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Vinylogous Mukaiyama–Michael Reactions between 2-Silyloxyfurans and Cyclic Enones or Unsaturated Oxo Esters

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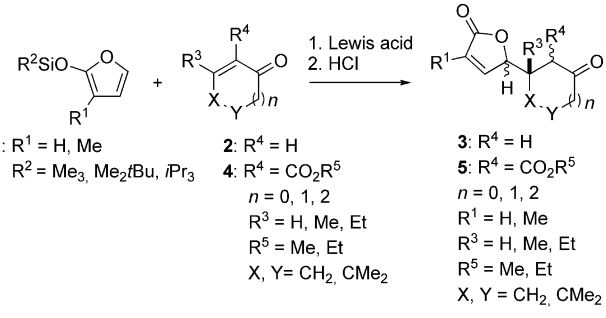
Lewis acid catalyzed vinylogous Mukaiyama–Michael (VMM) reactions between 2-(trialkylsilyloxy)furans **1** and α,β-unsaturated cyclic enones **2** or oxo esters **4** have been investigated. Both substrates proved to be useful Michael acceptors in the title reaction, giving the butenolides **3** and **5** in good yields. A comparative study between the α,β-unsaturated cyclic enones **2** and the oxo esters **4** as Michael acceptors showed better diasterecontrol with the latter class of compounds. In both series, crystal structures of the major isomers revealed *anti* relationships of newly formed stereogenic centers. From these data, two types of transition states could be proposed: an open TS with antiperiplanar orientation or a Diels–Alder-like TS with *exo* approach.

Introduction

Since the development of the Mukaiyama aldol reaction[1] and its vinylogous version (the addition of *O*-silyl dienolates),[2] the 2-(trialkylsilyloxy)furans **1** (Scheme 1) have emerged as attractive reagents for the introduction of γ-butenolides and γ-lactones, frameworks found in many natural products.[3] Lewis acid catalyzed vinylogous Mukaiyama aldol reactions with aldehydes have been extensively studied and have led to various strategies for diastereo- and enantioselective reactions.[2a] Because ketones are less reactive than aldehydes, vinylogous Mukaiyama aldol reactions between *O*-silylated dienolates and ketones have been limited to highly electrophilic ketones[4] and, more recently, cycloalkanones.[5]

Alternatively, vinylogous Mukaiyama–Michael (VMM) reactions between the 2-(trialkylsilyloxy)furans **1** and α,β-unsaturated carbonyl compounds have proven to be a valuable and complementary method for introducing γ-butenolides.[6] Since then, *acyclic Michael acceptors*, such as α,β-unsaturated imides,[6a–6f] aldehydes,[6g–6i] and ketones,[6j–6n] have been investigated for the development of stereocontrolled access to γ-butenolides.

In contrast, the use of *cyclic Michael acceptors* in VMM reactions with compounds **1** have attracted much less attention. *p*-Quinones[7] and *p*-quinols were found to be particularly useful Michael acceptors for the synthesis of benzofurans[8] and heterocyclic cage compounds,[9] respectively. Surprisingly, the use of α,β-unsaturated cyclic enones has been limited to 4-substituted cyclopent-2-en-1-ones[10,11] and cyclohex-2-en-1-one.[12] However, no detailed studies on the reactivity and the diastereoselectivity arising from reactions between silyloxyfurans and other cyclic enones **2** have been undertaken. Furthermore, to the best of our knowledge, no examples of VMM reactions between the silyloxyfurans **1** and the cyclic α,β-unsaturated oxo esters **4** have been reported. In view of the potential synthetic applications of the γ-butenolides **3** and **5** (Scheme 1),[3d,3e] here we report a study on the VMM reactions between the 2-(trialkylsilyloxy)furans **1** and the cyclic Michael acceptors **2** and **4**.



Scheme 1. VMM reactions between the 2-(trialkylsilyloxy)furans **1** and the cyclic α,β-unsaturated enones **2** or oxo esters **4**.

Results and Discussion

Studies on the Substituted Cycloalkenones 2 (R^4 = H)

Our investigation began with the identification of the optimal catalytic system in terms of efficiency and diastereoselectivity. For this purpose we chose the commercially

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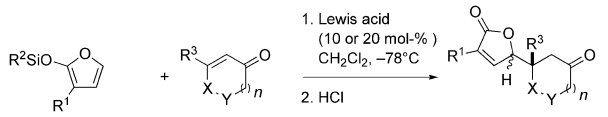
available cyclohex-2-en-1-one derivate **2a** as a Michael acceptor and 2-(trimethylsilyloxy)furan (TMSOF **1a**) as a γ-butenolide precursor (Scheme 2).



1a: R^1 = H; R^2 = Me_3
1b: R^1 = H; R^2 = Me_2tBu
1c: R^1 = H; R^2 = iPr_3
1d: R^1 = Me; R^2 = Me_2tBu
1e: R^1 = Me; R^2 = iPr_3

2a: n = 1; R^3 = H; X = Y = CH_2
2b: n = 0; R^3 = H; X = Y = CH_2
2c: n = 2; R^3 = H; X = Y = CH_2
2d: n = 1; R^3 = Me; X = Y = CH_2
2e: n = 1; R^3 = Me; X = CH_2; Y = CMe_2
2f: n = 1; R^3 = Et; X = Y = CH_2
2g: n = 1; R^3 = H; X = CMe_2; Y = CH_2

3a–g: R^1 = H
3a': R^1 = Me
n = 0, 1, 2
R^3 = H, Me, Et
X = CH_2, CMe_2
Y = CH_2, CMe_2

Scheme 2. VMM reactions between the 2-(trialkylsilyloxy)furans **1a–e** and the cyclic α,β-unsaturated enones **2a–g**.

We were delighted to find that the VMM reaction with the cyclohex-2-en-1-one **2a** afforded the γ-butenolide **3a** in good to excellent yields in the presence of a variety of Lewis acids (Table 1).[13] It is noteworthy that only the expected 1,4-addition product was observed in the crude mixture by ^{1}H NMR spectroscopy. Furthermore, the addition occurs exclusively at the 5-position in the furan ring.

Table 1. Screening of Lewis acid catalysts in the reaction between **1a** and **2a**.

Entry	Conditions	Yield [%][a]	*dr*[b]
1	$SnCl_4$, –78 °C	96	77:23
2	$Sn(OTf)_2$, –78 °C	95	73:27
3	$TiCl_4$, –78 °C	91	75:25
4	$Ti(OiPr)_4$, –78 °C to r.t.	n.r.[c]	–
5	$BF_3.OEt_2$, –78 °C	51	57:43
6	$Cu(OTf)_2$, –45 °C	77	70:30

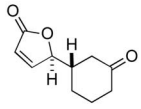
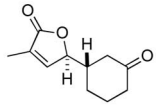
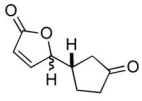
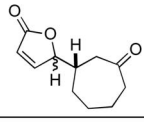
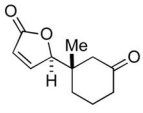
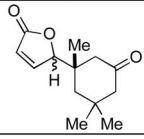
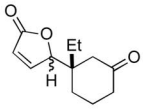
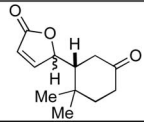
[a] Isolated yields. [b] Determined by HPLC on the crude mixtures. [c] No reaction.

Of the catalysts tested, $SnCl_4$ (10 mol-%) proved the most efficient, giving the butenolide **3a** in 96% yield and 77:23 diastereomeric ratio (Table 1, Entry 1). Other Lewis acids such as $Sn(OTf)_2$ and $TiCl_4$ also efficiently catalyzed the formation of the γ-butenolide **3a** (Entries 2–3) but with slightly lower stereocontrol. In contrast, the less reactive $Ti(OiPr)_4$ did not give any of the desired products, even at room temperature (Entry 4). Boron trifluoride–diethyl ether gave only poor diastereoselectivity and a moderate yield (Entry 5). Finally, copper(II) triflate was examined (Entry 6), but the reaction had to be carried out at –45 °C for completion to be reached. The γ-butenolide **3a** was isolated in good yield but with a lower selectivity than in the case of $SnCl_4$.

It has been reported that a single-electron transfer (SET) mechanism may operate in Mukaiyama–Michael reactions under $SnCl_4$ catalysis conditions, leading to a less stereoselective pathway.[14] To prevent such a mechanism, a test reaction between **1a** and **2a** was carried out in the presence of 1,4-dinitrobenzene (1 equiv.) and $SnCl_4$ (10 mol-%). No improvement in selectivity was observed even in the presence of this strong electron acceptor, indicating that a SET mechanism should not be operative.

In addition, Otera et al. have shown that Mukaiyama–Michael reactions of ketene silyl acetals incorporating bulky silyloxy groups produce high selectivities.[15] The nature of the silyl group was thus modified through the use of a 2-(*tert*-butyldimethylsilyl) group [i.e., TBSOF **1b**] (Table 2, Entry 2), which gave a higher diastereoselectivity than TMSOF **1a**. Use of 2-(triisopropylsilyloxy)furan (**1c**), however, led to a significant decrease in selectivity (Table 2, Entry 3).

Table 2. Vinylogous Mukaiyama–Michael reactions with the cyclic enones **2**.

Entry	Silyloxyfuran	Enone	Product	Yield[a] [%]	*dr*
1	**1a**	**2a**	 **3a**[c]	96	77:23[b]
2	**1b**	**2a**		86[d]	84:16[b]
3	**1c**	**2a**		90	60:40[b]
4	**1d**	**2a**	 **3a'**[c]	95[d]	76:24[b]
5	**1e**	**2a**		97	60:40[b]
6	**1b**	**2b**	 **3b**[e]	89[d]	69:31[b]
7	**1b**	**2c**	 **3c**[e]	85[d]	84:16[f]
8	**1b**	**2d**	 **3d**[c]	94[d]	92:8[b]
9	**1b**	**2e**	 **3e**[e]	42[d]	88:12[f]
10	**1b**	**2f**	 **3f**[e]	53[d]	88/12[f]
11	**1a**	**2g**	 **3g**[e]	62[g]	77:23[b]
12	**1b**	**2g**		90[d]	53:47[b]

[a] Isolated yields. [b] Determined by HPLC on the crude mixtures. [c] Major isomer, relative configuration determined by X-ray structure analysis (see Figure 1). [d] $SnCl_4$ (0.2 equiv.) was used. [e] The relative configurations of the major isomers were not determined. [f] Determined by ^{1}H NMR spectroscopy on the crude mixtures. [g] An 18% yield of the 1,2-addition product was isolated (*dr* = 53:47).

With the optimized conditions to hand, we studied the influence of a substituent on the silyloxyfuran component. The TBSOF **1d**, bearing a methyl group at C-3 (R^1 = Me), was thus investigated and found to furnish the γ-butenolide

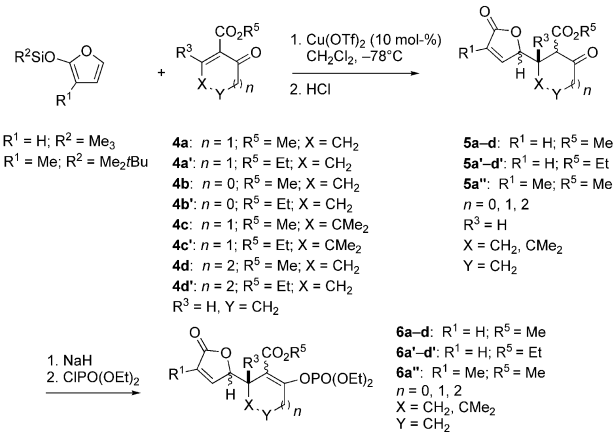
3a′ in excellent isolated yield, but with slightly lower diastereoselectivity (Table 2, Entry 4). As before, increasing the size of the silyl group, in the shape of the (triisopropylsilyloxy)furan **1e**, did not improve the diastereoselectivity (Table 2, Entry 5).

A series of cyclic enones was then examined in these VMM reactions. The influence of the enone ring size on stereoselectivity was examined with cyclopent-2-en-1-one (**2b**). The corresponding 1,4-adduct **3b** was obtained in good yield, but with only modest selectivity (Table 2, Entry 6).[16] Cyclohept-2-en-1-one (**2c**) also reacted efficiently with **1b** with good diastereocontrol (Table 2, Entry 7). It is worth mentioning that no 1,2-addition products were observed with these two cyclic enones **2b** and **2c**.

Various substituted cyclohex-2-en-1-ones – in particular, the cyclic enones **2d**–**f** bearing C-3 substituents (R^2 = Me, Et) – were then investigated. Interestingly, the use of 3-methylcyclohex-2-en-1-one (**2d**) allowed the formation of **3d**, containing a quaternary stereogenic center, with excellent selectivity (Table 2, Entry 8). In a similar way, the VMM reactions between the silyloxyfuran **1b** and isophorone (**2e**) (Table 2, Entry 9) or 3-ethylcyclohex-2-en-1-one (**2f**)[17] (Table 2, Entry 10) led to the corresponding γ-butenolides **3e** or **3f**, respectively, with good stereocontrol. Finally, the 4,4′-dimethylcyclohex-2-en-1-one (**2g**)[18] reacted with **1a** to give the Michael addition product **3g** in a 77:23 ratio, but with a small amount of aldol adduct as well (Table 2, Entry 11). In this case, the use of a bulkier silyl group on the furan derivative (i.e., **1b**) suppressed the aldol side reaction, but dramatically decreased the diastereoselectivity (Table 2, Entry 12).

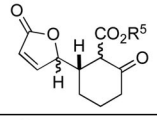
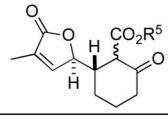
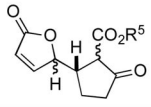
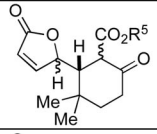
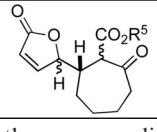
Studies on the Cyclic α,β-Unsaturated Oxo Esters 4 (R^4 = CO_2R^5)

Several examples of Lewis acid catalyzed Michael addition reactions with cyclic α,β-unsaturated oxo esters have been reported.[14a,19] To the best of our knowledge, however, no examples of VMM reaction between the silyloxyfurans **1** and the cyclic α,β-unsaturated oxo esters **4** have been reported. We thus turned our attention to a study of the VMM reactions between the silyloxyfurans **1** and the cyclic α,β-unsaturated oxo esters **4** (Scheme 3). Before we began our investigation, we realized that VMM reactions with the Michael acceptors **4** would form the β-oxo esters **5**, each



Scheme 3. Vinylogous Mukaiyama–Michael reactions between the 2-(trialkylsilyloxy)furans **1** and the cyclic α,β-unsaturated oxo esters **4**.

Table 3. Vinylogous Mukaiyama–Michael reactions with the cyclic α,β-unsaturated oxo esters **4**.

Entry	Silyloxyfuran	Oxo ester	Product	R^5	Yield[a] [%]	*dr*[b]
1	**1a**	**4a**		Me (**5a**)	83	95:5
2	**1a**	**4a'**		Et (**5a'**)	86	95:5
3	**1d**	**4a**		Me (**5a''**)[c]	70	>95:<5
4	**1a**	**4b**		Me (**5b**)	47	81:19
5	**1a**	**4b'**		Et (**5b'**)	65	85:15
6	**1a**	**4c**		Me (**5c**)	66	85:15
7	**1a**	**4c'**		Et (**5c'**)	69	89:11
8	**1a**	**4d**		Me (**5d**)	83	84:16
9	**1a**	**4d'**		Et (**5d'**)	78	84:16

[a] Isolated yields. [b] Determined by NMR spectroscopy on the corresponding phosphates **6** (see Experimental Section). [c] Major isomer, relative configuration determined by X-ray structure analysis (see Figure 1).

containing three stereogenic centers and potentially existing as a mixture of four diastereomers. Furthermore, in solution, the β-oxo esters **5** might exist in equilibrium with their enol forms, leading to two more diastereomers. Faced with the expected complexity of ^{1}H NMR spectra of compounds **5**, we thus decided to convert them into stable vinyl phosphates **6**, which should be more amenable to diastereomeric ratio estimation by ^{1}H NMR spectroscopy.

A series of α,β-unsaturated oxo esters (i.e., **4a**–**d** and **4a′**–**d′**) were synthesized to allow comparison of the results with those obtained with the analogous cyclic enones **2**.[20] Two sets of cyclic α,β-unsaturated oxo esters (methyl and ethyl esters) were tested as well, for comparison of the influence of the R^5 group on the diastereoselectivity. Copper(II) trifluoromethanesulfonate was chose in this study, because the doubly activated Michael acceptor was expected to be reactive enough without use of a strong Lewis acid such as $SnCl_4$. Moreover, the use of a copper(II) salt might allow the development of an asymmetric version of the reaction.[14a,19a,19b,21]

The results of the reactions between the silyloxyfurans **1a** and **1d** and the α,β-unsaturated ester **4a**–**d** and **4a′**–**d′**, catalyzed by $Cu(OTf)_2$ (10 mol-%) at –78 °C in dichloromethane, are given in Table 2. Most substrate combinations afforded the VMM products **5** with higher diastereoselectivities than had been obtained with the cycloalkenones **2a**–**g** (Table 2). The butenolides **5a** and **5a′**, for instance, were both obtained with excellent stereocontrol, whatever the nature of the R^5 group (Table 3, Entries 1, 2). In turn, the silyloxyfuran **1d**, which had given poor selectivity with the enone **2a** (Table 2, Entry 4), only gave one stereoisomer (i.e., **5a′′**) with the oxo ester **4a** (Table 3, Entry 3). Introduction of an ester function on cyclopentyl (**4b** and **4b′**, Table 3, Entries 4–5) and 4,4-dimethylcyclohexyl rings (**4c** and **4c′**, Table 3, Entries 6, 7) also improved the diastereoselectivities. Interestingly, in these examples, ethyl esters gave better results than their methyl counterparts. In contrast, no changes were observed in the cases of the seven-membered ring **4d** and **4d′**, whatever the nature of R^5 (Table 3, Entries 8,9).

Relative Stereochemistries of the Major Isomers

The relative configurations of the major diastereomers of four of our γ-butenolides (i.e., **3a**, **3a′**, **3d**, and **5a′′**) have been established by X-ray crystallographic analysis (Figure 1).[22]

In each case, the major isomer has the *anti* relative configuration. These data revealed that the introduction of a methyl group at the 3-position of the silyloxyfuran (compare **3a** and **3a′**) only affects the level of diastereocontrol (Table 2, Entries 2, 4), without changing the sense of the diastereoselectivity. The same conclusion can be drawn with **3a** and **3d**, the latter bearing a methyl group at the C-3 atom of the enone (Table 2, Entries 2, 8). Compounds **3a′** (Table 2, Entry 4) and **5a′′** (Table 3, Entry 3) also have the same relative configuration. These results show that the introduction of a second chelating group is beneficial in terms of increasing the diastereoselectivity and leads to the same major isomer.

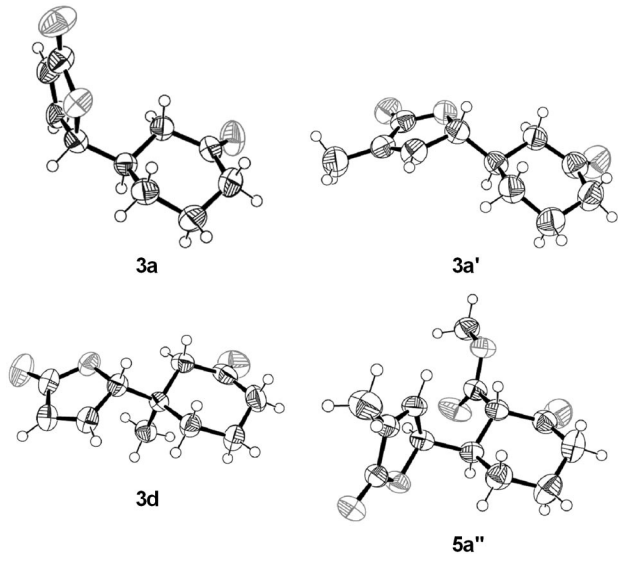


Figure 1. ORTEP representations of the major isomers of **3a**, **3a′**, **3d**, and **5a′′**.

Proposed Transition States

Lewis acid coordination with cyclic ketones is usually a nonselective process, because the participating lone pairs are positioned in similar steric and electronic environments (Figure 2). The lack of differentiation between $\mathbf{A_1}$ and $\mathbf{A_2}$ could be a possible explanation for the modest diastereoselectivity observed with cyclohex-2-en-1-one (**2a**). In contrast, two-point binding of the unsaturated β-oxo ester to the Lewis acid (i.e., **B**) is presumed, because this affords the most reactive of the possible catalyst–substrate complexes. In this chelate **B**, a high level of lone-pair differentiation is achieved. The metal center is then positioned close to the intracyclic double bond, which is probably a key feature for producing high diastereoselectivity as observed with substrates **4a** and **4a′**.

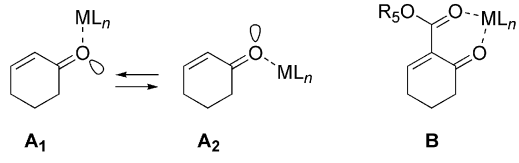


Figure 2. Coordination modes.

From the X-ray data, the *anti* relative configurations of the major isomers in the oxo ester series can thus be explained by transition states as depicted in Figure 3. At this stage of the study, we cannot conclude with certainty whether these additions proceed through an open geometry (**TS1** vs. **TS2**) or a Diels–Alder-type transition state (**TS3** vs. **TS4**).

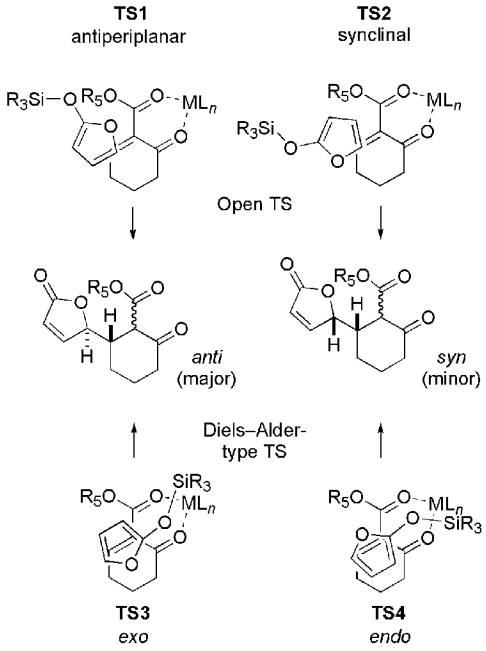


Figure 3. Proposed transition states.

Open transition states (**TS1** vs. **TS2**) have been proposed in order to account for the diastereocontrol in vinylogous Mukaiyama aldol reactions[23] and VMM reactions with cyclic acceptors.[8] In our case, an *antiperiplanar* (**TS1**) approach of the silyloxyfuran to the cyclic enone might explain the formation of the major *anti* isomers. **TS3** and **TS4**, reminiscent of a Diels–Alder-type transition state, cannot be excluded. The major *anti* isomers would then arise from an *exo* approach (**TS3**) of the silyloxyfuran to the cyclic enone. Such *exo* selectivity has previously been observed in studies of high-pressure-promoted Diels–Alder reactions involving cycloalkenones and silyloxyfurans[11] or 3-(methylsulfanyl)furan.[24] In our case, no Diels–Alder product was observed prior to hydrolysis of the crude mixture with HCl (1 M). Furthermore, no evidence of any Diels–Alder product was observed by ^{1}H NMR spectroscopy.[25] Further studies directed towards understanding of the origin and the sense of the stereocontrol are continuing.[26]

Conclusions

We have shown that vinylogous Mukaiyama–Michael reactions between the silyloxyfurans **1** and the cyclic enones **2** or the α,β-unsaturated cyclic oxo esters **4** constitute a valuable method for introducing γ-butenolides onto cycloalkene systems. In general, only 1,4-adducts were obtained, with the major diastereomers having *anti* relative configurations. X-ray data from this preliminary study revealed that both the six-membered cyclic enones **2** and the oxo esters **4** lead to the same major diastereomers, with better diastereocontrol in the latter case. At this stage it is still unclear whether the major isomers arise from open or Diels–Alder-like transition states, and further studies to address this point are currently in progress.

Experimental Section

General: All reactions were carried out under argon in dry solvents unless noted otherwise. Reactions were monitored by thin-layer chromatography on Merck silica gel plates (60 F_{254}) with a fluorescent indicator. Yields refer to chromatographically pure or crystalline compounds. All commercially available reagents were used without further purification. All solvents were dried and distilled before use: CH_2Cl_2 was distilled from P_2O_5, THF was distilled from sodium/benzophenone, methanol and ethanol were distilled from Mg/I_2, and NEt_3 was distilled from KOH. All separations were carried out under flash-chromatographic conditions on silica gel (Redi Sep prepacked column, 230–400 mesh) at medium pressure (20 psi) with use of a CombiFlash Companion. All new compounds gave satisfactory spectroscopic analyses (IR, ^{1}H NMR, ^{13}C NMR, HRMS). NMR spectra were determined with Bruker Avance 300 or Bruker Avance 500 instruments. ^{1}H NMR spectra are reported in parts per million (δ) relative to residual solvent peak. Data for ^{1}H are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, dd = double doublet, m = multiplet), coupling constant in Hz, and integration. ^{13}C NMR spectra were obtained with a Bruker Avance 300 (75.5 MHz) spectrometer and are reported in parts per million (δ) relative to the residual solvent peak. HRMS spectra were obtained with an ESI TOF Thermoquest AQA Navigator spectrometer. Infrared (IR) ($\tilde{\nu}$, cm^{-1}) spectra were recorded with a Fourier Perkin–Elmer Spectrum BX FT-IR instrument. Melting points were measured in capillary tubes and are uncorrected. Compounds **2a**–**e** and **2g** are commercially available. Compounds **2f**, **4a**–**d**, and **4′a**–**d** were prepared according to a reported procedure.[18]

General Procedure A. Lewis-Acid-Catalyzed Mukaiyama–Michael Additions to Cyclic Enones: The silyloxyfuran (1.3 equiv.) was added at –78 °C to a solution of the enone (1 equiv.) in dichloromethane (5 mL mmol^{-1}). A solution of the Lewis acid (0.1 equiv. or 0.2 equiv., 1 M in DCM) was then added at –78 °C, and the reaction mixture was stirred at this temperature until no more enone remained (TLC). The reaction was quenched with HCl solution (1 M) at –78 °C and the mixture allowed to warm to room temperature. It was diluted with water, and the aqueous layer was extracted with EtOAc (×3). The organic layer was dried with Na_2SO_4, filtered, and then concentrated under reduced pressure. The resulting residue was treated with THF/HCl (1 N) (1:1, v/v, 10 mL mmol^{-1}) at room temperature for 30 min. The reaction mixture was diluted with H_2O, extracted with EtOAc (×3), and dried with Na_2SO_4, and the solvent was evaporated. The crude mixture was purified through silica gel to afford the title compound.

General Procedure B. Cu-Catalyzed Mukaiyama–Michael Additions to Activated Cyclic Unsaturated Oxo Esters: $Cu(OTf)_2$ (0.1 equiv.) was suspended in CH_2Cl_2 (38 mL mmol^{-1}) under argon. A solution of enone (1 equiv.) in CH_2Cl_2 (0.8 mL mmol^{-1}) was added at room temp., and the mixture became homogeneous. The solution was cooled to –78 °C, and the silyloxyfuran (1.2 equiv.) was added. The reaction was monitored by TLC (usually 2–3 h). The reaction was quenched with aqueous saturated NH_4Cl at –78 °C and the mixture allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layers were dried with Na_2SO_4, filtered, and concen-

trated under reduced pressure. The resulting residue was treated by THF/HCl (1 N) (1:1, v/v, 10 mL mmol^{-1}) at room temperature for 30 min. The reaction mixture was diluted with H_2O, extracted with EtOAc (× 3), dried with Na_2SO_4, and filtered, and the solvent was evaporated. The crude mixture was purified through silica gel to afford the title compound.

General Procedure C. Phosphate Formation: A solution of the β-oxo ester (1 equiv.) in THF (4.5 mL mmol^{-1}) was added at 0 °C to a suspension of NaH (95%, 1.1 equiv.) in THF (4.5 mL mmol^{-1}). After the mixture had been kept at this temperature for 30 min, diethyl chlorophosphate (1.1 equiv.) was added, and the mixture was further stirred at 0 °C for 30 min. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (× 3). The organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography to afford the title compound.

5-(3-Oxocyclohexyl)furan-2(5*H*)-one (3a): This compound was prepared according to the General Procedure A from cyclohex-2-en-1-one (**2a**, 0.1 mL, 1.03 mmol) and 2-(*tert*-butyldimethylsilyloxy)-furan (**1b**, 285.9 mg, 1.44 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.21 mL, 0.21 mmol) in DCM (5 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a white solid (80.4 mg, 90%); m.p. 53–54 °C (major diastereomer). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 84:16): major: δ = 7.41 (dd, J = 1.5, 5.7 Hz, 1 H, C*H*=CH–CO), 6.18 (dd, J = 2.0, 5.8 Hz, 1 H, CH=C*H*–CO), 5.03 (m, 1 H, C*H*O), 2.44–2.36 (m, 1 H), 2.33–2.24 (m, 2 H), 2.24–2.18 (m, 1 H), 2.18–2.10 (m, 2 H), 1.97 (m, 1 H), 1.79–1.61 (m, 2 H) ppm; minor: δ = 7.44 (dd, J = 1.5, 5.8 Hz, 1 H, C*H*=CH–CO), 6.19 (dd, J = 2.0, 5.9 Hz, 1 H, CH=C*H*–CO), 4.29 (m, 1 H, C*H*O), 2.48 (m, 1 H), 1.89 (m, 1 H), 1.51 (m, 1 H) ppm, other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 209.2 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 154.1 (CH, *C*H=CH–CO), 122.3 (CH, CH=*C*H–CO), 83.4 (CH, *C*HO), 41.4 (CH_2), 41.0 (CH, *C*HCHO), 40.8 (CH_2), 27.5 (CH_2), 24.5 (CH_2) ppm; minor: δ = 209.1 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 154.0 (CH, *C*H=CH–CO), 122.4 (CH, CH=*C*H–CO), 85.2 (CH, *C*HO), 43.7 (CH_2), 41.3 (CH, *C*HCHO), 40.8 (CH_2), 25.3 (CH_2), 24.1 (CH_2) ppm. IR (film): $\tilde{\nu}$ = 3100, 2958, 2935, 1746, 1729, 1705 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 203 (100) [M + Na]. HRMS: calcd. for $C_{10}H_{12}NaO_3$ 203.0694; found 203.0676.

3-Methyl-5-(3-oxocyclohexyl)furan-2(5*H*)-one (3a′): This compound was prepared according to the General Procedure A from cyclohex-2-en-1-one (**2a**, 0.1 mL, 0.986 mmol) and 2-(*tert*-butyldimethylsilyloxy)-3-methylfuran (**1c**, 293 mg, 1.38 mmol) in the presence of tin(IV) chloride solution (0.2 mL) in DCM (5 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 5:5) to afford a white solid (181.9 mg, 95%); m.p. 73–74 °C (major diastereomer). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 76:24): major: δ = 6.98 (m, 1 H, C*H*=CH–CO), 4.88 (m, 1 H, C*H*O), 2.40 (m, 1 H), 2.32–2.23 (m, 2 H), 2.21–2.08 (m, 3 H), 1.96 (m, 1 H), 1.93 (s, 3 H, CH_3), 1.77–1.62 (m, 2 H) ppm; minor: δ = 7.02 (m, 1 H, C*H*=CH–CO), 4.76 (m, 1 H, C*H*O), 2.48–2.35 (m, 3 H), 2.31 (m, 1 H), 2.19–2.09 (m, 2 H), 1.89 (m, 1 H), 1.93 (s, 3 H, CH_3), 1.65 (m, 1 H), 1.49 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 209.6 (Cq, *C*=O), 173.6 (Cq, O–*C*=O), 146.3 (CH, *C*H=CH–CO), 131.2 (Cq, CH=*C*CH_3–CO), 83.2 (CH, *C*HO), 41.6 (CH_2), 41.5 (CH, *C*HCHO), 41.0 (CH_2), 27.7 (CH_2), 24.7 (CH_2), 10.6 (CH_3) ppm; minor: δ = 209.3 (Cq, *C*=O), 173.5 (Cq, O–*C*=O), 146.2 (CH, *C*H=CH–CO), 131.1 (Cq, CH=*C*CH_3–CO), 83.1 (CH, *C*HO), 43.9 (CH_2), 41.8 (CH, *C*HCHO), 41.1 (CH_2), 25.6 (CH_2), 24.3 (CH_2), 10.5 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3081, 2927, 1746, 1705 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 217 (100) [M + Na]. HRMS: calcd. for $C_{11}H_{14}NaO_3$ 217.0841; found 217.0831.

5-(3-Oxocyclopentyl)furan-2(5*H*)-one (3b): This compound was prepared according to the General Procedure A from cyclopent-2-en-1-one (**2b**, 70 μL, 0.819 mmol) and 2-(*tert*-butyldimethylsilyloxy)-furan (**1b**, 227.3 mg, 1.15 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.16 mL, 0.16 mmol) in DCM (4 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 5:5) to afford a colorless oil (120.9 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, ratio 69:31): major: δ = 7.47 (dd, J = 1.4, 5.7 Hz, 1 H, C*H*=CH–CO), 6.20 (dd, J = 1.9, 5.7 Hz, 1 H, CH=C*H*–CO), 5.08 (m, 1 H, C*H*O), 2.55 (m, 1 H), 2.45–2.32 (m, 2 H), 2.26–2.16 (m, 2 H), 2.04–1.89 (m, 2 H) ppm; minor: δ = 7.44 (dd, J = 1.4, 5.7 Hz, 1 H, C*H*=CH–CO), 6.21 (dd, J = 1.9, 5.8 Hz, 1 H, CH=C*H*–CO), 5.08 (m, 1 H, C*H*O), 2.52 (m, 1 H), 2.46–2.35 (m, 2 H), 2.25–2.15 (m, 3 H), 1.76 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 216.1 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 154.3 (CH, *C*H=CH–CO), 122.5 (CH, CH=*C*H–CO), 84.8 (CH, *C*HO), 39.3 (CH, *C*HCHO), 39.1 (CH_2), 37.7 (CH_2), 25.3 (CH_2) ppm; minor: 216.0 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 154.3 (CH, *C*H=CH–CO), 122.6 (CH, CH=*C*H–CO), 84.5 (CH, *C*HO), 40.3 (CH_2), 39.4 (CH, *C*HCHO), 37.6 (CH_2), 24.1 (CH_2) ppm. IR (film): $\tilde{\nu}$ = 3090, 2905, 1730 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 189 (100) [M + Na]. HRMS: calcd. for $C_9H_{10}NaO_3$ 189.0528; found 189.0523.

5-(3-Oxocycloheptyl)furan-2(5*H*)-one (3c): This compound was prepared by the General Procedure A from cyclohept-2-en-1-one (**2c**, 0.1 mL, 0.717 mmol) and 2-(*tert*-butyldimethylsilyloxy)furan (**1b**, 198.3 mg, 1 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.14 mL, 0.14 mmol) in DCM (4.4 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (119 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$, ratio 84:16): δ = 7.45 (dd, J = 1.3, 5.7 Hz, 1 H *min*, C*H*=CH–CO), 7.41 (dd, J = 1.2, 5.7 Hz, 1 H *maj*, C*H*=CH–CO), 6.19 (m, 1 H *maj* + 1 H *min*, CH=C*H*–CO), 4.98 (m, 1 H *maj*, C*H*O), 4.95 (m, 1 H *min*, C*H*O), 2.59–2.34 (m, 4 H *maj* + 4 H *min*), 2.13 (m, 1 H *maj* + 1 H *min*), 2.03 (m, 1 H *maj* + 1 H *min*), 1.93 (m, 2 H *maj* + 2 H *min*), 1.60 (m, 1 H *maj* + 1 H *min*), 1.40 (m, 2 H *maj* + 2 H *min*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 211.8 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 154.0 (CH, *C*H=CH–CO), 122.6 (CH, CH=*C*H–CO), 85.9 (CH, *C*HO), 43.4 (2 × CH_2), 38.4 (CH, *C*HCHO), 31.0 (CH_2), 27.9 (CH_2), 23.8 (CH_2) ppm; minor: δ = 211.9 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 154.0 (CH, *C*H=CH–CO), 122.7 (CH, CH=*C*H–CO), 86.2 (CH, *C*HO), 45.0 (CH_2), 43.8 (CH_2), 38.3 (CH, *C*HCHO), 32.3 (CH_2), 28.1 (CH_2), 23.7 (CH_2) ppm. IR (film): $\tilde{\nu}$ = 3091, 2927, 2858, 1745, 1693 cm^{-1}. MS (ESI+): *m*/*z* (%) = 217 (100) [M + Na]. HRMS: calcd. for $C_{11}H_{14}NaO_3$ 217.0841; found 217.0847.

5-(1-Methyl-3-oxocyclohexyl)furan-2(5*H*)-one (3d): This compound was prepared according to the General Procedure A from 3-methylcyclohex-2-en-1-one (**2d**, 0.07 mL, 0.60 mmol) and 2-(*tert*-butyldimethylsilyloxy)furan (**1b**, 168 mg, 0.85 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.12 mL, 0.12 mmol) in DCM (3 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 5:5) to afford a white solid (110 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$, ratio 92:8): major: δ = 7.46 (dd, J = 1.5, 5.8 Hz, 1 H, C*H*=CH–CO), 6.21 (dd, J = 2.0, 5.8 Hz, 1 H, CH=C*H*–CO), 4.82 (dd, J = 1.8, 1.8 Hz, 1 H, C*H*O), 2.40–2.24 (m, 3 H), 2.10–1.96 (m, 3 H), 1.88 (m, 1 H), 1.64 (m, 1 H), 0.95 (s, 3 H, CH_3) ppm; minor: δ = 4.78 (m, 1 H, C*H*O), 0.93 (s, 3 H, CH_3) ppm; other signals masked by major isomer. ^{13}C NMR

(75 MHz, $CDCl_3$): major: δ = 209.6 (Cq, *C*=O), 172.2 (Cq, O–*C*=O), 152.9 (CH, *C*H=CH–CO), 123.2 (CH, CH=*C*H–CO), 89.3 (CH, *C*HO), 47.8 (CH_2), 42.3 (Cq, *C*CH_3), 40.5 (CH_2), 32.7 (CH_2), 21.2 (CH_2), 20.1 (CH_3) ppm; minor: δ = 209.7 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 152.8 (CH, *C*H=CH–CO), 123.1 (CH, CH=*C*H–CO), 88.7 (CH, *C*HO), 49.9 (CH_2), 42.2 (Cq, *C*CH_3), 31.0 (CH_2), 21.1 (CH_2) ppm; other signals masked by major isomer. IR (film): $\tilde{\nu}$ = 3100, 2950, 1742, 1697 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 217 (100) [M + Na]. HRMS: calcd. for $C_{11}H_{14}NaO_3$ 217.0840; found 217.0841. M.p. 89–92 °C (major diastereomer).

5-(1,3,3-Trimethyl-5-oxocyclohexyl)furan-2(5*H*)-one (3e): This compound was prepared according to the General Procedure A from isophorone (**2e**, 70 mg, 0.506 mmol) and 2-(*tert*-butyldimethylsilyloxy)furan (**1b**, 130 mg, 0.66 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.1 mL, 0.1 mmol) in DCM (2.5 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (46.3 mg, 42%). ^1H NMR (300 MHz, $CDCl_3$, ratio 88:12): major: δ = 7.45 (dd, *J* = 1.6, 6.0 Hz, 1 H, C*H*=CH–CO), 6.20 (dd, *J* = 2.1, 5.9 Hz, 1 H, CH=C*H*–CO), 4.78 (dd, *J* = 1.7, 2.0 Hz, 1 H, C*H*O), 2.30 (d, *J* = 12.9 Hz, 1 H), 2.25 (d, *J* = 12.3 Hz, 1 H), 2.14 (dt, *J* = 13.7, 1.7 Hz, 1 H), 2.02 (dt, *J* = 13.7, 1.7 Hz, 1 H), 1.95 (d, *J* = 14.2 Hz, 1 H), 1.51 (dt, *J* = 14.2, 1.7 Hz, 1 H), 1.09 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3) ppm; minor: δ = 7.43 (dd, *J* = 1.5, 5.8 Hz, 1 H, C*H*=CH–CO), 6.20 (dd, *J* = 2.0, 5.9 Hz, 1 H, CH=C*H*–CO), 4.70 (dd, *J* = 1.7, 2.0 Hz, 1 H, C*H*O), 2.62 (d, *J* = 13.5 Hz, 1 H), 1.66 (d, *J* = 14.2 Hz, 1 H), 1.31 (dt, *J* = 12.3, 1.5 Hz, 1 H), 1.07 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 210.0 (Cq, *C*=O), 172.3 (Cq, O–*C*=O), 152.8 (CH, *C*H=CH–CO), 123.5 (CH, CH=*C*H–CO), 89.8 (CH, *C*HO), 53.5 (CH_2), 47.1 (CH_2), 47.8 (CH_2), 42.2 (Cq, *C*CH_3), 35.5 [Cq, *C*$(CH_3)_2$], 33.7 (CH_3), 29.1 (CH_3), 22.5 (CH_3) ppm; minor: δ = 172.4 (Cq, O–*C*=O), 152.9 (CH, *C*H=CH–CO), 123.5 (CH, CH=*C*H–CO), 53.7 (CH_2), 48.9 (CH_2), 43.4 (CH_2), 41.9 (Cq, *C*CH_3), 35.4 [Cq, *C*$(CH_3)_2$], 33.3 (CH_3), 29.2 (CH_3), 23.3 (CH_3) ppm; other signals masked by the major isomer. IR (film): $\tilde{\nu}$ = 3092, 2956, 1748, 1707 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 245 (100) [M + Na]. HRMS: calcd. for $C_{13}H_{18}NaO_3$ 245.1154; found 245.1155.

5-(1-Ethyl-3-oxocyclohexyl)furan-2(5*H*)-one (3f): This compound was prepared according to the General Procedure A from 3-ethylcyclohex-2-en-1-one (**2f**, 70 mg, 0.564 mmol) and 2-(*tert*-butyldimethylsilyloxy)furan (**1b**, 145 mg, 0.733 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.11 mL, 0.11 mmol) in DCM (2.8 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (62.4 mg, 53%). ^1H NMR (300 MHz, $CDCl_3$, ratio 88:12): major: δ = 7.46 (dd, *J* = 1.4, 5.8 Hz, 1 H, C*H*=CH–CO), 6.16 (dd, *J* = 2.1, 5.9 Hz, 1 H, CH=C*H*–CO), 4.95 (dd, *J* = 1.6, 2.0 Hz, 1 H, C*H*O), 2.28 (m, 2 H), 2.20 (m, 1 H), 2.02 (m, 5 H), 1.50 (m, 1 H), 1.36 (m, 1 H), 0.91 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3) ppm; minor: δ = 7.50 (dd, *J* = 1.5, 5.8 Hz, 1 H, C*H*=CH–CO), 6.18 (m, 1 H, CH=C*H*–CO), 4.91 (dd, *J* = 1.8, 1.9 Hz, 1 H, C*H*O), 0.89 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 210.2 (Cq, *C*=O), 172.5 (Cq, O–*C*=O), 153.2 (CH, *C*H=CH–CO), 123.2 (CH, CH=*C*H–CO), 87.2 (CH, *C*HO), 46.3 (CH_2), 44.8 (Cq, *C*CH_2CH_3), 40.6 (CH_2), 29.1 (CH_2), 26.9 (CH_2), 20.9 (CH_2), 7.65 (CH_3, CH_2CH_3) ppm; minor: δ = 153.3 (CH, *C*H=CH–CO), 86.6 (CH, *C*HO), 47.0 (CH_2), 44.6 (Cq, *C*CH_2CH_3), 28.5 (CH_2), 26.7 (CH_2) ppm; other signals masked by the major isomer. IR (film): $\tilde{\nu}$ = 3090, 2941, 2881, 1746, 1702 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 231 (100) [M + Na]. HRMS: calcd. for $C_{12}H_{16}NaO_3$ 231.0997; found 231.0995.

5-(2,2-Dimethyl-5-oxocyclohexyl)furan-2(5*H*)-one (3g): This compound was prepared according to the General Procedure A from 4,4-dimethylcyclohex-2-en-1-one (**2g**, 0.1 mL, 0.737 mmol) and 2-(trimethylsilyloxy)furan (**1a**, 0.16 mL, 0.96 mmol) in the presence of tin(IV) chloride solution (1 M in DCM, 0.076 mL, 0.076 mmol) in DCM (3.8 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 5:5) to afford **3g** as a white solid (95.2 mg, 62%) and the 1,2-addition product as a colorless oil (21.1 mg, 18%). ^1H NMR (300 MHz, $CDCl_3$, ratio 77:23): major: δ = 7.47 (dd, *J* = 1.5, 5.8 Hz, 1 H, C*H*=CH–CO), 6.12 (dd, *J* = 2.1, 5.8 Hz, 1 H, CH=C*H*–CO), 5.12 (m, 1 H, C*H*O), 2.46–2.36 (m, 1 H), 2.35–2.29 (m, 1 H), 2.28–2.21 (m, 1 H), 2.20–2.11 (m, 2 H), 1.73 (m, 2 H), 1.20 (s, 6 H, 2 × CH_3) ppm; minor: δ = 7.30 (dd, *J* = 1.6, 5.7 Hz, 1 H, C*H*=CH–CO), 6.10 (dd, *J* = 2.1, 5.7 Hz, 1 H, CH=C*H*–CO), 5.32 (m, 1 H, C*H*O), 2.00–1.86 (m, 2 H), 1.77 (m, 1 H), 1.58 (m, 1 H), 1.17 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3) ppm, other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 209.0 (Cq, *C*=O), 171.9 (Cq, O–*C*=O), 154.4 (CH, *C*H=CH–CO), 122.8 (CH, CH=*C*H–CO), 83.4 (CH, *C*HO), 48.9 (CH, *C*HCHO), 40.4 (CH_2), 38.8 (CH_2), 37.5 (CH_2), 32.4 [Cq, *C*$(CH_3)_2$], 29.5 (CH_3), 20.9 (CH_3) ppm; minor: δ = 209.8 (Cq, *C*=O), 172.7 (Cq, O–*C*=O), 156.0 (CH, *C*H=CH–CO), 122.1 (CH, CH=*C*H–CO), 81.7 (CH, *C*HO), 48.0 (CH, *C*HCHO), 39.8 (CH_2), 37.7 (CH_2), 35.6 (CH_2), 32.8 [Cq, *C*$(CH_3)_2$], 28.7 (CH_3), 21.7 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3117, 2950, 1748, 1733, 1702 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 231 (100) [M + Na]. HRMS: calcd. for $C_{12}H_{16}NaO_3$ 231.0997; found 231.0986. 1,2-Addition product 5-(1-hydroxy-4,4-dimethylcyclohex-2-enyl)furan-2(5*H*)-one: ^1H NMR (300 MHz, $CDCl_3$, ratio 53:47): δ = 7.49 (m, 1 H *maj* + 1 H *min*, C*H*=CH–CO), 6.19 (m, 1 H *maj* + 1 H *min*, CH=C*H*–CO), 5.74 (m, 1 H *min*, C*H*=CH), 5.70 (m, 1 H *maj*, C*H*=CH), 5.50 (dd, *J* = 10.1, 1.4 Hz, 1 H *maj*, C*H*=CH), 5.41 (d, *J* = 10 Hz, 1 H *min*, C*H*=CH), 4.96 (dd, *J* = 1.8, 1.7 Hz, 1 H *min*, C*H*O), 4.92 (dd, *J* = 1.8, 1.7 Hz, 1 H *maj*, C*H*O), 2.09 (br. s, 1 H *maj* + 1 H *min*, O*H*), 1.91–1.77 (m, 2 H), 1.74–1.60 (m, 4 H), 1.55–1.44 (m, 2 H), 1.03 (s, 3 H *maj* + 3 H *min*, CH_3), 0.97 (s, 3H *min*, CH_3), 0.95 (s, 3 H *maj*, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.9 (Cq, O–*C*=O), 153.2 (CH, *C*H=CH–CO), 144.3 (CH, *C*H=CH), 123.9 (CH, *C*H=CH), 123.1 (CH, CH=*C*H–CO), 88.6 (CH, *C*HO), 70.4 (Cq, *C*OH), 32.4 (CH_2), 32.0 [Cq, *C*$(CH_3)_2$], 29.8 (CH_3), 29.3 (CH_2), 26.9 (CH_3) ppm; minor: δ = 172.9 (Cq, O–*C*=O), 153.6 (CH, *C*H=CH–CO), 144.0 (CH, *C*H=CH), 124.6 (CH, *C*H=CH), 122.9 (CH, CH=*C*H–CO), 87.5 (CH, *C*HO), 70.7 (Cq, *C*OH), 32.7 (CH_2), 32.0 [Cq, *C*$(CH_3)_2$], 29.4 (CH_3), 29.3 (CH_2), 27.8 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3439, 2954, 1738 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 231 (100) [M + Na]. HRMS: calcd. for $C_{12}H_{16}NaO_3$ 231.0997; found 231.1002.

Methyl 2-Oxo-6-(5-oxo-2,5-dihydrofuran-2-yl)cyclohexanecarboxylate (5a): This compound was prepared as described in General Procedure B from methyl 6-oxocyclohex-1-enecarboxylate (**4a**, 60 mg, 0.384 mmol) in DCM (0.8 mL) and 2-(trimethylsilyloxy)furan (**1a**, 76 μL, 0.461 mmol) in the presence of copper(II) triflate (13.7 mg, 0.038 mmol) in DCM (1.4 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (76.4 mg, 83%). IR (film): $\tilde{\nu}$ = 2950, 1743, 1711 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 261 (100) [M + Na]. HRMS: calcd. for $C_{12}H_{14}NaO_5$ 261.0739; found 261.0742.

Methyl 2-(Diethoxyphosphoryloxy)-6-(5-oxo-2,5-dihydrofuran-2-yl)-cyclohex-1-enecarboxylate (6a): This compound was prepared as described in General Procedure C from the oxo ester **5a** (32.6 mg, 0.136 mmol) in solution in THF (0.7 mL), NaH (60% in oil, 6 mg, 0.15 mmol) in suspension in THF (0.7 mL), and diethyl chloro-

phosphate (23 μL, 0.15 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (34.2 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 95:5): major: δ = 7.45 (dd, J = 1.6, 5.7 Hz, 1 H, C*H*=CH–CO), 6.07 (dd, J = 2.1, 5.7 Hz, 1 H, CH=C*H*–CO), 5.14 (m, 1 H, C*H*O), 4.17 (m, 4 H, 2 × POCH_2), 3.74 (s, 3 H, CO_2CH_3), 3.36 (m, 1 H, C*H*CHO), 2.45 (m, 2 H), 1.84–1.52 (m, 4 H), 1.35 (m, 6 H, 2 × $POCH_2CH_3$) ppm; minor: δ = 7.37 (dd, J = 1.6, 5.9 Hz, 1 H, C*H*=CH–CO), 6.13 (dd, J = 2.2, 5.8 Hz, 1 H, CH=C*H*–CO), 3.07 (m, 1 H, C*H*CHO) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.6 (Cq, O–*C*=O), 166.5 (Cq, *C*O_2Me), 155.3 [d, $J_{P,C}$ = 7.1 Hz, Cq, *C*OP(OEt)$_2$], 154.8 (CH, *C*H=CH–CO), 121.8 (CH, CH=*C*H–CO), 114.0 (d, $J_{P,C}$ = 8.0 Hz, Cq, *C*CO_2Me), 84.9 (CH, *C*HO), 64.6 (d, $J_{P,C}$ = 6.2 Hz, CH_2, PO*C*H_2CH_3), 51.8 (CH_3, CO_2CH_3), 37.7 (CH, *C*HCHO), 28.4 (CH_2), 22.8 (CH_2), 19.4 (CH_2), 16.0 (d, $J_{P,C}$ = 7.8 Hz, CH_3, $POCH_2CH_3$) ppm. IR (film): $\tilde{\nu}$ = 2984, 1752, 1722, 1663 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 397 (100) [M + Na]. HRMS: calcd. for $C_{16}H_{23}NaO_8P$ 397.1028; found 397.1024.

Ethyl 2-Oxo-6-(5-oxo-2,5-dihydrofuran-2-yl)cyclohexanecarboxylate (5a′): This compound was prepared as described in General Procedure B from ethyl 6-oxocyclohex-1-enecarboxylate (**4a′**, 500 mg, 2.97 mmol) in DCM (7.4 mL) and 2-(trimethylsilyloxy)furan (**1a**, 0.58 mL, 3.56 mmol) in the presence of copper(II) triflate (107 mg, 0.297 mmol) in DCM (7 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (53 mg, 86%). IR (film): $\tilde{\nu}$ = 2940, 1745, 1711, 1641, 1613, 1220, 818 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 275 (100) [M + Na]. HRMS: calcd. for $C_{13}H_{16}NaO_5$ 275.0895; found 275.0899.

Ethyl 2-(Diethoxyphosphoryloxy)-6-(5-oxo-2,5-dihydrofuran-2-yl)-cyclohex-1-enecarboxylate (6a′): This compound was prepared as described in General Procedure C from the oxo ester **5a′** (53.9 mg, 0.214 mmol) in solution in THF (1 mL), NaH (60% in oil, 9.4 mg, 0.235 mmol) in suspension in THF (1 mL), and diethyl chlorophosphate (36 μL, 0.235 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (55 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 95:5): major: δ = 7.46 (dd, J = 1.5, 5.6 Hz, 1 H, C*H*=CH–CO), 6.06 (dd, J = 2.1, 5.2 Hz, 1 H, CH=C*H*–CO), 5.14 (m, 1 H, C*H*O), 4.28–4.09 (m, 6 H, CO_2CH_2 + 2 × POCH_2), 3.35 (m, 1 H, C*H*CHO), 2.44 (m, 2 H), 1.84–1.51 (m, 4 H), 1.39–1.21 (m, 9 H, $CO_2CH_2CH_3$, 2 × $POCH_2CH_3$) ppm; minor: δ = 7.37 (dd, J = 1.5, 5.7 Hz, 1 H, C*H*=CH–CO), 6.11 (dd, J = 2.1, 5.7 Hz, 1 H, CH=C*H*–CO), 5.10 (m, 1 H, C*H*O), 3.05 (m, 1 H, C*H*CHO) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.5 (Cq, O–*C*=O), 166.0 (Cq, *C*O_2Et), 154.9 [d, $J_{P,C}$ = 8.1 Hz, Cq, *C*O-P(OEt)$_2$], 154.8 (CH, *C*H=CH–CO), 121.9 (CH, CH=*C*H–CO), 114.3 (d, $J_{P,C}$ = 9.2 Hz, Cq, *C*CO_2Et), 84.9 (CH, *C*HO), 64.6 (d, $J_{P,C}$ = 5.3 Hz, CH_2, PO*C*H_2CH_3), 60.9 (CH_2, CO_2CH_2), 37.7 (CH, *C*HCHO), 28.3 (CH_2), 22.7 (CH_2), 19.5 (CH_2), 16.0 (d, $J_{P,C}$ = 6.9 Hz, CH_3, $POCH_2CH_3$), 14.1 (CH_3, $CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}$ = 2983, 1753, 1720, 1024 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 411 (100) [M + Na]. HRMS: calcd. for $C_{17}H_{25}NaO_8P$ 411.1185; found 411.1182.

Methyl 2-(4-Methyl-5-oxo-2,5-dihydrofuran-2-yl)-6-oxocyclohexanecarboxylate (5a′′): This compound was prepared as described in General Procedure B from methyl 6-oxocyclohex-1-enecarboxylate (**4a**, 50 mg, 0.32 mmol) in solution in DCM (0.4 mL), triisopropyl(3-methylfuran-2-yloxy)silane (**1d**, 97.7 mg, 0.384 mmol) in solution in DCM (0.4 mL), and copper(II) triflate (11.6 mg, 0.032 mmol) in DCM (0.8 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a white solid (56.7 mg, 70%). IR (film): $\tilde{\nu}$ = 3083–2860, 1736, 1703, 1649, 1610, 1222 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 275 (100) [M + Na]. HRMS: calcd. for $C_{13}H_{16}NaO_5$ 275.0895; found 275.0904.

Methyl 2-(Diethoxyphosphoryloxy)-6-(4-methyl-5-oxo-2,5-dihydrofuran-2-yl)cyclohex-1-enecarboxylate (6a′′): This compound was prepared as described in General Procedure C from the oxo ester **5a′′** (27.3 mg, 0.108 mmol) in solution in THF (1 mL), NaH (60% in oil, 4.8 mg, 0.12 mmol) in suspension in THF (0.55 mL), and diethyl chlorophosphate (18 μL, 0.1112 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (23 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio >95:<5): major: δ = 7.00 (m, 1 H, C*H*=CH–CO), 4.97 (m, 1 H, C*H*O), 4.16 (m, 4 H, 2 × POCH_2), 3.73 (s, 3 H, CO_2CH_3), 3.28 (m, 1 H, C*H*CHO), 2.44 (m, 2 H), 1.87 (t, J = 1.8 Hz, 3 H, CH_3), 1.84–1.54 (m, 4 H), 1.35 (m, 6 H, 2 × $POCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 173.7 (Cq, O–*C*=O), 166.7 (Cq, *C*O_2Me), 154.8 [d, $J_{P,C}$ = 7.3 Hz, Cq, *C*OP(OEt)$_2$], 147.0 (CH, *C*H=CH–CO), 130.5 (Cq, CH=*C*CH_3–CO), 114.3 (d, $J_{P,C}$ = 8.2 Hz, Cq, *C*CO_2Me), 82.7 (CH, *C*HO), 64.6 (d, $J_{P,C}$ = 6.5 Hz, CH_2, PO*C*H_2CH_3), 51.8 (CH_3, CO_2CH_3), 37.9 (CH, *C*HCHO), 28.3 (CH_2), 23.0 (CH_2), 19.4 (CH_2), 16.0 (d, $J_{P,C}$ = 7.3 Hz, CH_3, $POCH_2CH_3$), 10.6 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 2948, 1757, 1727, 1660, 1030 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 411 (100) [M + Na]. HRMS: calcd. for $C_{17}H_{25}NaO_8P$ 411.1185; found 411.1182.

Methyl 2-Oxo-5-(5-oxo-2,5-dihydrofuran-2-yl)cyclopentanecarboxylate (5b): This compound was prepared as described in General Procedure B from methyl 7-oxocyclopent-1-enecarboxylate (**4b**, 60 mg, 0.428 mmol) in DCM (1.1 mL), 2-(trimethylsilyloxy)furan (**1a**, 84 μL, 0.513 mmol), and copper(II) triflate (15.2 mg, 0.042 mmol) in DCM (1.1 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a yellow oil (45.3 mg, 47%). IR (film): $\tilde{\nu}$ = 2955, 1748, 1726, 1103 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 247 (100) [M + Na]. HRMS: calcd. for $C_{11}H_{12}NaO_5$ 247.0582; found 247.0586.

Methyl 2-(Diethoxyphosphoryloxy)-5-(5-oxo-2,5-dihydrofuran-2-yl)-cyclopent-1-enecarboxylate (6b): This compound was prepared as described in General Procedure C from the keto ester **5b** (20.6 mg, 0.092 mmol) in solution in THF (0.85 mL), NaH (60% in oil, 4 mg, 0.1 mmol) in suspension in THF (0.45 mL), and diethyl chlorophosphate (15.3 μL, 0.1 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (18.5 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 81:19): major: δ = 7.45 (dd, J = 5.7, 1.6 Hz, 1 H, C*H*=CH–CO), 6.18 (dd, J = 5.8, 2.1 Hz, 1 H, CH=C*H*–CO), 5.46 (m, 1 H, C*H*O), 4.31–4.17 (m, 4 H, 2 × POCH_2), 3.74 (s, 3 H, CO_2CH_3), 3.59 (m, 1 H, C*H*CHO), 2.69 (m, 2 H), 2.04 (m, 1 H), 1.64 (m, 2 H), 1.38 (m, 6 H, 2 × $POCH_2CH_3$) ppm; minor: 7.39 (dd, J = 5.7, 1.5 Hz, 1 H, C*H*=CH–CO), 6.14 (dd, J = 5.9, 2.1 Hz, 1 H, CH=C*H*–CO), 5.56 (m, 1 H, C*H*O), 4.31–4.17 (m, 4 H, 2 × POCH_2), 3.76 (s, 3 H, CO_2CH_3), 3.29 (m, 1 H, C*H*CHO), 2.78 (m, 2 H), 1.85 (m, 2 H), 1.38 (m, 6 H, 2 × $POCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.8 (Cq, O–*C*=O), 163.5 (Cq, *C*O_2Me), 161.7 [d, $J_{P,C}$ = 6.1 Hz, Cq, *C*OP(OEt)$_2$], 154.1 (CH, *C*H=CH–CO), 122.7 (CH, CH=*C*H–CO), 111.7 (d, $J_{P,C}$ = 8.8 Hz, Cq, *C*CO_2Me), 84.4 (CH, *C*HO), 65.2 (d, $J_{P,C}$ = 7.6 Hz, CH_2, PO*C*H_2CH_3), 65.1 (d, $J_{P,C}$ = 7.6 Hz, CH_2, PO*C*H_2CH_3), 51.4 (CH_3, CO_2CH_3), 43.7 (CH, *C*HCHO), 32.5 (CH_2), 20.7 (CH_2), 16.0 (d, $J_{P,C}$ = 6.4 Hz, CH_3, $POCH_2CH_3$) ppm IR (film): $\tilde{\nu}$ = 2952, 1751, 1714, 1697, 1649, 1018 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 383 (100) [M + Na]. HRMS: calcd. for $C_{15}H_{21}NaO_8P$ 383.0872; found 383.0880.

Ethyl 2-Oxo-5-(5-oxo-2,5-dihydrofuran-2-yl)cyclopentanecarboxylate (5b′): This compound was prepared as described in General

Procedure B from ethyl 7-oxocyclopent-1-enecarboxylate (**4b′**, 60 mg, 0.389 mmol) in DCM (1 mL), 2-(trimethylsilyloxy)furan (**1a**, 77 μL, 0.467 mmol), and copper(II) triflate (14.1 mg, 0.039 mmol) in DCM (1 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a slightly yellow oil (60 mg, 65%). IR (film): $\tilde{\nu}$ = 2980, 1746, 1716, 1098 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 261 (100) [M + Na]. HRMS: calcd. for $C_{12}H_{14}NaO_5$ 261.0739; found 261.00732.

Ethyl 2-(Diethoxyphosphoryloxy)-5-(5-oxo-2,5-dihydrofuran-2-yl)-cyclopent-1-enecarboxylate (6b′): This compound was prepared as described in General Procedure C from the oxo ester **5b′** (25.8 mg, 0.108 mmol) in solution in THF (1 mL), NaH (60% in oil, 4.8 mg, 0.119 mmol) in suspension in THF (0.55 mL), and diethyl chlorophosphate (18.2 μL, 0.119 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (25 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 85:15): major: δ = 7.45 (dd, *J* = 5.8, 1.5 Hz, 1 H, C*H*=CH–CO), 6.13 (dd, *J* = 5.8, 2.0 Hz, 1 H, CH=C*H*–CO), 5.46 (m, 1 H, C*H*O), 4.31–4.13 (m, 6 H, CO_2CH_2, 2 × $POCH_2$), 3.59 (m, 1 H, C*H*CHO), 2.69 (m, 2 H), 2.02 (m, 1 H), 1.62 (m, 1 H), 1.37 (m, 6 H, 2 × $POCH_2CH_3$), 1.29 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$) ppm; minor: δ = 7.38 (d, *J* = 5.7, 1.5 Hz, 1 H, C*H*=CH–CO), 6.17 (dd, *J* = 5.8, 2.1 Hz, 1 H, CH=C*H*–CO), 5.56 (m, 1 H, C*H*O), 4.31–4.13 (m, 6 H, CO_2CH_2, 2 × $POCH_2$), 3.28 (m, 1 H, C*H*CHO), 2.79 (m, 2 H), 1.82 (m, 2 H) 1.37 (m, 6 H, 2 × $POCH_2CH_3$), 1.30 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.8 (Cq, O–*C*=O), 163.0 (Cq, *C*O_2Et), 161.4 [d, $J_{P,C}$ = 6.7 Hz, Cq, *C*OP(OEt)$_2$], 154.1 (CH, *C*H=CH–CO), 122.7 (CH, CH=*C*H–CO), 111.9 (d, $J_{P,C}$ = 8.5 Hz, Cq, *C*CO_2Et), 84.4 (CH, *C*HO), 65.1 (d, $J_{P,C}$ = 7.1 Hz, CH_2, PO*C*H_2CH$_3$), 65.0 (d, $J_{P,C}$ = 7.1 Hz, CH_2, PO*C*H_2CH$_3$), 60.4 (CH_2, CO_2CH_2), 43.7 (CH, *C*HCHO), 32.5 (CH_2), 20.7 (CH_2), 16.0 (d, $J_{P,C}$ = 7.0 Hz, CH_3, POCH$_2$*C*H_3), 14.2 (CH_3, $CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}$ = 2983, 1753, 1714, 1693, 1649, 1020 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 397 (100) [M + Na]. HRMS: calcd. for $C_{16}H_{23}NaO_8P$ 397.1028; found 397.1012.

Methyl 3,3-Dimethyl-6-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)cyclohexanecarboxylate (5c): This compound was prepared as described in General Procedure B from methyl 3,3-dimethyl-6-oxocyclohex-1-enecarboxylate (**4c**, 60 mg, 0.329 mmol) in solution in DCM (1 mL), 2-(trimethylsilyloxy)furan (**1a**, 65 μL, 0.395 mmol), and copper(II) triflate (11.9 mg, 0.033 mmol) in DCM (0.7 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a white solid (57.8 mg, 66%). IR (film): $\tilde{\nu}$ = 3091–2949, 1738, 1642, 1606, 1217 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 289 (100) [M + Na]. HRMS: calcd. for $C_{14}H_{18}NaO_5$ 289.1052; found 289.1064.

Methyl 2-(Diethoxyphosphoryloxy)-5,5-dimethyl-6-(5-oxo-2,5-dihydrofuran-2-yl)cyclohex-1-enecarboxylate (6c): This compound was prepared as described in General Procedure C from the oxo ester **5c** (30 mg, 0.112 mmol) in solution in THF (1 mL), NaH (60% in oil, 4.9 mg, 0.123 mmol) in suspension in THF (0.6 mL), and diethyl chlorophosphate (19 μL, 0.123 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (32.1 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 85:15): major: δ = 7.35 (dd, *J* = 5.6, 1.6 Hz, 1 H, C*H*=CH–CO), 5.93 (dd, *J* = 5.7, 2.2 Hz, 1 H, CH=C*H*–CO), 5.30 (m, 1 H, C*H*O), 4.22–4.04 (m, 4 H, 2 × $POCH_2$), 3.66 (s, 3 H, CO_2CH_3), 2.94 (m, 1 H, C*H*CHO), 2.49 (m, 2 H), 2.13 (m, 1 H), 1.40–1.27 (m, 7 H, 2 × $POCH_2CH_3$), 1.19 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3) ppm; minor: 7.41 (dd, *J* = 5.7, 1.4 Hz, 1 H, C*H*=CH–CO), 6.08 (dd, *J* = 5.8, 2.1 Hz, 1 H, CH=C*H*–CO), 5.03 (m, 1 H, C*H*O), 4.22–4.04 (m, 4 H, 2 × $POCH_2$), 3.67 (s, 3 H, CO_2CH_3), 2.88 (m, 1 H, C*H*CHO), 1.17 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.8 (Cq, O–*C*=O), 167.3 (Cq, *C*O_2Me), 156.7 [d, $J_{P,C}$ = 8.5 Hz, Cq, *C*OP(OEt)$_2$], 156.2 (CH, *C*H=CH–CO), 120.8 (CH, CH=*C*H–CO), 110.8 (d, $J_{P,C}$ = 8.2 Hz, Cq, *C*CO_2Me), 82.2 (CH, *C*HO), 64.6 (d, $J_{P,C}$ = 6.7 Hz, CH_2, PO*C*H_2CH$_3$), 51.7 (CH_3, CO_2CH_3), 48.1 (CH, *C*HCHO), 31.9 [Cq, *C*(CH$_3$)$_2$], 31.2 (CH_2), 27.8 (CH_3), 27.2 (CH_3), 26.5 (CH_2), 16.0 (d, $J_{P,C}$ = 6.6 Hz, CH_3, POCH$_2$*C*H_3) ppm. IR (film): $\tilde{\nu}$ = 2954, 1757, 1704, 1276, 1022 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 425 (100) [M + Na]. HRMS: calcd. for $C_{17}H_{25}NaO_8P$ 425.1341; found 425.1345.

Ethyl 3,3-Dimethyl-6-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)cyclohexanecarboxylate (5c′): This compound was prepared as described in General Procedure B from ethyl 3,3-dimethyl-6-oxocyclohex-1-enecarboxylate (**4c′**, 60 mg, 0.305 mmol) in solution in DCM (1 mL), 2-(trimethylsilyloxy)furan (**1a**, 60 μL, 0.367 mmol), and copper(II) triflate (11 mg, 0.0305 mmol) in DCM (0.7 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (58.9 mg, 69%). IR (film): $\tilde{\nu}$ = 2962, 1752, 1639, 1607, 1216 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 303 (100) [M + Na]. HRMS: calcd. for $C_{15}H_{20}NaO_5$ 303.1208; found 303.1194.

Ethyl 2-(Diethoxyphosphoryloxy)-5,5-dimethyl-6-(5-oxo-2,5-dihydrofuran-2-yl)cyclohex-1-enecarboxylate (6c′): This compound was prepared as described in General Procedure C from the oxo ester **5c′** (24 mg, 0.085 mmol) in solution in THF (0.77 mL), NaH (60% in oil, 3.8 mg, 0.095 mmol) in suspension in THF (0.43 mL), and diethyl chlorophosphate (15 μL, 0.095 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (16.9 mg, 47%, 53% based on starting material). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 89:11): major: δ = 7.36 (dd, *J* = 5.6, 1.8 Hz, 1 H, C*H*=CH–CO), 5.93 (dd, *J* = 5.7, 2.1 Hz, 1 H, CH=C*H*–CO), 5.31 (m, 1 H, C*H*O), 4.22–4.06 (m, 6 H, CO_2CH_2, 2 × $POCH_2$), 2.95 (m, 1 H, C*H*CHO), 2.51 (m, 2 H), 2.15 (m, 1 H), 1.41–1.22 (m, 10 H, $CO_2CH_2CH_3$, 2 × $POCH_2CH_3$), 1.19 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3) ppm; minor: δ = 7.44 (dd, *J* = 5.6, 1.8 Hz, 1 H, C*H*=CH–CO), 6.08 (dd, *J* = 5.6, 2.1 Hz, 1 H, CH=C*H*–CO), 5.03 (m, 1 H, C*H*O), 2.87 (m, 1 H, C*H*CHO) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.8 (Cq, O–*C*=O), 167.0 (Cq, *C*O_2Et), 156.3 [Cq, *C*OP(OEt)$_2$], 156.3 (CH, *C*H=CH–CO), 120.9 (CH, CH=*C*H–CO), 111.1 (d, $J_{P,C}$ = 8.1 Hz, Cq, *C*CO_2Et), 82.2 (CH, *C*HO), 64.6 (d, $J_{P,C}$ = 6.2 Hz, CH_2, PO*C*H_2CH$_3$), 64.5 (d, $J_{P,C}$ = 5.6 Hz, CH_2, PO*C*H_2CH$_3$), 60.8 (CH_2, CO_2CH_2), 48.1 (CH, *C*HCHO), 31.9 [Cq, *C*(CH$_3$)$_2$], 31.2 (CH_2), 27.8 (CH_3), 27.2 (CH_3), 26.4 (CH_2), 16.1 (d, $J_{P,C}$ = 7.0 Hz, CH_3, POCH$_2$*C*H_3), 14.0 (CH_3, $CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}$ = 2975–2876, 1757, 1702, 1278, 1026 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 439 (100) [M + Na]. HRMS: calcd. for $C_{19}H_{29}NaO_8P$ 439.1498; found 439.1500.

Methyl 2-Oxo-7-(5-oxo-2,5-dihydrofuran-2-yl)cycloheptanecarboxylate (5d): This compound was prepared as described in General Procedure B from methyl 7-oxocyclohept-1-enecarboxylate (**4d**, 67.3 mg, 0.4 mmol), 2-(trimethylsilyloxy)furan (**1a**, 79 μL, 0.48 mmol), and copper(II) triflate (14.4 mg, 0.04 mmol) in DCM (2 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 5:5) to afford a colorless oil (84.3 mg, 83%). IR (film): $\tilde{\nu}$ = 2934–2863, 1745, 1698, 1436, 1158 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 275 (100) [M + Na]. HRMS: calcd. for $C_{13}H_{16}NaO_5$ 275.0895; found 275.0894.

Methyl 2-(Diethoxyphosphoryloxy)-7-(5-oxo-2,5-dihydrofuran-2-yl)-cyclohept-1-enecarboxylate (6d): This compound was prepared as described in General Procedure C from the oxo ester **5d** (49 mg, 0.194 mmol) in solution in THF (0.87 mL), NaH (60% in oil, 8.5 mg, 0.213 mmol) in suspension in THF (0.96 mL), and diethyl chlorophosphate (32 μL, 0.213 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (49.1 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 84:16): major: δ = 7.46 (dd, J = 1.6, 5.7 Hz, 1 H, C*H*=CH–CO), 6.08 (dd, J = 2.0, 5.8 Hz, 1 H, CH=C*H*–CO), 5.19 (m, 1 H, C*H*O), 4.07 (m, 4 H, 2 × POC*H*$_2$), 3.71 (s, 3 H, CO_2CH_3), 3.21 (m, 1 H, C*H*CHO), 2.84 (m, 1 H), 2.51 (m, 1 H), 1.90–1.62 (m, 6 H), 1.31 (m, 6 H, 2 × POCH$_2$C*H*$_3$) ppm; minor: δ = 7.60 (d, J = 5.5 Hz, 1 H, C*H*=CH–CO), 5.29 (d, J = 9.7 Hz, 1 H, C*H*O), 3.73 (s, 3 H, CO_2CH_3), 2.75 (m, 2 H), 2.61 (m, 1 H), 2.07 (m, 2 H) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.4 (Cq, O–*C*=O), 167.9 (Cq, *C*O$_2$Me), 156.9 [d, $J_{P,C}$ = 9 Hz, Cq, *C*OP(OEt)$_2$], 154.8 (CH, *C*H=CH–CO), 122.0 (CH, CH=*C*H–CO), 118.3 (d, $J_{P,C}$ = 7.6 Hz, Cq, *C*CO$_2$Me), 85.1 (CH, *C*HO), 64.5 (d, $J_{P,C}$ = 6.4 Hz, CH$_2$, PO*C*H$_2$CH$_3$), 63.5 (d, $J_{P,C}$ = 5.9 Hz, CH$_2$, POCH$_2$CH$_3$), 51.9 (CH$_3$, CO$_2$*C*H$_3$), 41.4 (CH, *C*HCHO), 32.0 (CH$_2$), 29.6 (CH$_2$), 27.8 (CH$_2$), 24.5 (CH$_2$), 23.5 (CH$_2$), 16.0 (d, $J_{P,C}$ = 6.3 Hz, CH$_3$, POCH$_2$*C*H$_3$), 15.9 (d, $J_{P,C}$ = 6.3 Hz, CH$_3$, POCH$_2$*C*H$_3$) ppm. IR (film): $\tilde{\nu}$ = 2929, 1755, 1714, 1028 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 411 (100) [M + Na]. HRMS: calcd. for $C_{17}H_{25}NaO_8P$ 411.1185; found 411.1184.

Ethyl 2-Oxo-7-(5-oxo-2,5-dihydrofuran-2-yl)cycloheptanecarboxylate (5d′): This compound was prepared as described in General Procedure B from ethyl 7-oxocyclohept-1-enecarboxylate (**4d′**, 60 mg, 0.329 mmol) in DCM (0.8 mL), 2-(trimethylsilyloxy)furan (**1a**, 65 μL, 0.395 mmol), and copper(II) triflate (11.9 mg, 0.033 mmol) in DCM (0.9 mL). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 6:4) to afford a colorless oil (68 mg, 78%). IR (film): $\tilde{\nu}$ = 2932, 1750, 1701, 1628, 1602, 1157 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 289 (100) [M + Na]. HRMS: calcd. for $C_{14}H_{18}NaO_5$ 289.1052; found 289.1042.

Ethyl 2-(Diethoxyphosphoryloxy)-7-(5-oxo-2,5-dihydrofuran-2-yl)-cyclohept-1-enecarboxylate (6d′): This compound was prepared as described in General Procedure C from the oxo ester **5d′** (21.7 mg, 0.081 mmol) in solution in THF (0.75 mL), NaH (60% in oil, 3.6 mg, 0.09 mmol) in suspension in THF (0.4 mL), and diethyl chlorophosphate (14 μL, 0.09 mmol). The crude mixture was purified through silica gel (heptane to heptane/EtOAc, 3:7) to afford a colorless oil (21.2 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$, ratio 84:16): major: δ = 7.46 (dd, J = 5.7, 1.6 Hz, 1 H, C*H*=CH–CO), 6.09 (dd, J = 5.8, 2.0 Hz, 1 H, CH=C*H*–CO), 5.21 (m, 1 H, C*H*O), 4.19 (q, J = 7.2 Hz, 2 H, CO$_2$CH$_2$), 4.14 (m, 4 H, 2 × POC*H*$_2$), 3.21 (m, 1 H, C*H*CHO), 2.84 (m, 1 H), 2.54 (m, 1 H), 1.96–1.60 (m, 6 H), 1.38–1.28 (m, 6 H, 2 × POCH$_2$C*H*$_3$), 1.30 (t, J = 7.2 Hz, 3 H, CO$_2$CH$_2$C*H*$_3$) ppm; minor: δ = 7.62 (dd, J = 5.8, 1.4 Hz, 1 H, C*H*=CH–CO), 6.08 (m, 1 H, CH=C*H*–CO), 5.29 (m, 1 H, C*H*O), 2.76–2.63 (m, 2 H) ppm; other signals masked by the major isomer. ^{13}C NMR (75 MHz, $CDCl_3$): major: δ = 172.4 (Cq, O–*C*=O), 167.5 (Cq, *C*O$_2$Et), 156.9 [d, $J_{P,C}$ = 8.9 Hz, Cq, *C*OP(OEt)$_2$], 154.7 (CH, *C*H=CH–CO), 122.1 (CH, CH=*C*H–CO), 118.7 (d, $J_{P,C}$ = 7.9 Hz, Cq, *C*CO$_2$Et), 85.1 (CH, *C*HO), 64.5 (d, $J_{P,C}$ = 6.0 Hz, CH$_2$, PO*C*H$_2$CH$_3$), 61.1 (CH$_2$, CO$_2$*C*H$_2$), 41.4 (CH, *C*HCHO), 31.9 (CH$_2$), 27.7 (CH$_2$), 24.6 (CH$_2$), 23.5 (CH$_2$), 16.1 (d, $J_{P,C}$ = 6.9 Hz, CH$_3$, POCH$_2$*C*H$_3$), 14.0 (CH$_3$, CO$_2$CH$_2$*C*H$_3$) ppm. IR (film): $\tilde{\nu}$ = 2930, 1753, 1704, 1273, 1018 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 425 (100) [M + Na]. HRMS: calcd. for $C_{18}H_{27}NaO_8P$ 425.1341; found 425.1333.

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