

Synthesis of Functionalized 2-Alkylidene-tetrahydrofurans Based on a [3+2] Cyclization/Bromination/Palladium(0) Cross-Coupling Strategy

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The bromination of 2-alkylidene-tetrahydrofurans and 2-alkylidene-pyrrolidines – readily available through one-pot [3+2] cyclization reactions – afforded 2-alkylidene-1'-bromotetrahydrofurans, 2-alkylidene-3-bromotetrahydrofurans and 2-alkylidene-1',3-dibromotetrahydrofurans and their pyrrolidine counterparts. 2-Alkylidene-1'-bromotetrahydrofurans

were functionalized by performing Suzuki and Heck reactions. 2-Alkylidene-1',3-dibromotetrahydrofurans were successfully employed in novel double-Suzuki reactions.

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Introduction

2-Alkylidene-tetrahydrofurans^[1,2] and 2-alkylidene-pyrrolidines^[3,4] are important building blocks in the synthesis of natural products. A number of synthetic transformations of 2-alkylidene-tetrahydrofurans have been reported, including, for example, cycloaddition,^[1a–1d] nucleophilic addition,^[1e,1f] cyclopropanation^[1g] and oxidative carbonylation reactions.^[1h–1j] The hydrogenation^[1k,2h,2i] of 2-alkylidene-tetrahydrofurans to give tetrahydrofurans has been applied to the synthesis of natural products such as methyl nonactate.^[2] The spiroketal chalcogran has been prepared from a bicyclic 2-alkylidene-tetrahydrofuran.^[5] We have a particular interest in the development of cyclization reactions of free and masked dianions, and have reported, along with others, a number of one-pot syntheses of 2-alkylidene-tetrahydrofurans by [3+2] cyclization of 1,3-dicarbonyl dianions and 1,3-bis-silyl enol ethers.^[6] In addition, the functionalization of 2-alkylidene-tetrahydrofurans by lithiation/alkylation^[7a,7b] and by BBr₃-mediated ring-opening reactions^[7c,7d] have been reported. Recently, we studied the functionalization of 2-alkylidene-tetrahydrofurans by bromination of the exocyclic double bond and subsequent Suzuki cross-coupling reactions.^[8] Herein, we wish to report full details of these studies; with regard to our preliminary communication, we have significantly extended the preparative scope. We also report double-Suzuki reactions of 2-alkylidene-1',3-dibromotetrahydrofurans which represent, to

the best of our knowledge, the first double-Suzuki reactions of 1,3-dibromoprop-1-enes. The products prepared are of considerable pharmacological relevance and also represent useful synthetic building blocks that are not readily available by other methods.

Results and Discussion

Our starting point was the development of a method for the bromination of the exocyclic double bond of 2-alkylidene-tetrahydrofurans and 2-alkylidene-pyrrolidines. The required starting materials, 2-alkylidene-tetrahydrofurans **2a–h**, were prepared in accord with our recently reported cyclization of 1-bromo-2-chloroethane with the dianions of 1,3-dicarbonyl compounds **1a–h** (Scheme 1, Table 1).^[9] 5-Vinyl-2-alkylidene-tetrahydrofuran **2i** is available by cyclization of dilithiated ethyl acetoacetate (**1b**) with 1,4-dibromo-2-butene.^[9] 2-Alkylidene-pyrrolidines **2j,k**, were also obtained by a known procedure: the reaction of the dianions of **1b,c** with 1-bromo-2-chloroethane gave the corresponding 6-chloro-1,3-dioxohexanoates. These dioxohexanoates were transformed into **2j,k** by nucleophilic displacement of the chloride group by treatment with NaN₃ and subsequent cyclization by treatment with PPh₃/THF (Staudinger-aza-Wittig reaction).^[10]

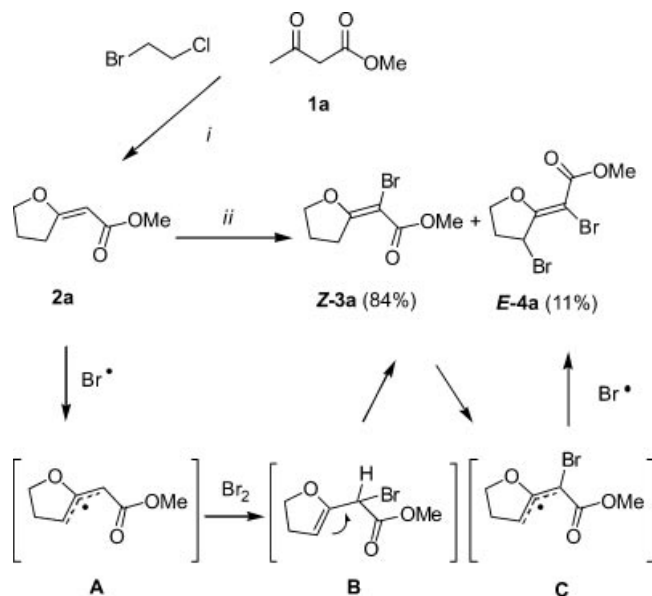
The bromination of 2-alkylidene-tetrahydrofuran **2a** was studied (Scheme 1). The reaction of **2a** with NBS (1.3 equiv.) resulted in the bromination of the double bond and the formation of the desired product **Z-3a**; the dibrominated side-product **E-4a** was also formed. Optimization of the reaction conditions showed that the use of NBS was mandatory; the employment of bromine was unsuccessful. In addition, the amount of NBS, the reaction time (3 h), temperature (reflux) and solvent (CCl₄) all proved to be important parameters. The formation of **Z-3a** can, in prin-

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ciple, proceed by a radical or a cationic mechanism. Notably, the reactions were carried out by using CCl_4 as the solvent under reflux; however, the use of a radical initiator, such as AIBN, was not required. In fact, the reaction conditions employed and the isolation of small amounts of the mono- and dibrominated products **4**, **5** and **6** suggest that a radical mechanism operates: the reaction of **2a** with a bromine radical ($\text{Br}^\bullet$) affords the allylic radical **A**. This reacts with bromine to give intermediate **B** which undergoes a double-bond migration to give the product **Z-3a**. A small amount of the latter is transformed into **E-4a** via the allylic radical **C**.



Scheme 1. Bromination of 2-alkylidene-tetrahydrofuran **2a**. Reagents and conditions: *i*: 1) 2.3 equiv. LDA, THF, 0 °C, 1 h; 2) $\text{Br}(\text{CH}_2)_2\text{Cl}$, $-78 \rightarrow 20$ °C, 14 h, then reflux, 12 h; *ii*: NBS (1.3 equiv.), CCl_4 , reflux, 3 h.

The bromination of other 2-alkylidene-tetrahydrofurans and -pyrrolidines has also been studied (Table 1). The reaction of **2b–d** with NBS (1.3 equiv.) afforded the desired products **3b–d** and the dibrominated side-products **4b,c**. Although the yield of **3c** was successfully improved by the employment of only 1.1 equiv. of NBS, the formation of side-products (**5c** and **4c**) could not be entirely avoided. The reaction of **2b** with an excess of NBS (3.0 equiv.) resulted in the selective formation of the dibrominated product **4b**, which was isolated in high yield as a separable mixture of (*E*)/(*Z*) isomers (**Z-4b**: 70%; **E-4b**: 23%).

The bromination (NBS, 1.3 equiv.) of benzoylacetone-derived 2-alkylidene-tetrahydrofuran **2e** exclusively gave the dibrominated product **4e**. The bromination of 2-alkylidene-tetrahydrofurans **2f,g** containing methyl and ethyl groups at the exocyclic double bond resulted in selective bromination of the C-3 carbon atom (**5f,g**) and in double bromination (**6f**). The bromination (NBS, 1.2 equiv.) of tetrahydro-2,3'-bifuranylidene-2'-one **2h**^[7a,9] afforded the monobromide **5h** (76%) and the dibromide **6h** (22%). Bromination of 2-alkylidene-tetrahydrofurans **2f–h** regioselectively occurred at the C-3 position, presumably as a result of steric hindrance

at the exocyclic double bond and the higher stability of the product containing an exocyclic double bond (conjugation to the carbonyl group). Bromination of 5-vinyl-2-alkylidene-tetrahydrofuran **2i** with NBS (1.6 equiv.) afforded the dibromide **4i**.

The reaction of isomerically pure (*Z*)-configured 2-alkylidene-pyrrolidine **2j** with NBS (1.3 equiv.) afforded a separable mixture of **3j** (66%) and **4j** (30%). Likewise, the bromination of **2k** with NBS (1.3 equiv.) gave **3k** (75%) and **4k** (19%). The use of a smaller amount of NBS resulted in a decrease in yield. These bromides (**3j**, **3k**, **4j** and **4k**) were obtained as inseparable mixtures of geometric isomers. The (*E*)-configured isomers were predominantly formed as a result of the formation of a stable intramolecular N–H $\cdots$ O hydrogen bond.

The configurations of the exocyclic double bond of 2-alkylidene-tetrahydrofurans **2** were established by NOESY experiments.^[7a,11] The structures of the bromo-2-alkylidene-tetrahydrofurans were elucidated by comparison of the chemical shifts of the C-2 carbon atom (O=C=C–Br) with those of related 2-alkylidene-tetrahydrofurans (Table 2). As expected, characteristic ^{13}C NMR shifts in the range of $\delta = 170.8\text{--}172.2$ ppm were observed for all (*Z*)-configured ester-derived 1'-bromo-2-alkylidene-tetrahydrofurans. The (*Z*)-configured 1',3-dibromo-2-alkylidene-tetrahydrofurans showed characteristic ^{13}C NMR resonances in the range of $\delta = 168.2\text{--}168.5$ ppm (for ester derivatives, except for **Z-4e**). In contrast, ^{13}C shifts were observed in the range of $\delta = 166.2\text{--}167.1$ ppm for (*E*)-configured 1',3-dibromo-2-alkylidene-tetrahydrofurans. In addition, general trends in the polarity of the (*E*)/(*Z*) diastereomers were deduced from TLC experiments. The chemical shifts of 2-alkylidene-pyrrolidines were compared with those reported for related compounds. In addition, NMR analysis of the intramolecular hydrogen bonds N–H $\cdots$ O was helpful for the assignment of the (*E*)/(*Z*) diastereomers (Table 3).

The palladium-catalyzed cross-coupling reactions of brominated 2-alkylidene-tetrahydrofurans **3a,d** and of 2-alkylidene-pyrrolidine **3k** were next studied (Scheme 2, Table 4). The Suzuki reaction of **3a** with $\text{PhB}(\text{OH})_2$ in the presence of $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%) afforded the desired 2-alkylidene-tetrahydrofuran **7a**. The best yields were obtained when $\text{Pd}(\text{PPh}_3)_4$, phenylboronic acid, K_3PO_4 and 1,4-dioxane (reflux) were used. The reaction of **3a** and **3d** with 4-tolyl-, 4-methoxyphenyl-, 4-chlorophenyl- and 2-thienylboronic acid afforded the functionalized 2-alkylidene-tetrahydrofurans **7b–j**. The acid **7k** was prepared by treatment of **7c** with BBr_3 in CH_2Cl_2 and subsequent heating with KOH in THF/ H_2O (1:1). The reaction of 2-alkylidene-pyrrolidine **3l** [(*E*)/(*Z*) mixture] with 4-chlorophenylboronic acid gave the isomerically pure (*Z*)-configured 2-alkylidene-pyrrolidine **7l**. All the Suzuki reactions proceeded in good to very good yields (48–92%), and with excellent (*E*) diastereoselectivity for 2-alkylidene-tetrahydrofurans **7a–k** and (*Z*) diastereoselectivity for 2-alkylidene-pyrrolidine **7l**.

The Suzuki reactions of dibromides **4a,b,e** were next studied (Scheme 3, Table 5). The reaction of **4a** with phenylboronic acid (3 equiv.) afforded a separable mixture of 2-

Table 1. Bromination of 2-alkylidene-tetrahydrofurans and 2-alkylidene-pyrrolidines.

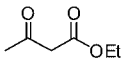
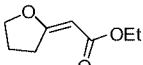
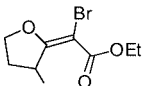
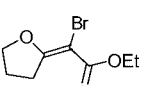
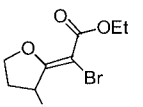
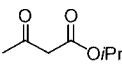
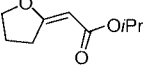
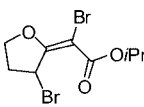
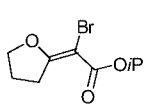
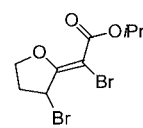
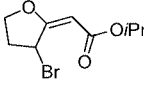
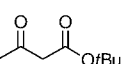
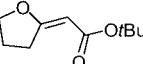
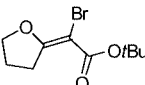
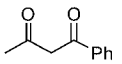
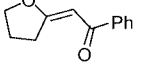
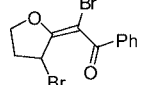
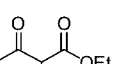
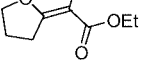
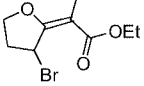
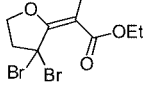
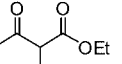
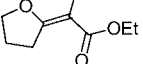
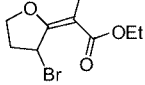
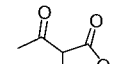
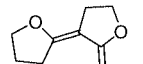
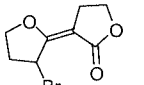
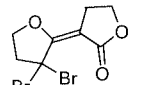
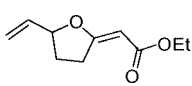
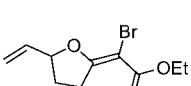
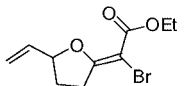
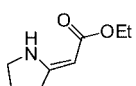
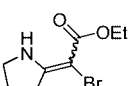
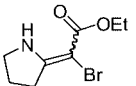
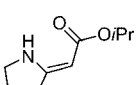
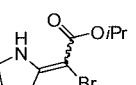
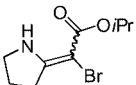
Entry	Substrate of 2	Substrate	Products 3, 4, 5, and 6 (%) ^[a]	NBS (equiv.)
1	 1b	 2b	 Z-4b (26%)  Z-3b (41%)  E-4b (15%)	1.3
2	1b	2b	Z-4b (70%) E-4b (23%)	3.0
3	 1c	 2c	 Z-4c (27%)  Z-3c (19%)  E-4c (26%)	1.3
4	1c	2c	 E-5c (21%) Z-3c (65%) E-4c (12%)	1.1
5	 1d	 2d	 Z-3d (73%)	1.3
6	 1e	 2e	 Z-4e (63%)	1.3
7	 1f	 2f	 5f (56%)  6f (12%)	1.1
8	 1g	 2g	 5g (80%)	1.1
9	 1h	 2h	 5h (76%)  6h (22%)	1.2

Table 1. (continued).

Entry	Substrate of 2	Substrate	Products 3 , 4 , 5 , and 6 (%) ^[a]	NBS (equiv.)
10	1b		 Z-4i (50%)  E-4i (26%)	1.6
11	1b		 3j (66%) (<i>E/Z</i> = 4:1)  4j (30%) (<i>E/Z</i> = 7:2)	1.3
12	1c		 3k (75%) (<i>E/Z</i> = 3:1)  4k (19%) (<i>E/Z</i> = 10:3)	1.3

[a] Yields of isolated products.

Table 2. C-2 chemical shifts of brominated 2-alkylidene-tetrahydrofurans.

Compound	δ [ppm] ^[a]	Compound	δ [ppm] ^[a]	Compound	δ [ppm] ^[a]
Z-3a	172.2	Z-4b	168.5	E-4a	167.0
Z-3b	171.7	Z-4c	168.3	E-4b	167.1
Z-3c	171.6	Z-4e	166.9	E-4c	166.9
Z-3d	170.8	Z-4i	168.2 ^[b]	E-4i	166.2 ^[b]

[a] Chemical shift (¹³C NMR, CDCl₃) of the C-2 carbon atom (O=C–Br). [b] Major diastereomer.

alkylidene-1',3-diaryltetrahydrofuran **9a** (41%) and furan **8a** (21%). Compound **9a** is formed by a double-Suzuki reaction of the 1,3-dibromoprop-1-ene moiety, which is, to the best of our knowledge, an unprecedented process. The formation of **8a** can be explained by Suzuki reaction of the alkenyl bromide, thermal elimination of hydrogen bromide and subsequent aromatization. The double-Suzuki reaction

Table 3. C-2 and N–H chemical shifts of brominated 2-alkylidene-pyrrolidines

Compound	δ [ppm] ^[a]	δ [ppm] ^[b]	Compound	δ [ppm] ^[a]	δ [ppm] ^[b]
E-3j	166.5	8.16	Z-3j	164.3	5.49
E-4j	167.1	8.07	Z-4j	163.7	5.45
E-3k	166.5	8.12	Z-3k	164.2	5.48
E-4k	166.5	7.75	Z-4k	162.0	5.41

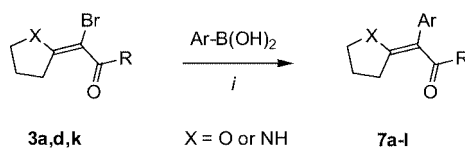
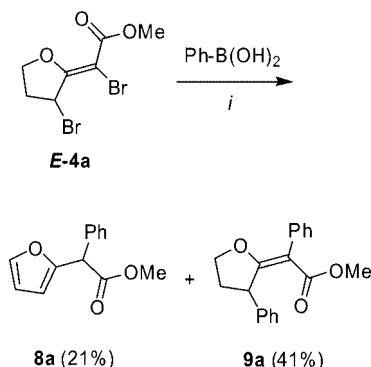
[a] Chemical shift (¹³C NMR, CDCl₃) of the C-2 carbon atom (HN=C=C–Br). [b] Chemical shift (¹H NMR, CDCl₃) of N–H.Scheme 2. Suzuki reactions of 2-alkylidene-tetrahydrofurans and 2-alkylidene-pyrrolidines. Reagents and conditions: *i*: ArB(OH)₂ (3 equiv.), Pd(PPh₃)₄ (3 mol-%), K₃PO₄ (6.0 equiv.), 1,4-dioxane, reflux, 6 h.

Table 4. Suzuki reactions of 2-alkylidene-tetrahydrofurans and 2-alkylidene-pyrrolidines.

7	X	R	Ar	7 [%] ^[a]	(<i>E</i>)/(<i>Z</i>)
a	O	OMe	Ph	79	>98:2
b	O	OMe	4-MeC ₆ H ₄	91	>98:2
c	O	OMe	4-(MeO)C ₆ H ₄	91	>98:2
d	O	OMe	4-ClC ₆ H ₄	92	>98:2
e	O	OMe	2-thienyl	62	>98:2
f	O	<i>Or</i> Bu	Ph	87	>98:2
g	O	<i>Or</i> Bu	4-MeC ₆ H ₄	88	>98:2
h	O	<i>Or</i> Bu	4-(MeO)C ₆ H ₄	77	>98:2
i	O	<i>Or</i> Bu	4-ClC ₆ H ₄	87	>98:2
j	O	<i>Or</i> Bu	2-thienyl	48 ^[b]	>98:2
k	O	OH	4-(HO)C ₆ H ₄	80 ^[c]	>98:2
l	NH	<i>Or</i> Pr	4-ClC ₆ H ₄	87	<2:98

[a] Yields of isolated products. [b] NMR yield (calcd. from a 1:1 mixture of **7j** and **3d**). [c] From **7c**: *i*: 1) BBr₃, CH₂Cl₂, 0 → 20 °C; 2) MeOH; *ii*: KOH, H₂O/THF (1:1), reflux.

of **4b** with 4-methoxyphenylboronic acid afforded the 2-alkylidene-tetrahydrofuran **9b** (Table 5). Likewise, **9c** was prepared by reaction of **4e** with phenylboronic acid.



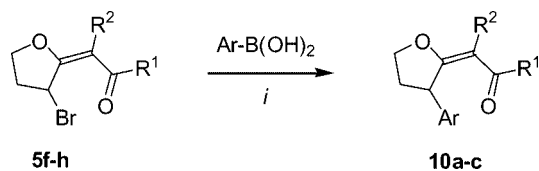
Scheme 3. Double-Suzuki reaction of 2-alkylidene-1',3-dibromotetrahydrofuran **E-4a**. Reagents and conditions: *i*: PhB(OH)₂ (3 equiv.), Pd(PPh₃)₄ (3 mol-%), K₃PO₄ (6 equiv.), 1,4-dioxane, reflux, 6 h.

Table 5. Double-Suzuki reactions of dibromides **4b,e**.

Entry	Substrate	Product (%) ^[a]
1		 9b (66%)
2		 9c (62%)

[a] Yields of isolated products, (*E*)/(*Z*) > 98:2.

The Suzuki reaction of monobromides **5f–h** afforded the (*E*)-configured 2-alkylidene-tetrahydrofurans **10a–c** in good yields (Scheme 4, Table 6); substitution occurred exclusively at the C-3 carbon atom.



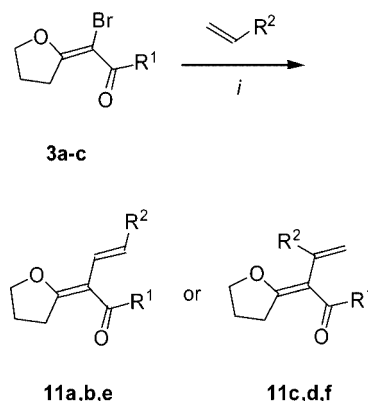
Scheme 4. Suzuki-reactions of 2-alkylidene-tetrahydrofurans **5f–h**. Reagents and conditions: *i*: Pd(PPh₃)₄ (3 mol-%), K₃PO₄ (6 equiv.), 1,4-dioxane, reflux, 6 h.

Table 6. Suzuki reactions of 2-alkylidene-3-bromotetrahydrofurans **5f–h**.

10	R ¹	R ²	Ar	10 [%] ^[a]
a	OEt	Me	4-ClC ₆ H ₄	52
b	OEt	Et	4-ClC ₆ H ₄	76
c		OCH ₂ CH ₂	Ph	55

[a] Yields of isolated products, (*E*)/(*Z*) > 98:2.

The Heck reactions of 2-alkylidene-tetrahydrofurans were next studied. The Heck reaction of **3a** with *tert*-butyl acrylate, acrylonitrile, styrene and 4-methoxystyrene afforded the alkenyl-substituted 2-alkylidene-tetrahydrofurans **11a–d** (Scheme 5, Table 7). 2-Alkylidene-tetrahydrofuran **11e** was prepared by the reaction of **3b** with *tert*-butyl acrylate. The reaction of **3c** with 4-methoxystyrene afforded **11f**. Notably, the regioselectivity observed in the reactions of styrene was different to that observed for acrylonitrile and *tert*-butyl acrylate for electronic reasons.



Scheme 5. Heck reactions of 2-alkylidene-tetrahydrofurans. Reagents and conditions: *i*: Pd(PPh₃)₄ (3 mol-%), NEt₃, DMF, 100 °C, 25 h.

Table 7. Heck reactions of 2-alkylidene-tetrahydrofurans.

11	R ¹	R ²	11 [%] ^[a]
a	OMe	CO ₂ <i>t</i> Bu	85
b	OMe	CN	47
c	OMe	Ph	56
d	OMe	4-(MeO)C ₆ H ₄	45
e	OEt	CO ₂ <i>t</i> Bu	51
f	O <i>i</i> Pr	4-(MeO)C ₆ H ₄	58

[a] Yields of isolated products.

In summary, we have reported the synthesis of 2-alkylidene-1'-bromotetrahydrofurans, 2-alkylidene-3-bromotetrahydrofurans and 2-alkylidene-1',3-dibromotetrahydrofurans and their pyrrolidine counterparts by bromination of 2-alkylidene-tetrahydrofurans and 2-alkylidene-pyrrolidines, which are readily available by one-pot [3+2] cyclization reactions. The 2-alkylidene-1'-bromotetrahydrofurans were functionalized by Suzuki and Heck reactions. 2-Alkylidene-1',3-dibromotetrahydrofurans were successfully employed in double-Suzuki reactions.

Experimental Section

General Comments: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. To record ^1H and ^{13}C NMR spectra the deuteriated solvents indicated were used. Mass spectroscopic (MS) data were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or by electrospray ionization (ESI). For preparative-scale chromatography silica gel (60–200 mesh) was used. Melting points are uncorrected.

Synthesis of Ethyl 2-[5-Vinyl-4,5-dihydrofuran-2(3H)-ylidene]acetate (2i): A THF solution of lithium diisopropylamide (LDA) was prepared by addition of *n*BuLi (78.51 mL, 15% in *n*-hexane, 125.0 mmol) to a solution of diisopropylamine (17.57 mL, 125.0 mmol) in THF (200 mL) at 0 °C. After stirring the mixture for 20 min, ethyl acetoacetate (**1b**) (6.32 mL, 50.0 mmol) was added at 0 °C. The mixture was stirred for 1 h at 0 °C and then this solution was slowly added to a solution of *trans*-1,4-dibromo-2-butene (12.834 g, 60.0 mmol) in THF (100 mL) at –78 °C. The temperature was allowed to rise to 20 °C over 14 h and the solution was stirred at room temperature for 24 h. The reaction mixture was poured into an aqueous solution of HCl (10%) and extracted with diethyl ether several times. The combined organic extracts were dried over Na_2SO_4 , filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) to give **E-2i** (3.633 g, 40%) and **Z-2i** (3.213 g, 35%) as yellowish oils (combined yield: 75%). Spectroscopic data of **E-2i**: ^1H NMR (CDCl_3 , 300 MHz): δ = 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.82–1.91 (m, 1 H, CH_2), 2.22–2.31 (m, 1 H, CH_2), 2.99–3.08 (m, 1 H, CH_2), 3.21–3.32 (m, 1 H, CH_2), 4.13 (q, J = 7.2 Hz, 2 H, OCH_2), 4.80 (q, J = 7.5 Hz, 1 H, OCH), 5.23 (dt, J = 10.5, 1.2 Hz, 1 H, $\text{CH}_2=\text{CH}$), 5.31 (dt, J = 9.9, 1.2 Hz, 1 H, $\text{CH}_2=\text{CH}$), 5.36 (t, J = 1.2 Hz, 1 H, $\text{CH}=\text{C}$), 5.80–5.91 (m, 1 H, $\text{CH}=\text{CH}_2$) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): δ = 14.1, 29.4, 29.8, 58.7, 83.4, 89.3, 116.9, 135.7, 168.0, 175.6 ppm. IR (neat): $\tilde{\nu}$ = 2983 (s), 2941 (m), 2903 (w), 1707 (s), 1644 (s), 1459 (m), 129 (m), 1392 (m), 1372 (s), 1348 (s), 1321 (m), 1284 (m), 1239 (m), 1164 (s), 1111 (s), 1047 (s), 1007 (s), 993 (s), 934 (m), 886 (s), 854 (w), 825 (s) cm^{-1} . MS (EI, 70 eV): m/z (%) = 182 (58) [$\text{M}]^+$, 153 (4), 137 (100), 108 (27), 95 (24). $\text{C}_{10}\text{H}_{14}\text{O}_3$ (182.219): calcd. C 65.92, H 7.74; found C 65.30, H 7.88. The synthesis of **Z-2i** has been reported previously.^[9]

General Procedure for the Reaction of 2-Alkylidene-tetrahydrofurans or 2-Alkylidene-pyrrolidines with *N*-Bromosuccinimide (NBS): *N*-Bromosuccinimide (1.1–3.0 equiv., see Table 1) was added to a CCl_4 solution (5 mL mmol $^{-1}$) of the 2-alkylidene-tetrahydrofuran or -pyrrolidine (**2**) (1 equiv.) at 20 °C. The reaction mixture was heated and stirred under reflux for 3 h. The reaction mixture was allowed to cool to ambient temperature and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give the brominated 2-alkylidene-tetrahydrofuran or -pyrrolidine (**3-6**).

Compounds 3a and 4a: Starting with **2a** (4.000 g, 28.0 mmol) and NBS (6.511 g, 36.6 mmol) in CCl_4 (40 mL), **Z-3a** (5.212 g, 84%) and **E-4a** (0.937 g, 11%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as yellowish and colorless solids, respectively.

Methyl 2-Bromo-2-[4,5-dihydrofuran-2(3H)-ylidene]acetate (Z-3a): ^1H NMR (CDCl_3 , 300 MHz): δ = 2.23 (quint, J = 7.2 Hz, 2 H, CH_2), 3.19 (t, J = 7.8 Hz, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 4.41 (t, J = 7.2 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): δ = 24.8, 32.3, 52.2, 73.0, 82.7, 164.7, 172.2 ppm. IR (KBr): $\tilde{\nu}$ = 2951 (w), 1699 (s), 1609 (s), 1435 (m), 1281 (s), 1213 (s), 1188 (m), 1073 (s), 973 (w), 925 (w), 879 (w), 770 (w), 759 (w) cm^{-1} . MS (EI,

70 eV): m/z (%) = 221 (^{81}Br), 72) [$\text{M}]^+$, 219 (^{79}Br), 71) [$\text{M}]^+$, 190 (63), 189 (100), 188 (71), 187 (93), 179 (10), 177 (10), 162 (3), 148 (60), 146 (59). $\text{C}_7\text{H}_9\text{BrO}_3$ (221.050): calcd. C 38.04, H 4.10; found C 38.19, H 3.64.

Methyl 2-Bromo-2-[3-bromo-4,5-dihydrofuran-2(3H)-ylidene]acetate (E-4a): ^1H NMR (CDCl_3 , 300 MHz): δ = 2.43–2.49 (m, 1 H, CH_2), 2.53–2.61 (m, 1 H, CH_2), 3.80 (s, 3 H, OCH_3), 4.74–4.76 (m, 1 H, OCH_2), 4.78–4.79 (m, 1 H, OCH_2), 5.20 (d, J = 5.4 Hz, 1 H, $\text{CH}-\text{Br}$) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): δ = 34.7, 48.4, 52.1, 73.8, 87.1, 162.0, 167.0 ppm. IR (KBr): $\tilde{\nu}$ = 2950 (w), 1706 (s), 1605 (s), 1433 (m), 1271 (s), 1204 (s), 1174 (s), 1057 (w), 1039 (s), 1027 (s), 1004 (w), 765 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 302 ($[2 \times ^{81}\text{Br}]$), 17) [$\text{M}]^+$, 300 (^{81}Br ^{79}Br), 34) [$\text{M}]^+$, 298 ($[2 \times ^{79}\text{Br}]$), 17) [$\text{M}]^+$, 271 (9), 269 (19), 267 (10), 241 (2), 221 (98), 219 (100), 189 (22), 187 (21), 161 (18), 159 (17), 133 (12), 131 (13), 81 (6), 79 (10). $\text{C}_7\text{H}_8\text{Br}_2\text{O}_3$ (299.946): calcd. C 28.03, H 2.69; found C 28.88, H 2.85.

Compounds 3b and 4b: Starting with **2b** (1.432 g, 9.2 mmol) and NBS (2.122 g, 11.92 mmol) in CCl_4 (25 mL), **Z-4b** (0.740 g, 26%), **Z-3b** (0.886 g, 41%) and **E-4b** (0.430 g, 15%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish and yellowish solids and as a yellowish oil, respectively.

Compound Z-4b: ^1H NMR (CDCl_3 , 300 MHz): δ = 1.36 (t, J = 7.2 Hz, 3 H, CH_3), 2.55–2.63 (m, 2 H, CH_2), 4.29 (dq, J = 2.1, 7.2 Hz, 2 H, OCH_2CH_3), 4.56–4.66 (m, 2 H, OCH_2), 5.81 (dd, J = 4.5, 1.5 Hz, 1 H, $\text{CH}-\text{Br}$) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): δ = 13.9, 36.8, 44.1, 61.7, 70.6, 87.1, 162.5, 168.5 ppm. IR (KBr): $\tilde{\nu}$ = 2933 (w), 1701 (s), 1616 (s), 1371 (w), 1274 (s), 1216 (s), 1189 (m), 1160 (w), 1069 (s), 1026 (w), 953 (w), 928 (w), 872 (w), 757 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 315 ($[2 \times ^{81}\text{Br}]$), 11) [$\text{M}]^+$, 313 (^{81}Br ^{79}Br), 33) [$\text{M}]^+$, 311 ($[2 \times ^{79}\text{Br}]$), 12) [$\text{M}]^+$, 271 (2), 269 (11), 267 (3), 235 (65), 233 (60), 207 (90), 205 (100), 189 (29), 187 (25), 161 (23), 159 (18), 148 (12), 146 (11), 133 (16), 131 (16). $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_3$ (313.973): calcd. C 30.60, H 3.21; found C 30.32, H 3.51.

Ethyl 2-Bromo-2-[4,5-dihydrofuran-2(3H)-ylidene]acetate (Z-3b): ^1H NMR (CDCl_3 , 300 MHz): δ = 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 2.23 (quint, J = 7.5 Hz, CH_2), 3.18 (t, J = 7.8 Hz, 2 H, CH_2), 4.23 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 4.40 (t, J = 7.2 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (CDCl_3 , 150 MHz): δ = 14.0, 24.6, 32.2, 60.8, 72.7, 83.0, 163.7, 171.7 ppm. IR (KBr): $\tilde{\nu}$ = 2995 (w), 2975 (w), 2907 (w), 1691 (s), 1608 (s), 1395 (w), 1374 (m), 1294 (s), 1276 (s), 1240 (w), 1194 (s), 1065 (s), 1038 (m), 953 (w), 931 (m), 874 (w), 762 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 236 (^{81}Br), 75) [$\text{M}]^+$, 234 (^{79}Br), 76) [$\text{M}]^+$, 207 (44), 205 (43), 190 (100), 188 (93), 164 (11), 162 (11), 148 (45), 146 (45), 110 (40), 81 (12), 79 (9). $\text{C}_8\text{H}_{11}\text{BrO}_3$ (235.077): calcd. C 40.88, H 4.72; found C 41.04, H 4.61.

Compound E-4b: ^1H NMR (CDCl_3 , 300 MHz): δ = 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 2.43–2.48 (m, 1 H, CH_2), 2.52–2.61 (m, 1 H, CH_2), 4.27 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 4.76 (dt, J = 8.7, 0.9 Hz, 2 H, OCH_2), 5.20 (d, J = 5.4 Hz, 1 H, $\text{CH}-\text{Br}$) ppm. ^{13}C NMR (CDCl_3 , 150 MHz): δ = 14.1, 35.2, 48.7, 61.5, 74.0, 87.9, 162.0, 167.1 ppm. IR (neat): $\tilde{\nu}$ = 2983 (m), 2938 (w), 2905 (m), 1737 (s), 1703 (s), 1660 (m), 1616 (s), 1471 (m), 1440 (m), 1371 (s), 1316 (m), 1283 (s), 1272 (s), 1206 (s), 1184 (s), 1157 (s), 1117 (m), 1094 (m), 1088 (s), 935 (m), 925 (m), 865 (w), 847 (w), 763 (m), 700 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 316 ($[2 \times ^{81}\text{Br}]$), 17) [$\text{M}]^+$, 314 (^{81}Br ^{79}Br), 37) [$\text{M}]^+$, 312 ($[2 \times ^{79}\text{Br}]$), 18) [$\text{M}]^+$, 271 (14), 269 (29), 267 (14), 241 (3), 235 (63), 233 (69), 207 (96), 205 (100), 189 (35), 187 (27), 161 (23), 159 (18), 148 (15), 146 (13), 133 (17), 131 (15),

81 (8), 79 (13). The exact molecular mass, $m/z = 311.8997 \pm 2$ ppm $[M]^+$, for $C_8H_{10}Br_2O_3$ was confirmed by HRMS (EI, 70 eV).

Ethyl 2-Bromo-2-[3-bromo-4,5-dihydrofuran-2(3H)-ylidene]acetate (4b): Starting with **2b** (0.300 g, 1.9 mmol) and NBS (1.026 g, 5.8 mmol) in CCl_4 (10 mL), **Z-4b** (0.423 g, 70%) and **E-4b** (0.138 g, 23%) were isolated after chromatography (silica gel, n -hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a slightly yellowish solid and a yellowish oil, respectively (combined yield: 93%).

Compounds 3c and 4c: Starting with **2c** (0.888 g, 5.22 mmol) and NBS (1.208 g, 6.79 mmol) in CCl_4 (20 mL), **Z-4c** (0.463 g, 27%), **Z-3c** (0.252 g, 19%) and **E-4c** (0.442 g, 26%) were isolated after chromatography (silica gel, n -hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish solid, yellowish oil and brownish oil, respectively.

Isopropyl 2-Bromo-2-[3-bromo-4,5-dihydrofuran-2(3H)-ylidene]acetate (Z-4c): 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.34$ (dd, $J = 6.3$, 1.5 Hz, 6 H, $2 \times CH_3$), 2.55–2.63 (m, 2 H, CH_2), 4.57–4.65 (m, 2 H, OCH_2), 5.13 (quint, $J = 6.3$ Hz, 1 H, CH), 5.79 (dt, $J = 4.5$, 0.9 Hz, 1 H, CH–Br) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 21.8$, 37.1, 44.4, 69.7, 70.7, 88.2, 162.1, 168.3 ppm. IR (neat): $\tilde{\nu} = 2983$ (w), 1694 (w), 1678 (m), 1616 (s), 1276 (s), 1217 (s), 1179 (m), 1109 (m), 1071 (s) cm^{-1} . MS (EI, 70 eV): m/z (%) = 329 ($[2 \times ^{81}Br]$, 12) $[M]^+$, 327 ($[^{81}Br \ ^{79}Br]$, 26) $[M]^+$, 325 ($[2 \times ^{79}Br]$, 12) $[M]^+$, 287 (29), 285 (57), 283 (29), 268 (18), 240 (1), 206 (99), 204 (100), 190 (9), 188 (29), 186 (19), 163 (4), 161 (18), 159 (14), 148 (10), 146 (9), 133 (11), 131 (11), 127 (2), 120 (2), 108 (3), 106 (3), 104 (3), 81 (3), 70 (8). The exact molecular mass, $m/z = 325.9153 \pm 2$ ppm $[M]^+$, for $C_9H_{12}Br_2O_3$ was confirmed by HRMS (EI, 70 eV).

Isopropyl 2-Bromo-2-[4,5-dihydrofuran-2(3H)-ylidene]acetate (Z-3c): 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.30$ (d, $J = 6.3$ Hz, 6 H, $2 \times CH_3$), 2.22 (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.17 (t, $J = 7.8$ Hz, 2 H, CH_2), 4.39 (t, $J = 7.2$ Hz, 2 H, OCH_2), 5.06 (quint, $J = 6.3$ Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 22.0$, 25.0, 32.5, 68.9, 72.9, 84.2, 163.8, 171.6 ppm. IR (neat): $\tilde{\nu} = 2982$ (s), 2938 (m), 2905 (m), 1732 (m), 1699 (s), 1690 (s), 1658 (m), 1612 (s), 1525 (w), 1462 (m), 1455 (m), 1427 (m), 1374 (m), 1355 (m), 1335 (m), 1276 (s), 1232 (s), 1211 (s), 1182 (s), 1147 (m), 1109 (m), 1067 (s), 1022 (m), 990 (w), 960 (m), 924 (m), 896 (w), 875 (w), 856 (w), 824 (w), 805 (w), 781 (m), 760 (m), 719 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 249 ($[^{81}Br]$, 26) $[M]^+$, 247 ($[^{79}Br]$, 26) $[M]^+$, 207 (84), 205 (88), 189 (90), 187 (88), 171 (7), 165 (12), 163 (14), 148 (29), 146 (29), 122 (8), 120 (8), 110 (17), 87 (18), 70 (33), 43 (100). The exact molecular mass, $m/z = 248.0048 \pm 2$ ppm $[M]^+$, for $C_9H_{13}BrO_3$ was confirmed by HRMS (EI, 70 eV). $C_9H_{13}BrO_3$ (249.104): calcd. C 43.40, H 5.26; found C 43.28, H 5.48.

Compound E-4c: 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.30$ (d, $J = 6.3$ Hz, 6 H, $2 \times CH_3$), 2.11–2.48 (m, 1 H, CH_2), 2.52–2.60 (m, 1 H, CH_2), 4.73–4.78 (m, 2 H, OCH_2), 5.07 (quint, $J = 6.3$ Hz, 1 H, CH), 5.20 (d, $J = 5.7$ Hz, 1 H, CH–Br) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 21.8$, 35.3, 48.8, 69.2, 74.0, 88.3, 161.7, 166.9 ppm. IR (neat): $\tilde{\nu} = 2982$ (s), 2937 (m), 2906 (m), 2883 (w), 1733 (s), 1702 (s), 1663 (m), 1615 (s), 1464 (m), 1440 (m), 1375 (s), 1315 (m), 1279 (s), 1208 (s), 1184 (s), 1159 (s), 1105 (s), 1061 (s), 1034 (s), 986 (m), 962 (w), 936 (m), 904 (m), 854 (w), 831 (w), 809 (w), 764 (w), 699 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 330 ($[2 \times ^{81}Br]$, 12) $[M]^+$, 328 ($[^{81}Br \ ^{79}Br]$, 26) $[M]^+$, 326 ($[2 \times ^{79}Br]$, 13) $[M]^+$, 288 (31), 286 (62), 284 (32), 271 (16), 269 (33), 267 (17), 249 (10), 247 (9), 241 (3), 207 (100), 205 (98), 191 (17), 189 (40), 187 (23), 163 (13), 161 (28), 159 (15), 148 (12), 146 (11), 133 (13), 131 (12), 108 (4), 106 (3), 87 (17), 70 (16), 43 (70). The exact molecular mass, $m/z = 325.9153 \pm 2$ ppm $[M]^+$, for $C_9H_{12}Br_2O_3$ was confirmed by HRMS (EI, 70 eV).

Compounds 3c, 4c, and 5c: Starting with **2c** (0.936 g, 5.5 mmol) and NBS (1.077 g, 6.05 mmol) in CCl_4 (20 mL), **E-5c** (0.281 g, 21%), **Z-3c** (0.888 g, 65%) and **E-4c** (0.219 g, 12%) were isolated after chromatography (silica gel, n -hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as yellowish oils.

Isopropyl 2-[3-Bromo-4,5-dihydrofuran-2(3H)-ylidene]acetate (E-5c): 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.27$ (d, $J = 6.3$ Hz, 6 H, $2 \times CH_3$), 2.43–2.50 (m, 2 H, CH_2), 4.38–4.50 (m, 2 H, OCH_2), 5.08 (quint, $J = 6.3$ Hz, 1 H, CH), 5.25 (s, 1 H, CH=C), 5.76–5.78 (m, CH–Br) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 21.9$, 22.0, 36.0, 43.0, 67.1, 69.6, 91.9, 166.3, 172.8 ppm. IR (neat): $\tilde{\nu} = 2981$ (m), 2935 (w), 2912 (w), 1701 (s), 1650 (s), 1464 (w), 1438 (w), 1375 (s), 1333 (w), 1302 (m), 1276 (m), 1246 (m), 1217 (w), 1179 (m), 1153 (m), 1127 (s), 1103 (s), 1060 (m), 1036 (s), 1008 (w), 958 (w), 888 (w), 834 (w), 705 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 250 ($[^{81}Br]$, 6) $[M]^+$, 248 ($[^{79}Br]$, 6) $[M]^+$, 208 (20), 207 (29), 206 (21), 205 (26), 191 (54), 190 (15), 189 (64), 188 (11), 187 (4), 164 (32), 162 (32), 161 (5), 159 (2), 148 (2), 146 (1), 133 (3), 131 (2), 127 (46), 110 (15), 109 (75), 108 (46), 97 (4), 83 (28), 81 (24), 70 (100). $C_9H_{13}BrO_3$ (249.104): calcd. C 43.40, H 5.26; found C 43.28, H 5.48.

tert-Butyl 2-Bromo-2-[4,5-dihydrofuran-2(3H)-ylidene]acetate (Z-3d): Starting with **2d** (0.700 g, 3.8 mmol) and NBS (0.879 g, 4.9 mmol) in CCl_4 (40 mL), **Z-3d** was isolated after chromatography (silica gel, n -hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a white solid (0.732 g, 73%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.51$ (s, 9 H, $OrBu$), 2.21 (quint, $J = 7.2$ Hz, 2 H, CH_2), 3.13 (t, $J = 7.8$ Hz, 2 H, CH_2), 4.37 (t, $J = 7.2$ Hz, 2 H, OCH_2) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 25.1$, 28.5, 32.5, 72.8, 81.7, 85.8, 163.4, 170.8 ppm. IR (KBr): $\tilde{\nu} = 2975$ (w), 1694 (s), 1613 (s), 1370 (m), 1295 (s), 1250 (w), 1243 (w), 1210 (m), 1170 (s), 1067 (s), 1039 (w), 1023 (w), 955 (w), 934 (w), 864 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 265 ($[^{81}Br]$, 18) $[M]^+$, 263 ($[^{79}Br]$, 19) $[M]^+$, 208 (98), 206 (100), 191 (48), 190 (92), 189 (54), 188 (93), 166 (9), 164 (10), 148 (26), 146 (26), 70 (12), 58 (57). The exact molecular mass, $m/z = 262.0205 \pm 2$ ppm $[M]^+$, for $C_{10}H_{15}BrO_3$ was confirmed by HRMS (EI, 70 eV). $C_{10}H_{15}BrO_3$ (263.131): calcd. C 45.65, H 5.75; found C 45.38, H 6.03.

2-Bromo-2-[3-bromo-4,5-dihydrofuran-2(3H)-ylidene]-1-phenylethanone (Z-4e): Starting with **2e** (0.600 g, 3.19 mmol), and NBS (0.738 g, 4.14 mmol) in CCl_4 (20 mL), **Z-4e** was isolated after chromatography (silica gel, n -hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish oil (0.692 g, 63%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.51$ –2.72 (m, 2 H, CH_2), 4.60–4.71 (m, 2 H, OCH_2), 5.60 (d, $J = 5.4$ Hz, 1 H, CH–Br), 7.41–7.55 (m, 3 H, $3 \times CH$ of Ph), 7.75 (d, $J = 3.9$ Hz, 2 H, $2 \times CH$ of Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 36.8$, 43.6, 70.5, 92.8, 127.7, 128.7, 132.0, 137.7, 166.9, 191.0 ppm. IR (neat): $\tilde{\nu} = 3059$ (w), 2998 (w), 2962 (w), 2906 (m), 1659 (s), 1653 (s), 1598 (s), 1584 (s), 1581 (s), 1570 (s), 1473 (w), 1444 (m), 1370 (m), 1311 (s), 1276 (s), 1220 (s), 1174 (s), 1161 (s), 1115 (w), 1076 (w), 1055 (m), 1017 (s), 964 (s), 931 (s), 909 (m), 882 (m), 836 (m), 815 (w), 794 (m), 741 (m), 687 (s), 654 (s), 522 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 348 ($[2 \times ^{81}Br]$, 7) $[M]^+$, 346 ($[^{81}Br \ ^{79}Br]$, 15) $[M]^+$, 344 ($[2 \times ^{79}Br]$, 7) $[M]^+$, 267 (36), 265 (36), 186 (100), 129 (11), 105 (68), 89 (6), 77 (76). $C_{12}H_{10}Br_2O_2$ (346.018): calcd. C 41.65, H 2.91; found C 41.35, H 3.60.

Compounds 5f and 6f: Starting with **2f** (0.100 g, 0.59 mmol) and NBS (0.115 g, 0.65 mmol) in CCl_4 (5 mL), **5f** (0.082 g, 56%) and **6f** (0.023 g, 12%) were isolated after chromatography (silica gel, n -hexane/EtOAc = 100:1 $\rightarrow$ 5:1) as slightly yellowish oils.

Ethyl 2-[3-Bromo-4,5-dihydrofuran-2(3H)-ylidene]propionate (5f): 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.30$ (t, $J = 7.2$ Hz, 3 H, CH_3), 1.85 (s, 3 H, CH_3), 2.43–2.49 (m, 2 H, CH_2), 4.22 (dq, $J = 7.2$,

2.7 Hz, 2 H, OCH₂CH₃), 4.39–4.54 (m, 2 H, OCH₂), 5.81 (m, 1 H, CH–Br) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 11.6, 14.3, 36.7, 45.1, 60.1, 69.1, 100.4, 167.1, 167.6 ppm. IR (neat): $\tilde{\nu}$ = 2984 (m), 2930 (w), 2904 (w), 1699 (s), 1644 (s), 1469 (w), 1441 (m), 1390 (w), 1369 (m), 1288 (s), 1212 (m), 1185 (m), 1170 (m), 1107 (s), 1082 (s), 1024 (m), 972 (w), 933 (w), 880 (w), 767 (w), 704 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 250 ([⁸¹Br], 29) [M]⁺, 248 ([⁷⁹Br], 34) [M]⁺, 205 (14), 203 (16), 169 (83), 141 (100), 123 (54), 99 (3), 97 (3), 95 (32), 83 (49), 68 (33). HRMS (ESI): calcd. for C₉H₁₃BrO₃ [M]⁺: 250.00276 (⁸¹Br), 248.00481 (⁷⁹Br); found 250.00210 (⁸¹Br), 248.00485 (⁷⁹Br). C₉H₁₃BrO₃ (249.104): calcd. C 43.40, H 5.26; found C 42.74, H 4.87.

Ethyl 2-[3,3-Dibromo-4,5-dihydrofuran-2(3H)-ylidene]propionate (6f): ¹H NMR (CDCl₃, 300 MHz): δ = 1.31 (t, J = 7.2 Hz, 3 H, CH₃), 2.21 (s, 3 H, CH₃), 3.27 (t, J = 6.3 Hz, 2 H, CH₂), 4.22 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 4.32 (t, J = 6.3 Hz, 2 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 14.2, 14.6, 50.4, 51.7, 60.5, 68.7, 103.2, 162.1, 167.2 ppm. IR (neat): $\tilde{\nu}$ = 2981 (w), 2931 (w), 2902 (w), 1713 (s), 1636 (m), 1443 (w), 1371 (w), 1318 (w), 1290 (m), 1279 (m), 1204 (m), 1174 (m), 1141 (s), 1103 (s), 1030 (w), 1001 (w), 738 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 328 ([⁸¹Br ⁷⁹Br], 11) [M]⁺, 326 ([2 × ⁷⁹Br], 2) [M]⁺, 285 (4), 283 (16), 281 (4), 249 (54), 247 (54), 221 (59), 219 (56), 205 (3), 204 (10), 203 (12), 202 (10), 201 (6), 177 (2), 175 (14), 173 (5), 169 (21), 167 (7), 165 (6), 141 (28), 139 (77), 129 (16), 123 (16), 108 (3), 95 (18), 83 (100), 66 (54). HRMS (ESI): calcd. for C₉H₁₂Br₂O₃ [M]⁺: 329.91127 (2 × ⁸¹Br), 327.91327 (⁸¹Br⁷⁹Br), 325.91532 (2 × ⁷⁹Br); found 329.90904 (2 × ⁸¹Br), 327.91240 (⁸¹Br⁷⁹Br), 325.91549 (2 × ⁷⁹Br).

Ethyl 2-[3-Bromo-4,5-dihydrofuran-2(3H)-ylidene]butyrate (5g): Starting with 2-[4,5-dihydro-furan-2(3H)-ylidene]butyric acid ethyl ester (2g) (1.000 g, 5.43 mmol) and NBS (1.063 g, 5.97 mmol) in CCl₄ (30 mL), **5g** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (1.140 g, 80%). ¹H NMR (CDCl₃, 300 MHz): δ = 0.99 (t, J = 7.4 Hz, 3 H, CH₃), 1.32 (t, J = 7.2 Hz, 3 H, CH₃), 2.29–2.38 (m, 2 H, CH₂), 2.42–2.49 (m, 2 H, CH₂), 4.18–4.27 (m, 2 H, OCH₂CH₃), 4.41–4.50 (m, 2 H, OCH₂), 5.81 (m, 1 H, CH–Br) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 12.7, 13.9, 19.2, 36.3, 45.1, 59.6, 68.8, 106.3, 166.8, 166.9 ppm. IR (neat): $\tilde{\nu}$ = 2975 (s), 2936 (m), 2905 (w), 2877 (w), 1696 (s), 1639 (s), 1448 (m), 1371 (m), 1307 (s), 1253 (s), 1212 (m), 1185 (s), 1105 (s), 1055 (m), 1032 (s), 990 (w), 951 (w), 877 (w), 780 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 264 ([⁸¹Br], 21) [M]⁺, 262 ([⁷⁹Br], 23) [M]⁺, 249 (3), 247 (3), 219 (14), 217 (15), 203 (5), 201 (4), 191 (5), 189 (5), 183 (100), 155 (57), 137 (50), 109 (21), 81 (15), 70 (50). C₁₀H₁₅BrO₃ (263.131): calcd. C 45.65, H 5.75; found C 45.05, H 5.55.

Compounds 5h and 6h: Starting with tetrahydro-2,3'-bifuranylidene-2'-one (**2h**) (0.200 g, 1.30 mmol) and NBS (0.277 g, 1.56 mmol) in CCl₄ (10 mL), **5h** (0.229 g, 76%) and **6h** (0.089 g, 22%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 20:1 → 1:1) as slightly yellowish solids.

3-Bromo-4,4',5,5'-tetrahydro-2,3'-bifuranylidene-2'-one (5h): ¹H NMR (CDCl₃, 300 MHz): δ = 2.46–2.52 (m, 2 H, CH₂), 2.75–3.02 (m, 2 H, CH₂), 4.31–4.39 (m, 2 H, OCH₂), 4.47–4.58 (m, 2 H, OCH₂), 5.82–5.84 (m, 1 H, CH–Br) ppm. ¹³C NMR (CDCl₃, 150 MHz): δ = 25.0, 36.1, 41.8, 65.3, 70.4, 95.7, 166.3, 171.1 ppm. IR (KBr): $\tilde{\nu}$ = 2910 (w), 1737 (s), 1683 (s), 1366 (m), 1254 (s), 1222 (m), 1184 (m), 1166 (m), 1080 (m), 1051 (s), 1029 (s), 993 (w), 931 (w), 670 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 234 ([⁸¹Br], 92) [M]⁺, 232 ([⁷⁹Br], 86) [M]⁺, 153 (100), 125 (14), 123 (20), 107 (32), 97 (23), 95 (39), 85 (14), 81 (23), 79 (34), 70 (35), 68 (40). The exact molecular mass, m/z = 231.9735 ± 2 ppm [M]⁺, for C₈H₉BrO₃ was confirmed by HRMS (EI, 70 eV).

3,3-Dibromo-4,4',5,5'-tetrahydro-2,3'-bifuranylidene-2'-one (6h): ¹H NMR (CDCl₃, 300 MHz): δ = 3.26 (t, J = 6.5 Hz, 2 H, CH₂), 3.33 (t, J = 7.5 Hz, 2 H, CH₂), 4.40 (t, J = 7.5 Hz, 2 H, OCH₂), 4.49 (t, J = 6.5 Hz, 2 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 150 MHz): δ = 26.2, 50.3, 51.0, 65.7, 70.5, 98.2, 163.0, 170.3 ppm. IR (KBr): $\tilde{\nu}$ = 2908 (w), 1738 (s), 1663 (s), 1224 (w), 1197 (w), 1149 (s), 1134 (m), 1070 (w), 1029 (m), 991 (w), 728 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 314 ([2 × ⁸¹Br], 2) [M]⁺, 312 ([⁸¹Br ⁷⁹Br], 6) [M]⁺, 310 ([2 × ⁷⁹Br], 3) [M]⁺, 234 (10), 233 (29), 232 (14), 231 (33), 189 (96), 188 (56), 187 (100), 186 (29), 185 (8), 184 (8), 180 (6), 178 (7), 177 (12), 175 (20), 173 (6), 153 (14), 150 (13), 148 (9), 123 (7), 121 (5), 112 (5), 107 (12), 95 (14), 81 (10), 79 (15), 77 (10), 68 (13), 66 (16). The exact molecular mass, m/z = 309.8840 ± 2 ppm [M]⁺, for C₈H₈BrO₃ was confirmed by HRMS (EI, 70 eV).

Ethyl 2-Bromo-2-[3-bromo-5-vinyl-4,5-dihydrofuran-2(3H)-ylidene]acetate (4i): Starting with **2i** (1.500 g, 8.23 mmol) and NBS (2.344 g, 13.17 mmol) in CCl₄ (30 mL), **Z-4i** (1.392 g, 50%) and **E-4i** (0.736 g, 26%) were isolated, each as a 10:1 mixture of *cis/trans* diastereomers, after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a colorless solid and a yellowish oil (combined yield: 76%), respectively.

Compound Z-4i: ¹H NMR (CDCl₃, 300 MHz): major diastereomer: δ = 1.36 (t, J = 7.2 Hz, 3 H, CH₃), 2.30–2.40 (m, 1 H, CH₂), 2.67 (dd, J = 14.4, 4.5 Hz, 1 H, CH₂), 4.29 (dq, J = 7.2, 2.4 Hz, 2 H, OCH₂), 5.29–5.35 (m, 1 H, CH), 5.38 (dt, J = 10.5, 0.9 Hz, 1 H, CH₂=CH), 5.53 (dt, J = 17.1, 1.2 Hz, 1 H, CH₂=CH), 5.83 (d, J = 5.4 Hz, 1 H, CH–Br), 5.89–6.00 (m, 1 H, CH=CH₂) ppm; minor diastereomer: δ = 1.29 (t, J = 7.2 Hz, 3 H, CH₃), 2.19–2.28 (m, 1 H, CH₂), 2.58 (dd, J = 15.0, 4.5 Hz, 1 H, CH₂), 4.18 (dq, J = 7.2, 2.1 Hz, 2 H, OCH₂), 5.14–5.24 (m, 1 H, CH), 5.31–5.35 (d, 1 H, CH₂=CH), 5.40–5.42 (d, 1 H, CH₂=CH), 5.80 (d, J = 5.4 Hz, 1 H, CH–Br), 5.81–5.88 (m, 1 H, CH=CH₂) ppm. ¹³C NMR (CDCl₃, 75 MHz): major diastereomer: δ = 14.2, 43.1, 44.5, 61.9, 83.6, 87.4, 120.1, 133.6, 162.9, 168.2 ppm; minor diastereomer: δ = 14.3, 42.1, 43.4, 59.8, 82.5, 87.4, 119.7, 134.2, 162.9, 166.8 ppm. IR (KBr): $\tilde{\nu}$ = 2983 (w), 1698 (s), 1651 (w), 1614 (s), 1445 (w), 1369 (w), 1323 (w), 1277 (s), 1234 (w), 1215 (s), 1186 (m), 1120 (m), 1067 (s), 992 (m), 958 (m), 939 (m), 927 (m), 864 (m), 847 (m), 756 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 342 ([2 × ⁸¹Br], 32) [M]⁺, 340 ([⁸¹Br ⁷⁹Br], 69) [M]⁺, 338 ([2 × ⁷⁹Br], 34) [M]⁺, 297 (7), 295 (12), 293 (6), 261 (29), 259 (74), 233 (45), 231 (50), 215 (100), 213 (100), 195 (25), 193 (27), 187 (28), 185 (26), 167 (28), 165 (29), 159 (17), 157 (16), 148 (23), 146 (29), 135 (9), 134 (15), 133 (14), 108 (10), 107 (17), 106 (21), 105 (9), 95 (11), 79 (52). The exact molecular mass, m/z = 337.9153 ± 2 ppm [M]⁺, for C₁₀H₁₂Br₂O₃ was confirmed by HRMS (EI, 70 eV).

Compound E-4i: ¹H NMR (CDCl₃, 300 MHz): major diastereomer: δ = 1.31 (t, J = 7.2 Hz, 3 H, CH₃), 2.30–2.40 (m, 1 H, CH₂), 2.56–2.62 (dd, J = 4.8, 14.4 Hz, 1 H, CH₂), 4.19–4.28 (m, 2 H, OCH₂), 5.22 (d, J = 5.7 Hz, 1 H, CH), 5.34–5.46 (m, 2 H, CH₂=CH), 5.51 (d, J = 17.1 Hz, 1 H, CH), 5.91–6.02 (m, CH=CH₂) ppm. ¹³C NMR (CDCl₃, 75 MHz): major diastereomer: δ = 14.0, 41.2, 48.7, 61.5, 86.5, 88.3, 119.3, 133.7, 162.0, 166.2 ppm; minor diastereomer: δ = 14.1, 41.2, 48.7, 61.0, 84.8, 88.3, 117.6, 135.0, 164.0, 171.0 ppm. IR (neat): $\tilde{\nu}$ = 2984 (m), 2935 (w), 2907 (w), 1705 (s), 1653 (m), 1616 (s), 1461 (w), 1430 (m), 1392 (w), 1369 (m), 1330 (s), 1299 (s), 1269 (s), 1194 (s), 1097 (m), 1056 (s), 1011 (s), 991 (s), 962 (m), 940 (s), 863 (w), 846 (w), 763 (m), 696 (w) cm^{–1}. MS (EI, 70 eV): m/z (%) = 342 ([2 × ⁸¹Br], 18) [M]⁺, 340 ([⁸¹Br ⁷⁹Br], 52) [M]⁺, 338 ([2 × ⁷⁹Br], 19) [M]⁺, 297 (9), 295 (24), 293 (8), 262 (11), 261 (44), 260 (12), 259 (31), 233 (26), 231 (28), 215 (100), 213 (69), 195 (23), 193 (28), 189 (11), 187 (34), 185 (22), 173 (9), 171 (11), 167

(36), 165 (37), 159 (17), 157 (14), 148 (22), 146 (28), 135 (38), 134 (15), 133 (13), 108 (11), 107 (22), 106 (17), 105 (8), 95 (13), 85 (25), 79 (43). The exact molecular mass, $m/z = 337.9153 \pm 2$ ppm $[M]^+$, for $C_{10}H_{12}Br_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{10}H_{12}Br_2O_3$ (340.011): calcd. C 35.33, H 3.56; found C 35.32, H 3.64.

Compounds 3j and 4j: Starting with **Z-2j** (0.290 g, 1.87 mmol) and NBS (0.432 g, 2.43 mmol) in CCl_4 (10 mL), **3j** [0.287 g, 66%, (*E*)/(*Z*) = 4:1] and **4j** [0.174 g, 30%, (*E*)/(*Z*) = 7:2] were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 $\rightarrow$ 1:1) as slightly brownish solids.

Ethyl 2-Bromo-2-(pyrrolidin-2-ylidene)acetate (3j): 1H NMR ($CDCl_3$, 300 MHz): (*E*) isomer: $\delta = 1.31$ (t, $J = 7.2$ Hz, 3 H, CH_3), 2.03 (quint, $J = 7.5$ Hz, 2 H, CH_2), 2.82 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.64 (t, $J = 6.9$ Hz, 2 H, CH_2-NH), 4.21 (q, $J = 7.2$ Hz, 2 H, OCH_2), 8.16 (br. s, 1 H, NH) ppm; (*Z*) isomer: $\delta = 1.31$ (t, $J = 7.2$ Hz, 3 H, CH_3), 2.17 (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.10 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.48 (t, $J = 7.5$ Hz, 2 H, CH_2-NH), 4.21 (q, $J = 7.2$ Hz, 2 H, OCH_2), 5.49 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): (*E*) isomer: $\delta = 14.3$, 21.3, 35.3, 48.6, 60.0, 71.1, 165.3, 166.5 ppm; (*Z*) isomer: $\delta = 14.2$, 23.9, 32.2, 45.7, 60.5, 75.5, 162.3, 164.3 ppm. IR (KBr): $\tilde{\nu} = 3346$ (br), 2985 (w), 2903 (w), 1634 (s), 1588 (s), 1477 (w), 1455 (w), 1442 (m), 1419 (m), 1368 (w), 1320 (m), 1282 (m), 1239 (s), 1069 (s), 1056 (m), 765 (m), 719 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 236 ($[^{81}Br]$, 18) $[M]^+$, 234 ($[^{79}Br]$, 16) $[M]^+$, 207 (2), 205 (2), 190 (15), 189 (21), 188 (29), 187 (18), 163 (5), 161 (8), 159 (3), 126 (2), 110 (100), 80 (36). The exact molecular mass, $m/z = 233.0052 \pm 2$ ppm $[M]^+$, for $C_8H_{12}BrNO_2$ was confirmed by HRMS (EI, 70 eV).

Ethyl 2-Bromo-2-(3-bromopyrrolidin-2-ylidene)acetate (4j): 1H NMR ($CDCl_3$, 300 MHz): (*E*) isomer: $\delta = 1.32$ (t, $J = 7.2$ Hz, 3 H, CH_3), 2.39–2.55 (m, 2 H, CH_2), 3.64–3.90 (m, 2 H, CH_2-NH), 4.21 (q, $J = 7.2$ Hz, 2 H, OCH_2), 5.10 (d, $J = 5.7$ Hz, 1 H, $CH-Br$), 8.07 (br. s, 1 H, NH) ppm; (*Z*) isomer: $\delta = 1.32$ (t, $J = 7.2$ Hz, 3 H, CH_3), 2.35–2.47 (m, 2 H, CH_2), 3.47–3.79 (m, 2 H, CH_2-NH), 4.21 (q, $J = 7.2$ Hz, 2 H, OCH_2), 5.45 (br. s, 1 H, NH), 5.83 (d, $J = 5.4$ Hz, 1 H, $CH-Br$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): (*E*) isomer: $\delta = 14.6$, 34.9, 46.9, 50.8, 61.1, 73.4, 162.5, 167.1 ppm; (*Z*) isomer: $\delta = 14.6$, 37.2, 44.0, 46.6, 61.1, 79.3, 160.0, 163.7 ppm. IR (KBr): $\tilde{\nu} = 3375$ (br), 2990 (w), 2974 (w), 1639 (s), 1592 (s), 1473 (w), 1464 (w), 1440 (m), 1422 (m), 1388 (w), 1367 (w), 1328 (m), 1317 (m), 1260 (s), 1231 (s), 1194 (m), 1182 (m), 1158 (w), 1093 (w), 1062 (s), 1043 (m), 1014 (w), 763 (m), 718 (w), 657 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 315 ($[2 \times ^{81}Br]$, 21) $[M]^+$, 313 ($[^{81}Br ^{79}Br]$, 47) $[M]^+$, 311 ($[2 \times ^{79}Br]$, 23) $[M]^+$, 298 (8), 296 (8), 269 (8), 267 (14), 265 (6), 234 (15), 232 (15), 206 (21), 204 (26), 202 (4), 190 (55), 188 (100), 186 (51), 162 (4), 160 (15), 158 (11). The exact molecular mass, $m/z = 310.9157 \pm 2$ ppm $[M]^+$, for $C_8H_{11}Br_2NO_2$ was confirmed by HRMS (EI, 70 eV).

Compounds 3k and 4k: Starting with **Z-2k** (0.550 g, 3.25 mmol) and NBS (0.752 g, 4.23 mmol) in CCl_4 (10 mL), **3k** [0.603 g, 75%, (*E*)/(*Z*) = 3:1] and **4k** [0.206 g, 19%, (*E*)/(*Z*) = 10:3] were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 $\rightarrow$ 1:1) as brownish solids.

Isopropyl 2-Bromo-2-(pyrrolidin-2-ylidene)acetate (3k): 1H NMR ($CDCl_3$, 300 MHz): (*E*) isomer: $\delta = 1.32$ (d, $J = 7.5$ Hz, 6 H, $2 \times CH_3$), 2.02 (quint, $J = 7.5$ Hz, 2 H, CH_2), 2.81 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.63 (t, $J = 7.2$ Hz, 2 H, CH_2-NH), 5.01 (sept, $J = 6.3$ Hz, 1 H, CH), 8.12 (br. s, 1 H, NH) ppm; (*Z*) isomer: $\delta = 1.32$ (d, $J = 7.5$ Hz, 6 H, $2 \times CH_3$), 2.17 (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.09 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.47 (t, $J = 6.9$ Hz, 2 H, CH_2-NH), 5.01 (sept, $J = 6.3$ Hz, 1 H, CH), 5.48 (br. s, 1 H, NH) ppm. ^{13}C

NMR ($CDCl_3$, 75 MHz): (*E*) isomer: $\delta = 21.6$, 22.1, 35.6, 48.7, 67.5, 72.0, 165.3, 166.5 ppm; (*Z*) isomer: $\delta = 22.2$, 23.3, 32.3, 45.8, 67.6, 76.8, 162.1, 164.2 ppm. IR (KBr): $\tilde{\nu} = 3377$ (br), 3350 (w), 3338 (w), 2975 (m), 2934 (w), 2882 (w), 1681 (w), 1639 (s), 1592 (s), 1465 (w), 1454 (w), 1439 (w), 1418 (w), 1384 (w), 1374 (w), 1348 (w), 1337 (w), 1311 (w), 1280 (s), 1240 (s), 1197 (w), 1180 (m), 1155 (w), 1144 (w), 1110 (s), 1077 (w), 1066 (w), 1034 (m), 985 (w), 762 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 249 ($[^{81}Br]$, 62) $[M]^+$, 247 ($[^{79}Br]$, 100) $[M]^+$, 207 (73), 205 (75), 190 (31), 189 (91), 188 (56), 187 (92), 161 (12), 134 (9), 132 (12), 109 (44), 80 (54). The exact molecular mass, $m/z = 247.0208 \pm 2$ ppm $[M]^+$, for $C_9H_{14}BrNO_2$ was confirmed by HRMS (EI, 70 eV).

Isopropyl 2-Bromo-2-(3-bromopyrrolidin-2-ylidene)acetate (4k): 1H NMR ($CDCl_3$, 300 MHz): (*E*) isomer: $\delta = 1.21$ (dd, $J = 7.0$, 2.8 Hz, 6 H, $2 \times CH_3$), 2.40–2.53 (m, 2 H, CH_2), 3.47–3.57 (m, 1 H, CH_2-NH), 3.65–3.73 (m, 1 H, CH_2-NH), 5.01 (quint, $J = 6.3$ Hz, 1 H, CH), 5.10 (d, $J = 6.3$ Hz, 1 H, $CH-Br$), 7.75 (br., 1 H, NH) ppm; (*Z*) isomer: $\delta = 1.31$ (dd, $J = 6.2$, 3.1 Hz, 6 H, $2 \times CH_3$), 2.27–2.34 (m, 2 H, CH_2), 3.47–3.78 (m, 2 H, CH_2-NH), 5.04 (sept, $J = 6.3$ Hz, 1 H, CH), 5.41 (br. s, 1 H, NH), 5.80 (d, $J = 5.1$ Hz, 1 H, $CH-Br$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): (*E*) isomer: $\delta = 22.0$, 34.7, 46.6, 50.7, 68.3, 73.7, 162.8, 166.5 ppm; (*Z*) isomer: $\delta = 22.1$, 37.0, 43.7, 46.5, 68.5, 80.2, 159.4, 162.0 ppm. IR (KBr): $\tilde{\nu} = 3376$ (br), 2977 (w), 1641 (s), 1598 (s), 1443 (w), 1421 (w), 1376 (w), 1334 (m), 1310 (w), 1276 (s), 1255 (s), 1236 (s), 1197 (m), 1180 (m), 1105 (s), 1064 (w), 1034 (m), 762 (w), 675 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 329 ($[2 \times ^{81}Br]$, 2) $[M]^+$, 327 ($[^{81}Br ^{79}Br]$, 6) $[M]^+$, 325 ($[2 \times ^{79}Br]$, 2) $[M]^+$, 287 (9), 285 (20), 283 (10), 267 (4), 249 (10), 247 (10), 207 (16), 206 (12), 205 (18), 204 (11), 190 (17), 189 (19), 188 (36), 187 (17), 186 (18), 163 (18), 161 (20), 126 (19), 107 (100), 80 (52), 69 (11). The exact molecular mass, m/z (%) = 324.9313 ± 2 ppm $[M]^+$, for $C_9H_{13}Br_2NO_2$ was confirmed by HRMS (EI, 70 eV).

General Procedure for the Suzuki Reaction of 2-Alkylidene-tetrahydrofurans and 2-Alkylidene-pyrrolidines with Arylboronic Acids: Potassium phosphate (K_3PO_4 , 6 equiv.), the boronic acid $Ar-B(OH)_2$ (3 equiv.) and tetrakis(triphenylphosphane)palladium(0) $[Pd(PPh_3)_4]$ (0.03 equiv.) were added to a 1,4-dioxane solution (3 mL mmol $^{-1}$) of the starting material **3**, **4** or **5** (1 equiv.) at 20 °C under argon. The reaction mixture was stirred under reflux for 6 h, and then cooled to 20 °C. Diethyl ether (10 mL mmol $^{-1}$) was added, and the resulting precipitate was filtered off and washed with diethyl ether. After concentration of the filtrate in vacuo, the residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give products **7**, **8** and **9**, or **10**.

Methyl 2-[4,5-Dihydrofuran-2(3*H*)-ylidene]2-phenylacetate (7a): Starting with **3a** (0.100 g, 0.45 mmol), phenylboronic acid (0.169 g, 1.36 mmol), K_3PO_4 (0.575 g, 2.71 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in 1,4-dioxane (5 mL), **7a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 5:1) as a slightly yellowish solid (0.077 g, 79%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.13$ (quint, $J = 7.2$ Hz, 2 H, CH_2), 3.28 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.66 (s, 3 H, $3 \times CH$ of Ph), 7.32–7.37 (m, 2 H, $2 \times CH$ of Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 24.0$, 31.6, 51.2, 72.1, 104.4, 126.6, 127.7, 130.5, 135.4, 168.7, 172.2 ppm. IR (KBr): $\tilde{\nu} = 2955$ (w), 1693 (s), 1616 (s), 1492 (w), 1437 (w), 1378 (w), 1318 (w), 1299 (s), 1274 (m), 1256 (w), 1230 (m), 1185 (s), 1116 (w), 1076 (s), 1017 (w), 974 (m), 931 (m), 903 (w), 784 (m), 766 (m), 702 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 218 (100) $[M]^+$, 186 (80), 159 (3). The exact molecular mass, $m/z = 218.0943 \pm 2$ ppm $[M]^+$, for $C_{13}H_{14}O_3$ was confirmed by HRMS (EI, 70 eV).

Methyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-2-(*p*-tolyl)acetate (7b): Starting with **3a** (0.100 g, 0.45 mmol), 4-tolylboronic acid (0.191 g, 1.36 mmol), K_3PO_4 (0.575 g, 2.71 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in 1,4-dioxane (5 mL), **7b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 5:1) as a yellowish solid (0.095 g, 91%). 1H NMR ($CDCl_3$, 300 MHz): δ = 2.12 (quint, J = 7.5 Hz, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 3.26 (t, J = 7.8 Hz, 2 H, CH_2), 3.65 (s, 3 H, OCH_3), 4.19 (t, J = 7.2 Hz, 2 H, OCH_2), 7.12–7.16 (m, 4 H, 4 × CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.1, 23.9, 31.4, 51.0, 72.0, 104.1, 128.4, 130.2, 132.3, 136.0, 168.7, 172.1 ppm. IR (KBr): $\tilde{\nu}$ = 2990 (w), 1699 (s), 1614 (s), 1514 (w), 1436 (w), 1301 (m), 1274 (w), 1252 (w), 1184 (s), 1074 (s), 981 (w), 931 (w), 818 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 232 (100) $[M]^+$, 200 (73), 173 (6), 159 (9). $C_{14}H_{16}O_3$ (232.279): calcd. C 72.39, H 6.94; found C 73.04, H 7.09.

Methyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-2-(4-methoxyphenyl)acetate (7c): Starting with **3a** (0.100 g, 0.45 mmol), 4-methoxyphenylboronic acid (0.213 g, 1.36 mmol), K_3PO_4 (0.575 g, 2.71 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.015 mmol) in 1,4-dioxane (5 mL), **7c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (0.102 g, 91%). 1H NMR ($CDCl_3$, 300 MHz): δ = 2.13 (quint, J = 7.2 Hz, 2 H, CH_2), 3.26 (t, J = 7.8 Hz, 2 H, CH_2), 3.66 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.20 (t, J = 7.2 Hz, 2 H, OCH_2), 6.89 (d, J = 11.7 Hz, 2 H, 2 × CH), 7.17 (d, J = 9.0 Hz, 2 H, 2 × CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.0, 31.5, 51.2, 55.0, 72.0, 103.7, 113.2, 127.5, 131.4, 158.0, 169.1, 172.3 ppm. IR (neat): $\tilde{\nu}$ = 2992 (w), 2951 (m), 2904 (w), 2837 (w), 1700 (s), 1613 (s), 1511 (s), 1460 (m), 1438 (m), 1376 (w), 1317 (m), 1300 (m), 1275 (m), 1241 (s), 1184 (s), 1105 (w), 1074 (s), 1035 (m), 981 (m), 934 (w), 831 (m), 800 (w), 775 (w), 734 (w), 593 (w), 533 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 248 (100) $[M]^+$, 232 (35), 216 (50), 200 (28), 188 (28), 173 (4), 159 (16). $C_{14}H_{16}O_4$ (248.278): calcd. C 67.73, H 6.50; found C 67.99, H 7.11.

Methyl 2-(4-Chlorophenyl)-2-[4,5-dihydrofuran-2(3H)-ylidene]acetate (7d): Starting with **3a** (0.100 g, 0.45 mmol), 4-chlorophenylboronic acid (0.219 g, 1.36 mmol), K_3PO_4 (0.575 g, 2.71 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in 1,4-dioxane (5 mL), **7d** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 5:1) as a slightly yellowish solid (0.105 g, 92%). 1H NMR ($CDCl_3$, 300 MHz): δ = 2.14 (quint, J = 7.5 Hz, 2 H, CH_2), 3.27 (t, J = 7.8 Hz, 2 H, CH_2), 3.66 (s, 3 H, OCH_3), 4.22 (t, J = 7.2 Hz, 2 H, OCH_2), 7.19 (d, J = 10.8 Hz, 2 H, 2 × CH), 7.30 (d, J = 13.5 Hz, 2 H, 2 × CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.9, 31.6, 51.2, 72.3, 103.2, 127.8, 132.2, 133.8, 155.0, 168.4, 172.8 ppm. IR (KBr): $\tilde{\nu}$ = 2951 (w), 1704 (s), 1614 (s), 1492 (m), 1436 (w), 1378 (w), 1310 (m), 1277 (w), 1256 (w), 1227 (w), 1187 (s), 1073 (s), 1014 (w), 981 (m), 933 (w), 829 (m), 783 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 254 ($[^{37}Cl]$, 31) $[M]^+$, 252 ($[^{35}Cl]$, 100) $[M]^+$, 223 (9), 222 (31), 221 (32), 220 (98), 193 (5), 191 (3), 189 (4), 181 (5), 179 (17), 139 (24), 137 (28), 129 (51), 125 (10), 123 (15), 101 (88). $C_{13}H_{13}ClO_3$ (252.697): calcd. C 61.79, H 5.19; found C 61.84, H 5.69.

Methyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-2-(thiophen-2-yl)acetate (7e): Starting with **3a** (0.100 g, 0.45 mmol), 2-thienylboronic acid (0.179 g, 1.36 mmol), K_3PO_4 (0.575 g, 2.71 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in 1,4-dioxane (5 mL), **7e** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 5:1) as a yellowish oil (0.063 g, 62%). M.p. 80 °C. 1H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (quint, J = 7.2 Hz, 2 H, CH_2), 3.26 (t, J = 7.8 Hz, 2 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.34 (t, J = 7.2 Hz, 2 H, OCH_2), 7.01 (dd, J = 3.6, 1.2 Hz, 1 H, CH), 7.12 (dd, J = 3.6, 1.2 Hz, 1 H, CH), 7.27 (dd, J = 3.6, 1.2 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.0, 32.2, 51.4, 72.7, 98.2, 124.6,

126.1, 127.1, 136.1, 168.2, 172.7 ppm. IR (neat): $\tilde{\nu}$ = 2952 (w), 1703 (s), 1610 (s), 1435 (m), 1377 (w), 1281 (s), 1231 (m), 1212 (m), 1184 (s), 1148 (w), 1121 (w), 1073 (s), 1025 (w), 975 (w), 928 (w), 877 (w), 765 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 224 (100) $[M]^+$, 192 (49), 164 (18). The exact molecular mass, m/z = 224.0507 ± 2 ppm $[M]^+$, for $C_{11}H_{12}O_3S$ was confirmed by HRMS (EI, 70 eV).

tert-Butyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-2-phenylacetate (7f): Starting with **3d** (0.150 g, 0.57 mmol), phenylboronic acid (0.209 g, 1.71 mmol), K_3PO_4 (0.726 g, 3.42 mmol) and $Pd(PPh_3)_4$ (0.20 g, 0.017 mmol) in 1,4-dioxane (5 mL), **7f** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 30:1) as a slightly yellowish oil (0.128 g, 87%). 1H NMR ($CDCl_3$, 300 MHz): δ = 1.44 (s, 9 H, *OrBu*), 2.11 (quint, J = 7.2 Hz, 2 H, CH_2), 3.21 (t, J = 7.8 Hz, 2 H, CH_2), 4.17 (t, J = 6.9 Hz, 2 H, OCH_2), 7.20–7.34 (m, 5 H, 5 × CH of Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.4, 28.5, 31.7, 71.9, 79.8, 106.4, 126.4, 127.6, 130.6, 136.2, 167.9, 170.7 ppm. IR (neat): $\tilde{\nu}$ = 3079 (w), 2974 (m), 2921 (w), 2907 (w), 1687 (s), 1608 (s), 1492 (m), 1474 (m), 1452 (m), 1420 (w), 1384 (m), 1368 (m), 1321 (m), 1301 (m), 1269 (m), 1251 (m), 1231 (m), 1157 (s), 1113 (m), 1063 (s), 1038 (s), 956 (m), 930 (m), 880 (w), 839 (m), 812 (m), 778 (m), 756 (m), 697 (m), 654 (w), 508 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 260 (23) $[M]^+$, 203 (100), 186 (79), 169 (4), 157 (1). The exact molecular mass, m/z = 260.1412 ± 2 ppm $[M]^+$, for $C_{16}H_{20}O_3$ was confirmed by HRMS (EI, 70 eV).

tert-Butyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-2-(*p*-tolyl)acetate (7g): Starting with **3d** (0.100 g, 0.38 mmol), tolylboronic acid (0.160 g, 1.14 mmol), K_3PO_4 (0.484 g, 2.28 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.014 mmol) in 1,4-dioxane (3 mL), **7g** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 30:1) as a yellowish solid (0.091 g, 88%). M.p. 56 °C. 1H NMR ($CDCl_3$, 300 MHz): δ = 1.45 (s, 9 H, *OrBu*), 1.97 (quint, J = 6.6 Hz, 2 H, CH_2), 2.09 (s, 3 H, CH_3), 3.20 (t, J = 7.8 Hz, 2 H, CH_2), 4.17 (t, J = 6.9 Hz, 2 H, OCH_2), 7.12–7.17 (m, 4 H, 4 × CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 23.0, 24.4, 28.5, 30.4, 72.0, 79.8, 106.3, 128.4, 130.5, 133.1, 135.9, 168.1, 170.4 ppm. IR (neat): $\tilde{\nu}$ = 2977 (m), 2936 (m), 2865 (w), 1693 (s), 1616 (s), 1515 (m), 1453 (m), 1428 (w), 1368 (m), 1320 (m), 1300 (m), 1251 (w), 1231 (w), 1162 (s), 1113 (w), 1067 (s), 1038 (w), 1017 (w), 960 (w), 934 (w), 822 (w), 806 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 274 (22) $[M]^+$, 218 (100), 200 (61), 184 (4), 172 (4), 159 (5). The exact molecular mass, m/z = 274.1569 ± 2 ppm $[M]^+$, for $C_{17}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV).

tert-Butyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-2-(4-methoxyphenyl)acetate (7h): Starting with **3d** (0.100 g, 0.38 mmol), 4-methoxyphenylboronic acid (0.179 g, 1.14 mmol), K_3PO_4 (0.484 g, 2.28 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.014 mmol) in 1,4-dioxane (3 mL), **7h** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as a slightly yellowish solid (0.085 g, 77%). 1H NMR ($CDCl_3$, 300 MHz): δ = 1.45 (s, 9 H, *OrBu*), 2.10 (quint, J = 7.2 Hz, 2 H, CH_2), 3.19 (t, J = 7.8 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 4.17 (t, J = 7.2 Hz, 2 H, OCH_2), 6.86 (d, J = 6.6 Hz, 2 H, 2 × CH), 7.19 (d, J = 6.9 Hz, 2 H, 2 × CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 24.5, 28.6, 31.8, 55.3, 71.9, 79.8, 105.9, 113.2, 128.6, 131.7, 158.0, 168.1, 170.3 ppm. IR (KBr): $\tilde{\nu}$ = 2982 (w), 2934 (w), 2906 (w), 1686 (s), 1612 (s), 1511 (s), 1457 (w), 1370 (m), 1316 (m), 1281 (m), 1240 (s), 1178 (s), 1160 (s), 1109 (w), 1066 (s), 1038 (m), 1016 (w), 959 (w), 935 (w), 838 (w), 806 (w), 783 (w), 593 (w), 537 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 290 (27) $[M]^+$, 234 (100), 216 (36), 200 (6), 188 (19), 159 (5). The exact molecular mass, m/z = 290.1518 ± 2 ppm $[M]^+$, for $C_{17}H_{22}O_4$ was confirmed by HRMS (EI, 70 eV).

tert-Butyl 2-(4-Chlorophenyl)-2-[4,5-dihydrofuran-2(3H)-ylidene]acetate (7i): Starting with **3d** (0.100 g, 0.38 mmol), 4-chloro-

phenylboronic acid (0.184 g, 1.14 mmol), K_3PO_4 (0.484 g, 2.28 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.014 mmol) in 1,4-dioxane (3 mL), **7i** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 30:1) as a slightly yellowish solid (0.097 g, 87%). M.p. 75 °C. 1H NMR ($CDCl_3$, 300 MHz): δ = 1.44 (s, 9 H, *OrBu*), 2.11 (quint, J = 7.5 Hz, 2 H, CH_2), 3.21 (t, J = 7.8 Hz, 2 H, CH_2), 4.18 (t, J = 7.2 Hz, 2 H, OCH_2), 7.19 (d, J = 6.6 Hz, 2 H, $2\times CH$), 7.27 (d, J = 8.4 Hz, 2 H, $2\times CH$) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 24.4, 28.5, 31.9, 72.2, 80.2, 105.3, 127.9, 132.1, 132.4, 134.7, 167.6, 171.1 ppm. IR (KBr): $\tilde{\nu}$ = 2972 (m), 1693 (s), 1623 (s), 1491 (m), 1391 (w), 1369 (m), 1313 (m), 1257 (m), 1232 (w), 1162 (s), 1071 (s), 1037 (m), 1015 (m), 959 (w), 932 (w), 838 (m), 805 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 296 ($[^{37}Cl]$, 6) $[M]^+$, 294 ($[^{35}Cl]$, 18) $[M]^+$, 240 (34), 238 (100), 223 (6), 222 (23), 221 (23), 220 (68), 204 (6), 192 (2), 181 (2), 179 (2), 151 (16), 139 (10), 137 (15), 129 (20). The exact molecular mass, m/z = 294.1023 $\pm$ 2 ppm $[M]^+$, for $C_{16}H_{19}ClO_3$ was confirmed by HRMS (EI, 70 eV).

tert-Butyl 2-[4,5-Dihydrofuran-2(3*H*)-ylidene]-2-(thiophen-2-yl)acetate (7j): Starting with **3d** (0.100 g, 0.38 mmol), 2-thienylboronic acid (0.150 g, 1.14 mmol), K_3PO_4 (0.484 g, 2.28 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.014 mmol) in 1,4-dioxane (3 mL), **7j** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 30:1) as a yellowish solid (1:1 mixture of **7j/3d**, calcd. yield of **7j**: 0.048 g, 48%). M.p. 99 °C. 1H NMR ($CDCl_3$, 300 MHz): δ = 1.51 (s, 9 H, *OrBu*), 2.13 (quint, J = 7.5 Hz, 2 H, CH_2), 3.13 (t, J = 7.8 Hz, 2 H, CH_2), 4.32 (t, J = 6.9 Hz, 2 H, OCH_2), 6.98 (t, J = 4.5 Hz, 1 H, CH), 7.21 (s, 1 H, CH), 7.22 (d, J = 4.2 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.0, 28.3, 32.3, 72.4, 80.6, 100.5, 124.0, 125.7, 126.6, 136.7, 167.0, 170.0 ppm. IR (neat): $\tilde{\nu}$ = 2977 (m), 1695 (s), 1613 (m), 1454 (w), 1370 (m), 1297 (m), 1253 (w), 1237 (w), 1208 (w), 1173 (s), 1151 (s), 1118 (m), 1070 (s), 1041 (w) cm^{-1} . MS (EI, eV): m/z (%) = 266 (24) $[M]^+$, 210 (100), 193 (16), 176 (8), 164 (25). The exact molecular mass, m/z = 266.0977 $\pm$ 2 ppm $[M]^+$, for $C_{14}H_{18}O_3S$ was confirmed by HRMS (EI, 70 eV).

2-[4,5-Dihydrofuran-2(3*H*)-ylidene]-2-(4-hydroxyphenyl)acetic Acid (7k): BBr_3 (0.525 g, 2.1 mmol) was added to a CH_2Cl_2 solution (5 mL) of **7c** (0.130 g, 0.5 mmol) at 0 °C. The reaction mixture was allowed to warm to 20 °C over 12 h and was then stirred at this temperature for 6 h. Methanol (5 mL) was slowly added to the reaction mixture and the solvents were removed in vacuo. An aqueous solution of KOH (0.069 g, 1.25 mmol in 7 mL H_2O) was added to a THF solution (7 mL) of the residue at 20 °C. The reaction mixture was refluxed for 4 h and cooled to 20 °C. An aqueous solution of HCl (10%, 10 mL) was added to the reaction mixture and the latter was extracted first with diethyl ether and then with dichloromethane. The combined organic layers were dried with Na_2SO_4 , filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc = 3:1 $\rightarrow$ 1:1) to give **7k** as a slightly yellowish solid (0.088 g, 80%). 1H NMR ($CDCl_3/[D_6]DMSO$ = 5:1, 300 MHz): δ = 2.10 (quint, J = 7.5 Hz, 2 H, CH_2), 3.21 (t, J = 7.8 Hz, 2 H, CH_2), 4.17 (t, J = 7.2 Hz, 2 H, OCH_2), 6.79 (d, J = 8.7 Hz, 2 H, $2\times CH$), 7.10 (d, J = 8.7 Hz, 2 H, $2\times CH$), 8.45 (s, 1 H, OH), 11.25 (br. s, 1 H, O=C-OH) ppm. ^{13}C NMR ($CDCl_3/[D_6]DMSO$ = 1:1, 75 MHz): δ = 23.1, 30.5, 70.7, 103.3, 113.6, 125.3, 130.5, 154.7, 170.2, 170.2 ppm. IR (KBr): $\tilde{\nu}$ = 3389 (br), 3138 (w), 3059 (w), 3018 (w), 2958 (m), 2912 (m), 2855 (w), 2830 (w), 2724 (w), 2632 (w), 2612 (w), 2559 (w), 1700 (m), 1674 (m), 1638 (s), 1608 (s), 1591 (s), 1516 (s), 1440 (m), 1375 (m), 1319 (s), 1237 (s), 1189 (s), 1102 (w), 1073 (s), 1025 (w), 955 (w), 931 (m), 829 (m), 769 (w), 597 (w), 531 (w), 467 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 220 (100) $[M]^+$, 202 (37),

176 (40), 161 (5), 93 (6), 77 (20). The exact molecular mass, m/z = 220.0736 $\pm$ 2 ppm $[M]^+$, for $C_{12}H_{12}O_4$ was confirmed by HRMS (EI, 70 eV).

Isopropyl 2-(4-Chlorophenyl)-2-(pyrrolidin-2-ylidene)acetate (7l): Starting with **3k** (0.150 g, 0.605 mmol), 4-chlorophenylboronic acid (0.292 g, 1.81 mmol), K_3PO_4 (0.771 g, 3.63 mmol) and $Pd(PPh_3)_4$ (0.021 g, 0.061 mmol) in 1,4-dioxane (5 mL), **7l** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 5:1) as a brownish oil (0.147 g, 87%). 1H NMR ($CDCl_3$, 300 MHz): δ = 1.23 (d, J = 6.3 Hz, 6 H, $2\times CH_3$), 1.97 (quint, J = 7.5 Hz, 2 H, CH_2), 2.57 (t, J = 7.8 Hz, 2 H, CH_2), 3.44 (t, J = 7.2 Hz, 2 H, CH_2NH), 5.00 (sept, J = 6.3 Hz, 1 H, CH), 6.77 (d, J = 6.9 Hz, 2 H, $2\times CH$), 7.17 (J = 6.6 Hz, 2 H, $2\times CH$), 7.87 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.2, 22.3, 32.3, 47.1, 65.4, 80.2, 116.7, 125.1, 129.4, 154.7, 166.6, 170.6 ppm. IR (neat): $\tilde{\nu}$ = 3374 (br), 2980 (s), 2936 (m), 2874 (w), 1731 (m), 1666 (s), 1605 (s), 1592 (s), 1489 (s), 1449 (m), 1438 (m), 1369 (s), 1340 (m), 1262 (s), 1222 (s), 1180 (m), 1163 (m), 1139 (m), 1105 (s), 1053 (m), 1002 (w), 081 (w), 829 (m), 773 (w), 661 (w), 641 (w), 507 (w).

Compounds 8a and 9a: Starting with **E-4a** (0.300 g, 1.0 mmol), phenylboronic acid (0.374 g, 3.0 mmol), K_3PO_4 (1.273 g, 6.0 mmol) and $Pd(PPh_3)_4$ (0.035 g, 0.030 mmol) in 1,4-dioxane (5 mL), **8a** (0.045 g, 21%) and **9a** (0.120 g, 41%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 10:1) as a colorless oil and a slightly yellowish solid, respectively.

Methyl 2-(Furan-2-yl)-2-phenylacetate (8a): 1H NMR ($CDCl_3$, 300 MHz): δ = 3.74 (s, 3 H, OCH_3), 5.03 (s, 1 H, CH), 6.19 (dd, J = 4.2, 0.75 Hz, 1 H, CH), 6.32 (dd, J = 3.3, 1.8 Hz, 1 H, CH), 7.29–7.38 (m, 6 H, $5\times CH$ of Ph, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.3, 52.6, 108.1, 110.3, 127.8, 128.5, 128.7, 136.0, 142.3, 151.6, 171.0 ppm. IR (neat): $\tilde{\nu}$ = 2992 (w), 2961 (w), 2936 (w), 2912 (w), 2839 (w), 1736 (s), 1646 (w), 1612 (m), 1586 (w), 1513 (s), 1463 (m), 1447 (w), 1392 (w), 1369 (w), 1325 (w), 1301 (m), 1249 (s), 1201 (m), 1177 (s), 1155 (s), 1100 (m), 1075 (w), 1033 (s), 932 (w), 880 (w), 822 (m), 742 (w), 532 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 216 (19) $[M]^+$, 187 (3), 157 (100), 102 (4), 77 (7). The exact molecular mass, m/z = 216.0786 $\pm$ 2 ppm $[M]^+$, for $C_{13}H_{12}O_3$ was confirmed by HRMS (EI, 70 eV).

Methyl 2-Phenyl-2-[3-phenyl-4,5-dihydrofuran-2(3*H*)-ylidene]acetate (9a): 1H NMR ($CDCl_3$, 300 MHz): δ = 2.08–2.13 (m, 1 H, CH_2), 2.49–2.63 (m, 1 H, CH_2), 3.48 (s, 3 H, OCH_3), 4.16–4.25 (m, 1 H, OCH_2), 4.31 (dt, J = 1.8, 8.7 Hz, 1 H, OCH_2), 5.12 (dd, J = 1.2, 8.7 Hz, 1 H, $CH-Ph$), 7.22–7.41 (m, 10 H, $10\times CH$ of $2\times Ph$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.1, 48.1, 51.1, 69.9, 106.0, 126.5, 126.76, 126.79, 127.8, 128.6, 130.4, 135.4, 142.0, 167.6, 172.5 ppm. IR (KBr): $\tilde{\nu}$ = 3026 (w), 2995 (w), 2951 (w), 2901 (w), 1703 (s), 1622 (s), 1603 (w), 1495 (w), 1450 (w), 1432 (w), 1376 (w), 1317 (w), 1299 (m), 1273 (w), 1254 (w), 1238 (w), 1201 (m), 1173 (s), 1075 (s), 1064 (s), 1029 (w), 1014 (w), 976 (m), 930 (w), 785 (m), 756 (w), 734 (w), 700 (m), 540 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 294 (82) $[M]^+$, 279 (12), 262 (100), 247 (18), 235 (4), 216 (13), 139 (19), 77 (68). The exact molecular mass, m/z = 294.1256 $\pm$ 2 ppm $[M]^+$, for $C_{19}H_{18}O_3$ was confirmed by HRMS (EI, 70 eV).

Ethyl (4-Methoxyphenyl)[3-(4-methoxyphenyl)-4,5-dihydrofuran-2(3*H*)-ylidene]acetate (9b): Starting with **Z-4b** (0.250 g, 0.796 mmol), 4-methoxyphenylboronic acid (0.749 g, 4.78 mmol), K_3PO_4 (0.015 g, 4.78 mmol) and $Pd(PPh_3)_4$ (0.046 g, 0.040 mmol) in 1,4-dioxane (5 mL), **9b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a slightly yellowish oil (0.184 g, 66%). 1H NMR ($CDCl_3$, 300 MHz): δ = 1.03 (t, J = 7.2 Hz, 3 H, CH_3), 2.02–2.08 (m, 1 H, CH_2), 2.45–2.58 (m, 1 H,

CH₂), 3.79 (s, 3 H, OCH₃), 3.82 (s, 3 H, OCH₃), 3.93–4.01 (dq, J = 7.2, 3.0 Hz, 2 H, OCH₂CH₃), 4.11–4.21 (m, 1 H, OCH₂), 4.26–4.32 (dt, J = 8.4, 1.8 Hz, 1 H, OCH₂), 5.04 (d, J = 7.8 Hz, 1 H, CH), 6.85–6.93 (m, 2 H, 2×CH), 7.17–7.20 (m, 1 H, CH), 7.24–7.28 (m, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 14.1, 34.3, 47.2, 55.05, 55.14, 59.8, 69.7, 105.8, 113.2, 113.9, 127.7, 127.9, 131.5, 134.0, 158.05, 158.10, 167.5, 172.0 ppm. IR (neat): $\tilde{\nu}$ = 3033 (w), 2983 (m), 2937 (m), 2908 (m), 2937 (w), 1734 (w), 1695 (s), 1609 (s), 1512 (s), 1462 (m), 1447 (m), 1371 (m), 1278 (s), 1245 (s), 1219 (s), 1175 (s), 1069 (s), 1033 (m), 956 (w), 933 (w), 879 (w), 832 (m), 809 (w), 789 (w), 760 (w), 735 (w), 591 (w), 543 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 368 (69) [M]⁺, 322 (100), 307 (29), 295 (16), 278 (38), 262 (10), 232 (12). The exact molecular mass, m/z = 368.1624 ± 2 ppm [M]⁺, for C₂₂H₂₄O₅ was confirmed by HRMS (EI, 70 eV).

1,2-Diphenyl-2-[3-phenyl-4,5-dihydrofuran-2(3H)-ylidene]ethanone (9c): Starting with **4e** (0.150 g, 0.434 mmol), phenylboronic acid (0.159 g, 1.302 mmol), K₃PO₄ (0.553 g, 2.60 mmol) and Pd(PPh₃)₄ (0.015 g, 0.013 mmol) in 1,4-dioxane (5 mL), **9c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish solid (0.091 g, 62%). ¹H NMR (CDCl₃, 300 MHz): δ = 2.09–2.17 (m, 1 H, CH₂), 2.54–2.66 (m, 1 H, CH₂), 4.36–4.41 (dd, J = 9.0, 4.8 Hz, 2 H, OCH₂), 4.77–4.81 (dd, J = 8.4, 3.3 Hz, 1 H, CH-Ph), 7.07–7.45 (m, 15 H, 15×CH of Ph) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 29.7, 47.7, 70.3, 113.8, 126.4, 126.5, 127.3, 127.6, 128.1, 128.5, 129.3, 129.9, 131.1, 136.8, 139.3, 141.8, 169.1, 195.8 ppm. IR (KBr): $\tilde{\nu}$ = 3055 (w), 3026 (w), 2982 (w), 2957 (w), 2922 (w), 2896 (w), 2852 (w), 1648 (s), 1598 (m), 1577 (w), 1553 (s), 1493 (w), 1448 (w), 1320 (w), 1291 (m), 1271 (w), 1203 (m), 1174 (s), 1113 (w), 1023 (w), 968 (s), 930 (m), 889 (s), 765 (w), 748 (w), 720 (w), 699 (s) cm⁻¹. MS (EI, 70 eV): m/z = 340 (100) [M]⁺, 263 (12), 235 (36). The exact molecular mass, m/z = 340.1463 ± 2 ppm [M]⁺, for C₂₄H₂₀O₂ was confirmed by HRMS (EI, 70 eV).

Ethyl 2-[3-(4-Chlorophenyl)-4,5-dihydrofuran-2(3H)-ylidene]propionate (10a): Starting with **5f** (0.200 g, 0.80 mmol), 4-chlorophenylboronic acid (0.377 g, 2.41 mmol), K₃PO₄ (1.023 g, 4.82 mmol) and Pd(PPh₃)₄ (0.028 g, 0.024 mmol) in 1,4-dioxane (10 mL), **10a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 3:1) as a slightly yellowish solid (0.117 g, 52%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.08 (t, J = 7.2 Hz, 3 H, CH₃), 1.92 (d, J = 0.6 Hz, 3 H, CH₃), 2.01 (ddt, J = 12.4, 5.7, 1.2 Hz, 1 H, CH₂), 2.43–2.57 (m, 1 H, CH₂), 3.98 (q, J = 7.2 Hz, 2 H, OCH₂), 4.11–4.21 (m, 1 H, OCH₂), 4.35 (dt, J = 8.5, 1.2 Hz, 1 H, OCH₂), 4.86 (d, J = 8.5 Hz, 1 H, CH), 7.10 (dd, J = 6.6, 1.8 Hz, 2 H, 2×CH of Ar), 7.26 (dd, J = 6.6, 1.8 Hz, 2 H, 2×CH of Ar) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 11.5, 14.2, 34.4, 47.0, 59.6, 68.8, 99.8, 128.3 (2 C), 128.6 (2 C), 132.0, 140.9, 168.2, 170.1 ppm. IR (neat): $\tilde{\nu}$ = 2982 (w), 2930 (w), 1737 (w), 1696 (s), 1641 (s), 1488 (w), 1452 (w), 1399 (w), 1390 (w), 1371 (w), 1289 (m), 1251 (w), 1216 (w), 1172 (m), 1089 (s), 1020 (w), 976 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 282 ([³⁷Cl], 27) [M]⁺, 280 ([³⁵Cl], 100) [M]⁺, 236 (19), 235 (38), 234 (61), 233 (13), 219 (6), 209 (18), 208 (5), 207 (43), 205 (23), 199 (89), 181 (5), 179 (6), 172 (23), 170 (15), 151 (17), 141 (18), 139 (16), 128 (38), 117 (21), 116 (20), 114 (48), 83 (36). HRMS (ESI): calcd. for C₁₅H₁₇ClO₃ ([M + 1]⁺): 283.09150 (³⁷Cl), 281.09445 (³⁵Cl); found 283.09119 (³⁷Cl), 281.09405 (³⁵Cl).

Ethyl 2-[3-(4-Chlorophenyl)-4,5-dihydrofuran-2(3H)-ylidene]butyrate (10b): Starting with **5g** (0.200 g, 0.76 mmol), 4-chlorophenylboronic acid (0.368 g, 2.28 mmol), K₃PO₄ (0.968 g, 4.56 mmol) and Pd(PPh₃)₄ (0.026 g, 0.023 mmol) in 1,4-dioxane (10 mL), **10b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc =

100:1 → 1:1) as a slightly yellowish oil (0.170 g, 76%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.08 (t, J = 7.2 Hz, 3 H, CH₃), 1.28 (t, J = 7.2 Hz, 3 H, CH₃), 2.00 (ddt, J = 12.4, 5.7, 1.3 Hz, 2 H, CH₂), 2.42 (q, J = 7.2 Hz, 2 H, CH₂), 4.09–4.24 (m, 3 H, 2×OCH₂), 4.34 (dt, J = 8.7, 1.4 Hz, 1 H, OCH₂), 4.86 (d, J = 8.3 Hz, 1 H, CH-Ar), 7.09 (d, J = 8.4 Hz, 2 H, 2×CH of Ar), 7.26 (d, J = 8.4 Hz, 2 H, 2×CH of Ar) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 13.6, 14.1, 19.6, 34.3, 46.9, 59.3, 68.8, 106.6, 128.1 (2 C), 128.7 (2 C), 129.3, 140.9, 169.9 ppm. IR (neat): $\tilde{\nu}$ = 2975 (s), 2934 (m), 2902 (m), 2875 (w), 1737 (m), 1694 (s), 1635 (s), 1489 (m), 1454 (m), 1400 (w), 1371 (m), 1310 (m), 1254 (s), 1215 (m), 1174 (s), 1099 (s), 1068 (m), 1036 (m), 1023 (m), 991 (w), 948 (w), 882 (w), 828 (w), 781 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 296 ([³⁷Cl], 12) [M]⁺, 294 ([³⁵Cl], 77) [M]⁺, 250 (18), 249 (34), 248 (100), 247 (81), 235 (6), 233 (35), 223 (15), 221 (18), 213 (64), 205 (20), 183 (3), 181 (17), 150 (4), 148 (37), 141 (10), 139 (9), 114 (25), 70 (42). C₁₆H₁₉ClO₃ (294.777): calcd. C 65.19, H 6.50; found C 64.50, H 6.33.

3-Phenyl-4,4',5,5'-tetrahydro-2,3'-bifuranylidene-2'-one (10c): Starting with **5h** (0.100 g, 0.43 mmol), phenylboronic acid (0.157 g, 1.29 mmol), K₃PO₄ (0.547 g, 2.57 mmol) and Pd(PPh₃)₄ (0.015 g, 0.013 mmol) in 1,4-dioxane (5 mL), **10c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 3:1) as a yellowish solid (0.054 g, 55%). ¹H NMR (CDCl₃, 300 MHz): δ = 2.11–2.18 (m, 1 H, CH₂), 2.46–2.60 (m, 1 H, CH₂), 2.97 (t, J = 7.8 Hz, 2 H, CH₂), 4.29 (t, J = 7.8 Hz, 2 H, OCH₂), 4.32–4.37 (m, 1 H, OCH₂), 4.45 (dt, J = 9.0, 1.5 Hz, 1 H, OCH₂), 4.97 (d, J = 8.4 Hz, 1 H, CH), 7.18–7.32 (m, 5 H, 5×CH of Ph) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 25.2, 33.7, 45.7, 65.0, 70.6, 94.6, 126.7, 126.9 (2 C), 128.6 (2 C), 141.1, 170.5, 171.8 ppm. IR (KBr): $\tilde{\nu}$ = 2999 (w), 2981 (w), 2913 (w), 1736 (s), 1675 (s), 1497 (w), 1482 (w), 1449 (w), 1370 (m), 1312 (w), 1253 (s), 1224 (m), 1191 (m), 1173 (m), 1028 (s), 990 (m), 942 (w), 758 (m), 702 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 230 (100) [M]⁺. HRMS (FTICR): calcd. for C₁₄H₁₄O₃ ([M + 1]⁺): 231.10212; found 231.10148.

General Procedure for the Heck Reaction of 2-Alkylidene-tetrahydrofurans: Triethylamine (NEt₃, 2 equiv.), the alkene (2 equiv.) and tetrakis(triphenylphosphane)palladium(0) [Pd(PPh₃)₄] (0.03 equiv.) were added to a DMF solution (5 mL mmol⁻¹) of **3** (1 equiv.) at 20 °C. The reaction mixture was heated and stirred at 100 °C for 25 h. The reaction mixture was allowed to cool to 20 °C and then poured into diethyl ether. The mixture was washed several times with water and the combined aqueous layers were extracted with diethyl ether. The combined organic layers were dried (Na₂SO₄), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give the products **11**.

1-tert-Butyl 5-Methyl 4-[4,5-Dihydrofuran-2(3H)-ylidene]pent-2-enedioate (11a): Starting with **3a** (0.050 g, 0.226 mmol), *tert*-butyl acrylate (0.05 mL, 0.34 mmol), NEt₃ (0.06 mL, 0.45 mmol), Pd(PPh₃)₄ (0.008 g, 0.007 mmol) in DMF (3 mL), **11a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.052 g, 85%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.50 (s, 9 H, *tert*-Bu), 2.14 (quint, J = 7.5 Hz, 2 H, CH₂), 3.25 (t, J = 7.8 Hz, 2 H, CH₂), 3.76 (s, 3 H, OCH₃), 4.44 (t, J = 7.2 Hz, 2 H, OCH₂), 6.41 (d, J = 16.2 Hz, 1 H, CH), 7.70 (d, J = 16.2 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 23.4, 28.2, 33.2, 51.3, 73.6, 79.6, 101.0, 119.1, 136.2, 167.8, 167.9, 177.8 ppm. IR (neat): $\tilde{\nu}$ = 2978 (m), 2934 (w), 1727 (s), 1711 (s), 1641 (w), 1622 (m), 1583 (m), 1477 (w), 1455 (m), 1440 (m), 1389 (m), 1369 (m), 1333 (w), 1305 (m), 1255 (s), 1242 (m), 1151 (s), 1124 (s), 1076 (m), 1052 (w), 993 (w), 976 (w), 847 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 268 (5) [M]⁺, 237 (6), 212 (44), 195 (26), 180 (100). The exact

molecular mass, $m/z = 268.1311 \pm 2$ ppm $[M]^+$, for $C_{14}H_{20}O_5$ was confirmed by HRMS (EI, 70 eV).

Methyl 4-Cyano-2-[4,5-dihydrofuran-2(3H)-ylidene]but-3-enoate (11b): Starting with **3a** (0.150 g, 0.68 mmol), acrylonitrile (0.09 mL, 1.36 mmol), NEt_3 (0.19 mL, 1.36 mmol) and $Pd(PPh_3)_4$ (0.039 g, 0.034 mmol) in DMF (3 mL), **11b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish oil (0.061 g, 47%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.18$ (quint, $J = 7.1$ Hz, 2 H, CH_2), 3.28 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.77 (s, 3 H, OCH_3), 4.48 (t, $J = 7.2$ Hz, 2 H, OCH_2), 6.04 (d, $J = 16.8$ Hz, 1 H, $CH=CH$), 7.44 (d, $J = 16.8$ Hz, 1 H, $CH=CH$) ppm. IR (neat): $\tilde{\nu} = 2957$ (w), 2906 (w), 2230 (w), 1603 (s), 1442 (m), 1287 (s), 1236 (w), 1212 (s), 1186 (s), 1075 (s), 1027 (w), 970 (w), 877 (m), 765 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 193 (1) $[M]^+$, 163 (73), 154 (76), 141 (45), 132 (10), 122 (64), 109 (13), 96 (96), 69 (100). The exact molecular mass, $m/z = 193.0739 \pm 2$ ppm $[M]^+$, for $C_{10}H_{11}NO_3$ was confirmed by HRMS (EI, 70 eV).

Methyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-3-phenylbut-3-enoate (11c): Starting with **3a** (0.100 g, 0.45 mmol), styrene (0.095 g, 0.91 mmol), NEt_3 (0.13 mL, 0.91 mmol) and $Pd(PPh_3)_4$ (0.027 g, 0.023 mmol) in DMF (3 mL), **11c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish oil (0.062 g, 56%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.13$ (quint, $J = 7.8$ Hz, 2 H, CH_2), 3.28 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 4.19 (t, $J = 7.2$ Hz, 2 H, OCH_2), 5.20 (d, $J = 1.5$ Hz, 1 H, $CH_2=C$), 5.79 (d, $J = 1.5$ Hz, 1 H, $CH_2=C$), 6.95–7.39 (m, 5 H, $5 \times CH$ of Ph) ppm. IR (neat): $\tilde{\nu} = 3079$ (w), 3060 (w), 3027 (m), 2976 (s), 2927 (s), 2858 (m), 1703 (s), 1639 (s), 1492 (m), 1446 (s), 1378 (m), 1350 (m), 1281 (m), 1239 (m), 1211 (m), 1185 (s), 1156 (m), 1119 (s), 1075 (s), 1049 (m), 980 (m), 927 (w), 829 (w), 760 (m), 701 (s) cm^{-1} . MS (EI, 70 eV): m/z (%) = 244 (100) $[M]^+$, 229 (10), 213 (14), 197 (11), 185 (34), 171 (35), 158 (16), 142 (39), 131 (9), 127 (29), 114 (49), 110 (14), 103 (19), 91 (19), 81 (8), 77 (24), 70 (70). HRMS (ESI): calcd. for $C_{15}H_{16}O_3$ ($[M + 1]^+$): 245.11777; found 245.11711.

Methyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-3-(4-methoxyphenyl)but-3-enoate (11d): Starting with **3a** (0.100 g, 0.45 mmol), 4-methoxystyrene (0.127 g, 0.91 mmol), NEt_3 (0.13 mL, 0.91 mmol) and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in DMF (3 mL), **11d** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish oil (0.055 g, 45%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.13$ (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.27 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.58 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.21 (t, $J = 7.2$ Hz, 2 H, OCH_2), 5.09 (d, $J = 1.5$ Hz, 1 H, $CH_2=C$), 5.71 (d, $J = 1.5$ Hz, 1 H, $CH_2=C$), 6.82 (d, $J = 9.0$ Hz, 2 H, $2 \times CH$ of Ar), 7.34 (d, $J = 9.0$ Hz, 2 H, $2 \times CH$ of Ar) ppm. IR (neat): $\tilde{\nu} = 2976$ (s), 2934 (m), 2895 (w), 2866 (m), 1705 (s), 1638 (m), 1609 (m), 1512 (s), 1460 (w), 1441 (m), 1381 (m), 1351 (w), 1297 (m), 1251 (s), 1216 (w), 1179 (s), 1151 (m), 1118 (s), 1078 (s), 1037 (s), 834 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 274 (100) $[M]^+$, 258 (42), 242 (18), 226 (36), 214 (45), 200 (35), 183 (9), 158 (40), 144 (25), 134 (47), 121 (14), 108 (7), 77 (21), 70 (21). The exact molecular mass, $m/z = 274.1205 \pm 2$ ppm $[M]^+$, for $C_{16}H_{18}O_4$ was confirmed by HRMS (EI, 70 eV).

1-tert-Butyl 5-Ethyl 4-[4,5-Dihydrofuran-2(3H)-ylidene]pent-2-enedioate (11e): Starting with **3b** (0.200 g, 0.85 mmol), *tert*-butyl acrylate (0.19 mL, 1.28 mmol), NEt_3 (0.24 mL, 1.70 mmol), $Pd(PPh_3)_4$ (0.050 g, 0.043 mmol) in DMF (3 mL), **11e** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish oil (0.123 g, 51%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.31$ (t, $J = 7.2$ Hz, 3 H, OCH_2CH_3), 1.39 (s, 9 H, $OrBu$), 2.13 (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.25 (t, $J = 7.8$ Hz, 2 H, CH_2), 4.23 (q, $J = 7.2$ Hz, 2 H, OCH_2CH_3), 4.44 (t, $J = 7.2$ Hz, 2 H, OCH_2), 6.43 (d, $J = 16.1$ Hz, 1 H, $CH=CH$), 7.70 (d, $J = 16.1$ Hz, 1 H, $CH=CH$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 14.4$, 23.5, 28.2, 33.2, 60.2, 73.5, 79.5, 101.2, 119.1, 136.3, 167.3, 167.9, 177.5 ppm. IR (neat): $\tilde{\nu} = 2978$ (s), 2934 (m), 2872 (m), 1728 (s), 1640 (m), 1623 (m), 1583 (w), 1477 (w), 1454 (m), 1423 (w), 1390 (m), 1370 (s), 1334 (m), 1302 (m), 1254 (s), 1151 (s), 1119 (s), 1072 (m), 1054 (m), 1026 (m), 868 (w), 846 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 282 (2) $[M]^+$, 237 (6), 226 (25), 209 (16), 180 (100), 151 (22), 136 (3), 107 (10). The exact molecular mass, $m/z = 282.1467 \pm 2$ ppm $[M]^+$, for $C_{15}H_{22}O_5$ was confirmed by HRMS (EI, 70 eV).

Isopropyl 2-[4,5-Dihydrofuran-2(3H)-ylidene]-3-(4-methoxyphenyl)but-3-enoate (11f): Starting with **3c** (0.100 g, 0.40 mmol), 4-methoxystyrene (0.112 g, 0.80 mmol), NEt_3 (0.11 mL, 0.80 mmol) and $Pd(PPh_3)_4$ (0.014 g, 0.012 mmol) in DMF (3 mL), **11f** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a yellowish oil (0.070 g, 58%). 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.03$ (d, $J = 6.3$ Hz, 6 H, $2 \times CH_3$), 2.12 (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.24 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 4.21 (t, $J = 7.2$ Hz, 2 H, OCH_2), 4.90 (sept, $J = 6.3$ Hz, 1 H, OCH), 5.11 (d, $J = 1.5$ Hz, 1 H, $CH_2=C$), 5.63 (d, $J = 1.5$ Hz, 1 H, $CH_2=C$), 6.80 (d, $J = 9.0$ Hz, 2 H, $2 \times CH$ of Ar), 7.31 (d, $J = 9.0$ Hz, 2 H, $2 \times CH$ of Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 21.8$, 24.2, 31.2, 55.3, 66.8, 72.0, 104.9, 113.4, 114.5, 127.1, 133.9, 142.0, 158.9, 167.9, 171.7 ppm. IR (neat): $\tilde{\nu} = 2978$ (m), 2931 (m), 2859 (w), 1694 (s), 1611 (s), 1510 (s), 1461 (m), 1376 (m), 1251 (s), 1178 (s), 1141 (m), 1108 (s), 1073 (s), 1035 (s), 984 (m), 961 (w), 934 (w), 896 (w), 837 (m), 807 (w), 794 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 302 (41) $[M]^+$, 259 (100), 243 (6), 231 (82), 227 (2), 215 (13), 201 (35), 185 (3), 148 (79), 135 (75). HRMS (ESI): calcd. for $C_{18}H_{22}O_4$ $[M]^+$: 302.15179; found 302.15236.

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