Regio- and Diastereoselective Synthesis of 2-Alkylidenetetrahydrofurans by Domino S_N/S_N' and S_N/S_N Reactions of 1,3-Dicarbonyl Dianions

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The domino C,O-cyclodialkylation reaction of dilithiated 1,3-dicarbonyl compounds with 1,4-dibromo-2-butene resulted in regio- and diastereoselective formation of 2-alkylidene-5-vinyltetrahydrofurans. The cyclization of 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane regio- and diastereoselectively afforded 2-alkylidenetetrahydrofurans under thermodynamic reaction control.

Introduction

Despite their potential simplicity, cyclization reactions of dianions[1] with 1,2-difunctional alkylhalides can suffer from various side reactions such as polymerization, elimination, monoalkylation, or reduction of the dielectrophile.[2] Recently, the two-step synthesis of annelated imidazoles by cyclization of dilithiated 2-methylbenzimidazole with 1-bromo-2-chloroethane has been reported.[3] As a result of a competing elimination pathway, relatively low yields were obtained compared with the formation of six-membered rings. Katritzky and co-workers have reported the cyclization of 1-bromo-2-chloroethane with the dianion of 2-methylindole, generated by the use of Lochmann−Schlosser- base.[4] Despite the simplicity of the idea, cyclization reactions of 1,3-dicarbonyl dianions[5,6] with 1,2-dihalides have, to the best of our knowledge, not been reported so far.[7] The reaction of 1,3-dicarbonyl dianions with 1,*n*-dibromoalkanes ($n = 3$ or higher) was reported to give mixtures of open-chain monoalkylated products and of 2:1-condensation products.[8] Not even open-chain products could be isolated in the reaction of 1,3-dicarbonyl dianions with 1,2-dibromo- or 1,2-diiodo*ethane*, because of a competing SET-process.[9] In fact, 1,2-dibromoethane has been used as a reagent for the oxidation of dianions.[10] In the presence of catalytic amounts of CuCl open-chain products were obtained, however, in only 25−33% yield.[11] Employment of 1,2-di*chloro*ethane resulted in elimination rather than nucleophilic substitution.[11] In the course of our interest[12] in the development of cyclization reactions of dianions we have recently shown[13] that 2-alkylidenetetrahydrofurans could be efficiently prepared by domino S_N/S_N reactions of 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane.[14,15] Herein, we wish to report full details of this methodology.

The reaction of 1,3-dicarbonyl dianions with 1,4-di*chloro*-2-butene has been reported to result only in formation of mixtures of open-chain products in low yields.[8] Recently, the K_2CO_3-mediated cyclization of dimethyl acetone-1,3-dicarboxylate with 1,4-dibromo-2-butene has been reported by Rodriguez[16a] and co-workers. We have recently reported the first, to our knowledge,

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domino S_N/S_N' reactions of 1,3-dicarbonyl dianions with 1,4-dibromo-2-butene. Herein, we wish to report full details of this cyclization reaction, which allows for a direct transformation of unsymmetrical and nonactivated 1,3-dicarbonyl compounds into 2-alkylidene-5-vinyltetrahydrofurans. Functionalized 2-alkylidenetetrahydrofurans represent important intermediates for the synthesis of biologically relevant tetrahydrofurans and natural products.[17]

Results and Discussion

Domino S_N/S_N Reactions. After much experimentation[14] we have recently developed conditions for the cyclization of the dianion of ethyl acetoacetate **1a** with 1,2-dihalides (Scheme 1). The following parameters were crucial to induce a cyclization and to prepare 2-alkylidenetetrahydrofuran **3a** in acceptable yield: (a) the use of 1-bromo-2-chloroethane **2** as the dielectrophile and (b) a proper tuning of the reaction temperature. At low temperature (−78 → 20 °C) the terminal carbon atom of the dianion chemo- and regioselectively attacked the alkyl bromide function of **2**. To induce the cyclization step, which proceeded regioselectively via the oxygen atom,[18] the reaction mixture was refluxed for 12−14 h. The exocyclic double bond was formed with high *E*-diastereoselectivity which can be explained by (a) minimization of the dipole−dipole repulsion of the oxygen atoms in the W-shaped intermediate **A**[19] and (b) the higher thermodynamic stability of the *E*-diastereomer.

To study the preparative scope of the cyclization, the substituents of the 1,3-dicarbonyl compounds were systematically varied (Table 1). Reaction of 1-bromo-2-choroethane **2** with the dianions of ethyl, methyl, *tert*-butyl, isobutyl, methoxyethyl, and benzyl acetoacetate afforded the 2-alkylidenetetrahydrofurans **3a**−**f** in good yields and with very good regio- and *E*-diastereoselectivities. Starting with the dianion of *N*,*N*-diethylacetylacetic amide the *E*-configured 2-alkylidenetetrahydrofuran **3g** was prepared. Reaction of **2** with the dianions of ethyl 2-methylacetoacetate, ethyl 2-ethylacetoacetate, and ethyl 2-butylacetoacetate afforded the tetrahydrofurans **3h**−**j** containing a methyl, ethyl, and butyl group at the exocyclic double bond, respectively. All products were formed with very good regio- and *E*-diastereoselectivities. The reaction of 1-bromo-2-chloroethane with methyl 3-oxopentanoate and ethyl 3-oxohexanoate afforded the 2-alkylidenetetrahydrofurans **3k,l** with again very good *E*-diastereoselectivities (despite the steric influence of the substituents R^1). Reaction of **2** with the dianions of the 2-acetyl-γ-butyrolactones **1m,n** afforded the interesting 2-alkylidenetetrahydrofurans **3m,n** with very good *E*-diastereoselectivities.

Scheme 1. Cyclization of 1,3-Dicarbonyl Dianions with 1-Bromo-2-chloroethane

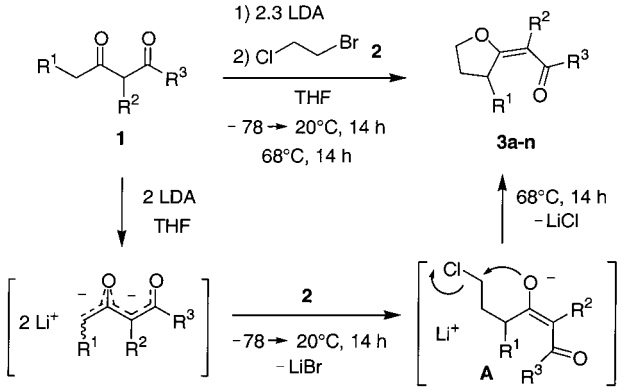
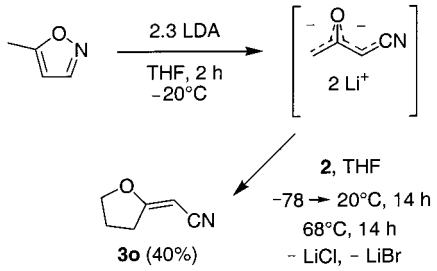


Table 1. Synthesis of 2-Alkylidenetetrahydrofurans 3

3	R^1	R^2	R^3	δ^a	δ^b	%[c]	*E*/*Z*
a	H	H	OEt	5.30	168.1	75	>98:2
b	H	H	OMe	5.32, 4.85	168.7	63	10:1
c	H	H	O(*t*-Bu)	5.25	167.2	74	>98:2
d	H	H	O(*i*-Bu)	5.30, 4.85	168.7	63	10:1
e	H	H	$O(CH_2)_2OMe$	5.33, 4.85	168.5	70	10:1
f	H	H	OCH_2Ph	5.37, 4.92	167.8	60	10:1
g	H	H	NEt_2	5.62	166.7	80	>98:2
h	H	Me	OEt		169.4	70	>98:2
i	H	Et	OEt		169.1	68	>98:2
j	H	Bu	OEt		169.1	60	>98:2
k	Me	H	OMe	5.23	168.4	68	>98:2
l	Et	H	OEt	5.20	168.0	80	>98:2
m	H	CH_2CH_2O			169.4	40	>98:2
n	H	$CH_2CH(Et)O$			168.8	62	>98:2

[a] Chemical shifts (^{1}H NMR) of the hydrogen atoms of the exocyclic double bond (major and minor isomer). [b] Chemical shifts (^{13}C NMR) of the carbonyl group. [c] Isolated yields

Scheme 2 Cyclization of the Dianion of α-Cyanoacetone with 1-Bromo-2-chloroethane



Treatment of 3-methylisoxazole with 2 equiv of LDA afforded the dianion of α-cyanoacetone.[20] Reaction of the latter with **2** afforded the *E*-configured 2-alkylidenetetrahydrofuran **3o** with very good diastereoselectivity (Scheme 2).

The geometry of the exocyclic double bond of 2-alkylidenetetrahydrofurans **3a**−**o** was established by NOESY experiments and by comparison of the chemical shifts of the hydrogen atoms of the exocyclic double bond (Table 1) with those of related compounds.[12,21] As expected, the chemical shifts strongly depend on the configuration of the double bond (for *E*-configured, ester-derived tetrahy-

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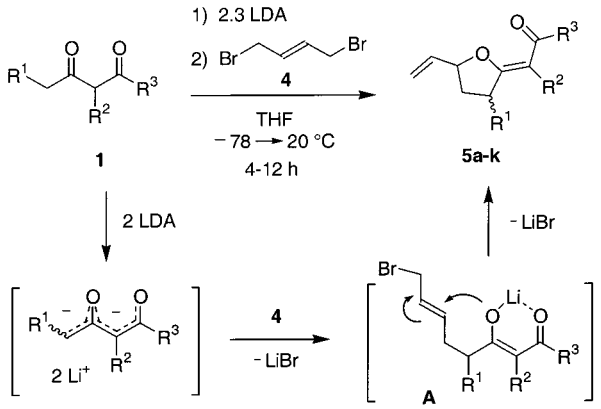
Scheme 3 Cyclization of 1,3-Dicarbonyl Dianions with 1,4-Dibromo-2-butene



drofurans $\delta = 5.30-5.40$; for *Z*-isomers $\delta = 4.80-4.90$). The configuration of **3h−j** and **3m,n**, containing tetrasubstituted exocyclic double bonds, was established by analysis of the ^{13}C NMR chemical shifts of the carbonyl carbons.[12,21] Additional evidence was obtained based on NOESY experiments.

Domino S_N/S_N' Reactions. The following parameters proved to be important for the cyclization of the dianion of ethyl acetoacetate **1a** with 1,4-dihalo-2-butenes: (a) the use of 1,4-di*bromo*-2-butene **4** rather than 1,4-di*chloro*-2-butene as the dielectrophile and (b) a proper tuning of the temperature to avoid the formation of open-chain products.[22] The reaction of a THF solution of **4** with the dianion of **1a** afforded the 2-alkylidene-5-vinyltetrahydrofuran **5a** in up to 60% yield. Formation of **5a** can be explained by a domino S_N/S_N' reaction, which involves regioselective attack of the terminal carbon of the dianion onto **4** and subsequent cyclization via the oxygen atom of the dianion (Scheme 3). The exocyclic double bond of **5a** was formed with very good *Z*-diastereoselectivity, which can be explained by chelation of a lithium ion by two oxygen atoms (intermediate **A**). In contrast to the synthesis of tetrahydrofurans **3**, the cyclization step was carried out at low temperature (kinetic reaction control). Therefore, no isomerization of the product to the thermodynamically more stable *E*-configured isomer occurred. However, a slow rearrangement (accompagnied by significant decomposition) was observed upon standing at room temperature for several days.

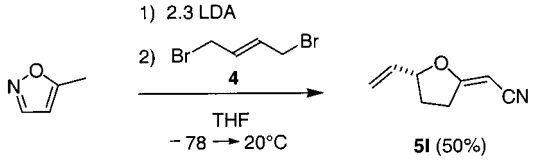
To study the preparative scope of our methodology, the substituents of the 1,3-dicarbonyl compounds were systematically varied (Scheme 3, Table 2). The reaction of **4** with the dianions of ethyl acetoacetate, *tert*-butyl acetoacetate, acetylacetone, and *N*,*N*-diethylacetylacetic amide afforded the *Z*-configured 2-alkylidene-5-vinyltetrahydrofurans **5a−d** in good yields and with very good stereoselectivities. Treatment of 1,4-dibromo-2-butene with the dianions of ethyl 2-methylacetoacetate, ethyl 2-ethylacetoacetate, and ethyl 2-butylacetoacetate resulted in formation of tetrahydrofurans **5e−g** with very good *Z*-diastereoselectivities. Reaction of **4** with the dianions of 2-acetyl-γ-butyrolactone and α-acetyltetralone afforded the 2-alkylidene-5-vinyltetrahydrofurans **5h** and **5i**, respectively. During the tedious purification of these products a complete isomerization into the more stable *E*-diastereomers occurred. The reaction of 1,4-dibromo-2-butene with the dianions of methyl 3-oxopentanoate and ethyl 3-oxohexanoate afforded the 2-alkylidene-5-vinyltetrahydrofurans **5j,k** in good yields and with very good *Z*-diastereoselectivities. The cyclization of 1,4-dibromo-2-butene with the dianion of α-cyanoacetone (Scheme 4) afforded the cyano-substituted 2-alkylidene-5-vinyltetrahydrofuran **5l** with very good regio- and *E*-diastereoselectivity (for comparison, see Scheme 2). The change from *Z*- to *E*-configuration of the exocyclic double bond can be explained by the fact that no chelation can occur, a result of the absence of a second carbonyl group.

Table 2. Synthesis of 2-Alkylidene-5-vinyltetrahydrofurans 5a−k

5	R^1	R^2	R^3	δ (CH)[a]	δ (C=O)[b]	Z/*E*	%[c]
a	H	H	OEt	4.75	164.5	>98:2	60
b	H	H	O(*t*-Bu)	4.68	164.2	>98:2	58
c	H	H	Me	4.96	200.1	>98:2	47
d	H	H	NEt_2	4.97	164.3	>98:2	73[d]
e	H	Me	OEt		166.6	>98:2	64
f	H	Et	OEt		167.9	>98:2	61
g	H	Bu	OEt		166.4	>98:2	32
h	H	$-CH_2CH_2O-$			168.3	<2:98	32
i	H	$-CH_2CH_2(C_6H_4)-$			187.9	<2:98	46
j	Me	H	OMe	4.70, 4.75	167.5	8:1	61
k	Et	H	OEt	4.70, 4.75	164.4	>98:2	53

[a] Chemical shifts (^1H NMR) of the hydrogen atoms of the exocyclic double bond (major and minor isomer). [b] Chemical shifts (^{13}C NMR) of the carbonyl group. [c] Isolated yields. The diastereoselectivities for **5j** and **5k** are 45:55 and 65:35, respectively. The configuration of the isomers could not be unambigiously assigned. [d] The starting material could not be completely separated.

Scheme 4. Cyclization of the Dianion of α-Cyanoacetone with 1,4-Dibromo-2-butene



The geometry of the exocyclic double bond of 2-alkylidenetetrahydrofurans **5a−l** was established by NOESY experiments, crystal structure analyses,[23] and comparison of the chemical shifts of the hydrogen atoms of the exocyclic double bond (Table 2) with those of tetrahydrofurans **3** and related compounds (Table 1).[12,21] For example, the chemical shifts of the *Z*-configured, ester-derived 2-alkylidenetetrahydrofurans **5a,b,j,k** appear in the range of $\delta = 4.65-4.80$. The configuration of tetrahydrofurans **5e−i** was established by comparison of the ^{13}C NMR chemical shifts of the carbonyl carbons with those of **3h−j** and **3m,n**.

From a methodology viewpoint, we have reported domino C,O-cyclodialkylation reactions of 1,3-dicarbonyl dianions. Very good regio- and *E*/*Z*-diastereoselectivities were observed giving rise to the formation of functionalized 2-alkylidenetetrahydrofurans, which are of biological relevance and of importance for natural product syntheses.

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Experimental Section

General Procedure for the Cyclization of 1-Bromo-2-chloroethane with 1,3-Dicarbonyl Dianions. To a THF solution of LDA (prepared by addition of 5.0 mmol of *n*-BuLi, 1.6 M in hexane, to a solution of diisopropylamine (0.57 mL, 5.0 mmol) in 50 mL of THF) was added ethyl acetoacetate (0.25 mL, 2.0 mmol) at 0 °C. The deep yellow, clear solution was stirred at 0 °C for 45 min. To this solution was added 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol) at −78 °C. The temperature was allowed to rise to ambient during 14 h, and the solution was subsequently refluxed for 14 h. To the solution was added hydrochloric acid (200 mL, 0.1 M), and the mixture was extracted with ether (4 × 150 mL). The organic layers were dried and filtered, the solvent of the filtrate was removed in vacuo, and the residue was purified by chromatography (silica gel, ether/petroleum ether 1:20 → 1:3) to give **3a** (234 mg, 75%, *E*/*Z* > 98:2) as a colorless oil. The diastereomeric ratios were determined by integration of the ^{1}H NMR spectra of the products.

2-(*E*)-(Ethoxycarbonylmethylidene)tetrahydrofuran (3a). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.08 (quint, J = 6.5 Hz, 2 H, 4-H), 3.10 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 4.15 (q, J = 7 Hz, 2 H, OCH_2-CH_3), 4.23 (t, J = 6.5 Hz, 2 H, H-5), 5.30 (t, J = 1.5, 1 H, CHC=O); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 14.02 (OCH_2CH_3), 23.44, 29.82 (C-3, C-4), 58.68 (OCH_2CH_3), 71.33 (C-5), 89.04 ($CHCO_2$-Et), 168.08 (C=O), 176.29 (C-2); MS (70 eV, EI) *m*/*z* 156 (M^+, 38), 111 (100), 69 (72). Anal. Calcd for $C_8H_{12}O_3$: C 61.52, H 7.74. Found: C 61.48, H 7.90.

2-(*E*)-(1-Methoxycarbonylmethylidene)tetrahydrofuran (3b). Starting with methyl acetoacetate (0.23 g, d = 1.077 g/cm^3, 0.22 mL, 2.1 mmol) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv.), **3b** was isolated by chromatography (silica gel, ether/petroleum ether 1:1) as a colorless oil (185 mg, 63%, *E*/*Z* = 10:1): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.09 (quint, J = 6.5 Hz, 2 H, 4-H), 3.11 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 3.66 (s, 3 H, OCH_3), 4.23 (t, J = 6.5 Hz, 2 H, 5-H), 5.32 (t, J = 1.5 Hz, 1 H, $CHCO_2Me$); *Z*-isomer: δ (=CH−) 4.85; ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 23.55, 29.96 (C-3, C-4), 50.26 (OCH_3), 71.55 (C-5), 88.82 ($CHCO_2CH_3$), 168.65 (C=O), 176.62 (C-2); IR (neat) $\tilde{\nu}$ 3383 (br), 3030 (w), 2993 (m), 2959 (m), 2912 (m), 1703 (s), 1648 (s), 1432 (m), 1352 (s), 1121 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 142 (M^+, 60). The exact molecular mass for $C_7H_{10}O_3$ *m*/*z* 142.0630 ± 2 mDa was confirmed by HRMS (70 eV, EI).

2-(*E*)-(*tert*-Butoxycarbonylmethylidene)tetrahydrofuran (3c). Starting with *tert*-butyl acetoacetate (2.0 mmol, 0.32 g) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv), **3c** was isolated by chromatography (silica gel, ether/petroleum ether 1:1) as a colorless oil (273 mg, 74%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.50 [s, 9 H, $C(CH_3)_3$], 2.08 (quint, J = 6.5 Hz, 2 H, 4-H), 3.10 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 4.20 (t, J = 6.5 Hz, 2 H, 5-H), 5.25 (t, J = 1.5 Hz, 1 H, CHC=O); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 27.74 [$C(CH_3)_3$], 23.44, 29.82 (C-3, C-4), 71.31 (C-5), 77.84 ($C(CH_3)_3$), 90.45 ($CHCO_2t$-Bu), 167.16 (C=O), 175.94 (C-2); MS (70 eV, EI) *m*/*z* 184 (M^+, 1), 128 (65), 69 (96). Anal. Calcd for $C_{10}H_{16}O_3$: C 65.19, H 8.75. Found: C 65.19, H 8.97.

2-(*E*)-(Isobutyloxycarbonylmethylidene)tetrahydrofuran (3d). Starting with isobutyl acetoacetate (2.0 mmol, 0.32 g, d = 0.980 g/cm^3, 0.32 mL) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv), **3d** was isolated by chromatography (silica gel, ether/petroleum ether 1:5) as a colorless oil (232 mg, 63%, *E*/*Z* = 10:1): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.93 (d, J = 6.5 Hz, 6 H, CH_3), 2.07 (quint, J = 6.5 Hz, 2 H, 4-H), 3.09 [m, 1 H, $OCH_2CH(CH_3)_2$], 3.82 [m, 4 H, 3-H, $OCH_2CH(CH_3)_2$], 4.20 (t, J = 6.5 Hz, 2 H, 5-H), 5.30 (t, J = 1.5 Hz, 1 H, CHC=O); *Z*-isomer δ (=CH−) 4.85; ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 19.16 [$CH(CH_3)_2$], 23.84 (C-4), 27.83 [$CH(CH_3)_2$], 30.20 (C-3), 69.54 [$OCH_2CH(CH_3)_2$] 71.69 (C-5), 89.62 (CHC=O), 168.68 (C=O), 176.49 (C-2); IR (neat) $\tilde{\nu}$ 2962 (m), 2876 (w), 1704 (s), 1646 (s), 1381 (m), 1112 (s), 1046 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 184 (M^+, 19), 129 (17), 128 (30), 111 (100), 69 (61). Anal. Calcd for $C_{10}H_{16}O_3$: C 65.19, H 8.75. Found: C 65.40, H 8.62.

2-(*E*)-[(2-Methoxyethoxycarbonyl)methylidene]tetrahydrofuran (3e). Starting with 2-methoxyethyl acetoacetate (0.32 g, d = 1.090 g/cm^3, 0.29 mL, 2.0 mmol) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv.), **3e** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (261 mg, 70%, *E*/*Z* = 10:1). The starting material could not be completely removed from the product. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.09 (quint, J = 6.5 Hz, 2 H, 4-H), 3.07 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 3.36 (s, 3 H, OCH_3), 3.55−3.60 (m, 2 H, OCH_2CH_2OMe), 4.17−4.29 (m, 4 H, OCH_2-CH_2OMe, 5-H), 5.33 (t, J = 1.5 Hz, 1 H, CHC=O); *Z*-isomer δ (=CH−) 4.85; ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 23.79, 30.28 (C-3, C-4), 58.96 (OCH_3), 62.34, 70.82, 71.84 (OCH_2), 89.30 (C=CH), 168.50 (C=O), 177.14 (C-2); MS (70 eV, EI) *m*/*z* 186 (M^+, 20). The exact molecular mass for $C_9H_{14}O_4$ *m*/*z* 186.0892 ± 2 mDa was confirmed by HRMS (70 eV, EI).

2-(*E*)-[(Benzyloxycarbonyl)methylidene]tetrahydrofuran (3f). Starting with benzyl acetoacetate (0.38 g, 0.35 mL, d = 1.112 g/cm^3, 2.0 mmol) and 1-bromo-2-chloroethane (2.2 mmol, 0.18 mL, 1.1 equiv), **3f** was isolated by chromatography (silica gel, ether/petroleum ether 1:5) as a colorless oil (262 mg, 60%, *E*/*Z* = 10:1). The starting material could not be completely removed from the product. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.09 (quint, J = 6.5 Hz, 2 H, 4-H), 3.13 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 4.23 (t, J = 6.5 Hz, 2 H, 5-H), 5.18 (s, 2 H, OCH_2Ph), 5.37 (t, J = 6.5 Hz, 1 H, $CHCO_2$), 7.26−7.36 (m, 5 H, Ph); *Z*-isomer δ 4.92 (=CH−); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 23.33, 29.62 (C-3, C-4), 64.62 (OCH_2Ph), 71.49 (C-5), 88.78 ($CHCO_2CH_2$), 127.44, 127.55, 128.01, 128.20 (Ph), 167.82 (C=O), 176.97 (C-2).

2-(*E*)-(2-Diethylamino-2-oxoethylidene)tetrahydrofuran (3g). Starting with *N*,*N*-diethylacetylacetic amide (0.31 g, 2.0 mmol) and 1-bromo-2-chloroethane (2.2 mmol, 0.18 mL, 1.1 equiv), **3g** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (293 mg, 80%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 [br, 6 H, $N(CH_2CH_3)_2$], 2.08 (quint, J = 6.5 Hz, 2 H, 4-H), 3.15 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 3.20−3.50 [m, 4 H, $N(CH_2CH_3)_2$], 4.16 (t, J = 6.5 Hz, 2 H, 5-H), 5.62 (t, J = 1.5 Hz, 1 H, CHC=O); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 12.92, 13.93 (CH_3), 23.60, 29.23 (C-4, C-3), 39.63, 41.59 [$N(CH_2CH_3)_2$], 70.13 (C-5), 88.32 (CHC=O), 166.65 (C=O), 173.30 (C-2); IR (neat) $\tilde{\nu}$ 3458 (br), 2976 (m), 2933 (m), 2897 (m), 1662 (s), 1600 (s), 1482 (m), 1429 (m), 1182 (m), 1114 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 183 (M^+, 35), 111 (100), 69 (38). Anal. Calcd for $C_{10}H_{17}NO_2$: C 65.54, H, 9.35. Found: C 65.27, H, 9.11.

2-(*E*)-[1-(Ethoxycarbonyl)ethylidene]tetrahydrofuran (3h). Starting with ethyl 2-methylacetoacetate (0.29 g, 2.0 mmol) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv), **3h** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (238 mg, 70%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.80 (s, 3 H, CH_3), 2.25 (quint, J = 6.5 Hz, 2 H, 4-H), 3.05 (m, 2 H, 3-H), 4.20 (t, J = 6.5 Hz, 2 H, 5-H), 4.17 (t, J = 7 Hz, 2 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 11.24 (OCH_2CH_3), 14.45 (CH_3), 24.52, 30.84 (C-3, C-4), 59.42 (OCH_2-CH_3), 71.18 (C-5), 97.52 (CCO_2Et), 169.36 (C=O), 170.25 (C-2); MS (70 eV, EI) *m*/*z* 170 (M^+, 70), 125 (100), 83 (81), 42 (71). Anal. Calcd for $C_9H_{14}O_3$: C 63.51, H 8.29. Found: C 63.80, H 7.99.

2-(*E*)-[1-(Ethoxycarbonyl)propylidene]tetrahydrofuran (3i). Starting with ethyl 2-ethylacetoacetate (2.0 mmol, 0.32 g) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv), **3i** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (251 mg, 68%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.90 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.25 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.05 (quint, J = 7 Hz, 2 H, 4-H), 2.30 (q, J = 7 Hz, 2 H, CH_2CH_3), 3.04 (t, J = 7 Hz, 2 H, 3-H), 4.01−4.30 (m, 4 H, 5-H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 13.77, 14.43 (CH_3), 19.39, 24.38 (C-4, C-3), 30.95 (CCH_2CH_3), 59.27 (OCH_2CH_3), 71.18 (C-5), 104.36 (CCO_2-Et), 169.10, 170.19 (C-2, C=O); IR (neat) $\tilde{\nu}$ 29962 (s), 2928 (s), 2961 (s), 1734 (m), 1655 (s), 1602 (m), 1457 (m), 1261 (s), 1076 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 184 (25). Anal. Calcd for $C_{10}H_{16}O_3$: C 65.19, H 8.75. Found: C 64.90, H 8.47.

2-(*E*)-[1-(Ethoxycarbonyl)pentylidene]tetrahydrofuran (3j). To a suspension of sodium hydride (0.50 g) in THF (50 mL) was added ethyl 2-butylacetoacetate (0.75 g, 4.0 mmol) at 0 °C, and the solution was stirred at 0 °C (1 h) and at 20 °C (1h). To the solution was added *n*-butyllithium (2.03 mL, 4.8 mmol, 2.35 M Lösung in *n*-hexane). After stirring for 1 h at 0 °C the solution was cooled to −78 °C, and 1-bromo-2-chloroethane (0.37 mL, 4.4 mmol, 1.1 equiv) was added. After warming to 20 °C during 14 h the solution was refluxed for 14 h. The solution was poured into an aqueous solution of hydrochloric acid (200 mL, 0.1 M), and the aqueous layer was extracted with ether (4 × 150 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, ether/petroleum ether 1:10 → 1:3) to give **3j** as a colorless oil (509 mg, 60%, *E*/*Z* > 98:2). The starting material could not be completely removed from the product. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.20 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.40−1.62 [m, 6 H, $(CH_2)_3$], 1.95 (quint, J = 6.5 Hz, 2 H, 4-H), 3.00 (t, J = 7 Hz, 2 H, 3-H), 4.02−4.20 (m, 4 H, 5-H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 13.91, 14.28 (CH_2CH_3), 22.26, 22.44, 24.28, 27.73, 30.86 ($CH_2CH_2CH_2CH_3$, C-4, C-3), 61.05 (OCH_2CH_3), 71.69 (C-5), 102.84 (*C*CO_2Et), 169.10, 170.32 (C-2, C=O); MS (70 eV, EI) *m*/*z* 212 (M^+, 100), 185 (22), 167 (50), 111 (28), 97 (55). The exact molecular mass for $C_{12}H_{20}O_3$ *m*/*z* 212.1412 ± 2 mDa was confirmed by HRMS (70 eV, EI).

2-(*Z*)-[(Methoxycarbonyl)methylidene]-3-methyltetrahydrofuran (3k). Starting with methyl 3-oxopentanoate (2.0 mmol, 0.26 g) and 1-bromo-2-chloroethane (2.2 mmol, 0.18 mL, 1.1 equiv), **3k** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (212 mg, 68%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (d, J = 7 Hz, 3 H, CH_3), 2.18−2.31 (m, 2 H, 4-H), 2.59 (q, J = 7 Hz, 1 H, 3-H), 3.65 (s, 3 H, OCH_3), 4.20−4.40 (m, 2 H, 5-H), 5.23 (s, 1 H, CHC=O); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 17.53 (CH_3), 31.52, 35.88 (C-3, C-4), 50.43 (OCH_3), 69.74 (C-5), 88.30 (*C*HC=O), 168.35 (C=O), 181.51 (C-2); IR (neat) $\tilde{\nu}$ 3344 (br), 3076 (m), 2961 (s), 1627 (s), 1441 (s), 1308 (s), 1268 (s), 1200 (s), 1112 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 156 (M^+, 50), 139 (27), 125 (89), 111 (45), 69 (100). Anal. Calcd for $C_8H_{12}O_3$: C 61.52, H 7.74. Found: C 61.41, H, 7.40.

2-(*Z*)-[(Ethoxycarbonyl)methylidene]-3-ethyltetrahydrofuran (3l). Starting with ethyl 3-oxohexanoate (2.0 mmol, 0.31 g) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv), **3l** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (293 mg, 80%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.0 (t, J = 7 Hz, 3 H, CH_3), 1.23 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.62−1.83 (m, 2 H, CH_2CH_3), 1.84−2.20 (m, 2 H, 4-H), 3.42−3.61 (m, 1 H, 3-H), 3.99−4.16 (m, 2 H, 5-H), 4.25 (q, J = 7 Hz, 2 H, OCH_2CH_3), 5.20 (s, 1 H, CHC=O); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 12.37 ($CHCH_2CH_3$), 14.38 (OCH_2CH_3), 24.94, 28.06, 42.92 (C-3, C-4, CCH_2CH_3), 59.08 (OCH_2CH_3), 69.99 (C-5), 89.16 (*C*HC=O), 167.99 (C=O), 180.67 (C-2); IR (neat) $\tilde{\nu}$ 2964 (s), 2903 (s), 1741 (s), 1714 (s), 1646 (s), 1463 (m), 1384 (m), 1151 (s), 1113 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 184 (M^+, 35), 111 (100), 69 (38). Anal. Calcd for $C_{10}H_{16}O_3$: C 65.19, H 8.75. Found: C 65.27, H 9.11.

2-(*E*)-(2-Oxotetrahydrofuran-3-ylidene)tetrahydrofuran (3m). Starting with 2-acetyl-γ-butyrolactone (0.26 g, 2.0 mmol) and 1-bromo-2-chloroethane (2.2 mmol, 0.18 mL, 1.1 equiv), **3m** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (123 mg, 40%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.10 (quint, J = 6.5 Hz, 2 H, 4-H), 2.87 (m, 2 H, (CH_2CH_2O), 3.09 (t, J = 6.5 Hz, 2 H, 3-H), 4.30 (2 x t, J = 6.5 Hz, 4 H, OCH_2CH_2, 5-H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 23.96, 24.96, 28.84 [C-3, C-4, CH_2(C=C)], 65.12, 72.39 (C-5, OCH_2), 92.84 (C=*C*CO_2), 169.40 (C=O), 173.00 (C-2); MS (70 eV, EI) *m*/*z* 154 (M^+, 20). The exact molecular mass for $C_8H_{10}O_3$ *m*/*z* 154.0630 ± 2 mDa was confirmed by HRMS (70 eV, EI).

2-(*E*)-(5-Ethyl-2-oxotetrahydrofuran-3-ylidene)tetrahydrofuran (3n). Starting with α-acetyl-γ-ethyl-γ-butyrolactone (2.0 mmol, 0.31 g) and 1-bromo-2-chloroethane (0.18 mL, 2.2 mmol, 1.1 equiv), **3n** was isolated by chromatography (silica gel, ether/petroleum ether 1:1) as a colorless oil (225 mg, 62%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, J = 7 Hz, 3 H, CH_3), 1.46−1.84 (m, 2 H, CH_2CH_3), 2.04 (quint, J = 6.5 Hz, 2 H, 4-H), 2.32−2.40 (m, 2 H, CH_2CHO), 2.98−3.06 (m, 2 H, 3-H), 4.21 (t, J = 6.5 Hz, 2 H, 5-H), 4.27 (m, 1 H, $OCHCH_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 8.61 (CH_3), 23.58, 28.51, 28.90, 30.09 (C-4, CH_2CHO, C-3, CH_2CH_3), 71.94 (C-5), 77.84 ($OCHCH_2CH_3$), 93.45 (C=CCO_2), 168.79 (C=O), 172.21 (C-2); IR (neat) $\tilde{\nu}$ 2968 (m), 2938 (m), 1739 (s), 1668 (s), 1457 (w), 1351 (m), 1254 (s), 1036 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 182 (M^+, 100), 153 (35), 125 (63), 96 (77), 43 (49). Anal. Calcd for $C_{10}H_{14}O_3$: C 65.91, H 7.74. Found: C 65.71, H 7.49.

2-(*E*)-(Cyanomethylidene)tetrahydrofuran (3o). Starting with 5-methylisoxazole (2.0 mmol, 0.17 g) and 1-bromo-2-chloroethane (2.2 mmol, 0.18 mL, 1.1 equiv), **3o** was isolated by chromatography (silica gel, ether/petroleum ether 1:3) as a colorless oil (87 mg, 40%, *E*/*Z* > 98:2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.11 (quint, J = 7 Hz, 2 H, 4-H), 2.70 (dt, J = 6.5 Hz, J = 1.5 Hz, 2 H, 3-H), 4.27 (t, J = 1.5 Hz, 1 H, C*H*CN), 4.37 (t, J = 7 Hz, 2 H, 5-H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 23.96, 30.79 (C-4, C-3), 65.09 (C-5), 73.88 (*C*HCN), 116.66 (CN), 176.85 (C-2); IR (neat) $\tilde{\nu}$ 3327 (br), 3088 (w), 2968 (m), 2912 (m), 2213 (s, CN), 1651 (s), 1391 (m), 1187 (s), 1200 (s), 1112 (s) cm^{-1}; MS (70 eV, EI) *m*/*z* 109 (M^+, 81), 68 (100), 42 (81). The exact molecular mass for C_6H_7NO *m*/*z* 109.0527 ± 2 mDa was confirmed by HRMS (70 eV, EI). Anal. Calcd for C_6H_7NO: C 66.04, H 6.47. Found: C 65.41, H 7.40.

General Procedure for the Cyclization of 1,3-Dicarbonyl Dianions with 1,4-Dibromo-2-butene. A THF solution of LDA (4.7 mmol) was prepared by addition of *n*-BuLi (8.0 mL, 18.4 mmol, 2.3 M solution in *n*-hexane) to a THF solution (50 mL) of diisopropylamine (2.6 mL, 18.4 mmol) at 0 °C. After the solution stirred for 20 min, ethyl acetoacetate (1.04 g, 8.0 mmol) was added at 0 °C. After stirring for 60 min, to the solution was added a THF solution (25 mL) of 1,4-dibromo-2-butene **4** (1.712 g, 8.0 mmol) at −78 °C. The employment of an inverse addition protocol was advantageous in many cases. The temperature was allowed to rise to ambient during 4−12 h, and the solution was stirred at 20 °C for 2 h. The reaction mixture was poured into an aqueous solution of hydrochloric acid (0.1 M) and was extracted with ether. The combined organic layers were dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/ether 3:2) to give **5a** (875 mg, 60%, *Z*/*E* > 98:2) as a colorless oil.

2-(Ethoxycarbonylmethylidene)-5-vinyltetrahydrofuran (5a). Starting with ethyl acetoacetate (1.04 g, 8.0 mmol), diisopropylamine (2.6 mL, 18.4 mmol), *n*-BuLi (8.0 mL, 18.4 mmol, 2.3 M solution in *n*-hexane), and 1,4-dibromo-2-butene (1.712 g, 8.0 mmol), 875 mg (60%, *Z*/*E* > 98:2) of **5a** was obtained as a colorless solid. The purification was effected by chromatography (silica gel, petroleum ether/ether 3:2). ^{1}H NMR (250 MHz, acetone-d_6) δ 1.18 (t, ^3J = 7 Hz, 3 H, CH_3), 1.69−1.86 (m, 1 H, 4-H), 2.15−2.34 (m, 1 H, 4-H), 2.75 (t, ^3J = 8 Hz, 2 H, 3-H), 4.01 (q, ^3J = 7 Hz, 2 H, OCH_2), 4.75 (s, 1 H, O=CCH), 4.98 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 5.19 [d, $^3J(Z)$ = 11 Hz, 1 H, C=CH], 5.36 [d, $^3J(E)$ = 18 Hz, 1 H, H_2C=CH], 5.94 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 18 Hz, 1 H, C*H*=CH_2]; ^{13}C NMR (62.9 MHz, acetone-d_6) δ 13.98 (CH_3), 28.91, 31.53 (CH_2), 58.06 (OCH_2), 85.98, 87.33 (C-5, O=*C*CH), 116.23 (CH=CH_2), 136.63 (*C*H=CH_2), 164.47 (C=O), 171.63 (C-2); MS (70 eV, EI) *m*/*z* 182 (73) $[M]^+$, 137 (100), 87 (85), 69 (100), 43 (55). The exact molecular mass for $C_{10}H_{14}O_3$ *m*/*z* 182.0943 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(1,1-Dimethylethoxycarbonylmethylidene)-5-vinyltetrahydrofuran (5b). Starting with *tert*-butyl acetoacetate (1.73 g, 10.95 mmol), diisopropylamine (3.55 mL, 25.0 mmol), *n*-BuLi (25.0 mmol, solution in *n*-hexane), and 1,4-dibromo-2-butene (2.58 g, 12.05 mmol), 1.33 g of **5b** (58%, *Z*/*E* > 98:2) was isolated as a colorless solid. The purification was effected by chromatography (silica gel, petroleum ether/ether 3:2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.40 (s, 9 H, CH_3), 1.68−1.84 (m, 1 H, 4-H), 2.13−2.29 (m, 1 H, 4-H), 2.71 (t, ^3J = 8 Hz, 2 H, 3-H), 4.68 (s, 1 H, O=CCH), 4.94 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 5.18 [d, $^3J(Z)$ = 11 Hz, 1 H, H_2C=CH], 5.36 [d, $^3J(E)$ = 18 Hz,

1 H, H_2C=CH], 5.93 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 18 Hz, 1 H, C*H*=CH_2]; ^{13}C NMR (62.9 MHz, acetone-d_6) δ 27.72 (CH_3), 28.93, 31.46 (CH_2), 77.31 [O*C*(CH_3)$_3$], 85.70, 89.04 (C-5, O=C*C*H), 116.10 (CH=CH_2), 136.70 (*C*H=CH_2), 164.16 (C=O), 170.68 (C-2); MS (70 eV, EI) *m*/*z* 210 (23) $[M]^+$, 154 (83), 137 (100), 87 (91), 69 (65), 68 (51), 57 (40). The exact molecular mass for $C_{12}H_{18}O_3$ *m*/*z* 210.1256 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(2-Oxopropylidene)-5-vinyltetrahydrofuran (5c). Starting with acetylacetone (1.60 g, 15.97 mmol), diisopropylamine (5.20 mL, 36.7 mmol), *n*-BuLi (36.7 mmol, solution in *n*-hexane), and 1,4-dibromo-2-butene (3.76 g, 17.57 mmol), **5c** was isolated as a colorless solid (1.14 g, 47%, *Z*/*E* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, acetone-d_6) δ 1.73−1.91 (m, 1 H, 4-H), 2.18−2.35 (m, 1 H, 4-H), partly overlaped by 2.22 (s, 3 H, CH_3), 2.78 (t, ^3J = 8 Hz, 2 H, 3-H), 4.96 (s, 1 H, O=CCH), 5.06 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 5.23 [d, $^3J(Z)$ = 11 Hz, 1 H, H_2C=CH], 5.37 [d, $^3J(E)$ = 18 Hz, 1 H, H_2C=CH], 5.98 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 18 Hz, 1 H, C*H*=CH_2]; ^{13}C NMR (62.9 MHz, MeOH-d_4) δ 30.01, 33.25 (CH_2), 30.53 (CH_3), 88.80 (C-5), 100.81 (O=C*C*H), 117.87 (CH=*C*H_2), 137.23 (*C*H=CH_2), 175.37 (C-2), 200.06 (C=O); MS (70 eV, EI) *m*/*z* 152 (24) $[M]^+$, 137 (27), 85 (54), 69 (100), 43 (70). The exact molecular mass for $C_9H_{12}O_2$ *m*/*z* 152.0837 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(2-Diethylamino-2-oxoethylidene)-5-vinyltetrahydrofuran (5d). Starting with *N*,*N*-diethylacetyl acetic amide (314 mg, 2.0 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*-BuLi (2.0 mL, 4.6 mmol, 2.3 M solution in *n*-hexane), and 1,4-dibromo-2-butene (424 mg, 11.3 mmol), **5d** was isolated as a colorless oil (305 mg, 73%, *Z*/*E* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). The starting material could not be completely removed. ^{1}H NMR (250 MHz, acetone-d_6) δ 0.95−1.26 (m, 6 H, CH_3), 1.73 (ddt, ^3J = ^3J = 9 Hz, ^2J = 13 Hz, 1 H, 4-H), 2.10−2.29 (m, 1 H, 4-H), 2.57−2.75 (m, 2 H, 3-H_2), 3.26−3.47 (m, 4 H, NCH_2), 4.83 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 4.97 (s, 1 H, O=CCH), 5.15 [d, $^3J(Z)$ = 11 Hz, 1 H, CH=C*H*$_2$], 5.35 [d, $^3J(E)$ = 17 Hz, 1 H, CH=C*H*$_2$], 5.90 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 17 Hz, 1 H, C*H*=CH_2]; ^{13}C NMR (62.9 MHz, acetone-d_6) δ 12.40, 26.09 (CH_3), 29.12, 29.21, 35.25, 35.32 (CH_2), 39.26, 41.46, 41.87 (NCH_2), 84.40 (C-5), 88.58, 115.72 (CH=*C*H_2), 129.16, 129.40 (CH, O=C*C*H), 136.99 (*C*H=CH_2), 164.33, 164.69 (C=O, C-2); MS (70 eV, EI) *m*/*z* 209 (43) $[M]^+$, 137 (100), 72 (28), 69 (72). The exact molecular mass for $C_{12}H_{19}O_2N$ *m*/*z* 209.1416 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(1-Ethoxycarbonylethylidene)-5-vinyltetrahydrofuran (5e). Starting with 2-acetylpropanoic acid ethylester (0.60 g, 4.16 mmol), diisopropylamine (1.34 mL, 9.5 mmol), *n*-BuLi (9.5 mmol, solution in *n*-hexane), and 1,4-dibromo-2-butene (0.98 g, 4.58 mmol), **5e** was isolated as a colorless oil (524 mg, 64%, *Z*/*E* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 3:2). ^{1}H NMR (250 MHz, acetone-d_6) δ 1.21 (t, ^3J = 6 Hz, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 1.73−1.96 (m, 1 H, 4-H), 2.14−2.31 (m, 1 H, 4-H), 2.68−2.81 (m, 2 H, 3-H), 4.07 (q, ^3J = 6 Hz, 2 H, OCH_2), 4.89 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 5.14 [d, $^3J(Z)$ = 11 Hz, 1 H, CH=C*H*$_2$], 5.34 [d, $^3J(E)$ = 17 Hz, 1 H, CH=C*H*$_2$], 5.91 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 17 Hz, 1 H, C*H*=CH_2]; ^{13}C NMR (62.9 MHz, acetone-d_6) δ 13.96, 14.09 (CH_3), 29.00, 30.23 (CH_2), 58.70 (OCH_2), 84.75 (C-5), 94.33 (C=*C*−CH_3), 115.48 (CH=CH_2), 137.26 (*C*H=CH_2), 166.60, 166.62 (C=O, C-2); MS (70 eV, EI) *m*/*z* 196 (77) $[M]^+$, 151 (93), 129 (38), 101 (84), 83 (100). The exact molecular mass for $C_{11}H_{16}O_3$ *m*/*z* 196.1099 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(1-Ethoxycarbonylpropylidene)-5-vinyltetrahydrofuran (5f). Starting with 2-acetylbutanoic acid ethylester (593 mg, 3.75 mmol), diisopropylamine (1.22 mL, 8.62 mmol), *n*-BuLi (8.62 mmol, solution in *n*-hexane) and 1,4-dibromo-2-butene (882 mg, 4.12 mmol), **5f** was isolated as a colorless oil (480 mg, 61%, *Z*/*E* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 3:2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (t, ^3J = 7 Hz, 3 H, CCH_2CH_3), 1.23 (t, ^3J = 6 Hz, 3 H, OCH_2CH_3), 1.79−1.90 (m, 1 H, 4-H), 2.19−2.36 (m, 1 H, 4-H), partly overlaped by 2.32 (q, ^3J = 7 Hz, 2 H, CH_2CH_3), 2.87−3.05 (m, 1 H, 3-H), 3.05−3.21 (m, 1 H, 3-H), 4.10 (q, ^3J = 6 Hz, 2 H, OCH_2CH_3), 4.87 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 5.18 [d, $^3J(Z)$ = 11 Hz, 1 H, CH=C*H*$_2$], 5.31 [d, $^3J(E)$ = 17 Hz, 1 H, CH=CH-*H*$_2$], 5.94 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 17 Hz, 1 H, C*H*=CH_2]; ^{13}C NMR (62.9 MHz, acetone-d_6) δ 13.37, 13.96 (CH_3), 19.24, 30.03, 30.62 (CH_2), 58.79 (O−CH_2), 83.13 (O−CH), 103.83 (C, OC=*C*), 115.80 (CH=*C*H_2), 137.17 (*C*H=CH_2), 167.89 (C=O), 169.72 (C-2); MS (70 eV, EI) *m*/*z* 210 (100) $[M]^+$, 165 (78), 157 (45), 149 (46), 143 (41), 115 (72), 97 (87). The exact molecular mass for $C_{12}H_{18}O_3$ *m*/*z* 210.1256 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(1-Ethoxycarbonylpentylidene)-5-vinyltetrahydrofuran (5g). Starting with 2-acetylhexanoic acid ethylester (560 mg, 3.0 mmol), diisopropylamine (0.98 mL, 6.9 mmol), *n*-BuLi (6.9 mmol, solution in *n*-hexane) and 1,4-dibromo-2-butene (705 mg, 3.3 mmol), **5g** was isolated as a colorless oil (224 mg, 32%, *Z*/*E* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 3:2). ^{1}H NMR (250 MHz, acetone-d_6) δ 0.88 (t, ^3J = 6 Hz, 3 H, CH_3), 1.18 (t, ^3J = 6 Hz, 3 H, CH_3), partly overlaped by 1.17−1.44 (m, 4 H, CH_2), 1.66−1.86 (m, 1 H, CH_2), 2.10−2.31 (m, 3 H, CH_2), 2.71−2.85 (m, 2 H, CH_2), 4.08 (q, ^3J = 6 Hz, 2 H, OCH_2CH_3), 4.88 [ddddd, ^3J = ^3J = ^3J = 6 Hz, $^4J(E)$ = $^4J(Z)$ = 1 Hz, 1 H, H-5], 5.14 [ddd, ^2J = $^4J(Z)$ = 1 Hz, $^3J(Z)$ = 10 Hz, 1 H, HC=C*H*$_2$], 5.35 [ddd, ^2J = $^4J(E)$ = 1 Hz, $^3J(E)$ = 18 Hz, 1 H, HC=C*H*$_2$], 5.92 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 10 Hz, $^3J(E)$ = 18 Hz, 1 H, *H*C=CH−H]; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.90, 14.31 (CH_3), 22.48, 28.95, 29.06, 29.84, 31.76 (CH_2), 59.38 (O−CH_2), 84.67 (O−CH), 100.95 (C, O−C=*C*), 116.70 (CH=*C*H_2), 136.20 (*C*H=CH_2), 166.41 (C=O), 167.12 (C-2); MS (70 eV, EI) *m*/*z* 238 (48) $[M]^+$, 195 (58), 193 (49), 149 (100), 85 (56), 57 (46). The exact molecular mass for $C_{14}H_{22}O_3$ *m*/*z* 238.1569 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(2-γ-Butyrolactonylidene)-5-vinyltetrahydrofuran (5h): Starting with 2-acetyl-γ-butyrolactone (384 mg, 3.0 mmol), diisopropylamine (0.97 mL, 6.9 mmol), *n*-BuLi (2.9 mL, 6.9 mmol, 2.38 M solution in *n*-hexane), and 1,4-dibromo-2-butene (708 mg, 3.3 mmol), **5h** was isolated as a colorless solid (175 mg, *E*/*Z* > 98:2, 32%). The product was purified two times by chromatography (silica gel, petroleum ether/ether 4:1). ^{1}H NMR (250 MHz, acetone-d_6) δ 1.78−1.96 (m, 1 H, O−CH−CH−*H*), 2.24−2.41 (m, 1 H, 4-H), 2.60−3.01 (m, 4 H, C=C−CH_2), 4.25 (t, ^3J = 8 Hz, 2 H, OCH_2), 4.96 (ddd, ^3J = ^3J = ^3J = 7 Hz, 1 H, 5-H), 5.23 [d, $^3J(Z)$ = 10 Hz, 1 H, HC=C*H*$_2$], 5.36 [d, $^3J(E)$ = 17 Hz, 1 H, HC=C*H*$_2$], 5.95 [ddd, ^3J = 7 Hz, $^3J(Z)$ = 10 Hz, $^3J(E)$ = 17 Hz, 1 H, *H*C=CH_2]; ^{13}C NMR (62.9 MHz, acetone-d_6) δ 24.79, 28.48, 29.74 (CH_2), 64.61 (O−CH_2), 84.49 (O−CH), 93.00 (C, O−C=*C*), 116.63 (CH=*C*H_2), 136.62 (*C*H=CH_2), 168.33 (C=O), 171.91 (C-2); MS (70 eV, EI) *m*/*z* 180 (38) $[M + H]^+$, 139 (49), 113 (100), 43 (71). The exact molecular mass for $C_{10}H_{12}O_3$ *m*/*z* 180.0786 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(1-Oxo-1,2,3,4-tetrahydronapht-2-ylidene)-5-vinyltetrahydrofuran (5i). Starting with α-acetyltetralone (372 mg, 2 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*-BuLi (2.0 mL, 4.6 mmol, solution in *n*-hexane), and 1,4-dibromo-2-butene (468 mg, 2.2 mmol)), **5i** was isolated as a colorless oil (220 mg, 46%, *E*/*Z* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 4:1). ^{1}H NMR (250 MHz, acetone-d_6) δ 1.80−1.98 (m, 1 H, CH_2), 2.22−2.47 (m, 1 H, CH_2), 2.70−2.97 (m, 4 H, CH_2), 2.98−3.22 (m, 1 H, CH_2), 3.27−3.43 (m, 1 H, CH_2), 4.95 (dt, ^3J = ^3J = 7 Hz, 1 H, 5-H), 5.23 [d, $^3J(Z)$ = 10 Hz, 1 H, HC=C*H*$_2$], 5.38 [d, $^3J(E)$ = 17 Hz, 1 H, HC=C*H*$_2$], 5.89 [ddd, ^3J = 7 Hz, $^3J(Z)$ = 10 Hz, $^3J(E)$ = 17 Hz, 1 H, *H*C=CH_2], 7.22−7.48 (m, 3 H, Ar−H), 7.92 (d, ^3J = 8 Hz, 1 H, Ar−H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 23.84, 28.58, 30.27, 31.62 (CH_2), 83.60 (O−CH), 106.58 (O−C=*C*), 117.36 (CH=*C*H_2), 126.54, 127.05, 127.83, 131.91 (Ar−CH), 135.08, 142.98 (Ar−C), 136.29 (*C*H=CH_2), 170.89 (C-2), 187.87 (C=O); MS (70 eV, EI) *m*/*z* 240 (100) $[M]^+$, 199 (25), 173 (79).

The exact molecular mass for $C_{16}H_{16}O_2$ *m/z* 240.1150 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(Methoxycarbonylmethylidene)-3-methyl-5-vinyltetrahydrofuran (5j). Starting with 3-oxopentanoic acid methylester (1.85 g, 14.2 mmol), diisopropylamine (4.64 mL, 32.7 mmol), *n*-BuLi (32.7 mmol, solution in hexane), and 1,4-dibromo-2-butene (3.35 g, 15.7 mmol), **5j** was isolated as a colorless oil (1.58 g, 61%, *Z*/*E* = 8:1, ds = 55:45). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, acetone-d_6]) δ 1.06 (d, ^3J = 6 Hz, 3 H, CCH_3), 1.21 (d, ^3J = 6 Hz, 3 H, C−CH_3), 1.43 (ddd, ^2J = ^3J = ^3J = 11 Hz, 1 H, CH_2), 1.82−2.01 (m, 1 H, CH_2), 2.29−2.50 (m, 2 × 1 H, CH_2, both isomers), 2.66−2.81 (m, 1 H, CH), 2.92−3.09 (m, 1 H, CH), 3.55 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 4.70, 4.75 (2 x s, 2 H, O=CCH), 4.86 (dt, ^3J = 11 Hz, ^3J = 6 Hz, 1 H, 5-H), 5.06 (dt, ^3J = ^3J = 6 Hz, 1 H, 5-H), 5.11−5.48 (m, 2 × 2 H, HC=CH_2, both isomers), 5.83−6.04 (m, 2 H, *H*C=CH_2, both isomers); ^{13}C NMR (62.9 MHz, acetone-d_6) δ 16.16, 17.50 (C-*C*H_3), 35.15, 36.25 (CH_2), 37.47, 38.78 (*C*H−CH_3), 49.43, 51.26 (OCH_3), 83.51, 84.07, 85.89, 86.23 (C-5, C=*C*HC=O), 115.84, 116.86 (CH=*C*H_2), 136.57, 136.66 (*C*H=CH_2), 165.11, 167.47 (C=O), 175.74, 175.75 (C-2); MS (70 eV, EI) *m/z* 182 (54) $[M]^+$, 151 (50), 101 (100), 81 (29), 69 (98), 41 (32). The exact molecular mass for $C_{10}H_{14}O_3$ *m/z* 182.0943 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-(Ethoxycarbonylmethylidene)-3-ethyl-5-vinyltetrahydrofuran (5k). Starting with 3-oxohexanoic acid ethylester (316 mg, 2.0 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*-BuLi (2.0 mL, 4.6 mmol, 2.36 M solution in *n*-hexane), and 1,4-dibromo-2-butene (426 mg, 2.0 mmol (petroleum ether/ether 5:1), **5k** was isolated as a colorless solid (224 mg, 53%, *Z*/*E* > 98:2, ds = 65:35). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, acetone-d_6) δ 0.95 (t, ^3J = 7 Hz, 2 × 3 H, CH_3, beide isomere), 1.18 (t, ^3J = 7 Hz, 2 × 3 H, CH_3, both isomers), 1.30−1.59 (m, 2 × 2 H, CH_2), 1.61−1.76 (m, 2 × 1 H, 4-H, both isomers), partly overlaped by 1.73−1.93 (m, 2 × 1 H, 4-H), 2.43 (ddd, ^3J = 6 Hz, ^3J = 8 Hz, ^2J = 13 Hz, 1 H, 3-H), 2.75−2.97 (m, 1 H, 3-H), 4.03 (q, ^3J = 7 Hz, 2 × 2 H, OCH_2, both isomers), 4.70 (s, 1 H, C=CHC=O), 4.75 (s, 1 H, C=CHC=O), 4.84 (ddd, ^3J = ^3J = 6 Hz, ^3J = 11 Hz, 1 H, 5-H), 5.05 (ddd, $^3J_1$ = $^3J_2$ = $^3J_3$ = 6 Hz, 1 H, 5-H), 5.17, 5.21 [2 × d, $^3J(Z)$ = 11 Hz, 2 × 1 H, CH=CH_2, both isomers], 5.33, 5.42 [d, $^3J(E)$ = 18 Hz, 2 × 1 H, CH=CH_2, both isomers], 5.84−6.04 (m, 2 × 1 H, C*H*=CH_2, both isomers); ^{13}C NMR (62.9 MHz, acetone-d_6) δ 11.04, 11.15 (CH_2*C*H_3), 13.96, 13.97 (OCH_2*C*H_3), 24.62, 25.70, 33.91, 35.20 (C-4, C*C*H_2CH_3), 44.54, 45.37 (C-3), 58.00, 58.01 (OCH_2), 83.65, 84.01, 86.54, 87.22 (C-5, C=*C*HC=O), 115.66, 116.52 (CH=*C*H_2), 136.71, 136.74 (*C*H=CH_2), 164.42, 164.43 (C=O) 174.23, 174.49 (C-2); MS (70 eV, EI) *m/z* 210 (65) $[M]^+$, 182 (54), 165 (100), 115 (52), 94 (46), 87 (71), 69 (83). The exact molecular mass for $C_{12}H_{18}O_3$ *m/z* 210.1256 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

2-Cyanomethylidene-5-vinyltetrahydrofuran (5l). Starting with 5-methylisoxazole (166 mg, 2.0 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*-BuLi (2.0 mL, 4.6 mmol, solution in *n*-hexane), and 1,4-dibromo-2-butene (470 mg, 2.2 mmol) **5l** was isolated as a colorless oil (135 mg, 50%, *E*/*Z* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.80−2.00 (m, 1 H, H-4), 2.20−2.40 (m, 1 H, H-4), 2.74 (t, ^3J = 6 Hz, 2 H, H-3), 4.27 (s, 1 H, C=C*H*CN), 4.99 (ddd, $^3J_1$ = $^3J_2$ = $^3J_3$ = 6 Hz, 1 H, H-5), 5.27 [d, $^3J(Z)$ = 11 Hz, 1 H, HC=CH_2], 5.37 [d, $^3J(E)$ = 17 Hz, 1 H, HC=CH_2], 5.87 [ddd, ^3J = 6 Hz, $^3J(Z)$ = 11 Hz, $^3J(E)$ = 17 Hz, 1 H, *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 29.83, 30.66 (CH_2), 65.36, 86.08 (CH, O−C=*C*, O−CH), 116.55 (C, CN), 117.97 (CH=*C*H_2), 135.04 (*C*H=CH_2), 176.11 (C, O−*C*=C); MS (70 eV, EI) *m/z* 135 (100) $[M]^+$, 134 (87), 120 (50), 67 (87), 53 (56). The exact molecular mass for C_8H_9NO *m/z* 135.0684 ± 2 mD (M^+) was confirmed by HRMS (EI, 70 eV).

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