JOC Article

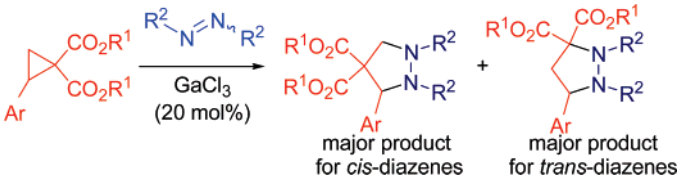
$GaCl_3$-Catalyzed Insertion of Diazene Derivatives into the Cyclopropane Ring[1]

Vadim S. Korotkov, Oleg V. Larionov, Anja Hofmeister, Jörg Magull, and Armin de Meijere*

Institut für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany

Armin.deMeijere@chemie.uni-goettingen.de

Received March 7, 2007



$GaCl_3$ has been found to efficiently catalyze the formal cycloadditions of diazene derivatives **6** onto 2-arylcyclopropane-1,1-dicarboxylates **5**, giving rise to the pyrazolidine derivatives **7**. The insertion into the cyclopropane ring proceeds with complete regioselectivity to furnish 5-arylpyrazolidine-1,2,3,3-tetracarboxylates exclusively; however, the *cis*-configured azo compound *N*-phenyltriazolinedione gave the two possible regioisomeric pyrazolidine derivatives in ratios varying from 1:1.5 to 1:3. Conceivable mechanisms of these transformations are being discussed.

Introduction

The selective catalytic activation of C−C σ-bonds has emerged as one of the most challenging problems in modern organic synthesis. The bonds in a cyclopropane ring, due to their inherent strain and unique electronic features,[2] undergo such an activation much more easily than those in alkanes and cycloalkanes of larger ring size. Among these reactions,[3] the cycloadditions of acceptor-substituted cyclopropanes to aldehydes,[4] imines,[5] nitrones,[6] allenes, acetylenes,[7] nitriles,[8] isocyanates,[9] and isothiocyanates[10] have recently attracted considerable attention, as they allow an easy assembly of valuable potentially biologically relevant five- and six-membered heterocycles, such as tetrahydrofurans and pyrroles. The other known type of reactions involving ring opening of acceptor-substituted cyclopropanes is a lanthanide(III)-catalyzed formal [3 + 1 + 1] cycloaddition with two molecules of an isocyanide.[11] It is particularly interesting that donor−acceptor-substituted cyclopropanes **1** can undergo reactions formally analogous to 1,3-dipolar additions onto double bonds. This type of reaction has been observed especially for aldehydes,[4] aldimines,[5a] ketimines,[5b] isocyanates,[9] and isothiocyanates.[10]

(1) Part 141 in the series "Cyclopropyl Building Blocks in Organic Synthesis". For part 140, see: Bagutski, V.; de Meijere, A. *Adv. Synth. Catal.* **2007**, 1247. Part 139: de Meijere, A.; Redlich, S.; Frank, D.; Magull, J.; Hofmeister, A.; Menzel, H.; König, B.; Svoboda, J. *Angew. Chem.* **2007**, *119*, 4658; *Angew. Chem., Int. Ed.* **2007**, *46*, 4574.

(2) (a) de Meijere, A. *Angew. Chem.* **1979**, *91*, 867−884; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. (b) Wiberg, K. B. *Introduction, Houben-Weyl Methods of Organic Chemistry*; de Meijere, A., Ed.; Thieme: Stuttgart, 1997; Vol. E17a, p 1ff.

(3) For a review concerning the ring-opening reactions of donor−acceptor-substituted cyclopropanes, see: Reissig, H. U.; Zimmer, R. *Chem. Rev.* **2003**, *103*, 1151.

(4) (a) Pohlhaus, P. D.; Johnson, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 16014. (b) Pohlhaus, P. D.; Johnson, J. S. *J. Org. Chem.* **2005**, *70*, 1057. (c) Min, S.; Yang, Y. H.; Bo, X. *Tetrahedron* **2005**, *61*, 1893. (d) Bernard, A. M.; Frongia, A.; Piras, P. P.; Secci, F.; Spiga, M. *Org. Lett.* **2005**, *7*, 4565. (e) Fuchibe, K.; Aoki, Y.; Akiyama, T. *Chem. Lett.* **2005**, *34*, 538.

(5) (a) Carson, C. A.; Kerr, M. A. *J. Org. Chem.* **2005**, *70*, 8242. (b) Wurz, R. P.; Charette, A. B. *Org. Lett.* **2005**, *7*, 2313. (c) Kang, Y.-B.; Tang, Y.; Sun, X.-L. *Org. Biomol. Chem.* **2006**, *4*, 299. (d) Christie, S. D. R.; Davoile, R. J.; Jones, R. C. F. *Org. Biomol. Chem.* **2006**, *4*, 2683. (e) Saigo, K.; Shimada, S.; Hasegawa, M. *Chem. Lett.* **1990**, 905.

(6) (a) Cardona, F.; Goti, A. *Angew. Chem.* **2005**, *117*, 8042; *Angew. Chem., Int. Ed.* **2005**, *44*, 7832. (b) Sibi, M. P.; Ma, Z. H.; Jasperse, C. P. *J. Am. Chem. Soc.* **2005**, *127*, 5764. (c) Ganton, M. D.; Kerr, M. A. *J. Org. Chem.* **2004**, *69*, 8554. (d) Young, I. S.; Kerr, M. A. *Angew. Chem.* **2003**, *115*, 3131; *Angew. Chem., Int. Ed.* **2003**, *42*, 3023.

(7) (a) Yadav, V. K.; Sriramurthy, V. *Org. Lett.* **2004**, *6*, 4495. (b) Yadav, V. K.; Sriramurthy, V. *Angew. Chem.* **2004**, *116*, 2723; *Angew. Chem., Int. Ed.* **2004**, *43*, 2669.

(8) (a) Yu, M.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 2563. (b) Yu, M.; Pagenkopf, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 8122. (c) Yu, M.; Pagenkopf, B. L. *Org. Lett.* **2003**, *5*, 5099.

(9) (a) Graziano, M. L.; Iesce, M. R. *J. Chem. Res.* (*S*) **1987**, 362. (b) Yamamoto, K.; Ishida, T.; Tsuji, J. *Chem. Lett.* **1987**, 1157.

(10) Graziano, M. L.; Cimminiello, G. *J. Chem. Res.* (*S*) **1989**, 42.

(11) Korotkov, V. S.; Larionov, O. V.; de Meijere, A. *Synthesis* **2006**, *21*, 3542.

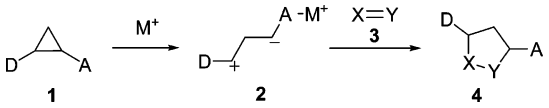
10.1021/jo0704816 CCC: $37.00
Published on Web 09/07/2007

TABLE 1. Scope of the $GaCl_3$-Catalyzed Formal Cycloaddition of Various 2-Arylcyclopropane-1,1-dicarboxylates onto Different Diazene Derivatives[a]

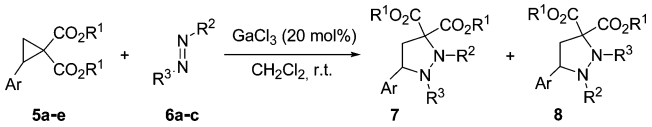
entry	cyclopropane	R^1, R^1	Ar	R^2-N=N-R^3	R^2	R^3	product	yield (%)
1	**5a**	Me, Me	Ph	**6a**	CO_2iPr	CO_2iPr	**7aa**	63
2	**5b**	Me, Me	4-MeC_6H_4	**6a**	CO_2iPr	CO_2iPr	**7ba**	52
3	**5c**	Me, Me	4-BrC_6H_4	**6a**	CO_2iPr	CO_2iPr	**7ca**	46
4	**5d**	Me, Me	4-ClC_6H_4	**6a**	CO_2iPr	CO_2iPr	**7da**	67
5	**5e**	Me, Me	4-$MeOC_6H_4$	**6a**	CO_2iPr	CO_2iPr	**7ea**	43
6	**5f**	CMe_2	Ph	**6a**	CO_2iPr	CO_2iPr	**7fa**	53
8	**5b**	Me, Me	4-MeC_6H_4	**6b**	CO_2Et	Ph	**7bb**, **8bb**	17, 6
9	**5a**	Me, Me	Ph	**6c**	Ph	Ph	**7ac**	42
10	**5b**	Me, Me	4-MeC_6H_4	**6c**	Ph	Ph	**7bc**	44
11	**5c**	Me, Me	4-BrC_6H_4	**6c**	Ph	Ph	**7cc**	41

[a] Reaction conditions: 20 mol % of $GaCl_3$, CH_2Cl_2, rt, 3 h.

SCHEME 1. Dissociative Mechanism of the Formal Cycloaddition of a Donor−Acceptor-Substituted Cyclopropane onto Compounds with Double Bonds



SCHEME 2. For Details, See Table 1



However, as has been shown by Pohlhaus et al. for the case of enantiomerically pure cyclopropane derivatives, the stereochemical information is transferred to the final products with high efficiency, and this rules out a pathway via an achiral dipolar intermediate of type **2** (Scheme 1). On the other hand, reactions of donor−acceptor-substituted cyclopropanes with compounds containing N−N double bonds have been largely neglected. Thus, Graziano et al. described a single example of a thermal reaction of a diazene derivative with a 2,2-dimethoxycyclopropanecarboxylate.[12] Further extension of these transformations would establish an efficient access to heterocyclic molecules of potential pharmacological interest and might provide insights into the mechanism of these formal cycloadditions.

Results and Discussion

Diisopropyl azodicarboxylate (**6a**, $R^2 = R^3 = CO_2iPr$) and dimethyl 2-phenylcyclopropanedicarboxylate (**5a**, Ar = Ph, R^1 = Me) were chosen as convenient reaction partners for initial experiments (Scheme 2).

Several Lewis acids ($Bi(OTf)_3$, $Sn(OTf)_2$, $InCl_3$) failed to catalyze the reaction completely, and with $Yb(OTf)_3$, only a trace of the desired product was isolated. Gratifyingly, the reaction was successful with added $GaCl_3$, with an optimum loading of 20 mol % (Figure 1). Further variations of the reaction conditions (solvent, concentrations and ratio of reagents, temperature, etc.) had little effect on the outcome of the reaction.

Under the optimized conditions, a number of 2-aryl-substituted cyclopropanedicarboxylates **5b**−**f** were treated with diisopropyl azodicarboxylate (**6a**), ethyl phenyldiazenecarboxylate (**6b**), and azobenzene (**6c**) to give the correspondingly substituted pyrazolidine derivatives **7** in yields ranging from 41 to 67% (Table 1) except for the product from **5b** and the unsymmetrically substituted diazene **6b**, which was obtained as a mixture of the two regioisomers **7bb** and **8bb** in a total yield of only 23% (Table 1, entry 8).

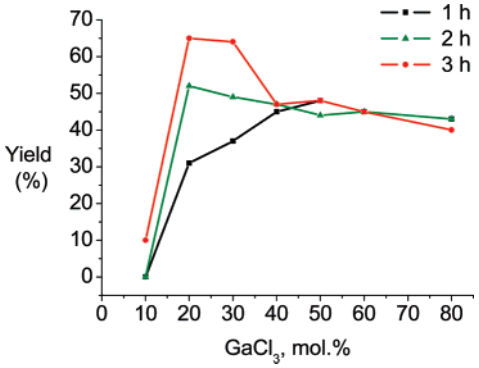
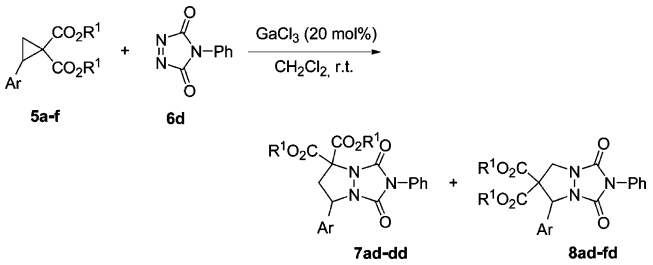


FIGURE 1. Dependence of the yields for the reaction of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**5a**) and diisopropyl azodicarboxylate (**6a**) in CH_2Cl_2 at rt on the loading of $GaCl_3$.

SCHEME 3. For Details, See Tables 1 and 2



However, all the diazene derivatives used above were naturally existing mixtures of minor amounts of *cis*- and major amounts of the thermodynamically favored *trans*-diastereomers. It was of particular interest to also investigate the reactivity of the cyclopropanes (**5a**−**e**) toward substances with fixed *cis*-configuration of the N,N double bond, as in 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **6d**).

Surprisingly, the reactions of cyclopropanes **5a**−**e** (Scheme 3) with PTAD **6d** led to separable mixtures of the expected products of insertion into the C(1)−C(2) cyclopropane bond (compounds **7ad**−**dd**) and the anomalous products of insertion into the C(2)−C(3) bond (compounds **8ad**−**dd**) in ratios varying from 1:1.5 to 1:3 (Table 2).

(12) Graziano, M. L.; Iesce, M. R.; Cermola, F. *J. Chem. Res. (S)* **1996**, 82.

SCHEME 4. Synthesis of Both Enantiomers of Cyclopropane 5a

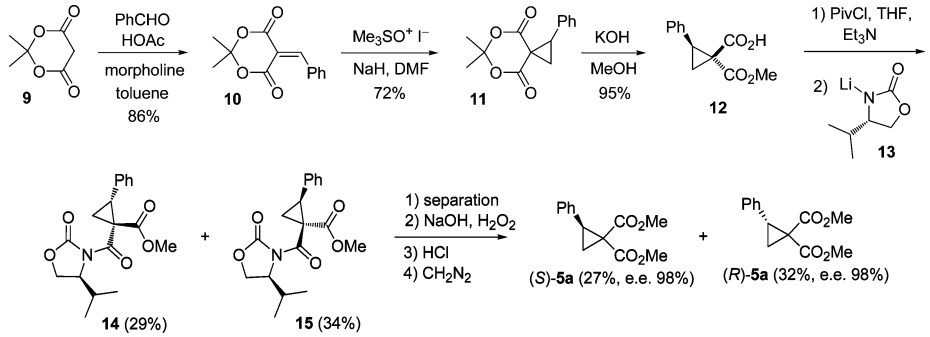


TABLE 2. Reaction of 2-Arylcyclopropanedicarboxylates 5 with *N*-Phenyltriazolinedione (PTAD, 6d)

entry	cyclopropane	R^1, R^1	Ar	products	yield (%) (**7**/**8** ratio)
1	**5a**	Me, Me	Ph	**7ad**, **8ad**	66 (1:3)
2	**5b**	Me, Me	4-MeC_6H_4	**7bd**, **8bd**	67 (1:1.7)
3	**5c**	Me, Me	4-BrC_6H_4	**7cd**, **8cd**	56 (1:1.5)
4	**5d**	Me, Me	4-ClC_6H_4	**7dd**, **8dd**	55 (1:2.2)
6	**5f**	CMe_2	Ph	**7fd**	34

Actually, the products of type **8** were favored in all cases except for that of the spirocyclic diester **5f**, in which not even a trace of the anomalous product of type **8** was observed in the ^{1}H NMR spectrum of the crude reaction mixture. The structures of products **7bd** and **8bd** were unambiguously established by means of an X-ray crystallographic analysis.[13]

In order to unveil the reason for the formation of the anomalous products **8ad**−**dd**, further experiments were carried out. Thus, $GaCl_3$ was added to solutions of pure **7ad** and **8ad**, respectively. No interconversion of **7ad** and **8ad** was observed according to the ^{1}H NMR spectra of solutions after 1, 2, 3, and even 24 h. This result is in accordance with the assumption that the insertions into the C(1)−C(2) and C(2)−C(3) bonds proceed along independent pathways under the reaction conditions. In order to gain additional mechanistic information, the enantiomerically enriched cyclopropanes (*R*)-**5a** and (*S*)-**5a** were synthesized from Meldrum's acid **9** (Scheme 4). Thus, the Knoevenagel product **10** from **9** and benzaldehyde was subjected to a Corey−Chaykovsky cyclopropanation, followed by base-catalyzed methanolysis to give the diacid monoester **12**. The latter was transformed into the chromatographically separable diastereomeric oxazolidinones **14** and **15**, which were hydrolyzed, and finally re-esterified with diazomethane.

The reaction of the enantiomerically pure cyclopropane (*R*)-**5a** with diisopropyl azodicarboxylate (**6a**) afforded the racemic product *rac*-**7aa**, according to HPLC analysis on a chiral column. Both the regular **7ad** as well as the anomalous **8ad** product of the reaction of (*S*)-**5a** with PTAD **6d** also proved to be racemic. Thus, these reactions must proceed via an achiral dipolar intermediate of type **2**. Apparently, diazene dipolarophiles possess a much lower nucleophilicity than imines as well as aldehydes and therefore fail to attack the cyclopropanes **5** at the C(2) atom in the presence of mild Lewis acids [Sn(II), Cu(II), Bi(III), etc.]. Gallium trichloride, on the other hand, being a powerful Lewis acid, may effect formation of the achiral dipolar ring-opened intermediate of type **2**, which can add, with its negatively charged terminus coming in first, onto the electron-deficient N,N double bond. This would then be succeeded by a ring closure leading to the racemic product **7** (Scheme 5). In accordance with this hypothesis, addition of gallium trichloride to a solution of the enantiomerically pure cyclopropane derivative (*R*)-**5a** in the absence of any diazene did not lead to any racemization (according to chiral-phase HPLC analysis) of the residual **5a**, while the net amount of available **5a** significantly decreased in the course of the experiment. Thus, the ring-opening event appears to be irreversible. Since formation of an intermediate of type **2′** featuring a primary carbocation is deemed highly unlikely, the anomalous byproduct **8d** must emerge along a different pathway.

Control experiments with **5a**, *N*-phenyltriazolinedione (PTAD), and azobisisobutyronitrile (AIBN) in the absence of $GaCl_3$ at elevated temperatures failed to elicit the formation of cycloaddition products, which rules out the possibility of a radical avenue. Therefore, the higher reactivity of the *cis*-configured PTAD **6d** over the *trans*-configured diazenes probably allows it to add to the least sterically congested methylene group of the cyclopropane **5**, so that the nucleophilic nitrogen of the PTAD further attacks the achiral benzylic carbocation center in the intermediate **18**, and this would account for the formation of the racemic product **8**. This pathway is less favorable for the *trans*-configured diazene derivatives due to the steric interaction between the substituent in **6** and the incoming nucleophile.

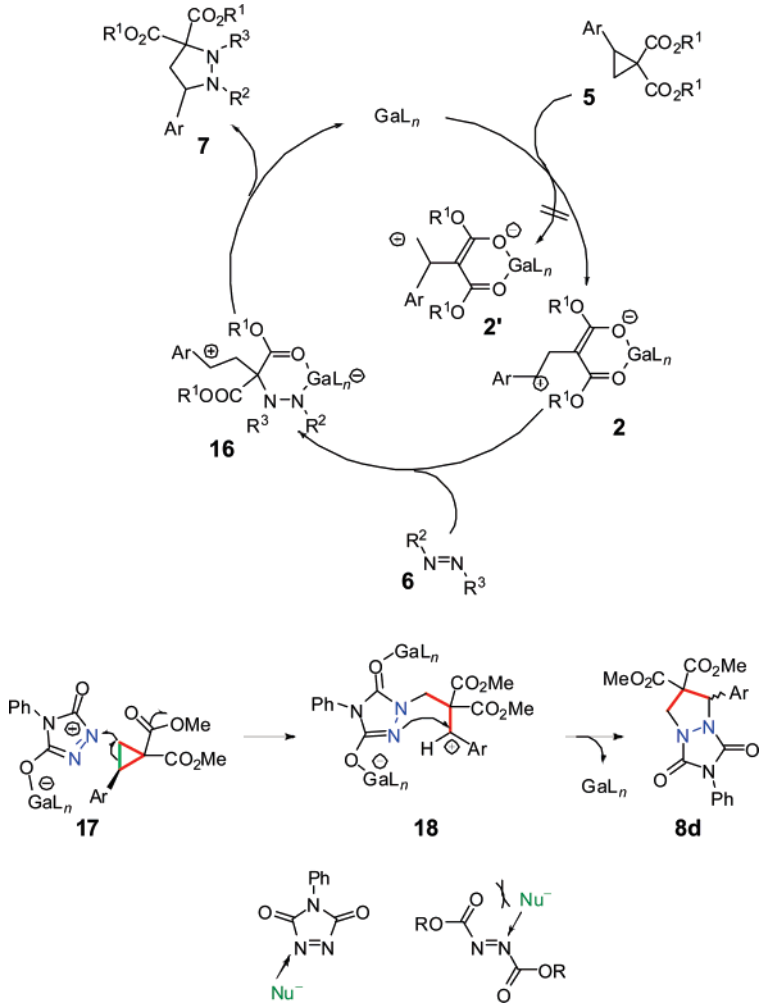
Experimental Section

General Procedure for the Synthesis of Diisopropyl 5-Aryl-3,3-di(methoxycarbonyl)pyrazolidine-1,2-dicarboxylates (GP1): To a mixture of the respective dimethyl 2-arylcyclopropane-1,1-dicarboxylate **5** (0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of $GaCl_3$ (30 mg, 0.17 mmol, 20 mol %) in CH_2Cl_2 (3.5 mL). The mixture was stirred at rt for 3 h, while monitoring the progress of the reaction by TLC, then directly applied onto a chromatographic column (silica gel) and eluted with diethyl ether/pentane (1:1) mixture to give the desired substituted pyrazolidine **7**.

Diisopropyl 3,3-Di(methoxycarbonyl)-5-phenylpyrazolidine-1,2-dicarboxylate (7aa): According to GP1, dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**5a**) (200 mg, 0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) gave 233 mg (63%) of the pyrazolidine **7aa** as a colorless oil: R_f = 0.33 (diethyl ether/pentane 1:1); ^{1}H NMR (250 MHz) δ 1.24−1.31 (m, 12 H), 2.92 (dd, J = 14, 4 Hz, 1 H), 3.31 (dd, J = 8, 14 Hz, 1 H), 3.48 (s, 3 H), 3.83 (s, 3 H), 4.92−5.06 (m, 2 H), 5.47 (dd, J = 4, 8 Hz, 1H), 7.23−7.45 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.8

(13) The X-ray cif files for these structures have been deposited at the Cambridge Crystallographic Data Center (CCDC): deposition numbers CCDC 637274 and 637275. Copies of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (e-mail: deposit@ccdc.cam.ac.uk; Internet: //www.ccdc.cam.ac.uk).

SCHEME 5. Proposed Mechanism for the $GaCl_3$-Catalyzed Formal Cycloaddition of Diazene Derivatives 6 to Cyclopropanes 5 and the Rationale for the Formation of the Anomalous Products of Type 8d



(CH_3), 21.9 (CH_3), 44.6 (CH_2), 53.0 (CH), 53.4 (CH), 61.2 (CH), 70.5 (CH_3), 70.8 (CH_3), 72.3 (C), 125.8 (CH), 127.3 (CH), 128.3 (CH), 139.5 (C), 153.3 (C), 156.9 (C), 166.5 (C), 168.9 (C) ppm; IR (film) $\tilde{\nu}$ 2983 cm^{-1}, 1751, 1707, 1456, 1375, 1276, 1180, 1107, 1020, 750, 701; LRMS (DCI) *m/z* = 890 ([2 M + NH_4^+], 8), 454 ([M + NH_4^+], 100), 437 ([M + H^+], 20), 222 (8); HRMS (APCI) [M + H^+] calcd for $C_{21}H_{29}N_2O_8$ 437.1924, found 437.1918.

Diisopropyl 3,3-Di(methoxycarbonyl)-5-(4-methylphenyl)-pyrazolidine-1,2-dicarboxylate (7ba): According to the GP1, dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (**5b**) (211 mg, 0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) gave 198 mg (52%) of the pyrazolidine **7ba** as a colorless oil: R_f = 0.30 (diethyl ether/pentane 1:1); ^{1}H NMR (300 MHz) δ 1.20−1.30 (m, 12 H), 2.31 (s, 3 H), 2.90 (dd, *J* = 4, 13 Hz, 1 H), 3.27 (dd, *J* = 8, 13 Hz, 1 H), 3.51 (s, 3 H), 3.82 (s, 3 H), 4.90−5.05 (m, 2 H), 5.40 (dd, *J* = 4, 8 Hz, 1 H), 7.12 (d, *J* = 8 Hz, 2 H), 7.26 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR (90.58 MHz) δ 21.8 (CH_3), 21.9 (CH_3), 22.1 (CH_3), 44.6 (CH_2), 53.0 (CH), 53.4 (CH), 61.0 (CH), 70.5 (CH_3), 70.7 (CH_3), 72.4 (C), 125.8 (CH), 129.0 (CH), 136.5 (C), 136.9 (C), 153.3 (C), 156.8 (C), 166.4 (C), 168.8 (C) ppm; IR (film) $\tilde{\nu}$ 2982 cm^{-1}, 1750, 1708, 1457, 1375, 1276, 1181, 1107, 1020, 913, 750; LRMS (ESI) *m/z* = 993 ([2 M + Na^+], 100), 473 ([M + Na^+], 36). Anal. Calcd for $C_{22}H_{30}N_2O_8$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.46; H, 6.78; N, 5.98.

Diisopropyl 5-(4-Bromophenyl)-3,3-di(methoxycarbonyl)-pyrazolidine-1,2-dicarboxylate (7ca): According to GP1, dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (**7c**) (266 mg, 0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) gave 201 mg (46%) of the pyrazolidine (**7ca**) as a colorless oil: R_f = 0.24 (diethyl ether/pentane 1:2); ^{1}H NMR (300 MHz) δ 1.22−1.29 (m, 12 H), 2.81 (dd, *J* = 4, 13 Hz, 1 H), 3.27 (dd, *J* = 8, 13 Hz, 1 H), 3.47 (s, 3 H), 3.89 (s, 3 H), 4.88−5.00 (m, 2 H), 5.37 (dd, *J* = 4, 8 Hz, 1 H), 7.27 (d, *J* = 8 Hz, 2 H), 7.76 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.86 (CH_3), 21.90 (CH_3), 21.93 (CH_3), 22.10 (CH_3), 44.6 (CH_2), 53.4 (CH), 53.7 (CH), 54.1 (CH), 71.0 (CH_3), 71.2 (CH_3), 72.8 (C), 121.2 (C), 128.0 (CH), 131.6 (CH), 139.4 (C), 153.6 (C), 156.7 (C), 166.5 (C), 168.7 (C) ppm; IR (film) $\tilde{\nu}$ 2983 cm^{-1}, 1750, 1707, 1635, 1559, 1540, 1456, 1374, 1106; LRMS (ESI) *m/z* = 1055 ([2 M + Na^+], 50), 1053 ([2 M + Na^+], 100), 1051 ([2 M + Na^+], 50), 539 ([M + Na^+], 30), 537 ([M + Na^+], 30). Anal. Calcd for $C_{21}H_{27}BrN_2O_8$: C, 48.94; H, 5.28; N, 5.44. Found: C, 48.73; H, 5.36; N, 5.21.

Diisopropyl 5-(4-Chlorophenyl)-3,3-di(methoxycarbonyl)-pyrazolidine-1,2-dicarboxylate (7da): According to GP1, dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (**5d**) (228 mg, 0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) gave 268 mg (67%) of the pyrazolidine **7da** as a colorless oil: R_f = 0.27 (diethyl ether/pentane 1:1); ^{1}H NMR (300 MHz) δ 1.24−1.32 (m, 12 H), 2.86 (dd, *J* = 4, 13 Hz, 1 H), 3.30 (dd, *J* = 8, 13 Hz, 1 H), 3.52 (s, 3 H), 3.82 (s, 3 H), 4.94−5.06 (m, 2 H), 5.43 (dd, *J* = 4, 8 Hz, 1 H), 7.28−7.40 (m, 4 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.82 (CH_3), 21.86 (CH_3), 21.88 (CH_3), 22.05 (CH_3), 44.6 (CH_2), 53.1 (CH), 53.4 (CH), 60.7 (CH), 70.6 (CH_3), 71.0 (CH_3), 72.3 (C), 127.1 (C), 127.3 (CH), 128.4 (CH), 133.1 (C), 153.1 (C), 156.8 (C), 166.4 (C), 168.6 (C) ppm; IR (film) $\tilde{\nu}$ 2983 cm^{-1}, 1749, 1708, 1640, 1494, 1454, 1375, 1282, 1179, 1106, 1015,

736; LRMS (ESI) m/z = 963 ([2 M + Na^+], 100), 493 ([M + Na^+], 24). Anal. Calcd for $C_{21}H_{27}ClN_2O_8$: C, 53.56; H, 5.78; N, 5.95. Found: C, 53.57; H, 5.50; N, 5.57.

Diisopropyl 3,3-Di(methoxycarbonyl)-5-(4-methoxyphenyl)-pyrazolidine-1,2-dicarboxylate (7ea): According to GP1, dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (**5e**) (225 mg, 0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) gave 170 mg (43%) of the pyrazolidine **7ea** as a colorless oil: R_f = 0.48 (diethyl ether/pentane 1:5); ^{1}H NMR (300 MHz) δ 1.23−1.30 (m, 12 H), 2.89 (dd, J = 4, 13 Hz, 1 H), 3.25 (dd, J = 8, 13 Hz, 1 H), 3.52 (s, 3 H), 3.78 (s, 3 H), 3.81 (s, 3 H), 4.92−5.04 (m, 2 H), 5.38 (dd, J = 4, 8 Hz, 1 H), 6.84 (d, J = 9 Hz, 2 H), 7.29 (d, J = 9 Hz, 2 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.80 (CH_3), 21.87 (CH_3), 21.89 (CH_3), 22.05 (CH_3), 44.6 (CH_2), 53.0 (CH), 53.3 (CH), 55.2 (CH), 60.7 (CH_3), 70.4 (CH_3), 70.7 (CH_3), 72.4 (C), 113.7 (CH), 127.1 (CH), 131.5 (C), 153.3 (C), 156.8 (C), 158.8 (C), 166.5 (C), 168.8 (C) ppm; IR (film) $\tilde{\nu}$ 2984 cm^{-1}, 1749, 1636, 1516, 1437, 1374, 1249, 1177, 1106; LRMS (ESI) m/z = 954 ([2 M + Na^+], 100), 489 ([M + Na^+], 12). Anal. Calcd for $C_{22}H_{30}N_2O_9$: C, 56.64; H, 6.48; N, 6.01. Found: C, 56.87; H, 6.20; N, 5.78.

Diisopropyl 8,8-Dimethyl-6,10-dioxo-3-phenyl-1,2-diaza-7,9-dioxaspiro[4.5]decane-1,2-dicarboxylate (7fa): According to GP1, 3,3-dimethyl-7-phenyl-2,4-dioxaspiro[2.5]octan-1,5-dione (**5f**) (210 mg, 0.85 mmol) and diisopropyl azodicarboxylate (**6a**) (242 mg, 1.2 mmol) gave 203 mg (53%) of the pyrazolidine **7fa** as a colorless oil: R_f = 0.34 (diethyl ether/pentane 1:1); ^{1}H NMR (300 MHz) δ 1.12−1.30 (m, 12 H), 1.73 (s, 3 H), 1.86 (s, 3 H), 2.96 (dd, J = 4, 13 Hz, 1 H), 3.13 (dd, J = 8, 13 Hz, 1 H), 4.94−5.06 (m, 2 H), 5.78 (dd, J = 4, 8 Hz, 1 H), 7.22−7.42 (m, 5 H) ppm; ^{13}C NMR (90.58 MHz) δ 21.6 (CH_3), 21.7 (CH_3), 21.8 (CH_3), 21.9 (CH_3), 27.7 (CH_3), 29.0 (CH_3), 46.9 (CH_2), 61.8 (CH), 65.0 (C), 71.2 (CH), 71.6 (CH), 72.4 (C), 125.8 (CH), 127.4 (CH), 128.3 (CH), 139.3 (C), 152.5 (C), 157.0 (C), 162.2 (C), 166.0 (C) ppm; IR (film) $\tilde{\nu}$ 2983 cm^{-1}, 1751, 1700, 1375, 1300, 1205, 1105, 961, 740, 701; LRMS (ESI) m/z = 919 ([2 M + Na^+], 48), 471 ([M + Na^+], 100), 401 (92); HRMS (ESI) [M + H^+] calcd for $C_{22}H_{29}N_2O_8$ 449.1924, found 449.1918.

Dimethyl 2-Ethoxycarbonyl-5-(4-methylphenyl)-1-phenylpyrazolidine-3,3-dicarboxylate (7bb) and Dimethyl 1-Ethoxycarbonyl-5-(4-methylphenyl)-2-phenylpyrazolidine-3,3-dicarboxylate (8bb): According to GP1, dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (**5b**) (211 mg, 0.85 mmol) and ethyl phenyldiazenecarboxylate (**6b**) (213 mg, 1.2 mmol) gave a mixture of **7bb** and **8bb** which were separated by column chromatography on silica gel (70 g, column 3 × 30 cm) eluting with pentane/diethyl ether 4:1 to 2:1).

Dimethyl 2-Ethoxycarbonyl-5-(4-methylphenyl)-1-phenylpyrazolidine-3,3-dicarboxylate (7bb): Light yellow oil, yield 60 mg (17%); R_f = 0.19 (diethyl ether/pentane 1:2); ^{1}H NMR (600 MHz) δ 1.13 (t, J = 7 Hz, 3 H), 2.28 (s, 3 H), 2.94 (dd, J = 10, 7 Hz, 1 H), 3.14 (dd, J = 10, 2 Hz, 1 H), 3.30 (s, 3 H), 3.76 (s, 3 H), 4.04−4.20 (m, 2 H), 4.93 (dd, J = 7, 2 Hz, 1 H), 6.80−7.40 (m, 9 H) ppm; ^{13}C NMR (151 MHz) δ 14.4 (CH_3), 21.1 (CH_3), 43.4 (CH_2), 52.7 (CH_3), 53.3 (CH_3), 62.3 (CH_2), 69.2 (CH), 72.3 (C), 116.4 (CH), 122.2 (CH), 126.0 (CH), 128.7 (CH), 129.0 (CH), 136.9 (C), 150.3 (C), 154.0 (C), 167.4 (C), 169.3 (C) ppm; IR (KBr) $\tilde{\nu}$ 2954 cm^{-1}, 1740, 1436, 1261, 1177, 1066, 1034, 802, 752, 697, 668; LRMS (ESI) m/z = 875 ([2 M + Na^+], 100), 449 ([M + Na^+], 35); HRMS (ESI) [M + H^+] calcd for $C_{23}H_{27}N_2O_6$ 427.1869, found 427.1864. Anal. Calcd for $C_{23}H_{26}N_2O_6$: C, 64.78; H, 6.15; N, 6.57. Found: C, 64.48; H, 6.00; N, 6.29.

Dimethyl 1-Ethoxycarbonyl-5-(4-methylphenyl)-2-phenylpyrazolidine-3,3-dicarboxylate (8bb): Light yellow oil, yield 20 mg (6%); R_f = 0.15 (diethyl ether/pentane 1:2); ^{1}H NMR (600 MHz) δ 1.19 (t, J = 7 Hz, 3 H), 2.35 (s, 3 H), 3.08 (dd, J = 10, 13 Hz, 1 H), 3.21 (dd, J = 8, 13 Hz, 1 H), 3.51 (s, 3 H), 3.86 (s, 3 H), 4.13−4.20 (m, 2 H), 5.14 (dd, J = 8, 10 Hz, 1 H), 7.04−7.07 (m, 1 H), 7.11−7.14 (m, 2 H), 7.16−7.22 (m, 4 H), 7.31 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR (151 MHz) δ 14.5 (CH_3), 21.1 (CH_3), 41.8 (CH_2), 53.0 (CH_3), 53.4 (CH_3), 60.7 (CH), 62.2 (CH_2), 78.3 (C), 121.9 (CH), 124.6 (CH), 126.7 (CH), 128.5 (CH), 129.2 (CH), 136.6 (C), 137.1 (C), 147.1 (C), 165.7 (C), 169.4 (C) ppm; IR (film) $\tilde{\nu}$ 2953 cm^{-1}, 1748, 1700, 1496, 1457, 1436, 1374, 1276, 1127, 1022, 912, 731; LRMS (ESI) m/z = 875 ([2 M + Na^+], 100), 449 ([M + Na^+], 13); HRMS (ESI) [M + H^+] calcd for $C_{23}H_{27}N_2O_6$ 427.1869, found 427.1864.

General Procedure for the Preparation of Dimethyl 5-Aryl-1,2-triphenylpyrazolidine-3,3-dicarboxylates (7ac−7cc) (GP2): A solution of $GaCl_3$ (30 mg, 0.17 mmol, 20 mol %) in CH_2Cl_2 (2 mL) was added dropwise to a solution of the respective dimethyl 2-arylcyclopropane-1,1-dicarboxylate (**5**) (0.85 mmol) and of azobenzene (**6c**) (309 mg, 1.7 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred for 2−3 h while monitoring the reaction progress by TLC, and then separated by column chromatography on silica gel, eluting with diethyl ether/pentane 1:4.

Dimethyl 1,2,5-Triphenylpyrazolidine-3,3-dicarboxylate (7ac): According to GP2, **5a** (200 mg, 0.85 mmol) and azobenzene (**6c**) (309 mg, 1.7 mmol) gave 150 mg (42%) of the pyrazolidine **7ac** as a colorless solid: R_f = 0.38 (diethyl ether/pentane 1:4), mp 127−128 °C; ^{1}H NMR (300 MHz) δ 3.14 (dd, J = 7, 13 Hz, 1 H), 3.39 (s, 3 H), 3.48 (dd, J = 8, 13 Hz, 1 H), 3.85 (s, 3 H), 4.92 (t, J = 7 Hz, 1 H), 6.88−7.61 (m, 15 H) ppm; ^{13}C NMR (75.5 MHz) δ 44.8 (CH_2), 52.7 (CH_3), 53.1 (CH_3), 67.8 (CH), 76.4 (C), 116 (CH), 117.8 (CH), 121.2 (CH), 121.5 (CH), 126.4 (CH), 127.3 (CH), 128.56 (CH), 128.62 (CH), 146.7 (C), 167.7 (C), 170.5 (C) ppm; IR (KBr) $\tilde{\nu}$ 2955 cm^{-1}, 2852, 1759, 1736, 1594, 1490, 1448, 1431, 1258, 1192, 1087, 756, 694, 518; LRMS (ESI) m/z = 855 ([2 M + Na^+], 4), 439 ([M + Na^+], 100). Anal. Calcd for $C_{25}H_{24}N_2O_4$: C, 72.10; H, 5.81; N, 6.73. Found: C, 71.81; H, 5.77; N, 6.58.

Dimethyl 5-(4-Methylphenyl)-1,2-diphenylpyrazolidine-3,3-dicarboxylate (7bc): According to GP2, dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (**5b**) (211 mg, 0.85 mmol) and azobenzene (**6c**) (309 mg, 1.7 mmol) gave 160 mg (44%) of the pyrazolidine **7bc** as a light yellow solid: R_f = 0.60 (diethyl ether/pentane 1:2), mp 104−105 °C (dec); ^{1}H NMR (300 MHz) δ 2.37 (s, 3 H), 3.06 (dd, J = 8, 13 Hz, 1 H), 3.39 (s, 3 H), 3.40−3.43 (m, 1 H), 3.80 (s, 3 H), 4.81 (t, J = 8 Hz, 1 H), 6.82−7.00 (m, 4 H), 7.12 (d, J = 8 Hz, 2H), 7.15−7.24 (m, 6 H), 7.41 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.1 (CH_3), 44.8 (CH_2), 52.8 (CH_3), 53.2 (CH_3), 67.5 (CH), 76.7 (C), 115.9 (CH), 118.0 (CH), 121.0 (CH), 121.7 (CH), 126.5 (CH), 127.3 (CH), 128.55 (CH), 128.64 (CH), 129.3 (CH), 137.0 (C), 146.9 (C), 170.6 (C) ppm; IR (KBr) $\tilde{\nu}$ 3025 cm^{-1}, 2952, 1734, 1595, 1496, 1490, 1436, 1260, 1172, 1088, 812, 749, 695, 668; LRMS (ESI) m/z = 883 ([2 M + Na^+], 5), 453 ([M + Na^+], 100); HRMS (ESI) [M + H^+] calcd for $C_{26}H_{27}N_2O_4$ 431.1971, found 431.1965. Anal. Calcd for $C_{26}H_{26}N_2O_4$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.36; H, 5.83; N, 6.30.

Dimethyl 5-(4-Bromophenyl)-1,2-diphenylpyrazolidine-3,3-dicarboxylate (7cc): According to GP2, dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (**5c**) (266 mg, 0.85 mmol) and azobenzene (**6c**) (309 mg, 1.7 mmol) gave 172 mg (41%) of the pyrazolidine **7cc** as a light yellow solid; R_f = 0.32 (diethyl ether/pentane 1:4); mp 144−145 °C; ^{1}H NMR (600 MHz) δ 3.04 (dd, J = 7, 13 Hz, 1 H), 3.38 (s, 3 H), 3.44 (dd, J = 8, 13 Hz, 1 H), 3.81 (s, 3 H), 4.84 (t, J = 8 Hz, 1 H), 6.87−6.98 (m, 4 H), 7.10−7.24 (m, 6 H), 7.40 (d, J = 8 Hz, 2 H), 7.51 (m, 2 H) ppm; ^{13}C NMR (151 MHz) δ 44.6 (CH_2), 52.8 (CH_3), 53.2 (CH_3), 67.4 (CH), 76.3 (C), 116.0 (CH), 117.5 (CH), 121.2 (CH), 121.5 (CH), 121.6 (CH), 128.3 (CH), 128.7 (CH), 129. 6 (C), 130.2 (C), 131.7 (CH), 167.7 (C) 170.4 (C) ppm; IR (KBr) $\tilde{\nu}$ 3025 cm^{-1}, 2953, 1772, 1749, 1594, 1490, 1436, 1263, 1168, 1102, 1009, 822, 790, 695; LRMS (ESI) m/z = 517 ([M + Na^+], 100); HRMS (ESI) [M + H^+] calcd for $C_{25}H_{24}BrN_2O_4$ 495.0919, found 495.0914, [M + K^+] calcd for $C_{25}H_{23}BrKN_2O_4$ 533.0478, found 533.0473.

General Procedure for the Preparation of Dimethyl 8-Aryl-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicar-

boxylates (7ad−fd) and Dimethyl 6-Aryl-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-7,7-dicarboxylates (8ad−ed) (GP3): A mixture of the respective dimethyl 2-arylcyclopropane-1,1-dicarboxylate (0.85 mmol) (**5**) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**6d**) (298 mg (1.7 mmol)) in CH_2Cl_2 (4 mL) was added dropwise to a solution of $GaCl_3$ (30 mg, 0.17 mmol, 20 mol %) in CH_2Cl_2 (1 mL). The mixture was stirred for 1−2 h, monitoring the progress of the reaction by TLC, and then subjected to column chromatography on silica gel, eluting with diethyl ether/pentane 1:2 to 5:1.

Dimethyl 2,4-Dioxo-8-(4-methylphenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7ad) and Dimethyl 2,4-Dioxo-3,6-diphenyl-1,3,5-triazabicyclo[3.3.0]octane-7,7-dicarboxylate (8ad): According to GP3, dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**5a**) (200 mg, 0.85 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**6d**) (298 mg, 1.7 mmol) gave a mixture, which was separated by chromatography on silica gel (70 g, column 3 × 30 cm).

Dimethyl 2,4-Dioxo-3,8-diphenyl-1,3,5-triazabicyclo[3.3.0]-octane-6,6-dicarboxylate (7ad): Colorless solid, yield 60 mg (17%), $R_f = 0.47$ (diethyl ether/pentane 5:1), mp 192−193 °C (dec); ^{1}H NMR (300 MHz) δ 3.25 (m, 1 H), 3.28 (m, 1 H), 3.87 (s, 3 H), 3.92 (s, 3 H), 5.19 (dd, $J = 8$, 9 Hz, 1 H), 7.30−7.55 (m, 10 H) ppm; ^{13}C NMR (75.5 MHz) δ 46.9 (CH_2), 54.0 (CH_3), 54.4 (CH_3), 59.2 (CH), 70.6 (C), 125.7 (CH), 126.2 (CH), 128.3 (CH), 128.7 (CH), 129.0 (CH), 129.1 (CH), 131.5 (C), 136.6 (C), 153.2 (CO), 153.5 (CO), 165.7 (COO), 167.0 (COO) ppm; IR (KBr) $\tilde{\nu}$ 3052 cm^{-1}, 2953, 2900, 1792, 1743, 1718, 1497, 1457, 1418, 1308, 1247, 1165, 758; LRMS (ESI) $m/z = 1250$ ([3 M + Na^+], 5), 841 ([2 M + Na^+], 100), 432 ([M + Na^+], 60). Anal. Calcd for $C_{21}H_{19}N_3O_6$: C, 61.61; H, 4.68; N, 10.26. Found: C, 61.33; H, 4.46; N, 10.15.

Dimethyl 2,4-Dioxo-3,6-diphenyl-1,3,5-triazabicyclo[3.3.0]-octane-7,7-dicarboxylate (8ad): Colorless solid, yield 170 mg (49%); $R_f = 0.57$ (diethyl ether/pentane 5:1), mp 179 °C; ^{1}H NMR (300 MHz) δ 3.44 (s, 3 H), 3.78 (s, 3 H), 4.28 (d, $J = 13$ Hz, 1 H), 4.46 (d, $J = 13$ Hz, 1 H), 5.83 (s, 1 H), 7.32−7.50 (m, 10 H) ppm; ^{13}C NMR (75.5 MHz) δ 49.7 (CH_2), 52.8 (CH_3), 54.0 (CH_3), 65.1 (C), 65.9 (CH), 125.9 (CH), 127.2 (CH), 128.4 (CH), 128.6 (CH), 129.0 (CH), 129.2 (CH), 131.5 (C), 134.8 (C), 156.2 (CO), 156.5 (CO), 164.7 (COO), 169.6 (COO) ppm; IR (KBr) $\tilde{\nu}$ 3014 cm^{-1}, 2953, 2871, 1734, 1653, 1506, 1409, 1318, 1260, 1140, 1098, 872, 769, 690; LRMS (ESI) $m/z = 1250$ ([3 M + Na^+], 15), 841 ([2 M + Na^+], 100), 432 ([M + Na^+], 95). Anal. Calcd for $C_{21}H_{19}N_3O_6$: C, 61.61; H, 4.68; N, 10.26. Found: C, 61.62; H, 4.44; N, 10.08.

Dimethyl 2,4-Dioxo-8-(4-methylphenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7bd) and Dimethyl 2,4-Dioxo-6-(4-methylphenyl)-3-phenyl-1,3,5-triazabicyclo-[3.3.0]-octane-7,7-dicarboxylate (8bd): According to GP3, dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (**5b**) (211 mg, 0.85 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**6d**) (298 mg, 1.7 mmol) gave a mixture, which was separated by chromatography on silica gel (70 g, column 3 × 30 cm).

Dimethyl 2,4-Dioxo-8-(4-methylphenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7bd): Colorless solid, yield 90 mg (25%), $R_f = 0.36$ (diethyl ether/pentane 5:1), mp 166−167 °C (dec); ^{1}H NMR (300 MHz) δ 2.35 (s, 3 H), 3.25 (d, $J = 8$ Hz, 2 H), 3.88 (s, 3 H), 3.92 (s, 3 H), 5.15 (t, $J = 8$ Hz, 1 H), 7.21 (d, $J = 8$ Hz, 2 H), 7.33 (d, $J = 8$ Hz, 2 H), 7.34−7.54 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.1 (CH_3), 46.9 (CH_2), 54.0 (CH_3), 54.3 (CH_3), 59.2 (CH), 70.6 (C), 125.7 (CH), 126.2 (CH), 128.2 (CH), 129.0 (CH), 129.7 (CH), 131.5 (C), 133.5 (C), 138.6 (C), 153.2 (CO), 153.5 (CO), 165.8 (COO), 167.0 (COO) ppm; IR (KBr) $\tilde{\nu}$ 3038 cm^{-1}, 2958, 1885, 1718, 1497, 1457, 1436, 1410, 1313, 1277, 1247, 1164, 770; LRMS (ESI) $m/z = 1291$ (5), 869 ([2 M + Na^+], 100), 446 ([M + Na^+], 30); HRMS (ESI) [M + H^+] calcd for $C_{22}H_{22}N_3O_6$ 424.1509, found 424.1503.

Dimethyl 2,4-Dioxo-6-(4-methylphenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-7,7-dicarboxylate (8bd): Colorless solid, yield 150 mg (42%), $R_f = 0.62$ (diethyl ether/pentane 5:1), mp 185−186 °C; ^{1}H NMR (300 MHz) δ 2.34 (s, 3 H), 3.49 (s, 3 H), 3.80 (s, 3 H), 4.29 (d, $J = 13$ Hz, 1 H), 4.46 (d, $J = 13$ Hz, 1 H), 5.81 (s, 1 H), 7.14−7.24 (m, 4 H), 7.44−7.52 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 21.1 (CH_3), 49.7 (CH_2), 52.8 (CH_3), 54.0 (CH_3), 65.1 (C), 65.8 (CH), 125.9 (CH), 127.1 (CH), 128.4 (CH), 129.2 (CH), 129.3 (CH), 131.5 (C), 131.8 (C), 138.9 (C), 156.2 (CO), 156.5 (CO), 164.8 (COO), 169.7 (COO) ppm; IR (KBr) $\tilde{\nu}$ 3057 cm^{-1}, 2962, 1772, 1734, 1718, 1506, 1410, 1261, 1096, 1019, 804, 701; LRMS (ESI) $m/z = 1291$ (20), 869 ([2 M + Na^+], 100), 446 ([M + Na^+], 70). Anal. Calcd for $C_{22}H_{21}N_3O_6$: C, 62.41; H, 5.00; N, 9.92. Found: C, 62.26; H, 4.94; N, 9.82.

Dimethyl 2,4-Dioxo-8-(4-bromophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7cd) and Dimethyl 2,4-Dioxo-6-(4-bromophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]-octane-7,7-dicarboxylate (8cd): According to GP3, dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (**5c**) (266 mg, 0.85 mmol) and of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**6d**) (298 mg, 1.7 mmol) gave a mixture, which was separated by chromatography on silica gel (70 g, column 3 × 30 cm).

Dimethyl 2,4-Dioxo-8-(4-bromophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7cd): Colorless solid, yield 140 mg (34%), $R_f = 0.46$ (diethyl ether/pentane 5:1), mp 179−180 °C; ^{1}H NMR (300 MHz) δ 3.23 (m, 2 H), 3.87 (s, 3 H), 3.90 (s, 3 H), 5.12 (dd, $J = 7$, 9 Hz, 1 H), 7.30−7.56 (m, 9 H) ppm; ^{13}C NMR (75.5 MHz) δ 46.6 (CH_2), 54.1 (CH_3), 54.4 (CH_3), 58.8 (CH), 70.6 (C), 122.7 (C), 125.7 (CH), 127.9 (CH), 128.4 (CH), 129.1 (CH), 131.3 (C), 132.2 (CH), 135.7 (C), 153.2 (CO), 153.8 (CO), 165.6 (COO), 166.9 (COO) ppm; IR (KBr) $\tilde{\nu}$ 2960 cm^{-1}, 1718, 1506, 1410, 1313, 1258, 1164, 769, 732; LRMS (ESI) $m/z = 999$ ([2 M + Na^+], 100), 510 ([M + Na^+], 76), 488 ([M + H^+], 6); HRMS (ESI) [M + H^+] calcd for $C_{21}H_{19}BrN_3O_6$ 488.0457, found 488.0452.

Dimethyl 2,4-Dioxo-6-(4-bromophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-7,7-dicarboxylate (8cd): Colorless solid, yield 90 mg (22%), $R_f = 0.63$ (diethyl ether/pentane 5:1), mp 167−168 °C; ^{1}H NMR (300 MHz) δ 3.52 (s, 3 H), 3.81 (s, 3 H), 4.24 (d, $J = 13$ Hz, 1 H), 4.47 (d, $J = 13$ Hz, 1 H), 5.80 (s, 1 H), 7.20−7.24 (m, 2 H), 7.28−7.32 (m, 2 H), 7.46−7.54 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 49.7 (CH_2), 53.0 (CH_3), 54.2 (CH_3), 65.0 (C), 65.4 (CH), 123.4 (C), 126.0 (CH), 128.6 (CH), 129.0 (CH), 129.3 (CH), 131.4 (C), 131.9 (CH), 134.0 (C), 156.3 (C), 156.5 (C), 164.7 (C), 169.5 (C) ppm; IR (KBr) $\tilde{\nu}$ 3328 cm^{-1}, 3000, 2950, 1727, 1653, 1594, 1559, 1496, 1437, 1412, 1301, 1232, 1100, 753, 694, 509; LRMS (ESI) $m/z = 1487$ ([3 M + Na^+], 35), 999 ([2 M + Na^+], 100), 550 (74), 510 ([M + Na^+], 13); HRMS (ESI) [M + H^+] calcd for $C_{21}H_{19}BrN_3O_6$ 488.0457, found 488.0452.

Dimethyl 2,4-Dioxo-8-(4-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7dd) and Dimethyl 2,4-Dioxo-6-(4-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo-[3.3.0]-octane-7,7-dicarboxylate (8dd): According to GP3, dimethyl 2-(4-chlorphenyl)cyclopropane-1,1-dicarboxylate (**5d**) (228 mg, 0.85 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**6d**) (298 mg, 1.7 mmol) gave a mixture which was separated by column chromatography on silica gel (70 g, column 3 × 30 cm).

Dimethyl 2,4-Dioxo-8-(4-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-6,6-dicarboxylate (7dd): Colorless solid, yield 64 mg (17%), $R_f = 0.43$ (diethyl ether/pentane 5:1), mp 195−196 °C (dec); ^{1}H NMR (300 MHz) δ 3.23 (m, 2 H), 3.86 (s, 3 H), 3.90 (s, 3 H), 5.13 (dd, $J = 7$, 9 Hz, 1 H), 7.30−7.56 (m, 9 H) ppm; ^{13}C NMR (75.5 MHz) δ 46.7 (CH_2), 54.1 (CH_3), 54.4 (CH_3), 58.7 (CH), 70.6 (C), 125.7 (CH), 126.2 (CH), 127.6 (CH), 128.4 (CH), 129.1 (CH), 129.2 (CH), 131.3 (C), 133.5 (C), 134.6 (C), 135.1 (C), 153.3 (CO), 153.8 (CO), 165.6 (COO), 167.0 (COO) ppm; IR (KBr) $\tilde{\nu}$ 2959 cm^{-1}, 1786, 1718, 1497, 1412, 1313, 1258, 1092, 769, 691; LRMS (ESI) $m/z = 461$ ([M + NH_4^+], 44), 444 ([M + H^+], 3), 162 (100). Anal. Calcd for $C_{21}H_{18}ClN_3O_6$: C, 56.83; H, 4.09; N, 9.47. Found: C, 56.83; H, 4.21; N, 9.23.

Dimethyl 2,4-Dioxo-6-(4-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo[3.3.0]octane-7,7-dicarboxylate (8dd): Colorless solid,

yield 150 mg (38%), R_f = 0.68 (diethyl ether/pentane 5:1), mp 166 °C; ^{1}H NMR (300 MHz) δ 3.51 (s, 3 H), 3.80 (s, 3 H), 4.23 (d, J = 13 Hz, 1H), 4.47 (d, J = 13 Hz, 1 H), 5.82 (s, 1 H), 7.24−7.49 (m, 9 H) ppm; ^{13}C NMR (75.5 MHz) δ 49.6 (CH_2), 52.9 (CH_3), 54.1 (CH_3), 65.0 (C), 65.3 (CH), 125.9 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 129.2 (CH), 131.3 (C), 131.4 (C), 135.1 (C), 156.2 (CO), 156.4 (CO), 164.6 (COO), 169.5 (COO) ppm; IR (KBr) $\tilde{\nu}$ 3013 cm^{-1}, 1734, 1506, 1419, 1300, 1260, 1091, 668; LRMS (DCI) m/z = 478 ([M + NH_3 + NH_4^+], 12), 461 ([M + NH_4^+], 100), 231 (44), 179 (84), 162 (100). Anal. Calcd for $C_{21}H_{18}ClN_3O_6$: C, 56.83; H, 4.09; N, 9.47. Found: C, 56.64; H, 4.30; N, 9.31.

2,2-Dimethyl-3,8-diphenyl-1,5,2′,4′-tetraoxospiro[(1,3-dioxane)-5,6′-(1′,3′,5′-triazabicyclo[3.3.0]octane] (7fd): According to GP3, 3,3-dimethyl-7-phenyl-2,4-dioxaspiro[2.5]octane-1,5-dione (**5f**) (210 mg, 0.85 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (298 mg, 1.7 mmol) (**6d**) gave 120 mg (34%) of **7fd** as a colorless solid: R_f = 0.49 (diethyl ether/pentane 5:1), mp 178−179 °C (dec); ^{1}H NMR (300 MHz) δ 1.83 (s, 3 H), 1.98 (s, 3 H), 3.13 (dd, J = 11, 13 Hz, 1 H), 3.31 (dd, J = 7, 13 Hz, 1 H), 5.34 (dd, J = 7, 11 Hz, 1 H), 7.34−7.52 (m, 10 H) ppm; ^{13}C NMR (75.5 MHz) δ 28.1 (CH_3), 29.3 (CH_3), 50.7 (CH_2), 60.6 (CH), 64.0 (C), 108.3 (C), 125.8 (CH), 126.5 (CH), 128.7 (CH), 129.1 (CH), 129.2 (CH), 131.0 (C), 135.4 (C), 154.3 (CO), 154.4 (CO), 163.7 (COO), 165.8 (COO) ppm; IR (KBr) $\tilde{\nu}$ 3010 cm^{-1}, 1787, 1717, 1491, 1411, 1315, 1267, 764, 747; LRMS (DCI) m/z = 860 ([2 M + NH_4^+], 3), 439 ([M + NH_4^+], 100). Anal. Calcd for $C_{22}H_{19}N_3O_6$: C, 62.70; H, 4.54; N, 9.97. Found: C, 62.42; H, 4.43; N, 10.06.

(1′*S*,2′*R*,4*S*)-4-Isopropyl-3-(1′-methoxycarbonyl-2′-phenylcyclopropylcarbonyl)oxazolidin-2-one (14) and (1′*R*,2′*S*,4*S*-4-Isopropyl-3-(1′-methoxycarbonyl-2′-phenylcyclopropylcarbonyl)-oxazolidin-2-one (15): A mixture of **14** and **15** was obtained from (*E*)-1-methoxycarbonyl-2-phenylcyclopropanecarboxylic acid[14] (**12**) (3.15 g, 14.3 mmol) and (4*S*)-4-isopropyloxazolidin-2-one (**13**) (1.85 g, 14.3 mmol) according to a published procedure.[15] This mixture was separated by column chromatography on silica gel, eluting with diethyl ether/pentane 1:4. **14:** Colorless solid, yield 1.4 g (29%), R_f = 0.08 (diethyl ether/pentane 1:4), mp 129−130 °C; ^{1}H NMR (300 MHz) δ −0.07 (d, J = 7 Hz, 3 H), 0.64 (d, J = 7 Hz, 3 H), 0.92 (dd, J = 7, 8 Hz, 1 H), 1.66−1.74 (m, 1 H), 1.78 (dd, J = 5, 9 Hz, 1 H), 2.36 (dd, J = 5, 8 Hz, 1 H), 3.42 (t, J = 8 Hz, 1 H), 3.72 (s, 3 H), 4.01 (dd, J = 1, 8 Hz, 1 H), 4.17 (t, J = 8 Hz, 1 H), 7.16−7.30 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 13.3 (CH_3), 17.8 (CH_3), 18.6 (CH_2), 26.2 (CH), 33.0 (CH), 39.9 (C), 52.6 (CH_3), 58.8 (CH), 63.3 (CH_2), 127.5 (CH), 128.2 (CH), 128.4 (CH), 133.6 (C), 153.3 (C), 165.0 (C), 169.7 (C) ppm; IR (film) $\tilde{\nu}$ 2970 cm^{-1}, 1787, 1736, 1690, 1388, 1366, 1279, 1209, 1151, 1104, 1052, 1012, 975, 752, 699; $[\alpha]^{20}_D$ = +212.0 (c = 1.0, $CHCl_3$); LRMS (ESI) m/z = 685 ([2 M + Na^+], 15), 354 ([M + Na^+], 100). Anal. Calcd for $C_{18}H_{21}N_2O_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.59; H, 6.26; N, 4.36. **15:** Colorless solid, yield 1.6 g (34%), R_f = 0.25 (diethyl ether/pentane 1:4), mp 128−129 °C; ^{1}H NMR (300 MHz) δ 0.80 (d, J = 7 Hz, 3 H), 0.82 (d, J = 7 Hz, 3 H), 1.79 (dd, J = 6, 9 Hz, 1 H), 2.14−2.24 (m, 1 H), 2.28 (dd, J = 6, 8 Hz, 1 H), 3.24−3.36 (m, 2 H), 3.71 (s, 3 H), 3.74 (m, 1 H), 3.87 (dd, J = 2, 9 Hz, 1 H), 7.06−7.32 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 15.1 (CH_3), 17.6 (CH_3), 18.5 (CH_2), 28.9 (CH), 32.1 (CH), 39.7 (C), 52.5 (CH_3), 58.5 (CH), 63.7 (CH_2), 127.3 (CH), 127.6 (CH), 128.1 (CH), 133.9 (C), 152.8 (C), 165.3 (C), 169.8 (C) ppm; IR (film) $\tilde{\nu}$ 2970 cm^{-1}, 1772, 1734, 1700, 1684, 1653, 1506, 1457, 1280, 1195, 1107, 870, 797, 758, 704; $[\alpha]^{20}_D$ = − 73.2 (c = 1.0, $CHCl_3$); LRMS (ESI) m/z = 685 ([2 M + Na^+], 26), 413 (25), 385 (32), 354 ([M + Na^+], 100). Anal. Calcd for $C_{18}H_{21}N_2O_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.41; H, 6.72; N, 4.01.

Synthesis of Both Enantiomers of Dimethyl 2-Phenylcyclopropane-1,1-dicarboxylate (5a): (1′*S*,2′*R*,4*S*)-4-Isopropyl-3-(1′-methoxycarbonyl-2′-phenylcyclopropylcarbonyl)oxazolidin-2-one (**15**) (200 mg, 0.6 mmol) was dissolved in a mixture of NaOH (4 g, 100 mmol), THF (21 mL), H_2O_2 (6 mL, 30%), and H_2O (14 mL). This solution was heated under reflux for 48 h, then THF was distilled off under reduced pressure. Saturated aqueous $NaHCO_3$ was added to this solution, and the solution obtained was washed twice with ethyl acetate, then the aqueous phase was acidified with diluted HCl, thrice extracted with ethyl acetate, and the organic phase was dried over Na_2SO_4. Then the solvent was distilled off, and an ethereal solution of CH_2N_2 (20 mL) obtained from *N*-nitroso-*N*-methylurea (1 g, 9.7 mmol) was added to the residue. After 24 h, the solvent was distilled off and the residue was purified by column chromatography on silica gel, eluting with diethyl ether/pentane 1:4.

Dimethyl (*R*)-2-Phenylcyclopropane-1,1-dicarboxylate ((*R*)-5a): Yield 45 mg (32%); $[\alpha]^{20}_D$ = +93.4 (c = 0.8, benzene); ^{1}H NMR (300 MHz) δ 1.74 (dd, J = 4, 3 Hz, 1 H), 2.20 (dd, J = 4, 3 Hz, 1 H), 3.21 (t, J = 4 Hz, 1 H), 3.40 (s, 3 H), 3.80 (s, 3 H), 7.20−7.30 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 19.0 (CH_2), 32.4 (CH), 36.8 (C), 52.1 (CH_3), 52.6 (CH_3), 127.2 (CH), 128.5 (CH), 128.9 (CH), 134.5 (C), 164.9 (C), 169.1 (C) ppm; IR (film) $\tilde{\nu}$ 3041 cm^{-1}, 2950, 1721, 1435, 1279, 1180, 1162, 1109.

Dimethyl (*S*)-2-Phenylcyclopropane-1,1-dicarboxylate ((*S*)-5a): Yield 38 mg (27%); $[\alpha]^{20}_D$ = −111.8 (c = 1.1, benzene), lit.[16] $[\alpha]^{20}_D$ = −124 (c = 2.23, benzene); ^{1}H NMR (300 MHz) δ 1.70 (dd, J = 4, 3 Hz, 1 H), 2.24 (dd, J = 4, 3 Hz, 1 H), 3.23 (t, J = 4 Hz, 1 H), 3.45 (s, 3 H), 3.80 (s, 3 H), 7.20−7.30 (m, 5 H) ppm; ^{13}C NMR (75.5 MHz) δ 18.9 (CH_2), 32.6 (CH), 36.9 (C), 52.4 (CH_3), 52.7 (CH_3), 127.3 (CH), 128.5 (CH), 128.8 (CH), 134.6 (C), 164.6 (C), 169.1 (C) ppm; IR (film) $\tilde{\nu}$ 3042 cm^{-1}, 2953, 1726, 1435, 1281, 1180, 1160, 1110.

Reaction of Dimethyl (*R*)-2-Phenylcyclopropane-1,1-dicarboxylate (*R*)-5a with Diisopropyl Azodicarboxylate (6a): According to GP1, dimethyl (*R*)-2-phenylcyclopropane-1,1-dicarboxylate ((*R*)-**5a**) (20 mg, 0.085 mmol), diisopropyl azodicarboxylate (**6a**) (30 mg, 0.15 mmol), and $GaCl_3$ (3 mg, 0.017 mmol, 20 mol %) in CH_2Cl_2 (0.5 mL) after purification by column chromatography on silica gel (3 g, column 1 × 10 cm) gave 18 mg (49%) of the pyrazolidine **7aa**, which was subjected to HPLC analysis on a chiral-phase 1A-Diacel column.

Reaction of Dimethyl (*S*)-2-Phenylcyclopropane-1,1-dicarboxylate (*S*)-5a with 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) (6d): According to the GP3, dimethyl (*S*)-2-phenylcyclopropane-1,1-dicarboxylate ((*S*)-**5a**) (15 mg, 0.064 mmol), 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (**6d**) (23 mg, 0.13 mmol), and $GaCl_3$ (2.5 mg, 0.014 mmol, 22 mol %) in CH_2Cl_2 (0.3 mL) gave a mixture which was separated by chromatography on silica gel (3 g, column 1 × 10 cm). The isolated 3 mg (12%) of the pyrazolidine **7ad** and 5 mg (19%) of the pyrazolidine **8ad** were subjected to HPLC on a chiral-phase 1A-Daicel column.

Acknowledgments. This work was supported by the State of Niedersachsen and the Fonds der Chemischen Industrie. V.S.K. and O.V.L. are indebted to the Degussa-Stiftung (Degussa AG) for graduate student fellowships. The authors thank Mr. Reinhard Machinek for the kinetic measurements by NMR spectroscopy.

Supporting Information Available: ^{1}H, ^{13}C NMR spectra and HPLC data for new compounds as well as detailed crystallographic information for **7bd** and **8bd**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0704816

(14) Izquierdo, M. L.; Arenal, I.; Bernabe, M.; Fernandez Alvarez, E. *Tetrahedron* **1985**, *41*, 215.

(15) Phoenix, S.; Bourque, E.; Deslongchamps, P. *Org. Lett.* **2000**, *2*, 4149.

(16) Corey, E. J.; Gant, T. G. *Tetrahedron Lett.* **1994**, *35*, 5373.