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Supporting Information for

Catalytic Deuteration of Aldehydes with D$_2$O

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1. General considerations

1.1 General experimental details

Unless otherwise indicated, reactions were conducted under an atmosphere of argon in 5 mL screw-capped vials that were oven dried (120 °C). Column chromatography was performed using Silicycle F60 40-63 µm silica gel. Analytical thin layer chromatography (TLC) was conducted with aluminum-backed EMD Millipore Silica Gel 60 F254 pre-coated plates. Visualization of developed plates was performed under UV light (254 nm) and/or using KMnO4, p-anisaldehyde, or ceric ammonium molybdate (CAM) stains.

1.2 Instrumentation

$^1$H and $^{13}$C spectra were recorded on a Bruker AVANCE 300 or 400 MHz spectrometer, as indicated. $^1$H NMR spectra were internally referenced to the residual solvent signal (e.g. CDCl$_3$ = 7.26 ppm). Data for $^1$H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. NMR yields for optimization studies were obtained by $^1$H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

1.3 Materials

Organic solvents were purified by rigorous degassing with nitrogen before passing through a PureSolv solvent purification system, and low water content was confirmed by Karl Fischer titration (<25 ppm for all solvents). RuHCl(CO)(PPh$_3$)$_3$ was obtained from Alfa Aesar or synthesized in house. $^3$D$_2$O was obtained from Cambridge Isotope Laboratories. Aldehydes were purchased from Sigma Aldrich, Oakwood, Alfa Aesar, and Combi-Blocks. Liquid aldehydes were distilled prior to use; solid aldehydes were used as received.
2. Experimental details

2.1 Representative General Procedure

Aldehyde (0.3 mmol) and RuHCl(CO)(PPh₃)₃ (14.3 mg, 0.015 mmol, 5 mol%) were dissolved in PhMe (1.5 mL, 0.2 M) in an oven-dried screw-cap vial. D₂O (27 μL, 1.5 mmol) was then added. The vial was sparged with argon and capped. The resulting solution was heated to 100 °C and stirred for 30 minutes. At the end of the reaction, the solvent was removed in vacuo and crude material was purified by column chromatography.

2.2 Product characterization

2-Napthaldehyde-α-D (2a) was prepared with the corresponding aldehyde (46.8 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 41.9 mg of 2a as a white solid (89% yield, 72% D). Characterization data matched those previously reported. ²¹H NMR (CDCl₃, 400 MHz) δ 8.35 (s, 1H), 8.02-7.90 (m, 4H), 7.67-7.57 (m, 2H). Residual formyl proton: δ 10.1.

4-Methylbenzaldehyde-α-D (2b) was prepared with the corresponding aldehyde (36.0 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 27.5 mg of 2b as a colorless oil (76% yield, 84% D). Characterization data matched those previously reported. ³¹H NMR (CDCl₃, 400 MHz) δ 7.78 (d, J = 8.04 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H). Residual formyl proton: δ 9.9.

6-Methoxy-2-napthaldehyde-α-D (2c) was prepared with the corresponding aldehyde (55.8 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 50.4 mg of 2c as a white solid (90% yield, 84% D). Characterization data matched those previously reported. ⁴¹H NMR (CDCl₃, 300 MHz) δ 8.21 (s, 1H), 7.90 (dd, J = 8.5, 1.6 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.21 (dd, J = 8.9, 2.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 3.93 (s, 3H). Residual formyl proton: δ 10.0.
**4-Methoxybenzaldehyde-α-D (2d)** was prepared with the corresponding aldehyde (40.8 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 33.2 mg of 2d as a colorless oil (81% yield, 84% D). Characterization data matched those previously reported.\(^5\) \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.83 (d, \(J = 8.8\) Hz, 2H), 6.99 (d, \(J = 8.8\) Hz, 2H), 3.88 (s, 3H). Residual formyl proton: \(\delta\) 9.8.

**3-Methoxybenzaldehyde-α-D (2e)** was prepared with the corresponding aldehyde (40.8 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 32.4 mg of 2e as a colorless oil (79% yield, 63% D). Characterization data matched those previously reported.\(^6\) \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.46-7.44 (m, 2H), 7.40-7.39 (m, 1H), 7.20-7.16 (m, 1H), 3.86 (s, 3H). Residual formyl proton: \(\delta\) 9.9.

**4-(Methylthio)benzaldehyde-α-D (2f)** was prepared with the corresponding aldehyde (45.6 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→10% EtOAc in hexane gradient to afford 42.1 mg of 2f as a colorless oil (92% yield, 74% D). Characterization data matched those previously reported.\(^7\) \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.77 (d, \(J = 8.6\) Hz, 2H), 7.31 (d, \(J = 8.5\) Hz, 2H), 2.52 (s, 3H). Residual formyl proton: \(\delta\) 9.9.

**Benzaldehyde-α-D (2g)** was prepared with the corresponding aldehyde (31.8 mg, 0.3 mmol) according to the general procedure. Reaction material was filtered through a short silica plug, and a crude \(^1\)H NMR was recorded. For volatility reasons, the product was not isolated (NMR yield is 68%, 55% D). Characterization data matched those previously reported.\(^8\) \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.90-7.88 (m, 2H), 7.64-7.60 (m, 1H), 7.49-7.54 (m, 2H). Residual formyl proton: \(\delta\) 10.0.

**Tert-butyl 3-formyl-1H-indole-1-carboxylate-α-D (2h)** was prepared with the corresponding aldehyde (73.5 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 10→20% EtOAc in hexane gradient to afford 65.6 mg of 2h as a white solid (89% yield, 44% D). Characterization data matched those previously reported.\(^9\) \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 8.28 (dd, \(J = 7.6\) Hz, 0.8 Hz, 1H), 8.22 (s, 1H), 8.14 (d, \(J = 7.9\) Hz, 1H), 7.40 (ddd, \(J = 8.6\) Hz, 7.3 Hz, 1.4 Hz, 1H), 7.36 (ddd, \(J = 8.5\) Hz, 7.6 Hz, 1.4 Hz, 1H), 1.70 (s, 9H). Residual formyl proton: \(\delta\) 10.0.
**N-methyl-2-pyrrolocarboxaldehyde-α-D** (2i) was prepared with the corresponding aldehyde (32.7 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 21.4 mg of 2i as a colorless oil (65% yield, 51% D). Characterization data matched those previously reported.\(^{10}\) \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 6.91 (dd, \(J = 4.0\) Hz, 1.6 Hz, 1H), 6.88-6.87 (m, 1H), 6.21 (dd, \(J = 4.0\) Hz, 1.6 Hz, 1H), 3.95 (s, 3H). Residual formyl proton: \(\delta\) 9.5.

**3,5-Di-tert-butyl-2-hydroxybenzaldehyde-α-D** (2j) was prepared with the corresponding aldehyde (70.2 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a gradient 1→4% EtOAc in hexane to afford 64.7 mg of 2j as a light yellow solid (92%, 75% D). Characterization data matched those previously reported.\(^{11}\) \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 11.67 (s, 1H), 7.60 (d, \(J = 3.0\) Hz, 1H), 7.35 (d, \(J = 3.2\) Hz, 1H), 1.43 (s, 9H), 1.33 (s, 9H). Residual formyl proton: \(\delta\) 9.8.

**4-Hydroxybenzaldehyde-α-D** (2k) was prepared with the corresponding aldehyde (36.6 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using a 2→8% EtOAc in hexane gradient to afford 35.0 mg of 2k as an off-white solid (95% yield, 80% D). Characterization data matched those previously reported.\(^{12}\) \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 10.59 (s, 1H), 7.75 (d, \(J = 8.7\) Hz, 2H), 6.92 (d, \(J = 8.7\) Hz, 2H). Residual formyl proton: \(\delta\) 9.7.

**Methyl-4-formylbenzoate-α-D** (2l) was prepared with the corresponding aldehyde (49.2 mg, 0.3 mmol) according to the general procedure. Purification was done by column chromatography using 20% EtOAc in hexane as the eluant to afford 32.2 mg of 2l as a white solid (60% yield, 14% D). Characterization data matched those previously reported.\(^{13}\) \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.18 (d, \(J = 8.1\) Hz, 2H), 7.94 (d, \(J = 8.6\) Hz, 2H), 3.95 (s, 3H). Residual formyl proton: \(\delta\) 10.0.

3. References

4. NMRs