69. Acid-Promoted Rearrangements of *N*-Substituted 8-Oxa-3-azatricyclo[3.2.1.$0^{2,4}$]octane-6,7-dicarboxylates: Remote Substituent Effects on the Regioselectivity of the *N*-Acylaziridine/Dihydrooxazone Rearrangement[1])

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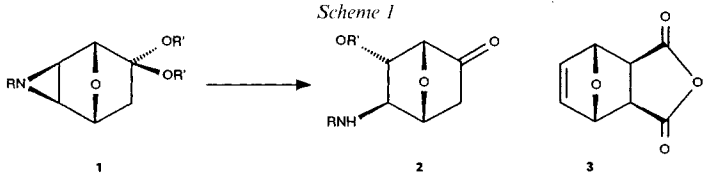
Preparations of dimethyl (1*RS*,2*SR*,4*RS*,5*SR*,6*SR*,7*RS*)- and dimethyl (1*RS*,2*SR*,4*RS*,5*SR*,6*RS*,7*SR*)-8-oxa-3-azatricyclo[3.2.1.$0^{2,4}$]octane-6,7-dicarboxylate (**15** and **18**, resp.) and of their *N*-(*tert*-butyloxy)carbonyl (**14**, **17**) and *N*-benzoyl (**16**, **19**) derivatives are described. While treatment with nucleophilic acids (HCl, HBr, AcOH) of the *exo,exo*-diesters **14** and **16** gave the corresponding products **23**–**27** of aziridine *trans*-addition, the *exo,endo*-diesters **17** and **19** led to the corresponding amino-lactones **63** (methyl (1*RS*,2*RS*,3*SR*,6*RS*,7*SR*,9*RS*)-2-{[(*tert*-butyloxy)carbonyl]amino}-5-oxo-4,8-dioxatricyclo[4.2.1.$0^{3,7}$]nonane-9-carboxylate) and **64** (methyl (1*RS*,2*RS*,3*SR*,6*RS*,7*SR*,9*RS*)-2-(benzoylamino)-5-oxo-4,8-dioxatricyclo[4.2.1.$0^{3,7}$]nonane-9-carboxylate). Under non-nucleophilic acidic conditions, the *N*-benzoylaziridine **16** was rearranged quantitatively into dimethyl (1*RS*,2*SR*,6*RS*,7*SR*,8*RS*,9*RS*)-4-phenyl-5,10-dioxa-3-azatricyclo[4.3.1.$0^{2,7}$]dec-3-ene-8,9-dicarboxylate (**31**), and **19** into dimethyl (1*RS*,2*SR*,6*SR*,7*SR*,8*SR*,9*SR*)-4-phenyl-3,10-dioxa-5-azatricyclo[5.2.1.$0^{2,6}$]dec-4-ene-8,9-dicarboxylate (**65**). Possible mechanisms of these highly selective reactions and rearrangements are discussed.

Introduction. – Derivatives of 7-oxabicyclo[2.2.1]heptane (= 7-oxanorbornane) have been used as starting material in the synthesis of natural products and compounds of biological interest [1] [2]. Recently, we presented a highly stereoselective method for the *trans*-aminohydroxylation of the double bond in 7-oxabicyclo[2.2.1]hept-5-en-2-one (a 'naked sugar' [1a]) which implies the acid-catalyzed rearrangement of aziridines **1** into the corresponding protected amino-hydroxy ketones **2** [3] *(Scheme 1)*. Compound **2** was transformed readily into optically pure 3-amino-3-deoxy-altrose derivatives [3]. Since the *Diels-Alder* adduct **3** of furan to maleic anhydride [4] can be transformed into optically active derivatives [5], we examined the possibility to introduce protected amino and hydroxy groups at centres C(5) and C(6) in a stereoselective fashion.

In 1933, *Alder* and *Stein* [6] reported that the treatment of *N*-phenylaziridine derivative **4** (in which the two ester functions are in a *trans*-configuration) with Ac_2O gave the

Scheme 1

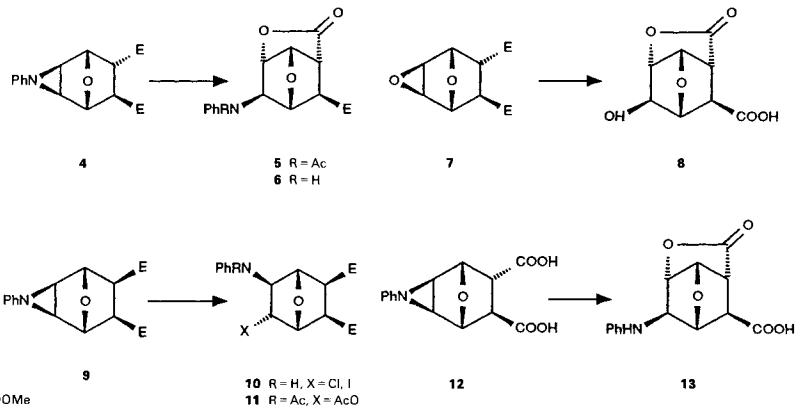


1 **2** **3**

R = PhCO, COOEt, COO(*t*-Bu); R' = Me, $PhCH_2$

[1]) This work was presented in part at the autumn meeting of the Swiss Chemical Society, Bern, Oct. 21, 1988.

Scheme 2



corresponding lactone **5** without skeleton rearrangement *(Scheme 2)*. Similarly, the same authors showed that treatment of **4** with aqueous acid gave **6** [7], and that the corresponding epoxide **7** furnished lactone **8** [6]. While the isomeric *exo,endo*-diesters of **4** and **7** reacted rapidly under acidic conditions to give lactones isomeric to **5** and **8**, respectively, the corresponding *exo,exo*-diesters were found to be much less reactive toward acids, in agreement with the hypothesis that the *endo*-carboxylic moieties in **4** and **7** participate in the heterolysis of the aziridine and epoxide rings, respectively[2]). In 1965, *Zefirov* and coworkers [10] reported that the *N*-phenylaziridine moiety of 7-oxanorbornane-2,3-dicarboxylate **9** added acids HX in a *trans*-fashion to give the corresponding adducts **10**, and that reaction of **9** with Ac_2O gave product **11** *(Scheme 2)*. Under similar conditions, the *exo,endo*-dicarboxylic acid **12** gave the (phenylamino)lactone **13** exclusively [10].

Since we wished to obtain amino alcohols derived from **3** in which the amino group bears a protective group more readily cleaved than the Ph substituent, we have developed first the syntheses of aziridines **14**–**19** and then explored their reactivity toward acids. We

report here that the *exo,exo*-diesters **14** and **16** add nucleophilic acids in a similar fashion as **9**. However, under non-nucleophilic conditions, the *N*-benzoyl derivative **16** underwent skeletal rearrangements and led to the exclusive formation of a tricyclic 6,7-dihydro-1,3,5-dioxazepine derivative. Interesting also was our finding that the *exo,endo*-diester **19** led either to the product of *trans*-aminohydroxylation, *via* a protected aminolactone (as in the case of reaction **12** → **13**), or to *cis*-aminohydroxylation through the highly stereoselective formation of a tricyclic 4,5-dihydrooxazole derivative, depending on the reaction conditions.

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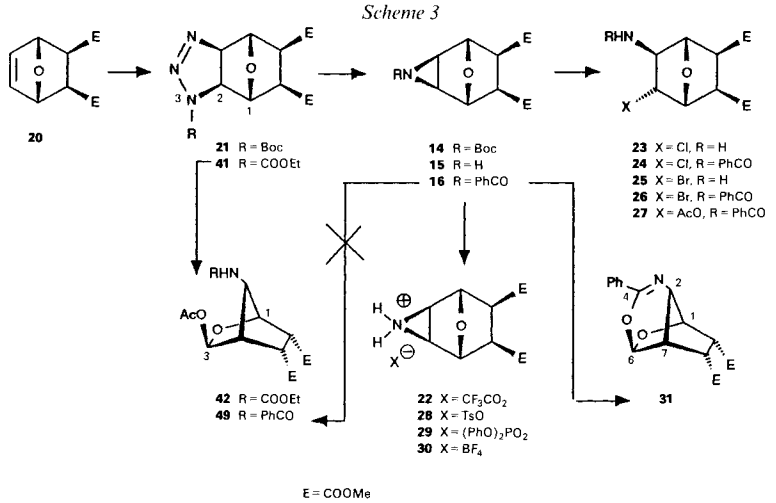
[2]) See also related lactonisations [8] [9].

Results and Discussion. – Cycloaddition (CH_2Cl_2, 37°, 3 d) of *tert*-butyl azidoformate to dimethyl 7-oxanorborn-5-en-2-*exo*,3-*exo*-dicarboxylate (**20**; obtained by treatment of anhydride **3** with MeOH/HCl) gave dihydrotriazole **21** (87%; *Scheme 3*). Irradiation of **21** with a high-pressure Hg lamp (quartz vessel, acetone) furnished the protected aziridine **14** (78%). Treatment of **14** with CF_3COOH in CH_2Cl_2 led to acidolysis of the carbamate and formation of salt **22** which was neutralized with aqueous $NaHCO_3$ solution to afford the unprotected aziridine **15**. The latter was benzoylated ($PhCOCl/Et_3N/CH_2Cl_2$) to **16** (69%).

Treatment of **14** with gaseous HCl in CH_2Cl_2 (20°) gave adduct **23** (99%) which was characterized as its benzamide **24** (72%; *Scheme 3*). The same compound (79%) was obtained on bubbling gaseous HCl through a CH_2Cl_2 solution of **16**. Similarly, **14** added at 20° 1 equiv. of HBr (30% in AcOH) to give the corresponding *trans*-bromo-amine **25** (98%) which was characterized as its benzamide **26** (68%). The same compound (86%) was also obtained on treating **16** with $HBr/AcOH/CH_2Cl_2$ (20°). In AcOH/

Scheme 3

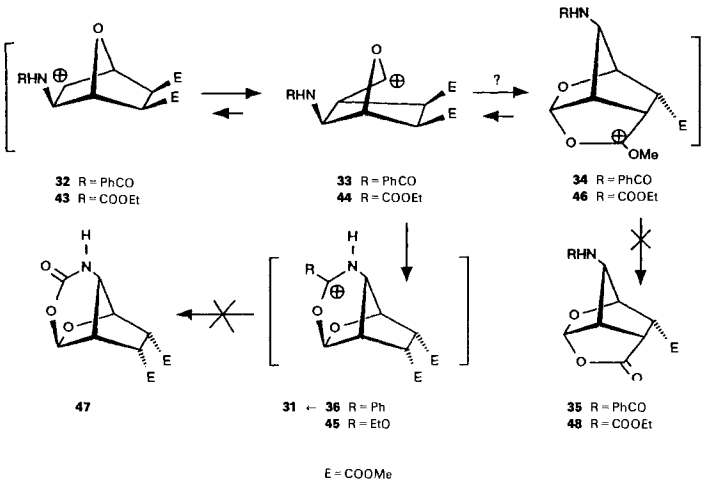


$CF_3CH(OH)CF_3$ 1:1 containing 0.5 equiv. of each CF_3SO_3H and $(CF_3SO_2)O$, adduct **27** was obtained from **16** in 30% yield together with *ca.* 60% of **31**. Less nucleophilic acids such as TsOH in EtOH, diphenyl hydrogen phosphate in CH_2Cl_2, or HBF_4 in EtOH did not give (20°) the corresponding product of aziridine addition but the stable salts **28**, **29**, and **30**, respectively (*Scheme 3*). Surprisingly, treatment of *N*-benzoylaziridine **16** with 70% aqueous $HClO_4$ in $CF_3CH(OH)CF_3$ at 20° gave the 6,7-dihydro-1,3,5-dioxazepine derivative **31** in 94% yield.

The structures of products **22**–**31** were given by their mode of formation and their spectral data (see *Exper. Part*). The relative configuration at C(2), C(3), C(5), and C(6) of the 7-oxanorbornane moieties was established unambiguously by the vicinal coupling constants ^3J(H,H) measured for the protons attached to these centres with the adjacent bridgehead protons H–C(1) and H–C(4) [11]. The 6,7-dihydro-1,3,5-dioxazepine moiety in **31** was confirmed by its IR ($\tilde{\nu}$(C=N) 1645 cm^{-1} [12]) and ^{13}C-NMR spectra (*s* at 157.1 ppm for O–C=N [13], *d* (^1J(C,H) = 170 Hz) at 98.2 ppm for OCHO).

The HCl and HBr additions duplicate the results reported by *Zefirov* and coworkers [10] for the *N*-phenylaziridine **9**. It is interesting to note, however, that no products arising from a *Wagner-Meerwein* rearrangement of the bicyclic skeleton have been observed in these acid-promoted aziridine-ring openings. Although the isomerization of 7-oxanorborn-2-yl-cation into 3-oxanorborn-2-yl-cation intermediates is expected to be a highly exothermic process [14] [15], it is retarded due to the inductive effect of the O(7) bridge and of the two carboxylic groups at C(2) and C(3) [16]. The isolation of stable aziridinium salts **28**–**30** is an illustration of that property which renders the acid-promoted heterolysis of the C–N bonds of aziridines **15** and **16** relatively difficult. Strongly acidic and ionizing media are thus required to induce it and to allow for the *Wagner-Meerwein* rearrangement **32** → **33** *(Scheme 4)*. With the nucleophilic acids HCl, HBr, and

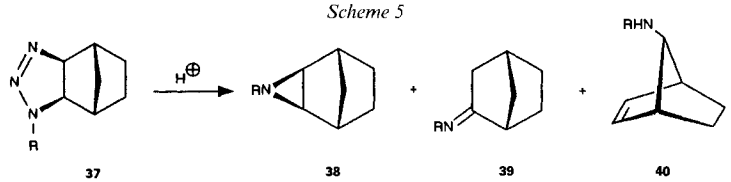
Scheme 4



AcOH, nucleophilic assistance to the C–N heterolysis intervenes and competes with the difficult σ(C–C) participation that leads to rearranged products. Most striking was the absence of lactone **35** under the strongly ionizing conditions leading to **31**. This result can be explained in terms of the alkoxycarbenium ion **33** that is quenched internally to give the more stable α-amino-α-alkoxybenzyl-cation intermediate **36** *(Scheme 4)*. This process can be more rapid than 'internal quenching' by the adjacent *endo*-ester group yielding the slightly less stable dialkoxycarbenium-ion intermediate **34**. Although lactone **35** was not observed, it is possible that **34** is present in equilibrium with ion **36** leading to **31** on deprotonation.

Triazolines **37** arising from cycloadditions of azides RN_3 to bicyclo[2.2.1]hept-2-ene have been reported to be decomposed under acidic conditions into mixtures of the corresponding aziridines **38**, imines **39**, and rearranged (norborn-2-en-7-yl)amines **40** [17] [18] *(Scheme 5)*. We found that dihydrotriazole **41** resulting from the reaction of ethyl azidoformate with **20** *(Scheme 3)* was stable in the presence of weak acids such as AcOH. However, with stronger acids such as CF_3SO_3H (generated by addition of $CF_3SO_3SiMe_3$ to a solution of **41** in CH_2Cl_2/AcOH at $-10°$), **41** was decomposed and rearranged into

Scheme 5

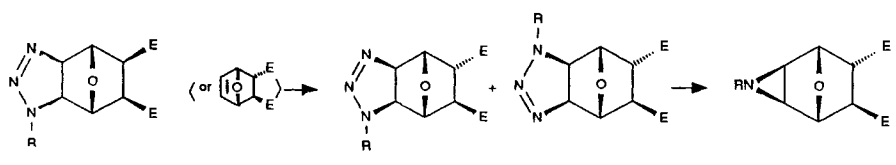


37 **38** **39** **40**

42 (88%; *Scheme 3*) in which the AcO group of the hemiacylal moiety is in the *exo*-position, as expected for an 'external quenching' of the corresponding alkoxy-carbenium intermediate **44** resulting from the *Wagner-Meerwein* rearrangement **43** → **44** *(Scheme 4)*. It is thus surprising to observe that 'internal quenching' of **44** either by the carbonyl group of the carbamate moiety leading to the expectedly stable carbenium-ion intermediate **45** or by the *endo*-ester group to give **46** did not occur, as no tricyclic carbamate **47** or lactone **48**, respectively, was found in the products. One should note also that no trace of hemiacylal **49** *(Scheme 3)* could be detected in the CF_3SO_3H-promoted rearrangement of **16** in pure AcOH.

The *exo,endo*-diesters **17**–**19** were synthesized in the following way *(Scheme 6)*: Cycloaddition of *tert*-butyl azidoformate to dimethyl 7-oxanorborn-5-en-2-*exo*,3-*endo*-dicarboxylate (**50**, obtained by K_2CO_3-catalyzed isomerization of **20** in MeOH, 20°) gave a 1:1 mixture of dihydrotriazoles **51** and **52** in modest yield (55%) due to relatively fast *retro-Diels-Alder* reaction of **50** giving furan and dimethyl fumarate. Direct isomerization of dihydrotriazole **21** with anhydrous $MeOH/CH_2Cl_2$ and 2-[(*tert*-butyl)imino]-2-(diethylamino)-1,3-dimethylperhydro-1,3,2λ^5-diazaphosphorinane on polystyrene gave a 3:2 mixture **51**/**52** from which **51** could be isolated pure in 53% yield by crystallization.

Scheme 6



21 R = Boc, E = COOMe
41 R = COOEt, E = COOMe

50 (for **51**/**52**)

51 R = Boc, E = COOMe
53 R = H, E = COOMe
55 R = H, E = COOEt
59 R = H, E = COOPr

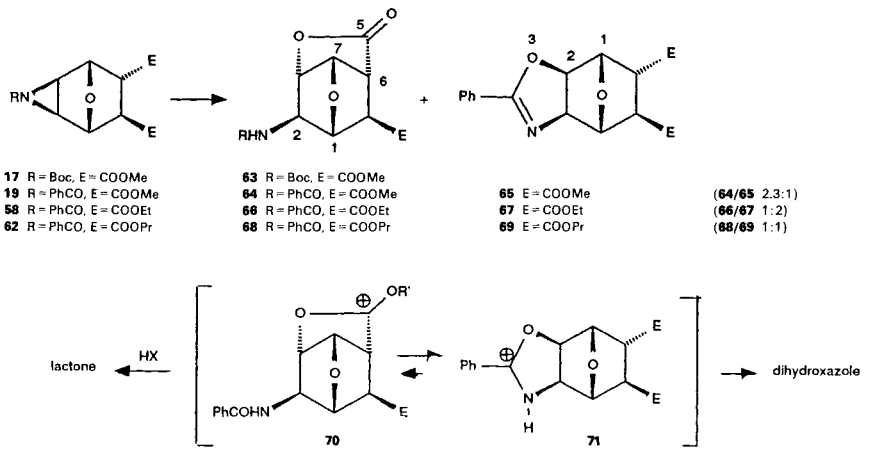
52 R = Boc, E = COOMe
54 R = H, E = COOMe
56 R = H, E = COOEt
60 R = H, E = COOPr

17 R = Boc, E = COOMe
18 R = H, E = COOMe
19 R = PhCO, E = COOMe
57 R = H, E = COOEt
58 R = PhCO, E = COOEt
61 R = H, E = COOPr
62 R = PhCO, E = COOPr

Irradiation of **51**/**52** led to aziridine **17** (74%). Alcaline methanolysis (K_2CO_3/anh. MeOH) of **41** was accompanied by isomerization leading to a 3:2 mixture **53**/**54**. Irradiation of **53**/**54** (Hg lamp, quartz, acetone, 0°) gave unprotected aziridine **18** (95%) which was benzoylated (PhCOCl, pyridine) to **19** (76%). For comparison purposes, we also synthesized the ethoxycarbonyl- and propyloxycarbonyl-substituted aziridines **58** and **62** *(Scheme 6)*. Treatment of **41** with K_2CO_3 in EtOH or PrOH gave the dihydrotriazoles **55**/**56** and **59**/**60**, respectively, which, on irradiation (→ **57** and **61**, resp.) and benzoylation, furnished the desired aziridines **58** and **62**, respectively.

Treatment of **17** with a small amount of CF_3CO_2H in CH_2Cl_2 (20°, 3 d) gave impure lactone **63** *(Scheme 7)*. A 90% yield of pure **63** was obtained by allowing pure dihydro-

Scheme 7



triazole **51** to react with a small amount of CF_3SO_3H (generated by addition of $CF_3SO_3SiMe_3$ to a stirred mixture of **51** in $CHCl_3/H_2O$). Similarly, treatment of **19** with $HBr/H_2O/AcOH/CH_2Cl_2$ (20°, 1 h) gave lactone **64** as unique product. Interestingly, in a less nucleophilic medium ($CF_3CH(OH)CF_3$/0.5 equiv. of CF_3SO_3H, 0.5 equiv. of $(CF_3SO_2)_2O$), **19** was rearranged readily and quantitatively (as determined by 360-MHz ^{1}H-NMR) to dihydrooxazole **65**[3]). A 2.3:1 mixture **64/65** was obtained by bubbling dry gaseous HCl through a CH_2Cl_2 solution of **19** (at 0°). Finally, the *N*-benzoylaziridines **58** and **62** bearing the more bulky ethoxycarbonyl and propyloxycarbonyl groups, respectively, gave, with gaseous HCl in anhydrous CH_2Cl_2, 1:2 and 1:1 mixtures of the corresponding lactones and dihydrooxazoles **66/67** and **68/69**, respectively. These results (*Scheme 7*, top) can be interpreted in terms of a facile formation of a cationic intermediate **70** due to the participation of the *endo*-ester group to the heterolysis of the aziridine moiety. In an ionizing and non-nucleophilic medium such as anh. $CF_3CH(OH)CF_3$ [18], **70** has the time to undergo an intramolecular S_N2 process leading to the expectedly more stable α-amino-α-alkoxybenzylic-ion intermediate **71** which gives the dihydrooxazoles on deprotonation (*Scheme 7*, bottom). In a nucleophilic medium containing H_2O or HCl, the nucleophile attacks competitively the R′ group in **70** leading to the observed lactones. This hypothesis was confirmed by comparing the behaviour of azirines **19**, **58**, and **62** bearing different alkoxycarbonyl groups. Thus, increasing the bulkiness of the R′ group in **70** made its quenching by the external nucleophile somewhat less competitive with the rearrangement **70** → **71**, leading to increased amounts of the corresponding dihydrooxazoles.

The structures of compounds **50**–**69** were established by their elemental analyses and spectral data (see *Exper. Part*). Distinction between isomeric dihydrotriazoles **51** and **52** was based on NOE measurements in their 360-MHz ^{1}H-NMR spectra (*e.g.*, irradiation of the signal of *t*-Bu of the Boc group of **51** (1.60 ppm) led to a NOE at 5.04 ppm (*s*,

[3]) Thermal rearrangement of *N*-benzoylaziridines into dihydrooxazoles have already been described [17a] [19]. This reaction can be catalyzed by I_2, thiocyanate, and azide anions [20], by Bu_3N [21], or by acids [22].

H–C(1))). The constitution of the dihydrooxazoles **65**, **67**, and **69** was based on the difference in δ(H) of H–C(6) and H–C(2). The latter, being geminal to the O-atom of the dihydrooxazole moiety and perturbed by the *endo*-carboxylate at C(9), is more deshielded. This attribution was confirmed by NOE measurements and by the protic-acid-induced shifts of the H–C(2) and H–C(6) signals on addition of HCl or TsOH (CH_2Cl_2 solutions), H–C(6) (geminal to the N-atom) being more deshielded than H–C(2) by protonation of the dihydrooxazole moiety (see *Exper. Part*).

Conclusion. – The acid-promoted rearrangements of *N*-substituted aziridines grafted to 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate systems have disclosed a number of unexpected subtleties of practical and theoretical interest. Some of the reactions presented here realize stereoselective methods for the *trans*- and *cis*-aminohydroxylation of the double bond of the inexpensive maleic anhydride/furan *Diels-Alder* adduct **3**.

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Experimental Part

1. *General.* See [23]. Column chromatography (FC = flash chromatography) and filtrations: Silica gel *Merck 7734* or *9385*. None of the procedures reported here have been optimized.

2. *3-tert-Butyl 6,7-Dimethyl (1RS,2SR,4RS,5SR,6SR,7RS)-8-Oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-3,6,7-tricarboxylate* (**14**). A soln. of **21** (1 g, 2.8 mmol) in acetone (150 ml) was irradiated (*Philips HPK 125 W*) in a quartz vessel cooled to 0° and under Ar bubbling for 1 h. After solvent evaporation, the residue was recrystallized from acetone/hexane (20°): 0.72 g (78%). Colourless crystals. M.p. 174–177° (dec.). IR (KBr): 2990, 2960, 2940, 1740, 1725, 1700, 1435, 1365, 1315, 1250, 1145, 1030, 1010, 925, 855, 815, 790. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.91 (*s*, H–C(1), H–C(5)); 3.70 (*s*, 2 MeO); 3.06 (*s*, H–C(6), H–C(7)); 2.70 (*s*, H–C(2), H–C(4)); 1.46 (*s*, *t*-Bu). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.3, 158.9, 81.3 (3*s*); 77.0 (*d*, ^1J(C,H) = 165, C(1), C(5)); 52.3 (*q*, ^1J(C,H) = 145, 2 MeO); 50.2 (*d* ^1J(C,H) = 140, C(2), C(4)); 36.3 (*d*, ^1J(C,H) = 190, C(6), C(7)); 28.0 (*q*, ^1J(C,H) = 125, Me_3C). CI-MS (NH_3): 345 (39), 328 (48, $M^{+\cdot}$), 289 (14), 272 (14), 254 (12), 229 (11), 228 (100), 227 (12), 145 (17), 106 (10), 83 (56). Anal. calc. for $C_{15}H_{21}NO_7$ (327.34): C 55.04, H 6.47, N 4.28; found: C 54.88, H 6.35, N 4.30.

3. *Dimethyl (1RS,2SR,4RS,5SR,6SR,7RS)-8-Oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**15**). CF_3COOH (0.3 ml; freshly distilled from P_4O_{10}) was added dropwise to a stirred soln. of **14** (0.1 g, 0.306 mmol) in anh. CH_2Cl_2 (1 ml) cooled to 0°. The temp. was allowed to reach 20° and the mixture stirred for 24 h. The mixture was poured into sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2 (10 ml, 5 times). After filtration on cotton, the solvent was evaporated: 67 mg (97%) of colourless crystals. Recrystallization from CH_2Cl_2/Et_2O/petroleum ether (20°) gave 50 mg (72%). Colourless crystals. M.p. 93.5–95°. IR (KBr): 3270, 3060, 3010, 2960, 1740, 1435, 1355, 1330, 1295, 1260, 1200, 1150, 1135, 1020, 990, 945, 930, 825, 800. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.68 (*s*, H–C(1), H–C(5)); 3.70 (*s*, 2 MeO); 3.05 (*s*, H–C(6), H–C(7)); 2.18 (*s*, H–C(2), H–C(4)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.7 (*s*); 77.3 (*d*, ^1J(C,H) = 170, C(1), C(5)); 52.2 (*q*, ^1J(C,H) = 150, MeO); 50.9 (*d* ^1J(C,H) = 140, C(6), C(7)); 30.4 (*d*, ^1J(C,H) = 160, C(2), C(4)). CI-MS (NH_3): 246 (4), 245 (33), 230 (3), 229 (11), 228 (100, [M + 1]$^+$), 200 (2), 190 (3), 168 (2), 83 (41), 80 (4). Anal. calc. for $C_{10}H_{13}NO_5$ (227.22): C 52.86, H 5.77, N 6.16; found: C 52.88, H 5.83, N 6.23.

4. *Dimethyl (1RS,2SR,4RS,5SR,6SR,7RS)-3-Benzoyl-8-oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**16**). CF_3COOH (1.5 ml, 19.6 mmol; freshly distilled from P_4O_{10}) was added dropwise to a stirred soln. of **14** (0.5 g, 1.53 mmol) in anh. CH_2Cl_2 cooled to 0°. After stirring at 20° for 1 d, the mixture was poured into sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2 (10 ml, 4 times). After solvent evaporation, the residue was dissolved in CH_2Cl_2 (4 ml) and cooled to 0°. Et_3N (0.425 ml, 3.06 mmol) was added, and then benzoyl chloride (0.355 ml, 3.06 mmol) was added dropwise. After stirring at 20° for 1 d, the mixture was poured into 1N HCl (10 ml) and extracted with CH_2Cl_2 (10 ml, 4 times). The extracts were combined and washed with sat. aq. $NaHCO_3$ soln. (10 ml). After

filtration (cotton), the solvent was evaporated and the residue purified by FC (CH_2Cl_2/Et_2O 1:1) to yield 350 mg (69%; R_f 0.13) of colourless crystals which could be recrystallized from CH_2Cl_2/Et_2O: 319 mg (63%). M.p. 195.5–196°. IR (KBr): 3070, 3020, 2990, 2950, 1735, 1675, 1455, 1435, 1380, 1330, 1255, 1215, 1190, 1165, 1050, 1025, 1000, 935, 920, 880, 820, 795, 780, 710. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.95–7.41 (*m*, 5 arom. H); 4.75 (*s*, H–C(1), H–C(5)); 3.65 (*s*, 2 MeO); 3.09 (*s*, H–C(6), H–C(7)); 3.06 (*s*, H–C(2), H–C(4)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 175.6 (*s*, PhCO); 170.0 (*s*, CO_2Me); 133.3 (*s*, C(arom.)); 132.2, 128.4, 128.1 (3 *d*, ^1J(C,H) = 160, 3 CH(arom.)); 76.6 (*d*, ^1J(C,H) = 160, C(1), C(5)); 52.3 (*q*, ^1J(C,H) = 145, MeO); 49.9 (*d*, ^1J(C,H) = 140, C(6), C(7)); 37.6 (*d*, ^1J(C,H) = 180, C(2), C(4)). CI-MS (NH_3): 350 (6), 349 (33), 334 (3), 333 (14), 332 (73), 331 (7, M^+), 300 (3), 187 (3), 122 (3), 106 (5), 105 (100), 94 (7), 82 (3), 78 (6), 77 (10). Anal. calc. for $C_{17}H_{17}NO_6$ (331.33): C 61.63, H 5.17, N 4.23; found: C 61.71, H 5.20, N 4.32.

5. *3-(*tert*-Butyl) 6,7-Dimethyl (1*RS,*2*SR,*4*RS,*5*SR,*6*RS,*7*RS*)*-8-Oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-3,6,7-tricarboxylate* (**17**). Same procedure as for **14**, starting with a 2:3 mixture **51**/**52**. Yield 74%, colourless oil. ^{1}H-NMR ($CDCl_3$, 360 MHz): 4.91 (*s*, H–C(1)); 4.82 (*d*, *J* = 5.0, H–C(5)); 3.78, 3.76 (2*s*, 2MeOH); 3.72 (*dd*, *J* = 5.0, 5.0, H–C(6)); 3.19 (*d*, *J* = 5.0, H–C(7)); 2.81 (*d*, *J* = 3.5, H–C(4)); 2.71 (*d*, *J* = 3.5, H–C(2)); 1.44 (*s*, *t*-Bu).

6. *Dimethyl (1*RS,*2*SR,*4*RS,*5*SR,*6*RS,*7*RS*)*-8-Oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**18**). A soln. of **53**/**54** (3 g, 11.8 mmol) in acetone (150 ml) was cooled to 0° and irradiated (quartz vessel, Ar bubbling, *Philips HPK 125*) for 3 h. Solvent evaporation gave 2.6 g (99%) of colourless oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.65 (*s*, H–C(1)); 4.58 (*d*, *J* = 5.5, H–C(5)); 3.76, 3.75 (2 *s*, 2MeO); 3.64 (*dd*, *J* = 5.5, 5.0, H–C(6)); 3.16 (*d*, *J* = 5.0, H–C(7)); 2.27, 2.18 (2*d*, *J* = 4.0, H–C(2), H–C(4)).

7. *Dimethyl (1*RS,*2*SR,*4*RS,*5*SR,*6*RS,*7*RS*)*-3-Benzoyl-8-oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**19**). Crude **18** was dissolved in anh. CH_2Cl_2 (16 ml) and pyridine (1.16 ml, 1.1 g). After cooling to 0°, benzoyl chloride (2 g, 14.1 ml) was added dropwise under stirring. After stirring at 20° for 1 d, the mixture was poured into 1N HCl (50 ml) and extracted with CH_2Cl_2 (30 ml, 5 times). The extracts were combined and washed with sat. aq. $NaHCO_3$ soln. (50 ml). After filtration (cotton), the solvent was evaporated and the yellowish residue purified by FC (silica gel, AcOEt/petroleum ether 2:1). The main fraction was recrystallized from CH_2Cl_2/Et_2O (20°): 2.95 g (76%). Colourless crystals. M.p. 126–127°. UV (MeCN): 210 (5550), 220 (8100), 230 (1350), 240 (1210), 250 (2300), 260 (1020), 270 (1020), 280 (770). IR (KBr): 3060, 3020, 3000, 2950, 1730, 1675, 1435, 1370, 1325, 1265, 1245, 1215, 1195, 1055, 995, 930, 915, 805, 760, 710. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.43–7.94 (*m*, 5 arom. H); 4.73 (*s*, H–C(1)); 4.66 (*d*, *J* = 5.0, H–C(5)); 3.79, 3.70 (2*s*, 2 MeO); 3.66 (*dd*, *J* = 4.5, 5.0, H–C(6)); 3.19 (*d*, *J* = 4.5, H–C(7)); 3.16 (*d*, *J* = 4.0, H–C(4)); 3.07 (*d*, *J* = 4.0, H–C(2)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 176.1, 171.2, 170.3, 133.3 (4 *s*); 132.4, 128.5, 128.1 (3 *d*, ^1J(C,H) = 163, CH(arom.)); 78.4 (*d*, ^1J(C,H) = 145, C(1)); 75.4 (*d*, ^1J(C,H) = 145, C(5)); 52.6, 52.5 (2 *q*, ^1J(C,H) = 145, 2 MeO); 50.7, 48.7 (2 *d*, ^1J(C,H) = 135, C(6), C(7)); 37.8, 36.3 (2*d*, ^1J(C,H) = 135, C(4), C(2)). Anal. calc. for $C_{17}H_{17}NO_6$ (331.33): C 61.63, H 5.17, N 4.23; found: C 61.71, H 5.23, N 4.23.

8. *3-*tert*-Butyl 8,9-Dimethyl (1*RS,*2*SR,*6*RS,*7*SR,*8*SR,*9*RS*)*-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene-3,8,9-tricarboxylate* (**21**). A mixture of **20** (5 g, 23.6 mmol) and *tert*-butyl azidoformate (4.4 g, 30.7 mmol) in CH_2Cl_2 (7 ml) was heated to 37° for 3 d in the dark. After solvent evaporation, the residue was recrystallized from CH_2Cl_2/Et_2O/hexane at 20°; 7.3 g (87%) of colourless crystals. M.p. 153–153.5° (dec.). UV (MeCN): 210 (1440), 220 (2400), 230 (4710), 240 (6630), 250 (5480), 260 (3170), 270 (1440), 280 (290). IR (KBr): 2980, 2950, 1730, 1710, 1520, 1435, 1390, 1250, 1210, 1175, 1175, 1145, 1010, 965, 930, 900, 870, 810. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.23 (*s*, H–C(7)); 5.04 (*s*, H–C(1)); 4.87, 4.01 (2 *d*, *J* = 8.0, H–C(6), H–C(2)); 3.72, 3.70 (2 *s*, 2 MeO); 3.14, 3.08 (2 *d*, *J* = 9.5, H–C(8), H–C(9)); 1.59 (*s*, *t*-Bu). CI-MS (NH_3): 356 (1, $M^{+\cdot}$ + 1), 289 (11), 273 (14), 272 (100), 229 (4), 228 (24), 195 (5), 168 (7), 167 (5), 145 (6), 83 (4). Anal. calc. for $C_{15}H_{21}N_3O_7$ (355.51): C 50.70, H 5.96, N 11.83; found: C 50.64, H 5.93, N 11.80.

9. *Dimethyl (1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS*)*-5-*exo*-*Amino-6-*endo*-*chloro-7-oxabicyclo[2.2.1]heptane-2-*exo*,*3-*exo*-*dicarboxylate* (**23**). Gaseous HCl was bubbled through a CH_2Cl_2 (18 ml) soln. of **14** (0.2 g, 0.61 mmol) cooled to 0° for 5 min. The mixture was allowed to stand at 20° for 24 h, then poured into sat. aq. $NaHCO_3$ soln. (20 ml), and extracted with CH_2Cl_2 (20 ml, 4 times). After filtration (cotton) and solvent evaporation, 159 mg (99%) of a colourless oil was obtained. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.96 (*d*, *J* = 5.0, H–C(4)); 4.56 (*s*, H–C(1)); 3.81 (*d*, *J* = 9.5, H–C(2)); 3.48–3.72 (*m*, H–C(6)); 3.72 (*s*, 2 MeO); 3.09 (*d*, *J* = 9.5, H–C(3)); 3.03 (br. *d*, H–C(5)).

10. *Dimethyl (1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS*)*-5-*exo*-*(Benzoylamino)-6-*endo*-*chloro-7-oxabicyclo[2.2.1]heptane-2-*exo*,*3-*exo*-*dicarboxylate* (**24**). 10.1. To a soln. of **23** (159 mg, 0.60 mmol) in anh. CH_2Cl_2 (4 ml) containing Et_3N (0.255 ml, 1.83 mmol) at 0°, PhCOCl (0.142 ml, 1.22 mmol) was added dropwise under vigourous stirring. After stirring at 20° under Ar for 24 h, the mixture was poured into 1N HCl (20 ml) and extracted with CH_2Cl_2 (20 ml, 4 times). After solvent evaporation, the residue was purified by FC (silica gel, Et_2O/CH_2Cl_2 1:1; R_f 0.58) yielding 163 mg (72%) of colourless crystals that could be recrystallized from Et_2O/CH_2Cl_2 (133 mg, 59%).

10.2. Gaseous HCl was bubbled through a CH_2Cl_2 (1 ml) soln. of **16** (8 mg, 0.024 mmol). After staying at 20° for 24 h, the soln. was washed with sat. aq. $NaHCO_3$ soln. and the aq. layer extracted with CH_2Cl_2 (5 ml, 4 times). The org. extracts were combined and evaporated. The residue was recrystallized from Et_2O/CH_2Cl_2: 7 mg (79%). Colourless crystals. M.p. 182–183°. IR (KBr): 3400, 3060, 3000, 2950, 1735, 1635, 1600, 1580, 1535, 1485, 1455, 1435, 1370, 1355, 1275, 1225, 1190, 1150, 1085, 1030, 1000, 915, 865, 805, 780, 695. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.82–7.43 (*m*, 5 arom. H); 6.47 (*d*, J = 8.0, NH); 5.03 (br. *d*, J = 5.0, 1.0, H–C(1)); 4.79 (*s*, H–C(4)); 4.35 (*dd*, J = 8.0, 3.0, H–C(5)); 3.99 (*dd*, J = 5.0, 3.0, H–C(6)); 3.91 (*d*, J = 9.5, H–C(2)); 3.73, 3.72 (2 *s*, 2 MeO); 3.29 (*d*, J = 9.5, H–C(3)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.7, 170.5 (2 *s*, 2 CO_2Me); 167.1 (*s*, Ph*C*O); 133.3 (*s*, C(arom.)); 132.0, 128.7, 127.1 (3 *d*, ^1J(C,H) = 160, CH(arom.)); 84.8 (*d*, ^1J(C,H) = 165, C(1)); 81.2 (*d*, ^1J(C,H) = 165, C(4)); 61.9 (*d*, ^1J(C,H) = 155, C(5)); 61.6 (*d*, ^1J(C,H) = 155, C(6)); 52.3 (*q*, ^1J(C,H) = 150, 2 MeO); 48.6 (*d*, ^1J(C,H) = 135, C(2)); 45.4 (*d*, ^1J(C,H) = 135, C(3)). CI-MS (NH_3): 388 (4), 387 (16), 386 (11), 385 (51), 371 (88), 370 (36), 369 (23), 368 (23), 368 (100, M^+), 333 (3), 332 (16), 331 (16), 300 (3), 230 (3), 122 (5), 106 (7), 105 (64), 94 (3), 77 (7). Anal. calc. for $C_{17}H_{18}ClNO_6$ (367.79): C 55.52, H 4.93, N 3.81; found: C 55.46, H 4.92, N 3.94.

11. *Dimethyl (1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS*)-5*-exo-*Amino-6*-endo-*bromo-7-oxabicyclo[2.2.1]heptane-2*-exo,*3*-exo-*dicarboxylate* (**25**). A 30% soln. of HBr in AcOH (0.132 ml) was added dropwise to a stirred soln. of **14** (50 mg, 0.153 mmol) in anh. CH_2Cl_2 (1 ml) cooled to 0°. After stirring at 20° for 24 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with CH_2Cl_2 (10 ml, 4 times). After filtration (cotton), the solvent was evaporated: 46 mg (98%). Colourless oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.94 (*d*, J = 5.0, H–C(1)); 4.51 (*s*, H–C(4)); 3.87 (*d*, J = 9.5, H–C(2)); 3.70 (*s*, 2 MeO); 3.70–3.67 (*m*, H–C(6)); 3.11 (br. *d*, H–C(5)); 3.06 (*d*, J = 9.5, H–C(3)).

12. *Dimethyl (1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS*)-5*-exo-*(Benzoylamino)-6*-endo-*bromo-7-oxabicyclo[2.2.1]heptane-2*-exo,*3*-exo-*dicarboxylate* (**26**). Same procedure as for **24**, starting with **16** (205 mg, 0.62 mmol) in CH_2Cl (8 ml) and 0.1 ml of 30% HBr in AcOH. The crude product was recrystallized from CH_2Cl_2/Et_2O: 219 mg (86%). Colourless crystals. M.p. 191–192°. The same compound was obtained in 86% yield by benzoylation (see **24**) of **25**. IR (KBr): 3300, 3060, 2950, 1735, 1640, 1535, 1435, 1280, 1225, 1195, 1180, 1030, 995, 910, 805, 790, 695. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.81–7.43 (*m*, arom. H); 6.51 (*d*, J = 8.5, NH); 5.01 (*dd*, J = 5.0, 1.0, H–C(1)); 4.76 (br. *s*, J = 1.0, H–C(1)); 4.43 (*dd*, J = 8.5, 3.0, H–C(5)); 3.99 (*d*, J = 9.5, H–C(2)); 3.92 (*ddd*, J = 3.0, 5.0, 1.0, H–C(6)); 3.73, 3.71 (2*s*, 2 MeO); 3.26 (*d*, J = 9.5, H–C(3)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.7, 170.4 (2*s*, 2 CO_2Me); 167.1 (*s*, Ph*C*O); 133.3 (*s*, C(arom.)); 132.1, 128,7, 127,1 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 84.8 (*d*, ^1J(C,H) = 165, C(1)); 81.3 (*d*, ^1J(C,H) = 165, C(4)); 62.2 (*d*, ^1J(C,H) = 155, C(5)); 52.4 (*q*, ^1J(C,H) = 150, 2 MeO); 50.5 (*d*, ^1J(C,H) = 160, C(6)); 48.5 (*d*, ^1J(C,H) = 140, C(2)); 47.1 (*d*, ^1J(C,H) = 140, C(3)). CI-MS (NH_3): 431 (23), 430 (6), 429 (22), 415 (15), 414 (61, $[M + NH_3]^+$), 413 (24), 412 (61, M^+), 334 (7), 333 (8), 332 (40), 300 (87), 178 (5), 122 (5), 106 (10), 105 (100), 94 (7), 91 (5), 77 (14). Anal. calc. for $C_{17}H_{18}NO_6$ (412.25): C 49.53, H 4.40, N 3.40; found: C 49.49, H 4.44, N 3.31.

13. *Dimethyl (1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS*)-5*-endo-*Acetoxy-6*-exo-*(benzoylamino)-7-oxabicyclo[2.2.1]heptane-2*-exo,*3*-exo-*dicarboxylate* (**27**). A 0.25M CH_3SO_3H and 0.25M $(CF_3SO_2)_2O$ soln. in $CF_3CH(OH)CF_3$ (2.5 ml) was added dropwise to a soln. of **16** (0.5 g, 1.5 mmol) in $CF_3CH(OH)CF_3$/AcOH 1:1 (24 ml). After staying at 20° for 24 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (50 ml) and extracted with CH_2Cl_2 (20 ml, 4 times). After solvent evaporation, the residue was separated and purified by FC (silica gel, AcOEt/CH_2Cl_2 2:1). The first fraction (R_f 0.44, UV) yielded 131 mg (33%) of **27**, the second fraction (R_f 0.41, UV) 317 mg (63%) of **31** (see below).

Data of **27**: Colourless crystals. M.p. 200.5–201°. IR (KBr): 3310, 1730, 1635, 1535, 1435, 1315, 1280, 1230, 1190, 1100, 1050, 1035, 910. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.81–7.42 (*m*, arom. H); 6.57 (*d*, J = 7.5, NH); 5.06 (*dd*, J = 5.0, 1.0, H–C(4)); 4.89 (*ddd*, J = 5.0, 2.5, 1.0, H–C(3)); 4.85 (*s*, J = 1.0, H–C(1)); 4.12 (*dd*, J = 7.5, 2.5, H–C(2)); 3.72 (*s*, 2MeO); 3.50 (*d*, J = 9.5, H–C(5)); 3.29 (*d*, J = 9.5, H–C(6)); 2.15 (*s*, AcO). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.7, 170.4, 170.0, 167.3 (4*s*, CO); 133.6 (*s*, C(arom.)); 131.9, 128.6, 127.1 (3*d*, ^1J(CH) = 160, 3 CH(arom.)); 84.6 (*d*, ^1J(C,H) = 165); 58.9 (*d*, ^1J(C,H) = 150); 52.3 (*q*, ^1J(C,H) = 145, MeO); 49.0 (*d*, J(C,H) = 1.30); 44.7 (*d*, ^1J(C,H) = 135); 20.6 (*q*, ^1J(C,H) = 135, *Me*CO). CI-MS (NH_3): 409 (12), 394 (5), 393 (20), 392 (100), 391 (30, M^+), 334 (4), 331 (7), 230 (4), 105 (42), 72 (4). Anal. calc. for $C_{19}H_{21}NO_8$ (263.37): C 59.50, H 5.82, N 3.85; found: C 57.86, H 5.47, N 3.95.

14. *(1*RS,*2*SR,*4*RS,*5*SR,*6*SR,*7*RS*)-6,7-Bis(methoxycarbonyl)-8-oxa-3-azoniatricyclo[3.2.1.0^{2,4}]octane* p-*Toluenesulfonate* (**28**). A soln. of TsOH (1.44 mmol, 274 mg) in EtOH (2 ml) was added to a soln. of **15** (326 mg, 1.44 mmol) in EtOH (4 ml). Addition of Et_2O led to precipitation of 500 mg (82%) of **28**. Colourless crystals. M.p. 196–197°. IR (KBr): 1735, 1565, 1525, 1430, 1380, 1365, 1350, 1275, 1215, 1125, 1035, 1010, 985, 930, 845, 810, 680.

^{1}H-NMR (MeOD, 250 MHz): 7.88–7.39 (*m*, arom. H); 5.24 (*s*, H–C(1), H–C(5)); 3.85 (*s*, H–C(6), H–C(7)); 3.83 (*s*, 2 MeO); 3.55 (*s*, H–C(2), H–C(4)); 2.54 (*s*, $CH_3C_6H_4$). ^{13}C-NMR (MeOD), 90.55 MHz): 171.6 (*s*, CO_2Me); 141.8 (*s*, C(arom.)); 129.9, 127.1 (2*d*, ^1J(C,H) = 160, 2 CH(arom.)); 77.4 (*d*, ^1J(C,H) = 170, C(1), C(5)); 52.9 (*q*, ^1J(C,H) = 150, MeO); 50.0 (*d*, ^1J = (C,H) = 150, (C6), C(7)); 35.8 (*d*, ^1J(C,H) = 195, C(2), C(4)); 21.3 (*q*, ^1J = (C,H) = 125, $CH_3C_6H_4$). CI-MS (NH_3): 229 (12), 228 (100, $[M - TsO]^+$), 200 (4), 196 (6), 190 (11), 170 (5), 168 (3), 108 (5), 91 (4), 83 (53), 80 (5). Anal. calc. for $C_{17}H_{21}NO_8S$ (399.42): C 51.12, H 5.30, N 3.51; found: C 51.14, H 5.31, N 3.62.

15. *(1RS,2SR,4RS,5SR,6SR7RS)-6,7-Bis(methoxycarbonyl)-8-oxa-3-azoniatricyclo[3.2.1.0^{2,4}]octane Diphenyl Phosphate* (**29**). A soln. of diphenyl hydrogen phosphate (187 mg, 079 mmol) in anh. CH_2Cl_2 (1 ml) was added to a soln. of **15** (170 mg) in anh. CH_2Cl_2 (1 ml). Addition of Et_2O induced the precipitation of 353 mg (94%) of **29**. Colourless crystals. M.p. 143–144°. IR (KBr): 3100, 1060, 3020, 1730, 1590, 1530, 1490, 1450, 1335, 1300, 1285, 1230, 1205, 1175, 1070, 995, 920, 905, 775, 690. ^{1}H-NMR (MeOD, 250 MHz): 7.46–72.0 (*m*, arom. H); 5.20 (*s*, H–C(1), H–C(5)); 3.83 (*s*, 2 MeOH); 3.74 (*s*, H–C(6), H–C(7)); 3.48 (*s*, H–C(2), H–C(4)). ^{13}C-NMR (MeOD, 90.55 MHz): 171.5 (*s*, CO_2Me); 154.2 (*s*, C(arom.)); 130.3, 124.6, 121.4 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 77.3 (*d*, ^1J(C,H) = 175, C(1), C(5)); 52.9 (*q*, ^1J(C,H) = 150, MeO); 50.0 (*d*, ^1J(C,H) = 140, C(6), C(7)); 35.3 (*d*, ^1J(C,H) = 200, C(4), C(2)). CI-MS (NH_3): 269 (11), 268 (100), 252 (9), 251 (49), 250 (51), 245 (14), 232 (5), 229 (14), 228 (77, $[M - (PhO)_2OPO]^+$, 77), 170 (21), 111 (5), 94 (40), 93 (41), 86 (5), 83 (54), 80 (11), 78 (49), 77 (14). Anal. calc. for $C_{22}H_{24}NO_9$ (477.41): C 55.35, H 5.07, N 2.93, P 6.49; found: C 55.46, H 5.16, N 2.97, P 6.59.

16. *(1RS,2SR,4RS,5SR,6SR,7RS)-6,7-Bis(methoxycarbonyl)-8-oxa-3-azoniatricyclo[3.2.1.0^{2,4}]octane Tetrafluoroborate* (**30**). HBF_4 (0.153 ml, 1.53 mmol) was added to a MeOH (4 ml) soln. of **15** (347 mg, 1.53 mmol). Addition of Et_2O induced precipitation of 382 mg (79%) of **30**. Colourless crystals. M.p. 193–195°. IR (KBr): 3300, 2800, 1735, 1525, 1430, 1380, 1365, 1350, 1320, 1275, 1220, 1080, 985, 930, 840, 810, 790, 755. ^{1}H-NMR (MeOD, 250 MHz): 5.24 (*s*, H–C(1), H–C(5)); 3.84 (*s*, 2 MeO); 3.82 (*s*, H–C(2), H–C(4)); 3.56 (*s*, H–C(6), H–C(7)). ^{13}C-NMR (MeOD, 90.55 MHz): 171.6 (*s*, CO_2Me); 77.3 (*d*, ^1J(C,H) = 175, C(1), C(5)); 52.9 (*q*, ^1J(C,H) = 145, MeO); 50.0 (*d*, ^1J(C,H) = 130, C(6), C(7)); 35.7 (*d*, ^1J(C,H) = 200, C(2), C(4)). CI-MS (NH_3): 246 (4), 245 (19), 229 (23), 228 (100, $[M - BF_4]^+$), 170 (9), 168 (4), 138 (3), 84 (5), 83 (63), 80 (7). Anal. calc. for $C_{10}H_{14}BF_4NO_5$ (315.03): C 38.13, H 4.48, N 4.45; found: C 38.29, H 4.55, N 4.58.

17. *Dimethyl (1RS,2SR,6RS,7SR,8RS,9RS)-4-Phenyl-5,10-dioxa-3-azatricyclo[4.3.1.0^{2,7}]dec-3-ene-8,9-dicarboxylate* (**31**). A 70% $HClO_4$ soln. in H_2O (0.1 ml) was added to a soln. of **16** (50 mg, 0.15 mmol) in $CF_3CH(OH)CF_3$ (5 ml). After staying at 20° for 1 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with CH_2Cl_2 (10 ml, 4 times). After filtration (cotton), the solvent was evaporated and the residue recrystallized from Et_2O/CH_2Cl_2: 46 mg (94%). Colourless crystals. M.p. 188–189.5°. IR (KBr): 3060 , 3010, 2950, 1735, 1645, 1580, 1435, 1370, 1335, 1290, 1240, 1225, 1200, 1130, 1065, 1030, 990, 955, 935, 915, 890, 865, 840, 800, 780, 700. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.93–7.34 (*m*, arom. H); 6.29 (br. *s*, H–C(6)); 5.01 (br. *dd*, *J* = 2.0, H–C(1)); 3.80 (*dd*, *J* = 1.0, 2.0, H–C(2)); 3.76, 3.71 (2*s*, 2 MeO); 3.37, 3.29 (2*dd*, *J* = 12.0, 3.5, H–C(8), H–C(9)); 2.80 (br. *d*, *J* = 3.5, 2.0, H–C(7)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 171.2 (*s*, CO_2Me); 169.1 (*s*, CO_2Me); 157.1 (*s*, C(4)); 131.9 (*s*, C(arom.)); 131.3, 128.2, 127.5 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 98.2 (*d*, ^1J(C,H) = 170, C(6)); 88.8 (*d*, ^1J(C,H) = 170, C(1)); 60.6 (*d*, ^1J(C,H) = 155, C(2)); 52.2 (*q*, ^1J(C,H) = 145, MeO); 52.0 (*q*, ^1J(C,H) = 145, MeO); 47.0, 40.9 (2 *dd*, ^1J(C,H) = 135, C(8), C(9)); 39.7 (*d*, ^1J(C,H) = 150, C(7)). CI-MS (NH_3): 339 (19), 332 (100, $[M+1]^+$, 100), 331 (3), 302 (4), 230 (11), 229 (61), 159 (4), 158 (23), 139 (6), 106 (6), 105 (36), 91 (14), 81 (8), 77 (15). Anal. calc. for $C_{17}H_{17}NO_6$ (331.33): C 61.63, H 5.17, N 4.23; found: C 61.60, H 5.22, N 4.14.

18. *3-Ethyl 8,9-Dimethyl (1RS,2SR,6RS,7SR,8SR,9RS)-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene-3,8,9-tricarboxylate* (**41**). A mixture of **20** (7 g, 33 mmol), ethyl azidoformate (5 g, 43.5 mmol), and $NaHCO_3$ (1 g) in CH_2Cl_2 (10 ml) was stirred at 37° for 2 d in the dark. The mixture was poured into sat. aq. $NaHCO_3$ soln. (100 ml) and extracted with CH_2Cl_2 (50 ml, 5 times). After drying ($MgSO_4$), the solvent was evaporated and the residue recrystallized from Et_2O/CH_2Cl_2: 9.8 g (91%). Colourless crystals. M.p. 143–143.5°. IR (KBr): 3020, 2980, 2950, 1730, 1515, 1430, 1385, 1340, 1250, 1215, 1070, 1055, 1030, 1010, 970, 920, 810. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.24 (*s*, H–C(7)); 5.06 (*s*, H–C(1)); 4.93 (*d*, *J* = 8.0, H–C(6)); 4.41 (*q*, *J* = 7.0, CH_3CH_2O); 4.04 (*d*, *J* = 8.0, H–C(2)); 3.72, 3.70 (2*s*, 2 MeO); 3.16, 3.10 (2*d*, *J* = 10.0, H–C(8), H–C(9)); 1.41 (*t*, *J* = 7.0, CH_3CH_2O). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 169.8, 150.8 (2*s*); 87.1 (*d*, ^1J(C,H) = 155, C(7)); 81.5 (*d*, ^1J(C,H) = 165, C(1)); 81.1 (*d*, ^1J(C,H) = 165, C(6)); 63.5 (*t*, ^1JC,H) = 145, CH_3CH_2O); 57.5 (*q*, ^1J(C,H) = 145, 2 MeO); 52.5 (*d*, ^1J(C,H) = 160, C(2)); 48.7, 48.0 (2 *dd*, ^1J(C,H) = 135, C(8), C(9)); 14.4 (*q*, ^1J(C,H) = 125, CH_3CH_2O). CI-MS (NH_3): 345 (3), 317 (7), 301 (14), 300 (100, $[M - N_2]^+$), 240 (11), 211 (7), 156 (6), 126 (10). Anal. calc. for $C_{13}H_{17}N_3O_7$ (327.30): C 47.71, H 5.24, N 12.84; found: C 47.74, H 5.23, N 12.90.

19. *Dimethyl (1*RS,*3*RS,*4*SR,*5*RS,*6*RS,*7*SR*)-3-*exo-*Acetoxy-7-*syn-*[(ethoxycarbonyl)amino]-2-oxabicyclo-[2.2.1]heptane-5-*endo-*6-*endo-*dicarboxylate* (**42**). $CF_3SO_3SiMe_3$ (55 µl) was added dropwise to a stirred soln. of **41** (0.5 g, 1.5 mmol) in CH_2Cl_2/Ac_2O 10:1 (5.5 ml) cooled to $-10°$ for 90 min (end of N_2 evolution). The soln. was poured into sat. aq. $NaHCO_3$ soln. (20 ml) and extracted with CH_2Cl_2 (20 ml, 5 times). After filtration (cotton), the solvent was evaporated and the residue purified by column chromatography (silica gel, *Lobar B*, 20°, Et_2O). The major fraction (R_f 0.4, positive test with 2,4-dinitrophenylhydrazine) gave 483 mg (88%) of **42**. Recrystallization from Et_2O ($-20°$) yielded 377 mg (69%). Colourless crystals. M.p. 60–62°. IR ($CHCl_3$): 3340, 3020, 3000, 2950, 1745, 1710, 1515, 1435, 1360, 1340, 1270, 1230, 1165, 1090, 1015, 965, 925, 880, 835. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.62 (*s*, H–C(3)); 5.58 (br. *d*, *J* = 9.0, NH); 4.43 (*d*, *J* = 2.0, H–C(1)); 4.15 (*q*, *J* = 7.0, CH_3CH_2O); 4.02 (*d*, *J* = 9.0, H–C(7)); 3.73, 3.70 (2*s*, 2 MeO); 3.32 (*dd*, *J* = 2.0, 11.0, H–C(6)); 3.08 (*dd*, *J* = 3.5, 11.0, H–C(5)); 2.81 (*s*, *J* = 3.5, H–C(4)); 2.12 (*s*, AcO); 1.28 (*t*, CH_3CH_2O). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.3, 169.3 (2*s*, $2CO_2Me$); 168.3 (*s*, $MeCO$); 155.9 (*s*, NCO_2Et); 95.2 (*d*, ^1J(C,H) = 180, C(3)); 82.7 (*d*, ^1J(C,H) = 170, C(1)); 61.3 (*t*, ^1J(C,H) = 150, CH_3CH_2O); 57.2 (*d*, ^1J(C,H) = 150, C(7)); 52.3, 51.9 (2*q*, ^1J(C,H) = 150, MeO); 46.7 (*d*, ^1J(C,H) = 135, C(2)); 46.2 (*d*, ^1J(C,H) = 150, C(5)); 41.0 (*d*, ^1J(C,H) = 130, C(4)); 21.1 (*q*, ^1J(C,H) = 130, $MeCO$); 14.6 (*q*, ^1J(C,H) = 130, CH_3CH_2O). CI-MS (NH_3): 378 (11), 377 (46), 359 (0.6, M^+), 316 (6), 301 (15), 300 (100), 299 (12), 247 (87), 240 (6), 212 (6), 186 (86), 144 (9), 80 (5). Anal. calc. for $C_{15}H_{21}NO_9$ (359.34): C 50.14, H 5.98, N 3.90; found: C 50.18, H 5.91, N 3.94.

20. *3-(*tert-*Butyl) 8,9-Dimethyl (1*RS,*2*SR,*6*RS,*7*SR,*8*RS,*9*RS*)-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene-3,8,9-tricarboxylate* (**51**) *and 3-(*tert-*Butyl) 8,9-Dimethyl (1*RS,*2*SR,*6*RS,*7*SR,*8*SR,*9*SR*)-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene-3,8,9-tricarboxylate* (**52**). A mixture of **21** (8 g, 22.5 mmol), CH_2Cl_2 (12 ml), MeOH (36 ml), and 2-[(*tert*-butyl)imino]-2-(ethylamino)-1,3-dimethylperhydro-1,3,2λ^5-diazaphosphorinane on polystyrene (0.8 g; *Fluka* No. 20026) was stirred at 20° for 3 h. After filtration (cotton), the solvent was evaporated and the residue purified by FC (silica gel, Et_2O). The main fraction contained a mixture of **51** (R_f 0.81) and **52** (R_f 0.74). Crystallization from Et_2O/CH_2Cl_2 (20°) gave 2.5 g (31%) of pure **51**. The mother-liquor gave a second crop of 1.73 g (22%) of **51**. The remaining mother-liquor contained a 3:1 mixture **52**/**51**.

Data of **52**: ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.22 (*s*, H–C(7)); 4.99 (*d*, *J* = 5.5, H–C(1)); 4.88 (*d*, *J* = 8.0, H–C(6)); 4.00 (*d*, *J* = 8.0, H–C(2)); 3.78 (*s*, 2 MeO); 3.68 (*dd*, *J* = 5.5, 5.0, H–C(9)); 3.24 (*d*, *J* = 5.0, H–C(8)).

Data of **51**: Colourless crystals. M.p. 135–138°. UV (MeCN): 210 (1380), 220 (2340), 230 (4570), 240 (6800), 250 (5480), 260 (3170), 270 (1440), 280 (320). IR (KBr): 2980, 1710, 1710, 1510, 1440, 1390, 1370, 1340, 1310, 1295, 1265, 1230, 1210, 1190, 1140, 1105, 1025, 1005, 980, 940, 905, 780, 760, 695. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.10 (*d*, *J* = 5.5, H–C(7)); 5.04 (*s*, H–C(1)); 4.87 (*d*, *J* = 8.0, H–C(6)); 4.11 (*d*, *J* = 8.0, H–C(2)); 3.81, 3.75 (*s*, 2 MeO); 3.63 (*dd*, *J* = 5.5, 5.4, H–C(8)); 3.15 (*d*, *J* = 5.4, H–C(9)); 1.60 (*s*, *t*-Bu). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 171.0, 170.5 (2*s*, COOMe); 149.5 (*s*, Me_3COCO); 84.2 (*d*, ^1JC,H) = 155, C(7)); 84.0 (*s*, Me_3C); 83.7 (*d*, ^1J(C,H) = 170, C(1)); 80.3 (*d*, ^1J(C,H) = 165, C(6)); 57.7 (*d*, ^1J(C,H) = 155, C(2)); 52.8 (*q*, ^1J(C,H) = 145, 2 MeO); 48.4 (*d*, ^1J(C,H) = 140, C(8)); 47.4 (*d*, ^1J(C,H) = 135, C(9)); 28.2 (*q*, ^1J(C,H) = 125, Me_3C). CI-MS (NH_3): 356 (4, M^+), 328 (8), 290 (8), 289 (55), 273 (13), 272 (100), 229 (86), 228 (48), 168 (12), 83 (16). Anal. calc. for $C_{15}H_{21}N_3O_7$ (355.25): C 50.70, H 5.96, N 11.83; found: C 50.67, H 5.89, N 11.87.

21. *Methyl (1*RS,*2*RS,*3*SR,*6*RS,*7*SR,*9*RS*)-2-{[(*tert-*Butyloxy)carbonyl]}amino}-5-oxo-4,8-dioxatricyclo-[4.2.1.0^{3,7}]nonane-9-carboxylate* (**63**). 21.1. Crude **17** (from irradiation of **51**/**52** (see above; 200 mg, 1.5 mmol)) was dissolved in CH_2Cl_2 (4.8 ml). After addition of CF_3CO_2H (0.12 ml), the mixture was allowed to stand at 20° for 3 d. It was poured into sat. aq. $NaHCO_3$ soln. (20 ml) and extracted with CH_2Cl_2 (20 ml, 5 times). After filtration (cotton), the solvent was evaporated: 220 mg (70%) of impure **63** as yellowish oil. Recrystallization from Et_2O/CH_2Cl_2 gave 114 mg (43%).

21.2. $CF_3SO_3SiMe_3$ (0.2 ml) was added to a stirred mixture of **51** (2 g, 5.6 mmol), $CHCl_3$ (40 ml), and H_2O (4 ml). After stirring at 20° for 10 min, the mixture was poured into sat. aq. $NaHCO_3$ soln. (50 ml) and extracted with CH_2Cl_2 (50 ml, 5 times). The extracts were combined and filtered (cotton) and the solvent evaporated. The residue was recrystallized from Et_2O/CH_2Cl_2 (20°): 1.6 g (90%). Colourless crystals. M.p. 174–176°. IR (KBr): 3280, 3000, 2985, 2920, 1795, 1730, 1700, 1670, 1520, 1360, 1335, 1280, 1240, 1225, 1150, 1070, 1055, 1045, 960, 920, 875. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.35 (*dd*, *J* = 5.0, 4.9, H–C(7)); 4.89 (*s*, H–C(1)); 4.80 (br. *s*, NH); 4.54 (*d*, *J* = 5.0, H–C(3)); 3.96 (br. *d*, *J* = 8.0, H–C(2)); 3.79 (*s*, MeO); 3.36 (*dd*, *J* = 4.9,2.0, H–C(6)); 3.09 (*d*, *J* = 2.0, H–C(9)); 1.48 (*s*, *t*-Bu). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 174.3, 169.2, 154.4 (3*s*); 84.4, 84.0 (2*d*, ^1J(C,H) = 170, C(1), C(7)); 80.7 (*s*); 80.7 (*d*, ^1J(C,H) = 165, C(3)); 58.9 (*d*, ^1J(C,H) = 150, C(2)); 53.1 (*q*, ^1J(C,H) = 145, MeO); 50.8 (*d*, ^1J(C,H) = 135, C(6)); 42.1 (*d*, ^1J(C,H) = 135, C(9)); 28.3 (*q*, ^1J(C,H) = 125, Me_2C). CI-MS (NH_3): 332 (18), 331 (100, $[M + NH_3]^+$), 314 (30), 313 (2, M^+), 275 (64), 274 (7), 258 (19), 257 (7), 214 (11), 213 (31), 181 (14), 169 (9), 112 (7). Anal. calc. for $C_{14}H_{19}NO_7$ (313.31): C 53.67, H 6.11, N 4.47; found: C 53.54, H 5.99, N 4.57.

22. *Dimethyl (1RS,2SR,6RS,7SR,8SR9SR)-* (**53**) *and (1RS,2SR,6RS,7SR,8SR,9SR)-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-dicarboxylate* (**54**). A mixture of **41** (29 g, 88.7 mmol), anh. CH_2Cl_2 (37 ml), anh. MeOH (74 ml), and anh. K_2CO_3 (14.5 g) was stirred at 20° for 2 h. The org. layer was washed with sat. aq. $NaHCO_3$ soln. The aq. layers were combined and extracted with CH_2Cl_2 (100 ml, 5 times). The org. extracts were combined, filtered (cotton), and the solvent evaporated. The residue was recrystallized from CH_2Cl_2/petroleum ether (20°): 15.1 g (67%). Colourless crystals. M.p. 126–127° (dec.). UV (MeCN): 210 (790), 220 (2340), 230 (4570), 240 (6800), 250 (5630), 260 (3300), 270 (1300), 280 (320). IR (KBr): 3050, 3330, 3010, 2950, 2840, 1730, 1500, 1435, 1385, 1300, 1280, 1250, 1220, 1180, 1155, 1010, 995, 910, 885, 810, 780. ^{1}H-NMR ($CDCl_3$, 360 MHz; primed numbering for minor isomer **54**): 7.98 (br. *d*, *J* = 2.0, 0.6 H, H–N(5)); 7.90 (br. *d*, 0.4 H, *J* = 2.0, H–N(5′)); 5.14 (*s*, 0.4 H, H–C(1′)); 5.04 (*d*, *J* = 5.4, 0.6 H, H–C(1)); 4.89 (*d*, *J* = 9.0, 0.4 H, H–C(2′)); 4.76 (*s*, 0.6 H, H–C(7)); 4.75 (*d*, *J* = 9.0, 0.6 H, H–C(2)); 4.65 (*d*, *J* = 5.4, 0.4 H, H–C(7′)); 3.86 (*dd*, *J* = 9.0, 0.4 H, 2.0, H–C(6′)); 3.81 (*s*, 1.8 H, MeO); 3.77 (*dd*, *J* = 9.0, 2.0, 0.6 H, H–C(6)); 3.77, 3.76 (2*s*, 1.2 H, 2 MeO); 3.74 (*s*, 1.8 H, MeO); 3.60 (*dd*, *J* = 5.5, 5.4, 0.6 H, H–C(9)); 3.57 (*dd*, *J* = 5.5, 5.4, 0.4 H, H–C(8′)); 3.22 (*d*, *J* = 5.0, 0.4 H, H–C(9′)); 3.13 (*d*, *J* = 5.0, 0.6 H, H–C(8)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 171.3, 170.7 (2*s*); 85.7 (*d*, ^1J(C,H) = 155, C(1), (C′)); 83.5 (*d*, ^1J(C,H) = 170, C(7′)); 82.9 (*d*, ^1J(C,H) = 155, C(7)); 82.4 (*d*, ^1J(C,H) = 170, C(2′)); 80.6 (*d*, ^1J(C,H) = 165, C(2)); 58.2 (*d*, ^1J(C,H) = 155, C(6)); 55.7 (*d*, ^1J(C, H) = 153, C(6′)); 52.7 (*q*, ^1J(C,H) = 145, MeO); 48.9 (*d*, ^1J(C,H) = 140, C(9)); 48.7 (*d*, ^1J = (C,H) = 140, (C(9′)); 48.3 (*d*, ^1J(C,H) = 135, C(8′)); 47.7 (*d*, ^1J(C,H) = 135, C(8)). CI-MS (NH_3): 256 (8, $M^{+\cdot}$), 230 (6), 229(12), 228 (100), 196 (9), 158 (9), 138 (5), 83 (20). Anal. calc. for $C_{10}H_{13}N_3O_5$ (255.23): C 47.06, H 5.13, N 16.44; found: C 47.16, H 5.13, N 16.47.

23. *Methyl (1RS,2RS,3SR,6RS,7SR,9RS)-2-(Benzoylamino)-5-oxo-4,8-dioxatricyclo[4.2.1.0^{3,7}]nonane-9-carboxylate* (**64**). A 30% soln. of HBr in AcOH (0.1 ml) and H_2O (200 µl) was added dropwise to a stirred soln. of **19** (100 mg, 0.30 mmol) in anh. CH_2Cl_2 (2 ml). After stirring at 20° for 1 d (→ precipitate), the mixture was poured into sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with CH_2Cl_2 (10 ml, 5 times). The solvent was evaporated and the residue recrystallized from CH_2Cl_2/EtOH (20°): 62 mg (65%). Colourless crystals. M.p. 205–206°. IR (KBr): 3370, 3020, 2960, 1770, 1730, 1630, 1575, 1520, 1485, 1440, 1385, 1345, 1290, 1265, 1235, 1190, 1160, 1080, 1045, 1030, 1015, 1005, 930, 875, 835, 800, 710. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.79–7.45 (*m*, arom. H); 6.32 (br. *d*, *J* = 8.0, NH); 5.42 (*dd*, *J* = 5.0, 4.9, H–C(7)); 5.01 (*s*, H–C(1)); 4.66 (*d*, *J* = 5.0, H–C(3)); 4.49 (*d*, *J* = 8.0, H–C(2)); 3.80 (*s*, MeO); 3.40 (*dd*, *J* = 4.9, 2.0, H–C(6)); 3.20 (*d*, *J* = 2.0, H–C(9)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 174.2, 169.1, 166.7 (3*s*, 3 CO); 133.4 (*s*, C(arom.)); 132.2 (*d*, ^1J(C,H) = 160, CH(arom.)); 128,8, 127,1 (2*d*, ^1J(C,H) = 155, 2 CH(arom.)); 84.2 (*d*, ^1J(C,H) = 165, C(7)); 84.0 (*d*, ^1J(C,H) = 165, C(1)); 80.9 (*d*, ^1J(C,H) = 170, C(3)); 57.9 (*d*, ^1J(C,H) = 150, C(2)); 53.2 (*q*, ^1J(C,H) = 150, MeOH); 50.9 (*d*, ^1J(C,H) = 135, C(6)); 42.1 (*d*, ^1J(C,H) = 160, C(9)). CI-MS (NH_3): 335 (24), 332 (15), 319 (17), 318 (100, $[M + 1]^+$), 317 (9, M^+), 212 (7), 106 (7), 105 (77), 94 (7), 83 (5), 78 (5), 77 (13). Anal. calc. for $C_{16}H_{15}NO_6$ (317.30): C 60.57, H 4.77, N 4.41; found: C 60.66, H 4.70, N 4.49.

24. *Dimethyl (1RS,2SR,6SR,7SR,8SR,9SR)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-ene-8,9-dicarboxylate* (**65**). A $CF_3CH(OH)CF_3$ soln. (250 µl) 0.25M in CF_3SO_3H and 0.25M in $(CF_3SO_2)O$ was added to a soln. of **19** (250 mg, 1.51 mmol) in anh. $CF_3CH(OH)CF_3$ (25 ml). After stirring at 20° for 24 h, CH_2Cl_2 (25 ml) was added and the mixture poured into sat aq. $NaHCO_3$ soln. (25 ml) and extracted with CH_2Cl_2 (25 ml, 4 times). After filtration (cotton), the solvent was evaporated. The residue (*ca.* 100% **65** by 360 MHz ^{1}H-NMR) was recrystallized from Et_2O/CH_2Cl_2 (20°): 383 mg (77%). Colourless crystals. M.p. 158.5–160.5°. IR (KBr): 3450, 3370, 3060, 3005, 2960, 2850, 1735, 1645, 1580, 1495, 1450, 1360, 1295, 1265, 1250, 1215, 1185, 1155, 1085, 1065, 1025, 1005, 980, 940, 925, 910, 890, 880, 870, 855, 815, 785, 770, 705, 685, 670. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.92–7.38 (*m*, arom. H); 4.91 (*d*, *J* = 5.0, H–C(1)); 4.90 (*s*, H–C(7)); 4.78 (*d*, *J* = 6.5, H–C(2)); 4.58 (*d*, *J* = 6.5, H–C(6)); 3.81, 3.76 (2*s*, 2 MeO); 3.62 (*dd*, *J* = 4.9, H–C(9)); 3.19 (*d*, *J* = 4.9, H–C(8)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 171.6, 170.6, 165.9 (3*s*); 131.6, 128.5, 128.3 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 126.9 (*s*, C(arom.)); 84.3 (*d*, ^1J(C,H) = 165, C(1)); 81.4 (*d*, ^1J(C,H) = 165, C(7)); 81.1 ^1J(*d*, (C,H) = 165, C(2)); 72.3 (*d*, ^1J(C,H) = 155, C(6)); 52.6 (*q*, ^1J(C,H) = 145, MeO); 47.9 (*d*, ^1J(C,H) = 140, C(9)); 47.5 (*d*, ^1J(C,H) = 140, C(8)). CI-MS (NH_3): 333 (18), 332 (100, $[M + 1]^+$), 331 (5, M^+), 230 (13), 229 (56), 158 (8), 149 (7), 145 (6), 126 (6), 117 (5), 105 (51), 95 (6), 11 (12). Anal. calc. for $C_{17}H_{17}NO_6$ (331.33): C 61.63, H 5.17, N 4.23; found: C 61.59, H 5.10, N 4.34.

25. *Diethyl (1RS,2SR,4RS,5SR,6RS,7RS)-3-Benzoyl-8-oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**58**). Pyridine (1.78 ml, 22.2 mmol) was added to a soln. of **57** (3.45 g, 11.1 mmol; see below) in anh. CH_2Cl_2 (15 ml). The soln. was cooled to 0° and benzoyl chloride (3.1 g, 22.2 mmol) added slowly under stirring. After stirring at 20° for 24 h, the mixture was poured into 1N HCl (50 ml) and extracted with CH_2Cl_2 (30 ml, 5 times). The org. extracts were combined and washed with sat. aq. $NaHCO_3$ soln. (50 ml). After filtration (cotton), the solvent was evaporated and the residue purified by FC (silica gel, AcOEt/petroleum ether 1:2): 3.31 g (83%; R_f 0.33). Colourless crystals which could be recrystallized from CH_2Cl_2/Et_2O (20°). M.p. 95–96°. IR (KBr): 3050, 2980,

2940, 1735, 1720, 1675, 1600, 1580, 1475, 1450, 1370, 1335, 1290, 1270, 1185, 1110, 1060, 1045, 1025, 970, 945, 925, 870, 825, 810, 760, 725, 700. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.43–7.94 (*m*, arom. H); 4.72 (*s*, H–C(1)); 4.67 (*d*, *J* = 4.9, H–C(5)); 4.28–4.10 (*m*, CH_3CH_2O); 3.65 (*dd*, *J* = 4.9, 5.0, H–C(6)); 3.19 (*d*, *J* = 5.0, H–C(7)); 3.17 (*d*, *J* = 4.0, H–C(4)); 3.08 (*d*, *J* = 4.0, H–C(2)); 1.33, 1.26 (2*t*, *J* = 7.0, $2CH_3CH_2O$). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 176.2 (*s*, Ph*C*O); 170.8, 169.8, (2*s*, $2CO_2Et$); 133.3 (*s*, C(arom.)); 132.4, 128.5, 128.0 (3*d*, ^1J(C,H) = 160, CH(arom.)); 78.5 (*d*, ^1J(C,H) = 170, C(1)); 75.3 (*d*, ^1J(C,H) = 170, C(5)); 61.7 (*t*, ^1J(C,H) = 150, CH_3CH_2O); 50.7 (*d*, ^1J(C,H) = 140, C(4)); 48.6 (*d*, ^1J(C,H) = 135, C(2)); 37.9 (*d*, ^1J(C,H) = 150, C(6)); 36.3 (*d*, ^1J(C,H) = 150, C(7)); 14.2, 14.1 (2*q*, ^1J(C,H) = 125, 2 CH_3). CI-MS (NH_3): 362 (5), 361 (27), 360 (100, $[M+1]^+$), 359 (3, $M^{+\cdot}$), 187 (6), 106 (3), 105 (32), 77 (4). Anal. calc. for $C_{19}H_{21}NO_6$ (359.38): C 63.50, H 5.89, N 3.90; found: C 63.37, H 5.86, N 3.82.

26. *Dipropyl (1RS,2SR,4RS,5SR,6RS,7RS)-3-Benzoyl-8-oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**62**). Same procedure as for **58** starting with 3.14 g (11.1 mmol) of **61** (see below): 1.29 g (58%). Colourless crystals. M.p. 70–71.5°. IR (KBr): 3420, 3060, 3020, 2960, 2920, 2880, 1740, 1675, 1595, 1575, 1465, 1450, 1375, 1340, 1320, 1305, 1285, 1270, 1245, 1210, 1190, 1105, 1060, 1050, 1030, 980, 970, 940, 920, 860, 820, 805, 785, 755, 695, 630. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.93–7.42 (*m*, arom. H); 4.71 (*s*, H–C(1)); 4.64 (*d*, *J* = 4.9, H–C(5)); 4.14–4.03 (*m*, $CH_3CH_2CH_2O$); 3.65 (*dd*, *J* = 5.0, 4.9, H–C(6)); 3.17 (*d*, *J* = 5.0, H–C(7)); 3.16 (*d*, *J* = 4.0, H–C(4)); 3.08 (*d*, *J* = 4.0, H–C(2)); 1.71–1.60 (*m*, $CH_3CH_2CH_2O$); 0.97, 0.90 (2*t*, *J* = 7.0, $CH_3CH_2CH_2O$). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 176.3, 170.9, 169.9 (3*s*); 133.4 (*s*, C(arom.)); 132.3, 128.4, 128.0 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 78.4, 75.4, (2*d*, ^1J(C,H) = 170, C(1), C(5)); 67.2 (*t*, ^1J(C,H) = 150, CH_2O); 50.9, 48.7 (2*d*, ^1J(C,H) = 140, C(6), C(7)); 37.8, 36.4 (2*d*, ^1J(C,H) = 195, C(2), C(4)); 21.9, 21.8 (2*t*, ^1J(C,H) = 130, CH_2); 10.3 (*q*, ^1J(C,H) = 130, 2 CH_3). CI-MS (NH_3): 390 (5), 389 (26), 388 (100, $[M+1]^+$), 387 (6, $M^{+\cdot}$), 187 (11), 178 (3), 106 (4), 105 (56), 94 (2), 77 (5). Anal. calc. for $C_{21}H_{25}NO_6$ (387.44): C 65.10, H 6.50, N 3.62; found: C 65.19, H 6.61, N 3.71.

27. *Ethyl (1RS,2RS,3SR,6RS,7SR,9RS)-2-(Benzoylamino)-5-oxo-4,8-dioxatricyclo[4.2.1.0^{3,7}]nonane-9-carboxylate* (**66**). At 0°, 30% HBr in AcOH (0.05 ml) was added to a stirred mixture of **58** (50 mg, 0.14 mmol) in CH_2Cl_2 (1 ml) and H_2O (0.1 ml). After stirring at 20° for 15 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with CH_2Cl_2 (15 ml, 5 times). The solvent was evaporated and the residue recrystallized from CH_2Cl_2/Et_2O (20°): 42 mg (91%). Colourless crystals. M.p. 187–189°. IR (KBr): 3370, 3060, 3020, 2980, 2960, 1770, 1635, 1600, 1570, 1520, 1480, 1460, 1445, 1380, 1345, 1320, 1285, 1260, 1230, 1210, 1180, 1155, 1095, 1075, 1045, 1035, 1005, 980, 940, 925, 900, 875, 850, 800, 755, 740, 710, 690. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.44–7.79 (*m*, arom. H); 6.35 (br. *d*, *J* = 8.5, NH); 5.41 (*dd*, *J* = 5.0, 4.9, H–C(7)); 4.99 (*s*, H–C(1)); 4.66 (*d*, *J* = 5.0 H–C(3)); 4.49 (*d*, *J* = 8.5, H–C(2)); 4.24 (*q*, *J* = 7.0, CH_3CH_2O); 3.40 (*dd*, *J* = 4.9, 1.5, H–C(6)); 3.18 (*d*, *J* = 1.5, H–C(9)); 1.31 (*t*, *J* = 7.0, CH_3CH_2O). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 174.3, 168.6, 166.7, 133.3 (4*s*); 132.2, 128.8, 127.1 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 84.2 (*d*, ^1J(C,H) = 170, C(8)); 84.1 (*d*, ^1J(C,H) = 170, C(6)); 80.9 (*d*, ^1J(C,H) = 170, C(4)); 62.4 (*t*, ^1J(C,H) = 150, CH_3CH_2O); 58.0 (*d*, ^1J(C,H) = 150, C(5)); 51.0 (*d*, ^1J(C,H) = 140, C(1)); 42.0 (*d*, ^1J(C,H) = 155, C(9)); 14.1 (*q*, ^1J(C,H) = 125, CH_3CH_2O). CI-MS (NH_3): 350 (6), 349 (23), 334 (3), 333 (19), 332 (100, $M^{+\cdot}$), 287 (4), 226 (7), 187 (3), 105 (64), 77 (6). Anal. calc. for $C_{17}H_{17}NO_6$ (331.33): C 61.63, H 5.17, N 4.23; found: C 61.44, H 5.22, N 4.30.

28. *Diethyl (1RS,2SR,6SR,7SR,8SR,9SR)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-ene-8,9-dicarboxylate* (**67**). Same procedure as for **65** starting with 250 mg (0.096 mmol) of **58**. Purification by FC (silica gel, CH_2Cl_2/Et_2O 1:1; R_f 0.62): 226 mg (90%). Recrystallization from CH_2Cl_2/Et_2O (4°): 199 mg (80%). Colourless crystals. M.p. 125–127.5°. IR (KBr): 3040, 2990, 2900, 1730, 1645, 1605, 1580, 1495, 1475, 1450, 1380, 1360, 1325, 1310, 1295, 1280, 1245, 1205, 1180, 1115, 2065, 1025, 1010, 1010, 995, 930, 895, 860, 805, 780, 705, 695. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.32–7.92 (*m*, arom. H); 4.92 (*d*, *J* = 6.0, H–C(1)); 4.90 (*s*, H–C(7)); 4.79 (*d*, *J* = 7.0, H–C(2)); 4.60 (*d*, *J* = 7.0, H–C(6)); 4.28–4.14 (*m*, CH_3CH_2O); 3.62 (*dd*, *J* = 6.0, 5.5, H–C(9)); 3.18 (*d*, *J* = 5.5, H–C(8)); 1.33, 1.27 (2*t*, *J* = 7.0, 2 CH_3CH_2O). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 171.2, 170.2, 166.0 (3*s*); 131.7, 128.5, 128.3 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 126.9 (*s*, C(arom.)); 84.5, 81.5 (2*d*, ^1J(C, H) = 170, C(1), C(7)); 81.2 (*d*, ^1J(C,H) = 160, C(6)); 75.3 (*d*, ^1J(C,H) = 155, C(2)); 61.7, 61.6 (2*t*, ^1J(C,H) = 150, 2 CH_3CH_2O); 48.0 (*d*, ^1J(C,H) = 140, C(9)); 47.5 (*d*, ^1J(C,H) = 140, C(8)); 14.2, 14.1 (2*q*, ^1J(C,H) = 125, 2 CH_3CH_2O). CI-MS (NH_3): 362 (5), 361 (28), 360 (100, $[M+1]^+$), 359 (4, M^+), 244 (10), 243 (34), 158 (3), 146 (6), 145 (5), 105 (17), 77 (3). Anal. calc. for $C_{19}H_{21}NO_6$ (359.38): C 63.50, H 5.89, N 3.90; found: C 63.48, H 5.86, N 3.99.

Hydrochloride **67**·*HCl*. Gaseous HCl was bubbled through a soln. of **67** (10 mg) in anh. CH_2Cl_2 (1 ml) for 5 min. The solvent was evaporated. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.59–8.48 (*m*, arom. H); 5.56 (br. *s*, H–C(6)); 5.33

(*s*, H–C(7)); 5.08 (*d*, *J* = 6.0, H–C(1)); 4.96 (br. *s*, H–C(2)); 4.16–4.32 (*m*, 2 CH_3CH_2O); 3.74 (*dd*, *J* = 6.0, 5.0, H–C(9)); 3.13 (*d*, *J* = 5.0, H–C(8)); 1.27–1.37 (*m*, 2 CH_3CH_2O).

p-*Toluenesulfonate* **67** · *TsOH*. TsOH (13 mg, 0.07 mmol) was added to a soln. of **67** (25 mg, 0.07 mmol) in anh. CH_2Cl_2 (1 ml). The solvent was evaporated. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.15–8.17 (*m*, arom. H); 5.57 (*d*, *J* = 7.0, H–C(6)); 5.28 (*s*, H–C(7)); 5.05 (*d*, *J* = 7.0, H–C(2)); 5.04 (*d*, *J* = 5.0, H–C(1)); 4.17–4.28 (*m*, 2 CH_3CH_2O); 3.68 (*dd*, *J* = 5.5, 5.0, H–C(9)); 3.17 (*d*, *J* = 5.5, H–C(8)); 2.34 (*s*, Me); 1.25–1.34 (*m*, 2 CH_3CH_2O).

29. *Propyl (1*RS,*2*RS,*3*SR,*6*RS,*7*SR,*9*RS*)-2-(Benzoylamino)-5-oxo-4,8-dioxatricyclo[4.2.1.0^{3,7}]nonane-9-carboxylate* (**68**). Same procedure as for **66**, starting with 50 mg (0.078 mmol) of **62**. Crystallization from Et_2O/petroleum ether (4°): 42 mg (99%). Colourless crystals. M.p. 167–168°. IR (KBr): 3340, 3060, 2960, 2865, 1780, 1730, 1640, 1600, 1575, 1520, 1480, 1440, 1420, 1280, 1255, 1170, 1060, 1040, 1025, 1015, 970, 910, 875, 810, 795, 775, 750, 715, 690. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.31–7.79 (*m*, arom. H); 6.33 (br. *d*, *J* = 8.0, NH); 5.42 (*d*, *J* = 5.0, 4.9, H–C(7)); 4.99 (*s*, H–C(1)); 4.67 (*d*, *J* = 5.0, H–C(3)); 4.50 (*d*, *J* = 8.0, H–C(2)); 4.16 (*q*, *J* = 6.5, $CH_3CH_2CH_2O$); 3.42 (*dd*, *J* = 4.9, 2.0, H–C(6)); 3.20 (*d*, *J* = 2.0, H–C(9)); 1.70 (*m*, $CH_3CH_2CH_2O$); 0.97 (*t*, *J* = 7.5, $CH_3CH_2CH_2O$). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 174.4, 168.7, 166.7, 133.3 (4*s*); 132.1, 128.7, 127.1 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 84.2 (*d*, ^1J(C,H) = 170, C(8)); 84.0 (*d*, ^1J(C,H) = 170, C(6)); 80.8 (*d*, ^1J(C,H) = 170, C(4)); 67.9 (*t*, ^1J(C,H) = 150, $CH_3CH_2CH_2O$); 58.0 (*d*, ^1J(C,H) = 150, C(5)); 52.0 (*d*, ^1J(C,H) = 140, C(1)); 42.1 (*d*, ^1J(C,H) = 155, C(9)); 21.8 (*t*, ^1J(C,H) = 125, $CH_3CH_2CH_2O$); 10.25, (*q*, ^1J(C,H) = 125, $CH_3CH_2CH_2O$). CI-MS (NH_3): 364 (7), 363 (25), 347 (23), 346 (100), 345 (11, [*M* + NH_3]$^+$), 301 (5), 105 (19), 94 (5), 77 (8). Anal. calc. for $C_{18}H_{19}NO_5$ (329.36): C 65.64, H 5.81, N 4.25; found: C 62.39, H 5.52, N 4.26.

30. *Dipropyl (1*RS,*2*SR,*6*SR,*7*SR,*8*SR,*9*SR*)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-ene-8,9-dicarboxylate* (**69**). Same procedure as for **67**, starting with 300 mg (0.275 mmol) of **62**. Purification by FC (silica gel, CH_2Cl_2/Et_2O 1:1; R_f 0.34): 291 mg (98%). Recrystallization from Et_2O/petroleum ether (4°): 258 mg (86%). Colourless crystals. M.p. 73–76.5°. IR (KBr): 3030, 3015, 2960, 2870, 1725, 1645, 1600, 1575, 1490, 1450, 1390, 1355, 1320, 1240, 1220, 1185, 1085, 1060, 1040, 1020, 1000, 990, 960, 925, 895, 860, 810, 775, 750, 700, 660, 635. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.37–7.93 (*m*, arom. H); 4.91 (*d*, *J* = 4.9, H–C(1)); 4.90 (*s*, H–C(7)); 4.73 (*d*, *J* = 7.0, H–C(2)); 4.59 (*d*, *J* = 7.0, H–C(6)); 4.18–4.05 (*m*, $CH_3CH_2CH_2O$); 3.64 (*dd*, *J* = 5.0, 4.9, H–C(9)); 3.19 (*d*, *J* = 5.0, H–C(8)); 1.80–1.62 (*m*, $CH_3CH_2CH_2O$); 1.07, 0.96 (2*t*, *J* = 7.5, 2 $CH_3CH_2CH_2O$). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 171.3, 170.3, 166.0 (3*s*); 131.7, 128.5, 128.3 (3*d*, ^1J(C,H) = 160, 3 CH(arom.)); 126.9 (*s*, C(arom.)); 84.4 (*d*, ^1J(C,H) = 170, C(1)); 81.4 (*d*, ^1J(C,H) = 160, C(7)); 81.2 (*d*, *J*(C,H) = 170, C(2)); 75.3 (*d*, *J*(C,H) = 150, C(6)); 67.2 (*t*, ^1J(C, H) = 150, $CH_3CH_2CH_2O$); 48.0 (*d*, ^1J(C,H) = 140, C(9)); 47.5 (*d*, ^1J(C,H) = 140, C(8)); 21.9 (*t*, ^1J(C,H) = 125, $CH_3CH_2CH_2O$); 10.3 (*q*, ^1J(C,H) = 125, $CH_3CH_2CH_2O$). CI-MS (NH_3): 390 (5), 389 (26), 388 (100, [*M* + 1]$^+$), 387 (4, *M*$^+$), 258 (7), 257 (26), 159 (3), 158 (4), 146 (4), 145 (4), 105 (13). Anal. calc. for $C_{21}H_{25}NO_6$ (387.44): C 65.10, H 6.50, N 3.62; found: C 65.15, H 6.42, N 3.44.

31. *Diethyl (1*RS,*2*SR,*6*RS,*7*SR,*8*SR,*9*SR*)- (**55**) *and (1*RS,*2*SR,*6*RS,*7*SR,*8*RS,*9*RS*)-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-dicarboxylate* (**56**). Anh. K_2CO_3 (2 g) was added to a stirred soln. of **41** (4 g, 12.2 mmol) in anh. EtOH (40 ml). After stirring at 20° for 4 h, CH_2Cl_2 (30 ml) was added and the mixture filtered. The soln. was poured into sat. aq. $NaHCO_3$ soln. (50 ml) and extracted with CH_2Cl_2 (50 ml, 5 times). The solvent was evaporated and the residue purified by FC (silica gel, AcOEt/petroleum ether 2:1): 3.13 g (90%). Colourless oil. ^{1}H-NMR ($CDCl_3$, 250 MHz; primed numbering for minor isomer **56**): 7.91 (br. *d*, *J* = 2.0, 0.6 H, H–N(5)); 7.82 (br. *d*, *J* = 2.0, 0.4 H, H–N(5′)); 5.13 (*s*, 0.4 H, H–C(1′)); 5.05 (*d*, *J* = 5.5, 0.6 H, H–C(1)); 4.90 (*d*, *J* = 9.0, 0.4 H, H–C(2′)); 4.77 (*d*, *J* = 9.0, 0.6 H, H–C(2)); 4.76 (*s*, 0.6 H, H–C(7)); 4.65 (*d*, *J* = 5.4, 0.4 H, H–C(7′)); 4.30–4.09 (*m*, 4.0 H, CH_3CH_2O); 3.87 (*dd*, *J* = 2.0, 9.0, 0.6 H, H–C(6)); 3.78 (*dd*, *J* = 2.0, 9.0, 0.4 H, H–C(6′)); 3.60 (*dd*, *J* = 5.5, 5.4, 0.6 H, H–C(9)); 3.57 (*dd*, *J* = 5.5, 5.4, 0.4 H, H–C(8′)); 3.21 (*d*, *J* = 5.5, 0.4 H, H–C(9′)); 3.12 (*d*, *J* = 5.5, 0.6 H, H–C(8)); 1.39–1.25 (*m*, 6.0 H, CH_3CH_2O).

32. *Dipropyl (1*RS,*2*SR,*6*RS,*7*SR,*8*SR,*9*SR*)- (**59**) *and (1*RS,*2*SR,*6*RS,*7*SR,*8*RS,*9*RS*)-10-Oxa-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-dicarboxylate* (**60**). Same procedure as for **53**/**54**, starting with **41** (1 g, 3.0 mmol) anh. K_2CO_3 (0.5 g), and PrOH (10 ml): 790 mg (83%). Colourless oil. ^{1}H-NMR ($CDCl_3$, 250 MHz; primed numbering for minor isomer **60**): 8.16 (br. *d*, *J* = 1.0, 0.6 H, H–N(5)); 8.02 (br. *d*, *J* = 1.0, 0.4 H, H–N(5′)); 5.11 (*s*, 0.4 H, H–C(1′)); 5.01 (*d*, *J* = 6.0, 0.6 H, H–C(1)); 4.87 (*d*, *J* = 9.0, 0.4 H, H–C(2′)); 4.76 (*d*, *J* = 9.0, 0.6 H, H–C(2)); 4.74 (*s*, 0.6 H, H–C(7)); 4.65 (*d*, *J* = 5.4, 0.4 H, H–C(7′)); 4.17–4.05 (*m*, 4.0 H, $CH_3CH_2CH_2O$); 3.86 (*dd*, *J* = 2.0, 9.0, 0.6 H, H–C(6)); 3.78 (*dd*, 0.4 H, *J* = 2.0, 9.0, H–C(6′)); 3.60 (*dd*, 0.6 H, *J* = 5.5, 5.4, H–C(9)); 3.56 (*dd*, *J* = 5.5, 5.4, 0.4 H, H–C(8′)); 3.20 (*d*, *J* = 5.5, 0.4 H, H–C(9′)); 3.11 (*d*, *J* = 5.5, 0.6 H, H–C(8)); 1.61–1.76 (*m*, 4.0 H, $CH_3CH_2CH_2O$); 1.02–0.90 (*m*, 6.0 H, $CH_3CH_2CH_2O$).

33. *Diethyl (1*RS,*2*SR,*4*RS,*5*SR,*6*RS,*7*RS*)-8-Oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**57**). A soln. of **55**/**56** (3.13 g, 11.1 mmol) in acetone (150 ml) was irradiated in a quartz vessel (*Philips HPK* 125) at 0° under

Ar bubbling for 3 h. The solvent was evaporated: 2.76 g (98%). Colourless oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.64 (*s*, H–C(1)); 4.59 (*d*, *J* = 4.9, H–C(5)); 4.21 (*q*, *J* = 7.0, CH_3CH_2O); 4.20 (*q*, CH_3CH_2O); 3.63 (*dd*, *J* = 5.0, 4.9, H–C(6)); 3.13 (*d*, *J* = 5.0, H–C(7)); 2.27 (*d*, *J* = 4.0, H–C(4)); 2.18 (*d*, *J* = 4.0, H–C(2)); 1.31 (*t*, *J* = 7.0, CH_3CH_2O); 1.28 (*t*, *J* = 7.0, CH_3CH_2O).

34. *Dipropyl (1*RS,*2*SR,*4*RS,*5*SR,*6*RS,*7*RS*)-8-Oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate* (**61**). Same procedure as for **57**, starting with 3.45 g (11.1 mmol) of **59**/**60**: 3.08 g (98%). Colourless oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.64 (*s*, H–C(1)); 4.58 (*d*, *J* = 4.9, H–C(5)); 4.14–4.07 (*m*, $CH_3CH_2CH_2O$); 3.64 (*dd*, *J* = 5.0, 4.9, H–C(6)); 3.14 (*d*, *J* = 5.0, H–C(7)); 2.28 (*d*, *J* = 4.0, H–C(4)); 2.18 (*d*, *J* = 4.0, H–C(2)); 1.63–1.72 (*m*, $CH_3CH_2CH_2O$); 0.96, 0.94 (2*t*, *J* = 7.5, 2 $CH_3CH_2CH_2O$).

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