SUPPORTING INFORMATION

Efficient labeling of sugars to provide of water soluble fluorescent tags

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General methods. Melting points were determined on a capillary point apparatus equipped with a digital thermometer. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with TMS for ^1H (300 MHz) and ^{13}C (75 MHz) as an internal reference. Coumarin-3 carboxyl acid was purchased from Acros; sugars, N-Fmoc-amino acid were purchased from Fluka, Acros and Aldrich and were used without further purification. All the reactions were carried out under microwave irradiation with a single mode cavity Discover Microwave Synthesizer (CEM Corporation, NC) producing a continuous irradiation at 2450 MHz. Elemental analyses were performed on a Carlo Erba-1106 instrument. Optical rotation values were measured with the use of sodium D line. Column chromatography was performed on silica gel (200-425 mesh). HPLC analyses were performed on Beckman system gold programmable solvent module 126 using Chirobiotic T column (4.6 x 250 mm), detection at 254 nm, flow rate 1.0 mL/min, and methanol as solvent.

3-(Benzotriazole-1-carbonyl)chromen-2-one, 4: Thionyl chloride (7.5 mmol) was added to a solution of 1*H*-benzotriazole (25 mmol) in dry THF (30 mL) at room temperature, and the reaction mixture was stirred for 20 min. To the reaction mixture was added coumarin-3-carboxylic acid (5 mmol) and stirred for 4 h at 25°C. The white precipitate formed during the reaction was filtered off, and the filtrate was concentrated under reduced pressure. The residue was diluted with EtOAc (150 ml) and the solution was washed with sat. Na_2CO_3 soln (3 × 50), sat. NaCl soln (50 mL), and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave 3-(benzotriazole-1-carbonyl)-chromen-2-one, which was recrystallized from CH_2Cl_2-hexanes for elemental analysis. White microcrystals (87%); mp 186–187 °C, ^1H NMR ($CDCl_3$): δ 7.41 (t, *J* =

7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 8.2 Hz, 1H), 7.64–7.80 (m, 3H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.34 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): 114.4, 117.2, 117.6, 120.5, 121.9, 125.3, 126.8, 129.6, 130.9, 131.2, 134.5, 146.2, 147.0, 154.9, 157.4, 162.6. Anal. Calcd for $C_{16}H_9N_3O$: C, 65.98; H, 3.11; N, 14.43. Found: C, 65.67; H, 3.10; N, 14.22.

(*S*)-2-Benzyloxycarbonylamino-6-[(2-oxo-2*H*-chromene-3-carbonyl)amino]hexanoic acid, N^{α}-Cbz-N^{ε}-Coumoyl-*L*-Lys-OH, 5: White microcrystals (89%); mp 144–145 °C, $[\alpha]^{23}_{D} = -8.54$ (c 1.68, DMF). ^{1}H NMR ($CDCl_3$): δ 1.37–1.56 (m, 2H), 1.58–1.74 (m, 2H), 1.75–2.40 (m, 2H), 3.33–3.58 (m, 2H), 4.34–4.45 (m, 1H), 5.09 (s, 2H), 5.75 (d, *J* = 8.0 Hz, 1H), 7.27–7.42 (m, 7H), 7.52–7.72 (m, 2H), 8.92 (s, 1H), 8.95–9.04 (m, 1H). ^{13}C NMR ($CDCl_3$): 22.3, 28.9, 31.5, 39.3, 53.6, 66.9, 116.5, 117.9, 118.5, 125.3, 128.0, 128.1, 128.4, 130.0, 134.1, 136.2, 148.8, 154.3, 156.3, 161.3, 162.1, 175.3. Anal. Calcd for $C_{24}H_{24}N_2O_7$: C, 63.71; H, 5.35; N, 6.19. Found: C, 63.82; H, 5.09; N, 6.04.

(*S*)-2-(9*H*-Fluoren-9-ylmethoxycarbonylamino)-6-[(2-oxo-2*H*-chromene-3-carbonyl)amino]hexanoic acid, N^{α}-Fmoc-N^{ε}-Coumoyl-*L*-Lys-OH, 6: White microcrystals (87%); mp 110–111 °C, $[\alpha]^{23}_{D} = -1.62$ (c 1.85, DMF), ^{1}H NMR (DMSO-d_6): δ 1.32–1.50 (m, 2H), 1.50–1.62 (m, 2H), 1.62–1.85 (m, 2H), 3.26–3.38 (m, 2H), 3.92–4.01(m, 1H), 4.17–4.36 (m, 3H), 7.22–7.54 (m, 6H), 7.60–7.80 (m, 4H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.96 (d, *J* = 7.4 Hz, 1H), 8.73 (t, *J* = 5.5 Hz, 1H), 8.84 (s, 1H). 12.62 (s, 1H). ^{13}C NMR (DMSO-d_6): 23.2, 28.6, 30.5, 46.7, 53.8, 65.6, 116.1, 118.5, 119.0, 120.1, 125.1, 125.3, 127.1, 127.7, 130.2, 134.0, 140.7, 143.8, 147.3, 153.8, 156.2, 160.4, 161.0, 174.0. Anal. Calcd for $C_{31}H_{28}N_2O_7$: C, 68.88; H, 5.22; N, 5.18. Found: C, 68.59; H, 5.11; N, 5.16.

General procedure for the preparation of (2-Oxo-2H-chromene-3-carbonyl)-α-aminoacyl)benzotriazoles, 7, 8: Thionyl chloride (1.2 mmol) was added to a solution of 1H-benzotriazole (4 mmol) in dry CH_2Cl_2 (15 mL) at 20 °C and the reaction mixture was stirred for 20 min. To the reaction mixture was added **5**, **6** (1 mmol) and the relevant mixtures were stirred for 1 h at room temperature. The white precipitate which formed during the reaction was filtered off, the filtrate was diluted with additional CH_2Cl_2 (80 ml) and the solution was washed with sat. Na_2CO_3 soln. (3 × 50), brine (50 mL), and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave **7**, **8** which were recrystallized from CH_2Cl_2-hexanes.

{(*S*)-1-(Benzotriazole-1-carbonyl)-5-[(2-oxo-2*H*-chromene-3-carbonyl)-amino]-pentyl}-carbamic acid benzyl ester, N^{α}-Cbz-N^{ε}-Coumoyl-*L*-Lys-Bt, 7: White microcrystals (79%); mp 156–157°C, ^{1}H NMR ($CDCl_3$): δ 1.50–1.80 (m, 4H), 1.96–2,12 (m, 1H), 2.13–2.28 (m, 1H), 3.36–3.48 (m, 1H), 3.48–3.64 (m, 1H), 5.13 (s, 2H), 5.69–5.83 (m, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 7.26–7.47 (m, 7H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.60–7.74 (m, 2H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.86 (s, 1H), 8.82–8.97 (m, 1H). ^{13}C NMR ($CDCl_3$): 22.3, 28.9, 31.6, 38.5, 54.6, 67.1, 114.4, 116.5, 118.2, 118.6, 120.3, 125.2, 126.4, 128.0, 128.1, 128.5, 129.8, 130.6, 131.1, 134.0, 136.2, 145.9, 148.6, 154.3, 156.2, 161.4, 162.0, 171.7. Anal. Calcd for $C_{30}H_{27}N_5O_6$: C, 65.09; H, 4.92; N, 12.65. Found: C, 64.91; H, 4.76; N, 12.59.

{(*S*)-1-(Benzotriazole-1-carbonyl)-5-[(2-oxo-2*H*-chromene-3-carbonyl)-amino]-pentyl}-carbamic acid 9*H*-fluoren-9-ylmethyl ester, N^{α}-Fmoc-N^{ε}-Coumoyl-*L*-Lys-Bt, 8: White microcrystals (82 %); mp 113–115°C, 1H NMR ($CDCl_3$): δ 1.40–1.90 (m, 4H),

1.95–2.15 (m, 1H), 2.15–2.23 (m, 1H), 3.40–3.68 (m, 2H), 4.20–4.35 (m, 2H), 4.36–4.48 (m, 1H), 5.71–5.83 (m, 1H), 6.20 (d, *J* = 7.7 Hz, 1H), 7.20–7.45 (m, 7H), 7.50–7.80 (m, 7H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.20–8.97 (m, 2H). ^{13}C NMR ($CDCl_3$): 22.4, 28.9, 31.6, 38.5, 47.1, 54.6, 67.1, 114.4, 116.4, 118.0, 118.5, 119.9, 120.2, 125.2, 126.4, 127.0, 127.6, 129.7,130.6, 131.1, 134.0, 141.2, 143.6, 146.0, 148.6, 154.3, 156.2, 161.4, 162.1, 171.7. Anal. Calcd for $C_{37}H_{31}N_5O_6$: C, 69.26; H, 4.87; N, 10.91. Found: C, 69.01; H, 4.76; N, 11.03.

1-*O*-Coumarin-3-carbonyl-2,3:5,6-di-*O*-isopropylidene-*α*-D-mannofuranose, 14: White solid (65%), mp 158.2–160.0 ^{o}C, ^{1}H NMR ($CDCl_3$): δ 1.35–1.40 (m, 6H), 1.46 (s, 3H), 1.52 (s, 3H), 4.06 (dd, *J* = 9.07, 4.4 Hz, 1H), 4.08–4.15 (m, 1H), 4.19 (dd, *J* = 7.8, 3.4 Hz, 1H), 4.40–4.48 (m, 1H), 4.89–4.98 (m, 2H), 6.36 (s, 1H), 7.32–7.40 (m, 2H), 7.62–7.71 (m, 2H), 8.54 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 24.6, 25.1, 25.9, 26.9, 66.8, 72.8, 79.2, 82.6, 85.0, 101.9, 109.4, 113.3, 116.8, 117.7, 124.9, 129.7, 134.8, 149.6, 155.3, 155.6, 156.4, 162.0. Anal. calcd for $C_{22}H_{24}O_9$: C, 61.11; H, 5.59; Found: C, 61.02; H, 5.54.

***N*-Coumarin-3-carbonyl-2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosylamine 16:** White solid (60%), mp 99–100 ^{o}C, ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 9H), 1.06 (s, 9H), 1.10 (s, 9H), 1.23 (s, 9H), 3.91–3.99 (m, 1H), 4.04–4.16 (m, 2H), 5.20–5.35 (m, 2H), 5.40–5.52 (m, 2H), 7.30–7.39 (m, 2H), 7.58–7.68 (m, 2H), 8.83 (s, 1H), 9.29 (d, *J* =9.1Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 26.7, 27.0, 27.1, 29.6, 38.6, 38.6, 38.7, 39.0, 60.7, 66.7, 67.7, 71.1, 72.7, 78.5, 116.7, 117.2, 118.3, 125.3, 130.0, 134.6, 149.5, 154.6, 160.6, 162.0, 176.8, 177.0, 177.0, 177.7. Anal. calcd for $C_{22}H_{24}O_9$: C, 62.87; H, 7.18; N, 2.04. Found: C, 62.69; H, 7.68; N, 2.07.

1-*O*-(N^{α}-(9-Fluorenylmethoxycarbonyl)-N^{δ}-(coumarin-3-carbonyl)-*L*-lysine)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, 19: The crude product was subjected to silica-gel column chromatography using ethyl acetate/hexanes (2:1) as eluent to afford white microcrystals (74%), mp 87.0-88.0 ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 3H), 1.37 (s, 3H), 1.43 (s, 3H), 1.48 (s, 3H), 1.52–1.98 (m, 4H), 3.46–3.60 (m, 2H), 3.98–4.16 (m, 4H), 4.22 (t, *J* = 7.1 Hz, 1H), 4.30–4.48 (m, 4H), 4.73 (d, *J* = 5.9 Hz, 1H), 4.80–4.90 (m, 1H), 5.65 (d, *J* = 7.8 Hz, 1H), 6.17 (s, 1H), 7.25–7.42 (m, 7H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.56–6.67 (m, 3H), 7.74 (dd, *J* = 7.3, 2.8 Hz, 2H), 8.82–8.96 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 22.3, 22.6, 24.6, 25.1, 25.9, 26.9, 29.0, 31.5, 38.9, 47.1, 53.7, 66.8, 67.0, 72.7, 79.2, 82.5, 85.0, 101.6, 109.3, 113.3, 116.5, 118.2, 118.5, 119.9, 125.1, 125.2, 127.0, 127.6, 129.7, 134.0, 141.2, 143.7, 143.9, 148.4, 154.3, 155.8, 161.4, 161.8, 171.1. Anal. calcd for $C_{43}H_{46}N_2O_{12}$: C, 65.97; H, 5.92; N, 3.58. Found: C, 65.57; H, 6.06; N, 3.40.

***N*-(N^{α}-(9-Fluorenylmethoxycarbonyl)-N^{δ}-(coumarin-3-carbonyl)-*L*-lysine)-2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosylamine, 20:** The crude product was subjected to silica-gel column chromatography using ethyl acetate/hexanes (1:3) as eluent to afford white microcrystals (40%), mp 117–119 ºC, $[\alpha]^{23}_{D}$ = +10.8 (*c* 1.16, DMF);^{1}H NMR ($CDCl_3$): δ 1.03 (s, 9H), 1.05 (s, 9H), 1.09 (s, 9H), 1.14 (s, 9H), 1.30–1.82 (m, 6H), 3.32–3.48 (m, 2H), 3.84–3.96 (m, 1H), 3.98–4.18 (m, 4H), 4.20–4.31 (m, 2H), 5.10–5.20 (m, 2H), 5.26 (t, *J* = 8.5 Hz, 1H), 5.35–5.41 (m, 1H), 5.60 (d, *J* = 7.7 Hz, 1H), 7.18-7.23 (m, 2H), 7.24–7.36 (m, 5H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.48–7.60 (m, 3H), 7.65 (t, *J* = 7.1 Hz, 2H), 8.85–8.89 (m, 1H), 8.91 (s, 1H). ^{13}C NMR ($CDCl_3$): 22.2, 27.0, 27.1, 27.2, 28.6, 29.7, 31.4, 38.6, 38.8, 38.9, 39.0, 47.1, 54.4, 60.8, 66.7, 67.2, 68.3, 71.2, 72.6, 77.2, 78.4, 116.5, 118.1, 118.7, 120.0, 125.2, 127.0, 127.1, 127.7, 129.9, 134.0, 141.2, 143.7, 148.9,

154.4, 161.5, 162.0, 172.5, 176.8, 177.0, 177.8, 178.2. Anal. calcd for $C_{57}H_{71}N_3O_{15}$: C, 65.94; H, 6.89; N, 4.04. Found: C, 66.07; H, 7.20; N, 3.75.