



Supporting Information

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Supporting Information

Solid-Phase Synthesis of Epigallocatechin Gallate Derivatives .

Hiroshi Tanaka, Haruko Miyoshi, Yu-Cheng Chuang, Yoshio Ando, Takashi Takahashi*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-S-35, Oookayama, Meguro, Tokyo 152-8552, Japan.

General Techniques

NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for ^1H , 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0 ppm) for internal tetramethylsilane for solutions in CDCl_3 . ^1H NMR spectrum data are reported as follows: CDCl_3 (7.26 ppm) or CD_3OD (3.30 ppm), acetone- d_6 (2.00 ppm), DMSO- d_6 (2.50 ppm). ^{13}C NMR spectrum data are reported as follows: CDCl_3 (77.1 ppm) or acetone- d_6 (30.3 ppm) as internal standard for D_2O . Multiplicities are reported by using the following abbreviations: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, br; broad, J ; coupling constants in Hertz.

IR spectra was recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important peaks are reported as the IR data given in cm^{-1} .

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by 10% ethanolic phosphomolybdic acid, *p*-anisaldehyde solution.

Merck silica gel was used for column chromatography.

Gel permeation chromatography (GPC) for qualitative analysis were performed on Japan Analytical Industry Model LC908 (recycling preparative HPLC), on a Japan Analytical Industry Model RI-5 refractive index detector and on a Japan Analytical Industry Model 310 ultra violet detector with a polystyrene gel column (JAIGEL-1H, 20mm x 600 mm), using chloroform as solvent (3.5 mL / min).

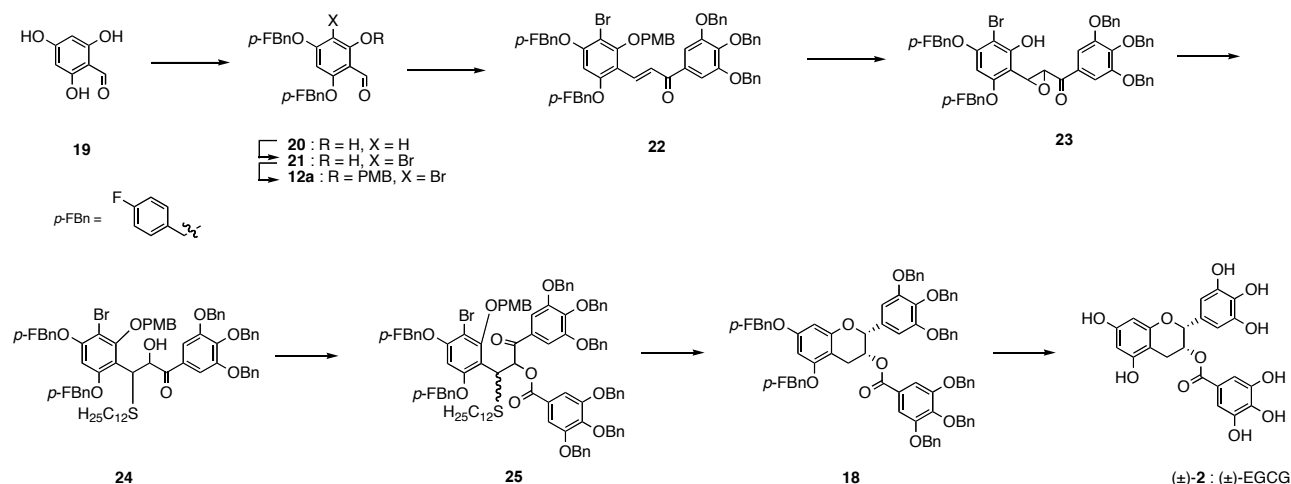
ESI-TOF Mass spectra were measured with Waters LCT PremierTM XE.

Dry dichloromethane was distilled from P_2O_5 . Dry triethylamine and dry acetonitrile were distilled from CaH_2 .

LC/MS were obtained on Hewlett-Packard Series 1100 (GL Science Inc. Inertsil ODS-3, 3 μm , 4.6 x 75 mm with a linear gradient of 10 % acetonitrile containing 0.1% formic acid/water containing 0.1% formic acid to 80% acetonitrile containing 0.1% formic acid/water containing 0.1% formic acid over 3 min, to 100% acetonitrile containing 0.1% formic acid further 10 min at 10 mL min⁻¹ flow rate).

Experimental Section

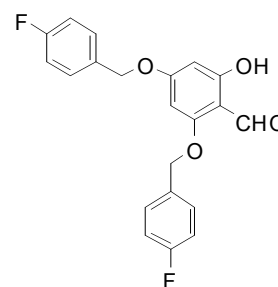
Solution-Phase Synthesis of Epigallocatechin-3-gallate (2)



2,4-Bis(4-fluorobenzoyloxy)-6-hydroxybenzaldehyde (20)

To a suspension of 2,4,6-trihydroxybenzaldehyde (**19**) (5.00 g, 26.3 mmol, 1.00 eq.) in DMF (55.0 mL) was added K_2CO_3 (8.36 g, 60.5 mmol, 2.30 eq.) at 0 °C under argon. After the reaction mixture was stirred at the same temperature for 5 min, a solution of 4-fluorobenzyl bromide (6.55 mL, 52.6 mmol, 2.00 eq.) in DMF (15.0 mL) was added dropwise to the reaction mixture. After being stirred at the room temperature for 16 h, the reaction mixture was poured into the mixture of 1 M aqueous HCl and ethyl acetate at 0 °C. The aqueous layer was extracted with two portions of ethyl acetate. The combined organic layers were washed with three portions of H_2O and brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with chloroform), and recrystallized from CH_2Cl_2 -hexane to afford benzaldehyde **20** (2.86 g, 7.65 mmol, 29% yield) as a white solid.

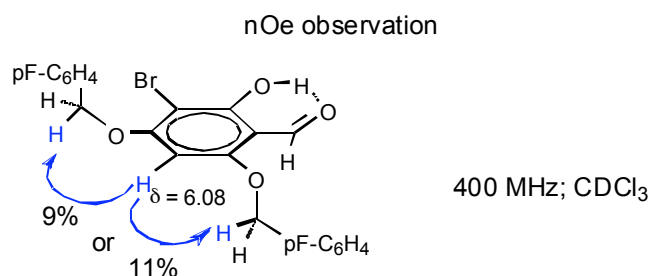
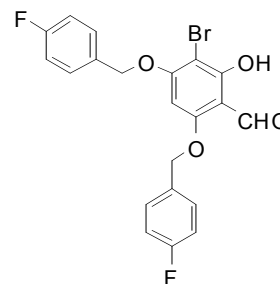
TLC R_f 0.49 (hexane/ethyl acetate = 2/1); ^1H NMR (400 MHz, CDCl_3) δ 12.50 (s, 1H), 10.14 (s, 1H), 7.38 (dd, J = 8.2 Hz, $J_{\text{H,F}}$ = 5.3 Hz, 2H), 7.37 (dd, J = 8.2 Hz, $J_{\text{H,F}}$ = 5.3 Hz, 2H), 7.09 (dd, J = 8.2 Hz, $J_{\text{H,F}}$ = 8.7 Hz, 4H), 6.10 (d, J = 1.9 Hz, 1H), 6.04 (d, J = 1.9 Hz, 1H), 5.04 (s, 2H), 5.03 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 166.9, 166.4, 162.8x2 ($J_{\text{C,F}}$ = 247 Hz), 162.5, 131.5 ($J_{\text{C,F}}$ = 3.0 Hz), 131.4 ($J_{\text{C,F}}$ = 3.0 Hz), 129.6 ($J_{\text{C,F}}$ = 8.4 Hz), 129.4 ($J_{\text{C,F}}$ = 8.4 Hz), 115.8 ($J_{\text{C,F}}$ = 21.3 Hz), 106.4, 94.2, 92.4, 70.0, 69.8; FT-IR (solid) 3037, 2873, 1624, 1575, 1510, 1291, 1153, 828, 795, 585, 504 cm^{-1} ; Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{F}_2\text{O}_4$: C, 68.11; H, 4.35. Found: C, 67.80; H, 4.47.



4,6-Bis(4-fluorobenzyloxy)-3-bromo-2-hydroxybenzaldehyde (**12a**)

To a solution of the benzaldehyde **20** (1.51 g, 4.09 mmol, 1.00 eq.) in CH_2Cl_2 (10.0 mL) was added dropwise a solution of bromine (209 μL , 4.09 mmol, 1.00 eq.) in CH_2Cl_2 at 0 °C under argon. After being stirred at the same temperature for 20 min, the reaction mixture was poured into the mixture of 10 wt% aqueous $\text{Na}_2\text{S}_2\text{O}_3$, saturated aqueous NaHCO_3 and ethyl acetate at 0 °C. The aqueous layer was extracted with two portions of ethyl acetate. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was recrystallized from CH_2Cl_2 -hexane to afford bromide **12a** (1.51 g, 3.37 mmol, 82% yield) as a pale yellow solid. Structure determination of the bromide **12a** was achieved by analysis of ^1H nOe spectra.

TLC R_f 0.41 (hexane/ethyl acetate = 2/1); ^1H NMR (400 MHz, CDCl_3) δ 12.94 (s, 1H), 10.12 (s, 1H), 7.40 (dd, $J = 8.2$ Hz, $J_{\text{H,F}} = 5.3$ Hz, 2H), 7.35 (dd, $J = 8.2$ Hz, $J_{\text{H,F}} = 5.3$ Hz, 2H), 7.09 (dd, $J = 8.2$ Hz, $J_{\text{H,F}} = 8.7$ Hz, 4H), 6.08 (s, 1H), 5.16 (s, 2H), 5.07 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.6, 164.0, 162.9 ($J_{\text{C,F}} = 247$ Hz), 162.7 ($J_{\text{C,F}} = 247$ Hz), 162.6, 162.1, 161.6, 131.1 ($J_{\text{C,F}} = 3.0$ Hz), 131.0 ($J_{\text{C,F}} = 3.0$ Hz), 129.4 ($J_{\text{C,F}} = 7.6$ Hz), 128.8 ($J_{\text{C,F}} = 8.4$ Hz), 116.0 ($J_{\text{C,F}} = 21.3$ Hz), 115.9 ($J_{\text{C,F}} = 22.1$ Hz), 106.8, 91.8, 89.7, 70.5, 70.3; FT-IR (solid) 3048, 2924, 1646, 1604, 1515, 1301, 1240, 1199, 1118, 972, 787, 716 cm^{-1} ; Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{BrF}_2\text{O}_4$: C, 56.14; H, 3.37. Found: C, 56.26; H, 3.37.



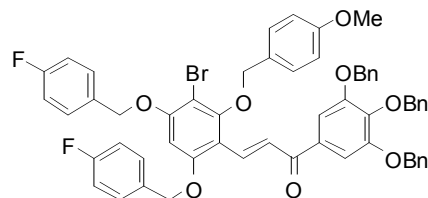
3-[4,6-Bis(4-fluorobenzyloxy)-3-bromo-2-(4-methoxybenzyloxy)phenyl]-1-[3,4,5-tris(benzyloxy)phenyl]prop-2-en-1-one (**22**)

To a suspension of benzaldehyde **12a** (894 mg, 1.99 mmol, 1.00 eq.) and Cs_2CO_3 (1.30 g, 3.98 mmol, 2.00 eq.) in DMF (10.0 mL) was added 4-methoxybenzyl chloride (565 μL , 4.15 mmol, 2.08 eq.) and sodium iodide (120 mg, 796 μmol , 0.40 eq.) at room temperature under argon. After being stirred at the same temperature for 11 h, the reaction mixture was poured into the mixture of H_2O and ethyl acetate. The aqueous layer was extracted with two portions of ethyl acetate. The combined organic layers were washed with two portions of H_2O and brine, dried over MgSO_4 , and concentrated *in vacuo*. The crude mixture was used for the next reaction without further purification.

To a solution of the above residue in THF (5.00 mL) was added 3',4',5'-tris(benzyloxy)acetophenone (**11a**) (829 mg, 1.89 mmol, 0.95 eq.) and sodium methoxide (322 mg, 5.97 mmol, 3.00 eq.) at room temperature. After being stirred at the same temperature for 3 h, the reaction mixture was poured into the mixture of H_2O and ethyl

acetate at 0 °C. The aqueous layer was extracted with two portions of ethyl acetate. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was recrystallized from CH₂Cl₂-hexane to afford chalcone **22** (1.62 g, 1.64 mmol, 82% yield in 2 steps) as a pale yellow solid.

TLC R_f 0.57 (toluene/acetone = 20/1); ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 15.9 Hz, 1H), 7.95 (d, *J* = 15.9 Hz, 1H), 7.31-7.45 (m, 21H), 7.22 (s, 2H), 7.10 (dd, *J* = 8.2 Hz, 8.7 Hz, 2H), 7.04 (dd, *J* = 8.2 Hz, 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.42 (s, 1H), 5.11 (s, 4H), 5.09 (s, 2H), 4.95 (s, 4H), 4.84 (s, 2H), 3.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.7, 162.7 (*J*_{C,F} = 248 Hz), 160.0, 158.9, 157.6, 157.5, 152.7, 142.5, 137.6, 136.7, 135.3, 133.8, 131.6x2 (*J*_{C,F} = 3.0 Hz), 130.8, 129.1 (*J*_{C,F} = 7.6 Hz), 128.9 (*J*_{C,F} = 8.4 Hz), 128.5, 128.2x2, 128.0x2, 127.8, 123.9, 115.9 (*J*_{C,F} = 21.3 Hz), 115.8 (*J*_{C,F} = 21.3 Hz), 114.0, 113.8, 108.3, 101.1, 96.0, 75.3, 75.2, 71.2, 70.6x2, 55.2; FT-IR (solid) 3031, 2936, 1643, 1586, 1251, 1184, 1159, 1093, 1031, 885, 799, 733, 698 cm⁻¹; Anal. Calcd for C₅₈H₄₇BrF₂O₈: C, 70.37; H, 4.79. Found: C, 70.22; H, 4.81.

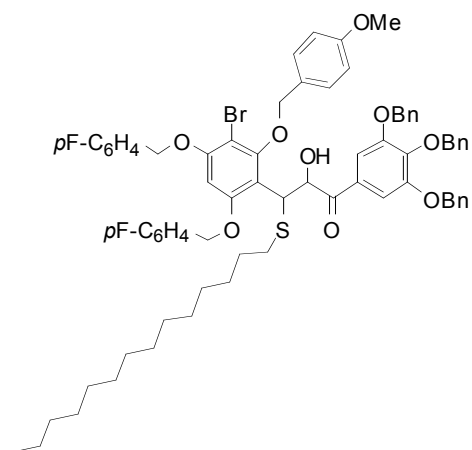


3-[4,6-Bis(4-fluorobenzyl)oxy]-3-bromo-2-(4-methoxybenzyl)oxyphenyl]-3-dodecylsulfanyl-2-hydroxy-1-[3,4,5-tris(benzyloxy)phenyl]propan-1-one (**24**)

To a solution of chalcone **22** (200 mg, 202 μmol, 1.00 eq.) in CH₂Cl₂ (3.00 mL) was added 30 wt% aqueous H₂O₂ (2.29 mL, 20.2 mmol, 100 eq.), 3 M aqueous KOH (1.00 mL) and Bu₄N · HSO₄ (137 mg, 404 μL, 2.00 eq.) at room temperature. After being stirred at the same temperature for 26 h, the reaction mixture was poured into saturated aqueous Na₂SO₃ and ethyl acetate at 0 °C. The aqueous layer was extracted with two portions of ethyl acetate. The combined organic layers were washed with saturated aqueous Na₂SO₃, brine, dried over Na₂SO₄, and concentrated *in vacuo*. The crude mixture was used for the next reaction without further purification.

To a solution of the crude in acetonitrile (2.02 mL) and CH₂Cl₂ (750 μL) was added 1-dodecanethiol (73.0 μL, 303 μmol, 1.50 eq.) and Zn(OTf)₂ (14.7 mg, 40.4 μmol, 0.20 eq.) at room temperature under argon. After being stirred at the same temperature for 15 min, the mixture was quenched by addition of triethylamine and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with 20% ethyl acetate in hexane) to afford a diastereo mixture of α-hydroxyketones **24** (210 mg, 174 μmol, 86% in 2 steps) as a white solid.

TLC R_f 0.45 (hexane/ethyl acetate = 3/1); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.02-8.31 (m, 45H), 6.96 (d, *J* = 8.2 Hz, 1.3H), 6.85 (d, *J* = 8.2 Hz, 0.7H), 6.75 (s, 0.32H), 6.66 (s, 0.09H), 6.62 (s, 0.59H), 6.25 (d, *J* = 7.7 Hz, 0.64H), 6.16 (d, *J* = 6.8 Hz, 0.05H), 6.09 (d, *J* = 7.3 Hz, 0.31H), 5.71 (br t, *J* = 9.7, 8.2 Hz, 0.38H), 5.61 (br t, *J* = 8.7 Hz, 0.62H), 4.77-5.29 (m, 12.4H), 4.57 (d, *J* = 9.7 Hz, 0.60H), 3.75 (s,

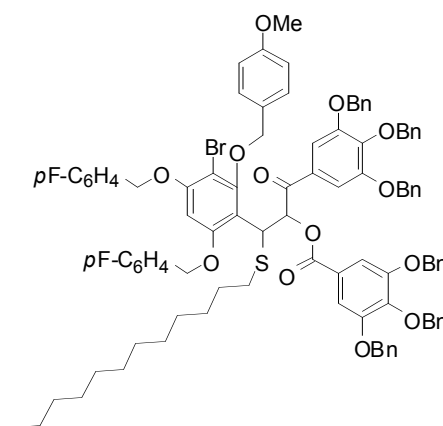


2.1H), 3.60 (s, 0.9H), 2.60-2.71 (m, 2H), 0.83-1.49 (m, 23H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 198.9, 198.7, 161.7 ($J_{\text{C,F}} = 244$ Hz), 161.6 ($J_{\text{C,F}} = 244$ Hz), 159.1, 156.7, 155.6, 155.2, 155.1, 154.8, 153.4, 151.8x2, 141.2, 141.0, 137.3, 136.5, 132.6 ($J_{\text{C,F}} = 2.3$ Hz), 132.5 ($J_{\text{C,F}} = 2.3$ Hz), 131.7, 131.5, 130.0, 129.6 ($J_{\text{C,F}} = 8.4$ Hz), 129.4 ($J_{\text{C,F}} = 7.6$ Hz), 128.8, 128.3, 128.1, 128.0x2, 127.9, 127.7, 127.6, 117.1, 115.2 ($J_{\text{C,F}} = 21.3$ Hz), 113.7, 107.1, 106.7, 99.1, 74.4, 74.3, 74.0, 73.5, 72.6, 70.3, 70.1, 69.9, 69.8x2, 69.4, 55.0, 54.8, 44.6, 40.4, 33.6, 33.4, 31.3, 29.7, 29.6, 29.0, 28.7, 28.6, 28.5, 28.4, 22.1; FT-IR (solid) 3471, 2924, 2855, 1674, 1608, 1589, 1514, 1103, 914, 824, 733, 697 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{70}\text{H}_{74}\text{F}_2\text{BrO}_9\text{S}$ $[\text{M}+\text{H}]^+$ 1207.4205, found 1207.4204.

3-[4,6-Bis(4-fluorobenzyloxy)-3-bromo-2-(4-methoxybenzyloxy)phenyl]-3-dodecylsulfanyl-1-[3,4,5-tris(benzyloxy)phenyl]propan-1-one-2-yl 3,4,5-tris(benzyloxy)benzoate (25)

To a solution of hydroxyketone **24** (195 mg, 162 μmol , 1.00 eq.) in pyridine (800 μL) was added 3,4,5-tris(benzyloxy)benzoic acid (**7a**) (92.5 mg, 210 μmol , 1.30 eq.), EDCI \cdot HCl (55.3 mg, 288 μmol , 1.78 eq.) and DMAP (3.90 mg, 32.4 μmol , 0.20 eq.) at room temperature under argon. After being stirred at the same temperature for 20 h, the reaction mixture was poured into 1 M aqueous HCl and ethyl acetate at 0 $^\circ\text{C}$. The aqueous layer was extracted with two portions of ethyl acetate. The combined organic layers were washed with 1 M aqueous HCl, saturated aqueous NaHCO_3 , brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with toluene) to afford a diastereo mixture of acyloxyketones **25** (219 mg, 134 μmol , 83% yield) as a white solid.

TLC R_f 0.51 (hexane/ethyl acetate = 2/1); ^1H NMR (400 MHz, CDCl_3) δ 6.70-7.65 (m, 46H), 6.40 (s, 0.05H), 6.13 (s, 0.36H), 5.94 (s, 0.59H), 5.39 (d, $J = 9.2$ Hz, 0.31H), 4.65-5.17 (m, 19.69H), 3.79 (s, 0.15H), 3.70 (s, 1.86H), 3.65 (s, 0.99H), 2.61-2.88 (m, 2H), 0.85-1.66 (m, 23H); FT-IR (solid) 3020, 2928, 1713, 1691, 1588, 1514, 1216, 1107, 927, 757, 669 cm^{-1} .

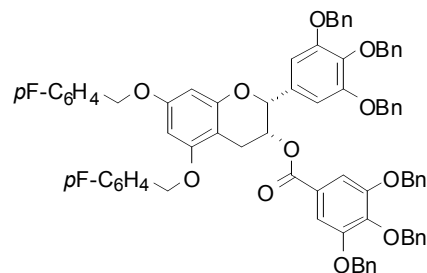


cis-5,7-Bis(4-fluorobenzyloxy)-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (18)

To a solution of acyloxyketone **25** (100 mg, 61.5 μmol , 1.00 eq.) in CH_2Cl_2 (1.50 mL) was added trifluoroacetic acid (300 μL) at -10 $^\circ\text{C}$ under argon. After being stirred at -10 $^\circ\text{C}$ for 2 h, the reaction mixture was treated with triethylsilane (200 μL). After being stirred at the same temperature for further 1 h, the reaction mixture was quenched by addition of triethylamine, diluted with toluene, and concentrated *in vacuo*. The residue was purified by gel permeation chromatography (GPC) to afford chroman **18** (64.7 mg, 53.2 μmol , 87% yield) as a white solid.

TLC R_f 0.43 (hexane/ethyl acetate = 2/1); ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.39 (m, 36H), 7.00-7.07 (m, 4H),

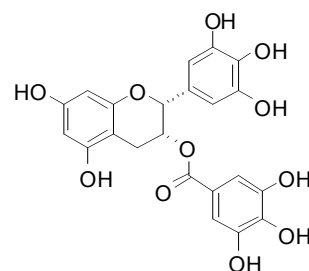
6.73 (s, 2H), 6.38 (d, $J = 1.9$ Hz, 1H), 6.30 (d, $J = 1.9$ Hz, 1H), 5.65 (br s, 1H), 5.04 (s, 1H), 4.66-5.01 (m, 16H), 3.10 (dd, $J_{\text{gem}} = 17.9$ Hz, $J = 4.4$ Hz, 1H), 3.03 (dd, $J_{\text{gem}} = 17.9$ Hz, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 162.6x2 ($J_{\text{C,F}} = 247$ Hz), 158.8, 158.0, 155.8, 153.0, 152.5, 142.9, 138.6, 137.8, 137.5, 137.0, 136.5, 133.2, 132.6 ($J_{\text{C,F}} = 3.0$ Hz), 129.4 ($J_{\text{C,F}} = 8.4$ Hz), 129.1 ($J_{\text{C,F}} = 8.4$ Hz), 128.6x2, 128.5, 128.4, 128.3, 128.2x2, 128.0, 127.9, 127.8, 127.6x2, 125.0, 115.6 ($J_{\text{C,F}} = 22.1$ Hz), 109.3, 106.9, 101.2, 94.8, 94.1, 78.1, 75.2, 75.1, 71.3, 71.2, 69.6, 69.5, 68.3, 26.3; FT-IR (solid) 3033, 2870, 1717, 1620, 1594, 1512, 1455, 1369, 1220, 1118, 909, 819, 734, 696, 502 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{78}\text{H}_{64}\text{F}_2\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 1215.4495, found 1215.4495.; Anal. Calcd for $\text{C}_{78}\text{H}_{64}\text{F}_2\text{O}_{11}$: C, 77.08; H, 5.31. Found: C, 76.76; H, 5.41.



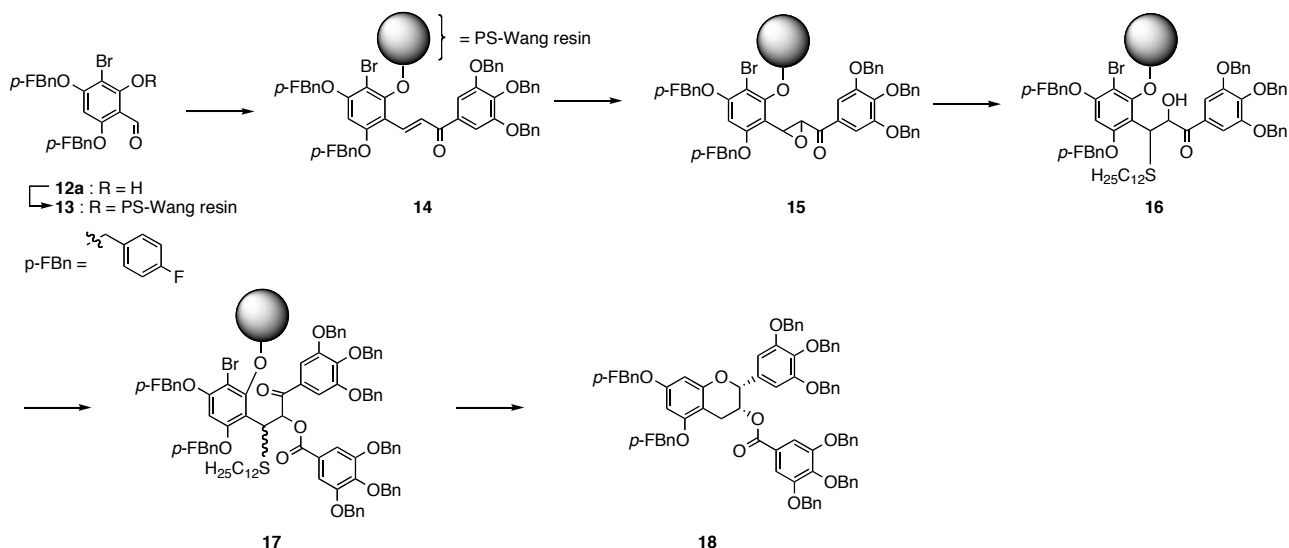
(±)-Epigallocatechin-3-gallate (**2**)

To a stirred solution of chroman **52** (9.10 mg, 7.45 μmol , 1.00 eq.) in THF/methanol (1:1, 2.00 mL) was added 20 wt% $\text{Pd}(\text{OH})_2$ (19.1 mg) and formic acid (5.00 μL) at room temperature. The reaction mixture was hydrogenolyzed for 29 h under hydrogen gas atmosphere. The reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with 10% methanol in CH_2Cl_2) to afford epigallocatechin-3-gallate (**1**) (2.80 mg, 6.11 μmol , 82% yield) as a white solid.

^1H NMR (400 MHz, acetone- $d_6/\text{D}_2\text{O} = 1/1$); δ 6.86 (s, 2H), 6.51 (s, 2H), 5.89 (s, 2H), 5.27 (br s, 1H), 4.89 (s, 1H), 2.87 (dd, $J_{\text{gem}} = 17.4$ Hz, $J = 4.4$ Hz, 1H), 2.76 (br d, $J_{\text{gem}} = 17.4$ Hz, 1H); ^{13}C NMR (100 MHz, acetone- $d_6/\text{D}_2\text{O} = 1/1$) δ 167.3, 157.0, 156.9, 156.8, 146.0, 145.7, 139.3, 133.0, 130.6, 121.0, 110.2, 106.8, 99.0, 96.5, 95.8, 77.9, 70.3, 26.4; FT-IR (solid) 3508, 1687, 1608, 1451, 1227, 1029, 730, 549 cm^{-1} .

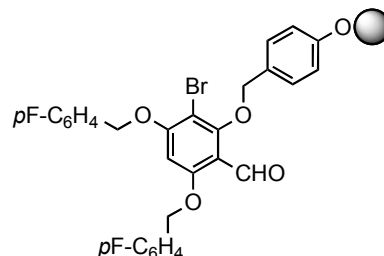


Solid-Phase Synthesis



Polymer-supported 4,6-bis(4-fluorobenzoyloxy)-3-bromo-2-hydroxybenzaldehyde (**13**)

PS-Wang-Br resin[®] (Novabiochem, 1.6 mmol/g loading, 140 mg) was placed in a syringe-shaped vessel. To this reaction vessel was added a suspension of hydroxybenzaldehyde **12a** (180 mg, 400 μmol) in DMF (2.00 mL), Cs_2CO_3 (130 mg, 400 μmol) and sodium iodide (15.0 mg, 120 μmol) at room temperature. After being shaken at the same temperature for 24 h, the solvent was removed and the resin was rinsed with DMF (10 min). The remained resin was washed consecutively with DMF/ H_2O (2:1, 10 min x 3), DMF (10 min x 3), methanol (10 min x 3), CH_2Cl_2 (10 min x 3), and dried under reduced pressure to afford polymer-supported benzaldehyde **13** (202.5 mg).



FT-IR (solid) 3025, 2909, 1685, 1615, 1104, 923, 851, 701, 576 cm^{-1} .

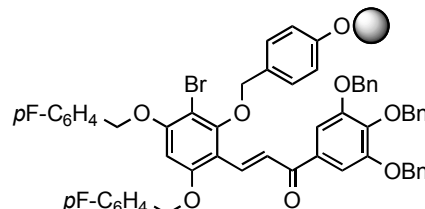
Procedure for Cleavage from PS resins

A part of the polymer-supported benzaldehyde **13** (84.8 mg) was placed in a syringe-shaped vessel. To this reaction vessel was added a solution of trifluoroacetic acid (50.0 μL) in CH_2Cl_2 (1.95 mL) at room temperature. After being shaken at the same temperature for 1 h, the reaction vessel was filtered and washed with CH_2Cl_2 (5 min x 3). The filtrate was concentrated *in vacuo*. The residue was purified by short-pad column chromatography (elution with chloroform) to afford benzaldehyde **12a** (20.3 mg, 45.2 μmol , 48% yield based on the resin).

Polymer-supported 3-[4,6-bis(4-fluorobenzyloxy)-3-bromo-2-(4-methoxybenzyloxy)phenyl]-1-[3,4,5-tris(benzyloxy)phenyl]prop-2-en-1-one (14)

Polymer-supported benzaldehyde **13** (118 mg, 62.5 μmol) was placed in a syringe-shaped vessel. To this reaction vessel was added 3',4',5'-tris(benzyloxy)acetophenone (**11a**) (329 mg, 750 μmol) in THF (1.20 mL) at room temperature. After being shaken for 15 min, the reaction mixture was added 0.5 M sodium methoxide in methanol (300 μL). After being shaken for 24 h, the solvent was removed and rinsed with THF (10 min). The remained resin was washed consecutively with THF (10 min x 3), methanol (10 min x 3), CH_2Cl_2 (10 min x 3), and dried under reduced pressure to afford polymer-supported chalcone **14**.

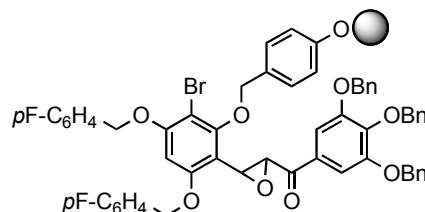
FT-IR (solid) 3028, 2925, 1655, 1583, 1174, 1104, 828, 740 cm^{-1} .



Polymer-supported 3-[4,6-bis(4-fluorobenzyloxy)-3-bromo-2-(4-methoxybenzyloxy)phenyl]-2,3-epoxy-1-[3,4,5-tris(benzyloxy)phenyl]propan-1-one (15)

The polymer-supported chalcone **14** was placed in a syringe-shaped vessel. To this reaction vessel was added 5.5 M *t*-butyl hydrogen peroxide in decane (380 μL , 2.09 mmol), CH_2Cl_2 (1.00 mL) and 2.5 M KOH in methanol (120 μL) at room temperature. After being shaken for 72 h, the solvent was removed and the resin was rinsed with CH_2Cl_2 (10 min). The remained resin was washed consecutively with methanol (10 min x 4), CH_2Cl_2 (10 min x 4), and dried under reduced pressure to afford the polymer-supported epoxide **15**.

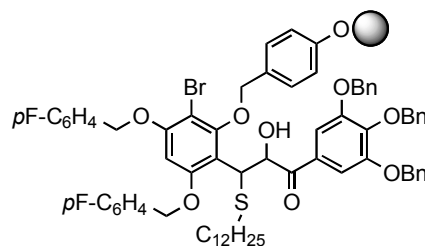
FT-IR (solid) 3464, 3027, 2921, 1676, 1610, 1158, 1078, 1028, 829, 739 cm^{-1} .



Polymer-supported 3-[4,6-bis(4-fluorobenzyloxy)-3-bromo-2-(4-methoxybenzyloxy)phenyl]-3-dodecylsulfanyl-2-hydroxy-1-[3,4,5-tris(benzyloxy)phenyl]propan-1-one (16)

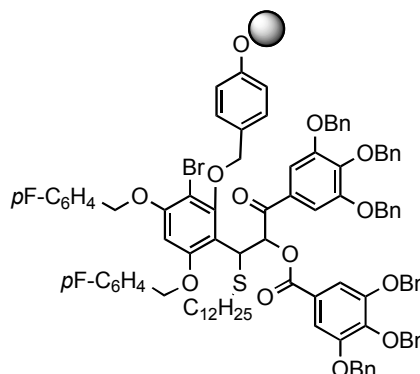
Polymer-supported epoxide **15** was placed in a syringe-shaped vessel. To this reaction vessel was added dodecanethiol (180 μL , 2.09 mmol), CH_2Cl_2 (750 μL) and 0.02 M $\text{Zn}(\text{OTf})_2$ in acetonitrile (750 μL , 15.0 μmol) at room temperature. After being shaken for 3 h, the solution was quenched by addition of triethylamine, and the solvent was removed and the resin was rinsed with CH_2Cl_2 (10 min). The remained resin was washed consecutively with acetonitrile (10 min x 2), methanol (10 min x 4), CH_2Cl_2 (10 min x 4), and dried under reduced pressure to afford polymer-supported hydroxyketone **16**.

FT-IR (solid) 3490, 3028, 2927, 1667, 1173, 1079, 1030, 829, 737 cm^{-1} .



Polymer-supported 3-[4,6-bis(4-fluorobenzyloxy)-3-bromo-2-(4-methoxybenzyloxy)phenyl]-3-dodecylsulfanyl-1-[3,4,5-tris(benzyloxy)phenyl]propan-1-one-2-yl 3,4,5-tris(benzyloxy)benzoate (17)

Polymer-supported α -hydroxyketone **16** was packed in MacroKan™. In flask, to a suspension of MacroKan™ and 3,4,5-tris(benzyloxy)benzoic acid (441 mg, 1.00 mmol), in pyridine/DMF (1:1, 5.00 mL) was added EDCI · HCl (192 mg, 1.00 mmol) and DMAP (36.6 mg, 300 μ mol) at 50 °C. After being stirred at the same temperature for 48 h, the reaction mixture was filtered and the MacroKan™ was rinsed with DMF (10 min). The MacroKan™ was washed consecutively with DMF (10 min x 3), DMF/H₂O (2:1, 10 min x 3), CH₂Cl₂ (10 min x 3), methanol (10 min x 3), and dried under reduced pressure to afford polymer-supported acyloxyketone **17**. FT-IR (solid) 3029, 2932, 1718, 1676, 1028, 1017, 828, 737, 702 cm⁻¹.



Procedure for the Release and cyclization of 17 to provide (18)

To a suspension of polymer-supported acyloxyketone **17** was added trifluoroacetic acid (0.600 mL) in CH₂Cl₂ (2.00 mL). After being stirred at -10 °C for 5 h, to the reaction mixture was added triethylsilane (0.400 mL). After being stirred at the same temperature for further 19 h, the reaction mixture was filtered. The remained resin was rinsed with ethyl acetate and the filtrate was concentrated *in vacuo*. The residue was purified by gel permeation chromatography (GPC) to afford chroman **18**.

Parallel synthesis of 60-membered EGCG analogues

General Procedure for Loading of 4,6-O-protective-2-hydroxybenzaldehyde

Each MiniKans™ contained PS-Wang-Br resin® (Novabiochem, 1.6 mmol/g loading, ca.70 mg) and color tag. To suspension of hydroxybenzaldehydes **12a-b** (0.2 M) and MiniKans™ in DMF was added Cs₂CO₃ (0.2 M) and sodium iodide (0.06 M) at room temperature. After being shaken at the same temperature for 24 h, the reaction mixture was filtered. The resin was washed with DMF/H₂O (2:1, 10 min x 3), DMF (10 min x 3), methanol (10 min x 3), CH₂Cl₂ (10 min x 3), and dried under reduced pressure to afford the polymer-supported benzaldehydes, respectively.

General Procedure for Cleavage from PS resins

To a MiniKans™ in 10 mL vial was added a solution of trifluoroacetic acid (50.0 μ L) in CH₂Cl₂ (1.95 mL) at room temperature. After being shaken at the same temperature for 1 h, MiniKans™ was filtered and washed with CH₂Cl₂ (5 min x 3). The filtrate was concentrated *in vacuo*. The residue was purified by short-pad column chromatography (elution with chloroform).

General Procedure for aldol condensation with ketones 11a-f

The 60 MiniKans™ were sorted and distributed into six sets of 10 MiniKans™. To a suspension of each set of MiniKans™ and ketones **11a-f** (7.50 mmol) in THF (12.0 mL) was added a solution of sodium methoxide (81.0 mg, 1.50 mmol) in methanol (3.00 mL) at room temperature. After being shaken for 36 h, the reaction mixture was filtered and the MiniKans™ were rinsed with THF (10 min). All MiniKans™ were pooled together, and washed consecutively with THF (10 min x 3), THF/H₂O (2:1, 10 min x 3), CH₂Cl₂ (10 min x 3), methanol (10 min x 3), and dried under reduced pressure.

Procedure for epoxidation

The 60 MiniKans™ in CH₂Cl₂ (50.0 mL) at room temperature were treated with a solution of 5.5 M *t*-butyl hydrogen peroxide in decane (19.0 mL) and a solution of 2.5 M KOH in methanol (19.0 mL). After being shaken for 72 h, the solvent was removed. The MiniKans™ were rinsed with CH₂Cl₂ (10 min). The MiniKans™ were washed consecutively with CH₂Cl₂ (10 min x 4), methanol (10 min x 4), and dried under reduced pressure.

Procedure for epoxide opening

The 60 MiniKans™ in dry CH₂Cl₂/acetonitrile (1:1, 80.0 mL) at room temperature were treated with dodecantiol (9.59 mL, 40.0 mmol) and Zn(OTf)₂ (291 mg, 800 μmol). After being vigorously shaken for 3 h, the solution was quenched by addition of triethylamine, and the solvent was removed and the MiniKans™ were rinsed with acetonitrile (10 min). The MiniKans™ were washed consecutively with acetonitrile (10 min x 3), CH₂Cl₂ (10 min x 3), methanol (10 min x 3), and dried under reduced pressure.

General Procedure for acylation with acid **7a-e**

The 60 MiniKans™ were sorted and distributed into five sets of 12 MiniKans™. To a suspension of each set of MiniKans™ and acids **7a-e** (3.00 mmol) in pyridine/DMF (1:1, 15.0 mL) was added EDCI • HCl (575 mg, 3.00 mmol) and DMAP (36.6 mg, 300 μmol) at room temperature. And the solution of acids **7a-e** was added to the reaction mixture at 50 °C. After being shaken at the same temperature for 48 h, the reaction mixture was filtered, and rinsed with DMF (10 min). All MiniKans™ were pooled together, and washed consecutively with DMF (10 min x 3), DMF/H₂O (2:1, 10 min x 3), CH₂Cl₂ (10 min x 3), methanol (10 min x 3), and dried under reduced pressure.

General Procedure for cleavage of the 60 polymer supported acyloxyketones

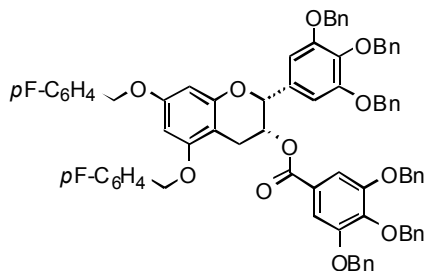
Each MiniKans™ was treated with a solution of trifluoroacetic acid (600 μL) in CH₂Cl₂ (2.00 mL) in the presence of PS-benzaldehyde resin (Argonaut, 1.13 mmol/g loading, 200 mg) at -10 °C. After the reaction mixture was shaken at the same temperature for 5 h, triethylsilane (400 μL) was added to the mixture. After being shaken at the same temperature for further 19 h, the reaction mixture was filtered to remove the MiniKans™. The MiniKans™ was rinsed with ethyl acetate. The filtrate was concentrated *in vacuo*. The residue was purified by gel permeation chromatography (GPC) to afford EGCG analogues.

Entry	aldehyd e	ketone	acid	Product	Crude yield(%)	Purity (%)	Isolated Yield (mg)	Isolated Yield (%)
1	12a	11a	7a	2	89	20	8.5	13
2	12a	11a	7b	5aab	129	27	10.8	17
3	12a	11a	7c	5aac	105	32	7.3	12
4	12a	11a	7d	5aad	114	16	3.1	5
5	12a	11a	7e	5aae	135	35	16.4	28
6	12a	11b	7a	5aba	87	15	8.0	13
7	12a	11b	7b	5abb	111	48	26.4	45
8	12a	11b	7c	5abc	143	51	14.3	26
9	12a	11b	7d	5abd	–	–	–	–
10	12a	11b	7e	5abe	118	49	21.6	39
11	12a	11c	7a	5aca	96	12	2.4	4
12	12a	11c	7b	5acb	108	22	6.5	12
13	12a	11c	7c	5acc	107	18	3.6	7
14	12a	11c	7d	5acd	115	31	3.2	6
15	12a	11c	7e	5ace	98	23	8.0	16
16	12a	11d	7a	5ada	64	23	5.7	10
17	12a	11d	7b	5adb	104	43	10.6	21
18	12a	11d	7c	5adc	152	57	20.3	44
19	12a	11d	7d	5add	111	45	8.7	18
20	12a	11d	7e	5ade	140	40	24.2	52
21	12a	11e	7a	5aea	142	7	1.5	3
22	12a	11e	7b	5aeb	110	48	8.3	16
23	12a	11e	7c	5aec	118	18	6.4	13
24	12a	11e	7d	5aed	85	9	–	–
25	12a	11e	7e	5aee	104	25	9.0	18
26	12a	11f	7a	5afa	93	11	3.6	6
27	12a	11f	7b	5afb	106	25	10.4	18
28	12a	11f	7c	5afc	141	15	8.0	15
29	12a	11f	7d	5afd	102	20	3.3	5
30	12a	11f	7e	5afe	152	18	9.4	18
31	12b	11a	7a	5baa	87	25	11.6	18
32	12b	11a	7b	5bab	80	27	9.0	15
33	12b	11a	7c	5bac	100	11	6.1	11
34	12b	11a	7d	5bad	75	18	4.0	7
35	12b	11a	7e	5bae	134	41	13.4	24
36	12b	11b	7a	5bba	100	8	–	–
37	12b	11b	7b	5bbb	173	22	10.2	18
38	12b	11b	7c	5bbc	117	40	10.1	20
39	12b	11b	7d	5bbd	66	23	4.6	9
40	12b	11b	7e	5bbe	99	47	16.1	32
41	12b	11c	7a	5bca	82	8	–	–
42	12b	11c	7b	5bcb	91	41	7.5	15
43	12b	11c	7c	5bcc	83	6	–	–
44	12b	11c	7d	5bcd	78	5	–	–
45	12b	11c	7e	5bce	87	6	–	–
46	12b	11d	7a	5bda	208	16	–	–
47	12b	11d	7b	5bdb	93	16	–	–
48	12b	11d	7c	5bdc	134	45	11.3	28
49	12b	11d	7d	5bdd	80	33	9.7	22

50	12b	11d	7e	5bde	73	59	10.3	25
51	12b	11e	7a	5bea	63	23	6.0	10
52	12b	11e	7b	5beb	85	32	10.8	19
53	12b	11e	7c	5bec	–	26	2.1	4
54	12b	11e	7d	5bed	96	26	3.5	6
55	12b	11e	7e	5bee	79	37	10.4	20
56	12b	11f	7a	5bfa	66	25	20.3	30
57	12b	11f	7b	5bfb	67	25	12.2	20
58	12b	11f	7c	5bfc	86	29	12.2	22
59	12b	11f	7d	5bfd	59	24	5.5	9
60	12b	11f	7e	5bfe	90	25	15.6	28

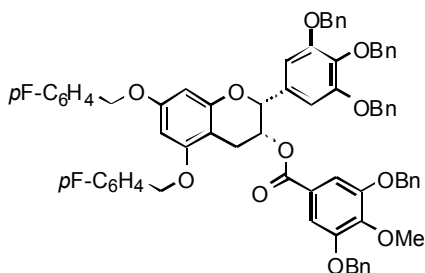
Epicatechin Analogues

Cis-5,7-bis(4-fluorobenzyloxy)-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (18)

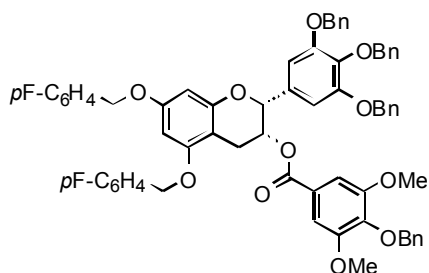


Yield 8.5 mg; Purity 32%; Retention Time 13.23 minutes;

Cis-5,7-bis(4-fluorobenzyloxy)-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5aab)

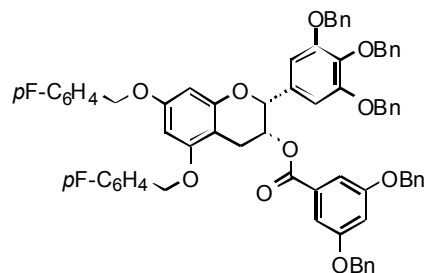


Yield 10.8 mg; Purity 27%; Retention Time 12.23 minutes; HRMS (ESI-TOF) calcd for $C_{72}H_{61}F_2O_{11}$ $[M+H]^+$ 1139.4182, found 1139.4186.



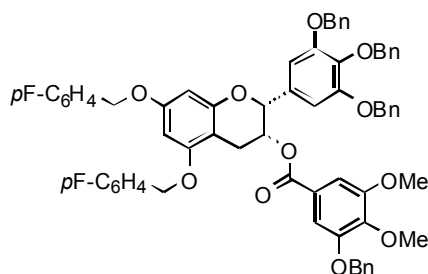
Cis-5,7-bis(4-fluorobenzyloxy)-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5aac)

Yield 7.3 mg; Purity 20%; Retention Time 11.67 minutes; MS (ESI-TOF) calcd for $C_{66}H_{57}F_2O_{11}$ $[M+H]^+$ 1063.4, found 1063.4.



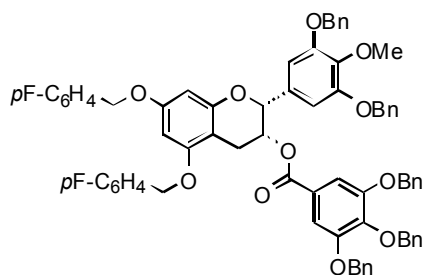
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,5-bis(benzyloxy)benzoate (Saad)**

Yield 3.1 mg; Purity 16%; Retention Time 12.75 minutes; HRMS (ESI-TOF) calcd for $C_{71}H_{59}F_2O_{10}$ $[M+H]^+$ 1109.4076, found 1109.4076.



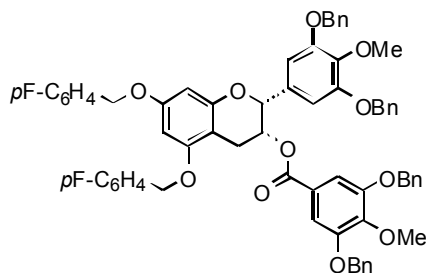
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (Saae)**

Yield 16.4 mg; Purity 35%; Retention Time 11.27 minutes; 1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.39 (m, 25H), 7.18x2 (t, J = 8.2, 8.7 Hz, 2H), 6.75 (s, 2H), 6.36 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 5.65 (br s, 1H), 5.05 (br s, 1H), 4.97-5.07 (m, 9H), 4.84 (d, J = 11.6 Hz, 2H), 4.72 (d, J = 11.6 Hz, 2H), 3.78 (s, 3H), 3.78 (s, 3H), 3.11 (dd, J_{gem} = 17.9 Hz, J = 4.3 Hz, 1H), 3.04 (dd, J_{gem} = 17.9 Hz, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 162.6x2 ($J_{C,F}$ = 246 Hz), 158.8, 158.0, 155.8, 153.3, 153.0, 151.8, 143.3, 138.6, 137.8, 137.0, 136.5, 133.3, 132.6 ($J_{C,F}$ = 2.3 Hz), 129.4 ($J_{C,F}$ = 7.6 Hz), 129.1 ($J_{C,F}$ = 7.6 Hz), 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 127.8x2, 127.5, 124.9, 115.6x2 ($J_{C,F}$ = 22.1 Hz), 109.1, 107.4, 106.9, 101.1, 94.8, 94.0, 78.0, 75.2, 71.4, 71.1, 69.6, 69.5, 68.4, 60.9, 56.4, 26.2; FT-IR (solid) 3421, 3032, 2932, 1713, 1590, 1511, 1220, 1107, 1001, 823, 754, 696 cm^{-1} ; MS (ESI-TOF) calcd for $C_{66}H_{57}F_2O_{11}$ $[M+H]^+$ 1063.4, found 1063.2.



***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (Saba)**

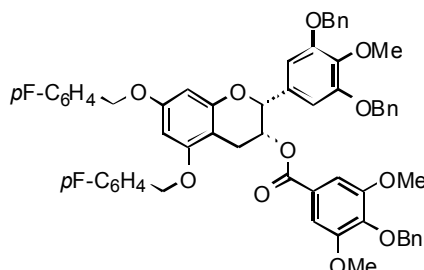
Yield 8.0 mg; Purity 15%; Retention Time 12.15 minutes; MS (ESI-TOF) calcd for $C_{72}H_{61}F_2O_{11}$ $[M+H]^+$ 1139.4, found 1139.3.



***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

3,5-bis(benzyloxy)-4-methoxybenzoate (5abb)

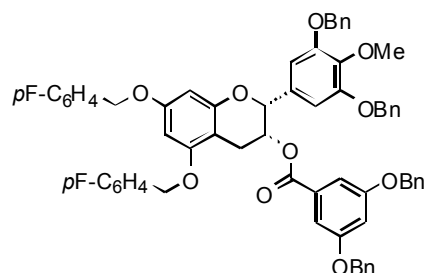
Yield 26.4 mg; Purity 48%; Retention Time 11.10 minutes; MS (ESI-TOF) calcd for C₂₆H₂₄F₂O₆ [M+H]⁺ 466.15, found 466.1.



***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

4-benzyloxy-3,5-dimethoxybenzoate (5abc)

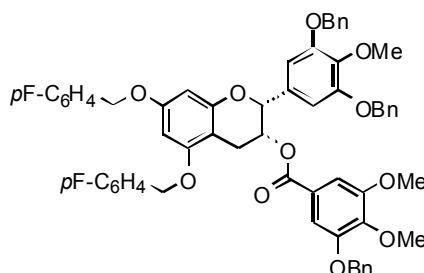
Yield 14.3 mg; Purity 51%; Retention Time 10.33 minutes; ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.43 (m, 19H), 7.18 (s, 2H), 7.03-7.11 (m, 4H), 6.78 (s, 2H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 5.62 (ddd, *J* = 1.5, 3.4, 4.4 Hz, 1H), 5.05 (br s, 1H), 4.88-5.02 (m, 10H), 3.84 (s, 3H), 3.76 (s, 6H), 3.10 (dd, *J*_{gem} = 17.9 Hz, *J* = 4.4 Hz, 1H), 3.04 (dd, *J*_{gem} = 17.9 Hz, *J* = 3.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 162.6x2 (*J*_{C,F} = 247 Hz), 158.7, 157.9, 155.7, 153.4, 152.7, 141.7, 139.9, 137.5, 137.0, 133.1, 132.7 (*J*_{C,F} = 3.0 Hz), 132.6 (*J*_{C,F} = 3.0 Hz), 129.4 (*J*_{C,F} = 8.4 Hz), 129.1 (*J*_{C,F} = 8.4 Hz), 128.6, 128.3x2, 128.0x2, 127.4, 125.2, 115.6x2 (*J*_{C,F} = 22.1 Hz), 107.4, 107.2, 101.1, 94.8, 94.0, 77.7, 75.0, 71.5, 69.6, 69.5, 68.6, 61.0, 56.4, 26.0; FT-IR (solid) 2999, 2935, 1712, 1590, 1509, 1223, 1129, 1102, 959, 833, 731, 696, 492 cm⁻¹; HRMS (ESI-TOF) calcd for C₆₀H₅₃F₂O₁₁ [M+H]⁺ 987.3556, found 987.3556.



***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

3,5-bis(benzyloxy)benzoate (5abd)

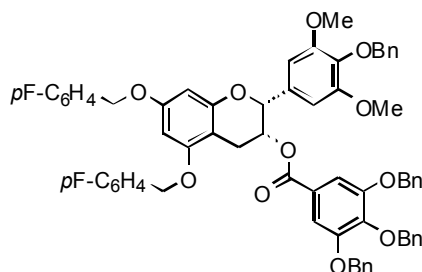
Yield - mg; Purity -%; Retention Time - minutes;



***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

3-benzyloxy-4,5-dimethoxybenzoate (5abe)

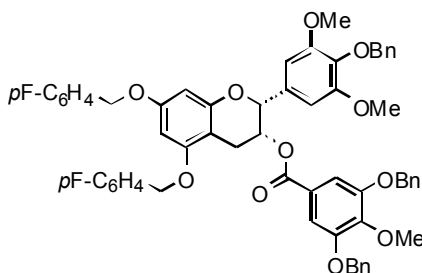
Yield 21.6 mg; Purity 49%; Retention Time 10.03 minutes; ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.37 (m, 20H), 7.18 (d, $J = 1.0$ Hz, 1H), 7.03-7.07 (m, 4H), 6.73 (s, 2H), 6.35 (d, $J = 1.9$ Hz, 1H), 6.29 (d, $J = 1.9$ Hz, 1H), 5.64 (br s, 1H), 4.99-5.07 (m, 7H), 4.87 (d, $J_{\text{gem}} = 12.1$ Hz, 2H), 4.76 (d, $J_{\text{gem}} = 12.1$ Hz, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 3.10 (dd, $J_{\text{gem}} = 17.9$ Hz, $J = 4.3$ Hz, 1H), 3.03 (dd, $J_{\text{gem}} = 17.9$ Hz, $J = 2.4$ Hz, 1H); FT-IR (solid) 3034, 2935, 1714, 1591, 1512, 1423, 1224, 1112, 1002, 827, 737, 697 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{60}\text{H}_{53}\text{F}_2\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 987.3556, found 987.3570.



***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

3,4,5-tris(benzyloxy)benzoate (5aca)

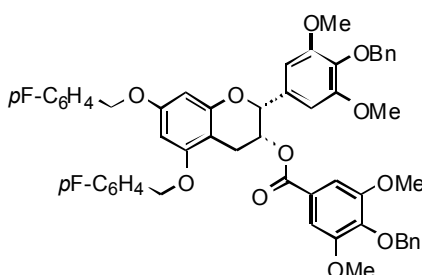
Yield 2.4 mg; Purity 12%; Retention Time 11.45 minutes; MS (ESI-TOF) calcd for $\text{C}_{66}\text{H}_{57}\text{F}_2\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 1063.4, found 1063.5.



***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

3,5-bis(benzyloxy)-4-methoxybenzoate (5acb)

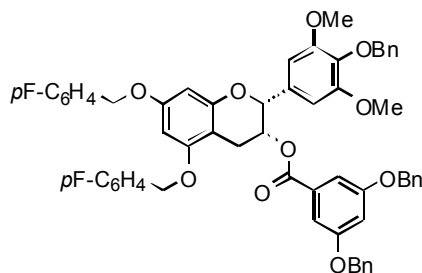
Yield 6.5 mg; Purity 22%; Retention Time 10.23 minutes; HRMS (ESI-TOF) calcd for $\text{C}_{60}\text{H}_{53}\text{F}_2\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 987.3556, found 987.3552.



***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

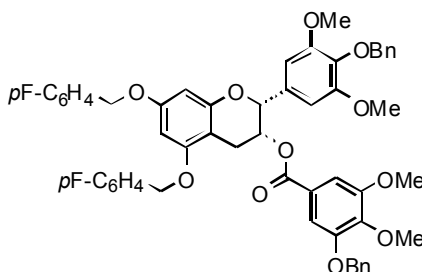
4-benzyloxy-3,5-dimethoxybenzoate (5acc)

Yield 3.6 mg; Purity 18%; Retention Time 9.38 minutes; HRMS (ESI-TOF) calcd for C₅₄H₄₉F₂O₁₁ [M+H]⁺ 911.3243, found 911.3243.



***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,5-bis(benzyloxy)benzoate (5acd)**

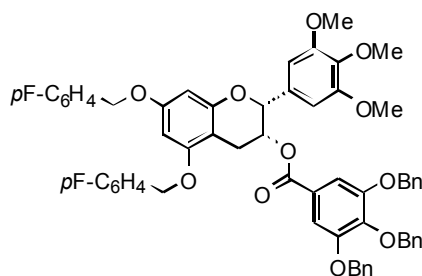
Yield 3.2 mg; Purity 31%; Retention Time 10.93 minutes; HRMS (ESI-TOF) calcd for C₅₉H₅₁F₂O₁₀ [M+H]⁺ 957.3450, found 957.3447.



***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

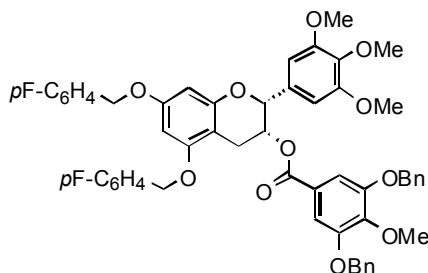
3-benzyloxy-4,5-dimethoxybenzoate (5ace)

Yield 8.0 mg; Purity 23%; Retention Time 9.12 minutes; HRMS (ESI-TOF) calcd for C₅₄H₄₉F₂O₁₁ [M+H]⁺ 911.3243, found 911.3224.



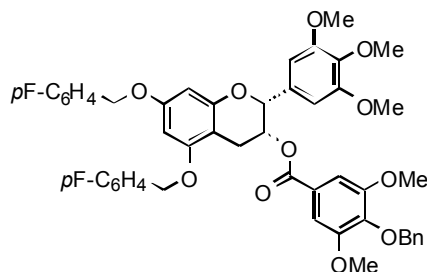
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5ada)**

Yield 5.7 mg; Purity 23%; Retention Time 10.28 minutes; HRMS (ESI-TOF) calcd for C₆₀H₅₃F₂O₁₁ [M+H]⁺ 987.3556, found 987.3552.



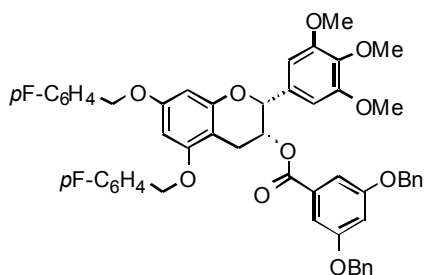
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5adb)**

Yield 10.6 mg; Purity 43%; Retention Time 8.95 minutes; ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.40 (m, 16H), 7.04 (t, *J* = 8.7 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.60 (s, 2H), 6.40 (d, *J* = 2.4 Hz, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 5.67 (br s, 1H), 4.99-5.09 (m, 9H), 3.89 (s, 3H), 3.78 (s, 3H), 3.53 (s, 6H), 3.11 (dd, *J*_{gem} = 17.9 Hz, *J* = 4.3 Hz, 1H), 3.04 (dd, *J*_{gem} = 17.9 Hz, *J* = 1.9 Hz, 1H); HRMS (ESI-TOF) calcd for C₅₄H₄₉F₂O₁₁ [M+H]⁺ 911.3243, found 911.3281.



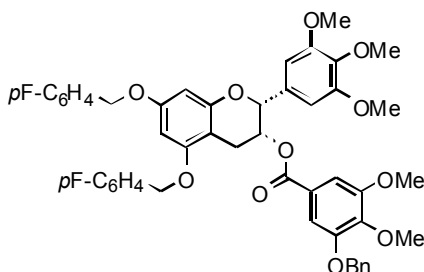
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5adc)**

Yield 20.3 mg; Purity 57%; Retention Time 8.08 minutes; ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.45 (m, 9H), 7.17 (s, 2H), 7.03-7.11 (m, 4H), 6.69 (s, 2H), 6.33 (d, *J* = 2.4 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 5.66 (br s, 1H), 5.09 (s, 1H), 5.06 (s, 2H), 5.00 (s, 2H), 4.98 (s, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 3.69 (s, 6H), 3.15 (dd, *J*_{gem} = 17.9 Hz, *J* = 3.9 Hz, 1H), 3.07 (dd, *J*_{gem} = 17.9 Hz, *J* = 2.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 162.6 (*J*_{C,F} = 247 Hz), 162.5 (*J*_{C,F} = 246 Hz), 158.7, 157.9, 155.7, 153.3, 153.2, 141.4, 138.1, 137.5, 137.3, 133.3, 132.6x2 (*J*_{C,F} = 3.0 Hz), 129.4 (*J*_{C,F} = 7.6 Hz), 129.1 (*J*_{C,F} = 7.6 Hz), 128.5, 128.3, 128.1, 125.2, 115.6 (*J*_{C,F} = 21.3 Hz), 115.5 (*J*_{C,F} = 21.3 Hz), 107.3, 104.1, 101.1, 94.8, 94.0, 78.0, 75.0, 69.5, 69.4, 68.6, 60.9, 56.3, 56.1, 26.2; FT-IR (solid) 2937, 1715, 1587, 1510, 1220, 1123, 1009, 825, 754 cm⁻¹; HRMS (ESI-TOF) calcd for C₄₈H₄₅F₂O₁₁ [M+H]⁺ 835.2930, found 835.2915.



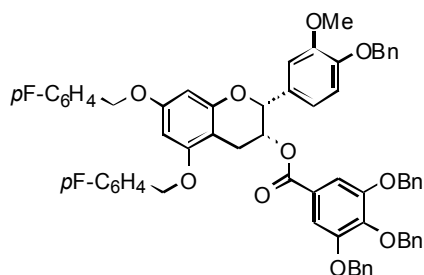
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3,5-bis(benzyloxy)benzoate (5add)**

Yield 8.7 mg; Purity 45%; Retention Time 9.63 minutes; ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.39 (m, 14H), 7.20 (d, J = 2.4 Hz, 2H), 7.03-7.07 (m, 4H), 6.75 (t, J = 2.4 Hz, 1H), 6.68 (s, 2Hc), 6.36 (d, J = 2.4 Hz, 1H), 6.26 (d, J = 2.4 Hz, 1H), 5.64 (t, J = 2.9 Hz, 1H), 5.07 (s, 1H), 4.99-5.00 (m, 8H), 3.80 (s, 3H), 3.67 (s, 6H), 3.05-3.17 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.3, 162.6x2 ($J_{\text{C,F}}$ = 247 Hz), 159.8, 158.8, 158.0, 155.7, 153.3, 138.1, 136.4, 133.2, 132.7 ($J_{\text{C,F}}$ = 3.0 Hz), 132.6 ($J_{\text{C,F}}$ = 3.0 Hz), 129.5 ($J_{\text{C,F}}$ = 8.4 Hz), 129.1 ($J_{\text{C,F}}$ = 8.4 Hz), 128.8, 128.3, 127.8, 115.6 ($J_{\text{C,F}}$ = 21.3 Hz), 108.8, 106.9, 104.1, 101.1, 95.1, 94.2, 78.2, 70.4, 69.6, 69.5, 68.8, 60.9, 56.1, 26.3; FT-IR (solid) 3431, 2928, 1719, 1591, 1510, 1221, 1125, 1050, 823, 736, 696, 667, 502 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{53}\text{H}_{47}\text{F}_2\text{O}_{10}$ $[\text{M}+\text{H}]^+$ 881.3137, found 881.3133.



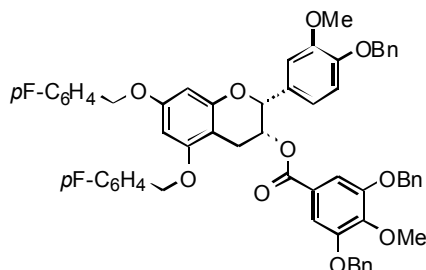
***Cis*-5,7-bis(4-fluorobenzyloxy)-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5ade)**

Yield 24.2 mg; Purity 40%; Retention Time 7.82 minutes; HRMS (ESI-TOF) calcd for $\text{C}_{48}\text{H}_{45}\text{F}_2\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 835.2930, found 835.2950.



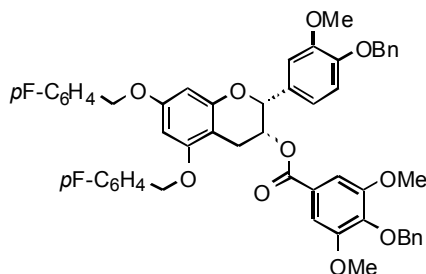
***Cis*-2-(4-benzyloxy-3-methoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5aea)**

Yield 1.5 mg; Purity 7%; Retention Time 11.52 minutes; MS (ESI-TOF) calcd for C₆₅H₅₅F₂O₁₀ [M+H]⁺ 1033.4, found 1033.3.



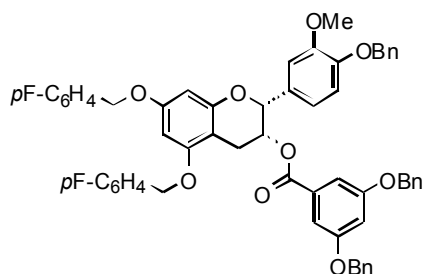
***Cis*-2-(4-benzyloxy-3-methoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5aeb)**

Yield 8.3 mg; Purity 48%; Retention Time 10.17 minutes; HRMS (ESI-TOF) calcd for C₅₉H₅₁F₂O₁₀ [M+H]⁺ 957.3450, found 957.3452.



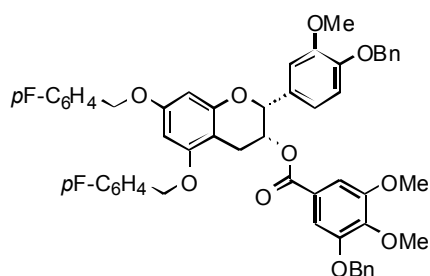
***Cis*-2-(4-benzyloxy-3-methoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5aec)**

Yield 6.4 mg; Purity 18%; Retention Time 9.32 minutes; ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.45 (m, 14H), 7.15 (s, 2H), 7.02-7.10 (m, 5H), 6.94 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.31 (d, *J* = 1.9 Hz, 1H), 6.24 (d, *J* = 1.9 Hz, 1H), 5.61 (br s, 1H), 5.12 (br s, 3H), 5.05 (s, 2H), 4.99 (s, 2H), 4.97 (s, 2H), 3.77 (s, 6H), 3.68 (s, 3H), 3.11 (dd, *J*_{gem} = 17.9 Hz, *J* = 4.3 Hz, 1H), 3.06 (dd, *J*_{gem} = 17.9 Hz, *J* = 2.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 162.6 (*J*_{C-F} = 247 Hz), 162.5 (*J*_{C-F} = 246 Hz), 158.7, 157.9, 155.8, 153.3, 149.7, 148.2, 141.4, 137.4, 137.1, 132.7 (*J*_{C-F} = 3.0 Hz), 132.6 (*J*_{C-F} = 3.0 Hz), 130.9, 129.4 (*J*_{C-F} = 7.6 Hz), 129.1 (*J*_{C-F} = 8.4 Hz), 128.6, 128.5, 128.3, 128.1, 127.9, 127.3, 125.2, 119.1, 115.6 (*J*_{C-F} = 22.1 Hz), 115.6 (*J*_{C-F} = 21.3 Hz), 113.4, 110.7, 107.3, 101.2, 94.8, 94.0, 77.7, 75.1, 71.1, 69.6, 69.5, 68.9, 56.3, 56.0, 26.1; FT-IR (solid) 2936, 1714, 1592, 1511, 1224, 1128, 1036, 825, 733, 697 cm⁻¹; HRMS (ESI-TOF) calcd for C₅₃H₄₇F₂O₁₀ [M+H]⁺ 881.3137, found 881.3141.



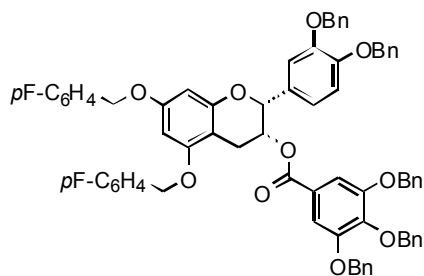
Cis-2-(4-benzyloxy-3-methoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,5-bis(benzyloxy)benzoate (5aed)

Yield mg; Purity 9%; Retention Time 10.83 minutes; HRMS (ESI-TOF) calcd for $C_{58}H_{49}F_2O_9$ $[M+H]^+$ 927.3, found 927.1.



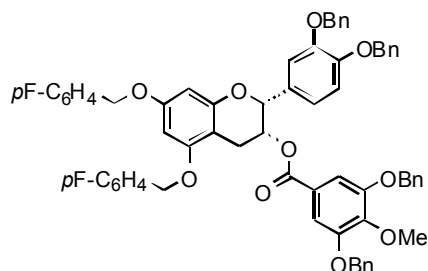
Cis-2-(4-benzyloxy-3-methoxyphenyl)-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5aee)

Yield 9.0 mg; Purity 25%; Retention Time 9.07 minutes; 1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.40 (m, 15H, aromatic-H), 7.15 (d, $J = 1.4$ Hz, 1H), 7.02-7.07 (m, 4H), 6.96 (d, $J = 1.9$ Hz, 1H), 6.89 (dd, $J = 8.7, 1.4$ Hz, 1H), 6.79 (d, $J = 8.7$ Hz, 1H), 6.35 (d, $J = 2.4$ Hz, 1H), 6.26 (d, $J = 2.4$ Hz, 1H), 5.62 (dd, $J = 4.3, 2.9$ Hz, 1H), 4.98-5.10 (m, 9H), 3.88 (s, 3H), 3.81 (s, 3H), 3.56 (s, 3H), 3.10 (dd, $J_{gem} = 17.9$ Hz, $J = 4.3$ Hz, 1H), 3.04 (dd, $J_{gem} = 17.9$ Hz, $J = 2.9$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 162.6 ($J_{CF} = 247$ Hz), 162.5 ($J_{CF} = 246$ Hz), 158.7, 158.0, 155.9, 153.2, 151.8, 149.6, 148.2, 143.2, 137.1, 136.6, 132.6x2 ($J_{CF} = 3.0$ Hz), 130.8, 129.4 ($J_{CF} = 8.4$ Hz), 129.1 ($J_{CF} = 7.6$ Hz), 128.7, 128.6, 128.2, 127.9, 127.8, 127.3, 124.9, 119.2, 115.6x2 ($J_{CF} = 21.3$ Hz), 113.8, 110.6, 109.1, 107.4, 101.2, 94.8, 94.0, 77.8, 71.1, 71.0, 69.6, 69.4, 68.7, 61.0, 56.3, 55.8, 26.2; FT-IR (solid) 3030, 2936, 1713, 1592, 1512, 1223, 1143, 1116, 1002, 821, 738, 698 cm^{-1} ; HRMS (ESI-TOF) calcd for $C_{53}H_{47}F_2O_{10}$ $[M+H]^+$ 881.3137, found 881.3142.



***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (**5afa**)**

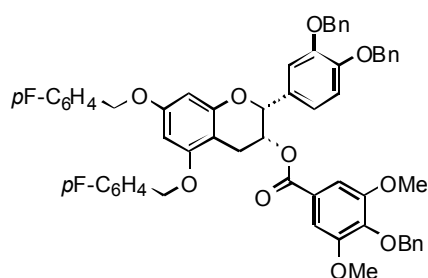
Yield 3.6 mg; Purity 11%; Retention Time 11.35 minutes; HRMS (ESI-TOF) calcd for $C_{71}H_{59}F_2O_{10}$ $[M+H]^+$ 1109.4076, found 1109.4076.



***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl**

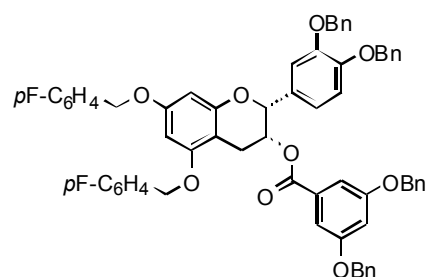
3,5-bis(benzyloxy)-4-methoxybenzoate (5afb**)**

Yield 10.4 mg; Purity 25%; Retention Time 11.28 minutes; HRMS (ESI-TOF) calcd for $C_{65}H_{50}F_2O_{10}$ $[M+H]^+$ 1033.3763, found 1033.3767.



***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (**5afc**)**

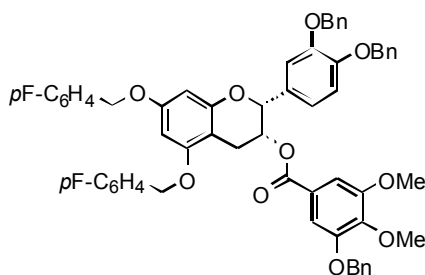
Yield 8.0 mg; Purity 15%; Retention Time 10.55 minutes; HRMS (ESI-TOF) calcd for $C_{59}H_{51}F_2O_{10}$ $[M+H]^+$ 957.3450, found 957.3464.



***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3,5-bis(benzyloxy)benzoate (**5afd**)**

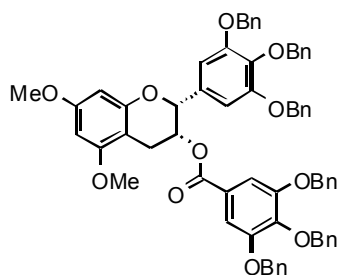
Yield 3.3 mg; Purity 20%; Retention Time 11.85 minutes;

MS (ESI-TOF) calcd for $C_{64}H_{53}F_2O_9$ $[M+H]^+$ 1103.4, found 1103.2.



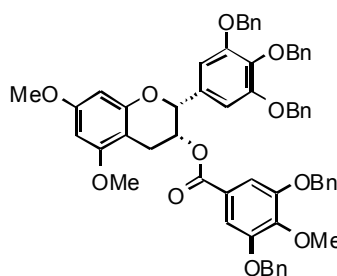
***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-bis(4-fluorobenzyloxy)chroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5afe)**

Yield 9.4 mg; Purity 18%; Retention Time 10.20 minutes; 1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.42 (m, 19H), 7.16 (d, $J = 1.9$ Hz, 1H), 7.02-7.07 (m, 6H), 6.94 (dd, $J = 1.9, 8.2$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.34 (d, $J = 2.4$ Hz, 1H), 6.26 (d, $J = 2.4$ Hz, 1H), 5.60 (s, 1H), 5.11 (s, 1H), 4.98-5.09 (m, 8H), 4.81 (d, $J_{gem} = 11.6$ Hz, 1H), 4.70 (d, $J_{gem} = 11.6$ Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.10 (dd, $J_{gem} = 17.9, 4.4$ Hz, 1H), 3.03 (dd, $J_{gem} = 17.9, 2.9$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 162.6 ($J_{CF} = 247$ Hz), 162.5 ($J_{CF} = 246$ Hz), 158.7, 158.0, 155.8, 153.2, 151.8, 149.1, 143.1, 137.2, 137.1, 136.6, 132.6x2 ($J_{CF} = 3.0$ Hz), 131.1, 129.4 ($J_{CF} = 8.4$ Hz), 129.1 ($J_{CF} = 8.4$ Hz), 128.7, 128.5, 128.4, 128.2, 127.8x2, 127.5, 127.3, 124.9, 121.3, 120.1, 115.6x2 ($J_{CF} = 21.3$ Hz), 114.8, 113.9, 109.1, 107.4, 101.1, 94.8, 94.0, 77.7, 71.4, 71.3, 71.1, 69.6, 69.4, 68.6, 61.0, 56.3, 26.1; FT-IR (solid) 3032, 2936, 1716, 1592, 1511, 1422, 1224, 1112, 1015, 824, 755, 697, 628 cm^{-1} ; HRMS (ESI-TOF) calcd for $C_{59}H_{51}F_2O_{10}$ $[M+H]^+$ 957.3450, found 957.3430.



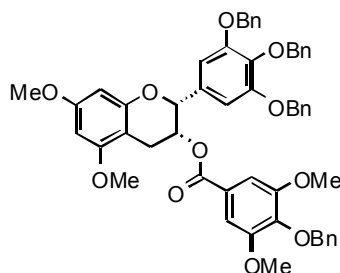
***Cis*-5,7-dimethoxy-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5baa)**

Yield 11.6 mg; Purity 25%; Retention Time 11.88 minutes; HRMS (ESI-TOF) calcd for $C_{66}H_{59}O_{11}$ $[M+H]^+$ 1027.4057, found 1027.4050.



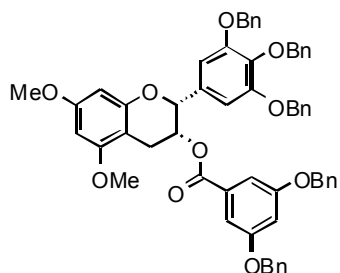
***Cis*-5,7-dimethoxy-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5bab)**

Yield 9.0 mg; Purity 27%; Retention Time 10.62 minutes; MS (ESI-TOF) calcd for C₆₀H₅₅O₁₁ [M+H]⁺ 951.4, found 951.4.



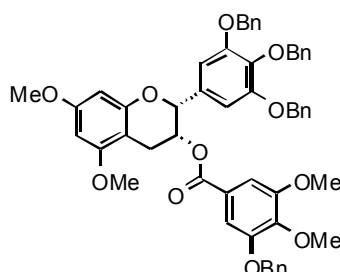
***Cis*-5,7-dimethoxy-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5bac)**

Yield 6.1 mg; Purity 11%; Retention Time 9.80 minutes; HRMS (ESI-TOF) calcd for C₅₄H₅₁O₁₁ [M+H]⁺ 875.3431, found 875.3434.



***Cis*-5,7-dimethoxy-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3,5-bis(benzyloxy)benzoate (5bad)**

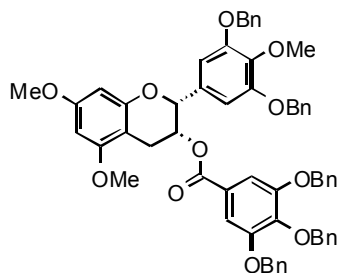
Yield 4.0 mg; Purity 18%; Retention Time 11.32 minutes; HRMS (ESI-TOF) calcd for C₅₉H₅₃O₁₀ [M+H]⁺ 921.3639, found 921.3639.



***Cis*-5,7-dimethoxy-2-[3,4,5-tris(benzyloxy)phenyl]chroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5bae)**

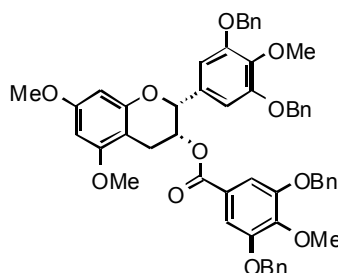
Yield 13.4 mg; Purity 41%; Retention Time 9.50 minutes; ¹H NMR (400 MHz, CDCl₃) δ 7.18-7.39 (m, 22H), 6.76 (s, 2H), 6.28 (d, *J* = 2.4 Hz, 1H), 6.16 (d, *J* = 2.4 Hz, 1H), 5.66 (br s, 1H), 4.97-5.05 (m, 5H), 4.86 (d, *J*_{gem} = 11.6 Hz, 2H), 4.72 (d, *J*_{gem} = 11.6 Hz, 2H), 3.80x2 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.06 (dd, *J*_{gem} = 17.9 Hz, *J* = 4.3 Hz, 1H), 3.00 (dd, *J*_{gem} = 17.9 Hz, *J* = 3.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.0, 159.9, 159.0, 155.6, 153.2, 153.0, 151.8, 143.3, 138.6, 137.9, 137.0, 136.5, 133.4, 128.7, 128.6x2, 128.5, 128.2, 127.9, 127.8x2, 127.6, 127.5, 125.0, 109.2, 107.5, 106.9, 100.3, 93.4, 92.1, 77.9, 75.2, 71.6, 71.4, 71.1, 68.5, 60.9, 56.4, 55.5x2, 26.0; FT-IR (solid) 3434, 2939, 1712, 1590, 1498, 1334, 1205, 1118, 1001, 812, 733, 696, 505 cm⁻¹; HRMS (ESI-TOF) calcd for C₅₄H₅₁O₁₁ [M+H]⁺

875.3431, found 875.3423.



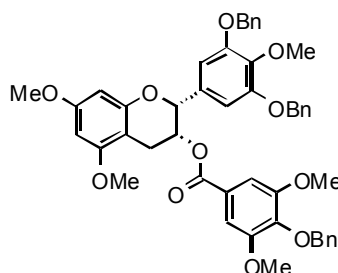
***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-dimethoxychroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5bba)**

Yield mg; Purity 8%; Retention Time 10.65 minutes; HRMS (ESI-TOF) calcd for $C_{60}H_{55}O_{11}$ $[M+H]^+$ 951.3744, found 951.3745.



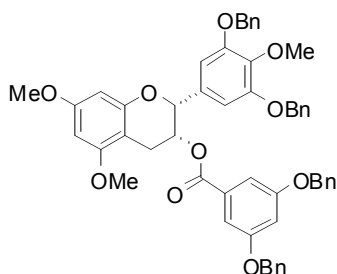
***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5bbb)**

Yield 10.2 mg; Purity 22%; Retention Time 9.25 minutes; HRMS (ESI-TOF) calcd for $C_{54}H_{51}O_{11}$ $[M+H]^+$ 875.3431, found 875.3439.



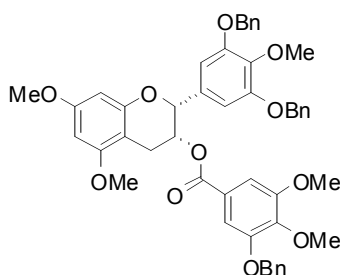
***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-dimethoxychroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5bbc)**

Yield 10.1 mg; Purity 40%; Retention Time 8.42 minutes; MS (ESI-TOF) calcd for $C_{48}H_{47}O_{11}$ $[M+H]^+$ 799.3, found 799.3.



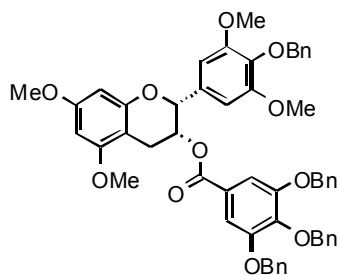
***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)benzoate (5bbd)**

Yield 4.6 mg; Purity 23%; Retention Time 10.00 minutes; HRMS (ESI-TOF) calcd for $C_{53}H_{49}O_{10}$ $[M+H]^+$ 845.3326, found 845.3321.



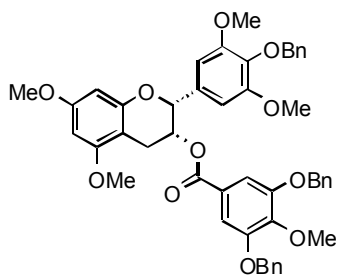
***Cis*-2-[3,5-bis(benzyloxy)-4-methoxyphenyl]-5,7-dimethoxychroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5bbe)**

Yield 16.1 mg; Purity 47%; Retention Time 8.12 minutes; HRMS (ESI-TOF) calcd for $C_{48}H_{47}O_{11}$ $[M+H]^+$ 799.3118, found 799.3121.



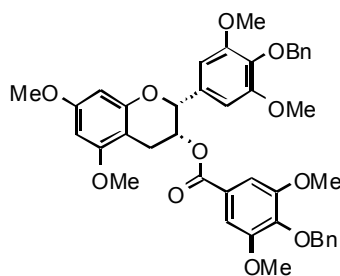
***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5bca)**

Yield mg; Purity 8%; Retention Time 9.67 minutes; HRMS (ESI-TOF) calcd for $C_{54}H_{51}O_{11}$ $[M+H]^+$ 875.3431, found 875.3430.



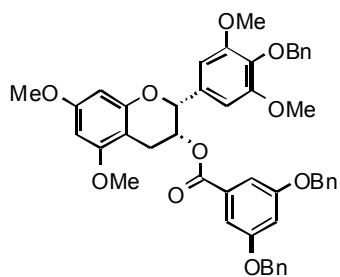
***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5bcb)**

Yield 7.5 mg; Purity 41%; Retention Time 8.28 minutes; ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.42 (m, 15H), 7.26 (s, 2H, a), 6.61 (s, 2H), 6.33 (d, $J = 2.4$ Hz, 1H), 6.17 (d, $J = 2.4$ Hz, 1H), 5.66 (br t, $J = 2.9$ Hz, 1H), 5.05-5.07 (m, 5H), 4.93 (s, 3H), 3.88 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.51 (s, 6H), 3.06 (dd, $J_{\text{gem}} = 17.9$ Hz, $J = 3.9$ Hz, 1H), 3.00 (dd, $J_{\text{gem}} = 17.9$ Hz, $J = 2.4$ Hz 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 159.9, 159.1, 155.7, 153.5, 152.1, 143.9, 137.9, 137.0, 136.6, 133.5, 128.7, 128.5, 128.2, 127.8x2, 127.6, 124.9, 109.4, 104.1, 100.3, 93.4, 92.1, 78.1, 75.0, 71.1, 68.5, 61.1, 56.0, 55.5x2, 26.2; FT-IR (solid) 3429, 3006, 2939, 1714, 1591, 1427, 1217, 1098, 1001, 847, 742, 698 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{48}\text{H}_{47}\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 799.3118, found 799.3119.



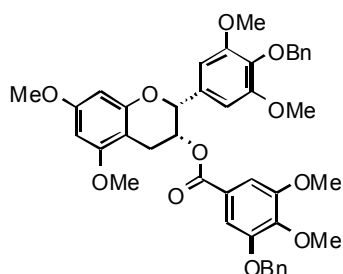
***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-dimethoxychroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5bcc)**

Yield mg; Purity 6%; Retention Time 7.33 minutes; MS (ESI-TOF) calcd for $\text{C}_{42}\text{H}_{43}\text{O}_{11}$ $[\text{M}+\text{H}]^+$ 723.2805, found 723.2798.



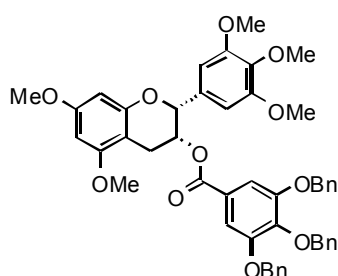
***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)benzoate (5bcd)**

Yield mg; Purity 5%; Retention Time 8.93 minutes; HRMS (ESI-TOF) calcd for $\text{C}_{47}\text{H}_{45}\text{O}_{10}$ $[\text{M}+\text{H}]^+$ 769.3013, found 769.3013.



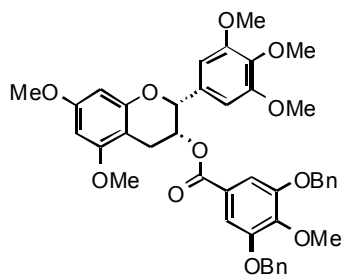
***Cis*-2-(4-benzyloxy-3,5-dimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5bce)**

Yield mg; Purity 6%; Retention Time 7.13 minutes; HRMS (ESI-TOF) calcd for $C_{42}H_{43}O_{11}$ $[M+H]^+$ 723.2805, found 273.2791.



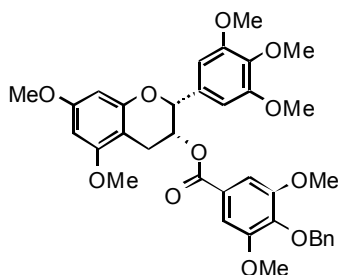
***Cis*-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5bda)**

Yield mg; Purity 16%; Retention Time 8.27 minutes; HRMS (ESI-TOF) calcd for $C_{48}H_{47}O_{11}$ $[M+H]^+$ 799.3118, found 799.3123.



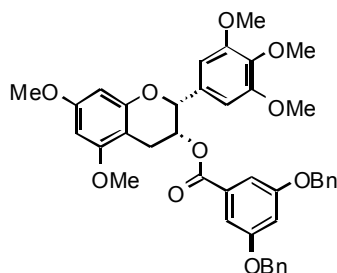
***Cis*-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5bdb)**

Yield mg; Purity 16%; Retention Time 6.95 minutes; HRMS (ESI-TOF) calcd for $C_{42}H_{42}O_{11}$ $[M+H]^+$ 723.3, found 723.3.



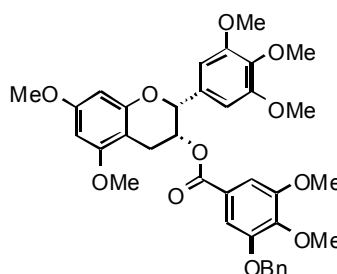
***Cis*-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5bdc)**

Yield 11.3 mg; Purity 45%; Retention Time 6.23 minutes; δ 7.28-7.44 (m, 5H), 7.16 (s, 2H), 6.69 (s, 2H), 6.25 (d, J = 2.4 Hz, 1H), 6.13 (d, J = 2.4 Hz, 1H), 5.66 (br s, 1H), 5.08 (s, 1H), 5.50 (s, 2H), 3.70-3.80 (m, 21H), 3.04-3.10 (m, 2H); HRMS (ESI-TOF) calcd for $C_{36}H_{39}O_{11}$ $[M+H]^+$ 647.2492, found 647.2480.



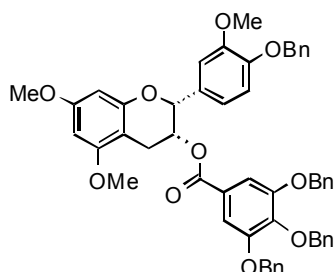
***Cis*-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3,5-bis(benzyloxy)benzoate (5bdd)**

Yield 9.7 mg; Purity 33%; Retention Time 7.60 minutes; HRMS (ESI-TOF) calcd for $C_{41}H_{41}O_{10}$ $[M+H]^+$ 693.2690, found 693.2700.



***Cis*-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)chroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5bde)**

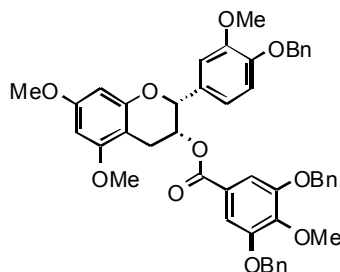
Yield 10.3 mg; Purity 59%; Retention Time 6.08 minutes; HRMS (ESI-TOF) calcd for $C_{36}H_{39}O_{11}$ $[M+H]^+$ 647.2492, found 647.2490.



***Cis*-2-(4-benzyloxy-3-trimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5bea)**

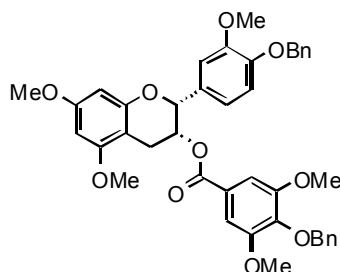
Yield 6.0 mg; Purity 23%; Retention Time 9.71 minutes; 1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.36 (m, 22H, aromatic-H), 6.93 (d, J = 1.5 Hz, 1H), 6.86 (dd, J = 1.5 Hz, 8.2 Hz, 1H), 6.77 (s, J = 8.2 Hz, 1H), 6.29 (d, J = 1.9 Hz, 1H), 6.15 (d, J = 1.9 Hz, 1H), 5.61 (br s, 1H), 5.09 (s, 1H), 5.00-5.07 (m, 8H), 3.80 (s, 3H), 3.79 (s, 3H, h), 3.47 (s, 3H), 3.05 (dd, J_{gem} = 17.9 Hz, J = 3.9 Hz, 1H), 3.04 (br d, J_{gem} = 17.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 159.8, 159.1, 155.8, 152.4, 149.6, 148.2, 142.5, 137.5, 137.1, 136.6, 131.0, 128.7, 128.6, 128.3, 128.1x2, 127.9, 127.8,

127.3, 125.1, 119.2, 113.8, 110.6, 109.2, 100.3, 93.3, 92.0, 77.8, 75.2, 71.1, 71.0, 68.7, 55.8, 55.5x2, 26.1; FT-IR (solid) 3031, 2937, 1715, 1593, 1429, 1217, 1145, 1116, 815, 753, 697, 474 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{53}\text{H}_{49}\text{O}_{10}$ $[\text{M}+\text{H}]^+$ 845.3326, found 845.3328.



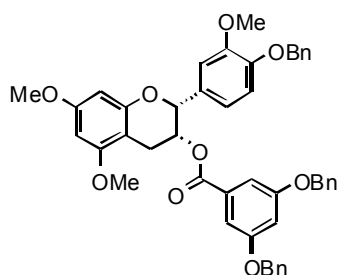
***Cis*-2-(4-benzyloxy-3-trimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5beb)**

Yield 10.8 mg; Purity 32%; Retention Time 8.23 minutes; HRMS (ESI-TOF) calcd for $\text{C}_{47}\text{H}_{45}\text{O}_{10}$ $[\text{M}+\text{H}]^+$ 769.3013, found 769.3012.



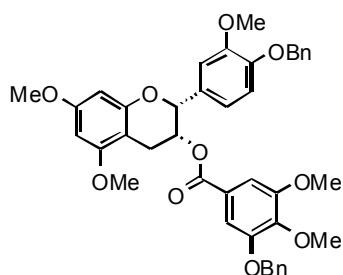
***Cis*-2-(4-benzyloxy-3-trimethoxyphenyl)-5,7-dimethoxychroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5bec)**

Yield 2.1 mg; Purity 25%; Retention Time 7.37 minutes; HRMS (ESI-TOF) calcd for $\text{C}_{41}\text{H}_{41}\text{O}_{10}$ $[\text{M}+\text{H}]^+$ 693.3, found 693.2.



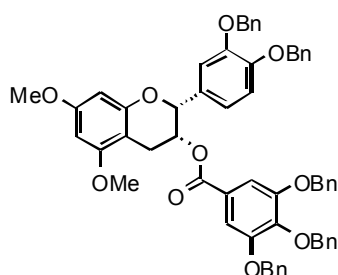
***Cis*-2-(4-benzyloxy-3-trimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)benzoate (5bed)**

Yield 3.5 mg; Purity 26%; Retention Time 8.92 minutes; HRMS (ESI-TOF) calcd for $\text{C}_{46}\text{H}_{43}\text{O}_9$ $[\text{M}+\text{H}]^+$ 739.2907, found 739.2903.



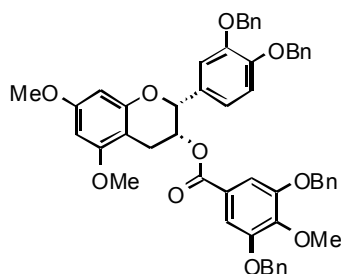
***Cis*-2-(4-benzyloxy-3-trimethoxyphenyl)-5,7-dimethoxychroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5bee)**

Yield 10.4 mg; Purity 37%; Retention Time 7.13 minutes; HRMS (ESI-TOF) calcd for $C_{41}H_{41}O_{10}$ $[M+H]^+$ 693.2700, found 693.2676.



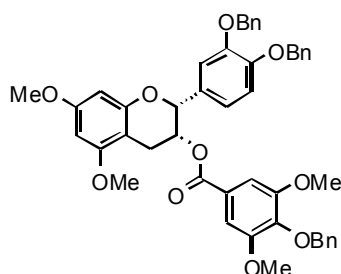
***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-dimethoxychroman-3-yl 3,4,5-tris(benzyloxy)benzoate (5bfa)**

Yield 20.3 mg; Purity 25%; Retention Time 10.82 minutes; HRMS (ESI-TOF) calcd for $C_{59}H_{53}O_{10}$ $[M+H]^+$ 921.3639, found 921.3638.



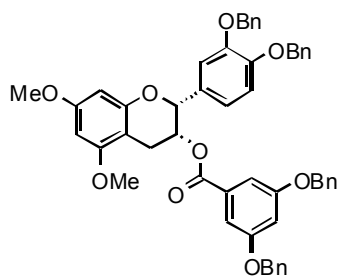
***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)-4-methoxybenzoate (5bfb)**

Yield 12.2 mg; Purity 25%; Retention Time 9.43 minutes; HRMS (ESI-TOF) calcd for $C_{53}H_{49}O_{10}$ $[M+H]^+$ 845.3326, found 845.3323.



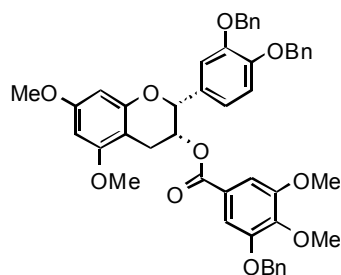
***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-dimethoxychroman-3-yl 4-benzyloxy-3,5-dimethoxybenzoate (5bfc)**

Yield 12.2 mg; Purity 29%; Retention Time 8.58 minutes; HRMS (ESI-TOF) calcd for $C_{47}H_{45}O_{10}$ $[M+H]^+$ 769.3013, found 769.3021.



***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-dimethoxychroman-3-yl 3,5-bis(benzyloxy)benzoate (5bfd)**

Yield 5.5 mg; Purity 24%; Retention Time 10.13 minutes; HRMS (ESI-TOF) calcd for $C_{52}H_{47}O_9$ $[M+H]^+$ 815.3220, found 815.3205.



***Cis*-2-[3,4-bis(benzyloxy)phenyl]-5,7-dimethoxychroman-3-yl 3-benzyloxy-4,5-dimethoxybenzoate (5bfe)**

Yield 15.6 mg; Purity 25%; Retention Time 8.25 minutes; 1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.38 (m, 16H, aromatic-H), 7.16 (d, J = 1.4 Hz, 1H), 7.07 (d, J = 1.9 Hz, 1H), 6.95 (dd, J = 1.9, 8.2 Hz, 1H), 6.85 (s, J = 8.2 Hz, 1H), 6.25 (d, J = 2.4 Hz, 1H), 6.13 (d, J = 2.4 Hz, 1H), 5.59 (br t, J = 2.9 Hz, 1H), 5.04-5.09 (m, 5H), 4.82 (d, J_{gem} = 11.6 Hz, 1H), 4.70 (d, J_{gem} = 11.6 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 9H), 3.04 (dd, J_{gem} = 17.4 Hz, J = 4.3 Hz, 1H), 2.99 (dd, J_{gem} = 17.4 Hz, J = 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 159.8, 159.0, 155.7, 153.1, 151.8, 149.1, 149.0, 143.1, 137.1, 136.6, 131.3, 128.7, 128.5, 128.4, 128.2, 127.8x2, 127.6, 127.4, 127.3, 125.0, 120.1, 114.9, 113.8, 109.1, 107.3, 100.3, 93.3, 92.0, 77.6, 71.4, 71.3, 71.0, 68.6, 60.9, 56.3, 55.5x2, 25.9; FT-IR (solid) 3447, 3008, 2939, 1715, 1596, 1455, 1220, 1118, 1025, 1006, 815, 752, 698 cm^{-1} ; HRMS (ESI-TOF) calcd for $C_{47}H_{45}O_{10}$ $[M+H]^+$ 769.3013, found 769.3026.

