Synthesis and chemical transformations of 2-cyclopropyl-2-diazoacetates*

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Methyl 2-cyclopropyl-2-diazoacetate was synthesized from acetylcyclopropane in few chemical steps in ~55% total yield. Its copper or rhodium-catalyzed dediazoniation exclusively proceeds through the intramolecular isomerization of generated cyclopropyl(methoxycarbonyl)carbene to 1-methoxycarbonylcyclobutene, irrespective of the presence or the absence of unsaturated compounds. However, in the presence of acrylates or strained cycloalkenes, this diazo ester is being slowly involved into the 1,3-dipolar cycloaddition, giving cyclopropyl-substituted pyrazolinecarboxylates, which in case of 1-pyrazolines easily lose nitrogen molecule to selectively afford 1-cyclopropylcyclopropanecarboxylate derivatives.

Key words: diazo esters, cyclopropylcarbene—cyclobutene isomerization, 1,3-cycloaddition, pyrazolinecarboxylates, dediazoniation, dicyclopropyls, cyclopropanes.

Diazo carbonyl compounds are valuable synthons for the fine organic synthesis and are widely used in the reactions, proceeding either with retention (mainly 1,3-dipolar cycloaddition reactions) or with elimination of nitrogen molecule.[1—3] In the latter case, the dediazoniation, assisted by the metal complex catalysts or by the Lewis acids, is the most efficient one. In particular, the catalytic dediazoniation of diazo compounds serves as a convenient method for the cyclopropanation of various unsaturated compounds or for the formation of the insertion products of the corresponding carbenes into C—H or C—heteroatom bonds.[3—5]

2-Cyclopropyl-2-diazoacetic acid esters can be of interest as the synthons for the preparation of cyclopropyl-substituted nitrogen-containing heterocycles or dicyclopropyl derivatives with various combinations of substituents in the small rings. However, in contrast to the most widely used diazoacetates and other diazo carbonyl compounds, capable of metal-catalyzed generating of the corresponding carbene intermediates, which further react in the [1+2]-cycloaddition or insertion into C—Y bonds with the suitable substrates, α-cyclopropyl-substituted diazo esters are less available, bear some specific properties, and are virtually not investigated for the synthetic purposes. To a certain extent, it can be attributed both to their low stability and to the ability of easy forming cyclopropylcarbenes to undergo isomerization to the corresponding cyclobutenes.[6,7] The similar transformations are characteristic of 2-diazoalkanecarboxylic acid esters, dediazoniation of which shows that the main competing with the interception of the corresponding carbenes process consists in the isomerization of the latter into alkenecarboxylates.[6,8]

In the present work, we elaborated a convenient method for the synthesis of 2-cyclopropyl-2-diazoacetic acid esters (**1**) from available acetylcyclopropane and studied some of their chemical transformations, in particular, 1,3-dipolar cycloaddition of methyl 2-cyclopropyl-2-diazoacetate (**1a**) to acrylates and strained cycloalkenes was investigated for the first time.

Results and discussion

2-Cyclopropyl-2-diazoacetic acid ester **1** can be prepared by decomposition of tosylhydrazones of the corresponding cyclopropyl-substituted α-ketoesters.[7] To obtain diazo esters devoid of substituents in cyclopropane ring, one can start from acetylcyclopropane (**2**) by its prior oxidation to α-keto acid **3** (Scheme 1). However, the described in the literature[9] method for the preparation of keto acid **3** by potassium permanganate oxidation of ketone **2** in the presence of Na_2CO_3 requires a prolong heating and slow addition of the oxidant (36 h at 50 °C). By changing of the order of addition of reagents (see Experimental) and by the use of KOH solution as the base, we were able to decrease the reaction time to 1 h and to increase the yield of ketoacid to 75%. Further methylation of the acid obtained with diazomethane and conver-

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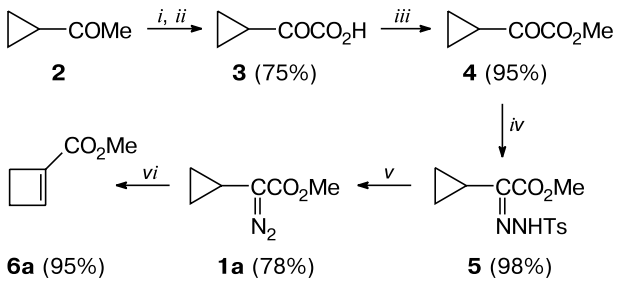
sion of keto ester **4** to tosylhydrazone **5** were carried out by the usual procedures (see Scheme 1). There is information on the synthesis of methyl 2-cyclopropyl-2-diazoacetate (**1a**) and its photolytic cleavage, though, neither the reaction conditions nor the yield of diazo compound **1a** were reported.[6] The later work[7] described the synthesis of methyl esters of *cis*- and *trans*-2-diazo-2-(2,3-dimethylcyclopropyl)acetic acid in ~38% yield, where MeONa in pyridine was used for the decomposition of the corresponding tosylhydrazones of α-keto esters. It can be assumed that the same procedure was applied for the synthesis of unsubstituted in the cyclopropane ring diazo ester **1a**. We changed the reaction conditions and found that the decomposition of tosylhydrazone **5** in acetonitrile assisted by triethylamine at 7 °C allows one to obtain diazo ester **1a** in up to 78% isolated yield (see Scheme 1). Similarly to the case of its dimethyl analog,[7] the obtained diazo ester contained 3—5% of methyl cyclobut-1-enecarboxylate (**6a**) as a by-product, which was formed by the partial dediazoniation of diazo ester **1a** and the intramolecular isomerization of cyclopropyl(methoxycarbonyl)carbene.

Scheme 1

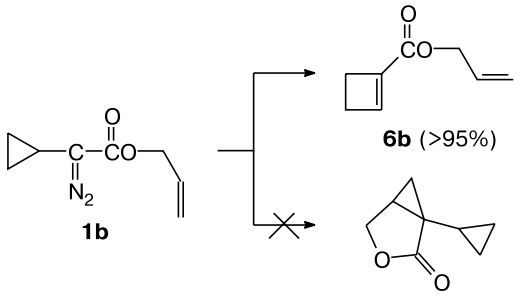


Reagents and conditions: *i*. $KMnO_4$, KOH, 60 °C, 1 h; *ii*. Dowex 50WX8-100 (H^+) resin; *iii*. CH_2N_2 in ether; *iv*. H_2NNHTs, MeOH; *v*. Et_3N, MeCN, 5—7 °C; *vi*. $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C or $(PhO)_3P{\cdot}CuCl$, CH_2Cl_2, 40 °C.

The carbene decomposition of diazo ester **1a,** catalyzed by the transition metal complexes, in particular $(PhO)_3P{\cdot}CuCl$ and $Rh_2(OAc)_4$, proceeds quite efficiently to give exclusively cyclobutenecarboxylate **6a** (see Scheme 1). Addition of various unsaturated compounds (cyclohexene, norbornene, and ethyl vinyl ether) into the reaction mixture does not lead to a noticeable formation of the corresponding products of cyclopropanation, always leaving cyclobutene **6a** virtually the only product.

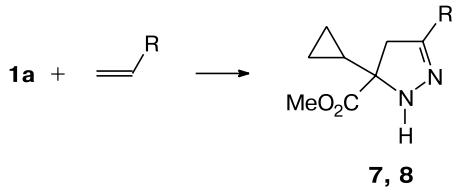
It is known, for example (see Ref. 5), that the catalytic decomposition of allyl esters of α-diazocarboxylic acids leads to the products of intramolecular cyclopropanation, *viz.,* to the corresponding 3-oxabicyclo[3.1.0]hexan-2-ones, in good yields. In order to investigate the competing processes of intramolecular cyclopropanation and cyclopropylcarbene—cyclobutene isomerization, we synthesized allyl ester of 2-cyclopropyl-2-diazoacetic acid (**1b**), applying procedure for the esterification of cyclopropanecarboxylic acids[10] with allyl alcohol and subsequent reactions similar to those used in the preparation of diazo ester **1a**. However, it turned out that the catalytic decomposition of obtained diazo ester **1b** in the presence of $(PhO)_3P{\cdot}CuCl$ or $Rh_2(OAc)_4$ did not lead to a noticeable formation of the bicyclic lactone, rather allyl cyclobut-1-enecarboxylate (**6b**) was the main product of the dediazoniation of **1b** (Scheme 2). Thus, if the photolysis (first of all, photosensitization) of α-cyclopropyldiazoacetates in the presence of olefins leads to a certain extent of intermolecular interception of forming cyclopropylcarbenes,[6,7] then the catalytic dediazoniation of α-cyclopropyl-substituted diazo esters, apparently, leaves not much hope of successful interception of carbenes with the other substrates.

Scheme 2



In contrast to inefficient catalytic cyclopropanation of olefins with cyclopropyl-containing diazo ester **1a**, its 1,3-dipolar cycloaddition reactions to unsaturated compounds, containing electron-withdrawing substituents or strained double bonds, proceed quite successfully. Thus the reaction of diazo ester **1a** with methyl acrylate or acrylonitrile leads to the corresponding functionally substituted 5-cyclopropyl-2-pyrazolines **7** and **8**, which were isolated by vacuum distillation in 60—65% yield (Scheme 3).

Scheme 3

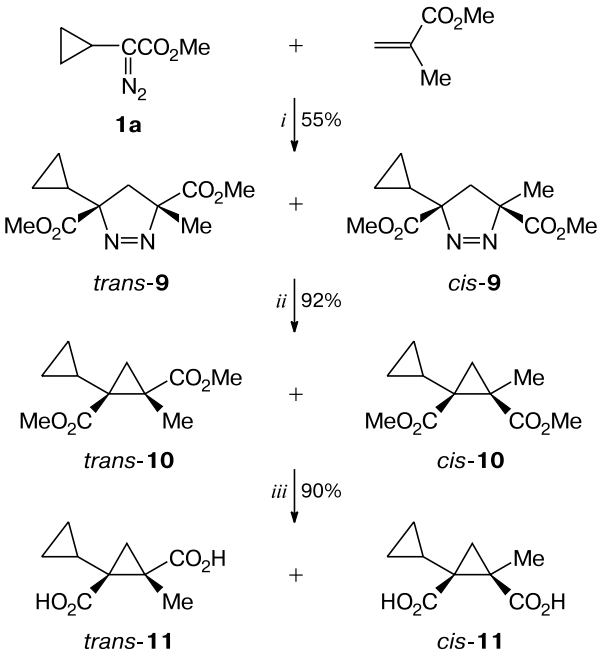


7: R = CO_2Me (65%)
8: R = CN (60%)

Conditions: 7—10 °C, 7 days.

The solvent-free storage of diazo ester **1a** with methyl methacrylate at 7—10 °C for 15 days leads to the formation of isomeric *cis*- and *trans*-1-pyrazolines **9** in the ratio ~1 : 2.2 (Scheme 4). In contrast to 2-pyrazolines **7** and **8**, the obtained pyrazolines **9** easily decompose with evolution of nitrogen even under mild heating. Thus they completely are converted to the corresponding 1-cyclopropylcyclopropane-1,2-dicarboxylates **10** for 1 h at 50 °C, retaining the ratio of *cis*- and *trans*-isomers close to that in the starting pyrazolines. The assignment of isomers was made based upon ^{1}H NMR spectroscopic data on the difference between chemical shifts of geminal protons in tetrasubstituted cyclopropane ring, which is much higher for *cis*-isomers **9** and **10** (Δδ 1.42 and 1.07, respectively) in comparison with the corresponding *trans*-isomers (Δδ 0.11 and 0.16). These regularities are also characteristic of the other close structures, containing cyclopropane-1,2-dicarboxylic acid fragment.[11] Cyclopropanedicarboxylates **10** obtained upon treatment with KOH in methanol, followed by acidification of the potassium salt, can be transformed to the corresponding *cis*- and *trans*-cyclopropanedicarboxylic acids **11** with retention of both cyclopropane fragments in the molecule.

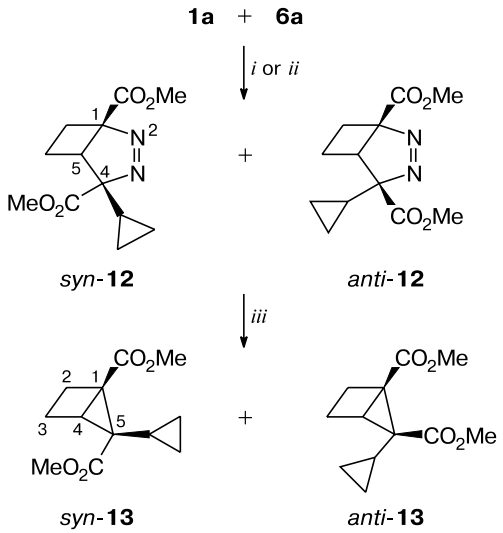
Scheme 4



Reagents and conditions: *i*. 7—10 °C, 14 days, solvent-free; *ii*. $CHCl_3$, 50 °C, 1 h; *iii*. KOH/MeOH, 60 °C, 2 h, then 1 *M* HCl.

It turned out that diazo ester **1a** can slowly react with the product of its own dediazoniation, *i.e.,* with cyclobutenecarboxylate **6a**, which, when the other interceptors of diazo esters **1** are used, can be a side process. Thus keeping of a mixture of diazo ester **1a** with the two-fold excess of cyclobutene **6a** at 5—7 °C for 14 days gives stereoisomeric bicyclic pyrazolines **12** in 35—38% yield with the ratio of *anti*- and *syn*-isomers being ~1 : 4.2 (Scheme 5).

Scheme 5



Reagents and conditions: *i*. 7—10 °C, 14 days, solvent-free; *ii*. 1000 MPa, 10 °C, 24 h; *iii*. C_6H_6, 80 °C, 1.5 h.

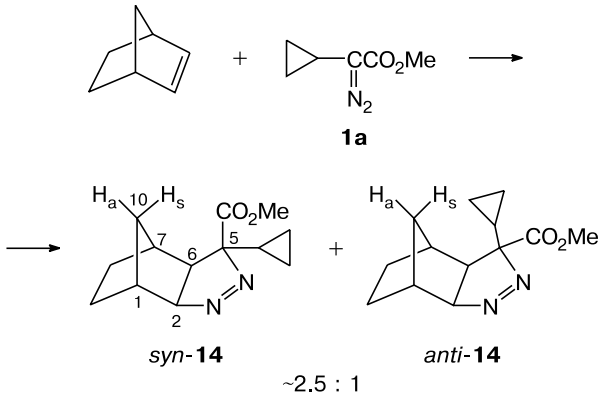
The effectivity of 1,3-dipolar cycloaddition of diazo ester **1a** to cyclobutene **6a** and, correspondingly, the yield of pyrazolines **12** are significantly higher (up to 75%), when the reaction is carried out under high pressure (1000 MPa, 10 °C, 24 h). Separation of the reaction mixture by preparative TLC on SiO_2 allowed us to isolate a pure *syn*-isomer **12** and to obtain an enriched with *anti*-isomer fraction (~80%). Similarly to the formation of pyrazolines **9**, we assumed that isomer with *trans*-arrangement of two ester substituents should be predominant in this reaction. In addition, the formation of *anti*-isomer **12** seems to be sterically less probable due to the strong overlap of H(6) proton and protons in the cyclopropyl substituent.

The dediazoniation of pyrazolines **12** in benzene at 80 °C gives 5-cyclopropyl-1,5-di(methoxycarbonyl)bicyclo[2.1.0]pentanes **13** in high yields, moreover, the individual *syn*-isomer **12** exclusively gives rise to *syn*-isomer **13**. The absence of isomeric unsaturated compounds (or at least their very low content) among reaction products makes it different from the dediazoniation of other such pyrazolines, for example, 2,3-diazabicyclo[3.2.0]hept-2-enes[12] or similar pyrazolines, formed by addition of diazo compounds, in particular, ethyl

diazoacetate, to 1-methoxycarbonylchlorotrifluorocyclobutene.[13]

1,3-Dipolar cycloaddition of diazo ester **1a** to norbornene at 7—10 °C proceeds also slow enough and, due to the side reactions, leads to a mixture of compounds, from which isomeric tricyclic pyrazolines **14** were isolated by column chromatography on SiO_2 in 40—45% yield and in ~1 : 2.5 ratio of *anti*- and *syn*-isomers (Scheme 6). A decrease of the reaction time by an increase in the temperature (50 °C, 4 days) decreases the yield of the target product to 30%. At the same time, conducting of the reaction under high pressure (1000 MPa, 15 °C, 48 h) not only accelerates the reaction, but also considerably increases the total yield of pyrazolines *anti*- and *syn*-**14** (to 75%).

Scheme 6



Conditions: 7—10 °C, 14 days or 1000 MPa, 15 °C, 36 h.

Polycyclic pyrazolines **14** were isolated as the individual compounds by column chromatography on SiO_2 with toluene—ethyl acetate (25 : 1) mixture as the eluent, with the minor *anti*-isomer being the least strongly held by the absorbent.

The structures of pyrazolines obtained were established based on ^1H and ^{13}C NMR spectra, mass spectra, and elemental analysis data. The assignment of tricyclic structure in both isomers to *exo*-configuration was made based on the low values of spin-spin coupling constant for vicinal protons H(1)—H(2) and on the presence of W-constant for the remote protons $H_a(10)$—$H_{endo}(2)$. The positions of substituents at C(5) were established by the presence of the nuclear Overhauser effect between protons of the cyclopropane ring and H(6) proton in major isomer and $H_s(10)$ proton in minor one.

In conclusion, methyl 2-cyclopropyldiazoacetate turned out to be inefficient in the direct catalytic cyclopropanation of unsaturated compounds due to the easy intramolecular isomerization of intermediate cyclopropyl(methoxycarbonyl)carbene to 1-methoxycarbonylcyclobutene. However, the reactions of 1,3-dipolar cycloaddition with the formation of cyclopropyl-substituted pyrazolinecarboxylates can be implemented for it. The latter, in case of 1-pyrazolines, containing electron-withdrawing substituents, easily lose nitrogen molecule to be selectively converted to the derivatives of 1-cyclopropylcyclopropanecarboxylates.

Experimental

^1H and ^{13}C spectra were recorded on a Bruker AC-200 (200 and 50.3 MHz), Bruker AM-300 (300 and 75.5 MHz), and Bruker DRX-500 (500 and 125.3 MHz, respectively) spectrometers in $CDCl_3$ solutions, containing 0.05% of Me_4Si as the internal standard; the COSY, NOESY, and HSQC experiments were performed on a Bruker DRX-500 spectrometer. Mass spectra were recorded on a Finnigan MAT INCOS-50 (EI, 70 eV, direct injection) and Finnigan LCQ (electro-spray ionization (ESI)) instruments for MeCN solutions. Elemental analysis data were obtained on a PerkinElmer Series II, 2400 C,H,N-analyzer. Thin layer chromatography was performed on silica gel 60 (Merck) plates with visualization in iodine chamber. Column chromatography was used for the preparative isolations (silica gel 60, 0.040—0.063 mm, Merck) with the substance—absorbent ratio being ~1 : 60. Acetylcyclopropane (99% purity) was synthesized according to the described procedure.[14] Chemically pure solvents (>99.6%) were used in this work without additional purification.

2-Cyclopropyl-2-oxoacetic acid (3). Acetylcyclopropane (**2**) (12.6 g, 0.15 mol) was added to a solution of $KMnO_4$ (44.2 g, 0.28 mol) in water (380 mL) with stirring, the mixture was heated to 30 °C and 10% aq. KOH (6 mL) was added to this, resulting in warming up of the reaction mixture to 60 °C, this temperature was further kept for 1 h. After the reaction was over, the mixture was filtered, the filtrate was concentrated, and the formed potassium salt was converted to the acid according to the described procedure[9] with the use of Dowex 50WX8-100 (H^+) ion-exchange resin. Acid **3** (12.9 g, 75%) was obtained, b.p. 96—98 °C (18 Torr). MS (EI), m/z (I_{rel} (%)): 114 (2) $[M]^+$, 69 (97) $[M - H_2O - CO]^+$, 41 (100). ^1H NMR ($CDCl_3$), δ: 1.32 (m, 4 H, CH_2CH_2); 2.93 (tt, 1 H, CH, J_{cis} = 7.4 Hz, J_{trans} = 5.0 Hz); 9.11 (br.s, OH). ^{13}C NMR ($CDCl_3$), δ: 15.31 (CH_2CH_2); 17.20 (CH); 160.91 (COO); 195.86 (CO).

Methyl 2-cyclopropyl-2-oxoacetate (4). A solution of diazomethane in ether (0.7 *M*, 93 mL, ~0.065 mol) was added to a stirred solution of keto acid **3** (6.84 g, 0.06 mol) in ether at 10 °C. After ether was evaporated and the residue was distilled *in vacuo*, keto ester **4** (7.29 g, 95%) was obtained, b.p. 94—96 °C (35 Torr); *cf.* Ref. 9: b.p. 85—90 °C (12 Torr). ^1H NMR ($CDCl_3$), δ: 1.21 (m, 4 H, CH_2CH_2); 2.75 (tt, 1 H, CH, J_{cis} = 7.7 Hz, J_{trans} = 4.7 Hz); 3.89 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 13.71 (CH_2CH_2); 18.28 (CH); 52.82 (OMe); 161.91 (COO); 194.0 (CO).

Tosylhydrazone of methyl 2-cyclopropyl-2-oxoacetate (5). A solution of keto ester **4** (16.64 g, 0.13 mol) in methanol (12 mL) was added dropwise to a solution of tosylhydrazine (24.18 g, 0.13 mol) in methanol (25 mL) at 30 °C and the reaction mixture was stirred at 50 °C for 6 h. After cooling, the formed crystals were filtered off and dried *in vacuo* to give tosylhydr-

azone **5** (37.73 g, 98%), m.p. 68—69 °C. MS (EI), m/z (I_{rel} (%)): 296 (25) $[M]^+$, 237 (10) $[M - CO_2Me]^+$, 141 (70), 53 (100). ^{1}H NMR ($CDCl_3$), δ: 0.76 (m, 4 H, CH_2CH_2); 1.92 (m, 1 H, CH); 2.42 (s, 3 H, Me); 3.83 (s, 3 H, OMe); 7.30, 7.78 (both d, 2 H each, C_6H_4, J = 7.7 Hz); 11.51 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 8.40 (CH_2CH_2); 12.47 (CH); 21.62 (Me); 52.64 (OMe); 127.78 (*m*-C); 129.60 (*o*-C); 135.49 (*p*-C); 139.88 (*ipso*-C); 144.20 (C=N); 162.47 (COO).

Methyl 2-cyclopropyl-2-diazoacetate (1a). Triethylamine (15 mL, 0.12 mol) was added to a stirred solution of tosylhydrazone **5** (11.82 g, 0.04 mol) in acetonitrile (25 mL) and this was stirred for 5 h at 5—7 °C. Then ice-cold water (400 mL) was added and the mixture was extracted with ether (75 mL), the organic layer was separated, dried with anhydrous Na_2SO_4, and the solvent was evaporated. The residue was re-distilled *in vacuo* (10^{-2} Torr) into a trap cooled with dry ice. Diazo ester **1a** (4.55 g, 78%) was obtained as bright yellow liquid, containing ~4% methyl cyclobut-1-enecarboxylate (**6a**). ^{1}H NMR ($CDCl_3$), δ: 0.55, 0.92 (both m, CH_2CH_2); 1.67 (tt, 1 H, CH, J_{cis} = 7.9 Hz, J_{trans} = 4.8 Hz); 3.76 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 4.36 (CH); 6.96 (CH_2CH_2); 51.61 (OMe); 59.87 (C=N_2); 167.75 (COO).

Allyl 2-cyclopropyl-2-diazoacetate (1b). The esterification of keto acid **3** was carried out similarly to the procedure used for the esterification of cyclopropanecarboxylic acids[10] with allyl alcohol. The following manipulations were carried out similarly to the preparation of diazo ester **1a**, the yield of the target **1b** was 62—65% calculated from keto acid **3**. ^{1}H NMR ($CDCl_3$), δ: 0.56, 0.92 (both m, CH_2CH_2); 1.66 (tt, 1 H, CH, J_{cis} = 7.9 Hz, J_{trans} = 4.8 Hz); 4.67 (dt, 2 H, OCH_2, ^3J = 5.5 Hz, $^4J \approx$ 1.5 Hz); 5.22 (dq, 1 H, =CH_a, J_{cis} = 10.3 Hz, $J \approx$ 1.5 Hz); 5.31 (dq, 1 H, =CH_b, J_{trans} = 17.0 Hz, $J \approx$ 1.5 Hz); 5.92 (ddt, 1 H, =CH, J_{cis} = 10.3 Hz, J_{trans} = 17.0 Hz, ^3J = 5.5 Hz).

Methyl cyclobut-1-enecarboxylate (6a). Diazo ester **1a** (1.96 g, 14 mmol) was slowly added to a stirred solution of $Rh_2(OAc)_4$ (31 mg, 0.07 mmol) (or 25 mg of $(PhO)_3PCuCl$) in CH_2Cl_2 (15 mL). After gas evolution was over, the solvent was evaporated to 1/4 of its initial volume, pentane (5 mL) was added, and the mixture was filtered through a short layer of silica gel. After the solvents were evaporated and the residue was distilled *in vacuo*, colorless liquid (1.49 g, 95%) was obtained, b.p. 74—76 °C (68 Torr), which, according to the ^{1}H NMR spectrum in $(CD_3)_2SO$, was identical to methyl cyclobutenecarboxylate **6a** described earlier.[15] ^{1}H NMR ($CDCl_3$), δ: 2.48 (ddd, 2 H, H(3), $J \approx$ 3.5 Hz, $J \approx$ 3.0 Hz, $J \approx$ 1.2 Hz); 2.72 (dd, 2 H, H(4), J = 3.5 Hz, J = 3.0 Hz); 3.72 (s, 3 H, OMe); 6.78 (t, 1 H, H(2), J = 1.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.01 (C(3)); 29.01 (C(4)); 51.03 (OMe); 138.38 (C(1)); 146.31 (C(2)); 162.45 (COO).

Allyl cyclobut-1-enecarboxylate (6b). Diazo ester **1b** (0.83 g, 5 mmol) was slowly added to a stirred solution of $Rh_2(OAc)_4$ (14 mg, 0.03 mmol) (or 11 mg of $(PhO)_3PCuCl$) in CH_2Cl_2 (10 mL). After gas evolution was over, the solvent was evaporated to 1/5 of its initial volume, pentane (2 mL) was added, the mixture was filtered through a short layer of silica gel, and the solvents were evaporated *in vacuo* at a residual pressure of 20 Torr. A slightly yellowish liquid was obtained (0.70 g), which virtually was a pure allyl cyclobutenecarboxylate **6b**. ^{1}H NMR ($CDCl_3$), δ: 2.46 (ddd, 2 H, H(3), $J \approx$ 3.5 Hz, $J \approx$ 3.0 Hz, $J \approx$ 1.2 Hz); 2.73 (dd, 2 H, H(4), J = 3.5 Hz, J = 3.0 Hz); 4.63 (dt, 2 H, OCH_2, ^3J = 5.5 Hz, $^4J \approx$ 1.5 Hz); 5.23 (dq, 1 H, =CH_a, J_{cis} = 10.4 Hz, $J \approx$ 1.5 Hz); 5.33 (dq, 1 H, =CH_b, J_{trans} = 17.1 Hz, $J \approx$ 1.5 Hz); 5.94 (ddt, 1 H, =CH, J_{cis} = 10.4 Hz, J_{trans} = 17.1 Hz, ^3J = 5.5 Hz); 6.80 (t, 1 H, H(2), J = 1.2 Hz).

5-Cyclopropyl-3,5-di(methoxycarbonyl)-4,5-dihydro-1*H*-pyrazole (7). A mixture of methyl acrylate (1.81 g, 21 mmol) and diazo ester **1a** (1.96 g, 14 mmol) was kept at 7—10 °C for 7 days. Then, the excess of methyl acrylate was evaporated and the residue was distilled *in vacuo*. Pyrazoline **7** (2.06 g, 65%) was obtained as colorless liquid, b.p. 147—150 °C (12 Torr). Found (%): C, 53.42; H, 6.48; N, 12.03. $C_{10}H_{14}N_2O_4$. Calculated (%): C, 53.09; H, 6.24; N, 12.38. MS (EI), m/z (I_{rel} (%)): 226 (5) $[M]^+$, 195 (7) $[M - OMe]^+$, 167 (85) $[M - CO_2Me]^+$, 135 (100) $[M - CO_2Me - MeOH]^+$. ^{1}H NMR ($CDCl_3$), δ: 0.49 (m, 4 H, CH_2CH_2); 1.35 (tt, 1 H, CH, J_{cis} = 8.2 Hz, J_{trans} = 5.6 Hz); 2.96 (dd, 1 H, $H_aC(4)$, ^2J = 17.4 Hz, ^5J = 0.8 Hz); 3.51 (d, 1 H, $H_bC(4)$, J = 17.4 Hz); 3.79, 3.83 (both s, 3 H each, 2 OMe); 8.53 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 1.13, 1.84 (CH_2CH_2); 17.35 (CH); 40.25 (C(4)); 52.10, 52.89 (2 OMe); 72.34 (C(5)); 142.30 (C(3)); 162.37, 174.15 (2 COO).

3-Cyano-5-cyclopropyl-5-methoxycarbonyl-4,5-dihydro-1*H*-pyrazole (8). The product was obtained similarly from acrylonitrile (1.11 g, 21 mmol) and diazo ester **1a** (1.96 g, 14 mmol). After distillation *in vacuo*, pyrazoline **8** (1.62 g, 60%) was obtained as colorless liquid, b.p. 136—139 °C (12 Torr). Found (%): C, 55.59; H, 5.48; N, 21.60. $C_9H_{11}N_3O_2$. Calculated (%): C, 55.95; H, 5.74; N, 21.75. MS (EI), m/z (I_{rel} (%)): 193 (5) $[M]^+$, 134 (100) $[M - CO_2Me]^+$, 106 (40) $[M - CO_2Me - N_2]^+$. ^{1}H NMR ($CDCl_3$), δ: 0.45, 0.56 (both m, 2 H each, CH_2CH_2); 1.34 (tt, 1 H, CH, J_{cis} = 8.1 Hz, J_{trans} = 5.7 Hz); 2.95 (dd, 1 H, $H_aC(4)$, ^2J = 17.3 Hz, ^5J = 0.8 Hz); 3.46 (d, 1 H, $H_bC(4)$, ^2J = 17.3 Hz); 3.82 (s, 3 H, OMe); 6.68 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 1.36, 2.14 (CH_2CH_2); 17.35 (CH); 42.39 (C(4)); 53.31 (OMe); 72.23 (C(5)); 113.85 (C≡N); 123.92 (C(3)), 173.33 (COO).

3-Cyclopropyl-3,5-di(methoxycarbonyl)-5-methyl-4,5-dihydro-3*H*-pyrazole (9). A mixture of diazo ester **1a** (0.56 g, 4 mmol) and methyl methacrylate (0.60 g, 6 mmol) was kept at 7—10 °C for 15 days. The excess of methyl methacrylate and partially formed cyclobutene **6a** were removed *in vacuo* (~0.1 Torr) at the temperature below 15 °C. The residue was dissolved in benzene (15 mL) and passed through a short layer of silica. After the solvent was evaporated, a viscous liquid (0.53 g) was obtained, which, according to the ^{1}H and ^{13}C NMR spectra, constituted a mixture of *cis*- and *trans*-pyrazolinedicarboxylates **9** (the yield was ~55%, the ratio of isomers, ~1 : 2.2) with small admixture (~5%) of other compounds. ***cis*-Isomer 9.** ^{1}H NMR ($CDCl_3$), δ: 0.20, 0.59, 0.69, 0.85 (all m, 1 H each, CH_2CH_2); 1.28, 2.70 (both d, 1 H each, $H_2C(4)$, ^2J = 13.5 Hz); 1.62 (m, 1 H, CH); 1.72 (s, 3 H, Me); 3.70, 3.78 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 1.31, 1.99 (CH_2CH_2); 17.53 (CH); 22.47 (Me); 36.45 (C(4)); 52.40, 52.49 (2 OMe); 95.92 (C(3)); 100.20 (C(5)); 170.00, 170.44 (2 COO). ***trans*-Isomer 9.** ^{1}H NMR ($CDCl_3$), δ: 0.21, 0.60 and 0.75 (all m, 1+2+1 H, CH_2CH_2); 1.56 (s, 3 H, Me); 1.70 (m, 1 H, CH); 1.88, 1.99 (both d, 1 H each, $H_2C(4)$, J = 13.7 Hz); 3.81, 3.82 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 1.05, 1.30 (CH_2CH_2); 16.49 (CH); 22.40 (Me); 34.40 (C(4)); 52.61, 52.65 (2 OMe); 96.68 (C(3)); 100.53 (C(5)); 170.65, 170.77 (2 COO).

Dimethyl 1-cyclopropyl-2-methylcyclopropane-1,2-dicarboxylate (10). Obtained in the preceding experiment reaction mixture (0.46 g) was heated in $CHCl_3$ (5 mL) at 50 °C for 1 h.

After the solvent was evaporated by microdistillation *in vacuo*, a mixture of *cis*- and *trans*-isomers of dimethyl 1-cyclopropyl-2-methylcyclopropane-1,2-dicarboxylate (0.37 g, 92%) was isolated in the ratio ~1 : 2.3, b.p. 116—119 °C (7 Torr). Found (%): C, 62.04; H, 7.49. $C_{11}H_{16}O_4$. Calculated (%): C, 62.25; H, 7.60. MS (EI), *m/z* (I_{rel} (%)): 212 $[M]^+$ (3), 180 $[M - MeOH]^+$ (11), 152 $[M - HCO_2Me]^+$ (35), 137 (32), 120 (37), 93 $[C_7H_9]^+$ (100). ***cis*-Isomer 10.** ^{1}H NMR ($CDCl_3$), δ: 0.21, 0.59, 0.38, 0.67 (all m, 1 H each, CH_2CH_2); 0.71, 1.78 (both d, 1 H each, $H_2C(3)$, ^2J = 5.1 Hz); 1.35 (m, 1 H, CH); 1.44 (s, 3 H, Me); 3.64, 3.67 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 3.51, 5.33 (CH_2CH_2); 10.60 (CH); 14.94 (Me); 21.67 (C(3)); 30.35 (C(1)); 39.67 (C(2)); 51.89, 51.95 (2 OMe); 172.37, 173.54 (2 COO). ***trans*-Isomer 10.** ^{1}H NMR ($CDCl_3$), δ: 0.19, 0.57, 0.29, 0.43 (all m, 1 H each, CH_2CH_2); 1.23, 1.39 (both d, 1 H each, $H_2C(3)$, J = 5.5 Hz); 1.28 (m, 1 H, CH); 1.34 (s, 3 H, Me); 3.71, 3.75 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 3.38, 5.08 (CH_2CH_2); 9.92 (CH); 16.37 (Me); 19.05 (C(3)); 31.63 (C(1)); 37.58 (C(2)); 51.87, 51.97 (2 OMe); 172.09, 172.18 (2 COO).

1-Cyclopropyl-2-methylcyclopropane-1,2-dicarboxylic acid (11). A solution of KOH (0.063 g, 1.1 mmol) in methanol (4 mL) was added to a solution of diester **10** (0.085 g, 0.4 mmol) (a mixture of isomers) in methanol (1 mL) and the mixture was heated at 60 °C for 2 h. Then, methanol was evaporated, water (8 mL) was added, this was acidified with 1 *M* HCl to pH 1—2 and extracted with ether (3×5 mL)). Etheral extract was dried with anhydrous $CaCl_2$. After evaporation of ether, acid **11** (0.067 g, ~90%) was obtained as yellowish oil (the ratio of *cis*- and *trans*-isomers, ~1 : 2.5). ^{1}H NMR (DMSO-d_6), δ: 0.04, 0.19, 0.32, 0.48 (all m, CH_2CH_2); 0.62, 1.41 (both d, $H_2C(3)$ in minor isomer, J = 5.2 Hz); 0.97, 1.16 (both d, $H_2C(3)$ in major isomer, J = 5.3 Hz); 1.20 (m, CH); 1.22 (s, Me in major isomer,); 1.28 (s, Me in minor isomer); 12.40 (br.s, COOH). ^{13}C NMR ($CDCl_3$), δ: for *trans*-isomer **11** 3.21, 5.30 (CH_2CH_2); 10.10 (CH); 16.49 (Me); 18.40 (C(3)); 30.79 (C(1)); 36.93 (C(2)); 172.44 (2 COO); for *cis*-isomer **11** 4.87, 10.71 (CH_2CH_2); 15.00, 15.10 (CH, Me); 20.71 (C(3)); 29.55 (C(1)); C(2) signal overlaps with DMSO signal; 172.30, 174.04 (2 COO).

4-Cyclopropyl-1,4-di(methoxycarbonyl)-2,3-diazabicyclo[3.2.0]hept-2-ene (12). ***A.*** A mixture of diazo ester **1a** (0.28 g, 2 mmol) and cyclobutenecarboxylate **6a** (0.45 g, 4 mmol) was kept at 7—10 °C for 14 days. The volatile compounds were evaporated *in vacuo* (0.1 Torr, 30 °C), The residue was dissolved in toluene (10 mL) and passed through a short column with SiO_2, eluting with toluene—AcOEt mixture (15 : 1). After evaporation of the solvents, a viscous yellowish liquid (0.20 g) was obtained, which, according to the ^{1}H NMR spectra, was predominantly a mixture of isomeric pyrazolines **12** (the ratio of *syn*- and *anti*-isomers, ~4.2 : 1).

B. Diazo ester **1a** (0.70 g, 5 mmol) and cyclobutene **6a** (0.78 g, 7 mmol) were placed in a PTFE-tube and a few drops of CH_2Cl_2 were added. The tube was placed into a high-pressure reactor, the pressure was adjusted to 1000 MPa, and this was kept for 24 h at 10 °C. After the experiment was over, the high-pressure unit was cooled to −20 °C, the pressure was released, and the reaction mixture was treated as described above. Isomeric pyrazolines **12** (0.96 g) were obtained (the yield, ~75%, the ratio of *syn*- and *anti*-isomers, ~4 : 1). A part of the reaction mixture was separated by preparative TLC (SiO_2, benzene—AcOEt, 5 : 1 as the eluent), collecting a fraction with R_f 0.47 (*syn*-**12**) and 0.53 (*anti*- and *syn*-**12** in the ratio ~3 : 1). ***syn*-Isomer 12.** Found (%): C, 57.51; H, 6.48; N, 10.85. $C_{12}H_{16}N_2O_4$. Calculated (%): C, 57.13; H, 6.39; N, 11.10. MS (ESI), *m/z*: MS 275 $[M + Na]^+$, MS/MS 247 $[M + Na - N_2]^+$. ^{1}H NMR ($CDCl_3$), δ: 0.21, 0.50, 0.66 (all m, 1+2+1 H, CH_2CH_2 in cyclopropane ring); 1.28 (tt, 1 H, CH in cyclopropane ring, J_{cis} = 8.5 Hz, J_{trans} = 5.4 Hz); 1.35 (dddd, 1 H, $H_a(6)$, ^2J = 13.1 Hz, J = 9.8 Hz, J = 7.8 Hz, $J_{5,6a}$ = 6.2 Hz); 2.17 (dddd, 1 H, $H_b(6)$, ^2J = 13.1 Hz, J = 10.4 Hz, $J_{5,6b}$ = 9.3 Hz, J = 5.1 Hz); 2.26 (dddd, 1 H, $H_a(7)$, ^2J = 13.2 Hz, J = 9.8 Hz, J = 5.1 Hz, $J_{5,7a}$ = 1.2 Hz); 2.74 (dddd, 1 H, $H_b(7)$, ^2J = 13.2 Hz, J = 10.4 Hz, J = 7.8 Hz, $J_{5,7b}$ = 1.0 Hz); 2.89 (ddt, 1 H, H(5), $J_{5,6b}$ = 9.3 Hz, $J_{5,6a}$ = 6.2 Hz, $^4J \approx$ 1.1 Hz); 3.82, 3.85 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 1.08, 1.75 (CH_2CH_2); 17.35 (CH); 19.34 (C(6)); 27.45 (C(7)); 39.78 (C(5)); 52.50, 52.84 (2 OMe); 98.00 (C(4)); 103.48 (C(1)); 168.89, 169.84 (2 COO). ***anti*-Isomer 12.** ^{1}H NMR ($CDCl_3$), δ: 0.57, 0.73, 1.16 (all m, 1+2+1 H, CH_2CH_2 in cyclopropane ring); 1.31 (m, 1 H, CH in cyclopropane ring); 2.06 (m, 2 H, H(6)); 2.32 (m, 1 H, $H_a(7)$); 2.78 (m, 1 H, $H_b(7)$); 3.30 (ddt, 1 H, H(5), $J_{5,6b}$ = 8.7 Hz, $J_{5,6a}$ = 7.0 Hz, $^4J \approx$ 1.1 Hz); 3.71, 3.74 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 1.36, 2.89 (CH_2CH_2); 13.17 (CH); 16.27 (C(6)); 26.98 (C(7)); 41.50 (C(5)); 52.69, 52.81 (2 OMe); 99.06 (C(4)); 100.07 (C(1)); 168.29, 171.01 (2 COO).

5-Cyclopropyl-1,5-di(methoxycarbonyl)bicyclo[2.1.0]pentane (13). A solution of pyrazolines **12** (0.129 g, 0.51 mmol) (the ratio of *syn*- and *anti*-isomers, ~4 : 1) in benzene (3 mL) was refluxed for 1.5 h, then passed through a short layer of silica gel, washed with benzene (3 mL), the solvent was evaporated *in vacuo* to give a mixture of *syn*- and *anti*-isomers (~4 : 1, ^{1}H and ^{13}C NMR spectra) of bicyclopentanedicarboxylate **13** (0.109 g, ~95%). In similar conditions, the thermolysis of pure *syn*-isomer **12** gives a single *syn*-isomer **13**. ***syn*-Isomer 13.** MS (EI), *m/z* (I_{rel} (%)): 224 (0.5) $[M]^+$, 210 (1.5), 196 (12), 165 (13) $[M - CO_2Me]^+$, 164 (10) $[M - HCO_2Me]^+$, 151 (15), 133 (17), 105 (20), 84 (100). ^{1}H NMR ($CDCl_3$), δ: 0.53, 0.72 (both m, 2 H each, CH_2CH_2); 1.21 (tt, 1 H, CH, J_{cis} = 8.5 Hz, J_{trans} = 5.4 Hz); 1.74 (dddd, 1 H, $H_a(3)$, ^2J = 11.7 Hz, J_{cis} = 5.8 Hz, J_{trans} = 3.6 Hz, $J_{3a,4} \approx$ 1.2 Hz); 2.02 (dddd, 1 H, $H_a(2)$, ^2J = 11.7 Hz, J_{cis} = 5.8 Hz, J_{trans} = 4.3 Hz, $J_{2a,4} \approx$ 1.2 Hz); 2.21 (dddd, 1 H, $H_b(3)$, ^2J = 11.7 Hz, J_{cis} = 10.5 Hz, J_{trans} = 4.3 Hz, $J_{3b,4}$ = 4.8 Hz); 2.53 (ddd, 1 H, $H_b(2)$, ^2J = 11.7 Hz, J_{cis} = 10.5 Hz, J_{trans} = 3.6 Hz); 2.79 (dt, 1 H, H(4), $J_{3b,4}$ = 4.8 Hz, $J_{3a,4} \approx J_{2a,4} \approx$ 1.2 Hz); 3.65, 3.66 (both s, 3 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 3.75, 6.21 (CH_2CH_2); 6.40 (CH); 16.84 (C(3)); 20.83 (C(2)); 34.03 (C(4)); 34.23 (C(5)); 43.25 (C(1)); 51.37, 51.55 (2 OMe); 170.05, 171.23 (2 COO). ***anti*-Isomer 13.** ^{1}H NMR ($CDCl_3$), δ: 1.30 (m, CH); 3.70, 3.77 (both s, 2 OMe); the rest of the signals overlap with the signals of the main *syn*-isomer. ^{13}C NMR ($CDCl_3$), δ: 3.70, 5.63 (CH_2CH_2); 10.41 (CH); 18.23 (C(3)); 23.22 (C(2)); 33.61 (C(4)); 34.38 (C(5)); 46.27 (C(1)); 51.31, 51.52 (2 OMe); 170.34, 171.35 (2 COO).

5-Cyclopropyl-5-methoxycarbonyl-3,4-diazatricyclo-[5.2.1.0^{2,6}]dec-3-ene (14). ***A.*** A mixture of norbornene (4.70 g, 0.05 mol), diazo ester **1a** (2.10 g, 0.015 mol), and CH_2Cl_2 (0.3 mL) was kept for 14 days at 7 °C. Then, the volatile compounds were evaporated *in vacuo* (~0.5 Torr). The residue (1.92 g) was obtained, which contained isomeric 3,4-diazatricyclodecenes **14** (*syn* : *anti* ≈ 2.5 : 1) with admixture of pyrazolines **12**. The reaction mixture obtained was separated by

column chromatography (SiO_2, toluene—AcOEt, 25 : 1 as the eluent), receiving initially the minor *anti*-isomer, then, a mixture of isomers, further, individual *syn*-isomer **14**, and, finally, a fraction, containing *syn*-isomer **14** together with pyrazolines **12**. After evaporation of the solvents, the eluates were analyzed by ^{1}H NMR spectroscopy.

B. A mixture of norbornene (0.94 g, 10 mmol), diazo ester **1a** (0.56 g, 4 mmol), and CH_2Cl_2 (0.3 mL) was placed into a PTFE-tube, which was placed in a high-pressure reactor and kept for 24 h at 1000 MPa. After the reaction was over, the pressure was released, the mixture was cooled to −20 °C, and the reaction mixture was concentrated *in vacuo* at ~0.2 Torr. The residue was dissolved in benzene (10 mL) and passed through a short layer of silica gel. After the solvent was evaporated, pyrazolines **14** (0.74 g, 78%) were obtained as a slightly yellowish liquid, which was a mixture of *syn*- and *anti*-isomers (~2.4 : 1). This was separated by chromatography as described earlier. ***syn*-Isomer 14.** Found (%): C, 66.19; H, 7.58; N, 12.24. $C_{13}H_{18}N_2O_2$. Calculated (%): C, 66.64; H, 7.74; N, 11.96. MS (EI), m/z (I_{rel} (%)): 234 (2) $[M]^+$, 206 (6) $[M - N_2]^+$, 178 (19), 146 (26), 105 (82), 91 (82), 79 (70), 59 (63); 41 (100). ^{1}H NMR ($CDCl_3$), δ: −0.12, 0.43, 0.72 (all m, 1+2+1 H, CH_2CH_2); 0.66 (dq, 1 H, *syn*-H(10), ^2J = 10.5 Hz, $J \approx$ 1.5 Hz); 0.89 (dq, 1 H, *anti*-H(10), ^2J = 10.5 Hz, $J \approx$ 1.8 Hz); 1.15 (m, 1 H, *endo*-H(8)); 1.31 (m, 1 H, *endo*-H(9)); 1.45 (m, 2 H, *exo*-H(8) and CH in cyclopropane ring); 1.58 (m, 1 H, *exo*-H(9)); 1.71 (dd, 1 H, H(6), ^3J = 6.8 Hz, $J \approx$ 1.8 Hz); 1.99 (m, 1 H, H(7)); 2.89 (m, 1 H, H(1), $^3J_{1,9exo}$ = 4.8 Hz); 3.83 (s, 3 H, OMe); 4.57 (dt, 1 H, H(2), ^3J = 6.8 Hz, $J \approx$ 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.33, 0.59 (CH_2CH_2); 18.69 (CH); 25.29 (C(9)); 28.68 (C(8)); 32.25 (C(10)); 38.16, 38.41 (C(1), C(7)); 47.63 (C(6)); 51.82 (OMe); 97.55 (C(2)); 98.69 (C(5)); 170.95 (COO). ***anti*-Isomer 14.** ^{1}H NMR ($CDCl_3$), δ: 0.45, 0.73, 1.10 (all m, 1+2+1 H, CH_2CH_2); 0.68 (m, 1 H, *syn*-H(10)); 1.00 (dq, 1 H, *anti*-H(10), ^2J = 10.5 Hz, $J \approx$ 1.5 Hz); 1.17 (m, 1 H, *endo*-H(8)); 1.30 (m, 2 H, *endo*-H(9), CH in cyclopropane ring); 1.46 (m, 1 H, *exo*-H(8)); 1.61 (m, 1 H, *exo*-H(9)); 2.01 (dd, 1 H, H(6), ^3J = 6.8 Hz, $J \approx$ 1.8 Hz); 2.38 (m, 1 H, H(7)); 2.99 (m, 1 H, H(1), $^3J_{1,9exo}$ = 4.8 Hz); 3.69 (s, 3 H, OMe); 4.63 (dt, 1 H, H(2), ^3J = 6.8 Hz, $J \approx$ 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 1.57 and 3.34 (CH_2CH_2); 12.80 (CH); 25.31 (C(9)); 28.72 (C(8)); 33.53 (C(10)); 36.85 C(7)); 38.52 (C(1)); 46.96 (C(6)); 52.36 (OMe); 97.70 (C(5)); 98.63 (C(2)); 171.59 (COO).

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