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Zirconium-catalyzed cyclopropanation of α-olefins mediated by $R'CO_2R''$ and Cl_nAlEt_{3-n}

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ABSTRACT

A Cp_2ZrCl_2-catalyzed one-pot cyclopropanation method has been developed to afford alkoxycyclopropanes and cyclopropanols from α-olefins involving esters of carboxylic acids and Cl_nAlEt_{3-n}.

1. Introduction

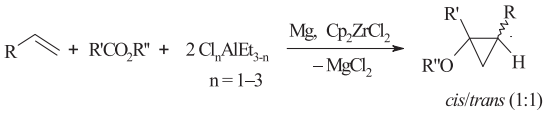
After the first synthesis of a cyclopropane derivative in 1884 by William Henry Perkin, the chemistry of these compounds has leapt forward since then. The interest of synthetic chemists to compounds bearing the cyclopropane ring is not accidental. Widely represented in nature, they play a fairly fundamental role due to their different biological activities. Many of them are applied as pesticides and insecticides (pyrethroids) to protect plants against various pests and rodents, as well as drugs in medical practice for treating many diseases.

In recent years, along with the well-known classical methods,[1] the catalytic methods for a synthesis of cyclopropane derivatives using organometallic compounds are especially popular and promising.[2,3] In continuation of our systematic studies on chemical transformations of organoaluminum compounds (OAC)[4] and also to elaborate an efficient catalytic one-pot preparative method to prepare substituted cyclopropanes we have examined the reaction of α-olefins with carboxylic esters involving alkylchloroalanes in the presence of zirconium and titanium-based metal complex catalysts. Now, we report the results of our further studies dealing with applications of the olefin cyclopropanation reaction.

2. Results and discussion

Recently, we found that the interaction between styrene and Cl_nAlEt_{3-n} (1:2 ratio, n=1–3) in the presence of carboxylic esters and metallic Mg as an acceptor of halogenide ions together with Cp_2ZrCl_2 catalyst (10 mol%) in THF (~20 °C, 8 h) leads to the formation of stereoisomeric (*cis*/*trans*)-1-alkoxy-1-alkyl-2-phenylcyclopropanes **1a**–**e** (1:1 molar ratio) in 40–52% total yield.[5]

The relative ease with which cyclopropane derivatives are formed, has stimulated continued exploration of these reactions. Therefore, along with styrene under optimized conditions, we have tested other aryl olefins, such as *ortho*-, *meta*-, *para*-methylstyrene, *para*-phenylstyrene, *ortho*-methoxystyrene and 1-vinyl naphthalene (Scheme 1, Table 1).



(a) R = Ph, R' = Me, R" = Et; (b) R = Ph, R' = Me, R" = Bu^n; (c) R = Ph, R' = Me, R" = allyl; (d) R = Ph, R' = Et, R" = Am^i; (e) R = Ph, R' = Am, R" = Me; (f) R = *o*-MePh, R' = Me, R" = Et; (g) R = *m*-MePh, R' = Me, R" = Et; (h) R = *p*-MePh, R' = Me, R" = Et; (i) R = *p*-PhPh, R' = Me, R" = Et; (j) R = *o*-OMePh, R' = Me, R" = Et; (k) R = Naphth, R' = Me, R" = Et.

Scheme 1.

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Table 1
Influence of the aryl olefin and carboxylate structure on the yield of alkoxycyclopropanes

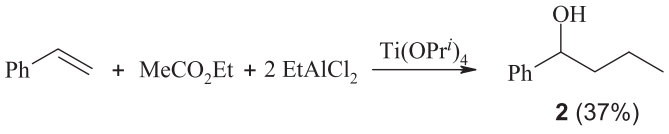
Entry	Product	Cl_nAlEt_{3-n}	R	R′	R″	cis/trans ratio	Yield[a] (%)
1	**1a**	$EtAlCl_2$	Ph	Me	Et	1:1	52
2	**1a**	Et_2AlCl	Ph	Me	Et	1:1	50
3	**1a**	$AlCl_3$	Ph	Me	Et	1:1	46
4	**1b**	$EtAlCl_2$	Ph	Me	^{n}Bu	1:1	50
5	**1c**	$EtAlCl_2$	Ph	Me	Allyl	1:1	40
6	**1d**	$EtAlCl_2$	Ph	Et	^{i}Am	1:1	49
7	**1e**	$EtAlCl_2$	Ph	^{n}Am	Me	1:1	40
8	**1f**	$EtAlCl_2$	*o*-MePh	Me	Et	1:1	45
9	**1g**	$EtAlCl_2$	*m*-MePh	Me	Et	1:1	49
10	**1h**	$EtAlCl_2$	*p*-MePh	Me	Et	1:1	52
11	**1i**	$EtAlCl_2$	*p*-PhPh	Me	Et	1:1	46
12	**1j**	$EtAlCl_2$	*o*-OMePh	Me	Et	1:1	44
13	**1k**	$EtAlCl_2$	Naphth	Me	Et	1:1	48

[a] Isolated yield.

The formation of the appropriate *cis*/*trans*-alkoxycyclopropanes **1a**–**k** clearly shows that the above reaction is general in nature (the assignment of a cis or trans prefix to any of these isomers has been done on the basis of the analysis of one-dimensional (^{1}H, ^{13}C) and two-dimensional (COSY, HMBC, HSQC) NMR spectra of the enriched fractions isolated by column chromatography).

We compared our method to transform styrene into isomeric phenylalkoxycyclopropanesand the well-known Kulinkovich reaction,[2,6] which allows the synthesis of cyclopropanols from esters using dialkyldialkoxytitanium reagents, generated in situ from Grignard reagents and titanium(IV) alkoxides. Certain analogy in approaches to the preparation of cyclopropane derivatives from carboxylic esters prompted us to modify this reaction using $EtAlCl_2$ (or Et_2AlCl) instead of Grignard reagent and $Ti(O^iPr)_4$ instead of Cp_2ZrCl_2.

However, the modified reaction provided evidence for the formation of acyclic secondary alcohol **2** in 37% yield, instead of the expected cyclopropanol (Scheme 2).



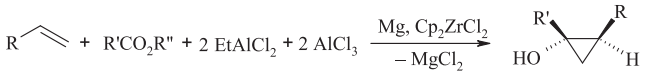
Scheme 2.

Taking into account all the above, and in order to use the developed method for the synthesis of alkyl substituted alkoxycyclopropanes **1**, we studied the interaction between Cl_nAlEt_{3-n}, carboxylic esters and aliphatic α-olefins including oct-1-ene, dec-1-ene, octa-1,7-diene, deca-1,9-diene, allyl benzene, 1-allyl naphthalene and 4-vinyl cyclohex-1-ene in the presence of Cp_2ZrCl_2 as a catalyst.

Amazingly, the reaction of oct-1-ene with ethyl acetate resulted in the formation of *cis*-1-methyl-2-hexylcyclopropanol **4a** in 42% yield (Scheme 3) instead of expected alkoxycyclopropanes as described above. This reaction proceeds in the presence of twofold excess of $EtAlCl_2$ (or Et_2AlCl) in combination with an equimolar amount of $AlCl_3$, metallic Mg and 10 mol % Cp_2ZrCl_2 as a catalyst and does not occur in the absence of $AlCl_3$. The yields of the products remain practically unchanged in the presence of Et_2AlCl (Table 2).

The structure of **4a** was confirmed by means of spectroscopic methods and by comparison with the known sample.[6,7]

The one-dimensional ^{1}H NMR spectra of compound **4a** has the characteristic signal of the cyclopropane hydrogen at 0.04 ppm and the singlet signal at 1.39 ppm belonging to the methyl protons. For the purpose of reliable NMR signal assignments and determination



4a–g

(a) R = Hex, R' = Me, R" = Et; (b) R = Oct, R' = Me, R" = Et; (c) R = Bn, R' = Me, R" = Et; (d) R = 1-NaphthMe, R' = Me, R" = Et; (e) R = Cyclohex-3-enyl, R' = Me, R" = Et; (f) R = Hex, R' = Et, R" = Am; (g) R = Hex, R' = Am, R" = Me.

Scheme 3.

Table 2
Influence of the aliphatic α-olefin and carboxylate structure on the yield of substituted cyclopropanols

Entry	Product	R	R′	R″	Yield[a] (%)
1	**4a**	Hex	Me	Et	42
2	**4b**	Oct	Me	Et	32
3	**4c**	Bn	Me	Et	45
4	**4d**	1-NaphthMe	Me	Et	40
5	**4e**	Cyclohex-3-enyl	Me	Et	32
6	**4f**	Hex	Et	^{n}Am	25
7	**4g**	Hex	^{n}Am	Me	22

[a] Isolated yield.

of the structure of **4a**, the homonuclear (HH COSY) and heteronuclear (HSQC, HMBC) two-dimensional experiments have been carried out.

In the HMBC spectra of **4a** the signals of the methyl protons [δ (*CH*$_3$) 1.39] were found to correlate with the signals of the quaternary carbon atom [δ (C-1) 55.50], the methine C atom [δ (C-2) 25.6] and the methylene C atom [δ (C-3) 20.2]. The IR spectrum of **4a** has absorption bands due to stretching vibrations of C–H bonds in the cyclopropane ring [3070 cm^{-1}] and the hydroxyl stretching vibrations [3360 cm^{-1}] as well.

The cis-orientation of the substituents at C-1 and C-2 in the cyclopropane fragment of **4a** is determined by the characteristic low-field signal of the methyl group [δ (CH$_3$) 20.46] in the ^{13}C NMR spectrum and by comparison with the known *cis*-1-methyl-2-phenylcyclopropanol[7] synthesized via the Kulinkovich reaction.

In an analogous fashion, dec-1-ene, allyl benzene, 1-allyl naphthalene, and 4-vinyl cyclohex-1-ene enter into Cp_2ZrCl_2-catalyzed reaction with alkylhalogenalanes and ethyl acetate furnishing appropriate substituted cyclopropanes **4b**–**e**. The structure of these products has been determined by analysis of their spectroscopic data. The ^{13}C NMR spectrum of **4e** exhibits diastereomeric signal splittings [δ(C-1) 55.57 (55.34) and δ(C-2) 29.28 (28.01) ppm] assigned to the cyclopropane moiety and also [δ(CH$_3$) 20.63 (20.48) and δ(C-5) 32.05 (31.38), δ(C-6) 126.52 (126.22), δ(C-7) 126.95 (126.87), δ(C-9) 31.12 (31.07) ppm] belonging to the methyl and cyclohexenyl substituents, respectively, due to the formation of two diastereomers with a new stereogenic center at C-4 (Fig. 1).

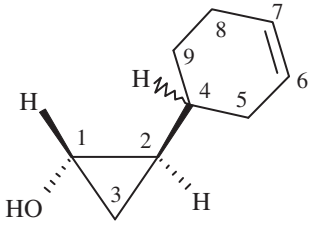
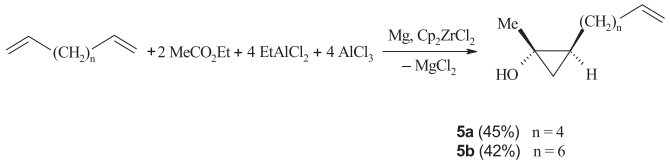


Fig. 1. Chemical structure of compound **4e**.

Cyclopropanation of α,ω-diolefins such as octa-1,7-diene and deca-1,9-diene under the same reaction conditions occurs exclusively at one terminal double bond (Scheme 3).

Thus, in the ^{13}C NMR spectrum of compound **5a**, along with the signals of the cyclopropane carbons [δ 20.16, 25.47, 55.49], the methyl substituent [δ 20.47] and the alkane chain, the signals of carbon atoms at δ 114.25 and 139.0 ppm indicating the terminal double bond are also observed. The ^{13}C NMR spectrum of compound **5b** has a similar picture. The mass spectra of **5a** and **5b** have the molecular ion peaks at m/z 154 $[M]^+$ and m/z 182 $[M]^+$, respectively. Despite our efforts, the second terminal double bond remains unchanged with increasing concentration of carboxylic ester and $EtAlCl_2$ in the reaction mixture (Scheme 4). Probably, π-interaction between the second double bond and the Al atom in the resulting organoaluminum compound prevents further reaction.



5a (45%) n = 4
5b (42%) n = 6

Scheme 4.

The catalytic cyclopropanation reaction of α-olefins with $EtAlCl_2$ (or Et_2AlCl) in the presence of $AlCl_3$ and carboxylic esters is feasible only in ethereal solvents. The reaction is best performed in tetrahydrofuran. In diethyl ether, dimethoxyethane or 1,4-dioxane, the chemical yields of the target cyclopropanols are significantly lower.

Therefore, it can be concluded that the Cp_2ZrCl_2-catalyzed interaction between aryl olefins, alkylhalogenalanes, and carboxylic esters affords aryl-substituted alkoxycyclopropanes unlike aliphatic α-olefins, which give rise to the corresponding substituted cyclopropanols.

This difference can be explained by the fact that primarily in the presence of α-olefin under reaction conditions the generation of coordinatively unsaturated complex 'Cp_2Zr^{+2}' occurs via reduction of Cp_2ZrCl_2 by Mg[8,9] giving rise to 2-aryl(alkyl)zirconacyclopropane **6**.[10]

In the case of aryl olefin, the subsequent transmetallation of 2-arylzirconacyclopropane **6** with $EtAlCl_2$ leads to the formation of 2-arylaluminacyclopropane **7**,[11] which is stabilized by intramolecular π-bonding between the aluminum atom and the aromatic ring of the original aryl olefin. The subsequent interaction between **7** and ester affords 2-oxoaluminacyclopentane **8**. Further skeleton rearrangements result in the formation of 2-arylalkoxycyclopropane **1**.

In the experiments with aliphatic α-olefins, the intermediates **6** do not undergo transmetallation to yield 2-alkylaluminacyclopropanes because of their low stability. They are coordinated to the ester molecule giving rise to oxazirconacyclopentane **9**. Further, the reaction proceeds according to the scheme proposed by Kulinkovich for $Ti(O^iPr)_4$ and EtMgBr.[2,6,7]

Subsequent migration of the alkoxide group in **9** to the Zr atom with the simultaneous closure of the three-membered ring leads to the formation of zirconium cyclopropanolate **10**. Transmetallation of the latter with $EtAlCl_2$ results in aluminum cyclopropanolate **11**, hydrolysis of which leads to the appropriate substituted cyclopropanols **4** (Scheme 5).

Formation of products with cis-oriented hydrocarbon substituents is the stereochemical feature of these reactions. Quantum-chemical study of the mechanism and diastereoselectivity of the Kulinkovich hydroxycyclopropanation reaction[12] has shown that formation of cyclopropanols with cis-configuration of the alkyl substituents is energetically more favorable. We believe that our method for the synthesis of cyclopropanols via the interaction between the aliphatic α-olefins, $EtAlCl_2$ and $R'CO_2R''$ in the presence Cp_2ZrCl_2 has similar regularities. When R of the α-olefin becomes the bulky aryl group, the increased repulsion between R and R′ decrease stereoselectivity of the reaction to give alkoxycyclopropanes **1** as a mixture of cis and trans isomers.

3. Conclusions

In conclusion, we have developed an effective one-pot method for cyclopropanation of α-olefins with the aid of $EtAlCl_2$ (or Et_2AlCl) and esters in the presence of Cp_2ZrCl_2 as a catalyst. The method allows the preparation of aryl-substituted alkoxycyclopropanes or alkylcyclopropanols in dependence upon reaction conditions.

Currently, we are engaged in studying this cyclopropanation reaction further in order to expand its scope and apply our research findings to a wide range of olefins and esters of carboxylic acids.

4. Experimental section

4.1. General

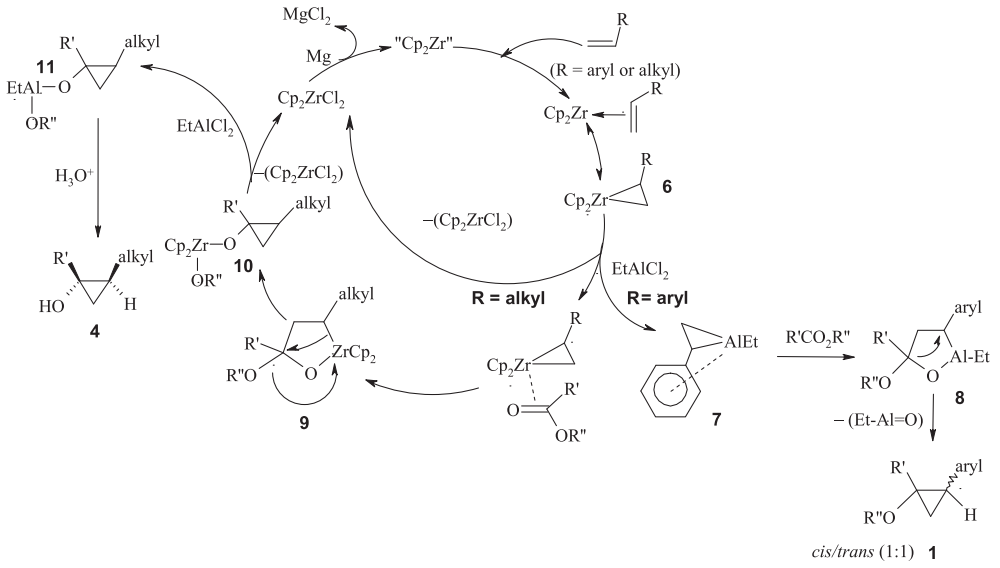
All reactions with organometallic compounds were carried out in a stream of dry argon. THF was dried by refluxing over metallic Na. All organometallic reagents $EtAlCl_2$, Et_2AlCl or $AlCl_3$ are commercially available and were used without additional purification.

Chromatographic analysis of compounds was performed on SHIMADZU GC-2014 instrument (capillary column 2 m×3 mm), 5% SE-30 on Chromaton N-AW-HMDS as the stationary phase, helium as a carrier gas (25 mL min^{-1}), temperature programming from 50 to 270 °C at a rate of 8 °C min^{-1}, evaporator temperature 300 °C, the temperature of the ion source 300 °C. Infrared spectra (IR) were recorded using FT-IR spectrometer Bruker Vertex 70 v (KBr pellet). Chromato-mass spectrometric analysis of compounds was performed on a Finnigan 4021 instrument (glass capillary column 50000×0.25 mm, stationary phase HP-5, helium as the carrier gas, temperature programming from 50 to 300 °C at a rate of 5 °C min^{-1}, evaporator temperature 280 °C, the temperature of the ion source 250 °C [EI, 70 eV]). Elemental analysis of the samples was carried out using Carlo Erba Elemental Analyzer model 1106. The one-dimensional (^1H, ^{13}C) and two-dimensional homo-(COSY) and heteronuclear (HSQC, HMBC) NMR spectra were recorded in $CDCl_3$ on a spectrometer Bruker Avance 400 [400.13 MHz (^1H) and 100.62 MHz (^{13}C)] in accordance with a standard Bruker protocol.

4.2. Cyclopropanation of aryl-substituted α-olefins mediated by $EtAlCl_2$ (Et_2AlCl or $AlCl_3$), RCO_2R' and Cp_2ZrCl_2 as a catalyst (general procedure)

The calcined and argon-filled 50 mL glass reactor equipped with magnetic stirrer was charged with THF (5 mL), Cp_2ZrCl_2 (1 mmol), magnesium (powder) (15 mmol), the corresponding aryl-substituted α-olefin (10 mmol), alkyl carboxylate (10 mmol), and $EtAlCl_2$ (Et_2AlCl or $AlCl_3$) (20 mmol) under a dry argon atmosphere at 0 °C. The reaction mixture was allowed to warm to rt (20–22 °C) and stirred for 10 h. Upon completion of the reaction and addition of hexane (5 mL), the reaction mixture was treated with 5–8% HCl solution. The organic layer was separated. The aqueous solution was extracted (10 mL×2) by diethyl ether. The resultant ether extract was combined with the organic layer, then was neutralized with Na_2CO_3 to pH ~7 and dried over $MgSO_4$. The end products were purified by column chromatography on silica gel SiO_2 (40–100 mesh grade, hexane/ethyl acetate 50:1 as eluent) and identified by means of spectroscopic methods.

*4.2.1. (cis/trans)-1-Ethoxy-1-methyl-2-(2-methylphenyl)cyclopropane (**1f**).* R_f 0.62 (hexane/ethyl acetate, 1:1) (0.86 g, 45% yield). IR (ν, cm^{-1}): 3428, 3043, 2971, 2922, 2867, 1551, 1486, 1302, 1284, 1218, 1165, 1102, 1053, 961, 872, 818, 731 cm^{-1}. MS m/z: 190 $[M]^+$.



Scheme 5.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54%. Found: C, 81.93; H, 9.25%.

*4.2.1.1. (cis)-1-Ethoxy-1-methyl-2-(2-methylphenyl)cyclopropane (cis-**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J=7.0 Hz, 3H, CH_3); 0.98 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 1.32–1.35 (m, 1H, CH_2, cyclopropane ring); 1.63 (s, 3H, CH_3); 2.35 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.49 (s, 3H, CH_3); 3.11 (dq, ^2J=9.0 Hz, ^3J=6.0 Hz, 1H, CH_2–O–); 3.46 (dq, ^2J=9.0 Hz, ^3J=6.0 Hz, 1H, CH_2–O–); 7.03–7.33 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 18.3, 20.2, 21.8, 28.5, 61.9, 62.6 [125.4, 125.6, 125.8, 126.2, 126.8, 127.3, 129.3, 129.7, 136.6, 137.1, 137.6, 138.7 arom (cis/trans)] ppm.

*4.2.1.2. (trans)-1-Ethoxy-1-methyl-2-(2-methylphenyl)cyclopropane (trans-**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.15 (s, 3H, CH_3); 1.30 (t, J=7.0 Hz, 3H, CH_3); 1.43 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 2.00 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.49 (s, 3H, CH_3); 3.66 (dq, ^2J=9.0 Hz, ^3J=6.0 Hz, 1H, CH_2–O–); 3.75 (dq, ^2J=9.0 Hz, ^3J=6.0 Hz, 1H, CH_2–O–); 7.03–7.33 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9, 16.1, 17.2, 20.3, 28.9, 61.8, 62.2 [125.4, 125.6, 125.8, 126.2, 126.8, 127.3, 129.3, 129.7, 136.6, 137.1, 137.6, 138.7 arom (cis/trans)] ppm.

*4.2.2. (cis/trans)-1-Ethoxy-1-methyl-2-(3-methylphenyl)cyclopropane (**1g**).* R_f 0.61 (hexane/ethyl acetate, 1:1) (0.93 g, 49% yield). MS m/z: 190 $[M]^+$. Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54%. Found: C, 81.90; H, 9.24%.

*4.2.2.1. (cis)-1-Ethoxy-1-methyl-2-(3-methylphenyl)cyclopropane (cis-**1g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 0.97 (t, J=7.0 Hz, 3H, CH_3); 1.28–1.32 (m, 1H, CH_2, cyclopropane ring); 1.54 (s, 3H, CH_3); 2.35 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.37 (s, 3H, CH_3); 2.68 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 3.05 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 6.99–7.21 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 21.0, 21.6, 30.5, 62.2, 62.9 [124.7, 125.5, 126.1, 126.7, 127.6, 127.9, 128.4, 129.4, 137.1, 137.7, 138.5, 138.7 arom (cis/trans)] ppm.

*4.2.2.2. (trans)-1-Ethoxy-1-methyl-2-(3-methylphenyl)cyclopropane (trans-**1g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.17 (s, 3H, CH_3); 1.26 (t, J=7.0 Hz, 3H, CH_3); 1.28 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 1.91 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.37 (s, 3H, CH_3); 3.45 (dq, ^2J=9.0 Hz, ^3J=6.0 Hz, 1H, CH_2–O–); 3.67 (dq, ^2J=9.0 Hz, ^3J=6.0 Hz, 1H, CH_2–O–); 7.03–7.33 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 16.1, 17.9, 21.4, 29.6, 61.8, 62.4 [124.7, 125.5, 126.1, 126.7, 127.6, 127.9, 128.4, 129.4, 137.1, 137.7, 138.5, 138.7 arom (cis/trans)] ppm.

*4.2.3. (cis/trans)-1-Ethoxy-1-methyl-2-(4-methylphenyl)cyclopropane (**1h**).* R_f 0.62 (hexane/ethyl acetate, 1:1) (0.99 g, 52% yield). IR ν 3432, 3046, 2975, 2927, 2870, 1517, 1442, 1392, 1279, 1231, 1125, 1067, 968, 879, 822, 733 cm^{-1}. MS m/z: 190 $[M]^+$. Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54%. Found: C, 81.91; H, 9.23%.

*4.2.3.1. (cis)-1-Ethoxy-1-methyl-2-(4-methylphenyl)cyclopropane (cis-**1h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 0.97 (t, J=7.0 Hz, 3H, CH_3); 1.27–1.31 (m, 1H, CH_2 cyclopropane ring); 1.53 (s, 3H, CH_3); 2.33 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.35 (s, 3H, CH_3); 3.06 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 3.54 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 7.08–7.28 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 20.8, 21.0, 21.6, 30.2, 62.1, 62.7 [127.5 (2C), 128.4 (4C), 128.9 (2C), 134.8, 135.4, 135.5, 135.6 arom (cis/trans)] ppm.

*4.2.3.2. (trans)-1-Ethoxy-1-methyl-2-(4-methylphenyl)cyclopropane (trans-**1h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.15 (s, 3H, CH_3); 1.25 (t, J=7.0 Hz, 3H, CH_3); 1.28 (t, J=6.0 Hz, 1H, CH_2); 1.90 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.35 (s, 3H, CH_3); 3.65 (q, J=7.0 Hz, 2H, CH_2); 7.06–7.21 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 16.1, 17.9, 21.0, 29.3, 61.8, 62.3 [127.5 (2C), 128.4 (4C), 128.9 (2C), 134.8, 135.4, 135.5, 135.6 arom (cis/trans)] ppm.

*4.2.4. (cis/trans)-1-Ethoxy-1-methyl-2-(4-phenylphenyl)cyclopropane (**1i**).* R_f 0.63 (hexane/ethyl acetate, 1:1) (0.99 g, 46% yield). MS m/z: 252 $[M]^+$. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%. Found: C, 85.53; H, 7.87%.

*4.2.4.1. (cis)-1-Ethoxy-1-methyl-2-(4-phenylphenyl)cyclopropane (cis-**1i**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, J=7.0 Hz, 3H, CH_3);

1.15 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.36–1.39 (m, 1H, CH_2 cyclopropane ring); 1.60 (s, 3H, CH_3); 2.01 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 3.15 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 3.58 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 7.28–7.69 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 21.3, 21.7, 30.4, 62.3, 63.1 [126.4 (2C), 126.9 (2C), 126.9 (2C), 127.0 (2C), 127.1 (2C), 128.1 (2C), 128.8 (2C), 128.8 (2C), 129.0 (2C), 137.9 (2C), 138.2, 138.2, 138.9 (2C), 141.0 (2C), 141.2 (2C) arom (cis/trans)] ppm.

*4.2.4.2. (trans)-1-Ethoxy-1-methyl-2-(4-phenylphenyl)cyclopropane (trans-**1i**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.15 (s, 3H, CH_3); 1.25 (t, J=7.0 Hz, 3H, CH_3); 1.28 (t, J=6.0 Hz, 1H, CH_2); 1.90 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.35 (s, 3H, CH_3); 3.65 (q, J=7.0 Hz, 2H, CH_2); 7.06–7.21 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 16.1, 17.9, 21.0, 29.3, 61.8, 62.3 [126.4 (2C), 126.9 (2C), 126.9 (2C), 127.0 (2C), 127.1 (2C), 128.1 (2C), 128.8 (2C), 128.8 (2C), 129.0 (2C), 137.9 (2C), 138.2, 138.2, 138.9 (2C), 141.0 (2C), 141.2 (2C) arom (cis/trans)] ppm.

*4.2.5. (cis/trans)-1-Ethoxy-1-methyl-2-(2-methoxylphenyl)cyclopropane (**1j**).* R_f 0.70 (hexane/ethyl acetate, 1:1) (0.91 g, 44% yield). MS *m/z*: 206 $[M]^+$. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. Found: C, 75.58; H, 8.72%.

*4.2.5.1. (cis)-1-Ethoxy-1-methyl-2-(2-methoxylphenyl)cyclopropane (cis-**1j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=7.0 Hz, 3H, CH_3); 1.00 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 1.31 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.59 (s, 3H, CH_3); 2.37 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 3.02 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 3.49 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–) [3.89, 3.90 (s, 6H, CH_3–O–, (*cis*/*trans*))]; 6.87–7.23 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 19.1 21.6, 25.3 [55.2, 55.6 (cis/trans)], 62.0, 62.7 [110.1 (2C), 120.0, 120.2, 126.3 (2C), 127.1, 127.2, 128.2 (2C), 158.5, 159.4 arom (cis/trans)] ppm.

*4.2.5.2. (trans)-1-Ethoxy-1-methyl-2-(2-methoxylphenyl)cyclopropane (trans-**1j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (dd, ^2J=7.0 Hz, ^3J=9.0 Hz, 1H, CH_2 cyclopropane ring); 1.12 (s, 3H, CH_3); 1.27 (t, J=7.0 Hz, 3H, CH_3); 1.35 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 2.30 (dd, $^3J_{trans}$=7.0 Hz, $^3J_{cis}$=9.0 Hz, 1H, CH cyclopropane ring); 3.72 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–); 3.82 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2–O–) [3.89, 3.90 (s, 6H, CH_3–O–, (*cis*/*trans*))]; 6.87–7.23 (m, 4H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9, 16.0, 17.8, 24.1 [55.2, 55.6 (cis/trans)], 61.6, 62.2 [110.1 (2C), 120.0, 120.2, 126.3 (2C), 127.1, 127.2, 128.2 (2C), 158.5, 159.4 arom (cis/trans)] ppm.

*4.2.6. (cis/trans)-1-Ethoxy-1-methyl-2-(1-naphthyl)cyclopropane (**1k**).* R_f 0.68 (hexane/ethyl acetate, 1:1) (1.09 g, 48% yield). IR ν 3430, 3046, 2974, 2927, 2871, 1925, 1580, 1509, 1402, 1219, 1126, 1068, 1021, 778 cm^{-1}. MS *m/z*: 226 $[M]^+$. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%. Found: C, 84.79; H, 7.95%.

*4.2.6.1. (cis)-1-Ethoxy-1-methyl-2-(1-naphthyl)cyclopropane (cis-**1k**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 (t, J=7.2 Hz, 3H, CH_3); 1.07 (t, J=6.0 Hz, 1H, CH_2 cyclopropane ring); 1.45 (dd, ^2J=6.0 Hz, ^3J=10.0 Hz, 1H, CH_2 cyclopropane ring); 1.74 (s, 3H, CH_3); 2.76 (dd, $^3J_{trans}$=6.0 Hz, $^3J_{cis}$=10.0 Hz, 1H, CH cyclopropane ring); 2.95 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2); 3.36 (dq,^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2); 7.20–8.39 (m, 7H, arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 18.2, 21.8, 28.5, 62.2, 62.7 [124.3, 124.6, 125.0, 125.1, 125.3, 125.3, 125.4, 125.8, 125.8, 126.0, 126.4, 126.9, 128.3, 128.6, 133.5, 133.5, 133.9, 134.0, 134.3, 135.6 arom (cis/trans)] ppm.

*4.2.6.2. (trans)-1-Ethoxy-1-methyl-2-(1-naphthyl)cyclopropane (trans-**1k**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (s, 3H, CH_3); 1.13 (dd, ^2J=7.0 Hz, ^3J=9.0 Hz, 1H, CH_2 cyclopropane ring); 1.59 (t, J=7.0 Hz, 1H, CH_2 cyclopropane ring); 2.48 (dd, $^3J_{trans}$=7.0 Hz, $^3J_{cis}$=9.0 Hz, 1H, CH); 3.67 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2); 3.84 (dq, ^2J=9.0 Hz, ^3J=7.0 Hz, 1H, CH_2); 7.20–8.39 (m, 7H, arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9, 16.2, 17.1, 28.1, 61.9, 62.6 [124.3, 124.6, 125.0, 125.1, 125.3, 125.3, 125.4, 125.8, 125.8, 126.0, 126.4, 126.9, 12.3, 128.6, 133.5, 133.5, 133.9, 134.0, 134.3, 135.6 arom (cis/trans)] ppm.

4.3. The reaction of styrene and $EtAlCl_2$ (or Et_2AlCl), RCO_2R' in the presence of $Ti(O^iPr)_4$ (general procedure)

The calcined and argon-filled 50 mL glass reactor equipped with magnetic stirrer was charged with THF (5 mL), $Ti(O^iPr)_4$ (1 mmol), magnesium (powder) (15 mmol), styrene (10 mmol), ethyl acetate (10 mmol), and $EtAlCl_2$ (or Et_2AlCl) (20 mmol) under a dry argon atmosphere at 0 °C. The reaction mixture was allowed to warm to rt (20–22 °C) and stirred for 10 h. Upon completion of the reaction and addition of hexane (5 mL), the reaction mixture was treated with 5–8% HCl solution. The organic layer was separated. The aqueous solution was extracted (10 mL×2) by diethyl ether. The resultant ether extract was combined with the organic layer, then was neutralized with Na_2CO_3 to pH ~7 and dried over $MgSO_4$. The end products were purified by column chromatography on silica gel SiO_2 (40–100 mesh grade, hexane/ethyl acetate 50:1 as eluent) and identified by means of spectral methods.

*4.3.1. α-Propylbenzenemethanol (**2**).* R_f 0.47 (hexane/ethyl acetate, 1:1) (0.55 g, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, 3H, CH_3, J=7.0 Hz); 1.29–1.83 (m, 4H, $2CH_2$), 4.67 (t, 1H, CH, J=6.0 Hz); 7.27–7.36 (m, 5H, CH–Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 19.0, 41.2, 74.4, 125.9, 127.5 (2C), 128.4 (2C), 145.0 ppm. MS *m/z*: 150 $[M]^+$. Anal. Calcd for $C_{10}H_{14}O$: C, 76.96; H, 9.39%. Found: C, 79.84; H, 8.92%.

4.4. Cyclopropanation of alkyl-substituted α-olefins (or α,ω-diolefins) mediated by $EtAlCl_2$ (or Et_2AlCl), RCO_2R' and Cp_2ZrCl_2 as a catalyst (general procedure)

The calcined and argon-filled 50 mL glass reactor equipped with magnetic stirrer was charged with THF (5 mL), Cp_2ZrCl_2 catalyst (1 mmol), magnesium (powder) (15 mmol), the corresponding alkyl-substituted α-olefin (10 mmol), alkyl carboxylate (10 mmol; 20 mmol for α,ω-diolefin), and $EtAlCl_2$ (or Et_2AlCl) (20 mmol; 40 mmol for α,ω-diolefin) and $AlCl_3$ (20 mmol; 40 mmol for α,ω-diolefin) under a dry argon atmosphere at 0 °C. The reaction mixture was allowed to warm to rt (20–22 °C) and stirred for additional 10 h. Upon completion of the reaction and addition of hexane (5 mL), the reaction mixture was treated with 5–8% HCl solution. The organic layer was separated. The aqueous solution was extracted (10 mL×2) by diethyl ether. The resultant ether extract was combined with the organic layer, then was neutralized with Na_2CO_3 to pH ~7 and dried over $MgSO_4$. The end products were purified by column chromatography on silica gel SiO_2 (40–100 mesh grade, hexane/ethyl acetate 4:1 as eluent) and identified by means of spectral methods.

*4.4.1. (cis)-1-Methyl-2-hexylcyclopropanol (**4a**).* R_f 0.55 (hexane/ethyl acetate, 1:1) (0.66 g, 42% yield). IR ν 3360 (OH), 3070 (C–H, cyclopropane ring) cm^{-1}. ^{1}H NMR δ 0.036 (t, 1H, CH_2, cyclopropane ring, $^2J \approx {}^3J$=6.0 Hz); 0.80–1.16 (m, 5H, CH, *H*-C-H (cyclopropane ring), CH_3); 1.18–1.35 (m, 10H, $5CH_2$), 1.39 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.2, 20.5, 22.6, 25.6, 29.2, 29.7, 29.9, 31.8,

55.5 ppm. MS *m*/*z*: 156 $[M]^+$. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%. Found: C, 76.77; H, 12.82%.

*4.4.2. (cis)-1-Methyl-2-octylcyclopropanol (**4b**).* R_f 0.55 (hexane/ethyl acetate, 1:1) (0.59 g, 32% yield). IR ν 3360 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.01 (m, 1H, CH_2, cyclopropane ring); 0.80–1.16 (m, 5H, CH, *H*–C–H (cyclopropane ring), CH_3); 1.15–1.35 (m, 14H, $7CH_2$); 1.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.4, 20.6, 22.6, 25.9, 29.4, 29.5, 29.6, 29.7, 29.9, 31.8, 55.3 ppm. MS *m*/*z*: 184 $[M]^+$. Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13%. Found: C, 78.09; H, 13.04%.

*4.4.3. (cis)-1-Methyl-2-benzylcyclopropanol (**4c**).* R_f 0.48 (hexane/ethyl acetate, 1:1) (0.73 g, 45% yield). IR ν 3380 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.30 (t, 1H, CH_2, cyclopropane ring, $^2J \approx {}^3J$=6.0 Hz); 0.99 (dd, 1H, CH_2, cyclopropane ring, ^2J=6.0 Hz, ^3J=10.0 Hz); 1.28–1.39 (m, 1H, CH, cyclopropane ring); 1.50 (s, 3H, CH_3); 2.57 (dd, 1H, CH_2–Ph, ^2J=15.2 Hz, ^3J=7.2 Hz), 2.68 (dd, 1H, CH_2–Ph, ^2J=15.2 Hz, ^3J=7.2 Hz); 7.19–7.45 (m, 5H, CH–Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 20.7, 26.08, 35.7, 55.8, 25.9, 125.9, 128.2 (2C), 128.4 (2C), 141.6 ppm. MS *m*/*z*: 162 $[M]^+$. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.77%. Found: C, 81.65; H, 8.68%.

*4.4.4. (cis)-1-Methyl-2-(1-naphthylmethyl)cyclopropanol (**4d**).* R_f 0.54 (hexane/ethyl acetate, 1:1) (0.85 g, 40% yield). IR ν 3380 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.37 (t, 1H, CH_2, cyclopropane ring, $^2J \approx {}^3J$=6.0 Hz); 1.05 (dd, 1H, CH_2, cyclopropane ring, ^2J=6.0 Hz, ^3J=10.0 Hz); 1.25–1.32 (m, 1H, CH, cyclopropane ring); 1.55 (s, 3H, CH_3); 3.05 (dd, 1H, CH_2, ^2J=12.0 Hz, ^3J=8.2 Hz); 3.14 (dd, 1H, CH_2, ^2J=12.0 Hz, ^3J=8.2 Hz); 7.46–8.12 (m, 7H, CH, arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 20.7, 25.0, 32.6, 55.9, 123.7, 125.2, 125.5, 125.7, 125.8, 126.7, 128.8, 132.0, 133.8, 137.5 ppm. MS *m*/*z*: 212 $[M]^+$. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%. Found: C, 84.96; H, 7.51%.

*4.4.5. (cis)-1-Methyl-2-(cyclohex-3-enyl)cyclopropanol (**4e**).* R_f 0.45 (hexane/ethyl acetate, 1:1) (0.49 g, 32% yield). IR ν 3380 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.09 (dd, $^2J \approx {}^3J \approx$ 5.2 Hz, 1H, CH_2, cyclopropane ring); 0.81 (m, 1H, CH_2, cyclopropane ring); 0.82–0.91 (m, 2H, CH_2); 0.92–0.98 (m, 1H, CH); 1.96–2.08 (m, 2H, C*H*$_2$–CH=CH); 1.14–1.37 (m, 1H, CH, cyclopropane ring); 1.42 and 1.44 (s, 3H, CH_3); 2.03–2.21 (m, 2H, C*H*$_2$–CH=CH); 5.62–5.63 (m, 2H, CH=CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 20.5 (20.6), 25.0, 28.0 (29.3), 31.1 (31.1), 31.4 (32.1), 35.3, 55.0 (55.6), 126.2 (126.5), 126.9 (127.0) ppm. MS *m*/*z*: 152 $[M]^+$. Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60%. Found: C, 78.83; H, 10.53%.

*4.4.6. (cis)-1-Ethyl-2-hexylcyclopropanol (**4f**).* R_f 0.55 (hexane/ethyl acetate, 1:1) (0.43 g, 25% yield). IR ν 3360 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.01 (m, 1H, CH_2, cyclopropane ring); 0.78 (m, 1H, CH_2, ring); 0.87 (m, 3H, CH_3); 1.02 (m, 1H, CH, ring); 1.06 (t, 3H, CH_3, J=7.2 Hz); 1.49–1.77 (m, 12H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.1, 14.0, 19.2, 22.6, 26.0, 27.0, 29.2, 29.5, 29.6, 31.8, 59.7 ppm. MS *m*/*z*: 170 $[M]^+$. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%. Found: C, 77.48; H, 12.93%.

*4.4.7. (cis)-1-Amyl-2-hexylcyclopropanol (**4g**).* R_f 0.55 (hexane/ethyl acetate, 1:1) (0.47 g, 22% yield). IR ν 3360 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.28 (m, 1H, CH_2, cyclopropane ring); 0.65 (m, 1H, CH_2, cyclopropane ring); 0.88 (t, 3H, CH_3, J=7.2 Hz); 0.95–1.00 (m, 1H, CH, cyclopropane ring); 1.49–1.77 (m, 12H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0 (2C), 19.5, 22.6, 22.7, 25.6, 25.9, 29.2, 29.5, 29.6, 31.8, 32.1, 34.1, 59.0 ppm. MS *m*/*z*: 212 $[M]^+$. Anal. Calcd for $C_{14}H_{28}O$: C, 79.22; H, 13.30%. Found: C, 79.08; H, 13.21%.

*4.4.8. (cis)-1-Methyl-2-(hex-5-enyl)cyclopropanol (**5a**).* R_f 0.49 (hexane/ethyl acetate, 1:1) (0.69 g, 45% yield). IR ν 3360 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.04 (t, 1H, CH_2, cyclopropane ring, $^2J \approx {}^3J$=5.8 Hz); 0.79–1.38 (m, 8H, CH, CH_2); 1.39 (s, 3H, CH_3); 2.00–2.27 (m, 2H, C*H*$_2$–CH=); 4.90–5.03 (m, 2H, CH_2=CH); 5.75–5.86 (m, H, CH=CH_2–) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 20.5, 25.5, 28.7, 29.1, 29.7, 33.7, 55.5, 114.3, 139.0 ppm. MS *m*/*z*: 154 $[M]^+$. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76%. Found: C, 77.75; H, 11.69%.

*4.4.9. (cis)-1-Methyl-2-(oct-7-enyl)cyclopropanol (**5b**).* R_f 0.49 (hexane/ethyl acetate, 1:1) (0.76 g, 42% yield). IR ν 3360 (OH), 3060 (C–H, cyclopropane ring) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.04 (t, 1H, CH_2, cyclopropane ring, $^2J \approx {}^3J$=5.8 Hz); 0.78–1.35 (m, 12H, CH, CH_2); 1.38 (s, 3H, CH_3); 2.00–2.05 (m, 2H, C*H*$_2$–CH=); 4.90–5.00 (m, 2H, CH_2=CH); 5.75–5.80 (m, H, CH=CH_2–) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 20.5, 25.5, 28.9, 29.1, 29.4, 29.6, 29.9, 33.8, 55.4, 114.1, 139.1 ppm. MS *m*/*z*: 182 $[M]^+$. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%. Found: C, 78.94; H, 12.08%.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.09.097.

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