SUPPLEMENTARY INFORMATION

4-*O*-Allyl-*myo*-inositol 1,3,5-*O*-orthobenzoate. *myo*-Inositol (5.00 g, 27 mmol) was taken up in DMSO (23 mL). To the suspension was added trimethylorthobenzoate (6.01 mL, 33.3 mmol) and *p*-toluene sulfonic acid (56 mg, 0.29 mmol). The suspension was stirred at 100 ºC for 5 h. The reaction was quenched with methylamine (0.9 mL) and the solvent removed under high vacuum. Crude *myo*-inositol 1,3,5-*O*-orthobenzoate (**2**, 7.6 g) was taken up in DMF (50 mL). The reaction mixture was cooled to -15 ºC and sodium hydride (60 % dispersion in mineral oil, 1.08 g, 27 mmol) added portion wise. The mixture was stirred at -15 ºC for 15 min, allowed to warm to rt and stirred for a further 30 min. Allyl bromide (2.34 mL, 27 mmol) was then added drop-wise and the reaction stirred for 24 h. The reaction was quenched by drop-wise addition of H_2O (5 mL) and the volume reduced under high vacuum. The residue was taken up in EtOAc and washed with H_2O (× 3) and then brine. The combined aqueous layers were back-extracted with EtOAc, and this solution was washed with H_2O (× 3) and brine. The organic layers were combined, dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude material was fractionated by chromatography on flash silica. Elution with hexane-EtOAc (7:3 → 0:1 v/v) yielded the *title compound* (6.03 g, 73 % over 2 steps) as a pale yellow oil; R_f (EtOAc) 0.72; ν_{max} (film)/cm^{-1} 3570, 3495, 3054, 2957, 2926, 2856 and 1452; δ_H (400 MHz, $CDCl_3$) 7.66-7.60 (2H, m, Ar ***H***), 7.42-7.26 (3H, m, Ar ***H***), 5.90 (1H, ddt, *J* 16.3, 10.3, 5.9, $OCH_2C\boldsymbol{H}CH_2$), 5.36 (1H, dq, *J* 15.7, 1.2, $OCH_2CHC\boldsymbol{H_a}H$), 5.32 (1H, dq, *J* 10.3, 1.2, $OCH_2CHC\boldsymbol{H_b}H$), 4.61 (1H, dtd, *J* 10.0, 4.1, 1.2, Ins 6-***H***), 4.52-4.47 (2H, m, 2 × Ins ***H***), 4.45-4.39 (2H, m, 2 × Ins ***H***), 4.21-4.16 (3H, m, Ins ***H*** + $OC\boldsymbol{H_2}CHCH_2$), 3.73 (1H, bd, *J* 10.3, Ins O***H***), 3.19 (1H, bd, *J* 11.8, Ins O***H***) ppm; δ_C (100 MHz, $CDCl_3$) 136.52 (Ar ***C***), 132.64 ($OCH_2\boldsymbol{C}HCH_2$), 129.70, 128.07 (2C), 125.17 (2C) (5 × Ar ***C***H), 119.56 ($OCH_2CH\boldsymbol{C}H_2$), 107.37 (Ph$\boldsymbol{C}O_3$), 76.02, 74.04, 73.53 (3 × Ins ***C***H), 71.99 ($O\boldsymbol{C}H_2CHCH_2$), 68.16, 67.69, 59.93 (3 × Ins ***C***H) ppm; HRMS (CI+) *m/z* (%) found $[M+H]^+$ 307.1189 (100), $C_{16}H_{19}O_6$ requires 307.1182.

2,6-*O*-Dibenzyl-4-*O*-allyl-*myo*-inositol 1,3,5-*O*-orthobenzoate. 4-*O*-Allyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (11.30 g, 36.9 mmol) was evaporated from MeCN (3 × 10 mL), taken up in DMF (100 mL) and cooled to -15 °C. Sodium hydride (60 % dispersion in mineral oil, 4.25 g, 111 mmol) was added portion-wise, the reaction stirred at -15 °C for 30 min then warmed to rt and benzyl bromide (13.2 mL, 111 mmol) was added drop-wise. The reaction was stirred at 60 °C for 12 h then quenched by drop-wise addition of H_2O (5 mL) and stirred for 30 min. The solvent volume was reduced under high vacuum, the residue dissolved in EtOAc and washed with H_2O (× 3) then brine. The organic phase was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude material was fractionated by chromatography on flash silica in a large sinter funnel. Elution with hexane-EtOAc (9:1 → 7:3 v/v) afforded the *title compound* (17.30 g, 97 %) as a yellow oil; R_f (hexane-EtOAc 1:1 v/v) 0.76; ν_{max} (film)/cm^{-1} 3054, 2957, 2927, 2856 and 1454; δ_H (400 MHz, $CDCl_3$) 7.66-7.22 (15H, m, Ar ***H***), 5.82 (1H, ddt, *J* 17.1, 10.7, 5.6, $OCH_2C\boldsymbol{H}CH_2$), 5.24 (1H, dq, *J* 17.2, 1.5, $OCH_2CHC\boldsymbol{H}H$), 5.18 (1H, dq, *J* 10.5, 1.2, $OCH_2CHC\boldsymbol{H}H$), 4.70 (2H, s, $OC\boldsymbol{H_2}Ph$), 4.67 (1H, d, *J* 11.8 OCH***H***Ph), 4.51 (1H, d, *J* 11.8, OCH***H***Ph), 4.55-4.52 (2H, m, 2 × Ins ***H***), 4.50 (1H, dq, *J* 3.8, 1.7, Ins ***H***), 4.47 (1H, dt, *J* 3.5, 1.6, Ins ***H***), 4.43 (1H, dt, *J* 3.7, 1.6, Ins ***H***), 4.13 (1H, ddt, *J* 12.7, 5.7, 1.7, OCH***H***$CHCH_2$), 4.10 (1H, t, *J* 1.4, Ins 2-***H***), 4.04 (1H, ddt, *J* 12.7, 5.7, 1.7, OCH***H***$CHCH_2$) ppm; δ_C (100 MHz, $CDCl_3$) 138.13, 137.77, 137.18 (3 × Ar ***C***), 134.13 ($OCH_2\boldsymbol{C}HCH_2$), 129.39, 128.42 (4C), 128.00 (2C), 127.94 (2C), 127.84, 127.75, 127.54 (2C), 125.39 (2C) (15 × Ar ***C***H), 117.56 ($OCH_2CH\boldsymbol{C}H_2$), 107.85 (Ph$\boldsymbol{C}O_3$), 73.83, 72.06, 71.92 (3 × Ins ***C***H), 71.49, 71.29, 70.71 [(2 × $O\boldsymbol{C}H_2Ph$) + $O\boldsymbol{C}H_2CHCH_2$], 69.05, 66.34, 60.41 (3 × Ins ***C***H) ppm; HRMS (CI+) *m/z* (%) found $[M+H]^+$ 487.2130 (100), $C_{30}H_{31}O_6$ requires 487.2121.

2,6-*O*-Dibenzyl-4-*O*-(prop-1-enyl)-*myo*-inositol 1,3,5-*O*-orthobenzoate. 2,6-*O*-Dibenzyl-4-*O*-allyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (5.40 g, 11.1 mmol) was evaporated from MeCN (3 × 5 mL), dissolved in DMSO (11 mL) and potassium *t*-butoxide (2.50 g, 22.2 mmol) added. The solution was stirred at 100 °C for 3 h. The reaction was cooled, diluted with H_2O (5 mL) and extracted with EtOAc. The organic layer was washed with H_2O (× 4), then brine, dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The *title compound* (5.40 g, 100 %) was isolated as a yellow oil and used without further purification; R_f (hexane-EtOAc 1:1 v/v) 0.76; ν_{max} (film)/cm^{-1} 3063, 3033, 2921, 1729, 1669, 1496 and 1453; δ_H (400 MHz, $CDCl_3$) 7.61-7.68 (2H, m, Ar ***H***), 7.22-7.46 (13H, m, Ar ***H***), 6.03 (1H, dq, *J* 6.1, 1.7, $OC\boldsymbol{H}CHCH_3$), 4.72 (2H, s, $OC\boldsymbol{H_2}Ph$), 4.67-4.62 (1H, m, Ins ***H***), 4.66 (1H, d, *J* 11.8, OCH***H***Ph), 4.50 (1H, d, *J* 12.2, OCH***H***Ph), 4.57-4.42 [5H, m, (4 × Ins ***H***) + $OCHC\boldsymbol{H}CH_3$], 4.10 (1H, t, *J* 1.6, Ins 2-***H***), 1.39 (3H, dd, *J* 6.8, 1.5, $OCHCHC\boldsymbol{H_3}$) ppm; δ_C (100 MHz, $CDCl_3$) 143.26 ($O\boldsymbol{C}HCHCH_3$), 137.83, 137.56, 136.93 (3 × Ar ***C***), 129.44, 128.42 (2C), 128.34 (2C), 128.04 (2C), 127.93 (2C), 127.80 (2C), 127.54 (2C), 125.36 (2C) (15 × Ar ***C***H), 107.83 (Ph$\boldsymbol{C}O_3$), 103.96 ($OCH\boldsymbol{C}HCH_3$), 75.17, 73.51, 71.94, 71.73 (4 × Ins ***C***H), 71.45, 71.10 (2 × $O\boldsymbol{C}H_2Ph$), 69.06, 65.59 (2 × Ins ***C***H), 14.17 ($OCHCH\boldsymbol{C}H_3$) ppm; HRMS (CI+) *m/z* (%) found $[M+H]^+$ 487.2130 (100) $C_{30}H_{31}O_6$ requires 487.2121.

2,6-*O*-Dibenzyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (3a). 2,6-*O*-Dibenzyl-4-*O*-(prop-1-enyl)-*myo*-inositol 1,3,5-*O*-orthobenzoate (17.41 g, 35.78 mmol) was taken up in MeCN (50 mL) and H_2O (5 mL). To the vigorously stirred solution was added *p*-toluene sulfonic acid (680 mg, 3.58 mmol). After 48 h the reaction was quenched with triethylamine (1.5 mL) and concentrated under vacuum. The residue was taken up in EtOAc, then washed with sat. $NaHCO_3$, H_2O (× 2) and brine. The organic layer was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude material was fractionated by chromatography on flash silica in a large sinter funnel. Elution with hexane-EtOAc (1:0 → 1:1 v/v)

afforded **3b** (12.61 g, 79 %) as a colourless oil; R_f (hexane-EtOAc 4:1 v/v) 0.16; ν_{max} (film)/cm^{-1} 3408, 3063, 3033, 2955, 2931, 2875, 1711, 1496 and 1453; δ_H (400 MHz, $CDCl_3$) 7.66-7.19 (15H, m, 15 × Ar ***H***), 4.82 (1H, d, *J* 12.5, PhCH***H***O), 4.68 (1H, d, *J* 12.5, PhCH***H***O), 4.58-4.53 [4H, m, (2 × Ins C***H***) + PhC***H***$_2$O], 4.50-4.47 (2H, m, 2 × Ins C***H***), 4.40-4.38 (1H, m, Ins C***H***), 3.94-3.93 (1H, m, Ins C***H***), 3.63 (1H, bs, Ins O***H***) ppm; δ_C (100 MHz, $CDCl_3$) 137.81, 136.79, 135.93 (3 × Ar ***C***), 129.46, 128.84 (2C), 128.75, 128.53 (2C), 128.11 (2C), 127.93 (5C), 125.37 (2C) (15 × Ar ***C***H), 107.32 (Ph***C***O$_3$), 74.46, 73.41 (2 × Ins ***C***H), 72.96 (O***C***H$_2$Ph), 71.29 (Ins ***C***H), 70.99 (O***C***H$_2$Ph), 68.67, 67.94, 65.07 (3 × Ins ***C***H) ppm; HRMS (ESI$^+$) *m/z* (%) found $[M+H]^+$ 447.1793 (100), $C_{27}H_{27}O_6$ requires 447.1808.

2,4,6-*O*-Tribenzyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (3b).[9] *myo*-Inositol 1,3,5-*O*-orthobenzoate (**2**, 200 mg, 0.75 mmol) was evaporated from MeCN (3 × 2 mL), taken up in DMF (2 mL) and cooled to -15 °C. Sodium hydride (60 % dispersion in mineral oil, 101 mg, 2.63 mmol) was added portion-wise, the reaction stirred at -15 °C for 30 min then warmed to rt and benzyl bromide (313 µL, 2.63 mmol) was added drop-wise. The reaction was stirred at 60 °C for 12 h then quenched by drop-wise addition of H_2O (5 mL) and stirred for 30 min. The crude material was taken up in EtOAc and washed with H_2O (× 3) then brine. The organic phase was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude material was fractionated by chromatography on flash silica in a large sinter funnel. Elution with hexane-EtOAc (9:1 → 7:3 v/v) afforded the *title compound* (338 mg, 84 %) as a yellow oil; R_f (EtOAc-hexane, 1:1 v/v) 0.76; δ_H (270 MHz, $CDCl_3$) 7.67-7.63 (2H, m), 7.35-7.24 (18H, m) (20 × Ar ***H***), 4.68 (2H, s, OC***H***$_2$Ph), 4.64 (2H, d, *J* 11.6, 2 × OCH***H***Ph), 4.56-4.44 (5H, m, 5 × Ins ***H***), 4.51 (2H, d, *J* 11.6, 2 × OCH***H***Ph), 4.14-4.12 (1H, m, Ins ***H***) ppm [lit.,[9] (200 MHz, $CDCl_3$) 7.60-7.71 (2H, m), 7.15-7.50 (18H, m), 4.37-4.80 (11H, m), 4.11 (t, 1H, t, *J* 2) ppm]; δ_C (100 MHz, $CDCl_3$) 138.10, 137.70 (2C), 137.21 (4 × Ar ***C***), 129.47, 128.48 (5C), 128.13 (3C), 128.01 (3C), 127.88 (2C), 127.69 (4C), 125.45 (2C) (20 × Ar ***C***H), 107.93 (Ph***C***O$_3$), 74.07 (2C), 71.98 (2C) (4 × Ins ***C***H), 71.68 (2C), 71.28 (3 × O***C***H$_2$Ph), 69.11, 66.20 (2 × Ins ***C***H) ppm; MS (CI$^+$) *m/z* (%) found $[M+H]^+$ 537 (100), $[M+NH_4]^+$ 551 (8).

2,6-*O*-Dibenzyl-4-O-(*tert*-butyldimethylsilyl)-*myo*-inositol 1,3,5-*O*-orthobenzoate (3c). 2,6-*O*-Dibenzyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (300 mg, 0.672 mmol) and imidazole (99 mg, 1.478 mmol) were evaporated from MeCN (3 × 1 mL) then taken up in dry DMF (5 mL) and Et_3N (93 µL, 0.672 mmol) added. The solution was cooled to 0 °C, before adding TbdmsCl (0.152 g, 1.008 mmol). The temperature was then raised to 100 °C and the reaction stirred for 48 h. The reaction was quenched with water (1 mL), stirred for a further 20 min and the solvent evaporated under reduced pressure. The residue was taken up in CH_2Cl_2 and washed with sat. $NaHCO_3$, water, then brine. The organic layer was dried (Mg_2SO_4), filtered and the filtrate evaporated to dryness under reduced pressure. The residue was fractionated by chromatography on flash silica. Elution with CH_2Cl_2-hexane (1:9 → 1:1 v/v) afforded the *title compound* (286 mg, 76 %) as an oil; R_f (CH_2Cl_2-hexane, 2:1 v/v) 0.55; δ_H (400 MHz, CDCl3) 7.72-7.67 (2H, m), 7.47-7.43 (2H, m), 7.40-7.29 (9H, m), 7.28-7.22 (2H, m) (15 × Ar ***H***), 4.77 (1H, d, *J* 12.6, CH***H***Ph), 4.73 (1H, d, *J* 12.6, CH***H***Ph), 4.65 (1 H, td, *J* 3.8, 1.7, Ins ***H***), 4.64 (1H, d, *J* 11.8, CH***H***Ph), 4.51-4.49 (1H, m, Ins ***H***), 4.49 (1H, d, *J* 11.8, CH***H***Ph), 4.44 (1H, td, *J* 3.7, 1.6, Ins ***H***), 4.38-4.33 (2H, m, 2 × Ins ***H***), 4.12 (1H, t, *J* 1.5, Ins 2-***H***), 0.80 (9H, s, SiC***Me$_3$***), 0.06 (6H, s, Si***Me***$_2$) ppm; δ_C (100 MHz, $CDCl_3$) 138.08, 137.76, 137.27 (3 × Ar ***C***), 129.36, 128.50 (2C), 128.36 (2C), 128.11 (2C), 127.96 (2C), 127.85, 127.77, 127.57 (2C), 125.43 (15 × Ar ***C***H), 107.67 (Ph***C***O$_3$), 74.29, 74.14, 72.03 (3 × Ins ***C***H), 71.45 (Ph***C***H$_2$O), 71.20 (Ins ***C***H), 71.00 (Ph***C***H$_2$O), 68.28, 65.34 (2 × Ins ***C***H), 25.56 (SiC***Me***$_3$), 17.83 (Si***C***Me$_3$), -4.77, -5.07 (Si***Me***$_2$) ppm; HRMS ES+) *m/z* (%) found $[M+H]^+$ 561.2677 (83), $[C_{33}H_{41}O_6Si]^+$ requires 561.2672; $[M+K]^+$ 599.2251 (25), $[M+Na]^+$ 583.2501.

2,6-*O*-Dibenzyl-4-*O*-*tert*-butyldiphenylsilyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (3d). 2,6-*O*-Dibenzyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (**3b**, 500 mg, 1.12 mmol) and imidazole (164 mg, 2.46 mmol) were evaporated from MeCN (3 × 1 mL) then taken up in dry DMF (3 mL) and Et_3N (155 µL, 1.12 mmol) was added. The reaction was cooled to 0 °C, before adding TbdpsCl (1.16 mL, 4.48 mmol). The reaction was heated to 100 °C and stirred for 72 h. The reaction was quenched with H_2 O (0.5 mL), stirred for a further 20 min and the solvent was evaporated. The remaining solids were taken up in CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$, H_2O and then brine. The organic layer was dried ($MgSO_4$), filtered and the filtrate evaporated to dryness. The residue was fractionated by chromatography on flash silica, eluting with EtOAc-hexane (1:9 v/v), followed by sublimation of the residual TbdpsOH contaminant (oil pump, heat gun) to give **3d** (645 mg, 84 %) as fine white crystals; R_f (hexane-EtOAc, 4:1 v/v) 0.52; mp 129-131 ºC (CH_2Cl_2-hexane); Found C, 75.5; H, 6.5. $C_{43}H_{44}O_6Si$ requires C, 75.4; H, 6.5 %; δ_H (500 MHz, $CDCl_3$) 7.71-7.67 (2H, m), 7.66-7.63 (4H, m), 7.52-7.47 (4H, m), 7.46-7.32 (13H, m), 7.31-7.27 (2H, m) (25 × Ar ***H***), 4.70 (1H, td, *J* 3.9, 1.7, Ins ***H***), 4.70 (1H, d, *J* 12.2, OCH***H***Ph), 4.67 (1H, d, *J* 12.6, OCH***H***Ph), 4.60 (1H, d, *J* 12.0, OCH***H***Ph), 4.48 (1H, dq, *J* 3.9, 1.9, Ins ***H***), 4.48 (1H, d, *J* 12.0, OCH***H***Ph), 4.39 (1H, td, *J* 3.7, 1.6, Ins ***H***), 4.24 (1H, tt, *J* 3.5, 1.7, Ins 5-***H***), 4.22 (1H, t, *J* 1.7, Ins 2-***H***), 4.19 (1H, dq, *J* 3.9, 1.9, Ins ***H***), 0.97 (9H, s, C***Me$_3$***) ppm; δ_C (125 MHz, $CDCl_3$) 138.09, 137.68, 137.16 (3 × Ar ***C***), 135.81 (2C), 135.73 (2C) (4 × Ar ***C***H), 133.16, 133.06 (2 × Ar ***C***), 130.17, 130.10, 129.38, 128.51 (2C), 128.49 (2C), 128.19 (2C), 127.94 (4C), 127.85 (4C), 127.76 (2C), 125.41 (2C) (21 × Ar ***C***H), 107.61 (Ph***C***O$_3$), 74.39, 73.61 (2 × Ins ***C***H), 72.05 (Ph***C***H$_2$O), 72.05 (Ins ***C***H), 70.99 (Ph***C***H$_2$O), 70.91, 68.72, 65.33 (3 × Ins ***C***H), 26.84 (SiC***C***H$_3$), 19.14 (Me$_3$***C***Si) ppm; HRMS (TOF ES$^+$) *m/z* (%) found $[M+H]^+$ 685.2970 (100), $C_{43}H_{45}O_6Si$ requires 685.2985; $[M+K]^+$ 748.3071 (32), $[M+Na]^+$ 707.2792 (94).

2,4-*O*-Bis[2,7-dibromo-9-(3-trifluoromethylphenyl) xanthen-9-yl]-*myo*-inositol 1,3,5-*O*-orthobenzoate (8). To *myo*-inositol orthobenzoate (**2**, 99 mg, 0.37 mmol) in MeCN (2 mL) was added a solution of 9-chloro-2,7-dibromo-9-(3-trifluoromethylphenyl)xanthene (0.574 g, 1.1 mmol) in pyridine-MeCN (10 mL, 1:1 v/v). The reaction was refluxed for 6.5 h, then cooled to rt and quenched with H_2O. After 30 min the solvent was stripped off and the residue dissolved in CH_2Cl_2. This solution was washed with sat. $NaHCO_3$ (× 2), then brine, dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The resultant pale yellow solids were triturated with hexane, discarding the filtrate. This material (0.336 g) was crystallised from EtOH-CH_2Cl_2 to give the *title compound* (248 mg, 46%) as fine crystallites; R_f ($CHCl_3$-hexane, 7:3 v/v) 0.41; mp > 250 ºC (EtOH-CH_2Cl_2); Found: C, 51.72; H, 2.50. $C_{53}H_{32}Br_4F_6O_8$ requires C, 51.73; H, 2.62 %; δ_H (360 MHz, $CDCl_3$) 7.92 (1H, bs), 7.66-7.61 (4H, m), 7.58-7.37 (7H, m), 7.36-7.28 (8H, m), 7.15-7.12 (3H, m), 7.09 (1H, d, *J* 2.3), 6.71 (1H, d, *J* 2.3) (25 Ar ***H***), 4.25 (1H, m, ex→td, *J* 4.0, 1.8, Ins 6-***H***), 4.04 (1H, t, *J* 1.8, Ins 2-***H***), 3.98 (1H, td, *J* 4.0, 1.8, Ins 4-***H***), 3.65 (1H, dq, *J* 4.0, 1.8, Ins ***H***), 3.40 (1H, dq, *J* 4.0, 1.8, Ins ***H***), 3.14 (1H, tt, *J* 3.7, 1.5, Ins 5-***H***), 2.58 (1H, d, *J* 8.4, ex, Ins O***H***) ppm; δ_C (90.6 MHz, $CDCl_3$) 150.16, 149.99, 149.77, 149.56, 147.74, 146.82, 136.50 (7 × Ar ***C***), 134.21, 134.03, 133.74 (2C), 133.36, 133.09, 132.92, 131.37 (8 × Ar ***C***H), 130.67 (2C, q, *J* 32.3, 2 × ***C***CF_3), 130.74, 129.63, 129.31, 129.00, 128.86, 128.14 (2C), 125.11 (2C) (9 × Ar ***C***H), 125.00 (q, *J* 3.5), 124.63 (q, *J* 3.6) (2 × Ar ***C***$HCCF_3$), 124.04 (Ar ***C***), 124.01 (q, *J* 272.3, ***C***F_3), 123.80 (Ar ***C***), 123.79 (q, *J* 272.6, ***C***F_3), 123.70-123.53 (2C, m, 2 × Ar ***C***$HCCF_3$), 123.05, 121.88 (2 × Ar ***C***), 119.15, 119.08, 118.59, 118.49 (4 × Ar ***C***H), 116.76, 116.73, 116.40, 116.13 (4 × Ar ***C***), 106.92 (Ph***C***O_3), 77.46, 75.45 (2 × Ar_3***C***O), 73.92, 73.70, 69.56, 68.80, 67.35, 61.66 (6 × Ins ***C***H) ppm; MS (ESI^+) *m/z* (%) found $[M+H]^+$ 1230.9 (44).

2-*O*-[2,7-Dibromo-9-(3-trifluoromethylphenyl)xanthen-9-yl]-*myo*-inositol 1,3,5-*O*-orthobenzoate (9). Method A: A solution of 2,4-di-Dtpx *myo*-inositol orthobenzoate (**8**, 122 mg, 0.099 mmol) in CH_2Cl_2 (5 mL) was cooled to -20 °C and DIBAL-H (1 M in hexanes, 0.6 mL, 0.60 mmol) was added. After 30 min a solution of sat. sodium potassium tartrate was added followed by sufficient CH_2Cl_2 to allow efficient mixing, and vigorous stirring continued for 1 h. The organic layer was separated, washed with sat. $NaHCO_3$ (× 2), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The residual gum (131 mg) was fractionated by medium pressure silica column chromatography. Elution with hexane-$CHCl_3$ (1:0 → 0:1 v/v), and then MeOH-$CHCl_3$ (0:1 → 1:9 v/v) afforded **9** (70 mg, 94%). **Method B:** *myo*-Inositol orthobenzoate (**2**, 85 mg, 0.32 mmol) was evaporated from pyridine (3 × 1 mL), then re-dissolved in pyridine (2 mL) and to this was added 9-chloro-2,7-dibromo-9-(3-trifluoromethylphenyl)xanthene (0.323 g, 0.62 mmol) and the reaction was stirred at rt for 18 h. The next day EtOH (5 mL) was added and the solvent stripped off under reduced pressure. The residue was taken up in CH_2Cl_2, washed with sat. $NaHCO_3$, dried ($MgSO_4$), and the solvent evaporated under reduced pressure, re-evaporating from EtOH (× 2). The residue was triturated with hexane and the filtrate discarded. The crude material (0.198 g) was fractionated by medium pressure silica column chromatography. Elution with hexane-$CHCl_3$ (1:0 → 0:1 v/v) afforded **9** (179 mg, 75 %) as a colourless amorphous solid; R_f (EtOH-$CHCl_3$, 1:19 v/v) 0.42; mp 97-99 ºC; δ_H (360 MHz, $CDCl_3$) 7.96 (1H, bs), 7.74-7.72 (2H, m), 7.61 (1H, bd, *J* 7.8), 7.58 (1H, bd, *J* 7.7), 7.49-7.41 (6H, m), 7.30 (2H, d, *J* 2.4), 7.14 (2H, d, *J* 8.8) (15 × Ar ***H***), 3.80 (2H, t, *J* 4.0, Ins 4-***H*** + Ins 6-***H***), 4.22 (1H, tt, *J* 3.8, 1.5, Ins 5-***H***), 3.80 (1H, t, *J* 1.9, Ins 2-***H***), 3.73 (2H, dt, *J* 4.6, 1.7, Ins 1-***H*** + Ins 3-***H***), 3.09 (2H, bs, ex, Ins 4-O***H*** + Ins 6-O***H***) ppm; δ_C (90.6 MHz, d_6-DMSO) 149.57 (2C), 148.64, 137.60 (4 × Ar ***C***), 133.56 (2C), 131.81 (2C), 131.52, 129.82, 129.27 (7 × Ar ***C***H), 128.96 (q, *J* 31.8, ***C***CF_3), 127.74 (2C), 125.29 (2C) (4 × Ar ***C***H), 124.56 (q, *J* 3.1, Ar ***C***$HCCF_3$), 124.13 (q, *J* 272.4, ***C***F_3), 123.52 (2 × Ar ***C***), 121.84 (q, *J* 3.3, Ar ***C***$HCCF_3$), 119.37 (2 × Ar ***C***H), 115.39 (2 × Ar ***C***), 106.32 (Ph***C***O_3), 74.77 [3C, (2 × Ins ***C***H) + Ar_3***C***O], 69.87, 66.52 (2C), 61.50 (4 × Ins ***C***H) ppm; HRMS (CI^+) *m/z* (%) found $[M+H]^+$ 746.9829 (49), $C_{33}H_{24}{}^{79}Br_2F_3O_7$ requires 746.9841.

2,6-*O*-Dibenzyl-inos-4-ose 1,3,5-*O*-orthobenzoate. 2,6-*O*-Dibenzyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (**3a**) (2.00 g, 4.47 mmol) was evaporated from MeCN (3 × 5 mL) and taken up in CH_2Cl_2 (20 mL). Dess Martin periodinane (3.80 g, 4.94 mmol) was added portion-wise and the suspension stirred for 3 h. Aqueous $Na_2S_2O_3$ (10 % w/v) was added and stirring continued for 10 min. The product was extracted with CH_2Cl_2 (× 2), and the combined organic layers washed successively with sat. $NaHCO_3$, H_2O and brine, before drying ($MgSO_4$) and evaporation to dryness under reduced pressure. The crude inos-4-ose (1.98 g, 100 %, pale yellow oil) was used without further purification; R_f (hexane-acetone, 7:3 v/v) 0.21; ν_{max} (film)/cm^{-1} 3064, 3033, 2969, 2873, 1766 1454 and 1342; δ_H (400 MHz, $CDCl_3$) 7.68-7.63 (3H, m, Ar ***H***), 7.43-7.20 (12H, m, Ar ***H***), 4.81-4.45 [8H, m, (4 × Ins ***H***) + (2 × OC***H***$_2$Ph)], 3.82-3.81 (1H, m, Ins ***H***) ppm; δ_C (100 MHz, $CDCl_3$) 200.01 (Ins ***C***=O), 137.14, 136.33, 135.66 (3 × Ar ***C***), 129.80, 128.67 (2C), 128.58 (2C), 128.45, 128.11, 128.05 (2C), 127.94 (2C), 127.89 (2C), 125.49 (2C) (15 × Ar ***C***H), 108.04 (O_3***C***Ph), 79.77, 77.40, 71.95 (3 × Ins ***C***H), 71.76, 71.49 (2 × O***C***H_2Ph), 70.46, 70.38 (2 × Ins ***C***H) ppm; HRMS (CI^+) *m/z* (%) found $[M+H]^+$ 445.1666 (100), $C_{27}H_{25}O_6$ requires 445.1651.

2,6-*O*-Dibenzyl-4-*C*-methyl-*myo*-inositol 1,3,5-*O*-orthobenzoate (10). Crude 2,6-*O*-Dibenzyl-inos-4-ose 1,3,5-*O*-orthobenzoate (1.00 g, 2.25 mmol) was evaporated from MeCN (3 × 4 mL), taken up in diethyl ether (10 mL) and cooled to –78 °C. Methylmagnesium bromide (3 M in ether, 0.9 mL, 2.7 mmol) was added drop-wise and the solution stirred for 30 min before warming to rt. After 3 h the reaction was quenched by slow addition of H_2O and extracted with CH_2Cl_2 (× 2). The organic layers were washed with 0.1 M HCl, sat. $NaHCO_3$ and brine, before drying ($MgSO_4$) and evaporating to dryness under reduced pressure. The crude material (0.98 g) was fractionated by chromatography on flash silica. Elution with ether-hexane (1:9 → 4:6 v/v) afforded **10**

(0.53 g, 77 % over 2 steps) as a clear oil; R_f (hexane-ether, 3:7 v/v) 0.69; ν_{max} (film)/cm^{-1} 3478, 3064, 3032, 2927, 1723, 1496 and 1455; δ_H (400 MHz, $CDCl_3$) 7.68-7.66 (2H, m), 7.46-7.34 (11H, m) 7.24-7.22 (2H, m) (15 × Ar ***H***), 4.82 (1H, d, *J* 12.5, 2-OC***H***HPh), 4.69 (1H, d, *J* 12.5, 2-OC***H***HPh), 4.63 (1H, d, *J* 11.6, 6-OC***H***HPh), 4.57 (1H, d, *J* 11.6, 6-OC***H***HPh), 4.53 (1H, t, *J* 3.9, Ins 6-***H***), 4.46 (1H, dq, *J* 3.6, 1.7, Ins 1-***H***), 4.32 (1H, bs, Ins 4-O***H***), 4.19 (1H, dt, *J* 3.7, 1.8, Ins 3-***H***), 4.04 (1H, dt, *J* 3.8, 1.9, Ins 5-***H***), 4.01 (1H, t, *J* 1.8, Ins 2-***H***), 1.67 (3H, s, Ins 4-C***H₃***) ppm; δ_C (100 MHz, $CDCl_3$) 137.89, 136.94, 135.67 (3 × Ar ***C***), 129.44, 128.84 (2C), 128.75, 128.51 (2C), 128.10 (2C), 127.97 (2C), 127.93 (3C), 127.88, 125.35 (15 × Ar ***C***H), 107.31 (O$_3$***C***Ph), 77.29, 74.67 (2 × Ins ***C***H), 72.96 (O***C***H$_2$Ph), 72.89 (Ins ***C***H), 71.04 (O***C***H$_2$Ph), 70.66 (Ins ***C***H), 69.58 (Ins ***C***), 66.20 (Ins ***C***H), 24.27 (Ins 4-***C***H$_3$) ppm; HRMS (ESI+) *m/z* (%) found $[M+H]^+$ 461.1959 (100), $C_{28}H_{29}O_6$ requires 461.1964.

1,3,4,5-O-Tetraacetyl-2,6-O-dibenzyl-4-C-methyl-*myo*-inositol. 2,6-*O*-Dibenzyl-4-*C*-methyl-*myo*-inositol (**14**, 60 mg, 0.16 mmol) and DMAP (2 mg, 0.02 mmol) were evaporated from pyridine (3 × 1 mL) and taken up in CH_2Cl_2 (1 mL). Acetic anhydride (127 µL, 1.28 mmol) and triethylamine (267 µL, 1.92 mmol) were added and the reaction mixture stirred for 2 h. The reaction was quenched by drop-wise addition of H_2O (0.5 mL) and stirred for a further 30 min before it was diluted with CH_2Cl_2, washed with H_2O, then brine, dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude material was fractionated by chromatography on flash silica. Elution with EtOAc-hexane (0:1 → 7:10 v/v) afforded the *title compound* (45 mg, 52 %) as a colourless oil; R_f (EtOAc) 0.90; δ_H (400 MHz, $CDCl_3$) 7.41-7.25 (10H, m, 10 × Ar ***H***), 6.14 (1H, d, *J* 3.6 Ins 3-***H***), 6.03 (1H, d, *J* 9.6, Ins 5-***H***), 5.09 (1H, dd, *J* 11.2, 2.8, Ins 1-***H***), 4.72-4.61 (4H, m, 2 × OC***H***$_2$Ph), 4.18 (1H, t, *J* 3.2, Ins 2-***H***), 3.99 (1H, t, *J* 10.0, Ins 6-***H***), 2.08 (3H, s), 2.02 (3H, s), 1.96 (3H, s), 1.91 (3H, s) (4 × OCO***Me***), 1.59 (3H, s, Ins 4-***Me***) ppm; δ_C (100 MHz, $CDCl_3$) 170.31, 169.70, 169.58, 169.35 (4 × O***C***OMe), 138.24, 137.99 (2 × Ar ***C***), 128.39 (2C), 128.33 (2C), 127.83, 127.64 (2C), 127.56, 127.25 (2C) (10 × Ar ***C***H), 84.52 (Ins 4-***C***), 76.77, 76.21 (2 × Ins ***C***H), 75.55, 74.97 (2 × O***C***H$_2$Ph), 72.86, 72.48, 70.32 (3 × Ins ***C***H), 22.33, 20.78, 20.74, 20.71 (4 × OCO***Me***), 17.42 (Ins 4-C***Me***) ppm.

$^{45}Ca^{2+}$ Flux Assay. L15 cells were obtained by stable exogenous expression of IP_3R1 in L fibroblasts.[19] The cells were cultured in Dulbecco's modified Eagle's medium supplemented with 10% foetal calf serum, 3.8 mM L-glutamine, 0.9% (v/v) non-essential amino acids, 85 IU/mL penicillin, 85 µg/mL streptomycin, and 20 mM HEPES, pH 7.4. $^{45}Ca^{2+}$ fluxes were performed on saponin-permeabilized cells.[20] The cells were seeded in 12-well clusters (*Costar*, Cambridge, MA) at a density of approximately 4 x 10^4 cm^2. Experiments were carried out on confluent monolayers of cells at the seventh day after plating. The cells were permeabilized by incubating them for 10 min with a solution containing 120 mM KCl, 30 mM imidazole hydrochloride, pH 6.8, 2 mM $MgCl_2$, 1 mM ATP, 1 mM EGTA, and 40 µg/mL saponin at 30 °C. The non-mitochondrial Ca^{2+} stores were loaded for 45 min at 30 °C in 120 mM KCl, 30 mM imidazole hydrochloride, pH 6.8, 5 mM $MgCl_2$, 5 mM ATP, 0.44 mM EGTA, 10 mM NaN_3, and 150 nM free $^{45}Ca^{2+}$ (28 µCi/mL). The cells were then washed twice with 1 mL of efflux medium containing 120 mM KCl, 30 mM imidazole hydrochloride, pH 6.8, 1 mM EGTA, and 10 µM thapsigargin. The efflux medium was replaced every 2 min, and the efflux was performed at 30 °C. At the end of the experiment, the $^{45}Ca^{2+}$ remaining in the stores was released by incubation with 1 mL of a 2 % sodium dodecyl sulfate solution for 30 min. Ca^{2+} release is plotted as the fractional loss (*i.e.*, the amount of Ca^{2+} released in 2 min divided by the total store Ca^{2+} content at that time). The latter value was calculated by summing in retrograde order the amount of tracer remaining in the cells at the end of the efflux and the amounts of tracer collected during the successive time intervals. The Ca^{2+} release provoked by IP_3 and 4-*C*-methyl IP_3 was normalized to the maximal releasable Ca^{2+}, measured by the addition of 10 µM A23187.