**L-1-*O*-Benzyl-*myo*-inositol (2b)**

L-1-*O*-Benzyl-2,3:5,6-di-*O*-cyclohexylidene-*myo*-inositol **(-)-1** (646mg, 1.5mmol) was allowed to react under the same condition as described for the preparation of **2a** to give **2b** (400mg, >99%). $^{1}$H NMR ($CD_3OD$) δ 3.03-3.22 (m, 3H), 3.52 (t, *J*=9.5 Hz, 1H), 3.66 (t, *J*=9.5 Hz, 1H), 4.07 (s, 1H), 4.55 (d, *J*=11.7 Hz, 1H), 7.15-7.35 (m, 5H). $^{13}$CNMR ($CD_3OD$) δ 70.8, 73.0, 73.2, 73.7, 74.1, 76.5, 81.1, 128.6, 129.1, 129.3, 139.9. IR (KBr) 3350, 2900, 1060, 1030 cm$^{-1}$. MS (EI) m/z 271 $(M+H)^+$. Anal.Calcd for $C_{13}H_{18}O_6$ : C, 57.77; H, 6.71. Found: C, 57.49; H, 6.75.

**L-1-*O*-Benzyl-2,3,4,5,6-penta-*O*-acetyl-*myo*-inositol (3b)**

**2b** (380mg, 1.4mmol) was allowed to react under the same condition as described for the preparation of **3a** to give **3b** (660mg, >99%). $^{1}$H NMR ($CDCl_3$) δ 1.99-2.01 (m, 12H), 2.20 (s, 3H), 3.60 (dd, *J*=10.1, 2.9 Hz, 1H), 4.40 (d, *J*=12.1 Hz), 4.66 (d, *J*=12.1 Hz, 1H), 4.94 (dd, *J*=15.5, 2.8 Hz, 1H), 5.08 (t, *J*=9.7 Hz, 1H), 5.39-5.52 (m, 2H), 5.76 (s, 1H), 7.22-7.34 (m, 5H). $^{13}$CNMR ($CDCl_3$) δ 20.5, 20.7, 20.8, 66.6, 69.1, 69.5, 70.9, 71.1, 71.8, 74.4, 127.8, 128.1, 128.5, 136.9, 169.6, 169.7, 169.8, 169.9, 170.0. IR (KBr) 2900, 1740, 1360, 1220, 1130 cm$^{-1}$. MS (EI) m/z 480 $(M+H)^+$. Anal.Calcd for $C_{23}H_{28}O_{11}$ : C, 57.50; H, 5.87. Found: C, 57.56; H, 5.91.

**L-2,3,4,5,6-Penta-*O*-acetyl-*myo*-inositol (4b)**

**3b** (620mg, 1.29mmol) was allowed to react under the same condition as described for the preparation of **4a** to give **4b** (490mg, 97%). $^{1}$H NMR ($CDCl_3$) δ 2.00 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.09 (s, 3H), 2.21 (s, 3H), 3.90 (dd, *J*=10.1, 2.9 Hz, 1H), 4.97 (dd, *J*=10.6, 2.7 Hz, 1H), 5.14 (t, *J*=9.7 Hz, 1H), 5.31 (t, *J*=9.9 Hz, 1H), 5.45 (t, *J*=10.1 Hz, 1H), 5.59 (t, *J*=2.9 Hz, 1H). $^{13}$CNMR ($CDCl_3$) δ 20.4, 20.5, 20.7, 20.8, 68.8, 69.2, 69.4, 70.5, 70.7, 72.5, 169.7, 169.8, 169.9, 170.2, 171.0. IR (KBr) 3400, 1740, 1370, 1220, 1030 cm$^{-1}$. MS (EI) m/z 391 $(M+H)^+$. Anal.Calcd for $C_{16}H_{22}O_{11}$-$2H_2O$:C, 48.12; H, 5.81. Found: C, 47.83; H, 5.58.

**L-2,3,6-Tri-*O*-acetyl-4,5-di-*O*-[bis(β-cyanoethyl)phosphoryl]-*myo*-inositol 1-[[(4,4'-Dimethoxytrityl)biotinyl-6-aminohexyl] (β-cyanoethyl)phosphate] (25b)**

**14b** (84mg, 0.12mmol) was allowed to react under the same condition as described for the preparation of **25a** to give **25b** (144mg, 83%). $^{1}$H NMR ($CDCl_3$) δ 1.36-1.67 (m, 14H), 2.03-2.29 (m, 11H), 2.43-2.45 (m, 1H), 2.70-2.82 (m, 10H), 3.07-3.20 (m, 3H), 3.79 (s, 6H), 4.02-4.29 (m, 15H), 4.67-4.81 (m, 3H), 5.22-5.26 (m, 1H), 5.49 (t, *J*=9.7

Hz, 1H), 5.63-5.73 (m, 2H), 5.99 (bs, 1H), 6.80 (d, *J*=8.4 Hz, 4H), 7.11-7.29 (m, 9H). IR (KBr) 2920, 1750, 1700, 1510, 1250, 1220, 1030 $cm^{-1}$.

**D-2,3,4,5,6-Penta-*O*-acetyl-*myo*-inositol**
**1-[[(4,4'-Dimethoxytrityl)biotinyl-6-aminohexyl] (β-cyanoethyl)phosphate] (26a)**

**4a** (258mg, 0.4mmol) was allowed to react under the same condition as described for the preparation of **25a** to give **26a** (133mg, 78%). $^1H$ NMR ($CDCl_3$) δ 1.22-1.66 (m, 14H), 1.96-2.27 (m, 18H), 2.42-2.47 (m, 1H), 2.67-2.71 (m, 2H), 3.05-3.18 (m, 3H), 3.79 (s, 6H), 4.01-4.30 (m, 6H), 4.68-4.74 (m, 1H), 5.05-5.22 (m, 2H), 5.44-5.52 (m, 2H), 5.71-5.76 (m, 2H), 5.97 (bs, 1H), 6.80 (d, *J*=8.8 Hz, 4H), 7.12-7.32 (m, 9H). IR (KBr) 2900, 1700, 1510, 1220, 1040 $cm^{-1}$. MS (FAB) m/z 1152 $(M+H)^+$.

**L-2,3,4,5,6-Penta-*O*-acetyl-*myo*-inositol**
**1-[[(4,4'-Dimethoxytrityl)biotinyl-6-aminohexyl](β-cyanoethyl)phosphate] (26b)**

**4b** (39mg, 0.1mmol) was allowed to react under the same condition as described for the preparation of **25a** to give **26b** (98mg, 85%). $^1H$ NMR ($CDCl_3$) δ 1.24-1.66 (m, 14H), 2.00-2.30 (m, 18H), 2.44 (d, *J*=12.8 Hz, 1H), 2.66-2.72 (m, 2H), 3.07-3.19 (m, 3H), 3.78 (s, 6H), 4.01-4.33 (m, 6H), 4.67-4.72 (m, 1H), 5.04-5.20 (m, 2H), 5.44-5.60 (m, 3H), 5.71 (s, 1H), 5.87-5.93 (m, 1H), 6.80 (d, *J*=8.8 Hz, 4H), 7.12-7.28 (m, 9H). IR (KBr) 2900, 1710, 1700, 1510, 1220, 1040 $cm^{-1}$.

**D-1,3,6-Tri-*O*-acetyl-4,5-di-*O*-[bis(β-cyanoethyl)phosphoryl]-*myo*-inositol**
**2-[[(4,4'-Dimethoxytrityl)biotinyl-6-aminohexyl] (β-cyanoethyl)phosphate] (27)**

**22a** (81mg, 0.12mmol) was allowed to react under the same condition as described for the preparation of **25a** to give **27** (173mg, 99%). $^1H$ NMR ($CDCl_3$) δ 1.24-1.87 (m, 14H), 2.03-2.19 (m, 11H), 2.42-2.46 (m, 1H), 2.70-2.78 (m, 8H), 2.95-3.23 (m, 5H), 3.79 (s, 6H), 4.08-4.30 (m, 15H), 4.66-5.05 (m, 4H), 5.50-5.67 (m, 2H), 6.04-6.22 (m, 2H), 6.80 (d, *J*=7.7 Hz, 4H), 7.11-7.28 (m, 9H). MS (EI) m/z 1440 $(M+H)^+$.

**1,3,4,5,6-Penta-*O*-acetyl-*myo*-inositol**
**2-[[(4,4'-Dimethoxytrityl)biotinyl-6-aminohexyl](β-cyanoethyl)phosphate] (28)**

**24a** (39mg, 0.1mmol) was allowed to react under the same condition as described for the preparation of **25a** to give **28** (59mg, 52%). $^1H$ NMR ($CDCl_3$) δ 1.20-1.74 (m, 14H), 2.02-2.46 (m, 19H), 2.81 (t, *J*=6.0 Hz, 2H), 3.08-3.20 (m, 3H), 3.79 (s, 5H), 4.16-4.34 (m, 6H), 5.02-5.24 (m, 4H), 5.48-5.54 (m, 4H), 5.90 (s, 1H), 6.80 (d, *J*=8.8 Hz, 4H), 7.12-7.28 (m, 9H). IR (KBr) 2920, 1750, 1500, 1220, 1030 $cm^{-1}$.

**L-1-*O*-[(Biotinyl-6-aminohexyl) hydrogen phosphoryl]-*myo*-inositol 4,5-bis(hydrogen phosphate) : Biotinylated L-*myo*-inositol 1,4,5-triphosphate.**

**25b** (135mg, 0.094mmol) was allowed to react under the same condition as described for the preparation of Biotinylated D-1,4,5-$IP_3$ to give the ammonium salts of Biotinylated L-1,4,5-$IP_3$ (27mg, 35%) as a white solid. $^1$H NMR ($D_2O$) δ 1.22-1.58 (m, 14H), 2.09 (t, *J*=7.1 Hz, 2H), 2.63 (d, *J*=13.0 Hz, 1H), 2.85 (dd, *J*=13.0, 4.9 Hz, 1H), 3.02 (d, *J*=6.6 Hz, 2H), 3.15-3.21 (m, 1H), 3.58 (d, *J*=8.1 Hz, 1H), 3.72-3.96 (m, 5H), 4.11-4.29 (m, 3H), 4.33-4.48 (m, 1H). $^{13}$CNMR ($D_2O$) δ 27.3, 27.9, 28.4, 30.3, 30.5, 30.9, 32.4, 38.2, 41.9, 42.3, 58.0, 62.9, 64.7, 69.1, 72.8, 73.4, 73.5, 78.2, 79.7, 81.1, 168.0, 179.3. IR (KBr) 3200, 2900, 1700, 1400, 1200, 1030 $cm^{-1}$. MS (FAB) m/z 746 $(M+H)^+$. FABHRMS Calcd m/z for $C_{22}H_{41}N_3O_{17}P_3S$ 744.1370. Found: 744.1306 $(M-H^+)$. Anal.Calcd for $C_{22}H_{42}N_6O_{17}P_3S$-$3NH_3$-$3H_2O$ : C, 31.06; H, 6.75; N, 9.88. Found: C, 30.90; H, 6.51; N, 10.00. $[\alpha]_D^{25}$ = +23.5 (c 0.1, $H_2O$)

**D-1-*O*-[(Biotinyl-6-aminohexyl) hydrogen phosphoryl]-*myo*-inositol : Biotinylated D-*myo*-inositol 1-phosphate.**

**26a** (125mg, 0.087mmol) was allowed to react under the same condition as described for the preparation of Biotinylated-D-1,4,5-$IP_3$ to give the ammonium salts of Biotinylated D-1-$IP_1$ (20mg, 30%) as a white solid. $^1$H NMR($D_2O$) δ 1.26-1.65 (m, 14H), 2.13 (t, *J*=6.8 Hz, 2H), 2.63 (d, *J*=13.0 Hz, 1H), 2.89 (dd, *J*=13.0, 4.9 Hz, 1H), 3.06 (t, *J*=6.6 Hz, 2H), 3.18-3.23 (m, 2H), 3.41-3.66 (m, 3H), 3.79 (d, *J*=6.6 Hz, 3H), 4.12 (s, 1H), 4.29-4.33 (m, 1H), 4.48-4.52 (m, 1H). $^{13}$CNMR ($D_2O$) δ 27.3, 27.9, 28.4, 30.3, 30.5, 30.9, 32.4, 38.2, 41.9, 42.4, 58.1, 62.9, 64.7, 69.0, 73.4, 74.0, 74.1, 74.9, 76.6, 78.7, 168.0, 179.3. IR (KBr) 3400, 2900, 1700, 1200, 1030 $cm^{-1}$. MS (FAB) m/z 586 $(M+H)^+$. FABHRMS Calcd m/z for $C_{22}H_{39}N_3O_{11}PS$ 584.2043. Found: 584.2057$(M-H^+)$. Anal.Calcd for $C_{22}H_{40}N_3O_{11}PS$-$NH_3$-$5/3H_2O$ : C, 41.77; H, 7.38; N, 8.86. Found: C, 42.10; H, 7.11; N, 8.46.

**L-1-*O*-[(Biotinyl-6-aminohexyl) hydrogen phosphoryl]-*myo*-inositol : Biotinylated L-*myo*-inositol 1-phosphate.**

**26b** (170mg, 0.148mmol) as allowed to react under the same condition as described for the preparation of Biotinylated-D-1,4,5-$IP_3$ to give the ammonium salts of Biotinylated-L-1-$IP_1$ (41mg, 46%) as a white solid. $^1$H NMR($D_2O$) δ 1.24-1.52 (m, 14H), 2.12 (t, *J*=6.8 Hz, 2H), 2.65 (d, *J*=13.0 Hz, 1H), 2.87 (dd, *J*=13.0, 4.9 Hz, 1H), 3.05 (t, *J*=6.6 Hz, 2H), 3.16-3.22 (m, 2H), 3.38-3.64 (m, 3H), 3.77-3.79 (m, 3H), 4.10-4.11 (m, 1H), 4.27-4.31 (m, 1H), 4.46-4.64 (m, 1H). $^{13}$CNMR ($D_2O$) δ 27.3, 27.9,

28.5, 30.4, 30.5, 30.9, 32.4, 38.2, 42.0, 42.4, 58.1, 62.9, 64.8, 69.1, 73.5, 74.1, 75.0, 76.7, 78.7, 78.8, 168.0, 179.3. IR (KBr) 3400, 2900, 1700, 1200, 1030 $cm^{-1}$. MS (FAB) m/z 586 $(M+H)^+$. FABHRMS Calcd m/z for $C_{22}H_{39}N_3O_{11}PS$ 584.2043. Found: 584.2083$(M-H^+)$ Anal.Calcd for $C_{22}H_{40}N_3O_{11}PS$-4/3$NH_3$-2$H_2O$: C, 41.01; H, 7.51; N, 9.42. Found: C, 41.20; H, 7.20; N, 9.24.

**D-2-*O*-[(Biotinyl-6-aminohexyl) hydrogen Phosphoryl] -*myo*-inositol 4,5-bis(hydrogen phosphate) : Biotinylated D-*myo*-inositol 2,4,5-triphosphate.**

**27** (135mg, 0.094mmol) as allowed to react under the same condition as described for the preparation of Biotinylated D-1,4,5-$IP_3$ to give the ammonium salts of Biotinylated D-2,4,5-$IP_3$ (31mg, 32%) as a white solid. $^1$H NMR ($D_2O$) δ 1.22-1.58 (m, 14H), 2.09 (t, *J*=7.1 Hz, 2H), 2.63 (d, *J*=13.0 Hz, 1H), 2.85 (dd, *J*=13.0, 4.9 Hz, 1H), 3.02 (d, *J*=6.6 Hz, 2H), 3.15-3.21 (m, 1H), 3.58 (d, *J*=8.1 Hz, 1H), 3.72-3.96 (m, 5H), 4.11-4.29 (m, 3H), 4.33-4.48 (m, 1H). $^{13}$CNMR ($D_2O$) δ 27.2, 27.9, 28.5, 30.3, 30.7, 30.9, 32.4, 38.4, 41.9, 42.3, 58.0, 63.1, 64.7, 69.5, 72.8, 73.7, 79.7, 81.1, 168.0, 179.3. IR (KBr) 3200, 2900, 1700, 1460, 1200, 1050 $cm^{-1}$. MS (FAB) m/z 746 $(M+H)^+$. FABHRMS Calcd m/z for $C_{22}H_{41}N_3O_{17}P_3S$ 744.1370. Found: 744.1327$(M-H^+)$. Anal.Calcd for $C_{22}H_{42}N_6O_{17}P_3S$-4$NH_3$-3$H_2O$ : C, 30.45; H, 6.97; N, 11.30. Found: C, 30.23; H, 6.60; N, 11.28. $[\alpha]_D^{25}$ = +23.2 (c 0.1, $H_2O$)

**2-*O*-[(Biotinyl-6-aminohexyl) hydrogen phosphoryl]-*myo*-inositol : Biotinylated D-*myo*-inositol 2-phosphate.**

**28** (59mg, 0.05 mmol) was allowed to react under the same condition as described for the preparation of Biotinylated D-1,4,5-$IP_3$ to give the ammonium salts of Biotinylated 2-$IP_1$ (20mg, 66%) as a white solid. δ 1.22-1.58 (m, 14H), 2.09 (t, *J*=7.1 Hz, 2H), 2.63 (d, *J*=13.0 Hz, 1H), 2.85 (dd, *J*=13.0, 4.9 Hz, 1H), 3.02 (t, *J*=6.6 Hz, 2H), 3.15-3.21 (m, 2H), 3.58 (d, *J*= 8.1 Hz, 1H), 3.72-3.96 (m, 5H), 4.11-4.29 (m, 3H), 4.33-4.48 (m, 1H). $^{13}$CNMR ($D_2O$) δ 27.3, 27.9, 28.4, 30.3, 30.5, 30.9, 32.4, 38.2, 41.9, 42.3, 58.0, 62.9, 64.7, 69.1, 72.8, 73.4, 78.2, 79.7, 81.2, 168.0, 179.3. IR (KBr) 3200, 2900, 1700, 1400, 1200, 1040 $cm^{-1}$. MS (FAB) m/z 586 $(M+H)^+$. FABHRMS Calcd m/z for $C_{22}H_{39}N_3O_{11}PS$ 584.2043. Found: 584.2056$(M-H^+)$. Anal.Calcd for $C_{22}H_{40}N_3O_{11}PS$-11/5$NH_3$-13/3$H_2O$ : C, 37.69; H, 7.94; N, 10.39. Found: C, 37.49; H, 7.54; N, 10.70.