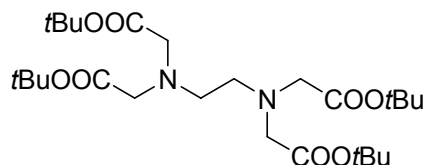


Supporting information



1

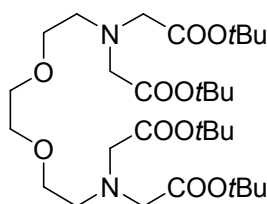
Compound 1

Ethylenediamine (2.9 g, 48.3 mmol) was dissolved in dry acetonitrile (100 mL) and K_2CO_3 (33.4 g, 241.5 mmol) was added. The mixture was cooled at 0 °C and *tert*-butylbromoacetate (39.6 g, 203 mmol) was added dropwise and the reaction warmed at r.t. After 72 h, the reaction was filtered, evaporated and the residue was dissolved in CH_2Cl_2 and washed with water (3x100 mL). The organic layer was dried over sodium sulphate and concentrated under vacuum to obtain a pale yellow oil (18.0 g, 72%).

1H NMR (300 MHz, $CDCl_3$, 298 K): 3.46 (s, 8H), 2.84 (s, 4H), 1.44 (s, 36H).

^{13}C NMR (75.4 MHz, $CDCl_3$, 298 K): 170.8, 80.9, 56.2, 52.6, 28.2.

MS (ESI+) Calc.d for $C_{26}H_{48}N_2O_8$: 516.3. Found: m/z (100%) 517.4 $[M+H]^+$.

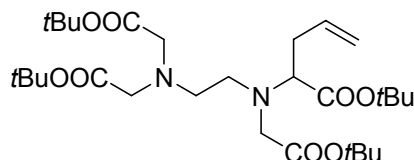


2

Compound 2

2,2'-(Ethylendioxy)bis(ethylamine) (5.0 g, 33.7 mmol) was dissolved in acetonitrile (100 mL) and K_2CO_3 (23.3 g, 168.5 mmol) was added. The mixture was cooled at 0 °C and *t*-butylbromoacetate (29.6 g, 152.0 mmol) was added dropwise. After 72 h the reaction was filtered, evaporated and the residue was dissolved in CH_2Cl_2 and washed with water (3x100 mL). The organic layer was dried over sodium sulphate and evaporated under vacuum to obtain the product as a pale yellow oil (15.5 g, 76%). 1H NMR (300 MHz, $CDCl_3$, 298 K): 3.56 (t, J = 5.8 Hz, 4H), 3.53 (s, 4H), 3.43 (s, 8H), 2.89 (t, J = 6.0 Hz, 4H), 1.40 (s, 36H).

^{13}C NMR (75.4 MHz, $CDCl_3$, 298 K): 170.8, 80.8, 70.5, 70.3, 56.7, 53.4, 28.2. MS (ESI+) Calc.d for $C_{30}H_{56}N_2O_{10}$: 604.4. Found: m/z (100%) 605.3 $[M+H]^+$.



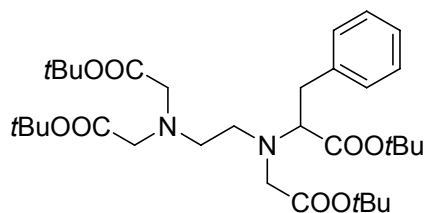
3a

Compound 3a Colourless oil (65%).

1H NMR (300 MHz, $CDCl_3$, 298 K): 5.82 (ddt, J_1 = 17.1, J_2 = 10.1, J_3 = 6.9 Hz, 1H), 5.05 (dd, J_1 = 17.2, J_2 = 1.8 Hz, 1H), 4.99 (dd, J_1 = 10.1, J_2 = 2.0 Hz, 1H), 3.45 (d, J = 17.4 Hz, 1H), 3.43 (s, 4H), 3.40 (t, J = 7.6 Hz, 1H), 3.29 (d, J = 17.4 Hz, 1H), 2.90-2.70 (m, 4H), 2.47-2.85 (m, 2H), 1.43 (s, 27H), 1.42 (s, 9H).

^{13}C NMR (75.4 MHz, $CDCl_3$, 298 K): 172.0, 171.3, 170.8, 135.0, 116.7, 81.1, 80.9, 80.6, 64.9, 56.3, 54.0, 53.2, 51.4,

35.1, 28.3, 28.2, 28.1. MS (ESI+) Calc.d for $C_{29}H_{52}N_2O_8$: 556.4. Found: m/z (100%) 557.4 $[M+H]^+$.



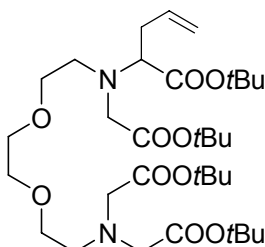
3b

Compound 3b

Colourless oil (62%).

^1H NMR (300 MHz, CDCl_3 , 298 K): 7.17-7.05 (m, 5H), 3.59 (dd, $J_1 = 11.6$ Hz, $J_2 = 8.8$ Hz, 1H), 3.50 (d, $J = 17.2$ Hz, 1H), 3.37 (d, $J = 17.5$ Hz, 2H), 3.34 (d, $J = 17.5$ Hz, 2H), 3.27 (d, $J = 17.1$ Hz, 1H), 2.94-2.62 (m, 6H), 1.37 (bs, 27H), 1.26 (s, 9H).

^{13}C NMR (75.4 MHz, CDCl_3 , 298 K): 171.7, 171.3, 170.8, 138.4, 129.6, 128.2, 126.3, 81.0, 80.8, 80.6, 66.7, 56.2, 53.9, 53.1, 51.5, 37.0, 28.31, 28.23, 28.22. MS (ESI+) Calc.d for $\text{C}_{33}\text{H}_{54}\text{N}_2\text{O}_8$: 606.4. Found: m/z (100%) 607.4 $[\text{M}+\text{H}]^+$.



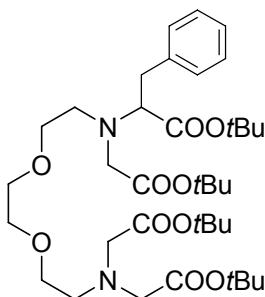
4a

Compound 4a

Pale yellow oil (70%).

^1H NMR (300 MHz, CDCl_3 , 298 K): 5.82 (ddt, $J_1 = 17.0$ Hz, $J_2 = 10.2$ Hz, $J_3 = 6.8$ Hz, 1H), 5.05 (dd, $J_1 = 17.1$ Hz, $J_2 = 1.8$ Hz, 1H), 4.99 (bd, $J = 10.4$ Hz, 1H), 3.58 (t, $J = 6.0$ Hz, 2H), 3.54 (s, 4H), 3.51 (t, $J = 6.4$ Hz, 2H), 3.45 (s, 4H), 3.44 (d, $J = 17.4$, 1H), 3.37 (t, $J = 7.5$, 1H), 3.34 (d, $J = 17.5$, 1H), 2.91 (t, $J = 6.0$, 2H), 2.94-2.79 (m, 2H), 2.47-2.27 (m, 2H), 1.42 (s, 27H), 1.41 (s, 9H).

^{13}C NMR (75.4 MHz, CDCl_3 , 298 K): 170.9, 170.2, 169.6, 133.8, 115.5, 79.9, 79.7, 79.3, 69.5, 69.2, 69.1, 69.07, 64.4, 55.5, 53.1, 52.1, 51.1, 34.0, 27.1, 27.0, 26.9. MS (ESI+) Calc.d for $\text{C}_{33}\text{H}_{60}\text{N}_2\text{O}_{10}$: 644.4. Found: m/z (100%) 667.2 $[\text{M}+\text{Na}]^+$.



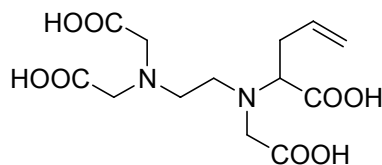
4b

Compound 4b

Colourless oil (78%).

^1H NMR (300 MHz, CDCl_3 , 298 K): 7.35-7.08 (m, 5H), 3.61-3.32 (m, 15H), 3.43 (s, 4H), 2.91 (dd, $J_1 = 13.5$ Hz, $J_2 = 8.3$ Hz, 1H), 2.86 (dd, $J_1 = 13.5$ Hz, $J_2 = 7.0$ Hz, 1H), 1.40 (bs, 36H).

^{13}C NMR (75.4 MHz, CDCl_3 , 298 K): 171.8, 171.3, 170.8, 138.3, 129.5, 128.1, 126.3, 81.0, 80.8, 80.6, 70.7, 70.5, 70.3, 70.2, 67.5, 56.7, 54.1, 53.4, 52.5, 37.0, 28.22, 28.16, 28.12. MS (ESI+) Calc.d for $\text{C}_{37}\text{H}_{62}\text{N}_2\text{O}_{10}$: 694.4. Found: m/z (100%) 717.6 $[\text{M}+\text{Na}]^+$.



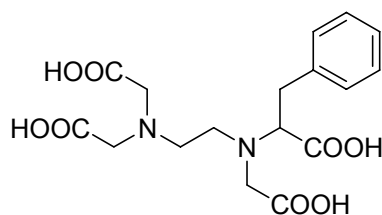
5a

Compound 5a White powder. M.p. 180-182 °C.

^1H NMR (300 MHz, D_2O , 298 K): 5.88 (ddt, $J_1 = 17.2$, $J_2 = 10.1$, $J_3 = 7.0$ Hz, 1H), 5.22 (dd, $J_1 = 17.1$, $J_2 = 1.5$ Hz, 1H), 5.16 (dd, $J_1 = 10.4$, $J_2 = 1.5$ Hz, 1H), 4.02 (s, 4H), 3.92 (t, $J = 7.0$ Hz, 1H), 3.86 (d, $J = 18.1$ Hz, 1H), 3.77 (d, $J = 18.1$ Hz, 1H), 3.55-3.41 (m, 2H), 3.37 (t, $J = 5.5$ Hz, 2H), 2.74-2.55 (m, 2H).

^{13}C NMR (75.4 MHz, D_2O , 298 K): 175.6, 173.3, 169.1, 135.5, 118.6, 64.7, 55.9, 53.9, 52.6, 51.2, 35.3.

Calc.d for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_8$: 332.1. Found: m/z (100%) 333.3 $[\text{M}+\text{H}]^+$.



5b

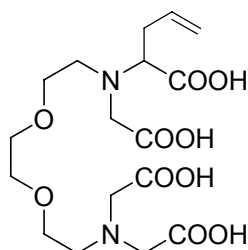
Compound 5b

White powder. M.p.= 190-192 °C.

^1H NMR (300 MHz, D_2O , 298 K): 7.33-7.16 (m, 5H), 3.46 (d, $J = 16.8$ Hz, 1H), 3.45 (dd, $J_1 = 8.2$, $J_2 = 6.8$ Hz, 1H), 3.29 (d, $J = 16.5$ Hz, 2H), 3.27 (d, $J = 16.8$ Hz, 2H), 3.10 (d, $J = 17.1$ Hz, 1H), 2.88-2.67 (m, 6H).

^{13}C NMR (75.4 MHz, D_2O , 298 K): 175.0, 174.7, 170.1, 137.4, 129.4, 129.1, 127.3, 67.0, 55.4, 53.0, 51.8, 49.4, 34.8.

MS (ESI+), Calc.d for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_8$: 382.1. Found: m/z (100%) 383.1 $[\text{M}+\text{H}]^+$.



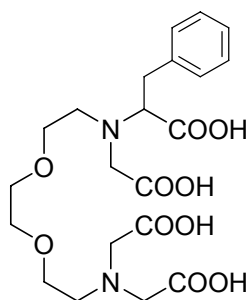
6a

Compound 6a Pale yellow gum.

^1H NMR (300 MHz, D_2O , 298 K): 5.75 (ddt, $J_1 = 17.1$ Hz, $J_2 = 10.1$ Hz, $J_3 = 7.0$ Hz, 1H), 5.25-5.13 (m, 2H), 4.36 (t, $J = 6.6$ Hz, 1H), 4.22 (d, $J = 17.8$ Hz, 1H), 4.18 (s, 4H), 4.12 (d, $J = 17.5$ Hz, 1H), 3.78-3.71 (m, 4H), 3.62-3.46 (m, 4H), 2.79 (dt, $J_1 = 15.3$ Hz, $J_2 = 7.0$ Hz, 1H), 2.71 (dt, $J_1 = 15.3$ Hz, $J_2 = 7.0$ Hz, 1H).

^{13}C NMR (75.4 MHz, D_2O , 298 K): 168.6, 167.7, 167.0, 129.9, 119.8, 68.51, 68.47, 65.1, 63.8, 63.7, 54.7, 54.3, 53.9, 52.2, 30.1.

MS (ESI+) Calc.d for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_{10}$: 420.2. Found: m/z (100%) 421.2 $[\text{M}+\text{H}]^+$, m/z (90%) 443.2 $[\text{M}+\text{Na}]^+$.



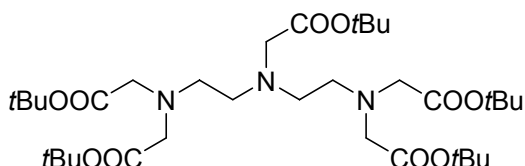
6b

Compound 6b

White amorphous solid.

^1H NMR (300 MHz, D_2O , 298 K): 7.32-7.17 (m, 5H), 4.35 (t, $J = 6.0$ Hz, 1H), 3.97 (s, 4H), 3.93 (m, 2H), 3.77-3.05 (m, 14H).

^{13}C NMR (75.4 MHz, D_2O , 298 K): 170.7, 169.6, 169.0, 134.9, 129.3(2CH), 127.9, 69.8, 69.7, 68.3, 64.9, 64.4, 56.2, 55.4, 54.4, 54.0, 33.0. M.p. 172-175 °C. MS (ESI+) Calc.d for $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_{10}$: 470.2. Found: m/z (100%) 471.1 $[\text{M}+\text{H}]^+$, m/z (90%) 493.2 $[\text{M}+\text{Na}]^+$. MS (ESI-) m/z (100%) 469.4 $[\text{M}-\text{H}]^-$.



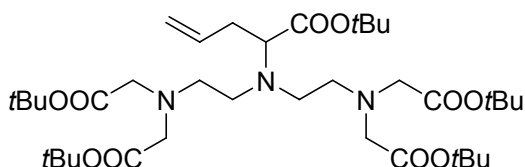
7

Compound 7

Diethylenetriamine (5.0g, 48.5 mmol) was dissolved in acetonitrile (100 mL) and K_2CO_3 (40.2 g, 291.0 mmol) was added. The mixture was cooled at 0 °C and *tert*-butylbromoacetate (55 g, 267 mmol) was added dropwise. After 72 h the reaction was filtered, the solvent evaporated and the residue dissolved in CH_2Cl_2 and washed with water (3x100 mL). The organic layer was dried over sodium sulphate and evaporated under vacuum to obtain a pale yellow oil (17.8 g, 55%).

^1H NMR (300 MHz, CDCl_3 , 298 K): 3.39 (s, 8H), 3.30 (s, 2H), 2.74 (bs, 8H), 1.40 (s, 45H).

^{13}C NMR (75.4 MHz, CDCl_3 , 298 K): 170.9, 170.8, 80.8 (2C), 56.2, 56.0, 53.0, 52.4, 28.2 (2CH₃). MS (ESI+) Calc.d for $\text{C}_{34}\text{H}_{63}\text{N}_3\text{O}_{10}$: 673.4. Found: m/z (100%) 674.3 $[\text{M}+\text{H}]^+$.



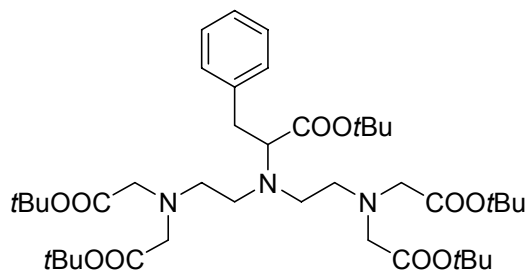
8a

Compound 8a Colourless oil (62%).

^1H NMR (300 MHz, CDCl_3 , 298 K): 5.82-5.67 (m, 1H), 5.02 (d, $J = 17.1$ Hz, 1H), 4.95 (d, $J = 9.8$ Hz, 1H), 3.40 (s, 8H), 3.30 (t, $J = 7.6$ Hz, 1H), 2.85-2.59 (m, 8H), 2.42 (dt, $J_1 = 14.1$ Hz, $J_2 = 7.0$ Hz, 1H), 2.25 (dt, $J_1 = 13.8$ Hz, $J_2 = 7.0$ Hz, 1H), 1.42 (s, 45H).

^{13}C NMR (75.4 MHz, CDCl_3 , 298 K): 170.8, 169.5, 134.4, 115.3, 79.6 (2C), 63.3, 54.9, 52.6, 49.4, 33.5, 27.1, 27.0.

MS (ESI+) Calc.d for $\text{C}_{37}\text{H}_{67}\text{N}_3\text{O}_{10}$: 713.5 Found: m/z (100%) 714.2 $[\text{M}+\text{H}]^+$.



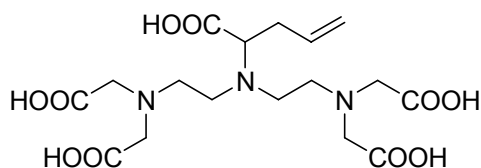
8b

Compound 8b

Colourless oil (435.2 mg, 57%).

^1H NMR (300 MHz, CDCl_3 , 298 K): 7.32-7.08 (m, 5H), 3.53 (dd, $J_1 = 8.0$, $J_2 = 7.0$ Hz, 1H), 2.97 (dd, $J_1 = 13.6$, $J_2 = 8.1$ Hz, 1H), 2.90-2.59 (m, 9H), 2.65 (s, 8H), 1.40 (s, 36H), 1.32 (s, 9H).

^{13}C NMR (75.4 MHz, CDCl_3 , 298 K): 171.9, 170.7, 138.9, 129.5, 128.0, 126.1, 80.8 (2C), 66.3, 56.1, 53.6, 50.4, 36.4, 28.2 (CH_3 , 2x*t*Bu). MS (ESI+) Calc.d for $\text{C}_{41}\text{H}_{69}\text{N}_3\text{O}_{10}$: 763.5. Found: m/z (100%) 764.3 $[\text{M}+\text{H}]^+$.



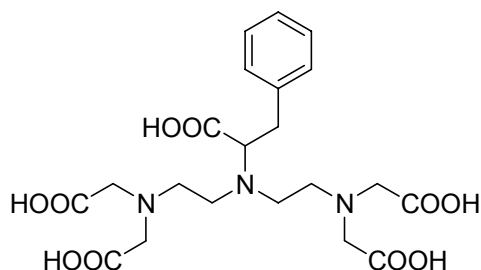
9a

Compound 9a

White gummy solid.

^1H NMR (300 MHz, D_2O , 298 K): 5.84 (ddt, $J_1 = 17.0$ Hz, $J_2 = 9.9$ Hz, $J_3 = 6.7$ Hz, 1H), 5.18 (d, $J = 17.2$ Hz, 1H), 5.11 (d, $J = 10.4$ Hz, 1H), 4.09 (s, 8H), 3.71 (t, $J = 7.0$ Hz, 1H), 3.48 (bt, $J = 6.1$ Hz, 4H), 3.17 (bt, $J = 6.2$ Hz, 4H), 2.61 (dt, $J_1 = 14.4$ Hz, $J_2 = 6.7$ Hz, 1H), 2.50 (dt, $J_1 = 14.7$ Hz, $J_2 = 6.8$ Hz, 1H).

^{13}C NMR (75.4 MHz, D_2O , 298 K): 173.9, 168.2, 132.9, 117.4, 61.6, 54.6, 52.2, 45.2, 31.4. MS (ESI+) Calc.d for $\text{C}_{17}\text{H}_{27}\text{N}_3\text{O}_{10}$: 433.2. Found: m/z (100%) 434.3 $[\text{M}+\text{H}]^+$.



9b

Compound 9b

White powder. (200 mg) M.p. 195-197 °C.

^1H NMR (300 MHz, CD_3OD , 298 K): 7.37 (d, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.23 (bt, 1H), 4.53 (bt, $J = 6.7$ Hz, 1H), 3.71 (s, 8H), 3.44-3.15 (m, 10H).

^{13}C NMR (75.4 MHz, CD_3OD , 298 K): 172.1, 170.7, 136.6, 129.2, 128.4, 126.8, 66.0, 54.5, 50.7, 50.1, 33.6. MS (ESI+) Calc.d for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_{10}$: 483.2. Found: m/z (100%) 482.2 $[\text{M}-\text{H}]^-$.