Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 61 (2005) 10868–10879
Tetrahedron

Lewis acid promoted reactions of γ,γ-dialkoxyallylic zirconium species with various carbonyl compounds

Hisanaka Ito,[a] Azusa Sato[b] and Takeo Taguchi[a,*]

[a]*Tokyo University of Pharmacy and Life Science, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan*
[b]*Tokyo Women's Medical University, 8-1 Kawada-cho, Shinjuku-ku, Tokyo 162-8666, Japan*

Received 3 August 2005; accepted 3 September 2005

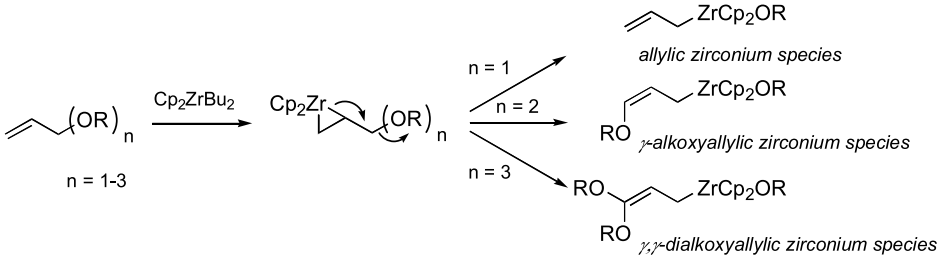
Available online 22 September 2005

Abstract—The reactions of γ,γ-dialkoxyallylic zirconium species with carbonyl compounds in the presence of Lewis acid are reported. The reactivity of γ,γ-dialkoxyallylic zirconium species and reaction pathway were strongly dependent on the structure and electrostatic nature of the carbonyl compounds.

1. Introduction

Although many kinds of allylic organometallics have been reported during the last three decades, development of novel preparative methods and their useful reactions is an important subject due to the importance of the carbon–carbon bond formation in the organic synthesis.[1] We have developed the preparative method for the allylic and related zirconium species from allyl ether derivatives with zirconocene–butene complex through β-elimination of alkoxyl group.[2–5] Our method for the generation of allylic zirconiums has some characteristic features: (1) zirconium species attack initially to the double bond of the allyl ether and the subsequent elimination of alkoxyl group provides the allylic zirconium.[6,7] Mechanism of this process is different from that of the reaction of low valent metal with allyl halide involving the direct oxidative insertion of metal to carbon–halogen bond. (2) Relatively stable allylic ether can be used as a precursor for the allylic organometallics. (3) A variety type of substrates can be used as a precursor (acrolein acetal and acrylic acid *ortho* ester etc.). Along with this line, we have reported the preparative method for the allylic zirconium,[2] alkoxyallylic zirconium,[3] and dialkoxyallylic zirconium species[4,5] from the corresponding allylic ethers (Scheme 1).

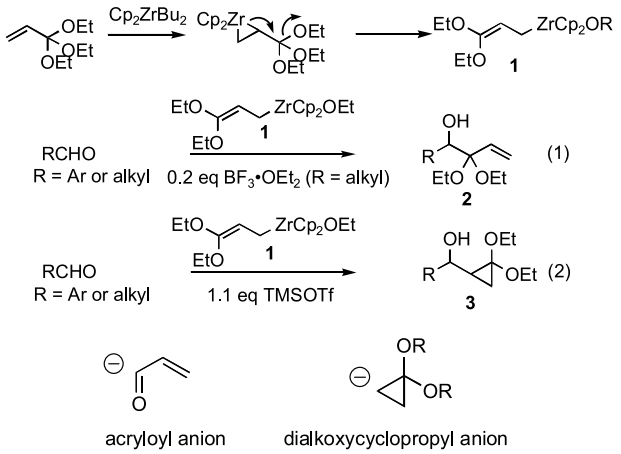
Among the reactions of allylic zirconium species with carbonyl compounds, we found interesting reactivities of γ,γ-dialkoxyallylic zirconium species and the detail of the reaction as α,β-unsaturated acyl anion equivalent have been reported.[4] γ,γ-Dialkoxyallylic zirconium species **1** react with aldehyde at the γ-position of zirconium in the absence or presence of 0.2–0.3 equiv of Lewis acid (Eq. 1 in Scheme 2). Therefore, this zirconium species **1** work as acryloyl anion equivalent.[10] On the other hand, in the presence of more than a stoichiometric amount of Lewis acid, *gem*-dialkoxycyclopropane derivatives **3** are formed in the reaction of **1** with aldehyde, in which **1** serves as



Scheme 1.

Keywords: Lewis acid; Zirconium species; Cyclopropane derivatives.
* Corresponding author. Tel./fax: +81 426 76 3257; e-mail: taguchi@ps.toyaku.ac.jp

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.09.009



Scheme 2.

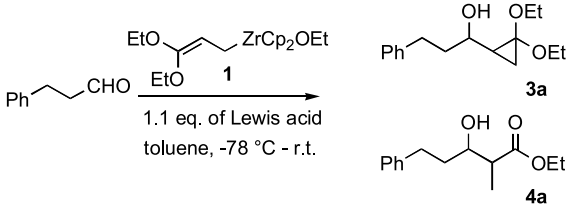
dialkoxycyclopropyl anion equivalent (Eq. 2 in Scheme 2). We report here the detail of the Lewis acid promoted reactions of γ,γ-dialkoxyallylic zirconium species with carbonyl compounds.[5]

2. Results and discussions

2.1. Reaction of γ,γ-diethoxyallylic zirconium species 1 with carbonyl compounds (1,2-addition)

γ,γ-Dialkoxyallylic zirconium species **1** can be prepared from triethyl orthoacrylate[8] with zirconocene–butene complex[9] by our reported procedure as shown in Scheme 2. Examination of Lewis acid for the preparation of *gem*-dialkoxycyclopropane derivatives by the reaction of the zirconium species **1** with aldehyde is summarized in Table 1. In the presence of stoichiometric amount of Lewis acid, the zirconium species **1** smoothly reacted with aldehydes to give the *gem*-diethoxycyclopropane derivatives **3** as a diastereomeric mixture. Regarding the Lewis acid, when $BF_3 \cdot OEt_2$ or $TiCl_4$ was employed, the reaction of **1** with 3-phenylpropionaldehyde gave **3a** in 75 and 57% yield, respectively, along with a small amount of uncyclized product **4a**[11] (entries 1 and 2). This result may support the following discussion for the mechanism of this reaction (vide infra). Trimethylsilyl trifluoromethanesulfonate (TMSOTf) smoothly promoted the reaction of **1** to give **3a** in 88% yield without the formation of **4a** (entry 3).

Table 1. Examination of Lewis acid for the reaction of **1**

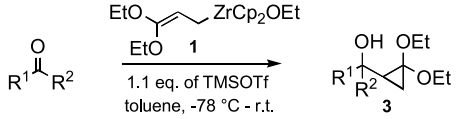


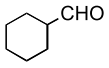
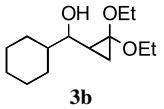
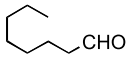
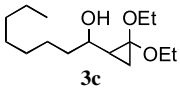
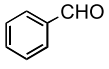
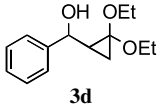
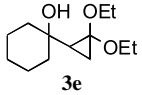
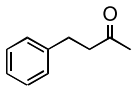
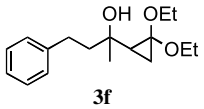
Entry	Lewis acid	Yield of **3a** (%)[a,b]
1	$BF_3 \cdot OEt_2$	75
2	$TiCl_4$	57
3	TMSOTf	88

[a] Isolated yield. Yield was based on **1**.
[b] Diastereomeric mixture (1:1–2:1).

Using TMSOTf, the reaction of **1** with other carbonyl compounds was examined (Table 2). The zirconium species **1** reacted with not only aliphatic aldehydes but also aromatic aldehydes to give the cyclopropane derivatives (**3b**, **3c**, and **3d**) in good yields (entries 1–3). Ketones also reacted with **1** to afford the adducts (**3e**, **3f**). Although the isolation yield was satisfactoly in the case of ketone, small amount of elimination product was obtained because of the adducts were relatively unstable due to the facile elimination of the hydroxyl group during silica gel column chromatography (entries 4, 5).

Table 2. TMSOTf-promoted reaction of **1** with carbonyl compounds



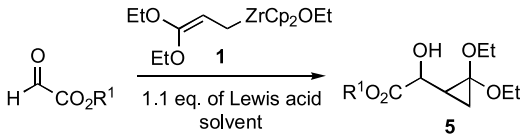
Entry	Carbonyl compound	Product	Yield (%)[a,b]
1		 **3b**	87
2		 **3c**	75
3		 **3d**	81
4		 **3e**	83
5		 **3f**	76

[a] Isolated yield. Yield was based on **1**.
[b] Diastereomeric mixture (1:1–2:1).

The reaction of γ,γ-diethoxyallylic zirconium species **1** with glyoxylate derivatives[12] was examined. Under the reaction conditions using TMSOTf (see Table 2), the desired product could not be obtained (Table 3, entry 1). In toluene, $Cu(OTf)_2$ or $Zn(OTf)_2$ which can be coordinated by two carbonyl groups also did not work well resulting in a complex mixture along with a significant amount of starting glyoxylate (entries 2 and 3). We found that the reaction proceeded smoothly in dichloromethane solvent. Thus, after the generation of **1** in toluene, the solvent was changed to dichloromethane for the reaction with glyoxylate and the best result was obtained in the case of $Cu(OTf)_2$ (entry 5).

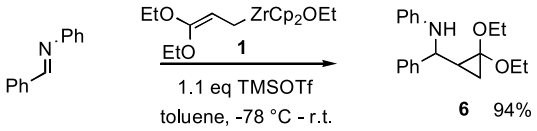
The reaction of the zirconium species **1** with imine derivatives was also examined (Scheme 3). Although **1** reacted with benzylideneaniline to give cyclopropane adduct **6** in 94% yield, unfortunately with other structurally similar imine derivatives such as naphthylideneaniline or benzylidene-*p*-methoxyaniline, clean reaction was not realized.

Table 3. Reaction of **1** with glyoxylate in the presence of Lewis acid



Entry	R^1	Lewis acid	Solvent	Product	Yield (%)[a,b]
1	*i*-Pr	TMSOTf	Toluene	—[c]	
2	*i*-Pr	$Cu(OTf)_2$	Toluene	—[c]	
3	*i*-Pr	$Zn(OTf)_2$	Toluene	—[c]	
4	*i*-Pr	TMSOTf	CH_2Cl_2	**5a**	52
5	*i*-Pr	$Cu(OTf)_2$	CH_2Cl_2	**5a**	85
6	*i*-Pr	$Zn(OTf)_2$	CH_2Cl_2	**5a**	55
7	Me	$Cu(OTf)_2$	CH_2Cl_2	**5b**	60
8	Et	$Cu(OTf)_2$	CH_2Cl_2	**5c**	78
9	Bn	$Cu(OTf)_2$	CH_2Cl_2	**5d**	60

[a] Isolated yield. Yield was based on **1**.
[b] Diastereomeric mixture (1:1–2:1).
[c] Complex mixture along with the recovery of glyoxylate.



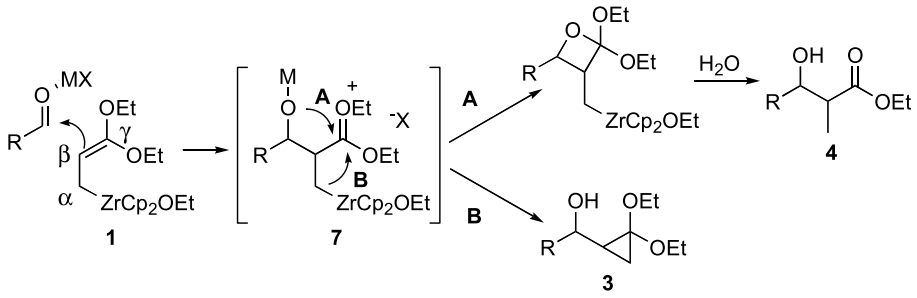
Scheme 3.

in the formation of the oxetane derivative, which after hydrolysis gave uncyclized product **4** as a by-product. The formation of cyclopropane derivatives in the reaction of alkoxyallylic tin derivatives with carbonyl compounds has also been reported.[13]

2.2. Reaction of γ,γ-diethoxyallylic zirconium species 1 with unsaturated carbonyl compounds

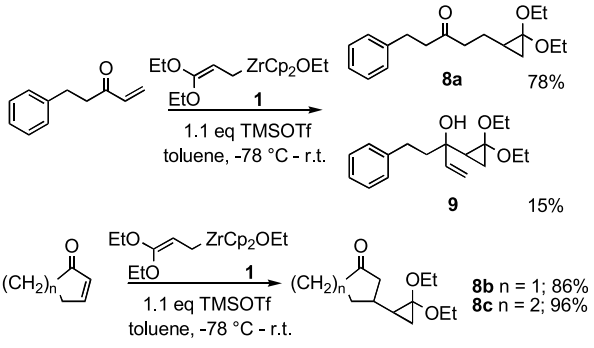
The reaction of γ,γ-diethoxyallylic zirconium species **1** with α,β-unsaturated ketone derivatives was examined. Under the TMSOTf-promoted conditions, with acyclic vinyl ketone, 5-phenylpent-1-en-3-one, the 1,4-addition reaction at the β-position of **1** proceeded predominantly to afford the cyclopropane **8a** in good yield (Scheme 5). With cycloalkenones, 1,4-adduct **8b** and **8c** were selectively obtained.

TMSOTf promoted reaction of **1** with benzyl acrylate as a typical model substrate of α,β-unsaturated ester was conducted (Scheme 6). Two products, diethoxycyclopropane **11** and diethoxycyclobutane **12** were obtained, although the yield was not good as a synthetic reaction. The reaction pathway to these products is possibly explained by considering the intermediate **10** derived through the 1,4-addition of the β-position of the zirconium species **1**. In the intermediate **10**, both nucleophilic centers competitively react to the carbenium ion site, that is, attack by ketene silyl acetal moiety provides the cyclobutane **12** (path B),[14]

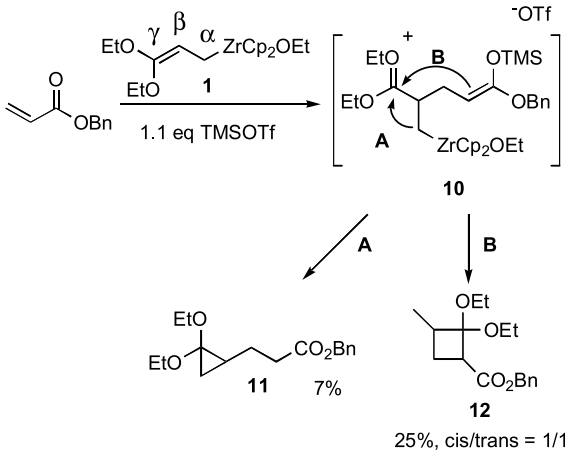


Scheme 4.

The reaction mechanism for the 1,2-addition of γ,γ-diethoxyallylic zirconium species **1** to the carbonyl compound is shown in Scheme 4. When less than a stoichiometric amount of Lewis acid is employed, the zirconium species **1** react at the γ-position with carbonyl compound through six-membered transition state, in which the activation of carbonyl group can be achieved by the coordination to the zirconium.[4] However, two geminal γ-ethoxy substituents of the zirconium species **1** makes the γ-position sterically hindered site and due to the ketene acetal structure the β-position should be electron rich site compared with allylic and γ-alkoxyallylic zirconium species. Therefore, in the presence of stoichiometric amount of Lewis acid, this zirconium species **1** react with activated carbonyl compound at the β-position as a ketene diethyl acetal leading to the formation of intermediate **7**. Subsequently, in the case of TMSOTf as Lewis acid, alkylzirconium part attacks to oxocarbenium ion moiety intramolecularly to give cyclopropane derivative **3** (path B). In the case of $BF_3 \cdot OEt_2$, competitive attack of the alkoxyl group in the intermediate **7** to the oxocarbenium ion resulted while the cyclopropane **11** is formed by the attack of alkylzirconium moiety (path A). To control the reaction pathway and to improve the product yield further reactions were conducted using various α,β-unsaturated carbonyl compounds such as lactone, amide, and *N*-acyloxazolidinone derivatives as described below.

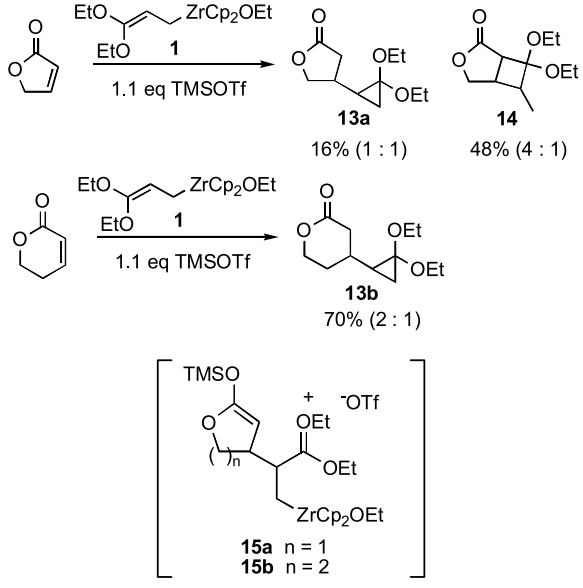


Scheme 5.



Scheme 6.

With α,β-unsaturated lactone derivatives the reaction proceeded smoothly. In the reaction of the zirconium species **1** with five-membered ring lactone, a mixture of the cyclopropane **13a** and the cyclobutane **14** were obtained in 16 and 48% yield, respectively. On the other hand, cyclopropane derivative **13b** was selectively obtained in the case of six-membered ring lactone. These results should be explained as follows. In both cases, 1,4-addition reaction at the β-position of the zirconium species **1** to the α,β-unsaturated lactone afforded the intermediate (**15a** or **15b**) having oxonium ion and silyl enol ether parts in the same molecule. In the case of six-membered ring lactone, it should be difficult to form the cyclobutane ring, because the oxonium ion and silyl enol ether are not close enough to react due to the equatorial oriented oxonium ion part on the pseudo chair like conformation of six-membered ring silyl enol ether (Scheme 7).

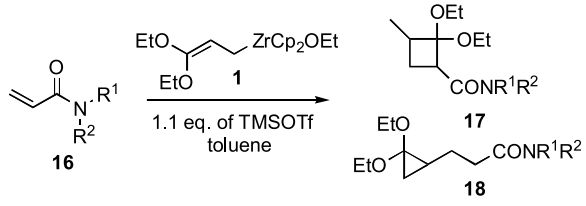


Scheme 7.

For the development of a highly selective method for the preparation of either cyclopropane or cyclobutane derivatives, we paid attention to the electron density of the ketene acetal moiety in the intermediate. Thus, an increase in the electron density of the ketene acetal moiety in the intermediate **10** by replacing one oxygen atom with electron-donating nitrogen atom would make path B favorable (Scheme 6). Therefore, as the substrate we adopted the acryl amide instead of ester for the selective construction of cyclobutane derivatives.

Results of the reaction of **1** with acryl amide derivatives **16** in the presence of TMSOTf are shown in Table 4. As expected, the reaction of **1** with *N*,*N*-dimethyl acrylamide smoothly proceeded to give cyclobutane derivative **17** exclusively (entry 1). In this reaction, the cis isomer was predominantly obtained. Improvement of the diastereoselectivity could be achieved by employing a more bulky substituent on the nitrogen atom ($R^1=R^2=$Bn or *i*-Pr, entries 2,3). The ratio of cyclobutane **17** and cyclopropane **18** was found to be affected by the electron density on the nitrogen atom. That is, when the electron density of the nitrogen atom was lowered by connecting to an aromatic ring, as in the case of *N*,*N*-diphenyl acrylamide, cyclopropane derivative **18** was obtained as a major product (entry 5). Under these conditions, the reaction did not proceed by introducing a substituent on the acryloyl moiety (crotonamide and methacrylamide) under these conditions.

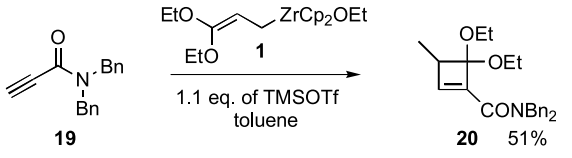
Table 4. Reaction of **1** with acrylamie derivatives



Entry	Amide		Yield (%)[a]	**17**/**18**[b]	**17**: cis/trans[b]
1	$R^1=R^2=$Me	**16a**	54	>95:5	82:18
2	$R^1=R^2=$Bn	**16b**	83	>95:5	>95:5
3	$R^1=R^2=$*i*-Pr	**16c**	56	>95:5	>95:5
4	$R^1=$Me, $R^2=$Ph	**16d**	85	>95:5	83:17
5	$R^1=R^2=$Ph	**16e**	61	25:75	85:15

[a] Isolated yield. Yield was based on **1**.
[b] Ration was determined by crude ^{1}H NMR.

The reaction of the zirconium species **1** with *N*,*N*-dibenzyl propiolamide (**19**) also proceeded to give the cyclobutene derivative **20** in 51% yield (Scheme 8).

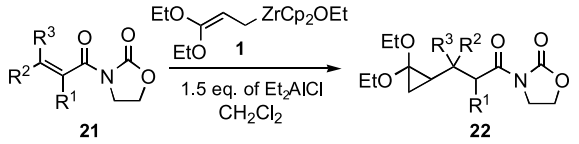


Scheme 8.

The selective construction of cyclopropane derivatives through path A in Scheme 6 was surveyed. To suppress the formation of cyclobutane derivatives through path B, α,β-unsaturated *N*-acyloxazolidinone derivatives **21**, which have oxazolidinone instead of dialkyl amine as the amide moiety, was used with the expectation of lowered nucleophilicity of ketene acetal moiety in the intermediate

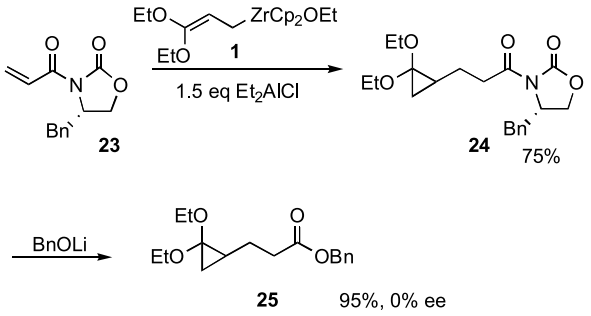
due to the decrease in the electron density as compared with *N*,*N*-dialkylamide. The results are summarized in Table 5.

Table 5. The reaction of **1** with acryloyl oxazolidinone derivatives



Entry	Substrate	Product	Yield (%)[a,b]
1	**21a**	**22a**	83
2	**21b**	**22b**	90 (1:1)
3	**21c**	**22c**	72 (7:3)
4	**21d**	**22d**	39

[a] Isolated yield. Yield was based on **1**.
[b] Ration was determined by crude ^{1}H NMR.



Scheme 9.

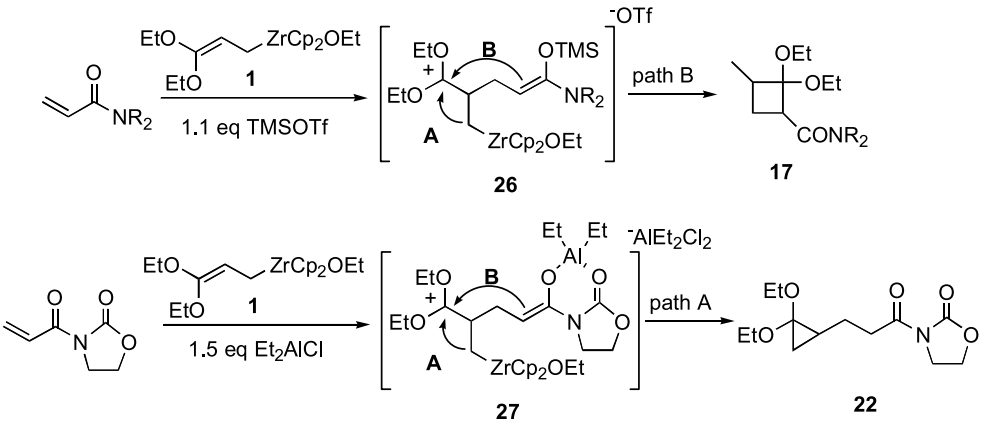
For the reaction to proceed, choice of solvent and Lewis acid was crucial. That is, since the 1,4-addition of **1** did not occur in toluene in which **1** was prepared, it was needed to change the solvent to dichloromethane before **1** was reacted with *N*-acyloxazolidinones. As a Lewis acid, diethylaluminum chloride worked nicely as compared with other Lewis acid such as trimethylsilyl triflate or titanium chloride. Thus, in the presence of 1.5 equiv of diethylaluminum chloride in dichloromethane, reaction of **1** with *N*-acryloyloxazolidinone **21a** gave the cyclopropane derivative **22a** as a sole product (entry 1). Under the similar conditions, **21b** or **21c**, which has substitent on the α,β-unsaturated carbonyl moiety, also reacted with **1** to give the cyclopropane **22** selectively in good yield, but the diastereoselectivity was low (entries 2 and 3). Surprisingly, sterically demanding β,β-disubstituted compound **21d** also reacted with **1** under these conditions to afford cyclopropane derivative **22d** in moderate yield.

The asymmetric reaction of **1** with chiral substrate **23** was also examined, but any chiral induction was not observed (Scheme 9).

The high selectivity for the formation of cyclopropane derivative **22** should be explained by the relatively lower electron density of the *N*,*O*-acetal moiety in the intermediate **27** as compared with that of the acrylamide which produced cyclobutane derivatives **17**. Thus, by changing the electronic nature of the residual group of the enoyl compound, selective formation of the *gem*-dialkoxycyclopropane **22** or cyclobutane **17** can be controlled through the 1,4-addition of **1** to an α,β-unsaturated carboxylic acid derivative (Scheme 10).

3. Conclusion

The addition reactions of γ,γ-dialkoxyallylic zirconium species **1** with various carbonyl compounds in the presence of Lewis acid were described. In the case of the reaction with aldehyde and ketones, 1,2-addition of the zirconium species **1** proceeded as dialkoxycyclopropyl anion equivalent. On the other hand, the reaction of **1** with α,β-unsaturated ester and amide derivatives gave cyclopropane and cyclobutane derivatives through 1,4-addition reaction. These compounds



Scheme 10.

could be obtained selectively by the appropriate choice of the substrate and reaction conditions.

4. Experimental

Zirconocene dichloride was purchased from Tokyo Kasei Kogyo. All reactions were conducted under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H NMR and $CDCl_3$ (77.01 ppm) for ^{13}C NMR as an internal standard, respectively. Mass spectra and HRMS were recorded by electron impact ionization at 70 eV. Column chromatography was performed on neutral silica gel (75–150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30×2.2 cm i.d. prepacked column (silica gel, 10 μm) with a UV or RI detector.

4.1. General procedure for generation of 1 and its reaction with aldehyde (ketone) or α,β-unsaturated carbonyl compounds in the presence of Lewis acid

Under argon atmosphere, to a solution of zirconocene dichloride (1.05 g, 3.6 mmol) in toluene (18 mL) was added *n*-butyllithium (1.46 M in hexane, 4.9 mL, 7.2 mmol) at −78 °C and the mixture was stirred at the same temperature for 1 h. A solution of triethyl orthoacrylate (522 mg, 3 mmol) in toluene (5 mL) was added to the reaction mixture at −78 °C and then the temperature was raised to ambient temperature. After being stirred for 3 h, were successively added a solution of carbonyl compound (3.6 mmol) in toluene (3 mL) at −78 °C and trimethylsilyl trifluoromethanesulfonate (0.6 mL, 3.3 mmol), and the whole was stirred at the same temperature for 10 min. The reaction temperature was raised to ambient temperature and the stirring was continued for 4.5 h. After addition of saturated aqueous ammonium chloride, the reaction mixture was extracted with ether for three times. Organic layer was washed with brine, dried with magnesium sulfate, and concentrated under vacuum. The residue was purified by neutral silica gel column chromatography to afford product. If the trimethylsilyl group could not be completely cleaved under the above mentioned procedure, the organic layer was washed several times with 1 N HCl. Although compound **3** is relatively stable under acid treatment in workup stage, it is labile during the purification by acidic silica gel column chromatography.

4.1.1. γ,γ-Diethoxyallylic zirconium species (1). ^{1}H NMR (300 MHz, benzene-d_6) δ 6.00–5.92 (10H, m), 4.50 (1H, t, J=8.7 Hz), 4.04 (2H, q, J=7.2 Hz), 3.91 (2H, q, J=7.0 Hz), 3.80 (2H, q, J=6.9 Hz), 1.97 (2H, d, J=8.7 Hz), 1.33 (3H, t, J=7.2 Hz), 1.25 (3H, t, J=6.9 Hz), 1.08 (3H, t, J=7.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 152.6, 110.7, 93.9, 68.8, 64.2, 64.0, 34.3, 20.1, 15.6, 15.1.

4.1.2. 1-(2,2-Diethoxycyclopropyl)-3-phenyl-1-propanol (3a). *Compound* **3a**-*less polar*. Colorless oil; IR (neat) 3468 ν cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.19 (5H, m), 3.88 (1H, dq, J=9.5, 7.1 Hz), 3.81 (1H, dq, J=9.3, 7.1 Hz), 3.64–3.54 (2H, m), 3.42 (1H, m), 2.86 (1H, ddd, J=14.2, 9.7, 6.3 Hz), 2.74 (1H, ddd, J=14.2, 9.5, 7.0 Hz), 2.45 (1H, br s), 1.99–1.91 (2H, m), 1.36 (1H, ddd, J=9.9, 8.2, 6.5 Hz), 1.23 (6H, t, J=7.1 Hz), 1.10 (1H, dd, J=9.9, 5.8 Hz), 0.81 (1H, dd, J=6.5, 5.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 128.3, 128.2, 125.7, 91.3, 72.1, 62.4, 61.9, 38.2, 32.1, 30.9, 17.3, 15.4, 15.3. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.54; H, 9.02.

Compound **3a**-*more polar*. Colorless oil; IR (neat) 3443 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.20 (5H, m), 3.82–3.71 (3H, m), 3.60 (1H, dq, J=9.5, 7.0 Hz), 3.54 (1H, dq, J=9.3, 7.0 Hz), 2.87 (1H, ddd, J=14.1, 7.5, 7.5 Hz), 2.75 (1H, ddd, J=14.1, 8.4, 8.4 Hz), 2.35 (1H, br s), 1.94–1.88 (2H, m), 1.34 (1H, ddd, J=10.0, 6.8, 5.8 Hz), 1.22 (3H, t, J=7.0 Hz), 1.20 (3H, t, J=7.0 Hz), 1.04 (1H, dd, J=10.0, 5.8 Hz), 1.00 (1H, dd, J=6.8, 5.8 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 142.2, 128.5, 128.3, 125.7, 91.3, 68.6, 62.2, 61.8, 38.8, 31.7, 30.5, 15.3, 15.2, 14.6. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.47; H, 9.22.

4.1.3. Cyclohexyl(2,2-diethoxycyclopropyl)methanol (3b). *Compound* **3b**-*less polar*. Colorless oil; IR (neat) 3476 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (1H, dq, J=9.5, 7.1 Hz), 3.78 (1H, dq, J=9.3, 7.1 Hz), 3.62–3.53 (2H, m), 3.06 (1H, br t, J=7.8 Hz), 2.35 (1H, br s), 1.97 (1H, br d, J=12.8 Hz), 1.84–1.72 (3H, m), 1.67 (1H, br d, J=11.0 Hz), 1.54–1.46 (1H, m), 1.34 (1H, ddd, J=9.6, 9.0, 6.4 Hz), 1.30–1.00 (5H, m), 1.22 (3H, t, J=7.2 Hz), 1.21 (3H, t, J=7.1 Hz), 1.10 (1H, dd, J=9.6, 5.7 Hz), 0.77 (1H, dd, J=6.4, 5.7 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 91.1, 77.4, 62.4, 61.8, 43.7, 29.3, 29.2, 29.1, 26.6, 26.2, 26.1, 18.3, 15.4, 15.3. Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.38; H, 10.97.

Compound **3b**-*more polar*. Colorless oil; IR (neat) 3443 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (1H, dq, J=9.5, 7.1 Hz), 3.77 (1H, dq, J=9.3, 7.1 Hz), 3.64–3.52 (3H, m), 1.89 (1H, br d, J=12.7 Hz), 1.81–1.72 (4H, m), 1.68 (1H, br d, J=12.0 Hz), 1.51–1.44 (1H, m), 1.37 (1H, ddd, J=9.6, 7.7, 5.0 Hz), 1.30–1.08 (5H, m), 1.22 (3H, t, J=7.1 Hz), 1.21 (3H, t, J=7.1 Hz), 1.02–0.98 (2H, m). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 91.3, 72.6, 62.3, 61.6, 44.0, 29.1, 29.0, 28.0, 26.6, 26.4, 26.3, 15.4, 15.3, 14.2. Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.10; H, 10.90.

4.1.4. 1-(2,2-Diethoxycyclopropyl)-1-octanol (3c). *Compound* **3c**-*less polar*. Colorless oil; IR (neat) 3471 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (1H, dq, J=9.5, 7.1 Hz), 3.77 (1H, dq, J=9.3, 7.1 Hz), 3.61–3.49 (2H, m), 3.31 (1H, m), 2.30 (1H, br s), 1.70–1.23 (13H, m), 1.21 (3H, t, J=7.1 Hz), 1.19 (3H, t, J=7.1 Hz), 1.06 (1H, dd, J=10.0, 5.7 Hz), 0.87 (3H, t, J=7.1 Hz), 0.76 (1H, dd, J=6.1, 6.0 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 91.4, 72.9, 62.4, 61.9, 36.5, 31.8, 31.1, 29.7, 29.3, 25.8, 22.7, 17.5, 15.4, 15.3, 14.1. Anal. Calcd for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found: C, 69.87; H, 11.98.

Compound **3c**-*more polar*. Colorless oil; IR (neat) 3435 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82–3.65 (3H, m), 3.58 (1H, dq, J=9.5, 7.1 Hz), 3.52 (1H, dq, J=9.3, 7.1 Hz), 2.25 (1H, br s), 1.60–1.23 (13H, m), 1.20 (6H, t, J=7.1 Hz), 1.01–0.93 (2H, m), 0.87 (3H, t, J=7.1 Hz). ^{13}C NMR

(125.7 MHz, $CDCl_3$) δ 91.4, 69.2, 62.2, 61.7, 37.2, 31.8, 30.5, 29.6, 29.3, 25.4, 22.7, 15.4, 15.3, 14.5, 14.1. Anal. Calcd for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found: C, 69.45; H, 11.84.

4.1.5. (2,2-Diethoxycyclopropyl)-phenylmethanol (3d). *Compound* **3d**-*less polar*. Colorless oil; IR (neat) 3420 ν cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.28 (5H, m), 4.45 (1H, dd, J=8.3, 1.2 Hz), 3.95 (1H, dq, J=9.5, 7.1 Hz), 3.82 (1H, dq, J=9.5, 7.1 Hz), 3.70 (1H, dq, J=9.5, 7.1 Hz), 3.59 (1H, dq, J=9.5, 7.1 Hz), 2.76 (1H, br s), 1.63 (1H, ddd, J=9.9, 8.5, 6.5 Hz), 1.31 (3H, t, J=7.1 Hz), 1.23 (3H, t, J=7.1 Hz), 1.16 (1H, dd, J=9.9, 5.9 Hz), 0.98 (1H, dd, J=6.5, 5.9 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 143.3, 128.4, 127.4, 125.9, 91.7, 74.5, 62.6, 62.1, 32.5, 17.8, 15.5, 15.3. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.99; H, 8.55.

Compound **3d**-*more polar*. White crystal; mp 40–41 °C. IR (KBr) 3235 $\nu$$cm^{-1}$. ^1H NMR (500 MHz, $CDCl_3$) δ 7.49–7.28 (5H, m), 4.76 (1H, d, J=6.7 Hz), 3.83 (1H, dq, J=9.5, 7.1 Hz), 3.71–3.62 (2H, m), 3.37 (1H, dq, J=9.5, 7.1 Hz), 2.65 (1H, br s), 1.57 (1H, ddd, J=9.9, 6.8, 6.8 Hz), 1.28 (3H, t, J=7.1 Hz), 1.19–1.12 (2H, m), 1.14 (3H, t, J=7.1 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 143.9, 128.2, 127.3, 125.8, 91.4, 71.6, 62.3, 61.8, 32.5, 15.7, 15.3, 15.2. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.04; H, 8.46.

4.1.6. 1-(2,2-Diethoxycyclopropyl)cyclohexanol (3e). Colorless oil; IR (neat) 3438 ν cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.87 (1H, dq, J=9.5, 7.1 Hz), 3.81 (1H, dq, J=9.5, 7.1 Hz), 3.59 (1H, dq, J=9.5, 7.1 Hz), 3.49 (1H, dq, J=9.5, 7.1 Hz), 2.98 (1H, s), 1.76–1.45 (8H, m), 1.41–1.25 (2H, m), 1.27 (1H, dd, J=10.4, 7.3 Hz), 1.23 (3H, t, J=7.1 Hz), 1.22 (3H, t, J=7.1 Hz), 1.17 (1H, dd, J=7.3, 5.7 Hz), 0.94 (1H, dd, J=10.4, 5.7 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 92.0, 68.4, 62.4, 62.2, 39.7, 37.1, 33.1, 25.8, 22.2, 21.9, 15.4, 15.3, 13.2. Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.22; H, 10.81.

4.1.7. 2-(2,2-Diethoxycyclopropyl)-4-phenyl-2-butanol (3f). *Compound* **3f**-*less polar*. Colorless oil; IR (neat) 3518 ν cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.17 (5H, m), 3.89 (1H, dq, J=9.5, 7.1 Hz), 3.83 (1H, dq, J=9.5, 7.1 Hz), 3.61 (1H, dq, J=9.5, 7.1 Hz), 3.51 (1H, dq, J=9.5, 7.1 Hz), 3.16 (1H, br s), 2.80–2.70 (2H, m), 1.90–1.76 (2H, m), 1.41 (3H, s), 1.29–1.20 (2H, m), 1.25 (3H, t, J=7.1 Hz), 1.23 (3H, t, J=7.1 Hz), 1.01 (1H, dd, J=10.2, 5.6 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 143.0, 128.4, 128.3, 125.6, 91.1, 69.2, 62.4, 62.2, 44.4, 33.0, 30.3, 29.3, 15.4, 15.3, 14.0. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.26; H, 9.52.

Compound **3f**-*more polar*. Colorless oil; IR (neat) 3509 ν cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.17 (5H, m), 3.88 (1H, dq, J=9.5, 7.1 Hz), 3.82 (1H, dq, J=9.5, 7.1 Hz), 3.61 (1H, dq, J=9.5, 7.1 Hz), 3.49 (1H, dq, J=9.5, 7.1 Hz), 3.14 (1H, br s), 2.90–2.69 (2H, m), 1.97–1.87 (2H, m), 1.31 (1H, dd, J=10.5, 7.3 Hz), 1.26 (3H, s), 1.24 (3H, t, J=7.1 Hz), 1.21 (3H, t, J=7.1 Hz), 1.18 (1H, dd, J=7.3, 5.6 Hz), 0.99 (1H, dd, J=10.5, 5.6 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 142.9, 128.3, 128.3, 125.6, 92.1, 69.8, 62.5, 62.1, 46.0, 33.6, 30.5, 25.9, 15.4, 15.3, 13.5. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.21; H, 9.47.

4.1.8. Isopropyl 2-(2,2-diethoxycyclopropyl)-2-hydroxyacetate (5a). *Compound* **5a**-*less polar*. Colorless oil; IR (neat) $\nu$$cm^{-1}$; 3478, 2979, 2934, 1731, 1452, 1376, 1255, 1195, 1108, 1054, 953. ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (1H, dq, J=6.0, 6.0 Hz), 3.89–3.80 (2H, m), 3.72 (1H, dq, J=9.2, 6.8 Hz), 3.63 (1H, dq, J=9.2, 7.2 Hz), 3.57 (1H, dq, J=9.2, 7.2 Hz), 2.97 (1H, d, J=6.8 Hz), 1.43 (1H, ddd, J=10.0, 8.4, 6.4 Hz), 1.26 (3H, d, J=6.0 Hz), 1.25 (3H, d, J=6.0 Hz), 1.22 (3H, t, J=7.2 Hz), 1.18 (3H, t, J=7.2 Hz), 1.10 (1H, dd, J=10.0, 6.4 Hz), 1.02 (1H, t, J=6.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.8, 90.5, 70.1, 69.2, 62.4, 62.1, 28.5, 21.8, 21.7, 16.1, 15.4, 15.2. ESI-MS *m/z*: 247 (M^++1). HRMS Calcd for $C_{12}H_{23}O_5$: 247.1545 (M^++1), found: 247.1556.

Compound **5a**-*more polar*. Colorless oil; IR (neat) $\nu$$cm^{-1}$; 3466, 2979, 2934, 1736, 1455, 1376, 1261, 1200, 1108, 1057, 959. ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (1H, dq, J=6.0, 6.0 Hz), 4.07 (1H, dd, J=7.6, 4.0 Hz), 3.80 (1H, dq, J=9.6, 7.2 Hz), 3.76 (1H, dq, J=9.2, 7.2 Hz), 3.58 (1H, dq, J=9.2, 7.2 Hz), 3.56 (1H, dq, J=9.6, 7.2 Hz), 3.00 (1H, d, J=4.0 Hz), 1.50 (1H, ddd, J=10.0, 7.6, 6.4 Hz), 1.27 (6H, d, J=6.0 Hz), 1.19 (3H, t, J=7.2 Hz), 1.17 (3H, t, J=7.2 Hz), 1.11 (1H, dd, J=10.0, 6.4 Hz), 1.04 (1H, t, J=6.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.3, 90.9, 69.4, 68.9, 62.3, 61.8, 28.2, 21.8, 21.7, 16.0, 15.3. ESI-MS *m/z*: 247 (M^++1). HRMS Calcd for $C_{12}H_{23}O_5$: 247.1545 (M^++1), found: 247.1561. Anal. Calcd for $C_{12}H_{22}O_5$: C, 58.52; H, 9.00. Found: C, 58.29; H, 8.60.

4.1.9. Methyl 2-(2,2-diethoxyxyclopropyl)-2-hydroxyacetate (5b). *Compound* **5b**-*less polar*. Colorless oil; IR (neat) $\nu$$cm^{-1}$; 3478, 2978, 1741, 1443, 1256, 1197, 1093, 1054, 940. ^1H NMR (400 MHz, $CDCl_3$) δ 3.93 (1H, dd, J=8.4, 5.2 Hz), 3.86–3.68 (2H, m), 3.77 (3H, s), 3.61 (1H, dq, J=9.2, 7.2 Hz), 3.55 (1H, dq, J=9.2, 7.2 Hz), 3.00 (1H, d, J=5.2 Hz), 1.46 (1H, ddd, J=10.4, 8.4, 6.4 Hz), 1.21 (3H, t, J=7.2 Hz), 1.18 (3H, t, J=7.2 Hz), 1.12 (1H, dd, J=10.4, 6.4 Hz), 1.01 (1H, t, J=6.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.5, 90.6, 70.2, 62.5, 62.1, 52.3, 28.3, 16.2, 15.3, 15.2. ESI-MS *m/z*: 219 (M^++1). HRMS Calcd for $C_{10}H_{19}O_5$: 219.1232 (M^++1), found: 219.1235.

Compound **5b**-*more polar*. Colorless oil; IR (neat) $\nu$$cm^{-1}$; 3460, 2977, 1742, 1445, 1380, 1255, 1200, 1056, 979, 939. ^1H NMR (400 MHz, $CDCl_3$) δ 4.15 (1H, d, J=7.6 Hz), 3.82–3.69 (2H, m), 3.78 (3H, s), 3.57 (1H, dq, J=9.6, 7.2 Hz), 3.53 (1H, dq, J=9.6, 7.2 Hz), 3.07 (1H, br s), 1.53 (1H, ddd, J=11.2, 7.6, 6.0 Hz), 1.18 (3H, t, J=7.2 Hz), 1.16 (3H, t, J=7.2 Hz), 1.10 (1H, dd, J=11.2, 6.0 Hz), 1.05 (1H, t, J=6.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.3, 91.1, 69.1, 62.7, 62.1, 52.6, 28.4, 16.1, 15.5, 15.4. ESI-MS *m/z*: 219 (M^++1). HRMS Calcd for $C_{10}H_{19}O_5$: 219.1232 (M^++1), found: 219.1237. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.61; H, 8.11.

4.1.10. Ethyl 2-(2,2-diethoxycyclopropyl)-2-hydroxyacetate (5c). *Compound* **5c**-*less polar*. Colorless oil; IR (neat) $\nu$$cm^{-1}$; 3480, 2978, 1937, 1738, 1449, 1369, 1255,

1195, 1093, 1053, 945. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (2H, q, J=7.2 Hz), 3.93 (1H, dd, J=8.4, 7.2 Hz), 3.85 (1H, dq, J=9.2, 7.2 Hz), 3.73 (1H, dq, J=9.6, 7.2 Hz), 3.64 (1H, dq, J=9.2, 7.2 Hz), 3.57 (1H, dq, J=9.6, 7.2 Hz), 2.93 (1H, d, J=7.2 Hz), 1.46 (1H, ddd, J=10.4, 8.4, 6.4 Hz), 1.30 (3H, t, J=7.2 Hz), 1.24 (3H, t, J=7.2 Hz), 1.19 (3H, t, J=7.2 Hz), 1.13 (1H, dd, J=10.4, 6.4 Hz), 1.04 (1H, t, J=6.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.2, 90.6, 70.1, 62.5, 62.1, 61.5, 28.4, 16.2, 15.4, 15.2, 14.2. ESI-MS m/z: 233 (M^++1). HRMS Calcd for $C_{11}H_{21}O_5$: 233.1389 (M^++1), found: 233.1389.

Compound **5c**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 3464, 2978, 2930, 1738, 1449, 1370, 1255, 1200, 1056, 944. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32–4.21 (2H, m), 4.15 (1H, dd, J=7.6, 2.0 Hz), 3.86–3.72 (2H, m), 3.64–3.52 (2H, m), 1.58–1.51 (1H, m), 2.96 (1H, br s), 1.30 (3H, td, J=7.2, 2.0 Hz), 1.20 (3H, td, J=7.2, 2.0 Hz), 1.19 (3H, td, J=7.2, 2.0 Hz), 1.13 (1H, ddd, J=10.4, 6.4, 2.0 Hz), 1.07 (1H, td, J=6.4, 2.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.7, 90.9, 68.8, 62.4, 61.9, 61.6, 28.2, 16.0, 15.3, 15.2, 14.2. ESI-MS m/z: 233 (M^++1). HRMS Calcd for $C_{11}H_{21}O_5$: 233.1389 (M^++1), found: 233.1381.

4.1.11. Benzyl 2-(2,2-diethoxycyclopropyl)-2-hydroxyacetate (5d). *Compound* **5d**-*less polar*. Colorless oil; IR (neat) νcm^{-1}; 3465, 2977, 2930, 1739, 1455, 1376, 1256, 1196, 1092, 1054, 993. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (5H, m), 5.26 (1H, d, J=12.4 Hz), 5.21 (1H, d, J=12.4 Hz), 4.02 (1H, dd, J=8.0, 7.2 Hz), 3.84 (1H, dq, J=9.6, 7.2 Hz), 3.67 (1H, dq, J=9.6, 7.2 Hz), 3.62 (1H, dq, J=9.6, 7.2 Hz), 3.48 (1H, dq, J=9.6, 7.2 Hz), 2.97 (1H, d, J=7.2 Hz), 1.48 (1H, ddd, J=10.4, 8.0, 6.0 Hz), 1.22 (3H, t, J=7.2 Hz), 1.15 (3H, t, J=7.2 Hz), 1.12 (1H, dd, J=10.4, 6.0 Hz), 1.06 (1H, t, J=6.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.0, 135.4, 128.6, 128.4, 128.3, 90.5, 70.1, 67.1, 62.5, 62.1, 28.2, 16.2, 15.4, 15.2. ESI-MS m/z: 295 (M^++1). HRMS Calcd for $C_{16}H_{22}O_5Na$: 317.1365 (M^++Na), found: 317.1396.

Compound **5d**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 3455, 2976, 2930, 1742, 1455, 1379, 1258, 1201, 1120, 1056, 981. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.29 (5H, m), 5.27 (1H, d, J=12.0 Hz), 5.20 (1H, d, J=12.0 Hz), 4.20 (1H, dd, J=8.0, 4.0 Hz), 3.79 (1H, dq, J=10.0, 7.2 Hz), 3.62 (1H, dq, J=9.6, 7.2 Hz), 3.56 (1H, dq, J=9.6, 7.2 Hz), 3.37 (1H, dq, J=10.0, 7.2 Hz), 2.98 (1H, d, J=4.8 Hz), 1.53 (1H, ddd, J=10.4, 8.0, 6.8 Hz), 1.19 (3H, t, J=7.2 Hz), 1.13 (1H, dd, J=10.4, 6.8 Hz), 1.08 (3H, t, J=7.2 Hz), 1.06 (1H, t, J=6.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.6, 135.2, 128.6, 128.5, 128.4, 90.8, 69.1, 67.2, 62.3, 61.8, 28.2, 16.2, 15.3, 15.2. ESI-MS m/z: 295 (M^++1). HRMS Calcd for $C_{16}H_{22}O_5Na$: 317.1365 (M^++Na), found: 317.1381.

4.1.12. *N*-[(2,2-Diethoxycyclopropyl)(phenyl)methyl]-aniline (6). *Compound* **6**-*less polar*. Colorless oil; IR (neat) νcm^{-1}; 3402, 2975, 1707, 1603, 1507, 1264, 1054, 750. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.22 (5H, m), 7.06 (2H, t, J=7.5 Hz), 6.63 (1H, t, J=7.5 Hz), 6.52 (2H, d, J=7.5 Hz), 4.49 (1H, br s), 4.11 (1H, d, J=8.6 Hz), 3.86–3.53 (4H, m), 1.57 (1H, ddd, J=10.3, 8.6, 6.7 Hz), 1.22 (3H, t, J=7.1 Hz), 1.20 (3H, t, J=7.1 Hz), 1.07 (1H, dd, J=10.3, 5.9 Hz), 0.92 (1H, dd, J=6.7, 5.9 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 147.8, 143.8, 129.0, 128.4, 126.7, 126.3, 117.2, 113.4, 91.5, 62.4, 61.8, 57.1, 34.0, 18.0, 15.4, 15.1. EI-MS m/z: 311 (M^+), 266 (M^+−OEt). Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.99; H, 8.11; N, 4.46.

Compound **6**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 3382, 2882, 1603, 1513, 1296, 1121, 1052, 747. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.23 (5H, m), 7.10 (2H, t, J=7.5 Hz), 6.66 (1H, t, J=7.5 Hz), 6.51 (2H, d, J=7.5 Hz), 4.35 (1H, br s), 4.17 (1H, d, J=9.7 Hz), 3.90 (1H, dq, J=9.4, 7.1 Hz), 3.65–3.58 (2H, m), 3.11 (1H, dq, J=9.4, 7.1 Hz), 1.52 (1H, ddd, J=9.7, 9.7, 6.7 Hz), 1.32 (3H, t, J=7.1 Hz), 1.20 (1H, dd, J=9.7, 5.6 Hz), 1.08 (3H, t, J=7.1 Hz), 0.96 (1H, dd, J=6.7, 5.9 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 147.8, 143.8, 129.0, 128.4, 126.7, 126.3, 117.2, 113.4, 91.5, 62.4, 61.8, 57.1, 34.0, 18.0, 15.4, 15.1. EI-MS m/z: 311 (M^+), 266 (M^+−OEt). Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.99; H, 8.11; N, 4.46.

4.1.13. 4-(2,2-Diethoxycyclopropyl)-1-phenyl-2-butanone (8a). Colorless oil; IR (neat) 1715 νcm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.16 (5H, m), 3.73–3.48 (4H, m), 2.90 (2H, t, J=7.8 Hz), 2.74 (2H, t, J=7.8 Hz), 2.55–2.41 (2H, m), 1.77–1.54 (2H, m), 1.20 (3H, t, J=7.1 Hz), 1.18 (3H, t, J=7.1 Hz), 1.11 (1H, dq, J=10.0, 7.0 Hz), 0.94 (1H, dd, J=10.0, 5.4 Hz), 0.43 (1H, dd, J=7.0, 5.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 209.9, 141.1, 128.5, 128.3, 126.0, 91.9, 62.2, 61.4, 44.2, 42.7, 29.8, 24.7, 22.7, 18.0, 15.4, 15.3. Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.40; H, 9.08.

4.1.14. 3-(2,2-Diethoxycyclopropyl)-5-phenyl-1-penten-3-ol (9). *Compound* **9**-*less polar*. Colorless oil; IR (neat) 3496 νcm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.16 (5H, m), 5.83 (1H, dd, J=17.3, 10.7 Hz), 5.31 (1H, dd, J=17.3, 1.7 Hz), 5.15 (1H, dd, J=10.7, 1.7 Hz), 3.88 (1H, dq, J=9.5, 7.1 Hz), 3.82 (1H, dq, J=9.5, 7.1 Hz), 3.62 (1H, dq, J=9.5, 7.1 Hz), 3.50 (1H, dq, J=9.5, 7.1 Hz), 3.35 (1H, s), 2.81 (1H, ddd, J=13.8, 9.9, 7.5 Hz), 2.66 (1H, ddd, J=13.8, 9.6, 7.8 Hz), 2.02–1.93 (2H, m), 1.37 (1H, dd, J=10.5, 7.3 Hz), 1.25 (3H, t, J=7.1 Hz), 1.20 (3H, t, J=7.1 Hz), 1.14 (1H, dd, J=7.3, 5.9 Hz), 0.95 (1H, dd, J=10.5, 5.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.9, 141.9, 128.4, 128.3, 125.6, 113.0, 92.2, 72.3, 62.6, 62.2, 44.8, 32.4, 30.2, 15.4, 15.3, 13.8. Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.38; H, 9.09.

Compound **9**-*more polar*. Colorless oil; IR (neat) 3494 νcm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.15 (5H, m), 6.05 (1H, dd, J=17.3, 10.7 Hz), 5.34 (1H, dd, J=17.3, 1.3 Hz), 5.16 (1H, dd, J=10.7, 1.3 Hz), 3.86 (1H, dq, J=9.5, 7.1 Hz), 3.76 (1H, dq, J=9.5, 7.1 Hz), 3.60 (1H, dq, J=9.5, 7.1 Hz), 3.48 (1H, dq, J=9.5, 7.1 Hz), 3.45 (1H, br s), 2.74 (1H, ddd, J=13.6, 12.4, 5.2 Hz), 2.66 (1H, ddd, J=13.6, 12.1, 4.9 Hz), 1.97 (1H, ddd, J=13.6, 12.1, 5.2 Hz), 1.80 (1H, ddd, J=13.6, 12.4, 4.9 Hz), 1.36 (1H, dd, J=10.4, 7.4 Hz), 1.24 (3H, t, J=7.1 Hz), 1.25–1.21 (1H, m), 1.20 (3H, t, J=7.1 Hz), 1.02 (1H, dd, J=10.4, 5.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.5, 142.9, 128.4, 128.3, 125.6, 112.2, 91.2, 72.1, 62.5, 62.3, 42.7, 32.4, 29.8, 15.3,

15.2, 13.6. Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.50; H, 9.12.

4.1.15. 3-(2,2-Diethoxycyclopropyl)cyclopentanone (8b). Colorless oil; IR (neat) 1742 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.70–3.37 (4H, m), 2.40–1.99 (4H, m), 1.97–1.81 (2H, m), 1.68–1.56 (1H, m), 1.13–1.06 (6H, m), 1.04–0.90 (2H, m), 0.51 (0.5H, t, J=5.7 Hz), 0.47 (0.5H, t, J=5.7 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 219.11, 219.00, 91.47, 91.35, 61.92, 61.86, 61.38, 61.30, 45.12, 44.09, 38.18, 38.01, 36.13, 29.70, 29.66, 29.59, 28.68, 17.24, 17.05, 15.24, 15.20, 15.11, 15.08. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.81; H, 9.89.

4.1.16. 3-(2,2-Diethoxycyclopropyl)cyclohexanone (8c). *Compound* **8c**-*less polar*. Colorless oil; IR (neat) 1714 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76–3.66 (2H, m), 3.73 (1H, dq, J=9.5, 7.1 Hz), 3.69 (1H, dq, J=9.5, 7.1 Hz), 2.58 (1H, br d, J=14.0 Hz), 2.34 (1H, br d, J=14.3 Hz), 2.25 (1H, ddd, J=14.2, 11.5, 6.0 Hz), 2.16 (1H, dd, J=14.0, 10.5 Hz), 2.06–2.00 (1H, m), 1.93–1.88 (1H, m), 1.71–1.43 (3H, m), 1.17 (3H, t, J=7.1 Hz), 1.16 (3H, t, J=7.1 Hz), 1.02–0.95 (2H, m), 0.54–0.48 (1H, m). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 211.5, 91.5, 62.1, 61.6, 48.2, 41.3, 38.3, 30.5, 30.3, 24.9, 17.3, 15.4, 15.3. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.81; H, 9.89.

Compound **8c**-*more polar*. Colorless oil; IR (neat) 1716 ν cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78–3.69 (2H, m), 3.53 (1H, dq, J=9.5, 7.1 Hz), 3.48 (1H, dq, J=9.5, 7.1 Hz), 2.42 (1H, br d, J=13.1 Hz), 2.34 (1H, br d, J=14.2 Hz), 2.26 (1H, ddd, J=13.8, 12.1, 5.6 Hz), 2.17–2.11 (1H, m), 2.07–2.00 (2H, m), 1.70–1.45 (3H, m), 1.18 (3H, t, J=7.1 Hz), 1.17 (3H, t, J=7.1 Hz), 1.01 (1H, ddd, J=9.8, 9.8, 6.2 Hz), 0.97 (1H, dd, J=9.8, 5.1 Hz), 0.48 (1H, dd, J=6.2, 5.1 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 211.7, 91.7, 62.3, 61.6, 47.3, 41.4, 38.6, 31.7, 30.7, 25.2, 17.1, 15.4, 15.3. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.71; H, 9.83.

4.1.17. Benzyl 3-(2,2-diethoxycyclopropyl)propanoate (11). Colorless oil; IR (neat) νcm^{-1}; 2975, 1737, 1455, 1263, 1166, 1054, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (5H, m), 5.12 (2H, s), 3.74–3.49 (4H, m), 2.46 (2H, td, J=7.2, 4.3 Hz), 1.82 (1H, sext, J=7.2 Hz), 1.66 (1H, sext, J=7.2 Hz), 1.21–1.11 (1H, m), 1.20 (3H, t, J=7.1 Hz), 1.17 (3H, t, J=7.1 Hz), 0.97 (1H, dd, J=10.0, 5.5 Hz), 0.47 (1H, t, J=5.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.3, 136.1, 128.5, 128.2, 91.8, 66.1, 62.2, 61.4, 34.1, 24.6, 23.9, 18.0, 15.4, 15.3. EI-MS *m*/*z*: 292 (M^+), 263 (M^+-Et), 247 (M^+-OEt), 201 (M^+-Bn). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.64; H, 8.41.

4.1.18. Benzyl 2,2-diethoxy-3-methylcyclobutanecarboxylate (12). *Compound trans*-**12**. Colorless oil; IR (neat) νcm^{-1}; 2975, 1738, 1455, 1329, 1226, 1188, 1132, 1051, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.27 (5H, m), 5.25 (1H, d, J=12.6 Hz), 5.09 (1H, d, J=12.6 Hz), 3.64–3.50 (2H, m), 3.37 (2H, q, J=7.1 Hz), 3.30 (1H, dd, J=9.2, 5.3 Hz), 2.73–2.62 (1H, m), 2.32 (1H, ddd, J=11.2, 10.0, 5.3 Hz), 1.41 (1H, ddd, J=11.2, 9.2, 7.3 Hz), 1.18 (3H, t, J=7.1 Hz), 1.10 (3H, t, J=7.1 Hz), 1.07 (3H, d, J=5.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.4, 136.6, 128.3, 127.9, 127.8, 102.3, 66.0, 56.8, 56.1, 40.7, 37.8, 22.9, 15.2, 15.1. EI-MS *m*/*z*: 292 (M^+). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.78; H, 8.24.

Compound cis-**12**. Colorless oil; IR (neat) νcm^{-1}; 2977, 1737, 1455, 1197, 1054, 975. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (5H, m), 5.20 (1H, d, J=12.5 Hz), 5.10 (1H, d, J=12.5 Hz), 3.61 (2H, dq, J=9.7, 7.1 Hz), 3.52–3.43 (2H, m), 3.38 (1H, dq, J=9.7, 7.0 Hz), 3.21 (1H, t, J=8.8 Hz), 2.53–2.43 (1H, m), 1.97 (1H, dt, J=11.3, 8.8 Hz), 1.79 (1H, dt, J=11.3, 8.8 Hz), 1.19 (3H, t, J=7.1 Hz), 1.11 (3H, t, J=7.0 Hz), 1.07 (3H, d, J=7.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.0, 136.3, 128.4, 128.1, 127.9, 103.9, 66.2, 57.7, 57.6, 47.5, 39.9, 22.3, 15.2, 15.1, 15.0. EI-MS *m*/*z*: 292 (M^+). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.78; H, 8.24.

4.1.19. 7,7-Diethoxy-6-methyl-4-oxabicyclo[3.2.0]heptan-2-one (14a). *Compound* **14a**-*less polar*. Colorless crystals; mp 60.5–62.0 °C. IR (KBr) νcm^{-1}; 2980, 1779, 1732, 1457, 1373, 1189, 1097, 1012. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.40 (1H, dd, J=9.9, 2.2 Hz), 4.26 (1H, dd, J=9.9, 7.7 Hz), 3.74 (1H, dq, J=9.4, 7.0 Hz), 3.51–3.42 (3H, m), 3.36 (1H, dd, J=7.7, 2.3 Hz), 2.96 (1H, qd, J=7.7, 2.2 Hz), 2.86–2.78 (1H, m), 1.21 (3H, t, J=7.0 Hz), 1.15 (3H, t, J=7.0 Hz), 1.10 (3H, d, J=7.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 175.32, 100.8, 67.6, 58.3, 56.8, 49.5, 41.3, 30.1, 15.0, 14.9, 10.0. EI-MS *m*/*z*: 214 (M^+). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.85; H, 8.34.

Compound **14a**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 2977, 2930, 1775, 1455, 1371, 1259, 1164, 1052, 928. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (1H, dd, J=9.4, 7.1 Hz), 4.22 (1H, dd, J=9.4, 2.1 Hz), 3.58 (1H, dq, J=9.8, 7.1 Hz), 3.54–3.41 (2H, m), 3.37 (1H, dq, J=9.4, 7.1 Hz), 3.28 (1H, d, J=8.1 Hz), 2.51–2.36 (2H, m), 1.19 (3H, t, J=7.1 Hz), 1.16 (3H, t, J=7.1 Hz), 1.15 (3H, d, J=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.7, 99.4, 73.3, 57.2, 56.7, 45.9, 46.1, 34.5, 15.0, 14.9, 14.2. EI-MS *m*/*z*: 214 (M^+). HRMS Calcd for $C_{11}H_{18}O_4$: 214.1205 (M^+), found: 214.1206.

4.1.20. 4-(2,2-Diethoxycyclopropyl)dihydro-2(3*H*)-furanone (13a). IR (neat) νcm^{-1}; 2977, 1779, 1458, 1372, 1267, 1166, 1054, 1018. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (1H, dd, J=8.8, 7.0 Hz), 4.09 (1H, dd, J=8.8, 6.7 Hz), 3.76–3.66 (2H, m), 3.58 (1H, dq, J=9.5, 7.1 Hz), 3.15 (1H, dq, J=9.3, 7.1 Hz), 2.71 (1H, dd, J=19.6, 10.7 Hz), 2.41–2.30 (2H, m), 1.23–1.16 (1H, m), 1.20 (3H, t, J=7.1 Hz), 1.19 (3H, t, J=7.1 Hz), 1.07 (1H, dd, J=9.9, 6.0 Hz), 0.61 (1H, t, J=6.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 177.0, 90.7, 72.7, 62.3, 61.8, 35.3, 35.0, 27.4, 17.1, 15.3, 15.2. EI-MS *m*/*z*: 215 (M^++1), 169 (M^+-OEt). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.64; H, 8.30.

4.1.21. 4-(2,2-Diethoxycyclopropyl)tetrahydro-2*H*-pyran-2-one (13b). *Compound* **13b**-*less polar*. Colorless oil; IR (neat) νcm^{-1}; 2976, 1739, 1446, 1399, 1285, 1252, 1221, 1196, 1060. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.44 (1H, dt, J=11.3, 4.1 Hz), 4.25 (1H, td, J=11.3, 4.1 Hz), 3.75 (1H, dq, J=9.4, 7.1 Hz), 3.72 (1H, dq, J=9.4, 7.1 Hz), 3.53 (1H, dq, J=9.4, 7.1 Hz), 3.44 (1H, dq, J=9.4, 7.1 Hz), 2.84 (1H, dd, J=17.5, 5.9 Hz), 2.31 (1H, dd, J=17.5, 9.4 Hz), 1.99–1.93 (1H, m), 1.76–1.65 (2H, m), 1.19 (3H, t, J=

7.1 Hz), 1.18 (3H, t, J=7.1 Hz), 1.05 (1H, dd, J=9.8, 5.5 Hz), 1.00 (1H, td, J=9.8, 5.5 Hz), 0.57 (1H, t, J=5.5 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 171.0, 91.2, 68.6, 62.2, 61.8, 36.7, 31.6, 30.0, 28.2, 17.3, 15.4, 15.3. HRMS Calcd for $C_{12}H_{20}O_4$: 228.1362 (M^+), found: 228.1340.

Compound **13b**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 2976, 1741, 1454, 1398, 1307, 1254, 1223, 1196, 1063. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (1H, dt, J=11.4, 4.2 Hz), 4.25 (1H, ddd, J=11.4, 10.1, 4.0 Hz), 3.80–3.68 (2H, m), 3.56 (1H, dq, J=9.5, 7.0 Hz), 3.47 (1H, dq, J=9.5, 7.0 Hz), 2.69 (1H, ddd, J=17.2, 7.1, 1.2 Hz), 2.31 (1H, dd, J=17.2, 9.9 Hz), 2.11–2.04 (1H, m), 1.80–1.65 (2H, m), 1.20 (3H, t, J=7.0 Hz), 1.19 (3H, t, J=7.0 Hz), 1.08–0.98 (2H, m), 0.60–0.52 (1H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.3, 91.3, 68.6, 62.3, 61.8, 35.7, 31.3, 30.2, 29.3, 17.1, 15.4, 15.3. EI-MS *m*/*z*: 229 (M^++1), 183 (M^+−OEt). HRMS Calcd for $C_{12}H_{20}O_4$: 228.1362 (M^+), found: 228.1368.

4.1.22. *N*,*N*-Dimethyl-2,2-diethoxy-3-methylcyclobutanecarboxamide (17a). *Compound* **17a**-*less polar*. Colorless oil; IR (neat) νcm^{-1}; 2977, 1650, 1398, 1263, 1192, 1054, 968, 659. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.46–3.42 (3H, m), 3.27–3.20 (2H, m), 3.10 (3H, s), 2.87 (3H, s), 2.32 (1H, ddq, J=9.8, 8.8, 6.8 Hz), 1.90 (1H, q, J=10.2 Hz), 1.75 (1H, dt, J=10.2, 8.8 Hz), 1.14 (3H, t, J=7.1 Hz), 1.07 (3H, t, J=7.0 Hz), 1.02 (3H, d, J=6.8 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 170.5, 104.2, 56.9, 56.2, 46.6, 38.1, 36.9, 35.4, 22.9, 15.4, 15.2, 14.3. EI-MS *m*/*z*: 229 (M^+), 200 (M^+−Et), 184 (M^+−OEt). HRMS Calcd for $C_{12}H_{23}NO_3$: 229.1678 (M^+), found: 229.1674.

Compound **17a**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 2975, 1649, 1393, 1226, 1134, 1060, 985. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59–3.48 (2H, m), 3.39 (1H, dd, J=8.3, 3.3 Hz), 3.34 (2H, q, J=7.1 Hz), 3.02 (3H, s), 2.93 (3H, s), 2.68–2.59 (1H, m), 2.33 (1H, ddd, J=10.0, 9.4, 3.3 Hz), 1.27 (1H, dt, J=10.0, 8.3 Hz), 1.21 (3H, t, J=7.1 Hz), 1.06 (3H, t, J=7.1 Hz), 1.02 (3H, d, J=5.9 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 171.2, 102.8, 56.6, 56.4, 44.4, 39.3, 37.3, 35.9, 24.2, 15.2, 15.1 14.5. EI-MS *m*/*z*: 229 (M^+), 184 (M^+−OEt). HRMS Calcd for $C_{12}H_{23}NO_3$: 229.1678 (M^+), found: 229.1664.

4.1.23. *N*,*N*-Dibenzyl-2,2-diethoxy-3-methylcyclobutanecarboxamide (17b). Colorless oil; IR (neat) νcm^{-1}; 2977, 1650, 1443, 1424, 1218, 1198, 1064, 702. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (2H, t, J=7.6 Hz), 7.32–7.22 (6H, m), 7.18 (2H, d, J=7.4 Hz), 5.41 (1H, d, J=14.1 Hz), 5.26 (1H, d, J=17.3 Hz), 5.15 (1H, d, J=17.3 Hz), 4.65 (1H, d, J=14.1 Hz), 3.39–3.32 (2H, m), 3.30–3.20 (2H, m), 3.11 (1H, dq, J=9.2, 7.0 Hz), 2.36–2.26 (1H, m), 2.03 (1H, dt, J=13.2, 10.2 Hz), 1.84 (1H, dt, J=10.2, 8.6 Hz), 1.09 (3H, t, J=7.1 Hz), 1.07 (3H, d, J=6.9 Hz), 1.01 (3H, t, J=7.0 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 171.0, 137.1, 137.0, 129.4, 128.9, 128.3, 127.4, 127.3, 126.5, 104.2, 57.1, 57.0, 48.8, 48.4, 46.9, 38.1, 23.3, 15.2, 14.4. EI-MS *m*/*z*: 381 (M^+), 336 (M^+−OEt), 290 (M^+−Bn). Anal. Calcd for $C_{24}H_{31}NO_3$: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.37; H, 8.10; N, 3.75.

4.1.24. 2,2-Diethoxy-*N*,*N*-diisopropyl-3-methylcyclobutanecarboxamide (17c). Colorless oil; IR (neat) νcm^{-1}; 2970, 1643, 1442, 1374, 1291, 1191, 1134, 1058. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57–4.46 (1H, m), 3.50–3.39 (4H, m), 3.42–3.31 (1H, m), 3.14 (1H, dd, J=10.0, 8.5 Hz), 2.35–2.24 (1H, m), 1.92 (1H, q, J=10.0 Hz), 1.75 (1H, dt, J=10.0, 8.5 Hz), 1.38 (3H, d, J=6.7 Hz), 1.36 (3H, d, J=6.8 Hz), 1.19 (3H, d, J=6.5 Hz), 1.17 (3H, t, J=7.0 Hz), 1.12 (3H, t, J=7.0 Hz), 1.12 (3H, d, J=6.4 Hz), 1.05 (3H, d, J=6.8 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.2, 103.9, 57.1, 56.9, 47.9, 47.8, 45.5, 38.0, 23.3, 20.9, 20.0, 19.5, 15.3, 15.2, 14.3. EI-MS *m*/*z*: 285 (M^+). Anal. Calcd for $C_{16}H_{31}NO_3$: C, 67.33; H, 10.95; N, 4.91. Found: C, 67.13; H, 10.87; N, 4.89.

4.1.25. 2,2-Diethoxy-*N*,3-dimethyl-*N*-phenylcyclobutanecarboxamide (17d). *Compound cis*-**17d**. Colorless oil; IR (neat) νcm^{-1}; 2975, 1657, 1496, 1387, 1190, 1054, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, t, J=7.2 Hz), 7.32–7.22 (3H, m), 3.53–3.41 (2H, m), 3.27 (3H, s), 3.13–3.04 (2H, m), 3.01–2.93 (1H, m), 2.29–2.19 (1H, m), 1.92–1.85 (1H, m), 1.79–1.69 (1H, m), 1.20 (3H, t, J=7.0 Hz), 1.09 (3H, d, J=6.9 Hz), 1.00 (3H, t, J=6.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.6, 144.0, 129.2, 128.0, 127.3, 103.6, 57.1, 56.3, 45.4, 38.8, 37.9, 23.5, 15.4, 15.0, 14.4. EI-MS *m*/*z*: 292 (M^++1), 262 (M^+−Et). Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.78; H, 8.67; N, 4.75.

Compound trans-**17d**. Colorless oil; IR (neat) νcm^{-1}; 2974, 1657, 1496, 1380, 1053, 701. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (2H, t, J=7.2 Hz), 7.29–7.21 (3H, m), 3.38–3.29 (2H, m), 3.28 (3H, s), 3.22 (1H, d, J=8.0 Hz), 2.83–2.72 (2H, m), 2.29–2.14 (2H, m), 1.26–1.25 (1H, m), 1.15 (3H, t, J=7.0 Hz), 0.95 (3H, d, J=6.9 Hz), 0.83 (3H, t, J=6.9 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 171.2, 144.2, 129.2, 128.8, 127.4, 102.3, 56.4, 55.7, 44.3, 39.5, 38.0, 24.8, 15.2, 15.1, 14.3. EI-MS *m*/*z*: 292 (M^++1), 262 (M^+−Et), 246 (M^+−OEt). Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 70.17; H, 8.68; N, 4.77.

4.1.26. 2,2-Diethoxy-3-methyl-*N*,*N*-diphenylcyclobutanecarboxamide (17e). White crystal; mp 87.5–88.4 °C. IR (KBr) νcm^{-1}; 2972, 1660, 1479, 1365, 1134, 1055, 982. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.13 (10H, m), 3.53–3.33 (3H, m), 2.93–2.82 (2H, m), 2.33 (1H, td, J=9.8, 1.8 Hz), 2.25 (1H, dq, J=2.8, 7.0 Hz), 1.29–1.21 (1H, m), 1.25 (3H, t, J=7.0 Hz), 0.99 (3H, d, J=6.8 Hz), 0.87 (3H, t, J=7.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.5, 143.2, 129.9, 128.8, 126.9, 125.8 103.0, 56.4, 55.9, 45.1, 39.4, 24.3, 15.3, 15.11, 14.4. EI-MS *m*/*z*: 353 (M^+). Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.78; H, 7.46; N, 4.15.

4.1.27. 3-(2,2-Diethoxycyclopropyl)-*N*,*N*-diphenylpropanamide (18e). Colorless oil; IR (neat) νcm^{-1}; 2975, 1732, 1675, 1593, 1492, 1369, 1273, 1054. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.22 (10H, m), 3.68–3.48 (4H, m), 2.39–2.32 (2H, m), 1.96–1.83 (1H, m), 1.68–1.57 (1H, m), 1.18 (3H, t, J=7.1 Hz), 1.16 (3H, t, J=7.1 Hz), 1.16–1.08 (1H, m), 0.91 (1H, dd, J=9.9, 5.4 Hz), 0.38 (1H, t, J=5.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 172.9, 142.9, 130.0–125.0 (aromatic), 92.0, 62.1, 61.4, 35.0, 25.0, 24.3, 17.9, 15.4, 15.3. EI-MS *m*/*z*: 353 (M^+), 324 (M^+−Et).

Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.43; H, 7.69; N, 4.07.

4.1.28. *N,N*-Dibenzyl-4,4-diethoxy-3-methyl-1-cyclobutene-1-carboxamide (20). Colorless oil; IR (neat) νcm^{-1}; 2975, 1639, 1611, 1421, 1219, 1188, 1048, 979. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.17 (10H, m), 6.44 (1H, s), 4.67 (1H, s), 4.65 (1H, s), 4.63 (1H, d, J=14.6 Hz), 4.50 (1H, d, J=14.6 Hz), 3.74 (1H, dq, J=9.4, 7.1 Hz), 3.72–3.64 (2H, m), 3.56 (1H, dq, J=9.4, 7.1 Hz), 2.98 (1H, q, J=7.0 Hz), 1.18 (6H, t, J=7.1 Hz), 1.12 (3H, d, J=7.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.5, 143.7, 142.3, 137.0, 136.9, 128.8, 128.7, 128.5, 128.4, 127.4, 127.3, 127.1, 105.0, 59.4, 59.3, 50.3, 47.9, 46.8, 15.4, 15.3, 13.8. EI-MS *m/z*: 379 (M^+). HRMS Calcd for $C_{24}H_{29}NO_3$: 379.2147 (M^+), found: 379.2134.

4.2. General procedure for the reaction of 1 with acryloyl oxazolidinone derivatives in the presence of Lewis acid

A solution of triethyl orthoacrylate (174 mg, 1 mmol) in toluene (2 mL) was added to a solution of 'Cp_2Zr' (1.2 mmol), prepared from Cp_2ZrCl_2 with *n*-BuLi at −78 °C. After being stirred for 3 h at room temperature, the solvent was removed in vacuo and CH_2Cl_2 (8 mL) was added to the residue. A solution of acryloyl oxazolidinone derivative (1.2 mmol) shown in Table 4 in CH_2Cl_2 (2 mL) and diethylaluminum chloride (1.0 M *n*-hexane solution, 1.5 mL, 1.5 mmol) were added to the mixture at −78 °C and then the mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with diethyl ether after addition of NH_4Cl aq and the extract was washed with brine, dried over $MgSO_4$. Purification of the residue, obtained by evaporation of the solvent, by neutral silica gel column chromatography (hexane–AcOEt) gave the product **22** shown in Table 5.

4.2.1. 3-[3-(2,2-Diethoxycyclopropyl)propanoyl]-1,3-oxazolidin-2-one (22a). Colorless oil; IR (neat) νcm^{-1}; 2976, 1782, 1700, 1389, 1212, 1053, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (2H, t, J=8.1 Hz), 4.01 (2H, t, J=8.1 Hz), 3.74–3.53 (4H, m), 3.09–2.94 (2H, m), 1.93–1.82 (1H, m), 1.70–1.59 (1H, m), 1.27–1.20 (1H, m), 1.19 (3H, t, J=7.0 Hz), 1.18 (3H, t, J=7.0 Hz), 0.97 (1H, dd, J=9.9, 5.6 Hz), 0.48 (1H, t, J=5.6 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.2, 153.5, 91.9, 62.1, 62.0, 61.4, 42.5, 34.9, 24.6, 23.1, 18.0, 15.4, 15.3. EI-MS *m/z*: 271 (M^+). Anal. Calcd for $C_{13}H_{21}NO_5$: C, 57.55; H, 7.80; N, 5.16. Found: C, 57.44; H, 7.83; N, 5.19.

4.2.2. 3-[3-(2,2-Diethoxycyclopropyl)-2-methylpropanoyl]-1,3-oxazolidin-2-one (22b). *Compound* **22b**-*less polar*. Colorless oil; IR (neat) νcm^{-1}; 2976, 1780, 1699, 1388, 1267, 1200, 1055. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42–4.36 (2H, m), 4.08–3.95 (2H, m), 3.82 (1H, tq, J=6.7, 6.7 Hz), 3.74–3.49 (4H, m), 1.79–1.61 (2H, m), 1.24–1.14 (10H, m), 0.95 (1H, dd, J=9.9, 5.4 Hz), 0.54 (1H, t, J=5.4 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 177.1, 153.1, 91.8, 62.6, 61.8, 61.3, 42.8, 37.2, 32.0, 22.9, 17.9, 16.5, 15.4. EI-MS *m/z*: 285 (M^+). Anal. Calcd for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.13; N, 4.91. Found: C, 58.85; H, 8.17; N, 4.93.

Compound **22b**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 2976, 1781, 1698, 1453, 1388, 1262, 1199, 1054, 1001, 954. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (2H, t, J=8.1 Hz), 4.02 (2H, t, J=8.1 Hz), 3.84 (1H, sext, J=6.9 Hz), 3.74–3.54 (4H, m), 2.09 (1H, ddd, J=13.9, 6.9, 4.9 Hz), 1.32 (1H, ddd, J=13.6, 9.4, 6.9 Hz), 1.22 (3H, d, J=6.9 Hz), 1.20 (3H, t, J=7.1 Hz), 1.18 (3H, t, J=7.1 Hz), 1.18–1.10 (1H, m), 0.99 (1H, dd, J=9.9, 5.5 Hz), 0.48 (1H, t, J=5.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 177.1, 153.1, 91.3, 62.1, 61.8, 61.4, 42.8, 37.4, 31.9, 23.3, 18.4, 17.3, 15.4, 15.3. EI-MS *m/z*: 285 (M^+), 256 (M^+−Et), 240 (M^+−OEt). HRMS Calcd for $C_{14}H_{23}NO_5$: 285.1576 (M^+), found: 285.1561.

4.2.3. 3-[3-(2,2-Diethoxycyclopropyl)butanoyl]-1,3-oxazolidin-2-one (22c). *Compound* **22c**-*less polar*. Colorless oil; IR (neat) νcm^{-1}; 2976, 1782, 1699, 1388, 1295, 1220, 1060. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (2H, t, J=8.0 Hz), 4.02 (2H, td, J=8.0, 3.4 Hz), 3.80–3.64 (2H, m), 3.55–3.40 (2H, m), 3.16 (1H, dd, J=15.5, 7.6 Hz), 2.75 (1H, dd, J=15.5, 6.2 Hz), 1.87–1.74 (1H, m), 1.17 (3H, t, J=7.1 Hz), 1.16 (3H, t, J=7.1 Hz), 1.07 (1H, td, J=10.0, 6.4 Hz), 1.06 (3H, d, J=6.9 Hz), 0.98 (1H, dd, J=10.0, 6.3 Hz), 0.48 (1H, t, J=6.3 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 172.3, 153.5, 92.3, 62.6, 61.4, 42.5, 42.4, 31.4, 30.1, 19.8, 17.8, 15.4. EI-MS *m/z*: 285 (M^+). Anal. Calcd for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.13; N, 4.91. Found: C, 58.66; H, 8.14; N, 4.91.

Compound **22c**-*more polar*. Colorless oil; IR (neat) νcm^{-1}; 2975, 1782, 1700, 1388, 1222, 1059, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (2H, t, J=8.1 Hz), 4.01 (2H, td, J=8.1, 2.4 Hz), 3.82–3.68 (2H, m), 3.58–3.42 (2H, m), 3.11 (1H, dd, J=15.4, 5.3 Hz), 2.83 (1H, dd, J=15.4, 8.7 Hz), 1.87–1.75 (1H, m), 1.19 (3H, t, J=7.1 Hz), 1.18 (3H, t, J=7.1 Hz), 1.10 (3H, d, J=6.6 Hz), 1.04 (1H, td, J=10.0, 6.5 Hz), 0.94 (1H, dd, J=9.9, 6.5 Hz), 0.57 (1H, t, J=6.5 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 172.8, 153.5, 91.9, 62.6, 61.9, 61.5, 42.6, 41.3, 31.6, 30.4, 20.5, 17.7, 15.5, 15.3. EI-MS *m/z*: 285 (M^+). Anal. Calcd for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.13; N, 4.91. Found: C, 58.63; H, 8.10; N, 4.88.

4.2.4. 3-[3-(2,2-Diethoxycyclopropyl)-3-methylbutanoyl]-1,3-oxazolidin-2-one (22d). Colorless oil; IR (neat) νcm^{-1}; 2976, 1780, 1698, 1391, 1361, 1219, 1052, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (2H, t, J=7.1 Hz), 4.07–3.98 (2H, m), 3.76 (1H, dq, J=9.5, 7.1 Hz), 3.74 (1H, dq, J=9.5, 7.1 Hz), 3.52–3.44 (2H, m), 3.16 (1H, d, J=15.3 Hz), 2.92 (1H, d, J=15.3 Hz), 1.28 (1H, dd, J=10.3, 8.0 Hz), 1.18 (3H, t, J=7.1 Hz), 1.17 (3H, t, J=7.1 Hz), 1.11 (3H, s), 1.07 (3H, s), 0.88–0.83 (2H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 172.1, 153.6, 91.5, 62.2, 61.6, 61.3, 45.3, 42.7, 35.0, 33.0, 26.6, 25.4, 15.5, 15.4, 14.3. EI-MS *m/z*: 299 (M^+), 270 (M^+−Et), 254 (M^+−OEt). Anal. Calcd for $C_{15}H_{25}NO_5$: C, 60.18; H, 8.42; N, 4.68. Found: C, 59.98; H, 8.31; N, 4.66.

4.2.5. (4*S*)-4-benzyl-3-[3-(2,2-diethoxycyclopropyl)propanoyl]-1,3-oxazolidin-2-one (24). Colorless oil; IR (neat) νcm^{-1}; 2975, 1784, 1700, 1388, 1269, 1211, 1054, 703. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (2H, t, J=7.1 Hz), 7.27 (1H, t, J=7.1 Hz), 7.21 (2H, d, J=7.6 Hz), 4.70–4.64 (1H, m), 4.20 (1H, dd, J=8.9, 7.7 Hz), 4.16 (1H, dd, J=8.9,

3.0 Hz), 3.80–3.51 (4H, m), 3.31 (1H, dt, $J=13.4$, 2.4 Hz), 3.11–2.95 (2H, m), 2.77 (1H, dt, $J=13.4$, 9.0 Hz), 1.97–1.88 (1H, m), 1.72–1.63 (1H, m), 1.30–1.24 (1H, m), 1.22 (3H, t, $J=7.1$ Hz), 1.19 (3H, t, $J=7.0$ Hz), 1.01 (1H, dd, $J=9.9$, 5.4 Hz), {0.53 (t, $J=5.4$ Hz), 0.51 (t, $J=5.4$ Hz) 1H}. ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 173.0, 153.4, 135.3, 129.4, 128.9, 127.3, 92.0, 66.2, 62.2, 61.5, 55.2, 37.9, 35.4, 24.7, 23.1, 18.0, 15.4, 15.3. EI-MS *m/z*: 361 (M^+), 316 (M^+-OEt). Anal. Calcd for $C_{20}H_{27}NO_5$: C, 66.46; H, 7.53; N, 3.88. Found: C, 66.21; H, 7.37; N, 3.89.

4.3. 3-(2,2-Diethoxycyclopropyl)-propionic acid benzyl ester (25). Under an argon atmosphere, to a solution of benzyl alcohol (19.1 mg, 0.18 mmol) in THF (1.5 mL) was added *n*-butyllithium (1.46 M in hexane, 0.09 mL, 0.13 mmol) at −78 °C and the mixture was stirred at 0 °C for 15 min. A solution of **24** (32 mg, 0.09 mmol) in THF (1 mL) was added to the reaction mixture at −78 °C and then the temperature was raised to ambient temperature. After being stirred for 1 h, saturated aqueous ammonium chloride was added to the mixture and the reaction mixture was extracted with ether for three times. Organic layer was washed with brine, dried over magnesium sulfate, and concentrated under vacuum. The residue was purified by neutral silica gel column chromatography to afford product **25** (25 mg, 0.084 mmol, 95%). Spectral data of **25** was identified with those of compound **11**.

References and notes

1. For reviews on preparation and reactions of allylic organometallic reagents, see: (a) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (c) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243. (d) Roush, W. R. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 2. (e) Yamamoto, Y. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 2. (f) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.
2. (a) Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 1295. (b) Ito, H.; Nakamura, T.; Taguchi, T.; Hanzawa, Y. *Tetrahedron* **1995**, *51*, 4507. (c) Ito, H.; Motoki, Y.; Taguchi, T.; Hanzawa, Y. *J. Am. Chem. Soc.* **1993**, *115*, 8835. (d) Ito, H.; Ikeuchi, Y.; Taguchi, T.; Hanzawa, Y.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 5469. (e) Ito, H.; Hanzawa, Y.; Taguchi, T. *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 217. (f) Ito, H. *Chemistry and Chemical Industry* **1995**, *48*, 155. (g) Hanzawa, Y.; Ito, H.; Taguchi, T. *Synlett* **1995**, 299–305.
3. Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 7873.
4. (a) Ito, H.; Taguchi, T. *Tetrahedron Lett.* **1997**, *38*, 5829. (b) Sato, A.; Ito, H.; Taguchi, T. *J. Org. Chem.* **2000**, *65*, 918. (c) Sato, A.; Ito, H.; Yamaguchi, Y.; Taguchi, T. *Tetrahedron Lett.* **2000**, *41*, 10239.
5. (a) Ito, H.; Kuroi, H.; Ding, H.; Taguchi, T. *J. Am. Chem. Soc.* **1998**, *120*, 6623. (b) Ito, H.; Sato, A.; Taguchi, T. *Tetrahedron Lett.* **1999**, *40*, 3217. (c) Ito, H.; Sato, A.; Kusanagi, T.; Taguchi, T. *Tetrahedron Lett.* **1999**, *40*, 3397.
6. *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; See also Ref. 1f.
7. Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835.
8. Stetter, H.; Uerdingen, W. *Synthesis* **1973**, 207.
9. Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.
10. Reviews of α,β-unsaturated acyl anion equivalent based on the heteroatom stabilized allylic and allenic anions; (a) Yamamoto, Y. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 2. (b) Yamamoto, H. In Trost, B. M., Fleming, I., Eds.; Comprehensive organic synthesis; Pergamon: Oxford, 1991; Vol. 2. Addition of α,β-unsaturated acyl zirconiums as unmasked acyl anions with aldehyde and ketone; (c) Harada, S.; Taguchi, T.; Tabuchi, N.; Narita, K.; Hanzawa, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1696 and references cited. See also; (d) Hanzawa, Y.; Tabuchi, N.; Taguchi, T. *Tetrahedron Lett.* **1998**, *39*, 8141. (e) Hanzawa, Y. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, 2002.
11. Hena, M. A.; Terauchi, S.; Kim, C.; Horiike, M.; Kiyooka, S. *Tetrahedron: Asymmetry* **1998**, *9*, 1883.
12. (a) Schuda, P. F.; Ebner, C. B.; Potlock, S. J. *Synthesis* **1987**, *12*, 1055. (b) Trova, M. P.; Gauuan, P. J. F.; Pechulis, A. D.; Bubb, S. M.; Bocckino, S. B.; Crapoc, J. D.; Dayc, B. J. *Bioorg. Med. Chem.* **2003**, *11*, 2695.
13. Examples for the cyclopropanation reaction of monoalkoxyallylic metals with carbonyl compounds. (a) Hoffmann, R. W.; Metternich, R. *Liebigs Ann. Chem.* **1985**, 2390. (b) Barrett, A. G. M.; Seefeld, M. A. *Tetrahedron* **1993**, *49*, 7857. (c) Marshall, J. A.; Luke, G. P. *J. Org. Chem.* **1991**, *56*, 483. (d) Marshall, J. A.; Jablonowski, J. A.; Luke, G. P. *J. Org. Chem.* **1994**, *59*, 7825.
14. For reviews on the [2+2]-cycloaddition of ketene acetal with α,β-unsaturated carbonyl compound, see: (a) *Carbocyclic four-membered ring compounds*; de Meijere, A., Ed.; Houben-Weyl Methods of Organic Chemistry; Thieme: Stuttgart, 1997; Vol. 17e/f. (b) Lee-Ruff, E.; Mladenova, G. *Chem. Rev.* **2003**, *103*, 1449. (c) Fruhauf, H.-W. *Chem. Rev.* **1997**, *97*, 523. (d) Crimmins, M. T.; Reinhold, T. L. *Org. React.* **1993**, *44*, 297. (e) Brannock, K. C.; Burpitt, R. D.; Thweatt, J. G. *J. Org. Chem.* **1964**, *29*, 940.