Synthesis of Benzofurans with Remote Bromide Functionality by Domino "Ring-Cleavage-Deprotection-Cyclization" Reactions of 2-Alkylidenetetrahydrofurans with Boron Tribromide

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JOC*Article*

Synthesis of Benzofurans with Remote Bromide Functionality by Domino "Ring-Cleavage-Deprotection-Cyclization" Reactions of 2-Alkylidenetetrahydrofurans with Boron Tribromide

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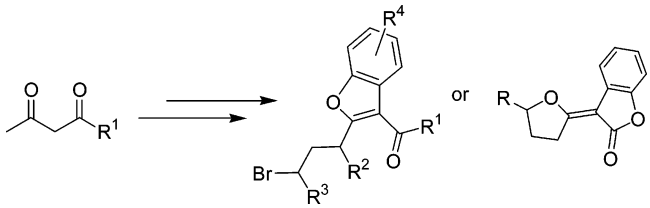

Bromination and subsequent Suzuki reactions of 2-alkylidenetetrahydrofurans, readily available by [3+2] cyclizations, afforded 1′-(2″-methoxyphenyl)-2-alkylidenetetrahydrofurans. Treatment of the latter with boron tribromide and subsequent addition of water resulted in the chemoselective formation of functionalized benzofurans containing a remote bromide functionality. The products are formed by a new domino "ring-cleavage-deprotection-cyclization" reaction. The addition of an aqueous solution of potassium *tert*-butoxide, rather than water, afforded saturated analogues of calycine by a "ring-cleavage-deprotection-ring-closure-lactonization" reaction.

Introduction

Functionalized benzofurans[1,2] represent important synthetic building blocks and occur in a variety of pharmacologically relevant natural products, such as diazonamide A, anigopreissin A (Figure 1), euparin (Figure 2), coumestrol (Figure 3), dehydrotremetone, or cicerfuran (Figure 4).[1] Synthetic amiodarone represents a potent antiarrythmic and antianginal drug that is used in the clinic.[3]

2-Alkylidenetetrahydrofurans represent useful synthetic building blocks.[4−6] We and others have reported a number of one-pot syntheses of 2-alkylidenetetrahydrofurans by [3+2] cyclizations of 1,3-dicarbonyl dianions and 1,3-bis-silyl enol ethers with 1,2-dielectrophiles,[7] and

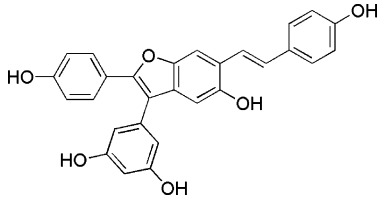

FIGURE 1. Anigopreissin A.

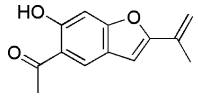

FIGURE 2. Euparin.

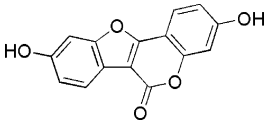

FIGURE 3. Coumesterol.

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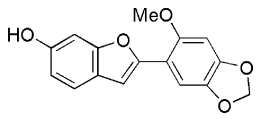
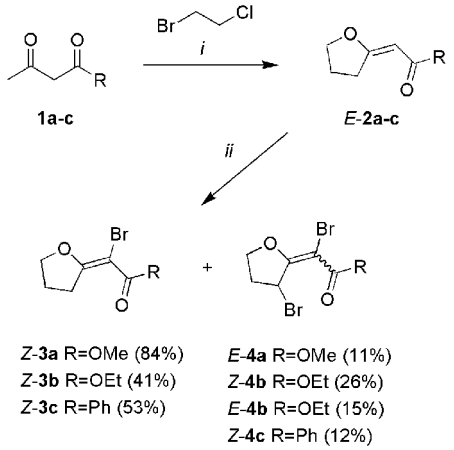


FIGURE 4. Cicerfuran.

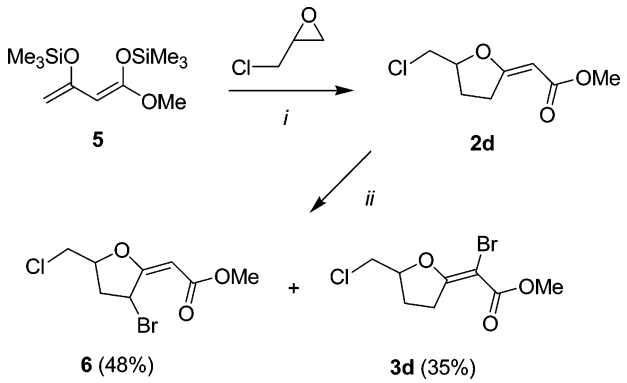
also by other methods.[8c−e] 2-Alkylidenetetrahydrofurans have been functionalized by lithiation and subsequent alkylations;[8a,b] in addition, the bromination of the exocyclic double bond and subsequent cross-coupling reactions have been reported.[8f] Recently, we have reported the synthesis of 6-bromo-3-oxoalkanoates by reaction of 2-alkylidenetetrahydrofurans with boron tribromide (BBr_3).[9] Herein, we wish to report the synthesis of benzofurans by BBr_3-mediated domino "ring-cleavage-deprotection-cyclization" reactions of 2-alkylidenetetrahydrofurans. In addition, the synthesis of calycine analogues,[10] based on Suzuki-cross-coupling and BBr_3 reactions, is reported. From a preparative viewpoint, our methodology allows a convenient access to functionalized benzofurans, containing a remote bromide functionality, which are not readily available by other methods. The chemistry reported herein complements our recently reported synthetic approach to benzofurans based on a "[3+2] cyclization/oxidation"[11] strategy. The reactions reported herein are of interest also from a methodology viewpoint: whereas the BBr_3-mediated cleavage of methylaryl ethers is well known and broadly used,[12] reactions of other ethers are more rare. Known examples include the formation of ω-bromoalkanols by ring-opening of cyclic ethers with BBr_3/MeOH,[13a] or the transformation of lactones into ω-halocarboxylic acids.[13b]

SCHEME 1. Bromination of 2-Alkylidenetetrahydrofurans 2a−c[a]



[a] (i) (1) 2.3 equiv of LDA, THF, 0 °C, 1 h, (2) $Br(CH_2)_2Cl$, −78 → 20 °C, 14 h, then reflux, 12 h; (ii) NBS (1.1−1.3 equiv), CCl_4, reflux, 3 h.

SCHEME 2. Bromination of 2-Alkylidenetetrahydrofuran 2d[a]



[a] (i) 2 equiv of $TiCl_4$, CH_2Cl_2, −78 → 20 °C; (ii) NBS (1.1 equiv), CCl_4, reflux, 3 h.

Results and Discussion

Our first aim was the synthesis of the required starting materials (Schemes 1 and 2). The reaction of 2-alkylidenetetrahydrofurans **2a−c**, prepared by cyclization of 1-bromo-2-chloroethane with the dianions of 1,3-dicarbonyl compounds **1a−c**,[8a,14] with NBS (1.1−1.3 equiv)

(3) (a) Wendt, B.; Ha, H. R.; Hesse, M. *Helv. Chim. Acta* **2002**, *85*, 2990. (b) Carlsson, B.; Singh, B. N.; Temciuc, M.; Nilsson, S.; Li, Y. L.; Mellin, C.; Malm, J. *J. Med. Chem.* **2002**, *45*, 623 and references therein. (c) Kwiecien, H.; Baumann, E. *J. Heterocycl. Chem.* **1997**, *34*, 1587. (d) Larock, R. C.; Harrison, L. W. *J. Am. Chem. Soc.* **1984**, *106*, 4218. (e) Mátyus, P.; Varga, I.; Rettegi, T.; Simay, A.; Kallay, N.; Károlyházy, L.; Kocsis, A.; Varro, A.; Penzes, I.; Papp, J. G. *Curr. Med. Chem.* **2004**, *1*, 61.

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(9) For an isolated example of the domino "ring-cleavage-deprotection-cyclization" reaction, see: (a) Bellur, E.; Langer, P. *Synlett* **2004**, 2172. For open-chained products: (b) Bellur, E.; Langer, P. *J. Org. Chem.* **2005**, *70*, 3819.

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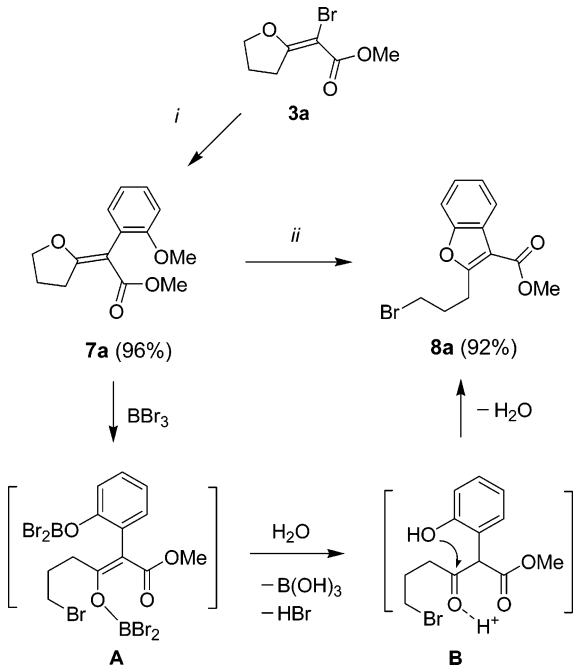
SCHEME 3. Synthesis of Benzofuran 8a[a]



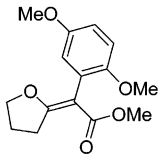
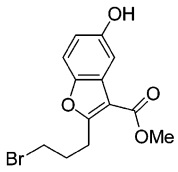
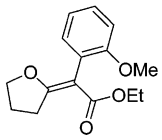
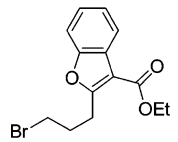
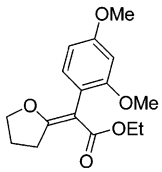
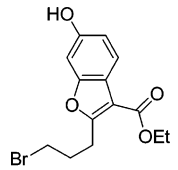
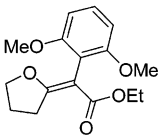
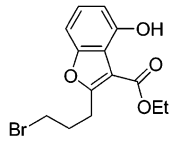
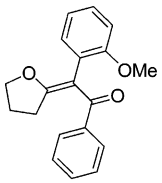
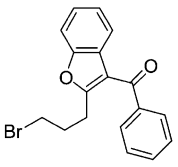
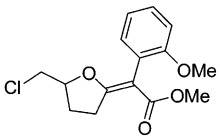
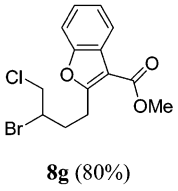
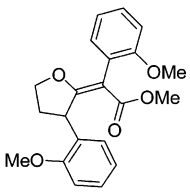
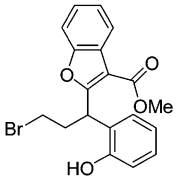
[a] (i) [2-(MeO)C_6H_4]B(OH)$_2$ (3.0 equiv), Pd(PPh$_3$)$_4$ (3 mol-%), K_3PO_4 (6.0 equiv), 1,4-dioxane, reflux, 6 h; (ii) (1) 4 equiv of BBr_3, CH_2Cl_2, 0 → 20 °C, 12 h, 20 °C, 6 h; (2) H_2O.

afforded the 1′-bromo-2-alkylidenetetrahydrofurans **3a**−**c** and the 1′,3-dibromo-2-alkylidenetetrahydrofurans **4a**−**c** (Scheme 1).

The NBS-mediated (1.1 equiv) bromination of 5-chloromethyl-2-alkylidenetetrahydrofuran **2d**, prepared by $TiCl_4$-mediated cyclization of 1,3-bis-silyl enol ether **5** with epichlorohydrin,[15] afforded the 1′-bromo-2-alkylidenetetrahydrofuran **3d** and the 1′,3-dibromo-2-alkylidenetetrahydrofuran **6** (Scheme 2). The desired product **3d** could be isolated in pure form when 1.1 equiv of NBS was employed; however, the formation of **6** could not be entirely avoided. The use of 1.3 equiv of NBS resulted in a decrease of the yield of **3d** and gave an inseparable mixture of **3d** and **6**.

The synthesis of functionalized benzofurans by sequential Suzuki and BBr_3 reactions was studied next (Scheme 3, Table 1). The Pd(PPh$_3$)$_4$ (3 mol-%) catalyzed Suzuki reaction of **3a** with (2-methoxyphenyl)boronic acid gave the desired 2-alkylidenetetrahydrofuran **7a** with excellent *E*-diastereoselectivity. Treatment of **7a** with BBr_3 afforded the benzofuran **8a**.[9a] We propose a mechanism that involves the formation of **8a** (Scheme 3). The latter is formed by BBr_3-mediated ring-opening of **7a** and cleavage of the arylmethyl ether to give intermediate **A**. Addition of water results in hydrolysis of the boronic ester moieties, to give boronic and hydrobromic acid (intermediate **B**), and subsequent acid-mediated cyclization and aromatization by extrusion of water. During the optimization, the use of an excess of BBr_3 (4 equiv) proved to be important.

TABLE 1. Synthesis of Benzofuran Derivatives

entry	substrate	% (**7**) [a, b]	% (**8**) [a]
1	**3a**	 **7b** (87%)	 **8b** (97%)
2	**3b**	 **7c** (93%)	 **8c** (84%)
3	**3b**	 **7d** (96%)	 **8d** (97%)
4	**3b**	 **7e** (87%)	 **8e** (92%)
5	**3c**	 **7f** (77%)	 **8f** (71%)
6	**3d**	 **7g** (96%)	 **8g** (80%)
7	**4a**	 **7h** (92%)	 **8h** (58%)

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

The preparative scope of our methodology was studied (Table 1). The Suzuki reaction of **3a** with 2,5-dimethoxyphenylboronic acid gave 2-alkylidenetetrahydrofuran **7b**.

(14) Langer, P.; Holtz, E.; Karimé, I.; Saleh, N. N. R. *J. Org. Chem.* **2001**, *66*, 6057.

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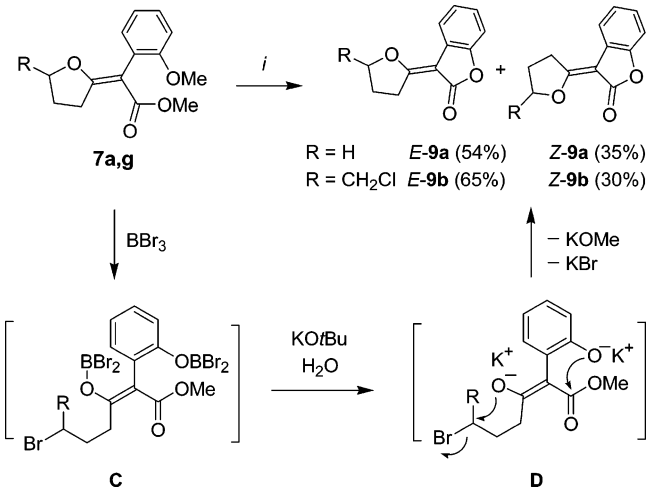
SCHEME 4. Lactonization of 7a,g[a]



[a] (i) (1) 4 equiv of BBr_3, CH_2Cl_2, 0 → 20 °C, 12 h, 20 °C, 6 h; (2) KO*t*Bu, H_2O (1 M), 1 h, 20 °C.

Treatment of the latter with BBr_3 afforded the benzofuran **8b**. The reaction of **3b** with 2-methoxyphenyl-, 2,4-dimethoxyphenyl-, and 2,6-dimethoxyphenylboronic acid afforded the functionalized 2-alkylidenetetrahydrofurans **7c**−**e**, which were transformed into **8c**−**e**. Likewise, the reaction of **3c** with 2-methoxyphenylboronic acid afforded **7f**, which was transformed into the 3-benzoylbenzofuran **8f** by treatment with BBr_3. 2-Alkylidenetetrahydrofuran **7g** was prepared by reaction of **3d** with 2-methoxyphenylboronic acid; treatment of **7g** with BBr_3 gave the benzofuran **8g**. The Suzuki reaction of dibromide **4a** with 2-methoxyphenylboronic acid afforded 2-alkylidene-1′,3-diaryltetrahydrofuran **7h**, which was formed by a double-Suzuki reaction of the 1,3-dibromoprop-1-ene moiety; the reaction of **7h** with BBr_3 afforded the benzofuran **8h**. All reactions proceeded in good to very good yields and with very good chemoselectivity. In addition, all Suzuki reactions proceeded with excellent *E*-diastereoselectivity.

The application of our methodology to the synthesis of 3-(dihydrofuran-2(3*H*)-ylidene)-3*H*-benzofuran-2-one **9a** and of 3-[(5-chloromethyl)dihydrofuran-2(3*H*)-ylidene]-3*H*-benzofuran-2-one **9b**, saturated analogues of calycine,[10] was studied next (Scheme 4).[8c] Treatment of **7a** and **7g** with BBr_3 (CH_2Cl_2) and subsequent addition of an aqueous solution of KO*t*Bu (1 M) afforded **9a** and **9b** as separable mixtures of *E*/*Z*-isomers, respectively. We propose a mechanism that involves the formation of **9a** and **9b** by BBr_3-mediated ring-cleavage of **7a**,**g** and cleavage of the arylmethyl ether (intermediate **C**). Addition of the aqueous solution of KO*t*Bu (KO*t*Bu + H_2O → KOH + *t*BuOH) results in hydrolysis of the boronic ester moieties (intermediate **D**) and subsequent base-mediated recyclization of the tetrahydrofuran moiety and lactonization. The formation of **9a**,**b** as a mixture of *E*/*Z*-isomers can be explained by keto−enol tautomerism of intermediate **C**.

In summary, we have reported a convenient and chemoselective formation of functionalized benzofurans containing a remote bromide functionality. The products are formed by a new BBr_3-mediated domino "ring-cleavage-deprotection-cyclization" reaction. The starting materials, 1′-(2″-methoxyphenyl)-2-alkylidenetetrahydrofurans, were prepared by bromination and subsequent Suzuki reactions of 2-alkylidenetetrahydrofurans available by [3+2] cyclizations. In addition, we have reported the synthesis of saturated analogues of calycine, prepared by reaction of 1′-(2″-methoxyphenyl)-2-alkylidenetetrahydrofurans with BBr_3 and subsequent addition of an aqueous solution of KO*t*Bu.

Experimental Section

General Procedure for the Reaction of 2-Alkylidenetetrahydrofurans with *N*-Bromosuccinimide (NBS). To a CCl_4-solution (5 mL/mmol) of the 2-alkylidenetetrahydrofuran **2** (1 equiv) was added *N*-bromosuccinimide (1.1 equiv) at 20 °C. The reaction mixture was heated and stirred at reflux for 3 h. The reaction mixture was then 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 bromo-2-alkylidenetetrahydrofurans **3**,**4**,**6**.

Synthesis of 3,4a. 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 Bromo(dihydrofuran-2(3*H*)-ylidene)acetate (*Z*-3a). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.23 (quint, J = 7.2 Hz, 2H, CH_2), 3.19 (t, J = 7.8 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 4.41 (t, J = 7.2 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.8, 32.3, 52.2, 73.0, 82.7, 164.7, 172.2. IR (KBr, cm^{-1}): ν = 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). MS (EI, 70 eV): *m*/*z* (%) = 221 (M^+ [^{81}Br], 72), 219 (M^+ [^{79}Br], 71), 190 (87), 162 (3). Anal. Calcd for $C_7H_9O_3Br$ (221.050): C, 38.04; H, 4.10. Found: C, 38.19; H, 3.64.

Methyl Bromo(3-bromodihydro-furan-2(3*H*)-ylidene)-acetate (*E*-4a). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43−2.49 (m, 1H, CH_2), 2.53−2.61 (m, 1H, CH_2), 3.80 (s, 3H, OCH_3), 4.74−4.76 (m, 1H, OCH_2), 4.78−4.79 (m, 1H, OCH_2), 5.20 (d, J = 5.4 Hz, 1H, CH−Br). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 34.7, 48.4, 52.1, 73.8, 87.1, 162.0, 167.0. IR (KBr, cm^{-1}): ν = 2950 (w), 1706 (s), 1605 (s), 1433 (m), 1271 (s), 1204 (s), 1174 (s), 1057 (w), 1039 (s), 1027 (s), 1004 (w), 765 (w). MS (EI, 70 eV): *m*/*z* (%) = 302 (M^+ [2 × ^{81}Br], 17), 300 (M^+ [^{81}Br^{79}Br], 34), 298 (M^+ [2 × ^{79}Br], 17), 269 (19), 241 (2), 221 (100), 189 (22), 161 (18). Anal. Calcd for $C_7H_8O_3Br_2$ (299.946): C, 28.03; H, 2.69. Found: C, 28.88; H, 2.85.

Synthesis of 3,4b. 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 solid, yellowish solid, and yellowish oil, respectively.

Ethyl Bromo(3-bromodihydrofuran-2(3*H*)-ylidene)acetate (*Z*-4b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, J = 7.2 Hz, 3H, CH_3), 2.55−2.63 (m, 2H, CH_2), 4.29 (dq, J = 2.1, 7.2 Hz, 2H, OCH_2CH_3), 4.56−4.66 (m, 2H, OCH_2), 5.81 (dd, J = 4.5, 1.5 Hz, 1H, CH−Br). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 36.8, 44.1, 61.7, 70.6, 87.1, 162.5, 168.5. IR (KBr, cm^{-1}): ν = 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). MS (EI, 70 eV): *m*/*z* (%) = 315 (M^+ [2 × ^{81}Br], 11), 313 (M^+ [^{81}Br^{79}Br], 33), 311 (M^+ [2 × ^{79}Br], 12), 269 (11), 235 (65), 305 (100), 189 (29), 161 (23). Anal. Calcd for $C_8H_{10}O_3Br_2$ (313.973): C, 30.60; H, 3.21. Found: C, 30.32; H, 3.51.

Ethyl Bromo(dihydrofuran-2(3*H*)-ylidene)acetate (*Z*-3b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (t, J = 7.2 Hz, 3H, CH_3), 2.23 (quint, J = 7.5 Hz, CH_2), 3.18 (t, J = 7.8 Hz, 2H, CH_2), 4.23 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.40 (t, J = 7.2 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.0, 24.6, 32.2, 60.8, 72.7, 83.0, 163.7, 171.7. IR (KBr, cm^{-1}): ν = 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). MS (EI, 70 eV): *m/z* (%) = 236 (M^+ [^{81}Br], 75), 234 (M^+ [^{79}Br], 76), 206 (44), 189 (100), 161 (5), 110 (40), 81 (12). Anal. Calcd for $C_8H_{11}O_3Br$ (235.077): C, 40.88; H, 4.72. Found: C, 41.04; H, 4.61.

***E*-4b.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (t, J = 7.2 Hz, 3H, CH_3), 2.43−2.48 (m, 1H, CH_2), 2.52−2.61 (m, 1H, CH_2), 4.27 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.76 (dt, J = 8.7, 0.9 Hz, 2H, OCH_2), 5.20 (d, J = 5.4 Hz, 1H, CH−Br). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.1, 35.2, 48.7, 61.5, 74.0, 87.9, 162.0, 176.1. IR (neat, cm^{-1}): ν = 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). MS (EI, 70 eV): *m/z* (%) = 316 (M^+ [2 × ^{81}Br], 17), 314 (M^+ [^{81}Br^{79}Br], 37), 312 (M^+ [2 × ^{79}Br], 18), 269 (29), 241 (3), 233 (6), 205 (100), 189 (35), 161 (23). The exact molecular mass *m/z* = 311.8997 ± 2 ppm [M^+] for $C_8H_{10}O_3Br_2$ was confirmed by HRMS (EI, 70 eV).

Synthesis of 3,4c. Starting with **2c** (0.400 g, 2.13 mmol) and NBS (0.416 g, 2.34 mmol) in CCl_4 (30 mL), ***Z*-4c** (0.087 g, 12%) and ***Z*-3c** (0.302 g, 53%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as yellowish oils.

2-Bromo-2-(3-bromodihydrofuran-2(3*H*)-ylidene)-1-phenylethanone (*Z*-4c). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.51−2.72 (m, 2H, CH_2), 4.60−4.71 (m, 2H, OCH_2), 5.60 (d, J = 5.4 Hz, 1H, CH−Br), 7.41−7.55 (m, 3H, 3 × CH of Ph), 7.75 (d, J = 3.9 Hz, 2H, 2 × CH of Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 36.8, 43.6, 70.5, 92.8, 127.7, 128.7, 132.0, 137.7, 166.9, 191.0. IR (neat, cm^{-1}): ν = 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). MS (EI, 70 eV): *m/z* (%) = 348 (M^+, [2 × ^{81}Br], 7), 346 (M^+ [^{81}Br^{79}Br], 15), 344 (M^+ [2 × ^{79}Br], 7), 267 (36), 186 (100). Anal. Calcd for $C_{12}H_{10}O_2Br_2$ (346.018): C, 41.65; H, 2.91. Found: C, 41.35; H, 3.60.

2-Bromo-2-(dihydrofuran-2(3*H*)-ylidene)-1-phenylethanone (*Z*-3c). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (quint, J = 7.5 Hz, 2H, CH_2), 2.94 (t, J = 7.8 Hz, 2H, CH_2), 4.45 (t, J = 7.2 Hz, 2H, OCH_2), 7.38−7.53 (m, 3H, 3 × CH of Ph), 7.61−7.71 (m, 2H, 2 × CH of Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.2, 32.7, 72.9, 91.3, 127.9 (2C), 128.5 (2C), 131.4, 139.2, 171.5, 191.8. IR (neat, cm^{-1}): ν = 2959 (w), 2927 (w), 1684 (s), 1646 (s), 1596 (s), 1448 (m), 1420 (w), 1312 (m), 1285 (m), 1253 (w), 1210 (s), 1183 (m), 1118 (w), 1075 (w), 1033 (m), 995 (w), 965 (w), 930 (w), 693 (w), 649 (w). MS (EI, 70 eV): *m/z* (%) = 267 (M^+, [^{81}Br], 22), 265 (M^+ [^{79}Br], 21), 186 (35), 162 (3), 146 (11), 129 (2), 105 (100), 77 (64), 70 (18).

Synthesis of 3d,6. Starting with **2d** (1.000 g, 5.25 mmol) and NBS (1.027 g, 5.77 mmol) in CCl_4 (50 mL), **6** (0.680 g, 48%) and **3d** (0.492 g, 35%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 2:1) as a yellowish oil and a white solid, respectively.

Methyl (3-Bromo-5-chloromethyldihydrofuran-2(3*H*)-ylidene)acetate (6). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.38−2.71 (m, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.79 (dd, J = 9.4, 4.9 Hz, 2H, CH_2−Cl), 5.03 (sext, J = 4.9 Hz, 1H, OCH), 5.33 (s, 1H, CH=C), 5.81 (d, J = 5.6 Hz, 1 H, CH−Br). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 38.3, 43.8, 50.5, 52.2, 79.9, 90.7, 166.0, 171.8. IR (neat, cm^{-1}): ν = 2953 (w), 1708 (s), 1653 (s), 1625 (m), 1436 (m), 1407 (w), 1358 (m), 1335 (w), 1284 (m), 1243 (w), 1215 (m), 1194 (m), 1164 (w), 1125 (s), 1071 (m), 1048 (m), 999 (w), 944 (w), 889 (w), 837 (w), 757 (w), 716 (w). MS (EI, 70 eV): *m/z* (%) = 272 (M^+ [^{81}Br^{37}Cl], 21), 270 (M^+ [^{81}Br^{35}Cl], 99), 268 (M^+ [^{79}Br^{35}Cl], 72), 239 (99), 189 (100), 157 (56), 139 (27), 125 (11), 110 (20), 101 (35), 81 (25).

Methyl Bromo(5-chloromethyldihydrofuran-2(3*H*)-ylidene)acetate (3d). mp = 40 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.11−2.22 (m, 1H, CH_2), 2.35−2.46 (m, 1H, CH_2), 3.09−3.21 (m, 1H, CH_2), 3.30−3.41 (m, 1H, CH_2), 3.63−3.73 (m, 2H, CH_2−Cl), 3.78 (s, 3H, OCH_3), 4.80−4.87 (m, 1H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.3, 31.9, 45.1, 52.1, 82.8, 82.9, 164.2, 171.1. IR (KBr, cm^{-1}): ν = 2953 (w), 1701 (s), 1614 (s), 1434 (m), 1346 (w), 1280 (s), 1221 (m), 1192 (m), 1122 (w), 1075 (s), 1037 (m), 883 (w), 760 (w), 748 (w), 738 (w). MS (EI, 70 eV): *m/z* (%) = 272 (M^+ [^{81}Br^{37}Cl], 8), 270 (M^+ [^{81}Br^{35}Cl], 48), 268 (M^+ [^{79}Br^{35}Cl], 39), 238 (100), 235 (72), 219 (5), 201 (14), 191 (5), 159 (23), 117 (11), 69 (36). Anal. Calcd for $C_8H_{10}BrClO_3$ (269.522): C, 35.65; H, 3.74. Found: C, 35.38; H, 4.00.

General Procedure for the Suzuki Reaction of 2-Alkylidenetetrahydrofurans with Arylboronic Acids. To a 1,4-dioxane solution (3 mL/mmol) of the bromo-2-alkylidenetetrahydrofuran (**3**,**4**) (1 equiv) were added potassium phosphate (K_3PO_4, 6 equiv), the boronic acid ($ArB(OH)_2$, 3 equiv), and $Pd(PPh_3)_4$ (0.03 equiv) at 20 °C. The reaction mixture was heated and stirred at reflux for 6 h. The reaction mixture was then allowed to cool to ambient temperature, and diethyl ether (10 mL/mmol) was added. The precipitate was filtered off, washed with diethyl ether, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give the aryl-substituted 2-alkylidenetetrahydrofurans **7**.

Methyl (Dihydrofuran-2(3*H*)-ylidene)-(2-methoxyphenyl)acetate (7a). Starting with **3a** (0.100 g, 0.45 mmol), 2-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, 0.014 mmol) in 1,4-dioxane (5 mL), **7a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish solid (0.107 g, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.12 (quint, J = 7.2 Hz, 2H, CH_2), 3.28 (t, J = 7.8 Hz, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 4.19 (t, J = 7.2 Hz, 2H, OCH_2), 6.90−6.98 (m, 2H, 2 × CH), 7.19 (d, J = 9.3 Hz, 1H, CH), 7.24−7.30 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.0, 31.1, 51.0, 55.5, 71.9, 100.4, 110.9, 120.1, 124.6, 128.3, 131.8, 157.1, 168.9, 171.5. IR (KBr, cm^{-1}): ν = 2943 (w), 1704 (s), 1623 (s), 1599 (w), 1492 (m), 1464 (w), 1435 (m), 1376 (w), 1315 (m), 1271 (m), 1244 (m), 1184 (s), 1114 (w), 1075 (s), 1068 (s), 1024 (m), 979 (m). MS (EI, 70 eV): *m/z* (%) = 248 (M^+, 100), 216 (25), 189 (57), 174 (7), 158 (3). Anal. Calcd for $C_{14}H_{16}O_4$ (248.278): C, 67.73; H, 6.50. Found: C, 67.51; H, 6.83.

Methyl (Dihydrofuran-2(3*H*)-ylidene)-(2,5-dimethoxyphenyl)acetate (7b). Starting with **3a** (0.100 g, 0.45 mmol), 2,5-dimethoxybenzeneboronic acid (0.253 g, 1.36 mmol), K_3PO_4 (0.576 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 = 50:1 → 1:1) as a yellowish solid (0.109 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (quint, J = 7.5 Hz, 2H, CH_2), 3.27 (t, J = 7.8 Hz, 2H, CH_2), 3.64 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 4.20 (t, J = 7.2 Hz, 2H, OCH_2), 6.77−6.86 (m, 3H, 3 × CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 24.2, 31.4, 51.3, 55.7, 56.5, 72.3, 100.5, 112.2, 112.8, 118.1, 125.9, 151.8, 153.3, 169.0, 171.9. IR (KBr, cm^{-1}): ν = 3009 (w), 2986 (w), 2953 (m), 2900 (w), 2837 (w), 1700 (s), 1621 (s), 1609 (s), 1497 (s), 1464 (m), 1428 (m), 1377 (w), 1306 (s), 1279 (s), 1236 (s), 1217 (s), 1185 (s), 1160 (m), 1137 (s), 1072 (s), 1053 (s), 1026 (m), 983 (w), 983 (w), 964 (m), 936 (w), 899 (w), 805 (m), 779 (w), 724 (w). MS (EI, 70 eV): *m/ z* (%) = 278 (M^+, 100), 247 (8), 231 (3), 219 (15), 217 (1), 204 (1), 155 (28), 91 (7), 77 (5), 70 (13). Anal. Calcd for $C_{15}H_{18}O_5$ (278.304): C, 64.74; H, 6.52. Found: C, 64.75; H, 6.75.

Ethyl (Dihydrofuran-2(3*H*)-ylidene)-(2-methoxyphenyl)acetate (7c). Starting with **3b** (0.200 g, 0.85 mmol), 2-methoxybenzeneboronic acid (0.400 g, 2.55 mmol), K_3PO_4 (1.085 g, 5.11 mmol), and $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) in 1,4-dioxane (8 mL), **7c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a slightly yellowish solid (0.207 g, 93%), mp = 59 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (t, J = 7.2 Hz, 3H, CH_3), 2.12 (quint, J =

7.5 Hz, 2H, CH_2), 3.27 (t, J = 7.8 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 4.13 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.18 (t, J = 7.2 Hz, 2H, OCH_2), 6.88−6.97 (m, 2H, 2 × CH), 7.18−7.29 (m, 2H, 2 × CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.6, 24.3, 31.4, 55.6, 59.6, 72.1, 101.1, 110.9, 120.3, 125.0, 128.4, 132.1, 157.4, 168.7, 171.4. IR (KBr, cm^{-1}): ν = 29.82 (m), 2958 (m), 2940 (m), 2900 (m), 2836 (w), 1697 (s), 1627 (s), 1603 (m), 1492 (s), 1462 (m), 1437 (m), 1371 (m), 1304 (s), 1267 (s), 1241 (s), 1185 (s), 1115 (m), 1069 (s), 1028 (m), 1008 (m), 955 (w), 933 (m), 876 (w), 849 (w), 782 (w), 755 (m), 647 (w). MS (EI, 70 eV): *m/z* (%) = 262 (M^+, 100), 217 (13), 216 (15), 189 (53), 91 (31). Anal. Calcd for $C_{15}H_{18}O_4$ (262.305): C, 68.69; H, 6.92. Found: C, 68.78; H, 6.81.

Ethyl (Dihydrofuran-2(3*H*)-ylidene)-(2,4-dimethoxyphenyl)acetate (7d). Starting with **3b** (0.150 g, 0.64 mmol), 2,4-dimethoxybenzeneboronic acid (0.355 g, 1.91 mmol), K_3PO_4 (0.813 g, 3.83 mmol), and $Pd(PPh_3)_4$ (0.022 g, 0.019 mmol) in 1,4-dioxane (10 mL), **7d** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a white solid (0.180 g, 96%), mp = 91 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (t, J = 7.2 Hz, 3H, CH_3), 2.11 (quint, J = 7.5 Hz, 2H, CH_2), 3.25 (t, J = 7.8 Hz, 2H, CH_2), 3.75 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.12 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.18 (t, J = 7.2 Hz, 2H, OCH_2), 6.48−6.51 (m, 2H, 2 × CH), 7.08−7.11 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.4, 24.1, 31.1, 55.1, 55.3, 59.4, 71.8, 98.5, 100.5, 103.9, 117.4, 132.1, 158.1, 159.9, 168.6, 171.09. IR (KBr, cm^{-1}): ν = 3000 (w), 2977 (w), 1690 (s), 1616, (s), 1584 (w), 1511 (m), 1464 (w), 1309 (m), 1289 (m), 1265 (m), 1209 (m), 1187 (m), 1167 (m), 1108 (w), 1069 (s), 1032 (m), 1008 (w), 947 (w), 819 (w). MS (EI, 70 eV): *m/z* (%) = 292 (M^+, 100), 246 (20), 231 (1), 219 (16), 190 (8). Anal. Calcd for $C_{16}H_{20}O_5$ (292.331): C, 65.74; H, 6.90. Found: C, 65.91; H, 6.87.

Ethyl (Dihydrofuran-2(3*H*)-ylidene)-(2,6-dimethoxyphenyl)acetate (7e). Starting with **3b** (0.170 g, 0.72 mmol), 2,6-dimethoxybenzeneboronic acid (0.403 g, 2.17 mmol), K_3PO_4 (0.921 g, 4.34 mmol), and $Pd(PPh_3)_4$ (0.025 g, 0.022 mmol) in 1,4-dioxane (10 mL), **7e** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish solid (0.182 g, 87%), mp = 82 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.15 (t, J = 7.2 Hz, 3H, CH_3), 2.11 (quint, J = 7.2 Hz, 2H, CH_2), 3.29 (t, J = 7.5 Hz, 2H, CH_2), 3.76 (s, 6H, 2 × OCH_3), 4.11 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.16 (t, J = 7.2 Hz, 2H, OCH_2), 6.59 (d, J = 8.4 Hz, 2H, 2 × CH), 7.22 (t, J = 8.4 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.7, 24.3, 31.3, 56.2, 59.5, 72.0, 96.3, 104.4, 113.8, 128.7, 158.4, 168.8, 171.8. IR (KBr, cm^{-1}): ν = 2976 (m), 2926 (m), 2855 (w), 1696 (s), 1630 (s), 1589 (m), 1468 (s), 1436 (m), 1378 (w), 1286 (m), 1248 (s), 1182 (s), 1112 (s), 1067 (s), 1030 (m), 931 (w), 746 (w). MS (EI, 70 eV): *m/z* (%) = 292 (M^+, 95), 263 (6), 219 (100), 204 (4), 190 (15), 188 (4), 173 (8), 157 (3), 137 (5). Anal. Calcd for $C_{16}H_{20}O_5$ (292.331): C, 65.74; H, 6.90. Found: C, 65.61; H, 6.24.

2-(Dihydrofuran-2(3*H*)-ylidene)-2-(2-methoxyphenyl)-1-phenyl-ethanone (7f). Starting with **3c** (0.100 g, 0.374 mmol), 2-methoxyphenylboronic acid (0.176 g, 1.12 mmol), K_3PO_4 (0.478 g, 2.25 mmol), and $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol) in 1,4-dioxane (10 mL), **7f** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 2:1) as a yellowish solid (0.085 g, 77%), mp = 123 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.16 (quint, J = 7.5 Hz, 2H, CH_2), 3.22 (t, J = 7.8 Hz, 2H, CH_2), 3.44 (s, 3H, OCH_3), 4.27 (t, J = 7.2 Hz, 2H, OCH_2), 6.63 (dd, J = 5.1, 1.2 Hz, 1H, CH), 6.94 (dt, J = 7.5, 1.2 Hz, 1H, CH), 7.11−7.18 (m, 3H, 3 × CH of Ar), 7.22−7.28 (m, 1H, CH), 7.45 (dt, J = 7.5, 1.5 Hz, 3H, 3 × CH of Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 24.2, 31.4, 54.8, 71.8, 108.5, 110.7, 120.2, 126.3, 127.0 (2C), 128.1 (2C), 128.2, 130.1, 131.8, 140.6, 156.3, 171.3, 196.1. IR (KBr, cm^{-1}): ν = 2992 (w), 2987 (w), 2936 (w), 1654 (s), 1595 (s), 1581 (s), 1487 (m), 1458 (m), 1443 (w), 1322 (m), 1300 (w), 1260 (s), 1249 (s), 1186 (s), 1114 (m), 1051 (w), 1022 (m), 967 (s), 932 (m), 889 (m), 760 (m), 712 (w), 712 (w), 663 (w). MS (EI, 70 eV): *m/z* (%) = 294 (M^+, 88), 263 (29), 217 (39, 189 (28), 171 (4), 157 (1), 105 (100), 91 (17), 77 (62).

Methyl (5-Chloromethyl-dihydrofuran-2(3*H*)-ylidene)-(2-methoxyphenyl)acetate (7g). Starting with **3d** (0.150 g, 0.56 mmol), 2-methoxyphenylboronic acid (0.262 g, 1.67 mmol), K_3PO_4 (0.709 g, 3.34 mmol), and $[Pd(PPh_3)_4]$ (0.019 g, 0.017 mmol) in 1,4-dioxane (5 mL), **7g** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (0.159 g, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.02−2.14 (m, 1H, CH_2), 2.19−2.31 (m, 1H, CH_2), 3.26−3.36 (m, 2H, CH_2), 3.54 (d, J = 5.1 Hz, 2H, CH_2−Cl), 3.60 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 4.58 (quint, J = 7.2 Hz, 1H, OCH), 6.87−6.96 (m, 2H, 2 × CH of Ar), 7.18−7.27 (m, 2H, 2 × CH of Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.6, 30.7, 45.4, 51.0, 53.3, 81.6, 100.9, 110.6, 120.0, 124.2, 128.3, 131.8, 157.0, 168.7, 170.3. IR (neat, cm^{-1}): ν = 2950 (w), 1704 (s), 1632 (s), 1492 (m), 1460 (m), 1435 (s), 1346 (w), 1308 (m), 1265 (m), 1244 (s), 1185 (s), 1116 (m), 1072 (s), 1026 (m), 926 (w), 755 (m). MS (EI, 70 eV): *m/z* (%) = 298 (M^+ [^{37}Cl], 33), 296 (M^+ [^{35}Cl], 100), 264 (50), 237 (58), 200 (7).

Methyl (2-Methoxyphenyl)-[3-(2-methoxyphenyl)-dihydrofuran-2(3*H*)-ylidene]acetate (7h). Starting with ***Z*-4a** (0.300 g, 1.0 mmol), 2-methoxybenzeneboronic acid (0.940 g, 6.0 mmol), K_3PO_4 (1.274 g, 6.0 mmol), and $[Pd(PPh_3)_4]$ (0.058 g, 0.05 mmol) in 1,4-dioxane (5 mL), **7h** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 2:1) as a white solid (0.325 g, 92%), mp = 112 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.58−2.05 (m, 1H, CH_2), 2.41−2.56 (m, 1H, CH), 3.43 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 4.04−4.18 (m, 1H, OCH_2), 4.24 (dt, J = 8.4, 1.8 Hz, 1H, OCH_2), 5.34 (dd, J = 8.7, 1.5 Hz, 1H, CH), 6.86−7.05 (m, 4H, 4 × CH), 7.19−7.32 (m, 2H, 2 × CH), 7.37−7.45 (m, 1H, CH), 7.81−7.85 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.7, 42.7, 50.9, 55.4, 55.6, 70.0, 101.9, 110.4, 111.0, 120.1, 120.2, 125.0, 127.0, 127.6, 128.4, 130.0, 131.8, 156.5, 157.3, 167.7, 172.7. IR (KBr, cm^{-1}): ν = 2946 (w), 1705 (m), 1631 (m), 1600 (s), 1577 (m), 1489 (s), 1461 (s), 1436 (s), 1402 (m), 1368 (s), 1344 (s), 1296 (m), 1270 (m), 1234 (s), 1197 (w), 1166 (m), 1109 (m), 1076 (s), 1054 (s), 1024 (s), 982 (w), 779 (m), 758 (s), 704 (w), 656 (m), 528 (w). MS (EI, 70 eV): *m/z* (%) = 354 (M^+, 100), 322 (39), 295 (25), 247 (32). The exact molecular mass *m/z* = 354.1467 ± 2 ppm [M^+] for $C_{21}H_{22}O_5$ was confirmed by HRMS (EI, 70 eV).

General Procedure for the Synthesis of Benzofurans by Reaction of 2-Alkylidenetetrahydrofurans with Borontribromide. To a CH_2Cl_2-solution (10 mL/mmol) of the 2-alkylidenetetrahydrofuran **7** (1 equiv) was added BBr_3 (4 equiv) at 0 °C. The reaction mixture was allowed to warm to 20 °C over 12 h and was stirred for 6 h at 20 °C. Water (15 mL/mmol substrate) was slowly added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL/mmol substrate). The combined organic extracts were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give **8**.

Methyl 2-(3′-Bromopropyl)benzofuran-3-carboxylate (8a). Starting with **7a** (0.150 g, 0.60 mmol) and BBr_3 (0.605 g, 2.42 mmol) in CH_2Cl_2 (6 mL), **8a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.163 g, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (quint, J = 7.2 Hz, 2H, CH_2), 3.35 (t, J = 7.5 Hz, 2H, CH_2), 3.47 (t, J = 6.9 Hz, 2H, CH_2−Br), 3.95 (s, 3H, OCH_3), 7.28−7.33 (m, 2H, 2 × CH), 7.42−7.45 (m, 1H, CH), 7.95−7.98 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.8, 30.8, 32.4, 51.4, 109.2, 110.9, 121.9, 123.9, 124.6, 125.8, 153.6, 164.5, 165.2. IR (neat, cm^{-1}): ν = 2952 (m), 1714 (s), 1593 (s), 1478 (m), 1451 (s), 1437 (s), 1386 (m), 1342 (w), 1284 (m), 1235 (s), 1174 (s), 1127 (w), 1106 (m), 1073 (s), 1010 (w), 959 (w), 935 (w), 861 (w), 790 (m), 752 (s). MS (EI, 70 eV): *m/z* (%) = 298 (M^+ [^{81}Br], 38), 296 (M^+ [^{79}Br], 39), 266 (7), 217 (16), 203 (10),

188 (100), 174 (5), 170 (29), 158 (47), 144 (4). Anal. Calcd for $C_{13}H_{13}BrO_3$ (297.148): C, 52.55; H, 4.41. Found: C, 52.84; H, 4.74.

Methyl 2-(3′-Bromopropyl)-5-hydroxybenzofuran-3-carboxylate (8b). Starting with **7b** (0.070 g, 0.25 mmol) and BBr_3 (0.504 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **8b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 5:1) as a white solid (0.076 g, 97%), mp = 154 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (quint, J = 7.05 Hz, 2H, CH_2), 3.33 (t, J = 7.5 Hz, 2H, CH_2), 3.47 (t, J = 6.6 Hz, 2H, CH_2−Br), 3.95 (s, 3H, OCH_3), 5.31 (broad s, 1H, OH), 6.83 (dd, J = 8.7, 2.4 Hz, 1H, CH), 7.30 (d, J = 8.7 Hz, 1H, CH), 7.46 (d, J = 2.4 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 150 MHz): δ 26.4, 30.2, 32.2, 50.8, 106.3, 108.4, 110.6, 112.9, 126.1, 147.4, 153.7, 163.9, 165.0. IR (KBr, cm^{-1}): ν = 3326 (s), 2962 (w), 2947 (w), 1687 (s), 1624 (w), 1605 (w), 1578 (m), 1488 (m), 1468 (s), 1441 (s), 1408 (m), 1382 (m), 1306 (m), 1267 (s), 1239 (m), 1224 (m), 1197 (m), 1169 (s), 1133 (w), 1111 (w), 1077 (m), 1048 (m), 955 (w), 867 (m), 816 (m), 789 (m), 731 (w), 664 (m), 623 (w). MS (EI, 70 eV): *m/z* (%) = 314 (M^+ [^{81}Br], 89), 312 (M^+ [^{79}Br], 92), 281 (7), 233 (6), 219 (6), 205 (100), 175 (18), 147 (8). The exact molecular mass *m/z* = 311.9997 ± 2 ppm [M^+] for $C_{13}H_{13}O_4Br$ was confirmed by HRMS (EI, 70 eV). Anal. Calcd for $C_{13}H_{13}BrO_4$ (313.147): C, 49.86; H, 4.18. Found: C, 50.14; H, 4.88.

Ethyl 2-(3′-Bromopropyl)benzofuran-3-carboxylate (8c). Starting with **7c** (0.080 g, 0.30 mmol) and BBr_3 (0.306 g, 1.2 mmol) in CH_2Cl_2 (3 mL), **8c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a slightly yellowish oil (0.078 g, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.46 (t, J = 7.2 Hz, 3H, CH_3), 2.36 (quint, J = 6.6 Hz, 2H, CH_2), 3.36 (t, J = 7.2 Hz, 2H, CH_2), 3.48 (t, J = 6.6 Hz, 2H, CH_2−Br), 4.42 (q, J = 7.2 Hz, 2H, OCH_2), 7.29−7.32 (m, 2H, 2 × CH), 7.44−7.47 (m, 1H, CH), 7.97−8.00 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.7, 27.2, 31.1, 32.7, 60.7, 109.6, 111.2, 122.2, 124.1, 124.8, 126.3, 153.9, 164.4, 165.3. IR (neat, cm^{-1}): ν = 2979 (w), 2931 (w), 1711 (s), 1593 (m), 1479 (w), 1451 (m), 1404 (w), 1380 (m), 1347 (w), 1283 (w), 1234 (s), 1176 (m), 1128 (w), 1104 (w), 1070 (s), 1012 (w), 789 (w), 751 (m). MS (EI, 70 eV): *m/z* (%) = 312 (M^+ [^{81}Br], 88) 310 (M^+ [^{79}Br], 95), 281 (17), 265 (14), 231 (7), 217 (3), 203 (27), 189 (4), 175 (100), 157 (36), 128 (15). HRMS (FT-ICR): calcd for $C_{14}H_{15}BrO_3$ [M^+]: 313.02623 (^{81}Br); 311.02828 (^{79}Br); found: 313.02576 (^{81}Br), 311.02779 (^{79}Br).

Ethyl 2-(3′-Bromopropyl)-6-hydroxybenzofuran-3-carboxylate (8d). Starting with **7d** (0.080 g, 0.27 mmol) and BBr_3 (0.549 g, 2.2 mmol) in CH_2Cl_2 (3 mL), **8d** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 5:1) as a white solid (0.085 g, 97%), mp = 132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.44 (t, J = 7.2 Hz, 3H, CH_3), 2.33 (quint, J = 7.05 Hz, 2H, CH_2), 3.31 (t, J = 7.5 Hz, 2H, CH_2), 3.47 (t, J = 6.6 Hz, 2H, CH_2−Br), 4.41 (q, J = 7.2 Hz, 2H, OCH_2), 4.97 (broad s, 1H, OH), 6.84 (dd, J = 8.7, 2.1 Hz, 1H, CH), 6.94 (d, J = 2.1 Hz, 1H, CH), 7.80 (d, J = 8.7 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$+d_6-DMSO, 150 MHz): δ 14.3, 26.7, 30.8, 32.6, 60.1, 97.8, 109.1, 113.1, 118.0, 121.7, 154.6, 155.5, 163.3, 164.2. IR (KBr, cm^{-1}): ν = 3304 (s), 2987 (w), 1676 (s), 1628 (m), 1594 (m), 1510 (w), 1495 (w), 1443 (s), 1406 (w), 1367 (m), 1301 (m), 1284 (m), 1262 (m), 1247 (m), 1196 (m), 1140 (m), 1113 (s), 1076 (s), 950 (w), 838 (w), 817 (w). MS (EI, 70 eV): *m/z* (%) = 328 (M^+ [^{81}Br], 97), 326 (M^+ [^{79}Br], 100), 297 (2%), 281 (9), 219 (75), 191 (88), 173 (19). The exact molecular mass *m/z* = 326.0154 ± 2 ppm [M^+] for $C_{14}H_{15}O_4Br$ was confirmed by HRMS (EI, 70 eV). Anal. Calcd for $C_{14}H_{15}BrO_4$ (327.174): C, 51.40; H, 4.62. Found: C, 51.30; H, 4.97.

Ethyl 2-(3′-Bromopropyl)-4-hydroxybenzofuran-3-carboxylate (8e). Starting with **7e** (0.070 g, 0.24 mmol) and BBr_3 (0.480 g, 1.92 mmol) in CH_2Cl_2 (3 mL), **8e** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a white solid (0.073 g, 92%); mp = 86 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.40 (t, J = 7.2 Hz, 3H, CH_3), 2.27 (quint, J = 7.05 Hz, 2H, CH_2), 3.23 (t, J = 7.5 Hz, 2H, CH_2), 3.41 (t, J = 6.6 Hz, 2H, CH_2−Br), 4.41 (q, J = 7.2 Hz, 2H, OCH_2), 6.70 (dd, J = 8.1, 0.9 Hz, 1H, CH), 6.88 (dd, J = 8.1 Hz, 0.9 Hz, 1H, CH), 7.12 (t, J = 8.1 Hz, 1H, CH), 10.40 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.5, 27.6, 31.0, 32.7, 62.5, 102.4, 109.5, 110.3, 113.7, 126.9, 151.5, 155.3, 163.8, 167.4. IR (KBr, cm^{-1}): ν = 3417 (w), 3146 (w), 3126 (w), 3068 (w), 3043 (w), 2974 (w), 2933 (w), 1667 (s), 1630 (m), 1595 (m), 1481 (m), 1420 (m), 1384 (m), 1353 (w), 1328 (w), 1284 (m), 1240 (m), 1201 (m), 1155 (w), 1084 (m), 1045 (m), 1022 (w), 769 (m), 750 (m), 728 (w). MS (EI, 70 eV): *m/z* (%) = 328 (M^+ [^{81}Br], 61), 326 (M^+ [^{79}Br], 62), 282 (100), 219 (14), 200 (7), 186 (4), 173 (38). The exact molecular mass *m/z* = 326.0154 ± 2 ppm [M^+] for $C_{14}H_{15}O_4Br$ was confirmed by HRMS (EI, 70 eV). Anal. Calcd for $C_{14}H_{15}BrO_4$ (327.174): C, 51.40; H, 4.62. Found: C, 52.15; H, 4.73.

3-Benzoyl-2-(3′-bromopropyl)benzofuran (8f). Starting with **7f** (0.050 g, 0.17 mmol) and BBr_3 (0.171 g, 0.68 mmol) in CH_2Cl_2 (3 mL), **8f** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (0.036 g, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.35 (quint, J = 7.1 Hz, 2H, CH_2), 3.10 (t, J = 7.4 Hz, 2H, CH_2), 3.44 (t, J = 6.8 Hz, 2H, CH_2−Br), 7.16−7.40 (m, 3H, 3 × CH), 7.47−7.64 (m, 4H, 4 × CH), 7.81−7.84 (m, 2H, 2 × CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.0, 31.0, 32.4, 111.1, 117.4, 121.5, 123.7, 124.6, 126.6, 128.6 (2C), 129.2 (2C), 132.9, 139.1, 153.7, 163.5, 191.9. IR (neat, cm^{-1}): ν = 2968 (m), 2925 (s), 2857 (m), 1730 (m), 1652 (s), 1573 (m), 1451 (s), 1377 (m), 1281 (m), 1242 (m), 1178 (m), 1117 (s), 1075 (w), 1017 (w), 937 (w), 899 (w), 753 (m), 700 (w). MS (EI, 70 eV): *m/z* (%) = 344 (M^+ [^{81}Br], 29), 342 (M^+ [^{79}Br], 30), 263 (17), 249 (40), 135 (90), 221 (159), 205 (10), 178 (13), 160 (10), 148 (100), 131 (12), 105 (44), 77 (32). HRMS (ESI): calcd for $C_{18}H_{15}BrO_2$ [M^+]: 344.02349 (^{81}Br), 342.02554 (^{79}Br); found: 344.02303 (^{81}Br), 342.02576 (^{79}Br).

Methyl 2-(3′-Bromo-4′-chlorobutyl)benzofuran-3-carboxylate (8g). Starting with **7g** (0.050 g, 0.17 mmol) and BBr_3 (0.171 g, 0.67 mmol) in CH_2Cl_2 (3 mL), **8g** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as a slightly yellowish oil (0.047 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21−2.34 (m, 1H, CH_2), 2.57−2.69 (m, 1H, CH_2), 3.31−3.42 (m, 1H, CH_2), 3.44−3.54 (m, 1H, CH_2), 3.80 (dd, J = 11.4, 8.4 Hz, 1H, CH_2−Cl), 3.97 (dd, J = 11.4, 4.8 Hz, 1H, CH_2−Cl), 3.97 (s, 3H, OCH_3), 4.14−4.22 (m, 1H, CH−Br), 7.30−7.33 (m, 2H, 2 × CH of Ar), 7.44−7.48 (m, 1H, CH of Ar), 7.96−7.99 (m, 1H, CH of Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.0, 33.5, 48.0, 51.6, 51.9, 109.4, 111.0, 122.0, 124.0, 124.7, 125.9, 153.9, 164.6, 164.8. IR (neat, cm^{-1}): ν = 2952 (w), 2926 (w), 1714 (s), 1594 (m), 1446 (m), 1383 (w), 1285 (w), 1237 (s), 1176 (m), 1106 (w), 1070 (s), 794 (w), 751 (m). MS (EI, 70 eV): *m/z* (%) = 348 (M^+ [^{81}Br^{37}Cl], 6), 346 (M^+ [^{81}Br^{35}Cl], 34), 344 (M^+ [^{79}Br^{35}Cl], 24), 314 (2), 229 (18), 203 (24), 189 (100), 169 (13), 159 (22), 131 (12), 114 (8). HRMS (ESI): calcd for $C_{14}H_{14}BrClO_3$ [M^+]: 345.97944 (^{81}Br), 343.98148 (^{79}Br); found: 345.96002 (^{81}Br), 343.98353 (^{79}Br).

Methyl 2-[3′-Bromo-1′-(2″-hydroxyphenyl)propyl]benzofuran-3-carboxylate (8h). Starting with **7h** (0.030 g, 0.085 mmol) and BBr_3 (0.129 g, 0.51 mmol) in CH_2Cl_2 (9 mL), **8h** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 4:1) as a colorless oil (0.019 g, 58%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.68−2.81 (m, 1H, CH_2), 2.84−2.95 (m, 1H, CH_2), 3.25−3.41 (m, 2H, CH_2−Br), 4.06 (s, 3H, OCH_3), 5.53 (t, J = 7.6 Hz, 1H, CH), 6.91−6.97 (m, 2H, 2 × CH), 7.13−7.19 (m, 1H, CH), 7.29−7.35 (m, 2H, 2 × CH), 7.45−7.50 (m, 2H, 2 × CH), 7.86−7.89 (m, 1H, CH), 7.91 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 30.6, 35.0, 35.3, 52.5, 111.3, 117.9, 120.9, 121.1, 122.1, 124.3, 124.5, 124.8, 125.2, 127.7, 128.8, 153.9, 154.5, 165.5, 167.1. IR (neat, cm^{-1}): ν = 3354 (br), 2974 (m), 2956 (m), 2928 (m), 2858 (w), 1738 (w), 1712 (s), 1688 (s), 1588 (m), 1482 (m), 1454 (s), 1368 (m), 1288 (m), 1239 (s), 1174 (s), 1154 (m), 1108 (s), 1069 (s), 1020 (m), 984 (w), 793 (w), 754 (s). MS (EI, 70 eV): *m/z* (%) = 390 (M^+ [^{81}Br], 18), 388 (M^+ [^{79}Br], 19), 356 (17), 329 (5), 281 (44), 263 (11), 249 (100), 221 (65), 205 (5), 134 (25), 107 (13). The exact molecular mass

m/z = 388.0310 ± 2 ppm [M^+] for $C_{19}H_{17}BrO_4$ was confirmed by HRMS (EI, 70 eV).

General Procedure for the Synthesis of 9 by Reaction of 2-Alkylidenetetrahydrofurans with Borontribromide. To a CH_2Cl_2-solution (10 mL/mmol) of the 2-alkylidenetetrahydrofuran (**7**) (1 equiv) was added BBr_3 (4 equiv) at 0 °C. The reaction mixture was allowed to warm to 20 °C over 12 h and was stirred for 12 h at 20 °C. The reaction mixture was then poured into an aqueous solution of KO*t*Bu (1 M, 10 mL/mmol). The mixture was stirred for 1 h and later extracted with CH_2Cl_2 (3 × 30 mL/mmol). The combined organic extracts were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give **9**.

3-(Dihydro-furan-2(3*H*)-ylidene)-3*H*-benzofuran-2-one (9a). Starting with **7a** (0.070 g, 0.282 mmol) and BBr_3 (0.283 g, 1.13 mmol) in CH_2Cl_2 (3 mL), ***E*-9a** and ***Z*-9a** were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as yellowish solids (0.031 g, 54%; 0.020 g, 35%).

***E*-9a.** mp = 170 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (quint, J = 7.5 Hz, 2H, CH_2), 3.37 (t, J = 7.8 Hz, 2H, CH_2), 4.62 (t, J = 7.2 Hz, 2H, OCH_2), 7.06−7.21 (m, 3H, 3 × CH of Ar), 7.60 (dd, J = 7.2, 1.2 Hz, 1H, CH of Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.5, 31.4, 75.0, 95.9, 110.0, 122.0, 123.5, 124.1, 126.7, 151.0, 169.8, 175.2. IR (KBr, cm^{-1}): ν = 2911 (w), 1750 (s), 1652 (s), 1611 (w), 1589 (w), 1479 (w), 1459 (m), 1420 (w), 1392 (m), 1247 (s), 1220 (m), 1166 (m), 1032 (m), 977 (s), 939 (m), 866 (m), 780 (m), 751 (m). MS (EI, 70 eV): m/z (%) = 202 (M^+, 100), 159 (10). The exact molecular mass m/z = 202.0630 ± 2 ppm [M^+] for $C_{12}H_{10}O_3$ was confirmed by HRMS (EI, 70 eV).

***Z*-9a.** mp = 106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (quint, J = 7.5 Hz, 2H, CH_2), 3.19 (t, J = 7.8 Hz, 2H, CH_2), 4.68 (t, J = 7.2 Hz, 2H, OCH_2), 7.06−7.25 (m, 4H, 4 × CH of Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.1, 32.4, 75.3, 95.9, 110.6, 119.6, 123.4, 124.7, 126.5, 151.3, 165.9, 172.9. IR (KBr, cm^{-1}): ν = 2958 (w), 2928 (w), 2855 (w), 1814 (w), 1760 (s), 1638 (s), 1457 (s), 1422 (w), 1392 (w), 1349 (w), 1308 (w), 1288 (w), 1245 (s), 1221 (m), 1192 (m), 1158 (w), 1133 (s), 1084 (s), 1028 (s), 997 (m), 976 (w), 924 (s), 868 (w), 776 (m), 750 (s). MS (EI, 70 eV): m/z (%) = 202 (M^+, 87), 159 (100). The exact molecular mass m/z = 202.0630 ± 2 ppm [M^+] for $C_{12}H_{10}O_3$ was confirmed by HRMS (EI, 70 eV).

3-(5-Chloromethyl-dihydro-furan-2(3*H*)-ylidene)-3*H*-benzofuran-2-one (9b). Starting with **7g** (0.050 g, 0.17 mmol) and BBr_3 (0.171 g, 0.67 mmol) in CH_2Cl_2 (3 mL), ***E*-9b** and ***Z*-9b** were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as yellowish solids (0.028 g, 65%; 0.013 g, 30%).

***E*-9b.** mp = 61 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.12−2.23 (m, 1H, CH_2), 2.39−2.52 (m, 1H, CH_2), 3.25−3.38 (m, 1H, CH_2), 3.52−3.60 (m, 1H, CH_2), 3.80 (d, J = 5.1 Hz, 1H, CH_2−Cl), 3.84 (d, J = 5.1 Hz, 1H, CH_2−Cl), 5.02−5.08 (m, 1H, OCH), 7.07−7.21 (m, 3H, 3 × CH of Ar), 7.61 (dd, J = 7.5, 1.2 Hz, 1H, CH of Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.1, 31.0, 45.3, 85.2, 96.3, 109.8, 122.0, 123.4, 126.8, 126.8, 150.8, 169.4, 173.3. IR (KBr, cm^{-1}): ν = 2976 (s), 2932 (w), 2866 (m), 1758 (s), 1746 (s), 1655 (s), 1612 (w), 1455 (s), 1378 (m), 1360 (m), 1296 (w), 1242 (s), 1206 (s), 1151 (s), 1118 (s), 1076 (m), 1015 (s), 964 (s), 933 (w), 874 (w), 832 (w), 752 (s). MS (EI, 70 eV): m/z (%) = 252 (M^+ [^{37}Cl], 20), 250 (M^+ [^{35}Cl], 73), 215 (20), 187 (8), 160 (100), 104 (25), 85 (76), 76 (26). HRMS (ESI): calcd for $C_{13}H_{11}ClO_3$ [M^+]: 252.03672 (^{37}Cl), 250.03967 (^{35}Cl); found: 252.03800 (^{37}Cl), 250.03903 (^{35}Cl).

***Z*-9b.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34−2.39 (m, 1H, CH_2), 2.45−2.58 (m, 1H, CH_2), 3.14−3.39 (m, 2H, CH_2), 3.86 (d, J = 0.9 Hz, 1H, CH_2−Cl), 3.87 (d, J = 1.8 Hz, 1H, CH_2−Cl), 5.13−5.19 (m, 1H, OCH), 7.08−7.23 (m, 4H, 4 × CH of Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.5, 31.0, 45.6, 85.1, 95.9, 110.5, 119.6, 123.3, 124.2, 126.6, 151.2, 167.3, 171.6. IR (KBr, cm^{-1}): ν = 2927 (w), 1756 (s), 1644 (s), 1459 (w), 1243 (m), 1140 (m), 1086 (m), 1014 (m), 938 (w), 777 (w), 747 (m). MS (EI, 70 eV): m/z (%) = 252 (M^+ [^{37}Cl], 2), 250 (M^+ [^{35}Cl], 12), 215 (12), 187 (7), 160 (100), 104 (35), 85 (86), 76 (24). HRMS (ESI): calcd for $C_{13}H_{11}ClO_3$ [M^+]: 252.03672 (^{37}Cl), 250.03967 (^{35}Cl); found: 252.03800 (^{37}Cl), 250.03903 (^{35}Cl).

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Supporting Information Available: Experimental procedures, spectroscopic data, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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