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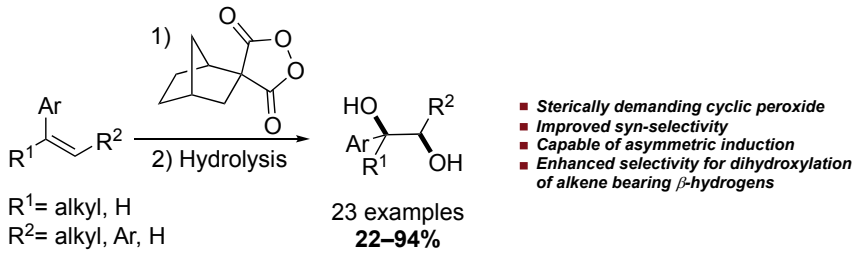
Syn-Dihydroxylation of Alkenes Using A Sterically Demanding Cyclic Diacyl Peroxide

Afsaneh Pilevar,[⊥] Abolfazl Hosseini,[⊥] Jonathan Becker,[‡] and Peter R. Schreiner*,[⊥]

[⊥]Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

[‡]Institute of Inorganic and Analytical Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

Abstract. The *syn*-dihydroxylation of alkenes is a highly valuable reaction in organic synthesis. Cyclic acyl peroxides (CAPs) have emerged recently as promising candidates to replace the commonly employed toxic metals for this purpose. Here we demonstrate that the structurally demanding cyclic peroxide spiro[bicyclo[2.2.1]heptane-2,4′-[1,2]dioxolane]-3′,5′-dione (**P4**) can be effectively used for the *syn*-dihydroxylation of alkenes. Reagent **P4** also shows an improved selectivity for dihydroxylation of alkenes bearing β-hydrogens as compared to other CAPs, where both diol and allyl alcohol products compete with each other. Furthermore, the use of enantiopure **P4** (labeled **P4'**) demonstrates the potential of **P4'** for a metal-free asymmetric *syn*-dihydroxylation of alkenes.

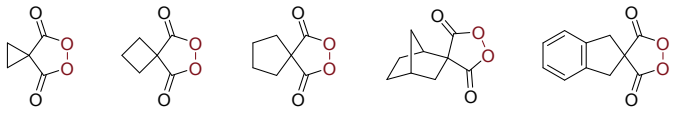


Introduction. The selective oxidation of olefins to the corresponding *syn*-diols has been the subject of intensive research.[1] Vicinal *syn*-diols are a common motif in a number of pharmaceutical and biologically active compounds as well as versatile intermediates in organic syntheses.[2] The *syn*-dihydroxylation of alkenes is generally performed using stoichiometric or catalytic amounts of transition metals, especially osmium and ruthenium based catalysts.[1a,3] However, the cost, toxicity, and environmental issues associated with these metals prompted scientists to develop sustainable metal-free strategies for alkene dioxygenation. While the metal free epoxidation of alkenes has been well established,[4] alkene *syn*-dioxygenation remains a difficult task. Recently, efficient organocatalytic *syn*-diacetoxylation of alkenes using aryl iodides as catalysts was reported, but these reactions often proceed with low diastereoselectivities.[5] Diacetoxylation of alkenes using $PhI(OAc)_2$ as oxidant requires strong acid catalyst (e.g., HOTf) and occurs with low diastereoselectivity.[6] Although recent efforts have led to some improvements,[7] literature precedents show that cyclic acyl peroxides (CAPs) are highly promising candidates for this purpose in terms of cost, atom economy, and prospects on stereoselectivity.

The chemistry of cyclic acyl peroxides (CAPs) has received strong impetus with the discovery of phthaloyl peroxide[8] and the thermolysis as well as photolysis of CAPs in general has been the subject of numerous studies over the last decades from both the synthetic and mechanistic point of view.[9] Notwithstanding the pioneering work of Greene and Adam,[10] the reactivity of cyclic peroxides toward nucleophiles as well as olefins still does not yet fully exploit the potency for novel carbon-oxygen bond forming reactions.[11] Dioxiranes[12] are known to give epoxides upon reaction with alkenes whereas 1,2-dioxetanes[13] and dimethyl α-peroxy lactones produce mixtures of peroxides, cycloadducts, and ene products.[11e,11f] Concurrently, with the growing attention for metal free organic reactions, CAPs have become attractive because of their potent ability in dioxygenation of electron-rich olefins under mild conditions. A few known CAPs have been employed with phthaloyl and cyclopropyl malonoyl peroxides resulting in appreciably increased reactivity,[14] with the latter being superior due to its higher relative reactivity, diastereoselectivity, and ease of preparation.[15] Tomkinson *et al.* demonstrated that the backbone structure of aliphatic CAPs plays a key role in reactivity and selectivity of a given reaction; cyclopropyl malonoyl peroxide hereby is particularly efficient.[14a,14b,16] Despite the great efforts made by Tomkinson and Siegel *et al.*[14c] for the metal free *syn*-

dihydroxylation of alkenes using established CAPs, there still remain some challenges concerning (1) the diastereoselectivities, (2) substrate scope, and (3) an asymmetric variant. Therefore, the synthesis and application of new peroxides with features that fulfill the above requirement remains a challenging task that must also take into account stability and safety. Additionally, simple manipulations of vicinal di-acids as starting materials do not necessarily deliver the corresponding cyclic peroxides due to an inappropriate torsion angle or O–O bond distance as well as their inherent propensity for decarboxylation.[14c,17] For instance, a phenyl group can readily be incorporated into **P3**, however, the resulting peroxide **P5** is unstable and gradually decomposes at room temperature. The low stability of **P5** could be attributed to the shortened O–O bond that increases the electrostatic repulsion of the peroxy oxygen lone pairs (Scheme 1).[17-18] Furthermore, the shortened O–O bond in **P5** implies a higher conjugation between the carbonyl group and peroxy oxygen that increases its electron density. It was reported that the increase in the ring strain (CO–C–CO angles) of the peroxide directly translates into increased reactivity.[14a] Although this could explain the reactivity trend of **P1** vs. **P3**, it is insufficient to explain the low stability of **P5**. We reason that the difference between internal CO–C–CO angles in the dicarboxylic acid starting materials and the resulting peroxides could also be taken as an indicator for peroxide stability;[19] for instance, this angle is 10.7 °[14a,20] in **P1**, about twice as large as in **P5** (5.2 °).

Scheme 1. Comparison of O–O bond length, $C(CO)_2$ inner angle and CO–O bond length (determined by single-crystal X-ray diffraction) in different CAPs.



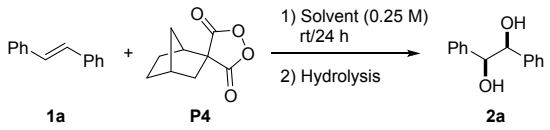
	P1	P2	P3	P4	P5
O-O bond (Å):	1.476	1.476	1.471	1.467	1.466
C(CO)₂ angle:	107.56	104.01	102.34	102.02	102.51
CO-O bond (Å):	1.390	1.392	1.377	1.382	1.375

Here we address several of the above-mentioned challenges with a readily prepared and safe CAP that proved highly versatile in olefin dioxygenation.

RESULTS AND DISCUSSION

We recently synthesized strained cyclic peroxide **P4** and applied it to the direct hydroxylation of aromatic substrates with good yields and appreciable regioselectivities.[15a] This promising results encouraged us to evaluate **P4** in alkene oxidation using *trans*-stilbene as the model substrate (Table 1). Various solvents were used and $CHCl_3$ gave the best results in terms of yield and diastereoselectivity of the resulting diol (Table 1, entries 1–5). Variation of temperature and the amount of peroxide as well as water did not affect the reaction much (Table 1, entries 6–9). In general, acceptable diastereoselectivities were observed in our initial screening although **P4** showed low reactivity at room temperature. It has been recently shown that fluorinated alcohols have beneficial effect on the rate and selectivity of alkene oxidation using CAPs[21] and we observed that perfluoro alcohols offered an appreciable increase in yield and selectivity using **P4** as oxidant. The yield for our test reaction increased to 50% with a 32:1 *syn:anti* ratio upon addition of 1 equiv of 2,2,2-trifluoroethanol (TFE). Further improvements were achieved when 3 equiv of TFE were added. Hexafluoroisopropanol (HFIP) on the other hand improved the yield but not the selectivity under the same conditions (Table 1, entries 10–13).

Table 1. Optimization of the dihydroxylation using peroxide **P4**.



no.	solvent	**P4** (equiv)	H_2O (equiv)	additive (equiv)	yield (%)[a]	*syn:anti*[b]
1	$CHCl_3$	1.2	1	–	38	28:1
2	Toluene	1.2	1	–	28	29:1
3	EtOAc	1.2	1	–	13[c]	n.d.
4	THF	1.2	1	–	14[c]	n.d.
5	CH_3CN	1.2	1	–	27	17:1
6[d]	$CHCl_3$	1.2	1	–	36	27:1

7	$CHCl_3$	1.2	2	–	32	21:1
8	$CHCl_3$	1	1	–	35	28:1
9	$CHCl_3$	1.5	1	–	35	20:1
10	$CHCl_3$	1.2	1	TFE (1)	50	32:1
11	$CHCl_3$	1.2	1	TFE (3)	70	34:1
12	$CHCl_3$	1.2	1	HFIP (1)	73[c]	28:1
13	$CHCl_3$	1.2	1	HFIP (3)	88	29:1
14	$CHCl_3$	1.2	1	PFB (1)	68	35:1
15	$CHCl_3$	1.2	1	PFB (3)	89	42:1
16	$CHCl_3$	1.2	1	PFB (6)	90	39:1
17	$CHCl_3$	1.2	1	PFB (10)	92	39:1

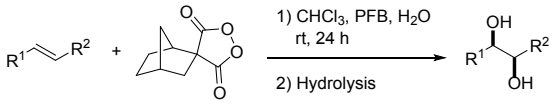
[a] Yield of isolated product. [b] Ratio determined by NMR. [c] Yield by NMR. [d] Reaction at 40 °C.

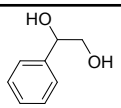
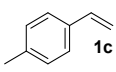
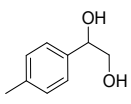
Significant improvement was finally achieved using 3 equiv of perfluoro-*tert*-butyl alcohol (PFB) at room temperature, leading to the formation of **2a** in 89% yield and a 42:1 *syn:anti* ratio (Table 1, entries 14–17). Therefore, the optimal conditions were established as alkene (1 equiv), **P4** (1.2 equiv), PFB (3 equiv) in $CHCl_3$ at room temperature.

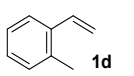
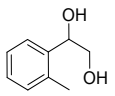
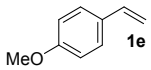
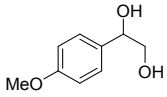
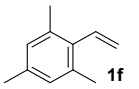
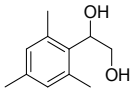
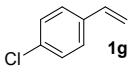
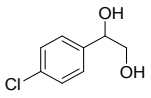
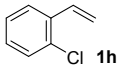
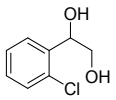
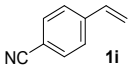
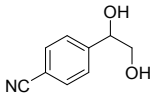
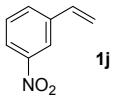
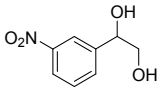
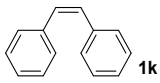
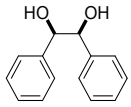
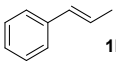
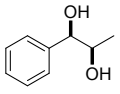
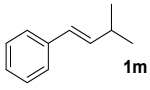
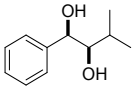
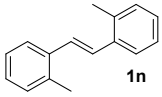
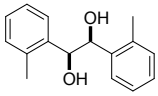
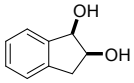
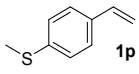
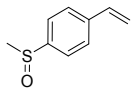
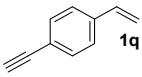
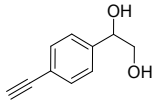
Having optimized the reaction conditions, we next explored the substrate scope, and a variety of substituted olefins were subjected to our standard conditions (Table 2). Treatment of styrene with **P4** in a chloroform-PFB mixture at room temperature produced 1-phenylethane-1,2-diol in 93% yield of isolated product (Table 2, entry 1). Similarly, styrenes bearing electron donating groups afforded high yields of the corresponding products (Table 2, entries 2–4). Sterically hindered 2,4,6-trimethylstyrene, however, led to lower conversion presumably due to the reduced accessibility of the double bond (Table 2, entry 5). Less nucleophilic *para* and *ortho*-chlorostyrenes also furnish the corresponding diols in high yields (Table 2, entries 6 and 7) while electron-deficient styrenes, such as *p*-cyanostyrene, react more slowly (Table 2, entries 8 and 9).

As shown in Table 2, the dihydroxylation of internal olefins provides access to products containing vicinal stereogenic centers with good to high diastereocontrol. A rather challenging substrate, *cis*-stilbene, afforded excellent yield but modest diastereoselectivity. The diastereoselectivity was improved to a 5:1 *syn:anti* ratio when the reaction was carried out in a toluene / PFB solvent mixture (1:1) at –15 °C, whereas no improvement was achieved using cyclopropyl malonoyl peroxide (Table 2, entry 10). Dihydroxylation of *trans*-β-methylstyrene afforded the desired product in 90% yield and a 5:1 *syn:anti* ratio (Table 2, entry 11). This result is marginally superior to using cyclobutane malonoyl peroxide (80%, 4:1 *syn:anti* ratio).[14b] This effect increases with an isopropyl terminus (81%, 11:1 *syn:anti* ratio) whereas only a modest change was observed with cyclobutane malonoyl peroxide (68%, 5:1 *syn:anti* ratio, Table 2, entry 12),[22] indicating that the steric hindrance of **P4** considerably affects the diastereoselectivity of the reaction. The steric sensitivity is also apparent when 2,2'-dimethyl-*trans*-stilbene was subjected to oxidation with **P4**: the *syn* product was isolated almost exclusively under the same reaction conditions (Table 2, entry 13); equally, indene provided exclusively the *syn* diol product in good yield due to the inherent ring strain that prevents the formation of the *anti* product (Table 2, entry 14). Similar to a previous report,[23] the reaction of *p*-vinylthioanisole preferably oxidized the sulfur atom and the alkene moiety remained intact (Table 2, entry 15). Treatment of *p*-ethynylstyrene with **P4** (Table 2, entry 16) gave only 27% yield of the corresponding diol. Aliphatic substrates thus far provide only low yields of the corresponding diols, apparently requiring a completely new optimization.

Table 2. Dihydroxylation of alkenes with cyclic peroxide **P4**.[a]



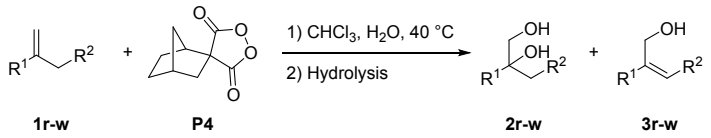
no.	substrate	product	yield (%)[b]	*syn:anti*[c]
1			93	–
2			94	–

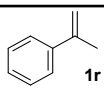
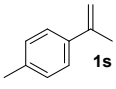
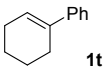
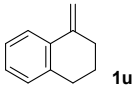
3			86	–
4			72	–
5			65	–
6			80[d]	–
7			71[d]	–
8			29[e]	–
9			22[e]	–
10			91 88 (92)[f,g]	4:1 5:1 (3:1)[f,g]
11			90	5:1
12			81	11:1
13			80	>75:1
14			74	100:0
15			76	–
16			27	–

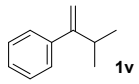
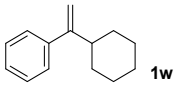
[a] *Reaction conditions:* Alkene (1 equiv), **P4** (1.2 equiv), $CHCl_3$ (0.25 M), PFB (3 equiv), H_2O (1 equiv) at room temperature for 24 h. [b] Yield of isolated product. [c] Ratio determined by NMR. [d] Reaction after 48 h. [e] Reaction after 72 h. [f] Reaction performed in toluene at –15 °C after 5 d. [g] The numbers in parentheses refer to the reaction using cyclopropyl malonoyl peroxide in toluene at –15 °C after 5 d.

Alkenes bearing β-hydrogens also are viable substrates, however, oxygenations with CAPs generally result in competitive formation of allyl alcohols, which decreases the yield of the desired diol.[14b] Having established conditions for alkene dihydroxylation, we next investigated the selectivity of **P4** in dihydroxylation of alkenes bearing β-hydrogens (Table 3). In fact, the presence of β-hydrogens allows the reaction to proceed through an alternative path to give the corresponding allyl alcohol (Scheme 2, **12t**). The optimized conditions in Table 2 were employed for hydroxylation of alkenes bearing β-hydrogens, however, no difference was observed in the presence or absence of PFB (Table 3, entry 1), and therefore, the reaction of **P4** with alkenes bearing β-hydrogens were carried out without PFB.

Table 3. Dihydroxylation of alkenes bearing β-hydrogens with **P4** under wet and dry conditions.[a]



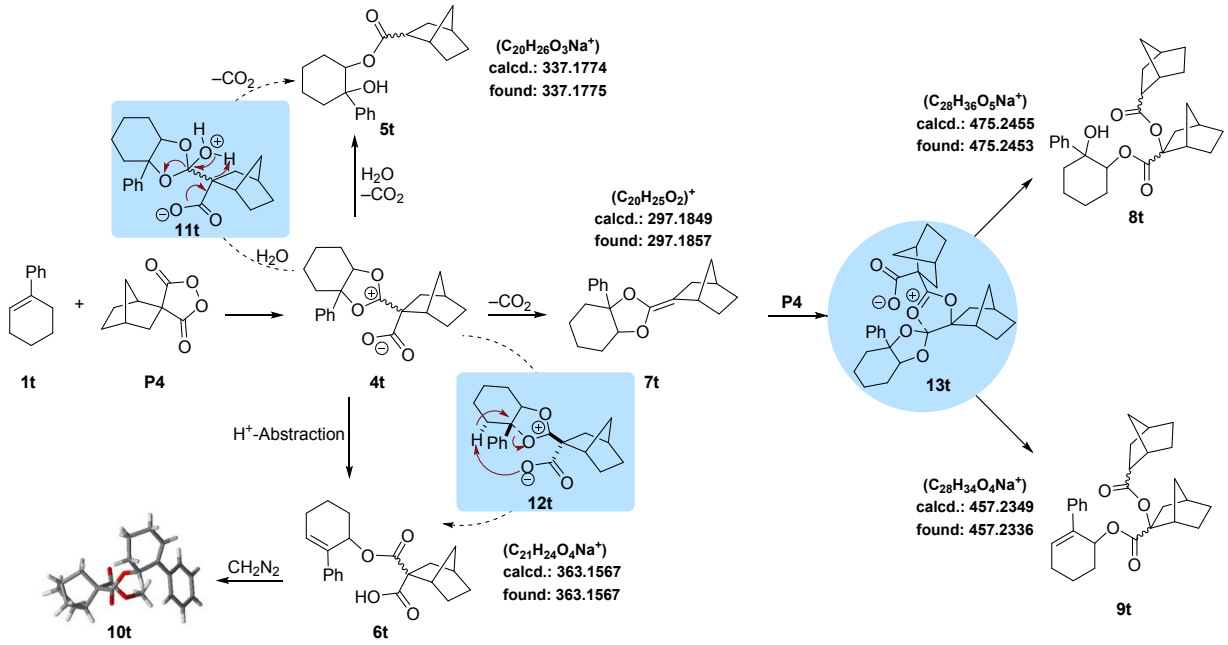
no.	substrate	"wet"		"dry"		time of hyd. (h)[d,e]
		Yield (%)[b]	*diol:allyl alc.*[c]	Yield (%)[b]	*diol:allyl alc.*[c]	
1	 **1r**	80 (92)[f,g]	4:1 (3:1)	26	1.6:1	48
2	 **1s**	78	4:1	24	1.6:1	48
3	 Ph **1t**	70 (72)[g]	2.6:1 (1.2:1)	30	1:5.5	120
4	 **1u**	81	2:1	20	1:>50	72

5	 **1v**	68[h]	pure diol[i]	–	–	48
6	 **1w**	66[h]	pure diol[i]	–	–	48

[a] *Reaction conditions:* Alkene (1 equiv), **P4** (1.2 equiv), $CHCl_3$ (0.6 M), H_2O (1 equiv) at 40 °C, reactions under dry conditions were performed in toluene. [b] Yield of isolated product. [c] Ratio determined by NMR. [d] Hydrolysis was performed using a mixture solution of NaOH (2 M) and 1,4-dioxane at 100 °C. [e] In all cases the same ratios of *diol:allyl alc.* were also obtained by hydrolysis of methylated esters in NaOMe/1,4-dioxane. [f] Reaction under standard conditions using PFB afforded 82% yield and a ratio of 3.7:1 *diol:allyl alcohol*. [g] Numbers in parentheses refer to the reaction using cyclopropyl malonoyl peroxide. [h] Yield of diol product. [i] No allyl alcohol product observed.

Based on the previously established mechanism,[24] water plays a critical role in the dihydroxylation reaction. However, the presence of β-hydrogens triggered an elimination reaction by the adjacent carboxylate anion (oxonium intermediate **12t**, Scheme 2) for which water is not needed to quench carbocation **12t**. Intrigued by the effect of water on the selectivity of the reaction, both wet and dry conditions were examined. With this in mind, performing the reactions under dry conditions should promote the formation of allyl alcohols. In general, better yields of the desired diol products were obtained using **P4** under wet conditions. The selectivity for diol formation is higher than that obtained for cyclobutane (70%, 2.5:1 of diol:allyl alcohol)[14b] or cyclopropyl malonoyl peroxides under the same reaction conditions (Table 3, entry 1). Good yields and selectivities were also observed for alkenes **1s**–**1u** for which **P4** proved superior. Interestingly, alkenes **1v** and **1w** gave only diol products under the same reaction conditions, without the formation of allyl products (Table 3, entries 5 and 6). The reactions under dry conditions were performed in dry toluene to avoid the hydrogen bond interaction.[25] The dry reaction conditions work in principle, however, were less efficient in terms of both yields and selectivities (Table 3).

Scheme 2. Proposed mechanism for the oxidation of alkene bearing β-hydrogens by **P4**.



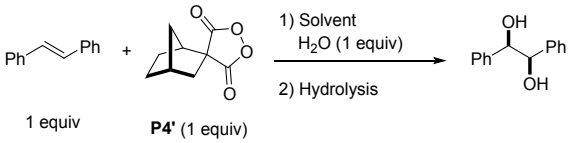
Inspection of Table 3 reveals that the preference for diol *vs* allyl alcohol formation is governed by the nature of the alkene where the stability of resulting carbocation as well as the steric environment of the β-hydrogens greatly affects the reaction outcome. For instance, the stabilized carbocation derived from **1r** affords high yield of diol product despite the existence of three β-hydrogens whereas less stable carbocation **4t** provides modest selectivity. Ready formation of the carbocation intermediates derived from alkenes **1v** and **1w** assisted by steric hindrance around the β-hydrogens led to the exclusive formation of dihydroxylated products. Even though the principal mechanism for alkene *syn*-dihydroxylations with CAPs has been thoroughly investigated,[24] the difficulty in hydrolyzing the resulting esters provoked our curiosity. For instance, the hydrolysis of the product mixture resulting from the reaction of **1t** with **P4** (mixture of dihydroxylated and allylic esters products) using aqueous sodium hydroxide did not proceed even after prolonged reaction times and elevated temperatures. Further investigation by GC-MS and NMR indicated that the dihydroxylated products were fully hydrolyzed whereas the allylic esters remained unreactive. Other bases like LiOH, KOH, and NaOMe/MeOH lead to incomplete hydrolysis of the allylic esters

products. This unexpected result prompted us to identify the reaction products before hydrolysis (Scheme 2). The products were isolated after a second esterification with diazomethane. Two major allyl alcohol and diol products (each containing *exo* and *endo*) were isolated; the *exo*-allyl structure was confirmed by X-ray crystallography. Note that mainly the decarboxylation product (**5t**, through intermediate **11t**) was obtained in the case of the diol product whereas the allyl oxidation product was isolated as a diester (**10t**, through intermediate **12t**). Surprisingly, the hydrolysis of the ester **10t** was easily accomplished at 100 °C overnight using a solution of NaOMe/1,4-dioxane, possibly due to its increased solubility in organic media.

To gain further insight into the underlying mechanism, samples of the reaction mixture were analyzed by HRMS as illustrated in Scheme 2. We suggest that the intermediate **4t** forms in the first step,[24] which undergoes proton elimination to give the corresponding allyl alcohol ester **6t**. An alternative pathway is the addition of water to intermediate **4t** and simultaneous decarboxylation to deliver the desired product **5t** or decarboxylation only to form **7t**. The latter may hydrolyze or react further with peroxide **P4** to give the desired products after hydrolysis. We reasoned that the formation of allyl product **6t** could be controlled by the ease of proton abstraction that is less favorable in the case of rigid and sterically hindered **P4** as compared to cyclobutane and cyclopropyl malonoyl peroxides. However, further evidence is needed to provide a full understanding of the mechanistic details.

Despite the considerable improvements in asymmetric metal catalyzed olefin *syn*-dihydroxylation, a stereoselective organocatalyzed variant remains elusive. We recently demonstrated a synthetic route for the preparation of enantiopure peroxide **P4** (which we label **P4'**), we naturally attempted the asymmetric dihydroxylation of alkenes using **P4'**. Performing the reaction under conditions used in Table 1 gave no *ee* (Table 4, entry 1), therefore subsequent reactions were carried out without the addition of PFB to minimize the effects of environment on the asymmetric induction (Table 4). The initial results are promising, demonstrating the potential of **P4'** as an organic reagent for replacing toxic and expensive metal catalysts, even though this will require a lot more work. To the best of our knowledge, this is the first example of the use of a chiral peroxide for the direct enantioenriched *syn*-dihydroxylation of alkenes.

Table 4. Assessment of asymmetric *syn*-dihydroxylation of *trans*-stilbene using chiral peroxide **P4'**.



no.	Solvent	*T* (°C)	Yield (%)[a]	*ee* (%)[b,c]
1[d]	$CHCl_3$/PFB	RT	85	0
2	$CHCl_3$	40	36	9
3	$CHCl_3$	RT	38	7
4	Toluene	40	30	9

[a] Yield of isolated product. [b] Determined by chiral HPLC. See Supporting Information for details. [c] ee of *syn* dihydroxylated product. [d] According to standard conditions of Table 2.

In conclusion, we have developed a high yielding olefin *syn*-dihydroxylation reaction enabled by a sterically demanding cyclic peroxide. High diastereoselectivities were observed for the dihydroxylation of a wide range of olefins with good to excellent yields. The diastereoselectivity was significantly boosted when sterically encumbered substrates were employed, a result that we ascribe to the bulky nature of **P4**. Moreover, the promising preliminary results for an asymmetric *syn*-dihydroxylation indicates the potential of reagents such as **P4** for developing a metal free variant of the well-established asymmetric *syn*-dihydroxylation of alkenes. Furthermore, this might be advantageously realized using chiral hydrogen bond donors, considering the low background reaction of **P4**. Future work will continue to explore the ability of the **P4** and related structures in the development of an asymmetric variant.

EXPERIMENTAL SECTION

General Remarks. All chemicals were purchased from TCI, Sigma Aldrich, Alfa Aesar, and Acros Organics in reagent grade and used without further purification. Alkenes **1m**,[26] **1q**,[27] **1u**, **1v**, **1w** were prepared according to literature procedures.[28] Peroxides **P4** and **P4'** were synthesized according to our previous report.[15a] All solvents were distilled before usage. Flash column chromatography was performed using MN silica gel 60 M (0.040 – 0.063 mm) or Büchi Reveleris Silica columns (0.040 mm). Analytical thin-layer chromatography (TLC) was performed using precoated polyester sheets Polygram® SIL G/UV254 from Macherey Nagel with a fluorescence indicator. Visualization of the TLC plate was accomplished by UV lamp at 254 nm, 5% phosphomolybdic acid in ethanol. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV600 or AV400 spectrometers at 298 K. Chemical shifts (δ) were expressed in ppm downfield from the internal standard tetramethylsilane (TMS, δ = 0.00 ppm) or to the respective solvent residual peaks ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm) and were reported as (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet, br = broad, etc). The coupling constants (*J*) were recorded in Hz. The progress of reactions was monitored by NMR or GC-MS analyses with a Quadrupol-MS HP MSD 5971(EI) and HP 5890A GC equipped with a J & W Scientific fused silica GC column (30 m × 0.250 mm, 0.25 micron DB–5MS stationary phase: 5% phenyl and 95% methyl silicone) using He (4.6 grade) as carrier gas; T-program standard 60 – 250 °C (15 °C/min heating rate), injector and transfer line 250 °C. HRMS were collected on a Bruker Mikro-TOF (ESI).

CAUTION: Organic peroxides are potentially dangerous compounds, the procedures must be handled with sufficient care; avoid exposure to strong heat or mechanical shock.

Preparation of Peroxide P5

Urea hydrogen peroxide (0.76 g, 8.05 mmol) was added to methanesulfonic acid (2.33 mL) and stirred in a water bath for 3 min. Indane-2,2-dicarboxylic acid[29] (0.56 g, 2.7 mmol) was added to the solution and the reaction stirred for 24 h in water bath.[14a] A mixture of ice/ethyl acetate (7 g/8 mL) was added to the reaction

mixture and stirred for 5 min. The phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 8 mL). The combined organic layers were successively washed with $NaHCO_3$ (2 × 4 mL) and brine (5 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure yielding **P5** (0.5 g, 91%) as a white solid. $^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.18 (m, 4H), 3.59 (s, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 174.4, 137.2, 128.2, 124.4, 46.3, 42.5 ppm.

General Procedure for Alkene Dihydroxylation

Alkene (0.5 mmol) was placed inside a 4 mL vial (screw top with solid green Thermoset cap with PTFE liner) equipped with a magnetic stirrer bar. $CHCl_3$ (2 ml), PFB (0.21 ml, 1.5 mmol), water (9 µl, 0.5 mmol) and **P4** (0.11 g, 0.6 mmol) were subsequently added. The liner was sealed and the material was stirred at room temperature for the indicated time. The reaction mixture was then diluted with EtOAc (10 mL) and stirred with a saturated solution of $Na_2S_2O_5$ (10 mL) for 2 h. After separation of the layers, the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (10 mL) and concentrated under reduced pressure. The residue was hydrolyzed using a mixture of NaOH (1 M, 10 ml) and THF (10 ml) at 60 °C (oil bath) for 24 h. THF was removed under reduced pressure and the basic phase was extracted with EtOAc (2 × 10 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated to give the crude product. The resultant crude mixture was then purified by column chromatography over silica gel.

General Procedure for the Dihydroxylation of Alkenes Bearing β-Hydrogens

Alkene (1 mmol) was placed inside a 4 mL vial (screw top with solid green Thermoset cap with PTFE liner) equipped with a magnetic stirrer bar. $CHCl_3$ (1.6 mL), water (0.018 g, 1 mmol) and **P4** (0.22 g, 1.2 mmol) were subsequently added. The liner was sealed and the vial was placed inside an oil bath heated to 40 °C for 24 h. The reaction mixture was then cooled to room temperature and diluted with EtOAc (15 mL) and stirred with a saturated solution of $Na_2S_2O_5$ (15 mL) for 2 h. After separation of the layers, the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (10 mL) and concentrated under reduced pressure. The residue was hydrolyzed using a mixture of NaOH (2 M, 15 ml) and 1,4-dioxane (15 mL) at 100 °C (oil bath) for the indicated time. 1,4-dioxane was removed under

reduced pressure and the basic phase was extracted with EtOAc (2 × 10 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated to give the crude product. The resultant crude mixture was then purified by column chromatography over silica gel.

Characterization data for alkenes **1m**, **1q**, **1u**, **1v**, **1w**:

*[(1E)-3-Methyl-1-butenyl]-benzene (**1m**)*: Colorless oil (0.28 g, 13%; pentane as an eluent); $^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.14 (m, 5H), 6.33 (d, *J* = 16.1 Hz, 1H), 6.19 (dd, *J* = 15.9, 6.7 Hz, 1H), 2.52 – 2.40 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.0, 128.5, 126.8, 126.8, 126.0, 31.5, 22.5 ppm.[26]

*1-Ethynyl-4-vinylbenzene (**1q**)*: Yellow oil (two steps, 0.53 g, 41%; pentane as an eluent); $^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 3.11 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.0, 136.1, 132.3, 126.1, 121.3, 115.1, 83.7, 77.7 ppm.[27]

*1-Methylene-1,2,3,4-tetrahydronaphthalene (**1u**)*: Colorless oil (1.4 g, 65%; pentane as an eluent); $^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.60 (m, 1H), 7.19 – 7.06 (m, 3H), 5.46 (d, *J* = 0.9 Hz, 1H), 4.94 (q, *J* = 1.4 Hz, 1H), 2.83 (t, *J* = 6.5 Hz, 2H), 2.56 – 2.50 (m, 2H), 1.91 – 1.83 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 143.5, 137.4, 134.8, 129.3, 127.6, 125.9, 124.3, 107.9, 33.3, 30.5, 23.9 ppm.[30]

*3-Methyl-2-phenyl-1-butene (**1v**)*: Colorless oil (1.7 g, 77%; pentane as an eluent); $^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.22 (m, 5H), 5.14 (s, 1H), 5.03 (t, *J* = 1.4 Hz, 1H), 2.89 – 2.77 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 155.8, 142.9, 128.1, 127.1, 126.6, 110.0, 32.3, 22.1 ppm.[31]

*1-Cyclohexyl-1-Phenylethene (**1w**)*: Colorless oil (2.2 g, 78%; pentane as an eluent); $^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 5.13 (d, *J* = 1.3 Hz, 1H), 5.00 (t, *J* = 1.4 Hz, 1H), 2.47 – 2.36 (m, 1H), 1.88 – 1.74 (m, 4H), 1.74 – 1.66 (m, 1H), 1.39 – 1.25 (m, 2H), 1.25 – 1.09 (m,

3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 155.0, 143.0, 128.1, 127.0, 126.6, 110.3, 42.6, 32.7, 26.9, 26.5 ppm.[32]

*(±)-Hydrobenzoin (**2a**)*: Colorless solid (0.1 g, 89%; *n*-hexane/ethyl acetate 4:1 as an eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.20 (m, 6H), 7.17 – 7.09 (m, 4H), 4.71 (s, 2H), 2.86 (s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.8, 128.2, 128.0, 126.9, 79.1 ppm.[14a]

*1-Phenylethane-1,2-diol (**2b**)*: Colorless solid (0.06 g, 93%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.27 (m, 5H), 4.82 (dd, *J* = 8.2, 3.5 Hz, 1H), 3.76 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.66 (dd, *J* = 11.3, 8.2 Hz, 1H), 2.74 (br s, 1H), 2.36 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.5, 127.5, 127.0, 125.0, 73.7, 67.1 ppm.[14a]

*1-p-Tolylethane-1,2-diol (**2c**)*: Colorless solid (0.07 g, 94%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.76 (dd, *J* = 8.3, 3.5 Hz, 1H), 3.75 – 3.59 (m, 2H), 2.96 (s, 1H), 2.59 (s, 1H), 2.34 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 137.9, 137.6, 129.3, 126.1, 74.7, 68.2, 21.2 ppm.[33]

*1-o-Tolylethane-1,2-diol (**2d**)*: Colorless solid (0.06 g, 86%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.25 – 7.12 (m, 3H), 5.06 (dt, *J* = 8.4, 2.9 Hz, 1H), 3.77 – 3.68 (m, 1H), 3.66 – 3.57 (m, 1H), 2.54 (d, *J* = 3.0 Hz, 1H), 2.34 (s, 3H), 2.27 (dd, *J* = 7.4, 4.3 Hz, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.5, 134.8, 130.5, 127.8, 126.3, 125.7, 71.4, 66.9, 19.0 ppm.[34]

*1-(4-Methoxyphenyl)ethane-1,2-diol (**2e**)*: Colorless solid (0.06 g, 72%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.24 (m, 2H), 6.92 – 6.85 (m, 2H), 4.75 (dd, *J* = 8.2, 3.7 Hz, 1H), 3.80 (s, 3H), 3.73 – 3.60 (m, 2H), 2.80 (br s, 1H), 2.51 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.4, 131.6, 126.3, 112.9, 73.3, 67.0, 54.3 ppm.[34]

*1-Mesitylethane-1,2-diol (**2f**):* Colorless solid (0.06 g, 65%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 6.83 (s, 2H), 5.25 (dd, *J* = 9.8, 3.8 Hz, 1H), 3.96 (dd, *J* = 11.5, 9.9 Hz, 1H),

3.60 (dd, *J* = 11.5, 3.8 Hz, 1H), 2.49 (br s, 2H), 2.40 (s, 6H), 2.25 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 137.2, 136.7, 132.5, 130.2, 72.7, 64.7, 20.7, 20.8 ppm.[14a]

1-(4-Chlorophenyl)ethane-1,2-diol ***(2g)***: Pale yellow solid (0.07 g, 80%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.18 (m, 4H), 4.72 (dd, *J* = 8.2, 3.4 Hz, 1H), 3.66 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.53 (dd, *J* = 11.3, 8.2 Hz, 1H), 2.54 (br s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl3): δ = 138.9, 133.7, 128.7, 127.5, 74.0, 67.9 ppm.[34]

1-(2-Chlorophenyl)ethane-1,2-diol ***(2h)***: Pale yellow solid (0.06 g, 71%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 5.25 (dd, *J* = 7.9, 3.1 Hz, 1H), 3.91 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.58 (dd, *J* = 11.4, 7.9 Hz, 1H), 2.34 (br s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 137.8, 131.9, 129.4, 129.0, 127.6, 127.1, 71.4, 66.2 ppm.[34]

1-(4-Cyanophenyl)ethane-1,2-diol ***(2i)***: Colorless solid (0.02 g, 29%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, Acetone-d_6): δ = 7.95 – 7.89 (m, 2H), 7.58 – 7.52 (m, 2H), 7.43 (br s, 1H), 6.82 (dd, *J* = 17.7, 10.9 Hz, 1H), 6.61 (br s, 1H), 5.92 (dd, *J* = 17.7, 0.9 Hz, 1H), 5.34 (dd, *J* = 10.9, 0.9 Hz, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d_6): δ = 168.6, 141.4, 137.3, 134.8, 128.9, 127.0, 116.2 ppm.[2a]

1-(3-Nitrophenyl)ethane-1,2-diol ***(2j)***: Colorless oil (0.02 g, 22%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, Acetone-d_6): δ = 8.31 (t, *J* = 2.0 Hz, 1H), 8.15 – 8.10 (m, 1H), 7.87 – 7.83 (m, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 4.93 – 4.86 (m, 1H), 4.76 (d, *J* = 4.0 Hz, 1H), 4.03 (t, *J* = 5.9 Hz, 1H), 3.75 – 3.61 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d_6): δ = 149.1, 146.4, 133.6, 130.1, 122.7, 121.8, 74.1, 68.4 ppm.[34]

meso-Hydrobenzoin ***(2k)***: Colorless solid (0.1 g, 91%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.14 (m, 10H), 4.74 (s, 2H), 2.14 (s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.8, 128.2, 128.1, 127.1, 78.1 ppm.[14a]

*1-Phenyl-1,2-propanediol (**2l**)*: White solid (0.07 g, 90%; *n*-hexane/ethyl acetate 3:1 as an eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.25 (m, 5H), 4.33 (d, *J* = 7.5 Hz, 1H), 3.88 – 3.78 (m, 1H), 3.01 (br s, 2H), 1.02 (d, *J* = 6.3 Hz, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.1, 127.5, 127.1, 125.9, 78.5, 71.2, 17.7.[14b]

*3-Methyl-1-phenyl-1,2-butanediol (**2m**)*: Colorless oil (0.07 g, 81%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.28 (m, 5H), 4.62 (d, *J* = 6.3 Hz, 1H), 3.48 (t, *J* = 5.3 Hz, 1H), 2.75 (s, 1H), 2.33 (s, 1H), 1.65 – 1.57 (m, 1H), 0.95 (dd, *J* = 6.9, 3.6 Hz, 6H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.6, 128.5, 127.9, 126.6, 80.4, 75.1, 29.2, 20.1, 16.3 ppm.

*1,2-Di-o-tolylethane-1,2-diol (**2n**)*: White solid (0.1 g, 80%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.61 – 7.59 (m, 2H), 7.22 – 7.09 (m, 4H), 6.92 – 6.90 (m, 2H), 4.95 (s, 2H), 3.02 (s, 2H), 1.65 (s, 6H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.0, 135.9, 130.2, 127.7, 127.2, 125.9, 74.6, 18.8 ppm.

*2,3-Dihydro-1H-indene-1,2-diol (**2o**)*: Colorless solid (0.05 g, 74%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.45 – 7.39 (m, 1H), 7.31 – 7.21 (m, 3H), 5.03 – 4.95 (m, 1H), 4.54 – 4.45 (m, 1H), 3.12 (dd, *J* = 16.3, 5.8 Hz, 1H), 2.95 (dd, *J* = 16.4, 3.6 Hz, 1H), 2.61 (br s, 1H), 2.52 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.0, 140.1, 128.9, 127.2, 125.4, 125.1, 76.0, 73.5, 38.7 ppm.[14a]

*1-(Methylsulfinyl)-4-vinylbenzene (**2ps**)*: Colorless solid (0.06 g, 76%; *n*-hexane/ethyl acetate 3:1 ⟶ 8:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.63 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.84 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.37 (dd, *J* = 10.9, 0.7 Hz, 1H), 2.72 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 144.8, 140.5, 135.7, 127.1, 123.8, 116.2, 44.0 ppm.[35]

*1-(4-Ethynylphenyl)ethane-1,2-diol (**2q**)*: Colorless solid (0.02 g, 27%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 4.82 (dd, *J* = 8.2,

3.4 Hz, 1H), 3.75 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.62 (dd, *J* = 11.3, 8.1 Hz, 1H), 3.08 (s, 1H), 2.52 (br s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.2, 132.3, 126.0, 121.8, 83.3, 77.4, 74.3, 67.9 ppm.[36]

2-Phenyl-1,2-propanediol ***(2r)***: Colorless oil (0.1 g, 64%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.42 (m, 2H), 7.39 – 7.33 (m, 2H), 7.30 – 7.24 (m, 1H), 3.76 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.60 (dd, *J* = 11.1, 7.7 Hz, 1H), 2.79 (s, 1H), 2.15 (dd, *J* = 7.9, 4.7 Hz, 1H), 1.51 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 145.0, 128.4, 127.2, 125.1, 74.9, 71.1, 26.0 ppm.[37]

2-Phenylprop-2-en-1-ol ***(3r)***: Colorless oil (0.02 g, 16%); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.42 (m, 2H), 7.39 – 7.27 (m, 3H), 5.47 (s, 1H), 5.35 (d, *J* = 1.1 Hz, 1H), 4.55 (s, 2H), 1.64 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 147.3, 138.5, 128.5, 128.0, 126.1, 112.6, 65.1 ppm.[38]

2-p-Tolylpropane-1,2-diol ***(2s)***:White solid (0.1 g, 62%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.29 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.74 – 3.68 (m, 1H), 3.56 (dd, *J* = 11.5, 6.2 Hz, 1H), 3.02 (s, 1H), 2.58 (br s, 1H), 2.34 (s, 3H), 1.49 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.1, 136.8, 129.1, 125.1, 74.8, 71.0, 26.0, 21.0 ppm.[39]

2-(p-Tolyl)prop-2-en-1-ol ***(3s)***: Colorless oil (0.02 g, 16%); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.33 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.44 (s, 1H), 5.31 (q, *J* = 1.4 Hz, 1H), 4.53 (s, 2H), 2.36 (s, 3H), 1.62 (s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 147.1, 137.8, 135.6, 129.2, 125.9, 111.8, 65.1, 21.1 ppm.[40]

1-Phenylcyclohexane-1,2-diol ***(2t)****:* White solid (0.1 g, 51%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.52 – 7.45 (m, 2H), 7.39 – 7.33 (m, 2H), 7.27 – 7.22 (m, 1H), 3.96 (ddd, *J* = 11.2, 4.5, 2.6 Hz, 1H), 2.62 (d, *J* = 1.8 Hz, 1H), 1.90 – 1.78 (m, 3H), 1.76 – 1.58 (m, 4H), 1.56 – 1.48 (m, 1H), 1.45 – 1.32 (m, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 146.4, 128.5, 127.0, 125.1, 75.8, 74.5, 38.5, 29.2, 24.4, 21.1 ppm.[41]

2-Phenyl-2-cyclohexen-1-ol ***(3t)***: White solid (0.03 g, 19%); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.44 (m, 2H), 7.36 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 6.16 (dd, *J* = 4.7, 3.4 Hz, 1H), 4.73 – 4.69 (m, 1H),

2.32 – 2.11 (m, 2H), 2.00 – 1.92 (m, 1H), 1.90 – 1.63 (m, 4H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.2, 139.1, 128.7, 128.6, 127.1, 126.0, 65.5, 31.6, 26.1, 17.4 ppm.[42]

*1-hydroxy-1-hydroxymethyl-1,2,3,4-tetrahydronaphthalene (**2u**)*: White solid (0.1 g, 54%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.49 (m, 1H), 7.25 – 7.16 (m, 2H), 7.14 – 7.06 (m, 1H), 3.76 – 3.58 (m, 2H), 2.90 – 2.71 (m, 2H), 2.46 – 2.23 (m, 3H), 1.97 – 1.68 (m, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.2, 137.7, 128.9, 127.7, 126.7, 126.3, 73.1, 69.1, 33.3, 29.7, 20.2 ppm.[43]

*1-Hydroxymethyl-3,4-dihydronaphthalene (**3u**)*: Colorless oil (0.04 g, 27%); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.33 (m, 1H), 7.25 – 7.14 (m, 3H), 6.12 (t, *J* = 4.5 Hz, 1H), 4.53 (s, 2H), 2.78 (t, *J* = 8.1 Hz, 2H), 2.37 – 2.28 (m, 2H), 1.51 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 136.5, 136.1, 133.1, 127.8, 127.2, 127.1, 126.5, 122.8, 64.0, 27.9, 22.9 ppm.[44]

*3-Methyl-2-phenylbutane-1,2-diol (**2v**)*: Colorless oil (0.12 g, 68%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.32 (m, 4H), 7.29 – 7.23 (m, 1H), 3.98 (d, *J* = 11.2 Hz, 1H), 3.81 (d, *J* = 11.3 Hz, 1H), 2.66 (s, 1H), 2.11 – 1.97 (m, 1H), 1.61 (br s, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.9, 128.2, 127.0, 126.2, 79.3, 68.4, 35.2, 17.4, 16.7 ppm.[45]

*1-Cyclohexyl-1-phenylethane-1,2-diol (**2w**)*: White solid (0.15 g, 66%; *n*-hexane/ethyl acetate 3:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.31 (m, 4H), 7.28 – 7.22 (m, 1H), 3.96 (d, *J* = 10.9 Hz, 1H), 3.81 (dd, *J* = 11.2, 7.6 Hz, 1H), 2.72 (s, 1H), 1.85 – 1.54 (m, 6H), 1.47 – 1.38 (m, 1H), 1.28 – 0.9 (m, 5H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 143.1, 128.1, 126.9, 126.2, 79.2, 68.1, 45.6, 27.2, 26.8, 26.6, 26.5, 26.3 ppm.[45]

*Methylated ester intermediate (**10t**)*: White solid (0.06 g, 16%; *n*-hexane/ethyl acetate 16:1 as eluent); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): *(mixture of endo/exo)* δ = 7.33 – 7.25 (m, 4H), 7.24 – 7.17 (m, 1H), 6.32 – 6.23 (m, 1H), 5.99 – 5.91 (m, 1H), 3.19 – 3.03 (s, 3H), 2.83 – 2.74 (m, 1H), 2.35 – 2.14 (m, 4H), 1.99 –

1.62 (m, 5H), 1.52 – 1.17 (m, 5H), 1.06 – 0.96 (m, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): *(major isomer)* δ = 171.8, 171.4, 139.6, 135.0, 131.2, 128.3, 127.0, 125.6, 67.7, 61.2, 51.9, 43.4, 39.6, 38.9, 36.3, 28.8, 27.7, 25.9, 25.1, 17.3 ppm.

*Ester intermediate (**5t**)*: White solid (0.17 g, 54%); $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$): *(mixture of endo/exo)* δ = 7.50 – 7.15 (m, 5H), 5.42 – 5.13 (m, 1H), 2.57 – 1.64 (m, 10H), 1.54 – 0.22 (m, 10H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 173.6, 173.6, 146.2, 146.1, 128.3, 128.3, 126.9, 126.8, 124.7, 124.6, 76.4, 75.9, 75.5, 75.4, 46.0, 45.8, 40.6, 40.2, 40.1, 39.9, 39.8, 39.6, 36.9, 31.7, 31.5, 29.0, 29.0, 27.4, 27.3, 24.5, 24.2, 24.2, 23.8, 21.1, 21.1 ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{26}O_3Na$ 337.1774, found 337.1775.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxx

Copies of ^{1}H and ^{13}C NMR spectra, X-ray crystallographic data for compound **P5** (CIF), X-ray crystallographic data for compound **10t** (CIF), and copies of chiral HPLC chromatographs for compound **2a** (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: prs@uni-giessen.de

ORCID

Peter R. Schreiner: 0000-0002-3608-5515

Notes

The authors declare no competing financial interest.

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References

(1) (a) Bataille, C. J. R.; Donohoe, T. J. Osmium-Free Direct *Syn*-Dihydroxylation of Alkenes. *Chem. Soc. Rev.* **2011**, *40*, 114–128. (b) Zang, C.; Liu, Y.; Xu, Z. J.; Tse, C. W.; Guan, X.; Wei, J.; Huang, J. S.; Che, C. M. Highly Enantioselective Iron-Catalyzed *cis*-Dihydroxylation of Alkenes with Hydrogen Peroxide Oxidant via an Fe^{III}-OOH Reactive Intermediate. *Angew. Chem. Int. Ed.* **2016**, *55*, 10253-10257. (c) Chow, T. W.-S.; Liu, Y.; Che, C.-M. Practical Manganese-Catalysed Highly Enantioselective *cis*-Dihydroxylation of Electron-Deficient Alkenes and Detection of a *cis*-Dioxomanganese(v) Intermediate by High Resolution ESI-MS Analysis. *Chem. Commun.* **2011**, *47*, 11204-11206. (d) Saisaha, P.; Pijper, D.; van Summeren, R. P.; Hoen, R.; Smit, C.; de Boer, J. W.; Hage, R.; Alsters, P. L.; Feringa, B. L.; Browne, W. R. Manganese Catalyzed *cis*-Dihydroxylation of Electron Deficient Alkenes with H_2O_2. *Org. Biomol. Chem.* **2010**, *8*, 4444-4450. (e) Borrell, M.; Costas, M. Mechanistically Driven Development of an Iron Catalyst for Selective *Syn*-Dihydroxylation of Alkenes with Aqueous Hydrogen Peroxide. *J. Am. Chem. Soc.* **2017**, *139*, 12821-12829.

(2) (a) Reddy, M. D.; Kobori, H.; Mori, T.; Wu, J.; Kawagishi, H.; Watkins, E. B. Gram-Scale, Stereoselective Synthesis and Biological Evaluation of (+)-Armillariol C. *J. Nat. Prod.* **2017**, *80*, 2561–2565. (b) Trost, B. M.; Knopf, J. D.; Brindle, C. S. Synthetic Strategies Employed for the Construction of Fostriecin and Related Natural Products. *Chem. Rev.* **2016**, *116*, 15035–15088.

(3) (a) Donohoe, T. J., Bataille, C. J. and Innocenti, P. Hydrogen-Bonding-Mediated Directed Osmium Dihydroxylation. In *Organic Reactions*; John Wiley and Sons Ltd.: 2012; Vol. 76. (b) Trindade, A. F.; Gois, P. M. P.; Afonso, C. A. M. Recyclable Stereoselective Catalysts. *Chem. Rev.* **2009**, *109*, 418–514. (c) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. Catalytic Asymmetric Dihydroxylation. *Chem. Rev.* **1994**, *94*, 2483–2547. (d) Bergstad, K.; Jonsson, S. Y.; Bäckvall, J.-E. A New Coupled Catalytic System for Dihydroxylation of Olefins by H_2O_2. *J. Am. Chem. Soc.* **1999**, *121*, 10424–10425. (e) Oldenburg, P. D.; Shteinman, A. A.; Que, L. Iron-Catalyzed Olefin *cis*-Dihydroxylation Using a Bio-Inspired N,N,O-Ligand. *J. Am. Chem. Soc.* **2005**, *127*, 15672–15673.

(4) (a) Wang, Z.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. An Efficient Catalytic Asymmetric Epoxidation Method. *J. Am. Chem. Soc.* **1997**, *119*, 11224–11235. (b) Limnios, D.; Kokotos, C. G. 2,2,2-Trifluoroacetophenone: An Organocatalyst for an Environmentally Friendly Epoxidation of Alkenes. *J. Org. Chem.* **2014**, *79*, 4270–4276. (c) Zhu, Y.; Wang, Q.; Cornwall, R. G.; Shi, Y. Organocatalytic Asymmetric Epoxidation and Aziridination of Olefins and Their Synthetic Applications. *Chem. Rev.* **2014**, *114*, 8199–8256. (d) Jana, N. K.; Verkade, J. G. Phase-Vanishing Methodology for Efficient Bromination, Alkylation, Epoxidation, and Oxidation Reactions of Organic Substrates. *Org. Lett.* **2003**, *5*, 3787–3790. (e) Wang, X.; Reisinger, C. M.; List, B. Catalytic Asymmetric Epoxidation of Cyclic Enones. *J. Am. Chem. Soc.* **2008**, *130*, 6070–6071.

(5) Zhong, W.; Liu, S.; Yang, J.; Meng, X.; Li, Z. Metal-Free, Organocatalytic *Syn* Diacetoxylation of Alkenes. *Org. Lett.* **2012**, *14*, 3336–3339.

(6) Kang, Y.-B.; Gade, L. H. The Nature of the Catalytically Active Species in Olefin Dioxygenation with $PhI(OAc)_2$: Metal or Proton? *J. Am. Chem. Soc.* **2011**, *133*, 3658–3667.

(7) (a) Bekkaye, M.; Su, Y.; Masson, G. Metal-Free Dioxygenation of Enecarbamates Mediated by a Hypervalent Iodine Reagent. *Eur. J. Org. Chem.* **2013**, *2013*, 3978–3982. (b) Schmidt, V. A.; Alexanian, E. J. Metal-Free, Aerobic Dioxygenation of Alkenes Using Hydroxamic Acids. *Angew. Chem. Int. Ed.* **2010**, *49*, 4491–4494.

(8) Russell, K. E. The Preparation of Phthalyl Peroxide and Its Decomposition in Solution. *J. Am. Chem. Soc.* **1955**, *77*, 4814–4815.

(9) (a) Adam, W. The Synthesis of Unusual Organic Molecules Using Cyclic Peroxides. New Synthetic Methods (3). *Angew. Chem. Int. Ed.* **1974**, *13*, 619–627. (b) Martin, M. M.; King, J. M. Preparation, Thermolysis, and Photolysis of Phenylmaleoyl Peroxide. *J. Org. Chem.* **1973**, *38*, 1588–1590. (c) Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriguez, O.; Rucktaeschel, R. Photochemical Transformations. XLIV. Cyclic Peroxides. Synthesis and Chemistry of α-Lactones. *J. Am. Chem. Soc.* **1972**, *94*, 1365–1367.
(10) (a) Greene, F. D. Cyclic Diacyl Peroxides. II. Reaction of Phthaloyl Peroxide with *cis*- and *trans*-Stilbene. *J. Am. Chem. Soc.* **1956**, *78*, 2250–2254. (b) Greene, F. D.; Rees, W. W. Cyclic Diacyl Peroxides. III. The Reaction of Phthaloyl Peroxide with Olefins. *J. Am. Chem. Soc.* **1958**, *80*, 3432–3437. (c) Greene, F. D.; Rees, W. W. Cyclic Diacyl Peroxides. V. Reaction of Phthaloyl Peroxide with Norbornylene. *J. Am. Chem. Soc.* **1960**, *82*, 890–893. (d) Greene, F. D.; Adam, W. Diacyl Peroxide–Olefin Reactions. Epoxidation of Tetramethylethylene by an Aroyl Peroxide. *J. Org. Chem.* **1964**, *29*, 136–139.
(11) (a) Greene, F. D.; Adam, W.; Knudsen, G. A. A Cyclic Peroxy Ester, β-Methyl-β-phenyl-β-peroxypropiolactone. *J. Org. Chem.* **1966**, *31*, 2087–2090. (b) Greene, F. D.; Rees, W. W. Cyclic Diacyl Peroxides. VI. Reaction of Phthaloyl Peroxide with Diarylacetylene. *J. Am. Chem. Soc.* **1960**, *82*, 893–896. (c) Adam, W.; Rios, A. Ionic Peroxide Reactions. Mechanism of the Reaction of Peroxycarbonates with Trivalent Phosphorus Nucleophiles. *J. Org. Chem.* **1971**, *36*, 407–411. (d) Adam, W.; Blancafort, L. Reaction of α-Peroxy Lactones with C, N, P, and S Nucleophiles: Adduct Formation and Nucleophile Oxidation by Nucleophilic Attack at and Biphilic Insertion into the Peroxide Bond. *J. Org. Chem.* **1997**, *62*, 1623–1629. (e) Adam, W.; Blancafort, L. Stereoselective Cycloaddition and Epoxidation of Enol Ethers by α-Peroxy Lactone as a Function of Steric and Stereoelectronic Effects. *J. Org. Chem.* **1996**, *61*, 8432–8438. (f) Adam, W.; Blancafort, L. Steric and Stereoelectronic Control of the Mode Selectivity as a Function of Alkene Structure in the Reaction with Dimethyl α-Peroxy Lactone: Cycloadducts and Ene Products versus Epoxides. *J. Am. Chem. Soc.* **1996**, *118*, 4778–4787.
(12) (a) Murray, R. W. Chemistry of Dioxiranes. 12. Dioxiranes. *Chem. Rev.* **1989**, *89*, 1187–1201. (b) Adam, W.; Saha-Möller, C. R.; Ganeshpure, P. A. Synthetic Applications of Nonmetal Catalysts for Homogeneous Oxidations. *Chem. Rev.* **2001**, *101*, 3499–3548.
(13) Adam, W.; Andler, S.; Heil, M. Novel Reactions of Disubstituted 1,2-Dioxetanes with Olefins as π-Nucleophiles: Cycloadditions via 1,6-Dipoles. *Angew. Chem. Int. Ed.* **1991**, *30*, 1365–1366.
(14) (a) Griffith, J. C.; Jones, K. M.; Picon, S.; Rawling, M. J.; Kariuki, B. M.; Campbell, M.; Tomkinson, N. C. O. Alkene *Syn* Dihydroxylation with Malonoyl Peroxides. *J. Am. Chem. Soc.* **2010**, *132*, 14409–14411. (b) Jones, K. M.; Tomkinson, N. C. O. Metal-Free Dihydroxylation of Alkenes Using Cyclobutane Malonoyl Peroxide. *J. Org. Chem.* **2012**, *77*, 921–928. (c) Yuan, C.; Axelrod, A.; Varela, M.; Danysh, L.; Siegel, D. Synthesis and Reaction of Phthaloyl Peroxide Derivatives, Potential Organocatalysts for the Stereospecific Dihydroxylation of Alkenes. *Tetrahedron Lett.* **2011**, *52*, 2540–2542.
(15) (a) Pilevar, A.; Hosseini, A.; Šekutor, M.; Hausmann, H.; Becker, J.; Turke, K.; Schreiner, P. R. Tuning the Reactivity of Peroxo Anhydrides for Aromatic C–H Bond Oxidation. *J. Org. Chem.* **2018**, *83*, 10070–10079. (b) Siegel, D. Phthaloyl Peroxide. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd., 2015. (c) Greene, F. D. Cyclic Diacyl Peroxides. I. Monomeric Phthaloyl Peroxide. *J. Am. Chem. Soc.* **1956**, *78*, 2246–2250.
(16) Alamillo-Ferrer, C.; Davidson, S. C.; Rawling, M. J.; Theodoulou, N. H.; Campbell, M.; Humphreys, P. G.; Kennedy, A. R.; Tomkinson, N. C. O. Alkene anti-Dihydroxylation with Malonoyl Peroxides. *Org. Lett.* **2015**, *17*, 5132–5135.
(17) Zhao, R.; Chang, D.; Shi, L. Recent Advances in Cyclic Diacyl Peroxides: Reactivity and Selectivity Enhancement Brought by the Cyclic Structure. *Synthesis* **2017**, *49*, 3357–3365.
(18) Bach, R. D.; Ayala, P. Y.; Schlegel, H. B. A Reassessment of the Bond Dissociation Energies of Peroxides. An ab Initio Study. *J. Am. Chem. Soc.* **1996**, *118*, 12758–12765.
(19) Schwarz, M.; Reiser, O. Metal or No Metal: That Is the Question! *Angew. Chem. Int. Ed.* **2011**, *50*, 10495-10497.
(20) Meester, M. A. M.; Schenk, H.; MacGillavry, C. H. The Crystal and Molecular Structure of Cyclopropane-1,1-dicarboxylic acid. *Acta Crystallographica Section B* **1971**, *27*, 630–634.
(21) Picon, S.; Rawling, M.; Campbell, M.; Tomkinson, N. C. O. Alkene Dihydroxylation with Malonoyl Peroxides: Catalysis Using Fluorinated Alcohols. *Org. Lett.* **2012**, *14*, 6250–6253.

(22) Jones, K. M. On the Metal-Free Dihydroxylation of Alkenes. PhD Thesis, Cardiff University, 2010.
(23) Gan, S.; Yin, J.; Yao, Y.; Liu, Y.; Chang, D.; Zhu, D.; Shi, L. Metal- and Additive-Free Oxygen-Atom Transfer Reaction: An Efficient and Chemoselective Oxidation of Sulfides to Sulfoxides with Cyclic Diacyl Peroxides. *Organic & Biomolecular Chemistry* **2017**, *15*, 2647–2654.
(24) Rawling, M. J.; Rowley, J. H.; Campbell, M.; Kennedy, A. R.; Parkinson, J. A.; Tomkinson, N. C. O. Mechanistic Insights into the Malonoyl Peroxide *Syn*-Dihydroxylation of Alkenes. *Chemical Science* **2014**, *5*, 1777–1785.
(25) Menger, F. M.; Vitale, A. C. Anion-Catalyzed Ester Aminolyses in a Hydrocarbon Solvent. *J. Am. Chem. Soc.* **1973**, *95*, 4931–4934.
(26) Lebedev, S. A.; Lopatina, V. S.; Petrov, E. S.; Beletskaya, I. P. Condensation of Organic Bromides with Vinyl Compounds Catalysed by Nickel Complexes in the Presence of Zinc. *J. Organomet. Chem.* **1988**, *344*, 253–259.
(27) Malkoch, M.; Thibault, R. J.; Drockenmuller, E.; Messerschmidt, M.; Voit, B.; Russell, T. P.; Hawker, C. J. Orthogonal Approaches to the Simultaneous and Cascade Functionalization of Macromolecules Using Click Chemistry. *J. Am. Chem. Soc.* **2005**, *127*, 14942–14949.
(28) Ohta, T.; Ikegami, H.; Miyake, T.; Takaya, H. BINAP-Ru(II) and BINAP-Rh(I)-Catalyzed Asymmetric Hydrogenation of Olefins without Heteroatom-Functionalities. *J. Organomet. Chem.* **1995**, *502*, 169–176.
(29) Müller, P.; Miao, Z. Synthesis of Functionalized Cycloprop[f]indenes via the Carbene Addition Route. *Helv. Chim. Acta* **1994**, *77*, 2051–2059.
(30) Phan, D. H. T.; Kou, K. G. M.; Dong, V. M. Enantioselective Desymmetrization of Cyclopropenes by Hydroacylation. *J. Am. Chem. Soc.* **2010**, *132*, 16354–16355.
(31) Adam, W.; Bosio, S. G.; Turro, N. J.; Wolff, B. T. Enecarbamates as Selective Substrates in Oxidations: Chiral-Auxiliary-Controlled Mode Selectivity and Diastereoselectivity in the [2+2] Cycloaddition and Ene Reaction of Singlet Oxygen and in the Epoxidation by DMD and *m*CPBA. *J. Org. Chem.* **2004**, *69*, 1704–1715.
(32) Walker, J. C. L.; Oestreich, M. Regioselective Transfer Hydrodeuteration of Alkenes with a Hydrogen Deuteride Surrogate Using $B(C_6F_5)_3$ Catalysis. *Org. Lett.* **2018**, *20*, 6411–6414.
(33) Emmanuvel, L.; Shaikh, T. M. A.; Sudalai, A. $NaIO_4$/LiBr-mediated Diastereoselective Dihydroxylation of Olefins: A Catalytic Approach to the Prevost−Woodward Reaction. *Org. Lett.* **2005**, *7*, 5071–5074.
(34) Bag, R.; Punniyamurthy, T. $K_2S_2O_8$-Mediated Dioxygenation of Aryl Alkenes Using N-Hydroxylamines and Air. *ChemistrySelect* **2018**, *3*, 6152–6155.
(35) Mäsing, F.; Mardyukov, A.; Doerenkamp, C.; Eckert, H.; Malkus, U.; Nüsse, H.; Klingauf, J.; Studer, A. Controlled Light-Mediated Preparation of Gold Nanoparticles by a Norrish Type I Reaction of Photoactive Polymers. *Angew. Chem. Int. Ed.* **2015**, *54*, 12612–12617.
(36) Ren, Q.; Tsunaba, K.; Kitamura, Y.; Nakashima, R.; Shibada, A.; Ikeda, M.; Kitade, Y. Synthesis of Ethynylbenzene-Substituted Glycol as a Versatile Probe for Labeling Oligonucleotides. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 1519–1522.
(37) Wang, Z.; Cui, Y.-T.; Xu, Z.-B.; Qu, J. Hot Water-Promoted Ring-Opening of Epoxides and Aziridines by Water and Other Nucleopliles. *J. Org. Chem.* **2008**, *73*, 2270–2274.
(38) Sun, X.; Frimpong, K.; Tan, K. L. Synthesis of Quaternary Carbon Centers via Hydroformylation. *J. Am. Chem. Soc.* **2010**, *132*, 11841–11843.
(39) Kim, J. H.; Čorić, I.; Palumbo, C.; List, B. Resolution of Diols via Catalytic Asymmetric Acetalization. *J. Am. Chem. Soc.* **2015**, *137*, 1778–1781.
(40) Li, C.; Chen, H.; Li, J.; Li, M.; Liao, J.; Wu, W.; Jiang, H. Palladium-Catalyzed Regioselective Aerobic Allylic C−H Oxygenation: Direct Synthesis of α,β-Unsaturated Aldehydes and Allylic Alcohols. *Adv. Synth. Catal.* **2018**, *360*, 1600–1604.
(41) King, S. B.; Sharpless, K. B. An Efficient Synthesis of Enantiomerically Pure *trans*-2-Phenylcyclohexanol. *Tetrahedron Lett.* **1994**, *35*, 5611–5612.
(42) Fristad, W. E.; Han, Y.-K.; Paquette, L. A. Silanes in Organic Synthesis: VI. Conversion of Unsubstituted and 2-Aryl Ketones to (1-Arylallyl)silanes. *J. Organomet. Chem.* **1979**, *174*, 27–40.

(43) Holland, H. L.; Destafano, D.; Ozog, J. Side Chain Hydroxylation of Aromatic Compounds by Fungi. Part 6. Biotransformation of Olefins by Mortierella Isabellina. *Biocatalysis* **1994**, *10*, 65–76.
(44) Campbell, M. M.; Abbas, N.; Sainsbury, M. Spiroheterocycles Derived from Tetralone. *Tetrahedron* **1985**, *41*, 5637–5644.
(45) Yang, B.; Lu, Z. Visible Light-Promoted Dihydroxylation of Styrenes with Water and Dioxygen. *Chem. Commun.* **2017**, *53*, 12634–12637.