SUPPORTING INFORMATION

SYNTHESIS OF 2,3-DIHYDROBENZO[1,4]DIOXINS AND -OXAZINS VIA A DOMINO WACKER-HECK REACTION

Lutz F. Tietze*[a], Kristina F. Wilckens[a], Sinem Yilmaz[a], Florian Stecker[a], and Julia Zinngrebe[a]

[a] Institute of Organic and Biomolecular Chemistry, Georg-August-University Göttingen, Tammannstraße 2, D-37077 Göttingen (Germany), ltietze@gwdg.de

TABLE OF CONTENTS

GENERAL EXPERIMENTAL METHODS 2

GENERAL PROCEDURES 2

SYNTHESIS OF THE MONOALLYL ETHERS 10–25 3

SYNTHESIS OF PHENOL 65 7

DOMINO WACKER-HECK REACTION 9

GENERAL EXPERIMENTAL METHODS

All reactions were performed under argon in flame-dried flasks. All solvents were dried and distilled prior to use by usual laboratory methods. All reagents obtained from commercial sources were used without further purification. Thin-layer chromatography (TLC) was performed on precoated silica gel SIL G/UV_{254} plates (Macherey–Nagel GmbH & Co. KG) and silica gel 60 (0.032–0.063 mm, Merck) was used for column chromatography. Phosphomolybdic acid in methanol (PMA) or vanillin in methanolic sulfuric acid were used as staining reagents for TLC. UV spectra were taken in CH_3CN or MeOH with a Perkin–Elmer Lambda 2 spectrometer. IR spectra were recorded as KBr pellets or as films with a Bruker IFS 25 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with Mercury–200, VXR–200, Unity–300, Inova–500, Unity Inova–600 (Varian) or AMX 300 (Bruker) spectrometer. Chemical shifts are reported in ppm with tetramethylsilane (TMS) as internal standard. Multiplicities of ^{13}C-NMR peaks were determined with the APT pulse sequence. Mass spectra were measured with a Finnigan MAT 95, TSQ 7000 or LCQ instrument.

GENERAL PROCEDURES

General Procedure A: **Allylation using K_2CO_3:** A suspension of anhydrous K_2CO_3 (0.95–1.1 eq.) and KI (1.1 eq.), or alternatively TBAI (cat.), in acetone (2 mL/mmol substrate) was treated with the respective substrate and stirred at room temperature until the end of gas release. Afterwards the allyl halide (1.1–2.0 eq.) was added and the resulting mixture stirred for 0.5–6 h at 25–60 °C. (TLC-Control). Then H_2O (5 mL/mmol) was added, the solution was neutralised with 1 N HCl and the aqueous phase was extracted with Et_2O (3 × 5 mL/mmol). The combined organic layers were dried over $MgSO_4$, the solvent removed under vacuum and the crude product purified by column chromatography on silica.

General Procedure B: **Allylation using NaH:** The substrate, dissolved in dry DMF (3 mL/mmol), was carefully treated with NaH (0.95 eq.) at 0 °C. After warming up to room temperature and the end of gas release, the respective ally halide as well as TBAI (cat.) were added and the reaction mixture stirred for 2–24 h at 25–80 °C (TLC-Control). Then H_2O (5 mL/mmol) was added, the solution neutralised with 1 N HCl and the aqueous phase extracted with Et_2O (3 × 5 mL/mmol). The combined organic layers were

washed with H_2O (15 mL/mmol) and saturated NaCl-solution, dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica.

General Procedure C: **Domino Wacker-Heck Reaction:** A mixture of palladium trifluoroacetate (0.1 eq.) and *p*-benzoquinone (4.0 eq.) in CH_2Cl_2 (0.4–0.5 mL/mmol substrate) was stirred for 10 min at room temperature. Then a solution of the phenol (1.0 eq.) and the respective coupling partner (2.0–5.0 eq.) in CH_2Cl_2 (0.4–0.5 mL/mmol) was added to the suspension and the mixture was stirred for 5 h–4 d at 25–60 °C. (TLC-Control). At the end of the reaction the mixture was treated with 1N HCl (50 mL/mmol) and the aqueous phase extracted with Et_2O (3 x 50 mL/mmol). The combined organic phases were washed with 1N NaOH (3 x 50 mL/mmol), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica.

SYNTHESIS OF THE MONOALLYL ETHERS 10–25

2-(2-Methylallyloxy)-phenol (10): According to general procedure **A**, catechol (**1**) (5.01 g, 45.5 mmol) was treated with K_2CO_3 (6.92 g, 50.1 mmol, 1.1 eq.), KI and 3-chloro-2-methylpropene (**26**) (4.94 g, 54.6 mmol, 5.34 mL, 1.2 eq.) under reflux for 4 h. After column chromatography on silica (P/EtOAc = 50:1 $\rightarrow$ 10:1) the desired compound **10** (3.90 g, 23.8 mmol, 52 %) was obtained as a colorless liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, 2'-CH_3), 4.51 (s, 2 H, 1'-H_2), 5.03 (m_c, 1 H, 3'-H), 5.10 (m_c, 1 H, 3'-H), 5.70 (s, 1 H, OH), 6.79–6.99 (m, 4 H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.37 (2'-CH_3), 72.59 (C-1'), 113.30 (C-3'), 112.11, 114.62 (C-3, C-6), 120.02, 121.63 (C-4, C-5), 140.38 (C-2') 145.60, 145.78 (C-1, C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 3536, 2919, 1597, 1501, 1454, 1373, 1259, 1219 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 197.0 (4.582), 199.5 (4.582), 215.5 (3.798), 276.0 (3.424) nm. **MS** (EI, 70 eV): m/z (%) = 164 (57) $[M]^+$, 109 (30) $[M–C_4H_7]^+$, 55 (100) $[C_4H_7]^+$. Calcd for **$C_{10}H_{12}O_2$**: 164.0837, Found: 164.0837 (EI-HRMS).

5-Methyl-2-(2-methylallyloxy)-phenol (11), 4-Methyl-2-(2-methylallyloxy)-phenol (19): According to general procedure **A**, 4-methoxycatechol (**2**) (6.24 g, 50.3 mmol) was treated with K_2CO_3 (6.95 g, 50.3 mmol, 1.0 eq.), KI and 3-chloro-2-methylpropene (**26**) (5.01 g, 55.3 mmol, 5.41 mL, 1.1 eq.) under reflux for 4 h. After purification by column chromatography on silica (P/EtOAc = 60:1) a 1:1 mixture of the two regioisomers **11** and **19** (5.68 g, 31.9 mmol, 63 %) was obtained as a colorless liquid. **^{1}H-NMR**

(300 MHz, $CDCl_3$): δ = 1.84, 1.86 (s, 3 H, 2'-CH_3), 2.27, 2.28 (s, 3 H, Ar-CH_3), 4.48, 4.49 (s, 2 H, 1'-H_2), 5.03 (m_c, 1 H, 3'-H_a), 5.10 (m_c, 1 H, 3'-H_b), 5.54, 5.65 (s, 1 H, OH), 6.59–6.88 (m, 3 H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.31, 19.35 (2'-CH_3), 20.72, 20.97 (Ar-CH_3), 72.51, 72.75 (C-1'), 112.08, 112.98, 114.21, 115.42 (C-3, C-6), 113.09, 113.10 (C-3'), 120.15, 121.71 (C-4[11], C-5[19]), 129.44, 131.31 (C-4[19], C-5[11]), 140.46, 140.56 (C-2'), 143.42 (C-1), 145.31, 145.59 (C-2') ppm. **IR** (Film): $\tilde{\nu}$ = 3543, 2920, 1594, 1512, 1454, 1377, 1272, 1232 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 199.0 (4.623), 281.5 (3.469) nm. **MS** (EI, 70 eV): m/z (%) = 178 (38) $[M]^+$, 123 (100) $[M–C_4H_7]^+$, 55 (77) $[C_4H_7]^+$. Calcd for **$C_{11}H_{14}O_2$**: 178.0994, Found: 178.0994 (EI-HRMS).

2-Methoxy-6-(2-methylallyloxy)-phenol (12), 3-Methoxy-2-(2-methylallyloxy)-phenol (20): According to general procedure **A**, 3-methoxycatechol (**3**) (7.04 g, 50.2 mmol) was treated with K_2CO_3 (6.94 g, 50.2 mmol, 1.0 eq.), KI and 3-chloro-2-methylpropene (**26**) (4.94 g, 55.3 mmol, 5.34 mL, 1.1 eq.) under reflux for 4 h. The two regioisomers **12** (5.11 g, 26.3 mmol, 52 %) and **20** (1.50 g, 7.72 mmol, 15 %) were obtained as colorless liquids after column chromatography on silica (P/EtOAc = 30:1 $\rightarrow$ 5:1). **12**: **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.87 (s, 3 H, 2'-CH_3), 3.85 (s, 3 H, OMe), 4.47 (s, 2 H, 1'-H_2), 4.99 (m_c, 1 H, 3'-H), 5.11 (m_c, 1 H, 3'-H), 5.83 (s, 1 H, OH), 6.47 (dd, J = 8.3, 1.1 Hz, 1 H, 3-H), 6.60 (dd, J = 8.3, 1.2 Hz, 1 H, 5-H), 6.92 (t, J = 8.3 Hz, 1 H, 4-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.66 (2'-CH_3), 55.77 (OMe), 76.84 (C-1'), 104.03, 108.00 (C-3, C-5), 113.36 (C-3'), 124.00 (C-4), 134.56 (C-1), 141.55 (C-2'), 149.57, 152.47 (C-6, C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 3518, 2943, 1596, 1480, 1310, 1268, 1200 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 200.5 (4.613), 267.5 (2.885) nm. **MS** (EI, 70 eV): m/z (%) = 194 (54) $[M]^+$, 139 (100) $[M–C_4H_7]^+$. Calcd for **$C_{11}H_{14}O_3$**: 194.0943, Found: 194.0943 (EI-HRMS). **20**: **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.83 (s, 3 H, 2'-CH_3), 3.89 (s, 3 H, OMe), 4.52 (s, 2 H, 1'-H_2), 4.99 (m_c, 1 H, 3'-H), 5.08 (m_c, 1 H, 3'-H), 5.56 (s, 1 H, OH), 6.54–6.61 (m, 2 H, 4-H, 5-H), 6.76 (t, J = 8.3 Hz, 1 H, 6-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.32 (2'-CH_3), 56.18 (OMe), 60.37 (C-1'), 105.06, 106.47 (C-4, C-6), 113.03 (C-3'), 118.88 (C-5), 135.16 (C-2), 140.66 (C-2'), 146.21, 147.35 (C-1, C-3) ppm. **IR** (Film): $\tilde{\nu}$ = 3517, 2939, 1619, 1507, 1480, 1363, 1284, 1214 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 202.0 (4.658), 269.5 (3.066) nm. **MS** (EI, 70 eV): m/z (%) = 194 (67) $[M]^+$, 139 (100) $[M–C_4H_7]^+$. Calcd for **$C_{11}H_{14}O_3$**: 194.0943, Found: 194.0943 (EI-HRMS).

2-Fluoro-6-(2-methylallyloxy)-phenol (13), 3-Fluoro-2-(2-methylallyloxy)-phenol (21): According to general procedure **A**, 3-fluorocatechol (**4**) (1.00 g, 7.81 mmol) was treated with K_2CO_3 (1.08 g, 7.81 mmol, 1.0 eq.), KI and 3-Chloro-2-methylpropene (**26**) (778 mg, 8.29 mmol, 841 µL, 1.1 eq.) under reflux for 6 h

to obtain the two regioisomers **13** (**21**) (688 mg, 3.77 mmol, 48 %) and **21** (**13**) (103 mg, 0.57 mmol, 8 %) as colorless liquids after column chromatography on silica (P/EtOAc = 100:1 → 50:1). **13** or **21**: **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.86 (s, 3 H, 2'-CH_3), 4.56 (s, 2 H, 1'-H_2), 5.01 (m_c, 1 H, 3'-H_a), 5.11 (m_c, 1 H, 3'-H_b), 5.81 (s, 1 H, OH), 6.63 (ddd, J = 11.3, 8.4, 1.5 Hz, 1 H, 4-H), 6.74 (dt, J = 8.2, 1.5 Hz, 1 H, 6-H), 6.89 (dt, J = 8.2, 6.0 Hz, 1 H, 5-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.46 (2'-CH_3), 77.55, 77.63 (C-1'), 108.02, 108.28 (C-3), 110.81, 110.85 (C-5), 114.30 (C-3'), 123.39, 123.51 (C-4), 133.41, 133.58 (C-1), 140.79 (C-2'), 149.77, 149.84 (C-6), 153.36, 156.62 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 3528, 2946, 1597, 1497, 1350, 1295, 1225 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 194.5 (4.567), 267.5 (3.004) nm. **MS** (EI, 70 eV): m/z (%) = 182 (29) $[M]^+$, 55 (100) $[C_4H_7]^+$. Calcd for **$C_{10}H_{11}FO_2$**: 182.0743. Found: 182.0743 (EI-HRMS).

3-Hydroxy-4-(2-methyl-allyloxy)-benzoic acid ethyl ester (14), 4-Hydroxy-3-(2-methyl-allyloxy)-benzoic acid ethyl ester (22): According to general procedure **A**, 3,4-dihydroxy-benzoic acid ethyl ester (**5**) (1.50 g, 8.23 mmol) was reacted with K_2CO_3 (1.25 g, 9.05 mmol, 1.1 eq.), TBAI and 3-chloro-2-methylpropene (**26**) (820 mg, 9.06 mmol, 887 µL, 1.1 eq.) under reflux for 6 h to provide a 4.1:1 mixture of regioisomers **14** and **22** (933 mg, 3.95 mmol, 48 %) as a white solid after column chromatography on silica (P/EtOAc = 50:1 → 10:1). Via a second column chromatography regioisomer **14** (556 mg, 2.35 mmol, 29 %) could partially be isolated from the mixture. **14**: **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.83 (s, 3 H, 2'-CH_3), 4.33 (q, J = 7.1 Hz, 2 H, OCH_2CH_3), 4.56 (s, 2 H, 1'-H_2), 5.04 (m_c, 1 H, 3'-H_a), 5.08 (m_c, 1 H, 3'-H_b), 5.73 (s, 1 H, OH), 6.86 (d, J = 8.4 Hz, 1 H, 5-H), 7.58 (dd, J = 8.3, 2.2 Hz, 1 H, 6-H), 7.61 (d, J = 2.0 Hz, 1 H, 2-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 14.31 (OCH_2CH_3), 19.31 (2'-CH_3), 60.73 (OCH_2CH_3), 72.58 (C-1'), 113.85 (C-3'), 111.07, 115.68, 122.55 (C-2, C-5, C-6), 123.80 (C-1), 139.65 (C-2'), 145.26 (C-3), 149.31 (C-4), 166.27 (CO_2Et) ppm. **IR** (Pellet): $\tilde{\nu}$ = 3489, 2980, 1692, 1614, 1514, 1448, 1371, 1267 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 206.0 (4.393), 216.0 (4.339), 256.5 (4.084), 292.5 (3.775) nm. **MS** (ESI): m/z (%) = 495.2 (36) $[2 \times M+Na]^+$, 275.1 (16) $[M+K]^+$, 259.1 (19) $[M+Na]^+$, 237.1 (100) $[M+H]^+$. Calcd for **$C_{13}H_{16}O_4$**: 237.11214 $[M+H]^+$. Found 237.11209 $[M+H]^+$ (ESI-HRMS).

3-Hydroxy-4-(2-methylallyloxy)-benzonitrile (15), 4-Hydroxy-3-(2-methylallyloxy)-benzonitrile (23): According to general procedure **B**, 3,4-dihydroxybenzonitrile (**6**) (500 mg, 3.70 mmol) was reacted with 3-bromo-2-methylpropene (**26**) (550 mg, 4.07 mmol, 410 µL, 1.1 eq.) within 3 h at 60 °C and a 3.2:1 mixture of the two product regioisomers (376 mg, 1.99 mmol, 54 %) was obtained as a white solid after column chromatography on silica (P/EtOAc = 30:1 → 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.83 (s,

3 H, 2'-CH_3), 4.53 (s, 2 H, 1'-H_2^{23}), 4.56 (s, 2 H, 1'-H_2^{15}), 5.02–5.11 (m, 2 H, 3'-H), 5.98 (s, 1 H, OH^{15}), 6.30 (s, 1 H, OH^{23}), 6.87 (m_c, 1 H, 5-H^{15}), 6.96 (d, J = 8.4 Hz, 1 H, 5-H^{23}), 7.07 (d, J = 1.9 Hz, 1 H, 2-H^{23}), 7.12–7.18 (m, 2 H, 6-H^{15}, 2-H^{23}), 7.20 (dd, J = 8.3, 1.9 Hz, 1 H, 6-H^{23}) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.20 (2'-CH_3), 72.72 (C-1'^{15}), 72.94 (C-1'^{23}), 103.04 (C-1^{23}), 104.47 (C-1^{15}), 112.09 (C-5^{15}), 114.20 (C-3'^{23}), 114.24 (C-3'^{15}), 115.17 (C-5^{23}), 115.34 (C-2^{23}), 117.74 (C-2^{15}), 118.94 (CN^{15}), 119.19 (CN^{23}), 125.39 (C-6^{15}), 126.98 (C-6^{23}), 139.13 (C-2'^{15}), 139.17 (C-2'^{23}), 145.60 (C-3^{15}), 145.96 (C-4^{23}), 149.30 (C-4^{15}), 150.00 (C-3^{23}) ppm. **IR** (Pellet): $\tilde{\nu}$ = 3349, 2229, 1580, 1510, 1290 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 212.0 (4.472), 251.5 (4.119), 287.5 (3.664), 292.0 (3.653) nm. **MS** (EI, 70 eV): m/z (%) = 189 (27) $[M]^+$, 55 (100) $[C_4H_7]^+$. Calcd for **$C_{11}H_{11}NO_2$**: 189.0790. Found: 189.0790 (EI-HRMS).

2-(2-Methylallyloxy)-5-nitro-phenol (16), 2-(2-Methylallyloxy)-4-nitro-phenol (24): According to general procedure **B**, 4-Nitrocatechol (**7**) (500 mg, 3.22 mmol) was reacted with 3-Bromo-2-methyl-propene (**26**) (479 mg, 3.55 mmol, 358 µL, 1.1 eq.) within 4 h at 80 °C and a 14.5:1 mixture of the two product regioisomers (396 mg, 1.89 mmol, 58 %) was obtained as a yellow solid after column chromatography on silica (P/EtOAc = 30:1 → 5:1). Main isomer **16:** **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.83 (s, 3 H, 2'-CH_3), 4.63 (s, 2 H, 1'-H_2), 5.07–5.11 (m, 2 H, 3'-H_2), 5.83 (s, 1 H, OH), 6.90 (m_c, 1 H, 5-H), 7.75–7.83 (m, 2 H, 2-H, 6-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.22 (2'-CH_3), 73.09 (C-1'), 110.20, 110.78 (C-2, C-5), 114.50 (C-3'), 116.76 (C-6), 138.97 (C-2'), 141.91 (C-1), 145.63 (C-3), 150.80 (C-4) ppm. **IR** (Pellet): $\tilde{\nu}$ = 3355, 1606, 1508, 1448, 1340, 1276 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 209.5 (4.054), 241.0 (3.907), 301.0 (3.754), 337.0 (3.830), 451.5 (2.435) nm. **MS** (EI, 70 eV): m/z (%) = 439.0 (59) $[2 \times M–2\ H+Na]^-$, 207.9 (98) $[M–H]^-$, 153.0 (100) $[M–C_4H_8]^-$. Calcd for **$C_{10}H_{11}NO_4$**: 208.06153 $[M–H]^-$. Found: 208.06160 $[M–H]^-$.

4-*tert*-Butyl-2-(2-methylallyloxy)-phenol (17), 5-*tert*-Butyl-2-(2-methylallyloxy)-phenol (25): According to general procedure **B**, 4-*tert*-butylcatechol (**8**) (1.50 g, 9.03 mmol) was treated with 3-bromo-2-methylpropene (**26**) (1.34 mg, 9.93 mmol, 1.00 mL, 1.1 eq.) for 2 h at room temperature to obtain a 1:1 mixture of regioisomers **17** and **25** (934 mg, 4.24 mmol, 47 %) as a colorless liquid after column chromatography on silica (P/EtOAc = 100:1 → 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.31, 1.32 (s, 9 H, $C(CH_3)_3$), 1.86, 1.87 (m_c, 3 H, 2'-CH_3), 4.50, 4.54 (s, 2 H, 1'-H_2), 5.04, 5.06, 5.12, 5.14 (m_c, 2 H, 3'-H_2), 5.60, 5.69 (s, 1 H, OH), 6.81 (d, J = 8.4 Hz, 1 H, 3-H^{25}, 6-H^{17}), 6.86 (dd, J = 8.5, 2.2 Hz, 1 H, 4-H^{25}/5-H^{17}), 6.89–6.96 (m, 3 H, Ar-H), 7.04 (d, J = 2.2 Hz, 6-H^{25}/3-H^{17}) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.36, 19.41 (2'-CH_3), 31.40, 31.51(C(CH_3)$_3$), 34.17, 34.32 ($C(CH_3)_3$, 72.70, 72.74 (C-1'), 109.81, 111.53, 112.22, 113.86, 116.40, 118.08 (C-3, C-6, C-4^{25}, C-5^{17}), 113.12, 113.34 (C-3'), 140.62,

140.70, 143.18, 143.36, 143.42, 144.90, 145.05, 145.13 (C-2', C-1, C-2, C-5[25], C-4[25]) ppm. **IR** (Film): $\tilde{\nu}$ = 3550, 2963, 1592, 1518, 1454, 1365, 1279, 1215 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 199.0 (4.691), 279.0 (3.500) nm. **MS** (DCI): m/z (%) = 255 (63) $[M+NH_3+NH_4]^+$, 238 (100) $[M+NH_4]^+$. Calcd for **$C_{14}H_{20}O_2$**: 243.13555 $[M+Na]^+$. Found: 243.13554 $[M+Na]^+$ (ESI-HRMS).

2,4-Di-*tert*-butyl-6-(2-methylallyloxy)-phenol (18): According to general procedure **B**, 3,5-di-*tert*-butylcatechol (**9**) (500 mg, 2.25 mmol) was reacted with 3-chloro-2-methylpropene (**26**) (224 mg, 2.47 mmol, 242 µL, 1.1 eq.) within 24 h at room temperature to provide the desired product **18** (317 mg, 1.15 mmol, 51 %) as a colorless crystalline solid after column chromatography on silica (P/EtOAc = 150:1 → 50:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, 2-C(CH_3)$_3$), 1.43 (s, 9 H, 4- C(CH_3)$_3$), 1.87 (s, 3 H, 2'-CH_3), 4.50 (s, 2 H, 1'-H_2), 5.03 (m_c, 1 H, 3'-H_a), 5.12 (m_c, 1 H, 3'-H_b), 5.93 (s, 1 H, OH), 6.82 (d, J = 2.3 Hz 1 H, 5-H), 6.93 (d, J = 2.3 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 19.51 (2'-CH_3), 29.47 (4-C(*C*H_3)$_3$), 31.63 (2-C(*C*H_3)$_3$) 34.56 (4-*C*(CH_3)$_3$), 34.88 (2-*C*(CH_3)$_3$), 73.06 (C-1'), 107.36 (C-5), 113.20 (C-3'), 115.89 (C-3), 134.58, 140.86, 141.25, 142.00, 145.20 (C-2', C-1, C-2, C-4, C-6) ppm. **IR** (Pellet): $\tilde{\nu}$ = 3455, 2958, 1595, 1421, 1362, 1302, 1252, 1219 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 201.5 (4.682), 278.5 (3.387) nm. **MS** (EI, 70 eV): m/z (%) = 276 (30) $[M]^+$, 173 (29) $[M–C_8H_{16}]^+$, 57 (46) $[C_4H_9]$. Calcd for **$C_{18}H_{28}O_2$**: 299.19815 $[M+Na]^+$. Found: 299.19826 $[M+Na]^+$ (ESI-HRMS).

SYNTHESIS OF PHENOL 65

(2-Hydroxy-phenyl)-carbamic acid *tert*-butyl ester (62): 2-Aminophenol (**61**) (2.00 g, 18.3 mmol) in THF (20 mL) was treated with di-*tert*-butyldicarbonate (4.20 g, 19.2 mmol, 4.42 mL, 1.05 eq.) and stirred for 13 h at room temperature. Then the solvent was removed in vacuum and the residue dissolved in H_2O (50 mL). The aqueous phase was extracted with EtOAc (3 × 50 mL) and the solvent removed in vacuum. The remaining solid was washed with CCl_4 to yield the protected phenol **62** (3.60 g, 17.2 mmol, 94 %) as colorless crystals. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.53 (s, 9 H, C(CH_3)$_3$), 6.68 (s, 1 H, NH), 6.86 (dt, J = 7.7, 1.8 Hz, 1 H, 5-H), 6.96 (dd, J = 8.1, 1.6 Hz 1 H, 3-H), 7.00–7.11 (m, 2 H, 4-H, 6-H), 8.17 (s, 1 H, OH) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 28.22 (C(*C*H_3)$_3$), 82.03 (*C*(CH_3)$_3$), 118.66, 120.74, 121.27, 125.47, 125.57 (C-1, C-3, C-4, C-5, C-6), 147.26 (C-2), 154.98 (*C*O_2C(CH_3)$_3$) ppm. **IR** (Pellet): $\tilde{\nu}$ = 3427, 3292, 1691, 1614, 1522, 1456, 1326, 1227 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 204.5 (4.576), 235.0 (4.026),

281.0 (3.550) nm. **MS** (ESI): m/z (%) = 441 (55) $[2\ M+Na]^+$, 232 (100) $[M+Na]^+$. Calcd for $\mathbf{C_{11}H_{15}NO_3}$: 232.09441 $[M+Na]^+$. Found: 232.09447 $[M+Na]^+$ (ESI-HRMS).

(2-Triisopropylsilanyloxyphenyl)-carbamic acid *tert*-butyl ester (63): A solution of **62** (1.29 g, 6.17 mmol) and imidazole (1.5 Äq, 630 mg, 9.25 mmol) in CH_2Cl_2 (20 mL) was treated with TIPS-Cl (1.78 g, 9.25 mmol, 1.98 mL, 1.5 eq.) and stirred for 20 h at room temperature. Afterwards H_2O (50 mL) was added and the reaction mixture extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with saturated aqueous NaCl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. After purification via column chromatography on silica (P/EtOAc = 100:1) the double protected phenol **63** (2.13 g, 5.83 mmol, 95 %) was received as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.12 (d, J = 7.3 Hz, 18 H, $CH(CH_3)_2$), 1.24–1.41 (m, 3 H, $CH(CH_3)_2$), 1.51 (s, 9 H, $C(CH_3)_3$), 6.78–6.89 (m, 2 H, 3-H, 5-H), 6.93 (dt, J = 6.9, 2.2 Hz, 1 H, 4-H), 7.11 (s, 1 H, OH), 7.99 (d, J = 8.0 Hz, 1 H, 6-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 12.68 ($CH(CH_3)_2$), 17.89 ($CH(CH_3)_2$), 28.29 ($C(CH_3)_3$), 80.00 ($C(CH_3)_3$), 117.29 (C-3), 118.48 (C-6), 121.52 (C-5), 122.16 (C-4), 129.81 (C-1), 143.88 (C-2), 152.75 ($CO_2C(CH_3)_3$) ppm. **IR** (Film): $\tilde{\nu}$ = 3438, 2946, 2869, 1735, 1598, 1450, 1367, 1328, 1265, 1234 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 206.5 (4.609), 237.0 (4.152), 280.0 (3.480) nm. **MS** (DCI): m/z (%) = 749 (100) $[2\ M+NH_4]^+$, 383 (95) $[M+NH_4]^+$, 366 (13) $[M+H]^+$. Calcd for $\mathbf{C_{20}H_{35}NO_3Si}$: 366.24590 $[M+H]^+$. Found: 366.24593 $[M+H]^+$ (ESI-HRMS).

(2-Methylallyl)-(2-triisopropylsilanyloxyphenyl)-carbamic acid *tert*-butyl ester (64): A solution of **63** (2.03 g, 5.55 mmol) in dry DMF (60 mL) was treated with 3-Brom-2-methylpropene (**26**) (2.25 g, 16.7 mmol, 1.68 mL, 3.0 eq.) and the resulting reaction mixture cooled to 0 °C before NaH (60 % in mineral oil, 244 mg, 6.11 mmol, 1.1 eq.) was added in small portions. After slow warming up to room temperature the mixture was stirred for further 3 h. Afterwards aqueous NH_4Cl solution (15 mL) and Et_2O (60 mL) were added carefully. The organic phase was washed with saturated aqueous NH_4Cl solution (2 × 60 mL), dried over Na_2SO_4 and the solvent was removed in vacuum. After column chromatography on silica (P/EtOAc = 100:1 → 95:5) alkene **64** (2.31 g, 5.50 mmol, 99 %) could be obtained as colorless crystals. **^{1}H-NMR** (300 MHz, DMSO-d_6, 100 °C): δ = 1.15 (d, 18 H, $CH(CH_3)_2$), 1.29–1.47 (m, 3 H, $CH(CH_3)_2$), 1.38 (s, 9 H, $C(CH_3)_3$), 1.75 (s, 3 H, 2'-CH_3), 2.98 (s, 2 H, 1'-H_2), 4.74 (m_c, 1 H, 3'-H_a), 4.80 (m_c, 1 H, 3'-H_b), 6.88–6.96 (m, 2 H, 3-H, 5-H), 7.11 (dd, J = 7.8, 1.7 Hz, 1 H, 6-H), 7.18 (ddd, J = 8.3, 7.3, 1.8 Hz, 1 H, 4-H) ppm. **^{13}C-NMR** (75.6 MHz, DMSO-d_6, 100 °C): δ = 11.84 ($CH(CH_3)_2$), 17.14 ($CH(CH_3)_2$), 19.31 (2'-CH_3), 27.35 ($C(CH_3)_3$), 53.80 (C-1'), 78.25 ($C(CH_3)_3$), 111.5 (C-3'), 118.2, 119.8, 127.2, 130.2 (C-3, C-6, C-5, C-4), 131.6 (C-1), 141.1 (C-2'), 150.6, 153.5 (C-2, $CO_2C(CH_3)_3$) ppm. **IR**

(Pellet): $\tilde{\nu}$ = , 2946, 2867, 1693, 1499, 1381, 1300 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 192.0 (4.559), 273.0 (3.284), 278.0 (3.250) nm. **MS** (EI, 70 eV): m/z (%) = 419 (47) $[M]^+$, 346 (100) $[M–C_4H_9O]^+$. Calcd for **$C_{24}H_{41}NO_3Si$**: 420.29285 $[M+H]^+$. Found: 420.29299 $[M+H]^+$ (ESI-HRMS).

(2-Hydroxyphenyl)-(2-methylallyl)- carbamic acid *tert*-butyl ester (65): TBAF·3 H_2O (1.91 g, 6.05 mmol, 1.25 eq.) was added to a solution of **64** (2.03 g, 4.84 mmol) in THF (50 mL) and the resulting mixture was stirred for 15 min at room temperature (TLC-Control). Afterwards the solvent was removed in vacuum and the crude product filtered over silica (P/EtOAc = 30:1 → 5:1) to yield alkene **65** (1.17 g, 4.44 mmol, 92 %) as a colorless crystalline solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.49 (s, 9 H, $C(CH_3)_3$), 1.72 (s, 3 H, 2'-CH_3), 4.16 (s, 2 H, 1'-H_2), 4.84–4.90 (m_c, 2 H, 3'-H_2), 6.90 (dt, J = 7.4, 1.5 Hz, 1 H, 5-H), 7.01 (dd, J = 8.2, 1.2 Hz, 1 H, 3-H), 7.10–7.19 (m, 2 H, 4-H, 6-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 20.09 (2'-CH_3), 28.11 ($C(CH_3)_3$), 56.63 (C-1'), 81.90 ($C(CH_3)_3$), 111.49 (C-3'), 119.47 (C-3), 120.94 (C-5), 125.51, 127.65 (C-4, C-6), 130.90 (C-1), 141.20 (C-2'), 150.95 (C-2), 155.53 ($CO_2C(CH_3)_3$) ppm. **IR** (Pellet): = 3248, 2973, 1651, 1597, 1513, 1403, 1294 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 274.0 (3.395) nm. **MS** (ESI): m/z (%) = 549.3 (27) $[2\ M+Na]^+$, 302.12 (100) $[M+K]^+$, 286.14 (37) $[M+Na]^+$. Calcd for **$C_{15}H_{21}NO_3$**: 286.14136 $[M+Na]^+$. Found: 286.14146 $[M+Na]^+$ (ESI-HRMS).

DOMINO WACKER-HECK REACTION

(*rac*)-(*E*)-5-(2-Methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-31) : According to general procedure **C**, phenol **10** (53.1 mg, 323 µmol) was reacted with methyl vinyl ketone (**27**) (45.3 mg, 647 µmol, 52.7 µL, 2.0 eq.), *p*-benzoquinone (140 mg, 1.29 mmol, 4.0 eq.) and palladium trifluoroacetate (10.8 mg, 32.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.35 mL) at room temperature for 10 h. Purification by column chromatography on silica (P/EtOAc = 5:1) yielded (*rac*)-**31** (66.2 mg, 285 µmol, 88 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, 2'-CH_3), 2.26 (s, 3 H, 1-H_3), 2.48 (ddd, J = 14.4, 8.3, 1.2 Hz, 1 H, 5-H_a), 2.65 (ddd, J = 14.5, 7.1, 1.5 Hz, 1 H, 5-H_b), 3.87 (d, J = 11.3 Hz, 1 H, 3'-H_a), 3.96 (d, J = 11.3 Hz, 1 H, 3'-H_b), 6.14 (dt, J = 15.9, 1.4 Hz, 1 H, 3-H), 6.76–6.93 (m, 5 H, 4-H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.37 (2'-CH_3), 27.08 (C-1), 38.81 (C-5), 70.43 (C-2'), 73.63 (C-3'), 117.00, 117.57 (C-5', C-8'), 121.22, 122.02 (C-6', C-7'), 134.64 (C-3), 141.26 (C-4), 141.97, 142.08 (C-4'a, C-8'a), 198.05 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2980 (C–H), 1674 (C=O), 1630, 1593 (C=C), 1494, 1362 (CH_3), 1264, 1201 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 200.0 (4.719), 217.5 (4.329), 278.0 (3.507), 331.0 (2.419)

nm. **MS** (EI, 70 eV): m/z (%) = 232 (30) $[M]^+$, 149 (100) $[M–C_5H_7O]^+$. Calcd for $\mathbf{C_{14}H_{16}O_3}$: 233.11722 $[M+H]^+$. Found: 233.11711 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(2-Methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-32): Phenol **10** (49.8 mg, 303 µmol) was reacted with methyl acrylate (**28**) (52.2 mg, 607 µmol, 55.0 µL, 2.0 eq.), *p*-benzoquinone (131 mg, 1.21 mmol, 4.0 eq.) and palladium trifluoroacetate (10.1 mg, 30.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.35 mL) at room temperature for 12 h following general procedure **C**. Purification by column chromatography on silica (P/EtOAc = 6:1) yielded (*rac*)-**32** (66.1 mg, 266 µmol, 88 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, 2'-CH_3), 2.48 (ddd, J = 14.4, 8.3, 1.3 Hz, 1 H, 4-H_a), 2.60 (ddd, J = 14.2, 7.2, 1.6 Hz, 1 H, 4-H_b), 3.74 (s, 3 H, OMe), 3.85 (d, J = 11.3 Hz, 1 H, 3'-H_a), 3.96 (d, J = 11.3 Hz, 1 H, 3'-H_b), 5.92 (dt, J = 15.7, 1.4 Hz, 1 H, 2-H), 6.79–6.92 (m, 4 H, Ar-H), 7.00 (ddd, J = 15.6, 8.2, 7.2 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.23 (2'-CH_3), 38.48 (C-4), 51.54 (OMe), 70.28 (C-2'), 73.58 (C-3'), 116.95, 117.64 (C-5', C-8'), 121.13, 121.98 (C-6', C-7'), 124.81 (C-2), 141.98, 142.07 (C-4'a, C-8'a), 142.61 (C-3), 166.38 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2981, 1724, 1659, 1594, 1494, 1436, 1264 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 201.0 (4.720), 277.5 (3.472) nm. **MS** (EI, 70 eV): m/z (%) = 248 (24) $[M]^+$, 149 (100) $[M–C_5H_7O_2]^+$. Calcd for $\mathbf{C_{14}H_{16}O_4}$: 249.11214 $[M+H]^+$. Found: 249.11214 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(2-Methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid ethyl ester ((*rac*)-33): Phenol **10** (70.0 mg, 426 µmol) was reacted with ethyl acrylate (**29**) (85.4 mg, 853 µmol, 92.7 µL, 2.0 eq.), *p*-benzoquinone (184 mg, 1.71 mmol, 4.0 eq.) and palladium trifluoroacetate (14.2 mg, 42.6 µmol, 0.1 eq.) in CH_2Cl_2 (0.45 mL) at 40 °C for 20 h following general procedure **C**. Purification by column chromatography on silica (P/EtOAc = 10:1) yielded (*rac*)-**33** (80.2 mg, 306 µmol, 72 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 1.33 (s, 3 H, 2'-CH_3), 2.48 (ddd, J = 14.2, 8.2, 1.2 Hz, 1 H, 4-H_a), 2.60 (ddd, J = 14.5, 7.3, 1.5 Hz, 1 H, 4-H_b), 3.85 (d, J = 11.3 Hz, 1 H, 3'-H_a), 3.97 (d, J = 11.3 Hz, 1 H, 3'-H_b), 4.20 (q, J = 7.2 Hz, 2 H, CH_2CH_3), 5.91 (dt, J = 15.6, 1.4 Hz, 1 H, 2-H), 6.79–6.92 (m, 4 H, Ar-H), 6.98 (ddd, J = 15.6, 8.1, 7.3 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 14.22 (OCH_2CH_3), 21.25 (2'-CH_3), 38.50 (C-4), 60.39 (OCH_2CH_3), 70.28 (C-2'), 73.63 (C-3'), 116.96, 117.65 (C-5', C-8'), 121.13, 121.98 (C-6', C-7'), 125.28 (C-2), 142.01, 142.09 (C-4'a, C-8'a), 142.24 (C-3), 165.99 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2981, 1719, 1656, 1594, 1369, 1264 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 200.5 (4.727), 278.0 (3.486) nm. **MS** (EI, 70 eV): m/z (%) = 262.2 (17) $[M]^+$, 149.1 (100) $[M–C_6H_9O_2]^+$. Calcd for $\mathbf{C_{15}H_{18}O_4}$: 263.12779 $[M+H]^+$. Found: 263.12771 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*/*Z*)-4-(2-Methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-ennitrile ((*rac*)-34): Phenol **10** (70.0 mg, 426 µmol) was reacted with acryl nitrile (**30**) (45.2 mg, 853 µmol, 92.7 µL, 2.0 eq.), *p*-benzoquinone (184 mg, 1.71 mmol, 4.0 eq.) and palladium trifluoroacetate (14.2 mg, 42.6 µmol, 0.1 eq.) in CH_2Cl_2 (0.45 mL) at 60 °C for 3 d following general procedure **C**. Purification by column chromatography on silica (P/EtOAc = 10:1) yielded **34** (*E*/*Z* = 5:1, 48.7 mg, 226 µmol, 44 %) as a mixture of the doublebond isomers as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.32, 1.34 (s, 3 H, 2'-CH_3), 2.44 (ddd, *J* = 14.5, 8.3, 1.2 Hz, 1 H, 4-$H_{a(E)}$), 2.59–2.76 (m, 1 H, 4-$H_{b(E)}$, 4-$H_{a(Z)}$), 2.84 (ddd, *J* = 14.9, 6.7, 1.2 Hz, 1 H, 4-$H_{b(Z)}$) 3.81–4.01 (m, 2 H, 3'-H_2), 5.42 (dt, *J* = 16.3, 1.5 Hz, 1 H, 2-$H_{(E)}$), 5.51 (dt, *J* = 11.0, 1.4 Hz, 1 H, 2-$H_{(Z)}$), 6.64 (ddd, *J* = 11.2, 8.6, 6.8, 1 H, 3-$H_{(Z)}$), 6.78 (m_c, 1 H, 3-$H_{(E)}$), 6.82–6.94 (m, 4 H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.16 (2'-CH_3), 39.15 (C-4), 70.18 (C-2'), 73.20 (C-3'), 103.41 (C-2), 116.82 (CN), 116.98, 117.51 (C-5', C-8'), 121.34, 122.09 (C-6', C-7'), 141.59, 141.85 (C-4'a, C-8'a), 149.46 (C-3) ppm. **IR** (Film): $\tilde{\nu}$ = 2981, 2225, 1636, 1594, 1494, 1464, 1386, 1264, 1205 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 200.5 (4.732), 277.5 (3.484) nm. **MS** (EI, 70 eV): m/z (%) = 215.1 (33) $[M]^+$, 149.1 (100) $[M–C_4H_4N]^+$. Calcd for **$C_{13}H_{13}NO_2$**: 238.08385 $[M+Na]^+$. Found: 238.08387 $[M+Na]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(8-Methoxy-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-35): Following general procedure **C**, phenol **12** (75.1 mg, 387 µmol) was reacted with methyl vinyl ketone (**27**) (54.2 mg, 773 µmol, 54.2 µL, 2.0 eq.), *p*-benzoquinone (167 mg, 1.55 mmol, 4.0 eq.) and palladium trifluoroacetate (10.8 mg, 38.7 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at room temperature within 5 h. After purification by column chromatography on silica (P/EtOAc = 8:3) the desired compound (*rac*)-**35** (79.5 mg, 303 µmol, 78 %) was obtained as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 2'-CH_3), 2.26 (s, 3 H, 1-H_3), 2.48 (ddd, *J* = 14.4, 8.0, 1.2 Hz, 1 H, 5-H_a), 2.65 (ddd, *J* = 14.5, 7.0, 1.3 Hz, 1 H, 5-H_b), 3.87–3.94 (m, 4 H, OMe, 3'-H_a), 4.04 (d, *J* = 11.2 Hz, 1 H, 3'-H_b), 6.15 (dt, *J* = 15.9, 1.2 Hz, 1 H, 3-H), 6.52 (m, 2 H, Ar-H), 6.82 (m, 2 H, Ar-H, 4-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.34 (2'-CH_3), 27.13 (C-1), 38.66 (C-5), 56.07 (OMe), 70.62 (C-2'), 73.67 (C-3'), 103.80, 110.30 (C-5', C-7'), 121.00 (C-6'), 131.64 (C-8'a), 134.73 (C-3), 141.21 (C-4), 142.64 (C-4'a), 148.83 (C-8'), 198.09 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2934, 1673, 1597, 1474, 1363, 1332, 1257, 1201, 1132, 1102, 983, 909, 768, 718 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 206.0 (4.703). **MS** (EI, 70 eV): m/z (%) = 262 (17) $[M]^+$, 179 (34) $[M–C_5H_7O]^+$. Calcd for **$C_{15}H_{18}O_4$**: 263.12779 $[M+H]^+$. Found: 263.12766 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(5-Methoxy-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)pent-3-en-2-one ((*rac*)-36): Following general procedure **C**, phenol **20** (77.6 mg, 401 µmol) was reacted with methyl vinyl ketone (**27**)

(56.1 mg, 801 µmol, 65.3 µL, 2.0 eq.), *p*-benzoquinone (173 mg, 1.60 mmol, 4.0 eq.) and palladium trifluoroacetate (13.2 mg, 40.1 µmol, 0.1 eq.) in CH_2Cl_2 (0.45 mL) at room temperature for 6 h. Purification by column chromatography on silica (P/EtOAc = 8:3) provided the desired compound (*rac*)-**36** (77.2 mg, 294 µmol, 74 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 2'-CH_3), 2.26 (s, 3 H, 1-H_3), 2.48 (ddd, *J* = 14.4, 8.0, 1.2 Hz, 1 H, 5-H_a), 2.65 (ddd, *J* = 14.5, 7.0, 1.3 Hz, 1 H, 5-H_b), 3.87–3.94 (m, 4 H, OMe, 3'-H_a), 4.04 (d, *J* = 11.2 Hz, 1 H, 3'-H_b), 6.15 (dt, *J* = 15.9, 1.2 Hz, 1 H, 3-H), 6.52 (m, 2 H, Ar-H), 6.82 (m, 2 H, Ar-H, 4-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.49 (2'-CH_3), 26.98 (C-1), 38.56 (C-5), 56.07 (OMe), 70.12 (C-2'), 73.67 (C-3'), 104.65 (C-6'), 109.66 (C-8'), 120.07 (C-7'), 131.60 (C-4'a), 134.68 (C-3), 141.31 (C-4), 142.79 (C-8'a), 149.31 (C-5'), 198.04 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2936, 1673, 1596, 1478, 1255, 1218 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 207.0 (4.701) nm. **MS** (ESI): m/z (%) = 285 $[M+Na]^+$, 236 $[M+H]^+$. Calcd for **$C_{15}H_{18}O_4$**: 263.12779 $[M+H]^+$. Found: 263.12779 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(8-Fluoro-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-37): According to general procedure **C**, phenol **13** (74.0 mg, 406 µmol) was reacted with methyl vinyl ketone (**27**) (56.9 mg, 812 µmol, 66.2 µL, 2.0 eq.), *p*-benzoquinone (176 mg, 1.62 mmol, 4.0 eq.) and palladium trifluoroacetate (13.5 mg, 40.6 µmol, 0.1 eq.) in CH_2Cl_2 (0.45 mL) for 5 h at room temperature. Purification by column chromatography on silica (P/EtOAc = 5:1) yielded the desired product (*rac*)-**37** (75.3 mg, 299 µmol, 74 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 2'-CH_3), 2.25 (s, 3 H, 1-H_3), 2.47 (dd, *J* = 14.6, 8.1 Hz, 1 H, 5-H_a), 2.63 (dd, *J* = 14.6, 7.0 Hz, 1 H, 5-H_b), 3.89 (d, *J* = 11.3 Hz, 1 H, 3'-H_a), 4.01 (d, *J* = 11.3 Hz, 1 H, 3'-H_b), 6.14 (d, *J* = 16.0 Hz, 1 H, 3-H), 6.60–6.71 (m, 2 H, Ar-H), 6.72–6.87 (m, 2 H, Ar-H, 4-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.18 (2'-CH_3), 27.13 (C-1), 38.62 (C-5), 70.34 (C-2'), 73.98 (C-3'), 108.04, 108.27 (C-7'), 112.82, 112.86 (C-5'), 120.57, 120.68 (C-6'), 130.94, 131.13 (C-8'a), 134.73 (C-3), 140.57 (C-4), 143.52, 143.56 (C-4'a), 149.99, 153.23 (C-8'), 197.87 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2983, 1674, 1597, 1497, 1476, 1363, 1314, 1253 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 198.5 (4.609), 214.5 (4.327), 269.0 (3.129), 275.0 (3.078) nm. **MS** (EI, 70 eV): m/z (%) = 250.1 (27) $[M]^+$, 167.0 (99) $[M–C_5H_7O]^+$, 43.0 (100) $[C_2H_3O]^+$. Calcd for **$C_{14}H_{15}FO_3$**: 251.10780 $[M+H]^+$. Found: 251.10788 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-3-Methyl-3-(4-oxo-pent-2-enyl)-2,3-dihydrobenzo[*b*][1,4]dioxin-6-carboxylic acid ethyl ester ((*rac*)-38): According to general procedure **C**, phenol **14** (100 mg, 423 µmol) was reacted with methyl vinyl ketone (**27**) (59.3 mg, 847 µmol, 69.0 µL, 2.0 eq.), *p*-benzoquinone (183 mg, 1.69 mmol, 4.0 eq.) and palladium trifluoroacetate (14.1 mg, 42.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) for 5 h at 60 °C.

Purification by column chromatography on silica (P/EtOAc = 4:1) yielded the desired product (*rac*)-**38** (114.9 mg, 378 µmol, 89 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 3-CH_3), 1.36 (t, J = 7.3 Hz, 3 H, $CO_2CH_2CH_3$), 2.27 (s, 3 H, 5'-H_3), 2.47 (ddd, J = 14.4, 8.3, 1.1 Hz, 1 H, 1'-H_a), 2.62 (ddd, J = 14.3, 7.0, 1.4 Hz, 1 H, 1'-H_b), 3.91 (d, J = 11.4 Hz, 1 H, 2-H_a), 4.01 (d, J = 11.4 Hz, 1 H, 2-H_b), 4.33 (q, J = 7.3 Hz, 2 H, $CO_2CH_2CH_3$), 6.15 (m_c, 1 H, 3'-H), 6.80 (ddd, J = 15.5, 8.0, 7.0 Hz, 1 H, 2'-H), 6.91 (m_c, 1 H, 8-H), 7.55–7.66 (m, 2 H, 5-H, 7-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 14.31 ($CO_2CH_2CH_3$), 21.26 (3-CH_3), 27.16 (C-5'), 38.80 (C-1'), 60.76 ($CO_2CH_2CH_3$), 70.63 (C-3), 73.71 (C-2), 116.78, 119.25, 123.19 (C-5, C-7, C-8), 124.45 (C-6), 134.82 (C-3'), 140.61 (C-2'), 141.46 (C-3), 146.12 (C-2), 166.00 (CO_2Et), 197.93 (C-4') ppm. **IR** (Film): $\tilde{\nu}$ = 2982, 1714, 1588, 1508, 1433, 1366, 1293, 1205 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 209.0 (4.556), 222.0 (4.558), 254.5 (4.067), 295.0 (3.680) nm. **MS** (ESI): m/z (%) = 327.1 (50) $[M+Na]^+$, 322.2 (63) $[M+NH_4]^+$, 305.2 (22) $[M+H]^+$. Calcd for **$C_{17}H_{20}O_5$**: 305.13835 $[M+H]^+$. Found: 305.13820 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(6,8-Di-*tert*-butyl-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one (*rac*)-39): Following general procedure **C**, phenol **18** (100 mg, 362 µmol) was converted with methyl vinyl ketone (**27**) (50.8 mg, 724 µmol, 59.0 µL, 2.0 eq.), *p*-benzoquinone (156 mg, 1.45 mmol, 4.0 eq.) and palladium trifluoroacetate (12.0 mg, 36.2 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at 40 °C for 4 d. Purification by column chromatography on silica (P/EtOAc = 10:1) provided (*rac*)-**39** (84.8 mg, 246 µmol, 68 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, $C(CH_3)_3$), 1.36 (s, 3 H, 2'-CH_3), 1.39 (s, 9 H, $C(CH_3)_3$), 2.25 (s, 3 H, 1-H_3), 2.55 (ddd, J = 14.1, 7.9, 1.2 Hz, 1 H, 5-H_a), 2.65 (ddd, J = 14.1, 7.3, 1.3 Hz, 1 H, 5-H_b), 3.86 (d, J = 11.1 Hz, 1 H, 3'-H_a), 3.94 (d, J = 10.9 Hz, 1 H, 3'-H_b), 6.17 (dt, J = 16.1, 1.3 Hz, 1 H, 3-H), 6.81 (d, J = 2.3 Hz, 1 H, 5'-H), 6.92 (m_c, J = 15.9, 7.5 Hz, 1 H, 4-H), 6.92 (d, J = 2.3 Hz, 1 H, 7'-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.26 (2'-CH_3), 26.75 (C-1), 29.76, 31.48 ($C(CH_3)_3$), 34.32, 35.11 ($C(CH_3)_3$), 39.59 (C-5), 70.18 (C-2'), 73.46 (C-3'), 112.21 (C-5'), 116.50 (C-7'), 134.82 (C-3), 137.67, 138.00, 141.36, 142.84 (C-6', C-8', C-4'a, C-8'a), 141.95 (C-4), 198.13 (C-2) ppm. **IR** (Pellet): $\tilde{\nu}$ = 2962, 1678, 1587, 1483, 1420, 1363, 1308, 1242 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 204.5 (4.763), 279.5 (3.474), 383.5 (3.476) nm. **MS** (ESI): m/z (%) = 367.2 (71) $[M+Na]^+$, 362.3 (100) $[M+NH_4]^+$, 345.2 (90) $[M+H]^+$. Calcd for **$C_{22}H_{32}O_3$**: 345.24242 $[M+H]^+$. Found: 345.24232 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(2,7-Dimethyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-40), (*rac*)-(*E*)-5-(2,6-Dimethyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-41): Following general procedure **C**, the mixture of regioisomers **11** and **19** (100 mg, 561 µmol) was reacted with methyl vinyl

ketone (**27**) (78.7 mg, 1.12 µmol, 91.5 µL, 2.0 eq.), *p*-benzoquinone (243 mg, 2.24 mmol, 4.0 eq.) and palladium trifluoroacetate (18.7 mg, 56.1 µmol, 0.1 eq.) in CH_2Cl_2 (0.55 mL) for 6 h at room temperature. Purification by column chromatography on silica (P/EtOAc = 8:1) yielded a mixture of the isomers (*rac*)-**40** and (*rac*)-**41** (110.4 mg, 448 µmol, 80 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.31 (s, 3 H, 2'-CH_3), 2.23–2.28 (m, 6 H, 1-H_3, Ar-CH_3), 2.40–2.51 (m, 1 H, 5-H_a), 2.58–2.69 (m, 1 H, 5-H_b), 3.80–3.87 (m, 1 H, 3'-H_a), 3.90–3.97 (m, 1 H, 3'-H_b), 6.08–6.18 (m_c, 1 H, 3-H), 6.60–6.90 (m, 4 H, 4-H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 20.60, 20.67 (Ar-CH_3), 21.34, 21.37 (2'-CH_3), 27.05 (C-1), 38.71, 38.83 (C-5), 70.46, 70.50 (C-2'), 73.42, 73.63 (C-3'), 116.61, 117.19, 117.31, 117.89, 121.78, 122.58 (C-5'^{40}, C-6'^{40}, C-8'^{40}, C-5'^{41}, C-7'^{41}, C-8'^{41}), 130.91, 131.70 (C-7'^{40}, C-6'^{41}), 134.62 (C-3), 139.58, 139.75 (C-4'a^{40}, C-8'a^{41}), 141.42 (C-4), 141.56, 141.65 (C-8'a^{40}, C-4'a^{41}), 198.06 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2979, 1674, 1593, 1506, 1426, 1362, 1279, 1215 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 202.5 (4.650), 283.5 (3.528) nm. **MS** (EI, 70 eV): m/z (%) = 246.2 (66) $[M]^+$, 163.1 (100) $[M–C_5H_7O]^+$. Calcd for **$C_{15}H_{18}O_3$**: 247.13287 $[M+H]^+$. Found: 247.13275 $[M+ H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-3-Methyl-3-(4-oxo-pent-2-enyl)-2,3-dihydrobenzo[*b*][1,4]dioxin-6-carbonitrile ((*rac*)-42), (*rac*)-(*E*)-2-Methyl-2-(4-oxopent-2-enyl)-2,3-dihydrobenzo[*b*][1,4]dioxin-6-carbonitrile ((*rac*)-43):
The mixture of regioisomers **15** and **23** (70.0 mg, 370 µmol) was reacted with methyl vinyl ketone (**27**) (51.9 mg, 740 µmol, 60.3 µL, 2.0 eq.), *p*-benzoquinone (160 mg, 1.48 mmol, 4.0 eq.) and palladium trifluoroacetate (13.5 mg, 37.0 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at 40 °C for 38 h following general procedure **C**. Purification by column chromatography on silica (P/EtOAc = 4:1) provided a mixture of the isomers (*rac*)-**42** and (*rac*)-**43** (86.9 mg, 338 µmol, 91 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33, 1.35 (s, 3 H, 3^{42}-CH_3/2^{43}-CH_3), 2.26, 2.27 (s, 3 H, 5'-H_3), 2.43–2.54 (m, 1 H, 1'-H_a), 2.55–2.66 (m, 1 H, 1'-H_b), 3.86–4.05 (m, 2 H, 2^{42}-H/3^{43}-H), 6.11 (m_c, 1 H, 3'-H), 6.70–6.83 (m, 1 H, 2'-H), 6.88-6.97 (m, 1 H, Ar-H), 7.12–7.21 (m, 2 H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.18, 21.24 (3-CH_3), 27.32, 27.39 (C-5'), 38.76, 38.85 (C-1'), 70.29, 70.57 (C-3^{42}, C-2^{43}), 74.25, 74.99 (C-2^{42}, C-3^{43}), 104.35, 105.19 (C-6), 118.00, 118.56 (C-8), 118.75, 118.80 (CN), 121.01, 121.54 (C-5^{42}, C-7^{43}), 125.75, 126.52 (C-7^{42}, C-5^{43}), 134.91, 134.95 (C-3'), 139.85, 139.90 (C-4a^{42}, C-8a^{43}), 142.26, 142.34 (C-8a^{42}, C-4a^{B}), 197.74, 197.77 (C-4') ppm. **IR** (Film): $\tilde{\nu}$ = 2983, 2225, 1674, 1581, 1506, 1424, 1363, 1286 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 212.5 (4.637), 219.0 (4.632), 250.0 (4.102), 296.0 (3.648) nm. **MS** (ESI): m/z (%) = 280 (100) $[M+Na]^+$, 258 (56) $[M+H]^+$. Calcd for **$C_{15}H_{15}NO_3$**: 258.11247 $[M+H]^+$. Found: 258.11262 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(2-Methyl-7-nitro-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-44), (*rac*)-(*E*)-5-(2-Methyl-6-nitro-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-45): According to general procedure **C,** the mixture of regioisomers **16** and **24** (70.0 mg, 335 µmol) was treated with methyl vinyl ketone (**27**) (46.9 mg, 669 µmol, 54.5 µL, 2.0 eq.), *p*-benzoquinone (145 mg, 1.34 mmol, 4.0 eq.) and palladium trifluoroacetate (11.1 mg, 33.5 µmol, 0.1 eq.) in CH_2Cl_2 (0.35 mL) at 40 °C for 18 h. Purification by column chromatography on silica (P/EtOAc = 8:3) yielded a mixture of the isomers (*rac*)-**44** and (*rac*)-**45** (86.7 mg, 313 µmol, 93 %) as a yellow oil. Main isomer *rac*-**44**: **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.36 (s, 3 H, 2'-CH_3), 2.28 (s, 3 H, 1-H_3), 22.53 (ddd, J = 14.4, 8.0, 1.3 Hz, 1 H, 5-H_a), 2.63 (ddd, J = 14.5, 7.1, 1.5 Hz, 1 H, 5-H_b), 3.97 (d, J = 11.5 Hz, 1 H, 3'-H_a), 4.06 (d, J = 11.5 Hz, 1 H, 3'-H_b), 6.17 (dt, J = 15.9, 1.4 Hz, 1 H, 3-H), 6.78 (m_c, J = 15.9, 7.1 Hz, 1 H, 4-H), 6.91–7.00 (m, 1 H, Ar-H), 7.73–7.85 (m, 2 H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.15 (2'-CH_3), 27.32 (C-1), 38.78 (C-5), 70.68 (C-2'), 74.33 (C-3'), 113.77 (C-8'), 117.06, 117.45 (C-5', C-6'), 135.04 (C-3), 139.74 (C-4), 141.72 (C-8'a), 142.34 (C-7'), 147.84 (C-4'a), 197.77 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2935, 1674, 1593, 1521, 1345, 1276 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 216.0 (3.403), 301.0 (2.797), 332.5 (2.798) nm. **MS** (EI, 70 eV): m/z (%) = 277.1 (52) $[M]^+$, 194.0 (100) $[M–C_5H_7O]^+$. Calcd for **$C_{14}H_{15}NO_5$**: 278.10230 $[M+H]^+$. Found: 278.10233 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-5-(7-*tert*-Butyl-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-46), (*rac*)-(*E*)-5-(6-*tert*-Butyl-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-pent-3-en-2-one ((*rac*)-47): The mixture of regioisomers **17** and **25** (80.0 mg, 363 µmol) was reacted with methyl vinyl ketone (**27**) (50.9 mg, 726 µmol, 59.2 µL, 2.0 eq.), *p*-benzoquinone (157 mg, 1.45 mmol, 4.0 eq.) and palladium trifluoroacetate (11.1 mg, 36.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) for 6 h at room temperature following general procedure **C**. A mixture of the isomers (*rac*)-**46** and (*rac*)-**47** (88.7 mg, 308 µmol, 85 %) was obtained after purification by column chromatography on silica (P/EtOAc = 5:1) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, $C(CH_3)_3$), 1.32, 1.33 (s, 3 H, 2'-CH_3), 2.26, 2.27 (s, 3 H, 1-H_3), 2.43–2.54 (m, 1 H, 5-H_a), 2.60–2.70 (m, 1 H, 5-H_b), 3.81–3.89 (m, 1 H, 3'-H_a), 3.91–3.99 (m, 1 H, 3'-H_b), 6.11–6.19 (m, 1 H, 3-H), 6.77–6.93 (m, 4 H, 4-H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.43, 21.47 (2'-CH_3), 27.02, 27.14 (C-1), 31.42 ($C(CH_3)_3$), 34.15, 34.21 ($C(CH_3)_3$), 38.87, 38.99 (C-5), 70.45, 70.55 (C-2'), 73.56, 73.73 (C-3'), 114.02, 114.52, 116.32, 116.82, 118.16, 118.96 (C-5'^{46}, C-6'^{46}, C-8'^{46}, C-5'^{47}, C-7'^{47}, C-8'^{47}), 134.61, 134.64 (C-3), 139.51, 139.60, 141.25, 141.29, 144.59, 145.42 (C-4'a, C-8'a, C-7'^{46}, C-6'^{47}), 141.42, 141.55 (C-4), 198.09, 198.12 (C-2) ppm. **IR** (Film): $\tilde{\nu}$ = 2964, 1675, 1590, 1504, 1421, 1362, 1275, 1201 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 202.0 (4.740), 281.0 (3.562) nm. **MS** (ESI): m/z

(%) = 311.2 (100), $[M+Na]^+$, 289.2 (71) $[M+H]^+$. Calcd for $\mathbf{C_{18}H_{24}O_3}$: 289.17982 $[M+H]^+$. Found: 289.17993 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(8-Methoxy-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-48): According to general procedure **C**, phenol **12** (76.3 mg, 393 µmol) was reacted with methyl acrylate (**28**) (67.6 mg, 786 µmol, 71.1 µL, 2.0 eq.), *p*-benzoquinone (170 mg, 1.57 mmol, 4.0 eq.) and palladium trifluoroacetate (13.1 mg, 39.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.45 mL) at room temperature within 7 h. Purification by column chromatography on silica (P/EtOAc = 8:3) yielded the desired compound (*rac*)-**48** (75.3 mg, 271 µmol, 69 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 2'-CH_3), 2.48 (ddd, J = 14.4, 8.3, 1.3 Hz, 1 H, 4-H_a), 2.62 (ddd, J = 14.3, 7.2, 1.4 Hz, 1 H, 4-H_b), 3.74 (s, 1 H, CO_2Me), 3.88 (s, 1 H, OMe), 3.90 (d, J = 11.2 Hz, 1 H, 3'-H_a), 4.03 (d, J = 11.2 Hz, 1 H, 3'-H_b), 5.92 (ddd, J = 15.7, 1.4 Hz, 1 H, 3-H), 6.47–6.56 (m, 2 H, 5'-H, 7'-H), 6.81 (dd, J = 8.4, 8.1 Hz, 1 H, 6'-H), 6.99 (ddd, J = 15.5, 8.0, 7.2 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.16 (2'-CH_3), 38.33 (C-4), 51.52 (CO_2CH_3), 56.02 (OMe), 70.48 (C-2'), 73.57 (C-3'), 103.71, 110.34 (C-5', C-7'), 120.89 (C-6'), 124.85 (C-2), 131.60 (C-8'a), 142.51 (C-3), 142.62 (C-4'a), 148.77 (C-8'), 166.36 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2950, 1723, 1659, 1597, 1499, 1474, 1332, 1284, 1201 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 206.0 (4.734), 262.0 (3.017) nm. **MS** (EI, 70 eV): m/z (%) = 278.2 (43) $[M]^+$, 179.1 (100) $[M–C_5H_7O_2]^+$. Calcd for $\mathbf{C_{15}H_{18}O_5}$: 279.12270 $[M+H]^+$. Found: 279.12265 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(5-Methoxy-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-49): Phenol **20** (100.0 mg, 515 µmol) was reacted with methyl acrylate (**28**) (88.6 mg, 1.03 mmol, 93.3 µL, 2.0 eq.), *p*-benzoquinone (223 mg, 2.06 mmol, 4.0 eq.) and palladium trifluoroacetate (17.1 mg, 51.5 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at room temperature within 36 h following general procedure **C**. After purification by column chromatography on silica (P/EtOAc = 4:1) the desired product (*rac*)-**49** (69.3 mg, 249 µmol, 48 %) was yielded as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.38 (s, 3 H, 2'-CH_3), 2.50–2.67 (m_c, 2 H, 4-H_2), 3.73 (s, 3 H, CO_2Me), 3.81–3.88 (m, 4 H, OMe, 3'-H_a), 3.97 (d, J = 11.3 Hz, 1 H, 3'-H_b), 5.91 (dt, J = 15.6, 1.4 Hz, 1 H, 2-H), 6.53 (m, 2 H, 6'-H, 8'-H), 6.78 (t, J = 8.3 Hz, 1 H, 7'-H), 6.98 (ddd, J = 15.6, 8.0 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.32 (2'-CH_3), 38.32 (C-4), 51.51 (CO_2CH_3), 56.11 (OMe), 69.92 (C-2'), 73.75 (C-3'), 104.68, 109.67 (C-6', C-8'), 119.97 (C-7'), 124.91 (C-2), 131.67 (C-8'a), 142.58 (C-3), 142.80 (C-4'a), 149.35 (C-5'), 166.35 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2950, 1723, 1659, 1597, 1478, 1384, 1281, 1200 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 205.5 (4.755) nm. **MS** (EI, 70 eV): m/z (%) = 278.1 (40) $[M]^+$, 179.1 (100) $[M–C_5H_7O_2]^+$. Calcd for $\mathbf{C_{15}H_{18}O_5}$: 279.12270 $[M+H]^+$. Found: 279.12269 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(8-fluoro-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-50): Following general procedure **C**, phenol **13** (100 mg, 549 µmol) was treated with methyl acrylate (**28**) (94.5 mg, 1.10 mmol, 99.5 µL, 2.0 eq.), *p*-benzoquinone (237 mg, 2.20 mmol, 4.0 eq.) and palladium trifluoroacetate (18.2 mg, 54.9 µmol, 0.1 eq.) in CH_2Cl_2 (0.55 mL) for 20 h at room temperature. Purification by column chromatography on silica (P/EtOAc = 10:1) yielded (*rac*)-**50** (107 mg, 401 µmol, 73 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 2'-CH_3), 2.47 (ddd, J = 14.3, 8.1 Hz 1.2 Hz, 1 H, 4-H_a), 2.60 (ddd, J = 14.5, 7.2, 1.4 Hz, 1 H, 4-H_b), 3.73 (s, 3 H, OMe), 3.88 (d, J = 11.3 Hz, 1 H, 3'-H_a), 4.01 (d, J = 11.3 Hz, 1 H, 3'-H_b), 5.91 (dt, J = 15.7, 1.4 Hz, 1 H, 2-H), 6.61–6.81 (m, 3 H, Ar-H), 6.97 (m_c, J = 15.5, 8.1, 7.2 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.07 (2'-CH_3), 38.33 (C-4), 51.52 (OMe), 70.24 (C-2'), 73.94 (C-3'), 107.98, 108.22 (C-7'), 112.87, 112.92 (C-5'), 120.52, 120.64 (C-6'), 125.03 (C-2), 130.96, 131.14 (C-8'a), 142.03 (C-3), 143.54, 143.59 (C-4'a), 150.00, 153.24 (C-8'), 166.25 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2951, 1724, 1660, 1597, 1497, 1476, 1314 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 199.0 (4.700), 269.0 (3.086), 275.0 (3.040) nm. **MS** (ESI): m/z (%) = 305.1 (100) $[M+K]^+$, 289.1 (57) $[M+Na]^+$, 267.1 (67) $[M+H]^+$. Calcd for **$C_{14}H_{15}FO_4$**: 267.10271 $[M+H]^+$. Found: 267.10262 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-3-(4-Methoxy-4-oxobut-2-enyl)-3-methyl-2,3-dihydrobenzo[*b*][1,4]-dioxin-6-carboxylic acid ethyl ester ((*rac*)-51): Phenol **14** (100 mg, 423 µmol) was treated with methyl acrylate (**28**) (72.9 mg, 847 µmol, 76.7 µL, 2.0 eq.), *p*-benzoquinone (183 mg, 1.69 mmol, 4.0 eq.) and palladium trifluoroacetate (14.1 mg, 42.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at 40 °C within 18 h according to general procedure **C**. Purification by column chromatography on silica (P/EtOAc = 7:1) provided (*rac*)-**51** (114.5 mg, 357 µmol, 84 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, 3-CH_3), 1.36 (t, J = 7.3 Hz, 3 H, $CO_2CH_2CH_3$), 2.47 (ddd, J = 14.4, 8.3, 1.2 Hz, 1 H, 1'-H_a), 2.58 (ddd, J = 14.4, 7.3, 1.5 Hz, 1 H, 1'-H_b), 3.74 (s, 3 H, OMe), 3.90 (d, J = 11.4 Hz, 1 H, 2-H_a), 4.00 (d, J = 11.3 Hz, 1 H, 2-H_b), 4.32 (q, J = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 5.92 (dt, J = 15.8, 1.4 Hz, 1 H, 3'-H_a), 6.88–7.03 (m, 2 H, 3'-H_b, 7-H), 6.91 (m_c, 1 H, 8-H), 7.54–7.60 (m, 2 H, 5-H, 7-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 14.31 ($CO_2CH_2CH_3$), 21.15 (3-CH_3), 38.48 (C-1'), 51.60 (OMe), 60.74 ($CO_2CH_2CH_3$), 70.49 (C-3), 73.68 (C-2), 116.74, 119.31, 123.15 (C-5, C-7, C-8), 124.42 (C-6), 125.10 (C-3'), 141.48 (C-3), 142.04 (C-2'), 146.13 (C-2), 166.04 (CO_2Et), 166.29 (C-4') ppm. **IR** (Film): $\tilde{\nu}$ = 2983, 1717, 1660, 1588, 1507, 1434, 1286, 1206 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 211.0 (3.549), 217.5 (3.521), 255.5 (3.051), 295.0 (2.684) nm. **MS** (EI, 70 eV): m/z (%) = 320.2 (23) $[M+H]^+$, 221.1 (100) $[M–C_5H_7O_2]^+$. Calcd for **$C_{17}H_{20}O_6$**: 321.13326 $[M+H]^+$. Found: 321.13332 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(6,8-Di-*tert*-butyl-2-methyl-2,3-dihydrobenzo[*b*][1,4]-dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-52): According to general procedure **C**, phenol **18** (100 mg, 362 µmol) was reacted with methyl acrylate (**28**) (62.3 mg, 724 µmol, 65.6 µL, 2.0 eq.), *p*-benzoquinone (156 mg, 1.45 mmol, 4.0 eq.) and palladium trifluoroacetate (12.0 mg, 36.2 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at 40 °C within 3 d. After purification by column chromatography on silica (P/EtOAc = 15:1) (*rac*)-**52** (112.8 mg, 313 µmol, 86 %) was provided as a white solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, $C(CH_3)_3$), 1.35 (s, 3 H, 2'-CH_3), 1.38 (s, 9 H, $C(CH_3)_3$), 2.58 (dd, J = 7.8, 1.2 Hz, 1 H, 4-H), 3.74 (s, 3 H, OMe), 3.83 (d, J = 11.1 Hz, 1 H, 3'-H_a), 3.93 (d, J = 11.1 Hz, 1 H, 3'-H_b), 5.90–5.98 (m, 1 H, 2-H), 6.79 (d, J = 2.4 Hz, 1 H, 5'-H), 6.91 (d, J = 2.4 Hz, 1 H, 7'-H), 7.05 (m_c, J = 15.5, 7.7 Hz, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.22 (2'-CH_3), 29.78, 31.49 ($C(CH_3)_3$), 34.31, 35.11 ($C(CH_3)_3$), 39.28 (C-4), 51.55 (OMe), 69.88 (C-2'), 73.38 (C-3'), 112.15 (C-5'), 116.46 (C-7'), 124.81 (C-2), 137.81, 138.03, 141.35, 142.74 (C-6', C-8', C-4'a, C-8'a), 142.99 (C-3), 166.40 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2955, 1728, 1660, 1588, 1419, 1310, 1241 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 205.0 (4.812), 284.0 (3.438), 280.0 (3.427) nm. **MS** (ESI): m/z (%) = 383.2 (24) $[M+Na]^+$, 378.3 (100) $[M+NH_4]^+$, 361.2 (45) $[M+H]^+$. Calcd for **$C_{22}H_{32}O_4$**: 361.23734 $[M+H]^+$. Found: 361.23715 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(2,7-Dimethyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-53), (*rac*)-(*E*)-4-(2,6-Dimethyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-54): A mixture of regioisomers **11** and **19** (100 mg, 561 µmol) was reacted with methyl acrylate (**28**) (96.6 mg, 1.12 mmol, 102 µL, 2.0 eq.), *p*-benzoquinone (243 mg, 2.24 mmol, 4.0 eq.) and palladium trifluoroacetate (18.7 mg, 56.1 µmol, 0.1 eq.) in CH_2Cl_2 (0.55 mL) for 9 h at room temperature following general procedure **C**. After purification by column chromatography on silica (P/EtOAc = 10:1) a mixture of the isomers (*rac*)-**53** and (*rac*)-**54** (114.6 mg, 437 µmol, 78 %) was obtained as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.30 (s, 3 H, 2'-CH_3), 2.25 (s, 3 H, Ar-CH_3), 2.41–2.51 (m, 1 H, 4-H_a), 2.54–2.64 (m, 1 H, 4-H_b), 3.74 (m, 3 H, OMe), 3.79–3.85 (m, 1 H, 3'-H_a), 3.90–3.96 (m, 1 H, 3'-H_b), 6.87–6.96 (m_c, 1 H, 2-H), 6.61–6.81 (m, 3 H, Ar-H), 6.93–7.06 (m, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 20.60, 20.66 (Ar-CH_3), 21.20, 21.23 (2'-CH_3), 38.39, 38.50 (C-4), 51.53 (OMe), 70.32, 70.36 (C-2'), 73.38, 73.58 (C-3'), 116.56, 117.25, 117.27, 117.95, 121.69, 122.54 (C-5'^{53}, C-6'^{53}, C-8'^{53}, C-5'^{54}, C-7'^{54}, C-8'^{54}), 124.75 (C-2) 130.80, 131.65 (C-7'^{53}, C-6'^{54}), 139.60, 139.76 (C-4'a^{53}, C-8'a^{54}), 141.58, 141.66 (C-8'a^{53}, C-4'a^{54}), 142.74 (C-3), 166.40 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2950, 1725, 1660, 1593, 1506, 1436, 1278 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 202.5 (4.354), 283.5 (3.160) nm. **MS** (EI, 70 eV): m/z (%) = 262.1 (46) $[M]^+$, 163.1 (100) $[M-C_5H_7O_2]^+$. Calcd for **$C_{15}H_{18}O_4$**: 263.12779 $[M+H]^+$. Found: 263.12777 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(7-Cyano-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-55), (*rac*)-(*E*)-4-(6-Cyano-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-56): Following general procedure **C,** the mixture of regioisomers **15** and **23** (70.0 mg, 370 µmol) was converted with methyl acrylate (**28**) (63.7 mg, 740 µmol, 67.1 µL, 2.0 eq.), *p*-benzoquinone (160 mg, 1.48 mmol, 4.0 eq.) and palladium trifluoroacetate (13.5 mg, 37.0 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at 40 °C for 38 h. Purification by column chromatography on silica (P/EtOAc = 5:1) provided a mixture of the isomers (*rac*)-**55** and (*rac*)-**56** (94.0 mg, 344 µmol, 93 %) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33, 1.34 (s, 3 H, 2'-CH_3), 2.42–2.64 (m, 2 H, 4-H_2), 3.74, 3.74 (s, 3 H, OMe), 3.84–4.05 (m, 2 H, 3'-H_2), 5.87–5.96 (m, 1 H, 2-H), 6.85–7.00 (m, 2 H, 3-H, 8'^{55}-H/5'^{56}-H), 7.10–7.20 (m, 2 H, 5'^{55}-H/8'^{56}-H, 6'^{55}-H/7'^{56}-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.07, 21.12 (2'-CH_3), 38.43, 38.55 (C-4), 51.63 (OMe), 70.16, 70.43 (C-2'), 74.17, 74.91 (C-3'), 104.27, 105.13 (C-7'^{55}/C-6'^{56}), 117.93, 118.57 (C-5'^{55}, C-8'^{56}), 118.81 (CN), 120.96, 121.56 (C-8'^{55}, C-5'^{56}), 125.35, (C-2) 125.68, 126.47 (C-6'^{55}, C-7'^{56}), 141.41 (C-3), 142.26, 142.32 (C-8'a^{55}, C-4'a^{56}), 146.22, 146.29 (C-4'a^{55}, C-8'a^{56}), 166.17 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2951, 2226, 1723, 1660, 1581, 1504, 1436, 1286 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 212.5 (4.632), 218.0 (4.610), 251.0 (4.059), 296.0 (3.625) nm. **MS** (EI, 70 eV): m/z (%) = 273.1 (16) $[M]^+$, 174 (100) $[M–C_5H_7O_2]^+$. Calcd for **$C_{15}H_{15}NO_4$**: 274.10738 $[M+H]^+$. Found: 274.10721 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(2-Methyl-7-nitro-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-57), (*rac*)-(*E*)-4-(2-methyl-6-nitro-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-58): The mixture of regioisomers **16** and **24** (70.0 mg, 335 µmol) was converted with methyl acrylate (**28**) (57.6 mg, 57 µmol, 60.6 µL, 2.0 eq.), *p*-benzoquinone (145 mg, 1.34 mmol, 4.0 eq.) and palladium trifluoroacetate (11.1 mg, 33.5 µmol, 0.1 eq.) in CH_2Cl_2 (0.35 mL) for 24 h at 40 °C according to general procedure **C**. Purification by column chromatography on silica (P/EtOAc = 5:1) yielded a mixture of the isomers (*rac*)-**57** and (*rac*)-**58** (87.2 mg, 297 µmol, 89 %) as a yellow oil. **57**: **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, 2'-CH_3), 2.50 (ddd, J = 14.3, 7.9, 1.2 Hz, 1 H, 4-H_a), 2.59 (ddd, J = 14.4, 7.4, 1.3 Hz, 1 H, 4-H_b), 3.75 (s, 3 H, OMe), 3.95 (d, J = 11.5 Hz, 1 H, 3'-H_a), 4.06 (d, J = 11.5 Hz, 1 H, 3'-H_b), 5.93 (dt, J = 15.7, 1.3 Hz, 1 H, 2-H), 6.88–7.01 (m, 2 H, 3-H, Ar-H), 7.75–7.80 (m, 2 H, Ar-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.05 (2'-CH_3), 38.46 (C-4), 51.66 (OMe), 70.54 (C-2'), 74.27 (C-3'), 113.80 (C-8'), 116.99, 117.38 (C-5', C-6'), 125.47 (C-2), 141.27 (C-3), 141.73 (C-8'a), 142.31 (C-7'), 147.85 (C-4'a), 166.16 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2951, 1724, 1660, 1593, 1521, 1435, 1345, 1275 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 209.0 (4.373), 243.5 (4.019), 301.0 (6.878) 296.0 (3.805) nm.

MS (EI, 70 eV): m/z (%) = 293.1 (28) $[M]^+$, 194.0 (100) $[M–C_5H_7O_2]^+$. Calcd for $\mathbf{C_{14}H_{15}NO_6}$: 294.09721 $[M+H]^+$. Found: 294.09721 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-4-(7-*tert*-Butyl-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-59), (*rac*)-(*E*)-4-(6-*tert*-Butyl-2-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)-but-2-enoic acid methyl ester ((*rac*)-60): A mixture of regioisomers **17** and **25** (80.0 mg, 363 µmol) was treated with methyl acrylate (**28**) (62.5 mg, 726 µmol, 65.8 µL, 2.0 eq.), *p*-benzoquinone (157 mg, 1.45 mmol, 4.0 eq.) and palladium trifluoroacetate (11.1 mg, 36.3 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) for 24 h at room temperature according to general procedure **C**. The mixture of the isomers (*rac*)-**115** and (*rac*)-**116** (92.8 mg, 305 µmol, 84 %) was obtained after purification by column chromatography on silica (P/EtOAc = 5:1) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, $C(CH_3)_3$), 1.31, 1.32 (s, 3 H, 2'-CH_3), 2.26, 2.44–2.54 (m, 1 H, 4-H_a), 2.55–2.65 (m, 1 H, 4-H_b), 3.74, 3.75 (s, 3 H, OMe), 3.80–3.87 (m, 1 H, 3'-H_a), 3.91–3.98 (m, 1 H, 3'-H_b), 5.88–5.97 (m, 1 H, 2-H), 6.77–6.93 (m, 3 H, Ar-H), 6.94–7.07 (m, 1 H, 3-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 21.31 (2'-CH_3), 31.42, 31.43 ($C(CH_3)_3$), 34.14, 34.21 ($C(CH_3)_3$), 38.53, 38.63 (C-4), 51.55 (OMe), 70.30, 70.38 (C-2'), 73.52, 73.69 (C-3'), 113.98, 114.59, 116.27, 116.87, 118.06, 118.91 (C-5'[59], C-6'[59], C-8'[59], C-5'[60], C-7'[60], C-8'[60]), 124.73, 142.78 (C-2), 139.52, 139.60, 141.26, 141.28, 144.48, 145.37 (C-4'a, C-8'a, C-7'[59], C-6'[60]), 142.79, 142.82 (C-3), 166.41, 166.43 (C-1) ppm. **IR** (Film): $\tilde{\nu}$ = 2963, 1726, 1659, 1590, 1503, 1436, 1275 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 202.5 (4.743), 281.5 (3.534) nm. **MS** (ESI, 70 eV): m/z (%) = 327.2 (100) $[M+Na]^+$, 305.2 (15) $[M+H]^+$. Calcd for $\mathbf{C_{18}H_{24}O_4}$: 305.17474 $[M+H]^+$. Found: 305.17495 $[M+H]^+$ (ESI-HRMS).

(*rac*)-(*E*)-2-Methyl-2-(4-oxopent-2-enyl)-2,3-dihydrobenzo[*b*][1,4]oxazin-4-carboxylic acid-*tert*-butyl ester ((*rac*)-66): Following general procedure **C**, phenol **65** (100 mg, 380 µmol) was converted with methyl vinyl ketone (**27**) (53.2 mg, 759 µmol, 61.9 µL, 2.0 eq.), *p*-benzoquinone (164 mg, 1.52 mmol, 4.0 eq.) and palladium trifluoroacetate (12.6 mg, 38.0 µmol, 0.1 eq.) in CH_2Cl_2 (0.40 mL) at 40 °C within 12 h. Purification by column chromatography on silica (P/EtOAc = 10:1) yielded (*rac*)-**66** (103.9 mg, 314 µmol, 83 %) as a yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.30 (s, 3 H, 2-CH_3), 1.54 (s, 9 H, $C(CH_3)_3$), 2.26 (s, 3 H, 5'-H_3), 2.47 (ddd, J = 14.3, 7.8, 1.3 Hz, 1 H, 1'-H_a), 2.55 (ddd, J = 14.3, 7.4, 1.3 Hz, 1 H, 1'-H_b), 3.57 (d, J = 13.6 Hz, 1 H, 3-H_a), 3.73 (d, J = 13.6 Hz, 1 H, 3-H_b), 6.14 (dm_c, J = 16.0 Hz, 1 H, 3'-H), 6.76–6.92 (m, 3 H, 2'-H, 6-H, 8-H), 7.00 (ddd, J = 7.6, 6.9, 1.5 Hz, 1 H, 7-H), 7.71 (s, 1 H, 5-H) ppm. **^{13}C-NMR** (75.6 MHz, $CDCl_3$): δ = 22.44 (2-CH_3), 26.91 (C-5'), 28.13 ($C(CH_3)_3$), 40.20 (C-1'), 49.15 (C-3), 75.51 (C-2), 81.68 ($C(CH_3)_3$), 117.19, 119.91 (C-6, C-8), 123.40 (C-5), 124.61 (C-7), 124.69 (C-4a), 134.48 (C-3'), 141.53 (C-2'), 144.95 (C-8a), 152.76 ($CO_2C(CH_3)_3$), 197.96 (C-4') ppm. **IR**

(Film): $\tilde{\nu}$ = 2974, 1696, 1674, 1377, 1252 cm^{-1}. **UV** (CH_3CN): λ_{max} (lg ε) = 211.5 (4.666), 282.5 (3.556) nm. **MS** (EI, 70 eV): m/z (%) = 331.2 (22) $[M]^+$, 231.2 (78) $[M–C_5H_9O_2]^+$, 148.1 (44) $[M–C_{10}H_{16}O_3]^+$. Calcd for **$C_{19}H_{25}NO_4$**: 370.14152 $[M+K]^+$. Found: 370.14146 $[M+K]^+$ (ESI-HRMS).