2,3-O-Cyclopentylidene-4,5-O-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-myo-inositol, 9. 2,3-O-Cyclopentylidene-1-O-tert-butyldiphenylsilyl-4,5-O-
(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-myo-inositol. 9. 2,3-
O-Cyclopentylidene-1-O-tetraethylpiperidin-4-yl-1,3-dioxan-2-yl)ethyl]oxy[(2-
cyanoethyloxy)phosphoryl]-2,3-
O-cyclopentylidene-4,5-O-
(xanthan-9-yldiene)-6-O-[(4-chlorophenyl)-4-ethoxy-
pyridin-4-yl]-myo-inositol, 18a. Dicyanoethyl phosphate 6 (2.0 g, 2.4 mmol) was taken up in MeCN-Et$_2$N (2:1 v/v; 30 mL) and stirred at rt for 16 h. The solution was evaporated under reduced pressure and the residue was re-evaporated from pyridine (3 × 10 mL). The residue was dissolved in MeCN (1.3 mL) and to this was added N-methylimidazolide (1.91 mL, 24 mmol, 10 eq.), followed by 3-(2,5,5-trimethyl-
1,3-dioxan-2-yl)ethan-1-ol (945 mg, 5.4 mmol, 2.3 eq.). A solution of mesitylene sulfonyl chloride (2.6 g, 12 mmol, 5 eq.) in pyridine (3.25 mL) was added drop-wise to the reaction mixture over a period of 5 min. After 30 min water (0.5 mL) was added and the solution concentrated under reduced pressure. The residue was dissolved in EtOAc (100 mL), washed with sat. NaHCO$_3$ (2 × 20 mL) and the aqueous washings were back-extracted with EtOAc (2 × 10 mL). The combined organic layers were dried (MgSO$_4$) and evaporated under reduced pressure. The residual oil was fractionated by MPLC (silica pre-treated with 1% pyridine-EtOAc) using a gradient of EtOAc-hexane (1:2 → 9:1 v/v) to afford the *title compound* as a colourless solid (0.24 g, 91%). TLC $R_t$ (EtOAc-hexane, 7:3 v/v) 0.40; $\delta_1$ (500 MHz, CDC$_13$) 7.69

**SUPPLEMENTARY INFORMATION**

2,3-O-Cyclopentylidene-4,5-O-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-myo-inositol, 8. 2,3-O-Cyclopentylidene-4,5-O-
(xanthan-9-yldiene)-6-O-[(4-chlorophenyl)-4-ethoxy-
pyridin-4-yl]-myo-inositol, 18a. Dicyanoethyl phosphate 6 (2.0 g, 2.4 mmol) was taken up in MeCN-Et$_2$N (2:1 v/v; 30 mL) and stirred at rt for 16 h. The solution was evaporated under reduced pressure and the residue was re-evaporated from pyridine (3 × 10 mL). The residue was dissolved in MeCN (1.3 mL) and to this was added N-methylimidazolide (1.91 mL, 24 mmol, 10 eq.), followed by 3-(2,5,5-trimethyl-
1,3-dioxan-2-yl)ethan-1-ol (945 mg, 5.4 mmol, 2.3 eq.). A solution of mesitylene sulfonyl chloride (2.6 g, 12 mmol, 5 eq.) in pyridine (3.25 mL) was added drop-wise to the reaction mixture over a period of 5 min. After 30 min water (0.5 mL) was added and the solution concentrated under reduced pressure. The residue was dissolved in EtOAc (100 mL), washed with sat. NaHCO$_3$ (2 × 20 mL) and the aqueous washings were back-extracted with EtOAc (2 × 10 mL). The combined organic layers were dried (MgSO$_4$) and evaporated under reduced pressure. The residual oil was fractionated by MPLC (silica pre-treated with 1% pyridine-EtOAc) using a gradient of EtOAc-hexane (1:2 → 9:1 v/v) to afford the *title compound* as a colourless solid (0.24 g, 91%). TLC $R_t$ (EtOAc-hexane, 7:3 v/v) 0.40; $\delta_1$ (500 MHz, CDC$_13$) 7.69

1-O-tetraethylpiperidin-4-yl)-1,3-dioxan-2-yl)ethyl]oxy[2-
cyanoethyloxy)phosphoryl]-2,3-O-cyclopentylidene-4,5-O-
(xanthan-9-yldiene)-6-O-[(4-chlorophenyl)-4-ethoxy-
pyridin-4-yl]-myo-inositol, 18a. Dicyanoethyl phosphate 6 (2.0 g, 2.4 mmol) was taken up in MeCN-Et$_2$N (2:1 v/v; 30 mL) and stirred at rt for 16 h. The solution was evaporated under reduced pressure and the residue was re-evaporated from pyridine (3 × 10 mL). The residue was dissolved in MeCN (1.3 mL) and to this was added N-methylimidazolide (1.91 mL, 24 mmol, 10 eq.), followed by 3-(2,5,5-trimethyl-
1,3-dioxan-2-yl)ethan-1-ol (945 mg, 5.4 mmol, 2.3 eq.). A solution of mesitylene sulfonyl chloride (2.6 g, 12 mmol, 5 eq.) in pyridine (3.25 mL) was added drop-wise to the reaction mixture over a period of 5 min. After 30 min water (0.5 mL) was added and the solution concentrated under reduced pressure. The residue was dissolved in EtOAc (100 mL), washed with sat. NaHCO$_3$ (2 × 20 mL) and the aqueous washings were back-extracted with EtOAc (2 × 10 mL). The combined organic layers were dried (MgSO$_4$) and evaporated under reduced pressure. The residual oil was fractionated by MPLC (silica pre-treated with 1% pyridine-EtOAc) using a gradient of EtOAc-hexane (1:2 → 9:1 v/v) to afford the *title compound* as a colourless solid (0.24 g, 91%). TLC $R_t$ (EtOAc-hexane, 7:3 v/v) 0.40; $\delta_1$ (500 MHz, CDC$_13$) 7.69
15. 7.64 (1H, dd, J 7.8, 1.8), 7.47-7.43 (2H, m), 7.30-7.26 (3H, m), 7.23 (1H, t, J 7.6) (8 × Ar H), 7.19 (2H, d, J 9.0), 6.81 (2H, d, J 8.9) (N-C6H4Cl), 4.76-4.70 (2H, m), 4.67-4.64 (1H, m), 4.57 (1H, m), 4.50 (1H, bt, J 7.4) (5 × Ins H), 4.46-4.25 (4H, m, 2 × POCH2), 4.08 (1H, m, Ins H), 3.63-3.54 [3H, m, OCH3Me + (2 × OCH2CH2Me)], 3.53 (1H, m, OCH3Me), 3.42-3.38 (2H, m, 2 × OCH2CH2Me), 3.35-3.30 (1H, m), 3.22-3.17 (2H, m), 3.04-2.99 (1H, m) (CH2NCH2), 2.85-2.75 (2H, m, CH2CN), 2.26-2.18 (2H, m, POCH2-dioxan), 2.12-1.90 (6H, m), 1.78-1.68 (6H, m) (6 × CH3). The crude residue was re-evaporated from pyridine (3 × v/v) then MeOH-EtOAc (0:1 v/v) to afford the title compound as a colourless solid (1.28 g, 77%). TLC Rf (EtOAc-hexane, 9:1 v/v) 0.35; δH (400 MHz, CDCl3) 7.20 (1H, d, J 8.8), 7.19 (1H, d, J 8.9), 6.86 (1H, d, J 9.0), 6.85 (1H, d, J 9.0) (N-C6H4Cl), 4.91 (0.5H, d, J 1.7) (5-CH2), 4.89 (0.5H, d, J 1.3) (5-CH2), 4.59-4.53 (1H, m, Ins H), 4.45 (0.5H, dd, J 5.5, 4.0), 4.42 (0.5H, dd, J 5.2, 4.2) (Ins H), 3.43-4.12 [5H, m, (2 × POCH2) + Ins 6-H], 4.06 (0.5H, t, J 5.2), 4.04 (0.5H, t, J 5.2) (Ins 3-H), 3.78 (1H, bt, J 8.4, 4-H), 3.76-3.69 (1H, m, OCH3Me), 3.64-3.55 [3H, m, OCH3Me + (2 × OCH2CH2Me)], 3.42-3.29 [5H, m, (2 × NCH2CH2) + (2 × OCH2CH2Me)] + Ins 5-H, 3.23-3.16 (1H, m), 3.14-3.05 (1H, m) (2 × NCH3), 3.00 (1H, bs, 4-CH2), 2.75 (1H, t, J 6.5), 2.72-2.59 (1H, m) (CH2CN), 2.12-1.93 (8H, m), 1.82-1.58 (6H, m) (7 × CH2), 1.38 (1.5H, s), 1.36 (1.5H, s) (dioxan-2-CH2), 1.25 (3H, t, J 7.0, OCH3Me), 1.03 (1.5H, s), 1.02 (1.5H, s), 0.83 (1.5H, s), 0.82 (1.5H, s) (Me2CH2) ppm; δC (125 MHz, CDCl3) 149.45 (0.5C), 149.32 (0.5C) (Ar C), 128.99, 128.96 (2 × Ar CH), 124.28 (0.5C), 124.24 (0.5C) (Ar C), 121.0 (acetel C), 117.2, 117.0 (2C) (4 × Ar CH), 142.4 (2H, C), 142.3 (3C, 2 × Ar CH), 122.64, 122.58 (2 × Ar C), 121.26 (0.5C), 121.21 (0.5C) (acetel C), 78.5, 73.88-73.78 (m, 3 × Ins CH), 70.99 (0.5C), 70.82 (0.5C) (acetelene C), 76.3, 76.0 (0.5C), 75.6, 75.38-75.34 (m, 3 × CH), 19.62-19.56 (m, CH3CN), 19.67-19.56 (m, 1H, Ins H), 15.0 (Me) ppm; LRMS (ESI+) m/z (% [M+Na]+ 869 (11), [M+H]+ 847 (100), [M-OEt]+ 801 (30), [M-C6H4ClCINO] 610 (30).

1-O-[3-(2,5,5-Trityl-1,1-dioxan-2-yl)ethoxy][2-cyclooctanyloxy]phosphoryl]-2,3-O-cyclopentylidene-6-O-[1-(4-chlorophenyl)-4-ethoxypiperidin-4-yl]-myo-inositol, 19a.

TFA-DCM (1:9 v/v, 4.7 mL, 3 eq.) was added to a solution of masked 3-oxobutyl phosphate 18a (2.00 g, 2.1 mmol) in pyrrole-DCM (1:9 v/v, 13.1 mL, 9 eq.). After 50 s the reaction was quenched with sat. NaHCO3 (100 mL) and extracted with CHCl3 (2 × 20 mL). The combined organic layers were dried (MgSO4) and concentrated under reduced pressure. The residual oil was fractionated by MPLC using a gradient of hexane-EtOAc (4:1 → 1:1 v/v) then MeOH-EtOAc (0:1→1:1 v/v) to afford the title compound as a colourless solid (1.28 g, 77%). TLC Rf (EtOAc-hexane, 9:1 v/v) 0.35; δH (400 MHz, CDCl3) 7.20 (1H, d, J 8.8), 7.19 (1H, d, J 8.9), 6.86 (1H, d, J 9.0), 6.85 (1H, d, J 9.0) (N-C6H4Cl), 4.91 (0.5H, d, J 1.7), 4.89 (0.5H, d, J 1.3) (5-CH2), 4.59-4.53 (1H, m, Ins 1-H), 4.45 (0.5H, dd, J 5.5, 4.0), 4.42 (0.5H, dd, J 5.2, 4.2) (Ins 2-H), 3.43-4.12 [5H, m, (2 × POCH2) + Ins 6-H], 4.06 (0.5H, t, J 5.2), 4.04 (0.5H, t, J 5.2) (Ins 3-H), 3.78 (1H, bt, J 8.4, 4-H), 3.76-3.69 (1H, m, OCH3Me), 3.64-3.55 [3H, m, OCH3Me + (2 × OCH2CH2Me)], 3.42-3.29 [5H, m, (2 × NCH2CH2) + (2 × OCH2CH2Me)] + Ins 5-H, 3.23-3.16 (1H, m), 3.14-3.05 (1H, m) (2 × NCH3), 3.00 (1H, bs, 4-CH2), 2.75 (1H, t, J 6.5), 2.72-2.59 (1H, m) (CH2CN), 2.12-1.93 (8H, m), 1.82-1.58 (6H, m) (7 × CH2), 1.38 (1.5H, s), 1.36 (1.5H, s) (dioxan-2-CH2), 1.25 (3H, t, J 7.0, OCH3Me), 1.03 (1.5H, s), 1.02 (1.5H, s), 0.83 (1.5H, s), 0.82 (1.5H, s) (Me2CH2) ppm; δC (125 MHz, CDCl3) 149.45 (0.5C), 149.32 (0.5C) (Ar C), 128.99, 128.96 (2 × Ar CH), 124.28 (0.5C), 124.24 (0.5C) (Ar C), 121.0 (acetel C), 117.2, 117.0 (2C) (4 × Ar CH), 142.4 (2H, C), 142.3 (3C, 2 × Ar CH), 122.64, 122.58 (2 × Ar C), 121.26 (0.5C), 121.21 (0.5C) (acetel C), 77.3, 75.81 (0.5C), 75.76 (0.5C), 74.37 (0.5C), 74.30 (0.5C), 73.69-73.52 (3C, m) (6 × Ins CH), 70.3 (OCH2CH2CH2O), 64.68 (0.5C, d, J 4.9), 64.52 (0.5C, d, J 5.3), 61.86 (0.5C, d, J 4.9),
1-O-(But-3-yn-3-yl[2-cyanoethoxy)phosphoryl]-2,3-
O-cyclopentylidene-6-O-[1-(4-chlorophenyl)-4-ethoxy-
piperidin-4-yl]-myo-inositol, 19b. TFA-DCM (1:9 v/v, 4.4 mL, 3 eq.) was added to a solution butylnyl phosphate 18b (1.15 g, 1.36 mmol) in pyrrole-DCM (1:9 v/v, 12.3 mL, 9 eq.) After 50 s the reaction was quenched with sat. NaHCO₃ (100 mL) and extracted with CHCl₃ (3 × 20 mL). The combined organic layers were dried (MgSO₄) and concentrated under reduced pressure. The residual oil was fractionated by MPLC using a gradient of MeOH–EtOAc (0:1 → 1:9 v/v) to afford the title compound as a colourless oil (308 mg, 70%). TLC R₅ (MeOH–EtOAc, 8:92 v/v) 0.58; δₛ (400 MHz, CDCl₃) 7.20 (2H, d, J 8.7), 6.89 (1H, d, J 8.5), 6.87 (1H, d, J 8.5) (N-C₆H₄Cl), 4.97 (1H, bd, J 8.7, 4.6), 4.47 (1H, t, J 4.0) (3 × Ins H), 4.30-4.13 (5H, m, 2 × POCH₃ + Ins H), 4.07 (1H, dt J 7.7, 5.1, Ins H), 3.81-3.73 (2H, OCH₂Me + Ins H), 3.66-3.59 (1H, quin, J 7.0, OCH₂CH₃), 3.34-3.31 (3H, m, 2 × NHCH₃ + Off), 3.23-3.19 (1H, m), 3.16-3.08 (1H, m, (2 × NCH₂H) ppm; δp (100 MHz, CDCl₃) 149.33 (0.5C), 149.29 (0.5C) ppm; δₛ (Ar, 95) 129.0 (2 × Ar CH), 124.28 (0.5), 124.23 (0.5C) (Ar, C), 120.1 (acetel C) 117.6 (2 × Ar CH), 116.35 (0.5C), 116.23 (0.5C) (CN), 100.2 (acetel C), 79.18 (0.5C), 79.10 (0.5C) (acetyl C), 77.33 (0.5C), 77.30 (0.5C), 76.05 (0.5C), 75.99 (0.5C), 74.2, 73.8, 73.54-73.46 (2C, m) (6 × Ins CH), 70.7 (acetylen C), 65.88 (0.5C, d, J 5.7), 65.73 (0.5C, d, J 5.7), 62.10 (0.5C, d, J 4.8), 61.97 (0.5C, d, J 4.8) (2 × POCH₃), 56.7 (OCH₃Me), 46.6, 46.39 (0.5C), 46.29 (0.5C) (CH₂NCH₂), 37.19, 37.06, 33.4, 32.96 (0.5C), 32.91 (0.5C), 23.8, 23.4 (6 × CH₂), 20.53-20.45 (m, CH₂CC), 19.49-19.42 (m, CH₂CN), 14.9 (Me) ppm; δ₝ (162 MHz, CDCl₃) -2.65 (0.5P), -2.76 (0.5P) ppm; LRMS (EI+) m/z (%) [M+H]+ 668.9 [100], [M-OEt]+ 610 (10).

1-O-[3-(2,5,5-Trimethyl-1,3-dioxan-2-yl)ethoxy[2-
cyanoethoxy]phosphoryl]-2,3-O-cyclopentylidene-4,5-O-bis[di(2-cyanoethoxy)phosphoryl]-6-O-[1-(4-
chlorophenyl)-4-ethoxy-piperidin-4-yl]-myo-inositol, 20a. Masked 3-oxobut-1-yl diol 19a (300 mg, 0.39 mmol) was evaporated from pyridine (3 × 5 mL) and the residue was redissolved in pyridine (0.8 mL) and MeCN (2.5 mL). To this was added N-methylimidazole (0.37 mL, 4.7 mmol, 12 eq.), followed by crude (CneO₂P)Cl (11, 521 mg, ca. 1.55 mmol, 4 eq.) in MeCN (1 mL). After 30 min the reaction was quenched with 3-hydroxypropionitrile (0.32 mL, 4.7 mmol, 12 eq.) and stirred for 15 min. The solvent was stripped off, the residue re-dissolved in MeCN (3 mL) and the solution cooled to 0°C. tert-Butyl hydroperoxide (5M in hexane, 1.24 mL, 6.2 mmol) was added, the mixture allowed to warm to rt and it was stirred for 2.5 h. The solution was diluted with water until turbidity appeared and fractionated through a column of silanised silica, eluting with a gradient of water-MeCN (1:0 → 0:1 v/v). The appropriate fractions were combined and the MeCN evaporated under reduced pressure. The resulting aqueous suspension was saturated with NaCl and extracted with CHCl₃ (× 3). The organic phase was dried (Na₂SO₄) and the solvent stripped off. The residual oil was fractionated by MPLC using a gradient of MeOH-DCM (0:1 → 5:9 v/v) to afford the title compound as a colourless oil (308 mg, 70%). TLC R₅ (MeOH–EtOAc, 8:92 v/v) 0.58; δₛ (400 MHz, CDCl₃) 7.20 (2H, d, J 8.7), 6.85 (2H, d, J 8.9) (N-C₆H₄Cl), 4.91-4.82 (2H, m), 4.64-4.58 (2H, m), 4.51 (0.5H, dd, J 4.2, 2.3), 4.49 (0.5H, dd, J 4.1, 2.6) (5 × Ins H), 4.43-4.27 (13H, m, (6 × POCH₃) + Ins H), 3.62-3.50 (4H, m, OCH₂Me + (2 × OCH₂CH₂Me)), 3.40-3.31 (4H, m, (2 × OCH₂CH₂Me) + (2 × NCH₂H) ppm; 3.16-3.03 (2H, m, 2 × NCH₂H), 2.90-2.74 (10H, 5 × CH₃CN), 2.15 (2H, t, J 7.4, POCH₂CH₂-dioxan), 2.11-1.82 (6H, m), 1.80-1.66 (6H, m) (6 × CH₂), 1.415 (1.5H, s), 1.412 (1.5H, s) (dioxan 2-Me), 1.28 (3H, t, J 7.0, OCH₃Me), 1.04 (1.5H, s), 1.03 (1.5H, s), 0.849 (1.5H, s), 0.848 (1.5H, s) (CMEO₂) ppm; δp (100 MHz, CDCl₃) 149.2 (Ar C), 129.0 (2 × Ar CH), 124.4 (Ar C), 120.8 (acetel C), 117.6 (2 × Ar CH), 117.09-116.50 (5, 5 × CN), 101.3, 97.5 (2 × acetel C), 81.60-81.29 (2C, m), 74.58 (0.5C), 74.50 (0.5C), 72.47-72.27 (2C, m), 70.8 (6 × Ins CH), 70.3 (OCH₂CH₂CH₂O), 65.08 (0.5C, d, J 6.5), 64.93 (0.5C, d, J 4.8), 63.21-63.14 (13m, m), 62.82-62.72 (2C, m), 62.5 (d, J 5.0), 62.25-62.16 (6m, 6 × POCH₃), 57.0 (OCH₃Me), 46.9, 46.6 (CH₂CH₂N), 39.46 (0.5C, d, J 6.5), 39.28 (0.5C, d, J 6.2), 36.2, 35.83 (0.5C), 35.78 (0.5C), 33.4, 33.0 (5 × CH₂), 29.9 (CMEO₂), 24.7, 23.9 (2 × CH₂), 22.9, 22.36 (0.5C), 22.33 (0.5C), 20.10 (0.5C) (3 × Me), 19.67-19.51 (m, 5 × CH₂CN), 15.1 (OCH₂Me) ppm; δₛ (162 MHz, CDCl₃) -2.66 (0.5P), -2.83 (0.5P), -3.48 (0.5P), -3.60 (0.5P), -3.71 (0.5P), -3.75 (0.5P) ppm; LRMS (EI+) m/z (%) [M+H]+ 1145.3549 (100), C₈H₁₀O₃N₄O₃P requires 1145.3670, [M+Na]+ 1167.3403 (70), [M-OEt]+ 1099.3141 (4) (C₈H₁₀O₃N₄O₃P requires 1109.2846 (12).
turbidity appeared and fractionated through a column of silanised silica, eluting with a gradient of water-MeCN (1:0 → 0:1 v/v). The appropriate fractions were combined and the MeCN evaporated under reduced pressure. The resulting aqueous suspension was saturated with NaCl and extracted with CHCl₃ (× 3). The organic phase was dried (Na₂SO₄) and the solvent stripped off. The residual oil was fractionated by MPLC using a gradient of MeOH-DCM (0:1 → 5:95 v/v) to afford the title compound as a colourless oil (270 mg, 77%).

TLC Rf (MeOH-DCM, 1:9 v/v) 0.38; δₕ (400 MHz, CDCl₃) 7.21 (2H, d, J 9.0), 6.86 (2H, d, J 8.9) (N-C₆H₅Cl), 4.97 (1H, bd, J 8.7), 4.96-4.86 (2H, m), 4.64-4.40 (2H, m), 4.54-4.50 (1H, m) (5 × Ins H), 4.45-4.31 [11H, m, (5 × POCH₂CH₂CN) + Ins H], 4.29-4.21 (2H, m, POCH₂CH₂CH₃), 3.63-3.52 (2H, m, OCH₃Me), 3.41-3.30 (2H, m), 3.17-3.05 (2H, m) (CH₂NCH₂), 2.87-2.80 (5 × CH₂CN), 2.66 (1H, td, J 6.4, 2.6), 2.65 (1H, td, J 6.8, 2.6) (CH₂CC), 2.12 (0.5H, t, J 2.8), 2.11 (0.5H, t, J 2.8) (CC), 2.07-2.00 (4H, m), 1.97-1.84 (2H, m), 1.82-1.70 (6H, m) (6 × CH₂), 1.30 (3H, t, J 7.0, OCH₃Me) ppm; δ (100 MHz, CDCl₃) 149.0 (Ar C), 128.9 (2 × Ar CH), 124.3 (Ar C), 120.7 (acetal C), 117.5 (2 × Ar CH), 91.91-91.66 (5 × C), 101.3 (acetal C), 81.42-82.12 (m, 2 × Ins CH), 79.2 (0.5C), 79.0 (0.5C) (acetylene C), 74.32 (0.5C), 74.23 (0.5C), 72.39-72.27 (m), 72.10 (0.5C), 72.06 (0.5C), 70.65, 70.55 [4 × Ins CH] + acetylene CH, 66.04-65.99 (m), 63.04-63.00 (m), 62.70-62.61 (2C, m), 62.37-62.27 (2C, m) (6 × POCH₂), 56.9 (OCH₃Me), 46.8, 46.5 (CH₂NCH₂), 35.94 (0.5C), 35.89 (0.5C), 35.69 (0.5C), 35.61 (0.5C), 33.3, 32.8, 23.8, 22.9 (6 × CH₂), 20.47-20.34 (m, 2 × CH₂CC), 19.47-19.40 (m, 5 × CH₂CN), 15.0 (Me) ppm; δ (162 MHz, CDCl₃) -3.09 (0.5P), -3.91 (1P), -3.54 (0.5P), -3.71 (1P) ppm; LRMS (ESI+) m/z (%) [M+Na]⁺ 1063.2 (83), [M+H]⁺ 1040.9 (100).

1-O-(But-3-ynyloxyphosphoryl)-myo-inositol 4,5-O-bisphosphate, 21. The fully protected butynyl InsP₂ 20b (180 mg, 0.17 mmol) was evaporated from MeCN (3 × 2 mL) and re-dissolved in MeCN (1.5 mL). TmsCl (0.44 mL, 3.5 mmol, 20 eq.) was added followed by Barton’s base (0.50 mL, 4.3 mmol, 25 eq). The reaction was stirred at rt for 1 h, then the solvent was evaporated under reduced pressure and the residue was evaporated from MeCN (3 × 5 mL). The resulting mixture was triturated with Et₂O under argon. The filtrate was evaporated to dryness and taken up in 1M methanolic ammonia (3 mL). The solution was evaporated under reduced pressure and the residue was dissolved in 80% acetic acid (10 mL). After 5 h, the solvent was stripped off under reduced pressure and the residue re-evaporated from EtOH (3 × 10 mL). The solids were triturated with DCM and then with MeCN to give the title compound as an amorphous colourless solid (69 mg, 83%). δ (400 MHz, CDCl₃) 4.13 (1H, t, J 1.3, Ins 2-H), 4.11 (1H, q, J 9.3, Ins H), 3.91-3.79 (4H, m, (2 × Ins H) + POCH₂), 3.72 (1H, t, J 9.6, Ins H), 3.55 (1H, dd, J 9.8, 2.6, Ins 1-H), 2.40 (2H, t, J 6.3, 2.6, CH₂CC), 2.26 (1H, t, J 2.6, CC) ppm; δ (100 MHz, CDCl₃) 82.0 (acetylene C), 78.2 (b), 76.7 (b), 75.6 (d, J 5.2), 70.9 (d, J 4.3), 70.62 (2C), 70.43 [6 × Ins CH] + acetylene CH, 63.8 (d, J 5.0, POCH₂), 20.1 (d, J 7.8, CH₂CC) ppm; δ (162 MHz, CDCl₃) -3.06 (2P), -3.27 ppm; HRMS (ESI+) m/z (%) found [M+H]⁺ 470.9870 (100), C₁₀H₁₄O₃P₂ requires 470.9859, [M+Na-H]⁻ 492.9682 (78), [M-H₂PO₃]⁻ 391.0207 (58).

1-O-(But-3-ynyloxyphosphoryl)-myo-inositol 4,5-O-bisphosphorothioate, 23. The fully protected butynyl InsP(S)₂ 22 (198 mg, 0.18 mmol) was evaporated from MeCN (3 × 2 mL) and re-dissolved in MeCN (1.6 mL). TmsCl (0.46 mL, 3.7 mmol, 20 eq.) was added followed by Barton’s base (0.54 mL, 4.6 mmol, 25 eq). The reaction was stirred at rt for 16 h, then the solvent was evaporated under reduced pressure and the residue was evaporated from MeCN (3 × 5 mL). The resulting mixture was triturated with Et₂O under argon. The filtrate was evaporated to dryness and taken up in 1M methanolic ammonia (3 mL). The solution was evaporated under reduced pressure and the residue was dissolved in 80% acetic acid (10 mL). After 5 h, the solvent was stripped off under reduced pressure and the residue re-evaporated from EtOH (3 × 10 mL). The solids were triturated with DCM and then with MeCN to give the title compound as an amorphous colourless solid (69 mg, 83%). δ (400 MHz, CDCl₃) 4.13 (1H, t, J 1.3, Ins 2-H), 4.11 (1H, q, J 9.3, Ins H), 3.91-3.79 (4H, m, (2 × Ins H) + POCH₂), 3.72 (1H, t, J 9.6, Ins H), 3.55 (1H, dd, J 9.8, 2.6, Ins 1-H), 2.40 (2H, t, J 6.3, 2.6, CH₂CC), 2.26 (1H, t, J 2.6, CC) ppm; δ (100 MHz, CDCl₃) 82.0 (acetylene C), 78.2 (b), 76.7 (b), 75.6 (d, J 5.2), 70.9 (d, J 4.3), 70.62 (2C), 70.43 [6 × Ins CH] + acetylene CH, 63.8 (d, J 5.0, POCH₂), 20.1 (d, J 7.8, CH₂CC) ppm; δ (162 MHz, CDCl₃) -3.06 (2P), -3.27 ppm; HRMS (ESI+) m/z (%) found [M+H]⁺ 1073.2245 (100), C₁₂H₁₆Cl₂N₂O₃P₂S₂ requires 1073.2276.
pressure. The residue was evaporated from MeCN (3 × 6 mL) and triturated with Et₂O under argon. The filtrate was evaporated to dryness and taken up in 1M methanolic ammonia (3 mL). The solution was evaporated under reduced pressure and the residue was dissolved in 80% acetic acid (10 mL). After 3 h, the solvent was stripped off under reduced pressure and the residue re-evaporated from EtOH (3 × 10 mL). The solids were triturated with DCM and then with MeCN to give the title compound as an off-white amorphous solid (74 mg, 82%). δ_H (400 MHz, CDCl₃) 4.45 (1H, q, J 10.1, Ins H), 4.23 (1H, t, J 2.6, Ins 2-H), 4.19 (1H, q, J 10.3, Ins H), 3.99-3.90 (3H, m, Ins H + POCH₂), 3.86 (1H, t, J 9.6, Ins H), 3.67 (1H, dd, J 9.8, 2.6, Ins 1-H), 2.49 (2H, td, J 6.3, 2.5, CH₂CC), 2.35 (1H, t, J 2.5, CCH) ppm; δ_C (100 MHz, CDCl₃) 82.0 (acycetylene C), 78.5 (b), 76.7 (b), 75.6 (d, J 6.0), 71.1 (d, J 3.9), 70.75, 70.66, 70.54 [(6 × Ins CH) + acetylene CH], 63.9 (d, J 5.1, POCH₂), 20.1 (d, J 8.3, CH₂CCH) ppm; δ_P (162 MHz, CDCl₃) 49.93 (2P), -0.62 (1P) ppm; HRMS (ESI-) m/z (%) found [M-H] - 502.9414 (45), C₁₀H₁₈O₁₅P₃S₂ requires 502.9402, [M-H 2PO₂S]- 407.0009 (100), [M+Na-H₂PO₂S]- 428.9803 (38), [M+Na-2H] - 524.9225 (31), [M+2Na-3H] - 546.9033 (22).
\[ 1^H-NMR \text{, expansion} \]
\[ \delta_H 3.7 - 5.5 \text{ ppm} \]

\[ 1^H-NMR \]
\[ (d_4-\text{AcOH-D}_2\text{O-CDCl}_3 \   4:2:1) \]

\[ 2 \times CH=CH \]

\[ 31^P-NMR \]
\[ (d_4-\text{AcOH-D}_2\text{O-CDCl}_3 \   4:2:1) \]

\[ 13^C-NMR \text{, expansion} \]
\[ \delta_C 60 - 82 \text{ ppm} \]

\[ 13^C-NMR \]
\[ (d_4-\text{AcOH-D}_2\text{O-CDCl}_3 \   4:2:1) \]
\[^{1}H\text{-NMR}\] (D$_2$O)

\[^{31}P\text{-NMR}\] (D$_2$O)

\[^{13}C\text{-NMR, expansion}\]
\[\delta: 63 - 83 \text{ ppm}\]

\[\delta: 19 - 21 \text{ ppm}\]

\[POCH_2\]

\[CH_2-C=\]

\[\text{POCH}_2\]

\[^{13}C\text{-NMR}\] (D$_2$O)

\[CH_2-C=\]
\[
\text{\textbf{\textsuperscript{1}H-NMR}} \quad \text{(D}_2\text{O)}
\]

\[
\text{\textbf{\textsuperscript{31}P-NMR}} \quad \text{(D}_2\text{O)}
\]

\[
\text{\textbf{\textsuperscript{13}C-NMR, expansion}}
\]

\[
\delta \text{ C = 63 – 83 ppm}
\]

\[
\delta \text{ C = 19.5 – 20.7 ppm}
\]