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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01784 • Publication Date (Web): 22 Aug 2019

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SO_2F_2-Mediated Epoxidation of Olefins with Hydrogen Peroxide

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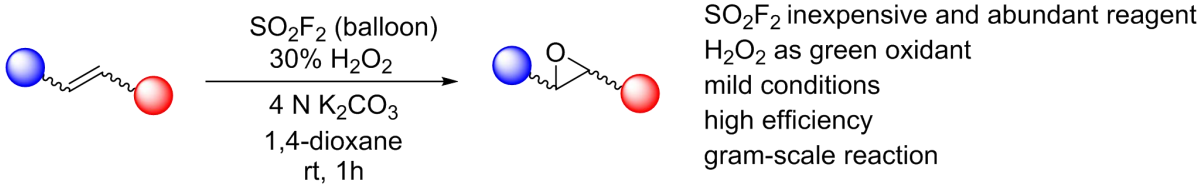
Supporting Information

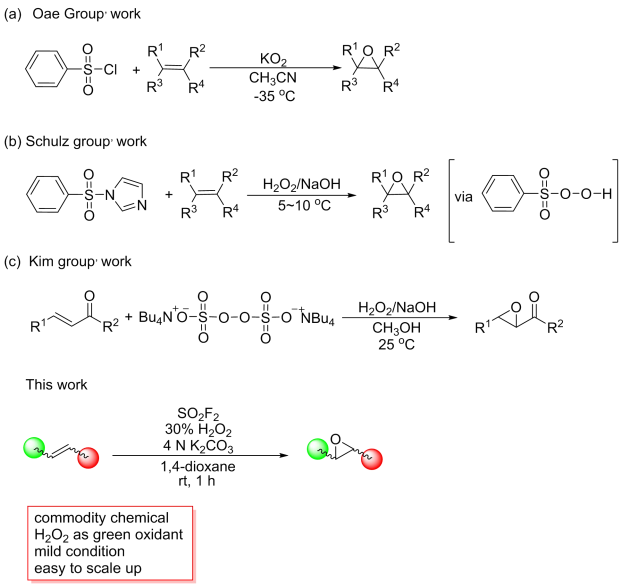


ABSTRACT: An inexpensive, mild, and highly efficient epoxidation protocol has been developed involving bubbling SO_2F_2 gas into a solution of olefin, 30% aqueous hydrogen peroxide and 4 N aqueous potassium carbonate in 1,4-dioxane at room temperature for 1 h with the formation of the corresponding epoxides in good to excellent yields. The novel $SO_2F_2/H_2O_2/K_2CO_3$ epoxidizing system is suitable to a variety of olefinic substrates including electron-rich and electron-deficient ones.

INTRODUCTION

Epoxides are versatile intermediates for the synthesis of a large number of valuable compounds and pharmaceuticals. The epoxidation of olefins is the most convenient method for the synthesis of epoxides[1]. Peracids and dioxiranes (for example 3-chloroperbenzoic acid and dimethyl dioxirane) are the most classic oxidants for this transformation[2]. Organo sulfonic peracid, as a new family of highly active oxidant species, was gradually recognized and investigated by chemists until recent decades[3]. Organo sulfonic peracids cannot be isolated because of their instability but they displayed some unique oxidizing properties[4]. In 1983, Oae[5] first reported the reaction of sulfonyl chlorides with KO_2 under argon atmosphere via a radical process leading to the formation of sulfonic peracid anions [Scheme 1. (a)]. Later, Schulz[6] disclosed in situ generation of organo sulfonic peracids through the reaction of arylsulfonyl imidazolides with 30% aqueous hydrogen peroxide in the presence of a base (NaOH or K_2CO_3). [Scheme 1. (b)]. It is noteworthy that the treatment of sulfonyl chlorides with H_2O_2 did not result in the formation of persulfonic acids[7]. In 2007, Kim[8] described the use of tetrabutylammonium peroxydisulfate as a kind of oxidant in the presence of H_2O_2 and NaOH [Scheme 1. (c)]. All the above in situ generated organo sulfonic peracids or peroxysulfate salt exhibited highly efficient epoxidizing abilities resulting in the smooth conversion of alkenes into epoxides. However, these known approaches for the in situ generation of sulfonic peracids still have disadvantages of the use of harsh reaction conditions and expensive or explosive reagents, and restricted substrate scope. Therefore, it is still a challenging task for chemists to develop inexpensive, mild, green and highly efficient approach for the epoxidation of olefins. On the other hand, sulfuryl fluoride gas (SO_2F_2) has been used as a fumigant for several decades, and its application as chemical reagent in organic synthesis was revived recently[9]. In 2014, Sharpless reported a new kind of click chemistry based on sulfur (VI) fluoride exchange (SuFEx) which offers a rapid and highly efficient access to diverse chemical functionality[10]. Sulfuryl fluoride is inexpensive and stable reagent (Currently, SO_2F_2 gas steel cylinder is commercially available in China). Since 2014, besides its application in SuFEx-based click reactions, SO_2F_2 has been widely used in other chemical transformations. Recently, Qin reported the elegant application of SO_2F_2 in the syntheses of a variety of compounds including aryl nitriles, heterocycles, ethenesulfonyl fluorides, diarylmethanes, arylcarboxylic acids, alkynes, nitriles and amides[11]. Over the past decade, we have been devoted to the study on the application of poly(per)fluorosulfonyl fluoride (R_fSO_2F, for example *n*-$C_4F_9SO_2F$) in organic synthesis[12]. In 2004, we reported an efficient epoxidizing system of $R_fSO_2F/H_2O_2/NaOH$. Inspired by our preliminary research results, we envisioned that SO_2F_2 will similarly be able to react with HOO^- anion to form an intermediate FSO_2OOH which will also serve as an efficient epoxidizing agent. Herein, we reports a highly efficient and mild SO_2F_2-mediated epoxidation of olefins with 30% H_2O_2 aqueous solution at room temperature.

Scheme 1. Previous Works for epoxidation of olefins using sulfur based oxidant

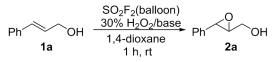


RESULTS AND DISCUSSION

To initiate our studies, we selected cinnamic alcohol (**1a**) as a model substrate to explore the optimum reaction conditions. The effect of base on epoxidation reaction was first investigated. A

variety of bases were used to perform the reaction in CH_3OH at room temperature. The molar ratio of **1a** : base : H_2O_2 is 1 : 8 : 8. When NaOH (4 N NaOH aqueous solution was used) was tested as a base, the corresponding epoxide product **2a** was obtained only in a low yield of 18% (Table 1, entry 1). The strong alkalinity of NaOH might cause the ring opening of epoxyl group resulting in the low yield of **2a**. Next, two weaker inorganic bases, $NaHCO_3$ (4 N aqueous solution) and K_2CO_3 (4 N aqueous solution) were then tested. To our delight, the yields of **2a** were dramatically increased to 70% and 75% respectively (Table 1, entries 2 and 3). The use of two organic bases, Et_3N and DBU, provided **2a** in slightly lower yields of 60% and 69% (Table 1, entries 4 and 5). In addition, use of solid K_2CO_3 and 1 N aqueous K_2CO_3 solution instead of 4 N aqueous K_2CO_3 solution had slightly reduced

Table 1. Reaction Condition Optimization for the Epoxidation of Cinnamic alcohol



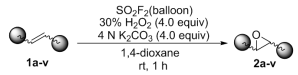
Entry[a]	base	solvent	yield[c]
1	NaOH (4 N)	MeOH	18%
2	$NaHCO_3$ (4 N)	MeOH	70%
3	K_2CO_3 (4 N)	MeOH	75%
4	NEt_3	MeOH	60%
5	DBU	MeOH	69%
6	K_2CO_3	MeOH	65%
7	K_2CO_3 (1 N)	MeOH	70%
8	K_2CO_3 (4 N)	1,4-dioxane	84%
9	K_2CO_3 (4 N)	Acetone	20%
10	K_2CO_3 (4 N)	CH_2Cl_2	trace
11	K_2CO_3 (4 N)	i-PrOH	15%
12	K_2CO_3 (4 N)	CH_3CN	10%
13[b]	K_2CO_3 (4 N)	1,4-dioxane	85%

[a]Reaction condition: To a 50 mL double-necked flask was added **1a** (0.5 mmol),solvent (2 mL), 8.0 equiv of 30% H_2O_2, then slowly added 8.0 equiv of base to the mixture, meanwhile, bubbling SO_2F_2 into the mixture by a balloon combined with syringe needle and stirred for 1 h at room temperature. [b]H_2O_2 : base = 4:4 (molar ratio), [c]isolated yield.

reactivity offering **2a** in 65% and 70% yields, respectively (Table 1, entries 6 and 7). K_2CO_3 (4 N) as base thus generated the best result. The further screening of solvents was subsequently performed. The results shown in Table 1 revealed that 1,4-dioxane was the best choice of solvent (Table 1, entries 8-12). It is of interest to note that, when the amounts of K_2CO_3 and H_2O_2 were reduced to 4 equivalents, it nearly has no any negative effect on the reaction (Table 1, entry 13). Therefore, the optimum reaction conditions are as follows: **1a** (0.50 mmol), 30% aqueous H_2O_2 (2.0 mmol), K_2CO_3 (4 N) (2.0 mmol), 1,4-dioxane (2 mL), bubbling SO_2F_2 gas (*Caution*! SO_2F_2 is toxic, and the reaction should be run in a fume hood) into the solution at room temperature for 1 h.

To further explore the application of the above methodology, an array of olefins were subjected to $SO_2F_2/H_2O_2/K_2CO_3$ epoxidizing system in dioxane at room temperature. Results were displayed in Table 2. Allylic alcohol, like cinnamyl alcohol **1a** (Table 2, entry 1), is a good substrate for this transformation. Then a variety of monosubstituted terminal olefins (**1b-1g**) was investigated, and the corresponding epoxides were smoothly formed in 75-87% yields (Table 2, entries 2-7). The ester group of **1c** was not hydrolyzed under the reaction conditions even after stirring for 24 h. Phenyloxy, benzyloxy and phenolic hydroxy groups are all tolerable to this system. For **1g**, the formation of aryl fluorosulfonate resulting from the reaction of phenolic hydroxy with SO_2F_2 was not observed. Two separated electron-rich double bonds in substrates **1h** (racemate) and **1i** (racemate) were successfully di-epoxidized leading to the formation of diepoxyl products in good yields (Table 2, entries 8 and 9). From their ^1H and ^{13}C NMR spectra, **2h** is still a racemate and **2i** is a mixture of diastereoisomers. Styrenes with different substituents (Cl, Br, OAc and NO_2) on benzene ring offered epoxides in moderate to good yields (Table 2, entries 10-13).

Table 2. Substrate Scope of SO_2F_2 - Mediated Epoxidation of Olefins



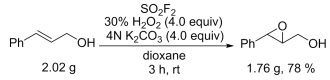
entry[a]	substrate	product	yield[c]	entry	substrate	product	yield[c]
1	1a	2a	85%	14	1n	2n	87%
2	1b	2b	87%	15	1o	2o	90%
3	1c	2c	82%	16[b]	1p	2p	75%
4	1d	2d	85%	17	1q	2q	92%
5	1e	2e	82%	18	1r	2r	81%[d]
6	1f	2f	83%	19	1s	2s	90%
7	1g	2g	75%	20	1t	2t	94%
8	1h	2h	85%	21	1u	2u	91%[e]
9	1i	2i	81%	22	1v	2v	89%[e]
10	1j	2j	61%				
11	1k	2k	63%				
12	1l	2l	65%				
13	1m	2m	80%				

[a]Reaction conditions: To a 50 mL double-necked flask was added **1** (0.5 mmol), dioxane (2 mL), 4.0 equiv of 30% H_2O_2, then slowly added 4.0 equiv of K_2CO_3 (4 N) to the mixture, finally bubbling SO_2F_2 into the mixture by a balloon and stirred for 1 h at room temperature.[b]reaction conditions: H_2O_2/K_2CO_3 = 8 : 8 (molar ratio) , reaction time 3 h. [c] isolated yield. [d]without SO_2F_2, 30% yield. [e]α : β isomer= 1.5 : 1.

For sterically hindered *trans*-stilbene (**1n**) and *cis*-stilbene (**1o**), the epoxidation proceeded very well with the formation of the corresponding epoxides in excellent yields (Table 2, entries 14 and 15). At the same time, the complete retention of configuration was observed for **2n** and **2o**. A tetrasubstituted sterically hindered olefin, tetra(4-cyanophenyl)ethylene (**1p**), provided the epoxide in 75% yield after 3 h when 8 equiv. of H_2O_2 and 8 equiv. of K_2CO_3 were used (Table 2, entry 16). $SO_2F_2/H_2O_2/K_2CO_3$ epoxidizing system is also amenable to the epoxidation of the challenging electron-deficient alkenes (entry 17-19). In the case of diethyl maleate (**1t**), an extremely electron-poor alkene, its epoxidation occurred smoothly affording *cis*-epoxyl product in 94% yield (Table 2, entry 20). As a comparison with results in literatures, it was reported that when **1t** was subjected to HOF and $Mn(OT_f)_2$/2-PyCOOH system for epoxidation, **2t** was obtained only with low to moderate yields[13]. It should be noted that in the epoxidation of **1r**, the Baeyer-Villiger[14] oxidation product was not observed. Finally, the epoxidation of two optically pure steroidal homoallylic alcohols **1u** and **1v** worked quite well (Table 2, entries 21 and 22), and the epoxides were afforded in 90% and 89% yields, respectively[15]. From their H-1 NMR spectra, both **2u** and **2v** are all mixtures of 5,6-α-epoxide and 5,6-β-epoxide with α : β isomer being 1.5 : 1.

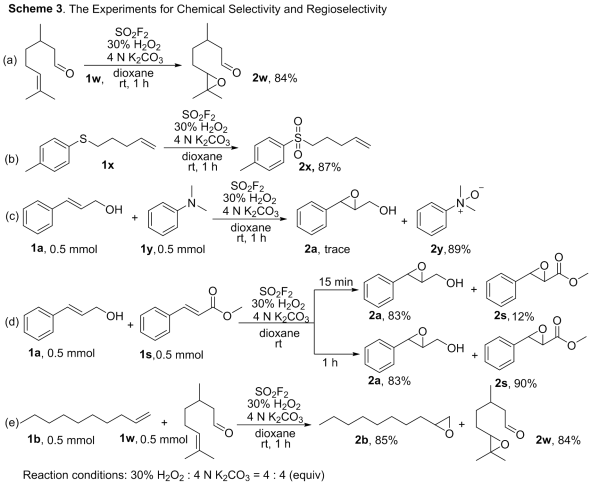
To demonstrate the potential application value of $SO_2F_2/H_2O_2/K_2CO_3$ epoxidizing system in organic synthesis, a gram-scale epoxidation of **1a** was examined. As shown in Scheme 2, the epoxidation of 2.02 grams of **1a** provided **2a** in 78% yield after 3 h at room temperature, which confirmed this method can be used in organic synthesis and even in industrial manufacturing.

Scheme 2. Gram-scale Epoxidation of Cinnamyl Alcohol

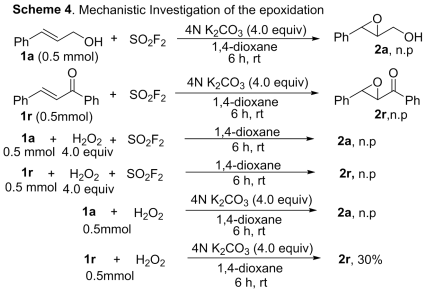


In order to explore the chemical selectivity, we subsequently investigated the reactions of two substrates with aldehyde group (**1w**) and thioether group (**1x**) with $SO_2F_2/H_2O_2/K_2CO_3$ system. Results were shown in Scheme 3. The double bond in **1w** can smoothly and quickly be epoxidized to **2w** in 84% yield with aldehyde group untouched [Scheme 3, (a)]. However, in the case of **1x**, only sulfur atom was selectively oxidized to sulfone and the double bond was kept inert [Scheme 3, (b)]. When the same amount of cinnamyl alcohol **1a** and *N*,*N*-dimethylaniline **1y** was subjected to $SO_2F_2/H_2O_2/K_2CO_3$ system, **2y** was selectively formed in 89% yield and **2a** was just detected in trace amount [Scheme 3, (b)]. The above results demonstrated that tertiary amine and thioether can be preferentially oxidized than olefinic double bond. Next, we used the same amount of cinnamyl alcohol **1a** and methyl cinnamate **1s** to study the regioselectivity [Scheme 3, (d)]. The results showed that electron-rich double bond is preferentially epoxidized than electron-deficient one. However, with the prolongation of reaction time, electron-deficient double bond was also efficiently epoxidized. The result in (e) of Scheme 3 indicated that $SO_2F_2/H_2O_2/K_2CO_3$ oxidation system did not have apparent selectivity to monosubstituted and trisubstituted double bonds.

Scheme 3. The Experiments for Chemical Selectivity and Regioselectivity



Scheme 4. Mechanistic Investigation of the epoxidation



To clarify the reaction mechanism, some control experiments are conducted (scheme 4). We selected cinnamyl alcohol (**1a**) as a representative electron-rich alkene, and chalcone (**1r**) as a representative electron-deficient alkene. In the absence of H_2O_2, no reaction was observed for **1a** and **1r**, indicating that H_2O_2 is an oxidant of the reaction. However, in the absence of sulfuryl fluoride or K_2CO_3, H_2O_2 cannot epoxidize cinnamyl alcohol. It showed that H_2O_2 reacts with SO_2F_2 in the presence of K_2CO_3 to form a new oxidant species, which enables alkene to be epoxidized. In addition, in the absence of SO_2F_2, chalcone can be epoxidized by H_2O_2/K_2CO_3 in much lower yield than by $SO_2F_2/H_2O_2/K_2CO_3$ system. This also showed that SO_2F_2 was involved in the epoxidation process.

Based on the above control experiments and literature descriptions[4, 5a, 7], a plausible epoxidation mechanism is outlined below. Firstly, H_2O_2 is deprotonated by K_2CO_3 to form anion HOO^-, which may attack SO_2F_2 through substitution reaction to provide fluorosulfonic peracid FSO_2OOH. Then in situ generated FSO_2OOH can epoxidize alkenes like traditional peracids. It has been reported in literatures[4,5a] that peroxysulfur species is not stable and can not be detected and isolated. Similarly, due to the instability of in situ generated FSO_2OOH, this oxidant species also was not detected nor isolated in the course of our study.

CONCLUSION

In conclusion, SO_2F_2-mediated epoxidation of a variety of electron-rich and electron-deficient alkenes with H_2O_2/K_2CO_3 was developed. The in situ generated fluorosulfonic peracid intermediate served as an oxidizing species in the epoxidation process. The main advantages of the epoxidation method is its inexpensiveness, high efficiency, environmentally benigh and mild reaction conditions. Neutral to weak alkaline reaction medium makes the novel method specially suitable for the epoxidation of acid-sensitive alkenes. In addition, $SO_2F_2/H_2O_2/K_2CO_3$ system can efficiently epoxidize extremely

electron-poor and highly sterically hindered olefinic substrates. Therefore, we expect it to be used as a practical alternative epoxidation system in organic synthesis.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. All reactions were performed in a double-necked flask. ^{1}H NMR spectra were recorded on 400 MHz and ^{13}C NMR spectra were recorded on 101 MHz, and tetramethylsilane as an internal standard. The chemical shifts are referenced to signals at 7.25 and 77.0 ppm ($CDCl_3$). Column chromatography was carried out on silica gel with petroleum ether/ethyl acetate as the eluent.

General procedure for the epoxidation of alkenes. To a 50 mL double-necked flask was added 0.5 mmol alkene, 2 mL dioxane, 30% H_2O_2 (0.23 mL, 2 mmol). Then K_2CO_3 (4 N aqueous solution. 0.5 mL, 2 mmol) was slowly added to the mixture. Meanwhile, SO_2F_2 gas was bubbling into the reaction mixture by a balloon combined with a syringe needle. The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was diluted with 5 mL of water, and extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was further purified through flash column chromatography using the mixture of petroleum ether and ethyl acetate as eluent.

3-Phenyl-2-oxiranemethanol (2a):[2c] colorless oil; 64 mg, 85 %; ^{1}H NMR (400 MHz, CDCl3) δ 7.39 – 7.19 (m, 5H), 4.04 (dd, *J* = 12.8, 2.5 Hz, 1H), 3.93 (d, *J* = 2.3 Hz, 1H), 3.79 (dd, *J* = 12.7, 3.9 Hz, 1H), 3.24 – 3.18 (m, 1H), 1.24 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.6, 128.5, 128.4, 125.7, 62.5, 61.1, 55.5.

2-Octyloxirane (2b):[2c] colorless oil; 68 mg, 87 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.71 (t, *J* = 4.5 Hz, 1H), 2.43 (dd, *J* = 5.1, 2.7 Hz, 1H), 1.51 – 1.46 (m, 2H), 1.25 (d, *J* = 8.9 Hz, 12H), 0.86 (d, *J* = 6.4 Hz, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 52.3, 47.0, 32.4, 31.8, 29.5, 29.4, 29.2, 25.9, 22.6, 14.0.

Diethyl 2-(oxiran-2-ylmethyl)propanedioate (2c):[16] colorless oil; 88 mg, 82 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 – 4.10 (m, 4H), 3.48 (dd, *J* = 8.6, 6.1 Hz, 1H), 2.96 (dp, *J* = 6.8, 2.2 Hz, 1H), 2.73 – 2.70 (m, 1H), 2.48 – 2.45 (m, 1H), 2.20 (ddd, *J* = 14.4, 8.6, 4.6 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.22 (td, *J* = 7.1, 3.8 Hz, 6H).^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.8, 168.8, 61.59, 61.56, 49.8, 48.9, 47.2, 31.6, 13.98, 13.95.

oxiran-2-ylmethyl 3-cyclohexylpropanoate (2d): colorless oil; 90 mg, 85 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (dd, *J* = 12.3, 3.0 Hz, 1H), 3.86 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.16 (dq, *J* = 6.4, 3.1 Hz, 1H), 2.80 (t, *J* = 4.5 Hz, 1H), 2.60 (dd, *J* = 4.9, 2.6 Hz, 1H), 2.31 (t, *J* = 7.9 Hz, 2H), 1.68 – 1.60 (m, 5H), 1.51 – 1.46 (m, 2H), 1.21 – 1.09 (m, 4H), 0.84 (td, *J* = 11.7, 8.6 Hz, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.8, 64.7, 49.3, 44.6, 37.1, 32.9, 32.2, 31.6, 26.5, 26.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}O_3$ 213.1485; Found: 213.1491.

2-[(Phenylmethoxy)methyl]oxirane (2e):[17] colorless oil; 67 mg, 82 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 4.58 (q, *J* = 11.9 Hz, 2H), 3.76 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.43 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.18 (dq, *J* = 6.4, 3.0 Hz, 1H), 2.79 (t, *J* = 4.6 Hz, 1H), 2.61 (dd, *J* = 5.1, 2.7 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.8, 128.4, 127.7, 73.3, 70.8, 50.9, 44.3.

phenoxyacetyl-2,3-epoxipropyl ester (2f):[24] colorless oil; 86 mg, 85 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 6.97 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.90 – 6.85 (m, 2H), 4.64 (d, *J* = 1.7 Hz, 2H), 4.51 (dd, *J* = 12.2, 2.9 Hz, 1H), 3.98 (ddd, *J* = 12.3, 6.4, 1.9 Hz, 1H), 3.18 (td, *J* = 4.1, 2.1 Hz, 1H), 2.79 (t, *J* = 4.5 Hz, 1H), 2.59 (dt, *J* = 4.8, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 157.6, 129.6, 121.8, 114.6, 65.6, 65.0, 49.0, 44.6.

2-(oxiran-2-ylmethyl)phenol (2g):[18] colorless oil; 56 mg, 75 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.8 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.00 (s, 1H), 6.92 – 6.82 (m, 2H), 3.29 (tt, *J* = 6.7, 2.8 Hz, 1H), 3.19 (dd, *J* = 15.1, 2.7 Hz, 1H), 2.91 (t, *J* = 4.2 Hz, 1H), 2.74 – 2.67 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.5, 131.0, 128.8, 123.2, 120.6, 117.0, 53.6, 48.1, 34.8.

2,4-Methano-2H-indeno[1,2-b:5,6-b']bisoxirene (2h):[2e] colorless solid; mp 179-181 ℃; 63 mg, 85 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 1H), 3.37 (d, *J* = 2.5 Hz, 1H), 3.23 (d, *J* = 3.4 Hz, 1H), 3.19 (d, *J* = 3.5 Hz, 1H), 2.65 (d, *J* = 4.4 Hz, 1H), 2.57 (dd, *J* = 8.2, 4.4 Hz, 1H), 2.46 (d, *J* = 3.4 Hz, 2H), 1.87 (dd, *J* = 15.4, 8.8 Hz, 1H), 1.80 – 1.78 (m, 1H), 1.42 – 1.37 (m, 1H), 0.82 (d, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 61.7, 58.6, 48.9, 48.7, 48.3, 44.6, 39.9, 39.1, 29.6, 26.9.

1,2-Epoxy-4-(2-oxiranyl)cyclohexane (2i):[2c] colorless oil; 50 mg, 81 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 – 3.00 (m, 2H), 2.84 – 2.56 (m, 2H), 2.53 – 2.37 (m, 1H), 2.22 – 1.98 (m, 2H), 1.84 (ddt, *J* = 16.3, 11.5, 6.1 Hz, 1H), 1.71 – 1.63 (m, 1H), 1.56 – 1.46 (m, 1H), 1.44 – 1.21 (m, 1H), 1.19 – 1.00 (m, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 55.9, 55.6, 55.5, 52.4, 52.4, 52.3, 52.2, 51.6, 51.5, 50.9, 50.8, 46.1, 46.0, 45.6, 45.3.

2-(4-Bromophenyl)oxirane (2j):[19] colorless oil; 61 mg, 61 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.83 – 3.79 (m, 1H), 3.13 (dt, *J* = 5.5, 2.9 Hz, 1H), 2.74 (dt, *J* = 5.5, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.7, 131.6, 127.1, 122.0, 51.8, 51.2.

2-(4-Chlorophenyl)oxirane (2k):[19] colorless oil; 49 mg, 63 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.21 – 7.16 (m, 2H), 3.81 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.12 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.73 (dd, *J* = 5.5, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.7, 131.6, 127.1, 122.0, 51.8, 51.2.

4-Methoxycarbonylstyrene oxide (2l):[19] colorless oil; 58 mg, 65 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.06 – 7.03 (m, 2H), 3.83 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.10 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.74 (dd, *J* = 5.4, 2.6 Hz, 1H), 2.26 (d, *J* = 1.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 169.4, 150.5, 135.2, 126.5, 121.7, 51.9, 51.2, 21.1.

2-(4-nitrophenyl)oxirane (2m):[19] colorless solid; mp 80-86 ℃; 66 mg, 80 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 3.93 (t, *J* = 3.3 Hz, 1H), 3.19 (t, *J* = 4.8 Hz, 1H), 2.74 (dd, *J* = 5.6, 2.5 Hz, 1H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.7, 145.3, 126.2, 123.8, 51.7, 51.4.

***trans*-Stilbeneoxide (2n)**:[1e] colorless solid; mp 66-68 ℃; 85 mg, 80 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (q, *J* = 6.2, 5.7 Hz, 10H), 3.89 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.1, 128.6, 128.3, 125.5, 62.9.

***cis*-Stilbeneoxide (2o)**:[1e] colorless solid; mp 66-69 ℃; 88 mg, 80 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 10H), 4.39 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 134.4, 127.8, 127.5, 59.8.

2,2,3,3-tetraphenyloxirane (2p): colorless solid; mp 402-404 ℃; 75 %, 159 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 8H), 7.30 (d, *J* = 8.2 Hz, 8H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.7, 132.2, 128.5, 117.8, 112.6, 73.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{30}H_{16}N_4O$ 449.1397; Found: 449.1375.

r*ac*-2-Oxiraneacetic Acid Phenylmethyl Ester (2q):[20] colorless oil; 82 mg, 92 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.0 Hz, 5H), 5.24 – 5.15 (m, 2H), 3.45 (dd, *J* = 4.2, 2.4 Hz, 1H), 2.97 – 2.89 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 135.0, 128.6, 128.6, 128.4, 67.2, 47.3, 46.3.

Phenyl(3-phenyl-2-oxiranyl)methanone (2r):[8] colorless solid; mp 86-88℃; 71 %, 90 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.63 – 7.57 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.37 (tq, *J* = 6.6, 3.6, 3.0 Hz, 5H), 4.29 (d, *J* = 1.9 Hz, 1H), 4.06 (d, *J* = 1.9 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.1, 135.5, 135.5, 134.0, 129.0, 128.9, 128.8, 128.3, 125.8, 61.0, 59.4.

1-Phenyl-2-methoxycarbonyloxirane (2s):[1e] colorless oil; 82 mg, 92 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.3, 2.0 Hz, 3H), 7.29 – 7.24 (m, 2H), 4.08 (d, *J* = 1.8 Hz, 1H), 3.81 – 3.78 (m, 3H), 3.50 (d, *J* = 1.9 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.6, 134.9, 129.0, 128.6, 125.8, 57.9, 56.6, 52.5.

Diethyl 2,3-oxiranedicarboxylate (2t):[13c] colorless oil; 93 mg, 94 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (ddq, *J* = 7.2, 5.4, 3.0 Hz, 4H), 3.60 (q, *J* = 3.0 Hz, 2H), 1.18 (tdd, *J* = 6.9, 4.2, 2.5 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 61.8, 52.4, 13.9.

3-hydroxy-9a,11b-dimethyltetradecahydrocyclopenta[1,2] phenanthro[8a,9-b]oxiren-9(2H)-one (2u):[21] colorless solid; mp 172-174 ℃; 89 %, 179 mg; mixture of diastereomers (α:β=60:40); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (m, J = 10.9, 0.6H), δ 3.6 (m, *J* = 4.7, 0.4H), 3.04 (d, 0.4H), 2.87 (d, 0.6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 220.9, 220.69, 220.66, 69.0, 68.2, 65.8, 63.3, 63.1, 58.7, 51.8, 51.4, 51.1, 47.6, 47.4, 42.8, 42.0, 39.6, 37.2, 35.7, 35.6, 35.0, 35.0, 32.4, 31.4, 31.4, 31.0, 30.9, 30.8, 29.4, 29.4, 27.6, 21.7, 21.6, 21.2, 19.9, 17.0, 15.9, 13.5, 13.4.

9a,11b-dimethyl-9-(6-methylheptan-2-yl) hexadecahydrocyclopenta[1,2]phenanthro[8a,9-b]oxiren-3-ol (2v):[2c] colorless solid; mp 142-144 ℃; 91 %, 90 mg; mixture of diastereomers (α:β=60:40); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (m, *J* = 10.5, 0.6H), 3.66 (m, *J* = 5.3, 0.6H), 2.87 (d, *J* = 4.3 Hz, 0.4H). 2.87 (d, *J* = 4.3 Hz, 0.6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 69.3, 68.6, 65.7, 63.7, 62.9, 59.3, 56.8, 56.2, 56.2, 55.8, 51.3, 42.5, 42.3, 42.3, 42.2, 39.8, 39.8, 39.5, 39.4, 37.2, 36.1, 35.7, 34.8, 32.6, 32.4, 31.0, 31.0, 29.9, 29.7, 28.8, 28.1, 28.04, 27.96, 24.2, 24.0, 23.8, 23.8, 22.8, 22.5, 22.0, 20.6, 18.6, 17.0, 15.9, 11.8, 11.7.

5-(3,3-dimethyloxiran-2-yl)-3-methylpentanal (2w):[22] colorless oil; 71.4 mg, 84 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 2.3 Hz, 1H), 2.67 – 2.63 (m, 1H), 2.41 – 2.34 (m, 1H), 2.22 (dddd, *J* = 16.2, 8.0, 3.8, 2.4 Hz, 1H), 2.07 (p, J = 6.7 Hz, 1H), 1.49 (ddd, *J* = 11.0, 7.1, 2.8 Hz, 2H), 1.45 – 1.35 (m, 2H), 1.25 (s, 3H), 1.21 (d, *J* = 1.5 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$) δ 202.6, 202.5, 64.2, 64.2, 58.3, 58.2, 50.9, 50.8, 33.5, 27.8, 26.3, 26.3, 24.8, 19.8, 19.7, 18.7, 18.6.

pent-4-en-1-ylsulfonyl)benzene (2x):[23] colorless oil; 97 mg, 87 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.62 (ddt, *J* = 13.3, 9.8, 6.7 Hz, 1H), 4.98 – 4.91 (m, 2H), 3.05 – 2.99 (m, 2H), 2.40 (s, 3H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.79 – 1.71 (m, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 144.6, 136.3, 136.1, 129.9, 128.0, 116.4, 55.5, 32.0, 21.8, 21.6.

N, N-dimethylaniline oxide (2y):[25] yellow solid; mp 148-150 ℃; 61 mg, 89 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (td, *J* = 7.8, 2.2 Hz, 2H), 7.10 – 6.96 (m, 3H), 3.21 (dd, *J* = 8.0, 2.3 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.9, 128.8, 128.5, 119.6, 62.8.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

^{1}H NMR and ^{13}C NMR spectra for all the products.

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ACKNOWLEDGMENTS

We are grateful for the financial support from the National Natural Science Foundation of China (21362022).

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