*Supplementary Materials*

# Practical Synthesis of C-1 Deuterated Aldehydes Enabled by NHC Catalysis

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## 1. Supplemnetary methods: General information

Commercial reagents and solvents were used as received, unless otherwise stated. Organic solution was concentrated under reduced pressure on a Büchi rotary evaporator. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography was performed on silica gel 200–300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas-beta®). The $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM 400 Spectrometer (400 and 100 MHz for $^{1}$H NMR and $^{13}$C NMR, respectively) and are internally referenced to residual solvent signals (note: $CDCl_3$ referenced at 7.26 ppm in $^{1}$H NMR; DMSO-$d^6$ referenced at 2.50 ppm in $^{1}$H NMR, respectively). Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for $^{13}$C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer. The NHC catalysts **5d, 5e** and **5s** were purchased from Adamas-beta, and **5a**[1], **5b**[2], **5c**[3], **5f**[4], **5g**[5], **5h**[6], **5i**[7], **5j**, **5k**[8], **5l**[9], **5m**[10], **5n**[10], **5o**[11], **5q**[11, 12], **5r**[9], **5t**[13], **5u**, **5v**[14], **5w**[15], **5x**, **5y**[9], **5z**[16], **5aa**, **5ab**[17], **5ac**, **5ad**[9], **5ae**[18], **5af**[9], **5ag**[19], **5ai**[20], **5aj**[21], **5ak**[11], **5al**[22, 23] were prepared according to literature procedures.

The level of deuterium incorporation in the product was determined by $^{1}$H NMR (**Supplementary Equation 1**) or $^{2}$H NMR (**Supplementary Equation 2**) spectroscopy. The integrals were calibrated against a peak corresponding to a position not expected to be labelled.[24]

**Supplementary Equation 1** was based on $^{1}$H NMR and used to calculate the extent of labelling for most of the deuterated products:

$$\%\ \text{Deuteration} = 100 - \left[ \left( \frac{\text{residual integral}}{\text{number of labelling sites}} \right) \times 100 \right]$$

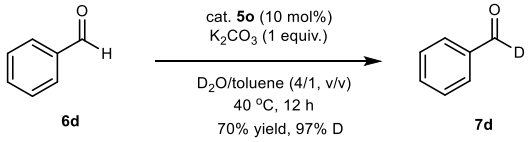
**Supplementary Equation 1**

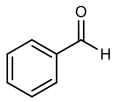
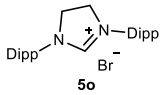
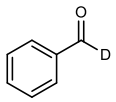
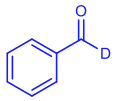
**Supplementary Equation 2** was based on $^{2}$H NMR and used to calculate the extent of labelling for the deuterated products containing some special sites where only slight deuterium incorporation occurred (**7h**, **7j**, **7z**, **7ao**, **7au**, **10a**, **10b**, **10d**, **10e**, **10f**, **12f**, **12i**, **12r**):

$$\%\ \text{Deuteration} = \text{integral of the needed peak}$$

**Supplementary Equation 2**

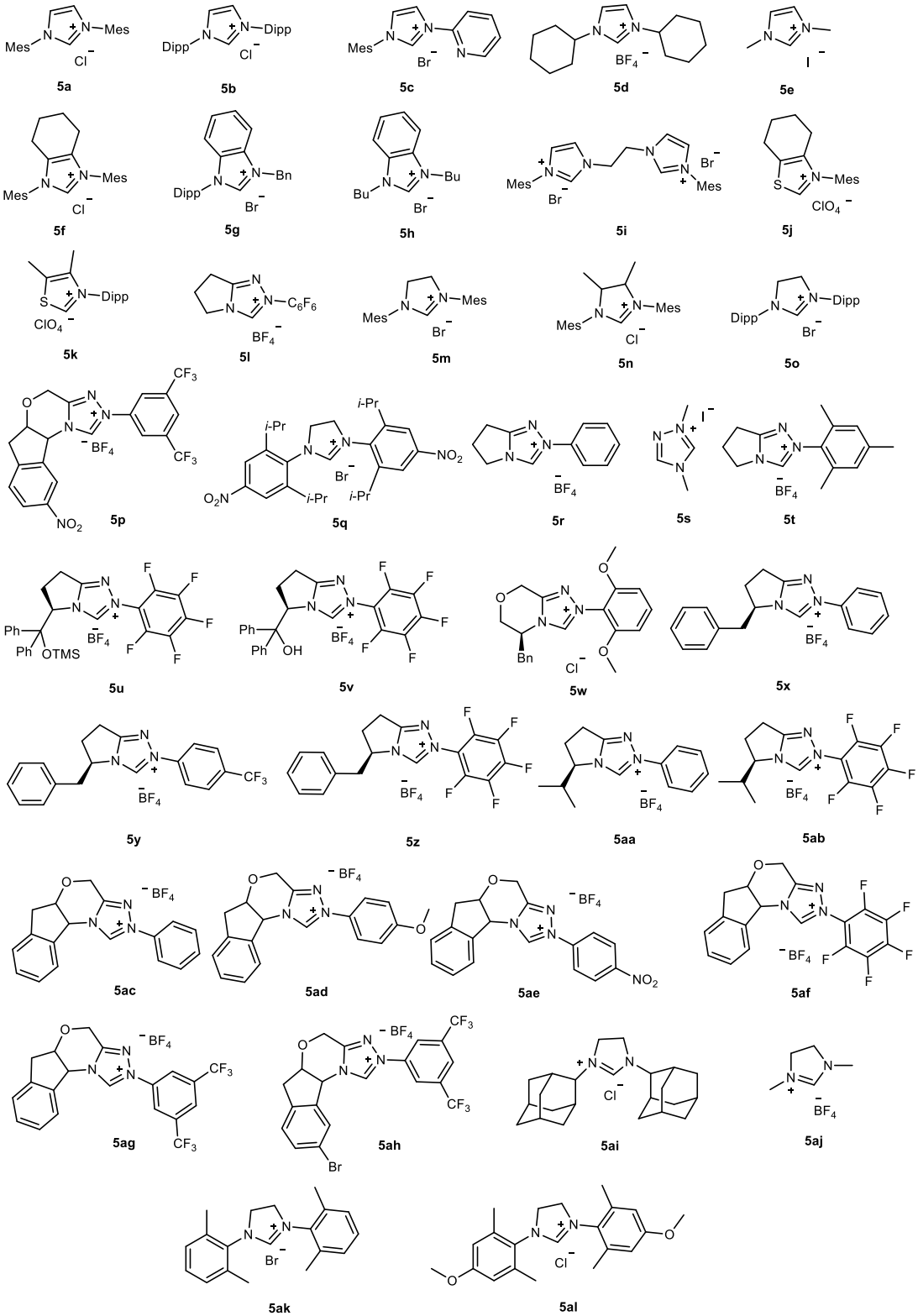
**2. *Supplementary Table 1.* The cost calculation for the preparation of deuterated benzaldehyde using the protocol developed in this work.**




| Compound | Vendor | Cost/g | MW | Quantity for producing 1 g product **7d** | Price for producing 1 g product **7d** |
|---|---|---|---|---|---|
|  | Sigma-Aldrich | $29.80/100g | 106 | 0.01335 mol × 106 = 1.42 g | $0.298/g × 1.42 g = $0.42 |
|  **5o** | Self preparation | $40/g | 427.1 | 0.01335 × 10 mol% × 427.1= 0.57 g | $40/g × 0.57 g = $22.8 |
| $D_2O$ | Sigma-Aldrich | $1,160/1kg | 20 | 1000 × 1.1/(107 × 70%) =14.7 g | $1.16/g × 14.7 = $17.05 |
| $K_2CO_3$ | Fisher | $24.66/500g | 138 | 0.01335 × 138 = 1.84 g | $0.049/g × 1.84 = $0.09 |
| Toluene (anhydrous) | Sigma-Aldrich | $45/2L | 92 | 3.3 mL | 0.0225/mL × 3.3 = $0.074 |
|  | Sigma-Aldrich | **$570/g** | 107 | | |
|  | Our method | **$40.43/g**[a] | 107 | | |

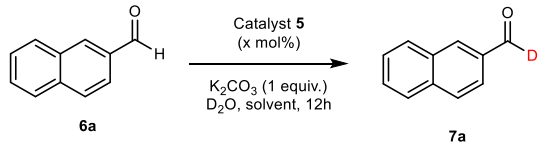
[a] If calculated based the cost of regents from China, the cost for 1g is ca. 88 RMB (ca. $13).

## 3. Optimization of the reaction conditions




***Supplementary Figure 1.*** Structures of NHC catalysts.

***Supplementary Table 2.*** Optimization of reaction conditions for aromatic aldehyde[a]

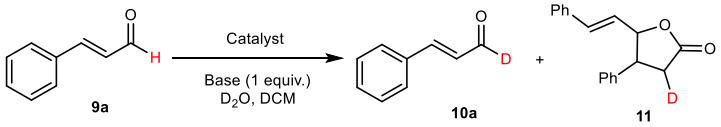



6a 7a

| Entry | Catalyst | Solvent | T (ºC) | Yield (%)[b] | D (%)[c] |
|---|---|---|---|---|---|
| 1 | - | THF | 60 | 98 | 0 |
| 2 | **5a** | THF | 60 | 40 | 99 |
| 3 | **5b-i** | THF | 60 | 0-99 | 5-80 |
| 4 | **5j** | THF | 60 | 40 | 11 |
| 5 | **5k** | THF | 60 | 26 | 98 |
| 6 | **5l** | THF | 60 | 15 | 90 |
| 7 | **5m** | THF | 60 | 50 | 94 |
| 8 | **5n** | THF | 60 | 26 | 99 |
| 9 | **5o** | THF | 60 | 48 | 98 |
| 10 | **5o** | THF | 40 | 58 | 97 |
| 11 | **5o** | THF | 25 | 96 | 8 |
| 12 | **5o** | $CH_2Cl_2$ | 40 | 80 | 98 |
| **13** | **5o** | **toluene** | **40** | **81** | **98** |
| 14[d] | **5o** | toluene | 40 | 73 | 98 |
| 15[e] | **5o** | toluene | 40 | 40 | 98 |
| 16[f] | **5o** | toluene | 40 | 82 | 97 |
| 17[g] | **5o** | toluene | 40 | 81 | 91 |

[a]Reaction conditions unless otherwise stated: **6a** (0.5 mmol), catalysts **5** (10 mol%) and $K_2CO_3$ (1.0 equiv) in $D_2O$ (1 mL) and solvent (0.25 mL) was vigorously stirred for 12 hours. [b]Isolated yield. [c]Determined by $^1H$ NMR. [d]5% catalyst was used. [e]20% catalyst was used. [f]0.5 mL $D_2O$ was used. [g]10 eq $D_2O$ was used.

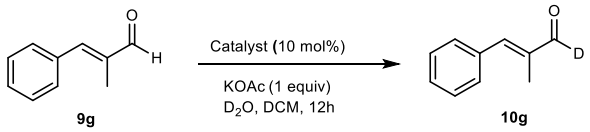
***Supplementary Table 3.*** Optimization of reaction conditions for cinnamaldehyde[a]




| Entry | Catalyst | Base | T(°C) | Yield (%)[b] | % D[d] | Yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | **5a** | $K_2CO_3$ | 40 | - | - | 50 |
| 2 | **5b** | $K_2CO_3$ | 40 | - | - | 50 |
| 3 | **5m** | $K_2CO_3$ | 40 | 60 | 0 | 10 |
| 4 | **5o** | $K_2CO_3$ | 40 | 80 | 0 | 0 |
| 5 | **5r** | $K_2CO_3$ | 40 | - | - | - |
| 6 | **5l** | KOAc | 40 | - | - | - |
| 7 | **5l** | DIPEA | 40 | 20 | 20 | - |
| 8 | **5s** | KOAc | 40 | 92 | 0 | - |
| 9 | **5t** | KOAc | 40 | 80 | 0 | - |
| 10 | **5u** | KOAc | 40 | 87 | 7 | - |
| 11 | **5v** | KOAc | 40 | 60 | 15 | - |
| 12 | **5w** | KOAc | 40 | 87 | 4 | - |
| 13 | **5x** | KOAc | 40 | 65 | 0 | - |
| 14 | **5y** | KOAc | 40 | 55 | 4 | - |
| 15 | **5z** | KOAc | 40 | 33 | 12 | - |
| 16 | **5aa** | KOAc | 40 | 80 | 0 | - |
| 17 | **5ab** | KOAc | 40 | 20 | 18 | - |
| 18 | **5ac** | KOAc | 40 | 40 | 40 | - |
| 19 | **5ad** | KOAc | 40 | 43 | 22 | - |
| 20 | **5ae** | KOAc | 40 | 72 | 0 | - |
| 21 | **5af** | KOAc | 40 | 50 | 32 | - |
| 22 | **5ag** | KOAc | 40 | 86 | 58 | - |
| 23 | **5ag** | KOAc | 60 | 95 | 45 | - |
| 24 | **5ah** | KOAc | 60 | 67 | 95 | - |
| 25 | **5p** | KOAc | 60 | 63 | 97 | - |

[a]Reaction conditions unless otherwise stated: **9a** (0.25 mmol), catalyst **5** (10 mol%) and KOAc (1.0 equiv) in $D_2O$ (1 mL) and DCM (0.25 mL) was vigorously stirred at 40 °C for 12 hours. [b]Yield of isolated product of **10a**. [c]Yield of isolated product of **11**. [d]Deuterium incorporations (%) were determined by $^1H$ NMR spectroscopy.

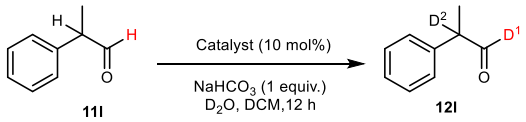
***Supplementary Table 4.*** Optimization of reaction conditions for other enals[a]




| Entry | Catalyst | T (°C) | Yield (%)[b] | % D[c] |
|---|---|---|---|---|
| 1 | **5a** | 25 | 98 | 0 |
| 2 | **5b** | 25 | 96 | 0 |
| 3 | **5m** | 25 | 92 | 0 |
| 4 | **5o** | 25 | 95 | 0 |
| 5 | **5r** | 25 | 94 | 15 |
| 6 | **5ag** | 25 | 89 | 67 |
| 7 | **5l** | 25 | 96 | 94 |
| 8 | **5l** | 40 | 95 | 98 |

[a]Reaction conditions unless otherwise stated: **9g** (0.25 mmol), catalyst **5** (10 mol%) and KOAc (1.0 equiv) in $D_2O$ (1 mL) and DCM (0.25 m) was vigorously stirred at 25 °C for 12 hours. [b]Yield of isolated product. [c]Deuterium incorporations (%) were determined by $^1H$ NMR spectroscopy.

***Supplementary Table 5.*** Optimization of reaction conditions for aliphatic aldehydes[a]



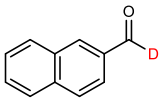

| Entry | Catalyst | T (°C) | Yield (%)[b] | % D[1c] | % D[2c] |
|---|---|---|---|---|---|
| 1 | **5a** | 40 | 35 | 12 | 37 |
| 2 | **5b** | 40 | 55 | 35 | 41 |
| 3 | **5c** | 40 | 71 | 30 | 84 |
| 4 | **5g** | 40 | - | - | - |
| 5 | **5h** | 40 | 65 | 0 | 76 |
| 6 | **5i** | 40 | 44 | 11 | 48 |
| 7 | **5j** | 40 | 52 | 40 | 97 |
| 8 | **5k** | 40 | 64 | 73 | 95 |
| 9 | **5l** | 40 | 39 | 60 | 97 |
| 10 | **5m** | 40 | 32 | 98 | 98 |
| 11 | **5n** | 40 | 33 | 95 | 98 |
| 12 | **5o** | 40 | 35 | 95 | 81 |
| 13 | **5ai** | 40 | 70 | 10 | 95 |
| 14 | **5aj** | 40 | 85 | 7 | 15 |
| 15 | **5ak** | 40 | 40 | 83 | 82 |
| 16 | **5al** | 40 | 65 | 18 | 45 |
| 17 | **5q** | 40 | 64 | 98 | 92 |
| **18** | **5q** | **30** | **73** | **99** | **97** |

[a]Reaction conditions unless otherwise stated **11l** (0.5 mmol), catalysts **5** (10 mol%) and $NaHCO_3$ (1.0 equiv) in $D_2O$ (1 mL) and DCM (0.25 mL) was vigorously stirred at 40 °C for 12 hours. [b]Yield of isolated product. [c]Deuterium incorporations (%) were determined by $^1H$ NMR spectroscopy.

## 4. Supplemnetary methods: Experiment procedures and product characterization

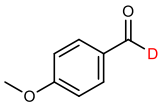
### 4.1 General procedure for deuteration of aldehydes catalyzed by NHC

Aldehyde (1 equiv), NHC catalyst (x mol%) and base (1 equiv) were dissolved in a mixture of $D_2O$ (1 mL) and organic solvent (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at specified temperature for 12 hours. After cooling to room temperature, the reaction was extracted with DCM, dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography to afford the deuterated product. The level of deuterium incorporation of the product was determined by $^1$H NMR spectroscopy. The integrals were calibrated against **Supplementary Equation 1** or **Supplementary Equation 2** (see page 2).



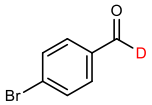

**2-Naphthaldehyde-*α*-*d*$_1$ (7a)**

2-Naphthaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7c** was obtained as a white solid in 81% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 0.02H), 8.30 (s, 1H), 7.99-7.87 (m, 4H), 7.65-7.55(m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.0 (t, *J* = 26.6 Hz), 136.4 (s), 134.6 (s), 134.0 (t, *J* = 3.5 Hz), 132.6 (s), 129.5 (s), 129.1 (s), 129.1 (s), 128.1 (s), 127.1 (s), 122.7 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.19 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_7DO$ [$(M)^+$]: 157.0638, found: 157.0639.




**4-Methoxybenzaldehyde-*α*-*d*$_1$ (7b)**

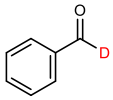
4-Methoxybenzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7a** was obtained as a colorless oil in 93% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 0.02H), 7.82 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.98 (dt, *J* = 8.8, 2.4 Hz, 2H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5 (t, *J* = 26.3 Hz), 164.6 (s), 132.0 (s), 129.9 (t, *J* = 3.5 Hz), 114.3 (s), 55.6 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.93 (s, 1D); HRMS (EI): m/z caled for $C_8H_7DO_2$ [$(M)^+$]: 137.0587, found: 137.0588.




**4-Bromobenzaldehyde-*α*-*d*$_1$ (7c)**

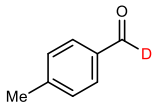
4-Bromobenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7b** was obtained as a

yellow solid in 86% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 0.02H), 7.73 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.66 (dt, *J* = 8.4, 2.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.8 (t, *J* = 26.8 Hz), 135.0 (t, *J* = 3.7 Hz), 132.4 (s), 131.0 (s), 129.8 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.00 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DBrO$ [$(M)^+$]: 184.9587, found: 184.9589.



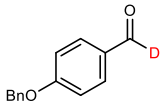

**Benzaldehyde-*α*-*d*$_1$ (7d)**

Benzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7d** was obtained as a colorless oil in 70% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 0.01H), 7.90-7.87 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.1 (t, *J* = 26.5 Hz), 136.3 (t, *J* = 3.6 Hz), 134.5 (s), 129.8 (s), 129.0 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.08 (s, 1D); HRMS (EI): m/z caled for $C_7H_5DO$ [$(M)^+$]: 107.0481, found: 107.0482.



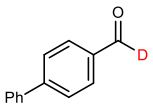

**4-Methylbenzaldehyde-*α*-*d*$_1$ (7e)**

4-Methylbenzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7e** was obtained as a colorless oil in 74% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 0.02H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 7.9 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.7 (t, *J* = 26.3 Hz), 145.6 (s), 134.1 (t, *J* = 3.6 Hz), 129.9 (s), 129.7 (s), 21.9 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.95 (s, 1D); HRMS (EI): m/z caled for $C_8H_7DO$ [$(M)^+$]: 121.0638, found: 121.0639.



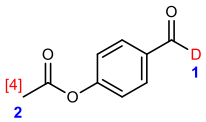

**4-Benzyloxybenzaldehyde-*α*-*d*$_1$ (7f)**

4-Benzyloxybenzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7f** was obtained as a yellow solid in 98% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 0.02H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.46-7.36 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5 (t, *J* = 26.2 Hz), 163.8 (s), 136.0 (s), 132.0 (s), 130.1 (t, *J* = 3.5Hz), 128.8 (s), 128.4 (s), 127.5 (s), 115.2 (s), 70.3 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.92 (s, 1D); HRMS (EI): m/z caled for $C_{14}H_{11}DO_2$ [$(M)^+$]: 213.0900, found: 213.0904.



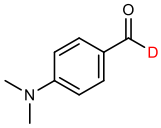

**[1,1'-Biphenyl]-4-carbaldehyde-*α*-*d*$_1$ (7g)**

[1,1'-biphenyl]-4-carbaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7g** was obtained as a white solid in 95% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 0.02H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.45-7.40 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.7 (t, *J* = 26.5 Hz), 147.2 (s), 139.7 (s), 135.1 (t, *J* = 3.5 Hz), 130.3 (s), 129.1 (s), 128.5 (s), 127.7 (s), 127.4 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.11 (s, 1D); HRMS (EI): m/z caled for $C_{13}H_9DO$ [$(M)^+$]: 183.0794, found: 183.0796.



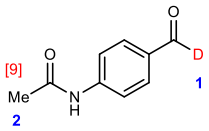

**4-Acetoxybenzaldehyde-*1,2-d*$_1$,*d*$_3$ (7h)**

4-Acetoxybenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7h** was obtained colorless as a oil in 47% yield with 97% D-incorporation at position 1 and 4% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 0.03H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 2.34 (s, 2.87H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.6 (t, *J* = 26.6 Hz), 168.7 (s), 155.4 (s), 133.9 (t, *J* = 3.6 Hz), 131.2 (s), 122.4 (s), 21.2 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.3 (s, 1D), 2.34 (s, 0.13D); HRMS (EI): m/z caled for $C_9H_7DO_3$ [$(M)^+$]: 165.0536, found: 165.0537.



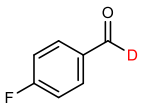

**4-Dimethylaminobenzaldehyde-*α*-*d*$_1$ (7i)**

4-Dimethylaminobenzaldehyde (0.5 mmol), **5ag** (30 mol%) and AcOK (1 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7i** was obtained as a white solid in 83% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 0.02H), 7.73 (d, *J* = 9.0 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 3.08 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.1 (t, *J* = 25.8 Hz), 154.4 (s), 132.0 (s), 125.0 (t, *J* = 3.4 Hz), 111.0 (s), 40.1 (s) ; $^2$H NMR (77 MHz, $CHCl_3$) δ 9.78 (s, 1D); HRMS (EI): m/z caled for $C_9H_{10}DNO$ [$(M)^+$]: 150.0903, found: 150.0903.



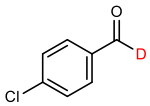

**4-Acetamidobenzaldehyde-*1,2-d*$_1$,*d*$_3$ (7j)**

4-Acetamidobenzaldehyde (0.5 mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7j** was obtained as a white solid in 64% yield with 99% D-incorporation at position 1 and 9% D-incorporation at position 2. $^1$H NMR (400 MHz, DMSO-*d*$_6$) δ 10.38 (s, 1H), 9.86 (s, 0.01H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 2.13-2.05 (m, 2.77H); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$) δ 191.2 (t, *J* = 26.7 Hz), 169.1 (s), 144.8 (s), 131.0 (s), 130.8 (s), 118.5 (s), 24.2-23.7 (m); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.86 (s, 1D), 2.05 (s, 0.28D); HRMS (EI): m/z caled for $C_9H_8DNO_2$ [$(M)^+$]: 164.0696 Found: 164.0696; $C_9H_7D_2NO_2$ [$(M)^+$]: 165.0759, found: 165.0758.



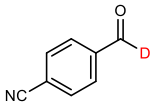

**4-Fluorobenzaldehyde-*α-d*$_1$ (7k)**

4-Fluorobenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7k** was obtained as a colorless oil in 50% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 0.01H), 7.87-7.83 (m, 2H), 7.14 (t, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.2 (t, *J* = 26.6 Hz), 166.6 (d, *J* = 256.7 Hz), 132.9 (t, *J* = 3.3 Hz), 132.3 (d, *J* = 9.7 Hz), 116.4 (d, *J* = 22.3 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.95 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DFO$ [$(M)^+$]: 125.0387, found: 125.0386.



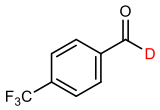

**4-Chlorobenzaldehyde-*α-d*$_1$ (7l)**

4-Chlorobenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7l** was obtained as a shite solid in 79% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 0.02H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 190.6 (t, *J* = 26.7 Hz), 141.0 (s), 134.6 (t, *J* = 3.7 Hz), 130.9 (s), 129.5 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.02 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DClO$ [$(M)^+$]: 141.0092, found: 141.0091.



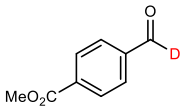
**4-Formylbenzonitrile-*α*-*d*$_1$ (7m)**

4-formylbenzonitrile (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7m** was obtained as a yellow solid in 75% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.02H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.4 (t, *J* = 27.2 Hz),138.7 (t, *J* = 3.7 Hz), 132.9 (s), 129.9 (s), 117.76 (s), 117.6(s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.13 (s, 1D); HRMS (EI): m/z caled for $C_8H_4DNO$ [$(M)^+$]: 132.0434, found: 132.0436.



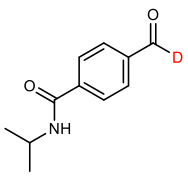
**4-(Trifluoromethyl)benzaldehyde-*α*-*d*$_1$ (7n)**

4-(Trifluoromethyl)benzaldehyde (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7n** was obtained as a yellow oil in 44% yield with 97% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.03H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.8 (t, *J* = 27.0 Hz), 138.6 (s), 135.6 (q, *J* = 32.6 Hz), 129.9 (s), 126.1 (q, *J* = 3.8 Hz), 123.4 (d, *J* = 272.9 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.15 (s, 1D); HRMS (EI): m/z caled for $C_8H_4DF_3O$ [$(M)^+$]: 175.0355, found: 175.0356.



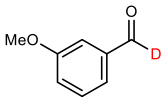
**Methyl 4-formylbenzoate-*α*-*d*$_1$ (7o)**

Methyl 4-formylbenzoate (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7o** was obtained as a white solid in 68% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.01H), 8.18 (d, *J* = 8.4, 2H), 7.94 (d, *J* = 8.4, 2H), 3.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.4 (t, *J* = 26.9 Hz), 166.1 (s), 139.1 (t, *J* = 3.6 Hz), 135.1 (s), 130.2 (s), 129.5 (s), 52.6 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.13 (s, 1D); HRMS (EI): m/z caled for $C_7H_9DO_3$: 165.0536, found: 165.0538.



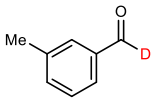
**4-Formyl-N-isopropylbenzamide-*α*-$d_1$ (7p)**

4-Formyl-N-isopropylbenzamide (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 ºC for 12 hours. **7p** was obtained as a white solid in 75% yield with 99% D-incorporation. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.07 (s, 0.01H), 8.45 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 4.15-4.07 (m, 1H), 1.17 (d, *J* = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 192.6 (t, *J* = 26.9 Hz), 164.5 (s), 139.8 (s), 137.5 (s), 129.3 (s), 127.9 (s), 41.2 (s), 22.2(s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.07 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_{12}DNO_2$ [$(M)^+$]: 192.1009, found: 192.1011.



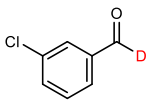

**3-Methoxybenzaldehyde-*α*-$d_1$ (7q)**

3-methoxybenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7q** was obtained as a yellow oil in 92% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 0.03H), 7.46-7.40 (m, 2H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.18-7.14 (m, 1H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.8 (t, *J* = 26.6 Hz), 160.2 (s), 137.7 (t, *J* = 3.6 Hz), 130.0 (s), 123.5 (s), 121.5 (s), 112.0 (s), 55.5 (d, *J* = 1.1 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.00 (s, 1D); HRMS (EI): m/z caled for $C_8H_7DO_2$ [$(M)^+$]: 137.0587, found: 137.0588.




***m*-Tolualdehyde-*α*-$d_1$ (7r)**

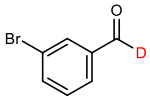
M-Tolualdehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7r** was obtained as a colorless oil in 91% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 0.02H), 7.70-7.67 (m, 2H), 7.46-7.39 (m, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.3 (t, *J* = 26.5 Hz), 138.9 (s), 136.4 (t, *J* = 3.5 Hz), 135.3 (s), 130.0 (s), 128.9 (s), 127.2 (s), 21.2 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.01 (s, 1D); HRMS (EI): m/z caled for $C_8H_7DO$ [$(M)^+$]: 121.0638, found: 121.0639.




**3-Chlorobenzaldehyde-*α*-$d_1$ (7s)**

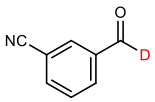
3-Chlorobenzaldehyde (0.5 mmol), **5o** (5 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7s** was obtained as a

colorless oil in 71% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 0.02H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.76 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.62-7.58 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5 (t, *J* = 27 Hz), 137.8 (t, *J* = 3.7 Hz), 135.5 (s), 134.4 (s), 130.4 (s), 129.3 (s), 128.0 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.98 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DClO$ [$(M)^+$]: 141.0092, found: 141.0091.




**3-Bromobenzaldehyde-*α*-*d*$_1$ (7t)**

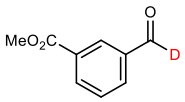
3-Bromobenzaldehyde (0.5 mmol), **5o** (5 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7t** was obtained as a colorless oil in 86% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 0.01H), 8.00 (t, *J* = 1.7 Hz, 1H), 7.80 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.76-7.72 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.4 (t, *J* = 26.9 Hz), 137.9 (t, *J* = 3.7 Hz), 137.3 (s), 132.4 (s), 130.6 (s), 128.4 (s), 123.4 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.02 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DBrO$ [$(M)^+$]: 184.9587, found: 184.9588.




**3-Formylbenzonitrile-*α*-*d*$_1$ (7u)**

3-Formylbenzonitrile (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. 3-formylbenzonitrile-*α*-*d*$_1$ was obtained as a yellow solid in 81% yield with 95% D-incorporation.

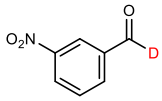
3-Formylbenzonitrile-*α*-*d*$_1$ (deuteration 95%, 0.40 mmol ), **5o** (10 mol%) and KOAc (0.40 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 ºC for 12 hours again. **7u** was obtained as a colorless solid in 59 % yield (for two steps) with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 0.01H), 8.16 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 188.7 (t, *J* = 27.2 Hz), 136.2 (s), 135.8 (t, *J* = 3.8 Hz), 132.3 (s), 132.1 (s), 129.1 (s), 116.6 (s), 112.7 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.06 (s, 1D); HRMS (EI): m/z caled for $C_8H_4DNO$ [$(M)^+$]: 132.0434, found: 132.0435.




**Methyl 3-formylbenzoate-*α*-*d*$_1$ (7v)**

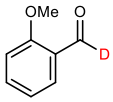
Methyl 3-formylbenzoate (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL).

Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7v** was obtained as a yellow oil in 59% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 0.01H), 8.54-8.52 (m, 1H), 8.29 (dt, *J* = 7.6, 1.6 Hz, 1H), 8.08 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.63 (t, *J* = 11.4, 1H), 3.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.1 (t, *J* = 26.8 Hz), 166.0 (s), 136.5 (d, *J* = 3.5 Hz), 135.2 (s), 133.1 (s), 131.3 (d, *J* = 7.1 Hz), 129.3 (s), 52.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.10 (s, 1D); HRMS (EI): m/z caled for $C_7H_9DO_3$[$(M)^+$]: 165.0536, found: 165.0538.



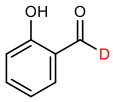

**3-Nitrobenzaldehyde-*α*-*d*$_1$ (7w)**

3-Nitrobenzaldehyde (0.5 mmol), **5o** (5 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7w** was obtained as a yellow solid in 55% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 0.01H), 8.72 (s, 1H), 8.51-8.48 (m, 1H), 8.24 (d, *J* = 7.6, 1H), 7.77 (t, *J* = 7.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.5 (t, *J* = 27.3 Hz), 148.8 (s), 137.3 (t, *J* = 3.8 Hz), 134.7 (s), 130.4 (s), 128.6 (s), 124.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.16 (s, 1D); HRMS (EI): m/z caled for $C_7H_4NDO_3$ [$(M)^+$]: 152.0332, found: 152.0333.




**2-Methoxybenzaldehyde-*α*-*d*$_1$ (7x)**

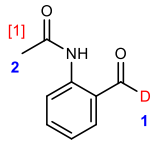
2-Methoxybenzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7x** was obtained as a yellow oil in 95% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 0.02H), 7.79 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.54-7.49 (m, 1H), 7.00-6.93 (m, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.5 (t, *J* = 27.5 Hz), 161.9 (s), 136.0 (s), 128.4 (s), 124.7 (t, *J* = 3.3 Hz), 120.6 (s), 111.6 (s), 55.6 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.43 (s, 1D); HRMS (EI): m/z caled for $C_8H_7DO_2$ [$(M)^+$]: 137.0587, found: 137.0588.




**Salicylaldehyde-*α*-*d*$_1$ (7y)**

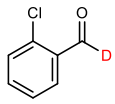
Salicylaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7y** was obtained as a colorless oil in 47% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.89 (s, 0.01H), 7.57-7.50 (m, 2H), 7.04-6.97 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.3 (t, *J* = 26.9 Hz), 161.7 (s), 137.0 (s), 133.7 (s), 120.6 (t. *J* = 3.0 Hz), 119.9 (s), 117.6 (s); $^{2}$H

NMR (77 MHz, $CHCl_3$) δ 9.94 (s, 1D); HRMS (EI): m/z caled for $C_7H_5DO_2$ [$(M)^+$]: 123.0431, found: 123.0432.



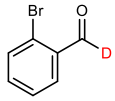

**N-(2-Formylphenyl)acetamide-*1,2-$d_1$,$d_3$* (7z)**

N-(2-Formylphenyl)acetamide (0.5 mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7z** was obtained as a yellow solid in 90% yield with 99% D-incorporation at position 1 and 1% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 9.92 (s, 0.01H), 8.74 (d, *J* = 8.5 Hz, 1H), 7.68 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.61 (dt, *J* = 8.5, 1.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 2.26 (s, 2.97H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.2 (t, *J* = 27.0), 169.6 (s), 140.9 (s), 136.2 (s), 136.0 (s), 122.8 (s), 121.3 (t, *J* = 3.0 Hz), 119.7 (s), 25.4 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.92 (s, 1D), 2.26-2.20 (m, 0.03D); HRMS (EI): m/z caled for $C_9H_8DNO_2$ [$(M)^+$]: 164.0696, found: 164.0697.



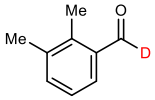

**2-Chloorbenzaldehyde-*α-$d_1$* (7aa)**

2-chloorbenzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7aa** was obtained as a yellow oil in 79% yield with 97% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 0.03H), 7.91 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.52 (dt, *J* = 8.1, 1.7 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.40-7.35 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.5 (t, *J* = 27.8 Hz), 138.0 (s), 135.1 (s), 132.4 (t, *J* = 3.5 Hz), 130.6 (s), 129.4 (s), 127.3 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.52 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DClO$ [$(M)^+$]: 141.0092, found: 141.0090.



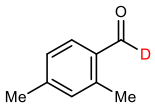

**2-Bromobenzaldehyde-*α-$d_1$* (7ab)**

2-Bromobenzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7ab** was obtained as a yellow oil in 93% yield with 99% D-incorporation. $^1$H NMR (400 MHz, DMSO) δ 10.33 (s, 0.01H), 7.90-7.87 (m, 1H), 7.63-7.60 (m, 1H), 7.45-7.37 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.4 (t, *J* = 27.9 Hz), 134.3 (s), 132.8 (s), 132.4 (t, *J* = 3.5 Hz), 128.8 (s), 126.9 (s), 126.1 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.40 (s, 1D); HRMS (EI): m/z caled for $C_7H_4DBrO$ [$(M)^+$]: 184.9587, found: 184.9586.



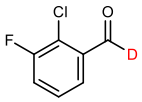

**2,3-Dimethylbenzalde-*α*-*d*$_1$ (7ac)**

2,3-Dimethylbenzalde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7ac** was obtained as a colorless oil in 83% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 0.02H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 2.58 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.9 (t, *J* = 26.4 Hz), 139.2 (s), 138.3 (s), 135.3 (s), 134.3(t, *J* = 3.4 Hz), 129.8 (s), 125.8 (s), 20.0 (s), 14.4 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.29 (s, 1D); HRMS (EI): m/z caled for $C_9H_9DO$ [$(M)^+$]: 135.0794, found: 135.0795.



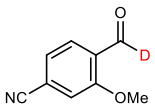

**2,4-DiMethylbenzaldehyde-*α*-*d*$_1$ (7ad)**

2,4-DiMethylbenzaldehyde (0.5 mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ad** was obtained as a colorless oil in 88% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 0.02H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 2.62 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.1 (t, *J* = 26.3 Hz), 144.6 (s), 140.6 (s), 132.6 (s), 132.4 (s), 132.06-131.9 (t, *J* = 3.4 Hz), 127.1 (s), 21.7 (s), 19.6 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.23 (s, 1D); HRMS (EI): m/z caled for $C_9H_9DO$ [$(M)^+$]: 135.0794, found: 135.0795.



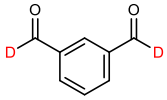

**2-Chloro-3-fluorobenzaldehyde-*α*-*d*$_1$ (7ae)**

2-Chloro-3-fluorobenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ae** was obtained as a white solid in 86% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 0.02H), 7.74-7.71 (m, 1H), 7.42-7.33 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 188.2 (td, *J* = 28.1, 3.8 Hz), 158.4 (d, *J* = 250.8 Hz), 133.9 (t, *J* = 3.5), 128.0 (d, *J* = 7.4 Hz), 124.9 (d, *J* = 18.5 Hz), 124.7 (d, *J* = 3.5 Hz), 121.8 (d, *J* = 21.4 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.49 (s, 1D); HRMS (EI): m/z caled for $C_7H_3DClFO$ [$(M)^+$]: 158.9997, found: 158.9998.



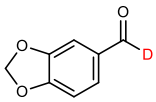
**4-Formyl-3-methoxybenzonitrile-*α*-$d_1$ (7af)**

4-Formyl-3-methoxybenzonitrile (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7af** was obtained as a yellow solid in 81% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 0.01H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.29 (s, 1H), 4.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 188.0 (t, *J* = 28.2 Hz), 161.3 (s), 129.2 (s), 127.5 (t, *J* = 3.4 Hz), 124.4 (s), 118.5 (s), 117.8 (s), 115.4 (s), 56.2 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.52 (s, 1D); HRMS (EI): m/z caled for $C_9H_6DNO_2$ [$(M)^+$]: 162.0540, found: 162.0541.



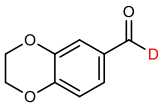
**Isophthalaldehyde-*1,3*-$d_{1,}d_1$ (7ag)**

Isophthalaldehyde (0.5 mmol), **5o** (20 mol%) and KOAc (1 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ag** was obtained as a white solid in 68% yield with 97.5% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.05H), 8.36 (s, 1H), 8.14 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.8 (t, *J* = 27 Hz), 135.9 (t, J = 3.7 Hz), 133.6 (s), 129.9 (s), 128.9 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.11 (s, 1D); HRMS (EI): m/z caled for $C_8H_4D_2O_2$ [$(M)^+$]: 136.0493, found: 136.0494.



**Piperonal-*α*-$d_1$ (7ah)**

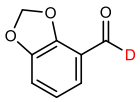
Piperonal (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7ah** was obtained as a colorless solid in 98% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 0.01H), 7.39 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.06 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.0 (t, *J* = 26.5 Hz), 153.1 (s), 148.7 (s), 131.8 (t, *J* = 3.6 Hz), 128.7 (s), 108.4(s), 106.9 (s), 102.1 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.82 (s, 1D); HRMS (EI): m/z caled for $C_8H_5DO_3$ [$(M)^+$]: 151.0380, found: 151.0381.



**1,4-Benzodioxin-6-carboxaldehyde-*α*-$d_1$ (7ai)**

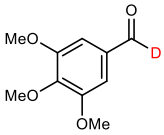
1,4-Benzodioxin-6-carboxaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7ai** was obtained as a

yellow solid in 99% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 0.02H), 7.40-7.37 (m, 2H), 6.98-6.95 (m, 1H), 4.34-4.28 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5 (t, *J* = 26.4 Hz), 149.3 (s), 143.9 (s), 130.6 (t, *J* = 3.6 Hz), 124.2 (s), 118.4 (s), 117.8 (s), 64.7 (s), 64.1 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.84 (s, 1D); HRMS (EI): m/z caled for $C_9H_7DO_3$ [$(M)^+$]: 165.0536, found: 165.0537.



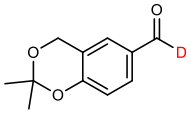
**2,3-(Methylenedioxy)benzaldehyde-*α*-*d*$_1$ (7aj)**

2,3-(Methylenedioxy)benzaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7aj** was obtained as a colorless solid in 81% yield with 97% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.03H), 7.25 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.99 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.10 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.7 (t, *J* = 27.1 Hz), 148.2 (s), 147.9 (s), 120.7 (s), 120.1 (s), 118.3 (t, *J* = 3.6 Hz), 112.4 (s), 101.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.15 (s, 1D);HRMS (EI): m/z caled for $C_8H_5DO_3$ [$(M)^+$]: 151.0380, found: 151.0381.



**3,4,5-Trimethoxybenzaldehyde-*α*-*d*$_1$ (7ak)**

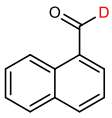
3,4,5-Trimethoxybenzaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ak** was obtained as a white solid in 88% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 0.01 H), 7.06 (s, 2H), 3.87 (s, 3H), 3.86 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.7 (t, *J* = 26.6 Hz), 153.6 (s), 143.5 (s), 131.6 (t, *J* = 3.2 Hz), 106.6 (s), 60.9 (d, *J* = 2.6 Hz), 56.2 (d, *J* = 2.5 Hz); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.82 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_{11}DO_4$ [$(M)^+$]: 197.0798, found: 197.0796.



**2,2-Dimethyl-4H-benzo[d][1,3]dioxine-6-carbaldehyde-*α*-*d*$_1$ (7al)**

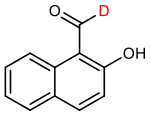
2,2-Dimethyl-4H-benzo[d][1,3]dioxine-6-carbaldehyde (0.5 mmol), **5o** (10 mol%), $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7al** was obtained as a in 88% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 0.02H), 7.66 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.51 (t, *J* = 0.8 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.86 (s, 2H), 1.53 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5 (t, *J* = 26.3 Hz),

156.8 (s), 130.4 (s), 129.3 (t, *J* = 3.4 Hz), 126.9 (s), 119.7 (s), 117.7 (s), 100.76 (s), 60.6 (s), 24.8 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.86 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_{11}DO_3$ [$(M)^+$]: 193.0849, found: 193.0850.



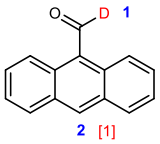

**1-Naphthaldehyde-*α*-*d*$_1$ (7am)**

1-Naphthaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7am** was obtained as a colorless oil in 88% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 0.01H), 9.23 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.83-7.80 (m, 2H), 7.63-7.59 (m, 1H), 7.53-7.44 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.2 (t, *J* = 26.5 Hz), 136.7 (s), 135.2 (s), 133.7 (s), 131.4-131.1 (m), 130.4 (s), 129.0 (s), 128.5 (s), 126.9 (s), 124.9 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.30 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_7DO$ [$(M)^+$]: 157.0638, found: 157.0638.




**2-Hydroxy-1-naphthaldehyde-*α*-*d*$_1$ (7an)**

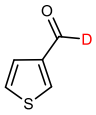
2-Hydroxy-1-naphthaldehyde (0.5 mmol), **5o** (20 mol%) and $NaHCO_3$ (1 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7an** was obtained as a white solid in 65% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 13.18 (s, 1H), 10.73 (s, 0.02H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.62-7.55 (m, 1H), 7.44-7.38 (m, 1H), 7.10 (d, *J* = 9.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 182.9 (t, *J* = 26.8 Hz), 165.0 (s), 139.1 (s), 132.9 (s), 129.5 (s), 129.1 (s), 127.8 (s), 124.5 (s), 119.2 (s), 118.6 (s), 111.2 (t, *J* = 2.5 Hz); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.70 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_7DO_2$ [$(M)^+$]: 173.0587, found: 173.0588.




**9-Anthraldehyde-*α*-*d*$_1$ (7ao)**

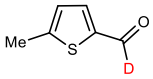
9-Anthraldehyde (0.5mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ao** was obtained as a yellow solid in 88% yield with 99% D-incorporation at position 1 and 1% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 0.01H), 8.89 (d, *J* = 9.0 Hz, 2H), 8.51 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.63-7.59 (m, 2H), 7.50-7.45 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.4 (t, *J* = 26.5 Hz ), 134.0 (s), 130.9 (s), 129.8 (s), 128.1 (s), 127.9 (s), 124.5 (s), 123.2 (t, *J* = 3.2

Hz), 122.3 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.41 (s, 1D); HRMS (EI): m/z caled for $C_{15}H_9DO$ [$(M)^+$]: 207.0794, found: 207.0796.



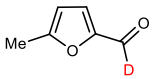
**Thiophene-3-carboxaldehyde-*α*-*d*$_1$ (7ap)**

Thiophene-3-carboxaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ap** was obtained as a yellow oil in 67% yield with 97% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 0.02H), 8.11 (dd, *J* = 2.8, 1.0 Hz, 1H), 7.53 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.36 (dd, *J* = 5.1, 2.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 184.7 (t, *J* = 26.8 Hz), 143.0 (t, *J* = 3.8 Hz), 136.8 (s), 127.4 (s), 125.4 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.94 (s, 1D); HRMS (EI): m/z caled for $C_5H_3DOS$ [$(M)^+$]: 113.0046, found: 113.0047.



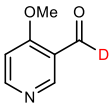
**5-Methylthiophene-2-carboxaldehyde-*α*-*d*$_1$ (7aq)**

5-Methylthiophene-2-carboxaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7aq** was obtained as a yellow oil in 84% yield with 97% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 0.03H), 7.57 (d, *J* = 3.6 Hz, 1H), 6.86 (d, *J* = 3.6 Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 182.4 (t, *J* = 26.9 Hz), 151.7 (s), 141.9 (t, *J* = 4.9 Hz), 137.4 (s), 127.1 (s), 16.3 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.78 (s, 1D); HRMS (EI): m/z caled for $C_6H_5DOS$ [$(M)^+$]: 127.0202, found: 127.0203.



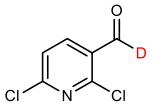
**5-Methyl furfural-*α*-*d*$_1$ (7ar)**

5-Methyl furfural (0.5 mmol), **5o** (20 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7ar** was obtained as a yellow oil in 50% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 0.02H), 7.16 (d, *J* = 3.5 Hz, 1H), 6.22 (d, *J* = 3.5 Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.6 (t, *J* = 27.9 Hz), 159.8 (s), 151.9 (t, *J* = 4.7 Hz), 123.9 (s), 109.5 (s), 14.1 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.53 (s, 1D); HRMS (EI): m/z caled for $C_6H_5DO_2$: 111.0431, found: 111.0432.



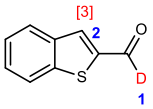
**4-Methoxy-3-pyridinecarboxaldehyde-*α*-*d*$_1$ (7as)**

4-Methoxy-3-pyridinecarboxaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7as** was obtained as a yellow solid in 98% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 0.02H), 8.82 (s, 1H), 8.58 (d, *J* = 5.9 Hz, 1H), 6.90 (d, *J* = 5.9 Hz, 1H), 3.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.4 (t, *J* = 27.8 Hz), 165.7 (s), 155.1 (s), 149.9 (s), 119.5 (t, *J* = 3.4 Hz), 106.3 (s), 54.9 (d, *J* = 1.3 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.42 (s, 1D); HRMS (EI): m/z caled for $C_7H_6DNO_2$ [$(M)^+$]: 138.0540, found: 138.0541.



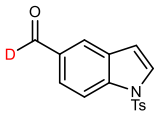

**2,6-Dichloro-3-pyridinecarbaldehyde-*α*-*d*$_1$ (7at)**

2,6-Dichloro-3-pyridinecarbaldehyde (0.5 mmol), **5o** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7at** was obtained as a white solid in 93% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.38 (d, *J* = 0.7 Hz, 0.02H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.7 (t, *J* = 28.6 Hz), 155.4 (s), 152.9 (s), 140.0 (s), 127.6 (t, *J* = 3.7 Hz), 124.2 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.41 (s, 1D); HRMS (EI): m/z caled for $C_6H_2DCl_2NO$ [$(M)^+$]: 175.9654, found: 175.9656.




**Benzothiophene-2-carboxaldehyde-*1,2-d*$_{1,}$*d*$_1$ (7au)**

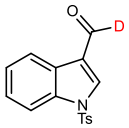
Benzothiophene-2-carboxaldehyde (0.5 mmol), **5o** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7au** was obtained as a yellow solid in 58% yield with 98% D-incorporation at position 1 and 3% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 0.02H), 8.0 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.51-7.45 (m, 1H), 7.44-7.38 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 184.5 (t, *J* = 27.4 Hz), 143.3 (t, *J* = 5.0 Hz), 142.7 (s), 138.6 (s), 134.6 (s), 128.2 (s), 126.3 (s), 125.3 (s), 123.3 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.10 (s, 1D), 8.03 (s, 0.03D); HRMS (EI): m/z caled for $C_9H_5DOS$ [$(M)^+$]: 163.0202, found: 163.0203.




**Tosyl-1H-indole-5-carboxaldehyde-*α*-*d*$_1$ (7av)**

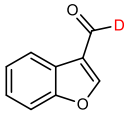
Tosyl-1H-indole-5-carboxaldehyde (0.5 mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7av** was obtained as a yellow solid in 85% yield with 99% D-incorporation. $^1$H NMR (400 MHz,

$CDCl_3$) δ 10.01 (s, 0.01H), 8.10 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 1.0 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 3.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.77 (dd, *J* = 3.7, 0.5 Hz, 1H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.5 (t, *J* = 26.4 Hz), 145.6 (s), 138.1 (s), 134.9 (s), 132.1 (t, *J* = 2.9 Hz), 130.9 (s), 130.1 (s), 128.0 (s), 126.9 (s), 125.2 (s), 124.8 (s), 113.9 (s), 109.4 (s), 21.6 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.01 (s, 1D); HRMS (EI): m/z caled for $C_{16}H_{12}DNO_3S$ [$(M)^+$]: 300.0679, found: 300.0681.



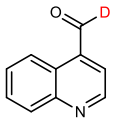

**Tosyl-1H-indole-3-carboxaldehyde-*α-d*$_1$ (7aw)**

Tosyl-1H-indole-3-carboxaldehyde (0.5 mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7aw** was obtained yellow solid in 62% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.01H), 8.25 (d, *J* = 9.1 Hz, 1H), 8.24 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.44-7.33 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.2 (t, *J* = 26.6), 146.2 (s), 136.3 (s), 135.2 (s), 134.3 (s), 130.4 (s), 127.3 (s), 126.3 (s), 125.1 (s), 122.6(s), 122.2 (t, *J* = 3.4), 113.3 (s), 21.7 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.09 (s, 1D); HRMS (EI): m/z caled for $C_{16}H_{12}DNO_3S$ [$(M)^+$]: 300.0679, found: 300.0681.




**3-Benzofurancarboxaldehyde-*α-d*$_1$(7ax)**

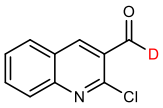
3-Benzofurancarboxaldehyde (0.5 mmol), **5m** (10 mol%) and $K_2CO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7ax** was obtained as a white solid in 56% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 0.01H), 8.28 (s, 1H), 8.22-8.18 (m, 1H), 7.58-7.54 (m, 1H), 7.45-7.37 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 184.5 (t, *J* = 26.7 Hz), 156.0 (s), 155.4 (s), 126.3 (s), 124.9 (s), 123.6 (t, *J* = 3.9 Hz), 122.9 (s), 122.6 (s), 111.7 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.20 (s, 1D); HRMS (EI): m/z caled for $C_9H_5DO_2$ [$(M)^+$]: 147.0431, found: 147.0432.




**4-Quinoline carboxaldehyde-*α-d*$_1$(7ay)**

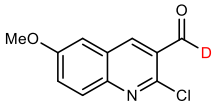
4-Quinoline carboxaldehyde (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7ay** was obtained as a white solid in 69% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.52 (s,

0.02H), 9.20 (d, *J* = 4.2 Hz, 1H), 9.03-9.01 (m, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.84-7.79 (m, 2H), 7.76-7.72 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.6 (t, *J* = 27.2 Hz), 150.5 (s), 149.3 (s), 136.7 (t, *J* = 3.7 Hz), 130.2 (s), 130.0 (s), 129.4 (s), 125.8 (s), 124.4 (s), 123.9 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.50 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_6DNO$ [$(M)^+$]: 158.0590, found: 158.0591.




**2-Chloroqinoline-3-carboxaldehyde-*α-d₁* (7az)**

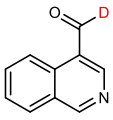
2-Chloroqinoline-3-carboxaldehyde (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (2 mL) and toluene (0.5 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7az** was obtained as a yellow solid in 73% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 0.01H), 8.73 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.90-7.84 (m, 1H), 7.63 (t, *J* = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 188.8 (t, *J* = 28.3 Hz), 150.1 (s), 149.6 (s), 140.3 (s), 133.6 (s), 129.7 (s), 128.6 (s), 128.2 (s), 126.5 (s), 126.3 (t, *J* = 3.4 Hz); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.58 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_5DClNO$ [$(M)^+$]: 192.0201, found: 192.0202.




**6-Methoxy2-Chloroqinoline-3-carboxaldehyde-*α-d₁* (7ba)**

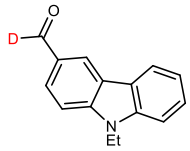
6-Methoxy2-Chloroqinoline-3-carboxaldehyde (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (2 mL) and toluene (0.5 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. 6-Methoxy-2-chloroqinoline-3-carboxaldehyde-*α-d₁* was obtained as a white solid in 93% yield with 94% D-incorporation.

6-Methoxy-2-Chloroqinoline-3-carboxaldehyde-*α-d₁* (deuteration 94%, 0.46 mmol), **5o** (10 mol%) and KOAc (0.46 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (2 mL) and toluene (0.5 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours.**7ba** was obtained as a yellow solid in 69 % yield (for two steps) with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 0.02H), 8.58 (s, 1H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.47 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.14 (d, *J* = 2.7 Hz, 1H), 3.93 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.1 (t, *J* = 27.8 Hz), 158.8 (s), 147.6 (s), 145.8 (s), 138.6 (s), 129.9 (s), 127.7 (s), 126.6 (s), 126.3 (t, *J* = 3.3 Hz), 106.4 (s), 55.8 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 10.56 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_7DClNO_2$ [$(M)^+$]: 222.0306, found: 222.0308.



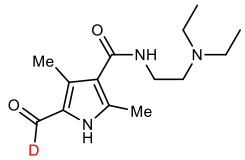

**Isoquinoline-4-carbaldehyde-*α-d₁*(7bb)**

Isoquinoline-4-carbaldehyde (0.5 mmol), **5o** (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7bb** was obtained as a yellow solid in 84% yield with 96% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 0.04H), 9.32 (s, 1H), 9.08 (d, *J* = 8.4 Hz, 1H), 8.84 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.83-7.77 (m, 1H), 7.67-7.61 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.5 (t, *J* = 26.8 Hz), 158.3 (s), 152.8 (s), 133.5 (s), 132.2 (s), 128.4 (s), 128.3 (s), 128.3 (s), 124.7 (t, *J* = 3.5 Hz), 124.3 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.30 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_6DNO$ [$(M)^+$]: 158.0590, found: 158.0591.



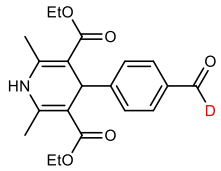

***N*-Ethyl-3-carbazolecarboxaldehyde-*α*-*d*$_1$ (7bc)**

*N*-Ethyl-3-carbazolecarboxaldehyde (0.5 mmol), **5o** (30 mol%) and $K_2CO_3$ (1 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **7bc** was obtained as a white solid in 88% yield with 97% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 0.03H), 8.58 (d, *J* = 1.2 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.00 (dd, *J* = 8.5, 1.4 Hz,1H), 7.56-7.51 (m, 1H), 7.46-7.43 (m, 2H), 7.35-7.30 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.6 (t, *J* = 26.1 Hz), 143.6 (s), 140.7 (s), 128.4 (s), 127.2 (s), 126.8 (s), 124.0 (s), 123.1 (s), 123.1 (s), 120.8 (s), 120.3 (s), 109.2 (s), 108.7 (s), 37.9 (s), 13.8 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.10 (s, 1D); HRMS (EI): m/z caled for $C_{15}H_{12}DNO$ [$(M)^+$]: 224.1060, found: 224.1062.



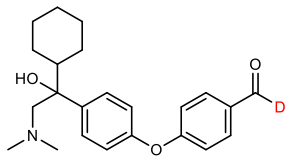

***N*-(2-(Diethylamino)ethyl)-5-formyl-2,4-dimethyl-1H-pyrrole-3-carboxamide-*α*-*d*$_1$ (7bd)**

*N*-(2-(Diethylamino)ethyl)-5-formyl-2,4-dimethyl-1H-pyrrole-3-carboxamide (0.5 mmol), **5m** (30 mol%) and $K_2CO_3$ (1.5 mmol, 3 equiv) was dissolved in a mixture of $D_2O$ (2 mL) and DCM (0.5 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **7be** was obtained as a yellow solid in 88% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 9.44 (s, 0.02H), 7.45 (s, 1H), 3.70-3.68 (m, 2H), 3.10 (s, 2H), 3.02 (q, *J* = 7.1 Hz, 4H), 2.52 (s, 3H), 2.49 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 6H); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$) δ 177.5-176.8 (m), 164.7 (s), 138.2 (s), 130.8 (t, *J* = 7.1 Hz), 127.7 (s), 118.8 (s), 50.6 (s), 46.7 (s), 35.1 (s), 12.6 (s), 9.7 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.49 (s, 1D); HRMS (EI): m/z caled for $C_{14}H_{22}DN_3O_2$ [$(M)^+$]: 266.1853, found: 266.1854.



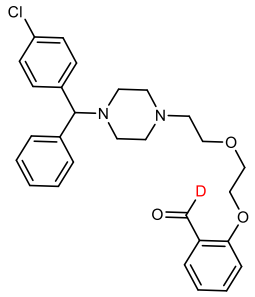
**4-(4-Formylphenyl)-1,4-dihydro-2,6-dimethyl-,3,5-diethyl ester-*α-d₁* (7be)**

4-(4-Formylphenyl)-1,4-dihydro-2,6-dimethyl-,3,5-diethyl ester **6be** (0.25 mmol), **5o** (20 mol%) and $K_2CO_3$ (0.5 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 ml). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7be** was obtained as a yellow solid in 73% yield with 96% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 0.04H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.35-6.32 (m, 1H), 5.06 (s, 1H), 4.11-4.02 (m, 4H), 2.32 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.2 (t, *J* = 29.4 Hz), 167.4 (s), 155.1 (s), 144.9 (s), 134.4 (s), 129.7 (s), 128.8 (s), 103.1 (s), 59.9 (s), 40.3 (s), 19.4 (s), 14.3 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.94 (s, 1D); HRMS (ESI): m/z caled for $C_{22}H_{23}DNO_5$ [$(M+H)^+$]: 359.1717, found: 359.1717.



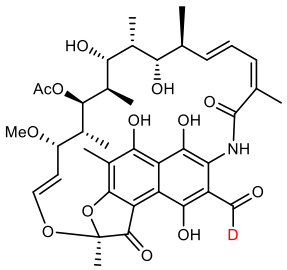
**4-(4-(2-(Dimethylamino)-1-(1-hydroxycyclohexyl)ethyl)phenoxy)benzaldehyde-*α-d₁* (7bf)**

4-(4-(2-(Dimethylamino)-1-(1-hydroxycyclohexyl)ethyl)phenoxy)benzaldehyde **6bf** (0.1 mmol), **5m** (15 mol%) and $K_2CO_3$ (0.1 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7bf** was obtained as a yellow oil in 55% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 0.02H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 3.81 (dd, *J* = 12.4, 6.6 Hz, 1H), 3.28 (t, *J* = 5.8 Hz, 1H), 2.95 (d, *J* = 8.3 Hz, 1H), 2.62 (s, 6H), 1.73-0.81 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5 (t, *J* = 26.4 Hz), 162.7 (s), 154.4 (s), 136.2 (s), 132.0 (s), 131.4 (s), 130.9 (s), 120.1 (s), 117.9 (s), 73.7 (s), 60.5 (s), 52.4 (s), 44.5 (s), 37.2 (s), 31.5 (s), 25.5 (s), 21.5 (s), 21.3 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.88 (s, 1D); HRMS (ESI): m/z caled for $C_{23}H_{29}DNO_3$ [$(M+H)^+$]: 369.2288, found: 369.2289.



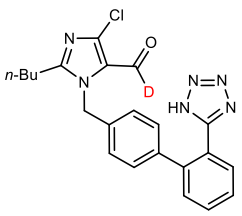
**2-(2-(2-(4-((4-Chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethoxy)ethoxy)benzaldehyde -*α-d₁* (7bg)**

2-(2-(2-(4-((4-Chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethoxy)ethoxy)benzaldehyde **6bg** (0.1 mmol), **5ag** (15 mol%) and AcOK (0.1 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7bg** was obtained as a yellow oil in 52% yield with 96% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 0.04H), 7.84 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.56-7.52 (m, 1H), 7.38-7.36 (m, 4H), 7.31-7.18 (m, 5H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.26-4.23 (m, 3H), 3.89-3.87 (m, 2H), 3.76 (t, *J* = 5.6 Hz, 2H), 2.72-2.48 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.4 (t, *J* = 29.5Hz), 161.1 (s), 141.7 (s), 140.9 (s), 135.9 (s), 132.8 (s), 129.1 (s), 128.8 (s), 128.8 (s), 128.5 (s), 127.7 (s), 127.4 (s), 125.0 (s), 121.1 (s), 112.8 (s), 75.1 (s), 69.4 (s), 68.1 (s), 68.0 (s), 57.4 (s), 53.7 (s), 50.5 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.50 (s, 1D); HRMS (ESI): m/z caled for $C_{28}H_{31}DClN_2O_3$ [$(M+H)^+$]: 480.2164, found: 480.2162.



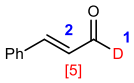

**3-Formyl rifamycin-*α*-*d*$_1$ (7bh)**

3-Formyl rifamycin (0.05 mmol), **5l** (20 mol%) and KOAc (0.1 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7bh** was obtained as a red solid in 60% yield with 97% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 13.75 (s, 1H), 13.19 (s, 1H), 12.66 (s, 1H), 12.33 (s, 1H), 10.67 (s, 0.03H), 6.62-6.49 (m, 2H), 6.24 (d, *J* = 12.7 Hz, 1H), 6.07 (dd, *J* = 15.0, 5.0 Hz, 1H), 5.16-5.09 (m, 1H), 4.94 (d, *J* = 10.6 Hz, 1H), 3.78 (d, *J* = 9.6 Hz, 1H), 3.62 (d, *J* = 4.8 Hz, 1H), 3.52-3.48 (m, 2H), 3.05 (s, 4H), 2.45-2.39 (m, 1H), 2.27 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 1.82 (s, 3H), 1.76-1.79 (m, 1H), 1.55 (dd, *J* = 9.8, 7.2 Hz, 1H), 1.36-1.41 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.67 (d, *J* = 6.9 Hz, 3H), -0.29 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.6 (s), 192.9-192.5 (m), 173.3 (s), 171.1 (s), 169.4 (s), 167.5 (s), 155.5 (s), 142.7 (s), 141.8 (s), 136.7 (s), 135.9 (s), 126.8 (s), 121.5 (s), 119.6 (s), 118.4 (s), 117.9 (s), 116.3 (s), 109.8 (s), 108.5 (s), 108.2 (s), 104.5 (s), 75.9 (s), 75.5 (s), 73.2 (s), 69.6 (s), 56.1 (s), 38.6 (s), 37.6 (s), 36.6 (s), 32.2 (s), 20.5 (s), 19.7 (s), 19.6 (s), 15.9 (s), 9.8 (s), 8.1 (s), 7.6 (s), 6.8 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 10.67 (s, 1D); HRMS (ESI): m/z caled for $C_{38}H_{46}DNNaO_{13}$ [$(M+Na)^+$]: 749.3008, found:749.3009.



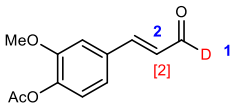
**2'-(2H-Tetrazol-5-yl)biphenyl-4-yl)methyl)-2-butyl-4-chloro-1H-imidazole-5-carbaldehyde-*α-d*$_1$ (7bi)**

2'-(2H-Tetrazol-5-yl)biphenyl-4-yl)methyl)-2-butyl-4-chloro-1H-imidazole-5-carbaldehyde (0.1 mmol), **5l** (20 mol%) and KOAc (0.2 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **7bi** was obtained as a white solid in 53% yield with 99% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 0.01H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.47 (s, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.63-1.55 (m, 2H), 1.34-1.24 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 178.2-177.4 (m), 155.3 (s), 154.9 (s), 143.2 (s), 140.7 (s), 139.2 (s), 135.3 (s), 131.3 (s), 130.8 (s), 129.6 (s), 128.2 (s), 126.7 (s), 124.1 (s), 122.9 (s), 48.0(s), 29.2 (s), 26.4 (s), 22.3 (s), 13.7 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.64 (s, 1D); HRMS (ESI): m/z caled for $C_{22}H_{21}DClN_6O$ [$(M+H)^+$]: 422.1606, found: 422.1605.



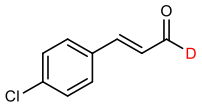

**(*E*)-Cinnamaldehyde-*1,2-d*$_{1,}$*d*$_2$ (10a)**

(*E*)-Cinnamaldehyde (0.25 mmol), **5p** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10a** was obtained as a yellow oil in 63% yield with 98% D-incorporation at position 1 and 5% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz,0.02H), 7.59-7.56 (m, 2H), 7.49 (d, *J* = 16.0 Hz, 1H), 7.46-7.43 (m, 3H), 6.73 (d, *J* = 16.0 Hz, 0.95H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.5 (t, *J* = 26.3), 152.8 (s), 134.0 (s), 131.3 (s), 129.1 (s), 128.5(s), 127.2 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.75 (s, 1D), 6.79 (s, 0.05D); HRMS (EI): m/z caled for $C_9H_7DO$ [$(M)^+$]: 133.0638, found: 133.0639.



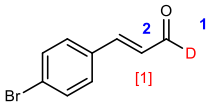

**(*E*)-4-Acetoxy-3-methoxycinnamaldehyde-*1,2-d*$_{1,}$*d*$_2$ (10b)**

(*E*)-4-Acetoxy-3-methoxycinnamaldehyde (0.25 mmol), **5p** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10b** was obtained as a brown solid in 40% yield with 95% D-incorporation at position 1 and 2% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.7 Hz, 0.05H), 7.44 (d, *J* = 15.9 Hz, 1H), 7.18-7.12 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 0.98H), 3.87 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.2 (t, *J* = 26.2 Hz), 168.7 (s), 151.9 (s), 151.6 (s), 142.2 (s), 133.0 (s), 128.7 (t, *J* = 3.6 Hz), 123.5 (s), 121.9 (s), 111.4 (s), 56.0 (d, *J* = 2.9 Hz), 20.7 (d, *J* = 2.1 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.73 (s, 1D), 6.72 (s, 0.02D); HRMS (EI): m/z caled for $C_{12}H_{11}DO_4$ [$(M)^+$]: 221.0798, found: 221.0780.



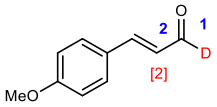

**(*E*)-4-Chlorocinnamaldehyde-*α-d*$_1$ (10c)**

(*E*)-4-Chlorocinnamaldehyde (0.25 mmol), **5p** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **10c** was obtained as a yellow solid in 40% yield with 97% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 7.6 Hz, 0.03H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 13.5 Hz, 1H), 7.41 (d, *J* = 6.2 Hz, 2H), 6.69 (d, *J* = 16.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.2 (t, *J* = 26.4 Hz), 151.1 (s), 137.3 (s), 132.5 (s), 129.6 (s), 129.5 (s), 128.9 (t, *J* = 3.8 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.75 (s, 1D); HRMS (EI): m/z caled for $C_9H_6DClO$ [$(M)^+$]: 167.0248, found: 167.0246.



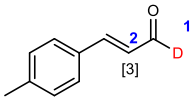

**(*E*)-4-Bromocinnamaldehyde-*1,2-d*$_{1,}$*d*$_2$ (10d)**

(*E*)-4-Bromocinnamaldehyde (0.25 mmol), **5p** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10d** was obtained as a brown solid in 33% yield with 97% D-incorporation at position 1 and 1% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 7.1 Hz, 0.03H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.45-7.37 (m, 3H), 6.70 (d, *J* = 16.0 Hz, 0.99H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.1 (t, *J* = 27.2 Hz), 151.1 (s), 132.9 (s), 132.4 (s), 129.8 (s), 129.0 (s), 125.7 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.76 (s, 1D), 6.76 (s, 0.01D); HRMS (EI): m/z caled for $C_9H_6DBrO$ [$(M)^+$]: 210.9743, found: 210.9744.



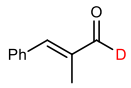

**(E)-4-Methoxycinnamaldehyde-*1,2-d*$_{1,}$*d*$_2$ (10e)**

(E)-4-Methoxycinnamaldehyde (0.25 mmol), **5p** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10e** was obtained yellow oil in 41% yield with 99% D-incorporation at position 1 and 2% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.8 Hz, 0.01H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 15.9 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 15.9 Hz, 0.98H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.5 (t, *J* = 26.1 Hz), 162.2 (s), 152.7 (s), 130.4 (s), 126.8 (s), 126.5 (t, *J* = 3.7 Hz), 114.6 (s), 55.5 (d, *J* = 4.2 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.68 (s, 1D), 6.65 (s, 0.02D); HRMS (EI): m/z caled for $C_{10}H_9DO_2$ [$(M)^+$]: 163.0744, found: 163.0743.



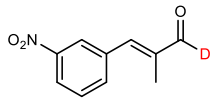
**(*E*)-4-Methylcinnamaldehyde-*α*-*d*$_1$ (10f)**

(*E*)-4-Methylcinnamaldehyde (0.25 mmol), **5p** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10f** was obtained as a yellow oil in 57% yield with 98% D-incorporation at position 1 and 3% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 7.8 Hz, 0.02H), 7.48-7.43 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.6 (t, *J* = 26.2 Hz), 153.0 (s), 142.0 (s), 131.3 (s), 129.9 (s), 128.6 (s), 127.7 (t, *J* = 3.8 Hz), 21.6 (d, *J* = 1.7 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.72 (s, 1D), 6.72 (s, 0.03D); HRMS (EI): m/z caled for $C_{10}H_9DO$ [$(M)^+$]: 147.0794, found: 147.0795.



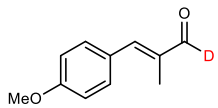

**alpha-Methylcinnamaldehyde-*α*-*d*$_1$ (10g)**

alpha-Methylcinnamaldehyde (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **10g** was obtained as a colorless oil in 95% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 0.02H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38-7.27 (m, 3H), 7.16 (s, 1H), 1.98 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.2 (t, *J* = 26.5 Hz), 149.8 (s), 138.3 (t, *J* = 3.5 Hz), 135.2 (s), 130.1 (s), 129.6 (s), 128.7 (s), 10.9 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.55 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_9DO$ [$(M)^+$]: 147.0794, found: 147.0795.




**(*E*)-2-Methyl-3-(3-nitrophenyl)acrylaldehyde-*α*-*d*$_1$ (10h)**

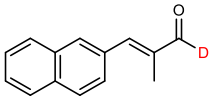
(*E*)-2-Methyl-3-(3-nitrophenyl)acrylaldehyde (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10h** was obtained as a white solid in 41% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 0.02H), 8.38 (s, 1H), 8.27-8.25 (m, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 2.11 (d, *J* = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.4 (t, *J* = 26.7 Hz), 148.5 (s), 146.0 (s), 140.6 (t, *J* = 3.6 Hz), 136.7 (s), 135.3 (s), 129.8 (s), 124.3 (s), 123.9 (s), 10.9 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.67 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_8DNO_3$ [$(M)^+$]: 192.0645, found: 192.0646.




**(*E*)-4-Methoxy-2-methylcinamaldehyde-*α*-*d*$_1$ (10i)**

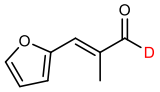
(*E*)-4-Methoxy-2-methylcinamaldehyde (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5

mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10i** was obtained as a yellow oil in 73% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 0.02H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.19 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.07 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.2 (t, *J* = 26.4 Hz), 160.8 (s), 149.9 (s), 136.1 (t, *J* = 3.5 Hz), 132.1 (s), 128.0 (s), 114.2 (s), 55.4 (d, *J* = 2.7 Hz), 10.9 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.57 (s, 1D); HRMS (EI): m/z caled for $C_{11}H_{11}DO_2$ [$(M)^+$]: 177.0900, found: 177.0901.



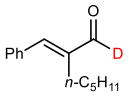

**(*E*)-2-Methyl-3-(naphthalen-2-yl)acrylaldehyde-*α*-*d*$_1$ (10j)**

(*E*)-2-Methyl-3-(naphthalen-2-yl)acrylaldehyde (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10j** was obtained as a white solid in 85% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 0.01H), 8.00 (s, 1H), 7.90-7.84 (m, 3H), 7.63 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.58-7.52 (m, 2H), 7.41 (s, 1H), 2.18 (d, *J* = 1.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.2 (t, *J* = 26.5 Hz), 149.8 (s), 138.4 (t, *J* = 3.5 Hz), 133.5 (s), 133.1 (s), 132.7 (s), 130.4 (s), 128.7 (s), 128.4 (s), 127.8 (s), 127.4 (s), 126.8 (s), 126.8 (s), 11.1 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.69 (s, 1D); HRMS (EI): m/z caled for $C_{14}H_{11}DO$ [$(M)^+$]: 197.0951, found: 197.0952.




**2-Methyl-3-(2-furyl)propenal-*α*-*d*$_1$ (10k)**

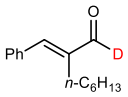
2-Methyl-3-(2-furyl)propenal (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **10k** was obtained as a yellow oil in 75% yield with 97% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 0.03H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.00 (s, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 6.54 (dd, *J* = 3.5, 1.8 Hz, 1H), 2.07 (d, *J* = 1.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.9 (t, *J* = 26.5 Hz), 151.6 (s), 145.3 (s), 135.4 (s), 134.9 (t, *J* = 3.6 Hz), 116.5 (s), 112.7 (s), 10.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.48 (s, 1D); HRMS (EI): m/z caled for $C_8H_7DO_2$ [$(M)^+$]: 137.0587, found: 137.0589.




**α-Amylcinnamaldehyde-*α*-*d*$_1$ (10l)**

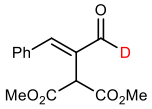
α-Amylcinnamaldehyde (0.25 mmol), **5l** (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **10l** was obtained as a

colorless oil in 96% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 0.01H), 7.51-7.36 (m, 5H), 7.20 (s, 1H), 2.54-2.50 (m, 2H), 1.54-1.45 (m, 2H), 1.39-1.30 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.3 (t, *J* = 26.4 Hz), 149.7 (s), 143.3 (t, *J* = 3.2 Hz), 135.0 (s), 129.7 (s), 129.5 (s), 128.8 (s), 32.1 (s), 28.0 (s), 24.7 (s), 22.4 (s), 14.0 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.52 (s, 1D); HRMS (EI): m/z caled for $C_{14}H_{17}DO$ [$(M)^+$]: 203.1420, found: 203.1421.



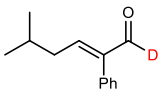

**α-Hexylcinnamaldehyde-*α-d₁* (10m)**

Hexylcinnamaldehyde (0.25 mmol), **5l** (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **10m** was obtained as a colorless oil in 92% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 0.01H), 7.51-7.36 (m, 5H), 7.20 (s, 1H), 2.55-2.50 (m, 2H), 1.53-1.44 (m, 2H), 1.42-1.25 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.3 (t, *J* = 26.4), 149.7 (s), 143.3 (t, *J* = 2.9 Hz), 135.0 (s), 129.7 (s), 129.5 (s), 128.8 (s), 31.5 (s), 29.6 (s), 28.3 (s), 24.8 (s), 22.6 (s), 14.1 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.57 (s, 1D); HRMS (EI): m/z caled for $C_{15}H_{19}DO$ [$(M)^+$]: 217.1577, found: 217.1578.




**(*E*)-Dimethyl 2-(3-oxo-1-phenylprop-1-en-2-yl)malonate-*α-d₁* (10n)**

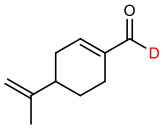
(*E*)-Dimethyl 2-(3-oxo-1-phenylprop-1-en-2-yl)malonate (0.25 mmol), **5l** (20 mol%), and KOAc (0.25 mmol, 1equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10n** was obtained as a yellow oil in 61% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 0.01H), 7.66 (s, 1H), 7.47-7.41 (m, 5H), 4.75 (s, 1H), 3.70 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.3 (t, *J* = 27.0 Hz), 167.6 (s), 152.7 (s), 135.0 (t, *J* = 3.0 Hz), 133.4 (s), 130.4 (s), 129.2 (s), 129.0 (s), 52.9 (d, *J* = 1.7 Hz), 49.1 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.65 (s, 1D); HRMS (EI): m/z caled for $C_{14}H_{13}DO_5$ [$(M)^+$]: 263.0904, found: 263.0903.




**5-Methyl-2-phenyl-2-hexenal-*α-d₁* (10o)**

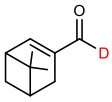
5-Methyl-2-phenyl-2-hexenal (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **10o** was obtained as a colorless oil in 80% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 0.02H), 7.46-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.18-7.14 (m, 2H), 6.77 (t, *J* = 7.5 Hz, 1H),

2.30-2.24 (m, 2H), 1.90-1.78 (m, 1H), 0.93 (d, $J$ = 6.7 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.4 (t, $J$ = 26.6 Hz), 155.6 (s), 144.6 (t, $J$ = 3.4 Hz), 132.8 (s), 129.5 (s), 128.2 (s), 127.9 (s), 38.6 (s), 28.5 (s), 22.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.67 (s, 1D); HRMS (EI): m/z caled for $C_{13}H_{15}DO$ [$(M)^+$]: 189.1264, found: 189.1265.



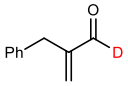
**(-)-Perillaldehyde-*α-d*$_1$ (10p)**

(-)-Perialdehyde (0.25 mmol), **5l** (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **10p** was obtained as a colorless oil in 75% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 0.02H), 6.82-6.81 (m, 1H), 4.77-4.76 (m, 1H), 4.72 (s, 1H), 2.49-2.37 (m, 2H), 2.26-2.18 (m, 2H), 2.13-2.06 (m, 1H), 1.92-1.87 (m, 1H), 1.74 (s, 3H), 1.48-1.38 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.6 (t, $J$ = 26.2 Hz), 150.6 (s), 148.3 (s), 141.2 (t, $J$ =3.5 Hz), 109.5 (s), 40.7 (s), 31.7 (s), 26.3 (s), 21.5 (s), 20.7 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.42 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_{13}DO$ [$(M)^+$]: 151.1107, found: 151.1109.



**(*1R*)-Myrtenal-*α-d*$_1$ (10q)**

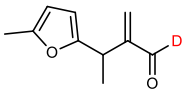
(*1R*)-Myrtenal (0.25 mmol), **5l** (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10q** was obtained as a colorless oil in 67% yield with 97% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 0.03H), 6.72-6.70 (m, 1H), 2.86 (t, $J$ = 5.6 Hz, 1H), 2.62-2.46 (m, 3H), 2.20-2.17 (m, 1H), 1.33 (s, 3H), 1.05 (d, $J$ = 9.2 Hz, 1H), 0.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.9 (t, $J$ = 26.3 Hz), 151.5 (t, $J$ = 3.6 Hz), 147.7 (s), 40.7 (s), 38.0 (s), 37.6 (s), 33.0 (s), 31.1 (s), 25.7 (s), 20.9 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.41 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_{13}DO$ [$(M)^+$]: 151.1107, found: 151.1109.



**2-Benzylacrylaldehyde-*α-d*$_1$ (10r)**

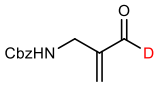
2-Benzylacrylaldehyde (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **10r** was obtained as a yellow oil in 50% yield with 96% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 0.04H), 7.33-7.17 (m, 5H), 6.11 (s, 1H), 6.07 (s, 1H), 3.57 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.7 (t, $J$ = 26.7 Hz), 149.7 (t, $J$ = 3.7 Hz), 138.1 (s), 135.2 (s), 129.2 (s), 128.6 (s),

126.5 (s), 34.1 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.65 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_9DO$ [$(M)^+$]: 147.0794, found: 147.0796.



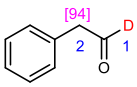

**2-Methylene-3-(5-methylfuran-2-yl)butanal-*α*-*d*$_1$ (10s)**

2-Methylene-3-(5-methylfuran-2-yl)butanal (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10s** was obtained as a yellow oil in 50% yield with 98% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 0.02H), 6.18 (s, 1H), 6.05 (s, 1H), 5.94 (d, *J* = 2.9 Hz, 1H), 5.86-5.85 (m, 1H), 4.04 (q, *J* = 7.1 Hz, 1H), 2.24 (s, 3H), 1.37 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.2 (t, *J* = 26.7 Hz), 154.7 (s), 152.4 (t, *J* = 3.7 Hz), 151.0 (s), 134.3 (s), 106.1 (s), 105.8 (s), 31.2 (s), 18.3 (s), 13.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.62 (s, 1D); HRMS (EI): m/z caled for $C_{10}H_{11}DO_2$ [$(M)^+$]: 165.0900, found: 165.0902.



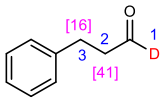

**Benzyl (2-formylallyl)carbamate-*α*-*d*$_1$ (10t)**

Benzyl (2-formylallyl)carbamate (0.25 mmol), **5l** (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **10t** was obtained as a yellow solid in 42% yield with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 0.01H), 7.38-7.30 (m, 5H), 6.44 (s, 1H), 6.12 (s, 1H), 5.21 (s, 1H), 5.10 (s, 2H), 4.00 (d, *J* = 6.3 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 193.7 (t, *J* = 24.5 Hz), 156.3 (s), 146.0 (s), 136.3 (s), 135.0 (s), 128.6 (s), 128.2 (s), 128.1 (s), 66.9 (s), 39.3 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.60 (s, 1D); HRMS (EI): m/z caled for $C_{12}H_{12}DNO_3$ [$(M)^+$]: 220.0958, found: 220.0959.



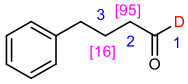

**Phenylacetaldehyde-*1,2*-*d*$_1$,*d*$_2$ (12a)**

Phenylacetaldehyde (0.5 mmol), **5q** (20 mol%) and KOAc (1.0 mmol, 2 equiv)was dis solved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **12a** was ob tained as a colorless oil in 48% yield with 98% D-incorporation at position 1 and 9 4% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 0.02H), 7.3 8 (t, *J* = 7.2 Hz, 2H), 7.34-7.29 (m, 1H), 7.25-7.21 (m, 2H), 3.68-3.66 (m, 0.12H); $^{1}$ $^{3}$C NMR (100 MHz, $CDCl_3$) δ 199.3 (t, *J* = 26.9 Hz), 131.8 (s), 129.6 (s), 129.0 (s) 127.4 (s), 49.9 (d, *J* = 12.6 Hz); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.74 (s, 1D), 3.62 (s, 2D); HRMS (EI): m/z caled for $C_8H_5D_3O$ [$(M)^+$]: 123.0763, found: 123.0764.



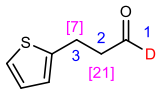

**3-Phenylpropionaldehyde-*1,2,3-d*$_1$,*d*$_2$,*d*$_2$ (12b)**

3-Phenylpropionaldehyde (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 30 °C for 12 hours. **12b** was obtained as a colorless oil in 51% yield with 98% D-incorporation at position 1, 41% D-incorporation at position 2 and 16% D-incorporation at position 3. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, *J* = 1.2 Hz, 0.02H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.29-7.21 (m, 3H), 2.99 (t, *J* = 7.4 Hz, 1.67H), 2.83-2.75 (m, 1.18H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.3 (t, *J* = 26.2 Hz), 140.5 (s), 128.7 (s), 128.4 (s), 126.3 (s), 45.1 (t, *J* = 3.7 Hz), 28.1 (d, *J* = 5.7 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.78 (s, 1D), 2.86 (s, 0.35D), 2.67 (s, 0.82D); HRMS (EI): m/z caled for $C_9H_9DO$ [$(M)^+$]: 135.0794, Found: 135.0799; $C_9H_8D_2O$ [$(M)^+$]: 136.0857, found: 136.0858; $C_9H_5D_5O$ [$(M)^+$]: 139.1045, found: 139.1049.




**Benzenebutanal-*1,2,3-d*$_1$,*d*$_2$,*d*$_2$ (12c)**

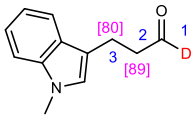
Benzenebutanal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **12c** was obtained as a colorless oil in 67% yield with 99% D-incorporation at position 1, 95% D-incorporation at position 2 and 16% D-incorporation at position 3. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 0.01H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24-7.16 (m, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.45-2.42 (m, 0.09H), 1.96 (t, *J* = 7.5 Hz, 1.68H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.2 (t, *J* = 25.8 Hz), 141.3 (s), 128.5 (s), 126.1 (s), 42.2 (s), 34.9 (d, *J* = 9.1 Hz), 23.5 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.80 (s, 1D), 2.43 (s, 1.92D), 1.94 (s, 0.37D); HRMS (EI): m/z caled for $C_{10}H_9D_3O$ [$(M)^+$]: 151.1076, Found: 151.1090; $C_{10}H_8D_4O$ [$(M)^+$]: 152.1139, Found: 152.1140; $C_{10}H_7D_5O$ [$(M)^+$]: 153.1202, found: 153.1190.




**3-Thienylpropionaldehyde-*1,2-d*$_1$,*d*$_2$ (12d)**

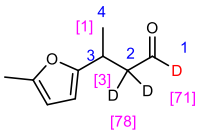
3-Thienylpropionaldehyde (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 30 °C for 12 hours. **12d** was obtained as a colorless oil in 69% yield with 98% D-incorporation at position 1, 21% D-incorporation at position 2 and 7% D-incorporation at position 3. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 0.02H), 7.13 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.82 (d, *J* = 3.3 Hz, 1H), 3.18 (t, *J* = 7.2 Hz, 1.86H), 2.84 (t, *J* = 7.3 Hz, 1.50H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.7 (t, *J* = 26.4), 143.0 (s), 127.0 (s), 124.8 (s), 123.6 (s), 45.2 (t, *J* = 3.7), 22.3 (d, *J* = 6.0 Hz); $^2$H

NMR (77 MHz, $CHCl_3$) δ 9.87 (s, 1D), 3.15 (s, 0.08D), 2.82 (s, 0.38D); HRMS (EI): m/z caled for $C_7H_7DOS$ [$(M)^+$]: 141.0359, found:141.0360.



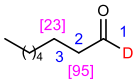

**3-(1-Methyl-1H-3-indolyl)propanal-*1,2,3-d*$_1$,*d*$_2$,*d*$_2$ (12e)**

3-(1-Methyl-1H-3-indolyl)propanal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **12e** was obtained as a yellow solid in 48% yield with 95% D-incorporation at position 1, 89% D-incorporation at position 2 and 80% D-incorporation at position 3. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 0.05H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.23-7.19 (m, 1H), 7.13-7.07 (m, 1H), 6.81 (s, 1H), 3.70 (s, 3H), 3.06 (t, *J* = 6.5 Hz, 0.42H), 2.80-2.75 (m, 0.24H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.6 (t, *J* = 26.2 Hz), 137.1 (s), 127.5 (s), 126.4 (s), 121.8 (s), 118.9 (s), 118.7 (s), 113.0 (s), 109.3 (s), 43.4 (m), 32.6 (s), 17.4 (m); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.88 (s, 1D), 3.07 (s, 1.78D), 2.80 (s, 1.73D); HRMS (EI): m/z caled for $C_{12}H_8D_5NO$ [$(M)^+$]: 192.1311, found: 192.1310.




**3-(5-Methyl-2-furanyl)butanal-*1,2,3,4-d*$_1$,*d*$_2$,*d*$_1$,*d*$_3$ (12f)**

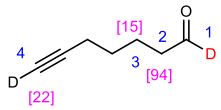
3-(5-Methyl-2-furanyl)butanal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **12f** was obtained as a colorless oil in 73% yield with 97% D-incorporation at position 1, 71% and 78% D-incorporation at position 2, 3% D-incorporation at position 3 and 1% D-incorporation at position 4. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 0.03H), 5.87 (d, *J* = 2.9 Hz, 1H), 5.85-5.84 (m, 1H), 3.40-3.33 (m, 1H), 2.79-2.73 (m, 0.32H), 2.58-2.52 (m, 0.24H), 2.24 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.9-201.1 (m), 156.4 (s), 150.8 (s), 105.8 (s), 104.8 (s), 49.2-45.8 (m), 27.8 (d, *J* = 5.1 Hz), 19.0 (s), 13.5 (d, *J* = 1.3 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.81 (s, 1D), 3.34 (s, 0.03D), 2.75 (s, 0.67D), 2.55 (s, 0.84D), 1.28 (s, 0.04D); HRMS (EI): m/z caled for $C_9H_9D_3O_2$: 155.1026, found: 155.1028.




**Octanal-*1,2,3-d*$_1$,*d*$_2$,*d*$_2$ (12g)**

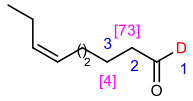
Octanal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **12g** was obtained as a colorless oil in 71% yield with 96% D-incorporation at position 1, 95% D-incorporation at position 2 and

23% D-incorporation at position 3. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 0.04 H), 2.41-2.20 (m, 0.1H), 1.58 (d, *J* = 6.5 Hz, 1.54 H), 1.35-1.22 (m, 8H), 0.86 (dd, *J* = 8.8, 4.9 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.9 (t, *J* = 26.6 Hz), 43.1 (m), 31.6 (s), 29.1(s), 29.0 (s), 22.6 (s), 21.9 (s), 14.0 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.74 (s, 1D), 2.34 (s, 2.00D), 1.54 (s, 0.34D); HRMS (EI): m/z caled for $C_8H_{13}D_3O$ [$(M)^+$]: 131.1389, found: 131.1385.



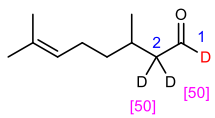

**6-Heptynal-*1,2,3,4-d$_1$,d$_2$,d$_2$,d$_1$* (12h)**

6-Heptynal (0.5 mmol), **5q** (10 mol%), $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. **12h** was obtained as a colorless oil in 64% yield with 98% D-incorporation at position 1, 89% D-incorporation at position 2, 16% D-incorporation at position 3 and 23% D-incorporation at position 4. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 0.02H), 2.48-2.41 (m, 0.21H), 2.26-2.18 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 0.64H), 1.78-1.70 (m, 1.74H), 1.61-1.52 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.1 (t, *J* = 23.5 Hz), 83.8 (s), 68.8 (s), 27.7 (s), 22.7 (s), 20.9 (s), 18.2 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.76 (s, 1D), 2.39 (s, 2.00D), 1.91 (s, 0.12D), 1.69 (s, 0.29D); HRMS (EI): m/z caled for $C_7H_9DO$ [$(M)^+$]: 111.0794, Found: 111.0793; $C_7H_7D_3O$ [$(M)^+$]: 113.0920, found: 113.0922.




**Cis-6-Nonenal-1,2-*d$_1$,d$_2$* (12i)**

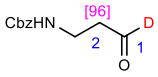
Cis-6-Nonenal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **12i** was obtained as a colorless oil in 72% yield with 96% D-incorporation at position 1, 73% D-incorporation at position 2 and 4% D-incorporation at position 3. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 0.04H), 5.41-5.34 (m, 1H), 5.33-5.26 (m, 1H), 2.42 (t, *J* = 7.4 Hz, 0.5H), 2.09-1.96 (m, 4H), 1.67-1.58 (m, 2H), 1.42-1.33 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.6 (d, *J* = 52.2 Hz), 132.2 (s), 128.4 (s), 43.6 (s), 29.1 (t, *J* = 7.6 Hz), 26.8 (s), 21.6-21.4 (m), 20.5 (s), 14.3 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.73 (s, 1D), 2.33 (s, 1.62D), 1.55 (s, 0.09D); HRMS (EI): m/z caled for $C_9H_{14}D_2O$ [$(M)^+$]: 142.1327, Found: 142.1322; $C_9H_{13}D_3O$ [$(M)^+$]: 143.1389, found: 143.1393.




**Citronellal-*1,2-d$_1$,d$_2$* (12j)**

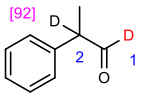
Citronellal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **12j** was obtained as a colorless oil in

78% yield with 96% D-incorporation at position 1 and 50% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 0.04H), 5.10-5.04 (m, 1H), 2.38 (dd, *J* = 15.9, 5.5 Hz, 0.50H), 2.21 (dd, *J* = 16.1, 8.0 Hz, 0.50H), 2.07-1.92 (m, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 1.40-1.21 (m, 2H), 0.96 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.8 (t, *J* = 25.8 Hz), 131.8 (s), 124.0 (s), 50.8 (t, *J* = 3.5 Hz), 36.9 (d, *J* = 4.3 Hz), 27.7 (d, *J* = 9.8 Hz), 25.7 (s), 25.4 (s), 19.8 (d, *J* = 6.5 Hz), 17.7 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.74 (s, 1D), 2.33 (s, 0.54D), 2.15 (s, 0.55D); HRMS (EI): m/z caled for $C_{10}H_{17}DO$ $[(M)^+]$: 155.1420, Found: 155.1424; $C_{10}H_{16}D_2O$ $[(M)^+]$: 156.1483, Found: 156.1474; $C_{10}H_{15}D_3O$ $[(M)^+]$: 157.1546, found: 157.1547.



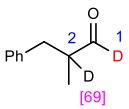

**Benzyl-4-oxobutanoate-*1,2-d*$_1$,*d*$_2$ (12k)**

Benzyl-4-oxobutanoate (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv), was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **12k** was obtained yellow solid in 55% yield with 99% D-incorporation at position 1 and 96% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 0.01H), 7.38-7.31 (m, 5H), 5.17 (s, 1H), 5.08 (s, 2H), 3.47 (d, *J* = 6.1 Hz, 2H), 2.70 (s, 0.08H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.4-200.7 (m), 156.4 (s), 136.4 (s), 128.6 (s), 128.2 (s), 128.1 (s), 66.8 (s), 43.9 (s), 34.4 (s), 29.7 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.84 (s, 1D), 2.72 (s, 1.91D), 1.55 (s, 0.09D); HRMS (EI): m/z caled for $C_{11}H_{10}D_3NO_3$ $[(M)^+]$: 210.1084, found: 210.1085.




**2-Phenylpropionaldehyde-*1,2-d*$_1$,*d*$_1$ (12l)**

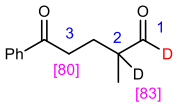
2-Phenylpropionaldehyde (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 30 °C for 12 hours. **12l** was obtained as a colorless oil in 73% yield with 98% D-incorporation at position 1 and 92% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 0.02H), 7.41-7.30 (m, 3H), 7.23-7.20 (m, 2H), 3.63 (q, *J* = 7.0 Hz, 0.08H), 1.45 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.9 (t, *J* = 26.6 Hz), 137.7 (s), 129.1 (s), 128.3 (s), 127.6 (s), 52.7-52.1 (m), 14.5 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.71 (s, 1D), 3.61 (s, 0.93D); HRMS (EI): m/z caled for $C_9H_8D_2O$ $[(M)^+]$: 136.0857, found: 136.0856.




**2-Methyl-3-phenylpropionaldehyde-*1,2-d*$_1$,*d*$_1$ (12m)**

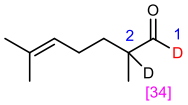
2-Methyl-3-phenylpropionaldehyde (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 30 °C for 12 hours. **12m** was

obtained as a colorless oil in 82% yield with 99% D-incorporation at position 1 and 69% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.3 Hz, 0.01H), 7.34-7.28 (m, 2H), 7.25-7.16 (m, 3H), 3.12-3.06 (m, 1H), 2.72-2.65 (m, 0.31H), 2.65-2.58 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.1 (td, *J* = 25.8, 9.1 Hz), 138.9 (d, *J* = 1.2 Hz), 129.1 (s), 128.6 (s), 126.4 (s), 47.9 (t, *J* = 3.5 Hz), 36.6 (d, *J* = 6.8 Hz), 13.2 (d, *J* = 7.5 Hz); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.76 (s, 1D), 2.68 (s, 0.75D); HRMS (EI): m/z caled for $C_{10}H_{10}D_2O$ [$(M)^+$]: 150.1014, found: 150.1018.



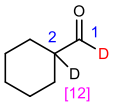

**2-Methyl-5-oxo-5-phenylpentanal-*1,2,4-d*$_1$,*d*$_1$,*d*$_2$ (12n)**

2-Methyl-5-oxo-5-phenylpentanal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **12n** was obtained as a colorless oil in 72% yield with 98% D-incorporation at position 1, 83% D-incorporation at position 2 and 80% D-incorporation at position 3. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 0.02H), 7.93-7.91 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 3.04-2.94 (m, 0.40H), 2.48-2.43 (m, 0.17H), 2.10 (dd, *J* = 14.2, 7.0 Hz, 1H), 1.85-1.78 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.5-203.9 (m), 199.4 (t, *J* = 6.2 Hz), 136.7 (s), 133.2 (s), 128.6 (s), 128.0 (s), 45.5 (t, *J* = 3.3 Hz), 35.5 (s), 24.6 (s), 13.5 (d, *J* = 7.9 Hz); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.63 (s, 1D), 2.94 (s, 1.68D), 2.41 (s, 0.84D); HRMS (EI): m/z caled for $C_{12}H_{10}D_4O_2$ [$(M)^+$]: 194.1245, found: 194.1275.



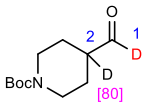

**2,6-Dimethyl-5-heptenal-*1,2-d*$_1$,*d*$_1$ (12o)**

2,6-Dimethyl-5-heptenal (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 50 °C for 12 hours. **12o** was obtained as a colorless oil in 64% yield with 98% D-incorporation at position 1 and 34% D-incorporation at position 2. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 1.8 Hz, 0.02H), 5.08-5.04 (m, 1H), 2.43 (t, *J* = 7.4 Hz, 0.24H), 2.36-2.29 (m, 0.57H), 2.23 (dd, *J* = 14.6, 7.3 Hz, 0.25H), 2.01 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.78-1.69 (m, 1H), 1.66 (s, 3H), 1.57 (s, 3H), 1.42-1.33 (m , 1H) 1.07 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.9 (t, *J* = 25.8 Hz), 132.7 (s), 123.4 (s), 45.6 (t, *J* = 3.3 Hz), 30.6 (s), 25.7 (s), 25.3 (s), 17.7 (s), 13.2 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 9.62 (s, 1D), 2.31 (s, 0.33D); HRMS (EI): m/z caled for $C_9H_{15}DO$ [$(M)^+$]: 141.1264, found: 141.1243.



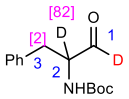

**Cyclohexanaldehyde-*1,2-d*$_1$,*d*$_1$ (12p)**

Cyclohexanaldehyde (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 30 °C for 12 hours. **12p** was obtained as a colorless oil in 70% yield with 99% D-incorporation at position 1 and 12% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 0.01H), 2.24-2.18 (m, 0.80H), 1.89-1.84 (m, 2H), 1.74-1.70 (m, 2H), 1.65-1.60 (m, 1H), 1.39-1.21 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.7 ((t, *J* = 25.8 Hz), 49.8 (t, *J* = 3.3 Hz), 25.9 (s), 25.9 (s), 25.0 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.64 (s, 1D), 2.22 (s, 0.03D); HRMS (EI): m/z caled for $C_7H_{11}DO$ [$(M)^+$]: 113.0951, found $C_7H_{11}DO$: 113.0952.



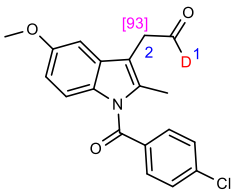

**1-(*tert*-Butoxycarbonyl)-4-formylpiperidine-*1,2-d$_1$,d$_1$* (12q)**

1-(*tert*-butoxycarbonyl)-4-formylpiperidine (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 30 °C for 12 hours. **12q** was obtained as a white solid in 76% yield with 99% D-incorporation at position 1, and 80% D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 0.01H), 3.97 (d, *J* = 8.2 Hz, 2H), 2.91 (t, *J* = 11.5 Hz, 2H), 2.42-2.37 (m, 0.19H), 1.86 (d, *J* = 10.7 Hz, 2H), 1.57-1.50 (m, 2H), 1.44 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.7 (t, *J* = 26.0 Hz), 154.7 (s), 79.7 (s), 47.8 (t, *J* = 3.5 Hz), 42.8 (m), 28.40 (s), 25.1 (d, *J* = 10.1 Hz); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.69 (s, 1D), 2.39 (s, 0.90D); HRMS (EI): m/z caled for $C_{11}H_{17}D_2NO_3$ [$(M)^+$]: 215.1490, found: 215.1489.



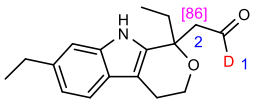

***tert*-Butyl N-(1-benzyl-2-oxoethyl)carbamate-*1,2,3-d$_1$,d$_1$,d$_2$* (12r)**

*tert*-Butyl N-(1-benzyl-2-oxoethyl)carbamate (0.5 mmol), **5q** (10 mol%) and $NaHCO_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 40 °C for 12 hours. Compound **12r** was obtained as a colorless oil in 86% yield with 98% D-incorporation at position 1, 82% D-incorporation at position 2. and 2% D-incorporation at position 3. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 0.02H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.31-7.27 (m, 1H), 7.21 (d, *J* = 6.9 Hz, 2H), 5.13 (s, 1H), 4.46 (d, *J* = 6.7 Hz, 0.15H), 3.15 (s, 2H), 1.48 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 199.2 (t, *J* = 27.5 Hz), 155.4 (s), 135.8 (s), 129.3 (s), 128.8 (s), 127.1 (s), 80.2 (s), 60.7 (m), 35.4 (s), 28.3 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.66 (s, 1D), 4.40 (s, 0.83D), 3.09 (s, 0.04D); HRMS (EI): m/z caled for $C_{13}H_{17}DNO_2$ [$(M\text{-}CDO)^+$]: 221.1400, found: 221.1401.



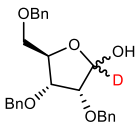

**2-(1-(4-Chlorobenzoyl)-5-methoxy-2-Methyl-1H-indol-3-yl)acetaldehyde-*1,2-d*$_1$,*d*$_2$ (12s)**

2-(1-(4-Chlorobenzoyl)-5-methoxy-2-Methyl-1H-indol-3-yl)acetaldehyde **11s** (0.1 mmol), **5q** (20 mol%) and AcOK (0.1 mmol, 1 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 ml) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 $^oC$ for 12 hours. **12s** was obtained as a tan solid in 60% yield with 99% D-incorporation at position 1 and 93% D-incorporation at position 2. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 0.01H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.87-6.84 (m, 2H), 6.69 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 0.14H), 2.38 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 197.8 (t, *J* = 26.8 Hz), 168.3 (s), 156.2 (s), 139.5 (s), 136.5 (s), 133.7 (s), 131.2 (s), 130.9 (s), 130.6 (s), 129.2 (s), 115.1 (s), 111.9 (s), 109.9 (s), 100.8 (s), 55.7 (s), 38.8 (m), 13.4 (s); $^2H$ NMR (77 MHz, $CHCl_3$) δ 9.72 (s, 1D), 3.68 (s, 1.78D); HRMS (ESI): m/z caled for $C_{19}H_{14}D_3ClNO_3$ [$(M+H)^+$]: 345.1085, found: 345.1089.




**2-(1,7-Diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetaldehyde-*1,2-d*$_1$,*d*$_2$ (12t)**

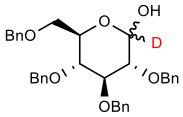
2-(1,8-Diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetaldehyde **11t** (0.1 mmol), **5q** (20 mol%) and AcOK (0.2 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **12t** was obtained liquid in 52% yield with 99% D-incorporation at position 1 and 86% D-incorporation at position 2. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 0.01H), 8.37 (s,1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 1H), 4.08-3.96 (m, 2H), 3.03 (s, 0.23H), 2.91-2.79 (m, 4H), 2.13-2.08 (m, 1H), 2.00-1.91 (m, 1H), 1.37 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 202.5 (t, *J* = 26.5 Hz,), 135.3 (s), 134.7 (s), 126.8 (s), 126.3 (s), 120.7 (s), 119.9 (s), 116.1 (s), 108.9 (s), 74.9 (s), 60.7 (s), 51.0 (d, *J* = 14.7 Hz), 31.2 (s), 24.1 (s), 22.4 (s), 13.9 (s), 7.8 (s); $^2H$ NMR (77 MHz, $CHCl_3$) δ 9.79 (s, 1D), 3.03 (s, 1.61D); HRMS (ESI): m/z caled for $C_{17}H_{18}D_3NO_2$ [$(M+H)^+$]: 275.1839, found: 275.1841.




**2,3,5-Tri-O-benzyl-α,β-D-ribofuranose-*1-d*$_1$ (12u)**

2,3,5-tri-O-benzyl-α,β-D-ribofuranose **11u** (0.1 mmol), **5af** (20 mol%), AcOK (0.1 mmol, 1 equiv) and $CD_3COOD$ (0.4 mmol, 4 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 80 °C for 12 hours. **12u** was obtained as a yellow oil in 55% yield with 95%

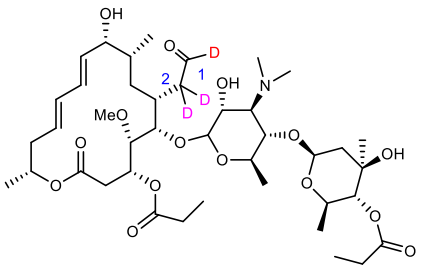
D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 15H), 5.34 (t, *J* = 9.7 Hz, 0.05H), 4.73-4.39 (m, 6H), 4.38-4.34 (m, 1H), 4.33-4.28 (m, 1H), 4.22 (dd, *J* = 6.7, 4.7 Hz, 1H), 4.18 (s, 1H), 4.00-3.95 (m, 2H), 3.85 (d, *J* = 4.6 Hz, 1H), 3.66 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.51-3.43 (m, 2H), 3.36 (s, 1H). $^{13}$C NMR (150 MHz, $CDCl_3$): **iso1**: δ 137.9 (s), 137.5 (s), 137.5 (s), 128.5 (s), 128.5 (s), 128.5 (s), 128.4 (s), 128.0 (s), 128.0 (s), 128.0 (s), 127.9 (s), 127.9 (s), 127.9 (s), 127.8 (s), 127.7 (s), 127.6 (s), 96.0 (t, *J* = 26.4 Hz,), 81.0 (s), 77.7 (s), 77.7 (s), 73.5 (s), 72.8 (s), 72.5 (s), 70.0 (s); **iso2**: δ 137.8 (s), 137.7 (s), 137.3 (s), 128.5 (s), 128.5 (s), 128.5 (s), 128.4 (s), 128.0 (s), 128.0 (s), 128.0 (s), 127.9 (s), 127.9 (s), 127.9 (s), 127.8 (s), 127.7 (s), 127.6 (s), 100.0 (t, *J* = 25.8 Hz), 80.9 (s), 80.7 (s), 77.2 (s), 72.5 (s), 72.3 (s), 69.4 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 5.33 (s, 1D); HRMS (ESI): m/z caled for $C_{26}H_{27}DNaO_5$ [$(M+Na)^+$]: 444.1897, found: 444.1898.




**2,3,4,6-*tetra*-*O*-Benzyl-α,β-D-glucopyranose-*1*-$d_1$ (12v)**

2,3,4,6-*tetra*-*O*-benzyl-α,β-D-glucopyranose **11v** (0.1 mmol), **5af** (40 mol%), AcOK (0.2 mmol, 2 equiv) and $CD_3COOD$ (0.8 mmol, 8 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 120 ºC for 12 hours. **12v** was obtained as a white solid in 83% yield with 91% D-incorporation.

2,3,4,6-*tetra*-*O*-benzyl-α,β-D-glucopyranose-*1*-$d_1$ (deuteration 91%, 0.083 mmol), **5af** (40 mol%) AcOK (0.17 mmol, 2 equiv) and $CD_3COOD$ (0.67 mmol, 8 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and toluene (0.25 ml) in a reaction vessel (5 ml). Then the reaction mixture was vigorously stirred at 120 °C for 12 hours. **12v** was obtained as a white solid in 77% yield (for two steps) with 99% D-incorporation. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.11 (m, 20H), 5.22 (s, 0.01H), 4.97-4.45 (m, 9H), 4.05-3.95 (m, 2H), 3.71-3.50 (m, 4H), 3.39 (d, *J* = 9.1 Hz, 1H), 3.25 (s, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) **iso1:** δ 138.5 (s), 138.4 (s), 138.0 (s), 137.70 (s), 128.5 (s), 128.4 (s), 128.4 (s), 128.4 (s), 128.1 (s), 128.0 (s), 128.0 (s), 127.9 (s), 127.9 (s), 127.9 (s), 127.7 (s), 127.7 (s), 127.7 (s), 127.6 (s), 97.1 (t, *J* = 24.5 Hz), 84.6 (s), 83.0 (s), 77.8 (s), 75.7 (s), 75.0 (s), 74.70 (s), 74.60 (s), 73.5 (s), 73.2 (s), 68.9 (s); **iso2:** δ 138.8 (s), 138.2 (s), 137.9 (s), 137.8 (s), 128.5 (s), 128.4 (s), 128.4 (S), 128.4 (S), 128.1 (s), 128.0 (s), 128.0 (s), 127.9 (s), 127.9 (s), 127.8 (s), 127.7 (s), 127.7 (s), 127.7 (s), 127.6 (s), 91.9 (t, *J* = 25.3 Hz), 81.7 (s), 79.9 (s), 77.7 (s), 75.7 (s), 75.0 (s), 73.5 (s), 73.2 (s), 70.2 (s), 68.6 (s); $^{2}$H NMR (77 MHz, $CHCl_3$) δ 5.24 (s, 1D, β anomer), 4.71 (s, 1D, α anomer); HRMS (ESI): m/z caled for $C_{34}H_{35}DNaO_6$ [$(M+Na)^+$]: 564.2472, found: 564.2471.

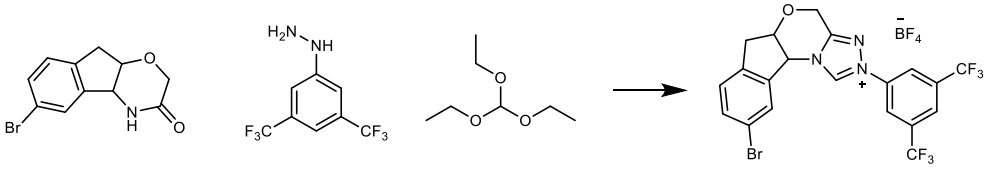


**Midecamycin-*1,2-d*$_1$,*d*$_2$ (12w)**

Midecamycin (0.1 mmol), **5l** (20 mol%) and AcOK (0.2 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **12w** was obtained as a white solid in 80% yield with 90% D-incorporation.

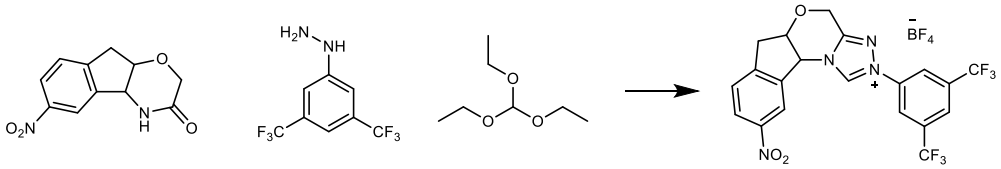
Midecamycin (deuteration 90%, 0.08 mmol), **5l** (20 mol%) and AcOK (0.16 mmol, 2 equiv) was dissolved in a mixture of $D_2O$ (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was vigorously stirred at 60 °C for 12 hours. **12w** was obtained as a white solid in 62% yield with 99% D-incorporation at position 1 and uncertain D-incorporation at position 2. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 0.01H), 6.61 (dd, *J* = 15.0, 10.7 Hz, 1H), 6.04 (dd, *J* = 14.9, 10.6 Hz, 1H), 6.08-6.00 (m, 1H), 5.75 (t, *J* = 13.0 Hz, 1H), 5.59 (dd, *J* = 15.1, 9.4 Hz, 1H), 5.13-5.00 (m, 3H), 4.60 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 7.1 Hz, 1H), 4.31 (s, 1H), 4.06 (dd, *J* = 9.4, 3.8 Hz, 1H), 3.84 (d, *J* = 9.2 Hz, 1H), 3.55-3.50 (m, 4H), 3.28-3.21 (m, 3H), 2.78-2.38 (m, 14-16H), 2.24 (d, *J* = 13.0 Hz, 1H), 2.12 (dd, *J* = 24.6, 11.5 Hz, 2H), 2.00 (d, *J* = 14.3 Hz, 1H), 1.84 (dd, *J* = 15.9, 12.0 Hz, 2H), 1.49-1.34 (m, 2H), 1.28-1.06 (m,17H), 1.02-0.84 (m, 4H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 202.5-200.1 (m), 174.4 (s), 173.9 (s), 169.9 (s), 135.8 (s), 132.9 (s), 131.9 (s), 127.5 (s), 103.6 (s), 96.9 (s), 84.8 (s), 77.6 (s), 75.9 (s), 73.2 (s), 72.9 (s), 71.6 (s), 69.4 (s), 69.0 (s), 68.7 (s), 63.5 (s), 62.5 (s), 42.2 (s), 41.9 (s), 41.6 (s), 41.0 (s), 37.1 (s), 33.5 (s), 30.4 (s), 28.7 (s), 27.6 (s), 27.6 (s), 25.4 (s), 20.4 (s), 18.8 (s), 17.7 (s), 14.7 (s), 9.3 (s), 8.9 (s); $^2$H NMR (77 MHz, $CHCl_3$) δ 9.66 (s, 1D), 2.37 (s, 1.60D); HRMS (ESI): m/z caled for $C_{41}H_{65}D_3NO_{15}$ [$(M+H)^+$]: 817.4777, found: 817.4795.

## 4.2 Preparation of catalysts 5ah and 5p



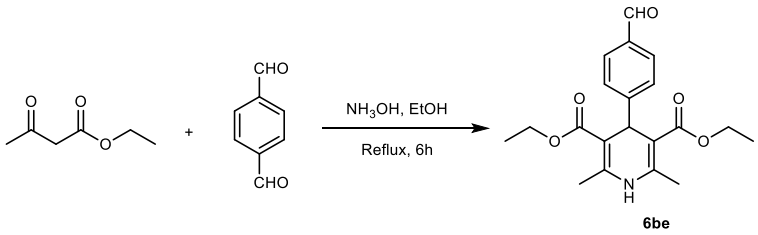

Following the modified procedure of reported literature,[9] a flame-dried round bottom flask was charged with 6-bromo-4,4a,9,9a-tetrahydroindeno[2,1-b][1,4]oxazin-3(2H) -one (1.0 g, 3.73 mmol) and $CH_2Cl_2$ (18 mL). Trimethyloxonium tetrafluoroborate (549 mg, 3.73 mmol) was added, and the reaction mixture stirred for 12 hours at 23 °C. 3,5-Bis(trifluoromethyl)phenylhydrazine (904 mg, 3.73 mmol) was then added and allowed to stir for 12 hours at ambient temperature. The solvent was evaporated and chlorobenzene (34 mL) was added, followed by triethyl orthoformate (1.55 ml, 9.26 mmol). The flask was equipped with a reflux condenser and heated to 110 °C and stirred at this temperature for 12 hours. At this time, additional triethylorthoformate (1.55 mL, 9.26 mmol) was added and stirring at 110 °C was continued for additional 12 hours. Upon cooling, concentrated in vacuo. The product was purified by flash column chromatography to get the title compound **5ah** as a tan solid (55% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 13.30 (s, 1H), 8.85 (s, 2H), 8.21 (s, 1H), 7.92 (s, 1H), 7.35-7.29 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 3.9 Hz, 1H), 5.10 (s, 2H), 5.02 (t, *J* = 4.4 Hz, 1H), 3.27 (dd, *J* = 17.3, 4.7 Hz, 1H), 3.11 (d, *J* = 17.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.1 (s), 144.6-142.7 (m), 139.1 (s), 137.2 (s), 136.3 (s), 133.7

(q, *J* = 34.8 Hz), 130.2 (d, *J* = 493.9 Hz), 126.8 (s), 124.0 (dd, *J* = 7.9, 4.2 Hz), 123.6 (s), 121.4 (d, *J* = 3.2 Hz), 121.2 (s), 120.9 (s), 77.7 (s), 62.2 (s), 60.4 (s), 37.2 (s); HRMS (EI): m/z caled for $C_{20}H_{12}BrF_6N_3O$ [$(M-H)^+$]: 503.0068, found: 503.0063.



Following the modified procedure of reported literature,[9] a flame-dried round bottom flask was charged with 6-nitro-4,4a,9,9a-tetrahydroindeno[2,1-b][1,4]oxazin-3(2H) –one (1.0 g, 4.27 mmol) and $CH_2Cl_2$ (21 mL). Trimethyloxonium tetrafluoroborate (769 mg, 4.27 mmol) was added, and thereaction mixture stirred for 12 hours at 23 °C. 3,5-bis(trifluoromethyl)phenylhydrazine (1,042 mg, 4.27 mmol) was then added and allowed to stir for 12 hours at ambient temperature. The solvent was evaporated and chlorobenzene (41 mL) was added, followed by triethyl orthoformate (1.78 mL, 10.69 mmol). The flask was equipped with a reflux condenser and heated to 110 °C and stirred at this temperature for 12 hours. At this time, additional triethylorthoformate (1.78 mL, 10.69 mmol) was added and stirring at 110 °C was continued for 12 more hours. Upon cooling, concentrated in vacuo. The product was purified by flash column chromatography to get the title compound **5p** as a tan solid (31% yield). $^1$H NMR (400 MHz, DMSO-*d*$_6$) δ 11.85 (s, 1H), 8.70 (s, 2H), 8.59 (d, *J* = 9.9 Hz, 2H), 8.32 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 3.9 Hz, 1H), 5.39 (d, *J* = 16.5 Hz, 1H), 5.17 (d, *J* = 16.5 Hz, 1H), 5.05 (t, *J* = 4.3 Hz, 1H), 3.60 (dd, *J* = 17.8, 4.6 Hz, 1H), 3.32 (d, *J* = 17.9 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$) δ 149.7 (s), 149.0 (s), 147.2 (s), 143.7 (s), 137.4 (s), 136.4 (s), 132.0 (d, *J* = 34.2 Hz), 125.9 (d, *J* = 171.6 Hz), 124.5 (m), 123.9 (s), 122.2 (m), 121.2 (s), 120.3 (s), 77.2 (s), 60.8 (s), 59.7 (s), 37.1 (s); HRMS (EI): m/z caled for $C_{20}H_{12}F_6N_4O_3$ [$(M-H)^+$]: 470.0814, found: 470.0815.

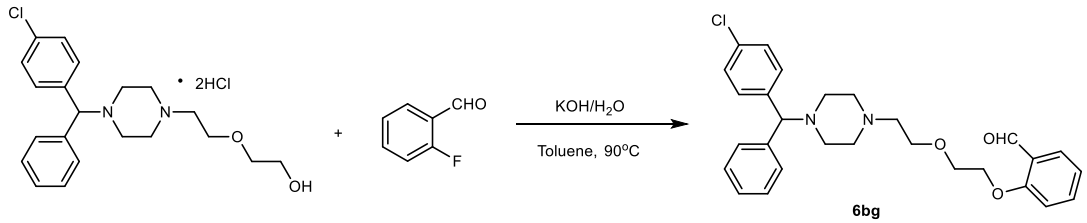
### 4.3 Preparation of substrates




Following the modified procedure of reported literature,[25] 1,4-phthalaldehyde (470 mg, 3.5 mmol), ethylacetoacetate (910 mg, 7 mmol), and ammonium hydroxide solution (364 μL, 2.6 mmol) in ethanol (2 mL) was stirred at reflux for 6 h. After completion of the reaction, as indicated by TLC, the reaction mixture was concentrated in vacuo. The crude product was purified by flash column chromatography (EtOAc/petroleum ether = 1/4). The title compound **6be** was obtained as a yellow solid (378 mg, 41%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.29 (s, 1H), 5.05 (s, 1H), 4.11-4.03 (m, 4H), 2.32 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 6H).

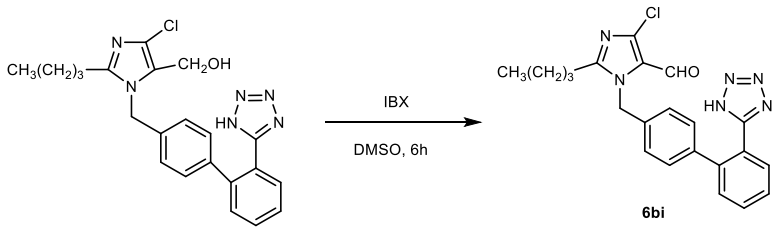

**6bf**

Following the modified procedure reported in literature,[26] In a flask were introduced *O*-desmethylvenlafaxine (670 mg, 2.55 mmol), DMF (3 mL), potassium carbonate (690 mg, 5 mmol) and 4-fluorobenzaldehyde (310 mg, 2.5 mmol). The resulting mixture was stirred at 120 °C overnight. The reaction mixture was diluted with water (30 mL) and the product was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed sequentially with 0.5 M aqueous NaOH solution (30 mL) and saturated aqueous $NaHCO_3$ solution (2 × 30 mL), and dried over anhydrous $MgSO_4$. The organic layer was filtered and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography using MeOH/DCM (1/50 - 1/10) as eluent to give the product **6bf** as a yellow oil (693 mg, 73%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 3.24 (t, *J* = 12.5 Hz, 1H), 2.96 (dd, *J* = 12.3, 3.1 Hz, 1H), 2.33-2.23 (m, 7H), 1.73-1.64 (m, 3H), 1.48 (t, *J* = 15.9 Hz, 3H), 1.33-1.21 (m, 2H), 0.95-0.80 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.6 (s), 163.1 (s), 153.7 (s), 137.4 (s), 131.9 (s), 131.2 (s), 130.8 (s), 119.7 (s), 117.5 (s), 74.1 (s), 61.0 (s), 51.9 (s), 45.5 (s), 38.1 (s), 31.2 (s), 26.0 (s), 21.6 (s), 21.3 (s).

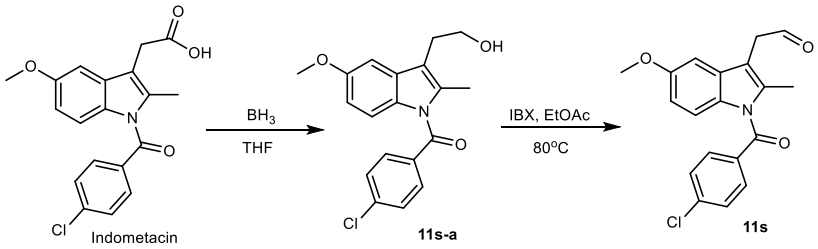



**6bg**

Following the modified procedure reported in literature,[27] hydroxyzine hydrochloride (1.12 g, 2.5 mmol) was diluted with toluene (10 mL), then 2-fluorobenzaldehyde (340 mg, 2.75 mmol), tetrabutylammonium bromide (TBAB) (200 mg, 0.66 mmol) and a solution of potassium hydroxide (560 mg, 10 mmol) in water (570 μL) were added. The reaction mixture was vigorously stirred at 90 °C under nitrogen overnight. When the reaction was completed, the solution was concentrated in vacuo. The crude residue was purified by silica gel chromatography to give product **6bg** (677 mg, 57% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.49 (d, *J* = 0.5 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.54-7.50 (m, 1H), 7.37-7.32 (m, 4H), 7.28-7.15 (m, 5H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.22 (m, 3H), 3.88-3.84 (m, 2H), 3.74 (t, *J* = 5.5 Hz, 2H), 2.72-2.44 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.8 (s), 161.2 (s), 142.0 (s), 141.2 (s), 135.9 (s), 132.6 (s), 129.2 (s), 128.7 (s), 128.6 (s), 128.4 (s), 127.8 (s), 127.2 (s), 125.1 (s), 121.0 (s), 112.8 (s), 75.3 (s), 69.3 (s), 68.9 (s), 68.1 (s), 57.6 (s), 53.8 (s), 51.3 (s).

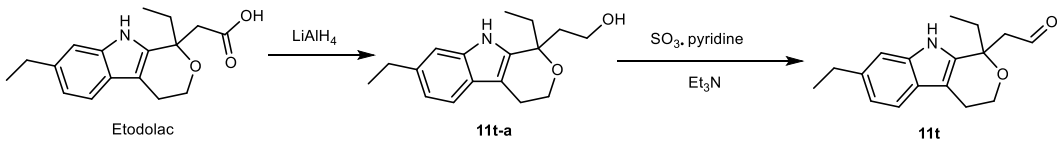



**(2'-(2H-Tetrazol-5-yl)biphenyl-4-yl)methyl)-2-butyl-4-chloro-1H-imidazole-5-carbaldehyde (6bi)**: Losartan (1.7 g, 4 mmol) and IBX (2-iodoxybenzoic acid, 1.345 g, 4.8 mmol) were added in DMSO (20 mL) and stirred at room temperature for 6 h. $CH_2Cl_2$ (120 mL) was added and the solution was washed with water (3 × 120 mL), saturated $NaHCO_3$ solution (3 × 120 mL), and brine (1 × 120 mL). The solvent was removed after drying ($Na_2SO_4$) in vacuo to yield the product **6bi** (888 mg, 53%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.90 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.62-7.54 (m, 1H), 7.54-7.46 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 5.49 (s, 2H), 2.79-2.48 (m, 2H), 1.67-1.65 (m, 2H), 1.41-1.21 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).




**Step 1:** Following the modified procedure reported in literature,[28] to a stirred solution of indometacin (1.0 g, 2.86 mmol) in THF (15 mL) was added a 1M solution of borane tetrahydrofuran complex (3 mL, 3.0 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 18 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (DCM/MeOH = 50/1) to give **11s-a** (734 mg, 74%) as a yellow solid.

**Step 2:** Following the modified procedure reported in literature,[28] To a stirred solution of **11s-a** (734 mg, 2.15 mmol) in EtOAc (7.34 mL) was added IBX (1.5 g, 5.3 mmol) at room temperature and the resulting mixture was heated at 80 °C for 2 h. The mixture was filtered and filtrate was concentrated under reduced pressure to give **11s** (490 mg, 66%) as a powder. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 2.1 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.87-6.84 (m, 2H), 6.69 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.82 (s, 3H), 3.72 (d, *J* = 2.0 Hz, 2H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 198.1 (s), 168.3 (s), 156.2 (s), 139.5 (s), 136.5 (s), 133.7 (s), 131.2 (s), 130.9 (s), 130.6 (s), 129.2 (s), 115.1 (s), 111.9 (s), 110.0 (s), 100.8 (s), 55.7 (s), 39.4 (s), 13.4 (s).

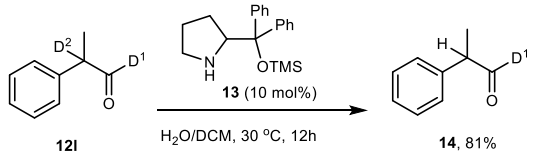


**Step 1:** Following the modified procedure reported in literature,[28] to a stirred solution of Etodolac (2.0 g, 6.97 mmol) in dry THF (15.5 mL) under nitrogen was added a solution of $LiAlH_4$ (800 mg, 21 mmol) in dry THF (10.5 mL) dropwise and the resulting mixture was warmed to room temperature and stirred overnight. The reaction was slowly quenched with EtOAc (30 mL) and poured into water. The resulting emulsion was filtered and the flitrate was extrated with EtOAc. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The organic layer was filtered and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography to give **11t-a** (1.14 g, 59%) as a yellow oil.

**Step 2:** Following the modified procedure reported in literature,[28] to a stirred solution of **11t-a** (1.14 g, 4.17 mmol) in $CH_3CN$ (5.38 mL), DMSO (5.38 mL) and $Et_3N$ (5.38 mL) was added pyridine sulfur trioxide (3.96 g, 24.8 mmol) and the resulting mixture was stirred at room temperature for 40 min. The mixture was poured into water and extracted with EtOAc. The combined organic layers were washed sequentially with 3% aquenes HCl solution, saturated aqueous $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. The organic layer was filtered and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography to give product **11t** (720 mg, 63%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.6 Hz, 1H), 8.43 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 6.7 Hz, 1H), 4.08-3.99 (m, 2H), 3.06 (d, *J* = 1.6 Hz, 2H), 2.91-2.81 (m, 4H), 2.16-2.08 (m, 1H), 1.99-1.94 (m, 1H), 1.38 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.4 (s), 135.2 (s), 134.6 (s), 126.6 (s), 126. 3 (s), 120.7 (s), 119.9 (s), 116.1 (s), 108.9 (s), 75.0 (s), 60.6 (s), 51.9 (s), 31.2 (s), 24.1 (s), 22.4 (s), 13.8 (s), 7.8 (s).

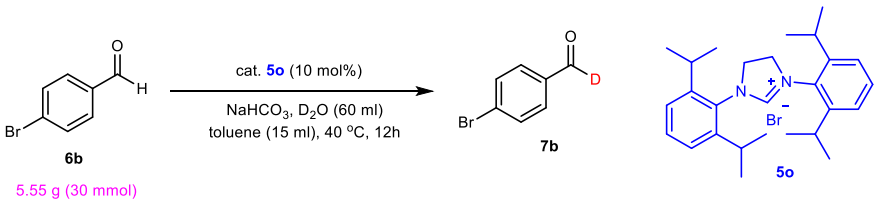
## 5. Synthetic applications

### 5.1 Recovery of hydrogen from deuterium at α-position of aldehyde (Figure 3)



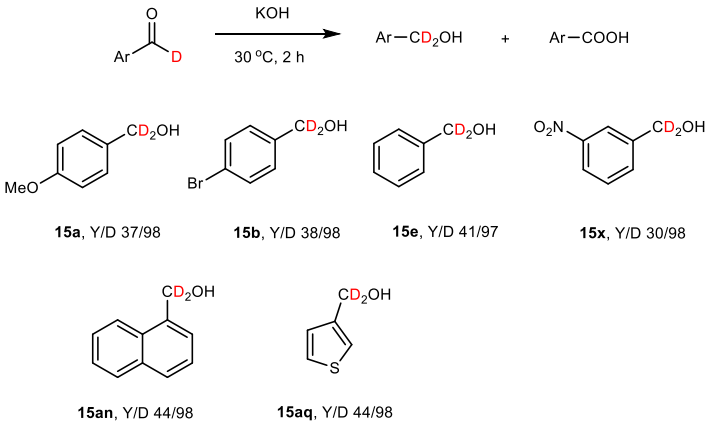

Compound **12l** (0.5 mmol, 68 mg, $D^1$ = 98%; $D^2$ = 97%) and organocatalyst **13** (16.3 mg, 10 mol%) was dissolved in a mixture $H_2O$ (1 mL) and DCM (0.25 ml). Then the reaction was vigorously stirred at 30 °C for 12 hours. After purification, compound **14** was obtained as a colorless oil in 81% yield with 98% D-incorporation. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 1.4 Hz, 0.02H), 7.41-7.37 (m, 2H), 7.35-7.28 (m, 1H), 7.24-7.21 (m, 2H), 3.64 (q, *J* = 7.1 Hz, 1H), 1.45 (d, *J* = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 200.8 (t, *J* = 26.6 Hz), 137.7 (s), 129.1 (s), 128.3 (s), 127.5 (s), 52.8 (t, *J* = 4.1 Hz,), 14.6 (s).

## 5.2 Gram-scale synthesis of deuterated aldehyde and recycling and subsequent use of recoved $D_2O$ (Figure 4)

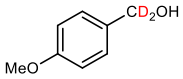



**Cycle 1**: A mixture of 4-Bromobenzaldehyde **6b** (30 mmol, 5.55 g), **5o** (10 mol%, 1.41 g) and $NaHCO_3$ (30 mmol, 2.52 g) in $D_2O$ (60 mL) and toluene (15 mL) was vigorously stirred at 40 °C for 12 hours. After cooling to room temperature, the reaction mixture was extracted with DCM for three time. The organic layers were combined and dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography. Deuterated aldehyde **7b** was obtained as a yellow solid in 86% yield with 98% D-incorporation.
**Cycle 2**: 4-Bromobenzaldehyde **6b** (30 mmol, 5.55 g) and **5o** (10 mol%, 1.41 g) were added to $D_2O$ (separated from **Cycle 1**) and toluene (15 mL). The reaction was vigorously stirred at 40 °C for 12 hours. After cooling to room temperature, the reaction was extracted with DCM for three time. The organic layers were combined and dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography. Deuterated aldehyde **7b** was obtained as a yellow solid in 90% yield with 98% D-incorporation.
**Cycle 3**: The same operation was carried out as **Cycle 2**. Deuterated aldehyde **7b** was obtained as a yellow solid in 91% yield with 95% D-incorporation.

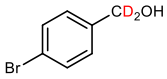
## 5.3 Preparation of deuterated benzyl alcohols through Cannizzaro reaction (Figure 4)



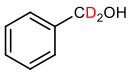

**General procedure:** According to the literature method,[29] the aromatic aldehyde (1.0 mmol) was added to a saturated solution of potassium hydroxide (4.0 mmol), and the mixture was stirred at room temperature for 1–2 hours. The thick slurry was diluted with water (10 mL), and the resulting mixture was extracted with $CH_2Cl_2$ (20 mL). The extracts were washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure to obtain the crude benzyl alcohol product. The crude products were purified by chromatography to obtain the pure product.



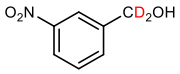

**4-Methoxybenzenemethan-*d*$_2$-ol (15a)**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (dt, *J* = 8.8, 2.8 Hz, 2H), 6.87 (dt, *J* = 8.8, 2.8 Hz, 2H), 4.54 (s, 0.03H), 3.78 (s, 3H), 2.19 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.2 (s), 133.1 (s), 128.7 (s), 113.9 (s), 64.2 (quint, *J* = 21.7 Hz), 55.3 (s).



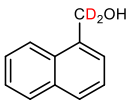

**4-Bromobenzenemethan-*d*$_2$-ol (15b)**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.60 (s, 0.04H), 2.06 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.6 (s), 131.6 (s), 128.7 (s), 121.5 (s), 63.8 (quint, *J* = 21.8 Hz).




**Benzenemethan-*d*$_2$-ol (15e)**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 4.64-4.62 (m, 0.03H), 2.27 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.8 (s), 128.6 (s), 127.7 (s), 127.1 (s), 64.6 (quint, *J* = 21.8 Hz).




**3-Nitrobenzenemethan-*d*$_2$-ol (15X)**: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 4.79 (s, 0.03H), 2.27 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.3 (s), 142.8 (s), 132.8 (s), 129.5 (s), 122.5 (s), 121.5 (s), 63.7-62.7 (m).

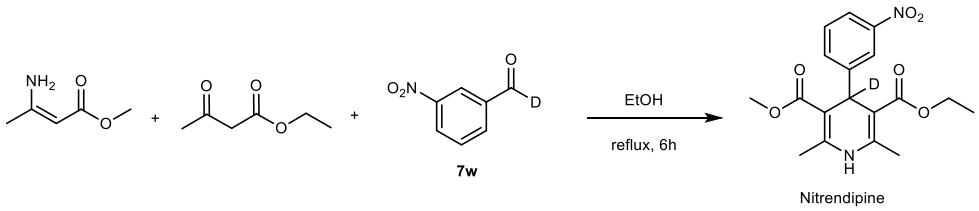



**1-Naphthalenemethan-*α*,*α*-*d*$_2$-ol (15an)**: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 1H), 7.89 (dd, *J* = 5.9, 3.6 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.57-7.50 (m, 2H), 7.49-7.41 (m, 2H), 5.03 (s, 0.04H), 2.41 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.2 (s), 133.8 (s), 131.8 (s), 128.7 (s), 128.6 (s), 126.4 (s), 125.9 (s), 125.5 (s), 125.4 (s), 123.7 (s), 62.8 (quint, *J* = 21.9 Hz).


**1-Thiophenemethan-*d*$_2$-ol (15aq)**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.25 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.10 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.68 (s, 0.03H), 1.70 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.1 (s), 126.8 (s), 126.3 (s), 122.1 (s), 60.5-59.5 (m).

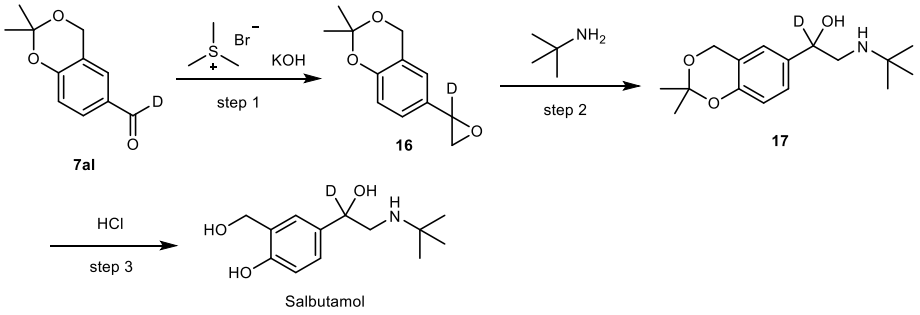
## 5.4 Preparation of deuterated pharmaceutical compounds

### 5.4.1 Procedure for the synthesis of nitrendipine




According to literature method,[30] a solution of the deuterated 3-nitrobenzaldehyde **7w** (76 mg, 0.5 mmol, 99% D), 3-amino-2-butanoate (0.5 mmol) and ethyl acetoacetate (0.5 mmol) in EtOH (1 mL) was stirred at reflux for 6 hours. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash column chromatography (EtOAc/petroleum ether = 1:4). The title compound was obtained as a yellow solid (144 mg, 78%), D-incorporation: 99%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.10 (t, *J* = 1.9 Hz, 1H), 8.01-7.97 (m, 1H), 7.65-7.60 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.10 (s, 1H), **5.08 (s, 0.01H)**, 4.12-4.04 (m, 2H), 3.63 (s, 3H), 2.35 (d, *J* = 2.3 Hz, 6H), 1.22 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.7 (s), 167.2 (s), 149.8 (s), 148.2 (s), 145.2 (s), 145.0 (s), 134.4 (s), 128.7 (s), 122.9 (s), 121.4 (s), 103.2 (s), 102.9 (s), 60.1 (s), 51.2 (s), 39.5 (t, *J* = 19.2 Hz), 19.6 (s), 19.5 (s), 14.3 (s); HRMS (ESI): m/z caled for $C_{18}H_{20}DN_2O_6$ [$(M+H)^+$]: 362.1462, found: 362.1461.

### 5.4.2 Procedure for the synthesis of salbutamol



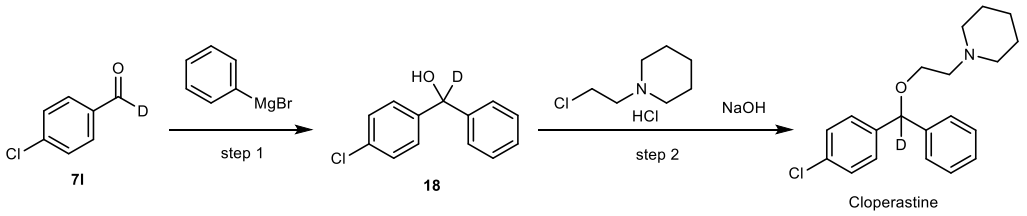

**Step 1:** According to the literature method,[31] a solution of trimethylsulfonium bromide (518 mg, 1.1 equiv) and KOH powder (219 mg, 1.3 equiv) in $CH_3CN$ (3 mL) was stirred at 50 °C for 10 min. Then aldehyde **7al** (579 mg, 3 mmol, 98% D) were added and stirred at 60 °C for another three hours. The reaction mixture then was cooled to room temperature, filtered and concentrated in vacuo. The crude product **16** was used without purification in the next step.

**Step 2:** According to the literature method,[31] compound **16** (400 mg) was dissolved in *tert*-butylamine (2 mL) and stirred at 110 °C for 15 hours. The reaction mixture was cooled to room temperature, concentrated in vacuo and added solvent (EtOAc/petroleum ether = 1/2). Then the reaction was refluxed until became clear, cooled to 30 °C for 1h, then cooled to 4 °C overnight, filtered and dried, **17** was obtained in 75% yield for two steps.

**Step 3:** According to the literature method,[31] compound **17** (60 mg) in 50% EtOH (0.8 mL) was added concentrated hydrochloric acid until the pH was adjusted to 5. The reaction mixture was stirred at 25 °C for 50 hours. NaOH (10%) was added until pH value was about 9-10. The reaction mixture was concentrated in vacuo, and the product was separated by preparative TLC. Salbutamol was obtained in 95% yield with 98% D-incorporation.) $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 7.32 (d, *J* = 2.2 Hz, 1H), 7.06 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.79

(d, *J* = 8.2 Hz, 1H), 4.46 (s, 2H), **4.28 (s, 0.02H)**, 2.84 (dd, *J* = 26.4, 12.2 Hz, 2H), 1.27 (s, 9H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 153.7 (s), 131.9 (s), 128.3 (s), 125.0 (s), 124.9 (s), 114.2 (s), 68.5 (m), 58.1 (s), 55.5 (s), 48.6 (s), 25.3 (s); HRMS (ESI): m/z caled for $C_{13}H_{20}DNO_3$ [$(M+H)^+$]: 241.1662, found: 241.1663.

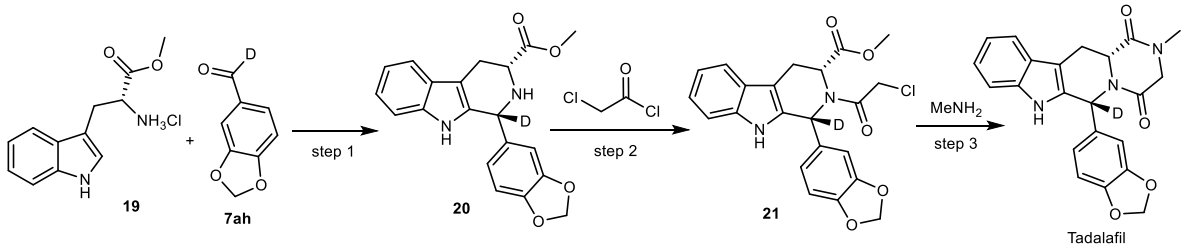
### 5.4.3 Procedure for the synthesis of cloperastine




**Step 1:** According to the literature method,[32] a solution of deuterated 4-chlorobenzaldehyde **7l** (140 mg, 1 mmol, 98% D) in dry THF (4 mL) was added dropwise phenyl magnesium bromide solution (1 M, 1.3 mL, 1.3 equiv) at 0 °C. After the addition was complete, the mixture was allowed to stir at room temperature for 4 hours. The reaction was quenched with 1 M HCl and extracted with EtOAc. The organic layer was washed with water followed by brine. The organic layer was dried with $MgSO_4$ and concentrated. The product was purified by flash chromatography with EtOAc/petroleum ether = 1:4, and **18** was obtained in 95% yield.

**Step 2:** According to the literature method,[33] to a solution of **18** (0.4 mmol) in $CH_2Cl_2$ (4 mL) was added 1-(2-chloroethyl) piperidine hydrochloride (120 mg, 0.6 mmol). The resulting solution was cooled at 0 °C followed by the addition of NaOH (48 mg, 1.2 mmol). After the mixture had been stirred for 20 min at 0 °C and then overnight at room temperature, it was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to get cloperastine (98 mg, 75% yield, 98% D-incorporation). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31-7.22 (m, 9H), **5.34 (s, 0.02H),** 3.57 (t, *J* = 5.9 Hz, 2H), 2.63 (t, *J* = 5.9 Hz, 2H), 2.42 (s, 4H), 1.59-1.53 (m, 4H), 1.43-1.38 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.4 (s), 140.6 (s), 132.7 (s), 128.1 (s), 128.1 (s), 128.0 (s), 127.3 (s), 126.6 (s), 82.9-82.7 (m), 66.7 (s), 58.2 (s), 54.7 (s), 25.6 (s), 23.9 (s); HRMS (ESI): m/z caled for $C_{20}H_{24}DClNO$ [$(M+H)^+$]: 331.1687, Found: 331.1690.

### 5.4.4 Procedure for the synthesis of tadalafil



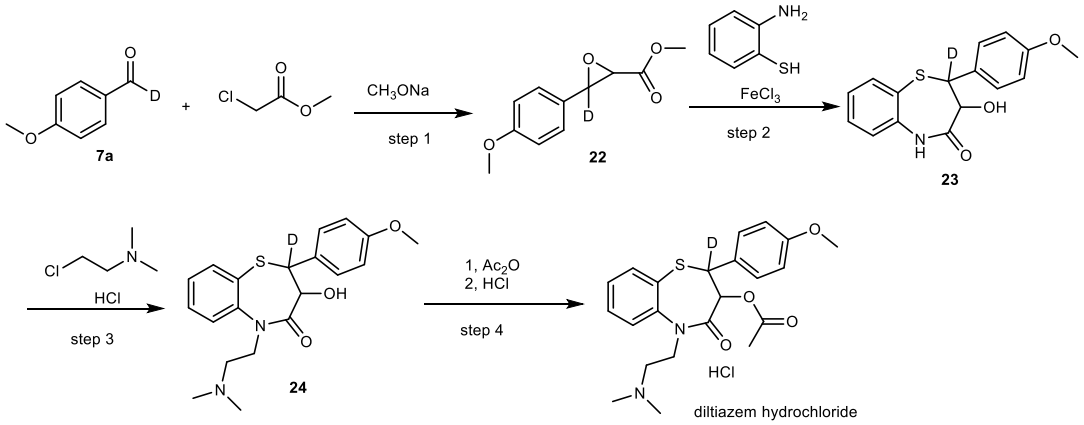

**Step 1:** According to the literature method,[34] D-tryptophan methyl ester hydrochloride **19** (400 mg, 1.57 mmol) was suspended in $CH_3CN$ (4 mL) and added deuterated piperonal **7ah** (284 mg, 1.87 mmol, 98% D) at room temperature. The mixture was stirred at 80 °C for 15

hours. The reaction mixture then was cooled to ambient temperature, filtered, and the solid washed with cold $CH_3CN$. The product was dried under vacuum at less than 60 °C to obtain compound **20** (308 mg, 80% yield).

**Step 2:** According to the literature method,[34] Compound **20** (270 mg, 0.7 mmol) were suspended in DCM (2.5 mL). The mixture was cooled to 0-5 °C, and triethylamine (194 mg, 1.82 mmol) were added. Subsequently, chloroacetyl chloride (108 mg, 0.95 mmol) in DCM (0.42 mL) were added dropwise, keeping the temperature under 10 °C. Then the reaction was stirred at 0-10 °C for 10 min. After completion of the reaction as monitered by TLC, water (0.4 mL) were added to quench the reaction. The mixture was stirred for 2 min and organic layer was separated, concentrated in vacuo. The resulting solid was washed with methanol to give the title compound **21** as a pale yellow solid (341 mg, 80% yield).

**Step 3:** According to the literature method,[34] a solution of **21** (214 mg, 0.5 mmol) and 25-30% $CH_3NH_2$ (a solution in water, 155.3 mg, 1.25 mmol, 2.5 equiv) in EtOH (1.5 mL) was heated to reflux for 45 min. The reaction mixture was cooled to room temperature, filtered, and the resulting solid was washed with water and methanol and dried to give deuterated tadalafil as a pale white solid (284 mg, 73% yield, 98% D-incorporation). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.05 (s, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 7.1 Hz, 1H), 6.88 (s, 1H), 6.79 (s, 2H), **6.14 (s, 0.02H)**, 5.93 (s, 2H), 4.40 (dd, *J* = 11.5, 4.1 Hz, 1H), 4.22-4.10 (m, 1H), 3.95 (d, *J* = 17.2 Hz, 1H), 3.53 (dd, *J* = 15.8, 4.5 Hz, 1H), 3.08-2.82 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 166.9 (s), 166.6 (s), 147.0 (s), 146.1 (s), 136.9 (s), 136.2 (s), 133.9 (s), 125.7 (s), 121.2 (s), 119.3 (s), 118.8 (s), 118.1 (s), 111.3 (s), 108.1 (s), 106.9 (s), 104.7 (s), 100.9 (s), 55.5 (s), 54.96 (m), 51.4 (s), 32.8 (s), 23.1 (s). HRMS (ESI): m/z caled for $C_{22}H_{19}DN_3O_4$ [$(M+H)^+$]: 391.1517, found: 391.1521.

### 5.4.5 Procedure for the synthesis of diltiazem hydrochloride




**Step 1**: According to the literature method,[35] sodium (126 mg, 5.48 mmol) was dissolved in methanol (1.32 mL), then *p*-anisaldehyde **7a** (450 mg, 3.31 mol, 98% D) and methyl chloroacetate (534 mg, 4.92 mmol) was added over 4.5 hours at 0 °C and stirring was continued for further 4 hours. The reaction mixture was poured into a solution of AcOH (60 mg) in water (7.5 mL) over 20 min at 0 °C. The reaction was stired for 1h, then the crystals were collected by filtration and washed with cold water and cold MeOH to give a crude product, which was recrystallized from hot MeOH to give **22** (922 mg, 67% yield).

**Step 2:** According to the literature method,[35] a solution of **22** (520 mg, 2.5 mmol) and 28% aqueous $FeCl_3$•$6H_2O$ (1 drop) in chlorobenzene (2.64 mL) was heated to 80-85 °C. 2-Aminothiophenol (328.6 mg, 2.62 mmol) was added over 30 min, and the resulting mixture was stirred at 115 °C for 45 min. $H_2O$ (1 drop) in MeOH (90 μL) were added and stirred at reflux for 30 min. Methanesulfonic acid (9.6 mg, 0.1 mmol) was then added and the reflux was maintained for an additional 18 hours. After cooling to room temperature, the solvent was concentrated under reduced pressure to give the crude benzothiazepinone **23** as a yellow powder. The residue was purified by column chromatography (cyclohexane : EtOAc = 8:2, v/v) to afford 20 mg white powder (yield: 69%).

**Step 3:** According to the literature method,[35] to a solution of benzothiazepinone **23** (414 mg, 1.41 mmol) in EtOAc (3.5 mL) was added 2-(dimethylamino) ethyl chloride hydrochloride (224 mg, 1.56 mmol). Under vigorous stirring were then added potassium carbonate (419 mg, 3.03 mmol) and $H_2O$ (64 mg). The resulting mixture was heated at reflux for 12 h. After cooling, the mixture was filtered to remove salts, and the filtrate was concentrated under reduced pressure to give the crude benzothiazepinone **24**. The residue was purified by column chromatography ($CH_2Cl_2$:MeOH = 98:2) to afford 366 mg of yellow oil (yield: 70%).

**Step 4:** According to the literature method,[36] a solution of **24** (0.317 mmol), $Ac_2O$ (1 mmol), $Et_3N$ (2 mmol) and DMAP (0.03 mmol) in $CH_2Cl_2$ (5 mL) was heated at reflux under $N_2$ for 5 hours. The solution was poured into a mixture of ice and brine. The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (10 mL). The combined organic layers were washed with 5% $NH_4OH$ (5 mL) solution, dried over $Na_2SO_4$ and evaporated. The residue was dissolved in MeOH (2 mL) and treated with a HCl solution in dioxane till pH was around 2. Ether (3 mL) was added to the resulting solution. The precipitate was collected by filtration and washed with 10% MeOH-ether to afford diltiazem hydrochloride (128 mg, 90% yield, 98% D). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.82-7.79 (m, 1H), 7.65 (dd, *J* = 5.5, 1.9 Hz, 2H), 7.46-7.39 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), **5.12 (s, 0.01H)**, 5.09 (s, 1H), 4.53-4.44 (m, 1H), 4.27-4.18 (m, 1H), 3.81 (s, 3H), 3.69-3.61 (m, 1H), 3.43-3.31 (m, 1H), 2.98 (d, *J* = 24.6 Hz, 6H), 1.87 (s, 3H); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 170.1 (s), 169.1 (s), 160.1 (s), 144.4 (s), 135.5 (s), 131.5 (s), 130.6 (s), 129.2 (s), 128.4 (s), 128.2 (s), 126.3 (s), 113.3 (s), 71.1 (s), 54.5 (s), 54.4 (s), 44.6 (s), 42.6 (s), 18.8 (s); HRMS (ESI): m/z caled for $C_{22}H_{26}DN_2O_4S$ [$(M+H)^+$]: 416.1754, found: 416.1759.

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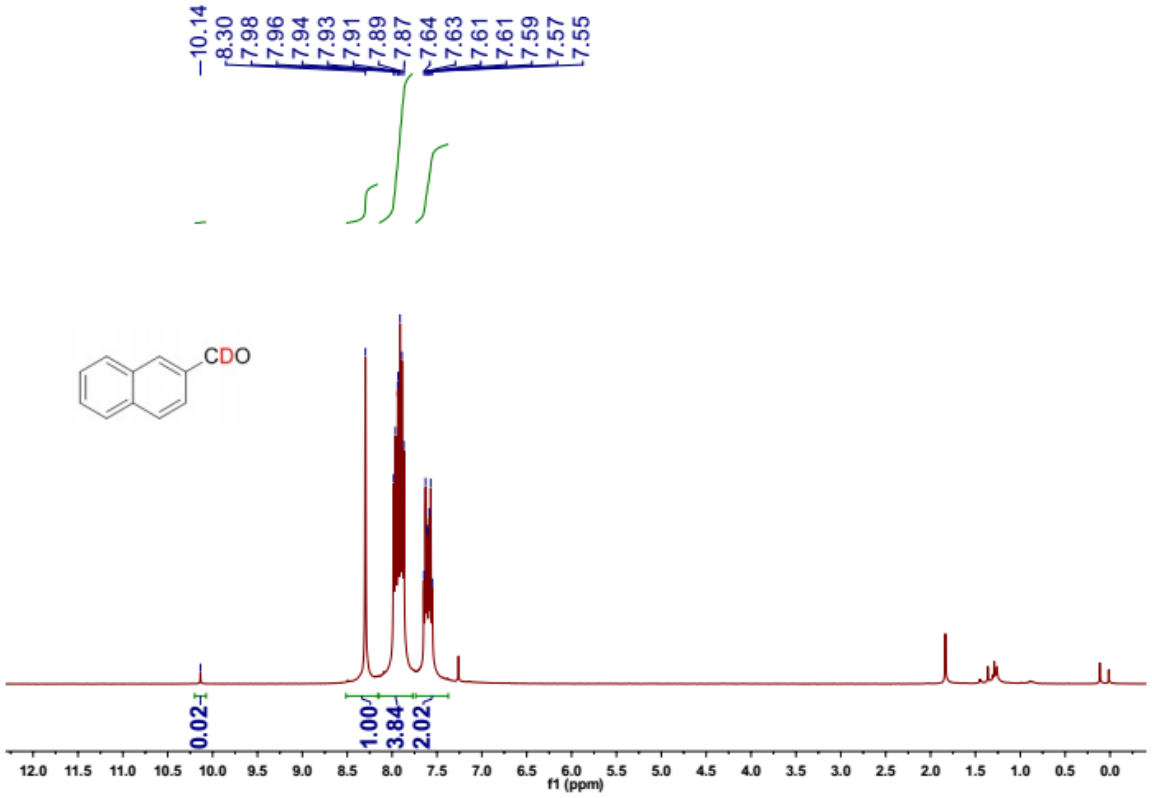
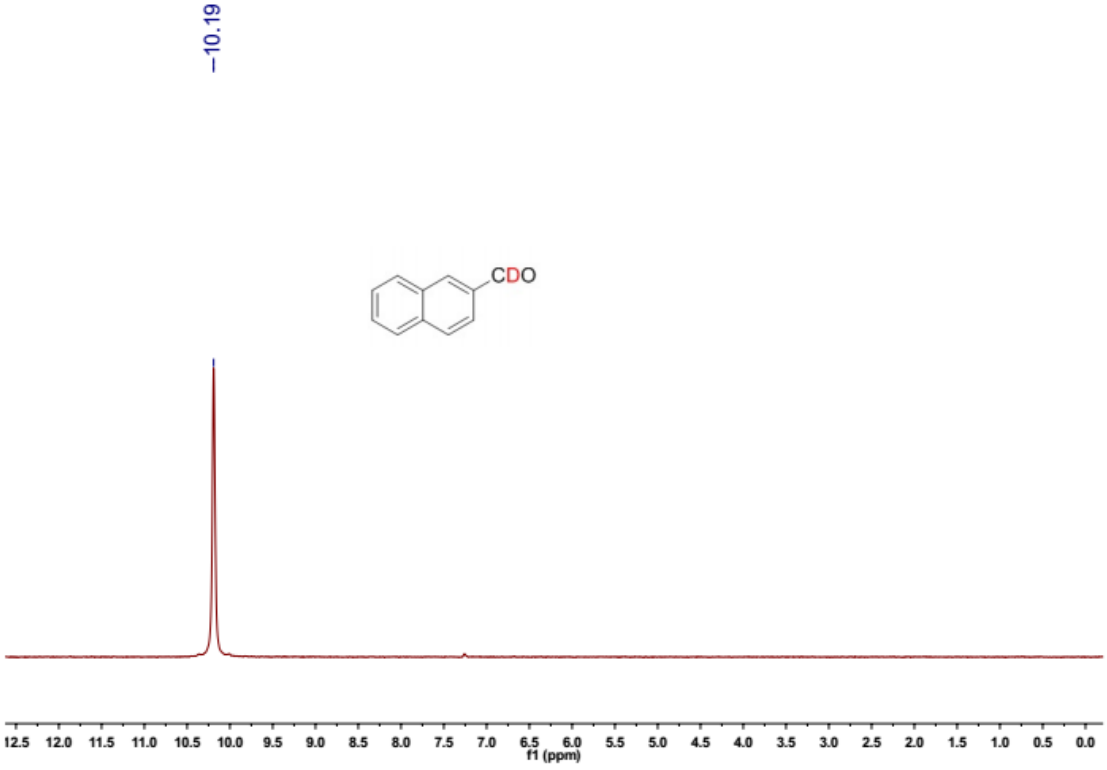
## 7. NMR Spectra

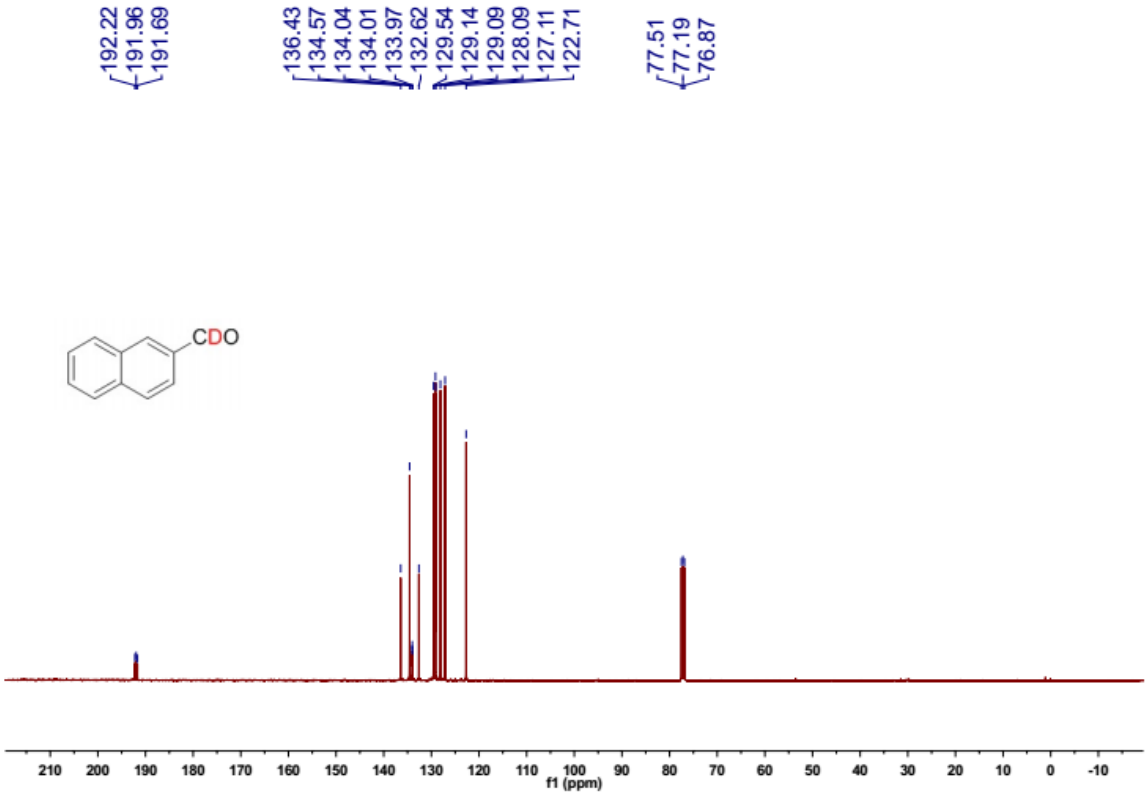
$^{1}$H NMR of deuterated aldehyde **7a**



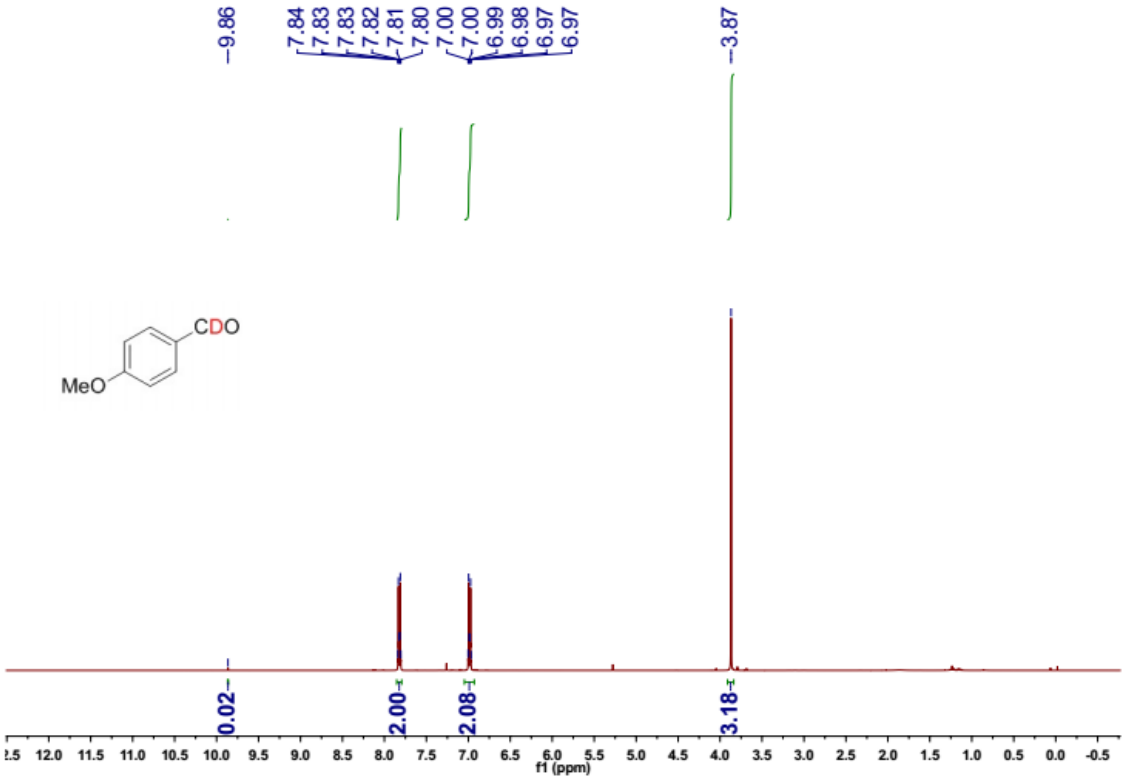

$^{2}$H NMR of deuterated aldehyde **7a**



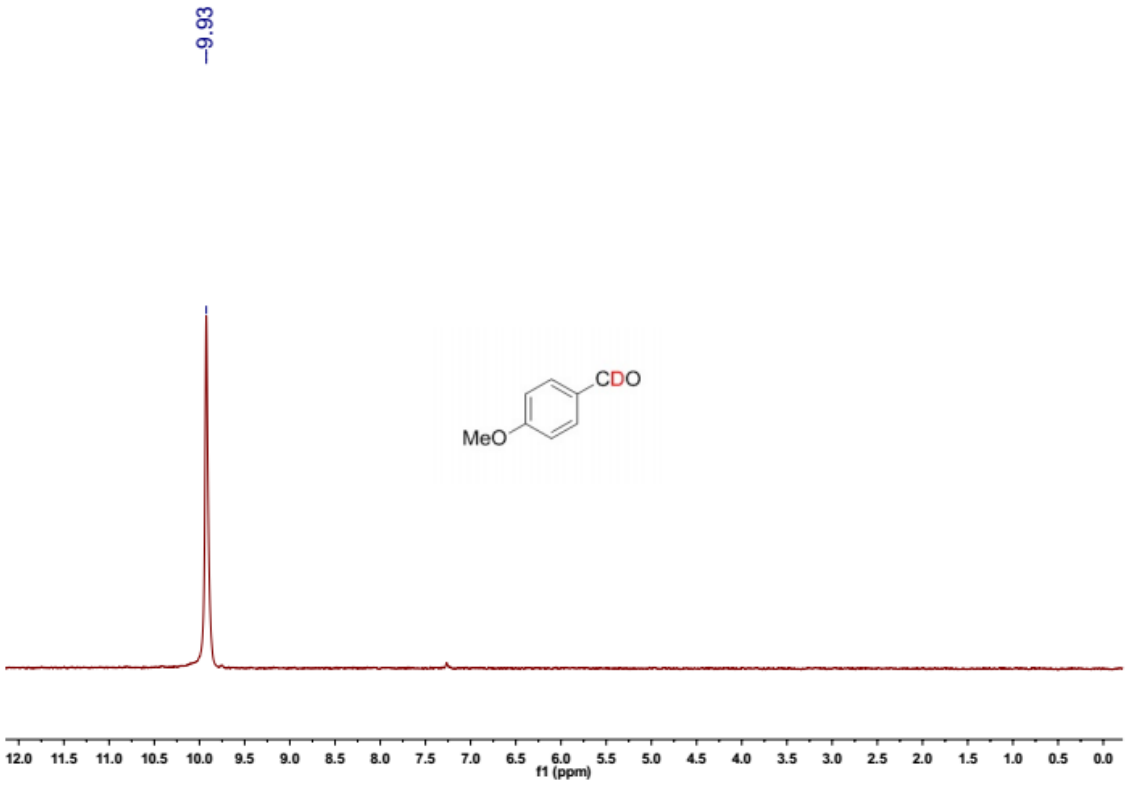
$^{13}$C NMR of deuterated aldehyde **7a**



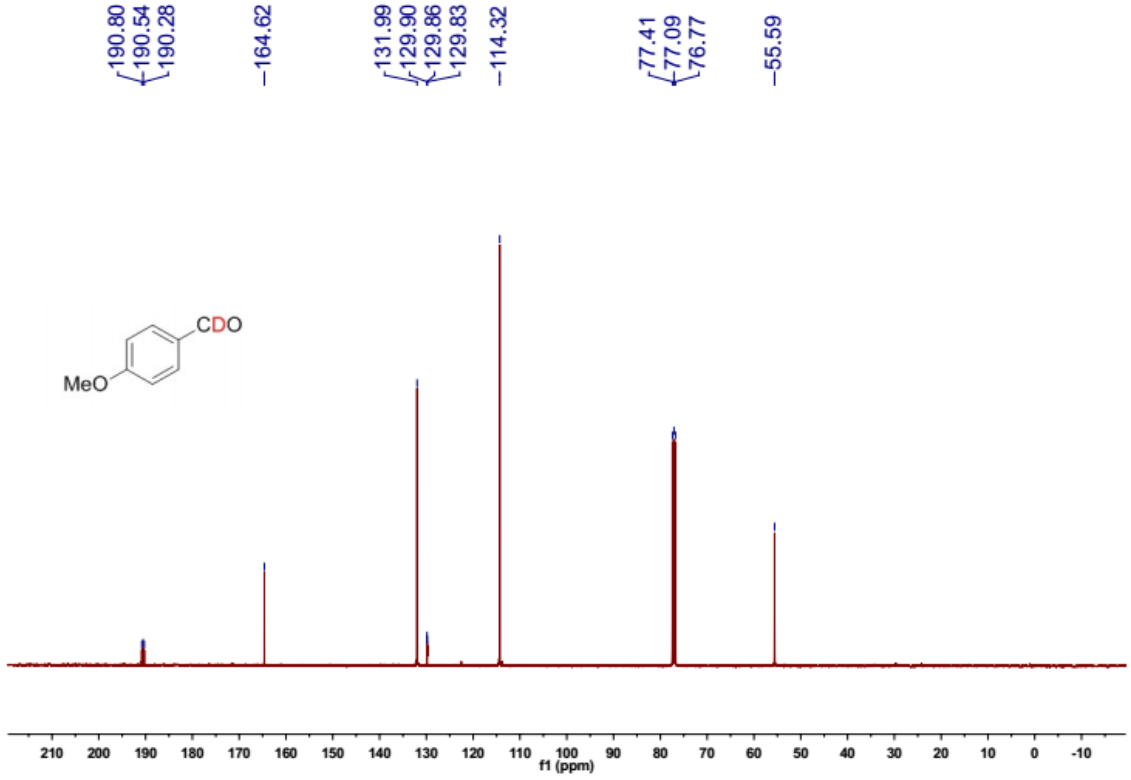
$^{1}$H NMR of deuterated aldehyde **7b**



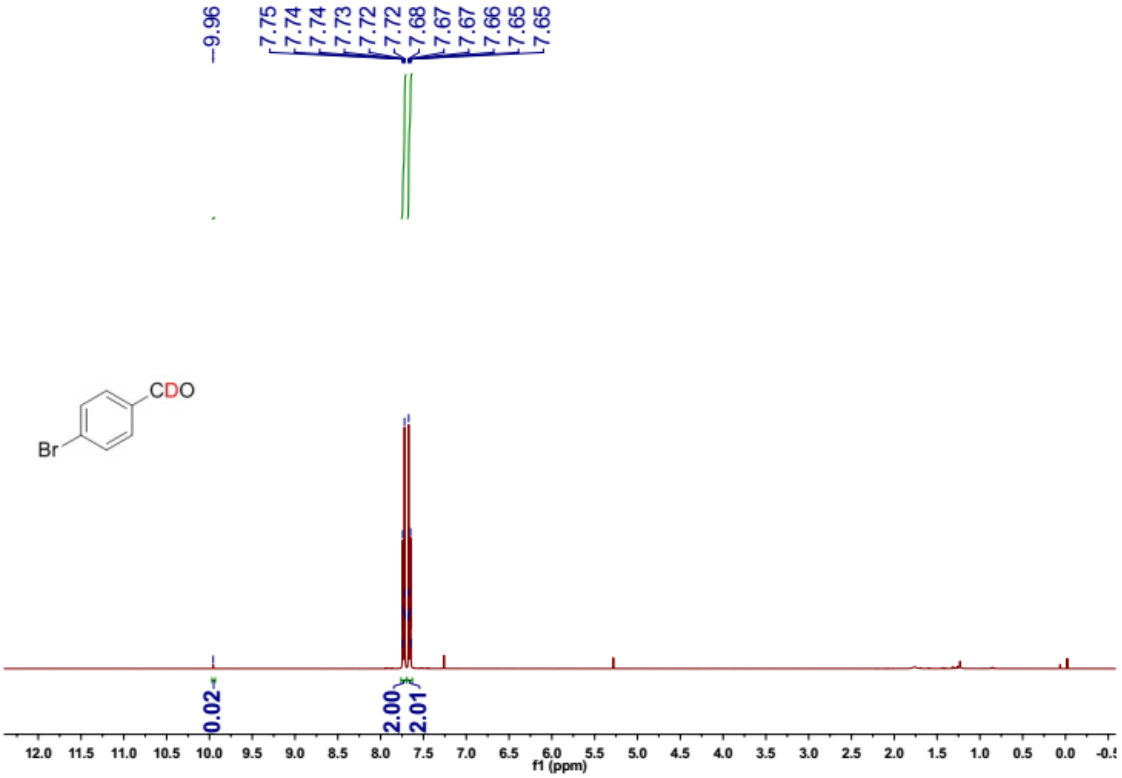

$^{2}$H NMR of deuterated aldehyde **7b**



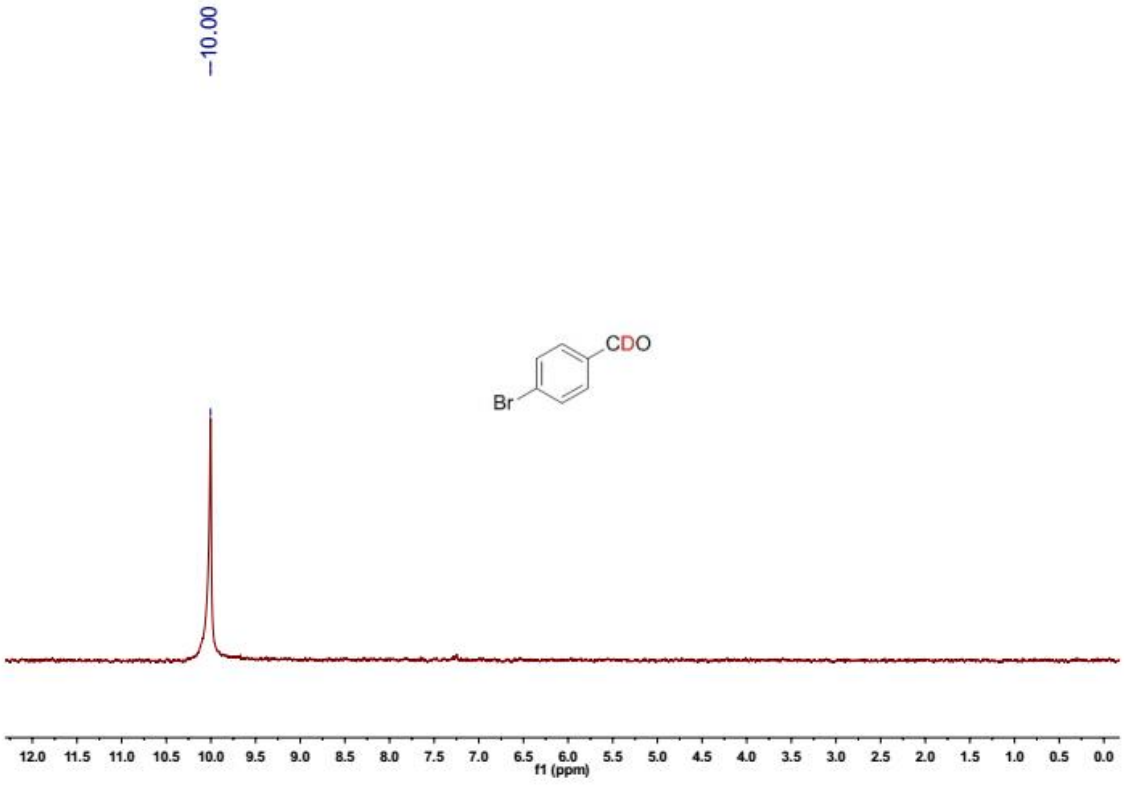
$^{13}$C NMR of deuterated aldehyde **7b**



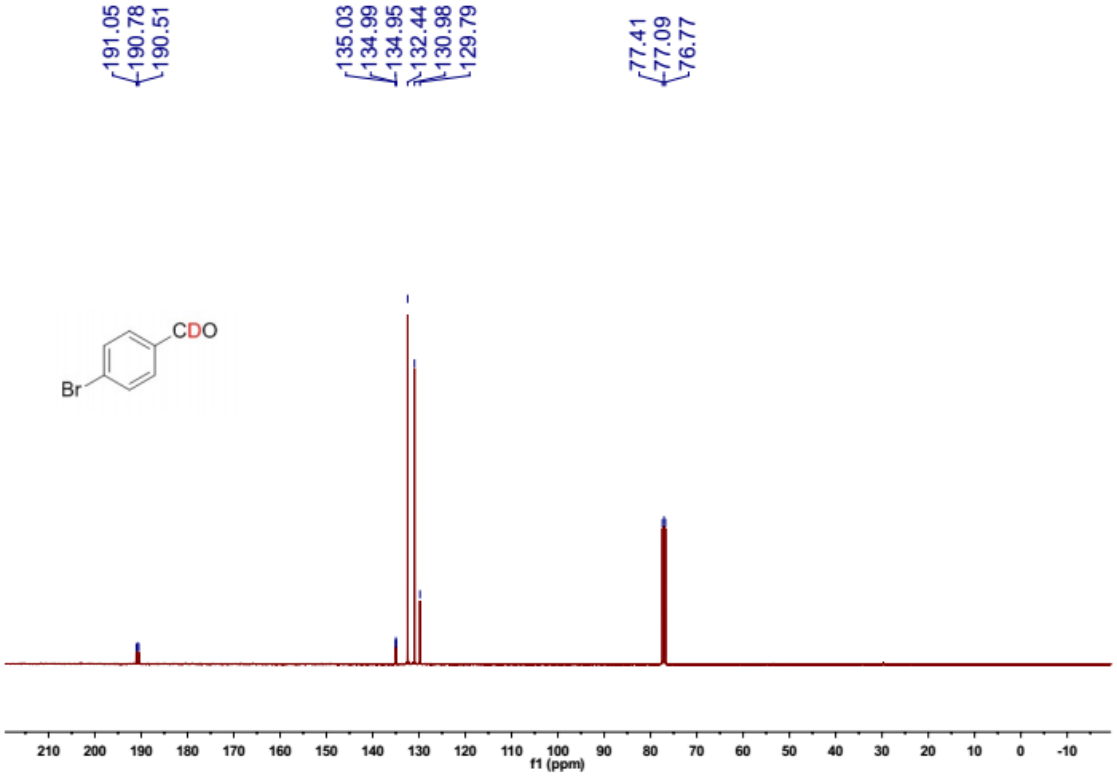
$^{1}$H NMR of deuterated aldehyde **7c**



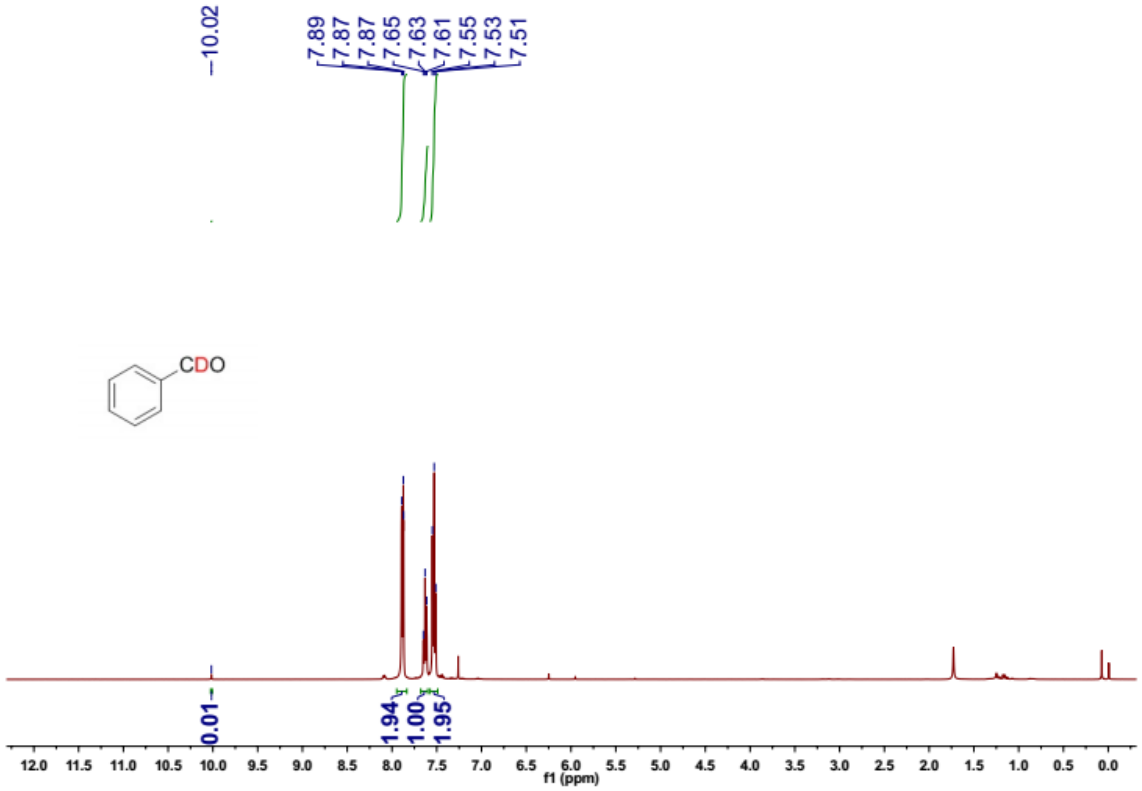

$^{2}$H NMR of deuterated aldehyde **7c**



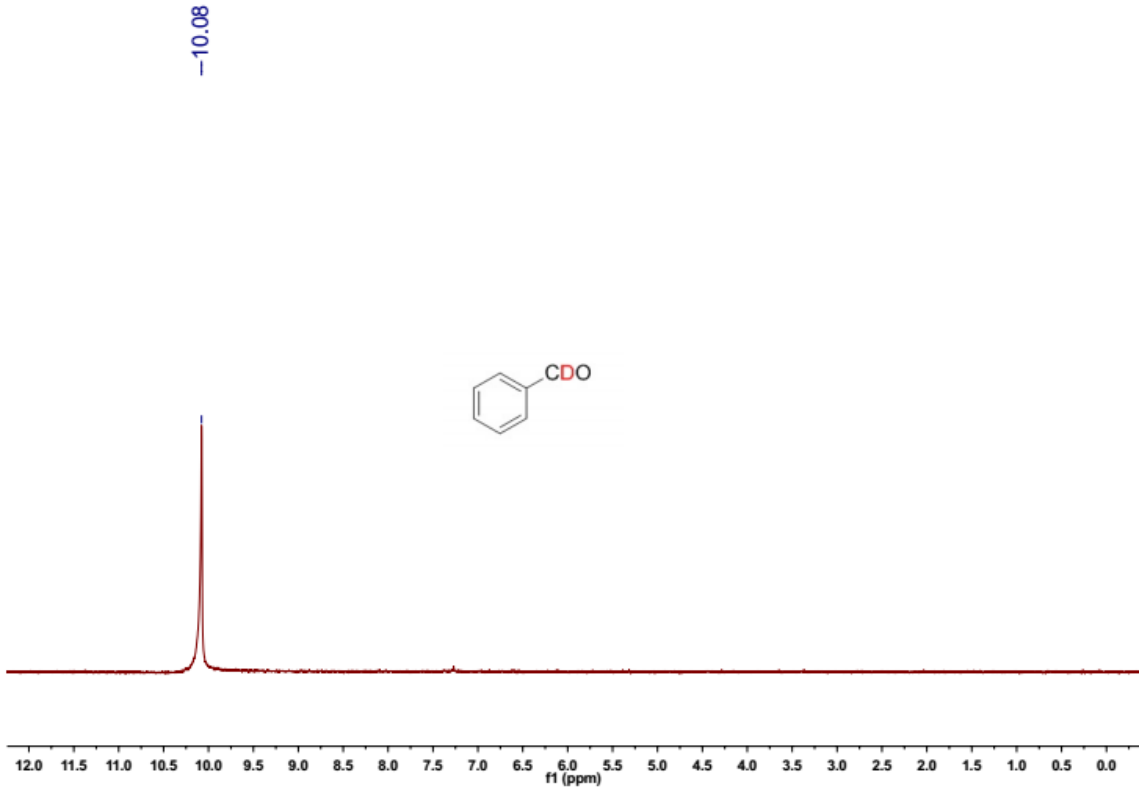
$^{13}$C NMR of deuterated aldehyde **7c**



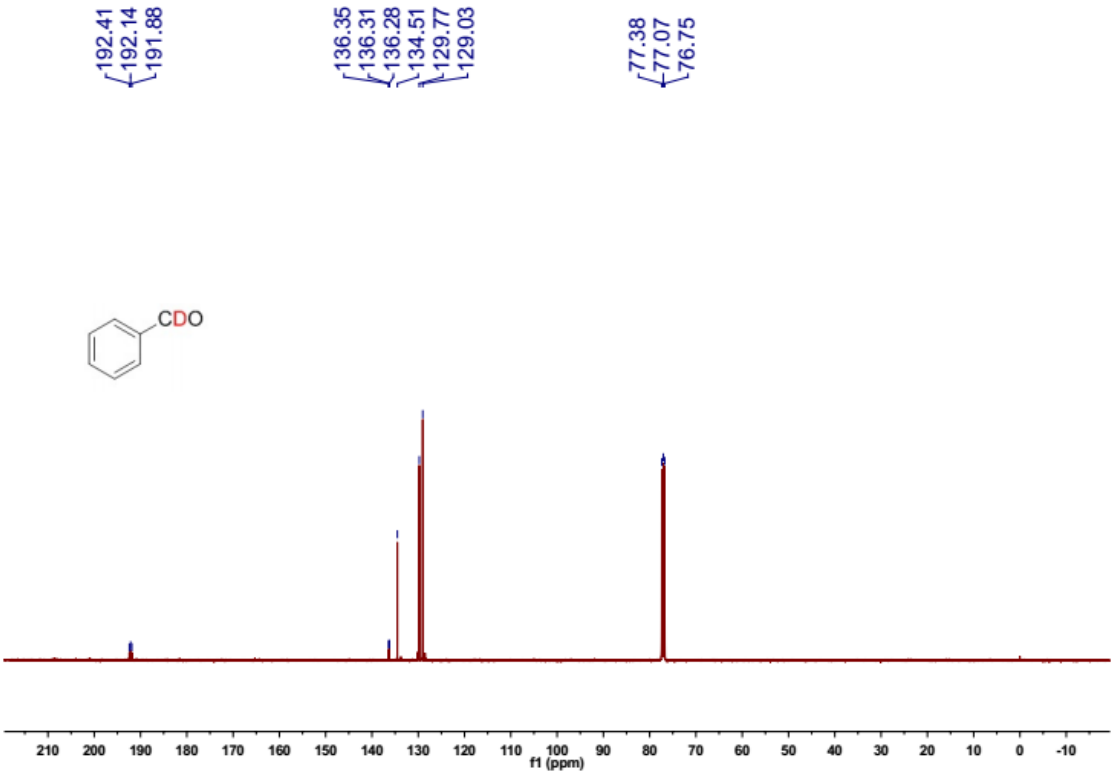
$^{1}$H NMR of deuterated aldehyde **7d**



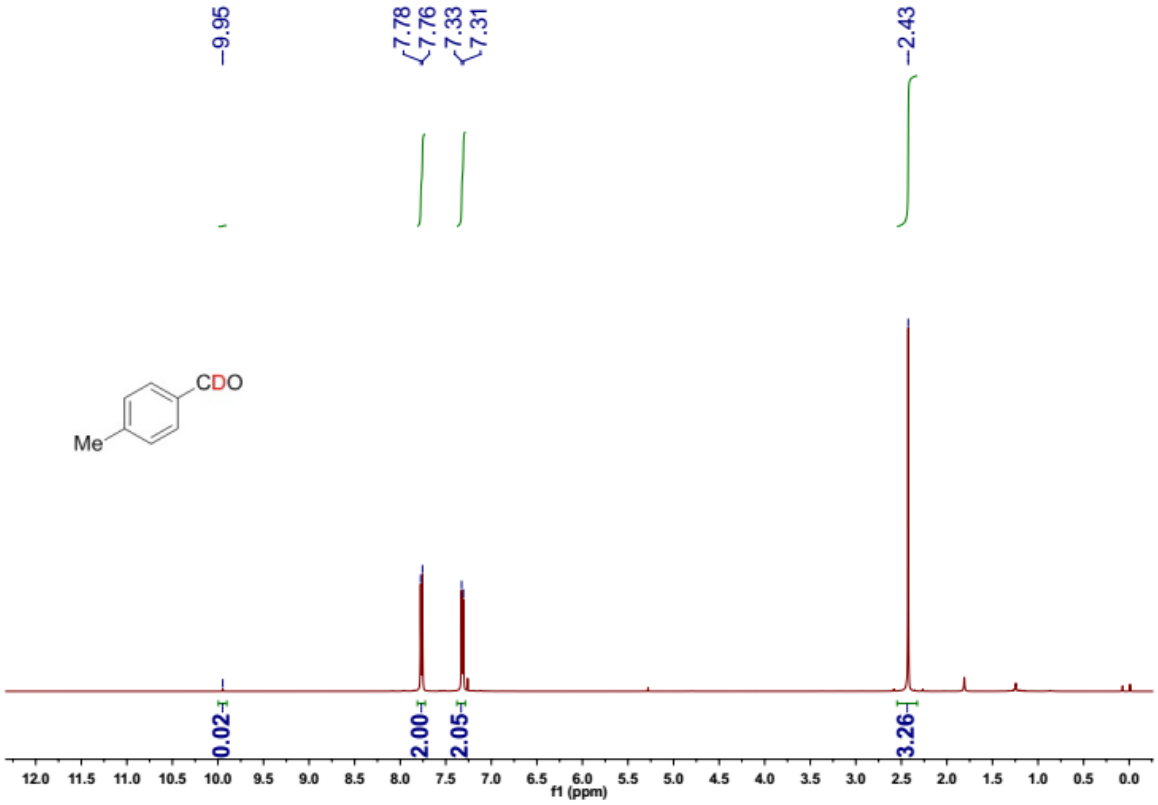

$^{2}$H NMR of deuterated aldehyde **7d**



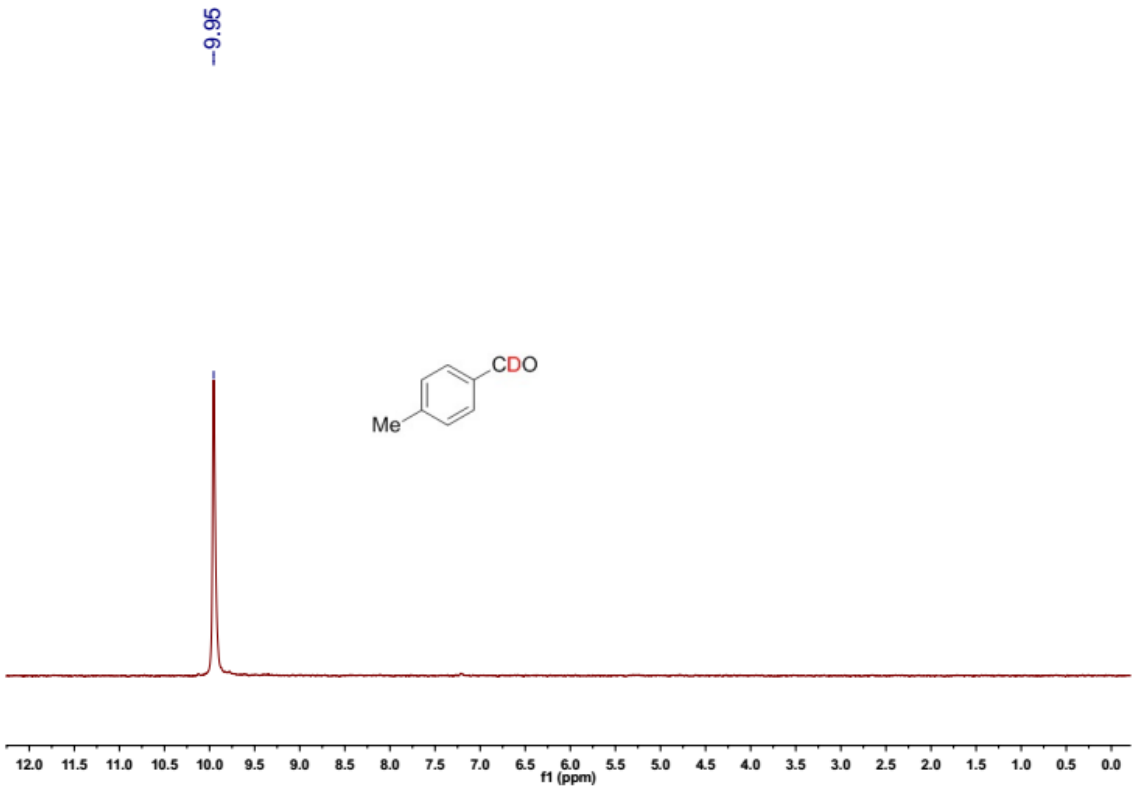
$^{13}$C NMR of deuterated aldehyde **7d**



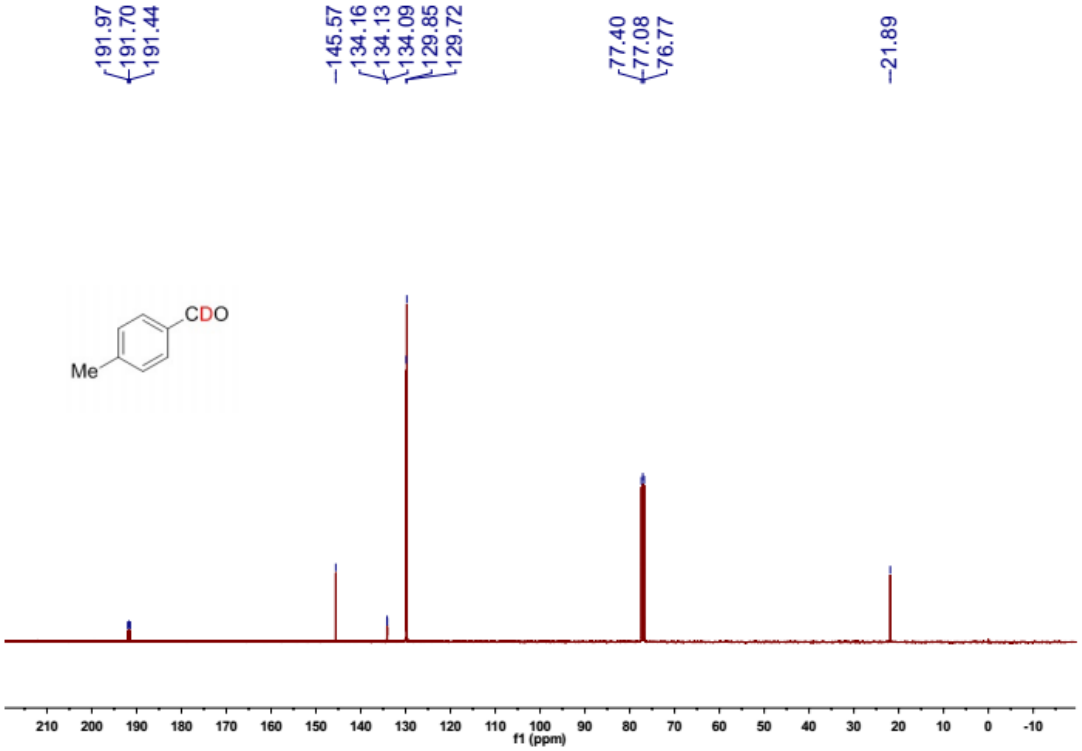
$^{1}$H NMR of deuterated aldehyde **7e**



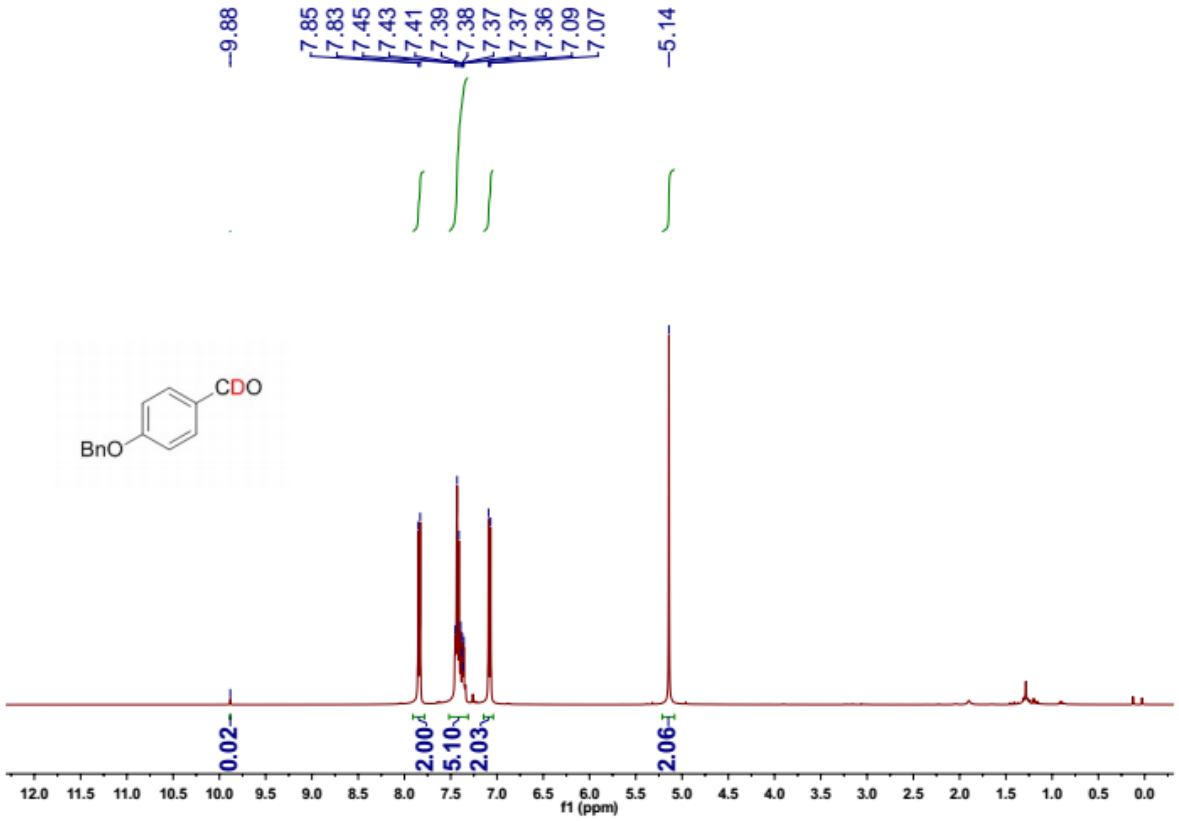

$^{2}$H NMR of deuterated aldehyde **7e**



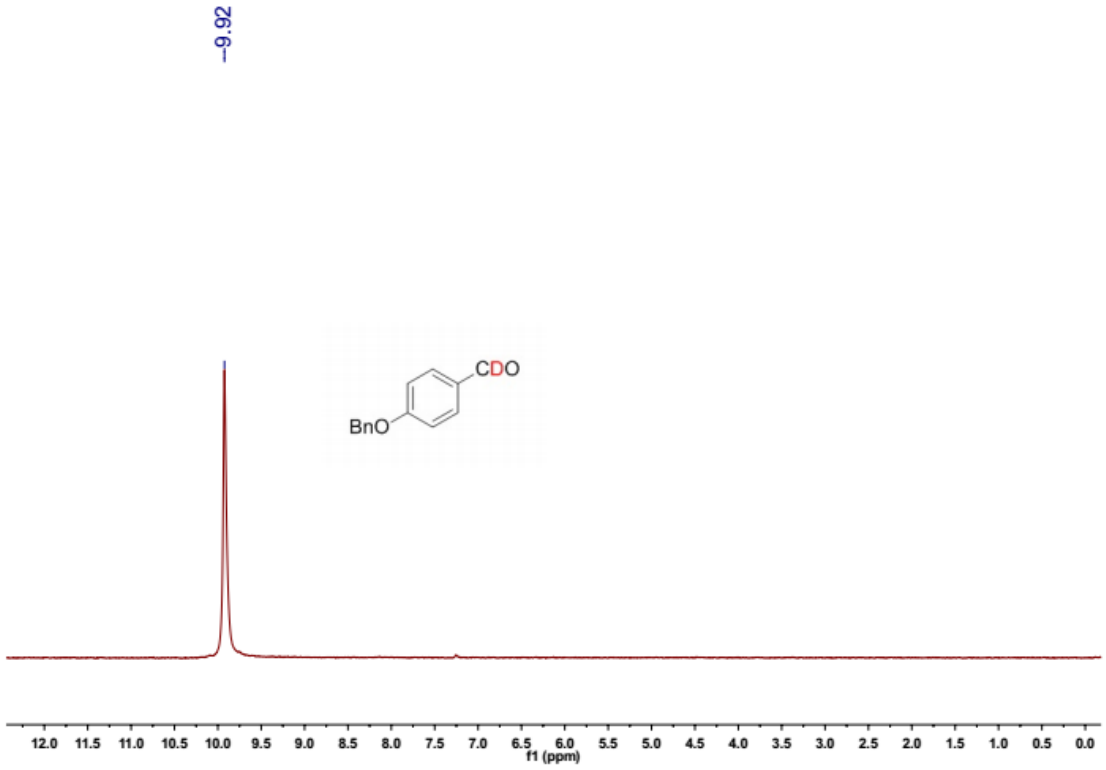
$^{13}$C NMR of deuterated aldehyde **7e**



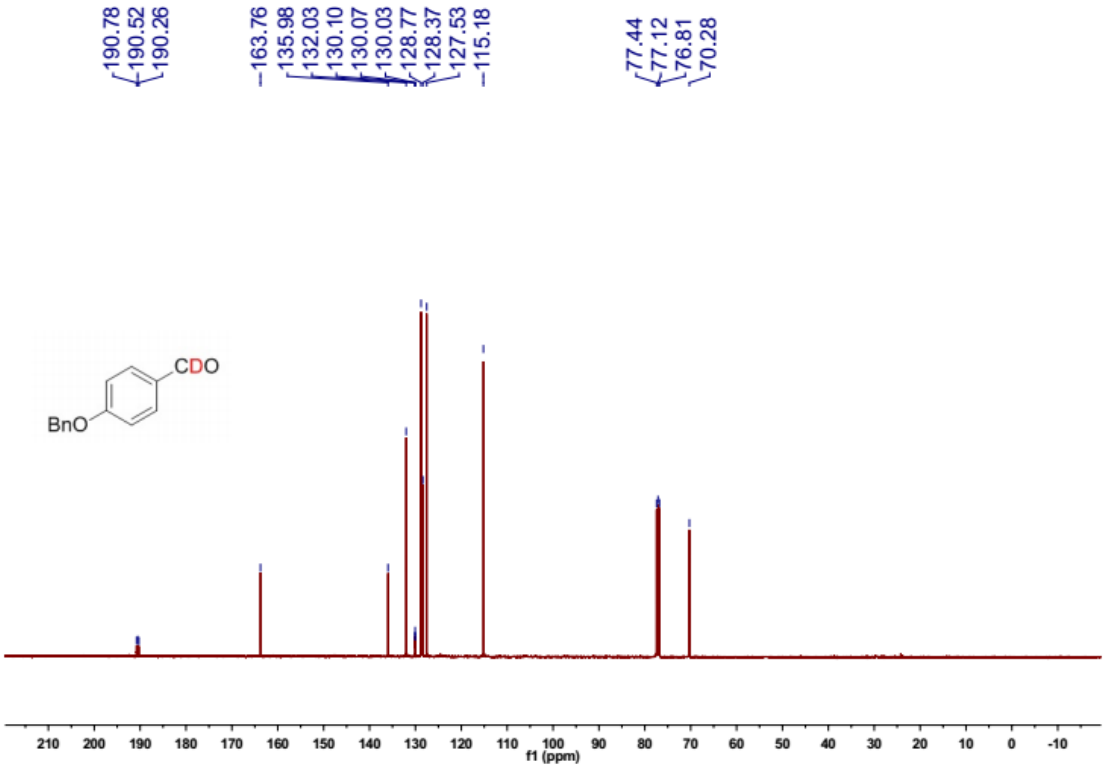
$^{1}$H NMR of deuterated aldehyde **7f**



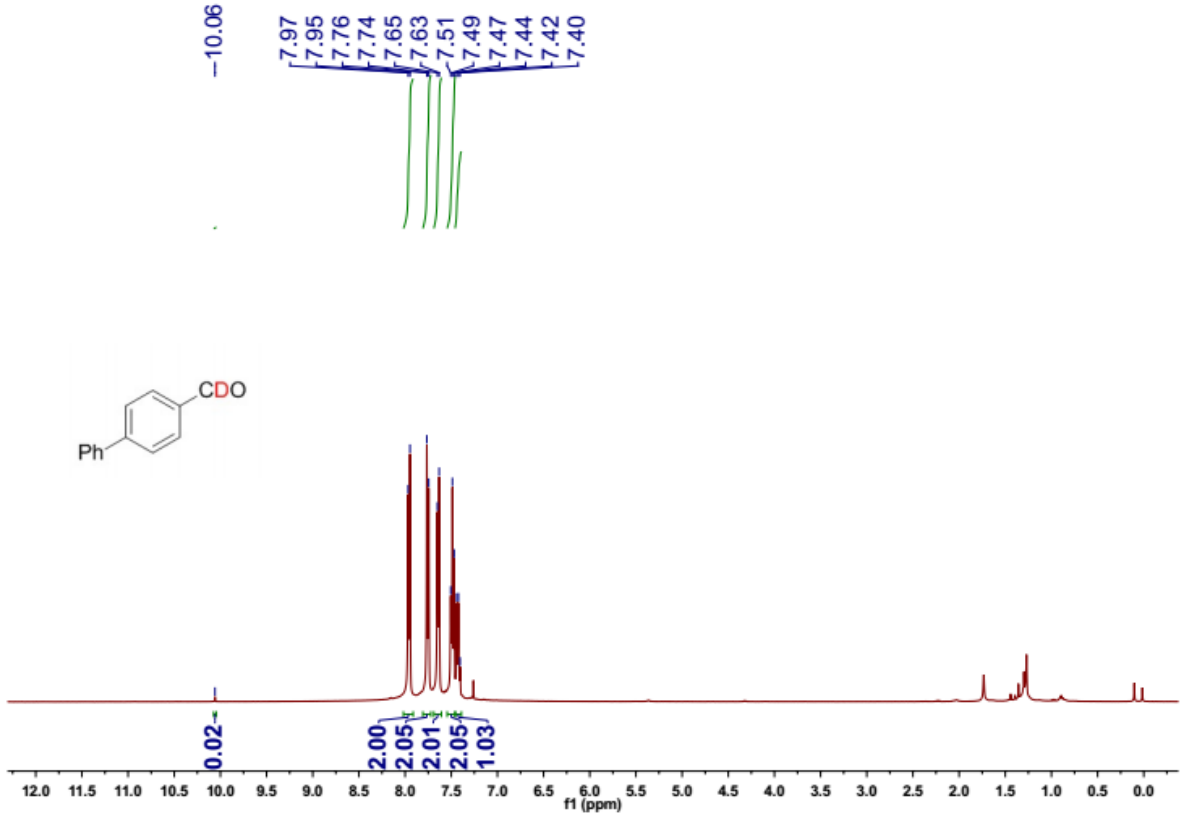

$^{2}$H NMR of deuterated aldehyde **7f**



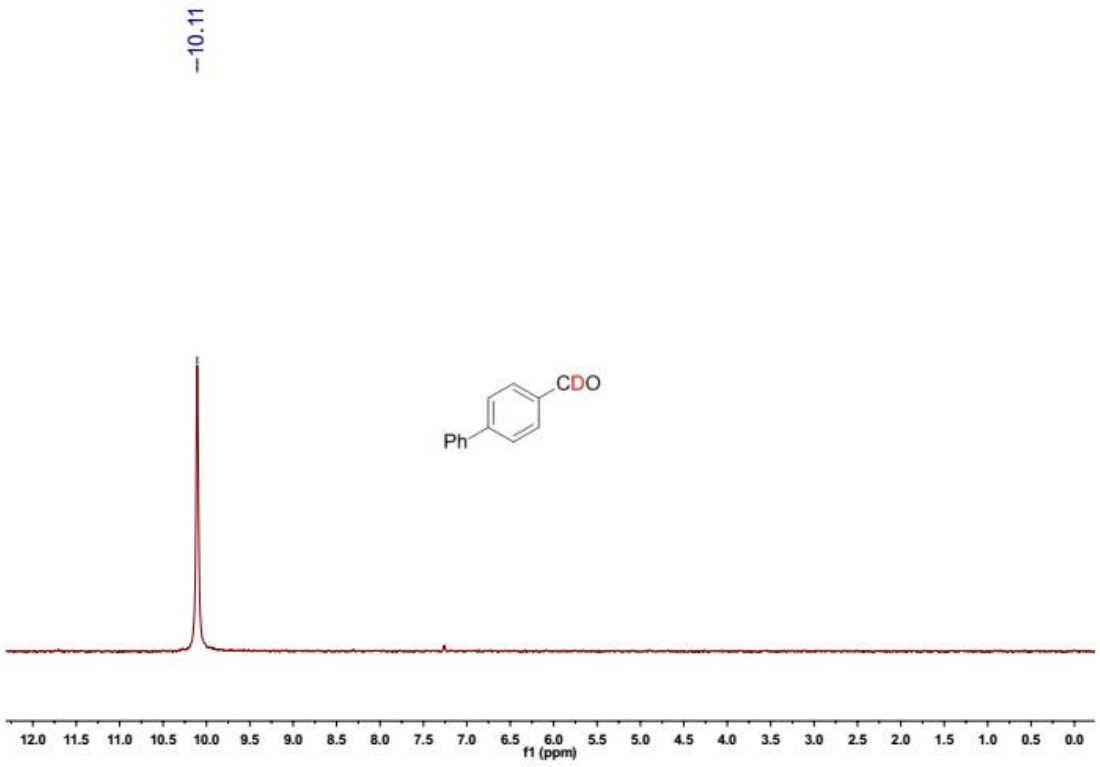
$^{13}$C NMR of deuterated aldehyde **7f**



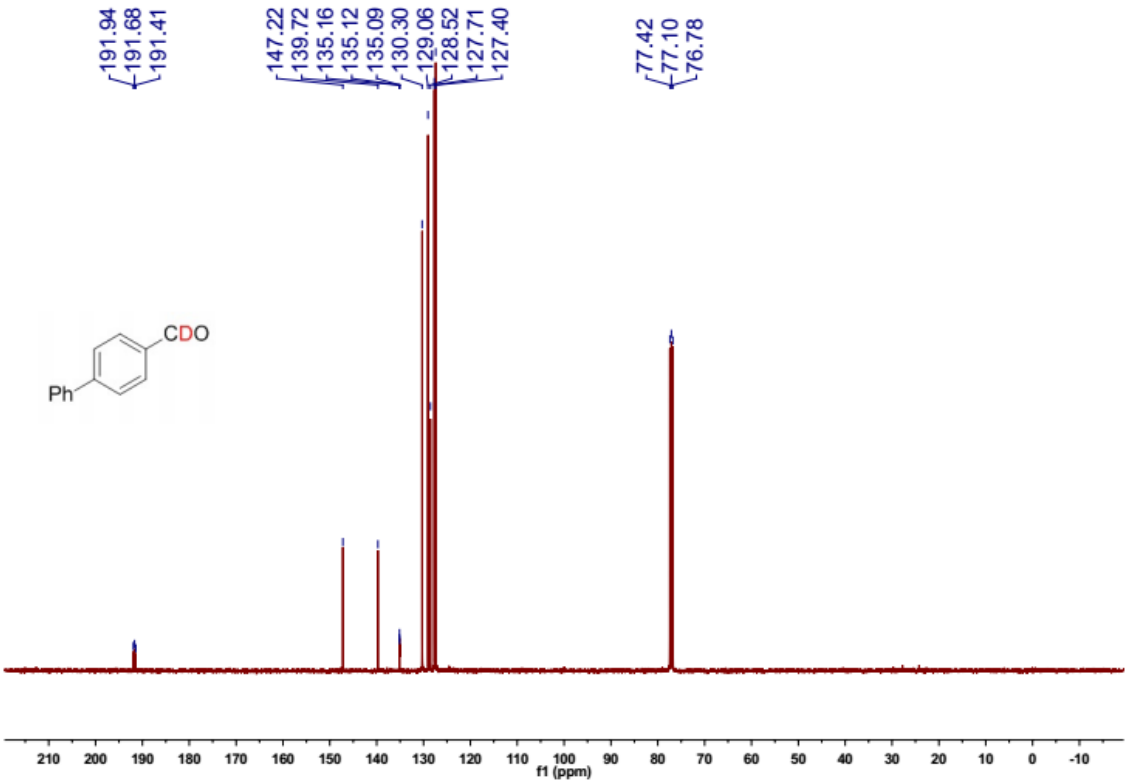
$^{1}$H NMR of deuterated aldehyde **7g**



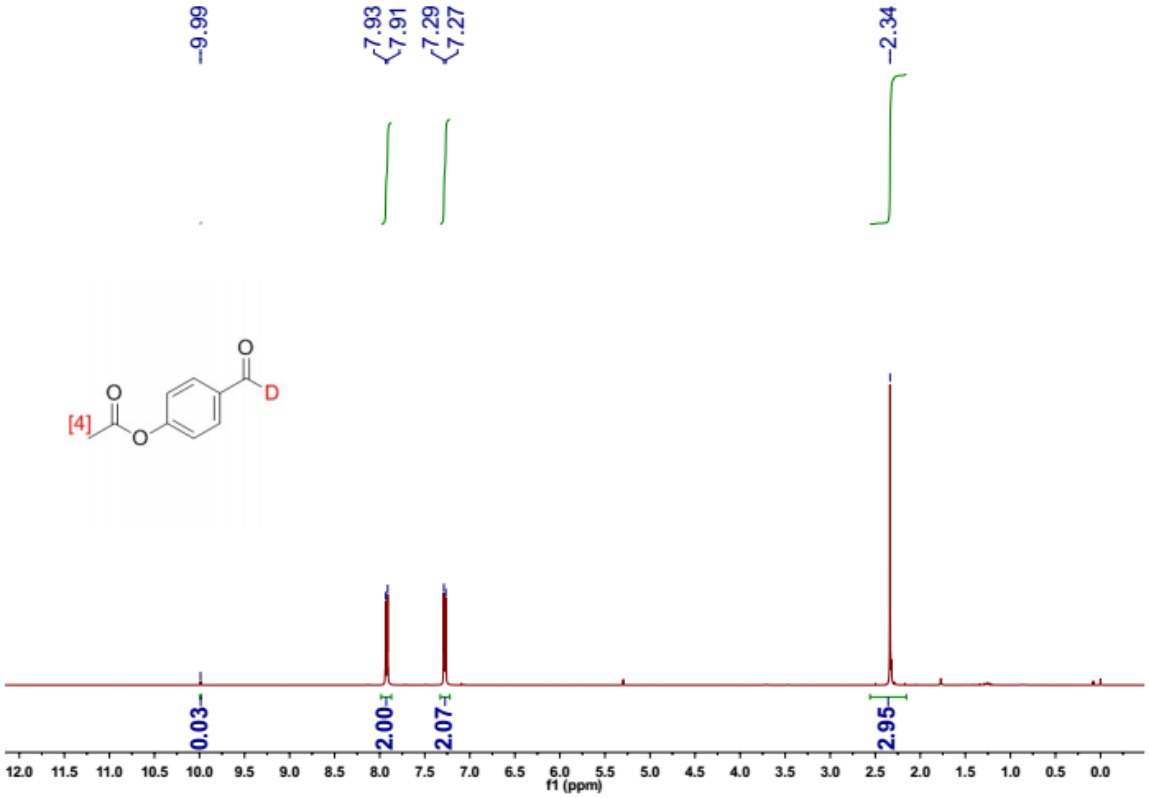

$^{2}$H NMR of deuterated aldehyde **7g**



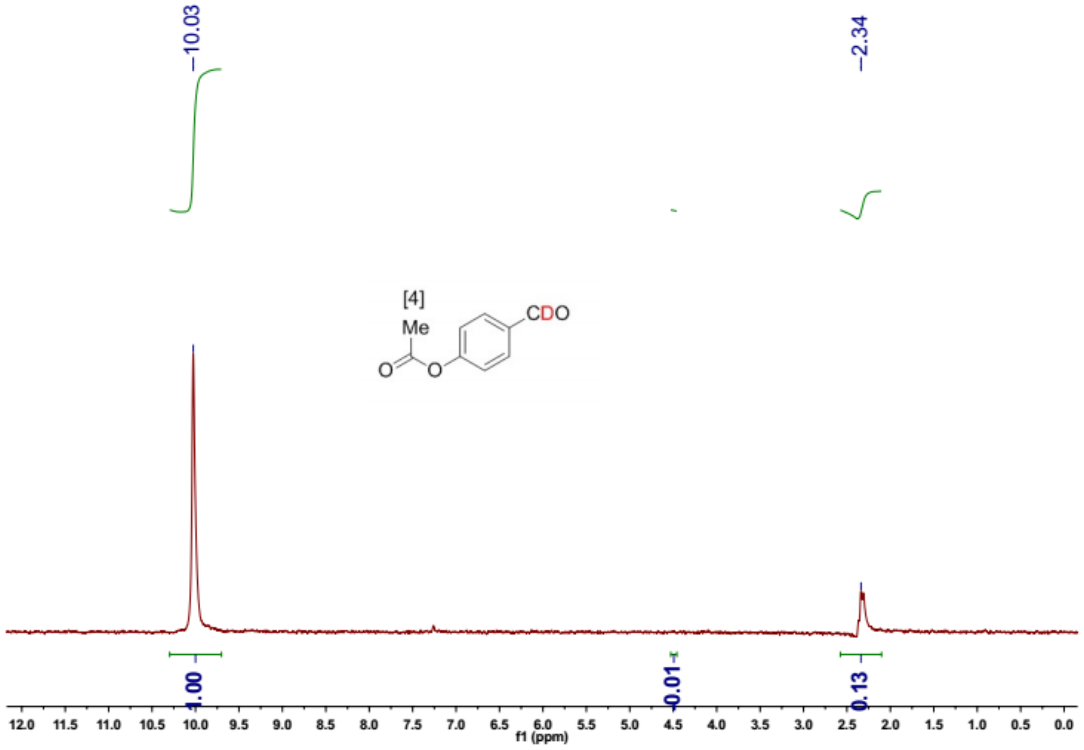
$^{13}$C NMR of deuterated aldehyde **7g**



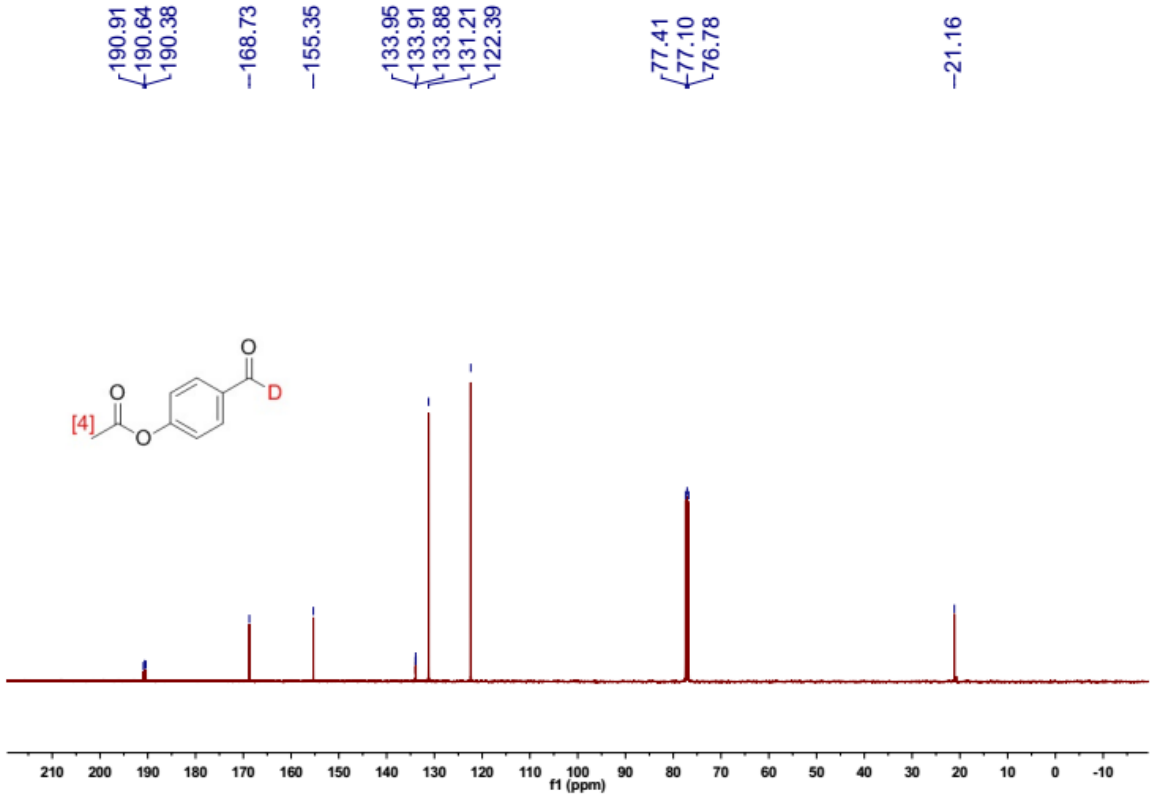
$^{1}$H NMR of deuterated aldehyde **7h**



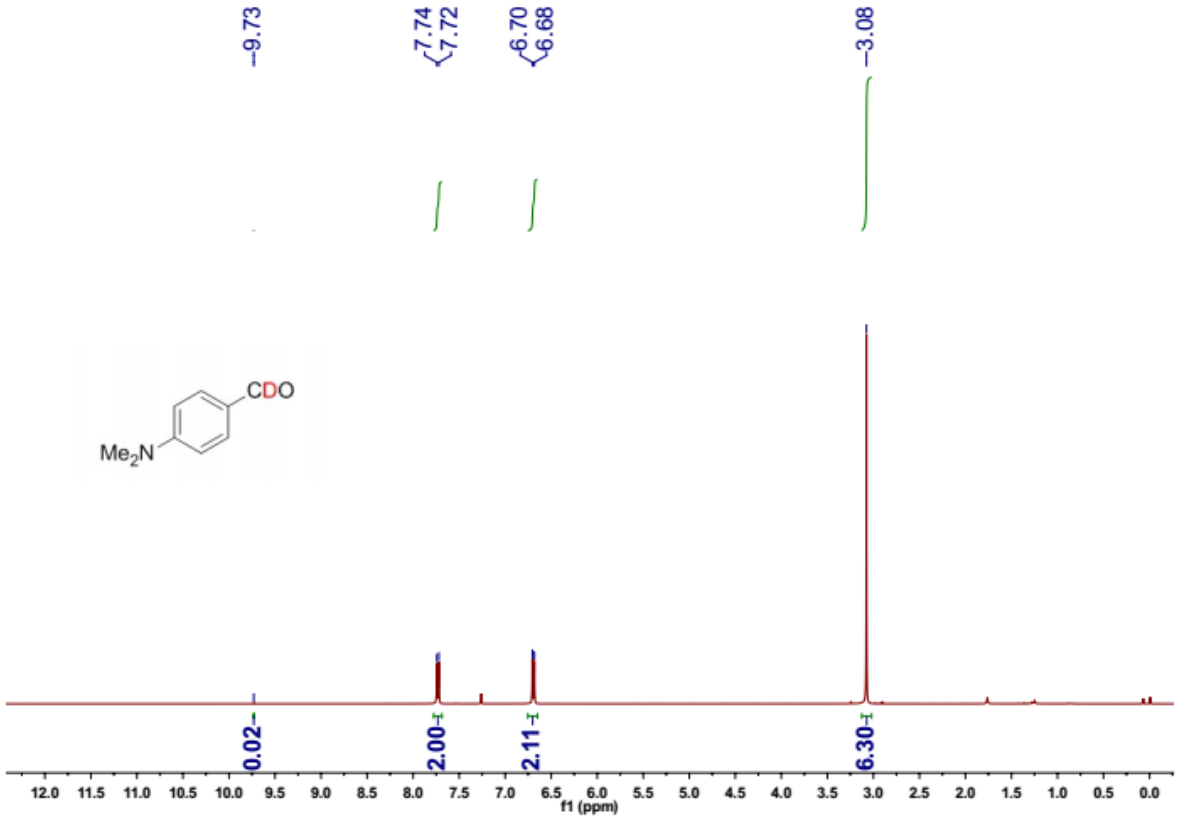

$^{2}$H NMR of deuterated aldehyde **7h**



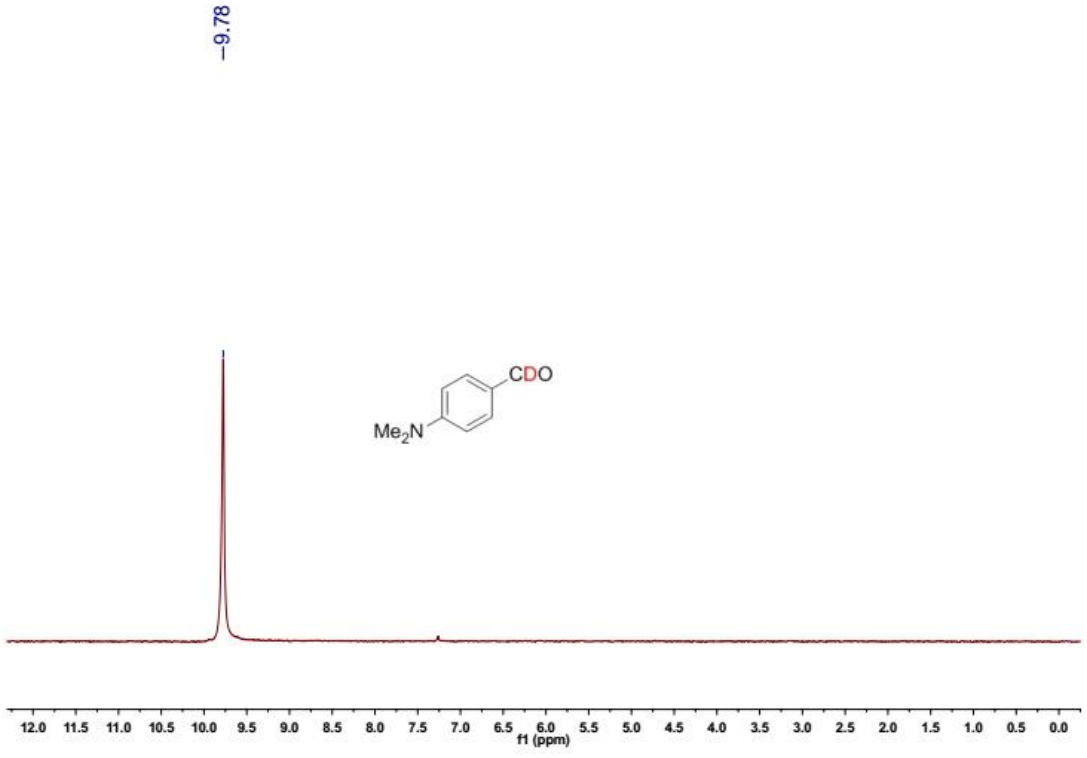
$^{13}$C NMR of deuterated aldehyde **7h**



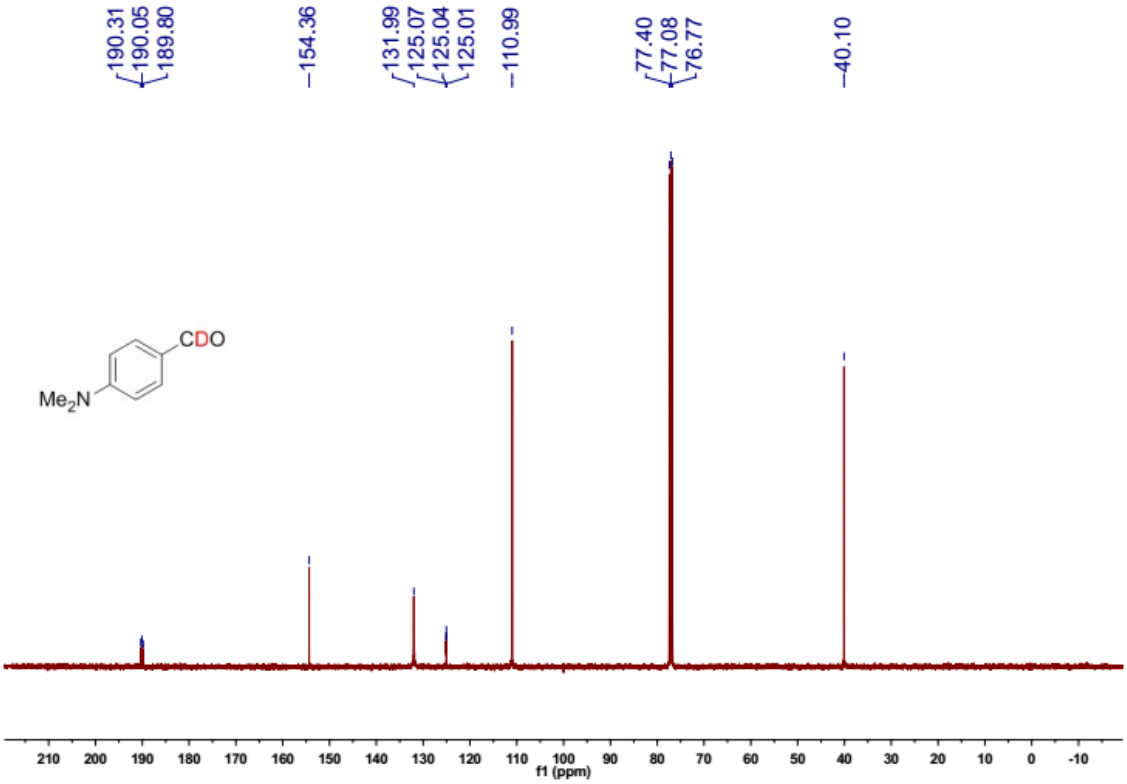
$^{1}$H NMR of deuterated aldehyde **7i**



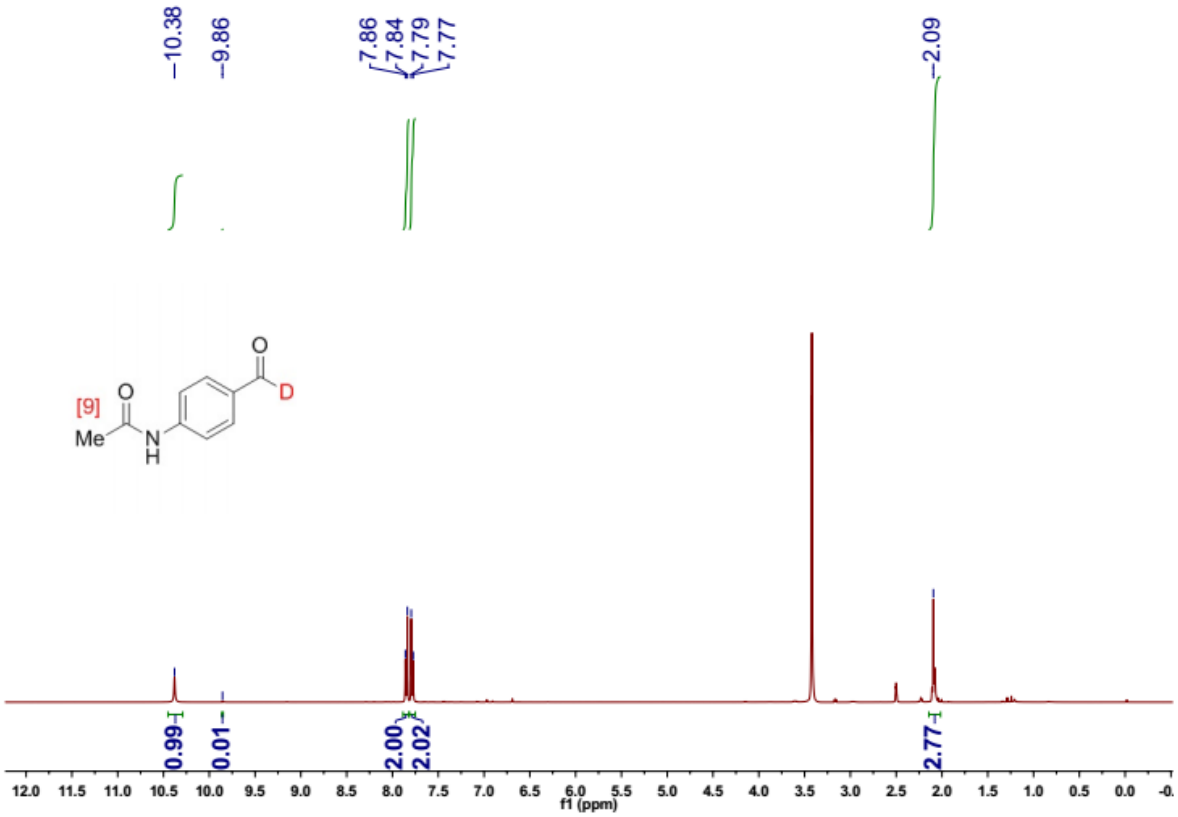

$^{2}$H NMR of deuterated aldehyde **7i**



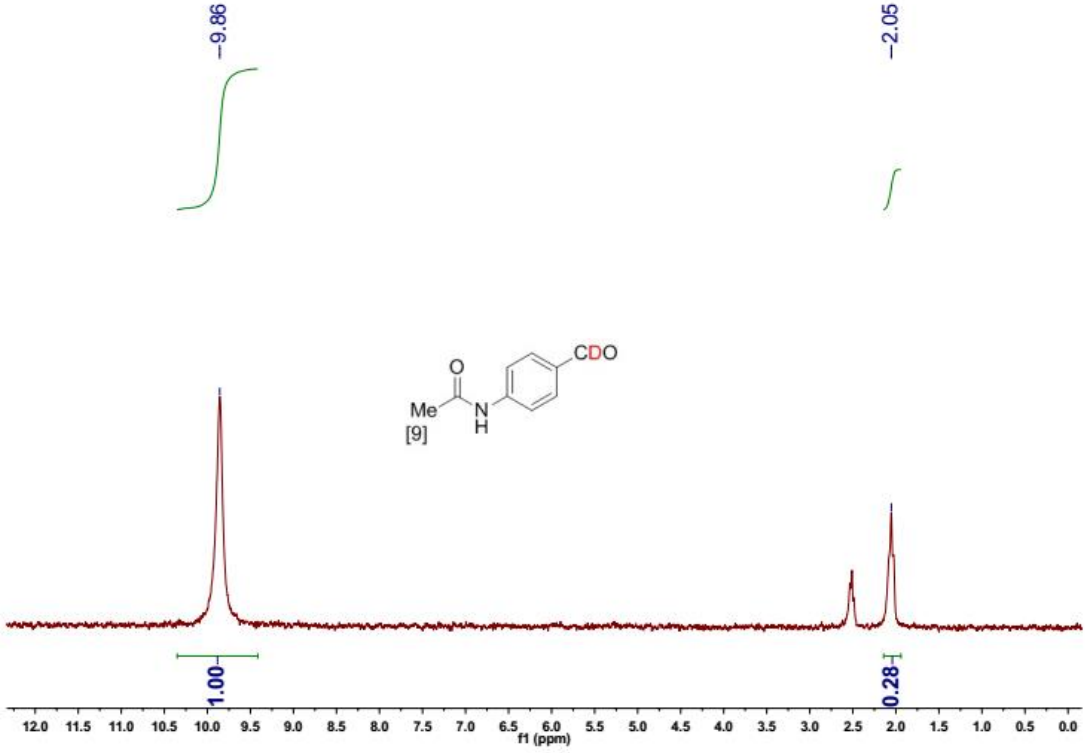
$^{13}$C NMR of deuterated aldehyde **7i**



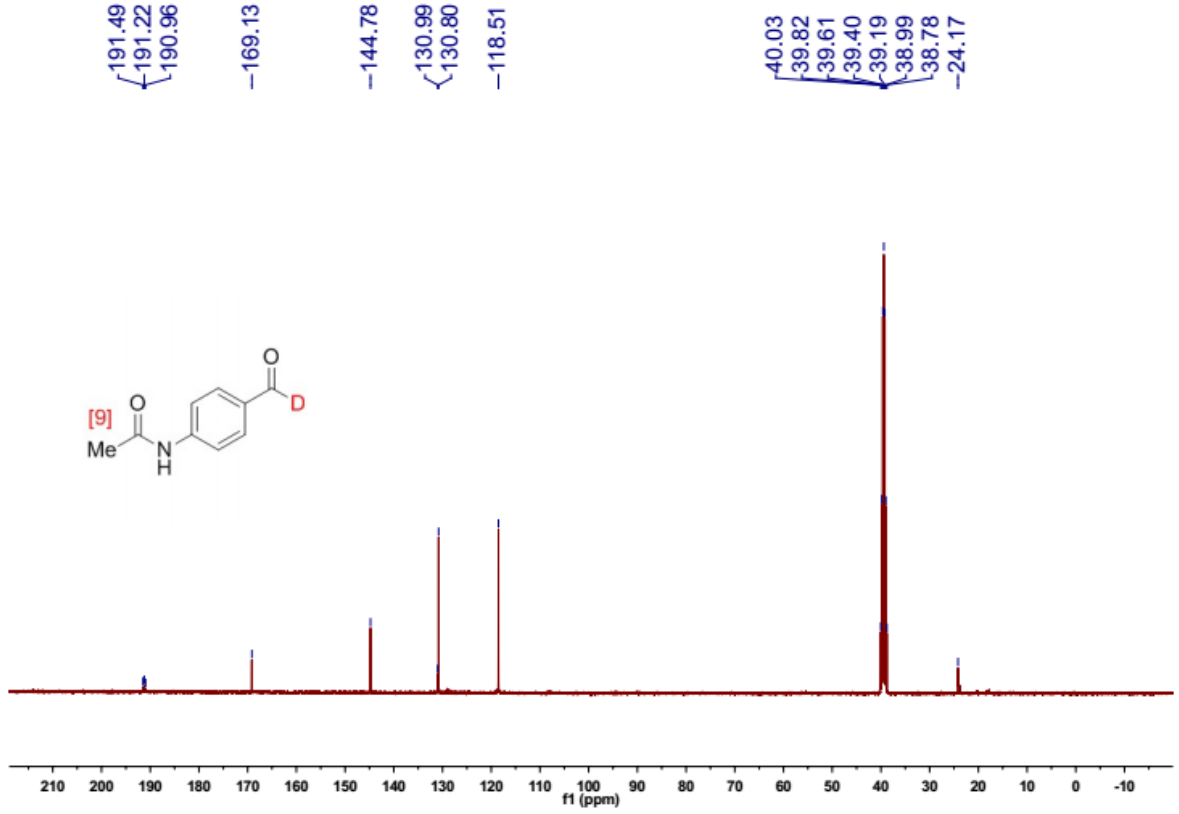
$^{1}$H NMR of deuterated aldehyde **7j**



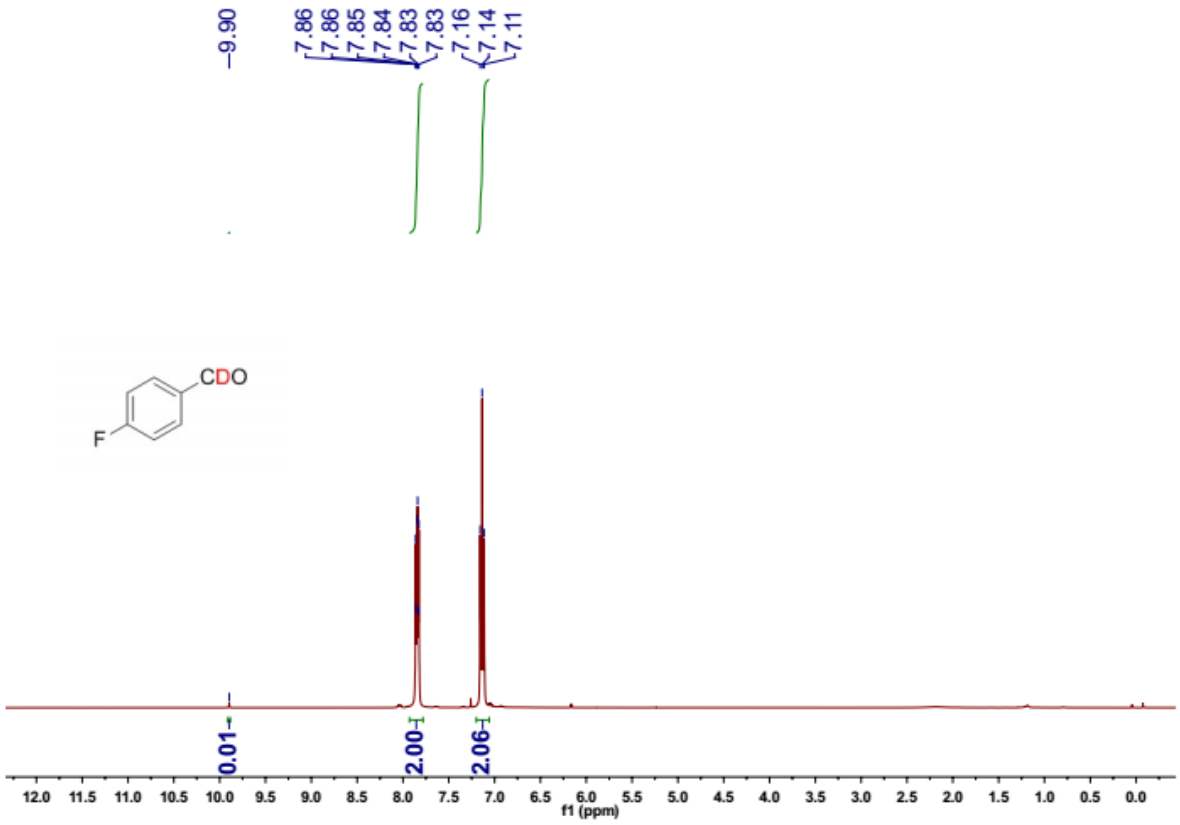

$^{2}$H NMR of deuterated aldehyde **7j** (The peak in δ 2.5 is the residue of DMSO-$d_6$)



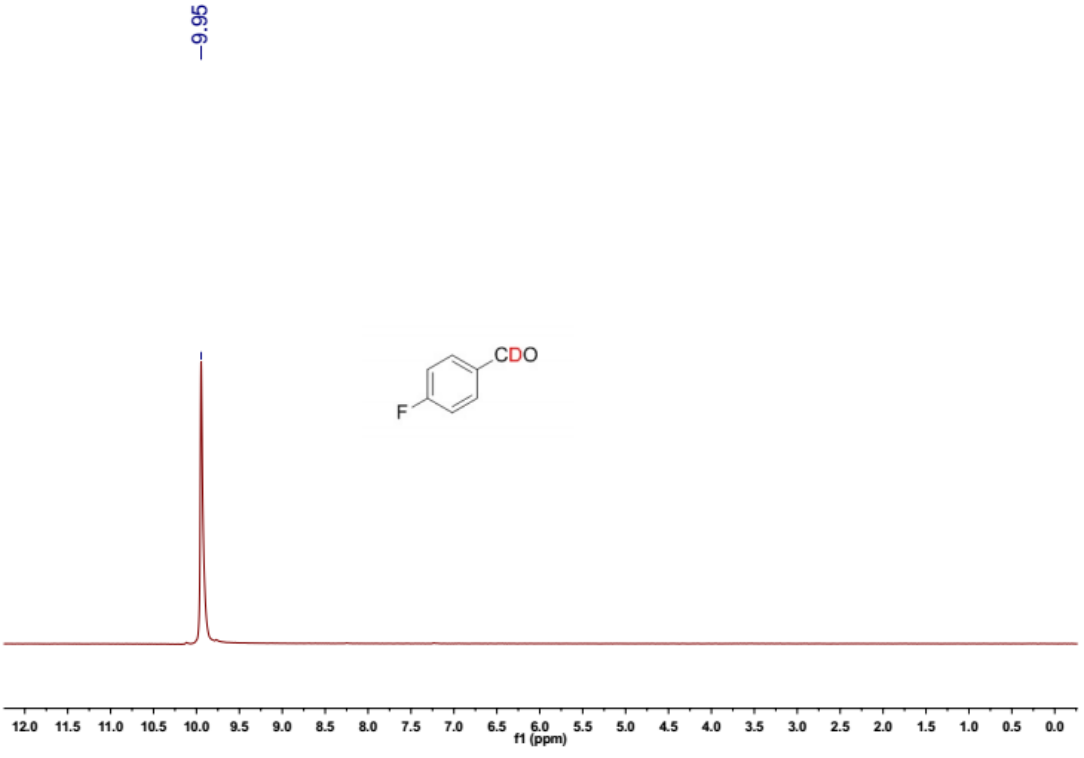
$^{13}$C NMR of deuterated aldehyde **7j**



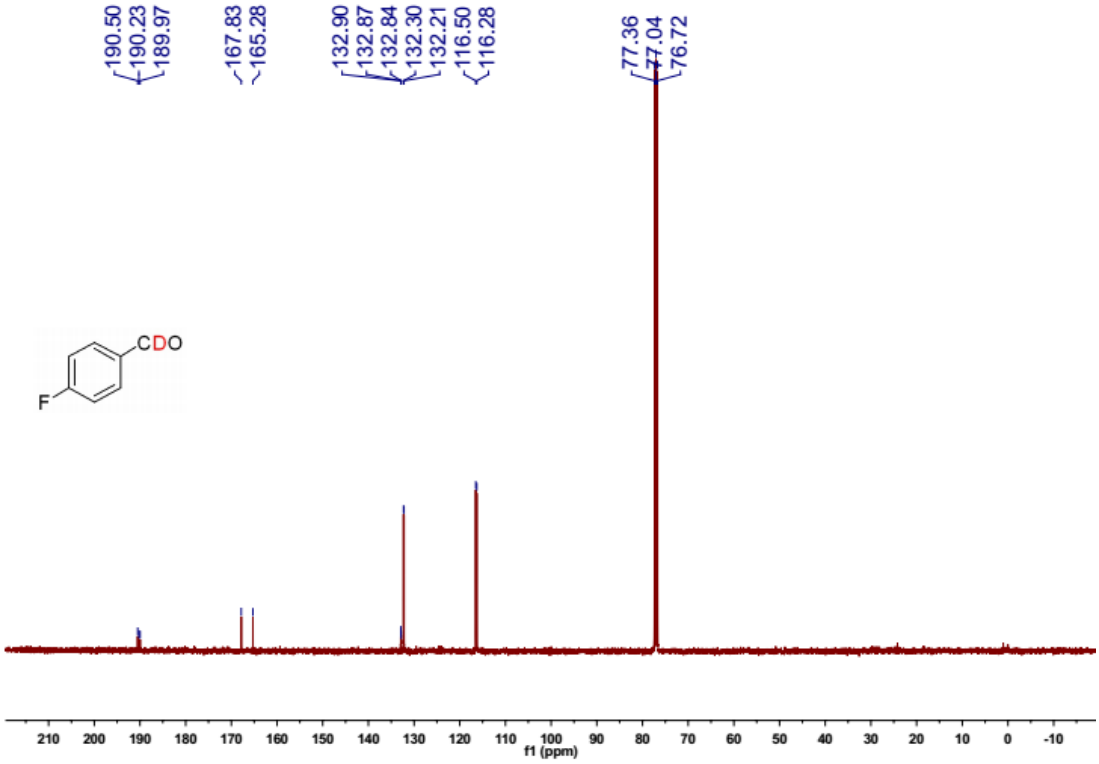
$^{1}$H NMR of deuterated aldehyde **7k**



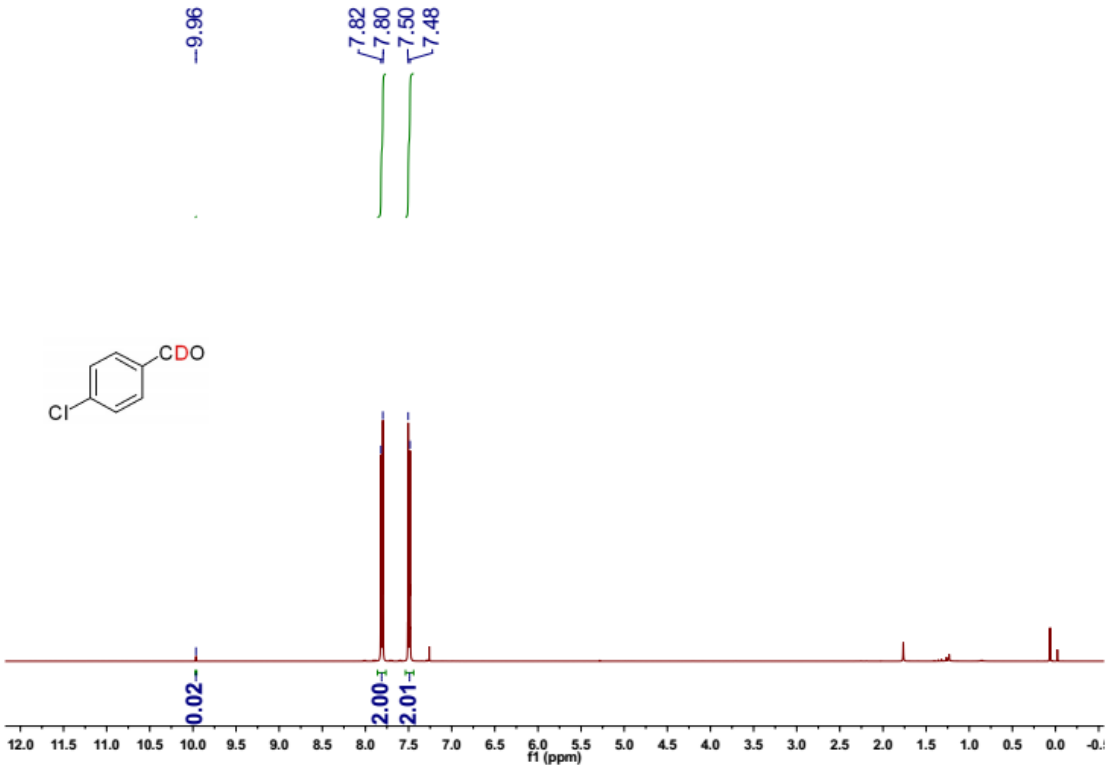

$^{2}$H NMR of deuterated aldehyde **7k**



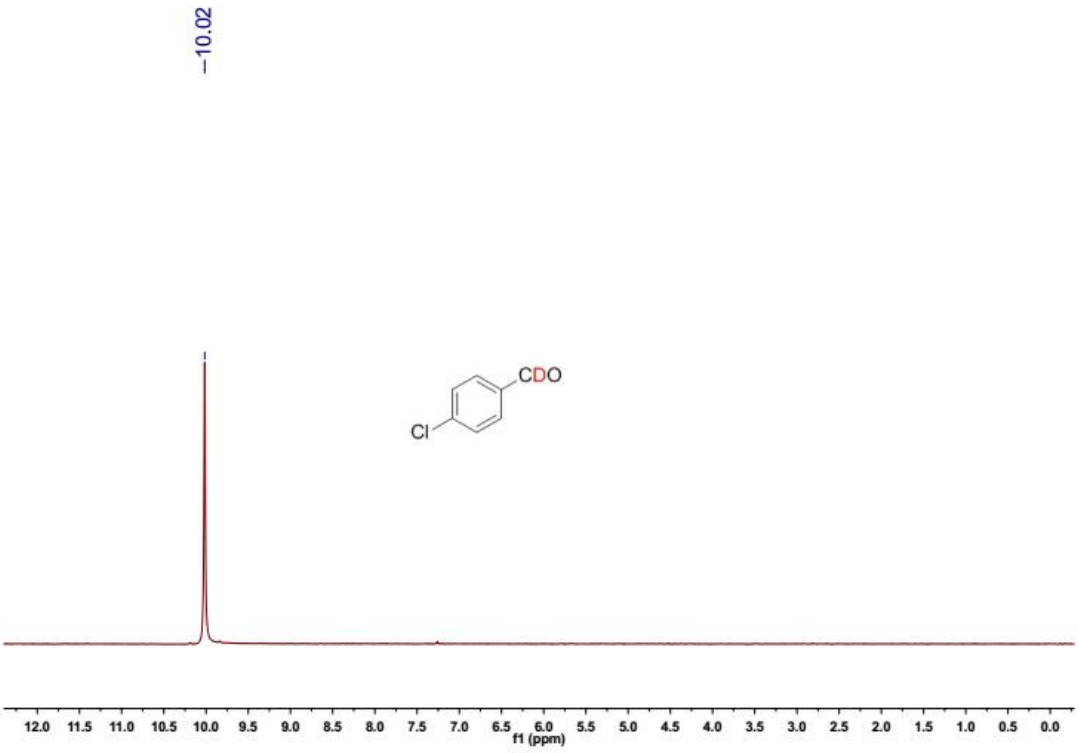
$^{13}$C NMR of deuterated aldehyde **7k**



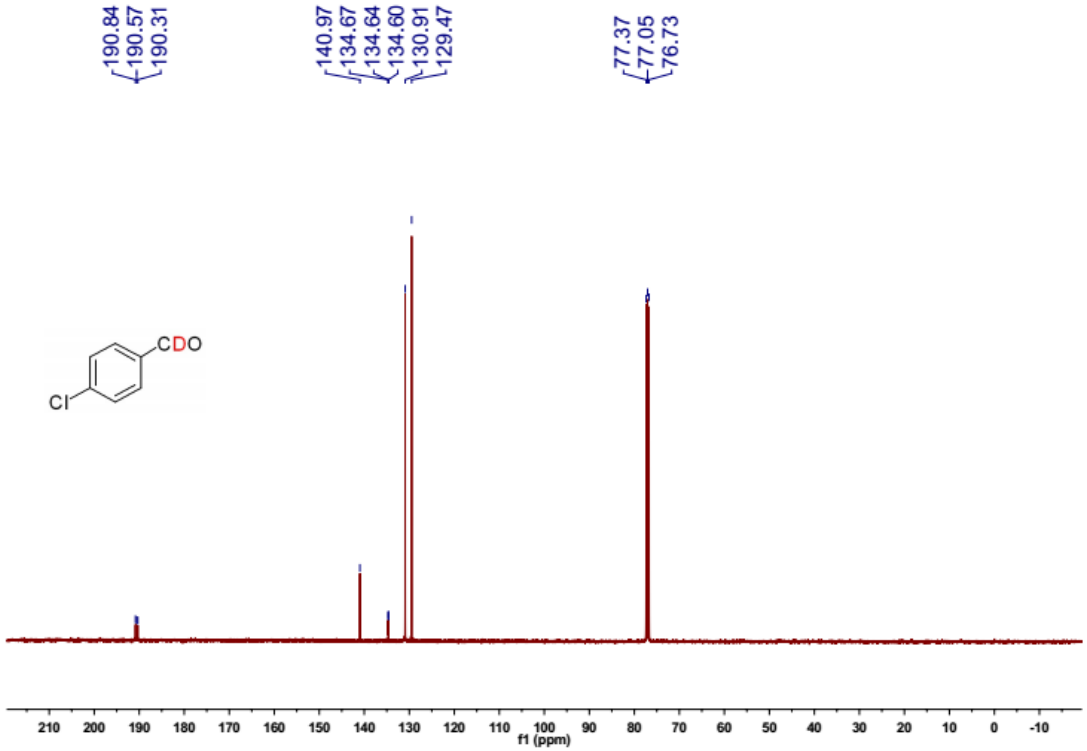
$^{1}$H NMR of deuterated aldehyde **7l**



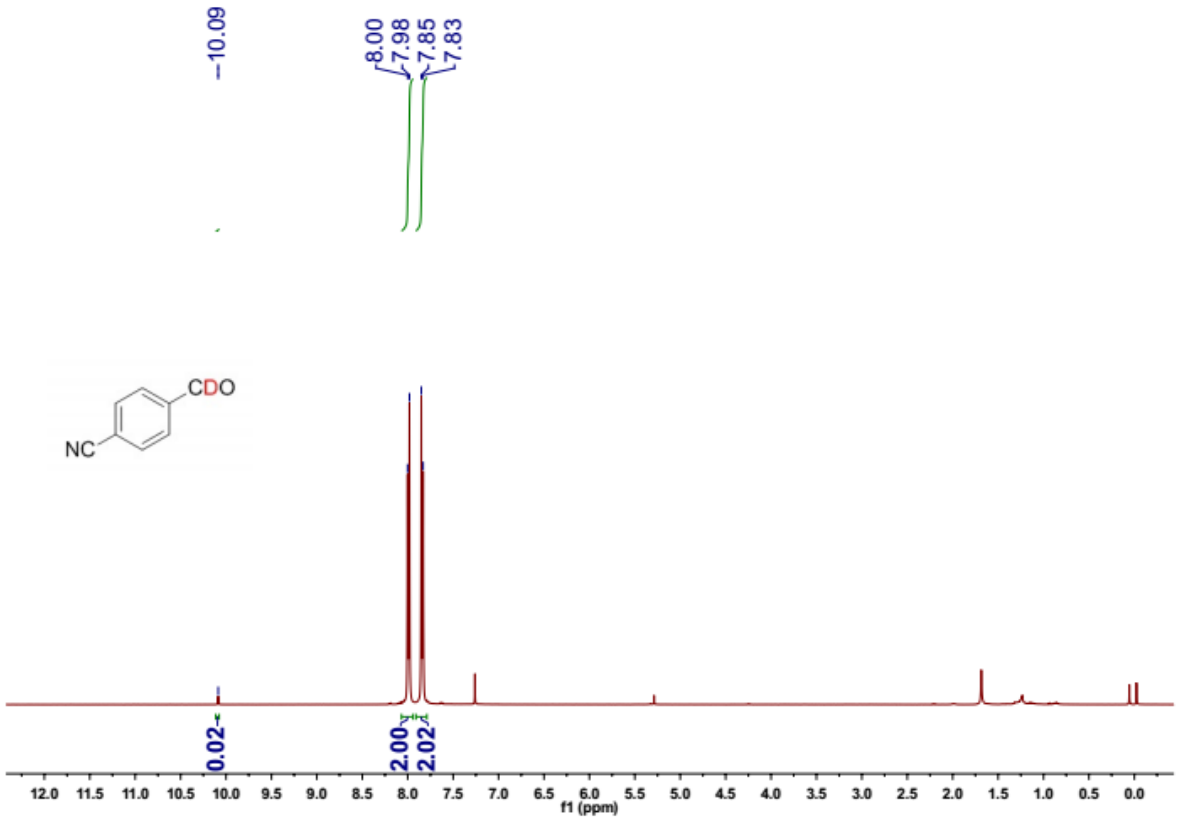

$^{2}$H NMR of deuterated aldehyde **7l**



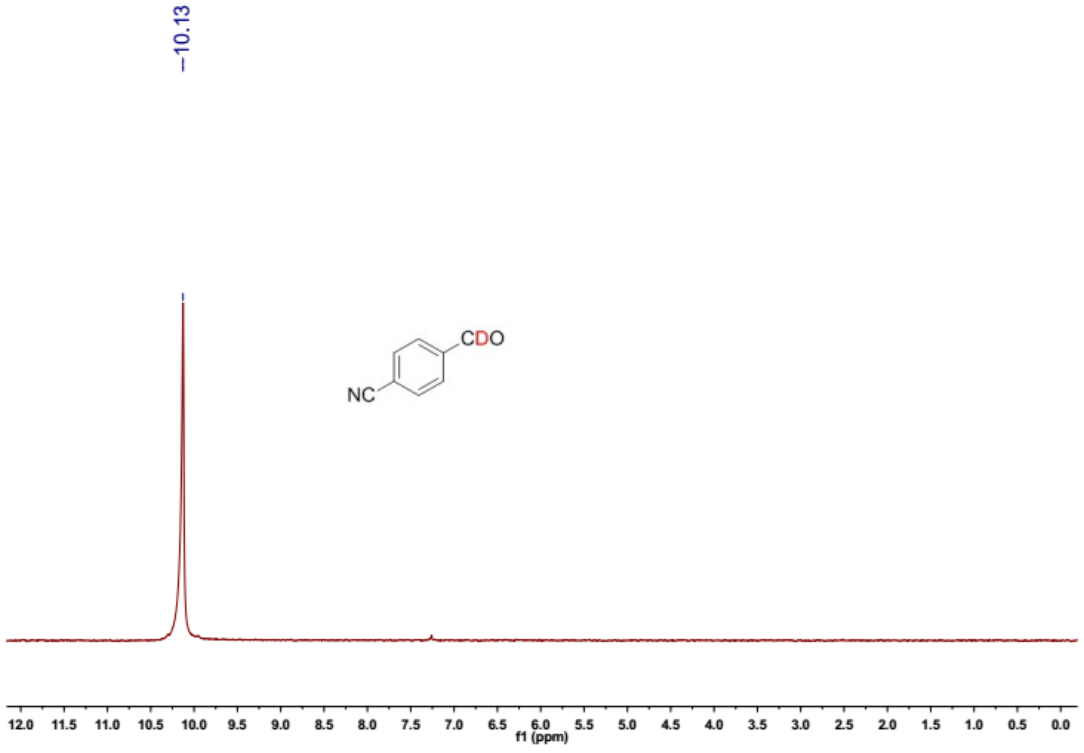
$^{13}$C NMR of deuterated aldehyde **7l**



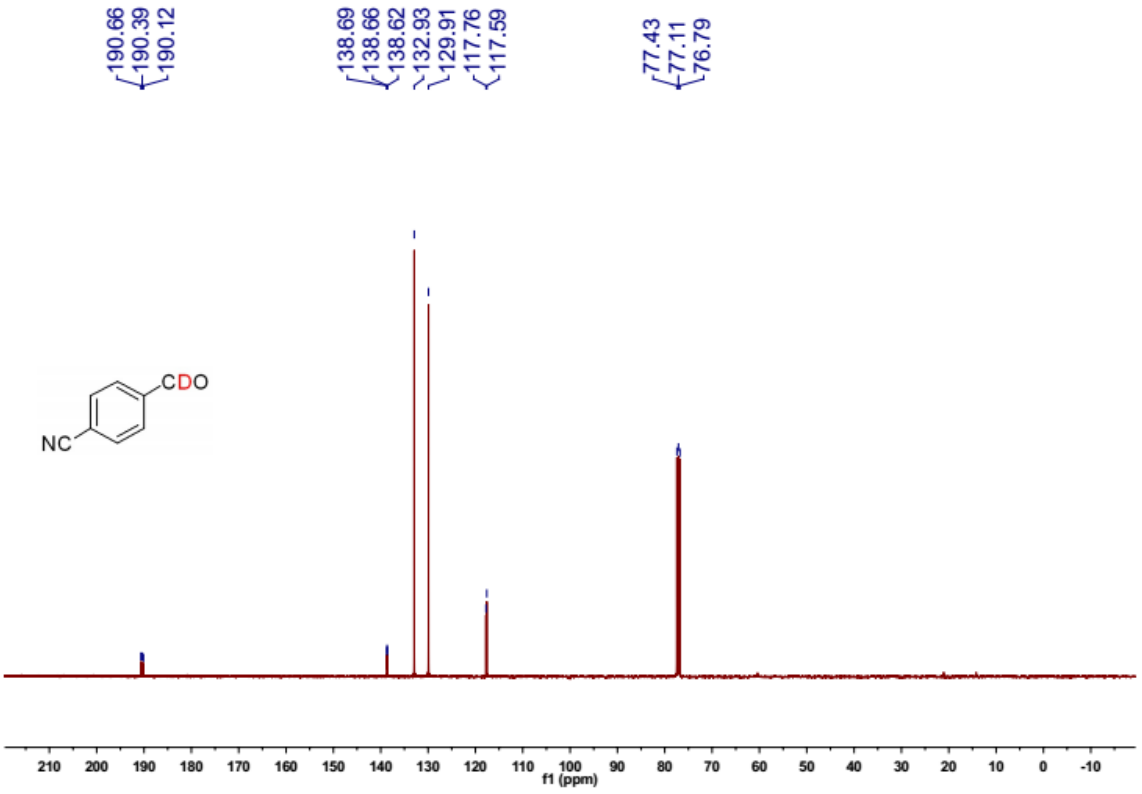
$^{1}$H NMR of deuterated aldehyde **7m**



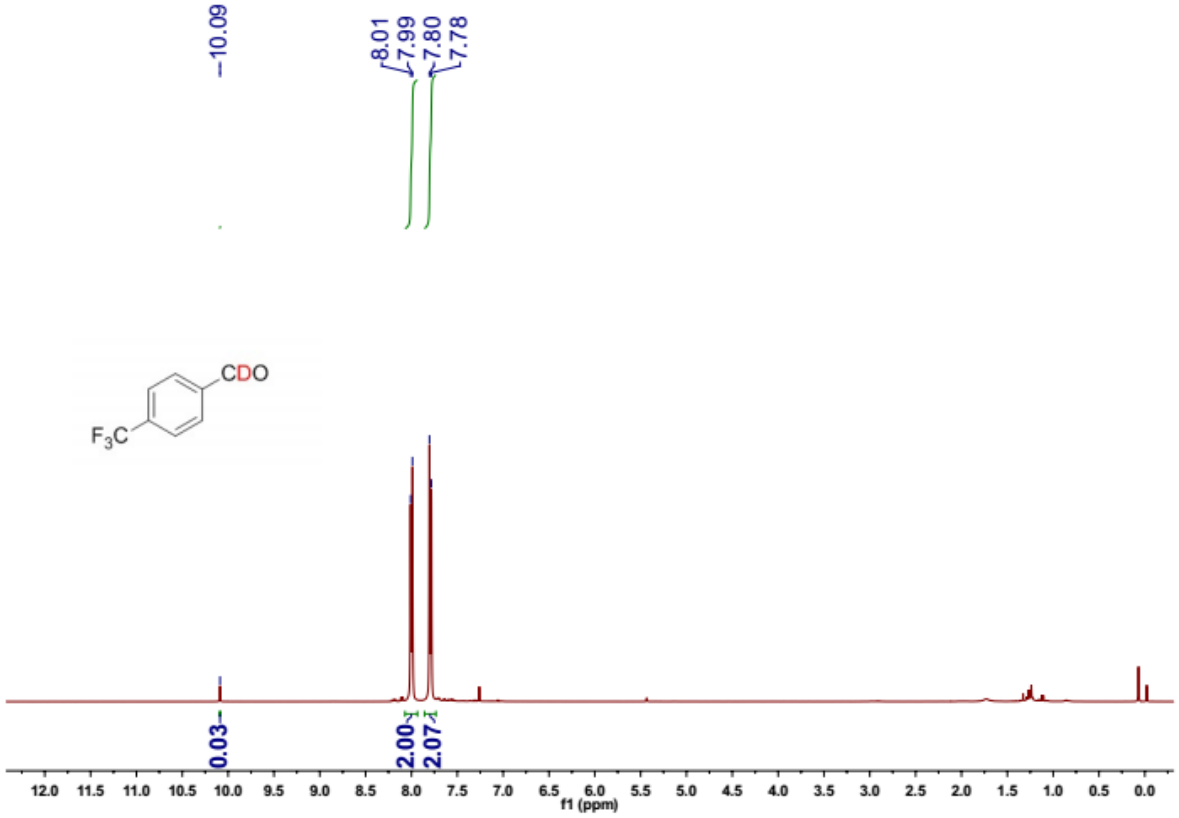

$^{2}$H NMR of deuterated aldehyde **7m**



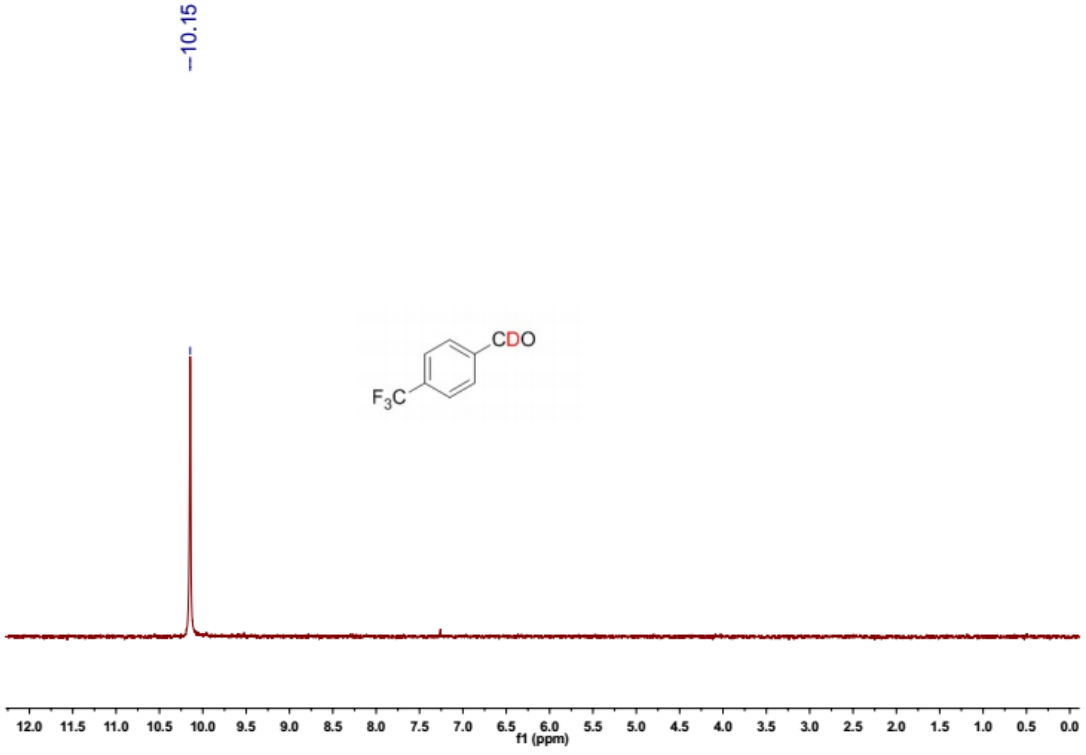
$^{13}$C NMR of deuterated aldehyde **7m**



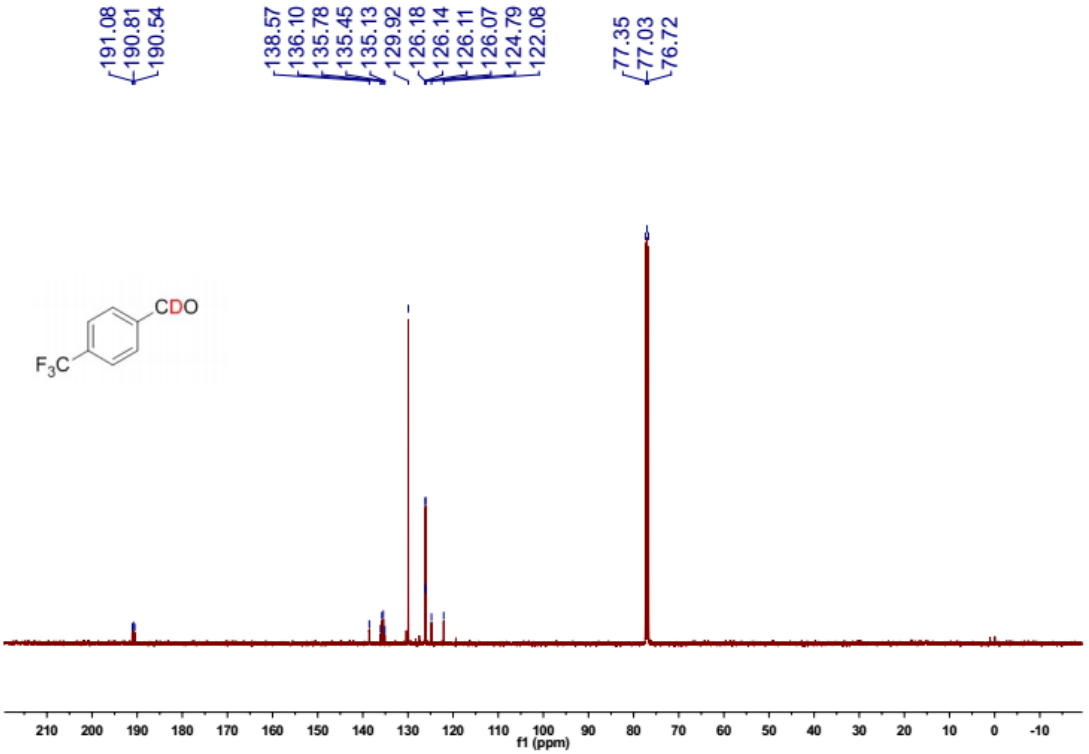
$^{1}$H NMR of deuterated aldehyde **7n**



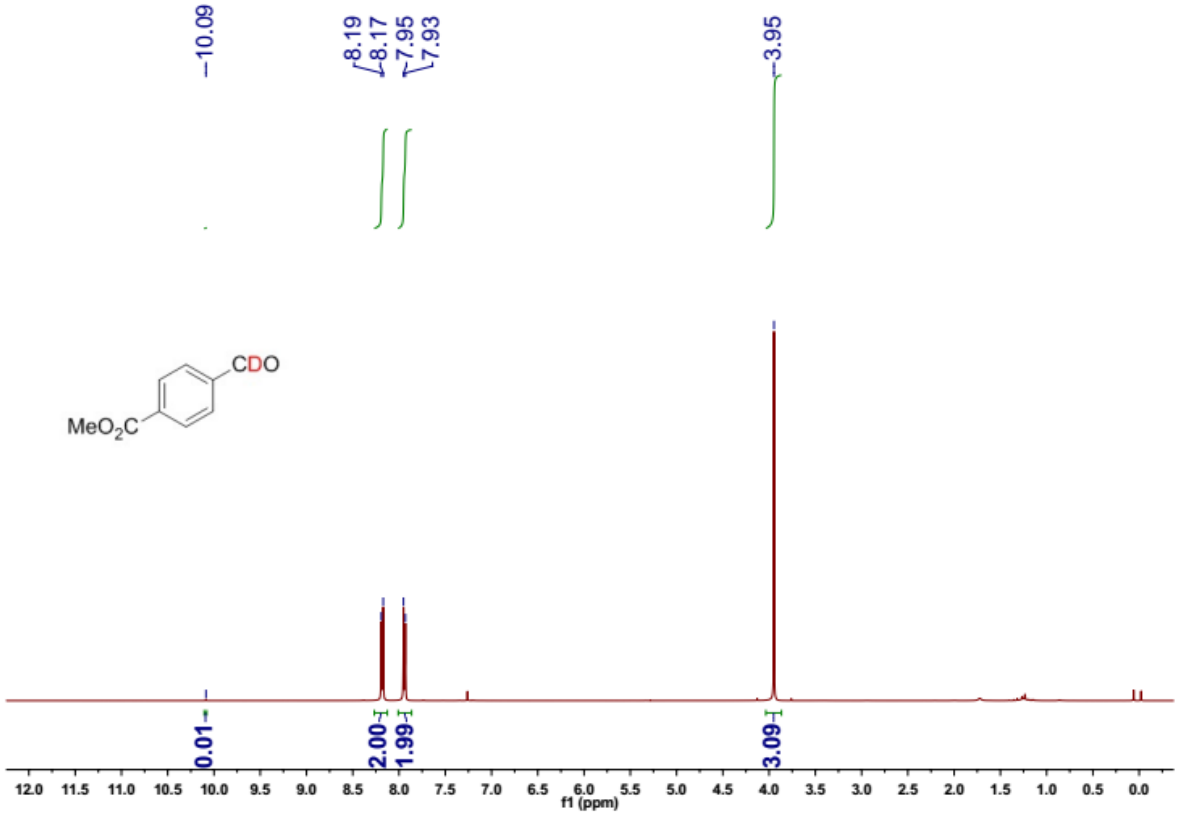

$^{2}$H NMR of deuterated aldehyde **7n**



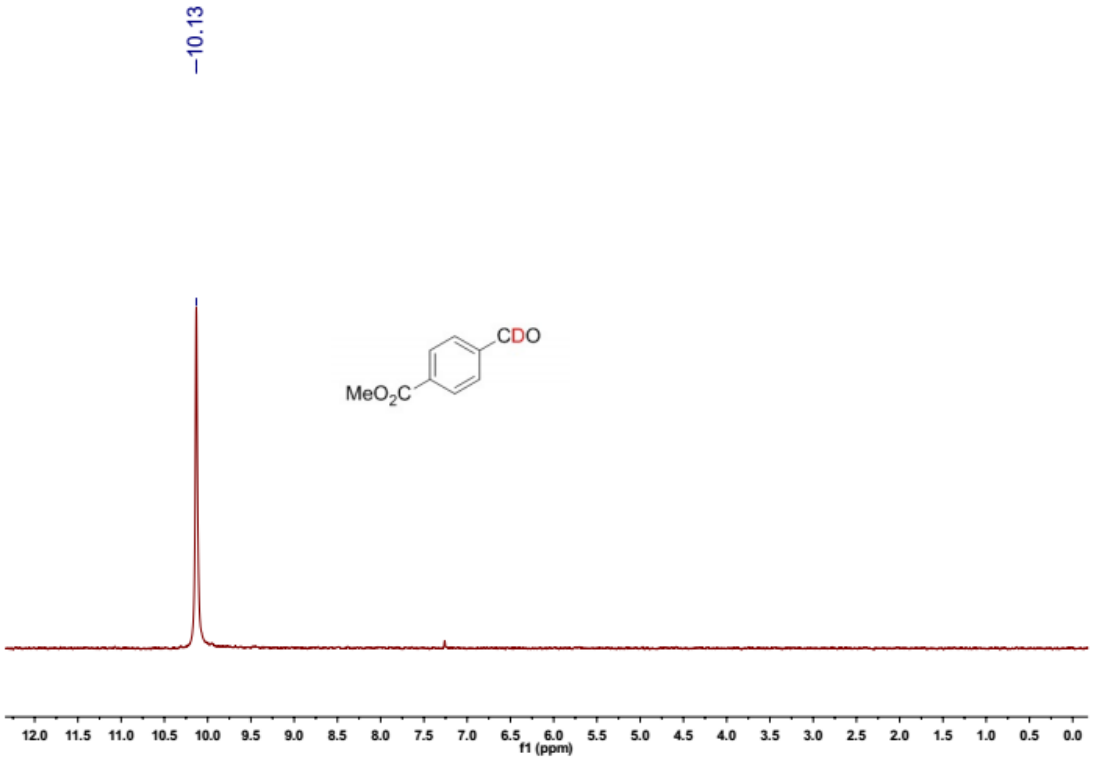
$^{13}$C NMR of deuterated aldehyde **7n**



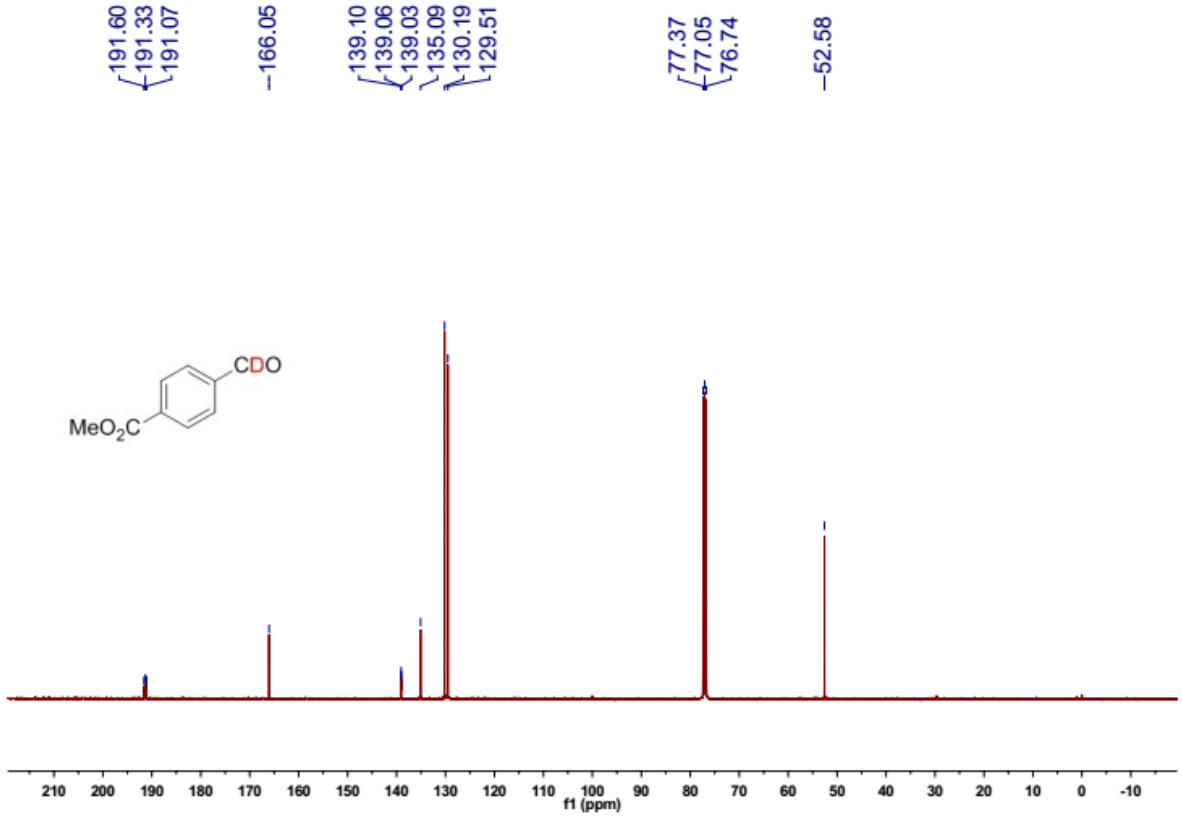
$^{1}$H NMR of deuterated aldehyde **7o**



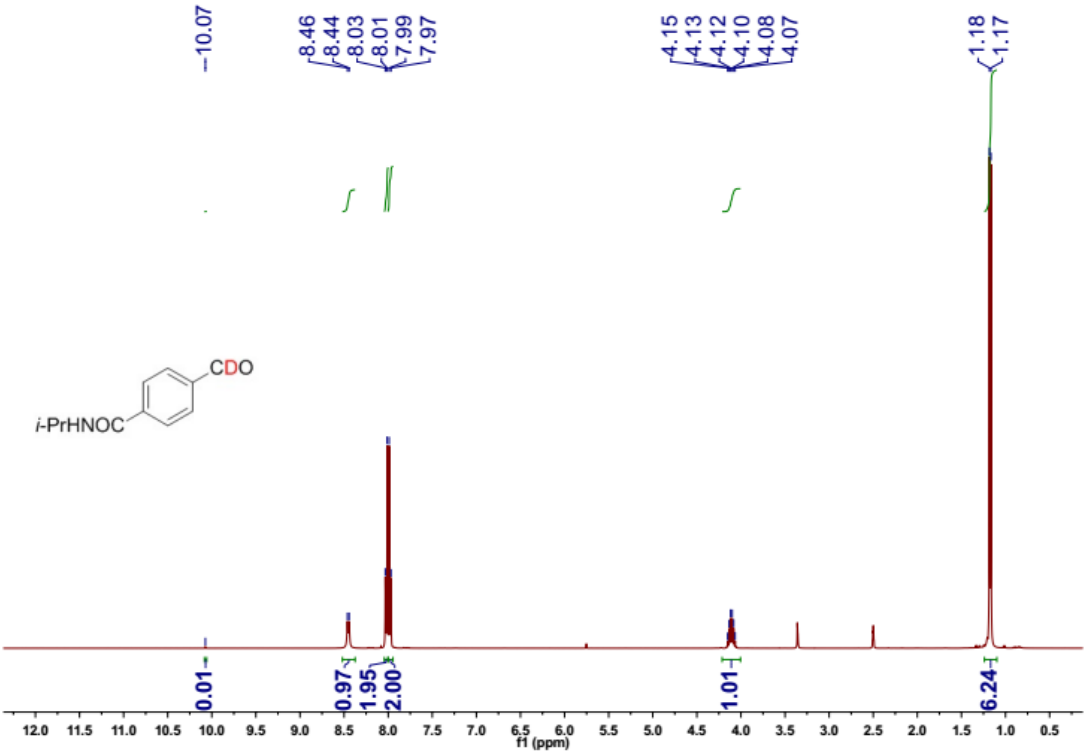

$^{2}$H NMR of deuterated aldehyde **7o**



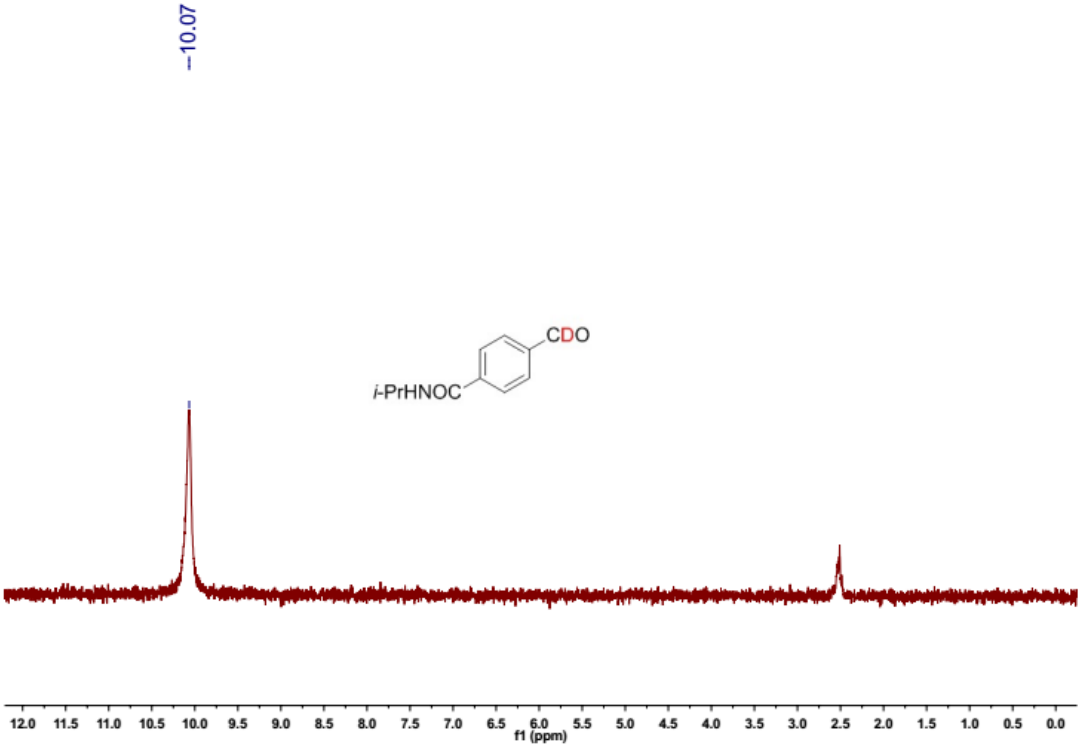
$^{13}$C NMR of deuterated aldehyde **7o**



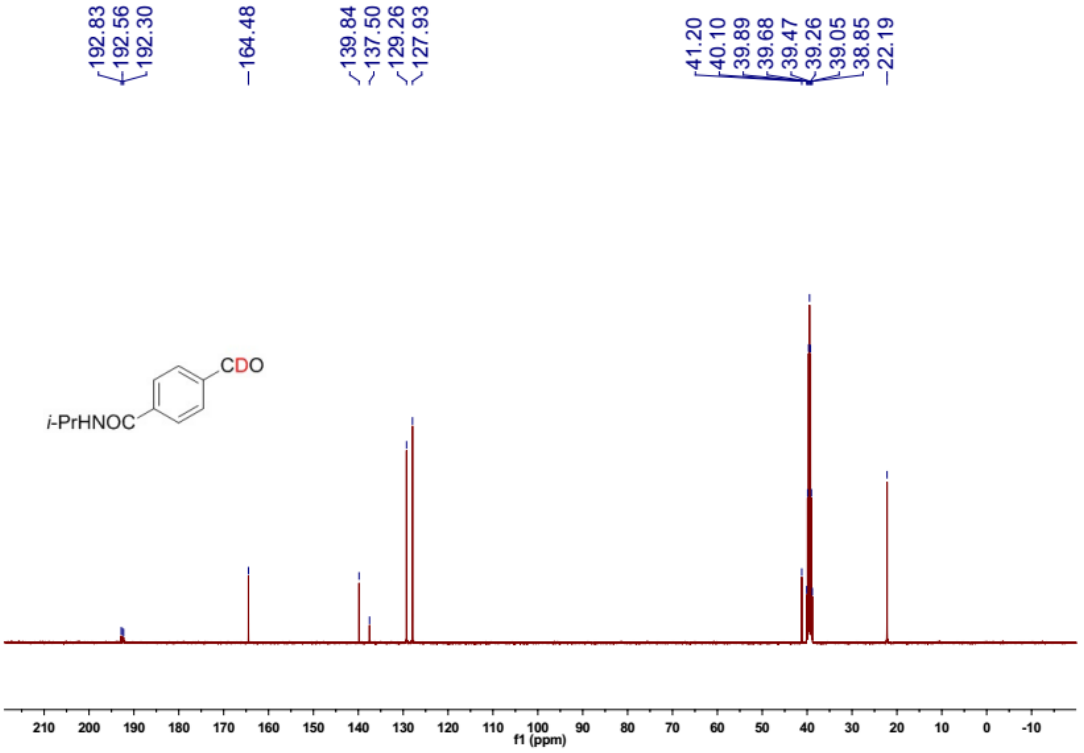
$^{1}$H NMR of deuterated aldehyde **7p**



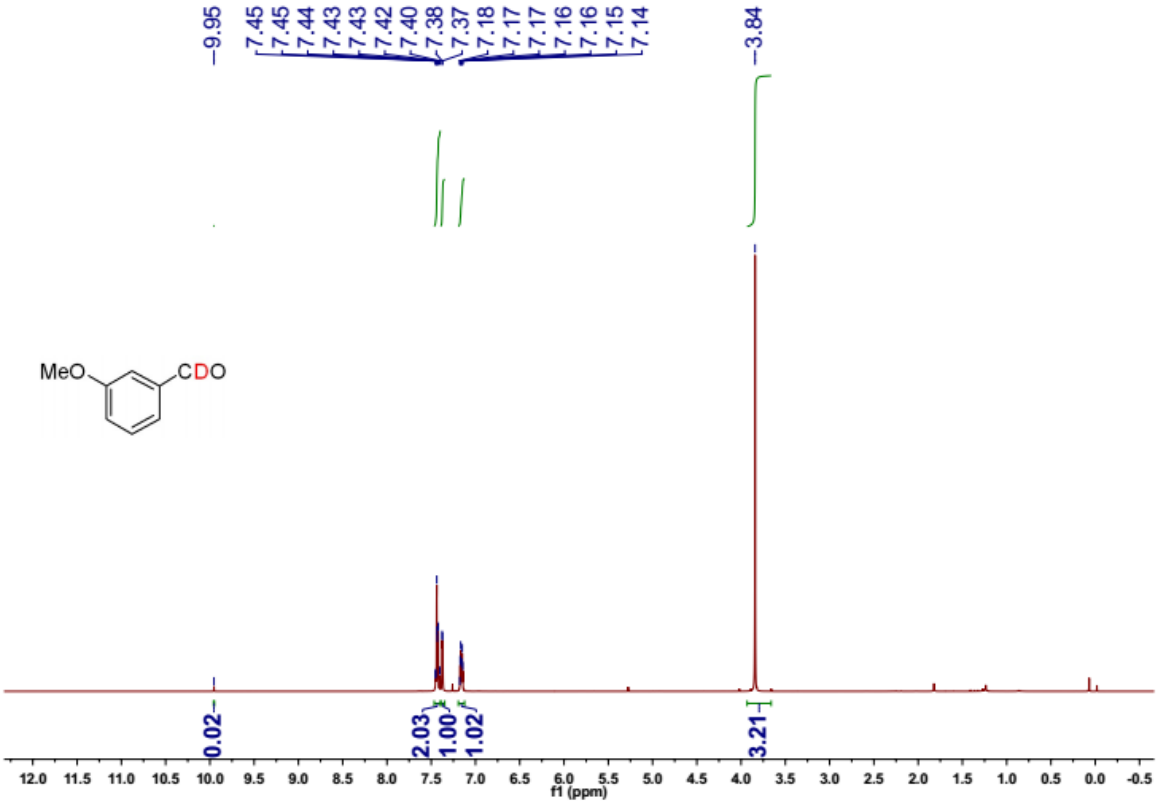

$^{2}$H NMR of deuterated aldehyde **7p** (The peak in δ 2.5 is the residue of DMSO-$d_6$)



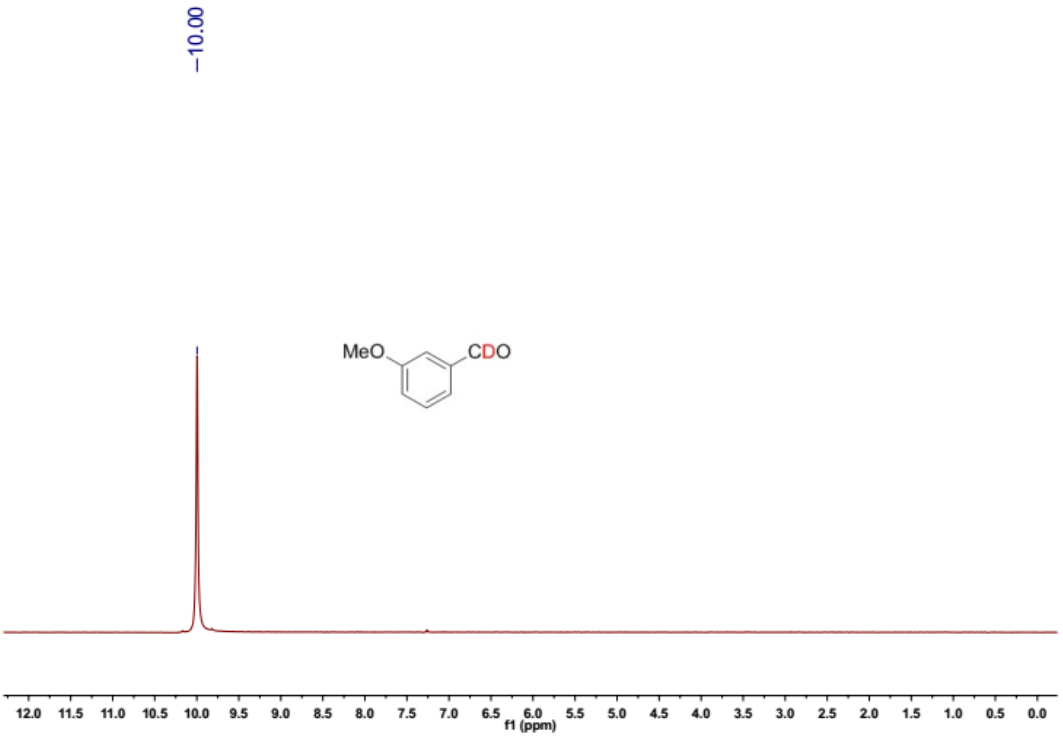
$^{13}$C NMR of deuterated aldehyde **7p**



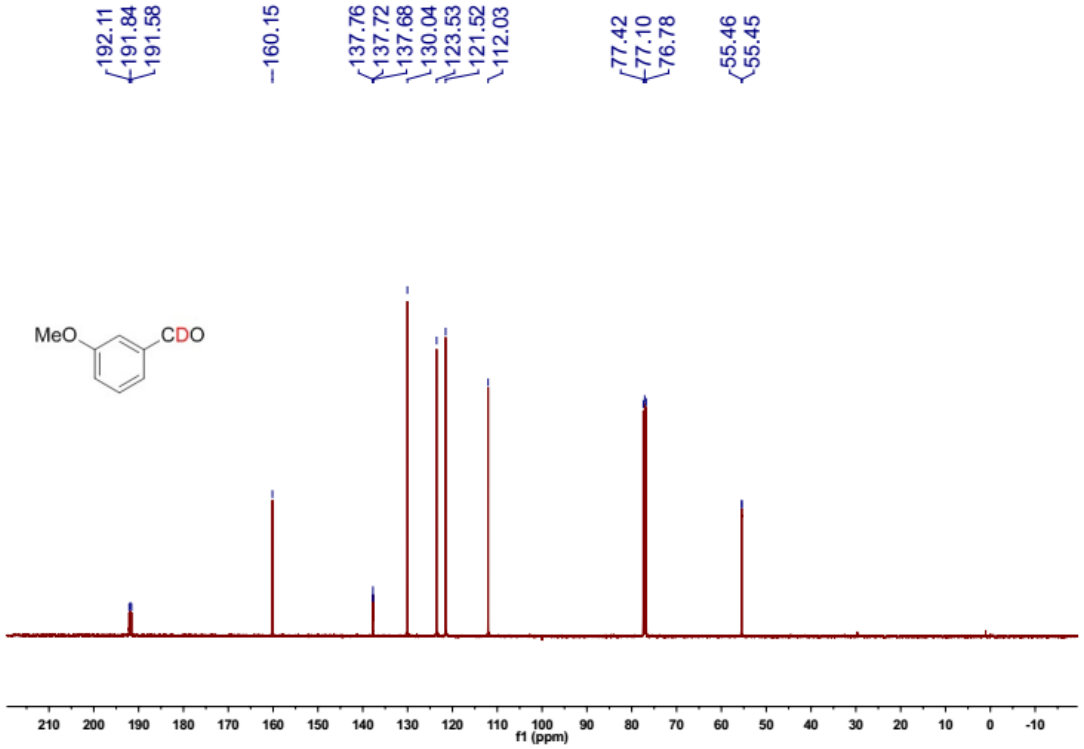
$^{1}$H NMR of deuterated aldehyde **7q**



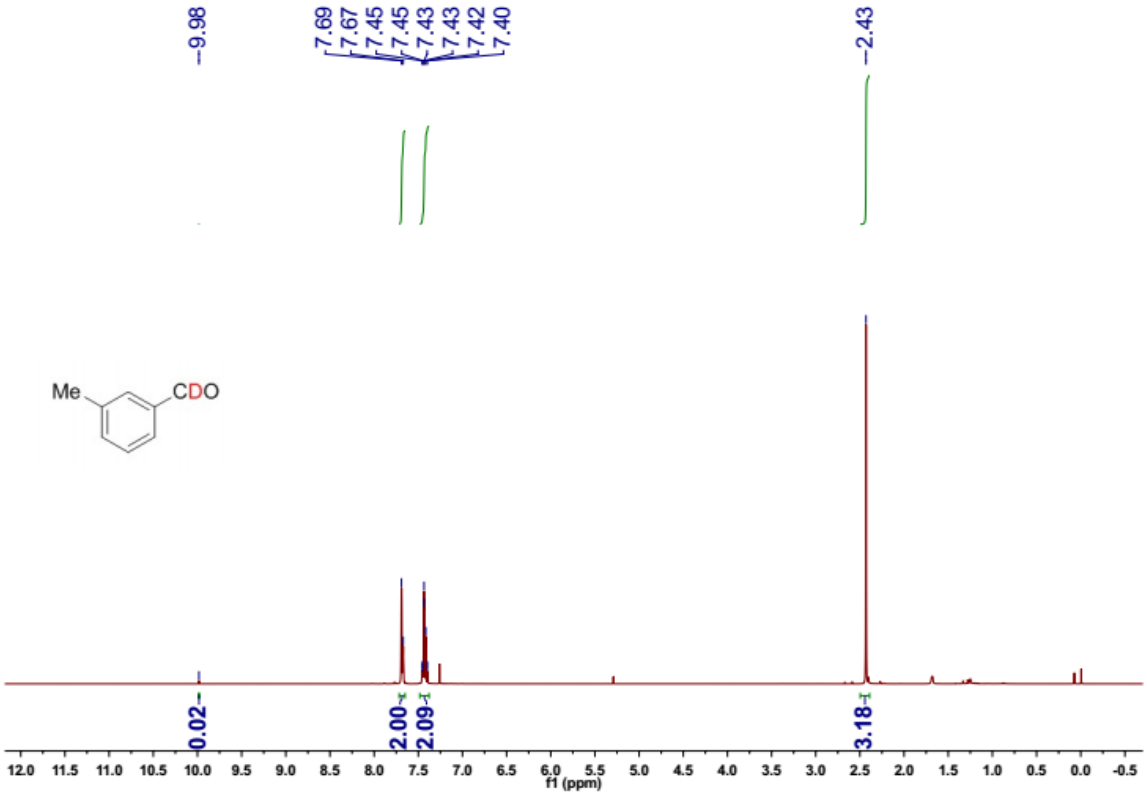

$^{2}$H NMR of deuterated aldehyde **7q**



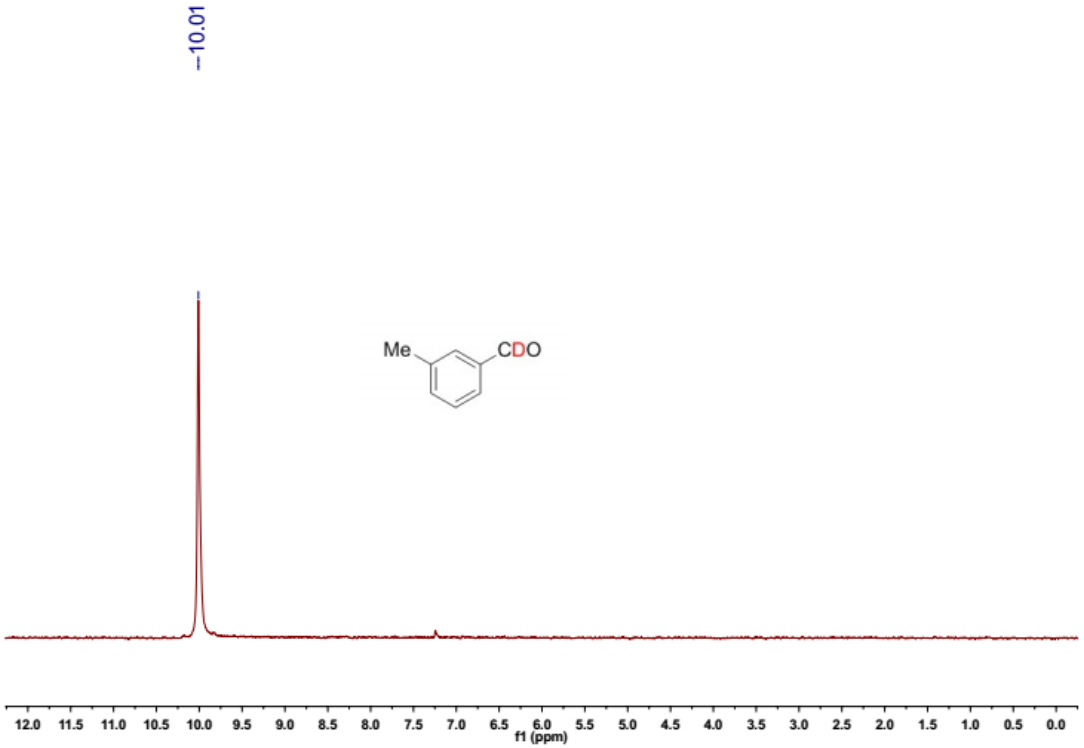
$^{13}$C NMR of deuterated aldehyde **7q**



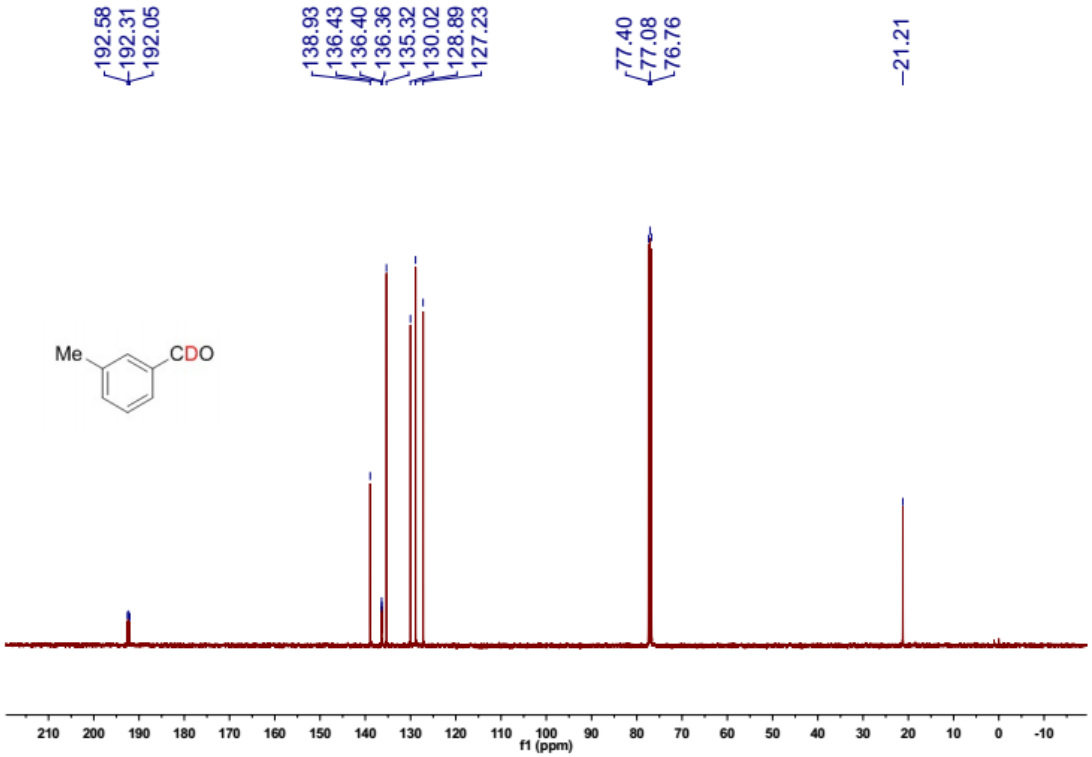
$^{1}$H NMR of deuterated aldehyde **7r**



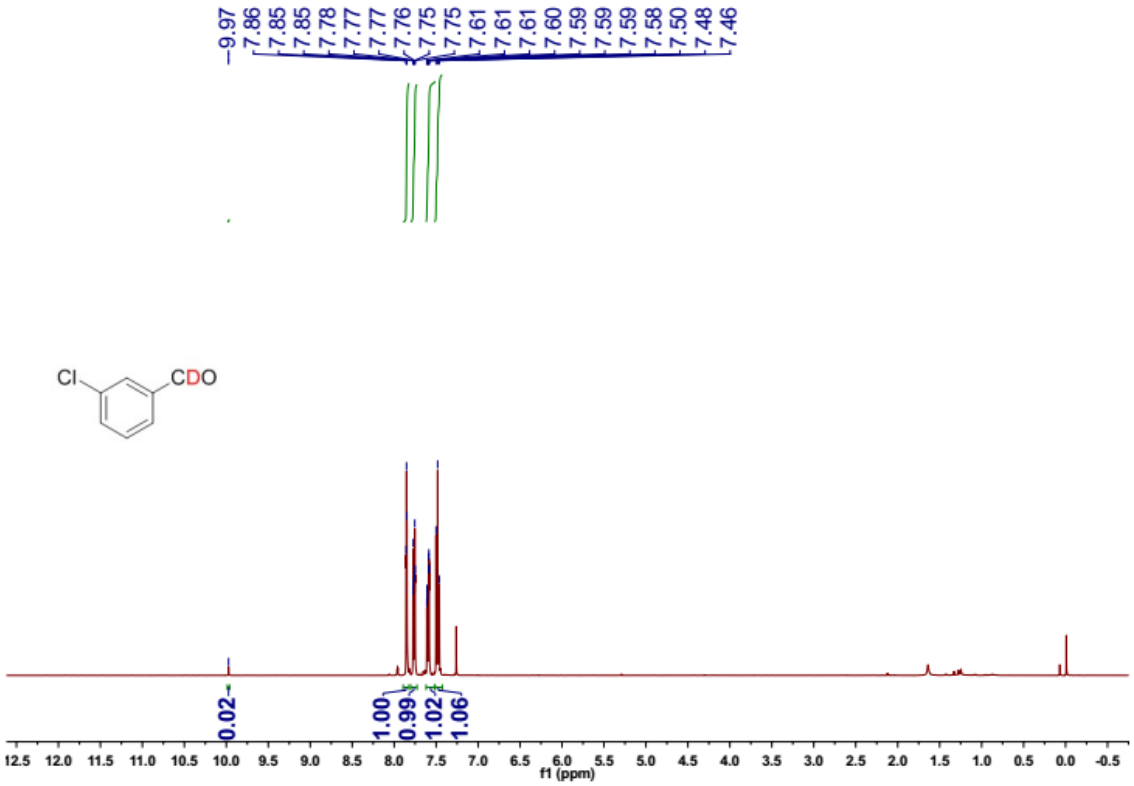

$^{2}$H NMR of deuterated aldehyde **7r**



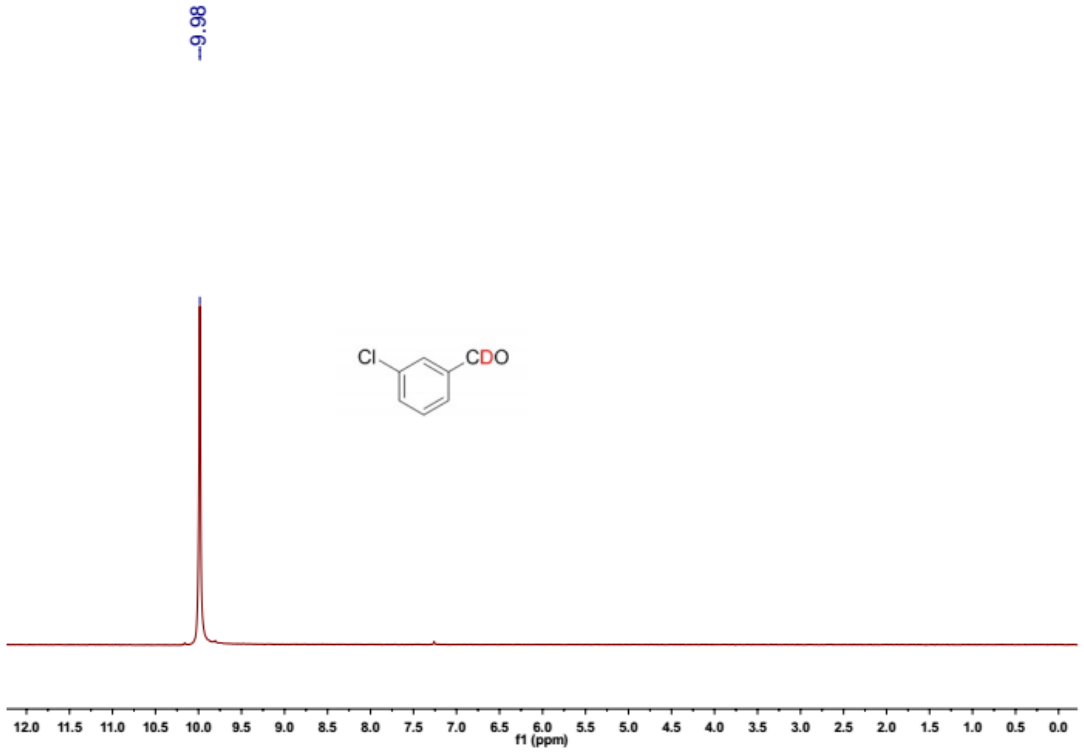
$^{13}$C NMR of deuterated aldehyde **7r**



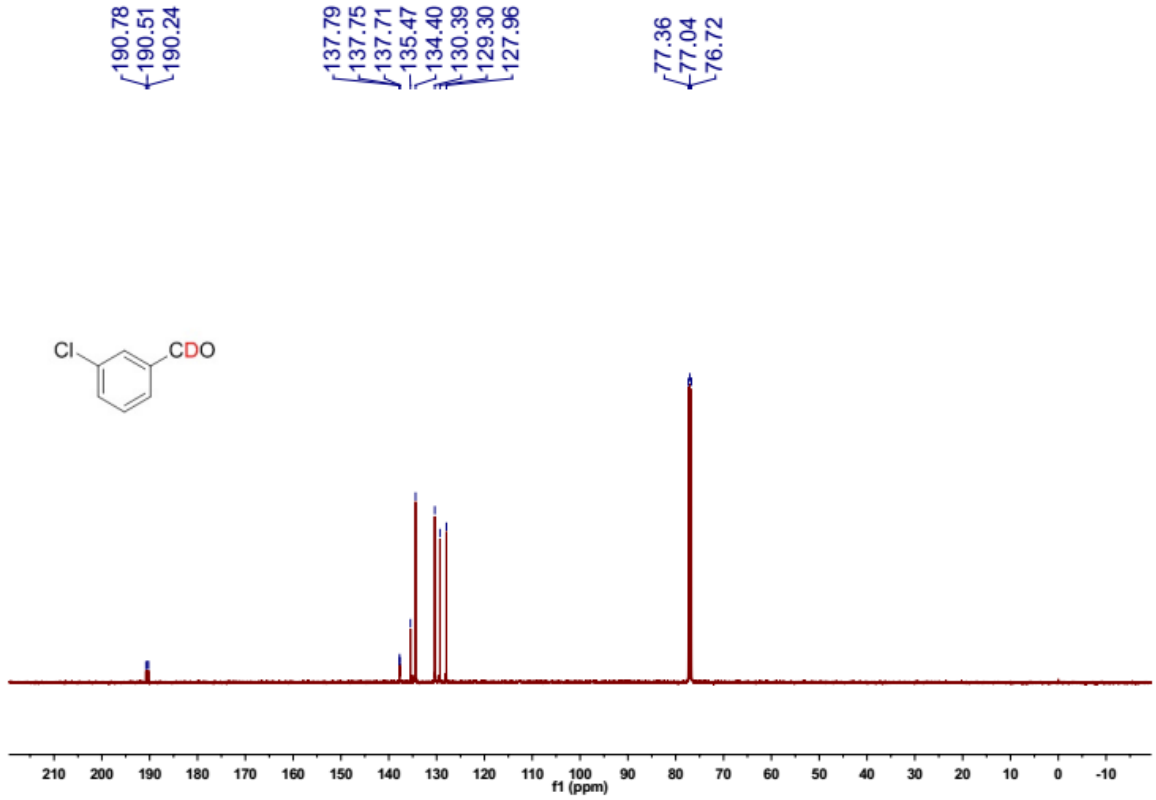
$^{1}$H NMR of deuterated aldehyde **7s**



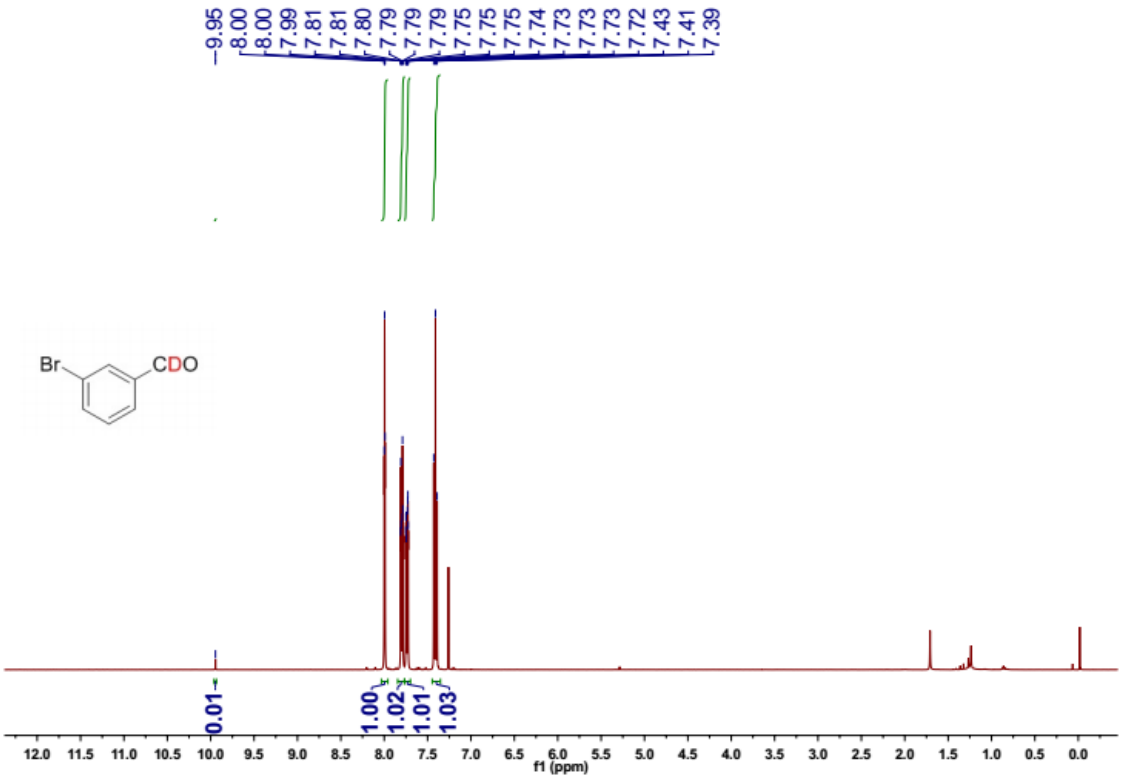

$^{2}$H NMR of deuterated aldehyde **7s**



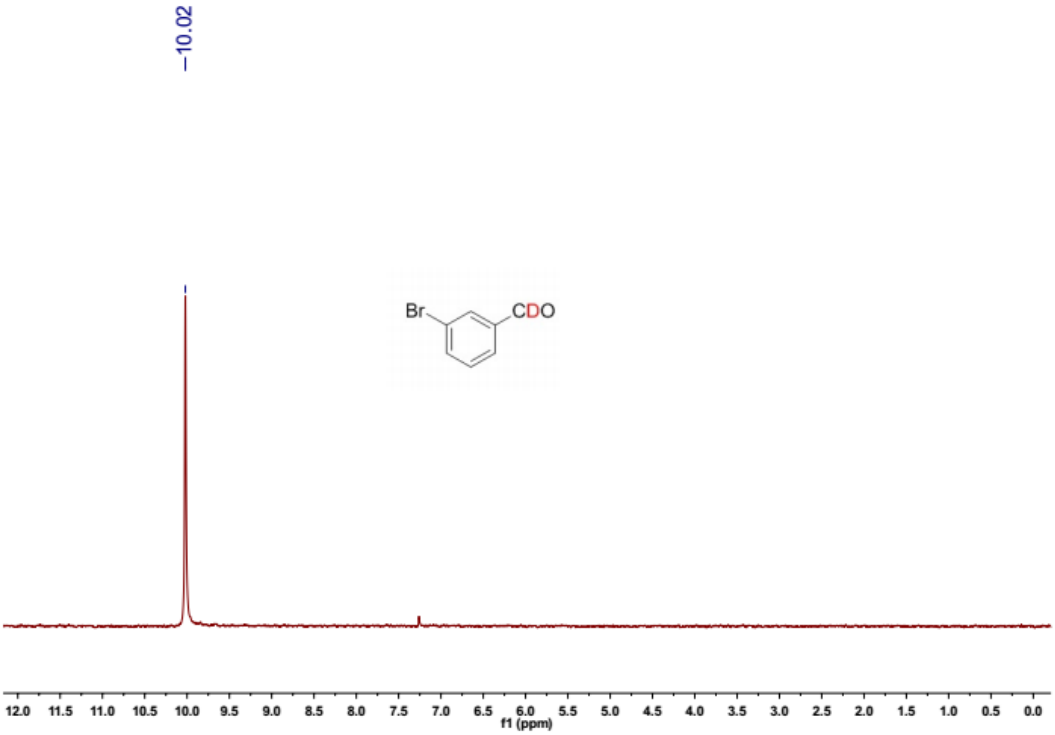
$^{13}$C NMR of deuterated aldehyde **7s**



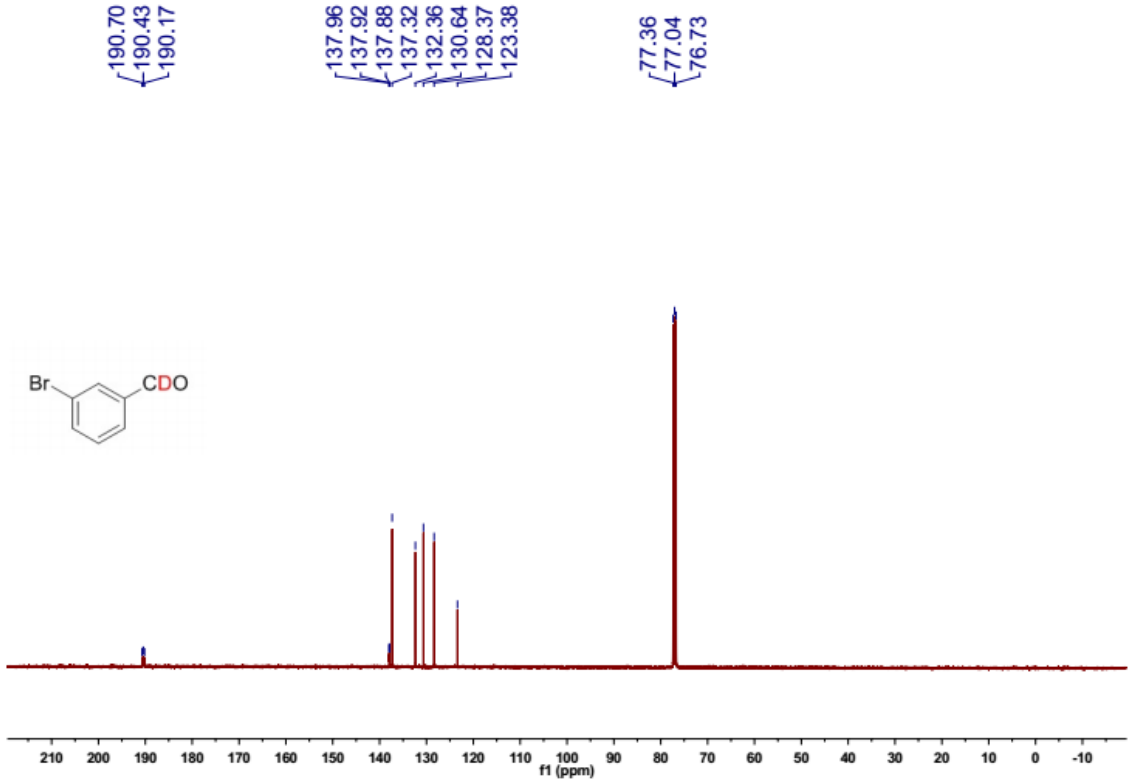
$^{1}$H NMR of deuterated aldehyde **7t**



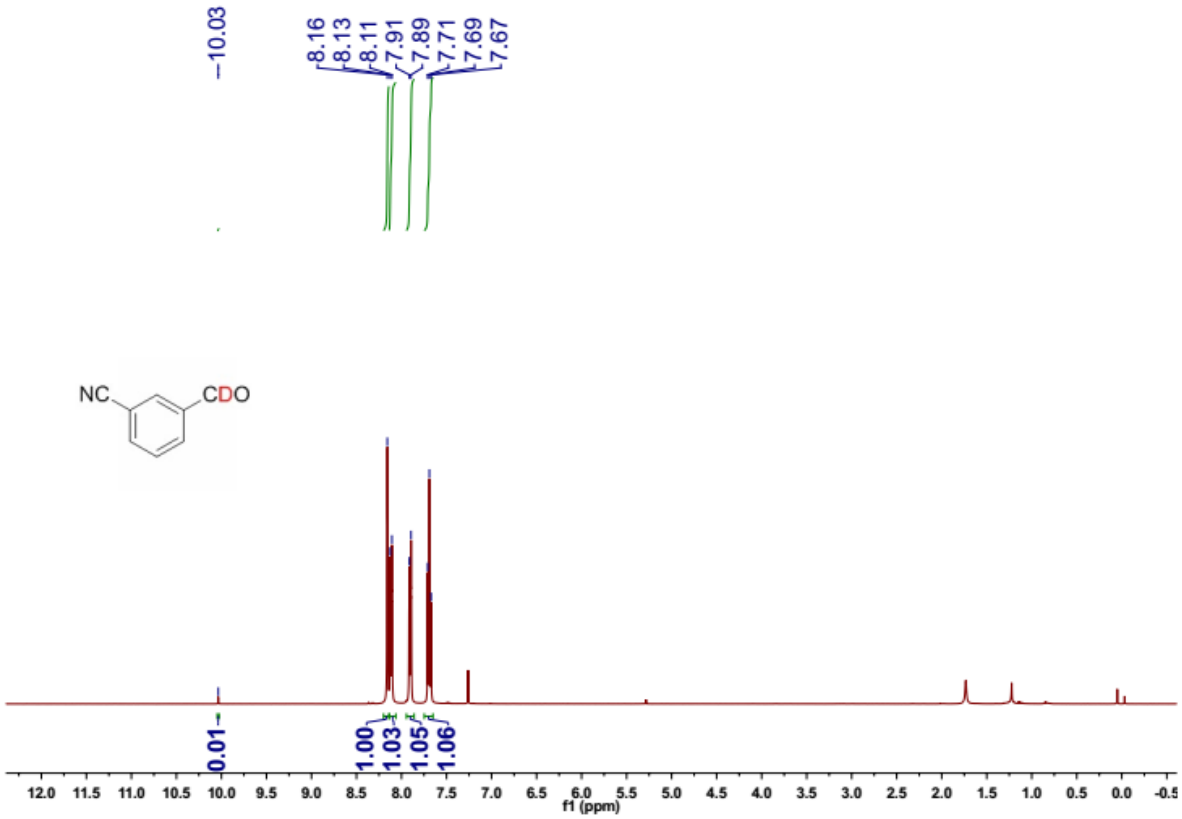

$^{2}$H NMR of deuterated aldehyde **7t**



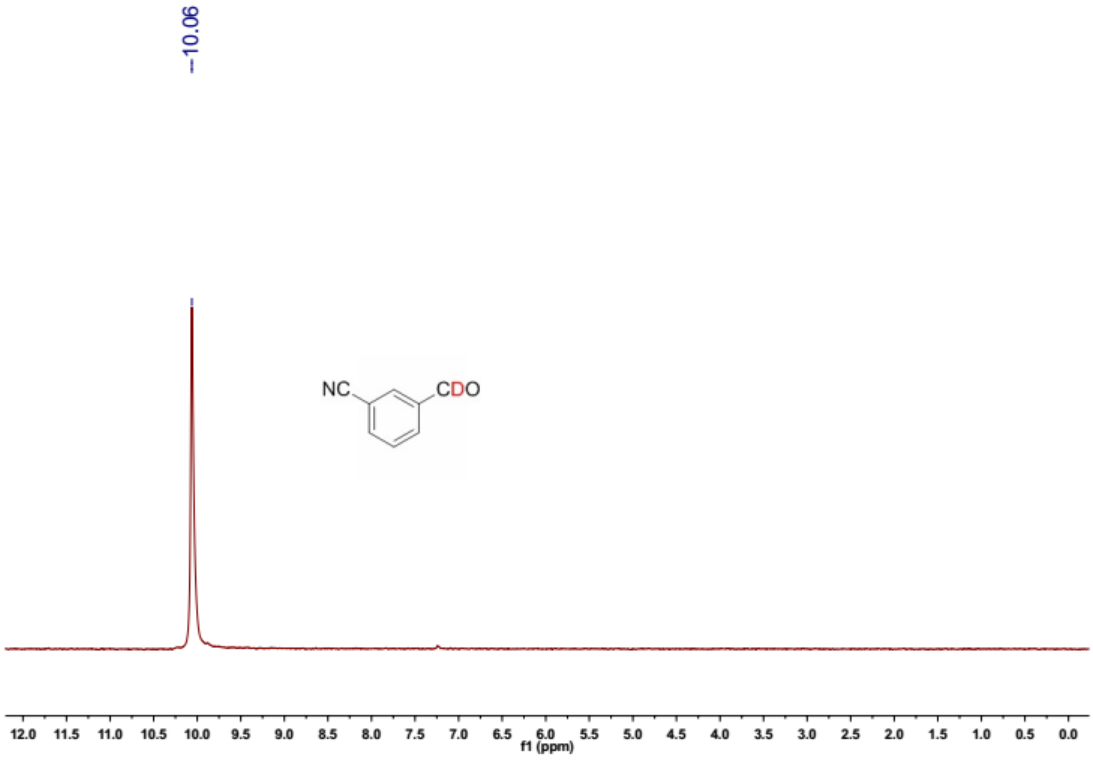
$^{13}$C NMR of deuterated aldehyde **7t**



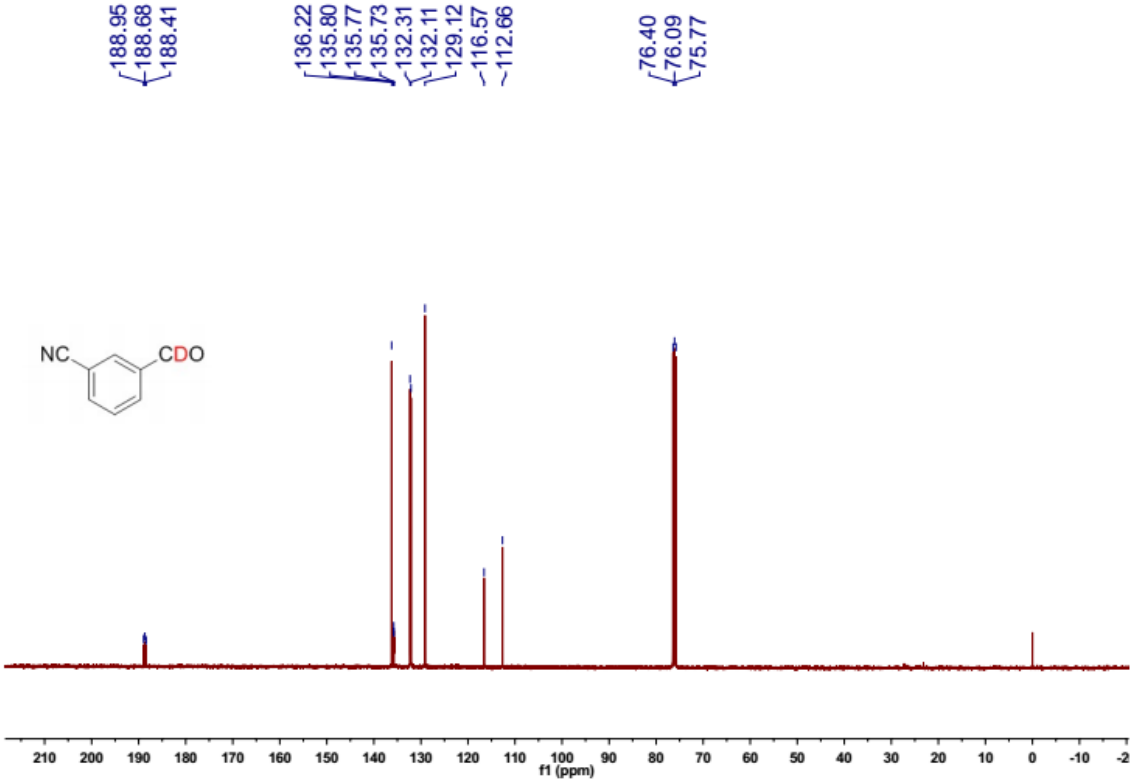
$^{1}$H NMR of deuterated aldehyde **7u**



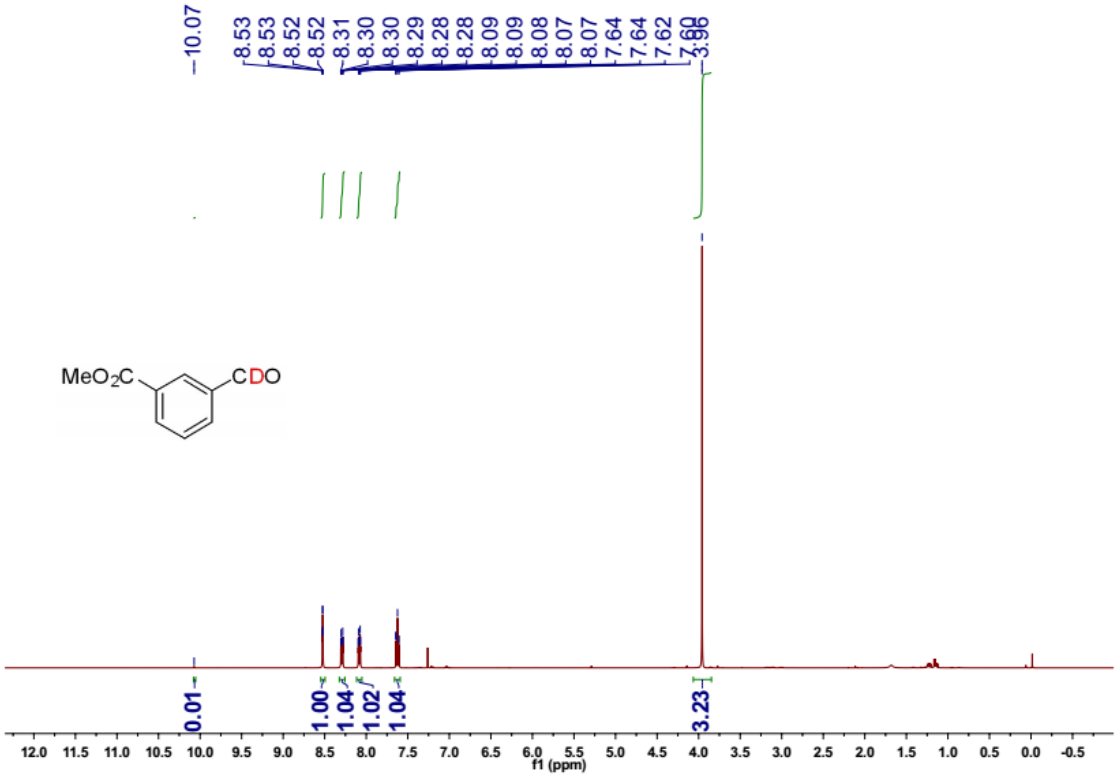

$^{2}$H NMR of deuterated aldehyde **7u**



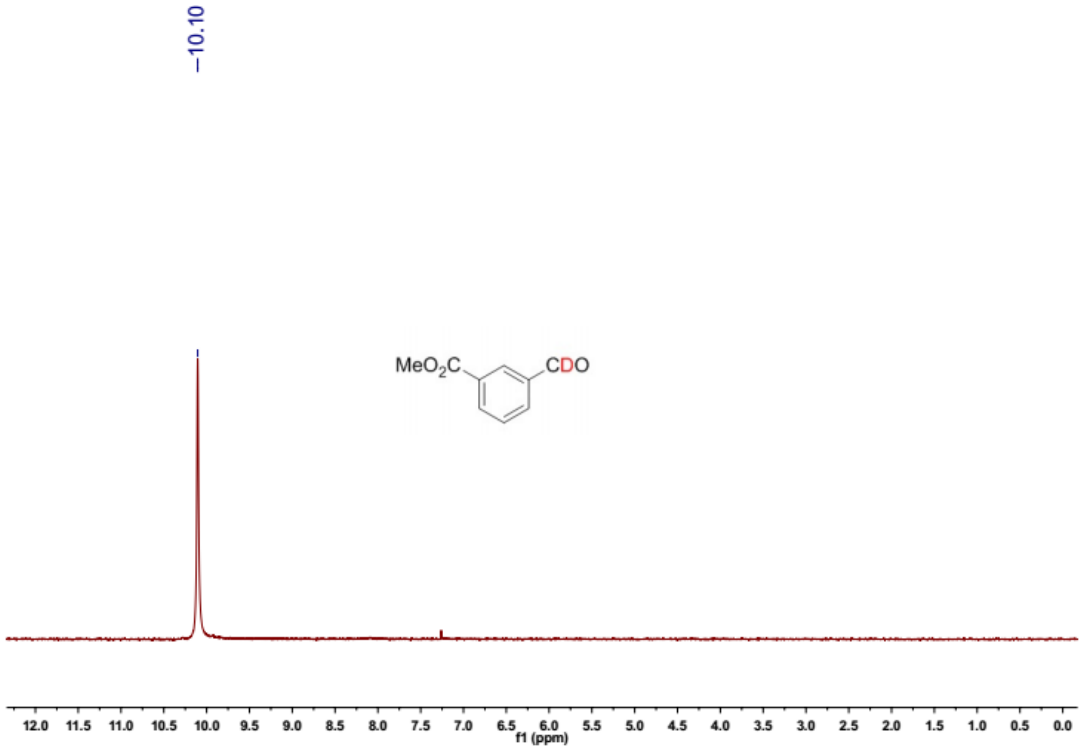
$^{13}$C NMR of deuterated aldehyde **7u**



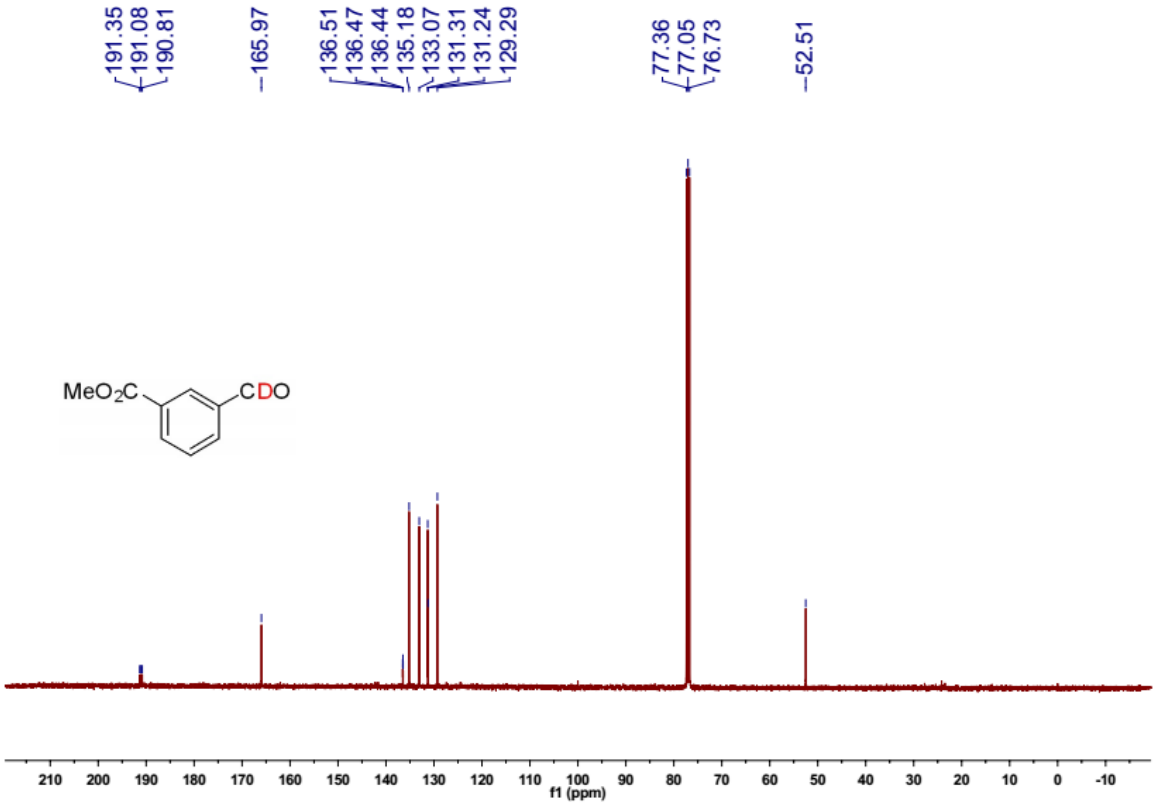
$^{1}$H NMR of deuterated aldehyde **7v**



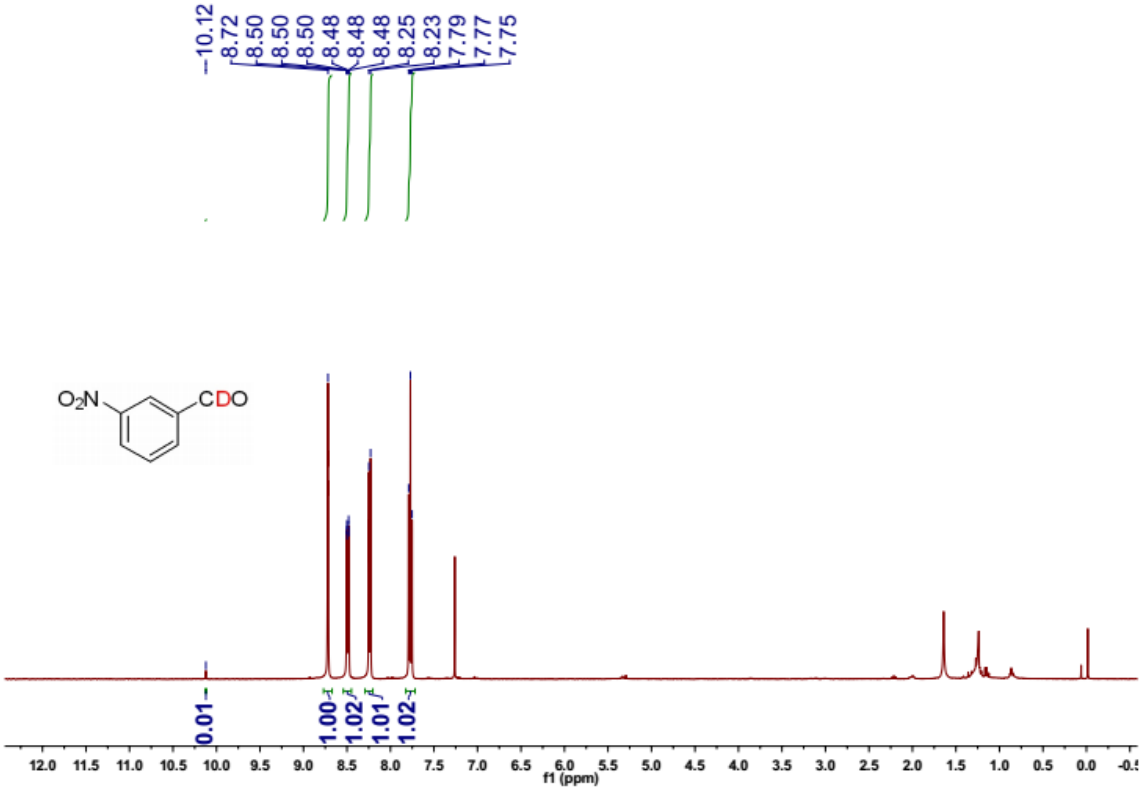

$^{2}$H NMR of deuterated aldehyde **7v**



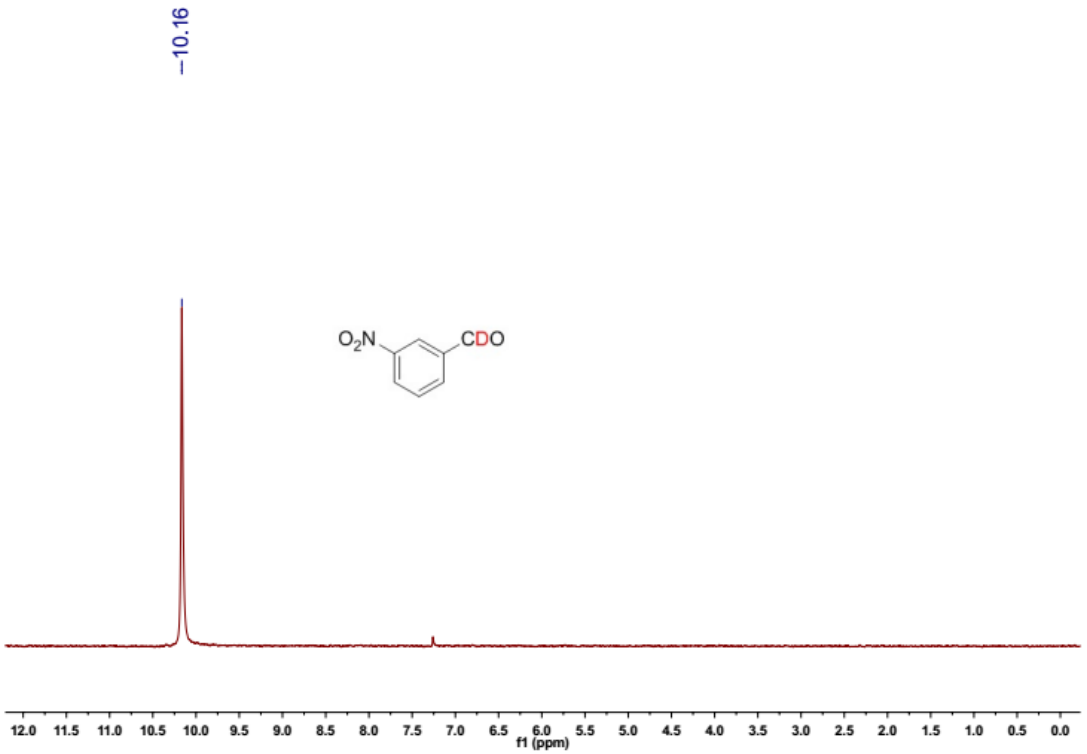
$^{13}$C NMR of deuterated aldehyde **7v**



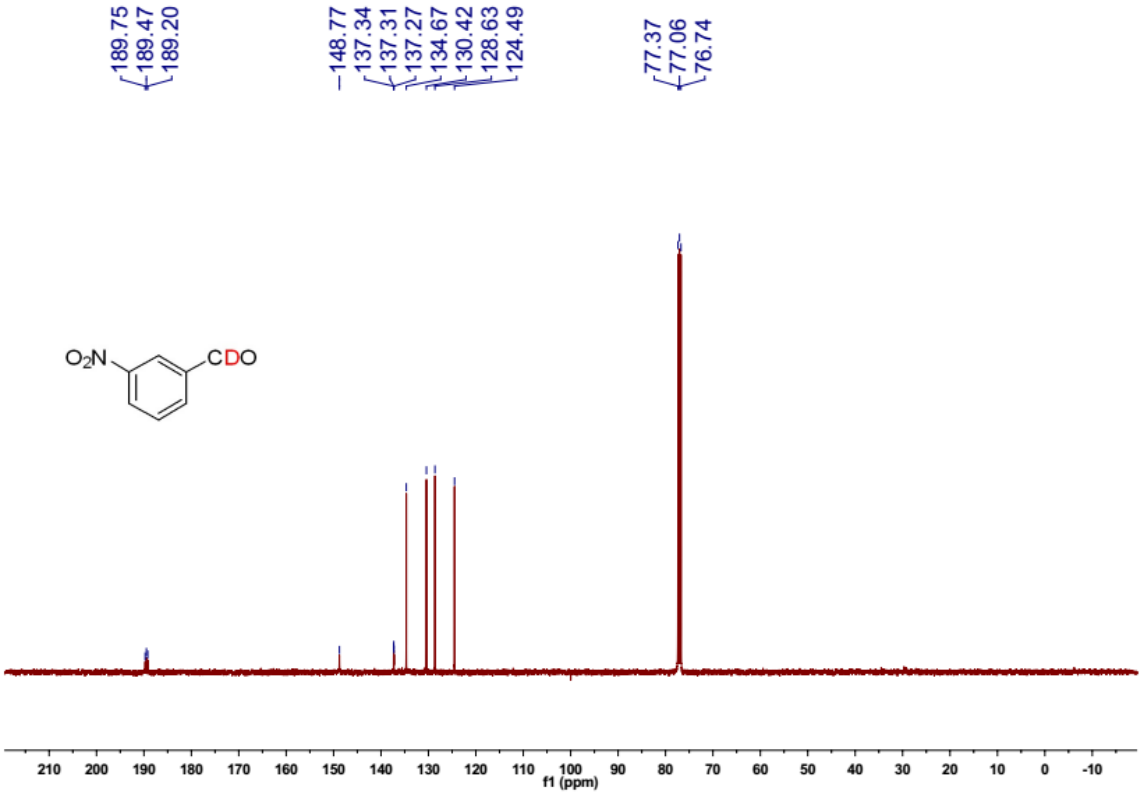
$^{1}$H NMR of deuterated aldehyde **7w**



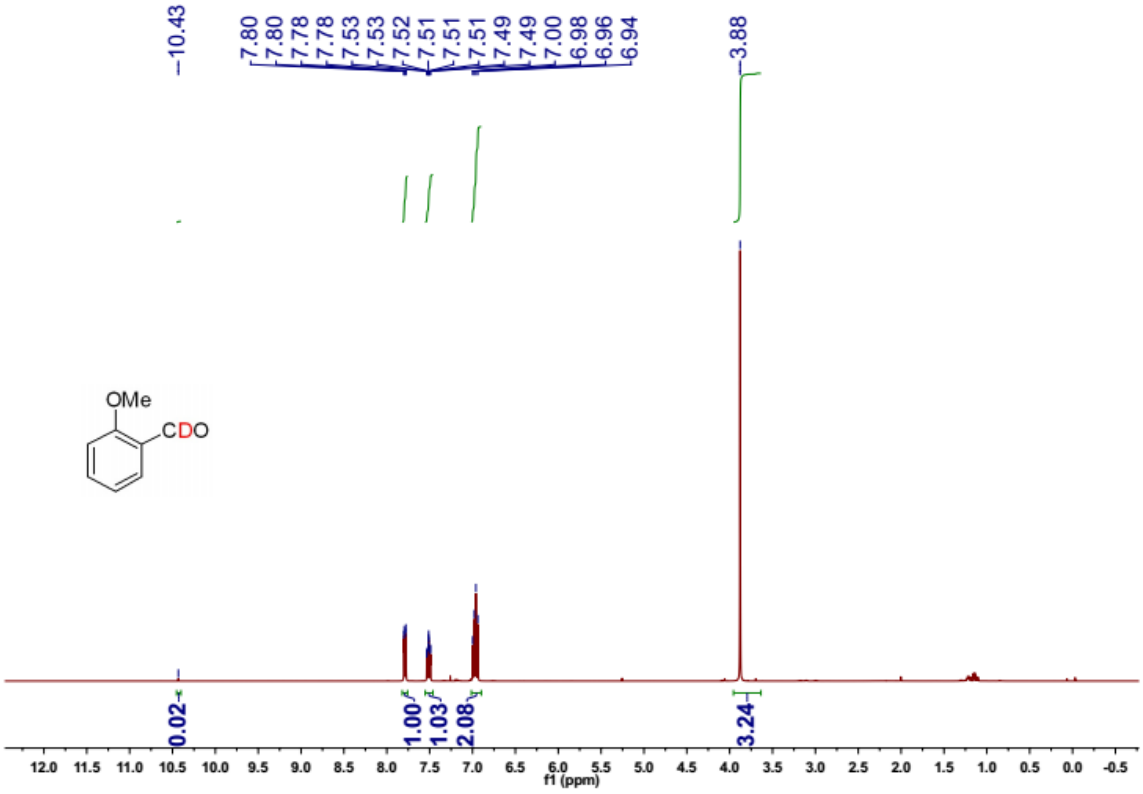

$^{2}$H NMR of deuterated aldehyde **7w**



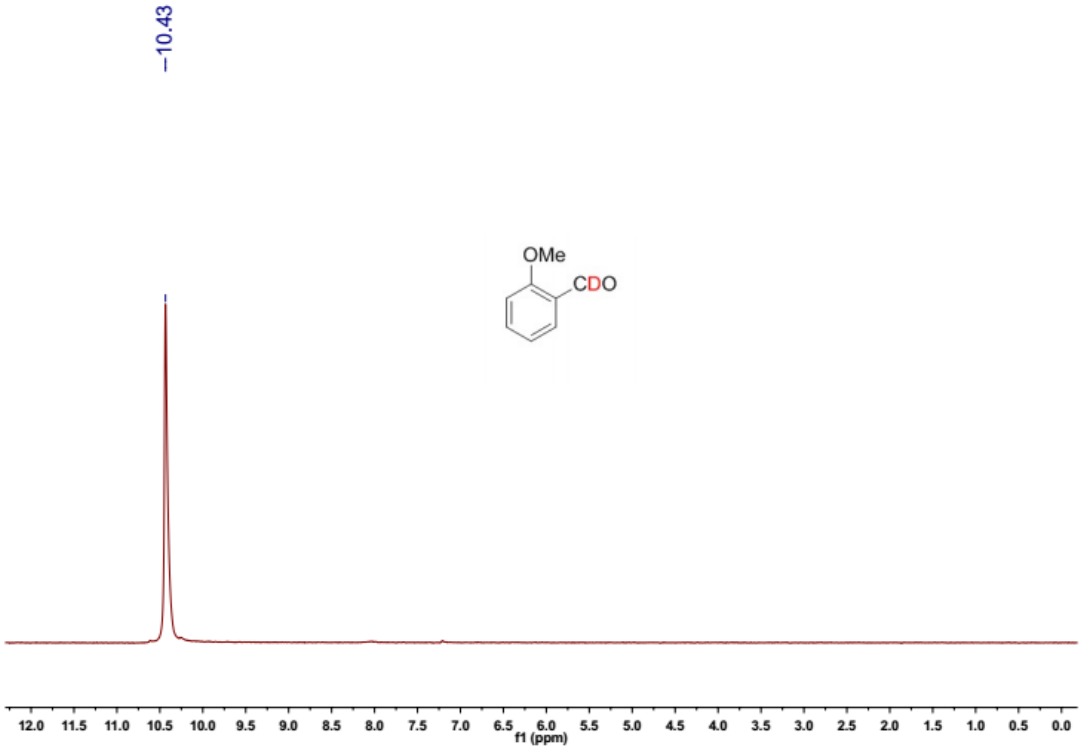
$^{13}$C NMR of deuterated aldehyde **7w**



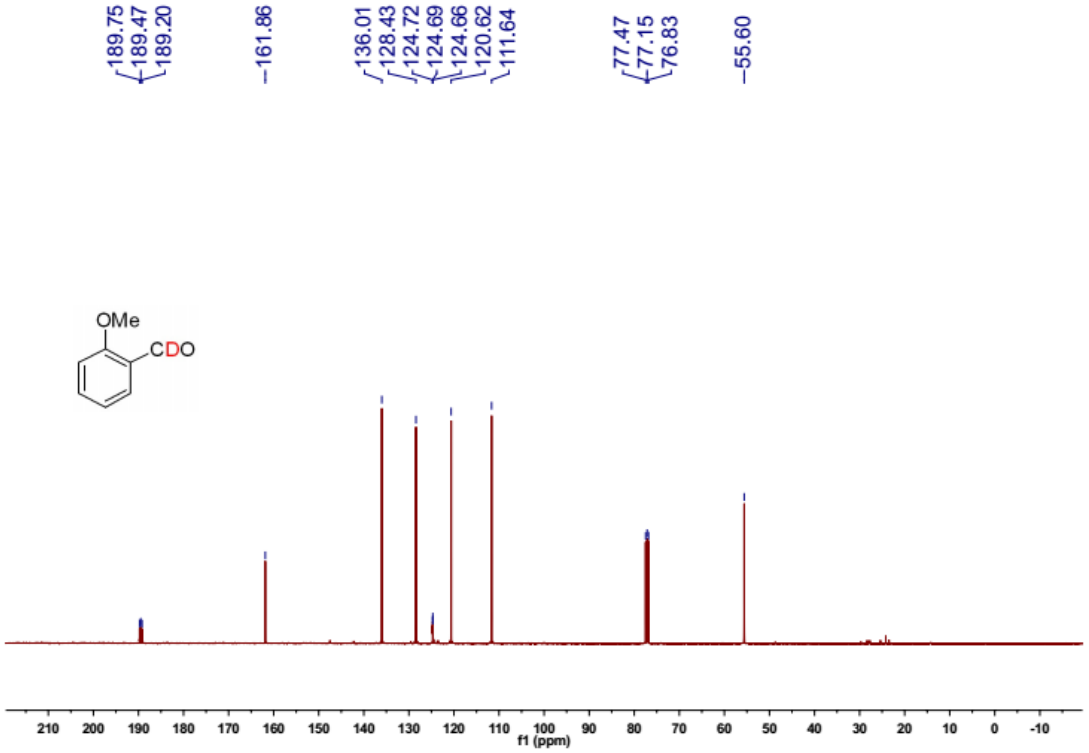
$^{1}$H NMR of deuterated aldehyde **7x**



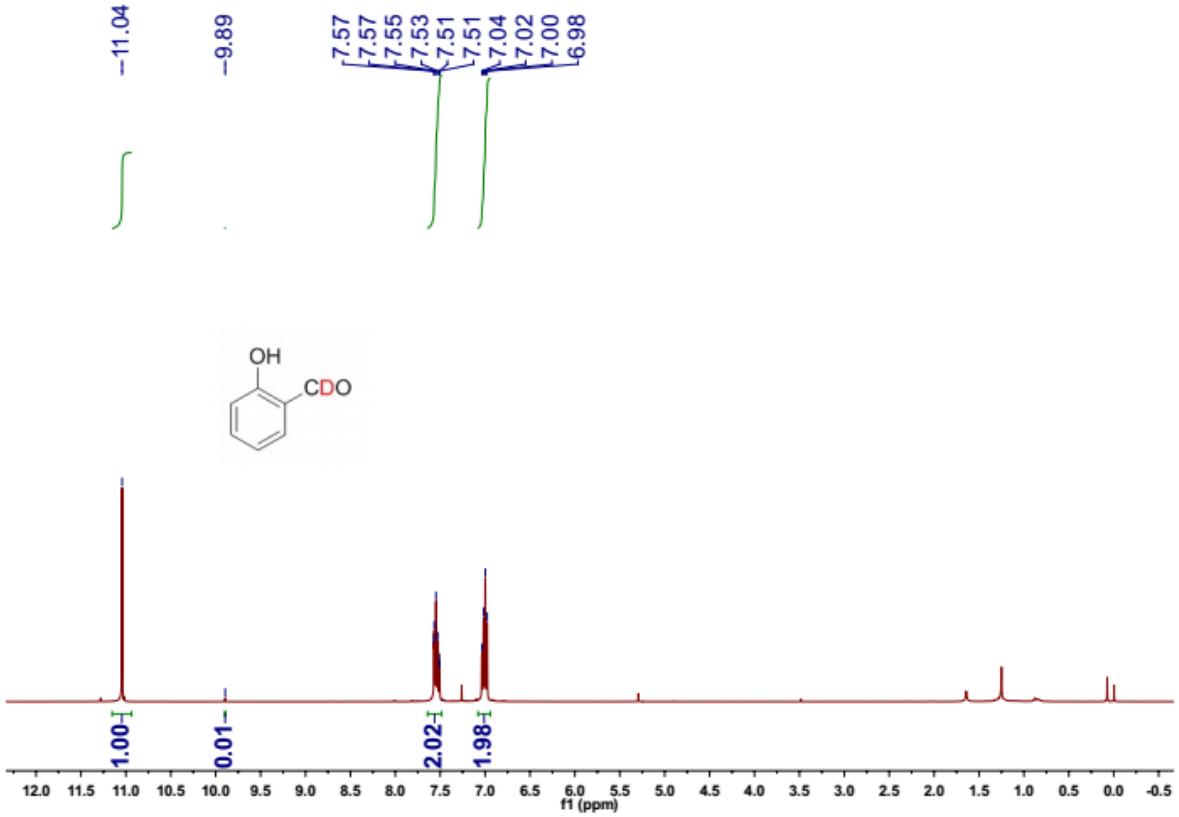

$^{2}$H NMR of deuterated aldehyde **7x**



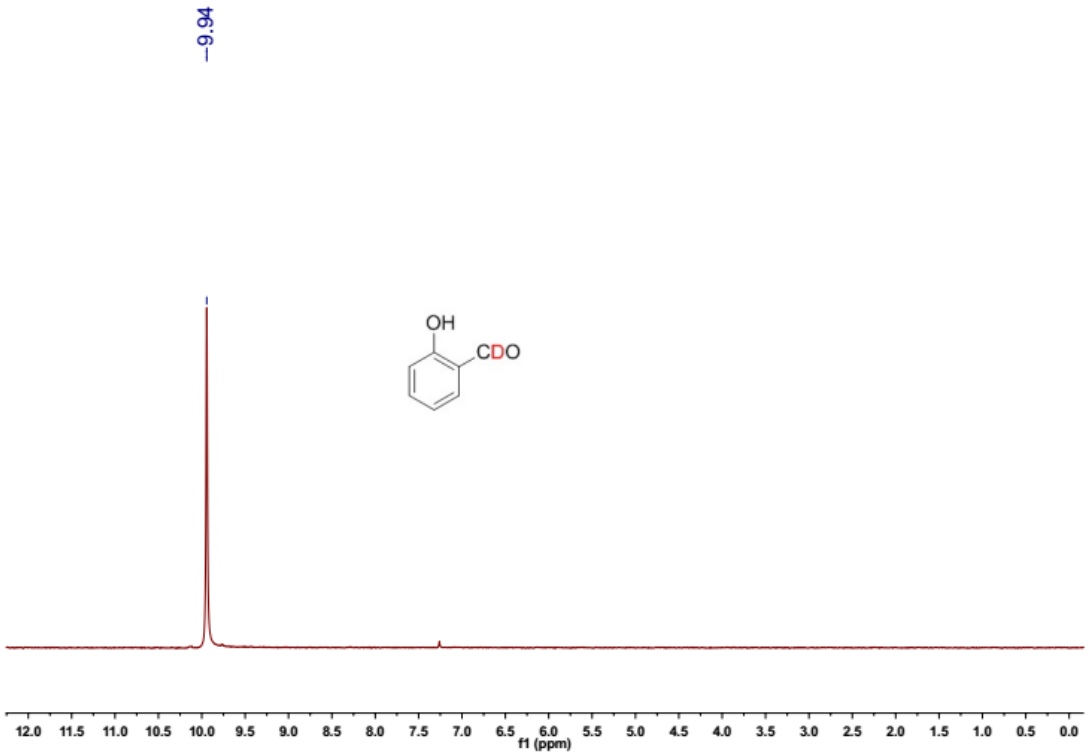
$^{13}$C NMR of deuterated aldehyde **7x**



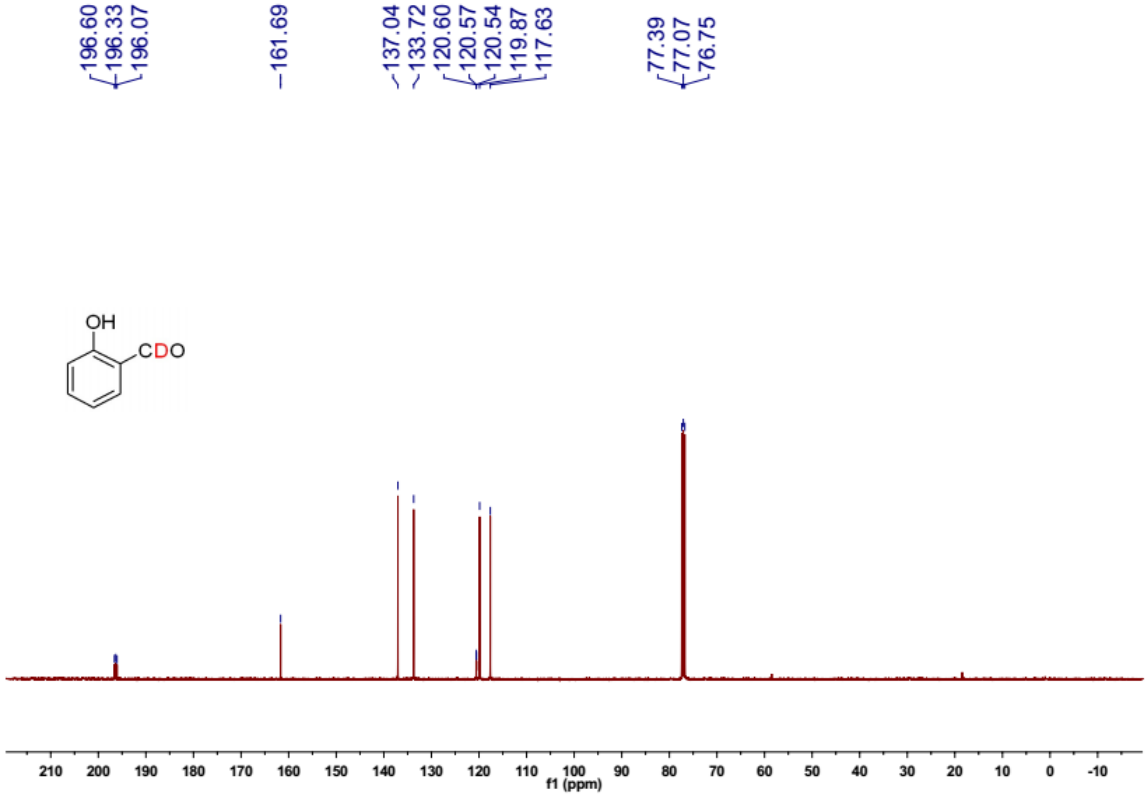
$^{1}$H NMR of deuterated aldehyde **7y**



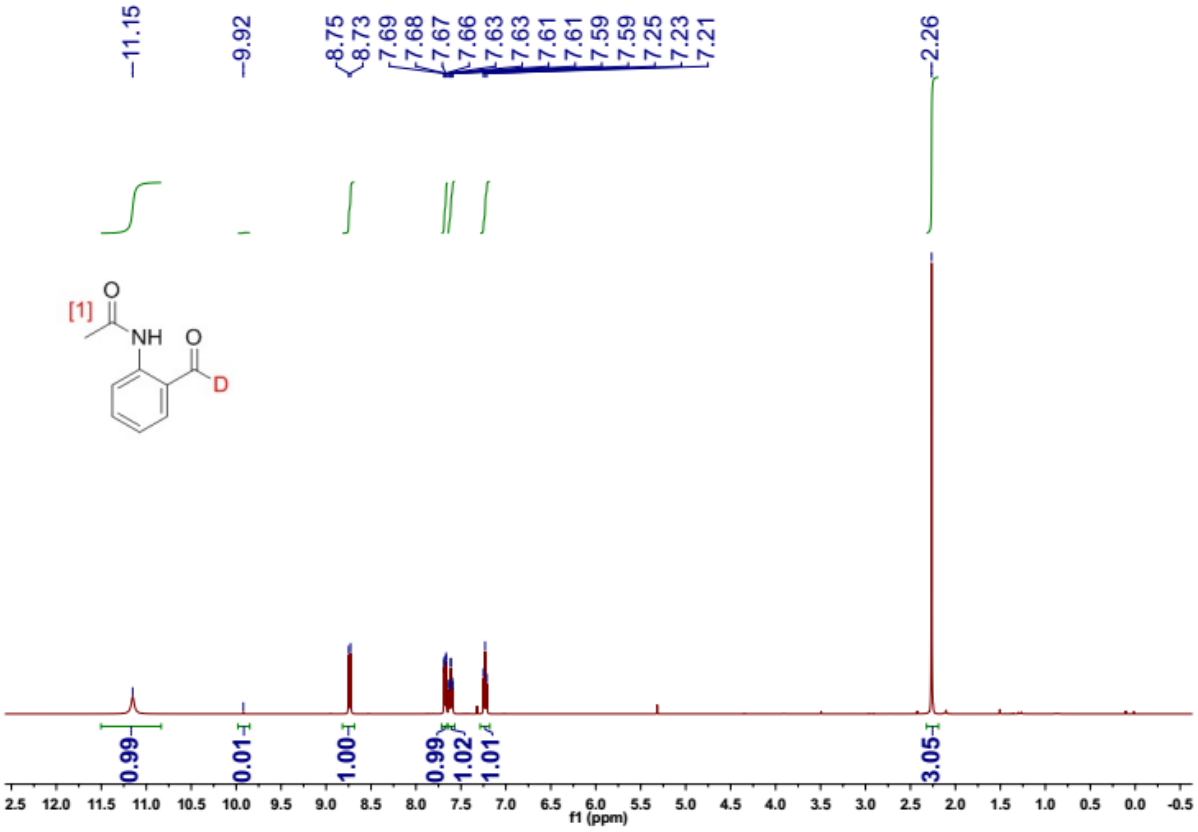

$^{2}$H NMR of deuterated aldehyde **7y**



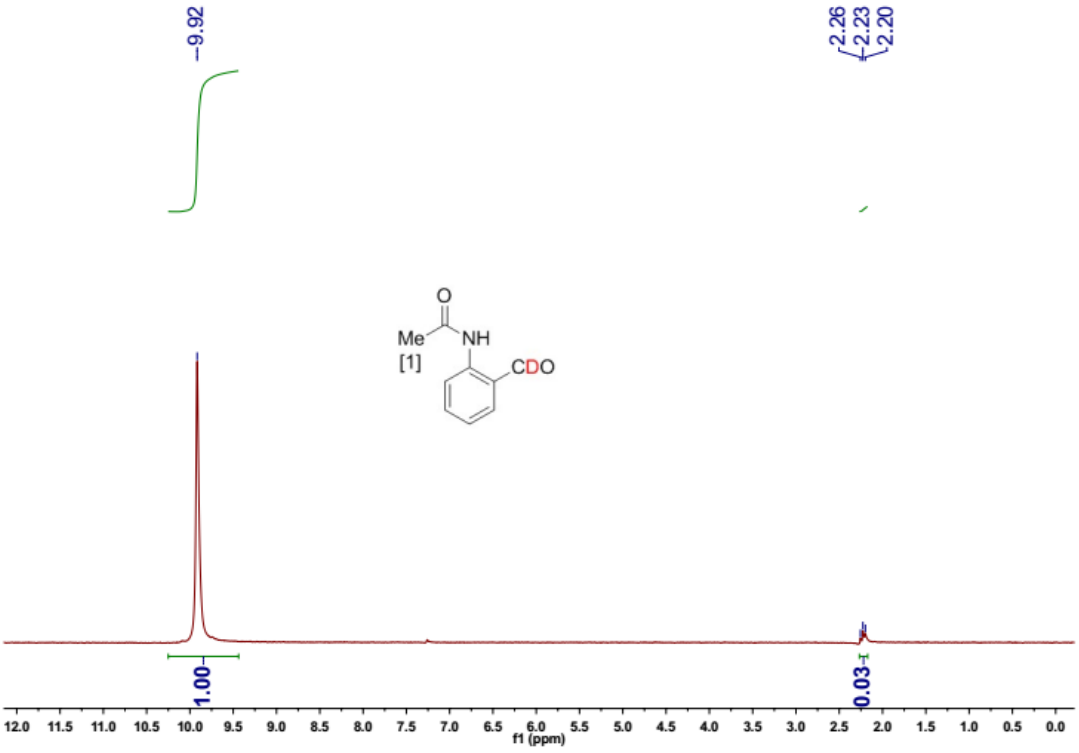
$^{13}$C NMR of deuterated aldehyde **7y**



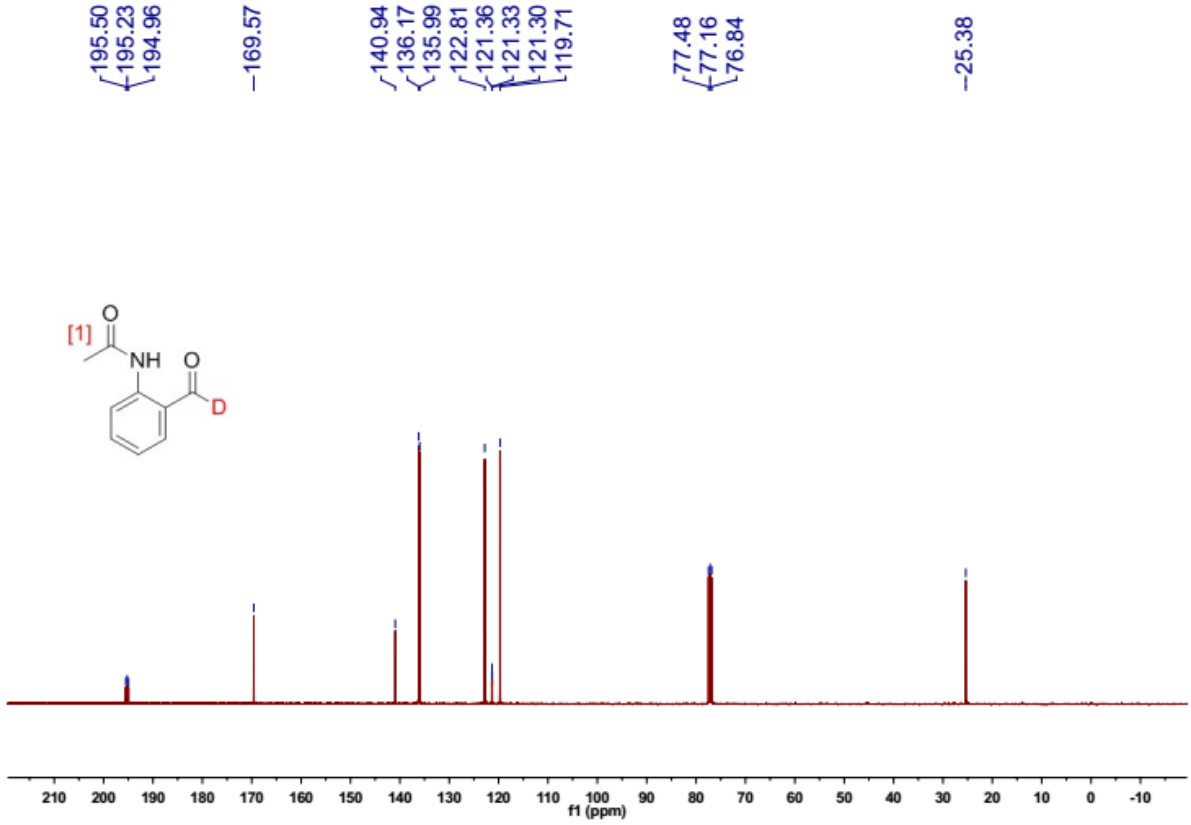
$^{1}$H NMR of deuterated aldehyde **7z**



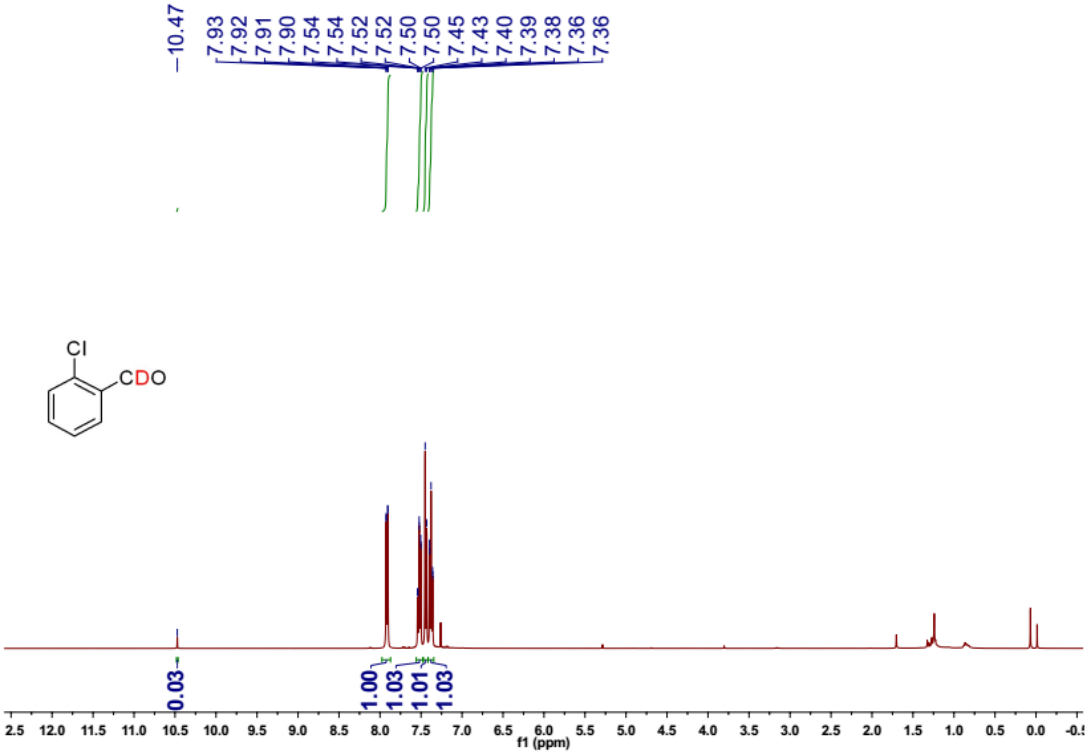

$^{2}$H NMR of deuterated aldehyde **7z**



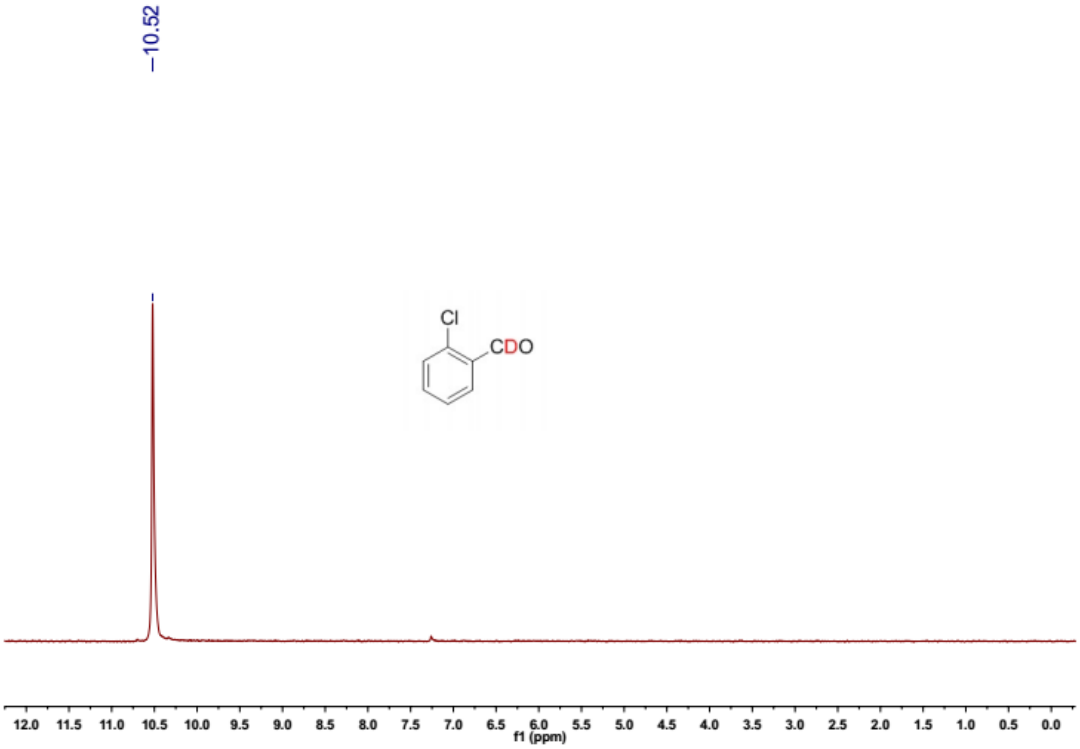
$^{13}$C NMR of deuterated aldehyde **7z**



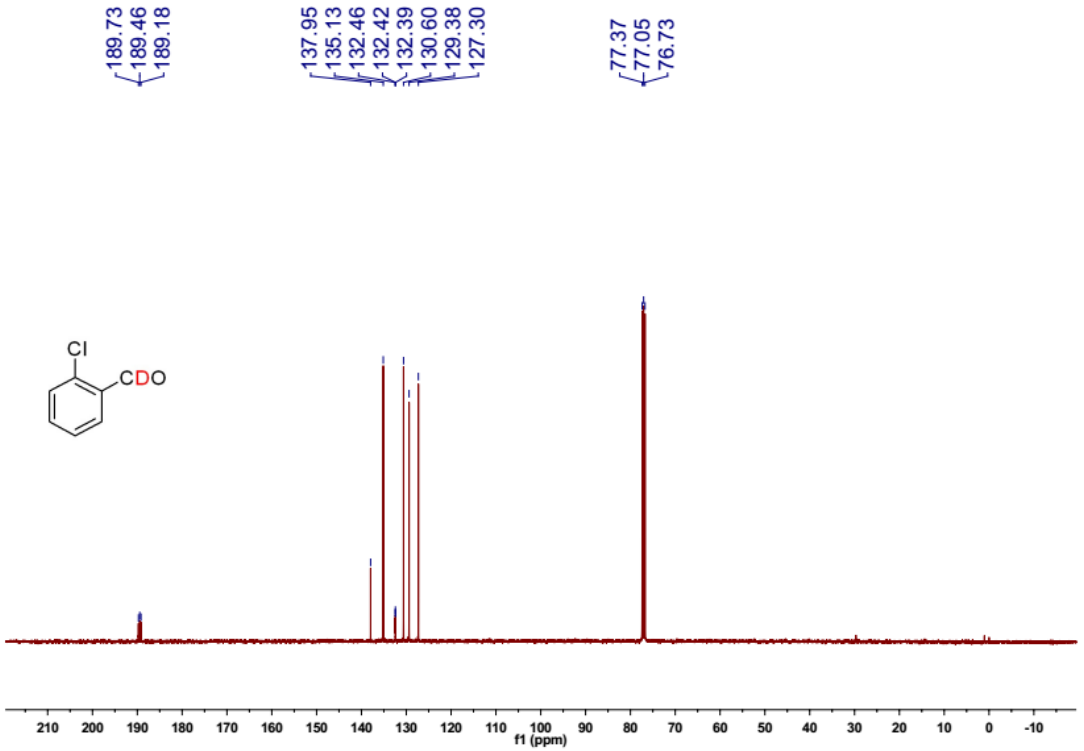
$^{1}$H NMR of deuterated aldehyde **7aa**



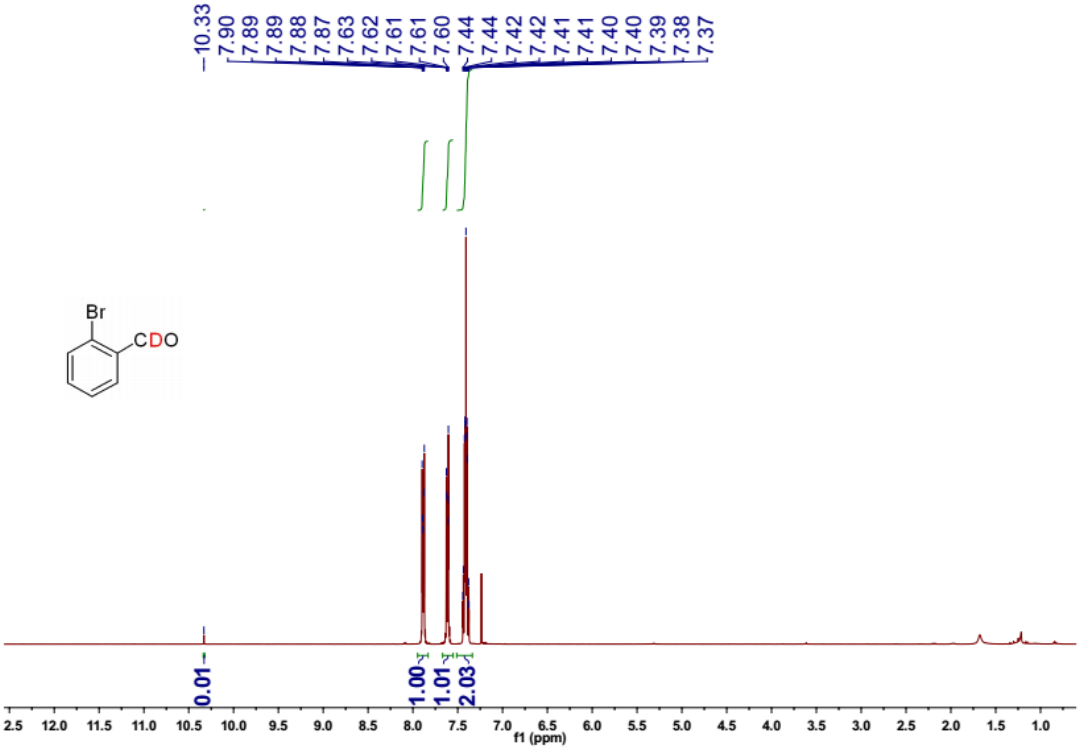

$^{2}$H NMR of deuterated aldehyde **7aa**



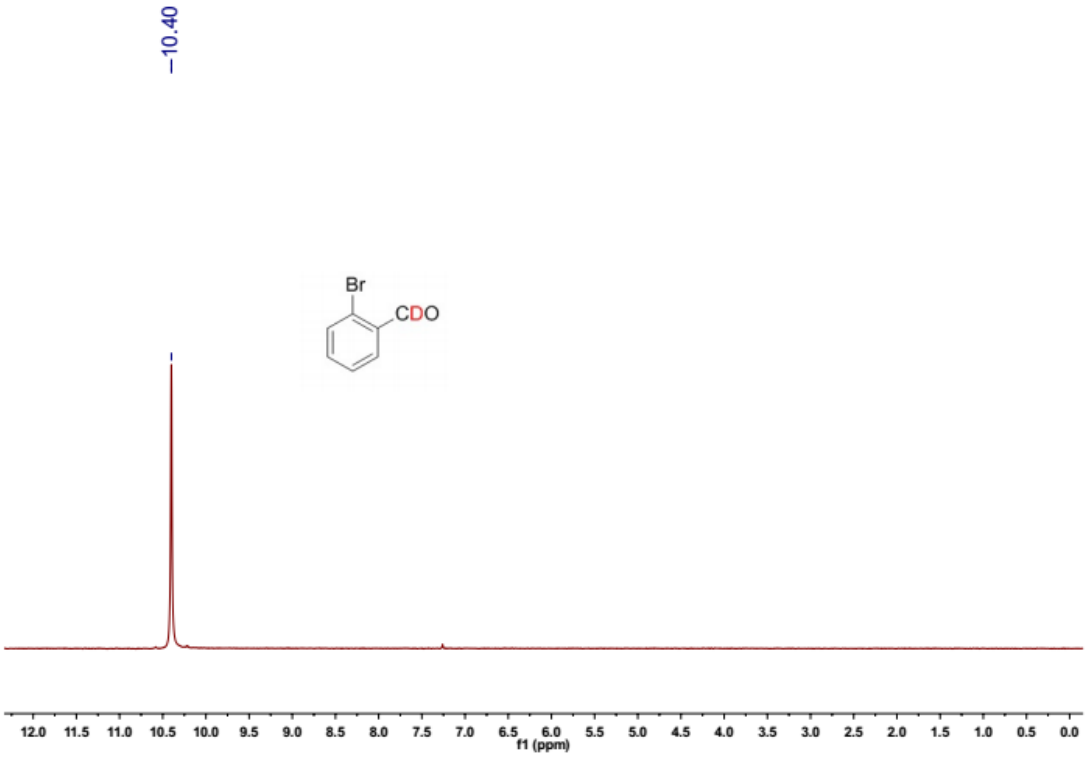
$^{13}$C NMR of deuterated aldehyde **7aa**



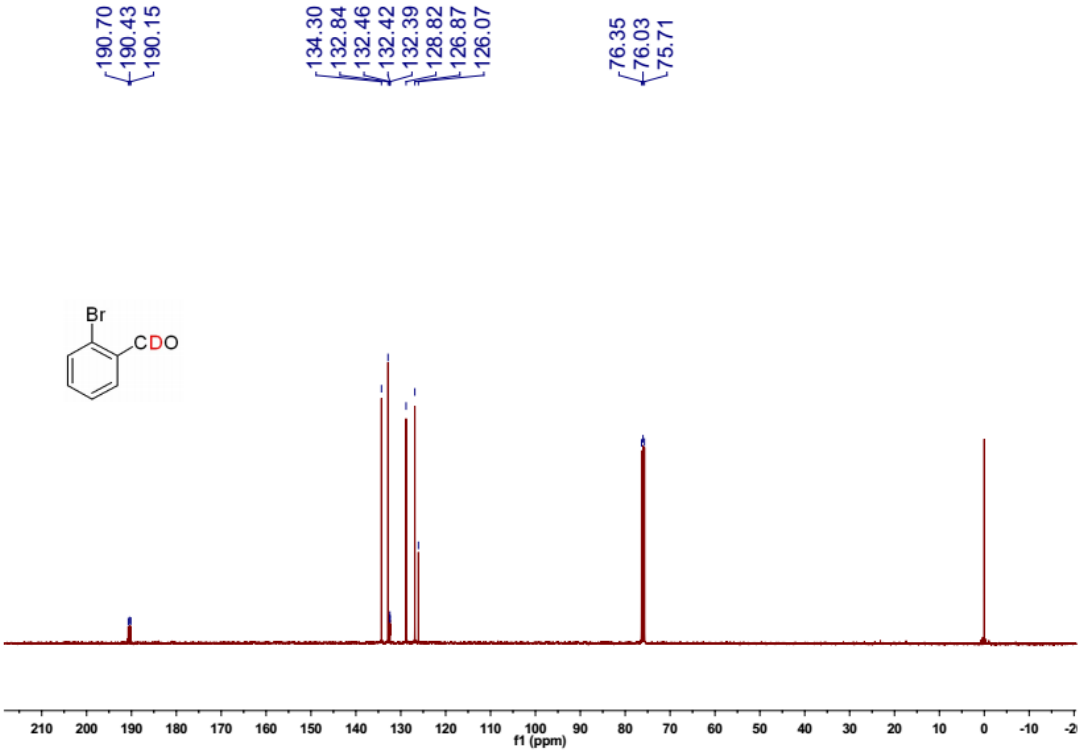
$^{1}$H NMR of deuterated aldehyde **7ab**



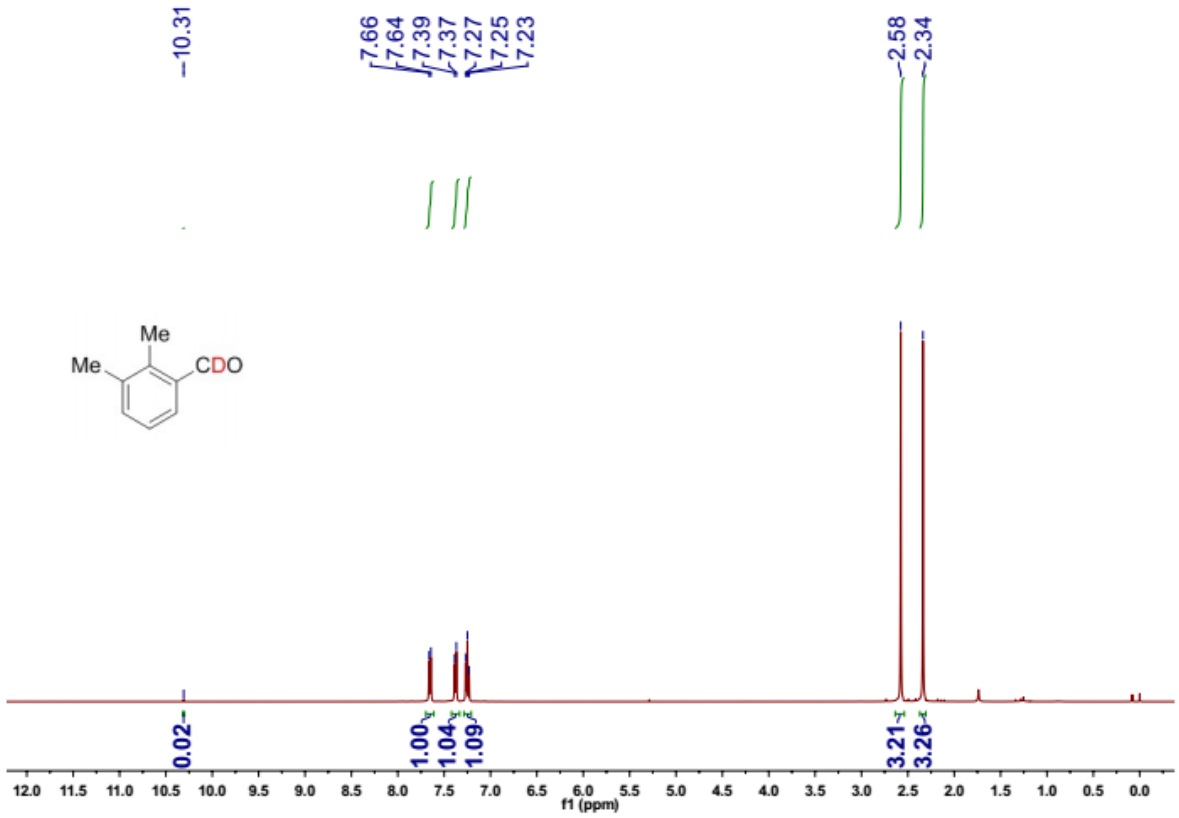

$^{2}$H NMR of deuterated aldehyde **7ab**



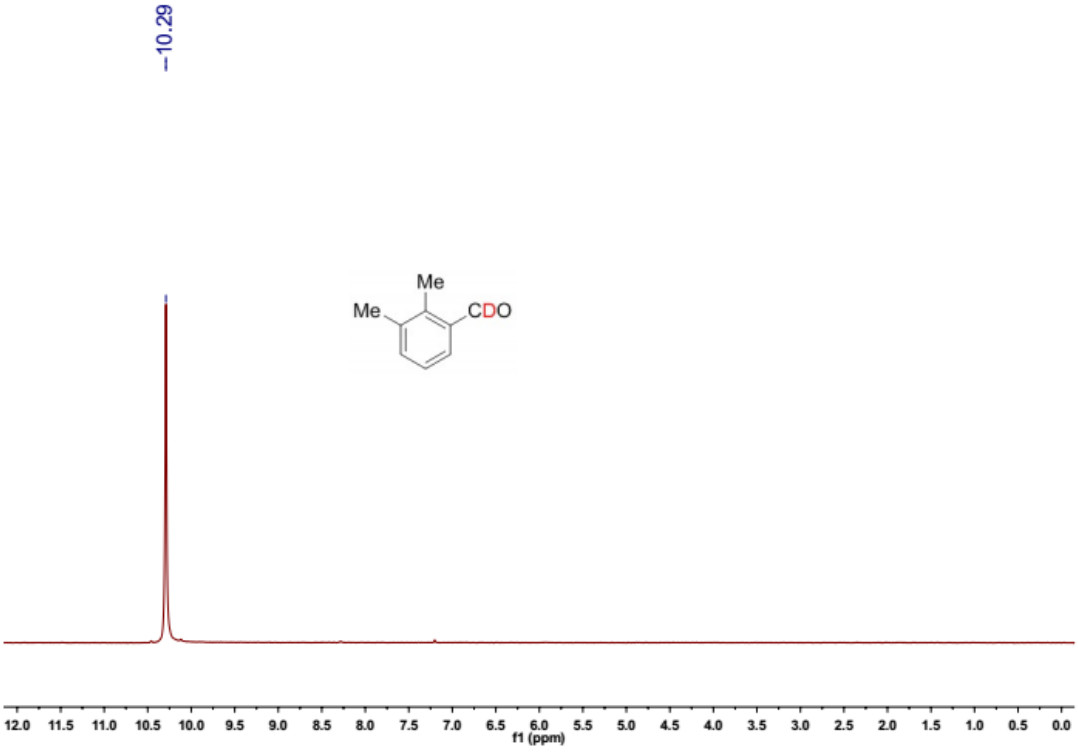
$^{13}$C NMR of deuterated aldehyde **7ab**



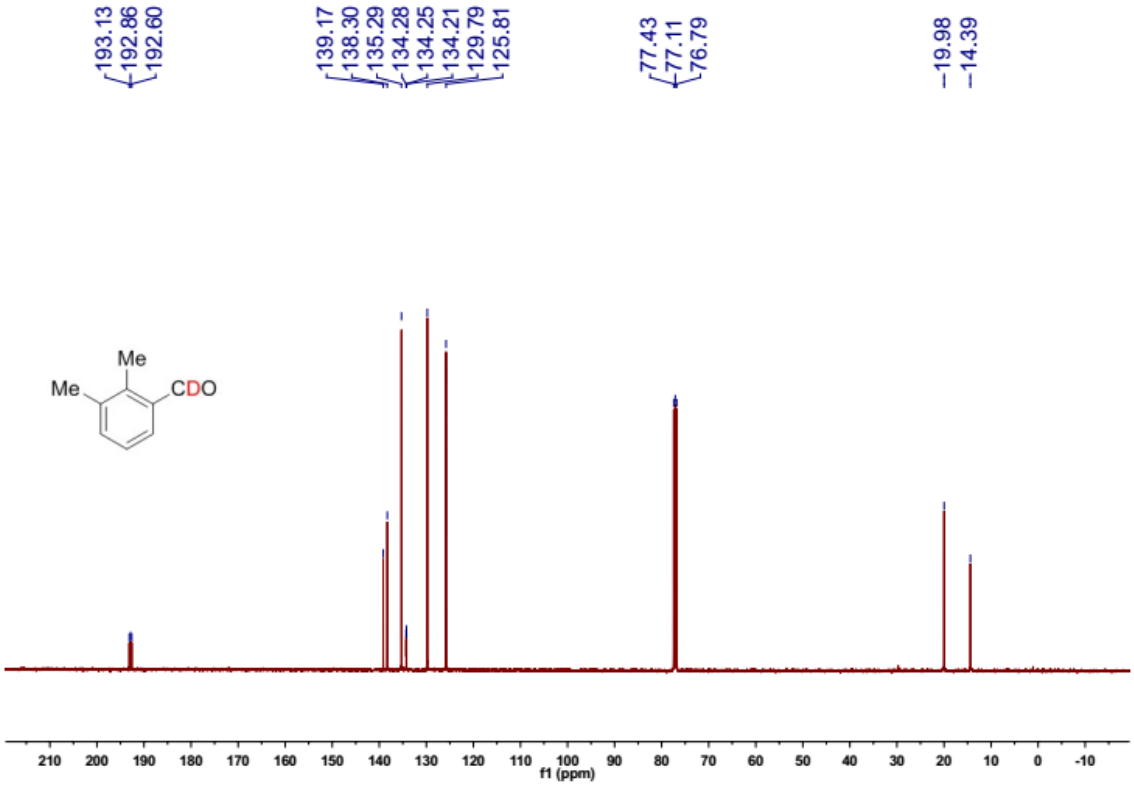
$^{1}$H NMR of deuterated aldehyde **7ac**



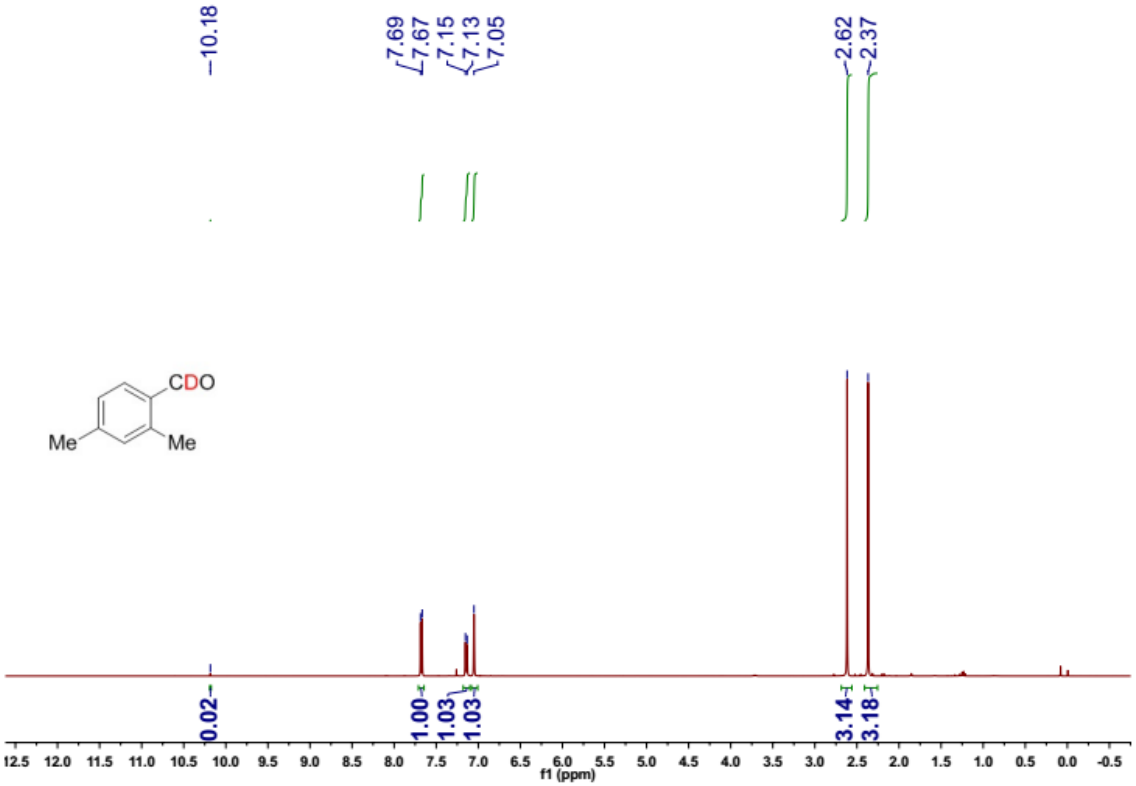

$^{2}$H NMR of deuterated aldehyde **7ac**



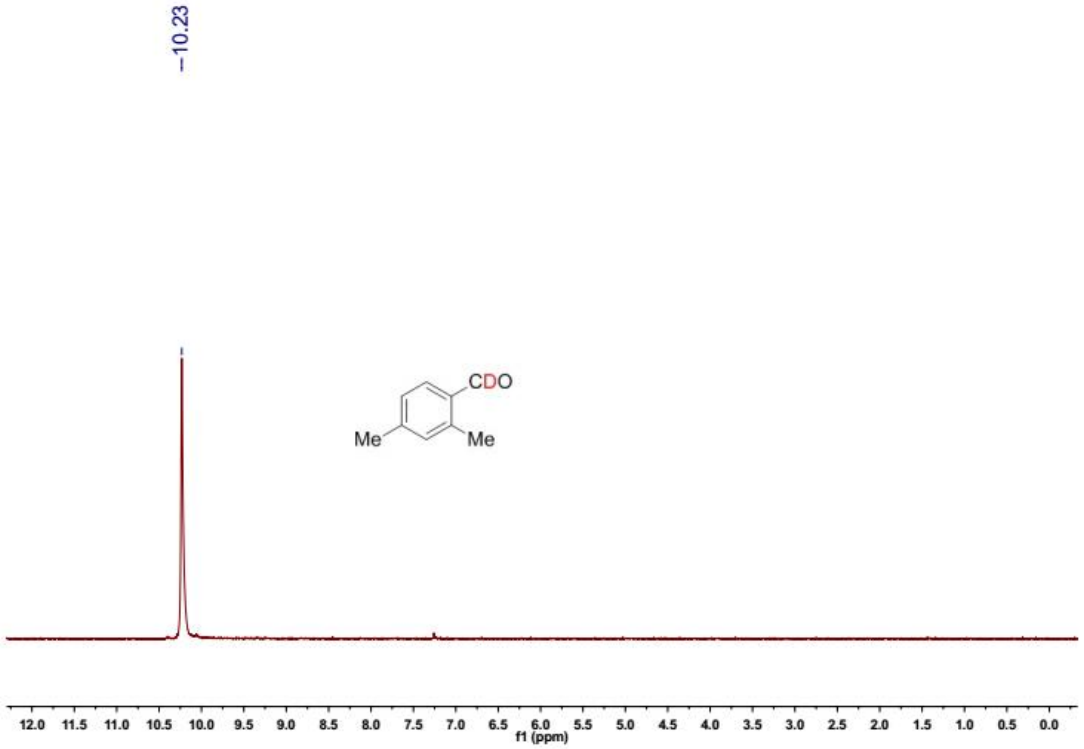
$^{13}$C NMR of deuterated aldehyde **7ac**



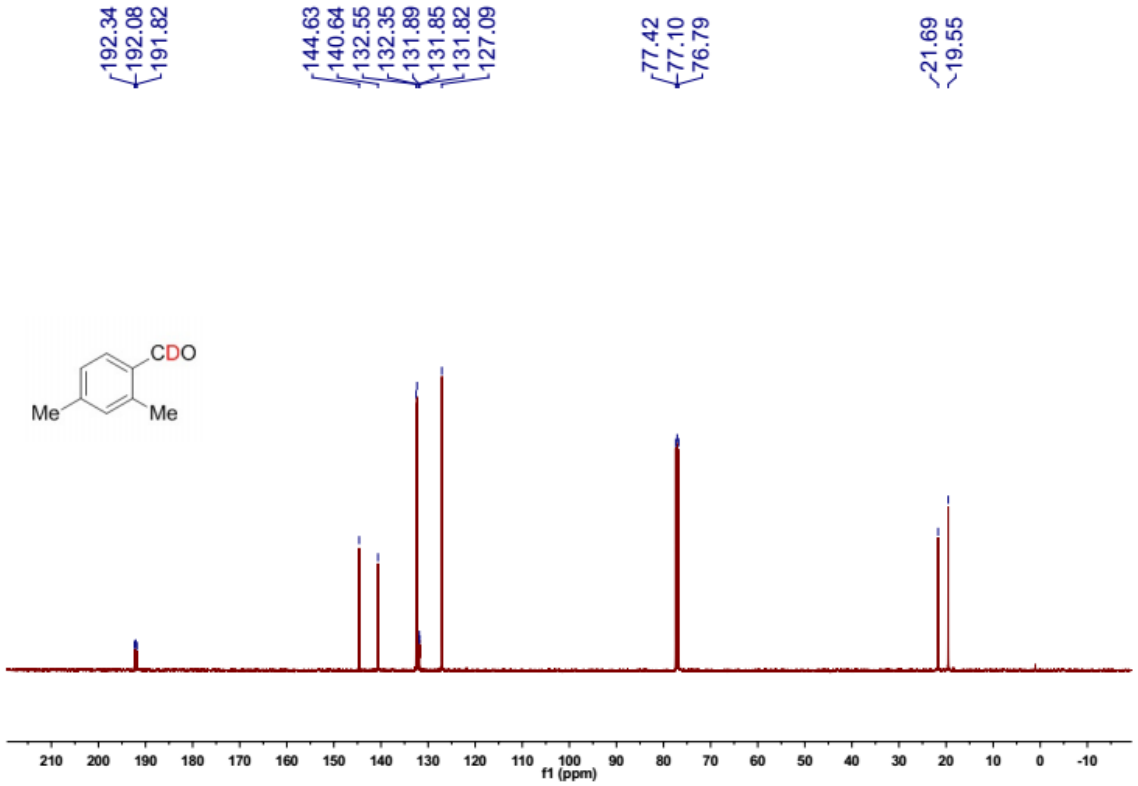
$^{1}$H NMR of deuterated aldehyde **7ad**



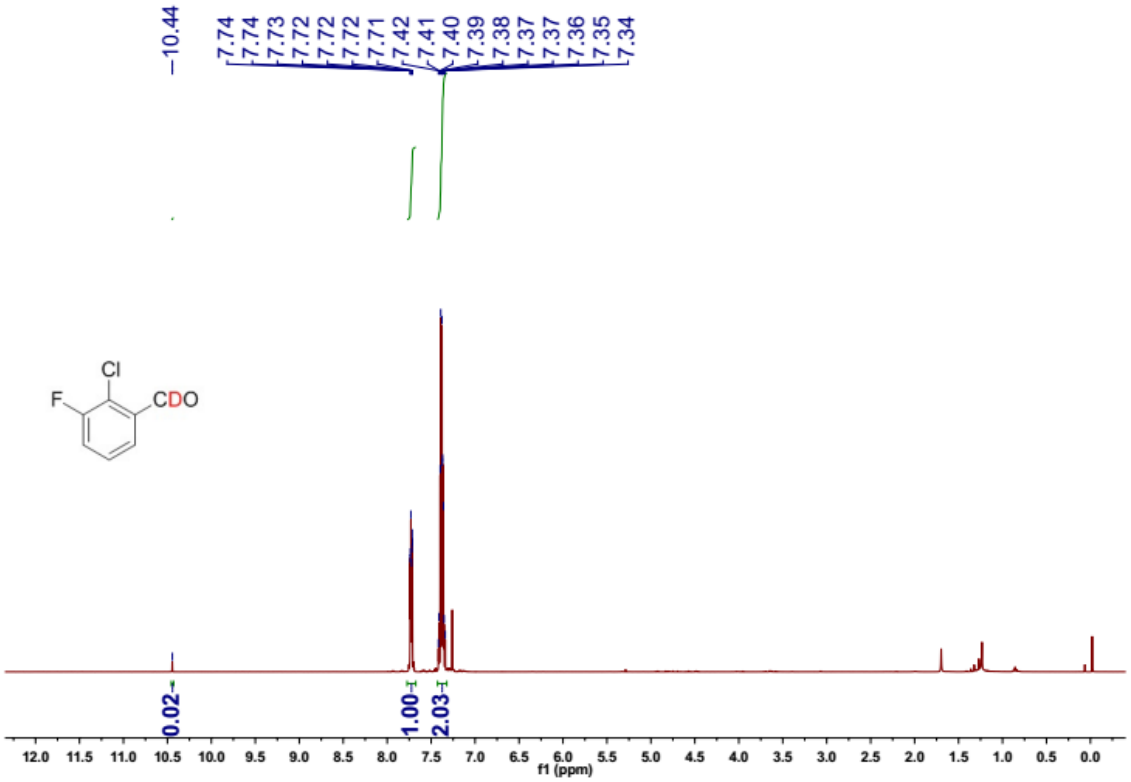

$^{2}$H NMR of deuterated aldehyde **7ad**



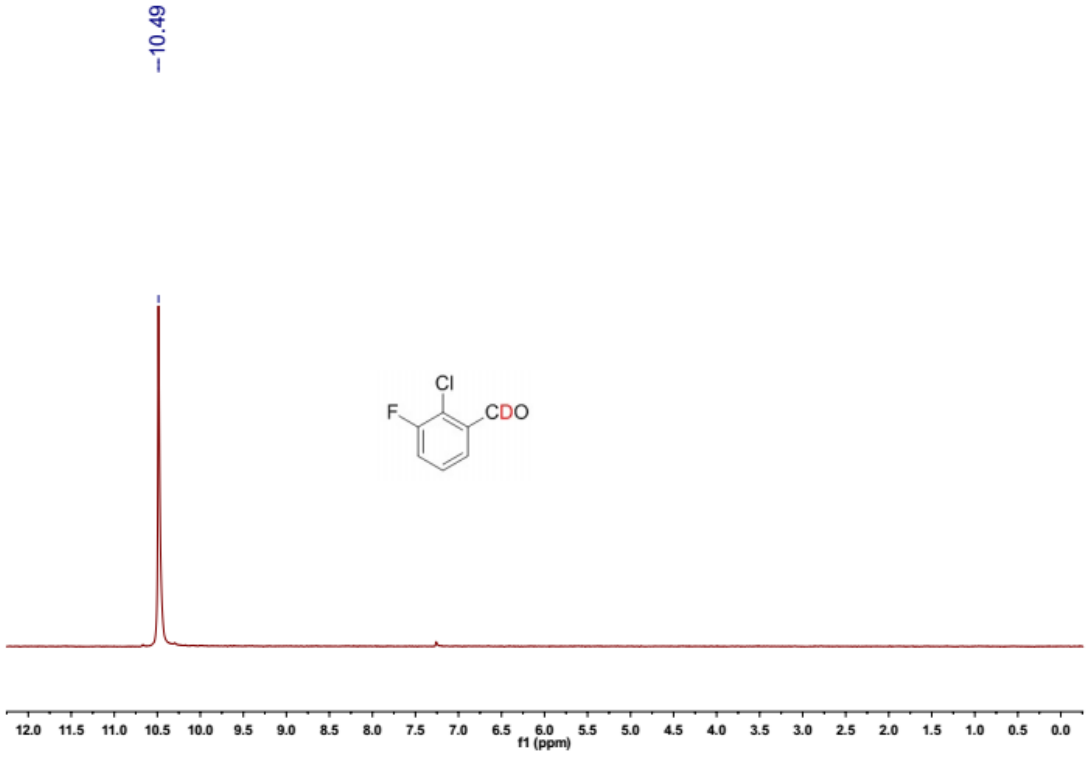
$^{13}$C NMR of deuterated aldehyde **7ad**



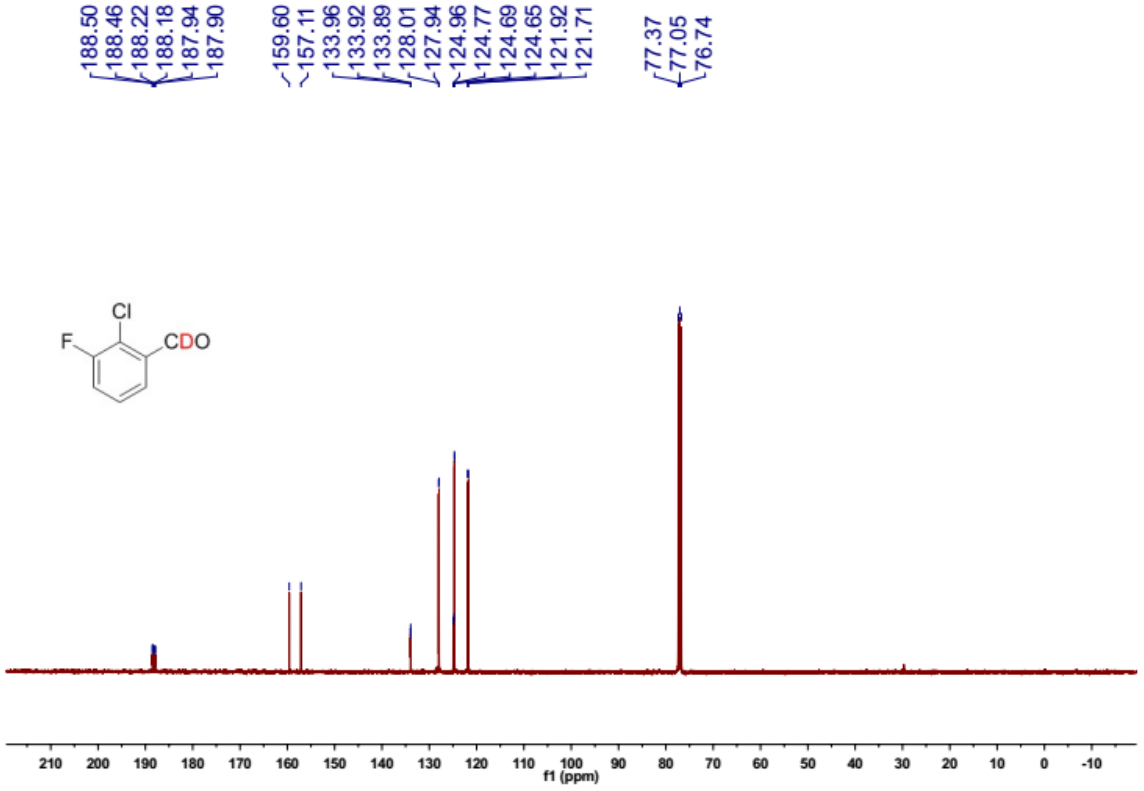
$^{1}$H NMR of deuterated aldehyde **7ae**



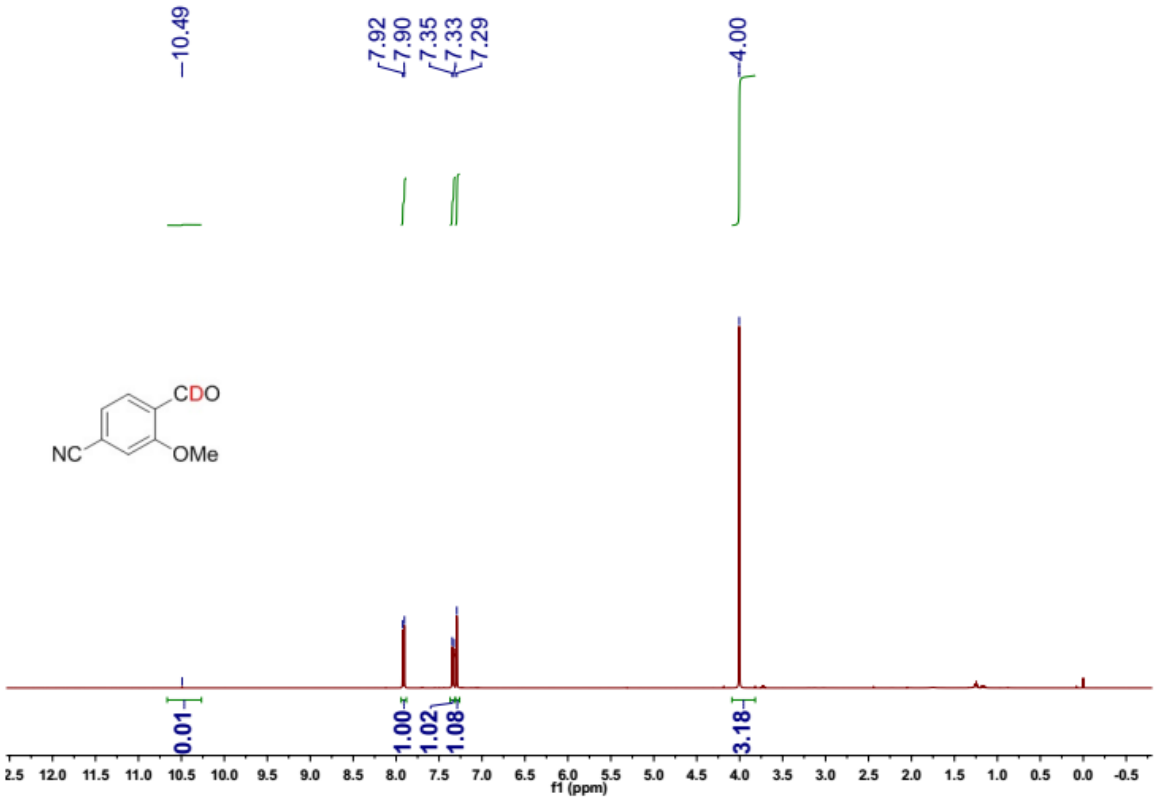

$^{2}$H NMR of deuterated aldehyde **7ae**



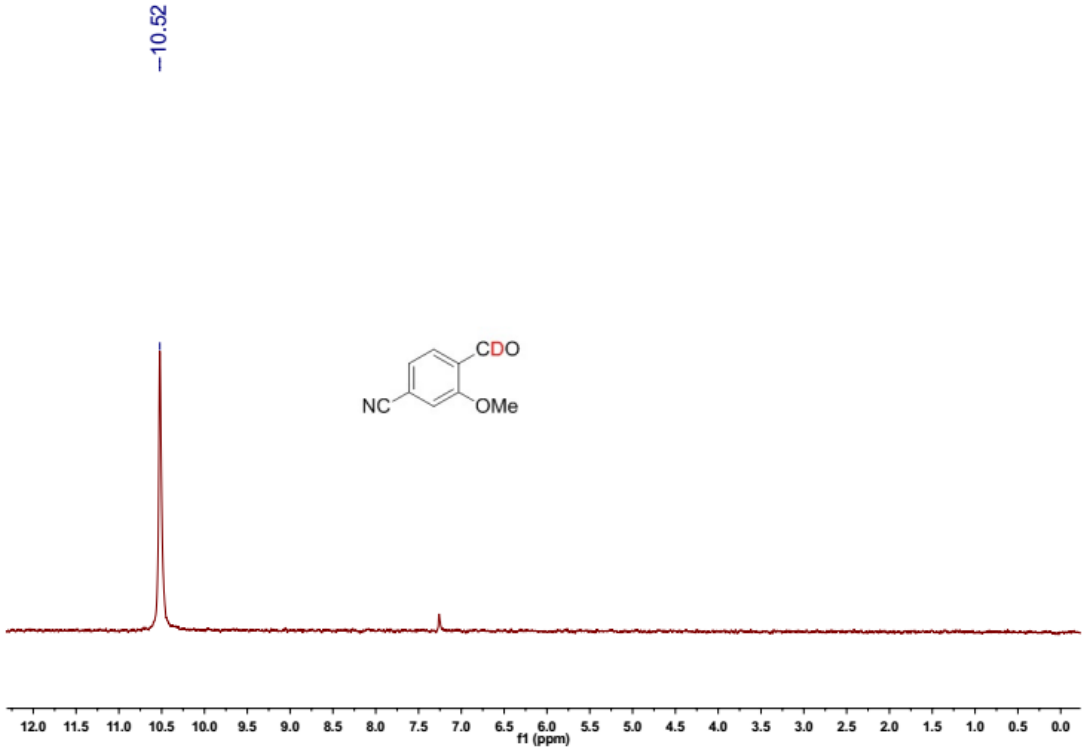
$^{13}$C NMR of deuterated aldehyde **7ae**



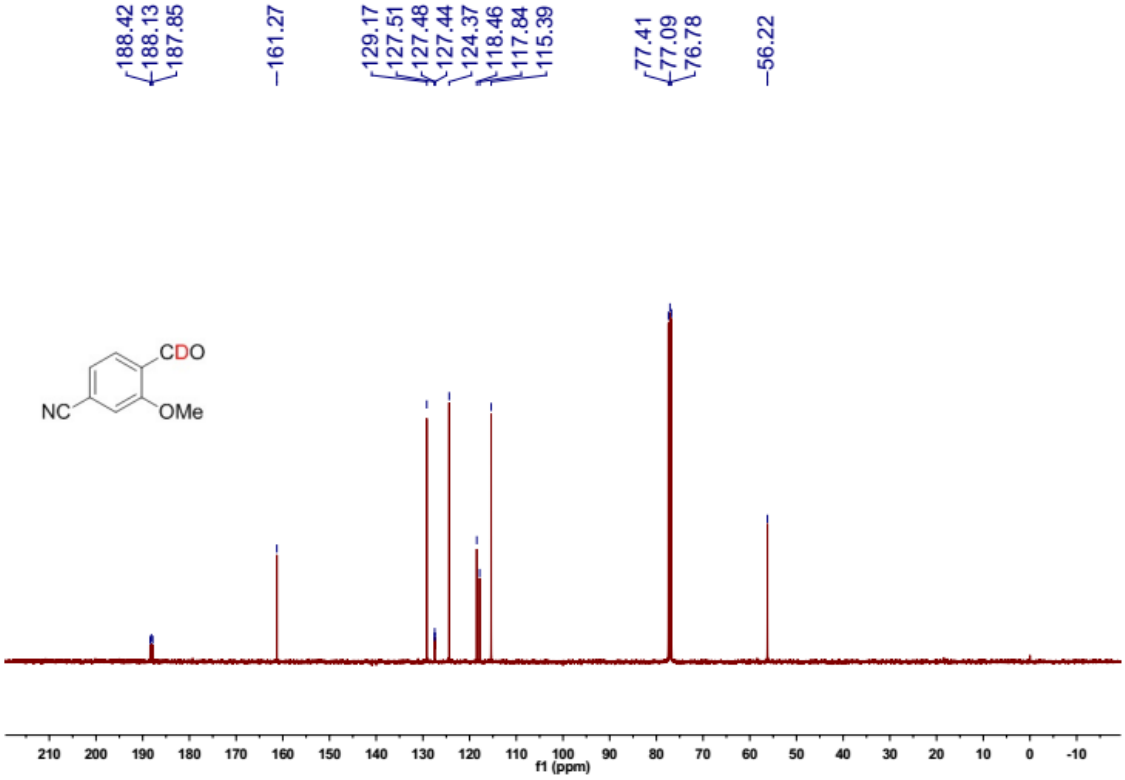
$^{1}$H NMR of deuterated aldehyde **7af**



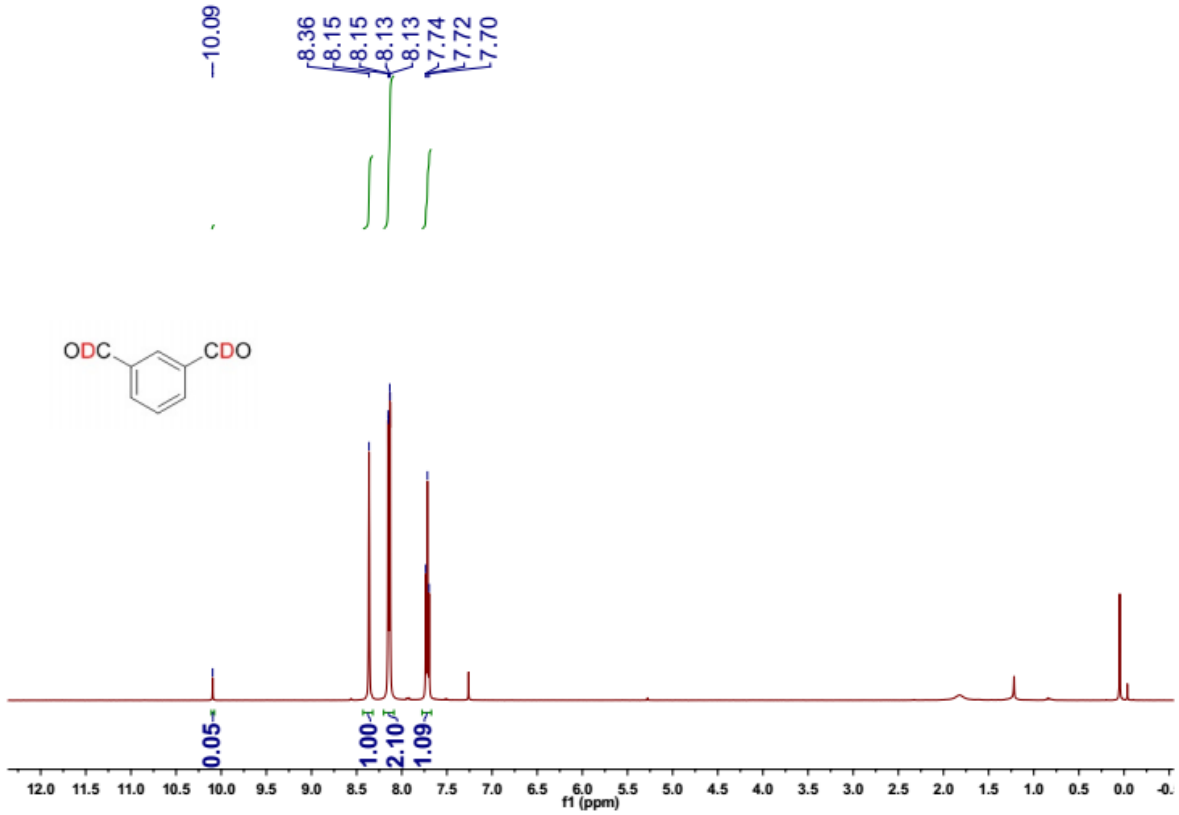

$^{2}$H NMR of deuterated aldehyde **7af**



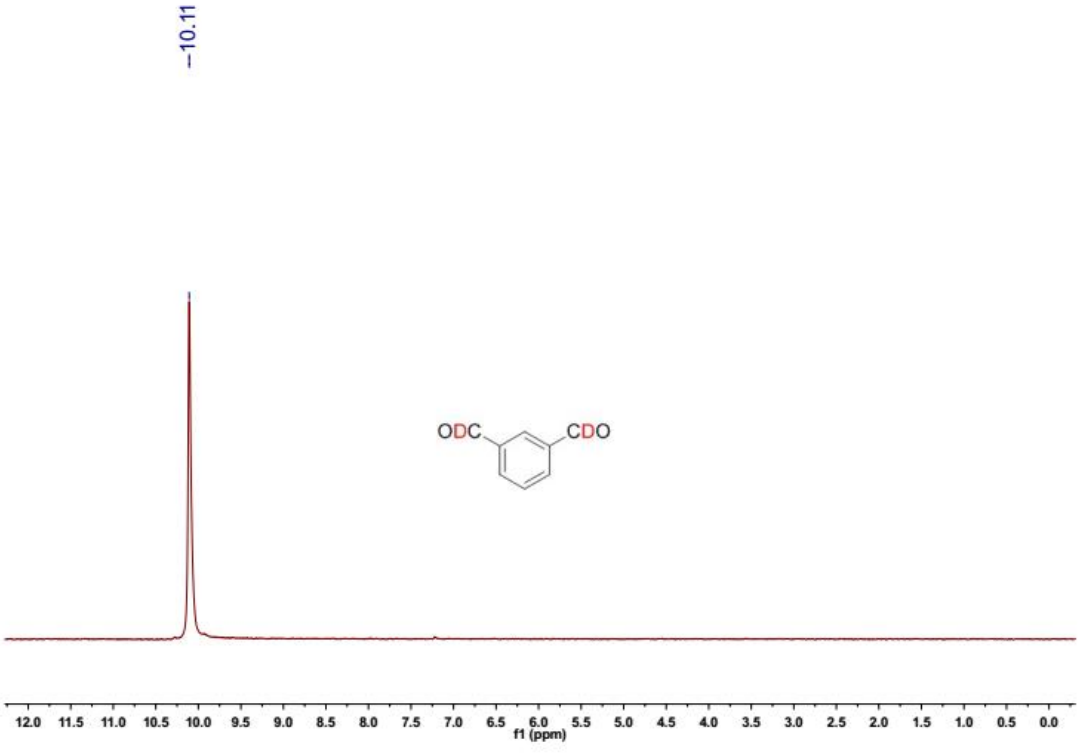
$^{13}$C NMR of deuterated aldehyde **7af**



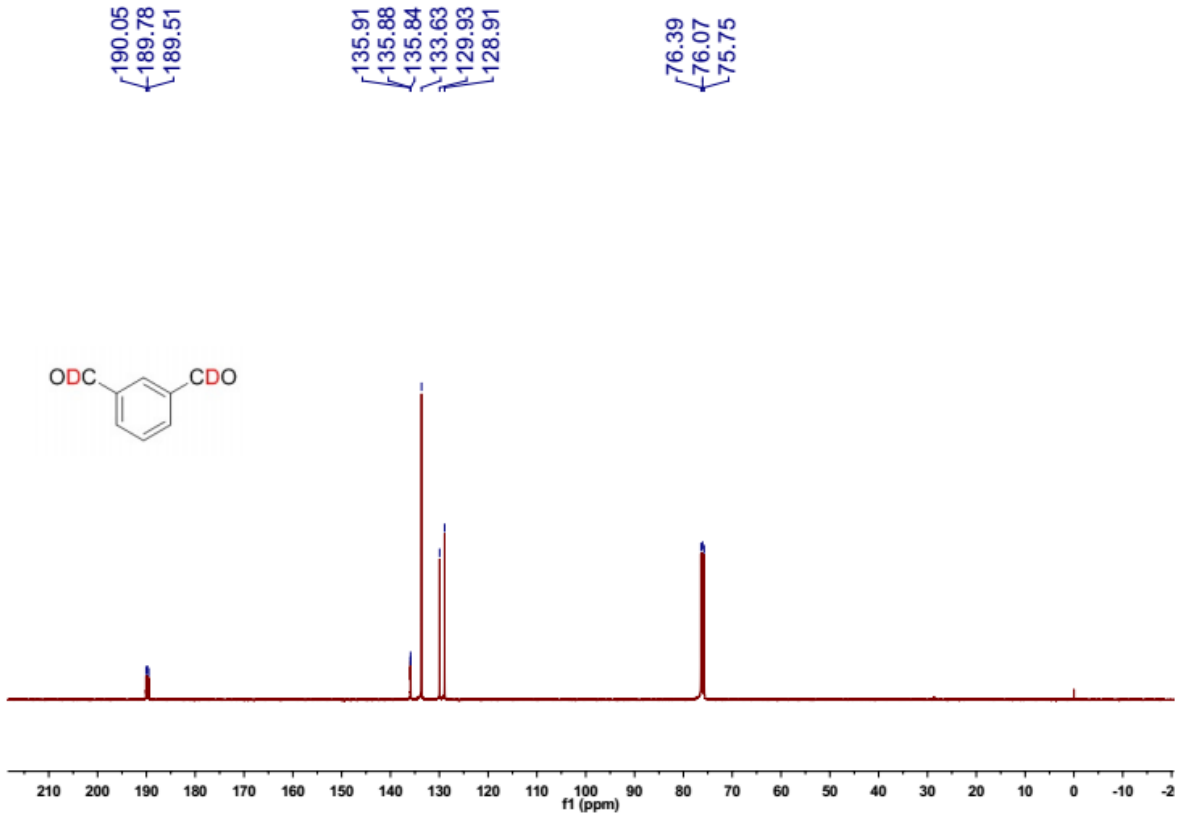
$^{1}$H NMR of deuterated aldehyde **7ag**



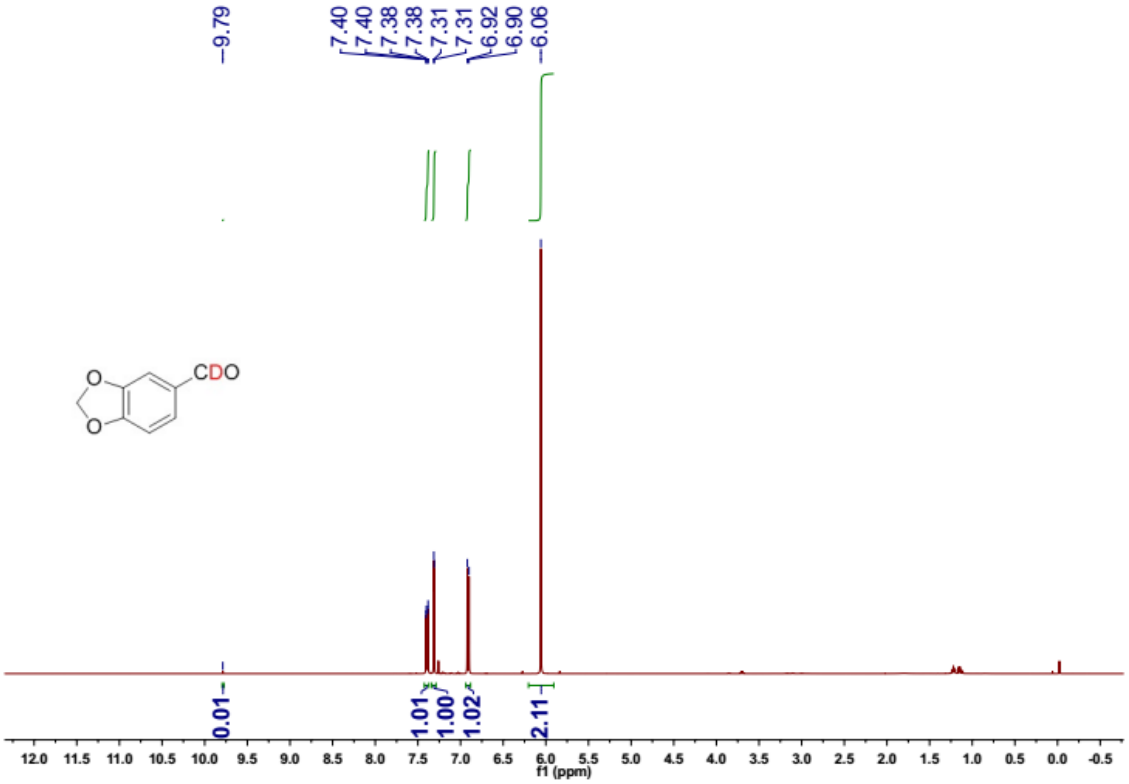

$^{2}$H NMR of deuterated aldehyde **7ag**



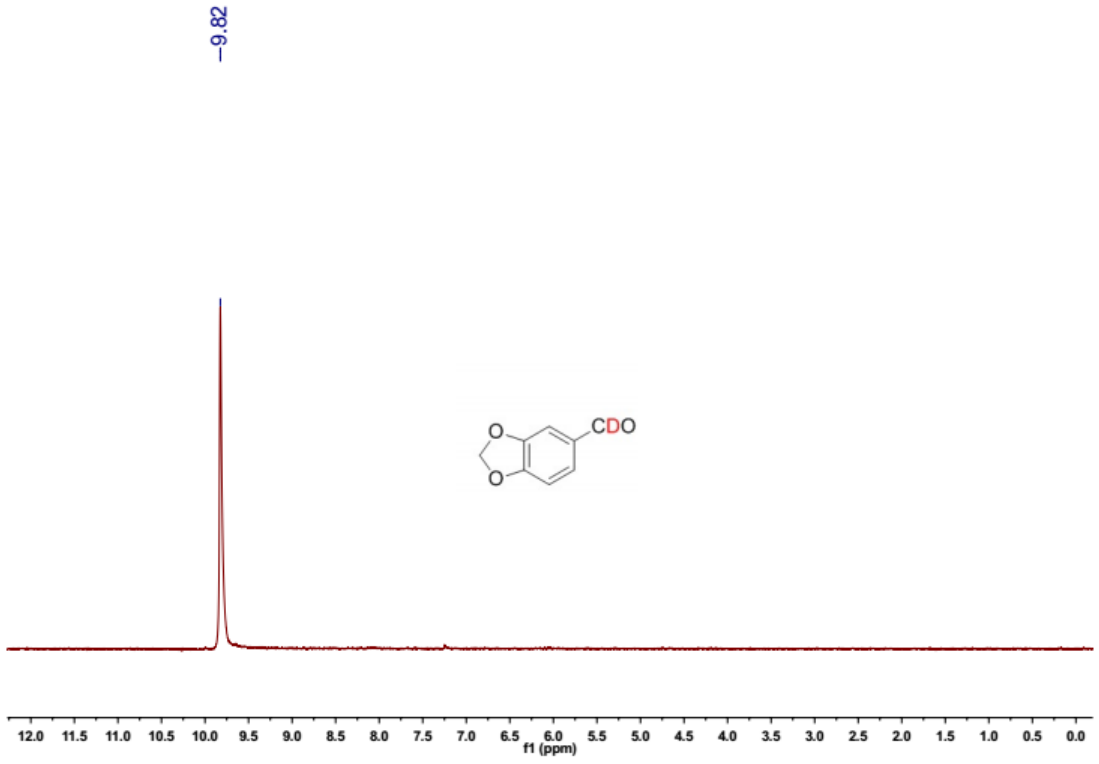
$^{13}$C NMR of deuterated aldehyde **7ag**



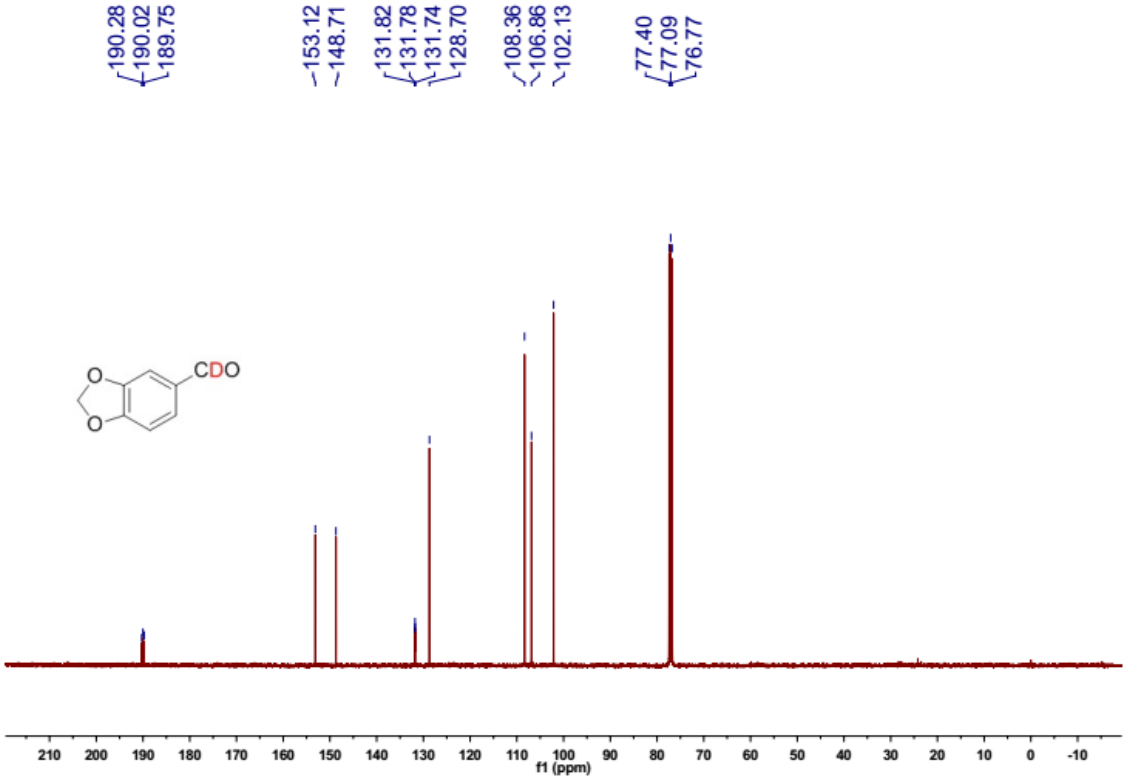
$^{1}$H NMR of deuterated aldehyde **7ah**



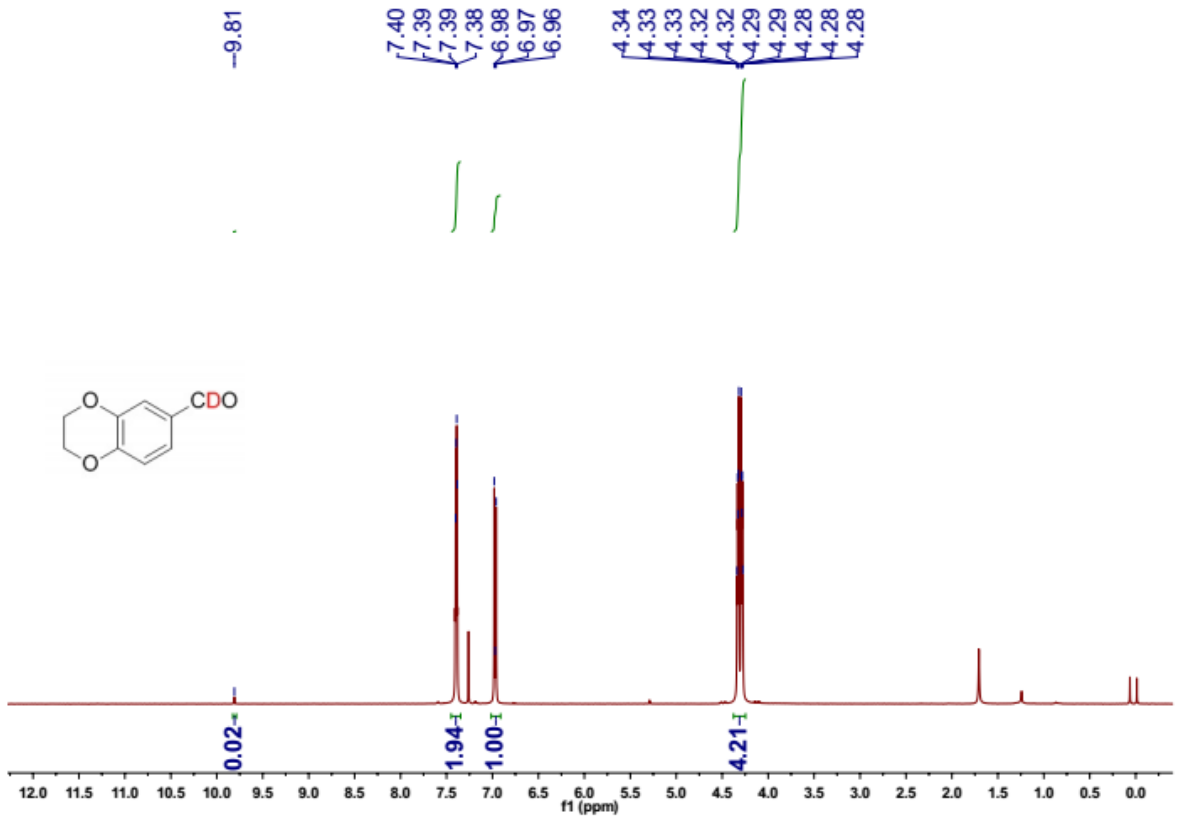

$^{2}$H NMR of deuterated aldehyde **7ah**



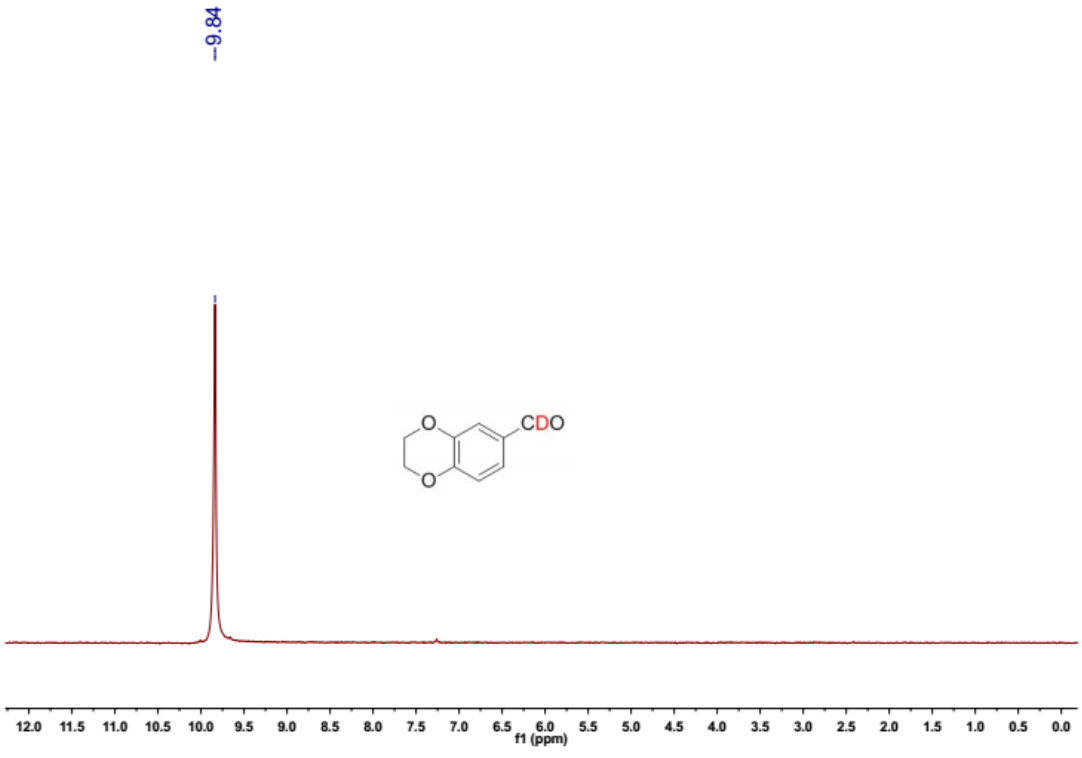
$^{13}$C NMR of deuterated aldehyde **7ah**



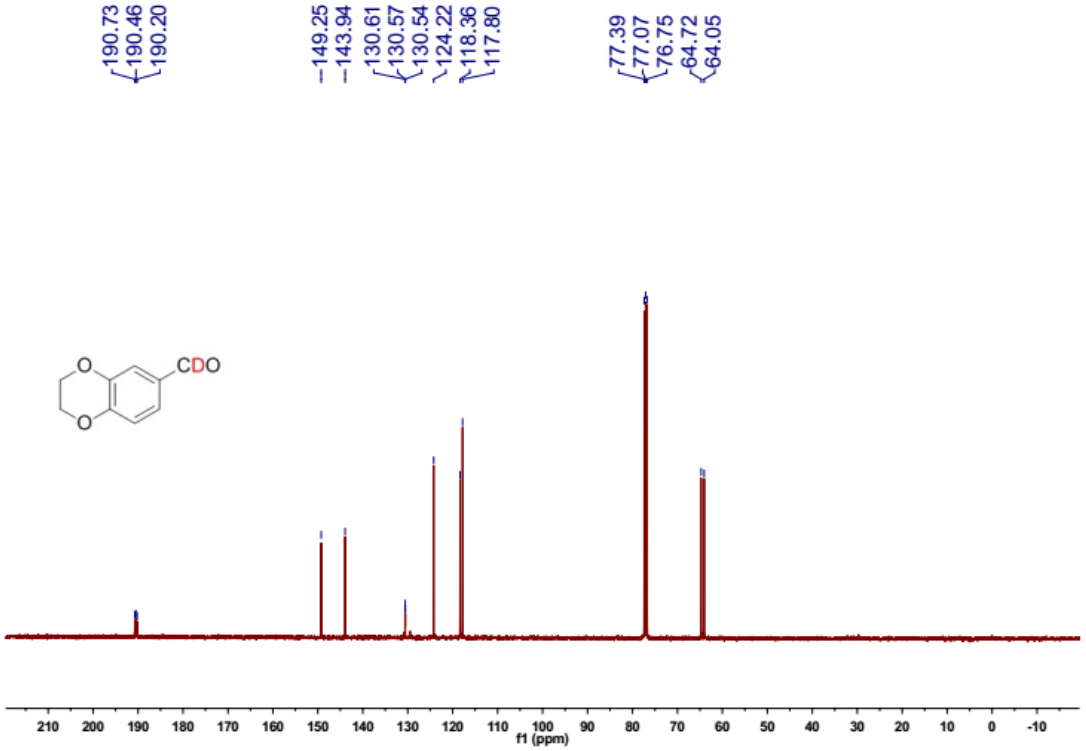
$^{1}$H NMR of deuterated aldehyde **7ai**



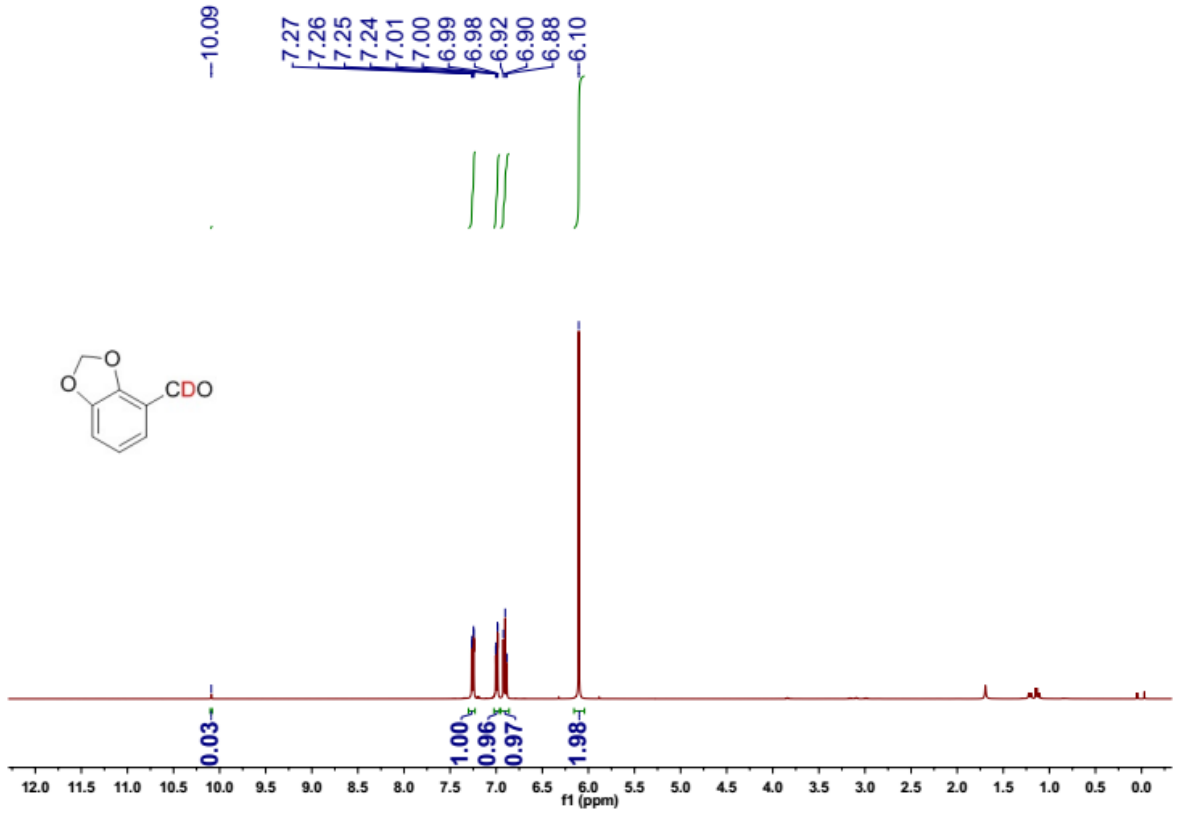

$^{2}$H NMR of deuterated aldehyde **7ai**



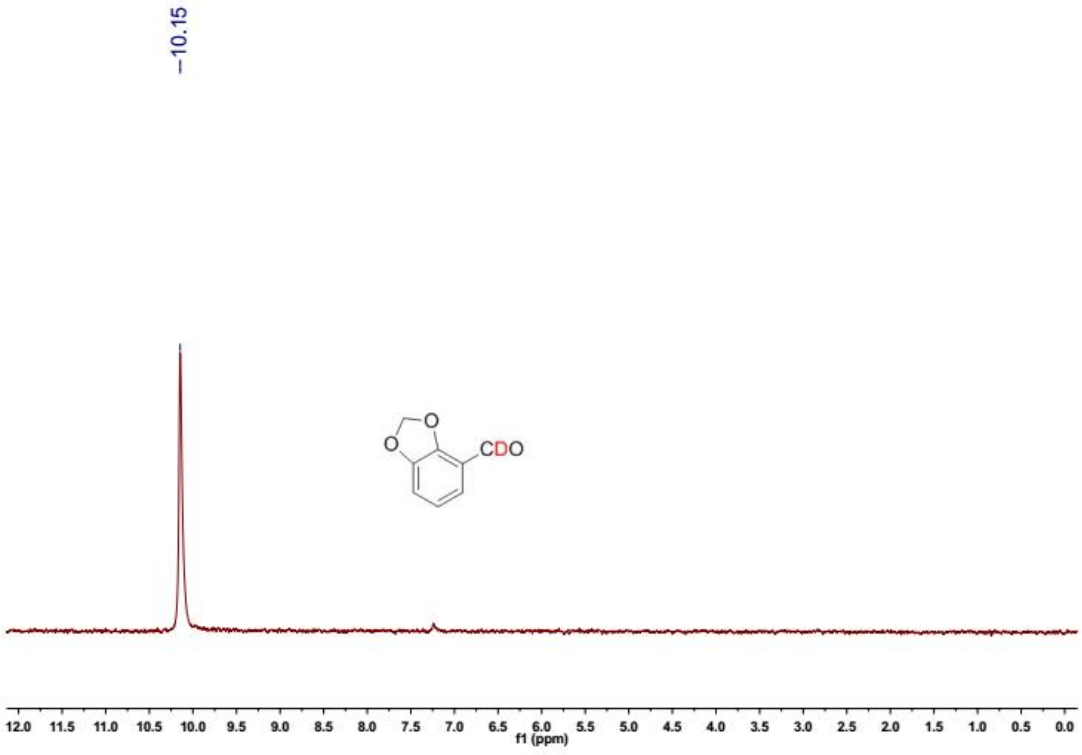
$^{13}$C NMR of deuterated aldehyde **7ai**



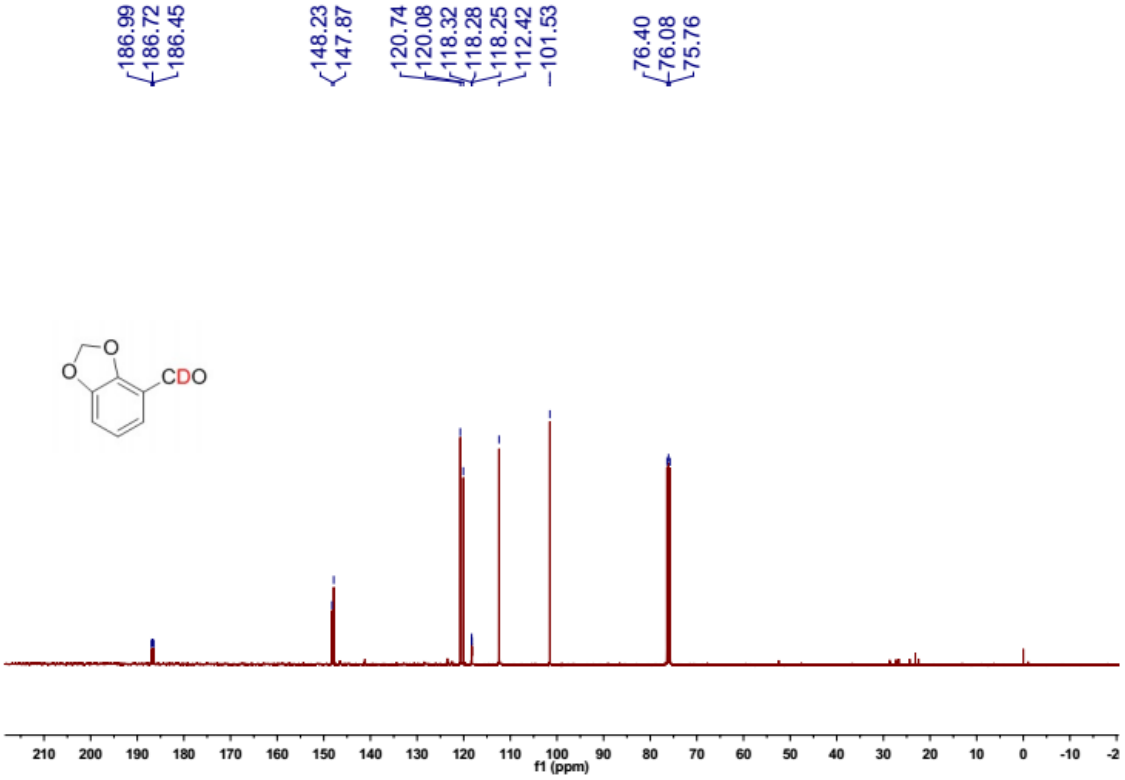
$^{1}$H NMR of deuterated aldehyde **7aj**



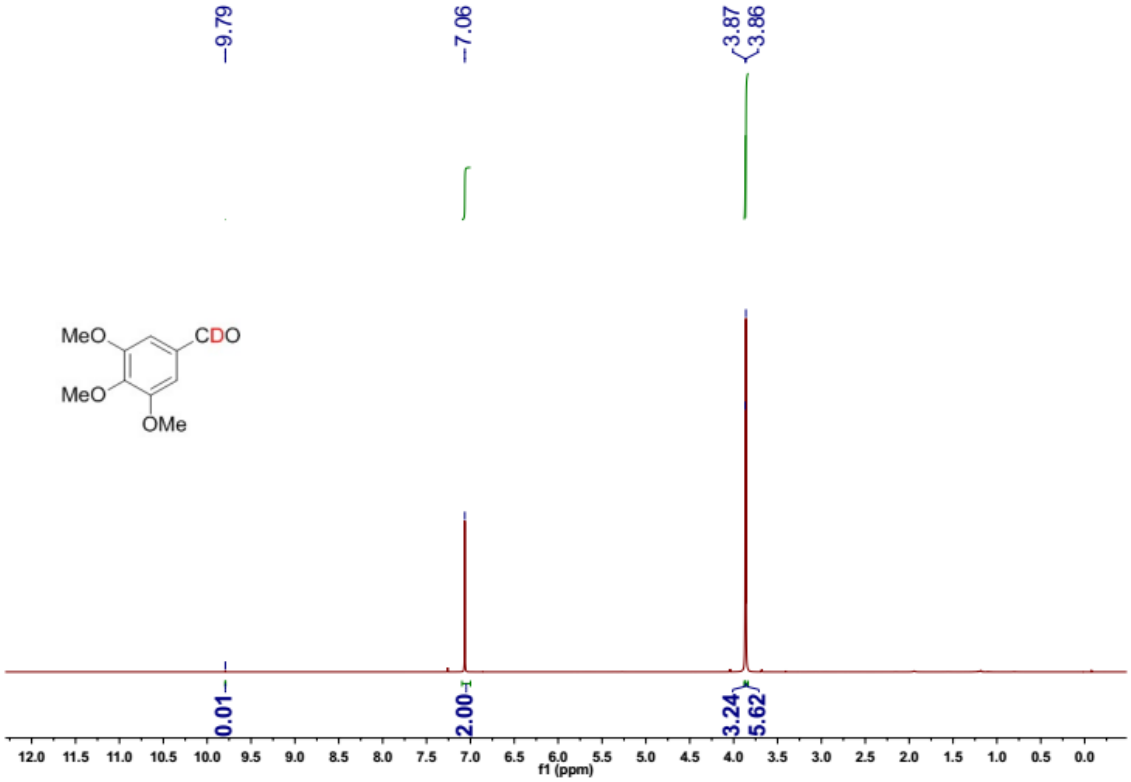

$^{2}$H NMR of deuterated aldehyde **7aj**



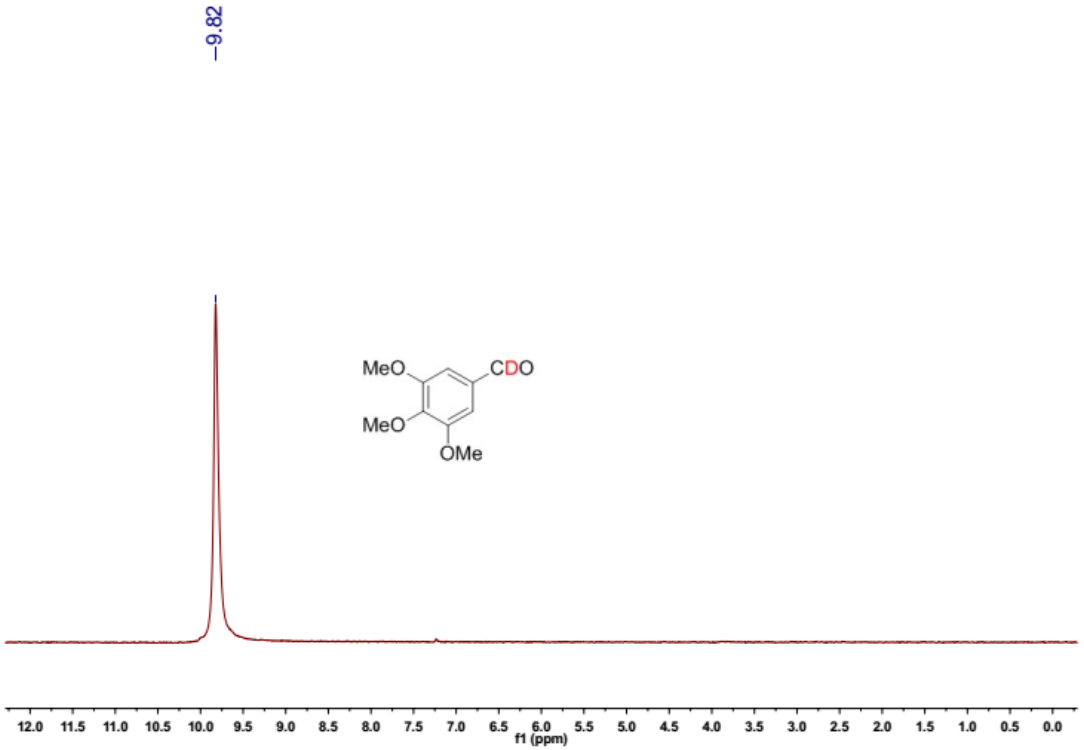
$^{13}$C NMR of deuterated aldehyde **7aj**



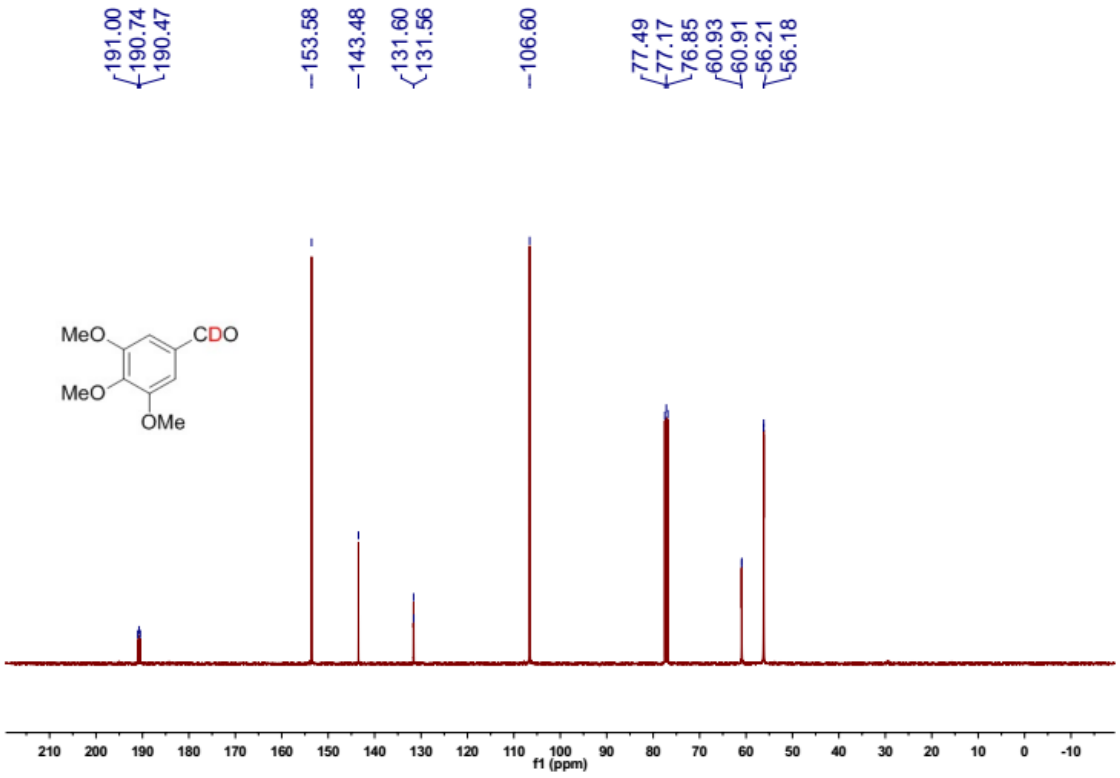
$^{1}$H NMR of deuterated aldehyde **7ak**



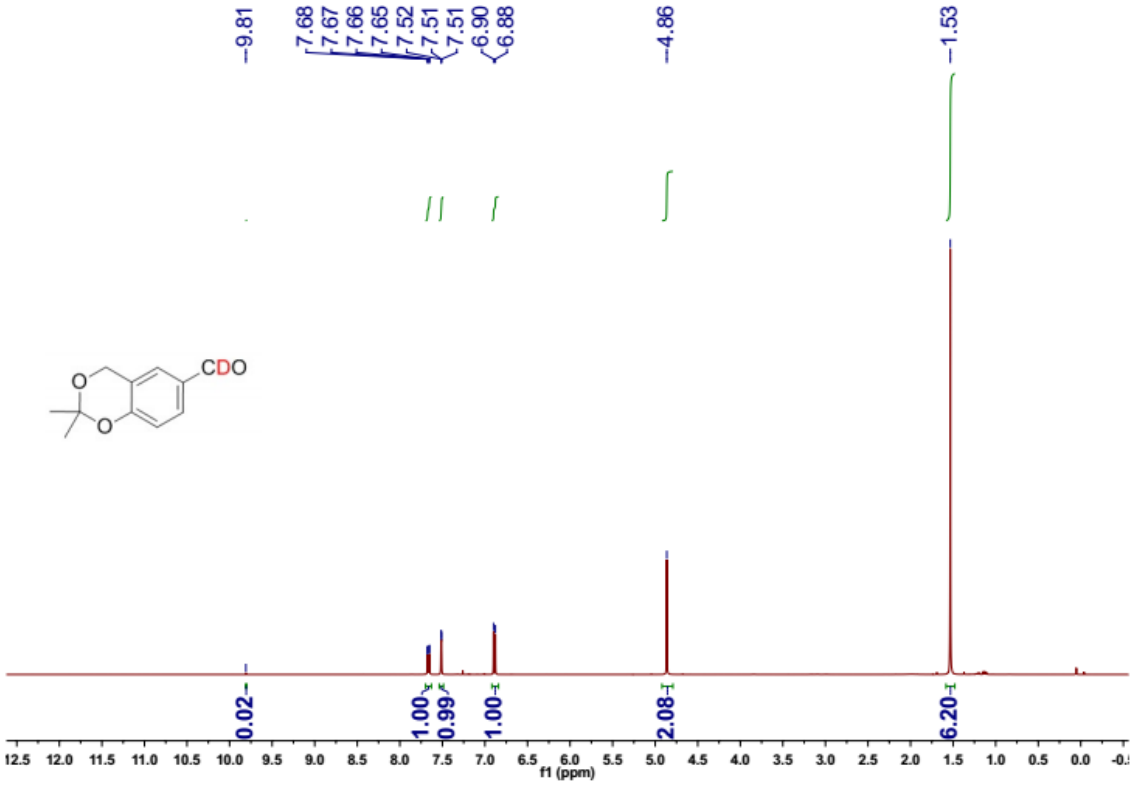

$^{2}$H NMR of deuterated aldehyde **7ak**



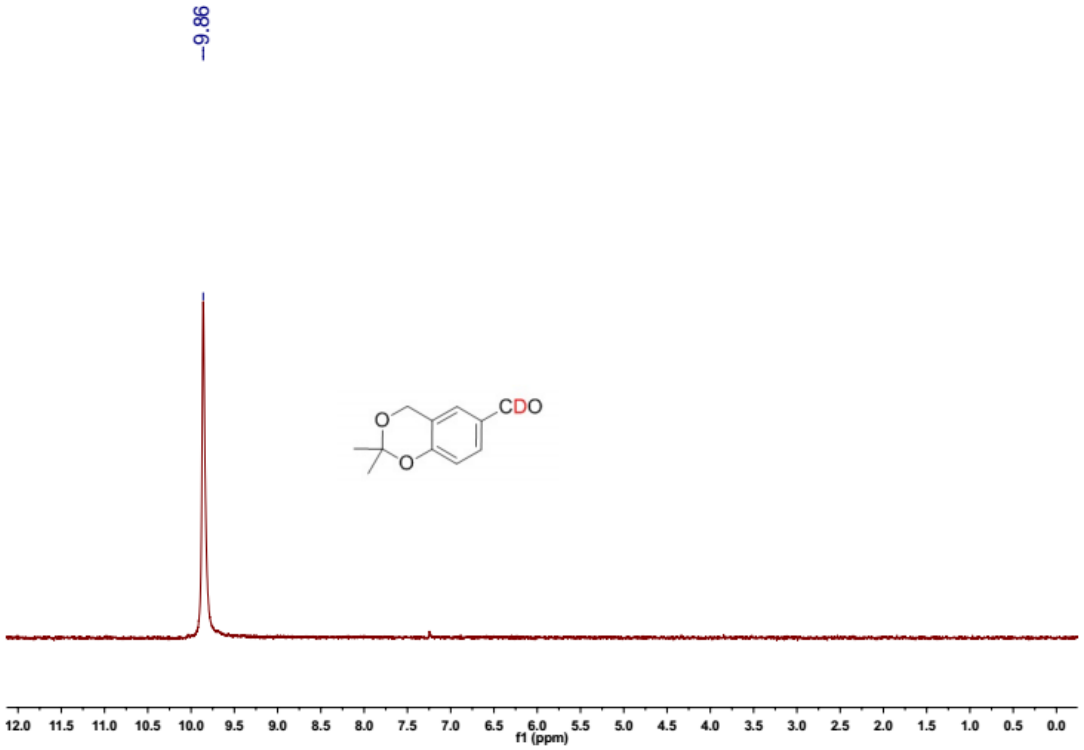
$^{13}$C NMR of deuterated aldehyde **7ak**



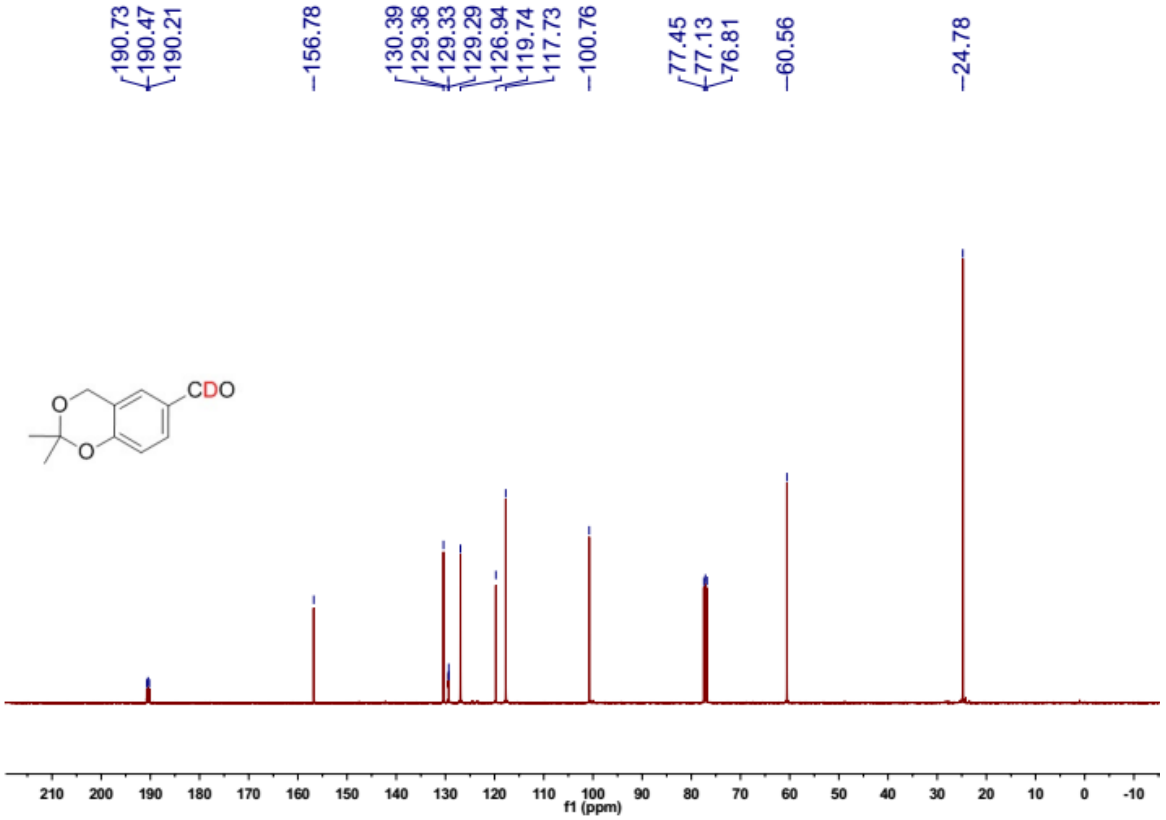
$^{1}$H NMR of deuterated aldehyde **7al**



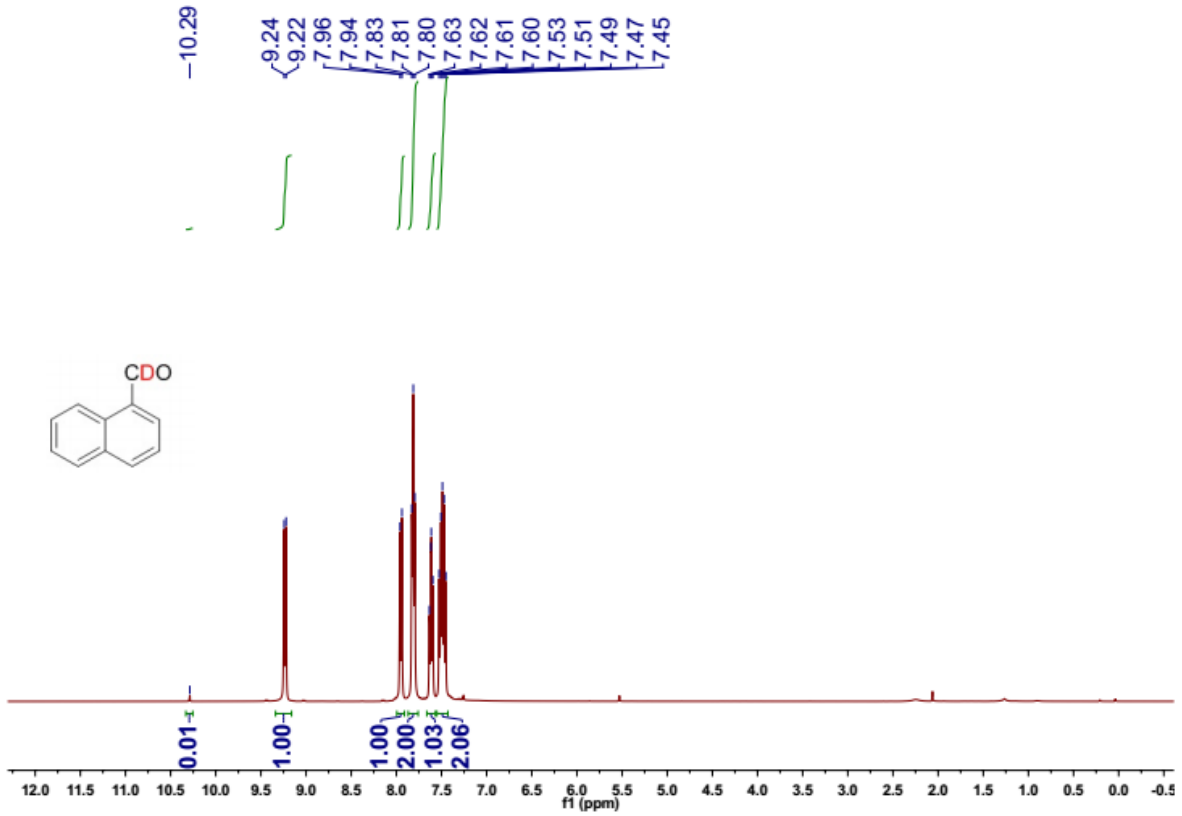

$^{2}$H NMR of deuterated aldehyde **7al**



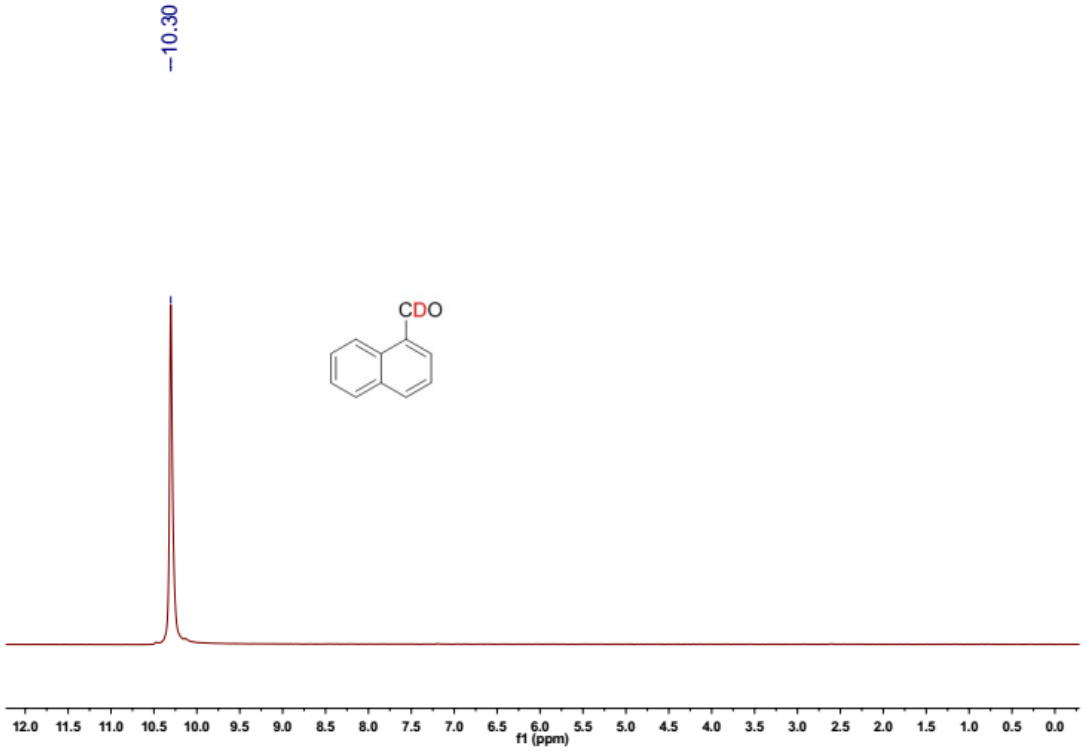
$^{13}$C NMR of deuterated aldehyde **7al**



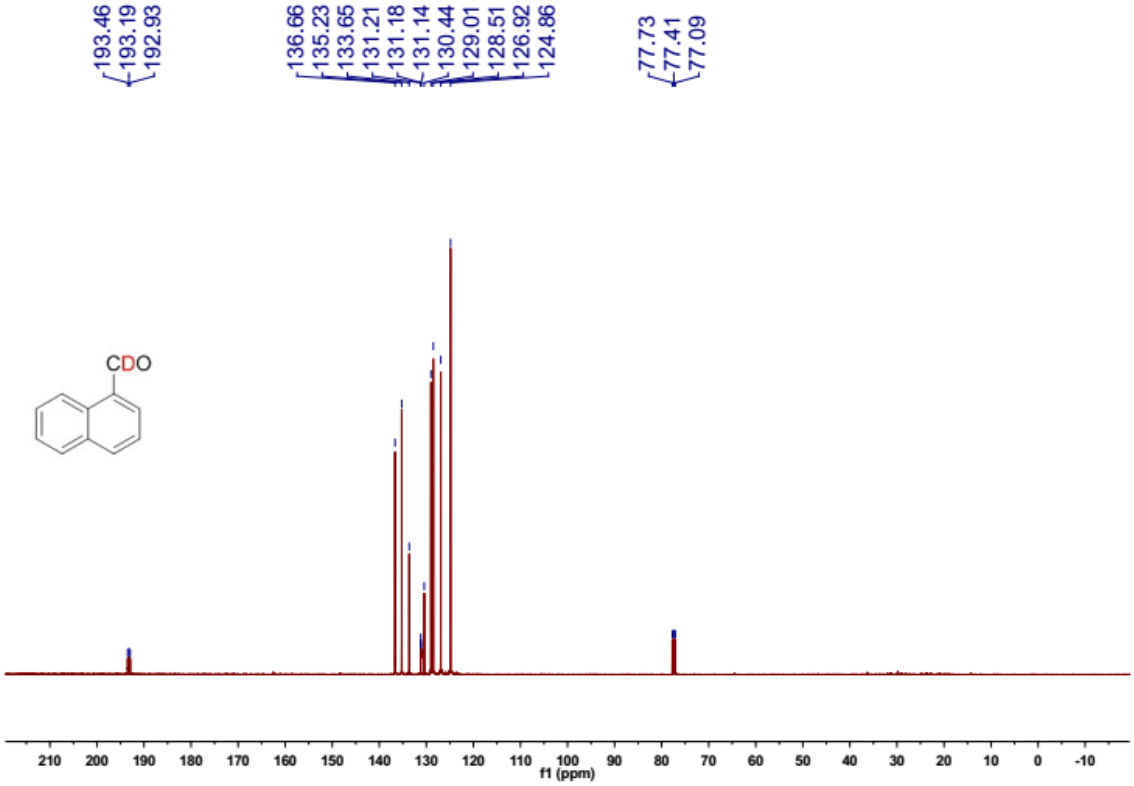
$^{1}$H NMR of deuterated aldehyde **7am**



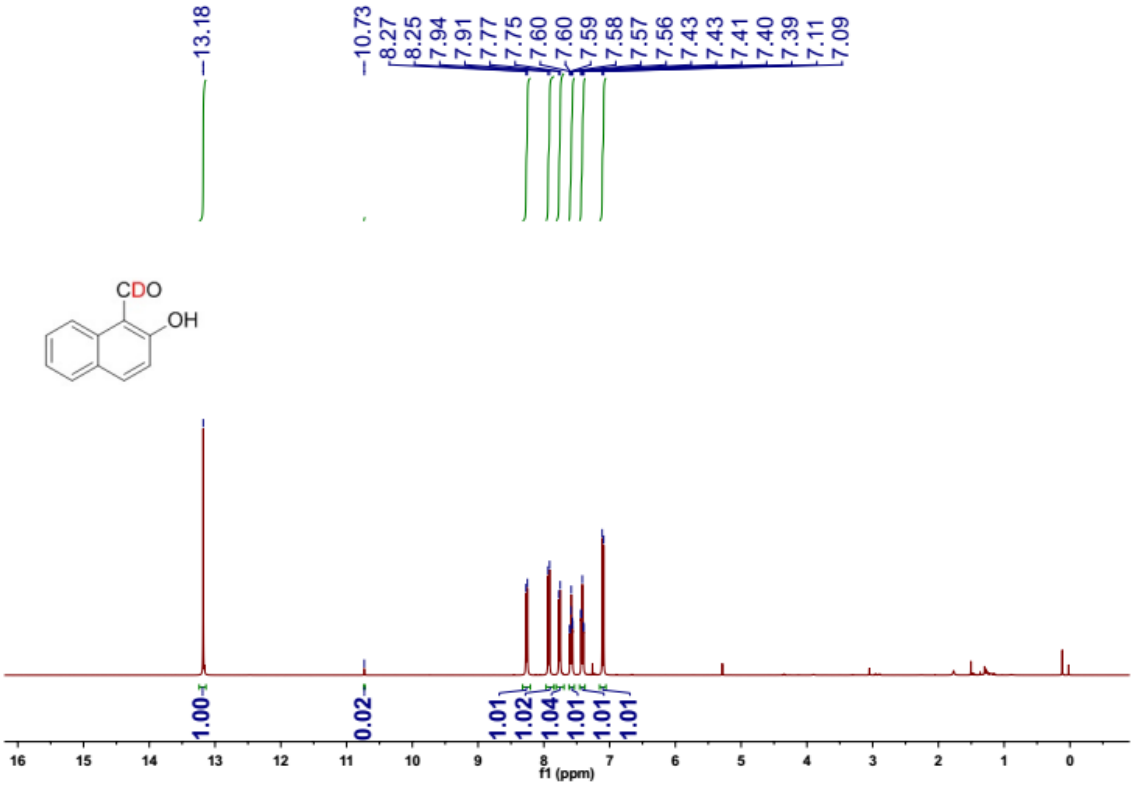

$^{2}$H NMR of deuterated aldehyde **7am**



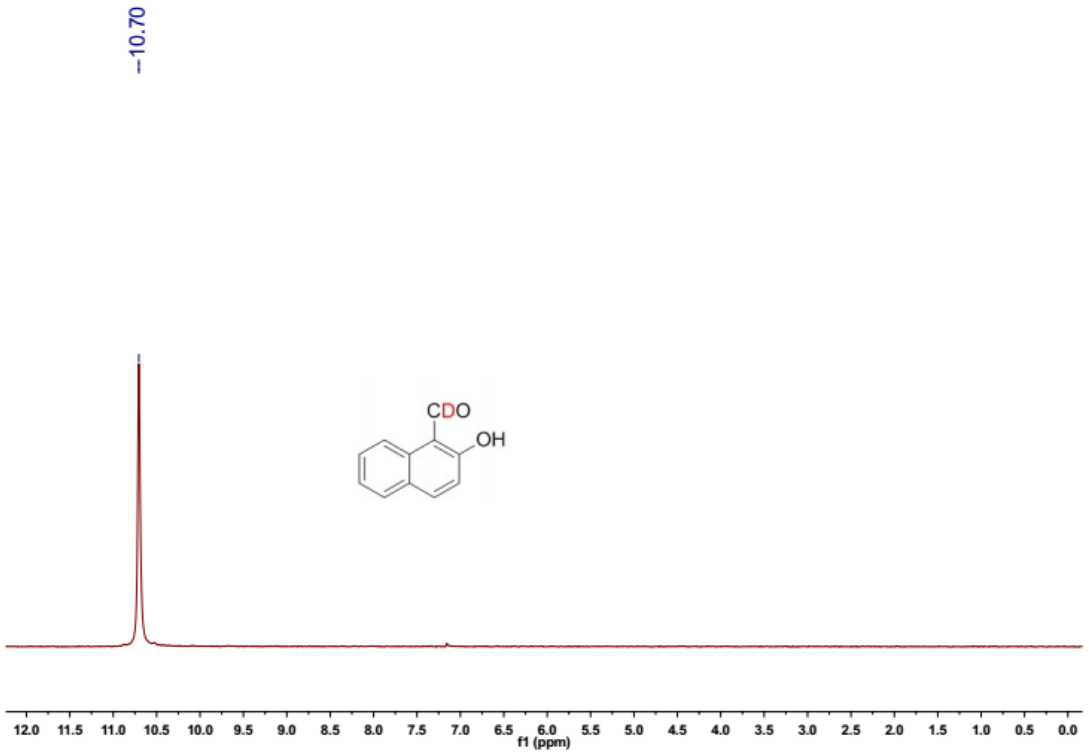
$^{13}$C NMR of deuterated aldehyde **7am**



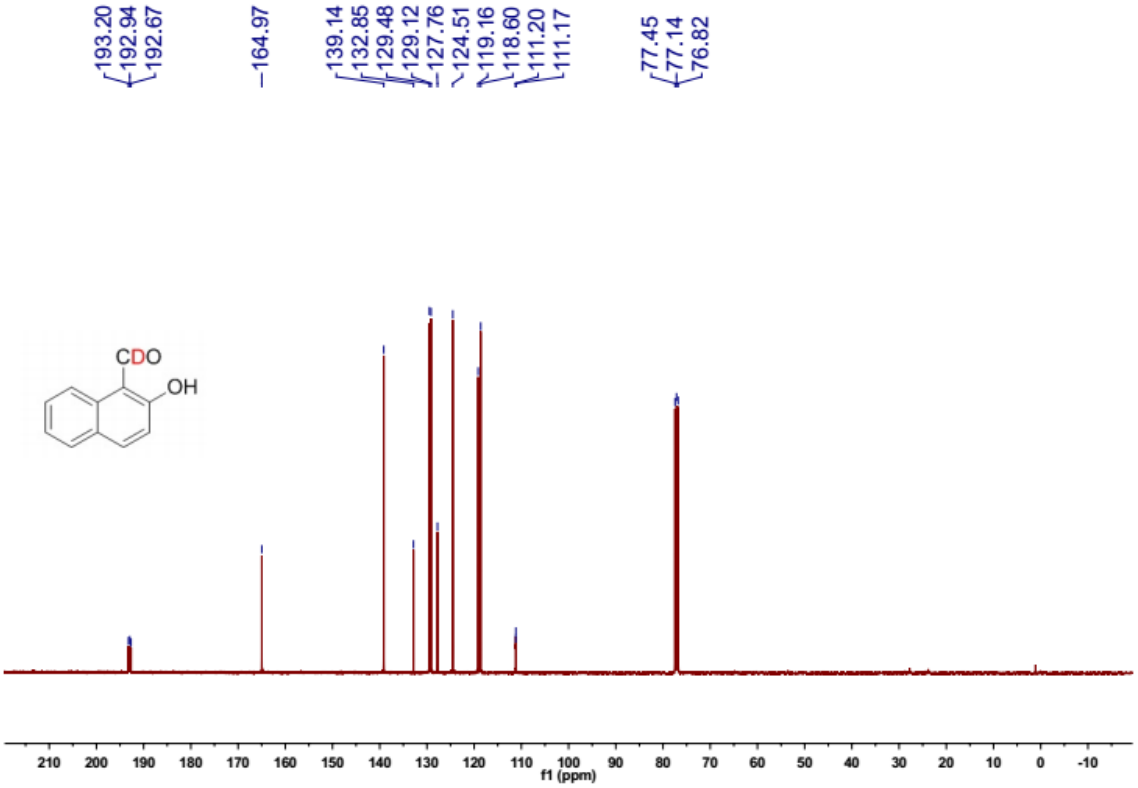
$^{1}$H NMR of deuterated aldehyde **7an**



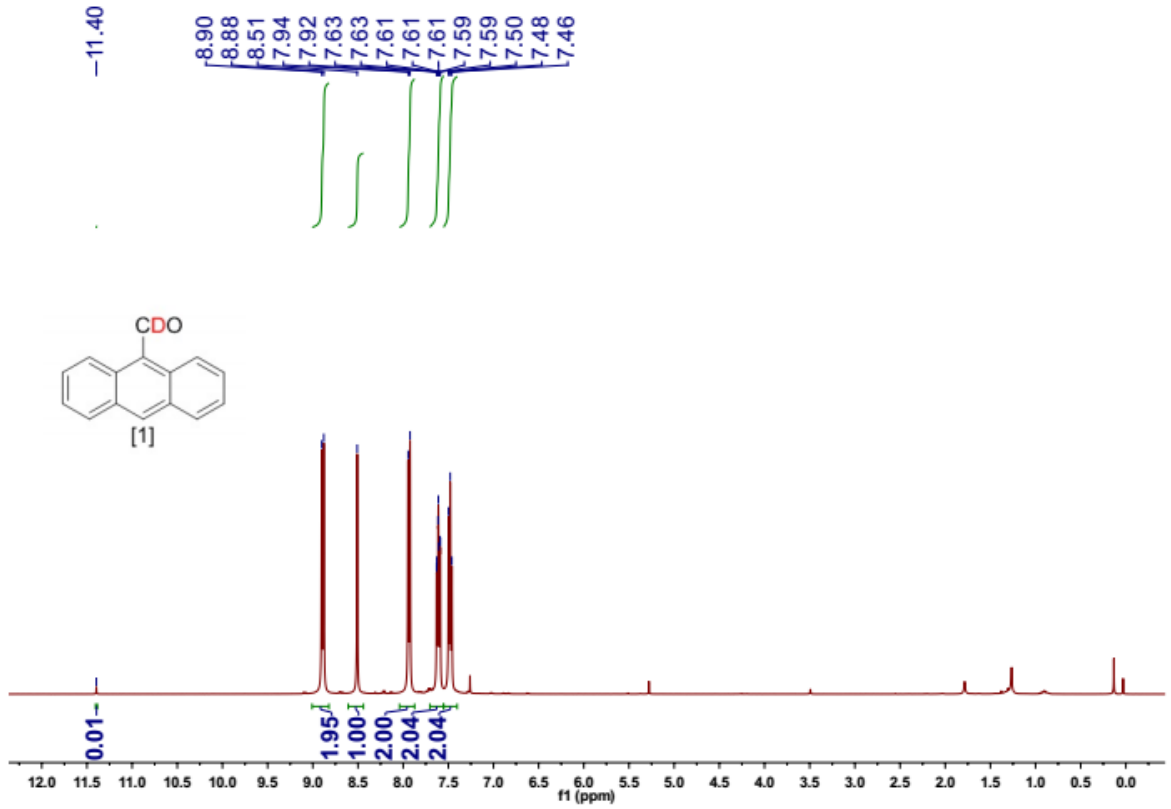

$^{2}$H NMR of deuterated aldehyde **7an**



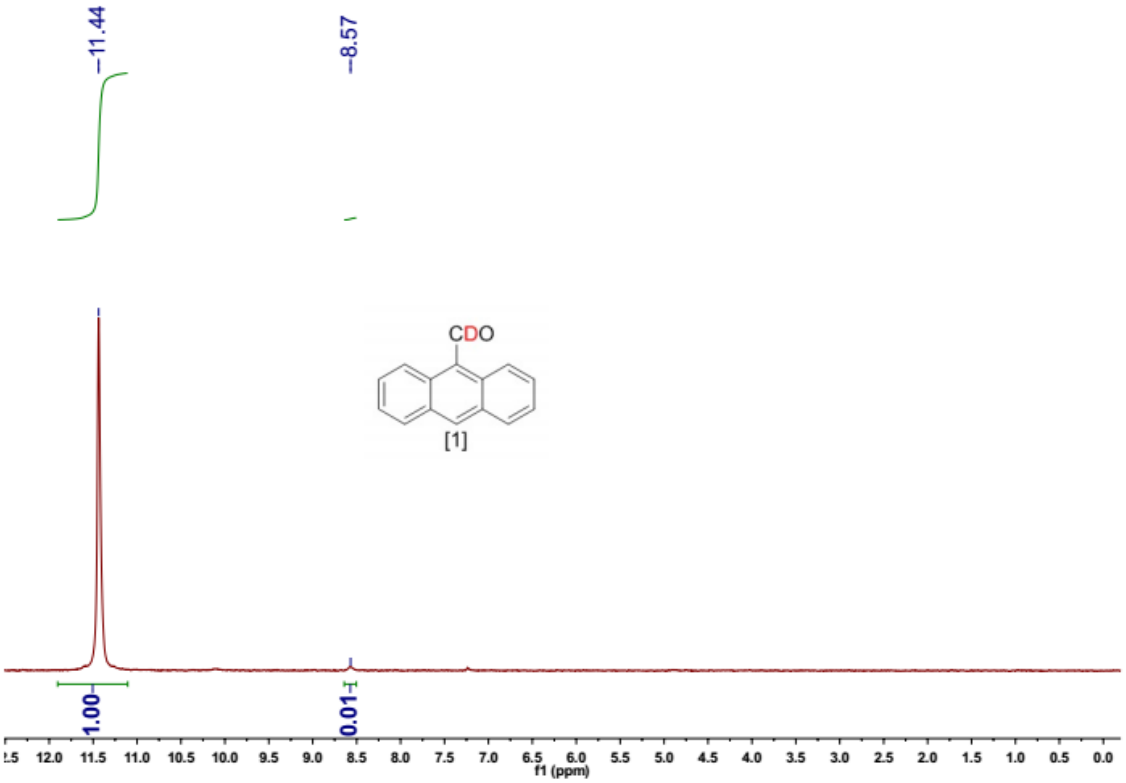
$^{13}$C NMR of deuterated aldehyde **7an**



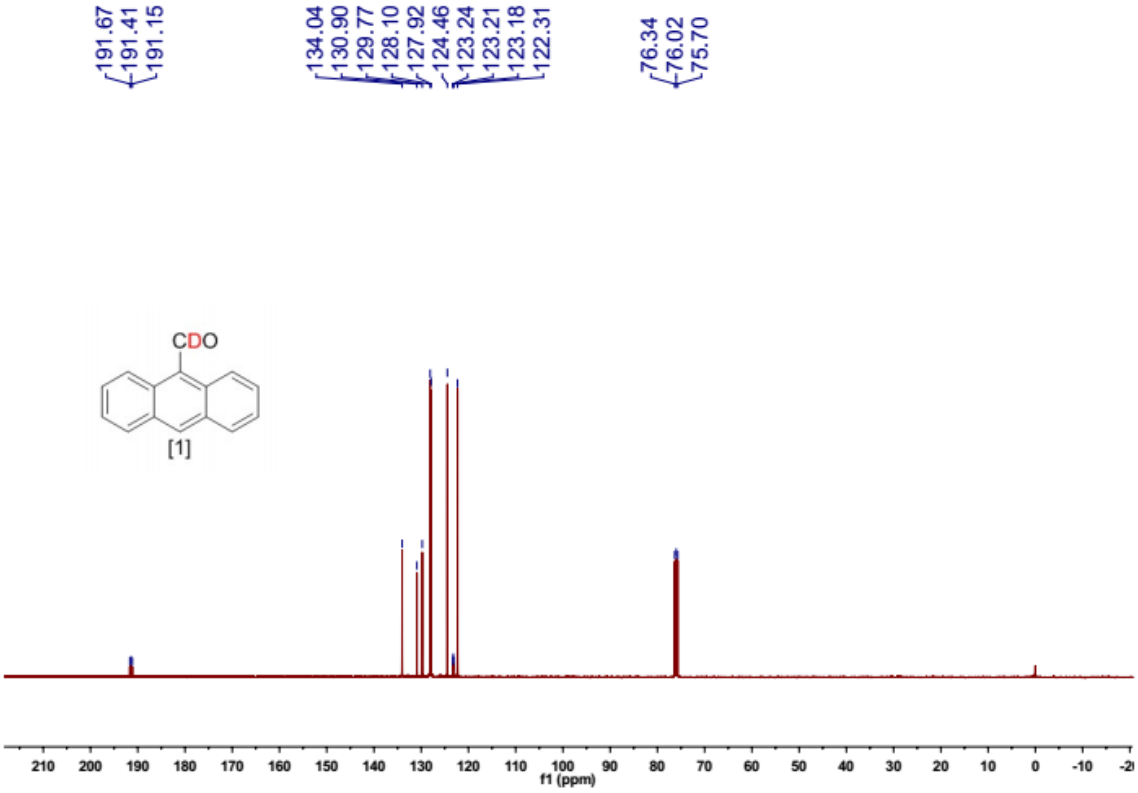
$^{1}$H NMR of deuterated aldehyde **7ao**



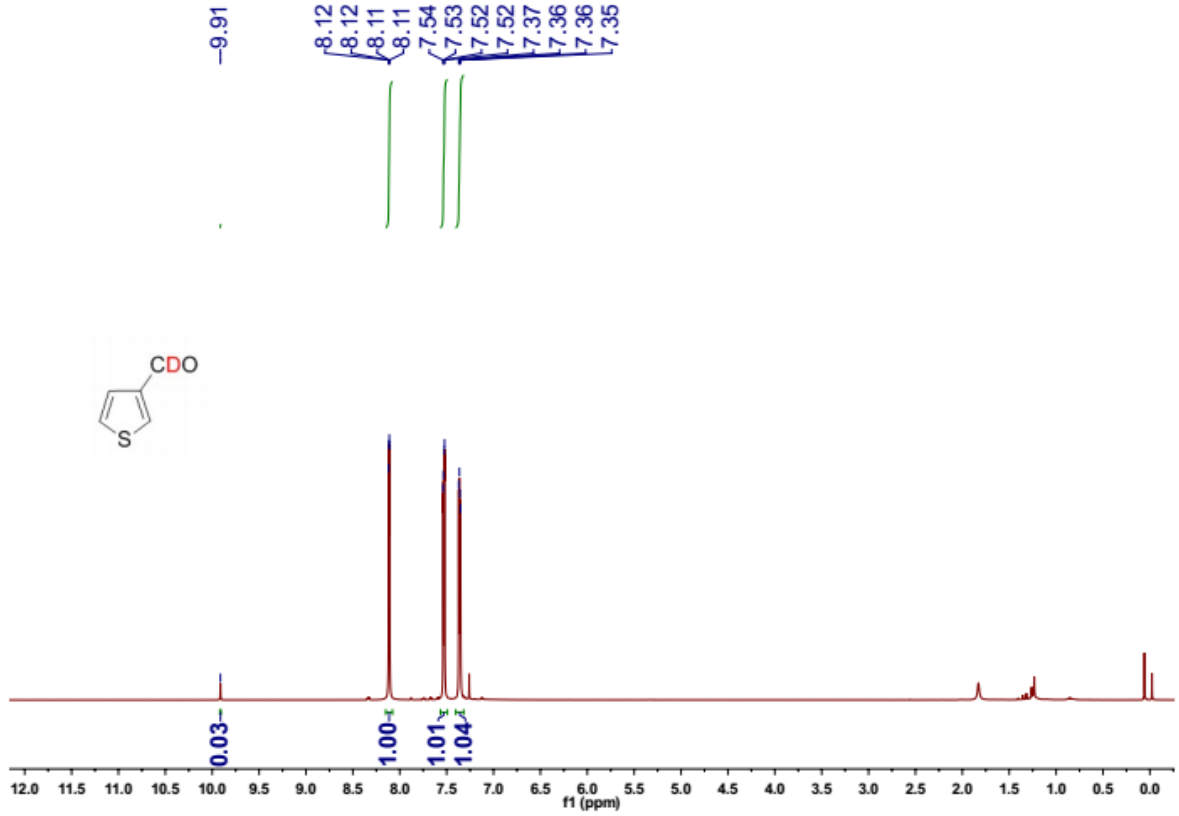

$^{2}$H NMR of deuterated aldehyde **7ao**



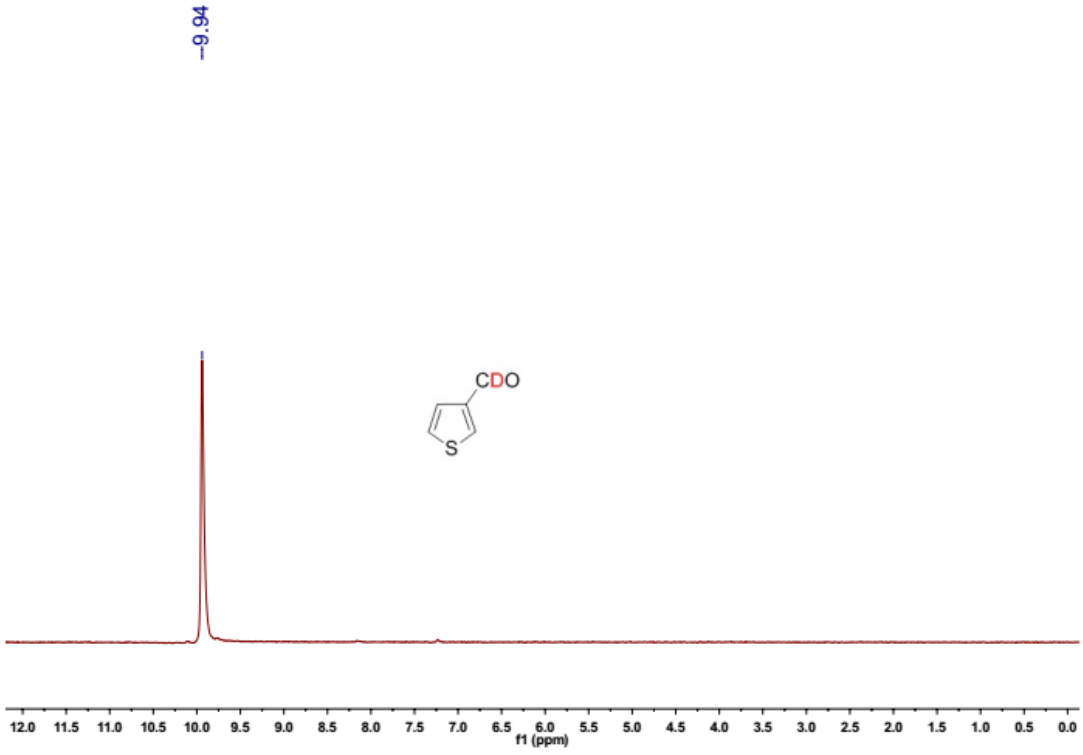
$^{13}$C NMR of deuterated aldehyde **7ao**



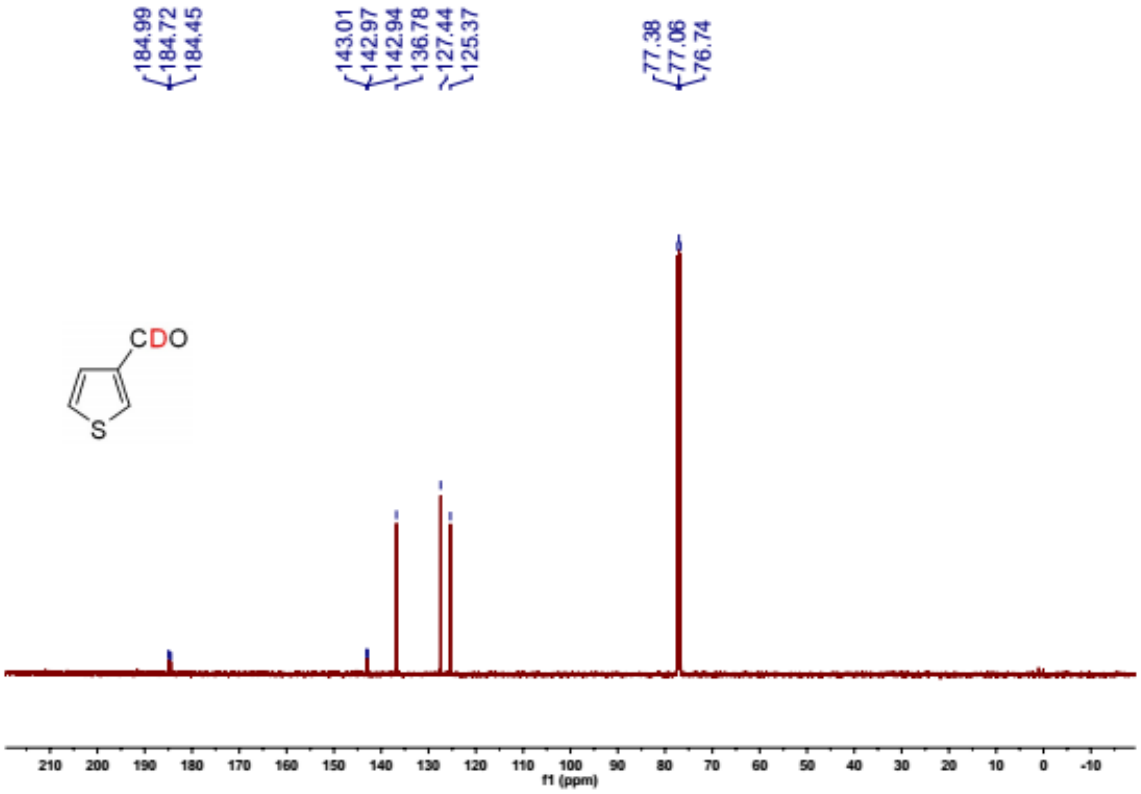
$^{1}$H NMR of deuterated aldehyde **7ap**



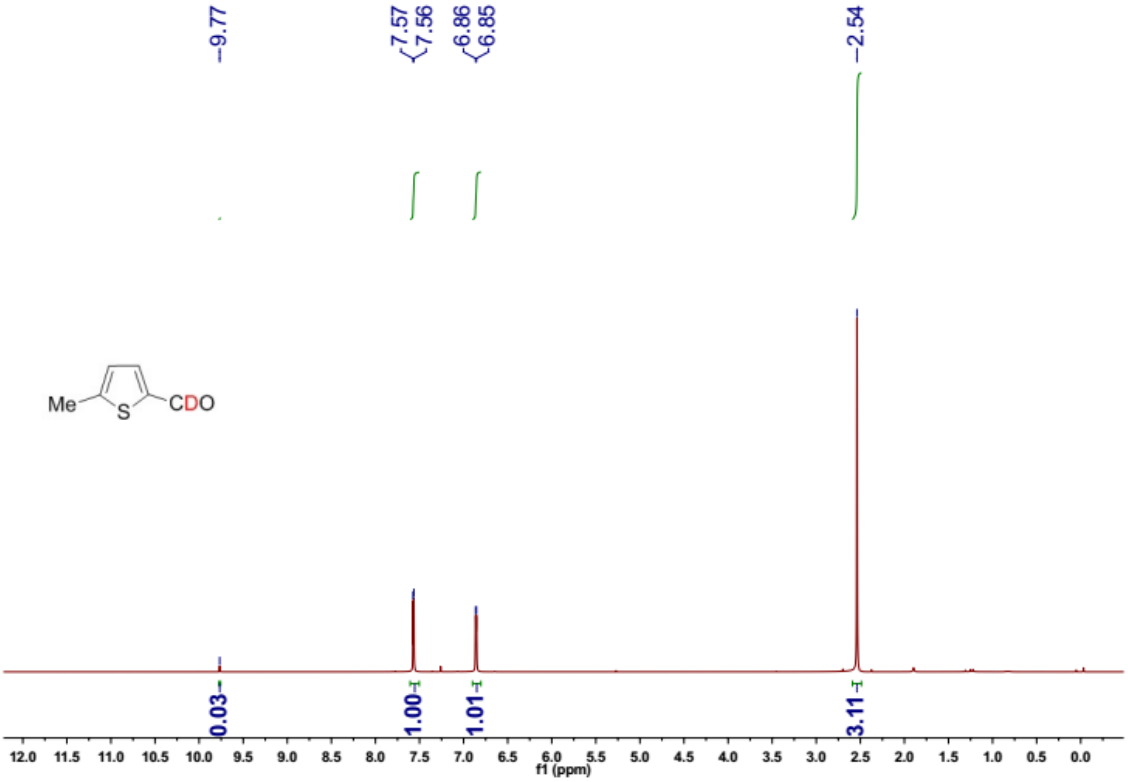

$^{2}$H NMR of deuterated aldehyde **7ap**



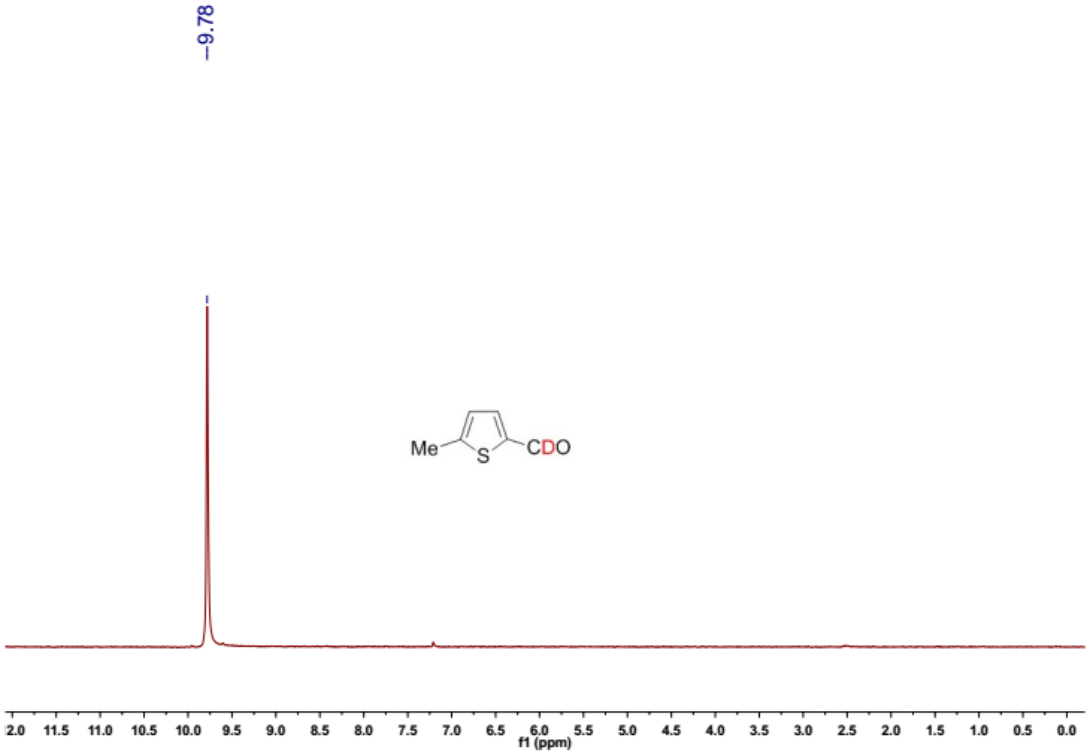
$^{13}$C NMR of deuterated aldehyde **7ap**



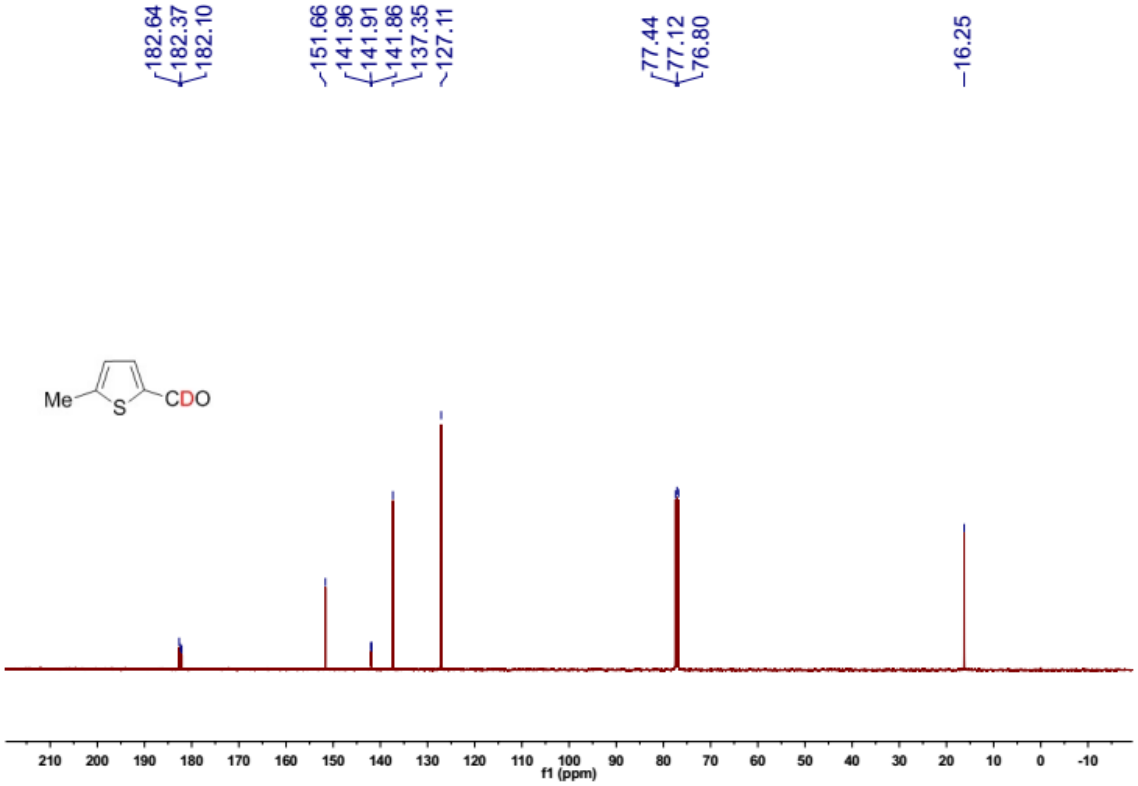
$^{1}$H NMR of deuterated aldehyde **7aq**



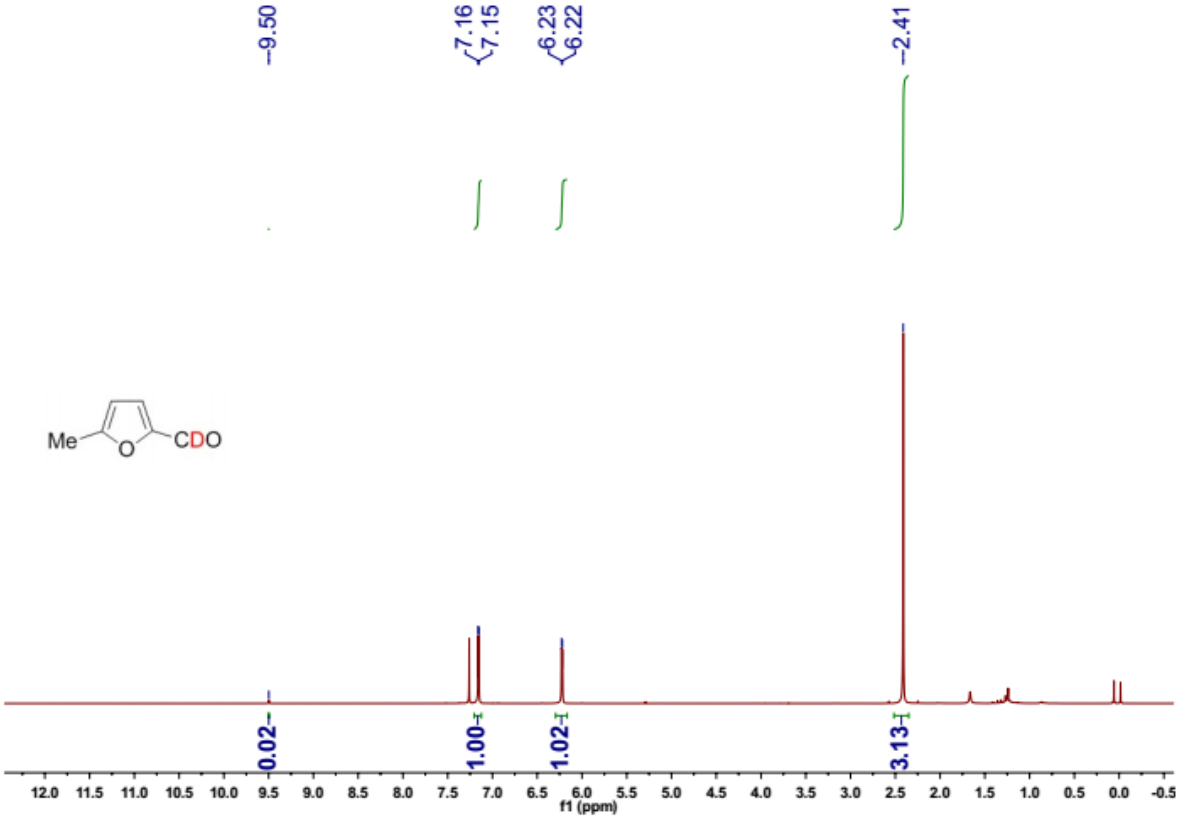

$^{2}$H NMR of deuterated aldehyde **7aq**



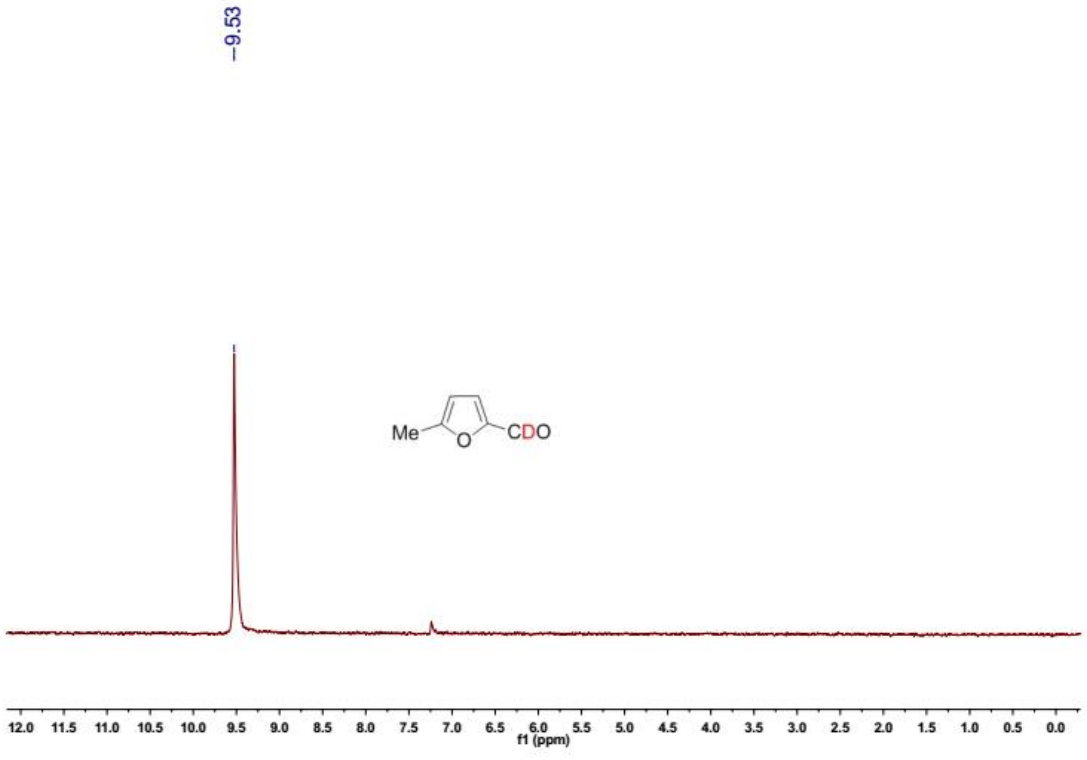
$^{13}$C NMR of deuterated aldehyde **7aq**



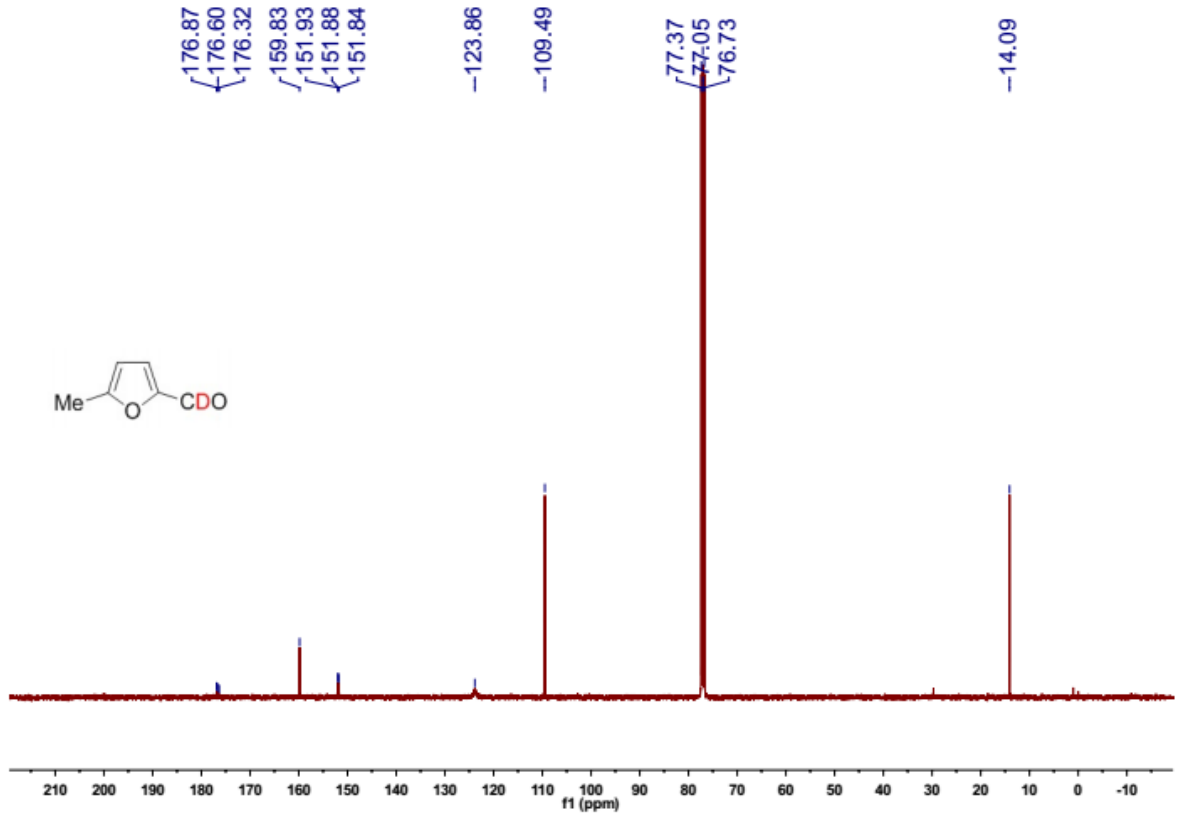
$^{1}$H NMR of deuterated aldehyde **7ar**



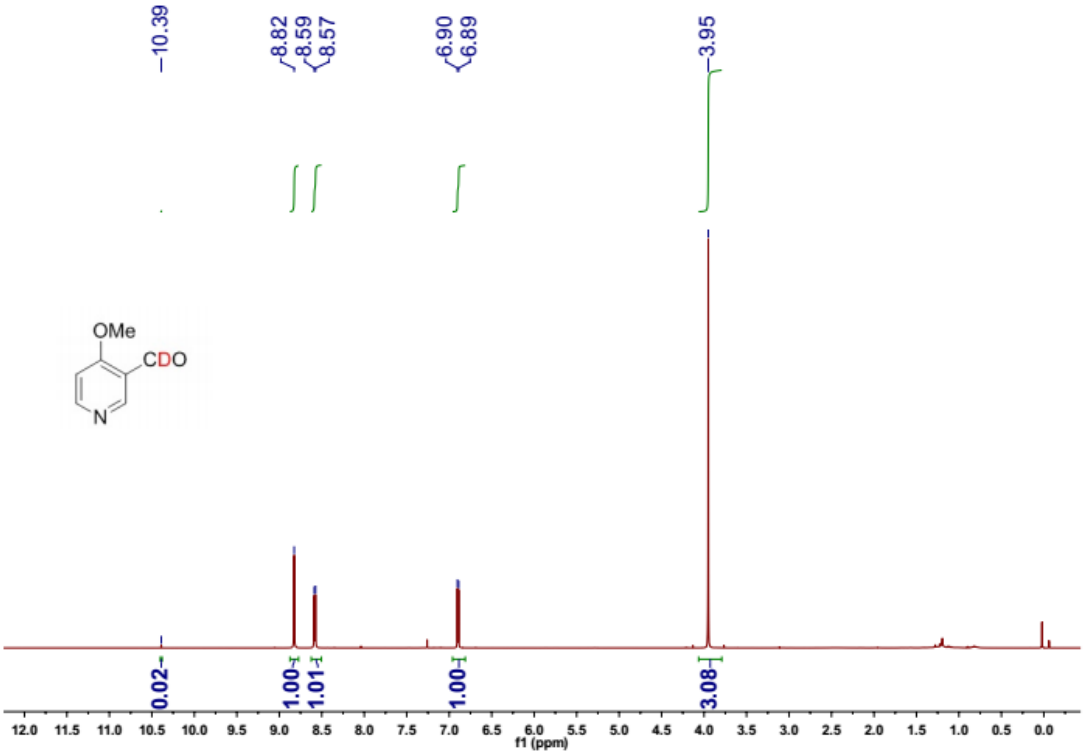

$^{2}$H NMR of deuterated aldehyde **7ar**



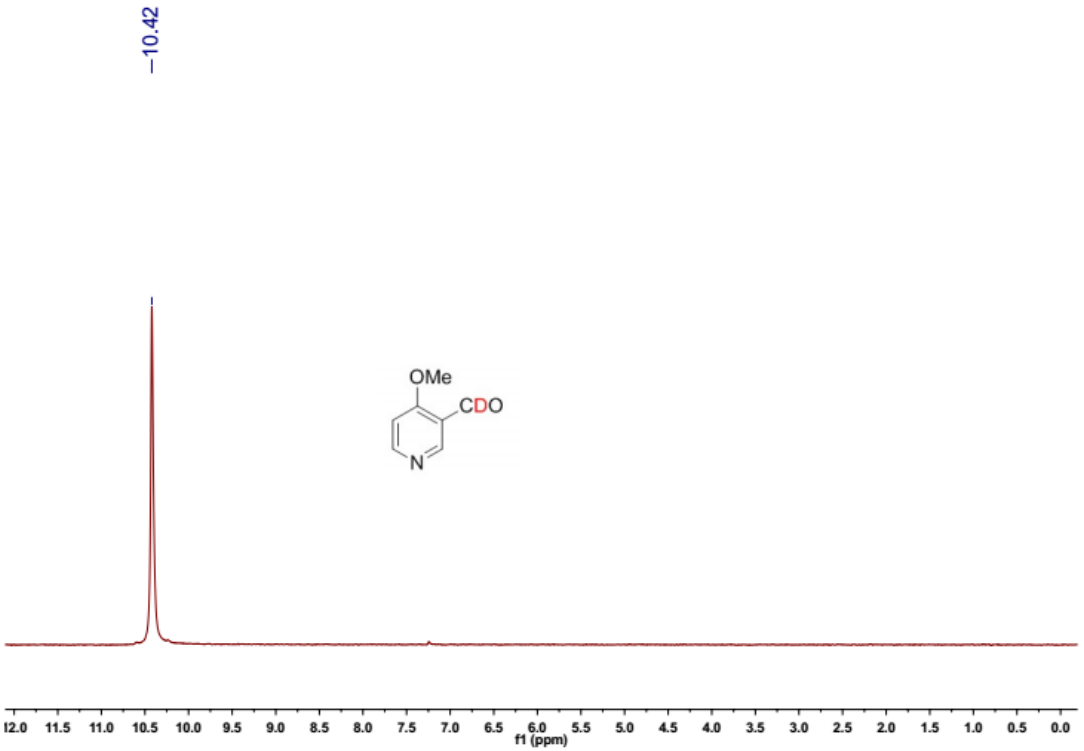
$^{13}$C NMR of deuterated aldehyde **7ar**



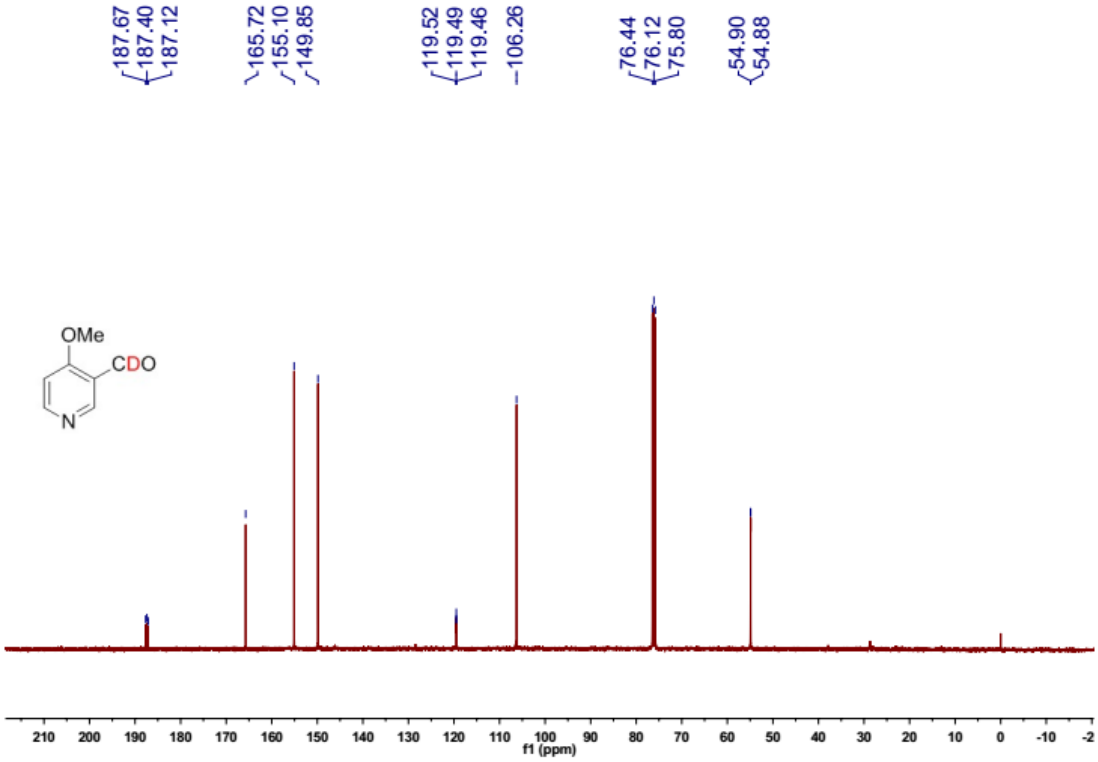
$^{1}$H NMR of deuterated aldehyde **7as**



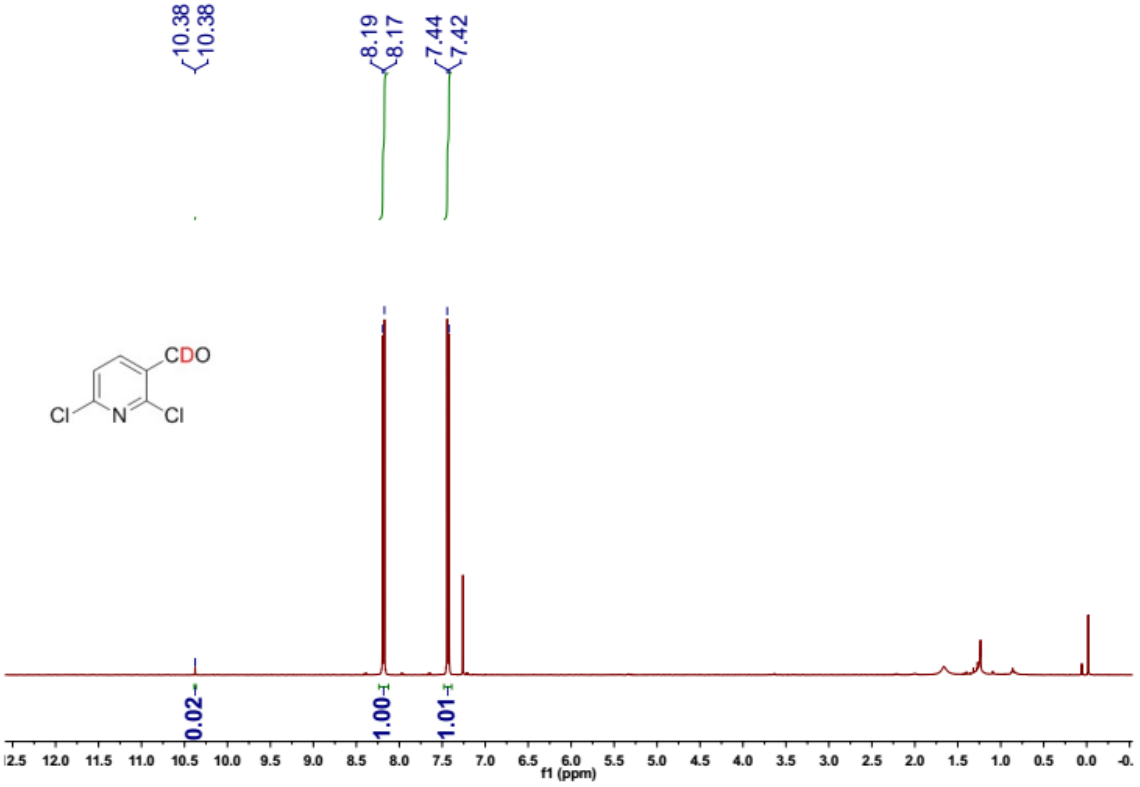

$^{2}$H NMR of deuterated aldehyde **7as**



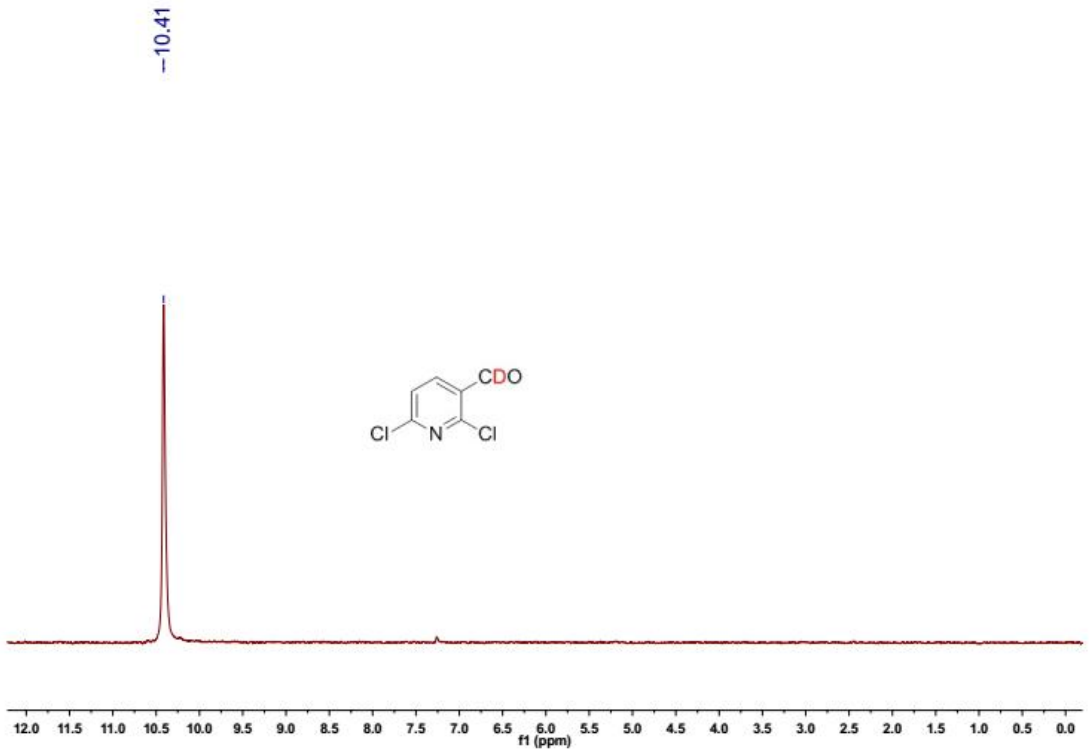
$^{13}$C NMR of deuterated aldehyde **7as**



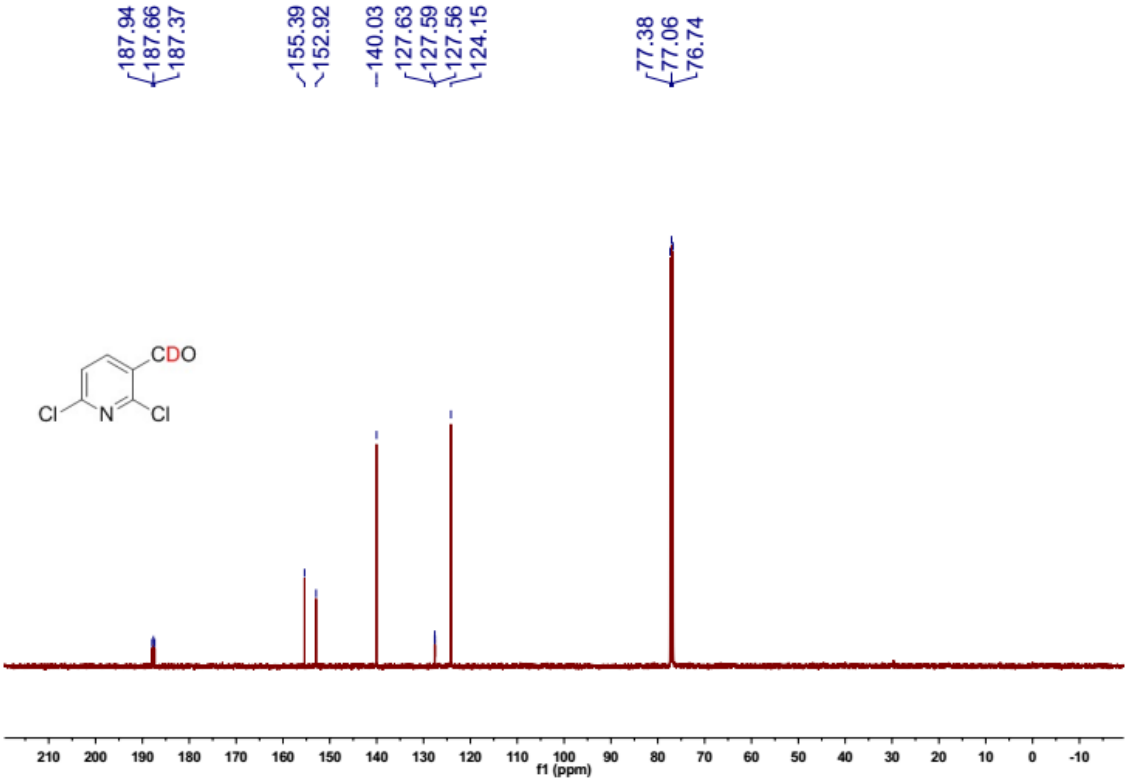
$^{1}$H NMR of deuterated aldehyde **7at**



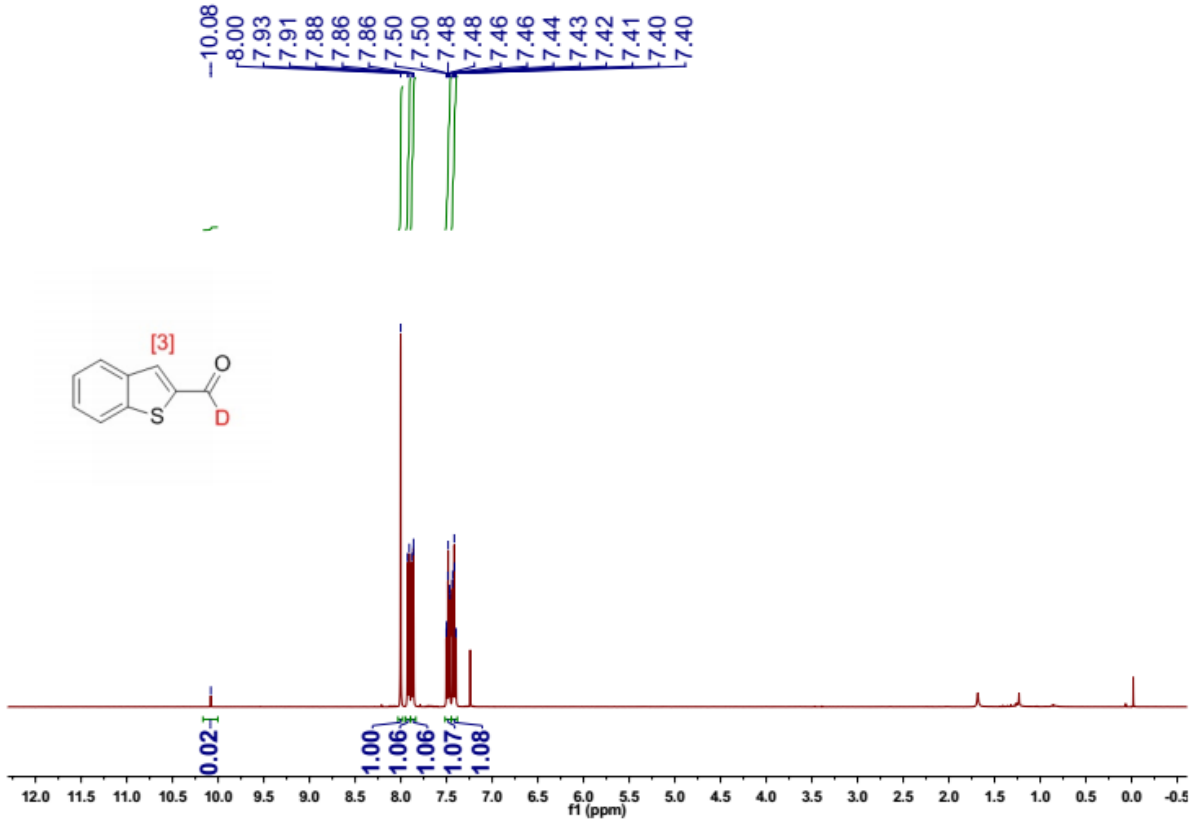

$^{2}$H NMR of deuterated aldehyde **7at**



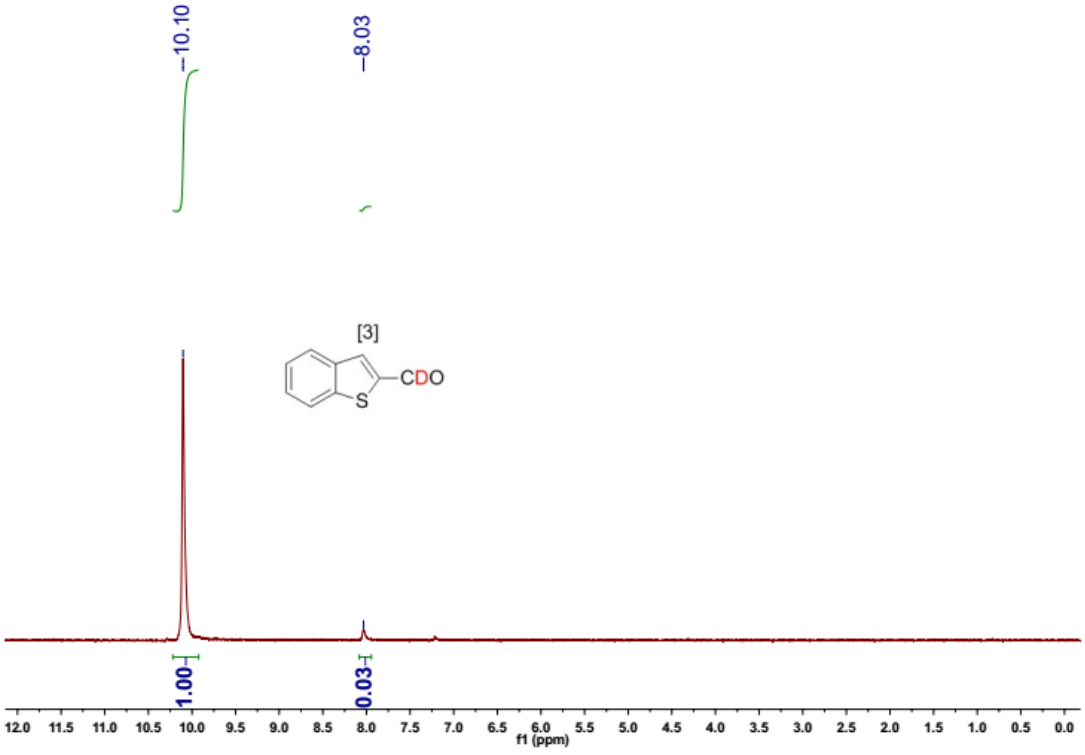
$^{13}$C NMR of deuterated aldehyde **7at**



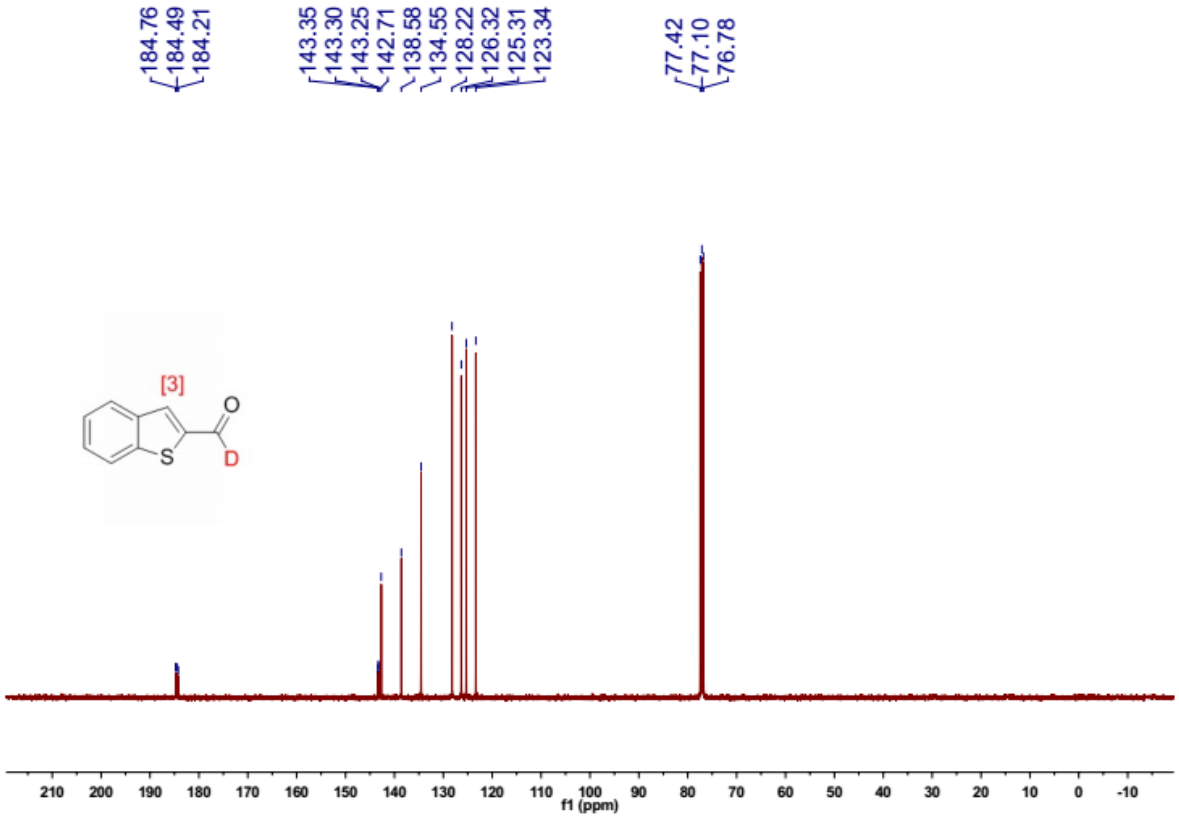
$^{1}$H NMR of deuterated aldehyde **7au**



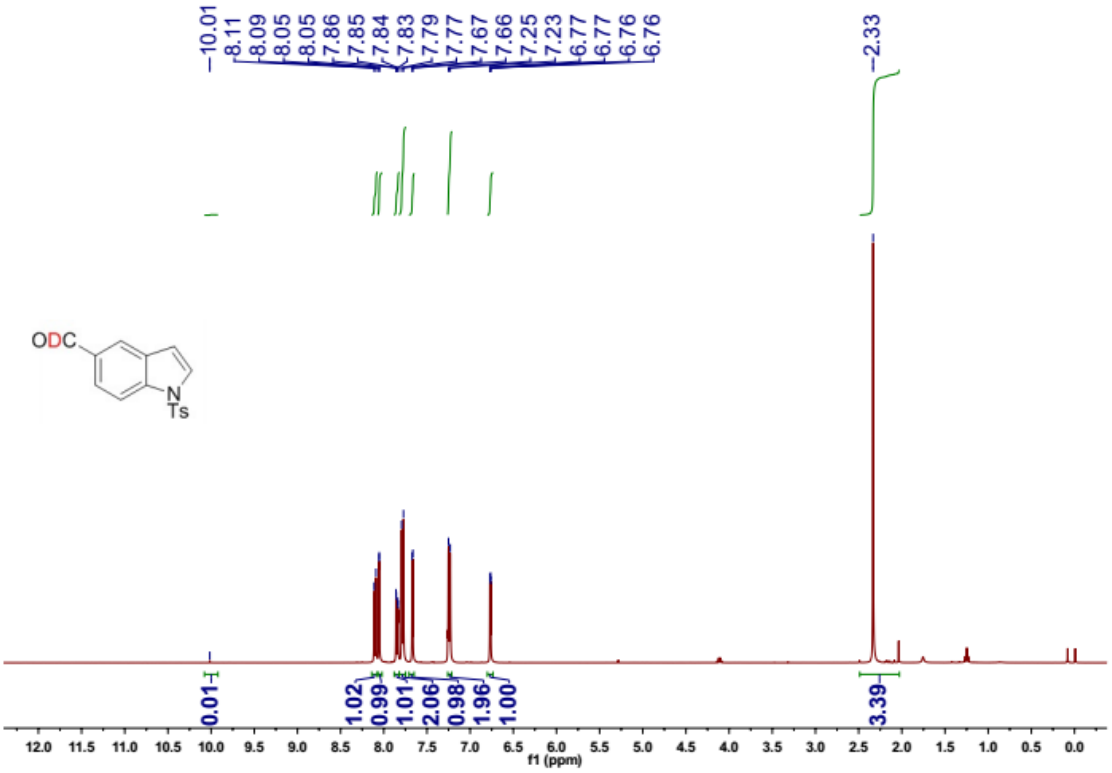

$^{2}$H NMR of deuterated aldehyde **7au**



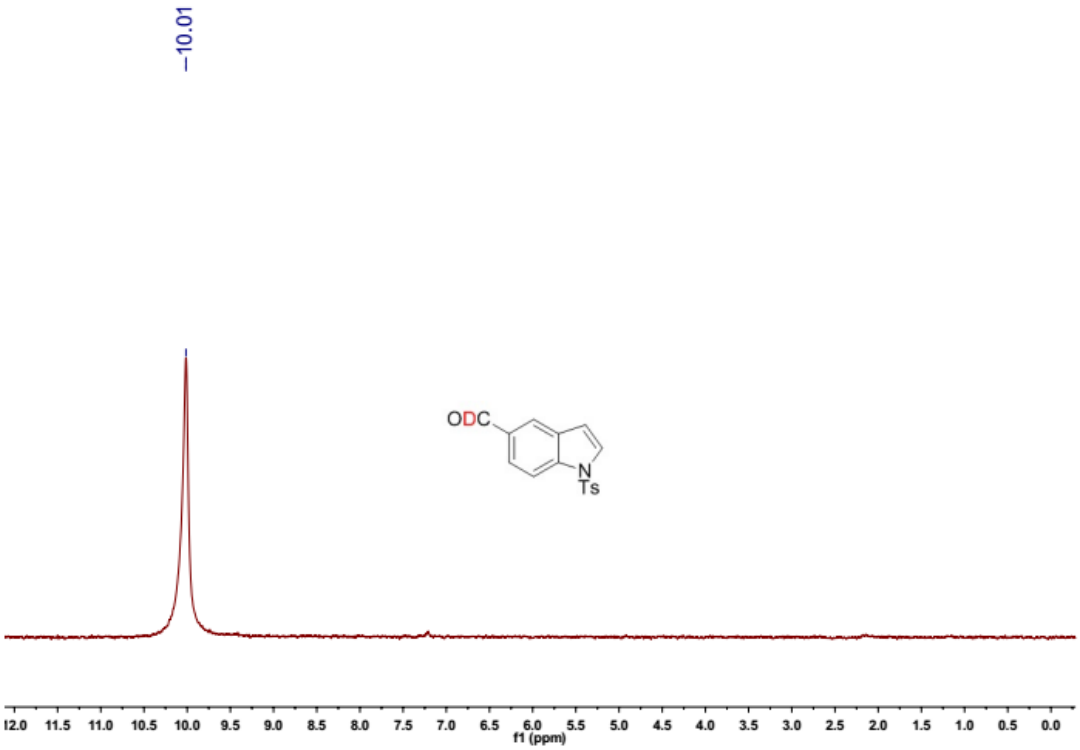
$^{13}$C NMR of deuterated aldehyde **7au**



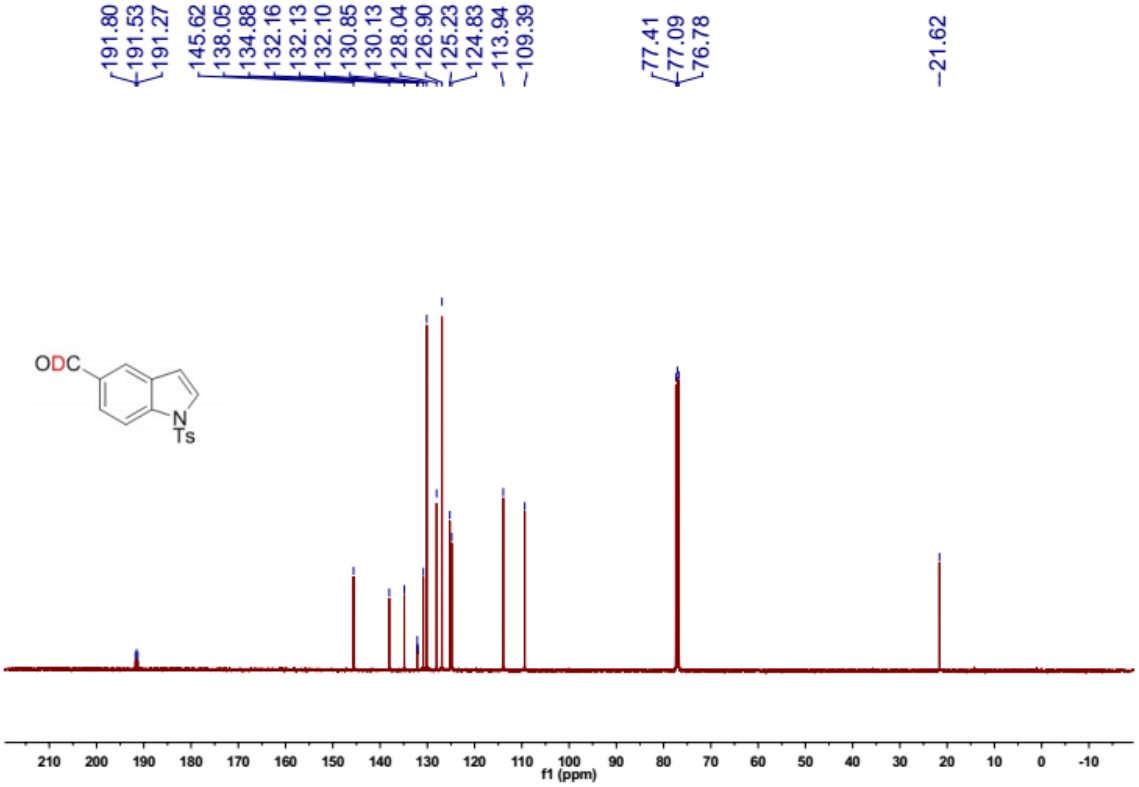
$^{1}$H NMR of deuterated aldehyde **7av**



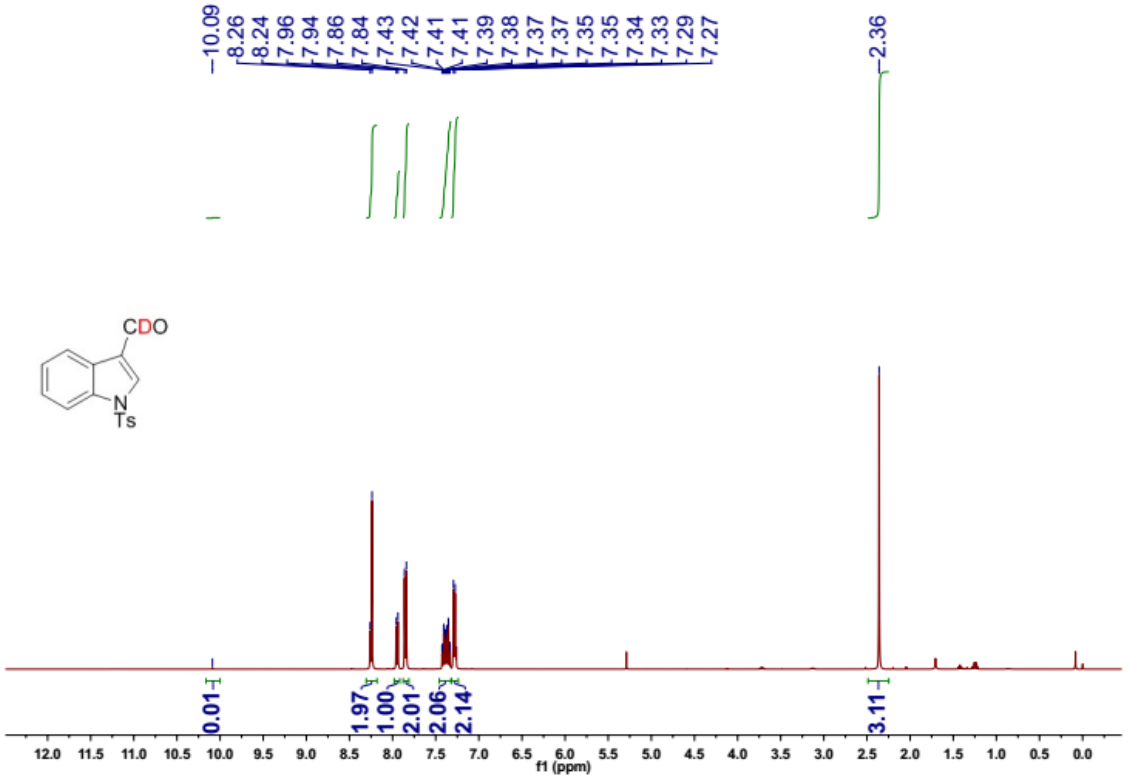

$^{2}$H NMR of deuterated aldehyde **7av**



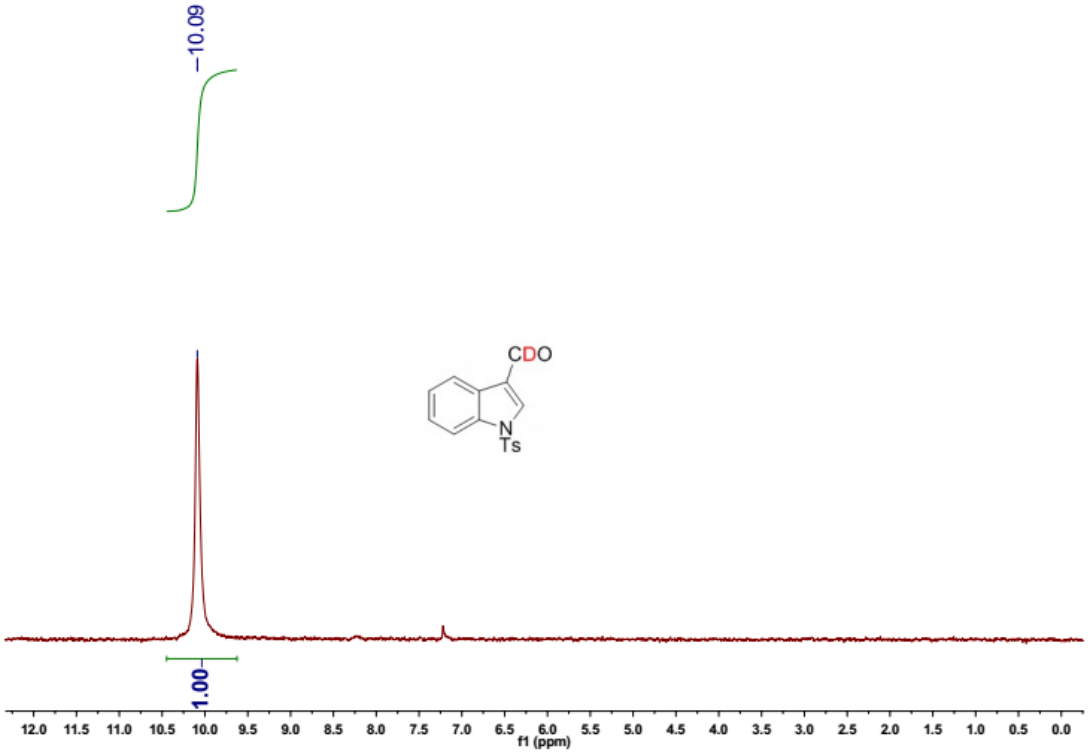
$^{13}$C NMR of deuterated aldehyde **7av**



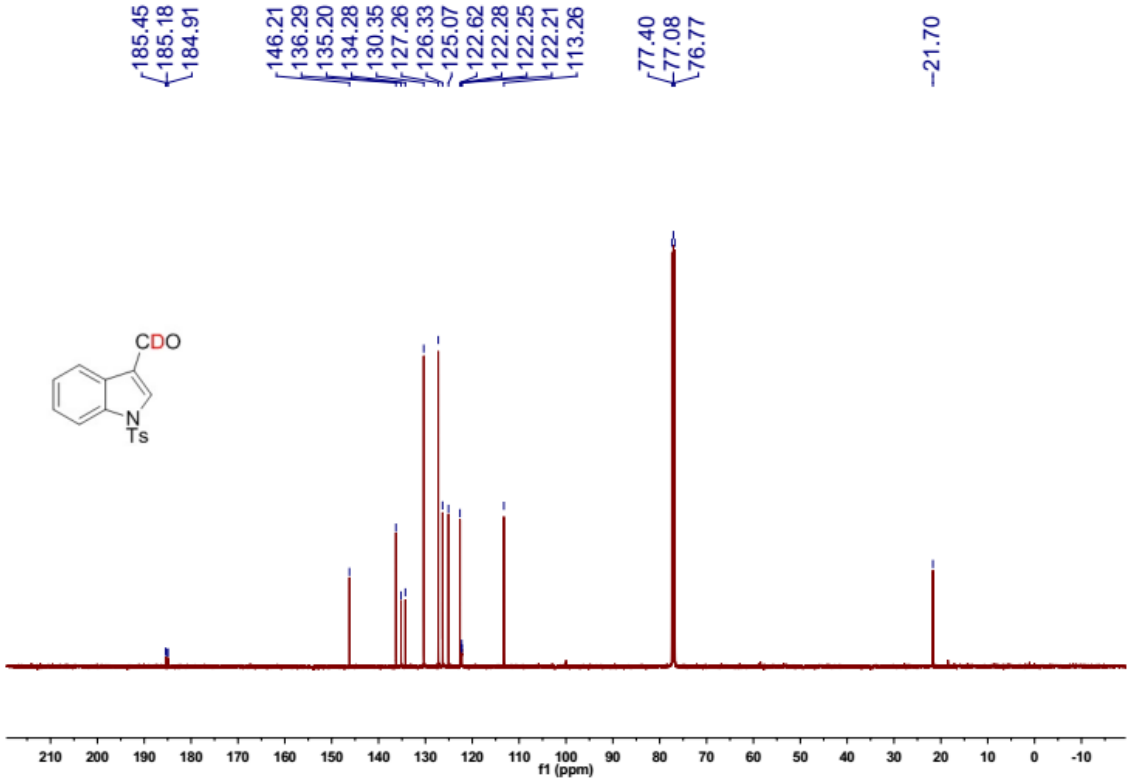
$^{1}$H NMR of deuterated aldehyde **7aw**



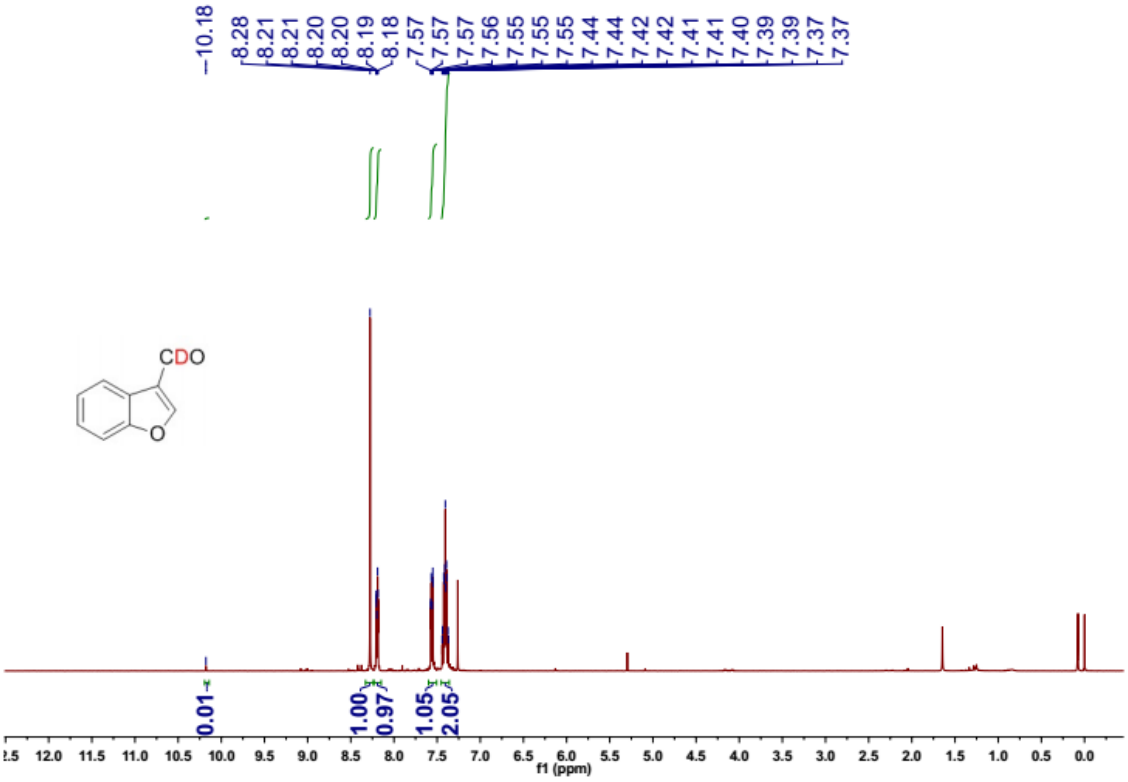

$^{2}$H NMR of deuterated aldehyde **7aw**



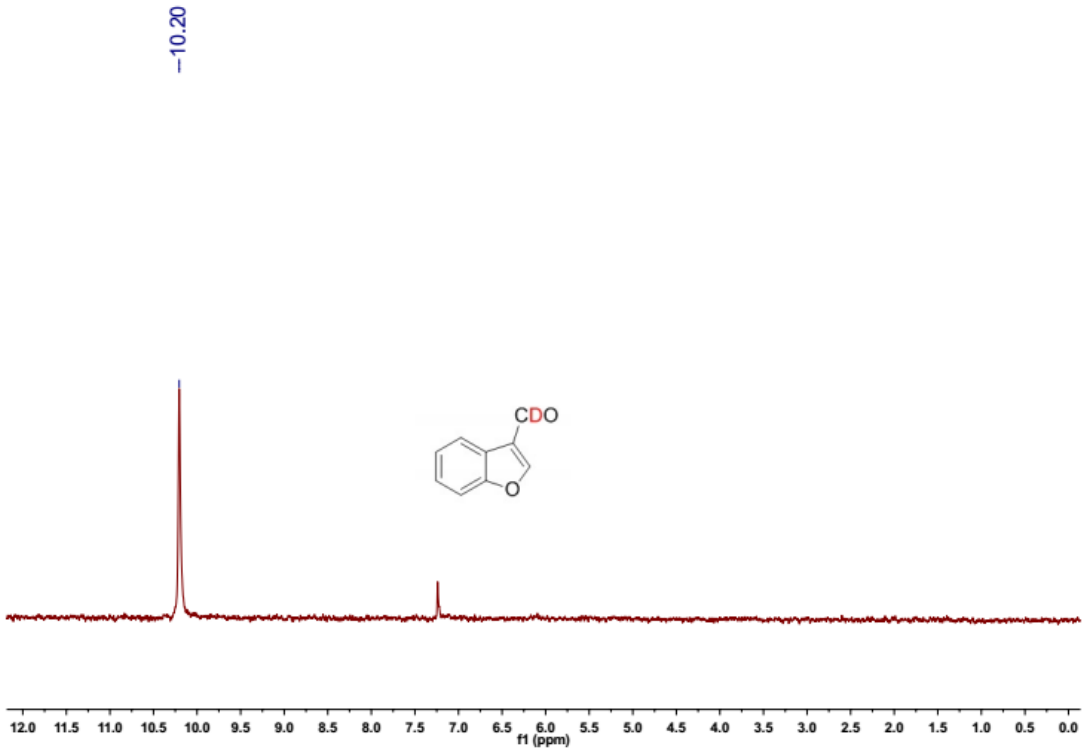
$^{13}$C NMR of deuterated aldehyde **7aw**



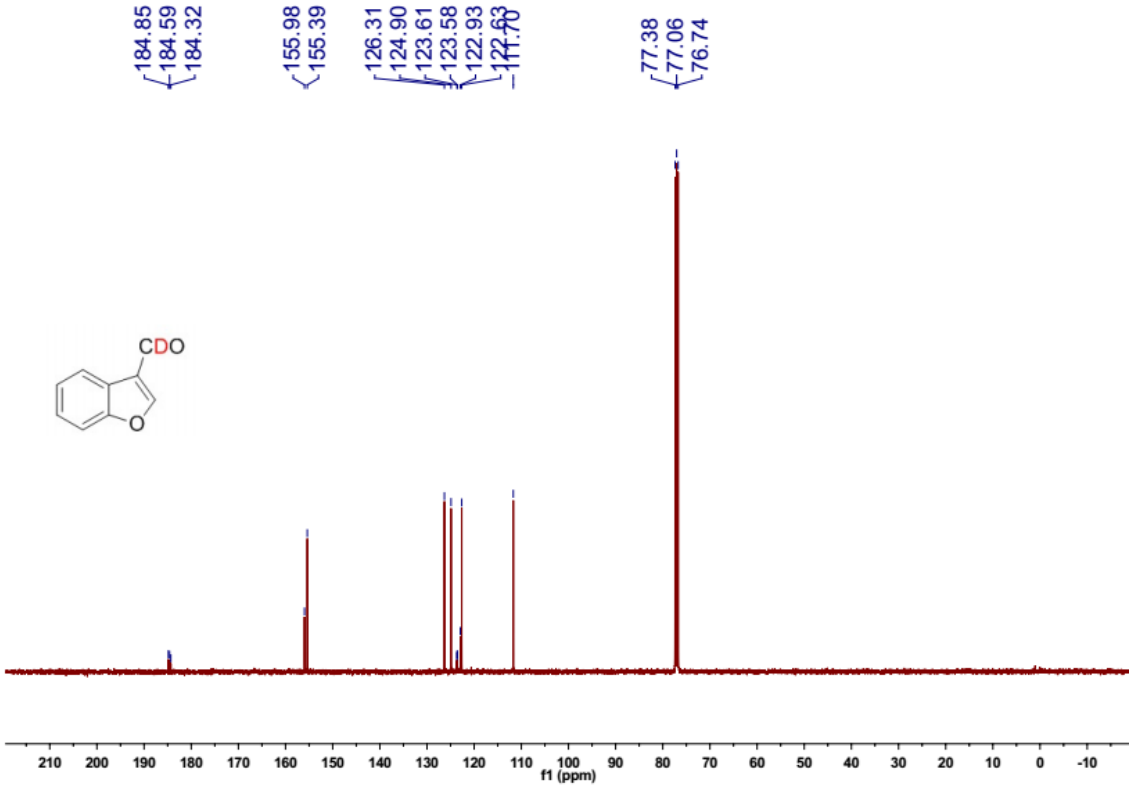
$^{1}$H NMR of deuterated aldehyde **7ax**



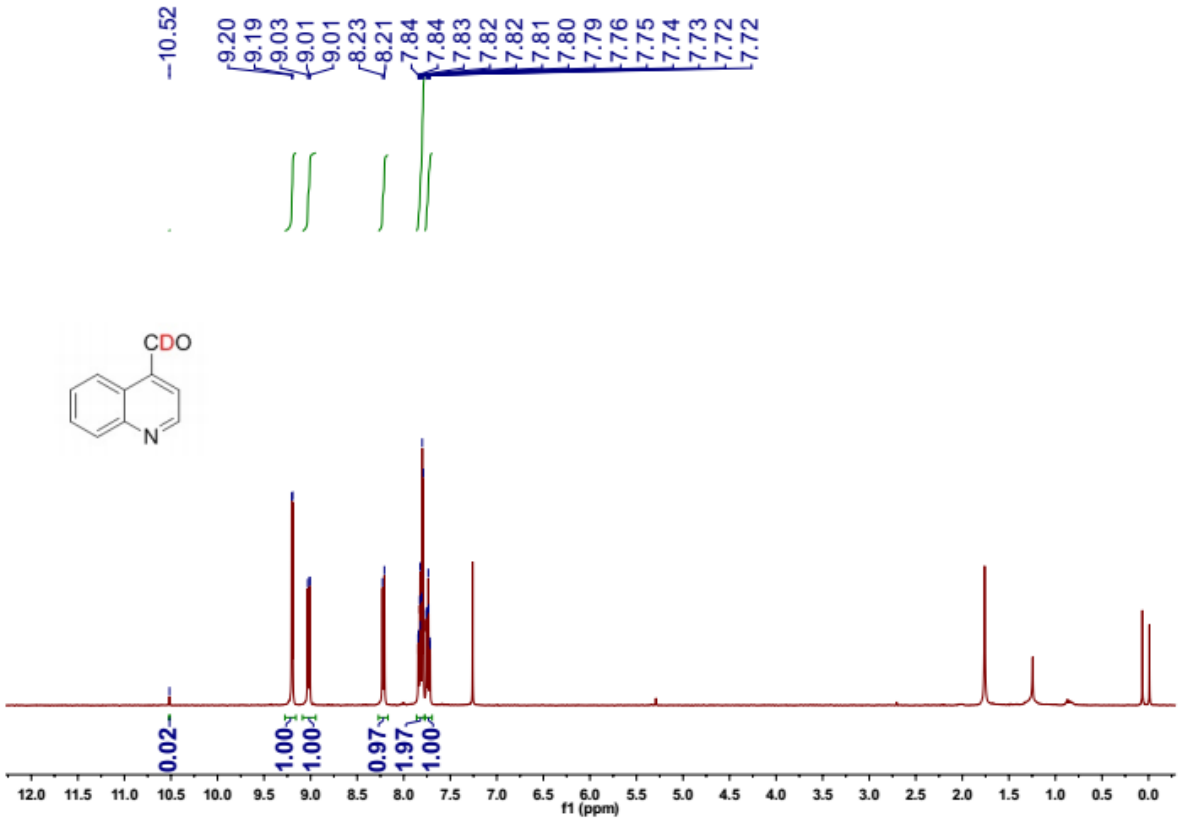

$^{2}$H NMR of deuterated aldehyde **7ax**



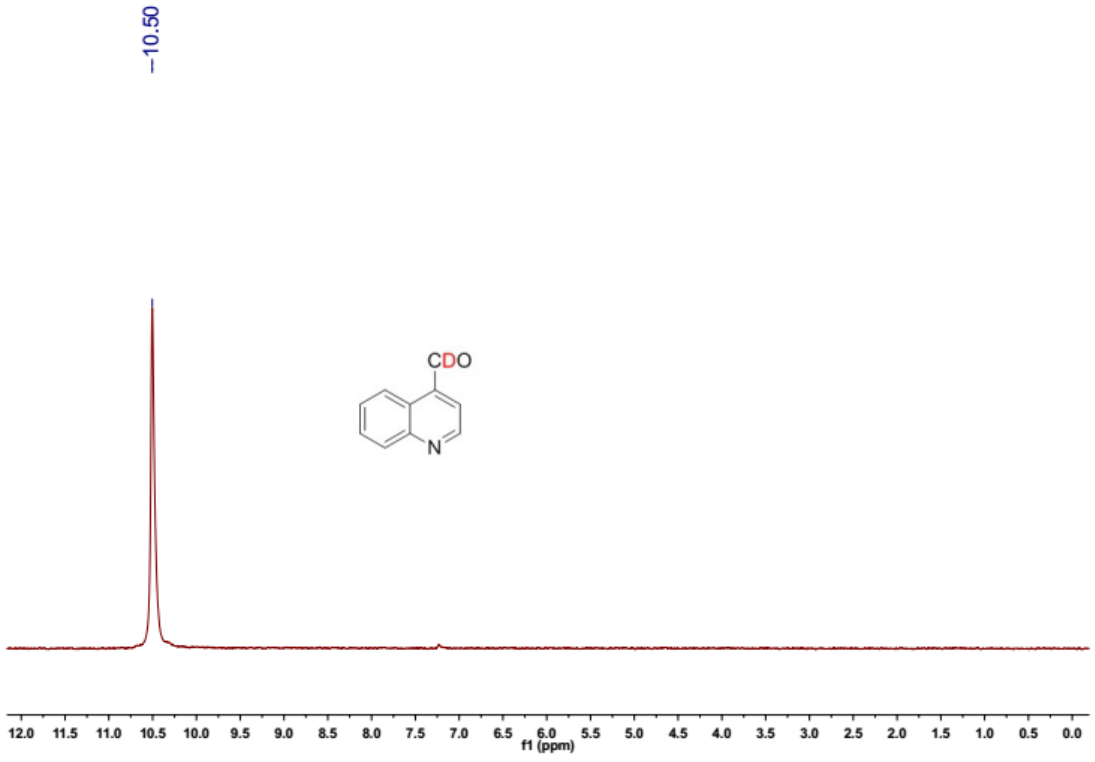
$^{13}$C NMR of deuterated aldehyde **7ax**



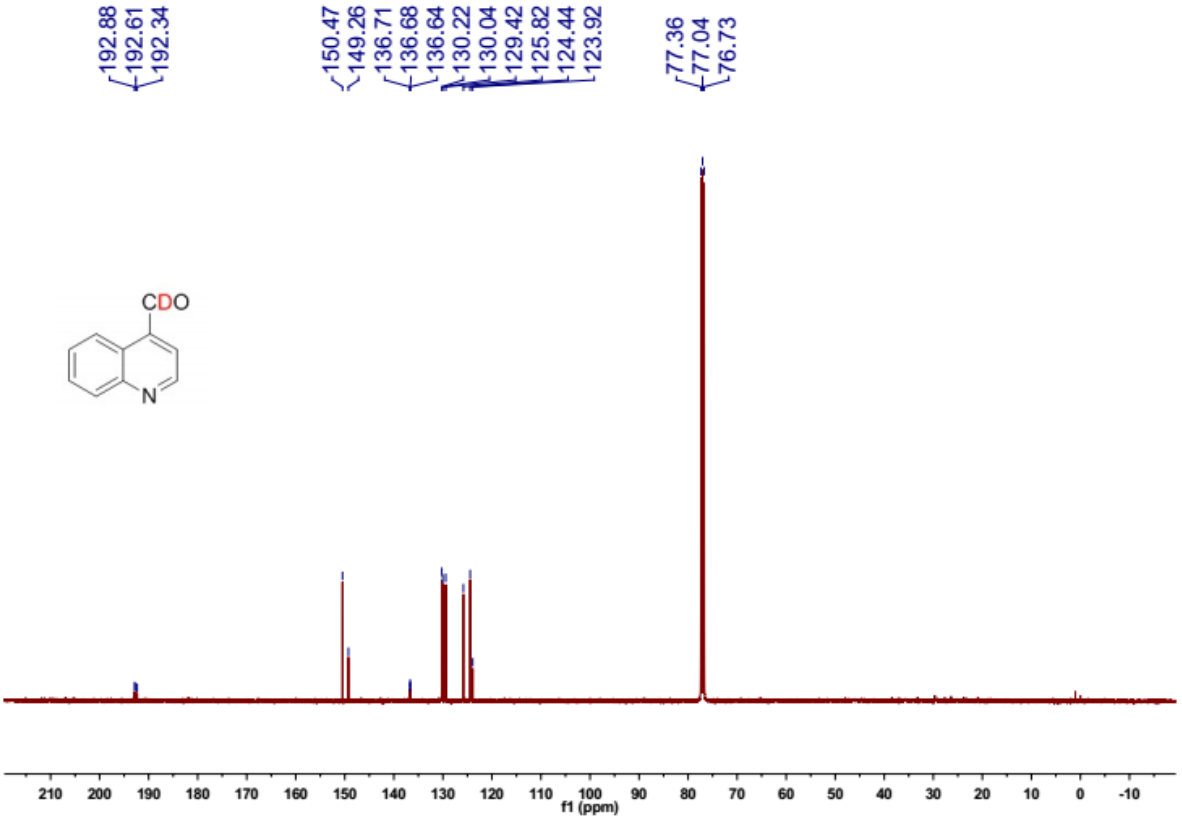
$^{1}$H NMR of deuterated aldehyde **7ay**



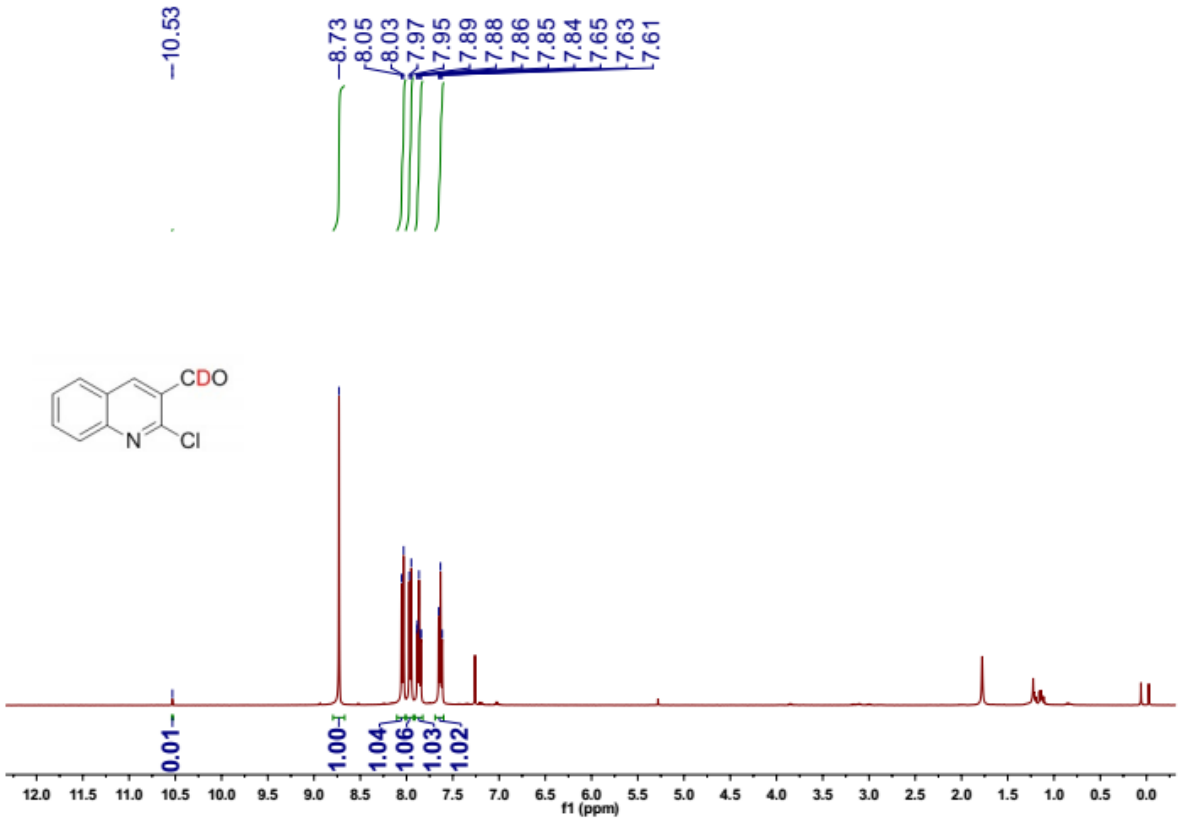

$^{2}$H NMR of deuterated aldehyde **7ay**



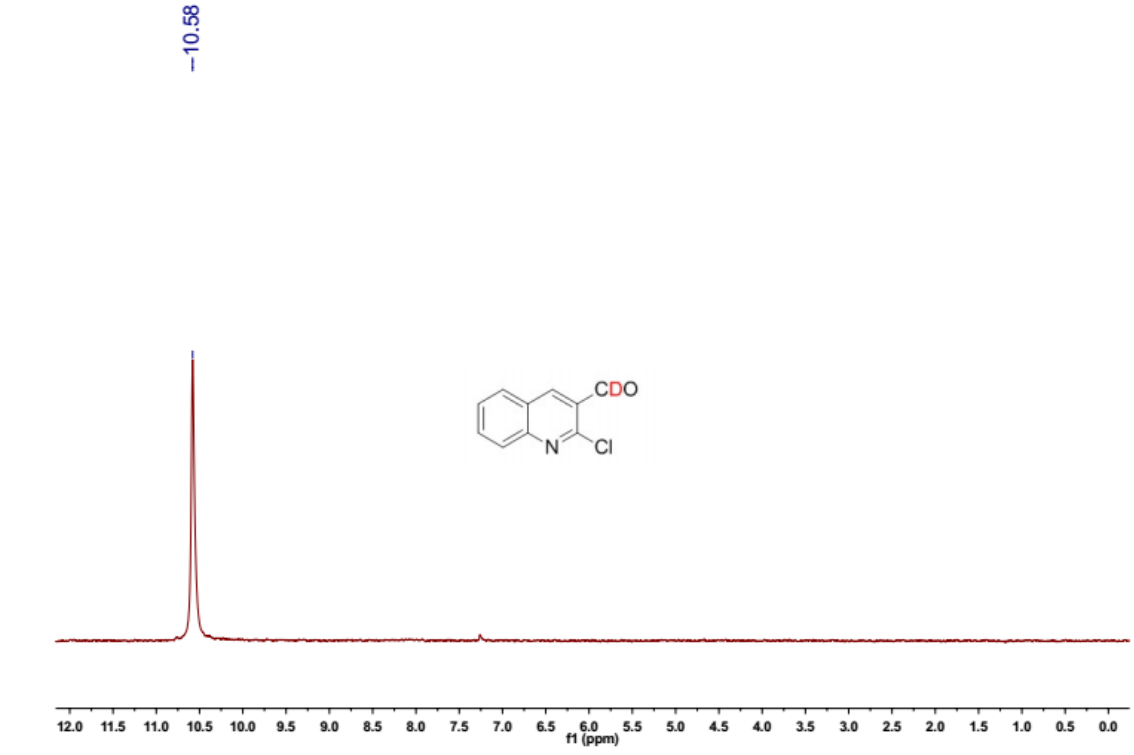
$^{13}$C NMR of deuterated aldehyde **7ay**



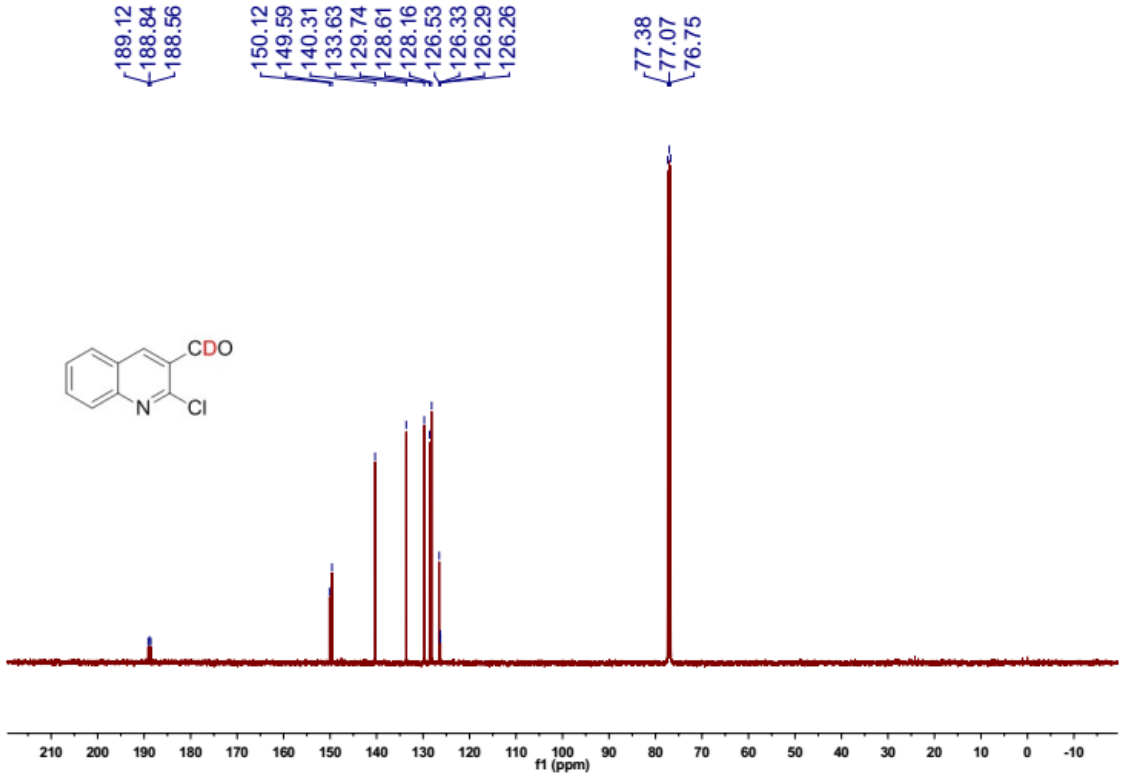
$^{1}$H NMR of deuterated aldehyde **7az**



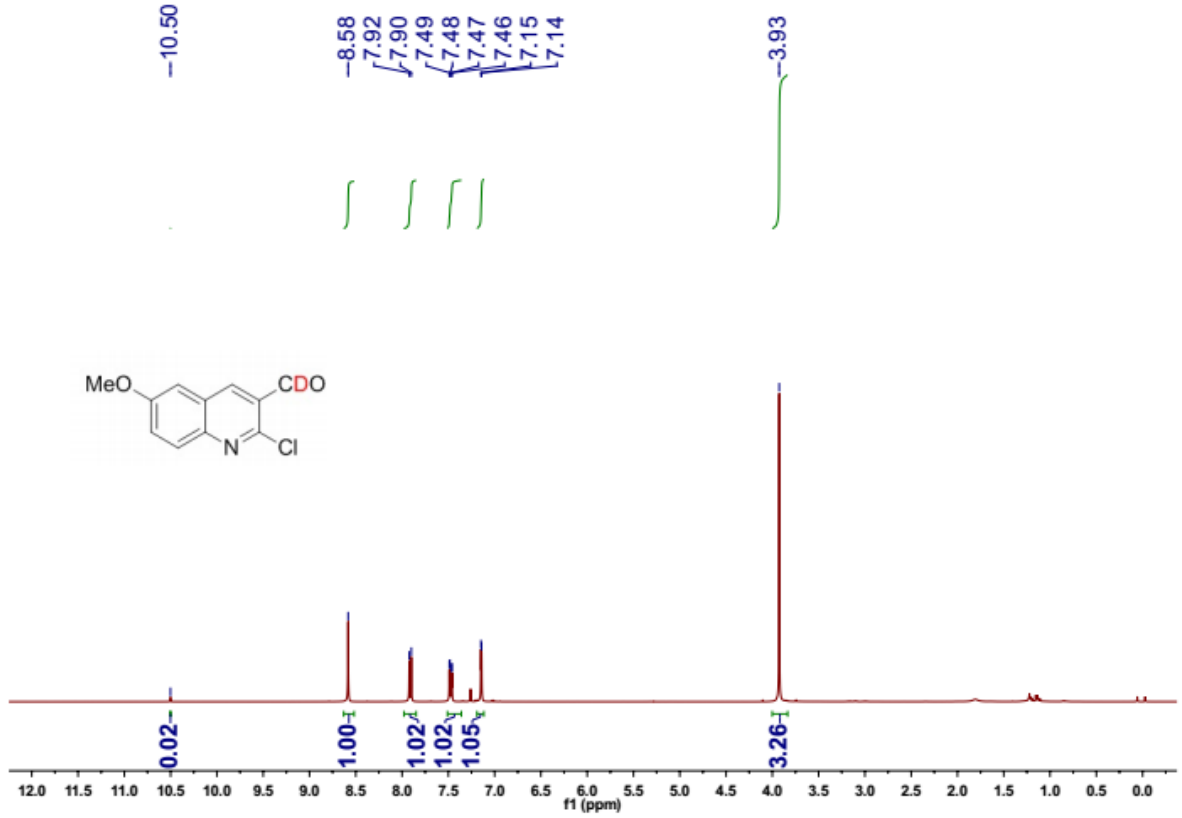

$^{2}$H NMR of deuterated aldehyde **7az**



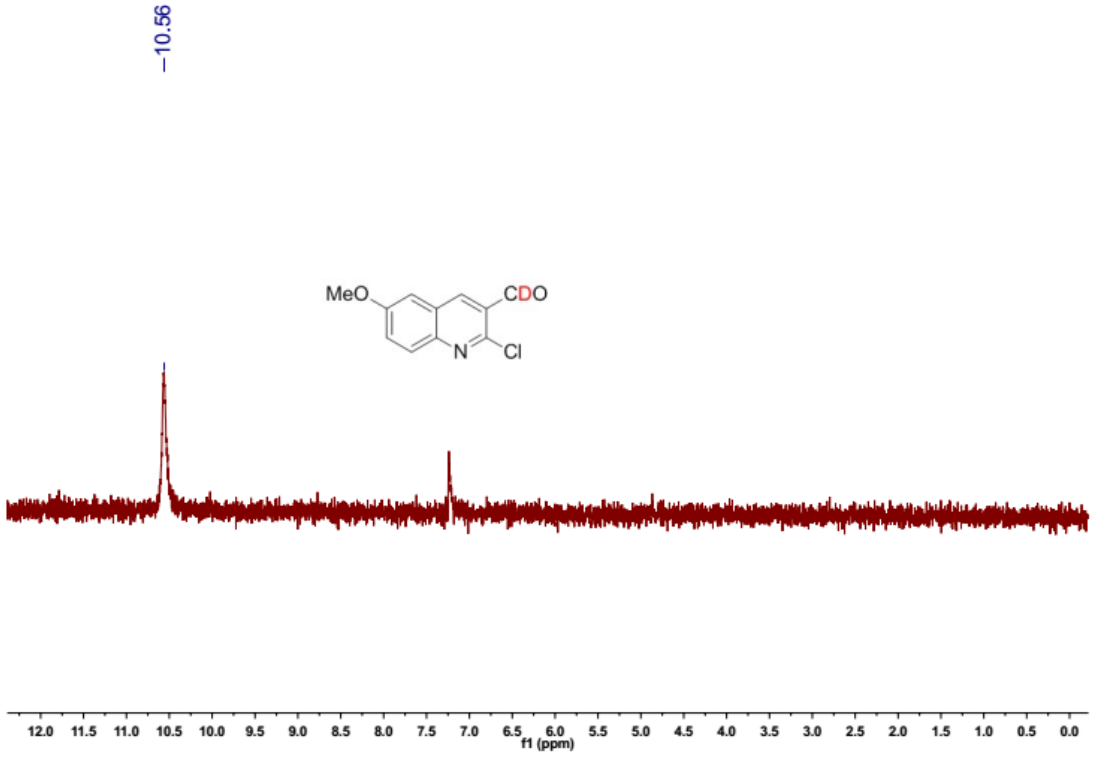
$^{13}$C NMR of deuterated aldehyde **7az**



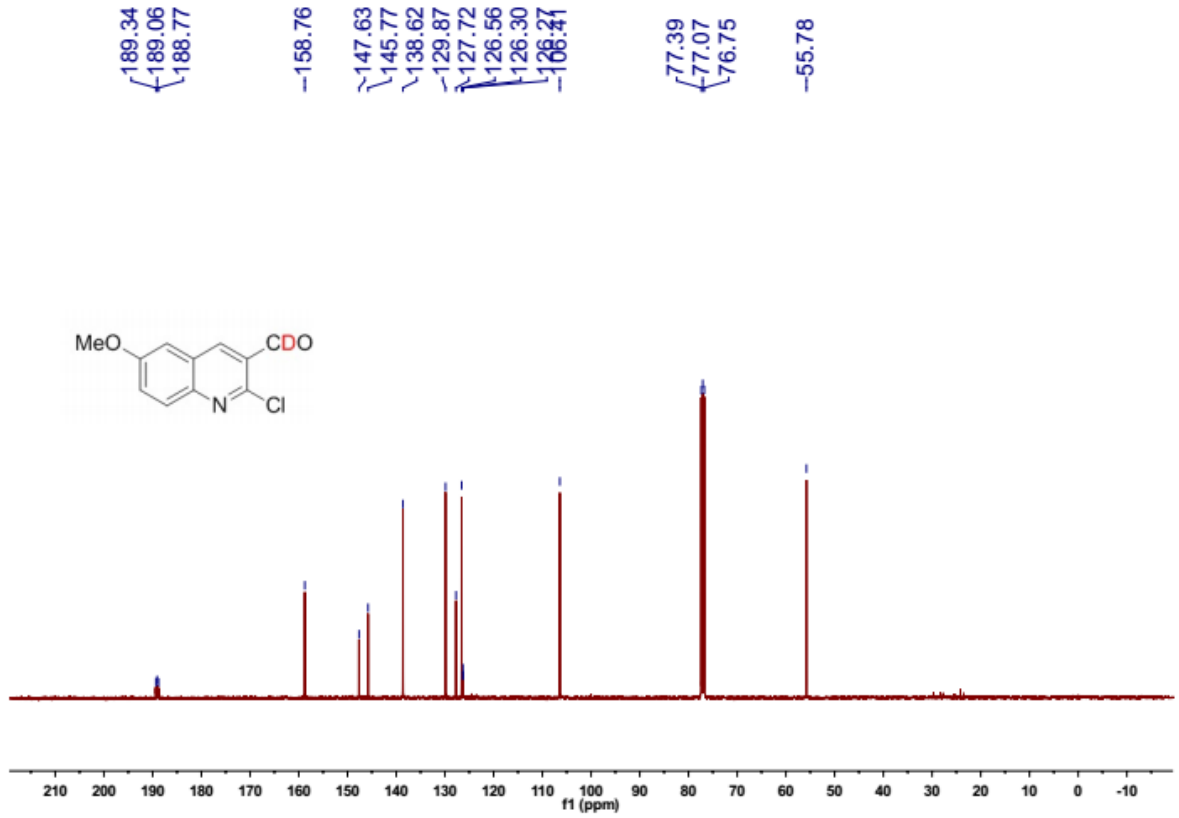
$^{1}$H NMR of deuterated aldehyde **7ba**



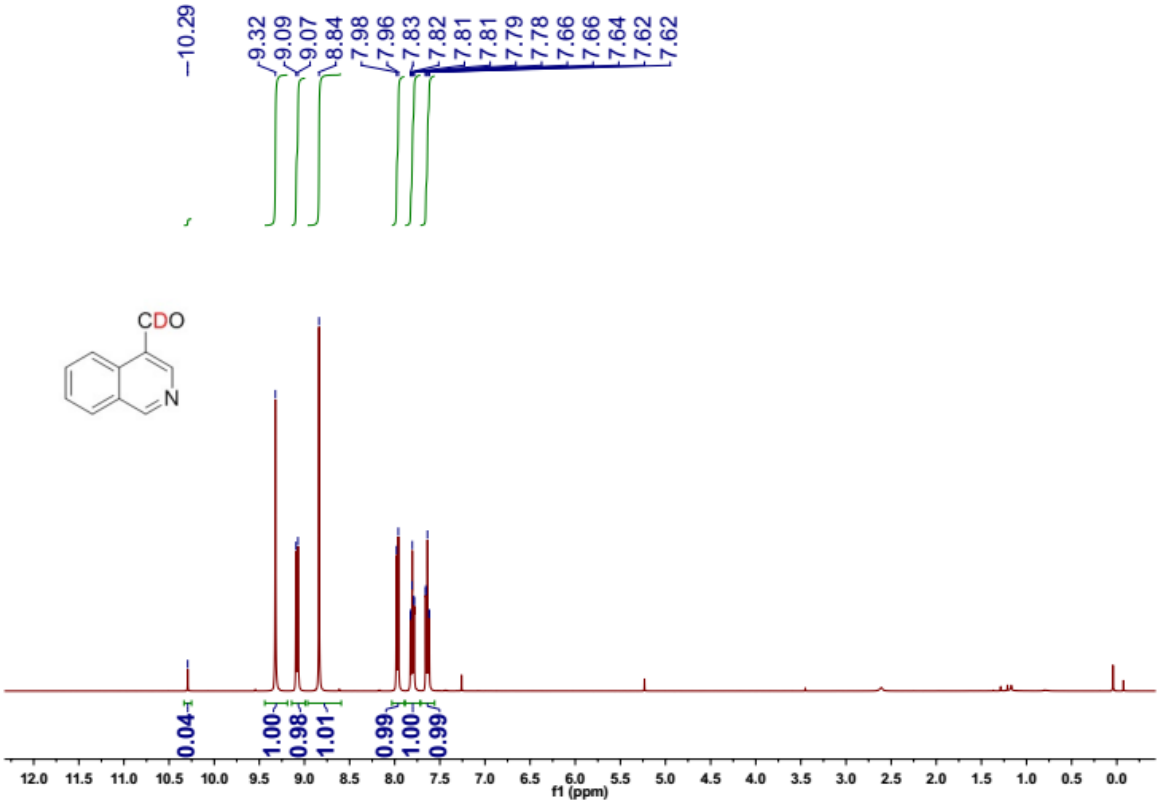

$^{2}$H NMR of deuterated aldehyde **7ba**



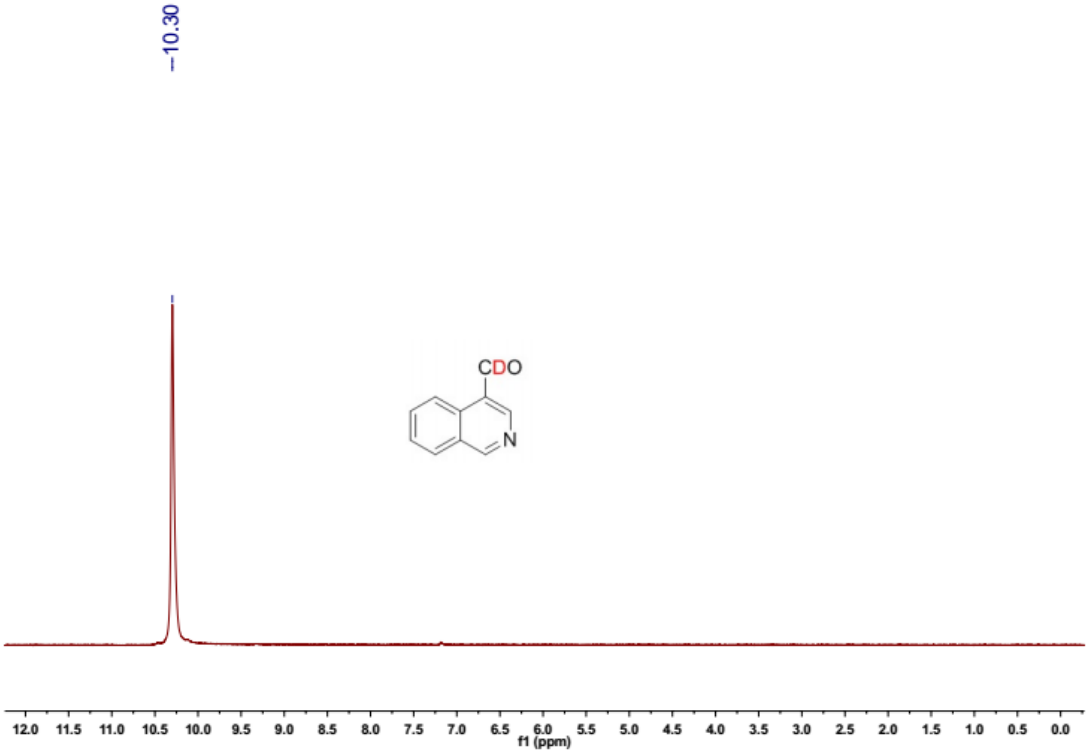
$^{13}$C NMR of deuterated aldehyde **7ba**



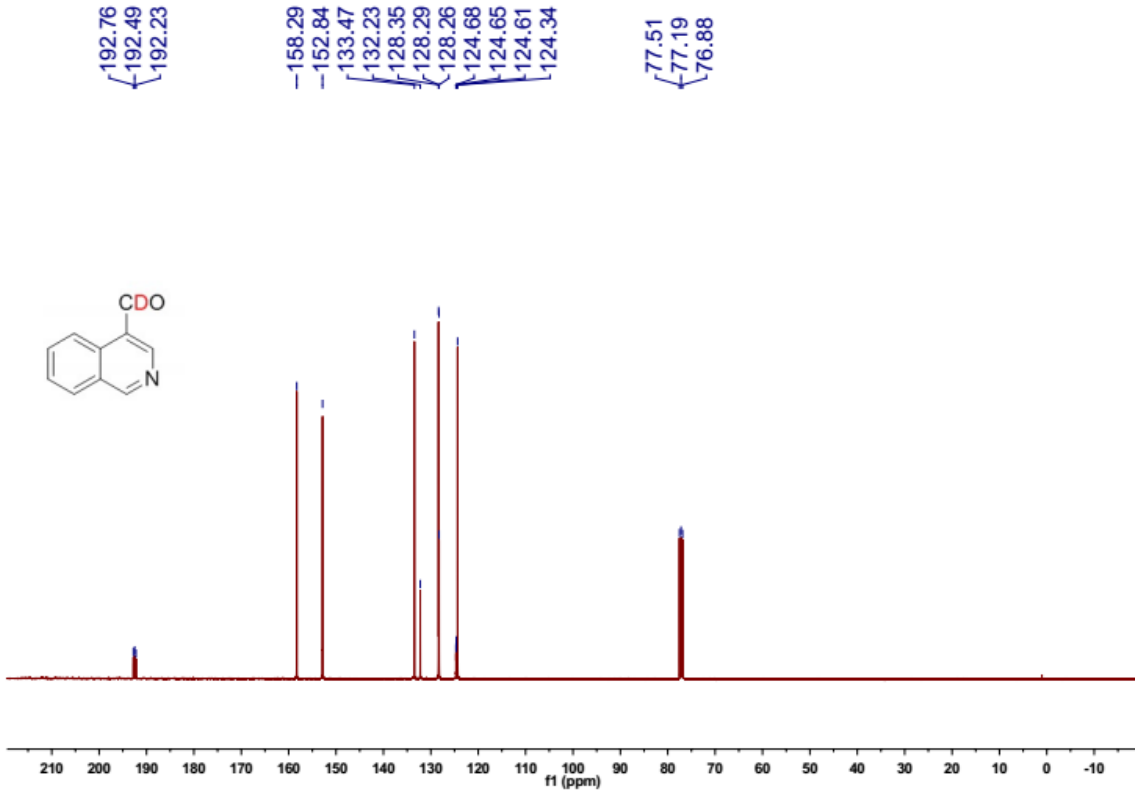
$^{1}$H NMR of deuterated aldehyde **7bb**



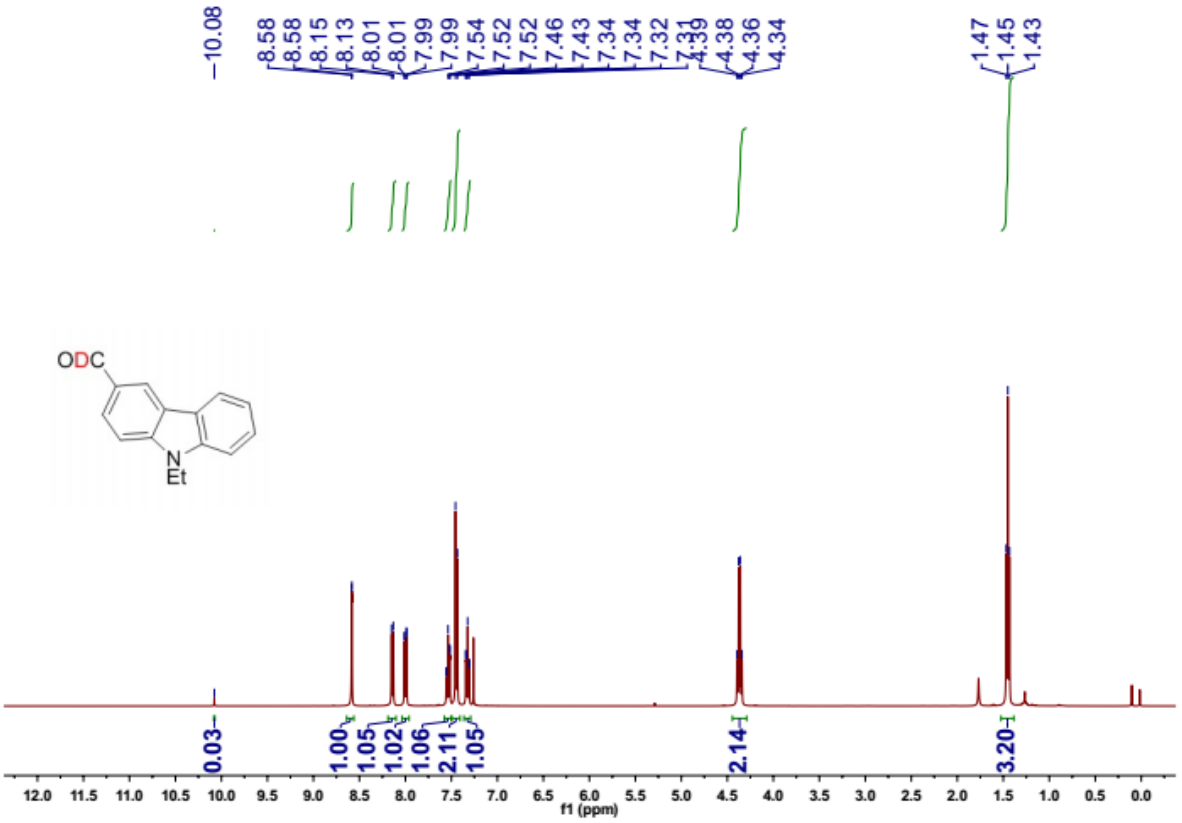

$^{2}$H NMR of deuterated aldehyde **7bb**



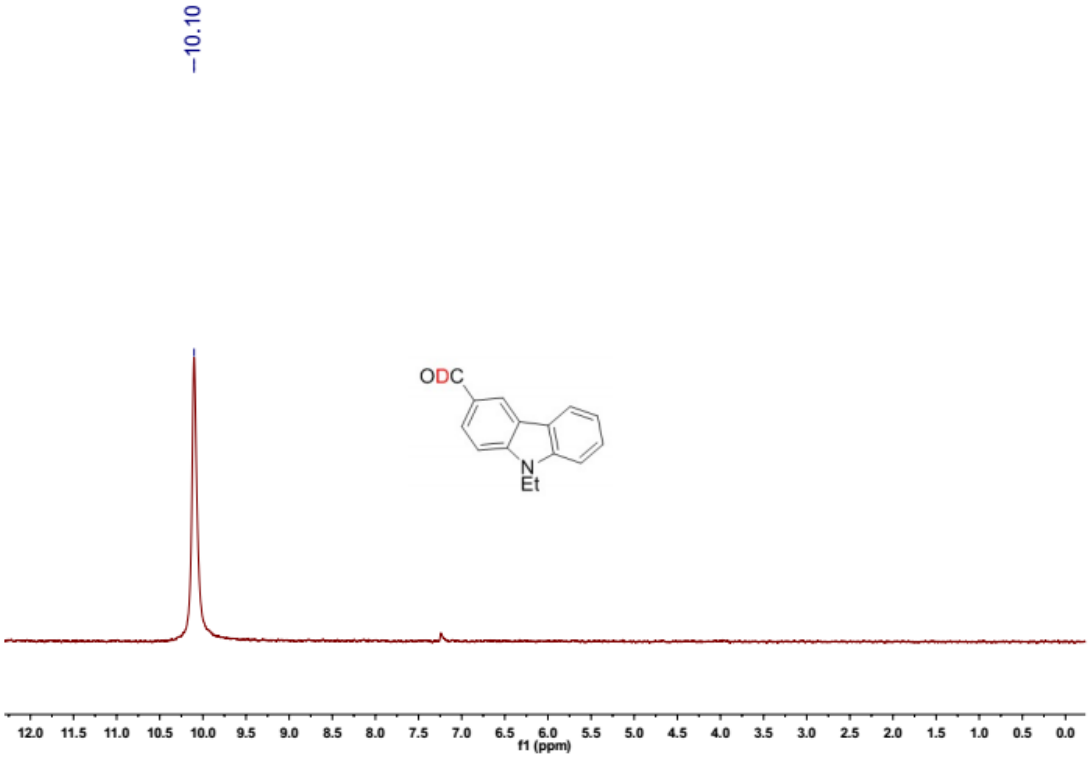
$^{13}$C NMR of deuterated aldehyde **7bb**



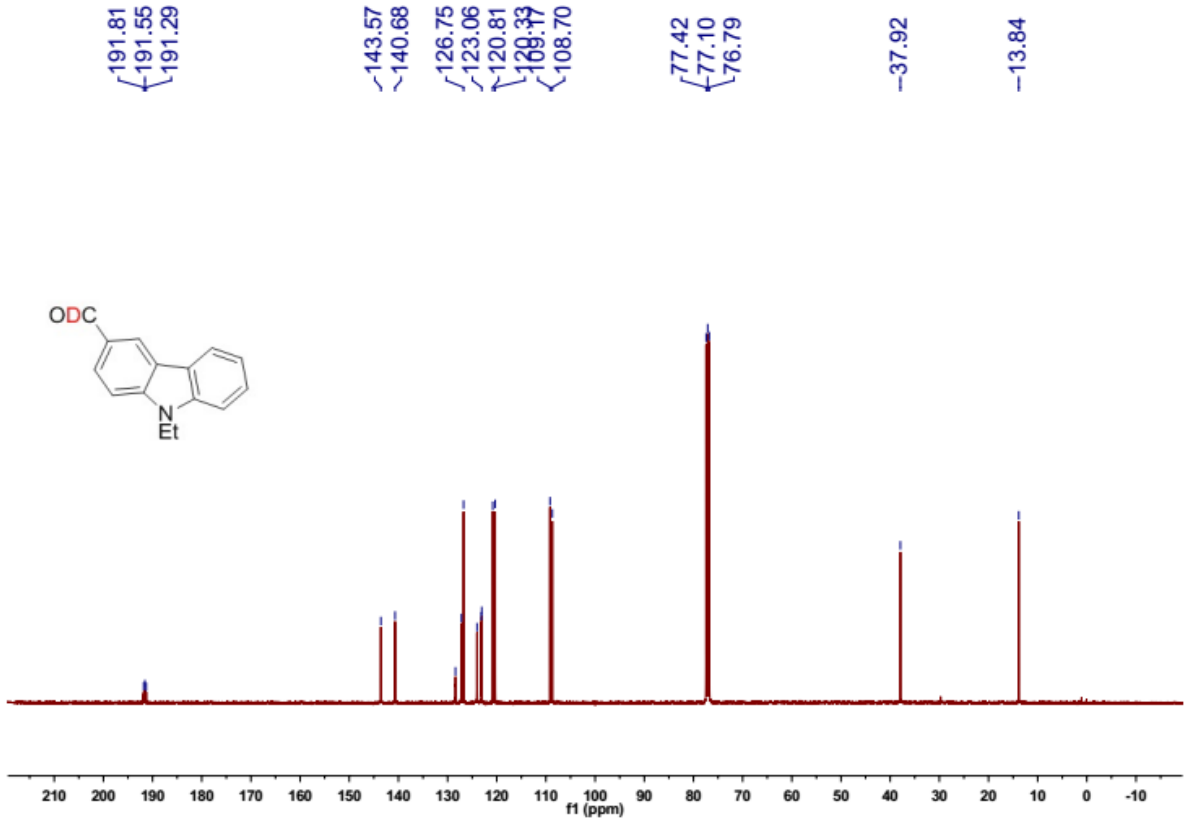
$^{1}$H NMR of deuterated aldehyde **7bc**



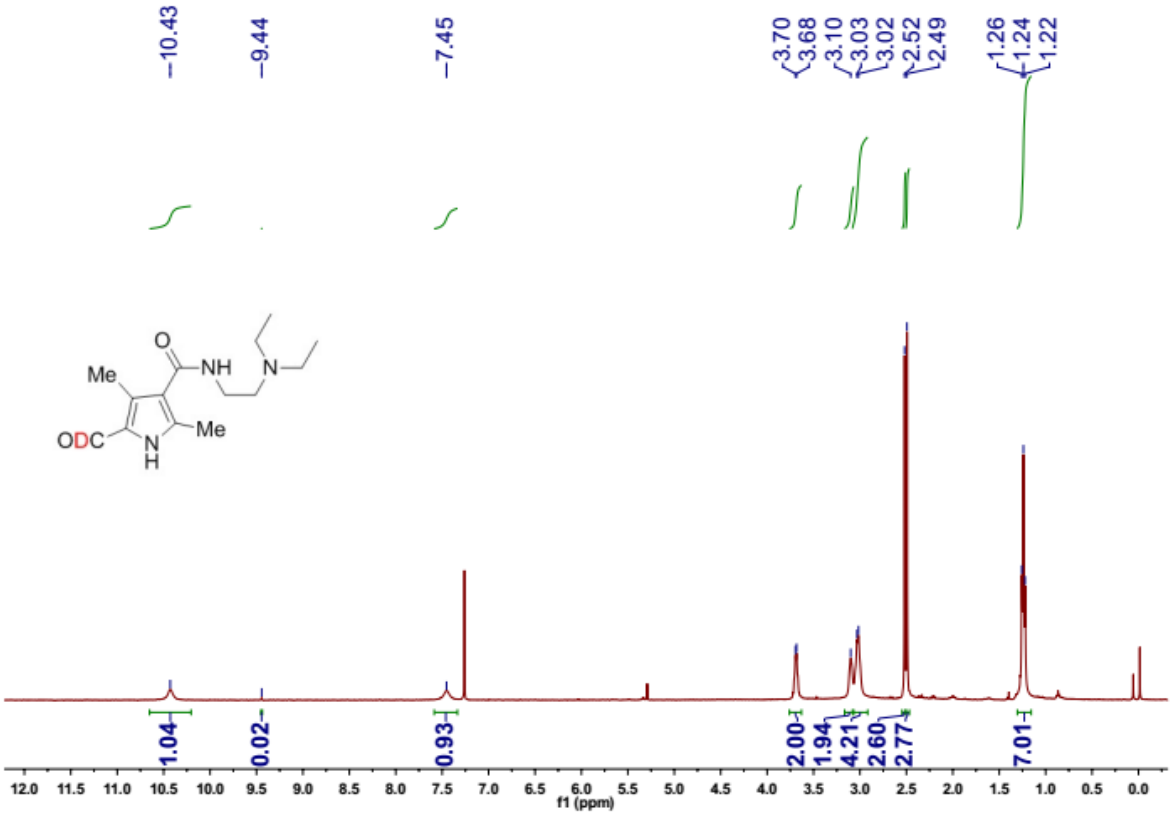

$^{2}$H NMR of deuterated aldehyde **7bc**



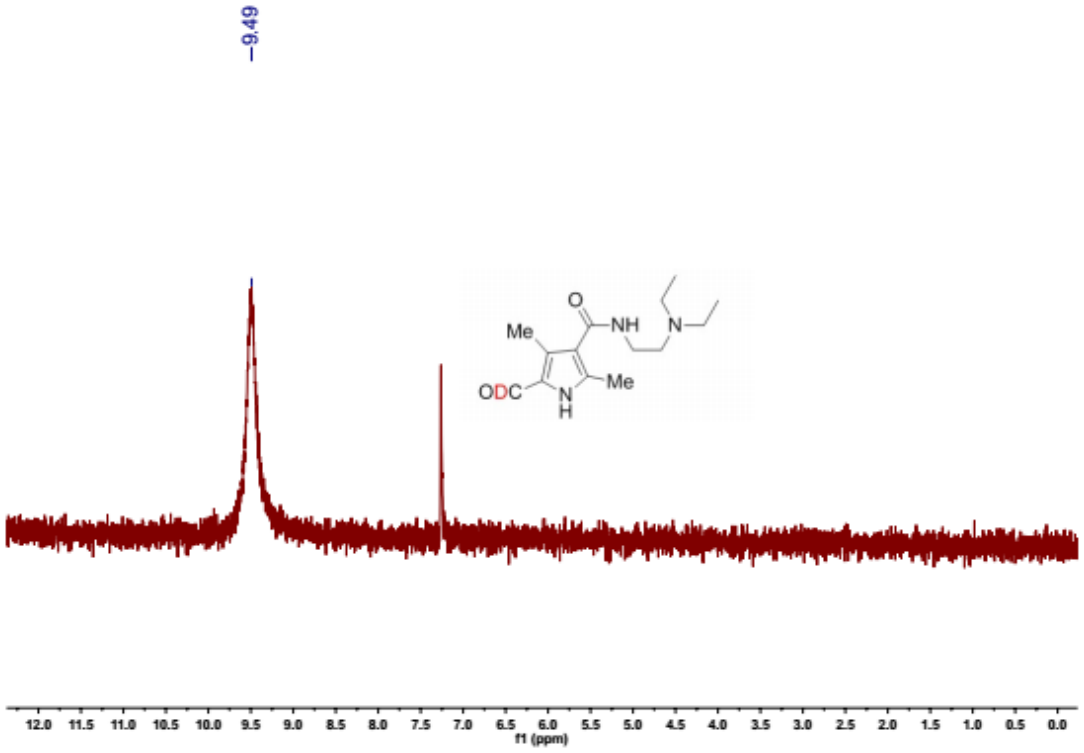
$^{13}$C NMR of deuterated aldehyde **7bc**



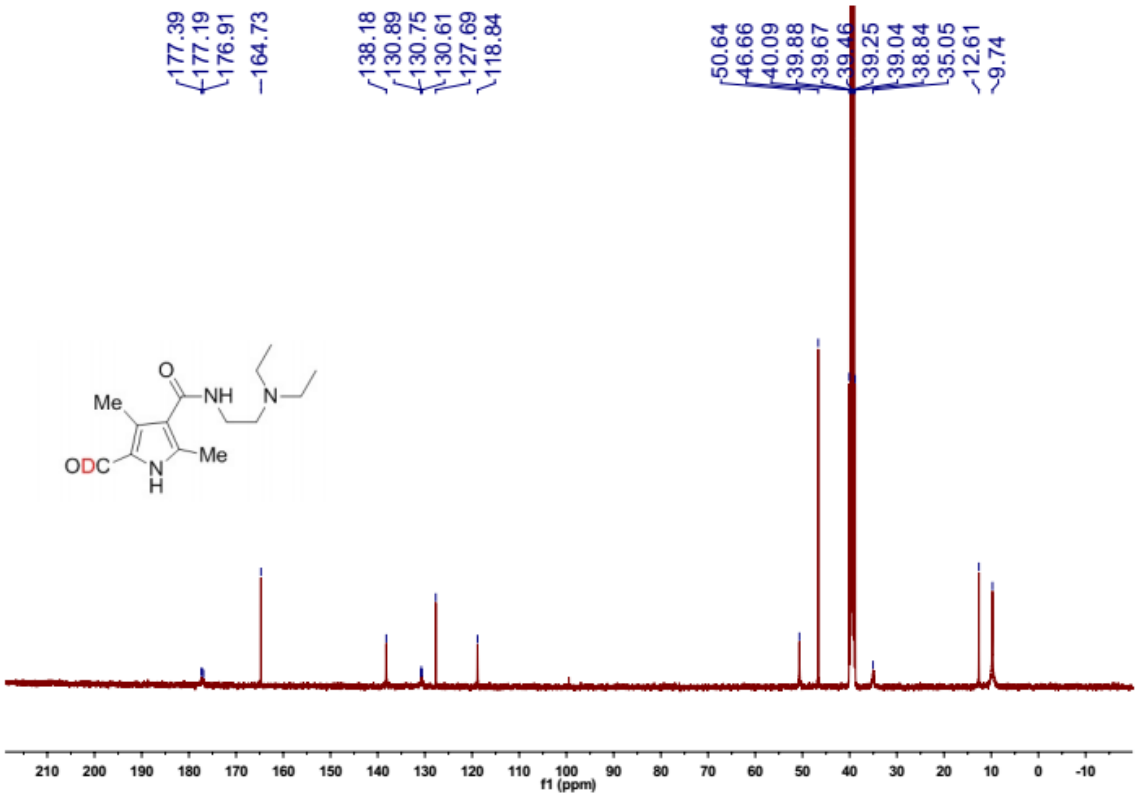
$^{1}$H NMR of deuterated aldehyde **7bd**



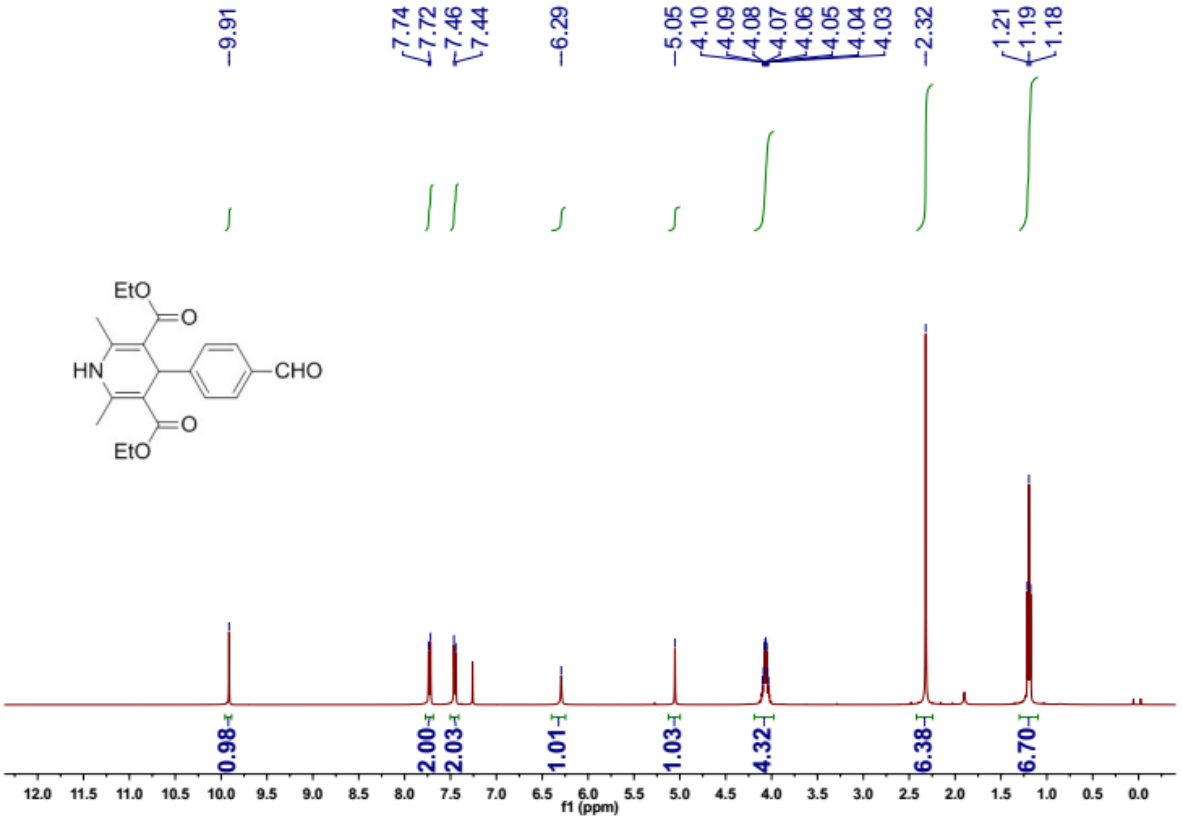

$^{2}$H NMR of deuterated aldehyde **7bd**



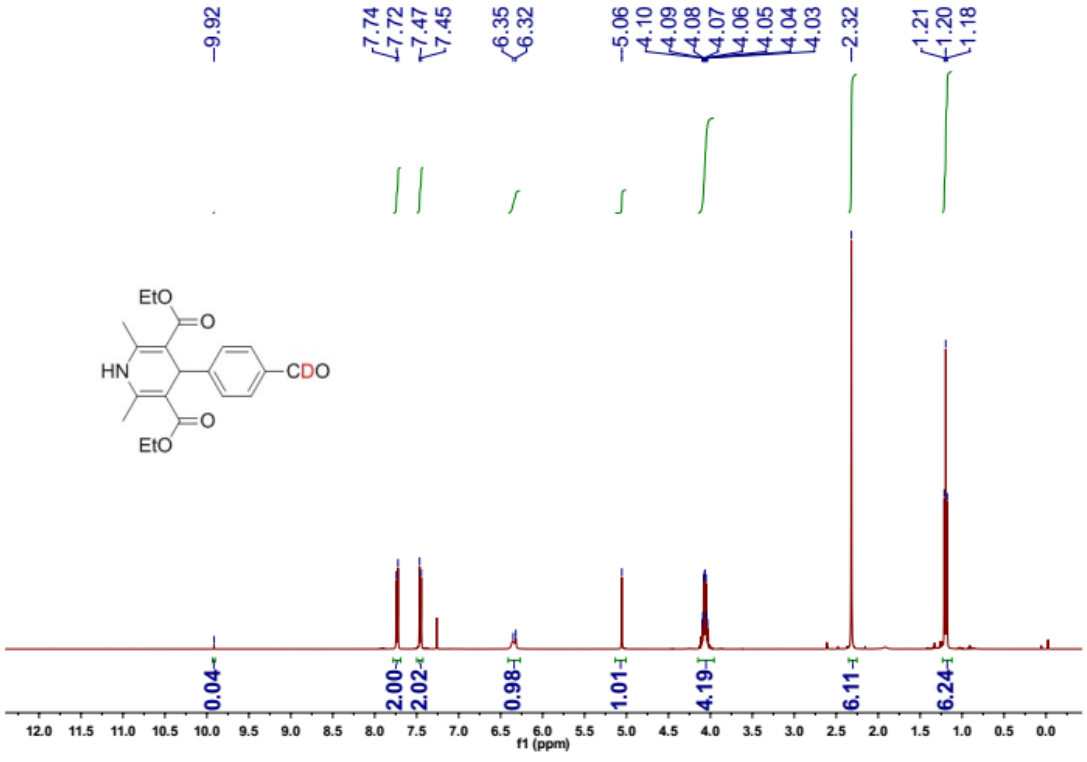
$^{13}$C NMR of deuterated aldehyde **7bd**



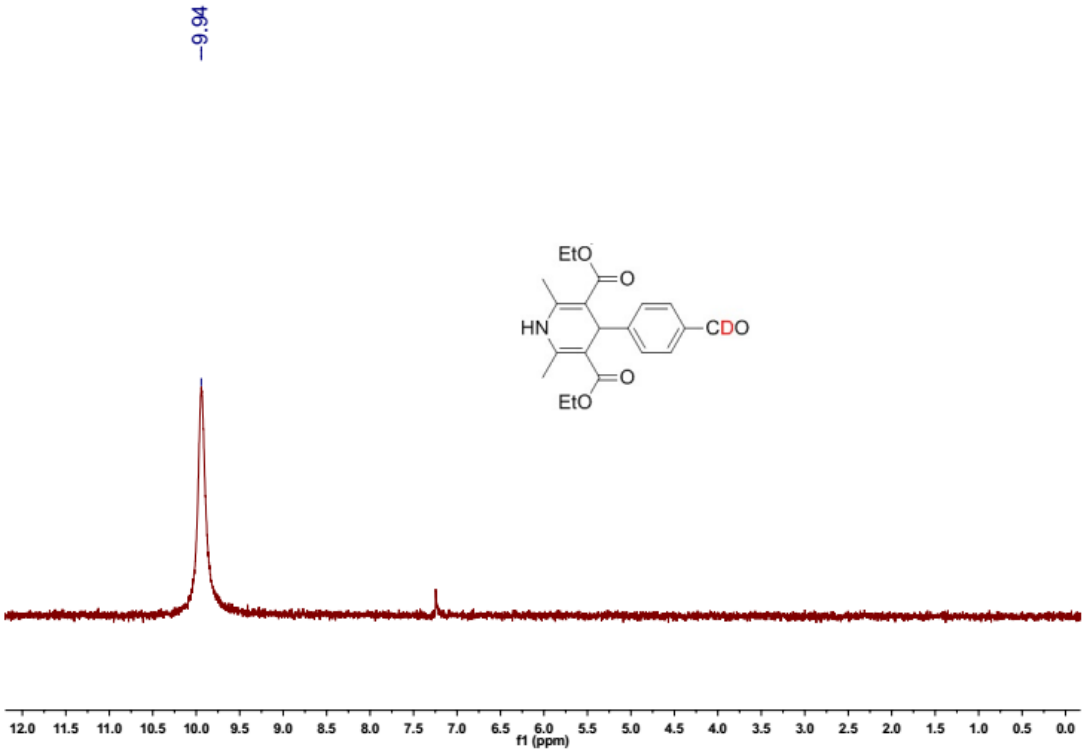
$^{1}$H NMR of aldehyde **6be**



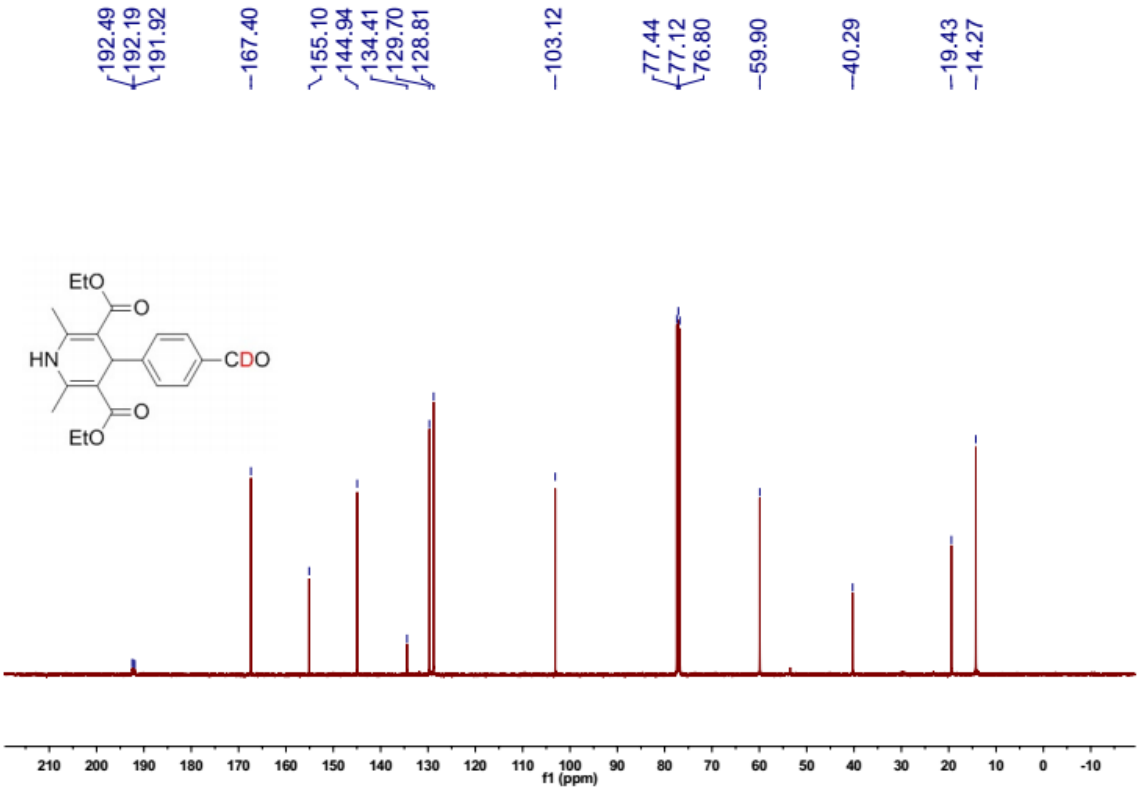

$^{1}$H NMR of deuterated aldehyde **7be**



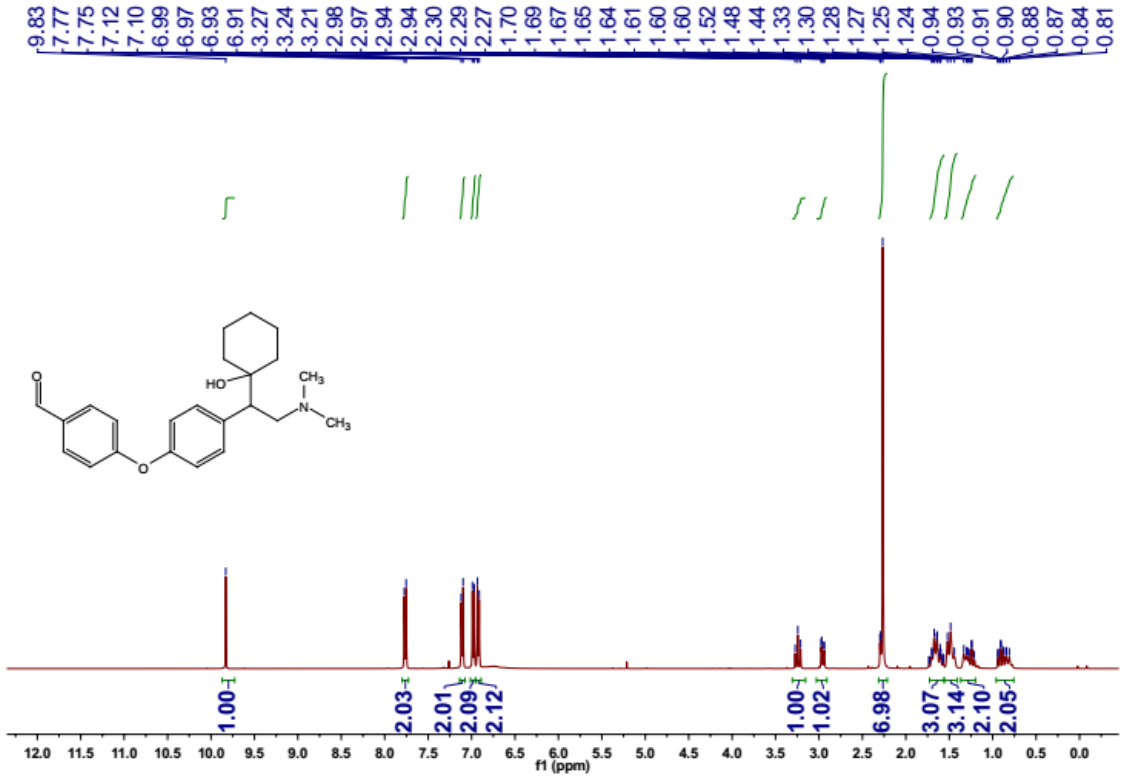
$^{2}$H NMR of deuterated aldehyde **7be**



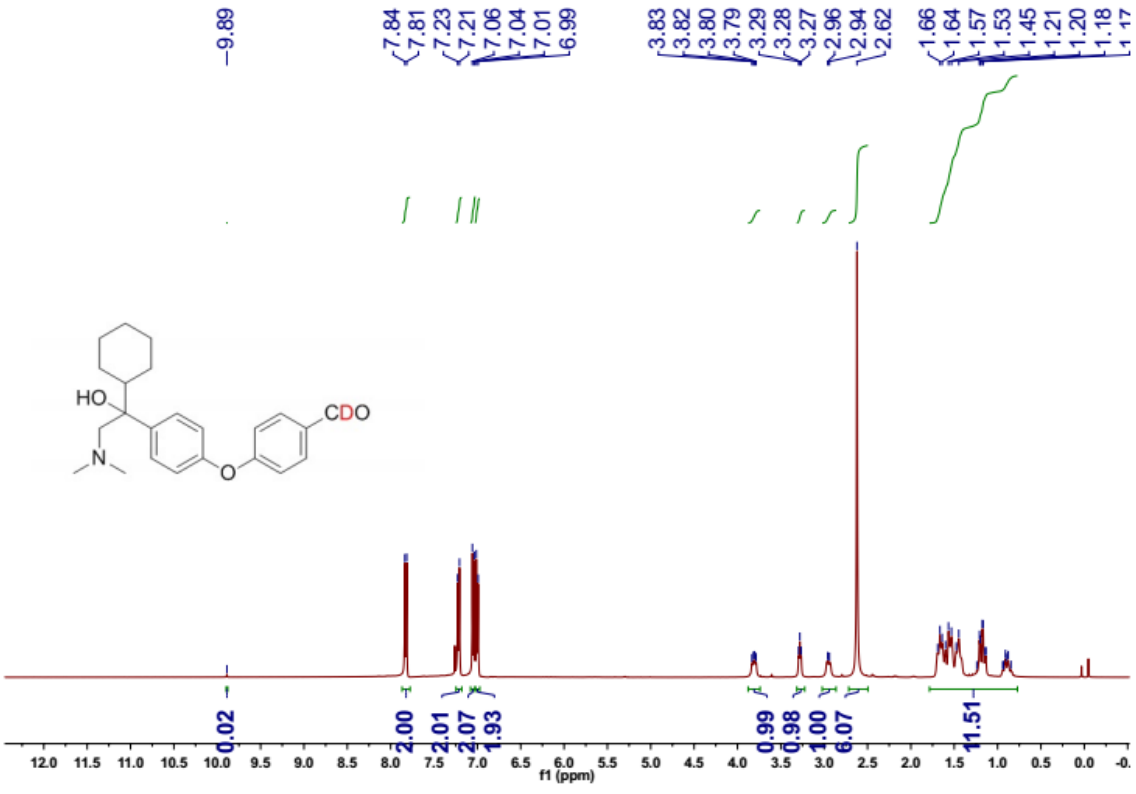

$^{13}$C NMR of deuterated aldehyde **7be**



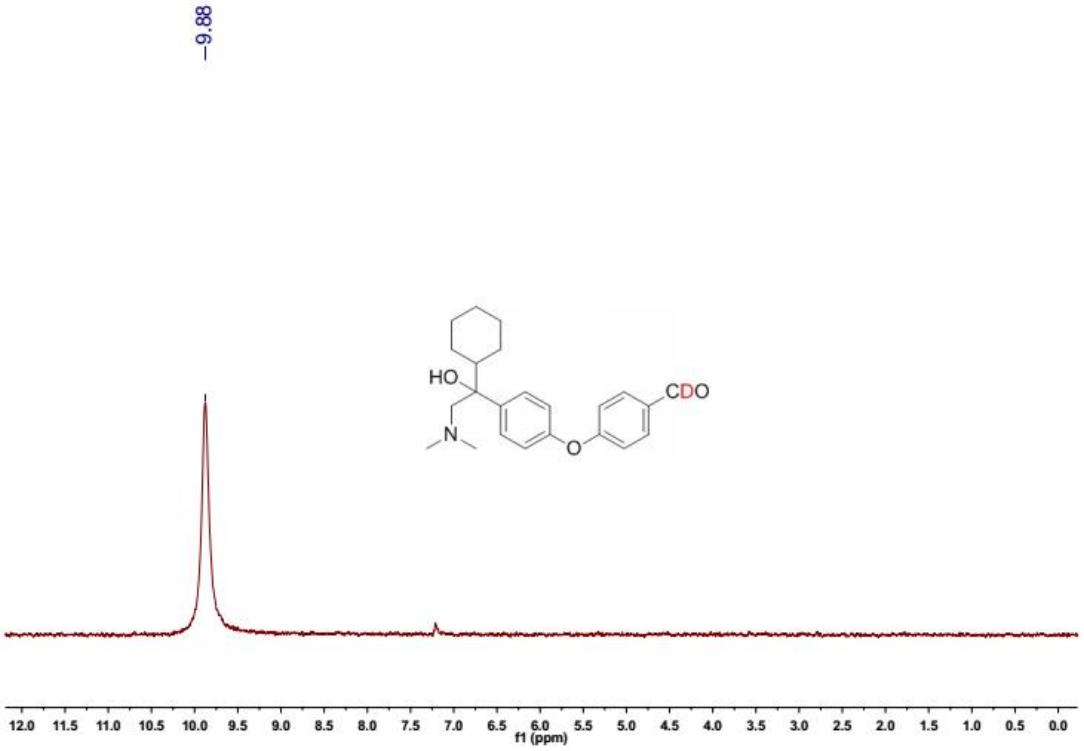
$^{1}$H NMR of aldehyde **6bf**



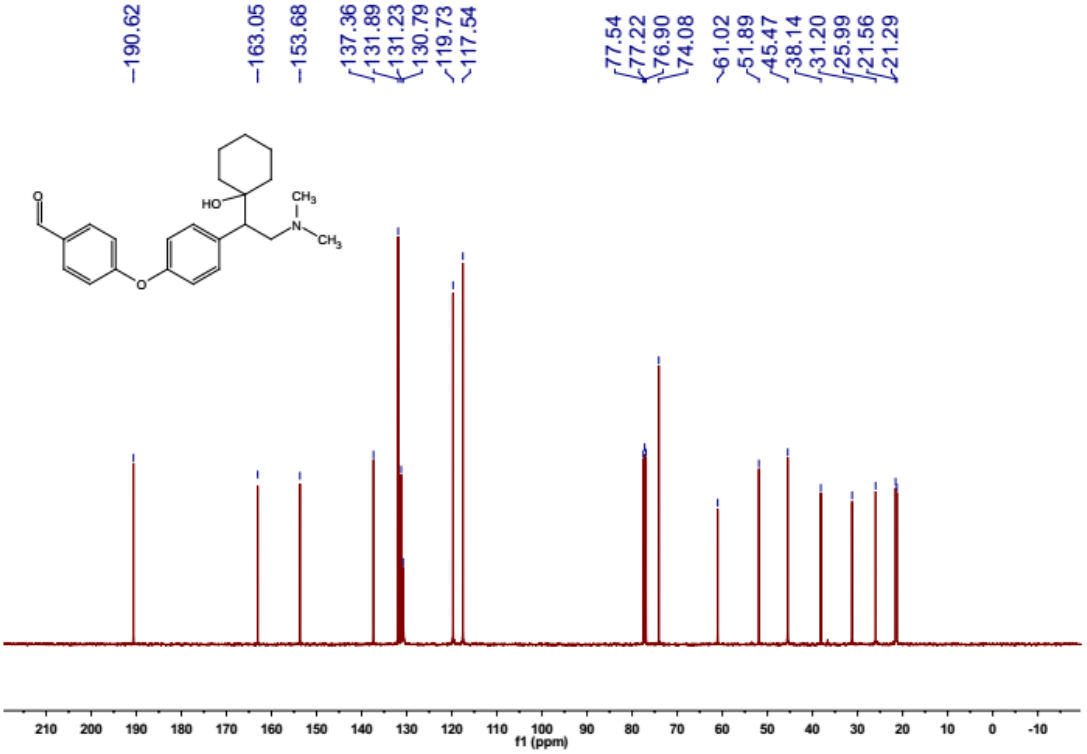

$^{1}$H NMR of deuterated aldehyde **7bf**



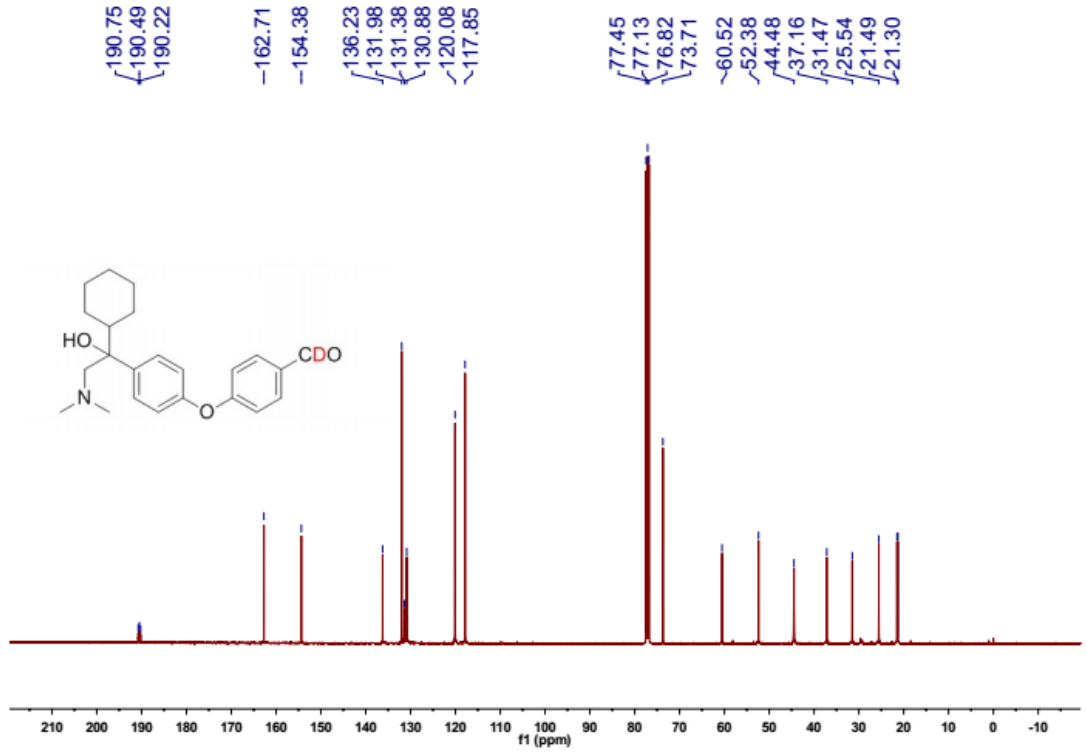
$^{2}$H NMR of deuterated aldehyde **7bf**



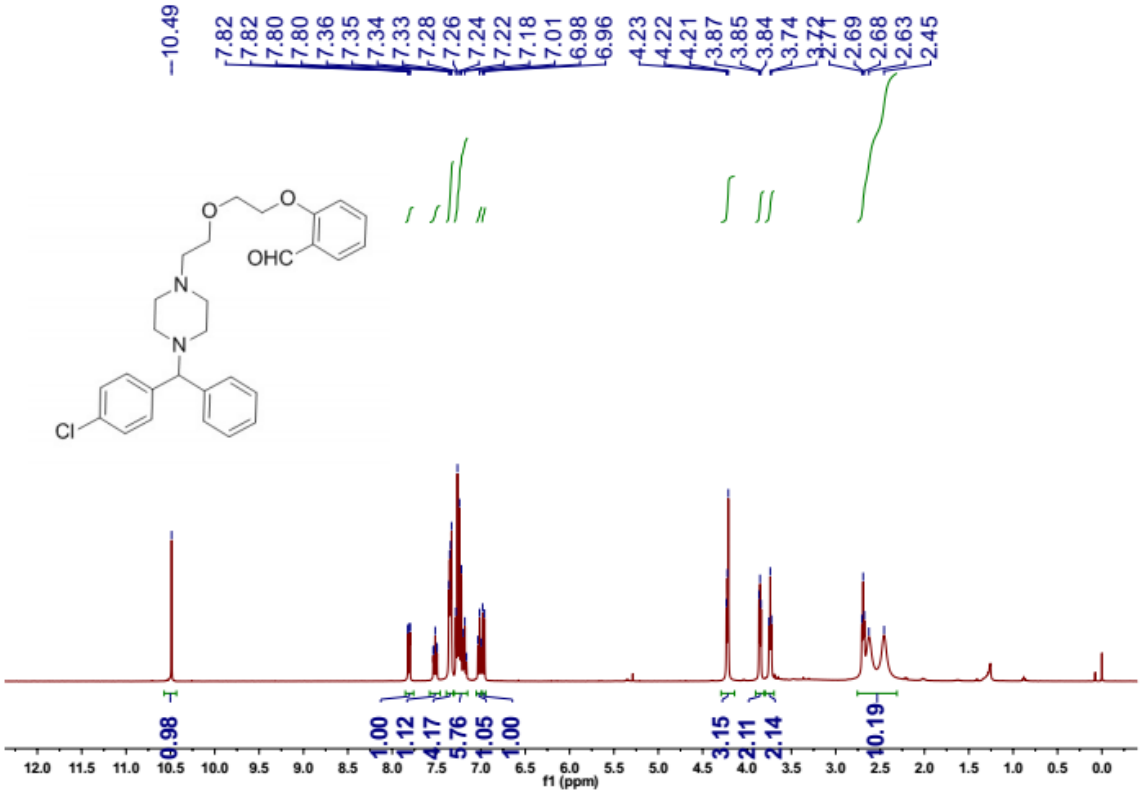
$^{13}$C NMR of aldehyde **6bf**



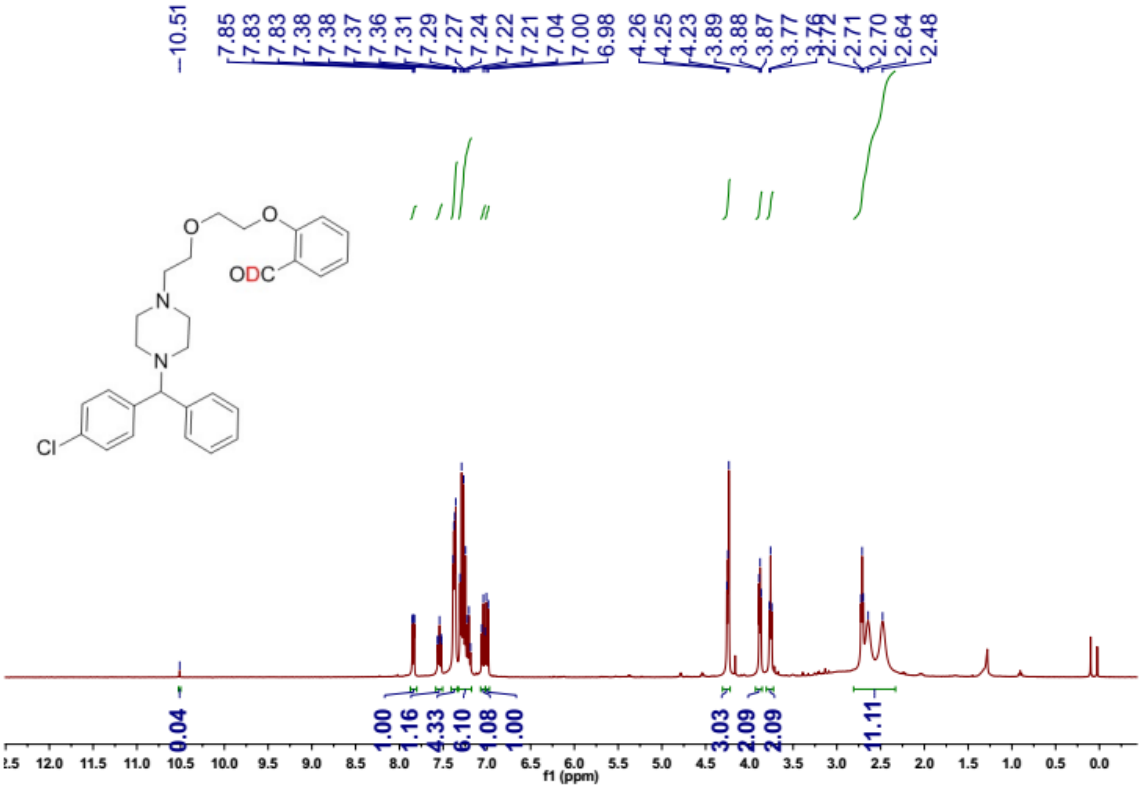

$^{13}$C NMR of deuterated aldehyde **7bf**



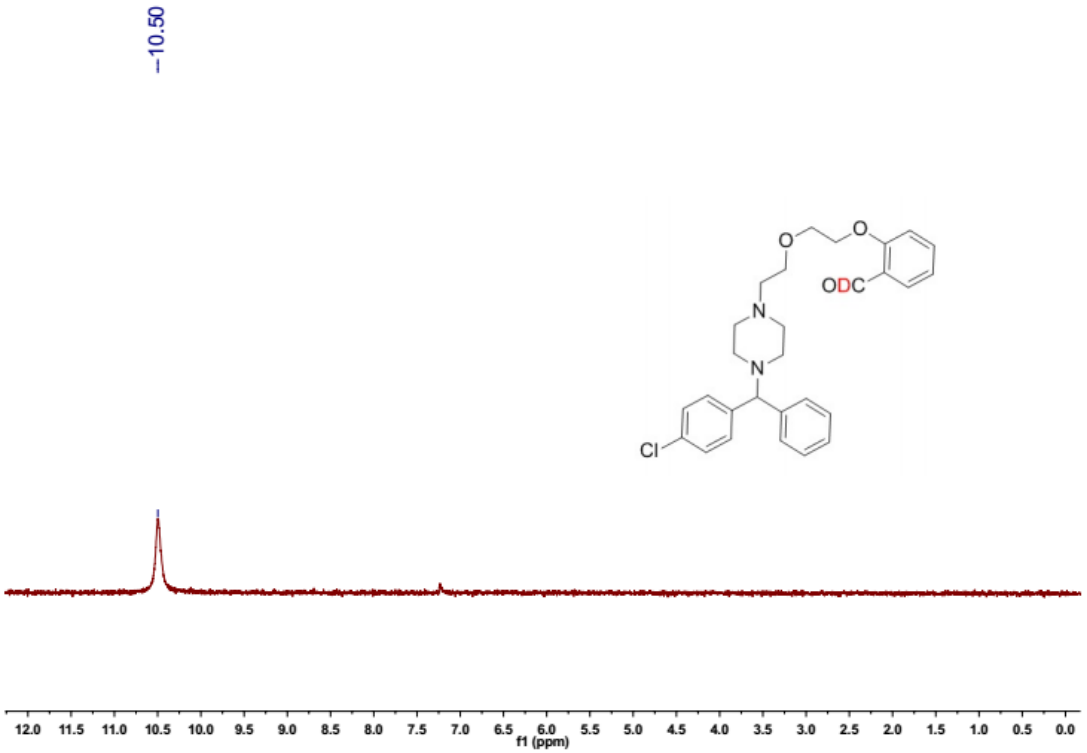
$^{1}$H NMR of aldehyde **6bg**



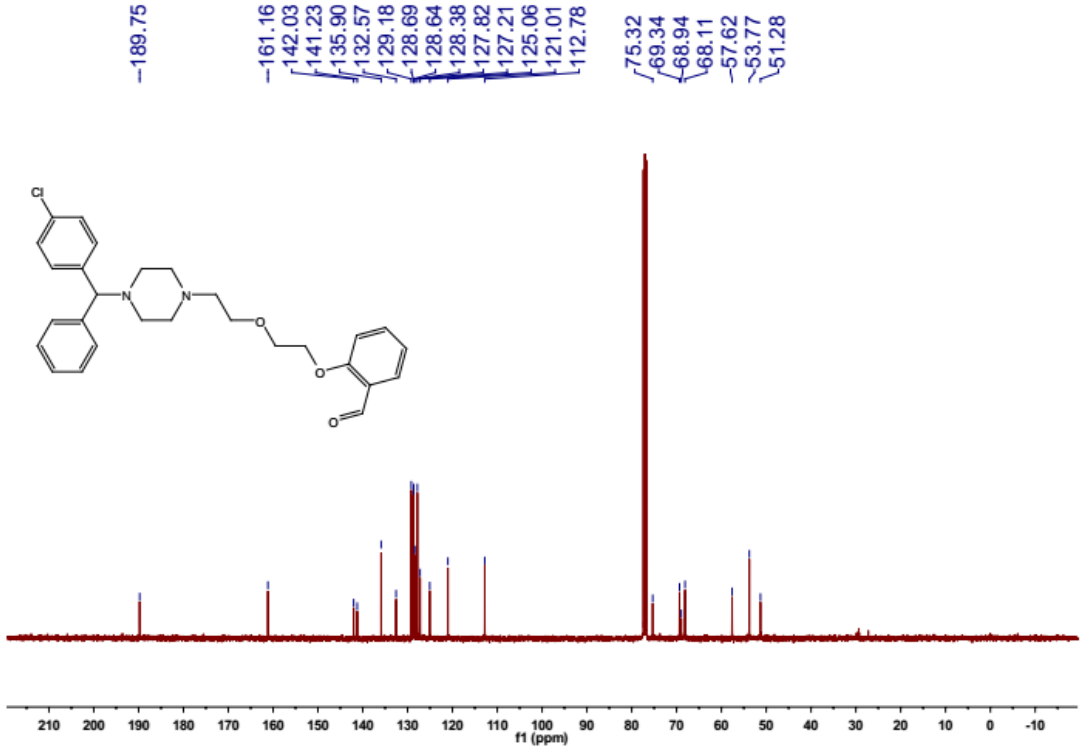

$^{1}$H NMR of deuterated aldehyde **7bg**



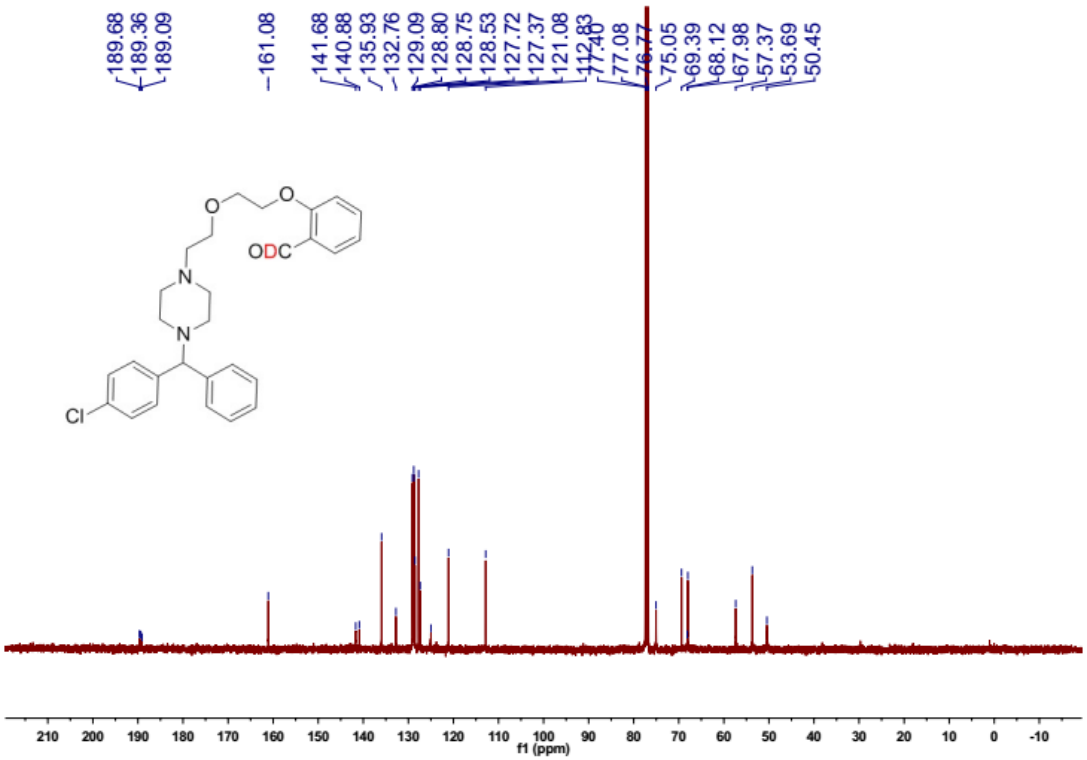
$^{2}$H NMR of deuterated aldehyde **7bg**



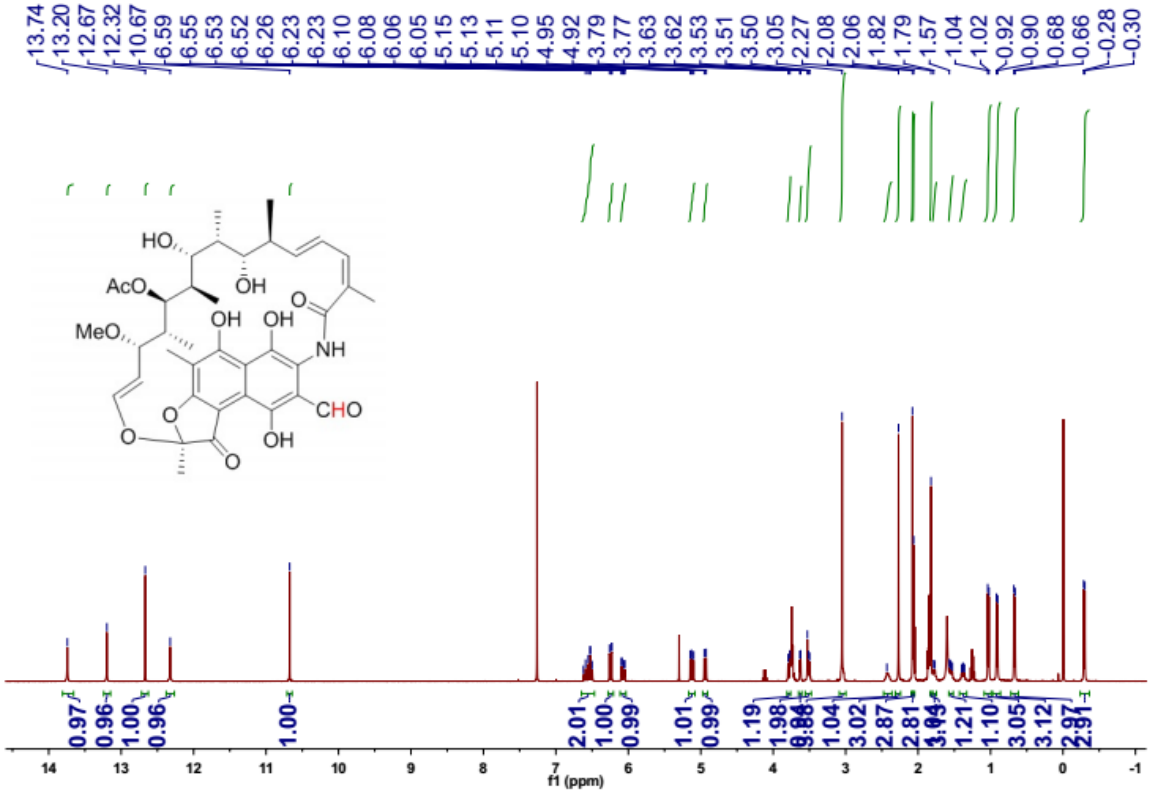
$^{13}$C NMR of aldehyde **6bg**



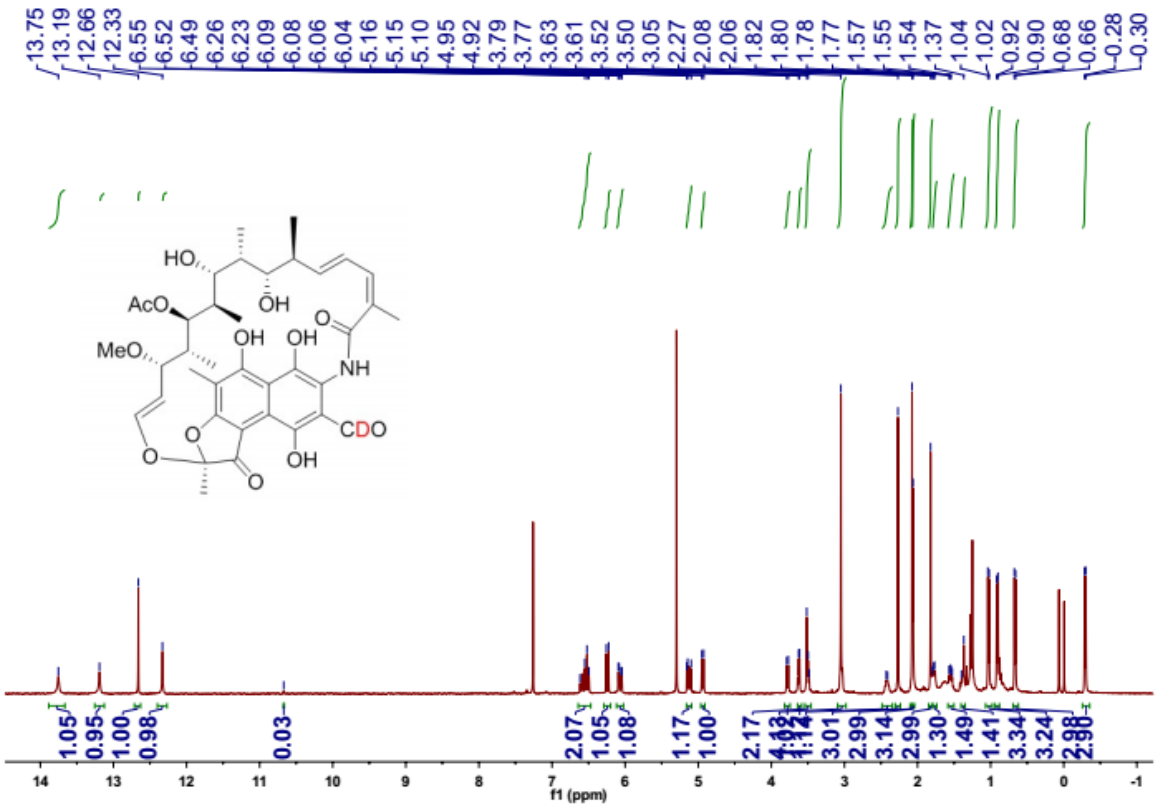

$^{13}$C NMR of deuterated aldehyde **7bg**



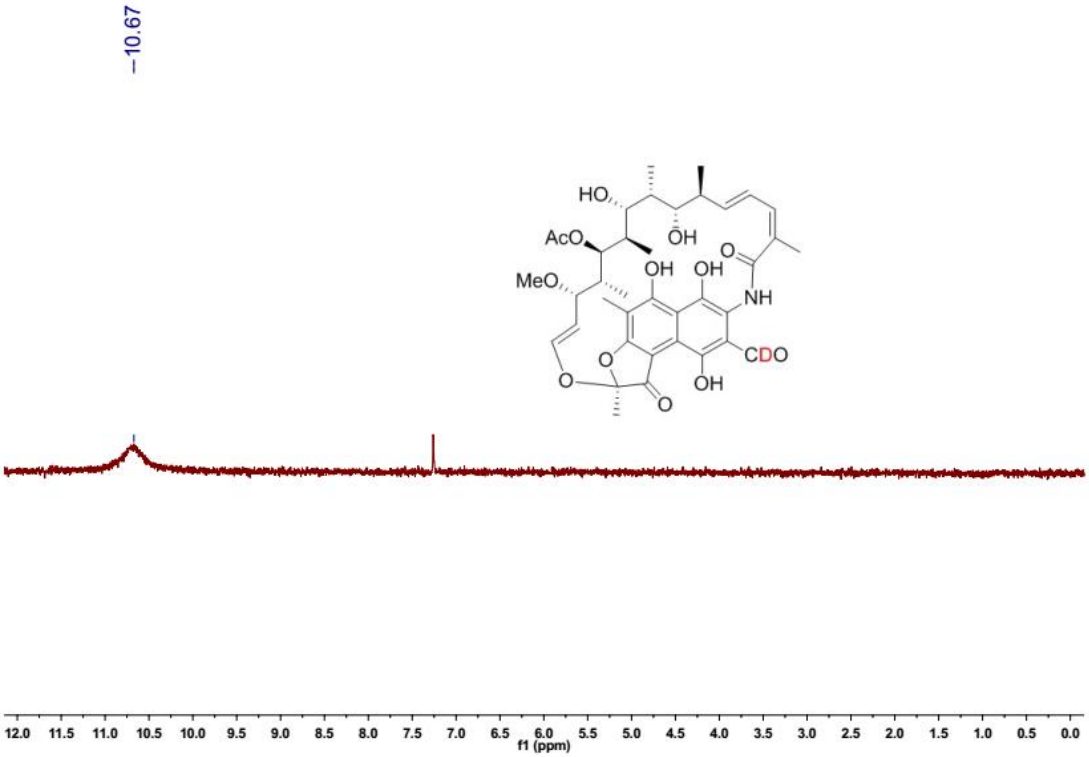
$^{1}$H NMR of 3-formyl rifamycin **6bh**



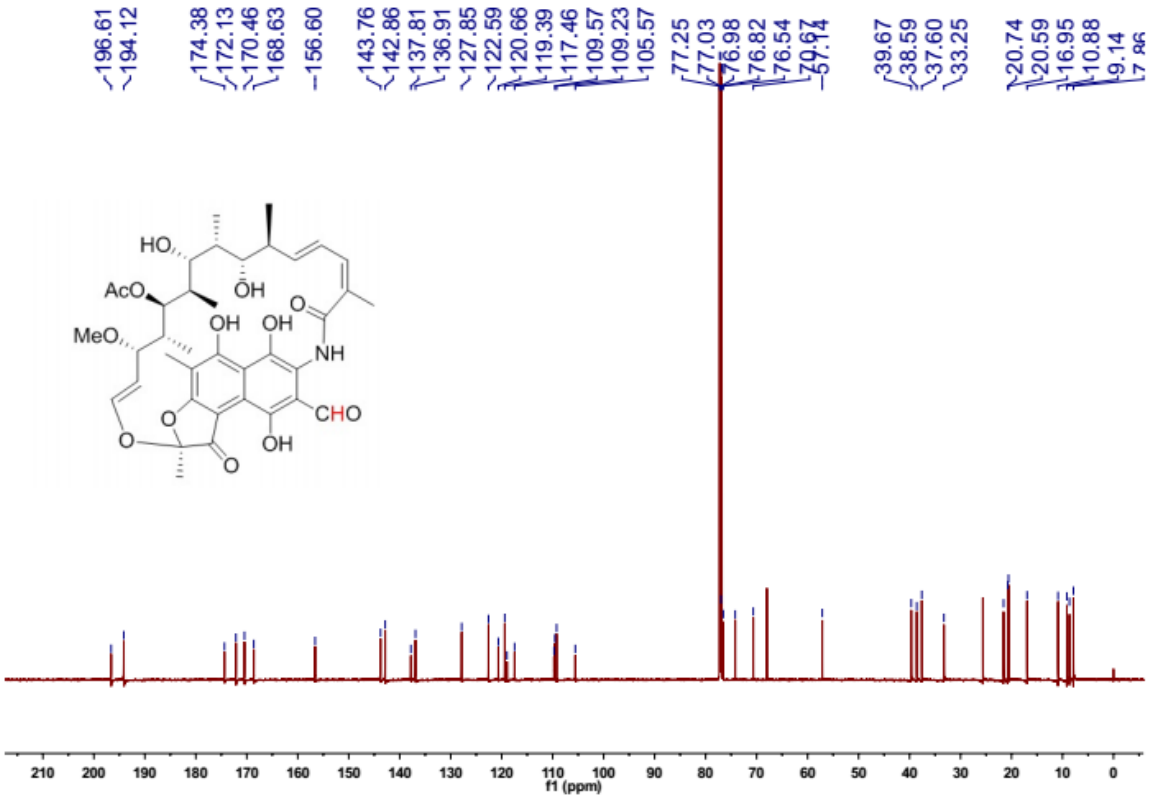

$^{1}$H NMR of deuterated 3-formyl rifamycin **7bh**



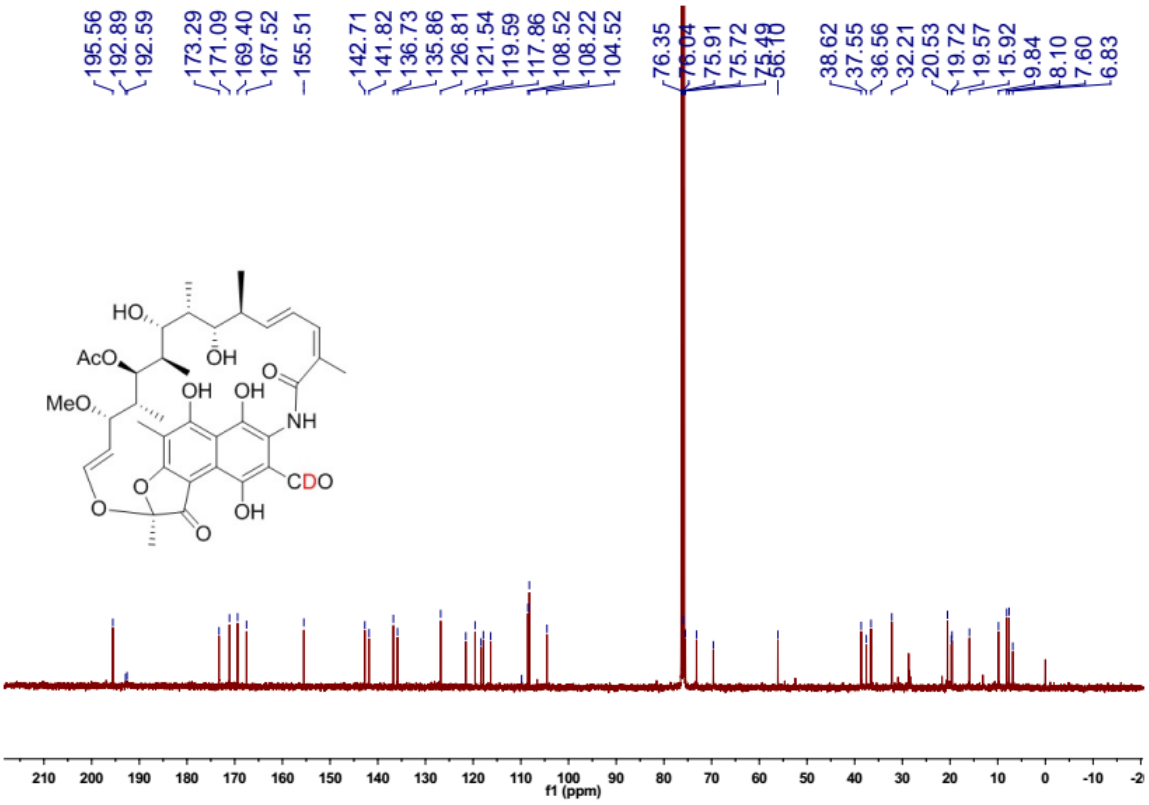
$^{2}$H NMR of deuterated aldehyde **7bh**



$^{13}$C NMR of 3-formyl rifamycin **6bh**

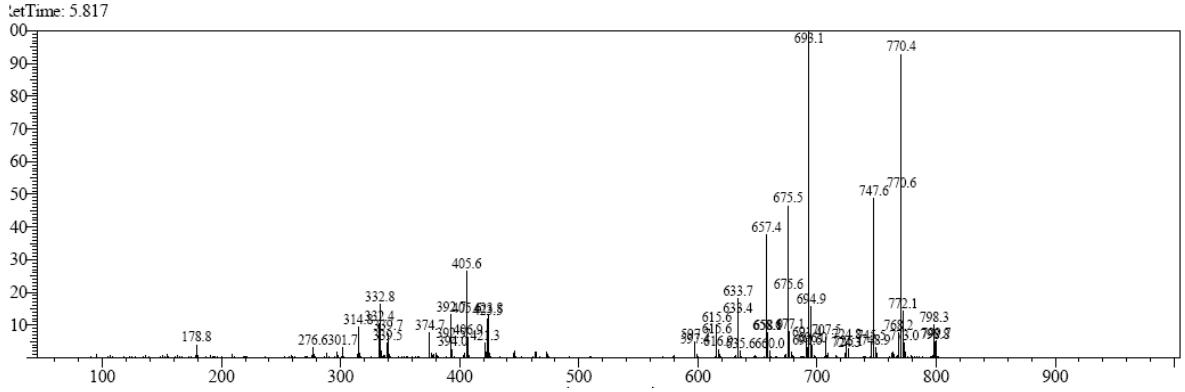



$^{13}$C NMR of deuterated 3-formyl rifamycin **7bh**

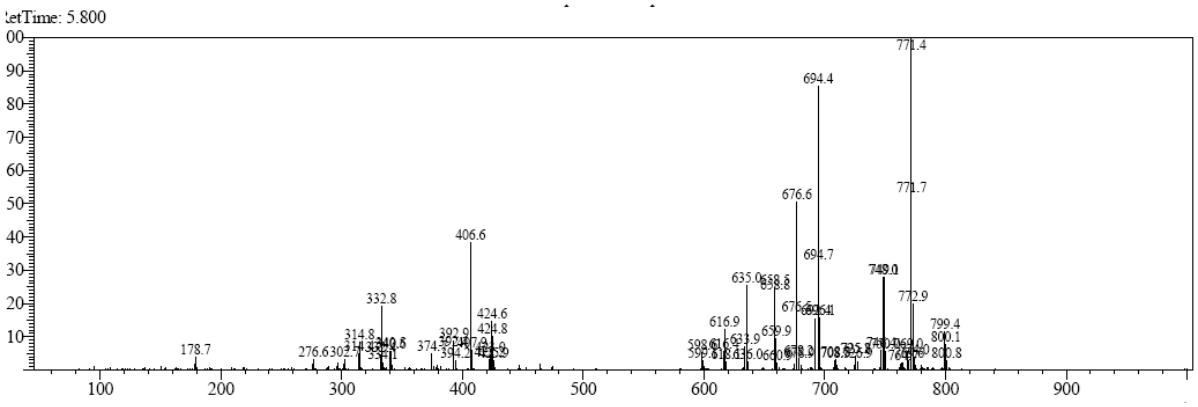


LRMS of 3-formyl rifamycin **6bh** and deuterated 3-formyl rifamycin **7bh**

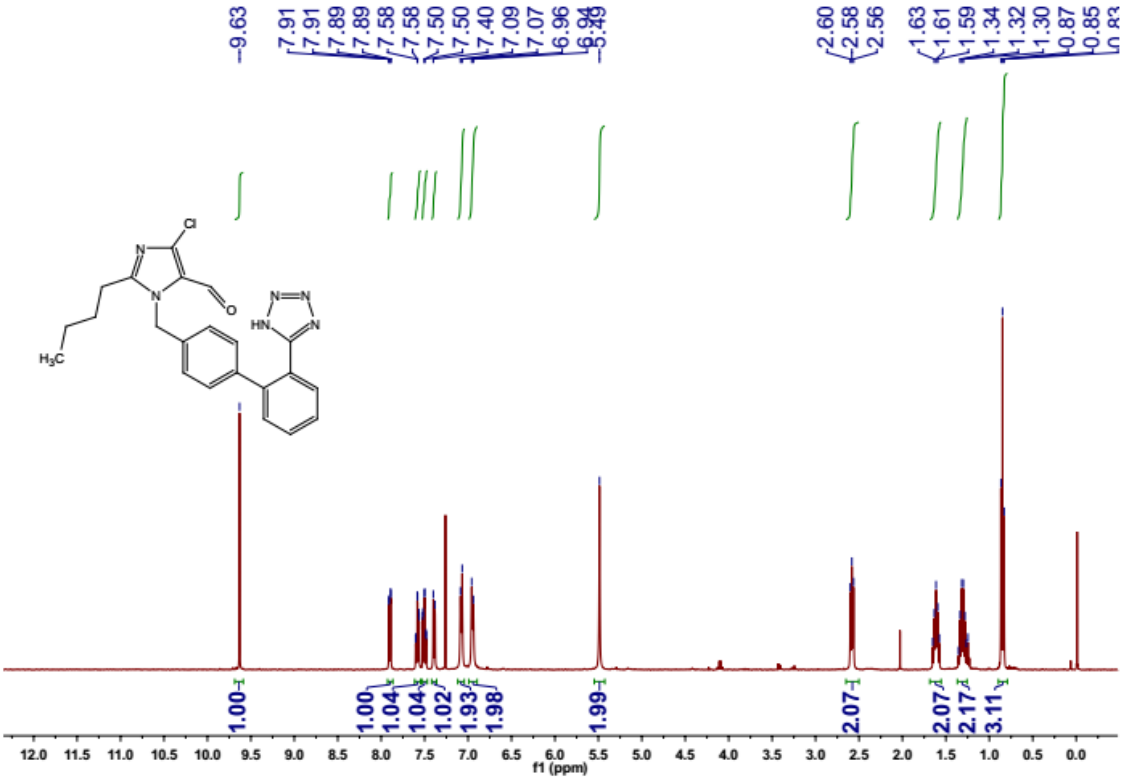
**6bh**: m/z caled for $C_{38}H_{46}NNa_2O_{13}$ [$(M-H+2Na)^+$]: 770.3, Found:770.4



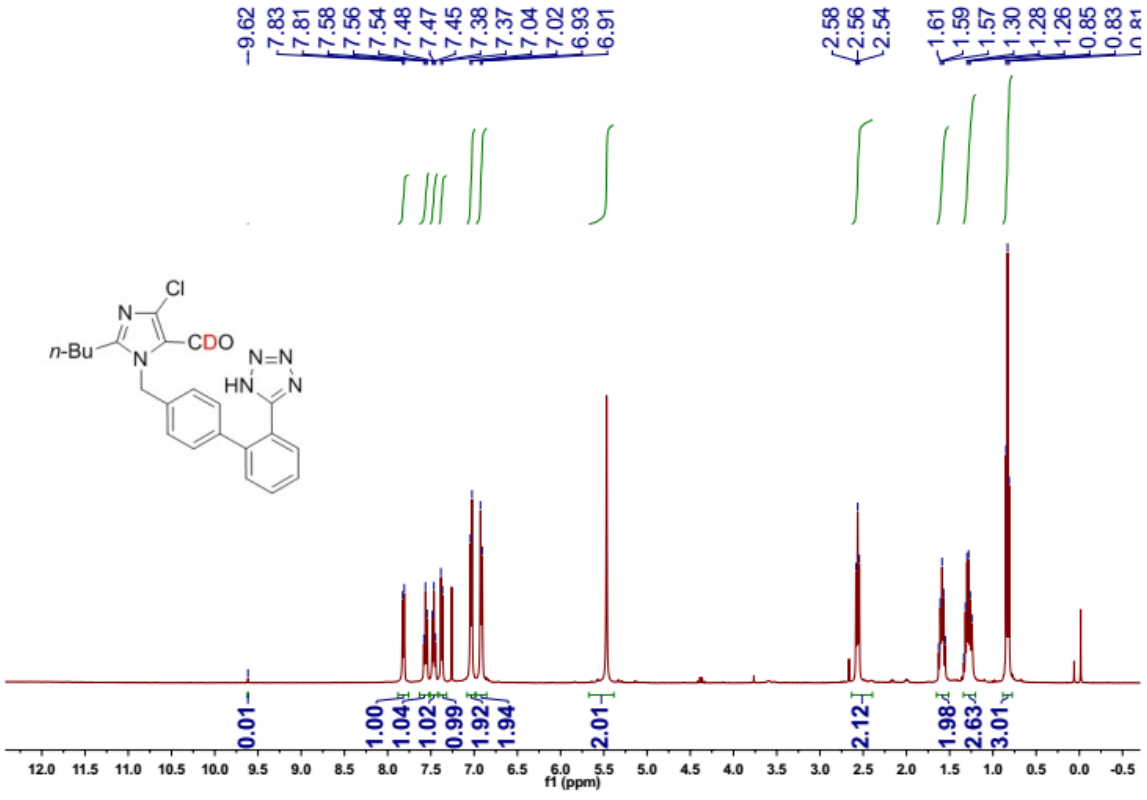

**7bh**: m/z caled for $C_{38}H_{45}DNNa_2O_{13}$ [$(M-H+2Na)^+$]: 771.3, Found:771.4



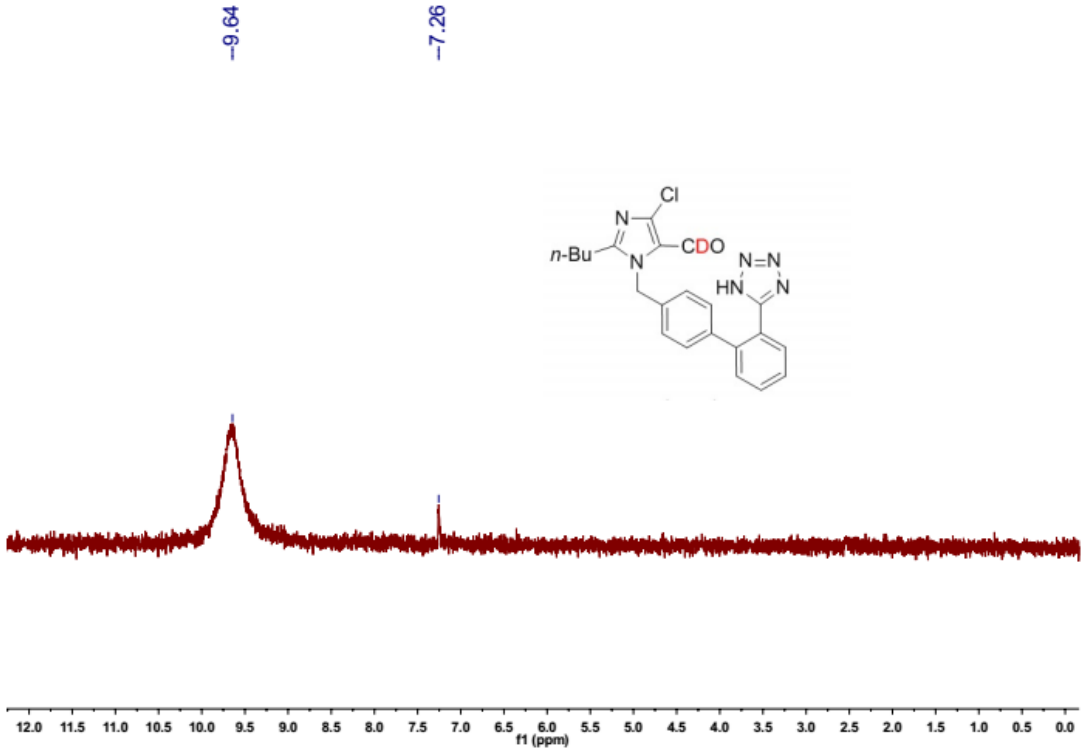
$^{1}$H NMR of aldehyde **6bi**



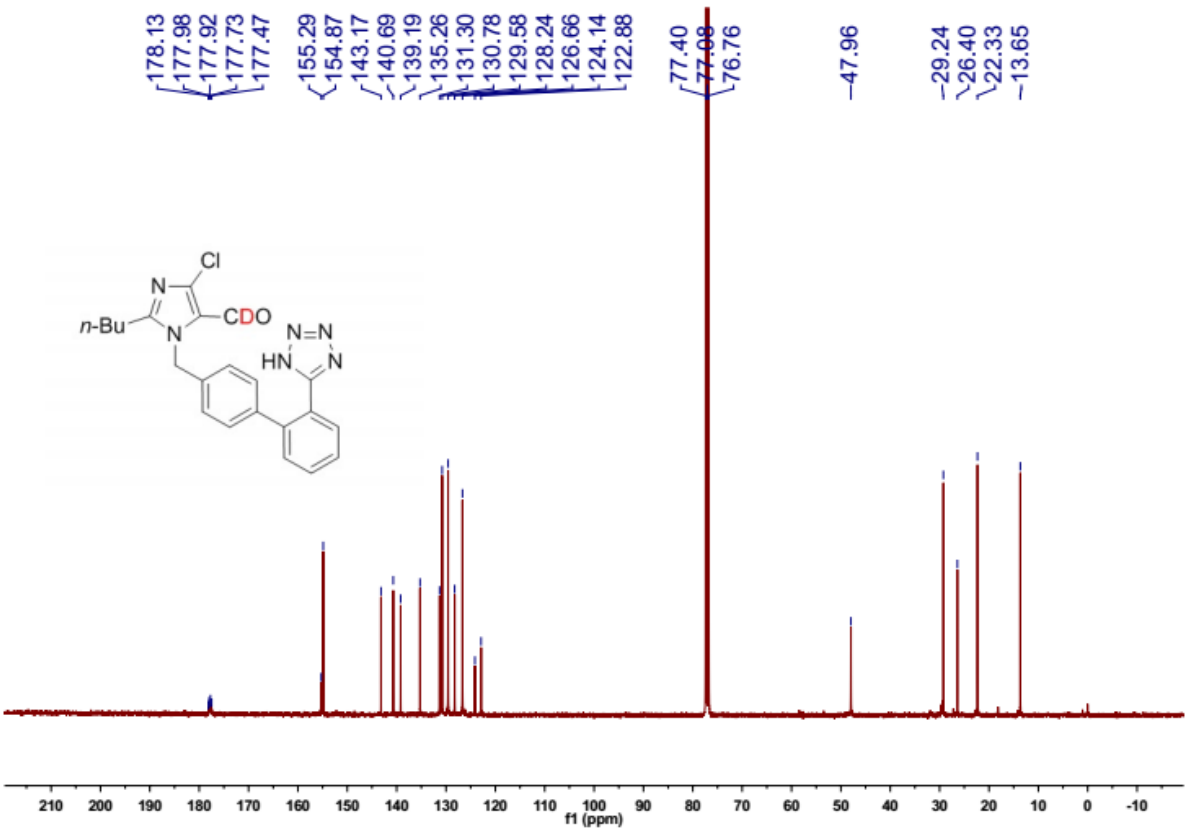

$^{1}$H NMR of deuterated aldehyde **7bi**



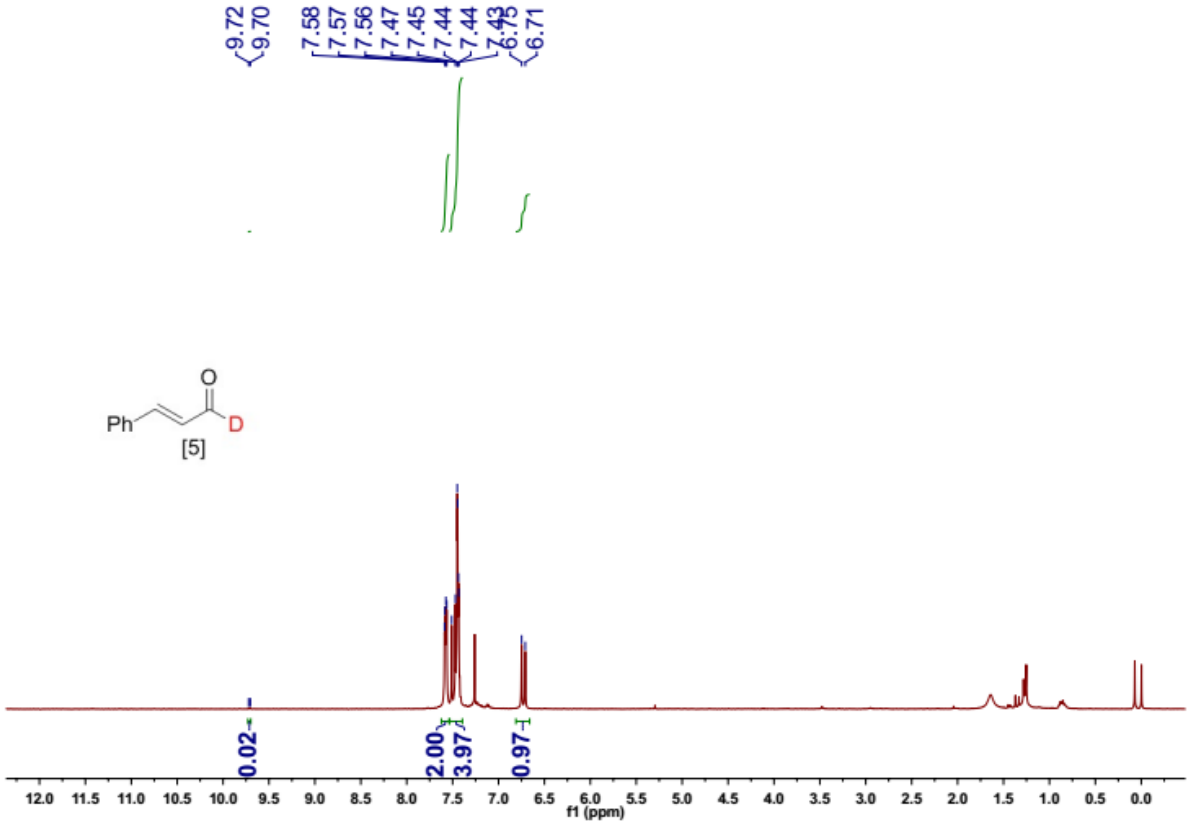
$^{2}$H NMR of deuterated aldehyde **7bi**



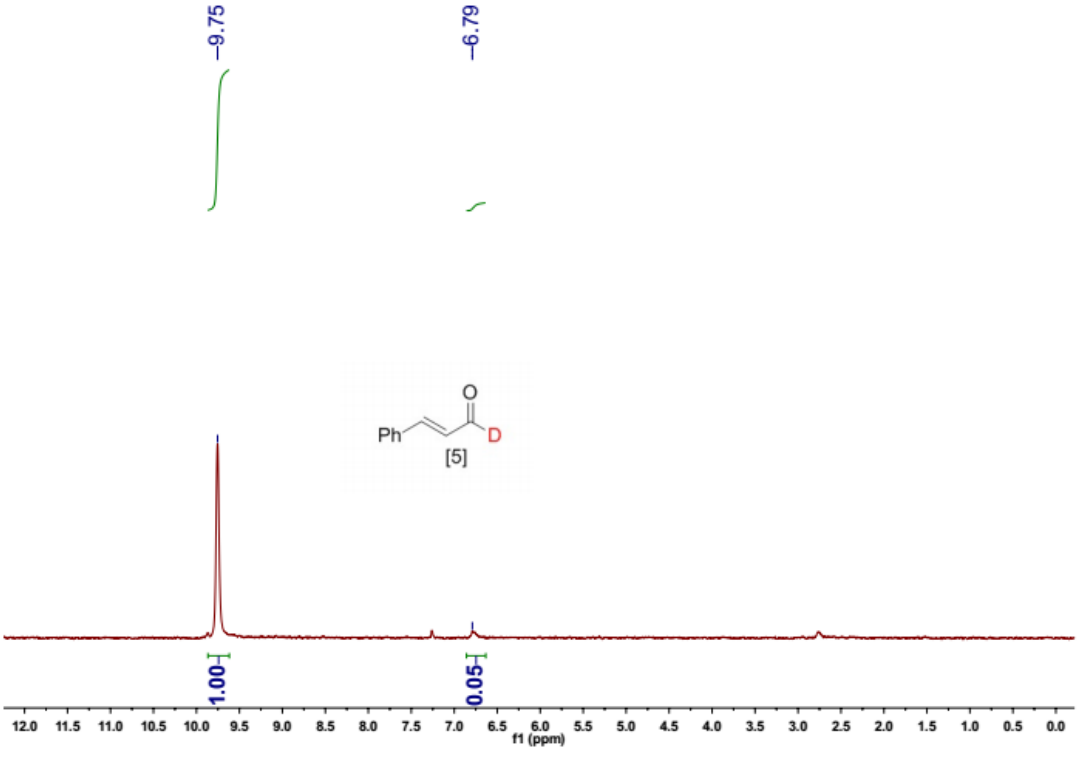

$^{13}$C NMR of deuterated aldehyde **7bi**



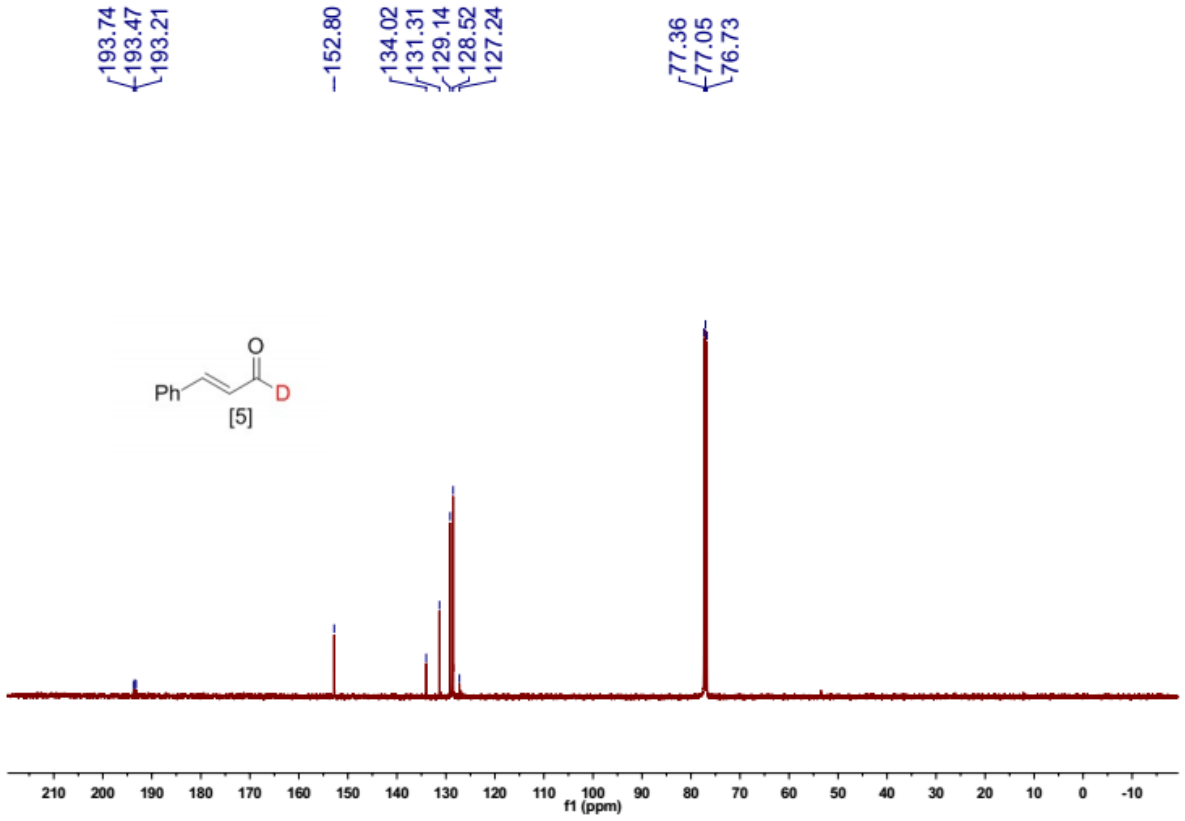
$^{1}$H NMR of deuterated aldehyde **10a**



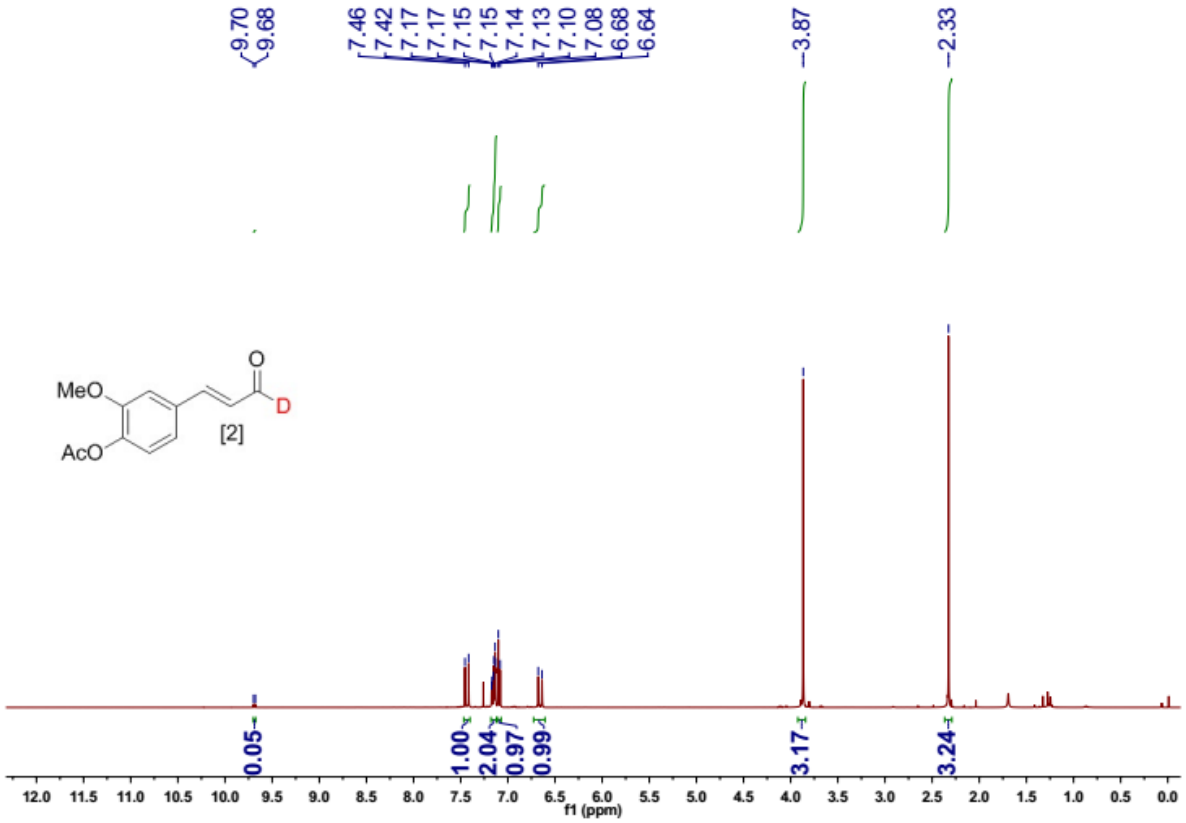

$^{2}$H NMR of deuterated aldehyde **10a**



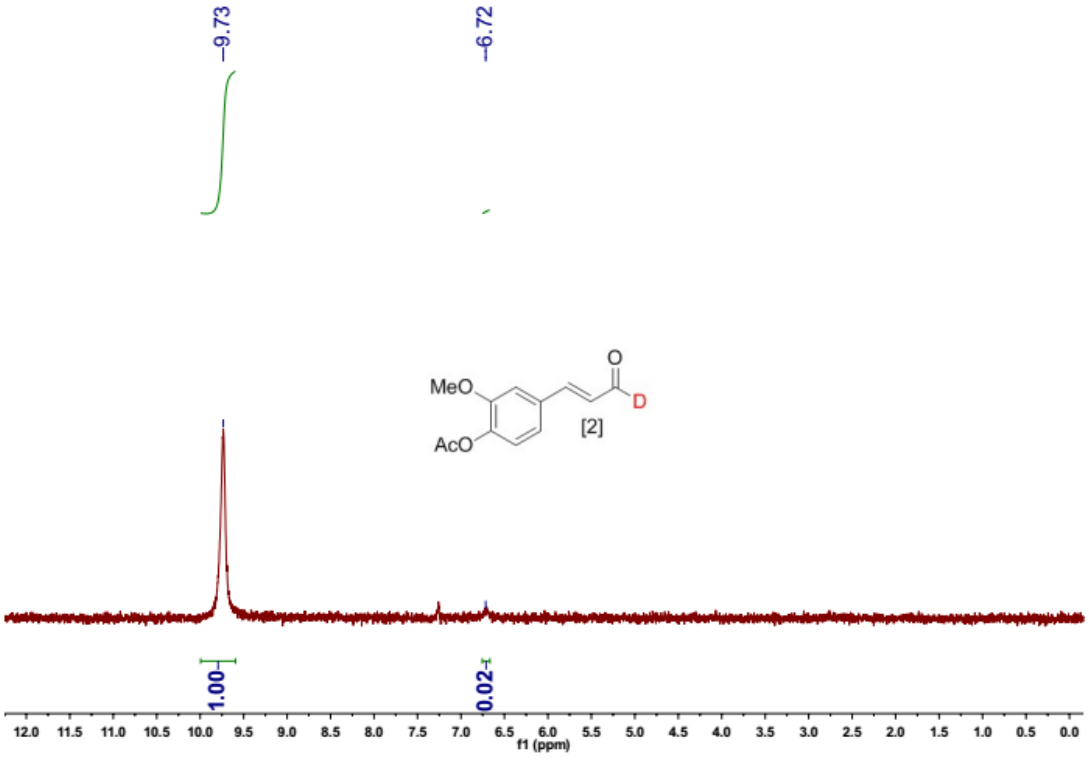
$^{13}$C NMR of deuterated aldehyde **10a**



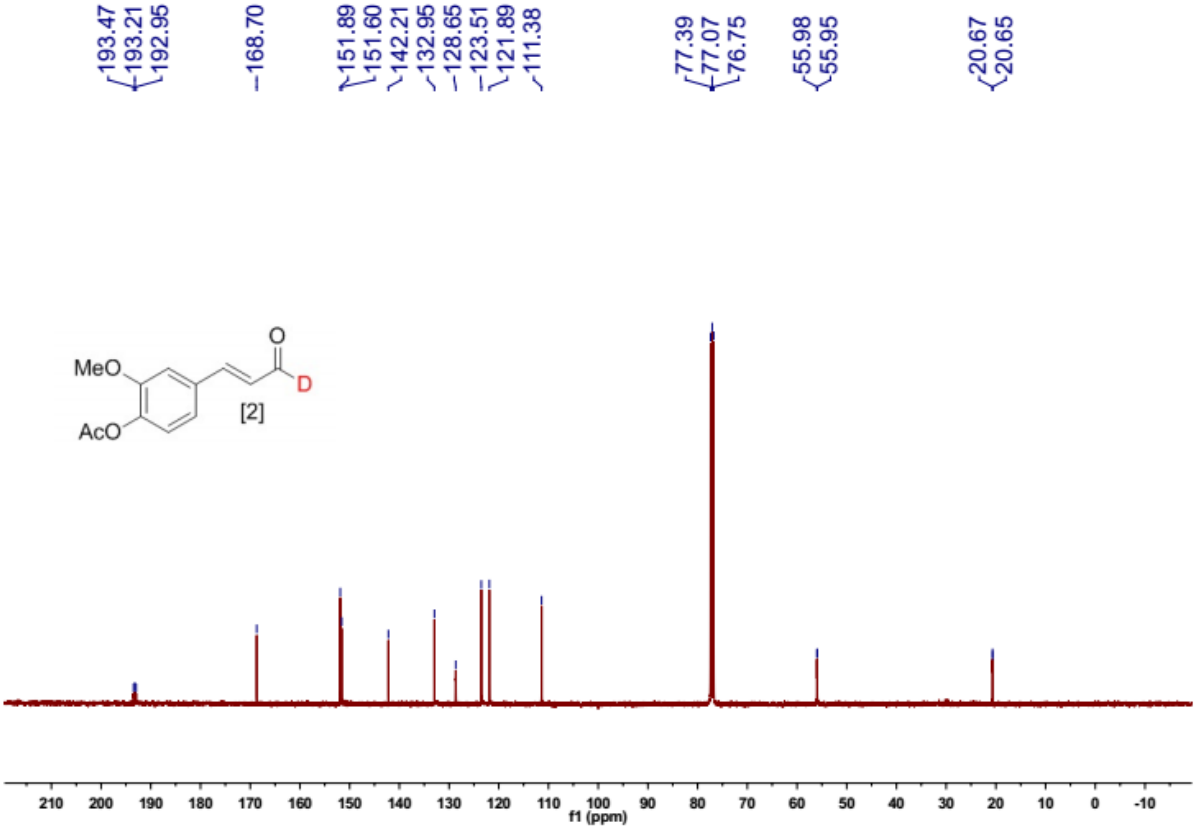
$^{1}$H NMR of deuterated aldehyde **10b**



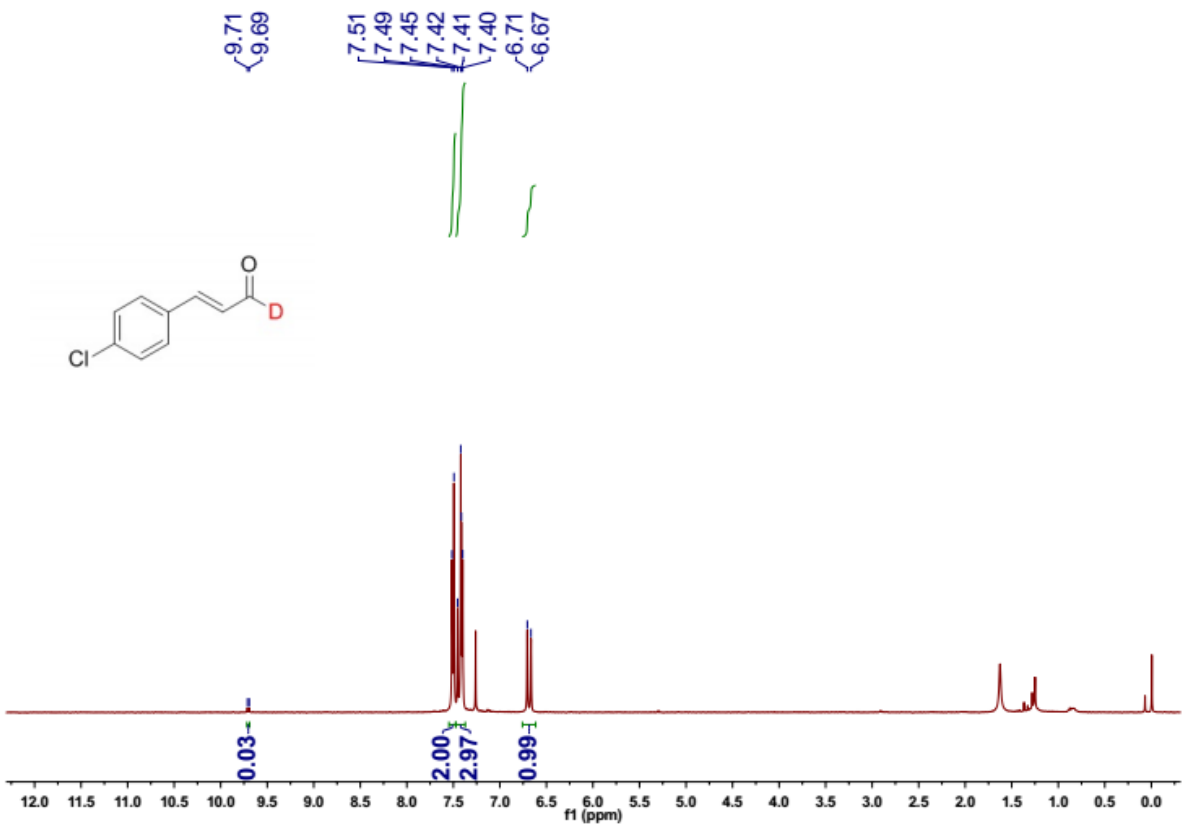

$^{2}$H NMR of deuterated aldehyde **10b**



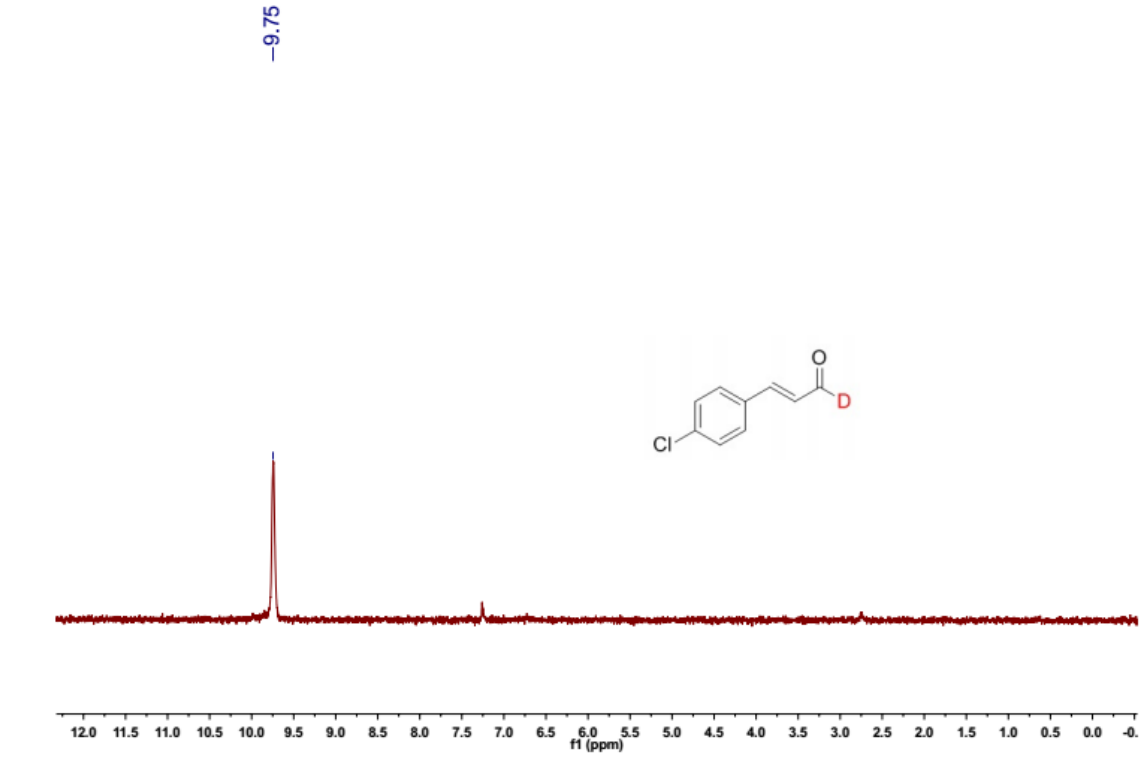
$^{13}$C NMR of deuterated aldehyde **10b**



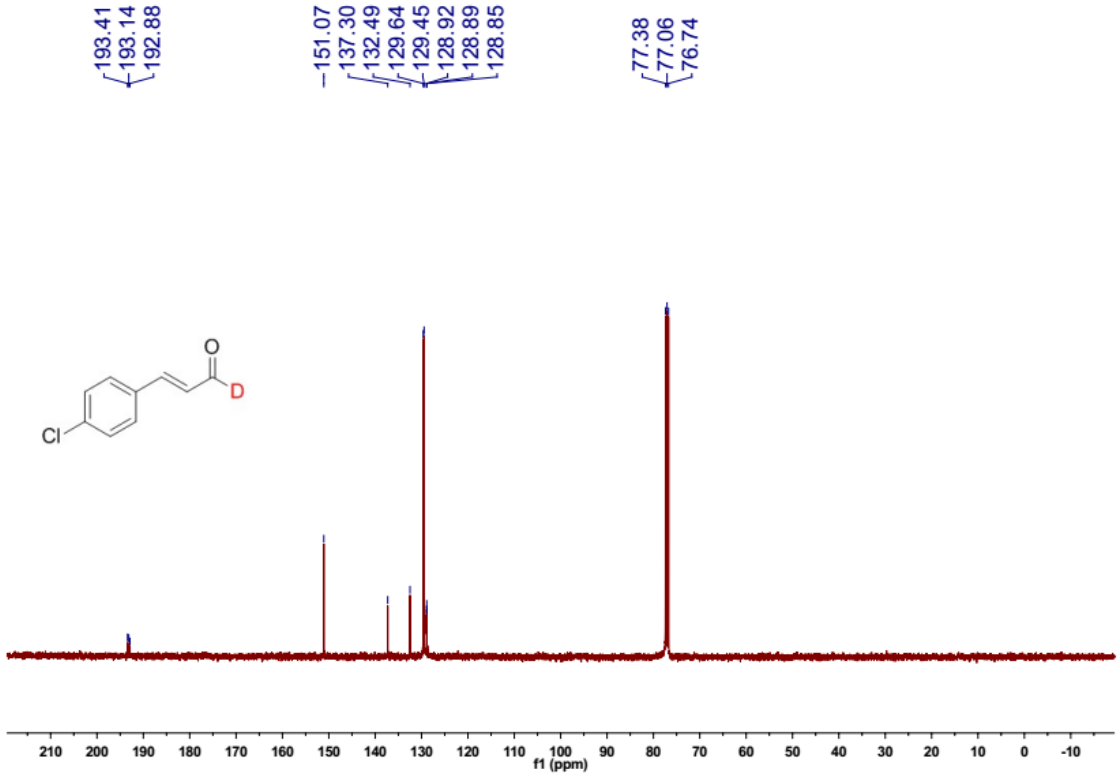
$^{1}$H NMR of deuterated aldehyde **10c**



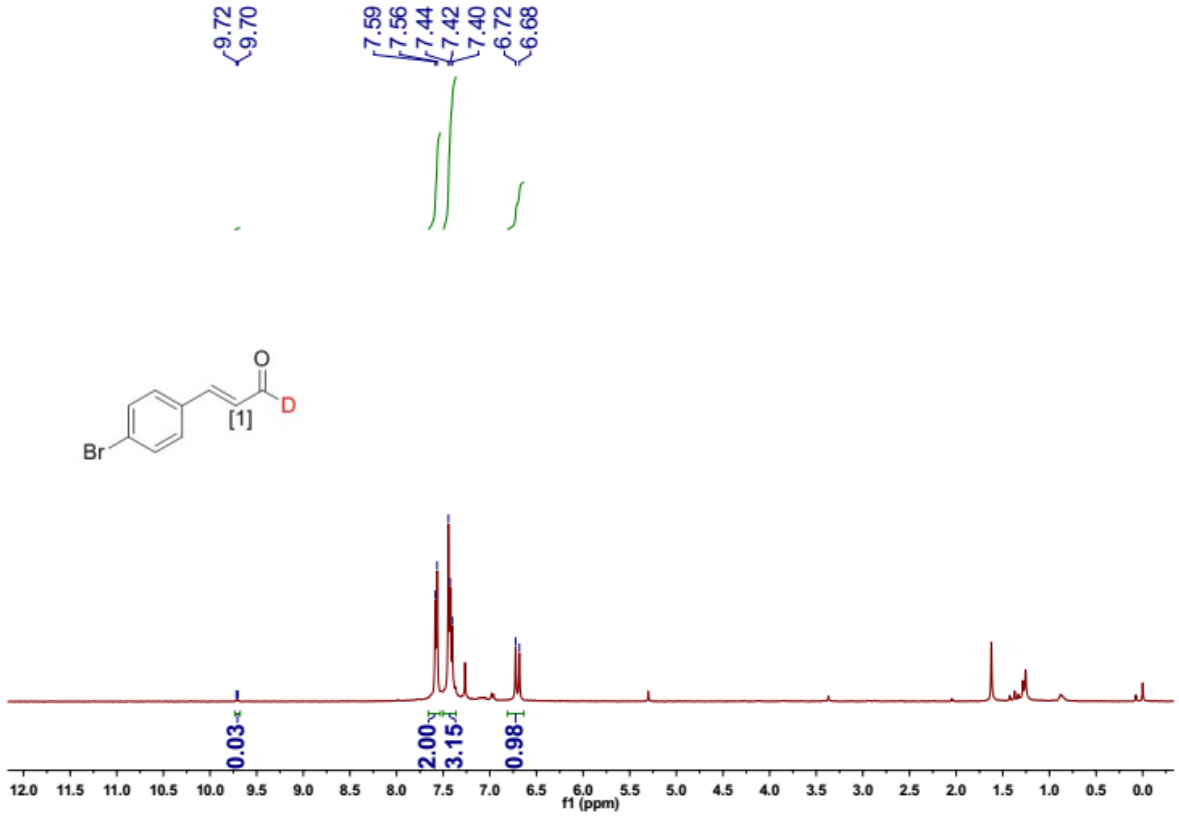

$^{2}$H NMR of deuterated aldehyde **10c**



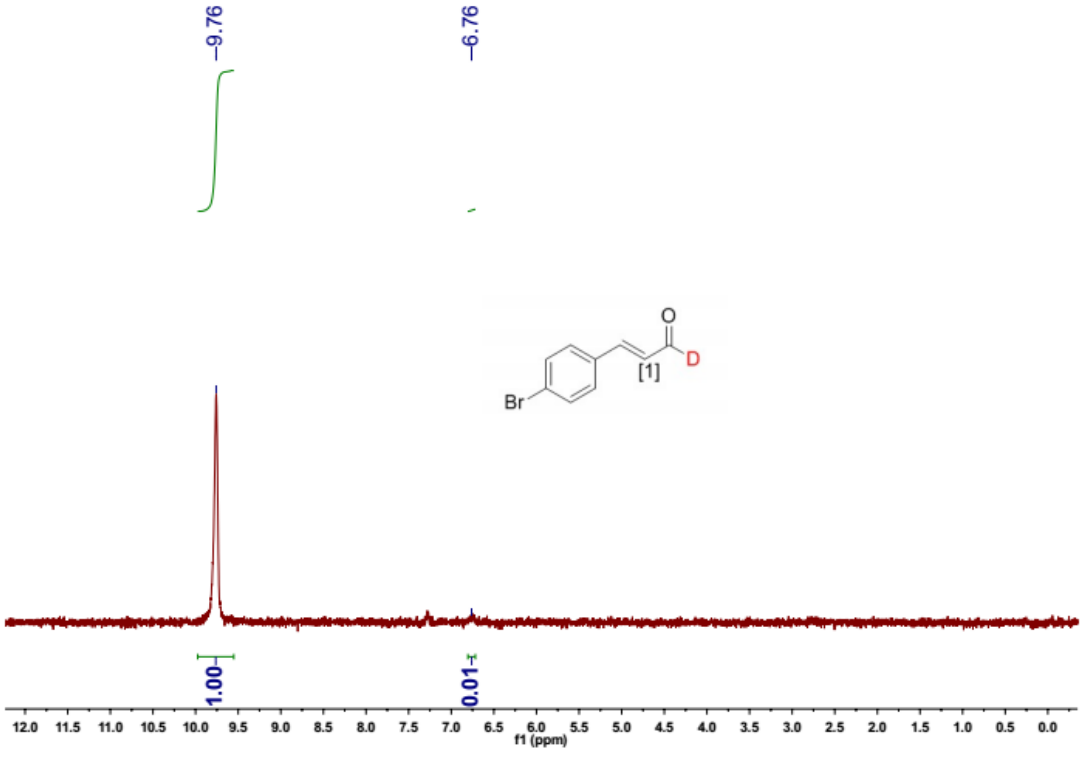
$^{13}$C NMR of deuterated aldehyde **10c**



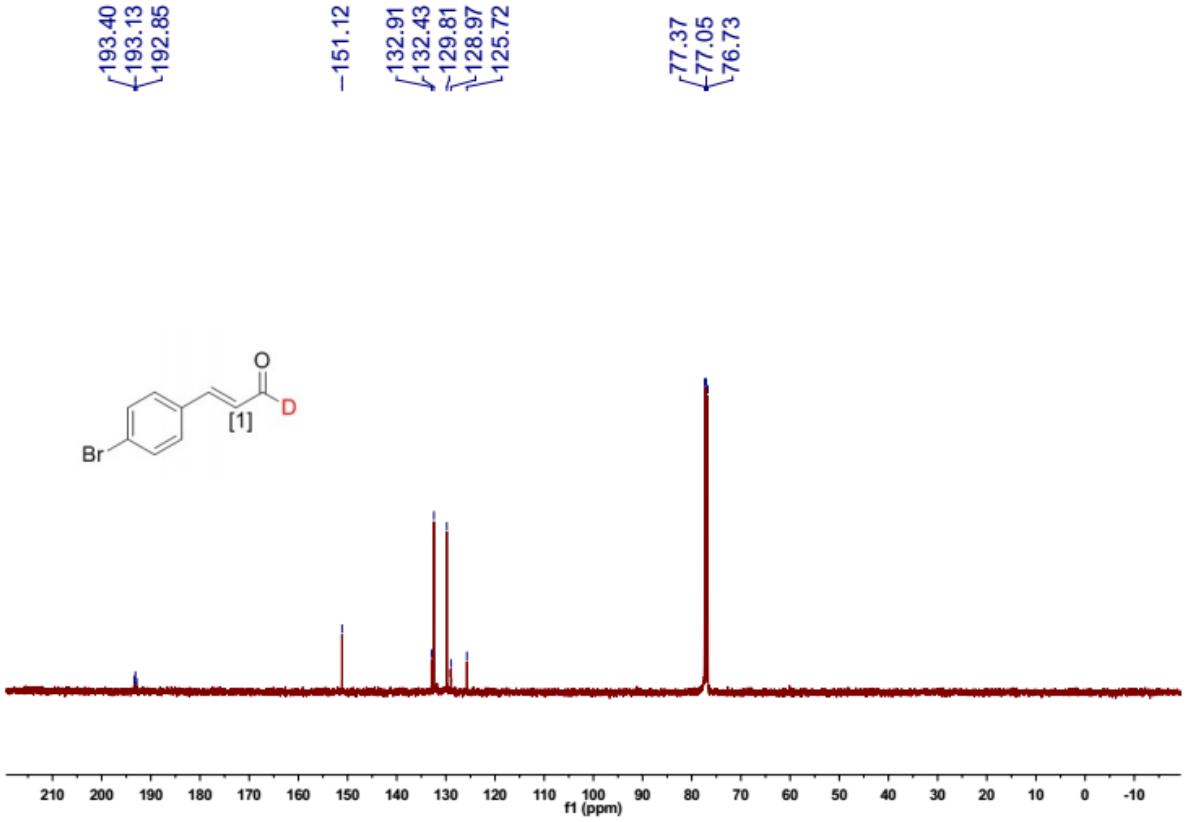
$^{1}$H NMR of deuterated aldehyde **10d**



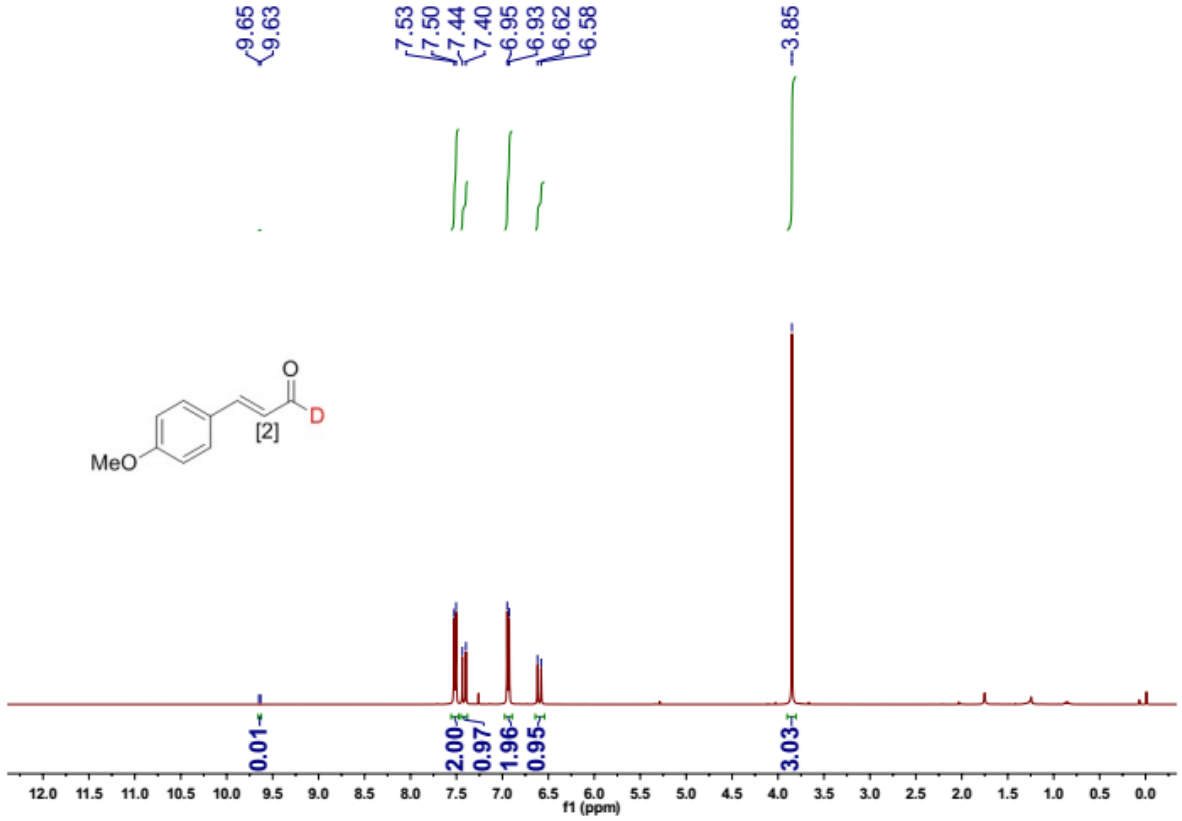

$^{2}$H NMR of deuterated aldehyde **10d**



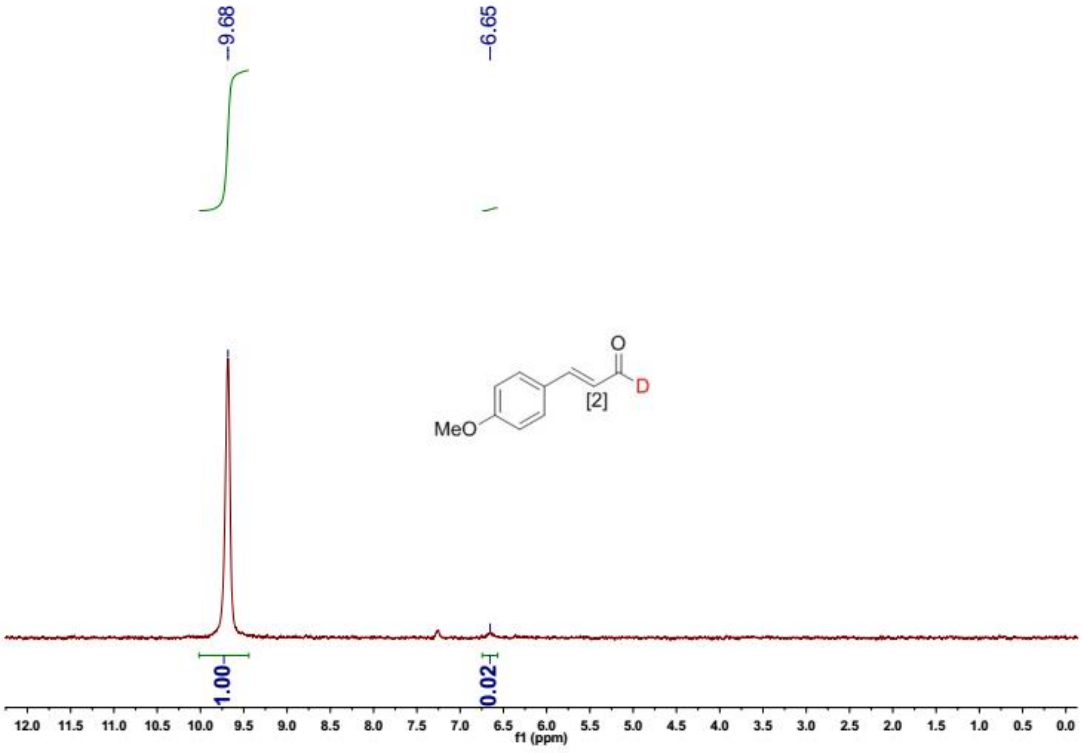
$^{13}$C NMR of deuterated aldehyde **10d**



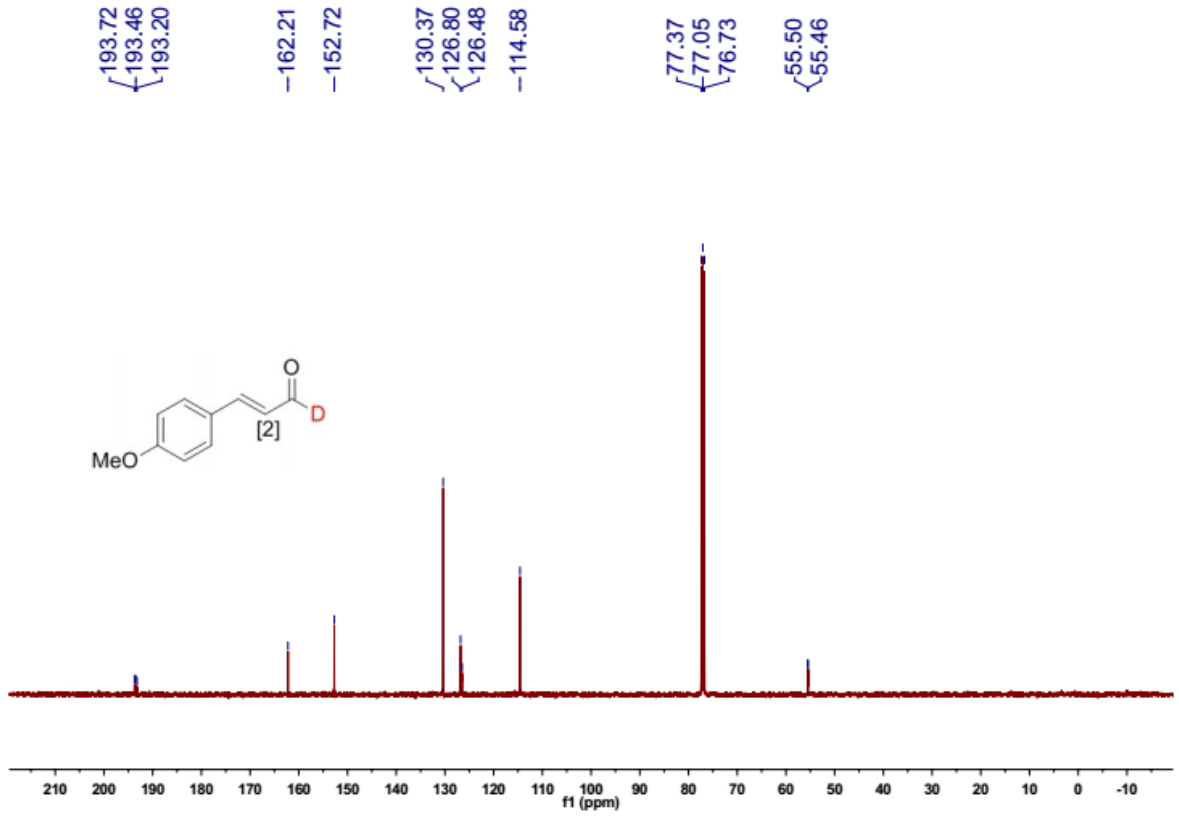
$^{1}$H NMR of deuterated aldehyde **10e**



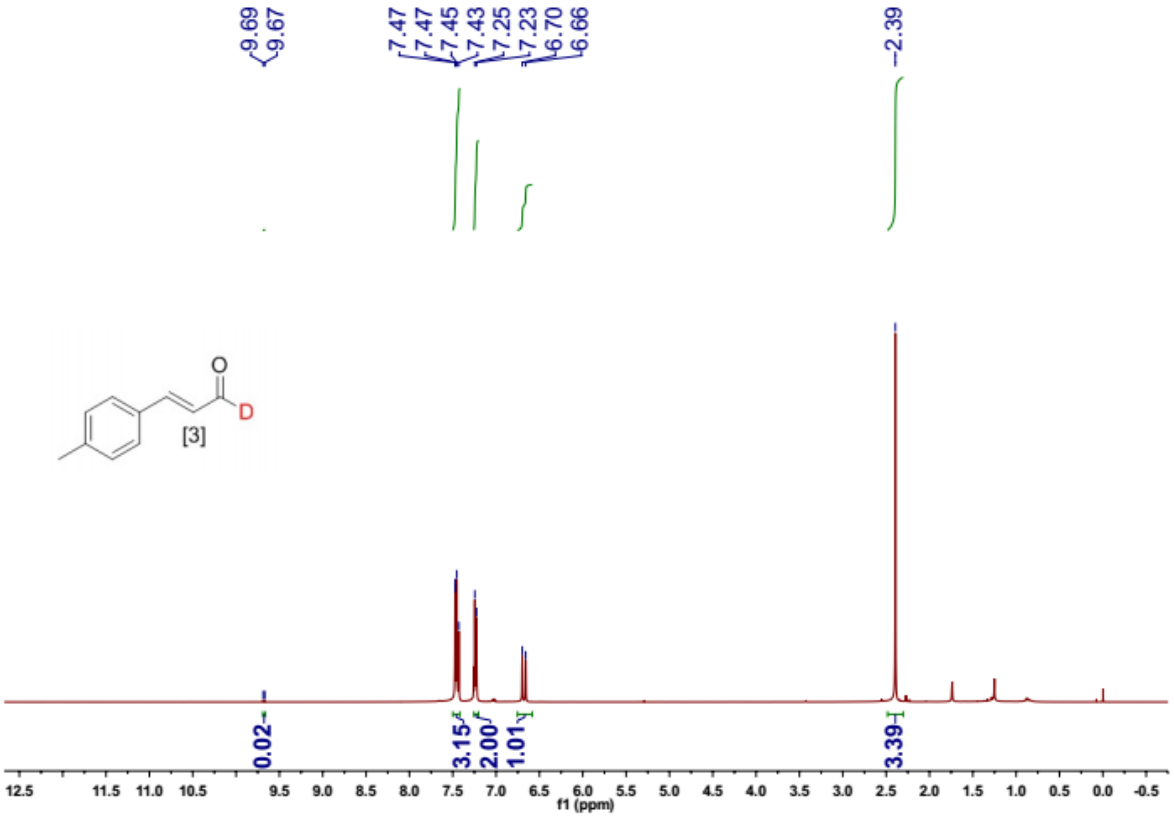

$^{2}$H NMR of deuterated aldehyde **10e**



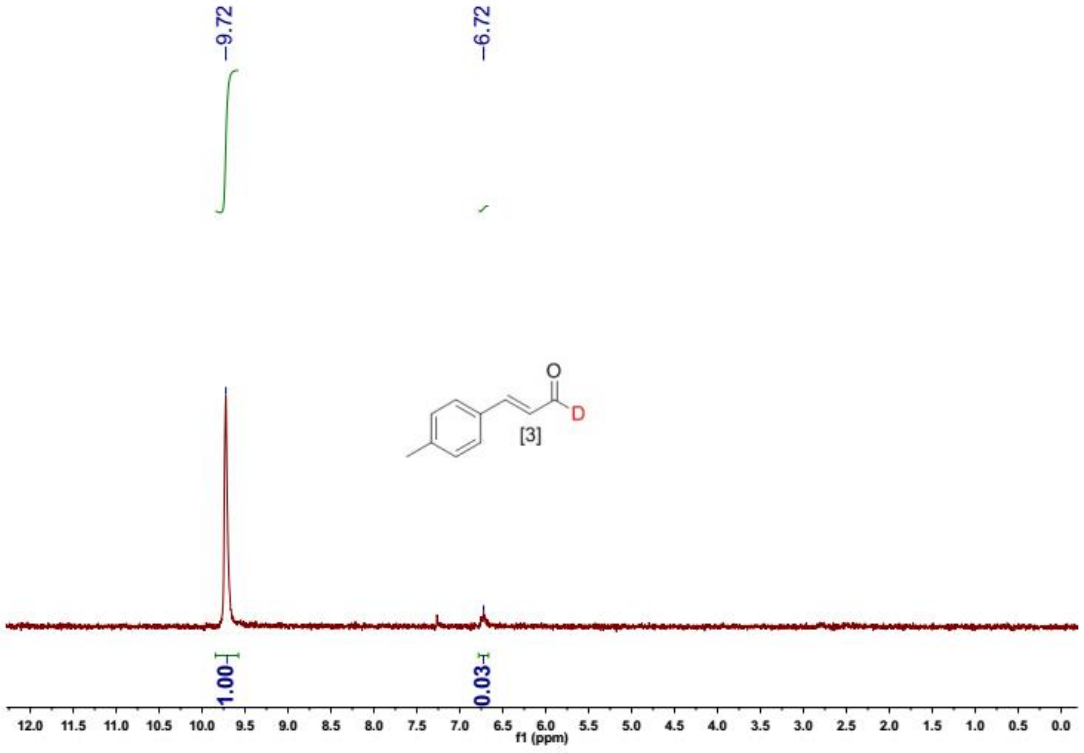
$^{13}$C NMR of deuterated aldehyde **10e**



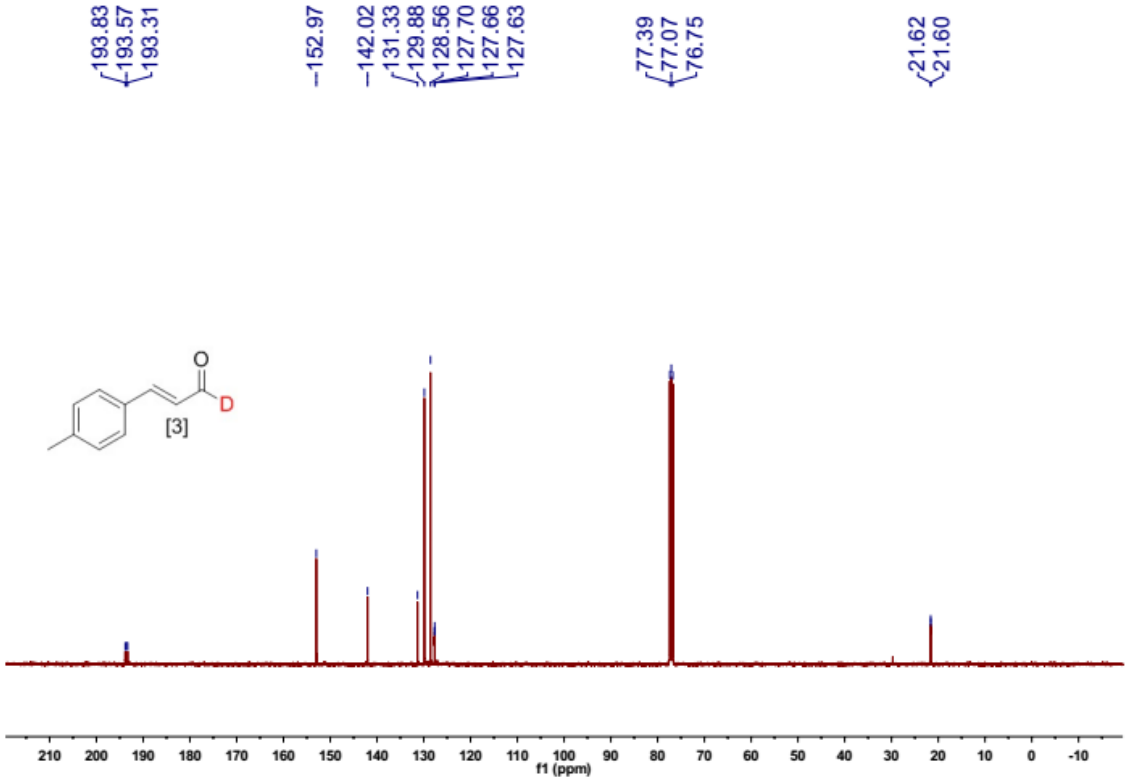
$^{1}$H NMR of deuterated aldehyde **10f**



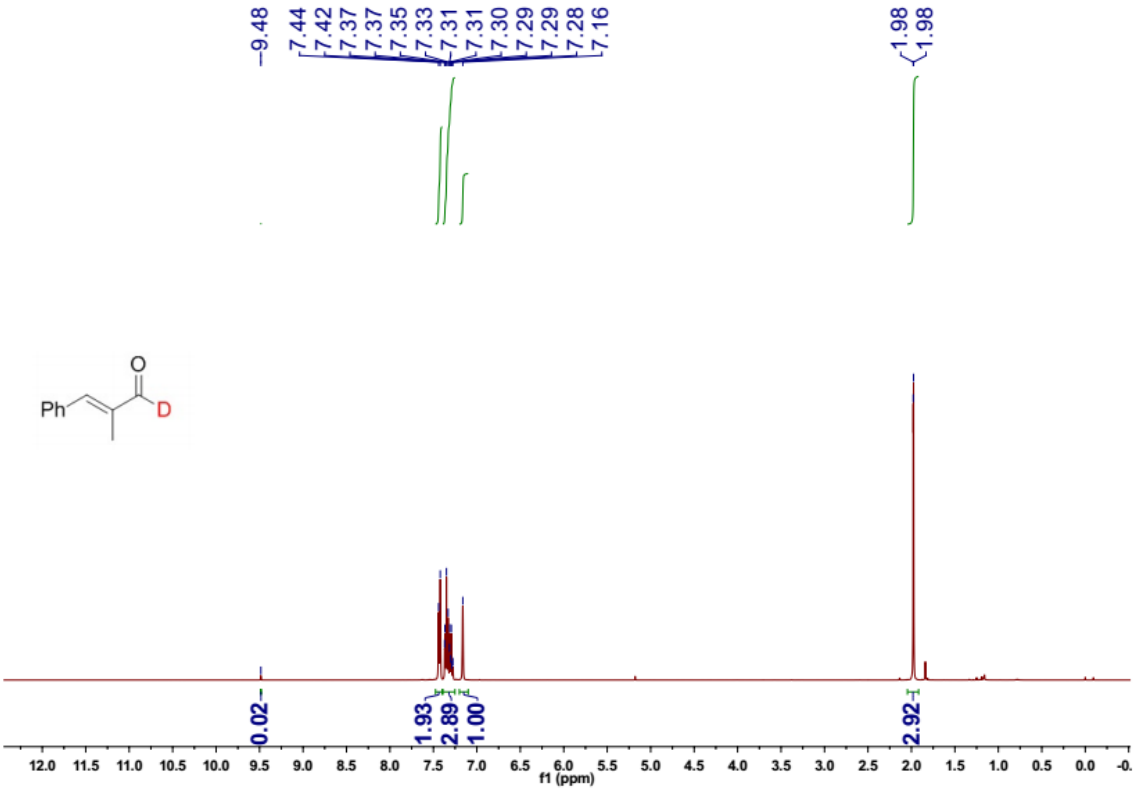

$^{2}$H NMR of deuterated aldehyde **10f**



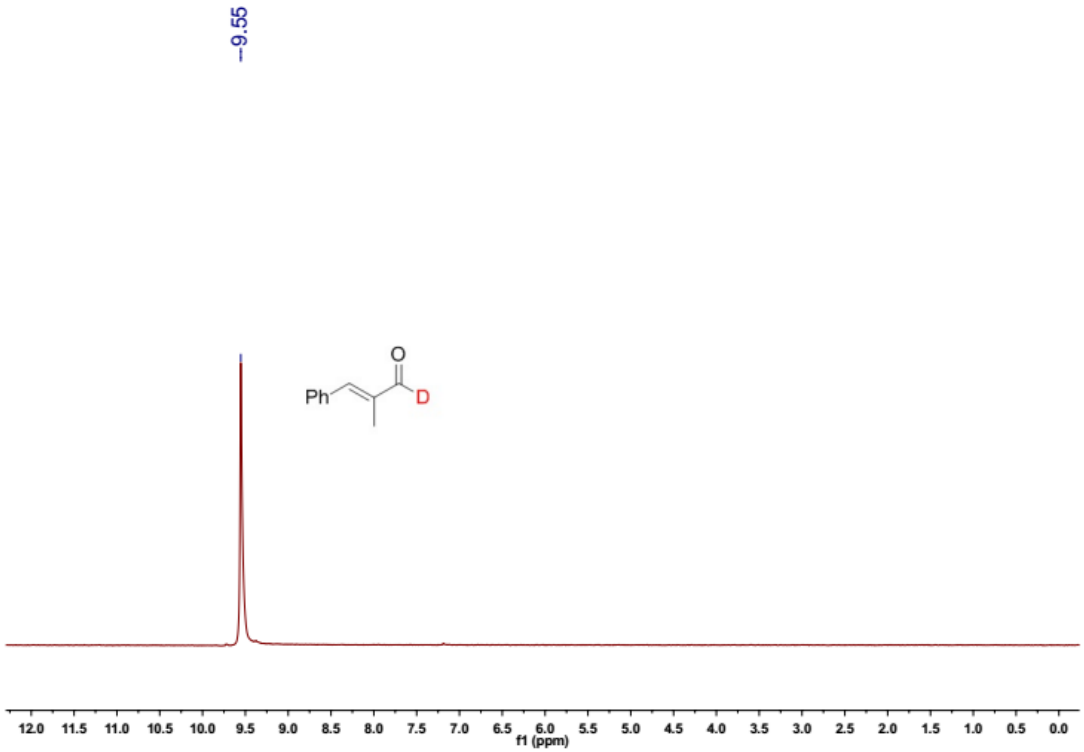
$^{13}$C NMR of deuterated aldehyde **10f**



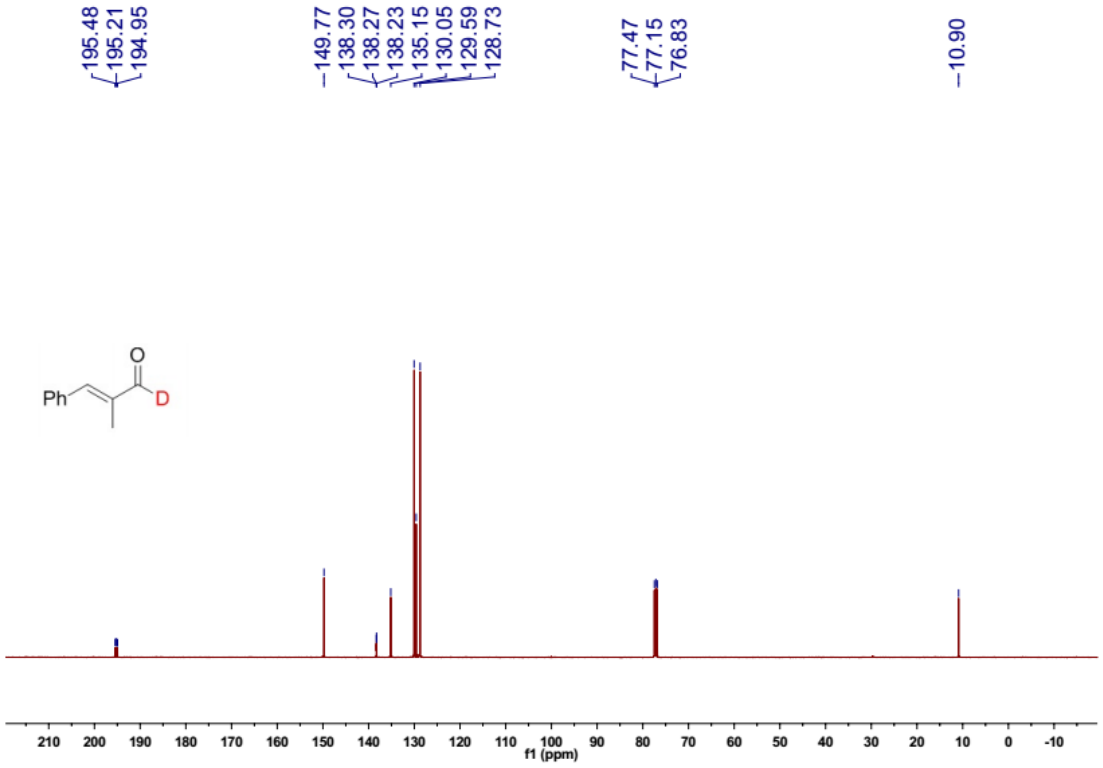
$^{1}$H NMR of deuterated aldehyde **10g**



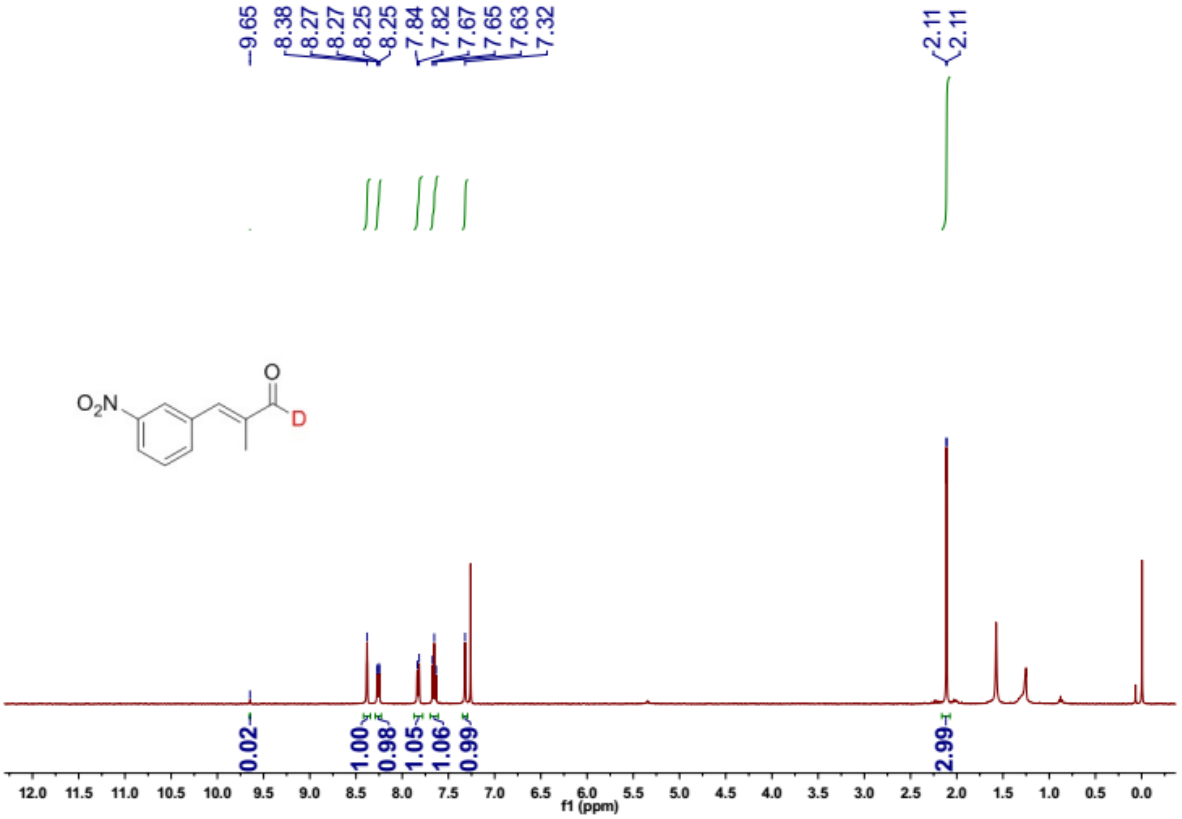

$^{2}$H NMR of deuterated aldehyde **10g**



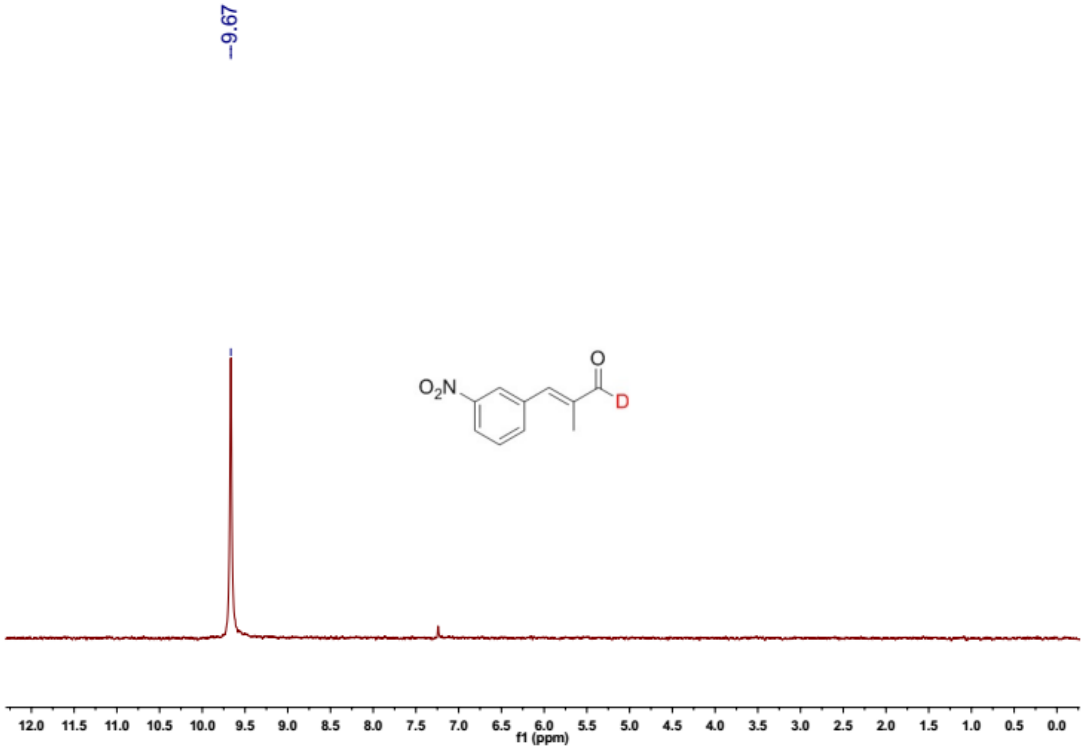
$^{13}$C NMR of deuterated aldehyde **10g**



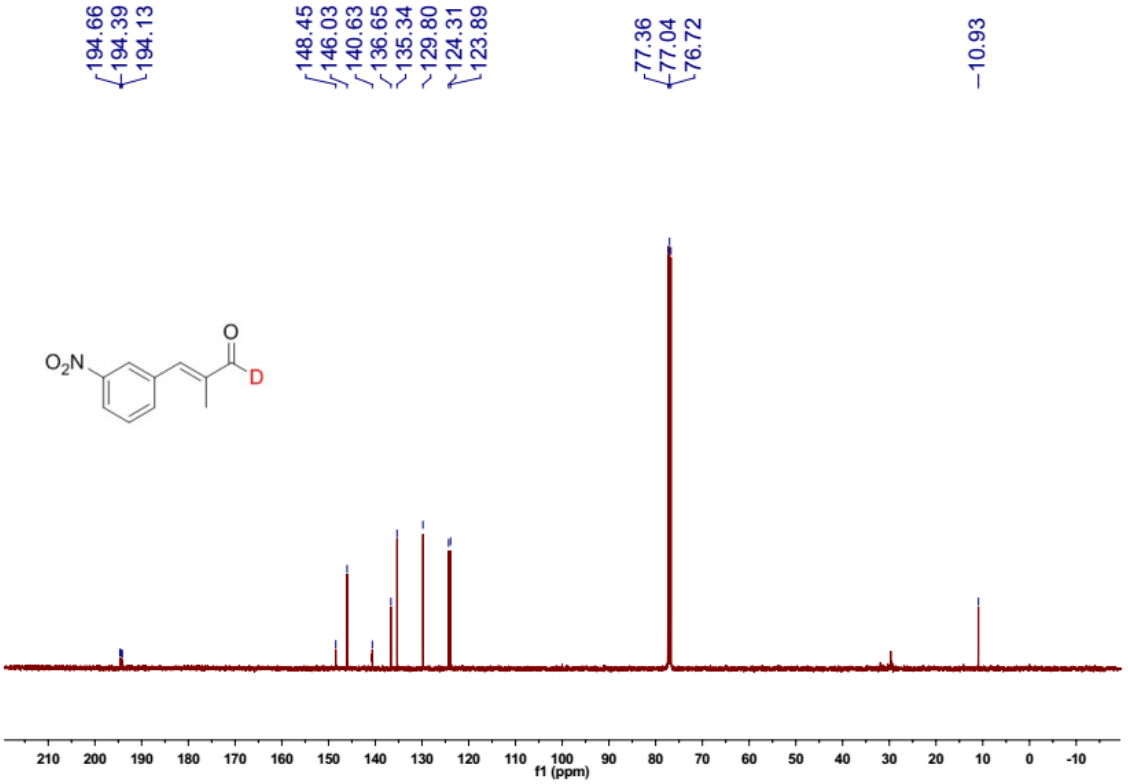
$^{1}$H NMR of deuterated aldehyde **10h**



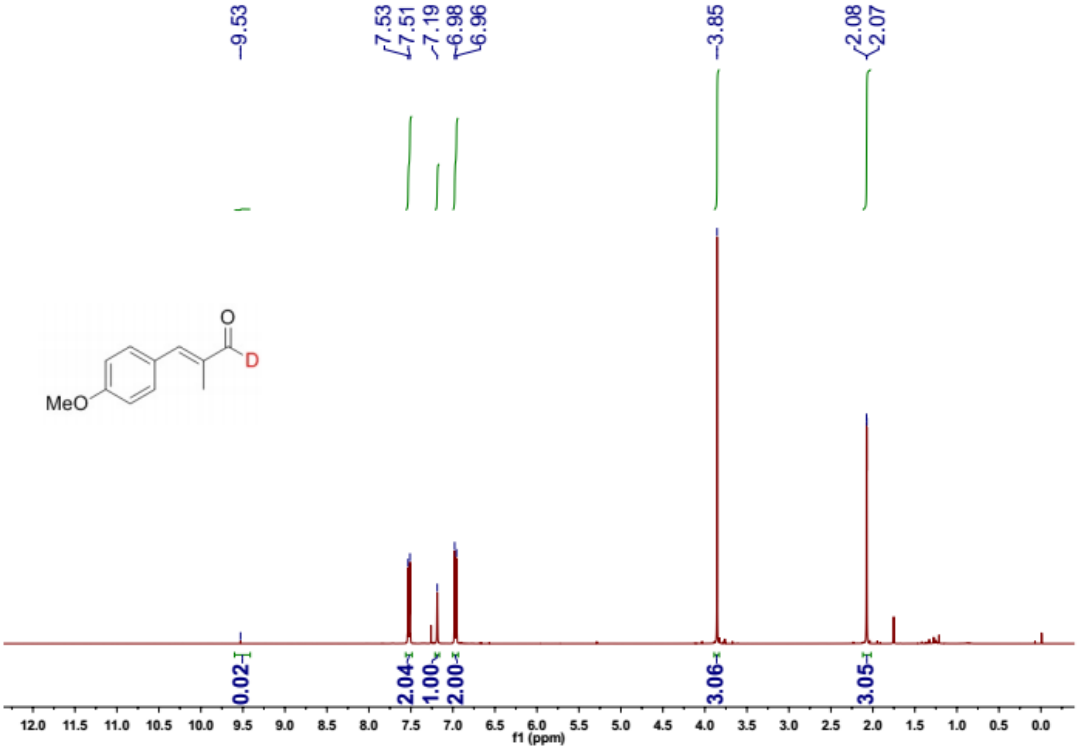

$^{2}$H NMR of deuterated aldehyde **10h**



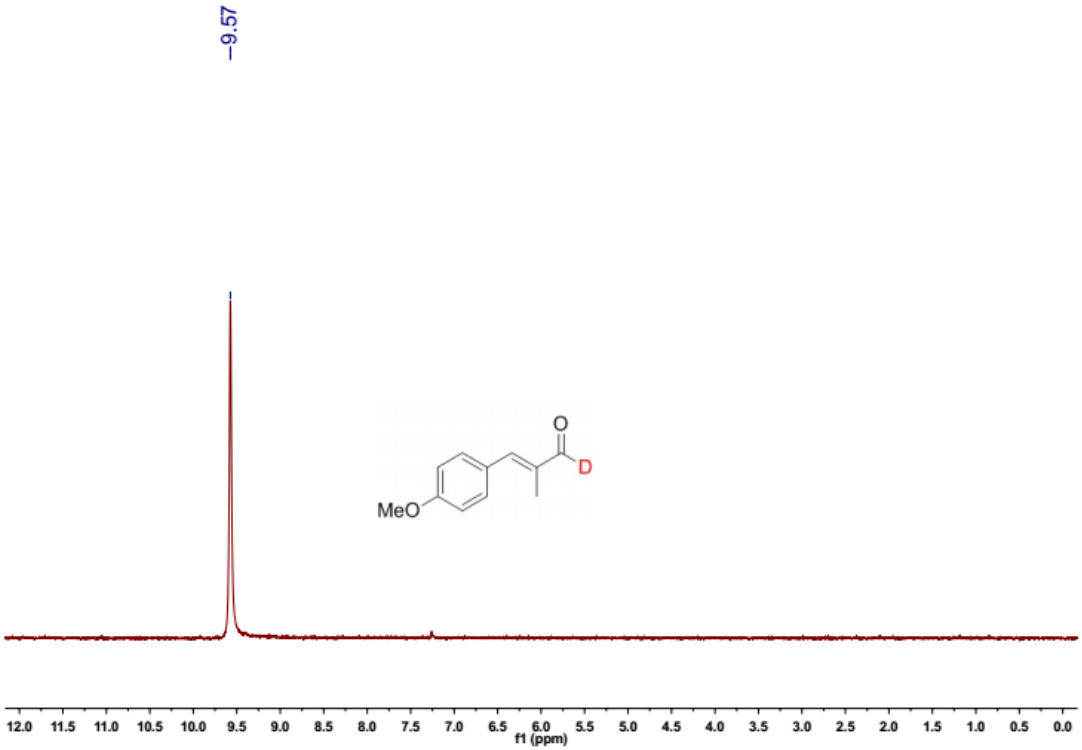
$^{13}$C NMR of deuterated aldehyde **10h**



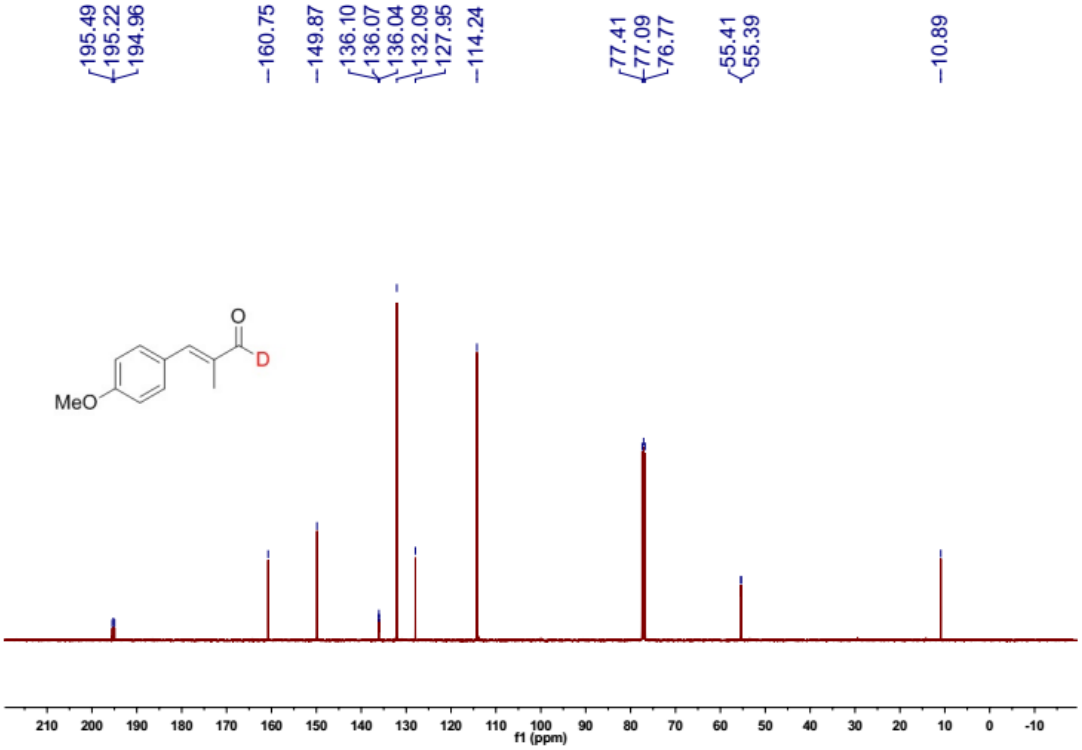
$^{1}$H NMR of deuterated aldehyde **10i**



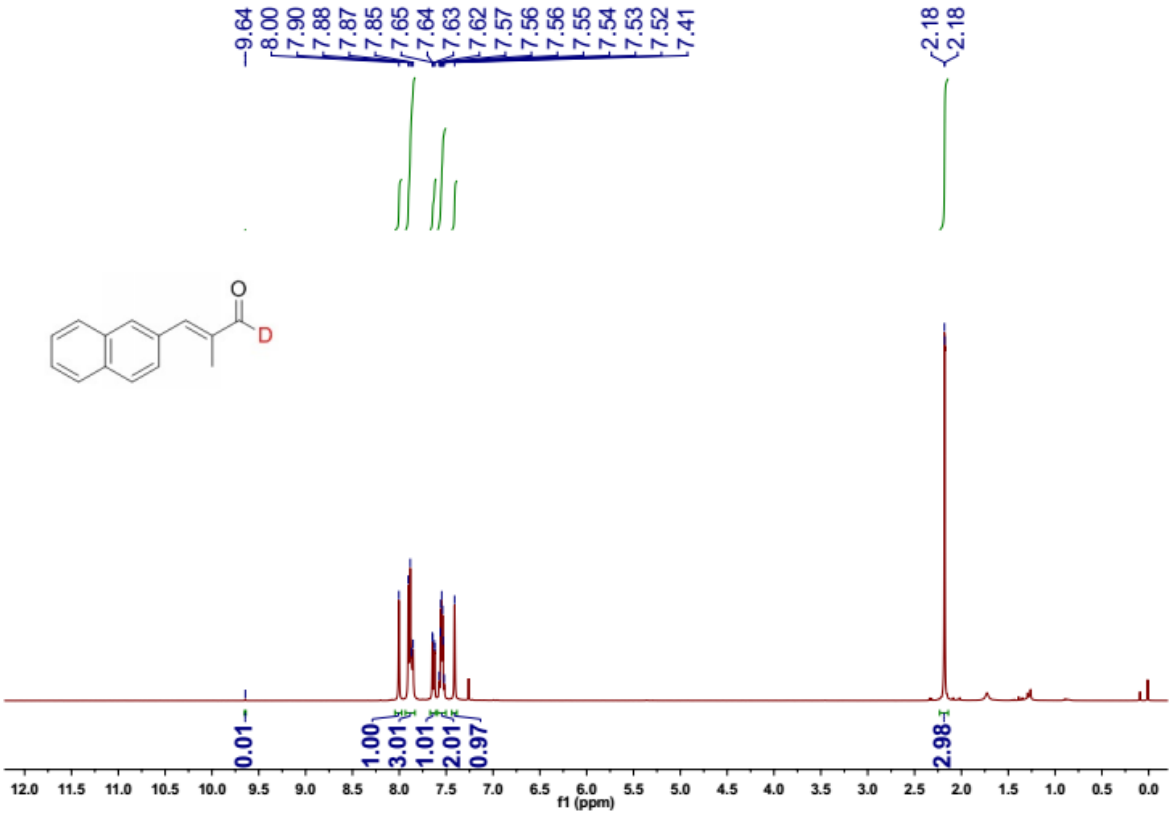

$^{2}$H NMR of deuterated aldehyde **10i**



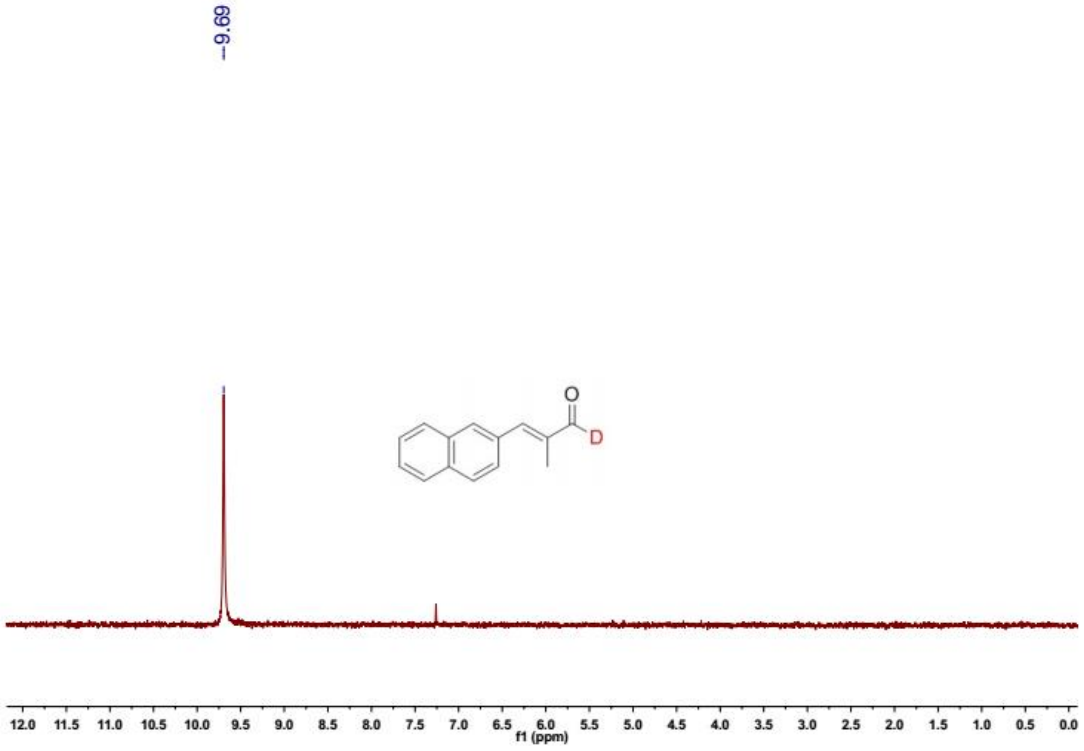
$^{13}$C NMR of deuterated aldehyde **10i**



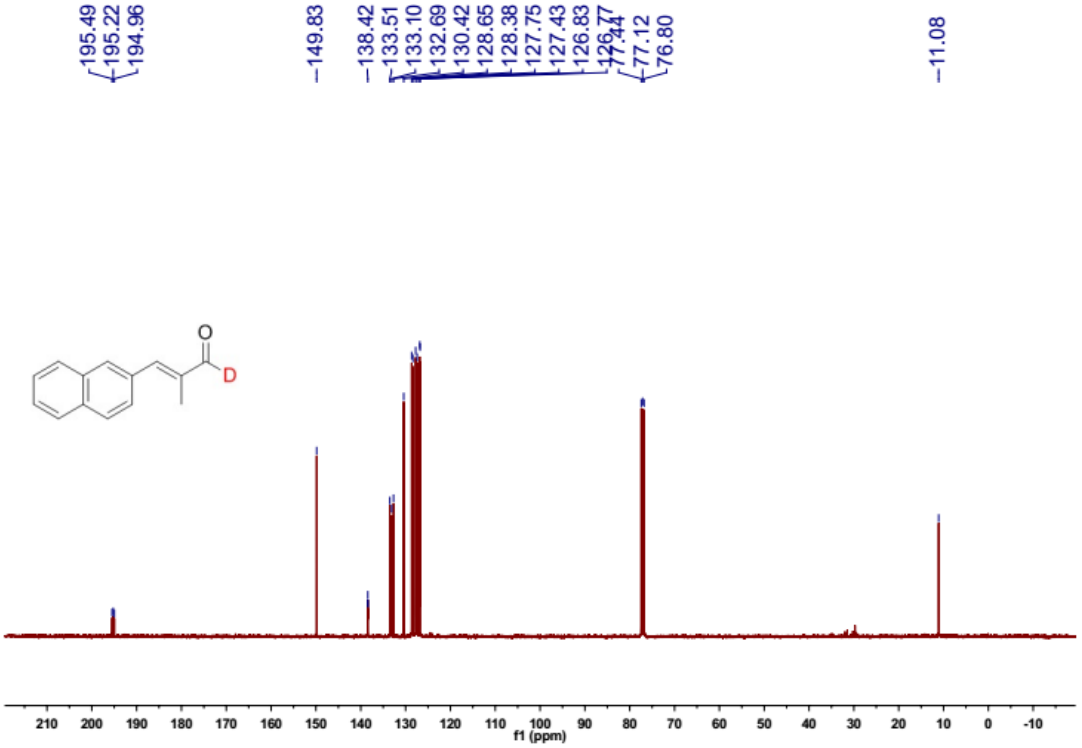
$^{1}$H NMR of deuterated aldehyde **10j**



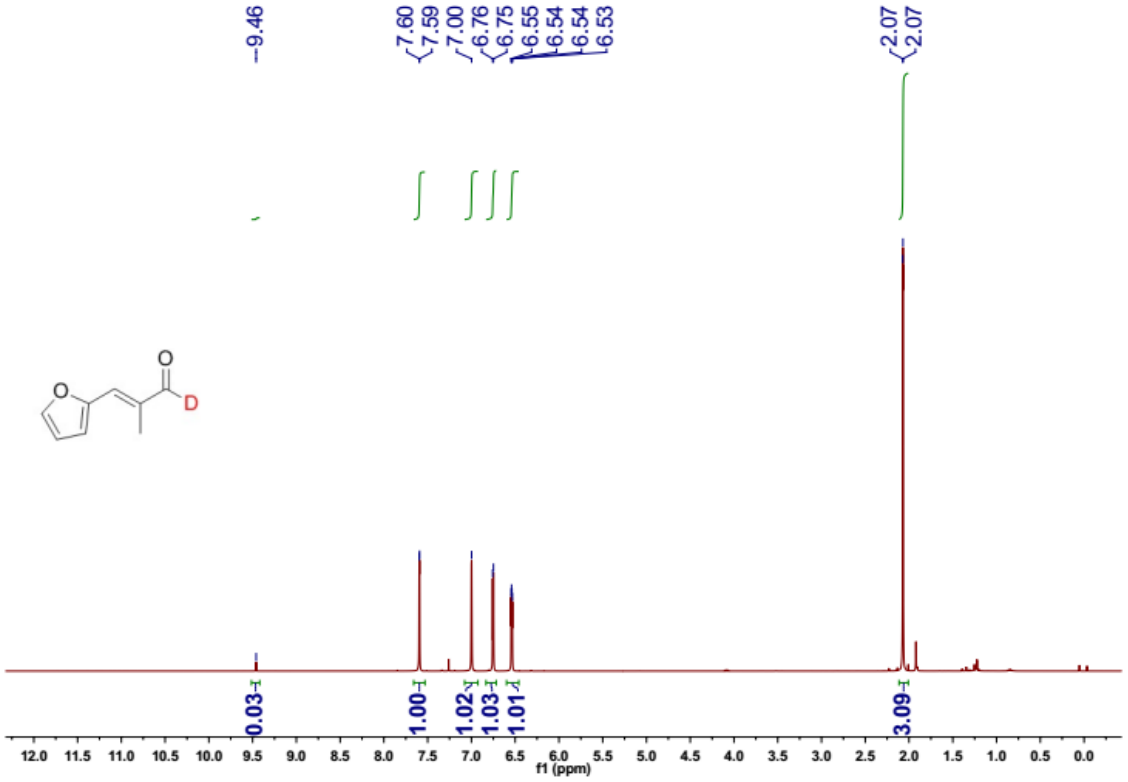

$^{2}$H NMR of deuterated aldehyde **10j**



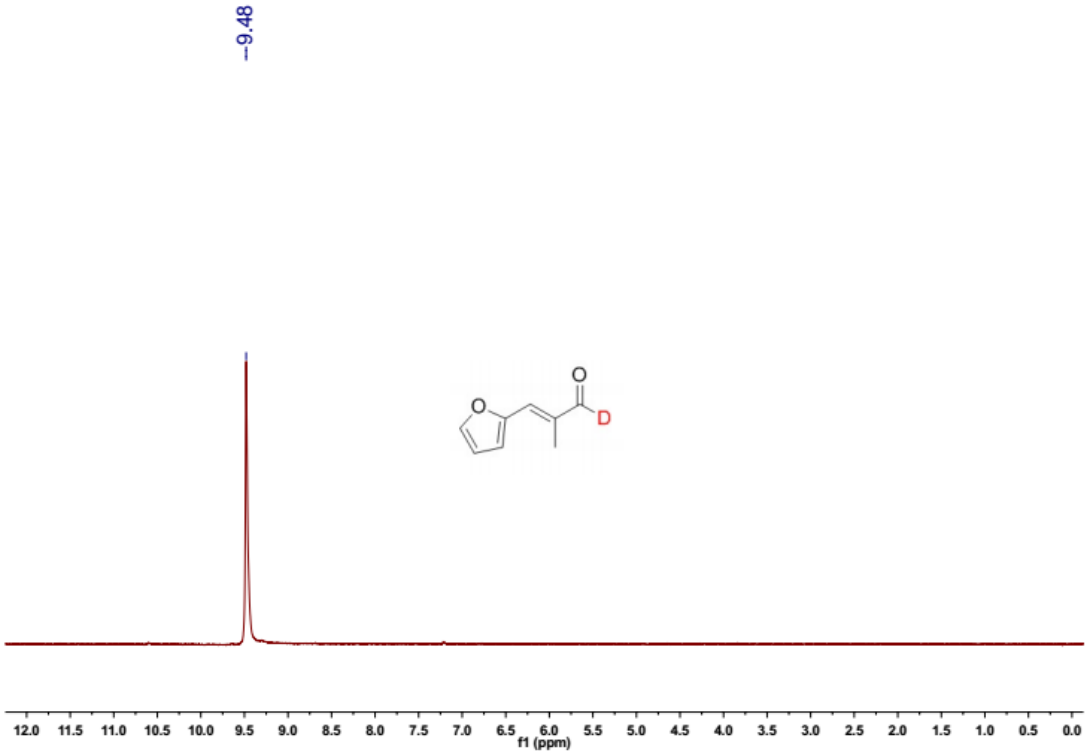
$^{13}$C NMR of deuterated aldehyde **10j**



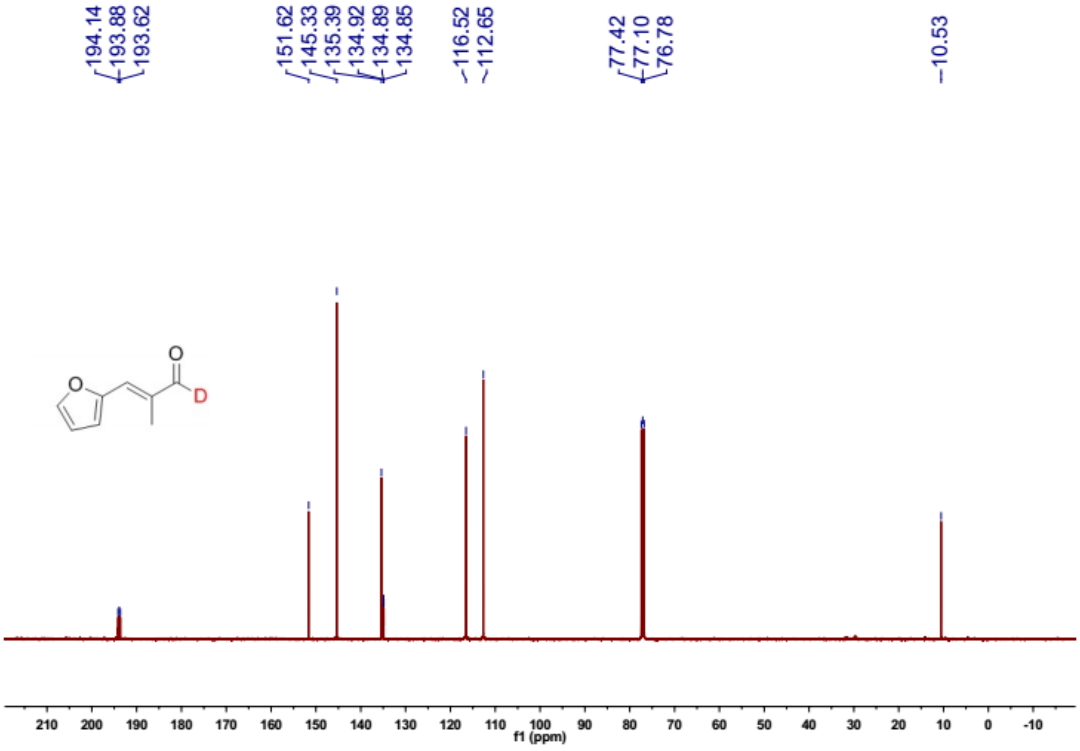
$^{1}$H NMR of deuterated aldehyde **10k**



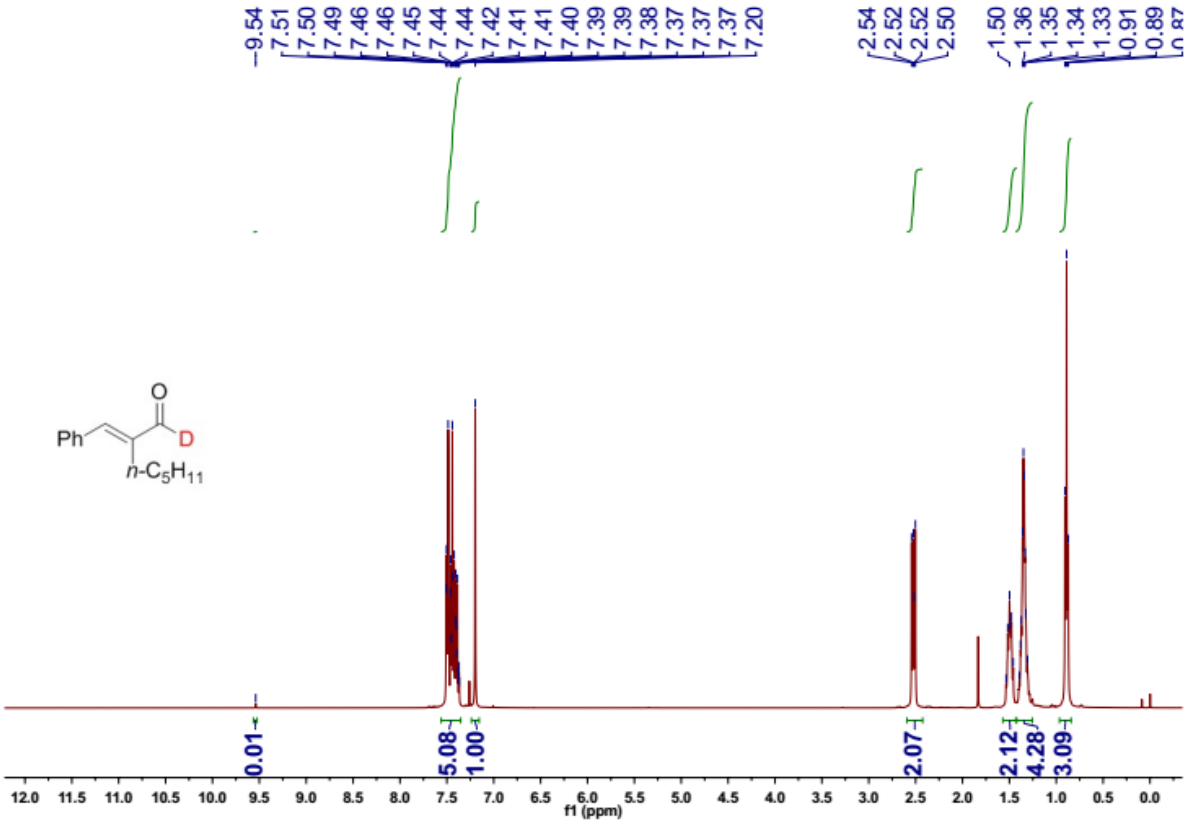

$^{2}$H NMR of deuterated aldehyde **10K**



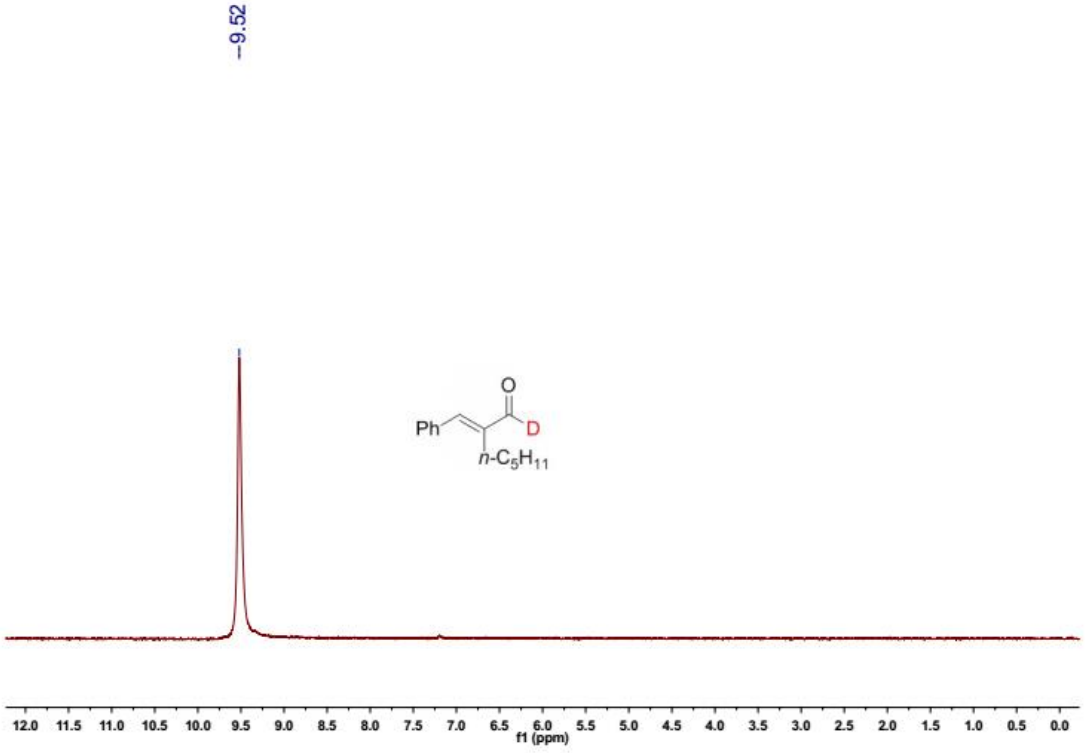
$^{13}$C NMR of deuterated aldehyde **10k**



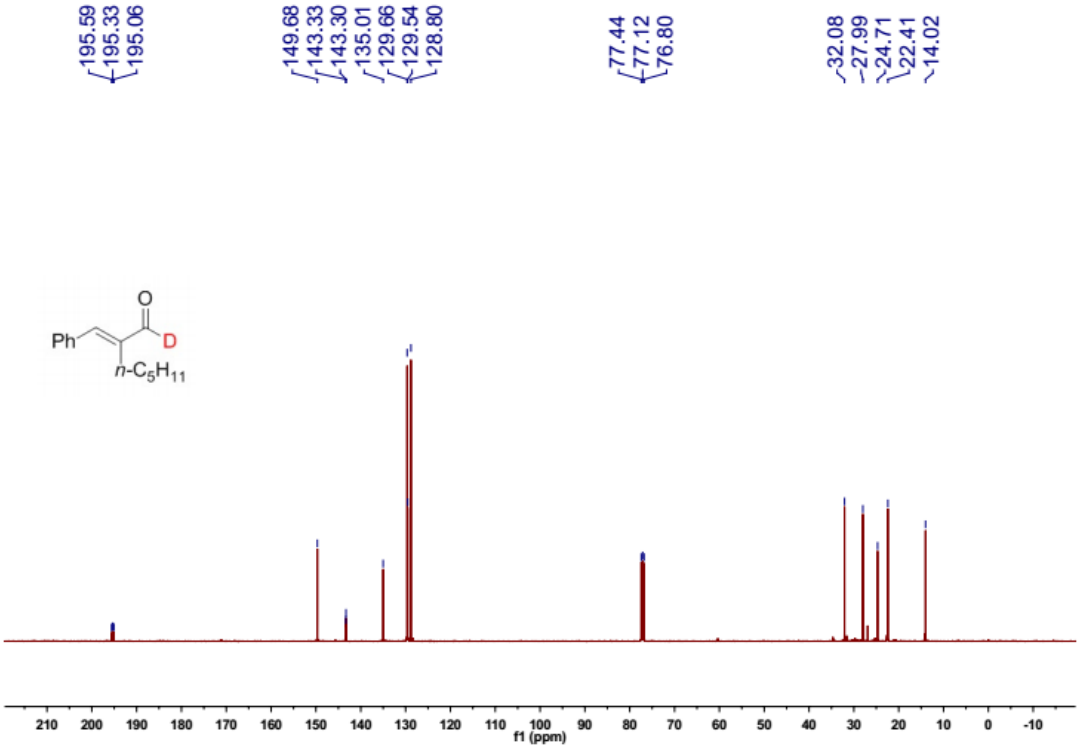
$^{1}$H NMR of deuterated aldehyde **10l**



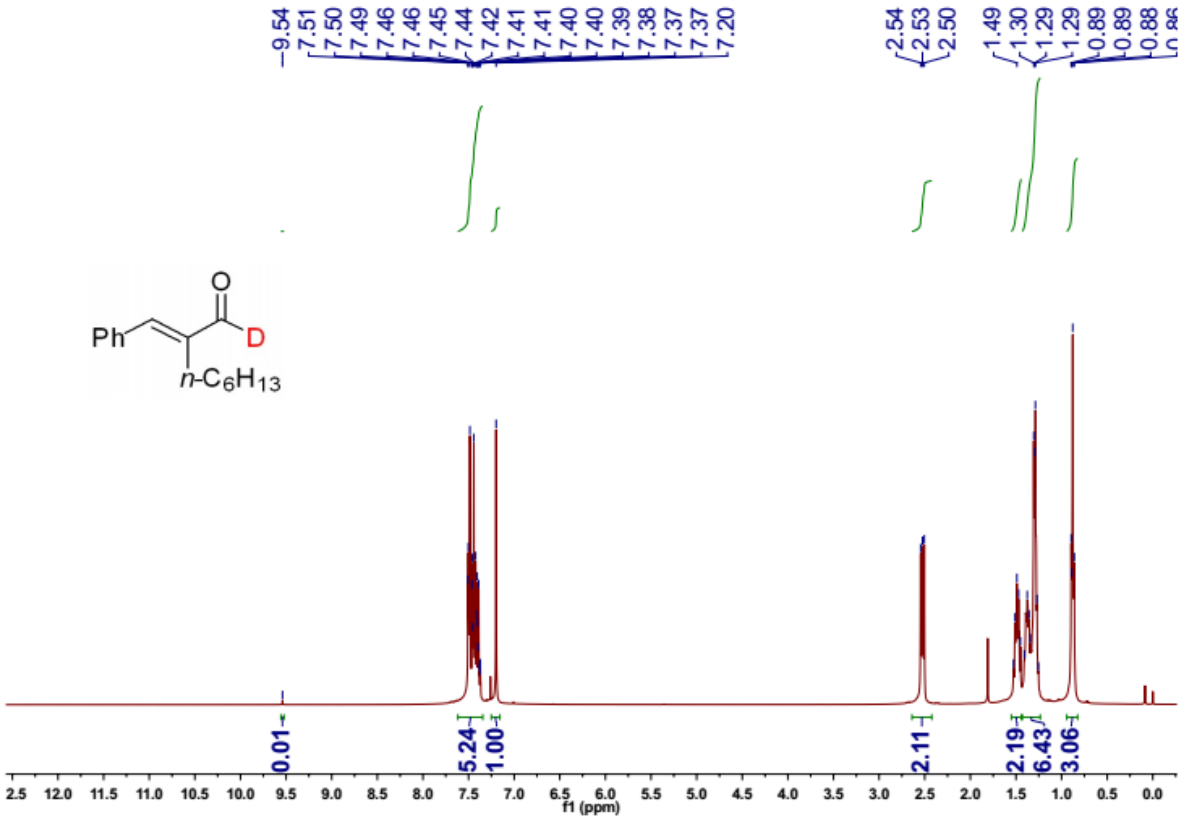

$^{2}$H NMR of deuterated aldehyde **10l**



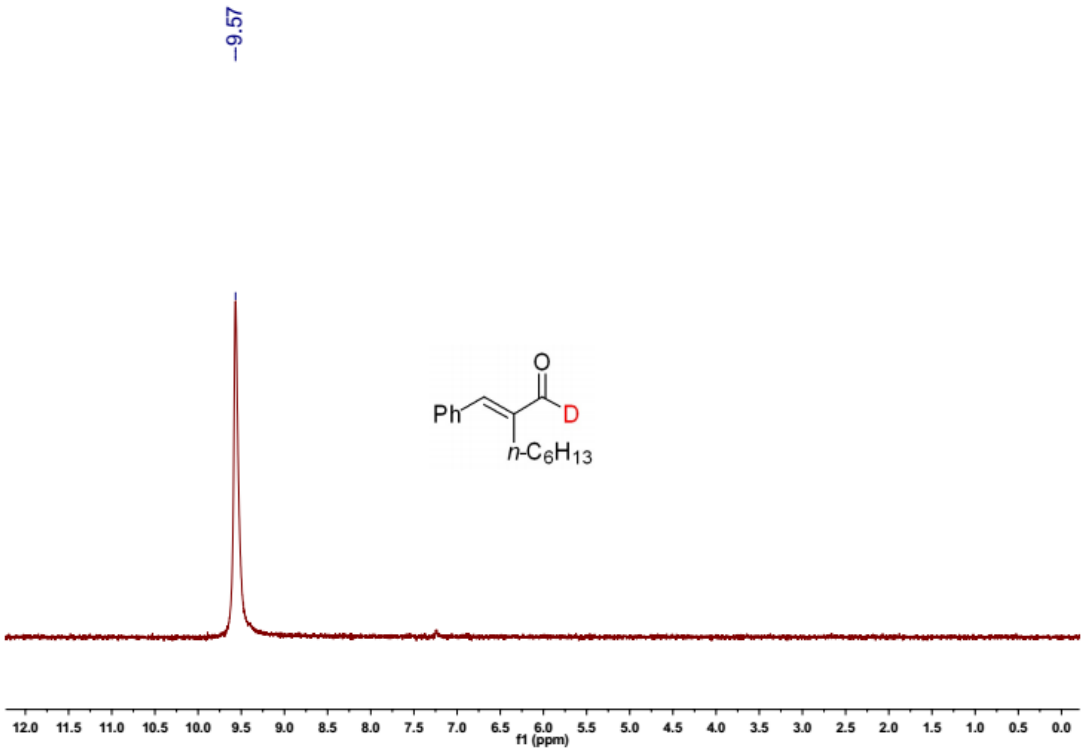
$^{13}$C NMR of deuterated aldehyde **10l**



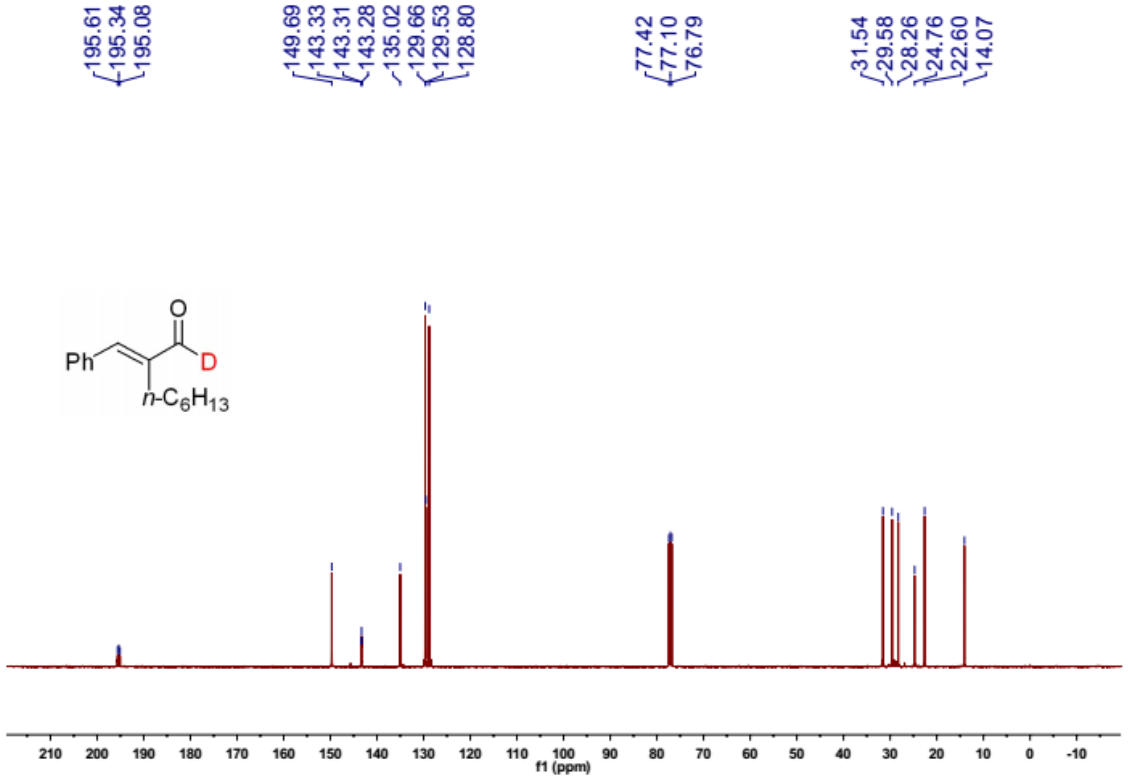
$^{1}$H NMR of deuterated aldehyde **10m**



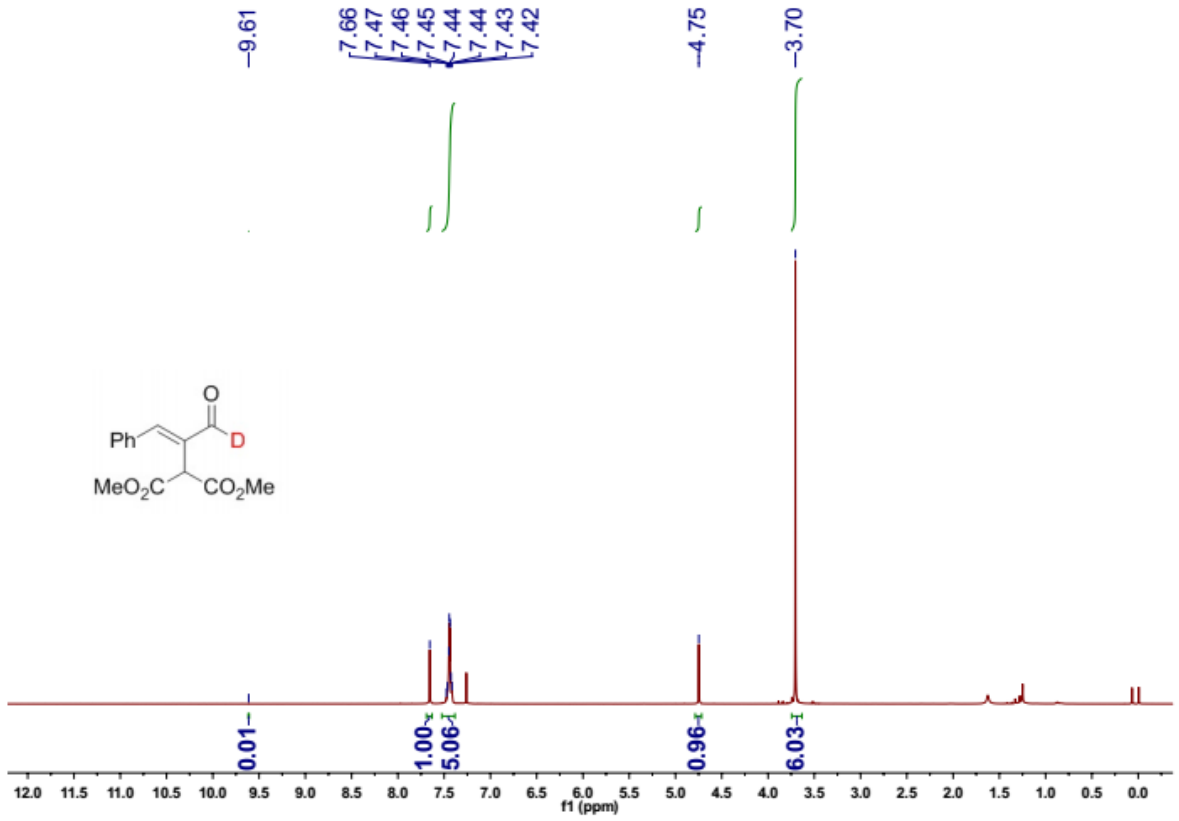

$^{2}$H NMR of deuterated aldehyde **10m**



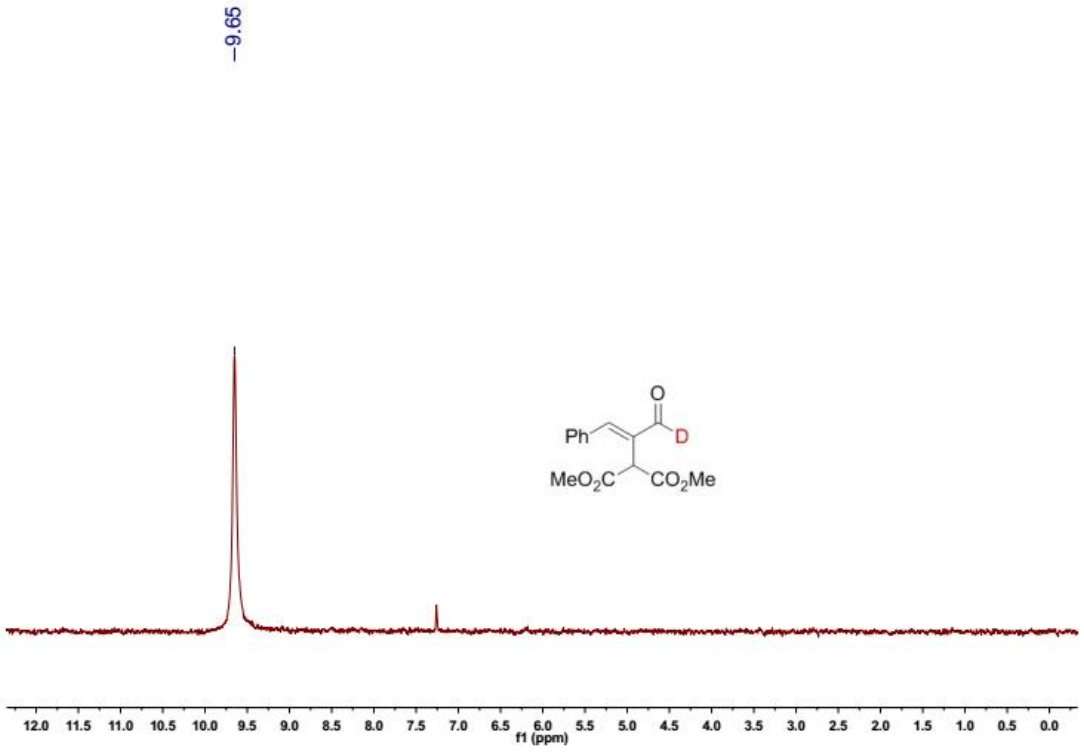
$^{13}$C NMR of deuterated aldehyde **10m**



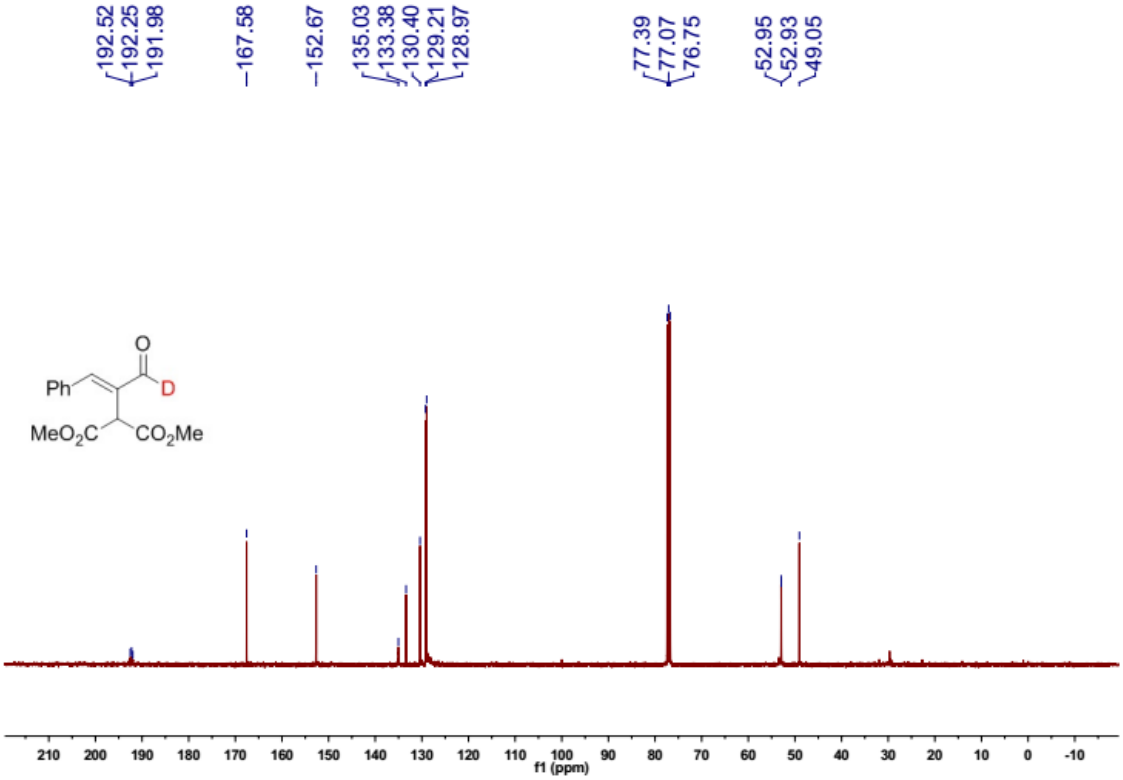
$^{1}$H NMR of deuterated aldehyde **10n**



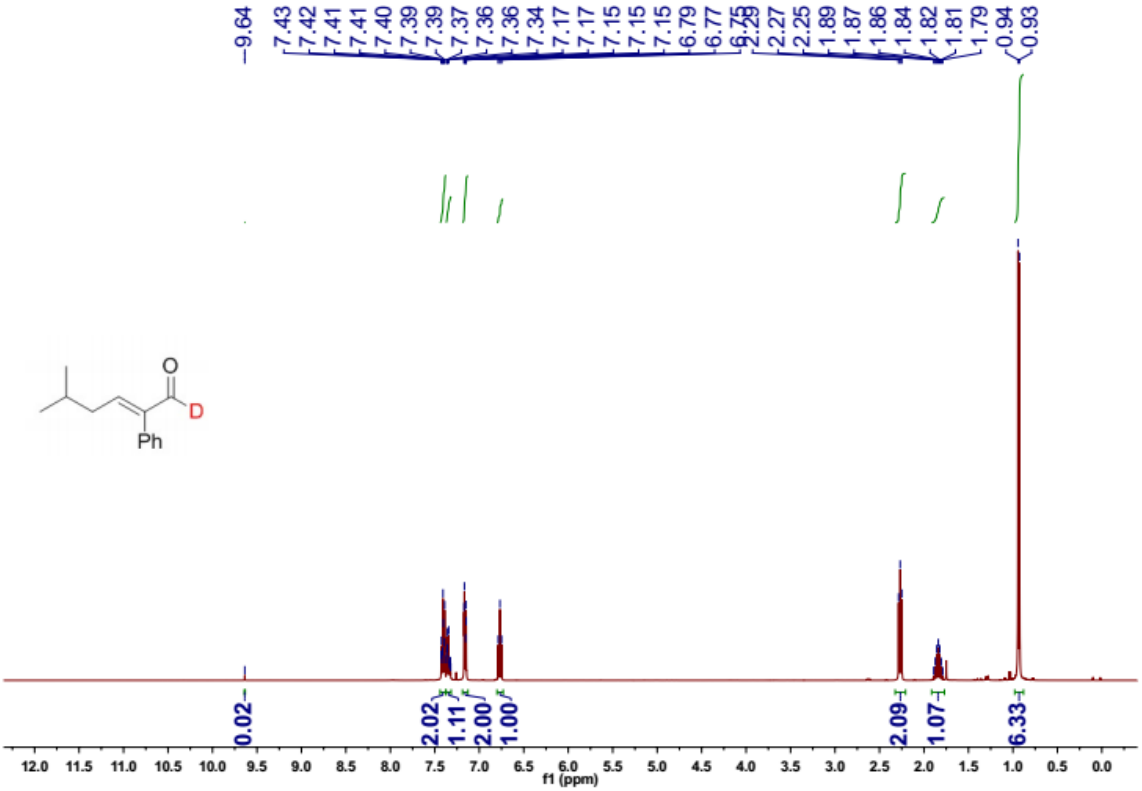

$^{2}$H NMR of deuterated aldehyde **10n**



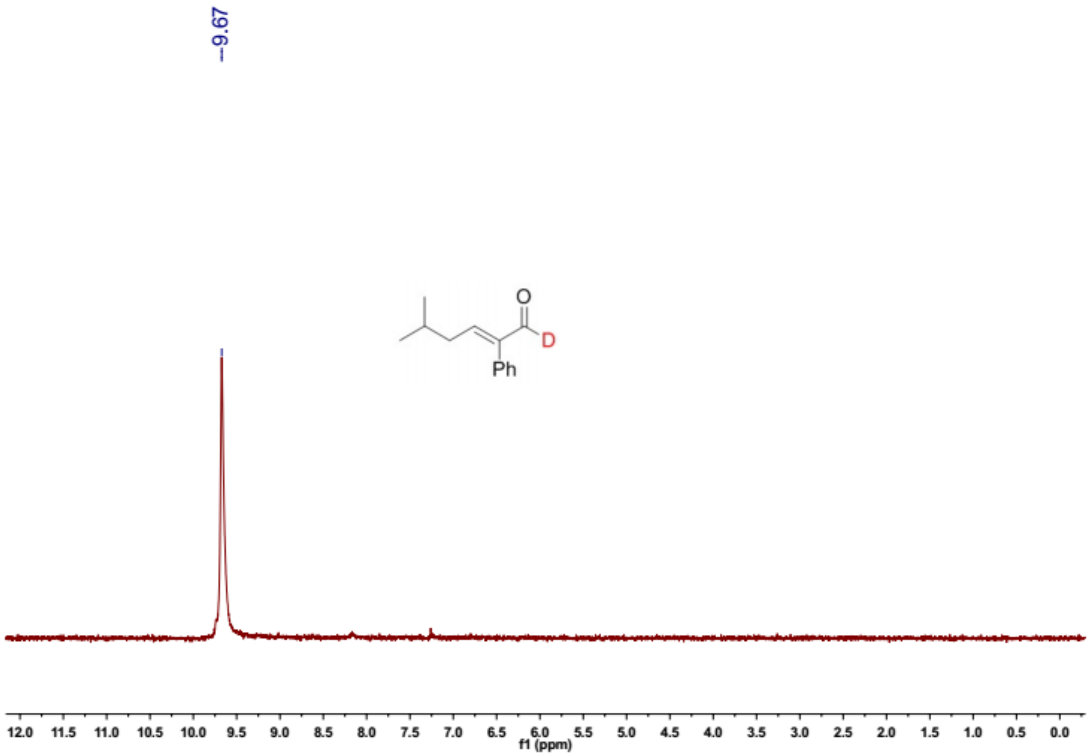
$^{13}$C NMR of deuterated aldehyde **10n**



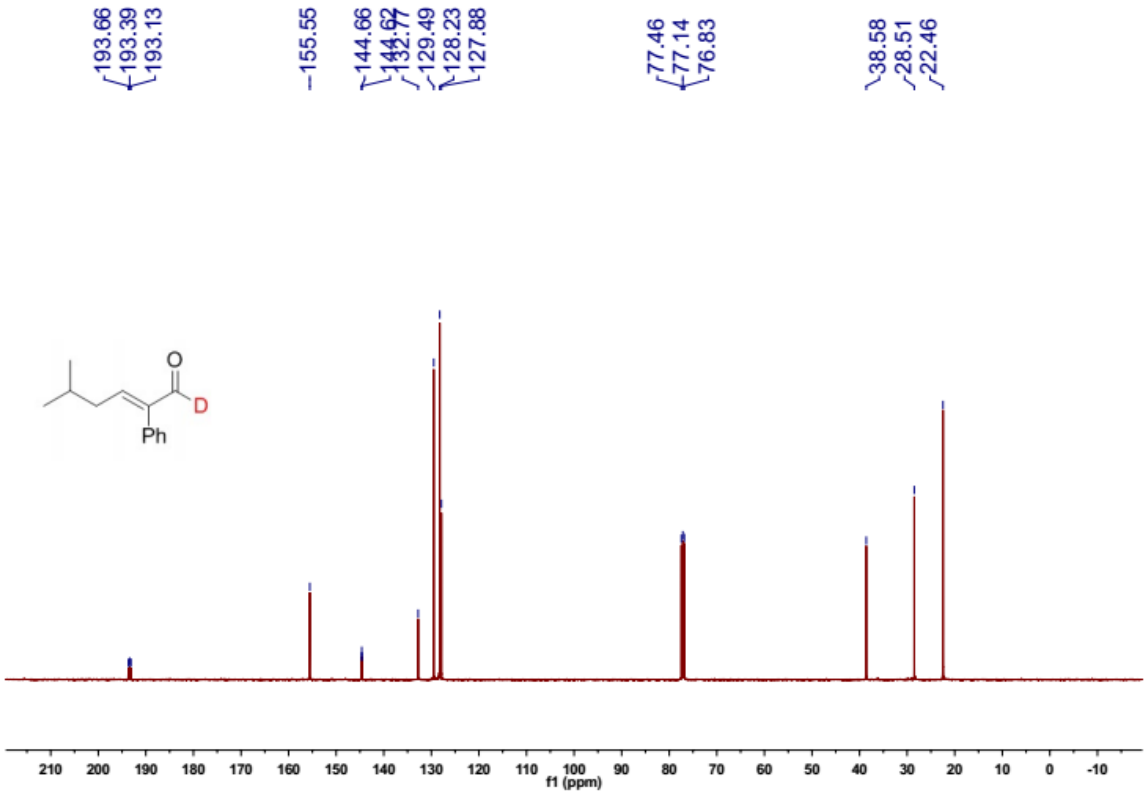
$^{1}$H NMR of deuterated aldehyde **10o**



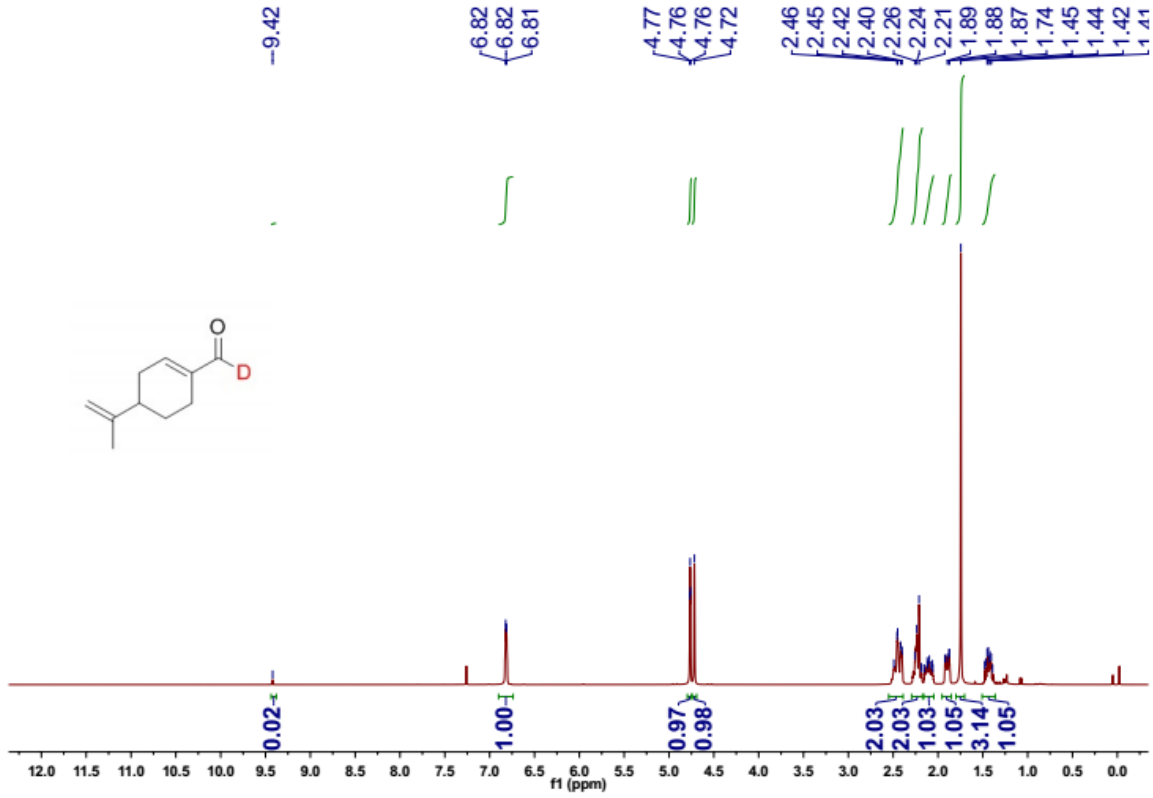

$^{2}$H NMR of deuterated aldehyde **10o**



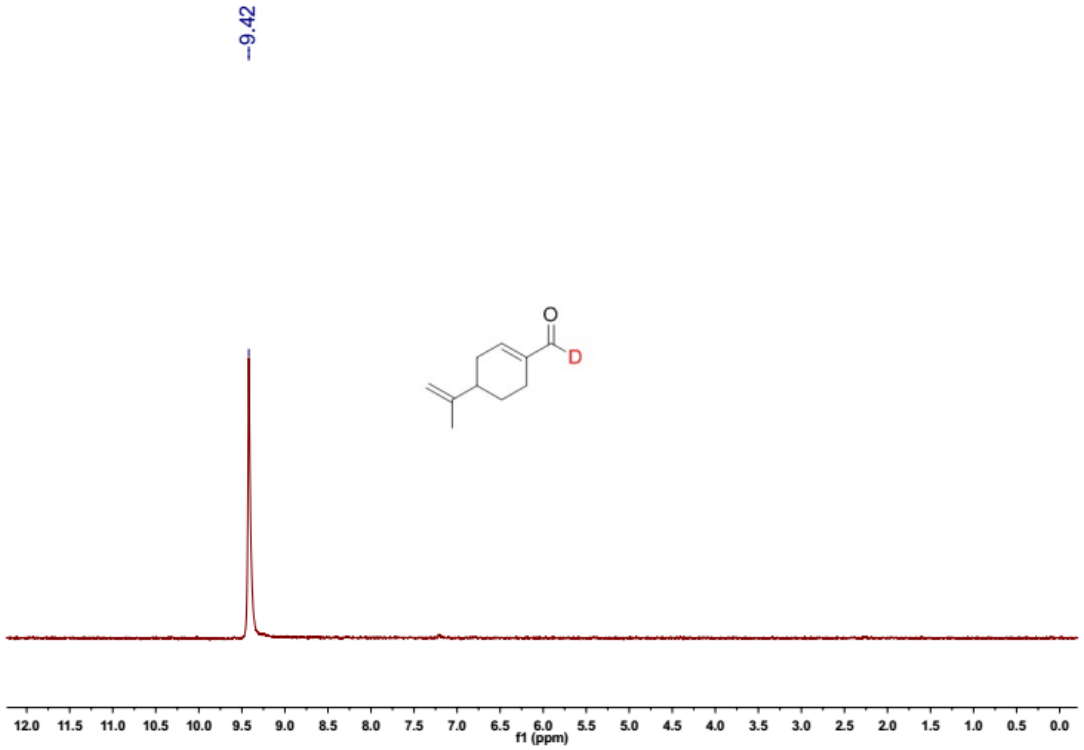
$^{13}$C NMR of deuterated aldehyde **10o**



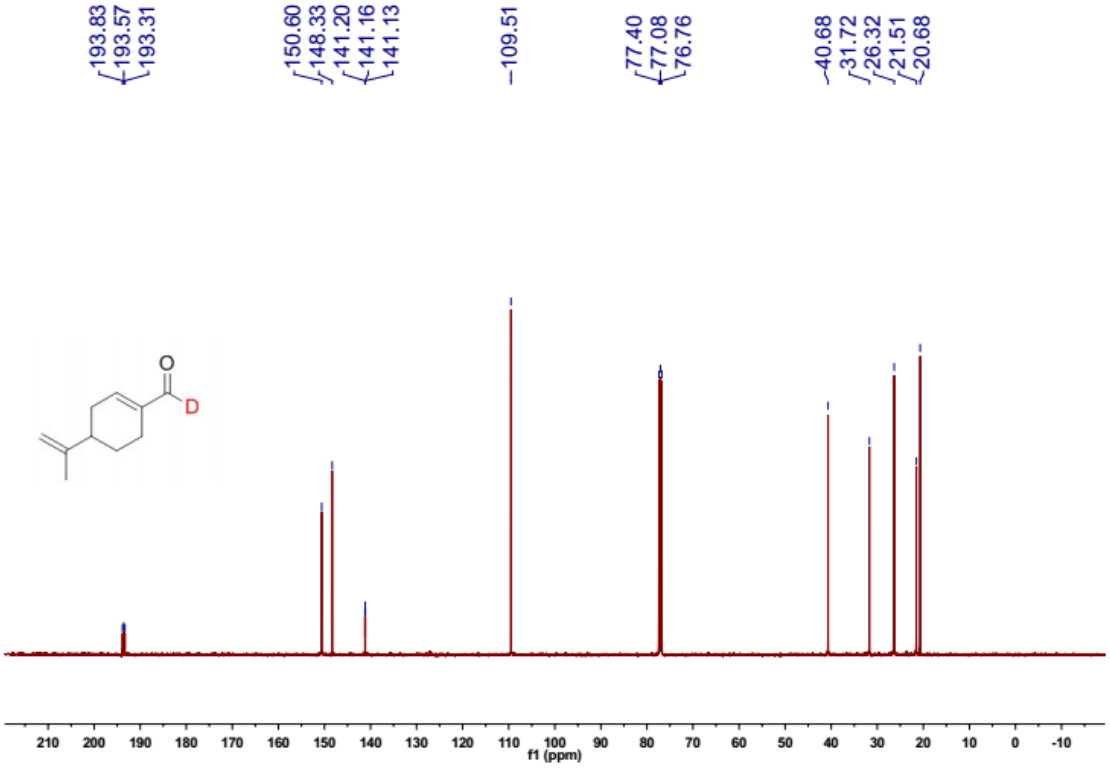
$^{1}$H NMR of deuterated aldehyde **10p**



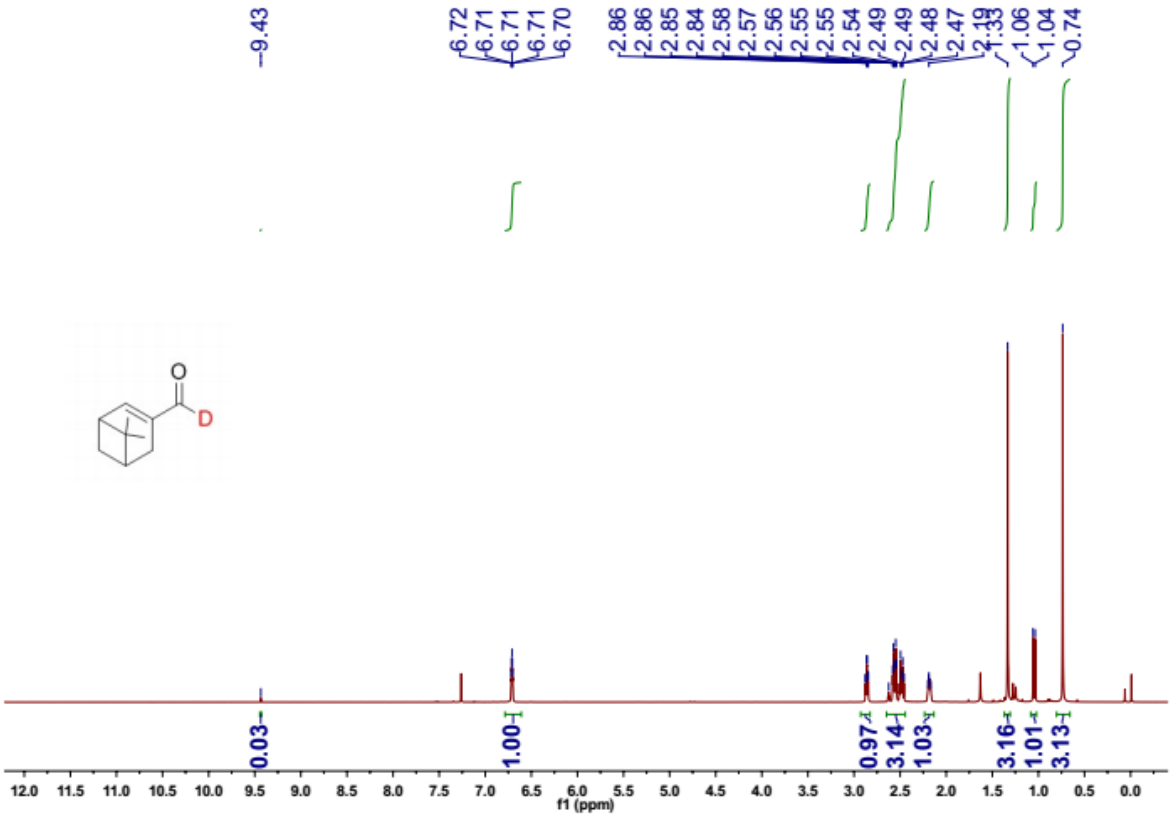

$^{2}$H NMR of deuterated aldehyde **10p**



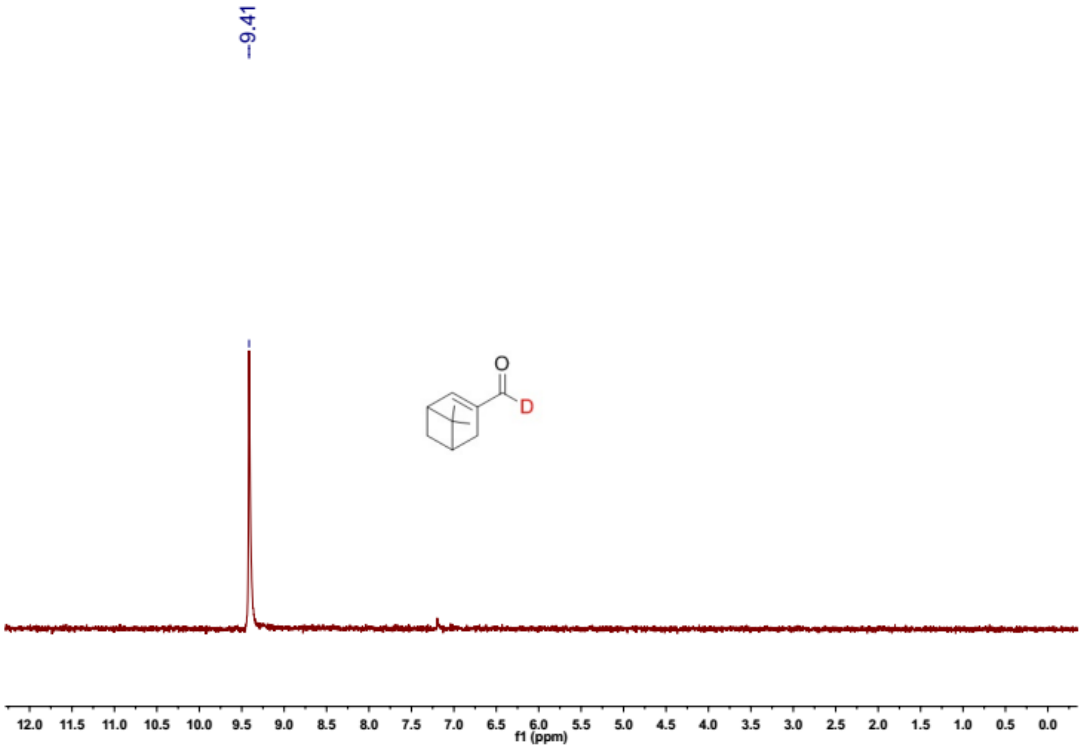
$^{13}$C NMR of deuterated aldehyde **10p**



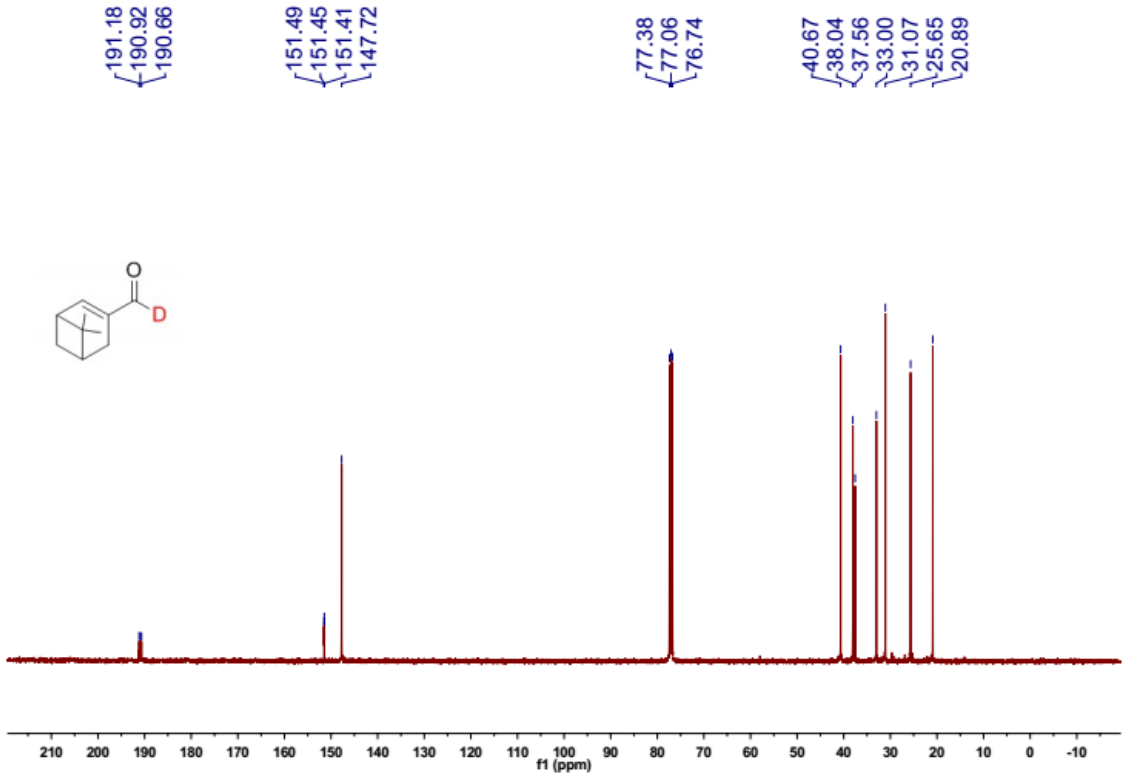
$^{1}$H NMR of deuterated aldehyde **10q**



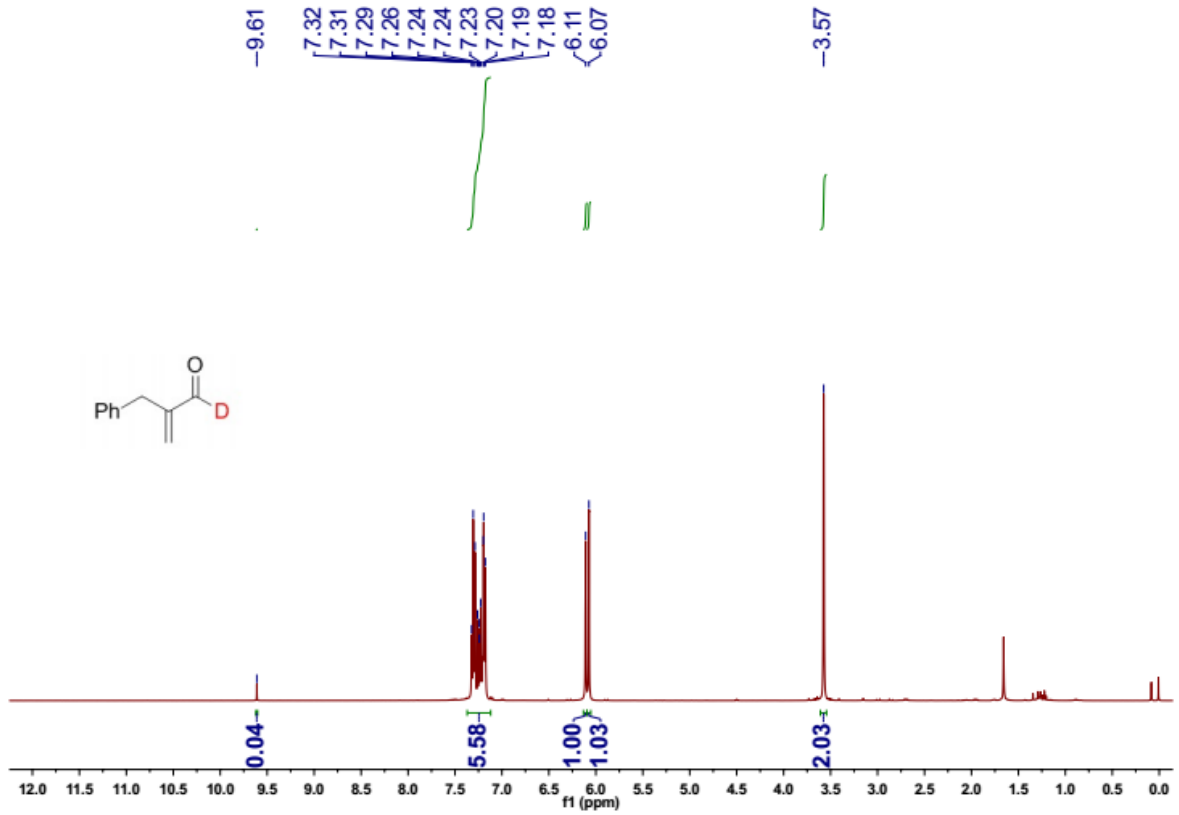

$^{2}$H NMR of deuterated aldehyde **10q**



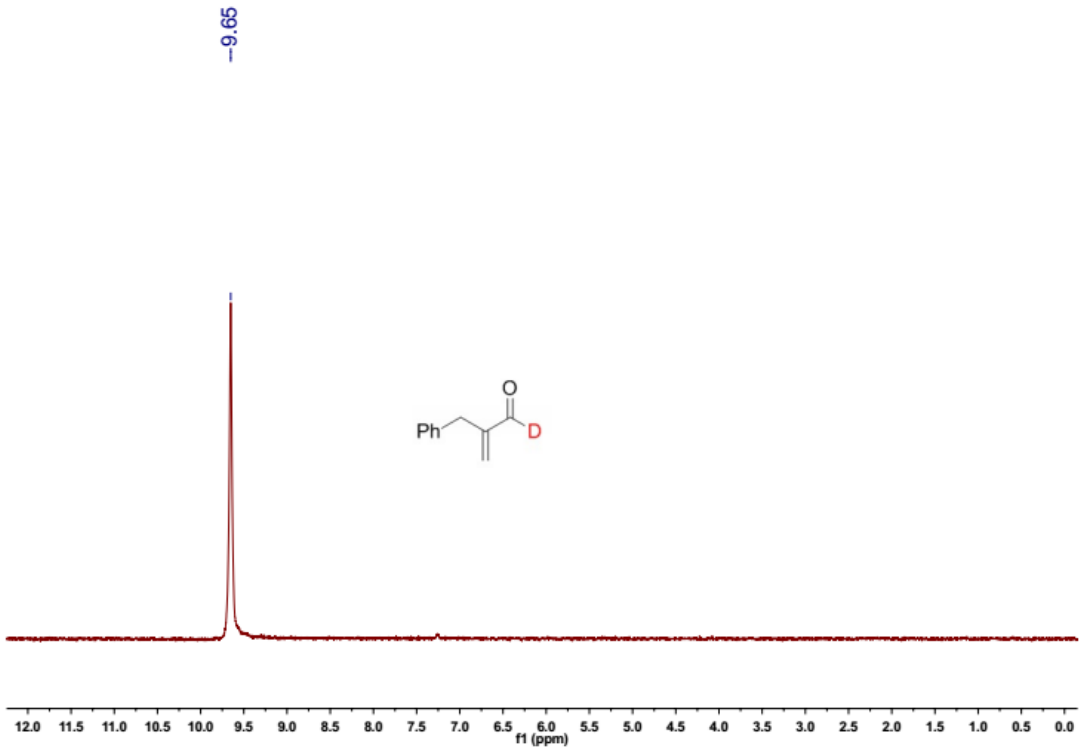
$^{13}$C NMR of deuterated aldehyde **10q**



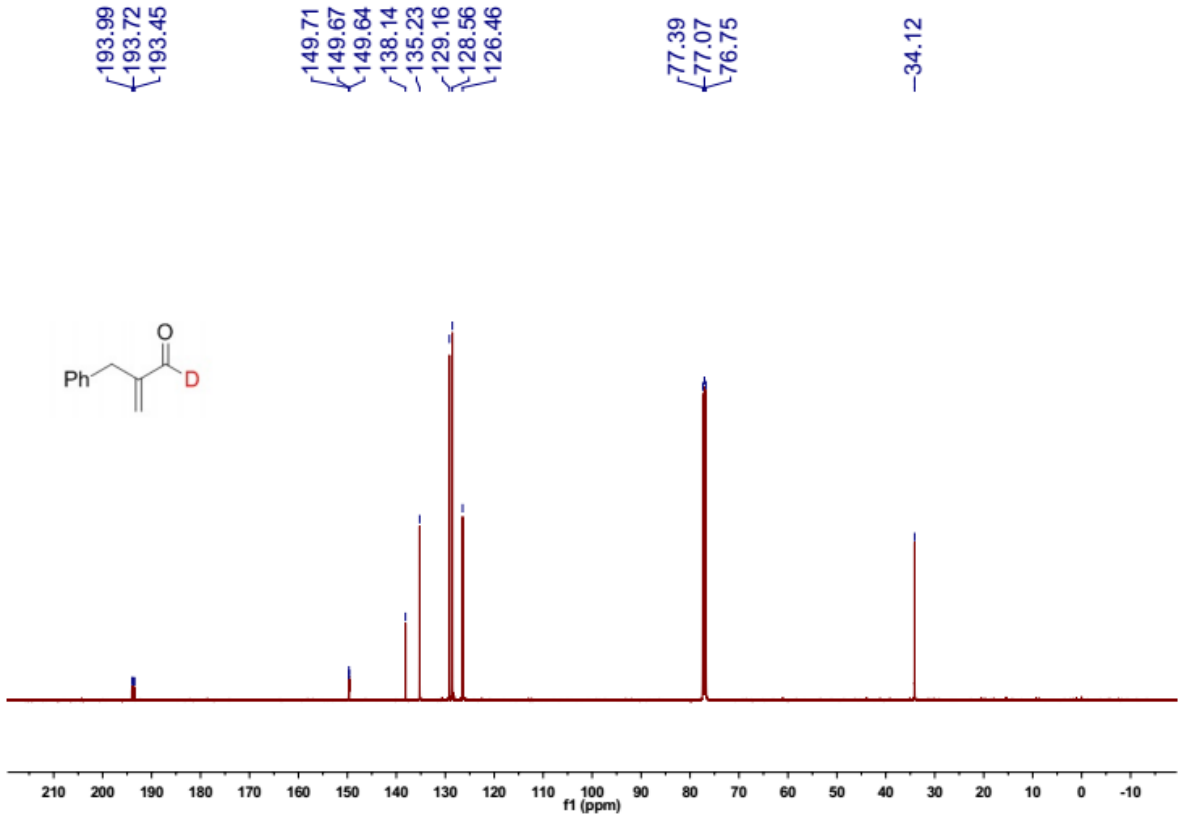
$^{1}$H NMR of deuterated aldehyde **10r**



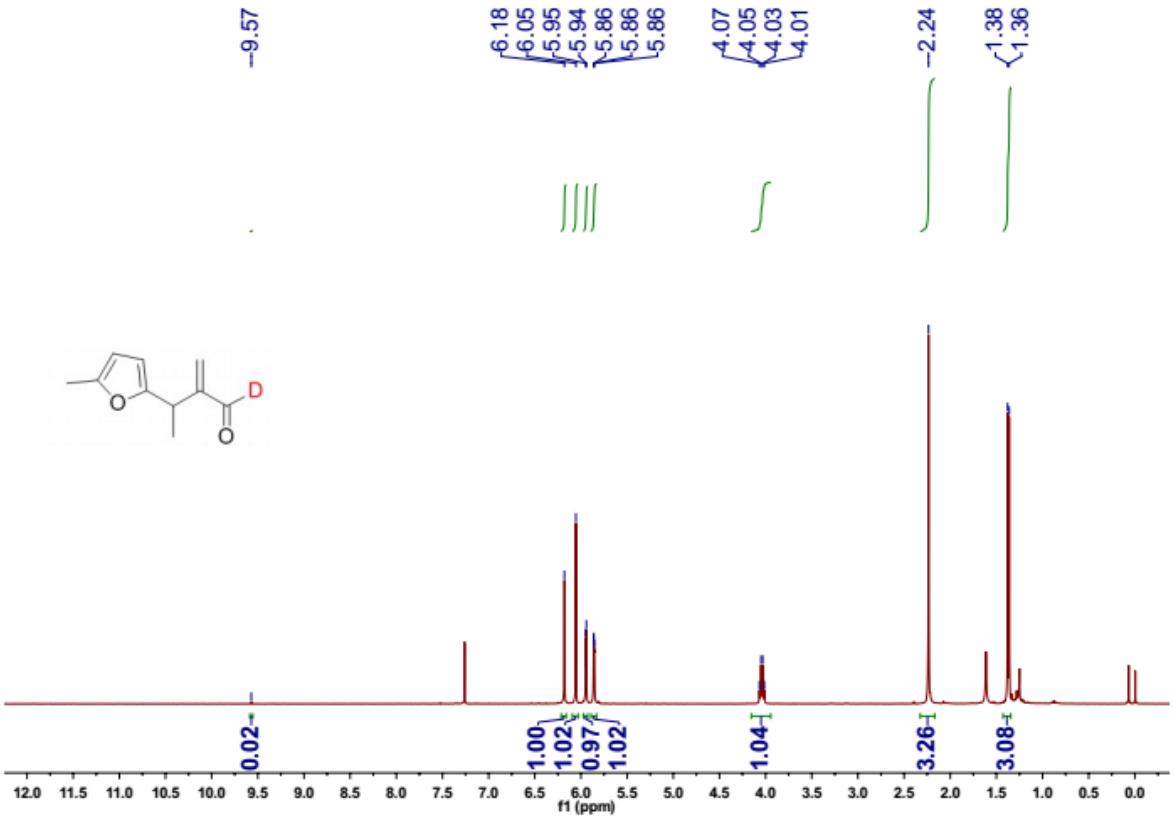

$^{2}$H NMR of deuterated aldehyde **10r**



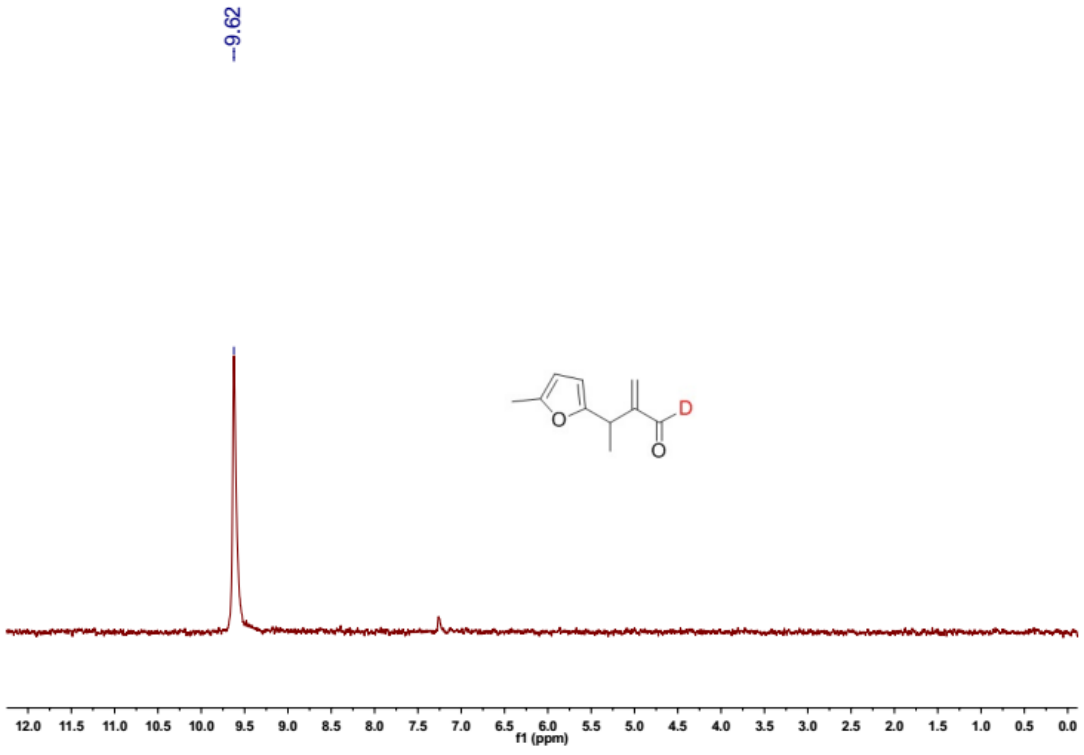
$^{13}$C NMR of deuterated aldehyde **10r**



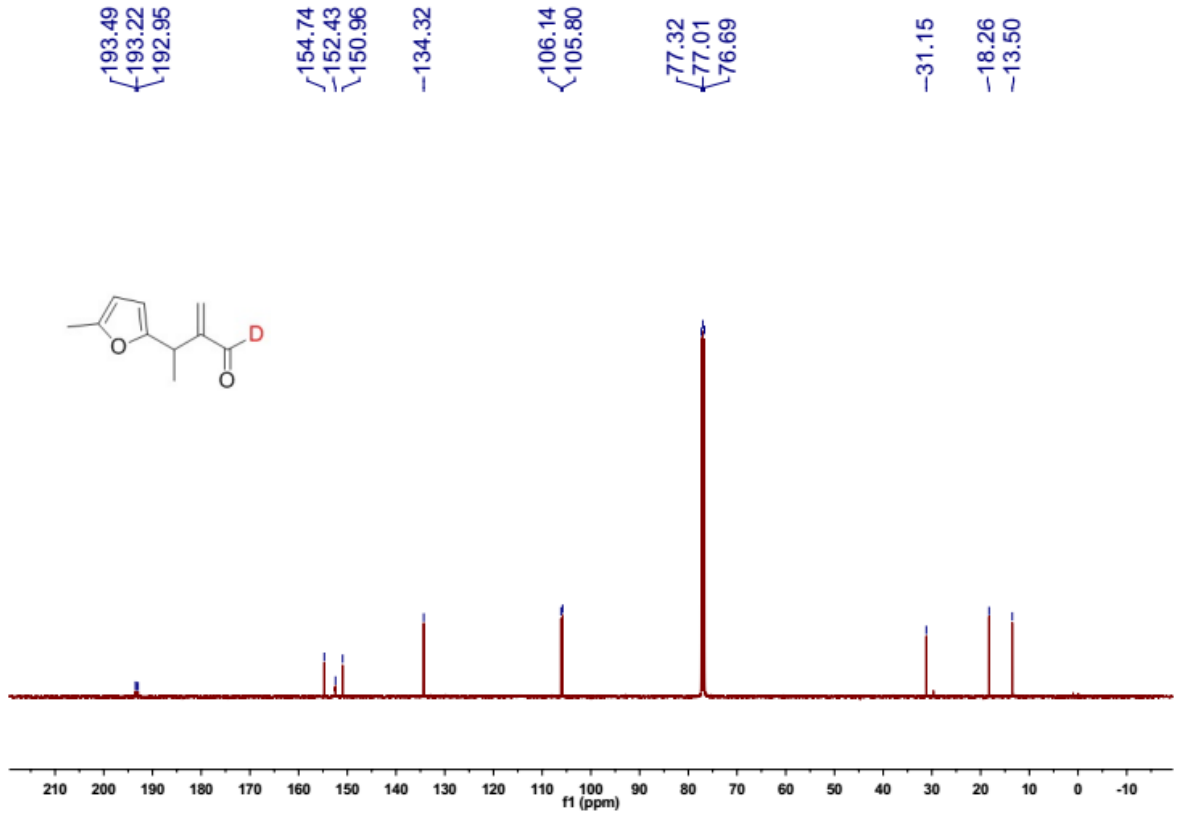
$^{1}$H NMR of deuterated aldehyde **10s**



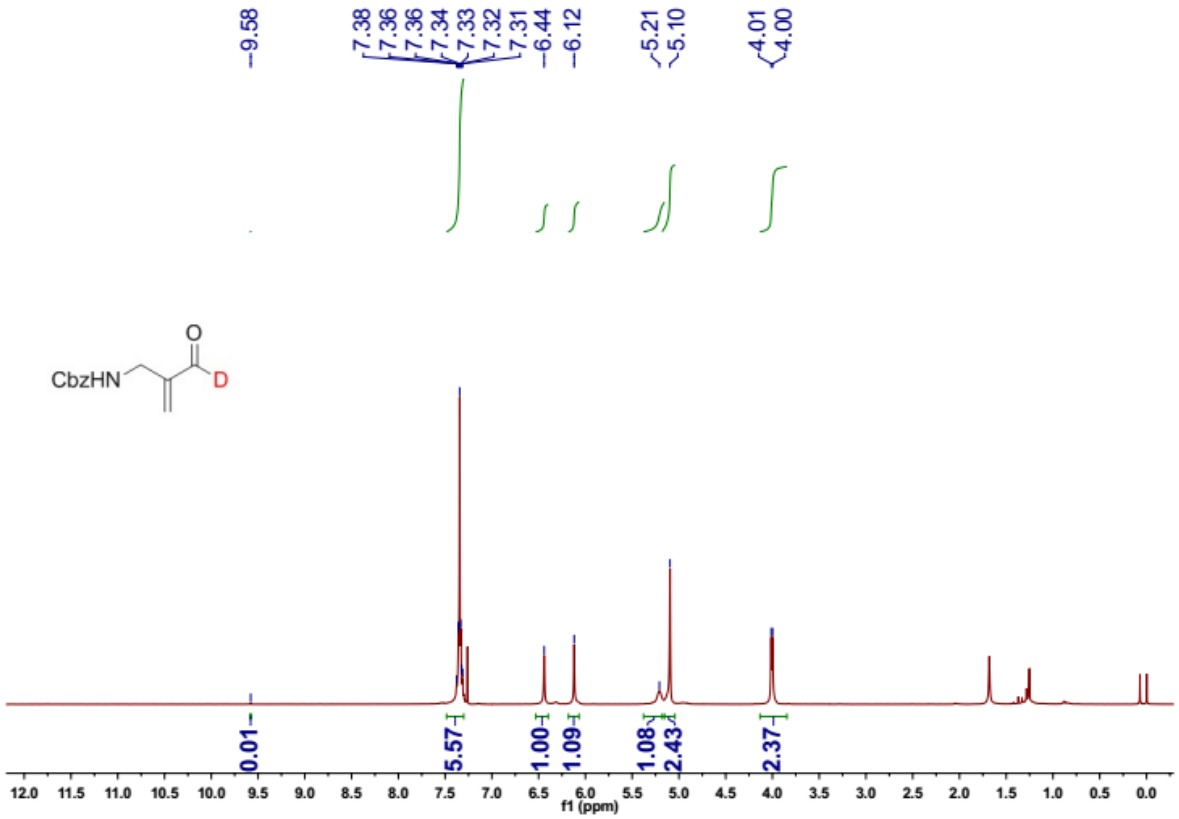

$^{2}$H NMR of deuterated aldehyde **10s**



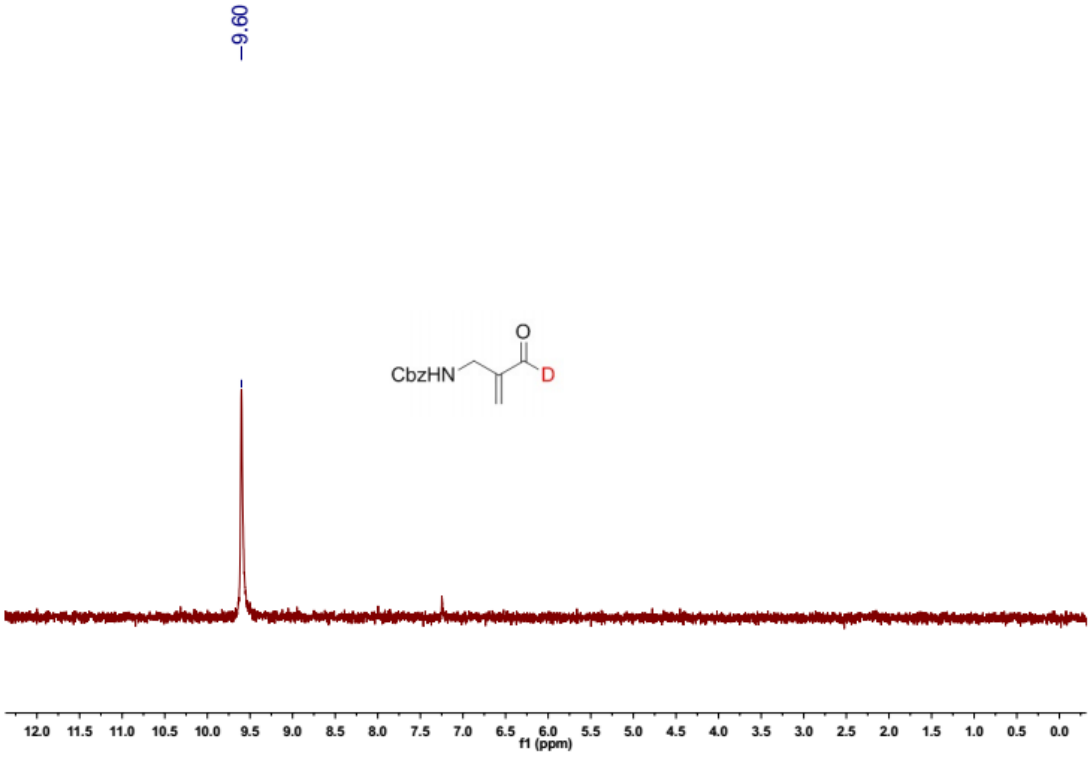
$^{13}$C NMR of deuterated aldehyde **10s**



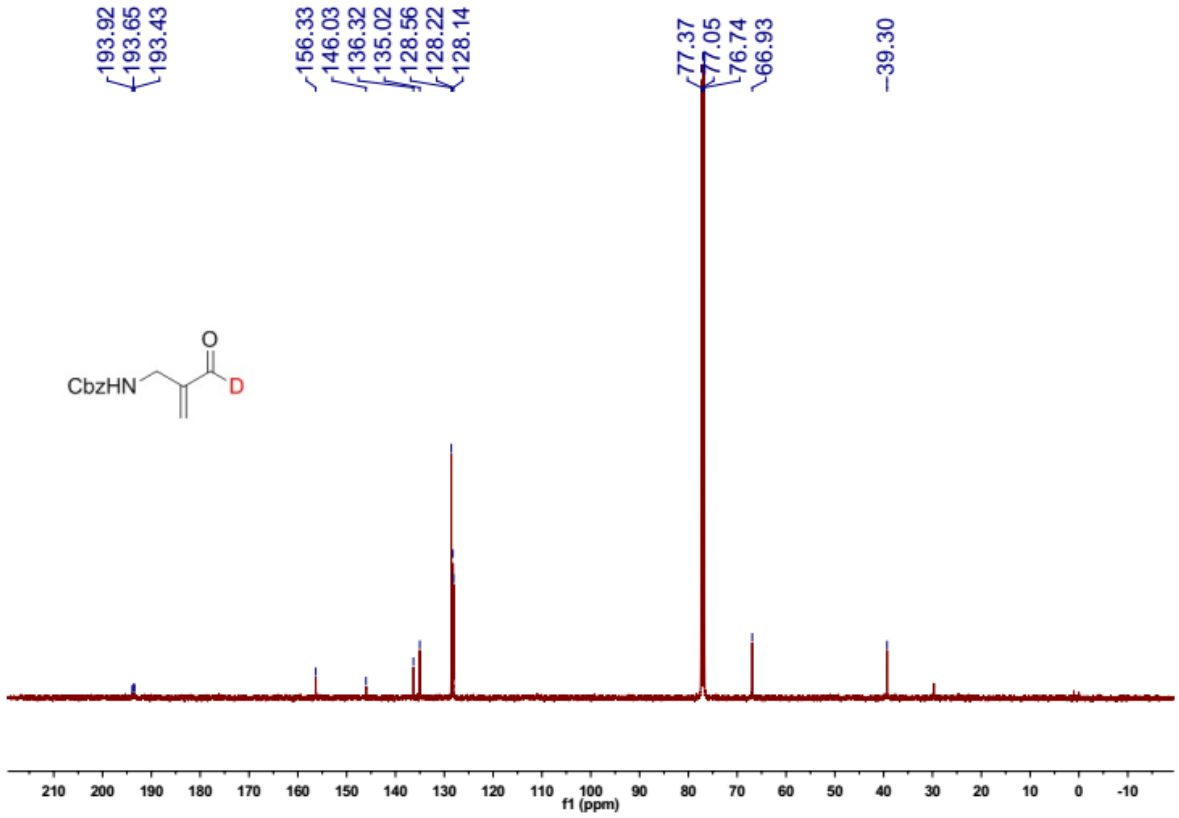
$^{1}$H NMR of deuterated aldehyde **10t**



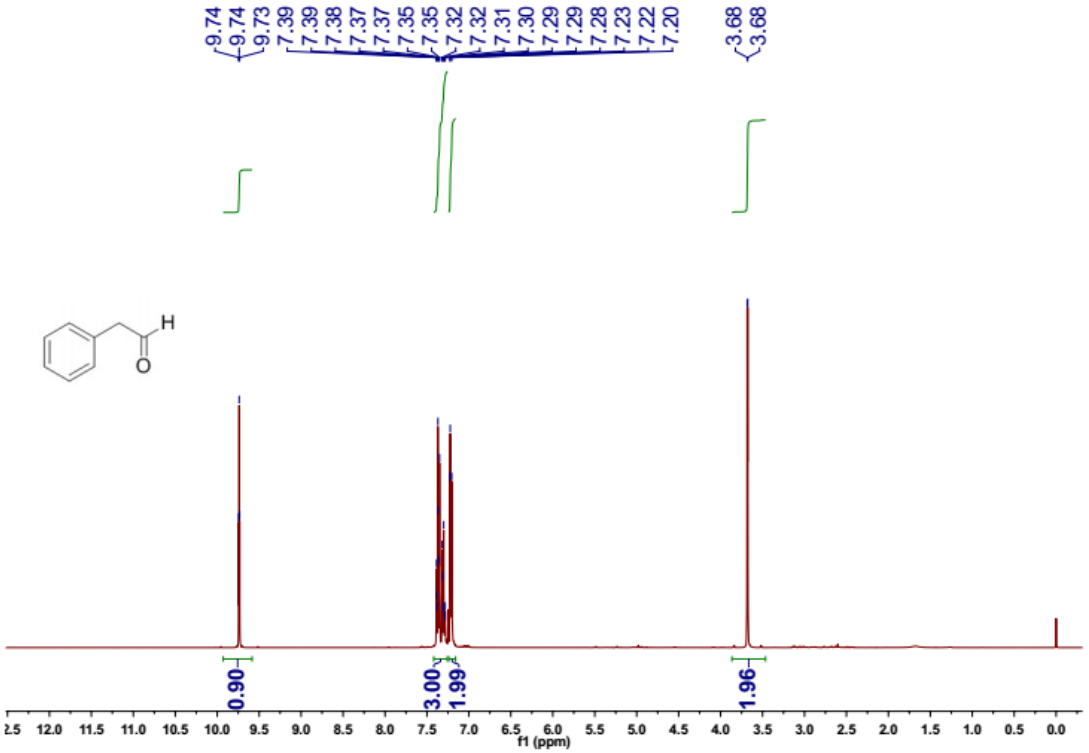

$^{2}$H NMR of deuterated aldehyde **10t**



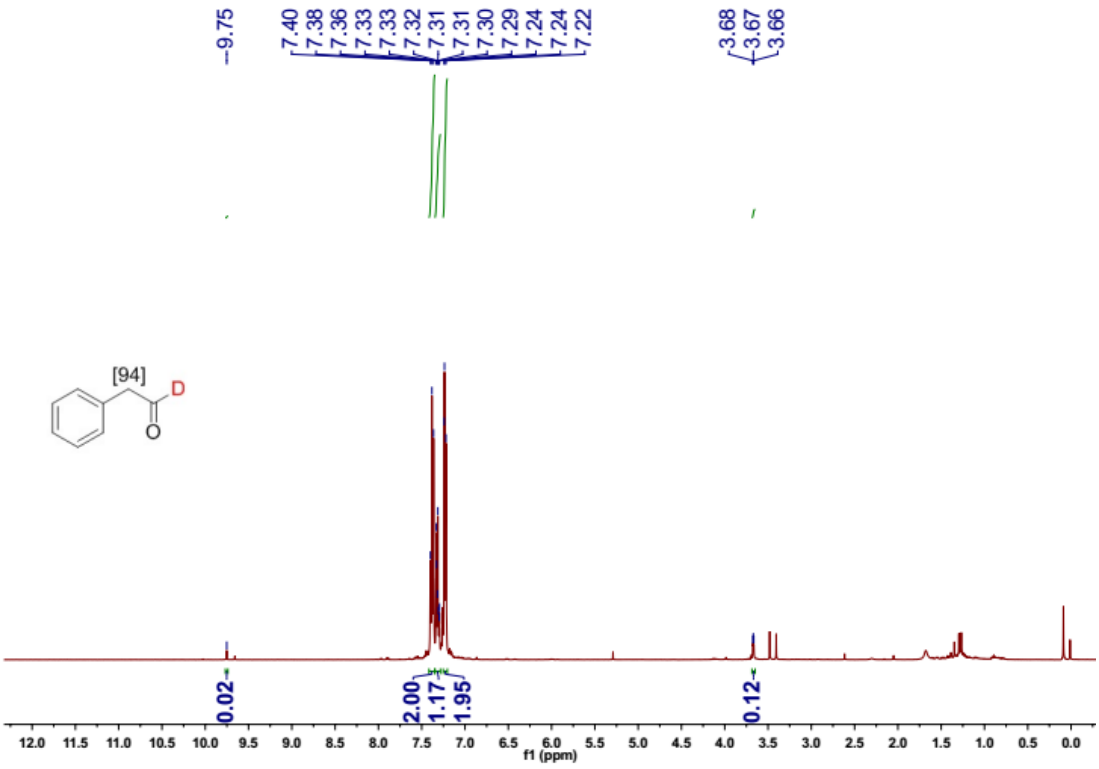
$^{13}$C NMR of deuterated aldehyde **10t**



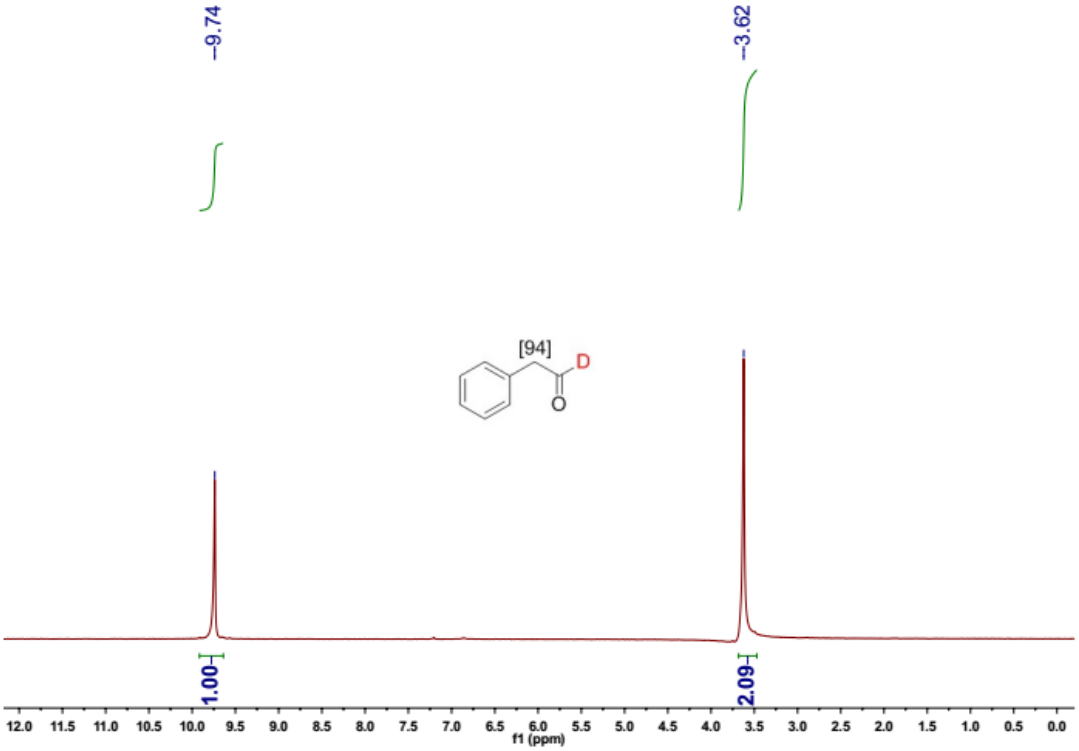
$^{1}$H NMR of aldehyde **11a**



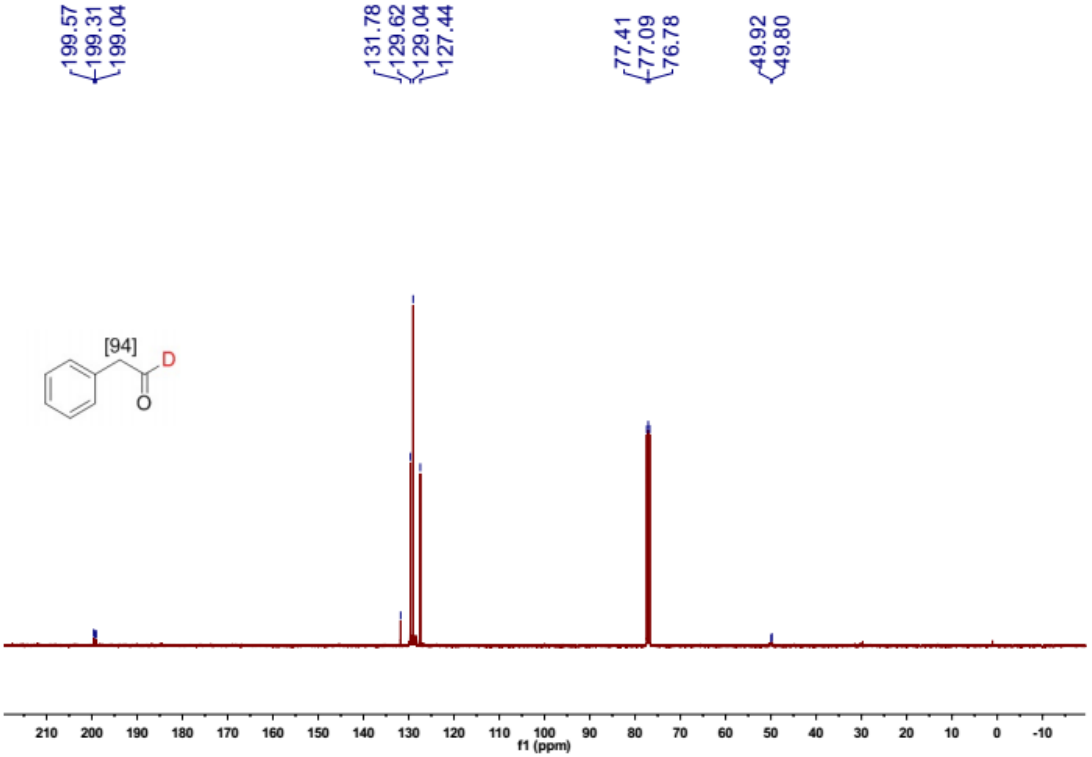

$^{1}$H NMR of deuterated aldehyde **12a**



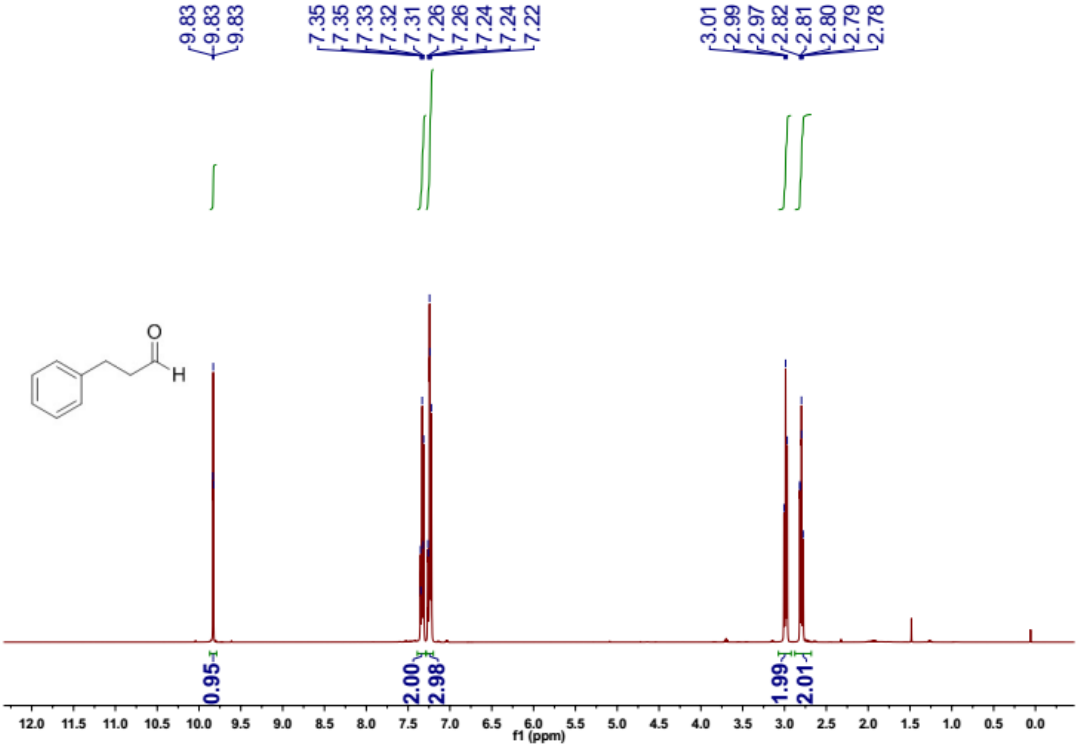
$^{2}$H NMR of deuterated aldehyde **12a**



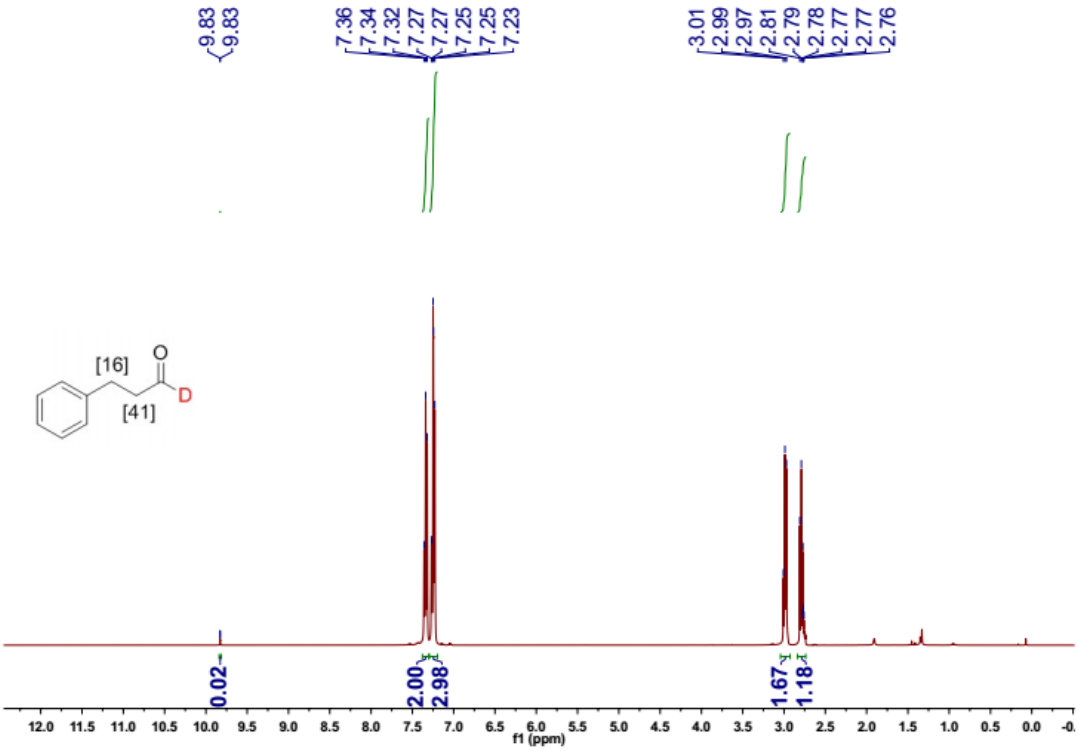

$^{13}$C NMR of deuterated aldehyde **12a**



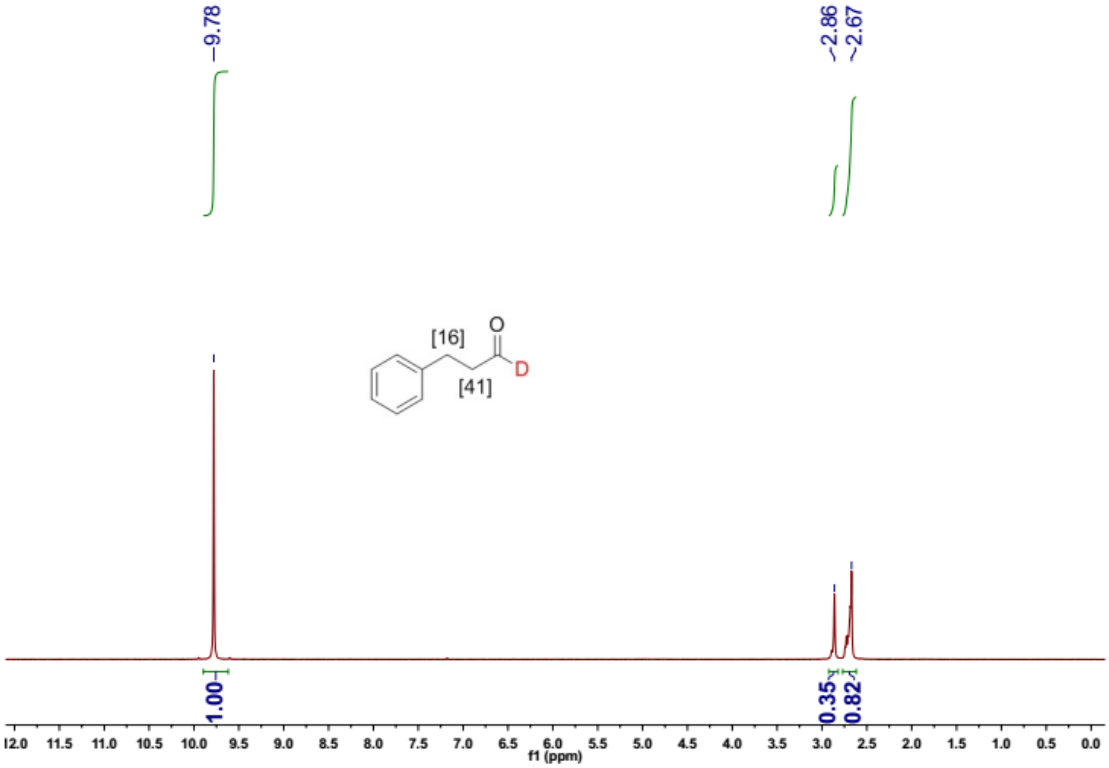
$^{1}$H NMR of aldehyde **11b**



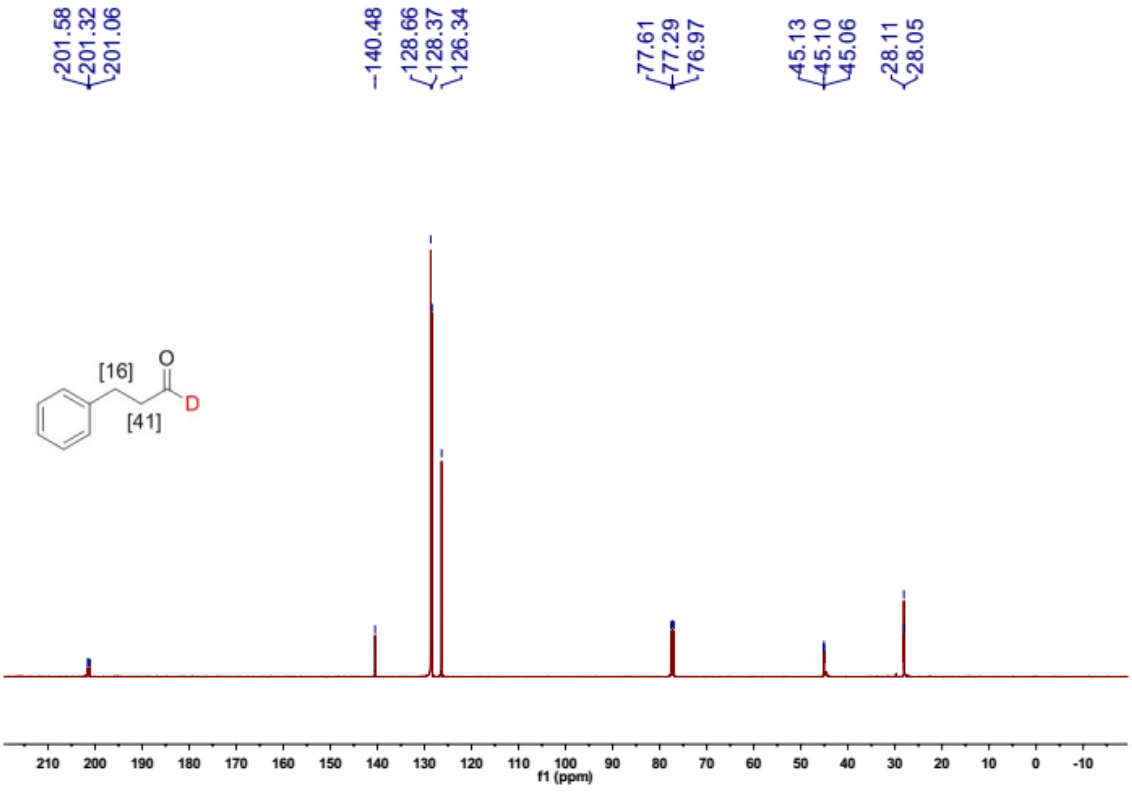

$^{1}$H NMR of deuterated aldehyde **12b**



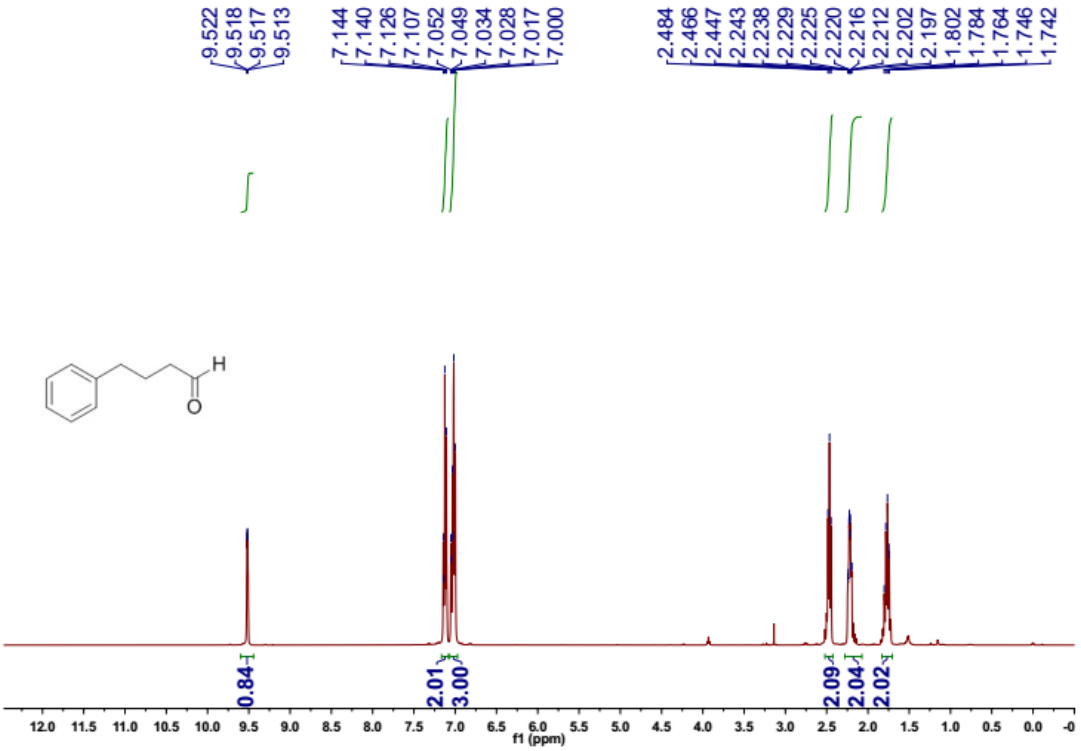
$^{2}$H NMR of deuterated aldehyde **12b**



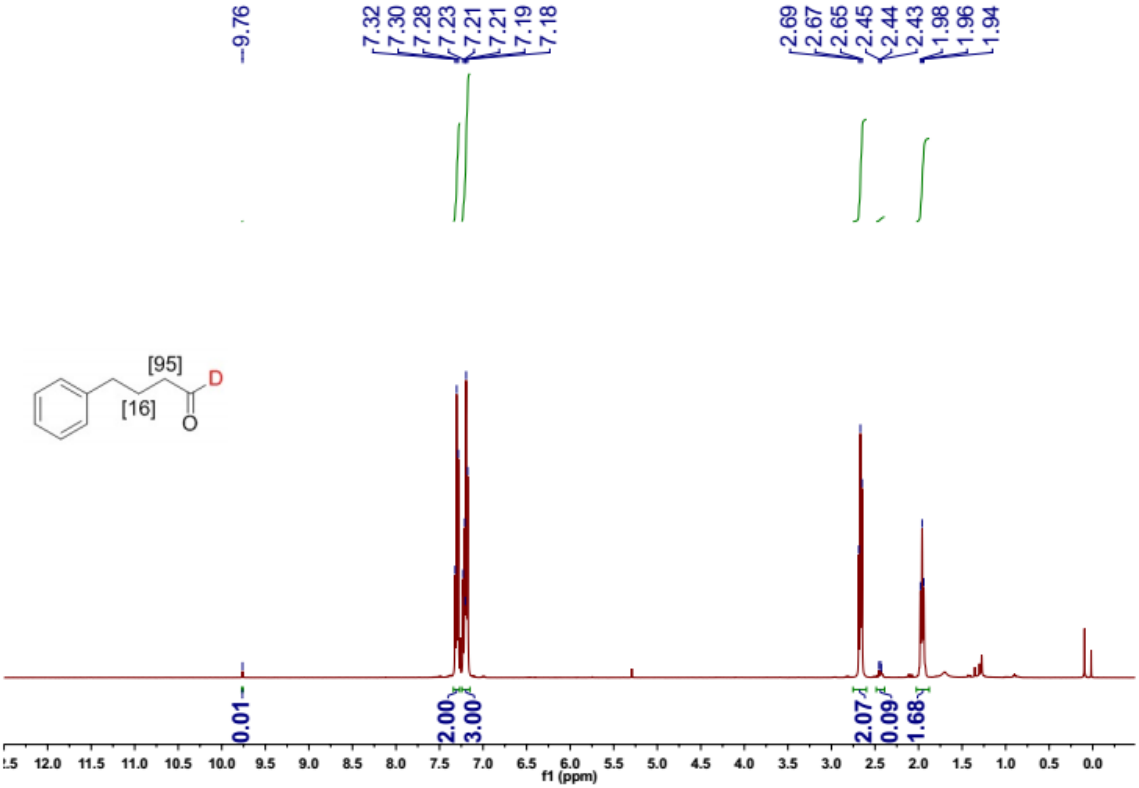

$^{13}$C NMR of deuterated aldehyde **12b**



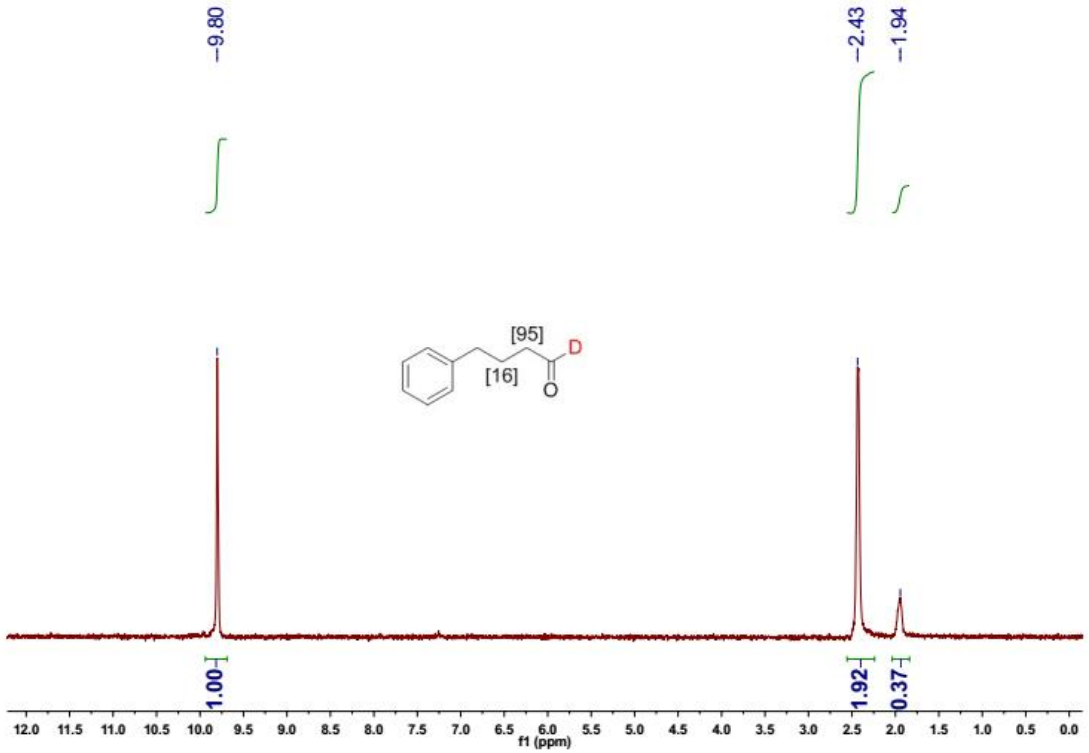
$^{1}$H NMR of aldehyde **11c**



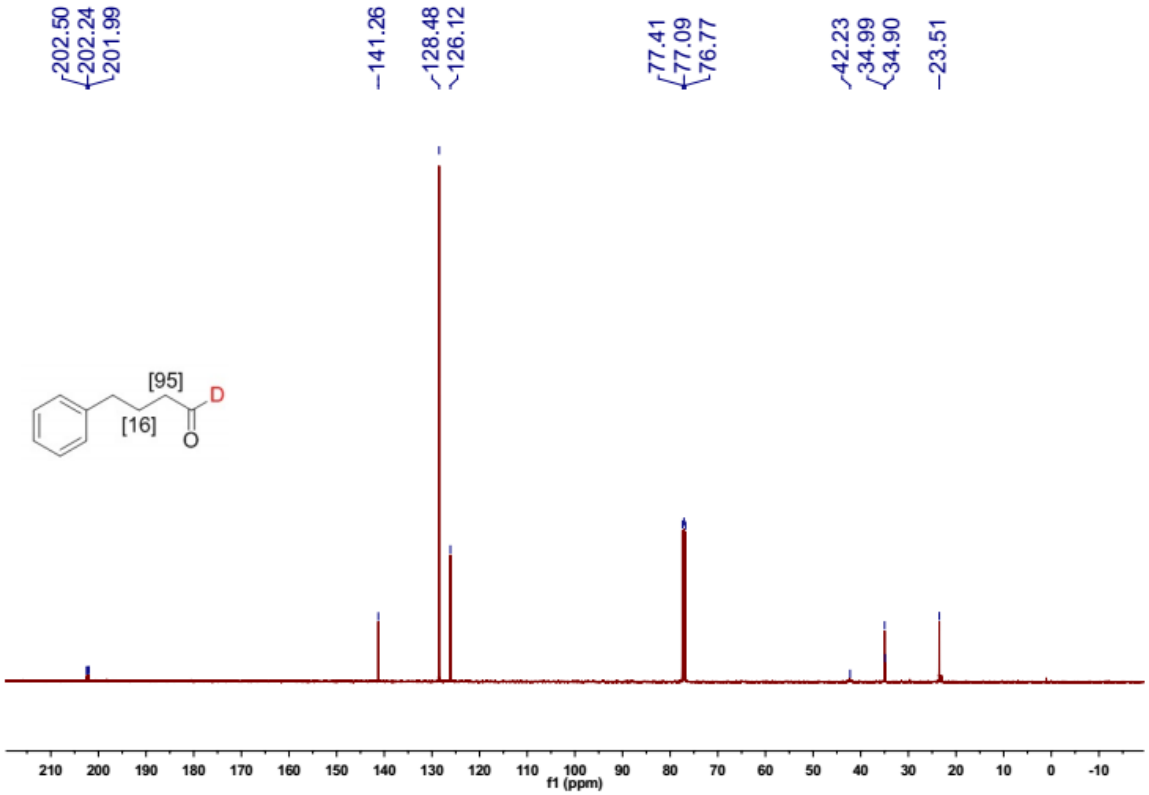

$^{1}$H NMR of deuterated aldehyde **12c**



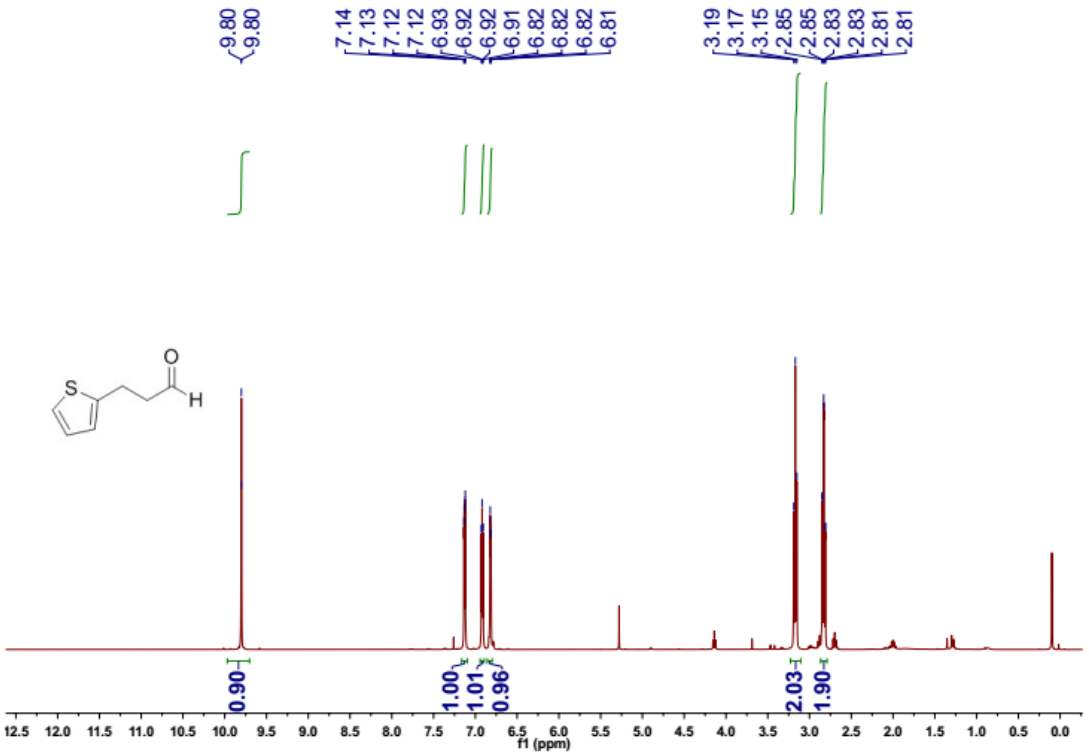
$^{2}$H NMR of deuterated aldehyde **12c**



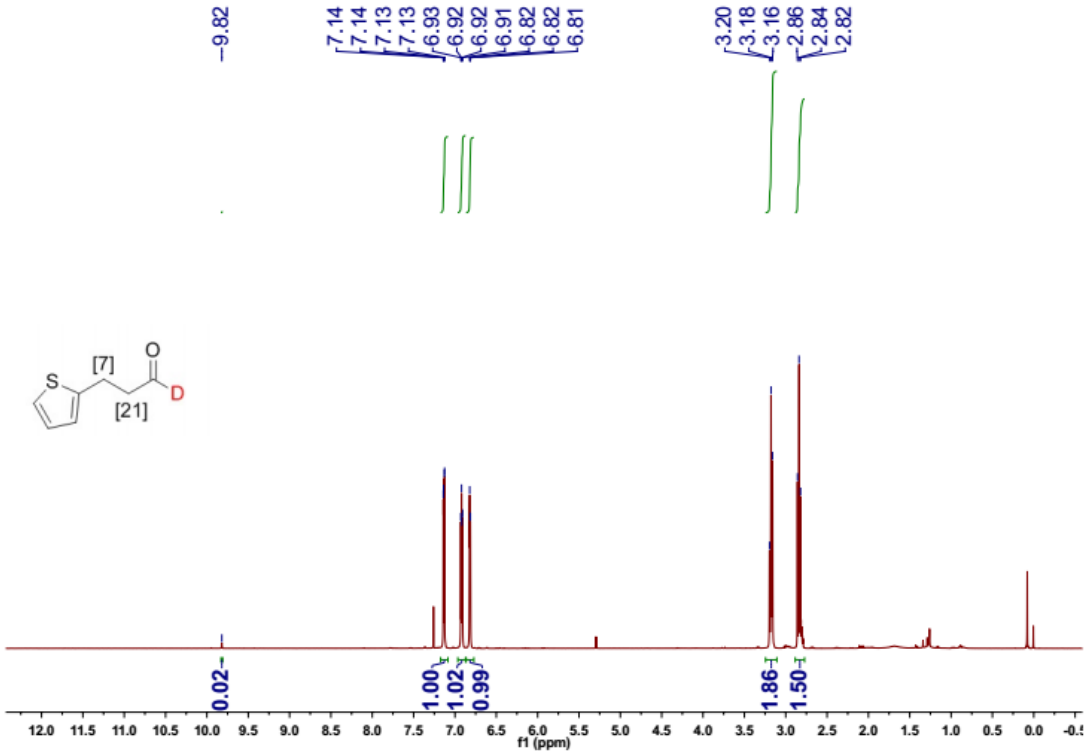

$^{13}$C NMR of deuterated aldehyde **12c**



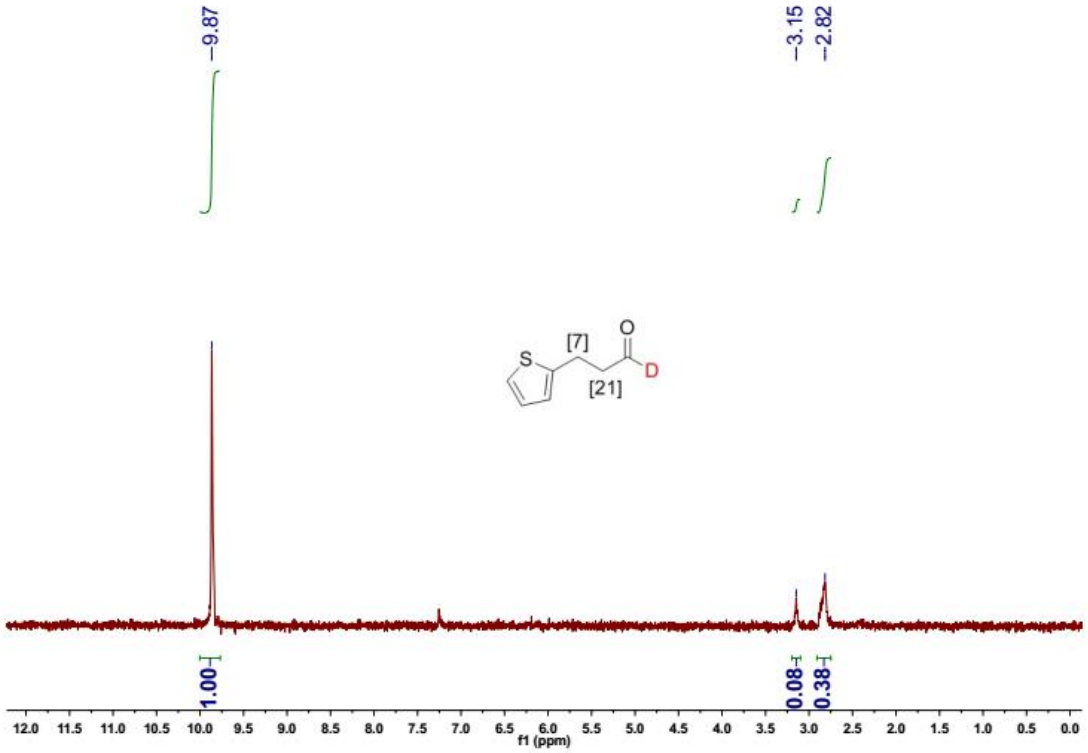
$^{1}$H NMR of aldehyde **11d**



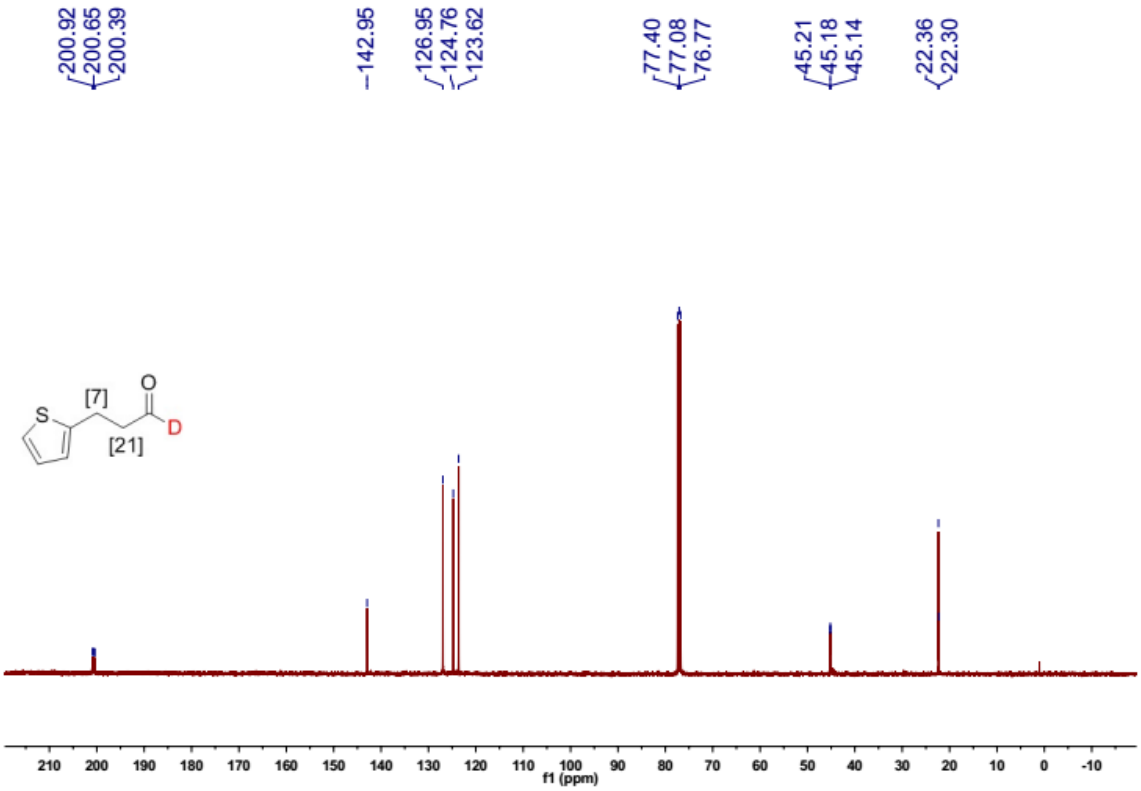

$^{1}$H NMR of deuterated aldehyde **12d**



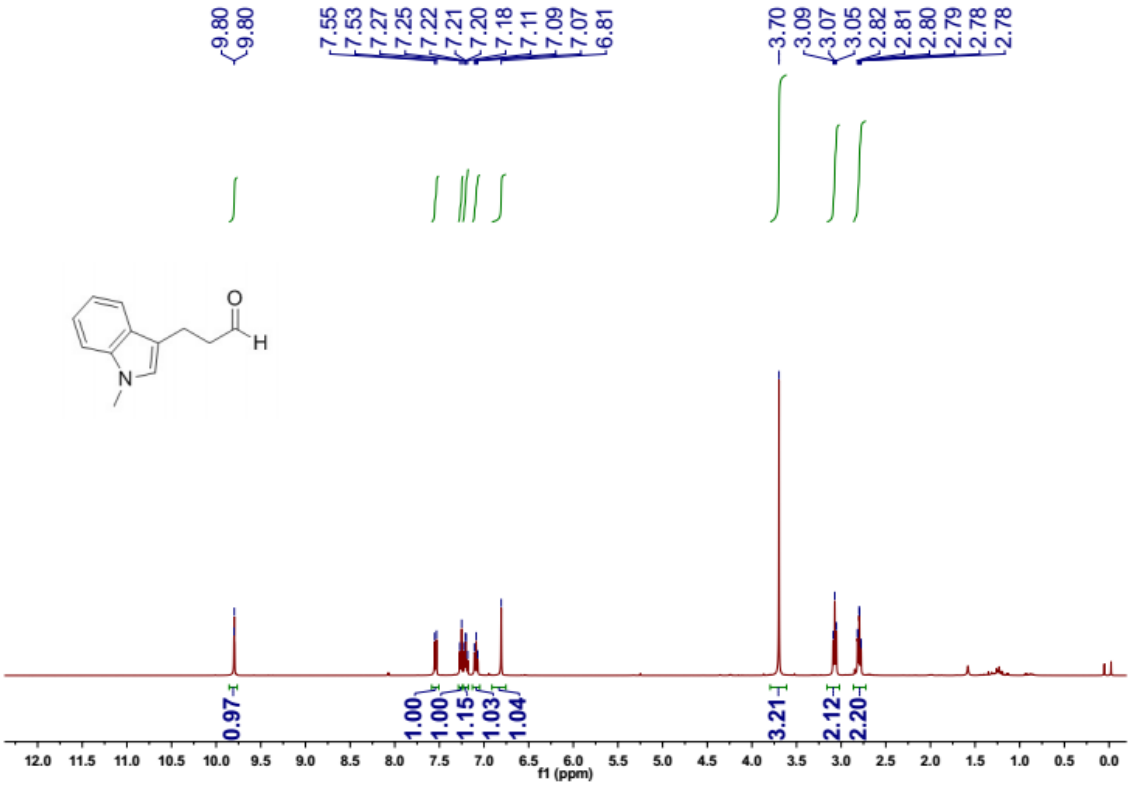
$^{2}$H NMR of deuterated aldehyde **12d**



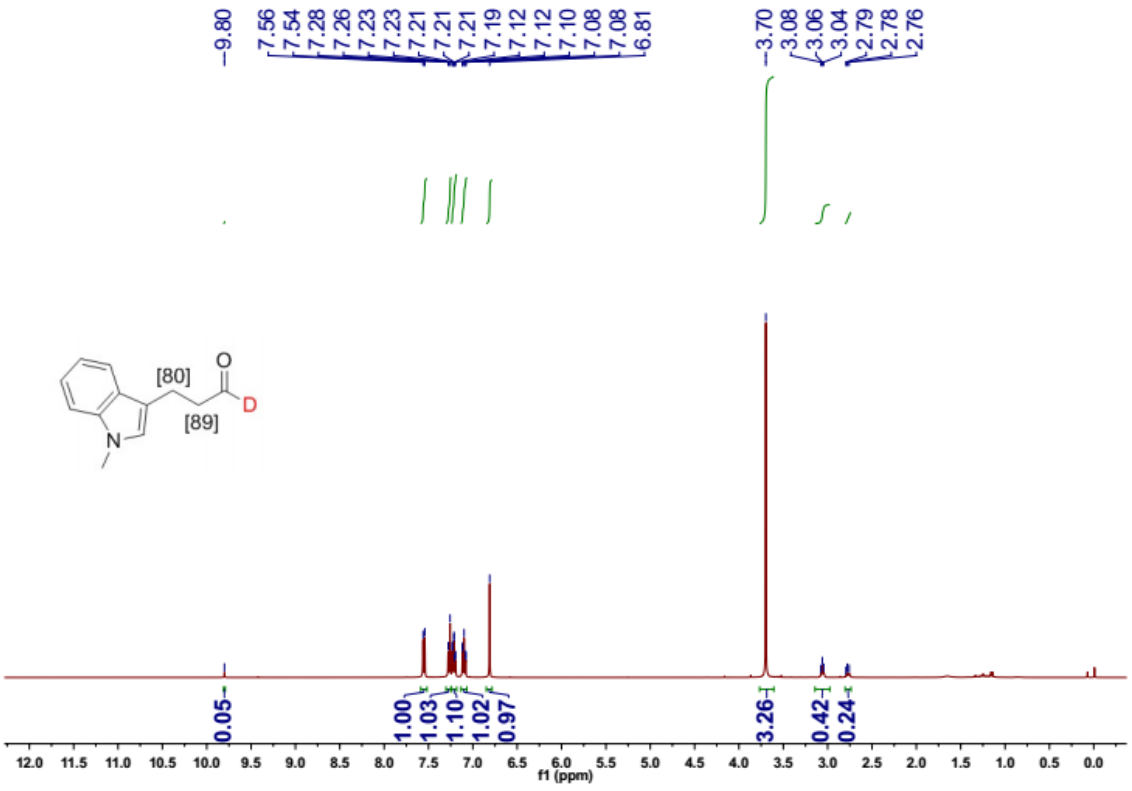

$^{13}$C NMR of deuterated aldehyde **12d**



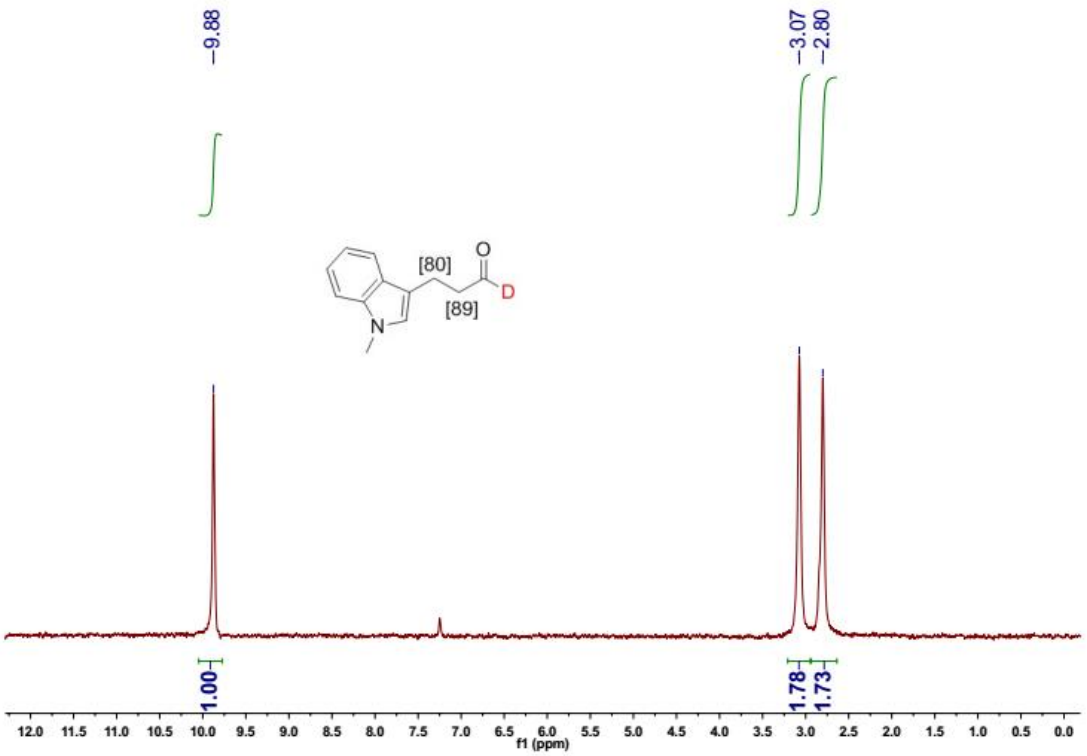
$^{1}$H NMR of aldehyde **11e**



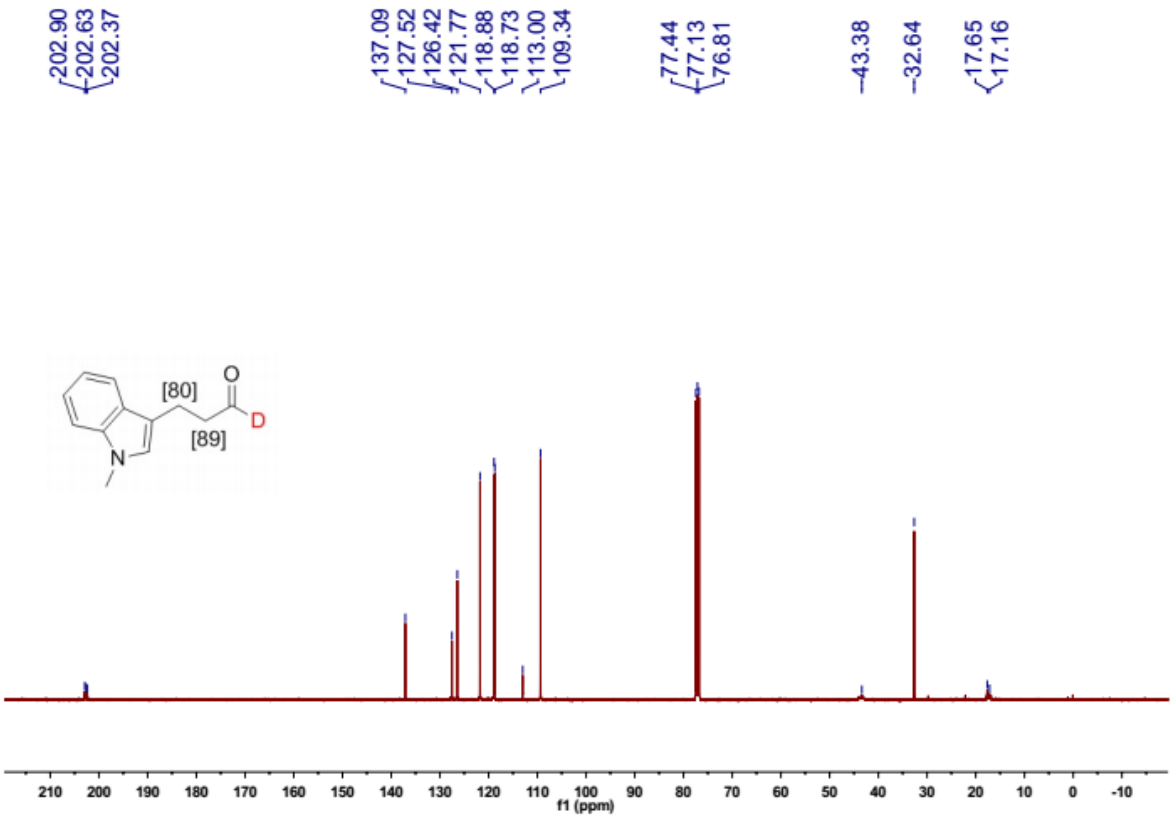

$^{1}$H NMR of deuterated aldehyde **12e**



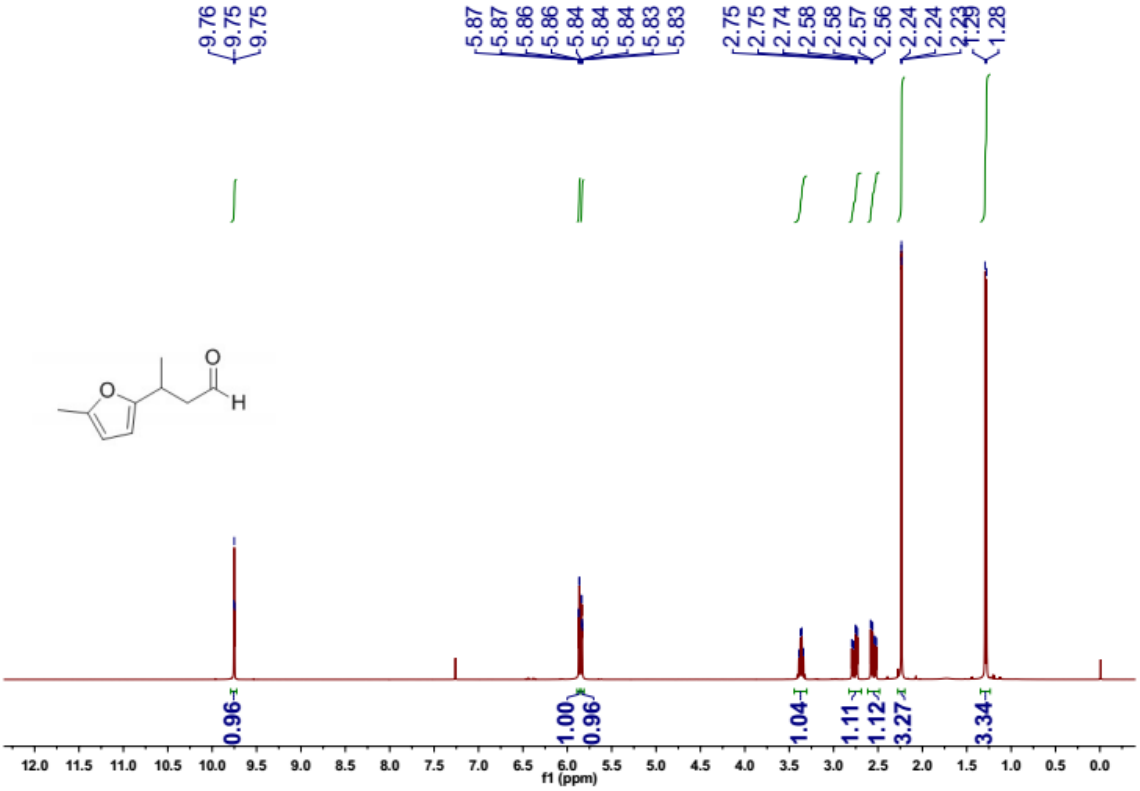
$^{2}$H NMR of deuterated aldehyde **12e**



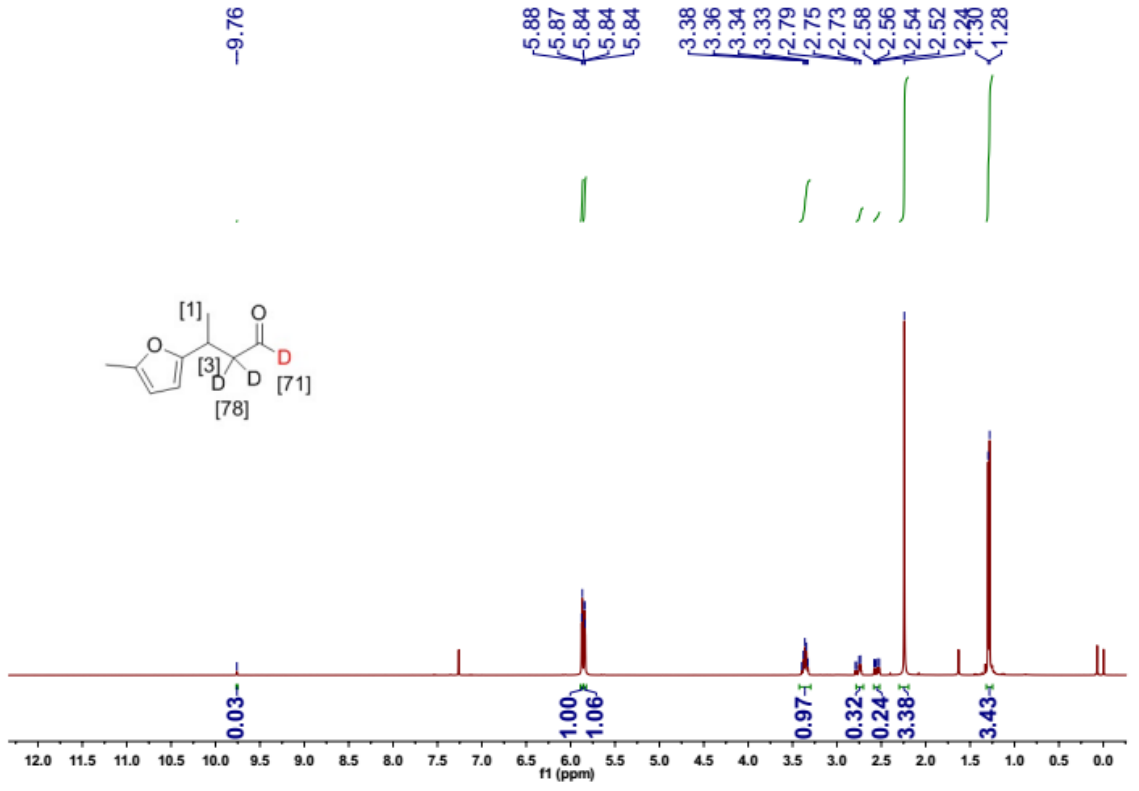

$^{13}$C NMR of deuterated aldehyde **12e**



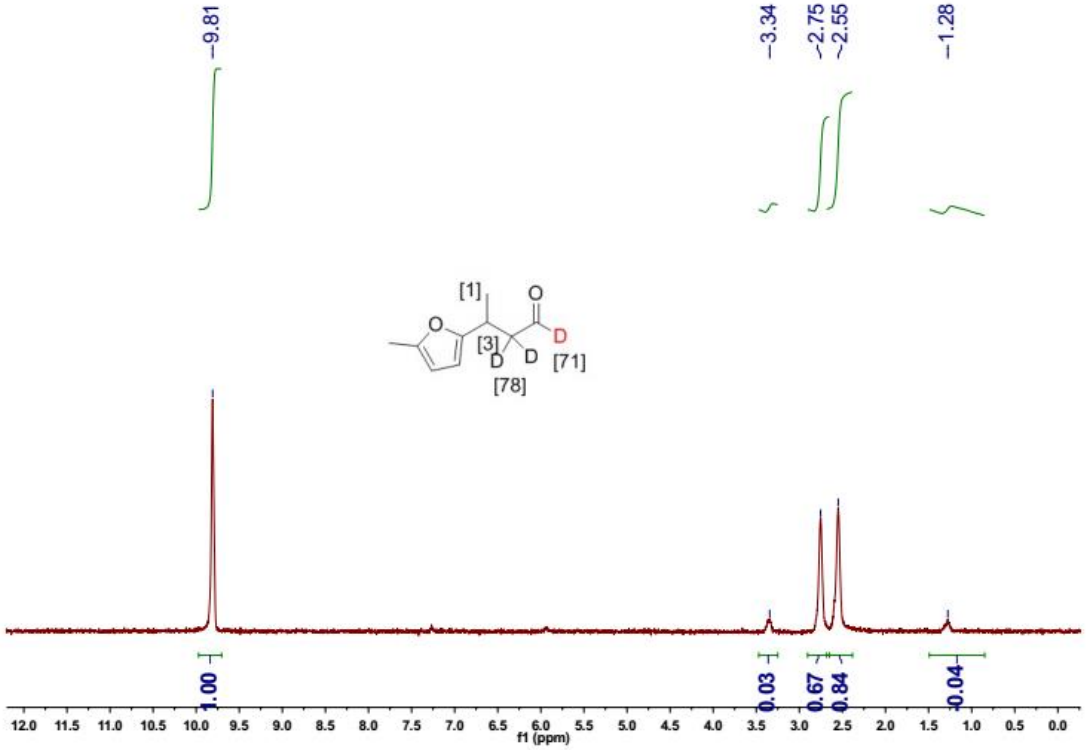
$^{1}$H NMR of aldehyde **11f**



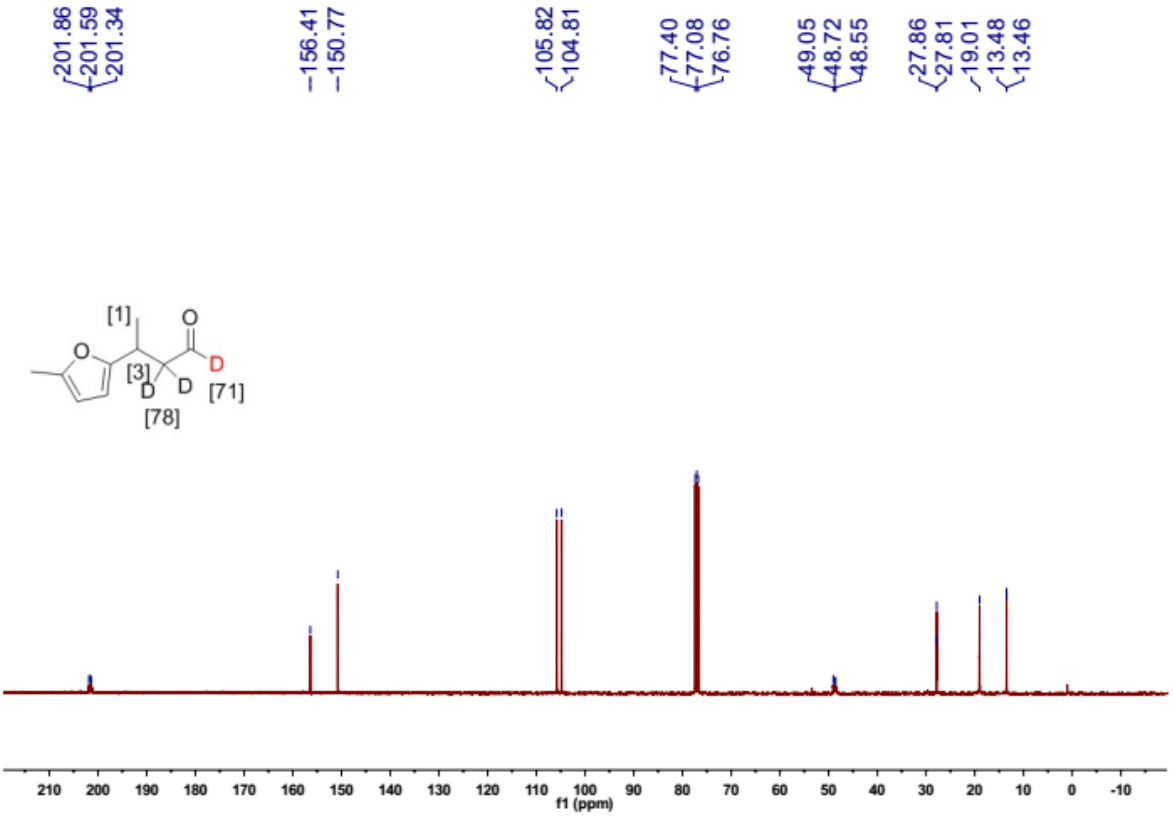

$^{1}$H NMR of deuterated aldehyde **12f**



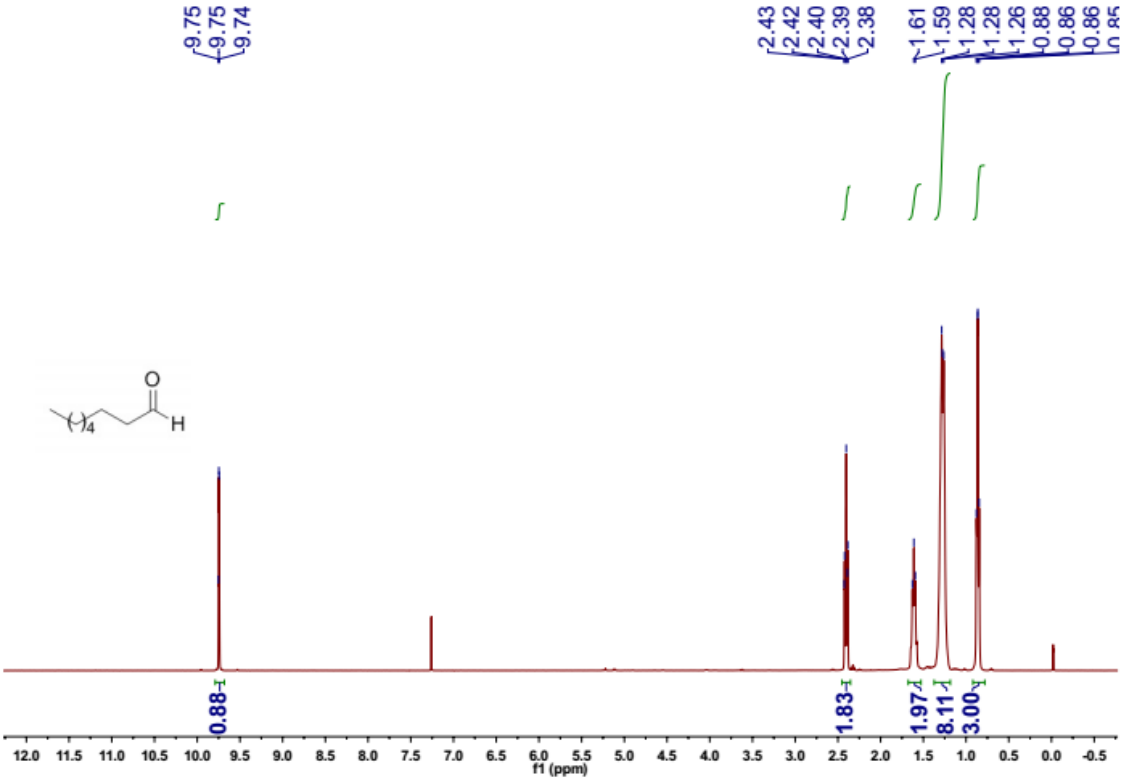
$^{2}$H NMR of deuterated aldehyde **12f**



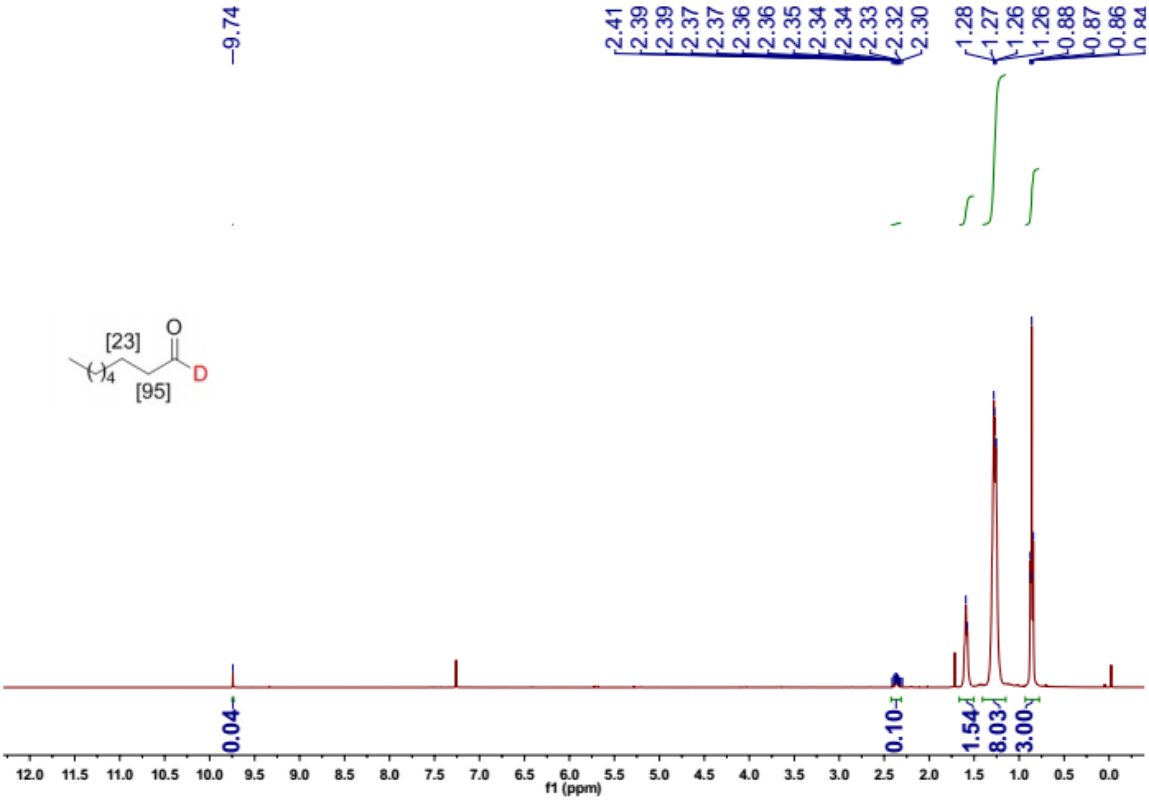

$^{13}$C NMR of deuterated aldehyde **12f**



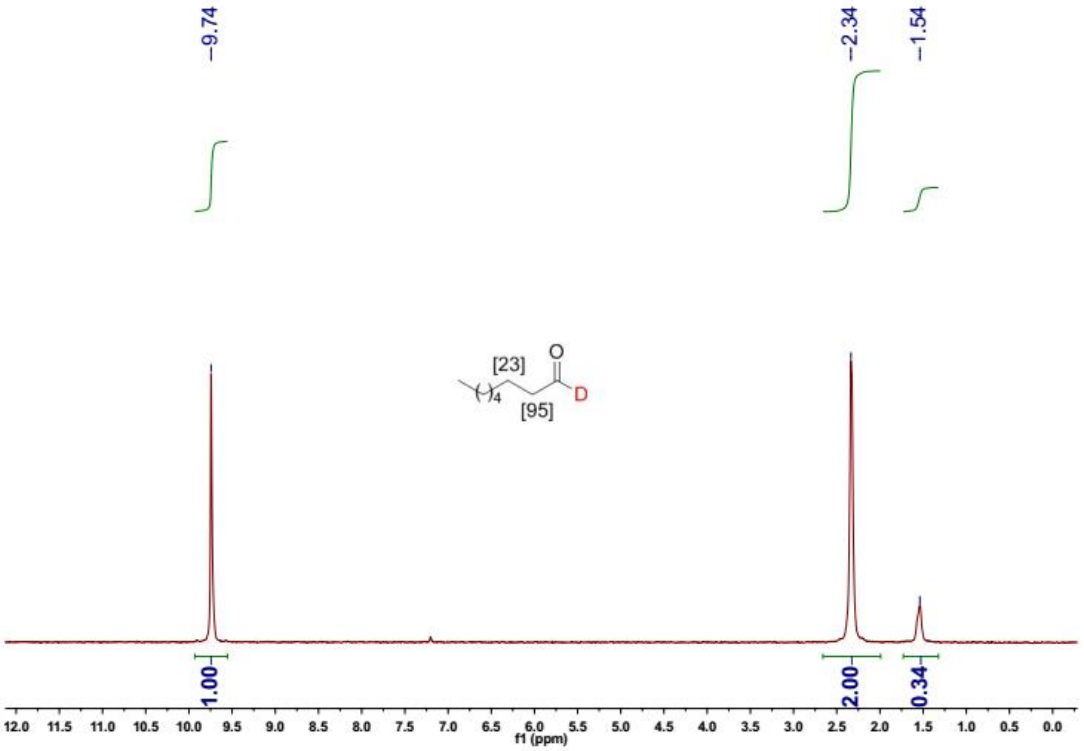
$^{1}$H NMR of aldehyde **11g**



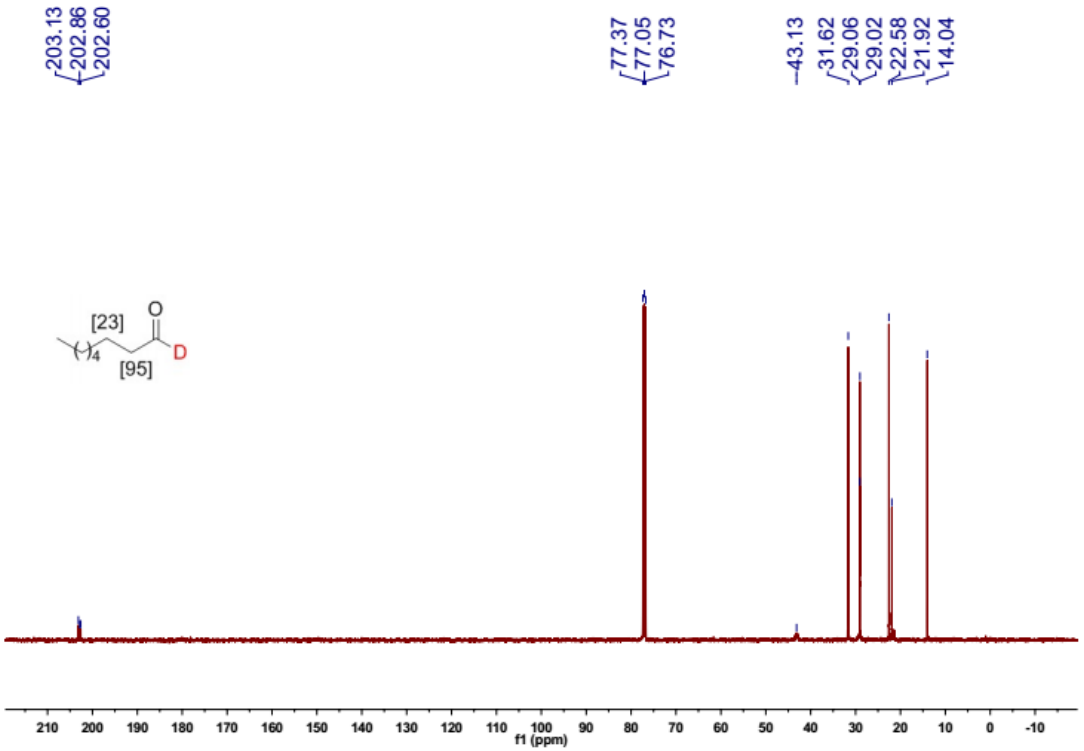

$^{1}$H NMR of deuterated aldehyde **12g**



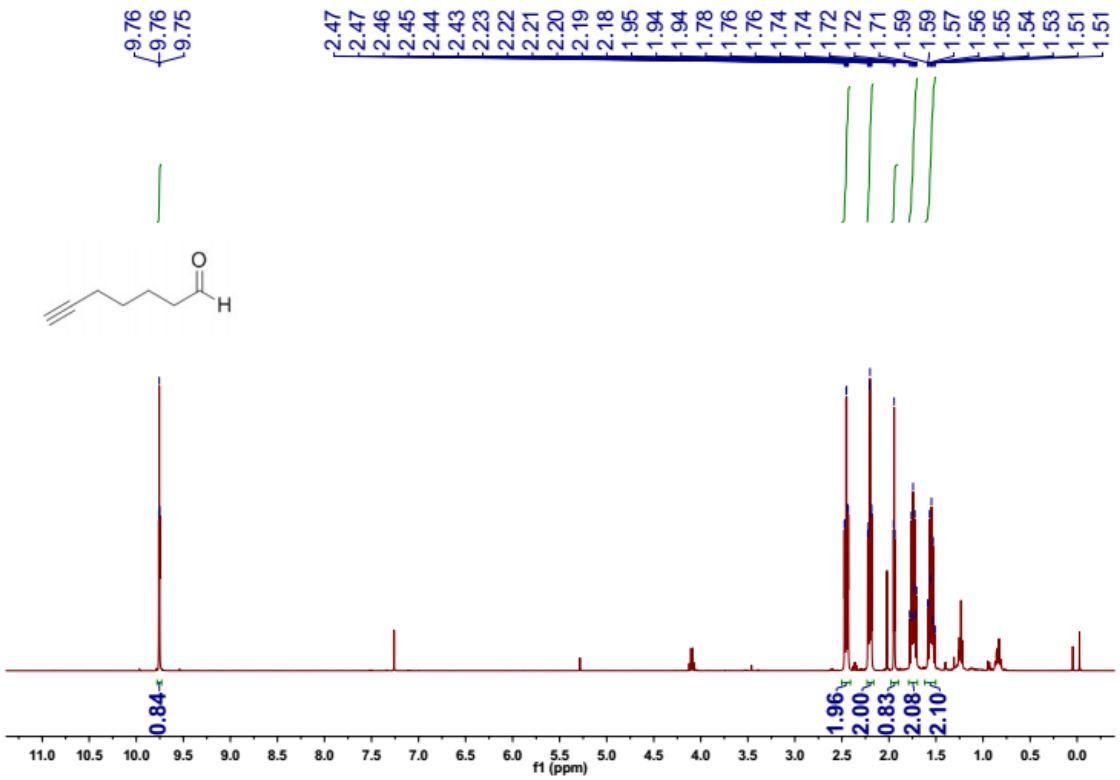
$^{2}$H NMR of deuterated aldehyde **12g**



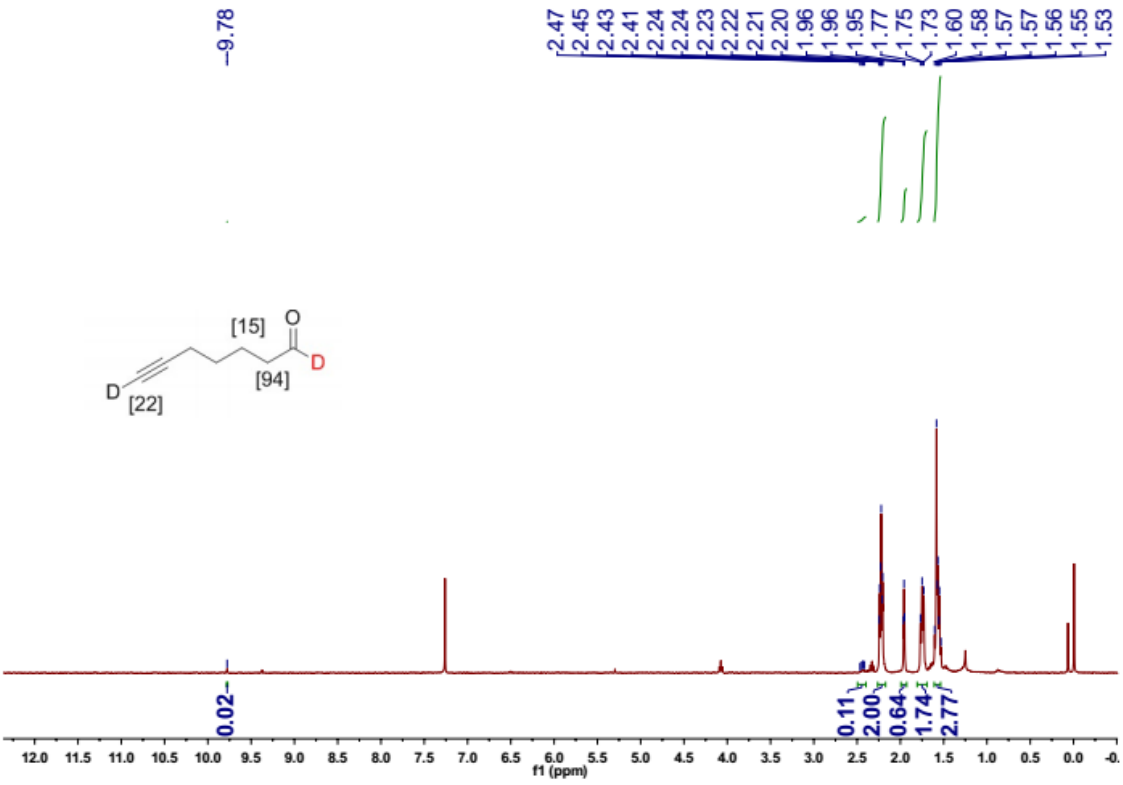

$^{13}$C NMR of deuterated aldehyde **12g**



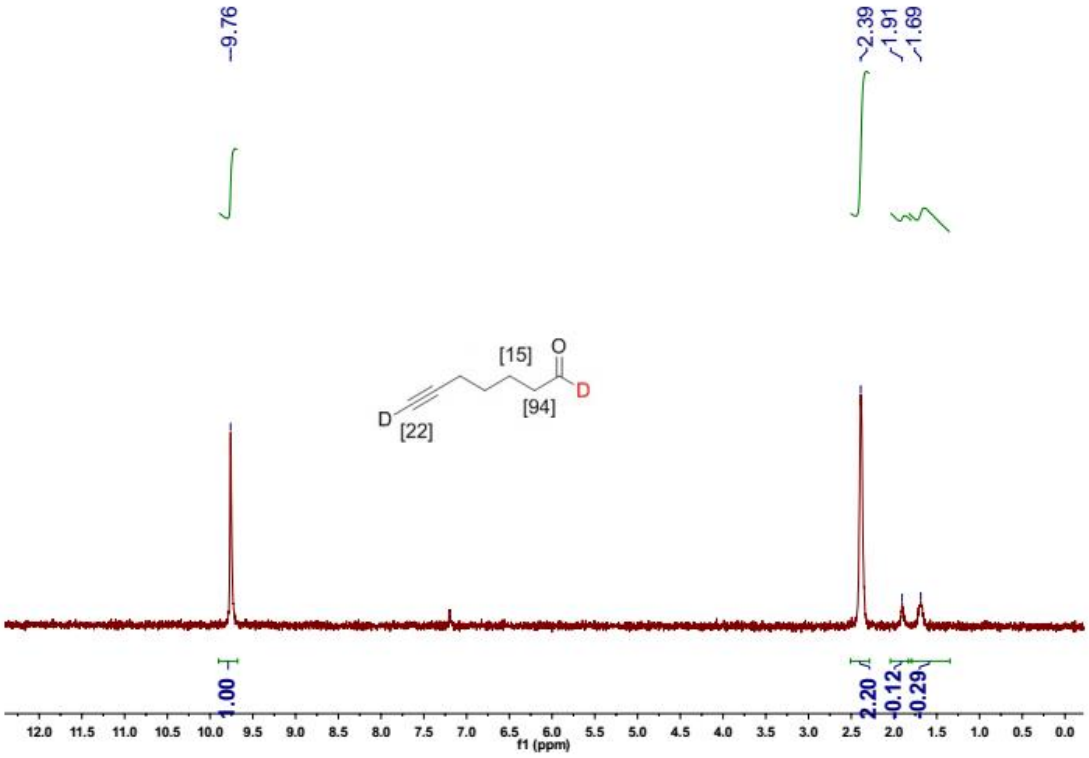
$^{1}$H NMR of aldehyde **11h**



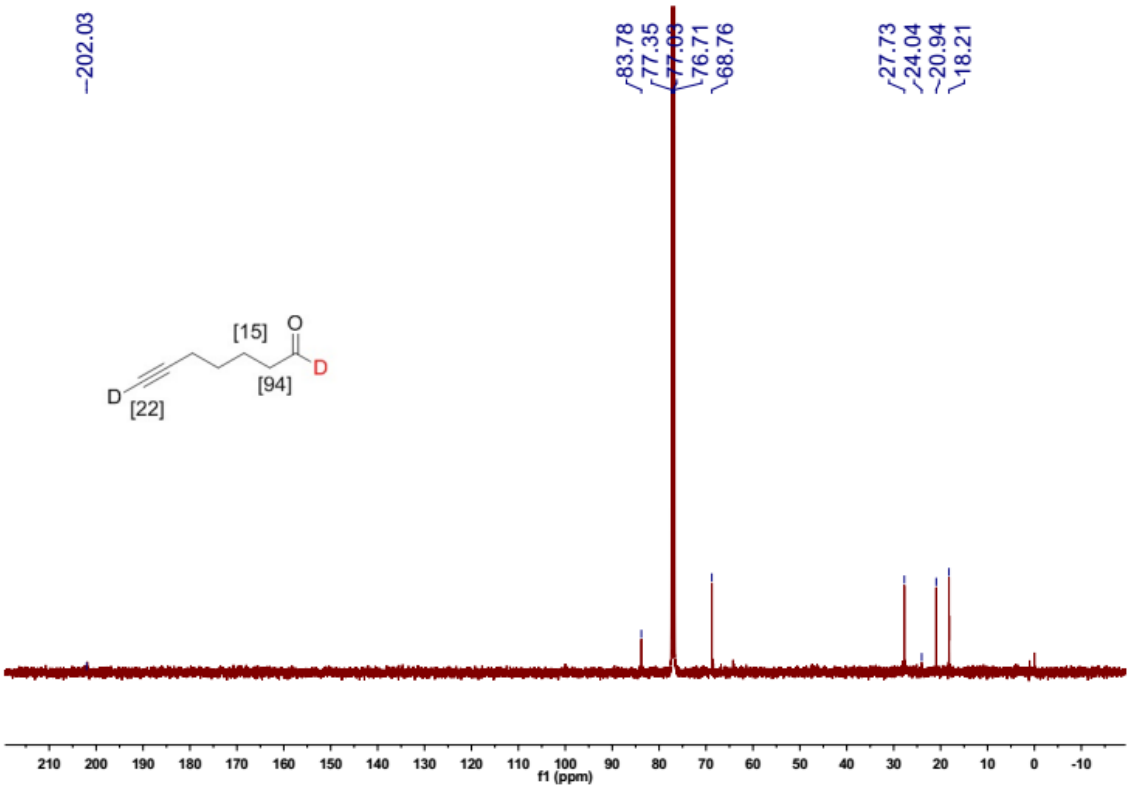

$^{1}$H NMR of deuterated aldehyde **12h**



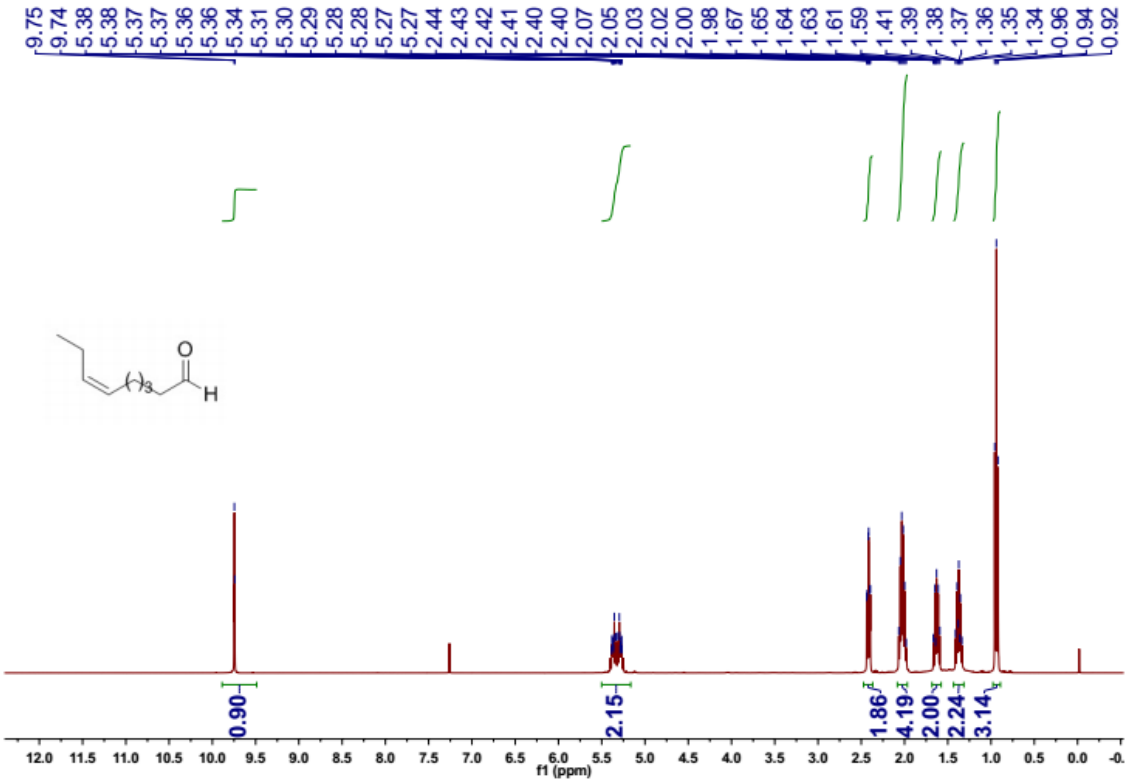
$^{2}$H NMR of deuterated aldehyde **12h**



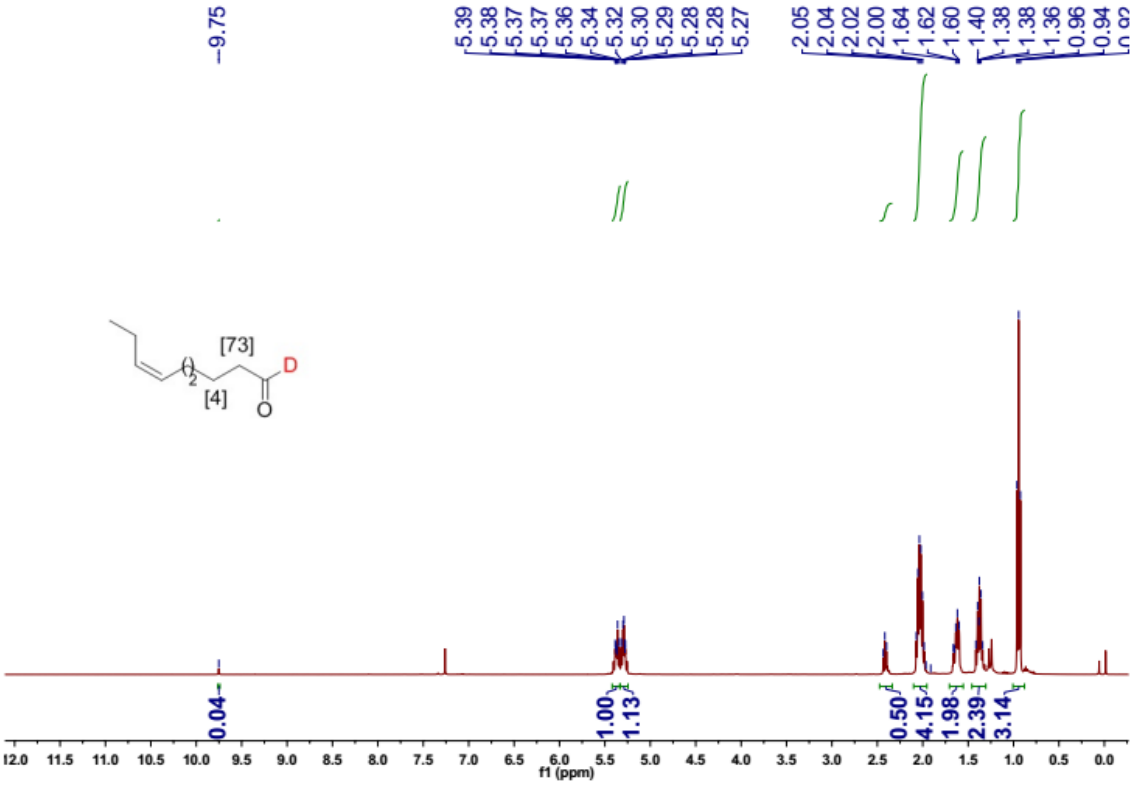

$^{13}$C NMR of deuterated aldehyde **12h**



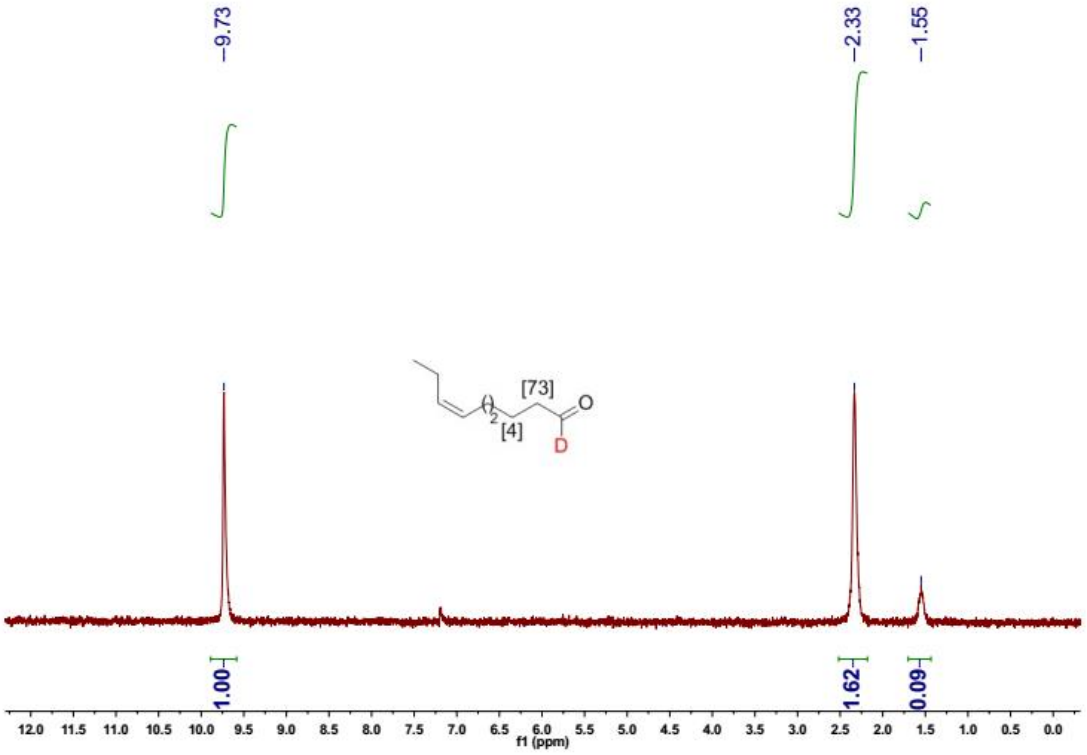
$^{1}$H NMR of aldehyde **11i**



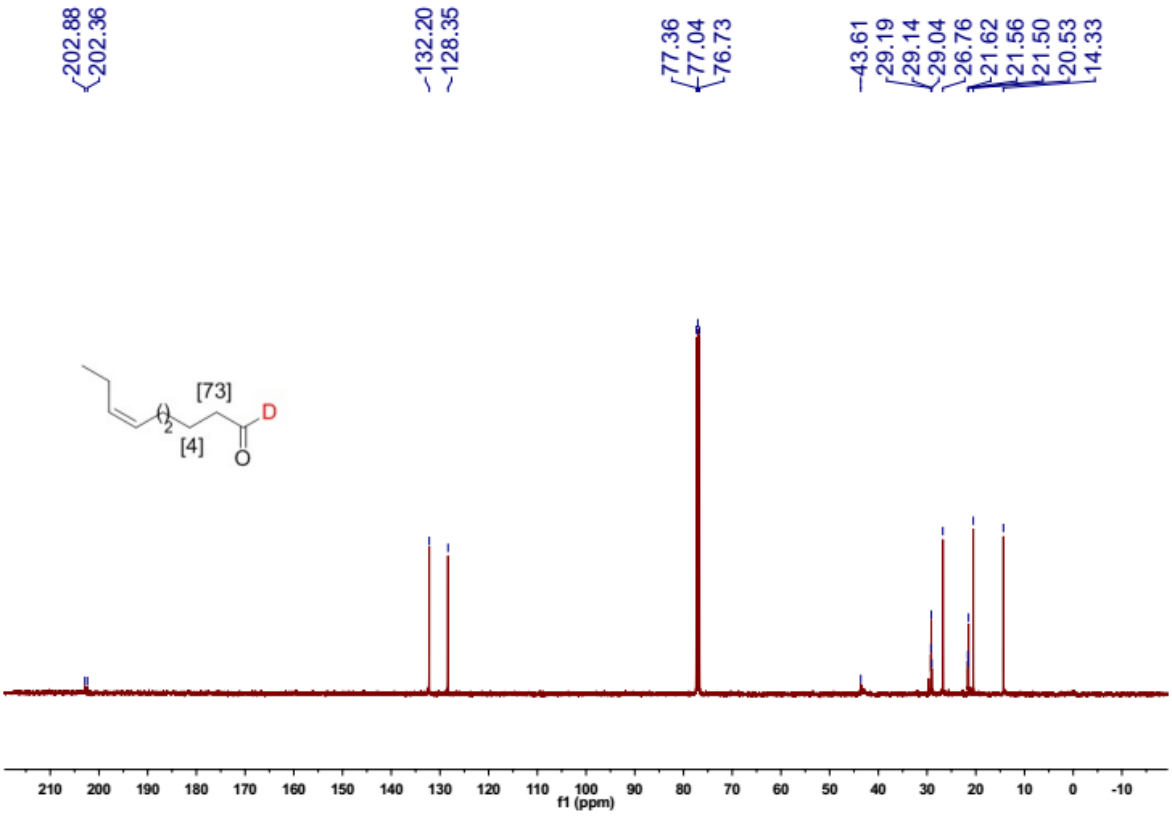

$^{1}$H NMR of deuterated aldehyde **12i**



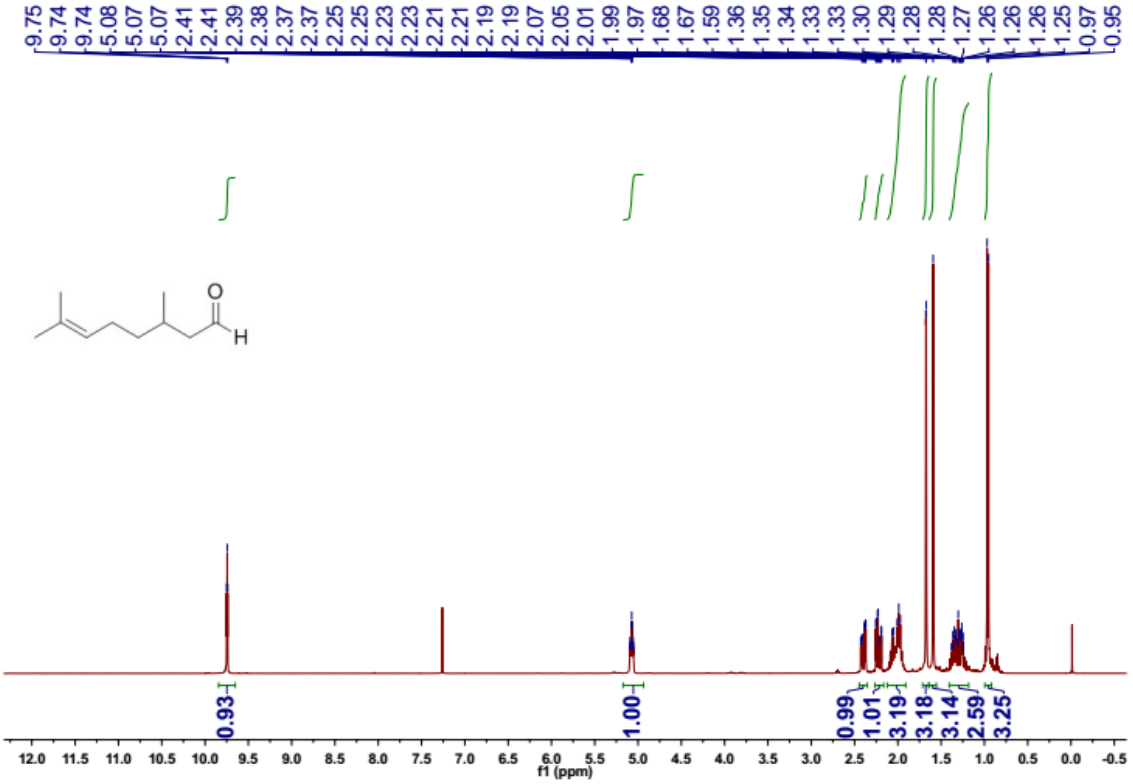
$^{2}$H NMR of deuterated aldehyde **12i**



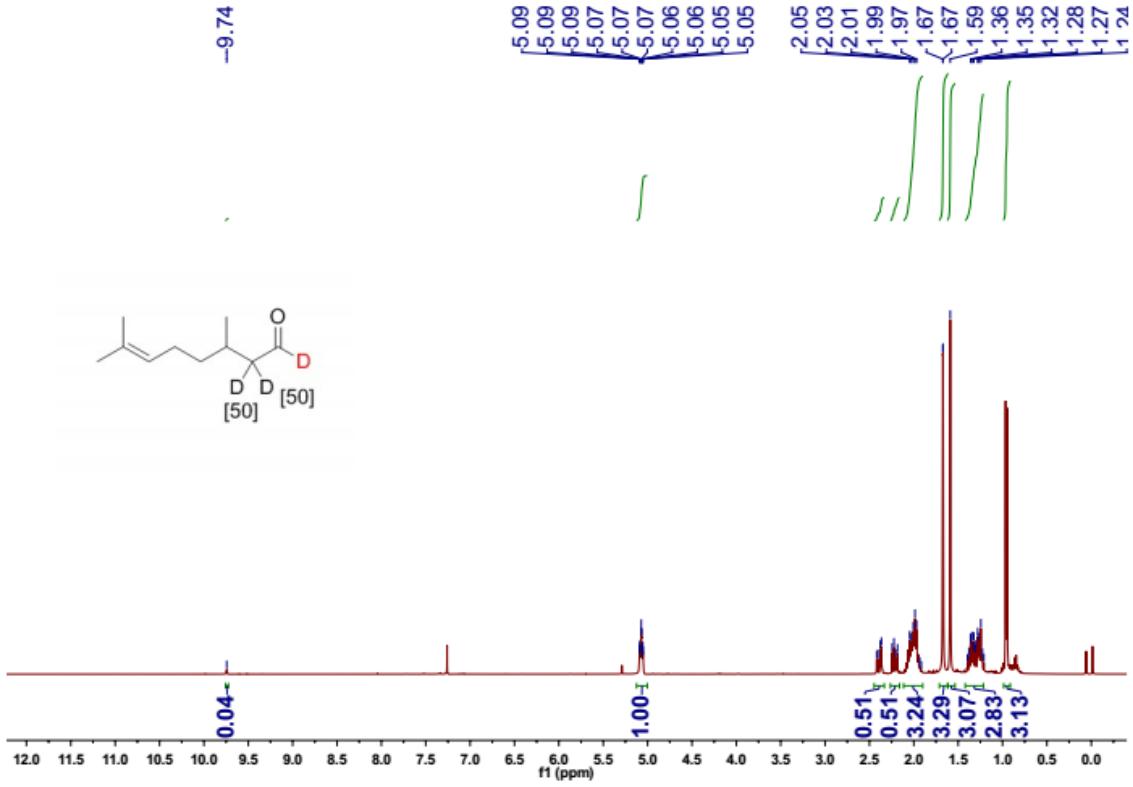

$^{13}$C NMR of deuterated aldehyde **12i**



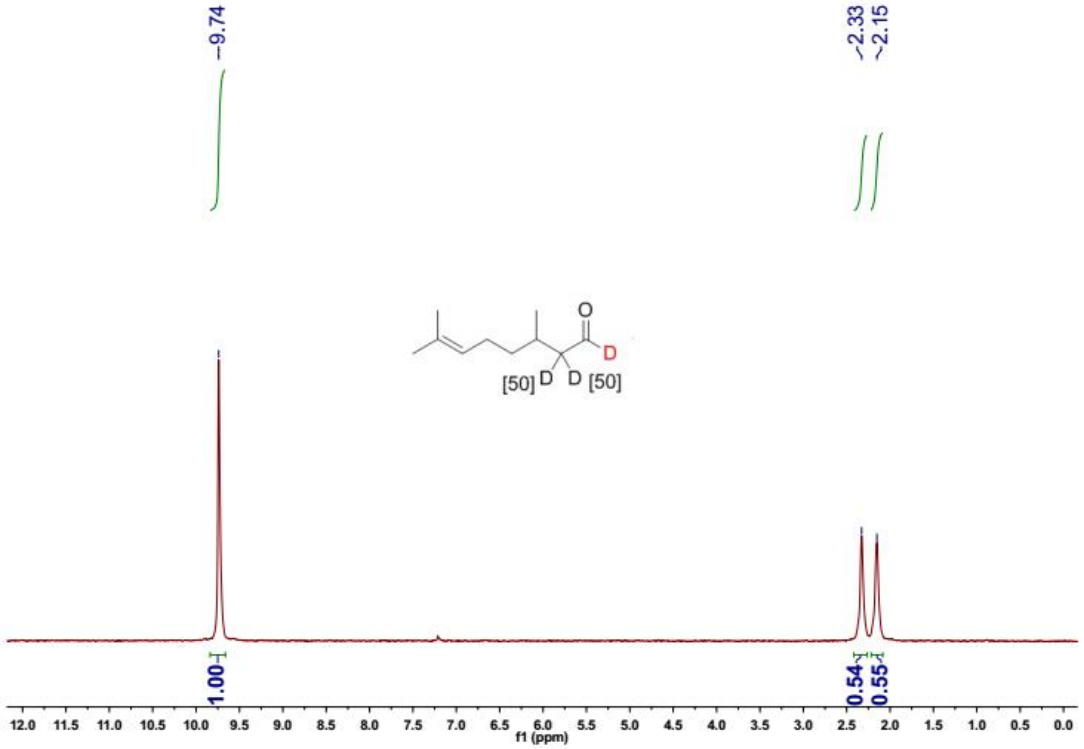
$^{1}$H NMR of aldehyde **11j**



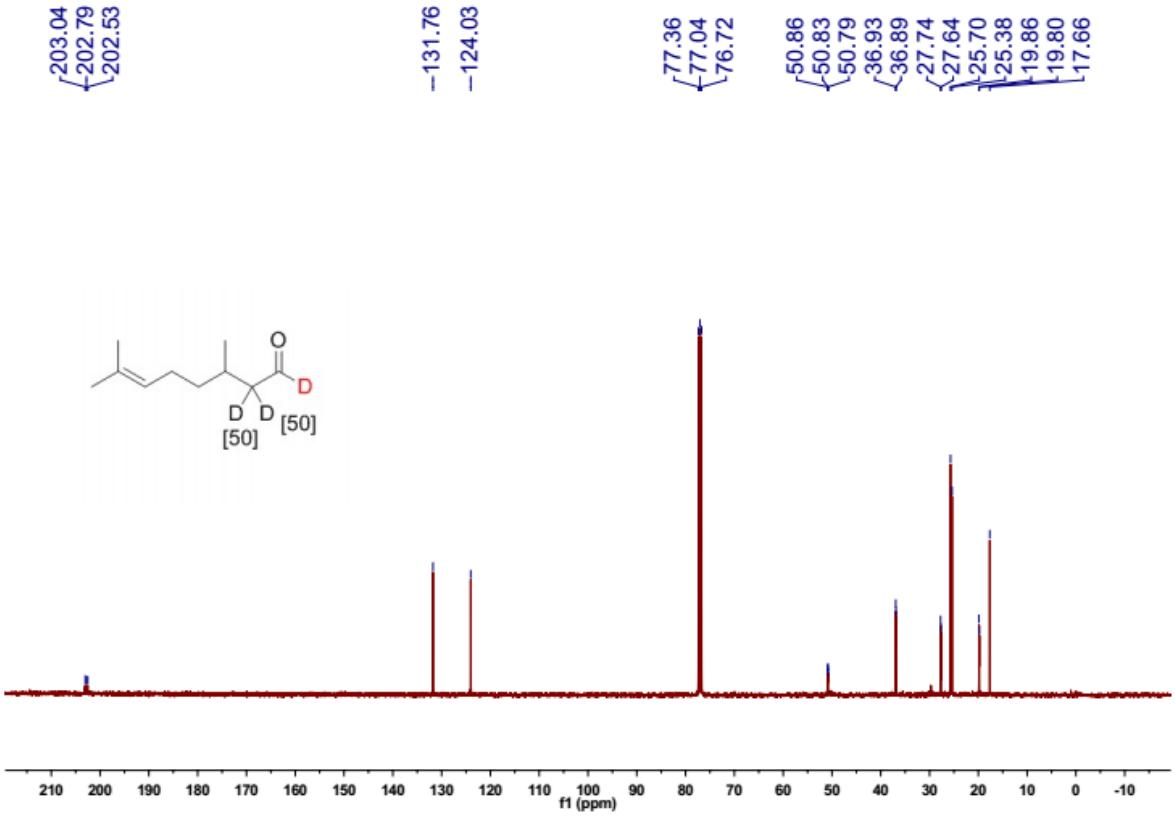

$^{1}$H NMR of deuterated aldehyde **12j**



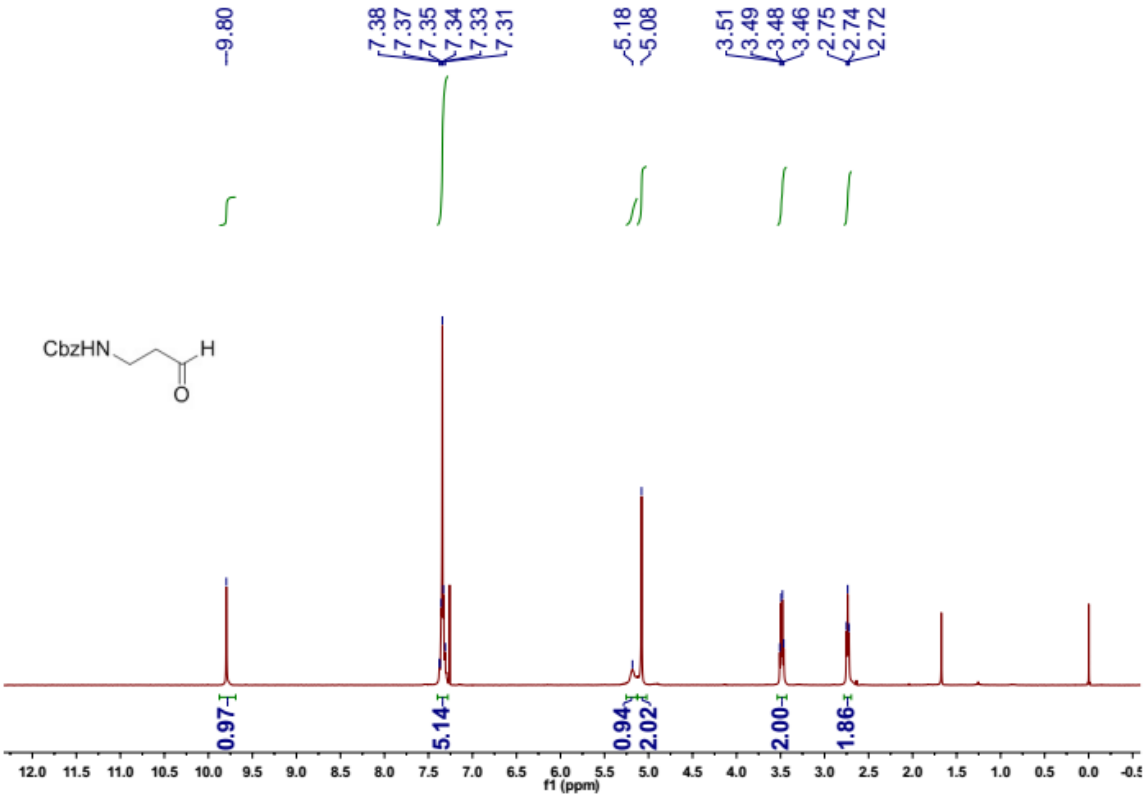
$^{2}$H NMR of deuterated aldehyde **12j**



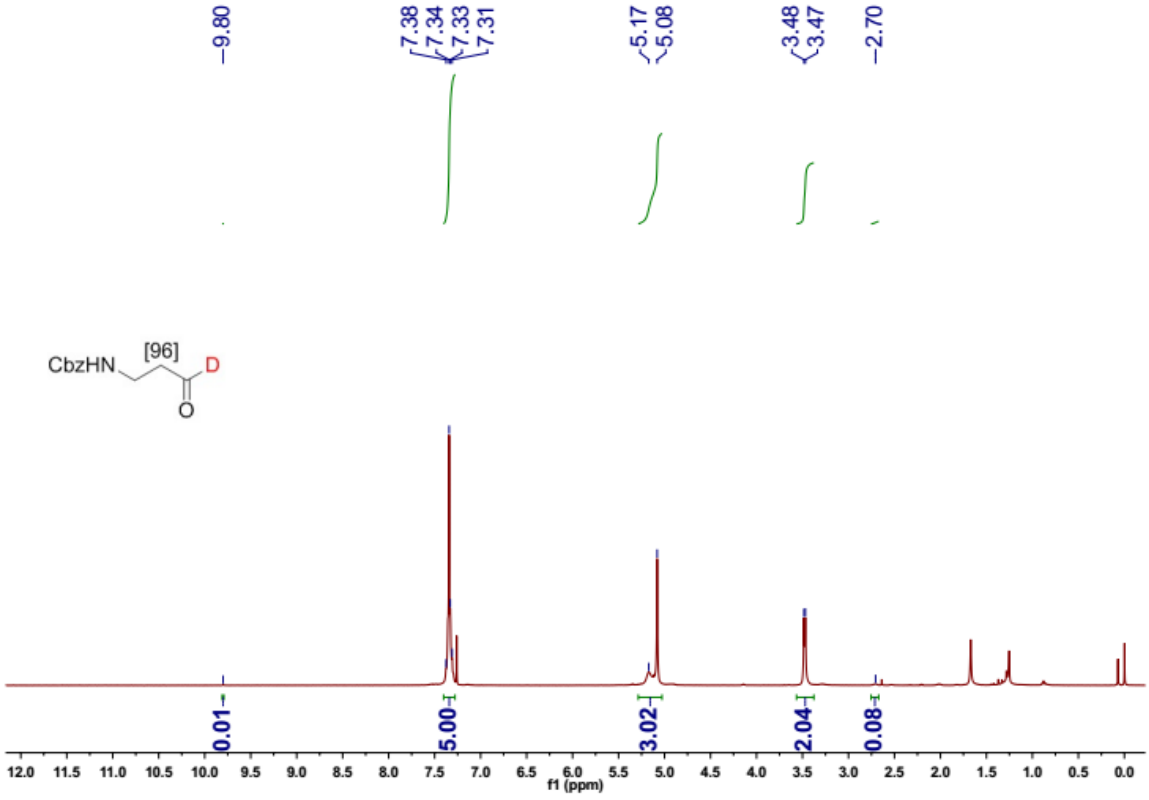

$^{13}$C NMR of deuterated aldehyde **12j**



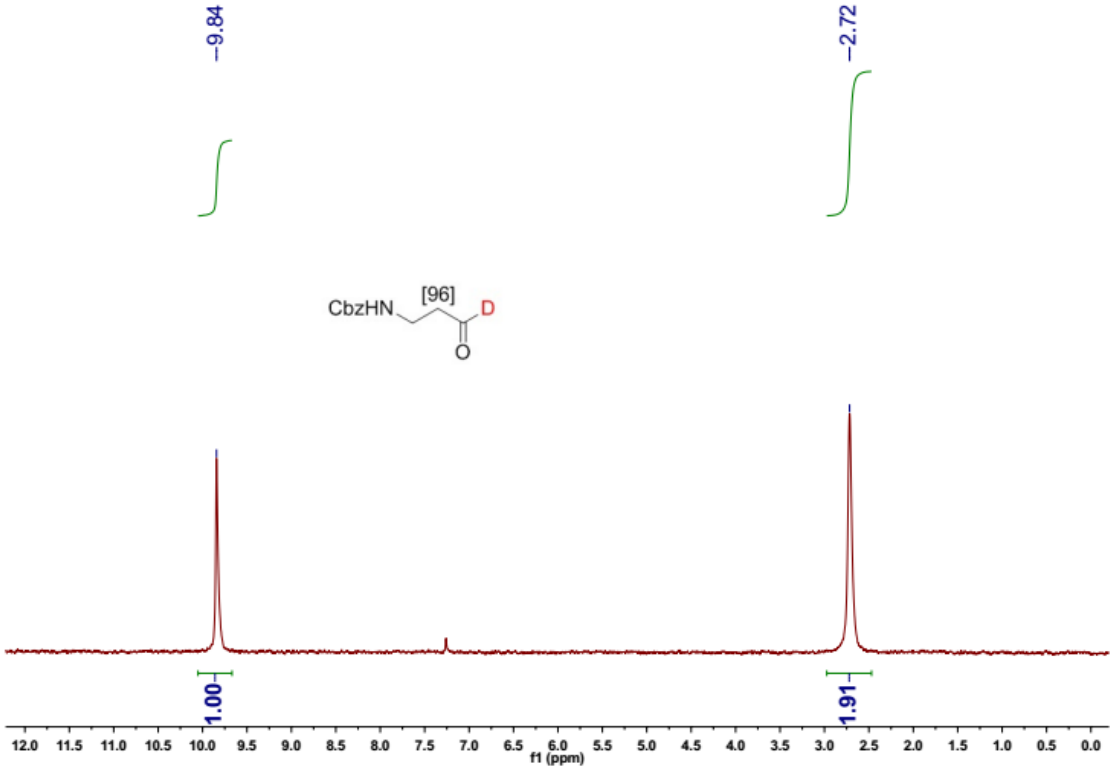
$^{1}$H NMR of aldehyde **11k**



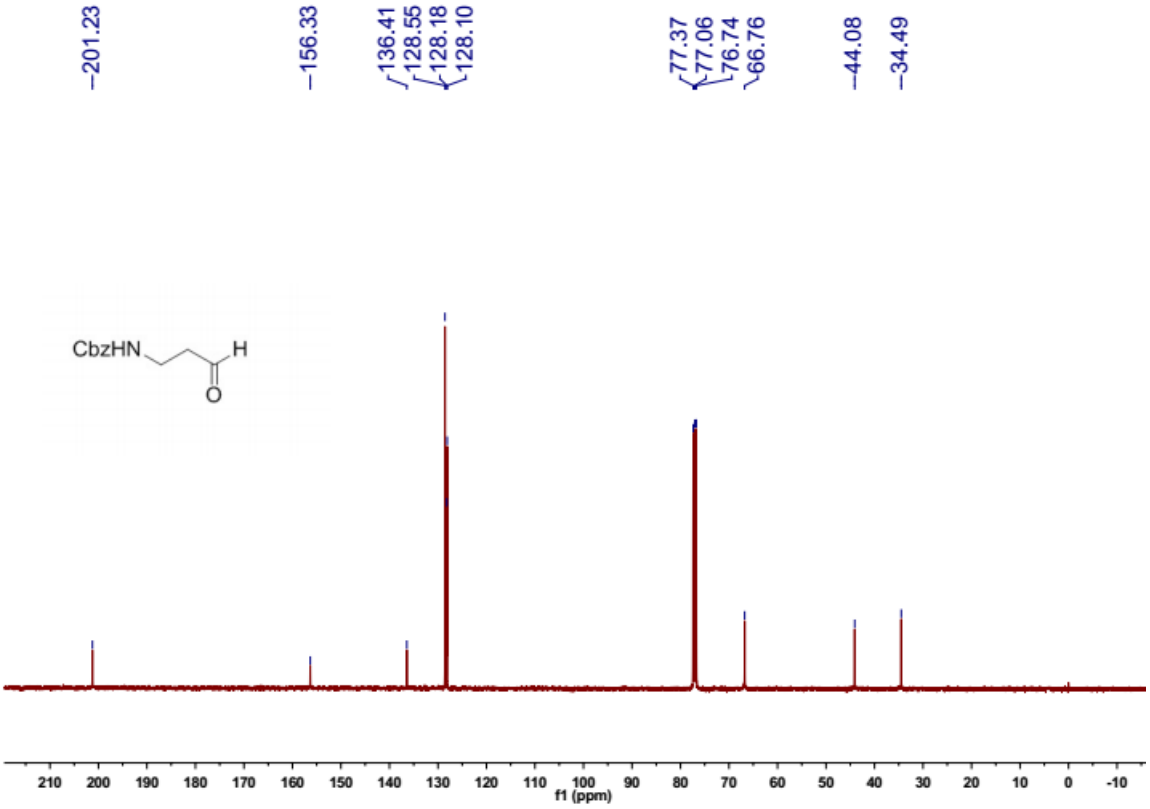

$^{1}$H NMR of deuterated aldehyde **12k**



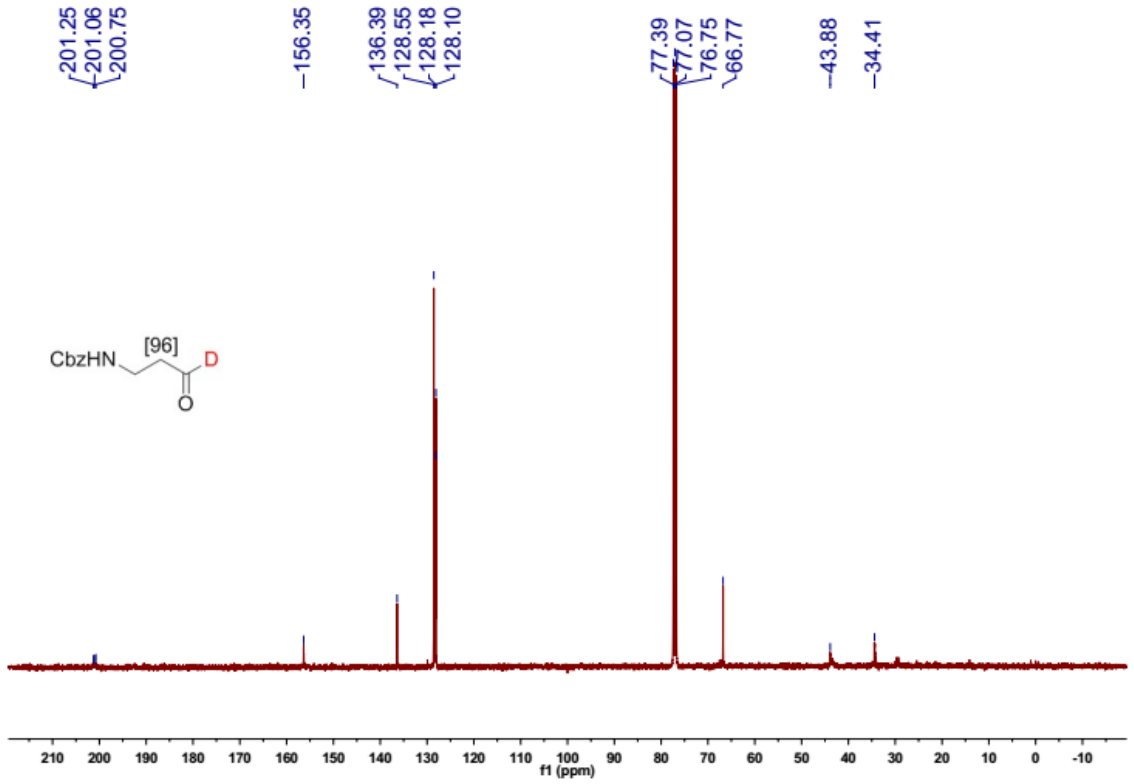
$^{2}$H NMR of deuterated aldehyde **12k**



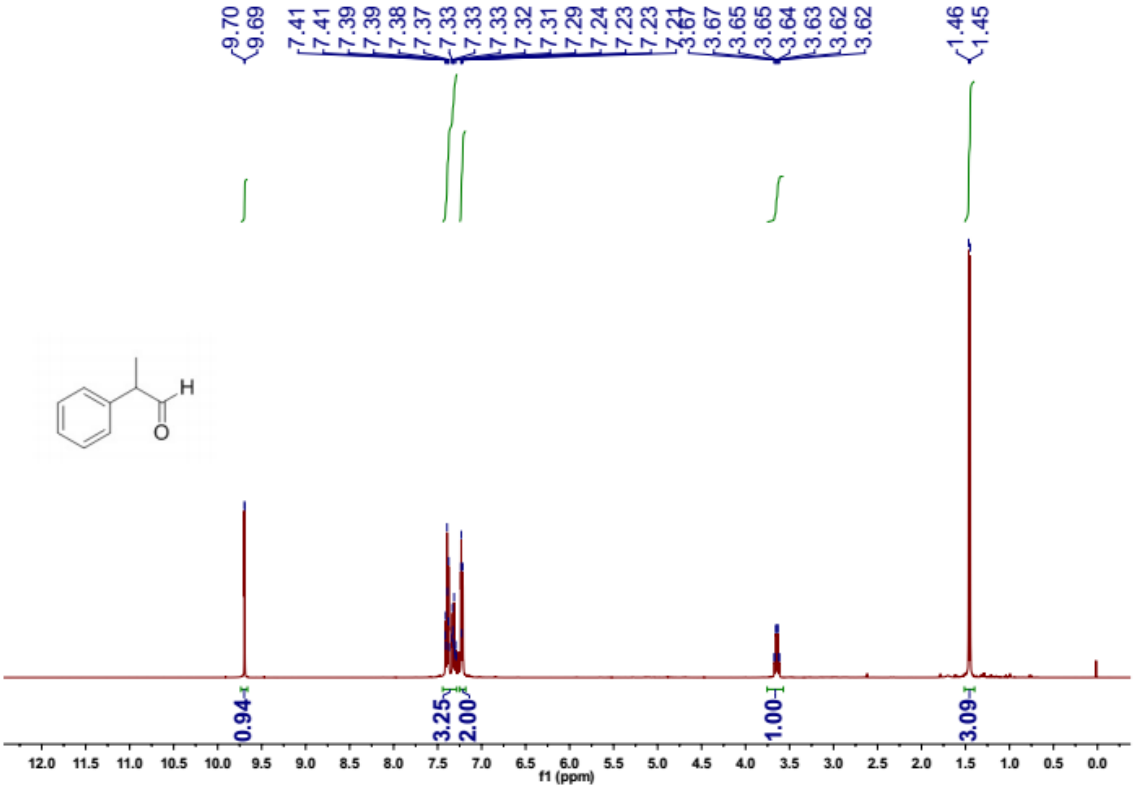
$^{13}$C NMR of aldehyde **11k**



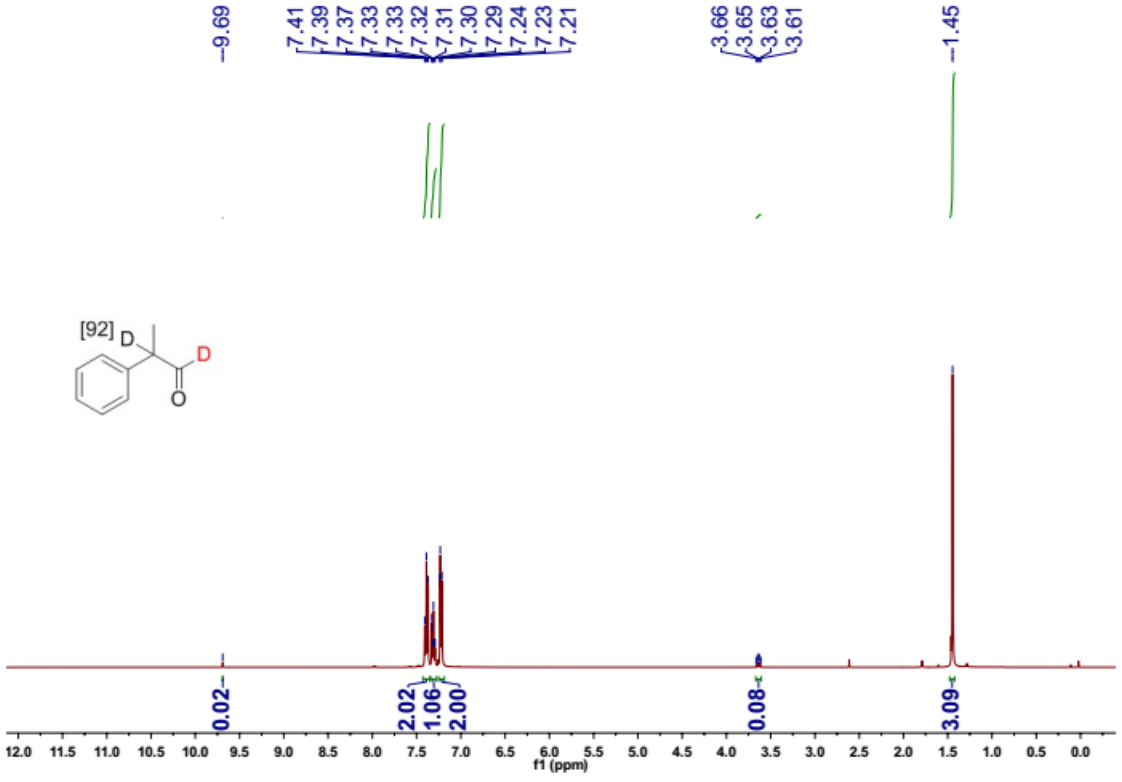

$^{13}$C NMR of deuterated aldehyde **12k**



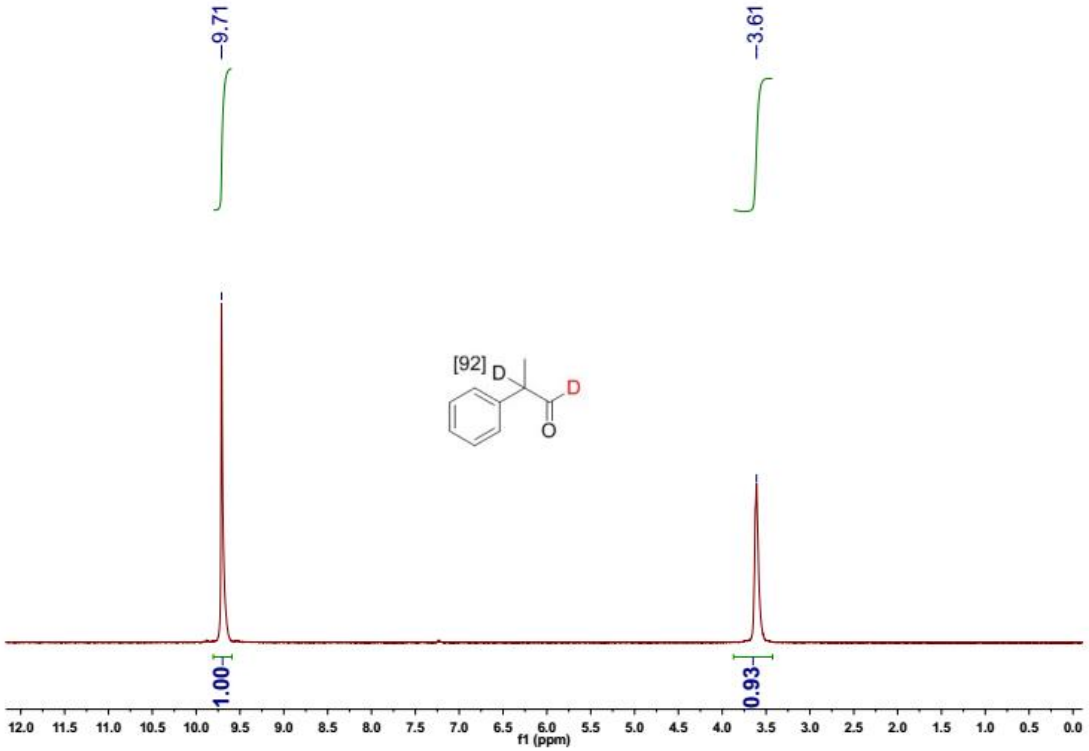
$^{1}$H NMR of aldehyde **11l**



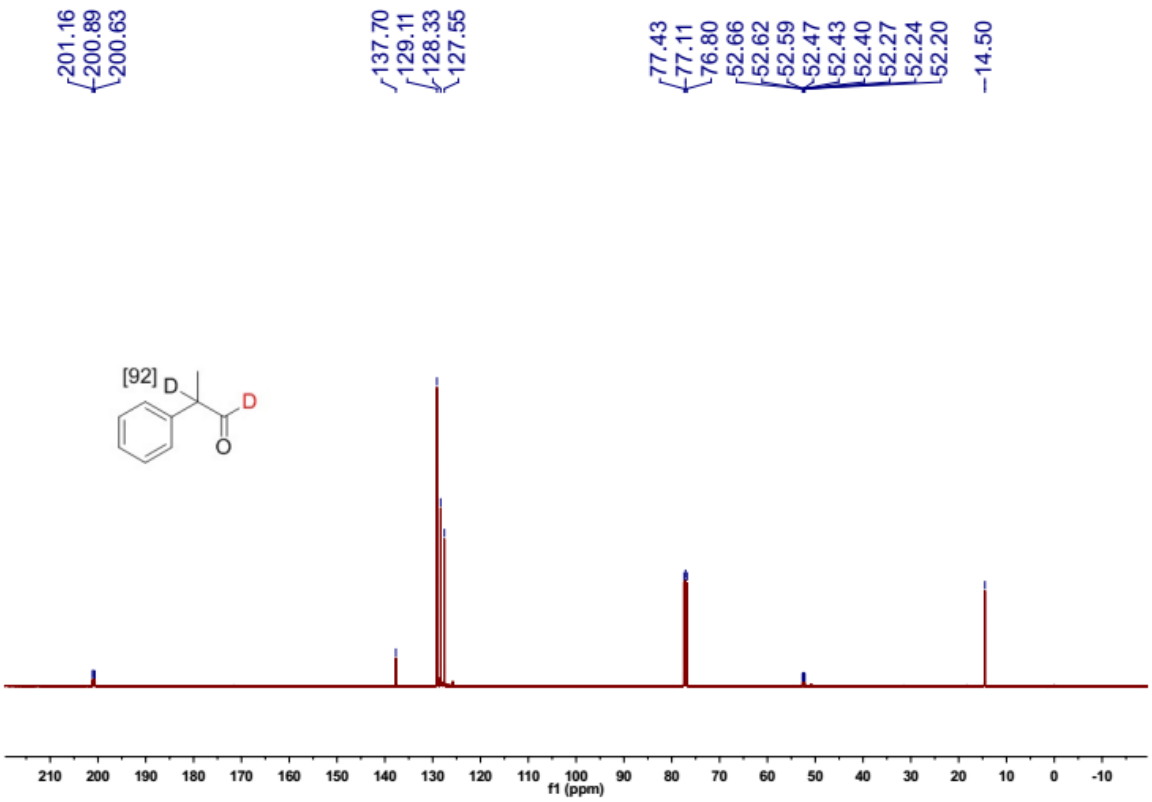

$^{1}$H NMR of deuterated aldehyde **12l**



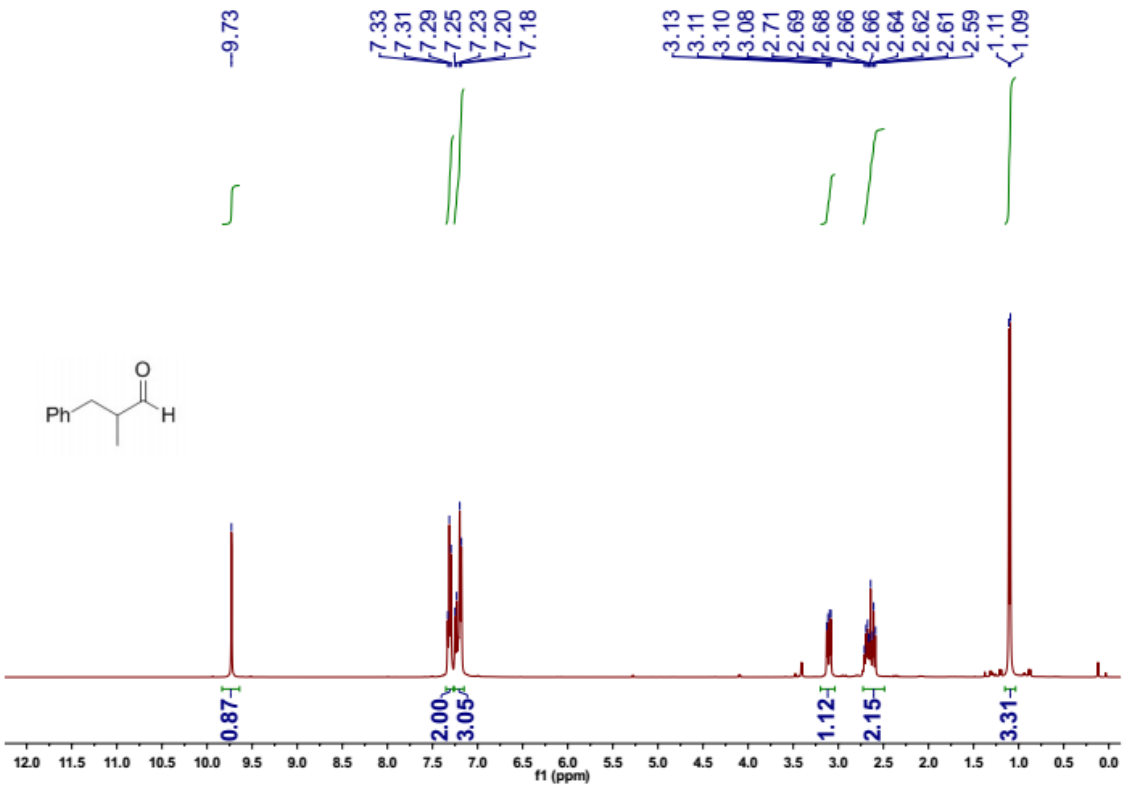
$^{2}$H NMR of deuterated aldehyde **12l**



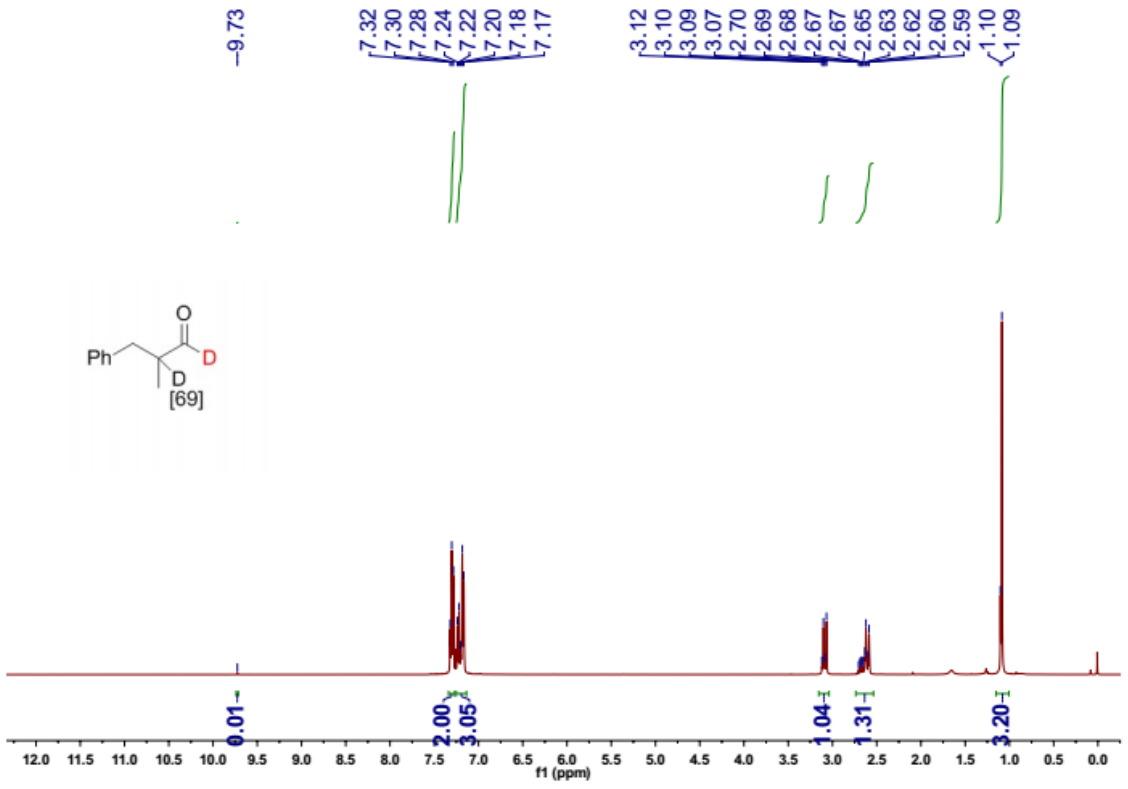

$^{13}$C NMR of deuterated aldehyde **12l**



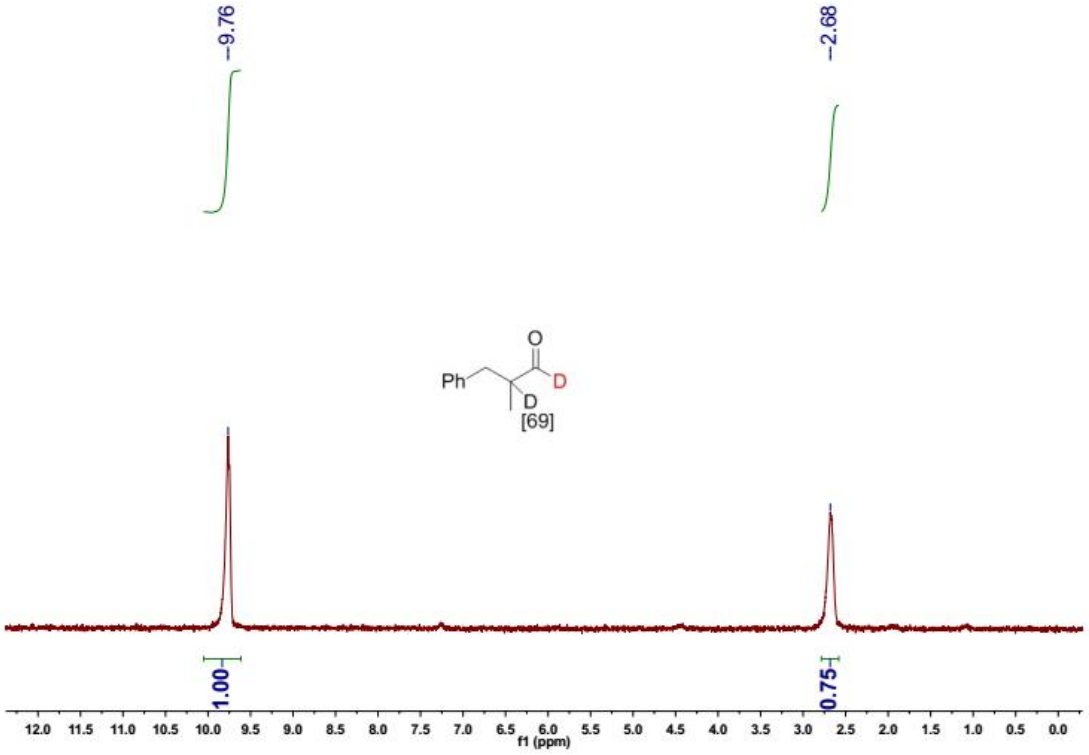
$^{1}$H NMR of aldehyde **11m**



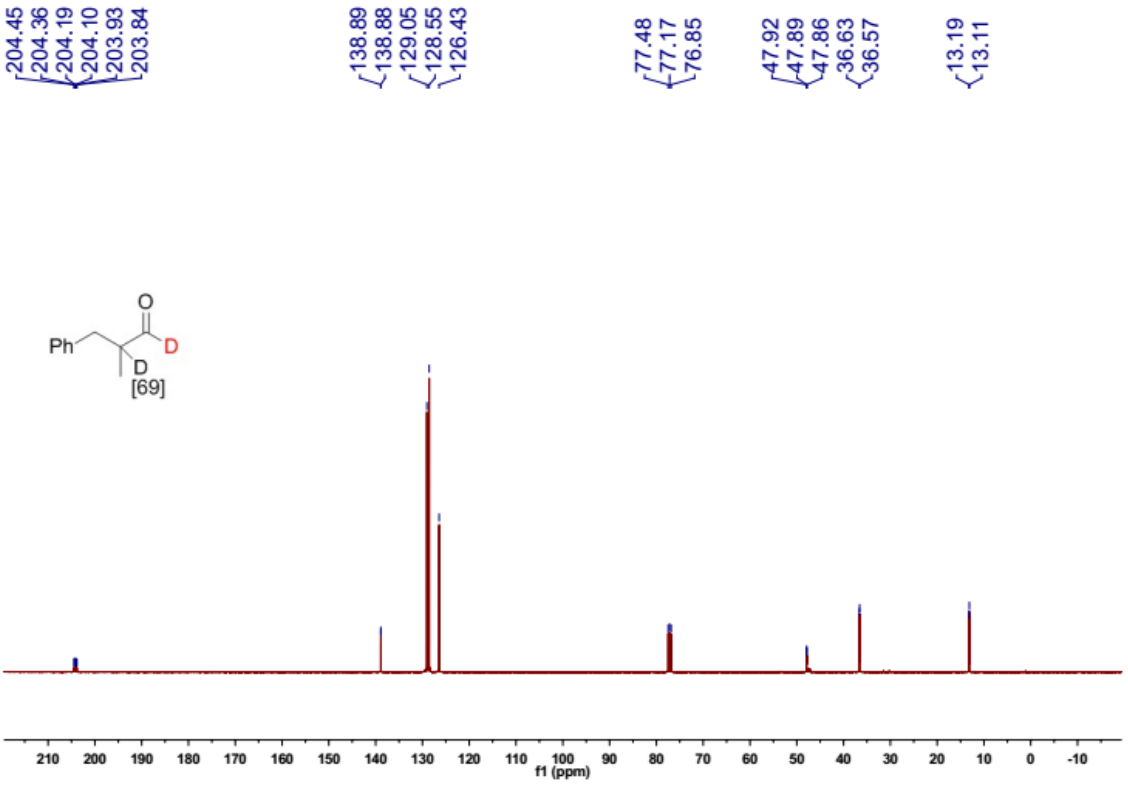

$^{1}$H NMR of deuterated aldehyde **12m**



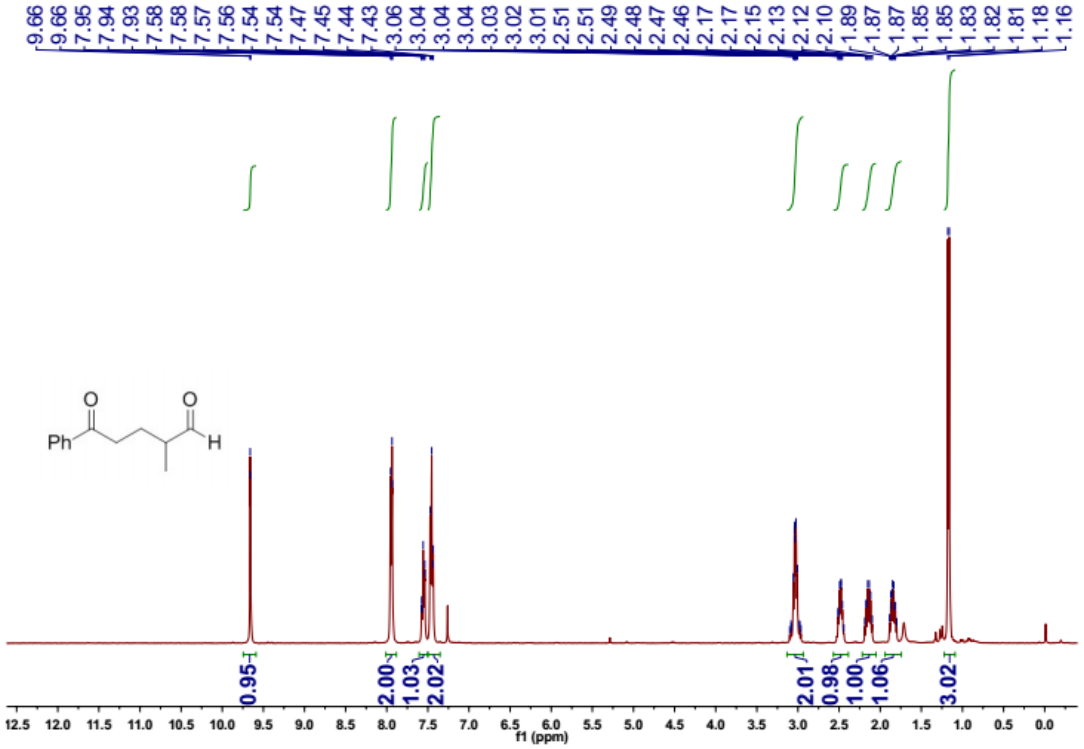
$^{2}$H NMR of deuterated aldehyde **12m**



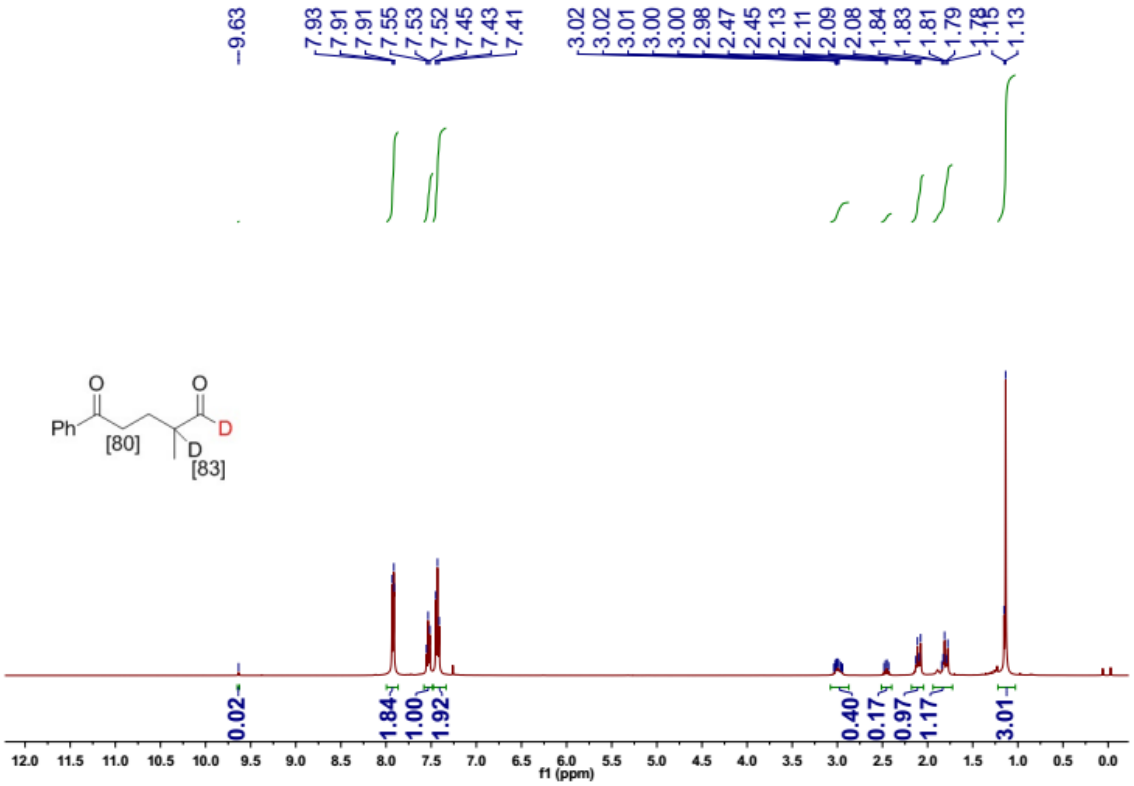

$^{13}$C NMR of deuterated aldehyde **12m**



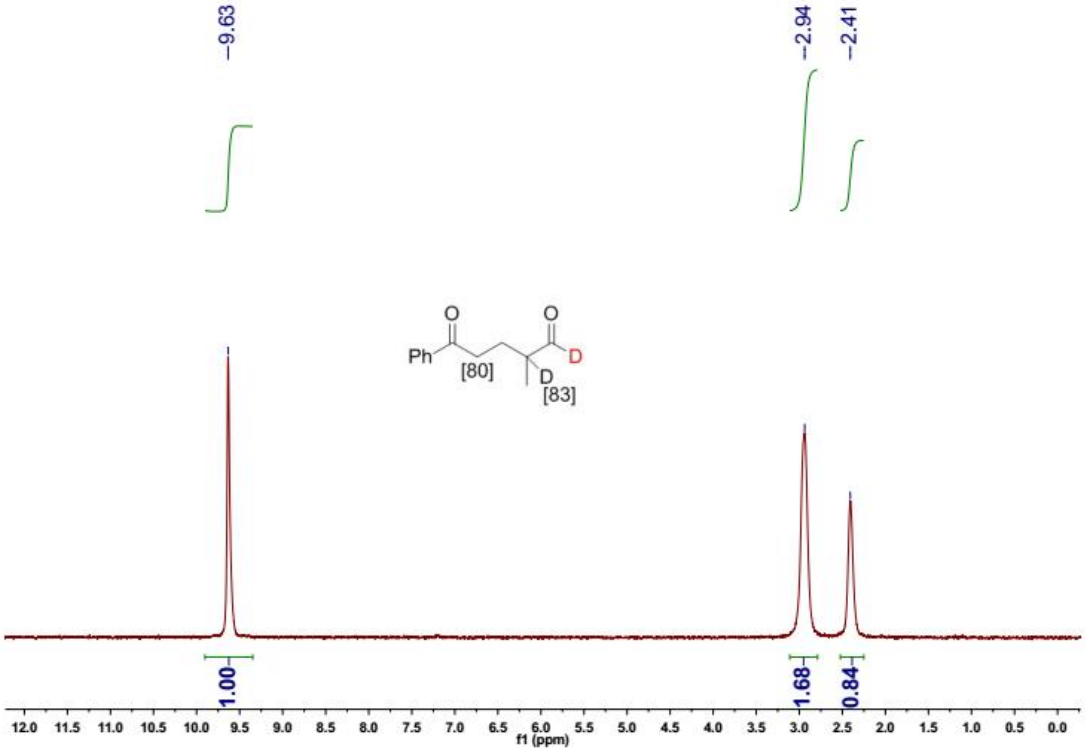
$^{1}$H NMR of aldehyde **11n**



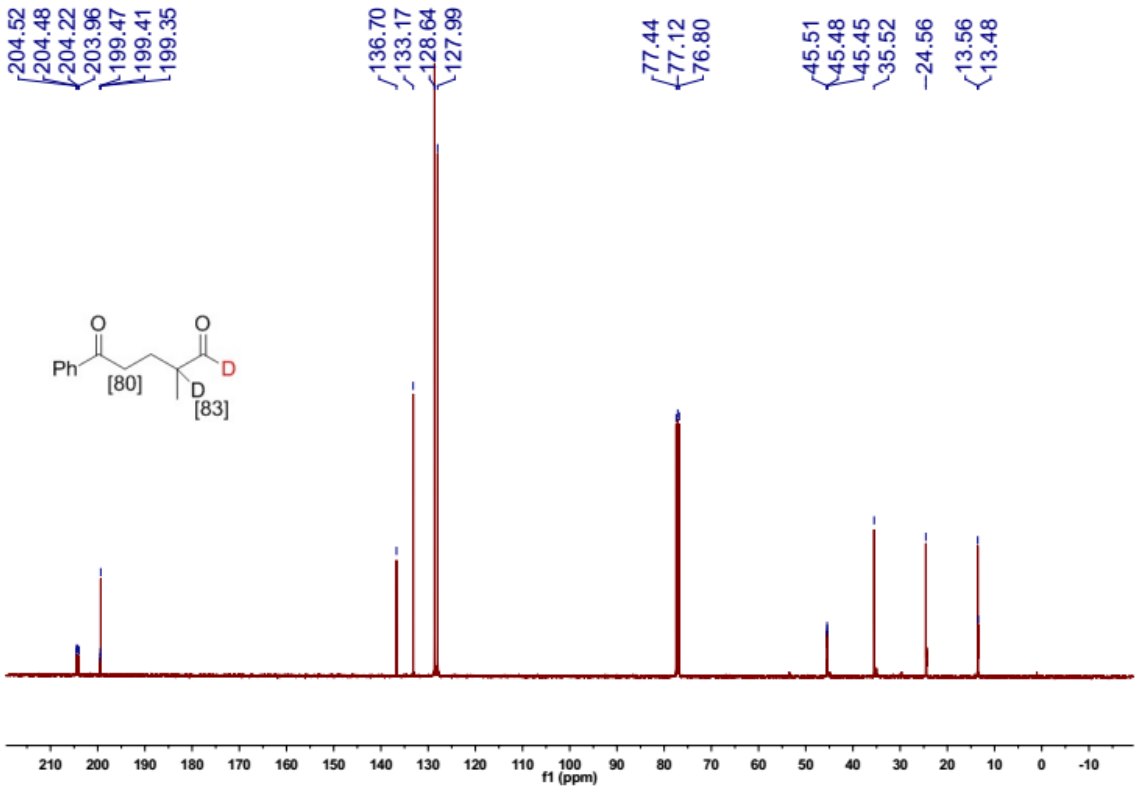

$^{1}$H NMR of deuterated aldehyde **12n**



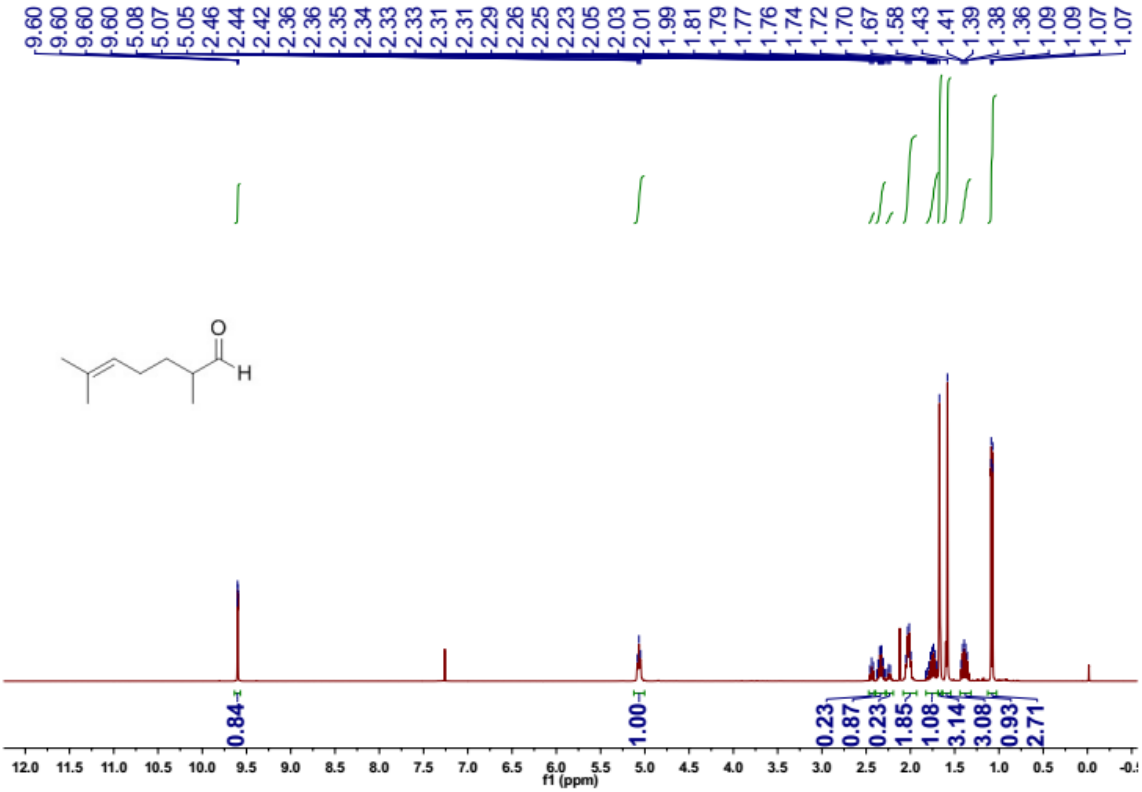
$^{2}$H NMR of deuterated aldehyde **12n**



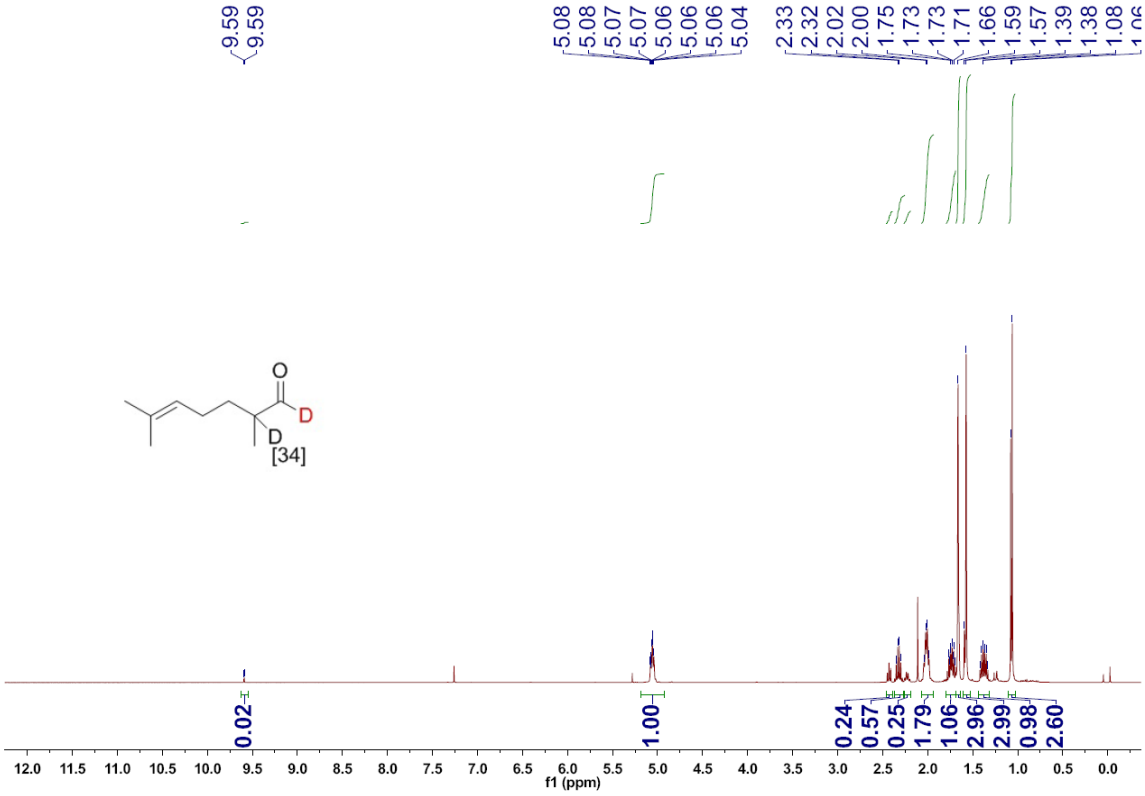

$^{13}$C NMR of deuterated aldehyde **12n**



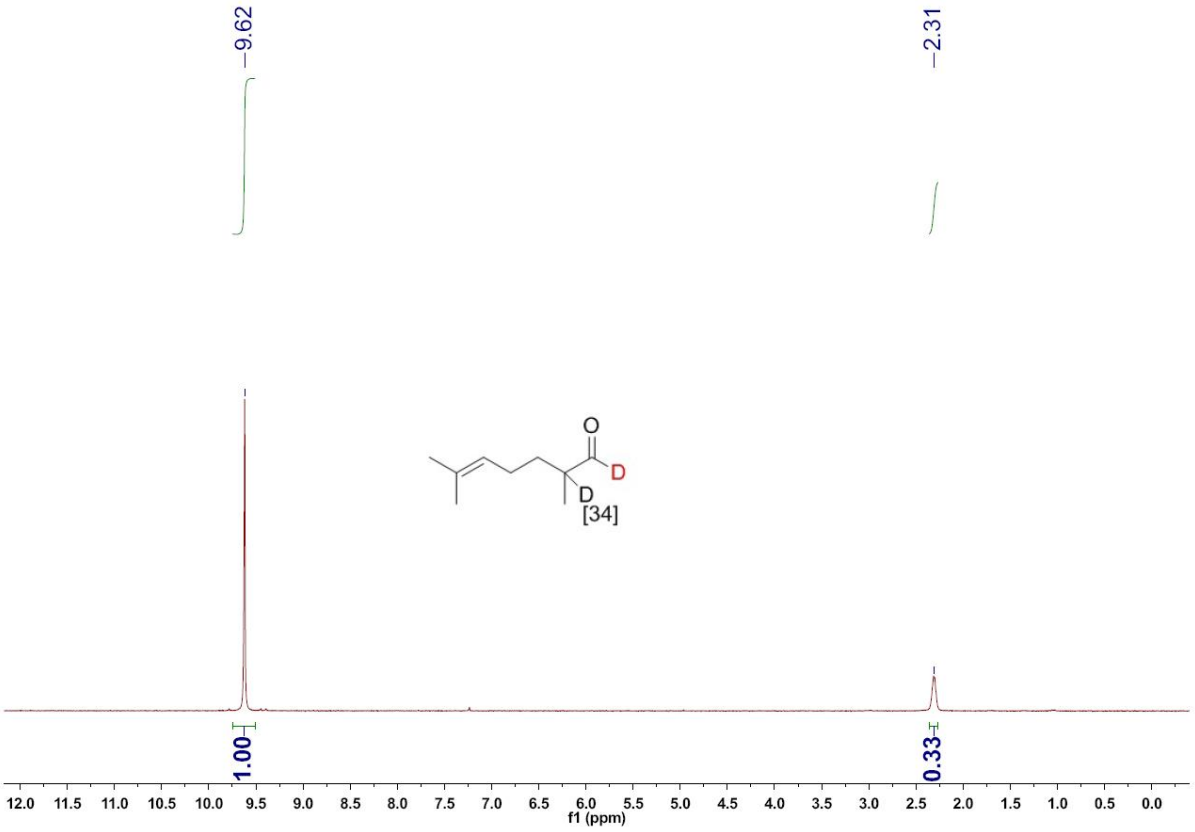
$^{1}$H NMR of aldehyde **11o**



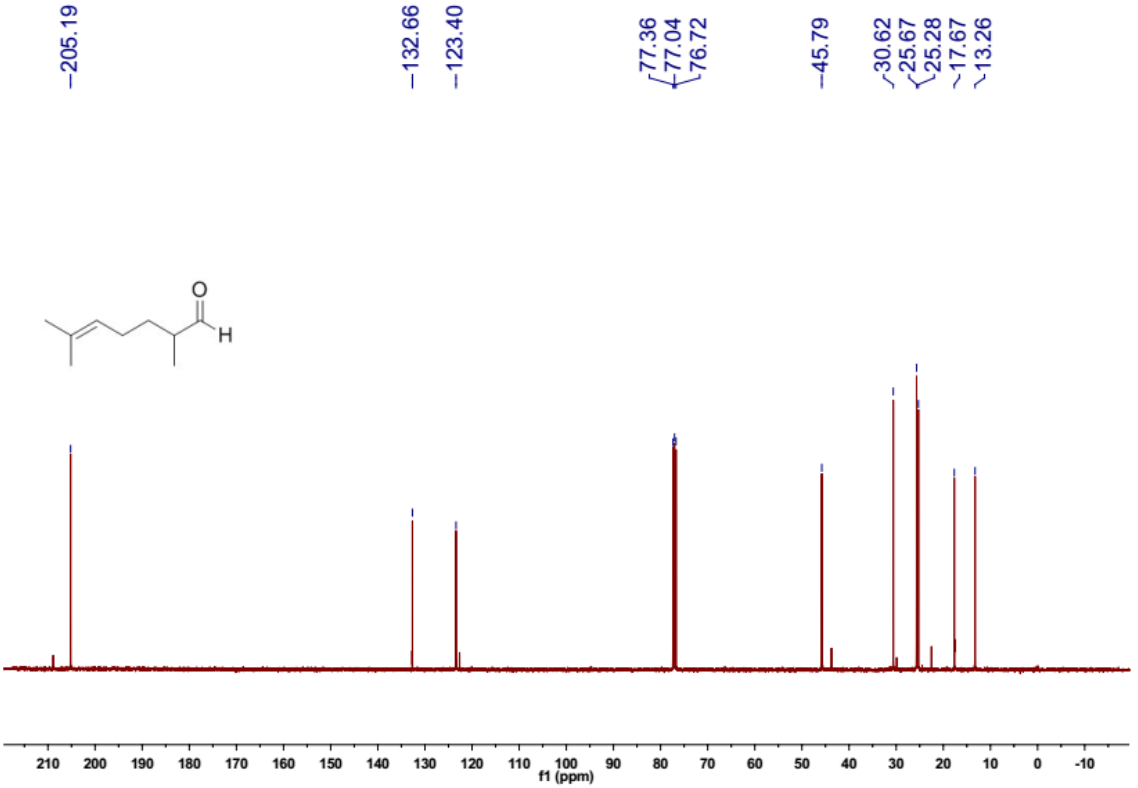

$^{1}$H NMR of deuterated aldehyde **12o**



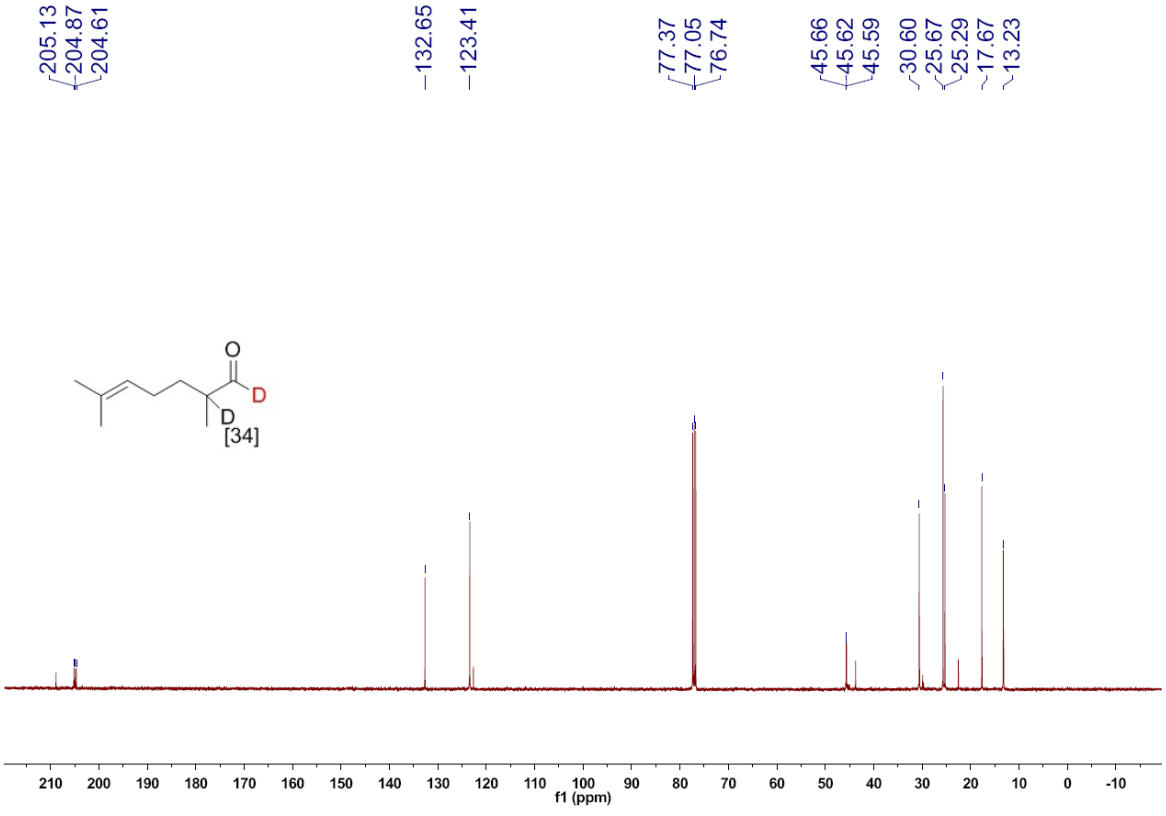
$^{2}$H NMR of deuterated aldehyde **12o**



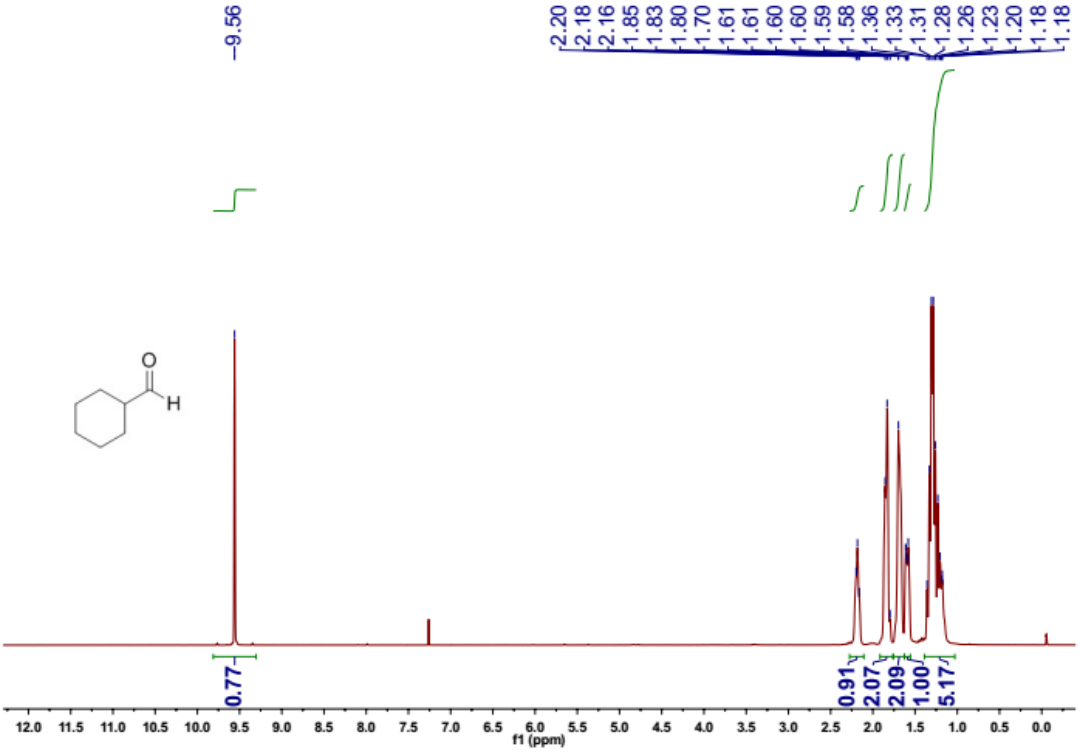
$^{13}$C NMR of aldehyde **11o**



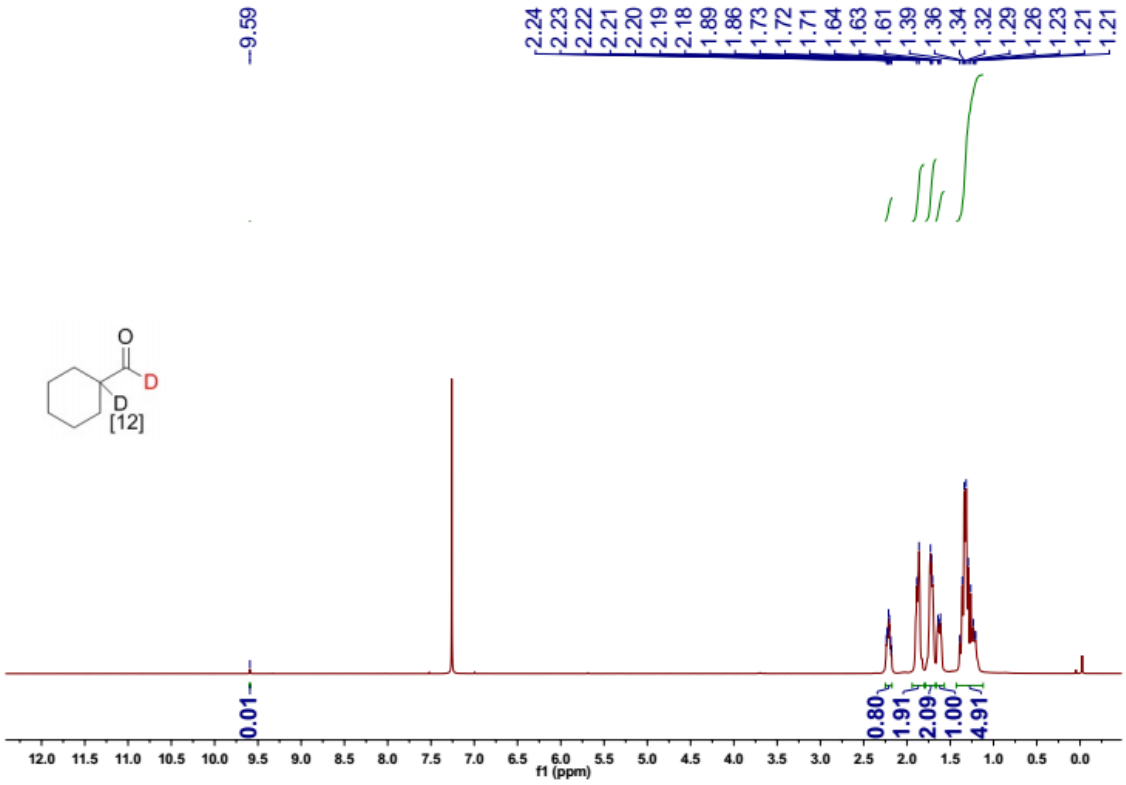

$^{13}$C NMR of deuterated aldehyde **12o**



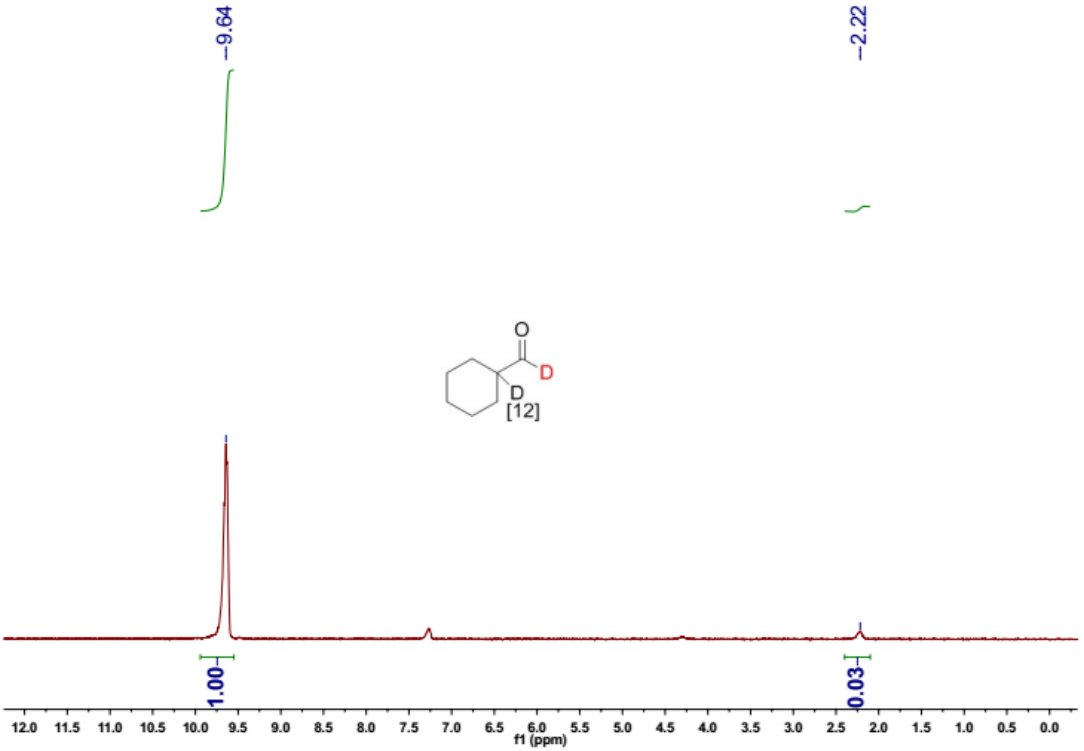
$^{1}$H NMR of aldehyde **11p**



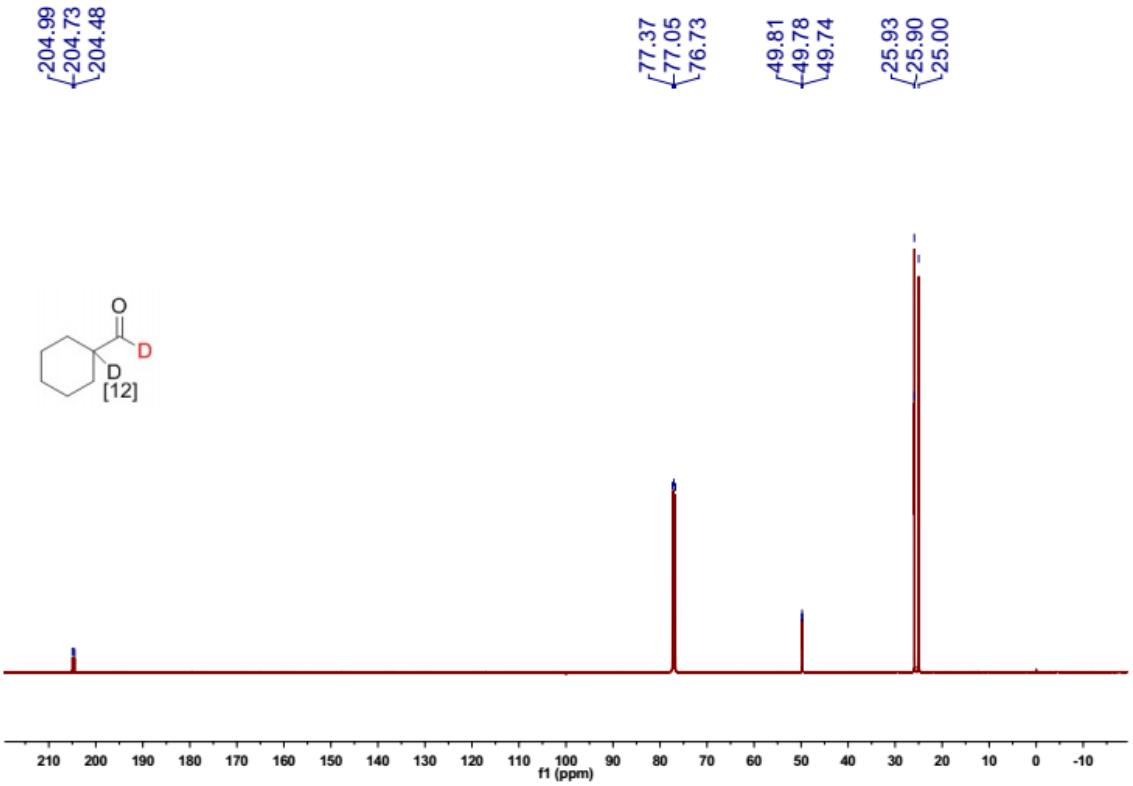

$^{1}$H NMR of deuterated aldehyde **12p**



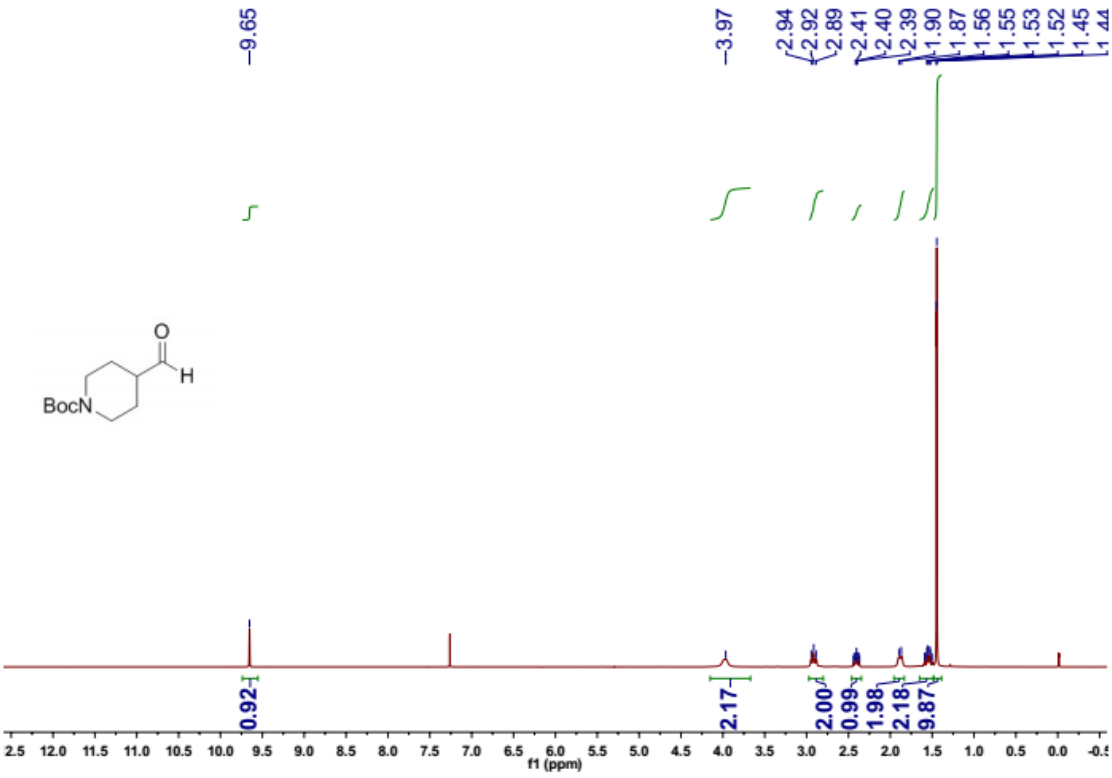
$^{2}$H NMR of deuterated aldehyde **12p**



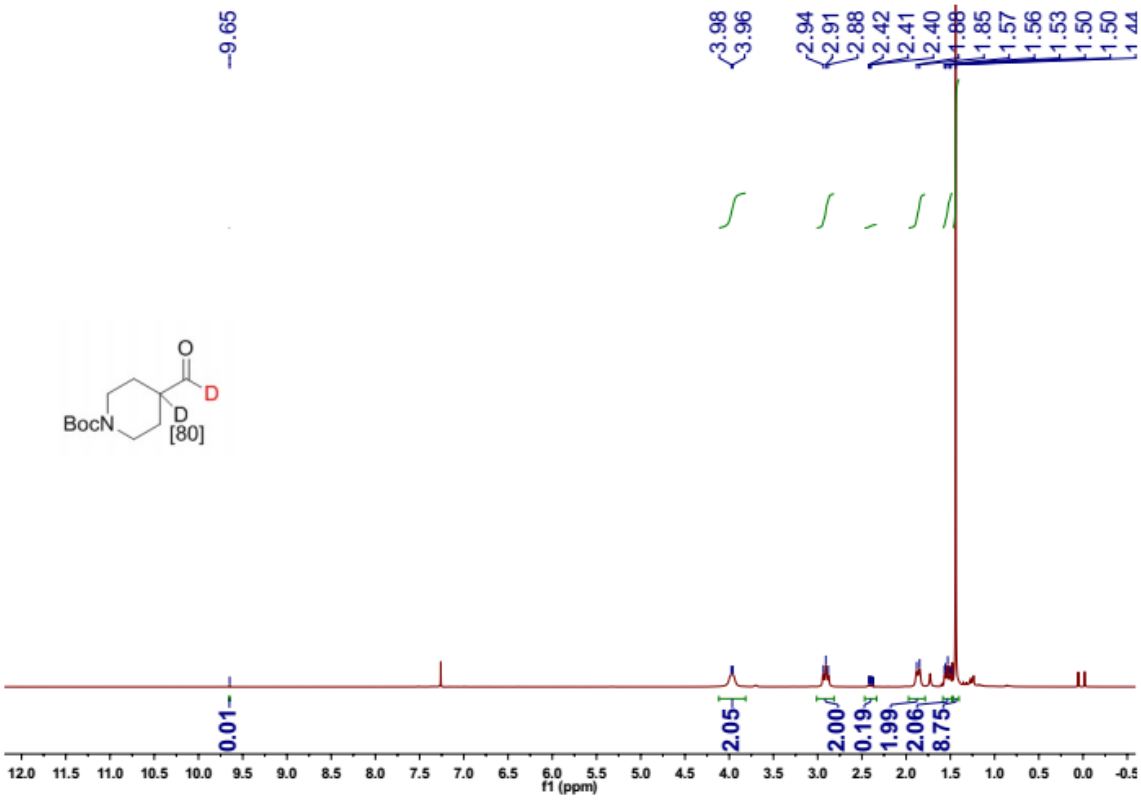

$^{13}$C NMR of deuterated aldehyde **12p**



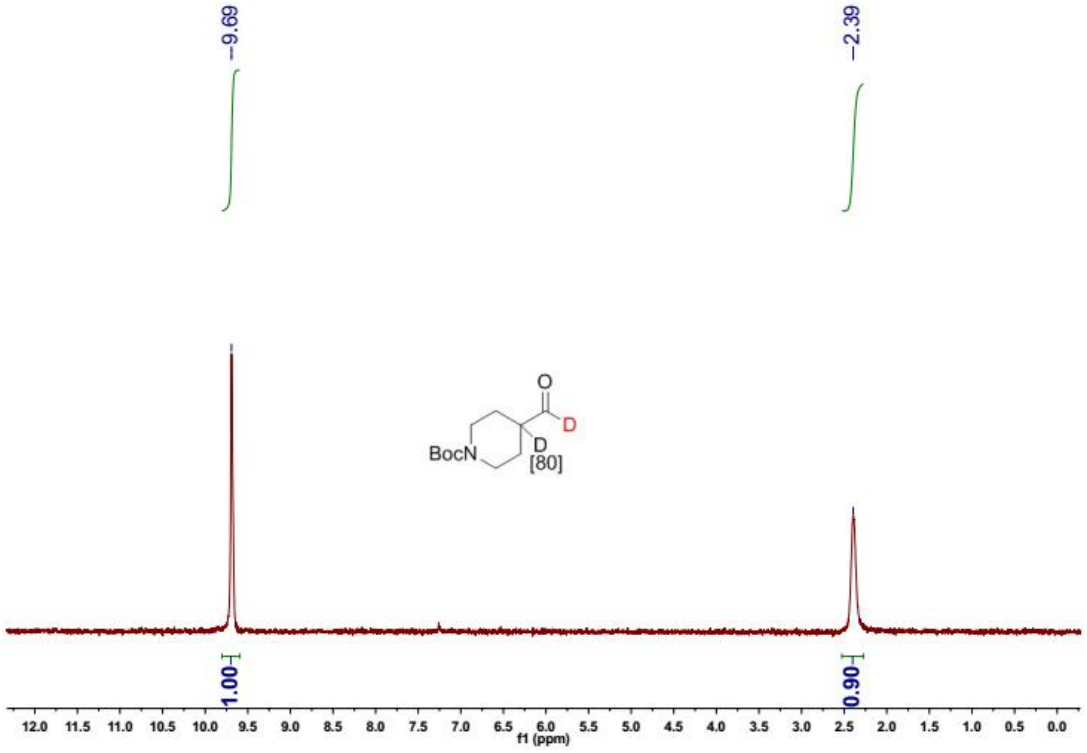
$^{1}$H NMR of aldehyde **11q**



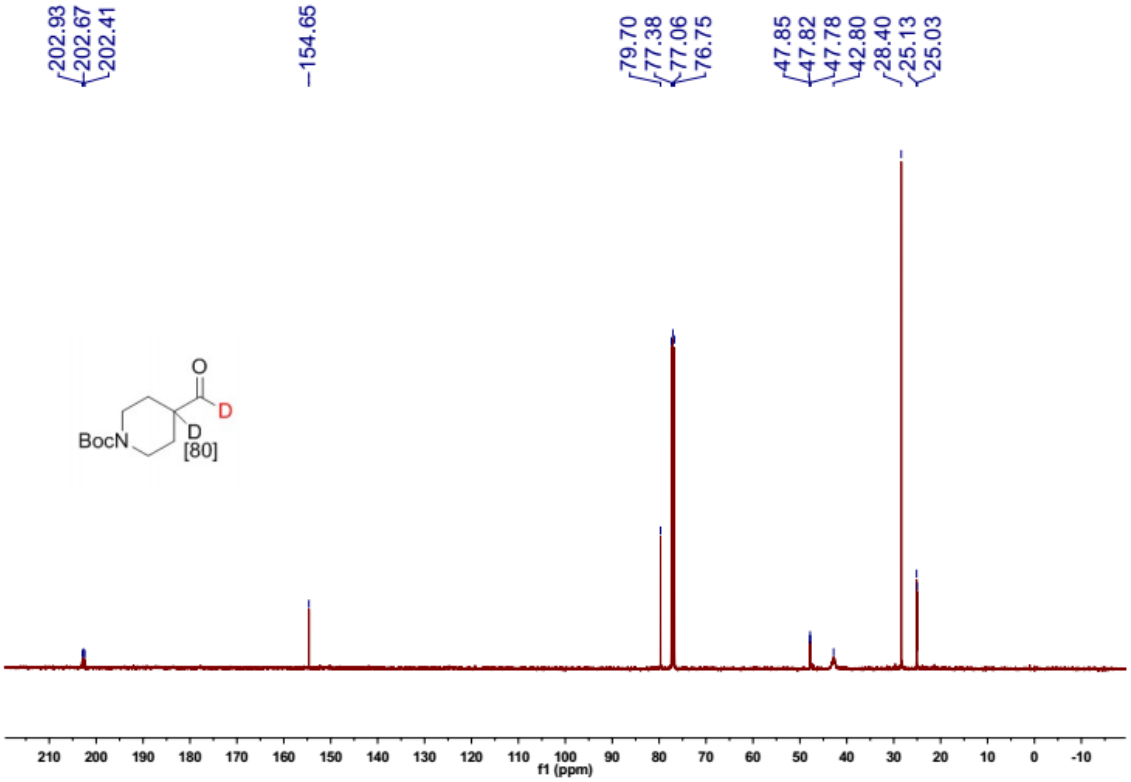

$^{1}$H NMR of deuterated aldehyde **12q**



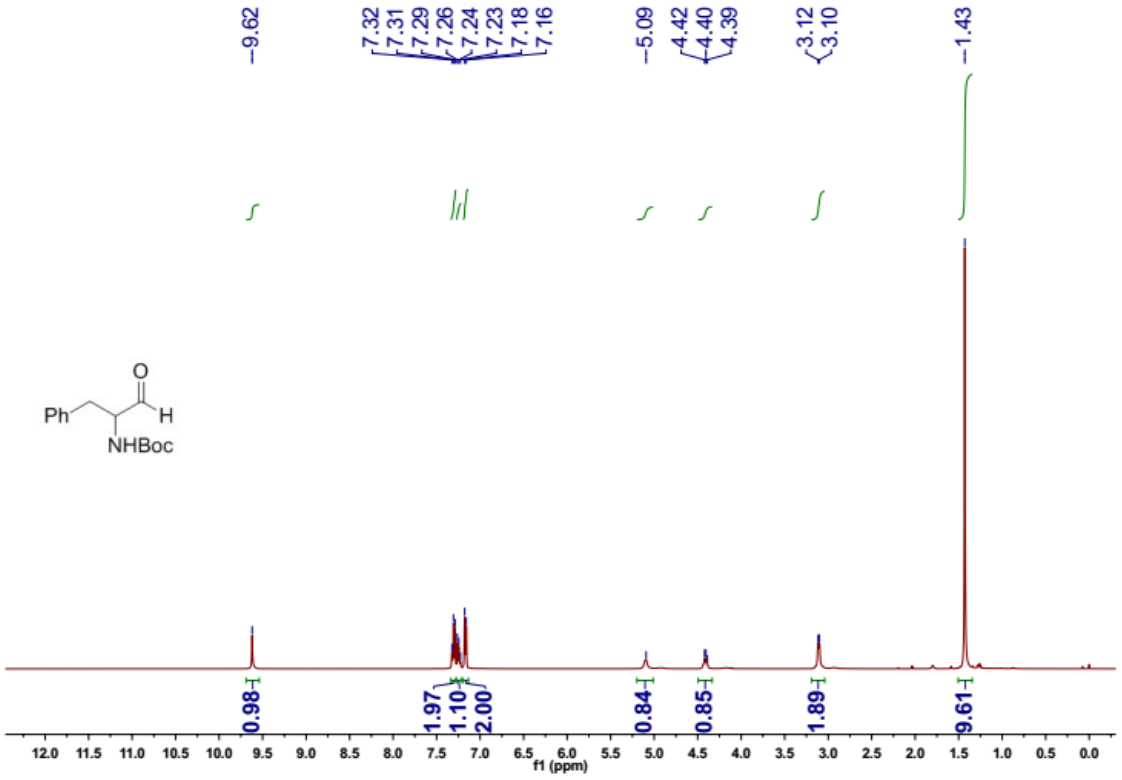
$^{2}$H NMR of deuterated aldehyde **12q**



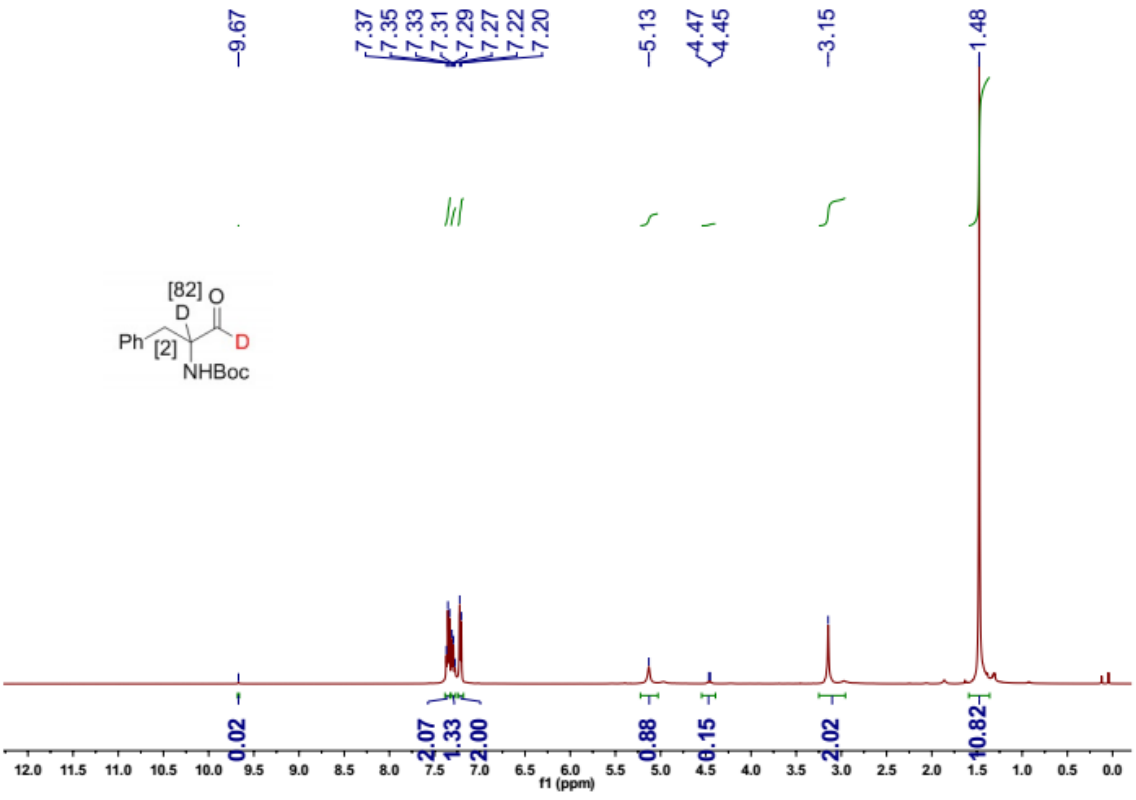

$^{13}$C NMR of deuterated aldehyde **12q**



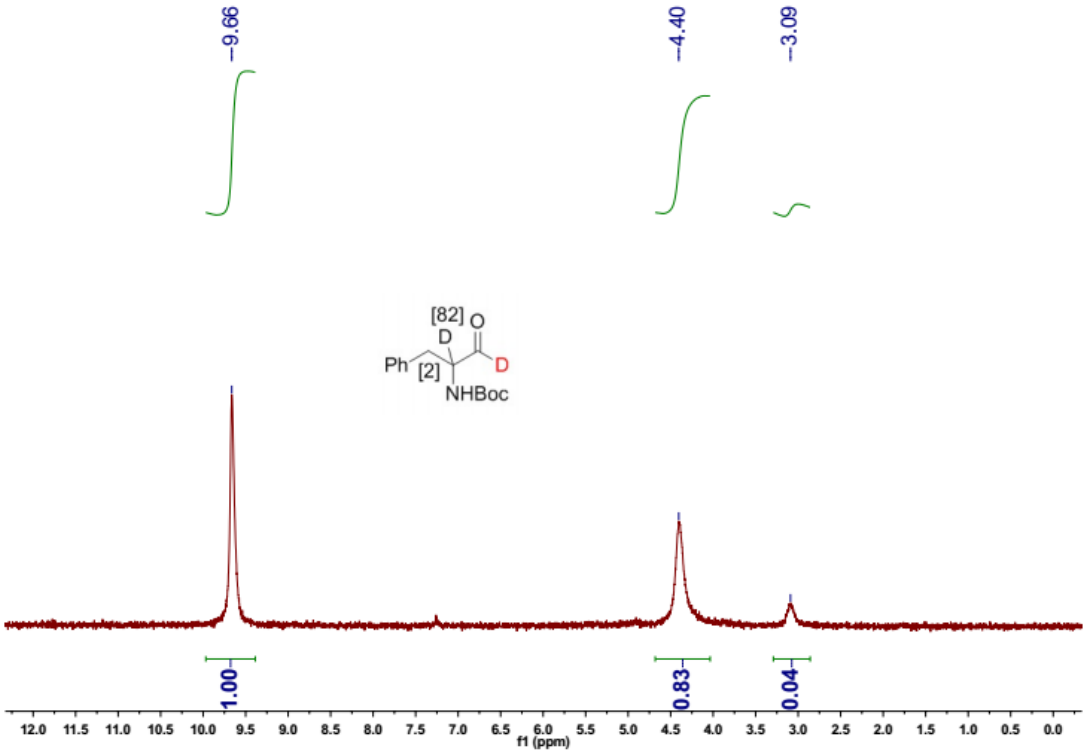
$^{1}$H NMR of aldehyde **11r**



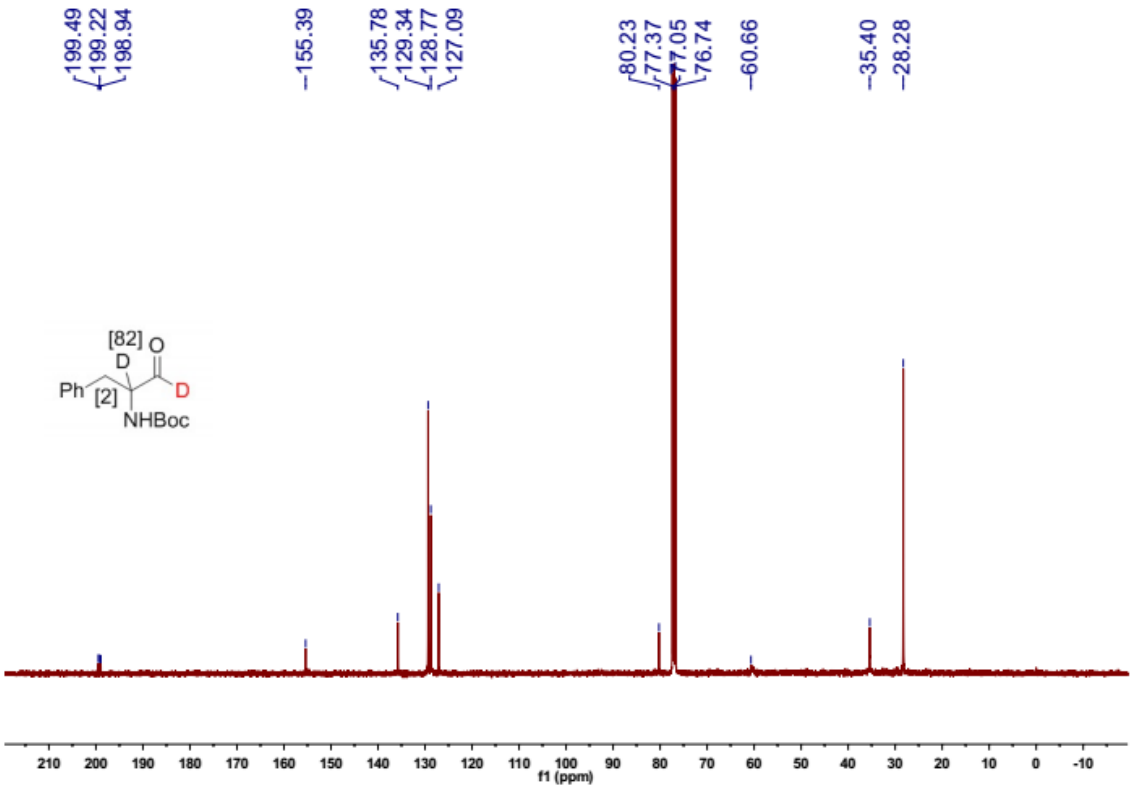

$^{1}$H NMR of deuterated aldehyde **12r**



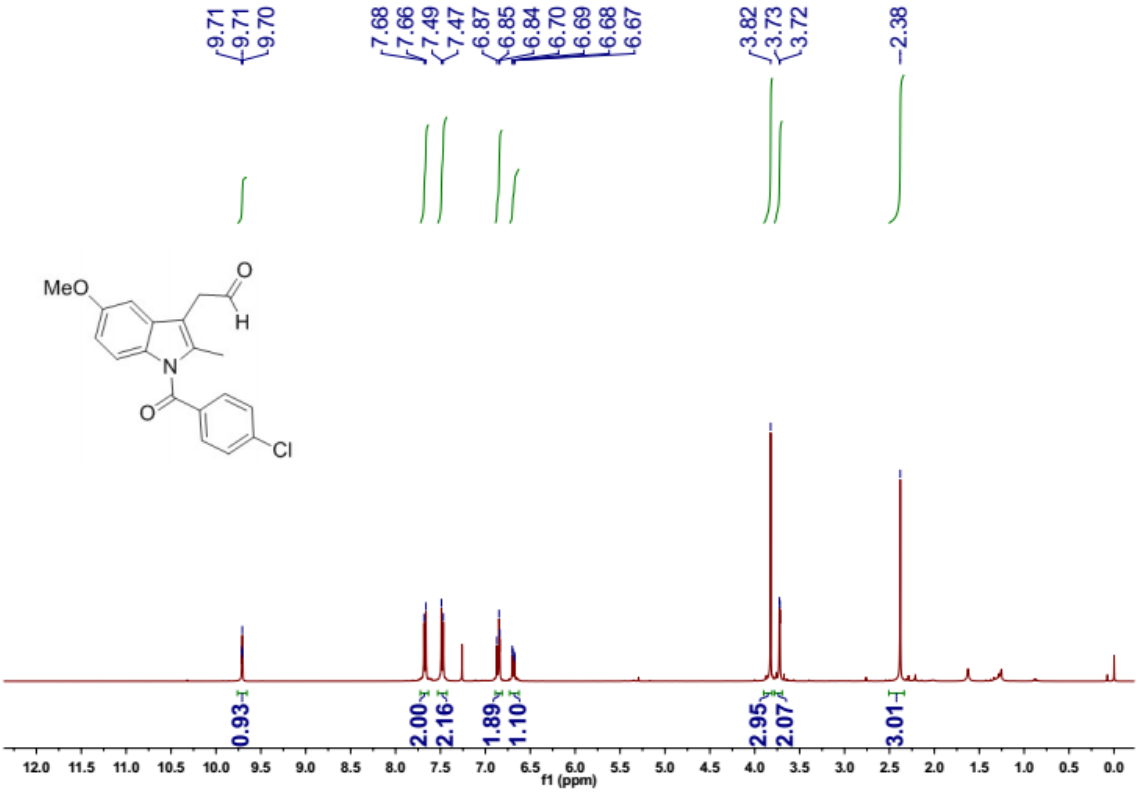
$^{2}$H NMR of deuterated aldehyde **12r**



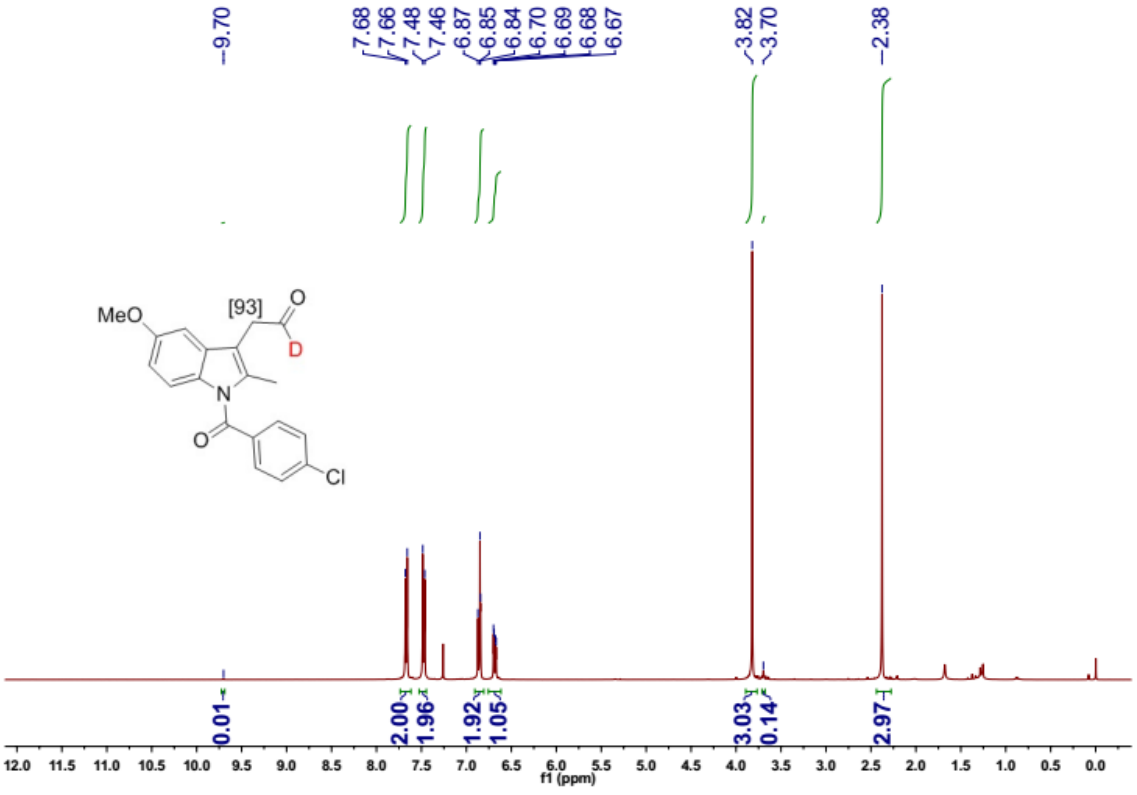

$^{13}$C NMR of deuterated aldehyde **12r**



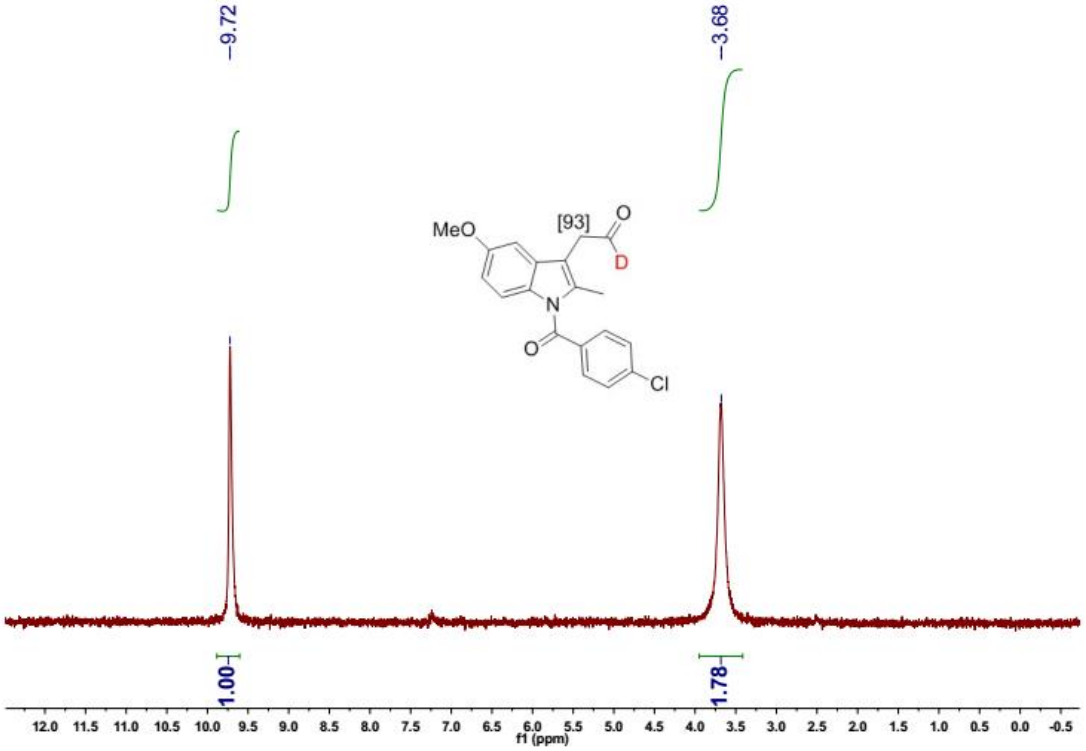
$^{1}$H NMR of aldehyde **11s**



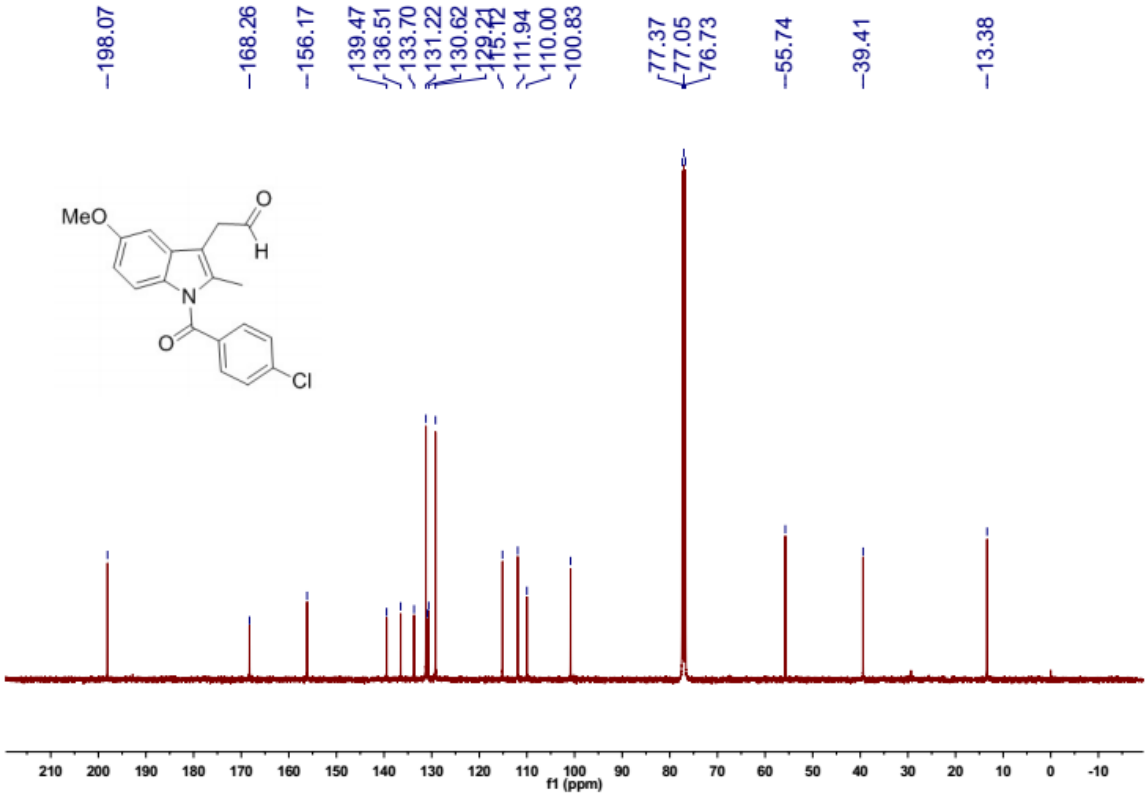

$^{1}$H NMR of deuterated aldehyde **12s**



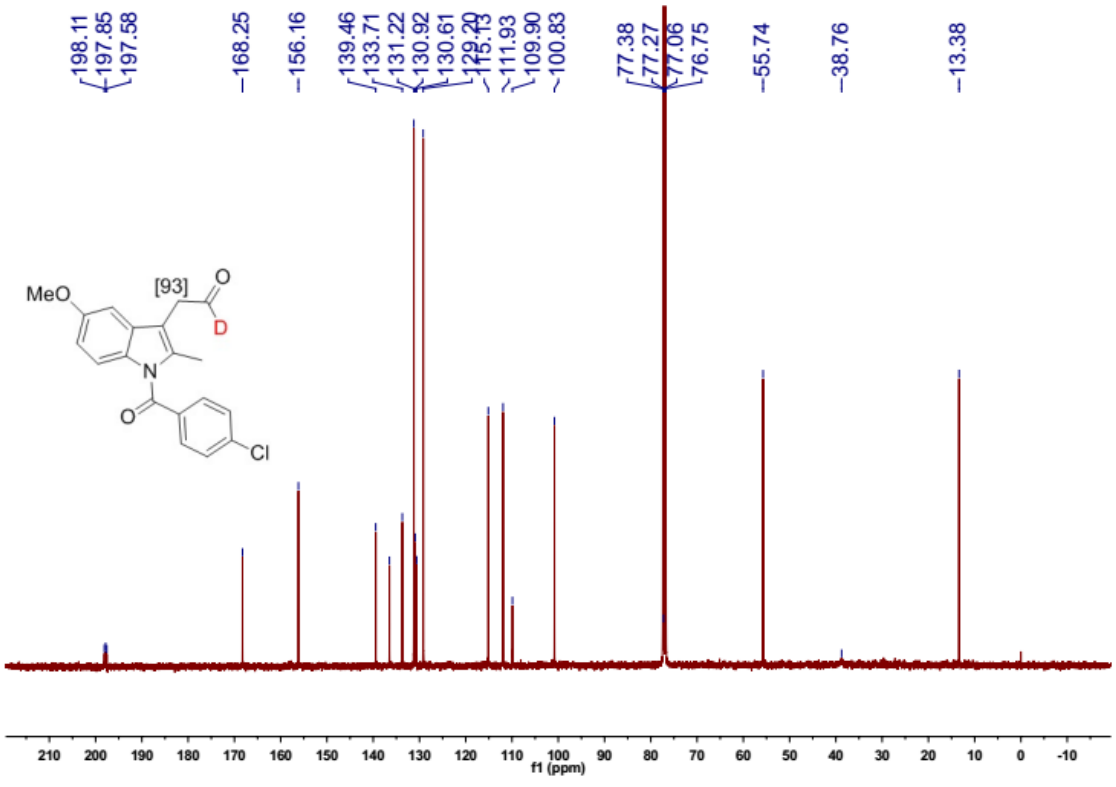
$^{2}$H NMR of deuterated aldehyde **12s**



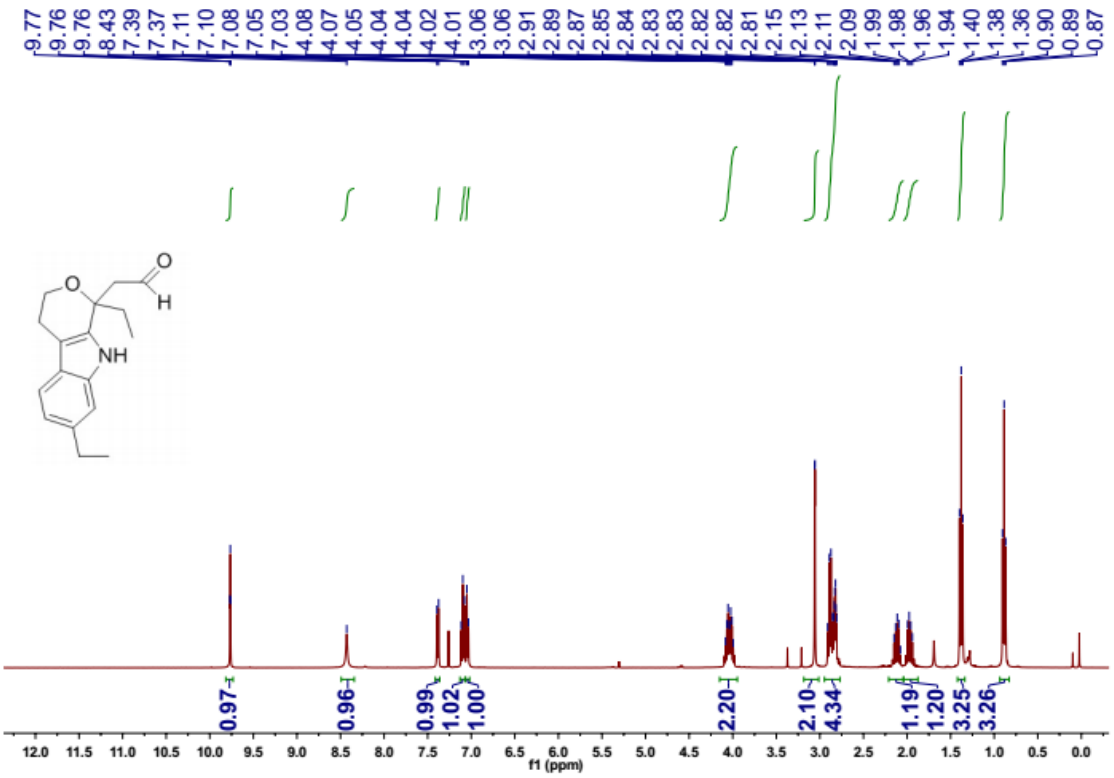
$^{13}$C NMR of aldehyde **11s**



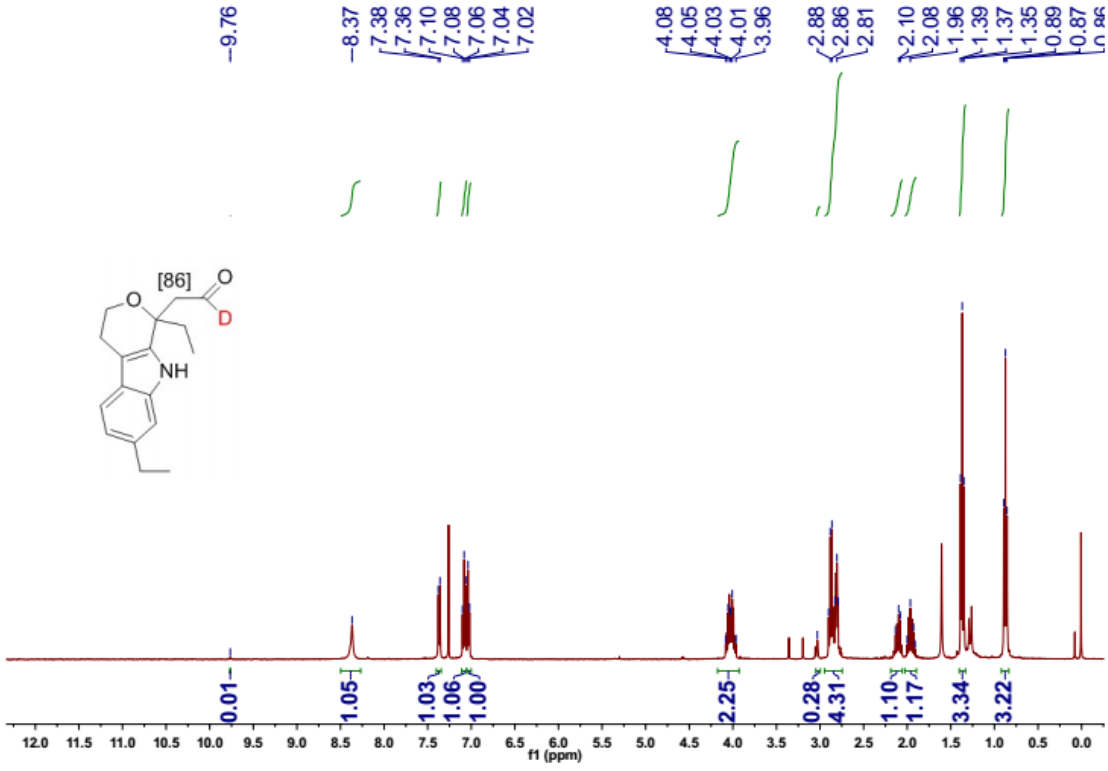

$^{13}$C NMR of deuterated aldehyde **12s**



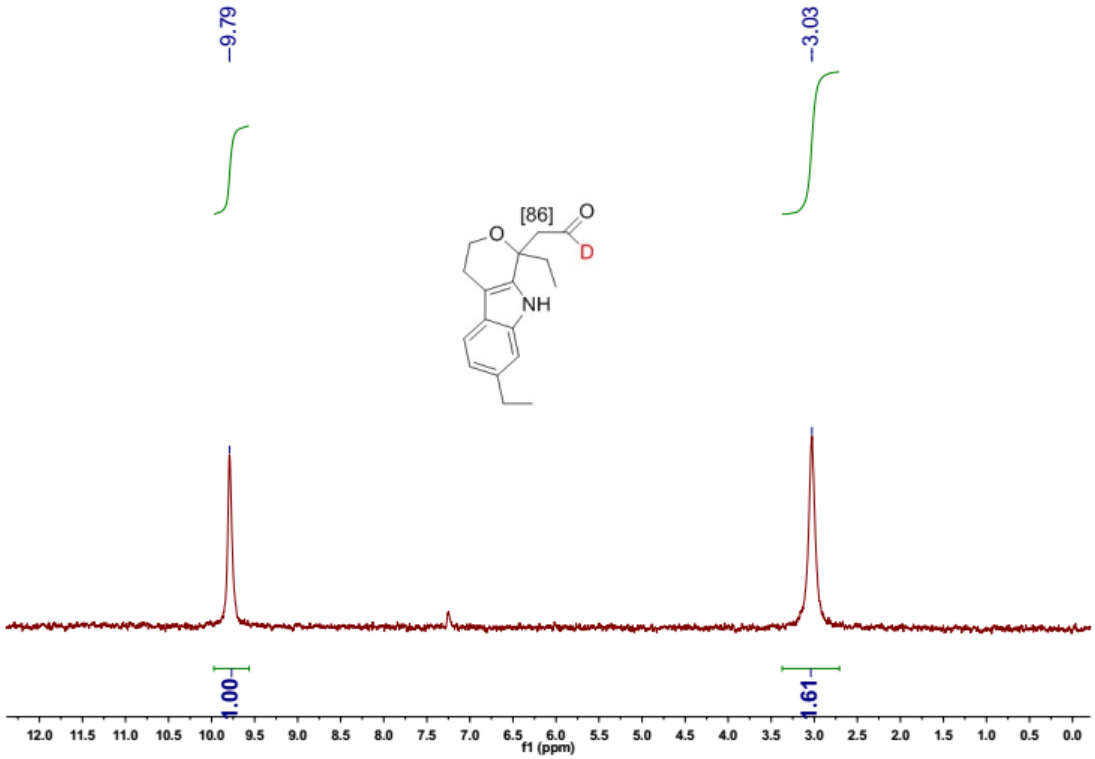
$^{1}$H NMR of aldehyde **11t**



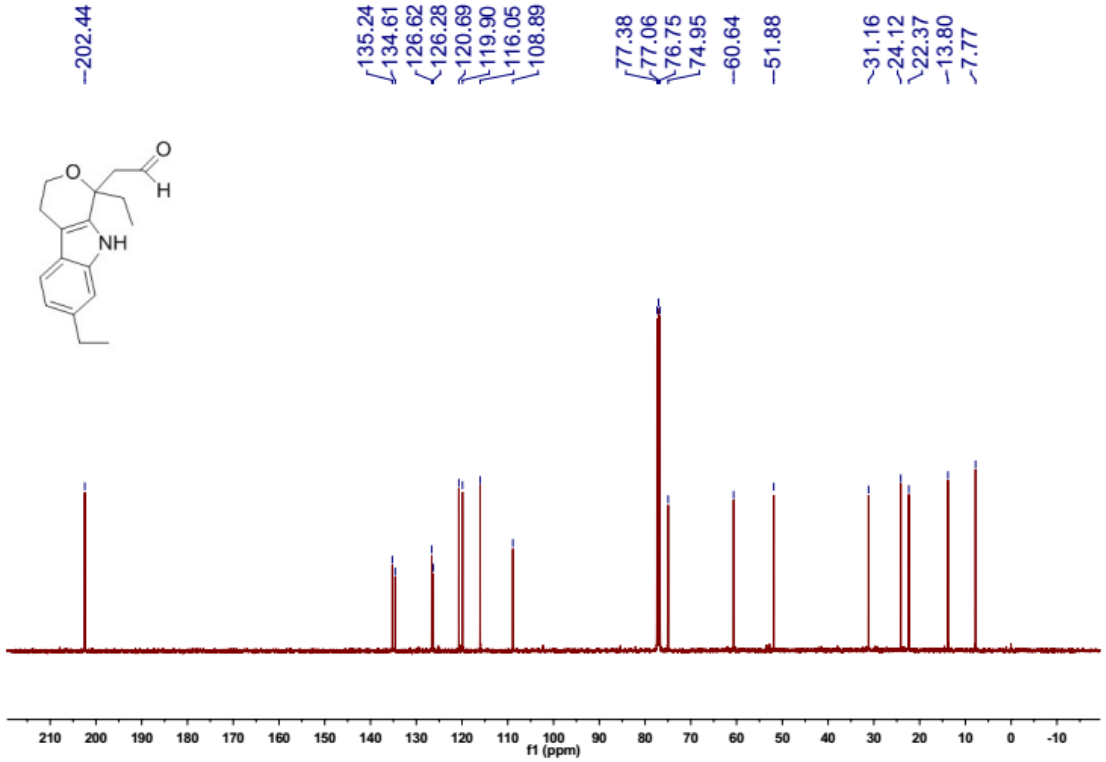

$^{1}$H NMR of deuterated aldehyde **12t**



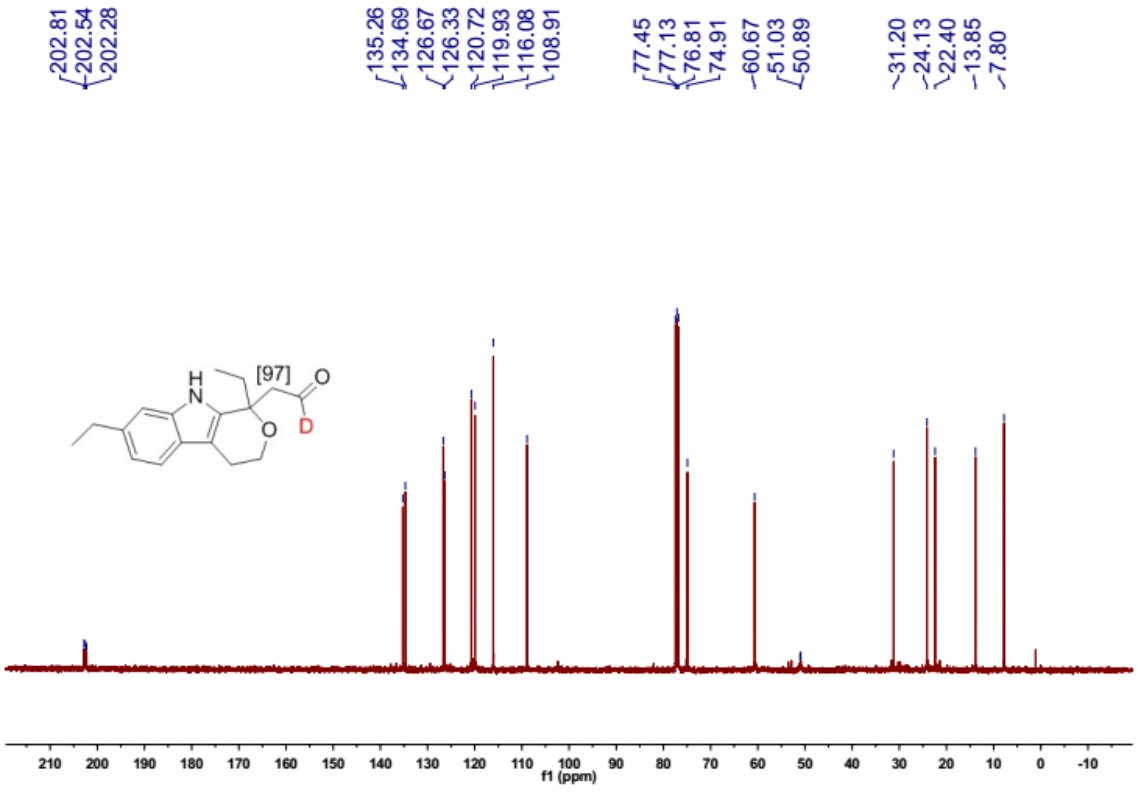
$^{2}$H NMR of deuterated aldehyde **12t**



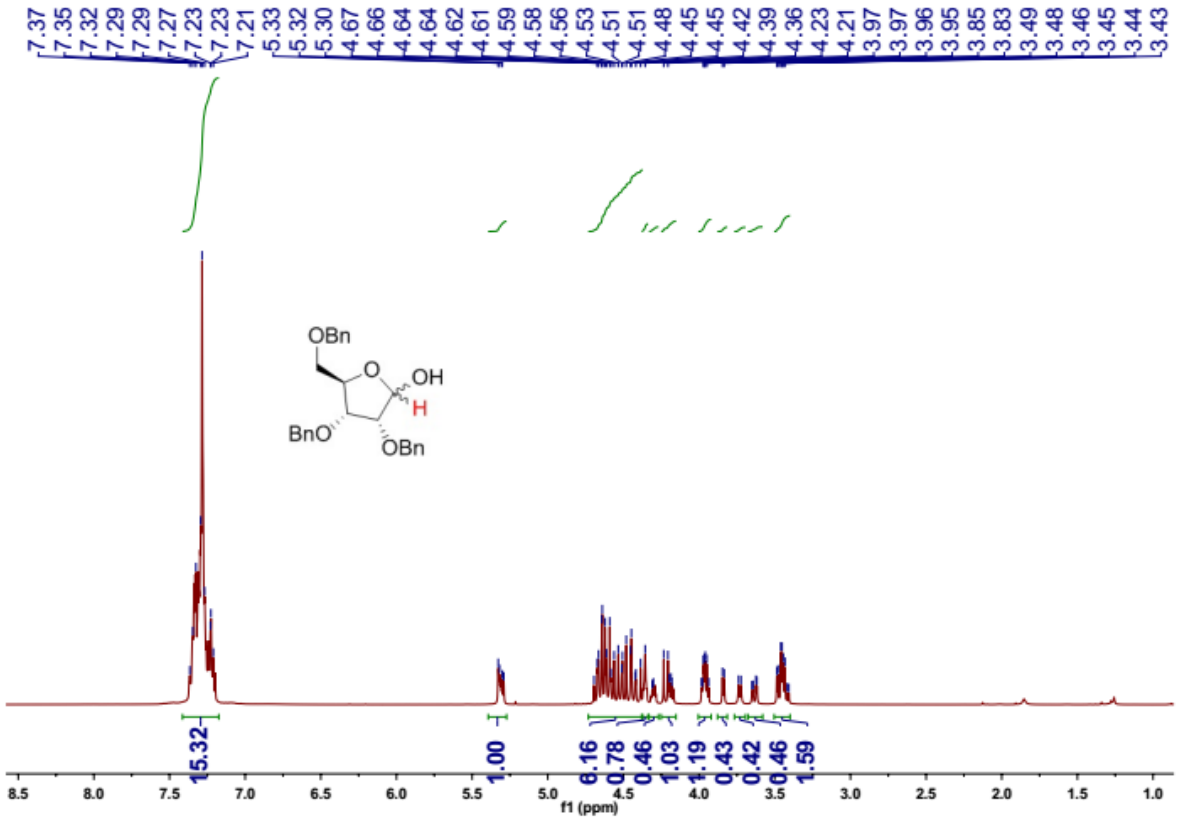
$^{13}$C NMR of aldehyde **11t**



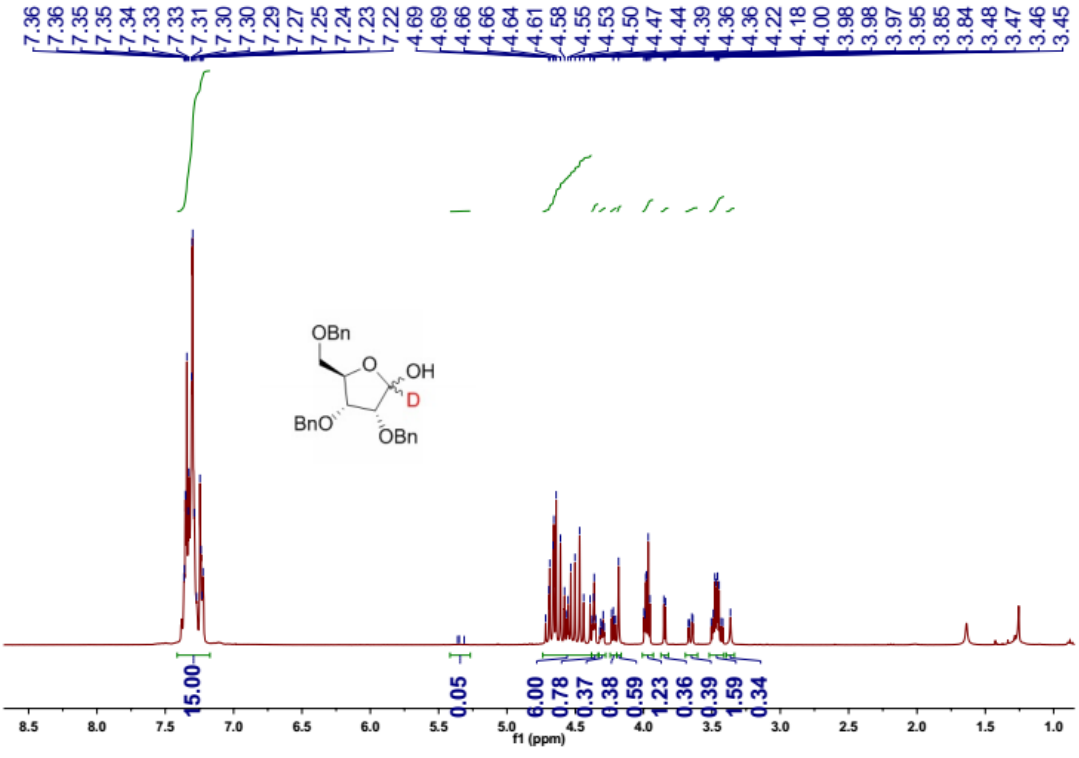

$^{13}$C NMR of deuterated aldehyde **12t**



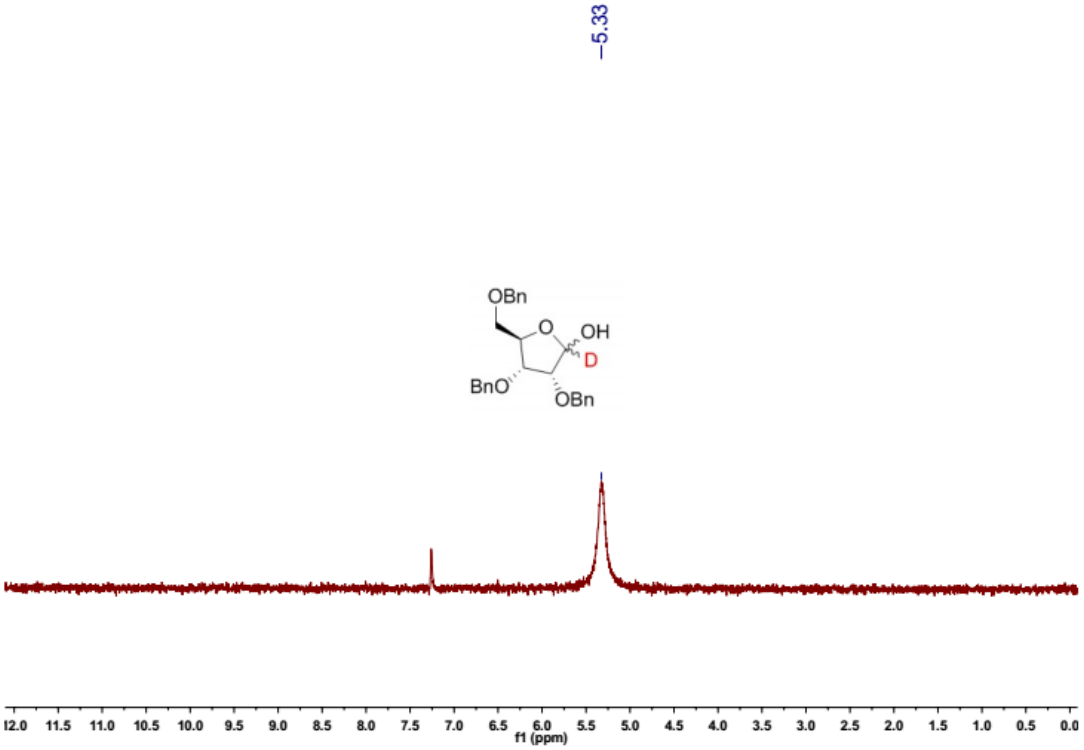
$^{1}$H NMR of ribofuranose **11u**



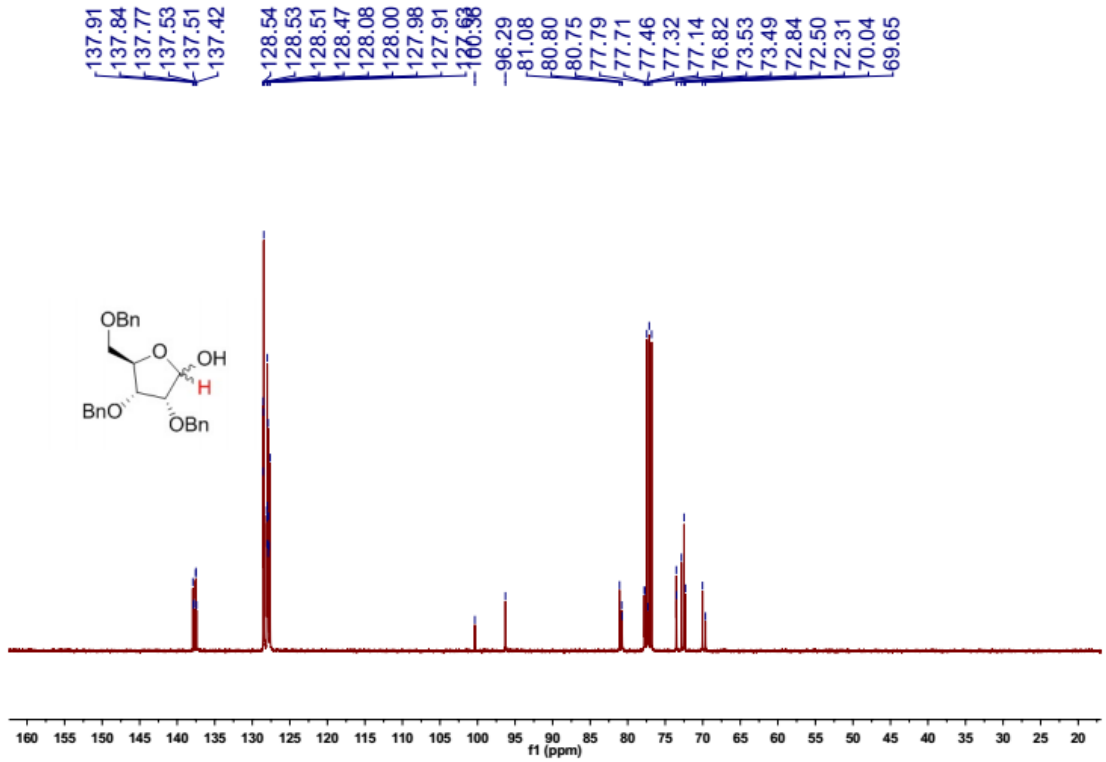

$^{1}$H NMR of deuterated ribofuranose **12u**



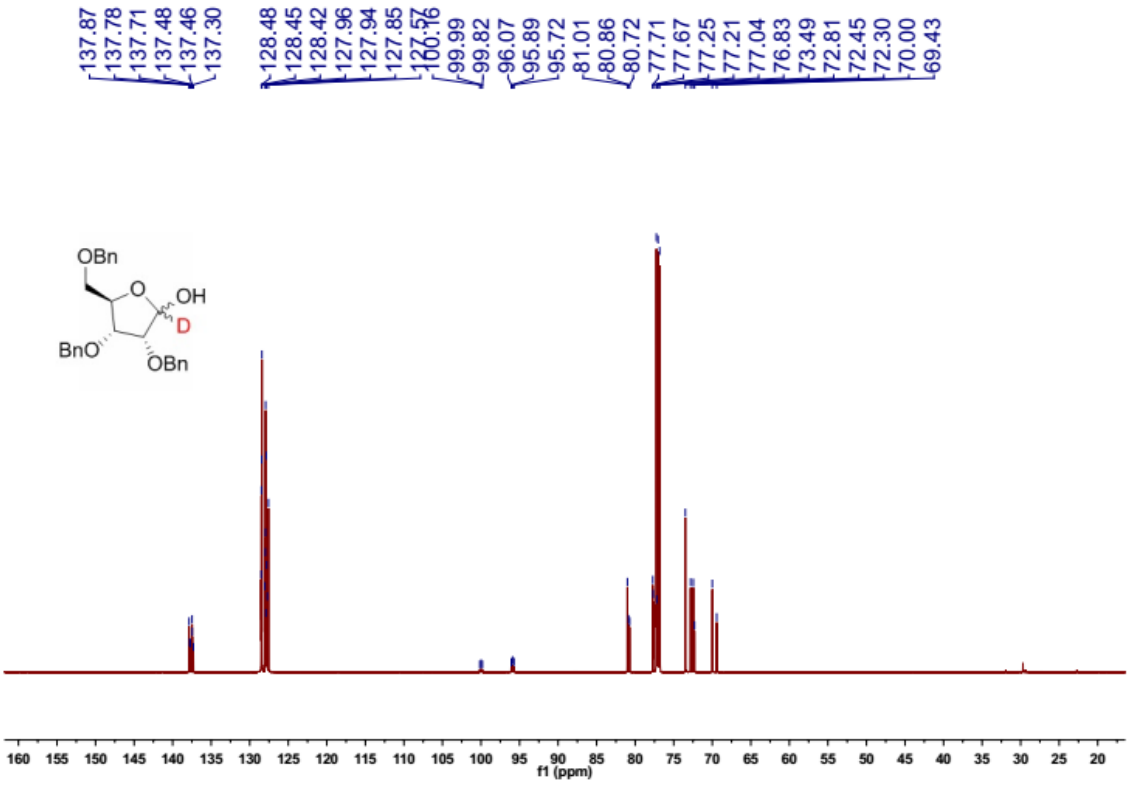
$^{2}$H NMR of deuterated aldehyde **12u**



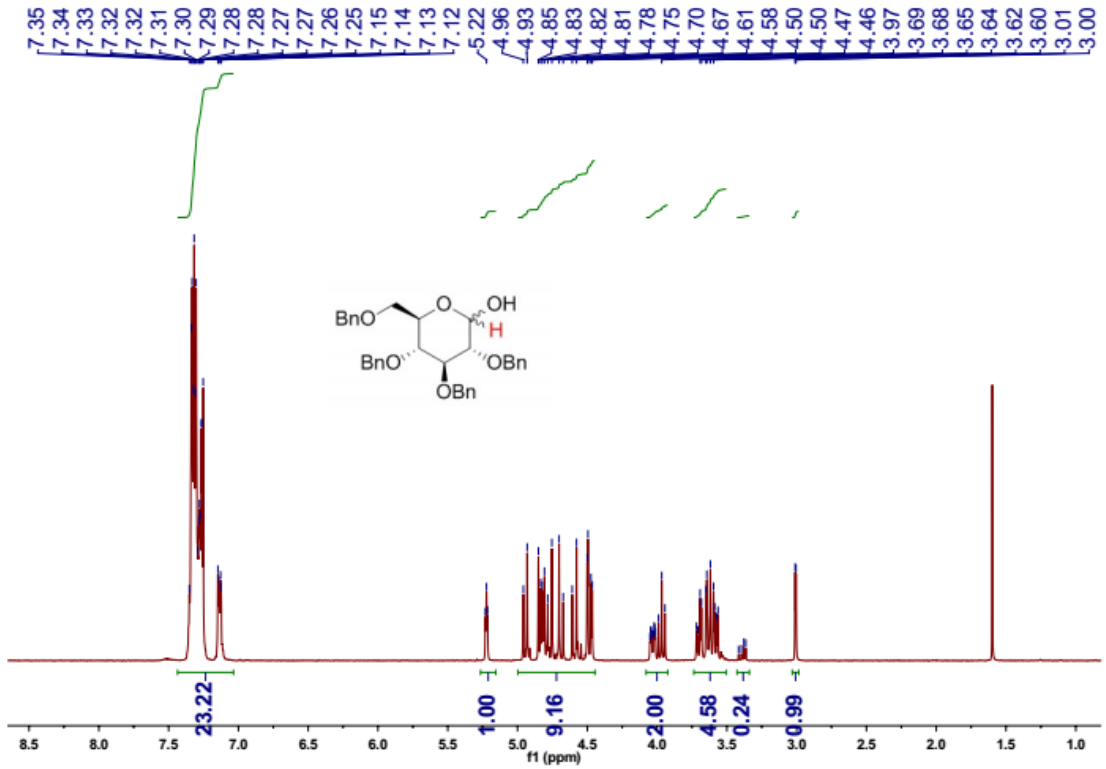
$^{13}$C NMR of ribofuranose **11u**



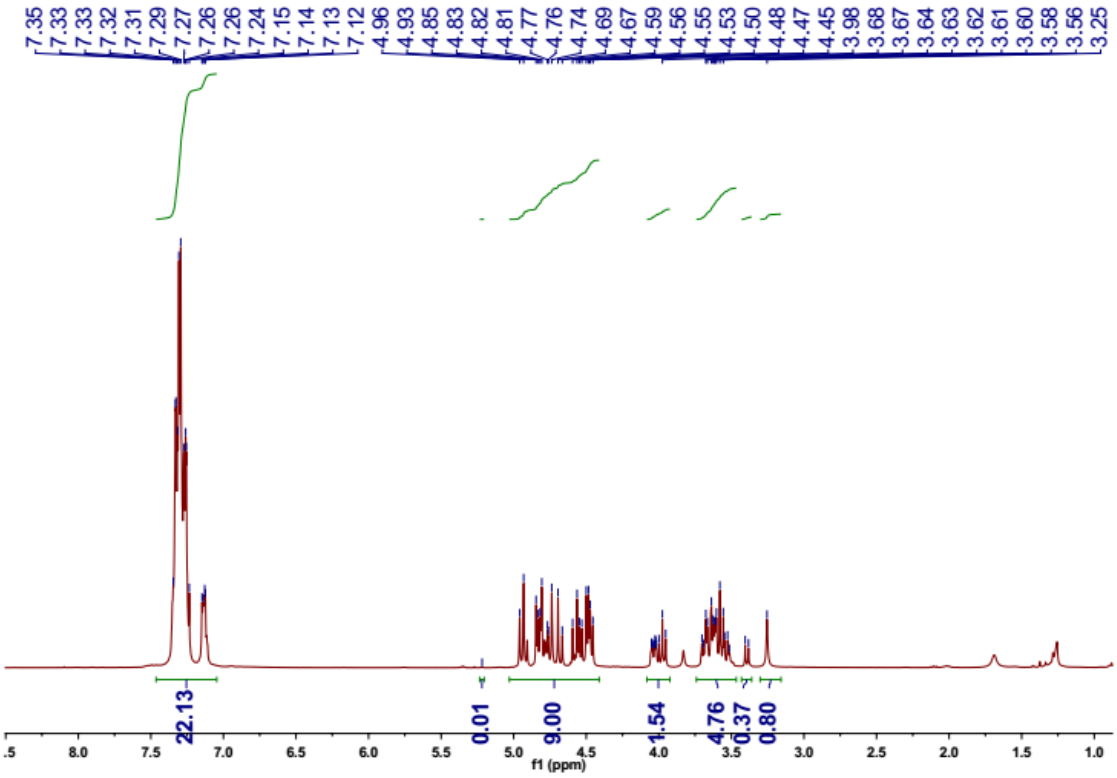

$^{13}$C NMR of deuterated ribofuranose **12u**



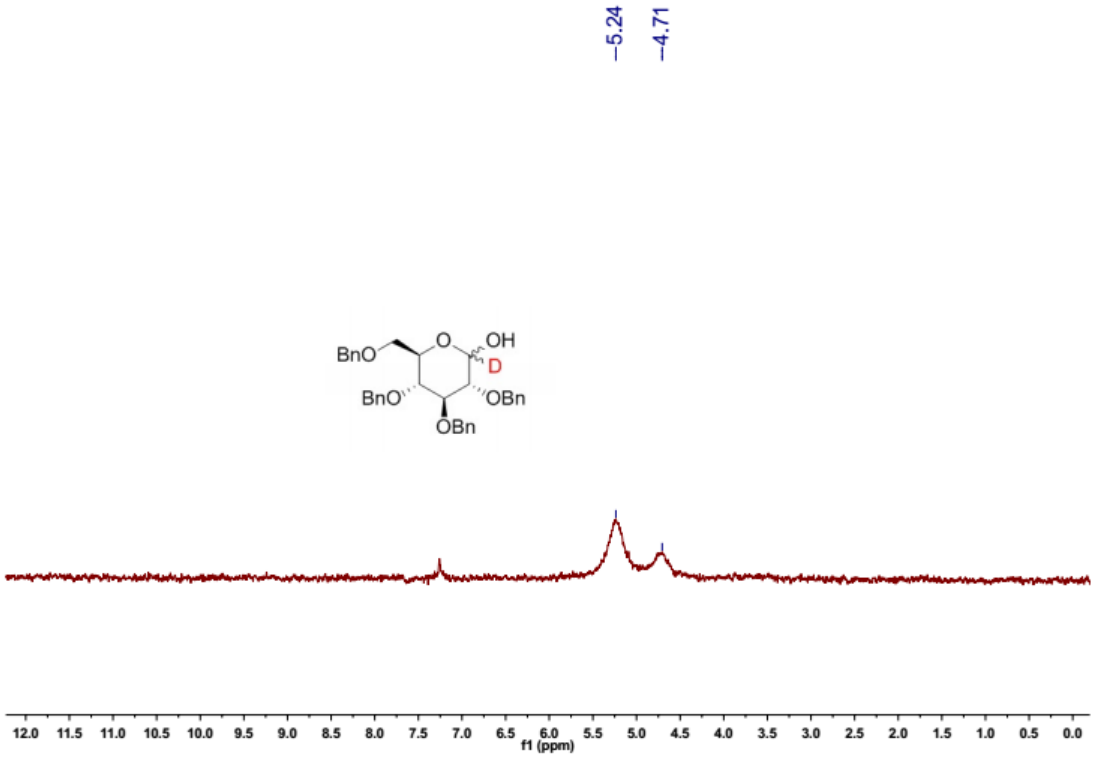
$^{1}$H NMR of glucopyranose **11v**



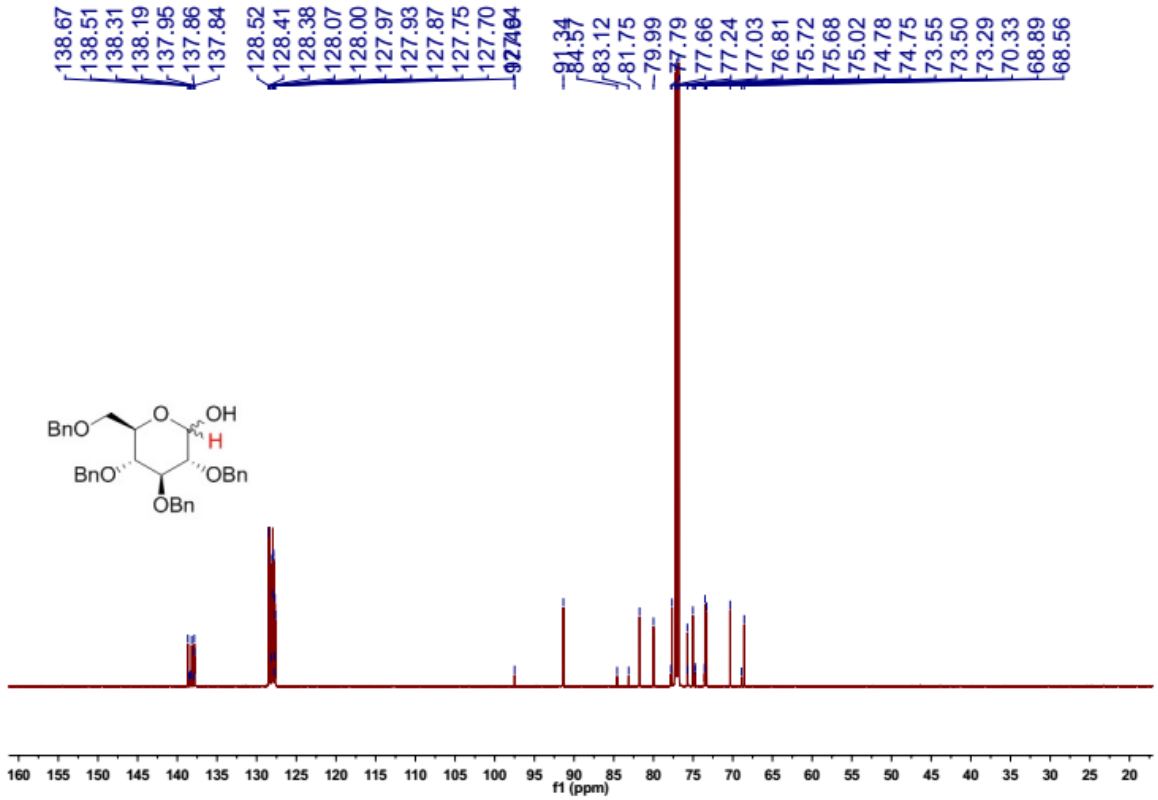

$^{1}$H NMR of deuterated glucopyranose **12v**



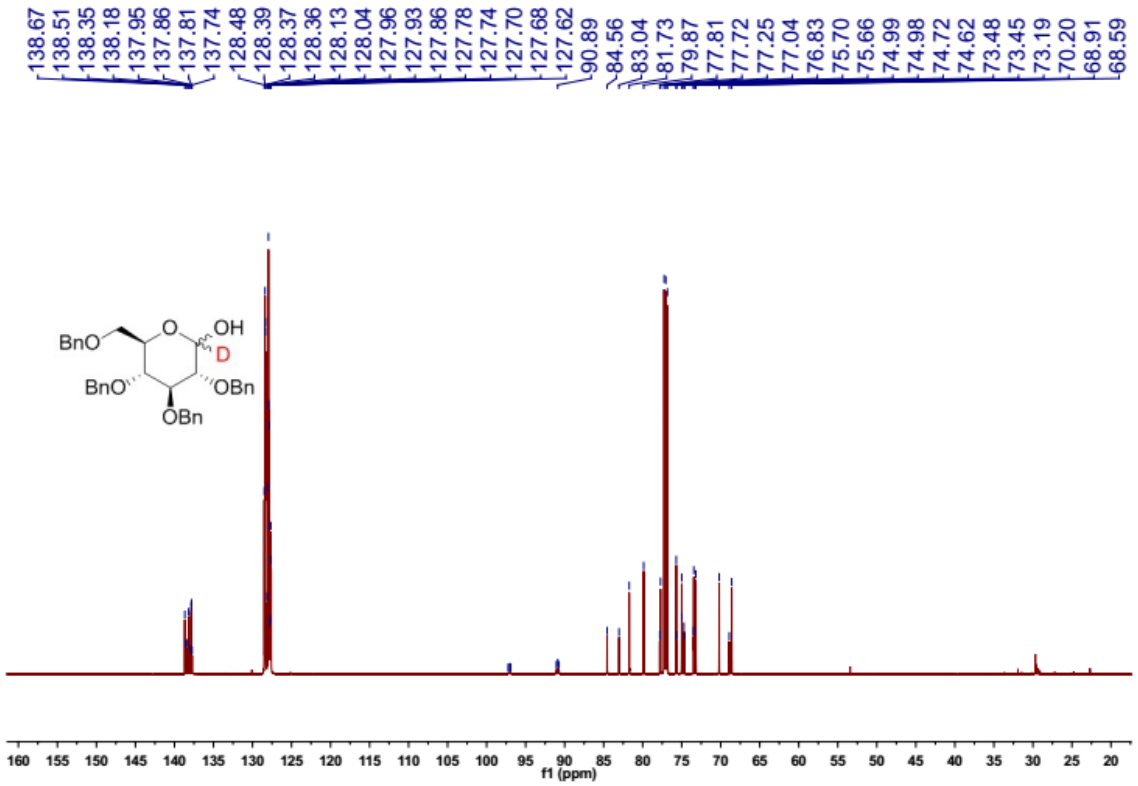
$^{2}$H NMR of deuterated aldehyde **12v**



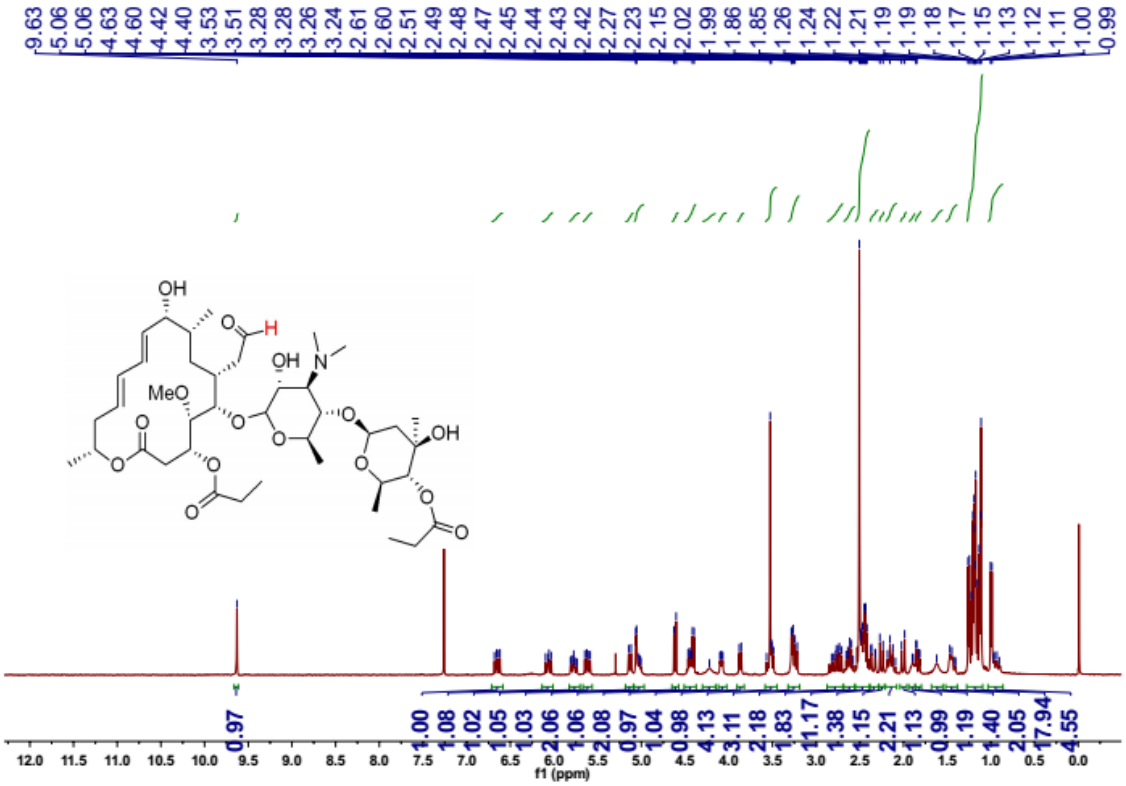
$^{13}$C NMR of glucopyranose **11v**



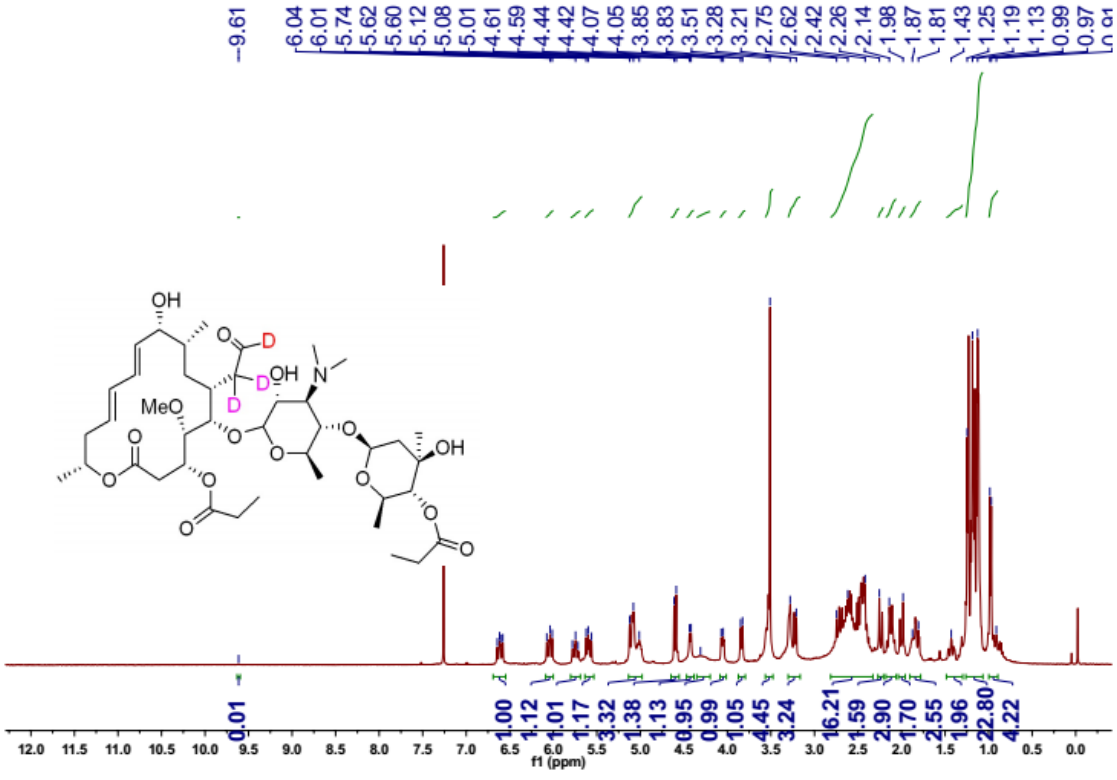

$^{13}$C NMR of deuterated glucopyranose **12v**



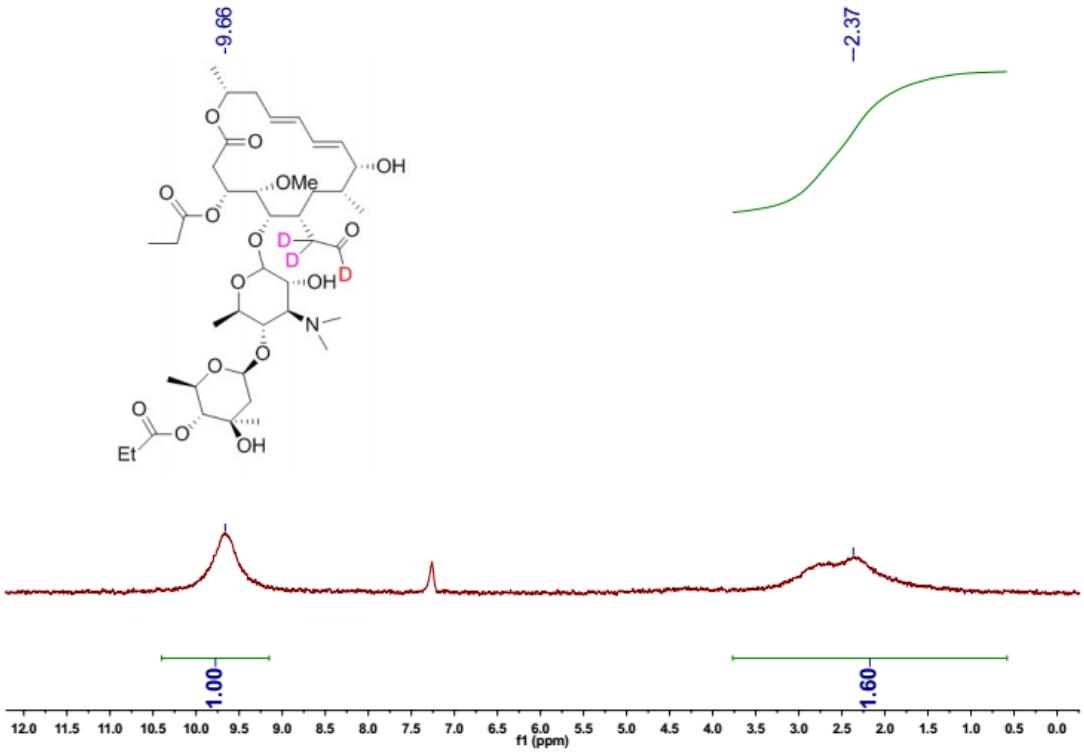
$^{1}$H NMR of midecamycin **11w**



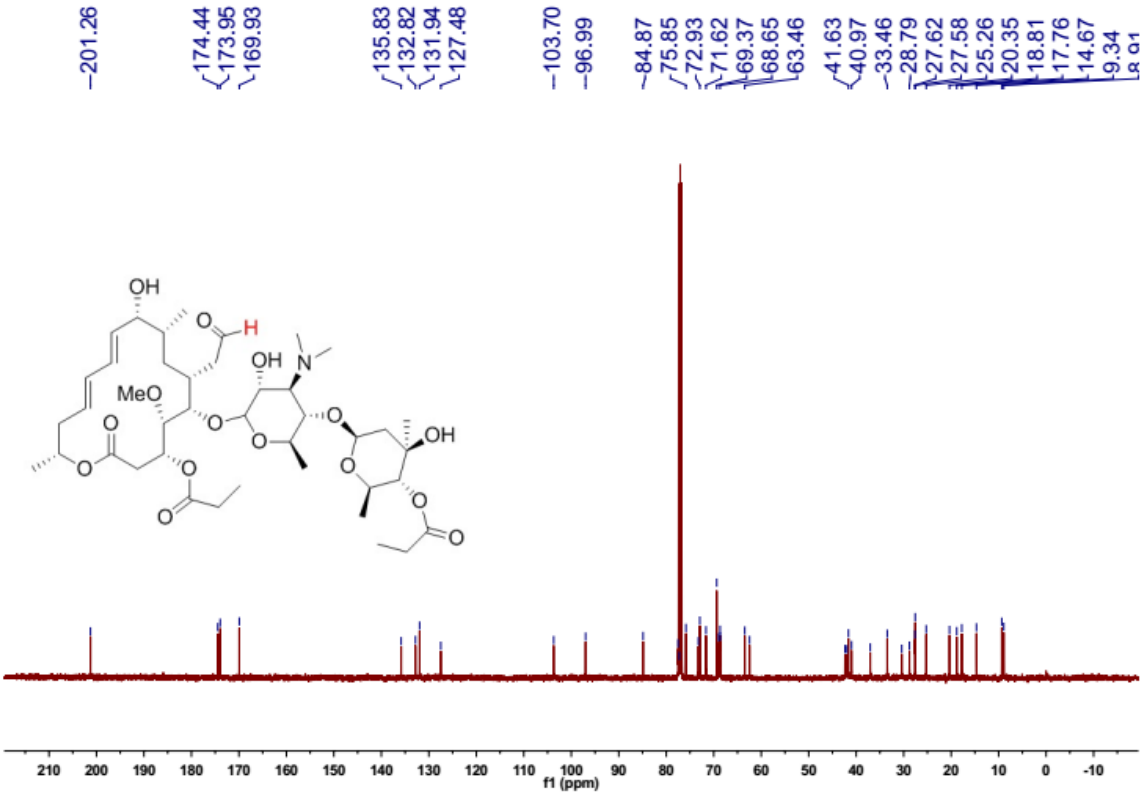
$^{1}$H NMR of deuterated midecamycin **12w**



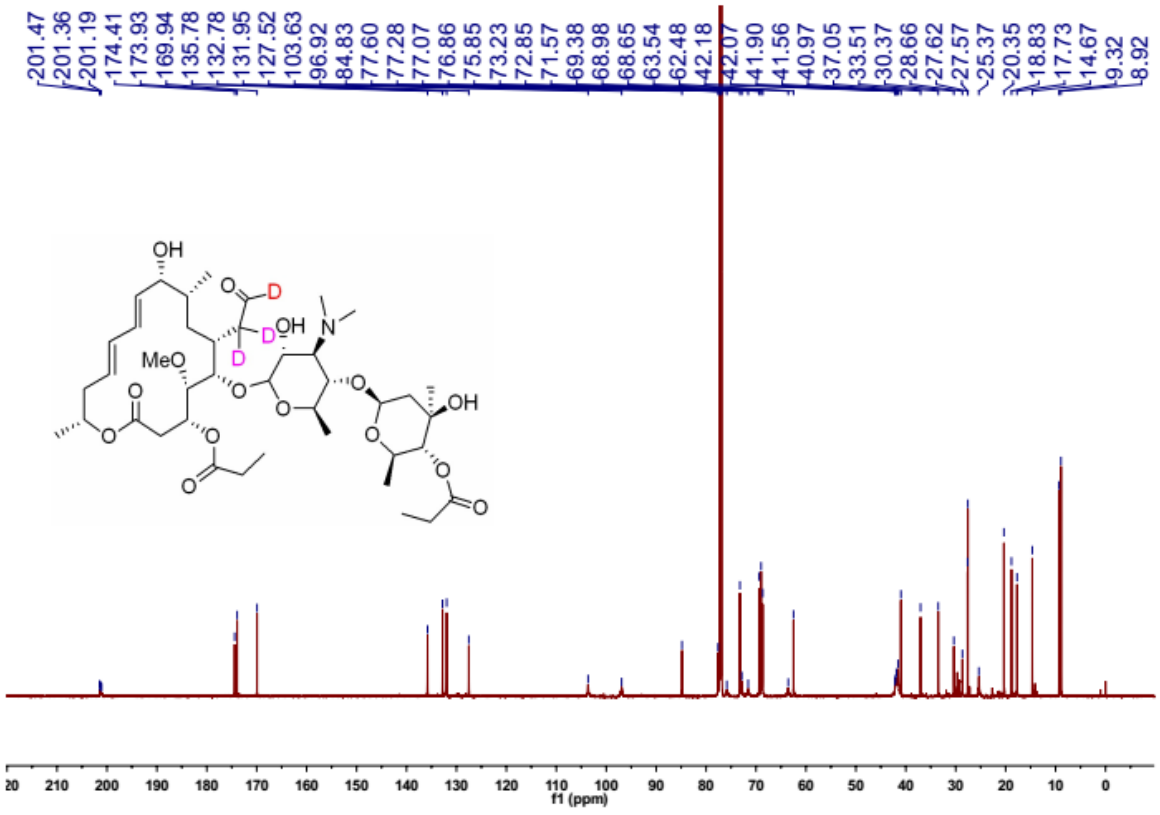
$^{2}$H NMR of deuterated aldehyde **12w**



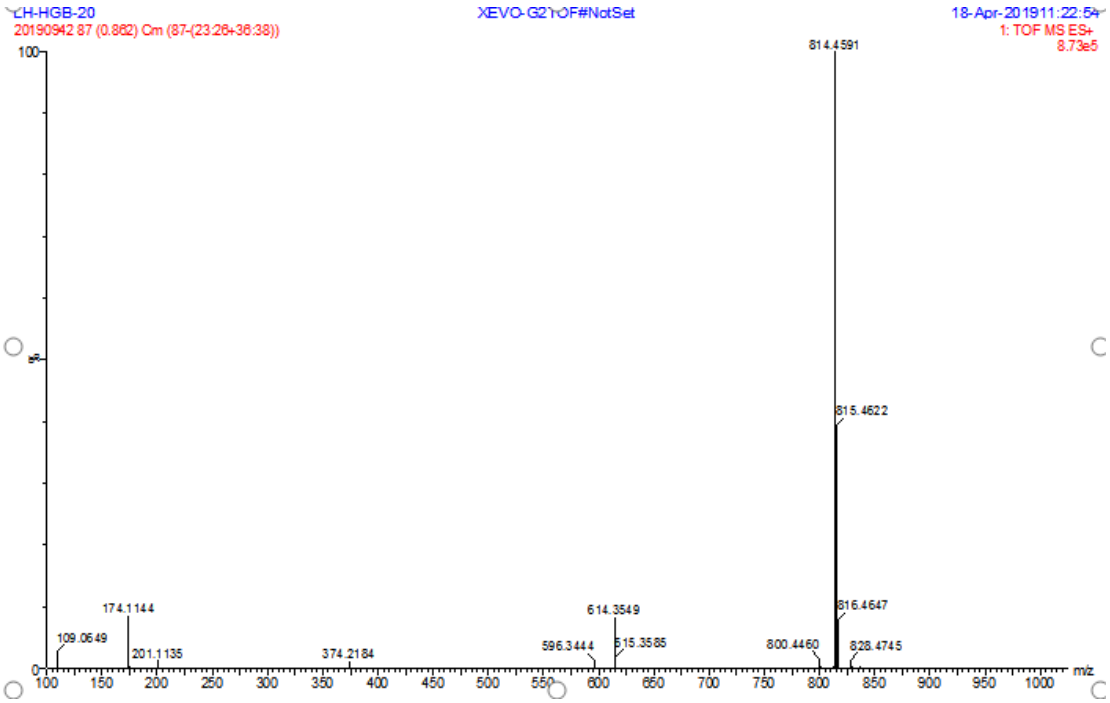
$^{13}$C NMR of midecamycin **11w**



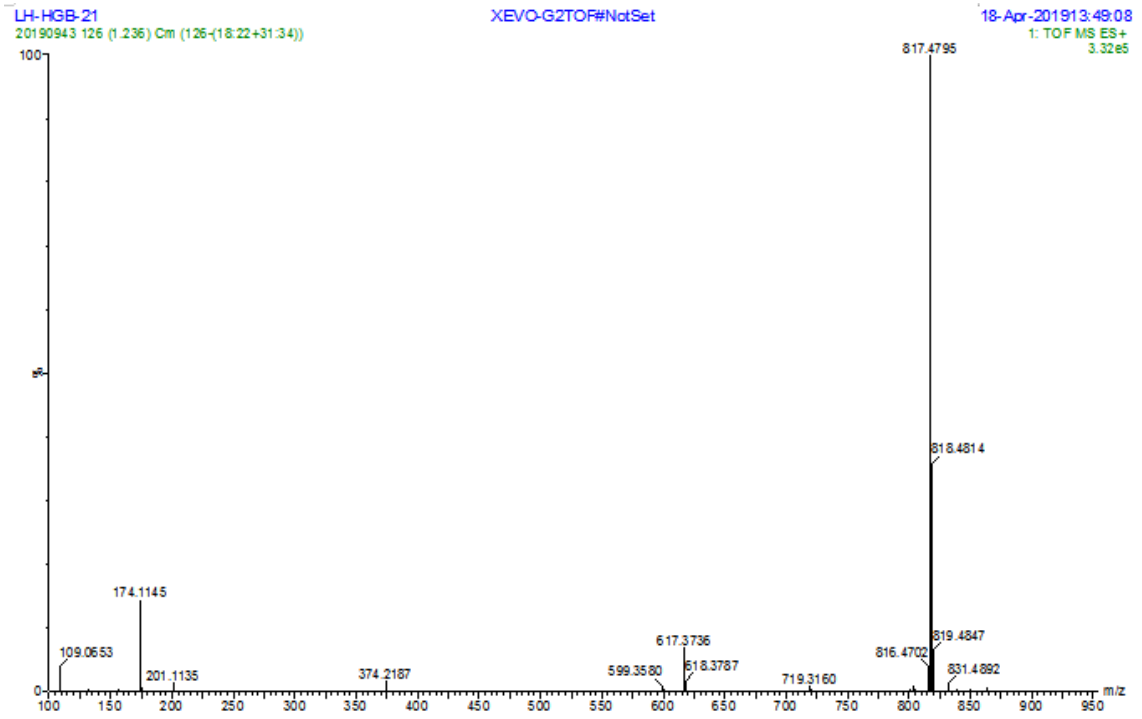

$^{13}$C NMR of deuterated midecamycin **12w**



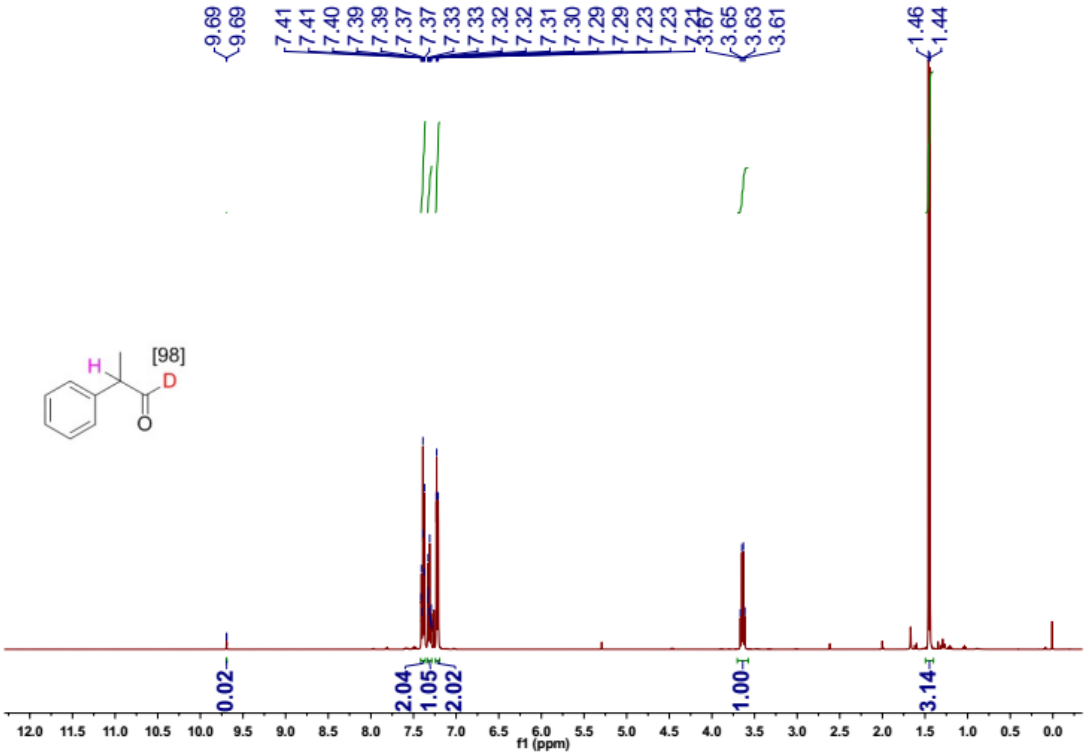
HRMS (ESI) of midecamycin **11w:**



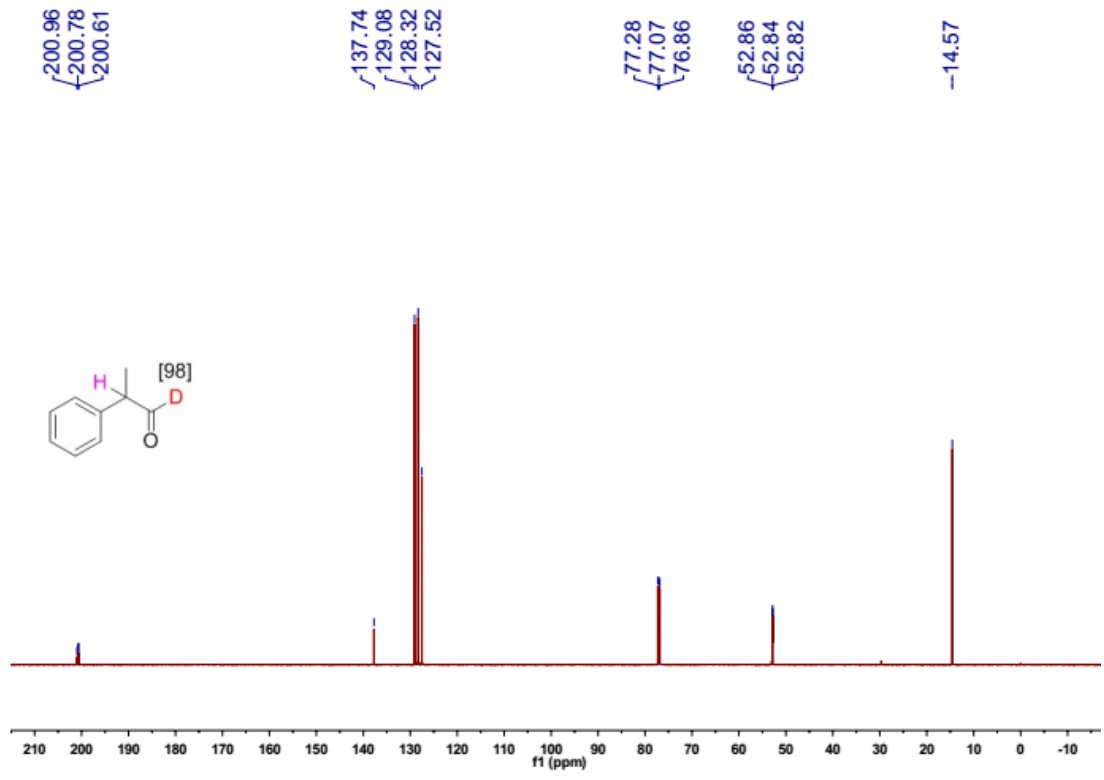

HRMS (ESI) of deuterated midecamycin **12w:**



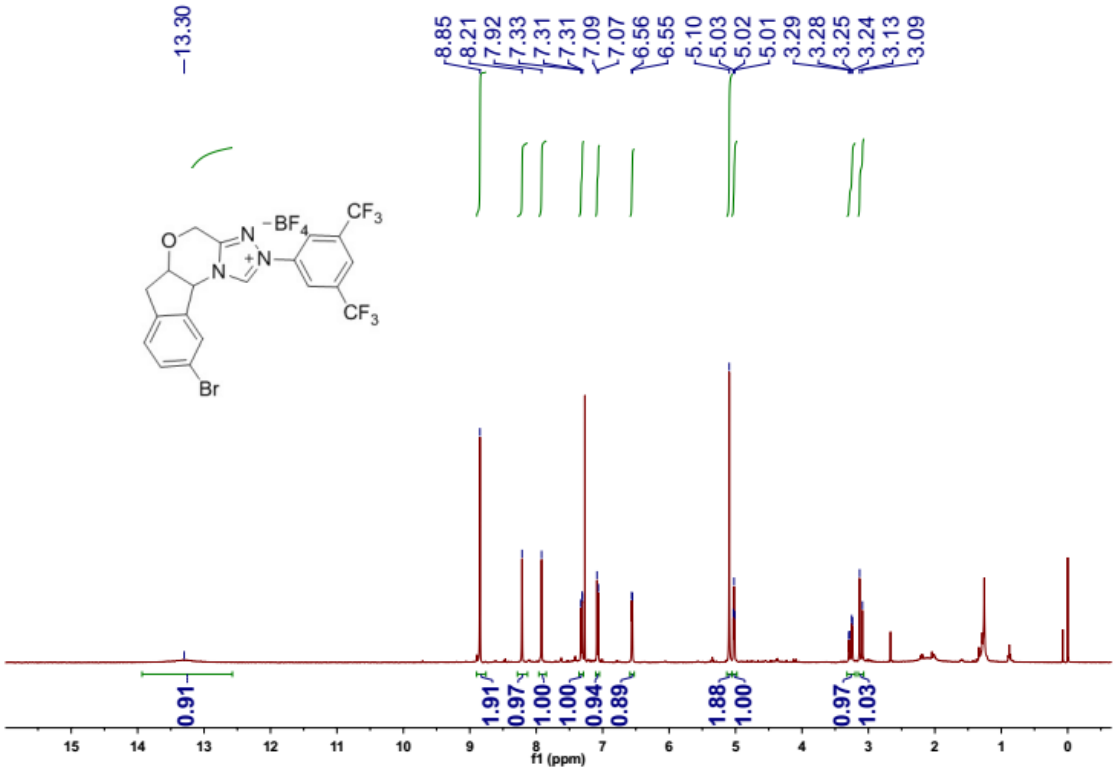
$^{1}$H NMR of **14**



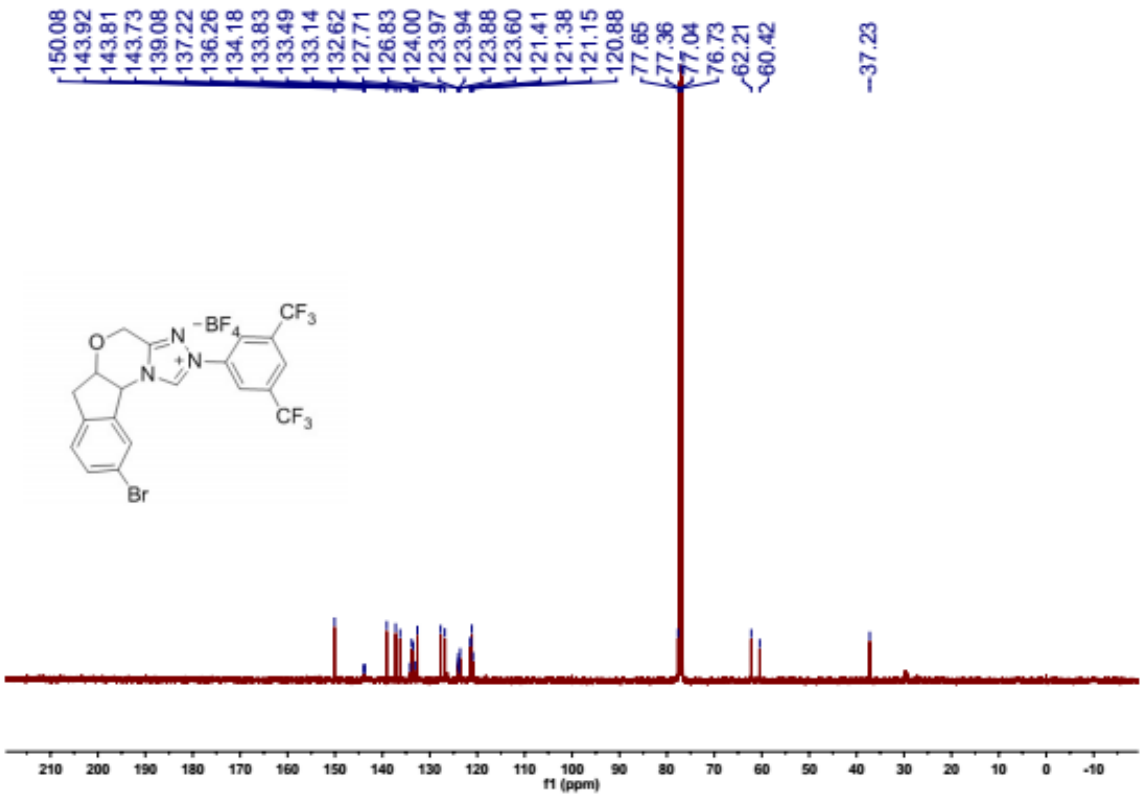

$^{13}$C NMR of **14**



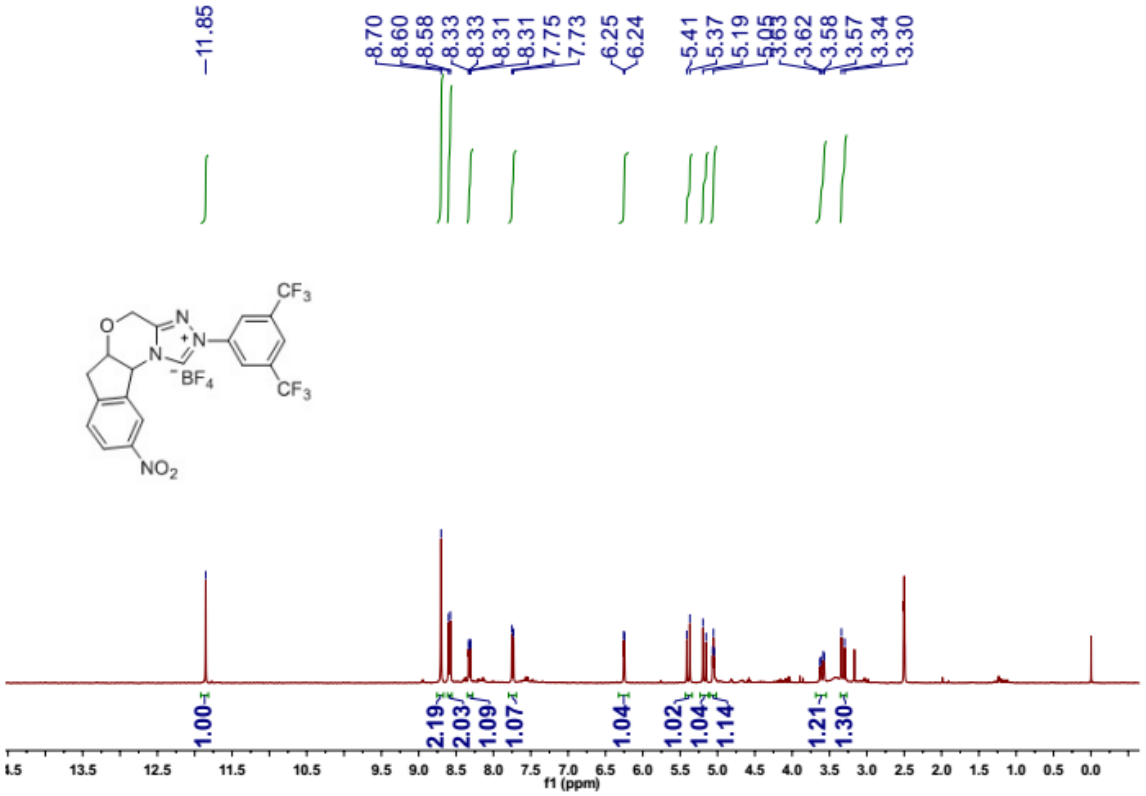
$^{1}$H NMR of **5ah**



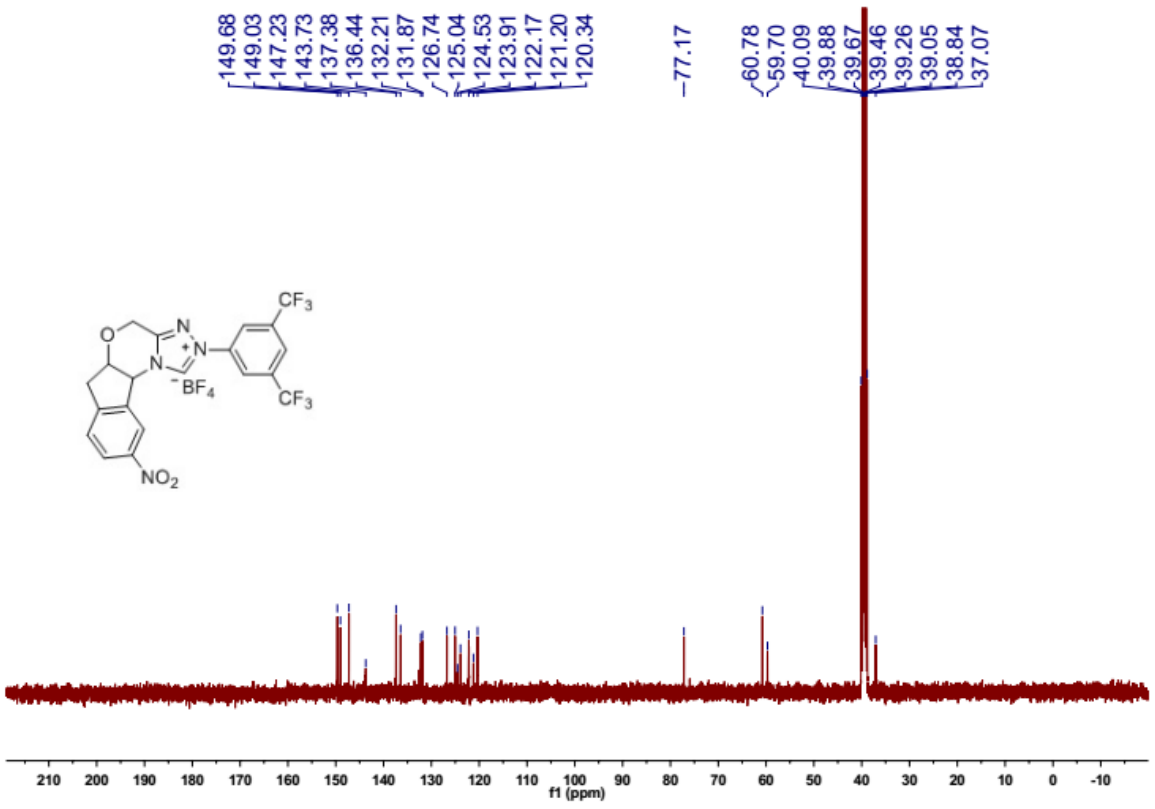

$^{13}$C NMR of **5ah**



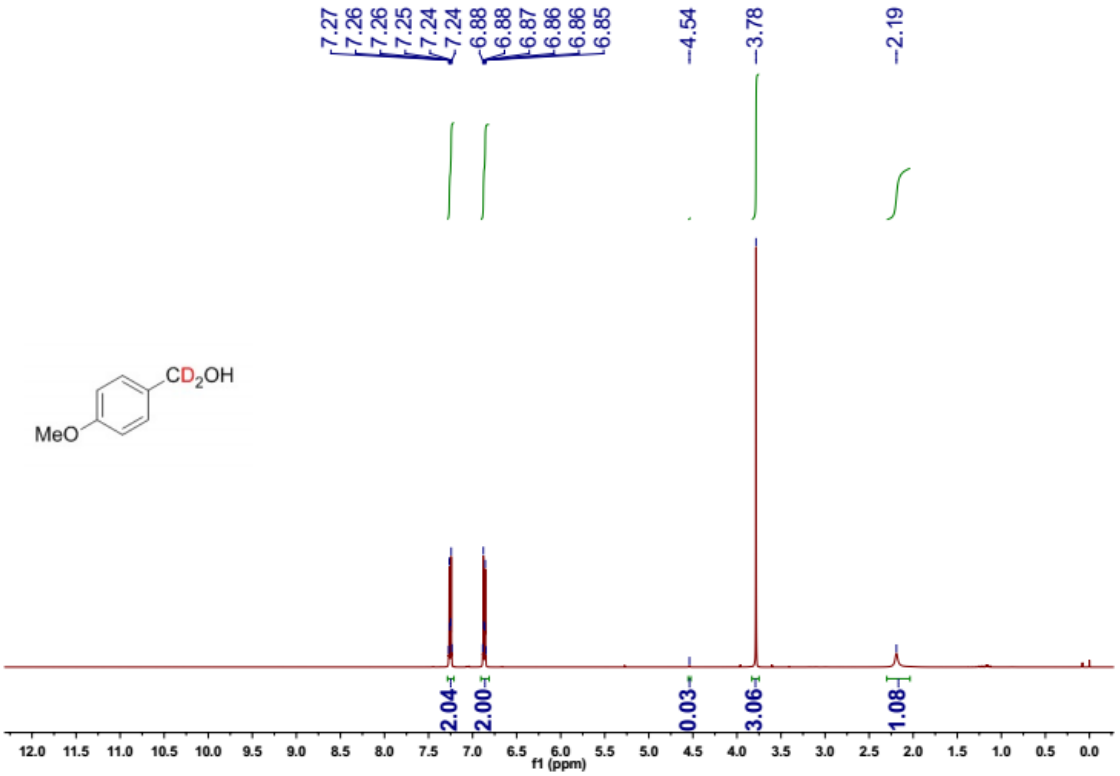
$^{1}$H NMR of **5p**



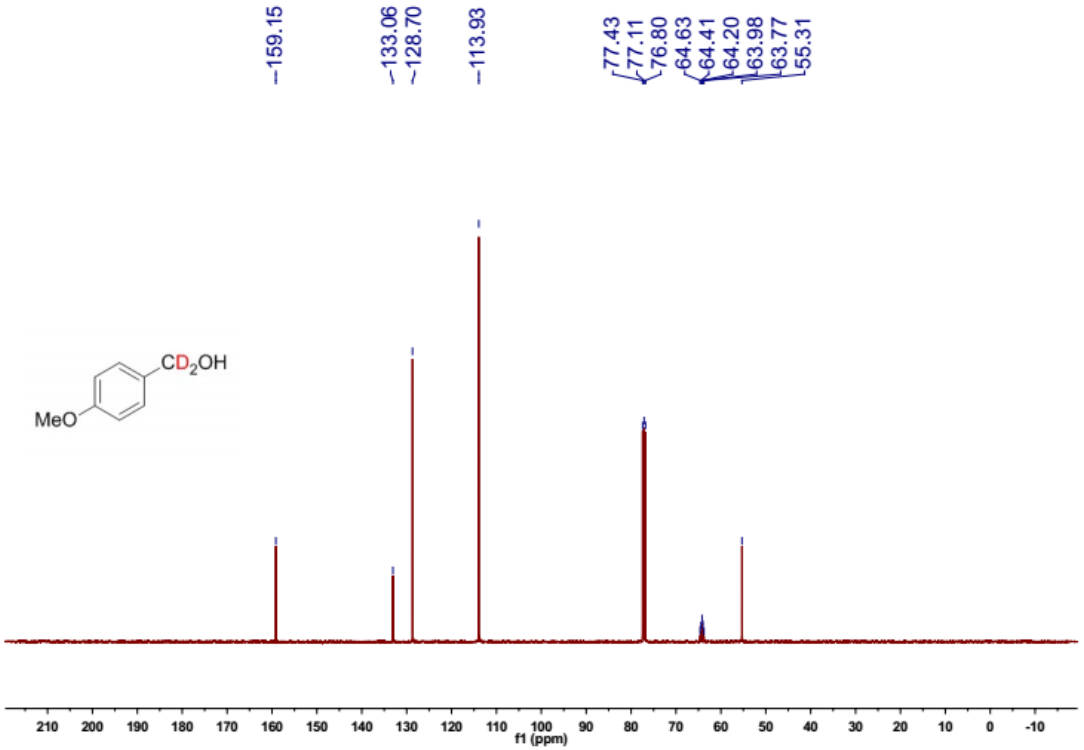

$^{13}$C NMR of **5p**



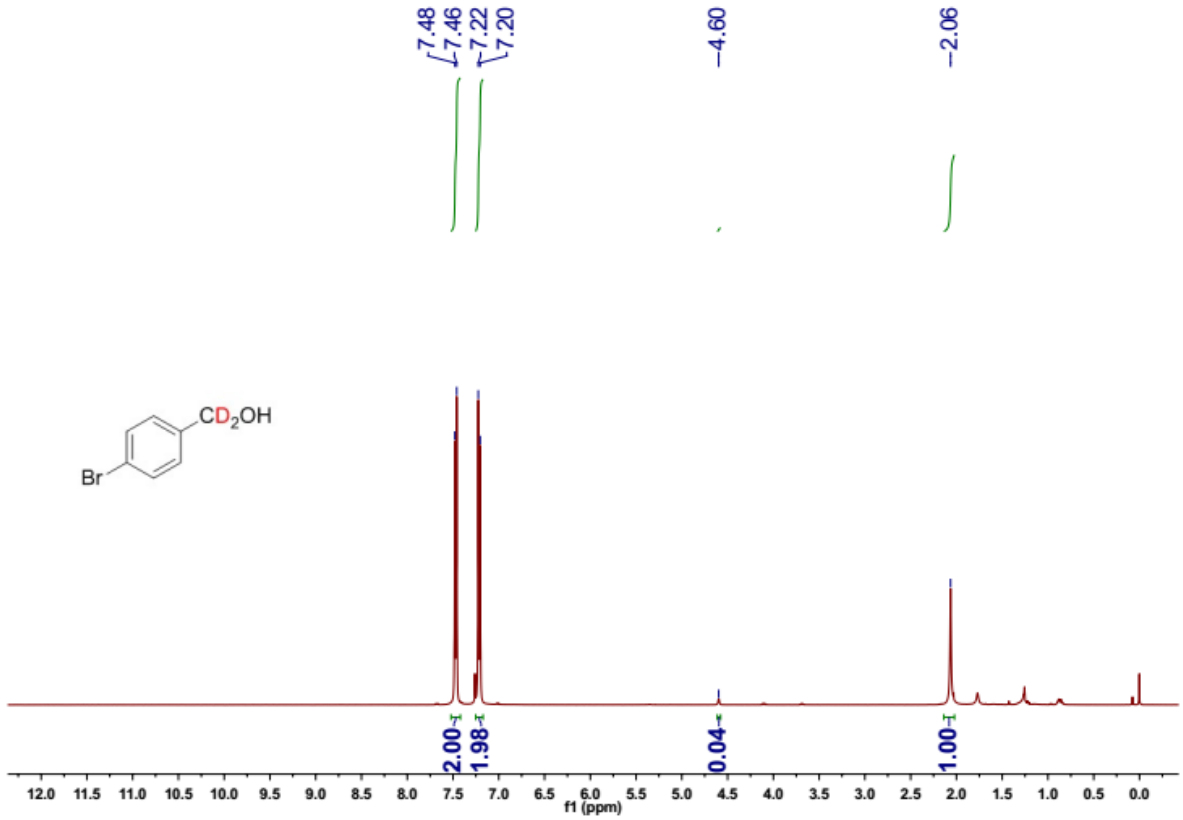
$^{1}$H NMR of **15a**



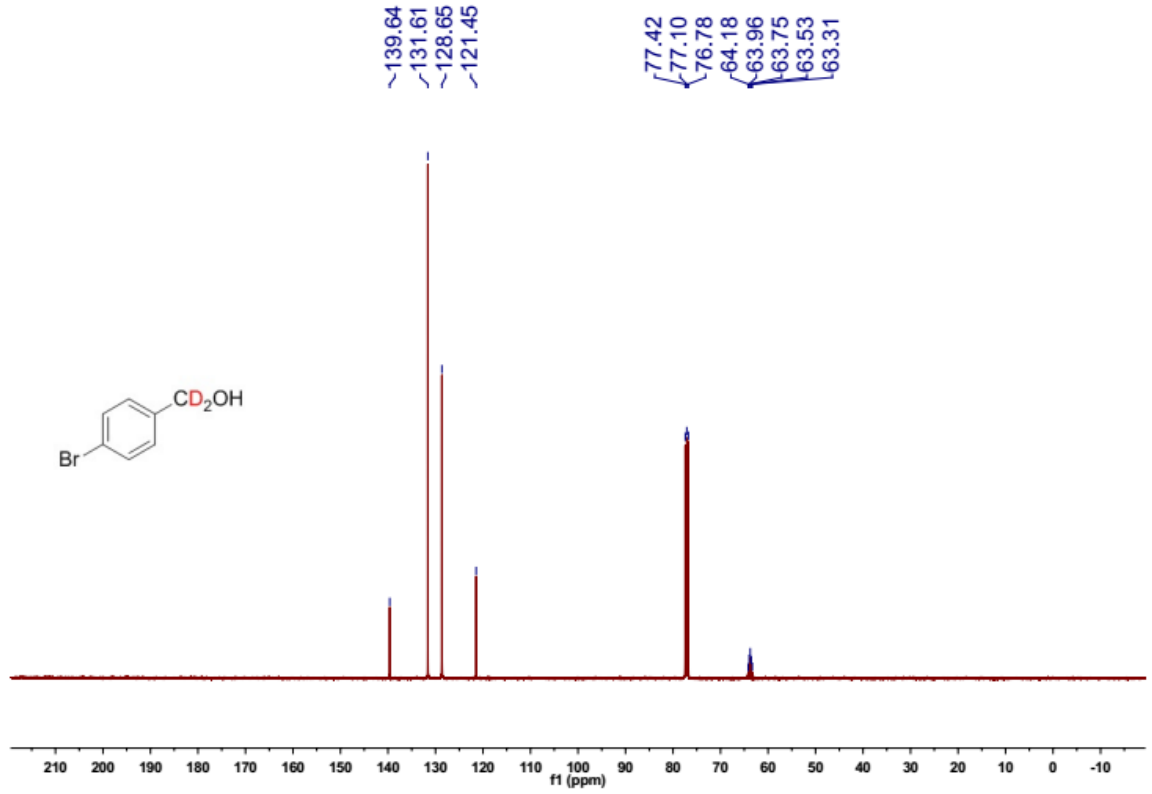

$^{13}$C NMR of **15a**



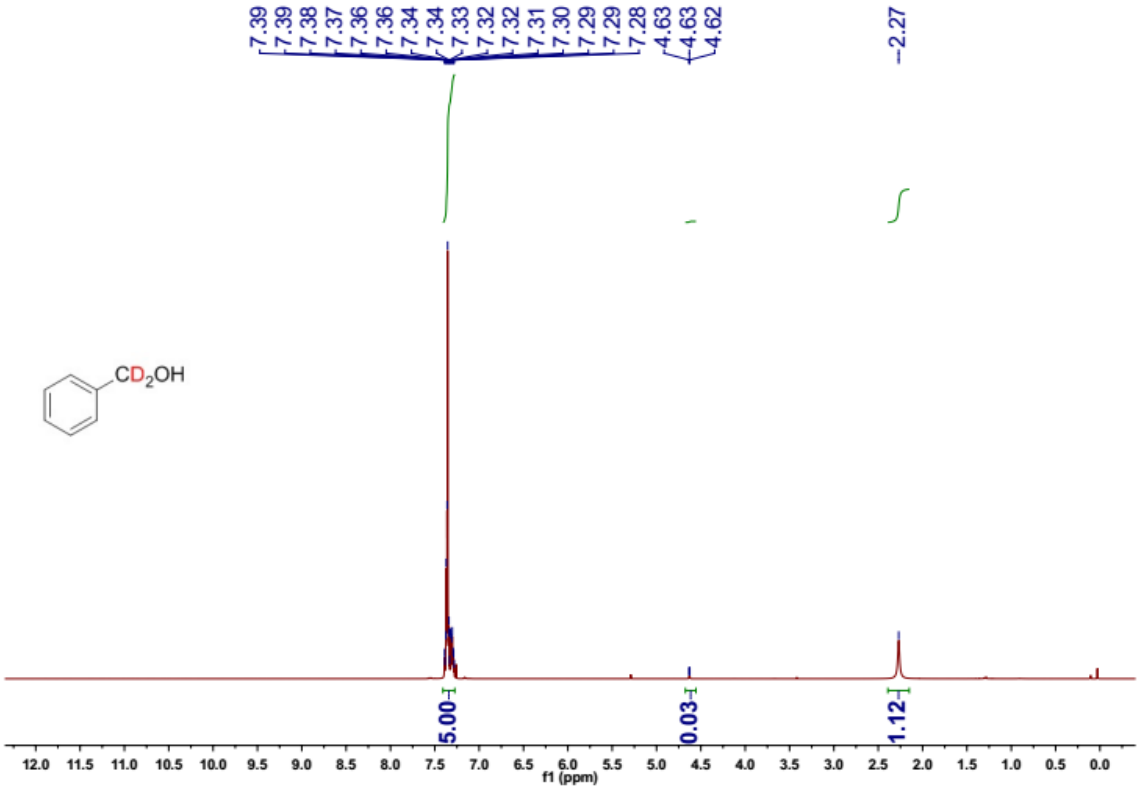
$^{1}$H NMR of **15b**



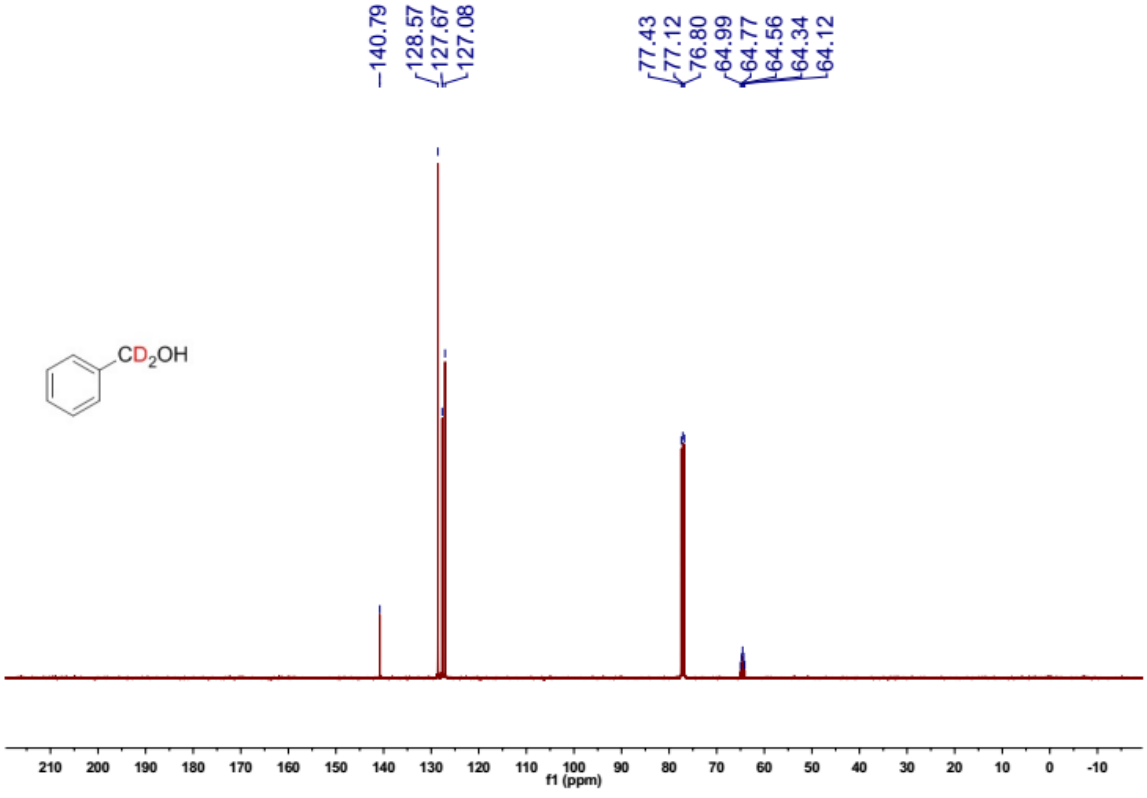

$^{13}$C NMR of **15b**



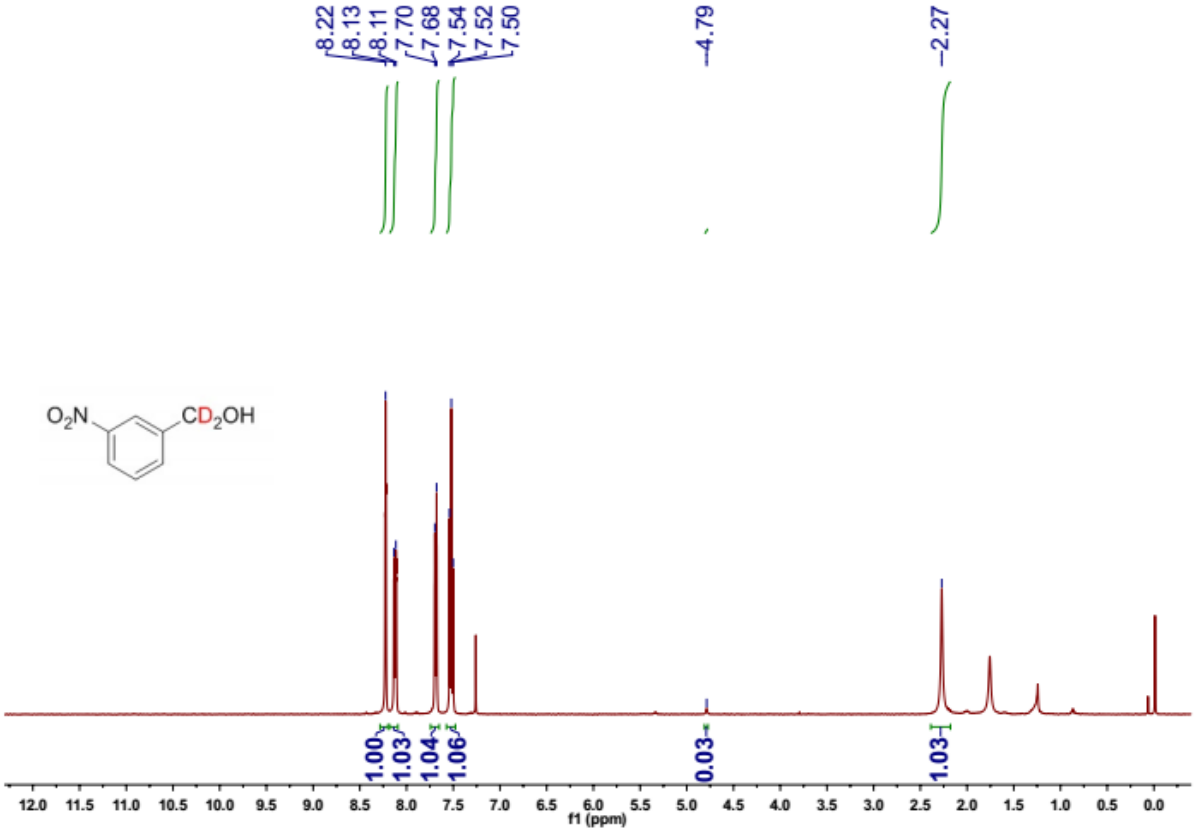
$^{1}$H NMR of **15e**



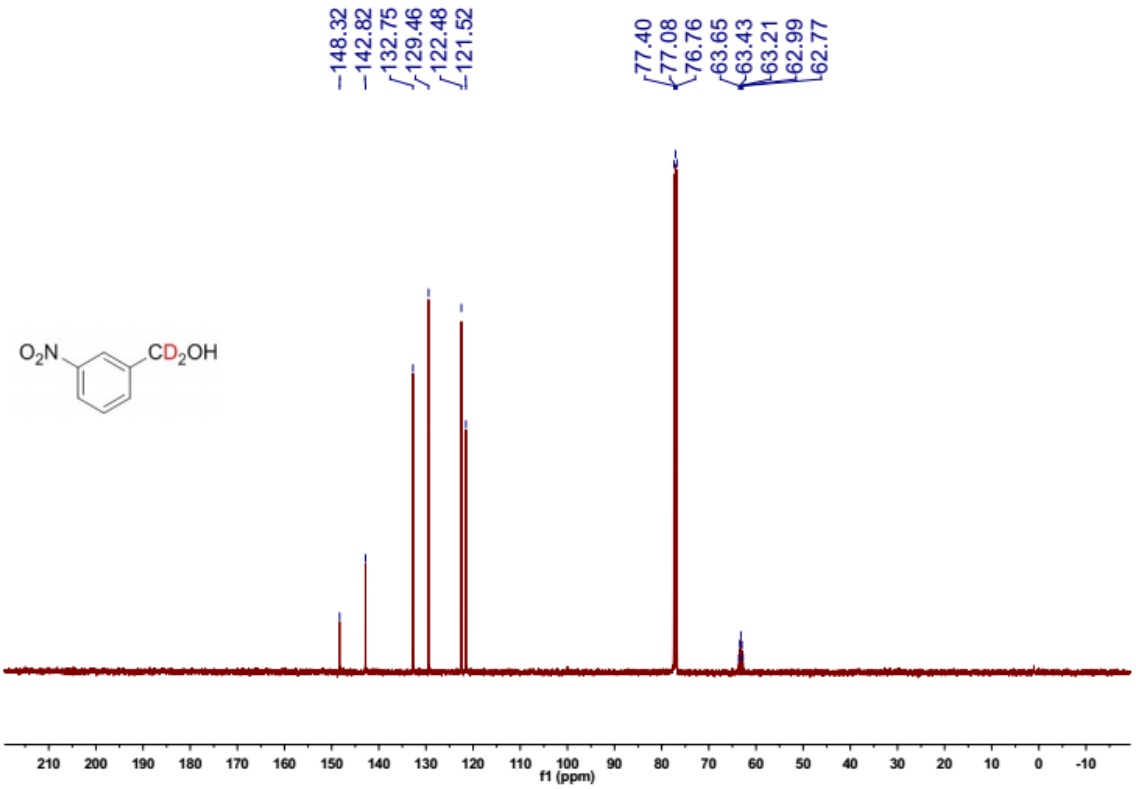

$^{13}$C NMR of **15e**



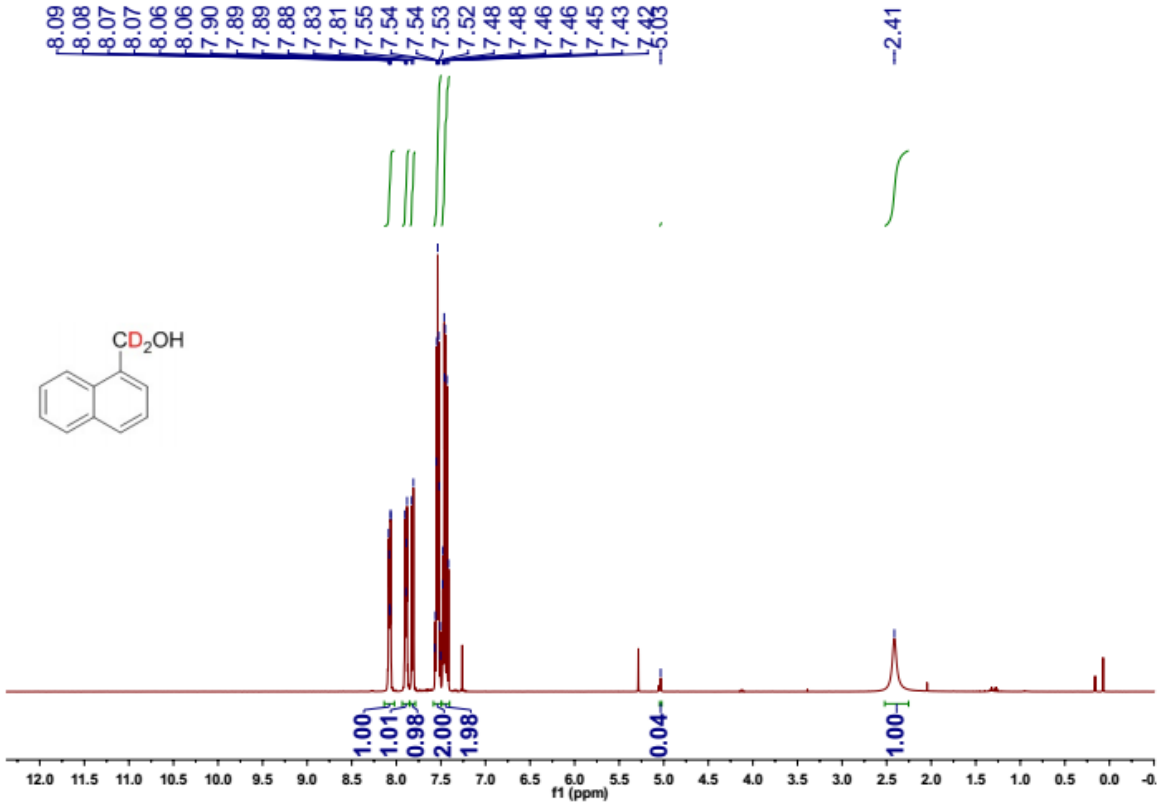
$^{1}$H NMR of **15x**



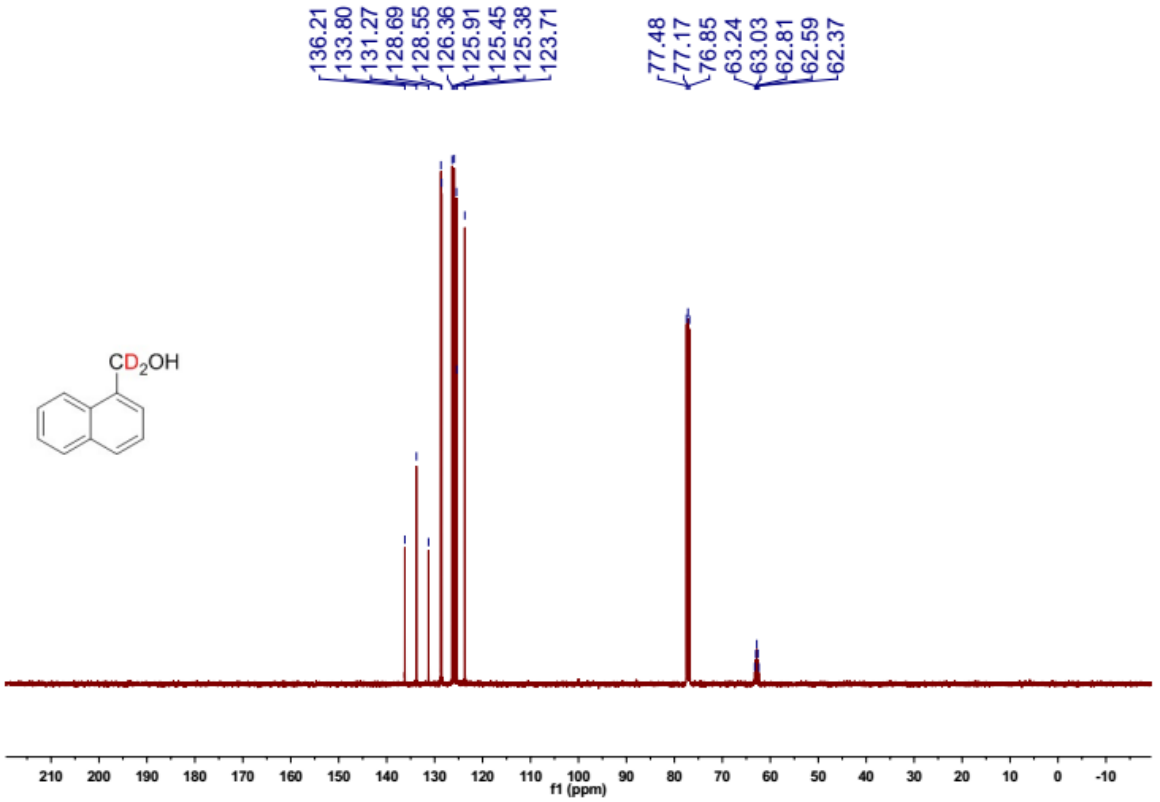

$^{13}$C NMR of **15x**



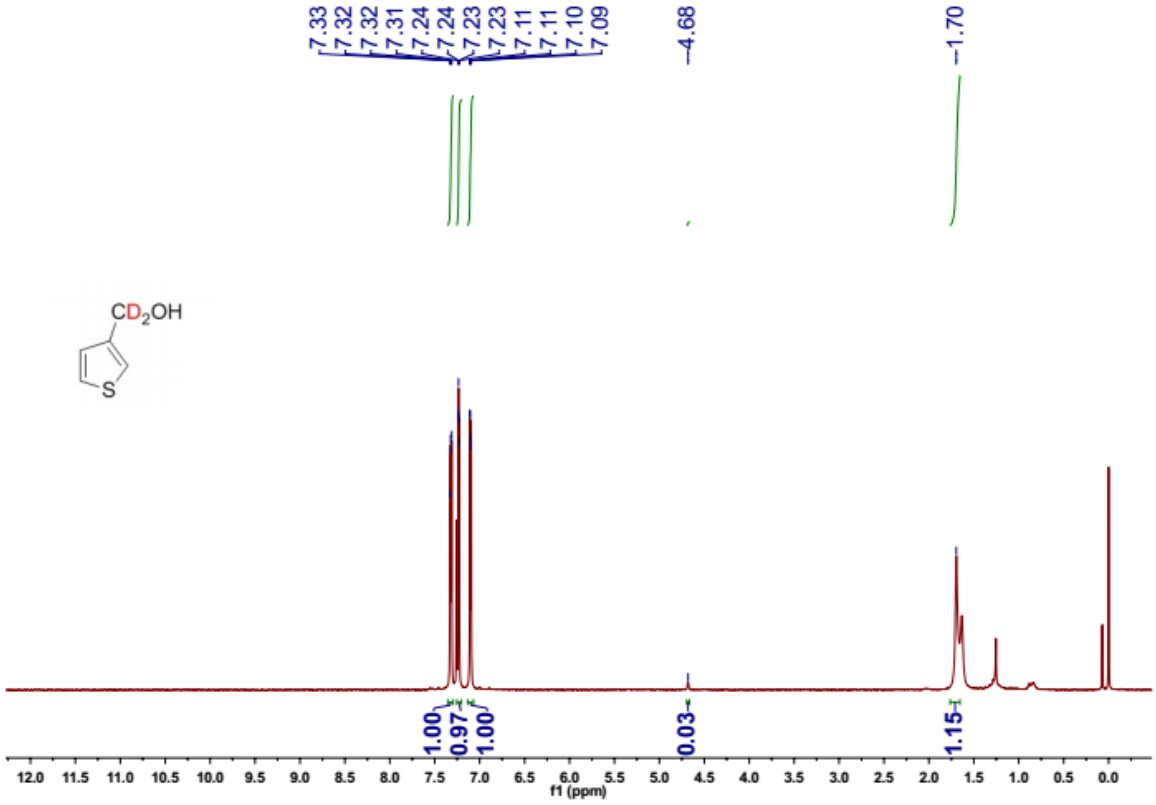
$^{1}$H NMR of **15an**



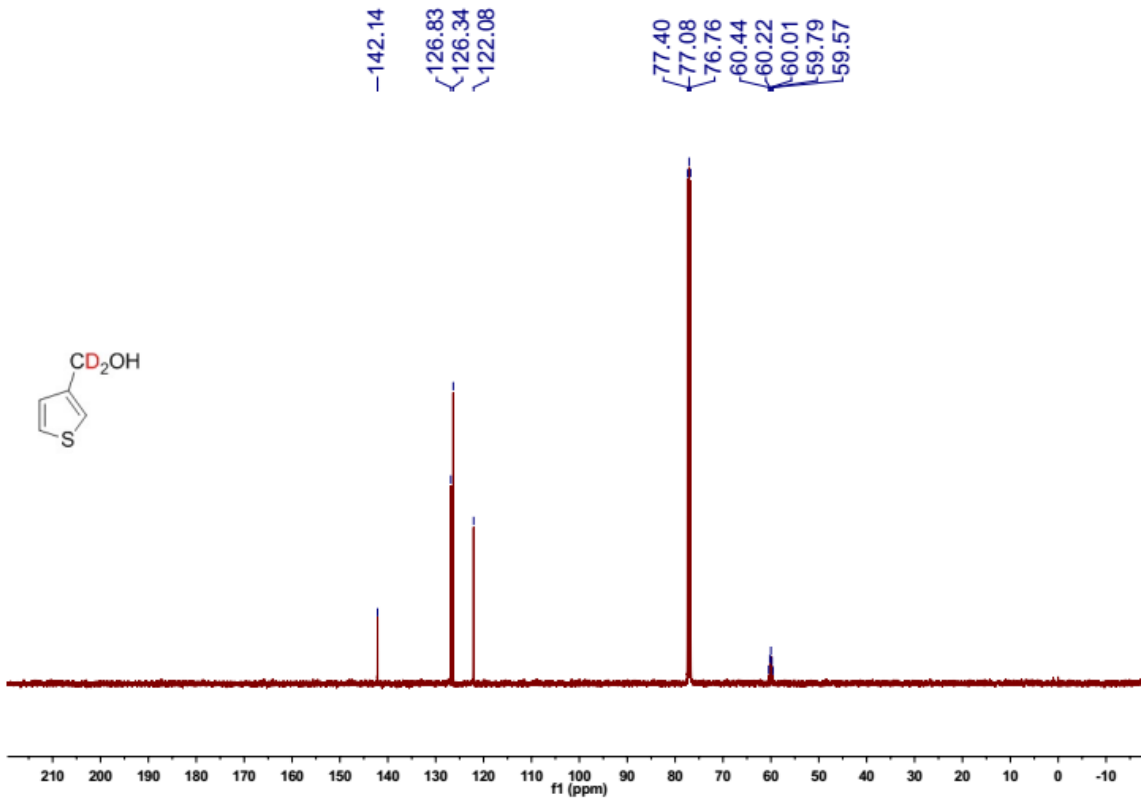

$^{13}$C NMR of **15an**



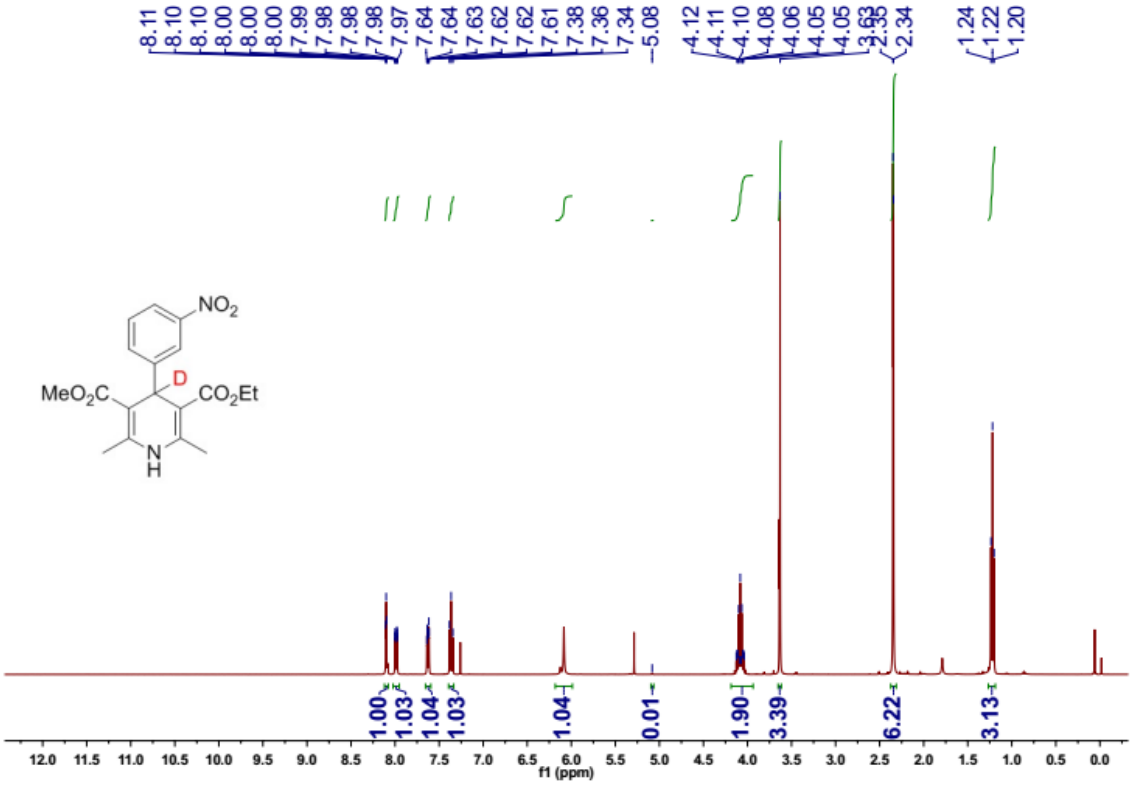
$^{1}$H NMR of **15aq**



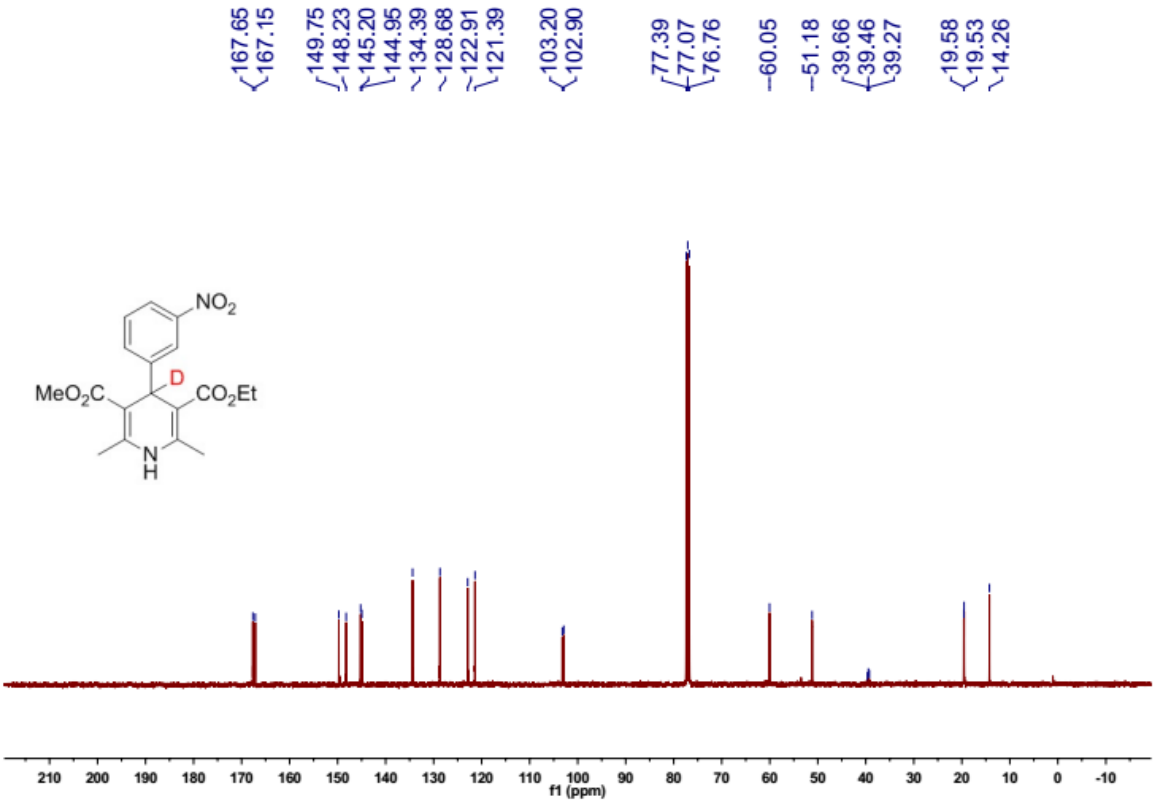

$^{13}$C NMR of **15aq**



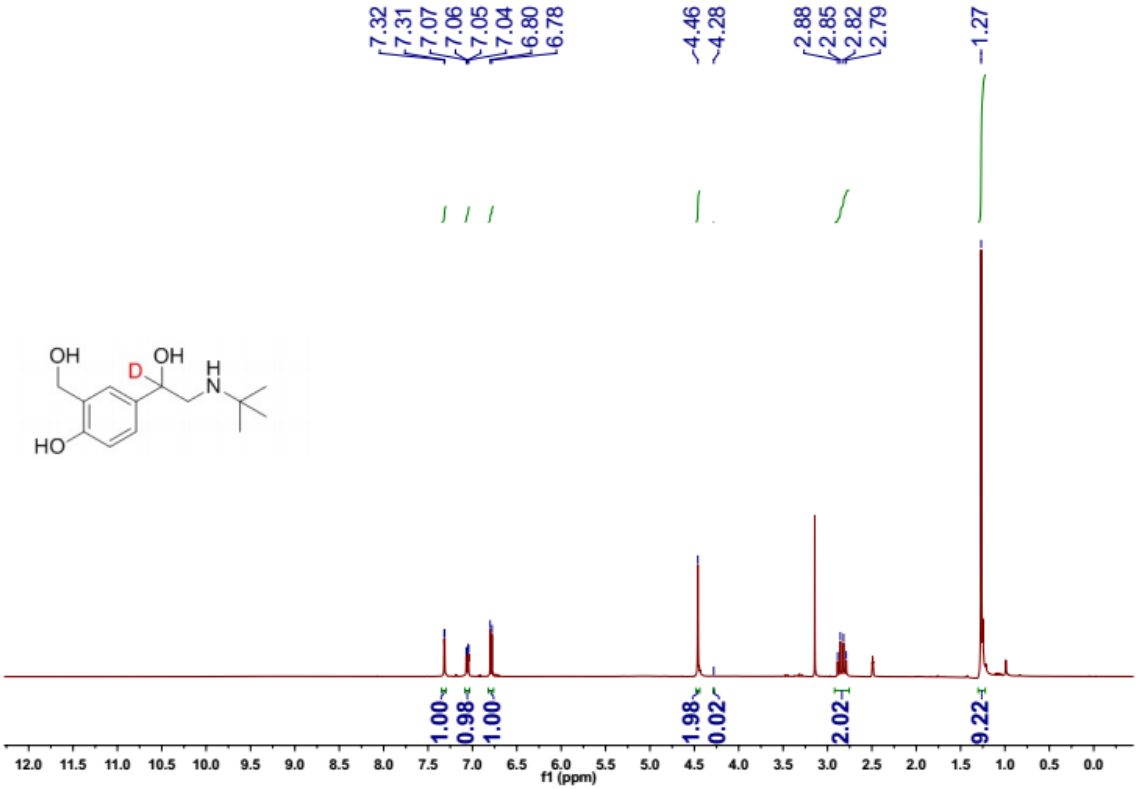
[1]H NMR of deuterated Nitrendipine



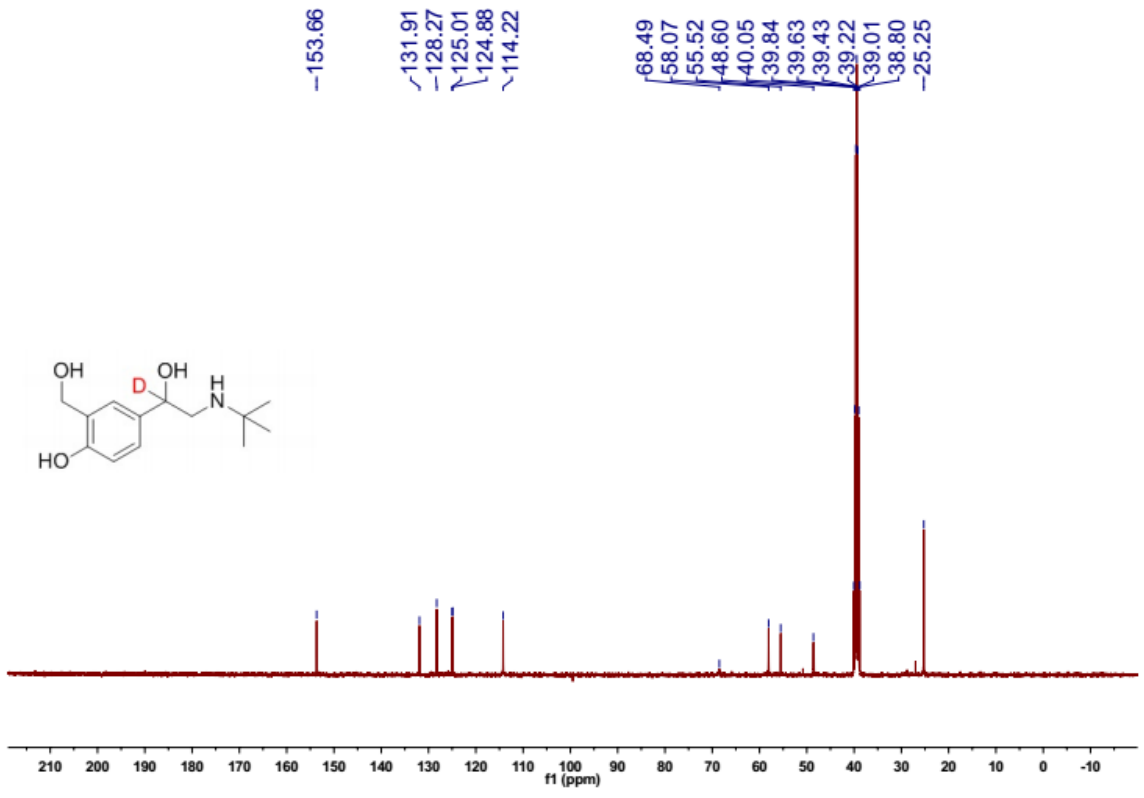

[13]C NMR of deuterated Nitrendipine



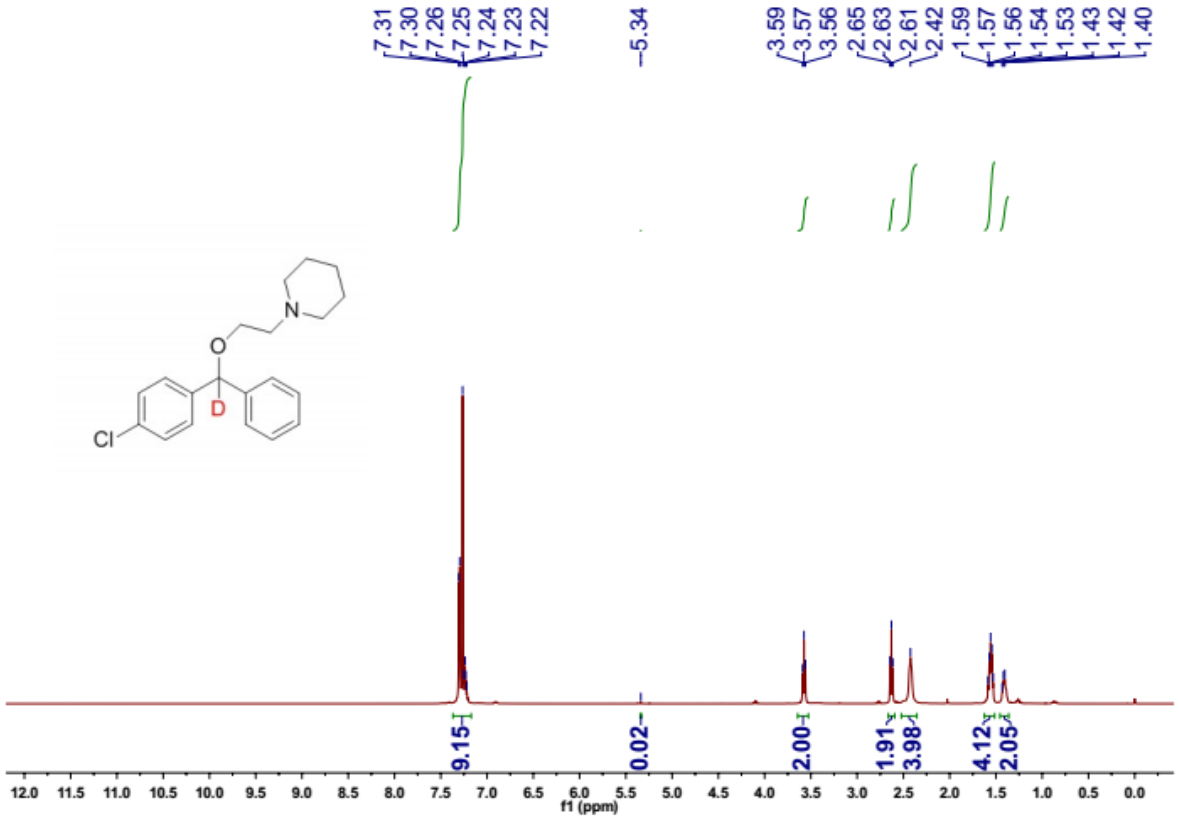
$^{1}$H NMR of deuterated Salbutamol



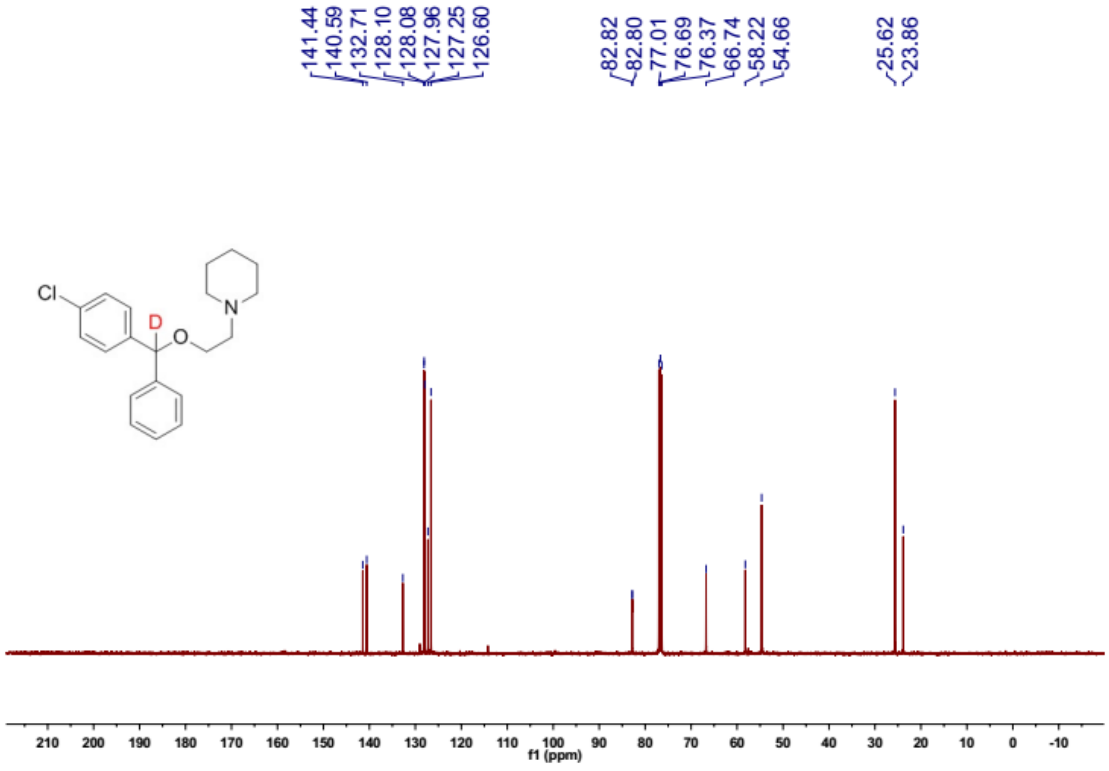

$^{13}$C NMR of deuterated Salbutamol



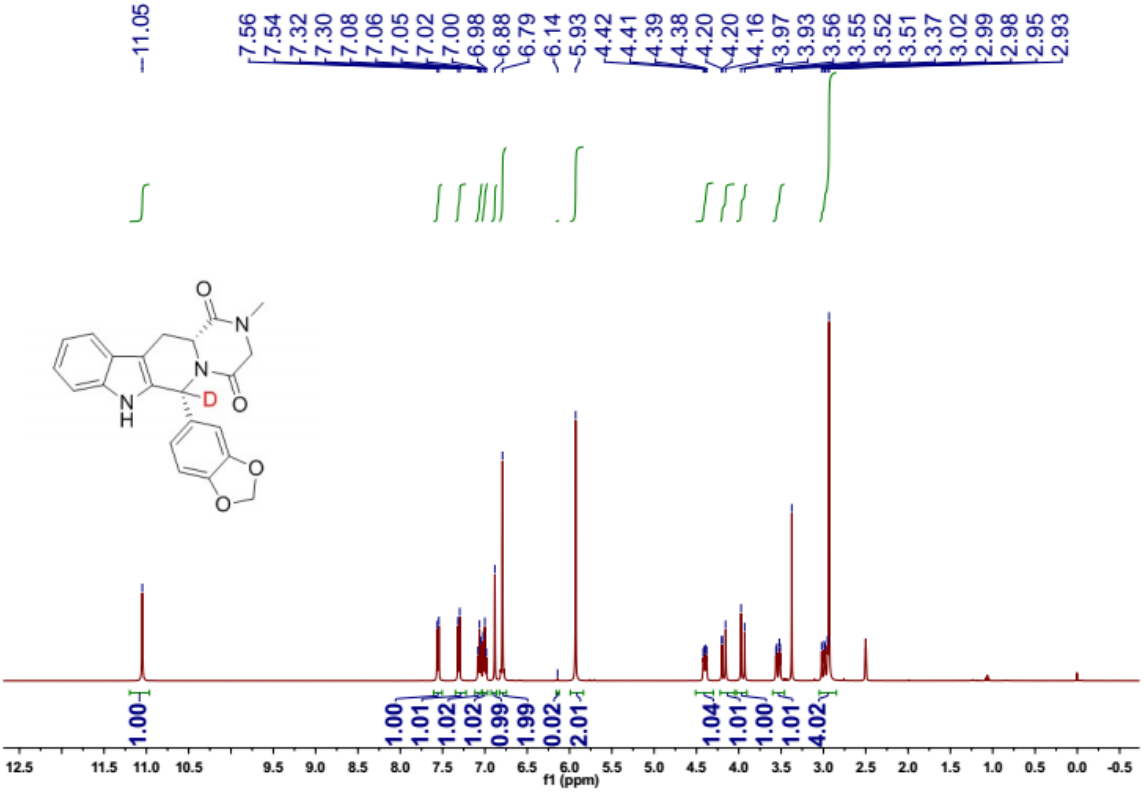
$^{1}$H NMR of deuterated Cloperastine



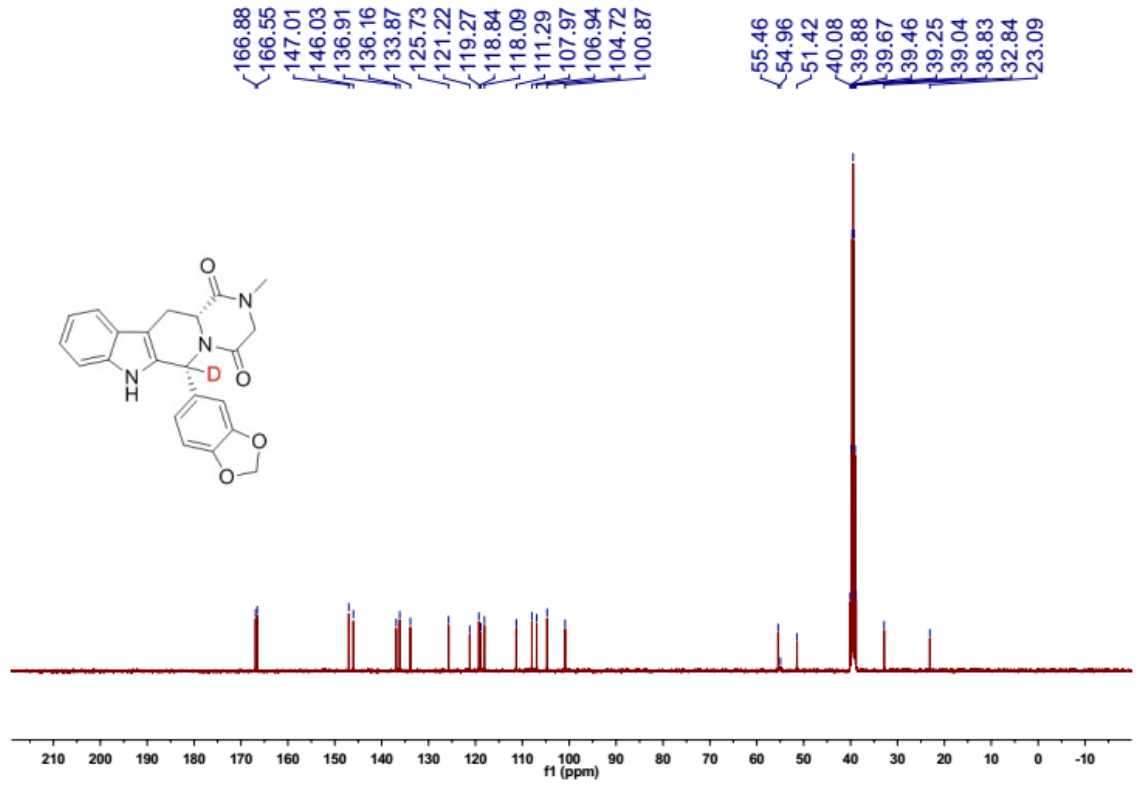

$^{13}$C NMR of deuterated Cloperastine



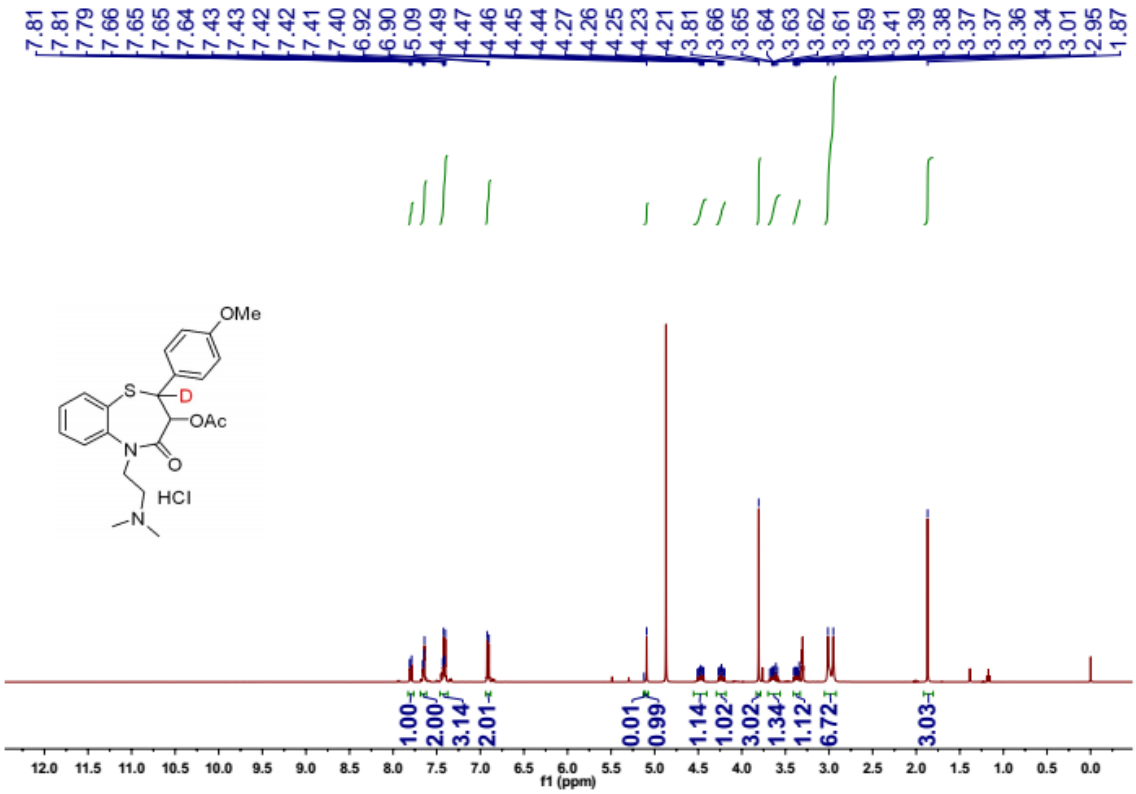
[1]H NMR of deuterated Tadalafil




[13]C NMR of deuterated Tadalafil



[1]H NMR of deuterated Diltiazem




[13]C NMR of deuterated Diltiazem