Supporting Information

Site-Selective Deuteration at α-Position of Enals by an Amine and Bis(phenylsulfonyl)methane Co-catalyzed H/D Exchange Reaction

Pengfei Qian, Shilei Zhang,* Fan Luo, Jiarui Wang, Xinyu Zhang, Xuejun Liu, Xiaodong Chen, Wei Wang* and Xiaobei Chen*

Table of Contents

1. General Information .................................................................................................................................... 2
2. Sensitivity assessment of the reaction ......................................................................................................... 2
3. Mechanism study ........................................................................................................................................ 4
4. Preparation of the starting materials ........................................................................................................... 6
5. Deuteration of enals .................................................................................................................................. 16
6. Applications of α-deuterated enals .......................................................................................................... 312
7. References ............................................................................................................................................... 388
8. NMR Spectra ........................................................................................................................................... 39
1. 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. Column 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, $^2$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on a Bruker AM 400 Spectrometer (400, 77, 151 and 565 MHz for $^1$H NMR, $^2$H NMR, $^{13}$C NMR and $^{19}$F NMR, respectively) and are internally referenced to residual solvent signals (note: CDCl$_3$ referenced at 7.26 ppm in $^1$H NMR, C$_6$F$_6$ referenced at -161.64 ppm in $^{19}$F NMR$^1$). 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. Mass spectra were obtained using a TOF MS instrument EI or ESI source.

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.

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

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

**Supplementary Equation 1**

**Supplementary Equation 2** was based on $^2$H NMR and used to calculate the extent of labelling for the deuterated products containing some special sites where only slight deuterium incorporation occurred ($5ae$, $5ah$, $5ai$, $5aj$):

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

**Supplementary Equation 2**

2. Sensitivity assessment of the reaction
Standard conditions: 1a (0.2 mmol), 2b (0.04 mmol) and cat. 3 (0.04 mmol) in DCM (1 mL) and D2O (0.5 mL) was vigorously stirred at 50 °C for 24 h.

<table>
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<th>Experiment</th>
<th>Description</th>
<th>Preparation</th>
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<tbody>
<tr>
<td>1</td>
<td>High c</td>
<td>n/(V-10%V)</td>
<td>0.9 mL DCM</td>
</tr>
<tr>
<td>2</td>
<td>Low c</td>
<td>n/(V+10%V)</td>
<td>1.1 mL DCM</td>
</tr>
<tr>
<td>3</td>
<td>High O2</td>
<td>+ air, Vair = 10 V</td>
<td>1.0 mL DCM + 10 mL air</td>
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<tr>
<td>4</td>
<td>Low O2</td>
<td>degassed</td>
<td>1.0 mL DCM + degassed</td>
</tr>
<tr>
<td>5</td>
<td>High T</td>
<td>T + 10 °C</td>
<td>1.0 mL DCM, T = 60 °C</td>
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<td>6</td>
<td>Low T</td>
<td>T - 10 °C</td>
<td>1.0 mL DCM, T = 40 °C</td>
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<td>Control</td>
<td>Standard conditions</td>
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<td>Big scale</td>
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<td>6.0 mmol of 1a</td>
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**Table S2. Results (yield) of sensitivity assessment of the reaction**

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<th>Yield 2 / %</th>
<th>Average Y. / %</th>
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**Table S3. Results (D value) of sensitivity assessment of reaction**

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<th>D. 1 / %</th>
<th>D. 2 / %</th>
<th>Average D. / %</th>
<th>Deviation / %</th>
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<td>Big scale</td>
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<td>99</td>
<td>99</td>
<td>4</td>
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3. Mechanism study

Preparation of compound 4o

According to our previously developed procedure (Chem. Commun., 2009, 4886), a solution of 1o (495 mg, 3.75 mmol), 2a (235.5 mg, 0.75 mmol) and 3 (48.7 mg, 0.15 mmol) in toluene (6 mL) was stirred at 0 °C for 72 h, then it was purified by column chromatography to give the desired product 4o.

$^1$H NMR of 4o:
$^1$H NMR of 2a:

A solution of 4o (22.4 mg, 0.05 mmol) and 3 (3.3 mg, 0.01 mmol) in CDCl₃ (0.5 mL) was stirred at rt for 12 h. The reaction mixture was directly detected by $^1$H NMR as follow:

From the $^1$H NMR we could find the typical peaks of cinnamaldehyde 1o and fluorobis(phenylsulfonyl)methane 2a. So this experiment can prove that the Michael addition reaction is reversible.
4. Preparation of the starting materials

Cinnamaldehydes (1a, 1c, 1d, 1g, 1i, 1j, 1k, 1o, 1r, 1s, 1t, 1u, 1w, 1z, 1ae), 9, 13, 17, 19 and nucleophiles 2b, 2c, 2d, 2e, 2f, 2g, 2h are commercially available. 2a, 3 and 12 were prepared according to literature procedures.

Procedure A: Synthesis of cinnamaldehydes via Heck reaction/deprotection

A mixture of aryl halide (1 mmol), acrolein diethyl acetal (3 mmol), K₂CO₃ (1.5 mmol), Bu₄N⁺OAc (2 mmol), KCl (1 mmol) and Pd(OAc)₂ (3 mol%) in DMF (4 mL) was stirred at 90°C under N₂, and the reaction was monitored by TLC. After the reaction was completed, it was cooled to room temperature and 2 N HCl (10 mL) was slowly added, and the mixture was stirred at room temperature for 30 min. Then the reaction was diluted with EtOAc and washed with H₂O. The organic layer was isolated and dried over Na₂SO₄. The solvent was concentrated under reduced pressure, and the crude product was purified by column chromatography to give the cinnamaldehyde products.

(E)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde (1e)

Following the general procedure A, the title compound was prepared from 4-iodobenzotrifluoride (5 mmol) as a light yellow solid (610 mg, 61% yield). The spectra data was consistent with the literature report. 5

1H NMR (400 MHz, CDCl₃): δ 9.66 (d, J = 7.5 Hz, 1H), 7.63 – 7.56 (m, 4H), 7.42 (d, J = 16.0 Hz, 1H), 6.68 (dd, J = 16.0, 7.5 Hz, 1H).

13C NMR (151 MHz, CDCl₃): δ 193.3, 150.4, 137.4, 132.7 (q, J = 33.2 Hz), 130.7, 128.7, 126.2 (q, J = 4.5 Hz), 123.8 (q, J = 271.8 Hz).

19F NMR (565 MHz, CDCl₃): δ -62.84 (s, 3F).

(E)-3-(2-fluorophenyl)acrylaldehyde (1f)

Following the general procedure A, the title compound was prepared from 1-fluoro-2-iodobenzene (5 mmol) as a light yellow liquid (530 mg, 71% yield). The spectra data was consistent with the literature report. 6
(E)-3-(2-chlorophenyl)acrylaldehyde (1h)

Following the general procedure A, the title compound was prepared from 1-chloro-2-iodobenzene (5 mmol) as a white solid (635 mg, 77% yield). The spectra data was consistent with the literature report.5

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3): & \; \delta 9.76 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 16.0 Hz, 1H), 7.67 (d, J = 7.3 Hz, 1H), \\
& \; 7.46 (d, J = 7.5 Hz, 1H), 7.39 – 7.38 (m, 2H), 6.71 (dd, J = 16.0, 7.7 Hz, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, CDCl}_3): & \; \delta 193.6, 148.0, 135.2, 132.1, 132.0, 130.5, 130.4, 127.9, 127.3.
\end{align*}
\]

(E)-3-(4-(trifluoromethoxy)phenyl)acrylaldehyde (1l)

Following the general procedure A, the title compound was prepared from 1-iodo-4-(trifluoromethoxy)benzene (4 mmol) as a light yellow liquid (695 mg, 80% yield). The spectra data was consistent with the literature report.7

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3): & \; \delta 9.72 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 16.1 Hz, 1H), 7.59 (t, J = 7.3 Hz, 1H), \\
& \; 7.48 – 7.38 (m, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 9.4 Hz, 1H), 6.79 (dd, J = 16.1, 7.6 Hz, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, CDCl}_3): & \; \delta 193.9, 161.2 (d, J = 254.8 Hz), 144.9 (d, J = 3.6 Hz), 132.9 (d, J = 8.9 Hz), \\
& \; 130.5 (d, J = 5.3 Hz), 128.8, 124.7 (d, J = 3.7 Hz), 122.1 (d, J = 11.4 Hz), 116.3 (d, J = 21.8 Hz).
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (565 MHz, CDCl}_3): & \; \delta -114.14 (s, 1F).
\end{align*}
\]

(E)-3-(3-oxoprop-1-en-1-yl)benzaldehyde (1m)

Following the general procedure A, the title compound was prepared from 3-bromobenzaldehyde (6 mmol) as a white solid (762 mg, 79% yield). The spectra data was consistent with the literature report.6

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3): & \; \delta 10.08 (s, 1H), 9.76 (d, J = 7.6 Hz, 1H), 8.08 (s, 1H), 7.96 (d, J = 7.6 Hz, 1H), \\
& \; 7.85 (d, J = 7.7 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 16.0 Hz, 1H), 6.81 (dd, J = 16.0, 7.6 Hz, 1H).
\end{align*}
\]
\( ^{13}\text{C\ NMR (151 MHz, CDCl}_3\): } \delta 193.2 \text{ (d, } J = 3.4 \text{ Hz), } 191.4 \text{ (d, } J = 1.9 \text{ Hz), } 150.6 \text{ (d, } J = 2.4 \text{ Hz), } 137.1, 135.0, 133.7, 132.0, 130.0, 129.9, 129.3.

\( (E)\)-methyl 4-(3-oxoprop-1-en-1-yl)benzoate (1n)

Following the general procedure A, the title compound was prepared from methyl 4-iodobenzoate (5 mmol) as a white solid (520 mg, 58% yield). The spectra data was consistent with the literature report.\(^9\)

\( ^{1}\text{H\ NMR (400 MHz, CDCl}_3\): } \delta 9.74 \text{ (d, } J = 7.6 \text{ Hz, 1H), } 8.09 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 7.63 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 7.50 \text{ (d, } J = 16.0 \text{ Hz, 1H), } 6.78 \text{ (dd, } J = 16.0, 7.6 \text{ Hz, 1H), } 3.94 \text{ (s, 3H).}

\( ^{13}\text{C\ NMR (151 MHz, CDCl}_3\): } \delta 193.4, 166.3, 150.9, 138.1, 132.2, 130.4, 130.3, 128.3, 52.4.

\( (E)\)-3-(o-tolyl)acrylaldehyde (1p)

Following the general procedure A, the title compound was prepared from 1-iodo-2-methylbenzene (5 mmol) as a light yellow liquid (580 mg, 79% yield). The spectra data was consistent with the literature report.\(^6\)

\( ^{1}\text{H\ NMR (400 MHz, CDCl}_3\): } \delta 9.72 \text{ (d, } J = 7.5 \text{ Hz, 1H), } 7.77 \text{ (d, } J = 15.8 \text{ Hz, 1H), } 7.59 \text{ (d, } J = 7.1 \text{ Hz, 1H), } 7.32 \text{ (d, } J = 6.9 \text{ Hz, 1H), } 7.24 \text{ (d, } J = 6.1 \text{ Hz, 2H), } 6.66 \text{ (dd, } J = 15.8, 7.5 \text{ Hz, 1H), } 2.48 \text{ (s, 3H).}

\( ^{13}\text{C\ NMR (151 MHz, CDCl}_3\): } \delta 193.9, 150.3, 137.9, 132.8, 131.1, 131.0, 129.6, 126.8, 126.6, 19.7.

\( (E)\)-3-(m-tolyl)acrylaldehyde (1q)

Following the general procedure A, the title compound was prepared from 1-iodo-3-methylbenzene (5 mmol) as a light yellow liquid (585 mg, 80% yield). The spectra data was consistent with the literature report.\(^6\)

\( ^{1}\text{H\ NMR (400 MHz, CDCl}_3\): } \delta 9.60 \text{ (d, } J = 7.7 \text{ Hz, 1H), } 7.35 \text{ (d, } J = 15.9 \text{ Hz, 1H), } 7.28 \text{ (s, 2H), } 7.23 - 7.15 \text{ (m, 2H), } 6.61 \text{ (dd, } J = 15.9, 7.7 \text{ Hz, 1H), } 2.30 \text{ (s, 3H).}

\( ^{13}\text{C\ NMR (151 MHz, CDCl}_3\): } \delta 193.8, 153.1, 138.9, 134.0, 132.2, 129.2, 129.0, 128.4, 125.8, 21.1.

\( (E)\)-3-(naphthalen-1-yl)acrylaldehyde (1x)

Following the general procedure A, the title compound was prepared from 1-iodonaphthalene (6 mmol) as a yellow solid (665 mg, 61% yield). The spectra data was consistent with the
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.86 (d, $J$ = 7.7 Hz, 1H), 8.34 (d, $J$ = 15.7 Hz, 1H), 8.19 (d, $J$ = 8.4 Hz, 1H), 7.94 (dd, $J$ = 18.0, 8.1 Hz, 2H), 7.83 (d, $J$ = 7.2 Hz, 1H), 7.66 – 7.49 (m, 3H), 6.85 (dd, $J$ = 15.7, 7.7 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.7, 149.3, 133.8, 131.6, 131.2, 131.0, 130.9, 129.0, 127.3, 126.4, 125.7, 125.5, 122.8.

Following the general procedure A, the title compound was prepared from 1,4-diiodobenzene (5 mmol) as a yellow solid (390 mg, 42% yield). The spectra data was consistent with the literature report.$^{10}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.74 (d, $J$ = 7.6 Hz, 2H), 7.64 (s, 4H), 7.49 (d, $J$ = 16.0 Hz, 2H), 6.77 (dd, $J$ = 16.0, 7.6 Hz, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.4, 150.9, 136.6, 129.8, 129.1.

(2$E$,2$'$E)-3,3'-((1,4-phenylene)diacrylaldehyde (1ag)

To a solution of 3-(3-nitrophenyl)-1-propanol (5.13 mmol) in DMSO (10 mL) and CH$_3$CN (15 mL) was added IBX (3.59 g, 12.83 mmol) and catalyst IV (259.6 mg, 1.03 mmol). The mixture was then stirred at room temperature until the reaction was completed monitored with TLC. H$_2$O (20 mL) was added to the
reaction mixture, the reaction mixture was diluted with EtOAc (80 mL) and washed with H2O (20 mL × 4), saturated brine (20 mL). The organic solution was dried over Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography to give aldehyde 1b as a white solid (569 mg, 63% yield for two steps). The spectra data was consistent with the literature report.8

1H NMR (400 MHz, CDCl3): δ 9.77 (d, J = 7.4 Hz, 1H), 8.42 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 16.0 Hz, 1H), 6.82 (dd, J = 16.0, 7.4 Hz, 1H).

13C NMR (151 MHz, CDCl3): δ 192.8, 149.1, 148.8, 135.7, 133.6, 130.9, 130.3, 125.4, 123.1.

(E)-3-(3,4-dimethoxyphenyl)acrylaldehyde (1v)

Following the same procedure for the synthesis of 1b as described above, the title compound 1v was obtained from 3-(3,4-dimethoxyphenyl)propanoic acid (1.05 g, 5 mmol) as a black solid (750 mg, 78% yield for two steps). The spectra data was consistent with the literature report.10

1H NMR (400 MHz, CDCl3): δ 9.64 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 15.8 Hz, 1H), 7.15 (dd, J = 8.3, 1.8 Hz, 1H), 7.07 (d, J = 1.8 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 6.60 (dd, J = 15.8, 8.3 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H).

13C NMR (151 MHz, CDCl3): δ 193.6, 152.9, 152.0, 149.4, 127.1, 126.7, 123.5, 111.1, 109.9, 56.1, 55.9.

(E)-3-(1-benzyl-1H-pyrrol-2-yl)acrylaldehyde (1y)

To a stirred solution of NaH (800 mg, 20 mmol) in DMF (20 ml) was added pyrrole-2-carboxyaldehyde (950 mg, 10 mmol) under N2 at 0 ºC. After 20 min, BnBr (2.38 mL, 20 mmol) was added. The reaction was slowly warmed up to room temperature and stirred for 3 h. H2O (10 mL) was slowly added to the reaction mixture at 0 ºC, the reaction mixture was diluted with DCM (80 mL) and washed with H2O (20 mL × 4), and saturated brine (20 mL). The organic solution was dried over Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography to give 1-benzyl-1H-pyrrole-2-carbaldehyde (1.73 g,
94% yield) as a dark red oil.

To a stirred solution of 1-benzyl-1H-pyrrole-2-carbaldehyde (1.73 g, 9.35 mmol) in THF (30 mL) under N₂ at 0 °C was added (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (6.02 g, 14 mmol), NaH (1.87 g, 46.75 mmol), and 18-crown-6 (200 mg). The reaction was slowly warmed to room temperature and stirred overnight. Then 1N HCl (80 mL) was added slowly to quench the reaction, the mixture was stirred for 30 min and neutralized with ammonia water then extracted with DCM (40 mL × 3). The combined organic solution was washed with saturated brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give aldehyde 1y as a black liquid (723 mg, 34% yield).

**1H NMR (400 MHz, CDCl₃):** δ 9.42 (d, J = 7.9 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.22 (d, J = 15.5 Hz, 1H), 7.03 (d, J = 7.3 Hz, 2H), 6.96 (s, 1H), 6.84 (d, J = 3.8 Hz, 1H), 6.41 (dd, J = 15.5, 7.9 Hz, 1H), 6.35 – 6.31 (m, 1H), 5.26 (s, 2H).

**13C NMR (151 MHz, CDCl₃):** δ 193.1, 139.7, 136.9, 129.1, 129.0, 128.5, 128.0, 126.1, 124.1, 114.6, 110.7, 50.9.

**HRMS (ESI-TOF):** m/z caled for C₁₄H₁₄NO [(M + H)⁺]: 212.1075, found: 212.1076

**((E)-3-(1-Benzyl-1H-imidazol-5-yl)acrylaldehyde (1aa)**

To a stirred solution of ((E)-3-(1H-imidazol-4-yl) acrylic acid (2.5 g, 18.1 mmol) in MeOH (25 mL) was added SOCl₂ (7.5 mL) dropwise at 0 °C. The reaction mixture was stirred at 80 °C for 6 h. The solvent was removed under reduced pressure. The residue was added saturated NaHCO₃ solution until pH = 7 and extracted with EtOAc (50 mL × 3). The combined organic solution was washed with saturated brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give the product methyl ((E)-3-(1H-imidazol-4-yl)acrylate as a white solid that was used directly in the next step without purification.

To a stirred solution of methyl ((E)-3-(1H-imidazol-4-yl)acrylate (18.12 mmol) in DMF (20 mL) was slowly added NaH (1.09 g, 27.18 mmol) slowly at 0 °C, followed by the addition of BnBr (3.41 g, 19.93 mmol).
The mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with H₂O (20 mL) at 0 °C and diluted with EtOAc (80 mL). The organic layer was separated and washed with H₂O (20 mL × 4) and saturated brine (20 mL). The combined organic solution was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give the product ([E]-methyl 3-(1-benzyl-1H-imidazol-5-yl)acrylate) as a white solid (1.9 g, 44% yield for two steps).

To a stirred solution of ([E]-methyl 3-(1-benzyl-1H-imidazol-5-yl)acrylate (1.9 g, 7.8 mmol) in dry DCM (55 mL) was added DIBAL-H (23.5 mL, 23.5 mmol, 1.0 M in hexanes) slowly under N₂ at -78 °C. After completion of reaction monitored by TLC, the mixture was quenched by slowly adding H₂O (8 mL). The mixture was allowed to warm to room temperature before it was poured into a suspension of NaHCO₃ (30 g) and MgSO₄ (30 g) in EtOAc (300 mL). After filtration, the filtrate was concentrated under reduced pressure. H₂O (20 mL) was added to the mixture, and the mixture was extracted with DCM (30 mL × 3), The combined organic solution was washed with saturated brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give ([E]-3-(1-benzyl-1H-imidazol-5-yl)prop-2-en-1-ol as colorless oil (1.6 g, 96% yield).

To a stirred solution of ([E]-3-(1-benzyl-1H-imidazol-5-yl)prop-2-en-1-ol (1.6 g, 7.5 mmol) in dry DCM (50 mL) was added Dess-Martin reagent (3.82 g, 9 mmol) slowly at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. The mixture was quenched by slowly adding saturated aqueous Na₂S₂O₅ (30 mL) and the aqueous phase was extracted with DCM (50 mL × 3). The combined organic solution was washed with saturated brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give aldehyde 1aa as light yellow solid (1.3 g, 82% yield).

**¹H NMR (400 MHz, CDCl₃):** δ 9.60 (d, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.41 – 7.30 (m, 4H), 7.22 (s, 1H), 7.20 – 7.15 (m, 2H), 6.76 (dd, J = 15.6, 8.0 Hz, 1H), 5.13 (s, 2H).

**¹³C NMR (151 MHz, CDCl₃):** δ 194.2, 146.2, 140.4, 137.9, 137.6, 129.3, 128.4, 128.1, 125.7, 125.2, 50.3.

**HRMS (ESI-TOF):** m/z cale for C₁₃H₁₃N₂O [(M + H)]⁺: 213.1028. found: 213.1029.

**([E]-3-(3-Phenylisoxazol-5-yl)acrylaldehyde (1ab)**

![Chemical Structure](image)
To a stirred solution of benzaldehydeoxime (1.5 g, 7.9 mmol), pent-4-yn-1-ol (529 mg, 6.3 mmol) and Et₃N (1.27 g, 12.6 mmol) in DCM (60 mL) was added aqueous NaClO (11-14% available chlorine, 66 mL). The mixture was stirred at room temperature for 10 h. H₂O (20 mL) was added and extracted with DCM (50 mL × 3). The combined organic solution was washed with saturated brine (50 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give 3-(3-phenylisoxazol-5-yl)propan-1-ol as light yellow solid (400 mg, 31% yield).

The second step followed the same procedure for the synthesis of 1b as described above. The title compound 1ab was obtained as a white solid (514 mg, 60% yield). The spectra data was consistent with the literature report.¹⁰

¹H NMR (400 MHz, CDCl₃):  δ 9.76 (d, J = 7.2 Hz, 1H), 7.83 (s, 2H), 7.49 (s, 3H), 7.37 (d, J = 16.1 Hz, 1H), 6.88 (dd, J = 16.1, 7.2 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 192.1, 165.8, 163.2, 133.3, 132.2, 130.5, 129.1, 128.1, 126.8, 105.0.

(E)-3-(1-Benzyl-1H-1,2,3-triazol-4-yl)acrylaldehyde (1ac)

To a stirred solution of BnN₃ (262 mg, 2.2 mmol) and pent-4-yn-1-ol (168 mg, 2.0 mmol) in t-BuOH (8 mL) and H₂O (8 mL) was added CuSO₄ꞏ5H₂O (50 mg, 0.2 mmol) and sodium ascorbate (198 mg, 1 mmol) in H₂O (1 mL). The reaction was stirred at room temperature for 2 h. H₂O (10 mL) was added and extracted with EtOAc (30 mL × 3). The combined organic solution were washed with saturated brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give the product 3-(1-benzyl-1H-1,2,3-triazol-4-yl)propan-1-ol that was used directly in the next step without purification.

The second step followed the same procedure for the synthesis of 1b as described above. The title compound 1ac was obtained as a white solid (307 mg, 75% yield for two steps). The spectra data was consistent with the literature report.¹⁰

¹H NMR (400 MHz, CDCl₃): δ 9.66 (d, J = 7.7 Hz, 1H), 7.69 (s, 1H), 7.48 (d, J = 16.1 Hz, 1H), 7.40 (s, 3H), 7.31 (s, 2H), 6.78 (dd, J = 16.1, 7.7 Hz, 1H), 5.57 (s, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 193.1, 143.8, 140.0, 133.9, 129.9, 129.4, 129.2, 128.2, 123.5, 54.5.
(E)-3-(1-Benzyl-1H-indol-3-yl)acrylaldehyde (1ad)

To a stirred solution of morpholine-trifluoroacetic acid (322 mg, 1.6 mmol), indole (936 mg, 8 mmol) in THF (60 mL) was added acrolein (1.34 g, 24 mmol). The reaction was stirred at room temperature for 24 h. Then DDQ (2.36 g, 10.4 mmol) was added and the reaction was continued to stir for 2 h. The reaction mixture was directly concentrated under reduced pressure and purified by column chromatography to give (E)-3-(1H-indol-3-yl)acrylaldehyde as a yellow solid (1.19 g, 88% yield).

A mixture of (E)-3-(1H-indol-3-yl)acrylaldehyde (1.19 g, 7 mmol), BnBr (1.44 g, 8.4 mmol) and K$_2$CO$_3$ (1.93 g, 14 mmol) in DMF (15 mL) was stirred at 80°C overnight. H$_2$O (20 mL) was added and extracted with EtOAc (80 mL), The organic layer was washed with H$_2$O (20 mL × 4) and saturated brine (20 mL). The organic solution was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography to give the aldehyde 1ad as a yellow solid (327 mg, 18% yield).

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.61 (d, $J$ = 7.9 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.65 (d, $J$ = 15.8 Hz, 1H), 7.49 (s, 1H), 7.36 – 7.28 (m, 6H), 7.18 – 7.16 (m, 2H), 6.76 (dd, $J$ = 15.8, 7.9 Hz, 1H), 5.35 (s, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 194.1, 146.3, 137.9, 135.7, 133.3, 129.1, 128.3, 127.1, 126.1, 124.6, 123.6, 122.1, 120.6, 113.0, 110.7, 50.6.

HRMS (ESI-TOF): m/z caled for C$_{18}$H$_{15}$NNaO [(M + Na)$^+$]: 284.1051. found: 284.1050.

(E)-3-(Ferrocenyl)acrylaldehyde (1af)

To a stirred solution of ferrocencarboxaldehyde (1.07 g, 5 mmol) in THF (20 mL) was added (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (3.22 g, 7.5 mmol), NaH (1.0 g, 25 mmol), and 18-crown-6 (100 mg) under N$_2$ at 0 °C. The reaction was slowly warmed up to room temperature and stirred overnight. Then 1N HCl (40 mL) was added slowly to quench the reaction, the mixture was stirred for 30 min and neutralized with ammonia water, then extracted with DCM (50 mL × 3). The combined organic solution was washed with saturated brine (30 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure.
pressure. The crude product was purified by column chromatography to give the aldehyde 1af as a black solid (850mg, 70% yield). The spectra data was consistent with the literature report.11

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 9.56 (d, J = 8.0 \text{ Hz}, 1H), 7.43 (d, J = 15.6 \text{ Hz}, 1H), 6.35 (dd, J = 15.6, 8.0 \text{ Hz}, 1H), 4.54 (d, J = 14.0 \text{ Hz}, 4H), 4.18 (s, 5H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)): \(\delta 193.2, 155.2, 126.4, 77.8, 71.9, 70.0, 69.2.

(2E,4E)-5-phenylpenta-2,4-dienal (1ah)

To a stirred solution of NaH (1.2 g, 30 mmol) in dry THF (120 mL) was added triethylphosphonoacetate (5.38 g, 24 mmol) dropwise under N\(_2\) at 0 °C. The mixture was stirred for 1 h before a solution of (E)-cinnamaldehyde (2.64 g, 20 mmol) in THF (20 mL) was added dropwise. The reaction was slowly warmed up to room temperature and stirred for 3 h. The reaction was quenched with saturated NH\(_4\)Cl (40 mL) and extracted with EtOAc (60 mL \(\times\) 3). The combined organic solution was washed with brine (40 mL), dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure to give the product (2E,4E)-ethyl 5-phenylpenta-2,4-dienoate that was used directly in the next step without purification.

To a stirred solution of (2E,4E)-ethyl 5-phenylpenta-2,4-dienoate (20 mmol) in dry DCM (60 mL) was added DIBAL-H (50 mL, 50 mmol, 1.0 M in hexanes) slowly under N\(_2\) at -78 °C. After completion of reaction monitored by TLC, the mixture was quenched by slowly adding H\(_2\)O (20 mL). The mixture was allowed to warm to room temperature before it was poured into a suspension of NaHCO\(_3\) (75 g) and MgSO\(_4\) (75 g) in EtOAc (750 mL). After filtration, the filtrate was concentrated under reduced pressure. H\(_2\)O (25 mL) was added to the mixture, and the mixture was extracted with DCM (60 mL \(\times\) 3). The combined organic solution was washed with saturated brine (40 mL), dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure to give the product (2E,4E)-5-phenylpenta-2,4-dien-1-ol that was used directly in the next step without purification.

To a solution of (2E,4E)-5-phenylpenta-2,4-dien-1-ol (20 mmol) in stirred dry DMSO (30 mL) was added IBX (7.0 g, 25 mmol) slowly at 0 °C, and the mixture was slowly warmed to room temperature and stirred overnight. Water (60 mL) was added and the mixture was filtered. The filtrate was extracted with EtOAc (80 mL). The organic layer was separated and washed with H\(_2\)O (20 mL \(\times\) 4), and saturated brine (20 mL). The combined organic solution was dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude
product was purified by column chromatography to give aldehyde 1ah as a light yellow liquid (1.85 g, 59% yield for three steps). The spectra data was consistent with the literature report.\textsuperscript{16}

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})}: \(\delta 9.62 (d, J = 8.0 \text{ Hz}, 1H), 7.51 (d, J = 7.0 \text{ Hz}, 2H), 7.43 - 7.34 \text{ (m, 3H)}, 7.31 - 7.25 \text{ (m, 1H)}, 7.05 - 6.99 \text{ (m, 2H)}, 6.28 (dd, J = 15.2, 8.0 \text{ Hz}, 1H).

\textbf{13C NMR (151 MHz, CDCl\textsubscript{3})}: \(\delta 193.6, 152.1, 142.4, 135.6, 131.6, 129.7, 128.9, 127.5, 126.2.

\textbf{(2E,4E)-5-(4-nitrophenyl)penta-2,4-dienal (1ai)}

Following the same procedure for the synthesis of 1ah as described above, the title compound 1ai was obtained from (E)-3-(4-nitrophenyl)acrylaldehyde (2.66 g, 15.0 mmol) as a yellow solid (1.67 g, 55% yield for three steps). The spectra data was consistent with the literature report.\textsuperscript{12}

\textbf{1H NMR (400 MHz, DMSO-\textsubscript{d6})}: \(\delta 9.64 (d, J = 8.0 \text{ Hz}, 1H), 8.25 (d, J = 8.4 \text{ Hz}, 2H), 7.88 (d, J = 8.4 \text{ Hz}, 2H), 7.60 - 7.40 \text{ (m, 2H)}, 7.31 (d, J = 14.7 \text{ Hz}, 1H), 6.38 (dd, J = 14.7, 8.0 \text{ Hz}, 1H).

\textbf{13C NMR (151 MHz, CDCl\textsubscript{3})}: \(\delta 193.2, 150.0, 147.9, 141.7, 139.0, 133.7, 130.2, 128.0, 124.3.

\textbf{(2E,4E)-5-(4-methoxyphenyl)penta-2,4-dienal (1aj)}

Following the same procedure for the synthesis of 1ah as described above, the title compound 1aj was obtained from (E)-3-(4-methoxyphenyl)acrylaldehyde (1 g, 6.17 mmol) as a yellow solid (724 mg, 64% yield for three steps). The spectra data was consistent with the literature report.\textsuperscript{17}

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})}: \(\delta 9.60 (d, J = 8.0 \text{ Hz}, 1H), 7.46 (d, J = 8.6 \text{ Hz}, 2H), 7.26 (d, J = 8.6 \text{ Hz}, 1H), 7.01 - 6.84 \text{ (m, 4H)}, 6.23 (dd, J = 15.1, 8.0 \text{ Hz}, 1H), 3.85 (s, 3H).

\textbf{13C NMR (151 MHz, CDCl\textsubscript{3})}: \(\delta 193.6, 161.0, 152.7, 142.3, 130.6, 129.2, 128.4, 124.1, 114.4, 55.4.

\section*{5. Deuteration of enals}

\textbf{General procedure}: a mixture of enal 1 (0.2 mmol), catalyst 3 (0.04 mmol) and 2b (0.04 mmol) in D\textsubscript{2}O (0.5 mL) and DCM (1 mL) was vigorously stirred at 50 °C for specified time. After cooling to room temperature, the reaction mixture was extracted with DCM (5 mL \(\times\) 3). The combined organic solution were dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated under reduced pressure. The residue was purified by column
chromatography to give the deuterated product 5. The level of deuterium incorporation for the product was determined by $^1$H NMR spectroscopy.

\[(E)-3-(4-nitrophenyl)acrylaldehyde-\text{-}\text{\textit{d}}_1\text{ (5a)}\]

Following the general procedure, 1a (35.4 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow solid (33.5 mg, 94% yield) with 95% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.78 (s, 1H), 8.31 – 8.29 (m, 2H), 7.75 – 7.73 (m, 2H), 7.53 (s, 1H), 6.81 (dd, $J$ = 16.1, 7.4 Hz, 0.05H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 192.9, 149.0, 148.8, 139.9, 131.5 (t, $J$ = 24.9 Hz), 129.1, 124.4.

$^2$H NMR (77 MHz, CHCl$_3$): $\delta$ 6.87 (s, 1D).

HRMS (EI-TOF): m/z caled for C$_9$H$_6$DNO$_3$ [(M)$^+$]: 178.0489, found: 178.0492.

Scale-up:
A mixture of 1a (1.06 g, 6 mmol), catalyst 3 (390 mg, 1.2 mmol) and 2b (355.2 mg, 1.2 mmol) in D$_2$O (15 mL) and DCM (20 mL) in sealed tube was vigorously stirred at 70 °C for 48 h. After cooling to room temperature, the reaction mixture was extracted with DCM (30 mL x 3). The combined organic solution was washed with saturated brine (20 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography to give 5a as a yellow solid (705 mg, 66% yield) with 99% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.78 (s, 1H), 8.31 – 8.29 (m, 2H), 7.74 – 7.72 (m, 2H), 7.55 – 7.49 (m, 1H), 6.81 (dd, $J$ = 16.1, 7.4 Hz, 0.01H).

\[(E)-3-(3-nitrophenyl)acrylaldehyde-\text{-}\text{\textit{d}}_1\text{ (5b)}\]

Following the general procedure, 1b (35.4 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow solid (32.7 mg, 92% yield) with 99% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.77 (s, 1H), 8.41 (s, 1H), 8.30 (d, $J$ = 8.2 Hz, 1H), 7.90 (d, $J$ = 8.2 Hz, 1H), 7.65 (t, $J$ = 8.0 Hz, 1H), 7.53 (s, 1H), 6.82 (dd, $J$ = 16.0, 7.6 Hz, 0.01H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 192.8, 148.9, 148.8 135.7, 133.6, 130.83 – 130.58 (m), 130.3, 125.2, 123.1.
HRMS (EI-TOF): m/z caled for C₉H₆DNO₃ [(M)+]: 178.0489, found: 178.0492.

(E)-3-(2-nitrophenyl)acrylaldehyde-α-d₁ (5c)

Following the general procedure, 1c (35.4 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow solid (33.5 mg, 94% yield) with 99% D-incorporation.

¹H NMR (400 MHz, CDCl₃): δ 9.78 (s, 1H), 8.11 (dd, J = 8.1, 0.9 Hz, 1H), 8.04 – 8.03 (m, 1H), 7.74 – 7.66 (m, 2H), 7.63 – 7.59 (m, 1H), 6.64 (dd, J = 15.8, 7.7 Hz, 0.01H).

¹³C NMR (151 MHz, CDCl₃): δ 193.3, 148.2, 147.4, 134.0, 132.5 (t, J = 24.8 Hz), 131.3, 130.2, 129.2, 125.4.

HRMS (EI-TOF): m/z caled for C₉H₆DNO₃ [(M)+]: 178.0489, found: 178.0487.

(E)-3-(3-(trifluoromethyl)phenyl)acrylaldehyde-α-d₁ (5d)

Following the general procedure, 1d (40.0 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a white solid (28.5 mg, 71% yield) with 99% D-incorporation.

¹H NMR (400 MHz, CDCl₃): δ 9.74 (s, 1H), 7.80 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.52 – 7.47 (m, 1H), 6.77 (dd, J = 16.0, 7.5 Hz, 0.01H).

¹³C NMR (151 MHz, CDCl₃): δ 193.3, 150.4, 134.9, 131.9 (q, J = 32.8 Hz), 131.2, 129.7, 129.6 (t, J = 24.9 Hz), 127.8 (q, J = 3.4 Hz), 125.4 (q, J = 3.7 Hz), 122.1 (q, J = 272.5 Hz).

¹⁹F NMR (565 MHz, CDCl₃): δ -62.77 (s, 3F).

HRMS (EI-TOF): m/z caled for C₁₀H₆DF₃O [(M)+]: 201.0512, found: 201.0510.

(E)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde-α-d₁ (5e)

Following the general procedure, 1e (40 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a light yellow liquid (31.4 mg, 78% yield) with 97% D-incorporation.
\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.76 (s, 1H), 7.72 – 7.66 (m, 4H), 7.52 – 7.49 (m, 1H), 6.78 (dd, \( J = 16.0, 7.6 \) Hz, 0.03H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \): 193.3, 150.3, 137.4, 132.8 (q, \( J = 33.2 \) Hz), 130.4 (t, \( J = 24.2 \) Hz), 128.7, 126.2 (q, \( J = 4.5 \) Hz), 123.8 (q, \( J = 271.8 \) Hz).

\( ^{19}F \) NMR (565 MHz, CDCl\(_3\)) \( \delta \): -62.88 (s, 3F).

HRMS (EI-TOF): m/z caled for C\(_{10}\)H\(_6\)DF\(_3\)O [(M)\(^+\)]: 201.0512, found: 201.0509.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.70 (s, 1H), 7.64 (s, 1H), 7.58 (t, \( J = 7.5 \) Hz, 1H), 7.42 (dd, \( J = 14.1, 6.8 \) Hz, 1H), 7.20 (t, \( J = 7.5 \) Hz, 1H), 7.16 – 7.09 (m, 1H), 6.78 (dd, \( J = 16.1, 7.7 \) Hz, 0.01H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \): 193.9, 161.3 (d, \( J = 254.8 \) Hz), 144.8 (d, \( J = 3.6 \) Hz), 133.0 (d, \( J = 8.9 \) Hz), 130.51 – 130.15 (m), 128.9, 124.8 (d, \( J = 3.6 \) Hz), 122.2 (d, \( J = 11.4 \) Hz), 116.5 (d, \( J = 22.0 \) Hz).

\( ^{19}F \) NMR (565 MHz, CDCl\(_3\)) \( \delta \): -114.15 (s, 1F).

HRMS (EI-TOF): m/z caled for C\(_9\)H\(_6\)DFO [(M)\(^+\)]: 151.0544, found: 151.0547.

\( \text{(E)} \)-3-(2-fluorophenyl)acrylaldehyde-\( \alpha \)-\( d_1 \) (5f)

Following the general procedure, 1f (30 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a light yellow liquid (26.9 mg, 89% yield) with 99% D-incorporation.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.69 (s, 1H), 7.59 – 7.54 (m, 2H), 7.44 (d, \( J = 1.9 \) Hz, 1H), 7.13 (t, \( J = 8.6 \) Hz, 2H), 6.65 (dd, \( J = 16.0, 7.7 \) Hz, 0.02H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \): 193.4, 165.5 (d, \( J = 254.2 \) Hz), 151.2, 130.4 (dd, \( J = 21.0, 6.0 \) Hz), 128.2 (t, \( J = 25.6 \) Hz), 116.3, 116.1.

\( ^{19}F \) NMR (565 MHz, CDCl\(_3\)) \( \delta \): -107.61(s, 1F).

HRMS (EI-TOF): caled for C\(_9\)H\(_6\)DFO [(M)\(^+\)]: 151.0544, found: 151.0546.
(E)-3-(2-chlorophenyl)acrylaldehyde-α-d₁ (5h)

Following the general procedure, 1h (33.2 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 108 h. The title compound was obtained as a white solid (26.3 mg, 79% yield) with 99% D-incorporation.

$^1$H NMR (400 MHz, CDCl₃): δ 9.77 (s, 1H), 7.94 (s, 1H), 7.67 (d, $J = 7.5$ Hz, 1H), 7.47 (d, $J = 7.5$ Hz, 1H), 7.40 – 7.31 (m, 2H), 6.71 (dd, $J = 16.0, 7.7$ Hz, 0.01H).

$^{13}$C NMR (151 MHz, CDCl₃): δ 193.7, 148.0, 135.3, 132.2, 132.1, 130.56 – 130.18 (m), 130.4, 128.0, 127.4.

HRMS (EI-TOF): m/z caled for C₉H₆DClO [(M)+]: 167.0248, found: 167.0246.

(Ε)-3-(4-chlorophenyl)acrylaldehyde-α-d₁ (5i)

Following the general procedure, 1i (33.2 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a white solid (28.7 mg, 86% yield) with 96% D-incorporation.

$^1$H NMR (400 MHz, CDCl₃): δ 9.71 (s, 1H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 3H), 6.69 (dd, $J = 16.0, 7.8$ Hz, 0.04H).

$^{13}$C NMR (151 MHz, CDCl₃): δ 193.4, 148.0, 137.2, 132.5, 129.7, 129.4, 128.7 (t, $J = 24.5$ Hz)

HRMS (EI-TOF): m/z caled for C₉H₆DClO [(M)+]: 167.0248, found: 167.0251.

(E)-3-(2-bromophenyl)acrylaldehyde-α-d₁ (5j)

Following the general procedure, 1j (41.8 mg, 0.2 mmol, deuteration 80%) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 48 h. The title compound was obtained as a yellow solid (33.8 mg, 80% yield) with 88% D-incorporation.

Following the general procedure, (E)-3-(2-bromophenyl)acrylaldehyde-α-d₁ (33.8 mg, 0.16 mmol, deuteration 80%) was used in the deuteration reaction, PhCOOH (3.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a yellow solid (23.2 mg, 55% yield for two steps) with 97% D-incorporation.

$^1$H NMR (400 MHz, CDCl₃): δ 9.78 (s, 1H), 7.93 – 7.88 (m, 1H), 7.66 (dd, $J = 7.8, 1.9$ Hz, 2H), 7.38 (t, $J = 7.3$ Hz, 1H), 7.31 – 7.27 (m, 1H), 6.68 (dd, $J = 15.8, 7.7$ Hz, 0.03H).
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.7, 150.7, 134.0, 133.8, 132.3, 130.6 ($t, J = 24.0$ Hz), 128.1 ($d, J = 13.4$ Hz), 125.9.


(5k)

Following the general procedure, 1k (41.8 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a yellow solid (37.6 mg, 89% yield) with 97% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.71 (s, 1H), 7.57 ($d, J = 8.4$ Hz, 2H), 7.43 ($d, J = 8.6$ Hz, 2H), 7.41 (s, 1H), 6.70 ($dd, J = 15.9, 7.6$ Hz, 0.03H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 193.4, 151.0, 132.9, 132.4, 129.8, 128.8 ($t, J = 24.4$ Hz), 125.7.

(E)-3-(4-(trifluoromethoxy)phenyl)acrylaldehyde-α-d1 (5l)

Following the general procedure, 1l (43.2 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a light yellow liquid (39.9 mg, 92% yield) with 98% D-incorporation.

$^1$H NMR (400 MHz, CDCl₃): δ 9.74 (s, 1H), 7.63 (d, $J = 8.7$ Hz, 2H), 7.48 (s, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 6.72 (dd, $J = 16.0$, 7.6 Hz, 0.02H).

$^{13}$C NMR (151 MHz, CDCl₃): δ 193.5, 151.2, 150.7, 132.6, 130.1, 129.1 (t, $J = 24.2$ Hz), 121.4, 120.5 (q, $J = 258.2$ Hz).

$^2$H NMR (77 MHz, CH₂Cl₂): δ 6.76 (s, 1D).

$^{19}$F NMR (565 MHz, CDCl₃): δ -57.54 (s, 3F).

HRMS (EI-TOF): m/z caled for C₁₀H₆DF₃O₂ [(M)+]: 217.0461, found: 217.0458.

(E)-3-(3-oxoprop-1-en-1-yl)benzaldehyde-α-d₁ (5m)

Following the general procedure, 1m (32.0 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 48 h. The title compound was obtained as a white solid (28.7 mg, 89% yield) with 58% D-incorporation.

Following the general procedure, (E)-3-(3-oxoprop-1-en-1-yl)benzaldehyde-α-d₁ (28.7 mg, 0.18 mmol, deuteration 58%) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as white solid (22.5 mg, 70% yield for two steps) with 95% D-incorporation.

$^1$H NMR (400 MHz, CDCl₃): δ 10.08 (s, 1H), 9.76 (s, 1H), 8.07 (s, 1H), 7.98 – 7.94 (m, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.56 – 7.52 (m, 1H), 6.81 (dd, $J = 16.0$, 7.5 Hz, 0.05H).

$^{13}$C NMR (151 MHz, CDCl₃): δ 193.3, 191.5, 150.6, 137.1, 135.0, 133.7, 132.0, 129.9, 130.20 – 129.47 (m), 129.3.

$^2$H NMR (77 MHz, CHCl₃): δ 6.86 (s, 1D).

HRMS (EI-TOF): m/z caled for C₁₀H₇DO₂ [(M)+]: 161.0587, found: 161.0590.

(E)-methyl 4-(3-oxoprop-1-en-1-yl)benzoate-α-d₁ (5n)

(E)-3-(3-oxoprop-1-en-1-yl)benzaldehyde-α-d₁ (5m)
Following the general procedure, 1n (38.0 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 48 h. The title compound was obtained as a white solid (30.6 mg, 80% yield) with 84% D-incorporation.

Following the general procedure, (E)-methyl 4-(3-oxoprop-1-en-1-yl)benzoate-α-d1 (30.6 mg, 0.16 mmol, deuteration 84%) was used in the deuteration reaction, PhCOOH (3.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a white solid (21 mg, 55% yield for two steps) with 96% D-incorporation.

**1H NMR (400 MHz, CDCl3):** δ 9.74 (s, 1H), 8.09 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.50 (s, 1H), 6.78 (dd, J = 16.0, 7.7 Hz, 0.04H), 3.94 (s, 3H).

**13C NMR (151 MHz, CDCl3):** δ 193.5, 166.4, 150.9, 138.2, 132.3, 130.4, 130.1 (t, J = 24.2 Hz), 128.5, 52.5.

**2H NMR (77 MHz, CHCl3):** δ 6.83 (s, 1D).

**HRMS (EI-TOF):** m/z calcd for C11H9DO3 [**(M)+]**: 191.0693, found: 191.0695.

(E)-cinnamaldehyde-α-d1 (5o)

Following the general procedure, 1o (26.4 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow liquid (21.3 mg, 80% yield) with 98% D-incorporation.

**1H NMR (400 MHz, CDCl3):** δ 9.71 (s, 1H), 7.57 (dd, J = 6.7, 2.9 Hz, 2H), 7.49 – 7.46 (m, 1H), 7.46 – 7.40 (m, 3H), 6.72 (dd, J = 16.0, 7.7 Hz, 0.02H).

**13C NMR (101 MHz, CDCl3):** δ 193.8, 152.8, 134.1, 131.4, 129.2, 128.6, 128.4 (t, J = 24.6 Hz).

**2H NMR (77 MHz, CHCl3):** δ 6.79 (s, 1D).

**HRMS (EI-TOF):** m/z calcd for C9H7DO [(M)+]: 133.0638, found: 133.0640.

(E)-3-(o-tolyl)acrylaldehyde-α-d1 (5p)

Following the general procedure, 1p (29.2 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow liquid (23.2 mg, 79% yield) with 94% D-incorporation.

**1H NMR (400 MHz, CDCl3):** δ 9.71 (s, 1H), 7.76 (s, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.23 (d, J = 7.4 Hz, 2H), 6.66 (dd, J = 15.8, 7.7 Hz, 0.06H), 2.47 (s, 3H).
$^{13}$C NMR (151 MHz, CDCl$_3$): δ 194.0, 150.3, 138.0, 132.9, 131.2 (d, $J = 2.9$ Hz), 129.68 – 129.23 (m), 127.0, 126.7, 19.9.

HRMS (EI-TOF): m/z calcd for C$_{10}$H$_9$DO [(M)$^+$]: 147.0794, found: 147.0796.

\begin{center}
\textbf{(E)-3-(m-tolyl)acrylaldehyde-$\alpha$-$d_1$ (5q)}
\end{center}

Following the general procedure, 1q (29.2 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow liquid (24.1 mg, 82% yield) with 96% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.69 (s, 1H), 7.45 (s, 1H), 7.37 (d, $J = 4.5$ Hz, 2H), 7.33 (t, $J = 5.7$ Hz, 1H), 7.26 (d, $J = 7.5$ Hz, 1H), 6.71 (dd, $J = 16.0$, 7.7 Hz, 0.04H), 2.39 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 194.0, 153.1, 138.9, 134.1, 132.2, 129.2, 129.1, 128.3 (t, $J = 24.2$ Hz), 125.8, 21.4.

HRMS (EI-TOF): m/z calcd for C$_{10}$H$_9$DO [(M)$^+$]: 147.0794, found: 147.0796.

\begin{center}
\textbf{(E)-3-(p-tolyl)acrylaldehyde-$\alpha$-$d_1$ (5r)}
\end{center}

Following the general procedure, 1r (29.2 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a light yellow solid (20.9 mg, 71% yield) with 98% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.68 (s, 1H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 2.6$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 2H), 6.68 (dd, $J = 15.9$, 7.7 Hz, 0.02H), 2.40 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 193.9, 153.0, 142.1, 131.4, 130.0, 128.7, 127.6 (t, $J = 24.3$ Hz), 21.7.

HRMS (EI-TOF): m/z calcd for C$_{10}$H$_9$DO [(M)$^+$]: 147.0794, found: 147.0792.

\begin{center}
\textbf{(E)-3-(2-methoxyphenyl)acrylaldehyde-$\alpha$-$d_1$ (5s)}
\end{center}

Following the general procedure, 1s (32.4 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a light yellow solid (25.1 mg, 77% yield) with 94% D-incorporation.
1H NMR (400 MHz, CDCl3): δ 9.68 (s, 1H), 7.83 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.79 (dd, J = 16.0, 7.9 Hz, 0.06H), 3.91 (s, 3H).

13C NMR (151 MHz, CDCl3): δ 194.7, 158.4, 148.3, 132.8, 129.18 – 128.75 (m), 129.0, 123.0, 121.0, 111.4, 55.7.

HRMS (EI-TOF): m/z caled for C10H9DO2 [(M)+]: 163.0744, found: 163.0746.

(E)-3-(4-methoxyphenyl)acrylaldehyde-α-d1 (5t)

Following the general procedure, 1t (32.4 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a yellow solid (30.6 mg, 94% yield) with 98% D-incorporation.

1H NMR (400 MHz, CDCl3): δ 9.66 (s, 1H), 7.53 (d, J = 8.7 Hz, 2H), 7.42 (s, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.61 (dd, J = 15.9, 7.8 Hz, 0.02H), 3.86 (s, 3H).

13C NMR (151 MHz, CDCl3): δ 193.9, 162.3, 152.8, 130.5, 126.9, 126.3 (t, J = 24.5 Hz), 114.7, 55.6.

2H NMR (77 MHz, CHCl3): δ 6.67 (s, 1D).

HRMS (EI-TOF): m/z caled for C10H9DO2 [(M)+]: 163.0744, found: 163.0742.

(E)-3-(4-(dimethylamino)phenyl)acrylaldehyde-α-d1 (5u)

Following the general procedure, 1u (35 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, toluene (1 mL) instead of DCM, and the reaction mixture was vigorously stirred at 80 °C for 48 h. The title compound was obtained as a yellow solid (23.2 mg, 66% yield) with 98% D-incorporation.

1H NMR (400 MHz, CDCl3): δ 9.59 (s, 1H), 7.49 – 7.43 (m, 2H), 7.37 (s, 1H), 6.71 – 6.67 (m, 2H), 6.54 (dd, J = 15.6, 7.9 Hz, 0.02H), 3.05 (s, 6H).

13C NMR (151 MHz, CDCl3): δ 193.8, 154.0, 152.5, 130.6, 123.6 (t, J = 24.2 Hz), 121.8, 111.8, 40.2.

HRMS (EI-TOF): m/z caled for C11H12DNO [(M)+]: 176.1060, found: 176.1063.

(E)-3-(3,4-dimethoxyphenyl)acrylaldehyde-α-d1 (5v)

Following the general procedure, 1v (38.4 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a black solid.
(34.3 mg, 89% yield) with 97% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.67 (s, 1H), 7.42 (s, 1H), 7.17 (d, $J = 8.3$ Hz, 1H), 7.08 (s, 1H), 6.91 (d, $J = 8.3$ Hz, 1H), 6.62 (dd, $J = 15.8$, 7.7 Hz, 0.03H), 3.94 (d, $J = 3.7$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 193.7, 152.9, 152.1, 149.5, 127.1, 126.67 – 126.35 (m), 123.6, 111.2, 109.9, 56.1, 56.0.

HRMS (EI-TOF): m/z caled for C$_{11}$H$_{11}$DO$_3$ [(M$^+$)]: 193.0849, found: 193.0847.

Following the general procedure, 1w (44 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a light yellow solid (30.1 mg, 68% yield) with 91% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.70 (s, 1H), 7.43 (s, 1H), 7.17 (dd, $J = 8.1$, 1.8 Hz, 1H), 7.14 (d, $J = 1.8$ Hz, 1H), 7.10 (d, $J = 8.1$ Hz, 1H), 6.67 (dd, $J = 15.9$, 7.6 Hz, 0.09H), 3.88 (s, 3H), 2.33 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 193.6, 168.8, 151.9, 151.7, 142.3, 133.0, 128.84 – 128.40 (m), 123.6, 122.0, 111.5, 56.0, 20.8.

$^2$H NMR (77 MHz, CHCl$_3$): δ 6.72 (s, 1D).

HRMS (EI-TOF): m/z caled for C$_{12}$H$_{11}$DO$_4$ [(M$^+$)]: 221.0798, found: 221.0800.

Following the general procedure, 1x (36.4 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a yellow solid (22.7 mg, 62% yield) with 98% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.84 (s, 1H), 8.31 (s, 1H), 8.18 (d, $J = 8.4$ Hz, 1H), 7.96-7.89 (m, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.64-7.50 (m, 3H), 6.83 (dd, $J = 15.6$, 7.7 Hz, 0.02H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 193.8, 149.3, 133.9, 131.7, 131.3, 131.0, 130.7 (t, $J = 24.6$ Hz), 129.1, 127.4, 126.5, 125.9, 125.6, 122.9.

HRMS (EI-TOF): m/z caled for C$_{13}$H$_{9}$DO [(M$^+$)]: 183.0794, found: 183.0791.
(E)-3-(1-benzyl-1H-pyrrol-2-yl)acrylaldehyde-α-d₁ (5y)

Following the general procedure, 1y (42.2 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a black solid (39 mg, 92% yield) with 85% D-incorporation.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl₃): } & \delta 9.41 (s, 1H), 7.35-7.28 (m, 3H), 7.21 (s, 1H), 7.03 (d, J = 7.3 \text{ Hz}, 2H), 6.95 (s, 1H), 6.83 (d, J = 3.8 \text{ Hz}, 1H), 6.40 (dd, J = 15.5, 7.9 \text{ Hz}, 0.15H), 6.34 – 6.29 (m, 1H), 5.25 (s, 2H). \\
\text{C NMR (151 MHz, CDCl₃): } & \delta 193.1, 139.7, 137.0, 129.1, 129.0, 128.6, 128.1, 126.2, 124.15 – 123.71 (m), 114.6, 110.8, 51.0. \\
\text{H NMR (77 MHz, CHCl₃): } & \delta 6.46 (s, 1D). \\
\text{HRMS (EI-TOF): } & m/z \text{ caled for C}_{14}H_{12}DNO } [(M)+]: 212.1060, \text{ found: 212.1057.}
\end{align*}
\]

(E)-3-(Furan-2-yl)acrylaldehyde-α-d₁ (5z)

Following the general procedure, 1z (24.4 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a white solid (17.3 mg, 70% yield) with 96% D-incorporation at α-position and 17% D-incorporation at C-5 position of furan.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl₃): } & \delta 9.62 (s, 1H), 7.57 (s, 1H), 7.24 – 7.19 (m, 1H), 6.77 (d, J = 3.3 \text{ Hz}, 1H), 6.59 (dd, J = 14.2, 6.3 \text{ Hz}, 0.04H), 6.54 (dd, J = 3.4, 1.8 \text{ Hz}, 0.83H). \\
\text{C NMR (151 MHz, CDCl₃): } & \delta 192.9, 150.5, 145.9, 137.7, 125.83 – 125.34 (m), 116.8, 116.7, 112.9. \\
\text{H NMR (77 MHz, CHCl₃): } & \delta 6.63 (s, 1.17D), \text{ two deuterium peaks are overlapped.} \\
\text{HRMS (EI-TOF): } & m/z \text{ caled for C}_7H_4D_2O_2 } [(M)+]: 124.0493, \text{ found: 124.0490.}
\end{align*}
\]

(E)-3-(1-Benzyl-1H-imidazol-5-yl)acrylaldehyde-α-d₁ (5aa)

Following the general procedure, 1aa (42.2 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a yellow solid (36.6 mg, 86% yield) with 92% D-incorporation.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl₃): } & \delta 9.41 (s, 1H), 7.35-7.28 (m, 3H), 7.21 (s, 1H), 7.03 (d, J = 7.3 \text{ Hz}, 2H), 6.95 (s, 1H), 6.83 (d, J = 3.8 \text{ Hz}, 1H), 6.40 (dd, J = 15.5, 7.9 \text{ Hz}, 0.15H), 6.34 – 6.29 (m, 1H), 5.25 (s, 2H). \\
\text{C NMR (151 MHz, CDCl₃): } & \delta 193.1, 139.7, 137.0, 129.1, 129.0, 128.6, 128.1, 126.2, 124.15 – 123.71 (m), 114.6, 110.8, 51.0. \\
\text{H NMR (77 MHz, CHCl₃): } & \delta 6.46 (s, 1D). \\
\text{HRMS (EI-TOF): } & m/z \text{ caled for C}_{14}H_{12}DNO } [(M)+]: 212.1060, \text{ found: 212.1057.}
\end{align*}
\]
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.60 (s, 1H), 7.62 (s, 1H), 7.41-7.36 (m, 3H), 7.33 (s, 1H), 7.23 (s, 1H), 7.22 – 7.16 (m, 2H), 6.77 (dd, $J$ = 15.6, 8.0 Hz, 0.08H), 5.14 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 193.6, 144.3, 139.2, 138.4, 135.2, 129.2, 128.6, 127.5, 126.8 (t, $J$ = 27.9 Hz), 122.9, 51.2.

HRMS (EI-TOF): m/z caled for C$_{13}$H$_{11}$DN$_2$O [$(M)+$]: 213.1012, found: 213.1015.

Following the general procedure, 1ab (39.8 mg, 0.2 mmol) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 48 h. The title compound was obtained as a white solid (30 mg, 75% yield) with 72% D-incorporation.

Following the general procedure, (E)-3-(3-Phenylisoxazol-5-yl)acrylaldehyde-α-d$_1$ (30 mg, 0.15 mmol, deuteration 72%) was used in the deuteration reaction, PhCOOH (3.7 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 72 h. The title compound was obtained as a white solid (19.6 mg, 49% yield for two steps) with 95% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.76 (s, 1H), 7.84 – 7.81 (m, 2H), 7.50 – 7.45 (m, 3H), 7.36  (s, 1H), 6.90 (s, 1H), 6.86 (s, 0.05H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 192.1, 165.8, 163.2, 133.2, 131.69 – 132.25 (m), 130.5, 129.1, 128.2, 126.8, 105.1.

HRMS (EI-TOF): m/z caled for C$_{12}$H$_{8}$DNO$_2$ [$(M)+$]: 200.0696, found: 200.0694.

Following the general procedure, 1ac (42.6 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a white solid (39.3 mg, 92% yield) with 98% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.64 (s, 1H), 7.78 (s, 1H), 7.46 (s, 1H), 7.40 – 7.37 (m, 3H), 7.31 – 7.29 (m, 2H), 6.77 (dd, $J$ = 15.9, 7.7 Hz, 0.02H), 5.57 (s, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.2, 147.3, 140.1, 134.1, 129.77 – 129.33 (m), 129.2, 129.1, 128.3, 123.9, 54.4.

HRMS (EI-TOF): m/z caled for C$_{12}$H$_{10}$DN$_3$O [$(M)+$]: 214.0965, found: 214.0963.
Following the general procedure, 1ad (52.2 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 60 h. The title compound was obtained as a yellow solid (50.3 mg, 96% yield) with 99% D-incorporation.

\[ {\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 9.60 \text{ (s, 1H), 7.94 – 7.88 (m, 1H), 7.64 (s, 1H), 7.49 (s, 1H), 7.36 – 7.19 (m, 6H), 7.19 – 7.14 (m, 2H), 6.76 (dd, } J = 15.6, 7.9 \text{ Hz, 0.01H), 5.35 (s, 2H).}} \]

\[ {\text{C NMR (151 MHz, CDCl}_3\text{): } \delta 194.2, 146.3, 138.0, 135.9, 133.5, 129.2, 128.4, 127.2, 126.3, 124.4 (t, } J = 23.9 \text{ Hz), 123.7, 122.2, 120.8, 113.0, 110.8, 50.8.}} \]

HRMS (EI-TOF): m/z calcd for C18H14DNO [(M)+]: 262.1216, found: 262.1220.

Following the general procedure, (E)-3-(1-Benzyl-1H-indol-3-yl)acrylaldehyde-\(\alpha\)-d\(1\) (5ae) was used in the deuteration reaction, PhCOOH (4.9 mg, 20 mol%) was added, toluene (1 mL) instead of DCM, and the reaction mixture was vigorously stirred at 80 °C for 48 h. The title compound was obtained as a yellow solid (46.1 mg, 75% yield) with 82% D-incorporation.

\[ {\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 9.57 \text{ (s, 0.82H), 7.61 (d, } J = 8.5 \text{ Hz, 1H), 7.59 – 7.52 (m, 2H), 7.41 – 7.38 (m, 2H), 7.32 (t, } J = 7.7 \text{ Hz, 1H), 7.19 (t, } J = 8.5 \text{ Hz, 2H), 7.13 (t, } J = 7.5 \text{ Hz, 1H), 6.32 (dd, } J = 16.1, 7.3 \text{ Hz, 0.04H), 5.01 – 4.94 (m, 1H), 1.75 (s, 3H), 1.73 (s, 3H).}} \]

\[ {\text{C NMR (151 MHz, CDCl}_3\text{): } \delta 193.4, 162.3 (d, } J = 247.1 \text{ Hz), 141.1, 137.6, 132.0 (d, } J = 8.0 \text{ Hz), 130.5, 129.95, 129.92, 129.7, 129.2 (t, } J = 24.6 \text{ Hz), 128.5, 124.8, 122.9, 121.1, 120.8, 116.1, 116.0, 112.6, 48.4, 21.9.}} \]

\[ {\text{H NMR (77 MHz, CHCl}_3\text{): } \delta 6.37 (s, 1D), 9.62 (s, 0.14D).}} \]

\[ {\text{F NMR (565 MHz, CDCl}_3\text{): } \delta -114.51 \text{ (s, 1F).}} \]

HRMS (EI-TOF): m/z calcd for C20H17DFNO [(M)+]: 308.1435, found: 308.1438.
(E)-3-((Ferrocenyl)acrylaldehyde-a-d1 (5af)

Following the general procedure, 1af (48.0 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a black solid (44 mg, 91% yield) with 98% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.55 (s, 1H), 7.41 (s, 1H), 6.34 (dd, $J = 15.6, 8.0$ Hz, 0.02H), 4.53 (dd, $J = 12.1, 1.6$ Hz, 4H), 4.16 (s, 5H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.3, 155.2, 126.2 (t, $J = 24.2$ Hz), 77.9, 72.0, 70.1, 69.3.

HRMS (EI-TOF): m/z calcd for C$_{13}$H$_{11}$DFeO [(M)$^+$]: 241.0301, found: 241.0303.

(2E,2'E)-3,3'-(1,4-phenylene)diacrylaldehyde-a-d1 (5ag)

Following the general procedure, 1ag (37.2 mg, 0.2 mmol) was used in the deuteration reaction, 3 (26.0 mg, 40 mol%), 2b (23.7 mg, 40 mol%), PhCOOH (9.8 mg, 40 mol%) and D$_2$O (1 mL) was added, the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a white solid (30.1 mg, 80% yield) with 99% D-incorporation.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.72 (s, 2H), 7.62 (s, 4H), 7.47 (s, 2H), 6.78 – 6.72 (m, 0.02H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.4, 150.8, 136.5, 129.74 – 129.21 (m), 129.1.

HRMS (EI-TOF): m/z calcd for C$_{12}$H$_8$D$_2$O$_2$ [(M)$^+$]: 188.0806, found: 188.0804.

(2E,4E)-5-phenylpenta-2,4-dienal-a-d1 (5ah)

Following the general procedure, 1ah (31.6 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a yellow liquid (26.7 mg, 84% yield) with 99% D-incorporation at α-position and 9% D-incorporation at γ-position.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.62 (s, 1H), 7.54 – 7.48 (m, 2H), 7.41-7.32 (m, 3H), 7.28 – 7.23 (m, 1H), 7.05 – 6.96 (m, 2H), 6.27 (dd, $J = 15.2, 8.0$ Hz, 0.01H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 193.7, 152.0, 142.5, 135.7, 131.4 (t, $J = 24.6$ Hz), 129.8, 129.0, 127.6, 126.3.

$^2$H NMR (77 MHz, CHCl$_3$): $\delta$ 6.33 (s, 1D), 7.07 (s, 0.09D).

HRMS (EI-TOF): m/z calcd for C$_{11}$H$_9$DO [(M)$^+$]: 159.0794, found: 159.0791.
(2E,4E)-5-(4-nitrophenyl)penta-2,4-dienal-α-d1 (5ai)

Following the general procedure, 1ai (40.6 mg, 0.2 mmol) was used in the deuteration reaction, and the reaction mixture was vigorously stirred at 50 °C for 24 h. The title compound was obtained as a yellow solid (27.7 mg, 68% yield) with 96% D-incorporation at α-position and 1% D-incorporation at γ-position.

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta 9.68 (s, 1H), 8.25 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 11.1 Hz, 1H), 7.18-7.04 (m, 2H), 6.37 (dd, J = 14.9, 7.4 Hz, 0.04H). \]

\[ ^13C \text{NMR (151 MHz, CDCl}_3\text{): } \delta 193.2, 149.9, 147.9, 141.7, 139.0, 133.3 (t, J = 24.8 Hz), 130.2, 128.0, 124.3. \]

\[ ^2H \text{NMR (77 MHz, CHCl}_3\text{): } \delta 6.42 (s, 1D), 7.20 (s, 0.01D). \]

HRMS (EI-TOF): m/z caled for C\textsubscript{11}H\textsubscript{8}DNO\textsubscript{3} [(M)+]: 204.0645, found: 204.0648.

(2E,4E)-5-(4-methoxyphenyl)penta-2,4-dienal-α-d1 (5aj)

Following the general procedure, 1aj (37.6 mg, 0.2 mmol) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, PhCOOH (4.9 mg, 20 mol%) was added, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound was obtained as a yellow solid (28.0 mg, 74% yield) with 99% D-incorporation at α-position and 10% D-incorporation at γ-position.

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta 9.59 (s, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 10.5 Hz, 1H), 6.99 – 6.84 (m, 4H), 6.22 (dd, J = 15.1, 8.0 Hz, 0.01H), 3.84 (s, 3H). \]

\[ ^13C \text{NMR (151 MHz, CDCl}_3\text{): } \delta 193.7, 161.1, 152.7, 142.4, 130.4 (t, J = 24.8 Hz), 129.3, 128.5, 124.2, 114.5, 55.5. \]

\[ ^2H \text{NMR (77 MHz, CHCl}_3\text{): } \delta 6.28 (s, 1D), 6.93 (s, 0.1D). \]

HRMS (EI-TOF): m/z caled for C\textsubscript{12}H\textsubscript{11}DO\textsubscript{2} [(M)+]: 189.0900, found: 189.0903.

6. Applications of α-Deuterated Enals

1-nitro-2-vinylbenzene-1,1-d\textsubscript{2} (8c)

\[ \text{PdOAc}_2, 4\text{A MS, 140 °C} \]
A clean, oven-dried screw cap reaction tube with previously placed magnetic stir-bar was charged with molecular sieves (4Å, 150 mg), 5c (89 mg, 0.5 mmol, 99% D-incorporation), Pd(OAc)$_2$ (9 mg, 8 mol%). Cyclohexane (2 mL) was added to this mixture by syringe. The tube was closed by screw cap and placed in a preheated oil bath at 140 °C. The reaction mixture was vigorously stirred for 6 h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube and the residue was washed with EtOAc (20 mL). The filtrate was concentrated and purified by column chromatography to give the title compound 8c as a yellow oil (37 mg, 49% yield) with 94% D-incorporation at D$_1$-position, and 4% D-incorporation at D$_2$-position.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J$ = 8.2 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.45 – 7.38 (m, 1H), 7.22 – 7.13 (m, 1H), 5.74 (dd, $J$ = 17.3, 6.2 Hz, 0.06H), 5.48 (dd, $J$ = 10.9, 5.9 Hz, 0.96H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 148.0, 133.5, 133.3, 132.6, 128.7, 128.5, 124.6, 118.7 (t, $J$ = 24.0 Hz).

$^2$H NMR (77 MHz, CHCl$_3$): $\delta$ 5.80 (d, $J$ = 2.6 Hz, 1D), 5.54 (d, $J$ = 1.2 Hz, 0.04D).

HRMS (EI-TOF): m/z caled for C$_8$H$_6$D$_1$NO$_2$ [(M$^+$)]: 150.0540, found: 150.0536.
(2E,4E)-5-(4-methoxyphenyl)penta-2,4-dienal-α-γ-d2 (11)

To a stirred solution of 5t (603 mg, 3.7 mmol, 98% D-incorporation) in THF (30 mL) was added 9 (2.38 g, 5.55 mmol), NaH (747 mg, 18.69 mmol), and 18-crown-6 (88 mg) under N2 at 0 ºC. The reaction was slowly warmed to room temperature and stirred overnight. 1N HCl (15 mL) was added slowly to quench the reaction, and the mixture was stirred for 30 min and neutralized with ammonia water, then extracted with DCM (30 mL × 3). The combined organic solution was washed with saturated brine (20 mL), dried over Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography to give the title compound 10 as a yellow solid (476 mg, 68% yield) with 98% D-incorporation.

1H NMR (400 MHz, CDCl3): δ 9.59 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.29 – 7.21 (m, 1H), 6.97 (s, 1H), 6.91 (d, J = 8.8 Hz, 2.02H), 6.23 (dd, J = 15.2, 8.0 Hz, 1H), 3.84 (s, 3H).

13C NMR (151 MHz, CDCl3): δ 193.8, 161.1, 152.8, 142.4, 130.7, 129.3, 128.5, 123.9 (t, J = 23.6 Hz), 114.6, 55.5.

HRMS (ESI-TOF): calculated for C12H12DO2 [(M + H)] +: 190.0978, found: 190.0979.

Following the general procedure, 10 (37.8 mg, 0.2 mmol, deuteration 98%) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, and the reaction mixture was vigorously stirred at 50 ºC for 96 h. The title compound 11 was obtained as a yellow solid (25 mg, 66% yield) with 98% D-incorporation at α- and γ-position.

1H NMR (400 MHz, CDCl3): δ 9.59 (s, 1H), 7.45 (d, J = 8.8 Hz, 2H), 7.24 (s, 1H), 6.96 (s, 1H), 6.91 (d, J = 8.8 Hz, 2.02H), 6.23 (dd, J = 15.2, 8.0 Hz, 1H), 3.84 (s, 3H).

13C NMR (151 MHz, CDCl3): δ 193.8, 161.1, 152.8, 142.4, 130.7, 129.3, 128.5, 123.9 (t, J = 23.6 Hz), 114.6, 55.5.

2H NMR (77 MHz, CHCl3): δ 6.94 (s, 1D), 6.28 (s, 1D).


(E)-3-(4-bromophenyl)acrylaldehyde-α-β-d2 (15)
A mixture of 12 (930 mg, 5 mmol, 98% D-incorporation) and 13 (2.13 g, 7 mmol) in toluene (40 mL) was vigorously stirred at 80 °C for 17 h under N₂. Then the reaction was concentrated under reduced pressure and purified by column chromatography to give the title compound 14 as a brown solid (606 mg, 57% yield) with 98% D-incorporation.

**1H NMR (400 MHz, CDCl₃):** δ 9.71 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 6.72 – 6.68 (m, 1H).

**13C NMR (151 MHz, CDCl₃):** δ 193.5, 150.9 (t, J = 23.6 Hz), 133.0, 132.6, 129.9, 129.0, 125.9.

**HRMS (ESI-TOF):** calculated for C₉H₇DBrO [(M + H)]⁺: 211.9821, found: 211.9824.

Following the general procedure, 14 (42.4 mg, 0.2 mmol, 98% D-incorporation) was used in the deuteration reaction, 2a (12.6 mg, 0.04 mmol) instead of 2b was used, and the reaction mixture was vigorously stirred at 50 °C for 96 h. The title compound 15 was obtained as a yellow solid (40.5 mg, 95% yield) with 98% D-incorporation at α- and β-position.

**1H NMR (400 MHz, CDCl₃):** δ 9.71 (s, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2.02H), 6.70 (dd, J = 8.4, 2.8 Hz, 0.02H).

**13C NMR (151 MHz, CDCl₃):** δ 193.5, 150.8 (t, J = 23.4 Hz), 133.0, 132.6, 129.9, 129.09 – 128.64 (m), 125.9.

**2H NMR (77 MHz, CHCl₃):** δ 7.46 (s, 1D), 6.75 (s, 1D).

**HRMS (ESI-TOF):** m/z caled for C₉H₆D₂BrO [(M + H)]⁺: 212.9884, found: 212.9883.

(E)-3-(4-bromophenyl)acrylaldehyde-1-2-3-d₃ (16)

Following the reported procedure, 15 (106 mg, 0.5 mmol), 23 (10 mol%) and KOAc (49.07 mg, 0.5 mmol) 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 60 °C for 12 h. The title compound 16 was obtained as a yellow solid (33 mg, 31% yield) with 98% D-incorporation at α- and β-position and 99% D-incorporation at aldehyde C1-
position.

1H NMR (400 MHz, CDCl3): $\delta$ 9.7 (s, 0.00H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2.02H), 6.70 (s, 0.02H).

13C NMR (101 MHz, CDCl3): $\delta$ 193.3 (t, $J = 26.6$ Hz), 150.8 (t, $J = 23.5$ Hz), 132.9, 132.5, 129.9, 128.97 – 128.48 (m), 125.8.

2H NMR (77 MHz, CHCl3): $\delta$ 9.75 (s, 1.03D), 7.46 (s, 1D), 6.74 (s, 1D).


Ethyl (2E,4E)-5-(4-bromophenyl)penta-2,4-dienoate-4-5-d2 (18)

Following the reported procedure,12 to a stirred solution of NaH (13.2 mg, 0.33 mmol) in dry THF (3 mL) was added 17 (74 mg, 0.33 mmol) dropwise under N2 at 0 °C. The mixture was stirred for 1 h before a solution of 15 (63.6 mg, 0.3 mmol) in THF (2 mL) was added dropwise. The reaction was slowly warmed to room temperature and stirred until completion monitored by TLC. The reaction was quenched with saturated NH4Cl (5 mL) and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic solution was washed with saturated brine (5 mL), dried over Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography to give the title compound 18 as light a yellow solid (55.5 mg, 65% yield) with 97% D-incorporation at γ-position and 98% D-incorporation at δ-position.

1H NMR (400 MHz, CDCl3): $\delta$ 7.47 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 15.6$ Hz, 1H), 7.31 (d, $J = 8.8$ Hz, 2H), 6.85 (s, 0.02H), 6.82 (d, $J = 6.8$ Hz, 0.03H), 6.00 (d, $J = 15.2$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 7.2$ Hz, 3H).

13C NMR (151 MHz, CDCl3): $\delta$ 167.0, 144.1, 138.85 – 138.34 (m), 135.0, 132.1, 128.7, 126.88 – 126.44 (m), 123.1, 122.0, 60.5, 14.4.

2H NMR (77 MHz, CHCl3): $\delta$ 6.87 (s, 2D), two deuterium peaks are overlapped.

HRMS (ESI-TOF): m/z caled for C13H12D2BrO2 [(M + H)⁺: 283.0303, found: 283.0301.

(E)-1-(buta-1,3-dien-yl)-4-nitrobenzene-3-d1 (20)
Following the reported procedure,\(^{14}\) to a stirred solution of 19 (129 mg, 0.36 mmol) in THF (2 mL) was added n-BuLi (0.16 mL, 0.39 mmol, 2.5 M in hexane) dropwise at 0 °C under N\(_2\). The reaction was slowly warmed to room temperature and stirred for 30 min, giving a dark red solution. 5a (53.4 mg, 0.3 mmol) in THF (1.0 mL) was then added dropwise at room temperature and stirred overnight. Then petroleum ether (5 mL) was added to the reaction mixture and stirred for 1 h. The reaction was filtered through celite and concentrated under reduced pressure. The crude product was purified by column chromatography to give the title compound 20 as a light yellow oil (24.2 mg, 46% yield) with 98% D-incorporation.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): δ 8.18 (d, \(J = 8.8\) Hz, 2H), 7.52 (d, \(J = 8.8\) Hz, 2H), 6.93 (dd, \(J = 15.6, 10.8\) Hz, 0.02H), 6.64 – 6.45 (m, 2H), 5.48 (d, \(J = 17.2\) Hz, 1H), 5.35 (d, \(J = 10.0\) Hz, 1H).

\(^{1}\)C NMR (151 MHz, CDCl\(_3\)): δ 146.8, 143.7, 136.4, 134.06 – 133.59 (m), 130.3, 126.9, 124.1, 120.9.

\(^{2}\)H NMR (77 MHz, CHCl\(_3\)): δ 6.90 (s, 1D).

HRMS (EI-TOF): m/z caled for C\(_{10}\)H\(_8\)DNO\(_2\) [(M)+]: 176.0696, found: 176.0697.

\((E)\)-1-(but-1-en-3-yn-1-yl)-4-nitrobenzene-2-\(d_1\) (21)

Following the reported procedure,\(^{15}\) to a stirred solution of 5a (178 mg, 1 mmol) and CBr\(_4\) (664 mg, 2 mmol) in anhydrous DCM (10 mL) was added Ph\(_3\)P (3.05 g, 4 mmol) in portions over a period of 20 min under N\(_2\) at 0 °C. The reaction mixture was turned brown and allowed to stir at 0 °C for 2 h. H\(_2\)O (5 mL) was added to the reaction mixture, and the reaction mixture was extracted with DCM (10 mL \(\times\) 3), the combined organic solution was washed with saturated brine (10 mL), dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude product was purified by column chromatography to give the compound \((E)\)-1-(4,4-dibromobuta-1,3-dien-1-yl)-4-nitrobenzene as a light yellow solid (315 mg, 95% yield) .

To a stirred solution of \((E)\)-1-(4,4-dibromobuta-1,3-dien-1-yl)-4-nitrobenzene (315 mg, 0.95 mmol) in anhydrous CH\(_2\)CN (4 mL) was added DBU (578 mg, 3.8 mmol) dropwise at room temperature. The reaction mixture was stirred for 16 h at rt, then the solvent was removed under reduced pressure. The crude product was purified by column chromatography to give the title compound 21 as a light yellow oil (64.4 mg, 39%
yield) with 98% D-incorporation.

**$^1$H NMR (400 MHz, CDCl$_3$):** $\delta$ 8.21 (d, $J$ = 8.8 Hz, 2H), 7.53 (d, $J$ = 8.8 Hz, 2H), 7.07 (s, 1H), 6.30 (dd, $J$ = 16.0, 2.4 Hz, 0.02H), 3.21 (s, 1H).

**$^{13}$C NMR (151 MHz, CDCl$_3$):** $\delta$ 147.8, 142.1, 140.6, 127.0, 124.3, 112.05 – 111.60 (m), 82.1, 82.0.

**$^2$H NMR (77 MHz, CHCl$_3$):** $\delta$ 6.34 (s, 1D).

**HRMS (EI-TOF):** m/z caled for C$_{10}$H$_6$DNO$_2$ [(M)$^+$]: 174.0540, found: 174.0542.
7. References


8. NMR Spectra

$^1$H NMR of 1b

$^{13}$C NMR of 1b
$^{1}H$ NMR of 1e

$^{13}C$ NMR of 1e
$^{19}$F NMR of 1e

$^1$H NMR of 1f
$^{13}\text{C}$ NMR of 1f

$^{19}\text{F}$ NMR of 1f
$^1$H NMR of $1h$

$^{13}$C NMR of $1h$
$^1$H NMR of 11

$^{13}$C NMR of 11
$^{19}F$ NMR of 11

$^1H$ NMR of 1m
$^{13}$CNMR of 1m

$^1$H NMR of 1n
$^{13}$C NMR of 1n

$^{1}$H NMR of 1p
$^{13}$C NMR of 1p

$^1$H NMR of 1q
$^{13}$C NMR of 1q

$^1$H NMR of 1v
$^{13}$C NMR of $1v$

$^1$H NMR of $1x$
$^{13}$C NMR of $1x$

$^1$H NMR of $1y$
$^{13}$C NMR of 1y

$^1$H NMR of 1z
$^1$H NMR of 1aa

$^{13}$C NMR of 1aa
$^1$H NMR of 1ab

$^{13}$C NMR of 1ab
$^1$H NMR of 1ac

$^{13}$C NMR of 1ac
$^1$H NMR of 1ad

$^{13}$C NMR of 1ad
$^1$H NMR of 1ag

$^{13}$C NMR of 1ag
$^1$H NMR of 1ah

$^{13}$C NMR of 1ah
$^1$H NMR of 1ai

13C NMR of 1ai
$^1$H NMR of 1aj

$^{13}$C NMR of 1aj
$^1$H NMR of $5a$

$^1$H NMR of scale up $5a$
$^{13}$C NMR of 5a

$^{2}$H NMR of 5a
$^1$H NMR of 5b

$^{13}$C NMR of 5b
$^1$H NMR of 5c

$^{13}$C NMR of 5c
$^1$H NMR of 5d

$^{13}$C NMR of 5d
$^{19}$F NMR of 5d

$^1$H NMR of 5e
\(^{13}\text{C}\) NMR of 5e

\(^{19}\text{F}\) NMR of 5e
$^1$H NMR of 5f

$^{13}$C NMR of 5f
$^{19}$F NMR of 5f

$^1$H NMR of 5g
$^{13}$C NMR of 5g

$^{19}$F NMR of 5g
$^1$H NMR of 5h

$^{13}$C NMR of 5h
$^1$H NMR of 5i

$^{13}$C NMR of 5i
$^1$H NMR of 5j

$^{13}$C NMR of 5j
$^{1}H$ NMR of 5k

$^{13}C$ NMR of 5k
$^1$H NMR of 5I

$^{13}$C NMR of 5I
$^2\text{H}$ NMR of 5l

$^{19}\text{F}$ NMR of 5l
\(^{1}H\) NMR of 5m

\(^{13}C\) NMR of 5m
$^2$H NMR of 5m

$^1$H NMR of 5n
$^{13}$C NMR of 5n

$^2$H NMR of 5n
$^1$H NMR of 5o

$^{13}$C NMR of 5o
$^2$H NMR of 5o

$^1$H NMR of 5p
$^{13}$C NMR of $5p$

$^1$H NMR of $5q$
$^{13}$C NMR of 5q

$^1$H NMR of 5r
$^{13}$C NMR of 5r

$^1$H NMR of 5s
$^{13}$C NMR of 5s

$^1$H NMR of 5t
$^{13}$C NMR of 5t

$^2$H NMR of 5t
$^1$H NMR of 5u

$^{13}$C NMR of 5u
$^1$H NMR of 5v

$^{13}$C NMR of 5v
$^1$H NMR of 5w

$^{13}$C NMR of 5w
$^2$H NMR of 5w

$^1$H NMR of 5x
$^{13}$C NMR of $5x$

$^1$H NMR of $5y$
$^{13}$C NMR of 5y

$^{2}$H NMR of 5y
$^1$H NMR of 5z

$^{13}$C NMR of 5z
$^2$H NMR of 5z

$^1$H NMR of 5aa
$^{13}$C NMR of 5aa

$^1$H NMR of 5ab
$^{13}$C NMR of $5_{\text{ab}}$

$^1$H NMR of $5_{\text{ac}}$
$^{13}$C NMR of 5ac

$^1$H NMR of 5ad
$^{13}$C NMR of 5ad

$^1$H NMR of 5ae
$^{13}$C NMR of 5ae

$^2$H NMR of 5ae
$^{19}$F NMR of 5ae

$^{1}$H NMR of 5af
$^{13}$C NMR of 5af

$^1$H NMR of 5ag
$^1$H NMR of 5ag

$^{13}$C NMR of 5ag

$^1$H NMR of 5ah

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

$^2$H NMR of 5ah
$^1$H NMR of 5ai

$^{13}$C NMR of 5ai
$^2\text{H NMR of 5ai}$

$^1\text{H NMR of 5aj}$
$^{13}$C NMR of 5aj

$^2$H NMR of 5aj
$^1$H NMR of 8c

$^{13}$C NMR of 8c
$^2$H NMR of 8c

$^1$H NMR of 10
$^{13}$C NMR of 10

$^1$H NMR of 11
$^{13}$C NMR of 11

2H NMR of 11
$^{1}H$ NMR of 14

$^{13}C$ NMR of 14
$^{1}H$ NMR of 15

$^{13}C$ NMR of 15
$^{2\text{H}}$ NMR of 15

$^{1\text{H}}$ NMR of 16
$^{13}\text{C} \text{ NMR of 16}$

$^{2}\text{H} \text{ NMR of 16}$
$^{1}H$ NMR of 18

$^{13}C$ NMR of 18
$^2$H NMR of 18

$^1$H NMR of 20
$^{13}$C NMR of 20

$^2$H NMR of 20
$^1$H NMR of 21

$^{13}$C NMR of 21
$^2$H NMR of 21