Formation of the double addition products of donor-acceptor cyclopropanes with 2-pyrazolines in the presence of Lewis acids

R. A. Novikov, Yu. V. Tomilov, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 135 6390. E-mail: tom@ioc.ac.ru

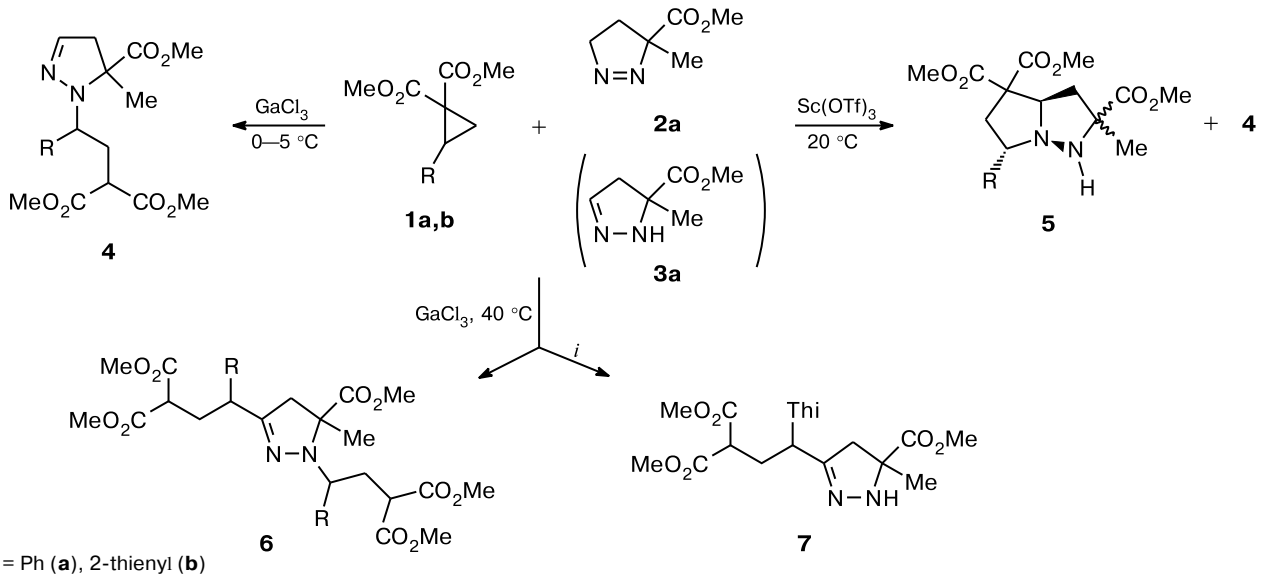
A reaction of excess of cyclopropane-1,1-dicarboxylates substituted at position 2 with 2-pyrazolines in the presence of 3 equiv. of $GaCl_3$ at 5 °C selectively resulted in the cyclopropanes double addition products, *viz.*, *N*-substituted 1,2-diazabicyclo[3.3.0]octanes. In this case, the first molecule of the starting cyclopropane formed the bicyclic system, whereas the second added at the N—H bond of the adduct formed. When catalytic amount of $Sc(OTf)_3$ was used in this reaction instead of $GaCl_3$ at 40 °C, besides the corresponding 1,2-diazabicyclo[3.3.0]-octanes, another type of cyclopropane double addition products, *viz.*, *N*-alkyl-2-pyrazolines, was formed, in which the alkyl chain was assembled from two molecules of the starting cyclopropane. A plausible mechanism for the transformations observed was suggested.

Key words: donor-acceptor cyclopropanes (cyclopropanedicarboxylates), 2-pyrazolines, catalysis, Lewis acids, double addition.

It is known that cyclopropanes with donor and acceptor substituents in the vicinal position are capable of the three-membered ring opening[1—5] by thermolysis or Lewis acid catalysis. A dipolar intermediate formed as a result of the cleavage of the σ-1,2-bond of cyclopropane ring can be involved in the formal [2+3]- or [3+3]-cycloaddition reaction with double and triple bonds, as well as with 1,3-dipoles with the formation of five- or six-membered rings, including those containing heteroatoms.

Recently, we have shown[6] that the reaction of substituted at position 2 cyclopropane-1,1-dicarboxylates **1** with 1- and 2-pyrazolines (**2** and **3**, respectively) was efficiently catalyzed by Sc and Yb triflates to furnish *N*-substituted 2-pyrazolines **4** and 1,2-diazabicyclo[3.3.0]octanes **5** (Scheme 1). In this case, the reaction of compounds **1**

Scheme 1



R = Ph (**a**), 2-thienyl (**b**)

i. R = 2-thienyl (Thi).

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with 1-pyrazolines **2** at 20 °C predominantly gave pyrazolines **4** (yields 61—66%), whereas with 2-pyrazolines **3**, diazabicyclooctanes **5** were predominantly formed (yields 57—61%). The use of anhydrous $GaCl_3$ also promoted the reaction of cyclopropanedicarboxylates **1** with pyrazolines, however, in this case the use of the equimolar amount of $GaCl_3$ with respect to the starting cyclopropane and the temperature reduced to 0—5 °C were required. These conditions gave *N*-substituted 2-pyrazolines **4** as the 1 : 1 adducts with both 1- and 2-pyrazolines (**2** and **3**).

However, when the temperature was increased from 5 to 40 °C, the reaction of cyclopropane-1,1-dicarboxylates **1** with pyrazolines **2** and **3** in the presence of $GaCl_3$ led not only to diazabicyclooctanes **5**, but also to 2-pyrazolines **6** and **7** containing an additional alkyl substituent at position 3 of the heterocycle,[7] with the latter becoming the major reaction products in excess cyclopropanedicarboxylate (see Scheme 1).

In the present work, the studies of the reaction of donor-acceptor cyclopropanes with 2-pyrazolines were continued and new directions for these transformations were found, which led to the formation of the products of double addition of cyclopropanes to pyrazoline molecule.

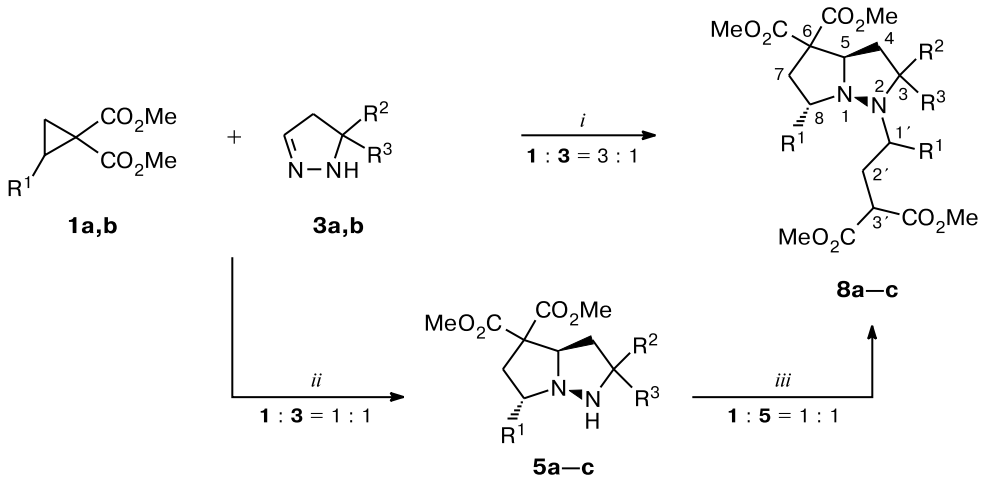
Results and Discussion

Earlier,[6,7] we have found that the reaction of 2-pyrazoline **3a** with 2-phenylcyclopropanedicarboxylate **1a** carried out in the presence of the equimolar amount of $GaCl_3$ at 5 and 20 °C led only to compounds **4a**, **5a**, and **6a** (see Scheme 1), the total yield of which was slightly higher 60% (Table 1, entries *3* and *4*). However, more thorough studies of the reaction mixture composition resulted in the isolation of yet another product, *viz.*, *N*-substituted 1,2-diazabicyclo[3.3.0]octane **8a** (Scheme 2), which was a mixture of four diastereomers (see below). This compound, like pyrazoline **6a**, was a product of the addition of two molecules of cyclopropane **1a** to one molecule of pyrazoline **3a**, therefore, it was logically to expect that an increase in the amount of the donor-acceptor cyclopropane would result in a noticeable increase in the yield of compound **8a**. In fact, when a three-fold excess of compound **1a** was used, the yield of *N*-substituted diazabicyclooctane reached 58% (see Table 1, entry *2*), with some amount of the starting cyclopropane undergoing polymerization in the course of the reaction.

It was very interesting to observe how the yields of the product of the double reaction of cyclopropanes **1a**,**b** with pyrazoline **3a** depended on the temperature of the process. Thus, at 40 °C compounds **8a**,**b** were formed in the minor amounts, whereas their isomers **6a**,**b** were obtained as the major products (see Table 1, entries *6* and *10*). Another pattern was observed at 5 °C: on the contrary, in this case bicyclic compounds **8a**,**b** noticeably predominated, whereas their isomers **6a**,**b** were formed in the minor amounts (see Table 1, entries *2* and *9*). At room temperature, poorly separable mixtures of the corresponding isomeric compounds were obtained in comparable amounts.

When 1-pyrazoline **2a** was used instead of 2-pyrazoline **3a**, no formation of compound **8a** was observed under all the range of conditions applied. No such a product was obtained in the reaction of *N*-substituted 2-pyrazoline **4a**

Scheme 2



Compound	R^1	Compound	R^2	R^3	Compound	R^1	R^2	R^3	Yield (%)	Compound	R^1	R^2	R^3
1a	Ph	**3a**	Me	CO_2Me	**5a**	Ph	Me	CO_2Me	61	**8a**	Ph	Me	CO_2Me
1b	2-Thienyl	**3b**	Ph	Ph	**5b**	2-Thienyl	Me	CO_2Me	57	**8b**	2-Thienyl	Me	CO_2Me
					5c	Ph	Ph	Ph	82	**8c**	Ph	Ph	Ph

i. $GaCl_3$ (3 equiv.), CH_2Cl_2, 5 °C, 10 min; *ii*. $Sc(OTf)_3$ (5 mol.%), CH_2Cl_2, 20 °C, 4 h; *iii*. $GaCl_3$ (1 equiv.), 5 °C, 10 min.

with cyclopropane **1a**, either. Thus, compounds **8** are the products of alkylation of the N—H bond in the initially formed diazabicyclooctanes **5**. Though for substituted cyclopropane-1,1-dicarboxylates, the cyclopropane ring opening reaction upon the action of nucleophilic agents and Lewis acids are studied much poorly than cycloaddition reactions, nonetheless, there are a number of examples demonstrating the addition of dipolar cyclopropanes at the N—H bond. Thus, in the presence of Et_2AlCl the donor-acceptor cyclopropanes react with ammonia, primary and secondary amines with the formation of γ-aminocarboxylic acid derivatives in from moderate to high yields.[8] Analogous process was also described for the azoles containing an N—H bond.[9] However, because of lower activity of the latter, the reaction under consideration required more drastic conditions: catalysis with lanthanum triflate under microwave irradiation, heating and increased pressure.

It turned out that an efficient addition of donor-acceptor cyclopropanes at the N—H bond can be also promoted by gallium trichloride. Earlier,[6] such a process has been already detected in the reaction of cyclopropanes **1** with pyrazoline **3a** in the presence of an equimolar amount of $GaCl_3$ with the formation of pyrazolines **4** (see Scheme 1). In the present work, it was shown that compounds containing a pyrazolidine fragment in the molecule could be involved in the analogous reaction. In fact, the reaction of cyclopropanes **1a**,**b** with diazabicyclooctanes **5a**,**b** in the presence of $GaCl_3$ led to the formation of compounds **8a**,**b** in 67—71% yields (see Table 1, entries *7* and *11*), in this case again the best result was obtained when reaction was carried out at 5 °C (entries *7* and *8*).

To increase the selectivity of preparation of *N*-substituted diazabicyclooctanes **8**, the process can be divided into two sequential steps: the first step would include the synthesis of diazabicyclooctane **5** by the reaction of cyclopropane **1** with 2-pyrazoline **3a** under catalysis with $Sc(OTf)_3$, in which no formation of cyclopropane double addition products would occur,[6] and then the reaction of cyclopropanedicarboxylate **1** with the synthesized diazabicyclooctane **5** already in the presence of $GaCl_3$ at 5 °C would be carried out.

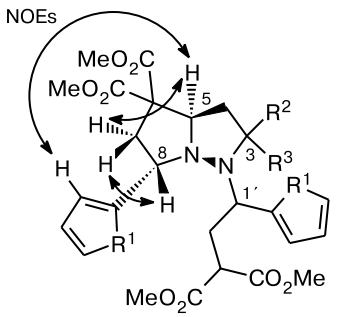
In contrast to pyrazoline **3a**, a direct reaction of excess cyclopropanedicarboxylate **1a** with 5,5-diphenylpyrazoline **3b** in the presence of $GaCl_3$ turned out to be low efficient (see Table 1, entry *12*). The yield of the double addition product **8c** can be increased several times by the use of the initially obtained diphenyldiazabicyclooctane **5c** (see Ref. 6) and by the increase of the reaction time (see Scheme 2 and Table 1, entry *13*). However, because of considerable steric hindrance created by two phenyl substituents at the NH group, even in this case the conversion of **5c** has proved not high enough, though the starting cyclopropane was completely spent out.

Substituted diazabicyclooctanes **8a**,**b** are formed as mixture of four out of eight possible diastereomers in approximately equal proportion. In this case, the isomeric compositions of the compounds formed in the direct reaction of donor-acceptor cyclopropane with pyrazoline and in its reaction with preliminary obtained diazabicyclooctane are completely identical. Unlike compounds **8a**,**b**, diphenyl-substituted diazabicyclooctane **8c** was obtained as a single isomer, that, apparently, can be attributed to the influence of steric factors.

Table 1. Yields of the reaction products of cyclopropanes **1** with pyrazolines **3** or diazabicyclooctanes **5** in the presence of $GaCl_3$[a]

Entry	Cyclopropane	Substrate	Molar ratio	*T*/°C	*t*/min	Yield (%)			
						4[b]	**5**[b]	**6**[c]	**8**[c]
1	**1a**	**3a**	1.3 : 1	5	10	20	37	9	10
2	**1a**	**3a**	3 : 1	5	10	23	5	12	58
3	**1a**	**3a**	1.3 : 1	20	5	17	9	36	15
4	**1a**	**3a**	3 : 1	20	5	19	3	43	24
5	**1a**	**3a**	1.3 : 1	40	5	8	7	48	6
6	**1a**	**3a**	3 : 1	40	5	6	6	78	8
7	**1a**	**5a**	1.3 : 1	5	10	—	—	—	71
8	**1a**	**5a**	1.3 : 1	20	5	—	—	—	63
9	**1b**	**3a**	3 : 1	5	10	25	10	13	50
10	**1b**	**3a**	3 : 1	40	1	14	22	49	12
11	**1b**	**5b**	1.3 : 1	5	10	—	—	—	67
12	**1a**	**3b**	3 : 1	5	30	2	8	—	9[d]
13	**1a**	**5c**	1.3 : 1	5	720	—	—	—	32[d]

[a] CH_2Cl_2, the molar ratio **1** : $GaCl_3$ = 1 : 1.
[b] A mixture of two diastereomers in the equal ratios.
[c] A mixture of four diastereomers in the equal ratios.
[d] Single isomer.



8a—c

8: R^1 = CH=CH (**a**), S (**b**); R^2 = Me, R^3 = CO_2Me (**a**, **b**); R^1 = CH=CH, R^2 = R^3 = Ph (**c**)

Fig. 1. Some characteristic cross-peaks in the 2D ^{1}H NOESY NMR spectra of compounds **8a**—**c**.

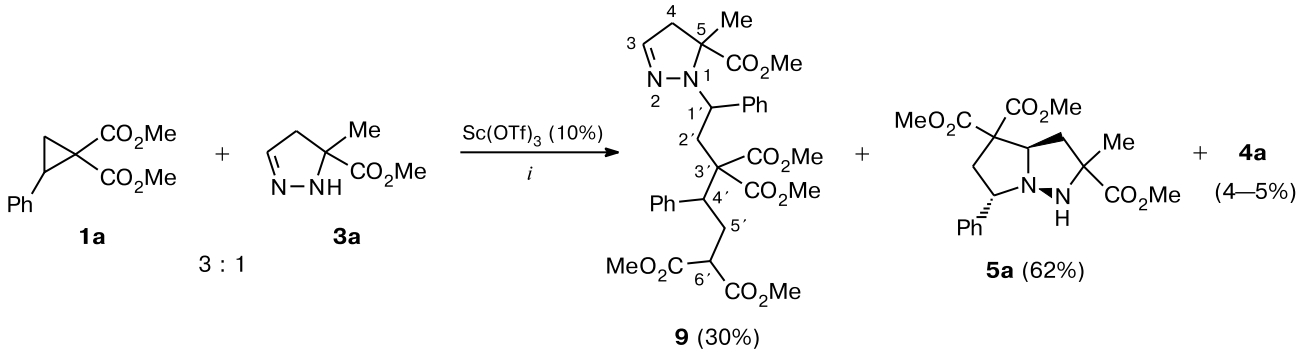
The structures and the isomeric composition of compounds **8a**—**c** were established using homo- and heteronuclear 1D and 2D NMR correlation spectra DEPT, COSY, TOCSY, NOESY, HSQC, and HMBC. The arrows in Fig. 1 show some characteristic cross-peaks in the 2D ^{1}H NOESY NMR spectra of compounds **8a**—**c**, demonstrating retention of stereochemistry of the 8-phenyl-1,2-diazabicyclo[3.3.0]octane fragment for all the diastereomers with respect to the starting compounds **5a**—**c** (see Ref. 6). In addition, we also found relative configuration of substituents at atoms C(3) and C(1′) for a number of examples, however, the stereochemistry of these centers was not unambiguously related to the configuration of atoms C(5) and C(8).

In the present work, we also obtained the third type of the double addition products of cyclopropane to pyrazolines. Thus, the reaction of equimolar amounts of pyrazoline **3a** and cyclopropanedicarboxylate **1a** catalyzed with $Sc(OTf)_3$ at room temperature resulted in the isolation of diazabicyclooctane **5a** and *N*-substituted pyrazoline **4a** as the only products.[6] However, an increase in the temperature to 40 °C and the use of a three-fold excess of the starting cyclopropane partially changed the course of the reaction. In this case, the yield of diazabicyclooctane **5a** remained virtually the same, but a long-chain *N*-alkylpyrazoline **9** was formed as the double addition product of cyclopropane **1a** to pyrazoline **3a** instead of most part of compound **4a** (Scheme 3).

This compound, like other double addition products **6** and **8**, was formed as a mixture of four stereoisomers in approximately equal ratio. The structure and the isomeric composition of compound **9** were established using homo- and heteronuclear 1D and 2D NMR correlation spectra DEPT, COSY, TOCSY, NOESY, HSQC and HMBC. For the ^{1}H and ^{13}C NMR spectra of all the isomers, the signals for the HC=N fragment found in the downfield regions of the spectra (δ_H 6.5—6.6 and δ_C 136—137) are characteristic, where signals for the isomeric compounds **6** and **8** are absent. We also found relative configurations of substituents at atoms C(5) and C(1′)[6], however, stereochemistry of these centers was not unambiguously related to the configuration of atoms C(1′) and C(4′).

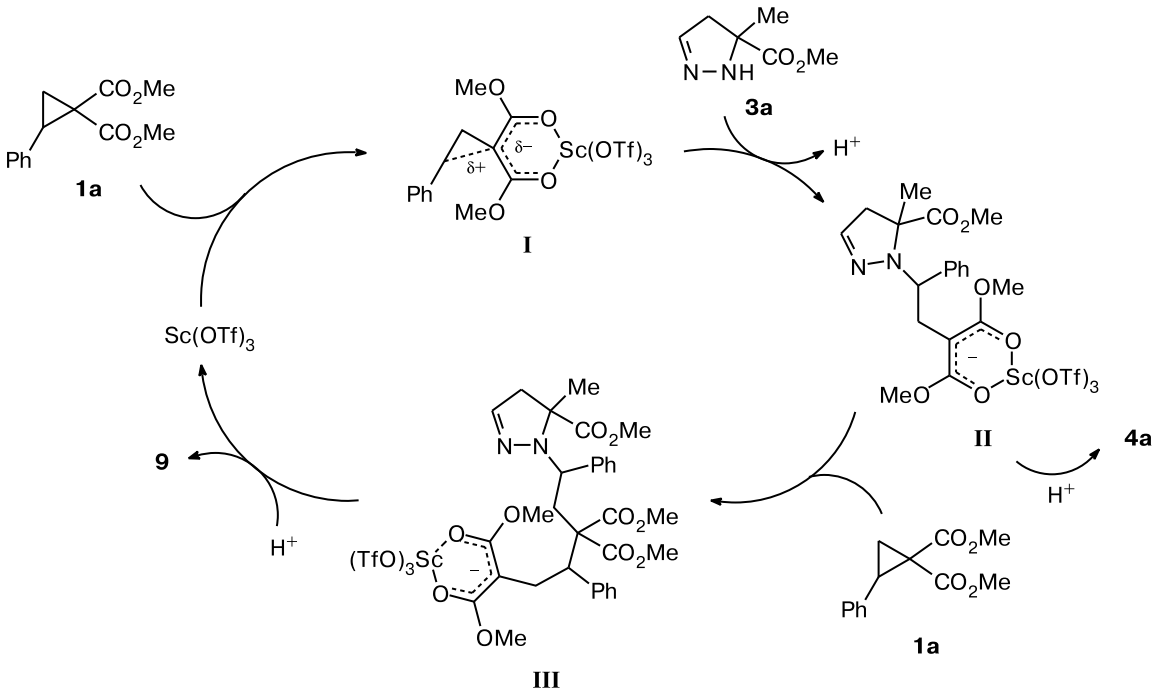
It could have been expected that compound **9** resulted from the further reaction of pyrazoline **4a** with the intermediate formed upon the opening of cyclopropane **1a** by the action of Lewis acid. However, such a suggestion had proved wrong, since an independent experiment showed that such a reaction did not take place under the same conditions. It is also difficult to picture this reaction as proceeding through the formation of the intermediate resulted from the initial reaction of two molecules of the donor-acceptor cyclopropane, since in the presence of $Sc(OTf)_3$ at 40 °C these cyclopropanes themselves gave no any dimeric products. Taking into account these observation, it can be suggested that the intermediate **I** can initially attack both nitrogen atoms of the starting 2-pyrazoline. Subsequent cyclization occurs upon attack at atom N(2), leading to diazabicyclooctanes.[6] The alkylation at atom N(1) leads to the intermediate **II**, which either irreversibly converts to pyrazoline **4** or, because of the pres-

Scheme 3



i. 40 °C, 12 h, CH_2Cl_2.

Scheme 4



ence of excess of donor-acceptor cyclopropane, adds a second molecule of **1**, that leads to the intermediate **III** and then to pyrazoline **9** (Scheme 4).

Theoretically, the intermediate **III**, similarly to the intermediate **II**, could have add another molecule of the donor-acceptor cyclopropane, however, no such products were observed in the reaction mixture. It should be noted that no examples of the formation of such products of addition to the substrate of two molecule of the donor-acceptor cyclopropane, directly bonded to each other, were described earlier. Therefore, the preparation of compound **9** is a new type of the reaction of the donor-acceptor cyclopropane **1a**. Note that similar cyclopropane **1b**, containing a thienyl substituent, does not give such a reaction.

In conclusion, in addition to the recently described method for the introduction of two donor-acceptor cyclopropane fragments at positions 1 and 3 of pyrazolines,[7] we found yet two more types of the reaction of the donor-acceptor cyclopropanes with 2-pyrazolines in the presence of Lewis acids, which were accompanied by the formation of cyclopropane double addition products, *viz.*, *N*-substituted 1,2-diazabicyclo[3.3.0]octanes and *N*-alkyl-2-pyrazolines, in which the alkyl chain was formed of two molecules of the starting cyclopropane. The use of different Lewis acids and varying the temperature allowed us to selectively obtain products with the different type of the double addition of cyclopropanes to 2-pyrazolines.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.1 and 100.6 MHz, respectively) for solutions in $CDCl_3$ containing 0.05% Me_4Si as an internal standard. Assignment of the signals and determination of the isomeric composition of compounds formed were performed using homo- and heteronuclear 1D and 2D correlation spectra DEPT, COSY, TOCSY, NOESY, XHCORR, HSQC, and HMBC. High resolution mass spectra (ESI-HRMS) were obtained on a micrOTOF instrument. Thin-layer chromatography was carried out on Silufol chromatographic plates (Merck). Silica gel 60 (0.040—0.063 mm, Merck) was used for preparative chromatography. Cyclopropanes **1a**,**b** were obtained by the Corey—Chaikovskii reaction.[10,11] Pyrazolines **3a**,**b** were synthesized according to the described procedures.[12,13] Diazabicyclooctanes **5a**—**c** were obtained by the formal [2+3] cycloaddition reaction of donor-acceptor cyclopropanes **1a**,**b** to pyrazolines **2a**,**b** using procedures developed by us earlier.[6] The Lewis acids $Sc(OTf)_3$ (Acros Organics) and $GaCl_3$ (Aldrich) were used in the work. All the manipulations with $GaCl_3$ were carried out under dry argon. Solvents of the reagent grade. (>99.5%) were used without additional purification. Dichloromethane was first stored over granulated KOH and then distilled over P_2O_5 under dry argon.

Reaction of dimethyl 2-arylcyclopropane-1,1-dicarboxylates (1) with 2-pyrazolines 3 and diazabicyclooctanes 5 in the presence of $GaCl_3$ (general procedure). Solid $GaCl_3$ (0.65 or 1.5 mmol) was added in one portion to a solution of cyclopropane **1a**,**b** (0.65 or 1.5 mmol (see Table 1)) and pyrazoline **3a**,**b** (0.5 mmol) or diazabicyclooctane **5a**—**c** (0.5 mmol) in anhydrous dichloromethane (3—5 mL) under argon at a required temperature and with vigorous stirring, then the stirring was continued during the

time indicated in Table 1. After that, the reaction mixture was diluted with 5% aqueous HCl at 0 °C to pH 3 and extracted with dichloromethane (3×10 mL). The organic layers were combined, dried with anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was separated by column chromatography on silica gel (eluent benzene—AcOEt), isolating compounds **4**—**8**. If necessary, the products additionally were purified using TLC on silica gel.

(5*R,8*S**)-Trimethyl 2-[3,3-bis(methoxycarbonyl)-1-phenylprop-1-yl]-3-methyl-8-phenyl-1,2-diazabicyclo[3.3.0]octane-3,6,6-tricarboxylate (8a).** ***A.*** The residue left after the carrying out the reaction of cyclopropane **1a** (0.35 g, 1.5 mmol) and 2-pyrazoline **3a** (71 mg, 0.5 mmol) in the presence of $GaCl_3$ (0.26 g, 1.5 mmol) (see Table 1, entry *2*) was separated by column chromatography on silica gel (eluent benzene—AcOEt, gradient from 20 : 1 to 5 : 1) to obtain pyrazoline **4a** (43 mg, 23%), diazabicyclooctane **5a** (9 mg, ~5%), substituted pyrazoline **6a** (36 mg, 12%), and substituted diazabicyclooctanes (5*R**,8*S**)-**8a** (four diastereomers **8aa**—**8ad** approximately in the equal ratio, totaling 0.18 g, 58%), of which three diastereomers were successfully isolated in the individual state, whereas the fourth only as a predominant isomer. In this case, all the diastereomers were characterized by the same relative configuration of substituents at atoms C(5) and C(8), however, we failed to unambiguously correlate stereochemistry of these centers with positions of substituents at atoms C(3) and C(1′). Compounds **4a**—**6a** and their isomeric composition were identical to those for the samples obtained earlier.[5,6]

B. The residue left after the carrying out the reaction of cyclopropane **1a** (152 mg, 0.65 mmol) and diazabicyclooctane **5a** (0.19 g, 0.5 mmol, a mixture of diastereomers (1 : 1)) in the presence of $GaCl_3$ (114 mg, 0.65 mmol) (see Table 1, entry *7*) was separated by column chromatography to obtained compound **8a** (totaling 0.22 g, 71%) with the same ratio of diastereomers as in entry ***A***.

Compound **8aa**. Colorless dense oil. HRMS (ESI): $[M + K]^+$, calculated for $C_{32}H_{38}N_2O_{10}K$ 649.2158, found 649.2152. ^{1}H NMR ($CDCl_3$), δ: 1.55 (m, 2 H, C(2′)H_2); 1.60 (s, 3 H, Me); 2.00 (dd, 1 H, H_a(4), ^2J = 12.4 Hz, ^3J = 12.0 Hz); 2.18 (dd, 1 H, H_a(7), ^2J = 14.5 Hz, ^3J = 7.2 Hz); 2.33 (dd, 1 H, H_b(4), ^2J = 12.4 Hz, ^3J = 5.4 Hz); 3.10 (dd, 1 H, H(3′), ^3J = 8.1 Hz, ^3J = 7.6 Hz); 3.10 (s, 3 H, OMe at C(3)); 3.33 (dd, 1 H, H_b(7), ^2J = 14.5 Hz, ^3J = 10.0 Hz); 3.49, 3.65 (both s, 3 H each, 2 OMe at C(3′)); 3.60 (dd, 1 H, H(1′), ^3J = 8.8 Hz, ^3J = 8.8 Hz, ^3J = 7.4 Hz); 3.71, 3.80 (both s, 3 H each, 2 OMe at C(6)); 4.18 (dd, 1 H, H(8), ^3J = 10.0 Hz, ^3J = 7.2 Hz); 4.47 (dd, 1 H, H(5), ^3J = 12.0 Hz, ^3J = 5.4 Hz); 7.19 (m, 2 H, H_p, 2 Ph); 7.28 (m, 4 H, H_m, 2 Ph); 7.36 (m, 2 H, H_o, Ph at C(8)); 7.56 (m, 2 H, H_o, Ph at C(1′)). ^{13}C NMR ($CDCl_3$), δ: 28.6 (Me); 37.5 (C(2′)); 39.4 (C(7)); 41.5 (C(4)); 49.0 (C(3′)); 51.6 (CO_2Me at C(3)); 52.2, 52.3 (2 CO_2Me at C(3′)); 52.99, 53.04 (2 CO_2Me at C(6)); 59.5 (C(6)); 60.5 (C(1′)); 69.7 (C(5)); 71.0 (C(3)); 72.7 (C(8)); 127.0 (C_p, Ph at C(1′)); 127.2 (C_p, Ph at C(8)); 127.9 (C_m, Ph at C(1′)); 128.0 (C_o, Ph at C(8)); 128.6 (C_m, Ph at C(8)); 129.1 (C_o, Ph at C(1′)); 141.6 (C_{ipso}, Ph at C(1′)); 143.5 (C_{ipso}, Ph at C(8)); 168.9, 169.87 (2 COO at C(3′)); 169.91, 171.5 (2 COO at C(6)); 173.4 (COO at C(3)).

Compound **8ab**. Colorless dense oil. HRMS (ESI): $[M + H]^+$, calculated for $C_{32}H_{39}N_2O_{10}$ 611.2599, found 611.2593. ^{1}H NMR ($CDCl_3$), δ: 1.32 (s, 3 H, Me); 1.58 (m, 2 H, CH_2(2′)); 1.75 (dd, 1 H, H_a(4), ^2J = 12.6 Hz, ^3J = 6.4 Hz); 2.23 (dd, 1 H, H_a(7), ^2J = 14.5 Hz, ^3J = 8.2 Hz); 2.79 (dd, 1 H, H_b(4), ^2J = 12.6 Hz, ^3J = 11.3 Hz); 3.10 (dd, 1 H, H(3′), ^3J = 9.2 Hz, ^3J = 6.2 Hz); 3.16 (dd, 1 H, H_b(7), ^2J = 14.5 Hz, ^3J = 9.5 Hz); 3.48, 3.63, 3.68, 3.71, 3.78 (all s, 3 H each, 5 OMe); 3.72 (m, 1 H, H(1′)); 3.85 (dd, 1 H, H(5), ^3J = 11.3 Hz, ^3J = 6.4 Hz); 4.23 (dd, 1 H, H(8), ^3J = 9.5 Hz, ^3J = 8.2 Hz); 7.17—7.48 (m, 8 H, 2 H_o, 4 H_m, 2 H_p, 2 Ph); 7.62 (m, 2 H, H_o, Ph at C(8)). ^{13}C NMR ($CDCl_3$), δ: 23.6 (Me); 36.6 (C(2′)); 38.8 (C(7)); 41.7 (C(4)); 48.7 (C(3′)); 52.1, 52.3, 52.5, 52.9, 53.1 (5 OMe); 59.3 (C(6)); 60.5 (C(1′)); 67.1 (C(5)); 69.4 (C(8)); 71.6 (C(3)); 127.1, 127.3 (C_p, 2 Ph); 128.1, 128.2, 128.6, 129.3 (C_o, C_m, 2 Ph); 142.9 (C_{ipso}, 2 Ph); 169.1 (COO at C(3′)); 170.0, 170.1 (COO, the ratio 3 : 1).

Compound **8ac**. Colorless dense oil. HRMS (ESI): $[M + K]^+$, calculated for $C_{32}H_{38}N_2O_{10}K$ 649.2158, found 649.2153. ^{1}H NMR ($CDCl_3$), δ: 1.05 (ddd, 1 H, H_a(2′), ^2J = 14.3 Hz, ^3J = 7.7 Hz, ^3J = 6.7 Hz); 1.33 (s, 3 H, Me); 1.89 (dd, 1 H, H_a(4), ^2J = 11.9 Hz, ^3J = 5.6 Hz); 1.92 (ddd, 1 H, H_b(2′), ^2J = 14.3 Hz, ^3J = 7.7 Hz, ^3J = 6.7 Hz); 2.38 (dd, 1 H, H_a(7), ^2J = 14.2 Hz, ^3J = 9.4 Hz); 2.72 (dd, 1 H, H_b(4), ^2J = 11.9 Hz, ^3J = 12.3 Hz); 3.19 (dd, 1 H, H_b(7), ^2J = 14.2 Hz, ^3J = 8.7 Hz); 3.42 (s, 3 H, CO_2Me at C(3)); 3.43 (t, 1 H, H(3′), ^3J = 7.7 Hz); 3.60, 3.71 (both s, 3 H each, CO_2Me at C(3′)); 3.74, 3.88 (both s, 3 H each, CO_2Me at C(6)); 3.85 (t, 1 H, H(1′), ^3J = 6.7 Hz); 4.42 (dd, 1 H, H(5), ^3J = 12.3 Hz, ^3J = 5.6 Hz); 4.62 (dd, 1 H, H(8), ^3J = 9.4 Hz, ^3J = 8.7 Hz); 7.01 (m, 2 H, H_o, Ph at C(1′)); 7.09 (m, 1 H, H_p, Ph at C(1′)); 7.13 (m, 2 H, H_m, Ph at C(1′)); 7.24 (m, 1 H, H_p, Ph at C(8)); 7.31 (m, 2 H, H_m, Ph at C(8)); 7.42 (m, 2 H, H_o, Ph at C(8)). ^{13}C NMR ($CDCl_3$), δ: 21.4 (Me); 36.9 (C(2′)); 37.4 (C(7)); 44.5 (C(4)); 50.0 (C(3′)); 52.1 (CO_2Me at C(3)); 52.25, 52.27 (CO_2Me at C(3′)); 53.0, 53.3 (CO_2Me at C(6)); 59.0 (C(6)); 61.5 (C(1′)); 66.7 (C(5)); 69.1 (C(8)); 71.2 (C(3)); 127.0 (C_p, Ph at C(1′)); 127.7 (C_p, Ph at C(8)); 128.02 (C_o, Ph at C(1′)); 128.06 (C_m, Ph at C(1′)); 128.2 (C_o, Ph at C(8)); 129.5 (C_m, Ph at C(8)); 141.2 (C_{ipso}, Ph at C(8)); 143.5 (C_{ipso}, Ph at C(1′)); 169.7, 170.2 (2 COO at C(3′)); 170.0, 171.5 (2 COO at C(6));176.5 (COO at C(3)).

(5*R,8*S**)-Trimethyl 2-[3,3-bis(methoxycarbonyl)-1-(2-thienyl)prop-1-yl]-3-methyl-8-(2-thienyl)-1,2-diazabicyclo[3.3.0]octane-3,6,6-tricarboxylate (8b).** ***A.*** The residue left after the carrying out the reaction of cyclopropane **1b** (0.36 g, 1.5 mmol) and 2-pyrazoline **3a** (71 mg, 0.5 mmol) in the presence of $GaCl_3$ (0.26 g, 1.5 mmol) (see Table 1, entry *9*) was separated by column chromatography on silica gel (eluent benzene—AcOEt (10 : 1)) to obtain pyrazoline **4b** (48 mg, 25%), diazabicyclooctane **5b** (19 mg, 10%), substituted pyrazoline **6b** (40 mg, 13%), and substituted diazabicyclooctanes **8b** (totaling 155 mg, 50%) (a mixture of four diastereomers in the equal ratios). Compounds **4b**—**6b** and their isomeric composition were identical to those for the samples obtained earlier.[5,6]

B. The residue left after the carrying out the reaction of cyclopropane **1b** (156 mg, 0.65 mmol) and diazabicyclooctane **5b** (0.19 g, 0.5 mmol, a mixture of diastereomers (1 : 1)) in the presence of $GaCl_3$ (114 mg, 0.65 mmol) (see Table 1, entry *11*) was separated by column chromatography on silica gel to obtain compound **8b** (208 mg, 67%) (a mixture of four diastereomers in the equal ratios).

Compound **8b** (a mixture of four diastereomers). Colorless dense oil. HRMS (ESI): $[M + Na]^+$, calculated for $C_{28}H_{34}N_2O_{10}S_2Na$ 645.1547, found 645.1543. ^{1}H NMR ($CDCl_3$), δ: 0.85, 0.88, 1.48, 1.56 (all s, 3 H*, 4 Me); 1.85 (dd, 1 H, H(4) in

* The integral intensities of the signal are given as calculated based on the intensities of a single proton of one isomer.

isomer *1*, J = 12.6 Hz, J = 6.4 Hz); 1.91 (dd, 1 H, H(4) in isomer *2*, J = 12.3 Hz, J = 12.2 Hz); 2.89 (dd, 1 H, H(4) in isomer *3*, J = 15.0 Hz, J = 7.9 Hz); 2.95 (dd, 1 H, H(4) in isomer *4*, J = 13.0 Hz, J = 10.1 Hz); 1.53—1.73 (m, 8 H, 4 C(2′)H_2); 4.13—4.35 (m, 6 H, 4 H(1′), 2 H(5)); 3.97—4.08 (m, 2 H, 2 H(5) or 2 H(8)); 4.53 (dd, 1 H, H(5) or H(8), J = 9.7 Hz, J = 6.6 Hz); 4.55—4.62 (m, 2 H, 2 H(5) or 2 H(8)); 4.65 (dd, 1 H, H(5) or H(8), J = 12.1 Hz, J = 5.5 Hz); 3.07—3.23 (m, 3 H, 3 H(7)); 3.23—3.37 (m, 5 H, 4 H(3′), H(7)); 2.26—2.84 (m, 8 H, 4 H(4), 4 H(7)); 3.10, 3.26, 3.40, 3.54, 3.57, 3.59, 3.659, 3.664, 3.70, 3.711, 3.716, 3.720, 3.75, 3.76, 3.77, 3.78, 3.79, 3.80, 3.81, 3.82 (all s, 3 H each, 5 CO_2Me in isomers *1—4*); 6.58—7.07 (m, 16 H, H(3″), H(4″), 2 thienyl); 7.11—7.25 (m, 8 H, H(5″)).

(5*R,8*S**)-Dimethyl 2-[3,3-bis(methoxycarbonyl)-1-phenylprop-1-yl]-3,3,8-triphenyl-1,2-diazabicyclo[3.3.0]octane-6,6-dicarboxylate (8c).** ***A.*** The residue left after the carrying out the reaction of cyclopropane **1a** (0.35 g, 1.5 mmol) and 2-pyrazoline **3b** (0.11 g, 0.5 mmol) in the presence of $GaCl_3$ (264 mg, 1.5 mmol) (see Table 1, entry *12*) was separated by column chromatography on silica gel (eluent benzene—AcOEt, gradient from 20 : 1 to 5 : 1) to obtain pyrazoline **4c** (5 mg, 2%), diazabicyclooctane **5c** (18 mg, 8%), and substituted diazabicyclooctane **8c** (31 mg, 9%) as a single isomer. Compounds **4c** and **5c** are identical to the samples obtained earlier.[5,6]

B. The residue left after the carrying out the reaction of cyclopropane **1a** (76 mg, 0.32 mmol) and diazabicyclooctane **5c** (114 mg, 0.25 mmol) in the presence of $GaCl_3$ (57 mg, 0.32 mmol) (see Table 1, entry *13*) was separated by column chromatography on silica gel (eluent benzene—AcOEt (10 : 1)) to obtain compound **8c** (55 mg, 32%) as colorless dense oil. HRMS (ESI): $[M + H]^+$, calculated for $C_{41}H_{43}N_2O_8$ 691.3014, found 691.3007. ^{1}H NMR ($CDCl_3$), δ: 1.88 (ddd, 1 H, H_a(2′), ^2J = 14.2 Hz, ^3J = 8.9 Hz, ^3J = 5.8 Hz); 2.22 (dd, 1 H, H_a(7), ^2J = 14.4 Hz, ^3J = 9.1 Hz); 2.67 (ddd, 1 H, H_b(2′), ^2J = 14.2 Hz, ^3J = 8.8 Hz, ^3J = 5.3 Hz); 2.70 (dd, 1 H, H_a(4), ^2J = 13.3 Hz, ^3J = 12.3 Hz); 3.06 (dd, 1 H, H(3′), ^3J = 8.9 Hz, ^3J = 5.3 Hz); 3.28 (dd, 1 H, H_b(4), ^2J = 13.3 Hz, ^3J = 6.6 Hz); 3.07 (dd, 1 H, H_b(7), ^2J = 14.4 Hz, ^3J = 8.9 Hz); 3.37 (dd, 1 H, H(1′), ^3J = 8.8 Hz, ^3J = 5.8 Hz); 3.57, 3.63, 3.78, 3.92 (all s, 3 H each, 4 OMe); 3.99 (dd, 1 H, H(8), ^3J = 9.1 Hz, ^3J = 8.9 Hz); 4.81 (dd, 1 H, H(5), ^3J = 12.3 Hz, ^3J = 6.6 Hz); 6.05 (m, 2 H, H_o, 1 Ph); 6.78 (m, 2 H, H_m, 1 Ph); 6.88 (m, 1 H, H_p, 1 Ph); 7.11—7.44 (m, 15 H, 3 Ph). ^{13}C NMR ($CDCl_3$), δ: 35.3 (C(2′)); 39.3 (C(7)); 49.8 (C(3′)); 51.2 (C(4)); 52.3, 53.0, 53.3 (4 OMe, the ratio 2 : 1 : 1); 59.6 (C(6)); 63.0 (C(1′)); 67.0 (C(8)); 69.8 (C(5)); 73.5 (C(3)); 125.5, 126.2, 126.3, 127.2 (C_o in all the Ph); 127.3, 127.4, 127.5, 128.2, 128.3 (3 C), 129.4 (C_m and C_p in all the Ph); 142.5, 143.3, 144.8, 151.5 (C_{ipso} in all the Ph); 169.9, 170.1, 170.3, 171.8 (4 COO).

Methyl 1-[3,3,6,6-tetra(methoxycarbonyl)-1,4-diphenylhex-1-yl]-5-methyl-4,5-dihydro-1*H*-pyrazol-5-carboxylate (9). The compound $Sc(OTf)_3$ (63 mg, 0.15 mmol) was added in one portion to a solution of cyclopropane **1a** (351 mg, 1.5 mmol) and pyrazoline **3a** (71 mg, 0.5 mmol) in anhydrous dichloromethane (5 mL) under argon and the reaction mixture was stirred for 12 h at 40 °C. Then, a 5% aq. HCl was added to pH 3 at 0 °C and extracted with CH_2Cl_2 (3×10 mL). The organic layers were combined, dried with anhydrous $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was separated by column chromatography on silica gel (eluent benzene—AcOEt, gradient from 20 : 1 to 5 : 1) to obtain pyrazoline **4a** (9 mg, 5%), diazabicyclooctane **5a** (117 mg, 62%), and substituted pyrazolines **9a—d** (totaling 92 mg, 30%) (a mixture of four diastereomers approximately in the equal ratios), of which two (**9c**,**d**) were obtained in the individual state, whereas another two (**9a**,**b**), as a mixture with each other. A mixture of isomers **9a,b**. Colorless dense oil. HRMS (ESI): $[M + Na]^+$, calculated for $C_{32}H_{38}N_2O_{10}Na$ 633.2419, found 633.2410; $[M + K]^+$, calculated for $C_{32}H_{38}N_2O_{10}K$ 649.2158, found 649.2161.

Isomer (5*R**,1′*R**)-**9a**. ^{1}H NMR ($CDCl_3$), δ: 0.82 (s, 3 H, Me); 1.99 (dd, 1 H, H_a(2′); ^2J = 14.4 Hz, ^3J = 3.3 Hz); 2.26 (ddd, 1 H, H_a(5′), ^2J = 13.0 Hz, ^3J = 9.8 Hz, ^3J = 5.6 Hz); 2.37 (dd, 1 H, H_a(4), ^2J = 17.3 Hz, ^3J = 1.9 Hz); 2.69 (ddd, 1 H, H_b(5′), ^2J = 13.0 Hz, ^3J = 9.5 Hz, ^3J = 3.2 Hz); 2.76 (dd, 1 H, H_b(4), ^2J = 17.3 Hz, ^3J = 2.4 Hz); 2.95 (dd, 1 H, H_b(2′), ^2J = 14.4 Hz, ^3J = 9.9 Hz); 3.07 (dd, 1 H, H(6′), ^3J = 9.5 Hz, ^3J = 5.6 Hz); 3.42 (dd, 1 H, H(4′), ^3J = 9.8 Hz, ^3J = 3.2 Hz); 3.45, 3.47, 3.70, 3.78, 3.88 (all s, 3 H each, 5 OMe); 4.69 (dd, 1 H, H(1′), ^3J = 9.9 Hz, ^3J = 3.3 Hz); 6.49 (dd, 1 H, H(3), ^3J = 2.4 Hz, ^3J = 1.9 Hz); 7.00—7.38 (m, 10 H, 2 Ph).

Isomer (5*S**,1′*R**)-**9b**. ^{1}H NMR ($CDCl_3$), δ: 1.56 (s, 3 H, Me); 2.07 (dd, 1 H, H_a(2′), ^2J = 14.6 Hz, ^3J = 4.4 Hz); 2.24 (ddd, 1 H, H_a(5′), ^2J = 13.2 Hz, ^3J = 11.9 Hz, ^3J = 4.0 Hz); 2.57 (dd, 1 H, H_a(4), ^2J = 17.7 Hz, ^3J = 1.1 Hz); 2.73 (ddd, 1 H, H_b(5′), ^2J = 13.2 Hz, ^3J = 9.8 Hz, ^3J = 1.4 Hz); 2.78 (s, 3 H, CO_2Me at C(5)); 2.93 (dd, 1 H, H_b(2′); ^2J = 14.6 Hz, ^3J = 9.4 Hz); 3.05 (dd, 1 H, H(6′), ^3J = 9.8 Hz, ^3J = 4.0 Hz); 3.14 (dd, 1 H, H_b(4), ^2J = 17.7 Hz, ^3J = 1.3 Hz); 3.49 (dd, 1 H, H(4′), ^3J = 11.9 Hz, ^3J = 1.4 Hz); 3.48, 3.53, 3.73, 3.78 (all s, 3 H each, 4 OMe); 4.32 (dd, 1 H, H(1′), ^3J = 9.4 Hz, ^3J = 4.4 Hz); 6.49 (dd, 1 H, H(3), ^3J = 1.3 Hz, ^3J = 1.1 Hz); 7.02 (m, 2 H, H_o, Ph at C(4′)); 7.10 (m, 2 H, H_m, Ph at C(4′)); 7.13 (m, 1 H, H_p, Ph at C(4′)); 7.16 (m, 1 H, H_p, Ph at C(1′)); 7.20 (m, 2 H, H_m, Ph at C(1′)); 7.31 (m, 2 H, H_o, Ph at C(1′)). ^{13}C NMR ($CDCl_3$), δ: 21.3 (Me); 31.5 (C(5′)); 41.0 (C(2′)); 47.0 (C(4)); 50.0 (C(4′)); 50.6 (C(6′)); 51.2 (CO_2Me at C(5)); 51.8, 51.9, 52.4, 52.5 (4 OMe); 57.0 (C(1′)); 61.1 (C(3′)); 67.7 (C(5)); 126.8 (br), 126.9 (2 C_p); 128.2, 128.3, 128.7 (2 C_m, C_o); 129.5 (br, C_o, Ph at C(4′)); 136.6 (C(3)); 138.4 (C_{ipso}, Ph at C(4′)); 145.1 (C_{ipso}, Ph at C(1′)); 169.3, 169.4, 169.5, 170.8 (4 COO); 172.3 (COO at C(5)).

Isomer (5*S**,1′*R**)-**9c**. Colorless dense oil. HRMS (ESI): $[M + Na]^+$, calculated for $C_{32}H_{38}N_2O_{10}Na$ 633.2419, found 633.2411; $[M + K]^+$, calculated for $C_{32}H_{38}N_2O_{10}K$ 649.2158, found 649.2164. ^{1}H NMR ($CDCl_3$), δ: 1.46 (s, 3 H, Me); 2.04 (dd, 1 H, H_a(2′), ^2J = 14.7 Hz, ^3J = 3.1 Hz); 2.43 (ddd, 1 H, H_a(5′), ^2J = 13.6 Hz, ^3J = 11.1 Hz, ^3J = 2.5 Hz); 2.56 (dd, 1 H, H_a(4), ^2J = 17.0 Hz, ^3J = 1.4 Hz); 2.56 (ddd, 1 H, H_a(5′), ^2J = 13.6 Hz, ^3J = 12.1 Hz, ^3J = 4.2 Hz); 2.72 (s, 3 H, CO_2Me at C(5)); 2.89 (dd, 1 H, H_b(2′), ^2J = 14.7 Hz, ^3J = 9.8 Hz); 2.93 (dd, 1 H, H(6′), ^3J = 11.1 Hz, ^3J = 4.2 Hz); 3.14 (dd, 1 H, H_b(4), ^2J = 17.0 Hz, ^3J = 1.7 Hz); 3.29 (dd, 1 H, H(4′), ^3J = 12.1 Hz, ^3J = 2.5 Hz); 3.53, 3.62, 3.73, 3.75 (all s, 3 H each, 4 OMe); 4.46 (dd, 1 H, H(1′), ^3J = 9.8 Hz, ^3J = 3.1 Hz); 6.55 (dd, 1 H, H(3), ^3J = 1.7 Hz, ^3J = 1.4 Hz); 7.03 (m, 2 H, H_o, Ph at C(4′)); 7.11 (m, 1 H, H_p, Ph at C(1′)); 7.16 (m, 1 H, H_p, Ph at C(4′)); 7.17 (m, 2 H, H_m, Ph at C(1′)); 7.21 (m, 2 H, H_m, Ph at C(4′)); 7.28 (m, 2 H, H_o, Ph at C(1′)). ^{13}C NMR ($CDCl_3$), δ: 21.2 (Me); 31.5 (C(5′)); 42.2 (C(2′)); 46.0 (C(4)); 49.9 (C(4′)); 50.3 (C(6′)); 51.1 (CO_2Me at C(5)); 51.8, 51.9, 52.5, 52.6 (4 OMe); 57.8 (C(1′)); 61.1 (C(3′)); 67.7 (C(5)); 126.80 (br), 126.83 (2 C_p); 127.9 (C_o, Ph at C(1′)); 128.2 (C_m, Ph at C(4′)); 128.5 (C_m, Ph at C(1′)); 129.5 (br, C_o, Ph at C(4′)); 136.9

(CH(3)); 137.5 (C_{ipso}, Ph at C(4′)); 141.7 (C_{ipso}, Ph at C(1′)); 169.4, 169.6, 170.5, 170.6 (4 COO); 172.2 (COO at C(5)).

Isomer (5*R**,1′*R**)-**9d**. Colorless dense oil. HRMS (ESI): $[M + Na]^+$, calculated for $C_{32}H_{38}N_2O_{10}Na$ 633.2419, found 633.2412; $[M + K]^+$, calculated for $C_{32}H_{38}N_2O_{10}K$ 649.2158, found 649.2160. ^{1}H NMR ($CDCl_3$), δ: 0.77 (s, 3 H, Me); 1.88 (dd, 1 H, H_a(2′), ^2J = 14.7 Hz, ^3J = 1.8 Hz); 2.37 (ddd, 1 H, H_a(5′), ^2J = 13.7 Hz, ^3J = 10.6 Hz, ^3J = 2.5 Hz); 2.37 (dd, 1 H, H_a(4), ^2J = 17.5 Hz, ^3J = 1.7 Hz); 2.63 (ddd, 1 H, H_b(5′), ^2J = 13.7 Hz, ^3J = 9.8 Hz, ^3J = 4.4 Hz); 2.88 (dd, 1 H, H_b(2′), ^2J = 14.7 Hz, ^3J = 10.3 Hz); 2.92 (dd, 1 H, H(6′), ^3J = 10.6 Hz, ^3J = 4.4 Hz); 3.26 (dd, 1 H, H(4′), ^3J = 9.8 Hz, ^3J = 2.5 Hz); 3.51 (dd, 1 H, H_b(4), ^2J = 17.5 Hz, ^3J = 1.3 Hz); 3.51, 3.57, 3.73, 3.77, 3.85 (all s, 3 H each, 5 OMe); 4.84 (dd, 1 H, H(1′), ^3J = 10.3 Hz, ^3J = 1.8 Hz); 6.58 (dd, 1 H, H(3), ^3J = 1.7 Hz, ^3J = 1.3 Hz); 7.00 (m, 2 H, H_o, Ph at C(4′)); 7.11 (m, 2 H, H_p, 2 Ph); 7.18 (m, 4 H, H_m, 2 Ph); 7.41 (m, 2 H, H_o, Ph at C(1′)). ^{13}C NMR ($CDCl_3$), δ: 22.2 (Me); 31.5 (C(5′)); 42.5 (C(2′)); 45.3 (C(4)); 50.6 (C(4′)); 50.5 (C(6′)); 51.75, 51.77, 51.9, 52.4, 52.6 (5 OMe); 59.1 (C(1′)); 61.4 (C(3′)); 70.5 (C(5)); 126.77, 126.80 (br, 2 C_p); 127.7 (C_o, Ph at C(1′)); 127.8, 128.6 (2 C_m); 129.5 (br, C_o, Ph at C(4′)); 136.4 (CH(3)); 137.4 (C_{ipso}, Ph at C(4′)); 145.5 (C_{ipso}, Ph at C(1′)); 169.5, 169.6, 170.3, 170.6 (4 COO), 171.7 (COO at C(5)).

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