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Green Organocatalytic Dihydroxylation of Alkenes

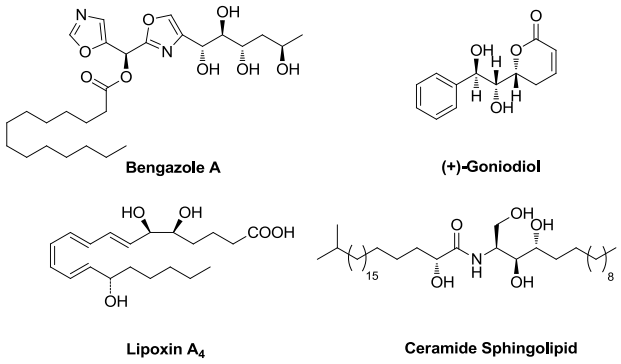
Alexis Theodorou,[a] Ierasia Triandafillidi,[a] and Christoforos G. Kokotos*[a]

Abstract: A cheap, green and metal-free one-pot procedure for the dihydroxylation of alkenes is described. H_2O_2 was employed as the oxidant and 2,2,2-trifluoroacetophenone as the organocatalyst, leading to a highly sustainable protocol, where a variety of homoallylic alcohols, amino-alkenes and double bonds were converted into the corresponding polyalcohols in high to excellent yields. This manifold takes advantage of an epoxidation reaction, followed by an *in situ* acidic treatment of the reaction mixture, upon which water ring opens the three-membered ring, leading to the desired products.

Introduction

1,2-Diols represent a repeatedly occurring moiety in numerous natural products and compounds with active biological properties. Bengazole A is a natural product isolated from a marine sponge that exhibits anthelmintic activity (Scheme 1).[1] Gonodiol is isolated from Goniothalamus gigantus and presents a selective cytotoxic potency against human lung carcinoma cells.[2] Lipoxin A_4 is a member of the bioactive family of Lipoxins, that derives from arachidonic acid, and has been shown to exhibit immunomodulatory and anti-inflammatory action,[3] while ceramides, which are isolated from female hair crabs have been shown to induce guard and copulatory behavior in male hair crabs.[4] Furthermore, glycerophospholipids and sphingophospholipids and their bilayers, important molecules in signal transmission and cell recognition, consist mainly by polyalcohols and aminoalcohols.[5] As a consequence of their synthetic versatility, a plethora of synthetic approaches have been devised for the synthesis of 1,2-alcohols. The most common methods include the two-step process, known as the Woodward-Prevost reaction (Scheme 2, path a), the direct dihydroxylation (path b) and ring opening of epoxides (path c). The Woodward-Prevost pathway relies on a substitution reaction taking place on an iodo-hydroxy compound.[6]

Unquestionably, the most studied pathway is the dihydroxylation of alkenes.[7] It is without say, that the most famous dioxygenation delivery methods are the OsO_4-catalyzed dioxygenation[8] and the Sharpless asymmetric dihydroxylation.[9] Unfortunately, the use of osmium suffers from its expense, toxicity and the volatility of the catalyst. Thus, a number of

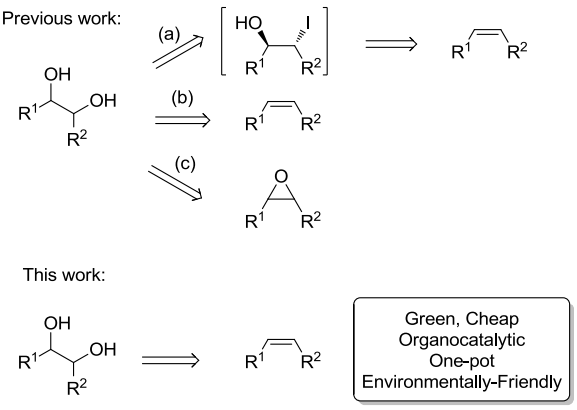


Scheme 1. Natural products containing the 1,2-diol motif.

reactions that mimic the action of the dihydroxylation has arised.[10] Notable success has been achieved with various transition metals including palladium,[11] iron,[12] ruthenium,[13] manganese,[14] copper[15] and boron.[16] Despite the widespread popularity of these reactions, the toxicity of metals and high levels of inorganic waste represent important limitations that have hindered its application on an industrial scale.

A few metal-free methods for the dihydroxylation of alkenes have been reported, using cyclic malonoyl peroxides[17] and fluorinated alcohols as catalysts.[18] In order to access *anti* 1,2-diols, pathway (c), ring-opening of epoxides, is the most widespread method. In addition, very recently, the use of malonoyl peroxides for the alkenes' *anti*-dihydroxylation was reported.[19]

Our group has contributed in the field of Organocatalysis and very recently reported a cheap, green metal-free and environmentally friendly protocol for oxidations, employing H_2O_2 as the oxidant and 2,2,2-trifluoroacetophenone as the



Scheme 2. Synthetic pathways to 1,2-diols.

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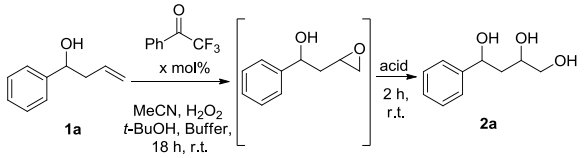
catalyst.[20] Except from the oxidation of silanes to silanols,[20a] azines and tertiary amines to *N*-oxides,[20b] and protected allylic alcohols,[20d] alkenes were readily oxidized in short reaction time.[20c] We envisaged we could introduce an one-pot protocol for the isolation of diols and polyalcohols, just by a ring opening reaction of the *in situ* formed intermediate-epoxides utilizing the aqueous environment required for the epoxidation (Scheme 2 bottom). Thus, our goal is to take advantage of a metal-free activation of H_2O_2 that could lead to the introduction of a sustainable protocol for the production of polyhydroxylated products.

Results and Discussion

Initially, we begun with our previous optimized reaction conditions for the epoxidation reaction,[20c] followed by addition of aqueous HCl (1N) in the reaction mixture. After addition of the acid, the reaction mixture was left stirring for 2 h at room temperature affording the desired triol **2a** in 55% yield (entry 1, Table 1). The presence of the organocatalyst is apparent, since omission of 2,2,2-trifluoroacetophenone from the reaction mixture led to traces of the product (Table 1, entry 2). This is expected, since H_2O_2 is a poor oxidant by itself and it has to be coupled with a catalyst to further activate it in order to perform the oxidation. The amount of MeCN and H_2O_2 was reinvestigated, in order this one-pot dihydroxylation to proceed in higher reaction yields (entries 1and 2-5, Table 1). Decreasing the catalyst loading to 5 mol% led to a noticeable decrease of reaction efficiency (Table 1, entry 6). Increasing the amount of catalyst to 20 mol% had no impact on the yield (Table 1, entry 7). Although, this already constitutes a highly sustainable metal-free process to access dihydroxylated alkenes from double bonds in one-pot, other acid promoters were also studied (entries 8-10, Table 1). Among them, (+)-camphorsulfonic acid (CSA) provided the best results.

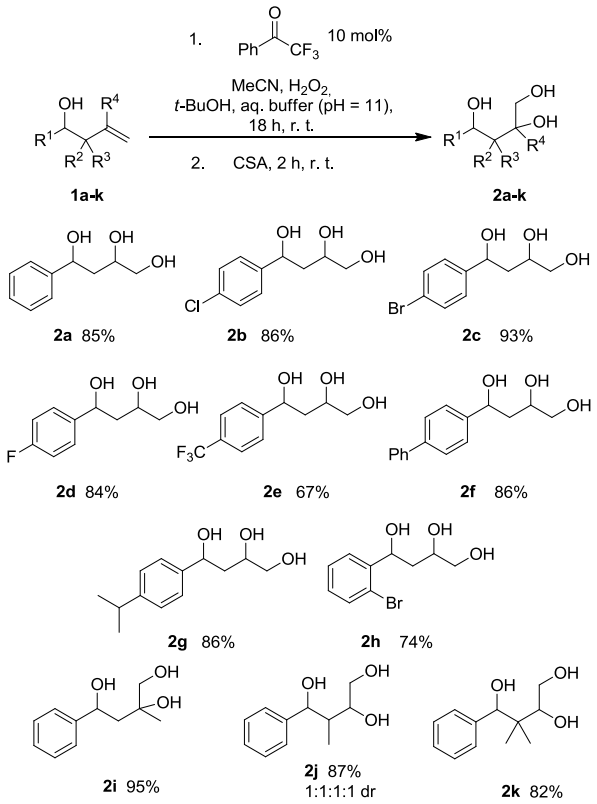
Having in hand the ideal reaction conditions, we turned our focus in exploring the substrate scope of this method (Scheme 3). In almost all cases, a 1:1 mixture of diastereomers was obtained. A number of homoallylic alcohols bearing an aromatic substituent were tested, providing the corresponding products in high yields (Scheme 3, **2a-h**). Various substituents at the *para* position had no significant impact in the reaction outcome. Both electron-rich and electron-poor aromatic moieties were employed leading to similarly high yields. In the case of *ortho*-substituted aromatic groups, the yield was slightly dropped, but still, high yield was obtained (compound **2h**). Changing the substitution pattern on the allylic moiety by building up on the steric hindrance did not alter the behavior of the reaction (compounds **2i-k**). Even quaternary dimethyl substituted carbon atom next to the alkene led to high yield of the product.

Table 1. Optimization of the reaction conditions for the organocatalytic dihydroxylation of alkenes.

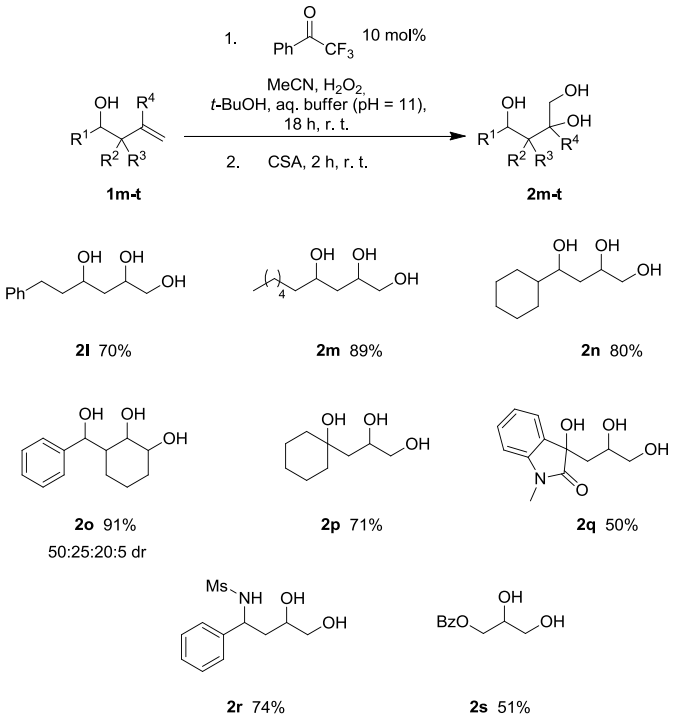


Entry	Catalyst mol (%)	MeCN, H_2O_2 (equiv.)	Acid	Yield (%)[a]
1	10	5	HCl	55
2	0	5	HCl	traces
3	10	8	HCl	58
4	10	12	HCl	62
5	10	16	HCl	69
6	5	16	HCl	57
7	20	16	HCl	69
8	10	16	AcOH	73
9	10	16	TFA	78
10	**10**	**16**	**(+)-CSA**	**85**

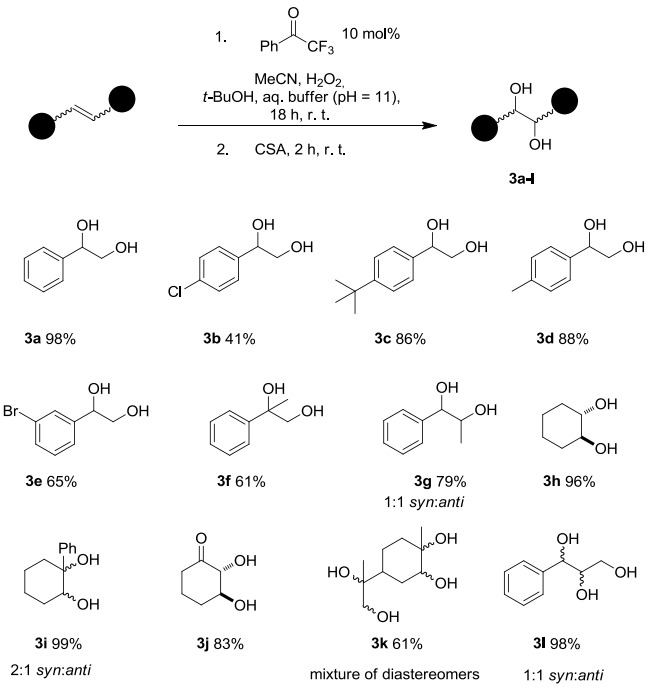
[a] Isolated yield. AcOH: acetic acid, TFA: trifluoroacetic acid, (+)-CSA: (+)-camphorsulfonic acid.



Scheme 3. Substrate scope of the organocatalytic dihydroxylation of alkenes.



Scheme 4. Substrate scope of the organocatalytic dihydroxylation of alkenes.



Scheme 5. Substrate scope of the organocatalytic dihydroxylation of alkenes.

Furthermore, the use of aliphatic side chains further expanded the substrate scope leading to high yields (compounds **2l-n**, Scheme 4). When the double bond is placed on a cyclic ring, almost quantitative dihydroxylation took place, leading to a mixture of four diastereomers (50:25:20:5, compound **2o**). Utilizing tetrasubstituted homoallylic alcohols led to dihydroxylation in good yields (compounds **2p** and **2q**). The lower yield in the case of **2q** can be attributed to the difficulty in the purification and isolation. The high versatility and sustainability of this process was further demonstrated in two additional examples (compounds **2r** and **2s**). Thus, the presence of a free hydroxy group is not necessary. Aiming at products that could be used as building blocks in lipids and sphingophospholipids, amino-alkenes and protected allylic alcohols were employed. Along with monoglycerides, diacetyl glycerol derivatives (DAG) and triacetyl glycerol compounds (TAG) are considered rich fuel additives that are used to improve cold flow and the viscosity properties of fuel when they are employed with gasoline.[21] Along these lines, we are glad to report that products **2r** and **2s**, which have high synthetic value, were isolated in good to high yields. In total, various substitution patterns were well tolerated, affording the dihydroxylated products in good to high yields.

In an effort to further expand the possibilities of this method, additional alkenes were tested (Scheme 5). Starting from a variety of substituted styrenes, diols **3a-3g** were isolated in good to excellent yields with sufficient purity (95%), after simple extractions. In most cases, no column chromatography was necessary, since all by-products, including acetamide, can be removed by simple extractions. When the aromatic moiety was replaced by an cyclic alkene, the desired diols were isolated in excellent yields (compounds **3g-3j**). Finally, poly-alcohol **3k** and triol **3l** were obtained in very good yields.

Conclusions

In conclusion, a highly sustainable one-pot green protocol for the dihydroxylation of alkenes is presented. H_2O_2, a green oxidant, since its only byproduct is water, was activated employing a cheap organic molecule (2,2,2-trilfuoroacetophenone) and a plethora of aromatic and aliphatic homoallylic alcohols were employed successfully leading to triols in high yields. Furthermore, simple alkenes, amino-alkenes and allylic alcohols were also excellent substrates for this transformation. In total, an easily-operated protocol for the intermolecular ring opening of epoxides, prepared *in situ* from alkenes, from water was demonstrated.

Experimental Section

General methods: Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F254 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F254). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Melting points were determined on a Buchi® 530 hot stage apparatus and are uncorrected. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Varian® Mercury (200 MHz, 50 MHz and 188 MHz

respectively), and are internally referenced to residual solvent signals. Data for 1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad signal, bs m = broad signal multiplet), coupling constant and integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ ppm). Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T: 0.25µm, I.D.: 0.25mm, L: 30m, Tmax: 350 ^{o}C, Column ID# 11475).

General Procedure A for the Synthesis of Homoallylic Alcohols: A flame dry round-bottom flask was charged with a solution of the allylbromide (0.61 mL, 7.00 mmol) in anhydrous THF (2 mL) under argon atmosphere. Zinc dust (210 mg, 7.00 mmol) was added slowly at 0 ^{o}C. A solution of aldehyde (2.00 mmol) in anhydrous THF (1 mL) was added to the reaction mixture. The resulting suspension was stirred for 2 hours at 0 ^{o}C and then overnight at room temperature. The reaction was quenched with saturated aqueous NH_4Cl carefully at 0 ^{o}C, filtered and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude homoallylic alcohol product was purified by column chromatography (5-20% EtOAc in Pet. Ether).

General Procedure B for the Synthesis of Homoallylic Alcohols: To a stirring solution of the magnesium (84 mg, 7.00 mmol) and I_2 (small crystal), allylbromide (0.61 mL, 7.00 mmol) in anhydrous THF (2 mL) was added slowly. The reaction mixture was heated at 60 ^{o}C for 1 hour. Aldehyde (2.00 mmol) was dissolved in anhydrous THF (1 mL) and added to the reaction mixture at 0 ^{o}C. The resulting suspension was stirred for 2 hours at 0 ^{o}C and then overnight at room temperature. The reaction was quenched with saturated aqueous NH_4Cl carefully at 0 ^{o}C, filtered and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude homoallylic alcohol product was purified by column chromatography (5-20% EtOAc in Pet. Ether).

1-Phenylbut-3-en-1-ol (1a).[22] Following Procedure A. Colorless oil; 72% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.38-7.25 (5H, m, ArH), 5.98-5.67 (1H, m, =CH), 5.22-5.06 (2H, m, $=CH_2$), 4.75-4.64 (1H, m, CHPh), 2.56-2.44 (2H, m, CH_2), 2.36 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$): *δ* 143.7, 134.2, 127.9, 127.0, 125.6, 117.3, 73.0, 43.2 ppm.

1-(4-Bromophenyl)but-3-en-1-ol (1b).[22] Following Procedure B. Colorless oil; 71% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.40 (2H, d, *J* = 8.4 Hz, ArH), 7.09 (2H, d, *J* = 8.4 Hz, ArH), 5.79-5.54 (1H, m, =CH), 5.11-4.98 (2H, m, $=CH_2$), 4.51 (1H, t, *J* = 6.7 Hz, CHPh), 3.57 (1H, s, OH), 2.36 (2H, t, *J* = 6.7 Hz, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.5, 133.6, 131.0, 127.3, 120.8, 118.0, 72.4, 43.1 ppm.

1-(4-Chlorophenyl)but-3-en-1-ol (1c).[22] Following Procedure B. Colorless oil; 52% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.26 (2H, d, *J* = 8.4 Hz, ArH), 7.17 (2H, d, *J* = 8.4 Hz, ArH), 5.82-5.57 (1H, m, =CH), 5.13-5.00 (2H, m, $=CH_2$), 4.57 (1H, t, *J* = 6.5 Hz, CHPh), 3.19 (1H, s, OH), 2.38 (2H, t, *J* = 6.5 Hz, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.1, 133.8, 132.7, 128.2, 127.0, 118.2, 72.4, 43.4 ppm.

1-(4-Fluorophenyl)but-3-en-1-ol (1d).[22] Following Procedure B. Colorless oil; 57% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.27-7.15 (2H, m, ArH), 7.04-6.89 (2H, m, ArH) 5.70 (1H, ddt, *J* = 16.6, 9.4 and 6.5 Hz, =CH), 5.12-4.96 ($=CH_2$), 4.58 (1H, t, *J* = 6.5 Hz, CHPh), 3.38 (1H, br s, OH), 2.39 (2H, t, *J* = 6.5 Hz, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 161.8 (d, *J* = 245.0 Hz), 139.5 (d, *J* = 3.0 Hz), 134.0, 127.3 (d, *J* = 8.0 Hz), 117.8, 114. 8 (d, *J* = 21.3 Hz), 72.5, 43.4 ppm. ^{19}F NMR ($CDCl_3$): *δ* -59.8 - -60.6 (m) ppm.

1-(4-(Trifluoromethyl)phenyl)but-3-en-1-ol (1e).[23] Following Procedure A. Colorless oil; 83% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.56 (2H, d, *J* = 8.2 Hz, ArH), 7.39 (2H, d, *J* = 8.2 Hz, ArH), 5.83-5.59 (1H, m, =CH), 5.18-5.04 (2H, m, $=CH_2$), 4.74 (1H, t, *J* = 6.4 Hz, CHPh), 3.27 (1H, s, OH), 2.46 (2H, t, *J* = 6.4 Hz, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 147.1, 133.3, 129.9 (q, *J* = 32.4 Hz), 126.1, 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.3 Hz), 119.0, 77.9, 43.4 ppm. ^{19}F NMR ($CDCl_3$): *δ* -7.52 (s) ppm.

1-([1,1'-Biphenyl]-4-yl)but-3-en-1-ol (1f).[24] Following Procedure B. Colorless oil; 67% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.74-7.37 (9H, m, ArH), 6.05-5.83 (1H, m, =CH), 5.33-5.18 (2H, m, $=CH_2$), 4.81 (1H, t, *J* = 6.5 Hz, CHPh), 3.20 (1H, br s, OH), 3.20 (2H, t, *J* = 6.5 Hz, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.8, 140.4, 139.9, 134.3, 128.5, 127.0, 126.7, 126.7, 126.1, 117.8, 72.9, 43.4 ppm.

1-(4-Isopropylphenyl)but-3-en-1-ol (1g).[24] Following Procedure A. Colorless oil; 42% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.29 (2H, d, *J* = 8.2 Hz, ArH), 7.21 (2H, d, *J* = 8.2 Hz, ArH), 5.95-5.70 (1H, m, =CH), 5.24-5.09 (2H, m, $=CH_2$), 4.70 (1H, t, *J* = 6.5 Hz, CHPh), 2.91 [1H, sept, *J* = 6.9 Hz, $CH(CH_3)_2$], 2.51 (2H, t, *J* = 6.5 Hz, CH_2), 1.98 (1H, br s, OH), 1.25 (6H, d, *J* = 6.9 Hz, 2 x CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 147.8, 141.2, 134.6, 126.2, 125.7, 117.6, 73.1, 43.4, 33.6, 23.8 ppm.

1-(2-Bromophenyl)but-3-en-1-ol (1h).[24] Following Procedure B. Colorless oil; 50% yield; ^{1}H NMR ($CDCl_3$): *δ* 756-7-47 (2H, m, ArH), 7.31 (1H, m, ArH), 7.11 (1H, td, *J* = 7.6 and 1.7 Hz, ArH), 5.97-5.75 (1H, m, =CH), 5.24-5.12 (2H, m, $=CH_2$), 5.07 (1H, dd, *J* = 8.3 and 3.8 Hz, CHPh) 2.68-2.53 (1H, m, C*H*H), 2.47 (1H, s, OH) 2.42-2.23 (1H, m, C*H*H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.6, 134.0, 132.3, 128.5, 127.3, 127.1, 121.5, 118.0, 71.6, 41.7 ppm.

3-Methyl-1-phenylbut-3-en-1-ol (1i).[25] Following Procedure A. Colorless oil; 87% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.40-7.22 (5H, m, ArH), 4.95-4.74 (3H, m, CHPh and $=CH_2$), 2.72 (1H, br s, OH), 2.43 (2H, d, *J* = 7.6 Hz, CH_2), 1.79 (3H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 143.9, 142.1, 128.1, 127.2, 125.6, 113.7, 71.3, 48.0, 22.2 ppm.

2-Methyl-1-phenylbut-3-en-1-ol (1j).[26] Following Procedure A. 1:1 mixture of diastereomers; Colorless oil; 92% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.38-7.22 (5H, m, ArH), 5.92-5.65 (1H, m, =CH), 5.25-4.98 (2H, m, $=CH_2$), 4.55 (0.5H, d, *J* = 5.7 Hz, OCHPh), 4.34 (0.5H, d, *J* = 7.7 Hz, OCHPh), 2.66-2.36 (2H, m, C*H*CH_3 and OH), 1.02 (1.5H, d, *J* = 6.8 Hz, CH_3), 0.88 (1.5H, d, *J* = 6.8 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.5, 142.3, 140.5, 140.2, 128.0, 127.8, 127.4, 127.1, 126.7, 126.4, 116.5, 115.2, 77.7, 77.1, 46.0, 44.5, 16.3, 14.1 ppm.

2,2-Dimethyl-1-phenylbut-3-en-1-ol (1k).[27] Following Procedure A. Colorless oil; 88% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.36-7.26 (5H, m, ArH), 5.92 (1H, dd, *J* = 17.4 and 7.8 Hz, =CH), 5.14 (1H, dd, *J* = 7.8 and 1.4 Hz, =C*H*H), 5.07 (1H, dd, *J* = 17.4 and 1.4 Hz, =C*H*H), 4.40 (1H, s, CHPh), 1.23 (1H, br s, OH), 1.02 (3H, s, CH_3) 0.97 (3H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 145.0, 140.7, 127.7, 127.4, 127.3, 113.7, 80.5, 42.1, 24.3, 21.0 ppm.

1-Phenylhex-5-en-3-ol (1l).[27] Following Procedure A. Colorless oil; 75% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.37-7.20 (5H, m, ArH), 5.97-5.75 (1H, m, =CH), 5.23-5.10 (2H, m, $=CH_2$), 3.77-3.62 (1H, m, OCH), 2.96-2.62 (2H, m, CH_2Ph), 2.43-2.04 (3H, m, OH and CH_2), 1.88-1.74 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 141.9, 134.5, 128.3, 128.2, 125.7, 118.0, 69.8, 41.9, 38.3, 31.9 ppm.

Dec-1-en-4-ol (1m).[28] Following Procedure A. Colorless oil; 35% yield; ^{1}H NMR ($CDCl_3$): *δ* 5.88-5.63 (1H, m, =CH), 5.08-4.92 (2H, m, $=CH_2$), 3.62-

3.46 (1H, m, OCH), 2.43-1.55 (3H, m, OH and CH_2), 1.59-1.12 (10H, m, 5 x CH_2), 0.81 (3H, t, *J* = 5.0 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 134.9, 117.4, 70.5, 41.8, 36.6, 31.7, 29.2, 25.5, 22.4, 13.9 ppm.

1-Cyclohexylbut-3-en-1-ol (1n).[27] Following Procedure A. Colorless oil; 87% yield; ^{1}H NMR ($CDCl_3$): *δ* 5.87 (1H, ddt, *J* = 15.0, 10.6 and 7.5 Hz, =CH), 5.18-5.02 (2H, m, =CH_2), 3.37-3.22 (1H, m, OCH), 2.20 (2H, m, =CHC*H*$_2$), 1.70-1.16 (12H, m, OH, CH and 5 x CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 135.4, 117.5, 74.7, 42.9, 38.6, 28.9, 27.9, 26.3, 26.1, 26.0 ppm.

Cyclohex-2-en-1-yl(phenyl)methanol (1o).[29] Following Procedure A. 1:1 mixture of diastereomers; Colorless oil; 56% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.43-7.22 (5H, m, ArH), 5.92-5.73 (1H, m, CH=), 5.47-5.31 (1H, m, =CH), 4.57 (0.5H, d, *J* = 7.0 Hz, CHPh), 4.52 (0.5H, d, *J* = 6.7 Hz, CHPh), 2.61-2.22 (2H, m, OH and CH), 2.09-1.92 (2H, m, CH_2) 1.88-1.65 (2H, m CH_2), 1.62-1.44 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.8, 130.0, 128.0, 127.2, 126.4, 126.2, 77.3, 42.8, 25.1, 23.9, 21.0 ppm.

1-Allylcyclohexan-1-ol (1p).[26] Following Procedure A. Colorless oil; 45% yield; ^{1}H NMR ($CDCl_3$): *δ* 5.98-5.73 (1H, m, =CH), 5.18-5.02 (2H, m, =CH_2), 2.20 (2H, d, *J* = 7.5 Hz, =CHC*H*$_2$), 1.73-1.10 (10H, m, 5 x CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 133.7, 118.4, 70.8, 46.6, 37.3, 25.7, 22.1 ppm.

3-Allyl-3-hydroxy-1-methylindolin-2-one (1q).[30] Following Procedure A. Yellow solid; 34% yield; ^{1}H NMR (CD_3OD): *δ* 7.40-7.26 (2H, m, ArH), 7.10 (1H, dd, *J* = 10.7 and 4.3 Hz, ArH), 6.94 (1H, d, *J* = 7.7 Hz, ArH), 5.40 (1H, m, =CH), 5.02-4.84 (3H, m, OH and =CH_2), 3.13 (3H, s, NCH_3), 2.65 (2H, m, CH_2) ppm. ^{13}C NMR (CD_3OD): *δ* 179.5, 144.5, 132.1, 131.8, 130.6, 124.9, 124.1, 119.9, 109.6, 77.2, 43.3, 26.3 ppm.

***N*-(1-Phenylbut-3-en-1-yl)methanesulfonamide (1r).**[31] Yellow oil; 32% yield (4 steps); ^{1}H NMR ($CDCl_3$): *δ* 7.33-7.16 (5H, m, ArH), 5.76-5.51 (2H, m, NH and =CH), 5.12-4.93 (2H, m, =CH_2), 4.53-4.35 (1H, m, NCHPh), 2.57-2.40 (5H, m, CH_3 and CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 141.4, 133.8, 129.0, 128.1, 126.9, 118.9, 57.9, 42.1, 41.9 ppm. MS (ESI) *m/z* 224 [$(M-H)^-$, 100%].

General Procedure for the One-pot Organocatalytic Oxidative Dihydroxylation of Alkenes (2a-2s, 3a-3l). Alkene (0.50 mmol) was placed in a round bottom flask and dissolved in tert-butanol (0.4 mL). 2,2,2-Trifluoro-1-phenylethanone (8.7 mg, 0.10 mmol), aqueous buffer solution (0.4 mL, 0.6M K_2CO_3 - 4x10^{-4}M EDTA disodium salt), acetonitrile (0.40 mL, 8.00 mmol) and 30% aqueous H_2O_2 (0.84 mL, 8.00 mmol) were added consecutively. The reaction mixture was left stirring for 18 hours at room temperature and then (+)-CSA (232 mg, 1.00 mmol) was added. The reaction mixture was stirred for 2 hours. The crude product was purified using flash column chromatography (50-100% EtOAc in Pet. Ether) to afford the desired product. Alternatively, if the starting alkene is fully consumed, after reaction completion, the reaction mixture can be diluted with CH_2Cl_2 (10 mL) and washed with HCl (1N, 10 mL) and brine (10 mL). The crude organic layers can be dried (Na_2SO_4) and the product can be obtained with sufficient purity.

4-Phenylbutane-1,2,4-triol (2a).[32] 1:1 mixture of diasteromers; Colorless oil; 85% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.26-7.14 (5H, m, ArH), 4.92-4.82 (0.5H, m, OCHPh), 4.77 (0.5H, dd, *J* = 9.1 and 3.6 Hz, OCHPh), 4.51 (2H, br s, 2 x OH), 3.98-3.72 (2H, m, OH and OCH), 3.49-3.26 (2H, m, OCH_2), 1.84-1.53 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 144.4, 143.9, 128.4, 128.3, 127.5, 127.2, 125.7, 125.5, 73.3, 71.7, 70.3, 69.1, 66.6, 66.3, 41.6, 41.3 ppm. MS (ESI) *m/z* 181 ($M-H^-$, 100%).

4-(4-Bromophenyl)butane-1,2,4-triol (2b). 1:1 mixture of diasteromers; Yellow solid; 86% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.40 (2H, d, *J* = 7.7 Hz, ArH), 7.17 (2H, d, *J* = 7.7 Hz, ArH), 5.05-4.89 (1H, m, OCHPh), 4.10-3.86 (1H, m, OCH), 3.70-3.42 (2H, m, OCH_2), 2.61 (3H, br s, 3 x OH), 1.97-1.62 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 143.4, 143.0, 131.4, 131.3, 127.4, 127.2, 121.1, 120.8, 72.7, 71.6, 69.6, 68.9, 66.4, 66.2, 41.3, 41.1 ppm. HRMS (ESI): *m/z* calcd. for $C_{10}H_{13}BrNaO_3$ $[M+Na]^+$ 282.9940; found 282.9940.

4-(4-Chlorophenyl)butane-1,2,4-triol (2c). 1:1 mixture of diasteromers; Low melting point solid; 93% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.23-7.15 (4H, m, ArH), 4.89-4.73 (1H, m, OCHPh), 4.41 (3H, br s, 3 x OH), 3.98-3.72 (1H, m, OCH), 3.55-3.28 (2H, m, OCH_2), 1.84-1.53 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.9, 142.4, 133.0, 132.7, 128.4, 128.4, 127.0, 126.8, 72.6, 71.6, 69.6, 68.9, 66.5, 66.2, 41.3, 41.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{10}H_{13}ClNaO_3$ $[M+Na]^+$ 239.0445; found 239.0444.

4-(4-Fluorophenyl)butane-1,2,4-triol (2d). 1:1 mixture of diasteromers; White solid; 84% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.29-7.17 (2H, m, ArH), 7.02-6.86 (2H, m, ArH), 4.91-4.76 (1H, m, OCHPh), 3.94-3.65 (4H, br s, OCH and 3 x OH), 3.54-3.32 (2H, m, OCH_2), 1.88-1.56 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 162.0 (d, *J* = 236.8 Hz), 161.9 (d, *J* = 236.8 Hz), 140.1 (d, *J* = 22.3 Hz), 140.0 (d, *J* = 22.3 Hz), 127.3 (d, *J* = 8.1 Hz), 127.0 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 3.0 Hz), 114.8 (d, *J* = 3.0 Hz), 72.7, 71.7, 69.7, 69.0, 66.5, 66.3, 41.5, 41.3 ppm. ^{19}F NMR ($CDCl_3$): *δ* -60.1 - -60.3 (m), -60.6 - -60.8 (m) ppm. HRMS (ESI): *m/z* calcd. for $C_{10}H_{13}FNaO_3$ $[M+H]^+$ 223.0741; found 223.0738.

4-(4-(Trifluoromethyl)phenyl)butane-1,2,4-triol (2e). 1:1 mixture of diasteromers; Colorless oil; 67% yield; ^{1}H NMR (80% $CDCl_3$:20% CD_3OD): *δ* 7.52 (2H, d, *J* = 8.1 Hz, ArH), 7.41 (2H, d, *J* = 8.1 Hz, ArH), 5.03-4.86 (1H, m, OCHPh), 3.92-3.78 (1H, m, OCH), 3.67 (3H, br s, 3 x OH), 3.55-3.32 (2H, m, OCH_2), 1.88-1.65 (2H, m, CH_2) ppm. ^{13}C NMR (80% $CDCl_3$:20% CD_3OD): *δ* 148.9, 148.3, 129.4 (q, *J* = 32.4 Hz), 129.1 (q, *J* = 32.2 Hz), 125.9, 125.7, 125.2 (q, *J* = 3.1 Hz), 125.1 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 271.9 Hz), 124.0 (q, *J* = 271.9 Hz), 72.6, 71.6, 69.8, 68.9, 66.4, 66.2, 41.6, 41.3 ppm. ^{19}F NMR (80% $CDCl_3$:20% CD_3OD): *δ* -15.05 (s), -15.08 (s); HRMS (ESI): *m/z* calcd. for $C_{11}H_{13}F_3NaO_3$ $[M+Na]^+$ 273.0709; found 273.0708.

4-([1,1'-Biphenyl]-4-yl)butane-1,2,4-triol (2f). 1:1 mixture of diasteromers; White solid; 86% yield; ^{1}H NMR (50% $CDCl_3$:50% CD_3OD): *δ* 7.44-7.22 (9H, m, ArH), 5.06-4.95 (0.5H, m, OCHPh) 4.94-4.83 (0.5H, m, OCHPh), 4.59 (3H, br s, 3 x OH), 4.15-4.02 (0.5H, m, OCH), 4.00-3.85 (0.5H, m, OCH), 3.68-3.36 (2H, m, OCH_2), 2.02-1.61 (2H, m, CH_2) ppm. ^{13}C NMR (50% $CDCl_3$:50% CD_3OD): *δ* 143.6, 143.0, 140.4, 140.3, 139.9, 139.6, 128.4, 126.8, 126.8, 126.6, 126.6, 126.5, 125.9, 125.6, 72.5, 71.1, 69.8, 68.8, 66.2, 65.9, 41.6, 41.2 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{18}NaO_3$ $[M+Na]^+$ 281.1148; found 281.1147.

4-(4-Isopropylphenyl)butane-1,2,4-triol (2g). 1:1 mixture of diasteromers; Yellow solid; 86% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.20 (2H, d, *J* = 8.3, ArH), 7.12 (2H, d, *J* = 8.3 Hz, ArH), 4.97-4.76 (1H, m, OCHPh), 4.52-3.81 (4H, m, 3 x OH and OCH), 3.57-3.33 (2H, m, OCH2), 2.83 [1H, sept, *J* = 6.9 Hz, $CH(CH_3)_2$], 1.93-1.57 (2H, m, CH_2), 1.19 (6H, d, *J* = 6.9 Hz, 2 x CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 148.2, 147.9, 141.8, 141.4, 126.4, 126.4, 125.7, 125.5, 73.6, 72.0, 70.4, 69.3, 66.8, 66.5, 41.2, 41.4, 33.7, 23.9 ppm. HRMS (ESI): *m/z* calcd. for $C_{13}H_{19}O_3$ $[M-H]^-$ 223.1340; found 223.1340.

4-(2-Bromophenyl)butane-1,2,4-triol (2h). 1:1 mixture of diasteromers; Yellow oil; 74% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.55-7.34 (2H, m, ArH), 7.28-7.15 (1H, m, ArH), 7.08-6.95 (1H, m, ArH), 5.33-5.10 (1H, m, OCHPh), 4.55-3.83 (4H, m, 3 x OH and OCH), 2.66-3.01 (2H, m, OCH_2), 1.89-1.50 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 143.0, 142.9, 132.5, 132.5, 128.8, 128.7, 127.8, 127.7, 127.2, 127.2, 121.3, 121.2, 72.6, 72.4, 69.9, 69.5,

66.6, 66.5, 39.7, 39.2 ppm. HRMS (ESI): *m/z* calcd. for $C_{10}H_{13}BrNa$ $[M+Na]^+$ 282.9940; found 282.9937.

2-Methyl-4-phenylbutane-1,2,4-triol (2i).[33] 55:45 mixture of diasteromers; Colorless oil; 95% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.29-7.18 (5H, m, ArH), 5.15-4.75 (2H, m, OH and OCHPh), 3.67 (1H, d, *J* = 11.3 Hz, CHHO), 3.47 (1H, d, *J* = 11.3 Hz, OCHH), 3.36 (2H, br s, 2 x OH), 2.08-1.96 (0.45H, m, C*H*H), 1.94-1.75 (0.55H, m, C*H*H), 1.76-1.64 (0.55H, m, C*H*H), 1.64-1.46 (0.45H, m, C*H*H), 1.20 (1.35H, s, CH_3), 1.13 (1.65H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 144.3, 144.1, 128.4, 127.5, 127.4, 125.7, 125.6, 73.6, 73.4, 71.5, 71.0, 70.2, 68.7, 46.8, 46.0, 25.0, 23.5 ppm. MS (ESI) *m/z* 195 ($M-H^-$, 100%).

3-Methyl-4-phenylbutane-1,2,4-triol (2j). 1:1:1:1 mixture of diasteromers; Viscous colorless oil; 87% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.32-7.10 (5H, m, ArH), 5.08 (0.5H, d, *J* = 2.1 Hz, OCHPh), 4.98 (0.5H, d, *J* = 2.5 Hz, OCHPh), 4.82 (2H, br s, OH), 4.54-4.44 (1H, m, OCH), 4.16-4.02 (0.25H, m, OC*H*H), 3.95-3.85 (0.25H, m, OC*H*H), 3.77-3.42 (2.5H, m, OCH_2 and OH), 1.98-1.76 (1H, m, C*H*CH_3), 0.69 (0.75H, d, *J* = 7.1 Hz, CH_3), 0.60 (0.75H, d, *J* = 7.0 Hz, CH_3), 0.52 (0.75H, d, *J* = 7.0 Hz, CH_3), 0.44 (0.75H, d, *J* = 6.9 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.8, 142.7, 142,4, 142.2, 128.4, 128.1, 128.0, 127.8, 127.7, 127.1, 127.0, 126.9, 126.8, 125.9, 125.7, 78.6, 76.7, 76.2, 75.8, 75.7, 74.2, 73.6, 72.4, 65.0, 64.9, 64.6, 64.4, 41.8, 41.6, 41.5, 41.4, 12.7, 10.9, 9.7 ppm. HRMS (ESI): *m/z* calcd. for $C_{11}H_{16}NaO_3$ $[M+Na]^+$ 219.0992; found 219.1001.

3,3-Dimethyl-4-phenylbutane-1,2,4-triol (2k). 1:1 mixture of diasteromers; White solid; 82% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.27-7.21 (5H, m, ArH), 5.15-5.12 (2H, br s, 2 x OH), 4.63 (1H, s, OCHPh), 3.75-3.42 (4H, m, OH, OCH and OCH_2), 0.84 (1.5H, s, CH_3), 0.76 (3H, s, CH_3), 0.58 (1.5H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 140.6, 128.1, 127.9, 127.5, 127.4, 127.4, 80.4, 80.2, 79.8, 77.6, 63.1, 62.7, 40.7, 39.8, 22.5, 21.1, 19.8, 15.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{12}H_{17}O_3$ $[M-H]^-$ 209.1183; found 209.1183.

6-Phenylhexane-1,2,4-triol (2l).[34] 1:1 mixture of diasteromers; Yellow oil; 70% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.32-7.10 (5H, m, ArH), 4.12-3.35 (7H, m, 3 x OH and 2 x OCH and OCH_2), 2.86-2.49 (2H, m, CH_2Ph), 1.85-1.68 (2H, m, CH_2), 1.66-1.43 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 141.9, 141.7, 128.3, 128.3, 125.8, 122.3, 72.3, 70.9, 69.2, 67.7, 66.8, 66.5, 39.5, 39.4, 39.0, 38.9, 32.0, 31.6 ppm. MS (ESI) *m/z* 209 ($M-H^-$, 100%).

Decane-1,2,4-triol (2m).[32] 1:1 mixture of diasteromers; Viscous orange oil; 89% yield; ^{1}H NMR ($CDCl_3$): *δ* 4.65-4.32 (3H, br s, 3 x OH), 3.98-3.67 (2H, m, 2 x OCH), 3.59-3.25 (2H, m, OCH_2), 1.57-1.12 (12H, m 6 x CH_2), 0.91-0.74 (3H, m, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 72.4, 71.6, 69.2, 68.2, 66.9, 66.5, 39.5, 39.0, 38.0, 37.8, 31.8, 29.3, 25.8, 25.4, 22.6, 14.0 ppm. MS (ESI) *m/z* 189 ($M-H^-$, 100%).

4-Cyclohexylbutane-1,2,4-triol (2n).[16] 1:1 mixture of diasteromers; Viscous white oil; 80% yield; ^{1}H NMR ($CDCl_3$): *δ* 4.07-3.87 (1H, m, OCH), 3.73-3.42 (3H, m, 1 x OCH and OCH_2), 2.73 (3H, br s, 3 x OH), 1.92-1.52 (5H, m, 1 x CH and 2 x CH_2), 0.42-0.83 (8H, m, 4 x CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 76.0, 72.7, 72.2, 69.4, 67.0, 66.6, 44.1, 43.9, 36.4, 35.8, 29.0, 28.8, 28.2, 28.0, 26.4, 26.2, 26.1 ppm. MS (ESI) *m/z* 187 ($M-H^-$, 100%).

3-(Hydroxy(phenyl)methyl)cyclohexane-1,2-diol (2o).[16] 50:25:20:5 mixture of diastereomers; Colorless oil; 91% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.31-7.12 (5H, m, ArH), 5.83 (2H, br s, 2 x OH), 5.10 (0.25H, d, *J* = 0.7 Hz, OCHPh), 4.96 (0.5H, d, *J* = 2.6 Hz, OCHPh), 4.76 (0.2H, d, *J* = 9.9 Hz, OCHPh), 4.52 (0.05H, d, *J* = 8.8 Hz, OCHPh), 3.98-3.76 (1H, m, OCH), 3.62-3-31 (1H, m, OCH), 2.24-0.90 (7H, m, OH and 3 x CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.8, 142.5, 142.4, 128.4, 128.1, 128.0, 127.1, 127.0, 126.9, 126.0, 125.8, 77.5, 77.4, 75.8, 75.8, 75.7, 75.5, 74.3, 72.7, 70.0, 48.7, 48.5, 41.9, 27.2, 27.1, 23.3, 22.8, 19.3, 19.2, 18.1, 18.0 ppm. MS (ESI) *m/z* 221 ($M-H^-$, 100%).

3-(1-Hydroxycyclohexyl)propane-1,2-diol (2p).[35] 1:1 mixture of diasteromers; Colorless solid; 71% yield; ^{1}H NMR ($CDCl_3$): *δ* 4.45 (1H, br s, OH), 4.06 (1H, ddd, *J* = 9.3 and 6.9 and 3.6 Hz, OCH), 3.56 (1H, dd, *J* = 11.6 and 3.3 Hz, OC*H*H), 3.46 (2H, br s, 2 x OH), 3.42 (1H, dd, *J* = 11.6 and 6.6 Hz, OC*H*H), 1.77-1.17 (12H, m, 6 x CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 72.2, 69.2, 67.1, 42.0, 39.7, 36.0, 25.7, 22.2, 22.0 ppm. MS (ESI) *m/z* 197 ($M+Na^+$, 100%).

3-(2,3-Dihydroxypropyl)-3-hydroxy-1-methylindolin-2-one (2q). 1:1 mixture of diasteromers; Orange oil; 50% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.49-7.38 (1H, m, ArH), 7.37-7.18 (1H, m, ArH), 7.13-6.96 (1H, m, ArH), 6.85-6.71 (1H, m, ArH), 5.07 (1H, br s, OH), 4.51-4.30 (1H, m, OCH), 4.17 (1H, br s, OH), 3.70-3.39 (3H, m, OH and OCH_2), 3.15 (1.5H, s, NCH_3), 3.12 (1.5H, s, NCH_3), 2.46-2.23 (1H, m C*H*H), 2.21-1.96 (1H, m, C*H*H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 178.7, 178.5, 142.6, 142.3, 130.7, 129.7, 124.3, 123.6, 123.5, 108.8, 108.7, 75.8, 75.7, 68.6, 68.3, 66.3, 66.2, 39.8, 39.2, 26.3, 26.2 ppm. HRMS (ESI): *m/z* calcd. for $C_{12}H_{14}NO_4$ $[M-H]^-$ 236.0928; found 236.0922.

***N*-(3,4-Dihydroxy-1-phenylbutyl)methanesulfonamide (2r).** 55:45 mixture of diasteromers; Colorless oil; 74% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.40-7.17 (5H, m, ArH), 6.57 (0.45H, d, *J* = 6.4 Hz, NH), 6.51 (0.55H, d, *J* = 8.8 Hz, NH), 4.83-4.55 (1H, m, NCHPh), 4.36-3.93 (2H, m, OH and OCH), 3.80-3.37 (3H, m, OH and OCH_2), 2.55 (1.65H, s, CH_3), 2.45 (1.35H, s, CH_3), 2.15-1.63 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 141.7, 141.2, 128.9, 128.0, 127.7, 126.9, 126.4, 70.2, 68.7, 66.5, 66.3, 56.7, 54.8, 41.6, 41.5, 40.1, 40.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{11}H_{16}NO_4S$ $[M-H]^-$ 258.0806; found 258.0805.

2,3-Dihydroxypropyl benzoate (2s).[36] Yellow oil. 51% yield; ^{1}H NMR ($CDCl_3$): *δ* 8.01 (2H, d, *J* = 7.0 Hz, ArH), 7.60-7.48 (1H, m, ArH), 7.46-7.33 (2H, m, ArH), 4.39 (2H, d, *J* = 5.4 Hz, OCH_2), 4.14-3.99 (1H, m, OH), 3.97-3.90 (1H, m, OCH), 3.82-3.50 (4H, m, 2 x OH and OCH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 167.7, 133.3, 129.7, 129.5, 128.4, 70.3, 65.6, 63.4 ppm. MS (ESI) *m/z* 219 ($M+Na^+$, 100%).

1-Phenylethane-1,2-diol (3a).[18] Colorless oil; 98% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.25 (5H, m, ArH), 4.75 (1H, dd, *J* = 7.8 and 3.9 Hz, OCHPh), 4.19 (2H, br s, 2 x OH), 3.70-3.51 (2H, m, OCH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 140.0, 128.4, 127.9, 126.0, 74.7, 67.8 ppm. MS (ESI) *m/z* 137 ($M-H^-$, 100%).

1-(4-Chlorophenyl)ethane-1,2-diol (3b).[37] Colorless oil; 41% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.36-7.17 (4H, m, ArH), 5.15-4.52 (3H, m, 2 x OH and PhCH), 3.79-3.42 (2H, m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): *δ* 138.8, 133.6, 128.6, 127.5, 73.9, 67.6 ppm. MS (ESI) *m/z* 171 ($M-H^-$, 100%).

1-(4-(tert-Butyl)phenyl)ethane-1,2-diol (3c).[38] White solid; 86% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.36 (2H, d, *J* = 8.4 Hz, ArH), 7.25 (2H, d, *J* = 8.4 Hz, ArH), 4.85-4.66 (1H, m, PhCH), 3.92-3.40 (4H, m, CH_2 and 2 x OH), 1.30 [9H, s, $C(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$): *δ* 150.8, 137.5, 125.8, 125.4, 74.9, 67.9, 34.5, 31.3 ppm. MS (ESI) *m/z* 193 ($M-H^-$, 100%).

1-(*p*-Tolyl)ethane-1,2-diol (3d).[37] White solid; 88% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.19 (2H, d, *J* = 8.2 Hz, ArH), 7.11 (2H, d, *J* = 8.2 Hz, ArH), 4.72 (1H, dd, *J* = 7.8 and 3.9 Hz, PhCH), 3.68 (2H, br s, 2 x OH), 3.69-3.52 (2H, m, CH_2), 2.32 (3H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 137.5, 137.3, 129.1,126.0, 74.5, 67.9, 21.1 ppm. MS (ESI) *m/z* 151 ($M-H^-$, 100%).

1-(3-Bromophenyl)ethane-1,2-diol (3e).[39] Colourless oil; 65% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.45 (1H, s, ArH), 7.42-7.35 (1H, m, ArH), 7.24-7.11 (2H, m, ArH), 5.39 (2H, br s, 2 x OH), 4.74 (1H, dd, *J* = 8.4 and 3.3 Hz, PhCH), 3.68 (1H, dd, *J* = 11.6 and 3.3 Hz, C*H*H), 3.55 (1H, dd, *J* = 11.6 and 8.4 Hz, PhC*H*H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 142.4, 131.0, 130.1, 129.1, 124.6, 122.6, 74.0, 67.7 ppm. MS (ESI) *m/z* 214 (M-H$^-$, 100%).

2-Phenylpropane-1,2-diol (3f).[38] Yellow oil; 61% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.48-7.21 (5H, m, ArH), 3.75 (1H, d, *J* = 11.3 Hz, C*H*H), 3.59 (1H, d, *J* = 11.3 Hz, C*H*H), 2.85 (2H, br s, 2 x OH), 1.50 (3H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 144.8, 128.5, 127.1, 125.0, 74.9, 70.9, 25.9 ppm. MS (ESI) *m/z* 151 (M-H$^-$, 100%).

1-Phenylpropane-1,2-diol (3g).[40] 1:1 mixture of diastereomers; Colourless oil; 79% yield; ^{1}H NMR ($CDCl_3$): *δ* 7.44-7.25 (5H, m, ArH), 4.66 (0.5H, d, *J* = 4.0 Hz, PhCH), 4.31 (0.5H, d, *J* = 7.7 Hz, PhCH), 4.21-3.92 (0.5H, m, CH), 3.91-3.76 (0.5H, m, CH), 3.43 (2H, br s, 2 x OH), 1.04-0.96 (3H, m, CH_3) ppm. ^{13}C NMR ($CDCl_3$): *δ* 140.9, 140.2, 128.4, 128.2, 128.0, 127.6, 126.8, 126.5, 79.4, 77.2, 72.2, 71.3, 18.6, 16.7 ppm. MS (ESI) *m/z* 151 (M-H$^-$, 100%).

***trans*-Cyclohexane-1,2-diol (3h).**[40] White solid; 96% yield; ^{1}H NMR ($CDCl_3$): *δ* 4.00 (2H, br s, 2 x OH), 3.38-3.23 (2H, m, 2 x C*H*OH), 2.13-1.84 (2H, m, 2 x C*H*H), 1.73-1.63 (2H, m, 2 x C*H*H), 1.36-1.07 (4H, m, 4 x C*H*H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 75.6, 32.8, 24.3 ppm. MS (ESI) *m/z* 115 (M-H$^-$, 100%).

1-Phenylcyclohexane-1,2-diol (3i).[40,41] White solid; 99% yield; 67:33 *syn*:*anti* mixture of diastereomers; ^{1}H NMR ($CDCl_3$): *δ* 7.59-7.23 (5H, m, ArH), 5.59 (0.33H, br s, OH), 3.94 (0.67H, dd, *J* = 10.7 and 4.6 Hz, CH), 3.73-3.69 (0.33H, m, CH), 3.05-2.88 (0.33H, m, OH), 2.75 (0.66H, br s, OH), 2.53-2.33 (0.66H, m, OH), 2.11-1.27 (8H, m, 8 x C*H*H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 146.3, 145.8, 128.5, 128.4, 127.5, 126.9, 126.1, 125.1, 75.7, 74.5, 74.4, 73.2, 38.4, 31.3, 29.2, 28.4, 24.3, 21.0, 21.0, 19.2 ppm. MS (ESI) *m/z* 191 (M-H$^-$, 100%).

***trans*-2,3-Dihydroxycyclohexan-1-one (3j).**[42] White solid; 83% yield; ^{1}H NMR ($CDCl_3$): *δ* 4.33 (2H, br s, 2 x OH), 4.03 (1H, d, *J* = 9.4 Hz, COCH), 3.54 (1H, ddd, *J* = 11.2, 9.4 and 4.5 Hz, C*H*OH), 2.54-2.22 (2H, m, 2 x C*H*H), 2.18-1.86 (2H, m, 2 x C*H*H), 1.84-1.32 (2H, m, 2 x C*H*H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 208.7, 81.9, 76.4, 38.8, 31.1, 21.0 ppm. MS (ESI) *m/z* 129 (M-H$^-$, 100%).

4-(1,2-Dihydroxypropan-2-yl)-1-methylcyclohexane-1,2-diol (3k).[43] White solid; Mixture of diastereomers; 61% yield; 1st set of isomers: 60:40 ^{1}H NMR ($CDCl_3$): 3.89-3.72 (1.6H, m, CH and OCH*H*), 3.62 (0.6H, d, *J* = 11.1 Hz,OC*H*H), 3.40 (0.4H, *J* = 10.7 Hz, OC*H*H), 3.27 (0.4H, *J* = 10.7 Hz, OC*H*H), 2.25-1.42 (11H, m, 4 x OH, CH and 6 x CHH), 1.37 (1.2H, s, CH_3), 1.27 (1.8H, s, CH_3), 1.23 (1.2H, s, CH_3), 1.21. (1.8H, s, CH_3); ^{13}C NMR ($CDCl_3$): *δ* 84.6, 84.2, 82.9, 82.7, 72.2, 71.9, 69.5, 66.8, 39.7, 37.8, 33.1, 31.8, 28.7, 24.6, 24.1, 23.5, 18.5. 2nd set of isomers: ^{1}H NMR (*d*-DMSO): *δ* 4.60-4.02 (2H, m, CH and OH), 3.98-3.40 (2.6H, m, CH, C*H*H and OH), 3.38-3.03 (1H, m, CH and C*H*H), 2.96-2.09 (1.4H, m, CH, C*H*H and OH), 2.01-1.21 (7H, m, CH and 6 x C*H*H), 1.07 (0.45H, s, CH_3), 1.00 (2.55H, s, CH_3), 0.87 (1.8H, s, CH_3), 0.70 (1.2H, s, CH_3) ppm. ^{13}C NMR (*d*-DMSO): *δ* 85.3, 81.2, 73.3, 73.2, 72.6, 72.6, 72.4, 69.6, 68.3, 68.3, 67.8, 67.8, 58.3, 47.3, 46.8, 42.4, 42.2, 40.6, 40.3, 40.2, 39.8, 36.1, 35.8, 33.5, 32.5, 30.1, 29.8, 28.9, 28.6, 28.0, 26.5, 24.2, 22.6, 22.2, 21.8, 21.3, 20.8, 20.2, 19.7 ppm. MS (ESI) *m/z* 203 (M-H$^-$, 100%).

1-Phenylpropane-1,2,3-triol (3l).[44] White solid; 98% yield; 1:1 mixture of diastereomers; ^{1}H NMR (*d*-DMSO): *δ* 7.44-7.12 (5H, m, ArH), 4.51 (0.5H, d, *J* = 4.7 Hz, PhCH) 4.41 (0.5H, d, *J* = 5.9 Hz, PhCH), 4.38 (2H, br s, 3 x OH), 3.58-3.20 (2.5H, m, CH and C*H*H), 3.13 (0.5H, dd, *J* = 10.9 and 6.3 Hz, C*H*H) ppm. ^{13}C NMR (*d*-DMSO): 143.6, 127.8, 127.6, 127.3, 126.8, 126.7, 126.7, 75.9, 75.5, 74.1, 72.9, 63.1, 62.6 ppm. MS (ESI) *m/z* 167 (M-H$^-$, 100%).

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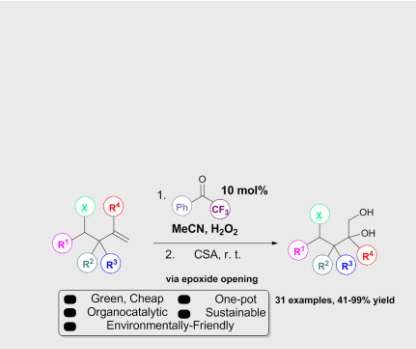
FULL PAPER

One-pot Magic. Green organocatalytic one-pot dihydroxylation of alkenes via an intermolecular ring opening from water of the in situ prepared epoxide.



Organocatalysis

*A. Theodorou, I. Triandafillidi, C. G. Kokotos**

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Green Organocatalytic One-pot Dihydroxylation of Alkenes

*Organocatalysis, Green Chemistry