SUPPORTING INFORMATION

Total Syntheses of the Telomerase-Inhibitors Dictyodendrin B, C and E

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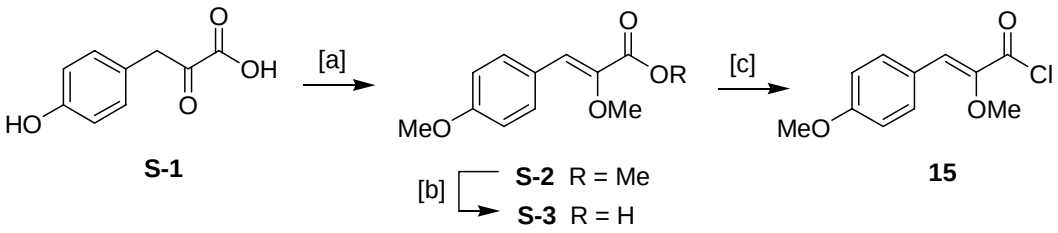
General: All reactions were carried out in flame-dried glassware under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O, DME (Mg-anthracene), CH_2Cl_2, 1,2-dichloroethane (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received unless otherwise stated.

NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm; residual CHD_2OD in CD_3OD: $\delta_H \equiv 3.31$ ppm; CD_3OD: $\delta_C \equiv 49.0$ ppm). *The coupling constants were not averaged. The proton spectra of the para-disubstituted phenyl groups are of AA'XX' spin systems. The*

splitting of signals of greatest intensity is quoted as the value of the coupling constant $^{3}J_{(AX)}$*, assuming that* $^{5}J_{(AX')}$ *is zero. Where indicated, the signal assignments are unambiguous*; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for ^{1}J(C,H) = 145 Hz; HMBC (*inv4gslplrnd*) for correlations via ^{n}J(C,H); HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

Starting Materials



Scheme S-1. Conditions: [a] (i) NaH, DMF, 2h; (ii) dimethyl sulfate, DMF, 67%; [b] NaOH, MeOH/H_2O (2:1), 87%; [c] oxalyl chloride, DMF cat., CH_2Cl_2, quant.

Methyl 2-methoxy-3-(4-methoxyphenyl)-2-propenoate (S-2).[1] To a suspension of NaH (1.60 g, 66.6 mmol) in dry DMF (15 mL) was added a solution of 4-hydroxyphenylpyruvic acid **S-1** (2.00 g, 11.1 mmol) in dry DMF (10 mL) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 2 h. Dimethyl sulfate (8.35 mL, 88.8 mmol) was then added and stirring continued for another 2 h. After completion of the reaction, water was introduced, the aqueous layer was extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with water and dried (Na_2SO_4). Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 1:4) afforded the title compound **S-2** as a pale yellow oil (1.66 g, 67%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.72 (d, J = 8.9 Hz, 2 H), 6.94 (s, 1 H), 6.91 (d, J = 8.9 Hz, 2 H), 3.82 (s, 3 H), 3.81 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 160.6, 144.3, 132.1, 126.5, 124.0, 114.3, 59.3, 55.6, 52.2; IR (film): $\tilde{\nu}$ = 3001, 2952, 2910, 2841, 1717, 1634, 1605, 1571, 1511, 1437, 1354, 1315, 1301, 1252, 1175, 1102, 1030, 834, 552, 521 cm^{-1}; MS (EI): *m/z* (%): 222 (100 $[M]^+$), 179 (52), 151 (53), 120 (18), 91 (14), 77 (16), 59 (9), 51 (11); HRMS (EI) *calcd.* for

[1] Kotsuki, H.; Saito, I.; Matsuura, T. *Tetrahedron Lett.* **1981**, *22*, 469-472.

$C_{12}H_{14}O_3$: 222.0892; *found*: 222.0894. *The stereochemical assignment of the configuration of the double bond is tentative*.

2-Methoxy-3-(4-methoxyphenyl)-2-propenoic acid (S-3). A solution of compound **S-2** (246 mg, 1.19 mmol) in MeOH (2.4 mL) and aq. NaOH (2 M, 1.2 mL) was stirred at ambient temperature for 2 h. For work up, the solution was acidified with aq. HCl (1 M) and the product was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4) and evaporated, and the residue was dried under high vacuum for several hours to afford the title acid **S-3** (216 mg, 87%) as a white solid. mp = 168-169 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 7.70 (d, J = 8.9 Hz, 2 H), 6.98 (s, 1 H), 6.91 (d, J = 8.9 Hz, 2 H), 3.02 (s, 3 H), 3.72 (s, 3 H); ^{13}C NMR (75 MHz, CD_3OD): δ = 167.8, 161.8, 145.3, 132.8, 127.4, 125.2, 115.1, 59.3, 55.7; IR (film): $\tilde{\nu}$ = 3000, 2975, 2938, 2837, 2515, 1684, 1603, 1569, 1509, 1443, 1425, 1249, 1175, 929, 822 cm^{-1}; MS (EI): *m/z* (%): 208 (100 $[M]^+$), 165 (36), 148 (18), 137 (20), 121 (14), 91 (11), 77 (18), 63 (6), 51 (11); HRMS (EI) *calcd.* for $C_{11}H_{12}O_4$: 208.0735; *found*: 208.0733. *The stereochemical assignment of the configuration of the double bond is tentative*.

1-(Bromoethyl)-4-methoxybenzene.[2] A mixture of 2-(methoxyphenyl)ethanol (18.2 g, 119 mmol) and PBr_3 (3.74 mL, 39.8 mmol) in toluene was refluxed for 2 h before it was allowed to reach ambient temperature. The organic phase was washed with sat. aq. $Na_2S_2O_3$/$NaHCO_3$ (1:1, 3 x 20 mL) and dried (Na_2SO_4) before the solvent was evaporated to give the title bromide as a colorless liquid (24.3 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.6 Hz, 2 H), 6.84 (d, J = 8.6 Hz, 2 H), 3.78 (s, 3 H), 3.51 (t, J = 7.6 Hz, 2 H), 3.08 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 130.9, 129.6, 113.9, 55.2, 38.5, 33.3; IR (film): $\tilde{\nu}$ = 3031, 3002, 2957, 2935, 2908, 2834, 1611, 1584, 1513, 1464, 1441, 1302, 1247, 1179, 1035, 821 cm^{-1}; MS (EI): *m/z* (%): 216 (16), 214 (17 $[M]^+$), 135 (19), 121 (100), 91 (7), 77 (6), 65 (4), 51 (3), 39 (3).

2,2,2-Trichloroethyl chlorosulfate.[3] SO_2Cl_2 (5.0 mL, 62 mmol) was added dropwise to a stirred solution of 2,2,2-trichloroethanol (6.0 mL, 62 mmol) and pyridine (5.0 mL, 62 mmol) in Et_2O (120 mL) at –20 °C. Once the addition was complete, the mixture was warmed to ambient temperature, and stirring was continued for 1 h. For work up, the reaction was carefully quenched with water (20 mL), the layers were separated, and the organic layer was dried ($MgSO_4$) and evaporated. The crude product was purified by distillation, yielding the title compound as a colorless oil (10.6 g, 69%, bp = 38 °C/0.04 mbar). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.92 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 91.3, 81.2; IR (film): $\tilde{\nu}$ 3021, 2963, 1420, 1376, 1193, 1088, 1045, 993, 875, 780, 729, 597 cm^{-1}; MS (EI): *m/z* (%): 213 (35), 129 (100), 119 (43), 117 (44), 99 (23), 77 (12), 61 (12), 49 (14), 29 (12).

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[2] Hori, M.; Ozeki, H.; Iwamura, T.; Shimizu, H.; Kataoka, T.; Iwata, N. *Heterocycles* **1990**, *31*, 23-26.

[3] Liu, Y.; Lien, I. F.; Ruttgaizer, S.; Dove, P.; Taylor, S. D. *Org. Lett.* **2004**, *6*, 209-212.

Preparation of the Common Synthesis Platform 18

3-Hydroxy-2-nitrophenylethanone (10).[4] 3-Hydroxyacetophenone (10.0 g, 73.4 mmol) was dissolved in ice-cold concentrated H_2SO_4 (30 mL). The resulting solution was cooled to –20 °C before a mixture of concentrated H_2SO_4 (4 mL) and HNO_3 (5 mL) was slowly added over 15 min. Once the addition was complete, the mixture was stirred for another 10 min before it was carefully poured on ice. After stirring for 30 min, the yellow precipitate was filtered off and recrystallized twice from ethanol to yield compound **10** as a beige solid (3.81 g, 29%). mp = 134-135 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.5 (s, 1 H), 7.60 (dd, J = 8.5, 7.4 Hz, 1 H), 7.22 (dd, J = 8.5, 1.3 Hz, 1 H), 6.84 (dd, J = 7.4, 1.3 Hz, 1 H), 2.52 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 155.1, 140.6, 137.0, 121.1, 118.1, 30.3; IR (film): $\tilde{\nu}$ = 3093, 1666, 1582, 1530, 1472, 1376, 1290, 798 cm^{-1}; MS (EI): *m/z* (%): 181 (48 $[M]^+$), 166 (100), 139 (13), 92 (36), 77 (8), 66 (24), 43 (97), 39 (35).

3-Isopropoxy-2-nitrophenylethanone (11). A suspension of ketone **10** (1.00 g, 5.52 mmol), isopropyl bromide (0.64 mL, 6.79 mmol) and K_2CO_3 (2.67 g, 19 mmol) in DMF (12 mL) was stirred at 100 °C for 3 h. For work up, water (80 mL) was added, the aqueous layer was extracted with *tert*-butyl methyl ether (3 x 20 mL), the combined organic layers were washed with water (5 x 20 mL) and aq. NaOH (2 M, 20 mL) before they were dried (Na_2SO_4) and evaporated, thus affording the title compound **11** as brown syrup which solidified upon standing at ambient temperature (1.22 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (m, 1 H), 7.35 (m, 1 H), 7.24 (m, 1 H), 4.65 (hept, J = 6.1 Hz, 1 H), 2.57 (s, 3 H), 1.35 (d, J = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.5, 150.0, 131.5, 130.8, 120.7, 119.4, 73.2, 27.9, 21.7; IR (film): $\tilde{\nu}$ = 3090, 2982, 2935, 1697, 1579, 1544, 1446, 1375, 1286, 1106, 949, 851, 790 cm^{-1}; MS (EI): *m/z* (%): 223 (8 $[M]^+$), 181 (30), 166 (100), 139 (9), 92 (8), 77 (3), 66 (8), 51 (3), 43 (63), 39 (11); HRMS (EI) *calcd.* for $C_{11}H_{13}NO_4$: 223.0844; *found*: 223.0846.

(2*E*)-3-Isopropoxy-2-nitrophenyl-3-(4-methoxyphenyl)-2-propenone (12). Sodium (294 mg, 12.8 mmol) was dissolved in MeOH (10 mL) before a solution of *p*-methoxybenzaldehyde (6.20 mL, 51.1 mmol) and ketone **11** (5.70 g, 25.6 mmol) in MeOH (10 mL) was added. The mixture was stirred at 70 °C for 2 h before it was slowly cooled to ambient temperature. The resulting precipitate was filtered off, washed successively with water (20 mL) and MeOH (20 mL), and dried under high vacuum to give chalcone **12** as a white solid (6.44 g, 74%). mp = 111-112 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 15.9 Hz, 1 H), 7.54-7.47 (m, 3 H), 7.26-7.20 (m, 2 H), 6.99 (d, J = 15.9 Hz, 1 H), 6.91 (m, 2 H), 4.67 (hept, J = 6.1 Hz, 1 H), 3.85 (s, 3 H), 1.37 (d, J = 6.1 Hz, 6 H); ^{13}C NMR

[4] Butenandt, A.; Hallmann, G.; Beckmann, R. *Chem. Ber.* **1957**, *90*, 1120-1124.

(100 MHz, $CDCl_3$): δ = 189.6, 162.2, 150.1, 147.0, 134.3, 131.1, 130.6, 126.9, 121.4, 120.2, 118.1, 114.5, 73.1, 55.4, 21.8; IR (film): $\tilde{\nu}$ = 2980, 2935, 2839, 1664, 1642, 1589, 1572, 1541, 1512, 1466, 1444, 1424, 1374, 1259, 1174, 1029, 977, 830, 799 cm^{-1}; MS (EI): *m/z* (%): 341 (14 $[M]^+$), 188 (23), 176 (8), 163 (55), 149 (38), 135 (38), 121 (100), 107 (17), 90 (9), 77 (11), 63 (3), 43 (18). HRMS (EI) *calcd.* for $C_{19}H_{19}NO_5$+Na ($[M+Na]^+$): 364.1160; *found*: 364.1157.

(3-Isopropoxy-2-nitrophenyl){4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]1*H*-pyrrol-3-yl}methanone (13). To a stirred suspension of NaH (2.11 g, 87.9 mmol) in dry THF (60 mL) was added a solution of TosMIC (5.70 g, 29.3 mmol) and chalcone **12** (5.00 g, 14.7 mmol) in THF (40 mL) at –30 °C. The mixture was stirred at –30 °C for 1 h and at ambient temperature for 2 h. After completion of the reaction, 2-bromoethyl-4-methoxybenzene (15.8 g, 73.3 mmol) was introduced and the solution was refluxed for 2 h. For work up, the reaction was quenched with water (20 mL) and the product was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 1:3) afforded pyrrole **13** as a pale yellow foam (6.27 g, 83%). mp = 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (m, 2 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 7.05 (m, 1 H), 6.97 (m, 2 H), 6.88 (dd, *J* = 1.0, 7.6 Hz, 1 H), 6.84-6.78 (m, 5 H), 6.56 (m, 1 H), 4.61 (hep, *J* = 6.1 Hz, 1 H), 4.01 (t, *J* = 7.0 Hz, 2 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 2.98 (t, *J* = 7.0 Hz, 2 H), 1.34 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 158.6, 158.4, 149.7, 141.0, 136.1, 130.7, 130.5, 129.9, 129.7, 129.5, 127.1, 126.7, 121.5, 121.2, 120.7, 117.3, 114.1, 113.3, 73.0, 55.2, 55.2, 52.0, 36.8, 21.8; IR (film): $\tilde{\nu}$ = 3124, 2979, 2935, 2836, 1643, 1611, 1537, 1514, 1465, 1443, 1383, 1288, 1247, 1179, 1034, 833 cm^{-1}; MS (EI): *m/z* (%): 514 (100 $[M]^+$), 322 (23), 160 (10), 135 (48), 121 (41), 105 (9), 77 (4), 43 (6); HRMS (EI) *calcd.* for $C_{30}H_{30}N_2O_{6+}$Na ($[M+Na]^+$): 537.2001; *found*: 537.1997.

(2-Amino-3-isopropoxyphenyl){4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]1*H*-pyrrol-3-yl}methanone (14). Aq. HCl (0.6 M, 21 mL, 12.5 mmol) was added to a suspension of compound **13** (4.67 g, 9.08 mmol) and iron powder (5.07 g, 90.8 mmol) in EtOH (90 mL) and the resulting suspension was refluxed for 2 h with vigorous stirring. The mixture was cooled to ambient temperature and filtered through a pad of Celite, the filtrate was diluted with EtOAc (200 mL) and successively washed with sat. aq. $NaHCO_3$ (50 mL) and brine (30 mL). Drying of the organic layer over Na_2SO_4 followed by evaporation of the solvent gave aniline **14** as a yellow foam (4.24 g, 96%). mp = 54-55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 2 H), 7.13 (dd, *J* = 1.2, 8.1 Hz, 1 H), 6.98 (m, 2 H), 6.86-6.81 (m, 5 H), 6.72 (d, *J* = 2.3 Hz, 1 H), 6.64 (d, *J* = 2.3 Hz, 1 H), 6.43 (m, 1 H), 6.02 (s, 2 H), 4.51 (hept, *J* = 6.1 Hz, 1 H), 4.03 (t, *J* = 7.0 Hz, 2 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 2.98 (t, *J* = 7.0 Hz, 2 H), 1.35 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.3, 158.5, 158.0, 144.9, 141.7, 129.7, 129.6, 129.2, 128.4, 127.5, 126.7, 125.3, 122.0, 120.8, 120.0, 115.5, 114.0, 113.6, 113.5, 70.9, 55.2, 55.1, 51.7, 37.0, 22.1; IR (film): $\tilde{\nu}$ = 3488, 3358, 3119, 3034, 2975, 2933, 2834, 1612,

1541, 1513, 1454, 1385, 1246, 1220, 1036, 833 cm^{-1}; MS (EI): *m/z* (%): 484 (69 $[M]^+$), 441 (10), 363 (100), 321 (42), 186 (15), 135 (23); HRMS (EI) *calcd.* for $C_{30}H_{33}N_2O_4$ (M+H): 485.2440; *found*: 485.2441.

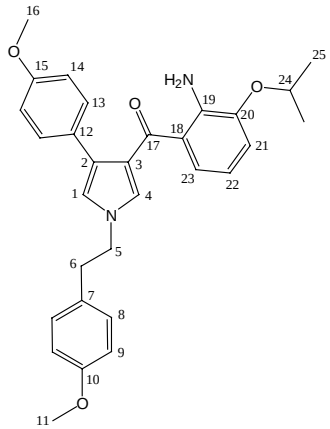


Table S-1. Tabular survey of the NMR data of amine **14** recorded in CD_2Cl_2. All assignments are unambiguous, cf. General; arbitrary numbering scheme as indicated in the insert.

position	δ_C [ppm] (150 MHz)	δ_H [ppm] (600 MHz)
1	120.5	6.68 (d, *J* = 2.3 Hz, 1H)
2	126.7	
3	122.4	
4	128.6	6.72 (d, *J* = 2.3 Hz, 1H)
5	52.1	4.08 (t, *J* = 7.0 Hz, 2H)
6	37.3	3.02 (t, *J* = 7.0 Hz, 2H)
7	130.4	
8	130.1	7.04 (m, 2H)
9	114.4	6.86 (m, 2H)
10	159.0	
11	55.5	3.794 (s, 3H)
12	128.2	
13	129.6	7.27 (m, 2H)
14	113.7	6.83 (m, 2H)
15	158.5	
16	55.5	3.792 (s, 3H)
17	193.5	
18	121.2	
19	142.1	
20	145.4	
21	116.0	6.87 (m, 1H)
22	114.0	6.46 (m, 1H)
23	125.7	7.13 (dd, *J* = 1.2, 8.1 Hz, 1H)
24	71.5	4.55 (sep, *J* = 6.1 Hz, 1H)
25	22.3	1.36 (d, *J* = 6.1 Hz, 6H)
NH_2		6.01 (s, 2H),

2-*N*-[2-Isopropoxy-6-({4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]-1*H*-pyrrol-3-yl}carbonyl)phenyl]-2-methoxy-3-(4-methoxyphenyl)-2-propenamide (16). Freshly distilled oxalyl chloride (0.70 mL, 8.26 mmol) was added dropwise to a suspension of acid **S–3** (1.29 g, 6.19 mmol) in CH_2Cl_2 (20 mL) at 0 °C under argon, followed by 4 drops of dry DMF. After 5 min, the cooling bath was removed and the mixture was stirred at ambient temperature for 1 h. The solvent was evaporated and the residue was dried *in vacuo*.

The crude acid chloride **15** thus formed was dissolved in CH_2Cl_2 (10 mL) and the resulting solution was added dropwise to a stirred solution containing aniline **14** (2.00 g, 4.13 mmol), freshly distilled Et_3N (2.90 mL, 20.7 mmol) and DMAP (50 mg, 0.619 mmol) in CH_2Cl_2 (20 mL) at ambient temperature. The mixture was stirred for 30 min before it was quenched with sat. aq. $NaHCO_3$ (5 mL). The layers were separated, the organic phase was washed successively with aq. HCl (3 M, 10 mL), sat. aq. $NaHCO_3$ (10 mL) and brine (5 mL) before it was dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 3:7 $\rightarrow$ 1:1) afforded amide **16** as a yellow foam (2.49 g, 89%). mp = 69-70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (s, 1 H), 7.61 (m, 2 H), 7.37 (m, 2 H), 7.08 (m, 1H), 7.00-6.94 (m, 6 H), 6.88-6.78 (m, 6 H), 6.54 (m, 1 H), 4.55 (hept, *J* = 6.1 Hz, 1 H), 4.00 (t, *J* = 7.1 Hz, 2 H), 3.81 (s, 3 H), 3.77 (s, 6 H), 3.66 (s, 3 H), 2.98 (t, *J* = 7.1 Hz, 2 H), 1.34 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.0, 162.1, 159.7, 158.5, 158.1, 151.4, 147.4, 137.6, 131.4, 131.0, 129.8, 129.7, 127.4, 126.8, 126.2, 125.3, 124.5, 121.8, 121.3, 120.8, 120.2, 115.2, 114.0, 114.0, 113.2, 71.1, 59.2, 55.2, 51.8, 36.9, 22.1; IR (KBr): $\tilde{\nu}$ = 3406, 3122, 2974, 2935, 2836, 1683, 1638, 1604, 1512, 1465, 1442, 1247, 1147, 1032, 851, 833, 785 cm^{-1}; MS (EI): *m/z* (%): 674 (51 $[M]^+$), 630 (8), 469 (12), 334 (40), 308 (16), 162 (17), 148 (100), 121 (22), 120 (18), 105 (8); HRMS (EI) *calcd.* for $C_{41}H_{42}N_2O_7$+Na ($[M+Na]^+$) 697.2889; *found*: 697.2886.

7-Isopropoxy-2-[methoxy-2-(4-methoxyphenyl)ethenyl]-3-{4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]-1*H*-pyrrol-3-yl}-1*H*-indole (17). *CAUTION: C_8K is pyrophoric and must be handled under Ar with care!* Dry DME (40 mL) was carefully added (*exothermic*!) to a mixture of $TiCl_3$ (2.85 g, 18.5 mmol) and C_8K (4.96 g, 36.7 mmol)[5] at 0 °C under argon and the resulting suspension was refluxed for 1.5 h. Dry pyridine (1.5 mL, 18.5 mmol) was introduced and reflux was continued for another 15 min. A solution of ketoamide **16** (2.49 g, 3.69 mmol) in dry DME (10 mL) was then introduced and the mixture was refluxed until TLC indicated complete conversion of the substrate (ca. 1.5 h). After reaching ambient temperature, the mixture was filtered through a plug of Celite layered on silica, which was carefully rinsed with EtOAc/PhMe (1:1, 150 mL), and the combined filtrates were

[5] (a) Fürstner, A.; Hupperts, A.; Ptock, A.; Janssen, E. *J. Org. Chem.* **1994**, 59, 5215. (b) A detailed procedure for the large scale preparation and handling of KC_8 is described in: Fürstner, A., in *Active Metals. Preparation. Characterization. Applications* (Fürstner, A., Ed.), VCH, Weinheim, **1995**, p.381

concentrated *in vacuo*. Purification of the residue by flash chromatography (EtOAc/hexanes, 1:6 + 1% 6 M NH_3/MeOH) yielded indole **17** as a yellow oil (1.68 g, 71%). The yield was raised to 93% when this reaction was performed on a somewhat smaller scale (278 mg of ketoamide **16**). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.55 (s, 1 H), 7.35 (m, 2 H), 7.08-7.02 (m, 4 H), 6.97-6.90 (m, 2 H), 6.82-6.76 (m, 5 H), 6.67-6.57 (m, 4 H), 5.93 (m, 1 H), 4.75 (hep, *J* = 6.1 Hz, 1 H), 4.15 (t, *J* = 7.0 Hz, 2 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 3.64 (s, 3 H), 3.34 (s, 3 H), 3.08 (t, *J* = 7.0 Hz, 2 H), 1.44 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 158.6, 157.9, 147.3, 144.4, 132.1, 131.1, 130.9, 130.2, 130.1, 129.8, 128.8, 128.3, 126.9, 124.6, 121.9, 120.4, 118.9, 114.5, 114.2, 113.9, 113.7, 112.7, 105.0, 70.8, 58.5, 55.5, 55.4, 52.0, 37.7, 22.5; IR (KBr): $\tilde{\nu}$ = 3480, 3429, 2974, 2933, 2834, 1609, 1575, 1547, 1511, 1463, 1454, 1441, 1248, 1177, 1034, 832, 784 cm^{-1}; MS (EI): *m/z* (%): 642 (44 [M]$^+$), 627 (100), 135 (36), 121 (11), 43 (2). HRMS (EI) *calcd.* for $C_{41}H_{42}N_2O_5$+Na ([M+Na]$^+$): 665.2991; *found*: 665.2987.

7-Isopropoxy-5-methoxy-1,4-bis-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-ethyl]-3,6-dihydro-pyrrolo[2,3-*c*]carbazole (18). In a water-cooled photoreactor, a solution of indole **17** (450 mg, 0.70 mmol) and nitrobenzene (1 mL) in MeCN (140 mL) was purged with argon for 30 min. After that time, Pd/C (10% w/w, 370 mg, 0.350 mmol) was added and the resulting suspension was irradiated with a medium pressure Hg-lamp (Hanovia, 250 W) (cooled by a stream of cold water) for 2.5 h. After completion of the reaction, the suspension was filtered through a silica/Celite pad, which was carefully rinsed with EtOAc/PhMe (1:1, 100 mL). The filtrate was evaporated and the residue was purified by flash chromatography (EtOAc/hexanes, 1:6) to afford pyrrolocarbazole **18** as a yellow solid (365 mg, 81%). mp = 173-174 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.54 (br s, 1 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.90 (s, 1 H), 6.79 (d, *J* = 7.6 Hz, 1 H), 6.73 (dd, *J* = 8.0, 7.6 Hz, 1 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.23 (d, *J* = 7.6 Hz, 1 H), 4.76 (hept, *J* = 6.0 Hz, 1 H), 3.93 (s, 3 H), 3.92 (s, 3 H), 3.84 (m, 2 H), 3.74 (s, 3 H), 3.66 (s, 3 H), 2.63 (m, 2 H), 1.45 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 159.6, 159.1, 158.4, 143.7, 140.6, 132.4, 132.0, 130.7, 130.6, 130.3, 129.8, 129.1, 128.9, 127.8, 124.9, 119.4, 118.7, 118.1, 117.1, 117.0, 115.2, 113.8, 113.7, 113.4, 106.9, 70.9, 61.4, 55.5, 55.3, 50.2, 37.0, 22.2; IR (film) $\tilde{\nu}$ = 3328, 2935, 2831, 1614, 1572, 1544, 1513, 1455, 1436, 1404, 1369, 1340, 1304, 1276, 1236, 1174, 1135, 1117, 1038, 1024, 1004, 931, 913, 874, 859, 834, 819, 783, 770, 734, 678 cm^{-1}. MS (EI): *m/z* (%): 484 (69 [M$^+$]), 441 (10), 363 (100), 321 (42), 186 (15), 135 (23).

Total Synthesis of Dictyodendrin C

7-Hydroxy-1,4-bis(4-hydroxyphenyl)-3-[2-(4-hydroxyphenyl)ethyl]pyrrolo[2,3-*c*]-carbazol-2,5(3*H*,6*H*)-dione (8). A solution of BBr_3 (1 M in CH_2Cl_2, 0.31 mL, 0.31 mmol) was added to a solution of compound **18** (20 mg, 0.031 mmol) and cyclohexene (0.063 mL, 0.620 mmol) in CH_2Cl_2 (8 mL) at –78 °C and the resulting mixture was allowed to reach ambient temperature over the course of 8 h. The reaction was quenched with aq. $KHSO_4$ (10% *w/w*, 2 mL) and NaOH (20% *w/w*, 1 mL) and the organic phase was washed with water. The aqueous phase was acidified with conc. HCl (2 mL) and extracted with *tert*-butyl methyl ether, the combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. Purification of the residue by preparative reverse-phase HPLC (Nucleodur 100-16-C-18/A, MeOH/H_2O) afforded compound **8** as a green-brown solid (8.5 mg, 49%). ^{1}H NMR (600 MHz, d_6-acetone): δ = 7.40 (m, 2 H), 7.32 (m, 2H), 6.98 (m, 2 H), 6.96 (m, 2 H), 6.68 (m, 2 H), 6.66 (dd, *J* = 7.8, 1.1 Hz, 1 H), 6.63 (t, *J* = 7.8 Hz, 1 H), 6.62 (m, 2 H), 5.95 (dd, *J* = 7.8, 1.1 Hz, 1 H), 3.45 (m, 2 H), 2.43 (m, 2 H); ^{13}C NMR (150 MHz, d_6-acetone): δ = 179.4, 171.8, 159.5, 158.5, 156.7, 149.6, 145.5, 134.8, 133.7, 133.3, 133.1, 130.6, 129.8, 129.8, 129.3, 126.2, 124.4, 123.9, 122.8, 118.1, 116.2, 115.9, 115.8, 115.6, 113.4, 110.2, 43.7, 34.6. IR (film): $\tilde{\nu}$ = 3312, 2925, 1687, 1582, 1511, 1436, 1392, 1357, 1217, 1168, 1106, 1080, 827, 780 cm^{-1}. MS (EI): *m/z* (%): 557 ([M+H]). HRMS (EI) *calcd*. for $C_{34}H_{24}N_2O_6$+Na ([M+Na]$^+$): 579.15321; *found*: 579.15271.

Phenol 19. BCl_3 (1 M solution in heptanes, 0.970 mL, 0.970 mmol) was added dropwise to a stirred solution of compound **18** (155 mg, 0.242 mmol) in dry CH_2Cl_2 at 0 °C under argon. After 1h, the reaction mixture was quenched with sat. aq. $NaHCO_3$ (5 mL), and vigorously stirred at RT for 30 min. The aqueous phase was extracted with CH_2Cl_2 (50 mL), the organic layers were washed with brine (2 mL), dried (Na_2SO_4), and evaporated. The residual solid was purified by recrystallisation in hot EtOAc/hexanes to afford the title compound **19** (109 mg, 75%) as a white solid. mp = 253-255 °C; ^{1}H NMR (400 MHz, acetone-d_6): δ = 9.87 (s, 1 H), 8.35 (s, 1 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 7.39 (d, *J* = 8.8 Hz, 2 H), 7.14 (d, *J* = 8.8 Hz, 2 H), 7.06 (s, 1 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 6.76-6.73 (m, 4 H), 6.70 (dd, *J* = 7.2, 0.4 Hz, 1 H), 6.56 (dd, *J* = 8.8, 7.6 Hz, 1 H), 6.25 (d, *J* = 8.4 Hz, 1 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 3.86 (m, 2 H), 3.72 (s, 3 H), 3.66 (s, 3 H), 2.64 (m, 2 H); ^{13}C NMR (100 MHz, THF-d_8): δ = 160.4, 159.8, 159.4, 143.6, 141.7, 133.3, 132.6, 131.6, 131.5, 130.4, 130.4, 129.8, 129.5, 129.2, 126.3, 120.4, 118.8, 118.4, 118.0, 117.2, 116.5, 114.2, 113.8, 108.8, 108.4, 68.2, 61.1, 55.5, 55.5, 55.3, 50.9, 37.8; IR (film) $\tilde{\nu}$ = 3437, 2926, 2838, 1733, 1606, 1576, 1548, 1513, 1462, 1440, 1403, 1347, 1301, 1282, 1243, 1229, 1174, 1162, 1135, 1106, 1091, 1063, 1033, 999, 935, 913, 850, 840, 784, 772, 731, 709, 682 cm^{-1}; MS (EI): *m/z* (%): 599 (42), 598 (100 [M$^+$]), 477 (25), 462 (16), 461 (11), 447 (12), 446 (33), 445 (11), 135 (21); HRMS (ESI$^+$) *calcd*. for $C_{38}H_{34}N_2O_5$+Na ([M+Na]$^+$): 621.2360; *found*: 621.2357.

Sulfate ester 20. A solution of 2,2,2-trichloroethyl chlorosulfate (66.5 mg, 0.270 mmol) in THF (1 mL) was added dropwise to a solution of phenol **19** (108 mg, 0.180 mmol) and DABCO (60.6 mg, 0.540 mmol) in THF (18 mL). After stirring for 3 days, the reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and brine (5 mL). The product was extracted with EtOAc (3 x 10 mL), dried (Na_2SO_4), and evaporated. The residue was purified by flash chromatography (EtOAc/hexanes, 3:7) to afford product **20** (104 mg, 71%) as a colorless oil. Remaining starting material (30 mg, 28%) could be re-isolated by a further elution of the silica gel column with EtOAc. Spectroscopic data for **20**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.79 (s, 1 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.33 (dd, *J* = 8.0, 0.4 Hz, 1 H), 7.10 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.94 (s, 1 H), 6.86 (dd, *J* = 8.0, 8.0 Hz, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 4.85 (s, 2 H), 3.93 (s, 3 H), 3.92 (s, 3 H), 3.86 (m, 2 H), 3.74 (s, 3 H), 3.64 (s, 3 H), 2.63 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.7, 159.2, 158.4, 140.3, 134.8, 132.3, 132.0, 130.7, 130.4, 130.0, 129.9, 129.7, 129.5, 127.7, 127.2, 124.3, 119.5, 119.3, 118.6, 116.9, 115.7, 114.5, 113.8, 113.7, 113.5, 95.8, 92.5, 81.0, 61.5, 55.5, 55.5, 55.2, 50.2, 37.0; IR (film) $\tilde{\nu}$ = 3414, 2933, 2835, 1609, 1570, 1548, 1512, 1461, 1441, 1404, 1357, 1304, 1285, 1241, 1192, 1159, 1104, 1085, 1029, 1006, 988, 932, 886, 860, 836, 810, 793, 784, 722 cm^{-1}; HRMS (ESI$^+$) *calcd*. for $C_{40}H_{35}N_2O_8SCl_3$+Na ([M+Na]$^+$): 831.1072; *found*: 831.1073.

Compound 21. BCl_3 (1 M solution in heptanes) was added dropwise to a solution of the polyphenol **20** (96.2 mg, 0.119 mmol) and *n*-Bu_4NI (351 mg, 0.950 mmol) in CH_2Cl_2 (12 mL) at 0 °C. After 30 min, the reaction mixture was quenched with sat. aq. $NaHCO_3$ (5 mL), diluted with EtOAc (20 mL), and vigorously stirred for 30 min. The layers were separated, the organic phase was washed with brine (2 mL), dried (Na_2SO_4), and evaporated to give a yellow oil which was used directly in the next step without further purification.

To a solution of this crude polyphenol in CH_3CN (12 mL) was added H_2O_2 (30% *w/w* solution in H_2O, 0.400 mL). After 1 h, the solvent was evaporated and the residue was purified by reverse-phase chromatography (Merck LiChroprep RP-18, eluent MeOH/H_2O 4:1) to afford quinone **21** (51.9 mg, 57% over 2 steps) as a brown syrup. ^{1}H NMR (400 MHz, CD_3OD): δ = 7.35 (dd, *J* = 7.9, 0.5 Hz, 1 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 6.82 (dd, *J* = 8.2, 8.1 Hz, 1 H), 6.65 (d, *J* = 8.6 Hz, 2 H), 6.57 (d, *J* = 8.5 Hz, 2 H), 6.37 (d, *J* = 8.3 Hz, 1 H), 5.13 (s, 2 H), 3.44 (m, 2 H), 2.39 (m, 2 H); ^{13}C NMR (150 MHz, CD_3OD): δ = 180.6, 173.0, 161.0, 159.4, 156.9, 150.3, 137.9, 134.8, 134.4, 133.9, 133.5, 131.9, 131.3, 130.9, 130.0, 127.7, 124.9, 123.9, 123.3, 122.0, 119.5, 118.2, 116.7, 116.2, 116.0, 114.3, 94.0, 81.9, 44.2, 34.9; IR (film) $\tilde{\nu}$ = 3263, 2926, 2851, 1694, 1599, 1511, 1476, 1437, 1395, 1319, 1202, 1163, 1107, 1086, 987, 895, 821, 796, 721 cm^{-1}; HRMS (ESI$^+$) *calcd*. for $C_{36}H_{25}N_2O_9SCl_3$+Na ([M+Na]$^+$): 789.0239; *found*: 789.0246.

Dictyodendrin C (3). Zn powder (pre-activated with HCl, 9.3 mg, 0.143 mmol) was added to a solution of sulfate ester **21** (21.9 mg, 0.0285 mmol) and HCO_2NH_4 (26.9 mg, 0.428 mmol)

in MeOH (2.9 mL) at ambient temperature. After the resulting mixture had been vigorously stirred for 30 min., the suspension was filtered through a pad of Celite and the filtrate was stirred for 4h under an atmosphere of oxygen (1 atm). The solvent was evaporated and the residue was purified by flash chromatography (CH_2Cl_2/MeOH 85/15). The fraction containing the product were combined and the CH_2Cl_2 was carefully evaporated. Excess aq. NH_4OH (5 drops) was then added and the mixture was concentrated to dryness to afford the ammonium salt of dictyodendrin C **3** (14.2 mg, 76%) as a golden solid. ^{1}H NMR (400 MHz, CD_3OD): δ = 7.32 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 6.72 (dd, *J* = 8.0, 8.0 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 2 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 6.15 (d, *J* = 8.0 Hz, 1 H), 3.43 (m, 2 H), 2.40 (m, 2 H); ^{13}C NMR (100 MHz, CD_3OD): δ = 180.8, 173.3, 160.3, 159.2, 156.9, 150.4, 140.7, 135.3, 134.0, 133.8, 133.6, 133.4, 131.0, 130.8, 130.5, 130.1, 126.8, 124.1, 123.8, 122.4, 122.0, 118.2, 116.4, 116.1, 116.0, 114.0, 44.2, 34.9; IR (film) $\tilde{\nu}$ = 3262, 2927, 1693, 1599, 1510, 1475, 1437, 1392, 1356, 1222, 1167, 1110, 1054, 1023, 917, 890, 809, 790, 777, 741, 721 cm^{-1}; HRMS (ESI$^-$) *calcd.* for $C_{34}H_{23}N_2O_9S$ ([M−NH_4]$^-$): 635.1119; *found*: 635.1102.

Total Synthesis of Dictyodendrin B

3→2 Aryl Migration: Preparation of 7-methoxy-2,4-bis(4-methoxyphenyl)-3-[2-(4-methoxy-phenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazole (24). A solution of substrate **23** (11 mg, 0.02 mmol), *p*-methoxybenzoxyl chloride (3 mg, 0.02 mmol) and $SnCl_4$ (0.002 mL, 0.021 mmol) in 1,2-dichloroethane (1.5 mL) was stirred at 80 °C for 2 h. The reaction was diluted with CH_2Cl_2 (5 mL) before it was quenched at ambient temperature with sat. aq. $NaHCO_3$ (5 mL). A standard extractive work up followed by flash chromatography (EtOAc/hexanes, 1:4) of the crude material afforded compound **24** as a colorless solid (7 mg, 64%). ^{1}H NMR (600 MHz, d_6-acetone): *δ* = 10.28 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.62 (m, 2H), 7.48 (m, 2H), 7.29 (s, 1H), 7.15 (m, 1H), 7.14 (m, 1H), 7.11 (m 2H), 7.06 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.56 (m, 2H), 6.29 (m, 2H), 4.02 (m, 5H), 3.90 (s, 3H), 3.87 (s, 3H), 3.66 (s, 3H), 2.19 (m, 2H). ^{13}C NMR (150 MHz, d_6-acetone): *see Table S-2*. IR (Film): $\tilde{\nu}$ = 2950, 2925, 2899, 2832, 1609, 1577, 1512, 1457, 1439, 1421, 1281, 1244, 1175, 1083, 1030, 834, 793, 753, 734 cm^{-1}. MS (EI): *m/z* (%): 582 (96 [M$^+$]), 461 (100), 430 (22), 121 (6). HR-MS (EI) *calcd* for $C_{38}H_{35}N_2O_4$ ([M+H]$^+$): 583.2596; *found*: 583.2591.

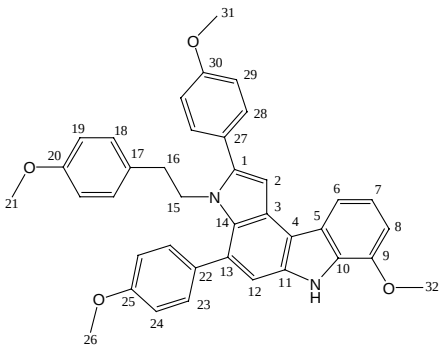
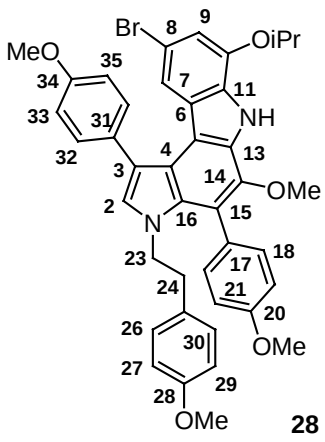


Table S-2. Tabular survey of the NMR data of compound **24** recorded in acetone-d_6. All assignments are unambiguous, cf. General; arbitrary numbering scheme as indicated in the insert.

position	δC [ppm]	δH [ppm]
1	144.2	
2	102.7	7.14 (m, 1H)
3	124.6	
4	114.4	
5	125.5	
6	114.6	7.91 (d, *J* = 7.8 Hz, 1H)
7	119.9	7.15 (m, 1H)
8	105.3	6.94 (d, *J* = 7.8 Hz, 1H)
9	146.9	
10	130.6	
11	135.9	
12	110.1	7.29 (s, 1H)
13	127.2	
14	131.0	
15	48.2	4.02 (m, 2H)
16	36.0	2.19 (m, 2H)
17	131.1	
18	130.1	6.29 (m, 2H)
19	114.3	6.56 (m, 2H)
20	159.1	
21	55.3	3.66 (s, 3H)
22	134.8	
23	131.8	7.62 (m, 2H)
24	114.5	7.11 (m 2H)
25	160.2	
26	55.8	3.90 (s, 3H)
27	126.9	
28	131.7	7.48 (m, 2H)
29	114.7	7.06 (m, 2H)
30	160.5	
31	55.7	3.87 (s, 3H)
32	55.8	4.02 (m, 3H)
NH		10.28 (s, 1H)

2-Bromo-7-isopropoxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)-ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazole (27). NBS (230 mg, 1.29 mmol) was added in one portion to a stirred solution of the pyrrolocarbazole **18** (830 mg, 1.29 mmol) in THF (26 mL) at 0 °C. After stirring for 30 min, the cooling bath was removed and the solution was allowed to reach ambient temperature over 10 min. The mixture was concentrated under reduced pressure to ca. 1/5 of the original volume and passed through a silica pad, which was rinsed with EtOAc/hexanes (1:2). The combined filtrates were evaporated and the solid thus obtained was recrystallized from hot EtOAc/hexanes to give the title compound **27** as an off-white solid (639 mg, 69%). mp = 201-202 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.54 (s, 1 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 7.41 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 8.1 Hz, 2 H), 6.77 (d, *J* = 7.7 Hz, 1 H), 6.72 (br s, 4 H), 6.67 (t, *J* = 8.0 Hz, 1 H), 5.85 (d, *J* = 8.1 Hz, 1 H), 4.74 (hept, *J* = 6.1 Hz, 1 H), 3.99 (m, 2 H), 3.95 (s, 3 H), 3.93 (s, 3 H), 3.75 (s, 3 H), 3.65 (s, 3 H), 2.58 (m, 2 H), 1.43 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 160.0, 159.9, 158.8, 144.0, 141.0, 133.3, 132.7, 131.1, 130.6, 130.1, 129.8, 129.6, 127.8, 124.9, 120.2, 119.2, 118.3, 118.1, 116.7, 114.9, 114.4, 114.2, 114.1, 114.0, 107.4, 71.2, 61.6, 55.8, 55.8, 55.6, 48.7, 36.0, 22.5; IR (film): $\tilde{\nu}$ = 3353, 2932, 2831, 1613, 1573, 1547, 1511, 1498, 1455, 1440, 1408, 1356, 1338, 1317, 1302, 1285, 1244, 1170, 1141, 1123, 1104, 1027, 1007, 933, 916, 862, 840, 820, 786, 753, 740, 686, 659 cm^{-1} ; MS (EI): *m/z* (%): 722 (10), 721 (42), 720 (100 [M$^+$]), 719 (43), 718 (93), 556 (14), 554 (13), 541 (12), 539 (11), 518 (10), 461 (8), 135 (56); HRMS (ESI$^+$) *calcd.* for $C_{41}H_{39}Br_1N_2O_5Na$ ([M+Na]$^+$): 741.1940; *found*: 741.1937.



28

The compound should be stored in a refrigerator to avoid migration of the bromine along the periphery of the heteroarene system, which ultimately furnishes the isomeric bromide **28** with the following spectroscopic properties: ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.55 (s, 1 H, N*H*), 7.51 (d, *J* = 8.6 Hz , 2 H, H(18,22)), 7.37 (d, *J* = 8.6 Hz, 2 H, H(32,36)), 7.08 (d, *J* = 8.5 Hz , 2 H, H(19-21)), 7.04 (d, *J* = 8.6 Hz, 2 H, H(33,35)), 6.89-6.92 (br s, 1 H, H(2)), 6.87 (d, *J* = 1.5 Hz, 1 H, H(9)), 6.70 (d, *J* = 8.6 Hz , 2 H, H(40,42)), 6.65 (d, *J* = 8.7 Hz , 2 H, H(39,43)), 6.01 (d, *J* = 1.5 Hz, 1 H, H(7)), 4.72 (hept, *J* = 6.0 Hz, 1 H, $(CH_3)_2CH$), 3.95 (s, 3 H, C(34)-OCH_3), 3.93 (s, 3 H, C(20)-OCH_3), 3.84 (m, 2 H, H(23)), 3.75 (s, 3 H, C(28)-OCH_3), 3.64 (s, 3 H, C(14)-OCH_3), 2.63 (m, 2 H, H(24)), 1.45 (d, *J* = 6.0 Hz, 6 H, $(CH_3)_2CH$); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 159.9 (C20), 159.8 (C34), 158.7 (C28), 144.3 (C10), 140.7 (C14), 132.6 (C18, C22), 132.6 (C32, C36), 130.8 (C25), 130.1 (C31), 130.0 (C26, C30), 129.5 (C11), 129.2 (C16), 128.9 (C2), 127.8 (C17), 125.7 (C6), 120.1 (C4), 119.7 (C7), 119.1 (C15), 117.1 (C3), 114.0 (C19, C21), 113.9 (C26, C30), 113.8 (C33, C35), 111.3 (C8), 110.1 (C9), 71.6 ($(CH_3)_2CH$), 61.7 (C14-OCH_3), 55.9 (C34-OCH_3), 55.8 (C20-OCH_3), 55.2 (C28-OCH_3), 50.5 (C23), 37.3 (C4), 22.3

((*C*H$_3$)$_2$CH); IR (film): $\tilde{\nu}$ = 3358, 2932, 2832, 1611, 1563, 1547, 1512, 1460, 1436, 1404, 1370, 1338, 1302, 1275, 1238, 1173, 1137, 1106, 1028, 1008, 932, 879, 836, 821, 789, 730, 713, 691, 667 cm^{-1}; MS (EI): *m/z* (%): 722 (16), 721 (55), 720 (100 [M$^+$]), 719 (54), 718 (85), 556 (16), 555 (10), 554 (15), 541 (13), 539 (11), 135 (47); HRMS (ESI$^+$) *calcd*. for $C_{41}H_{39}BrN_2O_5$+Na ([M+Na]$^+$): 741.1935; *found*: 741.1936.

{7-Isopropoxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-c]carbazol-2-yl}-(4-methoxyphenyl)methanol (29). MeLi (1.6 M in Et$_2$O, 0.59 mL, 0.946 mmol) was added dropwise to a stirred solution of the bromo-pyrrolocarbazole **27** (619 mg, 0.860 mmol) in dry THF (33 mL) at –78 °C under argon. After stirring for 15 min, *n*-BuLi (1.6 M in hexanes, 0.59 mL, 0.946 mmol) was added dropwise and stirring was continued for another 15 min before a solution of *p*-methoxybenzaldehyde (0.26 mL, 2.15 mmol) in dry THF (1 mL) was slowly introduced. After 15 min, the cooling bath was removed and the mixture was allowed to reach ambient temperature over 30 min. For work up, the reaction was carefully quenched with aq. NH_4Cl (1 mL) and brine (1 mL), the organic layer was dried ($MgSO_4$) and evaporated, and the residue was purified by flash chromatography (EtOAc/hexanes, 1:4) to furnish compound **29** as a white foam (647 mg, 97%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.58 (s, 1 H), 7.54-7.45 (m, 4 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.07-7.02 (m, 3 H), 6.98 (dd, *J* = 8.4, 2.8 Hz, 1 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 7.6 Hz, 1 H), 6.69 (dd, *J* = 8.0, 8.0 Hz, 1 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.31 (d, *J* = 8.8 Hz, 2 H), 6.03 (d, *J* = 2.8 Hz, 1 H), 5.80 (d, *J* = 8.0 Hz, 1 H), 4.76 (hept, J = 6.4 Hz, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 3.82 (m, 2 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.57 (s, 3 H), 2.54 (m, 1 H), 2.46 (d, *J* = 3.7 Hz, 1 H), 2.09 (m, 1 H), 1.45 (dd, *J* = 6.1, 1.4 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ =159.9, 159.8, 159.1, 158.4, 144.0, 141.4, 137.8, 134.8, 133.6, 133.5, 133.1, 133.0, 131.1, 130.2, 129.9, 129.5, 129.5, 127.9, 127.1, 125.1, 120.3, 119.2, 118.4, 118.4, 116.8, 115.7, 114.3, 114.1, 114.1, 113.9, 113.8, 113.6, 114.3, 114.1, 114.1, 113.9, 113.8, 113.6, 107.3, 71.2, 68.0, 61.3, 55.9, 55.8, 55.6, 55.5, 47.6, 36.0, 22.5; IR (film): $\tilde{\nu}$ = 3451, 2969, 2934, 2835, 1729, 1610, 1573, 1547, 1510, 1463, 1440, 1402, 1371, 1318, 1301, 1284, 1240, 1171, 1106, 1064, 1030, 1007, 953, 918, 875, 837, 804, 789, 770, 734, 709, 677 cm^{-1}; MS (EI): *m/z* (%): 778 (10), 777 (34), 776 (66 [M$^+$]), 655 (12), 626 (14), 612 (9), 534 (7), 506 (16), 449 (7), 135 (63), 134 (44), 121 (100), 119 (19), 91 (15), 65 (8); HRMS (ESI$^+$) *calcd*. for $C_{49}H_{48}N_2O_7$+Na ([M+Na]$^+$): 799.3359; *found*: 799.3352.

{7-Isopropoxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazol-2-yl}-(4-methoxyphenyl) methanone (30). TPAP (9.1 mg, 0.026 mmol) was added to a suspension of alcohol **29** (202 mg, 0.260 mmol), NMO (61.0 mg, 0.520 mmol) and activated molecular sieves (4Å, 600 mg) in dry CH_2Cl_2 under argon. The mixture was vigorously stirred for 2 h before it was filtered through a pad of Celite and the filtrate was evaporated. Purification of the residue by flash chromatography (EtOAc/hexanes, 1:4) afforded ketone **30** as a yellow foam (129 mg, 66%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.68 (s, 1 H), 7.59 (d, *J* = 8.8 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H),

7.10 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.66 (dd, *J* = 8.4, 8.4 Hz, 1 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 8.4 Hz, 2 H), 5.81 (d, *J* = 8.0 Hz, 1 H), 4.76 (hept, *J* = 6.0 Hz, 1 H), 3.96 (m, 2 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 2.55 (m, 2 H), 1.45 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 189.7, 163.3, 159.7, 159.2, 158.3, 143.8, 143.0, 136.3, 133.2, 132.4, 132.3, 131.8, 131.2, 130.8, 130.5, 129.7, 129.6, 128.8, 127.4, 124.6, 121.8, 119.5, 118.9, 118.2, 116.9, 115.7, 113.9, 113.6, 113.3, 113.3, 107.0, 70.9, 61.3, 55.5, 55.5, 55.5, 55.2, 47.6, 36.7, 22.2; IR (film): $\tilde{\nu}$ = 3344, 2969, 1934, 1835, 1596, 1572, 1533, 1510, 1462, 1439, 1420, 1384, 1371, 1350, 1316, 1285, 1239, 1170, 1153, 1106, 1063, 1028, 1008, 971, 932, 922, 905, 869, 836, 795, 781, 773, 733, 704 cm^{-1}; MS (EI): *m/z* (%): 775 (32), 774 (58 [M^+]), 654 (15), 653 (33), 640 (14), 595 (16), 135 (100), 121 (25); HRMS (ESI$^+$) *calcd.* for $C_{49}H_{47}N_2O_7$ ([M+H]$^+$): 775.3370; *found*: 775.3378.

Dimer 31. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.65 (s, 1 H), 7.63-7.49 (m, 8 H), 7.34 (d, *J* = 7.7 Hz, 1 H), 7.29 (d, *J* = 7.9 Hz , 1 H), 7.10 (m, 2 H), 7.07 (d, *J* = 8.4 Hz, 1 H), 7.01-6.98 (m, 3 H), 6.95 (d, *J* = 1.6 Hz, 1 H), 6.82 (dd, *J* = 7.5 Hz, 2 H), 6.73 (d, *J* = 8.9 Hz, 2 H), 6.64 (d, *J* = 8.9 Hz, 2 H), 6.63 (d, *J* = 6.7 Hz, 1 H), 6.61 (d, *J* = 8.8 Hz, 2 H), 6.59 (d, *J* = 8.6 Hz, 2 H) superimposed upon 6.58 (m, 1 H), 6.54 (d, *J* = 8.7 Hz, 2 H), 6.52 (d, *J* = 8.7 Hz, 2 H), 6.18 (m, 1 H), 6.09 (m, 1 H), 5.94 (d, *J* = 8.2 Hz, 1 H), 5.59 (d, *J* = 1.6 Hz, 1 H), 4.70 (hept, d = 6.0 Hz, 1 H), 4.27 (hept, *J* = 5.9 Hz, 1 H), 3.92 (s, 3 H), 3.89 (m, 4 H), 3.84 (s, 3 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 3.68 (s, 3 H), 2.77 (s, 3 H), 2.62 (s, 3 H), 2.53 (m, 4 H), 1.45 (d, *J* = 6.0 Hz, 3 H), 1.44 (d, *J* = 6.0 Hz, 3 H), 0.72 (d, *J* = 6.0 Hz, 3 H), 0.71 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 190.2, 189.7, 163.6, 163.5, 159.9, 159.7, 159.4, 159.1, 158.6, 145.0, 144.6, 143.3, 142.0, 136.8, 136.4, 134.5, 133.7, 133.4, 132.9, 132.9, 132.8, 132.7, 132.6, 132.6, 132.5, 132.1, 132.1, 132.0, 131.5, 131.4, 130.8, 130.7, 130.3, 130.2, 129.9, 129.5, 128.4, 128.0, 127.7, 125.1, 122.8, 122.3, 122.1, 120.3, 119.4, 119.3, 118.8, 118.3, 118.2, 117.3, 116.6, 116.3, 114.2, 114.2, 114.0, 113.8, 113.8, 113.6, 113.5, 113.5, 112.5, 110.2, 109.0, 71.3, 70.0, 61.6, 55.8, 55.8, 55.8, 55.7, 55.7, 55.4, 55.4, 54.7, 48.0, 47.9, 36.9, 36.8, 22.5, 22.3, 21.8, 21.6; IR (film) $\tilde{\nu}$ = 2969, 2932, 2834, 1733, 1597, 1574, 1533, 1511, 1462, 1440, 1421, 1371, 1348, 1285, 1239, 1172, 1108, 1027, 969, 928, 905, 835, 794, 781, 769, 732, 705 cm^{-1}; HRMS (ESI$^+$) *calcd*. for $C_{98}H_{91}N_4O_{14}$ [(M+H)$^+$]: 1547.6526; *found*: 1547.6499.

{7-Hydroxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazol-2-yl}-(4-methoxyphenyl)methanone (32). BCl_3 (1 M in heptanes, 1.32 mL, 1.32 mmol) was added dropwise to a stirred solution of compound **30** (256 mg, 0.330 mmol) in CH_2Cl_2 (16 mL) at –20 °C. After 1 h the reaction was quenched with vigorous stirring at that temperature with sat. aq. $NaHCO_3$ (3 mL) and the mixture was allowed to warm to ambient temperature. The organic layer was washed with brine (3 mL), dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (EtOAc/hexanes, 2:3) to afford compound **32** as a yellow oil (206 mg, 85%). ^{1}H NMR (400

MHz, CD_2Cl_2): δ = 8.68 (s, 1 H), 7.58 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.70 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 7.2 Hz, 1 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.58 (t, *J* = 8.0 Hz, 1 H), 6.52 (d, *J* = 8.8 Hz, 2 H), 5.81 (d, *J* = 8.0 Hz, 1 H), 5.25 (s, 1 H), 3.96 (m, 2 H), 3.91 (s, 3 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.69 (s, 3 H), 3.65 (s, 3 H), 2.52 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 190.3, 163.7, 159.9, 159.5, 158.6, 143.4, 141.6, 136.6, 133.5, 132.7, 132.6, 132.0, 131.8, 131.5, 130.8, 130.4, 129.9, 129.3, 129.0, 127.6, 125.6, 122.6, 119.9, 119.3, 118.7, 117.6, 116.0, 114.2, 113.9, 113.6, 109.561.5, 55.8, 55.8, 55.8, 55.5, 64.4, 47.9, 36.9; IR (film): $\tilde{\nu}$ = 3359, 2935, 1609, 1595, 1577, 1532, 1512, 1463, 1438, 1422, 1287, 1245, 1174, 1107, 1067, 1034, 966, 835 cm^{-1}; MS (EI): *m/z* (%): 733 (15), 732 (30 [M$^+$]), 612 (10), 611 (25), 598 (17), 135 (100), 121 (29), 105 (7); HRMS (ESI$^+$) *calcd.* for $C_{46}H_{41}N_2O_7$ ([M+H]$^+$): 733.2913; *found*: 733.2908.

Sulfuric acid 5-methoxy-2-(4-methoxybenzoyl)-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazol-7-yl ester 2,2,2-trichloroethyl ester (33). A solution of 2,2,2-trichloroethyl chlorosulfate (91 mg, 0.37 mmol) in CH_2Cl_2 (1 mL) was added in one portion to a stirred solution of phenol **32** (180 mg, 0.243 mmol) and DABCO (83 mg, 0.37 mmol) in CH_2Cl_2 (24 mL) at ambient temperature. Once the reaction was complete (2 h), sat. aq. NH_4Cl (4 mL) was added, the layers were separated, and the organic layer was washed with brine (2 mL) before being dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 1:3) gave compound **33** as a yellow foam (214 mg, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.82 (s, 1 H), 7.58 (d, *J* = 8.8 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 7.30 (dd, *J* = 8.0, 0.6 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.77 (dd, *J* = 8.4, 8.0 Hz, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.61 (d, *J* = 8.8 Hz, 2 H), 6.52 (d, *J* = 8.8 Hz, 2 H), 6.19 (d, *J* = 8.4 Hz, 1 H), 4.85 (s, 2 H), 3.95 (m, 2 H), 3.91 (s, 3 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.69 (s, 3 H), 3.65 (s, 3 H), 2.53 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 189.9, 163.8, 160.1, 159.7, 142.9, 137.0, 135.2, 133.5, 132.6, 131.9, 131.8, 131.1, 130.6, 129.9, 128.7, 127.6, 127.2, 124.7, 121.7, 120.0, 119.6, 119.1, 116.3, 115.4, 114.3, 113.9, 113.8, 113.7, 81.3, 61.7, 55.8, 55.8, 55.8, 55.5, 48.0, 37.0; IR (film): $\tilde{\nu}$ = 2935, 2835, 1597, 1572, 1533, 1511, 1462, 1442, 1417, 1351, 1311, 1286, 1243, 1193, 1173, 1158, 1106, 1068, 1030, 996, 965, 926, 885, 867, 836, 812, 794, 782, 770, 724 cm^{-1}; HRMS (ESI$^+$) *calcd.* for $C_{48}H_{42}Cl_3N_2O_{10}S_1$ ([M+H]$^+$): 943.1622; *found*: 943.1622.

Dictyodendrin B (2). BCl_3 (1 M in heptanes, 0.76 mL, 0.76 mmol) was added dropwise to a stirred solution of compound **33** (60 mg, 0.064 mmol) and (*n*-Bu)$_4$NI (282 mg, 0.0764 mmol) in CH_2Cl_2 (6.4 mL) at 0 °C under argon. The cooling bath was removed and the solution was stirred at ambient temperature for 1.5 h. The reaction was quenched with water (10 mL) and the resulting mixture was vigorously stirred for 1 h before it was diluted with EtOAc (20 mL). The organic layer was successively washed with sat. aq. Na_2SO_3 (5 mL) and brine (2 mL) before it was dried over Na_2SO_4 and evaporated. The residue was passed through a pad of

reverse-phase chromatography gel (LiChroprep RP-18, E. Merck, Darmstadt, 5 g), eluting with 3:1 MeOH/H_2O, and product **34** thus obtained was immediately processed in the next step without further characterization.

To a solution of this crude material and HCO_2NH_4 (24 mg, 0.38 mmol) in dry MeOH (6.4 mL) was added activated zinc dust (8.3 mg, 0.13 mmol). The suspension was vigorously stirred for 1 h before excess zinc was filtered off through a pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography (CH_2Cl_2/MeOH, 9:1 → 4:1). The pooled fractions were concentrated, and the residue was dissolved in water (1 mL). 4 Drops of ammonia (7 M in MeOH) were added, and the product was lyophilized to afford dicytodendrin B **2** (28 mg, 58% over both steps) as a yellow foam. ^{1}H NMR (600 MHz, CD_3OD): δ = 8.48 (s, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 9.0 Hz, 2 H), 7.18 (d, *J* = 7.8, 1.2 Hz, 1 H); 7.05 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 6.57 (dd, *J* = 7.8, 7.8 Hz, 1 H), 6.56 (d, *J* = 9.0 Hz, 2 H), 6.47 (d, *J* = 9.0 Hz, 2 H), 6.41 (d, *J* = 8.4 Hz, 2 H), 6.02 (dd, *J* = 8.4, 0.6 Hz, 1 H), 3.96 (t, *J* = 7.2 Hz, 2 H), 2.47 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (150 MHz, CD_3OD) δ = 192.0, 163.1, 158.7, 157.7, 156.8, 141.7, 138.8, 136.2, 134.3, 134.3, 134.0, 133.8, 132.0, 130.6, 129.3, 129.2, 127.1, 126.8, 125.8, 122.7, 118.9, 118.2, 117.2, 116.8, 116.1, 116.0, 115.6, 112.6, 48.4, 37.7; IR (film): $\tilde{\nu}$ = 3250, 1673, 1593, 1535, 1513, 1441, 1369, 1325, 1204, 1157, 1104, 1053, 1004, 921, 838, 798, 764, 724, 679 cm^{-1}. MS (ESI$^-$) *m/z*: 741 ([M–NH_4]$^-$); HRMS (ESI$^-$) *calcd*. for $C_{41}H_{29}N_2O_{10}S$ ([M–NH_4]$^-$): 741.1549; *found*: 741.1549.

Total Synthesis of Dictyodendrin E

Compound 41. A solution of 4-methoxybenzylmagnesium chloride (0.5 M in THF, 0.750 mmol, 1.5 mL) was added dropwise to a solution of 9-MeO-9-BBN (0.5 M in hexanes, 0.750 mmol, 1.5 mL) at −78 °C under argon. The cold bath was removed and the mixture was stirred at ambient temperature for 30 min. The resulting solution of borate **40** was diluted with DMF (5 mL) and freeze-thaw-degassed twice before bromide **27** (0.185 mmol, 133 mg) was added, followed by $Pd(OAc)_2$ (0.0185 mmol, 4.2 mg) and S-PHOS (0.0370 mmol, 15.2 mg). The resulting mixture was stirred at 110 °C (bath temperature) for 4.5 h until TLC indicated complete conversion of the substrate. The precipitated palladium black was filtered off through a pad of Celite, the filtrate was diluted with water (70 mL), and the product was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), and evaporated, and the residue was purified by flash chromatography (EtOAc/hexanes 1:6) to afford compound **41** (126 mg, 90%) as a white solid. mp = 225-226 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.51 (s, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 6.77 (d, *J* = 8.8 Hz, 1 H), 6.66 (dd, *J* = 8.8, 7.2 Hz, 1 H), 6.65 (d, *J* = 8.8

Hz, 2 H), 6.38 (d, *J* = 8.8 Hz, 2 H), 5.83 (d, *J* = 8.0 Hz, 1 H), 4.75 (hept, *J* = 6.0 Hz, 1 H), 3.91 (s, 3 H), 3.90 (s, 3 H), 3.81 (br s, 2 H), 3.73 (s, 3 H), 3.69 (s, 3 H) overlapping with 3.69 (m, 2 H), 3.62 (s, 3 H), 2.35 (m, 2 H), 1.43 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.4, 159.2, 143.6, 140.2, 136.6, 133.1, 132.6, 131.7, 130.7, 130.6, 129.6, 129.0, 128.4, 127.9, 124.9, 120.0, 118.7, 117.9, 116.5, 116.5, 114.9, 114.0, 113.7, 113.6, 113.5, 106.9, 70.8, 61.2, 55.5, 55.4, 55.3, 55.2, 46.6, 36.2, 30.3, 22.2; IR (film) $\tilde{\nu}$ = 3317, 2932, 2834, 1738, 1608, 1572, 1543, 1508, 1463, 1439, 1406, 1362, 1322, 1300, 1281, 1238, 1170, 1123, 1104, 1064, 1031, 1007, 970, 954, 836, 806, 792, 771, 754, 717 cm^{-1}; MS (EI): *m/z* (%): 762 (16), 761 (53), 760 (100 [M$^+$]), 745 (14), 639 (18), 596 (12), 581 (10), 543 (21), 135 (30), 121 (31); HRMS (ESI$^+$) calcd. for $C_{49}H_{48}N_2O_6$+Na ([M+Na]$^+$): 783.3405; *found*: 783.3400.

Compound 42. BBr_3 (1 M in CH_2Cl_2, 0.900 mL, 0.900 mmol) was added dropwise to a solution of compound **41** (68.5 mg, 0.0900 mmol) in CH_2Cl_2 (9 mL) at –78 °C under argon. The cold bath was removed and the mixture was allowed to reach ambient temperature. Upon completion of the reaction (30 min), the mixture was cooled to 0 °C, the reaction was quenched with 10% aq. $KHSO_4$ (6 mL) and vigorously stirred at ambient temperature for 30 min. The product was extracted with *tert*-butyl methyl ether (3 x 5 mL), the combined organic layers were washed with brine (2 mL), dried ($MgSO_4$), and evaporated to afford polyphenol **42** as an unstable blue foam which was not further purified. ^{1}H NMR (600 MHz, THF-d_8): δ = 7.37 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 6.79 (d, *J* = 8.5 Hz, 2 H), 6.55 (d, *J* = 8.6 Hz, 2 H), 6.50 (d, *J* = 7.5 Hz, 1 H), 6.47 (d, *J* = 8.4 Hz, 2 H), 6.42 (dd, *J* = 7.9, 7.7 Hz, 1 H), 6.34 (d, *J* = 8.4 Hz, 2 H), 5.94 (d, *J* = 7.4 Hz, 1 H), 3.74 (s, 2 H), 3.66 (t, *J* = 7.9 Hz, 2 H), 2.33 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR (150 MHz, THF-d_8): δ = 158.6, 157.7, 156.9, 156.8, 143.3, 137.8, 134.9, 133.9, 133.8, 131.7, 130.9, 130.4, 130.3, 130.3, 129.6, 129.6, 127.6, 127.3, 126.3, 118.6, 118.3, 117.7, 117.0, 116.3, 115.9, 115.9, 115.5, 115.5, 111.2, 108.6, 47.3, 37.2, 31.0; IR (film) $\tilde{\nu}$ = 3217, 2974, 1608, 1579, 1556, 1512, 1443, 1406, 1367, 1219, 1167, 1098, 1063, 1009, 832, 785, 721 cm^{-1}; HRMS (ESI$^+$) *calcd*. for $C_{41}H_{32}N_2O_6$+K ([M+K]$^+$): 687.1892; *found*: 687.1891.

Desulfated Dictyodendrin E (43). Freshly recrystallized DDQ (20.4 mg, 0.090 mmol) was added to a solution of phenol **42** (58.4 mg, 0.090 mmol) in THF (1.8 mL) and the resulting mixture was stirred for 30 min. For work up, the solvent was evaporated and the residue was purified by flash chromatography (EtOAc/hexanes, 3:2 → 4:1) to afford compound **43** (48.2 mg, 83% over 2 steps) as a red solid. mp = 253-255 °C; ^{1}H NMR (400 MHz, THF-d_8): δ = 11.17 (s, 1 H), 8.61 (s, 1 H), 8.59 (s, 1 H), 8.45 (s, 1 H), 7.84 (s, 1 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.8 Hz, 2 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 6.47 (d, *J* = 4.4 Hz, 2 H), 6.42 (d, *J* = 8.4 Hz, 2 H), 6.36 (d, *J* = 8.4 Hz, 2 H), 5.97 (s, 1 H), 5.54 (dd, *J* = 4.8, 4.4 Hz, 1 H), 3.46 (t, *J* = 7.3 Hz, 2 H), 2.29 (t, *J* = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, THF-d_8): δ = 176.5, 159.4, 158.9, 157.8, 157.5, 157.0, 149.0, 145.1, 142.5, 135.0, 133.2, 133.2, 133.1, 130.5, 129.7, 129.6, 129.0,

127.8, 126.7, 126.5, 126.2, 121.4, 118.3, 116.4, 116.0, 115.8, 115.6, 115.5, 114.2, 113.1, 109.1, 49.7, 33.6; IR (film) $\tilde{\nu}$ = 3218, 2956, 2921, 2223, 1697, 1605, 1560, 1508, 1442, 1394, 1370, 1342, 1259, 1211, 1166, 1137, 1077, 1034, 894, 804, 733 cm^{-1}; HRMS (ESI^+) *calcd*. for $C_{41}H_{30}N_2O_6$+K ($[M+K]^+$): 685.1736; *found*: 685.1732.

Compound 45. A solution of BCl_3 (1 M in heptanes, 0.580 mmol, 0.580 mL) was added dropwise to a solution of isopropyl ether **41** (0.145 mmol, 110 mg) in CH_2Cl_2 (7.3 mL) at –20 °C under argon. The mixture was allowed to warm to 0 °C over 1 h before 10% aq. $KHSO_4$ (3 mL) was added. The resulting mixture was vigorously stirred at ambient temperature for 15 min, the aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic phases were washed with brine (1 mL), dried ($MgSO_4$) and evaporated. The residue was purified by a quick filtration through a short silica pad (eluent: EtOAc) to give the rather unstable phenol **44** which was used directly in the next step.

2,2,2-Trichloroethyl chlorosulfate (0.290 mmol, 71.3 mg) was added to a solution of phenol **44** and DABCO (1.45 mmol, 170 mg) in THF (1.5 mL) and the mixture was stirred for 1 h. For work up, water (5 mL) was added, the aqueous layer was extracted with EtOAc (3 x 3 mL), and the combined organic phases were washed with brine (1 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (EtOAc/hexanes 1:4) to afford compound **45** (109 mg, 83% over two steps) as a yellow oil which rapidly turns red upon exposure to air. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.75 (s, 1 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.31 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.07 (d, *J* = 8.8 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.80 (dd, *J* = 8.0, 8.0 Hz, 1 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.39 (d, *J* = 8.8 Hz, 2 H), 6.24 (d, *J* = 8.4 Hz, 1 H), 4.84 (s, 2 H), 3.92 (s, 3 H), 3.90 (s, 3 H), 3.83 (s, 2 H), 3.74 (s, 3 H) superimposed upon 3.74-3.72 (m, 2 H), 3.72 (s, 3 H), 3.60 (s, 3 H), 2.36 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.6, 159.4, 158.3, 139.9, 137.3, 134.7, 133.1, 132.5, 131.4, 130.8, 130.4, 130.2, 129.9, 129.7, 129.6, 128.9, 127.7, 127.3, 123.8, 119.9, 119.4, 118.6, 116.5, 115.7, 114.2, 114.0, 113.8, 113.7, 113.5, 95.7, 92.5, 80.9, 61.3, 55.5, 55.5, 55.3, 55.2, 46.7, 36.2, 30.3; IR (film) $\tilde{\nu}$ = 3411, 2932, 2834, 1609, 1571, 1509, 1462, 1441, 1401, 1364, 1302, 1284, 1241, 1193, 1172, 1159, 1104, 1030, 1007, 993, 959, 886, 830, 809, 793, 775, 723 cm^{-1}; HRMS (ESI^+) *calcd*. for $C_{48}H_{43}N_2O_6SCl_3$+Na ($[M+Na]^+$): 951.1647; *found*: 951.1652.

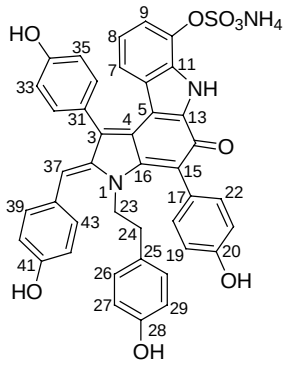
Compound 46. BCl_3 (1 M in heptanes, 1.20 mmol, 1.20 mL) was added dropwise to a stirred solution of compound **45** (0.120 mmol, 109 mg) and *n*-Bu_4NI (1.20 mmol, 443 mg) in CH_2Cl_2 (12 mL) at 0 °C. After the mixture had been stirred for 30 min, 10% aq. $KHSO_4$ (5 mL) was added to quench the reaction, and the resulting solution was vigorously stirred at ambient temperature for 30 min. The aqueous layer was extracted with EtOAc (3 x 15 mL), and the combined organic phases were washed with brine (2 mL), dried ($MgSO_4$) and evaporated. The residue was adsorbed on Celite and purified by reverse-phase chromatography (Merck LiChroprep RP-18). The tetrabutylammonium salts were eluted first (MeOH/H_2O, 1:1),

followed by the desired product **46** (eluent: MeOH), which was obtained as a red solid (88.2 mg, 85%). mp = 139-140 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 7.40 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.92 (d, *J* = 8.2 Hz, 2 H), 6.90 (d, *J* = 7.4 Hz, 2 H), 6.69 (t, *J* = 8.1 Hz, 1 H), 6.66 (d, *J* = 8.3 Hz, 2 H), 6.53 (d, *J* = 8.5 Hz, 2 H), 6.33 (d, *J* = 8.5 Hz, 2 H), 6.30 (d, *J* = 8.1 Hz, 1 H), 5.08 (s, 2 H), 3.75 (br s, 2 H), 3.68 (m, 2 H), 2.30 (m, 2 H); ^{13}C NMR (100 MHz, CD_3OD): δ = 159.1, 158.4, 157.2, 157.1, 138.1, 137.0, 136.7, 134.8, 134.6, 132.7, 132.5, 131.5, 131.2, 131.1, 130.8, 130.6, 129.1, 129.1, 127.9, 125.3, 118.9, 118.9, 118.1, 117.0, 116.8, 116.5, 116.3, 115.6, 114.4, 94.6, 82.5, 48.1, 37.8, 31.2; IR (film) $\tilde{\nu}$ = 3318, 2926, 1698, 1610, 1557, 1511, 1443, 1040, 1373, 1322, 1192, 1157, 1096, 1044, 992, 894, 829, 785, 723 cm^{-1}; HRMS (ESI^{+}) *calcd*. for $C_{43}H_{33}N_2O_9Cl_3S$+Na ([M+Na]$^{+}$): 881.0865; *found*: 881.0861.

Dictyodendrin E (5). A suspension of sulfate **46** (64.5 mg, 0.075 mmol), ammonium formate (28.4 mg, 0.45 mmol) and zinc powder (9.8 mg, 0.15 mmol) in MeOH (7.5 mL) was vigorously stirred for 1 h. The suspension was then filtered through a pad of Celite and the filtrate was evaporated.

To a solution of the residue in THF (7.5 mL) was added freshly recrystallized DDQ (17.0 mg, 0.075 mmol) and the resulting mixture was stirred at ambient temperature for 15 min before being evaporated. The crude product was adsorbed on silica and purified by flash chromatography: the side-products were eluted first with EtOAc before compound **5** was eluted with EtOAc/MeOH (4:1). The fractions containing the product were evaporated, the residue was taken up in MeOH, excess aq. NH_4OH was added, and all volatile materials were then evaporated to give dictyodendrin E **5** in form of its ammonium salt (42.1 mg, 75% over steps). ^{1}H NMR (400 MHz, CD_3OD): δ = 8.48 (s, 1 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 7.18 (d, *J* = 8.2 Hz, 2 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 7.12 (d, *J* = 7.7 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 4 H), 6.78 (d, *J* = 7.4 Hz, 2 H), 6.62 (dd, *J* = 8.0, 7.9 Hz, 1 H), 6.39 (br s, 4 H), 5.99 (s, 1 H), 5.75 (d, *J* = 8.2 Hz, 1 H), 3.47 (m, 2 H), 2.28 (m, 2 H); ^{13}C NMR (150 MHz, CD_3OD): δ = 170.0, 159.7, 159.5, 158.0, 157.9, 156.8, 148.9, 143.9, 140.0, 135.5, 134.3, 133.8, 133.5, 133.3, 132.8, 130.9, 130.1, 127.8, 127.2, 127.0, 126.3, 121.6, 121.3, 120.8, 117.6, 116.7, 116.6, 116.4, 116.3, 115.7, 114.4, 49.7, 34.2; IR (film) $\tilde{\nu}$ = 3184, 2209, 1563, 1509, 1441, 1387, 1370, 1339, 1219, 1166, 1139, 1110, 1078, 1053, 1021, 883, 809, 791, 778, 738 cm^{-1}; HRMS (ESI^{-}) *calcd*. for $C_{41}H_{29}N_2O_9S$ ([M–NH_4]$^{-}$): 725.1599; *found*: 725.1598.

Table S-3. Tabular survey of the ^{13}C NMR data (150 MHz, CD_3OH) recorded for Dictyodendrin E (**5**); Unless indicated otherwise, the assignments are unambiguous; arbitrary numbering scheme as indicated in the insert.



Position	Natural Product	Synthetic Product
2	158.9[a]	158.0
3	143.8	143.9
4	*n.d.*	134.3[b]
5	116.0	116.3
6	126.8	127.0
7	121.5	121.6
8	121.2	121.3
9	117.6	117.6
10	140.0	140.0
11	133.0	132.8
13	135.6	135.5
14	*n.d.*	170.0[b]
15	114.3	114.4
16	148.8	148.9
17	126.9	127.2
18 (22)	133.3	133.5
19 (21)	116.6	116.7
20	157.8	157.9
23	49.6	49.7
24	34.2	34.2
25	130.0	130.1
26 (30)	130.9	130.9
27 (29)	115.8	115.7
28	156.9	156.8
31	126.1	126.3
32 (36)	133.2	133.3
33 (35)	116.4	116.4
34	159.6	159.5

37	120.7	120.8
38	127.8	127.8
39 (43)	133.8	133.8
40 (42)	116.9	116.6
41	159.8[a]	159.7

[a] interchangeable. [b] tentative assignment. *n.d.:* Not detected.