Boc–Ser(Fmoc–Val)–OBzl (43). **43** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-valine derivative **82**. Yield: 93%; HPLC analysis at 230 nm: purity was higher than 96% (t_R = 36.4 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.3 Hz, 2H), 7.70-7.61 (m, 2H), 7.42-7.22 (m, 9H), 5.22-5.04 (m, 2H), 4.55-4.29 (m, 5H), 4.22 (t, J = 6.4 Hz, 1H), 4.06-3.98 (m, 1H), 2.14-1.96 (m, 1H), 1.40 (s, 9H), 0.97-0.84 (m, 6H); HRMS (FAB): calcd. for $C_{35}H_{40}N_2O_8Na$ $(M+Na)^+$: 639.2682, found: 639.2685.

Boc–Ser(Fmoc–D-Val)–OBzl (82). **82** was synthesized in the similar manner to **42**. Yield: 85%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 36.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.4 Hz, 2H), 7.70-7.61 (m, 2H), 7.40-7.27 (m, 9H), 5.24-5.11 (m, 2H), 4.54-4.43 (m, 2H), 4.42-4.29 (m, 3H), 4.24-4.20 (m, 1H), 4.06-3.98 (m, 1H), 2.12-1.96 (m, 1H), 1.40 (s, 9H), 0.93-0.82 (m, 6H); HRMS (FAB): calcd. for $C_{35}H_{40}N_2O_8Na$ $(M+Na)^+$: 639.2682, found: 639.2678.

Boc–Ser(Fmoc–Val)–OH (3). **3** was synthesized in the similar manner to **1**. Yield: 82%; HPLC analysis at 230 nm: purity was 94% (t_R = 32.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.1 Hz, 2H), 7.72-7.65 (m, 2H), 7.43-7.27 (m, 4H), 4.55-4.42 (m, 1H), 4.42-4.30 (m, 2H), 4.28-4.15 (m, 2H), 4.09 (d, J = 6.0 Hz, 1H), 2.25-2.06 (m, 1H), 1.40 (s, 9H), 0.93 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H); HRMS (FAB): calcd. for $C_{28}H_{34}N_2O_8Na$ $(M+Na)^+$: 549.2213, found: 549.2217.

Boc–Ser(Fmoc–Ile)–OBzl (45). **45** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-*allo*-isoleucine derivative **84**. Yield: 84%; HPLC analysis at 230 nm: purity was 89% (t_R = 38.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.66 (t, J = 6.6 Hz, 2H), 7.40-7.27 (m, 9H), 5.18 (d, J = 12.3 Hz, 1H), 5.11 (d, J = 12.3 Hz, 1H), 4.51-4.36 (m, 5H), 4.24-4.19 (m, 1H), 4.09 (d, J = 6.2 Hz, 1H), 1.88-1.75 (m, 1H), 1.39 (s, 9H), 1.28-1.15 (m, 2H), 0.97-0.87 (m, 6H); HRMS (FAB): calcd. for $C_{36}H_{42}N_2O_8Na$ $(M+Na)^+$: 653.2839, found: 653.2835.

Boc–Ser(Fmoc–D-*allo*-Ile)–OBzl (84). **84** was synthesized in the similar manner to **42**. Yield: 97%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.5 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.5 Hz, 2H), 7.68-7.65 (m, 2H), 7.40-7.27 (m, 9H), 5.19 (d, J = 12.3 Hz, 1H), 5.14 (d, J = 12.3 Hz, 1H), 4.51-4.47 (m, 2H), 4.39-4.36 (m, 3H), 4.26-4.20 (m, 2H), 1.92-1.78 (m, 1H), 1.40 (s, 9H), 1.36-1.12 (m, 2H), 0.94-0.83 (m, 6H); HRMS (FAB): calcd. for $C_{36}H_{42}N_2O_8Na$ $(M+Na)^+$: 653.2839, found: 653.2835.

Boc–Ser(Fmoc–Ile)–OH (5). **5** was synthesized in the similar manner to **1**. Yield: >99%; HPLC analysis at 230 nm: purity was 89% (t_R = 33.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.3 Hz, 2H), 7.69-7.66 (m, 2H), 7.40-7.27 (m, 4H), 4.51-4.48 (m, 1H), 4.14-4.31 (m, 3H), 4.24-4.13 (m, 3H), 1.93-1.86 (m, 1H), 1.40 (s, 9H), 1.28-1.16 (m, 2H), 0.99-0.90 (m, 6H); HRMS (FAB): calcd. for $C_{29}H_{36}N_2O_8Na$ $(M+Na)^+$: 563.2369, found: 563.2373.

Boc–Ser(Fmoc–Thr(*t*Bu))–OBzl (47). **47** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-*allo*-threonine derivative **86**. Yield: >99%; HPLC analysis at 230 nm: purity was 92% (t_R = 39.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.4 Hz, 2H), 7.69-7.64 (m, 2H), 7.40-7.30 (m, 9H), 5.20 (d, J = 12.5 Hz, 1H), 5.12 (d, J = 12.3 Hz, 1H), 4.55-4.35 (m, 5H), 4.25-4.16 (m, 3H), 1.40 (s, 9H), 1.15-1.08 (m, 12H); HRMS (FAB): calcd. for $C_{38}H_{46}N_2O_9Na$ $(M+Na)^+$: 697.3101, found: 697.3096.

Boc–Ser(Fmoc–D-*allo*-Thr(*t*Bu))–OBzl (86). **86** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.40-7.28 (m, 9H), 5.22-5.11 (m, 2H), 4.54-4.20 (m, 7H), 4.06-4.00 (m, 1H), 1.40 (s, 9H), 1.16 (s, 9H), 1.11 (d, J = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{38}H_{46}N_2O_9Na$ $(M+Na)^+$: 697.3101, found: 697.3096.

Boc–Ser(Fmoc–Thr(*t*Bu))–OH (7). **7** was synthesized in the similar manner to **1**. Yield: 89%; HPLC analysis at 230 nm: purity was 89% (t_R = 34.4 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2H), 7.70-7.66 (m, 2H), 7.41-7.28 (m, 4H), 4.46-4.20 (m, 8H), 1.42 (s, 9H), 1.16-1.12 (m, 12H); HRMS (FAB): calcd. for $C_{31}H_{40}N_2O_9Na$ $(M+Na)^+$: 607.2632, found: 607.2639.

Boc–Ser(Fmoc–Met)–OBzl (49). **49** was synthesized in the similar manner to **42**. Whether epimerization was occurred could not be determined because mixture of L-methionine derivative **49** and independently synthesized D-methionine derivative **88** was able to separate by neither RP-HPLC nor chiral HPLC. Yield: 89%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d,

J = 7.5 Hz, 2H), 7.71-7.61 (m, 2H), 7.43-7.23 (m, 9H), 5.16 (d, *J* = 12.4 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 4.56-4.17 (m, 7H), 2.62-2.40 (m, 2H), 2.14-1.98 (m, 4H), 1.97-1.82 (m, 1H), 1.39 (s, 9H); HRMS (FAB): calcd. for $C_{35}H_{40}N_2O_8SNa$ $(M+Na)^+$: 671.2403, found: 671.2407.

Boc–Ser(Fmoc–D-Met)–OBzl (88). **88** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 92% (t_R = 37.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.1 Hz, 2H), 7.73-7.58 (m, 2H), 7.46-7.24 (m, 9H), 5.20 (d, *J* = 12.5 Hz, 1H), 5.12 (d, *J* = 12.5 Hz, 1H), 4.55-4.17 (m, 7H), 2.60-2.38 (m, 2H), 2.12-1.98 (m, 4H), 1.93-1.79 (m, 1H), 1.39 (s, 9H); HRMS (FAB): calcd. for $C_{35}H_{40}N_2O_8SNa$ $(M+Na)^+$: 671.2403, found: 671.2410.

Boc–Ser(Fmoc–Met)–OH (9). **9** was synthesized in a similar manner to **8**. Yield: 70%; HPLC analysis at 230 nm: purity was 94% (t_R = 32.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.73-7.58 (m, 2H), 7.46-7.26 (m, 4H), 4.61-4.50 (m, 1H), 4.48-4.29 (m, 5H), 4.28-4.19 (m, 1H), 2.63-2.42 (m, 2H), 2.18-2.03 (m, 4H), 2.01-1.88 (m, 1H), 1.42 (s, 9H); HRMS (FAB): calcd. for $C_{28}H_{34}N_2O_8SNa$ $(M+Na)^+$: 581.1934, found: 581.1927.

Boc–Ser(Fmoc–Pro)–OBzl (50). **50** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-proline derivative **89**. Yield: 98%; HPLC analysis at 230 nm: purity was 95% (t_R = 38.5 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.81-7.76 (m, 2H), 7.64-7.52 (m, 2H), 7.39-7.29 (m, 9H), 5.21 (d, *J* = 12.3 Hz, 1H), 5.06 (d, *J* = 12.3 Hz, 1H), 4.62-4.14 (m, 7H), 3.44-3.39 (m, 2H), 2.23-2.12 (m, 1H), 1.98-180 (m, 3H), 1.36 (d, *J* = 3.1 Hz, 9H); HRMS (FAB): calcd. for $C_{35}H_{38}N_2O_8Na$ $(M+Na)^+$: 637.2526, found: 637.2531.

Boc–Ser(Fmoc–D-Pro)–OBzl (89). 89 was synthesized in the similar manner to **42**. Yield: 89%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.4 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80-7.75 (m, 2H), 7.63-7.53 (m, 2H), 7.41-7.28 (m, 9H), 5.21-5.10 (m, 2H), 4.48-4.33 (m, 4H), 4.26-4.11 (m, 3H), 3.47-3.37 (m, 2H), 2.16-2.09 (m, 1H), 1.88-1.80 (m, 3H), 1.38 (d, *J* = 4.8 Hz, 9H); HRMS (FAB): calcd. for $C_{35}H_{38}N_2O_8Na$ $(M+Na)^+$: 637.2526, found: 637.2531.

Boc–Ser(Fmoc–Pro)–OH (10). **10** was synthesized in the similar manner to **1**. Yield: >99%; HPLC analysis at 230 nm: purity was 95% (t_R = 32.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80-7.77 (m, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.41-7.31 (m, 4H), 4.67-4.58 (m, 1H), 4.45-4.16 (m, 6H), 3.59-3.51 (m, 1H), 3.45-3.37(M, 1H), 2.26-1.89 (m, 5H), 1.36 (d, *J* = 7.9 Hz, 9H); HRMS (FAB): calcd. for $C_{28}H_{32}N_2O_8Na$ $(M+Na)^+$: 547.2056, found: 547.2061.

Boc–Ser(Fmoc–Asp(O*t*Bu))–OBzl (51). **51** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-aspartic acid derivative **109**. Yield: >99%; HPLC analysis at 230 nm: purity was 88% (t_R = 38.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.66-7.63 (m, 2H), 7.40-7.27 (m, 9H), 5.19-5.09 (m, 2H), 4.52-4.34 (m, 5H), 4.24-4.21 (m, 2H), 2.80-2.72 (m, 1H), 2.67-2.59 (m, 1H), 1.44 (s, 9H), 1.40 (s, 9H); HRMS (FAB): calcd. for $C_{38}H_{44}N_2O_{10}Na$ $(M+Na)^+$: 711.2894, found: 711.2889.

Boc–Ser(Fmoc–D-Asp(O*t*Bu))–OBzl (90). **90** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 95% (t_R = 38.2 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.65-7.60 (m, 2H), 7.40-7.27 (m, 9H), 5.20 (d, *J* = 12.3 Hz, 1H), 5.11 (d, *J* = 12.9 Hz, 1H), 4.52-4.47 (m, 3H), 4.36-4.34 (m, 2H), 4.24-4.20 (m, 2H), 2.80-2.72 (m, 1H), 2.65-2.57 (m, 1H), 1.44 (s, 9H), 1.39 (s, 9H); HRMS (FAB): calcd. for $C_{38}H_{44}N_2O_{10}Na$ $(M+Na)^+$: 711.2894, found: 711.2900.

Boc–Ser(Fmoc–Asp(O*t*Bu))–OH (11). **11** was synthesized in the similar manner to **1**. Yield: >99%; HPLC analysis at 230 nm: purity was 92% (t_R = 33.3 min); ^{1}H NMR (DMSO-d_6, 300MHz) δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.68 –7.64 (m, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 4.60-4.54 (m, 2H), 4.34-4.29 (m, 3H), 4.25-4.20 (m, 2H), 2.88-2.81 (m, 1H), 2.74-2.65 (m, 1H), 1.44 (s, 9H), 1.42 (s, 9H); HRMS (FAB): calcd. for $C_{31}H_{38}N_2O_{10}Na$ $(M+Na)^+$: 621.2424, found: 621. 2420.

Boc–Ser(Fmoc–Asn(Trt))–OBzl (52). **52** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-asparagine derivative **90**. Yield: >99%; HPLC analysis at 230 nm: purity was 95% (t_R = 40.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79-7.77 (m, 2H), 7.66-7.62 (m, 2H), 7.39-7.17 (m, 24H), 5.11 (d, *J* = 1.3 Hz, 2H), 4.47-4.29 (m, 6H), 4.22-4.18 (m, 1H), 2.82 (d, *J* = 5.9 Hz, 2H), 1.37 (s, 9H); HRMS (FAB): calcd. for $C_{53}H_{51}N_3O_9Na$ $(M+Na)^+$: 896.3523, found: 896.3528.

Boc–Ser(Fmoc–D-Asn(Trt))–OBzl (90). **90** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 41.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.1 Hz, 2H), 7.65-7.63 (m, 2H), 7.39-7.19 (m, 24H), 5.17 (d, J = 11.5 Hz, 1H), 5.09 (d, J = 11.5 Hz, 1H), 4.50-4.28 (m, 6H), 4.24-4.17 (m, 1H), 2.81-2.79 (m, 2H), 1.36 (s, 9H); HRMS (FAB): calcd. for $C_{53}H_{51}N_3O_9Na$ $(M+Na)^+$: 896.3523, found: 896.3528.

Boc–Ser(Fmoc–Asn(Trt))–OH (12). **12** was synthesized in the similar manner to **1**. Yield: 96%; HPLC analysis at 230 nm: purity was 92% (t_R = 36.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.95-7.85 (m, 2H), 7.74-7.65 (m, 2H), 7.45-7.38 (m, 2H), 7.34-7.14 (m, 17H), 4.51-4.47 (m, 1H), 4.42-4.36 (m, 1H), 4.29-4.25 (m, 5H), 2.80-2.76 (m, 2H), 1.36 (s, 9H); HRMS (FAB): calcd. for $C_{46}H_{45}N_3O_9Na$ $(M+Na)^+$: 806.3054, found: 806.3058.

Boc–Ser(Fmoc–Glu(O*t*Bu))–OBzl (53). **53** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-glutamic acid derivative **92**. Yield: 98%; HPLC analysis at 230 nm: purity was 95% (t_R = 38.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.5 Hz, 2H), 7.68-7.64 (m, 2H), 7.40-7.27 (m, 9H), 5.17 (d, J = 12.5 Hz, 1H), 5.10 (d, J = 12.5 Hz, 1H), 4.50-4.43 (m, 3H), 4.36 (d, J = 6.6 Hz, 2H), 4.24-4.16 (m, 2H), 2.30 (t, J = 7.1 Hz, 2H), 2.13-2.02 (m, 1H), 1.92-1.81 (m, 1H), 1.44 (s, 9H), 1.40 (s, 9H); HRMS (FAB): calcd. for $C_{39}H_{46}N_2O_{10}Na$ $(M+Na)^+$: 725.3050, found: 725.3044.

Boc–Ser(Fmoc–D-Glu(O*t*Bu))–OBzl (92). **92** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 94% (t_R = 38.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2H), 7.73-7.60 (m, 2H), 7.40-7.28 (m, 9H), 5.20 (d, J = 12.3 Hz, 1H), 5.13 (d, J = 12.3 Hz, 1H), 4.24-4.16 (m, 2H), 1.44 (s, 9H), 1.39 (s, 9H); HRMS (FAB): calcd. for $C_{39}H_{46}N_2O_{10}Na$ $(M+Na)^+$: 725.3050, found: 725.3057.

Boc–Ser(Fmoc–Glu(O*t*Bu))–OH (13). **13** was synthesized in the similar manner to **1**. Yield: 99%; HPLC analysis at 230 nm: purity was 90% (t_R = 33.4 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.8 Hz, 2H), 7.41-7.29 (m, 4H), 7.45-7.48 (m, 1H), 4.38-4.33 (m, 4H), 4.28-4.20 (m, 2H), 2.32 (t, J = 7.2 Hz 2H), 2.20-2.06 (m, 1H), 1.45 (s, 9H), 1.41 (s, 9H); HRMS (FAB): calcd. for $C_{32}H_{40}N_2O_{10}Na$ $(M+Na)^+$: 636.2581, found: 636.2585.

Boc–Ser(Fmoc–Gln(Trt))–OBzl (54). **54** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-glutamine derivative **93**. Yield: 85%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 40.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.70-7.63 (m, 4H), 7.37 (t, J = 7.2 Hz, 4H), 7.28-7.18 (m, 18H), 5.13 (d, J = 12.5 Hz, 1H), 5.01 (d, J = 12.5 Hz, 1H), 4.47-4.36 (m, 4H), 4.22-4.08 (m, 3H), 2.41-2.39 (m, 2H), 2.12-1.95 (m, 1H), 1.90-1.76 (m, 1H), 1.38 (s, 9H); HRMS (FAB): calcd. for $C_{54}H_{53}N_3O_9Na$ $(M+Na)^+$: 910.3680, found: 910.3673.

Boc–Ser(Fmoc–D-Gln(Trt))–OBzl (93). **93** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 93% (t_R = 40.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.9 Hz, 2H), 7.67-7.60 (m, 4H), 7.37 (t, J = 7.1 Hz, 4H), 7.29-7.18 (m, 18H), 5.16-5.04 (m, 2H), 4.56-4.43 (m, 2H), 4.38-4.32 (m, 3H), 4.25-4.12 (m, 2H), 2.46-2.28 (m, 2H), 2.10-1.95 (m, 1H), 1.88-1.70 (m, 1H), 1.37 (s, 9H); HRMS (FAB): calcd. for $C_{54}H_{53}N_3O_9Na$ $(M+Na)^+$: 910.3680, found: 910.3677.

Boc–Ser(Fmoc–Gln(Trt))–OH (14). **14** was synthesized in the similar manner to **1**. Yield: 89%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 36.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.4 Hz, 2H), 7.66 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.31-7.16 (m, 17H), 4.53-4.31 (m, 4H), 4.27-4.18 (m, 3H), 2.49-2.35 (m, 2H), 2.16-2.01 (m, 1H), 1.94-1.80 (m, 1H), 1.38 (s, 9H); HRMS (FAB): calcd. for $C_{47}H_{47}N_3O_9Na$ $(M+Na)^+$: 820.3210, found: 820.3204.

Boc–Ser(Fmoc–His(Trt))–OBzl (55). **55** was synthesized in the same manner to **42**. Whether epimerization was occurred could not be determined because mixture of L-histidine derivative **55** and independently synthesized D-histidine derivative **94** was able to separate by neither RP-HPLC nor chiral HPLC. Yield: 78%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 35.2 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.81-7.68 (m, 2H), 7.64-7.56 (m, 2H), 7.42-7.17 (m, 20H), 7.14-6.95 (m, 6H), 5.17 (d, J = 12.3 Hz, 1H), 5.11 (d, J = 12.3 Hz, 1H), 4.61-4.34 (m, 4H), 4.32-4.20 (m, 2H), 4.17-4.04 (m, 1H), 3.20-2.81 (m, 2H), 1.32 (s, 9H); HRMS (FAB): calcd. for $C_{55}H_{52}N_4O_8Na$ $(M+Na)^+$: 919.3683, found: 919.3688.

Boc–Ser(Fmoc–D-His(Trt))–OBzl (94). **94** was synthesized in the same manner to **42**. Yield: 97%; HPLC analysis at 230 nm: purity was 88% (t_R = 34.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80 (d, J = 7.7 Hz, 2H), 7.63-7.54 (m, 2H), 7.50-7.07 (m, 26H), 5.17 (d, J = 12.4 Hz, 1H), 5.09 (d, J = 12.4 Hz, 1H), 4.56-4.45 (m, 3H),

4.45-4.32 (m, 2H), 4.28-4.19 (m, 1H), 4.18-4.10 (m, 1H), 3.24-3.09 (m, 1H), 3.01-2.89 (m, 1H), 1.37 (s, 9H); HRMS (FAB): calcd. for $C_{55}H_{52}N_4O_8Na$ $(M+Na)^+$: 919.3683, found: 919.3688.

Boc–Ser(Fmoc–His(Trt))–OH (15). **15** was synthesized in the same manner to **1**. Yield: 81%; HPLC analysis at 230 nm: purity was 89% (t_R = 31.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.5 Hz, 2H), 7.43-7.18 (m, 15H), 7.14-7.00 (m, 6H), 4.56-4.44 (m, 2H), 4.41-4.19 (m, 4H), 4.16-4.07 (m, 1H), 3.17-3.04 (m, 1H), 3.01-2.83 (m, 1H), 1.34 (s, 9H); HRMS (FAB): calcd. for $C_{48}H_{46}N_4O_8Na$ $(M+Na)^+$: 829.3213, found: 829.3208.

Boc–Ser(Fmoc–Lys(Boc))–OBzl (56). **56** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-lysine derivative **95**. Yield: >99%; HPLC analysis at 230 nm: purity was 95% (t_R = 38.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.1 Hz, 2H), 7.66 (t, J = 6.8 Hz, 2H), 7.42-7.26 (m, 9H), 5.17 (d, J = 12.1 Hz, 1H), 5.10 (d, J = 12.3 Hz, 1H), 4.49-4.35 (m, 5H), 4.21 (t, J = 7.0 Hz, 1H), 4.13-4.08 (m, 1H), 3.04-3.00 (m, 2H), 1.78-1.61 (m, 2H), 1.51-1.46 (m, 2H), 1.42 (s, 9H), 1.40 (s, 9H), 1.28 (s, 2H); HRMS (FAB): calcd. for $C_{41}H_{51}N_3O_{10}Na$ $(M+Na)^+$: 768.3472, found: 768.3468.

Boc–Ser(Fmoc–D-Lys(Boc))–OBzl (95). **95** was synthesized in the similar manner to **42**. Yield: 93%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2H), 7.68-7.64 (m, 2H), 7.40-7.27 (m, 9H), 5.20 (d, J = 12.1 Hz, 1H), 5.13 (d, J = 12.1 Hz, 1H), 4.50-4.35 (m, 5H), 4.24-4.19 (m, 1H), 4.12-4.08 (m, 1H), 3.01 (t, J = 6.6 Hz, 2H), 1.75-1.59 (m, 2H), 1.50-1.44 (m, 2H), 1.41 (s, 9H), 1.39 (s, 9H), 1.29 (s, 2H); HRMS (FAB): calcd. for $C_{41}H_{51}N_3O_{10}Na$ $(M+Na)^+$: 768.3472, found: 768.3480.

Boc–Ser(Fmoc–Lys(Boc))–OH (16). **16** was synthesized in the similar manner to **1**. Yield: 99%; HPLC analysis at 230 nm: purity was 91% (t_R = 33.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2H), 7.70-7.66 (m, 2H), 7.41-7.28 (m, 4H), 4.58-4.49 (m, 1H), 4.36-4.30 (m, 3H), 4.24-4.14 (m, 3H), 3.05 (t, J = 6.5 Hz, 2H), 1.85-1.66 (m, 2H), 1.45-1.37 (m, 20H), 1.29-1.28 (m, 2H); HRMS (FAB): calcd. for $C_{34}H_{45}N_3O_{10}Na$ $(M+Na)^+$: 678.3003, found: 678.2997.

Boc–Ser(Fmoc–Arg(Pmc))–OBzl (57). **57** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-arginine derivative **96**. Yield: 94%; HPLC analysis at 230 nm: purity was 97% (t_R = 38.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.66-7.62 (m, 2H), 7.39-7.26 (m, 9H), 5.15 (d, J = 12.1 Hz, 1H), 5.07 (d, J = 12.1 Hz, 1H), 4.48-4.35 (m, 5H), 4.22-4.17 (m, 1H), 4.10-4.05 (m, 1H), 3.15-3.11 (m, 2H), 2.64-2.60 (m, 2H), 2.56 (s, 3H), 2.55 (s, 3H), 2.08 (s, 3H), 1.80-1.70 (m, 3H), 1.60-1.42 (m, 3H), 1.38 (s, 9H), 1.27 (s, 6H); HRMS (FAB): calcd. for $C_{50}H_{61}N_5O_{11}SNa$ $(M+Na)^+$: 962.3986, found: 962.3978.

Boc–Ser(Fmoc–D-Arg(Pmc))–OBzl (96). **96** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.7 Hz, 2H), 7.65-7.62 (m, 2H), 7.39-7.26 (m, 9H), 5.16 (d, J = 12.3 Hz, 1 H), 5.08 (d, J = 12.7 Hz, 1H), 4.47-4.35 (m, 5H), 4.22-4.17 (m, 1H), 4.11-4.04 (m, 1H), 3.14-3.10 (m, 2H), 2.61 (t, J = 6.9 Hz, 2H), 2.56 (s, 3H), 2.55 (s, 3H), 2.07 (s, 3H), 1.79-1.68 (m, 3H), 1.59-1.43 (m, 3H), 1.38 (s, 9H), 1.26 (s, 6H); HRMS (FAB): calcd. for $C_{50}H_{61}N_5O_{11}SNa$ $(M+Na)^+$: 962.3986, found: 962.3978.

Boc–Ser(Fmoc–Arg(Pmc))–OH (17). **17** was synthesized in the similar manner to **1**. Yield: 88%; HPLC analysis at 230 nm: purity was 89% (t_R = 34.5 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.3 Hz, 2H), 7.67-7.63 (m, 2H), 7.39-7.26 (m, 4H), 4.50-4.44 (m, 1H), 4.36-4.34 (m, 3 H), 4.22-4.12 (m, 3H), 3.19-3.15 (m, 2H), 2.62 (t, J = 6.5 Hz, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 2.08 (s, 3H), 1.78 (t, J = 6.8 Hz, 2H), 1.67-1.44 (m, 4H), 1.38 (s, 9H), 1.27 (s, 6H); HRMS (FAB): calcd. for $C_{43}H_{55}N_5O_{11}SNa$ $(M+Na)^+$: 872.3516, found: 872.3525.

Boc–Ser(Fmoc–Phe)–OBzl (58). **58** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-phenylalanine derivative **97**. Yield: >99%; HPLC analysis at 230 nm: purity was 95% (t_R = 37.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.77 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H), 7.39-7.17 (m, 14H), 5.17 (d, J = 12.3 Hz, 1H), 5.11 (d, J = 12.3 Hz, 1H), 4.49-4.47 (m, 1H), 4.43-4.37 (m, 3H), 4.32-4.20 (m, 2H), 4.14 (t, J = 7.0 Hz, 1H), 3.13-3.06 (m, 1H), 2.93-2.85 (m, 1H), 1.40 (s, 9H); HRMS (FAB): calcd. for $C_{39}H_{40}N_2O_8Na$ $(M+Na)^+$: 687.2682, found: 687.2678.

Boc–Ser(Fmoc–D-Phe))–OBzl (97). **97** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 94% (t_R = 38.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.77 (d, J = 7.3 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.39-7.16 (m, 14H), 5.19 (d, J = 12.2 Hz, 1H), 5.12 (d, J = 12.2 Hz, 1H), 4.51-4.37 (m,

4H), 4.33-4.21 (m, 2H), 4.16-4.11 (m, 1H), 3.11-3.05 (m, 1H), 2.88-2.81 (m, 1H), 1.40 (s, 9H); HRMS (FAB): calcd. for $C_{39}H_{40}N_2O_8Na$ $(M+Na)^+$: 687.2682, found: 687.2678.

Boc–Ser(Fmoc–Phe)–OH (18). **18** was synthesized in the similar manner to **1**. Yield: >99%; HPLC analysis at 230 nm: purity was 90% (t_R = 32.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.77 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.31-7.16 (m, 7H), 4.51-4.43 (m, 2H), 4.39-4.11 (m, 5H), 3.26-3.16 (m, 1H), 2.99-2.88 (m, 1H), 1.41 (s, 9H); HRMS (FAB): calcd. for $C_{32}H_{34}N_2O_8Na$ $(M+Na)^+$: 597.2213, found: 597.2220.

Boc–Ser(Fmoc–Tyr(*t*Bu))–OBzl (59). **59** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-tyrosine derivative **98**. Yield: 91%; HPLC analysis at 230 nm: purity was 92% (t_R = 40.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.77 (d, J = 7.0 Hz, 2 H), 7.62-7.58 (m, 2 H), 7.40-7.28 (m, 9 H), 7.09 (d, J = 8.2 Hz, 2 H), 6.87-6.84 (m, 2 H), 5.20-5.09 (m, 2H), 4.82-4.81 (m, 1 H), 4.50-4.08 (m, 5H), 3.10-3.04 (m, 1H), 2.87-2.80 (m, 1H), 1.41 (s, 9H), 1.25 (s, 9H); HRMS (FAB): calcd. for $C_{43}H_{48}N_2O_9Na$ $(M+Na)^+$: 759.3258, found: 759.3262.

Boc–Ser(Fmoc–D-Tyr(*t*Bu))–OBzl (98). **98** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 2H), 7.40-7.25 (m, 9H), 7.07 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 5.20 (d, J = 12.3 Hz, 1H), 5.12 (d, J = 12.5 Hz, 1H), 4.53-4.49 (m, 1H), 4.46-4.35 (m, 3H), 4.32-4.19 (m, 2H), 4.15-4.10 (m, 1H), 3.07-3.01 (m, 1H) 2.84-2.76 (m, 1H), 1.40 (s, 9H), 1.25 (s, 9H); HRMS (FAB): calcd. for $C_{43}H_{48}N_2O_9Na$ $(M+Na)^+$: 759.3258, found: 759.3262.

Boc–Ser(Fmoc–Tyr(*t*Bu))–OH (19).[2k]

For details of synthesis and characterization of compound **19**, see ref. 2k.

Boc–Ser(Fmoc–Trp(Boc))–OBzl (60). **60** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-tryptophan derivative **99**. Yield: >99%; HPLC analysis at 230 nm: purity was 94% (t_R = 41.2 min); ^{1}H NMR (CD_3OD, 300MHz) δ 8.09 (d, J = 8.0 Hz, 1H), 7.80-7.69 (m, 2H), 7.64-7.46 (m, 3H), 7.43-7.13 (m, 11H), 5.16 (d, J = 12.4 Hz, 1H), 5.10 (d, J = 12.4 Hz, 1H), 4.59-4.49 (m, 2H), 4.48-4.41 (m, 2H), 4.36-4.06 (m, 3H), 3.29-3.15 (m, 1H), 3.13-3.00 (m, 1H), 1.58 (s, 9H), 1.40 (s, 9H); HRMS (FAB): calcd. for $C_{46}H_{49}N_3O_{10}Na$ $(M+Na)^+$: 826.3316, found: 826.3321.

Boc–Ser(Fmoc–D-Trp(Boc))–OBzl (99). 99 was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 91% (t_R = 41.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 8.15-8.05 (m, 1H), 7.81-7.68 (m, 2H), 7.67-7.59 (m, 1H), 7.58-7.45 (m, 3H), 7.43-7.14 (m, 11H), 5.21-5.02 (m, 2H), 4.62-4.43 (m, 4H), 4.36-4.05 (m, 3H), 3.28-3.13 (m, 1H), 3.11-3.05 (m, 1H), 1.58 (s, 9H), 1.39 (s, 9H); HRMS (FAB): calcd. for $C_{46}H_{49}N_3O_{10}Na$ $(M+Na)^+$: 826.3316, found: 826.3311.

Boc–Ser(Fmoc–Trp(Boc))–OH (20). 20 was synthesized in the similar manner to **1**. Yield: 91%; HPLC analysis at 230 nm: purity was 94% (t_R = 37.5 min); ^{1}H NMR (CD_3OD, 300MHz) δ 8.07 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.56-7.45 (m, 3H), 7.39-7.12 (m, 6H), 4.63-4.50 (m, 2H), 4.44-4.34 (m, 1H), 4.33-4.23 (m, 2H), 4.19-4.09 (m, 2H), 3.26-3.01 (m, 2H), 1.57 (s, 9H), 1.40 (s, 9H); HRMS (FAB): calcd. for $C_{39}H_{43}N_3O_{10}Na$ $(M+Na)^+$: 736.2846, found: 736.2840.

Boc–Thr(Fmoc–Gly)–OBzl (61). **61** was synthesized in a similar manner to **41**. Yield: 99%; HPLC analysis at 230 nm: purity was 87% (t_R = 35.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.40-7.27 (m, 9H), 5.45-5.42 (m, 1H), 5.17 (d, J = 12.3 Hz, 1H), 5.09 (d, J = 12.3 Hz, 1H), 4.41 (d, J = 2.7 Hz, 1H), 4.35 (d, J = 7.5 Hz, 2H), 4.23 (t, J = 7.1 Hz, 1H), 3.79 (d, J = 17.7 Hz, 1H), 3.71 (d, J = 17.7 Hz, 1H), 1.42 (s, 9H), 1.27 (d, J = 6.3 Hz, 3H); HRMS (FAB): calcd. for $C_{33}H_{36}N_2O_8Na$ $(M+Na)^+$: 611.2369, found: 611.2375.

Boc–Thr(Fmoc–Gly)–OH (21). **21** was synthesized in a similar manner to **1**. Yield: 95%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 30.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.40-7.28 (m, 4H), 5.44-5.41 (m, 1H), 4.34 (d, J = 6.6 Hz, 2H), 4.25-4.19 (m, 2H), 3.85 (s, 2H), 1.43 (s, 9H), 1.28 (d, J = 6.3 Hz, 3H); HRMS (FAB): calcd. for $C_{26}H_{30}N_2O_8Na$ $(M+Na)^+$: 521.1900, found: 521.1904.

Boc–Thr(Fmoc–Ala)–OBzl (62).[4b] **62** was synthesized in a similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-alanine derivative **100**. Yield: 81%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 36.1 min); ^{1}H NMR (CD_3OD,

400MHz) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.64 (dd, *J* = 13.6, 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32-7.23 (m, 7H), 5.46-5.42 (m, 1H), 5.14, 5.06 (2d, *J* = 12.3 Hz, 2H), 4.42 (d, *J* = 2.9 Hz, 1H), 4.37, 4.28 (2dd, *J* = 10.4 Hz, 7.0, 6.8 Hz, 2H), 4.20 (t, *J* = 6.8 Hz, 1H), 4.15 (q, *J* = 7.3 Hz, 1H), 1.43 (s, 9H), 1.30 (d, *J* = 7.3 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{34}H_{39}N_2O_8$ $(M+H)^+$: 603.2706, found: 603.2703.

Boc–Thr(Fmoc–D-Ala)–OBzl (100). **100** was synthesized in the similar manner to **44**. Yield: 86%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 36.0 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.40-7.28 (m, 9H), 5.43-5.39 (m, 1H), 5.16, 5.09 (2d, *J* = 12.2 Hz, 2H), 4.41 (d, *J* = 2.7 Hz, 1H), 4.39, 4.31 (2dd, *J* = 10.4 Hz, 7.2, 7.0 Hz, 2H), 4.24-4.20 (m, 1H), 4.12 (q, *J* = 7.3 Hz, 1H), 1.41 (s, 9H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.24 (d, *J* = 7.5 Hz, 3H); HRMS (FAB): calcd. for $C_{34}H_{38}N_2O_8Na$ $(M+Na)^+$: 625.2526, found: 625.2522.

Boc–Thr(Fmoc–Ala)–OH (22).[4b] **22** was synthesized in the similar manner to **1**. Yield: 98%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 30.5 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.33-7.29 (m, 2H), 5.42-5.39 (m, 1H), 4.39, 4.29 (2dd, *J* = 13.3 Hz, 7.2, 7.0 Hz, 2H), 4.24-4.18 (m, 3H), 1.41 (s, 9H), 1.35 (d, *J* = 7.3 Hz, 3H), 1.24 (d, *J* = 6.2 Hz, 3H); HRMS (FAB): calcd. for $C_{27}H_{32}N_2O_8Na$ $(M+Na)^+$: 535.2056, found: 535.2051.

Boc–Thr(Fmoc–Val)–OBzl (63). **63** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-valine derivative **101**. Yield: 94%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.2 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.66-7.62 (m, 2H), 7.37 (dt, *J* = 7.5 Hz, 0.5 Hz, 2H), 7.32-7.23 (m, 7H), 5.50-5.45 (m, 1H), 5.11, 5.04 (2d, *J* = 12.3 Hz, 2H), 4.43 (d, *J* = 2.8 Hz, 1H), 4.39-4.35 (m, 2H), 4.21 (t, *J* = 6.8 Hz, 1H), 3.98 (d, *J* = 7.0 Hz, 1H), 2.07-1.96 (m, 1H), 1.44 (s, 9 H), 1.24 (d, *J* = 6.4 Hz, 3H), 0.90, 0.89 (2d, *J* = 6.8, 6.6 Hz, 6H); HRMS (FAB): calcd. for $C_{36}H_{42}N_2O_8Na$ $(M+Na)^+$: 653.2839, found: 653.2833.

Boc–Thr(Fmoc–D-Val)–OBzl (101). **101** was synthesized in the similar manner to **44**. Yield: 89%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.4 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.1 Hz, 2H), 7.38 (dt, *J* = 7.5 Hz, 0.5 Hz, 2H), 7.32-7.25 (m, 7H), 5.46-5.41 (m, 1 H), 5.14, 5.08 (2d, *J* = 12.3 Hz, 2H), 4.43 (d, *J* = 2.7 Hz, 1H), 4.37 (d, *J* = 6.9 Hz, 2H), 4.23 (t, *J* = 6.9 Hz, 1H), 4.00 (d, *J* = 6.2 Hz, 1H), 2.09-2.00 (m, 1H), 1.43 (s, 9H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.88, 0.87 (2d, *J* = 6.8, 6.6 Hz, 6H); HRMS (FAB): calcd. for $C_{36}H_{42}N_2O_8Na$ $(M+Na)^+$: 653.2839, found: 653.2845.

Boc–Thr(Fmoc–Val)–OH (23).[2h]

For details of synthesis and characterization of compound **23**, see ref. 2h.

Boc–Thr(Fmoc–Leu)–OBzl (64). **64** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-leucine derivative **102**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.67-7.61 (m, 2H), 7.40-7.27 (m, 9H), 5.46-5.43 (m, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.04 (d, *J* = 12.6 Hz, 1H), 4.41-4.30 (m, 3H), 4.23-4.15 (m, 2H), 1.63-1.60 (m, 1H), 1.53-1.48 (m, 2H), 1.43 (s, 9H), 1.23 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.3 Hz, 3H); HRMS (FAB): calcd. for $C_{37}H_{44}N_2O_8Na$ $(M+Na)^+$: 667.2995, found: 667.2999.

Boc–Thr(Fmoc–D-Leu)–OBzl (102). **102** was synthesized in the similar manner to **44**. Yield: 96%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.2 Hz, 2 H), 7.66 (t, *J* = 6.6 Hz, 2H), 7.40-7.27 (m, 9H), 5.42-5.40 (m, 1H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.08 (d, *J* = 12.6 Hz, 1H), 4.41-4.33 (m, 3H), 4.25-4.12 (m, 2H), 1.66-1.59 (m, 1H), 1.51-1.46 (m, 2H), 1.41 (s, 9H), 1.26 (d, *J* = 6.3 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); HRMS (FAB): calcd. for $C_{37}H_{44}N_2O_8Na$ $(M+Na)^+$: 667.2995, found: 667.2991.

Boc–Thr(Fmoc–Leu)–OH (24). **24** was synthesized in the similar manner to **1**. Yield: 96%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 34.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 6.9 Hz, 2H), 7.41-7.29 (m, 4H), 5.39-5.35 (m, 1H), 4.43-4.32 (m, 2H), 4.25-4.15 (m, 3H), 1.66-1.52 (m, 3H), 1.41 (s, 9H), 1.23 (d, *J* = 6.3 Hz, 3H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3 H); HRMS (FAB): calcd. for $C_{30}H_{38}N_2O_8Na$ $(M+Na)^+$: 577.2526, found: 577.2520.

Boc–Thr(Fmoc–Ile)–OBzl (65). **65** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-*allo*-isoleucine derivative **103**. Yield: 92%; HPLC analysis at 230 nm: purity was 94% (t_R = 39.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31-7.26 (m, 7H),

5.48-5.46 (m, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.04 (d, *J* = 12.3 Hz, 1H), 4.42 (d, *J* = 2.7 Hz, 1H), 4.35 (d, *J* = 7.0 Hz, 2H), 4.20 (t, *J* = 6.8 Hz, 1H), 4.03 (d, *J* = 7.3 Hz, 1H), 1.82-1.72 (m, 1H), 1.44 (s, 9H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.18-1.11 (m, 2H), 0.89 (d, *J* = 7.4 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); HRMS (FAB): calcd. for $C_{37}H_{44}N_2O_8Na$ $(M+Na)^+$: 667.2995, found: 667.2991.

Boc–Thr(Fmoc–D-*allo*-Ile)–OBzl (103). **103** was synthesized in the similar manner to **42.** Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.69-7.65 (m, 2H), 7.40-7.27 (m, 9H), 5.44-5.41 (m, 1H), 5.15 (d, *J* = 11.9 Hz, 1H), 5.09 (d, *J* = 12.3 Hz, 1 H), 4.43-4.37 (m, 3H), 4.25-4.20 (m, 2H), 1.91-1.83 (m, 1H), 1.42 (s, 9H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.20-1.11 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H); HRMS (FAB): calcd. for $C_{37}H_{44}N_2O_8Na$ $(M+Na)^+$: 667.2995, found: 667.2991.

Boc–Thr(Fmoc–Ile)–OH (25). **25** was synthesized in the similar manner to **1**. Yield: 94%; HPLC analysis at 230 nm: purity was 93% (t_R = 33.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.3 Hz, 2 H), 7.69-7.63 (m, 2 H), 7.41-7.28 (m, 4H), 5.41-5.37 (m, 1H), 4.38 (d, *J* = 7.0 Hz, 2H), 4.23 (t, *J* = 6.8 Hz, 1H), 4.15 (d, *J* = 2.7 Hz, 1H), 4.08 (d, *J* = 6.6 Hz, 1H), 1.89-1.76 (m, 1H), 1.42 (s, 9H), 1.24 (d, *J* = 6.4 Hz, 3 H), 1.19-1.12 (m, 2H), 0.91 (d, *J* = 7.3 Hz, 3 H), 0.89 (d, *J* = 6.8 Hz, 3 H); HRMS (FAB): calcd. for $C_{30}H_{38}N_2O_8Na$ $(M+Na)^+$: 577.2526, found: 577.2520.

Boc–Thr(Fmoc–Ser(*t*Bu))–OBzl (66). **66** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-serine derivative **104**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.4 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 6.8 Hz, 2H), 7.41-7.23 (m, 9H), 5.48-5.45 (m, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.42-4,21 (m, 5H), 3.75-3.71 (m, 1H), 3.59-3.54 (m, 1H), 1.43 (s, 9H), 1.27 (d, *J* = 5.1 Hz, 3H), 1.16 (s, 9H); HRMS (FAB): calcd. for $C_{38}H_{46}N_2O_9Na$ $(M+Na)^+$: 697.3101, found: 697.3107.

Boc–Thr(Fmoc–D-Ser(*t*Bu))–OBzl (104). **104** was synthesized in the similar manner to **44**. Yield: 89%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.69-7.65 (m, 2H), 7.41-7.28 (m, 9H), 5.45-5.42 (m, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.41-4.22 (m, 5H), 3.69-3.64 (m, 1H), 3.59-3.55 (m, 1H), 1.41 (s, 9H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.16 (s, 9H); HRMS (FAB): calcd. for $C_{38}H_{46}N_2O_9Na$ $(M+Na)^+$: 697.3101, found: 697.3105.

Boc–Thr(Fmoc–Ser(*t*Bu))–OH (26). **26** was synthesized in the similar manner to **1**. Yield: 93%; HPLC analysis at 230 nm: purity was 92% (t_R = 34.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.68-7.67 (m, 2H), 7.41-7.28 (m, 4H), 5.43-5.40 (m, 1H), 4.37-4.18 (m, 5H), 3.81-3.76 (m, 1H), 3.59-3.55 (m, 1H), 1.43 (s, 9H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.57 (s, 9H); HRMS (FAB): calcd. for $C_{31}H_{40}N_2O_9Na$ $(M+Na)^+$: 607.2632, found: 607.2624.

Boc–Thr(Fmoc–Thr(*t*Bu))–OBzl (67). **67** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-*allo*-threonine derivative **105**. Yield: 86%; HPLC analysis at 230 nm: purity was 90% (t_R = 40.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 6.8 Hz, 2H), 7.68-7.62 (m, 2H), 7.40-7.23 (m, 9H), 5.47-5.32 (m, 1H), 5.14-4.99 (m, 2H), 4.42-4.35 (m, 3H), 4.26-4.17 (m, 1H), 4.14-4.06 (m, 2H), 1.43 (s, 9H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.16 (s, 9H), 1.14 (d, *J* = 5.1 Hz, 3H); HRMS (FAB): calcd. for $C_{39}H_{48}N_2O_9Na$ $(M+Na)^+$: 711.3258, found: 711.3252.

Boc–Thr(Fmoc–D-*allo*-Thr(*t*Bu))–OBzl (105). **105** was synthesized in the similar manner to **42**. Yield: 65%; HPLC analysis at 230 nm: purity was 88% (t_R = 40.0); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2 H), 7.68 (d, *J* = 7.3 Hz, 2 H), 7.41-7.28 (m, 9 H), 5.42-5.38 (m, 1 H), 5.17 (d, *J* = 12.5 Hz, 1 H), 5.09 (d, *J* = 12.3 Hz, 1 H), 4.41-4.37 (m, 3 H), 4.29-4.22 (m, 2 H), 4.03-4.00 (m, 1 H), 1.43 (s, 9 H), 1.30-1.28 (m, 3 H), 1.18 (s, 9 H), 1.09 (d, *J* = 6.4 Hz, 3 H); HRMS (FAB): calcd. for $C_{39}H_{48}N_2O_9Na$ $(M+Na)^+$:711.3258, found: 711.3253.

Boc–Thr(Fmoc–Thr(*t*Bu))–OH (27). **27** was synthesized in the similar manner to **1**. Yield: 83%; HPLC analysis at 230 nm: purity was 91% (t_R = 35.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.70-7.66 (m, 2H), 7.41-7.29 (m, 4H), 5.39-5.28 (m, 1H), 4.41-4.38 (m, 3H), 4.26-4.22 (m, 1H), 4.17-4.12 (m, 2H), 1.42 (s, 9H), 1.29 (d, *J* = 6.0 Hz, 3H). 1.17 (s, 9H), 1.13 (d, *J* = 6.2 Hz, 3H); HRMS (FAB): calcd. for $C_{32}H_{42}N_2O_9Na$ $(M+Na)^+$: 621.2788, found: 621.2792.

Boc–Thr(Fmoc–Met)–OBzl (69). **69** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-methionine derivative **107**. Yield: >99%; HPLC analysis at 230 nm: purity was 91% (t_R = 37.2 min); ^{1}H NMR (CD_3OD,

300MHz) δ 7.78 (d, J = 7.1 Hz, 2 H), 7.64 (t, J = 7.7 Hz, 2 H), 7.40-7.26 (m, 9 H), 5.51-5.37 (m, 1 H), 5.13 (d, J = 11.9 Hz, 1 H), 5.05 (d, J = 12.3 Hz, 1 H), 4.44-4.36 (m, 3 H), 4.30-4.16 (m, 2 H), 2.53-2.37 (m, 2 H), 2.06 (s, 3 H), 2.02-1.80 (m, 2 H), 1.42 (s, 9 H), 1.28-1.21 (m, 3 H); HRMS (FAB): calcd. for $C_{36}H_{42}N_2O_8SNa$ $(M+Na)^+$: 685.2560, found: 685.2555.

Boc–Thr(Fmoc–D-Met)–OBzl (107). **107** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 91% (t_R = 36.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2 H), 7.71-7.60 (m, 2 H), 7.40-7.28 (m, 9 H), 5.46-5.36 (m, 1 H), 5.18 (d, J = 12.3 Hz, 1 H), 5.09 (d, J = 12.3 Hz, 1 H), 4.44-4.33 (m, 3 H), 4.28-4.20 (m, 2 H), 2.50-2.38 (m, 2 H), 2.05 (s, 3 H), 2.01-1.89 (m, 1 H), 1.87-1.72 (m, 1 H), 1.40 (s, 9 H), 1.28-1.23 (m, 3 H); HRMS (FAB): calcd. for $C_{36}H_{42}N_2O_8SNa$ $(M+Na)^+$: 685.2560, found: 685.2554.

Boc–Thr(Fmoc–Met)–OH (29). **29** was synthesized in a similar manner to **8**. Yield: 73%; HPLC analysis at 230 nm: purity was 95% (t_R = 33.5 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.3 Hz, 2H), 7.68 (t, J = 6.8 Hz, 2H), 7.41-7.29 (m, 4H), 5.43-5.32 (m, 1H), 4.44-4.32 (m, 3H), 4.23 (t, J = 6.7 Hz, 2H), 2.54-2.41 (m, 2 H), 2.07 (s, 3H), 2.05-1.82 (m, 2H), 1.40 (s, 9H), 1.33-1.23 (m, 3 H); HRMS (FAB): calcd. for $C_{29}H_{36}N_2O_8SNa$ $(M+Na)^+$: 595.2090, found: 595.2097.

Boc–Thr(Fmoc–Pro)–OBzl (70). **70** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-proline derivative **108**. Yield: 86%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 37.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.1 Hz, 2H), 7.63-7.52 (m, 2H), 7.40-7.25 (m, 9H), 5.43-5.34 (m, 1H), 5.17-5.06 (m, 2H), 4.41-4.21 (m, 5H), 3.55-3.42 (m, 2H), 2.28-2.13 (m, 1H), 1.95-1.83 (m, 3H), 1.37 (s, 9H), 1.24-1.17 (m, 3H); HRMS (FAB): calcd. for $C_{36}H_{40}N_2O_8Na$ $(M+Na)^+$: 651.2682, found: 651.2688.

Boc–Thr(Fmoc–D-Pro)–OBzl (108). **108** was synthesized in the similar manner to **44**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 37.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80 (d, J = 7.5 Hz, 2H), 7.70-7.56 (m, 2H), 7.41-7.29 (m, 9H), 5.44-5.35 (m, 1H), 5.19-5.09 (m, 2H), 4.43-4.14 (m, 5H), 3.46-3.34 (m, 2H), 2.13-2.07 (m, 1H), 1.85-1.76 (m, 3H), 1.41 (s, 9H), 1.29-1.18 (m, 3H); HRMS (FAB): calcd. for $C_{36}H_{40}N_2O_8Na$ $(M+Na)^+$: 651.2682, found: 651.2676.

Boc–Thr(Fmoc–Pro)–OH (30). **30** was synthesized in the similar manner to **1**. Yield: 96%; HPLC analysis at 230 nm: purity was 90% (t_R = 31.6 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.81-7.77 (m, 2H), 7.68-7.56 (m, 2H), 7.41-7.29 (m, 4H), 5.38-5.27 (m, 1H), 4.44-4.11 (m, 5H), 3.61-3.54 (m, 1H), 3.45-3.37 (m, 1H), 2.30-2.18 (m, 1H), 2.05-1.88 (m, 3H), 1.36 (s, 9H), 1.23-1.12 (m, 3H); HRMS (FAB): calcd. for $C_{29}H_{34}N_2O_8Na$ $(M+Na)^+$: 561.2213, found: 561.2220.

Boc–Thr(Fmoc–Asp(O*t*Bu))–OBzl (71). **71** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-aspartic acid derivative **109**. Yield: >99%; HPLC analysis at 230 nm: purity was 92% (t_R = 40.2 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.1 Hz, 2H), 7.67-7.60 (m, 2H), 7.40-7.26 (m, 9H), 5.47-5.39 (m, 1H), 5.15-5.04 (m, 2H), 4.46-4.35 (m, 4H), 4.25-4.20 (m, 1H), 2.78-2.62 (m, 2H), 1.44 (s, 9H), 1.42 (s, 9H), 1.28-1.21 (m, 3H); HRMS (FAB): calcd. for $C_{39}H_{46}N_2O_{10}Na$ $(M+Na)^+$: 725.3050, found: 725.3057.

Boc–Thr(Fmoc–D-Asp(O*t*Bu))–OBzl (109). **109** was synthesized in the similar manner to **44**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.40-7.27 (m, 9H), 5.45-5.39 (m, 1H), 5.17 (d, J = 12.3 Hz, 1H), 5.10 (d, J = 12.5 Hz, 1H), 4.49-4.33 (m, 4H), 4.23 (t, J = 6.9 Hz, 1H), 2.78-2.70 (m, 1H), 2.59-2.50 (m, 1 H), 1.44 (s, 9H), 1.40 (s, 9H), 1.27-1.20 (m, 3H); HRMS (FAB): calcd. for $C_{39}H_{46}N_2O_{10}Na$ $(M+Na)^+$: 725.3050, found: 725.3046.

Boc–Thr(Fmoc–Asp(O*t*Bu))–OH (31). **31** was synthesized in the similar manner to **1**. Yield: 94%; HPLC analysis at 230 nm: purity was 92% (t_R = 35.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.68 -7.64 (m, 2H), 7.40-7.27 (m, 4H), 5.44-5.36 (m, 1H), 4.56-4.52 (m, 1H), 4.36-4.32 (m, 2H), 4.25-4.20 (m, 1H), 4.12-4.09 (m, 1H), 2.76-2.74 (m, 2H), 1.44 (s, 9H), 1.42 (s, 9H), 1.28-1.24 (m, 3H); HRMS (FAB): calcd. for $C_{32}H_{40}N_2O_{10}Na$ $(M+Na)^+$: 635.2581, found: 635.2585.

Boc–Thr(Fmoc–Asn(Trt))–OBzl (72). **72** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-asparagine derivative **110**. Yield: >99%; HPLC analysis at 230 nm: purity was 92% (t_R = 39.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, J = 7.9 Hz, 2H), 7.70-7.60 (m, 2H), 7.42-7.14 (m, 24H), 5.45-5.38 (m, 1H), 5.09-4.98 (m,

2H), 4.43-4.31 (m, 3H), 4.28-4.19 (m, 2H), 2.83-2.80 (m, 2H), 1.40 (s, 9H), 1.19 (d, *J* = 6.2 Hz, 3H); HRMS (FAB): calcd. for $C_{54}H_{53}N_3O_9Na$ $(M+Na)^+$: 910.3680, found: 910.3675.

Boc–Thr(Fmoc–D-Asn(Trt))–OBzl (110). 110 was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 40.2 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 6.4 Hz, 2H), 7.42-7.15 (m, 24H), 5.46-5.34 (m, 1H), 5.13-5.02 (m, 2H), 4.43-4.39 (m, 3H), 4.33-4.23 (m, 2H), 2.72 (d, *J* = 6.0 Hz, 2H), 1.37 (s, 9H), 1.21 (d, *J* = 6.2 Hz, 3H); HRMS (FAB): calcd. for $C_{54}H_{53}N_3O_9Na$ $(M+Na)^+$: 910.3680, found: 910.3675.

Boc–Thr(Fmoc–Asn(Trt))–OH (32). **32** was synthesized in the similar manner to **1**. Yield: 78%; HPLC analysis at 230 nm: purity was 94% (t_R = 36.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.42-7.15 (m, 19H), 5.45-5.33 (m, 1H), 4.53-4.41 (m, 2H), 4.31-4.23 (m, 2H), 4.16-4.11 (m, 1H), 2.89-2.74 (m, 2H), 1.40 (s, 9H), 1.20 (d, *J* = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{47}H_{47}N_3O_9Na$ $(M+Na)^+$: 820.3210, found: 820.3205.

Boc–Thr(Fmoc–Glu(O*t*Bu))–OBzl (73). **73** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-glutamic acid derivative **111**. Yield: 74%; HPLC analysis at 230 nm: purity was 94% (t_R = 38.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.40-7.25 (m, 9H), 5.50-5.41 (m, 1H), 5.13 (d, *J* = 12.3 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H) 4.42-4.31 (m, 3H), 4.24-4.13 (m, 2H), 2.28 (t, *J* = 7.2 Hz, 2H), 2.07-1.94 (m, 1H), 1.90-1.76 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H), 1.30-1.23 (m, 3H); HRMS (FAB): calcd.. for $C_{40}H_{48}N_2O_{10}Na$ $(M+Na)^+$: 739.3207, found: 739.3214.

Boc–Thr(Fmoc–D-Glu(O*t*Bu))–OBzl (111). **111** was synthesized in the similar manner to **44**. Yield: 88%; HPLC analysis at 230 nm: purity was 94% (t_R = 39.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.70-7.64 (m, 2H), 7.41-7.28 (m, 9H), 5.48-5.40 (m, 1H), 5.18 (d, *J* = 12.2 Hz, 1H), 5.10 (d, *J* = 12.2 Hz, 1H) 4.45-4.33 (m, 3H), 4.23 (t, *J* = 7.1 Hz, 1H), 4.18-4.11 (m, 1H), 2.27 (t, *J* = 7.6 Hz, 2 H), 2.07-1.94 (m, 1H), 1.81-1.69 (m, 1H), 1.44 (s, 9H), 1.41 (s, 9H), 1.28-1.24 (m, 3H); HRMS (FAB): calcd. for $C_{40}H_{48}N_2O_{10}Na$ $(M+Na)^+$: 739.3207, found: 739.3201.

Boc–Thr(Fmoc–Glu(O*t*Bu))–OH (33). **33** was synthesized in the similar manner to **1**. Yield: 90%; HPLC analysis at 230 nm: purity was 88% (t_R = 33.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.68 (t, *J* = 6.0 Hz, 2H), 7.41-7.29 (m, 4H), 5.47-5.34 (m, 1H), 4.38-4.31 (m, 2H), 4.25-4.21 (m, 2H), 4.15-4.10 (m, 1H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.13-2.00 (m, 1H), 1.92-1.87 (m, 1H), 1.44 (s, 9H), 1.41 (s, 9H), 1.25 (d, *J* = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{33}H_{42}N_2O_{10}Na$ $(M+Na)^+$: 649.2737, found: 649.2728.

Boc–Thr(Fmoc–Gln(Trt))–OBzl (74). **74** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-glutamine derivative **112**. Yield: >99%; HPLC analysis at 230 nm: purity was 95% (t_R = 41.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.66-7.61 (m, 2H), 7.39-7.16 (m, 24H), 5.48-5.44 (m, 1H), 5.11 (d, *J* = 12.5 Hz, 1H), 5.02 (d, *J* = 12.5 Hz, 1H), 4.41-4.35 (m, 2H), 4.23-4.08 (m, 3H), 2.45-2.28 (m, 2H), 2.05-1.95 (m, 1H), 1.82-1.72 (m, 1H), 1.41 (s, 9H), 1.28-1.21 (m, 3 H); HRMS (FAB): calcd. for $C_{55}H_{55}N_3O_9Na$ $(M+Na)^+$: 924.3836, found: 924.3830.

Boc–Thr(Fmoc–D-Gln(Trt))–OBzl (112). **112** was synthesized in the similar manner to **42**. Yield: >99%; HPLC analysis at 230 nm: purity was 93% (t_R = 40.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.67-7.65 (m, 2H), 7.39-7.18 (m, 24H), 5.46-5.43 (m, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.03 (d, *J* = 12.1 Hz, 1H), 4.42-4.37 (m, 2 H), 4.25-4.20 (m, 1H), 4.16-4.05 (m, 2H), 2.47-2.45 (m, 2H), 2.04-1.92 (m, 1H), 1.72-1.64 (m, 2H), 1.39 (s, 9H), 1.28-1.20 (m, 3H); HRMS (FAB): calcd. for $C_{55}H_{55}N_3O_9Na$ $(M+Na)^+$: 924.3836, found: 924.3830.

Boc–Thr(Fmoc–Gln(Trt))–OH (34). **34** was synthesized in the similar manner to **1**. Yield: 89%; HPLC analysis at 230 nm: purity was 94% (t_R = 36.9 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.68-7.65 (m, 2H), 7.39-7.16 (m, 19H), 5.47-5.41 (m, 1H), 4.40-4.31 (m, 2H), 4.24-4.19 (m, 2H), 4.12-4.11 (m, 1H), 2.45-2.29 (m, 2H), 2.06-1.97 (m, 1H), 1.89-1.79 (m, 1H), 1.39 (s, 9H), 1.23 (d, *J* = 6.0 Hz, 3H); HRMS (FAB): calcd. for $C_{48}H_{49}N_3O_9Na$ $(M+Na)^+$: 834.3367, found: 834.3362.

Boc–Thr(Fmoc–His(Trt))–OBzl (75). **75** was synthesized in the similar manner to **42**. Preparative HPLC with a 0.1% aqueous TFA–CH_3CN system was used for purification. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-histidine derivative **113**. Yield: 72%; HPLC analysis at 230 nm: purity was 93% (t_R = 35.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 6.7 Hz, 2H), 7.41-7.18 (m, 18H), 7.12-7.03 (m, 8H), 5.48-5.35 (m, 1H), 5.09 (d, *J* = 12.3 Hz,

1H), 5.02 (d, *J* = 12.3 Hz, 1H), 4.45-4.35 (m, 2H), 4.31-4.19 (m, 2H), 4.16-4.09 (m, 1H), 3.03-2.90 (m, 1H), 2.87-2.75 (m, 1H), 1.41 (s, 9H), 1.18 (d, *J* = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{56}H_{54}N_4O_8Na$ $(M+Na)^+$: 933.3839, found: 933.3836.

Boc–Thr(Fmoc–D-His(Trt))–OBzl (113). **113** was synthesized in the similar manner to **42**. Preparative HPLC with a 0.1% aqueous TFA–CH_3CN system was used for purification. Yield: >99%; HPLC analysis at 230 nm: purity was 93% (t_R = 35.3 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.64-7.54 (m, 2H), 7.45-7.20 (m, 18H), 7.17-7.09 (m, 8H), 5.47-5.37 (m, 1H), 5.14-5.01 (m, 2H), 4.50-4.35 (m, 3H), 4.30-4.22 (m, 1H), 4.21-4.11 (m, 1H), 3.02-2.89 (m, 1H), 2.86-2.74 (m, 1H), 1.41 (s, 9H), 1.31-1.20 (m, 3H); HRMS (FAB): calcd. for $C_{56}H_{54}N_4O_8Na$ $(M+Na)^+$: 933.3839, found: 933.3836.

Boc–Thr(Fmoc–His(Trt))–OH (35). **35** was synthesized in the similar manner to **1**. Preparative HPLC with a 0.1% aqueous TFA–CH_3CN system was used for purification. Yield: 77%; HPLC analysis at 230 nm: purity was 87% (t_R = 31.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.65-7.58 (m, 2H), 7.42-7.19 (m, 15H), 7.13-7.02 (m, 6H), 5.41-5.30 (m, 1H), 4.52-4.44 (m, 1H), 4.34-4.05 (m, 4H), 3.11-3.01 (m, 1H), 2.91-2.77 (m, 1H), 1.38 (s, 9H), 1.20 (d, *J* = 6.2 Hz, 3H); HRMS (FAB): calcd. for $C_{49}H_{48}N_4O_8Na$ $(M+Na)^+$: 843.3370, found: 843.3374.

Boc–Thr(Fmoc–Lys(Boc))–OBzl (76). **76** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-lysine derivative **114**. Yield: 98%; HPLC analysis at 230 nm: purity was 92% (t_R = 37.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.5 Hz, 2 H), 7.67-7.62 (m, 2 H), 7.04-7.25 (m, 9 H), 5.47-5.43 (m, 1H), 5.13 (d, *J* = 12.3 Hz, 1 H), 5.05 (d, *J* = 12.6 Hz, 1 H), 4.41-4.29 (m, 3H), 4.23-4.19 (m, 1H), 4.13-4.06 (m, 1H), 3.04-3.00 (m, 2H), 1.74-1.58 (m, 2H), 1.51-1.18 (m, 7H), 1.43 (s, 9H), 1.42 (s, 9H); HRMS (FAB): calcd. for $C_{42}H_{53}N_3O_{10}Na$ $(M+Na)^+$: 782.3629, found: 782.3624.

Boc–Thr(Fmoc–D-Lys(Boc))–OBzl (114). **114** was synthesized in the similar manner to **44**. Yield: >99%; HPLC analysis at 230 nm: purity was 94% (t_R = 37.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.3 Hz, 2 H), 7.69-7.65 (m, 2 H), 7.41-7.28 (m, 9 H), 5.43-5.41 (m, 1H), 5.17 (d, *J* = 12.5 Hz, 1 H), 5.09 (d, *J* = 12.1 Hz, 1 H), 4.44-4.31 (m, 3H), 4.25-4.20 (m, 1H), 4.11-4.04 (m, 1H), 3.03-3.00 (m, 2H), 1.71-1.50 (m, 1H), 1.45-1.21 (m, 5H), 1.42 (s, 9H), 1.41 (s, 9H), 1.27 (d, *J* = 6.4 Hz, 3 H); HRMS (FAB): calcd. for $C_{42}H_{53}N_3O_{10}Na$ $(M+Na)^+$: 782.3629, found: 782.3634.

Boc–Thr(Fmoc–Lys(Boc))–OH (36). **36** was synthesized in the similar manner to **1**. Yield: 96%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 35.1 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79 (d, *J* = 7.4 Hz, 2 H), 7.70-7.66 (m, 2 H), 7.41-7.29 (m, 4 H), 5.39-5.37 (m, 1H), 4.42-4.30 (m, 2H), 4.25-4.11 (m, 3H), 3.03 (t, *J* = 6.6 Hz, 2H), 1.81-1.63 (m, 1H), 1.52-1.28 (m, 5H), 1.42 (s, 9H), 1.41 (s, 9H), 1.24 (d, *J* = 6.4 Hz, 3 H); HRMS (FAB): calcd. for $C_{35}H_{47}N_3O_{10}Na$ $(M+Na)^+$: 692.3159, found: 692.3154.

Boc–Thr(Fmoc–Phe)–OBzl (78). **78** was synthesized in the similar manner to **44**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-phenylalanine derivative **116**. Yield: 94%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.3 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.39-7.35 (m, 2H), 7.31-7.18 (m, 12H), 5.45-5.39 (m, 1H), 5.13, 5.05 (2d, *J* = 12.3 Hz, 2H), 4.39 (d, *J* = 2.6 Hz, 1H), 4.36 (dd, *J* = 9.1, 6.2 Hz, 1H), 4.27-4.25 (m, 2H), 4.14 (t, *J* = 6.9 Hz, 1H), 3.02, 2.88 (2dd, *J* = 13.8 Hz, 9.2, 6.2 Hz, 2H), 1.44 (s, 9H), 1.14 (d, *J* = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{40}H_{43}N_2O_8$ $(M+H)^+$: 679.3019, found: 679.3015.

Boc–Thr(Fmoc–D-Phe)–OBzl (116). 116 was synthesized in the similar manner to **44**. Yield: 97%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 38.6 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.39-7.17 (m, 14H), 5.48-5.42 (m, 1H), 5.15, 5.07 (2d, *J* = 12.3 Hz, 2H), 4.43 (d, *J* = 2.7 Hz, 1H), 4.37 (dd, *J* = 9.9, 4.7 Hz, 1H), 4.30-4.21 (m, 2H), 4.14 (t, *J* = 7.0 Hz, 1H), 3.06, 2.75 (2dd, *J* = 13.9 Hz, 10.1, 4.7 Hz, 2H), 1.41 (s, 9H), 1.26 (d, *J* = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{40}H_{42}N_2O_8Na$ $(M+Na)^+$: 701.2839, found: 701.2843.

Boc–Thr(Fmoc–Phe)–OH (38). **38** was synthesized in the similar manner to **1**. Yield: 96%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 33.5 min); ^{1}H NMR (CD_3OD, 400MHz) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.61-7.58 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31-7.16 (m, 7H), 5.41-5.439 (m, 1H), 4.42 (dd, *J* = 9.4, 5.7 Hz, 1H), 4.30-4.20 (m, 3H), 4.14 (t, *J* = 7.0 Hz, 1H) 3.10, 2.90 (2 dd, *J* = 13.7 Hz, 9.5, 5.7 Hz, 2H), 1.44 (s, 9H), 1.18 (d, *J* = 7.3 Hz, 3H); HRMS (FAB): calcd. for $C_{33}H_{36}N_2O_8Na$ $(M+Na)^+$: 611.2369, found: 611.2375.

Boc–Thr(Fmoc–Tyr(*t*Bu))–OBzl (79). **79** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-tyrosine derivative **117**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 40.8 min); ^{1}H NMR

(CD_3OD, 300MHz) δ 7.77 (d, J = 7.5 Hz, 2H), 7.61-7.57 (m, 2H), 7.40-7.25 (m, 9H), 7.11 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.2 Hz, 2H), 5.45-5.41 (m, 1H), 5.15 (d, J = 12.2 Hz, 1H), 5.04 (d, J = 12.2 Hz, 1H), 4.41-4.30 (m, 2H), 4.28-4.19 (m, 2H), 4.15-4.08 (m, 1H), 3.03-2.96 (m, 1H), 2.86-2.79 (m, 1H), 1.44 (s, 9H), 1.30-1.20 (m, 12H), 1.15 (d, J = 6.2 Hz, 3H); HRMS (FAB): calcd. for $C_{44}H_{50}N_2O_9Na$ $(M+Na)^+$: 773.3414, found: 773.3418.

Boc–Thr(Fmoc–D-Tyr(*t*Bu))–OBzl (117). **117** was synthesized in the similar manner to **44**. Yield: >99%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 39.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.78 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.1 Hz, 2H), 7.40-7.25 (m, 9H), 7.10 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 5.46-5.43 (m, 1H), 5.16 (d, J = 12.0 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1H), 4.44-4.13 (m, 5H), 3.05-3.00 (m, 1H), 2.74-2.65 (m, 1H), 1.42 (s, 9H), 1.27 (d, J = 5.9 Hz, 3H), 1.24 (s, 9H); HRMS (FAB): calcd. for $C_{44}H_{50}N_2O_9Na$ $(M+Na)^+$: 773.3414, found: 773.3420.

Boc–Thr(Fmoc–Tyr(*t*Bu))–OH (39). **39** was synthesized in the similar manner to **1**. Yield: 76%; HPLC analysis at 230 nm: purity was 94% (t_R = 35.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.79-7.77 (m, 2H), 7.64-7.61 (m, 2H), 7.40-7.27 (m, 4H), 7.17-7.14 (m, 2H), 6.87-6.84 (m, 2H), 5.44-5.39 (m, 1H), 4.43-4.38 (m, 1H), 4.30-4.10 (m, 4H), 3.11-3.05 (m, 1H), 2.88-2.80 (m, 1H), 1.43 (s, 9H), 1.30-1.19 (m, 12H); HRMS (FAB): calcd. for $C_{37}H_{44}N_2O_9Na$ $(M+Na)^+$: 683.2945, found: 683.2939.

Boc–Thr(Fmoc–Trp(Boc))–OBzl (80). **80** was synthesized in the similar manner to **42**. Epimerization during the synthesis was not detected, confirmed by comparison with independently synthesized D-tryptophan derivative **118**. Yield: 94%; HPLC analysis at 230 nm: purity was 92% (t_R = 40.8 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.77-7.70 (m, 2H), 7.63-7.48 (m, 4H), 7.37-7.19 (m, 12H), 5.45-5.42 (m, 1H), 5.11 (d, J = 12.3 Hz, 1H), 5.03 (d, J = 12.3 Hz, 1H), 4.58-4.50 (m, 1H), 4.43-4.38 (m, 1H), 4.33-4.16 (m, 3H), 3.18-3.11 (m, 1H), 3.08-3.00 (m, 1H), 1.58 (s, 9H), 1.43 (s, 9H), 1.15 (d, J = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{47}H_{51}N_3O_{10}Na$ $(M+Na)^+$: 840.3472, found: 840.3476.

Boc–Thr(Fmoc–D-Trp(Boc))–OBzl (118). **118** was synthesized in the similar manner to **44**. Yield: 96%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 40.7 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.77-7.68 (m, 2H), 7.64-7.47 (m, 4H), 7.36-7.17 (m, 12H), 5.46-5.44 (m, 1H), 5.09 (d, J = 12.1 Hz, 1H), 5.00 (d, J = 12.1 Hz, 1H), 4.53-4.48 (m, 1H), 4.45-4.42 (m, 1H), 4.34-4.28 (m, 1H), 4.24-4.15 (m, 2H), 3.26-3.11 (m, 1H), 2.96-2.88 (m, 1H), 1.59 (s, 9H), 1.41 (s, 9H), 1.27 (d, J = 6.8 Hz, 3H); HRMS (FAB): calcd. for $C_{47}H_{51}N_3O_{10}Na$ $(M+Na)^+$: 840.3472, found: 840.3476.

Boc–Thr(Fmoc–Trp(Boc))–OH (80). **80** was synthesized in the similar manner to **1**. Yield: 91%; HPLC analysis at 230 nm: purity was higher than 95% (t_R = 37.0 min); ^{1}H NMR (CD_3OD, 300MHz) δ 7.75 (d, J = 7.7 Hz, 2H), 7.66-7.63 (m, 1H), 7.55-7.51 (m, 3H), 7.36-7.18 (m, 7H), 5.44-5.41 (m, 1H), 4.61-4.56 (m, 1H), 4.32-4.25 (m, 1H), 4.21-4.11 (m, 3H), 3.27-3.21 (m, 1H), 3.12-3.03 (m, 1H), 1.57 (s, 9H), 1.42 (s, 9H), 1.22 (d, J = 6.4 Hz, 3H); HRMS (FAB): calcd. for $C_{40}H_{45}N_3O_{10}Na$ $(M+Na)^+$: 750.3003, found: 750.3007.