Inter- and Intramolecular [2+2]-Photocycloaddition of Tetronates – Stereoselectivity, Mechanism, Scope and Synthetic Applications

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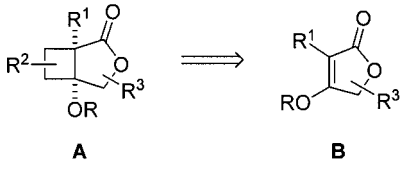
[2+2]-photocycloaddition reactions of various tetronates (**3**–**8**, **12**, **16**, **20**, **37**) have been examined. The tetronates were prepared from the corresponding tetronic acid by *O*-alkylation with an alkyl bromide or with an alcohol (Mitsunobu protocol). If the photocycloaddition reaction (λ = 254 nm, solvent: diethyl ether or *tert*-butyl alcohol) was carried out in an intramolecular fashion the tri- and tetracyclic products **21**–**23**, **27**–**36** were obtained in good yields (52–75%) and with excellent simple diastereoselectivity. The reaction tolerates a high degree of substitution at both the tetronate and at the alkene double bond. High facial diastereoselectivities were observed if stereogenic centers were present in the alkene tether (e.g. **7a** → **33**) or if the alkenyl substituent was attached to the stereogenic C5 carbon atom of the tetronate irradiation precursor (e.g. **20** → **32**). The reaction was also conducted in an intermolecular fashion. The methoxyethoxymethoxy (MEM) protecting group was suitable to protect the free tetronate hydroxy group. The photocycloaddition of tetronate **8** to cyclopentene was highly selective delivering the tricyclic products **39** in an 8:1 *exo*/*endo* ratio (59% yield). The products obtained from the intermolecular reaction underwent a de Mayo-like ring expansion delivering oxepane-diones **45**–**47** in good yields (74–84%). In mechanistic studies it was found that the formation of the photoproduct was supressed upon addition of piperylene. Furthermore, in the presence of acetone as a sensitizer the reaction could be conducted at λ = 300 nm. At this wavelength no conversion occurred under direct irradiation. These observations suggest the involvement of triplet intermediates in the reaction.

Introduction

The photochemical [2+2]-cycloaddition[1–4] of two alkene units is a highly useful reaction in organic synthesis since two new carbon–carbon bonds and up to four stereogenic centers are formed during this process. In the course of our studies towards the preparation of strained tetrahydrofurans by [2+2]-photocycloaddition we investigated the CuOTf-catalysed photocycloaddition of alkenes to enol ethers. Despite the fact that successful applications of this reaction are known,[5] we found that the lability of the enol ether moiety under the Lewis acidic reaction conditions accounts for a limited generality of this method. As a result of our efforts to circumvent this problem we have discovered the [2+2]-photocycloaddition of tetronates and alkenes under direct irradiation.[6] Although many suitable enone-type components for direct irradiation have been developed in the past,[1,3,7] no successful examples of tetronates in photocycloaddition reactions were known at this time.[8,9] In a recent program we investigated the preparation of a variety of bi-, tri- and tetracyclic heterocycles of general formula **A** from substituted tetronates **B** by inter- and intramolecular [2+2]-photocycloaddition reactions (Scheme 1).



Scheme 1. Tetronates **B** as precursors of oxygen-containing heterocycles of general formula **A**

In this paper, we report on the scope, mechanism and synthetic applicability of this reaction.

Results and Discussion

Preparation of the Substrates: The substrates employed in the [2+2]-photocycloaddition reactions were routinely prepared from the corresponding tetronic acids. Due to the inefficient photoreactions of tetronic acids in their unprotected form, the C4 hydroxy position had to be protected

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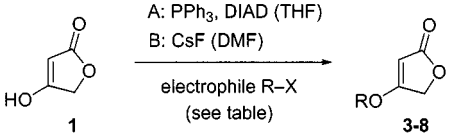
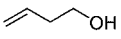
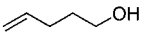
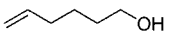
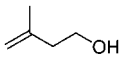
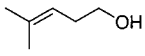
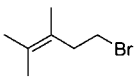
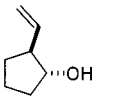
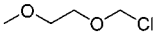
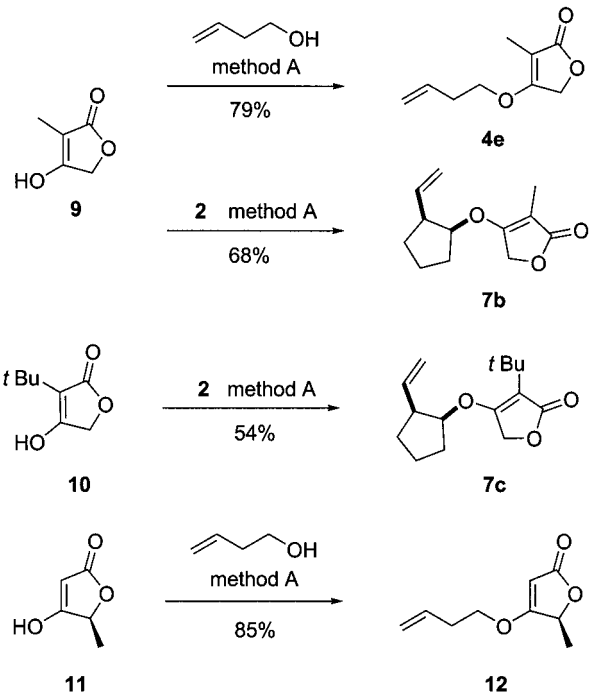
prior to the cycloaddition step. Although several methods are known to effect this transformation[10−13] we found two conditions sufficient to deliver all desired substrates. One method (method A) takes advantage of the relatively high acidity of tetronic acid [pK_a(H_2O) = 3.76][14] which allows to employ it as acidic component under Mitsunobu conditions (DIAD = diisopropyl diazenedicarboxylate).[12] Alternatively, cesium fluoride (CsF) in dimethylformamide (DMF) has been reported to be an efficient agent for the *O*-alkylation of tetronic acid (method B).[13] The substrates we have prepared via the described routes are summarized in Table 1.

Table 1. Preparation of *O*-substituted cycloaddition precursors from unsubstituted tetronic acid (**1**) by methods A and B



Entry	Method	Electrophile	Product	Yield
1	B		**3**	64%
2	A		**4a**	80%
3	A		**5**	85%
4	A		**6**	83%
5	A		**4b**	85%
6	A		**4c**	80%
7	B		**4d**	86%
8	A	 2	**7a**	77%
9	B		**8**	86%

While the parent tetronic acid (**1**) is a commercially available substance, its substituted derivatives had to be prepared. 3-Methyltetronic acid (**9**) was available from 2-methyl acetoacetate in a two-step one-pot procedure in 40% yield.[15] 3-*tert*-Butyltetronic acid (**10**) was prepared from tetronic acid (**1**) and *tert*-butyl alcohol under acidic conditions in 63% yield.[16] Enantiomerically pure (*S*)-(+)-5-methyltetronic acid (**11**) was obtained from (*S*)-(−)-ethyl lactate via a two-step procedure in an overall yield of 60%.[17] The tetronic acids were in turn used to synthesize



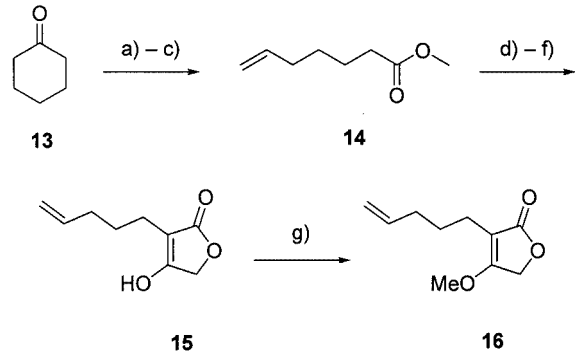
Scheme 2. Preparation of photocycloaddition precursors incorporating substituted tetronic acids **9**−**11**

the precursors **4e**, **7b**, **7c,** and **12** (Scheme 2) using the Mitsunobu protocol (method A). Except for compound **12** all chiral irradiation precursors were synthesized as racemates.

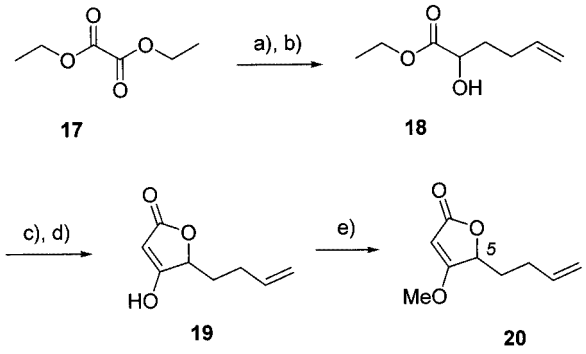
The substrates in which the alkene is attached to the tetronic acid core at C3 and C5 were accessible via short synthetic routes. In the former case (C3 substitution), methyl 6-oxohexanoate was prepared from cyclohexanone (**13**) following a procedure reported by Semple et al.[18] The aldehyde was transformed into the corresponding alkene (**14**) using standard Wittig conditions. Following a literature procedure reported for related compounds,[19] the tetronic acid core was subsequently installed by acylation with chloroacetyl chloride followed by base-assisted cyclization. The reaction sequence was not further optimized. The acid **15** obtained from this sequence was then converted into its methyl ester **16** by standard Mitsunobu chemistry (Scheme 3).

For the synthesis of the C5-substituted system, diethyl oxalate (**17**) was treated with homoallylmagnesium bromide at −78 °C to give the Grignard mono-addition product which was further reduced to the hydroxy ester **18**.[20] The hydroxy group was acetylated under standard conditions to give the corresponding acetate, which upon treatment with LiHMDS underwent a smooth Dieckmann condensation to give the tetronic acid **19** in 84% yield. Again, this compound was subsequently converted into its methyl ester **20** using standard Mitsunobu conditions (Scheme 4).

Irradiation Experiments: Intramolecular photocycloaddition reactions were carried out in dilute solutions (approx. 1 mM) using Et_2O or MeCN as standard solvents (irradiation source: Rayonet RPR-2537 Å). These conditions allowed for reaction times of less than one hour and re-



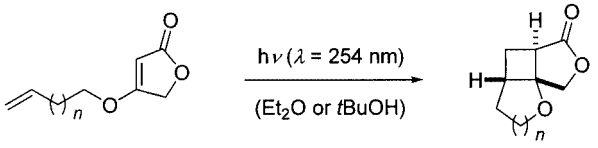
Scheme 3. Preparation of the C3-substituted methyl tetronate **16** from cyclohexanone (**13**): a) Ac_2O (neat), TSA, 60% b) O_3, MeOH, DMS, then HOAc/THF/H_2O (2:2:1), reflux, 48% c) $CH_3PPh_3^+I^-$, *n*BuLi in Et_2O, 46% d) TMS-Cl, LDA in THF e) $ClCH_2COCl$ in THF f) DBU in toluene then 1 M HCl, 27% from **14** g) MeOH, PPh_3, DIAD in THF, 92%



Scheme 4. Preparation of the C5-substituted methyl tetronate **20** from diethyl oxalate (**17**): a) C_4H_7MgBr in Et_2O, 83% b) $Na(CN)BH_3$ in EtOH/H_2O/HOAc, 7:3:1, 80% c) Ac_2O in py, 83% d) LiHMDS in THF, 84% e) MeOH, PPh_3, DIAD in THF, 94%.

sulted in clean conversions. In some cases it was favorable to use *tert*-butyl alcohol as a solvent to minimize side reactions caused by hydrogen abstraction from the solvent.

When the series of C4-substituted tetronates **4a**, **5** and **6** was subjected to the standard irradiation conditions we found that these substrates undergo an efficient photocycloaddition to give the desired tricyclic products. In the course of the reaction tetrahydrofuran **21**, tetrahydropyran **22**, and oxepane **23** were generated with the heterocyclic ring directly anellated to the cyclobutane unit (Scheme 5). As expected from literature precedence for related reactions,[3,21] the photocycloaddition proceeded exclusively to

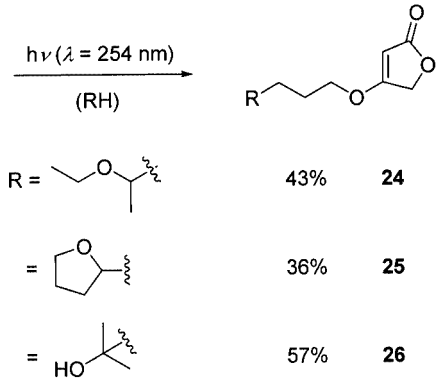


4a	*n* = 1	74%	**21**
5	*n* = 2	71%	**22**
6	*n* = 3	30%	**23**

Scheme 5. Formation of strained tetrahydrofurans, tetrahydropyrans and oxepanes by intramolecular [2+2]-PCA of tetronates **4a**, **5** and **6**

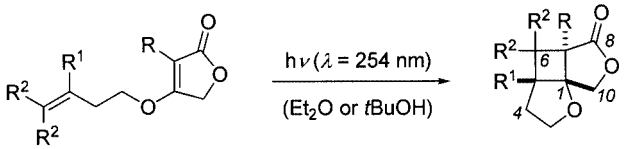
the straight photocycloaddition product. An indication for the formation of crossed photocycloaddition products was not found.

Starting from allyl tetronate **3** the formation of the straight photocycloaddition product was unlikely. The short chain connecting the reactive centers would in this reaction mode only allow for a highly strained oxa[2.2.0]hexane. The formation of the crossed cycloaddition product with an oxa[2.1.1]hexane core, however, was more likely and was therefore expected. Surprisingly, this product was not detected. Instead carbon radicals, which were generated from the solvent by hydrogen abstraction,[22] added to the terminal double bond to give the substituted tetronates **24**–**26** (Scheme 6). The hydrogen abstraction from isopropanol was most productive and gave the radical addition product in 57% yield.



Scheme 6. Products obtained from solvent addition to allyl tetronate (**3**) upon irradiation

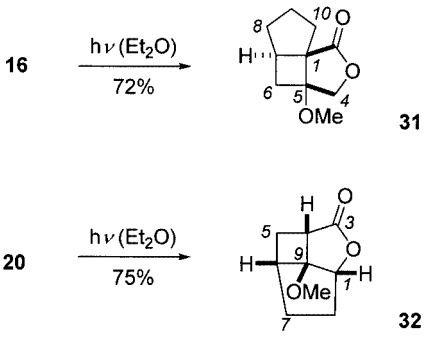
In a subsequent series of experiments we investigated the efficiency of the cycloaddition depending on the substitution pattern of appropriate 3-butenyl tetronate precursors (compounds **4**). The least substituted parent compound **4a** had given the photocycloaddition product **21** in 74% yield (Scheme 5). From the smooth formation of photoproducts **27**–**30** it can be concluded that the reaction is not sensitive towards the degree of substitution on either reactive center. Even the tetrasubstituted alkene **4d** underwent the [2+2]-photocycloaddition in 61% yield (Scheme 7). The simple diastereoselectivity was high in all cases, only one diastereoisomer was detected.



R = R² = H, R¹ = Me	**4b**	61%	**27**
R = R¹ = H, R² = Me	**4c**	52%	**28**
R = H, R¹ = R² = Me	**4d**	61%	**29**
R¹ = R² = H, R = Me	**4e**	76%	**30**

Scheme 7. Formation of substituted 2,9-dioxatricyclo[5.3.0^{1,5}]decanes **27**–**30** from tetronates **4b**–**4e**

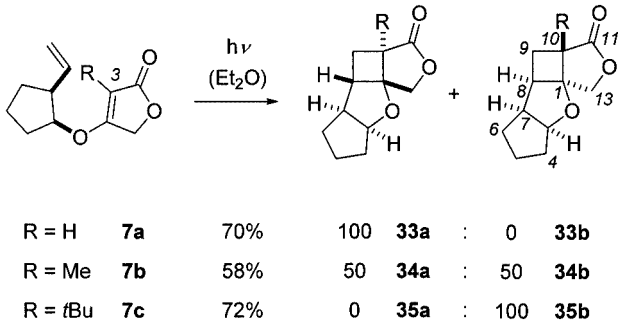
Irradiation of tetronates bearing the alkene tether attached to carbon atoms C3 (**16**) or C5 (**20**) of the tetronic acid core delivered the cycloaddition products **31** and **32** possessing the all-carbon [3.2.0]bicycloheptane backbone (Scheme 8). In both cases, diastereomerically pure compounds were isolated in good yields. The facial diastereoselectivity in the reaction of the 5-substituted tetronate **20** can be readily explained by an attack at the tetronate face to which the 3-butenyl chain is being directed by the stereogenic center at C5.



Scheme 8. Formation of tricyclic products **31** and **32** from C3-substituted tetronate **16** and C5-substituted tetronate **20**

In order to examine further the facial diastereoselectivity of the [2+2]-photocycloaddition, the substituted tetronate **7a**, bearing two stereocenters in the side chain, was prepared. The reaction would give access to the biologically relevant skeleton of the natural product *punctaporonin C*.[23] Upon irradiation, this compound, indeed, delivered a single product that was identified as compound **33a** (vide infra). In connection with a projected synthesis of the natural product we were also interested in the cycloaddition of the methyl-substituted analog **7b**. Again, under standard irradiation conditions, we observed a smooth conversion, but much to our surprise we found a 1:1 mixture of stereoisomers in the product. The structure of both compounds were elucidated by 2D NMR spectroscopy and were found to be the diastereomeric compounds **34a** and **34b**. Obviously, the course of the reaction is strongly influenced by the steric bulk of the C3 substituent of the tetronate. In order to verify this assumption we prepared compound **7c**, bearing a *tert*-butyl instead of the methyl group. Upon irradiation, this compound delivered one single cycloaddition product which was shown to be tetracycle **35b**. It appears to be possible to completely control the facial diastereoselectivity of these [2+2]-photocycloadditions by the size of the C3 substituent in the irradiation precursor (Scheme 9).

A preliminary explanation for the observed relative product configuration can be given on the basis of the relative size of the substituents at carbon atom C10 of the tetracyclic skeleton. In the *cis-anti-cis* products **33a**−**35a**, the eclipse of the rings anellated to the central tetrahydrofuran is avoided as the cyclopentane ring and the cyclobutane ring point to opposite directions. Inspection of molecular models show, however, that an unfavorable steric interaction can occur in these compounds due to the close proximity of the hydrogen atom H3 and the substituent at C10. The *cis-syn-cis* products (**33b**−**35b**) suffer from Pitzer (eclipsing) strain. The strain is particularly apparent at the C7-C8 bond where the two anellated ring bonds C7−C6 and C8−C9 are synperiplanar. Any interaction between H3 and the substituent at C10 is, however, avoided in these compounds (Figure 1).



Scheme 9. Investigation of the facial diastereoselectivity in the cycloaddition of tetronates **7a**−**7c**

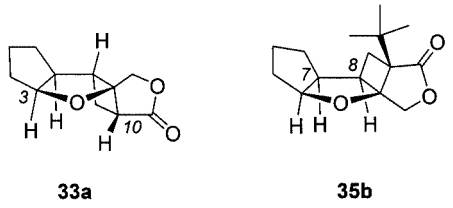
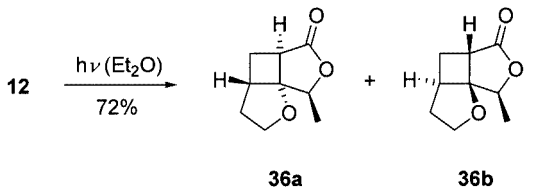


Figure 1. Stereochemical situation in the tetracyclic photocycloaddition products **33a** (*cis-anti-cis*-skeleton) and **35b** (*cis-syn-cis*-skeleton)

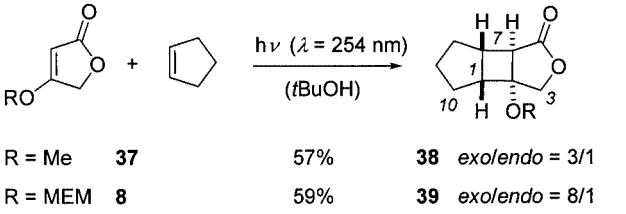
Under the premise that the steric interactions mentioned for compounds **33**−**35** are present in the transition states leading to the products (product control), it is apparent that **35b** is favored because the severe repulsion between the C10 *tert*-butyl group and hydrogen atom H3 is avoided while **33a** is preferred in the reaction of **7a** minimizing Pitzer strain at C7−C8. These arguments are in line with mechanistic proposals concerning the photocycloaddition (vide infra).

Efforts to control the facial diastereoselectivity by groups attached to the tetronate core proved to be less successful. Tetronate **12** was chosen because of its easy availability from literature known tetronic acid **11** and of the obvious charme of producing enantiomerically pure products. The photocycloaddition of compound **12** proceeded smoothly but without any differentiation of the diastereotopic faces to give a 1:1 mixture of the diastereoisomers **36a** and **36b** (Scheme 10). In comparison to literature known examples dealing with the stereocontrol exerted by γ-substituents of α,β-unsaturated carbonyl compounds in [2+2]-photocycloaddition reactions[24] this low degree of differentiation is somewhat surprising but not unprecedented.[8,9,25]



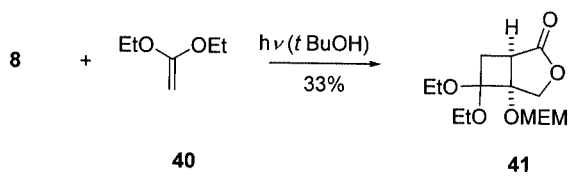
Scheme 10. Investigation of the facial diastereoselectivity in the cycloaddition of tetronate **12**

In order to extend tetronate photocycloadditions to intermolecular cycloadditions commercially available tetronate **37** was reacted with cyclopentene. After some optimization (concentration, solvent) the cycloaddition product **38** was obtained in greater than 50% yield and in an *exo*/*endo* ratio of 3:1. As already mentioned, the free tetronic acid reacted sluggishly. Still, it was desirable for consecutive reactions to have access to photocycloaddition products with a free hydroxy group at carbon atom C2. Following this consideration, the MEM protected tetronate **8** was subjected to the optimized irradiation conditions. The cycloaddition product **39** was obtained in yields similar to **38** and with an improved *exo*/*endo* selectivity (8:1, Scheme 11).



Scheme 11. Intermolecular cycloaddition of tetronates **8** and **37** and cyclopentene

In a series of experiments different alkenes as reaction partners were tested in the intramolecular [2+2]-photocycloaddition. It was found that the cyclopentene homologs cyclohexene and cyclooctene can be utilized giving the corresponding photoproducts in good yields. Electron rich olefins like the ketene diethylactetal **40** can also be employed giving bicyclic products such as **41** (Scheme 12). In this case the yield dropped, however, to 33%. Electron poor substrates (e.g. acrylonitrile, vinylcarbonate) did not give any of the expected photoproducts but unidentified side products accompanied by polymerization.



Scheme 12. Intermolecular cycloaddition of tetronate **8** and ketene diethyl acetal **40**

Proof of Configuration: Structural assignments were carried out on the basis of the structures of photoproducts **21** (Figure 2) and **33a** (Figure 3) that were unambiguously assigned by X-ray crystallographic analysis.[26]

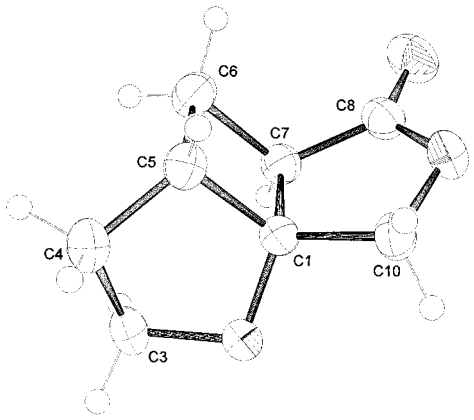


Figure 2. A molecule of 2,9-dioxatricyclo[5.3.0.0^{1,5}]decane (**21**) in the crystal

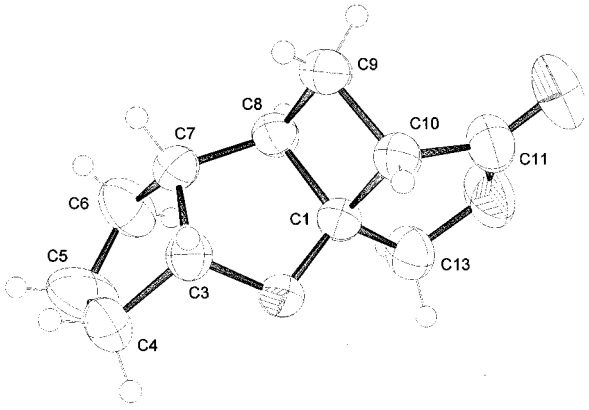
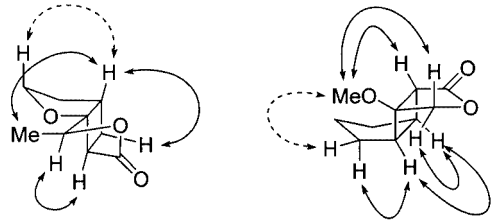


Figure 3. A molecule of 2,12-dioxatetracyclo[6.5.0.0^{3,7}.0^{1,10}]tridecan-11-one (**33a**) in the crystal

In addition to the structural assignment of compounds **21** and **33a** by X-ray diffraction, a set of 2D NMR experiments was carried out with these compounds. The NOESY contacts obtained from this study were used to assign the regio- and stereochemistry of the other cycloaddition products. The diagnostic contacts for the 2,9-dioxatricyclo[5.3.0.0^{1,5}] skeleton, as derived from compound **21**, were found between the protons at C5 and C10 (strong) as well as between the protons at C3 and C7 (strong). The structural assignments of photocycloaddition products **21**−**23** and **27**−**30** rest on these observations. The carbocyclic systems **31** and **32** were also unambiguously assigned by 2D NMR spectroscopy.

To distinguish between the two possible diastereoisomers in compounds **33**−**36** and **38**−**39** data obtained from NOESY experiments of compound **33a** were taken for comparison. According to the acquired data strong through space interaction of the protons at C3 and C10 as well as C8 and C13 accounted for the *cis-anti-cis* diastereoisomers whereas strong contacts between the protons connected to C3 and C13, C7 and C8 and C8 and C13 were characteristic for the *cis-syn-cis* diastereoisomers. It is worth to note that

in the latter diastereoisomers the C10 substituent does not produce any NOE contact to any proton, which indicates that it is obviously in a sterically uncrowded position (cf. Figure 1). As an illustration the NOE data for two representative cycloaddition products, compounds **36a** and *exo*-**38**, are given in Figure 4 (--- = medium, − = strong).



36a **38** (*exo*)

Figure 4. Structural assignments of photocycloaddition products **36a** and **38** (*exo*) on the basis of NOESY experiments

Mechanistic Investigations: [2+2]-Photocycloadditions under direct irradiation are usually initiated by the absorption of a photon resulting in the excitation of the molecule into its S_1 singlet state. After fast ISC the molecule reaches its T_1 triplet excited state, the lifetime of which is usually sufficient to allow photocycloadditions to occur.[27] Upon reaction with an appropriate alkene the critical 1,4-biradical is formed followed by cyclization to the final product. However, the biradicals can also revert to the starting materials thus, depending on the different rate constants, producing the final product.[4] In order to find out if the tetronate [2+2]-photocycloaddition follows the described reaction mechanism we carried out the photocycloaddition **4a** to **21** in the presence of various amounts of piperylene [$E(T_1)$ = 240 kJ/mol for (*Z*)- and 247 kJ/mol for (*E*)-piperylene] which is known to be an efficient triplet quencher.[28] As can be deduced from Figure 5 the formation of the photoproduct under standard irradiation conditions is decreased by an increasing amount of quencher added. This result strongly suggests the participation of an excited triplet state in the examined reaction. Upon irradiation in a 0.5 M solution of piperylene in Et_2O as a solvent the product formation was completely supressed.

It was also possible to carry out the reaction under sensitized conditions. When a sample of **4a** was irradiated under standard conditions using a 300 nm (Rayonet RPR-3000 Å) or 350 nm (Rayonet RPR-3500 Å) light source no conversion was observed and the starting material was recovered unchanged after 6 h of irradiation. In the presence of acetone [$E(T_1)$ = 332 kJ/mol] as a sensitizer the photocycloaddition took place upon irradiation at 300 nm to give one single product which was shown to be identical with product **21** obtained by direct irradiation. This finding also supports the involvement of a triplet intermediate. When benzophenone [$E(T_1)$ = 287 kJ/mol] or acetophenone [$E(T_1)$ = 310 kJ/mol] were employed as sensitizers under the same conditions no reaction was observed. The T_1 energy for the examined tetronate **4a** can thereby be estimated to be 310 kJ/mol < $E(T_1)$ < 332 kJ/mol. For the intramolecular reactions to **21** and **27**−**35** the triplet pathway consequently involves the initial cyclization to a five-membered ring and the intermediate formation of a 1,4-biradical. The 1,4-biradical can close to the product or if steric factors prohibit this ring closure (cf. **7c** → **35**) it can revert to the starting material. The diastereoselectivity is consequently controlled by both reaction steps.

Synthetic Applications: Apart from the direct application of the polycyclic ringsystems generated by the photocycloadditions in synthesis the highly strained products are also suitable for further transformations. As already mentioned in our earlier communication[6] one of the obvious applications is the use of the generated β-hydroxy lactone moiety in a retro-aldol ring expansion. This reaction leads to bicyclic oxepanediones and represents an useful expansion of the de Mayo methodology[29] which is usually carried out with β-diketo compounds and cannot be conducted with β-keto esters. In order to highlight this methodology, a small series of cycloaddition-ring opening reactions was conducted. MEM-protected tetronate **8** was irradiated under standard conditions in the presence of cyclopentene, cyclohexene and *cis*-cyclooctene to the corresponding

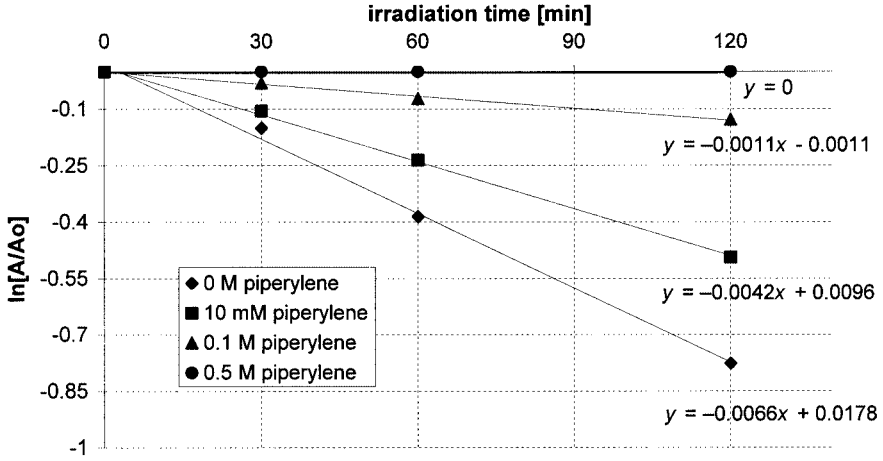
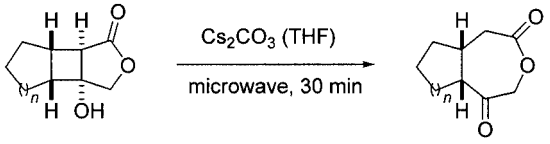


Figure 5. Quenching of the photocycloaddition of **4a** to **21** by various amounts of piperylene

cycloaddition products. These products were immediately deprotected with $TiCl_4$ in CH_2Cl_2 to give, after purification, the hydroxy lactones **42**−**44** in about 50% yield. For the five- and six-membered ring system one major product, the expected *exo* isomer, was isolated. In the cyclooctene case a 3:2:2:1 mixture of diastereoisomers (as determined by GC-MS) was obtained. Presumably, the reaction is not stereospecific for the larger ring and the four diastereoisomers are *cis*/*trans*-diastereoisomers of the *exo* and *endo* product. Compounds **42**−**44** were in turn submitted to Cs_2CO_3 in THF under microwave irradiation for 30 min and gave the ring-opened oxepane-diones **45**−**47** in good yields (Scheme 13).



n = 1	**42**	74%	**45**
n = 2	**43**	84%	**46**
n = 3	**44**	76%*	**47****

Scheme 13. Formation of oxepanediones **45**−**47** by retro aldol reaction of cycloaddition products **42**−**44** (* at 50% conversion based on recovered starting material; ** 1:1 diastereomeric mixture)

The stereochemistry remained unchanged in the course of this process. In the cyclohexene case prolonged reaction times or the use of stronger bases (NaH, LDA, KHMDS) sometimes produced epimerized products at the stereocenter adjacent to the newly formed carbonyl group. As expected, in the eight membered ring case the four diastereoisomers produced a mixture of only two ring-opened products in a ratio of 1:1.

Conclusion

In conclusion, the [2+2]-photocycloaddition of tetronates has been established as a useful addition to the synthetic methodology available to organic photochemists. The substrates involved are easily available or, in some cases, commercially available. The photocycloaddition step usually proceeds in good yields and excellent selectivity. It can be carried out in an intra- and an intermolecular fashion, tolerating various substitution patterns. The photocycloaddition can be conducted under direct irradiation (λ = 254 nm) or under sensitized conditions (λ = 300 nm, acetone as sensitizer) and is likely to proceed via the tetronate T_1 state. The reaction products obtained represent useful synthetic intermediates by themselves and can additionally be transformed into oxepane-diones by de Mayo-type retroaldol ring expansion.

Experimental Section

General: For general remarks, see ref..[30] All reactions involving sensitive chemicals were carried out under inert conditions using dried solvents. Microwave-assisted reactions were carried out in a microwave oven (CEM-corporation, model MarsX) using temperature controlled conditions. Irradiation experiments were conducted using dry solvents of spectroscopy grade quality (Merck Uvasol) that had been thoroughly degassed before use (exception: *tert*-butyl alcohol was of p.a. quality). Abbreviations: *n*-pentane (P), methanol (MeOH), ethanol (EtOH), ethyl acetate (EtOAc), tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM), *tert*-butyl alcohol (*t*BuOH), isopropanol (*i*PrOH), acetic acid anhydride (Ac_2O), methoxyethoxymethyl choride (MEM-Cl). Relevant literature known compounds: 5-Bromo-2,3-dimethylpent-2-ene,[31] **2**,[32] **3**,[13] **4a**,[11] **9**[15] **10**,[16] **11**,[17] **14**,[33] and **18**.[20] All other chemicals not mentioned in the following section were commercially available. Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically nonequivalent protons are marked as virtual (virt.).

5-(But-3-enyl)-4-hydroxyfuran-2(5*H*)-one (19): To a solution of ethyl-2-hydroxyhex-5-enoate (**18**, 1.60 g, 10.0 mmol) in pyridine (10 mL) was added Ac_2O (1.89 mL, 2.04 g, 20.0 mmol). The mixture was stirred at room temp. for 8 h and was then quenched by the addition of satd. NH_4Cl (30 mL). The mixture was extracted with EtOAc (3 × 30 mL) and the combined organic phases were washed with brine (20 mL) and then dried (Na_2SO_4). After filtration and evaporation of the solvent under reduced pressure crude ethyl 2-acetoxyhex-5-enoate (1.66 g, 8.30 mmol, 83%) was obtained as a yellow oil. This crude product was dissolved in THF (15 mL), cooled to −78 °C and then treated with a solution of LiHMDS (1 M in THF, 20.0 mL, 20.0 mmol). The resulting mixture was stirred at this temperature for 1 h and 2 M HCl (30 mL) was added. It was extracted with EtOAc (4 × 30 mL) and the combined organic layers were dried (Na_2SO_4). After filtration and evaporation of the solvent under reduced pressure crude 5-(but-3-enyl)-4-hydroxyfuran-2(5*H*)-one (**19**) was obtained as a yellow solid which was recrystallized from P/EtOAc to give the title compound as colorless, crystalline solid (1.07 g, 6.97 mmol, 84%, 70% from **18**). M.p. 55−56 °C; R_f = 0.40 (P/Et_2O, 1:1). ^1H NMR (360 MHz, [D_6]DMSO): δ = 1.50 (virt. quint, ^3J = ^2J = 7.2 Hz, 1 H), 1.87−1.97 (m, 1 H), 2.10 (virt. q, ^3J = ^2J = 7.2 Hz, 1 H), 4.80 (dd, ^3J = 4.1 Hz, 7.2 Hz, 1 H), 4.90 (s, 1 H), 5.00 (br. d, ^3J = 10.1 Hz, 1 H), 5.06 (br. d, ^3J = 18.0 Hz, 1 H), 5.84 (ddt, ^3J = 7.1 Hz, 10.1 Hz, 18.0 Hz, 1 H), 12.4−13.1 (br. s, 1 H, OH) ppm. ^{13}C NMR (90.6 MHz, [D_6]DMSO): δ = 28.1 (t), 30.5 (t), 77,6 (d), 87.9 (d), 115.5 (t), 137.4 (d), 173.0 (s), 181.8 (s) ppm. IR (KBr): $\tilde{\nu}$= 3387 (br. m , O−H), 2926 (s, C−H), 2690 (br. m), 1690 (vs, C=O), 1624 (vs), 1570 (vs), 1340 (m), 1290 (vs), 1174 (m), 1084 (m), 1023 (m), 996 (m), 930 (m), 912 (m), 814 (m). MS (70 eV, EI): *m*/*z* (%) =154 (1) [M^+], 136 (s), 126 (5), 112 (2), 100 (100), 83 (20), 72 (19), 69 (11), 55 (87). $C_8H_{10}O_3$ (154.16): calcd. C 62.33, H 6.54; found C 61.97, H 6.61.

4-Hydroxy-3-(pent-4-enyl)furan-2(5*H*)-one (15): This procedure was adapted from White et al.[19] To a solution of LDA (1 M in THF, 17.0 mL, 17.0 mmol) was added methyl hept-6-enoate (**14**, 2.40 g, 17.0 mmol) in a dropwise fashion and the mixture was stirred at this temperature for 1 h. During this period TMS-Cl (4.20 mL, 32.9 mol) was slowly added and the mixture was extracted with H_2O (2 × 20 mL). The remaining organic phase was dried (Na_2SO_4), filtered and the solvent was evaporated under reduced pressure to give a brown oil. The crude product was filtered through silica (P/EtOAc, 10:1, 100 mL) After evaporation of the solvent a yellow oil was obtained which was dissolved in toluene (40 mL). DBU (1.70 mL, 8.30 mmol) was added and the resulting brown mixture was stirred at room temp. for 18 h. MeOH (40 mL) and 1 M HCl (10

mL) were then added and the mixture was stirred for another 4 h. The volume was then reduced to ca. 5 mL and Et_2O (30 mL) and H_2O (5 mL) were added. The phases were separated and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was evaporated under reduced pressure. The remaining yellow oil was purified by column chromatography (silica, P/EtOAc, 1:1 as eluent) to yield the title compound **15** (0.76 g, 4.52 mmol, 27% from **14**) as colorless crystals. M.p. 89−94 °C; R_f = 0.80 (P/EtOAc, 1:1). ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.46 (virt. quint, ^3J = 7.7 Hz, 2 H), 2.00 (virt. q, ^3J = 7.7 Hz, 2 H), 2.08 (t, ^3J = 7.7 Hz, 2 H), 4.55 (s, 2 H), 4.93 (br. d, ^3J = 10.4 Hz, 1 H), 5.00 (br. d, ^3J = 16.7 Hz, 1 H), 5.75 (ddt, ^3J_d = 10.4 Hz, 16.7, ^3J_t = 7.7 Hz, 1 H), 11.71 (br. s, 1 H, OH) ppm. ^{13}C NMR (90.6 MHz, [D$_6$]DMSO): δ = 20.3 (t), 26.6 (t), 32.8 (t), 66.3 (t), 98.8 (s), 114.8 (t), 138.4 (d), 173.2 (s), 174.8 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3100 cm^{-1} (br. s, O−H), 3055 (C=C−H), 2939 (C−H), 1732 (vs, C=O), 1650 (vs,), 1442 (s), 1267 (s), 1097 (m), 1044 (s), 916 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (13) [M$^+$], 150 (8), 127 (10), 113 (92), 101 (75), 95 (48), 67 (100). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07859.

General Procedure for the Reaction of Tetronic Acids and Alcohols: To a solution of the tetronic acid (1.00 mmol), PPh_3 (262 mg, 1.00 mmol) and the alcohol (1.00 mmol) in 2.00 mL THF at room temp., DIAD (194 µL, 202 mg, 1.00 mmol) was added under vigorous stirring. The yellow mixture was stirred at this temperature for another 6 h. The solvent was then evaporated under reduced pressure and the remaining oil was purified by column chromatography to give the desired product.

4-(Pent-4-enyloxy)furan-2(5*H*)-one (5): Compound **5** was prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and 4-penten-1-ol (103 µL, 86.0 mg, 1.00 mmol) as pale yellow oil in a yield of 143 mg (0.85 mmol, 85%). R_f = 0.15 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.88 (quint, ^3J = 6.5 Hz, 2 H), 2.19 (virt. q, ^3J = 6.5 Hz, 2 H), 4.04 (t, ^3J = 6.5 Hz, 2 H), 4.62 (t, ^4J = 0.9 Hz, 2 H), 5.04 (br. d, ^3J = 10.2 Hz, 1 H), 5.06 (br. d, ^3J = 18.6 Hz, 1 H), 5.06 (t, ^4J = 0.9 Hz, 1 H), 5.80 (ddt, ^3J_d = 10.2 Hz, 18.6, ^3J_t = 6.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 27.5 (t), 29.6 (t), 67.8 (t), 72.0 (t), 88.8 (d), 116.0 (t), 136.7 (d), 173.5 (s), 179.3 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3120 (w, C=C−H), 3077 (w, C=C−H), 2943 (s, C−H), 1774 (vs, C=O), 1747 (vs), 1626 (vs), 1450 (m), 1371 (s), 1319 (s), 1238 (m), 1150 (vs), 1052 (vs), 980 (m), 882 (s), 803 (s). MS (70 eV, EI): *m*/*z* (%) = 168 (3) [M$^+$], 150 (2), 140 (10), 139 (14), 123 (12), 114 (42), 113 (43), 96 (12), 69 (100), 53 (24). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 63.96, H 7.14.

4-(Hex-5-enyloxy)furan-2(5*H*)-one (6): Compound **6** was prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and 5-hexen-1-ol (114 µL, 100 mg, 1.00 mmol) as pale yellow oil in a yield of 151 mg (0.83 mmol, 83%). R_f = 0.15 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.47−1.56 (m, 2 H), 1.72−1.82 (m, 2 H), 2.09 (virt. q, ^3J = 6.8 Hz, 2 H), 4.03 (t, ^3J = 6.8 Hz, 2 H), 4.60 (t, ^4J = 0.9 Hz, 2 H), 4.97 (br. d, ^3J = 10.2 Hz, 1 H), 5.01 (br. d, ^3J = 16.5 Hz, 1 H), 5.05 (t, ^4J = 0.9 Hz, 1 H), 5.78 (ddt, ^3J_d = 10.2 Hz, 16.5, ^3J_t = 6.8 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.8 (t), 27.8 (t), 33.0 (t), 67.8 (t), 72.7 (t), 88.7 (d), 115.2 (t), 137.8 (d), 173.5 (s), 179.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3120 (w, C=C−H), 3076 (w, C=C−H), 2940 (m, C−H), 1774 (vs, C=O), 1747 (vs), 1627 (vs), 1370 (m), 1319 (vs), 1239 (m), 1149 (s), 1052 (s), 882 (m), 802 (m). MS (70 eV, EI): *m*/*z* (%) = 182 (2) [M$^+$], 164 (1), 153 (8), 137 (3), 124 (2), 110 (4), 101 (4), 82 (9), 69 (35), 55 (100). $C_{10}H_{14}O_3$ (182.22): calcd. C 65.91, H 7.74; found C 65.85, H 7.81.

4-(3-Methylbut-3-enyloxy)furan-2(5*H*)-one (4b): Prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and 3-methyl-3-buten-1-ol (101 µL, 86.0 mg, 1.00 mmol) as pale yellow oil in a yield of 142 mg (0.85 mmol, 85%). R_f = 0.25 (P/DCM/EtOAc, 10:5:2). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.73 (s, 3 H), 2.44 (t, ^3J = 6.6 Hz, 2 H), 4.11 (t, ^3J = 6.6 Hz, 2 H), 4.57 (t, ^4J = 0.9 Hz, 2 H), 4.72 (s, 1 H), 4.81 (s, 1 H), 5.06 (s, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.3 (q), 36.1 (t), 67.7 (t), 70.8 (t), 88.7 (d), 112.8 (t), 140.4 (s), 173.3 (s), 179.2 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3120 (m, C=C−H), 2940 (m, C−H), 1774 (vs, C=O), 1748 (vs), 1628 (vs), 1367 (m), 1318 (s), 1236 (m), 1149 (s), 1054 (s), 972 (w), 884 (m). MS (70 eV, EI): *m*/*z* (%) =168 (1) [M$^+$], 140 (20), 123 (10), 96 (86), 69 (100), 53 (46). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 63.90, H 7.17.

4-(4-Methylpent-3-enyloxy)furan-2(5*H*)-one (4c): Prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and 4-methyl-3-penten-1-ol (116 µL, 100 mg, 1.00 mmol) as pale yellow oil in a yield of 146 mg (0.80 mmol, 80%). R_f = 0.25 (P/DCM/EtOAc, 10:5:2). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.60 (s, 3 H), 1.68 (s, 3 H), 2.42 (virt. q, ^3J = 7.0 Hz, 2 H), 3.96 (t, ^3J = 7.0 Hz, 2 H), 4.58 (t, ^4J = 0.9 Hz, 2 H), 5.03 (s, 1 H), 5.08 (tt, ^3J = 7.0, ^4J = 1.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 17.7 (q), 25.6 (q), 27.3 (t), 67.7 (t), 72.4 (t), 88.6 (d), 117.9 (s), 135.5 (d), 173.5 (s), 179.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3096 (m, C=C−H), 2934 (m, C−H), 1775 (vs, C=O), 1748 (vs), 1626 (vs), 1367 (m), 1317 (s), 1237 (m), 1149 (s), 1052 (s), 971 (w), 882 (w). MS (70 eV, EI): *m*/*z* (%) = 182 (2) [M$^+$], 167 (1), 154 (3), 138 (20), 123 (13), 110 (5), 82 (21), 69 (62), 55 (100). $C_{10}H_{14}O_3$ (182.22): calcd. C 65.91, H 7.74; found C 65.71, H 7.78.

4-(2-Vinylcyclopentanyloxy)furan-2(5*H*)-one (7a): Prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and *trans*-2-vinylcyclopentanol (**2**, 112 mg, 1.00 mmol) as colorless crystals in a yield of 150 mg (0.77 mmol, 77%). M.p. 87−89 °C; R_f = 0.15 (P/EtOAc, 8:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.61−2.08 (m, 6 H), 2.58−2.69 (m, 1 H), 4.53−4.62 (m, 3 H), 5.03 (t, ^4J = 1.0 Hz, 1 H), 5.08 (br. d, ^3J = 10.0 Hz, 1 H), 5.12 (br. d, ^3J = 18.3 Hz, 1 H), 5.84 (ddd, ^3J = 7.7 Hz, 10.0 Hz, 18.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.1 (t), 29.2 (t), 31.3 (t), 48.9 (d), 68.0 (t), 87.5 (d), 89.3 (d), 116.8 (t), 135.6 (d), 173.8 (s), 178.5 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3073 (w, C=C−H), 2976 (m, C−H), 1774 (vs, C=O), 1743 (vs), 1624 (vs), 1316 (s), 1235 (m), 1147 (s), 1050 (s), 926 (m), 800 (m). MS (70 eV, EI): *m*/*z* (%) = 194 (5) [M$^+$], 176 (3), 165 (5), 149 (8), 139 (11), 101 (14), 95 (75), 79 (100), 67 (70), 55 (18). $C_{11}H_{14}O_3$ (194.23): calcd. C 68.02, H 7.27; found C 67.83, H 6.90.

4-(But-3-enyloxy)-3-methylfuran-2(5*H*)-one (4e): Prepared from tetronic acid **9** (114 mg, 1.00 mmol) and 3-buten-1-ol (86.0 µL, 74.0 mg, 1.00 mmol) as pale yellow oil in a yield of 133 mg (0.79 mmol, 79%). R_f = 0.15 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.77 (t, ^4J = 1.4 Hz, 3 H), 2.46 (virt. q, ^3J = 6.6 Hz, 2 H), 4.17 (t, ^3J = 6.6 Hz, 2 H), 4.58 (s, 2 H), 5.09 (br. d, ^3J = 9.3 Hz, 1 H), 5.13 (br. d, ^3J = 18.3 Hz, 1 H), 5.77 (ddt, ^3J_d = 18.3 Hz, 9.3, ^3J_t = 6.6 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.4 (q), 33.8 (t), 65.9 (t), 69.8 (t), 98.6 (s), 118.3 (t), 132.7 (d), 171.3 (s), 175.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3079 (w, C=C−H), 2958 (m, C−H), 2923 (m, C−H), 1755 (vs, C=O), 1677 (vs), 1409 (s), 1389 (s), 1326 (s), 1251 (s), 1129 (s), 1048 (s), 920 (m), 756 (s). MS (70 eV, EI): *m*/*z* (%) = 168 (3) [M$^+$], 150 (1), 139 (9), 144 (4), 96 (3), 83 (12), 69 (7), 55 (100). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07868.

3-Methyl-4-(2-vinylcyclopentanyloxy)furan-2(5*H*)-one (7b): Prepared from tetronic acid **9** (114 mg, 1.00 mmol) and *trans*-2-vinylcyclopentanol (**2**, 112 mg, 1.00 mmol) as colorless crystals in a yield

of 142 mg (0.68 mmol, 68%). M.p. 51−53 °C; R_f = 0.25 (P/EtOAc, 8:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.62−2.06 (m, 6 H), 1.79 (s, 3 H), 2.53−2.63 (m, 1 H), 4.58 (br. s, 2 H), 4.69 (virt. t, ^3J = 4.0 Hz, 1 H), 5.09 (br. d, ^3J = 10.0 Hz, 1 H), 5.13 (br. d, ^3J = 16.8 Hz, 1 H), 5.84 (ddd, ^3J = 7.8 Hz, 10.0 Hz, 16.8 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.42 (q), 22.2 (t), 29.5 (t), 33.2 (t), 49.8 (d), 66.3 (t), 85.0 (d), 98.5 (s), 117.0 (t), 136.2 (d), 171.1 (s), 175.6 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3081 (w, C=C−H), 2941 (m, C−H), 1775 (vs, C=O), 1743 (vs), 1627 (vs), 1368 (m), 1320 (s), 1238 (m), 1151 (s), 1053 (s), 972 (m), 919 (m), 884 (m), 803 (m). MS (70 eV, EI): *m*/*z* (%) = 208 (5) [M^+], 179 (3), 114 (6), 103 (4), 95 (100), 79 (16), 67 (45), 55 (16). HRMS calcd. for $C_{12}H_{16}O_3$ 208.10994, found 208.10985.

3-*tert*-Butyl-4-(2-vinylcyclopentanyloxy)furan-2(5*H*)-one (7c): Prepared from tetronic acid **10** (156 mg, 1.00 mmol) and *trans*-2-vinylcyclopentanol (**2**, 112 mg, 1.00 mmol) as colorless crystals in a yield of 135 mg (0.54 mmol, 54%). M.p. 60−61 °C; R_f = 0.25 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.27 (s, 9 H), 1.62−2.01 (m, 6 H), 2.52−2.62 (m, 1 H), 4.42 (virt. t, ^3J = 4.4 Hz, 1 H), 4.61 (br. s, 2 H), 5.10 (br. d, ^3J = 10.0 Hz, 1 H), 5.14 (br. d, ^3J = 18.3 Hz, 1 H), 5.84 (ddd, ^3J = 8.0 Hz, 10.0 Hz, 18.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.2 (t), 28.8 (q), 29.4 (t), 31.4 (s), 33.2 (t), 49.9 (d), 64.6 (t), 84.8 (d), 110.3 (d), 117.1 (t), 136.4 (d), 170.2 (s), 173.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3071 (w, C=C−H), 2983 (s, C−H), 1741 (vs, C=O), 1647 (s), 1374 (s), 1241 (s), 1047 (s), 846 (m). MS (70 eV, EI): *m*/*z* (%) = 250 (3) [M^+], 157 (10), 141 (12), 95 (100), 79 (16), 67 (75), 55 (17). $C_{15}H_{22}O_3$ (250.33): calcd. C 71.97, H 8.86; found C 71.87, H 9.15.

(*S*)-(+)-4-(But-3-enyloxy)-5-methylfuran-2(5*H*)-one (12): Prepared from tetronic acid **11** (114 mg, 1.00 mmol) and 3-buten-1-ol (86.0 µL, 74.0 mg, 1.00 mmol) as pale yellow oil in a yield of 143 mg (0.85 mmol, 85%). R_f = 0.20 (P/DCM/EtOAc, 10:2:1). $[\alpha]_D^{20}$ = −6.6 (*c* = 0.10, $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.44 (d, ^3J = 6.8 Hz, 3 H), 2.51 (virt. q, ^3J = 6.6 Hz, 2 H), 3.96−4.08 (m, 2 H), 4.80 (q, ^3J = 6.8 Hz, 1 H), 5.00 (s, 1 H), 5.13 (br. d, ^3J = 10.0 Hz, 1 H), 5.15 (br. d, ^3J = 17.2 Hz, 1 H), 5.79 (ddt, ^3J_d = 10.0 Hz, 17.2, ^3J_t = 6.6 Hz,1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 17.8 (q), 32.7 (t), 71.6 (d), 75.3 (t), 88.1 (d), 118.1 (t), 132.7 (d), 172.6 (s), 182.3 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3117 (w, C=C−H), 3080 (w, C=C−H), 2984 (s, C−H), 2936 (m, C−H), 1755 (vs, C=O), 1630 (vs), 1450 (s), 1359 (s), 1295 (s), 1237 (s), 1161 (s), 1086 (s), 1058 (w), 952 (s), 900 (w), 804 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (1) [M^+], 137 (2), 126 (13), 113 (3), 96 (5), 69 (46), 55 (100). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 64.03, H 7.07.

5-(But-3-enyl)-4-methoxyfuran-2(5*H*)-one (20): Prepared from tetronic acid **19** (154 mg, 1.00 mmol) and MeOH (40.5 µL, 32.2 mg, 1.00 mmol) as pale yellow oil in a yield of 156 mg (0.94 mmol, 94%). R_f = 0.30 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.70 (virt. quint, ^2J = ^3J = 7.4 Hz, 1 H), 1.92−2.03 (m, 1 H), 2.20 (virt. q, ^3J = 7.4 Hz, 2 H), 3.87 (s, 3 H), 4.76 (dd, ^3J = 3.5 Hz, 7.4 Hz, 1 H), 5.01 (br. d, ^3J = 10.1 Hz, 1 H), 5.06 (d, ^4J = 0.8 Hz, 1 H), 5.07 (br. d, ^3J = 17.6 Hz, 1 H), 5.77 (ddt, ^3J_d = 10.1 Hz, 17.6, ^3J_t = 7.4 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 28.4 (t), 31.0 (t), 59.3 (q), 78.0 (d), 88.7 (d), 115.9 (t), 136.7 (d), 172.4 (s), 182.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3119 (w, C=C−H), 3078 (w, C=C−H), 2980 (m, C−H), 2945 (m, C−H), 1747 (vs, C=O), 1633 (vs), 1446 (m), 1376 (s), 1307 (s), 1245 (s), 1158 (s), 949 (s). MS (70 eV, EI): *m*/*z* (%) = 168 (4) [M^+], 140 (2), 126 (13), 114 (100), 113 (72), 96 (10), 85 (68), 69 (70), 59 (25). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07863.

4-Methoxy-3-(pent-4-enyl)furan-2(5*H*)-one (16): Prepared from tetronic acid **15** (168 mg, 1.00 mmol) and MeOH (40.5 µL, 32.2 mg, 1.00 mmol) as pale yellow oil in a yield of 167 mg (0.92 mmol, 92%). R_f = 0.25 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.60 (quint, ^3J = 7.7 Hz, 2 H), 2.07 (virt. q, ^3J = 7.7 Hz, 2 H), 2.25 (t, ^3J = 7.7 Hz. 2 H), 3.93 (s, 3 H), 4.65 (s, 2 H), 4.95 (br. d, ^3J = 10.5 Hz, 1 H), 5.01 (br. d, ^3J = 16.8 Hz, 1 H), 5.82 (ddt, ^3J_d = 10.1 Hz, 17.6, ^3J_t = 7.4 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 21.6 (t), 27.5 (t), 33.4 (t), 57.4 (q), 65.2 (d), 103.5 (s), 114.8 (t), 138.2 (d), 172.3 (s), 174.7 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3081 (w, C=C−H), 2931 (s, C−H), 1748 (vs, C=O), 1668 (vs), 1456 (m), 1384 (s), 1255 (m), 1097 (m), 1049 (s). MS (70 eV, EI): *m*/*z* (%) = 182 (13) [M^+], 167 (9), 153 (30), 140 (31), 128 (90), 127 (80), 113 (100), 99 (90), 82 (50), 69 (60), 53 (90). HRMS calcd. for $C_{10}H_{14}O_3$ 182.09430, found 182.09455.

General Procedure for the Reaction of Tetronic Acids and Alkyl Halides: To a solution of the tetronic acid (1.00 mmol) and CsF (304 mg, 2.00 mmol) in 10.0 mL DMF at room temp. was added the alkyl halide (2.00 mmol) and the yellow mixture was stirred at this temperature for another 10 h. The solvent was then evaporated under reduced pressure and the remaining residue was partitioned between H_2O (20 mL) and EtOAc (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and were dried (Na_2SO_4). After filtration the solvent was removed under reduced pressure and the remaining residue was purified by column chromatography to give the desired product.

4-(3,4-Dimethylpent-3-enyloxy)furan-2(5*H*)-one (4d): Prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and 5-bromo-2,3-dimethylpent-2-ene (354 mg, 2.00 mmol) as colorless crystals in a yield of 169 mg (0.86 mmol, 86%). M.p. 62−63 °C; R_f = 0.25 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.64−1.70 (m, 9 H), 2.52 (t, ^3J = 7.3 Hz, 2 H), 4.02 (t, ^3J = 7.3 Hz, 2 H), 4.62 (d, ^4J = 0.7 Hz, 2 H), 5.08 (s, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 18.8 (q), 20.3 (q), 20.7 (q), 33.4 (t), 67.9 (t), 71.3 (t), 88.7 (d), 121.8 (s), 128.4 (s), 173.7 (s), 179.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3098 (m, C=C−H), 2981 (m, C−H), 2937 (m, C−H), 1775 (vs, C=O), 1751 (vs), 1631 (vs), 1367 (s), 1328 (s), 1252 (m), 1154 (s), 1052 (s), 970 (s), 886 (s), 839 (m). MS (70 eV, EI): *m*/*z* (%) = 196 (8) [M^+], 181 (2), 152 (4), 137 (5), 101 (10), 96 (47), 81 (79), 69 (50), 55 (100). HRMS calcd. for $C_{11}H_{16}O_3$ 196.10994, found 196.10991.

4-(2-Methoxyethoxymethoxy)furan-2(5*H*)-one (8): Prepared from tetronic acid (**1**) (100 mg, 1.00 mmol) and MEM-Cl (249 mg, 2.00 mmol) as pale yellow oil in a yield of 162 mg (0.86 mmol, 86%); R_f = 0.15 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.38 (s, 3 H), 3.48−3.53 (m, 2 H), 3.73−3.84 (m, 2 H), 4.65 (d, ^4J = 0.8 Hz, 2 H), 5.25 (s, 2 H), 5.28 (s, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 59.1 (q), 67.8 (t), 69.3 (t), 71.3 (t), 91.5 (d), 95.9 (t), 173.4 (s), 176.7 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3121 (w, C=C−H), 2934 (s, C−H), 2887 (s), 1774 (vs, C=O), 1744 (vs), 1628 (vs), 1450 (m), 1374 (s), 1319 (s), 1222 (m), 1155 (vs), 1113 (vs), 1048 (s), 946 (s), 885 (s). MS (70 eV, EI): *m*/*z* (%) = 188 (1) [M^+], 157 (1), 143 (1), 112 (8), 100 (3), 89 (88), 82 (12), 69 (12), 59 (100), 54 (48). $C_8H_{12}O_3$ (188.18): calcd. C 51.06, H 6.43; found C 50.74, H 6.46.

General Irradiation Procedure for Intramolecular Cycloaddition: In a quartz vessel, a solution of the tetronate (0.1 mmol) in the specified solvent (100 mL) was irradiated at room temp. and 254 nm until GC analysis indicated complete conversion (0.5−3 h) (light source: Rayonet RPR-2537 Å). The solvent was then evaporated under reduced pressure and the remaining residue was purified by column chromatography to give the desired product.

2,9-Dioxatricyclo[5.3.0.0^{1,5}]decan-8-one (21): Prepared from tetronate **4a** (15.4 mg, 0.10 mmol) in Et_2O as colorless crystals in a yield of 11.4 mg (0.07 mmol, 74%); M.p. 88−90 °C; R_f = 0.20 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.80 (dd, ^3J = 5.4, ^2J = 12.7 Hz, 1 H), 1.95−2.05 (m, 2 H), 2.24 (ddd, ^3J = 4.4 Hz, 8.1 Hz, 12.8 Hz, 1 H), 2.94 (ddd, ^4J = 1.3, ^3J = 4.4 Hz, 10.4 Hz, 1 H), 2.99 (virt. q, ^3J = 8.1 Hz, 1 H), 3.95 (ddd, ^3J = 5.4 Hz, 11.5, ^2J = 8.9 Hz, 1 H), 4.22 (t, ^3J = 8.9 Hz, 1 H), 4.24 (d, ^2J = 9.8 Hz, 1 H), 4.33 (d, ^2J = 9.8 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 25.0 (t), 31.7 (t), 40.3 (d), 41.6 (d), 68.8 (t), 72.5 (t), 86.5 (s), 177.9 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2985 (m, C−H), 2876 (m, C−H), 1757 (vs, C=O), 1629 (w), 1472 (m), 1376 (s), 1293 (s), 1246 (m), 1190 (m), 1163 (s), 1140 (m), 1029 (vs), 991 (m), 960 (m). MS (70 eV, EI): *m*/*z* (%) = 154 (15) [M$^+$], 136 (2), 126 (12), 125 (9), 109 (7), 99 (25), 82 (10), 69 (10), 55 (100). $C_8H_{10}O_3$ (154.16): calcd. C 62.33, H 6.54; found C 62.07, H 6.71.

2,10-Dioxatricyclo[6.3.0.0^{1,6}]decan-9-one (22): Prepared from tetronate **5** (16.5 mg, 0.10 mmol) in *t*BuOH as pale yellow oil in a yield of 12.2 mg (0.07 mmol, 72%); R_f = 0.20 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.41−1.62 (m, 3 H), 1.90−2.04 (m, 2 H), 2.19−2.29 (m, 1 H), 2.29−2.38 (m, 1 H), 3.40 (dd, ^3J = 6.8 Hz, 9.7 Hz, 1 H), 3.53−3.63 (m, 1 H), 3.77−3.83 (m, 1 H), 4.27 (d, ^2J = 10.1 Hz, 1 H), 4.41 (d, ^2J = 10.1 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.6 (t), 25.5 (t), 28.2 (t), 36.0 (d), 40.9 (d), 64.5 (t), 76.6 (t), 79.6 (s), 177.3 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2944 (s, C−H), 2863 (m, C−H), 1770 (vs, C=O), 1626 (m), 1470 (m), 1455 (m), 1371 (m), 1281 (m), 1183 (m), 1107 (m), 1004 (s), 973 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (7) [M$^+$], 139 (15), 123 (10), 113 (52), 96 (40), 69 (39), 55 (100). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07878.

2,11-Dioxatricyclo[7.3.0.0^{1,7}]decan-10-one (23): Prepared from tetronate **6** (18.2 mg, 0.10 mmol) in *t*BuOH as pale yellow oil in a yield of 5.46 mg (0.03 mmol, 30%); R_f = 0.20 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.29−1.35 (m, 1 H), 1.69−1.80 (m, 3 H), 1.82−1.88 (m, 1 H), 1.93−2.04 (m, 3 H), 2.37−2.44 (m, 1 H), 3.04 (t, ^3J = 9.4 Hz, 1 H), 3.17−3.23 (m, 1 H), 3.81−3.90 (m, 1 H), 4.47 (d, ^2J = 9.9 Hz, 1 H), 4.51 (d, ^2J = 9.9 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.8 (t), 28.7 (t), 32.1 (t), 32.8 (t), 40.7 (d), 44.4 (d), 68.1 (t), 80.1 (t), 81.1 (q), 177.8 (q) ppm. IR (NaCl): $\tilde{\nu}$ = 2924 (s, C−H), 2853 (m, C−H), 1770 (vs, C=O), 1634 (m), 1456 (m), 1372 (m), 1304 (m), 1242 (w), 1176 (m), 1105 (m), 1019 (s). MS (70 eV, EI): *m*/*z* (%) = 182 (1) [M$^+$], 154 (5), 153 (4), 127 (3), 110 (6), 101 (3), 95 (4), 79 (10), 67 (20), 55 (100). HRMS calcd. for $C_{10}H_{14}O_3$ 182.09430, found 182.09417.

4-(4-Ethoxypentyloxy)furan-2(5*H*)-one (24): Prepared from tetronate **3** (138 mg, 1.00 mmol) in Et_2O as pale yellow oil in a yield of 92.0 mg (0.43 mmol, 43%); R_f = 0.10 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.17 (t, ^3J = 7.0 Hz, 3 H), 1.19 (t, ^3J = 7.0 Hz, 3 H), 1.53−1.60 (m, 2 H), 1.73−2.00 (m, 2 H), 3.37 (dq, ^2J_d = 9.2, ^3J_q = 7.0 Hz), 3.43 (virt. q, ^3J = 7.0 Hz, 1 H), 3.58 (dq, ^2J_d = 9.2, ^3J_q = 7.0 Hz, 1 H), 4.07 (dt, ^2J_d = 1.6, ^3J_t = 6.7 Hz, 1 H), 4.62 (s, 2 H), 5.07 (s, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 15.6 (q), 19.7 (q), 24.8 (t), 32.8 (t), 63.7 (t), 67.8 (t), 73.1 (t), 74.4 (d), 88.8 (d), 173.5 (s), 179.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3078 (w, C=C−H), 2924 (s, C−H), 1777 (vs, C=O), 1747 (vs), 1627 (vs), 1455 (m), 1373 (s), 1318 (m), 1148 (m), 1019 (m), 880 (m). MS (70 eV, EI): *m*/*z* (%) = 214 (0) [M$^+$], 199 (2), 170 (3), 153 (5), 142 (7), 126 (7), 115 (11), 99 (13), 73 (87), 69 (100), 59 (15). HRMS calcd. for $C_9H_{12}O_4$ [M$^+$ − CH_3] 199.09703, found 199.09711.

4-[3-(Tetrahydrofuran-2-yl)propoxy)furan-2(5*H*)-one (25): Prepared from tetronate **3** (138 mg, 1.00 mmol) in THF as pale yellow oil in a yield of 78.0 mg (0.36 mmol, 36%); R_f = 0.25 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.40−1.50 (m, 1 H), 1.60−1.69 (m, 2 H), 1.81−2.05 (m, 5 H), 3.73 (virt. q, ^3J = 7.0 Hz, 1 H), 3.78−3.90 (m, 2 H), 4.03−4.14 (m, 2 H), 4.62 (br. d, 2 H), 5.07 (s, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 25.5 (t), 25.7 (t), 31.4 (t), 31.6 (t), 67.8 (t), 67.8 (t), 72.8 (t), 78.6 (d), 88.8 (d), 173.6 (s), 179.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3056 (m, C=C−H), 2954 (s, C−H), 1770 (vs, C=O), 1746 (vs), 1626 (vs), 1455 (m), 1372 (m), 1319 (s), 1239 (m), 1149 (w), 1051 (s). MS (70 eV, EI): *m*/*z* (%) = 212 (1) [M$^+$], 184 (2), 169 (4), 153 (2), 129 (5), 113 (9), 97 (20), 84 (10), 71 (100), 55 (17). HRMS calcd. for $C_{11}H_{16}O_4$ 212.10486, found 212.10774.

4-(4-Hydroxy-4-methylpentyloxy)furan-2(5*H*)-one (26): Prepared from tetronate **3** (138 mg, 1.00 mmol) in *i*PrOH as colorless crystals in a yield of 114 mg (0.57 mmol, 57%); M.p. 72−74 °C; R_f = 0.15 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.25 (s, 6 H), 1.57 (dd, ^3J = 5.0 Hz, 8.0 Hz, 2 H). 1.84−1.95 (m, 2 H), 4.07 (t, ^3J = 6.4 Hz, 2 H), 4.62 (s, 2 H), 5.07 (s, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 23.5 (t), 29.4 (q), 39.4 (t), 67.8 (t), 70.4 (s), 73.3 (t), 88.8 (d), 173.6 (s), 179.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3458 (m br, OH), 3053 (m, C=C−H), 2973 (s, C−H), 1776 (vs, C=O), 1746 (vs), 1626 (vs), 1450 (m), 1366 (m), 1320 (s), 1237 (m), 1154 (w), 1053 (s), 910 (s). MS (70 eV, EI): *m*/*z* (%) = 200 (1) [M$^+$], 182 (4), 154 (5), 141 (3), 127 (7), 112 (8), 101 (10), 85 (29), 69 (56), 59 (100). HRMS calcd. for $C_{10}H_{16}O_4$ 200.10486, found 200.10474.

7-Methyl-2,9-dioxatricyclo[5.3.0.0^{1,5}]decan-8-one (30): Prepared from tetronate **4e** (16.8 mg, 0.10 mmol) in Et_2O as colorless crystals in a yield of 12.8 mg (0.08 mmol, 76%); M.p. 64−65 °C; R_f = 0.20 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.25 (s, 3 H), 1.61 (dd, ^2J = 13.2, ^3J = 7.9 Hz, 1 H), 1.79 (dd, ^2J = 12.7, ^3J = 5.5 Hz, 1 H), 1.99 (dddd, ^2J = 12.7, ^3J = 7.9 Hz, 9.3 Hz, 10.1 Hz, 1 H), 2.44 (dd, ^2J = 13.2, ^3J = 7.9 Hz, 1 H), 2.92 (virt. q, ^3J = 7.9 Hz, 1 H), 4.05 (ddd, ^2J = 9.3, ^3J = 5.5 Hz, 10.1 Hz, 1 H), 4.14 (d, ^2J = 10.4 Hz, 1 H), 4.22 (d, ^2J = 10.4 Hz, 1 H), 4.26 (virt. t, ^2J = ^3J = 9.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 15.1 (q), 31.2 (t), 33.4 (t), 39.5 (d), 44.2 (d), 69.7 (t), 71.0 (t), 88.0 (s), 181.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2969 (s, C−H), 1772 (vs, C=O), 1448 (m), 1378 (m), 1304 (m), 1231 (m), 1097 (s), 1029 (s), 979 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (11) [M$^+$], 150 (2), 139 (23), 123 (12), 112 (8), 98 (10), 81 (9), 69 (100), 55 (38). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07862.

5-Methyl-2,9-dioxatricyclo[5.3.0.0^{1,5}]decan-8-one (27): Prepared from tetronate **4b** (16.8 mg, 0.10 mmol) in Et_2O as colorless crystals in a yield of 10.6 mg (0.06 mmol, 61%); R_f = 0.20 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.30 (s, 3 H), 1.65 (virt. dt, ^3J_d = 6.0, ^2J_t = ^3J_t = 11.8 Hz, 1 H), 1.84−1.94 (m, 2 H), 2.24 (dd, ^2J = 13.2, ^3J = 10.4 Hz, 1 H), 2.92 (dd, ^3J = 4.1 Hz, 10.4 Hz, 1 H), 3.93 (ddd, ^2J = 9.3, ^3J = 6.0 Hz, 11.8 Hz, 1 H), 4.19 (virt. t, ^2J = ^3J = 9.3 Hz, 1 H), 4.21 (d, ^2J = 10.2 Hz, 1 H), 4.34 (d, ^2J = 10.2 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 21.4 (q), 31.9 (d), 38.2 (d), 39.5 (t), 46.2 (s), 68.0 (t), 68.7 (t), 87.4 (s), 178.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2961 (s, C−H), 2868 (C−H), 1779 (vs, C=O), 1447 (m), 1371 (m), 1280 (s), 1186 (m), 1148 (s), 1084 (m), 1066 (m), 1034 (s), 996 (s), 963 (m), 896 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (4) [M$^+$], 153 (1), 137 (1), 123 (3), 113 (5), 101 (8), 96 (100), 81 (12), 69 (23), 55 (34). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07861.

6,6-Dimethyl-2,9-dioxatricyclo[5.3.0.0^{1,5}]decan-8-one (28): Prepared from tetronate **4c** (18.2 mg, 0.10 mmol) in *t*BuOH as pale yellow

oil in a yield of 8.74 mg (0.05 mmol, 52%); R_f = 0.25 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.18 (s, 3 H), 1.19 (s, 3 H), 1.88−2.02 (m, 2 H), 2.53 (d, ^3J = 9.1 Hz, 1 H), 2.65 (d, ^4J = 1.1 Hz, 1 H), 3.82 (ddd, ^2J = 9.6, ^3J = 6.4 Hz, 10.9 Hz, 1 H), 4.22 (dt, ^3J_d = 1.8, ^2J_t = ^3J_t = 9.6 Hz, 1 H), 4.38 (d, ^2J = 10.2 Hz, 1 H), 4.45 (d, ^2J = 10.2 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.3 (q), 26.2 (q), 26.8 (t), 32.9 (s), 51.0 (d), 52.7 (d), 69.8 (t), 74.1 (t), 82.1 (s), 175.7 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2959 (s, C−H), 2870 (C−H), 1770 (vs, C=O), 1470 (m), 1371 (m), 1278 (m), 1172 (m), 1147 (s), 1030 (vs), 988 (m). MS (70 eV, EI): *m*/*z* (%) = 182 (4) [M$^+$], 167 (1), 154 (1), 138 (10), 123 (10), 100 (7), 96 (7), 91 (5) (2), 83 (100), 69 (14), 55 (52). $C_{10}H_{14}O_3$ (182.22): calcd. C 65.91, H 7.74; found C 65.64, H 7.71.

5,6,6-Trimethyl-2,9-dioxatricyclo[5.3.0.0^{1,5}]decan-8-one (29): Prepared from tetronate **4d** (19.6 mg, 0.10 mmol) in *t*BuOH as pale yellow oil in a yield of 12.0 mg (0.06 mmol, 61%); M.p. 77−79 °C; R_f = 0.30 (P/DCM/EtOAc, 10:2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.08 (s, 3 H), 1.14 (s, 3 H), 1.22 (s, 3 H), 1.64 (ddd, ^2J = 12.8, ^3J = 9.1 Hz, 11.1 Hz, 1 H), 2.26 (ddd, ^2J = 12.8, ^3J = 1.7 Hz, 6.4 Hz, 1 H), 3.80 (ddd, ^2J = 9.1, ^3J = 6.4 Hz, 11.1 Hz, 1 H), 4.15 (dt, ^3J_d = 1.7, ^2J_t = ^3J_t = 9.1 Hz, 1 H), 4.23 (d, ^2J = 10.5 Hz, 1 H), 4.40 (d, ^2J = 10.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 18.4 (q), 22.2 (q), 25.6 (q), 35.3 (s), 36.2 (t), 50.9 (s), 51.1 (d), 68.0 (t), 69.7 (t), 85.1 (s), 175.9 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2969 (s, C−H), 1769 (vs, C=O), 1629 (w), 1454 (m), 1370 (m), 1284 (m), 1163 (s), 1120 (m), 1033 (s), 985 (m). MS (70 eV, EI): *m*/*z* (%) = 196 (3) [M$^+$], 181 (2), 165 (2), 152 (5), 137 (7), 101 (8), 96 (100), 83 (48), 81 (40), 69 (28), 55 (79). $C_{11}H_{16}O_3$ (196.24): calcd. C 67.32, H 8.22; found C 67.00, H 7.94.

9-Methoxy-2-oxatricyclo[4.2.1.0^{4,9}]nonan-2-one (32): Prepared from tetronate **20** (16.8 mg, 0.10 mmol) in Et_2O as colorless crystals in a yield of 12.6 mg (0.07 mmol, 75%); M.p. 63−65 °C; R_f = 0.30 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.54 (dt, ^2J_d = 12.8, ^3J_t = 4.4 Hz, 1 H), 1.72−1.83 (m, 1 H), 2.02−2.11 (m, 1 H), 2.11−2.20 (m, 1 H), 2.22−2.32 (m, 1 H), 2.68 (ddd, ^2J = 12.8, ^3J = 10.0 Hz, 11.7 Hz, 1 H), 2.84−2.89 (m, 1 H), 3.13 (ddd, ^3J = 4.4 Hz, 11.7, ^4J = 1.6 Hz, 1 H), 3.32 (s, 3 H), 4.84 (dd, ^3J = 3.2 Hz, 6.4 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 23.8 (t), 31.2 (t), 32.8 (t), 37.0 (d), 38.4 (d), 52.4 (q), 87.7 (d), 92.6 (s), 177.9 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2940 (s, C−H), 1770 (vs, C=O), 1634 (vs), 1462 (m), 1353 (s), 1319 (s), 1268 (m), 1184 (vs), 1052 (vs), 1027 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (9) [M$^+$], 140 (2), 126 (13), 114 (100), 113 (42), 96 (28), 85 (23), 69 (15), 59 (45). HRMS calcd. for $C_9H_{12}O_3$ 168.07864, found 168.07875.

5-Methoxy-3-oxatricyclo[5.3.0.0^{1,5}]decan-2-one (31): Prepared from tetronate **16** (18.2 mg, 0.10 mmol) in Et_2O as colorless oil in a yield of 13.1 mg (0.07 mmol, 72%); R_f = 0.45 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.62−1.70 (m, 2 H), 1.85 (ddd, ^2J = 12.2, ^3J = 1.5 Hz, 7.3 Hz, 1 H), 1.91−2.12 (m, 4 H), 2.23 (dd, ^2J = 12.2, ^3J = 7.3 Hz, 1 H), 2.65 (virt. q, ^3J = 7.3 Hz, 1 H), 3.18 (s, 3 H), 4.27 (d, ^2J = 12.4 Hz, 1 H), 4.56 (dd, ^2J = 12.4, ^4J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 26.1 (t), 27.0 (t), 32.2 (t), 33.4 (t), 38.3 (d), 50.6 (q), 55.7 (s), 76.4 (s), 76.5 (t), 179.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2951 (s, C−H), 1759 (vs, C=O), 1466 (m), 1372 (m), 1263 (m), 1248 (m), 1140 (s), 1108 (m), 1066 (m), 1037 (s). MS (70 eV, EI): *m*/*z* (%) = 182 (3) [M$^+$], 167 (2), 153 (8), 140 (4), 137 (7), 128 (10), 113 (10), 109 (6), 95 (100), 91 (12), 79 (9), 67 (12), 53 (6). HRMS calcd. for $C_{10}H_{14}O_3$ 182.09430, found 182.09419.

2,12-Dioxatetracyclo[6.5.0.0^{3,7}.0^{1,10}]tridecan-11-one (33): Prepared from tetronate **7a** (19.4 mg, 0.10 mmol) in Et_2O as colorless crystals in a yield of 13.6 mg (0.07 mmol, 70%); M.p. 81−83 °C, R_f = 0.15 (P/EtOAc, 8:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.19−1.31 (m, 1 H), 1.54−1.64 (m, 1 H), 1.73−1.84 (m, 2 H), 1.85−1.91 (m, 1 H), 1.92−1.98 (m, 1 H), 2.10 (ddd, ^2J = 13.1, ^3J = 6.8 Hz, 10.4 Hz, 1 H), 2.22 (ddd, ^2J = 13.1, ^3J = 4.4 Hz, 6.8 Hz, 1 H), 2.40 (virt. q, ^3J = 6.8 Hz, 1 H), 2.81 (virt. t, ^3J = 6.8 Hz, 1 H), 2.98 (dd, ^3J = 4.4 Hz, 10.4 Hz, 1 H), 4.27 (d, ^2J = 9.6 Hz, 1 H), 4.34 (d, ^2J = 9.6 Hz, 1 H), 4.77 (virt. t, ^3J = 4.6 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.6 (t), 26.0 (t), 31.6 (t), 32.4 (t), 40.2 (d), 49.3 (d), 51.4 (d), 73.0 (t), 87.6 (d), 87.8 (s), 178.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2955 (s, C−H), 1779 (vs, C=O), 1626 (m), 1446 (m), 1372 (m), 1288 (m), 1230 (w), 1175 (m), 1031 (s), 958 (m). MS (70 eV, EI): *m*/*z* (%) = 194 (30) [M$^+$], 176 (5), 165 (23), 149 (10), 139 (45), 123 (47), 109 (115), 101 (20), 94 (90), 79 (100), 67 (56), 55 (70). HRMS calcd. for $C_{11}H_{14}O_3$ 194.09430, found 194.09410.

10-Methyl-2,12-dioxatetracyclo[6.5.0.0^{3,7}.0^{1,10}]tridecan-11-one (34): Prepared from tetronate **7b** (20.8 mg, 0.10 mmol) in Et_2O as colorless oil as a 1:1 diastereomeric mixture in a yield of 12.1 mg (0.06 mmol, 58%); *cis-anti-cis* diastereoisomer (**34a**): R_f = 0.25 (P/EtOAc, 9:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.27 (s, 3 H), 1.28−1.35 (m, 1 H), 1.59−1.95 (m, 6 H), 2.41−2.45 (m, 2 H), 2.72 (dd, ^3J = 6.6 Hz, 8.5 Hz, 1 H), 4.13 (d, ^2J = 10.5 Hz, 1 H), 4.24 (d, ^2J = 10.5 Hz, 1 H), 4.86 (virt. t, ^3J = 5.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 15.9 (q), 24.6 (t), 32.0 (t), 33.2 (t), 34.5 (t), 43.9 (s), 47.3 (d), 51.1 (d), 71.6 (t), 88.7 (d), 89.3 (s), 181.3 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2961 (s, C−H), 2869 (C−H), 1770 (vs, C=O), 1448 (s), 1377 (s), 1301 (m), 1221 (m), 1095 (s), 1027 (s). MS (70 eV, EI): *m*/*z* (%) = 208 (31) [M$^+$], 179 (30), 163 (22), 139 (23), 123 (65), 113 (12), 109 (19), 95 (44), 79 (63), 69 (100). HRMS calcd. for $C_{12}H_{16}O_3$ 208.10994, found 208.10986. *cis-syn-cis* diastereoisomer (**34b**): R_f = 0.20 (P/EtOAc, 9:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.21 (s, 3 H), 1.54−1.74 (m, 5 H), 1.87 (dd, ^2J = 13.1, ^3J = 8.2 Hz, 1 H), 1.91−1.97 (m, 1 H), 2.21 (dd, ^2J = 13.1, ^3J = 8.2 Hz, 1 H), 2.79−2.88 (m, 1 H), 2.95 (virt. q, ^3J = 8.2 Hz, 1 H), 4.04 (d, ^2J = 9.4 Hz, 1 H), 4.18 (d, ^2J = 9.4 Hz, 1 H), 4.78 (dt, ^3J_d = 2.1, ^3J_t = 7.0 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 15.6 (q), 25.7 (t), 27.4 (t), 28.8 (t), 33.8 (t), 40.3 (s), 43.1 (d), 45.1 (d), 72.5 (t), 90.3 (s), 92.2 (d), 181.2 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2958 (s, C−H), 2872 (C−H), 1769 (vs, C=O), 1449 (s), 1376 (s), 1296 (m), 1192 (m), 1097 (s), 1020 (s), 957 (m). MS (70 eV, EI): *m*/*z* (%) = 208 (30) [M$^+$], 179 (30), 139 (13), 123 (65), 113 (28), 109 (25), 95 (44), 79 (43), 69 (100). HRMS calcd. for $C_{12}H_{16}O_3$ 208.10994, found 208.10974.

10-*tert*-Butyl-2,12-dioxatetracyclo[6.5.0.0^{3,7}.0^{1,10}]tridecan-11-one (35): Prepared from tetronate **7c** (25.0 mg, 0.10 mmol) in Et_2O as colorless crystals in a yield of 18.0 mg (0.07 mmol, 72%); M.p. 59−61 °C, R_f = 0.25 (P/Et_2O = 4:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 1.45−1.88 (m, 5 H), 1.95−2.01 (m, 2 H), 2.21 (dd, ^2J = 12.1, ^3J = 8.2 Hz, 1 H), 2.72−2.79 (m, 1 H), 2.83 (virt. q, ^3J = 8.2 Hz, 1 H), 3.97 (d, ^2J = 8.8 Hz, 1 H), 4.02 (d, ^2J = 8.8 Hz, 1 H), 4.74 (virt. t, ^3J = 5.8 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.4 (t), 26.0 (t), 26.1 (q), 27.7 (t), 33.3 (t), 34.1 (s), 43.1 (d), 44.6 (d), 50.3 (s), 70.8 (t), 93.2 (d), 94.0 (s), 180.0 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2955 (s, C−H), 1769 (vs, C=O), 1634 (m), 1456 (m), 1362 (m), 1278 (m), 1164 (m), 1033 (s). MS (70 eV, EI): *m*/*z* (%) = 250 (2) [M$^+$] 221 (51), 193 (21), 165 (15), 123 (64), 111 (45), 95 (34), 79 (35), 67 (100), 55 (41). $C_{15}H_{22}O_3$ (250.33): calcd. C 71.97, H 8.86; found C 72.17, H 8.42.

10-Methyl-2,9-dioxatricyclo[5.3.0.0^{1,5}]decan-8-one (36): Prepared from tetronate **12** (16.8 mg, 0.10 mmol) in MeCN as a 1:1 diastereomeric mixture as colorless oil in a yield of 12.1 mg (0.07 mmol, 72%); diastereoisomer I (**36a**): R_f = 0.20 (P/DCM/EtOAc, 10:2:1). $[\alpha]_D^{20}$ = +43.8 (*c* = 0.10, $CHCl_3$). ^{1}H NMR

(360 MHz, $CDCl_3$): δ = 1.33 (d, ^3J = 6.8 Hz, 3 H), 1.71−2.03 (m, 3 H), 2.14 (ddd, ^2J = 12.2, ^3J = 4.0 Hz, 8.2 Hz, 1 H), 2.98 (ddd, ^3J = 4.0 Hz, 8.2, ^4J = 1.3 Hz, 1 H), 3.13 (virt. q, ^3J = 7.6 Hz, 1 H), 3.94 (ddd, ^2J = 11.1, ^3J = 7.4 Hz, 9.3 Hz, 1 H), 4.21−4.29 (m, 1 H), 4.56 (q, ^3J = 6.8 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.7 (q), 25.2 (t), 32.0 (t), 36.8 (d), 42.3 (d), 68.9 (t), 78.3 (d), 90.4 (s), 177.9 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2980 (m, C−H), 2870 (m, C−H), 1768 (vs, C=O), 1630 (w), 1448 (m), 1383 (m), 1287 (s), 1238 (m), 1176 (s), 1074 (s), 1050 (s), 975 (s), 919 (m). MS (70 eV, EI): *m*/*z* (%) =168 (2) [M^+], 153 (1), 140 (1), 137 (4), 126 (28), 113 (6), 96 (7), 81 (7), 69 (7), 55 (100). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 63.90, H 6.83. diastereoisomer II (**36b**): R_f = 0.15 (P/EtOAc, 9:1). $[\alpha]_D^{20}$ = −47.9 (*c* = 0.10, $CHCl_3$), ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.44 (d, ^3J = 6.6 Hz, 3 H), 1.78 (dd, ^2J = 12.1, ^3J = 5.3 Hz, 1 H), 1.95 (dt, ^2J_d = 12.1, ^3J_t = 7.8, 1 H), 2.02 (ddd, ^2J = 12.8, ^3J = 6.6 Hz, 7.8 Hz, 1 H), 2.24 (ddd, ^2J = 12.8, ^3J = 3.9 Hz, 7.8 Hz, 1 H), 2.97 (dd, ^3J = 3.9 Hz, 6.6 Hz, 1 H), 3.00 (virt. q, ^3J = 7.8 Hz, 1 H), 3.96 (ddd, ^2J = 7.8, ^3J = 4.0 Hz, 6.1 Hz, 1 H), 4.23 (virt. q, ^2J = ^3J = 7.8 Hz, 1 H), 4.59 (q, ^3J = 6.6 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 16.8 (q), 25.4 (t), 31.4 (t), 40.0 (d), 42.2 (d), 69.0 (t), 80.5 (d), 87.9 (s), 177.7 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2978 (m, C−H), 2869 (m, C−H), 1765 (vs, C=O), 1629 (w), 1448 (m), 1337 (m), 1283 (m), 1165 (s), 1071 (s), 1051 (s), 969 (m), 918 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (2) [M^+], 153 (1), 140 (1), 137 (4), 126 (18), 113 (6), 96 (17), 81 (7), 69 (8), 55 (100). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 64.09, H 6.98.

General Irradiation Procedure for Intermolecular Cycloaddition: In a quartz vessel, a solution of the tetronate (1.00 mmol) and the alkene (15.0 mmol) in the specified solvent (60 mL) was irradiated at room temp. and 254 nm for 10 h (light source: Rayonet RPR-2537 Å). The solvent was then evaporated under reduced pressure and the remaining residue was purified by column chromatography to give the desired product.

2-Methoxy-4-oxatricyclo[5.3.0.0^{2,6}]decan-5-one (38): Prepared from tetronate **37** (114 mg, 1.00 mmol) and cyclopentene (1.32 mL, 1.02 g, 15.0 mmol) in *t*BuOH as pale yellow oil in a yield of 104 mg (0.57 mmol, 57%, *exo*/*endo* = 3:1); *exo*-diastereoisomer: R_f = 0.15 (P/EtOAc, 4:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.47−1.56 (m, 1 H), 1.58−1.69 (m, 2 H), 1.82−1.94 (m, 2 H), 2.02 (dd, ^3J = 5.5 Hz, 13.1 Hz, 1 H), 2.54 (d, ^3J = 5.5 Hz, 1 H), 2.64 (virt. q, ^3J = 5.5 Hz, 1 H), 2.80 (virt. t, ^3J = 5.5 Hz, 1 H), 3.20 (s, 3 H), 4.32 (d, ^2J = 10.5 Hz, 1 H), 4.53 (d, ^2J = 10.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.9 (t), 26.2 (t), 32.9 (t), 37.3 (d), 44.6 (d), 47.0 (d), 50.7 (q), 76.6 (s), 77.0 (t), 178.0 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2951 (s, CH), 1754 (vs, C=O), 1470 (m), 1372 (m), 1266 (m), 1248 (m), 1185 (s), 1085 (m), 1030 (s), 998 (m), 934 (m), 905 (m). MS (70 eV, EI): *m*/*z* (%) = 182 (1) [M^+], 167 (1), 123 (5), 115 (100), 109 (3), 105 (2), 91 (10), 69 (13), 68 (12), 67 (18),65 (8), 53 (4). $C_{10}H_{14}O_3$ (182.22): calcd. C 65.91, H 7.74; found C 65.66, H 7.23. *endo*-diastereoisomer: R_f = 0.10 (P/EtOAc, 4:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.50−1.78 (m, 6 H), 3.02−3.08 (m, 1 H), 3.11−3.19 (m, 2 H), 3.24 (s, 3 H), 4.11 (d, ^2J = 10.3 Hz, 1 H), 4.43 (d, ^2J = 10.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 26.6 (t), 27.7 (t), 27.9 (t), 35.4 (d), 41.8 (d), 44.6 (d), 50.8 (q), 70.4 (t), 80.9 (s), 1761 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3442 (br vs, OH), 2959 (s, CH), 1769 (vs, C=O), 1373 (m), 1184 (vs), 1128 (s), 1030 (vs), 931 (m). MS (70 eV, EI): *m*/*z* (%) = 182 (1) [M^+], 167 (1), 153 (1), 137 (2), 123 (3), 115 (100), 109 (4), 91 (5), 83 (5), 67 (18). $C_{10}H_{14}O_3$ (182.22): calcd. C 65.91, H 7.74; found C 65.68, H 7.28.

2-(2-Methoxyethoxymethoxy)-4-oxatricyclo[5.3.0.0^{2,6}]decan-5-one (39): Prepared from tetronate **8** (188 mg, 1.00 mmol) and cyclopentene (1.32 mL, 1.02 g, 15.0 mmol) in *t*BuOH as pale yellow oil in a yield of 151 mg (0.59 mmol, 59%, *exo*/*endo* = 8:1); *exo*-diastereoisomer: R_f = 0.25 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.55−1.80 (m, 3 H), 1.82−1.91 (m, 2 H), 1.97 (dd, ^3J = 6.0 Hz, 13.0 Hz, 1 H), 2.64 (virt. q, ^3J = 6.2 Hz, 1 H), 2.70 (d, ^3J = 6.2 Hz, 1 H), 2.81 (virt. t, ^3J = 6.2 Hz, 1 H), 3.40 (s, 3 H), 3.53 (t, ^3J = 4.5 Hz, 2 H), 3.61−3.69 (m, 2 H), 3.79 (dt, ^2J_d = 11.4, ^3J_t = 4.1 Hz, 1 H), 4.39 (d, ^2J = 10.5 Hz, 1 H), 4.74 (d, ^2J = 10.5 Hz, 1 H), 4.73 (d, ^2J = 7.3 Hz, 1 H), 4.78 (d, ^2J = 7.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.9 (t), 26.3 (t), 32.9 (t), 37.8 (d), 46.1 (d), 47.7 (d), 59.0 (q), 67.8 (t), 71.6 (t), 76.6 (d), 79.4 (t), 91.8 (t), 177.8 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2949 (s, CH), 1774 (vs, C=O), 1470 (m), 1368 (s), 1247 (m), 1185 (m), 1106 (m), 1012 (s). MS (70 eV, EI): *m*/*z* (%) = 256 (1) [M^+], 197 (2), 189 (10), 151 (12), 123 (6), 105 (6), 89 (56), 77 (20), 67 (30), 59 (100).

6,6-Diethoxy-5-(2-methoxyethoxymethoxy)-3-oxabicyclo[3.2.0]-heptan-5-one (41): Prepared from tetronate **8** (188 mg, 1.00 mmol) and ketene diethyl acetal (**40**, 1.54 mL, 1.74 g, 15.0 mmol) in *t*BuOH as pale yellow oil in a yield of 100 mg (0.33 mmol, 33%) R_f = 0.35 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.21 (t, ^3J = 7.0 Hz, 3 H), 1.25 (t, ^3J = 7.0 Hz, 3 H), 1.97 (dd, ^2J = 13.0, ^3J = 7.4 Hz, 1 H), 2.64 (dd, ^2J = 13.0, ^3J = 10.9 Hz, 1 H), 3.29−3.33 (m, 1 H), 3.33 (dd, ^3J = 7.4 Hz, 10.9 Hz, 1 H), 3.40 (s, 3 H), 3.53−3.63 (m, 5 H), 3.67−3.72 (m, 1 H), 3.74−3.80 (m, 1 H), 4.41 (d, ^2J = 10.8 Hz, 1 H), 4.75 (d, ^2J = 10.8 Hz, 1 H), 4.85 (d, ^2J = 7.5 Hz, 1 H), 5.14 (d, ^2J = 7.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.9 (q), 15.3 (q), 31.1 (t), 36.6 (d), 57.7 (t), 58.6 (t), 59.0 (q), 67.4 (t), 71.6 (t), 74.2 (t), 85.9 (s), 93.0 (t), 101.4 (s), 176.4 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 2977 (s, C−H), 2932 (s, C−H), 1779 (vs, C=O), 1630 (m), 1452 (m), 1369 (s), 1310 (m), 1282 (s), 1249 (s), 1188 (vs), 1132 (vs), 1099 (vs), 1027 (vs), 848 (w). MS (70 eV, EI): *m*/*z* (%) = 304 (0) [M^+], 215 (7). 187 (2), 153 (2), 141 (9), 116 (13), 89 (33), 59 (100), 55 (78).

General Procedure for the Preparation of β-Hydroxy Lactones: A solution of the tetronate (1.00 mmol) and the alkene (15.0 mmol) in *t*BuOH (60 mL) was irradiated at room temp. and 254 nm for 10 h (light source: Rayonet 2537 Å). The solvent was then evaporated under reduced pressure and the remaining residue was directly dissolved in DCM (30 mL). $TiCl_4$ (0.33 mL, 0.57 g, 3.00 mmol) was added at room temp. and the resulting mixture was stirred for 6 h. Satd. aqueous $NaHCO_3$ (50 mL) was then added and the mixture was filtered. The organic phase was separated and the aqueous phase was extracted with DCM (3 × 30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was evaporated under reduced pressure. The remaining yellow oil was purified by column chromatography to yield the pure products.

2-Hydroxy-4-oxatricyclo[5.3.0.0^{2,6}]decan-5-one (42): Prepared from tetronate **8** (188 mg, 1.00 mmol) and cyclopentene (1.32 mL, 1.02 g, 15.0 mmol) as colorless crystals in a yield of 86.1 mg (0.53 mmol, 53%, *exo*/*endo* = 8:1); *exo*-diastereoisomer: M.p. 69−70 °C; R_f = 0.30 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.52−1.80 (m, 3 H), 1.84−2.06 (m, 3 H), 2.43 (d, ^3J = 6.5 Hz, 1 H), 2.63 (virt. q, ^3J = 6.5 Hz, 1 H), 2.85 (virt. t, ^3J = 6.5 Hz, 1 H), 4.39 (d, ^2J = 10.0 Hz, 1 H), 4.47 (d, ^2J = 10.0 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.9 (t), 26.1 (t), 32.9 (t), 37.5 (d), 48.4 (d), 49.6 (d), 72.1 (s), 81.9 (t), 178.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3425 (br vs, OH), 2945 (s, CH), 1738 (vs, C=O), 1622 (m), 1483 (m), 1269 (m), 1199 (m), 1163 (m), 1019 (vs). MS (70 eV, EI): *m*/*z* (%) = 168 (2) [M^+] 138 (5), 109 (6), 101 (95), 95 (10), 79 (15), 67 (100), 55 (40). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 64.14, H 7.12.

1-Hydroxy-9-oxatricyclo[6.3.0.0^{2,7}]undecan-8-one (43): Prepared from tetronate **8** (188 mg, 1.00 mmol) and cyclohexene (1.52 mL, 1.23 g, 15.0 mmol) as colorless oil in a yield of 95.2 g (0.52 mmol, 52%, *exo*/*endo* = 10:1); *exo*-diastereoisomer: R_f = 0.30 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.10−1.20 (m, 1 H), 1.22−1.44 (m, 1 H), 1.47−1.54 (m, 1 H), 1.55−1.83 (m, 4 H), 1.84−1.90 (m, 1 H), 2.23−2.32 (m, 1 H), 2.45 (virt. q, ^3J = 7.9 Hz, 1 H), 2.94 (d, ^3J = 7.9 Hz, 1 H), 4.43 (d, ^2J = 9.8 Hz, 1 H), 4.48 (d, ^2J = 9.8 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 21.4 (t), 21.7 (t), 22.5 (t), 25.3 (t), 29.5 (d), 40.9 (d), 49.7 (d), 75.1 (t), 80.7 (s), 177.7 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3418 (br vs, OH), 2934 (s, CH), 2856 (s, C−H), 1748 (vs, C=O), 1467 (m), 1450 (m), 1377 (m), 1276 (s), 1248 (m), 1185 (s), 1124 (m), 1007 (s), 990 (s), 906 (m). MS (70 eV, EI): *m*/*z* (%) = 182 (1) [M$^+$], 164 (1), 152 (4), 124 (6), 101 (100), 95 (5), 82 (10), 67 (34), 54 (11). HRMS calcd. for $C_{10}H_{14}O_3$ 182.09430, found 182.09416.

1-Hydroxy-12-oxatricyclo[8.3.0.0^{2,9}]tridecan-11-one (44): Prepared from tetronate **8** (188 mg, 1.0 mmol) and *cis*-cyclooctene (1.95 mL, 1.65 g, 15.0 mmol) as colorless oil in a yield of 114 mg (0.54 mmol, 54%, 1:2:1 diastereomeric mixture); R_f = 0.30 (P/EtOAc, 2:1); as inseparable mixture this compound was directly submitted to ring opening conditions

General Procedure for the Retro-Aldol Ring Expansion: A solution of the β-hydroxy lactone (1.00 mmol) and Cs_2CO_3 (2.00 mmol) in THF (20 mL) was transferred into a Teflon tube and irradiated in the microwave oven for 30 min. (temperature gradient: room temp. → 100 °C in 15 min at 800 W). The mixture was cooled to room temp., filtered and the solvent was removed under reduced pressure. The remaining oil was subjected to column chromatography to yield the desired products.

4-Oxabicyclo[5.3.0]decan-2,5-dione (45): Prepared from β-hydroxy lactone **42** (168 mg, 1.00 mmol) as colorless crystals in a yield of 125 mg (0.74 mmol, 74%, M.p. 94−96 °C; R_f = 0.50 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.10 (virt. q, ^3J = 8.0 Hz, 1 H), 1.52−1.68 (m, 2 H), 1.82−2.00 (m, 2 H), 2.31−2.47 (m, 2 H), 2.54−2.72 (m, 1 H), 2.85 (dd, ^2J = 13.2, ^3J = 5.2 Hz, 1 H), 3.44 (dt, ^3J_d = 3.5, ^3J_t = 8.2 Hz, 1 H), 4.51 (d, ^2J = 18.5 Hz, 1 H), 4.56 (d, ^2J = 18.5 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 23.0 (t), 24.5 (t), 32.5 (t), 36.0 (t), 39.5 (d), 50.7 (d), 73.5 (t), 171.9 (s), 206.9 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (s, CH), 1735 (vs, C=O), 1717 (vs, C=O), 1636 (vs), 1430 (m), 1320 (m), 1271 (m), 1170 (m), 1114 (m), 1071 (m). MS (70 eV, EI): *m*/*z* (%) = 168 (4) [M$^+$], 138 (10), 110 (6), 82 (46), 67 (100), 53 (41). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 64.03, H 7.18.

4-Oxa-bicyclo[5.4.0]undecan-2,5-dione (46): Prepared from β-hydroxy lactone **43** (182 mg, 1.00 mmol) as colorless crystals in a yield of 153 mg (0.84 mmol, 84%). M.p. 119−122 °C; R_f = 0.55 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.89−1.10 (m, 1 H), 1.16−1.30 (m, 1 H), 1.32−1.49 (m 1 H), 1.52−1.88 (m, 4 H), 2.06−2.13 (m, 1 H), 2.25−2.37 (m, 1 H), 2.38 (virt. t, ^2J = ^3J = 11.7 Hz, 1 H), 2.78 (dd, ^2J = 11.7, ^3J = 5.5 Hz, 1 H), 3.22 (virt. t, ^3J = 3.5 Hz, 1 H), 4.43 (d, ^2J = 18.3 Hz, 1 H), 4.49 (d, ^2J = 18.3 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 21.5 (t), 24.6 (t), 25.2 (t), 31.1 (t), 33.4 (d), 38.3 (t), 44.8 (d), 73.4 (t), 171.4 (s), 207.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2944 (s, CH), 2922 (s, C−H), 2878 (m, C−H), 2850 (m, C−H), 1732 (vs, C=O), 1727 (vs, C=O), 1449 (m), 1348 (m), 1283 (s), 1271 (s), 1242 (m), 1182 (m), 1144 (m), 1089 (m), 1070 (vs), 906 (s). MS (70 eV, EI): *m*/*z* (%) = 182 (8) [M$^+$], 152 (22), 139 (5), 124 (56), 96 (10), 82 (48), 81 (51), 67 (100), 54 (44). HRMS calcd. for $C_{10}H_{14}O_3$ 182.09430, found 182.09418.

11-Oxabicyclo[6.5.0]tridecan-9,12-dione (47): Prepared from the 1:2:1 diastereomeric mixture of β-hydroxy lactone **44** (210 mg, 1.00 mmol) as colorless oil in a yield of 80.0 mg (0.38 mmol, 38%, 76% b.r.s.m.) as a 1:1 diastereomeric mixture of *cis*/*trans* isomers together with 105 mg (0.50 mmol, 50%) of unchanged starting material. R_f = 0.55 (P/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.19−2.20 (m, 24 H), 2.31 (d, ^2J = 12.7 Hz, 1 H), 2.43 (dd, ^2J = 13.8, ^3J = 2.5 Hz), 2.55−2.65 (m, 2 H), 2.76 (dd, ^2J = 12.7, ^3J = 6.8 Hz, 1 H), 2.81 (dd, ^2J = 13.8, ^3J = 6.6 Hz, 1 H), 2.97 (dt, ^3J_d = 3.2, ^3J_t = 9.5 Hz, 1 H), 3.14 (ddd, ^3J = 3.5 Hz, 8.0 Hz, 11.7 Hz, 1 H), 4.44 (d, ^2J = 18.6 Hz, 1 H), 4.49 (d, ^2J = 18.6 Hz, 1 H), 4.50 (d, ^2J = 18.6 Hz, 1 H), 4.53 (d, ^2J = 18.6 Hz, 1 H) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 21.7 (t), 24.7 (t), 24.9 (t), 25.1 (t), 25.1 (t), 26.1 (t), 26.1 (t), 26.5 (t), 27.0 (t), 28.6 (t), 30.0 (t), 33.4 (d), 35.1 (t), 36.6 (d), 39.3 (t), 39.8 (t), 49.6 (d), 49.7 (d), 73.3 (t), 73.6 (t), 171.6 (s), 171.7 (s), 208.7 (s), 209.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2931 (vs, C−H), 2855 (s, C−H), 1755 (vs, C=O), 1716 (vs, C=O), 1481 (s), 1446 (s), 1362 (m), 1262 (m), 1171 (m), 1078 (s). MS (70 eV, EI): *m*/*z* (%) = 210 (10) [M$^+$], 180 (34), 167 (16), 152 (12), 124 (11), 110 (100), 96 (70), 81 (95), 67 (97), 55 (55). HRMS calcd. for $C_{12}H_{18}O_3$ 210.12560, found 210.12563.

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[26] Crystal structure analysis of compound **21**: $C_8H_{10}O_3$, M_r = 154.16, colorless fragment (0.32 × 0.34 × 0.51 mm^3), triclinic, $P\bar{1}$ (No. 2), a = 6.3159(3), b = 8.4407(4), c = 8.0125(5) Å, α = 101.315(2)°, β = 104.856(2)°, γ = 112.969(4)°, V = 358.46(4) Å^3, Z = 2, $D_{calcd.}$ = 1.428 g·cm^{-3}, F_{000} = 164, μ(Mo-K_α) = 0.109 mm^{-1}. Preliminary examination and data collection were carried out on an imaging plate device (NONIUS DIP2020) with a NONIUS cooling system at the window of a sealed tube (NONIUS FR590) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection were performed at 143 K within the Θ range of 2.78° < Θ < 25.34°. A total of 6003 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging (R_{int} = 0.068), 1231 [1195: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 141 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_o^2)^2$ and converged with $R1$ = 0.0444 [$I_o > 2\sigma(I_o)$], $wR2$ = 0.1212 [all data], GOF = 1.072, and shift/error < 0.001. Small extinction effects were corrected with the SHELXL-97 procedure [ε = 0.12(3)]. The final difference-Fourier map shows no striking features ($\Delta\rho_{e,\ min./max.}$ = +0.19/-0.19 e·Å^{-3}).

Crystal structure analysis of compound **33a**: $C_{11}H_{14}O_3$, M_r = 194.22, colorless fragment (0.56 × 0.64 × 0.89 mm^3), orthorhombic, *Pbca* (No. 61), a = 10.4048(5), b = 10.6301(5), c = 17.5821(8) Å, V = 1944.7(2) Å^3, Z = 8, $D_{calcd.}$ = 1.327 g·cm^{-3}, F_{000} = 832, μ(Mo-K_α) = 0.786 mm^{-1}. Preliminary examination and data collection were carried out on a four-circle diffractometer (NONIUS CAD4) at the window of a sealed tube (NONIUS FR590) with graphite-monochromated Cu-K_α radiation (λ = 1.5480 Å). Data collection were performed at 293 K within the range of 5.05° < Θ < 70.60°. A total of 7810 reflections were collected and corrected for Lorentz, polarization and decay (113 h, −29.6%) effects. No correction for absorption effects was applied. After rejecting 777 systematically absent intensities and merging (R_{int} = 0.044), 1842 [1622: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 127 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions (riding model). Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_o^2)^2$ and converged with $R1$ = 0.0537 [$I_o > 2\sigma(I_o)$], $wR2$ = 0.1573 [all data], GOF = 1.051, all parameters, and shift/error < 0.001. The final difference-Fourier map shows no striking features ($\Delta\rho_{min./max.}$ = +0.28/−0.25 e·Å^{-3}).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC-239366 (**33a**) and CCDC-239365 (**21**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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