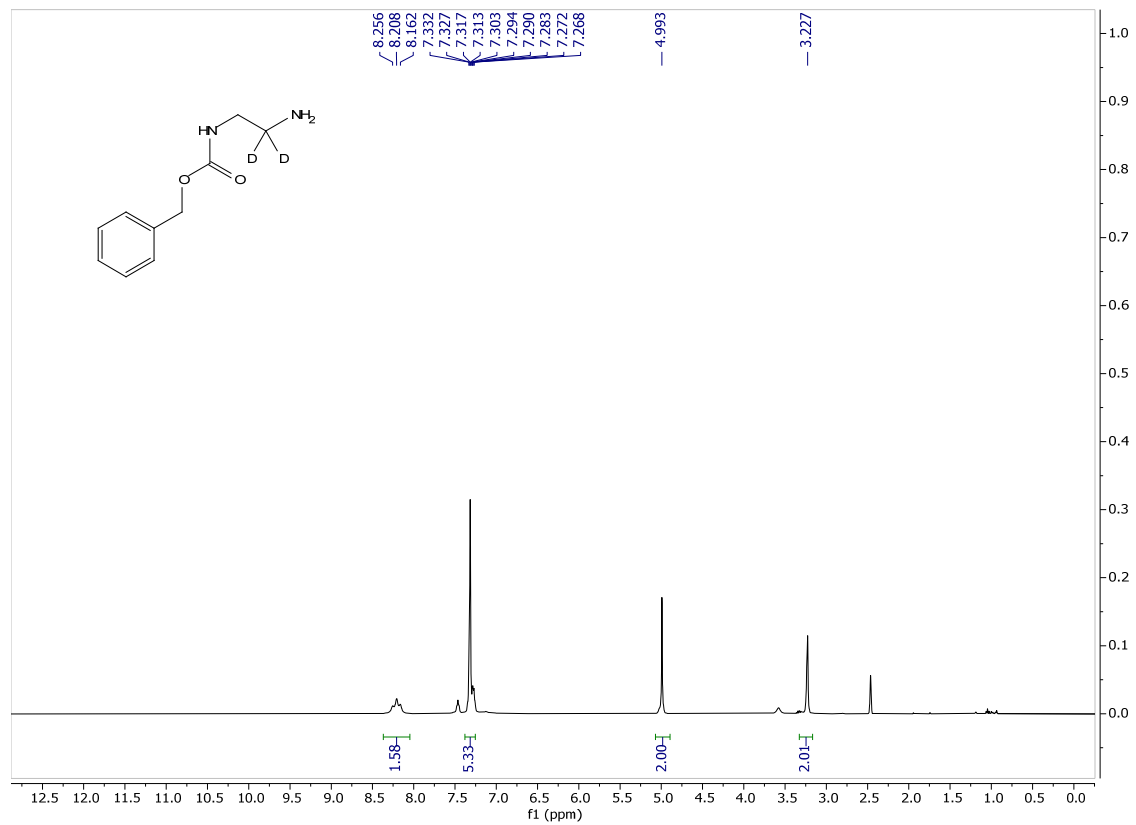
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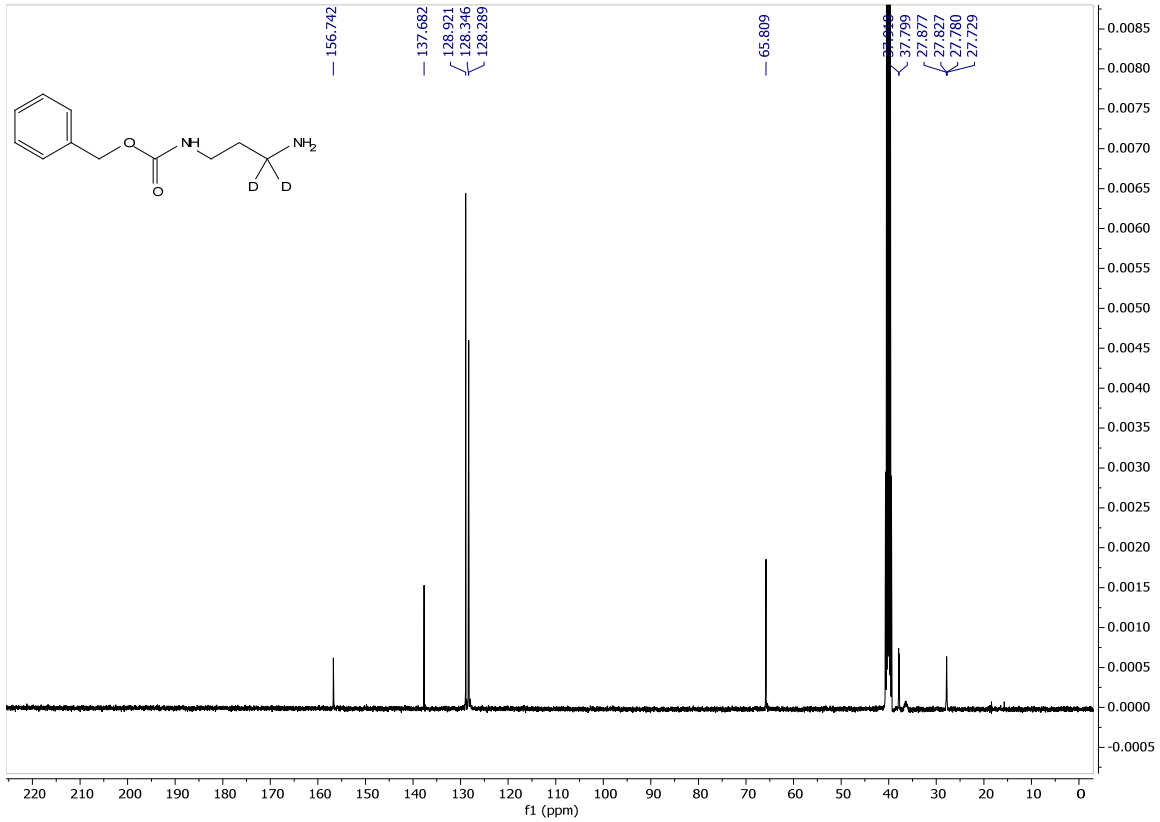
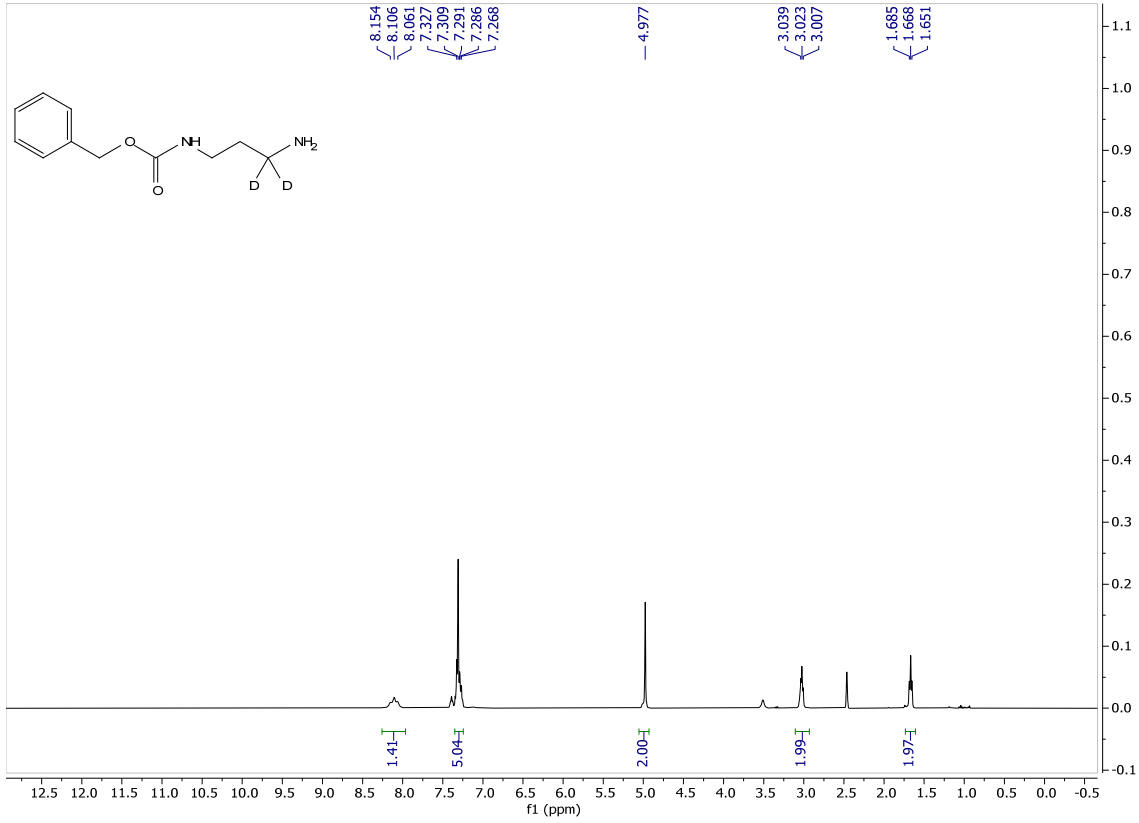
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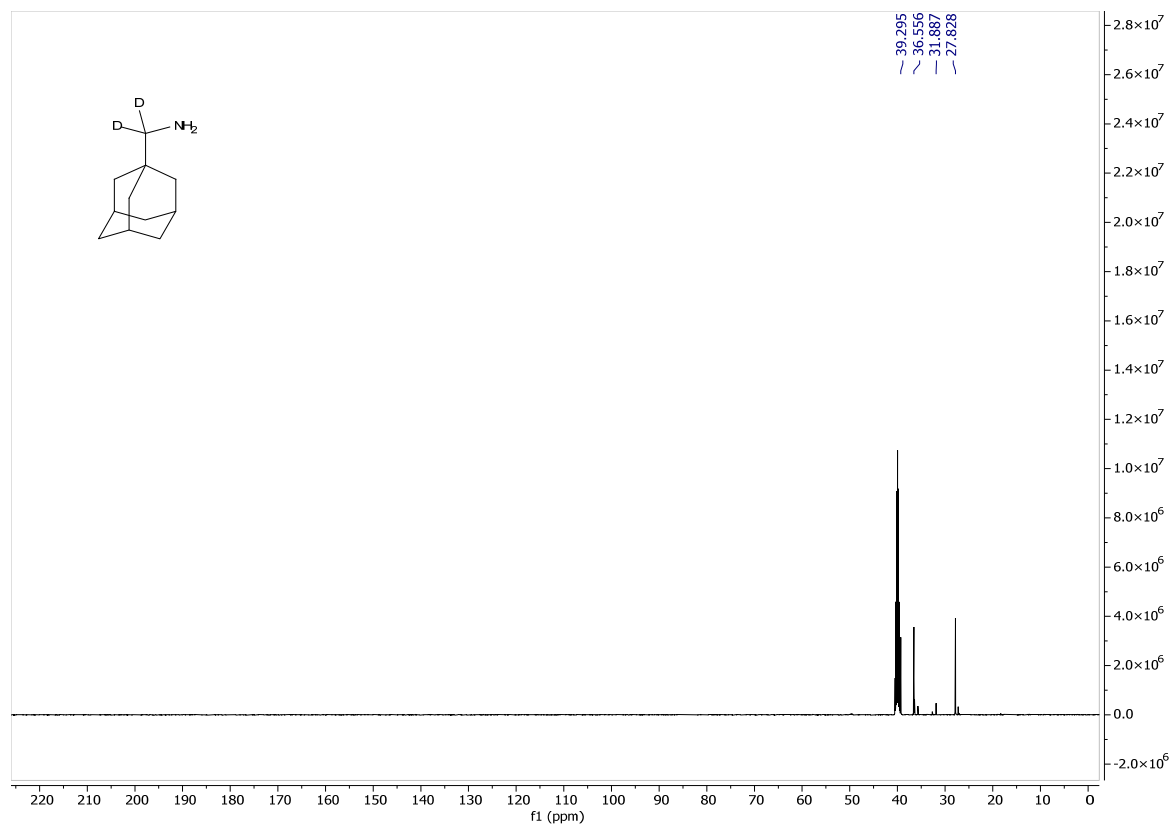
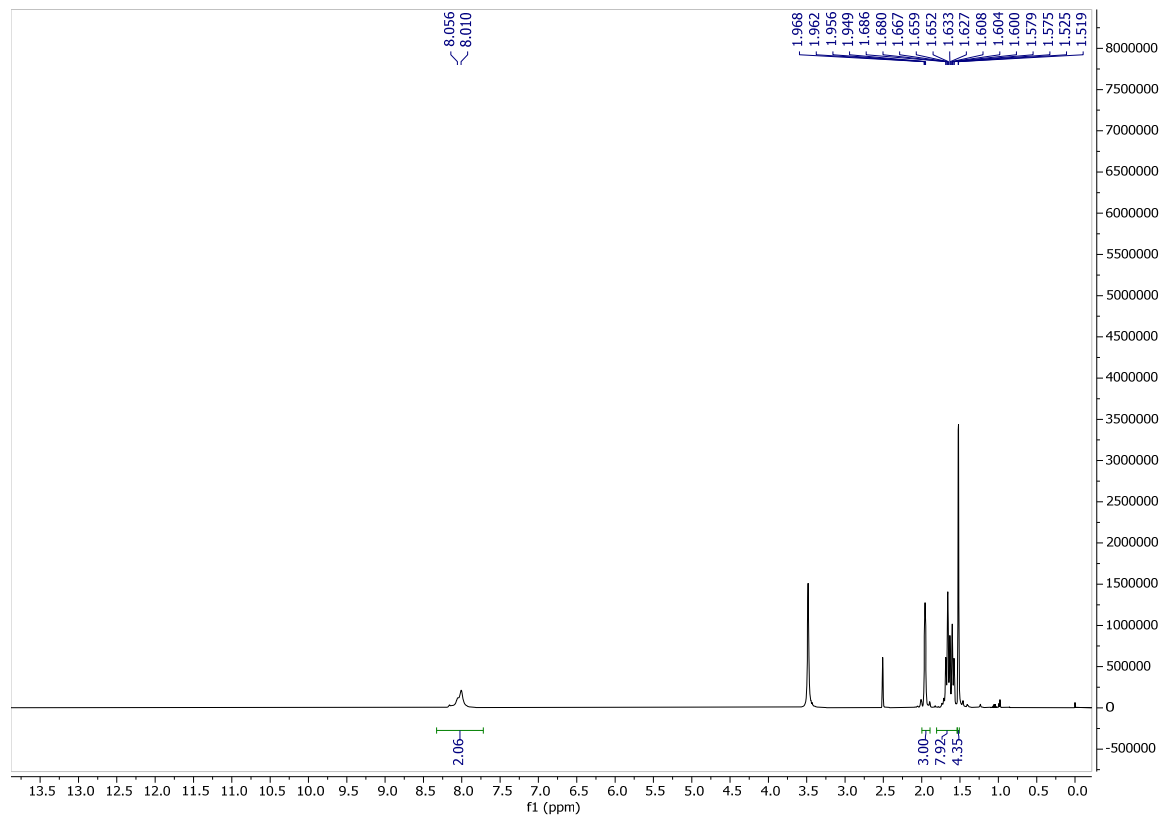
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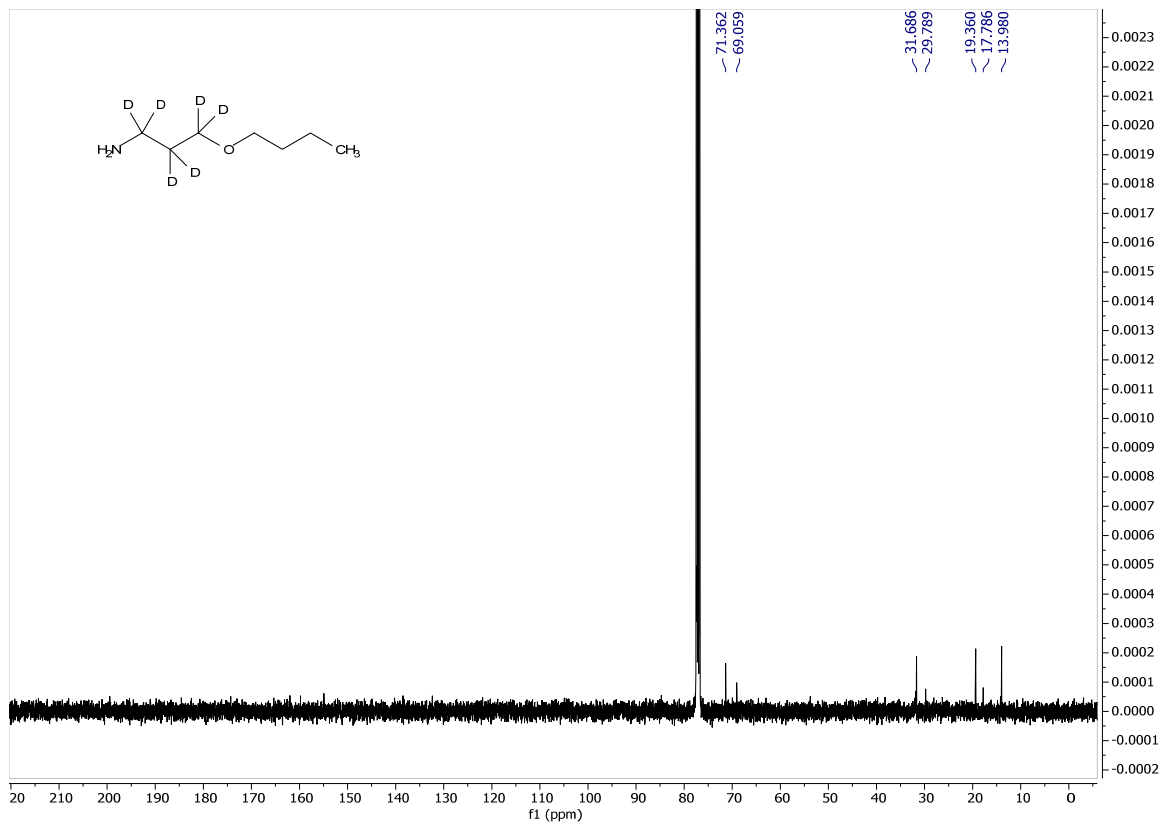
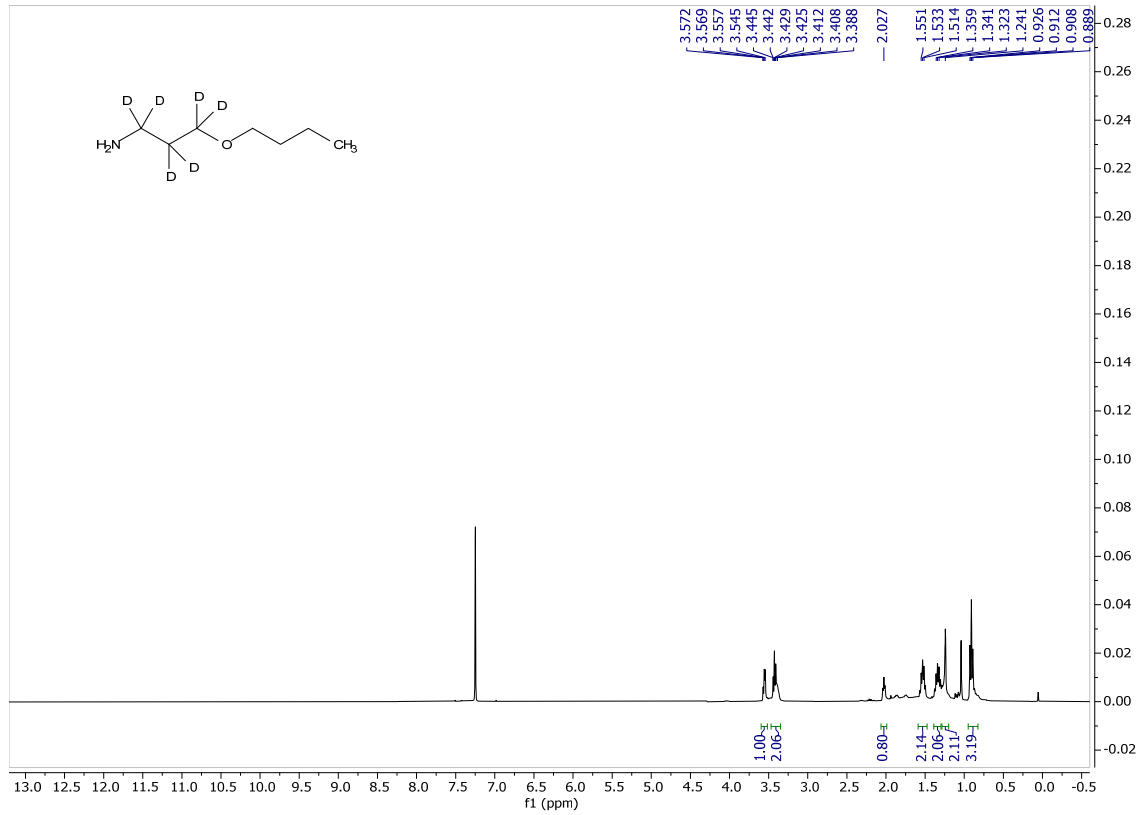
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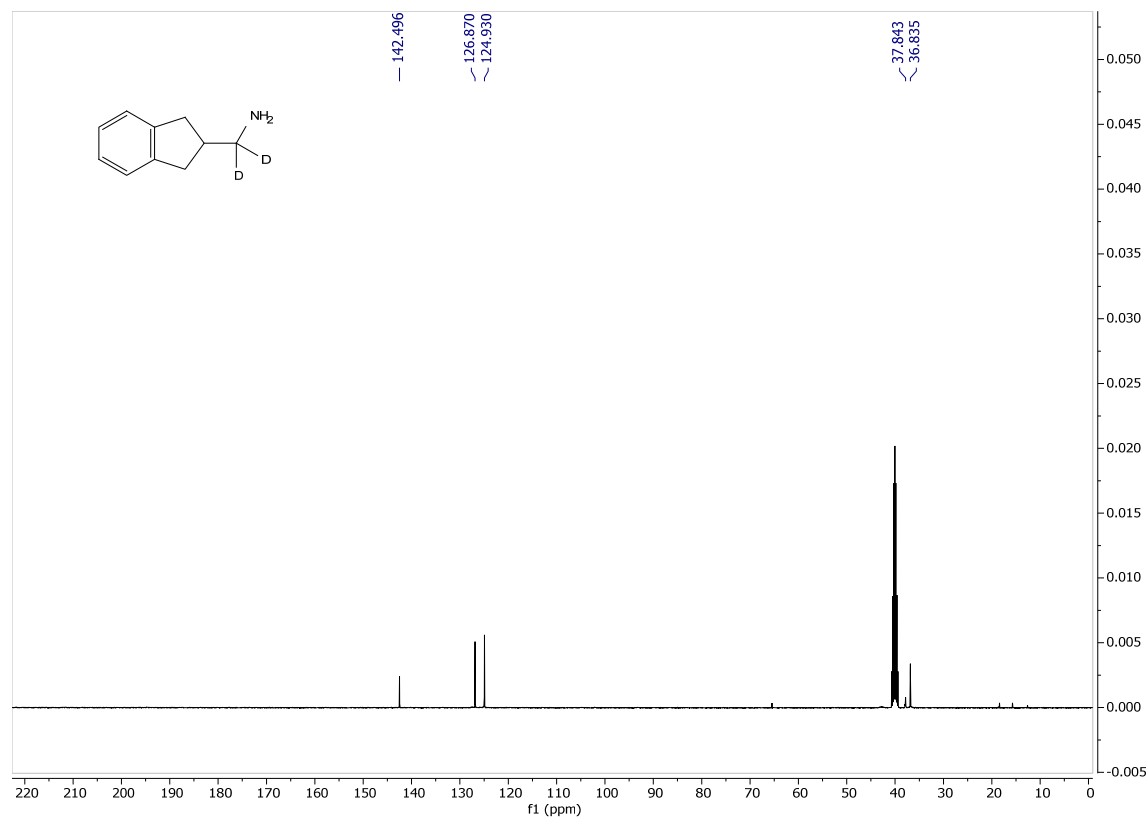
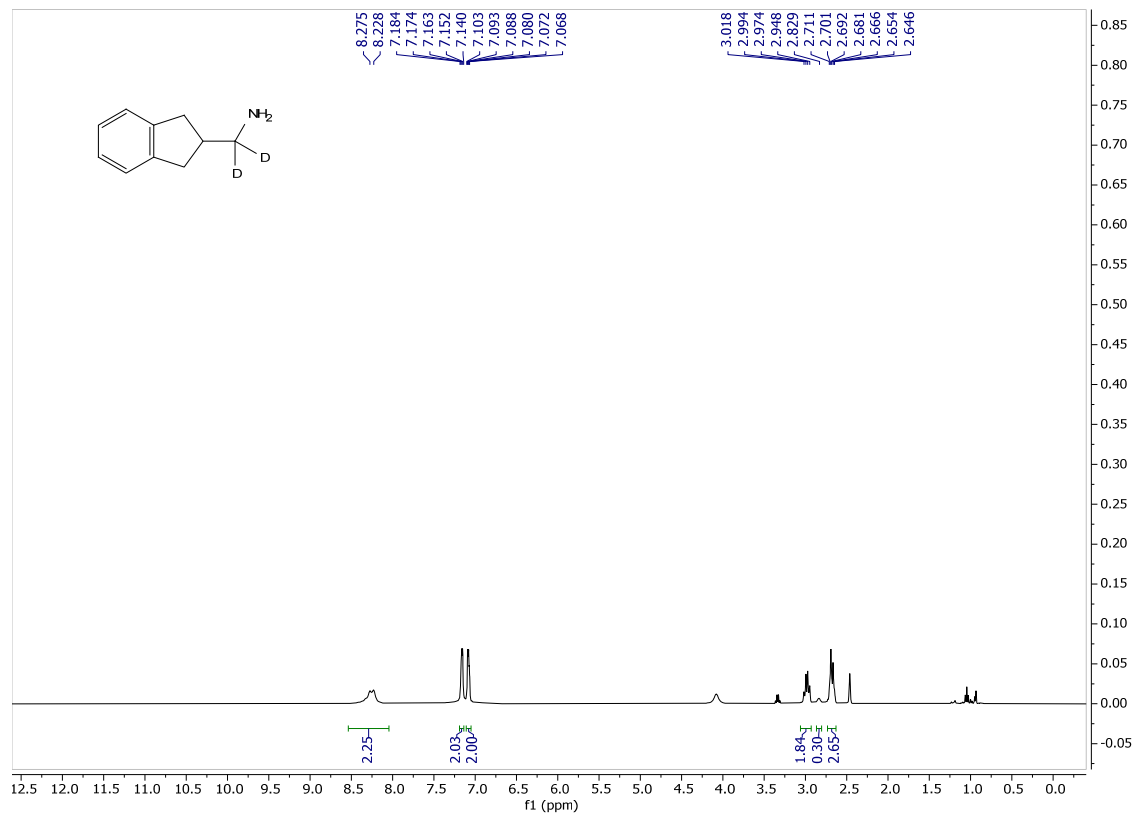
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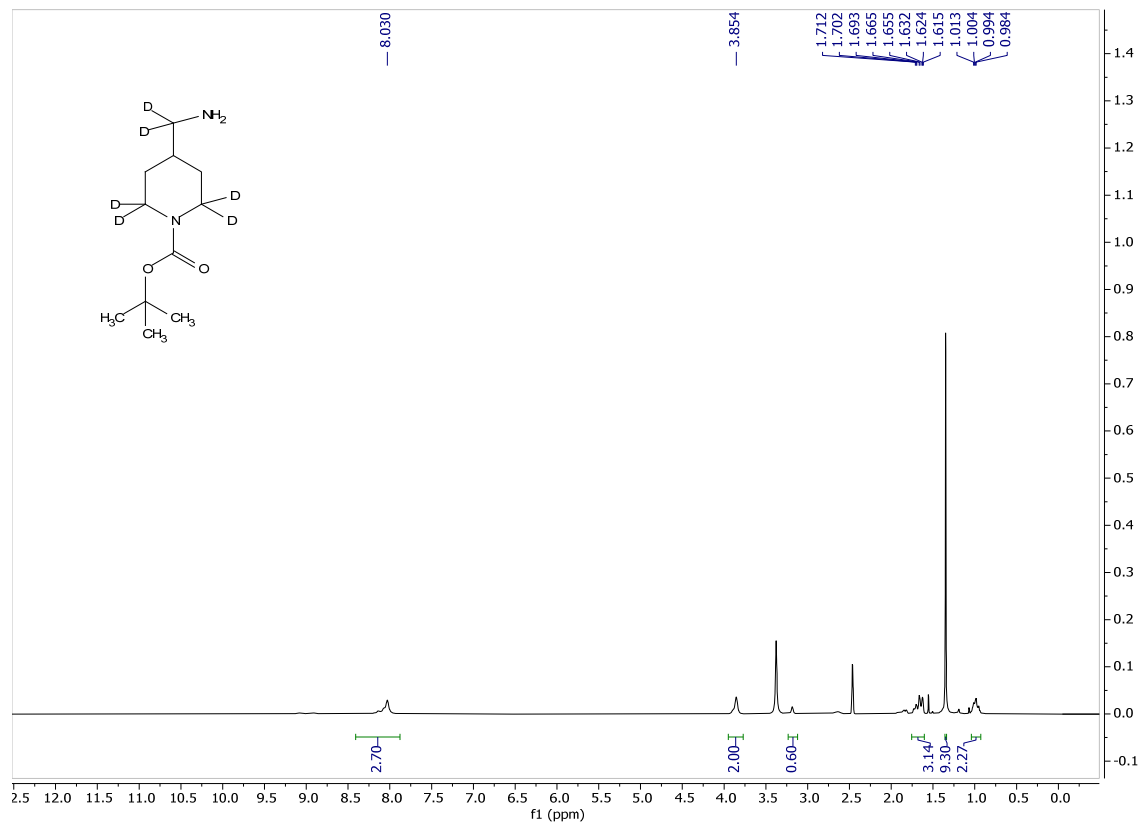
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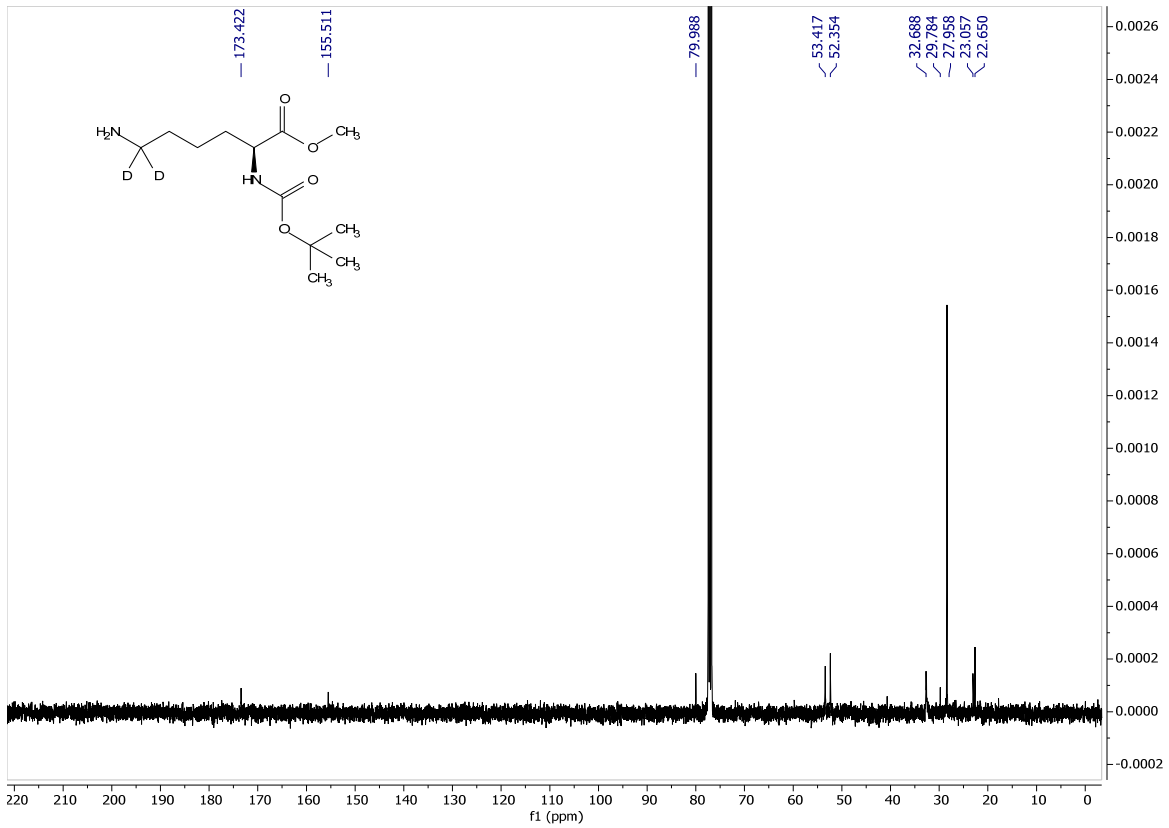
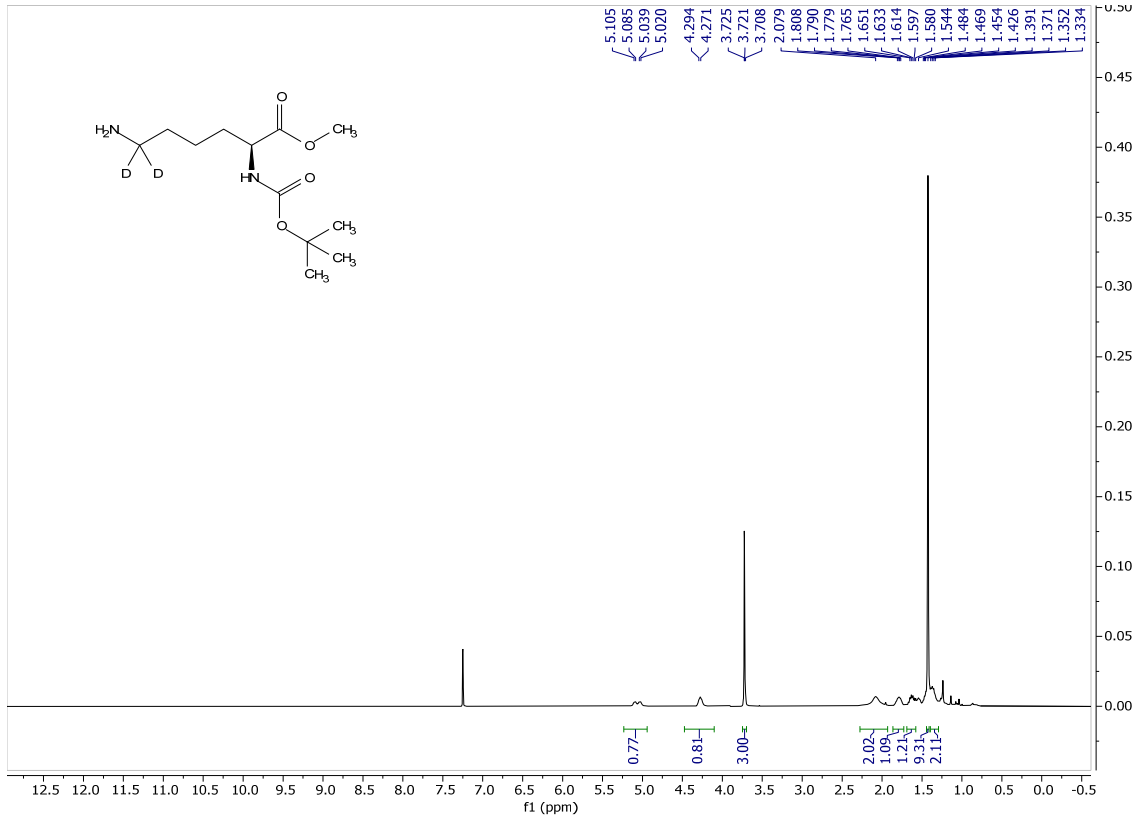
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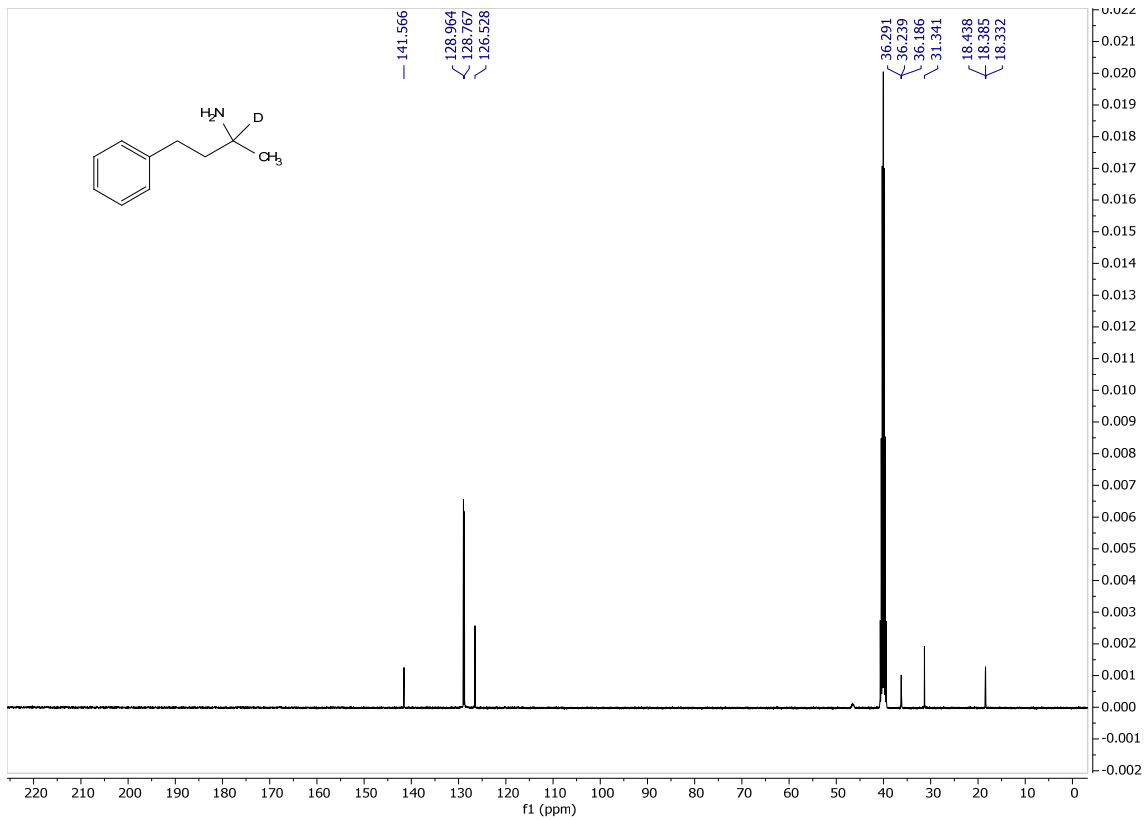
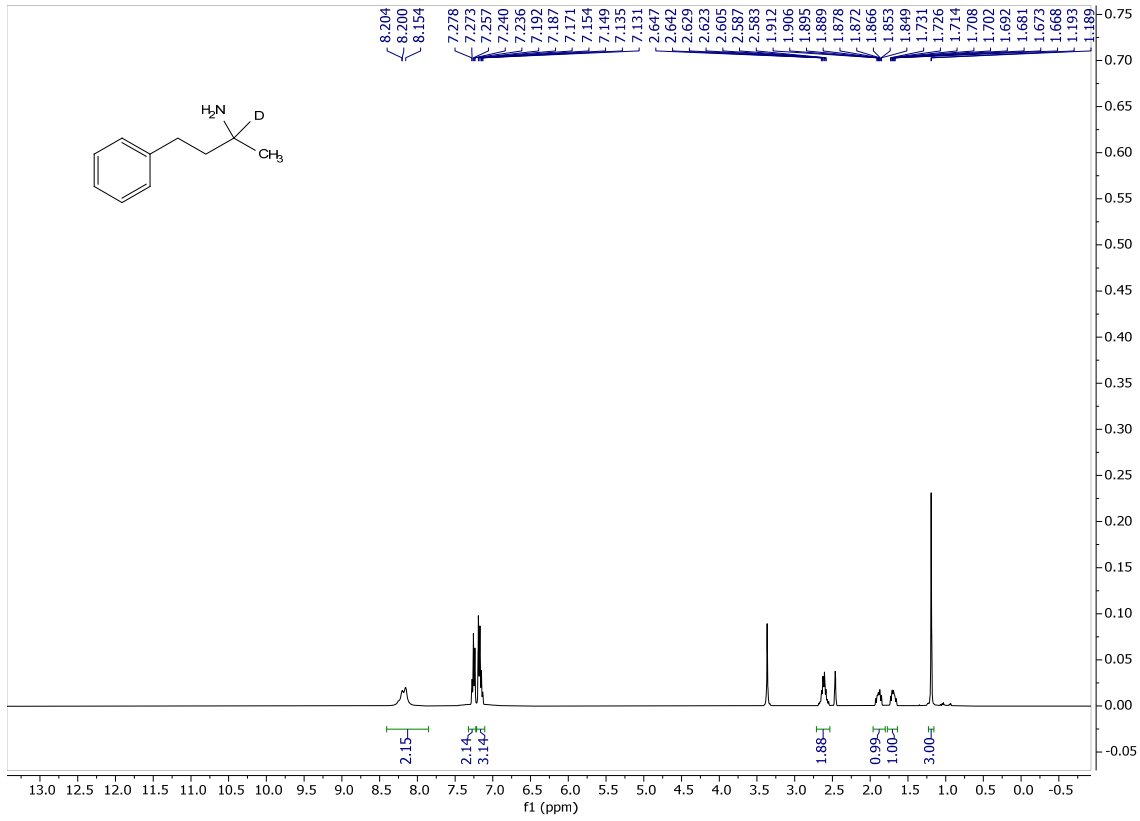
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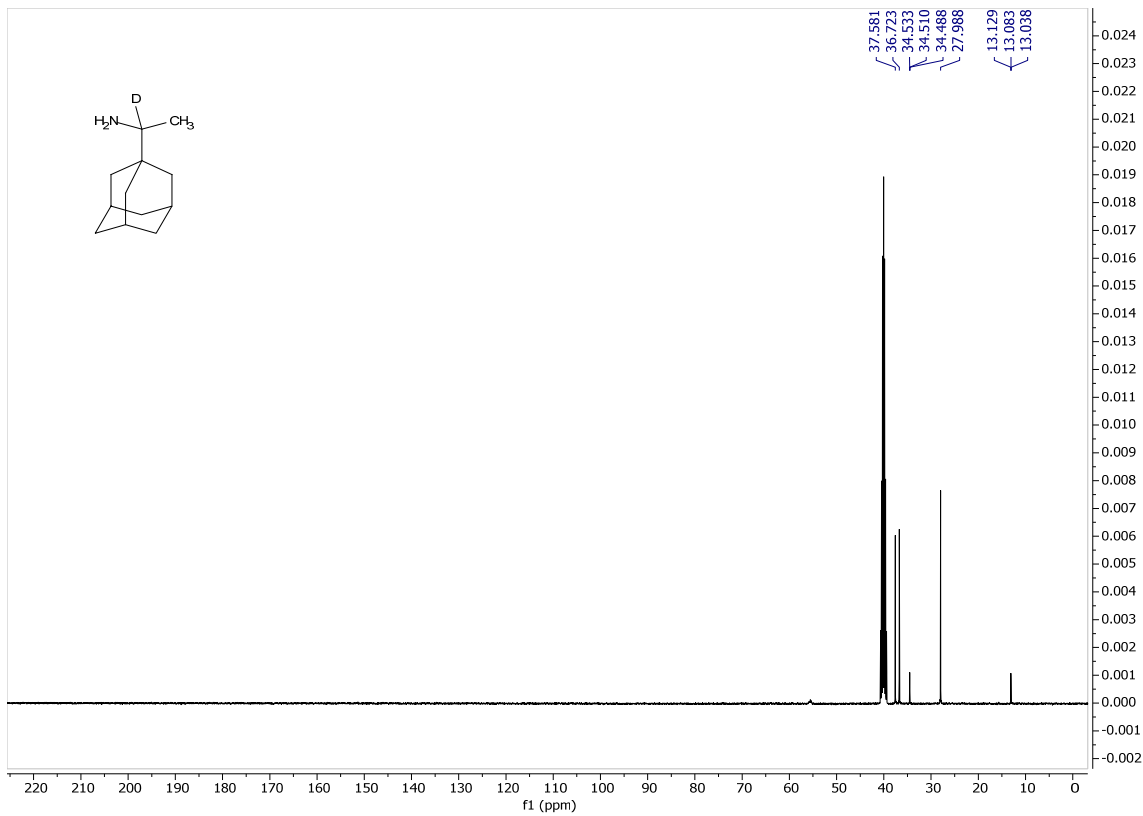
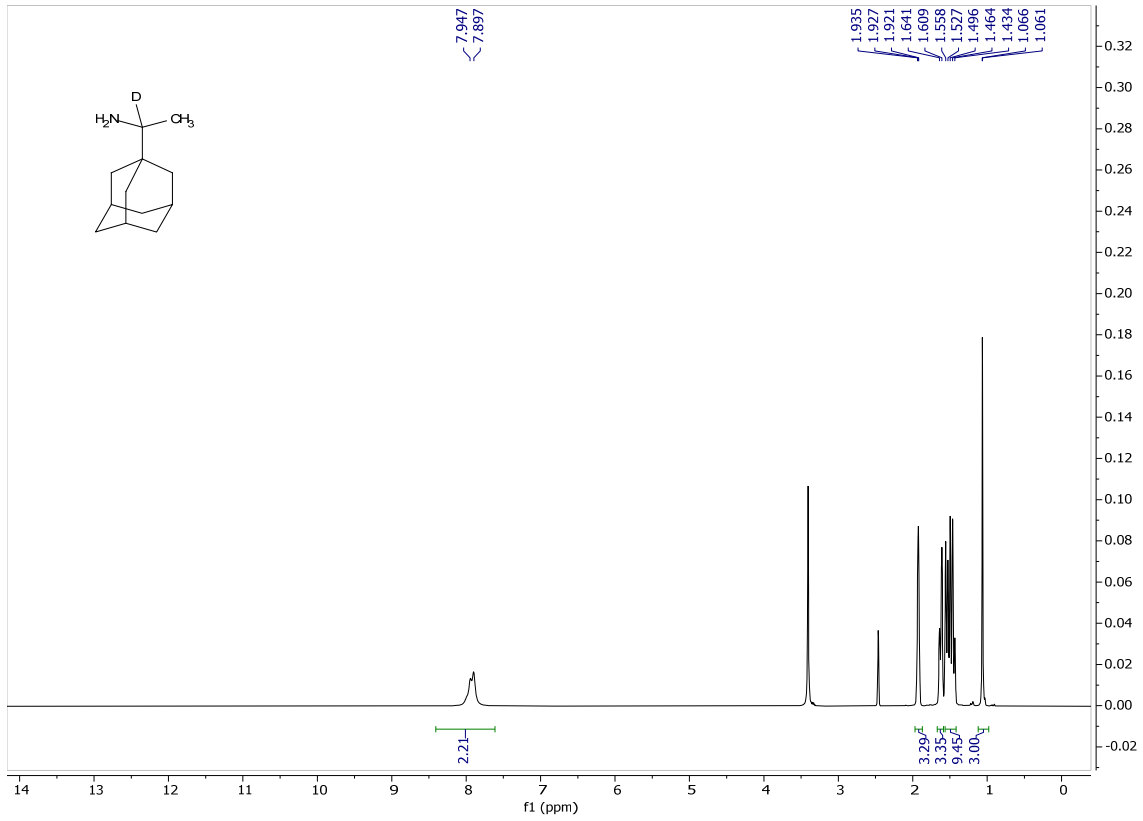
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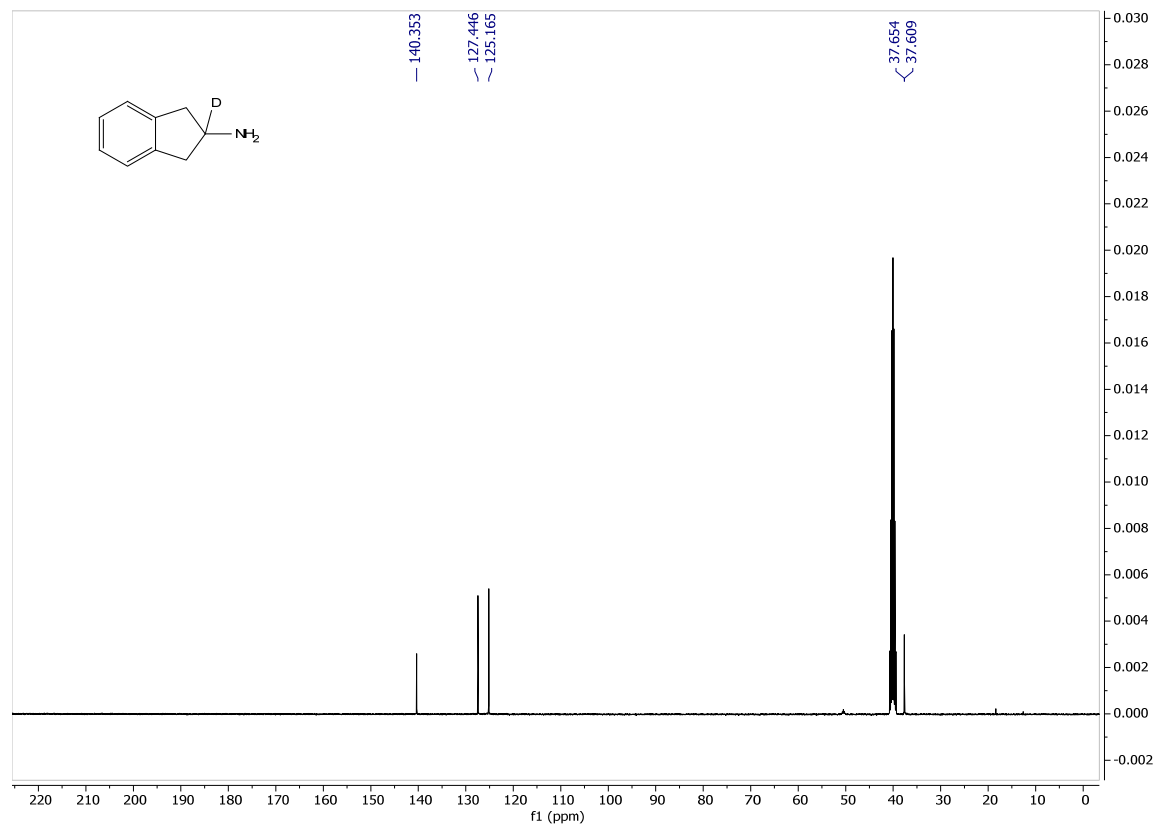
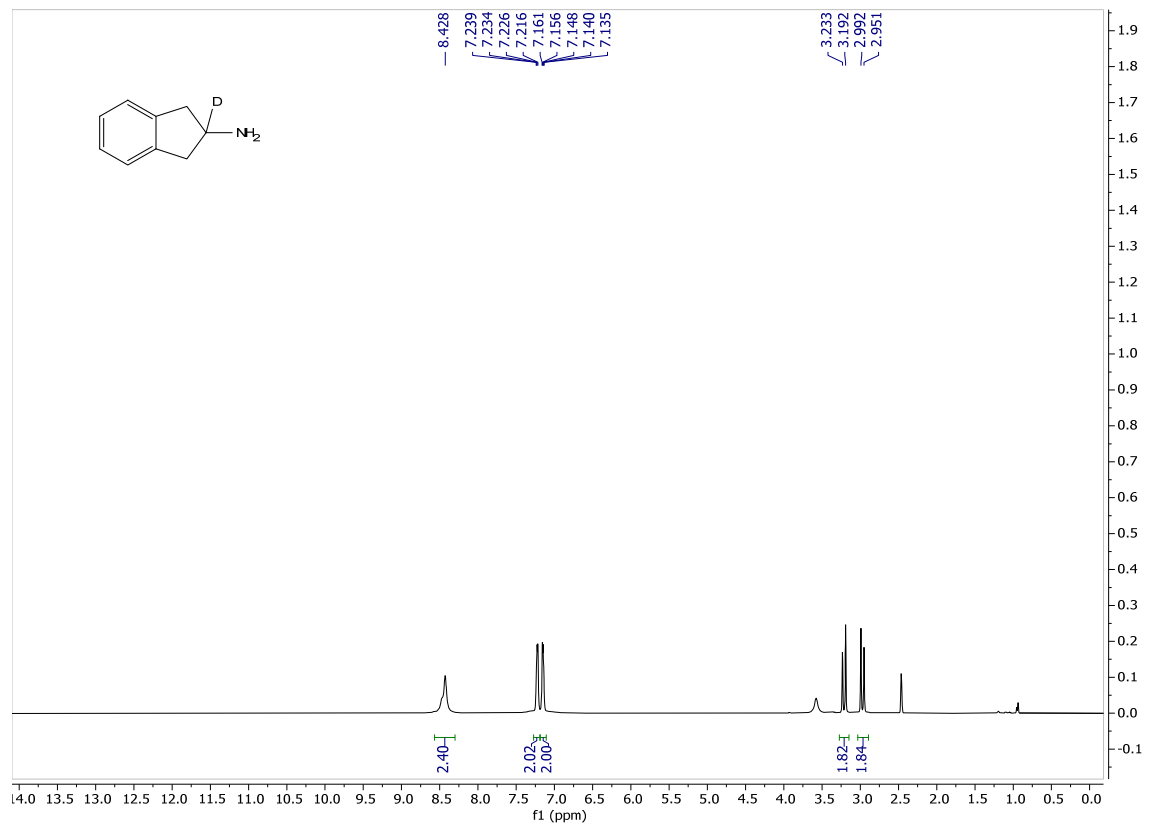
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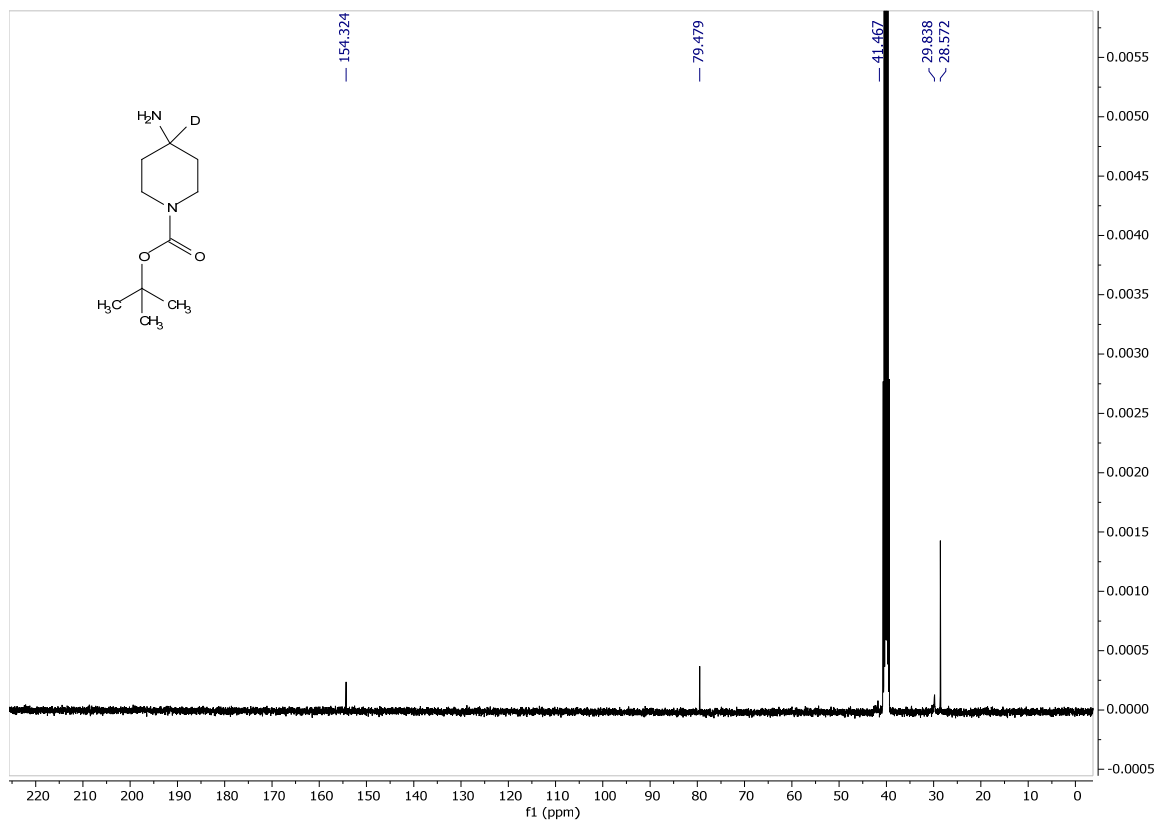
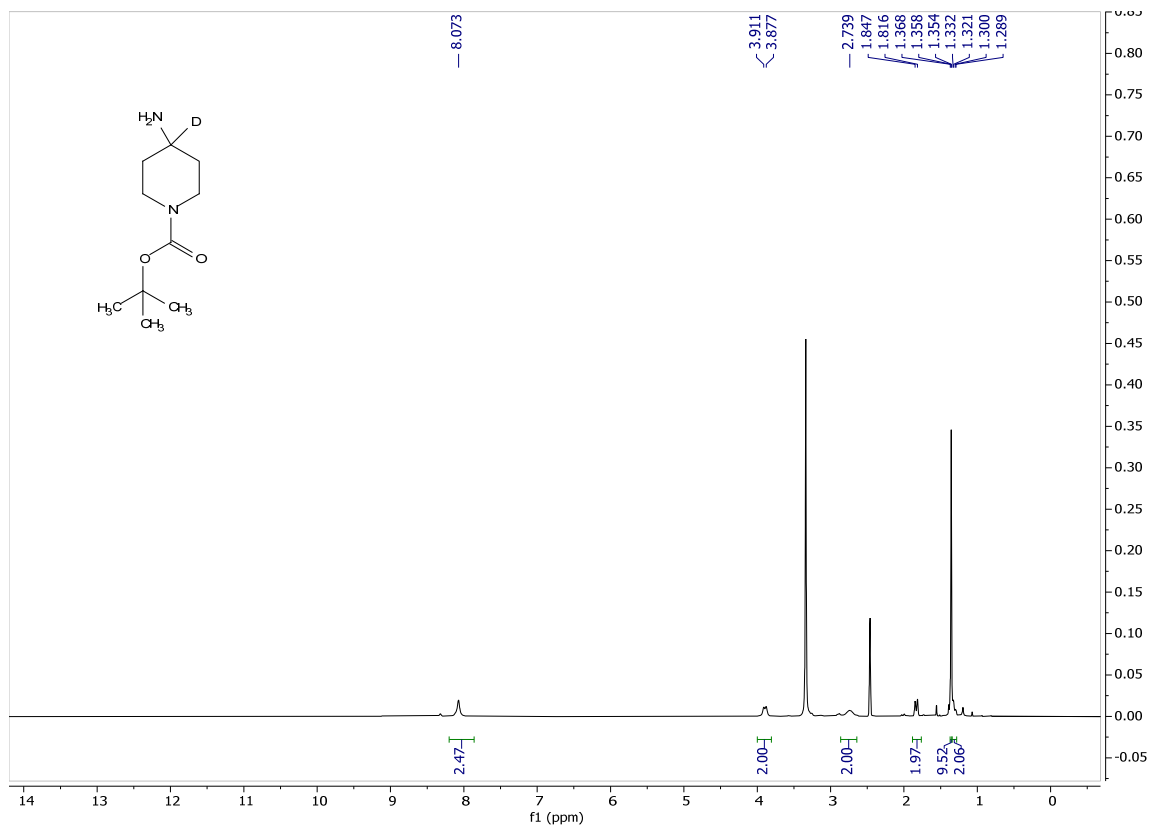
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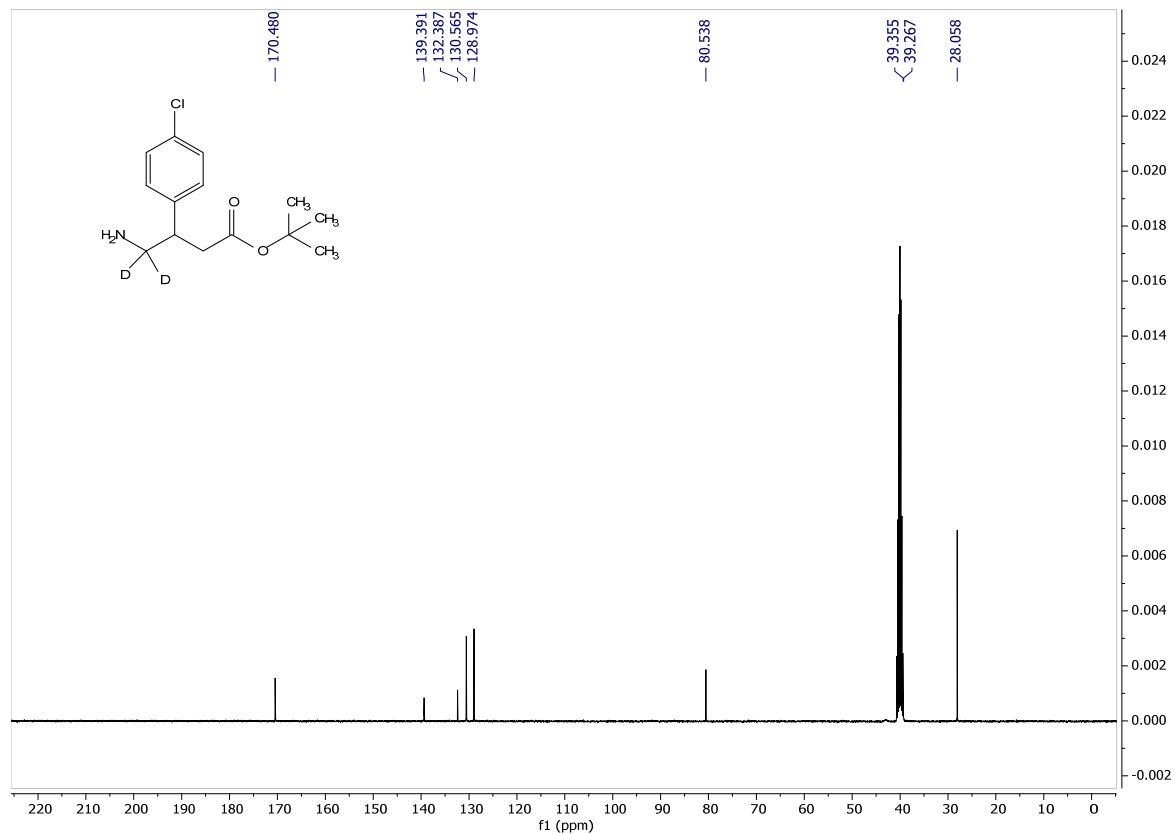
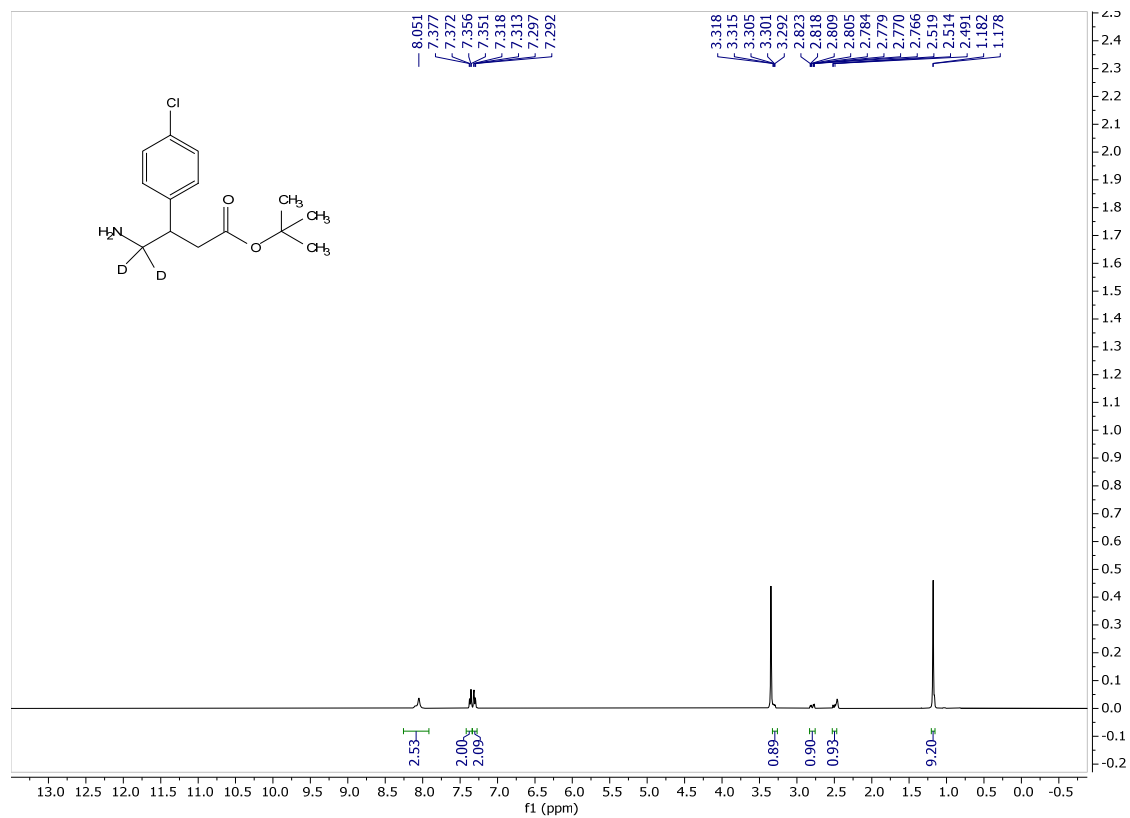
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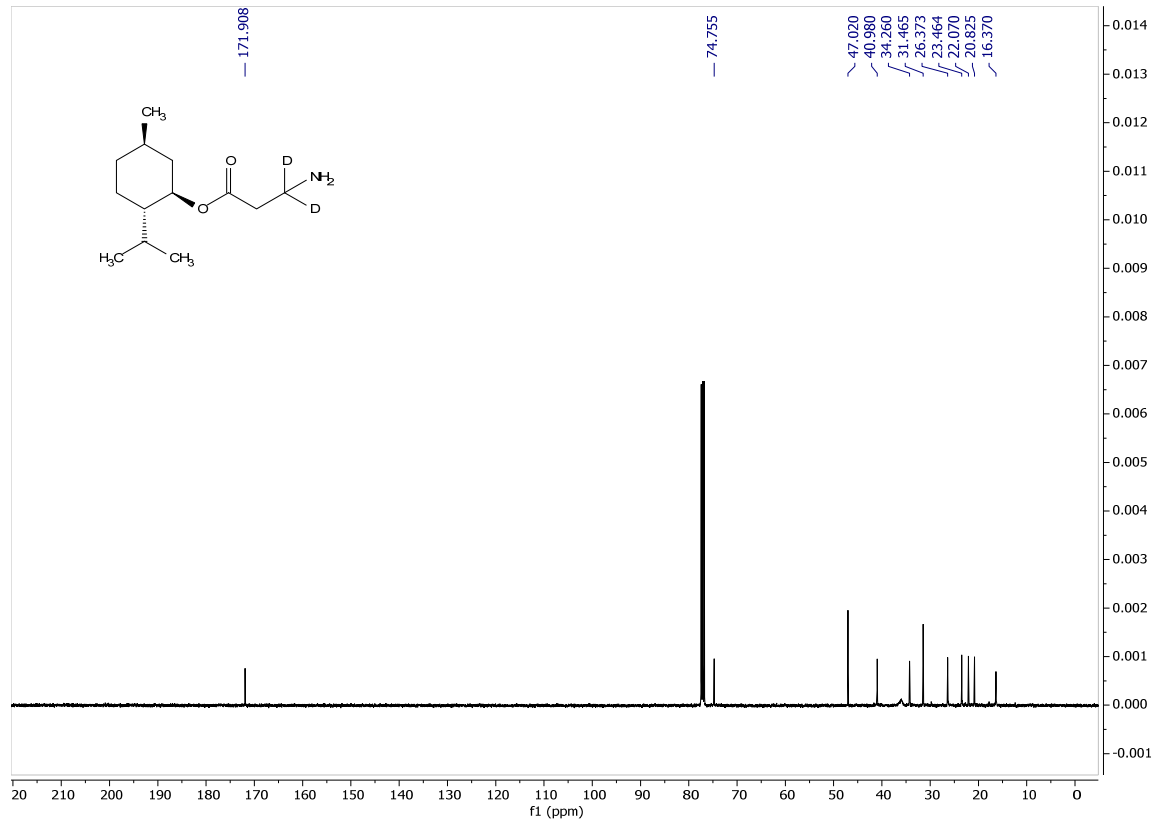
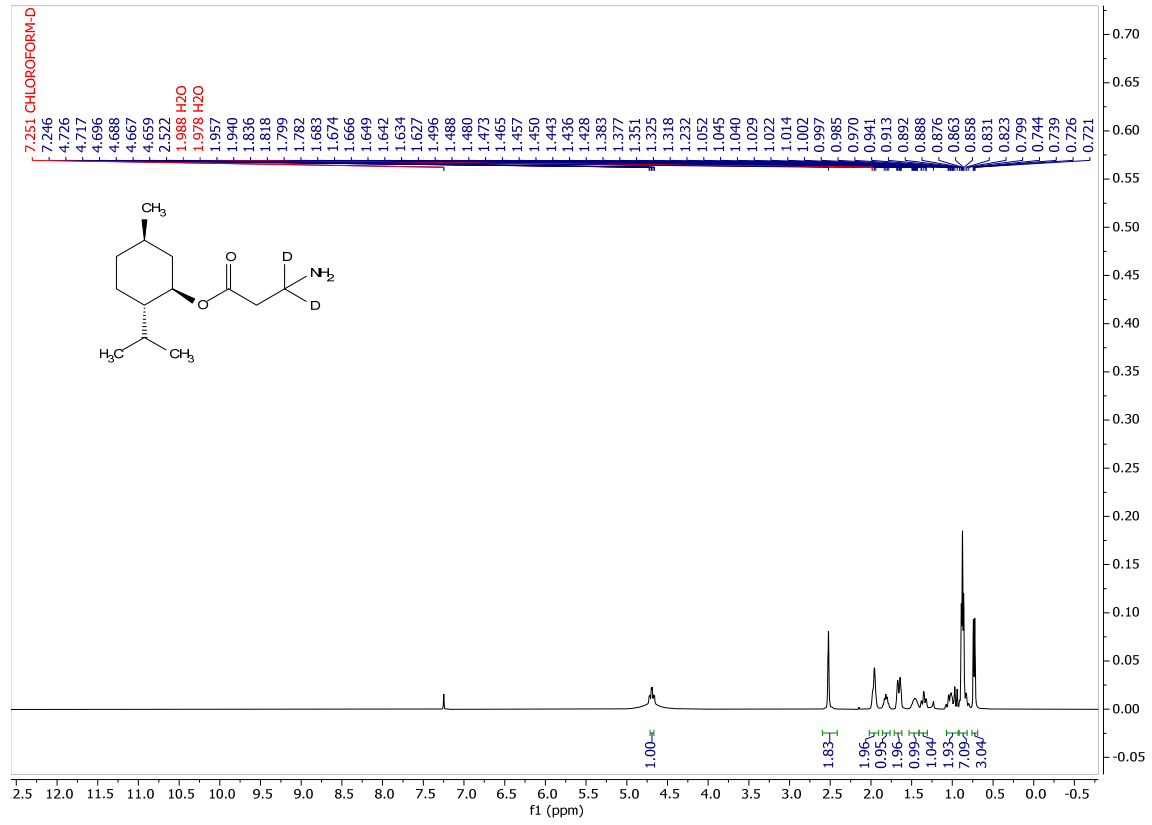
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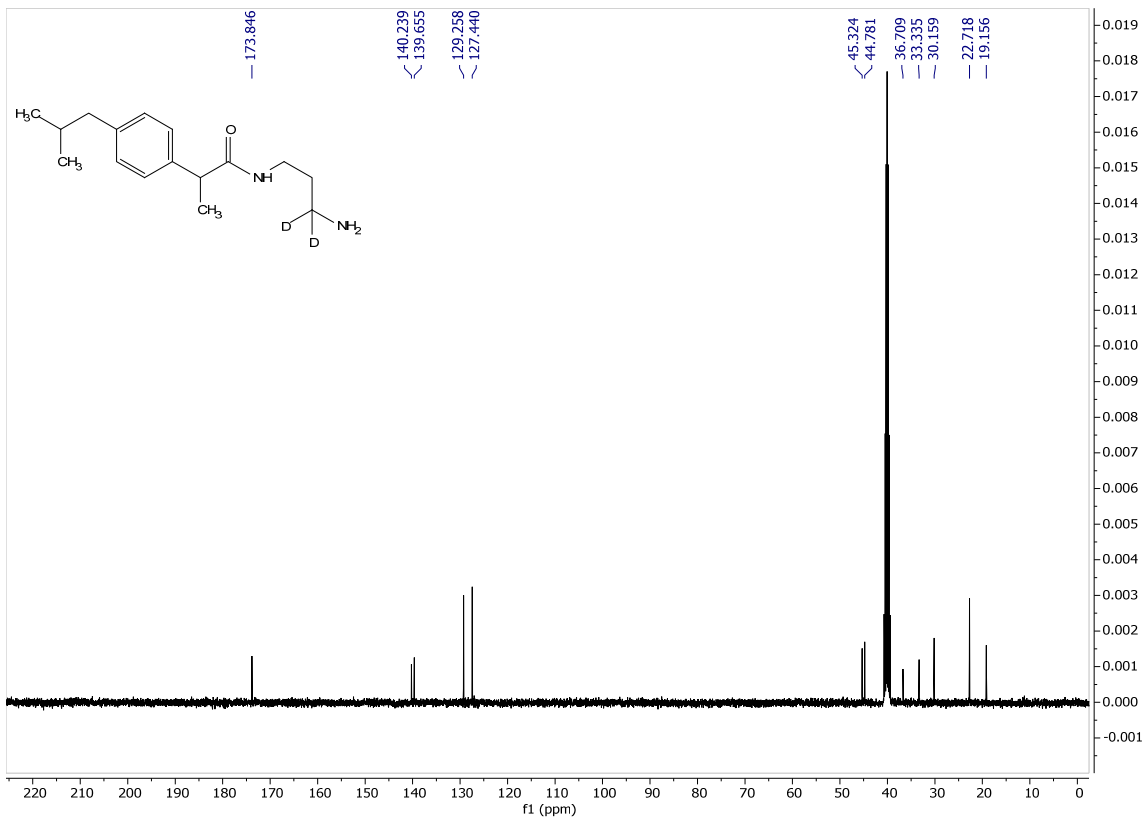
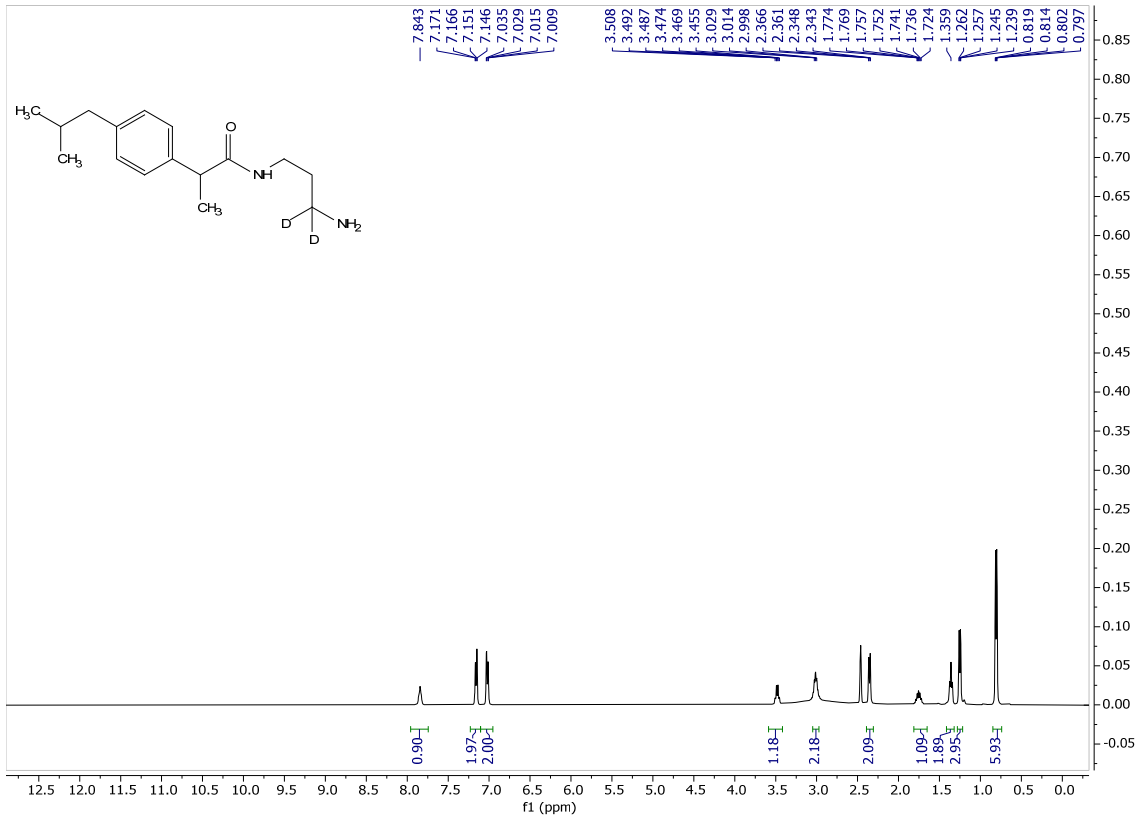
2ar



2as



2at



2au

