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PRACTICAL AND CHEMOSELECTIVE REDUCTION OF ACYL CHLORIDE TO ALCOHOL BY BOROHYDRIDE IN AQUEOUS DICHLOROMETHANE

Ramya Rajan, Sachin Badgujar, Kamaljit Kaur, Yashwardhan Malpani, and Pranab R. Kanjilal
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A simple methodology for the reduction of acid chlorides to their corresponding alcohols has been developed. Various carboxylic acids were converted to alcohols in excellent yields using $NaBH_4$-K_2CO_3 in a mixed solvent system of dichloromethane and water (1:1) in the presence of a phase-transfer catalyst at low temperature. The importance of the work is its simplicity, selectivity, excellent yield, and very short reaction time. This new reduction condition has proved to be an excellent chemoselective method for a range of acid chlorides in the presence of various functional groups.

Keywords: Acyl chloride; alcohol; aqueous dichloromethane; base; borohydride; phase-transfer catalyst

INTRODUCTION

Methodologies for functional group transformation are extremely important for the continued evolution of organic synthesis. While working on the preparation of potential agrochemicals, we were searching for efficient and chemoselective methods to prepare primary alcohols from carboxylic acids and their derivatives. In literature, a limited number of such methods is reported. These methods[1] describe the use of sodium borohydride alone or in combination with different Lewis acids or additives, or use of zinc borohydride or borane complexes for reduction of carboxylic acids or their different derivatives to the corresponding alcohols. Recently, Qiu and Zhang[2] reported preparation of alcohols from carboxylic acids and their derivatives using a combination of potassium borohydride and magnesium chloride. The methods reported in the literature suffer from one or more of the following limitations: long reaction times, high reaction temperatures, and use of either a large excess or expensive reagent. Moreover, these methods generally lack selectivity and reduce other functional groups in the substrate. Our literature search[3,4] revealed that carboxylic esters, acid chlorides, alkyl halides, and sulfonate esters can effectively be reduced by using a combination of sodium borohydride and

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polyethylene glycol (PEG)-400. The reactions needed high temperatures and long reaction times to complete. An isolated example of reduction of 6-chloronicotinoyl chloride to the corresponding alcohol was reported by Sivasankaran et al.[5] They used borohydride in aqueous dichloromethane in the presence of a carbonate base. However, the report does not offer a detailed study of the method, which required long reaction times. There are reports of borohydride reductions using different phase-transfer catalysts. Yadav and Lande,[6] in their studies of the kinetics of chemoselective reduction of citronellal, used sodium borohydride and tetraalkyl ammonium salts as phase-transfer catalysts in biphasic medium and reported that the rate of reduction with borohydride under phase-transfer catalytic conditions is very fast. They also explained the mechanism of reduction in the biphasic medium. PEGs are known as "poor chemist's crowns."[7] Recently, Cao et al.[8] reported reduction of aldehydes, ketones, and imines using sodium borohydride and PEG-400 as phase-transfer catalyst under solvent-free conditions. In another case, PEG-400 was used as phase-transfer catalyst in combination with $PdCl_2$ as cocatalyst for reduction of the acetylenic bond with borohydride.[9] Freedman[10] cited a large number of studies in which PEG had been used as a phase-transfer catalyst and that had industrial applications. Among the different phase-transfer catalysts, PEG-400 by far was much better, as reported by Cao et al.,[8] because of its low cost, stability, ready availability, and apparent lack of significant toxicological properties. In addition, compared with other phase-transfer catalysts, it has the most ability to solubilize inorganic salts because of its terminal polar hydroxyl groups.

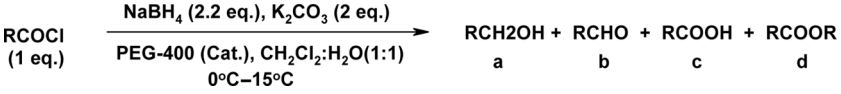
RESULTS AND DISCUSSION

Present Work

To make intermediates for our agrochemical research, we required a mild and selective method for reduction of acid chlorides to the corresponding alcohols. We wanted to explore the phase-transfer catalytic effect of PEG-400 in our studies using borohydride as the reducing agent in a biphasic medium (Scheme 1). In this work, the mechanistic considerations were not our primary interest; rather, we report a simple, selective, and efficient method that has been successfully scaled up to 200 g.

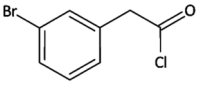
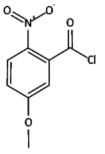
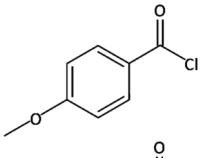
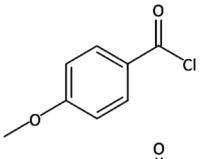
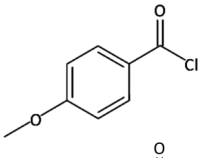
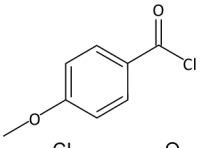
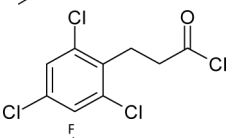
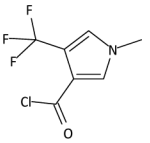
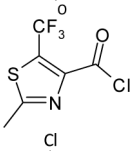
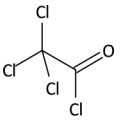
Thus, acid chloride and sodium borohydride were added simultaneously to a mixture of potassium carbonate and PEG-400 in a 1:1 mixture of dichloromethane and water at low temperature, and the corresponding alcohol was formed in excellent yield within 15 min. Table 1 shows the results of our explorations.

In our work, we studied different parameters, such as the effects of different molar ratios of reducing agent, different bases, and different solvents.



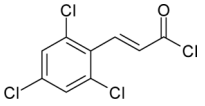
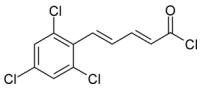
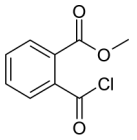
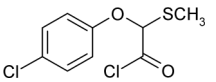
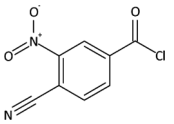
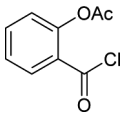
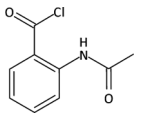
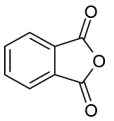
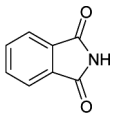
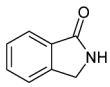
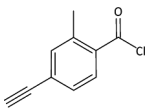
Scheme 1. Reduction of acid chloride to alcohol.

Table 1. Reduction of acid chlorides with $NaBH_4$-PEG 400 in the presence of K_2CO_3 in CH_2Cl_2: H_2O (1:1)

Entry	Substrate (1 mol equiv)	Mp (°C) (of product)	Reaction time	Temp. (°C)	Product yields a	b	C
1		—	15 min	0–15	86%	—	—
2		117	15 min	0–15	96%	—	—
3		—	15 min	0–15	95–98%[a–d]	—	—
4		—	16 h[e]	rt	93%	—	—
5		—	>30 min	0–15	98%[f]	—	—
6		—	8 h	0–15	18%	38%	8%[g]
7		55	15 min	0–15	94%	—	—
8		45	15 min	0–15	95%	—	—
9		75	15 min	0–15	95%	—	—
10		—	15 min	0–15	77% (volatile)		

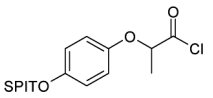
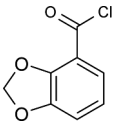
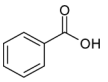
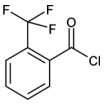
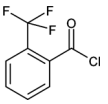
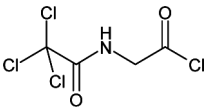
(*Continued*)

Table 1. Continued

Entry	Substrate (1 mol equiv)	Mp (°C) (of product)	Reaction time	Temp. (°C)	Product yields a	b	C
11		—	15 min	0–15	70%	—	—
12		90	15 min	0–15	56%	—	20%
13		—	15 min	0–15	Quant.[h]		
14		—	15 min	0–15	91%	—	—
15		—	15 min	0–15	97%	—	—
16		—	15 min	0–15	78%	—	10%
17		—	15 min	0–15	55%	—	40%
18		—	15 min	0–15	Phthalic acid		
19		—	15 min	0–15			
20		—	15 min	0–15	51%	40%	—

(*Continued*)

Table 1. Continued

Entry	Substrate (1 mol equiv)	Mp (°C) (of product)	Reaction time	Temp. (°C)	Product yields a	b	C
21		—	15 min	0–15	70%	—	—
22		—	15 min	0–15	93%	—	—
23		—	15 min	0–15	—	—	Recovered
24		—	15 min	0–15	93%	—	—
25		—	8 h[i]	15 °C art	25%	—	60%
26		—	15 min	0–15	60%	—	—

[a]Yield 98% (PTC-PEG-400).
[b]Yield 95% (PTC-TBAF).
[c]Yield 97% (PTC-TBAB).
[d]Yield 95% (PTC-18-Crown-6).
[e]Dry THF was used as solvent.
[f]KBH4 was used as reducing agent.
[g]Reaction was carried out without using any base, and along with the mixture of products the ester (**d**) derived from the starting acyl chloride and alcohol (**a**) was isolated in 35%.
[h]The desired alcohol was isolated along with the lactone in a ratio of 1:2. The lactone was derived from the intramolecular reaction of the reduced alcohol with the adjacent ester, thus proving that the ester functionality does not get reduced under this reaction condition.
[i]Reaction was carried out in toluene/water (1:1) as the solvent, keeping the rest of the conditions unchanged (11% starting acid chloride also was recovered along with the corresponding alcohol and acid).

Effect of Reducing Agent

The effects of different quantities of borohydride on the reaction rate and conversion are shown in Fig. 1. A portion of borohydride was added at the beginning to the reaction mixture, followed by simultaneous addition of the rest of the reagent along with acid chloride; otherwise, a substantial amount of the starting acid chloride was hydrolyzed to the starting acid. Our attempt to use potassium

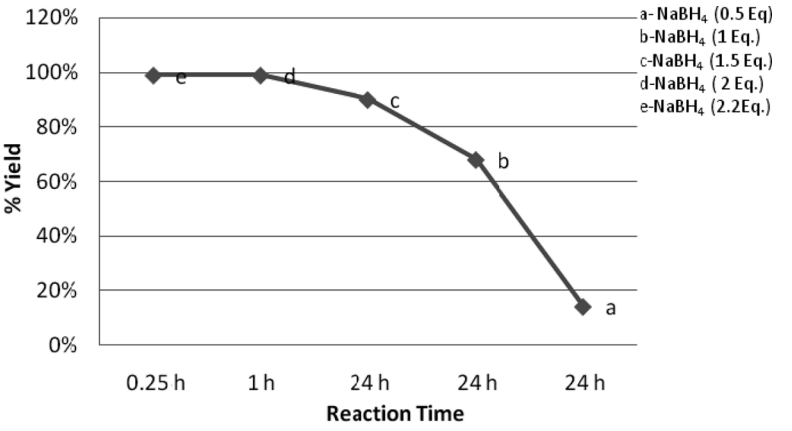


Figure 1. Effect of the concentration of $NaBH_4$ on the reduction of acid chloride.

borohydride in place of sodium borohydride (entry 5 in Table 1) did not prove to be beneficial because the reaction required longer time for completion and potassium borohydride is much more expensive.

Effect of Phase-Transfer Catalyst

Santaniello et al.[4] used 6 mL of PEG-400 and 1 mmol of substrate and reported the formation of $NaB(PEG)_2H_2$ as the reducing agent by reaction of borohydride and PEG-400 at 65–80 °C. In our case, we used a catalytic amount (20 mol%) of PEG-400 at low temperature. We assume that PEG-400, in our case, played the role of a phase-transfer catalyst like the tetraalkylammonium salts played in Yadav et al.'s work.[6] In our case, use of other phase-transfer catalysts like 18-C-6, tetrabutylammonium bromide (TBAB), or tetrabutylammonium fluoride (TBAF) gave similar results (entry 3) to PEG-400, and an attempt to carry out the reduction without use of any phase-transfer catalyst resulted in complete hydrolysis of acid chloride to the corresponding acid. PEG-400 was preferred over the other phase-transfer catalysts for the same reasons.

Effect of Base

Presence of a base is required for the reaction, and potassium carbonate was found to be the best. The effects of different quantities of potassium carbonate on the reaction rate and conversion are shown in Fig. 2. Other bases were also tried but found to be inferior (see Table 2). In the absence of the base, the reaction gave a

Table 2. Effects of different bases on reaction time, temperature, and product composition

Base	Reaction temperature	Reaction time	Product(s)
K_2CO_3	0–15 °C	15 min	**a** (exclusively)
Cs_2CO_3	RT	9 h	**a** (exclusively)
Na_2CO_3	RT	Overnight	Mixture of **a**, **b**, **c**, and **d** (ester)
TEA	RT	Overnight	Mixture of **a**, **b**, **c**, and **d** (ester)
Nil	0–15 °C	15 min	Mixture of **a**, **b**, **c**, and **d** (ester)

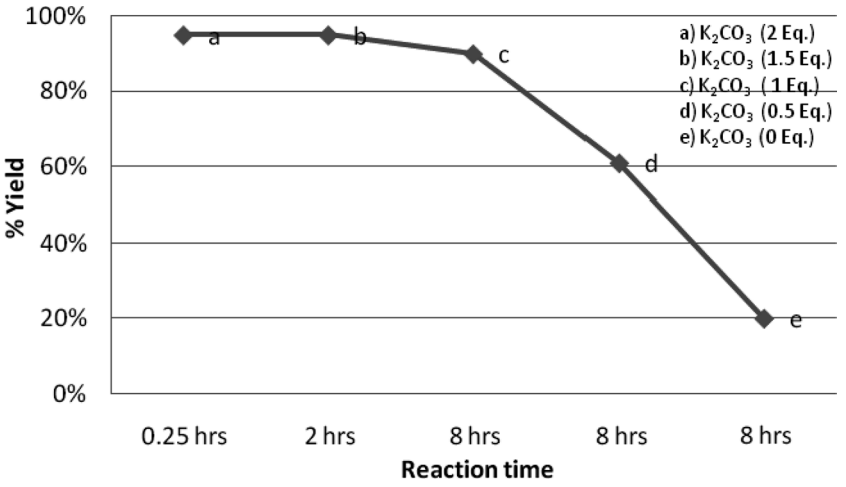


Figure 2. Effect of concentration of K_2CO_3 on the reduction of acid chloride.

mixture of the desired alcohol (a), the corresponding aldehyde (b), the starting acid (c), and an ester (d) derived from the reaction of the generated alcohol and the substrate (entry 6). At pH 11–12, as in our case, borohydride is stable for a couple of days.[11] We assume that in our case the base gives the stability to borohydride in aqueous solution in addition to quenching the hydrochloric acid generated from the reaction.

Effect of Solvent

Different solvents were also tried. The reaction did not proceed at all in CH_2Cl_2 alone, in tetrahydrofuran (THF) it required a very long time at rt (entry 4), and in a 1:1 mixture of toluene and water it gave rise to a mixture of products (entry 25). We proved by the titrimetric analysis that the borohydride–PEG complex is much more soluble in dichloromethane than in toluene.

Effect on Other Reducible Groups

Finally, we studied the effect of our reduction condition on other reducible functional groups in the substrates. Different acid chlorides were studied, and the borohydride–PEG combination under this reaction condition selectively reduces the acid chloride in the presence of other reducible functional groups as evident from entries 1–3 and 7–26. Anhydrides and imides were the exceptions. The anhydride was completely hydrolyzed to diacid (entry 18), whereas only one carbonyl group was reduced to methylene in imide (entry 19). Other combinations of borohydride with activators reduce other functional groups as well.[12–21]

CONCLUSION

In conclusion, our report describes a simple, rapid, and selective method to reduce acid chlorides to alcohols in excellent yields employing sodium borohydride and polyethylene glycol.

EXPERIMENTAL

All yields reported are isolated yields. The products were characterized by their melting points, wherever possible, and spectral and analytical data. ^{1}H NMR spectra were taken in $CDCl_3$ solution (for few cases in dimethylsulfoxide, DMSO) at ambient temperature in a 400-MHz multinuclear Bruker machine, and the chemical shift values are mentioned in δ. Purities of all the products were ≥96% and were checked by high-performance liquid chromatography (HPLC) in an Agilent-1200 series machine in a reverse-phase manner. They were also cross-checked in some cases by gas chromatography–mass spectrometry (GC-MS) on a Trace GC Ultra with DSQ on a Thermo Finnigan machine and in some cases by liquid chromatography–mass spectrometry (LC-MS) on a Surveyor HPLC with MSQ on a Thermo Finnigan machine. Infrared (IR) spectra were taken on a Shimadzu Prestige 21 machine with DRS 8000 in KBr. All experiments were carried out on a 0.5-g scale unless otherwise mentioned.

General Procedure for the Preparation of 4-hydroxymethyl-2-nitrobenzonitrile (15a)

A solution of 4-cyano-3-nitrobenzoic acid (0.5 g, 2.6 mmol) in dichloromethane (10 mL) was boiled with thionyl chloride (2.8 ml, 3.91 mmol) for 3 h. The reaction mixture turned to a dark solution. Excess thionyl chloride was distilled out under reduced pressure along with dichloromethane on a rotary evaporator. The resulting acid chloride was dissolved again in fresh and dry dichloromethane (2.5 mL) and was added dropwise to a precooled (0–15 °C) and stirred mixture of dichloromethane (2.5 mL) and water (2.5 mL) containing potassium carbonate (0.71 g, 5.2 mmol), PEG-400 (20 mol%), and a portion of sodium borohydride (0.2 eq.). The rest of the borohydride (2 eq.) was added simultaneously with the acid chloride solution over a period of 5 min. Stirring continued at the same temperature for another 10 min. The reaction mixture was diluted with water (25 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine (1 × 20 mL) and dried (Na_2SO_4). Evaporation of solvent afforded the desired alcohol (**15a**) as a gummy mass. Purification on a short column of silica gel provided the pure alcohol (0.45 g, 97%). Yield 97%; gummy mass; ^{1}H NMR ($CDCl_3$): 4.9 (s, 2H); 7.79 (d, J = 8 Hz, 1H), 7.88 (d, J = 8 Hz, 1H), 8.35 (s, 1H); (M^+ = 178.0). Exactly the same result was obtained when the reaction was carried out on a 200-g scale.

Selected Data

2-(3″-Bromophenyl) ethanol (1a). Yield 86%; gummy mass; ^{1}H NMR ($CDCl_3$): 2.84 (t, J = 8 Hz, 2H), 3.86 (t, J = 8 Hz, 2H), 7.16–7.18 (m, 2H), 7.35–7.39 (m, 2H).

(5″-Methoxy-2′-nitrophenyl) methanol (2a). Yield 96%; mp 117 °C; ^{1}H NMR ($CDCl_3$): 2.19 (br s, 1H), 3.91 (s, 3H), 4.99 (s, 2H), 6.89 (dd, J = 9.2 and 2.7 Hz, 1H), 7.22 (d, J = 2.7 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H); (M^+ = 183.1).

(4-Methoxyphenyl) methanol (3a). Yield 98%; gummy mass; ^{1}H NMR ($CDCl_3$): 3.8 (s, 3H), 4.6 (s, 2H), 6.89 (d, $J = 8$ Hz, 2H), 7.29 (d, $J = 8$ Hz, 2H); ($M^+ = 138.1$).

3-(2′,4′,6′-Trichlorophenyl) propan-1-ol (7a). Yield 94%; mp 55 °C; ^{1}H NMR ($CDCl_3$): 1.79–1.86 (m, 2H), 2.96–3.0 (m, $J = 8$ Hz, 2H), 3.73 (t, $J = 6$ Hz, 2H), 7.30 (s, 2H); ($M^+ = 238.1$).

(1-Methyl-4-trifluoromethyl-1H-pyrrol-3-yl) methanol (8a). Yield 95%; mp 45 °C; ^{1}H NMR ($CDCl_3$): 3.63 (s, 3H), 4.55 (s, 2H), 6.64 (s, 1H), 6.88 (s, 1H).

(2-Methyl-5-trifluoromethylthiazol-4-yl) methanol (9a). Yield 95%; mp 75 °C; ^{1}HNMR ($CDCl_3$): 2.17 (br s, 1H), 2.70 (s, 3H), 4.97 (s, 2H).

2,2,2-Trichloroethanol (10a). Yield 77% (volatile colorless liquid); ^{1}H NMR ($CDCl_3$) 2.85–3.15(br s, 1H), 4.15 (s, 2H); ($M^+ = 148.8$).

3-(2,4,6-Trichlorophenyl) prop-2-en-1-ol (11a). Yield 70%; gummy mass; ^{1}H NMR ($CDCl_3$): 4.39 (dd, $J = 1.6$ and 4.8 Hz, 2H), 6.39 (dt, $J = 16$ and 4.8 Hz, 1H), 6.57 (dt, $J = 16$ and 2 Hz, 1H), 7.34 (s, 2H); ($M^+ = 238.9$).

5-(2,4,6-Trichlorophenyl)-pent-2,4-dien-1-ol (12a). Yield 56%; mp 90 °C; ^{1}H NMR ($CDCl_3$): 1.43 (br s, 1H), 4.285 (d, $J = 5$ Hz, 2H), 6.03 (dt, $J = 15.6$ and 5 Hz, 1H), 6.463 (dd, $J = 10.8$ and 15.6 Hz, 1H), 6.53 (d, $J = 16$ Hz, 1H), 6.85 (dd, $J = 10.8$, 16 Hz, 1H), 7.33 (s, 2H); ($M^+ = 261.9$).

2-Hydroxymethylbenzoic acid methyl ester (13a). Yield (quantitative); gummy mass; ^{1}H NMR ($CDCl_3$): 3.89 (s, 3H), 5.09 (s, 2H), 7.57–7.61 (m, 3H), 7.89 (dd, $J = 4$ and 7.2 Hz, 1H).

2-(4-Chlorophenoxy)-2-methylsulfanylethanol (14a). Yield 91%; gummy mass; ^{1}H NMR ($CDCl_3$): 2.04 (s, 3H), 2.13 (t, $J = 7.6$ Hz, 1H), 3.85 (ddd, $J = 5.6$, 7.6, and 9.4 Hz, 1H), 4.03 (ddd, $J = 5.6$, 7.6, and 9.4 Hz, 1H), 5.18 (dd, $J = 5.6$ and 7.6 Hz, 1H), 6.98 (dd, $J = 5.6$ Hz, 2H), 7.28 (dd, $J = 5.6$ Hz, 2H).

Acetic acid-2-hydroxymethylphenyl ester (16a). Yield 78%; gummy mass; ^{1}H NMR ($CDCl_3$): 2.11 (s, 3H), 5.12 (s, 2H), 6.91–6.95 (m, 2H), 7.25–7.28 (m, 2H), 7.75 (s, 1H).

N-(2-Hydroxymethylphenyl)acetamide (17a). Yield 55%; gummy mass; ^{1}H NMR (DMSO): 2.45 (s, 3H), 3.52 (s, 2H), 7.63–7.66 (m, 2H), 7.96 (dd, $J = 8$ Hz, 1H), 8.16 (d, $J = 8$ Hz, 1H), ($M^+ = 166.13$).

2,3-Dihydroisoindol-1-one (19a). Yield (quantitative); gummy mass; ^{1}H NMR (DMSO): 5.42 (s, 2H), 7.59 (dd, $J = 8$ Hz, 1H), 7.69 (d, $J = 8$ Hz, 1H), 7.78 (dd, $J = 8$ Hz, 1H), 7.85 (d, $J = 8$ Hz, 1H).

(4-Ethynyl-2-methylphenyl) methanol (20a). Yield 46%; gummy mass; ^{1}H NMR (DMSO): 2.2 (s, 3H), 4.08 (s, 1H), 4.48 (d, $J = 5.2$ Hz, 2H), 5.15–5.18 (m, 1H), 7.25 (s, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 1H).

2-(4-Triisopropylsilanyloxyphenoxy) propan-1-ol (21a). Yield 70%; gummy mass; ^{1}H NMR ($CDCl_3$): 1.09 (d, $J = 7.2$ Hz, 18H), 1.22 (d, $J = 6$ Hz,

3H), 1.21–1.29 (m, 3H), 2.03 (br s, 1H), 3.64–3.75 (m, 2H), 4.33–4.37 (m, 1H), 6.79 (s, 4H).

Benzo[1,3]dioxol-4-yl-methanol (22a). Yield 93%; gummy mass; ^{1}H NMR ($CDCl_3$): 1.99 (br s, 1H), 4.68 (s, 2H), 5.96 (s, 2H), 6.76–6.86 (m, 3H).

(2-Trifluoromethylphenyl) methanol (24a). Yield 93%; gummy mass; ^{1}H NMR (DMSO): 4.67 (s, 2H), 5.47 (br s, 1H), 7.45 (dd, $J = 7.6$ Hz, 1H), 7.68 (dd, $J = 7.6$ Hz, 2H), 7.77 (d, $J = 7.6$ Hz, 1H).

2,2,2-Trichloro-N-(2-hydroxyethyl) acetamide (25a). Yield 60%; gummy mass; ^{1}H NMR (DMSO): 3.23–3.27 (m, 2H), 3.45–3.50 (m, 2H), 4.78 (t, $J = 4$ Hz, 1H), 8.88 (br s, 1H).

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