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SUPPORTING INFORMATION

Total Syntheses of (*S*)-(–)-Zearalenone and Lasiodiplodin Reveal Superior Metathesis Activity of Ruthenium Carbene Complexes with Imidazol-2-ylidene Ligands

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General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques unless stated otherwise. The solvents were dried by distillation over the drying agents indicated and were stored and transferred under Ar: CH_2Cl_2 (P_4O_{10}), toluene, benzene (Na/K), Et_2O, THF (magnesium/anthracene), EtOH, MeOH (Mg), HMPA (CaH_2), pyridine, Et_3N (KOH). Flash chromatography: Merck silica gel (230-400 mesh). Mp: Gallenkamp apparatus (uncorrected). NMR: Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: wavenumbers in cm^{-1}. Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka, Lancaster) were used as received.

METHOD A: Representative Procedure for Esterifications: 2-Vinyl-benzoic acid dec-9-enyl ester (7). A solution of the 9-decenol (200 µL, 1.1 mmol) and PPh_3 (288 mg, 1.1 mmol) in Et_2O (10 mL) is added dropwise at ambient temperature to a suspension of the carboxylic acid **6** (148 mg, 1 mmol)[15] and DEAD (173 µL, 1.1 mmol) in Et_2O (10 mL). After stirring for 3h the mixture is concentrated to a volume of ca. 5 mL and precipitated triphenylphosphine oxide is filtered off.

Drying of the filtrate over Na_2SO_4, evaporation of the solvent and flash chromatography of the residue (hexanes/ethyl acetate, 50:1) affords ester **7** as a colourless oil (216 mg, 75 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.85 (1 H, dd, J = 7.8, 1.2 Hz), 7.55 (1 H, dd, J = 7.2, 0.7 Hz), 7.51 - 7.37 (2H, m), 7.34 - 7.26 (1H, m), 5.79 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.63 (1H, dd, J = 17.4, 1.2 Hz), 5.32 (1H, dd, J = 11.0, 1.2 Hz), 5.02 - 4.87 (2H, m), 4.28 (2H, t, J = 6.7 Hz), 2.07 - 1.97 (2H, m), 1.78 - 1.67 (2H, m), 1.47 - 1.23 (10H, m); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 167.5, 139.5, 139.1, 135.9, 131.9, 130.2, 129.0, 127.3, 127.1, 116.3, 114.1, 65.2, 33.8, 29.3, 29.2, 29.0, 28.9, 28.6, 26.0; IR (neat) 3073, 2927, 2855, 1719, 1640, 1568, 1482, 1466, 1286, 1253, 1133, 1076, 991, 912, 770, 715 cm^{-1}; MS (EI) *m/z* (rel. intensity) 286 ([M^+], 12), 148 (100), 131 (16), 120 (7), 103 (12), 91 (3), 77 (9), 55 (13), 41 (11); HR-MS (EI) ($C_{19}H_{26}O_2$) *calcd.* 286.1933, *found* 286.1934; $C_{19}H_{26}O_2$ (286.41) *calcd.* C 79.68, H 9.15, *found* C 79.75, H 9.04.

METHOD B: Representative procedure for the RCM of styrene derivatives: 7,8,9,10,11,12,13,14-Octahydro-6-oxa-benzocyclotetradecen-5-one (**8**). Ruthenium carbene **5** (8.4 mg, 0.01 mmol) is added to a solution of ester **7** (57.2 mg, 0.2 mmol) in toluene (50 mL). The reaction mixture is stirred at 80 °C for 23 h. Evaporation of the solvent and flash chromatography of the crude material (hexanes/ethyl acetate, 30:1) affords product **8** as a colourless oil (38.6 mg, 75 %). The analytical data are in full agreement with those reported in the literature.[7e]

2-Hydroxy-4,6-dimethoxy-benzoic acid dec-9-enyl ester (**10**). Prepared according to procedure **A** using acid **9** (396 mg, 2 mmol),[2a] 9-decenol (400 µL, 2.2 mmol), PPh_3 (576 mg, 2.2 mmol) and DEAD (346 µL, 2.2 mmol). Colourless oil (454 mg, 67 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 12.06 (1 H, s), 6.08 (1 H, d, J = 2.4 Hz), 5.93 (1 H, d, J = 2.4 Hz), 5.78 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.02 - 4.87 (2H, m), 4.28 (2H, t, J = 6.5 Hz), 3.78 (6H, s), 2.07 - 1.98 (2H, m), 1.77 - 1.67 (2H, m), 1.48 - 1.22 (10 H, m); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 171.2, 165.9, 165.2, 162.2, 139.1, 114.1, 96.8, 93.3, 91.5, 65.2, 55.9, 55.4, 33.8, 29.4, 29.1, 29.0, 28.9, 28.5, 26.0; IR (neat) 3075, 3000, 2928, 2854, 1648, 1614, 1582, 1466, 1439, 1420, 1402, 1320, 1266, 1217, 1206, 1160, 1116, 1052, 995, 944, 910, 821, 705, 623 cm^{-1}; MS (EI) *m/z* (rel. intensity) 336 ([M^+], 13), 199 (8), 180 (100), 152 (12), 137 (6); HR-MS (EI) ($C_{19}H_{28}O_5$) *calcd.* 336.1937, *found* 336.1937; $C_{19}H_{28}O_5$ (336.43) *calcd.* C 67.83, H 8.39, *found* C 67.69, H 8.31.

METHOD C: Representative procedure for the formation of aryltriflates: 2,4-Dimethoxy-6-trifluoromethanesulfonyloxy-benzoic acid dec-9-enyl ester (11). Tf_2O (214 µL, 1.3 mmol) is added at 0 °C to a solution of compound **10** (212 mg, 0.63 mmol) in pyridine (3mL)/CH_2Cl_2 (3 mL). After stirring for 3 h, the reaction is quenched by the addition of water (10 mL), the aqueous phase is extracted with Et_2O (3 x 20 mL), the combined organic phases are washed with 1 N HCl (10 mL) and brine (10 ml), dried over Na_2SO_4, evaporated and the residue is purified by flash chromatography (hexanes/ethyl acetate, 10:1) affording product **11** as a pale yellow oil. (267 mg, 90 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.51 (1 H, d, J = 2.1 Hz), 6.43 (1 H, d, J = 2.1 Hz), 5.83 (1H, ddt, J = 16.9, 10.1, 6.7 Hz), 5.03 - 4.88 (2H, m), 4.27 (2H, t, J = 6.7 Hz), 3.85 (3H, s), 3.84 (3H, s), 2.08 - 2.01 (2H, m), 1.75 - 1.67 (2H, m), 1.46 - 1.27 (10 H, m); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 163.4, 162.8, 159.8, 148.3, 139.7, 118.9 (q, J = 320.4 Hz), 114.2, 110.8, 99.4, 98.8, 66.3, 56.8, 56.3, 34.1, 29.7, 29.5, 29.4, 29.3, 28.8, 26.2; IR (neat) 2929, 2856, 1731, 1622, 1580, 1501, 1467, 1424, 1332, 1272, 1247, 1216, 1160, 1144, 1110, 1064, 975, 911, 833, 763, 606 cm^{-1}; MS (EI) *m/z* (rel. intensity) 468 ([M$^+$], 7), 331 (100), 313 (92), 286 (8), 180 (45), 137 (11), 96 (5), 55 (13), 41 (10); HR-MS (CI) ($C_{20}H_{27}F_3O_7S$ + H) *calcd.* 469.1508, *found* 469.1509; $C_{20}H_{27}F_3O_7S$ (468.49) *calcd.* C 51.28, H 5.81, F 12.17, S 6.84, *found* C 51.40, H 5.88, F 12.28, S 6.62.

METHOD D: Representative procedure for Stille cross-coupling reactions: 2,4-Dimethoxy-6-vinyl-benzoic acid dec-9-enyl ester (12). LiCl (106 mg, 2.5 mmol) and tributylvinylstannane (146 µL, 0.5 mmol) are added to a solution of triflate **11** (116 mg, 0.247 mmol) in DMF (3 mL) at ambient temperature. Then $Pd(PPh_3)_2Cl_2$ (8.8 mg, 0.0125 mmol, 5 Mol-%) is introduced and stirring is continued for 14 h. For work-up, the reaction is quenched with H_2O (10 mL), the aqueous phase is extracted with ethyl acetate (3 x 10 mL), the combined organic phases are washed with sat. NH_4OH solution (2 x 10 mL) and brine (10 mL), dried over Na_2SO_4 and evaporated. The remaining crude product is purified by flash chromatography (hexanes/ethyl acetate 10:1) affording compound **12** as a colourless oil (70 mg, 82 %). The analytical data are compiled below.

METHOD E: Representative procedure for Heck-reactions with ethylene: Triflate **11** (94 mg, 0.2 mmol), LiCl (25 mg, 0.6 mmol), triethylamine (84 µL, 0.6 mmol) and $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol) were suspended in DMF (10 mL) in a 50 ml autoclave. The autoclave is pressured with ethylene (50 bar) and heated to 90 °C for 20 h. The autoclave is then cooled to ambient temperature and carefully vented. The mixture thus obtained is diluted with ethyl acetate (100 mL) and washed with water (20 mL) and brine (2 x 20 mL). Drying of the organic layer over Na_2SO_4, evaporation of the solvent and flash chromatography of the residue (hexanes/ethyl acetate, 10:1) affords product **12** as a colourless oil. (61 mg, 88 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.70 (1H, dd, J = 17.4, 11.0 Hz), 6.68 (1 H, d, J = 2.1 Hz), 6.42 (1 H, d, J = 2.1 Hz), 5.82 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.73 (1H, d, J = 17.4 Hz), 5.34 (1 H, d, J = 11.0 Hz), 5.04 - 4.79 (2H, m), 4.26 (2H, t, J = 6.6 Hz), 3.83 (3H, s), 3.79 (3H, s), 2.09 - 2.01 (2H, m), 1.76 -1.66 (2H, m), 1.47 - 1.27 (10H, m); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 168.0, 161.8, 158.3, 139.6, 137.6, 134.1, 117.0, 116.8, 114.2, 101.6, 98.5, 65.6, 56.2, 55.8, 34.2, 29.8, 29.6, 29.4, 29.3, 29.0, 26.3; IR (neat) 3075, 3001, 2928, 2854, 1724, 1639, 1633, 1601, 1578, 1459, 1423, 1383, 1323, 1292, 1263, 1231, 1204, 1161, 1101, 1062, 1034, 987, 914, 834, 637 cm^{-1}; MS (EI) *m/z* (rel. intensity) 346 ([M^+], 47), 208 (98), 191 (100), 179 (10), 163 (17), 148 (9), 133 (6), 91 (4), 77 (5), 55 (13), 41 (15); HR-MS (EI) ($C_{21}H_{30}O_4$) *calcd.* 346.2144, *found* 346.2142; $C_{21}H_{30}O_4$ (346.47) *calcd.* C 72.80, H 8.73, *found* C 72.68, H 8.84.

(*E*)-2,4-Dimethoxy-7,8,9,10,11,12,13,14-octahydro-6-oxa-benzocyclotetradecen-5-one (13). Prepared according to procedure **B** using diene **12** (69.2 mg, 0.2 mmol) and carbene **5** (8.4 mg, 0.01 mmol). Product **13** is isolated as a colourless oil (59.2 mg, 93 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.64 (1H, d, J = 2.1 Hz), 6.37 (1 H, d, J = 2.1 Hz), 6.34 (1H, d, J = 15.7 Hz), 6.15 (1H, dt, J = 15.7, 6.7 Hz), 4.36 (2H, t, J =5.1 Hz), 3.82 (3H, s), 3.78 (3H, s), 2.31 - 2.22 (2H, m), 1.73 -1.62 (2H, m), 1.59 - 1.26 (10H, m); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 168.2, 161.6, 157.7, 137.4, 134.2, 127.1, 116.6, 101.2, 97.5, 64.9, 56.2, 55.7, 30.7, 28.5, 27.0, 26.4, 25.3, 24.4, 23.7; IR (neat) 3000, 2933, 2854, 1724, 1651, 1600, 1579, 1458, 1424, 1380, 1347, 1327, 1291, 1266, 1232, 1203, 1159, 1094, 1049, 966, 832, 737, 638, 607 cm^{-1}; MS (EI) *m/z* (rel. intensity) 318 ([M^+], 100), 290 (4), 262 (15), 245 (6), 231 (6), 217 (17), 189 (21), 178 (17), 162 (12), 131 (7), 115 (10), 91 (7), 77 (7), 55 (12), 41

(15); HR-MS (EI) ($C_{19}H_{26}O_4$) *calcd.* 318.1831, *found* 318.1829; $C_{19}H_{26}O_4$ (318.41) *calcd.* C 71.67, H 8.23, *found* C 71.60, H 8.16.

2-Hydroxy-4,6-dimethoxy-benzoic acid 1-methyl-5-oxo-dec-9-enyl ester (**16**). Prepared according to procedure **A** using acid **9** (436 mg, 2.20 mmol), alcohol **15** (650 mg, 2.00 mmol),[37] PPh_3 (577 mg, 2.20 mmol) and DEAD (346 µL, 2.20 mmol). Ester **16** is isolated as a colourless oil (463 mg, 64 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 12.00 (1 H, s), 6.08 (1 H, d, J = 2.4 Hz), 5.97 (1 H, d, J = 2.4 Hz), 5.78 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.17 - 5.07 (1H, m), 5.05 - 4.92 (2H, m), 3.80 (6H, s), 2.47 - 2.36 (4H, m), 2.07 - 1.98 (2H, m), 1.77 - 1.55 (6H, m), 1.32 (3 H, d, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 210.6, 171.2, 166.1, 165.6, 162.8, 138.6, 115.1, 97.4, 93.6, 91.7, 72.1, 56.2, 55.8, 42.6, 42.1, 35.6, 33.5, 23.2, 20.0, 19.7; IR (neat) 3077, 2940, 1713, 1645, 1612, 1581, 1459, 1440, 1420, 1397, 1355, 1316, 1268, 1217, 1160, 1113, 1051, 994, 942, 916, 821, 784, 706, 622 cm^{-1}; MS (EI) *m/z* (rel. intensity) 364 ([M^+], 9), 198 (6), 180 (100), 167 (89), 125 (12), 112 (7), 97 (16), 69 (31), 55 (21), 41 (20); HR-MS (EI) ($C_{20}H_{28}O_6$) *calcd.* 364.1886, *found* 364.1886; $C_{20}H_{28}O_6$ (364.44) *calcd.* C 65.92, H 7.74, *found* C 65.87, H 7.81.

2,4-Dimethoxy-6-trifluoromethanesulfonyloxy-benzoic acid 1-methyl-5-oxo-dec-9-enyl ester (**17**). Prepared according to procedure **C** using phenol **16** (546 mg, 1.5 mmol) and Tf_2O (500 µL, 3 mmol). Triflate **17** is isolated as a colourless oil (681 mg, 92 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.51 (1 H, d, J = 2.1 Hz), 6.43 (1 H, d, J = 2.1 Hz), 5.78 (1H, ddt, J = 17.0, 10.2, 6.7 Hz), 5.16 - 5.04 (1H, m), 5.03 - 4.92 (2H, m), 3.85 (3H, s), 3.83 (3H, s), 2.46 - 2.26 (4H, m), 2.08 - 1.98 (2H, m), 1.73 - 1.52 (6H, m), 1.32 (3H, t, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 210.6, 163.2, 162.7, 159.7, 148.1, 138.6, 118.9 (q, J = 320.4 Hz), 115.1, 111.2, 99.2, 98.7, 73.1, 56.7, 56.3, 42.5, 42.1, 35.5, 33.5, 23.2, 19.8, 19.7; IR (neat) 3079, 2978, 2943, 2847, 1716, 1623, 1579, 1501, 1462, 1424, 1380, 1332, 1275, 1247, 1218, 1161, 1142, 1110, 1063, 974, 916, 833, 763, 607 cm^{-1}; MS (EI) *m/z* (rel. intensity) 496 ([M^+], 1), 331 (25), 313 (100), 180 (49), 166 (57), 152 (11), 137 (14), 125 (8), 112 (69), 97 (18), 83 (5), 69 (31), 55 (29), 41 (25); HR-MS (CI) ($C_{21}H_{27}F_3O_8S$ + H) *calcd.*

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[37] Perkins, M. V.; Jacobs, M. F.; Kitching, W.; Cassidy, P. J.; Lewis, J. A.; Drew, R. A. I. *J. Org. Chem.* **1992**, *57*, 3365.

497.1457, *found* 497.1449; $C_{21}H_{27}F_3O_8S$ (496.50) *calcd.* C 50.80, H 5.48, F 11.48, S 6.46, *found* C 50.74, H 5.55, F 11.30, S 6.52.

2,4-Dimethoxy-6-vinyl-benzoic acid 1-methyl-5-oxo-dec-9-enyl ester (18). **(I)** Prepared according to procedure **D** using **17** (372 mg, 0.75 mmol), tributylvinylstannane (438 μL, 1.5 mmol), LiCl (318 mg, 7.5 mmol) and $Pd(PPh_3)_2Cl_2$ (26.4 mg, 0.0375 mmol). Product **18** is isolated as a colourless oil (233 mg, 83 %).

(II). The same product was also prepared according to procedure **E** using **17** (496 mg, 1 mmol), triethylamine (420 μL, 3 mmol), LiCl (127 mg, 3 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) and ethylene (55 bar): Product **18** is isolated as a colourless oil (349 mg, 93 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.70 (1H, dd, J = 17.4, 11.0 Hz), 6.68 (1 H, d, J = 2.1 Hz), 6.42 (1 H, d, J = 2.1 Hz), 5.79 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.74 (1H, dd, J = 17.4 , 1.0 Hz), 5.33 (1 H, dd, J = 11.0, 1.0 Hz), 5.17 - 5.05 (1H, m), 5.04 - 4.93 (2H, m), 3.83 (3H, s), 3.79 (3H, s), 2.46 - 2.37 (4H, m), 2.08 - 1.99 (2H, m), 1.74 - 1.52 (6H, m), 1.31 (3H, t, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 210.5, 167.6, 161.7, 158.2, 138.6, 137.3, 133.9, 117.1, 117.0, 115.1, 101.4, 98.4, 71.9, 56.2, 55.8, 42.5, 42.1, 35.6, 33.5, 23.2, 20.1, 19.9; IR (neat) 3077, 2975, 2939, 2840, 1716, 1640, 1633, 1601, 1578, 1458, 1423, 1378, 1323, 1292, 1266, 1231, 1204, 1162, 1102, 1061, 1034, 988, 922, 835, 784, 637 cm^{-1}; MS (EI) *m/z* (rel. intensity) 374 ([M^+], 4), 208 (91), 191 (93), 179 (7), 167 (100), 125 (17), 112 (6), 97 (23), 91 (5), 77 (8), 69 (46), 55 (34), 41 (33); $C_{22}H_{30}O_5$ (374.48) *calcd.* C 70.56, H 8.07, *found* C 70.50, H 7.94.

(*E*)-2,4-Dimethoxy-7-methyl-7,8,9,10,13,14-hexahydro-12*H*-6-oxa-benzocyclotetradecene -5,11-dione (19). Prepared according to procedure **B** using diene **18** (74.8 mg, 0.2 mmol) and carbene **5** (8.4 mg, 0.01 mmol). Product **19** is isolated as a colourless solid (63.1 mg, 91 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.62 (1H, d, J = 2.1 Hz), 6.38 (1H, d, J = 2.1 Hz), 6.32 (1 H, dd, J = 15.6, 1.7 Hz), 6.05 (1H, ddd, J = 15.6, 10.0, 4.3 Hz), 5.31 - 5.20 (1H, m), 3.83 (3H, s), 3.80 (3H, s), 2.73 - 2.61 (1H, m), 2.46 - 1.96 (6H, m), 1.91 - 1.47 (5H, m), 1.30 (3H, d, J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 211.3, 167.6, 161.7, 157.9, 137.0, 133.9, 128.9, 116.8, 101.5, 97.8, 71.4, 56.3, 55.8, 44.3, 37.8, 35.4, 31.6, 22.1, 21.7, 20.1; IR (neat) 3016, 2974, 2945, 2929, 2889, 2851, 1712, 1650, 1596, 1579, 1460, 1444, 1421, 1377, 1348, 1325, 1297, 1269, 1235, 1205, 1188, 1158, 1129, 1101, 1083, 1044, 1028, 989, 969, 936, 879, 837, 819, 806, 783, 745, 647, 600 cm^{-1}; MS (EI) *m/z* (rel. intensity) 346 ([M^+], 51), 328 (23), 235 (26), 217 (100), 207 (31), 189 (82), 175 (10), 158 (13), 151 (39), 125 (13), 91 (6), 69 (7), 55 (25), 41 (14); HR-MS (EI) ($C_{20}H_{26}O_5$) *calcd.* 346.1780, *found* 346.1780; $C_{20}H_{26}O_5$ (346.42) *calcd.* C 69.34, H 7.56, *found* C 69.46, H 7.66.

Undeca-1,10-dien-6-one (**21**). A solution of 4-pentenylmagnesium bromide [freshly prepared from 5-bromo-1-pentene (1.89 mL, 16 mmol) and Mg (408 mg, 16.8 mmol) in Et_2O (25 mL)] is added to a refluxing solution of 5-cyano-1-pentene (951 mg, 10 mmol) in Et_2O (5 mL). After the addition is complete, reflux is continued for 3 h. The reaction is quenched by addition of 1 N HCl (30 mL), the aqueous layer is extracted with Et_2O (5 x 50 mL), the combined organic phases are dried over Na_2SO_4 and evaporated. Flash chromatography of the residue (hexanes/ethyl acetate, 10 : 1) affords ketone **21** as a colourless oil (1.465 g, 70 %). The analytical data correspond to those reported in the literature.[38]

2,2-Di-pent-4-enyl-[1,3]dioxolane. A solution of ketone **21** (1.660 g, 10.0 mmol), PPTS (225 mg, 1.00 mmol) and ethylene glycol (14.0 ml, 250 mmol) in toluene (100 ml) are refluxed for 4 h at in a Dean-Stark trap. The organic phase is then diluted with ethyl acetate, washed with sat. aq. $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography (hexanes/ethyl acetate, 10:1) affords the title compound as a colourless oil (2.057 g, 98 %). The analytical data are in full agreement with those reported in the literature.[39]

2-(3-Oxiranyl-propyl)-2-pent-4-enyl-[1,3]dioxolane (±)-(**22**). A solution of *m*-chloro perbenzoic acid (3.020 g, 17.5 mmol) in CH_2Cl_2 (100 mL) is added dropwise to a solution of the acetal described above (2.460 g, 11.7 mmol) in CH_2Cl_2 (100 mL) at ambient temperature. The mixture is stirred for 16 h prior to the addition of sat. aq. Na_2SO_3 (50 mL). The organic phase is separated,

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[38] Kitching, W.; Lewis, J. A.; Perkins, M. V.; Drew, R.; Moore, C. J.; Schurig, V.; König, W. A.; Francke, W. *J. Org. Chem.* **1989**, *54*, 3893.

[39] Nakahara, Y.; Fujita, A.; Ogawa, T. *Agric. Biol. Chem.* **1987**, *51*, 1009.

washed with sat. aq. Na_2CO_3 and dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography (hexanes/ethyl acetate, 4:1) affords epoxide (±)-**22** as a colourless oil (1.073 g, 41 %). A considerable amount of the starting material can be re-isolated (0.246 g, 10 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.81 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.04 - 4.91 (2H, m), 3.89 (4 H, s), 2.89 - 2.82 (1H, m), 2.72 - 2.66 (1H, dd, J = 5.0, 4.0 Hz), 2.44 - 2.38 (1H, dd, J = 5.0, 2.7 Hz), 2.09 - 1.99 (2H, m), 1.67 - 1.38 (10 H, m); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 139.2, 114.6, 111.7, 65.3, 52.3, 47.1, 37.2, 36.9, 34.3, 33.0, 23.5, 20.7; IR (neat) 3075, 3046, 2948, 2878, 1720, 1641, 1481, 1459, 1412, 1374, 1313, 1260, 1220, 1145, 1080, 1054, 996, 948, 913, 831, 649 cm^{-1}; MS (EI) *m/z* (rel. intensity) 226 ([M$^+$], < 1),157 (100), 141 (92), 127 (7), 113 (3), 99 (72), 85 (4), 67 (13), 55 (33), 41 (26); HR-MS (EI) ($C_{13}H_{22}O_3$ + H) *calcd.* 227.1647, *found* 227.1645; $C_{13}H_{22}O_3$ (226.32) *calcd.* C 68.99, H 9.80, *found* C 68.84, H 9.85.

(*S*)-2-(3-Oxiranyl-propyl)-2-pent-4-enyl-[1,3]dioxolane (*S*)-(**22**). (*S*,*S*)-Co^{III}(salen)(acetate) (89 mg, 0.135 mmol)[21] is added to a solution of (±)-**22** (1.221 g, 5.4 mmol) in THF (5 mL) under air. Water (195 µL, 10.8 mmol) is introduced and the solution is stirred at ambient temperature for 67 h. The solvent is evaporated and the residue is purified by Kugelrohr distillation (110 °C, 0.02 mbar) to yield optically active epoxide **22** (501 mg, 41 %). Determination of the optical purity by HPLC on a chiral column (Chiralcel OD-H, n-heptane/2-propanol = 95:5): ee ≥ 99 %. $[\alpha]^{20}_D = -6.1$ (2.32, CH_2Cl_2).

(*R*)-5-(2-Pent-4-enyl-[1,3]dioxolan-2-yl)-pentan-2-ol (**23**). A solution of $LiBEt_3H$ (7.5 mL, 1M in THF, 7.5 mmol) is added to a solution of (*S*)-(**22**) (339 mg, 1.5 mmol) in THF (20 mL) at 0 °C. The reaction mixture is stirred for 1 h and then quenched by careful addition of water (10 mL). Extraction with CH_2Cl_2 (3 x 10 mL), drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 2:1) affords alcohol **23** as a colourless oil (324 mg, 95 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.82 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.04 - 4.91 (2H, m), 3.89 (4 H, s), 3.79 - 3.73 (1H, m), 2.65 (1H, br s), 2.08 - 2.00 (2H, m), 1.63 - 1.55 (4H, m), 1.48 - 1.36 (6H, m), 1.14 (3H, d, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 139.3, 114.6, 111.9, 68.1, 65.2, 39.8, 37.3, 36.9, 34.3, 23.7, 23.5, 20.4; $[\alpha]^{20}_D = -6.8$ (1.05, CH_2Cl_2); IR (KBr) 3446, 3077, 2949, 2877, 1641, 1460, 1440, 1374, 1317, 1221, 1151, 1134, 1080, 1052, 994, 947, 914, 852, 814, 645 cm^{-1}; MS (EI) *m/z* (rel. intensity) 228 ([M$^+$], < 1), 213 (2), 159 (70), 141 (100), 125 (3), 115 (4), 99 (68), 86 (8), 69 (14), 55 (28), 41 (23); $C_{13}H_{24}O_3$ (226.32) *calcd.* C 68.38, H 10.59, *found* C 68.29, H 10.48.

(*R*)-*tert*-Butyl-dimethyl-(1-methyl-but-3-enyloxy)-silane (**26**). A solution of vinyl magnesium bromide (1 M in THF, 37.5 mL, 37.5 mmol) is added over 30 min to a suspension of (*R*)-methyloxirane **24** (1.75 ml, 25 mmol) and CuCl(COD) (518 mg, 2.5 mmol) in THF (25 mL) at -78 °C. The mixture is allowed to warm to ambient temperature overnight. The reaction is then quenched by addition of aq. sat. NH_4Cl (50 mL), the aqueous layer is extracted with Et_2O (3 x 100 mL), the combined organic phases are dried over Na_2SO_4. Careful evaporation of the solvent followed by distillation affords crude (*R*)-pent-4-en-2-ol **25** (b. p. 102 - 106 °C) as a colourless oil. This product is added to a stirred solution of TBSCl (5.43 g, 36 mmol) and imidazole (4.50 g, 66 mmol) in DMF (50 mL). After stirring for 20 h at ambient temperature, the reaction mixture is diluted with hexane (100 mL), the organic phase is washed with 1 N HCl (2 x 20 mL) and water (20 mL) and dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography (hexanes/ethyl acetate, 30:1) affords product **26** as a colourless oil (3.15 g, 63 % over 2 steps). The analytical data are in full agreement with those reported in the literature.[7e]

(*R*)-5-(*tert*-Butyl-dimethyl-silanyloxy)-hexanenitrile (**27**). A suspension of Cp_2ZrHCl (1.94 g, 7.5 mmol) in CH_2Cl_2 (20 mL) is stirred for 10 min at ambient temperature. The solid is allowed to settle and the solvent is removed via canula and replaced by fresh CH_2Cl_2 (20 mL). A solution of alkene **26** (600 mg, 3 mmol) in CH_2Cl_2 (15 mL) is added and the reaction mixture is stirred for 2 h prior to the additon of *t*-butylisonitrile (471 μL, 7.5 mmol) via syringe. After stirring for another 2 h at ambient temperature, a solution of iodine (760 mg, 3 mmol) in benzene (10 mL) is added at 0 °C and stirring is continued at 5 °C for 30 min. The reaction is then quenched by careful addition of sat. aq. $Na_2S_2O_3$ (50 mL). The resulting suspension is filtered through a pad of Celite and the filtrate is diluted with sat. aq. Na_2CO_3 (50 mL). Extraction of the aqueous layer with CH_2Cl_2 (3 x 50 mL), drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography of the crude material (hexanes/ethyl acetate, 30:1 → 20:1) affords nitrile **27** (525 mg, 77 %) as a pale yellow oil. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 3.89 - 3.79 (1H, m), 2.34 (2H, t, J = 7.0 Hz), 1.82 - 1.47 (4H, m), 1.13 (3H, d, J = 6.1 Hz), 0.89 (9H, s), 0.58 (3H, s), 0.51 (3H, s); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 120.2, 68.1, 38.7, 26.0, 23.9, 22.2, 18.3, 17.6, -4.3, - 4.8; $[\alpha]^{20}_D$ = −20.6 (2.46, CH_2Cl_2); IR (neat) 2957, 2930, 2885, 2857, 2246, 1472, 1463, 1375, 1361, 1256, 1139, 1096, 1059, 1024, 836, 807, 775 cm^{-1}; MS (EI) *m/z* (rel. intensity) 227 ([M$^+$], < 1), 212 (5), 170 (94), 159 (9), 129 (11), 115 (5), 100 (38), 96 (25), 75 (100), 59 (9), 45 (11); $C_{12}H_{25}NOSi$ (227.42) *calcd.* C 63.38, H 11.08, N 6.16; *found* C 63.30, H 11.15, 6.10.

(*R*)-10-(*tert*-Butyl-dimethyl-silanyloxy)-undec-1-en-6-one (**28**). A solution of 4-pentenyl magnesium bromide [freshly prepared from 5-bromo-1-pentene (680 μL, 5.73 mmol) and Mg (147 mg, 6.01 mmol) in Et_2O (25 mL)] is added to a refluxing solution of nitrile **27** (520 mg, 2.29 mmol) in Et_2O (5 mL). Reflux is continued for 4 h once the addition is complete. The reaction is then quenched by addition of sat. aq. NH_4Cl (30 mL), the aqueous layer is extracted with Et_2O (5 x 50 mL), the combined organic phases are dried over Na_2SO_4, the solvent is evaporated and the residue is purified by flash chromatography (hexanes/ethyl acetate, 30 : 1) affording ketone **28** as a colourless oil (465 mg, 68 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.79 (1H, ddt, J = 16.9, 10.1, 6.7 Hz), 5.06 - 4.93 (2H, m), 3.79 (1H, tq, 6.0, 6.1 Hz), 2.42 - 2.34 (4H, m), 2.08 - 1.99 (2H, m), 1.69 - 1.31 (6H, m), 1.10 (3H, d, J = 6.1 Hz), 0.88 (9H, s), 0.05 (6H, s); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 210.9, 138.7, 115.1, 68.7, 43.2, 42.1, 39.5, 33.5, 26.0, 23.9, 23.2, 20.5, 18.3, - 4.3, - 4.7; $[\alpha]^{20}_D$ = −10.9 (1.54, CH_2Cl_2); IR (neat) 3078, 2955, 2929, 2903, 2857, 1716, 1641, 1472, 1462, 1411, 1374, 1362, 1255, 1138, 1092, 1064, 1006, 912, 836, 808, 774, 710, 662 cm^{-1}; MS (EI) *m/z* (rel. intensity) 298 ([M$^+$], < 1), 283 (1), 241 (36), 199 (23), 157 (12), 145 (60), 119 (5), 107 (15), 93 (9), 75 (100), 67 (14), 55 (24), 41 (32); $C_{17}H_{34}O_2Si$ (298.54) *calcd.* C 68.39, H 11.48, *found* C 68.35, H 11.42.

(*R*)-*tert*-Butyl-dimethyl-[1-methyl-4-(2-pent-4-enyl-[1,3]dioxolan-2-yl)-butoxy]-silane. A solution of ketone **28** (412 g, 1.38 mmol), *p*-TsOH·H_2O (13.1 mg, 0.07 mmol) and ethylene glycol (2.30 mL, 41.4 mmol) in benzene (50 mL) is refluxed for 12 h in a Dean-Stark trap. The organic phase is diluted with ethyl acetate, washed with sat. aq. $NaHCO_3$ and dried over Na_2SO_4.

Evaporation of the solvent and flash chromatography of the residue (hexanes/ethyl acetate, 30:1) affords the title compound as a colourless oil (344 mg, 73 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.82 (1H, ddt, J = 16.9, 10.1, 6.7 Hz), 5.04 - 4.91 (2H, m), 3.89 (4 H, s), 3.85 - 3.74 (1H, m), 2.08 - 1.99 (2H, m), 1.62 - 1.31 (10H, m), 1.10 (3H, d, J = 6.1 Hz), 0.88 (9H, s), 0.05 (6H, s); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 139.3, 114.6, 112.0, 69.0, 65.3, 40.4, 37.6, 37.0, 34.3, 26.1, 24.0, 23.6, 20.5, 18.4, - 4.3, - 4.6; $[\alpha]^{20}_D = -10.3$ (1.12, CH_2Cl_2); IR (KBr) 3077, 2953, 2929, 2882, 2857, 1641, 1472, 1462, 1443, 1374, 1361, 1255, 1219, 1136, 1083, 1052, 1005, 947, 912, 836, 807, 774, 716, 660 cm^{-1}; MS (EI) *m/z* (rel. intensity) 342 ([M$^+$], < 1), 327 (1), 273 (59), 241 (7), 199 (7), 185 (11), 167 (36), 149 (33), 141 (100), 119 (19), 99 (33), 75 (40), 55 (15), 41 (10); $C_{19}H_{38}O_3Si$ (342.59) *calcd.* C 66.61, H 11.18, *found* C 66.49, H 11.08.

(*R*)-5-(2-Pent-4-enyl-[1,3]dioxolan-2-yl)-pentan-2-ol (**23**). To a solution of the acetal described above (338 mg, 0.99 mmol) in THF (20 mL) is added a solution of TBAF (1 M in THF, 2 mmol, 2 mL) at ambient temperature. After stirring for 24 h, the solvent is removed and the residue is taken up in 20 mL of brine. Extraction with Et_2O (3 x 20 mL), drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 2:1) affords alcohol **23** as a colourless oil (201 mg, 89 %). The analytical data are identical to those reported above.

(*S*)-2-Hydroxy-4,6-dimethoxy-benzoic acid 1-methyl-4-(2-pent-4-enyl-[1,3]dioxolan-2-yl)-butyl ester (**29**). Prepared according to procedure **A** using acid **9** (237 mg, 1.20 mmol), alcohol **23** (248 mg, 1.8 mmol), PPh_3 (315 mg, 1.20 mmol) and DEAD (191 µL, 1.20 mmol). Ester **29** is isolated as a colourless oil (314 mg, 71 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 12.02 (1 H, s), 6.08 (1 H, d, J = 2.4 Hz), 5.97 (1 H, d, J = 2.4 Hz), 5.78 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.17 - 5.06 (1H, m), 5.03 - 4.88 (2H, m), 3.88 (4H, s), 3.80 (6H, s), 2.07 - 1.98 (2H, m), 1.76 - 1.36 (10H, m), 1.32 (3 H, d, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 171.3, 166.1, 165.6, 162.8, 139.2, 114.6, 111.8, 97.5, 93.6, 91.7, 72.4, 65.2, 56.2, 55.8, 37.2, 36.8, 36.4, 34.2, 23.5, 20.0, 19.8; $[\alpha]^{20}_D = +19.5$ (1.12, CH_2Cl_2); IR (neat) 3075, 2948, 2878, 1646, 1613, 1582, 1459, 1440, 1420, 1396, 1355, 1316, 1269, 1217, 1160, 1114, 1077, 1052, 994, 946, 915, 867, 821, 784, 706, 622 cm^{-1}; MS (EI) *m/z* (rel. intensity)

408 ([M$^+$], 3), 339 (34), 280 (2), 211 (6), 181 (54), 169 (8), 141 (100), 99 (49), 69 (14), 55 (20), 41 (13); HR-MS (EI) ($C_{18}H_{26}O_5$) *calcd.* 408.2148, *found* 408.2143; $C_{22}H_{32}O_7$ (408.49) *calcd.* C 64.69, H 7.90, *found* C 64.78, H 7.81.

(*S*)-2,4-Dimethoxy-6-trifluoromethanesulfonyloxy-benzoic acid 1-methyl-4-(2-pent-4-enyl-[1,3]dioxolan-2-yl)-butyl ester (30). Prepared according to procedure **C** using compound **29** (281 mg, 0.69 mmol) and Tf_2O (228 µL, 1.38 mmol). Triflate **30** is isolated as a colourless oil (332 mg, 89 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.51 (1 H, d, J = 2.1 Hz), 6.44 (1 H, d, J = 2.1 Hz), 5.81 (1H, ddt, J = 17.0, 10.2, 6.7 Hz), 5.16 - 5.05 (1H, m), 5.04 - 4.90 (2H, m), 3.89 (4H, s), 3.86 (3H, s), 3.84 (3H, s), 2.09 - 1.99 (2H, m), 1.75 - 1.36 (10H, m), 1.31 (3H, t, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 163.2, 162.7, 159.7, 148.1, 139.3 118.9 (q, J = 320.5 Hz), 114.6, 111.8, 111.4, 99.3, 98.8, 73.5, 65.2, 56.8, 56.3, 37.3, 36.9, 36.4, 34.3, 23.5, 20.0, 19.9; $[\alpha]^{20}_D$ = +7.6 (0.99, CH_2Cl_2); IR (KBr) 3077, 2978, 2950, 2877, 2846, 1726, 1623, 1579, 1500, 1463, 1424, 1381, 1331, 1276, 1247, 1213, 1161, 1142, 1110, 1063, 974, 949, 915, 831, 815, 763, 606 cm^{-1}; MS (EI) *m/z* (rel. intensity) 540 ([M$^+$], < 1), 471 (32), 313 (18), 180 (9), 141 (100), 99 (34), 55 (8); HR-MS (CI) ($C_{23}H_{31}F_3O_9S$ + H) *calcd.* 541.1719, *found* 541.1721; $C_{23}H_{31}F_3O_9S$ (540.55) *calcd.* C 51.11, H 5.78, *found* C 51.19, H 5.70.

(*S*)-2,4-Dimethoxy-6-vinyl-benzoic acid 1-methyl-4-(2-pent-4-enyl-[1,3]dioxolan-2-yl)-butyl ester (31). Prepared according to procedure **E** using triflate **30** (313 mg, 0.58 mmol), triethylamine (243 µL, 1.74 mmol), LiCl (74 mg, 1.74 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 0.029 mmol) and ethylene (40 bar). Diene **31** is isolated as a colourless oil (199 mg, 82 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.71 (1H, dd, J = 17.3, 11.0 Hz), 6.67 (1 H, d, J = 2.2 Hz), 6.42 (1 H, d, J = 2.2 Hz), 5.81 (1H, ddt, 16.9, 10.2, 6.6 Hz), 5.74 (1H, dd, J = 17.3 , 0.5 Hz), 5.33 (1 H, dd, J = 11.0, 0.5 Hz), 5.18 - 4.92 (3H, m), 3.89 (4H, s) 3.83 (3H, s), 3.80 (3H, s), 2.08 - 2.00 (2H, m), 1.73 - 1.37 (10H, m), 1.31 (3H, t, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 167.6, 161.7, 158.3, 139.3, 137.4, 134.0, 117.3, 117.0, 114.6, 111.8, 101.5, 98.5, 72.3, 65.3, 56.3, 55.8, 37.3, 36.9, 36.5, 34.3, 23.5, 20.2, 20.1; $[\alpha]^{20}_D$ = +11.4 (1.45, CH_2Cl_2); IR (neat) 3075, 2974, 2947, 2877, 2841, 1719, 1639, 1601, 1578, 1458, 1423, 1382, 1322, 1292, 1266, 1230, 1204, 1161, 1103, 1060, 1035, 989, 915, 833 cm^{-1}; MS (EI) *m/z* (rel.

intensity) 418 ([M$^+$], 8), 349 (12), 208 (38), 191 (77), 141 (100), 99 (36), 69 (10), 55 (14), 41 (9); HR-MS (EI) ($C_{24}H_{34}O_6$) *calcd.* 418.2355, *found* 418.2355; $C_{24}H_{34}O_6$ (418.53) *calcd.* C 68.88, H 8.19, *found* C 69.04, H 8.12.

(*S*)-Zearalenone Derivative (32). Prepared according to general procedure **B** using diene **31** (83.6 mg, 0.2 mmol) and carbene **5** (8.4 mg, 0.01 mmol). Product **32** is isolated as a colourless solid (70.7 mg, 91 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.61 (1H, d, J = 2.1 Hz), 6.44 - 6.26 (3H, m) 5.21 - 5.12 (1H, m), 3.90 - 3.86 (4H, m), 3.81 (3H, s), 3.78 (3H, s), 2.45 - 2.33 (1H, m), 2.19 - 2.08 (1H, m) 1.83 - 1.41 (10H, m), 1.31 (3H, d, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 168.2, 161.5, 157.8, 136.8, 133.6, 126.0, 117.4, 112.0, 101.3, 97.7, 71.1, 64.6, 64.5, 56.3, 55.8, 35.6, 35.1, 33.5, 30.4, 21.5, 20.4, 20.0; $[\alpha]^{20}_D$ = +69.2 (0.79, CH_2Cl_2); IR (KBr) 2952, 2881, 2842, 1721, 1631, 1601, 1578, 1459, 1425, 1347, 1332, 1291, 1264, 1203, 1160, 1134, 1100, 1076, 1046, 968, 947, 831, 637 cm^{-1}; MS (EI) *m/z* (rel. intensity) 390 ([M$^+$], 31), 328 (26), 234 (24), 217 (26), 204 (26), 189 (51), 157 (11), 141 (25), 113 (12), 99 (100), 86 (10), 69 (4), 55 (24); HR-MS (EI) ($C_{22}H_{30}O_6$) calcd. 390.2042, found 390.2044. These analytical data are in full agreement with those reported in the literature.[7a]

Non-8-en-2-ol (33). A solution of 5-hexenylmagnesium bromide [freshly prepared from 6-bromo-1-hexene (2.8 g, 23 mmol) and Mg (558 mg, 23 mmol) in THF (25 mL)] is added over 30 min to a suspension of methyloxirane (1.19 mL, 17 mmol) and CuCl(COD) (480 mg, 2.3 mmol) in THF (15 mL) at -78 °C. The mixture is allowed to warm to ambient temperature overnight. The reaction is quenched by addition of aq. sat. NH_4Cl (30 mL) and the aqueous layer is extracted with Et_2O (3 x 30 mL). Drying of the combined organic phases with Na_2SO_4, evaporation of the solvent and flash chromatography of the residue (pentane/Et_2O, 4:1) affords alcohol **33** as a colourless oil (2.34 g, 98 %). The analytical data are in full agreement with those reported in the literature.[40]

2-Hydroxy-4,6-dimethoxy-benzoic acid 1-methyl-oct-7-enyl ester (34). Prepared according to procedure **A** using acid **9** (801 mg, 4.04 mmol), alcohol **33** (596 mg, 4.00 mmol), PPh_3 (1.060 g,

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[40] Shono, T.; Nishiguchi, I.; Ohmizu, H.; Mitani, M. *J. Am. Chem. Soc.* **1978**, *100*, 545.

4.04 mmol) and DEAD (655 µL, 4.16 mmol). Product **34** is isolated as a colourless oil (806 mg, 63 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 12.04 (1 H, s), 6.08 (1 H, d, J = 2.4 Hz), 5.97 (1 H, d, J = 2.4 Hz), 5.82 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.18 - 5.07 (1H, m), 5.04 - 4.88 (2H, m), 3.80 (3H, s), 3.79 (3H, s), 2.08 - 2.01 (2H, m), 1.77 - 1.35 (8H, m), 1.32 (3 H, d, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 171.3, 166.1, 165.6, 162.8, 139.5, 114.3, 97.5, 93.6, 91.7, 72.6, 56.2, 55.8, 36.2, 34.1, 29.3, 29.2, 25.4, 20.1; IR (neat) 3076, 2975, 2934, 2856, 1647, 1613, 1582, 1465, 1439, 1420, 1396, 1355, 1317, 1269, 1217, 1160, 1115, 1052, 995, 943, 912, 821, 782, 706, 623 cm^{-1}; MS (EI) *m/z* (rel. intensity) 322 ([M$^+$], 12), 198 (19), 180 (100), 152 (10), 137 (6); HR-MS (EI) ($C_{18}H_{26}O_5$) *calcd.* 322.1780, *found* 322.1780; $C_{18}H_{26}O_5$ (322.40) *calcd.* C 67.06, H 8.13, *found* C 67.25, H 7.93.

2,4-Dimethoxy-6-trifluoromethanesulfonyloxy-benzoic acid 1-methyl-oct-7-enyl ester (35). Prepared according to procedure **C** using compound **34** (484 mg, 1.5 mmol) and Tf_2O (500 µL, 3 mmol). Product **35** is isolated as a colourless oil (627 mg, 92 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.51 (1 H, d, J = 2.1 Hz), 6.44 (1 H, d, J = 2.1 Hz), 5.83 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.16 - 4.89 (3H, m), 3.84 (3H, s), 3.83 (3H, s), 2.10 - 2.01 (2H, m), 1.77 - 1.32 (8H, m), 1.31 (3H, t, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 163.1, 162.6, 159.6, 148.0, 139.5, 118.9 (q, J = 320.5 Hz), 114.3, 111.4, 99.2, 98.7, 73.6, 56.7, 56.3, 36.1, 34.1, 29.3, 29.2, 25.5, 19.9; IR (neat) 3079, 2978, 2934, 2857, 1727, 1623, 1580, 1501, 1466, 1424, 1382, 1332, 1276, 1247, 1217, 1161, 1142, 1111, 1064, 974, 913, 832, 816, 763, 606 cm^{-1}; MS (EI) *m/z* (rel. intensity) 454 ([M$^+$], 4), 331 (100), 313 (98), 286 (11), 180 (57), 169 (12), 152 (13), 137 (20), 124 (8), 82 (11), 69 (16), 55 (19), 41 (19); HR-MS (EI) ($C_{19}H_{25}F_3O_7S$) *calcd.* 454.1273, *found* 454.1270; $C_{19}H_{25}F_3O_7S$ (454.46) *calcd.* C 50.21, H 5.54, F 12.54, S 7.06, *found* C 50.23, H 5.49, F 12.62, S 7.08.

2,4-Dimethoxy-6-vinyl-benzoic acid 1-methyl-oct-7-enyl ester (36). **(I)** Prepared according to procedure **D** using triflate **35** (114 mg, 0.25 mmol), tributylvinylstannane (146 µL, 0.5 mmol), LiCl (106 mg, 2.5 mmol) and $Pd(PPh_3)_2Cl_2$ (8.8 mg, 0.0125 mmol). Product **36** is isolated as colourless oil (65 mg, 78 %). The analytical data are compiled below.

(II) The same compound was also prepared according to procedure **E** using triflate **35** (341 mg, 0.75 mmol), triethylamine (315 µL, 2.25 mmol), LiCl (96 mg, 2.25 mmol), $Pd(PPh_3)_2Cl_2$ (26 mg, 0.0375 mmol) and ethylene (40 bar). Product **36** is isolated as a colourless oil (229 mg, 92 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.72 (1H, dd, J = 17.4, 11.0 Hz), 6.68 (1 H, d, J = 2.2 Hz), 6.42 (1 H, d, J = 2.2 Hz), 5.83 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.74 (1H, dd, J = 17.4, 1.0 Hz), 5.33 (1 H, dd, J = 11.0, 1.0 Hz), 5.18 - 5.06 (1H, m), 5.04 - 4.92 (2H, m), 3.83 (3H, s), 3.79 (3H, s), 2.12 - 2.03 (2H, m), 1.69 -1.33 (8H, m), 1.33 (3H, t, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 167.6, 161.7, 158.2, 139.5, 137.3, 134.0, 117.3, 117.0, 114.3, 101.4, 98.5, 72.3, 56.2, 55.8, 36.3, 34.1, 29.3, 25.6, 25.5, 20.2; IR (neat) 3077, 2975, 2933, 2857, 1721, 1639, 1633, 1601, 1579, 1459, 1423, 1378, 1323, 1292, 1266, 1231, 1204, 1161, 1102, 1061, 1034, 988, 914, 833, 785, 637 cm^{-1}; MS (EI) *m/z* (rel. intensity) 332 ([M^+], 12), 208 (100), 191 (42), 163 (10), 148 (5), 133 (3), 118 (3), 91 (2), 77 (4), 55 (7), 41 (10); HR-MS (EI) ($C_{20}H_{28}O_4$) *calcd.* 332.1988, *found* 332.1989; $C_{20}H_{28}O_4$ (346.47) *calcd.* C 72.26, H 8.49, *found* C 72.18, H 8.41.

(*E*)-2,4-Dimethoxy-7-methyl-7,8,9,10,11,12-hexahydro-6-oxa-benzocyclododecen-5-one (37). Prepared according to procedure **B** using diene **36** (66.4 mg, 0.2 mmol) and carbene **5** (8.4 mg, 0.01 mmol). Product **37** is isolated as a colourless solid (41.9 mg, 69 %). mp = 119-120°C. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.40 (1H, d, J = 2.1 Hz), 6.38 (1H, d, J = 15.8 Hz), 6.36 (1H, d, J = 2.1 Hz), 5.85 (1H, dt, J = 15.8, 7.5 Hz), 5.14 - 5.03 (1H, m), 3.81 (3H, s), 3.79 (3H, s), 2.29 - 2.21 (2H, m), 1.98 - 1.78 (1H, m), 1.67 - 1.31 (7H, m), 1.26 (3H, d, J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 167.9, 161.7, 157.8, 139.3, 135.3, 129.4, 116.4, 103.5, 97.3, 72.5, 56.2, 55.8, 33.7, 32.2, 27.7, 25.1, 22.0, 20.2; IR (KBr) 3094, 3032, 2999, 2976, 2937, 2851, 1713, 1604, 1575, 1459, 1441, 1376, 1345, 1330, 1265, 1236, 1205, 1163, 1132, 1100, 1086, 1041, 1021, 986, 967, 946, 844, 634 cm^{-1}; MS (EI) *m/z* (rel. intensity) 304 ([M^+], 51), 289 (3), 261 (6), 207 (100), 196 (38), 178 (10), 162 (8), 149 (8), 131 (5), 115 (8), 103 (8), 91 (6), 69 (7), 55 (11), 43 (12); HR-MS (EI) ($C_{18}H_{24}O_4$) *calcd.* 304.1675 *found* 304.1677; $C_{18}H_{24}O_4$ (304.39) *calcd.* C 71.03, H 7.95, *found* C 71.15, H 7.93.

8,8-Dimethoxy-octan-2-ol (40). A solution of aldehyde **39** (12.62 g, 0.36 mol)[26] in Et_2O (70 mL) is added over a period of 3.5 h to a solution of MeMgCl (3.3 M in THF, 120 mL, 0.36 mol) at –10°C. Stirring is continued for 20 h at 0°C before the reaction is quenched by careful addition of chilled water (100 mL). The aqueous layer is extracted with Et_2O (5 x 100 mL), the combined organic phases are washed with brine, dried over Na_2SO_4 and evaporated. Flash chromatography of the crude product (hexane/ethyl acetate, 6:1) provides alcohol **40** as a colourless liquid (13.09 g, 95%). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 4.36 (1H, t, J = 5.6 Hz), 3.78 (1H, sext., J = 6.2 Hz), 3.31 (6H, s), 1.86 (1H, s), 1.58 (2H, m), 1.25-1.48 (8H, m), 1.18 (3H, d, J = 6.2 Hz); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 104.3, 67.6, 52.3 (2x), 39.0, 32.2, 29.3, 25.5, 24.4, 23.2; IR (film): 3430, 2940, 2860, 2830, 1465, 1385, 1370, 1195, 1125, 1070, 1055, 960 cm^{-1}; MS (EI) *m/z* (rel. intensity) 190 ([M^+], 0.1), 75 (100), 71 (26), 45 (15). $C_{10}H_{22}O_3$ (190.28) *calcd.* C 63.31, H 11.65; *found* C 62.96, H 11.64.

2,4-Dimethoxy-6-methyl-benzoic acid (7,7-dimethoxy-1-methyl-heptyl) ester (44). A suspension of acid **43** (1.96 g, 10.0 mmol) in toluene (6 mL) is treated with oxalyl chloride (1.31 mL, 15.0 mmol) for 16 h. All volatiles are removed in vacuo, the residue is dissolved in toluene (5 mL) which is subsequently distilled off in order to remove traces of acid and unreacted oxalyl chloride. A solution of the acid chloride thus formed in CH_2Cl_2 (40 mL) is added over a period of 3 h to a solution of alcohol **40** (1.88 g, 10.0 mmol) and DMAP (ca. 50 mg) in CH_2Cl_2 (30 mL) and pyridine (1.78 mL, 22 mmol). The resulting mixture is stirred for 26 h, the reaction is then quenched with aq. $NaHCO_3$ (5% w/w, 70 mL), the aqueous layer is repeatedly extracted with Et_2O, the combined organic layers are washed with brine, dried over Na_2SO_4 and evaporated. Traces of pyridine are removed by aceotropic distillation with toluene prior to flash chromatography of the crude material (hexane/ethyl acetate, 4:1). This affords ester **44** as a pale yellow syrup (3.17 g, 86%). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 6.31 (2H, s), 5.16 (1H, sext., J = 6.2 Hz), 4.35 (1H, t, J = 5.6 Hz), 3.79 (3H, s), 3.78 (3H, s), 3.31 (6H, s), 2.29 (3H, s), 1.26-1.72 (10H, m), 1.32 (3H, d, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 167.9, 161.1, 157.9, 137.5, 117.3, 106.5, 104.5, 96.2, 71.6, 55.7, 55.3, 52.6 (2x), 35.9, 32.4, 29.2, 25.3, 24.5, 20.1, 19.6; IR (film): 2940, 2860, 2840, 1720, 1605, 1590, 1495, 1465, 1420, 1370, 1340, 1325, 1290, 1275, 1230, 1205, 1160, 1130, 1095, 1055, 960, 830, 735, 610 cm^{-1}; MS (EI) *m/z* (rel. intensity) 368 ([M^+], 9), 197 (21), 196 (42), 180 (12), 179 (100), 178 (31), 75 (90), 71 (15), 41 (12). $C_{20}H_{32}O_6$ (368.45) *calcd.* C 65.19, H 8.75; *found* C 64.89, H 8.75.

2-Bis(phenylthio)methyl-4,6-dimethoxy-benzoic acid (7,7-dimethoxy-1-methyl-heptyl) ester (45). A solution of ester **44** (1.61 g, 4.4 mmol) in THF (13 mL) is added over a period of 5 min to a solution of LDA (1.40 g, 13.1 mmol) in THF (13 mL) at –78°C. After stirring for another 5 min, a solution of PhSSPh (2.09 g, 9.6 mmol) in THF (13 mL) is added at such a rate as to maintain the temperature of the reaction below –50°C. The mixture is then allowed to slowly warm to ambient temperature (5 h) and the reaction is quenched with HOAc (10 mL) and water (25 mL). The solvent is evaporated, the residue is dissolved in ethyl acetate (70 mL), the organic phase is successively washed water, aq. NaOH (5% *w/w*) and brine (ca. 20 mL each), dried over Na_2SO_4 and evaporated. The residue is purified by flash chromatography (hexane to remove residual PhSSPh, then hexane/ethyl acetate, 12:1) affording product **45** as a pale yellow syrup (2.45 g, 96%). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.33-7.40 (5H, m), 7.19-7.26 (5H, m), 6.83 (1H, d, J = 2.2 Hz), 6.35 (1H, d, J = 2.2 Hz), 5.74 (1H, s), 5.11 (1H, sext., J = 6.3 Hz), 4.31 (1H, t, J = 5.7 Hz), 3.77 (3H, s), 3.72 (3H, s), 3.29 (6H, s), 1.16-1.68 (10H, m), 1.20 (3H, d, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 166.9, 161.4, 158.1, 139.4, 134.5, 131.8, 131.7, 128.8, 127.5, 115.9, 104.5, 104.3, 98.8, 72.2, 55.8, 55.4, 52.6 (2x), 35.8, 32.4, 29.3, 25.3, 24.5, 19.9; IR (film): 3180, 3160, 2940, 2860, 2840, 1705, 1605, 1580, 1480, 1465, 1440, 1420, 1380, 1325, 1280, 1240, 1215, 1195, 1130, 1100, 1075, 1045, 1025, 1000, 955, 935, 835, 740, 690 cm^{-1}; MS (EI) *m/z* (rel. intensity) 553 (0.5), 552 (0.2), 475 (11), 304 (18), 303 (100), 194 (12), 193 (95), 109 (12), 75 (28), 71 (13). $C_{32}H_{40}O_6S_2$ (584.79) *calcd.* C 65.72, H 6.89, S 10.97; *found* C 65.62, H 7.02, S 10.92.

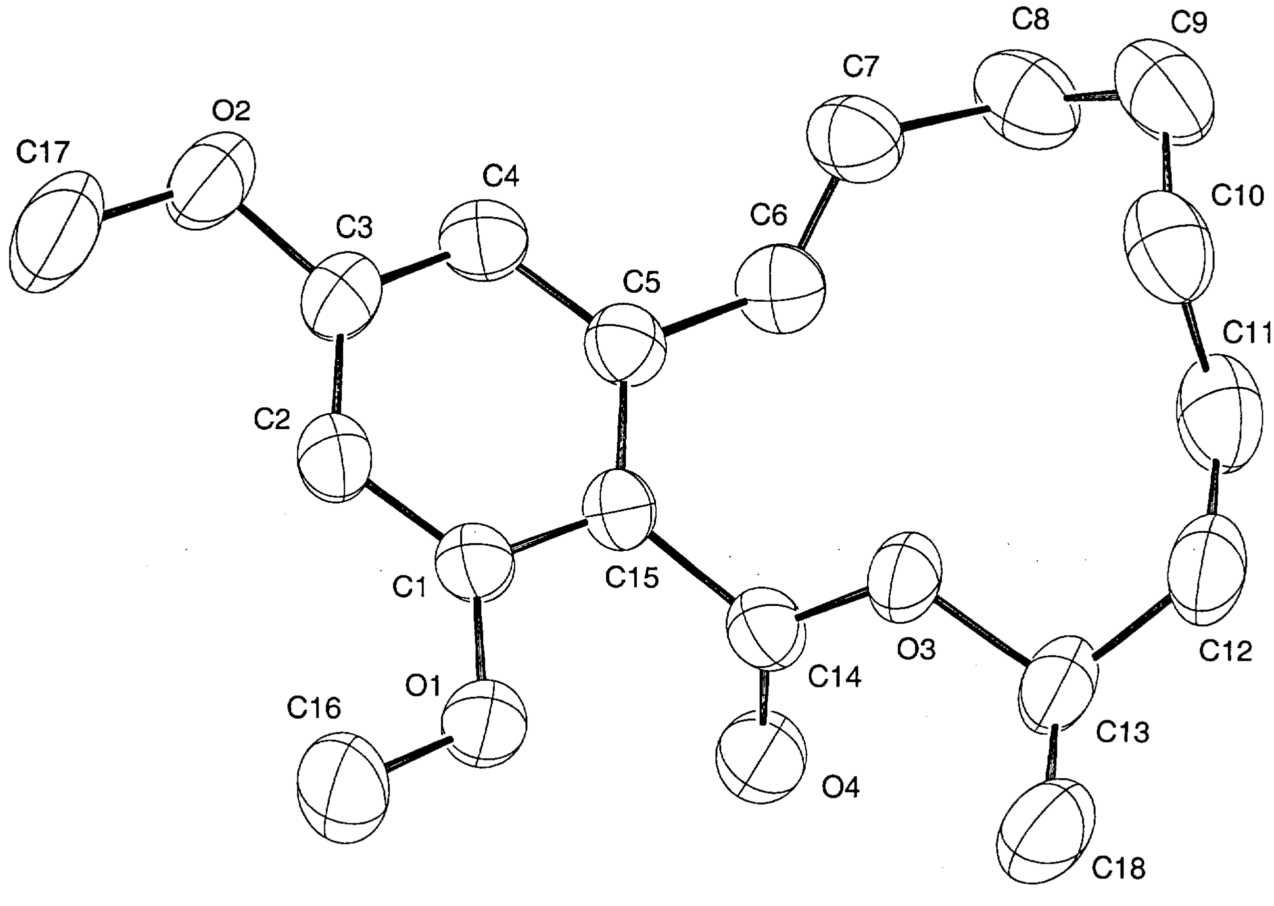
4,6-Dimethoxy-2-formyl-benzoic acid (7,7-dimethoxy-1-methyl-heptyl) ester (46). A solution of the dithioacetal **45** (1.17 g, 2.0 mmol) in acetone (10 mL) is added over a period of 5 min to a suspension of NBS (2.85 g, 16.0 mmol) and 2,6-lutidine (2.80 mL, 24.0 mmol) in acetone/water (4:1, 40 mL) at 0°C. The mixture is stirred for 30 min at ambient temperature and then quenched with a mixture of aq. sat. Na_2SO_3 (20 mL), hexane (20 mL) and CH_2Cl_2 (20 mL). The organic layer is separated, successively washed with aq. $Cu(NO_3)_2$ (5 M, 3 x 5 mL), aq. sat. $NaHCO_3$, water and brine, and dried over Na_2SO_4. Evaporation of the solvent in vacuo followed by flash chromatography of the residue (hexane/ethyl acetate, 12:1) affords product **46** as a colourless syrup (627 mg, 82%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.99 (1H, s), 6.97 (1H, d, J = 2.3 Hz), 6.70 (1H, d, J = 2.3 Hz), 5.22 (1H, s), 5.11 (1H, sext., J = 6.3 Hz), 3.87 (3H, s), 3.85 (3H, s), 3.31 (6H, s), 1.31-1.72 (10H, m), 1.36 (3H, d, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 189.9, 166.0, 161.7, 158.2, 135.3, 119.2, 104.5, 104.4, 104.0, 72.8, 56.1, 55.7, 52.6 (2x), 35.8, 32.4, 29.2, 25.2, 24.5, 19.9; IR (film) 2941, 2860, 1725, 1707, 1603, 1582, 1463, 1428, 1385, 1330, 1299, 1272, 1223, 1200, 1161, 1128, 1100, 1075, 1046, 961, 933, 916, 847, 787, 734, 710, 603 cm^{-1}; MS (EI) *m/z* (rel. intensity) 382 ([M$^+$], 0.3), 211 (14), 210 (17), 209 (89), 194 (12), 193 (100), 165 (13), 142 (15), 75 (66), 71 (17). $C_{20}H_{30}O_7$ (382.45) *calcd.* C 62.81, H 7.91; *found* C 62.46, H 8.03.

4,6-Dimethoxy-2-formyl-benzoic acid (1-methyl-7-oxo-heptyl) ester (47). A suspension of acetal **46** (1.91 g, 5.0 mmol) and Amberlyst-15 (200 mg) in acetone (20 mL) and H_2O (0.3 mL) is shaken at ambient temperature for 24 h. The resin is filtered off, the solvent is removed in vacuo and the residue is purified by flash chromatography (hexane/Et_2O, 2:1), thus affording dialdehyde **47** as a colourless syrup (1.26 g, 75%). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 9.98 (1H, s), 9.76 (1H, t, J = 1.8 Hz), 6.97 (1H, d, J = 2.3 Hz), 6.70 (1H, d, J = 2.3 Hz), 5.22 (1H, sext., J = 6.3 Hz), 3.88 (3H, s), 3.85 (3H, s), 2.42 (2H, dt, J = 7.3 and 1.7 Hz), 1.31-1.75 (8H, m), 1.36 (3H, d, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 202.4, 189.8, 165.9, 161.5, 158.0, 135.1, 118.5, 104.6, 104.1, 72.2, 56.0, 55.5, 43.5, 35.4, 28.6, 24.8, 21.7, 19.7; IR (film) 2980, 2940, 2860, 2740, 1735, 1705, 1600, 1590, 1460, 1440, 1430, 1380, 1330, 1300, 1275, 1225, 1200, 1160, 1100, 1045, 965, 935, 845, 785, 750, 710, 690, 630, 600 cm^{-1}; MS (EI) *m/z* (rel. intensity) 336 ([M$^+$], 0.1), 210 (17), 209 (100), 193 (28), 182 (11), 165 (11). $C_{18}H_{24}O_6$ (336.38) *calcd.* C 64.27, H 7.19; *found* C 63.80, H 7.50.

2,4-Dimethoxy-7-methyl-7,8,9,10,11,12-hexahydro-6-oxa-benzocyclododecen-5-one (*E,Z*-37). $TiCl_3$ (1.01 g, 6.56 mmol) is added to a suspension of bronze colored C_8K (1.75 g, 13.12 mmol)[33] in DME (100 mL). Once the exothermic reaction has ceased, the resulting mixture is refluxed for 1.5 h in order to complete the reduction process. The suspension of titanium-graphite thus formed is allowed to cool to ambient temperature. A solution of dialdehyde **47** (137 mg, 0.41 mmol) in DME (100 mL) is then introduced over a period of 10 h via a syringe pump. Once the addition is complete, the resulting mixture is refluxed for another 5.5 h. For work-up, insoluble residues are filtered off through a short pad of silica and are carefully rinsed with ethyl acetate (200 mL in several portions). The combined filtrates are evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 20:1) affording (*E*)-**37** and (*Z*)-**37** as colourless solids each. The analytical data of the *E*-isomer are identical in all respects with those of the material obtained by RCM (see above). The data of the *Z*-isomer are compiled below: mp = 80-81°C. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.47 (1H, ddq, J = 11.4, 2.6, 0.7 Hz), 6.35 (1H, dd, J = 2.3, 0.3 Hz), 6.20 (1H, dd, J = 2.3, 0.8 Hz), 5.51 (1H, dt, J = 11.4, 3.2 Hz), 5.04 (1H, ddq, J = 11.0, 6.1, 4.6 Hz), 3.78 (6H, s), 2.11 (1H, m), 1.89 (1H, m), 1.58 (2H, m), 1.43 (1H, m), 1.38 (2H, m), 1.32 (3H, d, J = 6.1 Hz), 1.20 (2H, m), 1.16 (1H, m); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 168.2, 160.9, 157.5, 138.7, 134.4, 128.4, 117.3, 105.8, 97.3, 69.9, 56.0, 55.4, 34.6, 27.3, 26.5, 24.4, 22.9, 20.9; IR (KBr) 3089, 3010, 3000, 2975, 2928, 2857, 1728, 1684, 1653, 1598, 1580, 1455, 1419, 1391, 1374, 1356, 1334, 1266, 1220, 1199, 1161, 1135, 1109, 1086, 1046, 1032, 936, 892, 871, 843, 830, 810, 792, 714, 689, 645, 609, 505 cm^{-1}; MS (EI) *m/z* (rel. intensity) 304 ([M^+], 24), 217 (10), 208 (17), 207 (100), 205 (15), 204 (10), 196 (32), 191 (11), 189 (10), 178 (12). HR-MS (EI) ($C_{18}H_{24}O_4$) *calcd.* 304.1675, *found* 304.1686.

2,4-Dimethoxy-7-methyl-7,8,9,10,11,12,13,14-octahydro-6-oxa-benzocyclododecen-5-one (Lasiodiplodinmethylether) (48). A suspension of compound **37** (94 mg, 0.309 mmol) and Pd/C (32 mg, 5 *w/w* %) in EtOH (20mL)/ethyl acetate (2 mL) was stirred under an atmosphere of H_2 for 20 h. Filtration over Celite, evaporation of the solvent and flash chromatography (hexanes/ethylacetate 10:1) affords product **48** as colourless crystals. (88 mg, 93 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 6.34 (1H, d, J = 2.1 Hz), 6.32 (1 H, d, J = 2.1 Hz), 5.27 - 5.16 (1H, m), 3.79 (3H, s), 3.78 (3H, s), 2.77 - 2.62 (1H, m), 2.58 - 2.47 (1H, m), 1.97 - 1.86 (1H, m) 1.74 - 1.56 (4H, m), 1.53 - 1.21 (7H, m), 1.31 (3H, d, J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 168.5, 161.5, 158.0, 143.0, 118.5, 106.2, 96.5, 72.2, 56.2, 55.6, 32.7, 30.8, 30.5, 26.9, 25.7, 24.7, 21.5, 19.6; IR (KBr) 3005, 2979, 2927, 2844, 1718, 1606, 1586, 1490, 1457, 1420, 1352, 1326, 1280, 1263, 1231, 102, 1161, 1131, 1106, 1088, 1057, 1030, 1001, 843, 829, 777, 646, 606 cm^{-1}; MS (EI) *m/z* (rel. intensity) 306 ([M^+], 84), 291 (8), 262 (6), 233 (3), 205 (14), 196 (100), 191 (39), 178 (14), 165 (13), 152 (77), 137 (7), 120 (8), 91 (7), 69 (17), 55 (10); HR-MS (EI) ($C_{18}H_{26}O_4$) *calcd.* 306.1831, *found* 306.1834. The analytical data are in full agreement with literature.[2a]

Figure S-1. ORTEP diagram of the molecular structure of compound (*E*)-**37**. Anisotropic displacement parameter ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity.



The complete lists of atomic coordinates, bond length and angles have been deposited with the Cambridge Crystallographic Data Center, Cambridge, U.K., under the deposition number **CCDC 146698** and may be obtained free of charge by applying to: „The Director, Cambridge Crystallographic Data Center, 12 Union Road, CB2 1EZ Cambridge, UK."

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{18}H_{24}O_4$	
Color	colorless	
Formula weight	304.37 g · mol^{-1}	
Temperature	293 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 11.3960(10) Å	α= 90°.
	b = 9.090(2) Å	β= 98.790(10)°.
	c = 16.616(2) Å	γ = 90°.
Volume	1701.0(5) Å^3	
Z	4	
Density (calculated)	1.189 Mg · m^{-3}	
Absorption coefficient	0.083 mm^{-1}	
F(000)	656 e	
Crystal size	0.67 x 0.52 x 0.17 mm^3	
θ range for data collection	2.48 to 26.28°.	
Index ranges	$-14 \leq h \leq 14$, $-11 \leq k \leq 0$, $0 \leq l \leq 20$	
Reflections collected	3567	
Independent reflections	3441 [R_{int} = 0.0298]	
Reflections with $I>2\sigma(I)$	1739	
Completeness to θ = 26.28°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3441 / 0 / 295	
Goodness-of-fit on F^2	0.983	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0430	wR^2 = 0.1011
R indices (all data)	R_1 = 0.1380	wR^2 = 0.1320
Largest diff. peak and hole	0.161 and -0.175 e · Å^{-3}	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	0.0475(1)	-0.0219(2)	0.1914(1)	0.069(1)
O(2)	0.1437(2)	-0.1327(2)	0.4789(1)	0.086(1)
O(3)	0.3397(1)	0.0961(2)	0.1688(1)	0.048(1)
O(4)	0.1858(1)	0.2496(2)	0.1649(1)	0.064(1)
C(1)	0.1152(2)	-0.0141(3)	0.2665(1)	0.048(1)
C(2)	0.0865(2)	-0.0849(3)	0.3349(1)	0.054(1)
C(3)	0.1631(2)	-0.0698(3)	0.4076(1)	0.056(1)
C(4)	0.2658(2)	0.0120(3)	0.4121(1)	0.053(1)
C(5)	0.2958(2)	0.0811(2)	0.3437(1)	0.044(1)
C(6)	0.4053(2)	0.1669(3)	0.3465(1)	0.050(1)
C(7)	0.5118(2)	0.1305(3)	0.3835(2)	0.056(1)
C(8)	0.6223(2)	0.2119(3)	0.3734(2)	0.066(1)
C(9)	0.6972(2)	0.1276(4)	0.3194(2)	0.073(1)
C(10)	0.6289(2)	0.0771(3)	0.2380(2)	0.066(1)
C(11)	0.5844(3)	0.2004(3)	0.1797(2)	0.071(1)
C(12)	0.5065(2)	0.1453(4)	0.1016(2)	0.068(1)
C(13)	0.3749(2)	0.1706(3)	0.0974(1)	0.056(1)
C(14)	0.2437(2)	0.1478(2)	0.1959(1)	0.045(1)
C(15)	0.2182(2)	0.0688(2)	0.2700(1)	0.042(1)
C(16)	-0.0589(3)	-0.1035(7)	0.1826(2)	0.104(2)
C(17)	0.0376(4)	-0.2153(7)	0.4798(2)	0.110(2)
C(18)	0.3012(3)	0.1098(4)	0.0218(2)	0.074(1)

Table 3. Bond lengths [Å] and angles [°].

O(1)-C(1)	1.366(2)	O(1)-C(16)	1.410(3)
O(2)-C(3)	1.364(3)	O(2)-C(17)	1.425(4)
O(3)-C(14)	1.331(2)	O(3)-C(13)	1.473(2)
O(4)-C(14)	1.205(2)	C(1)-C(2)	1.388(3)
C(1)-C(15)	1.388(3)	C(2)-C(3)	1.384(3)
C(2)-H(2)	0.939(19)	C(3)-C(4)	1.378(3)
C(4)-C(5)	1.386(3)	C(4)-H(4)	0.90(2)
C(5)-C(15)	1.401(3)	C(5)-C(6)	1.467(3)
C(6)-C(7)	1.316(3)	C(6)-H(6)	0.94(2)
C(7)-C(8)	1.492(3)	C(7)-H(7)	1.00(2)
C(8)-C(9)	1.535(4)	C(8)-H(8A)	0.99(3)
C(8)-H(8B)	1.03(3)	C(9)-C(10)	1.525(4)
C(9)-H(9A)	0.95(3)	C(9)-H(9B)	0.98(3)
C(10)-C(11)	1.517(4)	C(10)-H(10A)	1.00(2)
C(10)-H(10B)	1.02(3)	C(11)-C(12)	1.540(4)
C(11)-H(11A)	1.02(3)	C(11)-H(11B)	1.04(3)
C(12)-C(13)	1.509(3)	C(12)-H(12A)	0.92(3)
C(12)-H(12B)	1.04(2)	C(13)-C(18)	1.506(4)
C(13)-H(13)	0.99(2)	C(14)-C(15)	1.493(3)
C(16)-H(16A)	0.95(3)	C(16)-H(16B)	0.94(3)
C(16)-H(16C)	0.90(6)	C(17)-H(17A)	0.99(4)
C(17)-H(17B)	1.09(4)	C(17)-H(17C)	0.93(3)
C(18)-H(18A)	0.99(3)	C(18)-H(18B)	0.99(3)
C(18)-H(18C)	0.95(3)		

C(1)-O(1)-C(16)	118.6(2)	C(3)-O(2)-C(17)	118.7(2)
C(14)-O(3)-C(13)	116.64(16)	O(1)-C(1)-C(2)	123.62(19)
O(1)-C(1)-C(15)	115.02(18)	C(2)-C(1)-C(15)	121.35(19)
C(3)-C(2)-C(1)	118.2(2)	C(3)-C(2)-H(2)	120.0(12)
C(1)-C(2)-H(2)	121.8(12)	O(2)-C(3)-C(4)	115.3(2)
O(2)-C(3)-C(2)	123.5(2)	C(4)-C(3)-C(2)	121.2(2)
C(3)-C(4)-C(5)	120.9(2)	C(3)-C(4)-H(4)	118.9(14)
C(5)-C(4)-H(4)	120.2(14)	C(4)-C(5)-C(15)	118.59(19)
C(4)-C(5)-C(6)	122.0(2)	C(15)-C(5)-C(6)	119.38(19)
C(7)-C(6)-C(5)	126.9(2)	C(7)-C(6)-H(6)	117.6(12)
C(5)-C(6)-H(6)	115.4(12)	C(6)-C(7)-C(8)	123.8(2)
C(6)-C(7)-H(7)	121.2(13)	C(8)-C(7)-H(7)	114.9(13)

C(7)-C(8)-C(9)	111.9(2)	C(7)-C(8)-H(8A)	110.4(15)
C(9)-C(8)-H(8A)	107.1(15)	C(7)-C(8)-H(8B)	107.4(13)
C(9)-C(8)-H(8B)	112.2(13)	H(8A)-C(8)-H(8B)	108(2)
C(10)-C(9)-C(8)	114.5(2)	C(10)-C(9)-H(9A)	111.9(16)
C(8)-C(9)-H(9A)	105.0(16)	C(10)-C(9)-H(9B)	109.4(15)
C(8)-C(9)-H(9B)	109.6(15)	H(9A)-C(9)-H(9B)	106(2)
C(11)-C(10)-C(9)	114.8(2)	C(11)-C(10)-H(10A)	110.1(13)
C(9)-C(10)-H(10A)	108.7(12)	C(11)-C(10)-H(10B)	106.2(14)
C(9)-C(10)-H(10B)	111.1(13)	H(10A)-C(10)-H(10B)	105.5(19)
C(10)-C(11)-C(12)	113.1(2)	C(10)-C(11)-H(11A)	109.1(16)
C(12)-C(11)-H(11A)	110.7(15)	C(10)-C(11)-H(11B)	110.9(13)
C(12)-C(11)-H(11B)	108.0(13)	H(11A)-C(11)-H(11B)	105(2)
C(13)-C(12)-C(11)	115.5(2)	C(13)-C(12)-H(12A)	105.0(17)
C(11)-C(12)-H(12A)	108.3(17)	C(13)-C(12)-H(12B)	107.1(12)
C(11)-C(12)-H(12B)	112.7(12)	H(12A)-C(12)-H(12B)	108(2)
O(3)-C(13)-C(18)	108.5(2)	O(3)-C(13)-C(12)	106.53(19)
C(18)-C(13)-C(12)	113.9(2)	O(3)-C(13)-H(13)	105.9(12)
C(18)-C(13)-H(13)	109.7(11)	C(12)-C(13)-H(13)	111.9(12)
O(4)-C(14)-O(3)	123.47(19)	O(4)-C(14)-C(15)	124.00(18)
O(3)-C(14)-C(15)	112.51(18)	C(1)-C(15)-C(5)	119.80(18)
C(1)-C(15)-C(14)	119.74(18)	C(5)-C(15)-C(14)	120.44(18)
O(1)-C(16)-H(16A)	107.5(18)	O(1)-C(16)-H(16B)	106.9(19)
H(16A)-C(16)-H(16B)	118(3)	O(1)-C(16)-H(16C)	114(4)
H(16A)-C(16)-H(16C)	103(4)	H(16B)-C(16)-H(16C)	108(4)
O(2)-C(17)-H(17A)	105(2)	O(2)-C(17)-H(17B)	109(2)
H(17A)-C(17)-H(17B)	116(3)	O(2)-C(17)-H(17C)	102(2)
H(17A)-C(17)-H(17C)	108(3)	H(17B)-C(17)-H(17C)	115(3)
C(13)-C(18)-H(18A)	109.2(15)	C(13)-C(18)-H(18B)	111.4(15)
H(18A)-C(18)-H(18B)	107(2)	C(13)-C(18)-H(18C)	106.8(17)
H(18A)-C(18)-H(18C)	110(2)	H(18B)-C(18)-H(18C)	112(2)

Table 4. Anisotropic displacement parameters (Å^2).

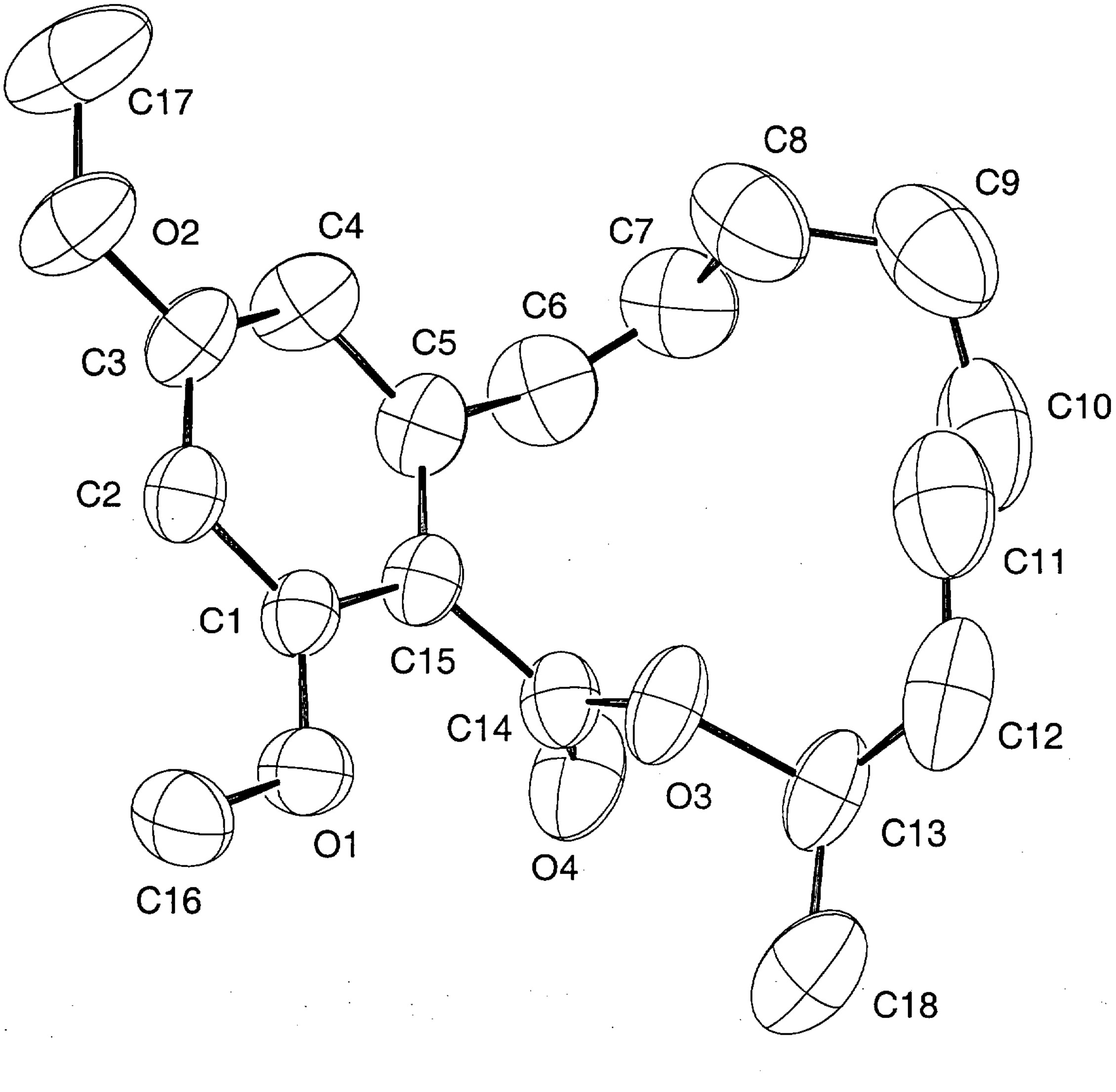
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.050(1)	0.112(1)	0.043(1)	0.008(1)	-0.001(1)	-0.022(1)
O(2)	0.073(1)	0.140(2)	0.045(1)	0.024(1)	0.005(1)	-0.034(1)
O(3)	0.049(1)	0.052(1)	0.048(1)	0.008(1)	0.021(1)	0.008(1)
O(4)	0.057(1)	0.072(1)	0.068(1)	0.020(1)	0.020(1)	0.022(1)
C(1)	0.039(1)	0.066(2)	0.038(1)	-0.002(1)	0.005(1)	0.000(1)
C(2)	0.041(1)	0.075(2)	0.046(1)	0.003(1)	0.009(1)	-0.011(1)
C(3)	0.053(1)	0.075(2)	0.039(1)	0.005(1)	0.011(1)	-0.005(1)
C(4)	0.047(1)	0.071(2)	0.039(1)	-0.002(1)	0.000(1)	-0.004(1)
C(5)	0.041(1)	0.047(1)	0.043(1)	-0.004(1)	0.007(1)	0.003(1)
C(6)	0.052(1)	0.046(1)	0.050(1)	-0.003(1)	0.005(1)	-0.002(1)
C(7)	0.050(1)	0.056(2)	0.060(2)	0.001(1)	-0.002(1)	-0.007(1)
C(8)	0.053(2)	0.058(2)	0.082(2)	-0.005(2)	-0.004(1)	-0.010(1)
C(9)	0.047(2)	0.068(2)	0.101(2)	0.006(2)	0.005(2)	-0.004(1)
C(10)	0.052(2)	0.056(2)	0.094(2)	0.000(2)	0.022(2)	0.004(1)
C(11)	0.062(2)	0.061(2)	0.094(2)	0.008(2)	0.027(2)	-0.008(1)
C(12)	0.066(2)	0.075(2)	0.070(2)	0.011(2)	0.034(1)	0.002(2)
C(13)	0.066(2)	0.055(2)	0.054(2)	0.014(1)	0.028(1)	0.007(1)
C(14)	0.038(1)	0.052(1)	0.046(1)	-0.002(1)	0.008(1)	0.004(1)
C(15)	0.037(1)	0.049(1)	0.042(1)	0.000(1)	0.012(1)	0.005(1)
C(16)	0.061(2)	0.195(5)	0.053(2)	-0.003(2)	-0.001(2)	-0.053(2)
C(17)	0.101(3)	0.170(4)	0.059(2)	0.027(3)	0.017(2)	-0.057(3)
C(18)	0.086(2)	0.090(3)	0.052(2)	0.009(2)	0.025(2)	0.008(2)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$).

	x	y	z	U_{eq}
H(2)	0.0186(18)	-0.144(2)	0.3326(11)	0.042(5)
H(4)	0.3140(19)	0.019(2)	0.4602(14)	0.056(6)
H(6)	0.3981(17)	0.254(2)	0.3160(13)	0.052(6)
H(7)	0.525(2)	0.040(3)	0.4178(14)	0.067(7)
H(8A)	0.672(2)	0.227(3)	0.4267(16)	0.084(8)
H(8B)	0.597(2)	0.314(3)	0.3501(14)	0.072(7)
H(9A)	0.730(2)	0.047(3)	0.3518(16)	0.080(9)
H(9B)	0.765(2)	0.189(3)	0.3098(14)	0.079(8)
H(10A)	0.561(2)	0.014(3)	0.2486(13)	0.066(7)
H(10B)	0.680(2)	0.011(3)	0.2078(14)	0.077(7)
H(11A)	0.655(3)	0.258(3)	0.1659(16)	0.100(9)
H(11B)	0.535(2)	0.276(3)	0.2073(15)	0.076(8)
H(12A)	0.527(2)	0.197(3)	0.0578(17)	0.094(9)
H(12B)	0.5184(18)	0.034(3)	0.0910(13)	0.060(7)
H(13)	0.3560(17)	0.276(2)	0.1034(12)	0.048(6)
H(16A)	-0.105(3)	-0.067(3)	0.2212(19)	0.093(10)
H(16B)	-0.092(3)	-0.099(3)	0.127(2)	0.110(10)
H(16C)	-0.049(5)	-0.198(7)	0.196(4)	0.23(3)
H(17A)	0.044(3)	-0.300(4)	0.443(2)	0.126(15)
H(17B)	-0.038(3)	-0.143(4)	0.463(2)	0.143(15)
H(17C)	0.047(3)	-0.249(3)	0.533(2)	0.110(10)
H(18A)	0.216(3)	0.130(3)	0.0235(16)	0.086(9)
H(18B)	0.310(2)	0.002(3)	0.0184(15)	0.089(10)
H(18C)	0.326(2)	0.159(3)	-0.0232(18)	0.097(9)

Figure S-2. ORTEP diagram of the molecular structure of compound (*Z*)-**37**. Anisotropic displacement parameter ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity.



The complete lists of atomic coordinates, bond length and angles have been deposited with the Cambridge Crystallographic Data Center, Cambridge, U.K., under the deposition number **CCDC 146697** and may be obtained free of charge by applying to: „The Director, Cambridge Crystallographic Data Center, 12 Union Road, CB2 1EZ Cambridge, UK."

Table 6. Crystal data and structure refinement.

Empirical formula	$C_{18}H_{24}O_4$	
Color	colorles	
Formula weight	304.37 $g \cdot mol^{-1}$	
Temperature	293 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 12.4040(10) Å	α= 90°.
	b = 8.859(3) Å	β= 108.310(10)°.
	c = 16.313(2) Å	γ = 90°.
Volume	1701.8(6) $Å^3$	
Z	4	
Density (calculated)	1.188 $Mg \cdot m^{-3}$	
Absorption coefficient	0.083 mm^{-1}	
F(000)	656 e	
Crystal size	0.63 x 0.63 x 0.46 mm^3	
θ range for data collection	2.66 to 27.44°.	
Index ranges	$-16 \leq h \leq 15$, $-11 \leq k \leq 0$, $0 \leq l \leq 21$	
Reflections collected	4011	
Independent reflections	3871 [R_{int} = 0.0291]	
Reflections with $I>2\sigma(I)$	1820	
Completeness to θ = 27.44°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3871 / 0 / 295	
Goodness-of-fit on F^2	0.966	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0473	wR^2 = 0.1194
R indices (all data)	R_1 = 0.1432	wR^2 = 0.1562
Largest diff. peak and hole	0.194 and -0.143 $e \cdot Å^{-3}$	

Table 7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	0.0937(1)	0.3174(2)	-0.0388(1)	0.058(1)
O(2)	-0.1900(1)	0.6423(2)	-0.2114(1)	0.078(1)
O(3)	0.2848(1)	0.5382(2)	0.0334(1)	0.061(1)
O(4)	0.3404(1)	0.4577(2)	-0.0764(1)	0.077(1)
C(1)	0.0595(2)	0.4414(3)	-0.0891(1)	0.045(1)
C(2)	-0.0524(2)	0.4810(3)	-0.1286(1)	0.051(1)
C(3)	-0.0768(2)	0.6098(3)	-0.1791(1)	0.056(1)
C(4)	0.0080(2)	0.6944(3)	-0.1940(2)	0.063(1)
C(5)	0.1216(2)	0.6551(3)	-0.1540(1)	0.055(1)
C(6)	0.2143(2)	0.7453(4)	-0.1706(2)	0.069(1)
C(7)	0.2532(3)	0.8739(4)	-0.1359(2)	0.079(1)
C(8)	0.2172(3)	0.9602(4)	-0.0714(3)	0.092(1)
C(9)	0.3146(4)	1.0212(5)	0.0019(3)	0.108(1)
C(10)	0.3922(3)	0.8995(5)	0.0556(3)	0.101(1)
C(11)	0.3406(3)	0.8167(5)	0.1169(3)	0.098(1)
C(12)	0.3988(3)	0.6711(5)	0.1552(2)	0.092(1)
C(13)	0.4017(2)	0.5475(4)	0.0910(2)	0.067(1)
C(14)	0.2678(2)	0.5007(3)	-0.0484(1)	0.050(1)
C(15)	0.1474(2)	0.5305(3)	-0.0995(1)	0.046(1)
C(16)	0.0092(2)	0.2199(3)	-0.0273(2)	0.065(1)
C(17)	-0.2230(3)	0.7737(6)	-0.2612(4)	0.111(2)
C(18)	0.4377(3)	0.3968(5)	0.1307(3)	0.094(1)

Table 8. Bond lengths [Å] and angles [°].

O(1)-C(1)	1.357(3)	O(1)-C(16)	1.415(3)
O(2)-C(3)	1.366(3)	O(2)-C(17)	1.405(4)
O(3)-C(14)	1.325(3)	O(3)-C(13)	1.461(2)
O(4)-C(14)	1.193(2)	C(1)-C(2)	1.379(3)
C(1)-C(15)	1.398(3)	C(2)-C(3)	1.384(3)
C(2)-H(2)	0.98(2)	C(3)-C(4)	1.375(3)
C(4)-C(5)	1.398(3)	C(4)-H(4)	0.94(2)
C(5)-C(15)	1.390(3)	C(5)-C(6)	1.492(3)
C(6)-C(7)	1.296(4)	C(6)-H(6)	0.98(3)
C(7)-C(8)	1.479(5)	C(7)-H(7)	0.95(3)
C(8)-C(9)	1.508(5)	C(8)-H(8A)	0.95(4)
C(8)-H(8B)	1.04(3)	C(9)-C(10)	1.525(6)
C(9)-H(9A)	0.98(4)	C(9)-H(9B)	0.99(4)
C(10)-C(11)	1.533(5)	C(10)-H(10A)	0.92(4)
C(10)-H(10B)	1.05(3)	C(11)-C(12)	1.514(5)
C(11)-H(11A)	1.07(4)	C(11)-H(11B)	0.95(2)
C(12)-C(13)	1.524(4)	C(12)-H(12A)	0.97(3)
C(12)-H(12B)	0.95(3)	C(13)-C(18)	1.490(5)
C(13)-H(13)	0.99(3)	C(14)-C(15)	1.488(3)
C(16)-H(16A)	0.98(3)	C(16)-H(16B)	0.99(2)
C(16)-H(16C)	0.96(3)	C(17)-H(17A)	1.09(3)
C(17)-H(17B)	0.83(5)	C(17)-H(17C)	0.96(4)
C(18)-H(18A)	1.03(3)	C(18)-H(18B)	1.03(4)
C(18)-H(18C)	0.94(3)		
C(1)-O(1)-C(16)	118.08(19)	C(3)-O(2)-C(17)	118.4(2)
C(14)-O(3)-C(13)	118.27(17)	O(1)-C(1)-C(2)	124.42(19)
O(1)-C(1)-C(15)	115.04(18)	C(2)-C(1)-C(15)	120.5(2)
C(1)-C(2)-C(3)	119.2(2)	C(1)-C(2)-H(2)	121.6(12)
C(3)-C(2)-H(2)	119.3(12)	O(2)-C(3)-C(4)	124.6(2)
O(2)-C(3)-C(2)	114.2(2)	C(4)-C(3)-C(2)	121.3(2)
C(3)-C(4)-C(5)	119.7(2)	C(3)-C(4)-H(4)	122.2(14)
C(5)-C(4)-H(4)	117.9(14)	C(15)-C(5)-C(4)	119.5(2)
C(15)-C(5)-C(6)	120.4(2)	C(4)-C(5)-C(6)	120.2(2)
C(7)-C(6)-C(5)	126.5(3)	C(7)-C(6)-H(6)	123.0(18)
C(5)-C(6)-H(6)	110.5(18)	C(6)-C(7)-C(8)	127.6(3)
C(6)-C(7)-H(7)	121.3(19)	C(8)-C(7)-H(7)	111.2(19)

C(7)-C(8)-C(9)	113.8(3)	C(7)-C(8)-H(8A)	110(3)
C(9)-C(8)-H(8A)	111(3)	C(7)-C(8)-H(8B)	106.2(17)
C(9)-C(8)-H(8B)	110.6(16)	H(8A)-C(8)-H(8B)	105(3)
C(8)-C(9)-C(10)	114.0(3)	C(8)-C(9)-H(9A)	105(2)
C(10)-C(9)-H(9A)	113(2)	C(8)-C(9)-H(9B)	111(2)
C(10)-C(9)-H(9B)	105(2)	H(9A)-C(9)-H(9B)	109(3)
C(9)-C(10)-C(11)	113.3(3)	C(9)-C(10)-H(10A)	111(2)
C(11)-C(10)-H(10A)	109(2)	C(9)-C(10)-H(10B)	107.5(14)
C(11)-C(10)-H(10B)	112.0(15)	H(10A)-C(10)-H(10B)	104(3)
C(12)-C(11)-C(10)	115.7(3)	C(12)-C(11)-H(11A)	106(2)
C(10)-C(11)-H(11A)	110(2)	C(12)-C(11)-H(11B)	105.5(15)
C(10)-C(11)-H(11B)	106.5(15)	H(11A)-C(11)-H(11B)	114(3)
C(11)-C(12)-C(13)	116.1(3)	C(11)-C(12)-H(12A)	109.0(19)
C(13)-C(12)-H(12A)	106.6(19)	C(11)-C(12)-H(12B)	108(2)
C(13)-C(12)-H(12B)	109(2)	H(12A)-C(12)-H(12B)	108(3)
O(3)-C(13)-C(18)	109.3(2)	O(3)-C(13)-C(12)	104.5(2)
C(18)-C(13)-C(12)	114.4(3)	O(3)-C(13)-H(13)	106.3(14)
C(18)-C(13)-H(13)	110.8(15)	C(12)-C(13)-H(13)	111.0(15)
O(4)-C(14)-O(3)	124.4(2)	O(4)-C(14)-C(15)	126.0(2)
O(3)-C(14)-C(15)	109.47(18)	C(5)-C(15)-C(1)	119.64(19)
C(5)-C(15)-C(14)	119.19(19)	C(1)-C(15)-C(14)	121.0(2)
O(1)-C(16)-H(16A)	105.6(17)	O(1)-C(16)-H(16B)	109.6(14)
H(16A)-C(16)-H(16B)	113(2)	O(1)-C(16)-H(16C)	110.6(14)
H(16A)-C(16)-H(16C)	118(2)	H(16B)-C(16)-H(16C)	100.7(19)
O(2)-C(17)-H(17A)	104.3(16)	O(2)-C(17)-H(17B)	113(3)
H(17A)-C(17)-H(17B)	105(4)	O(2)-C(17)-H(17C)	106(2)
H(17A)-C(17)-H(17C)	112(3)	H(17B)-C(17)-H(17C)	115(4)
C(13)-C(18)-H(18A)	114.6(17)	C(13)-C(18)-H(18B)	108(2)
H(18A)-C(18)-H(18B)	111(3)	C(13)-C(18)-H(18C)	110(2)
H(18A)-C(18)-H(18C)	101(3)	H(18B)-C(18)-H(18C)	112(3)

Table 9. Anisotropic displacement parameters ($Å^2$).
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.044(1)	0.053(1)	0.079(1)	0.007(1)	0.021(1)	-0.001(1)
O(2)	0.045(1)	0.104(2)	0.083(1)	0.032(1)	0.016(1)	0.013(1)
O(3)	0.033(1)	0.103(1)	0.048(1)	-0.008(1)	0.013(1)	-0.008(1)
O(4)	0.042(1)	0.117(2)	0.075(1)	-0.030(1)	0.024(1)	0.003(1)
C(1)	0.036(1)	0.054(1)	0.046(1)	-0.006(1)	0.014(1)	-0.002(1)
C(2)	0.038(1)	0.063(2)	0.052(1)	-0.003(1)	0.016(1)	-0.007(1)
C(3)	0.038(1)	0.080(2)	0.048(1)	0.007(1)	0.012(1)	0.003(1)
C(4)	0.057(2)	0.078(2)	0.058(2)	0.018(1)	0.025(1)	0.005(1)
C(5)	0.046(1)	0.072(2)	0.051(1)	0.000(1)	0.023(1)	-0.006(1)
C(6)	0.061(2)	0.081(2)	0.077(2)	0.009(2)	0.040(1)	-0.006(2)
C(7)	0.064(2)	0.078(2)	0.111(2)	0.015(2)	0.049(2)	-0.008(2)
C(8)	0.077(2)	0.072(2)	0.145(3)	-0.006(2)	0.062(2)	-0.014(2)
C(9)	0.093(3)	0.082(3)	0.169(4)	-0.027(3)	0.070(3)	-0.020(2)
C(10)	0.063(2)	0.123(3)	0.128(3)	-0.044(3)	0.044(2)	-0.040(2)
C(11)	0.068(2)	0.128(3)	0.109(3)	-0.043(3)	0.043(2)	-0.024(2)
C(12)	0.059(2)	0.155(4)	0.064(2)	-0.034(2)	0.021(2)	-0.026(2)
C(13)	0.034(1)	0.106(2)	0.057(2)	-0.001(2)	0.010(1)	-0.009(1)
C(14)	0.038(1)	0.058(1)	0.055(1)	-0.007(1)	0.018(1)	-0.007(1)
C(15)	0.036(1)	0.060(1)	0.045(1)	-0.004(1)	0.017(1)	-0.002(1)
C(16)	0.055(2)	0.056(2)	0.092(2)	0.003(2)	0.031(2)	-0.005(1)
C(17)	0.058(2)	0.138(4)	0.135(4)	0.069(3)	0.027(2)	0.026(2)
C(18)	0.059(2)	0.131(3)	0.085(2)	0.022(2)	0.013(2)	0.003(2)

Table 10. Hydrogen coordinates and isotropic displacement parameters (Å^2).

	x	y	z	U_{eq}
H(2)	-0.1152(18)	0.421(2)	-0.1207(12)	0.048(6)
H(4)	-0.0074(19)	0.776(3)	-0.2325(15)	0.068(7)
H(6)	0.243(2)	0.694(3)	-0.2124(19)	0.099(10)
H(7)	0.312(3)	0.925(4)	-0.1509(19)	0.105(10)
H(8A)	0.167(4)	1.039(5)	-0.099(3)	0.159(18)
H(8B)	0.168(3)	0.887(4)	-0.0483(18)	0.100(9)
H(9A)	0.280(3)	1.085(4)	0.036(2)	0.116(12)
H(9B)	0.365(3)	1.085(4)	-0.021(2)	0.116(12)
H(10A)	0.461(3)	0.939(4)	0.087(2)	0.124(12)
H(10B)	0.413(2)	0.825(3)	0.0125(17)	0.081(8)
H(11A)	0.344(3)	0.888(5)	0.171(3)	0.161(16)
H(11B)	0.266(2)	0.789(3)	0.0836(14)	0.065(7)
H(12A)	0.360(3)	0.629(3)	0.1932(19)	0.099(10)
H(12B)	0.475(3)	0.695(4)	0.189(2)	0.116(11)
H(13)	0.448(2)	0.578(3)	0.0547(16)	0.076(8)
H(16A)	0.050(2)	0.140(4)	0.0110(18)	0.091(9)
H(16B)	-0.038(2)	0.181(3)	-0.0842(16)	0.068(8)
H(16C)	-0.046(2)	0.276(3)	-0.0097(14)	0.066(7)
H(17A)	-0.189(3)	0.865(4)	-0.2162(19)	0.093(11)
H(17B)	-0.192(4)	0.783(6)	-0.300(3)	0.18(2)
H(17C)	-0.304(3)	0.773(4)	-0.281(2)	0.118(11)
H(18A)	0.445(3)	0.314(4)	0.088(2)	0.105(12)
H(18B)	0.382(3)	0.364(4)	0.163(2)	0.128(12)
H(18C)	0.513(3)	0.401(4)	0.168(2)	0.110(11)