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 satured solution of $NaHCO_3$ (20 ml). The aqueous phase was acidified with conc. HCl and extracted twice with diethyl ether (20 mL). After drying over $MgSO_4$, evaporation of the solvent and drying under high vacuum **4** was obtained as a pale yellow oil (1.78 g, 8.41 mmol, 60%). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 11.02 (s, br, 1H, COO*H*), 4.46 (t, ^3J = 6.1 Hz, 2H, OCH_2), 3.51 (t, ^3J = 6.1 Hz, 2H, BrCH_2), 3.48 (s, 2H, OCCH_2CO) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 171.54 (1C, *C*OOH), 165.88 (1C, *C*O), 64.84 (1C, O*C*H$_2$), 40.72 (1C, OC*C*H$_2$CO), 27.87 (1C, BrCH$_2$) ppm. MS (FAB, NBA): *m/z* = 211 $[M+H]^+$. $C_5H_7BrO_4$: calcd. C 28.46, H 3.34, Br 37.87, O 30.33; found C 28.39, H 3.44.

malonate precursor 16: ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 6.10 (s, br, 2H, N*H*), 4.51 (t, ^3J = 6.3 Hz, 4H, OCH_2), 3.26 (s, 2H, OCCH_2CO), 2.07 (m, 16H, CH_2COO^{t}Bu, CH_2CO), 1.82 (m, 16H, NHC(CH_2)$_3$, OCH$_2$CH_2), 1.28 (s, 54H, C(CH_3)$_3$) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 172.57 (6C, *C*OO^{t}Bu), 171.14 (2C, *C*ONH), 166.43 (2C, *C*O), 80.13 (6C, *C*(CH$_3$)$_3$), 64.29 (2C, O*C*H$_2$), 57.09 (2C, N*C*(CH$_2$)$_3$), 41.05 (1C, OC*C*H$_2$CO), 32.74 (2C, *C*H$_2$CO), 29.44 (6C, *C*H$_2$COO^{t}Bu), 29.35 (6C, NHC(*C*H$_2$)$_3$), 27.66 (18C, C(*C*H$_3$)$_3$), 24.17 (2C, OCH$_2$*C*H$_2$) ppm. MS (FAB, NBA): *m/z* = 1094 $[M+Na]^+$, 1071 $[M]^+$, 726 [M-6 ^{t}Bu]$^+$. $C_{55}H_{94}N_2O_{18}$: 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: ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 6.23 (s, br, 2H, CON*H*), 4.54 (t, ^3J = 6.5 Hz, 4H, OCH_2), 2.35 (t, ^3J = 6.6 Hz, 4H, CH_2CO), 2.24 (m, 12H, CH_2COO^{t}Bu), 2.19 (m, 4H, OCH$_2$CH_2), 1.99 (m, 12H, NHC(CH_2)$_3$), 1.44 (s, 54H, C(CH_3)$_3$) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 172.80 (6C, *C*OO^{t}Bu), 170.91 (2C, *C*ONH), 163.58 (2C, *C*O), 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, C_{60}-sp^2), 80.60 (6C, *C*(CH$_3$)$_3$), 71.44 (2C, C_{60}-sp^3), 66.63 (2C, O*C*H$_2$), 57.54 (2C, NH*C*(CH$_2$)$_3$), 51.96 (1C, OC*C*CO), 33.03 (2C, *C*H$_2$CO), 29.88 (6C, *C*H$_2$COO^{t}Bu), 29.78 (6C, NHC(*C*H$_2$)$_3$), 28.06 (18C, C(*C*H$_3$)$_3$), 24.50 (2C, OCH$_2$*C*H$_2$) ppm. MS (FAB, NBA): *m/z* = 1790 $[M]^+$, 720 $[C_{60}]^+$. UV/Vis (CH_2Cl_2): λ_{max} = 258, 325, 425, 496 nm.

deprotected monoadduct 16: ^{1}H-NMR (400 MHz, RT, THF-d_8): δ = 9.41 (s, br, 6H, COO*H*), 6.81 (s, br, 2H, CON*H*), 4.54 (t, ^3J = 6.6 Hz, 4H, OCH_2), 2.40 (t, ^3J = 6.5 Hz, 4H, CH_2CO), 2.26 (m, 12H, CH_2COOH), 2.13 (m, 4H, OCH$_2$CH_2), 2.02 (m, 12H, NHC(CH_2)$_3$) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 175.22 (6C, *C*OOH), 172.23 (2C, *C*ONH), 164.16 (2C, *C*O), 147.11, 146.49, 146.35, 146.26, 145.96, 145.80, 145.66, 145.06, 143.85,

144.19, 144.12, 144.09, 143.38, 143.13, 141.99, 140.43 (58C, C_{60}-sp^2), 73.27 (2C, C_{60}-sp^3), 68.21 (2C, O*C*H_2), 58.14 (2C, NH*C*$(CH_2)_3$), 53.95 (1C, OC*C*CO), 33.30 (2C, *C*H_2CO), 30.56 (6C, *C*H_2COOH), 28.86 (6C, NHC(*C*$H_2)_3$), 24.98 (2C, OCH$_2$*C*H_2) ppm. MS (FAB, NBA): *m/z* = 1453 $[M]^+$, 720 $[C_{60}]^+$. UV/Vis (DMSO): λ_{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, $CDCl_3$): δ = 11.30 (s, br, 1H, COO*H*), 4.08 (t, ^3J = 6.8 Hz, 2H, OC*H*$_2$), 3.36 (s, 2H, OCC*H*$_2$CO), 1.57 (m, 2H, C*H*$_2$), 1.22 (m, 6H, C*H*$_2$), 0.80 (t, ^3J = 6.9 Hz, 3H, C*H*$_3$) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 171.53 (1C, *C*O), 166.57 (1C, *C*O), 65.72 (1C, O*C*H$_2$), 40.78 (1C, OC*C*H$_2$CO), 31.06, 28.06, 25.12, 22.21 (4C, *C*H$_2$), 13.63 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 189 $[M+H]^+$. $C_9H_{16}O_4$: 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, $CDCl_3$): δ = 10.08 (s, br, 1H, COO*H*), 4.18 (t, ^3J = 6.8 Hz, 2H, OC*H*$_2$), 3.44 (s, 2H, OCC*H*$_2$CO), 1.66 (m, 2H, C*H*$_2$), 1.26 (m, 30H, C*H*$_2$), 0.88 (t, ^3J = 6.8 Hz, 3H, C*H*$_3$) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 170.65 (1C, *C*O), 167.34 (1C, *C*O), 66.22 (1C, O*C*H$_2$), 40.47 (1C, OC*C*H$_2$CO), 31.91 (1C, *C*H$_2$), 29.69 (5C, *C*H$_2$), 29.65 (2C, *C*H$_2$), 29.63, 29.55, 29.48, 29.35, 29.16, 28.36, 25.73, 22.68 (8C, *C*H$_2$), 14.11 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 357 $[M+H]^+$. $C_{21}H_{40}O_4$: 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, $CDCl_3$): δ = 9.01 (s, br, 1H, COO*H*), 4.96 (quin, ^3J = 6.7 Hz, 1H, OC*H*), 3.42 (s, 2H, OCC*H*$_2$CO), 1.54 (m, 4H, CHC*H*$_2$), 1.25 (m, 24H, C*H*$_2$), 0.88 (t, ^3J = 6.7 Hz, 6H, C*H*$_3$) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 171.07 (1C, *C*O), 167.08 (1C, *C*O), 76.78 (1C, *C*H), 40.70 (1C, OC*C*H$_2$CO), 33.85 (2C, *C*H$_2$), 31.82 (2C, *C*H$_2$), 29.42 (4C, *C*H$_2$), 29.20, 25.15, 22.63 (6C, *C*H$_2$), 14.09 (2C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 343 $[M+H]^+$. $C_{20}H_{38}O_4$: calcd. C 70.13, 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 ε-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 Et_2O and washed with 300 mL of H_2O. The aqueous layer was extracted twice with 200 mL Et_2O. 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 H_2SO_4 (180 mL) was added. The turbid aqueous solution was extracted with CH_2Cl_2 (3 x 200 mL), dried over anhydrous $MgSO_4$ and concentrated in vacuum to afford **23** as a pale yellow oil. To the residue of the toluene/Et_2O layers NaOH (16 g, 0.4 mol) and H_2O (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 H_2O and washed with Et_2O (3 x 100 mL). The aqueous layer was acidified with a slurry of 25 mL conc. H_2SO_4 in 100 mL of ice and then extracted with CH_2Cl_2 (3 x 100 mL). The organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed in vacuum to afford **23** as a pale yellow oil. (36.3 g, 0.16 mmol, 92.7 %). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 10.41 (s, br, 1H, COO*H*), 7.34 (m, 5H, arom.*H*), 4.51 (s, 2H, ArCH_2O), 3.48 (t, ^3J = 6.5 Hz, 2H, OCH_2), 2.37 (t, ^3J = 7.6 Hz, 2H, CH_2COOH), 1.66 (m, 4H, CH_2), 1.45 (m, 2H, CH_2) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 179.02 (1C, *C*OOH), 138.47 (1C, Ar*C*), 128.31 (2C, Ar*C*), 127.59 (2C, Ar*C*), 127.47 (1C, Ar*C*), 72.91 (1C, Ar*C*H_2O), 70.06 (1C, O*C*H_2), 33.89 (1C, *C*H_2COOH), 29.42, 25.75, 24.54 (3C, *C*H_2). MS (FAB, NBA): *m/z* = 223 $[M+H]^+$. $C_{13}H_{18}O_3$: calcd. C 70.24, H 8.16, O 21.59; found: C 70.09, H 8.18.

***tert*-butyl 6-(benzyloxy)hexanoate (24):** A solution of **23** (30 g, 0.135 mol) in dry CH_2Cl_2 (30 mL) was treated with condensed isobutene (100 mL at -60°C) and H_2SO_4 (2 mL). The resulting solution was stirred for three days at room temperature, then neutralized with a solution of K_2CO_3 (25 g) in H_2O (300 mL). The organic layer was washed with K_2CO_3 (saturated solution), citric acid (10 wt % in H_2O), and H_2O. After the mixture was dried over anhydrous $MgSO_4$, filtered, and concentrated, a pale yellow oil was obtained. (33.6 g, 0.12 mmol, 89.3 %). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 7.34 (m, 5H, arom.*H*), 4.51 (s, 2H, ArCH_2O), 3.48 (t, ^3J = 6.6 Hz, 2H, OCH_2), 2.22 (t, ^3J = 7.5 Hz, 2H, CH_2COO^{t}Bu), 1.62 (m, 4H, CH_2), 1.45 (s, 9H, C(CH_3)$_3$), 1.42 (m, 2H, CH_2) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 173.07 (1C, *C*OO^{t}Bu), 138.54 (1C, Ar*C*), 128.28 (2C, Ar*C*), 127.54 (2C, Ar*C*), 127.43 (1C, Ar*C*), 79.97 (1C, *C*(CH$_3$)$_3$), 72.86 (1C, Ar*C*H_2O), 70.19 (1C, O*C*H_2), 35.55 (1C, *C*H_2COO^{t}Bu), 29.48 (1C, *C*H_2), 28.15 (3C, C(*C*H$_3$)$_3$), 25.75, 24.97 (2C, *C*H_2). MS (FAB, NBA): *m/z* = 278 $[M]^+$. $C_{17}H_{26}O_3$: calcd. C 73.34, H 9.41, O 17.24; found: C 73.14, H 9.45.

***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 H_2 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, $CDCl_3$): δ = 3.63 (t, ^3J = 6.5 Hz, 2H, HOCH_2), 2.22 (t, ^3J = 7.4 Hz, 2H, CH_2COO^{t}Bu), 1.81 (s, br, 1H, O*H*), 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, $CDCl_3$): δ = 173.19 (1C, *C*OO^{t}Bu), 80.06 (1C, *C*(CH$_3$)$_3$), 62.54 (1C, HO*C*H$_2$), 35.41 (1C, *C*H$_2$COO^{t}Bu), 32.29 (1C, *C*H$_2$CH$_2$OH), 28.05 (3C, C(*C*H$_3$)$_3$), 25.15, 24.68 (2C, *C*H$_2$). 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_2Cl_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, $CDCl_3$): δ = 3.89 (m, 4H, OCH_2), 3.12 (s, 2H, OCCH_2CO), 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, $CDCl_3$): δ = 172.08 (1C, *C*O), 165.99 (2C, *C*O), 79.18 (1C, *C*(CH$_3$)$_3$), 64.81 (1C, O*C*H$_2$), 64.52 (1C, O*C*H$_2$), 40.89 (1C, OC*C*H$_2$CO), 34.59 (1C, *C*H$_2$CO), 30.78, 27.84, 27.60 (3C, *C*H$_2$), 27.38 (3C, *C*(CH$_3$)$_3$), 24.84, 24.70, 24.00, 21.88 (4C, *C*H$_2$), 13.29 (1C, *C*H$_3$) 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, $CDCl_3$): δ = 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_2CO), 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, $CDCl_3$): δ = 172.77 (1C, *C*O), 166.57 (2C, *C*O), 80.00 (1C, *C*(CH$_3$)$_3$), 65.62 (1C, O*C*H$_2$), 65.27 (1C, O*C*H$_2$), 41.58 (1C, OC*C*H$_2$CO), 35.29 (1C, *C*H$_2$CO), 31.88, 29.65, 29.61, 29.53, 29.47, 29.31, 29.16, 28.42, 28.15 (15C, *C*H$_2$), 28.05 (3C, C(*C*H$_3$)$_3$), 25.74, 25.27, 24.60, 22.64 (4C, *C*H$_2$), 14.06 (1C, *C*H$_3$) 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 (SiO_2; hexane/ethyl acetate, 90:12). (2.84 g, 5.39 mmol, 82 %. colourless oil). ^{1}H-NMR (300 MHz, RT, $CDCl_3$): δ = 4.91 (quin, ^3J = 6.3 Hz, 1H, OC*H*), 4.14 (t, ^3J = 6.7 Hz, 2H, OCH_2), 3.35 (s, 2H, OCCH_2CO), 2.22 (t, ^3J = 7.4 Hz, 2H, OCCH_2), 1.64 (m, 6H, CH_2), 1.55 (m, 2H, CH_2), 1.45 (s, 9H, CH_3), 1.26 (m, 26H, CH_2), 0.81 (t, ^3J = 6.6 Hz, 6H, CH_3) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 172.86 (1C, *C*O), 166.74 (1C, *C*O), 166.35 (1C, *C*O), 80.08 (1C, *C*$(CH_3)_3$), 75.97 (1C, *C*H), 65.28 (1C, O*C*H_2), 41.94 (1C, OC*C*H_2CO), 35.33 (1C, *C*H_2CO), 33.93 (2C, CH(*C*$H_2)_2$), 31.84, 29.48, 29.47, 29.23, 28.20 (9C, *C*H_2), 28.09 (3C, *C*$(CH_3)_3$), 25.30, 25.18 (3C, *C*H_2), 24.65 (1C, *C*H_2CH_2CO), 22.65 (2C, *C*H_2CH_3), 14.10 (2C, *C*H_3) ppm. MS (FAB, NBA): *m/z* = 512 $[M]^+$. $C_{30}H_{56}O_6$: 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 CH_2Cl_2 (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 %). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 7.91 (s, br, 1H, COO*H*), 4.15 (t, ^3J = 6.7 Hz, 2H, OCH_2), 4.14 (t, ^3J = 6.8 Hz, 2H, OCH_2), 3.38 (s, 2H, OCCH_2CO), 2.37 (t, ^3J = 7.4 Hz, 2H, OCCH_2), 1.65 (m, 6H, CH_2), 1.43 (m, 2H, CH_2), 1.30 (m, 6H, CH_2), 0.89 (t, ^3J = 6.9 Hz, 3H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, $CDCl_3$, RT): δ = 179.42 (1C, *C*O), 166.75 (1C, *C*O), 166.72 (1C, *C*O), 65.74 (1C, O*C*H_2), 65.23 (1C, O*C*H_2), 41.58 (1C, OC*C*H_2CO), 33.76 (1C, *C*H_2CO), 31.32, 28.36, 28.07, 25.40, 25.24, 24.15, 22.48 (7C, *C*H_2), 13.94 (1C, *C*H_3) ppm. MS (FAB, NBA): *m/z* = 303 $[M+H]^+$. $C_{15}H_{26}O_6$: 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). ^{1}H-NMR (300 MHz, RT, $CDCl_3$): δ = 10.10 (s, br, 1H, COO*H*), 4.15 (t, ^3J = 6.6 Hz, 2H, OCH_2), 4.13 (t, ^3J = 6.7 Hz, 2H, OCH_2), 3.37 (s, 2H, OCCH_2CO), 2.37 (t, ^3J = 7.4 Hz, 2H, OCCH_2), 1.66 (m, 6H, CH_2), 1.42 (m, 2H, CH_2), 1.26 (m, 30H, CH_2), 0.87 (t, ^3J = 6.7 Hz, 3H, CH_3) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 179.49 (1C, *C*O), 166.66 (1C, *C*O), 166.65 (1C, *C*O), 65.71 (1C, O*C*H_2), 65.19 (1C, O*C*H_2), 41.58 (1C, OC*C*H_2CO), 33.77 (1C, *C*H_2CO), 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, *C*H_2), 24.17 (1C, *C*H_2CH_2CO), 22.67 (1C,

*C*H$_2$), 14.09 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 472 [M+H]$^+$. $C_{27}H_{50}O_6$: calcd. C 68.90, H 10.71, O 20.40; found: C 69.07, H 10.77.

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). ^{1}H-NMR (300 MHz, RT, $CDCl_3$): δ = 10.82 (s, br, 1H, COO*H*), 4.91 (quin, ^3J = 6.3 Hz, 1H, OC*H*), 4.15 (t, ^3J = 6.7 Hz, 2H, OC*H*$_2$), 3.36 (s, 2H, OCC*H*$_2$CO), 2.37 (t, ^3J = 7.4 Hz, 2H, OCC*H*$_2$), 1.68 (m, 4H, CH(C*H*$_2$)$_2$), 1.53 (m, 4H, C*H*$_2$), 1.43 (m, 2H, C*H*$_2$), 1.26 (m, 24H, C*H*$_2$), 0.88 (t, ^3J = 6.8 Hz, 6H, C*H*$_3$) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 178.90 (1C, *C*O), 166.75 (1C, *C*O), 166.38 (1C, *C*O), 76.03 (1C, *C*H), 65.14 (1C, O*C*H$_2$), 41.93 (1C, OC*C*H$_2$CO), 33.93 (2C, CH(*C*H$_2$)$_2$), 33.68 (1C, *C*H$_2$CO), 31.84, 29.49, 29.48, 29.23, 28.14, 25.27, 25.19 (12C, *C*H$_2$), 24.20 (1C, *C*H$_2$CH$_2$CO), 22.65 (2C, *C*H$_2$CH$_3$), 14.09 (2C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 458 [M+H]$^+$. $C_{26}H_{48}O_6$: 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 (SiO_2, hexane/ethyl acetate, 15:10). (1.88 g, 2.17 mmol, 68 %, colourless oil). ^{1}H-NMR (300 MHz, RT, $CDCl_3$): δ = 5.90 (s, br, 1H, CON*H*), 4.13 (t, ^3J = 6.6 Hz, 2H, OC*H*$_2$), 4.12 (t, ^3J = 6.8 Hz, 2H, OC*H*$_2$), 3.36 (s, 2H, OCC*H*$_2$CO), 2.22 (t, ^3J = 7.7 Hz, 6H, C*H*$_2$COO^{t}Bu), 2.11 (t, ^3J = 7.4 Hz, 2H, OCC*H*$_2$), 1.95 (t, ^3J = 7.8 Hz, 6H, NHC(C*H*$_2$)$_3$), 1.63 (m, 6H, C*H*$_2$), 1.43 (s, 27H, C(C*H*$_3$)$_3$), 1.25 (m, 32H, C*H*$_2$), 0.87 (t, ^3J = 6.7 Hz, 3H, C*H*$_3$) ppm; ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 172.87 (3C, *C*OO^{t}Bu), 172.07 (1C, *C*ONH), 166.66 (1C, *C*O), 166.61 (1C, *C*O), 80.63 (3C, *C*(CH$_3$)$_3$), 65.67 (1C, O*C*H$_2$), 65.28 (1C, O*C*H$_2$), 57.28 (1C, NH*C*(CH$_2$)$_3$), 41.56 (1C, OC*C*H$_2$CO), 37.22 (1C, *C*H$_2$CO), 31.89 (1C, *C*H$_2$), 29.94 (3C, NHC(*C*H$_2$)$_3$), 29.79 (3C, *C*H$_2$COO^{t}Bu), 29.66, 29.64, 29.62, 29.55, 29.48, 29.33, 29.18, 28.43, 28.18 (14C, *C*H$_2$), 28.03 (9C, C(*C*H$_3$)$_3$), 25.75 (1C, *C*H$_2$), 25.48 (1C, *C*H$_2$CH$_2$CO), 25.23, 22.65 (2C, *C*H$_2$), 14.09 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 868 [M]$^+$, 696 [M-3^{t}Bu]$^+$. $C_{49}H_{89}NO_{11}$: calcd. 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 (SiO_2, hexane/ethyl acetate, 20:10 to 15:10). (1.20 g, 1.40 mmol, 64 %, colourless oil). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 5.91 (s, br, 1H, CON*H*), 4.91 (quin, ^3J = 6.2 Hz, 1H, OC*H*), 4.13 (t, ^3J = 6.7 Hz, 2H, OC*H*$_2$), 3.36 (s, 2H, OCC*H*$_2$CO), 2.22 (t, ^3J = 7.8 Hz, 6H,

C*H*$_2$COO^{t}Bu), 2.11 (t, ^3J = 7.6 Hz, 2H, OCC*H*$_2$), 1.97 (t, ^3J = 7.9 Hz, 6H, NHC(C*H*$_2$)$_3$), 1.64 (m, 4H, CHC*H*$_2$), 1.52 (m, 2H, C*H*$_2$), 1.43 (s, 27H, C(C*H*$_3$)$_3$), 1.41 (m, 2H, C*H*$_2$), 1.26 (m, 26H, C*H*$_2$), 0.88 (t, ^3J = 6.8 Hz, 6H, C*H*$_3$) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 173.40 (3C, *C*OO^{t}Bu), 172.59 (1C, *C*ONH), 167.20 (1C, *C*O), 166.85 (1C, *C*O), 80.69 (3C, *C*(CH$_3$)$_3$), 75.96 (1C, *C*H), 65.19 (1C, O*C*H$_2$), 57.20 (1C, NH*C*(CH$_2$)$_3$), 41.72 (1C, OC*C*H$_2$CO), 37.04 (1C, *C*H$_2$CO), 33.70 (2C, CH(*C*H$_2$)$_2$), 31.61, 30.04 (3C, *C*H$_2$), 29.71 (3C, NHC(*C*H$_2$)$_3$), 29.55 (3C, *C*H$_2$COO^{t}Bu), 29.43, 29.24, 29.22, 28.98, 27.98 (6C, *C*H$_2$), 27.80 (9C, C(*C*H$_3$)$_3$), 25.26 (1C, *C*H$_2$CH$_2$CO), 25.00, 24.91, 22.37 (5C, *C*H$_2$), 13.78 (2C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 854 [M]$^+$, 682 [M-3^{t}Bu]$^+$. $C_{48}H_{87}NO_{11}$: 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_2Cl_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, CON*H*), 6.15 (s, br, 3H, CON*H*), 3.98 (t, ^3J = 6.5 Hz, 2H, OC*H*$_2$), 3.96 (t, ^3J = 6.7 Hz, 2H, OC*H*$_2$), 3.24 (s, 2H, OCC*H*$_2$CO), 2.06 (m, 26H, C*H*$_2$COO^{t}Bu, OCC*H*$_2$), 1.81 (m, 24H, NHC(C*H*$_2$)$_3$), 1.50 (m, 6H, C*H*$_2$), 1.38 (m, 2H, C*H*$_2$), 1.30 (m, 83H, C(C*H*$_3$)$_3$, C*H*$_2$), 1.17 (m, 4H, C*H*$_2$), 0.71 (t, ^3J = 6.8 Hz, 3H, C*H*$_3$) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 172.87 (1C, *C*ONH), 172.75 (3C, *C*ONH), 172.32 (9C, *C*OO^{t}Bu), 166.38 (1C, *C*O), 166.35 (1C, *C*O), 80.09 (9C, *C*(CH$_3$)), 65.27 (1C, O*C*H$_2$), 65.04 (1C, O*C*H$_2$), 57.24 (1C, NH*C*(CH$_2$)$_3$), 57.07 (3C, NH*C*(CH$_2$)$_3$), 41.23 (1C, OC*C*H$_2$CO), 36.76 (1C, *C*H$_2$CO), 31.53 (3C, NHC(*C*H$_2$)$_3$), 31.34 (3C, *C*H$_2$CON), 31.06 (1C, *C*H$_2$), 29.49 (9C, NHC(*C*H$_2$)$_3$), 29.37 (9C, *C*H$_2$COO^{t}Bu), 28.73, 28.54 (2C, *C*H$_2$), 27.72 (27C, C(*C*H$_3$)$_3$), 25.27, 25.15 (2C, *C*H$_2$), 24.97 (1C, *C*H$_2$CH$_2$CO), 22.27 (1C, *C*H$_2$), 13.85 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 1724 [M]$^+$. $C_{91}H_{158}N_4O_{26}$: 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 (SiO_2, hexane/ethyl acetate, 20:10 to 13:10). (1.48 g, 0.78 mmol, 74 %, colourless oil). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 7.61 (s, br, 1H, CON*H*), 6.09 (s, br, 3H, CON*H*), 4.05 (t, ^3J = 6.6 Hz, 2H, OCH_2), 4.03 (t, ^3J = 6.6 Hz, 2H, OCH_2), 3.27 (s, 2H, OCCH_2CO), 2.09 (m, 26H, CH_2COO^{t}Bu, OCCH_2), 1.84 (m, 24H, NHC(CH_2)$_3$), 1.54 (m, 6H, CH_2), 1.33 (m, 83H, C(CH_3)$_3$, CH_2), 1.15 (m, 30H, CH_2), 0.77 (t, ^3J = 6.6 Hz, 3H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 172.88 (1C, *C*ONH), 172.66 (3C, *C*ONH), 172.38 (9C, *C*OO^{t}Bu), 166.46 (1C, *C*O), 166.43 (1C, *C*O), 80.25 (9C, *C*(CH$_3$)$_3$), 65.39 (1C, OCH$_2$), 65.13 (1C, OCH$_2$), 57.26 (1C, NH*C*(CH$_2$)$_3$), 57.16 (3C, NH*C*(CH$_2$)$_3$), 41.30 (1C, OC*C*H$_2$CO), 36.85 (1C, *C*H$_2$CO), 31.65 (4C, NHC(*C*H$_2$)$_3$, *C*H$_2$), 31.47 (3C, *C*H$_2$CON), 29.54 (1C, *C*H$_2$), 29.52 (9C, NHC(*C*H$_2$)$_3$), 29.42 (9C, *C*H$_2$COO^{t}Bu), 29.41, 29.38, 29.32, 29.25, 29.09, 28.96, 28.21, 27.99 (13C, *C*H$_2$), 27.83 (27C, C(*C*H$_3$)$_3$), 25.53 (1C, *C*H$_2$), 25.32 (1C, *C*H$_2$CH$_2$CO), 25.02, 22.42 (2C, *C*H$_2$), 13.88 (1C, *C*H$_3$) ppm; MS (FAB, NBA): *m/z* = 1892 [M]$^+$. $C_{103}H_{182}N_4O_{26}$: calcd. C 65.37, H 9.69, N 2.96, O 21.98; found: C 65.47, H 9.79, N 3.04.

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 (SiO_2, hexane/ethyl acetate, 13:10 to 10:10). (998 mg, 0.53 mmol, 69 %, colourless oil). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 7.57 (s, br, 1H, CON*H*), 6.09 (s, br, 3H, CON*H*), 4.84 (quin, ^3J = 6.3 Hz, 1H, C*H*), 4.08 (t, ^3J = 6.7 Hz, 2H, OCH_2), 3.29 (s, 2H, OCCH_2CO), 2.13 (m, 26H, CH_2COO^{t}Bu, OCCH_2), 1.88 (m, 24H, NHC(CH_2)$_3$), 1.60 (m, 4H, CH(CH_2)$_2$), 1.46 (m, 4H, CH_2), 1.37 (m, 83H, C(CH_3)$_3$, CH_2)), 1.19 (m, 24H, CH_2), 0.81 (t, ^3J = 6.8 Hz, 6H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 173.11 (1C, *C*ONH), 172.90 (3C, *C*ONH), 172.64 (9C, *C*OO^{t}Bu), 166.75 (1C, *C*O), 166.36 (1C, *C*O), 80.40 (9C, *C*(CH$_3$)$_3$), 75.72 (1C, *C*H), 65.18 (1C, OCH$_2$), 57.28 (1C, NH*C*(CH$_2$)$_3$), 57.23 (3C, NH*C*(CH$_2$)$_3$), 41.64 (1C, OC*C*H$_2$CO), 36.88 (1C, *C*H$_2$CO), 33.70 (2C, *C*H$_2$), 31.66 (3C, NHC(*C*H$_2$)$_3$), 31.62 (2C, *C*H$_2$), 31.53 (3C, *C*H$_2$CON), 29.60 (9C, NHC(*C*H$_2$)$_3$), 29.56 (9C, *C*H$_2$COO^{t}Bu), 29.25, 29.23, 29.00, 28.06 (7C, *C*H$_2$), 27.85 (27C, C(*C*H$_3$)$_3$), 25.36 (1C, *C*H$_2$CH$_2$CO), 25.06, 24.94, 22.41 (5C, *C*H$_2$), 13.87 (2C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 1878 [M]$^+$. $C_{102}H_{180}N_4O_{26}$: calcd. C 65.22, H 9.66, N 2.98, O 22.14; found: C 64.83, H 9.77, N 3.10.

C_{60} monoadduct 43: Prepared as described for compound **42** from **37** (500 mg, 0.58 mmol), C_{60} (498 mg, 0.69 mmol), CBr_4 (212 mg, 0.64 mmol) and DBU (96 µL, 0.64 mmol). Purification was obtained by flash column chromatography (SiO_2, toluene/ethyl acetate, 80:10 to 80:15). (488 mg, 0.31 mmol, 53 %, red brownish solid). ^{1}H-NMR (400 MHz, RT, $CDCl_3$):

δ = 5.90 (s, br, 1H, CON*H*), 4.50 (t, ^3J = 6.6 Hz, 2H, OCH_2), 4.49 (t, ^3J = 6.7 Hz, 2H, OCH_2), 2.22 (t, ^3J = 7.8 Hz, 6H, CH_2COO^{t}Bu), 2.13 (t, ^3J = 7.6 Hz, 2H, OCCH_2), 1.98 (t, ^3J = 7.8 Hz, 6H, NHC(CH_2)$_3$), 1.85 (m, 4H, OCH$_2$CH_2), 1.70 (m, 2H, CH_2), 1.44 (s, 27H, (CH_3)$_3$), 1.25 (m, 32H, CH_2), 0.88 (t, ^3J = 6.8 Hz, 3H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 172.88 (3C, *C*OO^{t}Bu), 171.96 (1C, *C*ONH), 163.67 (1C, *C*O), 163.59 (1C, *C*O), 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, C_{60}-sp^2), 80.69 (3C, *C*(CH$_3$)$_3$), 71.65 (2C, C_{60}-sp^3), 67.50 (1C, O*C*H$_2$), 67.13 (1C, O*C*H$_2$), 57.34 (1C, NH*C*(CH$_2$)$_3$), 49.87 (1C, OC*C*CO), 37.22 (1C, *C*H$_2$CO), 31.92 (1C, *C*H$_2$), 30.00 (3C, NHC(*C*H$_2$)$_3$), 29.83 (3C, *C*H$_2$COO^{t}Bu), 29.72, 29.70, 29.67, 29.62, 29.37, 29.22, 28.60, 28.35 (14C, *C*H$_2$), 28.06 (9C, C(*C*H$_3$)$_3$), 26.00 (1C, *C*H$_2$), 25.64 (1C, *C*H$_2$CH$_2$CO), 25.24, 22.69 (2C, *C*H$_2$), 14.14 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 1610 [M+Na]$^+$, 1587 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 254, 323, 425, 475 nm.

C_{60} monoadduct 44: Prepared as described for compound **42** from **38** (300 mg, 0.35 mmol), C_{60} (304 mg, 0.42 mmol), CBr_4 (130 mg, 0.39 mmol) and DBU (59 µL, 0.39 mmol). Purification was obtained by flash column chromatography (SiO_2, toluene/ethyl acetate, 90:10 to 70:10). (310 mg, 0.20 mmol, 56 %, red brownish solid). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 5.89 (s, br, 1H, CON*H*), 5.25 (m, 1H, OC*H*), 4.48 (t, ^3J = 6.8 Hz, 2H, OCH_2), 2.22 (t, ^3J = 7.8 Hz, 6H, CH_2COO^{t}Bu), 2.13 (t, ^3J = 7.7 Hz, 2H, OCCH_2), 1.97 (t, ^3J = 7.8 Hz, 6H, NHC(CH_2)$_3$), 1.87 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 1.68 (m, 6H, CHCH_2, CH_2), 1.44 (m, 29H, C(CH_3)$_3$, CH_2), 1.27 (m, 22H, CH_2), 0.88 (t, ^3J = 6.8 Hz, 6H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 173.01 (3C, *C*OO^{t}Bu), 172.08 (1C, *C*ONH), 163.70 (1C, *C*O), 163.29 (1C, *C*O), 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, C_{60}-sp^2), 80.69 (3C, *C*(CH$_3$)$_3$), 78.56 (1C, *C*H), 71.79 (2C, C_{60}-sp^3), 67.12 (1C, O*C*H$_2$), 57.31 (1C, NH*C*(CH$_2$)$_3$), 52.74 (1C, OC*C*CO), 37.16 (1C, *C*H$_2$CO), 33.87 (2C, CH(*C*H$_2$)$_2$), 31.83, 30.11 (3C, *C*H$_2$), 29.92 (3C, NC(*C*H$_2$)$_3$), 29.76 (3C, *C*H$_2$COO^{t}Bu), 29.63, 29.55, 29.48, 29.21, 28.35 (6C, *C*H$_2$), 28.01 (9C, C(*C*H$_3$)$_3$), 25.59 (1C, *C*H$_2$CH$_2$CO), 25.32, 25.18, 22.60 (5C, *C*H$_2$), 14.08 (2C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 1596 [M+Na]$^+$, 1573 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 254, 324, 425, 475 nm.

C_{60} monoadduct 45: Prepared as described for compound **42** from **39** (260 mg, 0.15 mmol), C_{60} (144 mg, 0.2 mmol), CBr_4 (56 mg, 0.17 mmol) and DBU (25 µL, 0.17 mmol). Purification was obtained by flash column chromatography (SiO_2, toluene/ethyl acetate, 30:10 to 15:10). (171 mg, 0.07 mmol, 47 %, red brownish solid). ^{1}H-NMR (400 MHz, RT, $CDCl_3$):

δ = 7.57 (s, br, 1H, CON*H*), 6.14 (s, br, 3H, CON*H*), 4.50 (t, ^3J = 6.5 Hz, 2H, OCH_2), 4.49 (t, ^3J = 6.4 Hz, 2H, OCH_2), 2.19 (m, 26H, CH_2COO^{t}Bu, OCCH_2), 1.95 (m, 24H, NHC(CH_2)$_3$), 1.84 (m, 4H, CH_2), 1.69 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.44 (m, 83H, C(CH_3)$_3$, CH_2), 1.26 (m, 4H, CH_2), 0.85 (t, ^3J = 6.7 Hz, 3H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 173.29 (1C, *C*ONH), 173.15 (3C, *C*ONH), 172.80 (9C, *C*OO^{t}Bu), 163.81 (1C, *C*O), 163.74 (1C, *C*O), 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, C_{60}-sp^2), 80.59 (9C, *C*(CH$_3$)), 71.65 (2C, C_{60}-sp^3), 67.47 (1C, OCH_2), 67.33 (1C, O*C*H$_2$), 57.58 (1C, NH*C*(CH$_2$)$_3$), 57.42 (3C, NH*C*(CH$_2$)$_3$), 52.36 (1C, OC*C*CO), 37.01 (1C, *C*H$_2$CO), 31.68 (3C, NHC(*C*H$_2$)$_3$), 31.30 (3C, *C*H$_2$CON), 30.75 (1C, *C*H$_2$), 29.72 (9C, NHC(*C*H$_2$)$_3$), 29.61 (9C, *C*H$_2$COO^{t}Bu), 28.47, 28.32 (2C, *C*H$_2$), 28.01 (27C, C(*C*H$_3$)$_3$), 25.55, 25.23 (2C, *C*H$_2$), 24.38 (1C, *C*H$_2$CH$_2$CO), 22.53 (1C, *C*H$_2$), 14.00 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 2466 [M+Na]$^+$, 2443 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 254.5, 324, 424.5, 476 nm.

C_{60} monoadduct 46: Prepared as described for compound **42** from **40** (600 mg, 0.32 mmol), C_{60} (302 mg, 0.42 mmol), CBr_4 (117 mg, 0.35 mmol) and DBU (52 µL, 0.35 mmol). Purification was obtained by flash column chromatography (SiO_2, toluene/ethyl acetate, 70:20 to 70:50). (366 mg, 0.14 mmol, 44 %, red brownish solid). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 7.63 (s, br, 1H, CON*H*), 6.04 (s, br, 3H, CON*H*), 4.51 (t, ^3J = 6.4 Hz, 2H, OCH_2), 4.50 (t, ^3J = 6.8 Hz, 2H, OCH_2), 2.20 (m, 26H, CH_2COO^{t}Bu, OCCH_2), 1.96 (m, 24H, NHC(CH_2)$_3$), 1.83 (m, 4H, CH_2), 1.71 (m, 2H, CH_2), 1.44 (m, 83H, C(CH_3)$_3$, CH_2), 1.25 (m, 30H, CH_2), 0.88 (t, ^3J = 6.8 Hz, 3H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, $CDCl_3$, RT): δ = 173.07 (1C, *C*ONH), 172.99 (3C, *C*ONH), 172.77 (9C, *C*OO^{t}Bu), 163.75 (1C, *C*O), 163.68 (1C, *C*O), 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, 142.13, 141.85, 140.88, 139.16, 139.10, 138.75 (58C, sp^2-*C*), 80.43 (9C, *C*(CH$_3$)$_3$), 71.66 (2C, sp^3-*C*), 67.44 (1C, OCH_2), 67.32 (1C, O*C*H$_2$), 57.57 (1C, NH*C*(CH$_2$)$_3$), 57.39 (3C, NH*C*(CH$_2$)$_3$), 52.42 (1C, OC*C*CO), 37.02 (1C, *C*H$_2$CO), 31.84 (3C, NHC(*C*H$_2$)$_3$), 31.73 (1C, *C*H$_2$), 31.63 (1C, *C*H$_2$), 31.62 (3C, *C*H$_2$CON), 29.74 (3C, *C*H$_2$), 29.71 (9C, NHC(*C*H$_2$)$_3$), 29.64 (9C, *C*H$_2$COO^{t}Bu), 29.61, 29.59, 29.56, 29.55, 29.29, 29.27, 29.14, 28.53, 28.28 (9C, *C*H$_2$), 28.02 (27C, C(*C*H$_3$)$_3$), 27.97, 25.51 (2C, *C*H$_2$), 25.23 (1C, *C*H$_2$CH$_2$CO), 24.84, 22.61 (2C, *C*H$_2$), 14.04 (1C, *C*H$_3$) ppm; MS (FAB, NBA): *m/z* = 2634 [M+Na]$^+$, 2611 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 254, 324, 424, 476 nm.

C_{60} monoadduct 47: Prepared as described for compound **42** from **41** (250 mg, 0.13 mmol), C_{60} (122 mg, 0.17 mmol), CBr_4 (48 mg, 0.14 mmol) and DBU (22 µL, 0.14 mmol). Purification was obtained by flash column chromatography (SiO_2; toluene/ethyl acetate, 70:20 to 70:50). (159 mg, 0.06 mmol, 47 %, red brownish solid). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 7.59 (s, br, 1H, CON*H*), 6.04 (s, br, 3H, CON*H*), 5.24 (quin, ^3J = 6.4 Hz, 1H, C*H*), 4.48 (t, ^3J = 7.1 Hz, 2H, OCH_2), 2.19 (m, 26H, CH_2COO^{t}Bu, OCCH_2), 1.95 (m, 24H, NHC(CH_2)$_3$), 1.69 (m, 4H, CH(CH_2)$_2$), 1.59 (m, 4H, CH_2), 1.43 (m, 83H, C(CH_3)$_3$, CH_2)), 1.25 (m, 24H, CH_2), 0.87 (t, ^3J = 6.9 Hz, 6H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 172.82 (3C, *C*ONH), 172.74 (1C, *C*ONH), 172.62 (9C, *C*OO^{t}Bu), 163.54 (1C, *C*O), 163.12 (1C, *C*O), 145.62, 145.36, 145.24, 145.20, 145.15, 145.13, 145.10, 144.80, 144.68, 144.64, 144.56, 144.53, 143.85, 143.82, 143.02, 142.98, 142.96, 142.94, 142.91, 142.17, 141.86, 140.89, 139.10, 138.72 (58C, sp^2-*C*), 80.55 (9C, *C*(CH$_3$)$_3$), 77.20 (1C, *C*H), 67.32 (1C, O*C*H$_2$), 57.42 (3C, NH*C*(CH$_2$)$_3$), 57.38 (1C, NH*C*(CH$_2$)$_3$), 49.08 (1C, OC*C*CO), 37.02 (1C, *C*H$_2$CO), 33.91 (2C, *C*H$_2$), 31.88 (2C, *C*H$_2$), 31.85 (3C, NHC(*C*H$_2$)$_3$), 31.70 (3C, *C*H$_2$CON), 29.79 (9C, NHC(*C*H$_2$)$_3$), 29.76 (9C, *C*H$_2$COO^{t}Bu), 29.65, 29.57, 29.48, 29.23, 28.44 (8C, *C*H$_2$), 28.07 (27C, C(*C*H$_3$)$_3$), 25.58 (1C, *C*H$_2$CH$_2$CO), 25.34, 24.91, 22.64 (6C, *C*H$_2$), 14.13 (2C, *C*H$_3$) ppm; MS (FAB, NBA): *m/z* = 2620 [M+Na]$^+$, 2597 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 254.5, 324, 424.5, 476 nm.

C_{60} 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/Et_2O. (259 mg, 0.18 mmol, 96 %). ^{1}H-NMR (400 MHz, RT, DMSO-d_6): δ = 12.05 (s, br, 3H, COO*H*), 7.14 (s, br, 1H, CON*H*), 4.39 (m, br, 4H, OCH_2), 2.09 (m, br, 8H, CH_2COOH, OCCH_2), 1.82 (m, br, 8H, NHC(CH_2)$_3$, CH_2), 1.51 (m, br, 4H, OCH$_2$CH_2), 1.36 (m, br, 32H, CH_2), 0.85 (m, br, 3H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 174.42 (3C, *C*OOH), 171.81 (1C, *C*ONH), 163.63 (1C, *C*O), 163.52 (1C, *C*O), 144.71, 144.13, 143.40, 142.53, 141.69, 141.30, 140.61, 140.35, 139.10, 138.85 (58C, C_{60}-sp^2), 71.42 (2C, C_{60}-sp^3), 67.12 (1C, O*C*H$_2$), 67.02 (1C, O*C*H$_2$), 56.34 (1C, NH*C*(CH$_2$)$_3$), 52.32 (1C, OC*C*CO), 38.13 (1C, *C*H$_2$CO), 31.73 (1C, *C*H$_2$), 29.97 (3C, NHC(*C*H$_2$)$_3$), 29.88 (3C, *C*H$_2$COOH), 29.69, 29.70, 29.60, 29.62, 29.33, 29.28, 28.54, 28.37 (14C, *C*H$_2$), 25.99 (1C, *C*H$_2$), 25.42 (1C, *C*H$_2$CH$_2$CO), 25.06, 22.57 (2C, *C*H$_2$), 14.23 (1C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 1419 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (DMSO): λ_{max} = 254, 323.5, 424.5 nm.

C_{60} 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/Et_2O. (218 mg, 0.16 mmol, 97 %). ^{1}H-NMR (400 MHz, RT, DMSO-d_6): δ = 11.89 (s, br, 3H, COO*H*),

7.04 (s, br, 1H, CON*H*), 5.18 (m, br, 1H, OC*H*), 4.41 (m, br, 2H, OCH_2), 2.18 (m, br, 8H, CH_2COOH, OCCH_2), 1.91 (m, br, 8H, NHC(CH_2)$_3$, CH_2), 1.65 (m, br, 8H, CHCH_2, CH_2), 1.41 (m, br, 2H, CH_2), 1.21 (m, br, 22H, CH_2), 0.85 (m, br, 6H, CH_3) ppm; ^{13}C-NMR (100.5 MHz, RT, DMSO-d_6): δ = 175.02 (3C, *C*OOH), 172.00 (1C, *C*ONH), 163.59 (1C, *C*O), 163.51 (1C, *C*O), 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_{60}-sp^2), 78.01 (1C, *C*H), 71.59 (2C, C_{60}-sp^3), 67.54 (1C, O*C*H$_2$), 56.69 (1C, NH*C*(CH$_2$)$_3$), 52.56 (1C, OC*C*CO), 37.99 (1C, *C*H$_2$CO), 33.98 (2C, CH(*C*H$_2$)$_2$), 31.89, 30.13 (3C, *C*H$_2$), 29.89 (3C, NHC(*C*H$_2$)$_3$), 29.71 (3C, *C*H$_2$COOH), 29.63, 29.48, 29.01, 28.37 (6C, *C*H$_2$), 25.61 (1C, *C*H$_2$CH$_2$CO), 25.37, 22.60 (5C, *C*H$_2$), 14.11 (2C, *C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 1405 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (DMSO): λ_{max} = 254, 323.5, 424.5 nm.

C_{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_2O. (112 mg, 0.06 mmol, 97 %). ^{1}H-NMR (400 MHz, RT, DMSO-d_6): δ = 12.01 (s, br, 9H, COO*H*), 8.05 (s, br, 1H, CON*H*), 7.16 (s, br, 3H, CON*H*), 4.51 (m, br, 4H, OCH_2), 2.11 (m, br, 26H, CH_2COOH, OCCH_2), 1.91 (m, br, 28H, NHC(CH_2)$_3$, CH_2), 1.51 (m, br, 6H, CH_2), 1.26 (m, br, 4H, CH_2), 0.84 (m, br, 3H, CH_3) ppm. MS (FAB, NBA): *m/z* = 1938 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (DMSO): λ_{max} = 254, 324, 424.5 nm.

C_{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_2O. (237 mg, 0.11 mmol, 98 %). ^{1}H-NMR (400 MHz, RT, DMSO-d_6): δ = 12.03 (s, br, 9H, COO*H*), 8.12 (s, br, 1H, CON*H*), 7.20 (s, br, 3H, CON*H*), 4.46 (m, br, 4H, OCH_2), 2.09 (m, br, 26H, CH_2COOH, OCCH_2), 1.81 (m, br, 30H, NHC(CH_2)$_3$, CH_2), 1.21 (m, br, 32H, CH_2), 0.82 (m, br, 3H, CH_3) ppm. MS (FAB, NBA): *m/z* = 2106 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (DMSO): λ_{max} = 254, 324, 424.5 nm.

C_{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_2O. (117 mg, 0.06 mmol, 97 %). ^{1}H-NMR (400 MHz, RT, DMSO-d_6): δ = 12.11 (s, br, 9H, COO*H*), 8.07 (s, br, 1H, CON*H*), 7.01 (s, br, 3H, CON*H*), 5.20 (m, br, 1H, C*H*), 4.41 (m, br, 2H, OCH_2), 2.13 (m, br, 26H, CH_2COOH, OCCH_2), 1.89 (m, 28H, NHC(CH_2)$_3$, CH(CH_2)$_2$), 1.51 (m, br, 6H, CH_2), 1.25 (m, br, 24H, CH_2), 0.87 (m, br, 6H, CH_3) ppm. MS (FAB, NBA): *m/z* = 2092 [M]$^+$, 720 [C_{60}]$^+$. UV/Vis (DMSO): λ_{max} = 254, 324, 424.5 nm.

2-(2-(2-(*tert*-Butyldimethylsilyloxy)ethoxy)ethoxy)-ethanol (54): To a stirred solution of triethylenglycol (8.88 mL, 66.6 mmol) and imidazole (11.40 g, 166.5 mmol) in dry DMF (45

mL), *tert*-butyldimethylsilylchloride (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 CH_2Cl_2 and Et_2O. The organic phases were combined and dried over $MgSO_4$. The product was purified by flash column chromatography (SiO_2; 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. ^{1}H-NMR (300 MHz, RT, $CDCl_3$): δ = 3.71 (t, ^3J = 5.3 Hz, 2H, SiOC*H*$_2$), 3.66 (dt, ^3J = 4.6 Hz, 2H, HOC*H*$_2$), 3.61 (m, 4H, OC*H*$_2$), 3.55 (t, ^3J = 4.6 Hz, 2H, OC*H*$_2$), 3.51 (t, ^3J = 5.3 Hz, 2H, OC*H*$_2$), 2.73 (s, br, 1H, O*H*), 0.83 (s, 9H, C(C*H*$_3$)$_3$), 0.01 (s, 6H, Si(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 72.58 (1C, O*C*H$_2$), 72.44 (1C, O*C*H$_2$), 70.69 (1C, O*C*H$_2$), 70.36 (1C, O*C*H$_2$), 62.60 (1C, SiO*C*H$_2$), 61.64 (1C, HO*C*H$_2$), 25.83 (3C, (C(*C*H$_3$)$_3$),18.27 (1C, *C*(CH$_3$)$_3$), -5.38 (2C, Si*C*H$_3$) ppm. MS (FAB, NBA): *m/z* = 265 [M]$^+$. $C_{12}H_{28}O_4Si$, calcd: C 54.50, H 10.67, O 24.20; found: C 54.62, H 10.75.

Malonic acid bis(2-(2-(2-(*tert*-butyldimethylsilyloxy)-ethoxy)ethoxy)ethyl ester (55): A solution of compound **54** (8.00 g, 30.25 mmol) in dry CH_2Cl_2 (400 mL) and NEt_3 (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 CH_2Cl_2 (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 NH_4Cl (2 x 200mL) and saturated $NaHCO_3$ (2 x 200mL). After drying over $MgSO_4$ and rotary evaporation of the solvent, flash column chromatography on SiO_2 (hexane/ethyl acetate, 70:30) yielded 5.30 g (8.88 mmol, 59%) of a pale yellow oil. ^{1}H-NMR (300 MHz, RT, $CDCl_3$): δ = 4.25 (m, 4H, OCOC*H*$_2$), 3.72 (m, 4H, OC*H*$_2$), 3.66 (m, 4H, OC*H*$_2$), 3.59 (m, 8H, OC*H*$_2$), 3.51 (m, 4H, OC*H*$_2$), 3.39 (s, 2H, OCC*H*$_2$CO), 0.84 (s, 18H, C(C*H*$_3$)$_3$), 0.09 (s, 12H, Si(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (75 MHz, RT, $CDCl_3$): δ = 166.83 (2C, *C*O), 73.07 (2C, O*C*H$_2$), 71.08 (2C, O*C*H$_2$), 71.03 (2C, O*C*H$_2$), 69.22 (2C, O*C*H$_2$), 64.96 (2C, O*C*H$_2$), 63.08, (2C, O*C*H$_2$), 41.62 (1C OC*C*H$_2$CO), 26.30 (6C, (C(*C*H$_3$)$_3$),18.73 (2C, *C*(CH$_3$)$_3$), -4.89 (4C, Si*C*H$_3$) ppm. MS (FAB, NBA): *m/z* =597 [M]$^+$. $C_{27}H_{56}O_{10}Si_2$: calcd. C 54.33, H 9.46, O 26.80; found C 54.42, H 9.51.

C_{60} monoadduct 60: DBU (141 µl, 0.95 mmol) was added dropwise to a solution of C_{60} (553 mg, 0.77 mmol), malonic acid bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl ester (250 mg, 0.63 mmol) and CBr_4 (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 (SiO_2; toluene/ethyl acetate, 30:70) and dried under vacuum to afford 288 mg (0.26 mmol, 41%) of a red brownish solid. ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 4.62 (m, 4H, OCOCH_2), 3.85 (m, 4H, OCH_2), 3.68 (m, 4H, OCH_2), 3.62 (m, 8H, OCH_2), 3.52 (m, 4H, OCH_2), 3.35 (s, 6H, OCH_3) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 163.44 (2C, *C*O), 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, C_{60}-sp^2) 71.87 (2C, *C*H_2OCH$_3$), 71.38 (2C, C_{60}-sp^3), 70.64 (2C, O*C*H$_2$), 70.60 (2C, O*C*H$_2$), 70.57 (2C, O*C*H$_2$), 68.72 (2C, O*C*H$_2$) 66.18 (2C, OCO*C*H$_2$), 59.02 (2C, O*C*H$_3$), 52.00 (1C, OC*C*CO) ppm. MS (FAB, NBA): *m/z* = 1115 [M]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 258, 326, 423 nm.

C_{70} monoadduct 61: DBU (36 µl, 0.24 mmol) was added dropwise to a solution of C_{70} (200 mg, 0.24 mmol), malonate derivative **55** (109 mg, 0.18 mmol) and CBr_4 (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 (SiO_2; toluene/ethyl acetate 85:15) and dried under vacuum to afford 97 mg (0.068 mmol, 37%) of a red brownish solid. ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 4.57 (t, ^3J = 4.8 Hz, 4H, OCOCH_2), 3.84 (t, ^3J = 4.8 Hz, 4H, OCH_2), 3.73 (t, ^3J = 5.4 Hz, 4H, OCH_2), 3.65 (m, 8H, OCH_2), 3.53 (t, ^3J = 5.4 Hz, 4H, OCH_2), 0.86 (s, 18H, C(CH_3)$_3$, 0.04 (s, 12H, Si(CH_3)$_2$) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 163.31 (2C, *C*O), 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, C_{70}-sp^2), 72.70 (2C, O*C*H$_2$) , 70.73 (2C, O*C*H$_2$), 68.68 (2C, O*C*H$_2$), 66.71 (1C, C_{70}-sp^3), 66.21 (2C, O*C*H$_2$), 66.10 (1C, C_{70}-sp^3), 62.64 (2C, O*C*H$_2$), 36.90 (1C OC*C*CO), 25.94 (6C, (C(*C*H$_3$)$_3$), 18.35 (2C, (*C*(CH$_3$)$_3$), -5.21 (4C, Si-*C*) ppm. MS (FAB, NBA): *m/z* =1436 [M]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 260 (sh), 308 (sh), 323, 328 (sh), 352, 369, 403, 460, 535 (sh), 607 (sh) nm.

C_{70} monoadduct 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 CH_2Cl_2 (50 mL), washed with a saturated solution of $NaHCO_3$ (100 mL) and water (100 mL). After drying over $MgSO_4$, filtrating and concentrating, the product was isolated as a red brownish solid. 32 mg (0.030 mmol, 80%). ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 4.59 (m, 4H, OCOCH_2), 3.87 (t, ^3J = 4.8 Hz, 4H, OCH_2), 3.72 (m, 8H, OCH_2), 3.67 (m, 4H, OCH_2), 3.59

(m, 4H, OC*H*$_2$), 2.78 (s, br, 2H, O*H*) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 163.66 (2C, *C*O), 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, O*C*H$_2$), 70.69 (2C, O*C*H$_2$), 70.33 (2C, O*C*H$_2$), 68.59 (2C, O*C*H$_2$), 66.69 (2C, C_{70}-sp^3), 66.06 (2C, O*C*H$_2$), 61.67 (2C, HO*C*H$_2$), 36.59 (1C OC*C*CO) ppm. MS (FAB, NBA): *m/z* = 1207 [M]$^+$. UV/Vis (CH_2Cl_2): λ_{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 CBr_4 (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 (SiO_2; 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, $CDCl_3$): δ = 4.55 (m, 8H, OCOC*H*$_2$), 3.83 (m, 8H, C*H*$_2$OSi), 3.74 (m, 8H, OC*H*$_2$), 3.66 (m, 16H, OC*H*$_2$), 3.54 (m, 8H, OC*H*$_2$), 0.87 (s, 36H, C(C*H*$_3$)$_3$), 0.04 (s, 24H, Si(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 163.43, 163.31 (4C, *C*O), 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, O*C*H$_2$), 67.45, 66.75 (4C, C_{70}-sp^3), 66.19, 62.69 (8C, O*C*H$_2$), 36.41 (2C, OC*C*CO), 25.95 (12C, C(*C*H$_3$)$_3$), 18.38 (4C, *C*(CH$_3$)$_3$), -5.21 (8C, Si(*C*H$_3$)$_2$) ppm. MS (FAB, NBA): *m/z* = 2030 [M]$^+$. UV/Vis (CH_2Cl_2): λ_{max} = 256 (sh), 282 (sh), 367, 401, 435 (sh), 467, 515 (sh), 635 (sh), 678 (sh) nm.

63b: ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 4.56 (m, 8H, OCOC*H*$_2$), 3.84 (m, 8H, C*H*$_2$OSi), 3.74 (m, 8H, OC*H*$_2$), 3.65 (m, 16H, OC*H*$_2$), 3.53 (m, 8H, OC*H*$_2$), 0.87 (s, 18H, C(C*H*$_3$)$_3$), 0.86 (s, 18H, C(C*H*$_3$)$_3$), 0.04 (s, 24H, Si(C*H*$_3$)$_2$), 0.04 (s, 24H, Si(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 163.44, 163.37 (4C, *C*O), 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, O*C*H$_2$), 67.06, 66.66 (4C, C_{70}-sp^3), 66.23, 62.67 (8C, O*C*H$_2$), 37.82 (2C, OC*C*CO), 25.94 (12C, C(*C*H$_3$)$_3$),

18.36 (4C, *C*(CH_3)$_3$), -5.23 (8C, Si(*C*H_3)$_2$) ppm. MS (FAB, NBA): *m/z* = 2030 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} = 255 (sh), 306 (sh), 331 (sh), 396, 433, 461, 525 (sh), 635 (sh) nm.

63c: ^{1}H-NMR (400 MHz, RT, $CDCl_3$): δ = 4.58 (m, 4H, OCOC*H*$_2$), 4.13 (m, 2H, OCOC*H*$_2$), 4.08 (m, 2H, OCOC*H*$_2$), 3.84 (t, ^3J = 4.8 Hz, 4H, C*H*$_2$OSi), 3.73, 3.68, 3.66 (3m, 20H, OC*H*$_2$), 3.62 (m 8H, OC*H*$_2$), 3.52 (m, 8H, OC*H*$_2$), 0.87 (s, 18H, C(C*H*$_3$)$_3$), 0.86 (s, 18H, C(C*H*$_3$)$_3$), 0.04 (s, 12H, Si(C*H*$_3$)$_2$), 0.03 (s, 12H, Si(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (100.5 MHz, RT, $CDCl_3$): δ = 163.48 (4C, *C*O), 154.38, 152.49, 151.39, 149.92, 140.45, 148.73, 147.45, 142.71, 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), 72.73, 72.69, 70.78, 70.75, 70.71, 69.60, 68.71, (16C, O*C*H$_2$), 68.54, 65.94 (4C, C_{70}-sp^3), 66.23, 62.67, 61.29 (8C, O*C*H$_2$), 36.39 (2C, OC*C*CO), 25.94, 25.90 (12C, C(*C*H$_3$)$_3$), 18.36, 18.34 (4C, *C*(CH$_3$)$_3$), -5.23, -5.29 (8C, Si(*C*H$_3$)$_2$) ppm. MS (FAB, NBA): *m/z* = 2030 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{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_2Cl_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): δ = 4.56 (m, 8H, OCOC*H*$_2$), 3.85 (m, 8H, C*H*$_2$OH), 3.65 (m, 8H, OC*H*$_2$), 3.59 (m, 16H, OC*H*$_2$), 3.49 (m, 8H, OC*H*$_2$), 2.55 (s, 4H, O*H*) ppm. ^{13}C-NMR (100.5 MHz, RT, THF-d_8): δ = 163.59, 163.45 (4C, *C*O), 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, O*C*H$_2$), 68.42, 68.00 (4C, C_{70}-sp^3), 62.14 (4C, HO*C*H$_2$), 37.85 (2C, OC*C*CO) ppm. MS (FAB, NBA): *m/z* = 1573 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{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): δ = 4.57 (m, 8H, OCOC*H*$_2$), 3.85 (m, 8H, C*H*$_2$OH), 3.66 (m, 8H, OC*H*$_2$), 3.62 (m, 8H OC*H*$_2$), 3.57 (m, 8H, OC*H*$_2$), 3.48 (m, 8H, OC*H*$_2$), 2.52 (s, 4H, O*H*) ppm. ^{13}C-NMR (100.5 MHz, RT, THF-d_8): δ = 164.17, 164.06 (4C, *C*O), 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, 144.59, 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, O*C*H_2), 68.25, 68.17 (4C, C_{70}-sp^3), 62.27 (4C, HO*C*H_2), 39.35 (2C, OC*C*CO) ppm. MS (FAB, NBA): *m/z* = 1573 $[M]^+$. UV/Vis (THF): λ_{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): δ = 4.58 (m, 8H, OCOC*H*$_2$), 3.86 (m, 8H, C*H*$_2$OH), 3.67 (m, 8H, OC*H*$_2$), 3.62 (m, 8H OC*H*$_2$), 3.58 (m, 8H, OC*H*$_2$), 3.49 (m, 8H, OC*H*$_2$), 2.53 (s, 4H, O*H*) ppm. ^{13}C-NMR (100.5 MHz, RT, THF-d_8): δ = 163.66 (4C, *C*O), 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, O*C*H_2), 68.03 (4C, C_{70}-sp^3), 62.14 (4C, HO*C*H_2), 37.87 (2C, OC*C*CO) ppm. MS (FAB, NBA): *m/z* = 1573 $[M]^+$. UV/Vis (THF): λ_{max} = 270, 328 (sh), 361, 398, 425 (sh), 476, 529 (sh), 615 (sh), 664 (sh) nm.