Reactions of donor-acceptor cyclopropanes or benzylidenemalonate with benzyl azide by generating gallium trichloride 1,2-zwitterionic complexes

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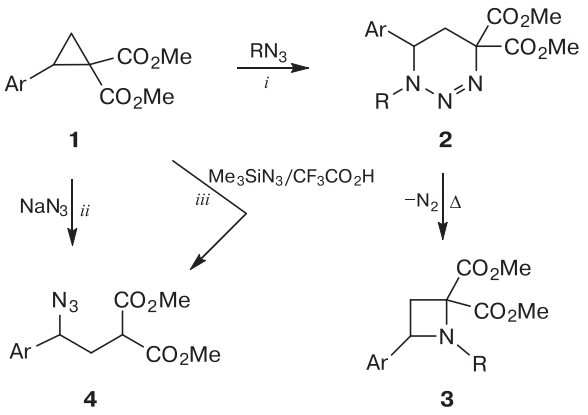
The reactions of 1,2-zwitterionic complexes, generated from 2-arylcyclopropane-1,1-dicarboxylates (ACDC) or benzylidenemalonate and gallium trichloride, with benzyl azide proceeds as a formal [3+2] cycloaddition to form dihydro-1,2,3-triazoles. The latter, when the reaction mixture is treated with 10% aqueous HCl, undergo retrocyclization with elimination of diazomalonate. The reaction of ACDC, benzyl azide, and $GaCl_3$ with simultaneous mixing of the reagents leads to the interception of the 1,3-zwitterion, with this stage being accompanied by both the cyclization to substituted 1,2,3-triazinine and the elimination of a nitrogen molecule to form 3,4-dihydro-2*H*-1,2-oxazine structure, which after acid hydrolysis gives substituted 3-hydroxypyrrolidin-2-one.

Key words: donor-acceptor cyclopropanes, 1,2-zwitterionic complexes, gallium trichloride, benzyl azide, N-heterocyclic compounds.

The last decade is characterized by the intensive development of donor-acceptor cyclopropane (DAC) chemistry.[1] New approaches to their synthesis are being elaborated, new types of reactivity are being studied, while DACs themselves are increasingly used in total syntheses of natural compounds. One of the interesting and important processes in DAC chemistry is the reaction of the generated from them 1,3-zwitterions with various substrates, which proceeds with the formation of six-membered carbo- and heterocycles.[2—6] A comparatively recent paper[7] was devoted to the formal [3+3] cycloaddition of 2-arylcyclopropane-1,1-dicarboxylates (ACDC, **1**) to azides in the presence of Lewis acids. The effect of various Lewis acids ($SnCl_4$, $FeCl_3$, $AlCl_3$ and $TiCl_4$) on the formation of substituted 1,2,3-triazinines **2** was studied (Scheme 1).

Scheme 1



Carrying out the reaction in the presence of $TiCl_4$ provides the best results in terms of the synthesis of triazinine derivatives **2** from ACDC and azides. The resulting triazinines upon heating undergo dediazotization to form azetidines **3** in moderate yields. The latter, in turn, can serve as convenient synthons in the design of biologically active compounds.[7] When azide anion acts as a nucleophile, for example, with the use of sodium azide[8] or trimethylsilyl azide[9] and CF_3CO_2H, ACDC undergoes nucleophilic ring opening to form the corresponding azido diesters **4** (see Scheme 1). This type of reactions accompanied by the three-membered ring opening at the substituted 1,2-bond is a traditional process of the transformation of ACDC treated with various nucleophilic agents.[8—11]

This work belongs to a series of publications[5,12—15] devoted to the study of the transformations of 1,2-zwitterionic intermediates generated from ACDC by treatment with $GaCl_3$. The generation of gallium 1,2-zwitterionic complexes **5** (Scheme 2) allows one to carry out reactions with various substrates, which were studied in the reactions of interception of primary 1,3-zwitterionic intermediates, but in other directions and with the formation of a different composition of products. In this regard, it was interest-

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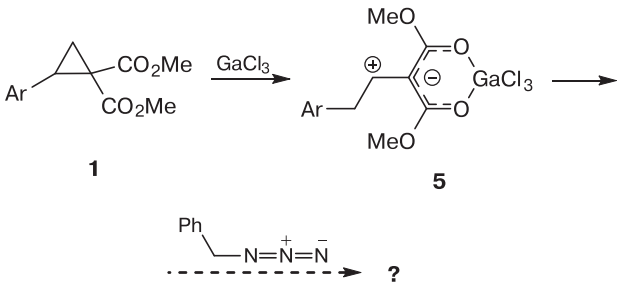
ing to study the reactivity of gallium complexes **5** in the reactions with azides.

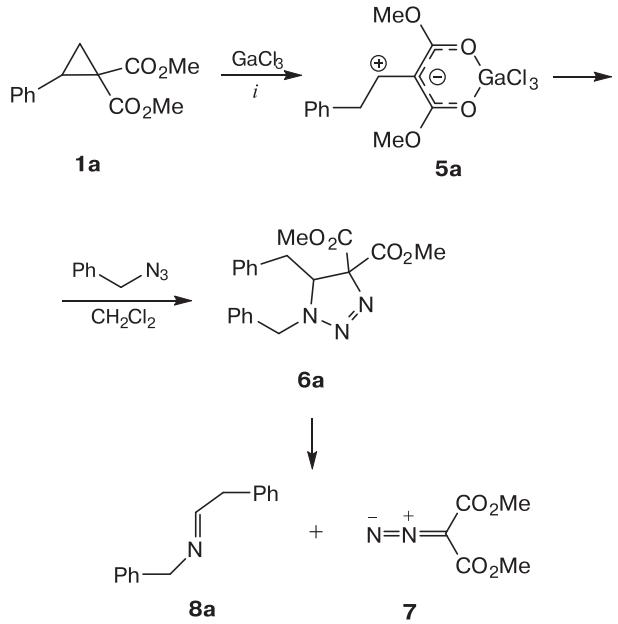
Scheme 2



Results and Discussion

Using the simplest ACDC **1a** as an example, we studied the reaction of 1,2-zwitterionic complex **5a** with benzyl azide under various conditions (Scheme 3, Table 1). In all cases, after the reaction mixtures were treated with 8—10% aqueous HCl at room temperature, the expected [3+2] cycloaddition product, dihydro-1,2,3-triazole **6a**, was formed in only 15—23% yield, while diazomalonate **7** turned out to be the main reaction product (see Table 1). It was logical to suppose that the appearance of diazomalonate could be a consequence of the decomposition of adduct **6a**, which at a certain stage could undergo partial retrocyclization[16] to form diazomalonate **7**

Scheme 3



Reagents and conditions: *i*. CH_2Cl_2, 0—5 °C, 15 min.

Table 1. Yields of dihydrotriazole **6a** and diazomalonate **7** in the reaction of complex **5a**, obtained by the reaction of **1a** with $GaCl_3$, with benzyl azide depending on the reaction conditions (solvent CH_2Cl_2, the reaction mixture was worked-up with 10% aqueous HCl)

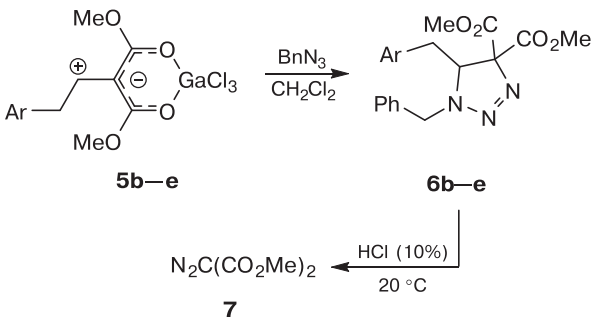
Ratio **1a** : BnN_3	Reaction conditions		Product yield (%)[a]	
	T/°C	*t*/min	**6a**	**7**
1 : 2	20	15	19[b]	36[b]
1 : 1	20	15	16	29
1 : 2	40	20	20[b]	39[b]
1 : 2	20	60	20	37
1 : 2	83[c]	10	15	40
1 : 2	−20	20	22	37

[a] The yields of dihydro-1,2,3-triazole **6a** and diazomalonate **7** were calculated from the ^{1}H NMR spectra with a weighed sample of 1,4-dinitrobenzene as an internal standard.
[b] Isolated yield.
[c] In 1,2-dichloroethane.

and imine **8a** (see Scheme 3). In fact, ^{1}H NMR spectroscopy showed the presence of phenylacetaldehyde as one of the products of acid hydrolysis of imine **8a** in the worked-up reaction mixture.

We carried out additional experiments to confirm the formation of diazomalonate **7** from dihydro-1,2,3-triazole **6a**. Thus, practically no changes were observed when compound **6a** (in CH_2Cl_2 at 20 °C) was treated with 10% aqueous HCl or kept in contact with anhydrous $GaCl_3$. However, if a solution of dihydro-1,2,3-triazole and $GaCl_3$ in dichloromethane is treated with 10% aqueous HCl, the appearance of diazomalonate **7** is clearly detected by ^{1}H NMR spectroscopy. Since it is obvious that the decomposition of dihydro-1,2,3-triazole occurs at the stage of the reaction mixture quenching, the work-up should be carried out at a lowered temperature and preceded by the decomposition of gallium trichloride with methanol.

Scheme 4



Ar = 4-ClC_6H_4 (**b**), 4-FC_6H_4 (**c**), 4-$O_2NC_6H_4$ (**d**), 4-MeC_6H_4 (**e**)

Table 2. Yields of dihydrotriazoles **6a—e** and diazomalonate **7** in the reaction of complexes **5**, obtained by the reaction of DAC **1a—e** with $GaCl_3$, with benzyl azide depending on the work-up conditions of the reaction mixture

Entry	Starting DAC	Work-up conditions[a]	Product yield (%)[b]	
			6a—e	**7**
1	**1a**	*A*	53	—
2	**1b**	*A*	54	—
3	**1c**	*A*	56	—
4	**1d**	*A*	59	—
5	**1e**	*A*	57	—
6	**1b**	*B*	16	36
7	**1c**	*B*	12	38
8	**1d**	*B*	4	72
9	**1e**	*B*	11	40

[a] Work-up conditions: *A*, MeOH, 0 °C; *B*, 10% HCl, 20 °C, 10—15 min.

[b] Reaction conditions: the ratio ACDC/$GaCl_3$ = 1 : 1, 5—20 °C, 15—60 min,[17] **5**/BnN_3 = 1 : 2, 20 °C, 10—15 min.

In fact, the reaction between 1,2-zwitterionic intermediate **5a** and benzyl azide at 20 °C and the subsequent treatment with methanol at 0 °C gives dihydro-1,2,3-triazole **6a** in up to 53% yield practically in the absence of diazomalonate **7**.

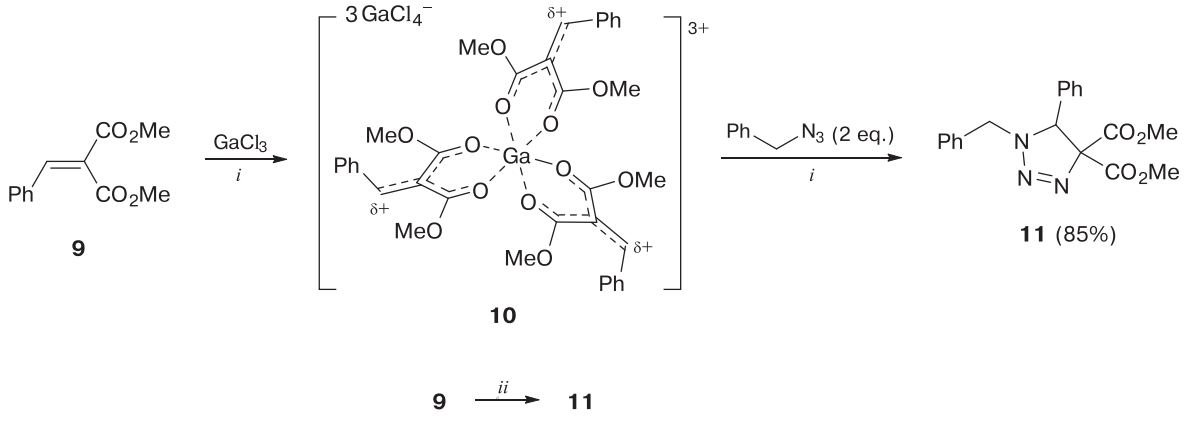
Next, we studied the reaction of benzyl azide with 1,2-zwitterionic complexes **5** (see Refs 12 and 13) obtained from ACDC **1b—e** containing both acceptor (Cl, F, NO_2) and donor (Me) substituents in the benzene ring. It turned out that in this case, the formal [3+2] cycloaddition also proceeded quite efficiently and the corresponding dihydro-1,2,3-triazoles **6b—e** were obtained in moderate yields after the low-temperature work-up of the reaction mixture with methanol, while their yield sharply decreased with the simultaneous appearance of diazomalonate **7** after treatment of the reaction mixture with 10% aqueous HCl (Scheme 4, Table 2).

We carried out a similar process between benzyl azide and benzylidenemalonate **9**, which also can form a 1,2-zwitterionic complex with $GaCl_3$ **10** with somewhat different structure (see Ref. 18). In this case, the [3+2] cycloaddition proceeded more efficiently, giving the corresponding dihydrotriazole **11** in high yield (Scheme 5), which, unlike 5-benzyl-substituted dihydrotriazoles **6a—e**, turned out to be a very stable compound and did not undergo fragmentation to diazomalonate even when the reaction mixture was treated with 10% aqueous HCl.

The methods for obtaining compounds of similar structure directly from arylidenemalonates and aryl azides described in the literature, despite the good yields of dihydrotriazoles, usually required prolonged reflux in a suitable solvent (up to 30 days).[19] The use of gallium trichloride significantly accelerates the formation of dihydro-1,2,3-triazole **11** (~ 10 min) and increases their yields. Thus, the advantages of the developed process are the short reaction time, the moderate temperature, and the simple procedure for isolation of the target compound.

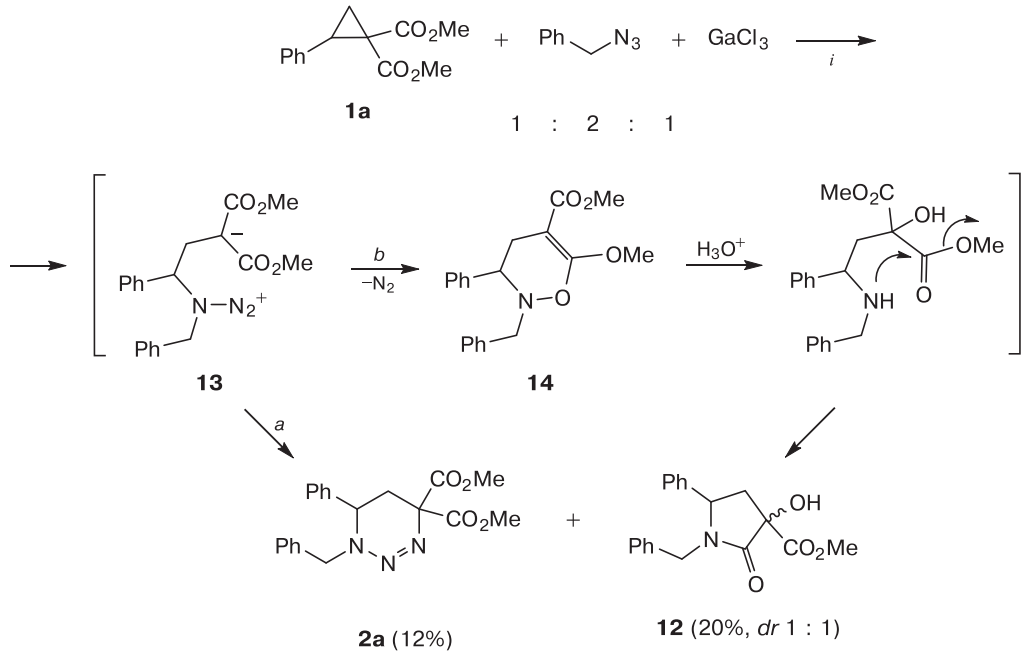
As noted earlier,[7] the reaction of ACDC with aryl azides in the presence of Lewis acids, in particular, $TiCl_4$, leads to 1,2,3-triazinines **2** (see Scheme 1). We carried out the reaction of ACDC **1a** and benzyl azide in the presence of $GaCl_3$ by simultaneous mixing of the reactants, *i.e.* when ACDC still mainly acts as a 1,3-zwitterion. Unfortunately, the yield of triazinine **2a** under these conditions turned out to be only about 12% due to the parallel processes of dimerization of ACDC **1a**. However, after the work-up of the reaction mixture, we isolated another product, previously undescribed 3-hydroxypyrrolidin-2-one **12** as approximately equal mixture of diastereomers

Scheme 5



Reagents and conditions: *i*. CH_2Cl_2, 10 min; *ii*. Ref. 19: 24—720 h, 25—100 °C, 50—67% yields.

Scheme 6



Conditions: *i*. 1,2-dichloroethane, 83 °C, 1 h.

(Scheme 6). Most likely, the same intermediate **13** (as a complex with $GaCl_3$) is the source of the formation of both triazinine **2a** and pyrrolidinone **12**. This intermediate either cyclizes to triazinine **2a** (path *a*) or loses a nitrogen molecule, giving 3,4-dihydro-2*H*-1,2-oxazine **14** (path *b*). The latter undergoes hydrolysis during the work-up of the reaction mixture to pyrrolidinone **12**, which is a mixture of two diastereomers in approximately equal proportions (see Scheme 6).

In the ^{1}H NMR spectrum, the signals of the cyclic CH_2 fragment of one of the isomers appear as a doublet at δ 2.58, whereas in the other isomer they are far apart (δ 2.18 and 2.90) and appear as a doublet of doublets with a geminal spin-spin coupling constant of 13.9 Hz.

Compounds with pyrrolidinone structure can be convenient synthons in the design of biologically active substances. Despite the low yield of pyrrolidinone **12**, the presented synthesis method allows one to obtain it from cyclopropane **1a** and benzyl azide in one experimental stage (the reaction conditions were not optimized).

In conclusion, using the model 2-arylcyclopropane-1,1-dicarboxylates **1**, we studied the reaction of gallium trichloride 1,2-zwitterionic complexes with benzyl azide as a 1,3-dipole, which leads to dihydro-1,2,3-triazoles. The latter, during the work-up of the reaction mixture with hydrochloric acid, undergo partial retrocyclization to form diazomalonate and the corresponding benzyl imines. At the same time, the use of the 1,2-zwitterionic complex derived from benzylidenemalonate and $GaCl_3$ gives a stable 5-phenyl-substituted triazoline in good yield, which does not undergo fragmentation to diazomalonate. If the reaction of ACDC **1a** and benzyl azide in the presence of $GaCl_3$ is carried out by simultaneous mixing of the reactants, in which the ACDC acts as a 1,3-zwitterion, the process proceeds with both the preservation of all three nitrogen atoms (cyclization to 1,2,3-triazinine) and the elimination of a nitrogen molecule to form in the end substituted 3-hydroxypyrrolidin-2-one.

Experimental

^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on Bruker AMX-III 400 (400.1, 100.6, and 40.5 MHz, respectively) and Bruker Avance-III HD 300 spectrometers (300.1, 75.5, and 30.4 MHz, respectively) for solutions in $CDCl_3$ containing 0.05% of Me_4Si as an internal standard. The assignment of signals and the determination of the isomeric composition of the compounds were carried out using homo- and heteronuclear 2D correlation spectra ^{1}H—^{1}H COSY and NOESY, ^{1}H—^{13}C edited-HSQC and HMBC, as well as ^{1}H—^{15}N HMBC. IR spectra were recorded on a Bruker ALPHA-T instrument in a solution of $CHCl_3$ in KBr cells (d = 1.0 mm). Mass spectra (electron impact (EI), 70 eV) were recorded on a Finnigan MAT INCOS-50 instrument. High-resolution mass spectra (electrospray ionization (ESI)) were recorded using a Bruker micro TOFII mass spectrometer. Thin layer chromatography was performed on Merck Silica gel 60 F_{254} plates. Silica gel 60 (0.040—0.063 mm) from Merck was used for

preparative chromatography. Anhydrous $GaCl_3$ used in the work was purchased from Aldrich handled in a dry argon atmosphere. The starting cyclopropanes **1a—e**,[1] benzyl azide,[20] and benzylidenemalonate[21] were synthesized according to the described procedures. Solvents with a purity of at least 99.5% were used without additional purification. Dichloromethane for the work with $GaCl_3$ was first dried over granulated KOH and then distilled over P_2O_5 under dry argon.

Synthesis of substituted dimethyl 1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylates 6a—e (general method). Gallium chloride (89 mg, 0.5 mmol) was added to a solution of 2-arylcyclopropane-1,1-dicarboxylate **1** (0.5 mmol) in anhydrous dichloromethane (1.5 mL) at 5 °C and the mixture was stirred at 5—25 °C for 10—75 min depending on the nature of the substituents in **1a—e**.[17] Then a solution of benzyl azide (133 mg, 1 mmol) in CH_2Cl_2 (1.5 mL) was added and the mixture was stirred at 20 °C for 10—15 min. Then, the reaction mixture was treated with methanol at 0 °C, the organic layer was separated and dried with anhydrous $MgSO_4$. The product was isolated by column chromatography on SiO_2, eluting first with benzene and then with a mixture of benzene—EtOAc, 40 : 1. The yields of dihydro-1,2,3-triazoles **6a—e** are given in Table 2. When the reaction mixture was quenched with 10% aqueous HCl, the isolation procedure was similar, but in this case diazomalonate was the main product.

Dimethyl 1,5-dibenzyl-1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylate (6a). The yield was 97.1 mg (53%), a colorless oil. IR (solution in $CHCl_3$), ν/cm^{-1}: 1739 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.70 (dd, 1 H, C$\underline{H}_2$CH, J = 14.1 Hz, J = 9.3 Hz); 3.06 (dd, 1 H, C$\underline{H}_2$CH, J = 14.1 Hz, J = 4.1 Hz); 3.78 and 3.85 (both s, 3 H each, 2 OCH_3); 4.01 and 5.08 (both d, 1 H each, CH_2N, ^2J = 15.4 Hz); 4.25 (dd, 1 H, CH, J = 9.3 Hz, J = 4.1 Hz); 6.71 (dd, 2 H, 2 CH_{Ar}, J = 7.4 Hz, J = 1.4 Hz); 7.18—7.36 (m, 8 H, 8 CH_{Ar}). ^{13}C NMR ($CDCl_3$), δ: 35.5 (CH_2), 52.9 and 53.6 (2 OCH_3), 53.1 (NCH_2), 60.8 (C(5)), 92.7 (C(4)) 127.0 and 127.7 (2 *p*-CH), 128.1, 128.4, 128.6 and 129.1 (*o*-CH and *m*-CH of two benzene rings), 134.1 and 136.7 (2 *ipso*-C), 165.6 and 166.6 (2 COO). HRMS: found: *m/z* 368.1615; $C_{20}H_{21}N_3O_4$; calculated [M]: M + H, 368.1605.

Dimethyl 1-benzyl-5-(4-chlorobenzyl)-1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylate (6b). The yield was 108.5 mg (54%), a colorless oil. IR (solution in $CHCl_3$), ν/cm^{-1}: 1740 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.71 (dd, 1 H, C$\underline{H}_2$CH, J = 14.2 Hz, J = 8.8 Hz); 3.00 (dd, 1 H, C$\underline{H}_2$CH, J = 14.2 Hz, J = 4.5 Hz); 3.78 and 3.85 (both s, 3 H each, 2 OCH_3); 4.08 and 5.09 (both d, 1 H each, CH_2N, ^2J = 15.5 Hz); 4.23 (dd, 1 H, CH, J = 8.8 Hz, J = 4.5 Hz); 6.75—6.83 (m, 2 H, 2 CH_{Ar}); 7.09 (d, 2 H, 2 CH_{Ar}, J = 8.2 Hz); 7.21—7.34 (m, 5 H, 5 CH_{Ar}). ^{13}C NMR ($CDCl_3$), δ: 34.5 (CH_2), 53.1 and 53.7 (2 OCH_3), 53.2 (NCH_2), 60.9 (C(5)), 92.7 (C(4)), 128.0, 128.6, 128.8 and 130.5 (*o*-CH and *m*-CH of two benzene rings), 128.1 (*p*-CH), 133.1, 134.2 and 135.2 (2 *ipso*-C and *p*-C), 165.6 and 166.6 (COO). HRMS: found: *m/z* 402.1230; $C_{20}H_{20}ClN_3O_4$; calculated [M]: M + H, 402.1215.

Dimethyl 1-benzyl-5-(4-fluorobenzyl)-1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylate (6c). The yield was 108.0 mg (56%), a colorless oil. IR (solution in $CHCl_3$), ν/cm^{-1}: 1738 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.71 (dd, 1 H, C$\underline{H}_2$CH, J = 14.3 Hz, J = 9.0 Hz); 3.02 (dd, 1 H, C$\underline{H}_2$CH, J = 14.3 Hz, J = 4.4 Hz); 3.78 and 3.85 (both s, 3 H each, 2 OCH_3); 4.06 and 5.10 (both d, 1 H each, CH_2N, ^2J = 15.5 Hz); 4.22 (dd, 1 H, CH, J = 9.0 Hz, J = 4.4 Hz); 6.76—6.84 (m, 2 H, 2 CH_{Ar}); 6.97—7.09 (m, 3 H, 3 CH_{Ar}); 7.11—7.20 (m, 2 H, 2 CH_{Ar}); 7.21—7.31 (m, 2 H, 2 CH_{Ar}). ^{13}C NMR ($CDCl_3$), δ: 34.4 (CH_2), 53.1 and 53.7 (2 OCH_3), 53.2 (NCH_2), 61.0 (C(5)), 92.7 (C(4)), 115.6 (d, *m*-CH, $^2J_{C,F}$ = 21.5 Hz), 128.1 (*o*-CH, *p*-CH), 128.6 (*m*-CH), 130.0 and 134.2 (2 *ipso*-C), 130.7 (d, *o*-CH, $^3J_{C,F}$ = 8.1 Hz); 161.8 (d, CF, $^1J_{C,F}$ = 240 Hz), 165.6 and 166.5 (2 COO). HRMS: found: *m/z* 386.1508; $C_{20}H_{20}FN_3O_4$; calculated [M]: M + H, 386.1511.

Dimethyl 1-benzyl-5-(4-nitrobenzyl)-1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylate (6d). The yield was 121.6 mg (59%), a colorless oil. IR (solution in $CHCl_3$), ν/cm^{-1}: 1738 (C=O), 1525 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 2.75 (dd, 1 H, C$\underline{H}_2$CH, J = 14.4 Hz, J = 9.1 Hz); 3.08 (dd, 1 H, C$\underline{H}_2$CH, J = 14.4 Hz, J = 4.2 Hz); 3.77 and 3.87 (both s, 3 H each, 2 OCH_3); 4.03 and 5.09 (both d, 1 H each, CH_2N, ^2J = 15.8 Hz); 4.31 (dd, 1 H, CH, J = 9.1 Hz, J = 4.2 Hz); 6.77—6.85 (m, 2 H, 2 CH_{Ar}); 7.16—7.37 (m, 7 H, 7 CH_{Ar}). ^{13}C NMR ($CDCl_3$), δ: 34.7 (CH_2), 53.0 and 53.8 (2 OCH_3), 53.3 (NCH_2), 60.8 (C(5)), 92.8 (C(4)), 123.8 (*m*-CH), 127.8, 128.8 and 129.9 (CH_{Ar}) 128.3 (*p*-CH), 134.0 and 144.2 (2 *ipso*-C), 147.1 (CNO_2), 165.5 and 166.4 (2 COO). HRMS: found: *m/z* 413.1436; $C_{20}H_{20}N_4O_6$; calculated [M]: M + H, 413.1456.

Dimethyl 1-benzyl-5-(4-methylbenzyl)-1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylate (6e). The yield was 151.9 mg (57%), a colorless oil. IR (solution in $CHCl_3$), ν/cm^{-1}: 1740 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.37 (s, 3 H, CH_3); 2.65 (dd, 1 H, C$\underline{H}_2$CH, J = 14.1 Hz, J = 9.4 Hz); 3.00 (dd, 1 H, C$\underline{H}_2$CH, J = 14.1 Hz, J = 4.1 Hz); 3.76 and 3.82 (both s, 3 H each, 2 OCH_3); 4.00 and 5.05 (both d, 1 H each, CH_2N, ^2J = 15.3 Hz); 4.22 (dd, 1 H, CH, J = 9.4 Hz, J = 4.1 Hz); 6.71—6.75 (m, 2 H, 2 CH_{Ar}); 7.07 and 7.13 (both br.d, 2 H each, C_6H_4, ^3J = 7.9 Hz); 7.18—7.25 (m, 3 H, 3 CH_{Ar}). ^{13}C NMR ($CDCl_3$), δ: 21.1 (CH_3), 34.9 (CH_2), 53.0 and 53.6 (both OCH_3), 53.1 (NCH_2), 61.0 (C(5)), 92.7 (C(4)), 127.9 (*p*-CH), 128.3, 128.4, 129.2 and 129.4 (*o*-CH and *m*-CH of two benzene rings), 133.7, 134.4 and 136.8 (2 *ipso*-C and *p*-C), 165.7 and 166.6 (2 COO). HRMS: found: *m/z* 382.1766; $C_{21}H_{23}N_3O_4$; calculated [M]: M + H, 382.1761.

Dimethyl 1-benzyl-5-phenyl-1,5-dihydro-4*H*-1,2,3-triazole-4,4-dicarboxylate (11). The reaction was carried out according to the general procedure, starting from dimethyl benzylidenemalonate **9** (0.11 g, 0.5 mmol) in CH_2Cl_2, sequentially adding $GaCl_3$ (88 mg, 0.5 mmol) and benzyl azide (133 mg, 1.0 mmol). The reaction mixture was refluxed for 10 min, cooled, and treated with 10% aqueous HCl to pH 3. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2×10 mL), and the organic extracts were dried without anhydrous $MgSO_4$. The solvent was removed *in vacuo*, the product was isolated by column chromatography on SiO_2, eluting first with benzene, then with benzene—EtOAc, 20: 1. Compound **11** (150 mg, 85%) was obtained as a colorless oil. Its spectral characteristics agree with the literature data.[19]

Methyl 1-benzyl-3-hydroxy-2-oxo-5-phenylpyrrolidine-3-carboxylate (12). Gallium chloride (44.2 mg, 0.25 mmol) was added to a solution of 2-phenylcyclopropane-1,1-dicarboxylate **1a** (58.6 mg, 0.25 mmol) and benzyl azide (66.5 mg, 0.5 mmol) in 1.2-dichloroethane (3 mL). The mixture was heated at 83 °C for 1 h, cooled, and treated with 10% aqueous HCl to pH 3. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2×10 mL), the organic extracts were dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*. The residue

was separated by column chromatography on SiO_2 (eluent: benzene—EtOAc, 20 : 1). The isolated products were 1,2,3-triazinine **2a** (11.0 mg, 12%) with the spectral characteristics corresponding to those described in the literature[7] and pyrrolidinone **12** (16.2 mg, 20%, a mixture of two diastereomers in a ratio of ~ 1 : 1), a colorless oil. IR (solution in $CHCl_3$), ν/cm^{-1}: 1715 (NC=O), 1745 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.18 (dd, 1 H, H_a(4), ^2J = 13.9 Hz, ^3J = 7.3 Hz); 2.58 (d, 2 H, H_2C(4), ^3J = = 7.5 Hz); 2.90 (dd, 1 H, H_b(4), ^2J = 13.9 Hz, ^3J = 7.6 Hz); 3.54 and 3.56 (both d, 1 H each, H_a (from NCH_2), ^2J = 15.0 Hz); 3.82 and 3.93 (both s, 3 H each, OCH_3); 4.00 (br.s, 2 H, OH); 4.46 (dd, 1 H, H(5), ^3J = 7.3 Hz, ^3J = 7.6 Hz); 4.58 (t, 1 H, H(5), J = 7.5 Hz); 5.07 and 5.11 (both d, 1 H each, H_b (from NCH_2), ^2J = 15.0 Hz); 6.99—7.45 (m, 20 H, 2 Ph of two isomers). ^{13}C NMR ($CDCl_3$), δ: 40.6 and 40.7 (C(4)), 44.8 and 45.1 (NCH_2), 53.3 and 53.6 (OCH_3), 58.4 and 58.9 (C(5)), 78.1 and 78.5 (C(3)), 127.6 and 127.8 (*p*-C of two isomers), 128.4, 128.6, 128.7 and 129.1 (*o*- and *m*-C of two isomers), 135.1, 135.2, 138.8 and 139.0 (*ipso*- C of two isomers), 171.1 and 171.5 (NC=O), 172.10 and 172.13 (COO). HRMS: found: *m*/*z* 326.1374; $C_{19}H_{19}NO_4$; calculated [M]: M + H, 326.1384.

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