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PAPER

Environmentally benign metal triflate-catalyzed reductive cleavage of the C–O bond of acetals to ethers

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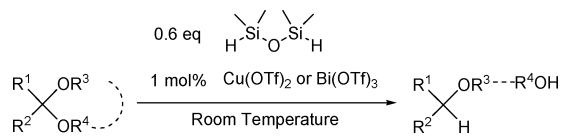
A protocol is described for the reductive cleavage of the C–O bond of aromatic and aliphatic acetals to ethers catalyzed by $Cu(OTf)_2$ or $Bi(OTf)_3$ at room temperature in excellent yields, without affecting aromatic rings, nitro, nitrile, ester and hydroxyl groups. This protocol represents an improvement in terms of atom economy compared to the previous methods, by distinctly decreasing the amount of the reducing reagent, 1,1,3,3-tetramethyldisiloxane (TMDS), and using a small amount of catalyst.

Introduction

Reductive cleavage of the C–O bond of acetals is one of the major methods in ether synthesis. It is widely applied not only as a deprotecting strategy but also in constructing building blocks in carbohydrate chemistry.[1] Various hydride sources have been introduced for the ring cleavage of acetals to ethers including $LiAlH_4$,[2] NaH,[3] DIBAL-H,[4] $NaBH_3CN$,[5] BH_3,[6] Et_3SiH[7] and $PhSiH_3$.[8] Nevertheless, most hydride sources in these reducing systems present drawbacks such as high price, incompatibility with other functionalities, necessity for rigorously anhydrous reaction conditions or release of pyrophoric and toxic gas in certain instances. Furthermore, most of these hydride sources are employed with Lewis acids which are extremely moisture-sensitive and have often to be used in stoichiometric or excessive amount, leading to hydrolysis of the acetal ring as a main side reaction.

Over the past decade, hydrosiloxane derivatives have emerged as attractive alternative reducing reagents since they are stable to moisture and air.[9] Moreover, hydrosiloxanes afford polysiloxanes as byproducts which are innocuous and easy to separate from the reaction medium.[10] In our laboratory, we previously described the reduction of phosphine oxides to phosphines,[11] nitriles to amines,[12] amides to aldehydes[13] using 1,1,3,3-tetramethyldisiloxane (TMDS) activated by titanium(IV) isopropoxide, as well as the reduction of nitro compounds to amines[14] activated by iron(III). Recently, in a preliminary study, we described the reduction of acetals to ethers[15] based on the use of a TMDS-Pd/C system in the presence of a Brønsted acid as co-catalyst. However, this procedure presented some drawbacks: Excessive amount of TMDS (3 equiv.), a large amount of expensive camphorsulfonic acid (30 wt%) and relatively high temperature (60 °C) were necessary to reach complete conversion. In addition, Pd/C is flammable under these conditions and its price dramatically increased during the past year.[16] Therefore, a more convenient, economic and eco-friendly alternative to the TMDS-Pd/C system was explored.

Metal triflates have been widely applied in numerous organic reactions.[17] So far, metal triflates have been developed as catalysts in reducing acetals with boranes or silanes.[18] To the best of our knowledge, they have never been employed with hydrosiloxanes. Herein, we report a straightforward, environmentally benign reduction of acetals to ethers catalyzed by $Cu(OTf)_2$ or $Bi(OTf)_3$, using only 0.6 equiv. of TMDS (1.2 Si–H mol/mol substrate) at room temperature (Scheme 1). A mechanistic consideration of the reaction process is also proposed.



Scheme 1 Reduction of acetals to ethers with TMDS catalyzed by $Cu(OTf)_2$ or $Bi(OTf)_3$.

Results and discussion

We started our investigation with the reduction of 2-phenyl-1,3-dioxane **1a** using TMDS in association with $Cu(OTf)_2$ in CH_2Cl_2 at room temperature. The results are summarized in Table 1.

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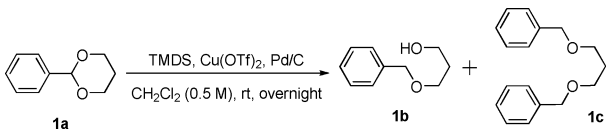
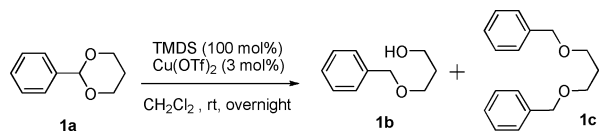
Table 1 Optimization of the reaction conditions



Entry	TMDS (mol%)	$Cu(OTf)_2$ (mol%)	Pd/C (mol%)	Conv.[a] (%)	**1b** : **1c**[b]
1	500	15	1	100	6 : 1
2	300	10	0.5	100	1 : 1
3	300	10	—	100	1 : 1
4	300	1	—	100	3 : 1
5	60	1	—	100	4 : 1
6[c]	60	1	—	100	5 : 1

[a] Determined by ^{1}H NMR after filtration and concentration. [b] Ratios of **1b** : **1c** were calculated after flash column chromatography. [c] The concentration of **1a** in CH_2Cl_2 was 0.2 M.

Table 2 Reduction of acetal **1a** in different solvents



Entry	Solvent	Conv.[a] (%)	**1b** : **1c**[a]
1	H_2O	100	nd[b]
2	EtOH	100	nd[b]
3	CH_2Cl_2	100	4 : 1
4	Toluene	95	3 : 2
5	THF	41	nd[b]

[a] Calculated after flash column chromatography. [b] No target products but only byproducts were detected after the reaction.

Initially, treatment of **1a** with 500 mol% TMDS in the presence of 15 mol% $Cu(OTf)_2$ and 1 mol% Pd/C overnight furnished the expected ring-opened product **1b** in excellent conversion and yield (Table 1, entry 1). However in this case, the formation of a minor byproduct **1c** was also detected. It is probably formed by further etherification of **1b**. Lowering the amount of TMDS, $Cu(OTf)_2$ and Pd/C to respectively 300 mol%, 10 mol% and 0.5 mol% resulted in full conversion of **1a** but also a drastic drop of the ratio of **1b** : **1c** (Table 1, entry 2). Interestingly, exclusion of Pd/C gave similar result (Table 1, entry 3). Moreover, a catalytic quantity of 1 mol% $Cu(OTf)_2$ completely converted **1a** and remarkably improved the selectivity of **1b** : **1c** to 3 : 1 (Table 1, entry 4). In addition, 60 mol% TMDS (1.2 Si–H mol/mol substrate) was sufficient to completely reduce **1a** with 1 mol% $Cu(OTf)_2$ (Table 1, entry 5). Less byproduct **1c** was formed at lower concentration (Table 1, entry 6).

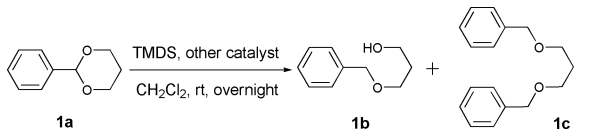
Solvent screening

In order to determine the best solvent required for optimum activity and selectivity, a set of experiments was performed to reduce acetal **1a** with 100 mol% TMDS and 3 mol% $Cu(OTf)_2$ in H_2O, EtOH, CH_2Cl_2, toluene and THF (Table 2).

With H_2O and EtOH as solvents, **1a** was completely converted. However, in this case, neither **1b** nor **1c** were detected after the reaction. (Table 2, entries 1–2). The sole identified product was the benzaldehyde formed by hydrolysis of **1a**.

The best result was obtained when the reaction was carried out in CH_2Cl_2. A complete conversion of **1a** and a 4 : 1 ratio for **1b** : **1c** were obtained (Table 2, entry 3). Although 95% of **1a** were converted when toluene was employed, the ratio **1b** : **1c** dropped to 3 : 2 (Table 2, entry 4). When THF was used, the conversion of the starting material remained lower than 50% and the formation of complex byproducts was observed (Table 2, entry 5). From these results, CH_2Cl_2 was found to be the best solvent for this protocol. It was therefore selected for further optimization.

Table 3 Effect of catalysts other than $Cu(OTf)_2$ employed in reducing acetal **1a**



Entry	Catalyst (mol%)	TMDS (mol%)	Conv.[a] (%)	**1b** : **1c**[b]
1	$Cu(acac)_2$ 10	300	0	—
2	TfOH 10	300	100	1 : 1
3	TMSOTf 10	300	100	1.5 : 1
4	$Bi(OTf)_3$ 1	60	100	8 : 1
5	$Yb(OTf)_3$ 1	60	0	—
6	$Gd(OTf)_3$ 1	60	0	—
7	$Eu(OTf)_3$ 1	60	0	—

[a] Determined by ^{1}H NMR after filtration and concentration. [b] Ratios of **1b**:**1c** were calculated after flash column chromatography.

Catalyst screening

A combination of TMDS with different catalysts was further studied. Acetal **1a** was not reduced in the presence of 300 mol% TMDS and 10 mol% $Cu(acac)_2$ (Table 3, entry 1), whereas 10 mol% TfOH or 10 mol% TMSOTf converted **1a** completely and led to the products **1b**, **1c** in the ratios of 1 : 1 and 1.5 : 1, respectively (Table 3, entries 2 and 3). In both cases, many unidentified by-products were detected. Similar results were obtained when the amount of TfOH or TMSOTf was decreased to 1 mol%. From these results we assumed that it was the triflic acid rather than the copper(II) cation that was indispensable to promote the reduction of acetals. However, the presence of Cu^{2+} is essential for the good selectivity of this reaction. When $Cu(OTf)_2$ was employed, much less by-products were generated in the reaction medium compared with TfOH and TMSOTf. In addition, $Cu(OTf)_2$ has the advantage to be easy to handle and much less hazardous than TfOH and the moisture-sensitive fuming liquid TMSOTf.

Treatment of the starting material **1a** with 60 mol% TMDS and 1 mol% $Bi(OTf)_3$ gave full conversion of **1a** and afforded a 8 : 1 ratio of **1b** : **1c** (Table 3, entry 4). This catalyst is even more selective toward the formation of **1b** than $Cu(OTf)_2$ (Table 1, entry 6). Consequently it would constitute a good substitute to $Cu(OTf)_2$. However, none of the lanthanide series metal triflate $Yb(OTf)_3$, $Gd(OTf)_3$ and $Eu(OTf)_3$ produced the expected ether **1b** (Table 3, entries 5–7). Similar lack of activity has already been reported in the literature for the regioselective ring opening

of 4,6-*O*-benzylidene acetals in hexopyranosides.[18d] Considering green chemistry principles, $Cu(OTf)_2$ and $Bi(OTf)_3$ have an edge over the other tested reagents as safe and efficient catalysts for TMDS activation.

Reduction of various acetals to the corresponding ethers

Cyclic and linear acetals bearing various functional groups were efficiently reduced under the optimized conditions (1 mol% of $Cu(OTf)_2$ or $Bi(OTf)_3$, 0.6 equiv. of TMDS in CH_2Cl_2 at room temperature). In all cases, the corresponding ethers were obtained in good to excellent yields (Table 4, entries 1–15). However, larger amounts of reagents (1.5 equiv. TMDS and 5 mol% $Cu(OTf)_2$) were necessary in some cases (Table 4, entry 15). It is worth to note that, in this case, the synthesized ether **12b** is a potential "green surfactant" since its precursor **12a** is synthesised from n-dodecanal and glycerol which are both abundant, inexpensive and derived from natural products.

With $Cu(OTf)_2$ as catalyst, cyclic benzylidene acetals were more difficult to be reduced than linear ones (Table 4, entries 1, 8 and 10). Indeed, further etherification of the formed alcohols with starting materials was observed as a dominant factor in limiting the reaction yields. Fortunately, the expected ethers were produced in excellent yields when $Bi(OTf)_3$ was used (Table 4, entries 2, 9 and 11). Hydroxyl groups (Table 4, entries 7, 12 and 15), nitro groups (Table 4, entries 8–9), nitriles (Table 4, entries 10, 11 and 13) and esters (Table 4, entries 12 and 14) were tolerated under this condition, which demonstrates the high chemoselectivity of the TMDS-metal triflate system.

Mechanistic considerations

It has long been known that the nucleophilic activation of hydrosiloxanes provides hypervalent silicate species that can act as powerful hydride donors.[9] The impressive efficiency of TMDS-metal triflate system in reducing acetals is presumably due to the transfer of a triflate group from the silicate to a nearby silicon atom in the presence of a nucleophile, *i.e.* the oxygen atom of an acetal. Nucleophilic substitution transfer that occurs in an intramolecular or intermolecular mode is repeated over and over again. Thus both of the two hydrogen atoms on TMDS are well activated and made full use of in the reduction of acetals. This type of nucleophile transfer has already been proposed by Lawrence *et al.* for the reduction of esters, ketones and aldehydes using polymethylhydrosiloxane (PMHS) in the presence of tetrabutylammonium fluoride (TBAF) as a catalyst.[19] Indeed the authors showed that F^- anion accelerated significantly the reduction reaction. Their system is quite similar to ours where TfO^- plays the role of the nucleophile (Fig. 1).

Conclusions

In summary, we have developed an efficient TMDS-metal triflate system for the reductive cleavage of the C–O bond of acetals. Using 60 mol% TMDS (1.2 Si–H mol/mol acetal) and 1 mol% $Cu(OTf)_2$ or $Bi(OTf)_3$, acetals are reduced to ethers in both high yields and selectivity. Key features of this protocol include operational simplicity, energy efficiency and environmental friendliness. Excellent functional group compatibility and chemoselectivity have also been achieved. Finally, an extension of this reducing system to regioselective carbohydrate deprotection strategy is being pursued.

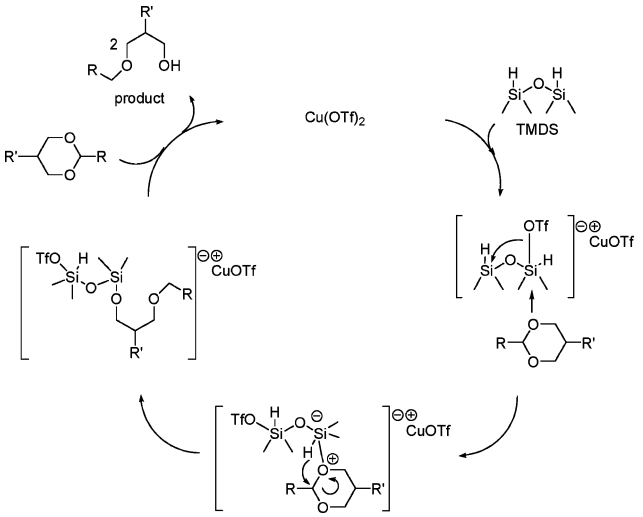


Fig. 1 Proposed mechanism for the $Cu(OTf)_2$-catalyzed reduction of acetals with TMDS.

Experimental

General

All purchased chemicals and reagents were of high commercially available grade. Solvents were purified by standard procedures. ^1H and ^{13}C NMR spectrum were recorded on Bruker ALX-300, DRX-300 or DRX 400 spectrometer in solvents using tetramethylsilane as the internal standard (chemical shifts in departs per million). All reactions were monitored by TLC (thin-layer chromatography) with detection by UV or by spraying with 6 N H_2SO_4 and charring at 300 °C. High resolution mass spectra (HRMS) were recorded on a Bruker Micro TOF-QII spectrometer using standard conditions.

General procedure for reduction of acetals

In a screw-capped vial, 1 mol% $Cu(OTf)_2$ and 60 mol% TMDS were introduced to a solution of 1 mmol acetal in CH_2Cl_2. The mixture was stirred at room temperature overnight. The reaction medium was diluted with 5 mL of CH_2Cl_2 and filtered over Celite®. The filtrate was concentrated *in vacuo* and then purified by silica column chromatography.

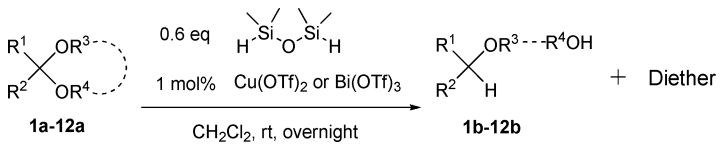
3-(Benzyloxy)propan-1-ol (1b)[18d]

Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.22 (m, 5H), 4.53 (s, 2H), 3.79 (t, *J* = 5.6 Hz, 2H), 3.67 (t, *J* = 5.8 Hz, 2H), 2.28 (brs, 1H), 1.99–1.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.1, 128.4, 127.7, 127.6, 73.3, 69.4, 61.9, 32.1.

1,3-Bis(benzyloxy)propane (1c)[20]

Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.25 (m, 10H), 4.53 (s, 4H), 3.63 (t, *J* = 6.3 Hz, 4H), 1.97 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 127.6, 127.4, 73.0, 67.3, 30.3.

Table 4 Reduction of acetals to ethers using TMDS catalyzed by $Cu(OTf)_2$ or $Bi(OTf)_3$



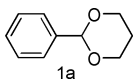
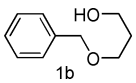
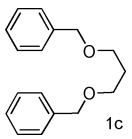
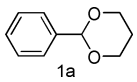
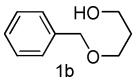
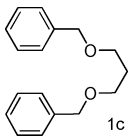
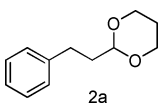
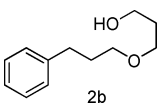
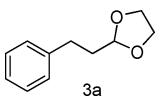
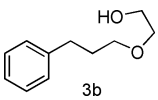
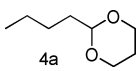
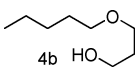
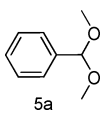
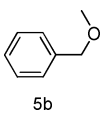
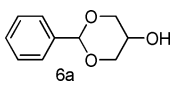
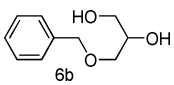
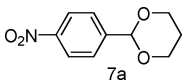
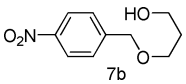
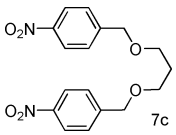
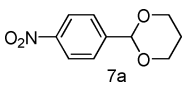
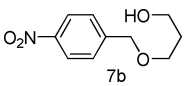
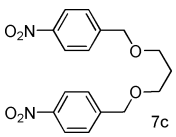
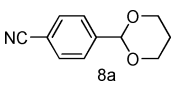
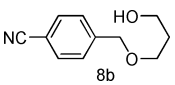
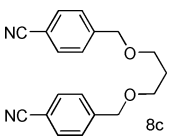
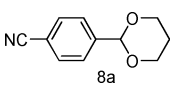
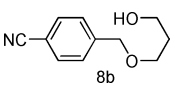
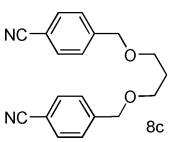
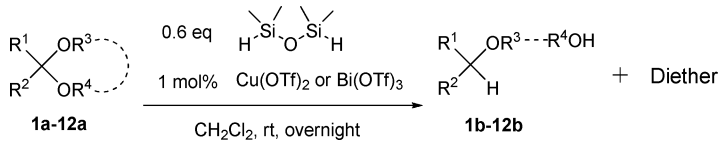
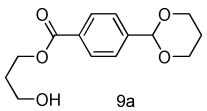
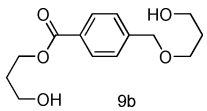
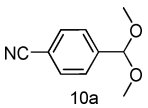
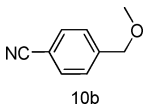
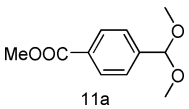
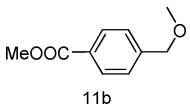
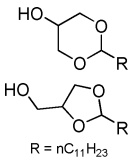
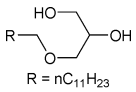
Entry	Acetal	Ether	Diether	Catalyst	Conv. (%)	Yield[a] **b** (%)	Selectivity[b]
1	 1a	 1b	 1c	$Cu(OTf)_2$	100	73	5 : 1
2	 1a	 1b	 1c	$Bi(OTf)_3$	100	89	8 : 1
3	 2a	 2b	—	$Cu(OTf)_2$	100	>99	—
4	 3a	 3b	—	$Cu(OTf)_2$	100	>99	—
5	 4a	 4b	—	$Cu(OTf)_2$	100	>99	—
6	 5a	 5b	—	$Cu(OTf)_2$	100	>99	—
7	 6a	 6b	—	$Cu(OTf)_2$	100	>99	—
8	 7a	 7b	 7c	$Cu(OTf)_2$	100	57	3 : 1[c]
9	 7a	 7b	 7c	$Bi(OTf)_3$	100	>99	>99 : 1
10	 8a	 8b	 8c	$Cu(OTf)_2$	100	61	3 : 1[c]
11	 8a	 8b	 8c	$Bi(OTf)_3$	100	>99	>99 : 1

Table 4 (*Contd.*)



Entry	Acetal	Ether	Diether	Catalyst	Conv. (%)	Yield[a] **b** (%)	Selectivity[b]
12	 9a	 9b	—	$Cu(OTf)_2$	100	85	—
13	 10a	 10b	—	$Cu(OTf)_2$	100	>99	—
14	 11a	 11b	—	$Cu(OTf)_2$	100	>99	—
15[d]	 R = $nC_{11}H_{23}$ 12a	 R = $nC_{11}H_{23}$ 12b	—	$Cu(OTf)_2$	100	72	—

[a] All products were isolated by column chromatography. [b] Ratios between ethers and diethers. [c] Determined by ^{1}H NMR after filtration and concentration under reduced pressure. [d] Reaction conditions: 150 mol% TMDS, 5 mol% $Cu(OTf)_2$, room temperature, overnight. As detected by gas chromatography, the ratio between six-membered and five-membered ring acetal is 3 : 2.

3-(3-Phenylpropoxy)propan-1-ol (2b)[15]

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–6.96 (m, 5H), 4.34 (brs, 1H), 3.66 (t, *J* = 5.4 Hz, 2H), 3.47 (t, *J* = 5.7 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.93–1.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 128.3, 128.2, 125.6, 70.0, 69.1, 60.9, 32.1, 32.1, 31.1.

2-(3-Phenylpropoxy)ethanol (3b)[15]

Colorless oil.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.12 (m, 2H), 7.12–7.00 (m, 3H), 3.62 (t, *J* = 4.5 Hz, 2H), 3.51–3.27 (m, 4H), 2.72 (s, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.91–1.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 128.4, 128.3, 125.8, 71.9, 70.4, 61.7, 32.2, 31.1.

3-(Pentyloxy)propan-1-ol (4b)[15]

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (brs, 1H), 3.69 (t, *J* = 6.1 Hz, 2H), 3.58–3.25 (m, 4H), 1.87–1.66 (m, 2H), 1.60–1.40 (m, 2H), 1.38–1.11 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 71.4, 70.1, 62.1, 31.1, 29.3, 28.2, 22.4, 13.9.

(Methoxymethyl)benzene (5b)[21]

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.01 (m, 5H), 4.30 (s, 2H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.0, 128.0, 127.3, 127.2, 74.2, 57.6.

3-(Benzyloxy)propane-1,2-diol (6b)[22]

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.10 (m, 5H), 4.43 (s, 2H), 3.86–3.34 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.4, 128.2, 127.5, 127.5, 73.7, 71.3, 70.7, 63.7.

3-(4-Nitrobenzyloxy)propan-1-ol (7b)[20]

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.52 (s, 2H), 3.74 (t, *J* = 5.6 Hz, 2H), 3.60 (t, *J* = 6.1 Hz, 2H), 2.03–1.67 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.8, 146.5, 128.2, 124.1, 72.4, 69.7, 61.3, 32.9.

1,3-Bis(4-nitro-benzyloxy)propane (7c)

Colorless oil. TLC: R_f 0.36 (cyclohexane/EtOAc = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.3 Hz, 4H), 7.38 (d, *J* = 8.3 Hz, 4H), 4.51 (s, 4H), 3.62 (t, *J* = 6.0 Hz, 4H), 1.84 (p, *J* = 5.9 Hz, 2H).

4-((3-Hydroxypropoxy)methyl)benzonitrile (8b)

Colorless oil. TLC: R_f 0.28 (cyclohexane/EtOAc = 3/2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 4.56 (s, 2H), 3.76 (t, *J* = 5.9 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 2.56 (brs, 1H), 1.96–1.79 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.9, 132.2, 127.6, 118.7, 111.2, 72.0, 69.0, 60.6, 32.2; HRESI MS: calcd for $C_{11}H_{14}NO_2$ ($[M+H]^+$) 192.1025, found 192.1021.

1,3-Bis(4-nitrile-benzyloxy)propane (8c)

Colorless oil. TLC: R_f 0.44 (cyclohexane/EtOAc = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.2 Hz, 4H), 7.42 (d, J = 8.1 Hz, 4H), 4.55 (s, 4H), 3.63 (t, J = 6.2 Hz, 4H), 1.96 (p, J = 6.3 Hz, 2H).

3-Hydroxypropyl 4-((3-hydroxypropoxy)methyl)benzoate (9b)

White Solid. TLC: R_f 0.25 (cyclohexane/EtOAc = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 4.58 (s, 2H), 4.49 (t, J = 6.2 Hz, 2H), 4.63–4.41 (m, 6H), 2.09–1.96 (m, 2H), 1.96–1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 143.9, 130.1, 129.7, 127.5, 72.9, 69.8, 62.1, 61.8, 59.4, 32.5, 32.2; HRESI MS: calcd for $C_{14}H_{20}NaO_5$ ([M+Na]$^+$) 291.1208, found 291.1205.

4-(Methoxymethyl)benzonitrile (10b)

White oil.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 4.48 (s, 2H), 3.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9, 132.0, 127.6, 118.6, 111.0, 73.4, 58.4.

Methyl 4-(methoxymethyl)benzoate (11b)

Colorless oil.^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 4.52 (s, 2H), 3.92 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 143.5, 129.7, 129.3, 127.2, 74.0, 58.3, 52.0.

3-(Dodecyloxy)propane-1,2-diol (12b)[23]

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93–3.82 (m, 1H), 3.81–3.63 (m, 2H), 3.60–3.38 (m, 4H), 1.74–1.51 (m, 2H), 1.36–1.12 (m, 18H), 0.85 (t, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 72.6, 72.1, 71.0, 64.4, 32.2, 30.0, 29.9, 29.8, 29.8, 29.6, 26.4, 23.0, 14.4.

3-Hydroxypropyl 4-(1,3-dioxan-2-yl)benzoate (9a)

To a solution of methyl 4-formylbenzoate (2.0 g, 12.2 mmol) in 25 mL propane-1,3-diol, 5 mol% of CSA (1*R*-10-camphorsulfonic acid) was added. After stirring for 16 h at 80 °C, the mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, filtered and concentrated. Silica column chromatography afforded **9a** as a white solid. TLC: R_f 0.20 (cyclohexane/EtOAc = 3/2); mp = 101.8 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09–7.95 (m, 2H), 7.64–7.44 (m, 2H), 5.53 (s, 1H), 4.45 (t, J = 6.2 Hz, 2H), 4.27 (dd, J = 11.2, 4.7 Hz, 2H), 4.07–3.88 (m, 2H), 3.74 (t, J = 6.1 Hz, 2H), 2.35–2.08 (m, 2H), 2.05–1.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 143.6, 130.5, 129.8, 126.3, 100.9, 67.6, 61.9, .59.3, 32.0, 25.9; HRESI MS: calcd for $C_{14}H_{18}NaO_5$ ([M+Na]$^+$) 289.1052, found 289.1047.

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