Supporting Information

Ruthenium-Catalyzed Selective α-Deuteration of Nitriles Using D_2O

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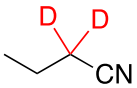
General experimental: All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBraun glove box. Chemicals were purchased from commercial vendors such as Sigma-Aldrich, Alfa-aesar, Central Drug House and used without further purification. ^{1}H, ^{13}C and ^{2}H spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz, ^{2}H: 61.4 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.

General procedure for the deuteration of aliphatic nitriles: To a screw cap scintillation vial aliphatic nitrile (0.5 mmol), catalyst **1** (0.2 to 0.5 mol%), and KO^{t}Bu (0.5 to 1 mol%) were charged in the nitrogen glove box. The vial was taken out and degassed D_2O (0.4 ml, 20 mmol) was added under argon atmosphere. The reaction vial was sealed and immersed into a pre-heated oil bath of 70 °C and the reaction mixture were stirred for 24 h. After the specified time the reaction mixture was cooled to room temperature, then extracted with dichloromethane (3 x 2mL). The combined organic phase is dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure provided pure products for further analysis.

Spectral data of aliphatic nitriles:

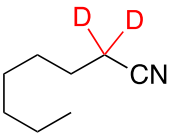
Acetonitrile-d_3 (3a, CD_3CN**):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (0.13H, CH_3), ^{13}C NMR (101 MHz, $CDCl_3$) δ 116.48 (*C*N), 1.26 (m, *C*H_3)

Butyronitrile (3b): Colorless liquid, Yield 30 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$)



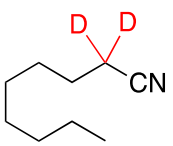
δ 2.30 (0.74H, α-CH_2), 1.67-1,69 (m, 2H, CH_2), 1.07 (t, *J* = 8 Hz, 3H, CH_3), ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.80 (*C*N), 19.13 (*C*H_2), 19.13 (m, α-*C*H_2) 13.36 (*C*H_3).

Octanenitrile (3c): Colorless liquid, Yield 56 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$)



δ 2.29 (0.38H, α-CH_2), 1.61 (m, 2H, β-CH_2), 1.41 (m, 2H, CH_2), 1.26 (m, 6H, CH_2), 0.83 (t, 3H, CH_3), ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.88 (*C*N), 31.49 (*C*H_2), 29.43 (*C*H_2), 25.49 (*C*H_2), 25.37 (*C*H_2), 22.51 (*C*H_2), 16.87 (m, α-*C*H_2), 14.00 (*C*H_3).

Nonanenitrile-2,2-d_2 (3d): Colorless liquid, Yield 66 mg (94%). ^{1}H NMR (400 MHz,



$CDCl_3$) δ 2.27 (m, 0.38H, CH_2), 1.57-1.62 (m, 2H, CH_2) 1.39-1.42 (m, 2H, CH_2), 1.24-1.26 (m, 8H, CH_2), 0.83-0.87 (m, 3H, CH_3). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 119.92 (*C*N), 31.72 (*C*H_2), 29.18 (*C*H_2), 28.99 (*C*H_2), 28.76 (*C*H_2), 25.21 (*C*H_2), 22.62 (*C*H_2), 16.70 (m, α-*C*H_2), 14.07 (*C*H_3).

Dodecanenitrile (3e): Colorless liquid, Yield 85 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (0.76H, α-C*H*$_2$), 1.57 (m, 2H, β-C*H*$_2$), 1.38 (m, 2H, C*H*$_2$), 1.23 (m, 14H, C*H*$_2$), 0.83 (s, 3H, C*H*$_3$), ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.84 (*C*N), 31.89 (*C*H_2), 29.55 (*C*H_2), 29.51 (*C*H_2), 29.30 (*C*H_2), 28.77 (*C*H_2), 28.63 (*C*H_2), 28.60 (*C*H_2), 25.29 (*C*H_2), 25.19 (*C*H_2), 22.67 (*C*H_2), 16.86 (m, α-*C*H_2), 14.08 (*C*H_3).

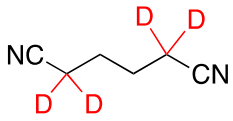
Undecanenitrile-2,2-*d*$_2$ (3f): Colorless liquid, Yield 77 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (0.72H, α-C*H*$_2$), 1.61-1.65 (m, 2H, C*H*$_2$), 1.41-1.45 (m, 2H, C*H*$_2$), 1.26-1.29 (m, 12H, C*H*$_2$), 0.87 (t, 3H, *J* = 8 Hz, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.85 (*C*N), 31.84 (*C*H_2), 29.45 (*C*H_2), 29.30 (*C*H_2), 29.25 (*C*H_2), 28.76 (*C*H_2), 25.36 (*C*H_2), 25.26 (*C*H_2), 22.65 (*C*H_2), 16.85 (m, α-*C*H_2), 14.07 (*C*H_3).

4-Phenylbutanenitrile-2,2-d$_2$ (3g): Colorless liquid, Yield 65 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.23 (m, 2H, ArC*H*), 7.07-7.14 (m, 3H, ArC*H*), 2.66 (d, 2H, *J* = 8 Hz, C*H*$_2$), 2.50 (m, 0.56H, α-C*H*$_2$), 1.83-1.88 (m, 2H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.74 (quat. *C*), 128.63 (Ar*C*H), 128.43 (Ar*C*H), 126.46 (Ar*C*H), 119.52 (*C*N), 34.30 (*C*H_2), 26.77 (*C*H_2), 16.09 (m, α-*C*H_2).

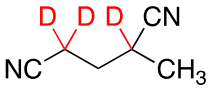
5-Phenylpentanenitrile-2,2-d2 (3h): Colorless liquid, Yield 72 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.36 (m, 2H, ArC*H*), 7.21-7.27 (m, 3H, ArC*H*), 2.70 (d, 2H, *J* = 8 Hz, C*H*$_2$), 2.36 (m, 1H, α-C*H*$_2$), 1.80-1.84 (m, 2H, C*H*$_2$), 1.69-1.73 (m, 2H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.24 (quat. *C*), 128.43 (Ar*C*H), 128.34 (Ar*C*H), 126.03 (Ar*C*H), 119.64 (*C*N), 34.94 (*C*H_2), 30.18 (*C*H), 24.70 (*C*H_2), 16.74 (m, α-*C*H_2).

Succinonitrile (3i): Light yellow liquid, Yield 38 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (0.27H, α-C*H*$_2$), ^{13}C NMR (101 MHz, $CDCl_3$) δ 116.48 (*C*N), 14.25 (m, α-*C*H_2).

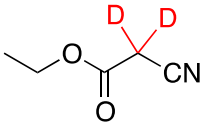
Glutaronitrile (3j): Light yellow liquid, Yield 44 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (0.34H, α-C*H*$_2$), 1.96 (s, 1.71H, β-C*H*$_2$), ^{13}C NMR (101 MHz, $CDCl_3$) δ 117.86 (*C*N), 21.35 (*C*H_2), 15.99 (m, α-*C*H_2).

Adiponitrile (3k): Light yellow liquid, Yield 50 mg (90%). ^{1}H NMR (400 MHz, 

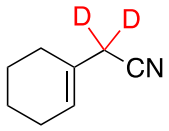
$CDCl_3$) δ 2.37 (0.46H, α-CH_2), 1.76 (s, 3.30H, β-CH_2), ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.83 (*C*N), 23.97 (β-*C*H_2), 16.33 (m, α-*C*H_2).

2-Methylpentanedinitrile (3l): Light yellow liquid, Yield 54 mg (86%). ^{1}H NMR (400 

MHz, $CDCl_3$) δ 2.76 (0.71H, α-C*H*), 2.52 (0.12H, α-CH_2), 1.89 (m, 1.85H, β-CH_2), 1.34 (m, 2.84H, CH_3), ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.10 (CH-*C*N), 118.08 (CH_2-*C*N), 29.34 (m, *C*H), 24.63 (*C*H_2), 17.38 (*C*H_3), 14.89 (m, α-*C*H_2).

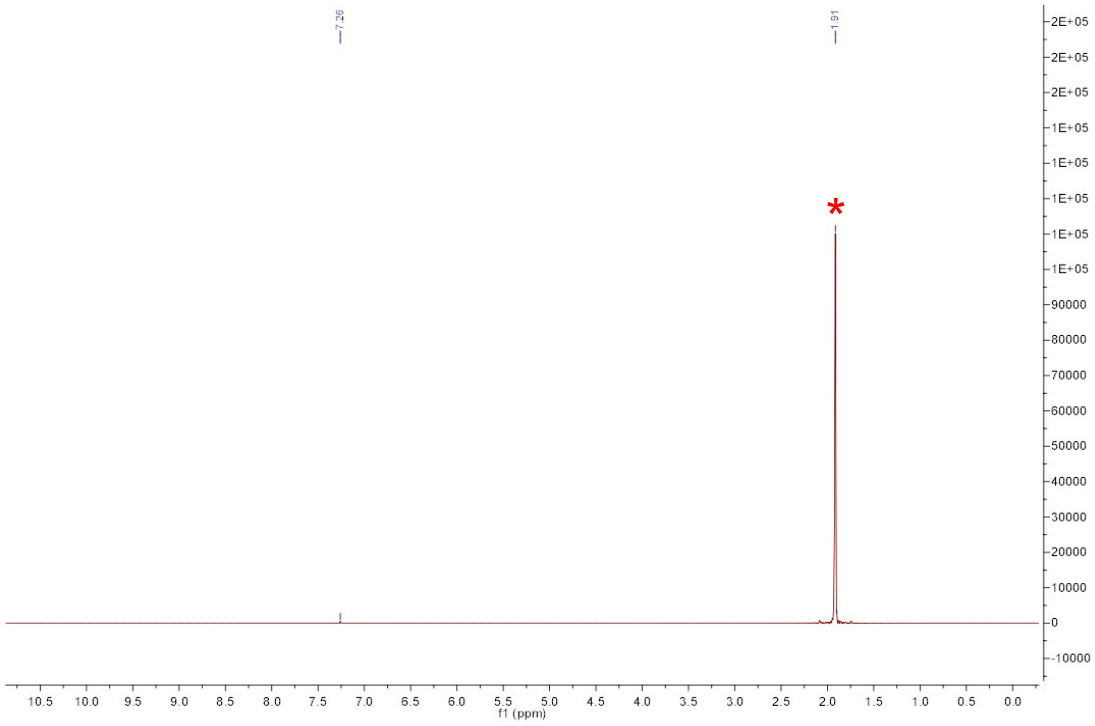
Ethyl 2-cyanoacetate (3m): Light yellow liquid, Yield 49 mg (85%). ^{1}H NMR (400 

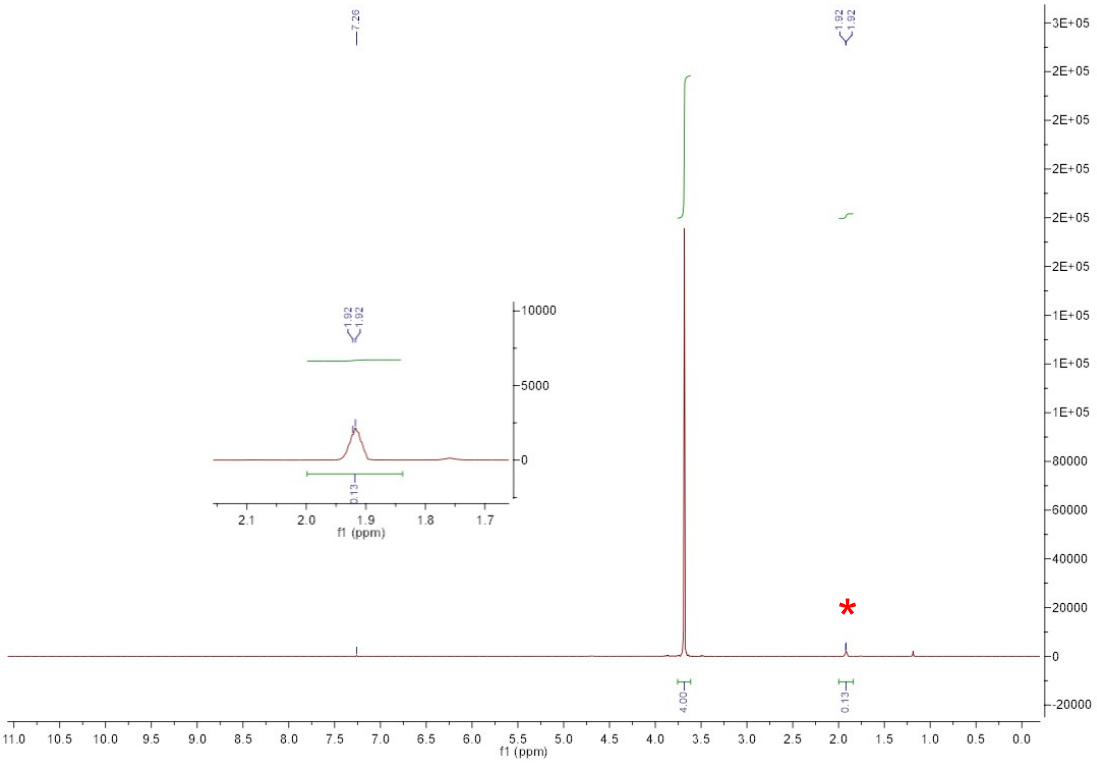
MHz, $CDCl_3$) δ 4.26 (q, *J* = 4 Hz, 2H, OCH_2), 3.44 (0.12H, α-CH_2), 1.30 (t, *J* = 4 Hz, 3H, CH_3) ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.07 (*C*=O), 113.23 (*C*N), 62.99 (O*C*H_2), 24.63 (m, α-*C*H_2), 13.97 (*C*H_3).

2-(Cyclohex-1-en-1-yl)acetonitrile (3n): Light yellow liquid, Yield 53 mg (85%). ^{1}H 

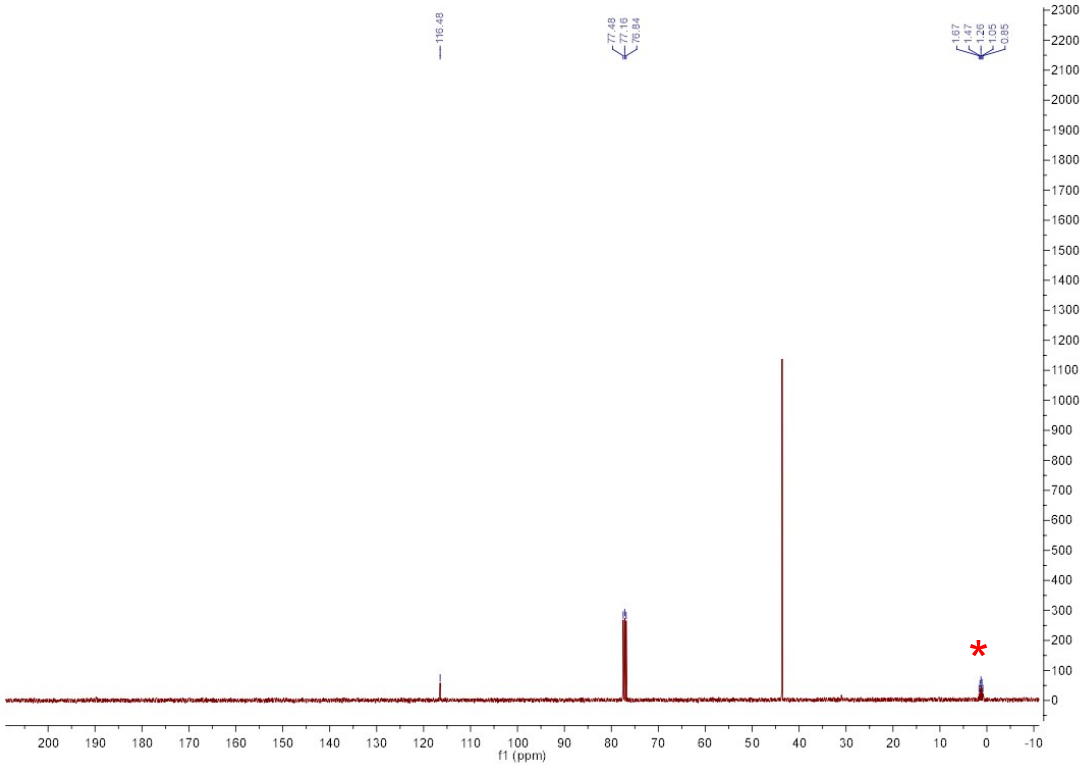
NMR (400 MHz, $CDCl_3$) δ 5.73 (0.73H, olefinic C*H*), 2.93 (0.11H, α-CH_2), 1.98 (s, 3.25H, CH_2), 1.61 (m, 4.14H, CH_2), ^{13}C NMR (101 MHz, $CDCl_3$) δ 126.97 (olefinic *C*=CH), 126.21 (olefinic quat. *C*), 117.75 (*C*N), 27.90 (*C*H_2), 25.54 (m, α-*C*H_2), 25.04 (*C*H_2), 22.38 (*C*H_2), 21.70 (*C*H_2).

^{1}H NMR spectrum of reference acetonitrile

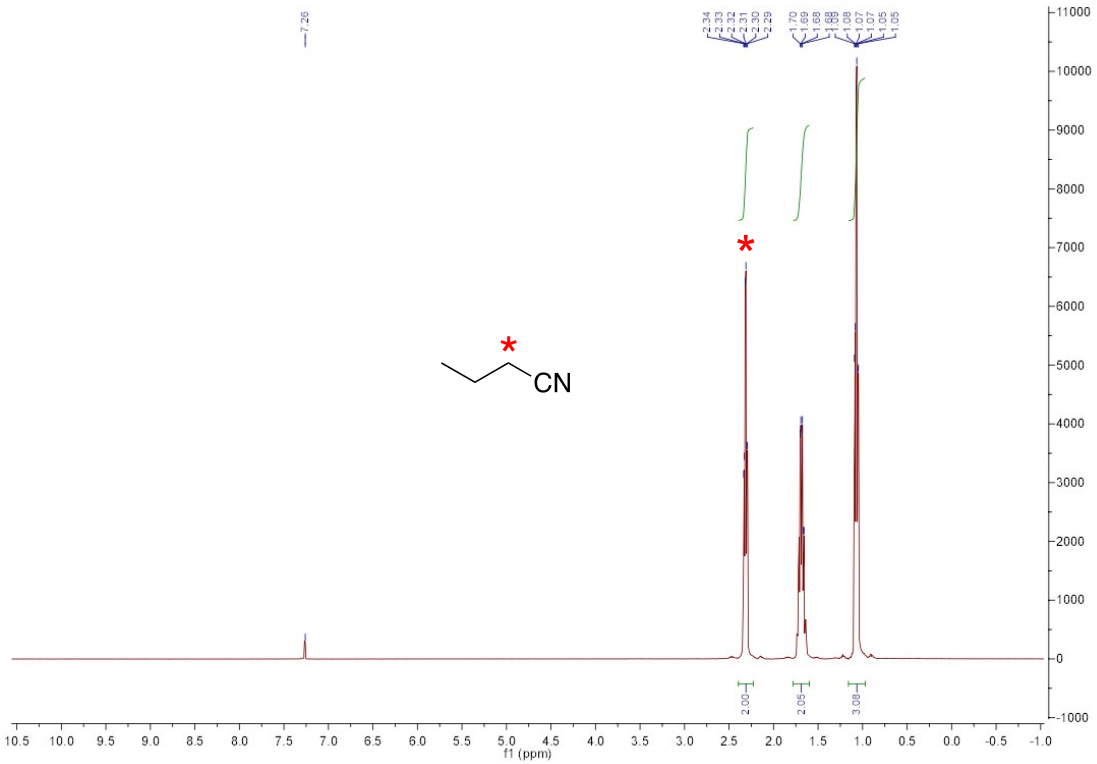

7.26
1.91
*
f1 (ppm)


7.26
1.92
1.92
*
4.00
0.13
f1 (ppm)

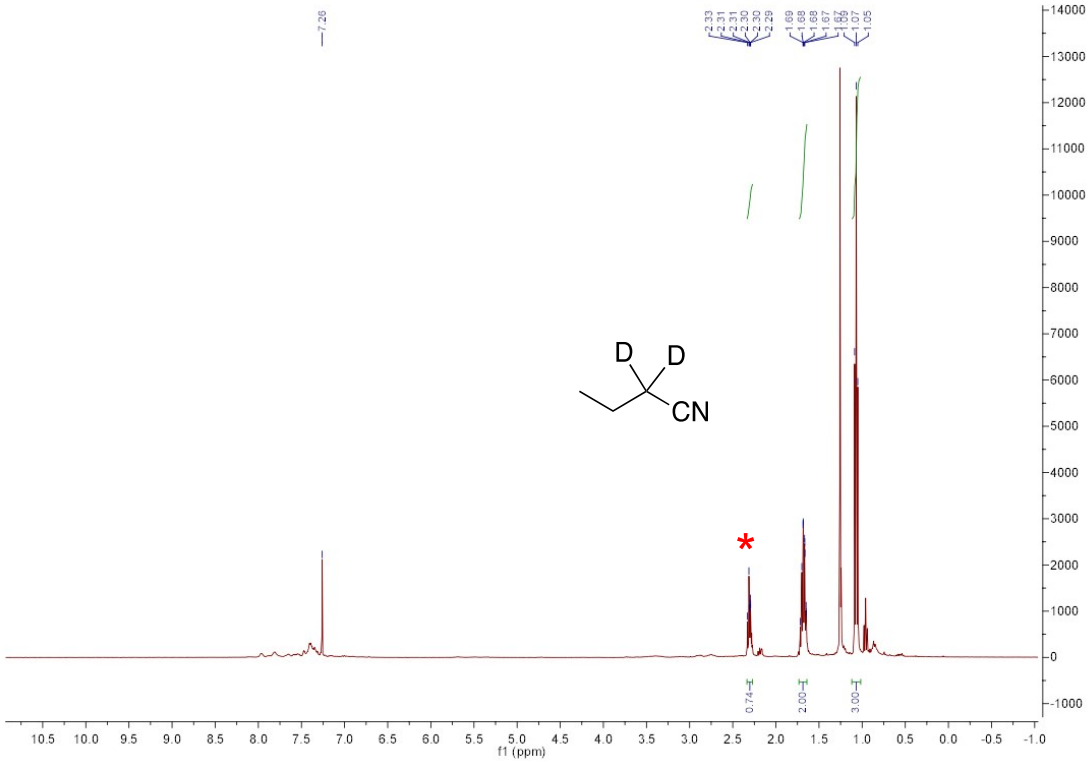
^{13}C NMR spectrum of acetonitrile-d_3 (**3a**):



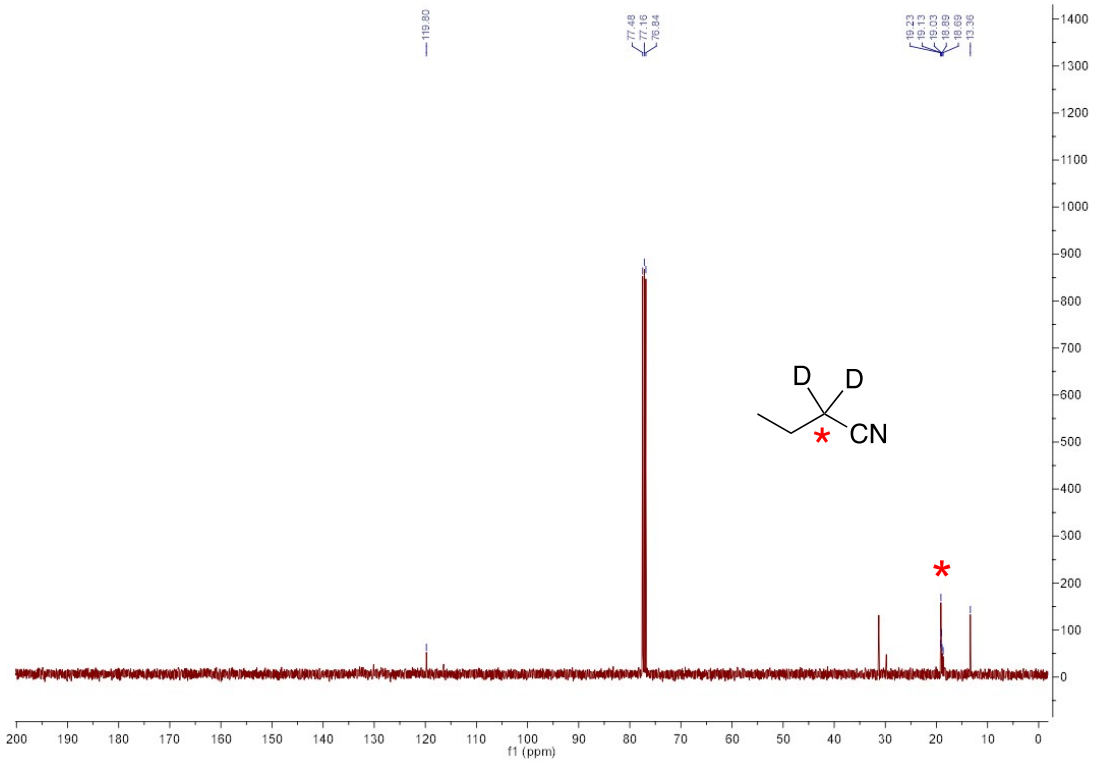
^{1}H NMR spectrum of reference butyronitrile



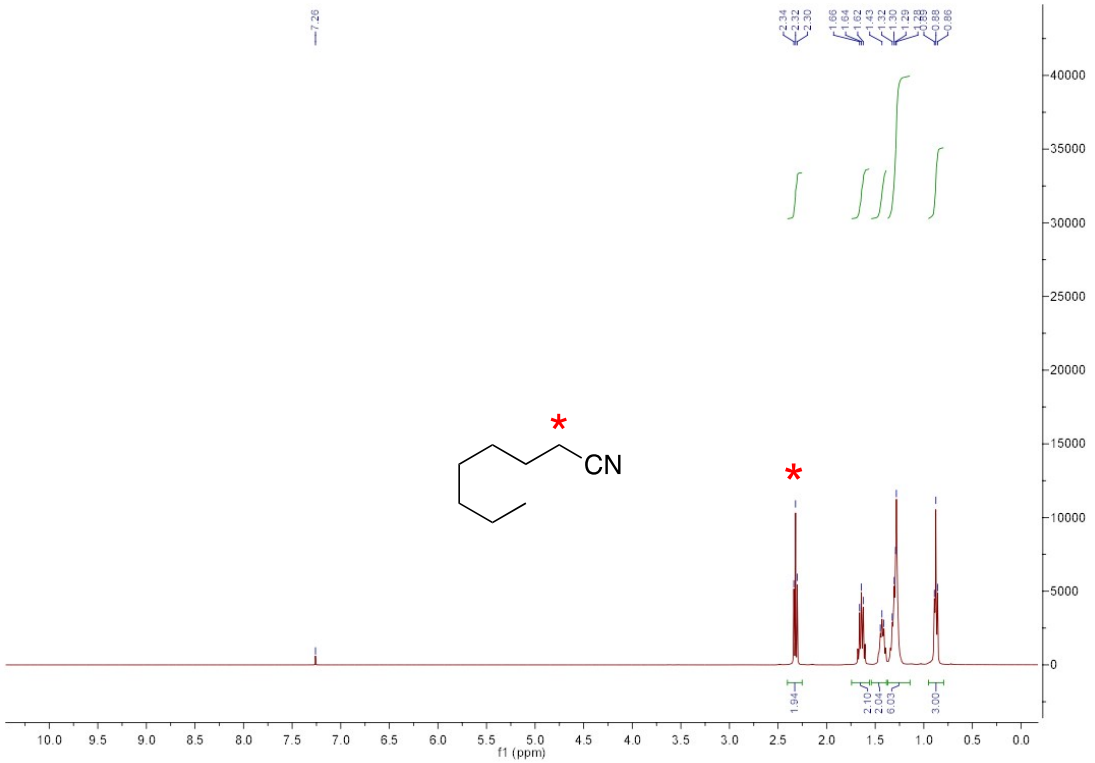
^{1}H NMR spectrum of butyronitrile-d_2 (**3b**):



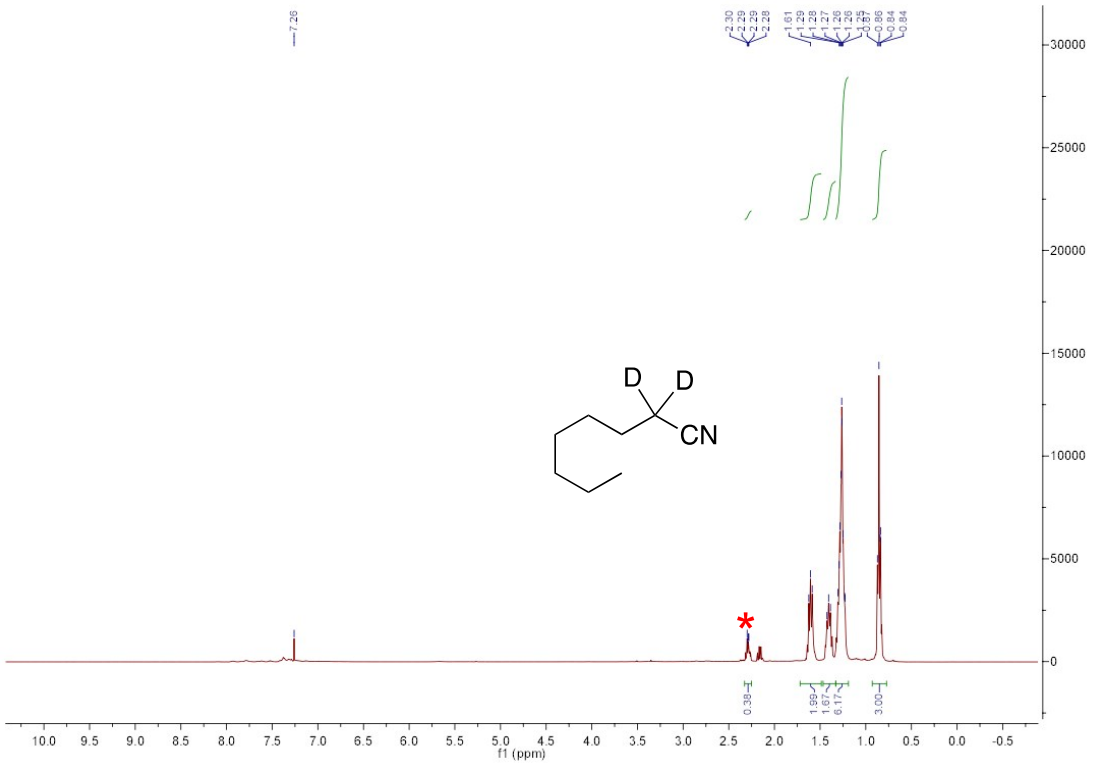
^{13}C NMR spectrum of butyronitrile-d_2 (**3b**):



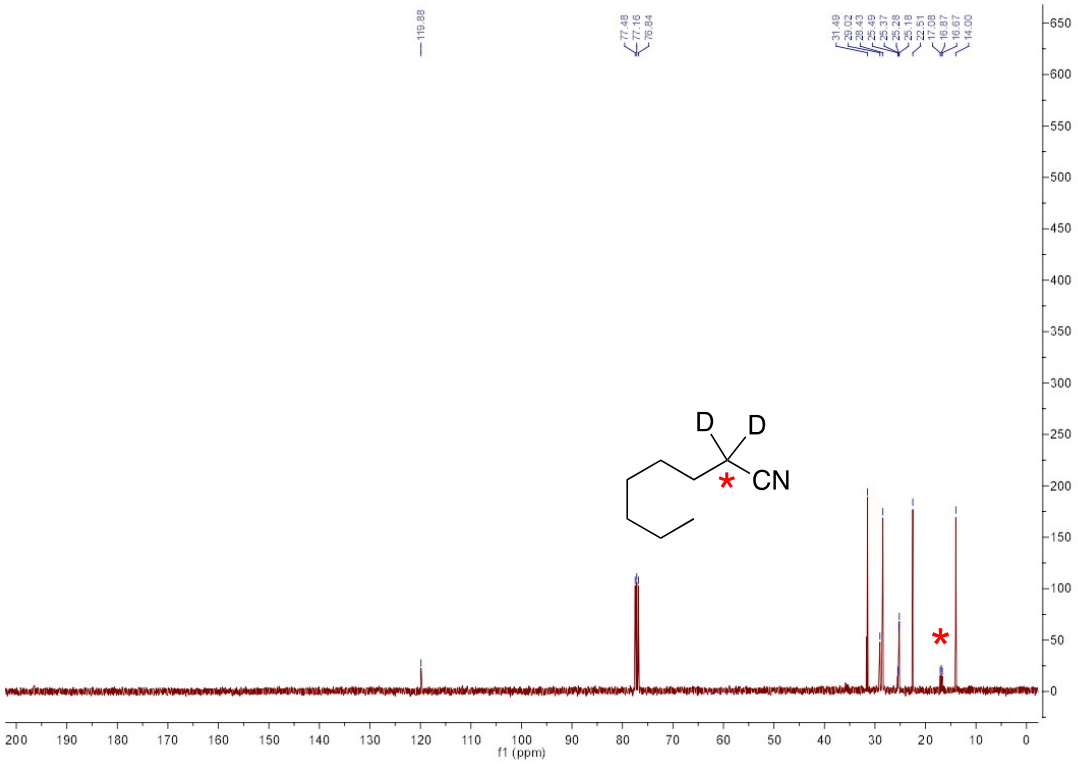
^{1}H NMR spectrum of reference octanenitrile



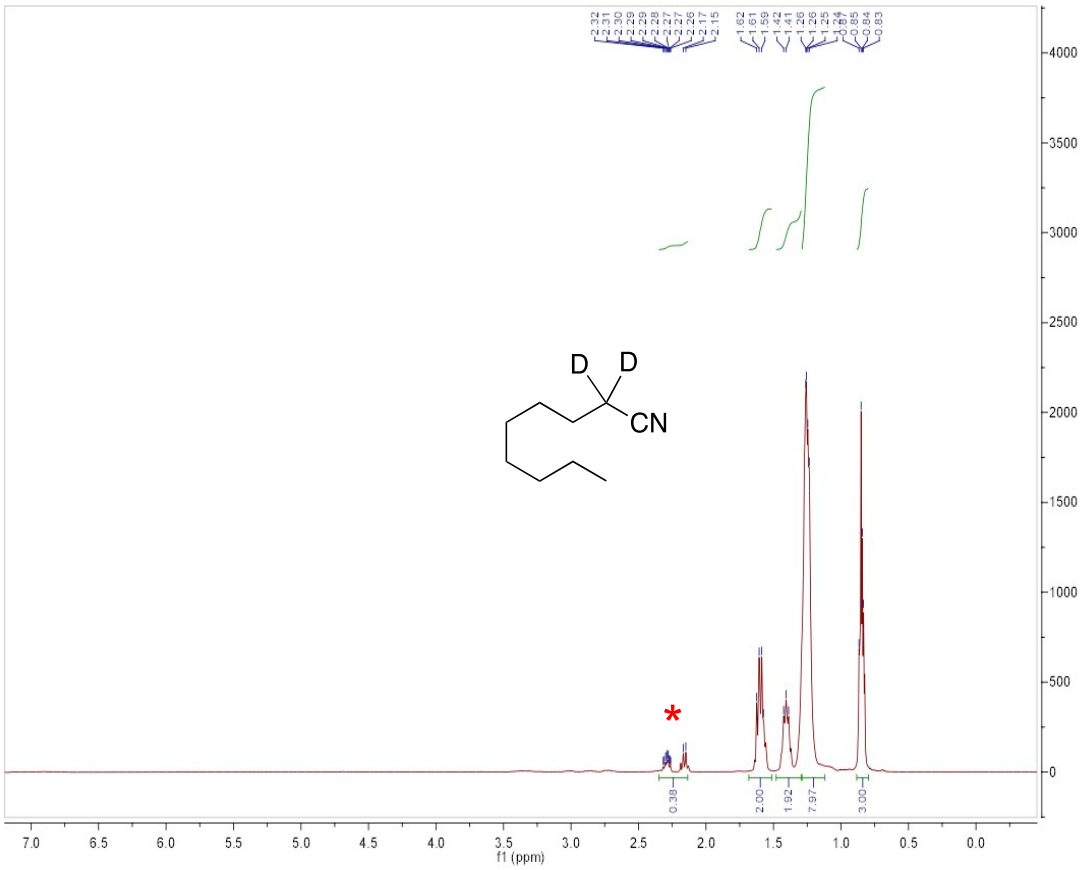
^{1}H NMR spectrum of octanenitrile-d_2 (**3c**):



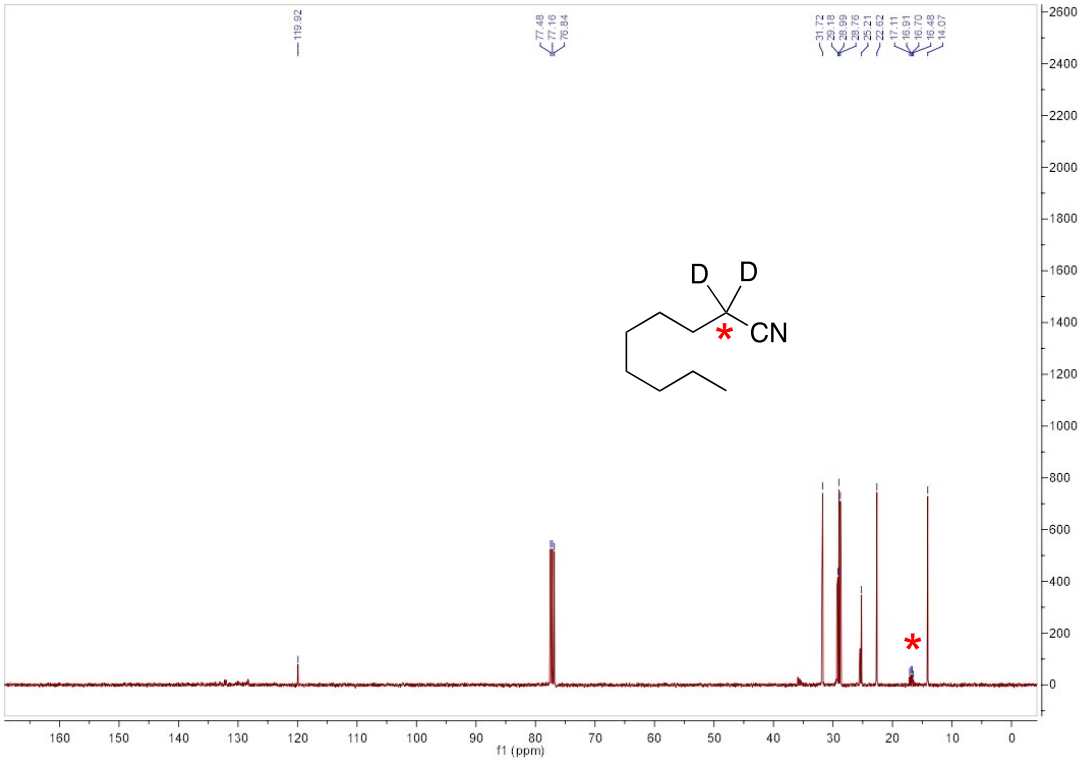
^{13}C NMR spectrum of octanenitrile-d_2 (**3c**):



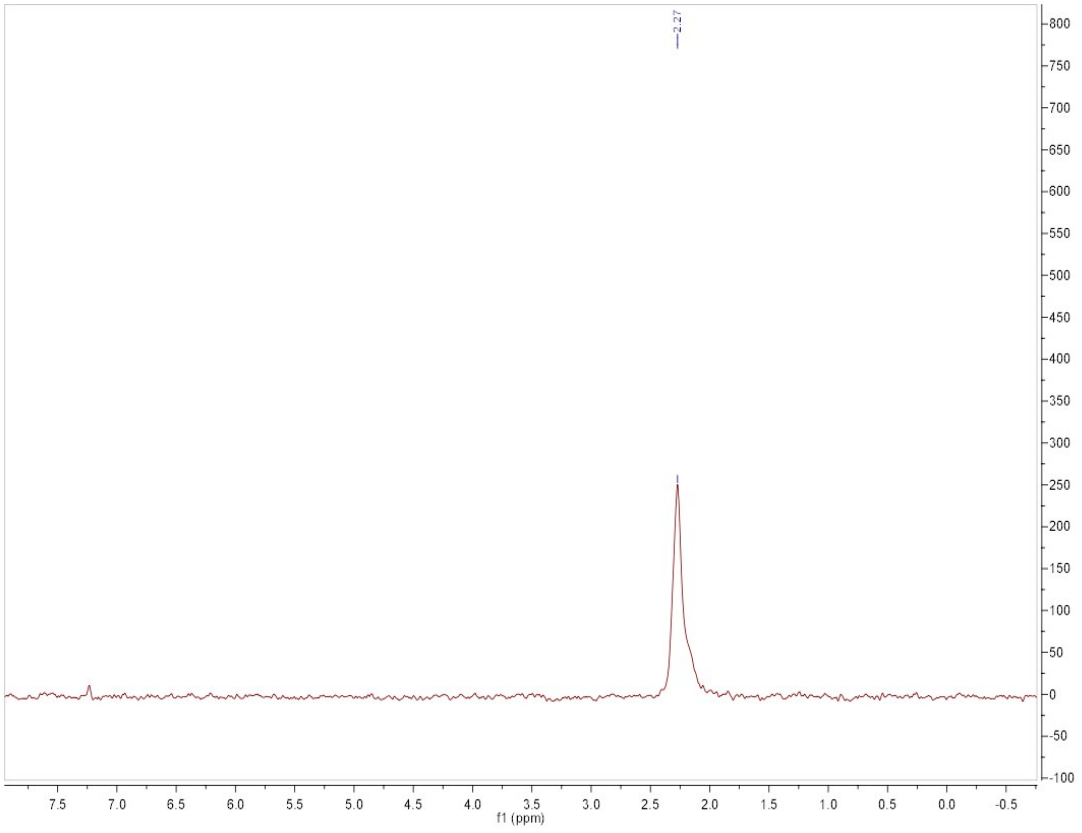
^{1}H NMR spectrum of nonanenitrile-d_2 (**3d**):



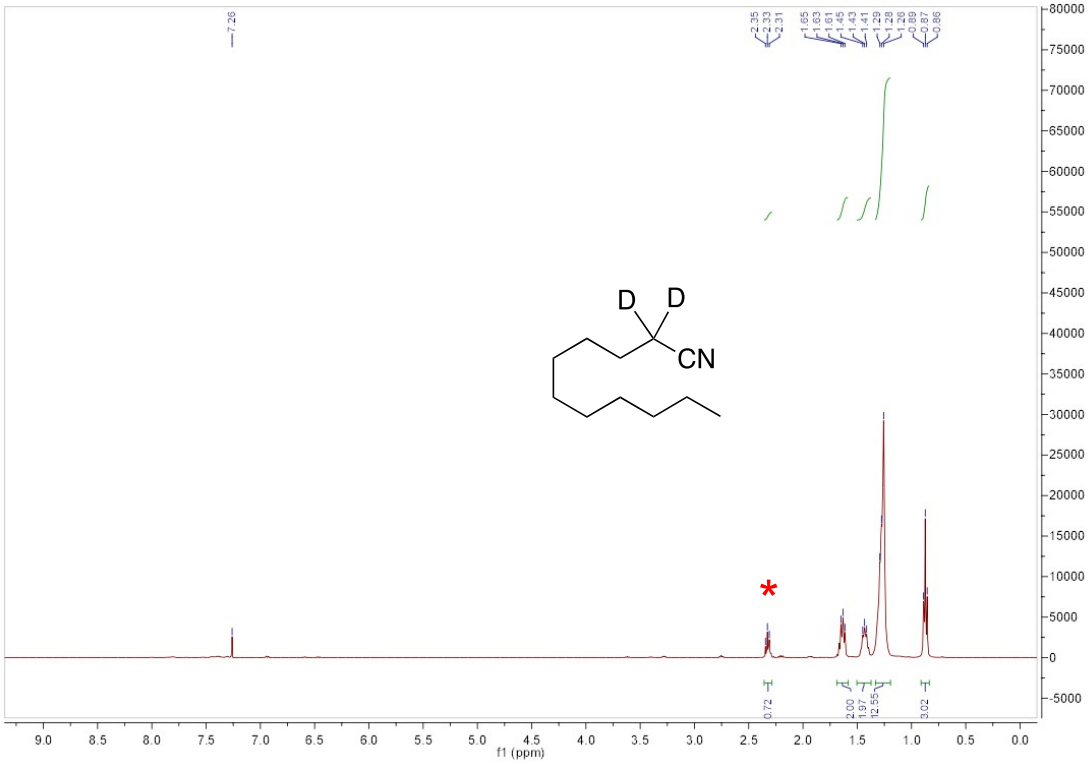
^{13}C NMR spectrum of nonanenitrile-d_2 (**3d**):



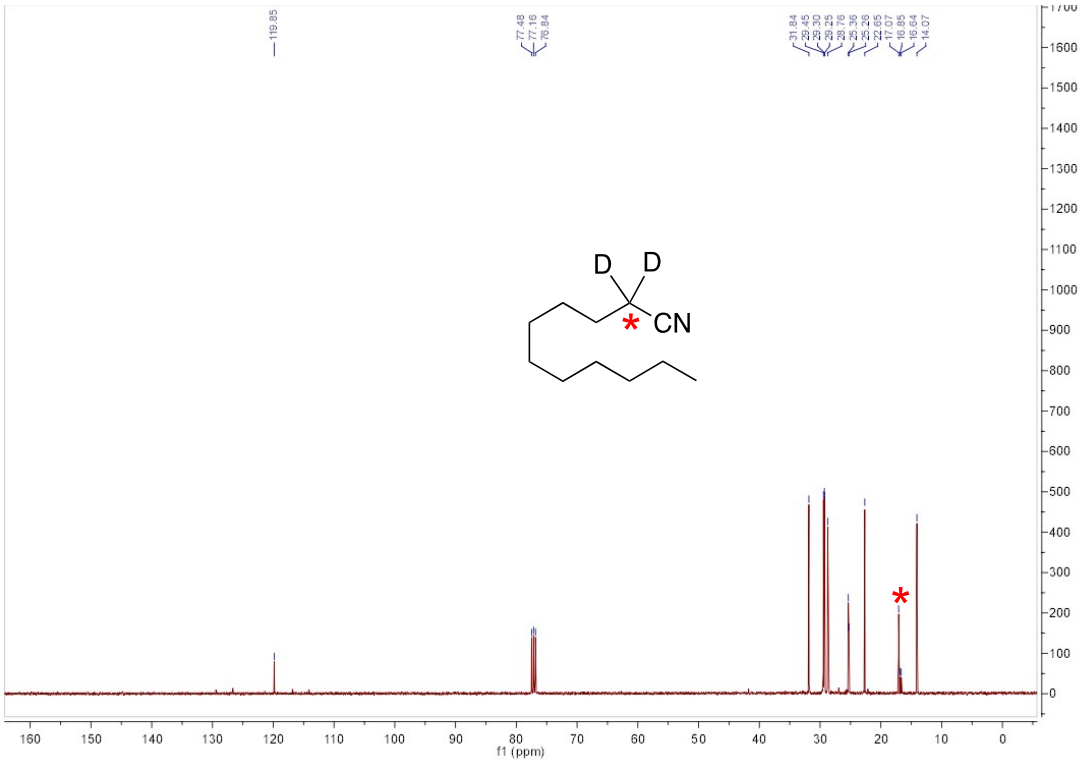
^{2}H NMR spectrum of nonanenitrile-d_2 (**3d**):



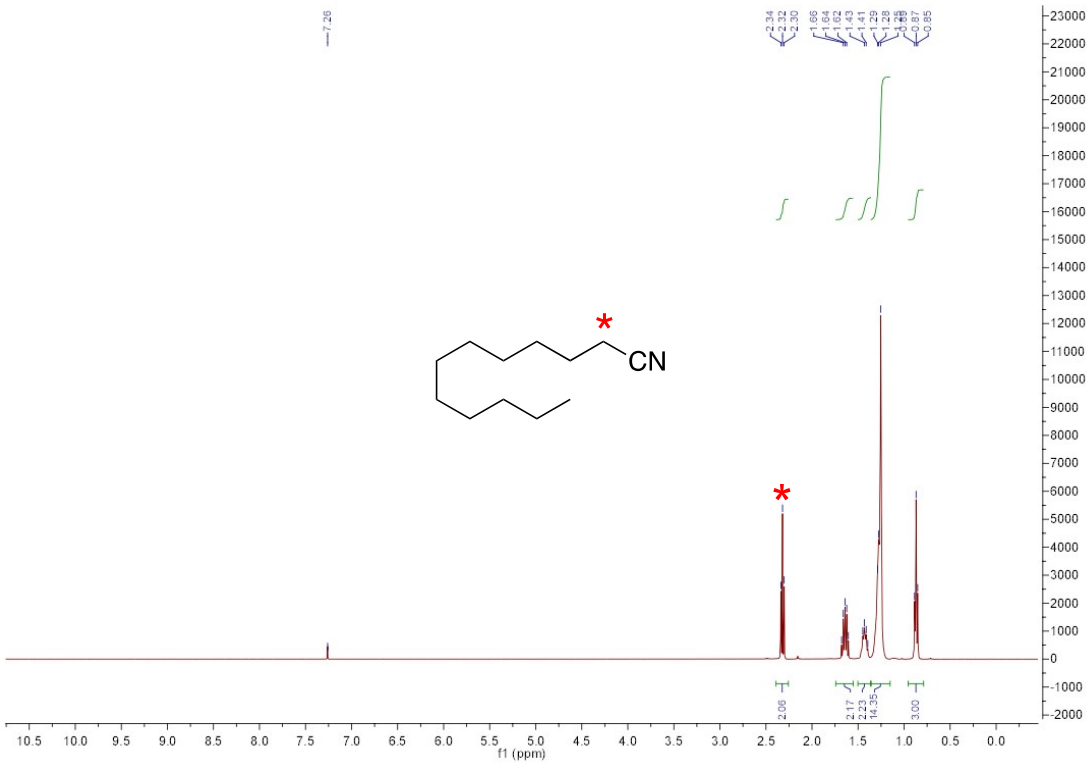
^{1}H NMR spectrum of undecanenitrile-d_2 (**3e**):



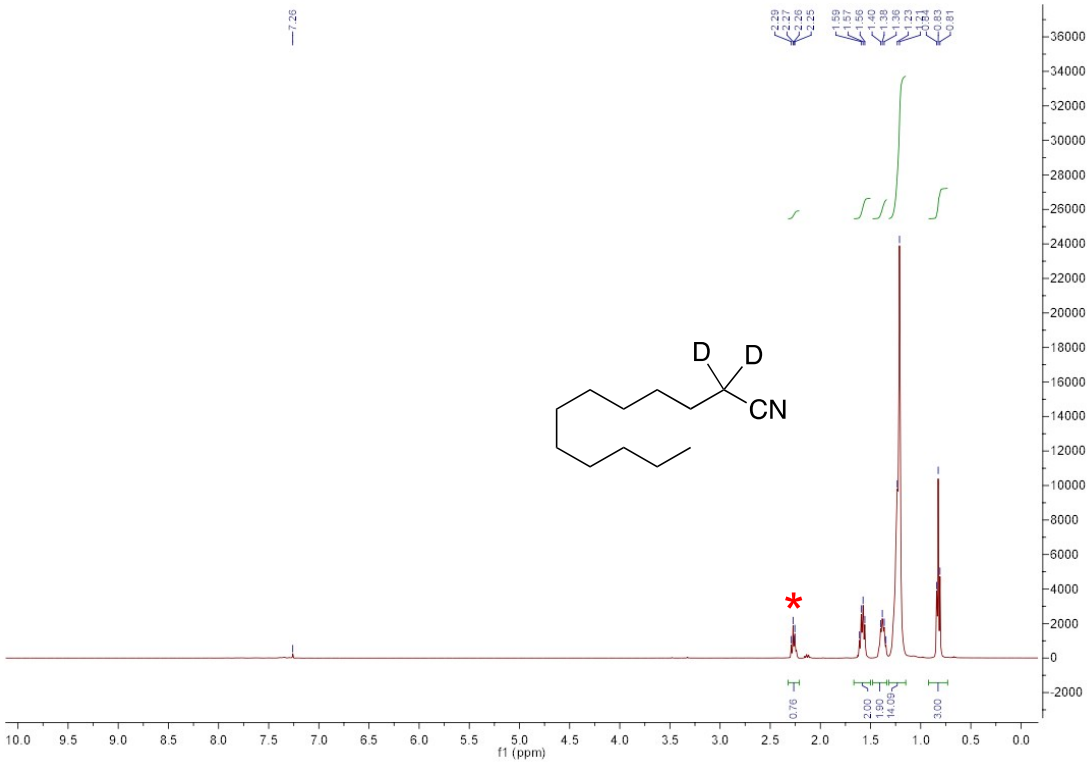
^{13}C NMR spectrum of undecanenitrile-d_2 (**3e**):



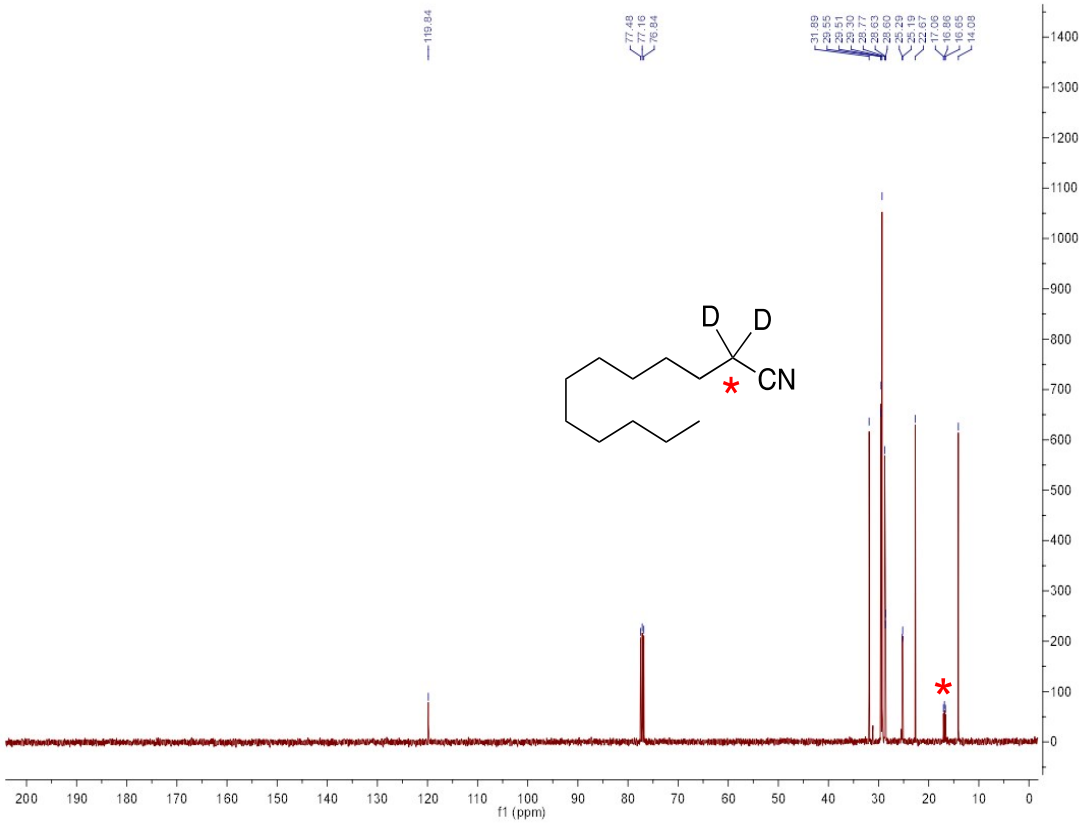
^{1}H NMR spectrum of reference dodecanitrile



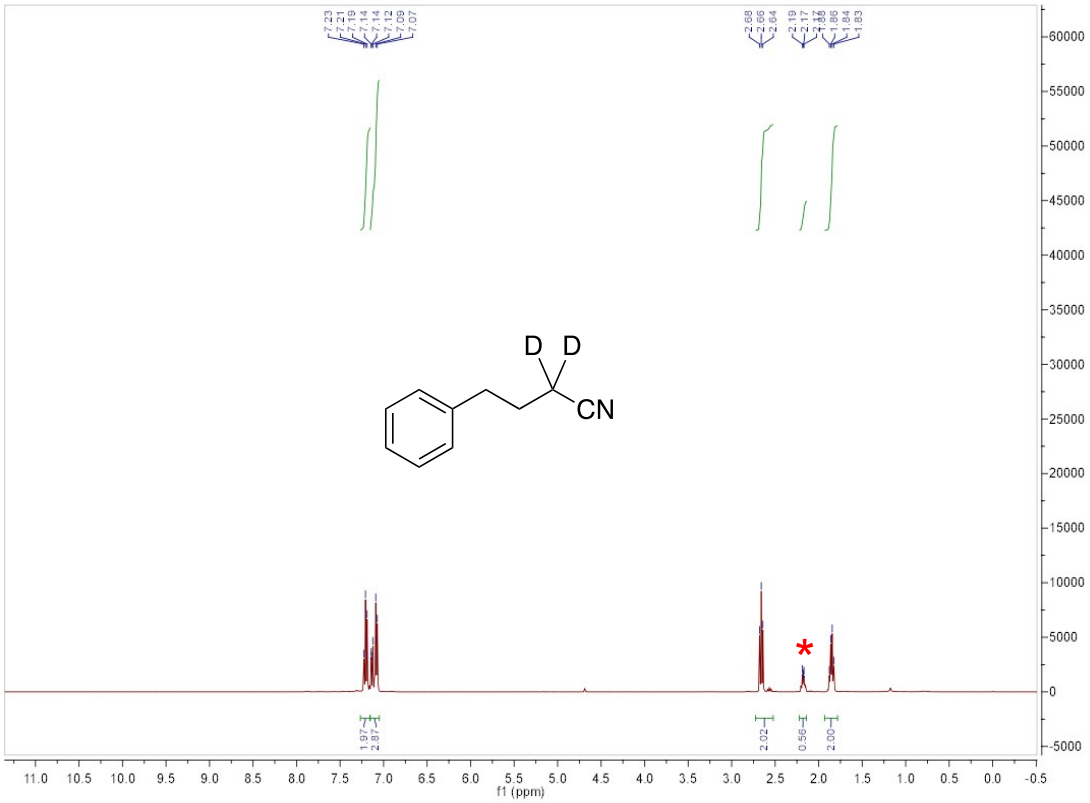
^{1}H NMR spectrum of dodecanitrile-d_2 (**3f**):



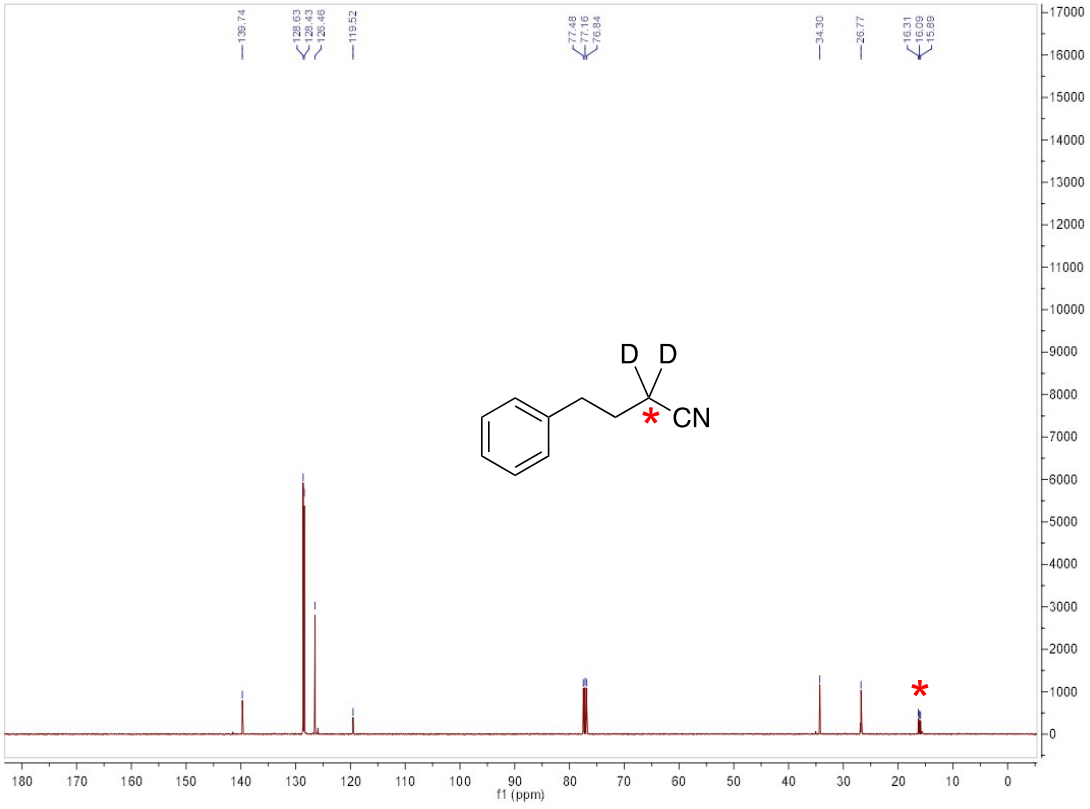
^{13}C NMR spectrum of dodecanitrile-d_2 (**3f**):



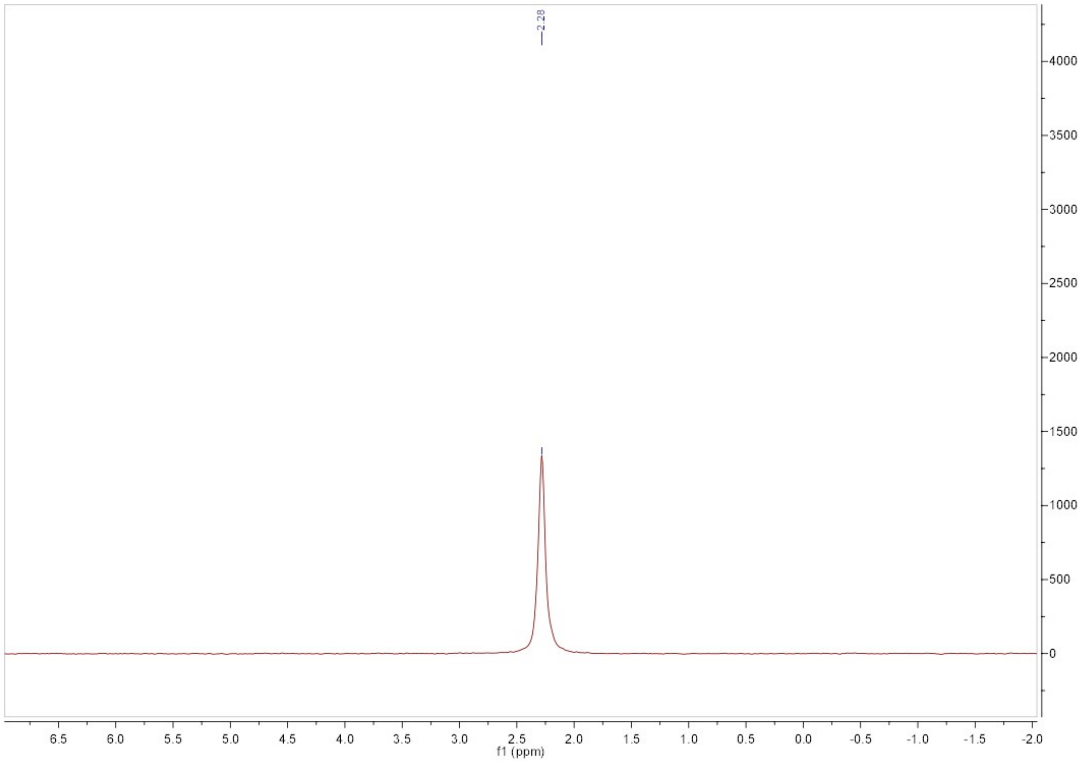
^{1}H NMR spectrum of 4-phenylbutanenitrile-d_2 (**4g**):



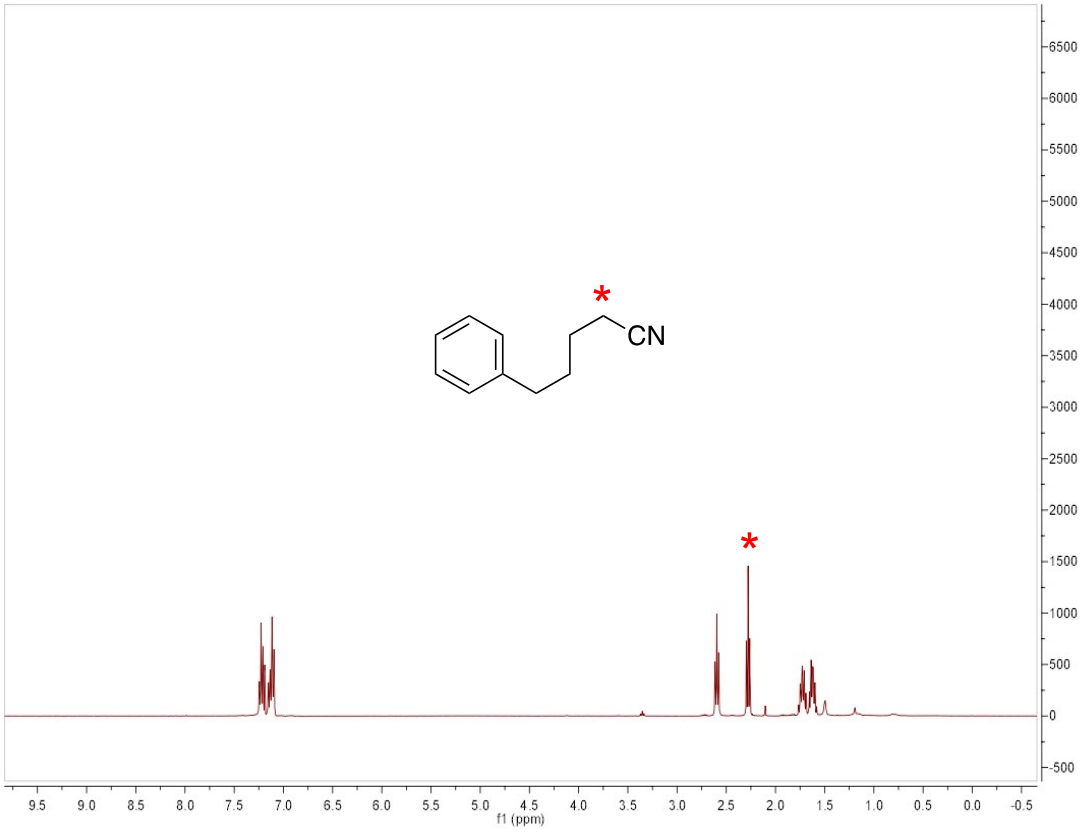
^{13}C NMR spectrum of 4-phenylbutanenitrile-d_2 (**4g**):



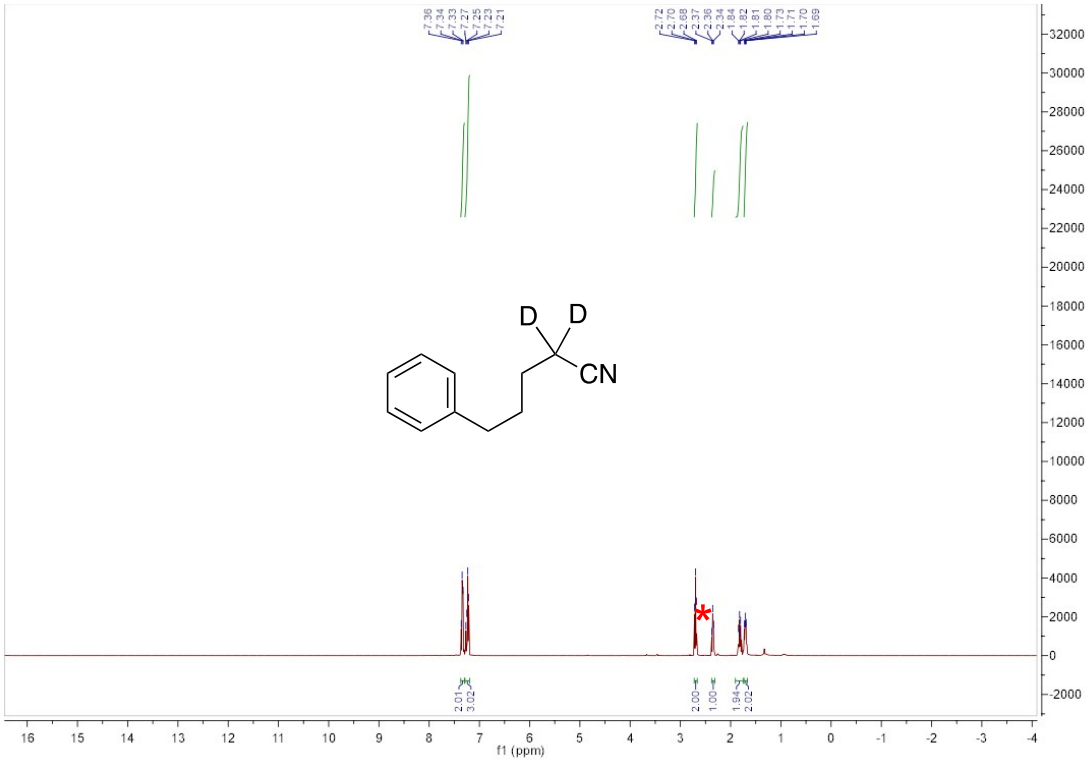
^{2}H NMR spectrum of 4-phenylbutanenitrile-d_2 (**4g**):



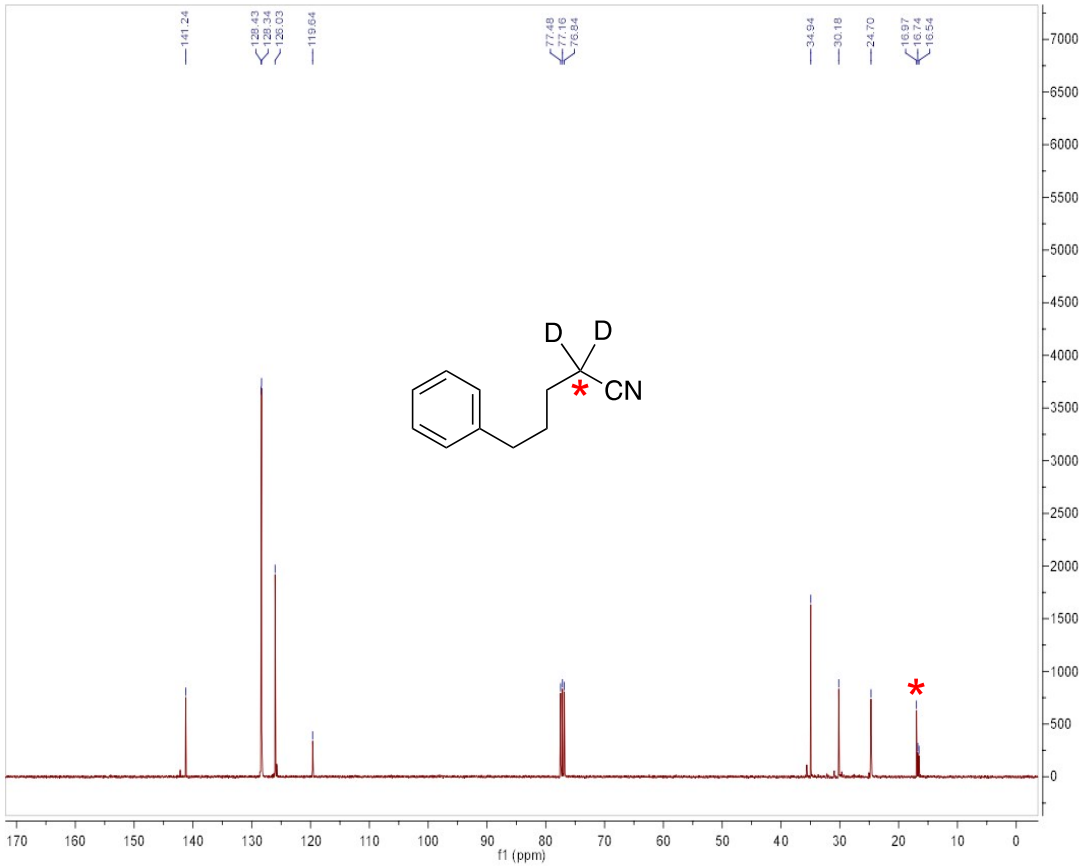
^{1}H NMR spectrum of reference 5-phenylpentanenitrile:



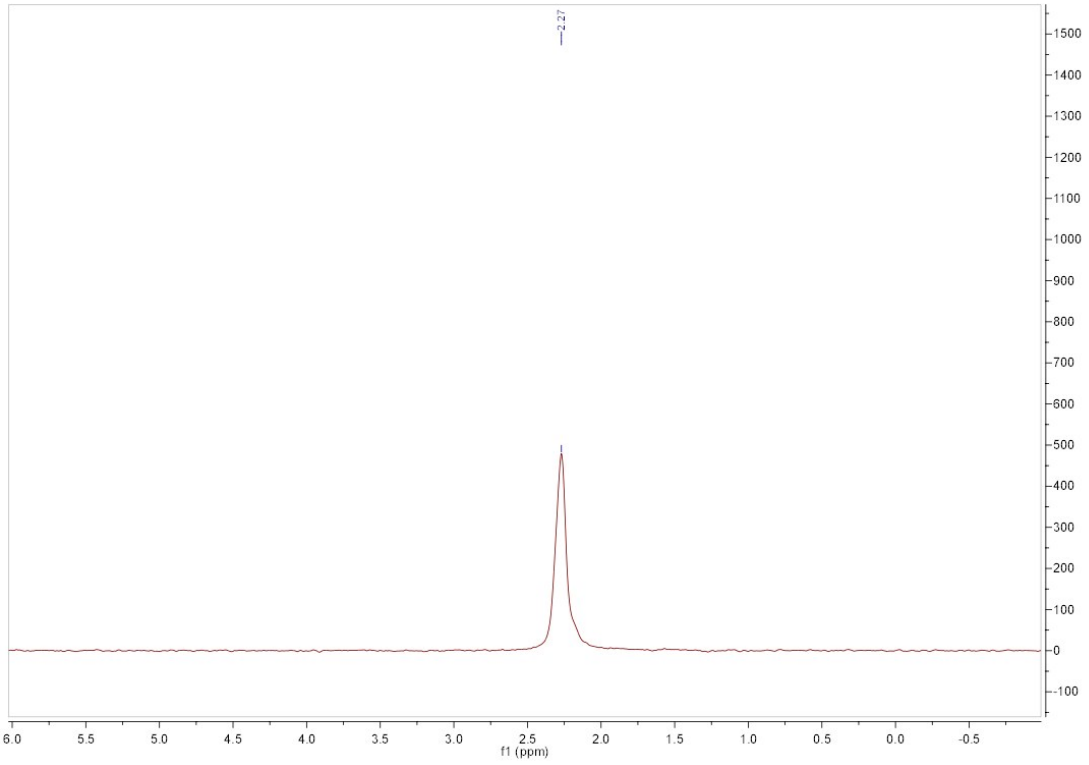
^{1}H NMR spectrum of 5-phenylpentanenitrile-d_2 (**3h**):



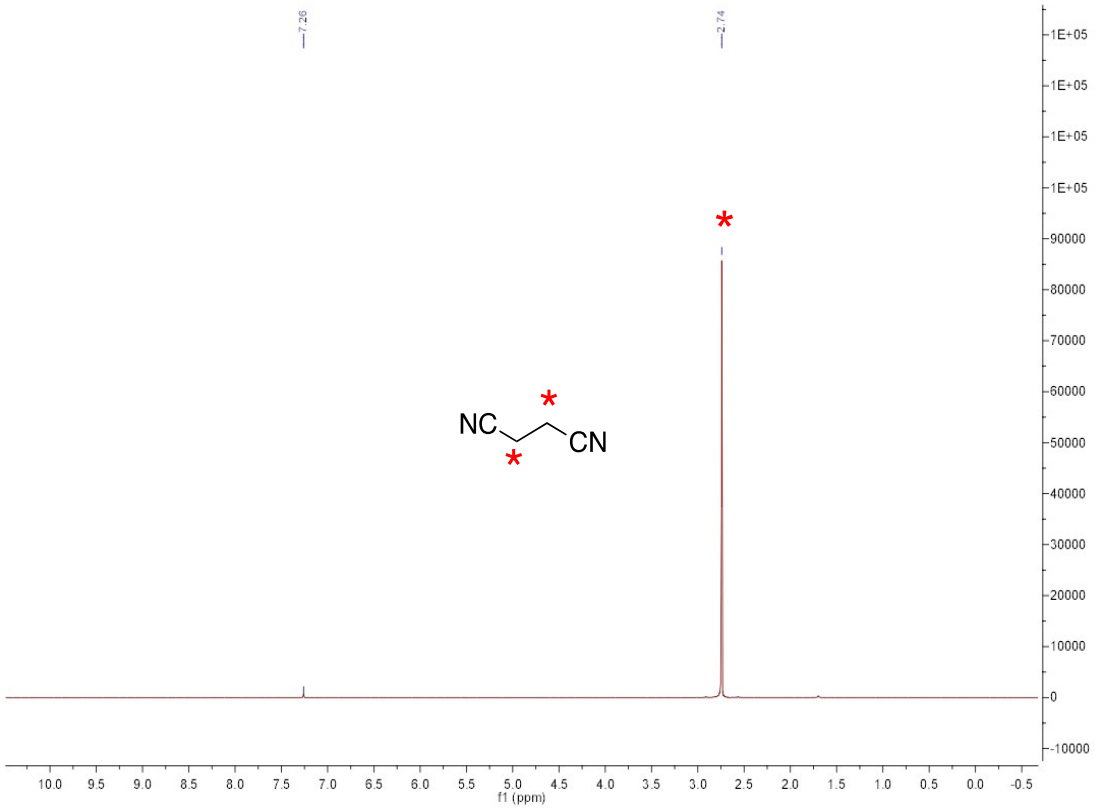
^{13}C NMR spectrum of 5-phenylpentanenitrile-d_2 (**3h**):



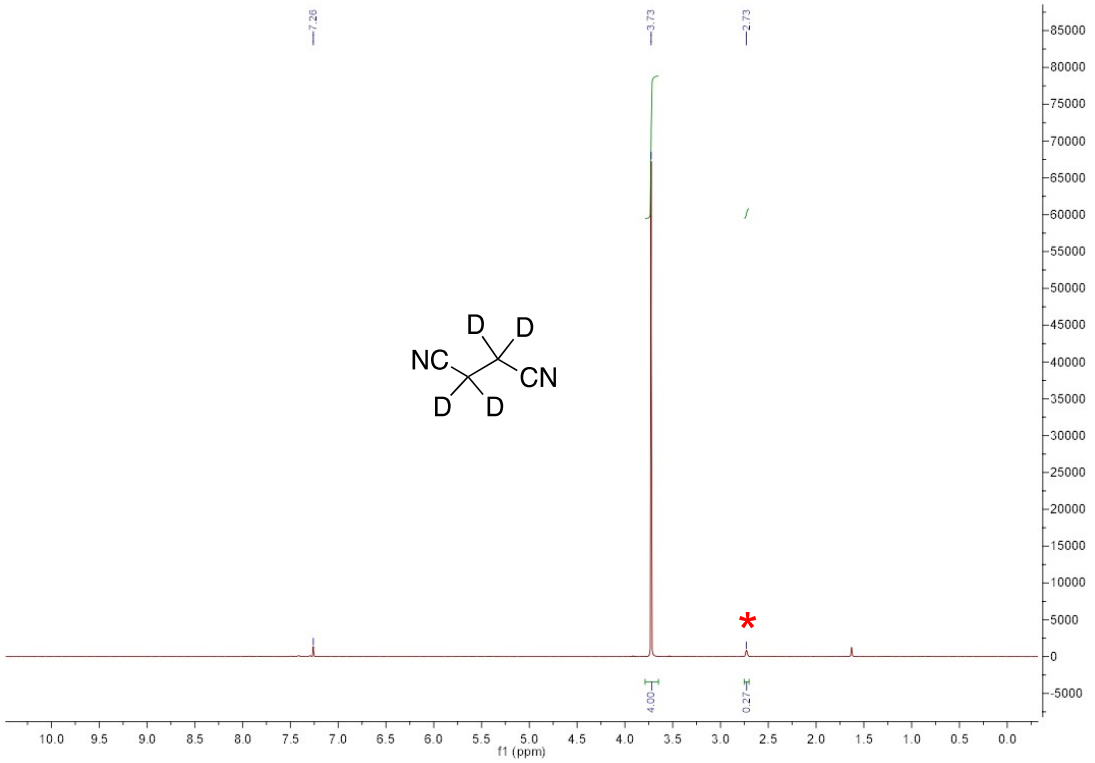
^{2}H NMR spectrum of 5-phenylpentanenitrile-d_2 (**3h**):



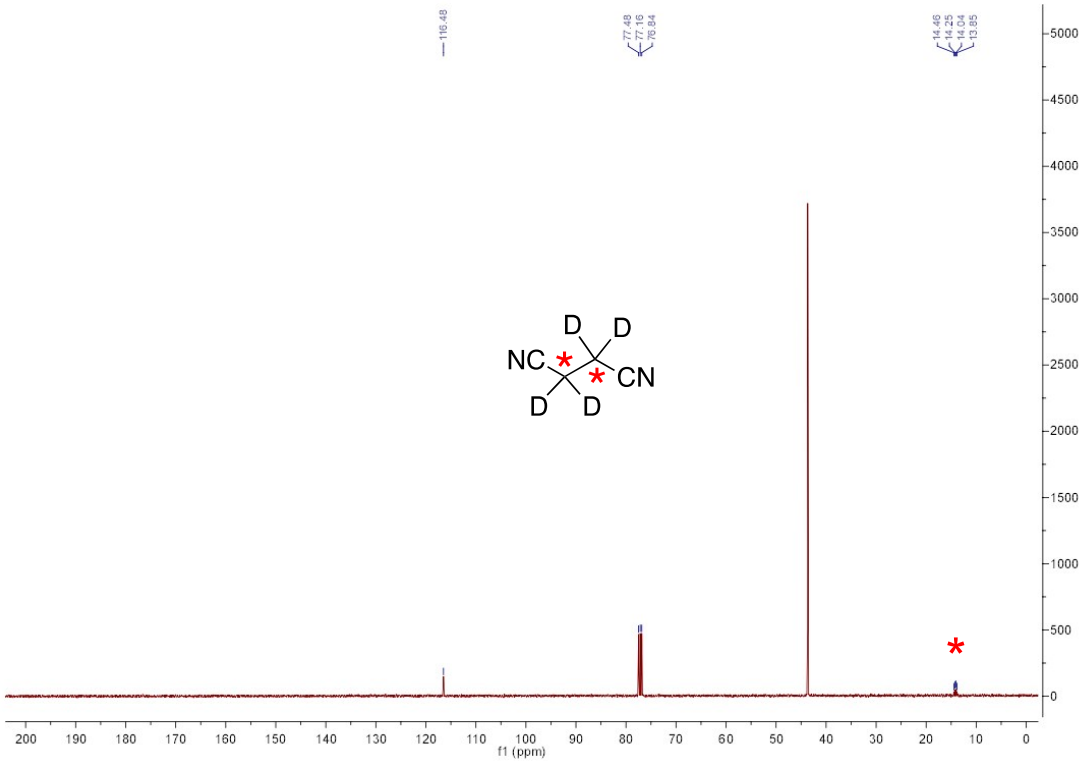
^{1}H NMR spectrum of reference succinonitrile


7.26
2.74
NC
CN
*
*
*
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

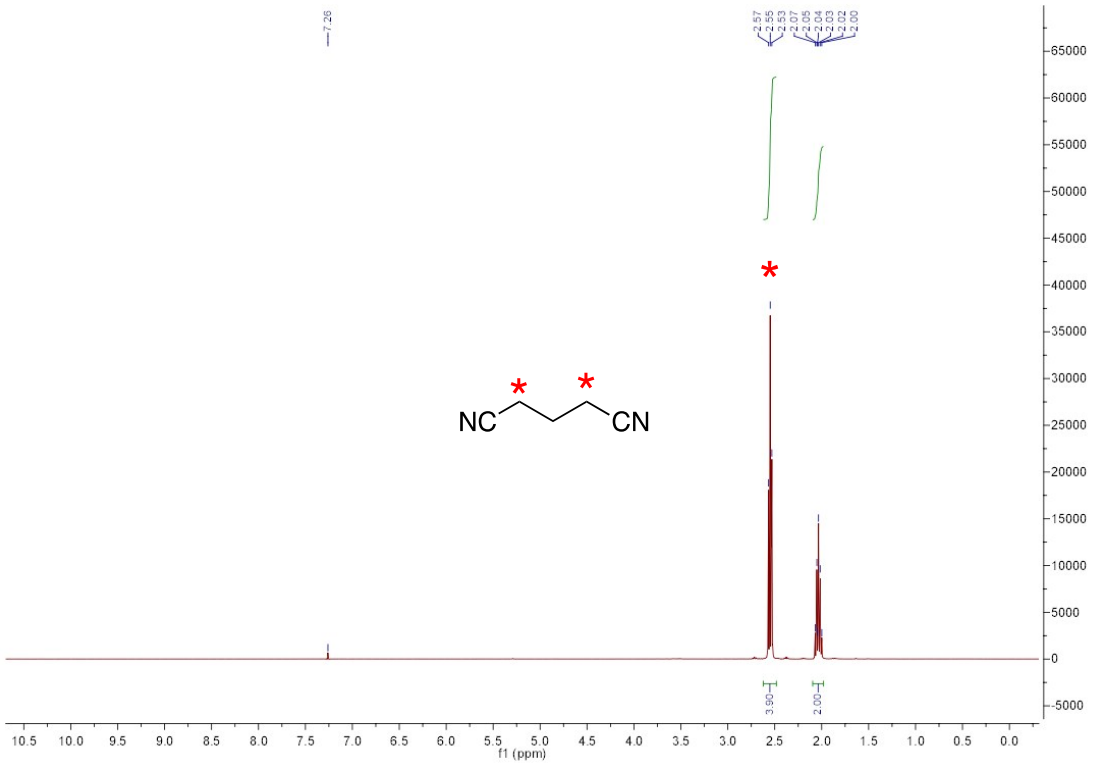
^{1}H NMR spectrum of succinonitrile-d_4 (**3l**):



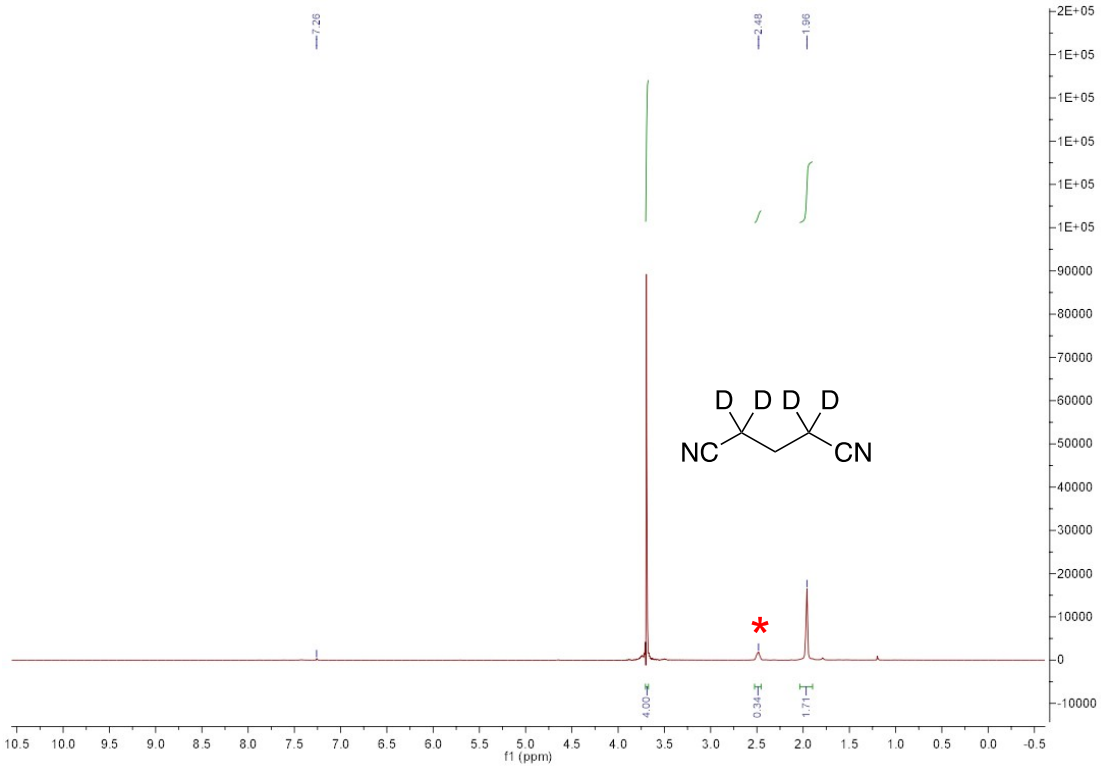
^{13}C NMR spectrum of succinonitrile-d_4 (**3l**):


116.48
77.48
77.16
76.84
14.46
14.25
14.04
13.85
D
D
NC
CN
D
D
*
*
*
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

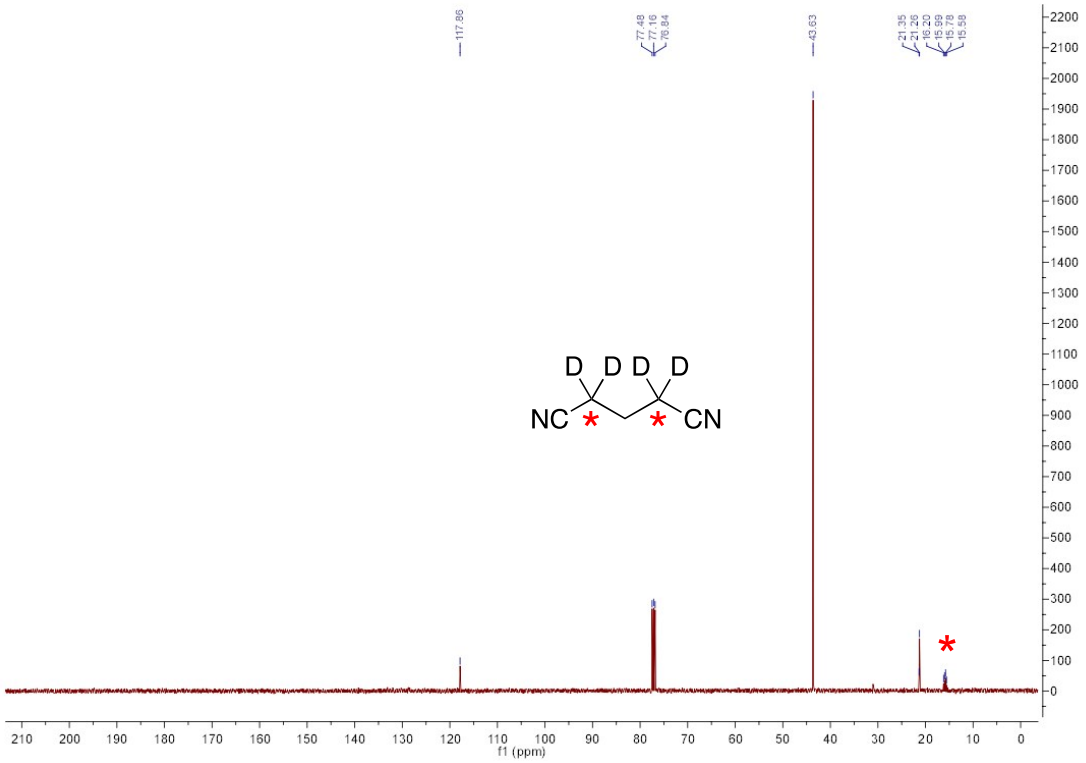
^{1}H NMR spectrum of reference glutaronitrile



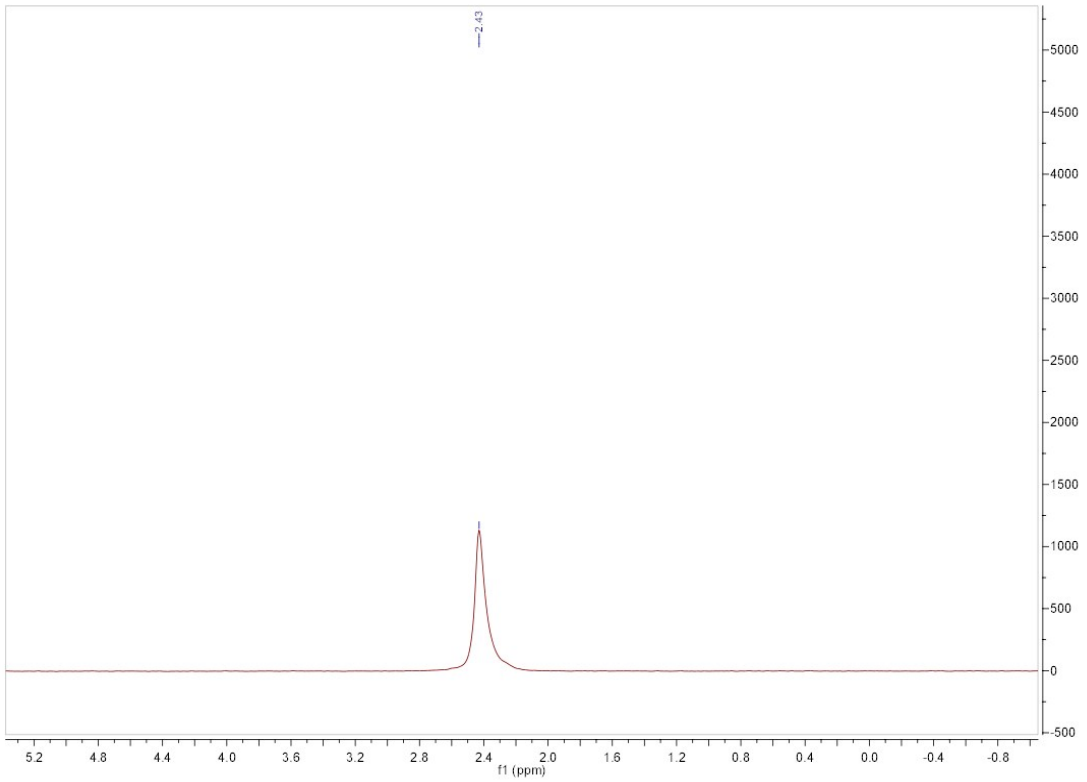
^{1}H NMR spectrum of glutaronitrile-d_4 (**3j**):



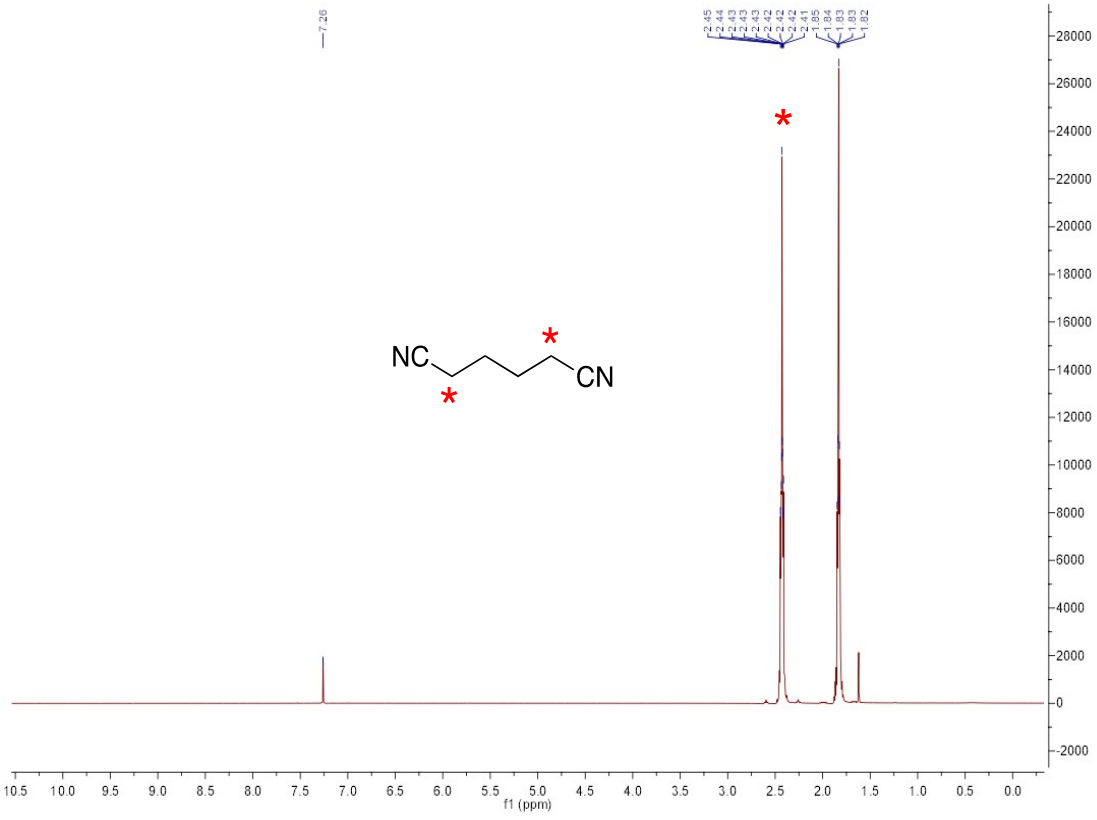
^{13}C NMR spectrum of glutaronitrile-d_4 (**3j**):



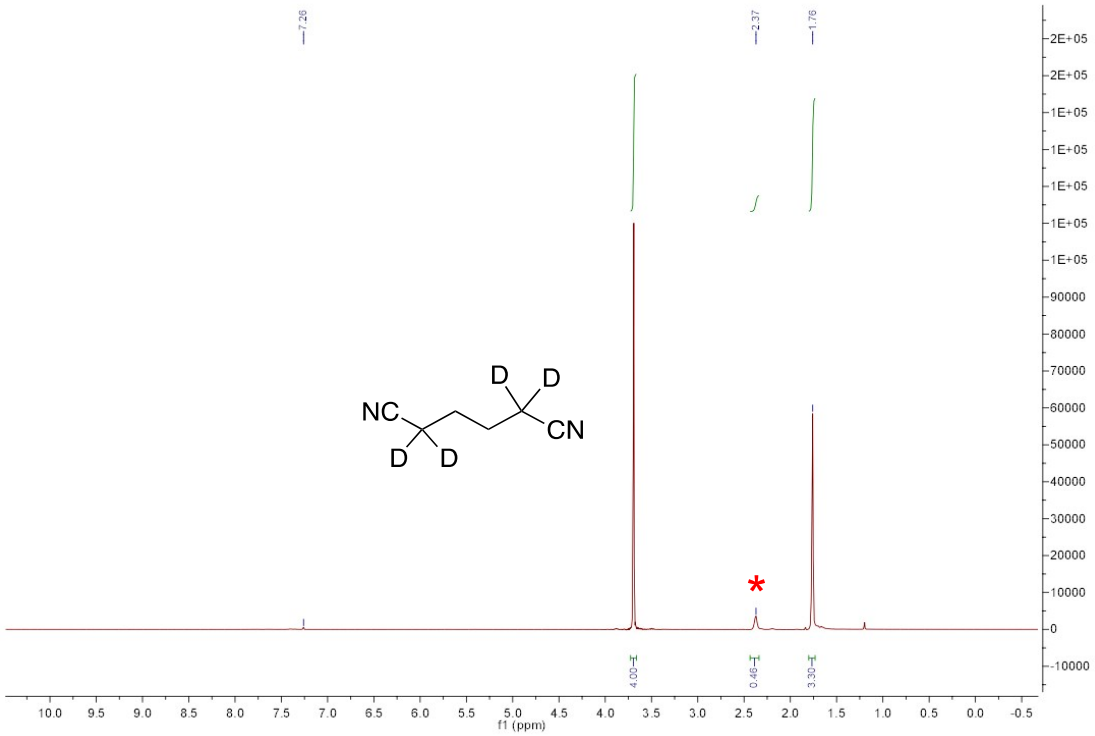
^{2}H NMR spectrum of glutaronitrile-d_4 (**3j**):



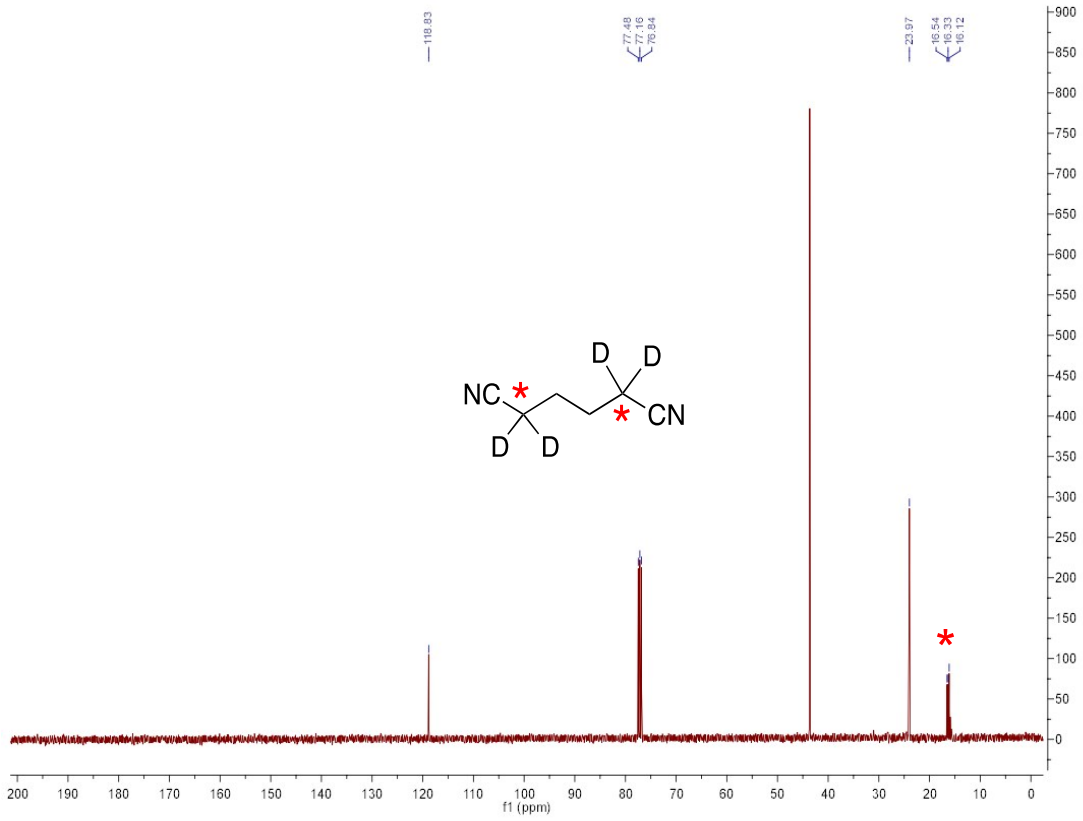
^{1}H NMR spectrum of reference adiponitrile



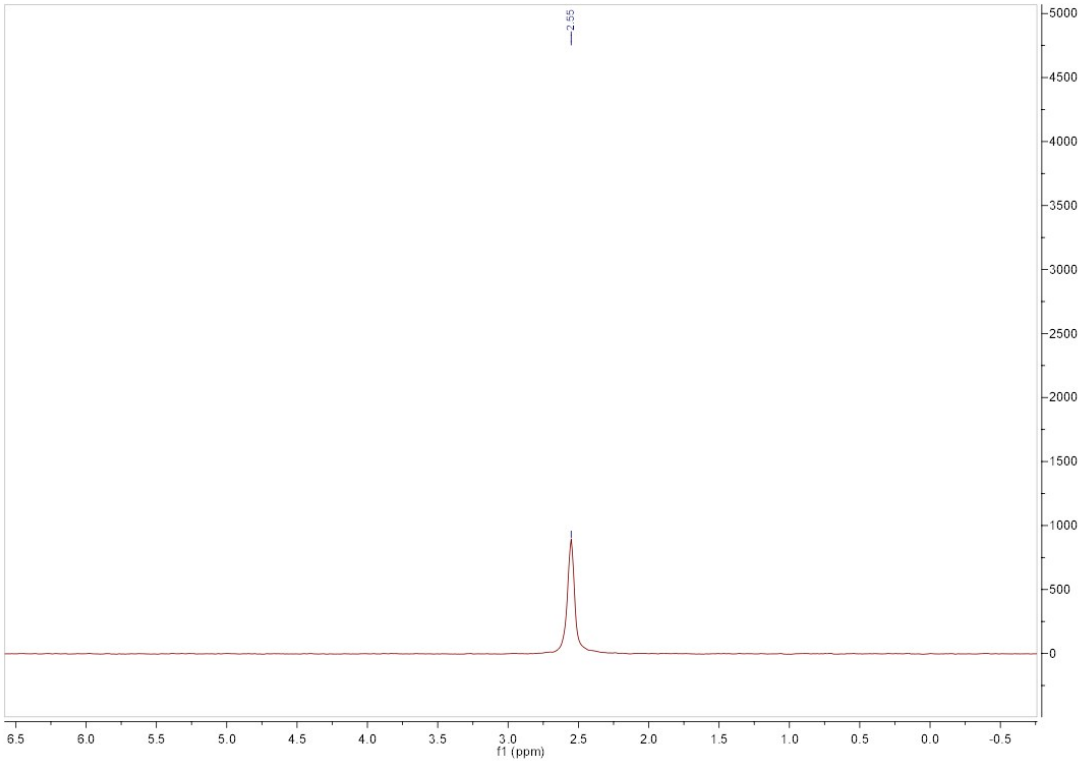
^{1}H NMR spectrum of adiponitrile-d_4 (**3k**):


7.26
2.37
1.76
D
D
NC
CN
D
D
*
4.00
0.46
3.30
f1 (ppm)

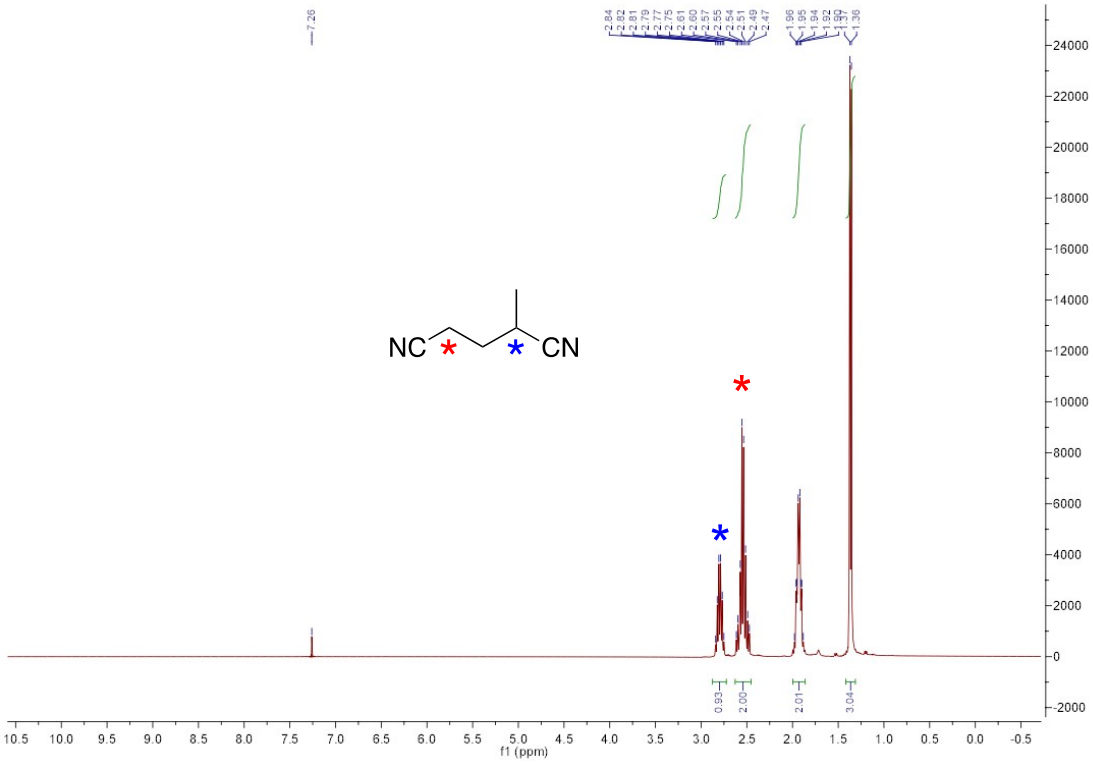
^{13}C NMR spectrum of adiponitrile-d_4 (**3k**):



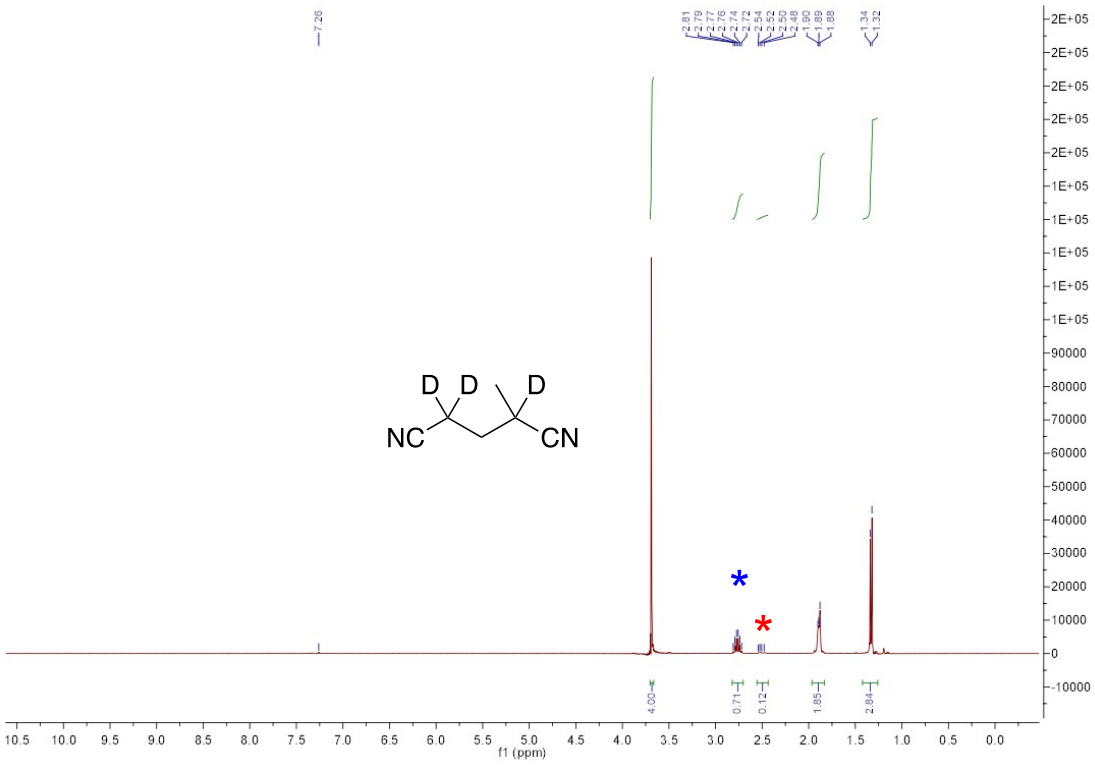
^{2}H NMR spectrum of adiponitrile-d_4 (**3k**):



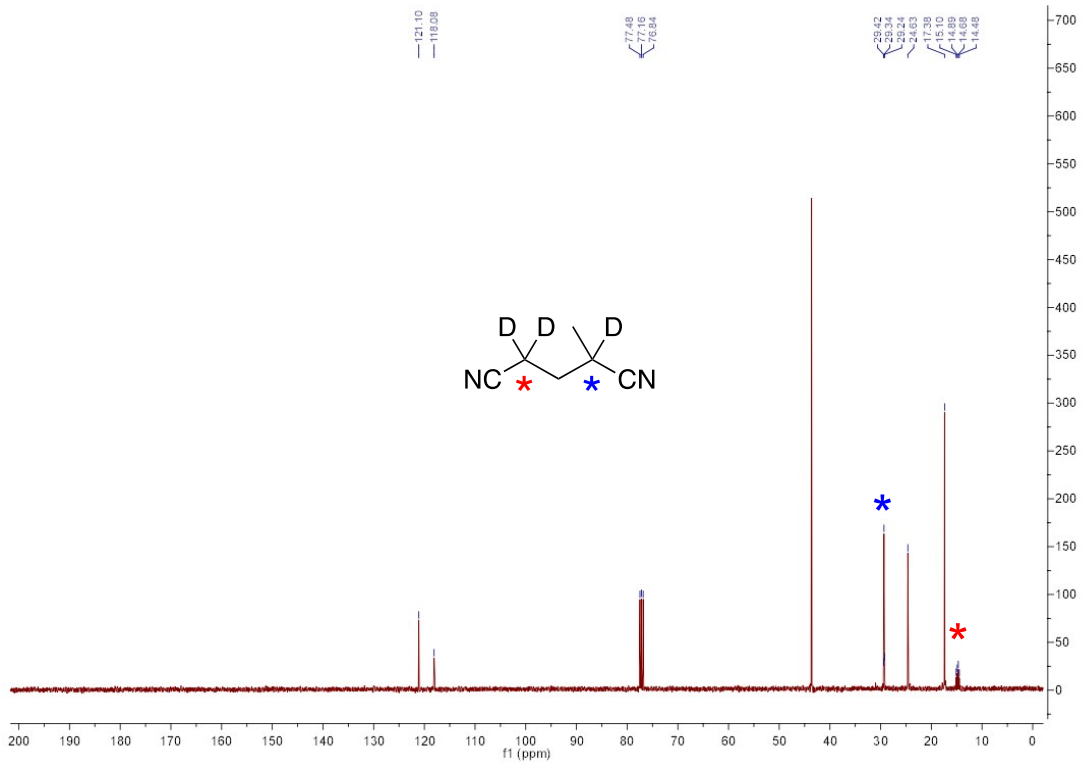
^{1}H NMR spectrum of reference 2-methylglutaronitrile



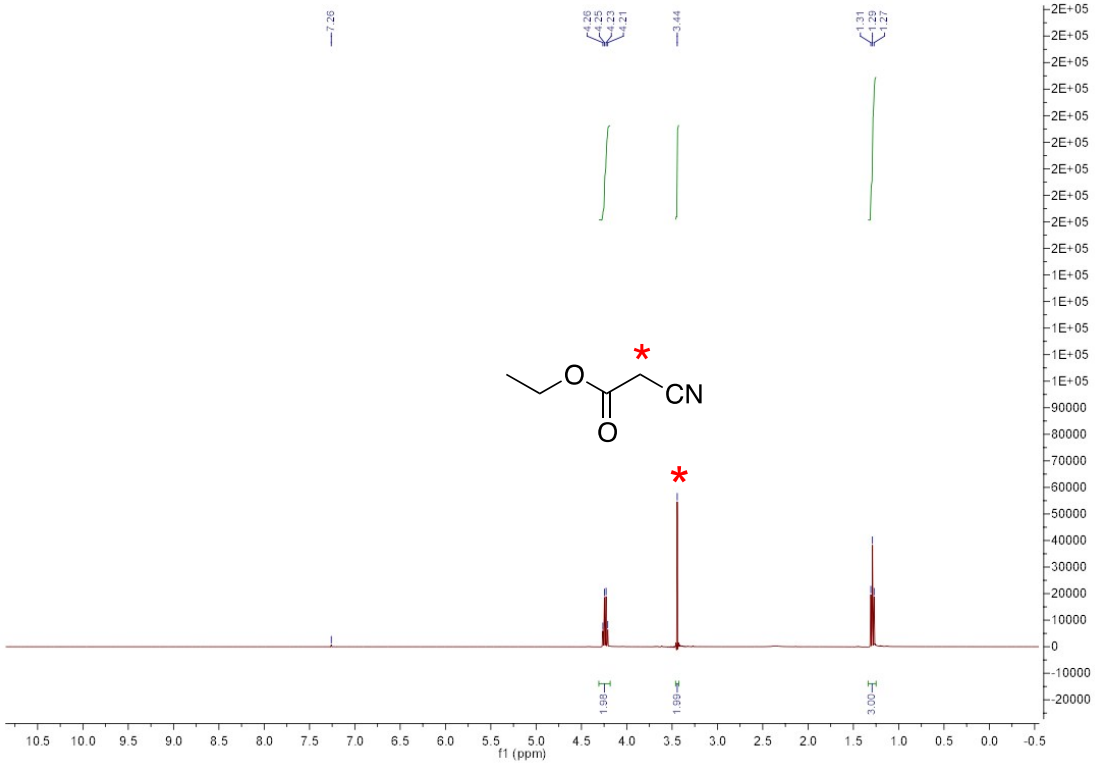
^{1}H NMR spectrum of 2-methylglutaronitrile-d_3 (**3l**):



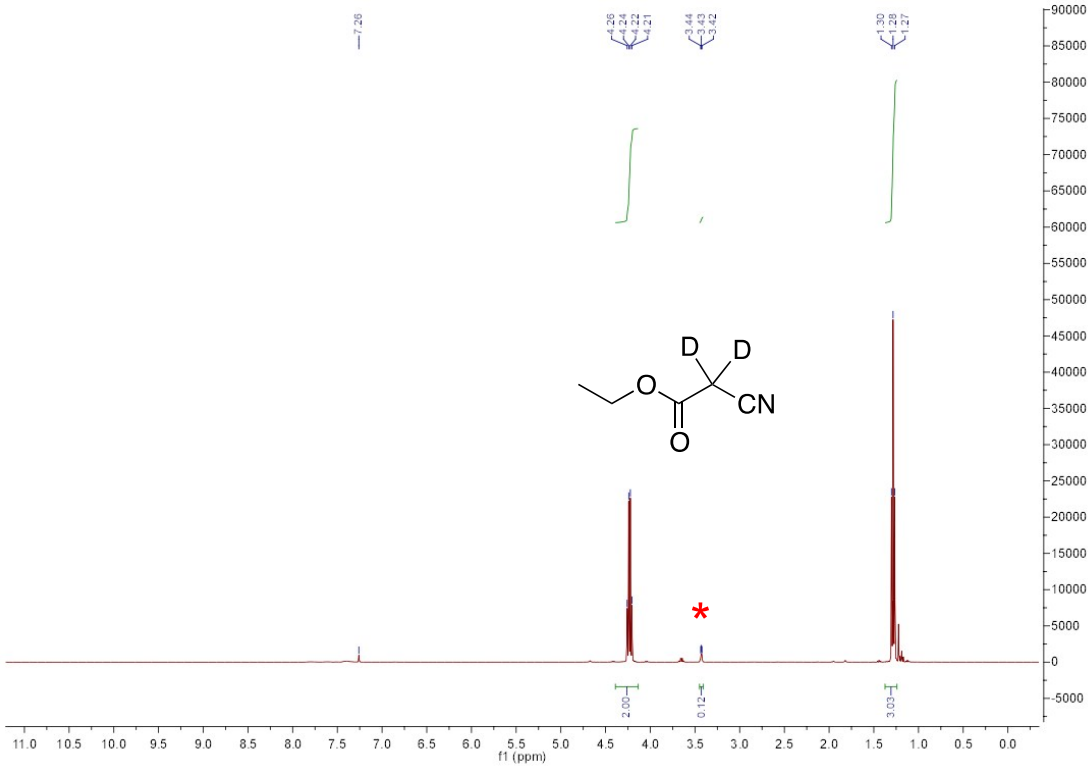
^{13}C NMR spectrum of 2-methylglutaronitrile-d_3 (**3l**):



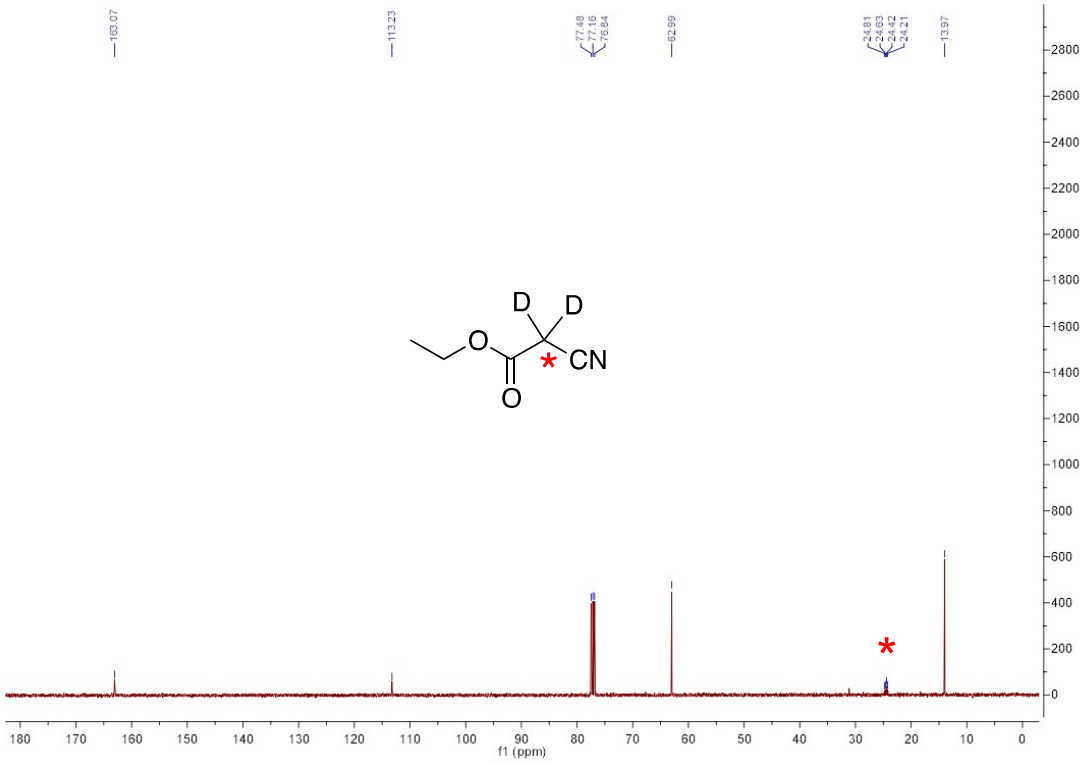
^{1}H NMR spectrum of reference ethylcyanoacetate



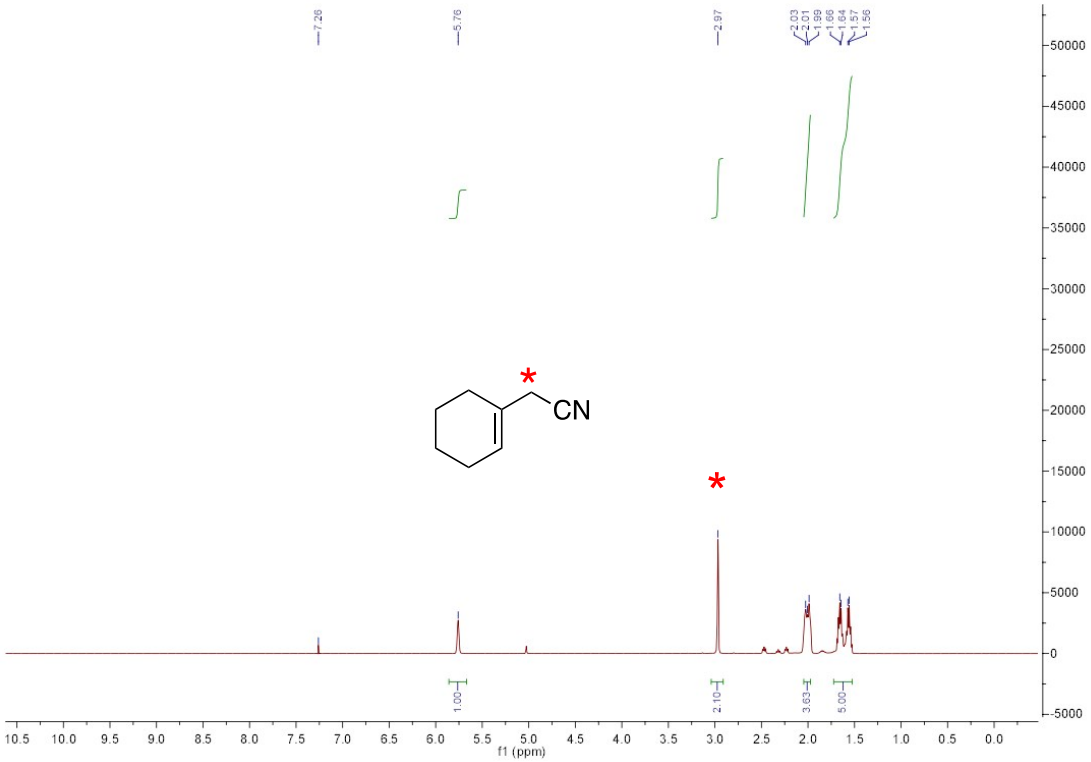
^{1}H NMR spectrum of ethylcyanoacetate-d_2 (**3m**):



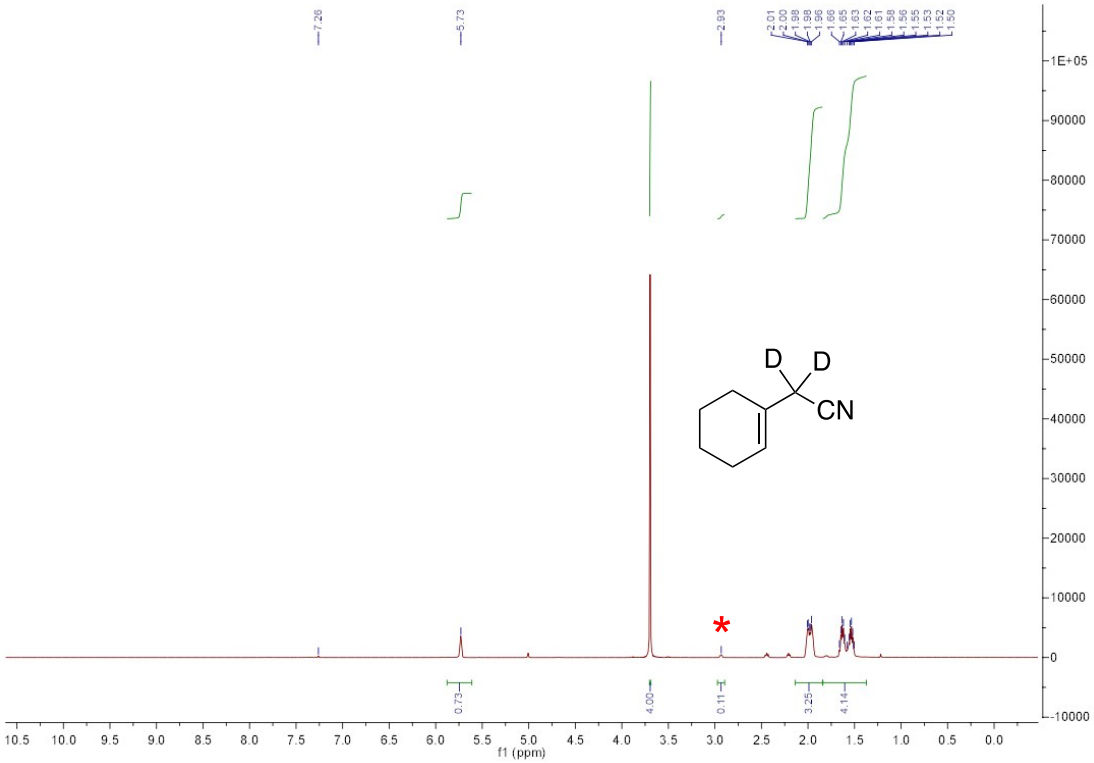
^{13}C NMR spectrum of ethylcyanoacetate-d_2 (**3m**):



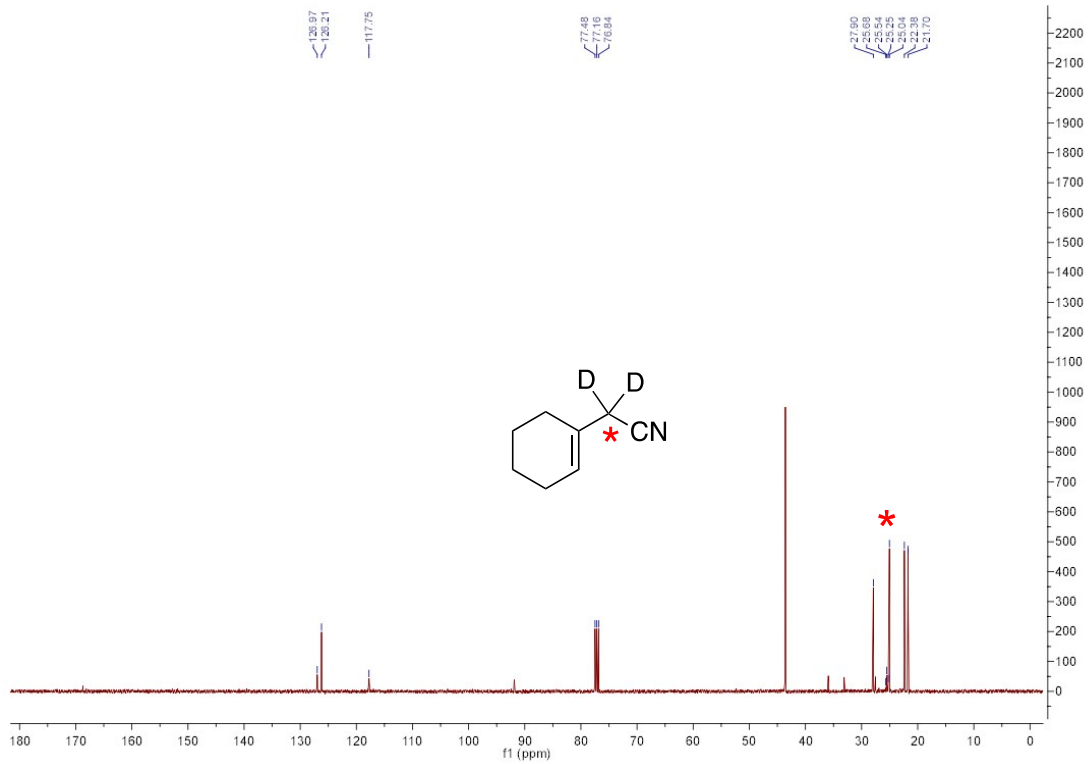
^{1}H NMR spectrum of reference 1-cyclohexenylacetonitrile



^{1}H NMR spectrum of 1-cyclohexenylacetonitrile-d_2 (**3n**):



^{13}C NMR spectrum of 1-cyclohexenylacetonitrile-d$_2$ (**3n**):

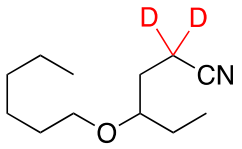


General procedure for the deuteration of heteroatom embedded aliphatic nitriles: To a screw cap scintillation vial heteroatom attached aliphatic nitrile (0.5 mmol), catalyst **1** (0.5 mol%), and KO^{t}Bu (1 mol%) were charged in the nitrogen glove box. The vial was taken out and degassed D_2O (0.4 ml, 20 mmol) was added under argon atmosphere. The reaction vial was sealed and immersed into a pre-heated oil bath of 70 °C and the reaction mixture were stirred for 24 h. After the specified time the reaction mixture was cooled to room temperature, then extracted with dichloromethane (3 x 2 mL). The combined organic phase is dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure provided pure products for further analysis.

Spectral data for deuterated heteroatom embedded aliphatic nitriles:

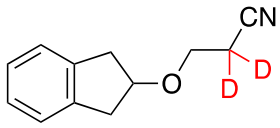
3-(Hexyloxy)propanenitrile-2,2-*d*$_2$ (4a): Colorless liquid, Yield 72 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58-3.63 (m, 2H, CH_2), 3.44-3.46 (m, 1.54H, β-CH_2), 2.56 (0.10H, α-CH_2), 1.54-1.56 (m, 2H, CH_2), 1.27-1.32 (m, 6H, CH_2), 0.85-0.88 (m, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.03 (*C*N), 71.58 (O*C*H$_2$), 65.16 (O*C*H$_2$), 31.65 (*C*H$_2$), 29.49 (*C*H$_2$), 25.73 (*C*H$_2$), 22.63 (*C*H$_2$), 18.70 (m, α-*C*H$_2$), 14.08 (*C*H$_3$).

4-(Hexyloxy)hexanenitrile-2,2-d_2 (4b): Colorless liquid, Yield 93 mg (93%). ^{1}H NMR



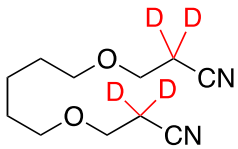
(400 MHz, $CDCl_3$) δ 3.36-3.56 (m, 3H, CH_2), 2.40 (0.22H, α-CH_2), 1.48-1.61 (m, 4H, CH_2), 1.23-1.31 (m, 6H, CH_2), 0.82-0.92 (m, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 117.77 (*C*N), 76.18 (O*C*H), 69.98 (O*C*H_2), 31.57 (*C*H_2), 29.81 (*C*H_2), 26.98 (*C*H_2), 25.70 (*C*H_2), 22.59 (*C*H_2), 22.54 (*C*H_2), 21.98 (m, α-*C*H_2), 13.97 (*C*H_2), 9.27 (*C*H_3).

3-((2,3-Dihydro-1H-inden-2-yl)oxy)propanenitrile-2,2-d2 (4c): Colorless liquid,



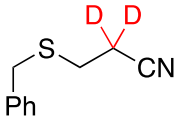
Yield 90 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.23 (m, 4H, ArC*H*), 4.32-4.42 (m, 1H, OCH_2), 3.71 (s, 2H, OCH_2), 3.16-3.21 (m, 2H, CH_2), 2.98-3.03 (m, 2H, CH_2), 2.58 (0.10H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 126.75, 124.76, 118.08 (*C*N), 51.02 (O*C*H_2), 63.57 (O*C*H), 39.27 (*C*H_2), 18.65 (m, α-*C*H_2).

3,3'-(Pentane-1,5-diylbis(oxy))bis(propanenitrile-2,2-d_2) (4d): Colorless liquid,



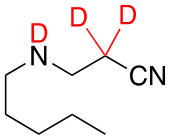
Yield 100 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59-3.62 (m, 4H, CH_2), 3.43-3.46 (m, 3.68H, β-CH_2) 2.56 (0.80H, α-CH_2), 1.55-1.59 (m, 4H, CH_2), 1.38-1.51 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.04 (*C*N), 71.10 (O*C*H_2), 65.02 (O*C*H_2), 29.09 (*C*H_2), 22.48 (*C*H_2), 18.57 (m, α-*C*H_2).

3-(Benzylthio)propanenitrile-2,2-d_2 (4e): Yellow liquid, Yield 82 mg (92%). ^{1}H



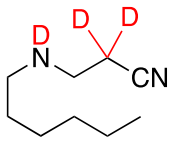
NMR (400 MHz, $CDCl_3$) δ 7.33-7.34 (m, 4H, ArC*H*), 7.25-7.30 (m, 1H, ArC*H*), 3.76 (s, 2H, CH_2) 2.72-2.74 (m, 2H, CH_2), 2.39 (m, 0.17H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.29 (quat. *C*), 128.93 (Ar*C*H), 128.68 (Ar*C*H), 127.24 (Ar*C*H), 129.50 (*C*N), 36.74 (*C*H_2), 35.19 (m, α-*C*H_2), 26.90 (*C*H_2).

3-(Pentylamino-*d*)propanenitrile-2,2-d_2 (4f): Yellow liquid, Yield 65 mg (90%). ^{1}H



NMR (400 MHz, $CDCl_3$) δ 2.82-2.89 (m, 2H, CH_2), 2.59 (t, 1.74H, *J* = 8 Hz, β-CH_2) 2.48 (0.30H, α-CH_2), 1.43-1.50 (m, 2H, CH_2), 1.29-1.33 (m, 4H, CH_2), 0.88 (t, 3H, *J* = 8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.86 (*C*N), 49.22 (*C*H_2), 44.90 (*C*H_2), 29.71 (*C*H_2), 29.48 (*C*H_2), 22.63 (*C*H_2), 18.30 (m, α-*C*H_2), 14.10 (*C*H_3).

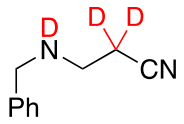
3-(Hexylamino-*d*)propanenitrile-2,2-d_2 (4g): Yellow liquid, Yield 69 mg (88%). ^{1}H



NMR (400 MHz, $CDCl_3$) δ 2.81-2.89 (m, 2H, CH_2), 2.58 (t, 1.56H, *J* =

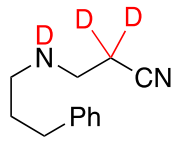
8 Hz, β-CH_2) 2.46 (0.66H, α-CH_2), 1.41-1.47 (m, 2H, CH_2), 1.26-1.32 (m, 6H, CH_2), 0.86 (t, 3H, J = 8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.84 (*C*N), 49.21 (*C*H_2), 44.87 (*C*H_2), 31.75 (*C*H_2), 29.96 (*C*H_2), 29.65 (*C*H_2), 22.64 (*C*H_2), 18.47 (m, α-*C*H_2), 14.09 (*C*H_3).

3-(Benzylamino-*d*)propanenitrile-2,2-d_2 (4h): Yellow liquid, Yield 70 mg (86%). ^{1}H



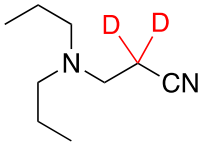
NMR (400 MHz, $CDCl_3$) δ 7.28-7.38 (m, 5H, ArC*H*), 3.83 (s, 2H, CH_2) 2.90-2.92 (m, 2H, CH_2), 2.50 (m, 0.62H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.37 (quat. *C*), 128.49 (Ar*C*H), 128.02 (Ar*C*H), 127.21 (Ar*C*H), 118.78 (*C*N), 52.97 (*C*H_2), 44.04 (*C*H_2), 18.39 (m, α-*C*H_2).

3-((3-Phenylpropyl)amino-*d*)propanenitrile-2,2-d_2 (4i): Yellow liquid, Yield 88 mg



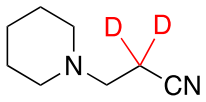
(92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.33 (m, 2H, ArC*H*), 7.20-7.23 (m, 3H, ArC*H*), 2.84-2.92 (m, 2H, CH_2), 2.65-2.71 (m, 4H, CH_2), 2.53 (m, 0.63H, α-CH_2), 1.80-1.88 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.88 (quat. *C*), 128.45 (Ar*C*H), 128.44 (Ar*C*H), 125.96 (Ar*C*H), 118.83 (*C*N), 48.51 (*C*H_2), 44.83 (*C*H_2), 33.49 (*C*H_2), 31.55 (*C*H_2), 18.52 (m, α-*C*H_2).

3-(Dipropylamino)propanenitrile-2,2-d_2 (4j): Yellow liquid, Yield 70 mg (90%). ^{1}H



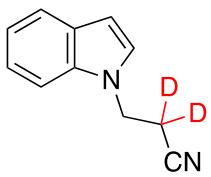
NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 1.82H, β–CH_2), 2.53 (m, 0.22H, α-CH_2), 2.38 (t, 4H, J = 8 Hz, CH_2), 1.38-1.49 (m, 4H, CH_2), 0.87 (t, 6H, J = 8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.28 (*C*N), 55.90 (*C*H_2), 49.60 (*C*H_2), 20.59 (*C*H_2), 16.12 (m, α-*C*H_2), 11.83 (*C*H_3).

3-(Piperidin-1-yl)propanenitrile-2,2-d_2 (4k): Yellow liquid, Yield 58 mg (83%). ^{1}H



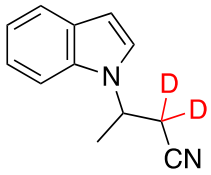
NMR (400 MHz, $CDCl_3$) δ 2.73 (m, 0.12H, α-CH_2), 2.50-2.61 (m, 2H, CH_2) 2.37-2.39 (m, 4H, CH_2), 1.51-1.57 (m, 4H, CH_2), 1.38-1.40 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.08 (*C*N), 54.00 (*C*H_2), 53.90 (*C*H_2), 26.04 (*C*H_2), 25.79 (*C*H_2), 24.26 (*C*H_2), 24.07 (*C*H_2), 15.21 (m, α-*C*H_2).

3-(1*H*-Indol-1-yl)propanenitrile-2,2-d_2 (4l): Brown solid, Yield 80 mg (93%). ^{1}H

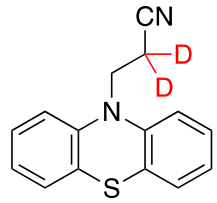


NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 1H, J = 8 Hz, ArC*H*), 7.16-7.35 (m, 4H, ArC*H*), 6.64 (d, 1H, J = 4 Hz, ArC*H*), 4.32 (s, 2H, CH_2), 2.69 (m, 0.12H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.23 (quat. *C*), 128.79 (quat. *C*), 127.50 (Ar*C*H), 122.04 (Ar*C*H), 121.29 (Ar*C*H), 119.99 (Ar*C*H), 117.44 (*C*N), 108.73 (Ar*C*H), 102. 52 (Ar*C*H), 41.60 (*C*H_2), 18.64 (m, α-*C*H_2).

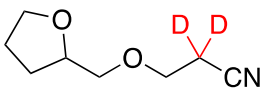
3-(1*H*-Indol-1-yl)butanenitrile-2,2-d$_2$ (4m): Brown solid, Yield 85 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64(d, 1H, *J* = 8 Hz, ArC*H*), 7.13-7.27 (m, 4H, ArC*H*), 6.55 (d, 1H, *J* = 4 Hz, ArC*H*), 4.73-4.78 (m, 2H, CH_2), 1.68 (d, 1H, *J* = 4 Hz, ArC*H*), 1.54 (m, 0.66H, α-CH_2).



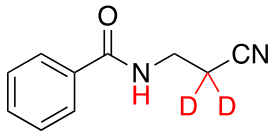
3-(10*H*-Phenothiazin-10-yl)propanenitrile-2,2-*d*$_2$ (4n): Yellow solid, Yield 118 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.29 (m, 4H, ArC*H*), 7.00-7.03 (t, 2H, *J* = 8 Hz, ArC*H*), 6.86-6.88 (d, 2H, *J* = 8 Hz, ArC*H*), 4.25 (s, 2H, CH_2), 2.84 (m, 0.42H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.97 (quat. *C*), 128.04 (Ar*C*H), 127.62 (Ar*C*H), 126.36 (quat. *C*), 123.57 (Ar*C*H), 117.62, (*C*N), 115.41 (Ar*C*H), 43.37 (*C*H$_2$), 16.44 (m, α-*C*H$_2$).



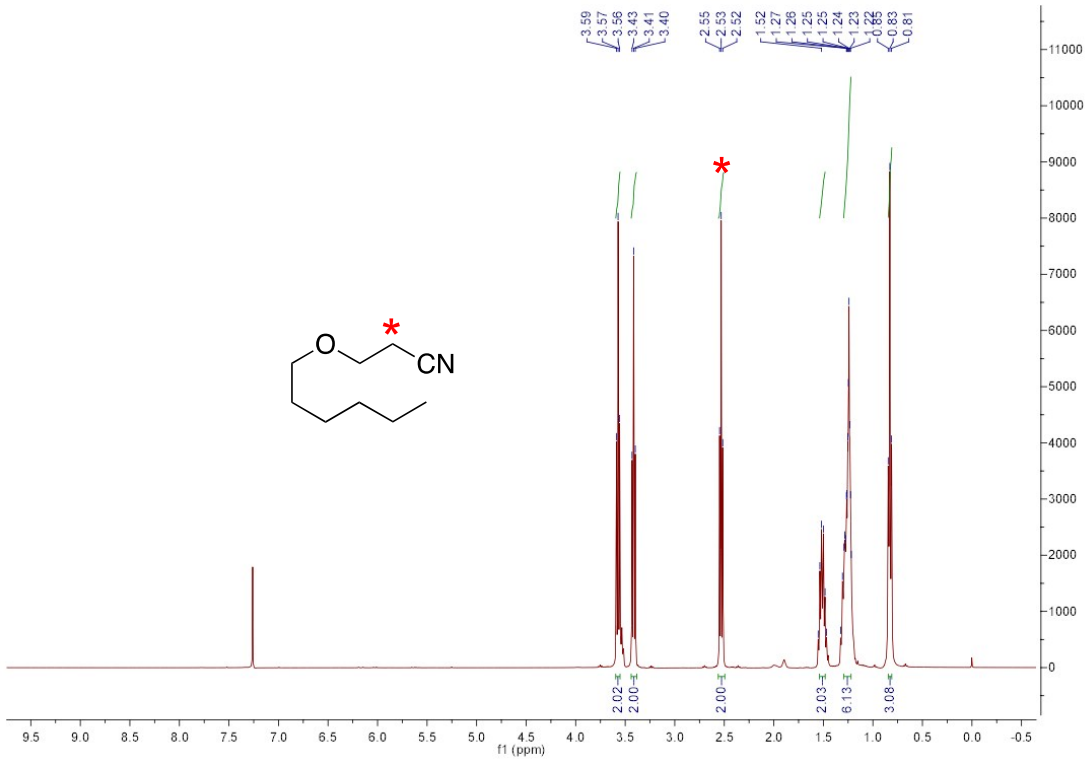
3-((Tetrahydrofuran-2-yl)methoxy)propanenitrile-2,2-*d*$_2$ (4o): Colorless liquid, Yield 68 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38-4.03 (m, 7H, OC*H* & OCH_2), 2.57 (0.07H, α-CH_2), 1.81-1.90 (m, 3H, CH_2) 1.56-1.63 (m, 1H, CH_2).



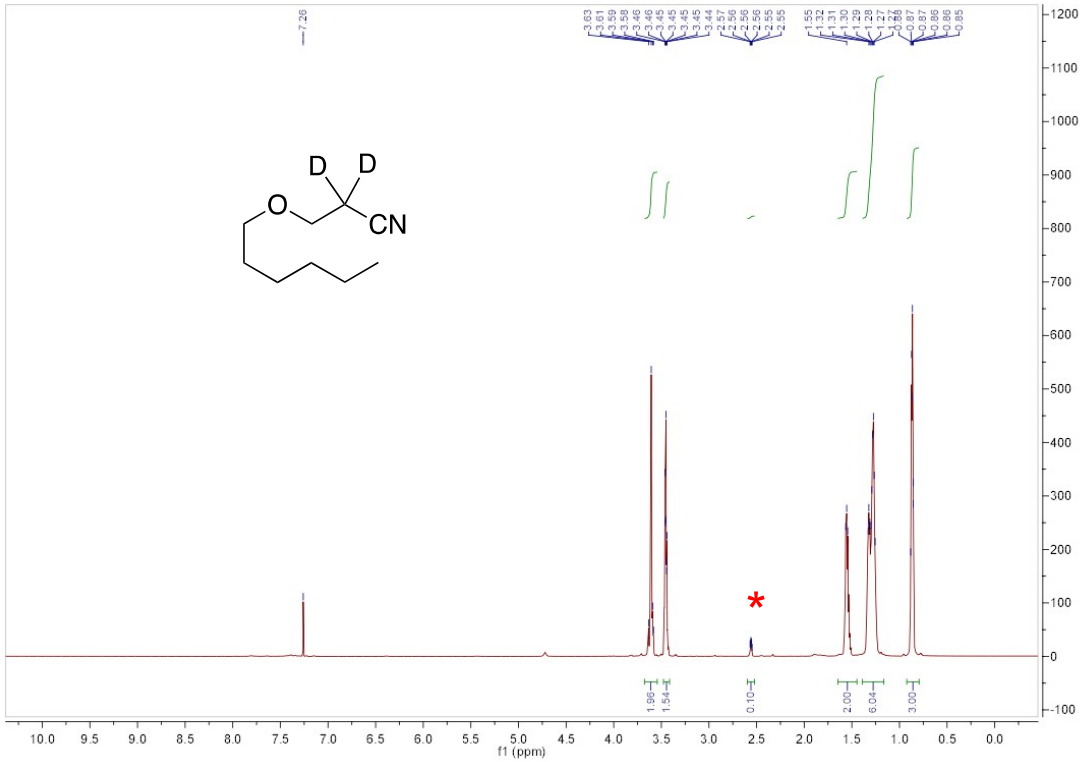
***N*-(2-Cyanoethyl-2,2-d$_2$)benzamide-d (4p):** Yellow solid, Yield 80 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.79 (m, 2H, ArC*H*), 7.48-7.51 (m, 1H, ArC*H*), 7.39-7.42 (m, 2H, ArC*H*), 3.66 (s, 2H, CH_2) 2.70 (m, 0.12H, α-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.15 (*C*=O), 133.65 (quat. *C*), 132.06 (Ar*C*H), 128.75 (Ar*C*H), 127.18 (Ar*C*H), 118.52 (*C*N), 36.01 (*C*H$_2$), 18.10 (m, α-*C*H$_2$).



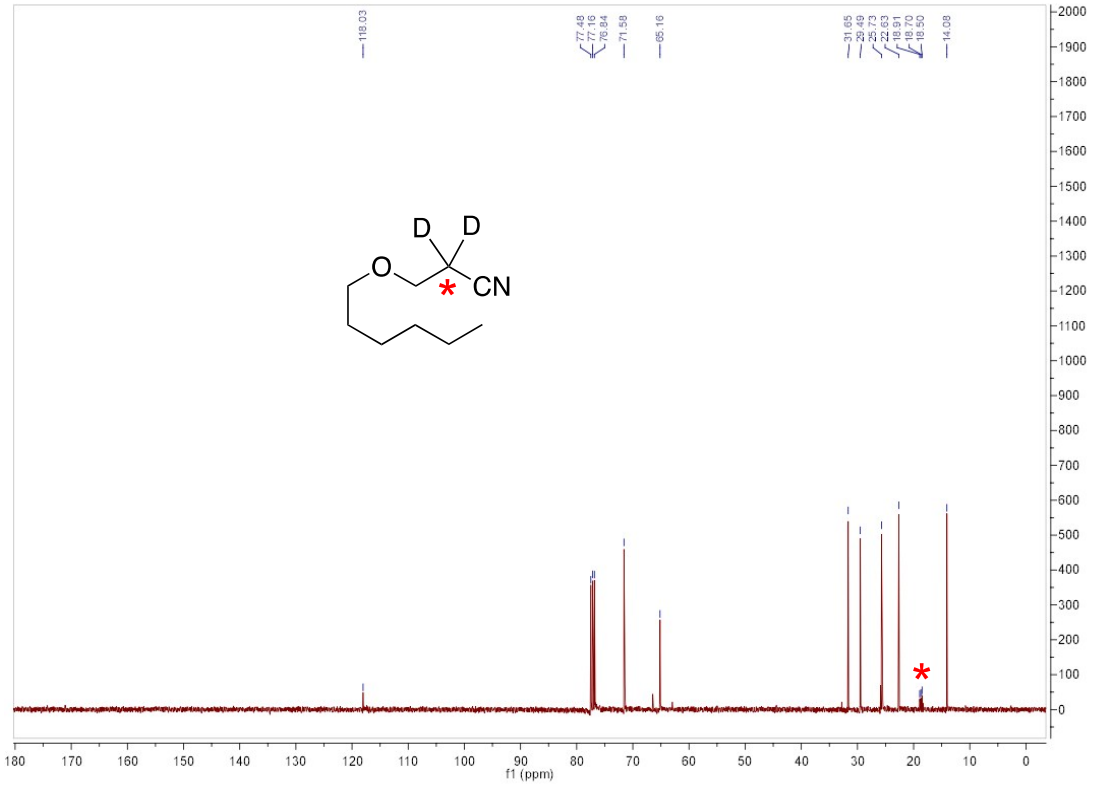
^{1}H NMR spectrum of reference 3-hexyloxypropanenitrile:



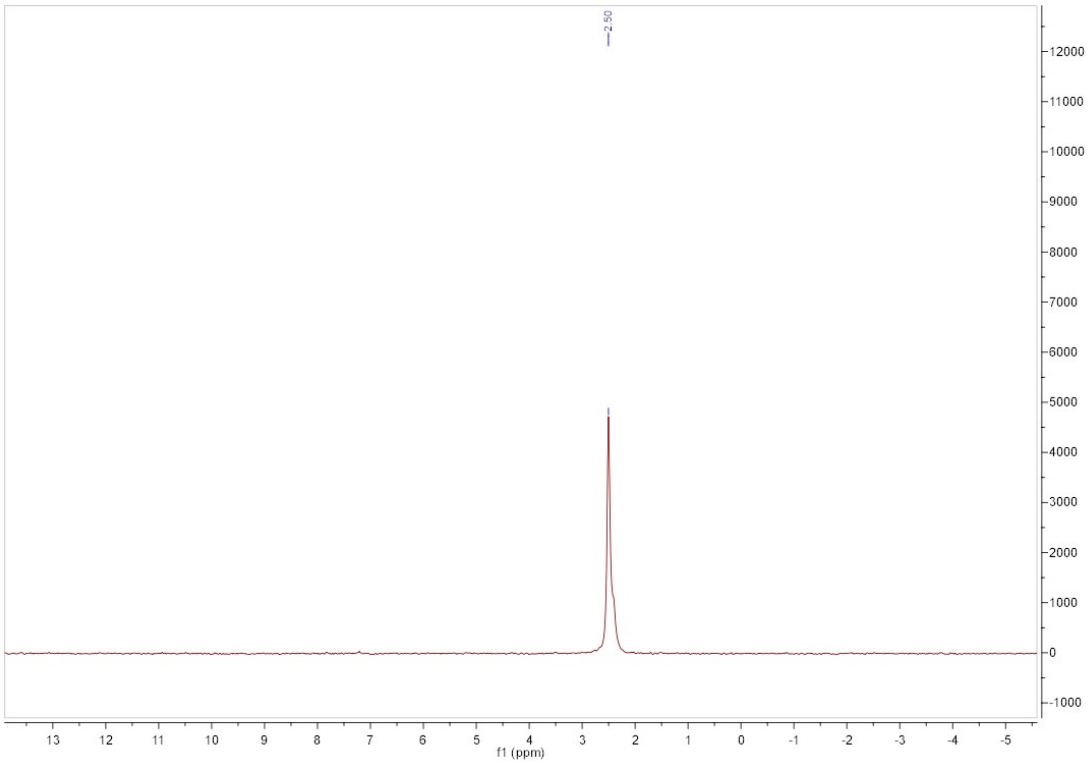
^{1}H NMR spectrum of 3-(hexyloxy)propanenitrile-2,2-d$_2$ (**4a**):



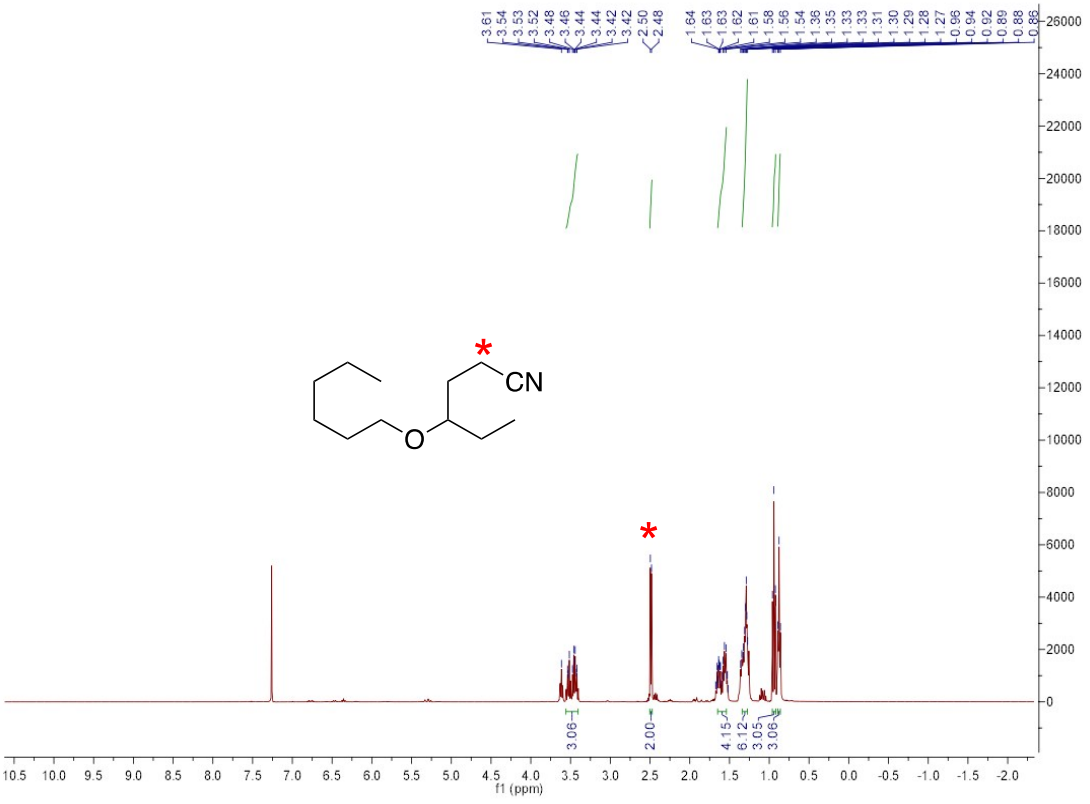
^{13}C NMR spectrum of 3-(hexyloxy)propanenitrile-2,2-d$_2$ (**4a**):



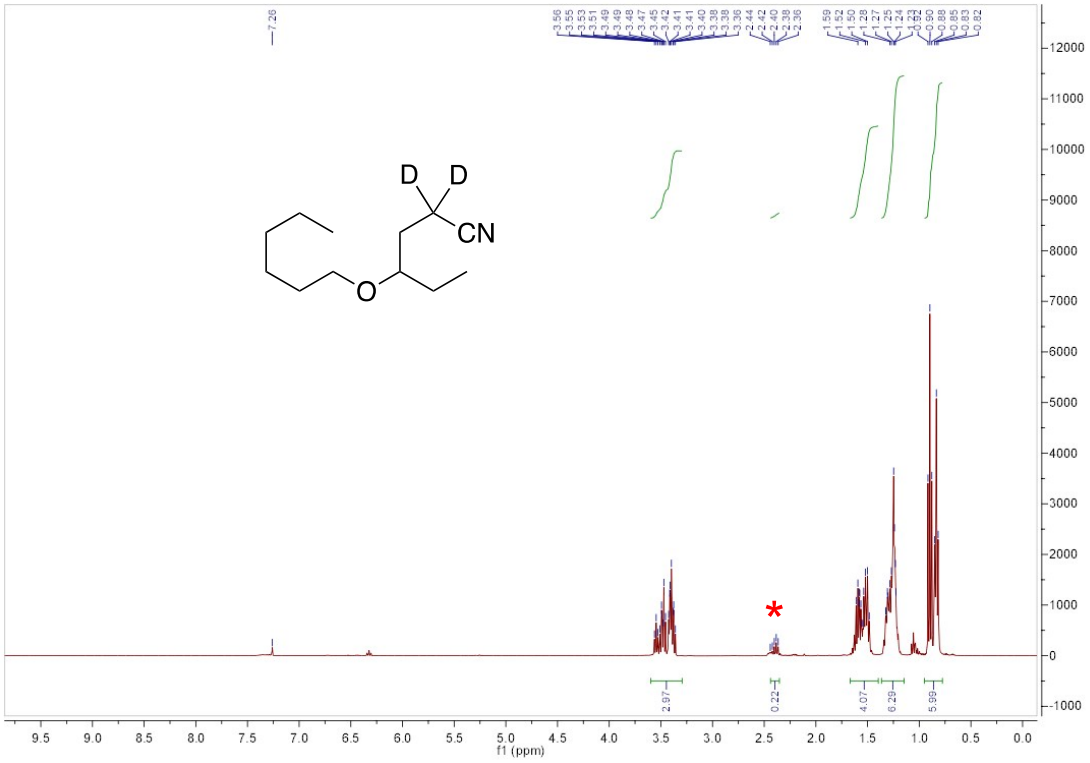
^{2}H NMR spectrum of 3-(hexyloxy)propanenitrile-2,2-d_2 (**4a**):



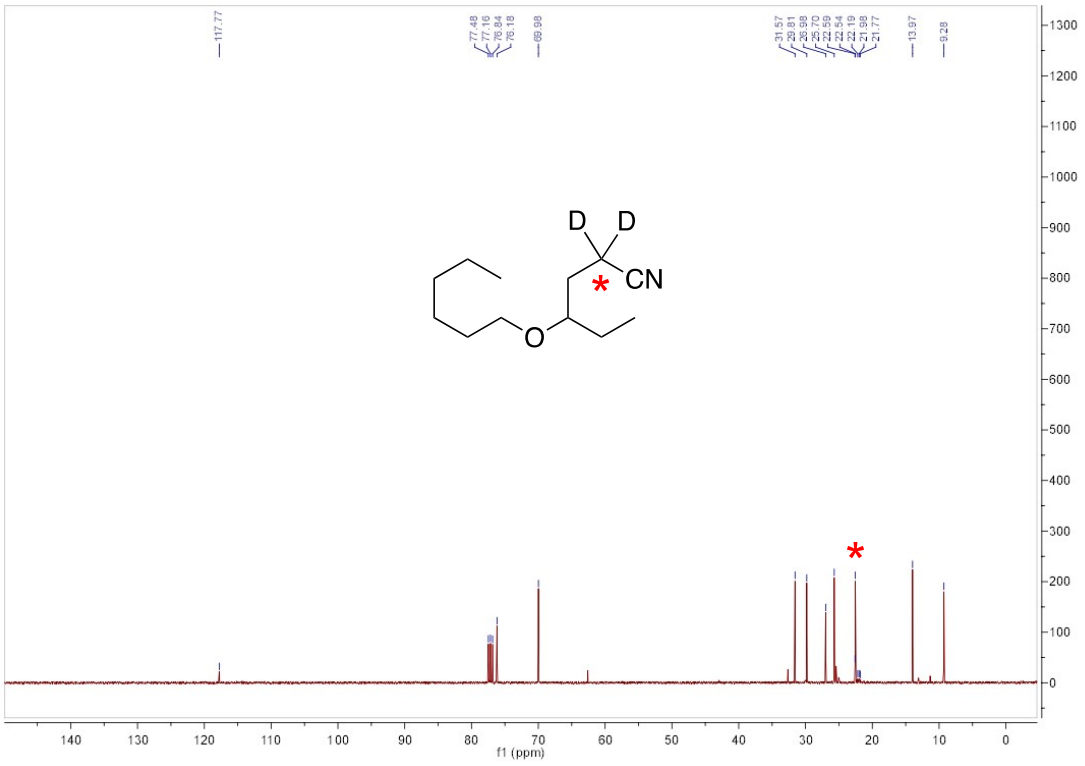
^{1}H NMR spectrum of reference 3-(hexyloxy)pentanenitrile:



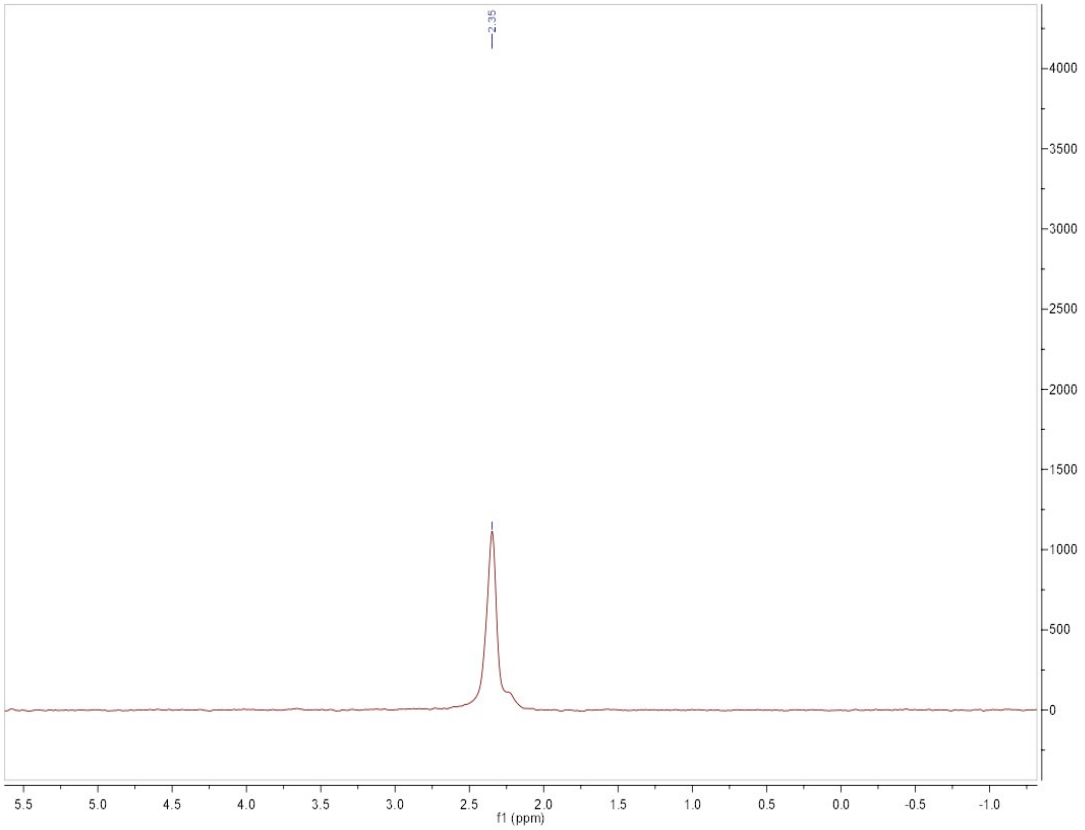
^{1}H NMR spectrum of 4-(hexyloxy)pentanenitrile-2,2-d_2 (**4b**):



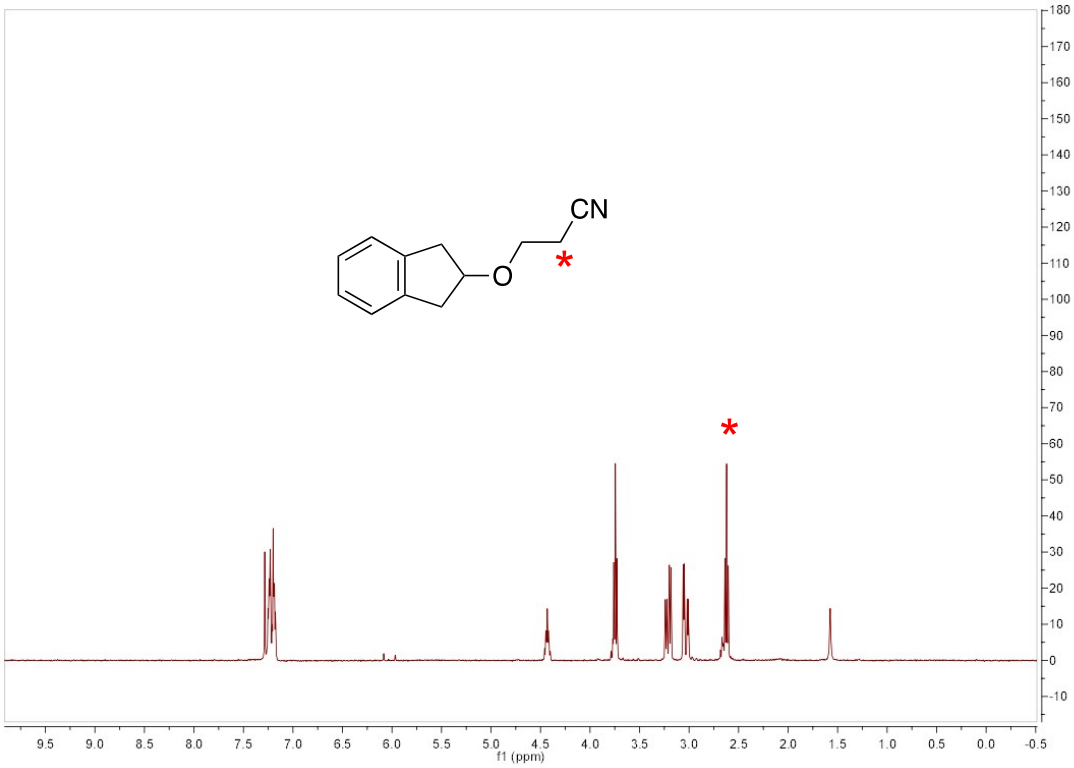
^{13}C NMR spectrum of 4-(hexyloxy)pentanenitrile-2,2-d_2 (**4b**):



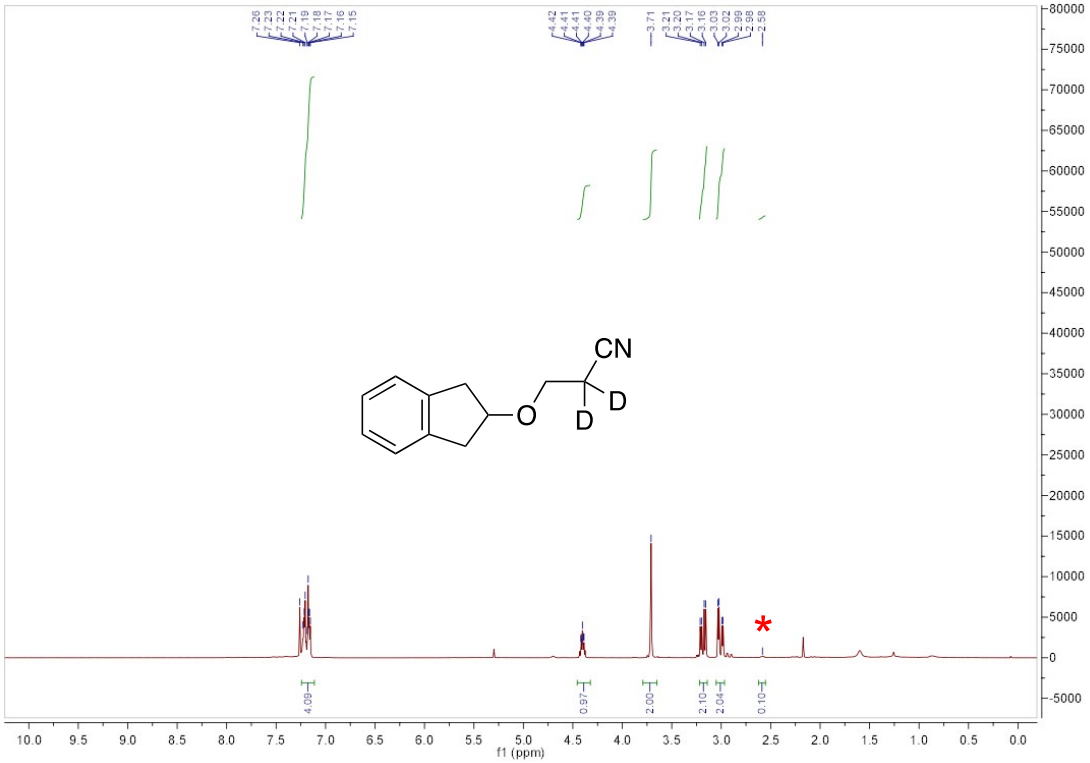
^{2}H NMR spectrum of 4-(hexyloxy)pentanenitrile-2,2-d_2 (**4b**):



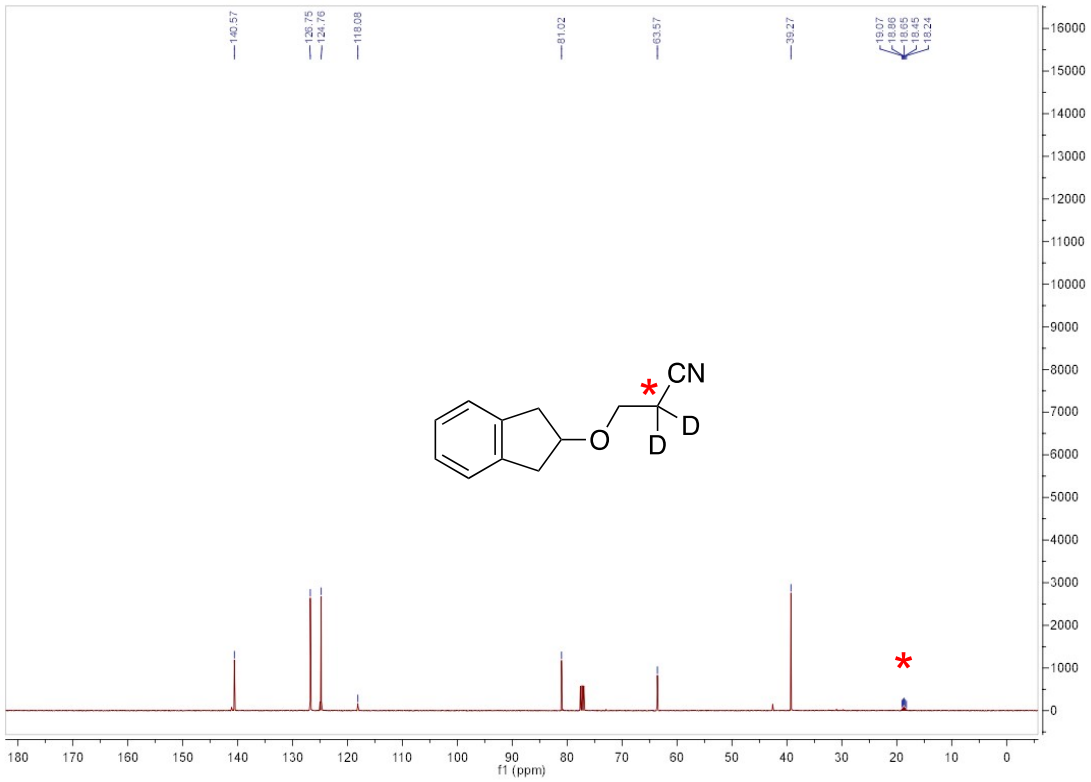
^{1}H NMR spectrum of reference 3-((2,3-dihydro-1*H*-inden-2-yl)oxy)propanenitrile:



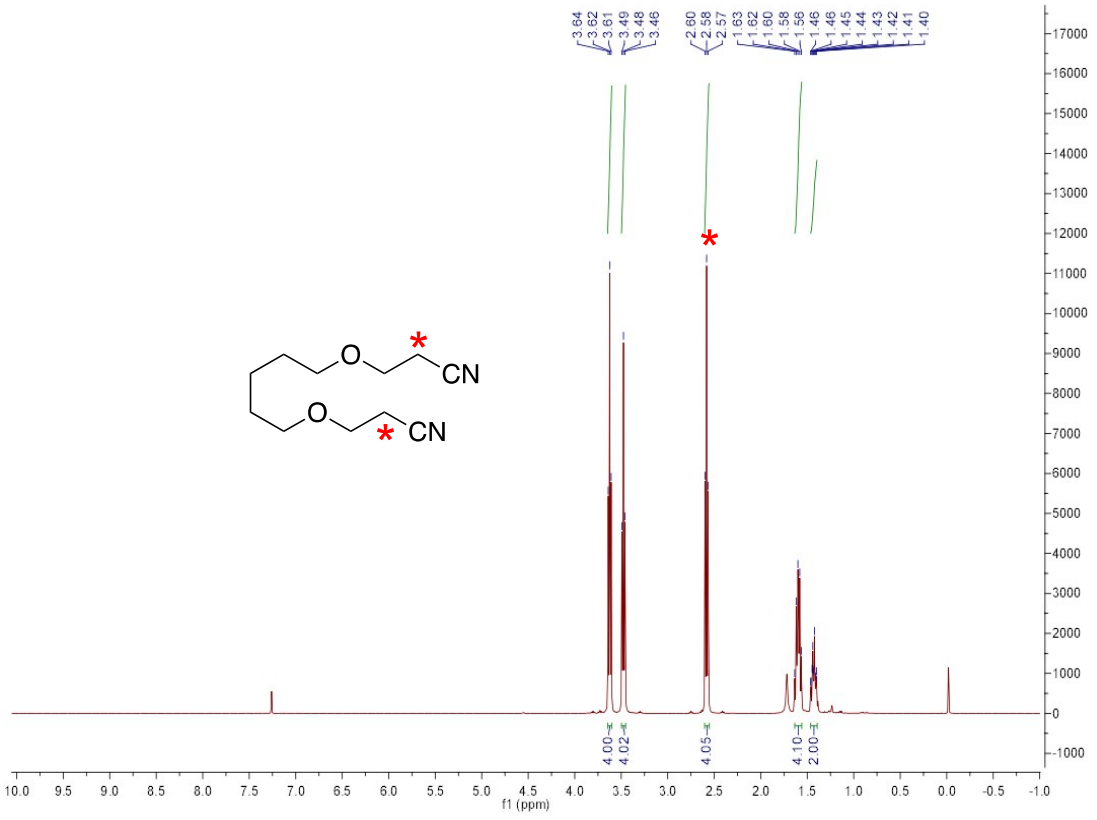
^{1}H NMR spectrum of 3-((2,3-dihydro-1H-inden-2-yl)oxy)propanenitrile-2,2-d_2 (**4c**):



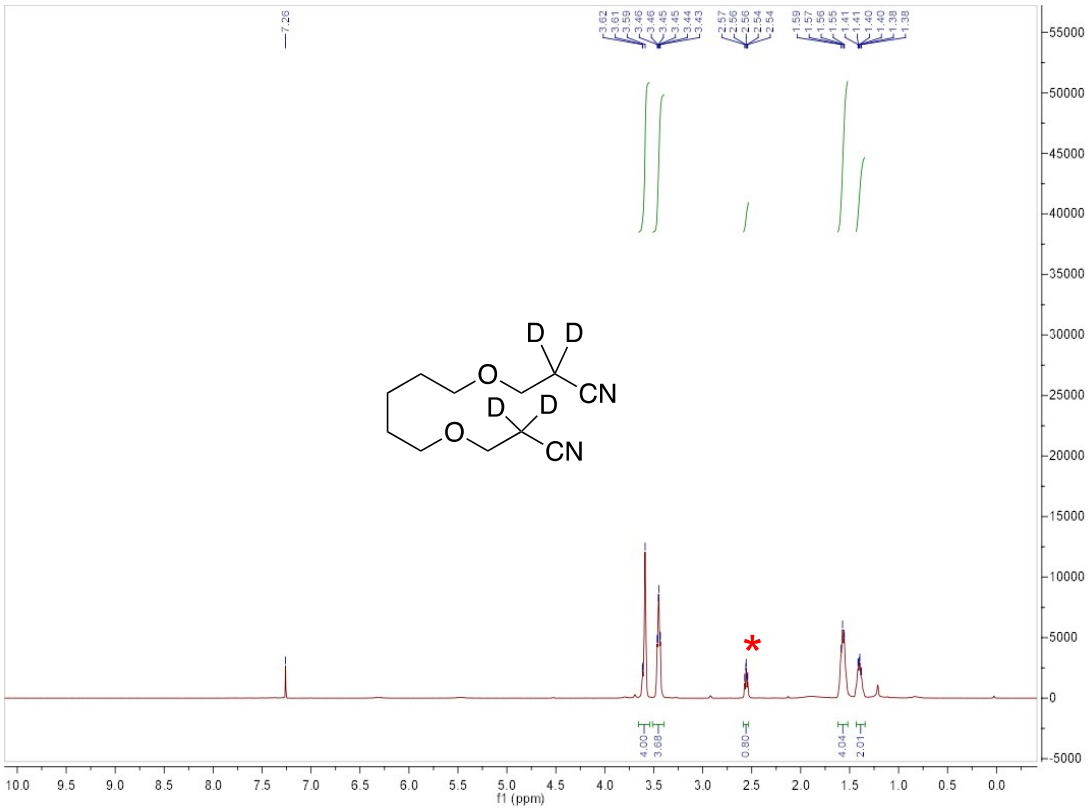
^{13}C NMR spectrum of 3-((2,3-dihydro-1H-inden-2-yl)oxy)propanenitrile-2,2-d$_2$ (**4c**):



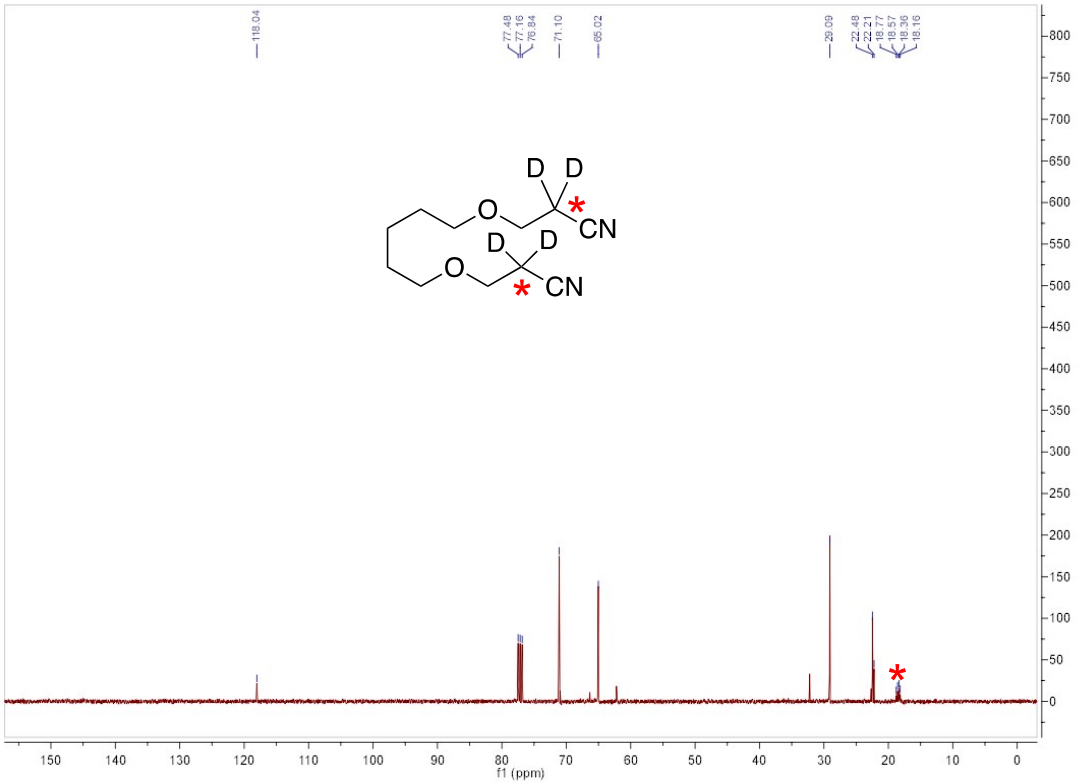
^{1}H NMR spectrum of reference 3,3'-(pentane-1,5-diylbis(oxy))dipropanenitrile:



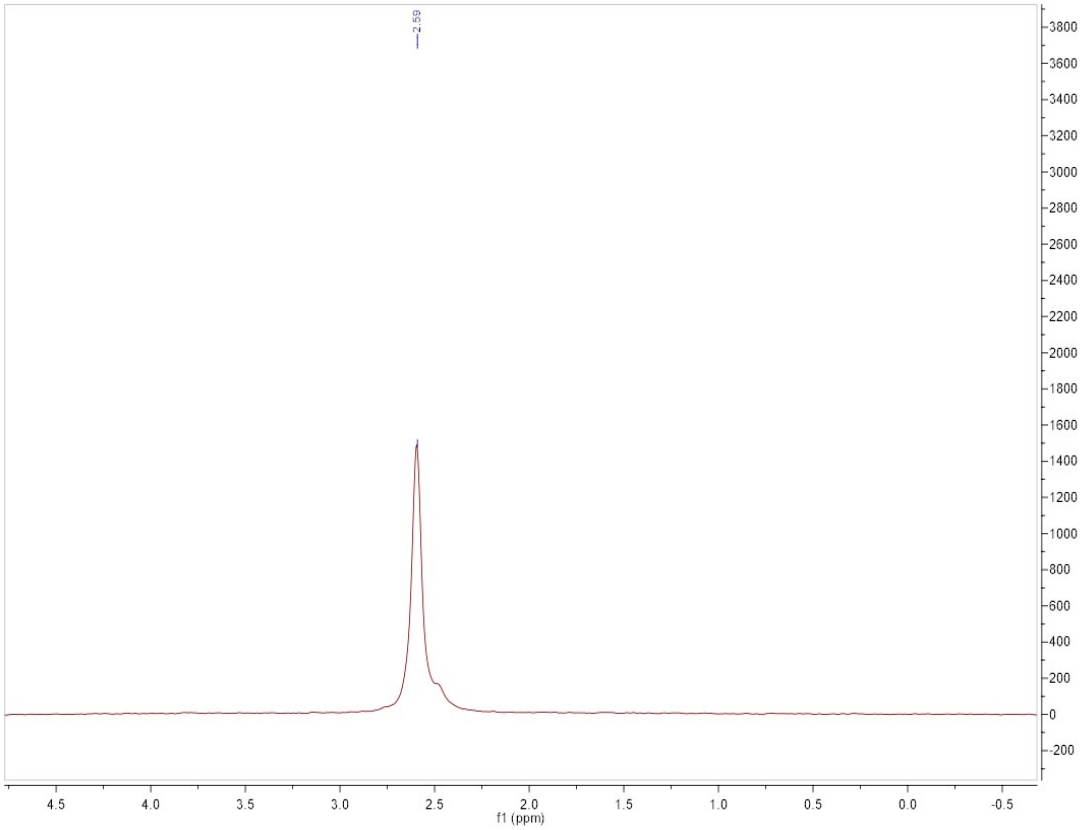
^{1}H NMR spectrum of 3,3'-(pentane-1,5-diylbis(oxy))bis(propanenitrile-2,2-d_2) (**4d**):



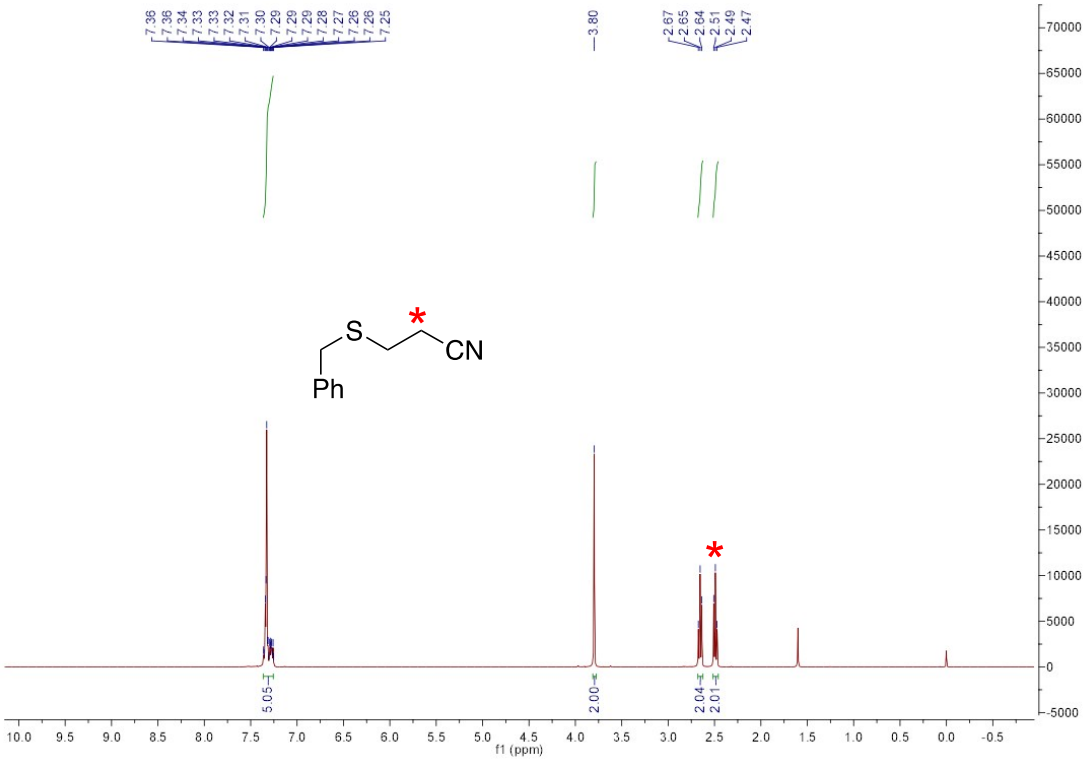
^{13}H NMR spectrum of 3,3'-(pentane-1,5-diylbis(oxy))bis(propanenitrile-2,2-d_2) (**4d**):



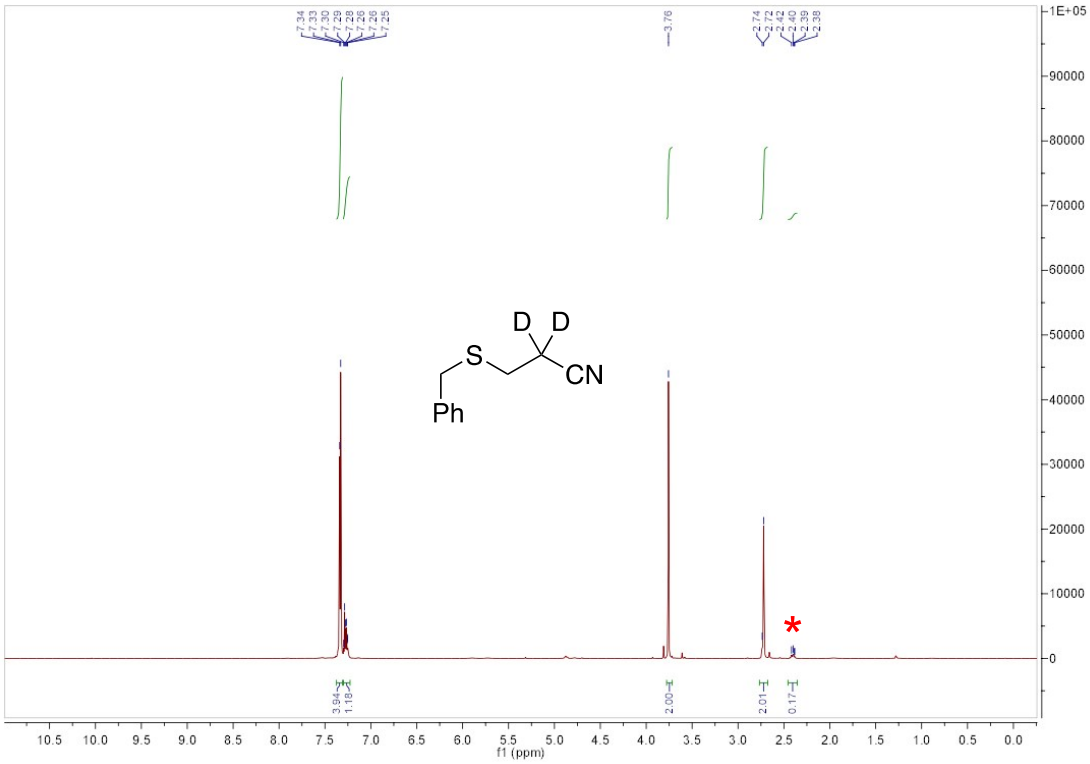
^{2}H NMR spectrum of 3,3'-(pentane-1,5-diylbis(oxy))bis(propanenitrile-2,2-d_2):



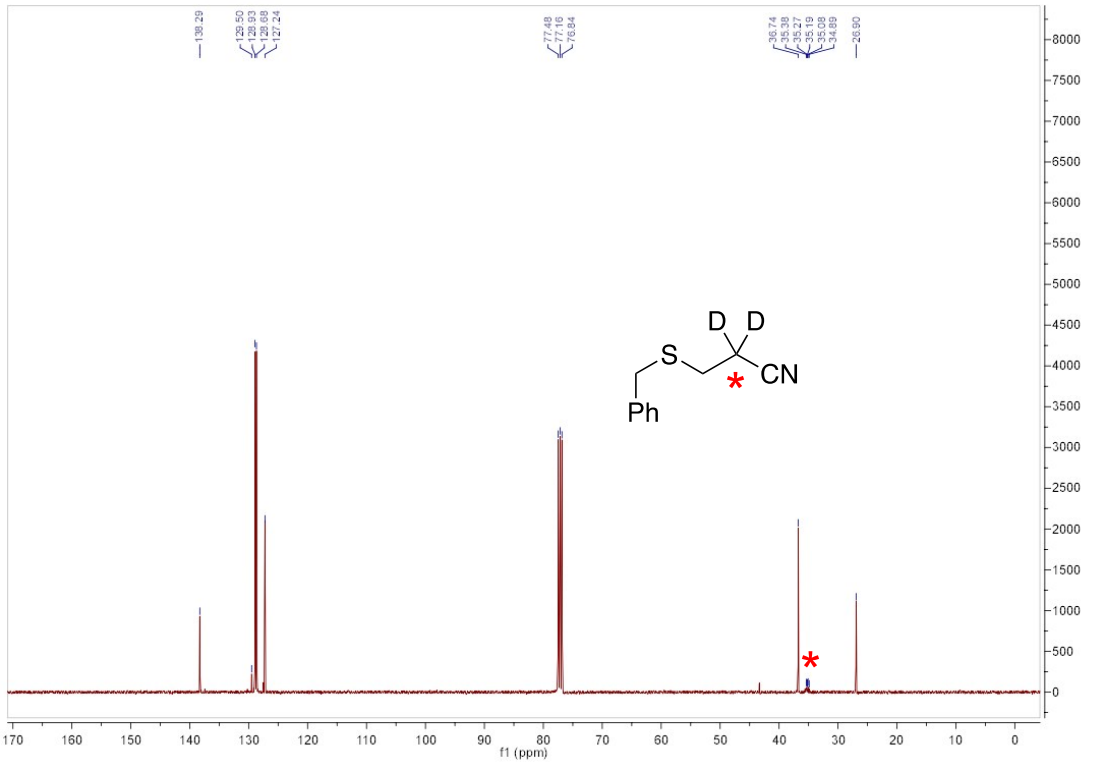
^{1}H NMR spectrum of reference 3-(benzylthio)propanenitrile:



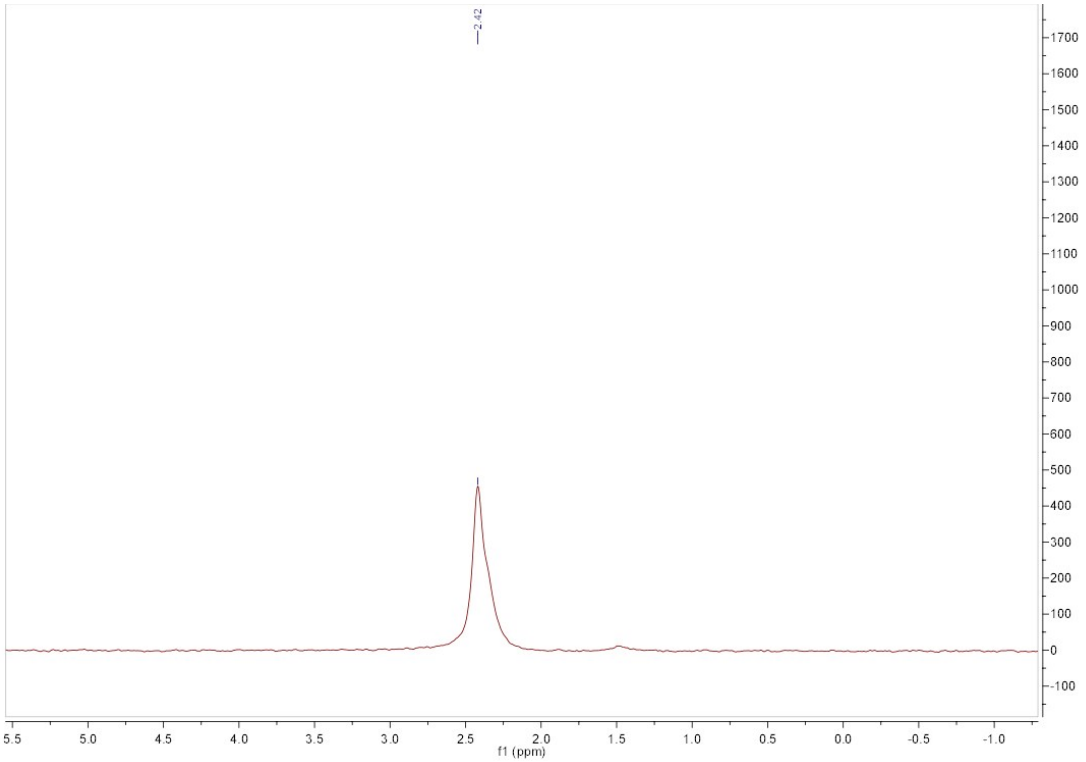
^{1}H NMR spectrum of 3-(benzylthio)propanenitrile-2,2-d_2 (**4e**):



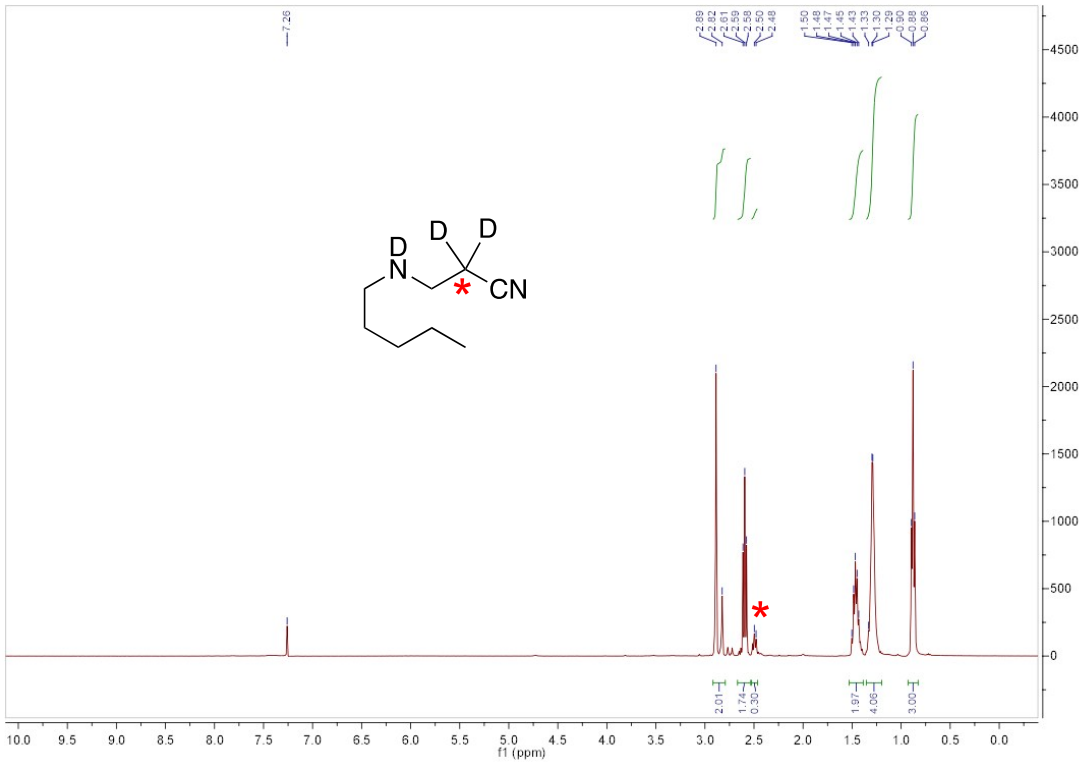
^{13}C NMR spectrum of 3-(benzylthio)propanenitrile-2,2-d_2 (**4e**):



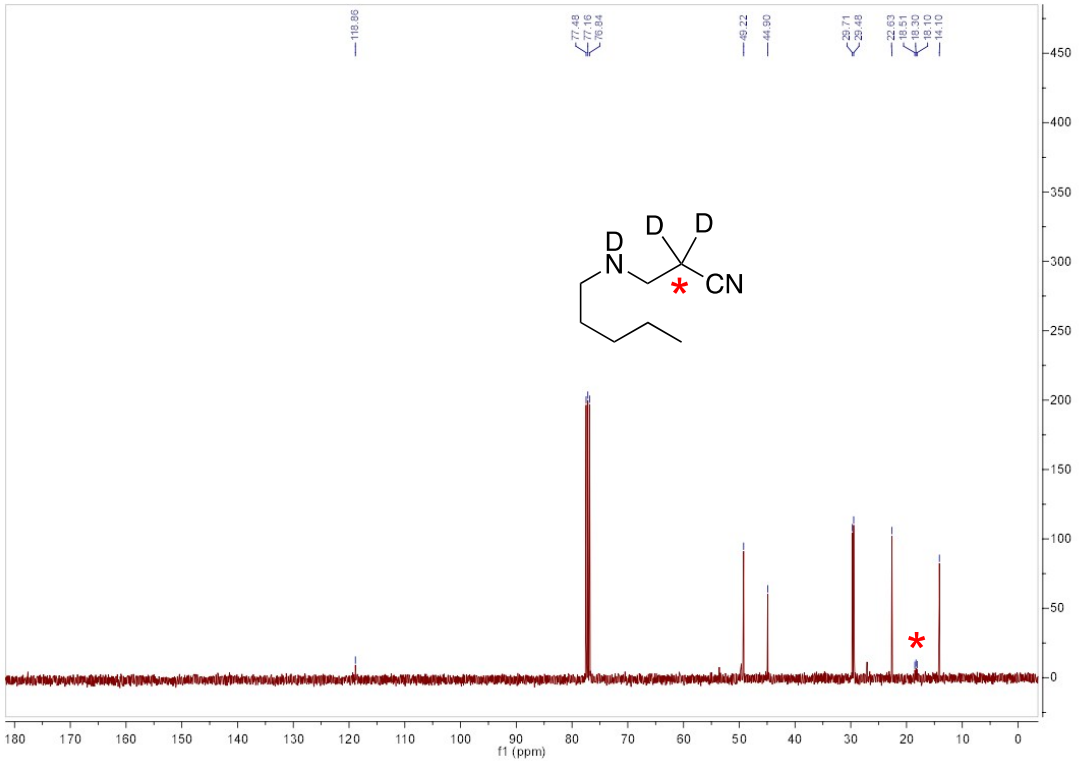
^{2}H NMR spectrum of 3-(benzylthio)propanenitrile-2,2-d_2 (**4e**):



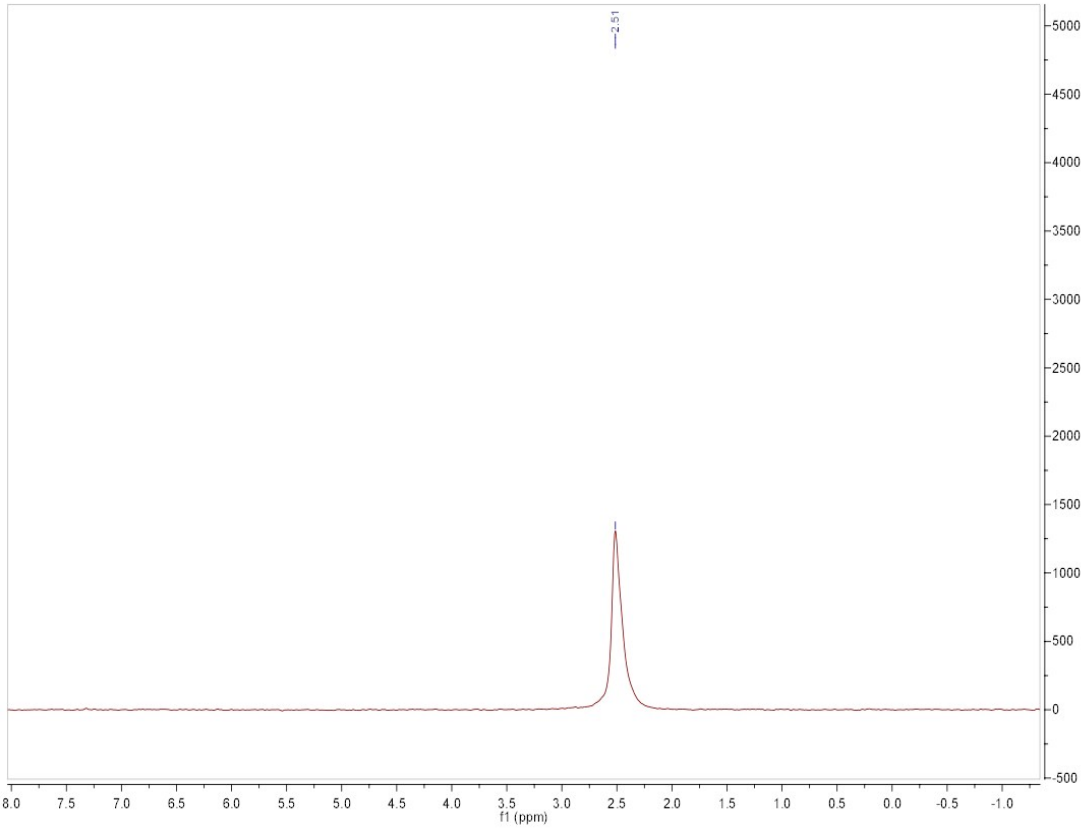
^{1}H NMR spectrum of 3-(pentylamino-*d*)propanenitrile-2,2-d_2 (**4f**):



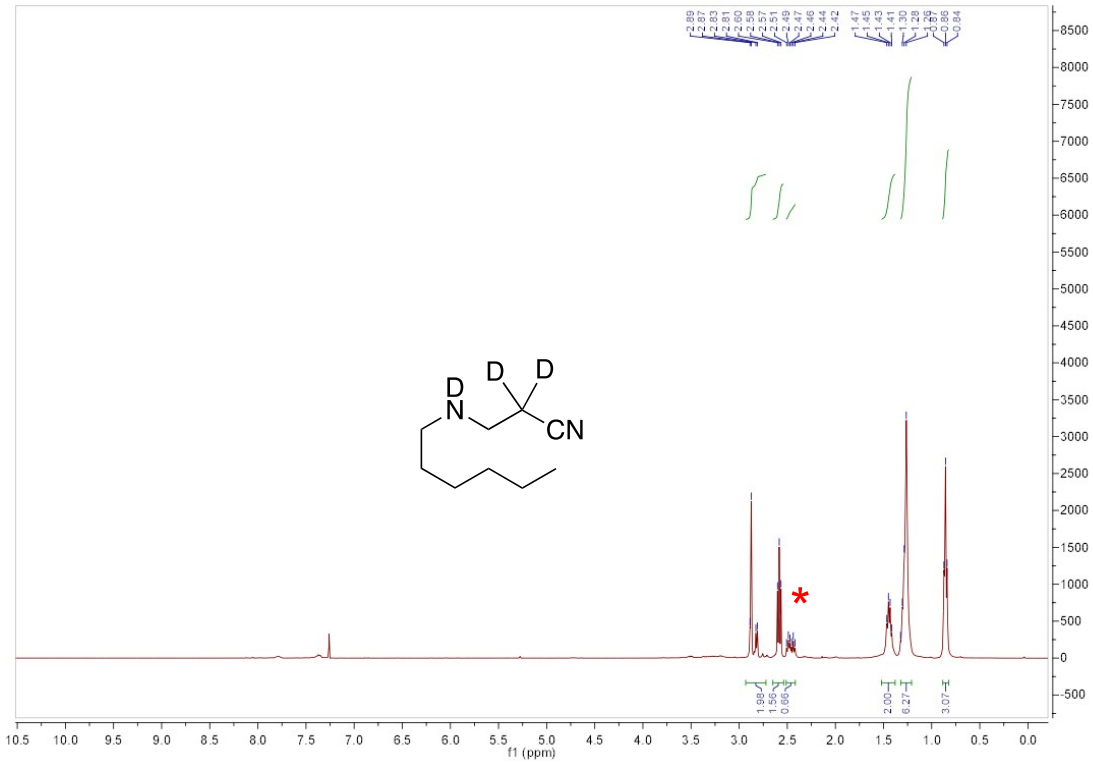
^{13}C NMR spectrum of 3-(pentylamino-*d*)propanenitrile-2,2-d_2 (**4f**):



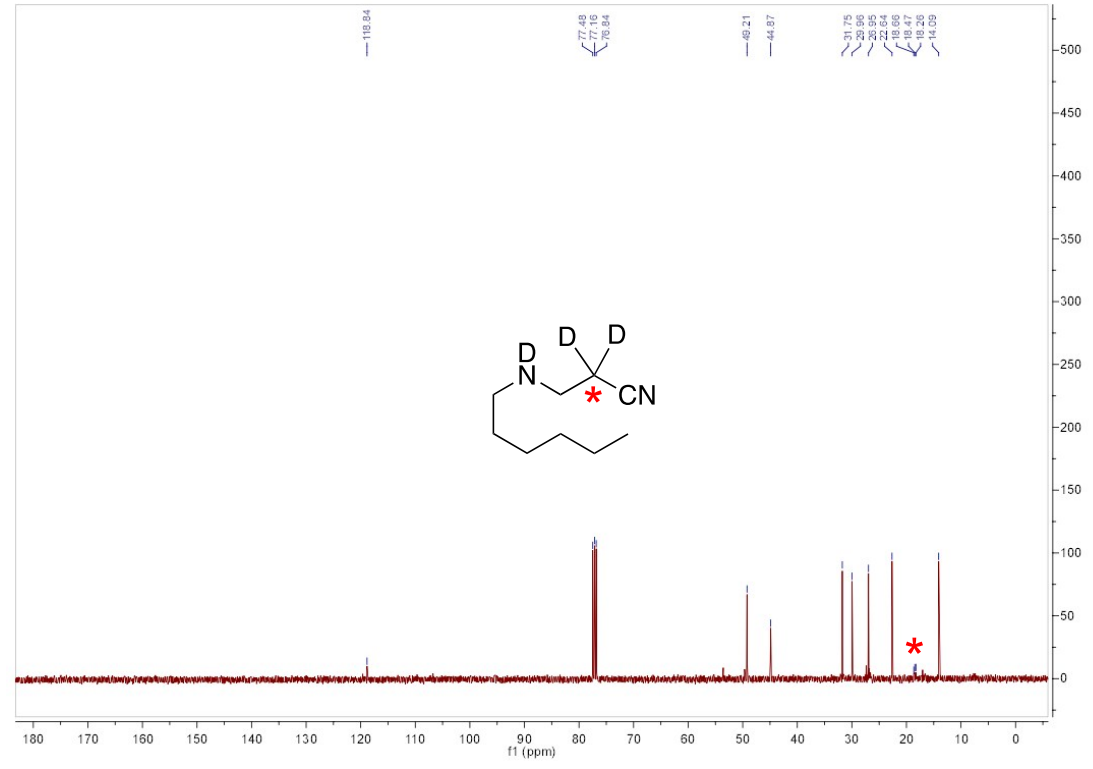
^{2}H NMR spectrum of 3-(pentylamino-*d*)propanenitrile-2,2-d_2 (**4f**):



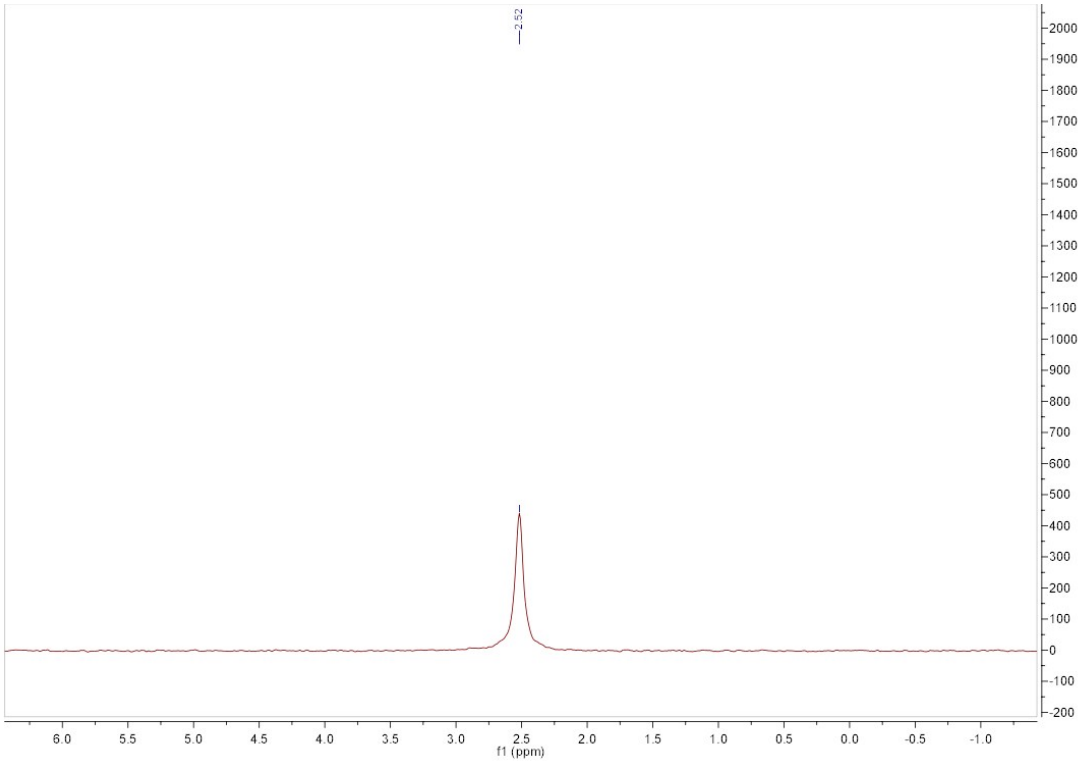
^{1}H NMR spectrum of 3-(hexylamino-*d*)propanenitrile-2,2-d_2 (**4g**):



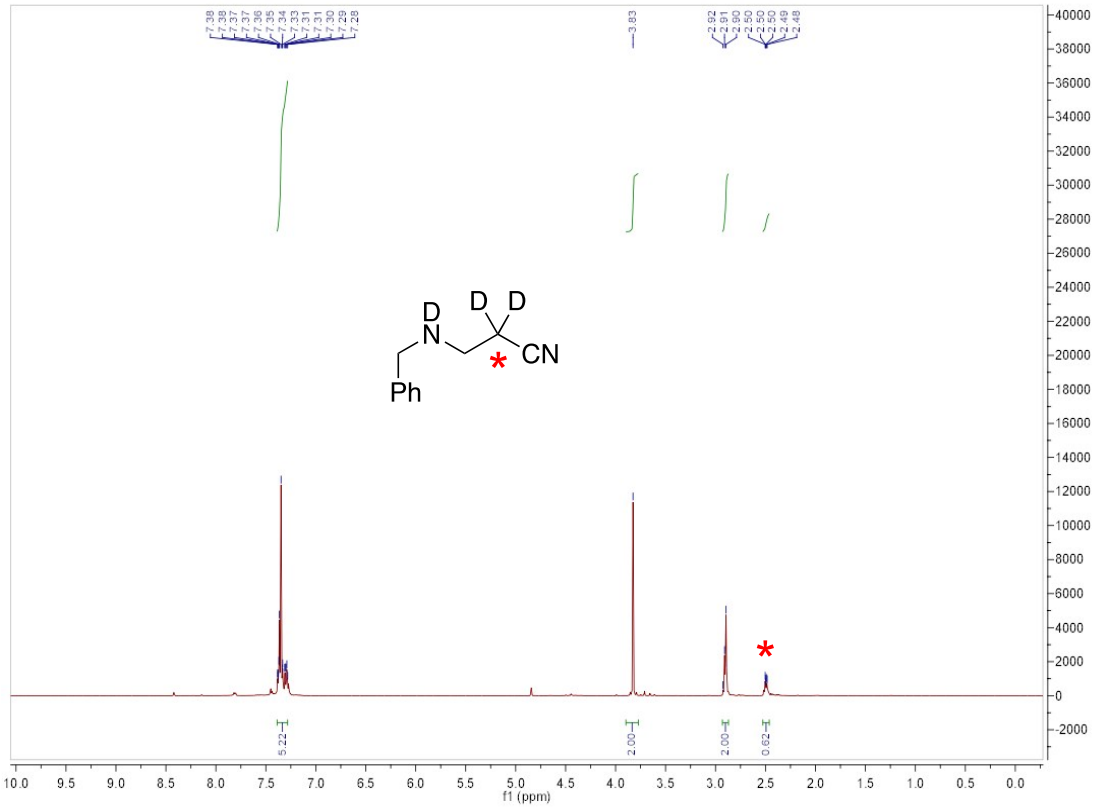
^{13}C NMR spectrum of 3-(hexylamino-*d*)propanenitrile-2,2-d_2 (**4g**):



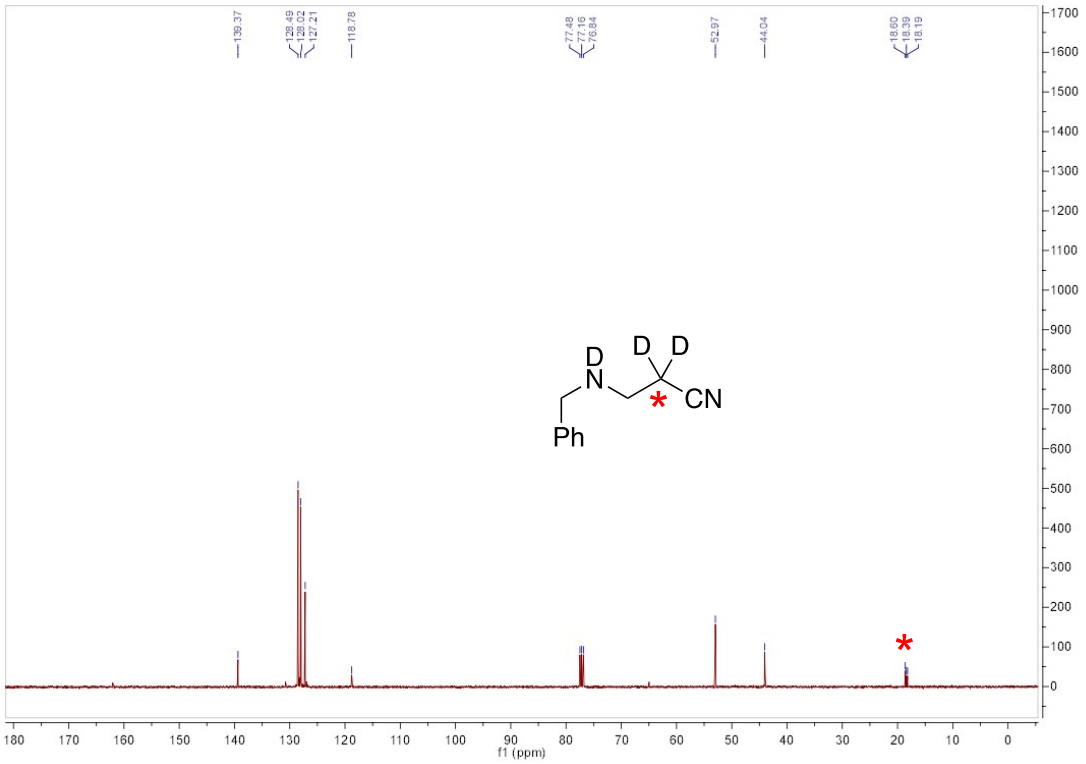
^{2}H NMR spectrum of 3-(hexylamino-*d*)propanenitrile-2,2-d_2 (**4g**):



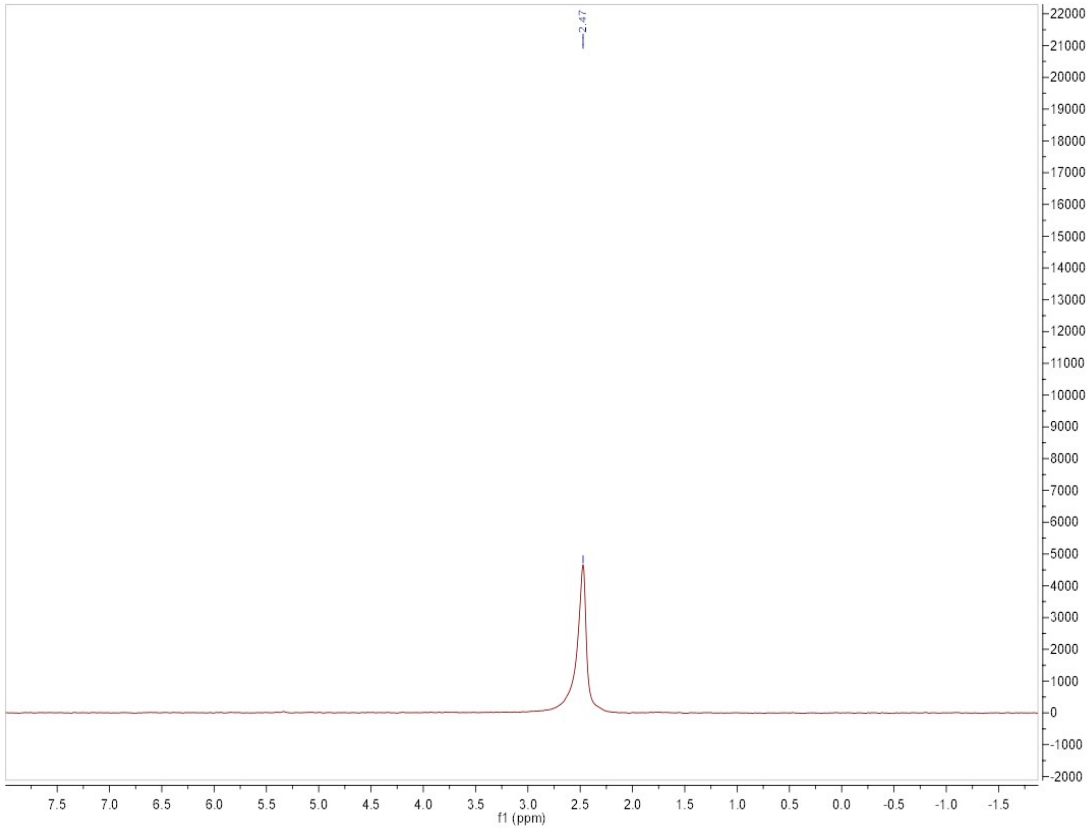
^{1}H NMR spectrum of 3-(benzylamino-*d*)propanenitrile-2,2-d_2 (**4h**):



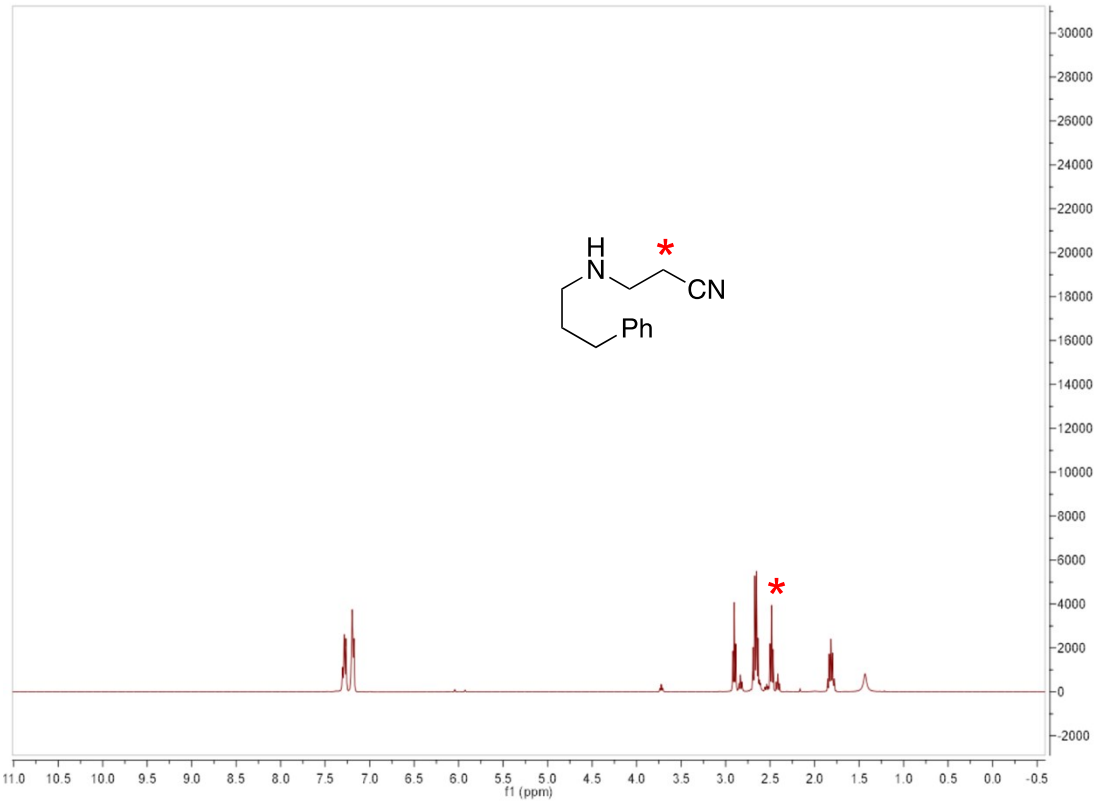
^{13}C NMR spectrum of 3-(benzylamino-*d*)propanenitrile-2,2-d_2 (**4h**):



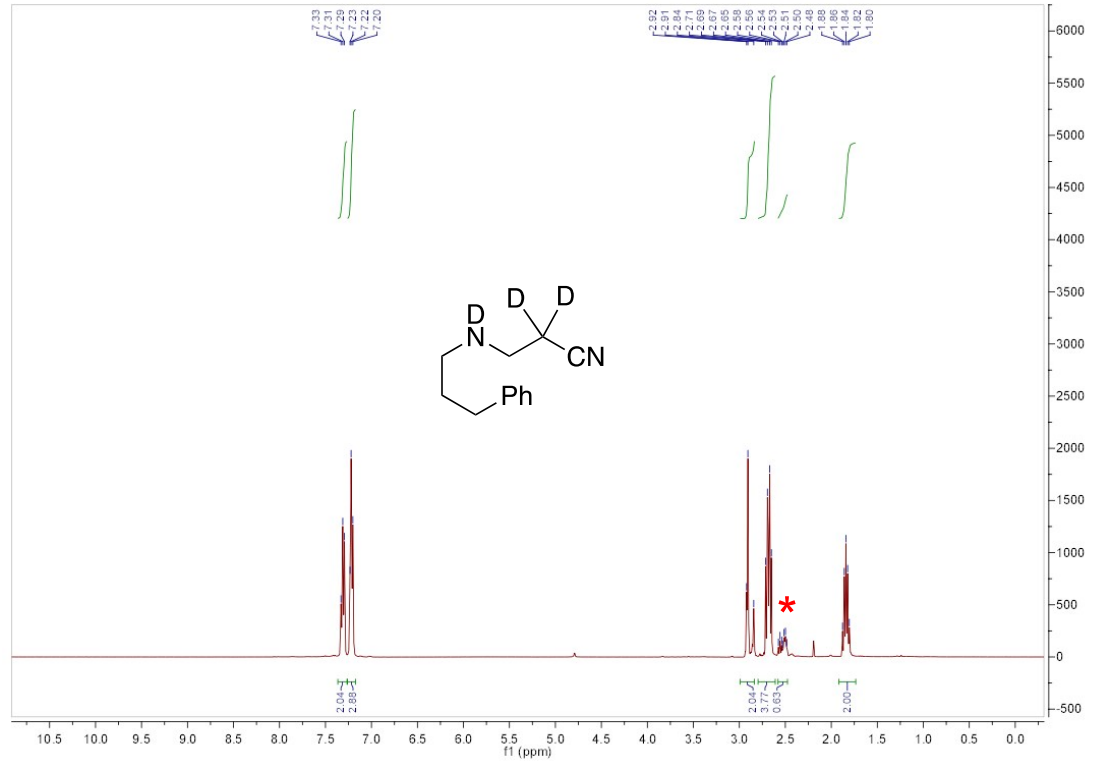
^{2}H NMR spectrum of 3-(benzylamino-*d*)propanenitrile-2,2-d_2 (**4h**):



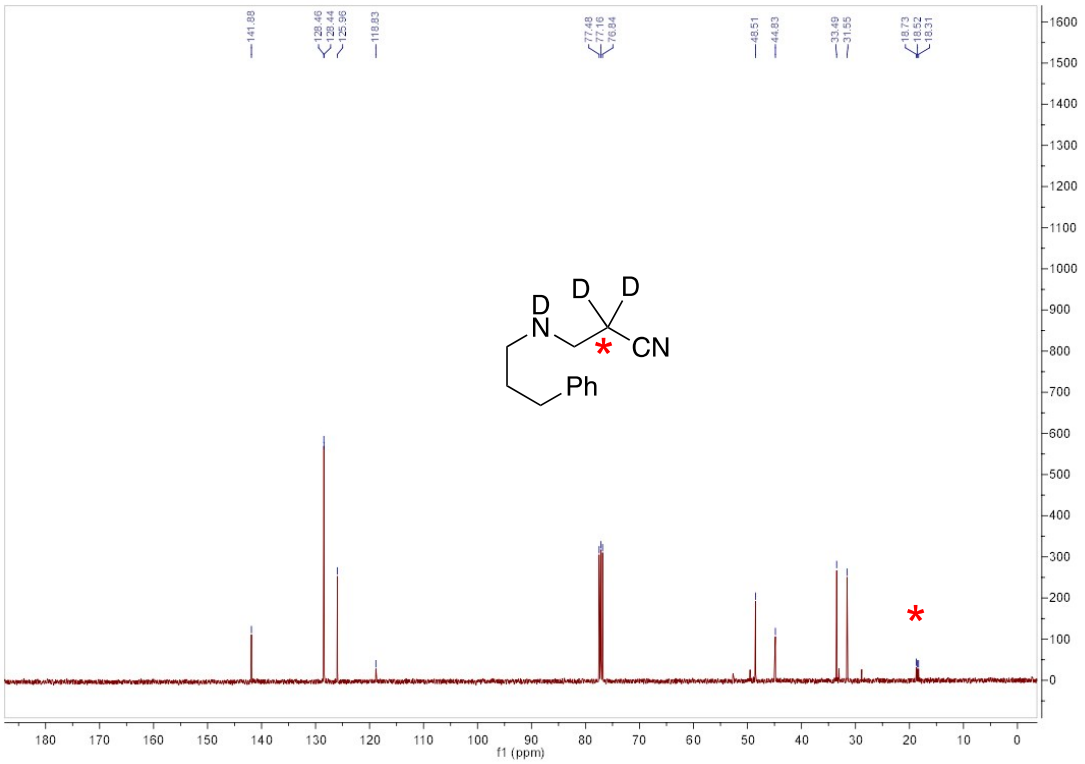
^{1}H NMR spectrum of reference 3-((3-phenylpropyl)amino)propanenitrile:



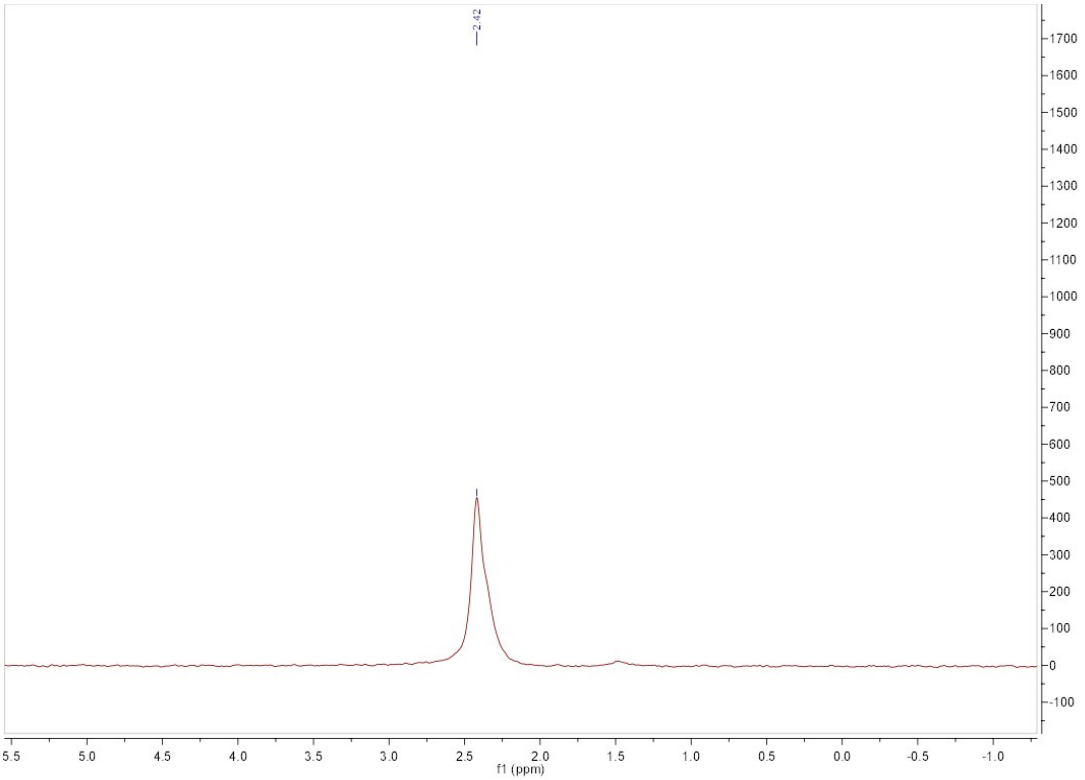
^{1}H NMR spectrum of 3-((3-phenylpropyl)amino-*d*)propanenitrile-2,2-d_2 (**4i**):



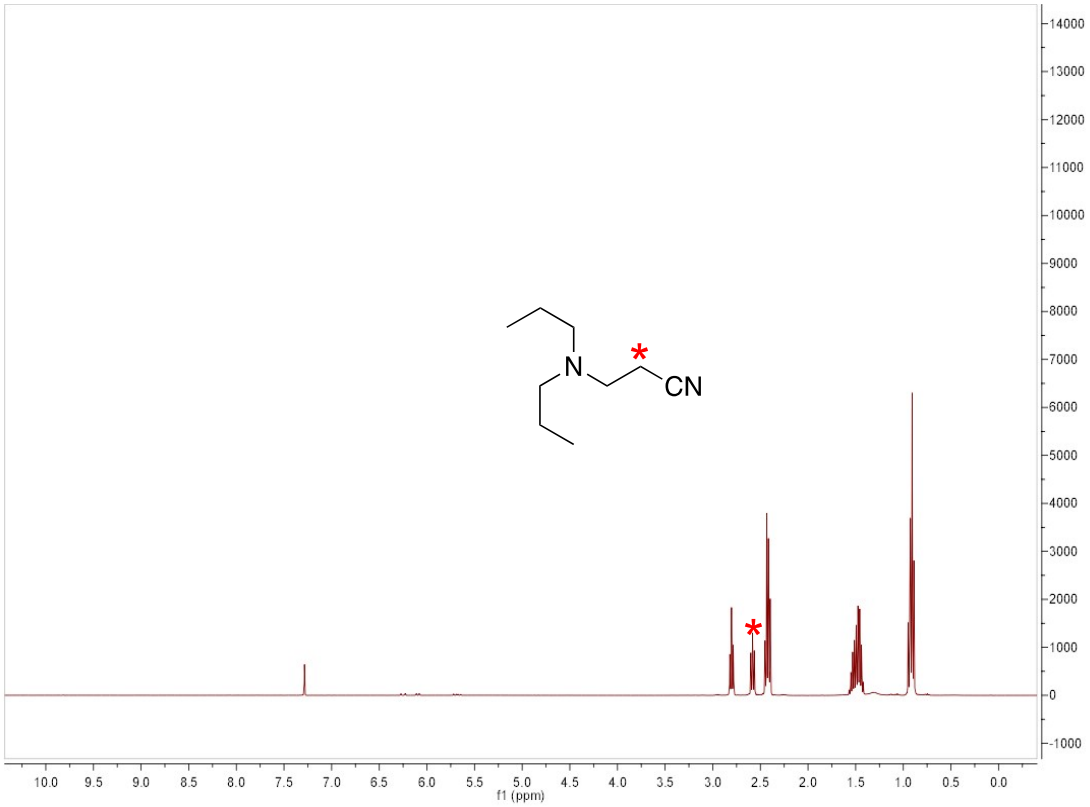
^{13}C NMR spectrum of 3-((3-phenylpropyl)amino-*d*)propanenitrile-2,2-d_2 (**4i**):



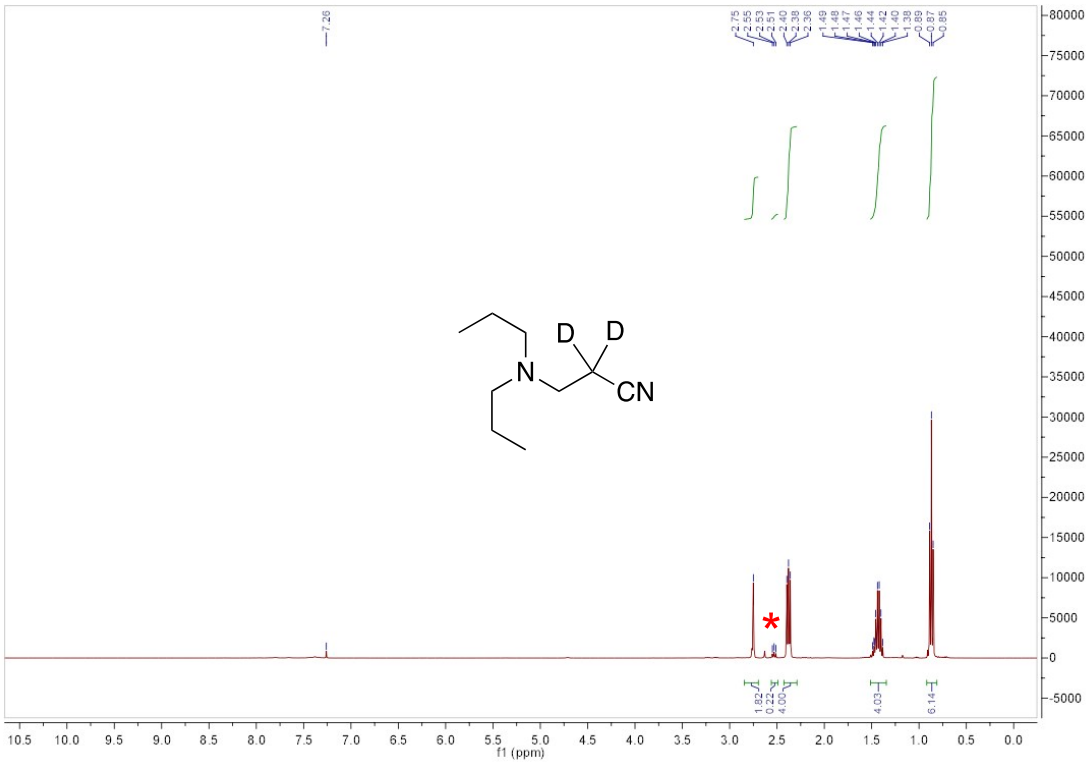
^{2}H NMR spectrum of 3-((3-phenylpropyl)amino-*d*)propanenitrile-2,2-d_2 (**4i**):



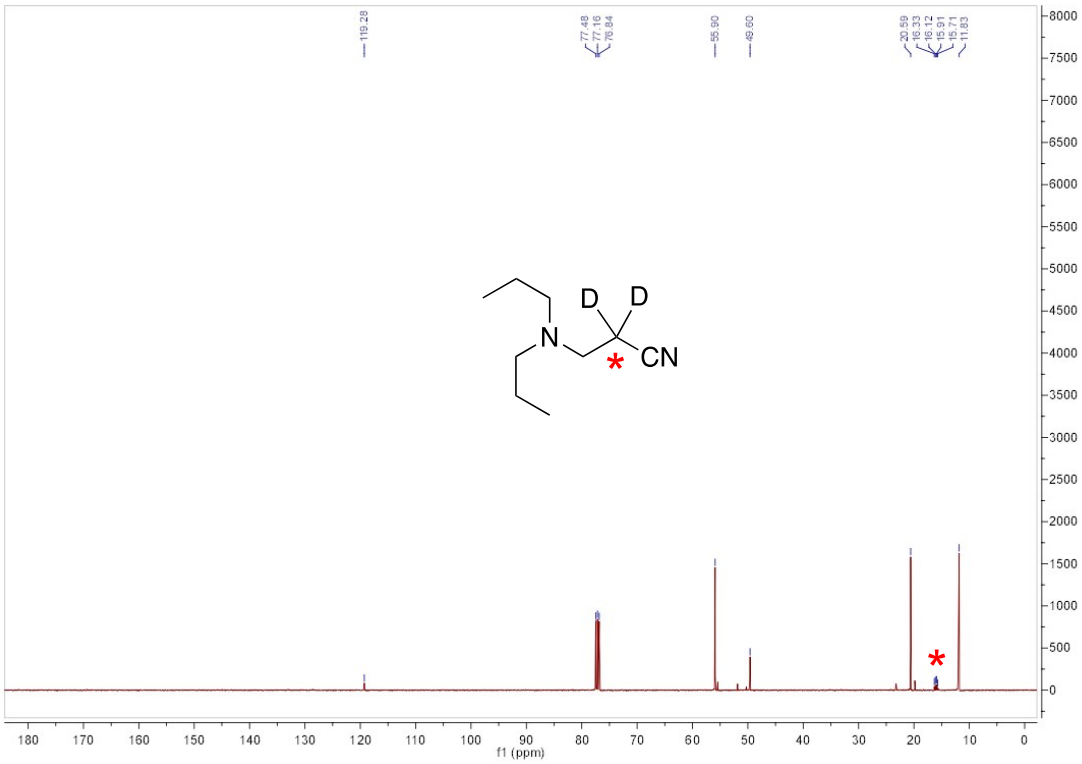
^{1}H NMR spectrum of reference 3-(dipropylamino)propanenitrile:



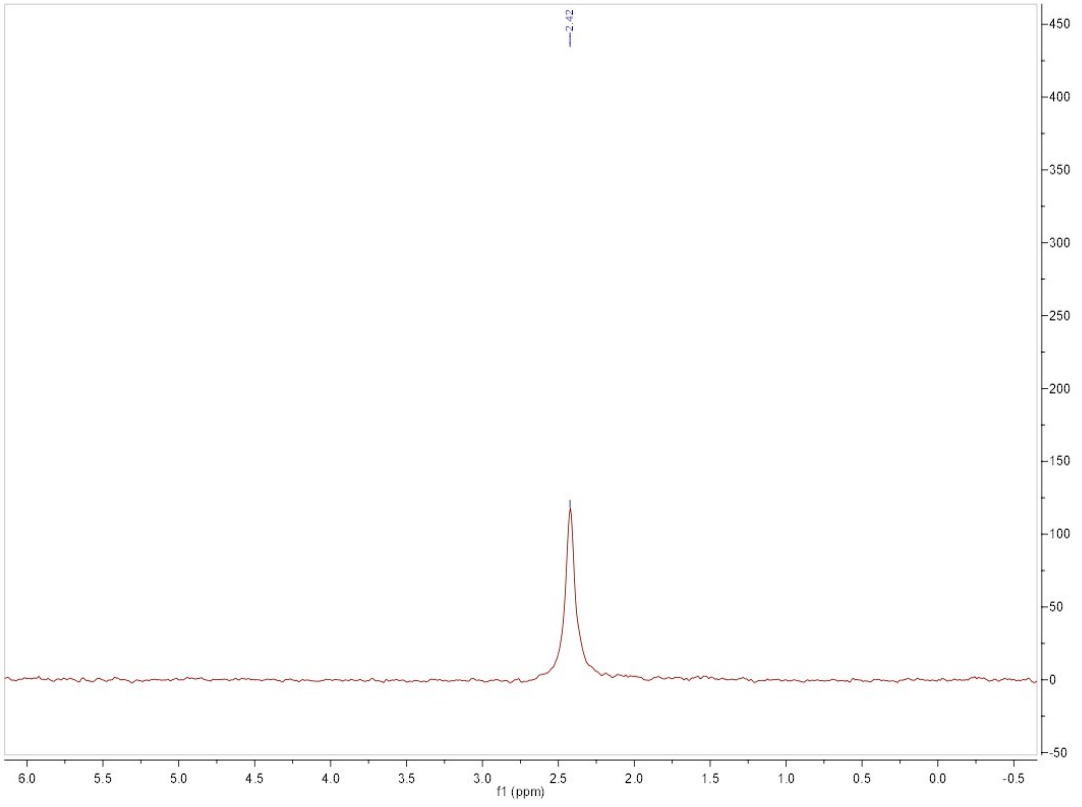
^{1}H NMR spectrum of 3-(dipropylamino)propanenitrile-2,2-d_2 (**4j**):



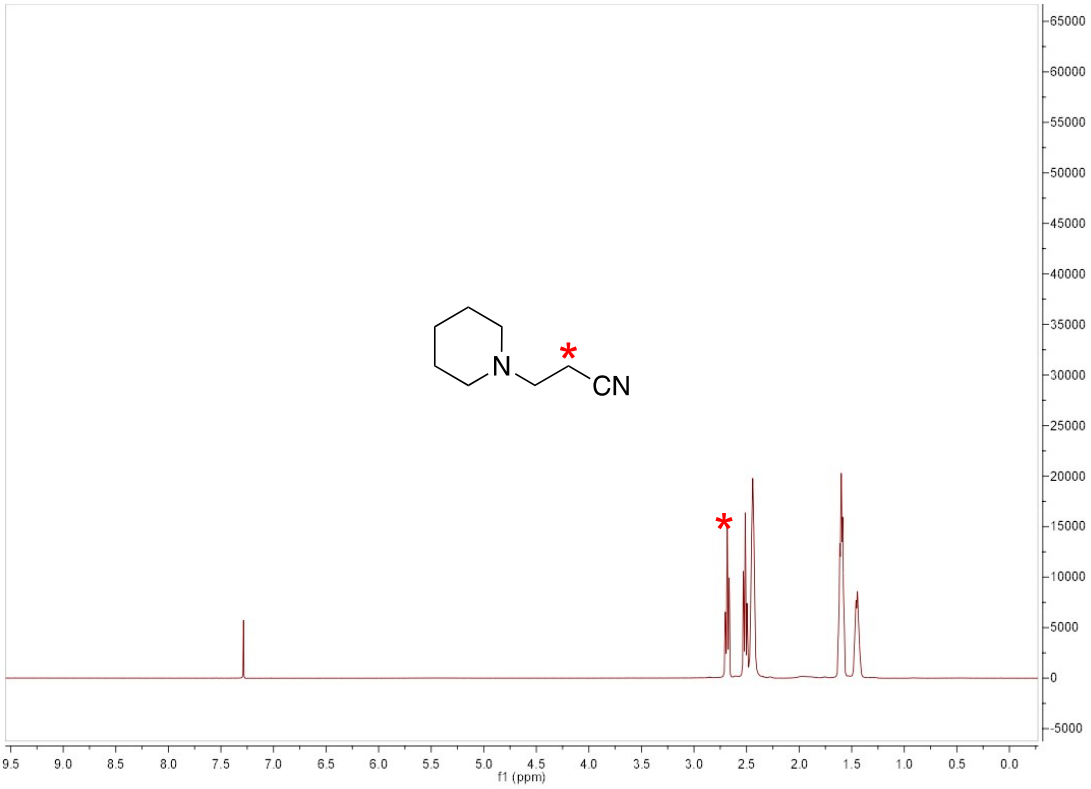
^{13}C NMR spectrum of 3-(dipropylamino)propanenitrile-2,2-d_2 (**4j**):



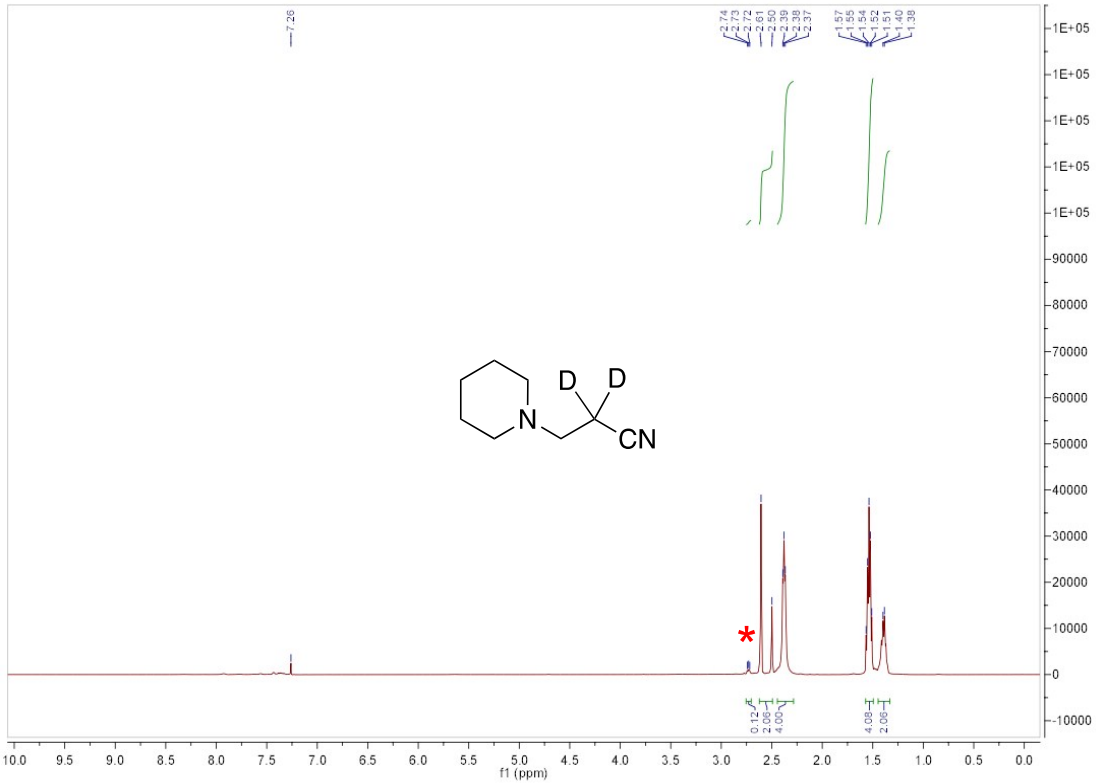
^{2}H NMR spectrum of 3-(dipropylamino)propanenitrile-2,2-d_2 (**4j**):



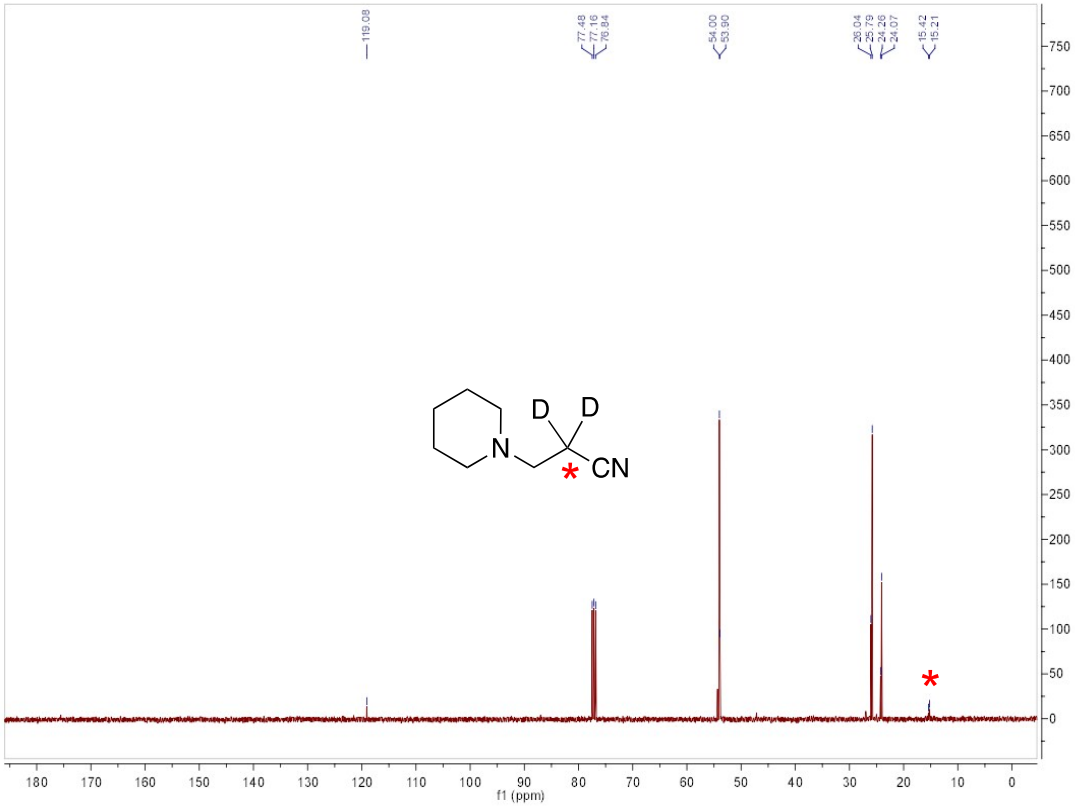
^{1}H NMR spectrum of reference 3-(piperidin-1-yl)propanenitrile:



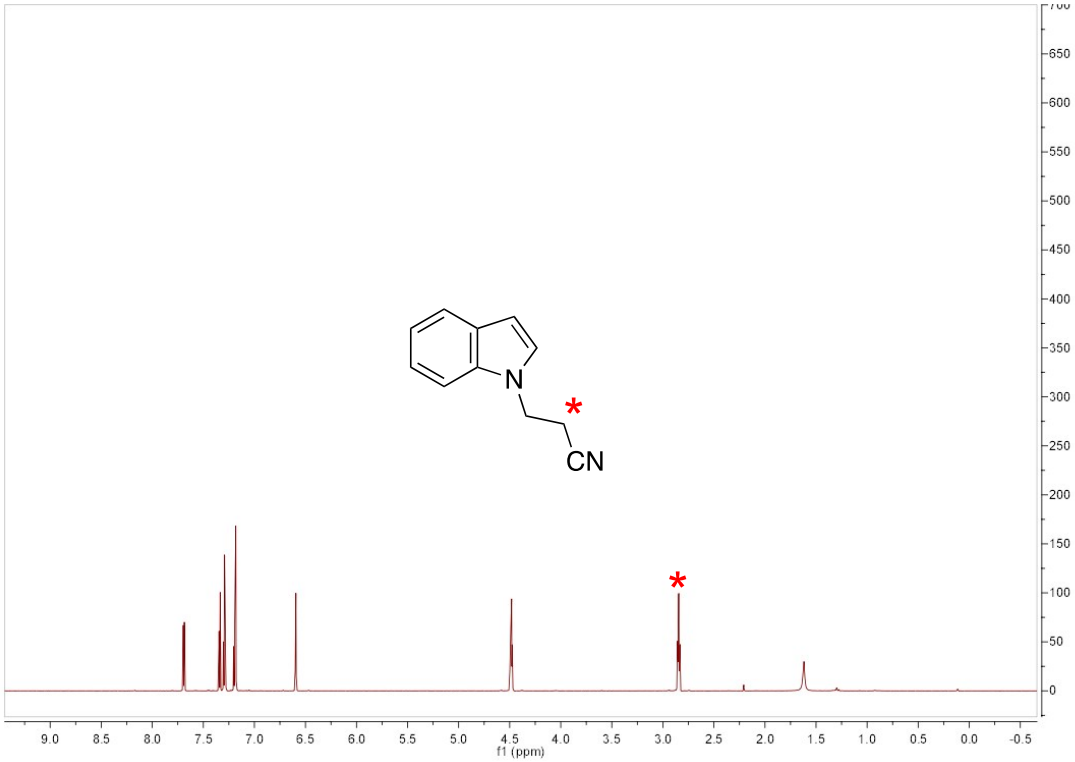
^{1}H NMR spectrum of 3-(piperidin-1-yl)propanenitrile-2,2-d_2 (**4k**):



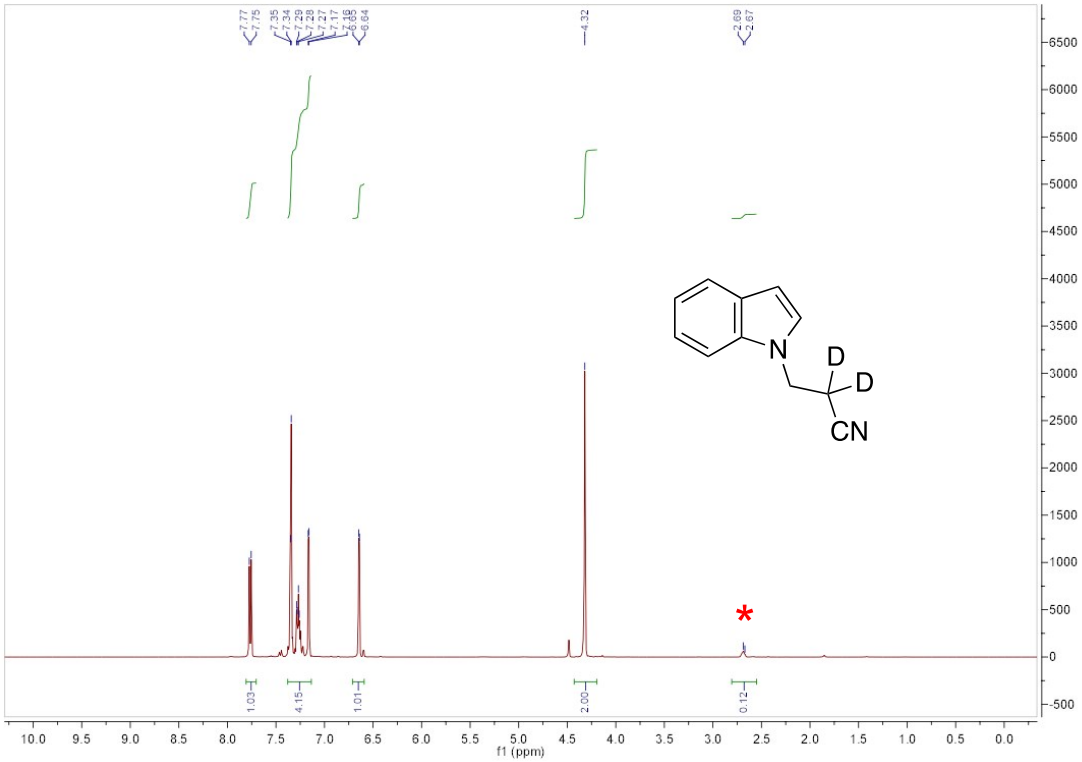
^{13}C NMR spectrum of 3-(piperidin-1-yl)propanenitrile-2,2-d_2 (**4k**):



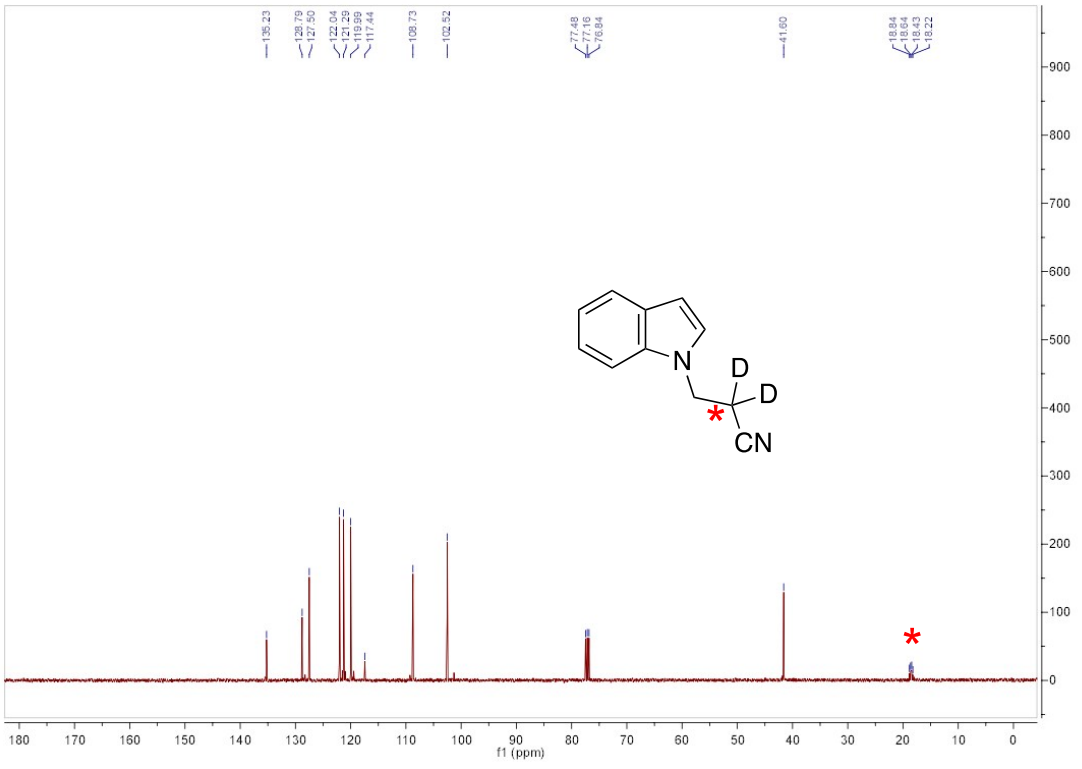
^{1}H NMR spectrum of reference 3-(1*H*-indol-1-yl)propanenitrile:



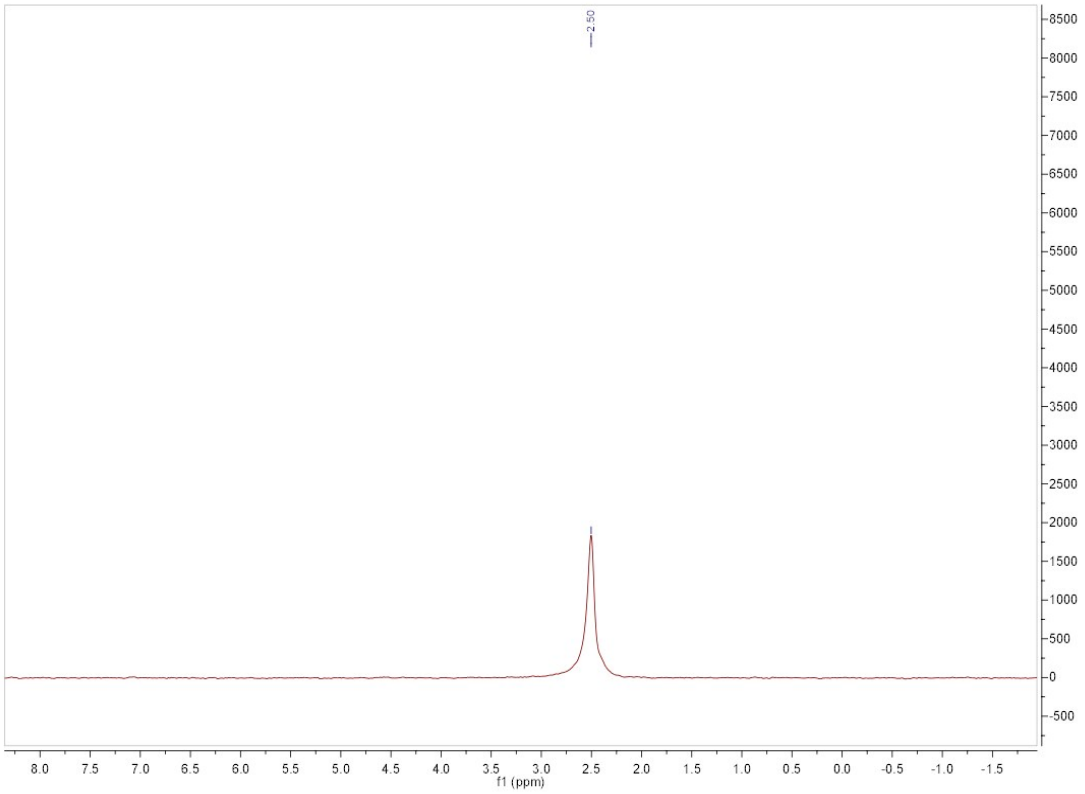
^{1}H NMR spectrum of 3-(1*H*-indol-1-yl)propanenitrile-2,2-d_2 (**4l**):



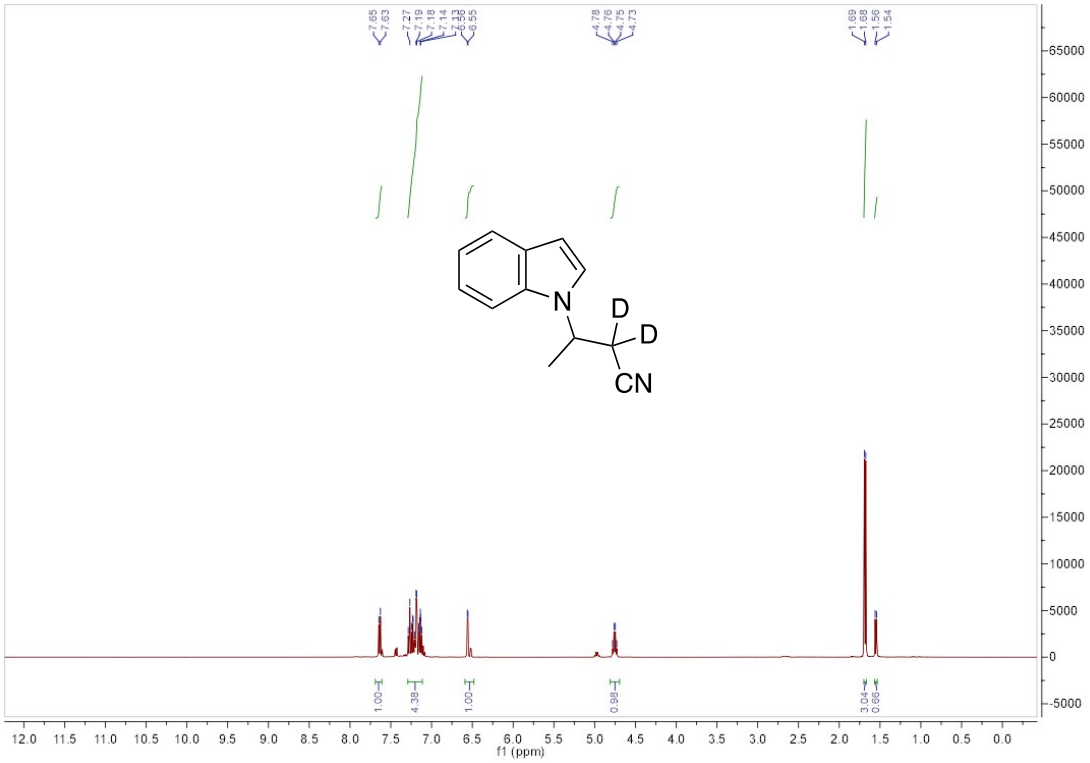
^{13}C NMR spectrum of 3-(1*H*-indol-1-yl)propanenitrile-2,2-d_2 (**4l**):



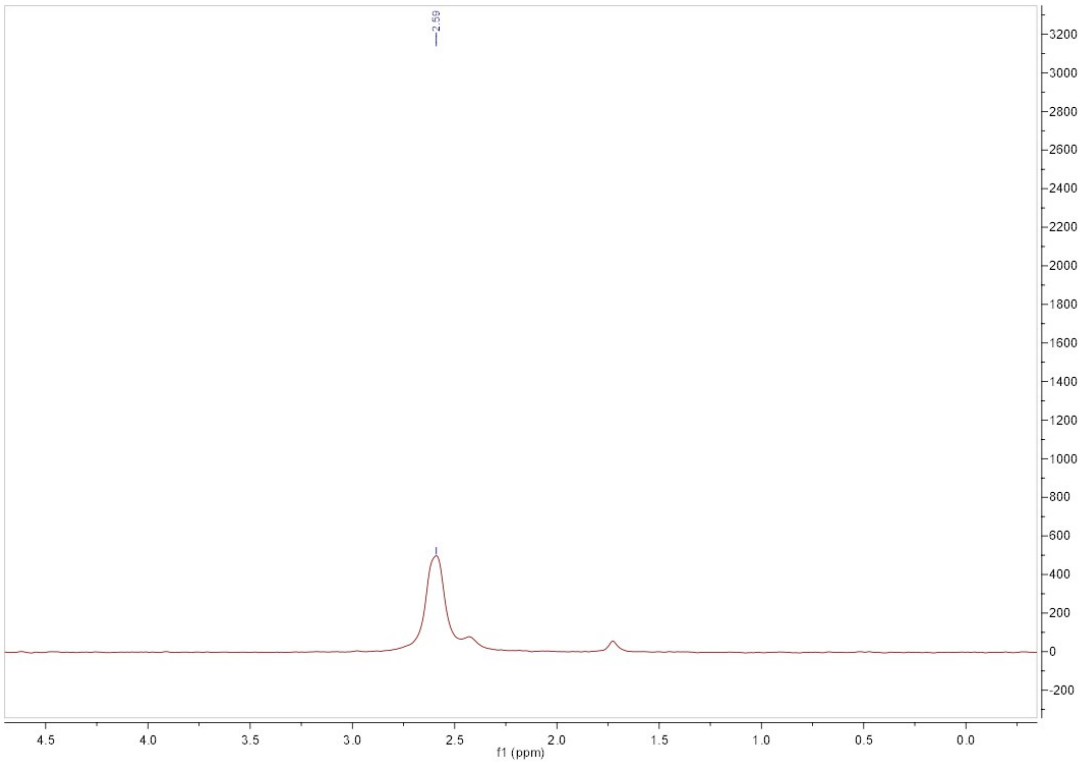
^{2}H NMR spectrum of 3-(1*H*-indol-1-yl)propanenitrile-2,2-d_2 (**4l**):



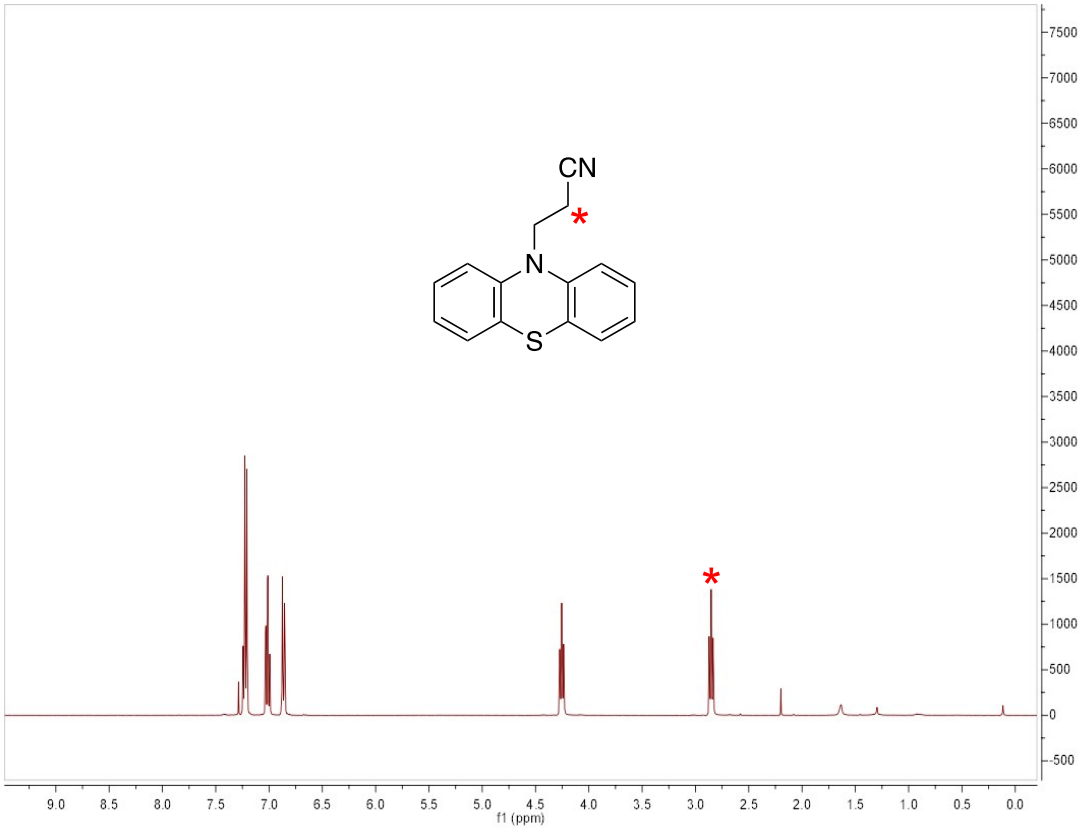
^{1}H NMR spectrum of 3-(1*H*-indol-1-yl)butanenitrile-2,2-d_2 (**4m**):



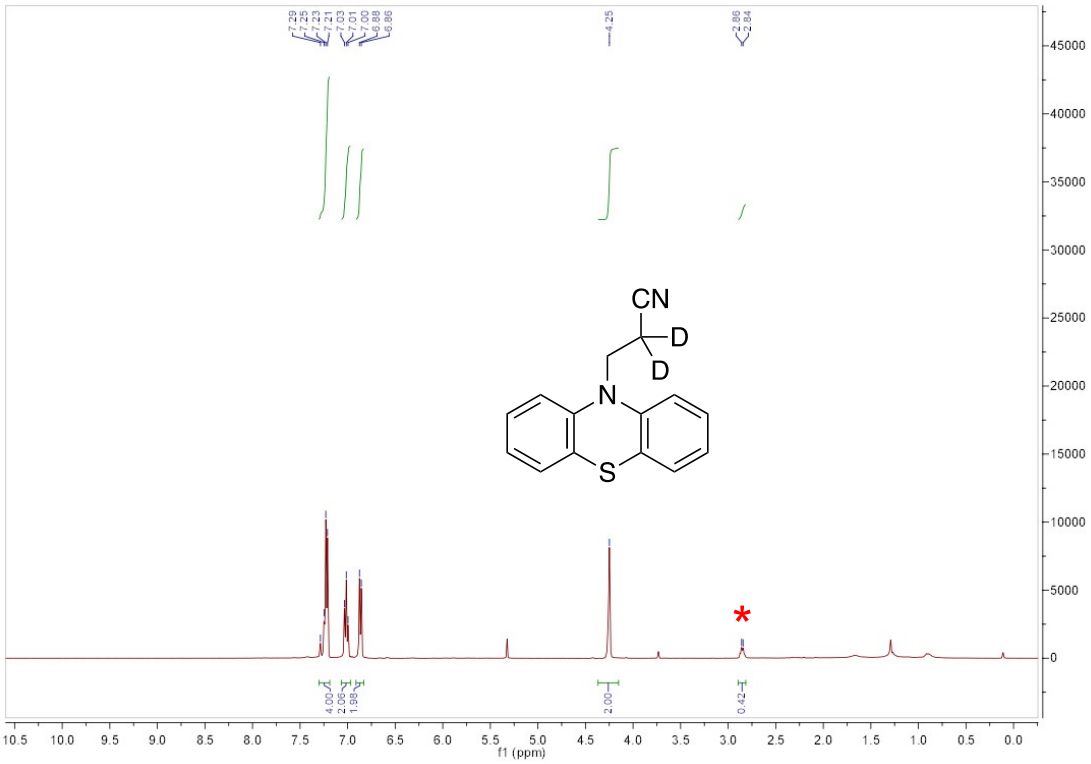
^{2}H NMR spectrum of 3-(1*H*-indol-1-yl)butanenitrile-2,2-d_2 (**4m**):



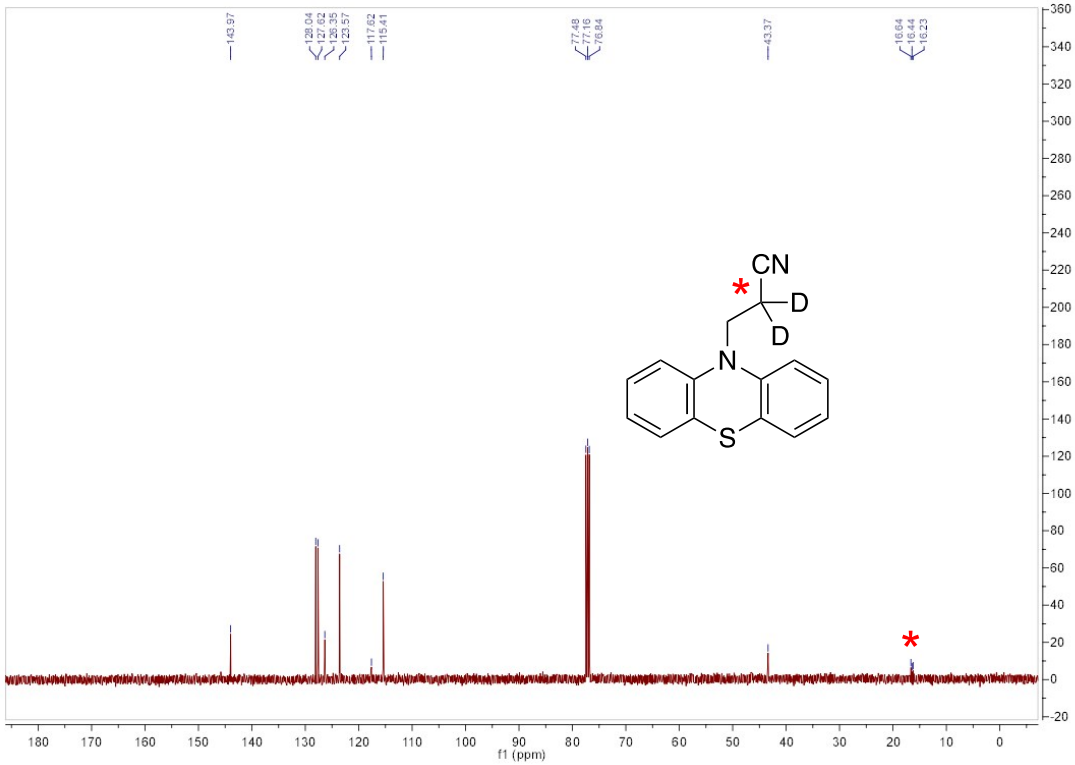
^{1}H NMR spectrum of reference 3-(10*H*-phenothiazin-10-yl)propanenitrile:



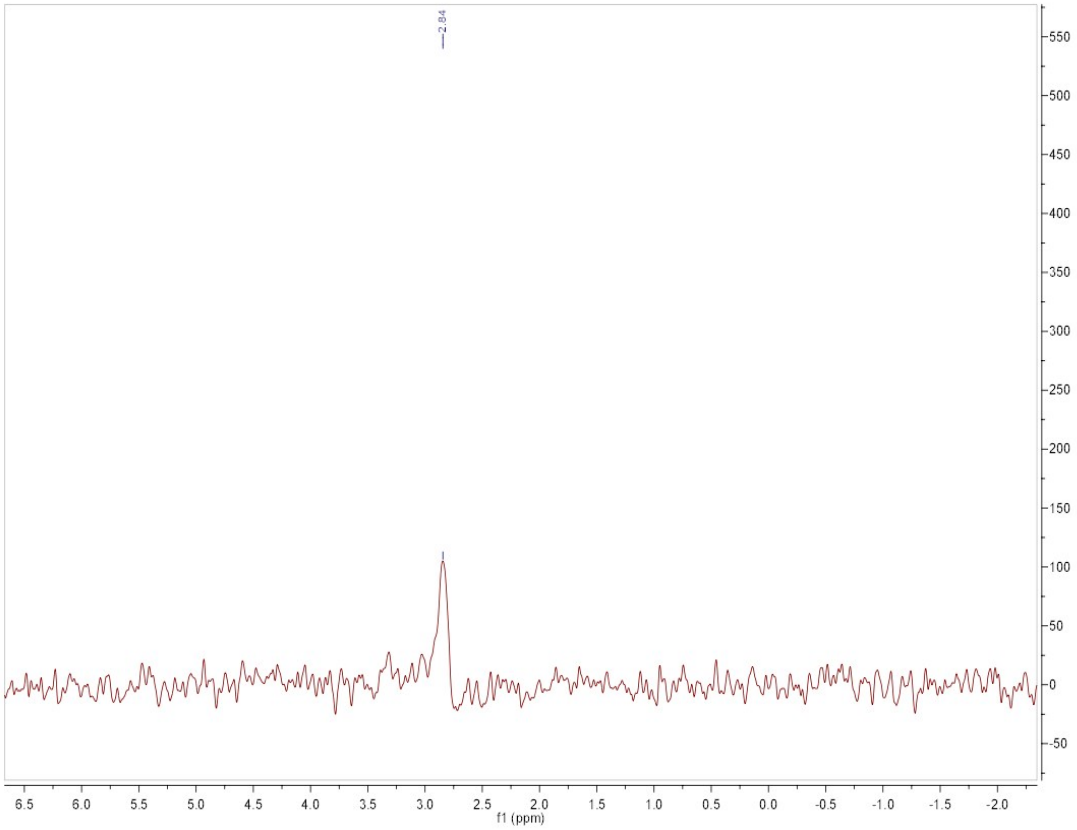
^{1}H NMR spectrum of 3-(10*H*-phenothiazin-10-yl)propanenitrile-2,2-d_2 (**4n**):



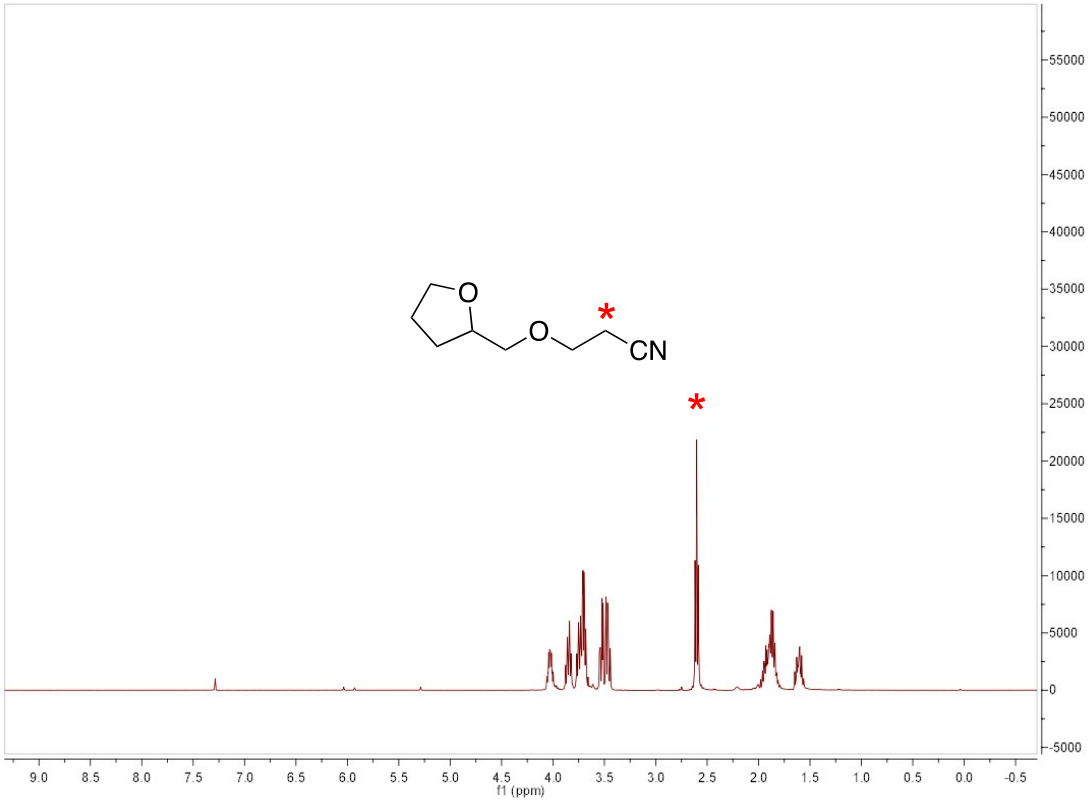
^{13}C NMR spectrum of 3-(10*H*-phenothiazin-10-yl)propanenitrile-2,2-d_2 (**4n**):



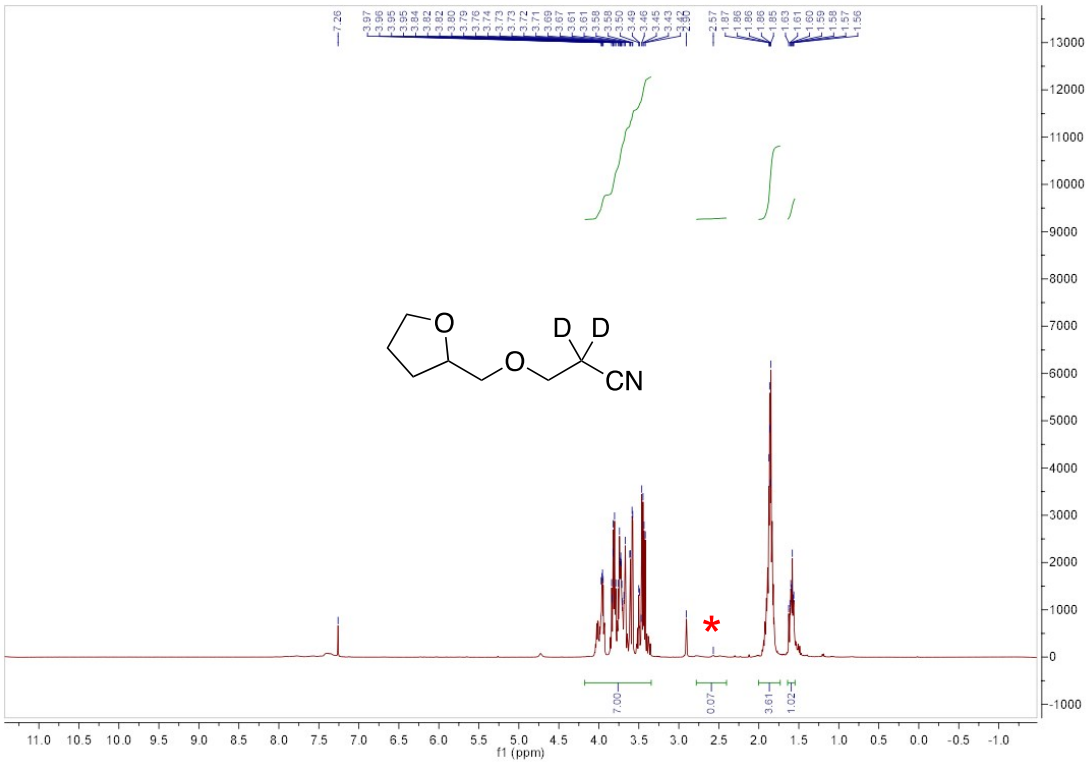
^{2}H NMR spectrum of 3-(10*H*-phenothiazin-10-yl)propanenitrile-2,2-d_2 (**4n**):



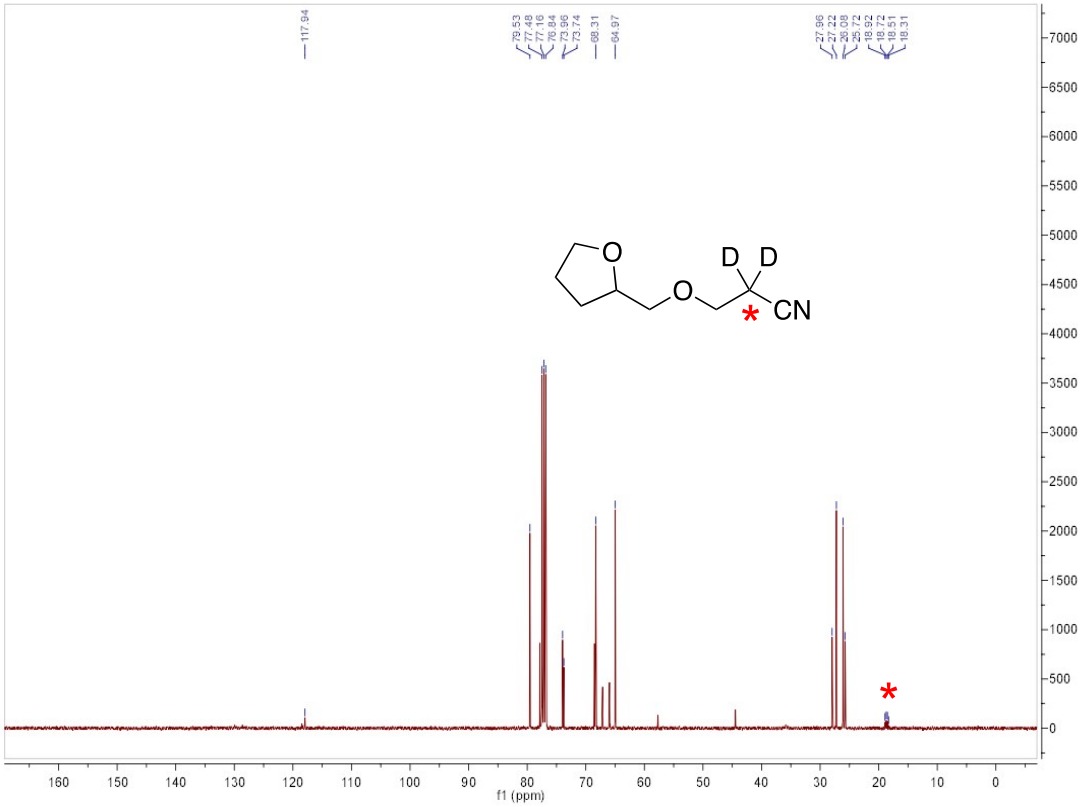
^{1}H NMR spectrum of reference 3-((tetrahydrofuran-2-yl)methoxy)propanenitrile:



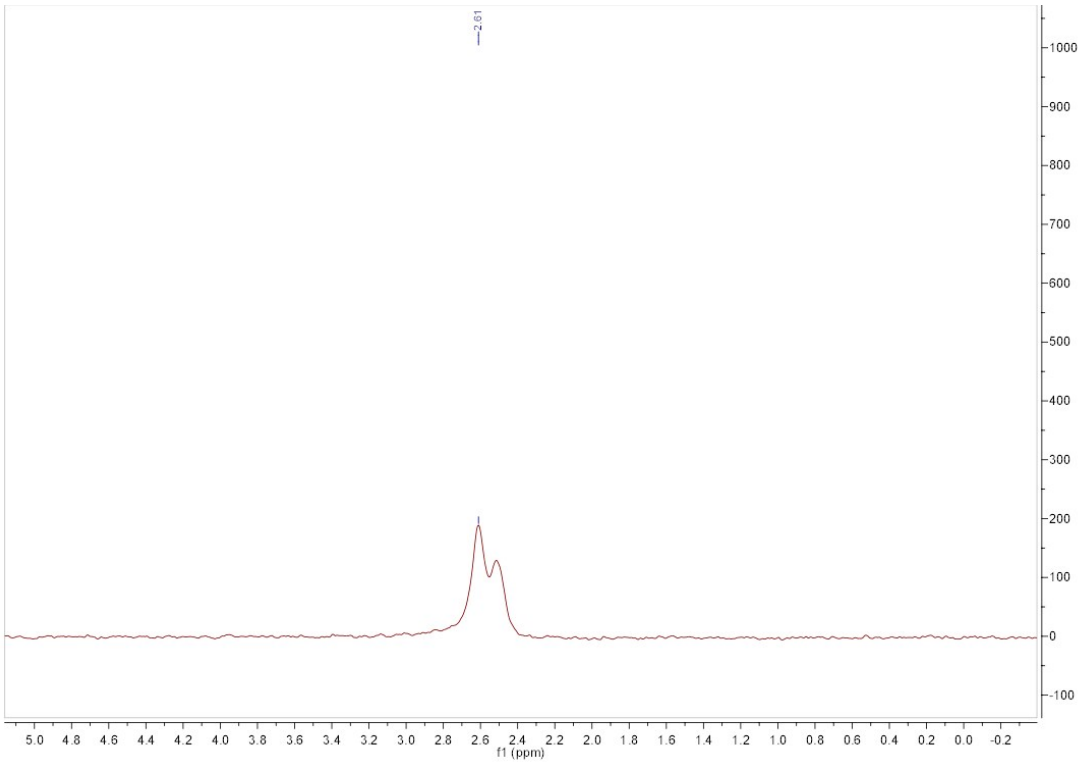
^{1}H NMR spectrum of 3-((tetrahydrofuran-2-yl)methoxy)propanenitrile-2,2-d_2 (**4o**):



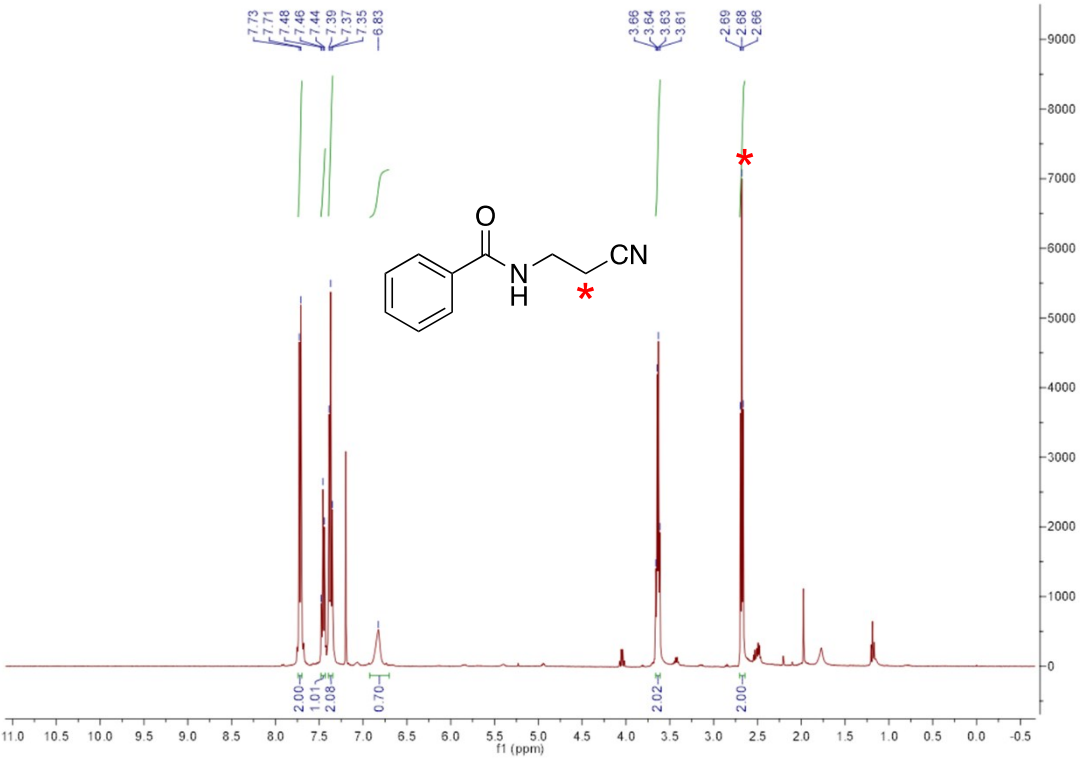
^{13}C NMR spectrum of 3-((tetrahydrofuran-2-yl)methoxy)propanenitrile-2,2-d_2 (**4o**):



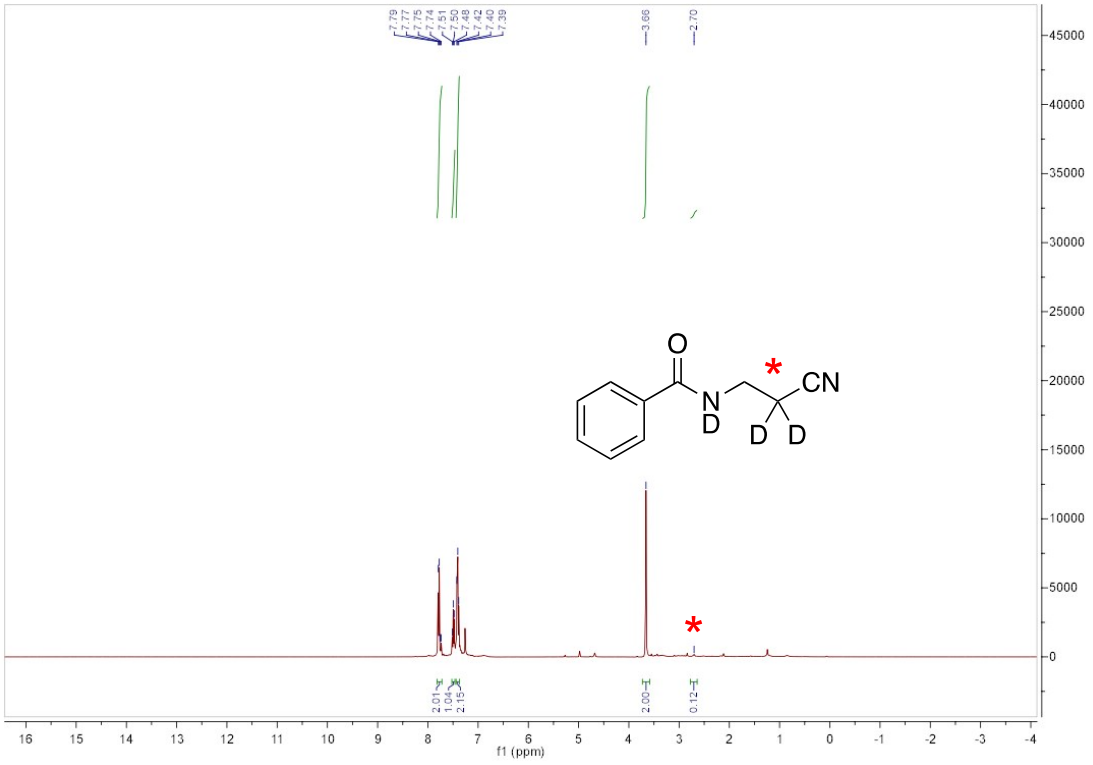
^{2}H NMR spectrum of 3-((tetrahydrofuran-2-yl)methoxy)propanenitrile-2,2-d_2 (**4o**):



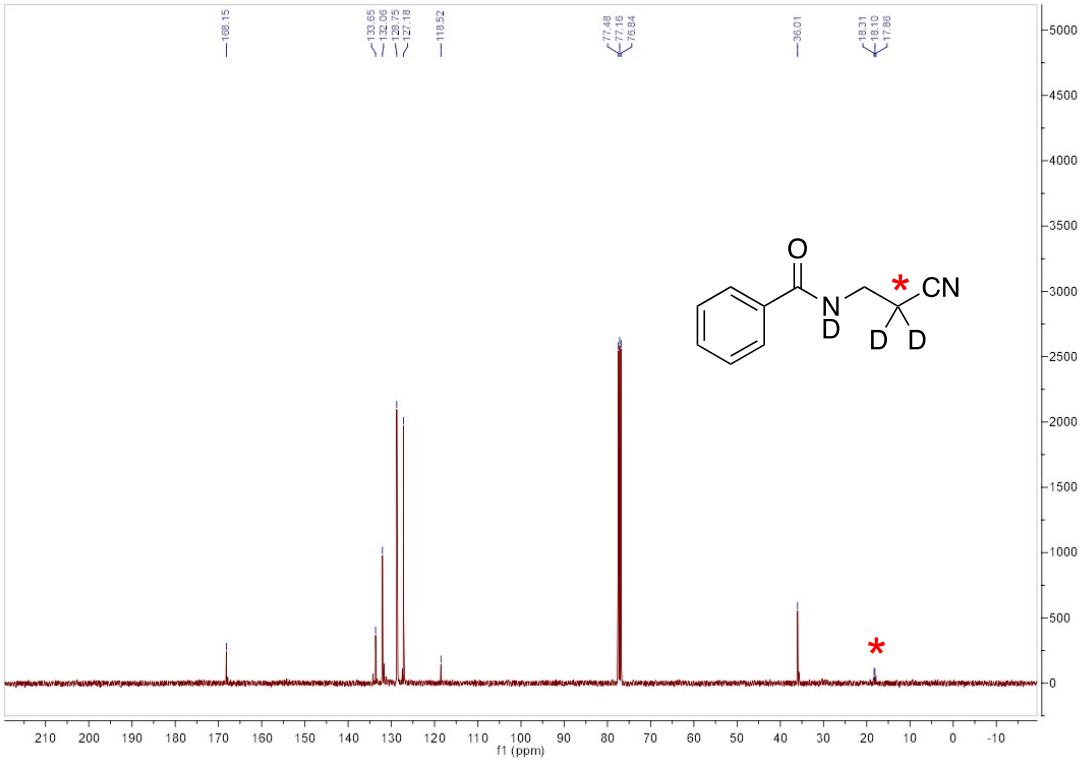
^{1}H NMR spectrum of reference *N*-(2-cyanoethyl)benzamide:



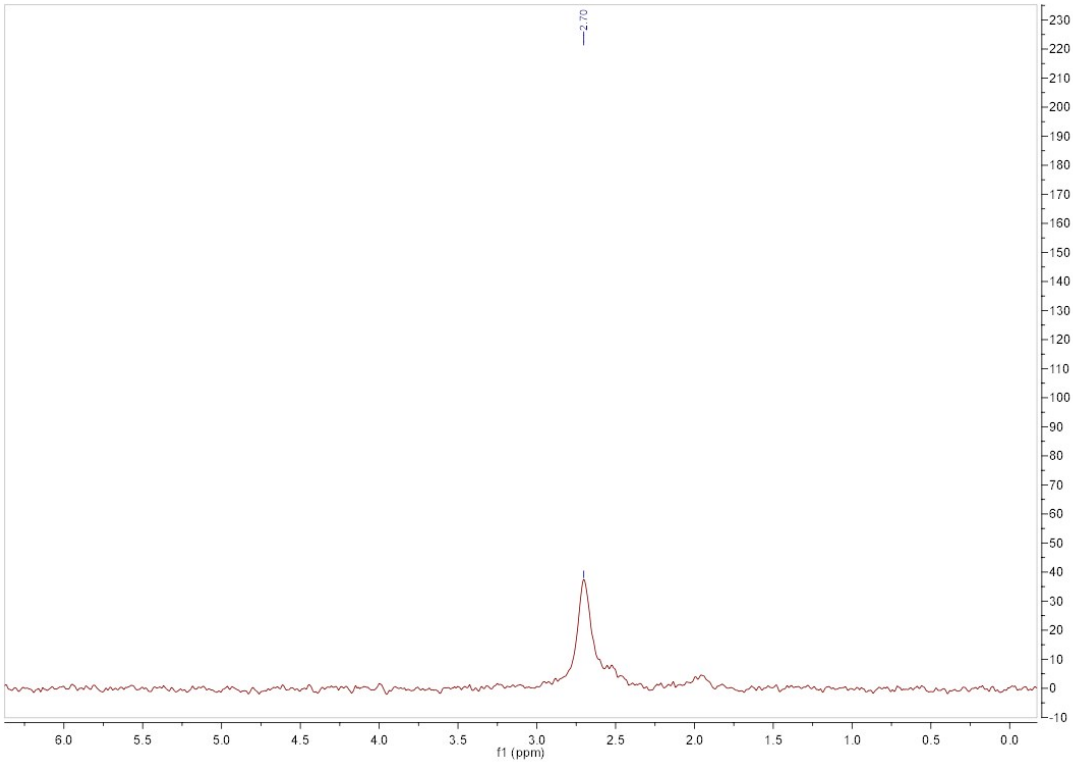
^{1}H NMR spectrum of *N*-(2-cyanoethyl-2,2-d$_2$)benzamide-d (**4n**):



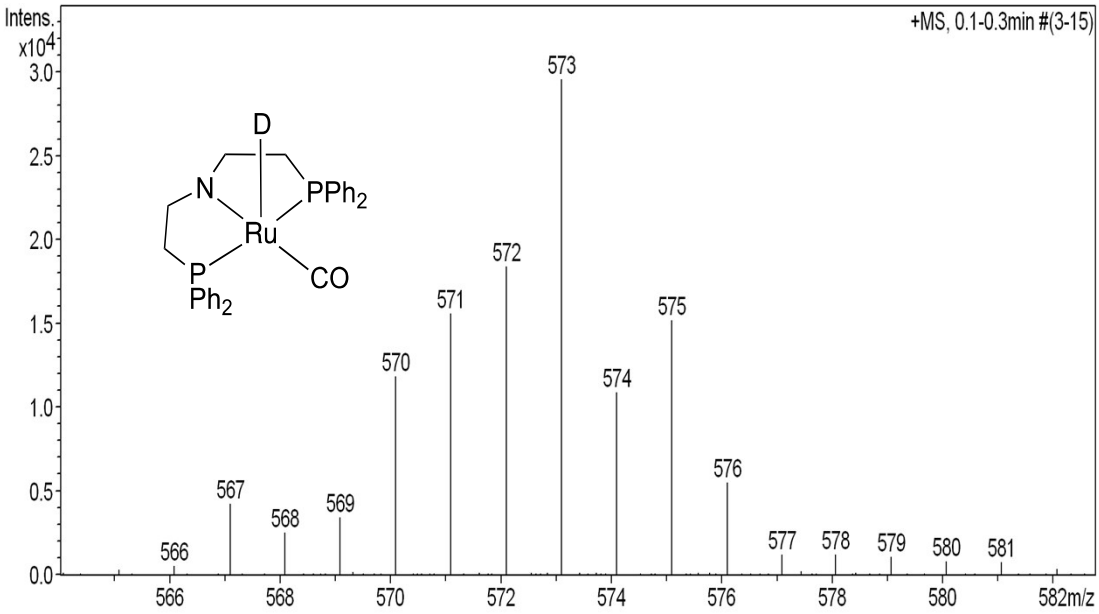
^{13}C NMR spectrum of *N*-(2-cyanoethyl-2,2-d$_2$)benzamide-d (**4n**):



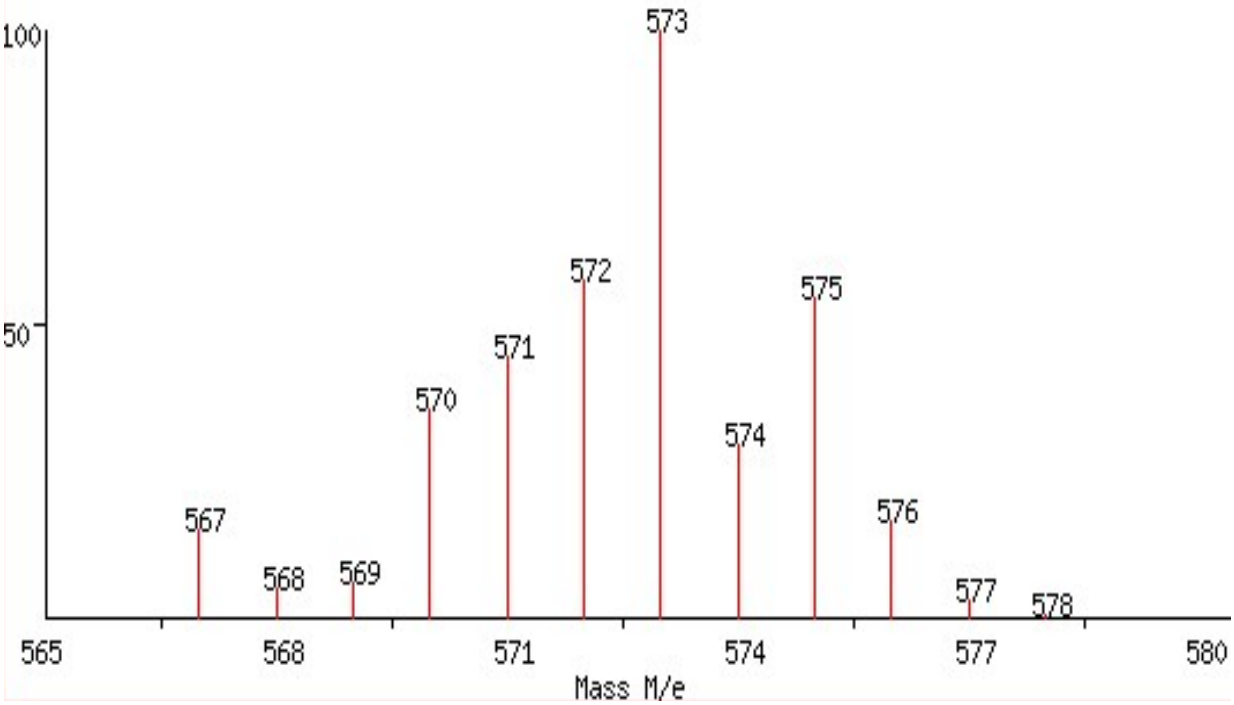
^{2}H NMR spectrum of *N*-(2-cyanoethyl-2,2-d$_2$)benzamide-d (**4n**):



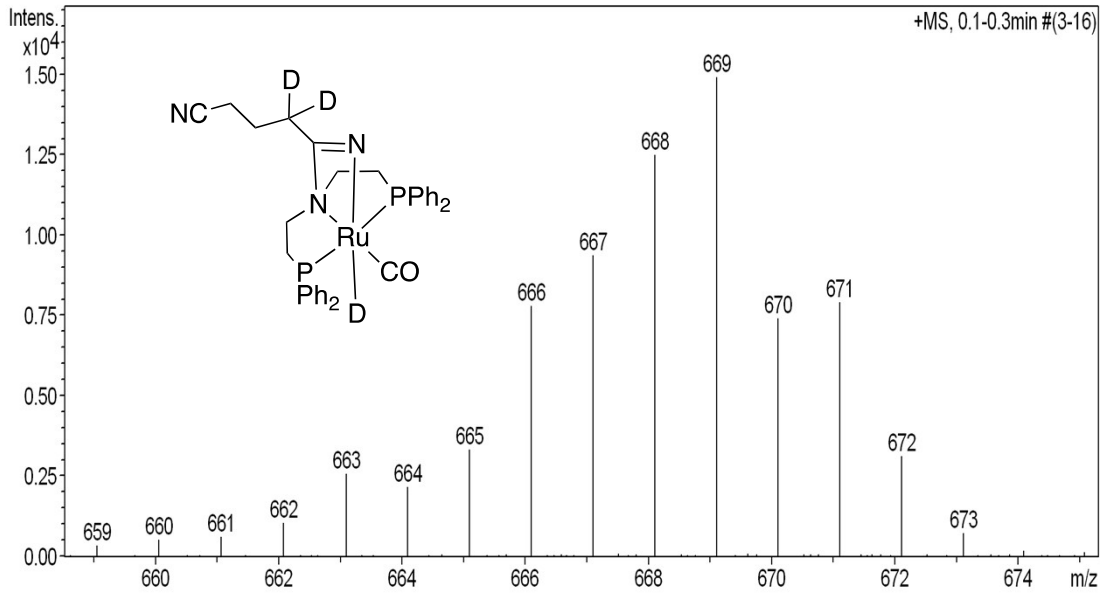
Experimental mass spectra of deuterated unsaturated Ru-pincer complex (**I-D)**
$C_{29}H_{28}DNOP_2Ru$ $(M+H)^+$**:** 573



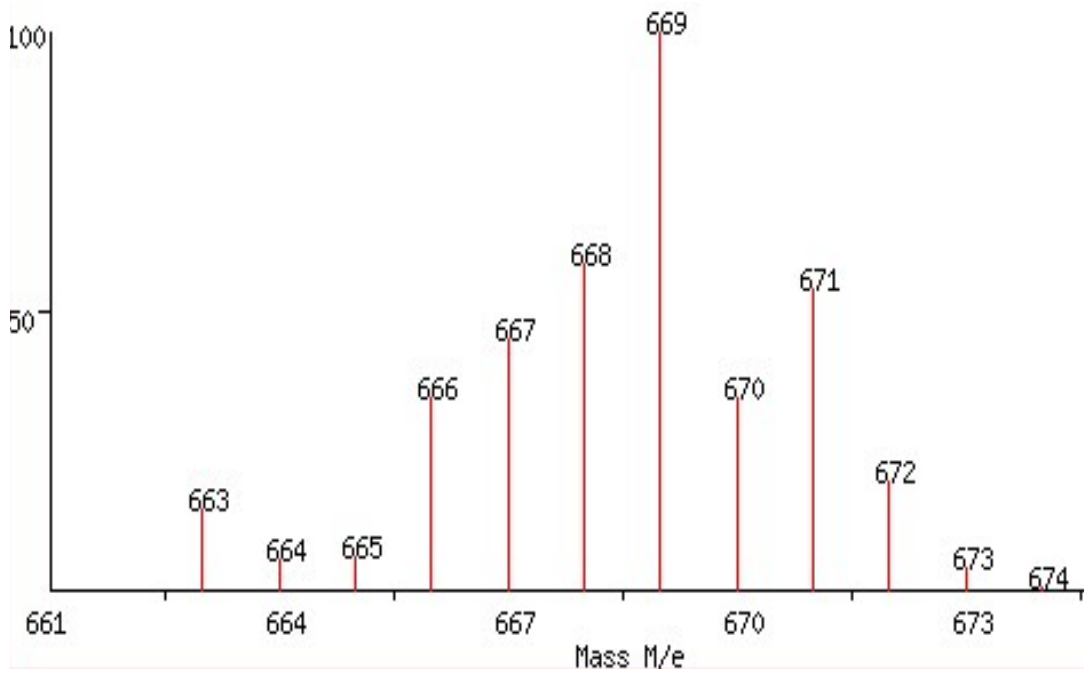
Theoretical mass spectra of deuterated unsaturated Ru-pincer complex (**I-D)**
$C_{29}H_{28}DNOP_2Ru$ $(M+H)^+$**:** 573



Experimental mass spectra of intermediate **(II-D_3)** $C_{34}H_{32}D_3N_3OP_2Ru$ $(M+H)^+$: 669



Theoretical mass spectra of intermediate **(II-D_3)** $C_{34}H_{32}D_3N_3OP_2Ru$ $(M+H)^+$: 669



Reference:

1. (a) B. Chatterjee, C. Gunanathan, *Chem. Comm.* 2014**, 50***,* 888-890; (b) A. Kaithal, B. Chatterjee, C. Gunanathan, *Org. Lett.* 2015, **17**, 4790-4793.