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Catalytic Reaction of 1-Chloropropenyl Butyl Ethers with Methyl Diazoacetate

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Abstract—Catalytic reaction of *trans*- and *cis*-1-chloropropenyl butyl ethers with methyl diazoacetate catalyzed by either $Rh_2(OAc)_3$, or $Cu(OTf)_2$, or $Cu(acac)_2$ in the presence of the imidazolium salts $[bmim]^+ Cl^-$, $[bmim]^+ BF_4^-$, and $[bmim]^+ PF_6^-$ was studied. The composition and ratio of products formed was shown to depend on the reaction conditions and the nature and ratio of the components of the catalytic system.

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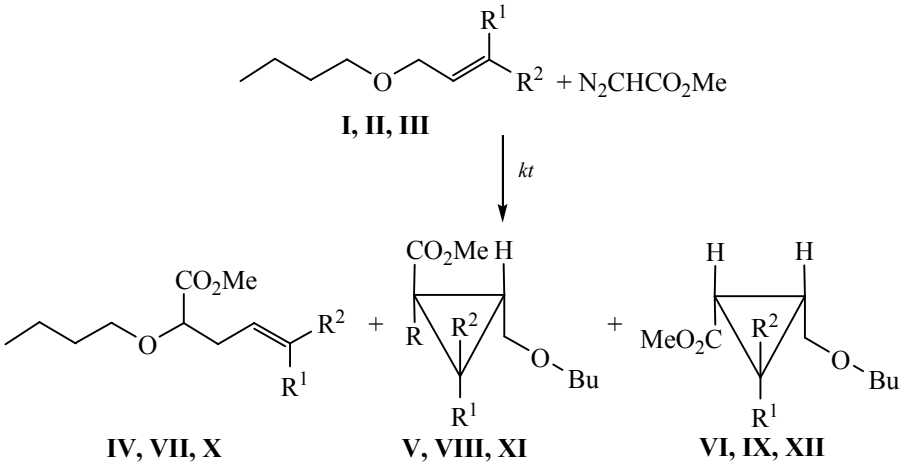
The reaction of alkyl diazoacetates with allyl halides or allyl ethyl ether in the presence of $Rh_2(OAc)_4$ is known to lead to both the products of C–X insertion of alkoxycarbonylcarbene as a result of the ylide [2,3]-rearrangement, and the cyclopropane adducts at C=C bond [1, 2]. In this study we investigated a reaction of allyl butyl ether (**I**), as well as *trans*- and *cis*-1-chloropropenyl butyl ethers **II** and **III** with methyl diazoacetate in the presence of $Rh_2(OAc)_4$, Cu $(OTf)_2$, or $Cu(acac)_2$ and imidazolium salts $[bmim]^+ Cl^-$, $[bmim]^+ BF_4^-$, and $[bmim]^+ PF_6^-$. The experiments were carried out by adding methyl diazoacetate to a solution of compound **I–III** in CH_2Cl_2 or $ClCH_2CH_2Cl$ at the molar ratio olefin:N_2CHCO_2Me:catalyst = 1:1:0.01.

The experiments showed that in the reaction of allyl butyl ether **I** with methyl diazoacetate in the presence of $Rh_2(OAc)_4$ and an imidazolium salt 1-methoxycarbonyl-2-butoxymethylcyclopropane formed as equimolar mixture of *trans*- and *cis*-isomers (**V, VI**) and methyl 2-butoxypent-4-enoate (**IV**) in 47% and 4% yields, respectively (Table 1).



I, IV–VI, $R^1 = R^2 = H$; **II, VII–IX**, $R^1 = H$, $R^2 = Cl$; **III, X–XII**, $R^1 = Cl$, $R^2 = H$.

Table 1. Effect of catalyst and temperature on the yield of the products in the reaction of allyl butyl ether with methyl diazoacetate[a]

Catalyst	Temperature, °C	Yield, % (*trans*:*cis*)	
		IV	**V/VI**
$Rh_2(OAc)_4$	40	4	47 (1:1)
$Rh_2(OAc)_4$/$[bmim]^+PF_6^-$	40	5	62 (1:1)
$Rh_2(OAc)_4$/$[bmim]^+BF_4^-$	40	19	57 (1:1)
$Rh_2(OAc)_4$/$[bmim]^+Cl^-$	40	8	41 (1:1)
$Cu(OTf)_2$	40	45	–
$Cu(OTf)_2$/$[bmim]^+PF_6^-$	40	18	5 (1:1)
$Cu(OTf)_2$/$[bmim]^+BF_4^-$	40	18	5 (1:1)
$Cu(OTf)_2$/$[bmim]^+Cl^-$	40	15	3 (1:1)
$Cu(OTf)_2$	75	38	–
$Cu(acac)_2$	75	27	–
$Cu(OAc)_2$	75	20	–
$Cu(OTf)_2$/$[bmim]^+PF_6^-$	75	32	5 (1:1)
$Cu(OTf)_2$/$[bmim]^+BF_4^-$	75	35	6 (1:1)
$Cu(OTf)_2$/$[bmim]^+Cl^-$	75	31	3 (1:1)

[a] Molar ratio of **I**:catalyst:$[bmim]^+X^-$ = 1:1:0.01:0.01, 3 h.

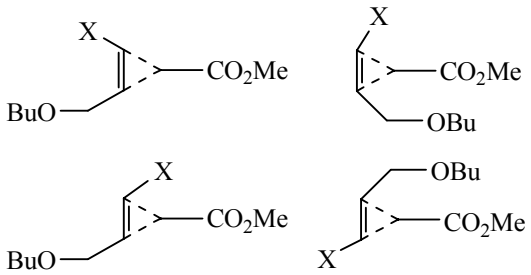
Table 2. Reaction condition and product yield in the reaction of compounds **II, III** with methyl diazoacetate[a]

Catalyst	*T*, °C	Yield, %			
		VII	**VIII/IX**	**X**	**XI/XII**
$Cu(OTf)_2$	40	–	–	–	–
$Cu(OTf)_2$	75	5	20 (3:1)	5	10 (5:1)
$Cu(acac)_2$	75	5	25 (2:1)	5	15 (XI)
$Rh_2(OAc)_4$	40	5	10 (3:1)	5	10 (5:1)
$Cu(OTf)_2$/$[bmim]^+PF_6^-$	40	–	–	–	–
$Cu(OTf)_2$/$[bmim]^+PF_6^-$	75	5	20 (2:1)	10	21 (5:1)
$Cu(acac)_2$/$[bmim]^+PF_6^-$	75	5	25 (2:1)	13	23 (XI)
$Rh_2(OAc)_4$[bmim]$^+PF_6^-$	40	10	18 (3:1)	10	15 (5:1)

[a] Molar ratio of **II,III**:catalyst:$[bmim]^+X^-$ = 1:1:0.01:0.01, 3 h.

The use of the imidazolium salts increases the overall yield of the reaction products, but the ratio of diastereomeric esters **V**:**VI** remains the same (Table 1). Compounds $Cu(OTf)_2$, $Cu(acac)_2$ and $Cu(OAc)_2$ catalyze the reaction of allyl butyl ether with methyl diazoacetate, resulting in a selective formation of **IV** in the yield of 20–45%. The products with cyclopropane ring were not detected in the reaction mixture. Use of a catalytic system of the $Cu(OTf)_2$–$[bmim]^+X^-$ type was found to be ineffective.

The *trans*- and *cis*-chloroallyl ethers **II** and **III** did not react with methyl diazoacetate at 40°C in methylene chloride in the presence of $Cu(OTf)_2$ or $[bmim]^+$ PF_6^-. However, the increase in the temperature or the use of other catalysts, like $Rh_2(OAc)_4$ and $Cu(acac)_2$, leads both to ethers **VII** and **X** and to the respective products of cyclopropanation **VIII**, **IX** and **XI**, **XII** in the yields of 5–13 and 10–25%, respectively (Table 2).



X = H, Cl.

The use of imidazolium salts as a co-catalyst had almost no effect on the selectivity and total yield of the reaction products of chloroallyl butyl ethers **II** and **III** with methyl diazoacetate (Table 2), but changed the ratio of the produced esters of cyclopropanecarboxylic acid **VIII**/**IX** and **XI**/**XII**.

Preferential formation of the cyclopropanes **VIII** and **XI** in the reaction of allyl ethers **II** and **III** with methyl diazoacetate is consistent with the known data about the reaction mechanism [3]. According to this mechanism, the cyclopropanation of olefins proceeds at the least hindered side with retention of the original configuration of the unsaturated compound.

In this case, the formation of products **VIII** and **XI** is preferable.

From the reaction mixture the mixtures of *trans*,*cis*-isomeric cyclopropanes **VIII**/**IX** and **XI**/**XII**, as well as individual products of the metoxycarbonylcarbene insertion **VII** and **X** were isolated by column chro-

matography. Their structures were confirmed using ^{1}H NMR spectroscopy and gas chromatography–mass spectrometry.

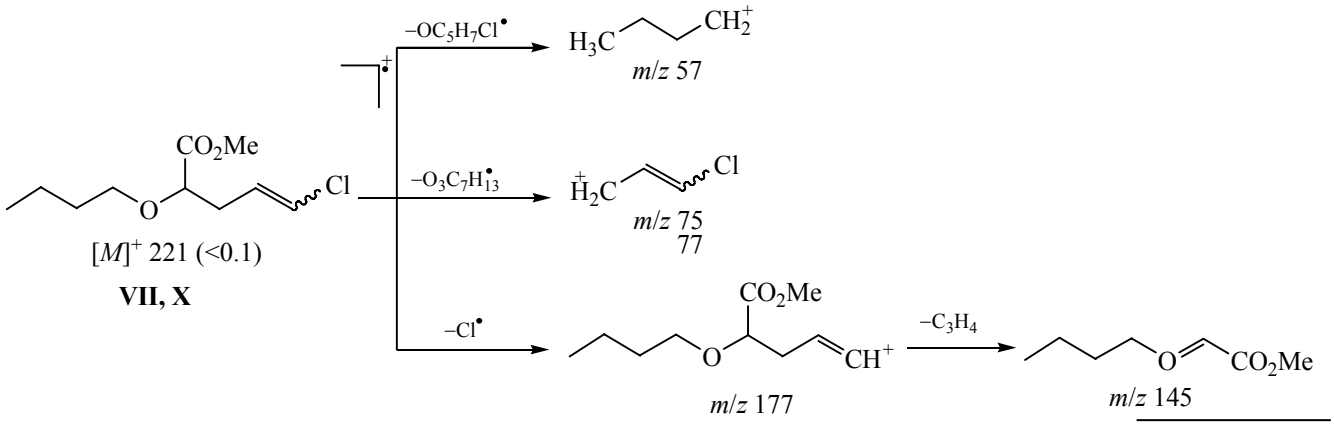
To assign the configuration of 1,2-disubstituted cyclopropanes **V**/**VI** the ^{13}C NMR spectra were the most informative: the signals of carbon atoms of cyclopropane ring of the *cis*-isomer resonated in a stronger field than those of the corresponding carbon atoms in the *trans*-isomer [4]. The *trans*-*cis* isomer ratio of methyl esters **V**/**VI** is 1:1, according to the integral intensity of the methoxy protons.

The characteristic signals in the ^{1}H NMR spectra of the trisubstituted cyclopropanes **VIII**, **IX**, **XI** and **XII** are those of the protons at C^1 and C^2 of the cyclopropane ring. Protons at the C^1 and C^2 atoms of compound **VIII** resonate as a doublet of doublets in the region of δ 1.88 ($^3J_{1-2}$ 9.0 and $^3J_{1-3}$ 2.3 Hz) and 3.63 ppm ($^3J_{1-2}$ 9.0 and $^3J_{1-3}$ 2.2 Hz), which corresponds to the *cis*-arrangement of methoxycarbonyl group and chlorine atom. Similarly, in the spectrum of the ester **IX** these signals are also doublets of doublets in the regions δ 1.81 ($^3J_{1-2}$ 2.6 and $^3J_{1-3}$ 9.5 Hz) and 3.52 ppm ($^3J_{1-2}$ 2.6 and $^3J_{1-3}$ 2.4 Hz), characteristic of the *trans* arrangement of the substituents in the cyclopropane ring. The assignment of signals in the spectra of the mixture of isomers **IX** and **XII** is similar. The resulting spectral data are consistent with those reported in the literature on the reaction of ethyl diazoacetate with allyl ethyl ether in the presence of $Rh_2(OAc)_4$ [2].

In the ^{1}H NMR spectra of compounds **VII** and **X** the signals of OCH_3 and CH groups are typical, which appear as a singlet at δ 3.8 ppm and a multiplet at δ 4.19–4.23 ppm respectively for compound **VII** and similarly for **X,** at δ 3.7 and 4.05–4.15 ppm, respectively. Chemical shifts of protons at the double bond and protons of *n*-C_4H_9O group of compounds **VII** and **X** are almost unchanged compared with original chloroallyl butyl ethers **II** and **III**. In the spectra of methyl (4*E*)- and (4*Z*)-2-butoxy-5-chloropent-4-enoates **VII** and **X** the proton signals of H^4 at the double bond appear at δ 6.25 and 6.15 ppm with coupling constants 12.7 and 6.7 Hz, respectively.

In the mass spectrum (EI) of compounds **VII** and **X** the molecular ion peak is absent (Scheme 1). The fragmentation occurs by three competing paths in equal amounts.

Scheme 1.



The main direction of the fragmentation consist in the loss of chloropropenoxy group, resulting in a cation with *m*/*z* = 57, which is the most intense in the spectra of compounds **VII** and **X**.

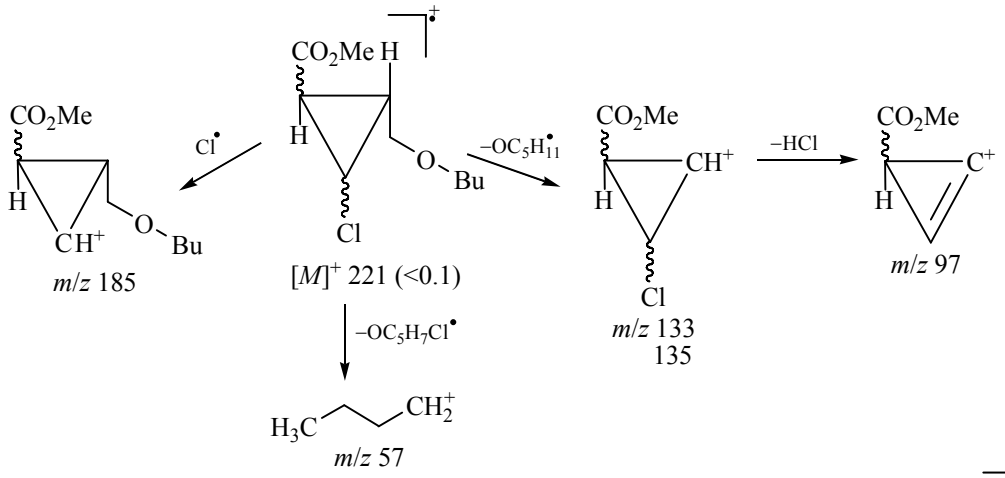
The mass spectra of compounds **VIII**/**IX** and **XI**/**XII** do not contain a peak of molecular ion *m*/*z* = 221 (Scheme 2).

The fragmentation of the *cis*- and *trans*-isomers is much alike. The most intense are the peaks containing the cyclopropane fragment (*m*/*z* = 97).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer (300.13 and 75.47 MHz respectively), solvent $CDCl_3$, internal standard Me_4Si. The mass spectra were recorded on a Thermo Finnigan MAT 95 XP mass spectrometers (EI, 70 eV, ionizing chamber temperature 250°C, the temperature of direct input 50–250°C, heating rate 10 K min^{-}1). The GLC analysis was performed on a Shimadzu GC-2014 chromatograph with a flame ionization detector, capil-

Scheme 2.



lary column DB35MS 25 m, carrier gas helium. The TLC analysis was performed on Silufol chromatographic plates (Merk), eluent petroleum ether–AcOEt, 7: 3). Preparative separation was carried out by column chromatography on silica gel, eluent petroleum ether with increasing content of ethyl acetate from 5 to 100%. The imidazolium salts $[bmim]^+ Cl^-$, $[bmim]^+ BF_4^-$, $[bmim]^+ PF_6^-$ used in the study and $Rh_2(OAc)_4$ were obtained by the methods described in [6–8], the catalyst $Cu(OTf)_2$ was commercially available.

Catalytic reaction of allyl ethers I–III with methyl diazoacetate (general procedure). To a solution of 1 mmol of unsaturated compound **I–III** and 0.01 mmol of a catalyst in 5 ml of a solvent (at 40°C methylene chloride or at 75°C dichloroethane) was added 1 mmol of methyl diazoacetate in 5 ml of the solvent and the mixture was refluxed for 3 h. Then the reaction mixture was passed through a thin layer of Al_2O_3, the solvent was removed at a reduced pressure. When an imidasolium salt was used, to the residue petroleum ether (bp 40–70°C) was added, and the catalytic system separated as a dark brown oil. The petroleum ether was removed at a reduced pressure and the residue was chromatographed on SiO_2.

Methyl 2-butoxypent-4-enoate (**IV**) was isolated by column chromatography, R_f 0.49. IR spectrum, ν, cm^{-1}: 758, 1018, 1124, 1200, 1300, 1458, 1745, 2853, 2924, 2955. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.85 t (3H, ^3J 7.2, CH_3), 1.28–1.47 m (2H, $C\underline{H}_2CH_3$), 1.48–1.62 m (2H, $C\underline{H}_2CH_2$), 2.40–2.44 t (2H, ^3J 6.3, $C\underline{H}_2CH$), 3.25–3.55 m (2H, OCH_2), 3.68 s (3H, OCH_3), 3.75–3.83 m (1H, $CH_2C\underline{H}$), 5.05–5.16 m (2H, $C\underline{H}_2CH$), 5.77 d.d.d (1H, $CH_2C\underline{H}$, ^3J 17, 10, 6.3). ^{13}C NMR spectrum, δ_C, ppm: 13.81 (CH_3), 19.19 (CH_2), 29.69 (CH_2), 37.35 (CH_2), 52.30 (OCH_3), 70.52 (CH_2), 78.92 (CHO), 117.78 ($\underline{C}H_2CH$), 133.43 ($CH_2C\underline{H}$), 165.39 (C=O). Mass-spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 186 (<0.1), 155 (12), 113 (58), 100 (34), 85 (56), 71 (54), 59 (32), 56 (100). *M* 186.1639.

Methyl 2-(butoxymethyl)cyclopropane carboxylate (**V, VI**) was isolated as a mixture of *trans-cis* isomers by column chromatography, R_f 0.34. IR spectrum, ν, cm^{-1}: 1109, 1177, 1205, 1271, 1389, 1437, 1734, 2933. Mass-spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 186 (<0.1), 113 (38), 100 (50), 85 (75), 59 (18), 56 (100). *M* 186.1635.

***trans*-V**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.90 m (3H, CH_3), 1.05, 1.12 m (2H, H^3), 1.30–1.65 m (6H, H^1, H^2, $C\underline{H}_2CH_2$, $C\underline{H}_2CH_3$), 3.25–3.55 m (2H, CH_2O), 3.66 c (3H, OCH_3), 3.75–3.90 m (2H, CH_2O). ^{13}C NMR spectrum, δ_C, ppm: 12.98 (C^3), 13.87 (CH_3), 18.23 (C^2), 19.13 ($C\underline{H}_2CH_3$), 21.77 (C^1), 29.68 (CH_2), 52.31 (OCH_3), 68.38 (OCH_2), 70.61 (OCH_2), 174.39 (CO_2).

***cis*-VI**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.90 m (3H, CH_3), 1.30–1.65 m (8H, H^1, H^2, $2H^3$, $C\underline{H}_2CH_2$, $C\underline{H}_2CH_3$), 3.25–3.55 m (2H, CH_2O), 3.67 s (3H, OCH_3), 3.75–3.90 m (2H, CH_2O). ^{13}C NMR spectrum, δ_C, ppm: 11.84 (C^3), 13.87 (CH_3), 17.22 (C^2), 19.13 ($C\underline{H}_2CH_3$), 20.81 (C^1), 29.68 (CH_2), 51.69 (OCH_3), 68.06 (OCH_2), 70.49 (OCH_2), 172.94 (CO_2).

Methyl (4*E*)-2-butoxy-5-chloropent-4-enoate (VII). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.92 т (3H, CH_3, ^3J 7.5), 1.28–1.47 m (2H, $C\underline{H}_2CH_3$), 1.48–1.62 m (2H, CH_2), 2.38–2.45 m (2H, $CH_2CHC\underline{H}_2$), 3.44 т (2H, CH_2O, ^3J 6.7), 3.8 s (3H, OCH_3), 4.19–4.23 m (1H,

CH), 5.95 d.d (1H, CH, ^3J 12.7, 6.0), 6.25 d (1H, CH, ^3J 6.0). ^{13}C NMR spectrum, δ_C, ppm: 13.72 (CH_3), 22.26 (CH_2), 32.90 (CH_2), 37.96 (CH_2), 52.55 (OCH_3), 64.26 (CH_2), 75.76 (CH), 121.39 (CHCl), 129.65 (CHCl), 165.5 (C=O). Mass-spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 221 (<0.1) , 145 (10), 130 (32), 101 (18), 85 (56), 87 (10), 75 (100), 69 (20).

Methyl *t*-3-butoxy-*c*-2-chlorocyclopropane-*r*-1-carboxylate (VIII). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 t (3H, CH_3, ^3J 7.5), 1.28–1.47 m (2H, $C\underline{H}_2CH_3$), 1.48–1.62 m (2H, CH_2), 1.88 d.d (1H, CH, $^3J_{1-2}$ 9.0, $^3J_{1-3}$ 2.3), 2.02–2.10 m (1H, CH), 3.44 t (2H, CH_2O, ^3J 6.7), 3.50–3.56 m (2H, CH_2O), 3.63 d.d (1H, CH, $^3J_{1-2}$ 9.0, $^3J_{1-3}$ 2.2); 3.64 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 13.72 (CH_3), 19.17 (CH_2), 22.26 (CH), 26.82 (CH), 31.58 (CH_2), 37.96 (CH), 52.71 (OCH_3), 68.06 (CH_2O), 71.56 (CH_2O), 165.42 (C=O).

Methyl *c*-3-butoxy-*t*-2-chlorocyclopropane-*r*-1-carboxylate (IX). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 t (3H, CH_3, ^3J 7.5), 1.28–1.47 m (2H, $C\underline{H}_2CH_3$), 1.48–1.62 m (2H, CH_2), 1.81 d.d (1H, CH, $^3J_{1-2}$ 2.6, $^3J_{1-3}$ 9.5), 1.94–2.00 m (1H, CH), 3.44 t (2H, CH_2O, ^3J 6.7), 3.50–3.56 m (2H, CH_2O), 3.52 d.d (1H, CH, $^3J_{1-2}$ 2.6, $^3J_{1-3}$ 2.4), 3.63 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 13.72 (CH_3), 19.17 (CH_2), 23.38 (CH), 27.58 (CH), 32.90 (CH_2), 37.96 (CH), 52.55 (OCH_3), 68.06 (CH_2O), 71.56 (CH_2O), 167.1 (C=O). Mass-spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 221 (<0.1), 185 (20), 147 (15), 128 (22), 113 (15), 97 (100), 85 (10), 57 (45).

Methyl (4*Z*)-2-butoxy-5-chloropent-4-enoate (X). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 t (3H, CH_3, ^3J 7.5), 1.27–1.45 m (2H, $C\underline{H}_2CH_3$), 1.47–1.60 m (2H, CH_2), 2.35–2.44 m (2H, CH_2), 3.36–3.66 m (1H, CH_2O), 4.05–4.15 m (1H, CH), 3.7 s (3H, OCH_3), 5.97 d.d (1H, CH, ^3J 6.7, 6.0), 6.15 d (1H, CH, ^3J 6.7). ^{13}C NMR spectrum, δ_C, ppm: 13.70 (CH_3), 22.16 (CH_2), 32.87 (CH_2), 37.97 (CH_2), 51.55 (OCH_3), 63.29 (CH_2), 74.79 (CH), 120.34 (CHCl), 164.24 (C=O). Mass-spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 221 (<0.1) , 145 (8), 130 (17), 101 (24), 85 (52), 87 (10), 75 (100), 69 (21).

Methyl *t*-3-butoxy-*t*-2-chlorocyclopropane-*r*-1-carboxylate (XI). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 t (3H, CH_3, ^3J 7.5), 1.28–1.47 m (2H, $C\underline{H}_2CH_3$), 1.48–1.62 m (2H, CH_2), 1.70 d.d (1H, CH, $^3J_{1-2}$ 2.6, $^3J_{1-3}$ 2.4), 2.05–2.10 m (1H, CH), 3.43–3.55 m (2H, CH_2O), 3.60 d.d (1H, CH, $^3J_{1-2}$ 9.0, $^3J_{1-3}$ 2.2), 3.81–3.90 m (2H, CH_2O), 3.67 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 13.71 (CH_3), 19.19 (CH_2), 23.87 (CH), 26.27 (CH), 32.85 (CH_2), 38.14 (CH), 53.32 (OCH_3), 69.18 (CH_2O), 72.13 (CH_2O), 169.2 (C=O).

Methyl *c*-3-butoxy-*c*-2-chlorocyclopropane-*r*-1-carboxylate (XII). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 t (3H, CH_3, ^3J 7.5), 1.28–1.47 m (2H, $C\underline{H}_2CH_3$), 1.48–1.62 m (2H, CH_2), 1.78 d.d (1H, CH, $^3J_{1-2}$ 9.6, $^3J_{1-3}$ 9.0), 2.05–2.10 m (1H, CH), 3.43–3.55 m (2H, CH_2O), 3.64 d.d (1H, CH, $^3J_{1-2}$ 9.6, $^3J_{1-3}$ 8.8), 3.81–3.90 m (2H, CH_2O), 3.70 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 13.70 (CH_3), 19.20 (CH_2), 24.18 (CH), 28.12 (CH), 32.86 (CH_2), 37.45 (CH), 52.55 (OCH_3), 69.18 (CH_2O), 72.13 (CH_2O), 171.1 (C=O). Mass-spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 221 (<0.1), 147 (18), 128 (25), 97 (54), 57 (100).

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