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

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

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. Then, the reaction mixture was allowed to cool down 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 $\rightarrow$ 1:1) as yellowish and colorless solids, respectively.

Methyl Bromo(dihydrofuran-2(3*H*)-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, OCH₂). ¹³C NMR (CDCl₃, 75 MHz): δ 24.8, 32.3, 52.2, 73.0, 82.7, 164.7, 172.2. IR (KBr, cm⁻¹): $\tilde{\nu} = 2951$ (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). MS (EI, 70 eV): m/z (%) = 221 (M⁺ [⁸¹Br], 72), 219 (M⁺ [⁷⁹Br], 71), 190 (63), 189 (100), 188 (71), 187 (93), 179 (10), 177 (10), 162 (3), 148 (60), 146 (59). Anal. calcd. for C₇H₉O₃Br (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): ¹H NMR (CDCl₃, 300 MHz): δ 2.43 – 2.49 (m, 1 H, CH₂), 2.53 – 2.61 (m, 1 H, CH₂), 3.80 (s, 3 H, OCH₃), 4.74 – 4.76 (m, 1 H, OCH₂), 4.78 – 4.79 (m, 1 H, OCH₂), 5.20 (d, $J = 5.4$ Hz, 1H, CH–Br). ¹³C NMR (CDCl₃, 75 MHz): δ 34.7, 48.4, 52.1, 73.8, 87.1, 162.0, 167.0. IR (KBr, cm⁻¹): $\tilde{\nu} = 2950$ (w), 1706 (s), 1605 (s), 1433 (m), 1271 (s), 1204 (s), 1174 (s), 1057 (w), 1039 (s), 1027 (s), 1004 (w), 765 (w). MS (EI, 70 eV): m/z (%) = 302 (M⁺ [2×⁸¹Br], 17), 300 (M⁺ [⁸¹Br ⁷⁹Br], 34), 298 (M⁺ [2×⁷⁹Br], 17), 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). Anal. calcd. for C₇H₈O₃Br₂ (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 CCl₄ (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 a slightly yellowish solid, yellowish solid and as a yellowish oil, respectively.

Ethyl Bromo(3-bromodihydro-furan-2(3*H*)-ylidene)acetate (*Z*-4b): ¹H NMR (CDCl₃, 300 MHz): δ 1.36 (t, $J = 7.2$ Hz, 3 H, CH₃), 2.55 – 2.63 (m, 2 H, CH₂), 4.29 (dq, $J = 2.1, 7.2$ Hz, 2 H, OCH₂CH₃), 4.56 – 4.66 (m, 2 H, OCH₂), 5.81 (dd, $J = 4.5, 1.5$ Hz, 1 H, CH–Br). ¹³C NMR (CDCl₃, 75 MHz): δ 13.9, 36.8, 44.1, 61.7, 70.6, 87.1, 162.5, 168.5. IR (KBr, cm⁻¹): $\tilde{\nu} = 2933$ (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). MS (EI, 70 eV): m/z (%) = 315 (M^+ [$2\times^{81}\text{Br}$], 11), 313 (M^+ [$^{81}\text{Br}^{79}\text{Br}$], 33), 311 (M^+ [$2\times^{79}\text{Br}$], 12), 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).

Anal. calcd. for $\text{C}_8\text{H}_{10}\text{O}_3\text{Br}_2$ (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**):** ^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). ^{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}): $\tilde{\nu} = 2995$ (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). MS (EI, 70 eV): m/z (%) = 236 (M^+ [^{81}Br], 75), 234 (M^+ [^{79}Br], 76), 207 (44), 205 (43), 190 (100), 188 (93), 164 (11), 162 (11), 148 (45), 146 (45), 110 (40), 81 (12), 79 (9). Anal. calcd. for $\text{C}_8\text{H}_{11}\text{O}_3\text{Br}$ (235.077): C, 40.88; H, 4.72; found: C, 41.04; H, 4.61.

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, 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}): $\tilde{\nu} = 2983$ (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). MS (EI, 70 eV): m/z (%) = 316 (M^+ [$2\times^{81}\text{Br}$], 17), 314 (M^+ [$^{81}\text{Br}^{79}\text{Br}$], 37), 312 (M^+ [$2\times^{79}\text{Br}$], 18), 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 $\text{C}_8\text{H}_{10}\text{O}_3\text{Br}_2$ 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 CCl₄ (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): ¹H NMR (CDCl₃, 300 MHz): δ 2.51 – 2.72 (m, 2 H, CH₂), 4.60 – 4.71 (m, 2 H, OCH₂), 5.60 (d, *J* = 5.4 Hz, 1 H, CH–Br), 7.41 – 7.55 (m, 3H, 3×CH of Ph), 7.75 (d, *J* = 3.9 Hz, 2 H, 2×CH of Ph). ¹³C NMR (CDCl₃, 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}): $\tilde{\nu}$ = 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). MS (EI, 70 eV): *m/z* (%) = 348 (M⁺ [2×⁸¹Br], 7), 346 (M⁺ [⁸¹Br ⁷⁹Br], 15), 344 (M⁺ [2×⁷⁹Br], 7), 267 (36), 265 (36), 186 (100), 129 (11), 105 (68), 89 (6), 77 (76). Anal. calcd. for C₁₂H₁₀O₂Br₂ (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): ¹H NMR (CDCl₃, 300 MHz): δ 2.21 (quint, *J* = 7.5 Hz, 2 H, CH₂), 2.94 (t, *J* = 7.8 Hz, 2 H, CH₂), 4.45 (t, *J* = 7.2 Hz, 2 H, OCH₂), 7.38 – 7.53 (m, 3 H, 3×CH of Ph), 7.61 – 7.71 (m, 2 H, 2×CH of Ph). ¹³C NMR (CDCl₃, 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}): $\tilde{\nu}$ = 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⁺ [⁸¹Br], 22), 265 (M⁺ [⁷⁹Br], 21), 200 (11), 198 (11), 186 (35), 162 (3), 148 (5), 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 CCl₄ (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 as white solid, respectively.

Methyl (3-Bromo-5-chloromethyldihydrofuran-2(3*H*)-ylidene)acetate (6): ¹H NMR (CDCl₃, 300 MHz): δ 2.38 – 2.71 (m, 2 H, CH₂), 3.73 (s, 3 H, OCH₃), 3.79 (dd, *J* = 9.4, 4.9 Hz, 2 H, CH₂–Cl), 5.03 (sext, *J* = 4.9 Hz, 1 H, OCH), 5.33 (s, 1 H, CH=C), 5.81 (d, *J* = 5.6 Hz, 1 H, CH–Br). ¹³C NMR (CDCl₃, 75 MHz): δ 38.3, 43.8, 50.5, 52.2, 79.9, 90.7, 166.0, 171.8. IR (neat, cm^{–1}): $\tilde{\nu}$ = 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⁺ [⁸¹Br³⁷Cl], 21), 270 (M⁺ [⁸¹Br³⁵Cl], 99), 268 (M⁺ [⁷⁹Br³⁵Cl], 72), 241 (19), 239 (99), 237 (79), 191 (31), 189 (100), 159 (27), 157 (56), 139 (27), 125 (11), 110 (20), 108 (19), 101 (35), 81 (25).

Methyl Bromo(5-chloromethyldihydrofuran-2(3*H*)-ylidene)acetate (3d): mp. = 40 °C. ¹H NMR (CDCl₃, 300 MHz): δ 2.11 – 2.22 (m, 1 H, CH₂), 2.35 – 2.46 (m, 1 H, CH₂), 3.09 – 3.21 (m, 1 H, CH₂), 3.30 – 3.41 (m, 1 H, CH₂), 3.63 – 3.73 (m, 2 H, CH₂–Cl), 3.78 (s, 3 H, OCH₃), 4.80 – 4.87 (m, 1 H, OCH). ¹³C NMR (CDCl₃, 75 MHz): δ 27.3, 31.9, 45.1, 52.1, 82.8, 82.9, 164.2, 171.1. IR (KBr, cm^{–1}): $\tilde{\nu}$ = 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⁺ [⁸¹Br³⁷Cl], 8), 270 (M⁺ [⁸¹Br³⁵Cl], 48), 268 (M⁺ [⁷⁹Br³⁵Cl], 39), 240 (21), 238 (100), 236 (72), 221 (2), 219 (5), 203 (13), 201 (14), 191 (5), 159 (23), 148 (25), 146 (22), 117 (11), 70 (36). Anal. calcd. for C₈H₁₀BrClO₃ (269.522): C, 35.65; H, 3.74; found: C, 35.38; H, 4.00.

General procedure for the Suzuki reaction of 2-alkyldienetetrahydrofurans with arylboronic acids: To a 1,4-dioxane solution (3 mL/mmol) of the bromo-2-alkyldienetetrahydrofuran (**3,4**) (1 equiv.) were added potassium phosphate (K₃PO₄, 6 equiv.),

the boronic acid ($\text{ArB}(\text{OH})_2$, 3 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (0.03 equiv.) at 20 °C. The reaction mixture was heated and stirred at reflux for 5 h. Then, the reaction mixture was allowed to cool down 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 (Dihydro-furan-2(3*H*)-ylidene)-(2-methoxy-phenyl)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 $\text{Pd}(\text{PPh}_3)_4$ (0.016 g, 0.014 mmol) in 1,4-dioxane (5 mL), **7a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 1:1) as a slightly yellowish solid (0.107 g, 96%). ^1H NMR (CDCl_3 , 300 MHz): δ 2.12 (quint, $J = 7.2$ Hz, 2 H, CH_2), 3.28 (t, $J = 7.8$ Hz, 2 H, CH_2), 3.63 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.19 (t, $J = 7.2$ Hz, 2 H, OCH_2), 6.90 – 6.98 (m, 2 H, $2\times\text{CH}$), 7.19 (d, $J = 9.3$ Hz, 1 H, CH), 7.24 – 7.30 (m, 1 H, 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}): $\tilde{\nu} = 2943$ (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 $\text{C}_{14}\text{H}_{16}\text{O}_4$ (248.278): C, 67.73; H, 6.50; found: C, 67.51; H, 6.83.

Methyl (Dihydro-furan-2(3*H*)-ylidene)-(2,5-dimethoxy-phenyl)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 $\text{Pd}(\text{PPh}_3)_4$ (0.016 g, 0.014 mmol) in 1,4-dioxane (5 mL), **7b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 $\rightarrow$ 1:1) as a yellowish solid (0.109 g, 87%). ^1H NMR (CDCl_3 , 300 MHz): δ 2.13 (quint, $J = 7.5$ Hz, 2 H, CH_2), 3.27 (t, $J =$

7.8 Hz, 2 H, CH₂), 3.64 (s, 3 H, OCH₃), 3.73 (s, 3 H, OCH₃), 3.77 (s, 3 H, OCH₃), 4.20 (t, J = 7.2 Hz, 2 H, OCH₂), 6.77 – 6.86 (m, 3 H, 3×CH). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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 C₁₅H₁₈O₅ (278.304): C, 64.74; H, 6.52; found: C, 64.75; H, 6.75.

Ethyl (Dihydro-furan-2(3*H*)-ylidene)-(2-methoxy-phenyl)acetate (7c): Starting with **3b** (0.200 g, 0.85 mmol), 2-methoxybenzeneboronic acid (0.400 g, 2.55 mmol), K₃PO₄ (1.085 g, 5.11 mmol) and Pd(PPh₃)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. ¹H NMR (CDCl₃, 300 MHz): δ 1.17 (t, J = 7.2 Hz, 3 H, CH₃), 2.12 (quint, J = 7.5 Hz, 2 H, CH₂), 3.27 (t, J = 7.8 Hz, 2 H, CH₂), 3.77 (s, 3 H, OCH₃), 4.13 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 4.18 (t, J = 7.2 Hz, 2 H, OCH₂), 6.88 – 6.97 (m, 2 H, 2×CH), 7.18 – 7.29 (m, 2 H, 2×CH). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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 C₁₅H₁₈O₄ (262.305): C, 68.69; H, 6.92; found: C, 68.78; H, 6.81.

Ethyl (Dihydro-furan-2(3*H*)-ylidene)-(2,4-dimethoxy-phenyl)acetate (7d): Starting with **3b** (0.150 g, 0.64 mmol), 2,4-dimethoxybenzeneboronic acid (0.355 g, 1.91 mmol), K₃PO₄ (0.813 g, 3.83 mmol) and Pd(PPh₃)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. ¹H NMR (CDCl₃, 300 MHz): δ 1.17 (t, *J* = 7.2 Hz, 3 H, CH₃), 2.11 (quint, *J* = 7.5 Hz, 2 H, CH₂), 3.25 (t, *J* = 7.8 Hz, 2 H, CH₂), 3.75 (s, 3 H, OCH₃), 3.81 (s, 3 H, OCH₃), 4.12 (q, *J* = 7.2 Hz, 2 H, OCH₂CH₃), 4.18 (t, *J* = 7.2 Hz, 2 H, OCH₂), 6.48 – 6.51 (m, 2 H, 2×CH), 7.08 – 7.11 (m, 1 H, CH). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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 C₁₆H₂₀O₅ (292.331): C, 65.74; H, 6.90; found: C, 65.91; H, 6.87.

Ethyl (Dihydro-furan-2(3*H*)-ylidene)-(2,6-dimethoxy-phenyl)acetate (7e): Starting with **3b** (0.170 g, 0.72 mmol), 2,6-dimethoxybenzeneboronic acid (0.403 g, 2.17 mmol), K₃PO₄ (0.921 g, 4.34 mmol) and Pd(PPh₃)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. ¹H NMR (CDCl₃, 300 MHz): δ 1.15 (t, *J* = 7.2 Hz, 3 H, CH₃), 2.11 (quint, *J* = 7.2 Hz, 2 H, CH₂), 3.29 (t, *J* = 7.5 Hz, 2 H, CH₂), 3.76 (s, 6 H, 2×OCH₃), 4.11 (q, *J* = 7.2 Hz, 2 H, OCH₂CH₃), 4.16 (t, *J* = 7.2 Hz, 2 H, OCH₂), 6.59 (d, *J* = 8.4 Hz, 2 H, 2×CH), 7.22 (t, *J* = 8.4 Hz, 1 H, CH). ¹³C NMR (CDCl₃, 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 (neat, cm⁻¹): $\tilde{\nu}$ = 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-(Dihydro-furan-2(3*H*)-ylidene)-2-(2-methoxy-phenyl)-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 $\rightarrow$ 2:1) as a yellowish solid (0.085 g, 77%), mp. = 123 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 2.16 (quint, J = 7.5 Hz, 2 H, CH_2), 3.22 (t, J = 7.8 Hz, 2 H, CH_2), 3.44 (s, 3 H, OCH_3), 4.27 (t, J = 7.2 Hz, 2 H, OCH_2), 6.63 (dd, J = 5.1, 1.2 Hz, 1 H, CH), 6.94 (dt, J = 7.5, 1.2 Hz, 1 H, CH), 7.11 – 7.18 (m, 3 H, 3 $\times$ CH of Ar), 7.22 – 7.28 (m, 1 H, CH), 7.45 (dt, J = 7.5, 1.5 Hz, 3 H, 3 $\times$ 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}): $\tilde{\nu}$ = 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-dihydro-furan-2(3*H*)-ylidene)-(2-methoxy-phenyl)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 $\rightarrow$ 1:1) as a slightly yellowish oil (0.159 g, 96%). 1H NMR ($CDCl_3$, 300 MHz): δ 2.02 – 2.14 (m, 1 H, CH_2), 2.19 – 2.31 (m, 1 H, CH_2), 3.26 – 3.36 (m, 2 H, CH_2), 3.54 (d, J = 5.1 Hz, 2 H, CH_2-Cl), 3.60 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.58 (quint, J = 7.2 Hz, 1 H, OCH), 6.87 – 6.96 (m, 2 H, 2 $\times$ CH of Ar), 7.18 – 7.27 (m, 2H, 2 $\times$ 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}): $\tilde{\nu}$ = 2950 (w), 17004 (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), 266 (17), 264 (50), 239 (16), 237 (58), 201 (7), 176 (10), 174 (13), 150 (13), 148 (39).

Methyl (2-Methoxy-phenyl)-[3-(2-methoxy-phenyl)-dihydro-furan-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 $[\text{Pd}(\text{PPh}_3)_4]$ (0.058 g, 0.05 mmol) in 1,4-dioxane (5 mL), **7h** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 $\rightarrow$ 2:1) as a white solid (0.325 g, 92%), mp. = 112 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 1.58 – 2.05 (m, 1 H, CH_2), 2.41 – 2.56 (m, 1 H, CH), 3.43 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.04 – 4.18 (m, 1 H, OCH_2), 4.24 (dt, J = 8.4, 1.8 Hz, 1 H, OCH_2), 5.34 (dd, J = 8.7, 1.5 Hz, 1 H, CH), 6.86 – 7.05 (m, 4 H, $4\times\text{CH}$), 7.19 – 7.32 (m, 2 H, $2\times\text{CH}$), 7.37 – 7.45 (m, 1 H, CH), 7.81 – 7.85 (m, 1 H, 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}): $\tilde{\nu}$ = 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 $\text{C}_{21}\text{H}_{22}\text{O}_5$ 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 CH₂Cl₂ (3×30 mL/mmol substrate). The combined organic extracts were dried (Na₂SO₄), 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 BBr₃ (0.605 g, 2.42 mmol) in CH₂Cl₂ (6 mL), **8a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.163 g, 92%). ¹H NMR (CDCl₃, 300 MHz): δ 2.34 (quint, *J* = 7.2 Hz, 2 H, CH₂), 3.35 (t, *J* = 7.5 Hz, 2 H, CH₂), 3.47 (t, *J* = 6.9 Hz, 2 H, CH₂-Br), 3.95 (s, 3 H, OCH₃), 7.28 – 7.33 (m, 2 H, 2×CH), 7.42 – 7.45 (m, 1 H, CH), 7.95 – 7.98 (m, 1 H, CH). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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⁺ [⁸¹Br], 38), 296 (M⁺ [⁷⁹Br], 39), 267 (7), 265 (7), 217 (16), 203 (10), 201 (6), 189 (100), 175 (5), 171 (29), 159 (47), 157 (22), 145 (4), 131 (34), 114 (12), 102 (37), 77 (14). Anal. calcd. for C₁₃H₁₃BrO₃ (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 BBr₃ (0.504 g, 2.0 mmol) in CH₂Cl₂ (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. ¹H NMR (CDCl₃, 300 MHz): δ 2.34 (quint, *J* = 7.05 Hz, 2 H, CH₂), 3.33 (t, *J* = 7.5 Hz, 2 H, CH₂), 3.47 (t, *J* = 6.6 Hz, 2 H, CH₂-Br), 3.95 (s, 3 H, OCH₃), 5.31 (broad s, 1 H, OH), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1 H, CH), 7.30 (d, *J* = 8.7 Hz, 1 H, CH), 7.46 (d, *J* = 2.4 Hz, 1

H, CH). ^{13}C NMR ($\text{CDCl}_3/\text{DMSO}-d_6$, 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}): $\tilde{\nu}$ = 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 ($\text{M}^+ [^{81}\text{Br}]$, 89), 312 ($\text{M}^+ [^{79}\text{Br}]$, 92), 283 (8), 281 (7), 233 (6), 219 (6), 205 (100), 175 (18), 147 (8), 77 (5). The exact molecular mass $m/z = 311.9997 \pm 2$ ppm [M^+] for $\text{C}_{13}\text{H}_{13}\text{O}_4\text{Br}$ was confirmed HRMS (EI, 70 eV). Anal. calcd. for $\text{C}_{13}\text{H}_{13}\text{BrO}_4$ (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 $\rightarrow$ 50:1) as a slightly yellowish oil (0.078 g, 84%). ^1H NMR (CDCl_3 , 300 MHz): δ 1.46 (t, $J = 7.2$ Hz, 3 H, CH_3), 2.36 (quint, $J = 6.6$ Hz, 2 H, CH_2), 3.36 (t, $J = 7.2$ Hz, 2 H, CH_2), 3.48 (t, $J = 6.6$ Hz, 2 H, $\text{CH}_2\text{-Br}$), 4.42 (q, $J = 7.2$ Hz, 2 H, OCH_2), 7.29 – 7.32 (m, 2 H, $2\times\text{CH}$), 7.44 – 7.47 (m, 1 H, CH), 7.97 – 8.00 (m, 1 H, 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}): $\tilde{\nu}$ = 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 ($\text{M}^+ [^{81}\text{Br}]$, 88), 310 ($\text{M}^+ [^{79}\text{Br}]$, 95), 283 (17), 281 (17), 267 (13), 265 (14), 231 (7), 217 (3), 203 (27), 201 (27), 189 (4), 175 (100), 157 (36), 131 (21), 129 (15), 91 (15), 77 (13). HRMS (FT-ICR): Calcd. for $\text{C}_{14}\text{H}_{15}\text{BrO}_3$ [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 BBr₃ (0.549 g, 2.2 mmol) in CH₂Cl₂ (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. ¹H NMR (CDCl₃, 300 MHz): δ 1.44 (t, *J* = 7.2 Hz, 3 H, CH₃), 2.33 (quint, *J* = 7.05 Hz, 2 H, CH₂), 3.31 (t, *J* = 7.5 Hz, 2 H, CH₂), 3.47 (t, *J* = 6.6 Hz, 2 H, CH₂-Br), 4.41 (q, *J* = 7.2 Hz, 2 H, OCH₂), 4.97 (broad s, 1 H, OH), 6.84 (dd, *J* = 8.7, 2.1 Hz, 1 H, CH), 6.94 (d, *J* = 2.1 Hz, 1 H, CH), 7.80 (d, *J* = 8.7 Hz, 1 H, CH). ¹³C NMR (CDCl₃+D₆-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): $\tilde{\nu}$ = 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⁺ [⁸¹Br], 97), 326 (M⁺ [⁷⁹Br], 100), 299 (24), 297 (25), 283 (9), 281 (9), 219 (75), 217 (25), 191 (88), 175 (10), 173 (19), 146 (14), 118 (7), 91 (7), 77 (6). The exact molecular mass *m/z* = 326.0154 ± 2 ppm [M⁺] for C₁₄H₁₅O₄Br was confirmed by HRMS (EI, 70 eV). Anal. calcd. for C₁₄H₁₅BrO₄ (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 BBr₃ (0.480 g, 1.92 mmol) in CH₂Cl₂ (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. ¹H NMR (CDCl₃, 300 MHz): δ 1.40 (t, *J* = 7.2 Hz, 3 H, CH₃), 2.27 (quint, *J* = 7.05 Hz, 2 H, CH₂), 3.23 (t, *J* = 7.5 Hz, 2 H, CH₂), 3.41 (t, *J* = 6.6 Hz, 2 H, CH₂-Br), 4.41 (q, *J* = 7.2 Hz, 2 H, OCH₂), 6.70 (dd, *J* = 8.1, 0.9 Hz, 1 H, CH), 6.88 (dd, *J* = 8.1 Hz, 0.9 Hz, 1 H, CH), 7.12 (t, *J* = 8.1 Hz, 1 H, CH), 10.40 (s, 1 H, OH). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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), 280 (100), 226 (4), 224 (4), 219 (2), 200 (7), 187 (4), 173 (38), 146 (6), 117 (9), 89 (16), 77 (6). The exact molecular mass $m/z = 326.0154 \pm 2$ ppm [M^+] for $\text{C}_{14}\text{H}_{15}\text{O}_4\text{Br}$ was confirmed by HRMS (EI, 70 eV). Anal. calcd. for $\text{C}_{14}\text{H}_{15}\text{BrO}_4$ (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 $\rightarrow$ 1:1) as a slightly yellowish oil (0.036 g, 71%). ^1H NMR (CDCl_3 , 300 MHz): δ 2.35 (quint, $J=7.1$ Hz, 2 H, CH_2), 3.10 (t, $J=7.4$ Hz, 2 H, CH_2), 3.44 (t, $J=6.8$ Hz, 2 H, $\text{CH}_2\text{-Br}$), 7.16 – 7.40 (m, 3 H, $3\times\text{CH}$), 7.47 – 7.64 (m, 4 H, $4\times\text{CH}$), 7.81 – 7.84 (m, 2 H, $2\times\text{CH}$). ^{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}): $\tilde{\nu}$ = 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), 235 (90), 221 (15), 205 (10), 178 (13), 160 (10), 148 (100), 131 (12), 105 (44), 77 (32). HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{15}\text{BrO}_2$ [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 $\rightarrow$ 10:1) as a slightly yellowish oil (0.047 g, 80%). ^1H NMR (CDCl_3 , 300 MHz): δ 2.21 – 2.34 (m, 1 H, CH_2), 2.57 – 2.69 (m, 1 H, CH_2), 3.31 – 3.42 (m, 1 H, CH_2), 3.44 – 3.54 (m, 1 H, CH_2), 3.80 (dd, $J=11.4, 8.4$ Hz, 1 H, $\text{CH}_2\text{-Cl}$), 3.97 (dd, $J=11.4, 4.8$ Hz, 1 H, $\text{CH}_2\text{-Cl}$), 3.97 (s, 3 H, OCH_3), 4.14 – 4.22 (m, 1

H, CH–Br), 7.30 – 7.33 (m, 2 H, 2×CH of Ar), 7.44 – 7.48 (m, 1 H, CH of Ar), 7.96 – 7.99 (m, 1 H, 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}): $\tilde{\nu}$ = 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^+ [$^{81}\text{Br}^{37}\text{Cl}$], 6), 346 (M^+ [$^{81}\text{Br}^{35}\text{Cl}$], 34), 344 (M^+ [$^{79}\text{Br}^{35}\text{Cl}$], 24), 315 (2), 313 (1), 229 (18), 203 (24), 189 (100), 171 (28), 169 (13), 159 (22), 131 (12), 114 (8), 102 (13), 77 (4). HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{14}\text{BrClO}_3$ [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 $\rightarrow$ 4:1) as a colorless oil (0.019 g, 58%). ^1H NMR (CDCl_3 , 300 MHz): δ 2.68 – 2.81 (m, 1 H, CH_2), 2.84 – 2.95 (m, 1 H, CH_2), 3.25 – 3.41 (m, 2 H, CH_2 –Br), 4.06 (s, 3 H, OCH_3), 5.53 (t, J = 7.6 Hz, 1 H, CH), 6.91 – 6.97 (m, 2 H, 2×CH), 7.13 – 7.19 (m, 1 H, CH), 7.29 – 7.35 (m, 2 H, 2×CH), 7.45 – 7.50 (m, 2 H, 2×CH), 7.86 – 7.89 (m, 1 H, CH), 7.91 (s, 1 H, 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}): $\tilde{\nu}$ = 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), 358 (16), 356 (17), 329 (5), 326 (5), 281 (44), 263 (11), 249 (100), 221 (65), 205 (5), 193 (13), 165 (14), 163 (11), 161 (23), 134 (25), 114 (20), 107 (13), 105 (14), 91 (11), 77 (22). The exact molecular mass m/z = 388.0310 ± 2 ppm [M^+] for $\text{C}_{19}\text{H}_{17}\text{BrO}_4$ was confirmed by HRMS (EI, 70 eV).

General procedure for the synthesis of 9 by reaction of 2-alkylidenetetrahydrofurans with borontribromide: To a CH₂Cl₂-solution (10 mL/mmol) of the 2-alkylidenetetrahydrofuran (**7**) (1 equiv.) was added BBr₃ (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. Then, the reaction mixture was poured into an aqueous solution of KO^tBu (1 M, 10 mL/mmol). The mixture was stirred for 1 h and later extracted with CH₂Cl₂ (3×30 mL/mmol). The combined organic extracts were dried (Na₂SO₄), 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 BBr₃ (0.283 g, 1.13 mmol) in CH₂Cl₂ (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. ¹H NMR (CDCl₃, 300 MHz): δ 2.28 (quint, *J* = 7.5 Hz, 2 H, CH₂), 3.37 (t, *J* = 7.8 Hz, 2 H, CH₂), 4.62 (t, *J* = 7.2 Hz, 2 H, OCH₂), 7.06 – 7.21 (m, 3 H, 3×CH of Ar), 7.60 (dd, *J* = 7.2, 1.2 Hz, 1 H, CH of Ar). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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 C₁₂H₁₀O₃ was confirmed by HRMS (EI, 70 eV).

Z-9a: mp. = 106 °C. ¹H NMR (CDCl₃, 300 MHz): δ 2.34 (quint, *J* = 7.5 Hz, 2 H, CH₂), 3.19 (t, *J* = 7.8 Hz, 2 H, CH₂), 4.68 (t, *J* = 7.2 Hz, 2 H, OCH₂), 7.06 – 7.25 (m, 4 H, 4×CH of Ar). ¹³C NMR (CDCl₃, 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): $\tilde{\nu}$ = 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 $\rightarrow$ 1:1) as yellowish oils (0.028 g, 65%; 0.013 g, 30%).

E-9b: mp. = 61 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 2.12 – 2.23 (m, 1 H, CH_2), 2.39 – 2.52 (m, 1 H, CH_2), 3.25 – 3.38 (m, 1 H, CH_2), 3.52 – 3.60 (m, 1 H, CH_2), 3.80 (d, J = 5.1 Hz, 1 H, CH_2-Cl), 3.84 (d, J = 5.1 Hz, 1 H, CH_2-Cl), 5.02 – 5.08 (m, 1 H, OCH), 7.07 – 7.21 (m, 3 H, 3 $\times$ CH of Ar), 7.61 (dd, J = 7.5, 1.2 Hz, 1 H, 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}): $\tilde{\nu}$ = 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), 162 (2), 160 (100), 121 (49), 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: 1H NMR ($CDCl_3$, 300 MHz): δ 2.34 – 2.39 (m, 1 H, CH_2), 2.45 – 2.58 (m, 1 H, CH_2), 3.14 – 3.39 (m, 2 H, CH_2), 3.86 (d, J = 0.9 Hz, 1 H, CH_2-Cl), 3.87 (d, J = 1.8 Hz, 1 H, CH_2-Cl), 5.13 – 5.19 (m, 1 H, OCH), 7.08 – 7.23 (m, 4 H, 4 $\times$ 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}): $\tilde{\nu}$ = 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^+

[³⁵Cl], 12), 215 (6), 187 (4), 160 (27), 145 (3), 131 (3), 121 (12), 104 (12), 85 (100), 77 (16).

HRMS (ESI): Calcd. for C₁₃H₁₁ClO₃ [M⁺]: 252.03672 (³⁷Cl), 250.03967 (³⁵Cl); found: 252.03800 (³⁷Cl), 250.03903 (³⁵Cl).

EB0568-1

(8b)

AKWEISZ

Current Data Parameters
NAME EB0568-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040804
Time 20.17
INSTRUM spect
PROBHD 5 mm TBC 1H-13
PULPROG zgpg
TD 32768
SOLVENT DMSO
CQ13 13C
RG 256
DS 0
SWH 39062.500 KHz
FIDRES 1.192093 KHz
AQ 0.4194932 sec
RG 812.7
SW 13.800 usec
SE 6.00 usec
TE 296.1 K
SI 2.0000000 sec
SFI 0.0000000 sec
RG 600.1330091 MHz
SF 600.1330091 MHz

F2 - Processing parameters
SI 32768
SF 150.9024790 MHz
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SSB 0
LB 2.00 Hz
GB 0
PC 1.00

EB0570-1

(8c)

AKWEISZ

Current Data Parameters
NAME EB0570-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040809
Time 17.04
INSTRUM spect
PROBHD 5 mm TBC 1H-13
PULPROG zgpg
TD 32768
SOLVENT DMSO
CQ13 13C
RG 256
DS 0
SWH 39062.500 KHz
FIDRES 1.192093 KHz
AQ 0.4194932 sec
RG 812.7
SW 13.800 usec
SE 6.00 usec
TE 296.1 K
SI 2.0000000 sec
SFI 0.0000000 sec
RG 600.1330091 MHz
SF 600.1330091 MHz

F2 - Processing parameters
SI 32768
SF 150.9023944 MHz
WDW EM
SSB 0
LB 2.00 Hz
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PC 1.00

EB0567-1

AKWEISZ

Current Data Parameters
NAME EB0567-1
EXNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time 20.26
INSTRUM spect
PROBHD 5 mm TBI 1H-13
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NS 128
DS 0
SWH 40983.605 Hz
FIDRES 1.250720 Hz
AQ 0.1998318 sec
RG 1625.5
DM 12.200 usec
DE 4.00 usec
TE 296.2 K
D1 2.00000000 sec
d11 0.01000000 sec
MCKEFT 0.00000000 sec
MCKEFT 0.01000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 4.00 usec
PL1 0.00 dB
SFO1 150.9181580 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 20.10 dB
SFO2 600.1310991 MHz

F2 - Processing parameters
SI 32768
SF 150.9024352 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

EB0569-1

AKWEISZ

Current Data Parameters
NAME EB0569-1
EXNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20040809
Time 19.02
INSTRUM spect
PROBHD 5 mm TBI 1H-13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 128
DS 0
SWH 40983.605 Hz
FIDRES 1.250720 Hz
AQ 0.1998318 sec
RG 1624.6
DM 12.200 usec
DE 4.00 usec
TE 296.2 K
D1 2.00000000 sec
d11 0.01000000 sec
MCKEFT 0.00000000 sec
MCKEFT 0.01000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 4.00 usec
PL1 0.00 dB
SFO1 150.9181480 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 20.10 dB
SFO2 600.1310991 MHz

F2 - Processing parameters
SI 32768
SF 150.9024352 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

EB 0366-3

2-9a

AK WEISZ

Current Data Parameters
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EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20031216
Time 15.21
INSTRUM spect
PROBHD 5 mm BBO 13C-1
PULPROG zgpg30
TD 65536
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NS 256
DS 9
SWH 37593.884 Hz
FIDRES 0.573639 Hz
AQ 0.8716921 sec
RG 25642.5
SFW 13.300 usec
DE 381.4 Hz
TE 2.0000000 sec
D11 0.0300000 sec
D12 0.0000000 sec
MCNMR 0.0150000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 0.00 dB
SFO1 150.909090 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 13.50 dB
PL13 13.50 dB
SFO2 600.1328000 MHz

F2 - Processing parameters
SI 32768
SF 150.909090 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Ernst-Moritz-Arns-Universität Greifswald
ARX300 - Kernresonanz-Spektrometer
13C-NMR-Spektrom (Protonenbreitbandkoppel)
E. Behr: EB0769-3
Lösungsmittel: Deuteriochloroform, CDCl3
Referenz: Lösungsmittel = 77.0 ppm
Messstemperatur: 298 K (25 °C)

E-9b

Current Data Parameters
NAME BE_EB0769-3
EXPNO 13
PROCNO 1
USER lag

F2 - Acquisition Parameters
Date_ 20030209
Time 10.11
INSTRUM spect
PROBHD 5 mm Maltus
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 896
DS 0
SWH 21798.131 Hz
FIDRES 0.460426 Hz
AQ 0.7537140 sec
RG 32768
SFW 23.000 usec
DE 32.86 usec
TE 298.0 K
D12 0.0000000 sec
D13 30.00 dB
D1 2.0000000 sec
CPDPRG2 waltz16
P13 110.00 usec
D11 0.0300000 sec
PL5 22.00 dB
P1 3.00 usec
SFO1 75.4761177 MHz
NUCLEUS 13C

F2 - Processing parameters
SI 32768
SF 75.4677532 MHz
WDW EM
SSB 0
LB 1.20 Hz
GB 0
PC 0.95