Malonic acid mono-2-bromoethyl ester (4): A solution of Meldrum's acid (2.03 g, 14.1 mmol) and 2-bromoethanol (1.00 mL, 14.1 mmol) in 10 mL of dry toluene was refluxed for two hours. The reaction mixture was washed with a saturated solution of NaHCO₃ (20 ml). The aqueous phase was acidified with conc. HCl and extracted twice with diethyl ether (20 mL). After drying over MgSO₄, evaporation of the solvent and drying under high vacuum was obtained as a pale yellow oil (1.78 g, 8.41 mmol, 60%). ¹H-NMR (400 MHz, RT, CDCl₃): δ = 11.02 (s, br, 1H, COOH), 4.46 (t, 3J = 6.1 Hz, 2H, OCH₂), 3.51 (t, 3J = 6.1 Hz, 2H, BrCH₂), 3.48 (s, 2H, OCC₂H₂CO) ppm. ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 171.54 (1C, COOH), 165.88 (1C, CO), 64.84 (1C, OCH₂), 40.72 (1C, OCCH₂CO), 27.87 (1C, BrCH₂) ppm. MS (FAB, NBA): m/z = 211 [M+H]⁺. C₅H₇BrO₄: calcd. C 28.46, H 3.34, Br 37.87, O 30.33; found C 28.39, H 3.44.

Malonate precursor 16: ¹H-NMR (400 MHz, RT, CDCl₃): δ = 6.10 (s, br, 2H, NH), 4.51 (t, 3J = 6.3 Hz, 4H, OCH₂), 3.26 (s, 2H, OCC₂H₂CO), 2.07 (m, 16H, C₆H₂COOᵗBu, C₆H₂CO), 1.82 (m, 16H, NHC(CH₃)₃, OCH₂CH₂), 1.28 (s, 54H, C(CH₃)₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 172.57 (6C, COOᵗBu), 171.14 (2C, CONH), 166.43 (2C, CO), 80.13 (6C, C(CH₃)₃), 64.29 (2C, OCH₂), 57.09 (2C, NC(CH₃)₃), 41.05 (1C, OCCH₂CO), 32.74 (2C, CH₂CO), 29.44 (6C, CH₂COOᵗBu), 29.35 (6C, NHC(CH₃)₃), 24.17 (2C, OCH₂CH₂) ppm. MS (FAB, NBA): m/z = 1094 [M+Na]⁺, 1071 [M]⁺, 726 [M-6ᵗBu]⁺. C₅₅H₹₄N₂O₁₈: calcd. C 61.66, H 8.84, N 2.61, O 26.88; found: C 61.45, H 8.99, N 2.65.

Protected monoadduct 16: ¹H-NMR (400 MHz, RT, CDCl₃): δ = 6.23 (s, br, 2H, CONH), 4.54 (t, 3J = 6.5 Hz, 4H, OCH₂), 2.35 (t, 3J = 6.6 Hz, 4H, CH₂CO), 2.24 (m, 12H, CH₂COOᵗBu), 2.19 (m, 4H, OCH₂CH₂), 1.99 (m, 12H, NHC(CH₃)₃), 1.44 (s, 54H, C(CH₃)₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 172.80 (6C, COOᵗBu), 170.91 (2C, CONH), 163.58 (2C, CO), 145.25, 145.18, 145.15, 145.11, 144.87, 144.65, 144.62, 144.59, 143.85, 143.07, 142.98, 142.95, 142.16, 141.83, 140.95, 138.99 (58C, C₆₀-sp²), 80.60 (6C, C(CH₃)₃), 71.44 (2C, C₆₀-sp³), 66.63 (2C, OCH₂), 57.54 (2C, NHC(CH₂)₃), 51.96 (1C, OCCCÖ), 33.03 (2C, CH₂CO), 29.88 (6C, CH₂COOᵗBu), 29.78 (6C, NHC(CH₂)₃), 28.06 (18C, C(CH₃)₃), 24.50 (2C, OCH₂CH₂) ppm. MS (FAB, NBA): m/z = 1790 [M⁺], 720 [C₆₀⁺]. UV/Vis (CH₂Cl₂): λₘₐₓ = 258, 325, 425, 496 nm.

Deprotected monoadduct 16: ¹H-NMR (400 MHz, RT, THF-d₈): δ = 9.41 (s, br, 6H, COOH), 6.81 (s, br, 2H, CONH), 4.54 (t, 3J = 6.6 Hz, 4H, OCH₂), 2.40 (t, 3J = 6.5 Hz, 4H, CH₂CO), 2.26 (m, 12H, CH₂COOH), 2.13 (m, 4H, OCH₂CH₂), 2.02 (m, 12H, NHC(CH₂)₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 175.22 (6C, COOH), 172.23 (2C, CONH), 164.16 (2C, CO), 147.11, 146.49, 146.35, 146.26, 145.96, 145.80, 145.66, 145.06, 143.85,
144.19, 144.12, 144.09, 143.19, 143.13, 141.99, 140.43 (58C, C\textsubscript{60}-sp\textsuperscript{2}), 73.27 (2C, C\textsubscript{60}-sp\textsuperscript{3}), 68.21 (2C, OCH\textsubscript{2}), 58.14 (2C, NHC(CH\textsubscript{2})\textsubscript{3}), 53.95 (1C, OCCCCO), 33.30 (2C, CH\textsubscript{2}CO), 30.56 (6C, CH\textsubscript{2}COOH), 28.86 (6C, NHC(CH\textsubscript{2})\textsubscript{3}), 24.98 (2C, OCH\textsubscript{2}CH\textsubscript{2}) ppm. MS (FAB, NBA): m/z = 1453 [M]+, 720 [C\textsubscript{60}]\textsuperscript{+}. UV/Vis (DMSO): \(\lambda_{\text{max}} = 254, 322, 424\) nm.

2-((hexyloxy)carbonyl)acetic acid (20): A mixture of 1-hexanol (1.42 g, 13.9 mmol) and meldrum’s acid (2 g, 13.9 mmol) was heated at 115 °C under vigorous stirring for 3 h. After cooling to room temperature, the product was washed with pentane (3 x 25 ml) and dried in vacuum to afford 20 as a white solid (2.54 g, 13.5 mmol, 97 %). \(^1\)H-NMR (300 MHz, RT, CDCl\textsubscript{3}): \(\delta = 11.30\) (s, br, 1H, COO\textsubscript{H}), 4.08 (t, \(^3\)J = 6.8 Hz, 2H, OCH\textsubscript{2}), 3.36 (s, 2H, OCC\textsubscript{H2}CO), 1.57 (m, 2H, CH\textsubscript{2}), 1.22 (m, 6H, CH\textsubscript{2}), 0.80 (t, \(^3\)J = 6.9 Hz, 3H, CH\textsubscript{3}) ppm; \(^13\)C-NMR (75 MHz, RT, CDCl\textsubscript{3}): \(\delta = 171.53\) (1C, C\textsubscript{O}), 166.57 (1C, C\textsubscript{O}), 65.72 (1C, O\textsubscript{C}H2), 40.78 (1C, OC\textsubscript{C}H2CO), 31.06, 28.06, 25.12, 22.21 (4C, CH\textsubscript{2}), 13.63 (1C, C\textsubscript{H3}) ppm. MS (FAB, NBA): m/z = 189 [M+H]+. C\textsubscript{9}H\textsubscript{16}O\textsubscript{4}: calcd. C 57.43, H 8.57, O 34.00; found C 57.09, H 8.63.

2-((octadecyloxy)carbonyl)acetic acid) (21): Prepared as described for compound 20 from 1-Octadecanol (4.69 g, 17.3 mmol) and meldrum’s acid (2.5 g, 17.3 mmol). (6.11 g, 17.1 mmol, 99 %, white solid). \(^1\)H-NMR (300 MHz, RT, CDCl\textsubscript{3}): \(\delta = 10.08\) (s, br, 1H, COO\textsubscript{H}), 4.18 (t, \(^3\)J = 6.8 Hz, 2H, OCH\textsubscript{2}), 3.44 (s, 2H, OCC\textsubscript{H2}CO), 1.66 (m, 2H, CH\textsubscript{2}), 1.26 (m, 30H, CH\textsubscript{2}), 0.88 (t, \(^3\)J = 6.8 Hz, 3H, CH\textsubscript{3}) ppm; \(^13\)C-NMR (75 MHz, RT, CDCl\textsubscript{3}): \(\delta = 170.65\) (1C, CO), 167.34 (1C, CO), 66.22 (1C, OCH\textsubscript{2}CO), 40.47 (1C, OCH\textsubscript{2}CO), 31.91 (1C, CH\textsubscript{2}), 29.68 (5C, CH\textsubscript{2}), 29.65 (2C, CH\textsubscript{2}), 29.63, 29.55, 29.48, 29.35, 29.16, 28.36, 25.73, 22.68 (8C, CH\textsubscript{2}), 14.11 (1C, CH\textsubscript{3}) ppm. MS (FAB, NBA): m/z = 357 [M+H]+. C\textsubscript{21}H\textsubscript{40}O\textsubscript{4}: calcd. C 70.74, H 11.31, O 17.95; found C 70.55, H 11.59.

2-((heptadecan-9-yloxy)carbonyl)acetic acid (22): Prepared as described for compound 20 from heptadecan-9-ol (3 g, 11.7 mmol) and meldrum’s acid (1.69 g, 11.7 mmol). (3.85 g, 11.2 mmol, 96 %, white solid). \(^1\)H-NMR (300 MHz, RT, CDCl\textsubscript{3}): \(\delta = 9.01\) (s, br, 1H, COO\textsubscript{H}), 4.96 (quin, \(^3\)J = 6.7 Hz, 1H, OCH\textsubscript{2}), 3.42 (s, 2H, OCH\textsubscript{2}CO), 1.54 (m, 4H, CHCH\textsubscript{2}), 1.25 (m, 24H, CH\textsubscript{2}), 0.88 (t, \(^3\)J = 6.7 Hz, 6H, CH\textsubscript{3}) ppm; \(^13\)C-NMR (75 MHz, RT, CDCl\textsubscript{3}): \(\delta = 171.07\) (1C, CO), 167.08 (1C, CO), 76.78 (1C, CH), 40.70 (1C, OCH\textsubscript{2}CO), 33.85 (2C, CH\textsubscript{2}), 31.82 (2C, CH\textsubscript{2}), 29.42 (4C, CH\textsubscript{2}), 29.20, 25.15, 22.63 (6C, CH\textsubscript{2}), 14.09 (2C, CH\textsubscript{3}) ppm. MS (FAB, NBA): m/z = 343 [M+H]+. C\textsubscript{20}H\textsubscript{38}O\textsubscript{4}: calcd. C 70.74, H 11.18, O 18.68; found C 69.88, H 11.21.

6-(benzyloxy)hexanoic acid (23): Freshly crushed 85 % KOH (49.2 g, 0.745 mol) was added to a solution of benzyl bromide (120 g, 0.7 mol) and \(\varepsilon\)-caprolactone (20.06 g, 0.176 mol) in
300 mL toluene. The mixture was heated at reflux for 48 h using a Dean-Stark apparatus, then
diluted with 200 mL of Et₂O and washed with 300 mL of H₂O. The aqueous layer was
extracted twice with 200 mL Et₂O. The organic layers were concentrated in vacuum to 150
mL and were set aside. The aqueous layer was cooled in an ice bath and 2M H₂SO₄ (180 mL)
was added. The turbid aqueous solution was extracted with CH₂Cl₂ (3 x 200 mL), dried over
anhydrous MgSO₄ and concentrated in vacuum to afford 23 as a pale yellow oil. To the
residue of the toluene/Et₂O layers NaOH (16 g, 0.4 mol) and H₂O (80 mL) was added and the
resulting mixture was heated at reflux for 24 h. The aqueous layer was separated, diluted to
250 mL with H₂O and washed with Et₂O (3 x 100 mL). The aqueous layer was acidified with
a slurry of 25 mL conc. H₂SO₄ in 100 mL of ice and then extracted with CH₂Cl₂ (3 x 100
mL). The organic layers were dried over anhydrous MgSO₄ and the solvent was removed in
vacuum to afford 23 as a pale yellow oil. (36.3 g, 0.16 mmol, 92.7 %). ¹H-NMR (400 MHz,
RT, CDCl₃): δ = 10.41 (s, br, 1H, COO⁻H), 7.34 (m, 5H, arom. H), 4.51 (s, 2H, ArCH₂O), 3.48
(t, ³J = 6.5 Hz, 2H, OCH₂), 2.37 (t, ³J = 7.6 Hz, 2H, CH₂COOH), 1.66 (m, 4H, CH₂), 1.45 (m, 2H,
CH₂) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 179.02 (1C, COOH), 138.47 (1C, ArC),
128.31 (2C, ArC), 127.59 (2C, ArC), 127.47 (1C, ArC), 72.91 (1C, ArCH₂O), 70.06
(1C, OCH₂), 33.89 (1C, CH₂COOH), 29.42, 25.75, 24.54 (3C, CH₂). MS (FAB, NBA): m/z =

**tert-butyl 6-(benzyloxy)hexanoate (24):** A solution of 23 (30 g, 0.135 mol) in dry CH₂Cl₂
(30 mL) was treated with condensed isobutene (100 mL at -60°C) and H₂SO₄ (2 mL). The
resulting solution was stirred for three days at room temperature, then neutralized with a
solution of K₂CO₃ (25 g) in H₂O (300 mL). The organic layer was washed with K₂CO₃
(saturated solution), citric acid (10 wt % in H₂O), and H₂O. After the mixture was dried over
anhydrous MgSO₄, filtered, and concentrated, a pale yellow oil was obtained. (33.6 g, 0.12
mmol, 89.3 %). ¹H-NMR (400 MHz, RT, CDCl₃): δ = 7.34 (m, 5H, arom.H), 4.51 (s, 2H,
ArCH₂O), 3.48 (t, ³J = 6.6 Hz, 2H, OCH₂), 2.22 (t, ³J = 7.5 Hz, 2H, CH₂COO'tBu), 1.62 (m, 4H,
CH₂), 1.45 (s, 9H, C(CH₃)₃), 1.42 (m, 2H, CH₂) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 173.07 (1C, COO'tBu), 138.54 (1C, ArC), 128.28 (2C, ArC), 127.59 (2C, ArC), 127.47 (1C, ArC), 72.91 (1C, ArCH₂O), 70.06
(1C, OCH₂), 33.89 (1C, CH₂COOH), 29.42, 25.75, 24.54 (3C, CH₂). MS (FAB, NBA): m/z =

**tert-butyl 6-hydroxyhexanoate (25):** A solution of 24 (26 g, 93 mmol) in dry methanol (300
mL) was treated with 10% palladium on carbon (3 g) and H₂ at room temperature. After 48 h,
the suspension was filtered through Celite and concentrated under reduced pressure to give 25.
as an oily product in quantitative yield. (17.6 g, 93 mmol, 100 %). $^1$H-NMR (300 MHz, RT, CDCl$_3$): $\delta = 3.63$ (t, $^3J = 6.5$ Hz, 2H, HOCH$_2$), 2.22 (t, $^3J = 7.4$ Hz, 2H, CH$_2$COO'Bu), 1.81 (s, br, 1H, OCH$_3$), 1.58 (m, 4H, CH$_2$), 1.43 (s, 9H, C(CH$_3$)$_3$), 1.40 (m, 2H, CH$_2$) ppm; $^{13}$C-NMR (75 MHz, RT, CDCl$_3$): $\delta =$ 173.19 (1C, COO'Bu), 80.06 (1C, C(CH$_3$)$_3$), 62.54 (1C, HOCH$_2$), 35.41 (1C, CH$_2$COO'Bu), 32.29 (1C, CH$_2$CH$_2$OH), 28.05 (3C, C(CH$_3$)$_3$), 25.15, 24.68 (2C, CH$_2$). MS (FAB, NBA): $m/z = 188$ [M$^+$]. C$_{10}$H$_{20}$O$_3$: calcd. C 63.80, H 10.71, O 25.50; found: C 63.53, H 10.59.

5-(tert-butoxycarbonyl)pentyl hexyl malonate (26): A solution of 20 (1 g, 5.31 mmol) and 25 (1 g, 5.31 mmol) in dry CH$_2$Cl$_2$ (150 mL) was cooled to 0 °C under nitrogen atmosphere. DMAP (64.9 mg, 0.53 mmol) and DCC (1.1 g, 5.31 mmol) were added subsequently. After stirring the solution under N$_2$ for 1 h at 0 °C, it was left at room temperature for another 24 h. Progress of the reaction was monitored by TLC. After evaporation of the solvent, the resulting product was purified by flash column chromatography (SiO$_2$; hexane/ethyl acetate, 100:30). The purified material was dried in vacuum affording 26 as a colourless oil. (1.43 g, 3.98 mmol, 75 %). $^1$H-NMR (400 MHz, RT, CDCl$_3$): $\delta = 3.89$ (m, 4H, OCH$_2$), 3.12 (s, 2H, OCCH$_2$CO), 1.97 (t, $^3J = 7.5$ Hz, 2H, OCCH$_2$), 1.41 (m, 6H, CH$_2$), 1.20 (s, 9H, CH$_3$), 1.08 (m, 8H, CH$_2$), 0.66 (t, $^3J = 6.4$ Hz, 3H, CH$_3$) ppm; $^{13}$C-NMR (100.5 MHz, RT, CDCl$_3$): $\delta =$ 172.08 (1C, CO), 165.99 (2C, CO), 79.18 (1C, C(CH$_3$)$_3$), 64.81 (1C, OCH$_2$), 64.52 (1C, OCH$_2$), 40.89 (1C, OCCH$_2$CO), 34.59 (1C, CH$_2$CO), 30.78, 27.84, 27.60 (3C, CH$_2$), 27.38 (3C, C(CH$_3$)$_3$), 24.84, 24.70, 24.00, 21.88 (4C, CH$_2$), 13.29 (1C, CH$_3$) ppm. MS (FAB, NBA): $m/z = 358$ [M$^+$]. C$_{19}$H$_{34}$O$_6$: calcd. C 63.66, H 9.56, O 26.78; found: C 63.91, H 9.78.

5-(tert-butoxycarbonyl)pentyl octadecyl malonate (27): Prepared as described for compound 26 from 21 (3.79 g, 10.64 mmol), 25 (2.00 g, 10.64 mmol), DCC (2.20 g, 10.64 mmol) and DMAP (130 mg, 1.06 mmol). Purification was obtained by flash column chromatography (SiO$_2$; hexane/ethyl acetate, 60:15). (4.54 g, 8.62 mmol, 81 %, colourless oil). $^1$H-NMR (300 MHz, RT, CDCl$_3$): $\delta = 4.13$ (t, $^3J = 6.7$ Hz, 2H, OCH$_2$), 4.12 (t, $^3J = 6.8$ Hz, 2H, OCH$_2$), 3.35 (s, 2H, OCCH$_2$CO), 2.20 (t, $^3J = 7.4$ Hz, 2H, OCCH$_2$), 1.63 (m, 6H, CH$_2$), 1.43 (s, 9H, CH$_3$), 1.25 (m, 32H, CH$_2$), 0.87 (t, $^3J = 6.4$ Hz, 3H, CH$_3$) ppm; $^{13}$C-NMR (75 MHz, RT, CDCl$_3$): $\delta = 172.77$ (1C, CO), 166.57 (2C, CO), 80.00 (1C, C(CH$_3$)$_3$), 65.62 (1C, OCH$_2$), 65.27 (1C, OCH$_2$), 41.58 (1C, OCCH$_2$CO), 35.29 (1C, CH$_2$CO), 31.88, 29.65, 29.61, 29.53, 29.47, 29.31, 29.16, 28.42, 28.15 (15C, CH$_2$), 28.05 (3C, C(CH$_3$)$_3$), 25.74, 25.27, 24.60, 22.64 (4C, CH$_2$), 14.06 (1C, CH$_3$) ppm. MS (FAB, NBA): $m/z = 527$ [M$^+$]. C$_{31}$H$_{58}$O$_6$: calcd. C 70.68, H 11.10, O 18.22; found: C 70.32, H 11.31.
5-(tert-butoxycarbonyl)pentyl heptadecan-9-yl malonate (28): Prepared as described for compound 26 from 22 (2.25 g, 6.57 mmol), 25 (1.24 g, 6.57 mmol), DCC (1.36 g, 6.57 mmol) and DMAP (81 mg, 0.66 mmol). Purification was obtained by flash column chromatography (SiO2; hexane/ethyl acetate, 90:12). (2.84 g, 5.39 mmol, 82 %). colourless oil. 1H-NMR (300 MHz, RT, CDCl3): δ = 4.91 (quin, 3J = 6.3 Hz, 1H, OCH), 4.14 (t, 3J = 6.7 Hz, 2H, OCH2), 3.35 (s, 2H, OCCO), 2.22 (t, 3J = 7.4 Hz, 2H, OCCH2), 1.64 (m, 6H, CH2), 1.55 (m, 2H, CH2), 1.45 (s, 9H, CH3), 1.26 (m, 26H, CH2), 0.81 (t, 3J = 6.6 Hz, 6H, CH3) ppm; 13C-NMR (75 MHz, RT, CDCl3): δ = 172.86 (1C, CO), 166.74 (1C, CO), 166.35 (1C, CO), 80.08 (1C, C(CH3)3), 75.97 (1C, CH), 65.28 (1C, OCH2CO), 41.94 (1C, OCH2CO), 35.33 (1C, CH2CO), 33.93 (2C, CH2), 31.84, 29.48, 29.47, 29.23, 28.20 (9C, CH2), 28.09 (3C, C(CH3)3), 25.30, 25.18 (3C, CH2), 24.65 (1C, CH2CH2CO), 22.65 (2C, CH2CH3), 14.10 (2C, CH3) ppm. MS (FAB, NBA): m/z = 512 [M]+. C30H56O6: calcd. C 70.27, H 11.01, O 18.72; found: C 69.89, H 11.10.

6-(2-((hexyloxy)carbonyl)acetoyloxy)hexanoic acid (29): Trifluoroacetic acid (2.4 mL, 31.0 mmol) was added to a solution of 26 (1.1 g, 3.07 mmol) in CH2Cl2 (50 mL). The reaction mixture was stirred for 12 h at room temperature and the progress of the reaction was monitored by TLC. The reaction mixture was concentrated and dried in vacuum to afford 29 as a white solid. (919 mg, 3.04 mmol, 99 %). 1H-NMR (400 MHz, RT, CDCl3): δ = 7.91 (s, br, 1H, COOH), 4.15 (t, 3J = 6.7 Hz, 2H, OCH2), 4.14 (t, 3J = 6.8 Hz, 2H, OCH2), 3.38 (s, 2H, OCCH2CO), 2.37 (t, 3J = 7.4 Hz, 2H, OCCH2), 1.65 (m, 6H, CH2), 1.43 (m, 2H, CH2), 1.30 (m, 6H, CH2), 0.89 (t, 3J = 6.9 Hz, 3H, CH3) ppm; 13C-NMR (100.5 MHz, CDCl3, RT): δ = 179.42 (1C, CO), 166.75 (1C, CO), 166.72 (1C, CO), 65.74 (1C, OCH2), 65.23 (1C, OCH2), 41.58 (1C, OCH2CO), 33.76 (1C, CH2CO), 31.32, 28.36, 28.07, 25.40, 25.24, 24.15, 22.48 (7C, CH2), 13.94 (1C, CH3) ppm. MS (FAB, NBA): m/z = 303 [M+H]+. C15H26O6: calcd. C 59.58, H 8.67, O 31.75. found: C 59.17, H 8.96.

6-(2-((octadecyloxy)carbonyl)acetoyloxy)hexanoic acid (30): Prepared as described for compound 29 from 27 (2.00 g, 3.80 mmol) and trifluoroacetic acid (2.9 mL, 38.0 mmol). (1.77 g, 3.76 mmol, 99 %, white solid). 1H-NMR (300 MHz, RT, CDCl3): δ = 10.10 (s, br, 1H, COOH), 4.15 (t, 3J = 6.6 Hz, 2H, OCH2), 4.13 (t, 3J = 6.7 Hz, 2H, OCH2), 3.37 (s, 2H, OCCH2CO), 2.37 (t, 3J = 7.4 Hz, 2H, OCCH2), 1.66 (m, 6H, CH2), 1.42 (m, 2H, CH2), 1.26 (m, 30H, CH2), 0.87 (t, 3J = 6.7 Hz, 3H, CH3) ppm; 13C-NMR (75 MHz, RT, CDCl3): δ = 179.49 (1C, CO), 166.66 (1C, CO), 166.65 (1C, CO), 65.71 (1C, OCH2), 65.19 (1C, OCH2), 41.58 (1C, OCH2CO), 33.77 (1C, CH2CO), 31.90, 29.67, 29.65, 29.64, 29.62, 29.56, 29.49, 29.34, 29.19, 28.43, 28.10, 25.76, 25.26 (17C, CH2), 24.17 (1C, CH2CH2CO), 22.67 (1C,
6-(2-((heptadecan-9-yloxy)carbonyl)acetoyloxy)hexanoic acid (31): Prepared as described for compound 29 from 28 (2.00 g, 3.80 mmol) and trifluoroacetic acid (2.9 mL, 38.0 mmol). (1.70 g, 3.72 mmol, 98 %, white solid). 1H-NMR (300 MHz, RT, CDCl 3): δ = 10.82 (s, br, 1H, COOH), 4.91 (quin, 3J = 6.3 Hz, 1H, OCH2), 4.15 (t, 3J = 6.7 Hz, 2H, OCH2), 3.36 (s, 2H, OCCH2CO), 2.37 (t, 3J = 7.4 Hz, 2H, OCCH2H), 1.68 (m, 4H, CH(CH2)2), 1.53 (m, 4H, CH2), 1.43 (m, 2H, CH2), 1.26 (m, 24H, CH2), 0.88 (t, 3J = 6.8 Hz, 6H, CH3) ppm; 13C-NMR (75 MHz, RT, CDCl3): δ = 178.90 (1C, CO), 166.75 (1C, CO), 166.38 (1C, CO), 76.03 (1C, CH2), 65.14 (1C, OCH2), 41.93 (1C, OCCH2CO), 33.93 (2C, CH(CH2)2), 33.68 (1C, CH2CO), 31.84, 29.49, 29.48, 29.23, 28.14, 25.27, 25.19 (12C, CH2), 24.20 (1C, CH2CH2CO), 22.65 (2C, CH2CH3), 14.09 (2C, CH3) ppm. MS (FAB, NBA): m/z = 458 [M+H]+. C26H48O6: calcd. C 68.38, H 10.59, O 21.02; found: C 68.36, H 10.80.

asymmetric malonate (G1) 37: Prepared as described for compound 36 from 30 (1.5 g, 3.19 mmol), 32 (1.32 g, 3.19 mmol), DMAP (78 mg, 0.64 mmol), 1-HOBt (431 mg, 3.19 mmol) and EDC (673 mg, 3.51 mmol). Purification was obtained by flash column chromatography (SiO2, hexane/ethyl acetate, 15:10). (1.88 g, 2.17 mmol, 68 %, colourless oil). 1H-NMR (300 MHz, RT, CDCl3): δ = 5.90 (s, br, 1H, CONH), 4.13 (t, 3J = 6.6 Hz, 2H, OCH2), 4.12 (t, 3J = 6.8 Hz, 2H, OCH2), 3.36 (s, 2H, OCCH2CO), 2.22 (t, 3J = 7.7 Hz, 6H, CH2COO' Bu), 2.11 (t, 3J = 7.4 Hz, 2H, OCCH2H), 1.95 (t, 3J = 7.8 Hz, 6H, NHC(CH2)3), 1.63 (m, 6H, CH2), 1.43 (s, 27H, C(CH3)3), 1.25 (m, 32H, CH2), 0.87 (t, 3J = 6.7 Hz, 3H, CH3) ppm; 13C-NMR (75 MHz, RT, CDCl3): δ = 172.87 (3C, COO' Bu), 172.07 (1C, CONH), 166.66 (1C, CO), 166.61 (1C, CO), 80.63 (3C, C(CH3)3), 65.67 (1C, OCH2), 65.28 (1C, OCH2), 57.28 (1C, NHC(CH2)3), 41.56 (1C, OCCH2CO), 37.22 (1C, CH2CO), 31.89 (1C, CH2), 29.94 (3C, NHC(CH2)3), 29.79 (3C, CH2COO' Bu), 29.66, 29.64, 29.62, 29.55, 29.48, 29.33, 29.18, 28.43, 28.18 (14C, CH2), 28.03 (9C, C(CH3)3), 25.75 (1C, CH2), 25.48 (1C, CH2CH2CO), 25.23, 22.65 (2C, CH2), 14.09 (1C, CH3) ppm. MS (FAB, NBA): m/z = 868 [M]+, 696 [M-3Bu]+. C49H89NO11: calced. C 67.78, H 10.33, N 1.61, O 20.27; found: C 67.93, H 10.58, N 1.64.

asymmetric malonate (G1) 38: Prepared as described for compound 36 from 31 (1 g, 2.19 mmol), 32 (0.91 g, 2.19 mmol), DMAP (54 mg, 0.44 mmol), 1-HOBt (296 mg, 2.19 mmol) and EDC (462 mg, 2.41 mmol). Purification was obtained by flash column chromatography (SiO2, hexane/ethyl acetate, 20:10 to 15:10). (1.20 g, 1.40 mmol, 64 %, colourless oil). 1H-NMR (400 MHz, RT, CDCl3): δ = 5.91 (s, br, 1H, CONH), 4.91 (quin, 3J = 6.2 Hz, 1H, OCH), 4.13 (t, 3J = 6.7 Hz, 2H, OCH2), 3.36 (s, 2H, OCCH2CO), 2.22 (t, 3J = 7.8 Hz, 6H,
CH$_2$COO'Bu), 2.11 (t, $^3J = 7.6$ Hz, 2H, OCCH$_2$), 1.97 (t, $^3J = 7.9$ Hz, 6H, NHC(CH$_3$)$_3$), 1.64 (m, 4H, CHCH$_2$), 1.52 (m, 2H, CH$_2$), 1.43 (s, 27H, C(CH$_3$)$_3$), 1.41 (m, 2H, CH$_2$), 1.26 (m, 26H, CH$_2$), 0.88 (t, $^3J = 6.8$ Hz, 6H, CH$_3$) ppm; $^{13}$C-NMR (100.5 MHz, RT, CDCl$_3$): δ = 173.40 (3C, COO'Bu), 172.59 (1C, CONH), 167.20 (1C, CO), 166.85 (1C, CO), 80.69 (3C, C(CH$_3$)$_3$), 75.96 (1C, CH), 65.19 (1C, OCH$_2$), 57.20 (1C, NH-C(CH$_2$)$_3$), 41.72 (1C, OCOCO'Bu), 37.04 (1C, CH$_2$CO), 33.70 (2C, CH(CCH$_2$)$_2$), 31.61, 30.04 (3C, CH$_2$), 29.43, 29.24, 29.22, 28.98, 27.98 (6C, CH$_2$), 27.80 (9C, C(CH$_3$)$_3$), 25.26 (1C, CH$_2$CH$_2$CO), 25.00, 24.91, 22.37 (5C, CH$_2$), 13.78 (2C, CH$_3$) ppm. MS (FAB, NBA): $m/z = 854$ [M]$^+$, 682 [M-3tBu]$^+$. C$_{48}$H$_{87}$NO$_{11}$: calcd. C 67.49, H 10.27, N 1.64, O 20.60; found: C 67.20, H 10.17, N 1.64.

**asymmetric malonate (G2) 39:** A solution of 29 (330 mg, 1.09 mmol) and 34 (1.57 g, 1.09 mmol) in dry CH$_2$Cl$_2$/THF = 1/1 (200 mL) was cooled to 0 °C under nitrogen atmosphere. DMAP (27 mg, 0.22 mmol), 1-HOBt (147 mg, 1.09 mmol) and EDC (230 mg, 1.20 mmol) were added subsequently. After stirring the solution under N$_2$ for 2 h at 0 °C, it was left at room temperature for another 48 h. Progress of the reaction was monitored by TLC. The organic phase was washed with water (2 x 150 mL) and dried over MgSO$_4$. After evaporation of the solvent, the resulting product was purified by flash column chromatography (SiO$_2$, hexane/ethyl acetate, 10:10 to 10:15). The purified material was dried in vacuum affording 39 as a colourless oil. (1.38 g, 0.80 mmol, 73 %). $^1$H-NMR (400 MHz, RT, CDCl$_3$): δ = 7.50 (s, br, 1H, CONH), 6.15 (s, br, 3H, CONH), 3.98 (t, $^3J = 6.5$ Hz, 2H, OCH$_2$), 3.96 (t, $^3J = 6.7$ Hz, 2H, OCH$_2$), 3.24 (s, 2H, OCCH$_2$CO), 2.06 (m, 26H, CH$_2$COO'Bu, OCCH$_2$), 1.81 (m, 24H, NHC(CH$_3$)$_3$), 1.50 (m, 6H, CH$_2$), 1.38 (m, 2H, CH$_2$), 1.30 (m, 83H, C(CH$_3$)$_3$, CH$_2$), 1.17 (m, 4H, CH$_2$), 0.71 (t, $^3J = 6.8$ Hz, 3H, CH$_3$) ppm; $^{13}$C-NMR (100.5 MHz, RT, CDCl$_3$): δ = 172.87 (1C, CONH), 172.75 (3C, CONH), 172.32 (9C, COO'Bu), 166.38 (1C, CO), 166.35 (1C, CO), 80.09 (9C, C(CH$_3$)), 65.27 (1C, OCH$_2$), 65.04 (1C, OCH$_2$), 57.24 (1C, NHC(CH$_3$)$_3$), 57.07 (3C, NHC(CH$_3$)$_3$), 41.23 (1C, OCCH$_2$CO), 36.76 (1C, CH$_2$CO), 31.53 (3C, NHC(CH$_3$)$_3$), 31.34 (3C, CH$_3$CON), 31.06 (1C, CH$_2$), 29.49 (9C, NHC(CH$_3$)$_3$), 29.37 (9C, CH$_2$COO'Bu), 28.73, 28.54 (2C, CH$_2$), 27.72 (27C, C(CH$_3$)$_3$), 25.27, 25.15 (2C, CH$_2$), 24.97 (1C, CH$_2$CH$_2$CO), 22.27 (1C, CH$_2$), 13.85 (1C, CH$_3$) ppm. MS (FAB, NBA): $m/z = 1724$ [M]$^+$. C$_{48}$H$_{87}$N$_4$O$_{26}$: calcd. C 63.39, H 9.24, N 3.25, O 24.13; found: C 63.01, H 8.98, N 3.38.

**asymmetric malonate (G2) 40:** Prepared as described for compound 39 from 30 (500 mg, 1.06 mmol), 34 (1.53 g, 1.06 mmol), DMAP (30 mg, 0.21 mmol), 1-HOBt (143 mg, 1.06 mmol) and EDC (224 mg, 1.17 mmol). Purification was obtained by flash column
chromatography (SiO₂, hexane/ethyl acetate, 20:10 to 13:10). (1.48 g, 0.78 mmol, 74 %, colourless oil). ¹H-NMR (400 MHz, RT, CDCl₃): δ = 7.61 (s, br, 1H, CONH), 6.09 (s, br, 3H, CONH), 4.05 (t, 3J = 6.6 Hz, 2H, OCH₂), 4.03 (t, 3J = 6.6 Hz, 2H, OCH₂), 3.27 (s, 2H, OCH₂), 2.09 (m, 26H, C₂H₂COO₂Bu, OCH₂), 1.84 (m, 24H, NHC(CH₂)₃), 1.54 (m, 6H, CH₂), 1.33 (m, 83H, C(C₃H₃)₃, CH₃), 1.15 (m, 30H, C₂H₂), 0.77 (t, 3J = 6.6 Hz, 3H, CH₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 172.88 (1C, CONH), 172.38 (9C, COO₂Bu), 166.46 (1C, CO), 166.43 (1C, CO), 80.25 (9C, C(CH₃)₃), 65.39 (1C, OCH₂), 65.13 (1C, OCH₂), 57.26 (1C, NHC(CH₂)₃), 57.16 (3C, NHC(CH₂)₃), 41.30 (1C, OC₂H₂CO), 36.85 (1C, CH₂CO), 31.65 (4C, NHC(CH₂)₃, CH₂), 31.47 (3C, CH₂CON), 29.54 (1C, CH₂), 29.52 (9C, NHC(CH₂)₃), 29.42 (9C, CH₂COO₂Bu), 29.41, 29.38, 29.32, 29.25, 29.09, 28.96, 28.21, 27.99 (13C, CH₂), 27.83 (27C, C(CH₃)₃), 25.53 (1C, CH₂), 25.32 (1C, CH₂CH₂CO), 25.02, 22.42 (2C, CH₂), 13.88 (1C, CH₃) ppm. MS (FAB, NBA): m/z = 1892 [M]+.


asymmetric malonate (G2) 41: Prepared as described for compound 39 from 31 (350 mg, 0.77 mmol), 34 (1.10 g, 0.77 mmol), DMAP (19 mg, 0.15 mmol), 1-HOBt (104 mg, 0.77 mmol) and EDC (162 mg, 0.85 mmol). Purification was obtained by flash column chromatography (SiO₂, hexane/ethyl acetate, 13:10 to 10:10). (998 mg, 0.53 mmol, 69 %, colourless oil). ¹H-NMR (400 MHz, RT, CDCl₃): δ = 7.57 (s, br, 1H, CONH), 6.09 (s, br, 3H, CONH), 4.84 (quin, 3J = 6.3 Hz, 1H, CHJ), 4.08 (t, 3J = 6.7 Hz, 2H, OCH₂), 3.29 (s, 2H, OCH₂CO), 2.13 (m, 26H, CH₂COO₂Bu, OCH₂), 1.84 (m, 24H, NHC(CH₂)₃), 1.60 (m, 4H, CH(CH₂)₂), 1.46 (m, 4H, CH₂), 1.37 (m, 83H, C(CH₃)₃, CH₂), 1.15 (m, 30H, C₂H₂), 0.81 (t, 3J = 6.8 Hz, 6H, CH₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 173.11 (1C, CONH), 172.90 (3C, CONH), 172.64 (9C, COO₂Bu), 166.75 (1C, CO), 166.36 (1C, CO), 80.40 (9C, C(CH₃)₃), 75.72 (1C, CH), 65.18 (1C, OCH₂), 57.28 (1C, NHC(CH₂)₃), 57.23 (3C, NHC(CH₂)₃), 41.64 (1C, OC₂H₂CO), 36.88 (1C, CH₂CO), 33.70 (2C, CH₂), 31.66 (3C, NHC(CH₂)₃), 31.62 (2C, CH₂), 31.53 (3C, CH₂CON), 29.55 (6C, NHC(CH₂)₃), 29.56 (9C, CH₂COO₂Bu), 29.25, 29.23, 29.00, 28.06 (7C, CH₂), 27.85 (27C, C(CH₃)₃), 25.36 (1C, CH₂CH₂CO), 25.02, 24.94, 22.41 (5C, CH₂), 13.87 (2C, CH₃) ppm. MS (FAB, NBA): m/z = 1878 [M]+. C₁₀₂H₁₈₀N₄O₂₆: calcd. C 65.22, H 9.66, N 2.98, O 22.14; found: C 64.83, H 9.77, N 3.10.

C₆₀ monoadduct 43: Prepared as described for compound 42 from 37 (500 mg, 0.58 mmol), C₆₀ (498 mg, 0.69 mmol), CBr₄ (212 mg, 0.64 mmol) and DBU (96 μL, 0.64 mmol). Purification was obtained by flash column chromatography (SiO₂, toluene/ethyl acetate, 80:10 to 80:15). (488 mg, 0.31 mmol, 53 %, red brownish solid). ¹H-NMR (400 MHz, RT, CDCl₃):
δ = 5.90 (s, br, 1H, CONH), 4.50 (t, 3 J = 6.6 Hz, 2H, OCH2), 4.49 (t, 3 J = 6.7 Hz, 2H, OCH2), 2.22 (t, 3 J = 7.8 Hz, 6H, CH2COO'Bu), 2.13 (t, 3 J = 7.6 Hz, 2H, OCCH2), 1.98 (t, 3 J = 7.8 Hz, 6H, NHC(CH2)), 1.85 (m, 4H, OCH2CH2), 1.70 (m, 2H, CH2), 1.44 (s, 27H, (CH3)3), 1.25 (m, 32H, C60-sp3), 0.88 (t, 3 J = 6.8 Hz, 3H, CH3) ppm; 13C-NMR (100.5 MHz, RT, CDCl3): δ = 172.88 (3C, COO'Bu), 171.96 (1C, CONH), 163.67 (1C, CO), 163.59 (1C, CO), 145.37, 145.33, 145.25, 145.16, 145.14, 144.67, 144.63, 144.59, 143.86, 143.09, 143.06, 143.07, 143.00, 142.97, 142.19, 141.88, 140.93, 138.98, 138.93 (58C, C60-sp2), 80.69 (3C, C(CH3)3), 71.65 (2C, C60-sp3), 67.50 (1C, OCH2), 67.13 (1C, OCH2), 57.34 (1C, NHC(CH2)), 49.87 (1C, OCCO), 37.22 (1C, CH2CO), 31.92 (1C, CH2), 30.00 (3C, NHC(CH2)), 29.83 (3C, CH2COO'Bu), 29.72, 29.70, 29.67, 29.62, 29.37, 29.22, 28.60, 28.35 (14C, CH2), 28.06 (9C, C(CH3)3), 26.00 (1C, CH2), 25.64 (1C, CH2COCH2), 25.24, 22.69 (2C, CH2), 14.14 (1C, CH3) ppm. MS (FAB, NBA): m/z = 1610 [M+Na]+, 1587 [M]+, 720 [C60]+. UV/Vis (CH2Cl2): λmax = 254, 323, 425, 475 nm.

C60 monoadduct 44: Prepared as described for compound 42 from 38 (300 mg, 0.35 mmol), C60 (304 mg, 0.42 mmol), CBr4 (130 mg, 0.39 mmol) and DBU (59 μL, 0.39 mmol). Purification was obtained by flash column chromatography (SiO2, toluene/ethyl acetate, 90:10 to 70:10). (310 mg, 0.20 mmol, 56% , red brownish solid). 1H-NMR (400 MHz, RT, CDCl3): δ = 5.89 (s, br, 1H, CONH), 5.25 (m, 1H, OCH2), 4.48 (t, 3 J = 6.8 Hz, 2H, OCH2), 2.22 (t, 3 J = 7.8 Hz, 6H, CH2COO'Bu), 2.13 (t, 3 J = 7.7 Hz, 2H, OCCH2), 1.97 (t, 3 J = 7.8 Hz, 6H, NHC(CH2)), 1.87 (m, 2H, CH2), 1.78 (m, 2H, CH2), 1.68 (m, 6H, CHCH2, CH2), 1.44 (m, 29H, C(CH3)3, CH2), 1.27 (m, 22H, CH2), 0.88 (t, 3 J = 6.8 Hz, 6H, CH3) ppm; 13C-NMR (100.5 MHz, RT, CDCl3): δ = 173.01 (3C, COO'Bu), 172.08 (1C, CONH), 163.70 (1C, CO), 163.29 (1C, CO), 145.61, 145.46, 145.33, 145.25, 144.93, 144.77, 144.75, 144.65, 143.95, 143.94, 143.18, 143.09, 143.05, 142.28, 141.98, 141.00, 139.11, 138.89 (58C, C60-sp3), 80.69 (3C, C(CH3)3), 78.56 (1C, CH), 71.79 (2C, C60-sp3), 67.12 (1C, OCH2), 57.31 (1C, NHC(CH2)), 52.74 (1C, OCCO), 37.16 (1C, CH2CO), 33.87 (2C, CH(CH2)), 31.83, 30.11 (3C, CH2), 29.92 (3C, NC(CH2)), 29.76 (3C, CH2COO'Bu), 29.63, 29.55, 29.48, 29.21, 28.35 (6C, CH2), 28.01 (9C, C(CH3)3), 25.59 (1C, CH2CH2CO), 25.32, 25.18, 22.60 (5C, CH2), 14.08 (2C, CH3) ppm. MS (FAB, NBA): m/z = 1596 [M+Na]+, 1573 [M]+, 720 [C60]+. UV/Vis (CH2Cl2): λmax = 254, 323, 425, 475 nm.

C60 monoadduct 45: Prepared as described for compound 42 from 39 (260 mg, 0.15 mmol), C60 (144 mg, 0.2 mmol), CBr4 (56 mg, 0.17 mmol) and DBU (25 μL, 0.17 mmol). Purification was obtained by flash column chromatography (SiO2, toluene/ethyl acetate, 30:10 to 15:10). (171 mg, 0.07 mmol, 47%, red brownish solid). 1H-NMR (400 MHz, RT, CDCl3):
δ = 7.57 (s, br, 1H, CONH), 6.14 (s, br, 3H, CONH), 4.50 (t, 3J = 6.5 Hz, 2H, OCH2), 4.49 (t, 3J = 6.4 Hz, 2H, OCH2), 2.19 (m, 26H, CH2COO′Bu, OCCH2), 1.95 (m, 24H, NH(C(H)3)), 1.84 (m, 4H, CH2), 1.69 (m, 2H, CH2), 1.47 (m, 2H, CH2), 1.44 (m, 83H, C(CH3), CH2), 1.26 (m, 4H, CH2), 0.85 (t, 3J = 6.7 Hz, 3H, CH3) ppm; 13C-NMR (100.5 MHz, RT, CDCl3): δ = 173.29 (1C, CONH), 173.15 (3C, CONH), 172.80 (9C, COO′Bu), 163.81 (1C, O), 163.74 (1C, CO), 145.67, 145.53, 145.43, 145.32, 145.26, 145.12, 144.95, 144.83, 144.76, 144.68, 144.65, 143.95, 143.91, 143.53, 143.13, 143.05, 142.26, 141.98, 141.00, 139.12, 139.03, 139.00 (58C, C60-sp2), 80.59 (9C, (CH3)), 71.65 (2C, C60-sp3), 67.47 (1C, OCH2), 67.33 (1C, OCH2), 57.58 (1C, NH(C(H)2)), 57.42 (3C, NH(C(H)2)), 52.36 (1C, OCCC0), 37.01 (1C, CH2CO), 31.68 (3C, NH(C(H)2)), 31.30 (3C, C(H)2CON), 30.75 (1C, CH2), 29.72 (9C, NH(C(H)2)), 29.61 (9C, CH2COO′Bu), 28.47, 28.32 (2C, CH2), 28.01 (27C, C(CH3)), 25.55, 25.23 (2C, CH2), 24.38 (1C, CH2CH2CO), 14.00 (1C, CH3) ppm. MS (FAB, NBA): m/z = 2466 [M+Na]+, 2443 [M]+, 720 [C60]+. UV/Vis (CH2Cl2): λmax = 254.5, 324, 424.5, 476 nm.

C60 monoadduct 46: Prepared as described for compound 42 from 40 (600 mg, 0.32 mmol), C60 (302 mg, 0.42 mmol), CBr4 (117 mg, 0.35 mmol) and DBU (52 μL, 0.35 mmol). Purification was obtained by flash column chromatography (SiO2, toluene/ethyl acetate, 70:20 to 70:50). (366 mg, 0.14 mmol, 44%, red brownish solid). 1H-NMR (400 MHz, RT, CDCl3): δ = 7.63 (s, br, 1H, CONH), 6.04 (s, br, 3H, CONH), 4.51 (t, 3J = 6.4 Hz, 2H, OCH2), 4.50 (t, 3J = 6.8 Hz, 2H, OCH2), 2.20 (m, 26H, CH2COO′Bu, OCCH2), 1.96 (m, 24H, NH(C(H)3)), 1.83 (m, 4H, CH2), 1.71 (m, 2H, CH2), 1.44 (m, 83H, C(CH3), CH2), 1.25 (m, 30H, CH2), 0.88 (t, 3J = 6.8 Hz, 3H, CH3) ppm; 13C-NMR (100.5 MHz, CDCl3, RT): δ = 173.07 (1C, CONH), 172.99 (3C, CONH), 172.77 (9C, COO′Bu), 163.75 (1C, CO), 163.68 (1C, CO), 145.48, 145.26, 145.19, 145.16, 145.11, 145.09, 144.80, 144.63, 144.62, 144.59, 144.55, 144.53, 143.83, 143.81, 143.02, 142.95, 142.93, 142.90, 142.15, 141.85, 141.85, 140.88, 139.16, 139.10, 138.75 (58C, sp2-C), 80.43 (9C, C(CH3)), 71.66 (2C, sp3-C), 67.44 (1C, OCH2), 67.32 (1C, OCH2), 57.57 (1C, NH(C(H)2)), 57.39 (3C, NH(C(H)2)), 52.42 (1C, OCCC0), 37.02 (1C, CH2CO), 31.84 (3C, NH(C(H)2)), 31.73 (1C, CH2), 31.63 (1C, CH2), 31.62 (3C, CH2CON), 29.74 (3C, CH2), 29.71 (9C, NH(C(H)2)), 29.64 (9C, CH2COO′Bu), 29.61, 29.59, 29.56, 29.55, 29.29, 29.27, 29.14, 28.53, 28.28 (9C, CH2), 28.02 (27C, C(CH3)), 27.97, 25.51 (2C, CH2), 25.23 (1C, CH2CH2CO), 24.84, 22.61 (2C, CH2), 14.04 (1C, CH3) ppm; MS (FAB, NBA): m/z = 2634 [M+Na]+, 2611 [M]+, 720 [C60]+. UV/Vis (CH2Cl2): λmax = 254.5, 324, 424.5, 476 nm.
**C₆₀ monoadduct 47:** Prepared as described for compound 42 from 41 (250 mg, 0.13 mmol), C₆₀ (122 mg, 0.17 mmol), CBr₄ (48 mg, 0.14 mmol) and DBU (22 μL, 0.14 mmol). Purification was obtained by flash column chromatography (SiO₂; toluene/ethyl acetate, 70:20 to 70:50). (159 mg, 0.06 mmol, 47 %, red brownish solid). ¹H-NMR (400 MHz, RT, CDCl₃): δ = 7.59 (s, br, 1H, CONH), 6.04 (s, br, 3H, CONH), 5.24 (quin, 3J = 6.4 Hz, 1H, CH), 4.48 (t, 3J = 7.1 Hz, 2H, OCH₂), 2.19 (m, 26H, C₂H₂COO-tBu, OCC₂H₂), 1.95 (m, 24H, NHC(C₂H₂)₃), 1.69 (m, 4H, CH(CH₂)₂), 1.59 (m, 4H, CH₂), 1.43 (m, 83H, C(CH₃)₃, CH₂), 1.25 (m, 24H, C₂H₂), 0.87 (t, 3J = 6.9 Hz, 6H, C₃H₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 172.82 (3C, CONH), 172.74 (1C, CONH), 172.62 (9C, COO-tBu), 163.54 (1C, O), 163.12 (1C, CO), 145.62, 145.36, 145.24, 145.20, 145.15, 145.13, 145.10, 144.80, 144.68, 144.64, 144.56, 144.53, 143.82, 143.82, 142.98, 142.92, 142.94, 142.91, 142.17, 141.86, 140.89, 139.10, 138.72 (58C, sp²-C), 80.55 (9C, (CH₃)₃), 77.20 (1C, C₂H), 67.32 (1C, OCH₂), 57.42 (3C, NHC(C₂H₂)₃), 57.38 (1C, NHC(C₂H₂)₃), 49.08 (1C, OCOBu), 37.02 (1C, C₂H₂CO), 33.91 (2C, C₂H₂), 31.88 (2C, CH₂), 31.85 (3C, NHC(C₂H₂)₃), 31.70 (3C, CH₂COO-tBu), 29.79, 29.76 (9C, CH₂COO-tBu), 29.65, 29.57, 29.48, 29.23, 28.44 (8C, CH₂), 28.07 (27C, C(CH₃)₃), 25.58 (1C, CH₂CH₂CO), 25.34, 24.91, 22.64 (6C, CH₂), 14.13 (2C, CH₃) ppm; MS (FAB, NBA): m/z = 2620 [M+Na]⁺, 2597 [M⁺], 720 [C₆₀⁺]. UV/Vis (CH₂Cl₂): λmax = 254.5, 324, 424.5, 476 nm.

**C₆₀ monoadduct 49:** Prepared as described for compound 48 from 43 (300 mg, 0.19 mmol) and formic acid (25 mL). Purification was obtained by reprecipitation from MeOH/Et₂O. (259 mg, 0.18 mmol, 96 %). ¹H-NMR (400 MHz, RT, DMSO-d₆): δ = 12.05 (s, br, 3H, COO⁻H), 7.14 (s, br, 1H, CONH), 4.39 (m, br, 4H, OCH₂), 2.09 (m, br, 8H, CH₂COOH, OCC₂H₂), 1.82 (m, br, 8H, NHC(CH₂)₃, CH₂), 1.51 (m, br, 4H, OCH₂CH₂), 1.36 (m, br, 32H, CH₂), 0.85 (m, br, 3H, CH₃) ppm; ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 174.42 (3C, COOH), 171.81 (1C, CONH), 163.63 (1C, CO), 163.52 (1C, CO), 144.71, 144.13, 143.40, 142.53, 141.69, 141.30, 140.61, 140.35, 139.10, 138.85 (58C, C₆₀·sp²), 71.42 (2C, C₆₀·sp³), 67.12 (1C, OCH₂), 67.02 (1C, CH₂), 56.34 (1C, NHC(CH₂)₃), 52.32 (1C, OCCC₂O), 38.13 (1C, CH₂CO), 31.73 (1C, CH₂), 29.97 (3C, NHC(CH₂)₃), 29.88 (3C, CH₂COOH), 29.69, 29.70, 29.60, 29.62, 29.33, 29.28, 28.54, 28.37 (14C, CH₂), 25.99 (1C, CH₂), 25.42 (1C, CH₂CH₂CO), 25.06, 22.57 (2C, CH₂), 14.23 (1C, CH₃) ppm. MS (FAB, NBA): m/z = 1419 [M⁺], 720 [C₆₀⁺]. UV/Vis (CH₂Cl₂): λmax = 254.5, 324, 424.5 nm.

**C₆₀ monoadduct 50:** Prepared as described for compound 48 from 44 (250 mg, 0.16 mmol) and formic acid (25 mL). Purification was obtained by reprecipitation from MeOH/Et₂O. (218 mg, 0.16 mmol, 97 %). ¹H-NMR (400 MHz, RT, DMSO-d₆): δ = 11.89 (s, br, 3H, COO⁻H),
Supplementary material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2007

7.04 (s, br, 1H, CON\textsubscript{H}), 5.18 (m, br, 1H, OCH\textsubscript{H}), 4.41 (m, br, 2H, OCH\textsubscript{2}), 2.18 (m, br, 8H, CH\textsubscript{2}COOH, OCC\textsubscript{H}), 1.91 (m, br, 8H, NH(C(H\textsubscript{2})\textsubscript{3}, CH\textsubscript{2}), 1.65 (m, br, 8H, CHCH\textsubscript{2}, CH\textsubscript{2}), 1.41 (m, br, 2H, CH\textsubscript{2}), 1.21 (m, br, 22H, CH\textsubscript{2}), 0.85 (m, br, 6H, CH\textsubscript{3}) ppm; \textsuperscript{13}C-NMR (100.5 MHz, RT, DMSO-d\textsubscript{6}): \(\delta = 175.02 \) (3C, COOH), 172.00 (1C, CON\textsubscript{H}), 163.59 (1C, CO), 163.51 (1C, CO), 144.88, 144.76, 144.36, 144.01, 143.76, 143.35, 143.08, 142.28, 141.88, 141.00, 139.11, 138.79 (58C, C\textsubscript{60}-sp\textsuperscript{2}), 78.01 (1C, CH), 71.59 (2C, C\textsubscript{60}-sp\textsuperscript{3}), 67.54 (1C, OCH\textsubscript{2}), 56.69 (1C, NHCC(CH\textsubscript{2})\textsubscript{3}), 52.56 (1C, OCC\textsubscript{H}), 37.99 (1C, C\textsubscript{H}2CO), 33.98 (2C, CH(C\textsubscript{H}2)\textsubscript{2}), 31.89, 30.13 (3C, CH\textsubscript{2}), 29.89 (3C, NH(C(H\textsubscript{2})\textsubscript{3}), 29.71 (3C, C\textsubscript{2}COOH), 29.63, 29.48, 29.01, 28.37 (6C, CH\textsubscript{2}), 25.37, 22.60 (5C, CH\textsubscript{2}), 14.11 (2C, CH\textsubscript{3}) ppm. MS (FAB, NBA): \textit{m/z} = 1405 [M] \textsuperscript{+}, 720 [C\textsubscript{60}]\textsuperscript{+}. UV/Vis (DMSO): \(\lambda_{\text{max}} = 254, 323.5, 424.5 \) nm.

\textbf{C\textsubscript{60} monoadduct 51}: Prepared as described for compound 48 from 45 (150 mg, 0.06 mmol) and formic acid (35 mL). Purification was obtained by reprecipitation from MeOH/Et\textsubscript{2}O. (112 mg, 0.06 mmol, 97\%). \textsuperscript{1}H-NMR (400 MHz, RT, DMSO-d\textsubscript{6}): \(\delta = 12.01 \) (s, br, 9H, COO\textsubscript{H}), 8.05 (s, br, 1H, CON\textsubscript{H}), 7.16 (s, br, 3H, CON\textsubscript{H}), 4.51 (m, br, 4H, OCH\textsubscript{2}), 2.11 (m, br, 26H, CH\textsubscript{2}COOH, OCC\textsubscript{H}), 1.91 (m, br, 28H, NHC(CH\textsubscript{2})\textsubscript{3}, CH\textsubscript{2}), 1.51 (m, br, 6H, CH\textsubscript{2}), 1.26 (m, br, 4H, CH\textsubscript{2}), 0.84 (m, br, 3H, CH\textsubscript{3}) ppm. MS (FAB, NBA): \textit{m/z} = 1938 [M] \textsuperscript{+}, 720 [C\textsubscript{60}]\textsuperscript{+}. UV/Vis (DMSO): \(\lambda_{\text{max}} = 254, 324, 424.5 \) nm.

\textbf{C\textsubscript{60} monoadduct 52}: Prepared as described for compound 48 from 46 (300 mg, 0.11 mmol) and formic acid (50 mL). Purification was obtained by reprecipitation from MeOH/Et\textsubscript{2}O. (237 mg, 0.11 mmol, 98\%). \textsuperscript{1}H-NMR (400 MHz, RT, DMSO-d\textsubscript{6}): \(\delta = 12.03 \) (s, br, 9H, COO\textsubscript{H}), 8.12 (s, br, 1H, CON\textsubscript{H}), 7.20 (s, br, 3H, CON\textsubscript{H}), 4.46 (m, br, 4H, OCH\textsubscript{2}), 2.09 (m, br, 26H, CH\textsubscript{2}COOH, OCC\textsubscript{H}), 1.81 (m, br, 30H, NHC(CH\textsubscript{2})\textsubscript{3}, CH\textsubscript{2}), 1.21 (m, br, 32H, CH\textsubscript{2}), 0.82 (m, br, 3H, CH\textsubscript{3}) ppm. MS (FAB, NBA): \textit{m/z} = 2106 [M] \textsuperscript{+}, 720 [C\textsubscript{60}]\textsuperscript{+}. UV/Vis (DMSO): \(\lambda_{\text{max}} = 254, 324, 424.5 \) nm.

\textbf{C\textsubscript{60} monoadduct 53}: Prepared as described for compound 48 from 47 (150 mg, 0.06 mmol) and formic acid (35 mL). Purification was obtained by reprecipitation from MeOH/Et\textsubscript{2}O. (117 mg, 0.06 mmol, 97\%). \textsuperscript{1}H-NMR (400 MHz, RT, DMSO-d\textsubscript{6}): \(\delta = 12.11 \) (s, br, 9H, COO\textsubscript{H}), 8.07 (s, br, 1H, CON\textsubscript{H}), 7.01 (s, br, 3H, CON\textsubscript{H}), 5.20 (m, br, 1H, CH), 4.41 (m, br, 2H, OCH\textsubscript{2}), 2.13 (m, br, 26H, CH\textsubscript{2}COOH, OCC\textsubscript{H}), 1.89 (m, 28H, NH(C(H\textsubscript{2})\textsubscript{3}), CH(CH\textsubscript{2})\textsubscript{2}), 1.51 (m, br, 6H, CH\textsubscript{2}), 1.25 (m, br, 24H, CH\textsubscript{2}), 0.87 (m, br, 6H, CH\textsubscript{3}) ppm. MS (FAB, NBA): \textit{m/z} = 2092 [M] \textsuperscript{+}, 720 [C\textsubscript{60}]\textsuperscript{+}. UV/Vis (DMSO): \(\lambda_{\text{max}} = 254, 324, 424.5 \) nm.

\textbf{2-(2-(2-(tert-Butyldimethylsilyloxy)ethoxy)ethoxy)ethanol (54)}: To a stirred solution of triethyleneglycol (8.88 mL, 66.6 mmol) and imidazole (11.40 g, 166.5 mmol) in dry DMF (45
tert-butyldimethylsilyl chloride (10.04 g, 66.6 mmol) dissolved in dry DMF (30 mL) was slowly added at 0°C. The reaction mixture was stirred for 1 h at 0°C followed by stirring for 15 h at room temperature and the progress of the reaction was monitored by TLC. The reaction mixture was diluted with water and successively washed with CH₂Cl₂ and Et₂O. The organic phases were combined and dried over MgSO₄. The product was purified by flash column chromatography (SiO₂; hexane/ethyl acetate, 75:25). The purified material was dried under vacuum to afford 8.50 g (32.1 mmol, 48%) of a pale yellow viscous oil. 

1H-NMR (300 MHz, RT, CDCl₃): δ = 3.71 (t, 3J = 5.3 Hz, 2H, SiOC₂H₂), 3.66 (dt, 3J = 4.6 Hz, 2H, HOC₂H₂), 3.61 (m, 4H, OCH₂), 3.55 (t, 3J = 4.6 Hz, 2H, OCH₂), 3.51 (t, 3J = 5.3 Hz, 2H, OCH₂), 2.73 (s, br, 1H, OH), 0.83 (s, 9H, C(CH₃)₃), 0.01 (s, 6H, Si(CH₃)₂) ppm. 

13C-NMR (75 MHz, RT, CDCl₃): δ = 72.58 (1C, OOC₂H₂), 72.44 (1C, OOC₂H₂), 70.69 (1C, OCH₂), 70.36 (1C, OCH₂), 62.60 (1C, SiOCH₂), 61.64 (1C, HOCH₂), 25.83 (3C, (C(CH₃)₃), 18.27 (1C, C(CH₃)₃), -5.38 (2C, SiCH₃) ppm. MS (FAB, NBA): m/z = 265 [M]+. C₁₂H₂₈O₄Si, calcd: C 54.50, H 10.67, O 24.20; found: C 54.62, H 10.75.

Malonic acid bis(2-(2-(tert-butyldimethylsilyloxy)ethoxy)ethoxy)ethyl ester (55): A solution of compound 54 (8.00 g, 30.25 mmol) in dry CH₂Cl₂ (400 mL) and NEt₃ (2.44 mL, 30.25 mmol) were cooled in the ice bath under nitrogen. Malonyl dichloride (1.47 mL, 15.13 mmol) was diluted in dry CH₂Cl₂ (20 mL) and added dropwise over a period of 2 h via a dropping funnel. The reaction mixture was stirred for another 2 h at 0°C followed by stirring for 20 h at room temperature. The mixture was extracted with saturated NH₄Cl (2 x 200mL) and saturated NaHCO₃ (2 x 200mL). After drying over MgSO₄ and rotary evaporation of the solvent, flash column chromatography on SiO₂ (hexane/ethyl acetate, 70:30) yielded 5.30 g (8.88 mmol, 59%) of a pale yellow oil. 

1H-NMR (300 MHz, RT, CDCl₃): δ = 4.25 (m, 4H, OCOCH₂), 3.72 (m, 4H, OCH₂), 3.66 (m, 4H, OCH₂), 3.59 (m, 8H, OCH₂), 3.51 (m, 4H, OCH₂), 3.39 (s, 2H, OCOC₂H₂CO), 0.84 (s, 18H, C(CH₃)₃), 0.09 (s, 12H, Si(CH₃)₂) ppm. 

13C-NMR (75 MHz, RT, CDCl₃): δ = 166.83 (2C, CO), 73.07 (2C, OCH₂), 71.08 (2C, OCH₂), 71.03 (2C, OCH₂), 69.22 (2C, OCH₂), 64.96 (2C, OCH₂), 63.08, (2C, OCH₂), 41.62 (1C OCH₂CO), 26.30 (6C, (C(CH₃)₃), 18.73 (2C, C(CH₃)₃), -4.89 (4C, SiCH₃) ppm. MS (FAB, NBA): m/z =597 [M]+. C₂₃H₅₈O₁₀Si₂: calcd. C 54.33, H 9.46, O 26.80; found C 54.42, H 9.51.

C₆₀ monoadduct 60: DBU (141 µl, 0.95 mmol) was added dropwise to a solution of C₆₀ (553 mg, 0.77 mmol), malonic acid bis(2-(2-methoxyethoxy)ethoxy)ethyl ester (250 mg, 0.63 mmol) and CBr₄ (208 mg, 0.63 mmol) in dry toluene (250 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 20 h and the progress of the reaction
was monitored by TLC. The product was isolated by flash column chromatography (SiO₂; toluene/ethyl acetate, 30:70) and dried under vacuum to afford 288 mg (0.26 mmol, 41%) of a red brownish solid. ¹H-NMR (400 MHz, RT, CDCl₃): δ = 4.62 (m, 4H, OCOCH₂), 3.85 (m, 4H, OCH₂), 3.68 (m, 4H, OCH₂), 3.62 (m, 8H, OCH₂), 3.52 (m, 4H, OCH₂), 3.35 (s, 6H, OCH₃) ppm. ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 163.44 (2C, CO), 145.21, 145.13, 144.84, 144.63, 144.57, 143.83, 143.03, 142.97, 142.92, 142.15, 141.81, 140.86, 139.02 (58C, C₆₀-sp²), 71.87 (2C, C₆₀-sp³), 71.38 (2C, C₆₀-sp³), 70.64 (2C, OCH₂), 70.60 (2C, OCH₂), 70.57 (2C, OCH₂), 68.72 (2C, OCH₂), 66.18 (2C, OCOCH₂), 59.02 (2C, OCH₃), 52.00 (1C, OCCC) ppm. MS (FAB, NBA): m/z = 1115 [M]+. UV/Vis (CH₂Cl₂): λ max = 258, 326, 423 nm.

C₇₀ monooadduct 61: DBU (36 µl, 0.24 mmol) was added dropwise to a solution of C₇₀ (200 mg, 0.24 mmol), malonate derivative 55 (109 mg, 0.18 mmol) and CBr₄ (64 mg, 0.19 mmol) in dry toluene (250 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 20 h and the progress of the reaction was monitored by TLC. The product was isolated by flash column chromatography (SiO₂; toluene/ethyl acetate, 85:15) and dried under vacuum to afford 97 mg (0.068 mmol, 37%) of a red brownish solid. ¹H-NMR (400 MHz, RT, CDCl₃): δ = 4.57 (t, 3J = 4.8 Hz, 4H, OCOCH₂), 3.84 (t, 3J = 4.8 Hz, 4H, OCH₂), 3.73 (t, 3J = 5.4 Hz, 4H, OCH₂), 3.65 (m, 8H, OCH₂), 3.53 (t, 3J = 5.4 Hz, 4H, OCH₂), 0.86 (s, 18H, C(C(CH₃)₃), 0.04 (s, 12H, Si(C(CH₃)₃)) ppm. ¹³C-NMR (100.5 MHz, RT, CDCl₃): δ = 163.31 (2C, CO), 155.00, 151.27, 151.09, 150.63, 150.51, 149.25, 149.19, 149.02, 148.66, 148.48, 148.43, 148.40, 147.54, 147.45, 147.23, 146.93, 146.37, 145.85, 145.20, 145.12, 144.81, 143.86, 143.77, 143.47, 142.77, 142.22, 141.56, 140.77, 136.84, 133.45, 132.75, 130.86, 130.73 (68C, C₇₀-sp²), 72.70 (2C, OCH₂), 70.73 (2C, OCH₂), 68.68 (2C, OCH₂), 66.71 (1C, C₇₀-sp³), 66.21 (2C, OCH₂), 66.10 (1C, C₇₀-sp³), 62.64 (2C, OCH₂), 36.90 (1C OCCC), 25.94 (6C, (C(CH₃)₃)), 18.35 (2C, (C(CH₃)₃), -5.21 (4C, Si-C) ppm. MS (FAB, NBA): m/z = 1436 [M]+. UV/Vis (CH₂Cl₂): λ max = 260 (sh), 308 (sh), 323, 328 (sh), 352, 369, 403, 460, 535 (sh), 607 (sh) nm.

C₇₀ monooadduct 62: The protected alcohol 61 (50 mg, 0.038 mmol) was dissolved in THF (10 mL) and 2N HCl (1mL) was added under vigorous stirring. The progress of the reaction was monitored by TLC. After complete deprotection the solution was diluted with CH₂Cl₂ (50 mL), washed with a saturated solution of NaHCO₃ (100 mL) and water (100 mL). After drying over MgSO₄, filtrating and concentrating, the product was isolated as a red brownish solid. 32 mg (0.030 mmol, 80%). ¹H-NMR (400 MHz, RT, CDCl₃): δ = 4.59 (m, 4H, OCOCH₂), 3.87 (t, 3J = 4.8 Hz, 4H, OCH₂), 3.72 (m, 8H, OCH₂), 3.67 (m, 4H, OCH₂), 3.59
(m, 4H, OCH2), 2.78 (s, br, 2H, OH) ppm. $^{13}$C-NMR (100.5 MHz, RT, CDCl3): $\delta = 163.66$ (2C, CO), 155.28, 151.55, 151.38, 150.93, 150.79, 149.55, 149.47, 149.33, 148.94, 148.78, 148.71, 148.68, 147.81, 147.71, 147.50, 147.20, 146.65, 146.16, 146.10, 145.06, 144.14, 144.02, 143.74, 143.03, 142.97, 142.49, 141.82, 141.05, 137.01, 133.69, 132.97, 131.08, 131.04, 130.95 (68C, C_{70}-sp^{2}), 72.67, (2C, OCH2), 70.69 (2C, OCH2), 70.33 (2C, OCH2), 68.59 (2C, OCH2), 66.69 (2C, C_{70}-sp^{3}), 66.06 (2C, OCH2), 61.67 (2C, HOCH2), 36.59 (1C OCCCCO) ppm. MS (FAB, NBA): $m/z = 1207$ [M]$^+$. UV/Vis (CH2Cl2): $\lambda_{max} = 238, 261$ (sh), 308 (sh), 322, 328 (sh), 352, 370, 405, 460, 534 (sh), 607 (sh) nm.

C_{70} bisadducts 63a-c: DBU (113 µL, 0.75 mmol) was added dropwise to a solution of C_{70} (211 mg, 0.25 mmol), malonate derivative 55 (344 mg, 0.58 mmol) and CBr4 (200 mg, 0.60 mmol) in dry toluene (250 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 20 h and the progress of the reaction was monitored by TLC. After chromatographic purification (SiO2; toluene/ethyl acetate, 95:5 to 80:20; HPLC; toluene/ethyl acetate, 87:13) the pure regioisomers were obtained as dark solids. 63a (2´clock) 25 mg (12.5 µmol, 5%), 63b (5´clock) 152 mg (75.0 µmol, 30%), 63c (12´clock) 66 mg (32.5 µmol, 13%).

63a: $^{1}$H-NMR (400 MHz, RT, CDCl3): $\delta = 4.55$ (m, 8H, OCOCH2), 3.83 (m, 8H, CH2OSi), 3.74 (m, 8H, OCH2), 3.66 (m, 16H, OCH2), 3.54 (m, 8H, OCH2), 0.87 (s, 36H, C(CH3)3), 0.04 (s, 24H, Si(CH3)2) ppm. $^{13}$C-NMR (100.5 MHz, RT, CDCl3): $\delta = 163.43, 163.31$ (4C, CO), 156.05, 155.34, 151.86, 151.18, 150.27, 149.87, 149.00, 148.37, 147.96, 147.35, 146.91, 146.84, 144.03, 143.95, 143.33, 142.95, 142.83, 142.36, 141.71, 140.96, 140.65, 140.40, 139.36, 137.53, 136.96, 133.57, 133.03, 132.52, 132.42, 130.67 (66C, C_{70}-sp^{2}), 72.73, 70.76, 68.71 (16C, OCH2), 67.45, 66.75 (4C, C_{70}-sp^{3}), 66.19, 62.69 (8C, OCH2), 36.41 (2C, OCCCCO), 25.95 (12C, C(CH3)3), 18.38 (4C, C(CH3)3), -5.21 (8C, Si(CH3)2) ppm. MS (FAB, NBA): $m/z = 2030$ [M]$^+$. UV/Vis (CH2Cl2): $\lambda_{max} = 256$ (sh), 282 (sh), 367, 401, 435 (sh), 467, 515 (sh), 635 (sh), 678 (sh) nm.

63b: $^{1}$H-NMR (400 MHz, RT, CDCl3): $\delta = 4.56$ (m, 8H, OCOCH2), 3.84 (m, 8H, CH2OSi), 3.74 (m, 8H, OCH2), 3.65 (m, 16H, OCH2), 3.53 (m, 8H, OCH2), 0.87 (s, 18H, C(CH3)3), 0.86 (s, 18H, C(CH3)3), 0.04 (s, 24H, Si(CH3)2), 0.04 (s, 24H, Si(CH3)2) ppm. $^{13}$C-NMR (100.5 MHz, RT, CDCl3): $\delta = 163.44, 163.37$ (4C, CO), 155.51, 154.97, 152.97, 152.14, 151.63, 151.21, 150.46, 149.93, 148.95, 147.51, 146.46, 146.36, 146.27, 145.06, 144.89, 144.44, 143.51, 143.28, 142.47, 142.13, 141.50, 141.37, 140.66, 140.43, 137.79, 135.79, 132.92, 132.84, 131.36, 131.08 (66C, C_{70}-sp^{2}), 72.74, 70.78, 70.76, 70.73, 68.71 (16C, OCH2), 67.06, 66.66 (4C, C_{70}-sp^{3}), 66.23, 62.67 (8C, OCH2), 37.82 (2C, OCCCCO), 25.94 (12C, C(CH3)3),
18.36 (4C, C(CH$_3$)$_3$), -5.23 (8C, Si(CH$_3$)$_2$) ppm. MS (FAB, NBA): $m/z = 2030$ [M]$^+$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 255$ (sh), 306 (sh), 331 (sh), 396, 433, 461, 525 (sh), 635 (sh) nm.

**63c**: $^1$H-NMR (400 MHz, RT, CDCl$_3$): $\delta = 4.58$ (m, 4H, OCOC$_2$H$_2$), 4.13 (m, 2H, OCOC$_2$H$_2$), 4.08 (m, 2H, OCOC$_2$H$_2$), 3.84 (t, $^3$J = 4.8 Hz, 4H, CH$_2$OSi), 3.73, 3.68, 3.66 (3m, 6H, CH$_2$OSi), 3.62 (m 8H, OCH$_2$), 3.52 (m, 8H, OCH$_2$), 0.87 (s, 18H, C(CH$_3$)$_3$), 0.86 (s, 18H, C(CH$_3$)$_3$), 0.04 (s, 12H, Si(CH$_3$)$_2$), 0.03 (s, 12H, Si(CH$_3$)$_2$) ppm. $^{13}$C-NMR (100.5 MHz, RT, CDCl$_3$): $\delta = 163.48$ (4C, CO), 154.38, 152.49, 151.39, 149.92, 140.45, 148.73, 147.45, 142.13, 142.10, 141.89, 141.54, 137.35, 136.71, 135.24, 131.73, 131.20, 130.59 (66C, C$_{70}$-sp$^2$), 73.95, 71.39, 69.39, 67.85, 67.63, 67.42 (20C, OCH$_2$), 68.42, 68.00 (4C, C$_{70}$-sp$^3$), 37.85 (2C, OC$_2$CO) ppm. MS (FAB, NBA): $m/z = 1573$ [M]$^+$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 270$, 326 (sh), 361, 399, 425 (sh), 475, 529 (sh), 613 (sh), 667 (sh) nm.

**C$_{70}$ bisadducts 64a-c**: The protected alcohol 63a-c (50 mg, 0.025 mmol) was dissolved in THF (5 mL) and 1N HCl (1 mL) was added under vigorous stirring. The progress of the reaction was monitored by TLC. After complete deprotection the solution was diluted with CH$_2$Cl$_2$ (50 mL), washed with a saturated solution of NaHCO$_3$ (100 mL) and with water (100 mL). After drying over MgSO$_4$ the solution was concentrated and dried under vacuum for further 24 h. **64a** (2’clock) 28 mg (0.018 mmol, 72%), **64b** (5’clock) 30 mg (0.019 mmol, 77%), **64c** (12’clock) 26 mg (0.016 mmol, 65%).

**64a**: $^1$H-NMR (400 MHz, RT, THF-d$_8$): $\delta = 4.56$ (m, 8H, OCOC$_2$H$_2$), 3.85 (m, 8H, CH$_2$OH), 3.65 (m, 8H, OCH$_2$), 3.59 (m, 16H, OCH$_2$), 3.49 (m, 8H, OCH$_2$), 2.55 (s, 4H, OH) ppm. $^{13}$C-NMR (100.5 MHz, RT, THF-d$_8$): $\delta = 163.59$, 163.45 (4C, CO), 157.06, 156.34, 152.70, 152.04, 151.17, 151.11, 149.84, 149.79, 149.17, 149.13, 148.73, 148.12, 147.60, 147.55, 144.72, 144.22, 143.71, 143.57, 143.24, 142.41, 142.07, 141.89, 141.41, 141.20, 140.49, 140.18, 138.76, 138.19, 134.36, 133.79, 133.31, 133.18, 131.37, (66C, C$_{70}$-sp$^2$), 73.95, 71.39, 69.39, 67.85, 67.63, 67.42 (20C, OCH$_2$), 68.42, 68.00 (4C, C$_{70}$-sp$^3$), 62.14 (4C, HOCH$_2$), 37.85 (2C, OCCCCO) ppm. MS (FAB, NBA): $m/z = 1573$ [M]$^+$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 258$ (sh), 282 (sh), 366, 401, 435 (sh), 467, 518 (sh), 634 (sh), 675 (sh) nm.

**64b**: $^1$H-NMR (400 MHz, RT, THF-d$_8$): $\delta = 4.57$ (m, 8H, OCOC$_2$H$_2$), 3.85 (m, 8H, CH$_2$OH), 3.66 (m, 8H, OCH$_2$), 3.62 (m, 8H OCH$_2$), 3.57 (m, 8H, OCH$_2$), 3.48 (m, 8H, OCH$_2$), 2.52 (s, 4H, OH) ppm. $^{13}$C-NMR (100.5 MHz, RT, THF-d$_8$): $\delta = 164.17$, 164.06 (4C, CO), 157.03, 156.47, 154.20, 153.52, 152.92, 152.58, 151.83, 151.16, 150.15, 148.83, 147.68, 147.64,
147.57, 146.71, 146.17, 145.78, 145.60, 144.68, 144.17, 143.64, 143.30, 142.85, 142.51, 141.89, 141.73, 139.55, 137.09, 134.13, 134.00, 132.48, 132.23 (66C, C$_{70}$-sp$^2$), 74.14, 71.58, 71.57, 69.57, 68.02, 67.80, 67.58 (20C, OCH$_2$), 68.25, 68.17 (4C, C$_{70}$-sp$^3$), 62.27 (4C, HOCH$_2$), 39.35 (2C, OCCCO) ppm. MS (FAB, NBA): $m/z$ = 1573 [M]$^+$. UV/Vis (THF): $\lambda_{\text{max}}$ = 258 (sh), 306 (sh), 331 (sh), 394, 433, 462, 524 (sh), 633 (sh) nm.
64c: $^1$H-NMR (400 MHz, RT, THF-d$_8$): $\delta$ = 4.58 (m, 8H, OCOCH$_2$), 3.86 (m, 8H, CH$_2$OH), 3.67 (m, 8H, OCH$_2$), 3.62 (m, 8H OCH$_2$), 3.58 (m, 8H, OCH$_2$), 3.49 (m, 8H, OCH$_2$), 2.53 (s, 4H, OH) ppm. $^{13}$C-NMR (100.5 MHz, RT, THF-d$_8$): $\delta$ = 163.66 (4C, CO), 155.38, 153.38, 152.22, 150.63, 150.12, 149.52, 148.38, 143.51, 143.46, 143.07, 142.17, 138.65, 137.58, 136.11, 132.40, 131.94, 131.33 (66C, C$_{70}$-sp$^2$), 73.95, 71.40, 69.40, 67.85, 67.63, 67.41, 67.16 (20C, OCH$_2$), 68.03 (4C, C$_{70}$-sp$^3$), 62.14 (4C, HOCH$_2$), 37.87 (2C, OCCCO) ppm. MS (FAB, NBA): $m/z$ = 1573 [M]$^+$. UV/Vis (THF): $\lambda_{\text{max}}$ = 270, 328 (sh), 361, 398, 425 (sh), 476, 529 (sh), 615 (sh), 664 (sh) nm.