SUPPORTING INFORMATION

Asymmetric Synthesis of the Fully Functional Macrolide Core of Salicylihalamide: Remote Control of Olefin Geometry during RCM

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General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. 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 (Na/K), Et_2O, THF (magnesium/anthracene), MeOH and EtOH (Mg), HMPA (CaH_2), pyridine and Et_3N (KOH). Flash chromatography: Merck silica gel (230-400 mesh). Mp: Gallenkamp apparatus (uncorrected). NMR: Spectra were recorded on a Bruker DPX 300, AMX 400 or DMX 600 spectrometer in the solvent indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Nicolet FT-7199, wavenumbers in cm^{-1}. MS: Finnigan MAT 8200 (70 eV) or Finnigan MAT SSQ 7000 (70 eV). HRMS: MAT 95 (70 eV). Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka, Lancaster) were used as received.

Starting Materials. 5-Hydroxy-2,2-dimethyl-benzo[1,3]dioxin-4-one (**4**),[6] trifluoro-methanesulfonic acid 2,2-dimethyl-4-oxo-4*H*-benzo[1,3]dioxin-5-yl ester (**5**),[7a] 5-allyl-2,2-dimethyl-benzo[1,3]dioxin-4-one (**6**),[9] and (4*S*, 5*R*)-4-methyl-5-phenyl-3-propionyl-oxazolidin-2-one (**8**)[32] were prepared according to the literature cited.

[32] Toyota, M.; Hirota, M.; Nishikawa, Y.; Fukumoto, K.; Ihara, M. *J. Org. Chem.* **1998**, *63*, 5895.

2-Allyl-6-hydroxy-benzoic acid (7). A solution of BCl_3 (1 M in CH_2Cl_2, 30 mL, 30 mmol) is slowly added to a solution of compound **6** (1.00 g, 4.54 mmol) in CH_2Cl_2 (80 mL) at 0 °C and the resulting mixture is stirred for 5 h at ambient temperature. The organic phase is diluted with ethyl acetate (50 mL), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and flash chromatography (hexanes/ethyl acetate/acetic acid, 10:1:1) affords acid **7** as colourless crystals (0.78 g, 96 %). mp = 98-99°C. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 11.15 - 10.75 (1H, br s), 7.38 (1H, dd, J = 8.2, 7.7 Hz), 6.90 (1H, dd, J = 8.2, 0.9 Hz), 6.79 (1H, dd, J = 7.7, 0.9 Hz), 6.02 (1H, ddt, J = 17.0, 10.2, 6.3 Hz), 5.07 - 4.96 (2H, m) 3.76 (2H, d, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 175.2, 163.6, 144.3, 137.3, 135.6, 122.7, 116.5, 115.7, 110.6, 40.1; IR (KBr) 3047, 2853, 2704, 2589, 1643, 1606, 1576, 1441, 1410, 1309, 1293, 1275, 1237, 1193, 1169, 1124, 1068, 1014, 1002, 915, 814, 792, 757, 707, 573 cm^{-1}; MS (EI) *m/z* (rel. intensity) 178 ([M^+], 33), 160 (100), 132 (24), 115 (3), 104 (26), 77 (12), 63 (4), 51 (11); HR-MS (EI) ($C_{10}H_{10}O_3$) *calcd.* 178.0630, *found* 178.0632; $C_{10}H_{10}O_3$ (178.20) *calcd.* C 67.41, H 5.66; *found* C 67.53, H 5.75.

(4*S*, 5*R*)-3-((2*R*)-2,5-Dimethyl-hex-4-enoyl)-4-methyl-5-phenyl-oxazolidin-2-one (9). A solution of substrate **8** (6.64 g, 28.5 mmol) in THF (20 mL) is slowly added to a solution of LiHMDS (5.24 g, 31.3 mmol) in THF (150 mL) at −78 °C. Stirring is continued at that temperature for 30 minutes prior to the addition of 3,3-dimethylallyl bromide (11.6 mL, 100.6 mmol) at −5 °C. The mixture is kept at 0 °C for 16 h before the reaction is quenched by addition of aq. sat. NH_4Cl. Extraction with Et_2O, drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 15:1) affords product **9** as a colourless oil (7.27 g, 85 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 7.47 - 7.30 (5H, m), 5.65 (1H, d, J = 7.4 Hz), 5.19 - 5.11 (1H, m), 4.77 (1H, dq, J = 7.4, 6.6 Hz), 3.79 (1H, dq, J = 6.8, 6.8 Hz), 2.45 -2.33 (1H, m), 2.23 -2.11 (1H, m), 1.68 (3H, s), 1.62 (3H, s), 1.15 (3H, d, J = 6.8 Hz), 0.83 (3H, d, 6.6 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 176.9, 153.1, 134.2, 134.1, 129.0, 128.9, 126.1, 121.5, 79.0, 55.0, 38.2, 32.7, 25.8, 17.9, 16.6, 14.7; $[\alpha]^{20}_D$ = −33.6 (1.32, CH_2Cl_2); IR (neat) 3065, 3034, 2973, 2933, 2877, 1782, 1700, 1607, 1497, 1456, 1383, 1368, 1344, 1305, 1241, 1231, 1287, 1198, 1146, 1122, 1090, 1068, 1027,

987, 959, 767, 725, 700 cm^{-1}; MS (EI) *m/z* (rel. intensity) 301 ([M^+], 27), 286 (2), 257 (2) 233 (99), 214 (2), 178 (17), 159 (26), 134 (30), 124 (11), 118 (37), 109 (14), 96 (100), 81 (26), 69 (21), 55 (29), 41 (29); HR-MS (EI) ($C_{18}H_{23}NO_3$) *calcd*. 301.1678, *found* 301.1679; $C_{18}H_{23}NO_3$ (301.39) *calcd*. C 71.73, H 7.69, N 4.65; *found* C 71.63, H 7.78, N 4.61.

(2*R*)-2,5-Dimethyl-hex-4-enoic acid (10). Aqueous H_2O_2 (30 % w/w, 24.1 mL) and a suspension of $LiOH{\cdot}H_2O$ (4.43 g, 105.5 mmol) in water (20 mL) are added at 0 °C to a solution of compound **9** (15.78 g, 52.4 mmol) in THF (150 mL) and water (50 mL). The reaction is quenched after 4 h by addition of a solution of Na_2SO_3 (30.3 g, 240 mmol) in water (100 mL). After stirring for additional 45 minutes, the organic solvent is evaporated and the remaining aqueous phase is washed with CH_2Cl_2. Acidification of the aqueous phase with diluted HCl to pH 1, extraction with Et_2O, drying of the combined organic phases over Na_2SO_4 and evaporation of the solvent affords product **10** as a colourless oil (7.40 g, 99 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 10.50 - 10.00 (1H, br s), 5.12 - 5.04 (1H, m), 2.52 - 2.28 (2H, m), 2.19 - 2.08 (1H, m), 1.67 (3H, s), 1.59 (3H, s), 1.14 (3H, d, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 183.0, 134.0, 120.9, 39.8, 31.8, 25.8, 17.8, 16.3; $[\alpha]^{20}_D = -8.8$ (2.08, CH_2Cl_2); IR (KBr) 2975, 2935, 2661, 1710, 1463, 1417, 1378, 1338, 1287, 1245, 1226, 1185, 1125, 1083, 1049, 933, 856, 812, 778, 625 cm^{-1}; MS (EI) *m/z* (rel. intensity) 142 ([M^+], 24), 124 (2), 109 (1), 97 (3), 87 (5), 81 (5), 74 (17), 69 (100), 55 (10), 41 (55); HR-MS (EI) ($C_8H_{14}O_2$) *calcd*. 142.0994, *found* 142.0993.

(2*R*)-2,5-Dimethyl-hex-4-enoyl chloride (11). Chloroenamine **12** (3.50 g, 26.3 mmol) is slowly added via syringe to a solution of acid **10** (3.11 g, 21.90 mmol) in CH_2Cl_2 (40 mL). After stirring for 90 minutes the solvent is evaporated in vacuo affording acid chloride **11** as a colourless oil. The crude product is dissolved in THF (35 mL) and directly used in the next step.

(4*R*)-4,7-Dimethyl-3-oxo-oct-6-enoic acid methyl ester (13). A solution of *n*-BuLi (1.6 M in hexane, 53.0 mL, 84.3 mmol) is added at −78 °C to a solution of diisopropylamine (10.75

ml, 76.7 mmol) in THF (200 mL). The reaction mixture is stirred for 30 minutes at −20 °C prior to the slow addition of methyl acetate (6.10 ml, 76.7 mmol) at −78 °C. After stirring for 1 h, a solution of acid chloride **11** (21.90 mmol, crude) in THF (35 mL) is added and the reaction mixture is quickly warmed to ambient temperature. After 2 h the reaction is quenched by addition of aq. sat. NH_4Cl. Extraction with Et_2O, drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 15:1) affords keto ester **13** as a colourless oil (3.50 g, 81 %). According to NMR, the product consists of a 9:1 mixture of keto-enol tautomers. NMR-Data for major keto-form: ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.09 - 5.02 (1H, m), 3.69 (3H, s), 3.47 (2H, s), 2.69 - 2.58 (1H, m), 2.36 - 2.24 (1H, m), 2.14 - 2.02 (1H, m), 1.69 (3H, s), 1.61 (3H, s), 1.07 (3H, d, J = 7.0 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 206.6, 168.1, 134.4, 121.2, 52.4, 48.1, 47.2, 31.5, 25.8, 17.9, 15.8; $[\alpha]^{20}_D$ = −35.1 (1.54, CH_2Cl_2); IR (KBr) 2971, 2934, 1752, 1715, 1653, 1626, 1450, 1438, 1405, 1377, 1318, 1237, 1195, 1155, 1119, 1039, 1006, 849, 842, 805, 778, 739, 703, 658 cm^{-1}; MS (EI) *m/z* (rel. intensity) 198 ([M^+], 18), 180 (8), 166 (4), 143 (13), 130 (54), 125 (31), 109 (20), 101 (29), 96 (25), 81 (14), 74 (15), 69 (100), 55 (38), 41 (56); HR-MS (EI) ($C_{11}H_{18}O_3$) *calcd*. 198.1256, *found* 198.1254; $C_{11}H_{18}O_3$ (198.26) *calcd*. C 66.64, H 9.15; *found* C 66.52, H 9.08.

(3*S*,4*R*)-3-Hydroxy-4,7-dimethyl-oct-6-enoic acid methyl ester (14). A stainless steel autoclave (50 mL) is charged with a solution of compound **13** (594 mg, 3 mmol) in MeOH (20 mL). After addition of [(*R*)-BINAP·$RuCl_2$]$_2$·NEt_3 (3.1 mM in THF, 8 mL, 0.025 mmol, 0.8 mol %) the autoclave is pressurized with H_2 (4 atm) and the reaction mixture is stirred for 4 h at 80 °C. After venting the autoclave, the solvent is removed in vacuo and the residue is purified by flash chromatography (hexanes/ethyl acetate, 6:1) affording product **14** (575 mg, 96 %) as a colourless oil. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.14 (1H, ddsept, J = 7.8, 6.8, 1.4 Hz), 3.83 (1H, dddd, J = 9.5, 6.1, 4.0, 2.6 Hz), 3.68 (3H, s), 2.82 (1H, d, J = 4.0 Hz), 2.50 (1H, dd, J = 16.1, 2.9 Hz), 2.38 (1H, dd, J = 16.1, 9.6 Hz), 2.15 (1H, ddd, J = 14.2, 6.8, 4.8 Hz), 1.89 (1H, ddd, J = 14.2, 8.6, 7.8 Hz), 1.70 (3H, q, 1.3 Hz), 1.61 (3H, d, J = 0.8 Hz), 1.59 (1H, dddq, J = 8.4, 6.1, 4.8, 6.8 Hz), 0.86 (3H, d, J = 6.8 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz)

δ 174.1, 133.0, 123.0, 72.0, 52.0, 39.6, 38.5, 31.2, 25.9, 17.9, 15.3; $[\alpha]^{20}_D$ = –20.5 (1.29, CH_2Cl_2); IR (neat) 3472, 2964, 2925, 2881, 1739, 1438, 1405, 1377, 1339, 1288, 1260, 1196, 1170, 1113, 1051, 1018, 990, 880, 846 cm^{-1}; MS (EI) *m/z* (rel. intensity) 200 ([M^+], 11), 182 (55), 167 (9), 150 (14), 122 (40), 109 (62), 107 (56), 103 (24), 93 (25), 81 (22), 69 (84), 55 (57), 41 (100), 29 (37); HR-MS (EI) ($C_{11}H_{20}O_3$) *calcd*. 200.1412, *found* 200.1413; $C_{11}H_{20}O_3$ (200.28) *calcd*. C 65.97, H 10.07; *found* C 66.11, H 9.98.

(3*S*,4*R*)-3-Methoxymethoxy-4,7-dimethyl-oct-6-enoic acid methyl ester (15). *N*,*N*-Dimethylaminopyridine (35 mg, 0.29 mmol), diisopropylethylamine (1.52 mL, 8.7 mmol) and MOMCl (0.66 mL, 8.7 mmol) are added to a solution of compound **14** (580 mg, 2.9 mmol) in CH_2Cl_2 (60 mL). Stirring at ambient temperature is continued for 40 h. After dilution with ethyl acetate (200 mL) the organic phase is washed with brine (2 x 50 mL), dried over Na_2SO_4, evaporated and the crude product is purified by flash chromatography (hexanes/ethyl acetate, 10:1) affording product **15** as a colourless oil (637 mg, 90 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.15 - 5.08 (1H, m), 4.61 (2H, s), 3.95 - 3.87 (1H, m), 3.65 (3H, s), 3.30 (3H, s), 2.44 (1H, d, J = 7.4 Hz), 2.43 (1H, d, 4.9 Hz), 2.08 - 1.95 (1H, m), 1.88 - 1.75 (2H, m), 1.70 (3H, s), 1.60 (3H, s), 0.86 (3H, d, J = 6.5 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 172.7, 133.0, 123.0, 96.7, 78.8, 55.8, 51.8, 37.7, 36.7, 31.5, 25.9, 17.9, 14.5; $[\alpha]^{20}_D$ = –15.6 (1.90, CH_2Cl_2); IR (KBr) 2962, 2932, 2889, 2824, 1742, 1673, 1437, 1378, 1343, 1290, 1272, 1214, 1194, 1173, 1150, 1100, 1043, 976, 919, 857, 821 cm^{-1}; MS (EI) *m/z* (rel. intensity) 244 ([M^+], < 1), 212 (12), 194 (3), 182 (18), 167 (3), 155 (4), 139 (6), 121 (19), 103 (23), 81 (9), 69 (33), 55 (24), 45 (100), 41 (25), 29 (9); HR-MS (CI) ($C_{13}H_{24}O_3$ + H) *calcd*. 245.1753, *found* 245.1754; $C_{13}H_{24}O_4$ (244.33) *calcd*. C 63.91, H 9.90; *found* C 64.06, H 10.05.

(5*S*,6*R*)-5-Methoxymethoxy-6,9-dimethyl-3-oxo-dec-8-enoic acid *tert*-butyl ester (16). A solution of *tert*-butyl acetate (2.11 mL, 15.66 mmol) in THF (10 mL) is slowly added to a solution of LiHMDS (2.62 g, 15.66 mmol) in THF (100 mL) at –45 °C. The temperature is raised to –30 °C over a period of 90 minutes. A solution of compound **15** (636 mg, 2.60 mmol) in THF (20 mL) is then added at –40 °C. Stirring is continued for 3h while the

temperature is raised again to −30 °C. Quenching with aq. sat. NH_4Cl, extraction with Et_2O, drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethylacetate 10:1) affords product **16** as a colourless oil (839 mg, 98 %). According to NMR, the product consists of a 13:1 mixture of the keto-enol tautomers. NMR-Data for major keto-form: ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.16 - 5.08 (1H, m), 4.58 (2H, s), 4.01 - 3.94 (1H, m), 3.37 (2H, s), 3.29 (3H, s), 2.73 (1H, dd, J = 16.2, 8.7 Hz), 2.52 (1H, dd, J = 16.2, 3.2 Hz), 2.04 - 1.92 (1H, m), 1.87 - 1.76 (2H, m), 1.70 (3H, s), 1.59 (3H, s), 1.45 (9H, s), 0.86 (3H, d, J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 202.5, 166.7, 133.0, 122.9, 96.7, 81.9, 77.7, 55.9, 51.9, 44.4, 37.6, 31.7, 28.1, 25.9, 18.0, 14.5; $[\alpha]^{20}_D$ = −18.1 (1.29, CH_2Cl_2); IR (neat) 2975, 2931, 2824, 1738, 1717, 1643, 1456, 1408, 1393, 1369, 1319, 1286, 1253, 1212, 1150, 1099, 1040, 944, 919, 840 cm^{-1}; MS (EI) *m/z* (rel. intensity) 328 ([M^+], < 1), 296 (2), 266 (1), 240 (25), 223 (5), 210 (15), 181 (9), 139 (15), 123 (14), 109 (22), 97 (15), 81 (10), 69 (32), 57 (72), 45 (100), 41 (31), 29 (13); HR-MS (CI) ($C_{18}H_{32}O_5$ + H) *calcd*. 329.2328, *found* 329.2328; $C_{18}H_{32}O_5$ (328.45) *calcd*. C 65.82, H 9.82; *found* C 65.70, H 9.74.

(3*R*,5*S*,6*R*)-3-Hydroxy-5-methoxymethoxy-6,9-dimethyl-dec-8-enoic acid *tert*-butyl ester (17). A stainless steel autoclave (50 mL) is charged with a solution of keto ester **16** (827 mg, 2.52 mmol) in MeOH (20 mL). After addition of [(*R*)-BINAP·$RuCl_2$]$_2$·NEt_3 (3.1 mM in THF, 10 mL, 0.031 mmol, 1.2 mol%) the autoclave is pressurized with H_2 (80 atm) and the reaction mixture is stirred for 6.5 h at 25 °C. After the autoclave has been ventured, the solvent is removed in vacuo and the residue is purified by flash chromatography (hexanes/ethyl acetate, 4:1) affording product **17** (777 mg, 93 %) as a colourless oil. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.16 - 5.08 (1H, m), 4.67 (1H, d, J = 6.8 Hz), 4.60 (1H, d, J = 6.8 Hz), 4.15 - 4.06 (1H, m), 3.67 - 3.60 (1H, m), 3.55 - 3.30 (1H, br s), 3.36 (3H, s), 2.41 (1H, dd, J = 15.7, 4.6 Hz), 2.32 (1H, dd, J = 15.7, 7.9 Hz), 1.98 - 1.78 (3H, m), 1.70 (3H, s), 1.69 - 1.41 (2H, m), 1.60 (3H, s), 1.44 (9H, s), 0.86 (3H, d, J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 172.0, 132.8, 123.2, 96.0, 81.0, 80.5, 67.8, 56.1, 43.2, 36.8, 36.5, 31.7, 28.2, 25.9, 18.0, 14.1; $[\alpha]^{20}_D$ = −41.5 (1.20, CH_2Cl_2); IR (KBr) 3468, 2971, 2932, 1729, 1632, 1455, 1392, 1368, 1340, 1302, 1258,

1214, 1151, 1097, 1034, 951, 917, 844, 774 cm^{-1}; MS (EI) *m/z* (rel. intensity) 330 ([M^+], <1), 242 (29), 224 (14), 212 (42), 183 (20), 145 (38), 123 (13), 115 (61), 95 (21), 81 (14), 69 (44), 57 (63), 45 (100); HR-MS (CI) ($C_{18}H_{34}O_5$ + H) *calcd*. 331.2484, *found* 331.2485; $C_{18}H_{34}O_5$ (330.47) *calcd*. C 65.42, H 10.37; *found* C 65.36, H 10.45.

(3*S*,5*S*,6*R*)-5-Methoxymethoxy-6,9-dimethyl-dec-8-ene-1,3-diol (18). $LiAlH_4$ (114 mg, 3 mmol) is added to a solution of compound **17** (330 mg, 1 mmol) in Et_2O (50 mL) at 0 °C. Careful addition of aq. sat. NH_4Cl (20 mL) after 6 h, extraction with Et_2O (3 x 50 mL), drying of the combined organic phases over Na_2SO_4, evaporation of the solvent and flash chromatography of the residue (hexanes/ethyl acetate, 1:1 → 1:2) affords diol **18** as a colourless oil (255 mg, 98 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.15 - 5.07 (1H, m), 4.67 (1H, d, J = 6.6 Hz), 4.62 (1H, d, J = 6.6 Hz), 4.05 - 3.95 (1H, m), 3.81 - 3.65 (4H, m), 3.37 (3H, s), 3.20 - 2.85 (1H, br s), 1.98 - 1.78 (3H, m), 1.74 - 1.61 (3H, m), 1.70 (3H, s), 1.59 (3H, s), 1.55 - 1.46 (1H, m), 0.86 (3H, d, J = 6.0 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 132.9, 123.1, 95.9, 81.9, 72.2, 61.6, 56.2, 39.3, 36.8, 36.7, 31.9, 25.8, 17.9, 13.8; $[\alpha]^{20}_D = -51.1$ (1.19, CH_2Cl_2); IR (neat) 3386, 2961, 2931, 2888, 1658, 1442, 1377, 1212, 1151, 1097, 1037, 969, 918, 864, 822, 724 cm^{-1}; MS (EI) *m/z* (rel. intensity) 260 ([M^+], < 1), 228 (5), 210 (2), 198 (8), 183 (10), 165 (2), 141 (7), 124 (8), 110 (14), 101 (43), 95 (17), 83 (17), 69 (34), 55 (29), 45 (100), 41 (25), 29 (12); $C_{14}H_{28}O_4$ (260.37) *calcd*. C 64.58, H 10.84, *found* C 64.46, H 10.95.

(3*S*,5*S*,6*R*)-1-(4-Methoxy-benzyloxy)-5-methoxymethoxy-6,9-dimethyl-dec-8-en-3-ol (19). A solution of diol **18** (294 mg, 1.13 mmol) in DMF (10 mL) is added to a suspension of NaH (109 mg, 4.52 mmol) in DMF (15 mL). The mixture is stirred for 75 minutes before PMBCl (153 µL, 1.13 mL) is added via syringe. After stirring for another 90 minutes, the reaction is quenched by addition of diethylamine (5 drops). The reaction mixture is diluted with ethyl acetate (50 ml) and the organic phase is washed with brine (3 x 20 mL). Drying over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 2:1) affords product **19** as a colourless oil (345 mg, 85 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 7.25 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 5.16 - 5.07 (1H, m), 4.67 (1H, d, J = 6.7 Hz), 4.60 (1H, d,

J = 6.6 Hz), 4.42 (2H, s), 3.94 - 3.84 (1H, m), 3.79 (3H, s), 3.69 - 3.53 (3H, m), 3.50 - 3.25 (1H, br s), 3.36 (3H, s), 1.97 - 1.49 (7H, m), 1.71 (3H, s), 1.59 (3H, s), 0.86 (3H, d, J = 6.3 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 159.6, 132.7, 131.0, 129.6, 123.3, 114.0, 95.9, 81.1, 73.1, 69.7, 68.3, 56.1, 55.5, 37.5, 37.1, 36.8, 31.8, 25.9, 17.9, 14.1; $[\alpha]^{20}_D$ = −26.0 (1.32, CH_2Cl_2); IR (KBr) 3463, 2930, 1613, 1586, 1514, 1463, 1442, 1375, 1302, 1248, 1210, 1173, 1152, 1096, 1036, 969, 917, 821, 773, 756, 707, 637, 571, 518 cm^{-1}; MS (EI) *m/z* (rel. intensity) 380 ([M^+], < 1), 348 (1), 247 (1), 227 (2), 197 (4), 176 (2), 151 (1), 137 (13), 121 (100), 101 (7), 69 (7), 55 (4), 45 (15); $C_{22}H_{36}O_5$ (380.52) *calcd*. C 69.44, H 9.54; *found* C 69.46, H 9.48.

2-Allyl-6-hydroxy-benzoic acid (1*R*,3*S*,4*R*)-1-[2-(4-methoxy-benzyloxy)-ethyl]-3-methoxymethoxy-4,7-dimethyl-oct-6-enyl ester (23a). A solution of alcohol **19** (152 mg, 0.4 mmol) and PPh_3 (210 mg, 0.8 mmol) in Et_2O (15 mL) is added dropwise at ambient temperature to a solution of the carboxylic acid **7** (142 mg, 0.8 mmol) and DEAD (126 μL, 0.8 mmol) in Et_2O (25 mL). After stirring for 20h, the mixture is concentrated to a volume of ca. 5 mL and precipitated triphenylphosphine oxide is removed by filtration. Drying over Na_2SO_4, evaporation and flash chromatography (hexanes/ethyl acetate, 20:1) affords ester **23a** as a colourless oil (190 mg, 88 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 11.09 (1H, s), 7.31 (1H, dd, J = 8.0, 7.5 Hz), 7.21 (2H, d, J = 8.6 Hz), 6.84 (1H, d, J = 8.0 Hz), 6.81 (2H, d, J = 8.6 Hz), 6.73 (1H, d, J = 7.5 Hz), 5.98 (1H, ddt, J = 17.1, 10.2, 6.1 Hz), 5.62 - 5.53 (1H, m), 5.12 - 5.05 (1H, m), 5.01 (1H, dd, J = 10.2, 1.6 Hz), 4.93 (1H, dd, J = 17.1, 1.6 Hz), 4.64 (1H, d, J = 6.8 Hz), 4.55 (1H, d, J = 6.8 Hz), 4.38 (2H, s), 3.76 (3H, s), 3.69 (1H, d, J = 6.0 Hz), 3.64 (1H, d, J = 6.0 Hz), 3.60 - 3.49 (3H, m), 3.33 (3H, s), 2.12 - 1.48 (7H, m), 1.63 (3H, s), 1.56 (3H, s), 0.87 (3H, d, J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 171.1, 162.7, 159.6, 143.0, 138.3, 134.3, 132.8, 130.8, 129.6, 123.1, 122.7, 116.3, 115.5, 113.9, 113.3, 96.9, 78.5, 73.0, 72.4, 66.8, 55.5, 54.5, 40.3, 37.4, 35.5, 35.2, 31.8, 25.7, 17.9, 13.8; $[\alpha]^{20}_D$ = −15.1 (1.02, CH_2Cl_2); IR (neat) 3374, 3059, 2960, 2928, 1723, 1656, 1608, 1578, 1514, 1450, 1374, 1302, 1249, 1222, 1165, 1098, 1039, 999, 917, 818, 767, 712, 573 cm^{-1}; MS (EI) *m/z* (rel. intensity) 540 ([M^+], < 1), 508 (2), 387 (1), 330 (1), 298 (2), 211 (2), 179 (3), 161 (7), 139

(1), 121 (100), 109 (1), 69 (4), 45 (10); $C_{32}H_{44}O_7$ (540.70) *calcd*. C 71.08, H 8.20; *found* C 71.15, H 8.12.

2-Allyl-6-methoxy-benzoic acid (1*R*,3*S*,4*R*)-1-[2-(4-methoxy-benzyloxy)-ethyl]-3-methoxymethoxy-4,7-dimethyl-oct-6-enyl ester (23b). A solution of diene **23a** (54.0 mg, 0.1 mmol) and trimethylsilyl diazomethane (2 M in hexane, 250 µL, 0.5 mmol) in THF (4 mL) and MeOH (2 mL) is stirred at ambient temperature. Additional trimethylsilyl diazomethane (2 M in hexane, 250 µL, 0.5 mmol) is added after 38 h, and stirring is continued for another 8 h. The reaction is quenched by addition of a few drops of acetic acid. Evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 10:1 → 4:1) affords compound **23b** as a colourless oil (29.8 mg, 54 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 7.33 - 7.24 (3H, m), 6.89 - 6.78 (4H, m), 6.02 - 5.85 (1H, m), 5.45 - 5.34 (1H, m), 5.13 - 5.01 (3H, m), 4.69 (2H, s), 4.46 (1H, d, J = 11.4 Hz), 4.42 (1H, d, J = 11.4 Hz), 3.80 (3H, s), 3.79 (3H, s), 3.69 - 3.55 (3H, m), 3.37 (3H, s), 3.34 (2H, d, J = 6.5 Hz), 2.12 - 1.67 (7H, m), 1.60 (3H, s), 1.52 (3H, s), 0.87 (3H, d, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 168.0, 159.6, 156.6, 138.5, 137.0, 132.5, 131.2, 130.5, 129.6, 124.7, 123.3, 121.9, 116.4, 114.0, 109.2, 97.1, 78.5, 72.9, 71.1, 66.8, 55.9, 55.8, 55.6, 37.7, 37.5, 35.6, 35.4, 32.0, 25.8, 17.8, 14.0.

2-Allyl-6-methoxymethoxy-benzoic acid (1*R*,3*S*,4*R*)-1-[2-(4-methoxy-benzyloxy)-ethyl]-3-methoxymethoxy-4,7-dimethyl-oct-6-enyl ester (23c). Diisopropylethylamine (261 µL, 1.5 mmol) and MOMCl (76 µL, 1 mmol) are added to a solution of compound **23a** (54.0 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) and the mixture is stirred for 18 h. After dilution with ethyl acetate (20 mL), the organic phase is washed with brine (2 x 10 mL). Drying over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 10:1) affords product **23c** as a colourless oil (49.2 mg, 84 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 7.33 - 7.24 (3H, m), 7.02 (1H, d, J = 8.4 Hz), 6.93 - 6.84 (3H, m), 6.03 - 5.86 (1H, m), 5.47 - 5.36 (1H, m), 5.18 (1H, d, J =6.8 Hz), 5.12 (1H, d, J =6.8 Hz), 5.10 - 5.02 (3H, m), 4.69 (2H, s), 4.46 (1H, d, J = 11.4 Hz), 4.42 (1H, d, J = 11.4 Hz), 3.79 (3H, s), 3.68 - 3.55 (3H, m), 3.43 (3H, s), 3.38 (3H, s), 3.36 (2H, d, J = 6.5 Hz), 2.12 - 1.68 (7H, m), 1.59 (3H, s), 1.51 (3H, s), 0.87

(3H, d, J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 167.8, 159.6, 154.2, 138.6, 136.9, 132.6, 131.1, 130.4, 129.5, 125.5, 123.3, 122.9, 116.5, 114.0, 112.6, 97.0, 94.9, 78.4, 73.0, 71.2, 66.8, 56.3, 55.9, 55.5, 37.7, 37.5, 35.6, 35.3, 32.0, 25.8, 17.8, 14.0; IR (neat) 2959, 2931, 1726, 1639, 1612, 1585, 1513, 1465, 1442, 1376, 1301, 1249, 1208, 1155, 1097, 1036, 947, 919, 821, 755, 580 cm^{-1}; MS (EI) *m/z* (rel. intensity) 584 ([M$^+$], < 1), 539 (3), 507 (2), 416 (4), 403 (3), 371 (3), 305 (1), 223 (2), 205 (10), 161 (7), 121 (100), 69 (3), 45 (15).

2-Allyl-6-(*tert*-butyl-dimethyl-silanyloxy)-benzoic acid (1*R*,3*S*,4*R*)-1-[2-(4-methoxy-benzyloxy)-ethyl]-3-methoxymethoxy-4,7-dimethyl-oct-6-enyl ester (23d). A solution of diene **23a** (103 mg, 0.19 mmol), imidazole (129 mg, 1.90 mmol) and TBSCl (229 mg, 1.52 mmol) in DMF (10 mL) is stirred for 24 h at ambient temperature. The reaction mixture is diluted with ethyl acetate (50 mL) and the organic phase is washed with brine (3 x 20 mL). Drying over Na_2SO_4, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 15:1) affords product **23d** as a colourless oil (111 mg, 89 %). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 7.26 (2H, d, J =8.6 Hz), 7.18 (1H, dd, J = 8.2, 7.9 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.82 (1H, d, J = 7.9 Hz), 6.74 (1H, d, J = 8.2 Hz), 6.02 - 5.87 (1H, m), 5.27 - 5.18 (1H, m), 5.11 - 5.01 (3H, m), 4.65 (1H, d, J = 6.8 Hz), 4.60 (1H, d, J = 6.8 Hz), 4.45 (1H, d, J = 11.4 Hz), 4.39 (1H, d, J = 11.4 Hz), 3.79 (3H, s), 3.65 - 3.52 (3H, m), 3.40 - 3.32 (2H, m), 3.35 (3H, s), 2.20 - 2.09 (1H, m), 2.05 - 1.92 (2H, m), 1.88 - 1.68 (4H, m), 1.61 (3H, s), 1.52 (3H, s), 0.98 (9H, s), 0.86 (3H, d, J = 6.3 Hz), 0.25 (6H, s); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 168.0, 159.5, 152.9, 138.8, 137.1, 132.7, 131.2, 130.1, 129.5, 127.3, 123.3, 122.1, 117.3, 116.4, 114.0, 96.6, 78.9, 72.8, 72.2, 67.0, 55.9, 55.5, 37.8, 37.5, 35.3, 35.2, 31.6, 26.0, 25.8, 18.8, 17.9, 14.2, -3.9; $[\alpha]^{20}_D$ = −12.4 (1.02, CH_2Cl_2); IR (neat) 3077, 2955, 2930, 2887, 2858, 1728, 1639, 1613, 1594, 1584, 1514, 1464, 1408, 1376, 1362, 1282, 1250, 1172, 1155, 1099, 1062, 1037, 917, 838, 785, 743, 716, 668, 579 cm^{-1}; MS (EI) *m/z* (rel. intensity) 654 ([M$^+$], < 1), 597 (1), 486 (2), 331 (1), 301 (2), 275 (9), 235 (8), 203 (3), 137 (1), 121 (100), 69 (5), 45 (13); $C_{38}H_{58}O_7Si$ (654.96) *calcd*. C 69.69, H 8.93; *found* C 69.57, H 9.05.

(7*R*,9*S*,10*R*)-4-Hydroxy-7-[2-(4-methoxy-benzyloxy)-ethyl]-9-methoxymethoxy-10-methyl-7,8,9,10,11,14-hexahydro-6-oxa-benzocyclododecen-5-one (24a). Carbene **21** (2.1 mg, 0.0025 mmol, 5 mol%) is added to a solution of diene **23a** (27.0 mg, 0.05 mmol) in toluene (50 mL) at 80 °C. Additional catalyst **21** (2.1 mg, 0.0025 mmol, 5 mol%) is added after 2 h. The reaction is stopped after 20 h upon addition of ethoxy-ethene (1 mL). Evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 10:1) affords (*Z*)-**24a** as a colourless oil (16.6 mg, 69 %). ^{1}H-NMR (C_6D_6, 300 MHz) δ 11.69 (1H, s), 7.23 - 7.17 (2H, m), 6.98 - 6.95 (2H, m), 6.83 - 6.76 (2H, m), 6.48 - 6.43 (1H, m), 5.75 - 5.65 (1H, m), 5.18 - 5.03 (2H, m), 4.55 (1H, d, J = 6.9 Hz), 4.49 (1H, d, J = 6.9 Hz), 4.48 - 4.40 (1H, m), 4.25 (1H, d, J = 11.5 Hz), 4.20 (1H, d, J = 11.5 Hz), 3.74 - 3.68 (1H, m), 3.34 - 3.28 (2H, m), 3.30 (3H, s), 3.23 (3H, s), 2.90 - 2.82 (1H, m), 2.07 - 1.62 (7H, m), 0.88 (3H, d, J = 6.6 Hz); ^{13}C-NMR (C_6D_6, 75.5 MHz) δ 171.7, 163.8, 159.7, 144.7, 134.6, 131.5, 130.9, 129.5, 127.9, 123.0, 116.8, 114.0, 113.0, 95.9, 76.5, 74.1, 72.9, 66.4, 55.3, 54.7, 36.0, 35.5, 35.2, 35.0, 32.2, 13.8; IR (neat) 2956, 2932, 1657, 1606, 1576, 1513, 1449, 1361, 1295, 1247, 1217, 1165, 1098, 1038, 992, 916, 816, 770, 714, 669, 662 cm^{-1}; MS (EI) *m/z* (rel. intensity) 484 ([M^{+}], 1), 452 (5), 439 (4), 303 (3), 286 (2), 176 (1), 150 (1), 121 (100), 77 (2), 45 (9).

(7*R*,9*S*,10*R*)-4-Methoxy-7-[2-(4-methoxy-benzyloxy)-ethyl]-9-methoxymethoxy-10-methyl-7,8,9,10,11,14-hexahydro-6-oxa-benzocyclododecen-5-one (24b). Carbene **21** (2.3 mg, 0.0027 mmol, 5 mol%) is added to a solution of diene **23b** (29.8 mg, 0.054 mmol) in toluene (50 mL) at 80 °C. The reaction is stopped after 90 minutes upon addition of ethoxy-ethene (1 mL). Evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 4:1) affords product **24b** as a colourless oil (25.0 mg, 93 %). The macrocycle is formed as a mixture of *E*/*Z*-isomers (66/34). **(*E*)-24c**: ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.30 (2H, d, J = 8.6 Hz), 7.03 - 6.91 (1H, m), 6.82 (2H, d, J = 8.6 Hz), 6.55 (1H, d, J = 7.5 Hz), 6.34 (1H, d, J = 7.6 Hz), 5.91 - 5.80 (1H, m), 5.48 - 5.21 (2H, m), 5.03 (1H, d, J = 6.7 Hz), 4.81 (1H, d, J = 6.7 Hz), 4.48 - 4.44 (1H, m), 4.43 (2H, s), 3. 89 - 3.78 (1H, m), 3.75 - 3.63 (2H, m) 3.35 (3H, s), 3.29 (3H, s), 3.25 - 3.15 (1H, m), 3.17 (3H, s), 2.20 - 1.86 (4H, m), 1.80 - 1.52 (3H, m), 0.87 (3H, d, J = 6.6 Hz); ^{13}C-NMR (C_6D_6, 75.5 MHz) δ 168.0, 159.6, 157.1, 139.6, 131.6, 131.5,

129.7, 129.2, 129.0, 128.9, 123.0, 114.1, 109.6, 97.1, 79.6, 72.8, 72.1, 66.8, 55.4, 55.0, 54.7, 38.1, 38.0, 37.2, 36.4, 34.4, 13.6; **(*Z*)-24c:** ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.31 (2H, d, J = 8.6 Hz), 7.03 - 6.91 (1H, m), 6.82 (2H, d, J = 8.6 Hz), 6.63 (1H, d, J = 7.5 Hz), 6.38 (1H, d, J = 7.6 Hz), 5.91 - 5.80 (1H, m), 5.48 - 5.21 (2H, m), 4.88 (1H, d, J = 6.7 Hz), 4.73 (1H, d, J = 6.7 Hz), 4.29 (2H, s), 4.13 - 4.02 (2H, m), 3.56 - 3.50 (2H, m), 3.30 (3H, s), 3.29 (3H, s), 3.25 (3H, s), 2.96 - 2.87 (1H, m), 2.20 - 1.86 (4H, m), 1.80 - 1.52 (3H, m), 0.89 (3H, d, J = 6.6 Hz); ^{13}C-NMR (C_6D_6, 75.5 MHz) δ 166.5, 160.3, 157.6, 140.3, 131.3, 130.4, 129.6, 129.5, 128.8, 125.9, 122.9, 114.0, 110.0, 97.2, 78.0, 73.0, 72.1, 66.7, 55.6, 55.3, 54.7, 36.7, 36.5, 36.1, 32.9, 32.2, 13.6; IR (neat) 3064, 2956, 2929, 2839, 1725, 1612, 1597, 1584, 1513, 1468, 1439, 1380, 1362, 1301, 1273, 1250, 1173, 1154, 1098, 1069, 1039, 972, 951, 916, 820, 758, 728, 698, 637, 503 cm^{-1}; MS (EI) *m/z* (rel. intensity) 498 ([M^+], < 1), 466 (4), 453 (7), 436 (2), 300 (13), 245 (5), 215 (4), 176 (12), 135 (5), 121 (100), 95 (3), 77 (3), 55 (3), 45 (16).

(7*R*,9*S*,10*R*)-7-[2-(4-Methoxy-benzyloxy)-ethyl]-4,9-bis-methoxymethoxy-10-methyl-7,8,9,10,11,14-hexahydro-6-oxa-benzocyclododecen-5-one (24c). Carbene **21** (2.9 mg, 0.0035 mmol, 5 mol%) is added to a solution of diene **23c** (41.0 mg, 0.07 mmol) in toluene (50 mL) at 80 °C. Additional catalyst **21** (2.9 mg, 0.0035 mmol, 5 mol%) is introduced after 1 h. The reaction is stopped after 2 h upon addition of ethoxy-ethene (1 mL). Evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 4:1) affords product **24c** as a colourless oil (33.8 mg, 91 %). The macrocycle is formed as a mixture of *E*/*Z*-isomers (68/32). **(*E*)-24c**: ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.34 - 7.26 (2H, m), 7.01 - 6.87 (2H, m), 6.84 - 6.77 (2H, m), 6.58 - 6.53 (1H, m), 5.92 - 5.82 (1H, m), 5.48 - 5.21 (2H, m), 5.02 (1H, d, J = 6.7 Hz), 4.84 - 4.72 (3H, m), 4.47 - 4.43 (1H, m), 4.40 (2H, s), 3.92 - 3.51 (4H, m), 3.35 (3H, s), 3.29 (3H, s), 3.11 (3H, s), 2.18 - 1.57 (7H, m), 0.87 (3H, d, J = 6.9 Hz); ^{13}C-NMR (C_6D_6, 75.5 MHz) δ 167.9, 159.7, 154.9, 139.6, 131.5, 131.3, 129.8, 129.4, 129.2, 126.5, 123.9, 114.1, 113.2, 97.1, 94.5, 79.7, 72.8, 72.2, 66.7, 55.7, 55.4, 54.8, 38.1, 38.0, 36.8, 36.2, 34.4, 13.6; **(*Z*)-24c**: ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.34 - 7.26 (2H, m), 7.01 - 6.87 (2H, m), 6.84 - 6.77 (2H, m), 6.66 - 6.62 (1H, m), 5.92 - 5.82 (1H, m), 5.48 - 5.21 (2H, m), 4.92 (1H, d, J = 6.7 Hz), 4.84 - 4.72 (3H, m), 4.29 (2H, s), 4.11 - 3.98 (2H, m), 3.92 - 3.51 (2H, m), 3.30 (3H,

s), 3.29 (3H, s), 3.17 (3H, s), 2.94 - 2.85 (1H, m), 2.18 - 1.57 (7H, m), 0.88 (3H, d, J = 6.9 Hz); ^{13}C-NMR (C_6D_6, 75.5 MHz) δ 166.5, 159.7, 155.3, 140.3, 131.5, 131.4, 130.5, 129.6, 129.0, 126.0, 124.0, 114.0, 113.9, 97.3, 94.9, 78.0, 73.0, 72.0, 66.7, 55.9, 55.3, 54.8, 37.1, 36.8, 36.2, 32.9, 32.2, 13.6; IR (KBr) 2956, 1724, 1612, 1599, 1583, 1513, 1462, 1442, 1423, 1402, 1375, 1359, 1302, 1271, 1249, 1208, 1171, 1154, 1116, 1095, 1066, 1039, 971, 937, 920, 808, 769, 729, 697, 638, 596, 572, 515 cm^{-1}; MS (EI) *m/z* (rel. intensity) 528 ([M$^+$], < 1), 496 (2), 483 (7), 436 (2), 347 (5), 330 (2), 315 (1), 285 (1), 176 (2), 152 (4), 137 (1), 121 (100), 77 (1), 55 (2), 45 (18).

(7*R*,9*S*,10*R*)-4-(*tert*-Butyl-dimethyl-silanyloxy)-7-[2-(4-methoxy-benzyloxy)-ethyl]-9-methoxymethoxy-10-methyl-7,8,9,10,11,14-hexahydro-6-oxa-benzocyclododecen-5-one (24d). Carbene **21** (5.9 mg, 0.007 mmol, 5 mol%) is added to a solution of diene **23d** (91.6 mg, 0.14 mmol) in toluene (70 ml) at 80 °C. The reaction is stopped after 1 h upon addition of ethoxy-ethene (1 mL). Evaporation of the solvent and flash chromatography (hexanes/ethyl acetate, 15:1) affords product **24d** as a colourless oil (76.4 mg, 91 %). The macrocycle is formed as a mixture of *E*/*Z*-isomers (40/60). **(*E*)-24d**: ^{1}H-NMR (C_6D_6, 600 MHz) δ 7.27 (2H, d, J = 9.0 Hz), 6.91 (1H, dd, J = 8.2, 7.6 Hz), 6.84 - 6.82 (2H, m), 6.70 (1H, d, J = 8.2 Hz), 6.56 (1H, d, J = 7.6 Hz), 5.78 - 5.74 (1H, m), 5.40 - 5.36 (2H, m), 5.06 (1H, d, J = 6.7 Hz), 4.81 (1H, d, J = 6.7 Hz), 4.40 - 4.37 (1H, m), 4.35 (2H, s), 3.76 - 3.70 (1H, m), 3.60 - 3.57 (2H, m), 3.35 (3H, s), 3.31 (3H, s), 3.21 - 3.17 (1H, m), 2.31 - 2.24 (1H, m), 2.19 - 2.00 (3H, m), 1.73 - 1.69 (2H, m), 1.64 - 1.60 (1H, m), 1.00 (9H, s), 0.89 (3H, d, J = 6.8 Hz), 0.21 (3H, s), 0.10 (3H, s); ^{13}C-NMR (C_6D_6, 151 MHz) δ 168.2, 159.7, 153.4, 139.2, 131.4, 131.3, 129.4, 129.2, 129.1, 129.0, 123.6, 118.4, 114.0, 97.4, 79.5, 72.8, 72.5, 66.7, 55.4, 54.7, 38.3, 38.1, 36.6, 35.4, 34.5, 26.1, 18.6, 13.8, - 3.9, - 4.2; **(*Z*)-24d**: ^{1}H-NMR (C_6D_6, 600 MHz) δ 7.26 (2H, d, J = 9.0 Hz), 6.97 (1H, dd, J = 8.2, 7.6 Hz), 6.82 - 6.80 (2H, m), 6.73 (1H, d, J = 8.2 Hz), 6.62 (1H, d, J = 7.6 Hz), 5.88 - 5.84 (1H, m), 5.35 - 5.30 (1H, m), 5.26 - 5.20 (1H, m), 4.97 (1H, d, J = 6.7 Hz), 4.76 (1H, d, J = 6.7 Hz), 4.39 (1H, d, J = 11.5 Hz), 4.32 (1H, d, J = 11.5 Hz), 4.08 - 4.02 (2H, m), 3.55 - 3.52 (2H, m), 3.31 (3H, s), 3.30 (3H, s), 2.91 - 2.87 (1H, m), 2.12 - 1.90 (4H, m), 1.81 - 1.75 (1H, m), 1.74 - 1.70 (1H, m), 1.69 - 1.62 (1H, m),

1.04 (9H, s), 0.90 (3H, d, J = 6.8 Hz), 0.25 (3H, s), 0.17 (3H, s); ^{13}C-NMR (C_6D_6, 151 MHz) δ 166.5, 159.7, 154.1, 141.0, 131.3, 130.4, 129.8, 129.3, 128.9, 127.2, 123.4, 118.0, 114.0, 97.6, 77.9, 72.8, 71.4, 67.0, 55.3, 54.7, 37.0, 36.7, 36.5, 33.1, 32.3, 26.0, 18.5, 13.7, - 4.0, - 4.3; IR (KBr) 3064, 2956, 2931, 2897, 2857, 1727, 1613, 1593, 1582, 1514, 1463, 1382, 1362, 1282, 1251, 1172, 1155, 1100, 1065, 1040, 972, 914, 860, 839, 784, 733, 696, 670, 508 cm^{-1}; MS (EI) *m/z* (rel. intensity) 598 ([M^+], < 1), 553 (1), 541 (6), 341 (4), 262 (4), 207 (5), 121 (100), 45 (16).