General: Abbrevations used: GP (general procedure), HV (high vacuum, 0.01-0.001 Torr), rt (room temperature). THF was distilled over K; CH_2Cl_2 was used in puriss. quality dried over molecular sieve (4Å). Solvents for work-up and flash chromatography: pentane, hexane and ethyl acetate were distilled over sikkon, diethylether over $Fe(SO_4)$/KOH and CH_2Cl_2 over P_4O_{10}. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates. The compounds were visualized by $UV_{254\ nm}$ light or iodine or by dipping in/spraying with phosphomolybdic acid solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \bullet 4H_2O$ (10 g), H_2SO_4 (60 mL), H_2O (940 mL)]. Flash chromatography was carried out using silica gel 60 (0.040-0.063 mm). Melting points were measured in open glass capillaries with a Totolli apparatus and are uncorrected. Optical rotations $[\alpha]_D$ were determined at rt. IR spectra are given in cm^{-1}. ^1H and ^{13}C spectra were measured on 500/400/300/200 or 125/100/75 MHz spectrometers, respectively. Elemental analyses were performed by the Microanalytical Service Laboratory of the Laboratorium für Organische Chemie (ETH).

(4*R*,5*R*)-5-[(Chloro-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol (2). Triphenylphosphine (4.5 g, 17.0 mmol) and TADDOL **1** (4.0 g, 8.6 mmol) were dissolved in anhydrous CH_2Cl_2 (15 mL) under argon atmosphere. Pyridine (1.4 mL, 17.0 mmol) and CCl_4 (1.7 mL, 17.0 mmol) were added and the reaction mixture was stirred for 3 d at rt. After concentration to a volume of ca. 5 mL the solution was flash chromatographed (silica gel (250 g), pentane/Et_2O 4:1) and the obtained product recrystallized (pentane/Et_2O 6:1 (20 mL)) to yield **2** (3.0 g, 72%) as a white solid: R_f 0.58 (pentane/Et_2O 4:1); mp 133-135 °C; $[\alpha]_D^{rt}$ = -17.8 (*c* = 1.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, CH_3); 1.07 (s, CH_3); 1.82 (s, OH); 5.12 (d, *J* = 5.9 Hz, CH); 5.36 (d, *J* = 5.9 Hz, CH); 7.15-7.42 (m, 18 arom. H); 7.47-7.51 (m, 2 arom. H). All analytical data were in accordance with the literature values.[1]

(4*S*,5*S*)-2,2-Dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolan-4,5-dimethylamine (5). Dichloro-TADDOL **3** (5.0 g, 9.95 mmol), NH_4Cl (30 equiv, 15.94 g, 0.298 mol) and a magnetic stirring bar were placed in an evacuated and argon filled autoclave (250 mL). The autoclave was cooled to -78 °C and NH_3 (44 g, 2.44 mol) was condensed in. The reaction mixture was stirred at 85 °C for 2 d (25 bar). The autoclave was cooled to rt and the unreacted NH_3 was vented. The crude product was dissolved in CH_2Cl_2 and H_2O and neutralized with 1N HCl. The organic phase was washed with sat. $NaHCO_3$, H_2O, sat. NaCl, dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. According to ^1H NMR data, the crude product consisted of starting compound (17%), bicyclic product (1*S*,5*S*)-3,3-dimethyl-6,6,8,8-tetraphenyl-2,4-dioxa-7-azabicyclo[3,3,0]octane[1] (20%) and desired TADDAMIN **5** (63%). The crude product was flash chromatographed (silica gel (100 g), Et_2O) to yield **5** (2.9 g, 63%) as a white solid: R_f 0.10 (Et_2O); mp 198 - 200 °C; $[\alpha]_D^{rt}$ = - 45.2 (*c* = 1.0, $CHCl_3$). The analytical data matched those of the literature.[1]

(4*S*,5*R*)-5-[(Chloro-diphenyl)methyl]-N,N,2,2-tetramethyl-α,α-diphenyl-1,3-dioxolane-4-methanamin (7). Preparation as described elsewhere.[1] Recrystallization (pentane) leads to analytically pure **7**: mp 130-131 °C; $[\alpha]_D^{rt}$ = -36.4 (*c* = 1.18, $CHCl_3$); IR ($CHCl_3$) 3089, 3059, 3007, 2937, 2869, 2832, 2789, 1598, 1493, 1446, 1380, 1370, 1335, 1318, 1169, 1064, 1027, 924, 886, 861, 843, 631; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75 (s, CH_3); 1.23 (s, CH_3); 1.64 (s, $N(CH_3)_2$); 4.91 (d, *J* = 7.1 Hz, CH); 5.25 (d br., *J* = 5.8 Hz, CH); 7.14-7.36 (m, 18 arom. H), 7.59-7.61 (m, 2 arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.07, 27.51, 40.41 br. (CH_3); 73.80 (C); 78.11, 82.69 (CH); 107.66 (C); 126.16, 126.22, 126.94, 127.16, 127.28, 127.39, 128.11, 129.32 (CH); 130.47, 136.80, 144.36 (C); EI-MS *m/z* 512.1 (M, 0.3), 265.1 (4), 237.1 (11), 210.1 (100), 179.0 (40), 165.0 (25), 118.0 (11); Anal. Calcd for $C_{33}H_{34}NO_2Cl$ (512.09): C, 77.40; H, 6.69; N, 2.74; Cl,

[1] Seebach, D.; Beck, A. K.; Hayakawa, M.; Jaeschke, G.; Kühnle, F. N. M.; Nägeli, I.; Pinkerton, A. B.; Rheiner, P. B.; Duthaler, R. O.; Rothe, P. M.; Weigand, W.; Wünsch, R.; Dick, S.; Nesper, R.; Wörle, M.; Gramlich, V. *Bull. Soc. Chim. Fr.* **1997**, *134*, 315.

6.92. Found: C, 77.40; H, 6.74; N, 2.78; Cl, 7.02. For details of the X-ray structure determination see CCDC 118715 and the Table.

(4*S*,5*R*)-5-Benzhydryl-*N*,*N*,2,2-tetramethyl-α,α-diphenyl-1,3-dioxolane-4-methanamine (8). A solution of the chloroamine **7** (125 mg, 0.244 mmol) and diphenylphosphine (0.3 mL, 1.73 mmol, 7 equiv) in anhydrous THF (2 ml) were warmed to 60 °C (oil bath) and kept at this temperature for 24 h. The mixture was cooled to rt and H_2O (ca. 5 mL) and Et_2O (ca. 10 mL) were added. The organic layer was separated and the aqueous phase was extracted two times with Et_2O (ca. 20 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel (50 g), pentane/Et_2O 19:1) to give **8** (55 mg, 47%) as a white foam: mp 68-70 °C; $[\alpha]_D^{rt}$ = -83.5 (*c* = 0.65, $CHCl_3$); IR ($CHCl_3$) 3089, 3061, 3008, 2989, 2933, 2870, 2835, 2792, 1707, 1600, 1494, 1449, 1380, 1370, 1166, 1085, 1072, 1033, 1020, 1007, 890, 878 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.65 (s, CH_3); 1.27 (s, CH_3); 1.96 (s, $N(CH_3)_2$); 4.16 (dd, *J* = 8.7, *J* = 2.0 Hz, OCH); 4.38 (s, CH); 4.85 (d, *J* = 8.7 Hz, OCH); 7.10-7.33 (m, 16 arom. H); 7.39-7.49 (m, 2 arom. H); 7.62-7.65 (m, 2 arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.27, 27.43, 40.96 (CH_3); 51.00 (CH); 73.29 (C); 76.45, 81.04 (CH); 107.47 (C); 125.89, 126.42, 126.54, 126.56, 126.65, 126.97, 128.00, 128.14, 128.45, 130.45, 131.07, 131.96 (CH); 136.40, 138.31, 140.75, 144.35 (C); FAB-MS *m/z* 478.1 (M+1, 12), 433.0 (M-$N(CH_3)_2$, 9), 420.1 (7), 400.1 (27), 375.0 (7), 237.0 (18), 224.1 (12), 210.1 (100), 179.0 (22), 167.0 (27).

(4*S*,5*R*)-5-[(Diphenyl-phenylsulfonyl)methyl]-*N*,*N*,2,2-tetramethyl-α,α-diphenyl-1,3-dioxolane-4-methanamin (9). Thiophenol (2 mL, 20 mmol, 40 equiv) and chloroamine **7** (250 mg, 0.49 mmol) were warmed to 60 °C (oil bath) and kept at this temperature for 24 h. 1N NaOH (ca. 10 mL) and CH_2Cl_2 (ca. 10 mL) were added, the organic layer separated and the aqueous layer extracted twice with CH_2Cl_2 (10-15 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure (remaining thiophenol was removed under HV). The residue was purified by flash chromatography (silica gel (80 g), pentane→pentane/Et_2O 97:3) and trituration with pentane (10 mL) gave **9** (65 mg., 27%) as a white foam. For analytical purposes a sample of **9** was recrystallized from *i*-PrOH: R_f 0.27 (hexane/ethylacetate 9:1); mp 97-98 °C. $[\alpha]_D^{rt}$ = -99.2 (*c* = 0.90, $CHCl_3$); IR ($CHCl_3$) 3059, 2932, 2869, 2832, 2789, 1598, 1493, 1442, 1380, 1370, 1334, 1173, 1066, 1053, 1036, 1025, 1011, 923, 883, 839; ^1H NMR (400 MHz, $CDCl_3$) δ 0.49 (s, CH_3); 0.96 (s, CH_3); 1.75-2.20 (2d br., $N(CH_3)_2$); 4.65 (d, *J* = 7.6 Hz, CH); 5.30 (d br., CH); 6.70-7.65 (m, 22 arom. H); 8.10-8.16 (m, 2 arom. H); 8.25-8.55 (s br. 1 arom. H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.74, 27.48, 41.44 br. (CH_3); 68.51, 74.35 (C); 77.22, 83.38 (CH); 107.13 (C); 125.57, 126.09 br., 126.58, 126.71, 126.95, 127.39, 127.65, 127.69, 129.51, 132.87 (CH); 134.18 (C); 136.60 (CH); 137.87, 139.47, 143.63 (C); ESI-MS (pos. mode) *m/z* 586.5 (M+1), 541.1 (M-$N(CH_3)_2$), 483.3, 431.3, 210.0, 146.1. Anal. Calcd for $C_{39}H_{39}NO_2S$ (585.81): C, 79.96; H, 6.71; N, 2.39; S, 5.47. Found: C, 79.96; H, 6.61; N, 2.39; S, 5.65.

(4*R*,5*S*)-5-[(Anilino-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol (10). Aniline (0.25 ml, 2.5 mmol, 5 equiv) was added to a solution of monochloride **2** (243 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) and the mixture was stirred for 5 d at rt. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica gel (70 g), pentane/Et_2O 95:5→pentane/Et_2O 8:2) to give **10** (217 mg, 80%) as a white solid. For analytical purposes a sample of **10** was recrystallized from pentane/Et_2O: R_f 0.65 (hexane/ethylacetate 8:2); mp 192-193 °C; $[\alpha]_D^{rt}$ = -73.6 (*c* = 1.24, $CHCl_3$); IR ($CHCl_3$) 3588, 3354, 3062, 1958, 1601, 1496, 1447, 1424, 1381, 1371, 1326, 1082, 1052, 890; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, CH_3); 1.13 (s, CH_3); 4.42 (d, *J* = 8.1 Hz, CH); 4.75 (d, *J* = 8.1 Hz, CH); 5.17, 5.62 (2s, OH, NH); 6.27 (d, *J* = 7.8 Hz, 2 arom. H); 6.63 (t, *J* = 7.3 Hz, 1 arom. H); 6.81-6.88 (m, 2 arom. H); 7.03-7.42 (m, 16 arom. H); 7.57-7.64 (m, 4 arom. H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.61, 27.22 (CH_3); 68.07 (C); 82.21 (CH); 108.32,

(C); 118.66, 119.74, 126.67, 127.18, 127.28, 127.33, 127.46, 127.59, 127.96, 128.22, 128.32, 129.32, 130.56 (CH); 140.14, 142.49, 143.33, 144.12, 146.01 (C); FAB-MS *m/z* 1084.1 (2M+2, 2), 542.5 (M+1, 20), 464.3 (5), 258.1 (100), 237.1 (6), 179.0 (5); Anal. Calcd for $C_{37}H_{35}NO_3$ (541.69): C, 82.04; H, 6.51; N, 2.59. Found: C, 82.10; H, 6.72; N, 2.64. For details of the X-ray structure determination see CCDC 118719 and the Table.

(4*R*,5*S*)-5-{[(4-tert-Butyl)phenoxy-diphenyl]methyl}-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol (11). Monochloride **2** (243 mg, 0.5 mmol) and 4-tert-butylphenol (376 mg, 2.5 mmol, 5 equiv) were dissolved in CH_2Cl_2 (5 mL) and NEt_3 (0.15 mL, 1.0 mmol, 2 equiv) was added. The mixture was stirred under reflux for 16 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica gel (50 g), pentane/Et_2O 95:5) to give **11** (140 mg, 47%) as a white solid. For analytical purposes a sample of **11** was recrystallized from MeOH (*Caution:* Decomposition of the product with MeOH to the monomethylether-derivative if there are traces of monochloride **2** present; also decomposition with MeOH when additional hydrochloric acid is added.): R_f 0.53 (hexane/ethylacetate 8:2); mp 154-155 °C; $[\alpha]_D^{rt}$ = -50.5 (*c* = 0.65, $CHCl_3$); IR ($CHCl_3$) 3402, 3061, 3008, 2967, 2904, 1602, 1508, 1495, 1447, 1382, 1372, 1174, 1082, 1047, 1032, 1015, 889, 840; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, CH_3); 1.09 (s, CH_3); 1.15 (s, $C(CH_3)$); 4.40 (d, *J* = 8.1, CH); 4.76 (d, *J* = 8.1, CH); 5.92 (s, OH); 6.49-6.53 (m, 2 arom. H); 6.91-6.96 (m, 2 arom. H); 7.04-7.10 (m, 3 arom. H); 7.15-7.26 (m, 5 arom. H); 7.32-7.45 (m, 8 arom. H); 7.70-7.75 (m, 4 arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.84, 27.18, 31.29 (CH_3); 34.04, 77.44 (C); 81.68, 82.20 (CH); 88.62, 108.86 (C); 121.45, 125.29, 126.98, 127.07, 127.14, 127.23, 127.40, 127.70, 127.73, 127.88, 128.05, 128.57, 130.24, 130.35 (CH); 137.98, 138.48, 143.70, 145.97, 146.15, 151.30 (C); FAB-MS *m/z* 449.1 (7), 391.1 (16), 315.1 (24), 267.1 (58), 237.1 (100), 191.1 (31), 183.1 (56), 179.1 (72), 167.1 (74), 104.9 (54); Anal. Calcd for $C_{41}H_{42}O_4$ (598.80): C, 82.24; H, 7.07. Found: C, 82.00; H, 7.13.

(4*R*,5*R*)-5-[(Fluoro-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-diphenylmethanol (12). DAST (0.81 g, 5.0 mmol) was added dropwise to a solution of TADDOL **1** (2.33 g, 5.0 mmol) in CH_2Cl_2 (60 mL) under argon at -78 °C. The solution was stirred and allowed to warm up to rt overnight. H_2O was added and the organic phase was dried ($MgSO_4$). The solvent was evaporated under reduced pressure. The residue was flash chromatographed (silica gel, toluene/pentane 1:1) to yield 12% of the difluoride **13** and **12** (1.38 g, 59%) as colorless crystals: mp 138 - 140 °C; IR ($CHCl_3$) 3570, 3092, 3060, 3008, 2939, 1953, 1893, 1814, 1599, 1494, 1449, 1382, 1371, 1329, 1163, 1086, 1046, 1002, 975, 906, 870; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 3H), 1.26 (s, 3H), 2.47 (d, *J* = 3.5 Hz, 1H), 5.11-5.23 (m, 2H), 7.01-7.50 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3 (d, $^5J_{CF}$ = 7.0 Hz), 28.3, 78.5, 80.5 (d, $^2J_{CF}$ = 26.7 Hz), 81.3 (d, $^3J_{CF}$ = 2.1 Hz), 98.8 (d, $^1J_{CF}$ = 183.1 Hz), 112.1, 124.7, 124.8, 125.7, 125.8, 126.1, 126.2, 126.6, 126.8, 126.9, 127.2, 127.4, 127.5, 127.6, 127.7, 127.9, 128.2, 128.3, 141.2 (d, $^2J_{CF}$= 23.4 Hz), 141.4 (d, $^2J_{CF}$ = 22.9 Hz), 143.9, 145.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -156.2 (m, 1F, 1CF); MS (EI) *m/z* 451 (M-F, 1), 286 (3), 285 (16), 210 (3), 209 (19), 208 (52), 207 (70), 200 (14), 199 (88), 198 (4), 197 (11), 186 (8), 185 (54), 184 (15), 183 (100), 182 (20), 181 (7), 180 (14), 179 (52), 178 (29), 177 (3), 168 (3), 167 (20), 166 (6), 165 (20), 106 (3), 105 (40); $[\alpha]_D^{rt}$ = + 61.1 (*c* = 1.2, $CHCl_3$); Anal. Calcd for $C_{31}H_{29}FO_3$ (468.57): C, 79.46; H, 6.24. Found: C, 79.49, H, 6.27. For details of the X-ray structure determination see CCDC 118716 and the Table.

(4*R*,5*R*)-4,5-Di[(fluoro-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane (13). DAST (2.41 g, 15.0 mmol) was added dropwise to a solution of TADDOL **1** (2.33 g, 5.0 mmol) in CH_2Cl_2 (60 mL) under argon at -78 °C. The solution was stirred and allowed to warm up to rt overnight. H_2O was added and the organic phase was dried ($MgSO_4$). The solvent was evaporated under reduced pressure. The residue was flash chromatographed (silica gel, toluene/pentane 1:1) to yield **13** (1.98 g, 84%) as colorless crystals: mp 139-140 °C; IR ($CHCl_3$) 3093, 3064, 3040, 3008, 2942, 1952, 1870, 1808, 1600, 1495,

1450, 1382, 1371, 1332, 1297, 1155, 1136, 1100, 1048, 1034, 1001, 985, 946, 905, 853; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 6 H), 5.27 (d, $^3J_{HF}$ = 28.3 Hz, 2H), 6.97-7.07 (m, 10H), 7.20-7.32 (m, 6H), 7.43-7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (m), 80.8 (dd, $^2J_{CF}$ = 24.2 Hz, $^3J_{CF}$ = 2.8 Hz), 99.5 (d, $^1J_{CF}$ = 186.3 Hz), 114.0, 124.7, 124.8, 126.1, 126.2, 127.2, 127.4, 127.9, 128.3, 140.6 (d, $^2J_{CF}$ = 24.4 Hz), 141.6 (d, $^2J_{CF}$ = 23.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -164.6 (d, $^3J_{HF}$ = 28.3 Hz, 2F, 2 CF); MS (EI) *m/z* 471 (M+1, 0.01), 455 (1), 287 (1), 286 (10), 285 (49), 202 (1), 201 (17), 200 (100), 187 (1), 186 (14), 185 (88), 181 (1), 180 (9), 179 (58), 178 (22), 168 (1), 167 (7), 166 (4), 165 (18); $[\alpha]_D^{rt}$ = + 108.3 (*c* = 1.2, $CHCl_3$); Anal. Calcd for $C_{31}H_{28}F_2O_2$ (470.56): C, 79.13; H, 6.00. Found: C, 79.03; H, 5.89.

General Procedure (GP 1) for the Preparation of Trityl-Derivatives 14a, 14b and 15: A solution of monochloride **2** or dichloride **3** (1 equiv) in CH_2Cl_2 (0.2-1.25 M) was treated with the corresponding amine and stirred at rt for 5 d. H_2O was added and the aqueous layer extracted twice with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography.

(4*R*,5*S*)-2,2-Dimethyl-5-{[4-(methylamino)phenyl-diphenyl]methyl}-α,α-diphenyl-1,3-dioxolan-4-methanol (14a). Monochloride **2** (4.85 g, 10.0 mmol) was dissolved in CH_2Cl_2 (8 mL) and treated with N-methylaniline (10.7 g, 100 mmol), according to GP 1 yielding **14a** (3.0 g, 54%) after flash chromatography (silica gel (80 g), pentane/Et_2O 9:1) as a beige solid. Trituration with hot *i*–PrOH gave an analytically pure sample (white solid): R_f 0.30 (hexane/ethylacetate 8:2); mp 223-225 °C; $[\alpha]_D^{rt}$ = +7.1 (*c* = 1.05, $CHCl_3$); IR ($CHCl_3$) 3500, 3059, 3007, 2934, 1613, 1520, 1493, 1447, 1381, 1371, 1324, 1163, 1061, 1042, 880; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.40 (s, CH_3); 1.41 (s, CH_3); 1.94 (s, 1H, OH or NH); 2.78 (s, NCH_3); 3.66 (s, 1H, OH or NH); 4.63 (d, *J* = 8.4 Hz, CH); 5.43 (d, *J* = 8.4 Hz, CH); 6.44 (d, *J* = 9.0 Hz, 2 arom. H); 7.09-7.45 (m, 20 arom. H); 7.74-7.79 (m, 2 arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.41, 27.62, 30.59 (CH_3); 59.94, 76.79 (C); 79.42, 83.97 (CH); 106.67 (C); 111.89, 125.81, 126.08, 126.84, 127.02, 127.32, 127.48, 127.54, 127.60, 127.76, 128.07, 130.08, 131.48, 131.61 (CH); 131.85, 143.04, 143.86, 145.91, 146.15, 147.54 (C); FAB-MS *m/z* 1111.7 (2M+1, 2), 568.4 (M+13, 17), 556.4 (M+1, 29), 378.2 (11), 302.2 (9), 285.2 (14), 272.2 (100), 237.2 (12), 179.2 (11); Anal. Calcd for $C_{38}H_{37}NO_3$ (555.72): C, 82.13; H, 6.71; N, 2.52. Found: C, 82.25; H, 6.88; N, 2.54.

(4*R*,5*S*)-5-[(4-Anilinophenyl-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolan-4-methanol (14b). Mono chloride **2** (485 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with diphenylamine (1.70 g, 10 mmol), according to GP 1 yielding **14b** (510 mg, 83%) after flash chromatography (silica gel (80 g), pentane/Et_2O 9:1) as a solid of slight beige color. A sample of **14b** was recrystallized from MeOH for analytical purposes (white solid): R_f 0.46 (hexane/ethylacetate 8:2); mp 200-202 °C; $[\alpha]_D^{rt}$ = -2.5 (*c* = 1.74, $CHCl_3$); IR ($CHCl_3$) 3503, 3428, 3059, 3008, 2935, 1597, 1514, 1497, 1447, 1381, 1372, 1316, 1061, 1041, 875; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.43 (s, CH_3); 1.42 (s, CH_3); 1.86 (s, 1H, OH or NH); 4.63 (d, *J* = 8.4 Hz, CH); 5.48 (d, *J* = 8.4 Hz, CH); 5.66 (s, 1H, NH or OH); 6.88-6.94 (m, 3 arom. H); 7.03-7.06 (m, 2 arom. H); 7.10-7.27 (m, 15 arom. H); 7.34-7.45 (m, 7 arom. H); 7.75-7.79 (m, 2 arom. H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.42, 27.61 (CH_3); 60.16, 76.81 (C); 79.28, 83.99 (CH); 106.73 (C); 116.62, 118.00, 121.16, 126.09, 126.19, 126.92, 126.95, 127.57, 127.58, 127.67, 127.84, 127.96, 129.31, 130.32, 131.11, 131.73 (CH); 135.85, 141.33, 142.69, 143.03, 144.11, 145.16, 145.79 (C); FAB-MS *m/z* 618.8 (M+1, 13), 347.3 (8), 334.3 (100), 237.3 (6), 179.2 (6), 104.9 (10); Anal. Calcd for $C_{43}H_{39}NO_3$ (617.79): C, 83.60; H, 6.36; N; 2.27. Found: C, 83.52; H, 6.52; N, 2.28. For details of the X-ray structure determination see CCDC 118718 and the Table.

(4*S*,5*S*)-2,2-Dimethyl-*N*,*N*',α,α,α',α'-hexaphenyl-1,3-dioxolane-4,5-di(p-methylaniline) (15). Dichloride **3** (2.52 g, 5.0 mmol) and diphenylamine (8.46 g, 50 mmol) were dissolved in CH_2Cl_2 (5 mL) and treated according to GP 1 yielding **15** (2.75 g, 72%) after flash chromatography (silica gel (150 g), pentane/Et_2O 4:1) as a solid of slight beige color. A sample of **15** was recrystallized for analytical purposes from pentane/Et_2O (white solid): R_f 0.20 (pentane/Et_2O 8:2); mp 168-169 °C; $[\alpha]_D^{rt}$ = -65.4 (*c* = 1.0, $CHCl_3$); IR ($CHCl_3$) 3427, 3089, 3056, 3007, 2936, 1598, 1514, 1497, 1446, 1399, 1379, 1368, 1316, 1172, 1060, 1036, 877, 822, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 2 CH_3); 5.57 (s, 2H); 5.96 (s, 2H); 6.65-6.82 (m, 4 arom. H); 6.86-7.40 (m, 34 arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.46 (CH3); 62.44 (C); 81.56 (CH); 108.54 (C); 116.35, 117.33, 120.65, 125.35, 125.78, 127.13, 127.28, 129.30, 130.19, 131.30 (CH); 140.44, 143.01 (C); FAB-MS *m/z* 769.1 (M+1, 42), 667.2 (6), 501.1 (9), 376.1 (22), 364.1 (8), 348.1 (27), 334.1 (100), 270.1 (14), 258.1 (10), 241.1 (10), 237.1 (15), 179.1 (24), 165.1 (15); Anal. Calcd for $C_{55}H_{48}N_2O_2$ (769.00): C, 85.90; H, 6.29; N, 3.64. Found: C, 86.07; H, 6.32; N, 3.72.

General Procedure (GP 2) for the Condensation Reaction of TADDAMIN 5 with Aldehydes. TADDAMIN **5**, the aldehyde[1] (2 equiv) and *p*-toluenesulfonic acid (PTSA) (ca. 10 mol%) were dissolved in toluene and refluxed until the total consumption of the aldehyde was observed (3-7 d, TLC control). After cooling to rt, the solvent was evaporated under reduced pressure. The crude product was redissolved in Et_2O, washed with H_2O, sat. NaCl and dried ($MgSO_4$). The solvent was removed under reduced pressure to provide yellow solid which was flash chromatographed.

2-({[{(4*S*,5*S*)-5-[{[(Z)-1-(2-Hydroxyphenyl)methylidene]amino}(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)methyl]imino}methyl)phenol (16a): TADDAMIN **5** (500 mg, 1.08 mmol), salicylaldehyde (263 mg, 2.15 mmol) and PTSA (35 mg, 0.18 mmol) were dissolved in toluene (20 mL) and refluxed for 3 d. According to ^{1}H NMR, the crude product consisted of 21% monocondensation product and 79% **16a**. This crude product was flash chromatographed (silica gel (100 g), pentane/CH_2Cl_2 1:9) to yield **16a** (39o mg, 54%) as a yellow solid: R_f 0.27 (CH_2Cl_2/pentane 1:1); mp 209-210 °C; $[\alpha]_D^{rt}$ = +41.5 (*c* = 0.6, $CHCl_3$); IR (KBr) 3048, 2988, 2928, 1620, 1580, 1490, 1444, 1369, 1279, 1234, 1153, 1058, 867, 757, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 6H), 5.49 (s, 2H), 6.83-6.94 (m, 8H), 7.01-7.04 (m, 4H), 7.08-7.25 (m, 14H), 7.36-7.41 (m, 2H), 8.2 (s, 2H), 13.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 32.5, 72.5, 74.4, 80.7, 107.8, 117.1, 118.8, 119.2, 126.2, 126.4, 126.99, 127.8, 128.6, 129.6, 132.5, 132.8, 143.5, 145.1, 161.2, 169.1; FAB-MS *m/z* 673 (M, 82), 552 (11), 431 (15), 386 (100), 345 (8), 286 (38), 237 (11), 179 (34), 122 (6); Anal. Calcd for $C_{45}H_{40}N_2O_4$ (672.81): C, 80.33; H, 5.99; N, 4.16. Found: C, 80.07; H, 6.23; N, 4.13.

2,4-Di-(*tert*-butyl)-6-({[{(4*S*,5*S*)-5-[[({(Z)-1-[3,5-di(*tert*-butyl)-2-hydroxyphenyl]-methylidene}amino](diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)-methyl]imino}methyl)phenol (16b) and 2-({[{(4*S*,5*S*)-5-[amino(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)-methyl]imino}methyl)-4,6-di(*tert*-butyl)phenol (A) (monocondensation product): TADDAMIN **5** (581 mg, 1.25 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (590 mg, 2.5 mmol) and PTSA (23 mg, 0.12 mmol) were dissolved in toluene (23 mL) and refluxed for 7 d. The crude product was flash chromatographed (silica gel (100 g), pentane/CH_2Cl_2 1:1→pentane/CH_2Cl_2 1:9) to yield **16b** (749 mg, 67%) and monocondensation product **A** (194 mg, 23%) both as yellow solids.

16b: R_f 0.67 (pentane/CH_2Cl_2 8:2); mp 182-183 °C; $[\alpha]_D^{rt}$ = +45.5 (*c* = 1.0, $CHCl_3$); IR (KBr) 3056, 2956, 2867, 1617, 1589, 1467, 1439, 1361, 1272, 1250, 1206, 1172, 1056, 1000, 878, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.30 (s, 18H), 1.59 (s, 18H), 5.44 (s, 2H), 6.87-6.88 (m, 2H), 6.92-6.95 (m, 4H), 7.02-7.09 (m, 9H), 7.11-7.16 (m, 9H), 7.47

[1] Preparation of aldehyde derivatives: Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Fepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939-1942.

(d, J = 2.4 Hz, 2H), 8.32 (s, 2H), 14.3 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 29.6, 31.5, 34.2, 35.2, 73.4, 80.3, 106.7, 118.3, 125.8, 126.1, 126.6, 127.1, 127.3, 127.8, 128.6, 129.3, 136.7, 140.2, 143.4, 145.8, 158.4, 170.1; FAB-MS *m/z* 897 (M, 16), 664 (4), 498 (21), 428 (10), 398 (100), 342 (5), 320 (9), 274 (5), 237 (10), 179 (18); Anal. Calcd for $C_{61}H_{72}N_2O_4$ (897.24): C, 81.66; H, 8.09; N, 3.12. Found: C, 81.54; H, 8.06; N, 3.12.

A: R_f 0.32 (pentane/CH_2Cl_2 1:9); mp 139-141°C; $[\alpha]_D^{rt}$ = +63.6 (c = 1.0, $CHCl_3$); IR (KBr) 2923, 2856, 1628, 1567, 1473, 1445, 1367, 1273, 1178, 1090, 1034, 945, 828, 784, 628; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 3H), 0.90 (s, 3H), 1.27 (s, 9H), 1.54 (s, 9H), 4.87 (d, J = 7.1 Hz, 1H), 5.09 (d, J = 7.1 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 7.1-7.4 (m, 20H), 7.43 (d, J = 2.5 Hz, 1H), 8.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 27.8, 29.4, 31.5, 32.5, 34.2, 35.2, 62.8, 72.5, 82.2, 82.7, 109.2, 118.4, 126.3, 126.8, 126.91, 126.94, 127.0, 127.4, 127.5, 127.7, 127.8, 127.9, 128.7, 128.8, 129.7, 130.6, 136.9, 140.3, 143.5, 143.96, 144.9, 149.4, 158.2, 169.6; FAB-MS *m/z* 681 (M, 100), 399 (34), 237 (12), 182 (28), 104 (8); Anal. Calcd for $C_{46}H_{52}N_2O_3$ (680.92): C, 81.14; H, 7.70; N, 4.11. Found: C, 81.24; H, 7.81; N, 4.11.

2-(*tert*-Butyl)-6-({[{(4*S*,5*S*)-5-[({(*Z*)-1-[3-(*tert*-butyl)-2-hydroxy-5-methylphenyl]-methylidene}amino)(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)-methyl]imino}methyl)-4-methylphenol (16c): TADDAMIN **5** (500 mg, 1.08 mmol), 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (414 mg, 2.15 mmol) and PTSA (17 mg, 0.09 mmol) were dissolved in toluene (23 mL) and refluxed for 5 d. According to ^{1}H NMR, the crude product consisted of 8% monocondensation product and 92% **16c**. The crude product was flash chromatographed (silica gel (100 g), pentane/CH_2Cl_2 1:1) to yield **16c** (330 mg, 37%) as a yellow solid: R_f 0.27 (pentane/CH_2Cl_2 8:2); mp 245-246 °C; $[\alpha]_D^{rt}$ = +37.9 (c = 0.6, $CHCl_3$); IR (KBr) 3058, 2950, 2914, 1619, 1594, 1492, 1439, 1371, 1317, 1266, 1236, 1211, 1166, 1051, 1006, 700; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.1 (s, 6H), 1.55 (s, 18H), 2.25 (s, 6H), 5.43 (s, 2H), 6.81 (d, J = 1.5 Hz, 2H), 6.89-6.97 (m, 6H), 7.04-7.10 (m, 6H), 7.13-7.19 (m, 10H), 8.21 (s, 2H), 14.21 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 27.7, 29.5, 34.9, 73.7, 80.4, 107.3, 118.8, 126.0, 126.2, 126.6, 127.0, 127.6, 128.5, 129.5, 130.6, 130.8, 137.1, 143.4, 145.3, 158.4, 169.4; FAB-MS *m/z* 813 (M, 14), 456 (31), 386 (9), 356 (100), 278 (9), 237 (25), 179 (34), 105 (5); Anal. Calcd for $C_{55}H_{60}N_2O_4$ (813.08): C, 81.25; H, 7.44; N, 3.45. Found: C, 81.14; H, 7.29; N, 3.47.

(4*R*,5*R*,4'*R*,5'*R*)-[5-({2-[2-(2-{[5-(Hydroxy-diphenyl-methyl)-2,2-dimethyl-[1,3]-ioxolan-4-yl]-diphenyl-methoxy}-ethoxy)-ethoxy]-ethoxy}-diphenyl-methyl)-2',2'-dimethyl-[1',3']-dioxolan-4'-yl]-diphenyl-methanol (17) and (4*R*,5*R*)-(5-{Diphenyl-[2-(2-vinyloxy-ethoxy)-ethoxy]-methyl}-2,2-dimethyl-[1,3]-di-oxolan-4-yl)-diphenyl-methanol (B). According to an analogous procedure,[1] KO*t*Bu (1.45 g, 12.87 mmol) was added to TADDOL **1** (3.00 g, 6.44 mmol) in THF. After 10 minutes stirring triethyleneglycol ditosylate (2.95 g, 6.44 mmol) was added and the reaction mixture refluxed for 9 h. After cooling to rt, THF was evaporated under reduced pressure and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The organic layer was separated, washed with H_2O (100 mL), sat. NaCl, dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel (100 g), CH_2Cl_2) to yield **17** (1.00 g, 30%) and side product **B** (0.80 g, 21%) both as white solids.

17: Recrystallization from CH_2Cl_2/Et_2O (430 mg, 13%): R_f 0.07 (CH_2Cl_2); mp 232-235 °C; $[\alpha]_D^{rt}$ = -10.0 (c = 1.00, $CHCl_3$); IR ($CHCl_3$) 3370, 3062, 3007, 2889, 1495, 1446, 1372, 1170, 1086, 1050, 892, 873, 639; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 1.00 (s, 3 H), 2.82-2.87 (m, 2 H), 3.41-3.77 (m, 10 H), 4.20 (d, J = 8.2 Hz, 2 H), 4.56 (d, J = 8.2 Hz, 2 H), 6.14 (s, 2 H), 7.13-7.40 (m, 32 H), 7.52-7.55 (m, 4 H), 7.63-7.66 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.82, 27.02, 63.82, 69.87, 70.75, 77.42, 80.14, 81.56, 84.63, 108.58, 126.79, 126.94, 127.21, 127.58, 127.68, 127.87,

[1] Kyba, E. P.; Gokel, G. W.; Jong, F. D.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.

127.91, 128.36, 128.78, 129.83, 130.19, 136.69, 139.14, 143.96, 146.57; FAB-MS *m/z* 1047 (M, 20), 763 (33), 599 (37), 431 (59), 267 (69), 237 (100); Anal. Calcd for $C_{68}H_{70}O_{10}$ (1047.31): C, 77.99; H, 6.74. Found: C, 76.49; H, 6.83.

B: Recrystallization from MeOH (620 mg, 17%), white needles: R_f 0.36 (CH_2Cl_2); mp 145-147 °C; $[\alpha]_D^{rt}$ = -14.0 (*c* = 1.06, $CHCl_3$); IR ($CHCl_3$) 3370, 3062, 3007, 2935, 1636, 1618, 1495, 1447, 1381, 1372, 1322, 1170, 1136, 1086, 1049, 1023, 983, 892, 874, 818, 639; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 1.00 (s, 3 H), 2.88-2.93 (m, 1 H), 3.93-3.47 (m, 7 H), 4.00 (dd, *J* = 2.1, 6.8 Hz, 1 H), 4.19 (dd, *J* = 2.1, 14.2 Hz, 1 H), 4.22 (d, *J* = 8.0 Hz, 1 H), 4.58 (d, *J* = 8.2 Hz, 1 H), 6.16 (s, 1 H), 6.50 (dd, *J* = 7.2, 14.3 Hz, 1 H), 7.18-7.41 (m, 16 H), 7.53-7.65 (m, 2 H), 7.65-7.67 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.82, 27.02, 63.70, 67.41, 69.70, 69.93, 77.45, 80.10, 81.58, 84.71, 86.75, 108.65, 126.80, 126.85, 126.98, 127.23, 127.62, 127.71, 127.88, 127.93, 128.40, 128.78, 129.84, 130.21, 136.62, 139.08, 143.94, 146.58, 151.80; FAB-MS *m/z* 581 (M, <0.1), 267 (54), 237 (100), 179 (84), 167 (76), 105 (91); Anal. Calcd for $C_{37}H_{40}O_6$ (580.73): C, 76.53; H, 6.94. Found: C, 76.51; H, 6.82.

(3a*R*,15a*R*)-2,2-Dimethyl-4,4,15,15-tetraphenylperhydro[1,3]dioxolo[4,5-*l*][1,4,7,10]tetraoxacyclotetradecine (18). NaH (210 mg, 8.6 mmol) was added to a solution of TADDOL **1** (1.00 g, 2.15 mmol) in THF (60 mL) at rt. The mixture was stirred for 10 minutes, then triethyleneglycol ditosylate (980 mg, 2.15 mmol) was added and the reaction was refluxed for 16 h. After cooling to rt, THF was evaporated under reduced pressure and the residue was dissolved in Et_2O (100 mL) and H_2O (100 ml). The organic layer was washed with H_2O (100 mL), sat. NaCl, dried ($MgSO_4$) and the solvent was evaporated under reduced pressure to give a crude product which was purified by flash chromatography (silica gel (20 g), CH_2Cl_2) yielding **18** (710 mg, 58%) as a white solid: R_f 0.35 (CH_2Cl_2); mp 155-157 °C; $[\alpha]_D^{rt}$ = +41.0 (*c* = 1.06, $CHCl_3$); IR ($CHCl_3$) 3059, 3007, 2932, 2874, 1600, 1494, 1446, 1380, 1371, 1320, 1169, 1131, 1096, 1024, 940, 894, 871, 816, 638; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 6 H), 2.90-2.94 (m, 2 H), 3.27-3.88 (m, 10 H), 4.20 (s, 2 H), 7.20-7.28 (m, 10 H), 7.39-7.44 (m, 6 H), 7.82-7.85 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.00, 64.26, 70.44, 71.41, 80.94, 84.11, 106.40, 126.63, 126.98, 127.21, 127.28, 129.89, 130.51, 139.63, 142.00; FAB-MS *m/z* 580.3 (M, 24), 503 (13), 431 (25), 343 (18), 237 (84), 179 (100); Anal. Calcd for $C_{37}H_{40}O_6$ (580.73): C, 76.53; H, 6.94. Found: C, 76.64; H, 7.15. For details of the X-ray structure determination see CCDC 118717 and the Table.

General Procedure (GP 3) for the Preparation of the Oxazolin-Derivatives 19a and 19b: The half-ester of (*R,R*)-tartaric acid acetonide[1] was treated with 3 equiv PhMgBr to give (4*R*,5*R*)-2,2-dimethyl-5-(hydroxy-diphenyl)methyl-1,3-dioxolane-4-carbonic acid[2] **C**. Phenylglycinol (1 equiv) and **C** (1 equiv) were dissolved in CH_2Cl_2 (0.2 M) and NEt_3 (1 equiv.) and CCl_4 (3 equiv.) were added. A solution of triphenylphosphine (1 equiv) in CH_2Cl_2 (0.3-0.4 M) was added dropwise over 3 h and the reaction mixture was stirred for 1 h. After further addition of NEt_3 (2 equiv) and CCl_4 (3 equiv), again triphenylphosphine (2 equiv) in CH_2Cl_2 (0.3-0.4 M) was added dropwise over 3 h and the reaction mixture stirred for 16 h. The solvent was removed under reduced pressure and the crude product was stirred in Et_2O whereupon a brown solid precipitated. After filtration the solvent was removed under reduced pressure and the resulting brown oil was purified by flash chromatography. For analytical purposes the compounds were recrystallized.

(4*R*,5*R*)-2,2-Dimethyl-5-[(*R*)-4-phenyloxazolin-2-yl]-α,α-diphenyl-1,3-dioxolane-4-methanol (19a). According to GP 3, a mixture of (*R*)-phenylglycinol (1.04 g, 7.60 mmol), carboxylic acid **C** (2.50 g, 7.60 mmol), NEt_3 (1.06 mL, 7.60 mmol) and CCl_4 (2.0 mL, 20.7 mmol) in CH_2Cl_2 (40 mL) were treated with a solution of triphenylphosphine (2.00 g, 7.60 mmol) in CH_2Cl_2 (20 mL). Further addition of NEt_3 (2.1 mL, 15.2 mmol), CCl_4 (4.0 mL, 41.4 mmol) and a solution of

[1] Musich, J. A.; Rapport, H. *J. Am. Chem. Soc.* **1978**, *100*, 4865.
[2] Seebach, D.; Devaquet, E.; Ernst, A.; Hayakawa, M.; Kühnle, F. N. M.;Schweizer, W. B.; Weber, B. *Helv. Chim. Acta* **1995**, *78*, 1636.

triphenylphosphine (4.00 g, 15.2 mmol) in CH_2Cl_2 (50 mL). Treatment with Et_2O (150 mL) gave 5.0 g of crude product. After flash chromatography (silica gel (60 g); pentane/Et_2O 1:2) **19a** (1.28 g, 39%) was isolated as a white solid. Recrystallization (25 mL MeOH): R_f 0.26 (pentane/Et_2O 1:2); mp 182-185 °C; $[\alpha]_D^{rt}$ = +18.3 (*c* = 1.0, $CHCl_3$); IR ($CHCl_3$) 3744, 3648, 3566, 3062, 3008, 1952, 1800, 1665, 1601, 1494, 1449, 1384, 1374, 1254, 1178, 1162, 1062, 1033, 982, 929, 902, 870, 823, 652, 634; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.47 (s, CH_3CO); 1.61 (s, CH_3CO), 3.37 (s, OH); 3.84 (m, 1 H, C*H*HO or CHN); 4.36 (m, 1 H, C*H*HO or CHN); 4.65 (d, *J* = 7.2 Hz, CHO); 4.94 (m, 1 H, C*H*HO or CHN); 5.63 (d, *J* = 7.2 Hz, CHO); 7.03-7.59 (m, 15 arom. H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 26.43, 26.80 (CH_3); 69.38, 71.65 (CH); 74.78 (CH_2); 82.06 (CH); 111.65 (C); 126.31, 126.31, 126.63, 127.23, 127.36, 127.57, 127.93, 128.07, 128.57 (CH); 141.27, 144.98, 166.07 (C); FAB-MS *m/z* 859 (2M, 20), 430 (M+1, 100), 412 (12), 307 (7), 246 (12) 189 (8); Anal. Calcd for $C_{27}H_{27}NO_4$ (429.52): C, 75.50; H, 6.34; N, 3.26. Found: C, 75.26; H, 6.60; N, 3.29.

(4*R*,5*R*)-2,2-Dimethyl-5-[(*S*)-4-phenyloxazolin-2-yl]-α,α-diphenyl-1,3-dioxolane-4-methanol (19b)

According to GP 3, a mixture of (*S*)-phenylglycinol (0.84 g, 6.10 mmol), carboxylic acid **C** (2.00 g, 6.10 mmol), NEt_3 (0.85 mL, 6.10 mmol) and CCl_4 (1.8 mL, 18.6 mmol) in CH_2Cl_2 (40 mL) were treated with a solution of triphenylphosphine (1.60 g, 6.09 mmol) in CH_2Cl_2 (20 mL). Further addition of NEt_3 (1.7 mL, 12.2 mmol), CCl_4 (1.8 mL, 18.6 mmol) and a solution of triphenylphosphine (3.20 g, 12.2 mmol) in CH_2Cl_2 (50 mL). Treatment with Et_2O (100 mL) gave 4.2 g of crude product. After flash chromatography (silica gel (60 g); pentane/Et_2O 1:2) **19b** (1.26 g, 48%) was isolated as a white solid. Recrystallization (20 mL MeOH): R_f 0.25 (pentane/Et_2O 1:2); mp 185-188 °C; $[\alpha]_D^{rt}$ = -10.6 (*c* = 1.17, $CHCl_3$); IR ($CHCl_3$) 3564, 3063, 2991, 1952, 1884, 1810, 1606, 1600, 1494, 1473, 1449, 1384, 1374, 1260, 1173, 1068, 988, 870; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, CH_3CO); 1.59 (s, CH_3CO), 3.37 (s, OH); 3.84 (m, 1 H, C*H*HO or CHN); 4.45 (m, 1 H, C*H*HO or CHN); 4.71 (d, *J* = 7.2 Hz, CHO); 4.89 (m, 1 H, C*H*HO or CHN); 5.60 (d, *J* = 7.2 Hz, CHO); 6.96-7.61 (m, 15 arom. H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.27, 26.77 (CH_3); 69.41, 71.79 (CH); 74.91 (CH_2); 76.69 (C); 81.95 (CH); 111.54 (C); 126.20, 126.62, 127.15, 127.22, 127.36, 127.54, 128.12, 128.54 (CH); 141.26, 142.34, 145.17, 165.88 (C); FAB-MS *m/z* 859 (2M, 7), 430 (M+1, 100), 412 (13), 307 (6), 246 (15) 189 (6); Anal. Calcd for $C_{27}H_{27}NO_4$ (429.52): C, 75.50; H, 6.34; N, 3.26. Found: C, 75.40; H, 6.60; N, 3.22.

Crystallographic Structural Determination. Each crystal was mounted on a glass fiber in a random orientation. The intensities for **7** and **14b** were collected on a *Syntex-P21* four circle diffractometer (graphite monochromatized Mo*K*α radiation, λ = 0.7107 Å), for **10** and **12** on a *Picker-Stoe* four circle diffractometer (graphite monochromatized Cu*K*α radiation, λ = 1.5418 Å) and for **18** on a Enraf-Nonius-CAD-4 four circle diffractometer (graphite monochromatized Mo*K*α radiation, λ = 0.7107 Å). The structures were solved by direct methods with SHELXS-86[1] and refined in full-matrix least-squares (SHELXL-93[2] for **7**, **10**, **12**, **14b** and SHELXL-92[2] for **18**). H-Atoms were calculated at idealized positions and included in the structure factor calculation with fixed isotropic displacement parameters. The Crystallographic Information Files (cif-files) have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

[1] Sheldrick, G. M.; Krüger, C.; Goddard, R.; in *Crystallographic Computing 3*; Oxforg University Press, 1985, p. 175-189.
[2] Sheldrick, G. M.; SHELXL92 and SHELXL93. Programs for Crystal Structure Refinement, University of Göttingen, Germany.

Table. Crystal Data and Data Collection Parameters

data	7	10	12	14b	18
formula	$C_{33}H_{34}ClNO_2$	$C_{37}H_{35}NO_3$	$C_{31}H_{29}FO_3$	$C_{43}H_{39}NO_3$	$C_{37}H_{40}O_6$
formula weight (g/mol)	512.06	541.69	468.54	617.80	580.69
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
crystal dimensions [mm]	0.6 x 0.5 x 0.5	0.4 x 0.3 x 0.2	0.3 x 0.2 x 0.2	0.3 x 0.3 x 0.1	0.4 x 0.4 x 0.6
crystal system	monoclinic	monoclinic	orthorhombic	triclinic	orthorhombic
space group	*C*2	$P2_1$	$P2_12_12_1$	*P*1	$P2_12_12_1$
2θ range [°]	3 < 2θ < 38	6 < 2θ < 100	6 < 2θ < 100	4 < 2θ < 40	1 < 2θ < 50
a [Å]	18.956(8)	13.358(7)	6.352(4)	8.767(5)	9.794(4)
b [Å]	10.874(5)	16.52(1)	17.70(2)	10.193(6)	15.857(4)
c [Å]	40.63(2)	15.07(1)	22.23(1)	10.307(6)	23.870(4)
α [deg]	90	90	90	85.26(5)	90
β [deg]	93.60(4)	98.10(5)	90	65.43(5)	90
γ [deg]	90	90	90	84.44(5)	90
V [$Å^3$]	8358(7)	3293(4)	2500(3)	832.8(8)	3707(2)
Z	12	4	4	1	4
ρ_{calc} [g cm^{-3}]	1.221	1.173	1.245	1.232	1.040
μ [mm^{-1}]	0.167	0.605	0.675	0.076	0.070
Total reflections measured	3779	3536	1522	1680	3667
independent reflections	3625	3536	1522	1680	3667
reflections observed	3122	2903	1428	1269	2460
no. of variables	953	783	321	431	389
criterion	I > 2σ(I)	I > 2σ(I)	I > 2σ(I)	I > 2σ(I)	I > 3σ(I)
final *R* [%]	3.02	5.91	4.57	3.35	6.22
wR_2 [%]	6.94	17.20	13.00	7.23	19.92
goodness of fit	0.946	0.914	0.973	0.859	1.116
Δρ (max, min) [$eÅ^{-3}$]	0.155, -0.144	0.352, -0.219	0.232, -0.158	0.112, -0.111	0.439, -0.224
CCDC	118715	118719	118716	118718	118717