Supplementary Materials

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

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1. Supplementary 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$,^8$, 5k$,^9$, 5l$,^{10}$, 5m$,^{10}$, 5n$,^{10}$, 5o$,^{11,12}$, 5r$,^9$, 5t$,^{13}$, 5u$,^{14}$, 5v$,^{15}$, 5x$,^{16}$, 5y$,^{17}$, 5za$,^{18}$, 5ac, 5ad$,^9$, 5ae$,^{18}$, 5af$,^9$, 5ag$,^{19}$, 5ai$,^{20}$, 5aj$,^{21}$, 5ak$,^{11}$, 5at$,^{22}$, 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:

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

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.

![Chemical reaction](image)

| Compound          | Vendor          | Cost/g         | MW | Quantity for producing 1 g product 7d | Price for producing 1 g product 7d |
|-------------------|-----------------|----------------|----|--------------------------------------|-----------------------------------|
| ![Chemical structure](image) | Sigma-Aldrich    | $29.80/100g    | 106| $0.298/g × 1.42 g = $0.42            |                                   |
| ![Chemical structure](image) | Self preparation | $40/g          | 427.1| $0.01335 × 10 mol% × 427.1 = 0.57 g = $22.8 |
| ![Chemical structure](image) | Sigma-Aldrich    | $1.160/1kg     | 20 | 1000 × 1.1/(107 × 70%) = 14.7 g = $17.05 |
| ![Chemical structure](image) | Fisher          | $24.66/500g    | 138| $0.01335 × 138 = 1.84 g = $0.09 |
| Toluene (anhydrous) | Sigma-Aldrich    | $45/2L         | 92 | 0.0225/mL × 3.3 mL = $0.074 |
| ![Chemical structure](image) | Sigma-Aldrich    | $570/g         | 107|                                   |
| ![Chemical structure](image) | Our method       | $40.43/g       | 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**

| Entry | Catalyst | Solvent | T (°C) | Yield (%)<sup>b</sup> | D (%)<sup>c</sup> |
|-------|----------|---------|--------|------------------------|-------------------|
| 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       | CH₂Cl₂  | 40     | 80                     | 98                |
| 13    | 5o       | toluene | 40     | 81                     | 98                |
| 14<sup>d</sup> | 5o   | toluene | 40     | 73                     | 98                |
| 15<sup>e</sup> | 5o   | toluene | 40     | 40                     | 98                |
| 16<sup>f</sup> | 5o   | toluene | 40     | 82                     | 97                |
| 17<sup>g</sup> | 5o   | toluene | 40     | 81                     | 91                |

<sup>a</sup>Reaction conditions unless otherwise stated: 6a (0.5 mmol), catalysts 5 (10 mol%) and K₂CO₃ (1.0 equiv) in D₂O (1 mL) and solvent (0.25 mL) was vigorously stirred for 12 hours. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by <sup>1</sup>H NMR. <sup>d</sup>5% catalyst was used. <sup>e</sup>20% catalyst was used. <sup>f</sup>0.5 mL D₂O was used. <sup>g</sup>10 eq D₂O was used.
**Supplementary Table 3.** Optimization of reaction conditions for cinnamaldehyde

![Catalyst Base Diagram]

| Entry | Catalyst | Base   | T(°C) | Yield (%)<sup>b</sup> | % D<sup>d</sup> | Yield (%)<sup>c</sup> |
|-------|----------|--------|-------|------------------------|----------------|------------------------|
| 1     | 5a       | K₂CO₃  | 40    | -                      | -              | 50                     |
| 2     | 5b       | K₂CO₃  | 40    | -                      | -              | 50                     |
| 3     | 5m       | K₂CO₃  | 40    | 60                     | 0              | 10                     |
| 4     | 5o       | K₂CO₃  | 40    | 80                     | 0              | 0                      |
| 5     | 5r       | K₂CO₃  | 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             | -                      |

<sup>a</sup>Reaction conditions unless otherwise stated: 9a (0.25 mmol), catalyst 5 (10 mol%) and KOAc (1.0 equiv) in D₂O (1 mL) and DCM (0.25 mL) was vigorously stirred at 40 °C for 12 hours. <sup>b</sup>Yield of isolated product of 10a. <sup>c</sup>Yield of isolated product of 11. <sup>d</sup>Deuterium incorporations (%) were determined by ¹H NMR spectroscopy.
**Supplementary Table 4.** Optimization of reaction conditions for other enals

![Chemical Structure](image)

| Entry | Catalyst | T (°C) | Yield (%)<sup>b</sup> | % D<sup>c</sup> |
|-------|----------|--------|------------------------|---------------|
| 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            |

<sup>a</sup>Reaction conditions unless otherwise stated: 9g (0.25 mmol), catalyst 5 (10 mol%) and KOAc (1.0 equiv) in D<sub>2</sub>O (1 mL) and DCM (0.25 mL) was vigorously stirred at 25 °C for 12 hours.  
<sup>b</sup>Yield of isolated product.  
<sup>c</sup>Deuterium incorporations (%) were determined by <sup>1</sup>H NMR spectroscopy.
Supplementary Table 5. Optimization of reaction conditions for aliphatic aldehydes

![Diagram of reaction](image)

| Entry | Catalyst | T (°C) | Yield (%)\(^b\) | % D\(^1\)\(^c\) | % D\(^2\)\(^c\) |
|-------|----------|--------|------------------|----------------|----------------|
| 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: III (0.5 mmol), catalysts 5 (10 mol%) and NaHCO\(_3\) (1.0 equiv) in D\(_2\)O (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 \(^1\)H NMR spectroscopy.
4. Supplementary 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$_2$O (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-$\alpha$-d$_1$ (7a)](image)

2-Naphthaldehyde ($0.5$ mmol), 5o (10 mol%) and K$_2$CO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_7$DO [(M)$^+$]: 157.0638, found: 157.0639.

![4-Methoxybenzaldehyde-$\alpha$-d$_1$ (7b)](image)

4-Methoxybenzaldehyde (0.5 mmol), 5o (10 mol%) and K$_2$CO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_8$H$_7$DO$_2$ [(M)$^+$]: 137.0587, found: 137.0588.

![4-Bromobenzaldehyde-$\alpha$-d$_1$ (7c)](image)

4-Bromobenzaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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 calcd for C$_7$H$_5$DO [(M)$^+$]: 184.9587, found: 184.9589.

**Benzaldehyde-$\alpha$-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$_2$O (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 calcd for C$_7$H$_5$DO [(M)$^+$]: 107.0481, found: 107.0482.

**4-Methylbenzaldehyde-$\alpha$-d$_1$ (7e)**

4-Methylbenzaldehyde (0.5 mmol), 5o (10 mol%) and K$_2$CO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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 calcd for C$_8$H$_7$DO [(M)$^+$]: 121.0638, found: 121.0639.

**4-Benzylxybenzaldehyde-$\alpha$-d$_1$ (7f)**

4-Benzylxybenzaldehyde (0.5 mmol), 5o (10 mol%) and K$_2$CO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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, $J = 3.5$Hz), 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 calcd for C$_{14}$H$_{11}$DO$_2$ [(M)$^+$]: 213.0900, found: 213.0904.
[1,1′-Biphenyl]-4-carbaldehyde-α-d₄ (7g)

[1,1′-biphenyl]-4-carbaldehyde (0.5 mmol), 5o (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.11 (s, 1D); HRMS (EI): m/z calcd for C₁₃H₈DO [(M)⁺]: 183.0794, found: 183.0796.

4-Acetoxybenzaldehyde-1,2-d₁,3 (7h)

4-Acetoxybenzaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv), was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.3 (s, 1D), 2.34 (s, 0.13D); HRMS (EI): m/z calcd for C₉H₇DO₃ [(M)⁺]: 165.0536, found: 165.0537.

4-Dimethylaminobenzaldehyde-α-d₁ (7i)

4-Dimethylaminobenzaldehyde (0.5 mmol), 5ag (30 mol%) and AcOK (1 mmol, 2 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.78 (s, 1D); HRMS (EI): m/z calcd for C₉H₁₀DNO [(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. ^1H 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); ^13C 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); ^2H NMR (77 MHz, CHCl_3) δ 9.86 (s, 1D), 2.05 (s, 0.28D); HRMS (EI): m/z caled for C_9H_8D_NO_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. ^1H 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); ^13C 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); ^2H 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 white solid in 79% yield with 98% D-incorporation. ^1H 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); ^13C 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); ^2H NMR (77 MHz, CHCl_3) δ 10.02 (s, 1D); HRMS (EI): m/z caled for C_7H_4DCIO [(M)^+]: 141.0092, found: 141.0091.
4-Formylbenzonitrile-α-\textit{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\textsubscript{2}O (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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 10.09 (s, 0.02H), 7.99 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{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); \textsuperscript{2}H NMR (77 MHz, CHCl\textsubscript{3}) δ 10.13 (s, 1D); HRMS (EI): m/z caled for C\textsubscript{8}H\textsubscript{4}DN\textsubscript{O}\[(M)^+\]: 132.0434, found: 132.0436.

4-(Trifluoromethyl)benzaldehyde-α-\textit{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\textsubscript{2}O (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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 10.09 (s, 0.03H), 8.00 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 190.8 (t, J = 27.2 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); \textsuperscript{2}H NMR (77 MHz, CHCl\textsubscript{3}) δ 10.15 (s, 1D); HRMS (EI): m/z caled for C\textsubscript{8}H\textsubscript{4}DF\textsubscript{3}O\[(M)^+\]: 175.0355, found: 175.0356.

Methyl 4-formylbenzoate-α-\textit{d}_1 (7o)
Methyl 4-formylbenzoate (0.5 mmol), 5o (10 mol%) and NaHCO\textsubscript{3} (0.5 mmol, 1 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{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); \textsuperscript{2}H NMR (77 MHz, CHCl\textsubscript{3}) δ 10.13 (s, 1D); HRMS (EI): m/z caled for C\textsubscript{7}H\textsubscript{6}DO\textsubscript{3}: 165.0536, found: 165.0538.
4-Formyl-N-isopropylbenzamide-α-d1 (7p)

4-Formyl-N-isopropylbenzamide (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. 7p was obtained as a white solid in 75% yield with 99% D-incorporation. ¹H NMR (400 MHz, DMSO-d₆) 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); ¹³C NMR (100 MHz, DMSO-d₆) 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); ²H NMR (77 MHz, CHCl₃) δ 10.07 (s, 1D); HRMS (EI): m/z caled for C₁₁H₁₂DNO₂ [(M)+]: 192.1009, found: 192.1011.

![3-Methoxybenzaldehyde-α-d1 (7q)](image)

3-Methoxybenzaldehyde-α-d1 (7q)

3-methoxybenzaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv), was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.00 (s, 1D); HRMS (EI): m/z caled for C₆H₅DO₂ [(M)+]: 137.0587, found: 137.0588.

![M-Tolualdehyde-α-d1 (7r)](image)

M-Tolualdehyde-α-d1 (7r)

M-Tolualdehyde (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 0.02H), 7.70-7.67 (m, 2H), 7.46-7.39 (m, 2H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.01 (s, 1D); HRMS (EI): m/z caled for C₇H₇DO [(M)+]: 121.0638, found: 121.0639.

![3-Chlorobenzaldehyde-α-d1 (7s)](image)

3-Chlorobenzaldehyde-α-d1 (7s)

3-Chlorobenzaldehyde (0.5 mmol), 5o (5 mol%) and NaHCO₃ (0.5 mmol, 1 equiv), was dissolved in a mixture of D₂O (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. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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); \(^2H\) NMR (77 MHz, CHCl\(_3\)) \( \delta \) 9.98 (s, 1D); HRMS (EI): m/z calcd for C\(_7\)H\(_5\)DCIO [(M)+]: 141.0092, found: 141.0091.

**3-Bromobenzaldehyde-\( \alpha \)-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\(_2\)O (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. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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); \(^2H\) NMR (77 MHz, CHCl\(_3\)) \( \delta \) 10.02 (s, 1D); HRMS (EI): m/z calcd for C\(_7\)H\(_5\)DBrO [(M)+]: 184.9587, found: 184.9588.

**3-Formylbenzonitrile-\( \alpha \)-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\(_2\)O (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-\( \alpha \)-d\(_1\) was obtained as a yellow solid in 81% yield with 95% D-incorporation.

3-Formylbenzonitrile-\( \alpha \)-d\(_1\) (deuteration 95%, 0.40 mmol), 5o (10 mol%) and KOAc (0.40 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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 again. 7u was obtained as a colorless solid in 59 % yield (for two steps) with 99% D-incorporation. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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); \(^2H\) NMR (77 MHz, CHCl\(_3\)) \( \delta \) 10.06 (s, 1D); HRMS (EI): m/z calcd for C\(_8\)H\(_7\)DNO [(M)+]: 132.0434, found: 132.0435.

**Methyl 3-formylbenzoate-\( \alpha \)-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\(_2\)O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.10 (s, 1D); HRMS (EI): m/z caled for C7H9DO3[(M)+]: 165.0536, found: 165.0538.

3-Nitrobenzaldehyde-a-d1 (7w)
3-Nitrobenzaldehyde (0.5 mmol), 5o (5 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.16 (s, 1D); HRMS (EI): m/z caled for C7H4NDO3[(M)+]: 152.0332, found: 152.0333.

2-Methoxybenzaldehyde-a-d1 (7x)
2-Methoxybenzaldehyde (0.5 mmol), 5o (10 mol%) and K2CO3 (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 189.5 (t, J = 27.5 Hz), 161.9 (s), 136.0 (s), 128.4 (s), 124.7 (s, J = 3.3 Hz), 126.0 (s), 111.6 (s), 55.6 (s); 2H NMR (77 MHz, CHCl3) δ 10.43 (s, 1D); HRMS (EI): m/z caled for C8H7DO2[(M)+]: 137.0587, found: 137.0588.

Salicylaldehyde-a-d1 (7y)
Salicylaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO3 (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) δ 11.04 (s, 1H), 9.89 (s, 0.01H), 7.57-7.50 (m, 2H), 7.04-6.97 (m, 2H); 13C NMR (100 MHz, CDCl3) 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); 2H
N-(2-Formylphenyl)acetamide-1,2-d1,d3 (7z)
N-(2-Formylphenyl)acetamide (0.5 mmol), 5m (10 mol%) and K2CO3 (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 195.2 (t, J = 7.3 Hz, 1H), 132.4 (t, J = 8.5 Hz, 1H), 122.8 (s), 121.3 (t, J = 3.0 Hz), 119.7 (s), 25.4 (s); 2H NMR (77 MHz, CHCl3) δ 9.92 (s, 1D), 2.26-2.20 (m, 0.03D); HRMS (EI): m/z caled for C7H3DO2 [(M)+]: 123.0431, found: 123.0432.

2-Chloorbenzaldehyde-α-d1 (7aa)
2-chloorbenzaldehyde (0.5 mmol), 5o (10 mol%) and K2CO3 (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.52 (s, 1D); HRMS (EI): m/z caled for C7H4DCIO [(M)+]: 141.0092, found: 141.0090.

2-Bromobenzaldehyde-α-d1 (7ab)
2-Bromobenzaldehyde (0.5 mmol), 5o (10 mol%) and K2CO3 (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.40 (s, 1D); HRMS (EI): m/z caled for C7H4DBrO [(M)+]: 184.9587, found: 184.9586.
2,3-Dimethylbenzaldehye-\(\alpha\)-d\(\text{i}\) (7ac)

2,3-Dimethylbenzaldehyde (0.5 mmol), 5o (10 mol%) and K\(_2\)CO\(_3\) (0.5 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \(\delta\) 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); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 192.9 (t, \(J = 26.3\) 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\(_3\)) \(\delta\) 10.29 (s, 1D); HRMS (EI): m/z caled for C\(_{13}\)H\(_{20}\)DO [(M)\(^+\)]: 135.0794, found: 135.0795.

2,4-DiMethylbenzaldehyde-\(\alpha\)-d\(\text{i}\) (7ad)

2,4-DiMethylbenzaldehyde (0.5 mmol), 5m (10 mol%) and K\(_2\)CO\(_3\) (0.5 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \(\delta\) 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); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 10.23 (s, 1D); HRMS (EI): m/z caled for C\(_{13}\)H\(_{20}\)DO [(M)\(^+\)]: 135.0794, found: 135.0795.

2-Chloro-3-fluorobenzaldehyde-\(\alpha\)-d\(\text{i}\) (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\(_2\)O (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\(_3\)) \(\delta\) 10.44 (s, 0.02H), 7.74-7.71 (m, 1H), 7.42-7.33 (m, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 188.2 (td, \(J = 28.1, 3.8\) Hz), 158.4 (d, \(J = 250.8\) Hz), 133.9 (t, \(J = 3.5\) Hz), 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\(_3\)) \(\delta\) 10.49 (s, 1D); HRMS (EI): m/z caled for C\(_7\)H\(_3\)DClFO [(M)\(^+\)]: 158.9997, found: 158.9998.
4-Formyl-3-methoxybenzonitrile-α-d₁ (7af)
4-Formyl-3-methoxybenzonitrile (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 188.0 (t, J = 7.6 Hz, 1H), 136.0493. HRMS (EI): m/z caled for C₉H₆DNO₂ [(M)⁺]: 162.0540, found: 162.0541.

Isophthalaldehyde-1,3-d₁,d₁ (7ag)
Isophthalaldehyde (0.5 mmol), 5o (20 mol%) and KOAc (1 mmol, 2 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 189.8 (t, J = 27 Hz), 135.9 (t, J = 3.7 Hz), 133.6 (s), 129.9 (s), 128.9 (s); ²H NMR (77 MHz, CHCl₃) δ 10.11 (s, 1D); HRMS (EI): m/z caled for C₉H₄D₃O₂ [(M)⁺]: 136.0493, found: 136.0494.

Piperonal-α-d₁ (7ah)
Piperonal (0.5 mmol), 5o (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.82 (s, 1D); HRMS (EI): m/z caled for C₉H₈DO₃ [(M)⁺]: 151.0380, found: 151.0381.

1,4-Benzodioxin-6-carboxaldehyde-α-d₁ (7ai)
1,4-Benzodioxin-6-carboxaldehyde (0.5 mmol), 5o (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 9.84 (s, 1D); HRMS (EI): m/z caled for C$_8$H$_7$DO$_3$ [(M$^+$)]: 165.0536, found: 165.0537.

2,3-(Methylenedioxy)benzaldehyde-$\alpha$-$d_1$ (7aj)
2,3-(Methylenedioxy)benzaldehyde (0.5 mmol), 5o (10 mol%) and K$_2$CO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 186.7 (t, $J = 26.3$ Hz), 153.0 (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$_3$) $\delta$ 9.82 (s, 1D); HRMS (EI): m/z caled for C$_8$H$_7$DO$_3$ [(M$^+$)]: 151.0380, found: 151.0381.

3,4,5-Trimethoxybenzaldehyde-$\alpha$-$d_1$ (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$_2$O (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$_3$) $\delta$ 9.79 (s, 0.01 H), 7.06 (s, 2H), 3.87 (s, 3H), 3.86 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 9.82 (s, 1D); HRMS (EI): m/z caled for C$_{13}$H$_{11}$DO$_4$ [(M$^+$)]: 197.0798, found: 197.0796.

2,2-Dimethyl-4H-benzo[d][1,3]dioxine-6-carbaldehyde-$\alpha$-$d_1$ (7al)
2,2-Dimethyl-4H-benzo[d][1,3]dioxine-6-carbaldehyde (0.5 mmol), 5o (10 mol%), K$_2$CO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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); \(^1\)H NMR (77 MHz, CHCl\(_3\)) \( \delta \) 9.86 (s, 1D); HRMS (EI): m/z caled for C\(_{11}\)H\(_1\)DO\(_3\) [(M)\(^+\)]: 193.0849, found: 193.0850.

![Anthraldehyde-\(\alpha\)-\(d\)](image)

1-Naphthaldehyde-\(\alpha\)-\(d\) \((7\text{am})\)

1-Naphthaldehyde (0.5 mmol), 5o (10 mol\%) and K\(_2\)CO\(_3\) (0.5 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 10.30 (s, 1D); HRMS (EI): m/z caled for C\(_{11}\)H\(_2\)DO [(M)\(^+\)]: 157.0638, found: 157.0638.

![2-Hydroxy-1-naphthaldehyde-\(\alpha\)-\(d\)](image)

2-Hydroxy-1-naphthaldehyde (0.5 mmol), 5o (20 mol\%) and NaHCO\(_3\) (1 mmol, 2 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 10.70 (s, 1D); HRMS (EI): m/z caled for C\(_{11}\)H\(_2\)DO\(_2\) [(M)\(^+\)]: 173.0587, found: 173.0588.

![9-Anthraldehyde-\(\alpha\)-\(d\)](image)

9-Anthraldehyde (0.5 mmol), 5m (10 mol\%) and K\(_2\)CO\(_3\) (0.5 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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).
Thiophene-3-carboxaldehyde-α-d₁ (7ap)
Thiophene-3-carboxaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 184.7 (t, J = 3.5 Hz, 1H), 143.0 (t, J = 3.8 Hz), 136.8 (s), 127.4 (s), 125.4 (s); ²H NMR (77 MHz, CHCl₃) δ 9.94 (s, 1D); HRMS (EI): m/z caled for C₅H₅DOS [(M⁺): 113.0046, found: 113.0047.

5-Methylthiophene-2-carboxaldehyde-α-d₁ (7aq)
5-Methylthiophene-2-carboxaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 182.4 (t, J = 3.6 Hz, 1H), 151.7 (s), 141.9 (t, J = 4.9 Hz), 137.4 (s), 127.1 (s), 16.3 (s); ²H NMR (77 MHz, CHCl₃) δ 9.78 (s, 1D); HRMS (EI): m/z caled for C₆H₅DOS [(M⁺): 127.0202, found: 127.0203.

5-Methyl furfural-α-d₁ (7ar)
5-Methyl furfural (0.5 mmol), 5o (20 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.53 (s, 1D); HRMS (EI): m/z caled for C₆H₅DO₂: 111.0431, found: 111.0432.

4-Methoxy-3-pyridinecarboxaldehyde-α-d₁ (7as)
4-Methoxy-3-pyridinecarboxaldehyde (0.5 mmol), 5o (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 187.4 (t, J = 27.8 Hz), 165.7 (s), 155.1 (s), 145.9 (s), 119.5 (t, J = 3.4 Hz), 106.3 (s), 54.9 (d, J = 1.3 Hz); ²H NMR (77 MHz, CHCl₃) δ 10.42 (s, 1D); HRMS (EI): m/z calcd for C₇H₇NO₂ [(M⁺)⁺]: 138.0540, found: 138.0541.

2,6-Dichloro-3-pyridinecarbaldehyde-α-d₁ (7at)

2,6-Dichloro-3-pyridinecarbaldehyde (0.5 mmol), 5o (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.41 (s, 1D); HRMS (EI): m/z calcd for C₉H₇Cl₂NO [(M⁺)⁺]: 175.9654, found: 175.9656.

Benzothiophene-2-carboxaldehyde-1,2-d₁,d₁ (7au)

Benzothiophene-2-carboxaldehyde (0.5 mmol), 5o (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.10 (s, 1D), 8.03 (s, 0.03D); HRMS (EI): m/z calcd for C₀H₂DOS [(M⁺)⁺]: 163.0202, found: 163.0203.

Tosyl-1H-indole-5-carboxaldehyde-α-d₁ (7av)

Tosyl-1H-indole-5-carboxaldehyde (0.5 mmol), 5m (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz,
CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.01 (s, 1D); HRMS (EI): m/z caled for C₁₆H₁₂DNO₃S [(M)+]: 300.0679, found: 300.0681.

Tosyl-1H-indole-3-carboxaldehyde-α-d₁ (7aw)
Tosyl-1H-indole-3-carboxaldehyde (0.5 mmol), 5m (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.09 (s, 1D); HRMS (EI): m/z caled for C₁₆H₁₂DNO₃S [(M)+]: 300.0679, found: 300.0681.

3-Benzofurancarboxaldehyde-α-d₁(7ax)
3-Benzofurancarboxaldehyde (0.5 mmol), 5m (10 mol%) and K₂CO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.20 (s, 1D); HRMS (EI): m/z caled for C₉H₅DO₂ [(M)+]: 147.0431, found: 147.0432.

4-Quinoline carboxaldehyde-α-d₁(7ay)
4-Quinoline carboxaldehyde (0.5 mmol), 5o (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.50 (s, 1D); HRMS (EI): m/z caled for C10H6DNO [(M)+]: 158.0590, found: 158.0591.

2-Chloroquinoline-3-carboxaldehyde-α-d1 (7az)
2-Chloroquinoline-3-carboxaldehyde (0.5 mmol), 5o (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.58 (s, 1D); HRMS (EI): m/z caled for C10H5DCINO [(M)+]: 192.0201, found: 192.0202.

6-Methoxy2-Chloroquinoline-3-carboxaldehyde-α-d1 (7ba)
6-Methoxy2-Chloroquinoline-3-carboxaldehyde (0.5 mmol), 5o (10 mol%) and KOAc (0.5 mmol, 1 equiv) was dissolved in a mixture of D2O (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-chloroquinoline-3-carboxaldehyde-α-d1 was obtained as a white solid in 93% yield with 94% D-incorporation.
6-Methoxy-2-Chloroquinoline-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 D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 10.56 (s, 1D); HRMS (EI): m/z caled for C11H5DCINO2 [(M)+]: 222.0306, found: 222.0308.

Isoquinoline-4-carboxaldehyde-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 D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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), 124.7 (t, J = 3.5 Hz), 124.3 (s); ²H NMR (77 MHz, CHCl₃) δ 10.30 (s, 1D); HRMS (EI): m/z caled for C₁₀H₈DNO [(M⁺): 158.0590, found: 158.0591.

\[ \text{N-Ethyl-3-carbazolecarboxaldehyde-}α-d₁ (7bc) \]

N-Ethyl-3-carbazolecarboxaldehyde (0.5 mmol), 5o (30 mol%) and K₂CO₃ (1 mmol, 2 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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), 108.7 (s), 37.9 (s), 13.8 (s); ²H NMR (77 MHz, CHCl₃) δ 10.10 (s, 1D); HRMS (EI): m/z caled for C₁₅H₁₂DNO [(M⁺): 224.1060, found: 224.1062.

\[ \text{N-(2-(Diethylamino)ethyl)-5-formyl-2,4-dimethyl-1H-pyrrole-3-carboxamide-}α-d₁ (7bd) \]

N-(2-(Diethylamino)ethyl)-5-formyl-2,4-dimethyl-1H-pyrrole-3-carboxamide (0.5 mmol), 5m (30 mol%) and K₂CO₃ (1.5 mmol, 3 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, DMSO-d₆) 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); ²H NMR (77 MHz, CHCl₃) δ 9.49 (s, 1D); HRMS (EI): m/z caled for C₁₄H₂₂D₃N₃O₂ [(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 K₂CO₃ (0.5 mmol, 2 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.94 (s, 1D); HRMS (ESI): m/z caled for C₂₂H₂₃DΝO₅ [(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 K₂CO₃ (0.1 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.88 (s, 1D); HRMS (ESI): m/z caled for C₂₃H₂₉DNO₃ [(M+H)+]: 369.2288, found: 369.2289.

2-(2-(4-((4-Chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethoxy)ethoxy)benzaldehyde-α-d₁ (7bg)
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 D₂O (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. 7bg was obtained as a yellow oil in 52% yield with 96% D-incorporation. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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), 128.5 (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); ²H NMR (77 MHz, CHCl₃) δ 10.50 (s, 1D); HRMS (ESI): m/z caled for C₂₅H₂₃DCIN₂O₃ [(M+H)⁺]: 480.2164, found: 480.2162.

3-Formyl rifamycin-α-d₁ (7bh)
3-Formyl rifamycin (0.05 mmol), 5l (20 mol%) and KOAc (0.1 mmol, 2 equiv) was dissolved in a mixture of D₂O (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. 7bh was obtained as a red solid in 60% yield with 97% D-incorporation. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 10.67 (s, 1D); HRMS (ESI): m/z caled for C₃₈H₄₆DN₃NaO₁₃ [(M+Na)⁺]: 749.3008, found:749.3009.
2’-(2H-Tetrazol-5-yl)biphenyl-4-yl)methyl)-2-butyl-4-chloro-1H-imidazole-5-carbaldehyde de-o-d1 (7bi)

2’-(2H-Tetrazol-5-yl)biphenyl-4-yl)methyl)-2-butyl-4-chloro-1H-imidazole-5-carbaldehyde (0.1 mmol), 5i (20 mol%) and KOAc (0.2 mmol, 2 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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, 0.05H), 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); 13C NMR (100 MHz, CDCl3) 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), 48.0 (s), 29.2 (s), 26.4 (s), 22.3 (s), 13.7 (s); 2H NMR (77 MHz, CHCl3) δ 9.64 (s, 1D); HRMS (ESI): m/z caled for C22H21DClN6O [(M+H)⁺]: 422.1606, found: 422.1605.

(E)-Cinnamaldehyde-1,2-d1,d2 (10a)

(E)-Cinnamaldehyde (0.25 mmol), 5p (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 193.5 (t, J = 26.3), 152.8 (s), 152.8 (s), 134.0 (s), 131.3 (s), 129.1 (s), 128.5 (s), 137.2 (s); 2H NMR (77 MHz, CHCl3) δ 9.75 (s, 1D), 6.79 (s, 0.05D); HRMS (ESI): m/z caled for C35H35DO [(M+)⁺]: 133.0638, found: 133.0639.

(E)-4-Acetoxy-3-methoxycinnamaldehyde-1,2-d1,d2 (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 D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 193.2 (t, J = 26.2 Hz), 168.7 (s), 151.9 (s), 151.6 (s), 143.2 (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); 2H NMR (77 MHz, CHCl3) δ 9.73 (s, 1D), 6.72 (s, 0.02D); HRMS (ESI): m/z caled for C12H11D1O4 [(M+)⁺]: 221.0798, found: 221.0780.
(E)-4-Chlorocinnamaldehyde-α-d₁ (10c)

(E)-4-Chlorocinnamaldehyde (0.25 mmol), 5p (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D₂O (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 oil in 40% yield with 97% D-incorporation. 1H NMR (400 MHz, CDCl₃) 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); 13C NMR (100 MHz, CDCl₃) 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); 1H NMR (77 MHz, CHCl₃) δ 9.75 (s, 1D); HRMS (EI): m/z caled for C₉H₆DCIO [(M)+]: 167.0248, found: 167.0246.

(E)-4-Bromocinnamaldehyde-1,2-d₁,d₂ (10d)

(E)-4-Bromocinnamaldehyde (0.25 mmol), 5p (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. 1H NMR (400 MHz, CDCl₃) 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); 13C NMR (100 MHz, CDCl₃) 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); 1H NMR (77 MHz, CHCl₃) δ 9.76 (s, 1D), 6.76 (s, 0.01D); HRMS (EI): m/z caled for C₉H₆DBrO [(M)+]: 210.9743, found: 210.9744.

(E)-4-Methoxycinnamaldehyde-1,2-d₁,d₂ (10e)

(E)-4-Methoxycinnamaldehyde (0.25 mmol), 5p (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. 1H NMR (400 MHz, CDCl₃) 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); 13C NMR (100 MHz, CDCl₃) 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); 1H NMR (77 MHz, CHCl₃) δ 9.68 (s, 1D), 6.65 (s, 0.02D); HRMS (EI): m/z caled for C₁₀H₈DO₂ [(M)+]: 163.0744, found: 163.0743.
(E)-4-Methylcinnamaldehyde-α-d1 (10f)
(E)-4-Methylcinnamaldehyde (0.25 mmol), 5p (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 9.72 (s, 1D), 6.72 (s, 0.03D); HRMS (EI): m/z calcd for C10H9DO [(M)+]: 147.0794, found: 147.0795.

alpha-Methylcinnamaldehyde-α-d1 (10g)
alpha-Methylcinnamaldehyde (0.25 mmol), 5l (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 9.55 (s, 1D); HRMS (EI): m/z calcd for C10H9DO [(M)+]: 147.0794, found: 147.0795.

(E)-2-Methyl-3-(3-nitrophenyl)acrylaldehyde-α-d1 (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 D2O (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. 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 2H NMR (77 MHz, CHCl3) δ 9.67 (s, 1D); HRMS (EI): m/z calcd for C10H9DNO3 [(M)+]: 192.0645, found: 192.0646.

(E)-4-Methoxy-2-methylcinnamaldehyde-α-d1 (10i)
(E)-4-Methoxy-2-methylcinnamaldehyde (0.25 mmol), 5l (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D2O (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL).
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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 9.57 (s, 1D); HRMS (EI): m/z caled for C$_{11}$H$_{11}$DO [(M)$^+$]: 177.0900, found: 177.0901.

(E)-2-Methyl-3-(naphthal-2-yl)acrylaldehyde-$\alpha$-d$_1$ (**10j**)

(E)-2-Methyl-3-(naphthal-2-yl)acrylaldehyde (0.25 mmol), **5l** (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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), 11.1 (s); $^2$H NMR (77 MHz, CHCl$_3$) $\delta$ 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-$\alpha$-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$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 9.48 (s, 1D); HRMS (EI): m/z caled for C$_8$H$_7$DO [(M)$^+$]: 137.0587, found: 137.0589.

$\alpha$-Amylcinnamaldehyde-$\alpha$-d$_1$ (**10l**)

$\alpha$-Amylcinnamaldehyde (0.25 mmol), **5l** (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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 133.4 (s), 130.4 (s), 129.2 (s), 129.0 (s), 52.9 (d, $J = 6.8$ Hz, 3H), 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 calcd for C$_{15}$H$_{15}$DO [(M)$^+$]: 217.1577, found: 217.1578.

(E)-Dimethyl 2-(3-oxo-1-phenylprop-1-en-2-yl)malonate-$\alpha$-$d_1$ (10n)

(E)-Dimethyl 2-(3-oxo-1-phenylprop-1-en-2-yl)malonate (0.25 mmol), 5l (20 mol%), and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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 calcd for C$_{14}$H$_{13}$DO$_5$ [(M)$^+$]: 263.0904, found: 263.0903.

5-Methyl-2-phenyl-2-hexenal-$\alpha$-$d_1$ (10o)

5-Methyl-2-phenyl-2-hexenal (0.25 mmol), 5l (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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), 6.62 (d, $J = 1.7$ Hz, 1H), 6.59-6.52 (m, 2H), 6.01-5.89 (m, 1H), 4.71 (s, 1H), 3.85 (s, 1H), 3.13-3.05 (m, 2H), 2.34-2.22 (m, 4H), 1.98-1.88 (m, 2H), 1.54-1.43 (m, 2H), 1.39-1.30 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H).
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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 9.67 (s, 1D); HRMS (EI): m/z caled for C\(_{13}\)H\(_{15}\)DO [(M)\(^+\)]: 189.1264, found: 189.1265.

**(-)-Perillaldehyde-\(\alpha\)-\(d\)_\(_1\) (10p)**

(-)-Perillaldehyde (0.25 mmol), 51 (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 9.42 (s, 1D); HRMS (EI): m/z caled for C\(_{10}\)H\(_{13}\)DO [(M)\(^+\)]: 151.1107, found: 151.1109.

**\((IR)\)-Myrtenal-\(\alpha\)-\(d\)_\(_1\) (10q)**

\((IR)\)-Myrtenal (0.25 mmol), 51 (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 9.41 (s, 1D); HRMS (EI): m/z caled for C\(_{10}\)H\(_{13}\)DO [(M)\(^+\)]: 151.1107, found: 151.1109.

**2-Benzylacrylaldehyde-\(\alpha\)-\(d\)_\(_1\) (10r)**

2-Benzylacrylaldehyde (0.25 mmol), 51 (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D\(_2\)O (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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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$_3$) $\delta$ 9.65 (s, 1D); HRMS (EI): m/z caled for C$_{10}$H$_9$DO [(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), 5I (10 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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), 5I (20 mol%) and KOAc (0.25 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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 dissolved in a mixture of D$_2$O (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 obtained as a colorless oil in 48% yield with 98% D-incorporation at position 1 and 94% D-incorporation at position 2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.75 (s, 0.02H), 7.38 (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); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 9.74 (s, 1D), 3.62 (s, 2D); HRMS (EI): m/z caled for C$_8$H$_8$D$_2$O [(M)+]: 123.0763, found: 123.0764.
3-Phenylpropionaldehyde-1,2,3-d₁,d₂,d₂ (12b)
3-Phenylpropionaldehyde (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.78 (s, 1D), 2.86 (s, 0.35D), 2.67 (s, 0.82D); HRMS (EI): m/z caled for C₉H₆O [(M)+]: 135.0794, Found: 135.0799; C₉H₈D₂O [(M)+]: 136.0857, found: 136.0858; C₉H₈D₂O [(M)+]: 139.1045, found: 139.1049.

Benzenebutanal-1,2,3-d₁,d₂,d₂ (12c)
Benzenebutanal (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.80 (s, 1D), 2.43 (s, 1.92D), 1.94 (s, 0.37D); HRMS (EI): m/z caled for C₁₀H₈D₃O [(M)+]: 151.1076, Found: 151.1090; C₁₀H₈D₃O [(M)+]: 152.1139, Found: 152.1140; C₁₀H₇D₂O [(M)+]: 153.1202, found: 153.1190.

3-Thienylpropionaldehyde-1,2-d₁,d₂ (12d)
3-Thienylpropionaldehyde (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H
NMR (77 MHz, CHCl$_3$) $\delta$ 9.87 (s, 1D), 3.15 (s, 0.08D), 2.82 (s, 0.38D); HRMS (EI): m/z caled for C$_{12}$H$_9$D$_5$O$_2$: 141.0359, found: 141.0360.

3-(1-Methyl-1H-3-indolyl)propanal-1,2,3-d$_1$,$d$$_2$,$d$$_3$ (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$_2$O (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL). Then the reaction mixture was dissolved in a mixture of D$_2$O (1 mL) and DCM (0.25 mL) in a reaction vessel (5 mL) and NaHCO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 9.88 (s, 1D), 3.07 (s, 1.78D), 2.80 (s, 1.73D); HRMS (EI): m/z caled for C$_{12}$H$_9$D$_5$NO [(M)$^+$]: 192.1311, found: 192.1310.

3-(5-Methyl-2-furanyl)butanal-1,2,3,4-d$_1$,$d$$_2$,$d$$_3$,$d$$_4$ (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$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_9$H$_9$D$_3$O$_2$: 155.1026, found: 155.1028.

Octanal-1,2,3-d$_1$,$d$$_2$,$d$$_3$ (12g)
Octanal (0.5 mmol), 5q (10 mol%) and NaHCO$_3$ (0.5 mmol, 1 equiv) was dissolved in a mixture of D$_2$O (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. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta 9.74 \) (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\textsubscript{3}) \( \delta 202.9 \) (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); \( ^2H \) NMR (77 MHz, CHCl\textsubscript{3}) \( \delta 9.74 \) (s, 1D), 2.34 (s, 2.00D), 1.54 (s, 0.34D); HRMS (EI): m/z caled for C\textsubscript{8}H\textsubscript{13}D\textsubscript{3}O [(M)+]: 131.1389, found: 131.1385.

**6-Heptynal-1,2,3,4-d\textsubscript{1},d\textsubscript{2},d\textsubscript{2},d\textsubscript{1} (12h)**

6-Heptynal (0.5 mmol), 5q (10 mol%), NaHCO\textsubscript{3} (0.5 mmol, 1 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta 9.77 \) (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\textsubscript{3}) \( \delta 202.1 \) (t, \( J = 23.5 \) Hz), 83.8 (s), 68.8 (s), 27.7 (s), 22.7 (s), 20.9 (s), 18.2 (s); \( ^2H \) NMR (77 MHz, CHCl\textsubscript{3}) \( \delta 9.76 \) (s, 1D), 2.39 (s, 2.00D), 1.91 (s, 0.12D), 1.69 (s, 0.29D); HRMS (EI): m/z caled for C\textsubscript{7}H\textsubscript{13}DO [(M)+]: 111.0794, Found: 111.0793; C\textsubscript{7}H\textsubscript{13}D\textsubscript{3}O [(M)+]: 113.0920, found: 113.0922.

**Cis-6-Nonenal-1,2-d\textsubscript{1},d\textsubscript{2} (12i)**

Cis-6-Nonenal (0.5 mmol), 5q (10 mol%) and NaHCO\textsubscript{3} (0.5 mmol, 1 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta 9.75 \) (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\textsubscript{3}) \( \delta 202.6 \) (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); \( ^2H \) NMR (77 MHz, CHCl\textsubscript{3}) \( \delta 9.73 \) (s, 1D), 2.33 (s, 1.62D), 1.55 (s, 0.09D); HRMS (EI): m/z caled for C\textsubscript{9}H\textsubscript{14}D\textsubscript{2}O [(M)+]: 142.1327, Found: 142.1322; C\textsubscript{9}H\textsubscript{13}D\textsubscript{3}O [(M)+]: 143.1389, found: 143.1393.

**Citronellal-1,2-d\textsubscript{1},d\textsubscript{2} (12j)**

Citronellal (0.5 mmol), 5q (10 mol%) and NaHCO\textsubscript{3} (0.5 mmol, 1 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) δ 202.8 (t, J = 31.9 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); ²H NMR (77 MHz, CHCl₃) δ 9.74 (s, 1D), 2.33 (s, 0.54D), 2.15 (s, 0.55D); HRMS (EI): m/z calced for C₁₅H₁₇DO [(M)⁺]: 210.1084. Found: 210.1084.

**Benzyl-4-oxobutanoate-1,2-d₁,d₂ (12k)**
Benzyl-4-oxobutanoate (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv), was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) δ 201.4-200.7 (m), 156.4 (s), 136.4 (s), 128.3 (s), 128.2 (s), 128.1 (s), 66.8 (s), 43.9 (s), 34.4 (s), 29.7 (s); ²H NMR (77 MHz, CHCl₃) δ 9.84 (s, 1D), 2.72 (s, 1.91D), 1.55 (s, 0.09D); HRMS (EI): m/z calced for C₁₅H₁₆D₂O [(M)⁺]: 210.1084, found: 210.1085.

**2-Phenylpropionaldehyde-1,2-d₁,d₁ (12l)**
2-Phenylpropionaldehyde (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.71 (s, 1D), 3.61 (s, 0.93D); HRMS (EI): m/z calced for C₉H₈D₂O [(M)⁺]: 136.0857, found: 136.0856.

**2-Methyl-3-phenylpropionaldehyde-1,2-d₁,d₁ (12m)**
2-Methyl-3-phenylpropionaldehyde (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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 calcd for C$_{10}$H$_{10}$D$_2$O [(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$_2$O (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 calcd for C$_{12}$H$_{10}$D$_4$O$_2$ [(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$_2$O (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 calcd for C$_9$H$_{15}$DO [(M$^+$)]: 141.1264, found: 141.1243.

**Cyclohexanaldehyde-1,2-d$_1$,d$_1$ (12p)**
Cyclohexanaldehyde (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 204.7 (t, J = 25.8 Hz), 49.8 (t, J = 3.3 Hz), 25.9 (s), 25.9 (s), 25.0 (s); ²H NMR (77 MHz, CHCl₃) δ 9.67 (s, 0D), 202.7 (t, J = 10.7 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); ²H NMR (77 MHz, CHCl₃) δ 9.69 (s, 1D), 2.39 (s, 0.90D); HRMS (EI): m/z caled for C₁₁H₁₃D₂NO₃ [(M)+]: 215.1490, found: 215.1489.

tert-Butyl N-(1-benzyl-2-oxoethyl)carbamate-1,2,3-d₁,d₁,d₂ (12r)

tert-Butyl N-(1-benzyl-2-oxoethyl)carbamate (0.5 mmol), 5q (10 mol%) and NaHCO₃ (0.5 mmol, 1 equiv) was dissolved in a mixture of D₂O (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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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); ²H NMR (77 MHz, CHCl₃) δ 9.66 (s, 1D), 4.40 (s, 0.83D), 3.09 (s, 0.04D); HRMS (EI): m/z caled for C₁₃H₁₇DNO₂ [(M-CDO)⁺]: 221.1400, found: 221.1401.
2-(1-(4-Chlorobenzoyl)-5-methoxy-2-Methyl-1H-indol-3-yl)acetaldehyde-\textit{I}, 2-\textit{d}_{1}, 2-\textit{d}_{2} (12s)

2-(1-(4-Chlorobenzoyl)-5-methoxy-2-Methyl-1H-indol-3-yl)acetaldehyde \textit{11s} (0.1 mmol), \textit{5q} (20 mol\%) and AcOK (0.1 mmol, 1 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. 12\textit{s} was obtained as a tan solid in 99% D-incorporation at position 1 and 93% D-incorporation at position 2. \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 9.70 (s, 0.01H), 7.67 (d, \textit{J} = 8.5 Hz, 2H), 7.47 (d, \textit{J} = 8.4 Hz, 2H), 6.87-6.84 (m, 2H), 6.69 (dd, \textit{J} = 8.9, 2.5 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 0.14H), 2.38 (s, 3H); \textit{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 197.8 (t, \textit{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); \textit{2}H NMR (77 MHz, CHCl\textsubscript{3}) δ 9.72 (s, 1D), 3.68 (s, 1.78D); HRMS (ESI): m/z caled for C\textsubscript{19}H\textsubscript{14}D\textsubscript{3}ClNO\textsubscript{3} [(M+H)+]: 345.1085, found: 345.1089.

2-(1,7-Diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetaldehyde-\textit{I}, 2-\textit{d}_{1}, 2-\textit{d}_{2} (12t)

2-(1,8-Diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetaldehyde \textit{11t} (0.1 mmol), \textit{5q} (20 mol\%) and AcOK (0.2 mmol, 2 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. 12\textit{t} was obtained liquid in 52% yield with 99% D-incorporation at position 1 and 86% D-incorporation at position 2. \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 9.76 (s, 0.01H), 8.37 (s,1H), 7.37 (d, \textit{J} = 7.7 Hz, 1H), 7.08 (t, \textit{J} = 7.5 Hz, 1H), 7.03 (d, \textit{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, \textit{J} = 7.6 Hz, 3H), 0.87 (t, \textit{J} = 7.4 Hz, 3H); \textit{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 202.5 (t, \textit{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, \textit{J} = 14.7 Hz), 31.2 (s), 24.1 (s), 22.4 (s), 13.9 (s), 7.8 (s); \textit{2}H NMR (77 MHz, CHCl\textsubscript{3}) δ 9.79 (s, 1D), 3.03 (s, 1.61D); HRMS (ESI): m/z caled for C\textsubscript{17}H\textsubscript{18}D\textsubscript{3}NO\textsubscript{2} [(M+H)+]: 275.1839, found: 275.1841.

2,3,5-Tri-O-benzyl-\alpha,\beta-D-ribofuranose-\textit{I}-\textit{d}_{1} (12u)

2,3,5-tri-O-benzyl-\alpha,\beta-D-ribofuranose \textit{11u} (0.1 mmol), \textit{5af} (20 mol\%), AcOK (0.1 mmol, 1 equiv) and CD\textsubscript{3}COOD (0.4 mmol, 4 equiv) was dissolved in a mixture of D\textsubscript{2}O (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. 12\textit{u} was obtained as a yellow oil in 55% yield with 95%
D-incorporation. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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: $\delta$ 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), 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: $\delta$ 137.8 (s), 137.7 (s), 137.3 (s), 128.5 (s), 128.5 (s), 128.4 (s), 128.0 (s), 128.0 (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$_3$) $\delta$ 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$_3$COOD (0.8 mmol, 8 equiv) was dissolved in a mixture of D$_2$O (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 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$_3$COOD (0.67 mmol, 8 equiv) was dissolved in a mixture of D$_2$O (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$_3$) $\delta$ 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: $\delta$ 138.5 (s), 138.4 (s), 138.0 (s), 137.70 (s), 128.5 (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), 127.6 (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: $\delta$ 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), 127.6 (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$_3$) $\delta$ 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), S_1 (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 (deuterium 90%, 0.08 mmol), S_1 (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. ^1H 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); ^13C 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); ^2H 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_{3}NO_{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). ^1H 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); ^13C 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_{6}N_{3}O [(M-H)^+]: 503.0068, found: 503.0063.

Following the modified procedure of reported literature, a flame-dried round bottom flask was charged with 6-nitro-4,4a,9,9a-tetrahydroindenol[2,1-b][1,4]oxazin-3(2H) –one (1.0 g, 4.27 mmol) and CH_{2}Cl_{2} (21 mL). Trimethyloxonium tetrafluoroborate (769 mg, 4.27 mmol) was added, and the reaction 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 triethyl orthoformate (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}BrF_{6}N_{3}O3 [(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).
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 NaHCO₃ solution (2 × 30 mL), and dried over anhydrous MgSO₄. 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%). 1H NMR (400 MHz, CDCl₃) 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), 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); 13C NMR (100 MHz, CDCl₃) 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).

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). 1H NMR (400 MHz, CDCl₃) 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); 13C NMR (100 MHz, CDCl₃) 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-carboxaldehyde (6bi): Losartan (1.7 g, 4 mmol) and IBX (2-idoxybenzoic acid, 1.345 g, 4.8 mmol) were added in DMSO (20 mL) and stirred at room temperature for 6 h. CH₂Cl₂ (120 mL) was added and the solution was washed with water (3 × 120 mL), saturated NaHCO₃ solution (3 × 120 mL), and brine (1 × 120 mL). The solvent was removed after drying (Na₂SO₄) in vacuo to yield the product 6bi (888 mg, 53%). ¹H NMR (400 MHz, CDCl₃) 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 indomethacin (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. ¹H NMR (400 MHz, CDCl₃) 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), ¹³C NMR (100 MHz, CDCl₃) 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, 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 LiAlH₄ (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 filtrate was extracted with EtOAc. The combined organic layers were washed with brine and dried over anhydrous MgSO₄. 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, to a stirred solution of 11t-a (1.14 g, 4.17 mmol) in CH₃CN (5.38 mL), DMSO (5.38 mL) and Et₃N (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% aqueous HCl solution, saturated aqueous NaHCO₃ solution and brine, and dried over anhydrous MgSO₄. 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%).

**5. Synthetic applications**

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

Compound 12l (0.5 mmol, 68 mg, D¹ = 98%; D² = 97%) and organocatalyst 13 (16.3 mg, 10 mol%) was dissolved in a mixture H₂O (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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (150 MHz, CDCl₃) 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 recovered D$_2$O (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$_2$O (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 times. 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$_2$O (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 times. 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, 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$_2$Cl$_2$ (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-d₂-ol (15a): $^1$H NMR (400 MHz, CDCl₃) 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, CDCl₃) 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-d₂-ol (15b): $^1$H NMR (400 MHz, CDCl₃) δ 7.47 (dt, $J = 8.3$ Hz, 2H), 7.21 (dt, $J = 8.4$ Hz, 2H), 4.60 (s, 0.04H), 2.06 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 139.6 (s), 131.6 (s), 128.7 (s), 121.5 (s), 63.8 (quint, $J = 21.8$ Hz).

Benzenemethan-d₂-ol (15e): $^1$H NMR (400 MHz, CDCl₃) δ 7.41-7.27 (m, 5H), 4.60-4.42 (m, 0.03H), 2.27 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 140.8 (s), 128.6 (s), 127.1 (s), 64.6 (quint, $J = 21.8$ Hz).

3-Nitrobenzenemethan-d₂-ol (15X): $^1$H NMR (400 MHz, CDCl₃) 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, CDCl₃) 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-a,a-d₂-ol (15an): $^1$H NMR (400 MHz, CDCl₃) 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), 4.21 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) 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-d₂-ol (15aq): $^1$H NMR (400 MHz, CDCl₃) 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, CDCl₃) 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,\textsuperscript{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%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta 8.10 (t, J = 1.9 \text{ Hz}, 1H), 8.01-7.97 (m, 1H), 7.65-7.60 (m, 1H), 7.36 (t, J = 7.9 \text{ Hz}, 1H), 6.10 (s, 1H), 5.08 (s), 4.12-4.04 (m, 2H), 3.63 (s, 3H), 2.35 (d, J = 2.3 \text{ Hz}, 6H), 1.22 (t, J = 7.1 \text{ Hz}, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta 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 \text{ Hz}), 19.6 (s), 19.5 (s), 14.3 (s); HRMS (ESI): m/z caleed for C\textsubscript{18}H\textsubscript{20}DN\textsubscript{2}O\textsubscript{6} [(M+H)\textsuperscript{+}]: 362.1462, found: 362.1461.

### 5.4.2 Procedure for the synthesis of salbutamol

![Chemical structure of salbutamol with reaction steps]

**Step 1:** According to the literature method,\textsuperscript{31} a solution of trimethylsulphonium bromide (518 mg, 1.1 equiv) and KOH powder (219 mg, 1.3 equiv) in CH\textsubscript{3}CN (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,\textsuperscript{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 1 h, 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,\textsuperscript{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.) \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}) \( \delta 7.32 (d, J = 2.2 \text{ Hz}, 1H), 7.06 (dd, J = 8.2, 2.2 \text{ Hz}, 1H), 6.79
(d, \( J = 8.2 \) Hz, 1H), 4.46 (s, 2H), 4.28 (s, 0.02 H), 2.84 (dd, \( J = 12.2 \) Hz, 2H), 1.27 (s, 9H); \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)) \( \delta \) 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

![Diagram of cloperastine synthesis]

**Step 1:** According to the literature method,\(^{32}\) a solution of deuterated 4-chlorobenzaldehyde 71 (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\(_2\)Cl\(_2\) (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\(_2\)O and extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), 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\(_3\)) \( \delta \) 7.31-7.22 (m, 9H), 5.34 (s, 0.02 H), 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\(_3\)) \( \delta \) 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

![Diagram of tadalafil synthesis]

**Step 1:** According to the literature method,\(^{34}\) D-tryptophan methyl ester hydrochloride 19 (400 mg, 1.57 mmol) was suspended in CH\(_3\)CN (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$_3$CN. 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, 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, a solution of 21 (214 mg, 0.5 mmol) and 25-30% CH$_3$NH$_2$ (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$_3$O$_4$ [(M+H)$^+$]: 391.1517, found: 391.1521.

### 5.4.5 Procedure for the synthesis of diltiazem hydrochloride

![Diagram of the synthesis of diltiazem hydrochloride]

**Step 1:** According to the literature method, 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 stirred 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, a solution of 22 (520 mg, 2.5 mmol) and 28% aqueous FeCl₃·6H₂O (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. H₂O (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, 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 H₂O (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 (CH₂Cl₂:MeOH = 98:2) to afford 366 mg of yellow oil (yield: 70%).

**Step 4:** According to the literature method, a solution of 24 (0.317 mmol), Ac₂O (1 mmol), Et₃N (2 mmol) and DMAP (0.03 mmol) in CH₂Cl₂ (5 mL) was heated at reflux under N₂ 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 CH₂Cl₂ (10 mL). The combined organic layers were washed with 5% NH₄OH (5 mL) solution, dried over Na₂SO₄ 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). ¹H NMR (400 MHz, CD₃OD) 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); ¹³C NMR (100 MHz, CD₃OD) 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 C₂₂H₂₆DN₂O₄S [(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 7e
$^1$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
$^{1}\text{H NMR of deuterated aldehyde 7g}$

$^{2}\text{H NMR of deuterated aldehyde 7g}$
$^{13}$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
$^{13}\text{C NMR of deuterated aldehyde 7i}$
$^1$H NMR of deuterated aldehyde $7j$

$^2$H NMR of deuterated aldehyde $7j$ (The peak at $\delta$ 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 71

$^2$H NMR of deuterated aldehyde 71
$^{13}$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
$^1\text{H NMR of deuterated aldehyde 7t}$

$^2\text{H NMR of deuterated aldehyde 7t}$
$^{13}$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 $7w$

![Deuterated Aldehyde 7w H NMR](image)

$^2$H NMR of deuterated aldehyde $7w$

![Deuterated Aldehyde 7w 2H NMR](image)
$^{13}$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

![NMR Spectroscopy Image]
$^1$H NMR of deuterated aldehyde 7aa

$^2$H NMR of deuterated aldehyde 7aa
$^{13}$C NMR of deuterated aldehyde 7aa

![Carbon-13 NMR spectrum of deuterated aldehyde 7aa](image-url)
$^1$H NMR of deuterated aldehyde 7ab

$^2$H NMR of deuterated aldehyde 7ab
$^{13}$C NMR of deuterated aldehyde 7ab
\(^1\text{H NMR of deuterated aldehyde 7ac}\)

\(^2\text{H NMR of deuterated aldehyde 7ac}\)
$^{13}$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 $7\text{ah}$

$^2$H NMR of deuterated aldehyde $7\text{ah}$
$^{13}$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 $7_{aj}$
$^1$H NMR of deuterated aldehyde 7ak

$^2$H NMR of deuterated aldehyde 7ak
$^{13}$C NMR of deuterated aldehyde 7ak

![NMR Spectrum Image]

Chemical shifts: 191.00, 131.60, 143.48, 153.58, 156.60, 177.49, 177.17, 145.85, 120.81, 66.21
$^1$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 \textbf{7aq}

\[\text{Me}_n\text{CDO}\]

\(^2\)H NMR of deuterated aldehyde \textbf{7aq}

\[\text{Me}_n\text{CDO}\]
$^{13}$C NMR of deuterated aldehyde 7aq
$^1\text{H NMR}$ of deuterated aldehyde 7ar

$^2\text{H NMR}$ 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
^1H NMR of deuterated aldehyde 7bc

^2H NMR of deuterated aldehyde 7bc
$^{13}$C NMR of deuterated aldehyde 7be
$^1$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

13C 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 $6bh$

![H NMR of 3-formyl rifamycin 6bh](image)

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

![H NMR of deuterated 3-formyl rifamycin 7bh](image)
$^2$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 $6_{bh}$ and deuterated 3-formyl rifamycin $7_{bh}$

$6_{bh}$: m/z caled for $\text{C}_{38}\text{H}_{46}\text{NNa}_2\text{O}_{13}$ [(M-H+2Na)$^+$]: 770.3, Found: 770.4

$7_{bh}$: m/z caled for $\text{C}_{38}\text{H}_{45}\text{DNNa}_2\text{O}_{13}$ [(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
\[^{13}\text{C} \text{NMR of deuterated aldehyde 10i}\]
$^1$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
¹H NMR of deuterated aldehyde 10m

²H 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
$^1\text{H NMR of aldehyde } {\textbf{11a}}$

$^1\text{H NMR of deuterated aldehyde } {\textbf{12a}}$
$^2$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
$^2\text{H NMR of deuterated aldehyde } 12\text{b}$

$^{13}\text{C NMR of deuterated aldehyde } 12\text{b}$
$^1$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

13C 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
$^1\text{H NMR of aldehyde 11k}$

$^1\text{H NMR of deuterated aldehyde 12k}$
$^2$H NMR of deuterated aldehyde 12k

![H NMR spectrum of deuterated aldehyde 12k](image-url)
$^{13}$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 $\text{I10}$

$^{13}$C NMR of deuterated aldehyde $\text{I20}$
$^1$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**

![Aldehyde 11r NMR spectrum](image)

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

![Deuterated aldehyde 12r NMR spectrum](image)
$^2$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
\textsuperscript{13}C NMR of aldehyde 11t

\textsuperscript{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
\textbf{13C NMR of glucopyranose 11v}

\textbf{13C 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