Supplementary Material (ESI) for *Soft Matter*
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Relationship between molecular structure, gelation behaviour and gel properties of Fmoc-dipeptides

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SUPPORTING INFORMATION

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Preparation of Fmoc-dipeptides. Fmoc-dipeptides were prepared by coupling two protected amino acids. This is exemplified for the formation of FmocLeucineGlycine. Isobutylchloroformate (0.316 mL, 2.44 mmol) was added to a solution of FmocLeucine-OH (0.86 g, 2.44 mmol) and *N*-methylmorpholine (NMM, 0.27 mL, 2.44 mmol) in chloroform (20 mL) at -10 ^{o}C. After stirring for 3 minutes, HCl.H_2N-Glycine-O^{t}Bu (0.41 g, 2.44 mmol) and NMM (0.27 mL, 2.44 mmol) in chloroform (5 mL) were added. The reaction was allowed to warm to room temperature and then stirred overnight. The organic layer was then partitioned between chloroform (50 mL) and water. The organic phase was washed sequentially with water, 0.2 M HCl (aq), 0.2 M $NaHCO_3$ (aq) and brine. After drying with sodium sulfate, the organic solvent was removed *in vacuo* to give the product in high purity.

The *tert*-butyl protecting group was removed by dissolving the Fmoc-dipeptide in chloroform (5 mL) and adding trifluoroacetic acid (5 mL). After stirring overnight, the product was collected by precipitation into cold diethyl ether and filtration. This afforded the product in high purity and yield.

Full Characterisation Data for the Fmoc-Dipeptides used in this study are detailed below:

t-Butyl Protected Dipeptides

Fmoc-Ala-Ala-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.15 (1H, NHCHCH$_3$, d, ^{3}J=7.0 Hz), 7.88 (2H, 2ArH,d, ^{3}J= 7.5 Hz), 7.73 (2H, 2ArH, t, ^{3}J=7.5 Hz), 7.48 (1H, NHCHCH$_3$, d, ^{3}J=7.9 Hz), 7.42 (2H, 2ArH, t, ^{3}J=7.4 Hz), 7.33 (2H, 2ArH, t, ^{3}J= 7.4 Hz), 4.30 (2H, CHCH$_2$, d, ^{3}J=6.9 Hz), 4.23 (1H, CHCH$_2$, t, ^{3}J=6.8 Hz), 4.04-4.14 (2H, 2CH (2Ala), m), 1.40 (9H,$(CH_3)_3$, s), 1.27 (3H, CH_3 (Ala),d, ^{3}J= 5.1 Hz), 1.22 (3H,CH_3 (Ala),d, ^{3}J= 5.0 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 16.9 (CH_3 (Ala)), 18.2 (CH_3 (Ala)), 27.6 ($3CH_3$,$C(CH_3)_3$), 46.6 (CHCH$_2$), 48.2 (CH (Ala)), 49.5(CH (Ala)), 65.6 (CHCH$_2$), 80.2 (4^{o}C, C$(CH_3)_3$), 120.0 (ArCH), 120.1 (ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4^{o}C), 143.8 (Ar 4^{o}C), 143.9

(Ar 4°C), 155.6 (4°C, C=O ester), 171.7 (4°C, C=O amide), 172.3 (4°C, C=O amide). $C_{25}H_{30}N_2O_5$ m/z (ES) 461 $[M+Na]^+$, Mp 56-58 °C.

Fmoc-Ala-Gly-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.15 (1H, NHCH$_2$, t, ^3J=5.6 Hz), 7.88 (2H, 2ArH,d, ^3J= 7.5 Hz), 7.73 (2H, 2ArH, t, ^3J=6.8 Hz), 7.52 (1H, NHCHCH$_3$, d, ^3J=7.9 Hz), 7.42 (2H, 2ArH, t, ^3J=7.4 Hz), 7.33 (2H, 2ArH, t, ^3J= 7.4 Hz), 4.25 (2H, CHCH$_2$, d, ^3J=6.9 Hz), 4.20 (1H, CHCH$_2$, t, ^3J=6.5 Hz), 4.10 (1H, NHCHCH$_3$,qn, ^3J=7.1 Hz), 3.75 (1H, CH (Gly), dd, ^3J=5.8 Hz, ^2J=17.4 Hz), 3.65 (1H, CH (Gly), dd, ^3J=5.9 Hz, ^2J=17.4 Hz), 1.40 (9H,$(CH_3)_3$, s), 1.27 (3H, CH$_3$ (Ala),d, ^3J= 7.2 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.2 (CH$_3$ (Ala)), 27.7 (3CH$_3$,C$(CH_3)_3$), 40.0 (CH$_2$ (Gly)), 46.6 (CH (Ala)), 49.8 (CHCH$_2$), 65.6 (CHCH$_2$), 80.5 (4°C, C$(CH_3)_3$), 120.1 (2ArCH),125.3 (2ArCH),127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4°C), 143.8 (Ar 4°C), 143.9 (Ar 4°C), 155.6 (4°C, C=O ester), 168.8 (4°C, C=O amide), 172.9 (4°C, C=O amide). $C_{24}H_{28}N_2O_5$ m/z (ES) 391 $[(M-{}^tBu)+Na+H]^+$ Mp 104-107 °C.

Fmoc-Ala-Val-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.90 (2H, 2ArH, d, ^3J=7.5 Hz), 7.88 (1H, NHCHCH$(CH_3)_2$, d, ^3J= 8.3 Hz), 7.73 (2H, 2ArH, t, ^3J= 7.7 Hz), 7.50 (1H, NHCHCH$_3$, d, ^3J= 7.8 Hz), 7.42 (2H, 2ArH, t, ^3J=7.4 Hz), 7.31 (2H, 2ArH, ^3J=7.4 Hz), 4.25 (2H, CHCH$_2$, d, ^3J=6.8 Hz), 4.20 (1H, CHCH$_2$, t, ^3J=6.8 Hz), 4.18 (1H, CH, t, ^3J= 7.4 Hz), 4.03 (1H, CH (Ala), dd, ^3J=6.0Hz, ^3J=7.9 Hz), 2.02 (1H, CH (Val), m), 1.40 (9H, $(CH_3)_3$, s), 1.22 (3H, CH$_3$, d, ^3J=7.1Hz), 0.88 (6H, $(CH_3)_2$ (Val), m). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.4 (CH$_3$ (Val)), 18.7 (CH$_3$ (Val)), 19.4 (CH$_3$ (Ala)), 28.1 (3CH$_3$,C$(CH_3)_3$), 30.4 (CH (Val)), 47.1 (CHCH$_2$), 50.1 (CH,(Val)), 58.3 (CH (Ala)), 66.1 (CHCH$_2$), 81.0 (4°C, C$(CH_3)_3$), 120.5 (2ArCH), 125.7 (ArCH), 125.8 (ArCH), 127.5 (2ArCH), 128.1(2ArCH), 141.2 (2Ar 4°C), 144.3 (Ar 4°C), 144.4 (Ar 4°C), 156.1 (4°C, C=O ester), 170.9 (4°C, C=O amide), 173.3 (4°C, C=O amide). $C_{27}H_{33}N_2O_5$ m/z (ES) 489 $[M+Na]^+$ Mp 113-115 °C.

Fmoc-Val-Gly-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.25 (1H, NH, t, ^3J=5.8 Hz), 7.90 (2H, 2ArH , d, ^3J= 7.5 Hz), 7.75 (1H, NH, t, ^3J= 7.6 Hz), 7.42 (4H, 4ArH, m), 7.31 (2H, 2ArH, m), 4.25 (3H, CHCH$_2$ and CHCH$_2$, m), 3.88 (1H, CH (Val), m), 3.80 (1H, CH (Gly), dd, ^3J=6.1Hz, ^2J=11.2 Hz), 3.68 (1H, CH (Gly), dd, ^3J=5.7 Hz,

^{2}J=11.5 Hz), 2.02 (1H, CH (Val), m), 1.40 (9H, $(CH_3)_3$, s), 0.88 (6H, $(CH_3)_2$ (Val), m). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.7 (CH_3 (Val)), 19.7 (CH_3 (Val)), 28.2 ($3CH_3$,$C(CH_3)_3$), 30.8 (CH (Val)), 41.9 (CH_2 (Gly)) 47.1 (<u>CH</u>CH_2), 60.6 (CH,(Val)), 66.2 (CH<u>CH_2</u>), 81.0 (4^oC, <u>C</u>$(CH_3)_3$), 120.5 (2ArCH), 125.9 (2ArCH), 127.5 (2ArCH), 128.1 (2ArCH), 141.2 (2Ar 4^oC), 144.3 (Ar 4^oC), 144.4 (Ar 4^oC), 156.6 (4^oC, C=O ester), 169.3 (4^oC, C=O amide), 172.1 (4^oC, C=O amide). $C_{26}H_{32}N_2O_5$ m/z (ES) 475 $[M+Na]^+$ Mp 154-155 ^oC.

Fmoc-Leu-Ala-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.18 (1H, <u>NH</u>$CHCH_3$, d, ^{3}J=7.0 Hz), 7.88 (2H, 2ArH, d, ^{3}J= 7.6 Hz), 7.73 (2H, 2ArH,d, ^{3}J= 7.1 Hz), 7.47 (1H, $NHCHCH_2CH(CH_3)_2$, t, ^{3}J= 8.8 Hz), 7.43 (2H, 2ArH,d, ^{3}J= 7.5 Hz), 7.32(2H, 2ArH,d, ^{3}J= 7.5 Hz), 4.20-4.30 (3H, <u>CH</u>CH_2 and CH<u>CH_2</u>, m), 4.04-4.15 (2H, CH_2(Leu), m), 1.68 (1H, CH(Leu), q, ^{3}J= 6.9 Hz), 1.48 (2H, CH_2(Leu), m), 1.40 (9H,$(CH_3)_3$, s), 1.27 (3H, CH_3(Ala), d, ^{3}J= 7.3 Hz), 0.88 (3H, CH_3(Leu), d, ^{3}J= 6.6 Hz), 0.85 (3H, CH_3(Leu), d, ^{3}J= 6.6 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 16.8 (CH_3 (Ala)), 21.4 (CH (Leu)), 23.1(CH_3 (Leu)), 24.1 (CH_3 (Leu)), 27.7 ($3CH_3$,$C(CH_3)_3$), 40.8 (CH_2 (Leu)), 46.7 (CH (Ala)), 48.3 (<u>CH</u>CH_2), 52.6 (CH,(Leu)), 65.6 (CH<u>CH_2</u>), 80.2 (4^oC, <u>C</u>$(CH_3)_3$), 120.0 (2ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4^oC), 143.7 (Ar 4^oC), 143.9 (Ar 4^oC), 155.9 (4^oC, C=O ester), 171.6 (4^oC, C=O amide), 172.2 (4^oC, C=O amide). $C_{28}H_{36}N_2O_5$ m/z (ES) 503[$(M+Na]^+$ Mp 127-129 ^oC.

Fmoc-Phe-Ala-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.40 (1H, <u>NH</u>$CHCH_2Ph$, d, ^{3}J=7.0 Hz), 7.88 (2H, 2ArH, d, ^{3}J= 7.6 Hz), 7.58-7.66 (3H, 3ArH, m), 7.25-7.41 (8H, 8ArH, m), 7.19 (1H, $NHCHCH_3$, t, ^{3}J= 7.3Hz), 4.30 (1H,CH(Phe), dt, ^{3}J= 11.0 Hz, ^{4}J=3.2 Hz), 4.07- 4.18 (4H,<u>CH</u>CH_2,CH<u>CH_2</u> and CH(Ala), m), 3.04 (1H, CH(Phe), dd, ^{2}J= 13.8 Hz, ^{4}J= 3.4 Hz), 2.77 (1H, CH(Phe), dd, ^{2}J= 13.6 Hz, ^{3}J= 11.3 Hz), 1.40 (9H,$(CH_3)_3$, s), 1.30 (3H,CH_3(Ala), d, ^{3}J= 7.3 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 16.9 (CH_3 (Ala)), 27.6 ($3CH_3$,$C(CH_3)_3$), 37.5 (CH_2 (Phe)), 46.5 (CH (Ala)), 48.4 (<u>CH</u>CH_2), 55.8 (CH,(Phe)), 65.6 (CH<u>CH_2</u>), 80.3 (4^oC, <u>C</u>$(CH_3)_3$), 120.0 (2ArCH),125.2 (ArCH), 125.3 (ArCH), 126.2(ArCH (Phe)), 127.0 (2ArCH), 127.6 (2ArCH), 128.0 (2ArCH,(Phe)), 129.2 (2ArCH,(Phe)),138.2(Ar 4^oC), 140.6 (2Ar

4°C), 143.7 (2Ar 4°C), 155.8 (4°C, C=O ester), 171.5 (4°C, C=O amide), 171.7 (4°C, C=O amide). $C_{31}H_{34}N_2O_5$ m/z (ES) 516 $[(M+H]^+$, Mp 107-110 °C.

Fmoc-Leu-Gly-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.18 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.73 (2H, 2ArH,d, ^3J= 7.3 Hz, ^4J= 3.2Hz), 7.50(1H, NHCHCH$_2$CH(CH$_3$)$_2$, t, ^3J= 8.5 Hz), 7.41 (2H, 2ArH, dd, ^3J= 7.4 Hz), 7.28-7.34 (2H, 2ArH, m), 4.20-4.30 (3H, CHCH$_2$ and CHCH$_2$, m), 4.03-4.10 (1H, NHCH(Leu), m), 3.75 (1H, CH(Gly), dd, ^3J= 5.8 Hz, ^2J= 11.7 Hz), 3.65 (1H, CH(Gly), dd, ^3J= 5.9 Hz, ^2J= 11.7 Hz), 1.70-1.58 (1H, CH(Leu), m), 1.58-1.42 (2H, CH$_2$(Leu),m), 1.40 (9H,(CH$_3$)$_3$, s), 0.88 (3H, CH$_3$(Leu), d, ^3J= 6.6 Hz), 0.85 (3H, CH$_3$(Leu), d, ^3J= 6.5 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 21.3 (CH (Leu)), 23.0(CH$_3$ (Leu)), 24.1 (CH$_3$ (Leu)), 27.7 (3CH$_3$,C(CH$_3$)$_3$), 40.7 (CH$_2$ (Leu)), 41.4 (CH$_2$ (Gly)), 46.7 (CHCH$_2$), 52.8 (CH,(Leu)), 65.5 (CHCH$_2$), 80.5 (4°C, C(CH$_3$)$_3$), 120.0 (ArCH), 120.1 (ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.9 (4°C, C=O ester), 168.8 (4°C, C=O amide), 172.7 (4°C, C=O amide). $C_{27}H_{34}N_2O_5$ m/z (ES) 489$[(M+Na]^+$ Mp 128-131 °C.

Fmoc-Phe-Gly-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.18 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.67 (3H, 3ArH,t, ^3J=8.9 Hz), 7.35-7.41 (2H, 2ArH, m), 7.33 (2H, 2ArH,d, ^3J=7.2 Hz), 7.30 (2H, 2ArH,d, ^3J=7.5 Hz), 7.27 (2H, 2ArH,d, ^3J=7.4 Hz), 4.27 (2H, CH$_2$(Phe), dd, ^3J= 10.9, Hz, ^4J= 3.6 Hz),), 4.05-4.15 (3H, CHCH$_2$ and CHCH$_2$, m), 3.75 (1H, CH(Gly), dd, , ^2J= 17.4 Hz, ^3J= 5.9 Hz), 3.65 (1H, CH(Gly), dd, ^2J= 17.5Hz, ^3J= 5.9 Hz,), 3.04 (1H, CH(Phe), dd, ^2J= 13.7 Hz, ^4J= 3.5 Hz), 2.77 (1H, CH(Phe), dd, ^2J= 13.6 Hz, ^3J= 11.1 Hz), 1.40 (9H,(CH$_3$)$_3$, s). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 27.7 (3CH$_3$,C(CH$_3$)$_3$), 37.4 (CH$_2$ (Phe)), 41.4 (CH$_2$ (Gly)), 46.5 (CHCH$_2$), 56.0 (CH,(Phe)), 65.6 (CHCH$_2$), 80.6 (4°C, C(CH$_3$)$_3$), 120.0 (2ArCH), 125.2 (ArCH), 125.3 (ArCH), 126.2 (ArCH), 127.0 (2ArCH), 127.6 (ArCH), 128.0 (2ArCH), 129.2 (2ArCH), 138.2 (2Ar 4°C), 140.6 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.8 (4°C, C=O ester), 168.8 (4°C, C=O amide), 172.0 (4°C, C=O amide). $C_{30}H_{32}N_2O_5$ m/z (ES) 523$[(M+Na]^+$ Mp 160-163 °C.

Fmoc-Phe-Val-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.08 (1H, NHCH$_2$, d, ^3J=8.2 Hz), 7.87 (2H, 2ArH, d, ^3J= 7.3 Hz), 7.62 (3H, 3ArH, dt, ^3J=8.9 Hz, ^4J=7.5), 7.40 (2H, 2ArH, m), 7.33 (1H, NHCHCH$(CH_3)_2$, d, ^3J= 8.2 Hz), 7.18-7.34 (5H, 5ArH, m), 7.18 (1H, ArH, t, ^3J= 7.4, m), 4.39 (1H, CHNH, m), (3H, CHNH + CH_2OCO, m), 4.14 (3.01 (1H, CHPhe, dd, ^2J= 13.8 Hz, ^4J=3.6 Hz), 2.79 (1H, CHPhe, dd, ^2J= 13.7 Hz, ^4J=11.04 Hz), 2.08 (1H, CH$(CH_3)_2$, m), 1.41 (9H, $(CH_3)_2$, s), 0.90 (6H, $(CH_3)_2$, m). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.5 (CH_3, val),19.1 (CH_3, val), 28.1 ($3CH_3$,C$(CH_3)_3$), 30.5 (CHC$(CH_3)_2$), 37.9 (CH_2 (Phe)), 47.0 (CHCH$_2$), 58.4 (CH,(Phe)), 66.1 (CHCH$_2$), 81.1 (4^{o}C, C$(CH_3)_3$), 120.5 (ArCH), 125.7 (2ArCH), 126.7 (ArCH), 127.5 (2ArCH), 128.5 (2ArCH), 129.7 (2ArCH), 138.6 (2Ar 4^{o}C), 141.1 (Ar 4^{o}C), 144.2 (Ar 4^{o}C), 156.2 (4^{o}C, C=O ester), 170.9 (4^{o}C, C=O amide), 172.4 (4^{o}C, C=O amide). $C_{33}H_{37}N_2O_5$ m/z (ES) 565 $[(M+Na]^+$.

Fmoc-Leu-Phe-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.14 (1H, NHCHCH$_2$Ph, d, ^3J= 7.4 Hz), 7.89 (2H, 2ArH, d, ^3J= 7.5 Hz), 7.73 (2H, 2ArH, d, ^3J=7.3 Hz), 7.41 (3H, 3ArH, m), 7.31 (2H, 2ArH, td, ^2J=4.2 Hz, ^3J=7.3 Hz), 7.14-7.24 (5H, 4ArH, NHCHCH$_2$CH$(CH_3)_2$, m), 4.27-4.38 (2H, CH(Phe) and CHCH$_2$, m), 4.18-4.25 (2H, CHCH$_2$, m), 4.05-4.11 (1H, CHNH (Leu) m), 2.88- 3.05 (2H, CH_2 (Phe), m), 1.57 (1H, CH (Leu), q, ^3J=6.9 Hz), 1.32-1.46 (2H, CH_2 (Leu), m), 1.32 (9H, $CH_3)_3$, s), 0.88 (3H, CH_3, (Leu), d, ^3J=6.6 Hz), 0.87 (3H, CH_3, (Leu), d, ^3J=6.5 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 21.4 (CH (Leu)), 23.0 (CH_3 (Leu)), 24.1 (CH_3 (Leu)), 27.5 ($3CH_3$,C$(CH_3)_3$), 36.7 (CH_2 (Phe)), 40.8 (CH_2 (Leu)), 46.7 (CHCH$_2$), 52.8 (CH,(Leu)), 54.0(CH (Phe)), 65.5 (CHCH$_2$), 80.5 (4^{o}C, C$(CH_3)_3$), 120.0 (2ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH),128.1(2ArCH), 129.1 (3ArCH),137.1 (Ar 4^{o}C), 140.7 (2Ar 4^{o}C), 143.7 (Ar 4^{o}C), 143.9 (Ar 4^{o}C), 155.8 (4^{o}C, C=O ester), 170.3 (4^{o}C, C=O amide), 172.2 (4^{o}C, C=O amide). $C_{34}H_{40}N_2O_5$ m/z (ES) 558 $[(M+H)]^+$, Mp163-165 ^{o}C.

Fmoc-Phe-Phe-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.38 (1H, NHCHCH$_2$Ph, d, ^3J= 7.4 Hz), 7.87 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.59-7.67 (2H, 2ArH,m), 7.57 (1H, NHCHCH$_2$Ph, d, ^3J=8.9 Hz), 7.41 (2H, 2ArH, td, ^3J=7.4 Hz, ^4J=2.9 Hz), 7.15-7.34 (12H, 12ArH, m), 4.38 (1H, CH(Phe), dd, ^3J=7.3 Hz, ^3J=7.4 Hz), 4.29 (1H, CH(Phe),

ddd, ^{3}J=7.1 Hz, ^{3}J=8.9 Hz, ^{4}J=3.6 Hz), 4.07-4.18 (3H, $CHCH_2$, m), 2.94-3.04 (3H,CH_2(Phe),CH(Phe),m), 2.72-2.80 (1H, CH(Phe),m), 1.38 (9H, $CH_3)_3$, s). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 27.5 ($3CH_3$,$C(CH_3)_3$), 36.8 (CH_2 (Phe)), 37.4 (CH_2 (Phe)), 46.5 (<u>CH</u>CH_2), 54.2 (CH,(Phe)), 55.8 (CH,(Phe)), 65.6 (CH<u>CH_2</u>), 80.6 (4^oC, <u>C</u>$(CH_3)_3$), 120.0 (2ArCH), 125.2 (ArCH), 125.3 (ArCH), 126.2 (ArCH (Phe)), 126.5 (ArCH (Phe)), 127.0 (2ArCH), 127.6 (2ArCH), 128.0 (2ArCH,(Phe)), 128.1 (2ArCH,(Phe)), 129.2 (4ArCH,(Phe)),137.1(Ar 4^oC), 138.2 (Ar 4^oC), 140.6 (2Ar 4^oC), 143.7 (2Ar 4^oC), 155.7 (4^oC, C=O ester), 170.3 (4^oC, C=O amide), 171.6 (4^oC, C=O amide). $C_{37}H_{38}N_2O_5$ m/z (ES) 592 $[(M+H)^+$, Mp 135-137 ^oC

Fmoc-Dipeptides

Fmoc-Ala-Ala-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 8.12 (1H, <u>NH</u>$CHCH_3$, d, ^{3}J=7.4 Hz), 7.89 (2H, 2ArH(a),d, ^{3}J= 7.5 Hz),7.73 (2H, 2ArH(a), t, ^{3}J=7.3 Hz), 7.48 (1H, <u>NH</u>$CHCH_3$, d, ^{3}J=7.8 Hz), 7.42 (2H, 2ArH(b), t, ^{3}J=7.3Hz), 7.33 (2H, 2ArH(b), t, ^{3}J= 7.5 Hz), 4.20-4.30 (4H, <u>$CHCH_2$</u>, <u>CH</u>CH_3, m), 4.10 (1H, $CHCH_3$ (Ala), t, ^{3}J= 7.4 Hz), 1.27 (3H, CH_3 (Ala),d, ^{3}J= 7.3 Hz), 1.22 (3H,CH_3 (Ala),d, ^{3}J= 7.1 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ17.1 (CH_3 (Ala)), 18.1 (CH_3 (Ala)), 46.6(<u>CH</u>CH_2) 48.2 (CH (Ala)), 49.5 (CH (Ala)), 65.6 (CH<u>CH_2</u>), 120.1 (2ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4^oC), 143.8 (2Ar 4^oC), 155.6 (4^oC, C=O acid), 172.3 (4^oC, C=O amide), 174.0 (4^oC, C=O amide). $C_{21}H_{22}N_2O_5$ m/z (ES) 383 $[M+H]^{+,}$ Mp 189-190 ^oC.

Fmoc-Ala-Gly-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ12.60 (1H, COOH, (br) s), 8.11 (1H, <u>NH</u>CH_2, t, ^{3}J=5.6 Hz), 7.88 (2H, 2ArH(a),d, ^{3}J= 7.5 Hz), 7.73 (2H, 2ArH(a), t, ^{3}J=7.1 Hz), 7.52 (1H, <u>NH</u>$CHCH_3$, d, ^{3}J=7.8 Hz), 7.42 (2H, 2ArH(b), t, ^{3}J=7.1Hz), 7.33 (2H, 2ArH(b), t, ^{3}J= 7.4 Hz), 4.20-4.30 (3H, <u>$CHCH_2$</u>, m), 4.10 (1H, NH<u>CH</u>CH_3, qn, ^{3}J=7.2 Hz), 3.80 (1H, <u>CH</u> (Gly), dd, ^{2}J=17.5 Hz, ^{3}J=6.0 Hz), 3.70 (1H, <u>CH</u> (Gly), dd, , ^{2}J=17.5 Hz^{3}J=5.7 Hz), 1.25 (3H, CH_3 (Ala),d, ^{3}J= 7.2 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.2 (CH_3 (Ala)), 40.6 (CH_2 (Gly)), 46.6 (<u>CH</u>CH_2), 49.8 (CH (Ala)), 65.6 (CH<u>CH_2</u>), 120.1 (2ArCH),125.3 (2ArCH),127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4^oC), 143.8 (Ar 4^oC), 143.9 (Ar 4^oC), 155.6 (4^oC, C=O

acid), 171.1 (4°C, C=O amide), 172.8 (4°C, C=O amide). $C_{20}H_{20}N_2O_5$ m/z (ES) 369 $[(M+H]^+$ Mp 135-136 °C.

Fmoc-Ala-Val –OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 7.90 (2H, 2ArH, d, ^3J=7.5 Hz), 7.88 (1H, NH, d, ^3J= 8.5 Hz), 7.73 (2H, 2ArH, t, ^3J= 8.0 Hz), 7.50 (1H, NHCHCH$_3$, d, ^3J= 7.8 Hz), 7.42 (2H, 2ArH, t, ^3J=7.4 Hz), 7.31 (2H, 2ArH, ^3J=7.4 Hz), 4.25 (2H, CHCH$_2$, d, ^3J=7.0 Hz), 4.20 (1H, CHCH$_2$, t, ^3J=7.0 Hz), 4.18 (1H, CH, t, ^3J= 7.4 Hz), 4.03 (1H, CH (Ala), dd, ^3J=5.5Hz, ^3J=8.1 Hz), 2.02 (1H, CH (Val), q, ^3J=6.6Hz), 1.22 (3H, CH$_3$, d, ^3J=7.1Hz), 0.88 (6H, $(CH_3)_2$ (Val), d, ^3J=6.8). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.4 (CH_3 (Val)), 18.6 (CH_3 (Val)), 19.5 (CH_3 (Ala)), 30.4 (CH (Val)), 47.1 (CHCH$_2$), 50.3 (CH,(Val)), 57.5 (CH (Ala)), 66.1 (CHCH$_2$), 120.6 (2ArCH), 125.7 (ArCH), 125.8 (ArCH), 127.5 (2ArCH), 128.1 (2ArCH), 141.2 (2Ar 4°C), 144.3 (Ar 4°C), 144.4 (Ar 4°C), 156.1 (4°C, C=O acid), 173.2 (4°C, C=O amide), 173.3 (4°C, C=O amide). $C_{27}H_{33}N_2O_5$ m/z (ES) 433 $[M+Na]^+$ Mp 182-183 °C.

Fmoc -Val-Gly-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 8.25 (1H, NH, t, ^3J=5.6 Hz), 7.90 (2H, 2ArH , d, ^3J= 7.5 Hz), 7.75 (1H, NH, t, ^3J= 8.5 Hz), 7.42 (4H, 4ArH, m), 7.31 (2H, 2ArH, dd, ^3J=6.9 Hz, ^3J=5.6 Hz), 4.25 (3H, CHCH$_2$, m), 3.88 (1H, CH (Val), dd, ^3J=8.5, ^3J=7.6 Hz), 3.80 (1H, CH (Gly), dd, ^3J=5.8Hz, ^2J=17.4 Hz), 3.68 (1H, CH (Gly), dd, ^3J=5.6 Hz, ^2J=17.5 Hz), 2.02 (1H, CH (Val), q, ^3J=6.8 Hz), 0.89 (3H, (CH_3) (Val), d, ^3J=6.8), 0.88 (3H, (CH_3) (Val), d, ^3J=6.8). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 18.7 (CH_3 (Val)), 19.6 (CH_3 (Val)), 30.8 (CH (Val)), 41.1 (CH_2 (Gly)), 47.2 (CHCH$_2$), 60.6 (CH,(Val)), 66.2 (CHCH$_2$), 120.5 (2ArCH), 125.9 (2ArCH), 127.5 (2ArCH), 128.1 (2ArCH), 141.2 (2Ar 4°C), 144.3 (Ar 4°C), 144.4 (Ar 4°C), 156.6 (4°C, C=O acid), 171.5 (4°C, C=O amide), 172.1 (4°C, C=O amide). $C_{22}H_{24}N_2O_5$ m/z (ES) 397 $[M+H]^+$ Mp 194-195 °C.

Fmoc-Leu-Ala–OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ12.50 (1H, COOH, (br) s), 8.12 (1H, NHCHCH$_3$, d, ^3J=7.1 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.5 Hz), 7.73 (2H, 2ArH,d, ^3J= 7.0 Hz), 7.47 (1H, NHCHCH$_2$CH$(CH_3)_2$, t, ^3J= 8.6 Hz), 7.43 (2H, 2ArH,d, ^3J= 7.4 Hz), 7.32(2H, 2ArH,td, ^3J= 7.4 Hz, ^4J= 2.6 Hz), 4.16-4.30 (4H,

CHCH2, CH (Leu), m), 4.04-4.15 (1H, CH (Leu), m), 1.68 (1H, CH (Ala), q, ^{3}J= 6.8 Hz),1.48 (2H, 2CH (Leu), m), 1.27 (3H, CH_3 (Ala), d, ^{3}J= 7.3 Hz), 0.88 (3H, CH_3 (Leu), d, ^{3}J= 6.6 Hz),0.85 (3H, CH_3 (Leu), d, ^{3}J= 6.6 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 17.1 (CH_3 (Ala)), 21.4 (CH (Leu)), 23.1(CH_3 (Leu)), 24.1 (CH_3 (Leu)), 40.7 (CH_2 (Leu)), 46.7 (CH (Ala)), 47.4 (CHCH$_2$), 52.7 (CH,(Leu)), 65.5 (CHCH$_2$), 120.1 (2ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4^{o}C), 143.7 (Ar 4^{o}C), 143.9 (Ar 4^{o}C), 155.8 (4^{o}C, C=O acid), 172.1 (4^{o}C, C=O amide), 173.9 (4^{o}C, C=O amide). $C_{24}H_{28}N_2O_5$ m/z (ES) 503[(M+H]$^{+}$ Mp 180-181 ^{o}C.

Fmoc-Phe-Ala-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 8.37 (1H, NHCHCH$_2$Ph, d, ^{3}J=7.0 Hz), 7.88 (2H, 2ArH, d, ^{3}J= 7.6Hz), 7.58-7.66 (3H, 3ArH, m), 7.41 (2H, 2ArH, td, ^{3}J=7.4 Hz, ^{4}J=3.2 Hz), 7.33 (2H, 2ArH, t, ^{3}J=6.4 Hz), 7.30 (2H, 2ArH, d, ^{3}J=6.4 Hz), 7.25 (2H, 2ArH, t, ^{3}J=7.4 Hz), 7.19 (1H, NHCHCH$_3$, t, ^{3}J= 7.3Hz), 4.30 (1H,CH (Phe), td, ^{3}J= 11.1 Hz, ^{4}J=3.4 Hz), 4.24 (1H,CH(Ala), d, ^{3}J= 7.3Hz), 4.07- 4.16 (3H,CHCH$_2$, m), 3.04 (1H, CH (Phe), dd, ^{2}J= 13.8 Hz, ^{4}J= 3.4 Hz), 2.77 (1H, CH (Phe), dd, ^{2}J= 13.7 Hz, ^{3}J= 11.1 Hz), 1.30 (3H, CH$_3$(Ala), d, ^{3}J= 7.3 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 17.1 (CH_3 (Ala)), 37.4 (CH_2 (Phe)), 46.5 (CH (Ala)), 47.5 (CHCH$_2$), 55.8 (CH,(Phe)), 65.6 (CHCH$_2$), 120.0 (2ArCH),125.2 (ArCH), 125.3 (ArCH), 126.2(ArCH (Phe)), 127.0 (2ArCH), 127.6 (2ArCH), 128.0 (2ArCH,(Phe)), 129.2 (2ArCH,(Phe)),138.2(Ar 4^{o}C), 140.6 (2Ar 4^{o}C), 143.7 (2Ar 4^{o}C), 155.8 (4^{o}C, C=O acid), 171.4 (4^{o}C, C=O amide), 174.0 (4^{o}C, C=O amide). $C_{27}H_{26}N_2O_5$ m/z (ES) 459[M]$^{+}$ Mp 205-206 ^{o}C.

Fmoc-Leu-Gly-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ12.50 (1H, COOH, (br) s), 8.14 (1H, NHCH$_2$, d, ^{3}J=5.8 Hz), 7.88 (2H, 2ArH, d, ^{3}J= 7.6 Hz), 7.73 (2H, 2ArH,d, ^{3}J= 7.1 Hz), 7.50 (1H, NHCHCH$_2$CH$(CH_3)_2$, t, ^{3}J= 8.5 Hz), 7.41 (2H, 2ArH, dd, ^{3}J= 7.4 Hz), 7.28-7.34 (2H, 2ArH, m), 4.20-4.30 (3H, CHCH$_2$, m), 4.03-4.10 (2H, CH_2 (Leu), m), 3.75 (1H, CH (Gly), dd, ^{2}J= 11.7 Hz, ^{3}J= 5.9 Hz), 3.65 (1H, CH (Gly), dd, ^{2}J= 11.8 Hz, ^{3}J= 5.8 Hz),1.58-1.70 (1H, CH (Leu),m), 1.42-1.58 (1H, CH (Leu),m), 0.88 (3H, CH_3 (Leu), d, ^{3}J= 6.6 Hz),0.85 (3H, CH_3 (Leu), d, ^{3}J= 6.6 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 21.3 (CH (Leu)), 23.0(CH_3 (Leu)), 24.1 (CH_3 (Leu)), 40.6 (CH_2 (Leu)), 40.7 (CH_2 (Gly)), 46.7 (CHCH$_2$), 52.9 (CH,(Leu)), 65.5 (CHCH$_2$),

120.0 (ArCH), 120.1 (ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.9 (4°C, C=O acid), 171.0 (4°C, C=O amide), 172.6 (4°C, C=O amide). $C_{23}H_{26}N_2O_5$ m/z (ES) 411 $[(M+H]^+$ Mp 149-150 °C.

Fmoc-Phe-Gly-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 8.33 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.60-7.65 (3H, 3ArH, m), 7.35-7.41 (2H, 2ArH, m), 7.33 (2H, 2ArH,d, ^3J=7.2 Hz), 7.30 (2H, 2ArH,d, ^3J=7.5 Hz), 7.27 (2H, 2ArH,d, ^3J=7.4 Hz), 7.19 (1H, NHCHCH$_2$Ph, d, ^3J= 7.3 Hz), 4.27 (1H, CH (Phe), d, ^4J= 3.6 Hz), 4.05-4.15 (3H, CHCH$_2$, m), 3.75 (1H, CH (Gly), dd, , ^2J= 17.6 Hz, ^3J= 5.9 Hz), 3.65 (1H, CH (Gly), dd, ^2J= 17.7 Hz, ^3J= 5.9 Hz,), 3.04 (1H, CH (Phe), dd, ^2J= 13.7 Hz, ^4J= 3.6 Hz), 2.77 (1H, CH (Phe), dd, ^2J= 13.7 Hz, ^3J= 11.1 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 37.5 (CH$_2$ (Phe)), 40.7 (CH$_2$ (Gly)), 46.5 (CHCH$_2$), 56.0 (CH,(Phe)), 65.6 (CHCH$_2$), 120.0 (2ArCH), 125.2 (ArCH), 125.3 (ArCH), 126.2 (ArCH), 127.0 (2ArCH), 127.6 (ArCH), 128.0 (2ArCH), 129.2 (2ArCH), 138.2 (2Ar 4°C), 140.6 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.8 (4°C, C=O acid), 171.1 (4°C, C=O amide), 172.0 (4°C, C=O amide). $C_{26}H_{24}N_2O_5$ m/z (ES) 467 $[(M+Na]^+$ Mp 188-189 °C.

Fmoc-Leu-Phe-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.70 (1H, COOH, (br) s), 8.14 (1H, NHCHCH$_2$Ph, d, ^3J= 7.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.5 Hz), 7.73 (2H, 2ArH, d, ^3J=7.3 Hz), 7.41 (2H, 2ArH, t, ^3J=7.6 Hz), 7.31 (2H, 2ArH, t, ^3J=7.4 Hz), 7.14-7.24 (6H, 5ArH, NHCHCH$_2$CH$(CH_3)_2$, m), 4.42 (1H, CH (Phe), ddd, ^3J=5.4 Hz, ^3J=8.0 Hz ^4J=2.8 Hz), 4.17-4.33 (3H, CHCH$_2$, m), 4.01-4.08 (1H, CH(Leu), m), 3.05 (1H, CH (Phe), dd, ^2J=13.9 Hz, ^3J=5.3 Hz), 2.92 (1H, CH (Phe), dd, ^2J=13.9 Hz, ^3J=5.2 Hz), 1.57 (1H, CH(Leu), q, ^3J=6.6 Hz), 1.32-1.46 (2H, CH$_2$ (Leu), m), 0.87 (3H, CH$_3$, (Leu), d, ^3J=6.6 Hz), 0.87 (3H, CH$_3$, (Leu), d, ^3J=6.5 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 21.4 (CH (Leu)), 23.0 (CH$_3$ (Leu)), 24.1 (CH$_3$, (Leu)), 36.6 (CH$_2$ (Phe)), 40.7 (CH$_2$ (Leu)), 46.7 (CHCH$_2$), 52.9 (CH,(Leu)), 53.2 (CH (Phe)), 65.5 (CHCH$_2$), 120.0 (ArCH), 120.1 (ArCH), 125.3 (2ArCH), 126.3 (ArCH), 127.0 (ArCH), 127.6 (2ArCH), 128.1(2ArCH), 129.1 (3ArCH),137.3 (Ar 4°C), 140.7 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.7 (4°C, C=O acid), 172.2 (4°C, C=O

amide), 172.7 (4°C, C=O amide). $C_{30}H_{32}N_2O_5$ m/z (ES) 523 $[(M+Na)]^+$ Mp 170-171 °C.

Fmoc-Phe-Val-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.03 (1H, NHCHCH$_2$Ph, d, ^3J=8.5 Hz), 7.87 (2H, 2ArH, d, ^3J=7.2 Hz), 7.61 (3H, 3ArH, dt, ^3J=8.2 Hz, ^4J=10.8 Hz), 7.4 (2H, 2ArH, m), 7.23-7.36 (6H, NH+5ArH, m), 7.19 (1H, ArH, t, ^3J=7.3 Hz), 4.40 (1H, CHCH$_2$, m), 4.01-4.03 (4H, NH+CH+CH$_2$, m), 3.01 (1H, CHPh, dd, ^2J=13.9 Hz, ^4J=3.65 Hz), 2.70 (1H, CHPh, dd, ^2J=16.8 Hz, ^4J=11.04 Hz), 2.09 (1H, CH(CH$_3$)$_2$, m), 0.90 (6H, CH$_3$)$_2$, m). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 173.3 (4°C, C=O amide), 172.3 (4°C, C=O amide), 156.2 (4°C, C=O acid), 144.2 (ArH), 144.1 (ArH), 141.1 (ArH), 138.6 (ArH), 129.7 (ArH), 128.5 (ArH), 128.1 (ArH), 127.5 (ArH), 126.7 (ArH), 125.8 (ArH), 120.5 (ArH), 66.1 (CH<u>CH$_2$</u>), 57.6 (CHPh), 56.3 (CHPh), 47.0 (CH<u>CH</u>), 37.8 (CH$_2$Ar), 30.4 (CH(CH$_3$)$_2$), 19.5 (CH$_3$, val), 18.4 (CH$_3$, val) $C_{26}H_{24}N_2O_5$ m/z (ES) 509 $[(M+Na)]^+$.

Fmoc-Phe-Phe-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.75 (1H, COOH, (br) s), 8.26 (1H, <u>NH</u>CHCH$_2$Ph, d, ^3J= 7.8 Hz), 7.87 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.63 (2H, 2ArH, t, ^3J= 8.5 Hz), 7.57 (1H, <u>NH</u>CHCH$_2$Ph, t, ^3J=8.9 Hz), 7.41 (2H, 2ArH, td, ^3J=7.4 Hz, ^4J=2.5 Hz),), 7.15-7.34 (12H, 12ArH, m), 4.45-4.52 (1H, CH (Phe), m), 4.28 (1H, CH (Phe), ddd, ^2J=7.1 Hz, ^3J=9.0 Hz, ^4J=3.7 Hz), 4.07-4.18 (3H, CHCH$_2$ m), 3.09(1H,CH (Phe), dd, ^2J=14.0 Hz, ^3J=5.2 Hz), 2.95 (2H, CH$_2$ (Phe), ddd, ^2J=14.0 Hz, ^3J=8.7 Hz, ^3J=5.3 Hz), 2.70-2.77 (1H, CH (Phe),m). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 36.7 (CH$_2$ (Phe)), 37.4 (CH$_2$ (Phe)), 46.5 (<u>CH</u>CH$_2$), 53.4 (CH,(Phe)), 55.9 (CH,(Phe)), 65.6 (CH<u>CH$_2$</u>), 120.0 (2ArCH), 125.2 (ArCH), 125.3 (ArCH), 126.2 (ArCH (Phe)), 126.4 (ArCH (Phe)), 127.0 (2ArCH), 127.6 (2ArCH), 128.0 (2ArCH,(Phe)), 128.1 (2ArCH,(Phe)), 129.2 (4ArCH,(Phe)), 137.3 (Ar 4°C), 138.1 (Ar 4°C), 140.6 (2Ar 4°C), 143.7 (2Ar 4°C), 155.6 (4°C, C=O acid), 171.5 (4°C, C=O amide), 172.7 (4°C, C=O amide). $C_{33}H_{30}N_2O_5$ m/z (ES) 536 $[(M+H)]^+$ Mp 177-179 °C.