Synthesis of Functionalised Aromatic Oligamide Rods

Electronic Supplementary material

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Additional Experimental Details and Characterisation

Methyl-3-propyloxy-4-nitrobenzoate 3b

(Procedure A) methyl-3-hydroxy-4-nitrobenzoate **2** (600 mg, 3.0 mmol), K_2CO_3 (510 mg, 3.7 mmol), anhydrous DMF (15 mL), 1-bromopropane (450 μL, 5.0 mmol). Purification by column chromatography (silica, 30 g, 20% EtOAc–CH_2Cl_2) gave the product (563 mg, 77%) as a bright yellow solid yield; m.p. 56-57°C (Found C 55.40, H 5.50, N 5.80%. calcd C 55.20, H 5.50, N 5.90%); R_f 0.6 (CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 1.07 (3H, t, J = 7.4, CH_3) 1.88 (2H, tq, J = 6.8 and 7.0, CH_2), 3.96 (3H, s, CO_2Me), 4.13 (2H, t, J = 6.3, CH_2), 7.67 (1H, d, J 8.2, ArCH), 7.73 (1H, s, Ar CH), 7.81 (1H, d, J 8.3, ArCH); δ_C (75 MHz, $CDCl_3$) 10.4, 14.2, 22.3, 52.8, 71.4, 115.5, 121.1, 125.1, 134.7, 142.6, 151.9, 165.3; υ_{max}/cm^{-1} (solid state) = 3082, 2956, 2882, 1727 (CO), 1589 (Ar C=C); ESI-MS *m/z* 239.1 $[M+H]^+$.

Methyl 3-benzyloxy-4-nitrobenzoate 3c

To a stirred solution of methyl-3-hydroxy-4-nitrobenzoate **2** (1.00 g, 5.1 mmol), benzyl alcohol (0.52 mL, 5.0 mmol) and triphenylphosphine (1.97 g, 7.5 mmol) in anhydrous THF (10 mL) in an atmosphere of nitrogen at 0°C was added dropwise DIAD (1.47 mL, 7.5 mmol). The reaction mixture was allowed to warm to room temperature, stirred for 15 h, concentrated and purified by column chomatography (silica, 40g, CH_2Cl_2). The resultant solid was recrystalised from the minimu amount of hexane yield the product (0.92 g, 66%) as yellow-white crystals; m.p. 85–87°C (Found: C, 62.70; H, 4.55; N, 4.80%. $C_{15}H_{13}NO_5$ requires: C, 62.72; H, 4.56; N, 4.88 %); R_f 0.70 (2 % MeOH in CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 3.95 (3H, s, CO_2Me) 5.28 (2H, s, benzylic CH_2), 6.69 (1H, d, J = 8.6, ArCH), 7.47-7.33 (5H, m, ArCH), 7.84 (2H, t, J = 7.3, ArCH); δ_C (75 MHz, $CDCl_3$) 53.30, 71.76, 116.43, 122.11, 125.82, 127.57, 128.85, 129.18, 135.19, 135.41, 143.19, 151.83, 165.57; υ_{max}/cm^{-1} (solid state) = 3118, 3062, 2964 (CH), 1731 (CO); ESI-HRMS found *m/z* 310.0697 $[M+Na]^+$, $C_{15}H_{13}NNaO_5$ requires 310.0686.

Methyl-3-(1-napthyl)methoxy-4-nitro-benzoate 3d

(Procedure A) methyl-3-hydroxy-4-nitrobenzoic acid **2** (1.87 g, 9.5 mmol), 1-chloromethylnaphthalene (2.04 g, 11.5 mmol), potassium carbonate (4.00 g, 26.0 mmol) and dimethylformamide (30 mL) to yield the prodcut (2.80 g, 87%) as a yellow powder; m.p. 144–146°C; R_f 0.80 (30% Et_2O in CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 3.95 (3H, s, CO_2Me), 5.70 (2H, s, napthyl-CH_2), 7.47 (1H, t, J = 7.3, ArCH), 7.52 (1H, t, J = 6.9 Hz, ArCH), 7.57 (1H, t, J = 6.9, ArCH), 7.67-7.70 (2H, m, ArCH), 7.82 (1H, d, J = 8.3, ArCH), 7.85 (1H, d, J = 8.3, ArCH), 7.88 (1H, d, J = 7.9, ArCH), 7.96 (1H, s, ArCH), 8.04 (1H, d, J = 8.3 Hz, ArCH); δ_C (75 MHz, $CDCl_3$) 52.8, 70.1, 116.1, 121.8, 123.2, 125.3, 125.4, 126.1, 126.4, 126.7, 128.8, 129.4, 130.3, 131.0, 133.7, 134.8, 142.9, 151.4,

165.1. υ_{max}/cm^{-1} (solid state) = 3427, 3060, 2954, 1919, 1723, 1606, 1515, 1435, 1305, 1245, 1112, 984, 795, 632; ESI-HRMS found *m/z* 360.0834 $[M+Na]^+$, $C_{10}H_{15}NO_5$ requires 360.0842.

Methyl-3-(2-napthyl)methoxy-4-nitro-benzoate 3e

(Procedure A) methyl-3-hydroxy-4-nitrobenzoic acid **2** (2.6 g, 13.5 mMol), 2-bromomethylnaphthalene (3.3 g, 14.9 mmol), potassium carbonate (5.2 g, 34.0 mmol), and DMF to yield the product (4.4 g, 97%) as a yellow powder; m.p. 152–154 °C; R_f 0.8 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 3.94 (3H, s, CO_2Me), 5.43 (2H, $ArCH_2O$), 7.46-7.50 (2H, m, ArCH), 7.55 (1H, d, *J* = 8.5, ArCH), 7.69 (1H, d, *J* = 8.4, ArCH), 7.81-7.92 (6H, m ArCH). δ_C (75 MHz, $CDCl_3$) 53.3, 72.0, 116.6, 122.2, 125.1, 125.8, 126.7, 126.8, 128.2, 128.5, 129.1, 132.9, 133.6, 133.7, 135.2, 143.3, 151.9, 165.5. υ_{max}/cm^{-1} (solid state) = 3439, 3007, 2957, 2860, 1740, 1726, 1613, 1519, 1349, 1300, 1236, 1110, 1014, 975, 760, 744; HRMS found *m/z* 360.0840 $[M+Na]^+$, $C_{10}H_{15}NO_5$ requires 360.0842.

-Propyloxy-4-nitro benzoic acid 4b

(Using minor modifications to procedure B) A solution of methyl-3-propyloxy-4-nitrobenzoate (326.3 mg, 1.4 mmol) and NaOH (1 equivalent) in H_2O–methanol (1:3, 10 mL) was stirred at room temperature for 20 hours. The reaction mixture was acidified to pH 1 (1M HCl) and the precipitated product was filtered and dried under vacuum to give the product (214 mg, 68%) as a white/ cream powder; m.p. 194–195°C; δ_H (500 MHz, CD_3OD) 0.97 (3H, t, *J* = 7.4, CH_3), 1.75 (2H, tq, *J* = 6.6 and 7.1, CH_2), 4.07 (2H, t, *J* = 6.3, CH_2), 7.60 (1H, d, *J* = 8.2, ArCH), 7.72 (1H, s, ArCH), 7.73 (1H, d, *J* = 5.2, ArCH); δ_C (75 MHz, CD_3OD) 8.9, 21.6, 22.4, 70.7, 114.9, 120.8, 124.1, 135.0, 151.1; ν_{max}/cm^{-1} (solid state) = 2970 (COOH), 1688, 1611, 1588, 1528, 1492, 1438, 1396, 1354, 1301, 1251; ESI-HRMS found *m/z* 224.0564 $[M-H]^-$, $C_{10}H_{11}N0_5$ requires 224.0637.

3-Benzyloxy-4-nitrobenzoic acid 4c

(Using minor modifications to procedure B) methyl-3-benzyloxy-4-nitro benzoate (250 mg, 0.87 mmol), 1M NaOH (1.5 mL, excess) in methanol (15 mL) was heated at reflux (65 ^oC) for 12 h. On cooling, the reaction mixture was acidified (1N HCl, ~2 mL) to ~ pH 1, precipitating the desired acid (191 mg, 80.3 %) as a pale cream paste that was collected by filtration and dried under a high vacuum; m.p. 210–212°C (Found: C, 60.95; H, 4.00; N, 5.00%. $C_{14}H_{11}NO_5$ requires: C, 61.54; H, 4.06; N, 5.13%); R_f 0.31 (15% MeOH in CH_2Cl_2); δ_H (500 MHz, CD_3OD) 5.22 (s, 2H, CH_2), 7.22 (t, 1H, *J* = 7.3 Hz, ArCH), 7.28 (t, 2H, *J* = 7.2 & 7.7 Hz, ArCH), 7.36 (d, 2H, *J* = 7.4 Hz, ArCH), 7.60 (d, 1H, *J* = 8.3 Hz, ArCH), 7.74 (d, 1H, *J* = 8.3 Hz, ArCH), 7.80 (s, 1H, ArCH); δ_C (300 MHz, CD_3OD) 72.59, 117.61, 123.26, 126.29, 128.75, 129.60, 129.95, 137.04, 137.40, 144.73, 152.60,

167.86; ν_{max}/cm^{-1} (solid state) = 3411 (broad, COOH), 1692 (CO), 1530, 1431; ESI-HRMS found *m/z* 272.0556 $[M-H]^-$, $C_{14}H_{10}NO_5$ requires 272.0553.

3-(1-napthyl)methoxy-4-nitro-benzoic acid 4d

(Procedure B) methyl-3-(1-napthyl)methoxy-4-nitro-benzoate **3d** (0.54 g, 1.59 mmol), 10% aqueous sodium hydroxide (10 mL), THF (40 mL), and methanol (40 mL) to yield product (0.50 g, quant.) as an off-white powder; m.p. 218–220°C; δ_H (300 MHz, DMSO-d_6) 5.85 (2H, s, napthyl CH_2), 7.52-7.62 (3H, m, ArCH), 7.67-7.71 (2H, m, ArCH), 7.95-8.03 (3H, m, ArCH), 8.09-8.16 (2H, m, ArCH); δ_C (75 MHz, DMSO-d_6) 69.8, 116.5, 122.0, 124.3, 125.3, 125.7, 126.5, 126.8, 127.0, 128.8, 129.4, 131.3, 131.6, 133.6, 136.0, 142.7, 150.9, 166.1; υ_{max}/cm^{-1} (solid state) = 3065, 2657, 1714, 1614, 1524, 1492, 1350, 1256, 1152, 1051, 1001, 785, 743, 526; ESI-HRMS found *m/z* 322.0712 $[M-H]^-$, $C_{18}H_{12}NO_5$ requires 322.0721.

3-(2-napthyl)methoxy-4-nitro-benzoic acid 4e

(Procedure B) **3e** (2.70 g, 8.0 mmol), 10% aqueous sodium hydroxide (10 mL), THF (40 mL), and methanol (40 mL) to yield a crystalline yellow powder (2.60 g, quant) m.p. 252–253 °C (Found: C, 63.55; H, 4.05; N, 3.95%. $C_{18}H_{12}NO_5.H_2O$ requires: C, 63.34; H, 4.43; N, 4.10%); δ_H (300 MHz, DMSO-d_6) 5.56 (2H, s, naphthyl-CH_2), 7.51-7.60 (3H, m, ArCH), 7.67 (1H, dd *J* = 8.3 and 1.5, ArCH), 7.89-8.02 (6H, m, ArCH); δ_C (75 MHz, DMSO-d_6) 71.2, 116.4, 122.0, 125.5, 125.7, 126.6, 126.7, 126.8, 129.0, 128.2, 128.6, 133.0, 133.7, 136.0, 142.7, 150.9, 166.1; υ_{max}/cm^{-1} (solid state) = 3058, 2911, 2613, 1694, 1607, 1521, 1492, 1427, 1350, 1310, 1254, 1035, 955, 814, 777, 623. ESI-MS 322 $[M-H]^+$.

Methyl 3-propyloxy-4-aminobenzoate 5b

To a stirred solution of methyl-3-propoxy-4-nitrobenzoate **3b** (300 mg, 1.3 mmol) in anhydrous methanol (10 mL), under an atmosphere of nitrogen, was added 10% palladium on charcoal (30 mg). The nitrogen atmosphere was evacuated under vacuum and hydrogen gas (1 L, excess) introduced *via* a balloon. The reaction mixture was stirred for 12 h, filtered through a celite pad, concentrated and dried under vacuum to givethe product (260 mg, 99%) as a cream white solid; m.p. 52–53°C (Found: C, 62.9; H, 7.1; N, 6.6%. $C_{11}H_{15}NO_3$ requires: C, 63.14; H, 7.23; N, 6.69%); δ_H (500 MHz, $CDCl_3$) 1.06 (3H, t, *J* = 7.7, CH_3), 1.85 (2H, tq, *J* = 6.8 and 7.6, CH_2), 3.86 (3H, s, CO_2Me), 4.01 (2H, t, *J* = 6.4, CH_2), 4.22 (2H, s, NH_2), 6.66 (1H, d, = *J* 8.9, ArCH), 7.44 (1H, s, ArCH), 7.53 (1H, d, *J* = 7.9, ArCH); δ_C (75 MHz, $CDCl_3$) 10.6, 22.6, 51.7, 69.9, 112.1, 113.1, 119.5, 123.9, 141.2, 145.5, 167.4; υ_{max}/cm^{-1} (solid state) = 3499, 3371, 2950, 2874, 1690 (CO), 1432; ESI-MS *m/z* 210.1 $[M+H]^+$.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-nitro-benzoylamido)-benzoate 6aa

(Procedure C) **4a** (150 mg, 0.67 mmol), **5a** (140 mg, 0.67 mmol), chloroform (8 mL), Cl_2PPh_3 (533 mg, 1.60 mmol). The reaction mixture was then heated at reflux (61 ^oC) for 48 hours before being concentrated and purified by column chromatography (5% EtOAc in CH_2Cl_2) to yield the product (233 mg, 84%) as a pale yellow solid; m.p. 108–110°C (Found: C, 60.50; H, 5.85; N, 6.55 %. $C_{21}H_{24}N_2O_7$ requires: C, 60.57; H, 5.81; N, 6.73 %); R_f 0.61 (5% EtOAc in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.46 (d, 6H, J = 1.5 Hz, CH_3), 1.48 (d, 6H, J = 5 Hz, CH_3), 3.96 (s, 3H, CO_2Me), 4.83 (m, 2H, $\underline{CH}CH_3$), 7.38 (d, 1H, J = 8.3, ArCH), 7.64 (d, J = 1.7, ArCH), 7.72 (d, J = 1.6, ArCH), 7.77 (d, 1H, J = 8.5, ArCH), 7.91 (d, 1H, J = 8.3, ArCH), 8.63 (d, 1H, J = 8.5, ArCH), 8.83 (s, 1H, NH); δ_C (75 MHz, $CDCl_3$): 22.23, 22.60, 52.62, 72.24, 73.49, 113.42, 115.79, 117.56, 119.24, 123.62, 126.21, 132.56, 139.92, 143.22, 146.25, 151.97, 163.58, 167.05; ν_{max}/cm^{-1} (solid state) = 3389 (NH), 3080, 2990 (CH), 1703, 1674 (CO); ESI-HRMS found *m/z* 417.1661[M+H$^+$], $C_{21}H_{25}N_2O_7$ requires 417.1656.

Methyl-3-isopropoxy-4-(3-benzyloxy-4-nitro-benzoylamido)-benzoate 6ac

(Procedure C) **5a** (683.4 mg, 3.26 mMol), **4c** (1.17 g, 4.27 mMol), Cl_2PPh_3 (6.0 g, 18.5 mmol) and chloroform (70 mL) to yield a yellow solid (1.3 g, 87%); m.p. 132–133 °C (Found C 64.45, H 5.40, N 6.00%. $C_{25}H_{24}N_2O_7$ requires: C 64.65, H 5.21, N 6.03%); R_f = 0.8 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.44 (6H, d, J = 6.0, iPrCH_3), 3.91 (3H, s, CO_2Me), 4.78 (1H, sept, J = 6.0, iPrCH), 5.33 (2H, s, BenzylCH_2), 7.32-7.49 (6H, m, ArCH), 7.60 (1H, s, ArCH), 7.72 (1H, d, J = 8.5, ArCH), 7.79 (1H, s, ArCH), 7.95 (1H, d, J = 8.3, ArCH), 8.57 (1H, d, J = 8.5, ArCH), 8.78 (1H, br, NH) δ_C (75 MHz, $CDCl_3$) 22.2, 52.2, 71.5, 71.9, 113.1, 114.9, 117.7, 119.0, 123.3, 125.9, 126.0, 127.2, 128.5, 128.9, 132.1, 134.9, 139.9, 142.1, 145.9, 152.2, 162.9, 166.6. υ_{max}/cm^{-1} (solid state) = 3422, 3072, 2981, 1718, 1677, 1596, 1513, 1264, 1114, 993, 872, 762, 607; ESI-MS [M+H]$^+$ *m/z* 465.3.

Methyl-3-propoxy-4-(3-benzyloxy-4-nitro-benzoylamido)-benzoate 6bc

(Procedure C) **5c** (193.1 mg, 0.7 mmol), **4b** (150.0 mg, 0.7 mmol), chloroform (40 mL), Cl_2PPh_3 (600 mg, 1.8 mmol). Purification (SiO_2 chromatography) afforded the product (307.8 mg, 94%) as a yellow solid; m.p. 194–196°C (Found: C, 64.0; H, 5.0; N, 5.65 %. $C_{25}H_{24}N_2O_7$ requires: C, 64.65; H, 5.21; N, 6.03%); δ_H (500 MHz, $CDCl_3$) 1.11 (3H, t, J = 7.4, CH_3), 1.92 (2H, tq, J = 7.0 and 6.9, CH_2), 3.92 (3H, s, CO_2Me), 4.14 (2H, t, J = 6.4, CH_2), 5.33 (2H, s, benzylic-CH_2), 7.36 (1H, d, J = 7.0, ArCH), 7.41 (3H, dd, J = 7.7 and 7.5, ArCHs), 7.48 (2H, d, J = 7.2, ArCH), 7.60 (1H, s, ArCH), 7.75 (1H, d, J = 8.4, ArCH), 7.79 (1H, s, ArCH), 7.95 (1H, d, J = 8.3, ArCH), 8.57 (1H, d, J = 8.4, ArCH), 8.76 (1H, s, NH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.6, 22.5, 52.2, 70.5, 71.4, 111.7, 114.8, 117.7, 118.7, 123.3, 125.9, 126.1, 127.1, 128.5, 128.8, 131.4, 134.9, 139.8, 142.0,

147.0, 152.2, 162.9, 166.6; ν_{max}/cm^{-1} (solid state) 3424 (NH), 3073, 2967, 2878, 2620, 1938, 1682 (CO), 1592 (Ar C=C), 1531 (NO_2); ESI-HRMS found *m/z* 465.1664 $[M+H]^+$, $C_{25}H_{25}N_2O_7$ requires 465.1656.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-amino-benzoylamido)-benzoate 7aa

To a stirred solution of **6aa** (100 mg, 0.24 mmol) in anhydrous methanol (7 mL), under an atmosphere of nitrogen, was added palladium on charcoal catalyst (10 mg, 10% catalyst). The nitrogen atmosphere was evacuated under vacuum and hydrogen gas (1 L, excess) introduced *via* a balloon. The reaction mixture was stirred for 6 h until TLC indicated the reaction was complete. The mixture was passed through a celite pad, concentrated and dried under high vacuum to yield the product (74 mg, 79.8%) as a cream solid; m.p. 148–149°C; R_f 0.30 (5% EtOAc in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.44 (d, 6H, *J* 6.1 Hz, CH_3), 1.46 (d, 6H, *J* 6.1 Hz, CH_3), 3.95 (s, 3H, CO_2Me), 4.75 (m, 2H, CH), 6.83 (d, 1H, *J* = 8.1, ArCH), 7.30 (d, 1H, *J* = 8.1, ArCH), 7.50 (d, 1H, *J* = 1.7, ArCH), 7.61 (d, 1H, *J* = 1.7, ArCH), 7.74 (d, 1H, *J* = 8.5, ArCH), 8.66 (d, 1H, *J* = 8.5, ArCH), 8.79 (s, 1H, NH); δ_C (75 MHz, $CDCl_3$) 22.2, 52.1, 70.8, 71.6, 112.3, 113.0, 113.6, 118.4, 119.8, 123.4, 124.1, 124.4, 133.5, 141.4, 144.8, 145.5, 165.1, 166.9; ν_{max}/cm^{-1} (solid state) 3503, 3433, 3365 (NH_2), 2972 (CH), 1711 (CO); ESI-HRMS found *m/z* 387.1916 $[M+H^+]$, $C_{21}H_{27}N_2O_5$ requires 387.1914.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-amino-benzoylamido)-benzoate 7aa

(Alternative preparation using procedure D) **6aa** (0.47 g, 1.13 mmol), $SnCl_2.H_20$ (1.20 g, 5.65 mmol), ethyl acetate (30 mL). Yield: 385 mg, 88% (data as above).

Methyl-3-isopropoxy-4-(3-benzyloxy-4-amino-benzoylamido)-benzoate 7ac

(Procedure C) **6ac** (1.00 g, 2.15 mmol), $SnCl_2.H_20$ (2.50 g, 11.1 mmol) and ethyl acetate (90 mL) to yield a yellow oil (0.81 g, 87%) that solidified upon standing overnight; m.p. 152–154 °C; R_f = 0.65 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.41 (6H, d *J* = 6 Hz, *I*Pr CH_3), 3.89 (3H, s, CO_2Me), 4.31 (2H, br, NH_2), 4.72 (1H, sept *J* = 6Hz, *i*PrCH), 5.14 (2H, s, -CH_2Ph) 6.74 (1H,d *J* = 8.2Hz, ArCH), 7.26-7.57 (6H, m, ArCH), 7.56 (2H, d *J* = 6Hz, ArCH), 7.71 (1H, d *J* = 8.5 Hz, ArCH), 8.62 (1H, d *J* = 8.5 Hz, ArCH), 8.74 (1H, br, NH); δ_C (75 MHz, $CDCl_3$) 22.1, 51.9, 70.4, 71.6, 111.2, 113.1, 113.3, 118.3, 120.2, 123.3, 123.8, 124.3, 126.8, 127.6, 128.1, 128.4, 128.6, 133.4, 136.4, 140.7, 145.5, 145.8, 164.9, 166.8; ν_{max}/cm^{-1} (solid state) 3483, 3457, 3321, 2944, 1720, 1707, 1654, 1595, 1516, 1346, 1263, 1133, 1013, 763, 626; ESI-HRMS found *m/z* 435.1910 $[M+H]^+$, $C_{25}H_{26}N_2O_6$ requires 435.1914.

Methyl-3-propoxy-4-(3-benzyloxy-4-amino-benzoylamido)-benzoate 7bc

(Procedure D) **6bc** (150.0 mg, 0.3 mmol), $SnCl_2.2H_2O$ (380.0 mg, 1.7 mmol) afforded the product (108.3 mg, 83%) as a slightly yellow solid; m.p. 140–142°C (Found: C, 68.85; H, 5.9; N, 6.0%. $C_{25}H_{26}N_2O_5$ requires: C, 69.11; H, 6.03; N, 6.45 %); δ_H (500 MHz, $CDCl_3$)

1.12 (3H, t, *J* = 7.3, CH_3), 1.92 (2H, tq, *J* = 6.9 and 6.7, CH_2), 3.91 (3H, s, CO_2Me), 4.11 (2H, t, *J* = 6.2, CH_2), 4.26 (2H, s, NH_2), 5.16 (2H, s, benzylic-CH_2), 6.75 (1H, d, *J* = 8.0, ArCH), 7.29 (1H, d, *J* = 7.8, ArCH), 7.42-7.36 (3H, m, ArCHs), 7.46 (2H, d, *J* = 7.0, ArCH), 7.56 (2H, s, ArCH), 7.72 (1H, d, *J* = 8.2, Ar 6-CH), 8.62 (1H, d, *J* = 8.4, ArCH), 8.73 (1H, s, NH); δ_C (75 MHz, $CDCl_3$) 11.1, 23.0, 52.5, 70.7, 70.9, 111.59, 111.9, 113.9, 118.6, 118.7, 120.7, 123.9, 124.5, 124.9, 128.2, 128.7, 129.1, 133.1, 136.9, 141.1, 146.4, 147.2, 165.4, 167.3; ν_{max}/cm^{-1} (solid state) 3477, 3436, 3339, 2967, 2947, 2871, 1625 (CO), 1598; ESI-HRMS found *m/z* 433.1769 $[M-H]^-$, $C_{25}H_{25}N_2O_5$ requires 433.1842.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-(3-isopropoxy-4-nitro-benzoylamido)-benzoylamido)-benzoate 8aaa

(Procedure C) **7aa** (0.436 g, 1.23 mmol), **4a** (0.348 mg, 1.54 mmol), Cl_2PPh_3 (2.200g, 6.81 mmol), and chloroform (50 mL) to yield a faint yellow solid (0.579 mg, 84%); m.p. 192–193 °C; R_f 0.8 (30% Et_2O in CH_2Cl_2), δ_H (300 MHz, DMSO-d_6), 1.37-1.34 (18H, m, 3 x *i*PrCH$_3$), 3.86 (3H, s, CO_2Me), 4.80-4.73 (2H, m, *i*PrCH), 4.96 (1H, sept *J* = 6.0 Hz, *i*PrCH), 7.65-7.56 (5H, m, ArCH) 7.81 (1H, s, ArCH), 7.99 (1H, d *J* = 8.4, ArCH), 8.09 (1H, d *J* = 8.1, ArCH), 8.22 (1H, d *J* = 8.4, ArCH), 9.37 (1H, s, NH), 9.70 (1H, s, NH); δ_C (75 MHz, $CDCl_3$) 22.2, 22.6, 52.6, 72.2, 72.3, 73.5, 112.2, 113.5 ,115.8, 117.6, 119.0, 119.2, 119.5, 123.7, 125.5, 126.3, 131.0, 131.7, 133.3, 139.9, 143.3, 146.2, 147.0, 152.0, 163.7, 184.8, 167.2; ν_{max}/cm^{-1} (solid state) 3432, 2982, 1713, 1683, 1595, 1349, 1111, 1004, 844, 763, 604; ESI-HRMS found *m/z* 594.2439 $[M+H]^+$, $C_{31}H_{35}N_3O_9$ requires 594.2439.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-(3-benzyloxy-4-nitro-benzoylamido)-benzoylamido)-benzoate 8aac

(Procedure C) **7aa** (55 mg, 0.14 mmol), **4c** (39 mg, 0.14 mmol), Cl_2PPh_3 (114 mg, 0.342 mmol), chloroform (5 mL). Reaction was heated at reflux (65 ^oC) for 24 h. Purification by column chromatography (10 % EtOAc in CH_2Cl_2) afforded target material (66 mg, 73.5%) as a pale yellow solid; m.p. 200–202°C (Found: C, 66.3; H, 5.5; N, 6.05%. $C_{35}H_{35}N_3O_9$ requires: C, 65.51; H, 5.50; N, 6.55 %); R_f 0.42 (10% EtOAc in CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 1.46 (d, 12H, *J* = 6.0 Hz, 2 x CH_3), 3.92 (s, 3H, CO_2Me), 4.80 (m, 2H, CH), 5.35 (s, 2H, benzylic-CH_2), 7.36 (t, 1H, *J* = 7.3, ArCH), 7.40 (m, 4H, ArCH), 7.49 (d, 2H, *J* = 7.5, ArCH), 7.62 (dd, 2H, *J* = 12.0 and 1.4, ArCH), 7.73 (dd, 1H, *J* = 8.4 and 1.4, ArCH), 7.80 (d, 1H, *J* = 1.1, ArCH), 7.97 (1H, d, *J* = 8.2, ArCH), 8.63 (t, 2H, *J* = 7.5, ArCH), 8.77 (s, 1H, NH), 8.86 (s, 1H, NH); δ_C (75 MHz, $CDCl_3$) 22.63, 52.54, 71.83, 72.24, 72.34, 112.26, 113.50, 115.23, 118.11, 118.99, 119.13, 119.61, 123.73, 125.50, 126.48, 127.55, 128.93, 129.26, 131.06, 131.65, 133.32, 135.29, 140.18, 142.48, 146.17, 147.06, 152.61, 163.41, 164.76, 167.20; ν_{max}/cm^{-1} (solid state) 3425 (NH), 2977 (CH),

1715, 1678 (CO), 1517; ESI-HRMS found *m/z* 664.2271 $[M+Na]^+$, $C_{35}H_{35}N_3NaO_9$ requires 664.2266.

Methyl-3-isopropoxy-4-(3-benzyloxy-4-(3-(1-napthyloxy)-4-nitro-benzoylamido)-benzoylamido)-benzoate 8acd

(Procedure C) **7ac** (0.25 g, 0.576 mmol) **4d** (0.25 g, 1.34 mmol), Cl_2PPh_3 (1.60g, 4.95 mmMol) and chloroform (75 mL) to yield the product (0.32 g, 75%) as a yellow solid; m.p. 182–183 °C (Found: C, 66.2; H, 5.1; N, 5.35%. $C_{43}H_{37}N_3O_9.2H_2O$ requires: C, 66.57; H, 5.33; N, 5.42%); R_f = 0.8 (30% Et_2O in CH_2Cl_2); δ_H (300 Mhz, $CDCl_3$) 1.45 (6H, d, *J* = 6.0, *i*Pr CH_3), 3.92, (3H, s, CO_2Me), 4.78 (1H, sept *J* = 6.0, *i*PrCH), 5.26 (2H, s, Benzyl CH_2), 5.65 (2H, s, napthyl CH_2), 7.27-7.64 (12H, m, ArCH), 7.73 (1H, d, *J* = 8.5 Hz, ArCH), 7.77 (1H, s, ArCH), 7.84-7.91 (4H, m, ArCH), 8.02 (1H, d *J* = 8 Hz, ArCH), 8.62 (1H, d, *J* = 8.5 Hz, ArCH), 8.67 (1H, d *J* = 8.5 Hz, ArCH), 8.77 (1H, br, NH), 8.87 (1H, br NH); δ_C (75 MHz, $CDCl_3$) 22.3, 52.1, 70.2, 71.7, 71.9, 111.6, 113.2, 114.5, 118.2, 118.7, 119.2, 119.4, 123.4, 125.3, 126.0, 126.2, 126.7, 126.8, 127.9, 128.8, 129.0, 129.6, 130.2, 131.0, 131.1, 133.0, 133.8, 135.6, 139.4, 145.8, 147.8, 163.0, 164.2, 166.8. ν_{max}/cm^{-1} (solid state) 3483, 3422, 3330, 2978, 1707, 1596, 1516, 1484, 1349, 1264, 1111, 1001, 954, 849, 764, 702, 604. ESI-MS *m/z* 740 $[M+H]^+$, 762 $[M+Na]^+$.

Methyl-3-propoxy-4-(3-benzyloxy-4-(3-isopropoxy-4-nitro-benzoylamido)-benzoylamido)-benzoate 8bca

(Procedure C) **7bc** (75.4 mg, 0.2 mmol), **4a** (40.6 mg, 0.2 mmol), chloroform (20 mL), Cl_2PPh_3 (200 mg, 0.6 mmol) afforded the product (97.0 mg, 86%) as a yellow solid; m.p. 197–199 °C; δ_H (500 MHz, $CDCl_3$) 1.14 (3H, t, *J* 7.4, CH_3), 1.37 (6H, d, *J* = 6.0, CH_3), 4.15 (2H, t, *J* = 6.5, CH_2), 1.95 (2H, tq, *J* = 7.1 and 6.9, CH_2), 3.92 (3H, s, CO_2Me), 4.67 (1H, hep, *J* = 7.0, CH), 5.26 (2H, s, benzylic-CH_2), 7.49-7.43 (6H, m, ArCH), 7.68 (2H, d, *J* = 9.8, ArCH), 8.75 (1H, s, NH), 7.79-7.74 (3H, m, ArCH), 8.62 (1H, d, *J* = 8.4, ArCH), 8.68 (1H, d, *J* = 8.3, ArCH), 8.86 (1H, s, NH); δ_C (75 MHz, $CDCl_3$) 8.8, 19.9, 20.7, 50.3, 68.6, 69.7, 71.2, 109.5, 109.7, 113.2, 115.7, 116.6, 117.2, 117.5, 121.5, 123.3, 123.9, 126.1, 127.1, 127.1, 128.8, 129.1, 130.2, 133.7, 137.2, 141.0, 145.1, 145.8, 149.6, 161.3, 162.4, 164.9; ν_{max}/cm^{-1} (solid state) 3606, 3430 (NH_2), 2966, 2933, 2876, 1709 (CO), 1599, 1525, 1488 (NO_2); ESI-HRMS found *m/z* 640.2326 $[M-H]^-$, $C_{35}H_{34}N_3O_9$ requires 640.2373.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-(3-isopropoxy-4-amino-benzoylamido)-benzoylamido)-benzoate 9aaa

(Procedure D), **8aaa** (0.414 g, 0.74 mmol) $SnCl_2.H_2O$ (1.012 g, 4.49 mmol) and ethyl acetate (40mL) to yield the product (0.329 g, 83%) as a pale yellow oil that solidified upon standing; m.p. 182–183 °C; R_f = 0.65 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.40-1.46 (18H, 3 x *i*PrCH$_3$), 3.91 (3H, s, CO_2Me), 4.70 (1H, sept, *J* = 6.0, *i*PrCH) 4.74-

4.81 (2H, m, 2 different *i*PrCH), 6.75 (1H, d, *J* = 8.1, ArCH), 7.28 (1H, d *J* = 8.1, ArCH), 7.40 (1H, d *J* = 8.5, ArCH), 7.45 (1H, s, ArCH), 7.60 (2H, s, ArCH), 7.72 (1H, d, *J* = 8.5, ArCH), 8.63 (1H, d, *J* = 8.5, ArCH), 8.71 (1H, d, *J* = 8.5, ArCH), 8.73 (1H, br, NH), 8.87 (1H, br, NH). δ_C (75 MHz, $CDCl_3$) 22.2, 52.0, 70.8, 71.7, 71.8, 111.8, 112.3, 113.1, 113.6, 118.5, 118.6, 118.9, 119.9, 123.3, 123.9, 124.8, 129.1, 132.7, 133.1, 141.5, 144.8, 145.7, 146.3, 164.6, 165.1, 166.8. ν_{max}/cm^{-1} (solid state) 3356, 2975, 2618, 2250, 1595, 1513, 1346, 871, 749, 594. HRMS (M+H) Found 564.2713 calculated 564.2704.

Methyl-3-isopropoxy-4-(3-isopropoxy-4-(3-benzyloxy-4-amino-benzoylamido)-benzoylamido)-benzoate 9aac

(Procedure D) **8aac** (71 mg, 0.1mmol), $SnCl_2.H_20$ (125 mg, 0.6mmol). Purification by column chronatography (40% Et_2O in CH_2Cl_2) yielded the product (61 mg, 89%) as a pale yellow solid; m.p. 198–199°C (Found: C, 68.7; H, 6.15; N, 6.6%. $C_{35}H_{37}N_3O_7$ requires: C, 68.72; H, 6.10; N, 6.87 %); R_f 0.35 (40% Et_2O in CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 1.45 (2xd, 12H, *J* 6.1 Hz, CH_3), 3.91 (s, 3H, CO_2Me), 4.78 (m, 2H, CH), 5.18 (s, 2H, Benzylic CH_2), 7.30 (dd, 1H, *J* 1.7 and 8.1 Hz, ArCH), 7.39 (m, 4H, ArCH), 7.46 (d, 2H, *J* 7.2 Hz, ArCH), 7.57 (d, 1H, 1.7 Hz, ArCH), 7.60 (t, 2H, *J* 1.9 Hz, ArCH), 7.72 (dd, 1H, *J* 1.6 and 8.4 Hz, ArCH), 8.62 (1H, *J* 8.5 Hz, ArCH), 8.68 (d, 1H, *J* = 8.4, ArCH), 8.73 (s, 1H, NH), 8.87 (s, 1H, NH); δ_C (75 MHz, $CDCl_3$): 22.23, 52.09, 70.53, 71.72, 71.83, 111.26, 111.84, 113.10, 113.45, 118.52, 118.71, 118.91, 120.26, 123.32, 123.99, 124.86, 127.78, 128.29, 128.55, 129.17, 132.67, 133.14, 136.48, 140.77, 145.75, 145.94, 146.38, 164.67, 165.05, 166.85; ν_{max}/cm^{-1} (solid state) 3469, 3434, 3358 (NH), 2977, 2950 (CH), 1704, 1688 (CO); ESI-HRMS found 612.2704 *m/z* $[M+H]^+$, $C_{35}H_{37}N_3O_9$ requires 612.2704.

Methyl-3-isopropoxy-4-(3-benzyloxy-4-(3-(1-napthyloxy-4-amino-benzoylamido)-benzoylamido)-benzoate 9acd

(Procedure D) **9acd** (103.3 mg, 0.14 mmol), $SnCl_2.H_20$ (235.3 mg, 1.04 mmol), and ethyl acetate (50 mL) to yield product (66.5 mg, 67%) as a yellow oil that solidified upon standing; m.p. 260–262 °C; R_f = 0.65 (30% Et_2O in CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 1.46 (6H, d, *J* = 6.0, iPrCH_3), 3.00 (2H, br, NH_2), 3.91 (3H, s, CO_2Me), 4.77 (1H, sept, *J* = 6.0, iPrCH), 5.25 (2H, s, ArCH_2O-), 5.42 (2H, s, ArCH_2O-), 6.68 (1H, d, *J* = 8.1, ArCH), 7.18 (1H, t, *J* = 8.3, ArCH), 7.28-7.36 (3H, m, ArCH), 7.46-7.55 (7H, m, ArCH), 7.54 (1H, s, ArCH), 7.55 (1H, s, ArCH), 7.71-7.73 (2H, singlet with buried doublet, ArCH), 7.87-7.92 (2H, m, ArCH), 8.05 (1H, m, ArCH), 8.63 (1H, d, *J* = 8.5, ArCH), 8.73 (1H, d, *J* = 8.4, ArCH), 8.78 (1H, br, NH), 8.88 (1H, br, NH); δ_C (75 MHz, $CDCl_3$) 22.2, 52.1, 69.3, 71.4, 71.9, 110.8, 111.2, 113.2, 113.5, 118.6, 118.7, 119.5, 121.0, 123.4, 123.7, 123.8, 125.0, 125.3, 126.1, 126.6, 127.4, 127.8, 128.7, 128.8, 128.9, 129.3, 129.5, 131.9, 132.3, 133.1, 133.8, 135.9, 141.0, 145.8, 145.9, 147.5, 164.5, 165.1, 166.8; ν_{max}/cm^{-1} (solid state) 3481, 3450, 3358, 2977, 1712, 1662, 1594, 1515, 1438, 1250, 1204, 1130,

1006, 873, 796, 750, 618; ESI-HRMS found 710.2853 *m/z* $[M+H]^+$, $C_{43}H_{39}N_3O_9$ requires 710.2861.

Methyl-3-isopropoxy-4-(3-benzyloxy-4-(3-(2-napthyloxy-4-amino-benzoylamido)-benzoylamido)-benzoate 9ace

(Procedure D) **8ace** (185.5 mg, 0.25 mmol), $SnCl_2.H_20$ (364.3 mg, 1.61 mmol) and ethyl acetate (60 mL) to yield a yellow oil the solidified upon cooling (128.6 mg, 72%); m.p. 148–150°C; R_f = 0.65 (30% Et_2O in CH_2Cl_2) δ_H (300 MHz, $CDCl_3$) 1.45 (6H, d, *J* = 6.1, iPrCH_3), 3.91 (3H, s, CO_2Me), 4.20 (2H, br, NH_2), 4.75 (1H, sept, *J* = 6.1, iPr CH), 5.18 (2H, s, Benzyl CH_2), 5.24 (2H, s, naphthyl-CH_2), 6.70 (1H, d, *J* = 8.1, ArCH), 7.25-7.54 (11H, m, ArCH), 7.60 (1H, s, ArCH), 7.70-7.74 (2H, m, ArCH), 7.85-7.90 (4H, m, ArCH), 8.62 (1H, d, *J* = 8.5, ArCH), 8.71 (1H, d, *J* = 8.5, ArCH), 8.73 (1H, br, NH), 8.87 (1H, br, NH). δ_C (75 MHz, $CDCl_3$) 22.6, 52.5, 71.1, 71.7, 72.3, 111.3, 111.6, 113.7, 113.9, 119.0, 119.1, 119.9, 121.3, 123.7, 124.2, 125.4, 126.0, 126.7, 126.8, 127.4, 128.2, 128.4, 128.9, 129.1, 129.3, 129.7, 132.6, 133.5, 133.7, 134.2, 136.4, 141.2, 146.2, 146.3, 147.8, 164.9, 165.4, 167.2. υ (cm^{-1} solid state) 3569, 3429, 2969, 1678, 1598, 1528, 1440, 1354, 1272, 1111, 994, 881, 849, 614; ESI-HRMS found 710.2853 *m/z* $[M+H]^+$, $C_{43}H_{39}N_3O_9$ requires 710.2861.

Methyl-3-propoxy-4-(3-benzyloxy-4-(3-isopropoxy-4-amino-benzoylamido)-benzoylamido)-benzoate 9bca

(procuedure C) **8bca** (70 mg, 0.1 mmol), $SnCl_2$ (126.5 mg, 0.6 mmol) afforderd the product (62.3 mg, 94%) as a yellow solid; m.p. 208°C; δ_H (500 MHz, $CDCl_3$) 1.13 (3H, t, *J* 7.3, CH_3) 1.33 (6H, d, *J* 5.9, CH_3), 1.94 (2H, tq, J 7.2 and 6.9, CH_2), 3.92 (3H, s, CO_2Me), 4.14 (2H, t, *J* 6.3, CH_2), 4.53 (1H, hep, *J* 6.1, CH), 5.25 (2H, s, benzylic CH_2), 6.67 (1H, d, *J* 8.0, Ar CH), 8.86 (1H, s, NH), 7.42-7.20 (4H, m, ArCH), 7.43 (1H, s, ArCH), 7.49-7.46 (5H, m, ArCH), 7.56 (1H, s, NH), 7.74 (2H, d, *J* 8.4, NH_2), 8.62 (1H, d, *J* 8.4, ArCH), 8.71 (2H, d, *J* 5.4, ArCH); ν_{max}/cm^{-1} (solid state) 3433, 3378 (NH), 2977, 1701 (CO), 1603, 1520, 1272; ESI-HRMS found *m/z* 634.2524 $[M+Na]^+$, $C_{35}H_{37}N_3O_7$.Na 634.2529.

3-Isopropoxy-4-(3-isopropoxy-4-(3-benzyloxy-4-amino-benzoylamido)-benzoylamido)-benzoic acid 10aac

(Procedure B) **9aac** (45mg, 0.07mmol). Target acid was recrystallised by slow cooling of a MeOH/THF/H_20 mix and isolated (29 mg, 66%) as a yellow crystalline solid; m.p. 230–232°C; δ_H (300 MHz, MeOD:$CDCl_3$): 1.48 (d, 12H, *J* = 6.0, 2 x CH_3), 4.82 (m, 2H, CH), 5.31 (s, 2H, Benzylic CH_2), 7.43 (m, 8H, ArCH), 7.59 (d, 1H, *J* = 1.8, ArCH), 7.67 (dd, 2H *J* = 1.7 and 7.2, ArCH), 7.72 (dd, 1H, *J* = 8.5 and 1.8 Hz, ArCH), 8.48 (d, 1H, *J* = 7.3, ArCH), 8.52 (d, 1H, *J* = 7.3, ArCH); δ_C (75 MHz, $CDCl_3$): 22.1, 22.2, 59.6, 69.9, 71.8, 111.7, 112.7, 114.3, 120.4, 121.1, 121.7, 122.6, 127.0, 127.7, 128.1, 128.8, 129.9, 132.5,

132.9, 137.3, 145.7, 147.7, 148.0, 164.6, 164.7, 167.3; ν_{max}/cm^{-1} (solid state) ~3200 (broad, COOH), 3434, 3357 (NH), 2968, 2924, 2850 (CH), 1670, 1597 (CO); ESI-HRMS found 620.2389 *m/z* $[M+Na]^+$, $C_{34}H_{35}N_3NaO_7$ requires 6120.2367.

3-Isopropoxy-4-(3-benzyloxy-4-(3-(1-naphthyl)oxy-4-amino-benzoylamido)-benzoylamido)-benzoic acid 10acd

(Procedure B) **9acd** (92.2 mg, 0.13 mmol), aqueous NaOH (1 mL), THF (4 mL), methanol (4 mL) afforded the product (76.3 mg, 84%) as a pale beige solid; m.p. 225-226°C; δ_H (300 MHz, DMSO- d_6) 1.36 (6H, d, *J* = 6.0, iPrCH_3), 4.76 (1H, hep, *J* = 6, iPrCH), 5.34 (2H, s, benzylicCH_2), 5.58 (2H, s, benzylic CH_2), 6.73 (1H, d, *J* = 8.2, ArCH), 7.18-7.40 (4H, m, ArCH), 7.51-7.75 (11H, m, ArCH), 7.93-8.01 (2H, m, ArCH), 8.13-8.25 (3H, m, ArCH), 9.20 (1H, s, NH), 9.33 (1H, s, NH); δ_C (75 MHz, DMSO-d_6) 22.09, 68.5, 70.6, 71.8, 111.5, 112.0, 112.9, 114.4, 120.5, 121.2, 121.7, 122.5, 124.1, 125.8, 126.3, 126.8, 127.8, 128.3, 128.8, 128.9, 131.4, 132.0, 132.8, 133.6, 137.1, 144.8, 148.1, 164.8, 164.9, 167.3; ν_{max}/cm^{-1} (solid state) 3431, (NH), 2929, 1688 (CO), 1598, 1513, 1427, 1348, 1261, 1122, 1014, 872; ESI-HRMS found 696.2711 *m/z* $[M+H]^+$, $C_{42}H_{38}N_3O_7$ requires 696.2704.

3-propoxy-4-(3-benzyloxy-4-(3-isopropoxy-4-amino-benzoylamido)-benzoylamido)-benzoic acid 10bca

(Procedure B) **9bca** (53.2 mg, 0.087 mmol), aqueous NaOH (1 mL), THF (4 mL), methanol (4 mL) afforded the product (45.7 mg, 88%) as a pale beige solid; m.p. 231-232°C; δ_H (300 MHz, DMSO-d_6) 1.01 (3H, t, *J* = 7.3, PrCH_3), 1.25 (6H, d, *J* 6.0, iPrCH_3), 1.80 (2H, m, PrCH_2), 4.03 (2H, t, *J* = 6.3, PrCH_2), 4.48 (1H, hep, *J* = 6.0, iPrCH), 5.30 (2H, s, benzylicCH_2), 5.41 (2H, s, NH_2), 6.68 (1H, d, *J* = 8.3, ArCH), 7.32-7.43 (5H, m, ArCH), 7.47-7.62 (5H, m, ArCH), 7.76 (1H, s, ArCH), 7.82 (1H, d, *J* = 8.1, ArCH), 8.18 (1H, d, *J* = 8.3, ArCH), 9.10 (1H, s, NH), 9.26 (1H, s, NH); δ_C (75 MHz, DMSO-d_6) 10.83, 22.2, 22.5, 70.0, 70.6, 70.7, 108.8, 111.9, 113.1, 113.2, 120.5, 121.2, 121.6, 121.7, 122.0, 122.1, 127.9, 128.4, 129.8, 130.4, 131.6, 137.1, 143.5, 143.7, 149.1, 149.6, 152.0, 157.3, 164.5, 164.9, 169.8; ν_{max}/cm^{-1} (solid state) 3433, 2971, 1665, 1602, 1514, 1384, 1259, 1119; ESI-HRMS found 598.2560 *m/z* $[M+H]^+$, $C_{34}H_{36}N_3O_7$ requires 598.2548.

Tetramer 11aaaa

(Procedure C) **9aaa** (186.0 mg, 0.35 mmol), **4a** (115.4 mg, 0.51 mmol), Cl_2PPh_3 (553.4 mg, 1.71 mmol), and chloroform (40 mL) afforded product (185 mg, 73%) as a pale yellow solid; m.p. 225–226°C (Found: C, 62.3; H, 6.15; N, 6.85%. $C_{41}H_{46}N_4O_{11}$ requires: C, 62.43; H, 6.15; N, 7.10%); R_f = 0.8 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.32-1.49 (24H, 4 different *i*Pr CH_3), 3.91 (3H, s, CO_2Me), 4.75-4.86 (4H, m, *i*PrCH), 7.32-7.46 (3H, m, ArCH), 7.60-7.63 (3H, m, ArCH), 7.68-7.74 (2H, m, ArCH), 7.87 (1H, d *J* 8.3 Hz, ArCH), 8.60-8.70 (3H, nested doublets, ArCH), 8.78 (1H, br NH), 8.85 (1H, br,

NH), 8.86 (1H, br, NH). δ_C (75 MHz, $CDCl_3$) 22.1, 22.2, 22.6, 52.5, 72.2, 72.3, 72.4, 73.6, 112.2, 112.3, 113.6, 115.9, 116.9, 117.7, 118.9, 119.3, 119.6, 123.7, 125.4, 126.2, 130.3, 130.9, 131.8, 132.5, 133.5, 139.8, 143.4, 146.2, 146.9, 147.1, 152.0, 163.7, 167.8, 167.9, 167.2. ν_{max}/cm^{-1} (solid state) 3433, 2975, 2622, 1671, 1598, 1513, 1264, 1112, 986, 872, 794, 596; ESI-MS mz/ 771 $[M+H]^+$, 794$[M+Na]^+$.

Tetramer 11acde

(Procedure C) **9acd** (81.1 mg, 0.114 mmol), **4e** (86.5 mg, 0.26 mmol), Cl_2PPh_3 (318.4 mg, 0.98 mmol), and chloroform (40 mL) to yield product (75.2 mg, 65%) as a yellow solid; m.p. 256–257°C (Found: C, 70.45; H, 5.10; N, 5.35%. $C_{42}H_{47}N_3O_7$ requires: C, 70.92; H, 5.07; N, 5.35%); R_f = 0.8 (30% Et_2O in CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 1.47 (6H, d, *J* = 6.0, iPrCH_3), 3.92 (3H, s, CO_2Me), 4.78 (1H, sept, *J* = 6.0, iPr CH), 5.06 (2H, s, ArCH_2O-), 5.29 (2H, s, ArCH_2O-), 5.56 (2H, s, ArCH_2O-), 6.80 (1H, d, *J* = 8.3, ArCH), 7.28 (1H, t, *J* = 8.4 Hz, ArCH), 7.43-7.55 (16H, m, ArCH), 7.61 (1H, s, ArCH), 7.72-7.84 (3H, m, ArCH), 7.87-7.90 (6H, m, ArCH), 8.02 (1H, d, *J* = 8.3, ArCH), 8.57 (1H, br, NH), 8.59 (1H, d, *J* = 8.4 Hz, ArCH), 8.63 (1H, d, *J* = 8.5 Hz, ArCH), 8.74 (1H, d, *J* = 8.4, ArCH), 8.88 (1H, br, NH), 8.89 (1H, br, NH). δ_C (75 MHz, $CDCl_3$) 22.3, 52.1, 70.9, 71.3, 71.5, 71.9, 111.3, 111.5, 113.2, 114.0, 118.2, 118.7, 119.0, 119.2, 119.5, 120.3, 123.2, 123.3, 124.8, 125.4, 125.7, 126.3, 126.4, 127.0, 127.9, 128.1, 128.7, 129.0, 129.3, 130.0, 130.3, 131.4, 131.6, 133.3, 134.0, 138.9, 142.0, 146.1, 145.8, 151.8, 162.8, 164.3, 164.4, 166.8; ν_{max}/cm^{-1} (solid state) 3432, 3068, 2971, 1728, 1688, 1596, 1516, 1426, 1349, 1194, 1123, 1025, 1000, 869, 747, 605. ESI-MS *m/z* 1015 $[M+H]^+$, 1037 $[M+Na]^+$.

Tetramer 12aaaa

(Procedure D) **11aaaa** (111.8 mg, 0.15 mmol), $SnCl_2.H_20$ (371.4 mg, 1.65 mmol), ethyl acetate (30 mL) and methanol (1 mL) afforeded a pale yellow oil (98.7 mg, 92%) that solidified upon standing; m.p. 206–207°C; R_f = 0.65 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.40-1.49 (24H, m, 4 x *i*PrCH_3), 3.1 (2H, br, NH_2), 3.92 (3H, s, CO_2Me), 4.67-4.85 (4H, m, 4 x *i*PrCH), 6.75 (1H, d, *J* = 8.1, ArCH), 7.28 (1H, d, ArCH), 7.40-7.47 (3H, nested doublets, ArCH), 7.60-7.62 (3H, overlapping singlets, ArCH), 7.73 (1H, d, *J* = 8.5, ArCH), 8.63 (1H, d, *J* = 8.5, ArCH), 8.67-8.71 (2H, overlapped doublets, ArCH), 8.74 (1H, br, NH), 8.85 (1H, br, NH), 8.87 (1H, br, NH). δ_C (75 MHz, $CDCl_3$) 22.6, 52.5, 71.3, 72.2, 72.3, 112.2, 112.8, 113.6, 114.0, 119.0, 119.1, 119.2, 119.3, 119.4, 120.4, 123.7, 124.4, 125.3, 129.5, 130.0, 132.8, 1333.2, 133.5, 141.9, 145.3, 146.2, 146.8, 146.9, 165.0, 165.2, 165.6, 167.2; ν_{max}/cm^{-1} (solid state) 3434, 3358, 3199, 2976, 1710, 1672, 1598, 1514, 1348, 1266, 1112, 985, 872, 750, 598; ESI-HRMS found 741.3505 *m/z* $[M+H]^+$, $C_{41}H_{48}N_4O_9$ requires 741.3494.

Pentamer 13aaaaa

(Procedure C), **12aaaa** (38.7 mg, 0.054 mmol), **4a** (35.3 mg, 0.156 mmol), Cl_2PPh_3 (214.5 mg, 0.66 mmol), and chloroform (30 mL), to yield product (33.5 mg, 68%) as a pale yellow solid; m.p. 248–249°C; R_f = 0.8 (30% Et_2O in CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 1.44-1.53 (30H, nested doublets, iPrCH_3), 3.91 (3H, s, CO_2Me), 4.75-4.87 (5H, nested septuplets, iPrCH), 7.32-7.46 (4H, m, ArCH), 7.60-7.65 (4H, m, ArCH), 7.70 (1H, s, ArCH), 7.72 (1H, d, *J* = 8.8, ArCH), 7.88 (1H, d *J* = 8.3, ArCH), 8.63 (1H, d, *J* = 8.5, ArCH), 8.65-8.71 (3H, m, ArCH), 8.78 (1H, br, NH), 8.85-8.87 (3H, br, NH). δ_C (75 MHz, $CDCl_3$) 22.1, 22.2, 22.6, 52.5, 72.3, 72.4, 73.6, 112.3, 113.6, 115.9, 116.7,119.0, 119.2, 119.3, 119.4, 119.6, 123.7, 125.4, 126.2, 130.1, 130.2, 130.9, 131.9, 132.6, 132.7, 133.5, 146.2, 147.0, 147.1, 152.0, 163.7, 164.8, 164.9, 165.0, 167.2; ν_{max}/cm^{-1} (solid state) 3434, 2978, 1673, 1595, 1519, 1266, 1111, 986, 874, 746, 602. ESI-HRMS found 948.4004 *m/z* $[M+H]^+$, $C_{51}H_{57}N_5O_{13}$ requires 948.4026.

Additional Structural Data

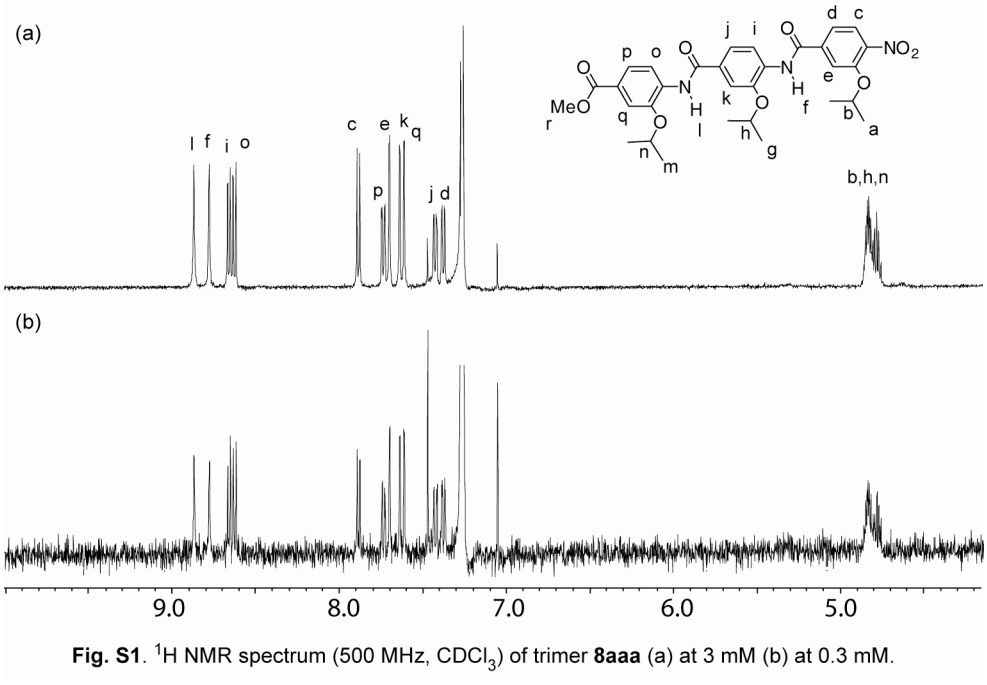

Fig. S1. ^1H NMR spectrum (500 MHz, $CDCl_3$) of trimer **8aaa** (a) at 3 mM (b) at 0.3 mM.

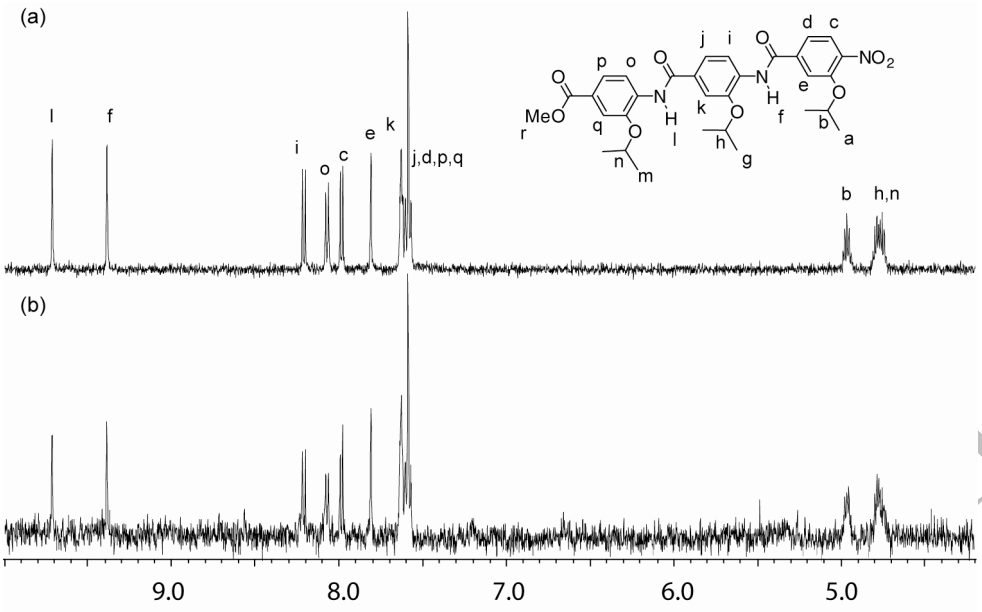

Fig. S2. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of trimer **8aaa** (a) at 2 mM (b) at 0.2 mM.

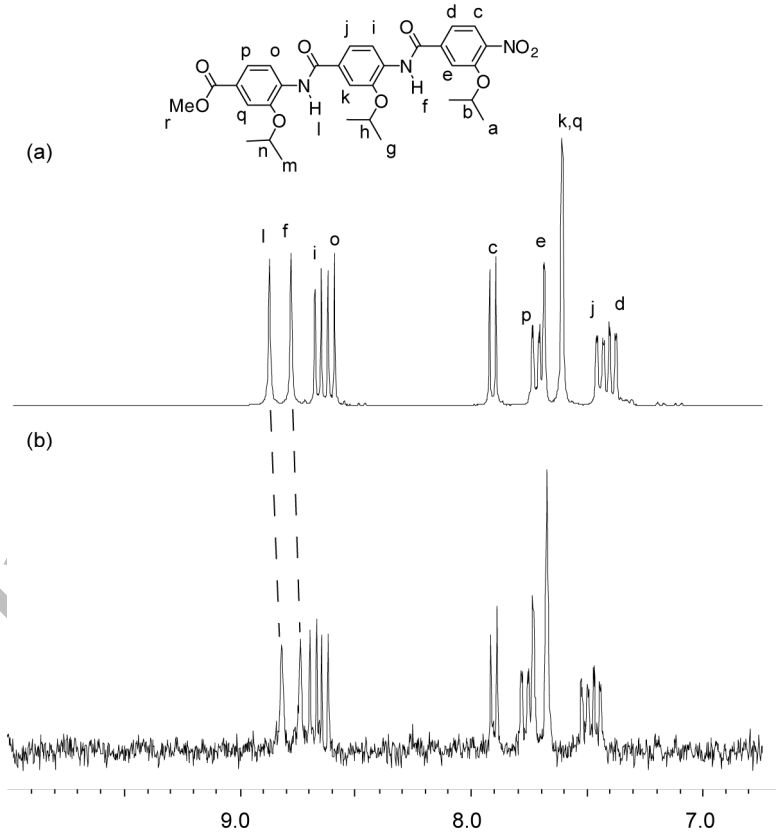

Fig. S3. ^{1}H NMR spectrum (300 MHz, $C_2D_2Cl_4$) of trimer **8aaa** (a) at 303 K (b) at 373 K

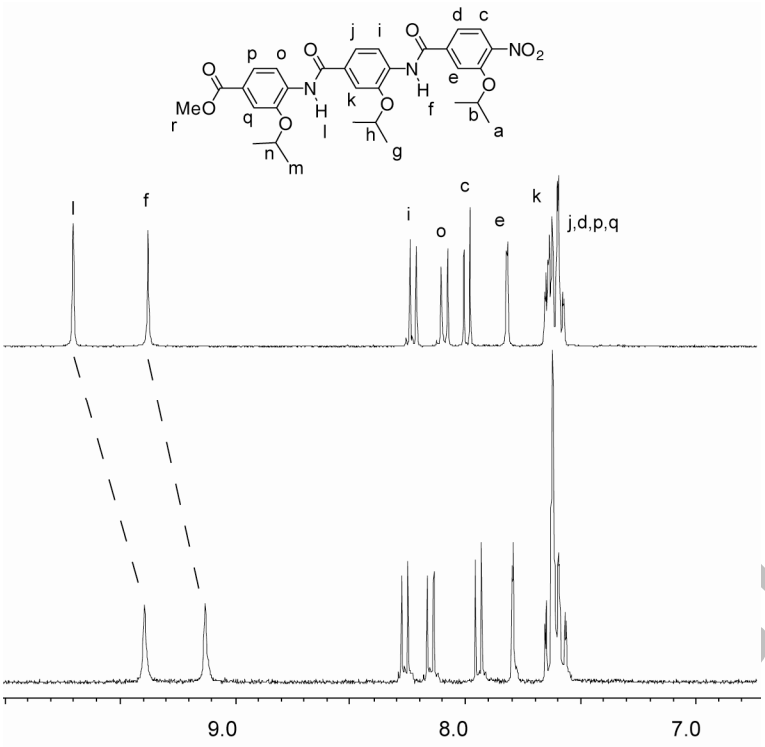

Fig. S4. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of trimer **8aaa** (a) at 303 K (b) at 373 K