Electronic Supporting Information for

**An Environmentally Friendly Procedure for the Aqueous Oxidation of
Benzyl Alcohols to Aldehydes with Dibromodimethylhydantoin
(DBDMH) and Cyclodextrin – Scope and Mechanistic Insights**

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Materials and Methods

Proton NMR spectra were recorded using a Bruker 300 MHz instrument, with the singlet peak of HDO at 4.79 ppm as reference. All reagents, substrates, and solvents were obtained from Sigma Aldrich and used as received. Four different cyclodextrin solutions were screened: α -cyclodextrin, β -cyclodextrin, methyl β -cyclodextrin and γ -cyclodextrin dissolved in deuterated water (D_2O). A cyclodextrin-free D_2O solution was used as the control. The same procedure was adopted for all the cyclodextrins and the control.

Standard Reaction Conditions

To a clean and dry small vial, a solution of substrate **1** (15.0 μmol , 1.0 equivalent) was made using an aqueous cyclodextrin solution (1.0 mL) in D_2O . DBDMH **3** (4.3 mg, 15.0 μmol , 1.0 equivalent) was added to the reaction mixture and sonicated to make sure that the reagents were well suspended. The reaction mixture was heated at 60 $^\circ\text{C}$ with occasional shaking to maintain the homogeneity of the solution. After the desired period of time, the ^1H NMR spectrum of the reaction mixture was recorded to determine the percent conversion.

NMR Analysis

proton peaks
integrated for
starting material

proton peak
integrated for
product

Figure 1. ^1H NMR peaks of protons (marked in red) integrated for the starting material **1** and product **2**.

The percent conversion of each reaction was calculated based on the following equation:

$$\% \text{ Conversion} = \left[\frac{\text{Integration of the product peak}}{(\text{Integration of the product peak}) + (\text{Integration of the starting material peak}/2)} \right] \times 100\%$$

The starting material NMR peak used in this equation corresponds to 2 benzylic protons of compound **1** and the product peak used for this equation corresponds to the 1 aldehyde proton of the product **2** (Figure 1). The integrations of the NMR peaks were the relative areas under the curve measured against a calibrated standard corresponding to the anomeric protons of the cyclodextrin hosts.

Kinetic Isotope Effect Experiments

Two separate solutions of substrate **1a** and **d2-1a** (15.0 μmol , 1.0 equivalent) were made using 5 mM aqueous α -cyclodextrin solution (1.0 mL, 5.0 μmol , 0.33 equivalents) in D_2O . DBDMH **3** (4.3 mg, 15.0 μmol , 1.0 equivalent) was added to the reaction mixtures and sonicated to make sure that the reagents were well suspended. The reaction mixtures were heated at 60 $^\circ\text{C}$ with occasional shaking to maintain the homogeneity of the solutions for 1 hour. ^1H NMR spectra of the reaction mixtures were recorded to determine the percent conversions.

Percent conversions of alcohol substrates **1a** and **d2-1a** to aldehyde **2a**

Substrate	Equivalents of substrate	Equivalents of compound 3	% Conversion ^b	k_H/k_D
1a	15 μmol	15 μmol	26	3.2
d2-1a	15 μmol	15 μmol	8	

^a Percent conversions were calculated based on the ^1H NMR analysis of the reaction mixture.

^b The reaction was run with α -cyclodextrin (0.33 equivalents) for 0.5 hours at 60 $^\circ\text{C}$

Table Demonstrating Catalyst Reusability

Number of Re-runs of Catalyst	Starting Material 1a (%) ^a	Br-benzyl alcohol (%) ^a	Br-Aldehyde (%) ^a	Acid bromide (%) ^a	Product 2a (%) ^a

1st	15	-	-	10	75
2nd	-	-	-	26	74
3rd	-	-	22	16	62

^a Percent conversions were calculated based on ¹H NMR analysis of the reaction mixture.

¹H NMR SPECTRA

Benzyl alcohol 1a

4-methyl benzyl alcohol 1b

3-methyl benzyl alcohol 1c

4-chloro benzyl alcohol 1d

4-trifluoromethyl benzyl alcohol 1e

3-bromo benzyl alcohol 1f

4-bromo benzyl alcohol 1g

4-nitro benzyl alcohol 1h

2-nitro benzyl alcohol 1i

4-iodo benzyl alcohol 1j

2-chloro-5-methylhydroxy pyridine 1k

2-chloro benzyl alcohol 1l

4-methoxy benzyl alcohol 1m

¹H NMR Spectra Demonstrating Catalyst Reusability

¹H NMR Spectra Demonstrating Reactivity of Reagent 3 in the Presence of Cyclodextrin

¹H NMR Spectra Demonstrating Reactivity of Reagent 3 in the Presence of Cyclodextrin and One Equivalent of 1a

Table Illustrating the %N-Br bond dissociation of reagent 3 in the Presence of Cyclodextrin and One Equivalent of 1a at standard reaction conditions (Calculated based on the NMR peak integrals of 3 and 4)

<i>CDs (0.33 eq.)</i>	<i>3 (rt, 0 mins)</i>	<i>3 + 1a (60°C, 0.5 hrs)</i>
α-CD	50	58
β-CD	66	66
mβ-CD	68	69
γ-CD	11	14
control	100	100