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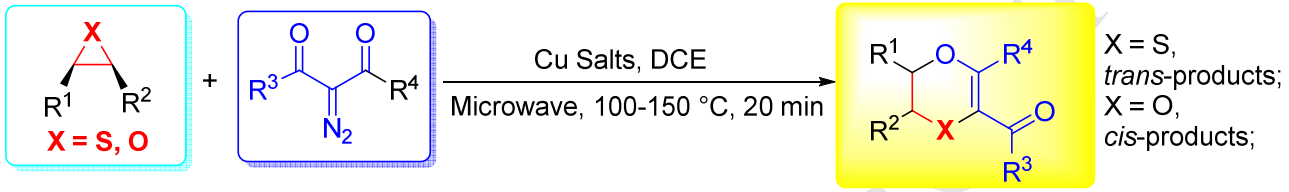

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Microwave-assisted copper-catalyzed stereoselective ring expansion of three-membered heterocycles with α-diazo-β-dicarbonyl compounds

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ABSTRACT

Microwave-assisted copper-catalyzed ring expansions of three-membered heterocycles with α-diazo-β-dicarbonyl compounds were investigated. Thiiranes generated 3-acyl-5,6-dihydro-1,4-oxathiines in the presence of copper sulfate and *trans*-3-acyl-5,6-dihydro-1,4-oxathiines as stereospecific products for 1,2-disubstituted *cis*-thiiranes through an intramolecular S_N2 process. Oxiranes gave rise to 2-acyl-5,6-dihydro-1,4-dioxines under the catalysis of copper hexafluoroacetylacetonate and *cis*-3-acyl-5,6-dihydro-1,4-dioxines as stereospecific products for 1,2-disubstituted *cis*-oxiranes via an intimate ion-pair mechanism. The current method provides a direct and simple strategy in efficient preparation of 3-acyl-5,6-dihydro-1,4-oxathiines and 2-acyl-5,6-dihydro-1,4-dioxines, important agents in medicinal and agricultural chemistry, from readily available thiiranes and oxiranes, respectively.

1. Introduction

5,6-Dihydro-1,4-oxathiines and 1,4-dioxines are important and indispensable structural units in medicinal and agricultural chemistry.[1-3] 5,6-Dihydro-1,4-oxathiine-3-carboxanilides are commercial fungicides and active anti-HIV agents.[1-3] *N*-Aryl-3-methyl-5,6-dihydro-1,4-dioxine-2-carboxamides are the oxygen analogues of effective fungicide 5,6-dihydro-2-methyl-*N*-phenyl-1,4-oxathiine-3-carboxamide (Vitavax) and have the fungicidal activity against bean rust, a major disease of cereal crops.[4] Meanwhile, 2-[(4-methylphenyl)amino]-2-oxoethyl 5,6-dihydro-1,4-dioxine-2-carboxylate is a potential cruzain inhibitor to treat American trypanosomiasis.[5] Thus, such compounds are a kind of valuable fungicide candidates.

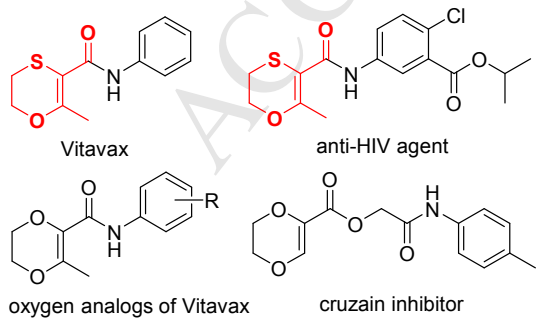

Figure 1. Biologically active molecules containing 1,4-oxathiines and 1,4-dioxines

3-Acyl-5,6-dihydro-1,4-oxathiines have been synthesized mainly through the displacement of ethyl 2-chloro-3-oxobutanoate with 2-mercaptoethanol and subsequent cyclization.[6] This is a general method for the preparation of Vitavax. Alternative method is the cyclization of (*E*/*Z*)-2-chloro-2-(2-hydroxyethylthio)butenamides under the treatment of LiHMDS to afford 3-acyl-5,6-dihydro-1,4-oxathiines in low yields.[7] Hetero-Diels-Alder cycloadditions of 2,4-dioxopentane-3-thione and electron-rich enolic ethers have also been applied in the synthesis of 3-acyl-5,6-dihydro-1,4-oxathiines.[8]

Previously reported synthesis of 5,6-dihydro-1,4-dioxine-2-carboxylic acid derivatives generally required multi-step reactions or under harsh conditions. For example, Dekeyser and his coworkers prepared 5,6-dihydro-1,4-dioxine-2-carboxylic acid derivatives from glycol and 3-chloroprop-1-yne through five steps in 1998.[4] Two years later, Hahn and his coworkers developed a method for their synthesis from 3-ethoxy-1,1,1-trifluoropropan-2-one via six steps.[9] Moreover, Blanchot and his coworkers realized a two-step synthetic route, but they used BuLi and organotin reagents in their reactions.[10] The aforementioned methods hardly realized highly efficient preparation of 5,6-dihydro-1,4-dioxine-2-carboxylic acid derivatives in high yields. Recently, Achard and his coworkers reported a direct preparation of 5,6-dihydro-1,4-dioxine-2-carboxylic acid derivatives from epoxides and diazo compounds under the catalysis of $[CpRu(CH_3CN)_3][BArF]$.[11] But the Ru catalyst is expensive and the diazo substrates are limited to diazoketoesters only. In our

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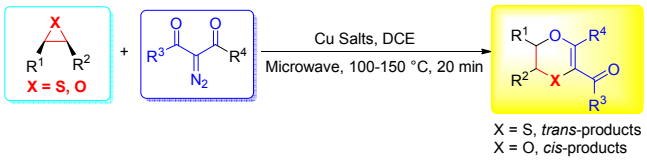
continuing interest in the synthesis of heterocycles through ring expansion of small heterocycles,[12] we realized inexpensive copper-catalyzed synthesis of 3-acyl-5,6-dihydro-1,4-oxathiines and 2-acyl-5,6-dihydro-1,4-dioxines from thiiranes and oxiranes, respectively, with α-diazo-β-dicarbonyl compounds, including both diazoketoesters and diazodiketones. 1,2-Disubstituted *cis*-thiiranes and oxiranes show completely opposite stereoselectivity in the ring expansions (Scheme 1). Herein, we present our results.



Scheme 1. Synthesis of 5,6-dihydro-1,4-oxathiines and 1,4-dioxines through the ring expansion of thiiranes and oxiranes with α-diazo-β-dicarbonyl compounds.

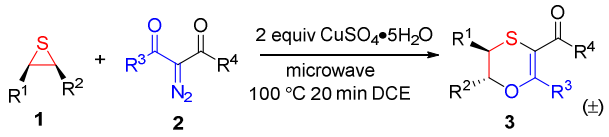
2. Results and Discussion

2.1. Synthesis of 3-acyl-5,6-dihydro-1,4-oxathiines through the ring expansion of thiiranes and α-diazo-β-dicarbonyl compounds

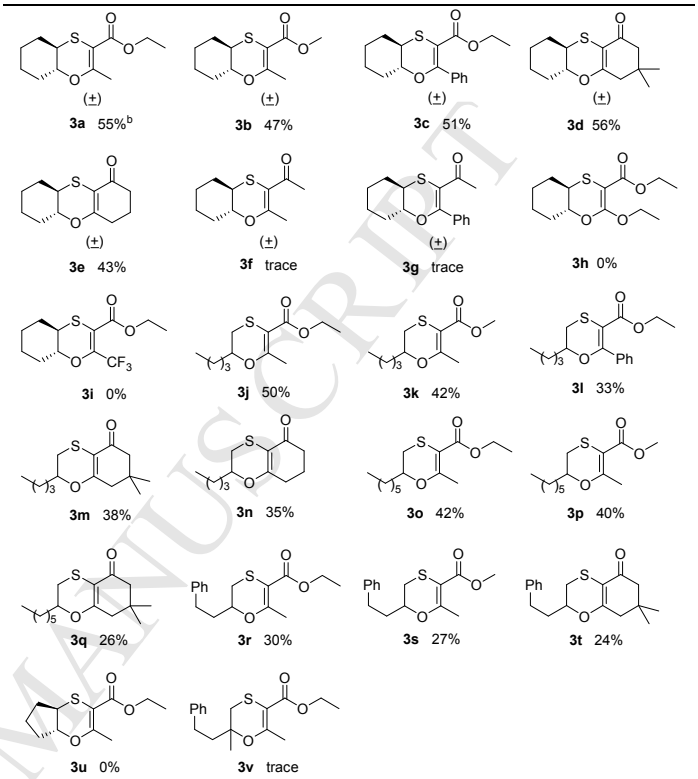
Initially, 7-thiabicyclo[4.1.0]heptane (**1a**) and ethyl 2-diazo-3-oxobutanoate (**2a**) were employed as the model substrates to optimize reaction conditions. Both $Rh_2(OAc)_4$, $Pd(OAc)_2$, $Zn(OAc)_2$, $Cu(hfacac)_2 \cdot xH_2O$, $Cu(CH_3CN)_4PF_6$, $(CF_3SO_3)_2Cu$, and $CuSO_4 \cdot 5H_2O$ salt catalysts and $BF_3 \cdot OEt$, $FeCl_3$, and $AlCl_3$ Lewis acid catalysts were attempted. Different solvents 1,2-dichloroethane (DCE), toluene, dioxane, and acetonitrile were screened. The optimum reaction conditions were finally identified as follows: **1a**:**2a** = 2:1 in the presence of 2 equiv. of $CuSO_4 \cdot 5H_2O$ in DCE as solvent at 100 °C for 20 min microwave irradiation.[13]

Under the optimized reaction conditions, the reaction scope was evaluated (Table 1). The reactions of 7-thiabicyclo[4.1.0]heptane (cyclohexene sulfide) (**1a**) and different α-diazo-β-dicarbonyl compounds **2** indicated that diazoketoesters (alkyl 2-diazo-3-oxobutanoates and 2-diazo-3-oxo-3-phenylpropanoate) and cyclic diazodiketones (2-diazocyclohexane-1,3-diones) generated the corresponding desired products **3a-e** in *trans*-configuration in moderate yields. Their stereostructure was determined by the single crystal X-ray diffraction analysis of the representative compound **3c**.[13] However, linear diazodiketones (3-diazo-2,4-pentanedione and 2-diazo-1-phenyl-1,3-butanedione), diethyl 2-diazomalonate, and electron-deficient ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate failed in the reaction. Products **3f,g** were obtained in trace amounts and products **3h,i** were not observed. Capozzi and coworkers previously synthesized *cis*-1-(3-methyl-4a,7,8,8a-tetrahydro-6*H*-pyrano[2,3-*b*][1,4]oxathiine-2-yl)ethan-1-one by the hetero-Diels-Alder reaction of 2,4-dioxopentane-3-thione and dihydropyrane.[8] Currently, we synthesized ethyl *trans*-3-acyl-4a,5,6,7,8,8a-hexahydrobenzo[*b*][1,4]oxathiines. Both diazoketoesters and cyclic diazodiketones were reacted with monosubstituted thiiranes to afford the corresponding desired products **3j-t** in low to moderate yields. However, no reaction occurred for 6-thiabicyclo[3.1.0]hexane (cyclopentene sulfide) and ethyl 2-diazo-3-oxobutanoate. For 1,1-disubstituted 1-methyl-1-(2-phenylethyl)thiirane, only a trace amount of product **3v** was obtained possibly due to the steric hindrance of 1,1-disubstituted thiirane.

Table 1. Synthesis of 3-acyl-5,6-dihydro-1,4-oxathiines **3** from thiiranes **1** and α-diazo-β-dicarbonyl compounds **2**[a]

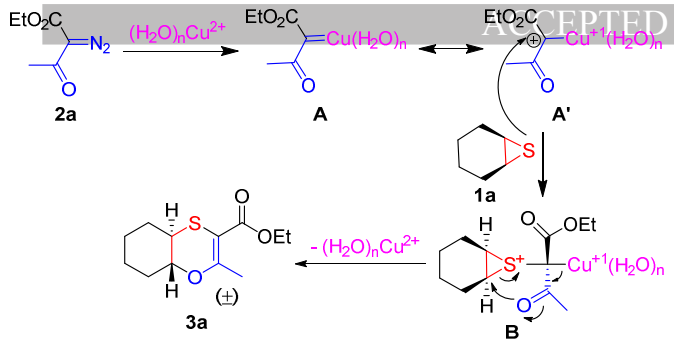


1 **2** **3**



[a] Reaction conditions: Diazo compounds **2** (0.3 mmol) and thiiranes **1** (0.6 mmol) were added in DCE (1.0 mL) in a 10 mL microwave tube, then $CuSO_4 \cdot 5H_2O$ (0.6 mmol) was added, and the reaction mixture was stirred at 100 °C for 20 mins under microwave irradiation in a sealed vessel. All yields are isolated yields.

On the basis of the stereostructure of products **3a-e**, we proposed the following mechanism for reactions of thiiranes **1** and α-diazo-β-dicarbonyl compounds **2**. The reaction of cyclic thiirane **1a** and diazo compound **2a** is selected as an example to present the mechanism (Scheme 2). Diazo compound **2a** first reacts with $CuSO_4 \cdot 5H_2O$ to generate a metal carbene intermediate A by loss of nitrogen. Thiirane **1a** nucleophilically attacks the intermediate **A** and further forms a metal sulfonium ylide intermediate **B**. Accompanied by the departure of the copper complex, the original ketonic carbonyl isomerizes into an enolate, which nucleophilically attacks the thiirane from the backside of the C-S bond, leading to the cleavage of the C-S bond to generate the ring expansion product **3a**. During the ring-opening reaction, the configuration of the attacked carbon is inverted as the enolate anion attacks from the back of the three-membered ring, resulting in the formation of *trans*-product **3a** from *cis*-thiirane **1a**. For monosubstituted thiiranes, since the thiirane ring in the intermediates **B** is partially positively charged, the enolate anion is more nucleophilic to attack the carbon atom with more substituents,[14,15] and 6-substituted products **3j-3t** are generated.



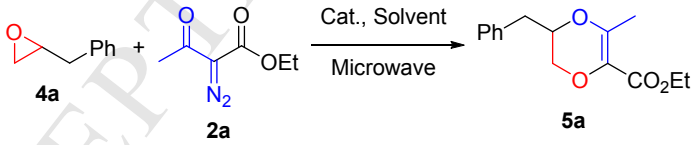
Scheme 2. Mechanistic rationale on the stereospecific ring expansion of 7-thiabicyclo[4.1.0]heptane (**1a**) and different α-diazo-β-dicarbonyl compounds **2** in the presence of copper sulfate pentahydrate.

2.2. Synthesis of 2-acyl-5,6-dihydro-1,4-dioxines through the ring expansion of oxiranes and α-diazo-β-dicarbonyl compounds

After success in the synthesis of 3-acyl-5,6-dihydro-1,4-oxathiines **3** from thiiranes **1** with α-diazo-β-dicarbonyl compounds **2** through the ring expansion reactions,[13] we turned our attention to the synthesis of 2-acyl-5,6-dihydro-1,4-dioxines from oxiranes and α-diazo-β-dicarbonyl compounds. We first chose the reaction of 2-benzyloxirane (**4a**) and ethyl 2-diazo-3-oxobutanoate (**2a**) as a model reaction to optimize the reaction conditions. Because many reactions between small heterocyclic rings and diazo compounds share the feature of excessive diazo compounds,[16,17] we decided to use 1.5 equiv of diazo compound **2a**. We started our optimization by simply mixing the two reactants and a metal catalyst together at room temperature, but after 3 h, no reaction occurred. Then we mixed both the reagents and different metal catalysts together in various refluxing solvents, but we did not get any new products. After all these attempts, we found that diazo compound **2a** decomposed easily and fast, having no opportunity to react with epoxide **4a**. Thus, we attempted to use a syringe pump to inject **2a** dropwise into a solution of **4a** and a catalyst. Gratifyingly, we isolated the desired product ethyl 3-methyl-5-phenylmethyl-5,6-dihydro-1,4-dioxine-2-carboxylate (**5a**) in a low yield. After a series of optimizations, we still did not get a satisfied yield (detailed results not shown here), so we tried to use microwave to assist our reaction because microwave can selectively heat polar reactants.[18]

With the assistance of microwave irradiation, we screened various inexpensive copper catalysts, such as $Cu(acac)_2$, $Cu(hfacac)_2 \cdot xH_2O$, $CuSO_4 \cdot 5H_2O$, and $Cu(OTf)_2$ (Table 2, entries 1–10). $Cu(hfacac)_2 \cdot xH_2O$ was discovered as the best catalyst (Table 2, entry 7). The encouraging results prompted us to optimize the reaction conditions further. The yield also varied with temperature, reaction time, and solvents. The yield was improved when the reaction temperature was raised from 100 °C to 150 °C (Table 2, entries 2, 4, 6, and 7). Shortening the reaction time from 60 min to 40 min, 30 min, or 20 min had a positive influence on the yield of **3a** (Table 2, entries 7, 11, 12 and 13). However, further shortening time to 15 min to 10 min caused decrease of the yield due to unfinished reaction with lots of reagents remained (Table 2, entries 14 and 15). But the yield decreased for the 20 min. reaction when the temperature was further increased to 160 °C (Table 2, entry 16). For solvent optimization, 1,2-dichloroethane (DCE), toluene, and dichloromethane (DCM) were screened (Table 2, entries 7, 8, and 17). Toluene caused a mussy system after reaction and dichloromethane could not reach the best reaction temperature due to its low boiling point. Adjusting the equivalent of oxirane **4a** and diazo compound **2a** did not produce a good effect to the yield of **5a** (Table 2, entries 18 and 19). Finally, after all these optimizations, we selected to use 1.5 equiv. of 2-diazo-3-oxobutanoate (**2a**) to react with one equivalent of 2-benzyloxirane (**4a**) under the catalysis of 10 mol% $Cu(hfacac)_2 \cdot xH_2O$ at 150 °C in DCE with the assistance of microwave irradiation for 20 min. (Table 2, entry 13).

Table 2. Optimization for the reaction of 2-benzyloxirane (**4a**) and ethyl 2-diazo-3-oxobutanoate (**2a**) under microwave irradiation [a]



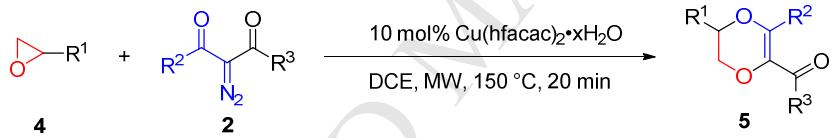
Entry	Catalyst (10 mol%)	Time/Min	Solvent	Temperature/°C	Yield/%[b]
1	$Cu(acac)_2$	60	DCE	100	10
2	$Cu(hfacac)_2 \cdot xH_2O$	60	DCE	100	8
3	$Cu(acac)_2$	60	DCE	120	8
4	$Cu(hfacac)_2 \cdot xH_2O$	60	DCE	120	20
5	$Cu(acac)_2$	60	DCE	135	11
6	$Cu(hfacac)_2 \cdot xH_2O$	60	DCE	130	21
7	$Cu(hfacac)_2 \cdot xH_2O$	60	DCE	150	26
8	$Cu(hfacac)_2 \cdot xH_2O$	60	Toluene	150	8
9	$CuSO_4 \cdot 5H_2O$	60	DCE	150	8
10	$Cu(OTf)_2$	60	DCE	150	13
11	$Cu(hfacac)_2 \cdot xH_2O$	40	DCE	150	24
12	$Cu(hfacac)_2 \cdot xH_2O$	30	DCE	150	32

13	$Cu(hfacac)_2 \cdot xH_2O$	20	DCE	150	49 (45 [d])
14	$Cu(hfacac)_2 \cdot xH_2O$	15	DCE	150	31
15	$Cu(hfacac)_2 \cdot xH_2O$	10	DCE	150	28
16	$Cu(hfacac)_2 \cdot xH_2O$	20	DCE	160	27
17	$Cu(hfacac)_2 \cdot xH_2O$	20	DCM	70	10
18[C]	$Cu(hfacac)_2 \cdot xH_2O$	40	DCE	150	35
19[C]	$Cu(hfacac)_2 \cdot xH_2O$	20	DCE	150	23

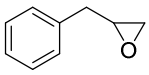
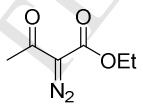
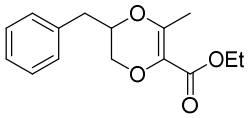
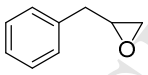
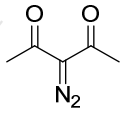
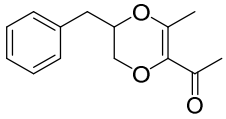
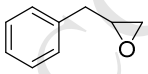
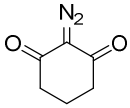
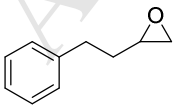
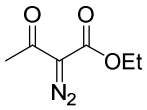
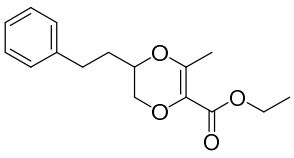
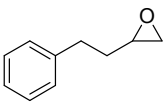
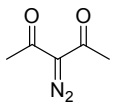
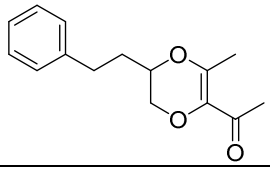
[a]Without special notes, reaction conditions: diazo compound **2a** (1.5 equiv). [b]The yield is determined by ^{1}H NMR with 4-iodonitrobenzene as an internal standard. [c]3 equiv of **2a**. [d]Isolated yield.

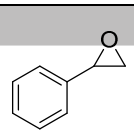
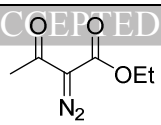
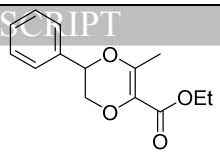
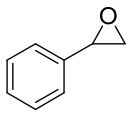
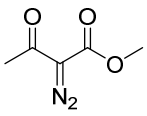
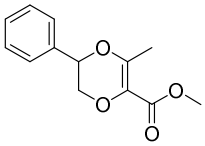
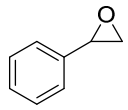
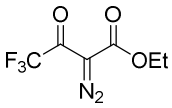
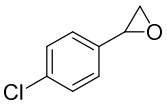
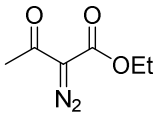
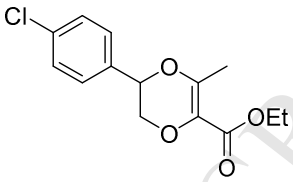
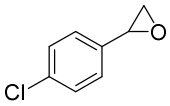
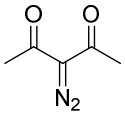
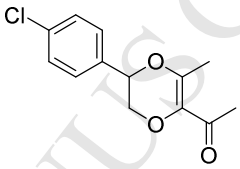
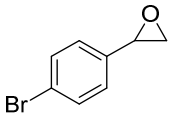
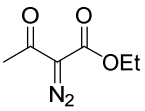
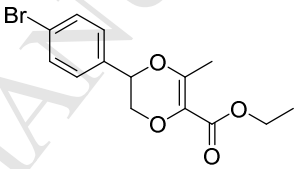
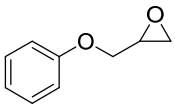
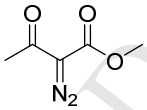
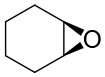
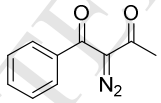
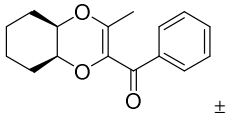
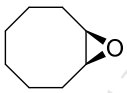
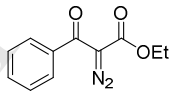
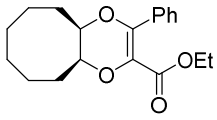
With the optimal conditions for the preparation of ethyl 5-benzyl-3-methyl-5,6-dihydro-1,4-dioxine-2-carboxylate (**3a**), we evaluated the scopes of oxiranes **4** and diazo compounds **2**. The results are present in Table 3. The reactivity between varies of oxiranes **4** and diazo compounds **2** suggested that both 2-alkyl and 2-aryloxiranes **4** can react with diazoketoesters (**2a, d, g**), except for ones with strong electron-withdrawing groups (**2e**), and linear diazodiketones (**2b,f**), affording the corresponding 5,6-dihydro-1,4-dioxine-2-carboxylates **5a, d, f, g, i, k, n** and 5,6-dihydro-1,4-dioxin-2-yl ketones **5b, e, j, m**, respectively. Comparison with the reactions of different oxiranes **4** with ethyl 2-diazo-3-oxobutanoate (**2a**) and 3-diazopentane-2,4-dione (**2b**) indicated that the more electron-withdrawing the diazo compounds are, the lower yields obtained (Table 3, entries 1, 2, 4, 5, 9, and 10). The reaction of 2-phenyloxirane (**4c**) and ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate (**2e**) further supports this conclusion (Table 3, entry 8). However, 2-(phenoxymethyl)oxirane (**1f**) did not produce the corresponding product **5l** (Table 3, entry 12). We supposed that it was because there were two different oxygen atoms in oxirane **1f** so that there might exist a competitive coordination with copper in the catalyst between them, resulting in no desired product **5l** generated in the reaction. Furthermore, a cyclic diazodiketone compound 2-diazocyclohexane-1,3-dione (**2c**) was attempted, but it failed to undergo the reaction (Table 3, entry 3).

Table 3. Synthesis of 2-acyl-5,6-dihydro-1,4-dioxines **5** from oxiranes **4** and α-diazo-β-dicarbonyl compounds **2**



4 **2** **5**

Entry	Oxirane	**4**	Diazo compound	**2**	Product	**5**	Isolated yield/%
1		**4a**		**2a**		**5a**	45
2		**4a**		**2b**		**5b**	31
3		**4a**		**2c**	-	**5c**	NR
4		**4b**		**2a**		**5d**	42
5		**4b**		**2b**		**5e**	24

6		**4c**		**2a**		**5f**	40
7		**4c**		**2d**		**5g**	18
8		**4c**		**2e**	-	**5h**	NR
9		**4d**		**2a**		**5i**	27
10		**4d**		**2b**		**5j**	20
11		**4e**		**2a**		**5k**	27
12		**4f**		**2d**	-	**5l**	NR
13		**4g**		**2f**	 ±	**5m**	10
14		**4h**		**2g**	 ±	**5n**	33

To identify the regioselectivity and structures of products **5a,b,d-g,i-k** in the reactions, we performed 2D HMBC NMR spectrum of the representative product **5i**, of which the structure is **5iA** or **5iB** (Figure 2). The spectrum showed that a weak interaction between the CH_3 group (2.26 ppm) and the benzylic carbon (75.05 ppm) and a ^3J coupling between the methylene group (4.20 ppm) in 1,4-dioxine and C(sp^2) attached to the carboxylate group, indicating that product **5i** should possess the structure of **5iA**. The results suggest that products **5** were generated through the enolate attacking on the more substituted carbon atom of oxiranes **4** because the oxirane ring possesses positive charge, similar to protonated or Lewis acid-coordinated oxiranes, after the oxygen in the oxirane ring nucleophilically attacks the metallocarbenes generated from diazo compounds **2** and copper catalyst (*vide post* Scheme 3).

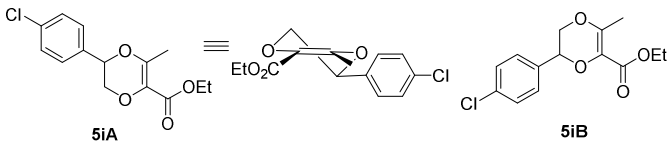
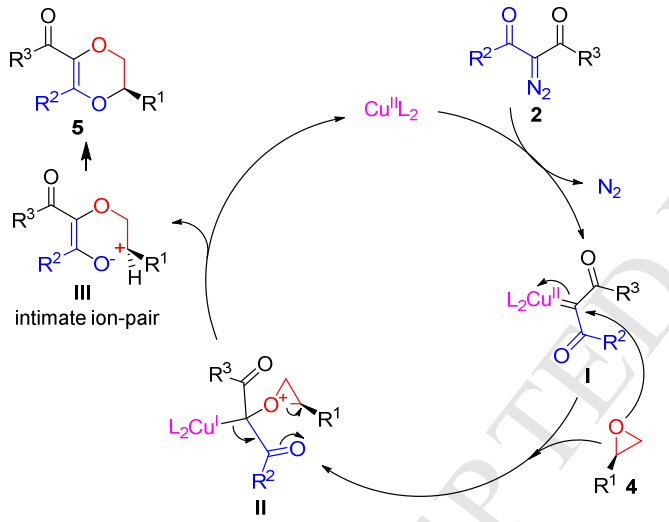


Figure 2. Two possible structures of product **5i.**

For 1,2-disubstituted *cis*-oxiranes, 7-oxabicyclo[4.1.0]heptane (cyclohexene oxide) (**4g**) afforded the corresponding *cis*-product **5m**, of which *cis*-configuration was determined from the coupling constant (J = 2.9 Hz) of the protons on the carbon atoms next to the oxygen atoms (positions 4a and 8a in **5m**) by comparison with previously reported data (Table 3, entry 13).[11,19] To further verify the stereosturcture of product **5m**, the reaction of 9-oxabicyclo[6.1.0]nonane (cyclooctene oxide) (**4h**) and ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2g**) was performed under the catalysis of $Cu(hfacac)_2 \cdot xH_2O$, affording the desired product **5n** (Table 3,

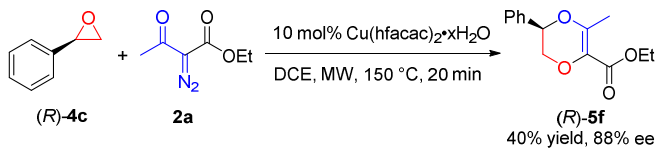
entry 14). Product **5n** shows the identical ^{1}H NMR data to the previously reported *cis*-product **5n** obtained in the same reaction under the catalysis of [CpRu(CH_3CN)$_3$][BArF].[11]

The results in the ring expansion of 1,2-disubstituted *cis*-oxiranes **4** are obviously different from those in the ring expansion of thiiranes **1**.[13] For the reactions of thiiranes **1**, the ring expansion undergoes an intramolecularly bimolecular substitution (S_N2), generating *trans*-products **3** from 1,2-disubstituted *cis*-thiiranes **1**. However, in the current reactions, 1,2-disubstituted *cis*-oxiranes **4** afforded the corresponding *cis*-products **5**. The results suggests that the reaction should undergo an intimate ion-pair mechanism rather than the S_N2 mechanism. To explain the ring expansion reaction between oxiranes **4** and diazo compounds **2**, we proposed the mechanism shown in Scheme 3. First of all, diazo compounds **2** coordinate with Cu(hfacac)$_2$·xH_2O and discharge a molecule of nitrogen, generating metallocarbenes **I**. Then, oxiranes **4** attack the electron-deficient metallocarbenes **I** to produce metal oxonium ylide intermediates **II**. The intermediates **II** undergo the cleavage of the more substituted C-O bond of the oxirane ring because the substituents can stabilize the positive charged carbocations and simultaneous release of the copper catalyst to form enolate anions. That is, intimate ion-pairs **III** are generated and further combine the enolates and carbocations to afford six-membered ring products **5** through the intimate ion-pair process.



Scheme 3. Mechanistic rationale on the stereospecific ring expansion of oxiranes **5** and α-diazo-β-dicarbonyl compounds **2** under the catalysis of Cu(hfacac)$_2$·xH_2O.

To further verify the intimate ion-pair process, we tested the reaction of enantiopure substrate (*R*)-phenyloxirane [(*R*)-**4c**] and ethyl 2-diazo-3-oxobutanoate (**2a**) and obtained the corresponding product (*R*)-**5f** with 88% e.e., supporting the intimate ion-pair mechanism (Scheme 4). On the basis of *cis*-selectivity in the reaction of cyclohexene oxide (**4g**) and cyclooctene oxide (**4h**) and the intimate ion-pair mechanism, the optical product **3f** can be assumed as the R configuration.



Scheme 4. Ring expansion with enantiopure epoxide (*R*)-**4c**.

When thiirane **1a** was used as starting material under the conditions for oxiranes (Cu(hfacac)$_2$·xH_2O, 150 °C, DCE), the thiirane **1a** decomposed completely without observation of the corresponding *cis*-oxathiine. Even the reaction was conducted at 100 °C. No desired product was observed as well, but some thiirane **1a** remained.

Finally, we hoped to extend the strategy into the reactions of aziridines and α-diazo-β-dicarbonyl compounds **2**, attempting to synthesize 3-acyl-5,6-dihydro-1,4-oxazines through similar ring expansion reactions. However, after many attempts in different solvents under the catalysis of various transition metal catalysts, applied in the reactions of thiiranes and oxiranes, no desired product was observed.

3. Conclusion

In conclusion, we successfully provided a convenient and economic synthetic preparation of important 3-acyl-5,6-dihydro-1,4-oxathiine and 2-acyl-5,6-dihydro-1,4-dioxine derivatives from readily available thiiranes and oxiranes with α-diazo-β-dicarbonyl compounds under the catalysis of commercial available and inexpensive copper catalysts. The assistance of microwave irradiation shortens the reaction time extremely to only 20 min. In addition, the substrate scope expanded to not only diazoketoesters, but also diazodiketones. The two ring expansion reactions showed completely different stereoselectivities for 1,2-disubstituted *cis*-three-membered heterocycles because thiiranes underwent the bimolecular nucleophilic substitution mechanism, while oxiranes took place the intimate ion-pair process. However, aziridines produced complex mixtures under similar conditions. Although the yields are from low to moderate, the current methods provide a direct and simple strategy in efficient preparation of 3-acyl-5,6-dihydro-1,4-oxathiines and 2-acyl-5,6-dihydro-1,4-dioxines.

4. Experimental Section

4.1 General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. DCE was refluxed over CaH_2 and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical. Petroleum ether (PE) used for column chromatography is 60–90 °C fraction, and the removal of residue solvent was accomplished under rotovap. Reactions were monitored by thin-layer chromatography (TLC) on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light, as well as other TLC stains (10% phosphomolybdic acid in ethanol; 1% potassium permanganate in water; 10 g of iodine absorbed on 30 g of silica gel). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard, and the chemical shifts (δ) are reported in parts per million (ppm). All coupling constants (J) in ^{1}HNMR are absolute values given in hertz (Hz) with peaks labeled as single (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), and multiplet (m). The IR spectra (KBr pellets, v [cm^{-1}]) were taken on a Nicolet 5700 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. Specific rotation was determined on an Anton Paar MCP200 polarimeter. All microwave reactions were conducted in CEM Discover SP micromave system equipped with an infrared temperature detector. The enantiomeric

excess was determined by chiral HPLC analysis using an Agilent 1260 LC instrument with Daicel Chiralpak AD-H column with a mixture of hexane and isopropanol (90:10, *v/v*) as eluent at a flow rate of 1.0 mL/min. at 254 nm.

All analytic data of thiiranes **1** and 3-acyl-5,6-dihydro-1,4-oxatiines **3** were reported previously in our previous communications. Analytic data of oxiranes **4** and diazo compounds **2** are provided in electronic supporting information.

4.2 General procedure for the synthesis of 2-acyl-5,6-dihydro-1,4-dioxines 5

In a 10 mL reaction tube, oxirane **4** (0.2 mmol), diazo compound **2** (0.3 mmol) and $Cu(hfacac)_2 \cdot xH_2O$ (9.54 mg, 0.02 mmol) were dissolved in 2 mL of dries DCE. The reaction mixture was stirred and irridated in a microwave reactor at 150 °C for 20 min. After the solution was concentrated under reduced pressure, the resulting residue was purified by silica gel column chromatography with a mixture of petroleum ether/EtOAc (15:1 to 50:1, *v/v*) as eluent to give pure product **5**.

4.2.1 Ethyl 5-benzyl-3-methyl-5,6-dihydro-1,4-dioxine-2-carboxylate (5a)

Yellow oil. Yield, 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.20 (m, 5H, ArH), 4.30–4.22 (m, 3H, CH_2 & CH), 4.05 (dd, *J* = 11.0, 2.4 Hz, 1H in CH_2), 3.71 (dd, *J* = 11.0, 6.3 Hz, 1H in CH_2), 3.00 (dd, *J* = 14.0, 6.6 Hz, 1H in CH_2), 2.84 (dd, *J* = 14.0, 6.9 Hz, 1H in CH_2), 2.24 (s, 3H, CH_3), 1.33 (t, *J* = 6.9 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 147.0, 136.2, 129.3, 128.6, 126.8, 124.8, 74.7, 66.0, 60.5, 37.2, 17.8, 14.4. IR (KBr) 1711, 1635 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{15}H_{18}NaO_4^+$ $[M+Na]^+$: 285.1103; found: 285.1102.

4.2.2 1-(5-Benzyl-3-methyl-5,6-dihydro-1,4-dioxin-2-yl)ethan-1-one (5b)

Yellow oil. Yield, 30.4%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.19 (m, 5H, ArH), 4.24 (dddd, *J* = 6.9, 6.7, 2.2, 2.2 Hz, 1H, CH), 4.02 (dd, *J* = 11.1, 2.3 Hz, 1H in CH_2), 3.67 (dd, *J* = 11.1, 6.4 Hz, 1H in CH_2), 3.02 (dd, *J* = 13.9, 6.3 Hz, 1H in CH_2), 2.82 (dd, *J* = 13.9, 7.3 Hz, 1H in CH_2), 2.22 (s, 3H, CH_3), 2.21 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 145.6, 136.2, 132.5, 129.3, 128.6, 126.9, 74.8, 65.5, 37.3, 27.5, 17.7. IR (KBr) 1735 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{14}H_{17}O_3^+$$[M+H]^+$: 233.1178; found: 233.1189.

4.2.3 Ethyl 3-methyl-5-phenethyl-5,6-dihydro-1,4-dioxine-2-carboxylate (5d)

Yellow oil. Yield, 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.16 (m, 5H, ArH), 4.30–4.21 (m, 2H, CH_2), 4.08 (dd, *J* = 11.0, 2.3 Hz, 1H in CH_2), 4.04–3.97 (m, 1H, CH), 3.67 (dd, *J* = 11.0, 6.9 Hz, 1H in CH_2), 2.88–2.69 (m, 1H in CH_2), 2.25 (s, 3H, CH_3), 1.96 (dddd, *J* = 14.2, 8.6, 8.6, 5.8 Hz, 1H, in CH_2), 1.82 (dddd, *J* = 14.0, 9.1, 7.3, 5.0 Hz, 1H in CH_2), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 147.1, 140.8, 128.5, 128.4, 126.1, 124.6, 73.2, 66.8, 60.5, 32.2, 31.0, 17.8, 14.4. IR (KBr) 1731, 1682 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{16}H_{21}O_4^+$$[M+H]^+$: 277.1440; found: 277.1434.

4.2.4 1-(3-Methyl-5-phenethyl-5,6-dihydro-1,4-dioxin-2-yl)ethan-1-one (5e)

Yellow oil. Yield, 24%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.03 (m, 5H, ArH), 3.98 (dd, *J* = 10.9, 2.4 Hz, 1H in CH_2), 3.92 (ddt, *J* = 8.7, 4.8, 2.3 Hz, 1H, CH), 3.58 (dd, *J* = 10.9, 6.8 Hz, 1H in CH_2), 2.82–2.63 (m, 2H, CH_2), 2.16 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.88 (dddd, *J* = 14.2, 8.6, 8.6, 5.7 Hz, 1H, CH), 1.74 (dddd, *J* = 13.9, 9.0, 7.4, 4.7 Hz, 1H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 145.6, 140.9, 132.4, 128.5, 128.4, 126.2, 73.3, 66.4, 32.2, 31.0, 27.5, 17.8. IR (KBr) 1689, 1597 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{15}H_{19}O_3^+$ $[M+H]^+$: 247.1334; found: 247.1325.

4.2.5 Ethyl 3-methyl-5-phenyl-5,6-dihydro-1,4-dioxine-2-carboxylate (5f)

Yellow oil. Yield, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.33 (m, 5H, ArH), 5.03 (dd, *J* = 8.4, 2.4 Hz, 1H, CH), 4.38–4.26 (m, 3H, 1H in CH_2 & CH_2), 3.79 (dd, *J* = 11.3, 8.4 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3), 1.38 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 147.7, 135.8, 128.8, 128.8, 126.3, 125.0, 76.0, 68.5, 60.6, 17.8, 14.4. IR (KBr) 1738 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{14}H_{17}O_4^+$ $[M+H]^+$: 249.1127; found: 249.1120.

4.2.6 Ethyl (*R*)-3-methyl-5-phenyl-5,6-dihydro-1,4-dioxine-2-carboxylate ((*R*)-5f)

Yellow oil. Yield, 41%. $[\alpha]^{20}_D$ = -24.3 (c, 1.10, CH_2Cl_2). 88% ee (Daicel Chiralpak AD-H column with a mixture of hexane and isopropanol (90:10, *v/v*) as eluent at a flow rate of 1.0 mL/min. at 254 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.33 (m, 5H, ArH), 5.03 (dd, *J* = 8.4, 2.4 Hz, 1H, CH), 4.38–4.26 (m, 3H, 1H in CH_2 & CH_2), 3.79 (dd, *J* = 11.3, 8.4 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3), 1.38 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 147.7, 135.8, 128.8, 128.8, 126.3, 125.0, 76.0, 68.5, 60.6, 17.8, 14.4. IR (KBr) 1738 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{14}H_{17}O_4^+$ $[M+H]^+$: 249.1127; found: 249.1122.

4.2.7 Methyl 3-methyl-5-phenyl-5,6-dihydro-1,4-dioxine-2-carboxylate (5g)[11]

Yellow oil. Yield, 18%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H, ArH), 4.94 (d, *J* = 8.0 Hz, 1H, CH), 4.23 (d, *J* = 11.2 Hz, 1H in CH_2), 3.75 (s, 3H, CH_3), 3.70 (dd, *J* =11.2, 8.0 1H in CH_2), 2.28 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 148.0, 135.7, 128.8, 128.8, 126.3, 125.7, 76.0, 68.4, 51.7, 17.7.

4.2.8 Ethyl 5-(4-chlorophenyl)-3-methyl-5,6-dihydro-1,4-dioxine-2-carboxylate (5i)

Yellow oil. Yield, 26.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.20 (d, *J* = 7.7 Hz, 2H, ArH), 4.91 (dd, *J* = 8.0, 1.6 Hz, 1H, CH), 4.29–4.14 (m, 3H, CH_2 & CH_2), 3.65 (dd, *J* = 11.2, 8.4 Hz, 1H in CH_2), 2.26 (s, 3H, CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 147.4, 134.7, 134.3, 129.0, 127.6, 125.1, 75.2, 68.3, 60.7, 17.8, 14.4. IR (KBr): 1736, cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{14}H_{16}ClO_4^+$ $[M+H]^+$: 283.0737; found: 283.0761.

4.2.9 1-(5-(4-Chlorophenyl)-3-methyl-5,6-dihydro-1,4-dioxin-2-yl)ethan-1-one (5j)

Yellow oil. Yield, 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H, ArH), 7.26 (d, *J* = 8.8 Hz, 2H, ArH), 4.97 (dd, *J* = 8.0, 1.6 Hz, 1H, CH), 4.24 (d, *J* = 11.2 Hz, 1H in CH_2), 3.80–3.63 (dd, *J* = 12.1, 3.9 Hz, 1H in CH_2), 2.30 (s, 3H, CH_3), 2.24 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 195.5, 145.9, 132.6, 130.9, 129.0, 128.5, 127.6, 75.3, 67.9, 27.6, 17.6. IR (KBr) 1724, 1690 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{13}H_{14}ClO_3^+$ $[M+H]^+$: 253.0631; found: 253.0617.

4.2.10 Ethyl 5-(4-bromophenyl)-3-methyl-5,6-dihydro-1,4-dioxine-2-carboxylate (5k)

Yellow oil. Yield, 27%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.07 (m, 5H, ArH), 4.90 (dd, *J* = 8.2, 2.4 Hz, 1H, CH), 4.28–4.16 (m, 3H, 1H in CH_2 & CH_2), 3.65 (dd, *J* = 11.2, 8.2 Hz, 1H in CH_2), 2.26 (s, 3H, CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 147.4, 134.9, 131.9, 127.9, 125.1, 122.8, 75.3, 68.2, 60.7, 17.8, 14.4. IR (KBr) 1735 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{14}H_{16}BrO_4^+$ $[M+H]^+$: 327.0232; found: 277.0228.

4.2.11 *rel*(4a*R*,8a*S*)-(3-Methyl-4a,5,6,7,8,8a-hexahydrobenzo[*b*][1,4]dioxin-2-yl)(phenyl)methanone (5m)

Yellow oil. Yield, 10%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78–7.69 (m, 2H, ArH), 7.51–7.48 (m, 3H, ArH). 4.19 (ddd, *J* = 7.6, 2.9, 2.4 Hz, 1H, CH), 4.09 (ddd, *J* = 6.4, 3.0, 2.9 Hz, 1H, CH), 2.17 (s, 3H, CH_3), 1.82–1.34 (m, 8H,

4CH_2). ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.3, 144.3, 137.9, 131.2, 129.7, 128.3, 127.4, 72.4, 69.1, 26.7, 26.4, 20.9, 19.9, 16.8. IR (KBr) 1734, 1665 cm^{-1}. HRMS (ESI) *m/z*: calcd. for $C_{16}H_{19}O_3^+$ $[M+H]^+$: 259.1134; found: 259.1135.

4.2.12 Ethyl *rel*(4a*R*,10a*S*)-3-phenyl-4a,5,6,7,8,9,10,10a-octahydrocycloocta[*b*][1,4]dioxine-2-carboxylate (5n)[11]

Yellow oil, yield 33%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 (s, 5H), 4.42 (dt, *J* = 9.0 and 2.8 Hz, 1H), 4.21 (dt, *J* = 9.0 and 2.8 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 2.18 – 1.89 (m, 3H), 1.97 – 1.42 (m, 9H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Acetone) δ 163.6, 145.9, 135.8, 129.8, 129.1, 128.0, 125.8, 76.4, 74.1, 60.2, 28.2, 28.0, 26.1, 25.6, 23.8, 23.1, 13.8.

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Supplementary Material

General procedures for preparation of oxiranes **1** and diao compounds **2**, analytical data of oxiranes **1** and diazo compounds **2**, copies of ^{1}H and ^{13}C NMR spectra of diazo compounds **2**, oxiranes **4**, and products **5**, and copies of HPLC profiles for the enantiomeric excessive determination of products (*R*)-**5f.** The Supplementary Material is available free of charge on http://dx. doi: 10.1021/xxxxxx.

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