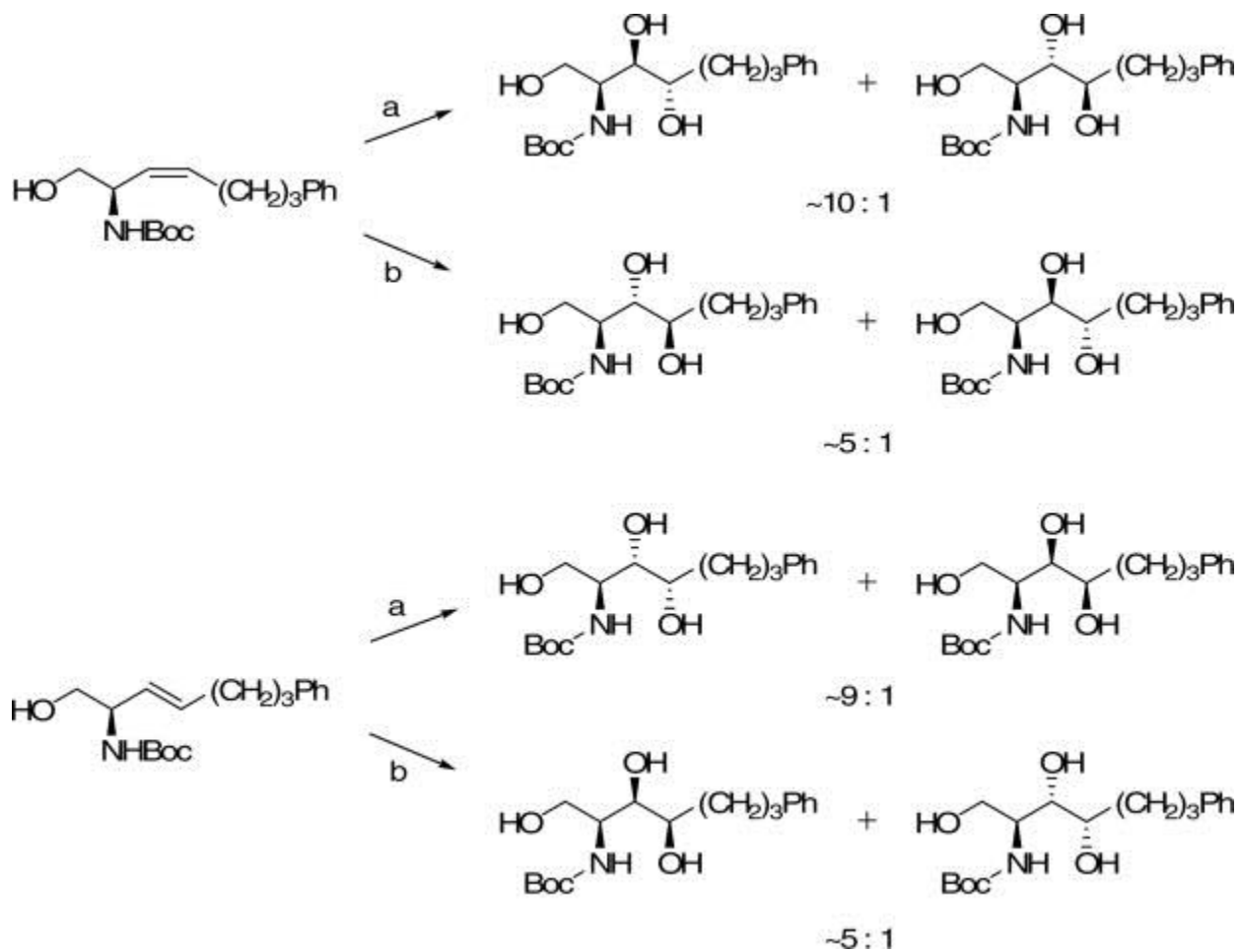
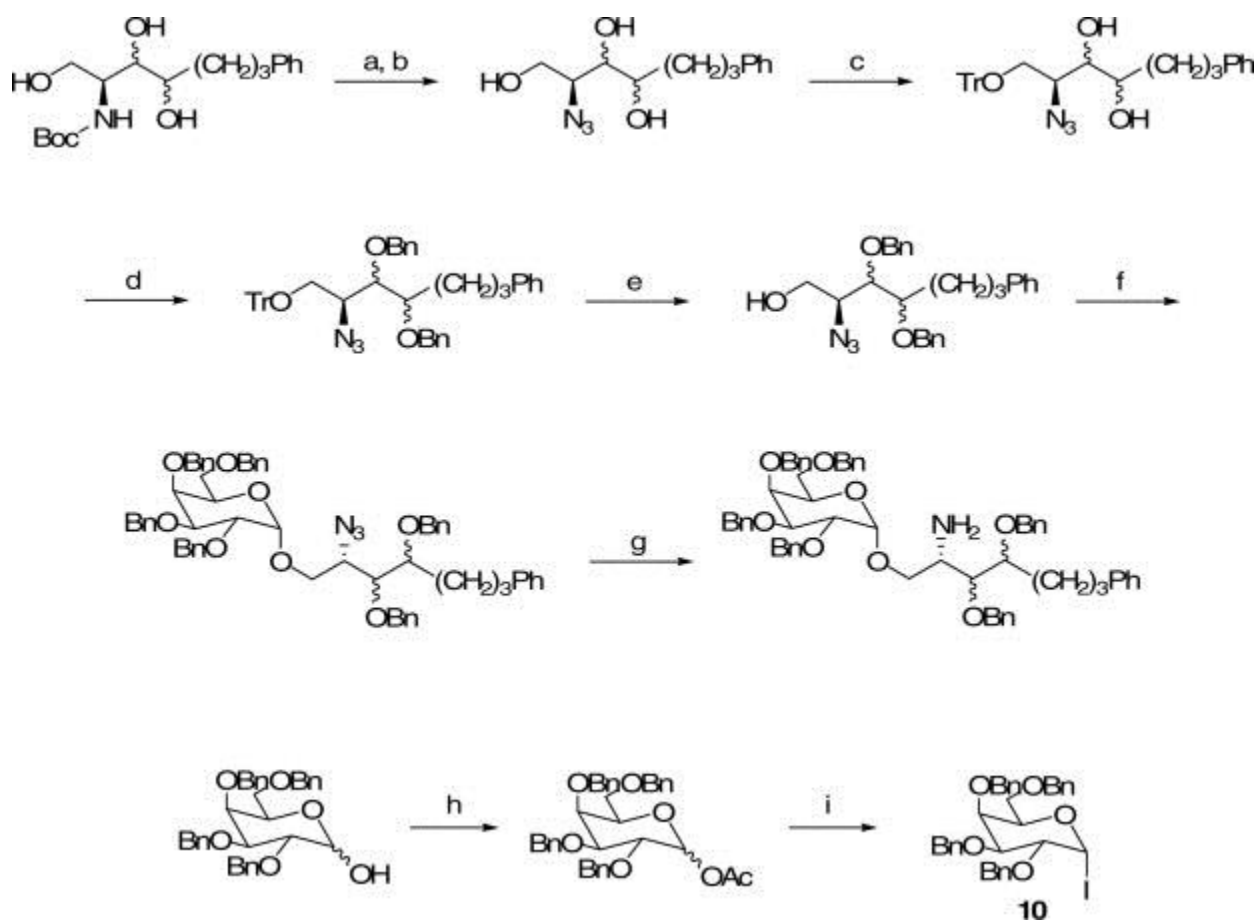


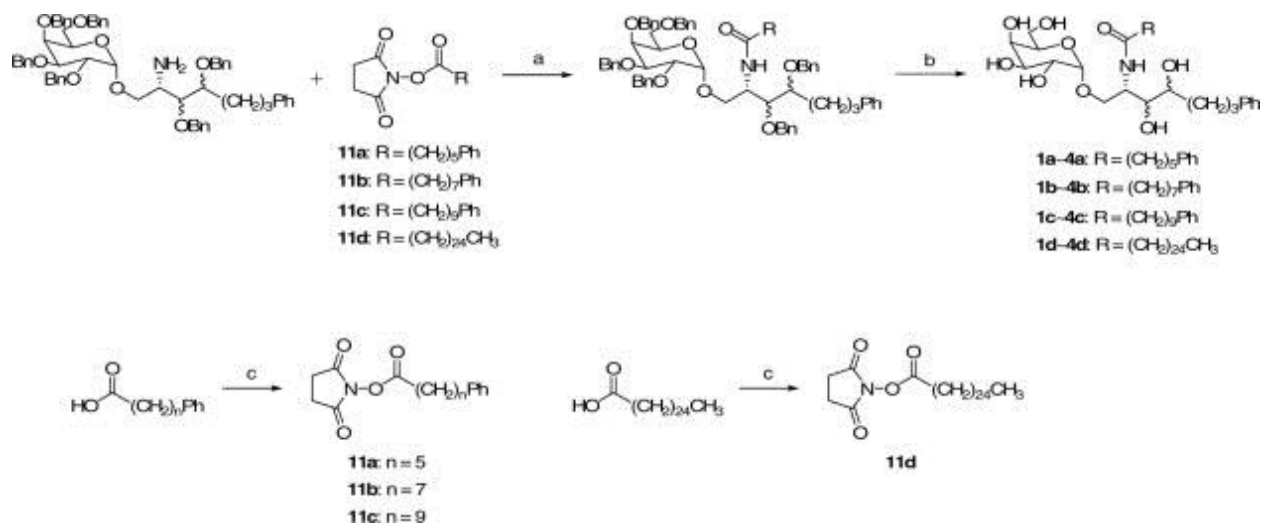
Supplementary Scheme 1. Reagents and conditions: (a) **9**, *n*-BuLi, THF, -78 °C–rt, 88%; (b) **9**, KHMDS, THF, MeOH, -78 °C–rt, 93%; (c) aq AcOH, rt, 94–95%; (d) PPh<sub>3</sub>, toluene, reflux, 99%.



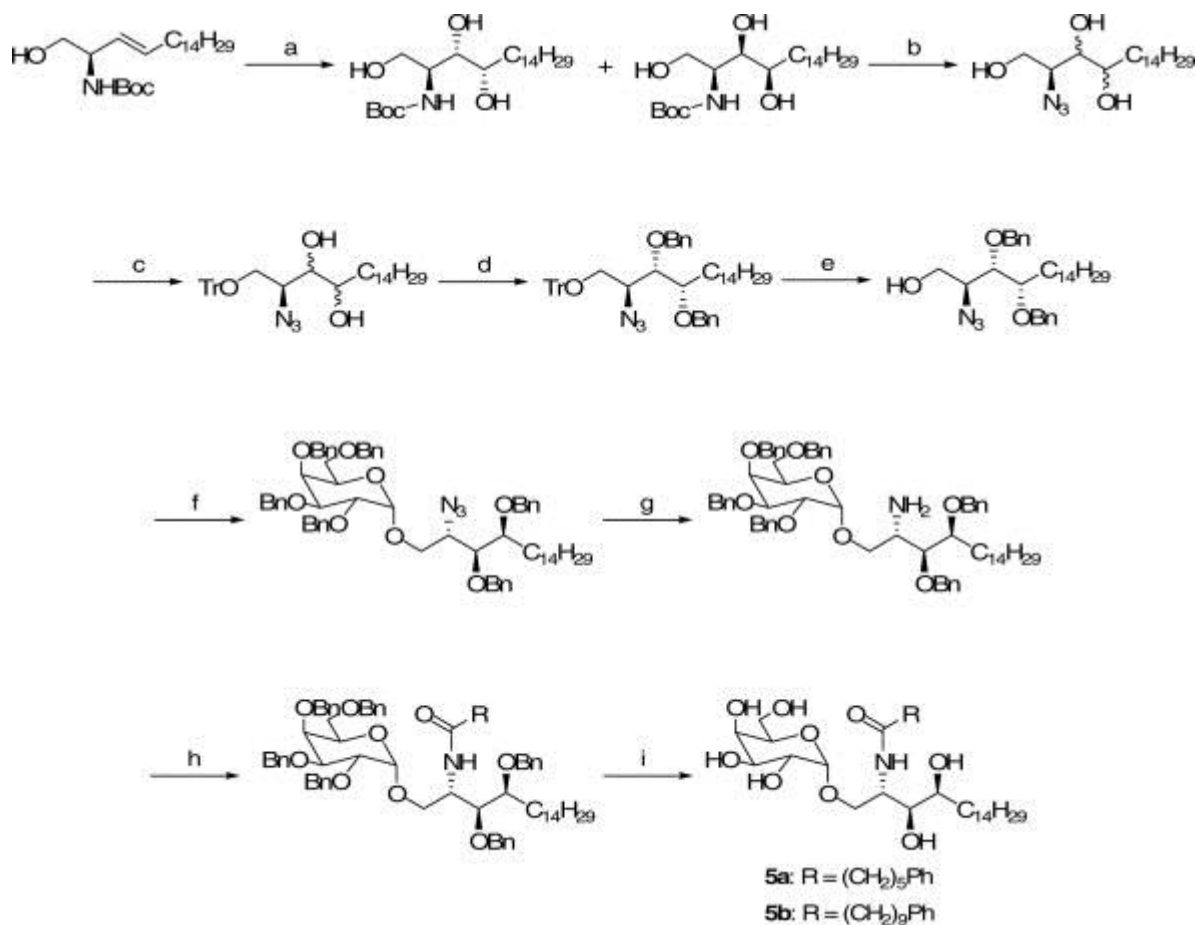
Supplementary Scheme 2. Reagents and conditions: (a) AD-mix- $\alpha$ ,  $\text{CH}_3\text{SO}_2\text{NH}_2$ , *t*-BuOH,  $\text{H}_2\text{O}$ , rt, 93–98%; (b) AD-mix- $\beta$ ,  $\text{CH}_3\text{SO}_2\text{NH}_2$ , *t*-BuOH,  $\text{H}_2\text{O}$ , rt, 97–99%.



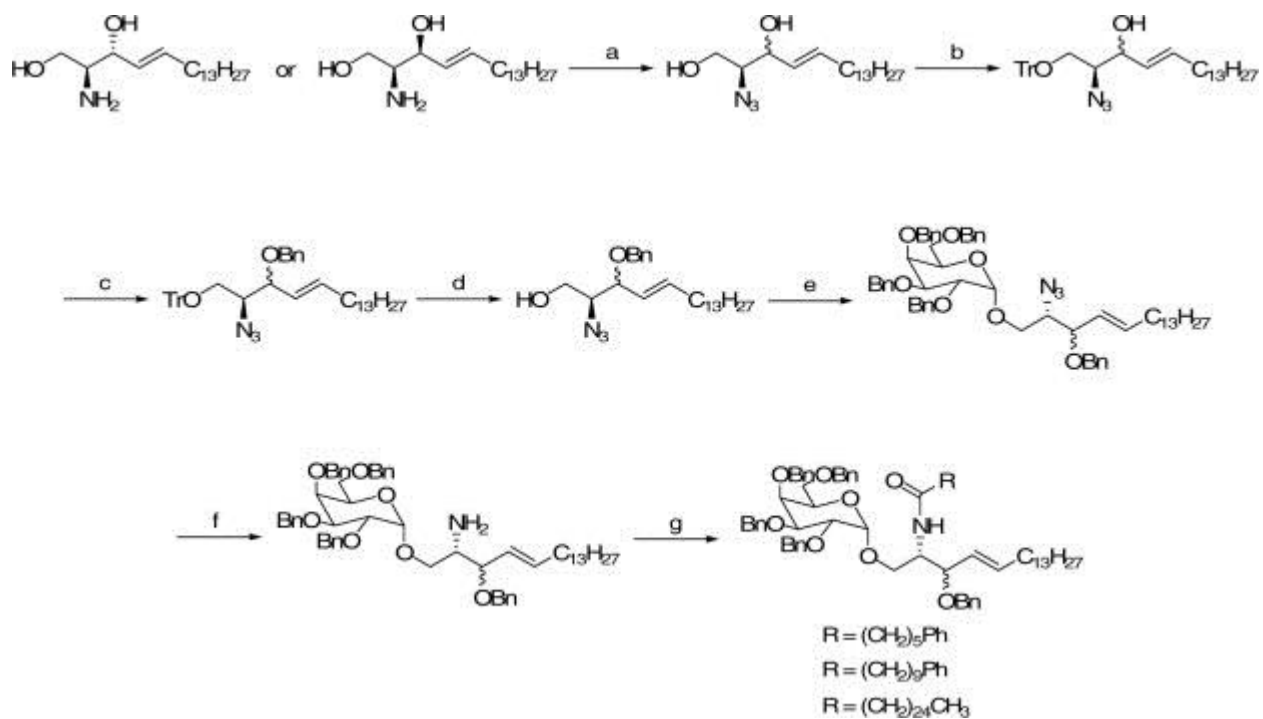
Supplementary Scheme 3. Reagents and conditions: (a) aq HCl, MeOH, rt; (b) TfN<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, CuSO<sub>4</sub>, H<sub>2</sub>O, MeOH, rt, 85–91% for two steps; (c) TrCl, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, rt, 84–90%; (d) BnBr, NaH, TBAI, THF, DMF, rt, 91–97%; (e) BF<sub>3</sub>·Et<sub>2</sub>O, toluene, MeOH, rt, 84–97%; (f) **10**, 4 Å molecular sieves, TBAI, DIPEA, benzene, 65 °C, 87–92%; (g) (i) PMe<sub>3</sub>, THF, rt; (ii) 1 N NaOH, rt, 84–90%; (h) Ac<sub>2</sub>O, pyridine, CH<sub>2</sub>Cl<sub>2</sub>, rt, 98%; (i) TMSI, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C.



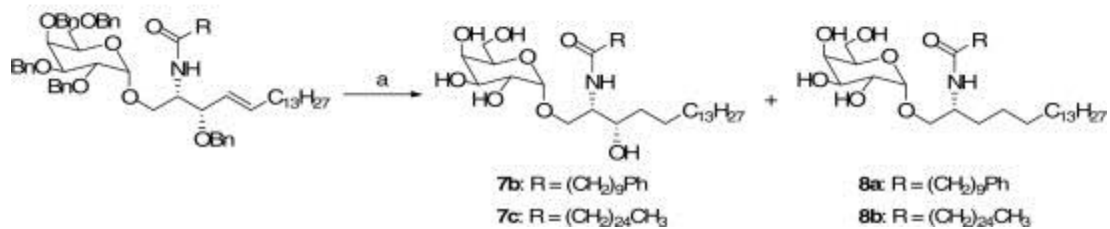
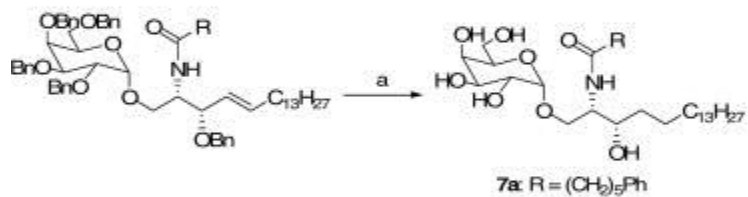
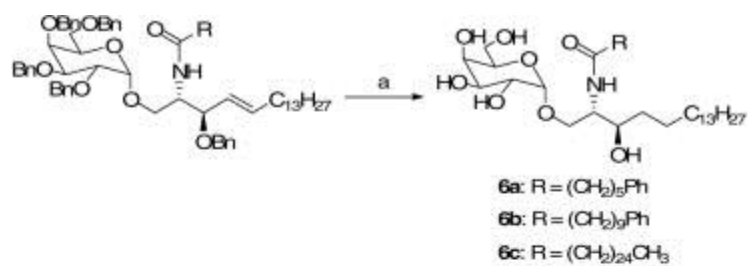
Supplementary Scheme 4. Reagents and conditions: (a) Et<sub>3</sub>N, THF, rt, 88–96%; (b) H<sub>2</sub>, Pd(OH)<sub>2</sub>/C, MeOH, CH<sub>2</sub>Cl<sub>2</sub>, rt, 83–96%; (c) *N*-hydroxysuccinimide, EDC·HCl, CH<sub>2</sub>Cl<sub>2</sub>, reflux, 95–99%.



Supplementary Scheme 5. Reagents and conditions: (a) AD-mix- $\alpha$ , CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>, *t*-BuOH, H<sub>2</sub>O, rt, 75%; (b) (i) aq HCl, MeOH, rt; (ii) TfN<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, CuSO<sub>4</sub>, H<sub>2</sub>O, MeOH, rt, 90%; (c) TrCl, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, rt, quant.; (d) BnBr, NaH, TBAI, THF, DMF, rt, 94%; (e) BF<sub>3</sub>·Et<sub>2</sub>O, toluene, MeOH, rt, 80%; (f) **10**, 4 Å molecular sieves, TBAI, DIPEA, benzene, 65 °C, 79%; (g) (i) PMe<sub>3</sub>, THF, rt; (ii) 1 N NaOH, rt, 84%; (h) **11**, Et<sub>3</sub>N, THF, rt, 88%; (i) H<sub>2</sub>, Pd(OH)<sub>2</sub>/C, MeOH, CH<sub>2</sub>Cl<sub>2</sub>, rt, 92–93%.



Supplementary Scheme 6. Reagents and conditions: (a) (i) aq HCl, MeOH, rt; (ii) TfN<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, CuSO<sub>4</sub>, H<sub>2</sub>O, MeOH, rt, 80–88%; (b) TrCl, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, rt, quant.; (c) BnBr, NaH, TBAI, THF, DMF, rt, 78–96%; (d) BF<sub>3</sub>·Et<sub>2</sub>O, toluene, MeOH, rt, 83%; (e) **10**, 4 Å molecular sieves, TBAI, DIPEA, benzene, 65 °C, 76–80%; (f) (i) PMe<sub>3</sub>, THF, rt; (ii) 1N NaOH, rt, 86%; (g) **11**, Et<sub>3</sub>N, THF, rt, 63–90%.



Supplementary Scheme 7. Reagents and conditions: (a) H<sub>2</sub>, Pd(OH)<sub>2</sub>/C, MeOH, CH<sub>2</sub>Cl<sub>2</sub>, rt.