第 4 章　総括

以上、本研究では芳香族第三級アミドの立体特性を活かすことで、らせんと環状の 2 種類の構造から、分子認識への応用を志向したフォルダマーを創製した。

第 2 章では、らせんの内部空間を拡張するために、*N*-アルキルベンズアニリドをリンカー(第二級アミド結合もしくは三重結合)で連結した 2 種類のオリゴマーを創製した(Figure IV-1)。第二級アミド結合をもつオリゴマーは、らせん上下で分子内水素結合を形成したらせん構造をとっていることが示唆され、UV スペクトルにおいて、鎖長伸長に伴う極大吸収波長の長波長シフト化が観察されたことから、硬直ならせん構造をとっていると考えられた。三重結合をもつオリゴマーは、溶媒の極性に依存して、2 種類のコンフォメーションをとることが示唆された。低極性溶媒中でらせん構造をとることから、らせん構造への driving force は予想していた疎溶媒効果ではないことが分かった。

どちらのオリゴマーについても、キラルなゲスト分子の添加によるらせんの不斉誘起は観察されなかった。第二級アミド結合をリンカーにもつオリゴマーは、分子内水素結合形成のために、水素結合によるゲスト分子の包接は期待できなかった。また、三重結合をリンカーにもつオリゴマーは疎水性のキラルなゲスト分子とは相互作用しなかったが、低極性溶媒中でアニオン、カチオンとは相互作用していることが NMR 測定より確認された。また本らせんオリゴマーはゲスト分子非存在下でもらせん構造を形成する、1. 2. 3 項 Figure I-30 (b)に相当する系であり、ゲスト分子包接による構造変化が大きくないことから、NMR や UV 測定での変化はわずかであった。

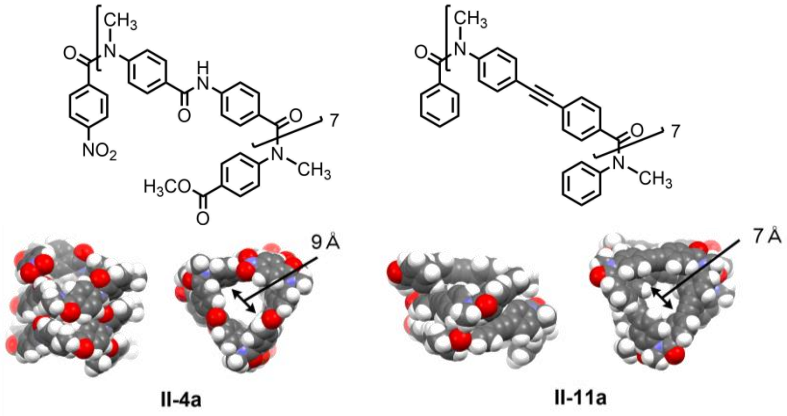

Figure IV-1. Optimized conformations of **II-4a** and **II-11a**.

第 3 章では、第三級アミド結合を導入することで、環状キノリンオリゴアミドの創製を行った。期待した通り、cis 型をとる第三級アミド結合を導入することでキノリンオリゴアミドのらせん構造は歪み、新たに環状ペンタマー、ヘキサマー、ヘプタマーを創製することに成功した。合成した非環状のオリゴアミドのうち、環化反応が進行しないアミノ酸もいくつかあり、第三級アミド結合を適切な数・位置で導入し、らせんオリゴアミドの末端の配向を制御することが重要であった。いずれの環状キノリンオリゴアミドも、全て部分的にらせん構造をもっており、そのらせん性を最大限高めるような立体構造をとっていた(Figure IV-2)。結晶構造ではらせん形成のため、包接空間をもっていなかったが、環状ヘプタマーは溶液中、水素結合形成様式により複数のコンフォメーションで存在していると考えられた。ゲスト

分子の添加によりコンフォメーションを変化させて相互作用することも予想され、今後ゲスト認識についても検討していきたいと考えている。

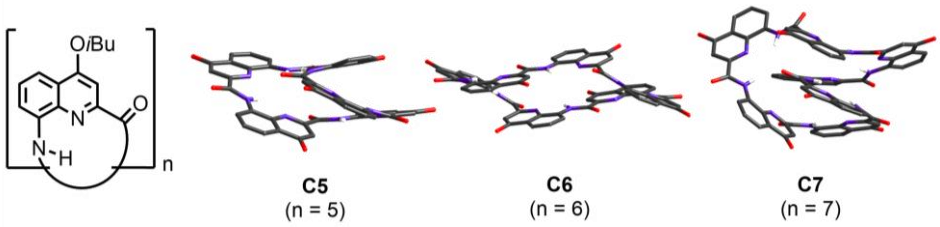

Figure IV-2. Crystal structures of cyclic quinoline oligoamides **C5** - **C7**.

以上、本研究ではらせん状、環状フォルダマーを創製し、その立体構造を明らかとした。本知見により、芳香族第三級アミド結合がフォルダマーの骨格としても、フォルダマー合成のための補助基としても有用であることが示された。

第 5 章　実験項

General

All reagents were purchased from Sigma-Aldrich Chemical Co., Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co., or Kanto Kagaku Co., Inc. Silica Gel 60 N (spherical, neutral) for column chromatography was purchased from Kanto Kagaku Co., Inc. Unless otherwise noted, the original materials were used directly from commercial supplies without any purification. Dry dichloromethane, chloroform, diisopropylethylamine were distilled from CaH_2 prior to use. Recycling preparative HPLC was purchased by LC-9201R/U (Japan Analytical Industry Co. Ltd.). ^{1}H, ^{13}C and ^{1}H-^{1}H ROESY NMR spectra were recorded on JEOL JNM-AL 400, Bruker Avance II 600, and Bruker Avance III 600 spectrometer by using residual solvent resonances $CHCl_3$ (7.26 ppm), CH_2Cl_2 (5.32 ppm), DMSO (2.50 ppm) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ) relative to the signal of the NMR solvent used. ^{1}H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Coupling constants (*J*) are reported in hertz. Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br). ^{1}H-^{1}H ROESY spectra utilized a mixing time of 0.3 s. Positive values were depicted in black and negative values were depicted in red. Mass spectral data were obtained on a Bruker Daltonics micro TOF-2focus in the positive ion detection mode. X-Ray crystallographic data were collected at Ochanomizu University on a Bruker SMART APEX II ULTRA diffractometer equipped with a CCD detector using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, or at the Center for Analytical Instrumentation in Chiba University on a Bruker SMART APEX II ULTRA diffractometer equipped with a CCD detector and graphite-monochromated Cu Kα (λ = 0.71073 Å) radiationor, or at the BL38B1 station of SPring-8 (Hyogo, *J*apan) using a Rayonix MX225 CCD area detector with synchrotron radiation (λ = 0.85 Å) or at the IECB X-ray facility on a Rigaku MM07 rotating anode (800kW) at the Cu Kα wavelength equipped with a RAPID SPIDER image plate for detection and varimax HF optics. Images collected at Spring-8 were processed using software HKL2000 (HKL Research). Structure solution and refinement were performed by using SHELXT-2014/51 and SHELXL-2017/12. The data collected at the IECB were processed with the Rigaku CrystalClear 1.36 suite. The crystal structures were solved by direct methods SHELXS-97 or intrinsic phasing method SHELXT and refined by full-matrix least-squares SHELXL-97[124)]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at their calculated positions. UV spectra were recorded with a JASCO V-650, and CD spectra were recorded with a JASCO J-820 spectropolarimeter using a 2 mm quartz cell. The concentration of each solution in CD experiments was adjusted so that the absorbance of the oligomer was 1 at the maximum absorption wavelength in the examined solvent.

Synthesis of Compound **II-12**: Triethylamine (5 mL, 1.2 eq.) was added to a solution of methyl *p*-aminobenzoate (4.60 g, 30.4 mmol) in dichloromethane (70 mL), and the mixture was stirred at 0°C. A solution of *p*-nitrobenzoyl chloride (5.64 g, 1.0 eq.) in dichloromethane (70 mL) was added to the cold amine solution and the mixture was stirred at rt for 12 h, then washed successively with 2 M HCl, sat. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was recrystallized from ethyl acetate /*n*-hexane to give **II-12** (7.96 g, 26.5 mmol, 87%) as a colorless powder; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1 H), 8.39 (d, *J* = 9.2 Hz, 2 H), 8.20 (d, *J* = 8.7 Hz, 2 H), 7.99 (d, *J* = 9.2 Hz, 2 H), 7.95 (d, *J* = 9.2 Hz, 2 H), 3.85 (s, 3 H).

Synthesis of Compound **II-13a**: A solution of **II-12** (299 mg, 1.00 mmol) in DMF (10 mL) was added to a suspension of NaH (60 %, 79.9 mg, 2.0 eq., washed with *n*-hexane twice) in DMF (9 mL) at 0°C. The solution was stirred at rt for 30 min, and then MeI (514 mg, 3.6 eq.) was added to it at 0°C. The resulting solution was stirred at rt for 3 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate /*n*-hexane 1:1) to give **II-13a** (231 mg, 0.74 mmol, 74%) as a yellow powder; ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 2 H), 7.92 (d, *J* = 8.8 Hz, 2 H), 7.45 (d, *J* = 9.2 Hz, 2 H), 7.08 (d, *J* = 8.7 Hz, 2 H), 3.89 (s, 3 H), 3.55 (s, 3 H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 166.0, 148.3, 147.9, 141.6, 131.0, 129.7, 128.8, 126.6, 123.4, 52.5, 38.2.

Synthesis of Compound **II-13b**: A solution of **II-12** (2.52 g, 8.39 mmol) in DMF (50 mL) was added at 0°C to a suspension of NaH (60 %, 512 mg, 1.5 eq., washed with n-hexane twice) in DMF (9 mL). The solution was stirred at rt for 30 min. 1-Iodopropane (4.59 g, 3.2 eq.) was added at 0°C. The resulting solution was stirred at rt for 8 h and heated at 50°C for 16 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate / *n*-hexane 1 : 5) to give **II-13b** (1.48 g, 4.33 mmol, 56%) as a yellow amorphous solid; ^{1}H NMR(400 MHz,$CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 2 H), 7.92 (d, *J* = 8.8 Hz, 2 H), 7.45 (d, *J* = 9.2 Hz, 2 H), 7.08 (d, *J* = 8.7 Hz, 2 H), 3.94 (m, 2H), 3.89 (s, 3 H), 1.66 (sext, *J* = 7.4 Hz, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, CDCl3) δ 168.2, 166.0, 148.2, 146.7, 142.1, 131.0, 129.6, 129.0, 127.5, 123.4, 52.5, 52.0, 21.1, 11.4. HRMS (ESI+) m/z calcd for $C_{18}H_{19}N_2O_5$ $[M+H]^+$ 343.1288, found 343.1295.

Synthesis of Compound **II-13c**: A solution of **II-12** (5.00 g, 16.6 mmol) in DMF (25 mL) was added to a suspension of NaH (60 %, 880 mg, 1.3 eq., washed with *n*-hexane twice) in DMF (5 mL) at 0°C. The solution was stirred at rt for 5 min, and then 1-Iodo-2-methylpropane (4 mL, 2.1 eq.) was added to the mixture at 0°C. The resulting solution was stirred at 80°C for 5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over MgSO4, filtered and concentrated *in vacuo.* The residue was purified by silica gel column chromatography (ethyl acetate / chloroform = 1:1) to give **II-13c** (1.09 g, 3.06 mmol, 18%) as a yellow oil. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2 H), 7.90 (d, *J* = 8.2 Hz, 2 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 7.08 (d, *J* = 8.2 Hz, 2 H), 3.85 (d, *J* = 7.8 Hz, 2 H), 1.90 (nonuplet, *J* = 6.6 Hz, 1 H), 0.96 (d, *J* = 6.6 Hz, 6 H) ; 13C NMR (150 MHz, CDCl3) δ 168.5, 166.0, 148.1, 146.8, 142.3, 131.0, 129.6,

128.9, 127.4, 123.4, 56.9, 52.5, 27.2, 20.3.

Synthesis of Compound **II-13d**: A solution of **II-12** (105 mg, 0.35 mmol) in DMF (2 mL) was added at 0°C to a suspension of NaH (60 %, 15.7 mg, 0.39 mmol, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at rt for 30 min, and then 1-Iodooctane (172 mg, 0.72 mmol) was added at 0°C. The resulting solution was stirred at rt for 2 h at 80°C. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate / dichloromethane=1/40) to give **II-13d** (82.2 mg, 0.20 mmol, 57%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2 H), 7.92 (d, *J* = 8.7 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.08 (d, *J* = 8.7 Hz, 2 H), 3.96 (dd, *J* = 7.8, 7.8 Hz, 2 H), 3.89 (s, 3 H), 1.62 (sext, *J* = 7.3 Hz, 2 H), 1.34-1.25 (m, 10 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 166.0, 148.2, 146.7, 142.1, 131.0, 129.7, 129.0, 127.5, 123.4, 52.5, 50.6, 31.9, 29.4, 29.3, 27.8, 27.0, 22.7, 14.2. HRMS (ESI+) m/z calcd for $C_{23}H_{29}N_2O_5$ $[M+H]^+$ 413.2071, found 413.2077.

Synthesis of Compound **II-13f**: Triethylamine (1 mL, 7.17 mmol) was added to a solution of **II-18** (1.0073 g, 3.24 mmol) in dichloromethane (10 mL), and the mixture was stirred at 0°C. A solution of *p*-nitrobenzoyl chloride (659.7 mg, 3.56 mmol) in dichloromethane (10 mL) was added to the cold amine solution and the mixture was stirred at rt for 6 h. The mixture was washed successively with 2 M hydrochloric acid, 2 M NaOH and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-13f** (1.4354 g, 3.12 mmol, 96%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2 H), 7.87 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 6.8 Hz, 2 H), 4.13 (d, *J* = 12.8 Hz, 1 H), 3.94 (d, *J* = 12.8 Hz, 1 H), 3.88 (s, 3 H), 3.76-3.57 (m, 6 H), 3.53-3.49 (m, 3 H), 3.35 (s, 3 H), 1.21 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 166.2, 148.2, 142.2, 132.2, 130.7, 129.8, 128.5, 127.8, 123.4, 73.3, 72.0, 70.9, 70.6, 68.4, 59.1, 56.7, 52.4, 17.4. HRMS (ESI+) m/z calc*d* for $C_{23}H_{28}N_2NaO_8$ $[M+Na]^+$ 483.1738, found 483.1729.

Synthesis of Compound **II-14a**: LiI (870 mg, 21 eq.) was added to a solution of **II-13a** (96.8 mg, 0.31 mmol) in pyridine (10 mL) and the resulting mixture was stirred for 41 h at 115°C. The mixture was cooled to 0°C, diluted with dichloromethane (50 mL), washed with 2 M HCl (70 mL). The aqueous layer was repeatedly extracted with dichloromethane, and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate / *n*-hexane 4 : 1) to give **II-14a** (84.2 mg, 0.28 mmol, 90%) as a pale yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (*d*, *J* = 8.7 Hz, 2H), 7.98 (*d*, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 3.56 (s, 3H).

Synthesis of Compound **II-14b**: LiI (109 mg, 5.1 eq.) was added to a solution of **II-13b** (55.0 mg, 0.16 mmol) in pyridine (3 mL) and the resulting mixture was stirred for 4 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed with 2 M HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-14b** (57.2 mg, quant.) as a colorless amorphous solid; ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2 H), 7.98 (d, *J* = 8.7 Hz, 2 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 2 H),

3.89 (m, 2H), 3.95 (m, 2 H), 1.67 (sext, *J* = 7.3 Hz, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 168.3, 148.3, 147.5, 142.0, 131.7, 129.7, 128.0, 127.6, 123.4, 52.1, 21.1, 11.4. HRMS (ESI+) m/z calcd for $C_{17}H_{17}N_2O_5$ $[M+H]^+$ 329.1132, found 329.1129.

Synthesis of Compound **II-14c**: LiI (328 mg, 5 eq.) was added to a solution of **II-13c** (173 mg, 0.49 mmol) in pyridine (4 mL) and the resulting mixture was stirred for 5 days at 115°C. The mixture was cooled to 0°C, and was diluted with dichloromethane. The organic layer was washed with 2 M HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-14c** (147 mg, 0.43 mmol, 88%) as a brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 3.86 (d, *J* = 7.8 Hz, 2H), 1.91 (nonuplet, *J* = 6.6 Hz, 1 H), 0.96 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 168.6, 148.2, 147.6, 142.2, 131.6, 129.6, 127.9, 127.5, 123.5, 57.0, 52.5, 27.2, 20.3.

Synthesis of Compound **II-14d**: LiI (147 mg, 1.10 mmol) was added to a solution of **II-13d** (89.9 mg, 0.22 mmol) in pyridine (2.5 mL) and the resulting mixture was stirred for 3 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was and washed with 2 M HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-14d** (86.8 mg, quant.) as a brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 2 H), 7.97 (d, *J* = 8.7 Hz, 2 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, 2 H), 3.97 (dd, *J* = 7.8, 7.8 Hz, 2 H), 1.62 (sext, *J* = 7.3 Hz, 2 H), 1.32-1.25 (m, 10 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 168.2, 148.3, 147.5, 142.0, 131.7, 129.7, 128.0, 127.6, 123.4, 50.7, 31.9, 29.3, 29.3, 27.8, 27.0, 22.7, 14.2.; HRMS (ESI+) m/z calcd for $C_{22}H_{27}N_2O_5$ $[M+H]^+$ 399.1914, found 399.1916.

Synthesis of Compound **II-14f**: LiI (899.5 mg, 6.72 mmol) was added to a solution of **II-13f** (460.8 mg, 1.32 mmol) in pyridine (15 mL) and the resulting mixture was stirred for 4 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was and washed with 2 M HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-14f** (590.4 mg, quant.) as a brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 2 H), 7.92 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 4.16 (d, *J* = 12.8 Hz, 1 H), 3.98 (br, 1 H), 3.78-3.74 (m, 1 H), 3.70-3.48 (m, 8 H), 3.45 (s, 3 H), 1.22 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 168.7, 148.3, 142.1, 131.6, 131.3, 129.8, 127.8, 127.0, 123.4, 73.3, 72.0, 70.9, 70.6, 68.4, 59.1, 56.8, 17.4. HRMS (ESI+) m/z calcd for $C_{22}H_{26}N_2NaO_8$ $[M+Na]^+$ 469.1581, found 469.1583.

Synthesis of Compound **II-15a**: A solution of **II-13a** (199 mg, 0.63 mmol) in dry methanol (12 mL) was hydrogenated with Pd-C (10%, 20.4 mg) for 80 min at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-15a** (194 mg, quant.) as a pale pink solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 8.2Hz, 2H), 3.89 (s, 3H), 3.49 (s, 3H).

Synthesis of Compound **II-15b**: A solution of **II-13b** (37.1 mg, 0.11 mmol) in MeOH (3 mL) was hydrogenated with Pd-C (10%, 5.3 mg) for 90 min at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated

in vacuo to give **II-15b** (31.8 mg, 0.10 mmol, 94%) as a colorless amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 8.7 Hz, 2H), 3.89 (m, 2H), 3.89 (s, 3H), 3.78 (br, 2H), 1.64 (sext, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 166.6, 149.1, 148.3, 131.3, 130.6, 127.4, 12.0, 125.3, 113.8, 52.3, 51.1, 21.3, 11.5. HRMS (ESI+) m/z calcd for $C_{18}H_{21}N_2O_3$ $[M+H]^+$ 313.1547, found 313.1556.

Synthesis of Compound **II-15c**: A solution of **II-13c** (197 mg, 0.55 mmol) in ethyl acetate (6 mL) was hydrogenated with Pd-C (10%, 26 mg) for 4 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-15c** (157 mg, 87%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 8.2Hz, 2H), 3.80 (d, *J* = 7.8 Hz, 2H), 1.94 (nonuplet, *J* = 6.6 Hz, 1 H), 0.93 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 166.6, 149.2, 148.3, 131.2, 130.5, 127.1, 126.8, 125.4, 113.8, 57.1, 52.3, 27.4, 20.4.

Synthesis of Compound **II-15d**: A solution o**f II-13d** (1.15 g, 2.81 mmol) in dry methanol (30 mL) was hydrogenated with Pd-C (10%, 262 mg) for 5 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-15d** (1.11 g, quant.) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 2 H), 7.07 (d, *J* = 8.7 Hz, 2 H), 6.40 (d, *J* = 8.7 Hz, 2 H), 3.91 (dd, *J* = 7.8, 7.8 Hz, 2 H), 3.79 (s, 3 H), 1.62 (sext, *J* = 7.3 Hz, 2 H), 1.34-1.25 (m, 10 H), 0.85 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 166.6, 149.0, 148.4, 131.2, 130.6, 127.3, 127.0, 125.1, 113.7, 52.3, 50.7, 31.9, 29.4, 29.3, 28.0, 27.1, 22.7, 14.2. HRMS (ESI+) m/z calcd for $C_{23}H_{31}N_2O_3$ $[M+H]^+$ 383.2329, found 383.2338.

Synthesis of Compound **II-15f**: A solution of **II-13f** (48.6 mg, 0.11 mmol) in dry methanol (1.5 mL) was hydrogenated with Pd-C (10%, 5.8 mg) for 8 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-15f** (45.1 mg, quant.) as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.86(d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 6.49 (d, *J* = 8.2 Hz, 2 H), 4.15 (dd, *J* = 14.4, 4.0 Hz, 1 H), 3.94 (m, 1 H), 3.87 (s, 3 H), 3.85-3.49 (m, 9 H), 3.45 (s, 3 H), 1.19 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 166.7, 150.2, 148.5, 131.3, 130.4, 127.0, 126.9, 125.0, 113.7, 74.2, 72.0, 70.8, 70.6, 68.5, 59.1, 57.0, 52.2, 17.8. HRMS (ESI+) m/z calcd for $C_{23}H_{30}N_2NaO_6$ $[M+Na]^+$ 453.1996, found 453.1985.

Synthesis of Compound **II-1a**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.98 g, 1.9 eq.) and *N*,*N*-dimethyl-4-aminopyridine (1.24 g, 1.9 eq.) were added to a solution of **II-14a** (1.80 g, 5.99 mmol) and **II-15a** (1.55 g, 1.1 eq.) in DMF (10 mL). The resulting mixture was stirred at rt for 12 h. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was washed with ethyl acetate to give **II-1a** (2.50 g, 4.41 mmol, 81%) as a white powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 7.8Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.88 (s, 3H), 3.55 (s, 3H), 3.52(s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 168.4, 166.3, 164.3, 149.2, 148.5, 147.3, 141.7, 139.3, 133.2, 131.6, 130.8, 130.3, 129.7,

128.6, 128.0, 127.1, 126.5, 123.5, 119.1, 52.4, 38.4, 38.3. HRMS (ESI+) m/z calcd for $C_{31}H_{26}N_4NaO_7$ $[M+Na]^+$ 589.1694, found 589.1685.

Synthesis of Compound **II-1b**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (316 mg, 1.65 mmol) and *N*,*N*-dimethyl-4-aminopyridine (199 mg, 1.63 mmol) were added to a solution of **II-14b** (415 mg, 1.26 mmol) and **II-15b** (390 mg, 1.25 mmol) in DMF (12 mL). The resulting mixture was stirred for 4 h at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate / n-hexane =1 / 5) to give **II-1b** (616 mg, 0.99 mmol, 87%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 3.92 (m, 4H), 3.88 (s, 3H), 1.65 (sext, *J* = 7.3 Hz, 4H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.2, 166.4, 164.3, 148.2, 148.0, 142.1, 139.2, 133.3, 131.9, 130.7, 130.1, 129.6, 128.6, 128.0, 127.9, 127.3, 123.4, 119.1, 52.4, 52.1, 21.2, 21.1, 11.5, 11.4.; HRMS (ESI+) m/z calcd for $C_{35}H_{35}N_4O_7$ $[M+H]^+$ 623.2500, found 623.2486.

Synthesis of Compound **II-1c**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (153 mg, 2.0 eq.) and *N*,*N*-dimethyl-4-aminopyridine (2.4 mg, 5 mol%) were added to a solution of **II-14c** (138 mg, 0.40 mmol) and **II-15c** (151 mg, 1.2 eq.) in dichloromethane (4 mL). The resulting mixture was stirred overnight at rt and diluted with dichloromethane.The organic layer was washed successively with 2 M HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate/chloroform =1/5) to give **II-1c** (221 mg, 0.34 mmol, 84%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2 H), 7.87 (d, *J* = 8.2 Hz, 2 H), 7.84 (s, 1 H), 7.72 (d, *J* = 8.7 Hz, 2 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 7.40 (d, *J* = 8.7 Hz, 2 H), 7.24 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 2 H), 7.08 (d, *J* = 8.2 Hz, 2 H), 3.83 (m, 4 H), 1.91 (m, 2 H), 0.95 (d, *J* = 6.6 Hz, 6 H), 0.93 (d, *J* = 6.6 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 168.5, 166.3, 164.3, 148.2, 148.1, 142.3, 139.1, 133.2, 132.1, 130.7, 130.1, 129.6, 128.5, 127.9, 127.8, 127.2, 123.5, 119.1, 57.0, 52.4, 27.3, 27.2, 20.4, 20.3.

Synthesis of Compound **II-1d**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (44.0 mg, 0.23 mmol) and *N*,*N*-dimethyl-4-aminopyridine (27.9 mg, 0.23 mmol) were added to a solution of **II-14d** (71.8 mg, 0.18 mmol) and **II-15d** (76.8 mg, 0.20 mmol) in DMF (2 mL). The resulting mixture was stirred for 5 h at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate / dichloromethane =1 / 5) to give **II-1d** (117.8 mg, 0.15 mmol, 86%) as a yellow solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.7 Hz, 2 H), 7.64 (s, 1 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.41 (d, *J* = 8.7 Hz, 2 H), 7.28 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 2 H), 7.06 (d, *J* = 8.2 Hz, 2 H), 3.94 (m, 4 H), 3.88 (s, 3 H), 1.61 (m, 4 H), 1.38-1.15 (m, 20 H), 0.86 (dt, *J* = 7.2, 2.2 Hz, 6 H); 13C NMR (150 MHz, $CDCl_3$) δ 169.6, 168.1, 166.4, 164.3, 148.3, 148.1, 146.0, 142.2, 139.2, 133.4, 132.0, 130.7, 130.2, 129.6, 128.6, 128.1, 128.0, 127.3, 123.4, 119.1, 52.4, 50.7, 31.9, 31.9, 29.4, 29.4, 29.3, 29.3, 28.0, 27.8, 27.1,

27.0, 22.7, 14.2. HRMS (ESI+) m/z calcd for $C_{45}H_{55}N_4O_7$ $[M+H]^+$ 763.4065, found 763.4048.

Synthesis of Compound **II-1f**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (30.3 mg, 0.16 mmol) and *N*,*N*-dimethyl-4-aminopyridine (21.1 mg, 0.17 mmol) were added to a solution of **II-14f** (36.2 mg, 0.08 mmol) and II-15f (45.1 mg, 0.10 mmol) in DMF (2 mL). The resulting mixture was stirred for 20 h at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate/methanol =15/1) to give **II-1f** (45.9 mg, 0.06 mmol, 72%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2 H), 7.85 (d, *J* = 8.7 Hz, 2 H), 7.82 (s, 1 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 7.23 (d, *J* = 8.7 Hz, 2 H), 4.16(dd, *J* = 10.5, 3.7 Hz, 2 H), 3.96 (m, 2 H),3.87 (s, 3 H), 3.75-3.47 (m, 18 H), 3.36 (s, 3 H), 3.33 (s, 3 H), 1.21 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 166.5, 164.6, 149.3, 148.3, 142.2, 139.5, 133.0, 131.8, 130.5, 130.3, 129.8, 128.3, 128.2, 127.7, 127.4, 123.4, 119.0, 73.9, 73.5, 72.0, 70.9, 70.9, 70.6, 70.5, 68.5, 68.3, 59.2, 59.1, 56.8, 56.6, 52.3, 17.7, 17.4. HRMS (ESI+) m/z calcd for $C_{45}H_{54}N_4NaO_{13}$ $[M+Na]^+$ 881.3580, found 881.3577.

Synthesis of Compound **II-16**: 2-Nitrobenzenesulfonyl chloride (1.4687 g, 6.63 mmol) was added to a solution of methyl *p*-aminobenzoate (1.0069 g, 6.66 mmol) in dry pyridine (5 mL) at 0°C, and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo*, then the residue was poured into 2 M hydrochloric acid, and extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated to give **II-16** (2.0189 g, 6.00 mmol, 90%) as a red solid ; ^{1}H NMR (400 MHz,DMSO-d_6) δ 11.3 (s, 1 H), 8.04 (d, *J* = 6.4 Hz, 1 H), 8.01 (d, *J* = 8.2 Hz, 1 H), 7.89 (d, *J* = 7.2 Hz, 1 H), 7.87 (d, *J* = 8.7 Hz, 2 H), 7.82 (d, *J* = 7.3 Hz, 1 H), 7.24 (d, *J* = 8.7 Hz, 2 H), 3.79 (s, 3 H).

Synthesis of Compound **II-17**: Diethyl azodicarboxylate (40% in toluene, 345.6 mg, 0.79 mmol) in dry tetrahydrofuran (1 mL) was added to a mixture of **II-16** (132.0 mg, 0.39 mmol), (*R*)-2-(methoxyethoxyethoxy)propanol (73.5 mg, 0.41 mmol), and triphenylphosphine (210.2 mg, 0.80 mmol) in dry tetrahydrofuran (3 mL) under an argon atmosphere at 0°C. The reaction mixture was stirred for 2 days at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/n-hexane=2/1) to give **II-17** (146.7 mg, 0.30 mmol, 75%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2 H), 7.61 (m, 2 H), 7.52 (d, *J* = 7.2 Hz, 1 H), 7.44 (td, *J* = 6.4, 2.3 Hz, 1 H), 7.38 (d, *J* = 8.8 Hz, 2 H), 3.91 (s, 3 H), 3.87 (m, 2 H), 3.63-3.39 (m, 9 H), 3.37 (s, 3 H), 1.18 (t, *J* = 6.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 148.0, 143.5, 133.9, 132.1, 131.8, 131.3, 130.7, 129.6, 129.0, 124.1, 74.9, 72.0, 70.7, 70.6, 68.3, 59.2, 57.0, 52.5, 17.4. HRMS (ESI+) m/z calcd for $C_{22}H_{28}N_2NaO_9S$ $[M+Na]^+$ 519.1408, found 519.1407.

Synthesis of Compound **II-18**: A solution of 10 (1.7309 g, 3.49 mmol) in dry acetonitrile (20 mL) and cesium carbonate (1.4856 g, 4.57 mmol) were added to a solution of benzenethiol (0.5 mL, 4.90 mmol) in acetonitrile (10 mL). The mixture was stirred for 1 h at 45°C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column

chromatography (silica gel, ethyl acetate/n-hexane=1/1) to give **II-18** (1.0073 g, 3.27 mmol, 93%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 2 H), 6.56 (d, *J* = 8.7 Hz, 2 H), 4.88 (br, 1 H), 3.84 (s, 3 H), 3.79-3.71 (m, 2 H), 3.70-3.60 (m, 4 H), 3.59-3.55 (m, 3 H), 3.39 (s, 3 H), 3.30-3.25 (m, 1 H), 3.11-3.05 (m, 1 H), 1.23 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 152.3, 131.6, 118.0, 111.7, 74.3, 72.0, 70.8, 70.6, 68.0, 59.2, 51.6, 48.4, 17.9. HRMS (ESI+) m/z calcd for $C_{16}H_{25}NNaO_5$ $[M+Na]^+$ 334.1625, found 334.1628.

Synthesis of Compound **II-19a**: LiI (123.4 mg, 5.1 eq.) was added to a solution of **II-1a** (99.8 mg, 0.18 mmol) in pyridine (5 mL), and the resulting mixture was stirred for 4 days at 115°C. After removal of the solvent *in vacuo*, the residue was dissolved in water and the solution was poured into 2 M HCl. The gray precipitates was collected and dried to give **II-19a** (82.3 mg, 0.15 mmol, 83%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.2 (s, 1H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 4H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8Hz, 2H), 3.43 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.2, 167.7, 166.6, 164.7, 148.7, 147.6, 146.5, 142.5, 140.3, 132.6, 130.7, 130.1, 129.5, 129.2, 128.8, 128.0, 126.9, 126.6, 123.2, 119.1, 37.6. HRMS (ESI+) m/z calcd for $C_{30}H_{25}N_4O_7$ $[M+H]^+$ 553.1718, found 553.1706.

Synthesis of Compound **II-19b**: LiI (55.2 mg, 5.1 eq) was added to a solution of **II-1b** (51.4 mg, 0.08 mmol) in pyridine (1.5 mL) and the resulting mixture was stirred for 4 days at 115°C. After removal of the solvent *in vacuo*, the residue was poured into 2 M HCl and the precipitate was collected by filtration to give **II-19b** (48.6 mg, 97%) as a yellow-brown solid; ^{1}H NMR(400 MHz,$CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2 H), 7.93 (d, *J* = 8.7 Hz, 2 H), 7.76 (s, 1 H), 7.71 (d, *J* = 8.7 Hz, 2 H), 7.43 (d, *J* = 6.9 Hz, 4 H), 7.29 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, 2 H), 3.93 (m, 4 H), 3.95 (m, 2 H), 1.65 (m, 4 H), 0.94 (m, 6 H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.0, 167.8, 166.7, 164.8, 147.5, 147.4, 145.0, 142.8, 140.2, 132.9, 131.1, 130.2, 129.4, 129.3, 128.8, 128.3, 127.9, 127.5, 125.8, 123.3, 119.2, 50.9, 50.9, 20.6, 20.5, 11.2, 11.2. HRMS (ESI+) m/z calcd for $C_{34}H_{33}N_4O_7$ $[M+H]^+$ 609.2344, found 609.2343.

Synthesis of Compound **II-19c**: LiI (94 mg, 5 eq.) was added to a solution of **II-1c** (91 mg, 0.14 mmol) in pyridine (2 mL) and the resulting mixture was stirred for 5 days at 115°C. The mixture was cooled to 0°C, and was diluted with dichloromethane. The mixture was washed with 2 M HCl and the organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-19c** (104 mg, 0.16 mmol, quant.) as a brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 3.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.6, 168.7, 164.6, 148.5, 148.1, 142.3, 139.4, 133.1, 131.8, 131.3, 130.0, 129.6, 129.2, 128.7, 127.8, 127.5, 127.3, 127.2, 123.5, 119.4, 57.1, 27.3, 27.2, 20.3, 20.3.

Synthesis of Compound **II-19d**: LiI (36.2 mg, 0.27 mmol) was added to a solution of **II-1d** (34.7 mg, 0.05 mmol) in pyridine (1.5 mL) and the resulting mixture was stirred for 4 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with CH2Cl2 and washed with 2 M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-19d** (34.1 mg, quant.) as a brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 2 H), 7.72 (d, *J* = 8.7 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.29 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 8.7 Hz, 2 H), 7.09 (d, *J* = 8.7 Hz, 2 H), 3.97 (m, 4 H), 1.61 (m, 4 H), 1.38-1.15 (m, 20 H), 0.86 (t, *J* = 6.8 Hz, 6 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 169.3, 168.2, 164.5, 148.2, 146.8, 142.1, 139.6, 139.3, 133.3, 131.8, 131.2, 130.1, 129.6, 128.7, 128.0, 127.9, 127.3, 125.1, 123.4, 119.2, 50.7, 31.9, 31.9, 29.4, 29.4, 29.3, 29.3, 27.9, 27.8, 27.0, 27.0, 22.7, 14.2. HRMS (ESI+) m/z calcd for $C_{44}H_{53}N_4O_7$ $[M+H]^+$ 749.3909, found 749.3903.

Synthesis of Compound **II-19f**: LiI (199.7 mg, 1.49 mmol) was added to a solution of **II-1f** (240.6 mg, 0.28 mmol) in pyridine (3 mL) and the resulting mixture was stirred for 4 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane and washed with 2 M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-19f** (272.8 mg, quant.) as a brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2 H), 7.95 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 2 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.44 (d, *J* = 8.2 Hz, 2 H), 7.33-7.25 (m, 6 H), 4.17 (d, *J* = 11.4 Hz, 2 H), 3.97 (m, 2 H), 3.75-3.47 (m, 18 H),3.36 (s, 3 H), 3.33 (s, 3 H), 1.21 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.0, 165.1, 163.1, 149.2, 148.1, 146.0, 142/1. 140.0, 131.1, 131.0, 130.1, 129.8, 128.8, 128.0, 127.5, 127.4, 123.4, 119.4, 73.9, 73.4, 71.9, 71.8, 70.8, 70.7, 70.4, 70.4, 68.2, 68.1, 59.1, 59.0, 56.6, 56.4, 53.6, 36.8, 31.7, 17.6, 17.4. HRMS (ESI+) m/z calcd for $C_{44}H_{52}N_4NaO_{13}$ $[M+Na]^+$ 867.3423, found 867.3426.

Synthesis of Compound **II-20a**: A solution of **II-1a** (41.2 mg, 0.07 mmol) in THF (5 mL) was hydrogenated with Pd-C (10%, 4.9 mg) for 19 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-20a** (38.0 mg, quant.) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.75 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 3.53 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 166.4, 164.9, 161.5, 149.2, 148.6, 139.7, 131.6, 131.2, 131.1, 130.8, 130.2, 128.2, 127.9, 126.6, 126.5, 126.5, 124.5, 119.1, 113.8, 52.4, 38.4, 38.3. HRMS (ESI+) m/z calcd for $C_{31}H_{29}N_4O_5$ $[M+H]^+$ 537.2132, found 537.2123.

Synthesis of Compound **II-20b**: A solution of **II-1b** (63.9 mg, 0.10 mmol) in MeOH (5 mL) was hydrogenated with Pd-C (10%, 9.7 mg) for 90 min at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-20b** (62.8 mg, 0.10 mmol, quant.) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.71 (s, 1 H), 7.68 (d, *J* = 8.7 Hz, 2 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.29 (d, *J* = 8.7 Hz, 2 H), 7.10 (m, 6 H), 6.40 (d, *J* = 8.7 Hz, 2 H), 3.90 (m, 4 H), 3.88 (s, 3 H), 3.86 (br, 2H), 1.63 (m, 4 H), 0.93 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 149.9, 166.4, 165.0, 148.5, 148.0, 148.0, 139.8, 131.7, 131.4, 131.1, 130.7, 130.0, 128.2, 128.0, 127.3, 127.2, 124.9, 119.1, 113.7, 52.4, 52.2, 52.1, 21.2, 21.2, 11.5, 11.5. HRMS (ESI+) m/z calcd for $C_{35}H_{37}N_4O_5$ $[M+H]^+$ 593.2758, found 593.2744.

Synthesis of Compound **II-20c**: A solution of **II-1c** (122 mg, 0.19 mmol) in ethyl acetate (3 mL) was hydrogenated with Pd-C (10%, 21 mg) for 6 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-20c** (104 mg, 89%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.2Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.2Hz, 2H), 6.38 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 3.84 (d, *J* = 6.6 Hz, 2H), 3.79 (d, *J* = 6.6 Hz, 2H), 1.92 (m, 2 H), 0.93 (d, *J* =

6.6 Hz, 6 H), 0.92 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.3, 166.5, 165.0, 148.5, 148.3, 139.6, 131.8, 131.6, 131.3, 130.8, 130.2, 128.2, 127.9, 127.3, 127.3, 125.4, 119.1, 113.9, 57.2, 57.1, 52.5, 27.4, 27.4, 20.5, 20.4.

Synthesis of Compound **II-20d**: A solution of **II-1d** (356.4 mg, 0.47 mmol) in dry ethyl acetate (5 mL) was hydrogenated with Pd-C (10%, 61.7 mg) for 7 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-20d** (342.3 mg, quant.) as a white solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2 H), 7.81 (s, 3 H), 7.68 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.28 (d, *J* = 8.7 Hz, 2 H), 7.09 (m, 6 H), 6.39 (d, *J* = 8.7 Hz, 2 H), 3.93 (m, 4 H), 3.88 (s, 3 H), 1.61 (m, 4 H), 1.38-1.15 (m, 20 H), 0.85 (dt, *J* = 6.7, 2.3 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.7, 166.4, 164.9, 148.4, 148.1, 148.1, 139.6, 131.7, 131.6, 131.2, 130.7, 130.2, 128.1, 127.9, 127.3, 127.3, 125.1, 119.0, 113.8, 52.4, 50.8, 50.6, 31.9, 29.4, 29.4, 29.3, 29.3, 28.0, 27.9, 27.1, 27.0, 22.7, 14.2. HRMS (ESI+) m/z calcd for $C_{45}H_{57}N_4O_5$ $[M+H]^+$ 733.4323, found 733.4307.

Synthesis of Compound **II-20f**: A solution of **II-1f** (246.3 mg, 0.29 mmol) in dry ethyl acetate (4 mL) was hydrogenated with Pd-C (10%, 30.6 mg) for 24 h at rt. The reaction mixture was filtered on Celite, and the filtrate wasconcentrated *in vacuo* to give **II-20f** (231.1 mg, 0.28 mmol, 97%) as a yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.99 (s, 1 H), 7.86 (d, *J* = 8.7 Hz, 2 H), 7.66 (d, *J* = 8.7 Hz, 2 H), 7.46(d, *J* = 8.7 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7,24 (m, 4 H), 7.13 (d, *J* = 8.7 Hz, 2 H), 6.39 (d, *J* = 8.7 Hz, 2 H), 4.15 (m, 2 H), 3.97 (m, 2 H), 3.88 (s, 3 H), 3.82 (s, 2 H), 3.75-3.46 (m, 18 H), 3.36 (s, 3 H), 3.33 (s, 3 H), 1.20 (t, *J* = 6.4 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.2, 166.5, 165.2, 149.4, 148.6, 139.9, 131.4, 131.3, 130.5, 130.3, 128.0, 127.6, 127.4, 124.8, 119.0, 113.7, 74.4, 73.9, 72.0, 72.0, 71.0, 70.9, 70.6, 70.4, 68.5, 68.4, 60.6, 59.2, 59.1, 56.8, 52.3, 21.2, 17.7, 17.7, 14.3. HRMS (ESI+) m/z calcd for $C_{45}H_{56}N_4NaO_{11}$ $[M+Na]^+$ 851.3838, found 851.3832.

Synthesis of Compound **II-2a**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (40.5 mg, 0.21 mmol) and *N*,*N*-dimethyl-4-aminopyridine (25.2 mg, 0.21 mmol) were added to a solution of **II-19a** (89.3 mg, 0.16 mmol) and **II-20a** (85.1 mg, 0.16 mmol) in DMF (1 mL). The resulting mixture was stirred for 31 h at rt and heated at 50°C for 19 h. After removal of the solvent *in vacuo*, the residue was extracted with THF. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo.* THF was added to the residue and the resulting pale yellow precipitates was collected and dried to give **II-2a** (45.4 mg, 26%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.3 (s, 1H), 10.3 (s, 1H), 10.3 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.80 (m, 8H), 7.59 (m, 8H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.27 (m, 12H), 3.79 (s, 3H), 3.42 (s, 3H), 3.40 (s, 3H), 3.40 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.2, 167.8, 165.6, 164.9, 149.1, 147.9, 147.6, 146.5, 142.5, 140.5, 140.4, 140.3, 132.6, 131.9, 130.9, 130.8, 130.6, 130.0, 129.5, 128.8, 128.7, 126.9, 126.9, 126.8, 126.6, 123.2, 119.2, 119.2, 119.1, 52.2, 37.8, 37.6. HRMS (ESI+) m/z calcd for $C_{61}H_{50}N_8NaO_{11}$ $[M+Na]^+$ 1093.3491, found 1093.3463.

Synthesis of Compound **II-2b**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (138 mg, 0.72 mmol) and N,N-dimethyl-4-aminopyridine (89.8 mg, 0.74 mmol) were added to a solution of **II-19b** (223 mg, 0.37 mmol) and **II-20b** (234 mg, 0.39 mmol) in DMF (4 mL). The resulting mixture was stirred for 5 days. After removal of the

solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 4 / 1) to give **II-2b** (264 mg, 0.22 mmol, 61%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1 H), 8.83 (s, 1 H), 8.65 (s, 1 H), 8.00 (d, *J* = 8.7 Hz, 2 H), 7.88 (d, *J* = 8.7 Hz, 2 H), 7.76 (m, 4 H), 7.59 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.44 (m, 6 H), 7.07 (m, 12 H), 3.87 (m, 8 H), 3.86 (s, 3 H), 1.63 (m, 8 H), 0.92 (m, 12 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.1, 167.7, 165.6, 165.0, 147.8, 147.6, 146.4, 142.8, 140.4, 140.3, 140.2, 132.9, 132.2, 131.2, 130.9, 130.1, 129.4, 129.3, 128.8, 128.7, 127.9, 127.6, 127.4, 127.1, 123.2, 119.2, 119.1, 52.2, 51.0, 50.9, 20.6, 20.6, 20.5, 11.2, 11.2. HRMS (ESI+) m/z calcd for $C_{69}H_{66}N_8NaO_{11}$ $[M+Na]^+$ 1205.4743, found 1205.4719.

Synthesis of Compound **II-2c**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (63 mg, 2.1 eq.) and *N*,*N*-dimethyl-4-aminopyridine (1.5 mg, 8 mol%) were added to a solution of **II-19c** (101 mg, 0.16 mmol) and **II-20c** (93 mg, 1.0 eq.) in dichloromethane (3 mL). The resulting mixture was stirred for 2 days at rt and diluted with dichloromethane. The organic layer was washed successively with 2 M HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate/chloroform =1/1) to give **II-2c** (56 mg, 0.05 mmol, 30%) as a white solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 9.31 (s, 1 H), 9.08 (s, 1 H), 8.79 (s, 1 H), 8.00 (d, *J* = 7.2 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 7.8 Hz, 2 H), 7.59 (d, *J* = 7.8 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H)m 7.41 (d, *J* = 8.4 Hz, 2 H), 7.16 (m, 6 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 7.07 (d, *J* = 9.0 Hz, 2 H), 7.00 (m, 8 H), 3.86 (s, 3 H), 3.83 (m, 4 H), 3.77 (d, *J* = 7.2 Hz, 2 H), 7.73 (d, *J* = 7.2 Hz, 2 H), 1.89 (m, 4 H), 0.93 (m, 24 H).

Synthesis of Compound **II-2d**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (175.5 mg, 0.92 mmol) and *N*,*N*-dimethyl-4-aminopyridine (110.2 mg, 0.90 mmol) were added to a solution of **II-19d** (330.0 mg, 0.44 mmol) and **II-20d** (342.2 mg, 0.47 mmol) in DMF (5 mL). The resulting mixture was stirred for 2 days at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate/n-hexane=2/1) to give **II-2d** (480.2 mg, 0.33 mmol, 74%) as a yellow solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.64 (br, 1 H), 8.41 (br, 1 H), 8.33 (br, 1 H), 8.00 (d, *J* = 8.7 Hz, 2 H), 7.89 (d, *J* = 8.7 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 4 H), 7.63 (d, *J* = 8.7 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 6.8 Hz, 2 H), 7.30-7.20 (m, 4 H), 7.16-7.01 (m, 12 H), 3.90 (m, 8 H), 3.86 (s, 3 H), 1.61 (m, 8 H), 1.40-1.20 (m, 40 H), 0.86 (m, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 166.4, 165.6, 165.1, 164.9, 148.1, 148.0, 146.7, 142.3, 140.2, 139.4, 139.2, 132.9, 132.8, 132.0, 131.7, 131.2, 131.0, 130.7, 130.1, 130.0, 129.6, 128.9, 128.8, 128.6, 128.2, 128.0, 127.8, 127.6, 127.4, 127.3, 127.2, 123.4, 120.1, 119.8, 119.2, 119.0, 52.4, 50.8, 50.8, 50.7, 31.9, 29.4, 29.4, 29.4, 29.4, 29.3, 27.9, 27.9, 27.8, 27.1, 27.0, 27.0, 22.8, 14.3. HRMS (ESI+) m/z calcd for $C_{89}H_{107}N_8O_{11}$ [M+H]+ 1463.8054, found 1463.8035.

Synthesis of Compound **II-2f**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (108.8 mg, 0.57 mmol) and *N*,*N*-dimethyl-4-aminopyridine (70.0 mg, 0.57 mmol) were added to a solution of **II-19f** (236.7 mg, 0.28

mmol) and **II-20f** (231.1 mg, 0.28 mmol) in DMF (4 mL). The resulting mixture was stirred for 24 h at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate/methanol =10/1) to give **II-2f** (353.6 mg, 0.21 mmol, 76%) as a pale yellow solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.46 (br, 1 H), 8.43 (br, 1 H), 8.33 (br, 1 H), 8.02 (d, *J* = 8.7 Hz, 2 H), 8.75 (d, *J* = 8.7 Hz, 2 H), 7.69 (d, *J* = 8.7 Hz, 4 H), 7.61 (d, *J* = 8.7 Hz, 2 H), 7.47 (d, *J* = 8.2 Hz, 4 H), 7.38 (m, 4 H), 7.22 (m, 12 H), 4.13 (m, 4 H), 3.92 (m, 4 H), 3.85 (s, 3 H), 3.75-3.40 (m, 36 H), 3.35 (s, 3 H), 3.31 (s, 3 H), 3.30 (s, 3 H), 3.28 (s, 3 H), 1.19 (d, *J* = 6.0 Hz , 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 170.2, 170.2, 166.5, 165.8, 165.2, 162.7, 149.2, 148.2, 142.2, 140.3, 139.8, 139.7, 132.7, 132.2, 132.0, 131.6, 131.5, 131.1, 130.5, 130.3, 130.1, 129.9, 129.8, 128.6, 128.5, 128.4, 128.0, 127.6, 127.5, 127.3, 123.4, 119.7, 119.1, 77.4, 77.2, 76.9, 74.0, 73.9, 72.0, 71.9, 71.9, 71.9, 70.9, 70.9, 70.9, 70.6, 70.5, 70.5, 70.4, 68.4, 68.3, 68.3, 68.2, 60.5, 59.2, 59.1, 59.0, 59.0, 56.8, 56.7, 56.5, 52.3, 36.7, 31.6, 29.8, 21.2, 17.7, 17.6, 17.4, 14.3. HRMS (ESI+) m/z calcd for $C_{89}H_{107}N_8O_{23}$ $[M+H]^+$ 1655.7444, found 1655.7416.

Synthesis of Compound **II-21d**: A solution of **II-2d** (51.9 mg, 0.04 mmol) in dry ethyl acetate (6 mL) was hydrogenated with Pd-C (10%, 10.5 mg) for 24 h at rt. The reaction mixture was filtered on Celite, and the filtrate was concentrated *in vacuo* to give **II-21d** (44.2 mg, 0.03 mmol, 87%) as a white solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.70 (br, 2 H), 8.43 (br, 1 H), 7.88 (d, *J* = 8.7 Hz, 2 H), 7.73 (d, *J* = 8.7 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 4 H), 7.62 (d, *J* = 8.7 Hz, 2 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 6.8 Hz, 2 H), 7.31-7.18 (m, 8 H), 7.18-7.01 (m, 12 H), 6.38 (d, *J* = 8.7 Hz, 2 H), 3.89 (m, 8 H), 3.86 (s, 3 H), 1.61 (m, 8 H), 1.40-1.20 (m, 40 H), 0.86 (m, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.0, 169.8, 166.4, 165.7, 165.2, 148.6, 148.0, 140.1, 139.5, 139.4, 131.8, 131.6, 131.2, 131.0, 130.7, 129.9, 129.6, 128.7, 128.6, 128.4, 127.9, 127.5, 127.2, 124.9, 120.0, 119.9, 119.2, 113.7, 52.4, 50.8, 50.7, 31.8, 29.4, 29.4, 29.3, 29.3, 28.1, 27.9, 27.8, 27.1, 27.0, 22.7, 22.7, 14.2. HRMS (ESI+) m/z calcd for $C_{89}H_{109}N_8O_9$ $[M+H]^+$ 1433.8312, found 1433.8313.

Synthesis of Compound **II-22f**: LiI (33.0 mg, 0.25 mmol) was added to a solution of **II-2f** (79.0 mg, 0.05 mmol) in pyridine (2 mL) and the resulting mixture was stirred for 6 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane and washed with 2 M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-22f** (71.9 mg, 88%) as a brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 9.00 (br, 2 H), 8.83 (br, 1 H), 8.00 (m, 2 H), 7.78 (m, 6 H), 7.50 (m, 8 H), 7.18 (m, 16 H), 4.12 (m, 8H), 3.95 (m, 8 H), 3.70-3.50 (m, 36 H), 3.33-3.26 (m, 12 H), 1.20-1.10 (m, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.4, 165.3, 148.1, 142.2, 140.1, 132.2, 131.3, 131.0, 130.8, 130.0, 129.9, 129.8, 129.0, 128.7, 128.2, 127.8, 127.6, 127.4, 127.3, 123.4, 120.0, 119.7, 119.3, 74.0, 71.8, 71.7, 71.6, 70.8, 70.7, 70.6, 70.5, 70.4, 70.3, 68.3, 68.1, 59.1, 59.1, 59.0, 59.0, 56.5, 56.5, 56.4, 17.6, 17.6, 17.4. HRMS (ESI+) m/z calcd for $C_{88}H_{104}N_8NaO_{23}$ $[M+Na]^+$ 1663.7107, found 1663.7100.

Synthesis of Compound **II-3d**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (30.6 mg, 0.16 mmol) and *N*,*N*-dimethyl-4-aminopyridine (19.5 mg, 0.16 mmol) were added to a solution of **II-14d** (84.6 mg, 0.11 mmol) and **II-21d** (117.9 mg, 0.08 mmol) in DMF (4 mL). The resulting mixture was stirred for 36 h at rt. After removal of

the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by GPC to give **II-3d** (33.1 mg, 0.02 mmol, 19%) as a pale brown solid; ^{1}H NMR(400 MHz, DMSO-d_6) δ 10.28-10.24(m, 5 H), 8.06 (d, *J* = 7.8 Hz, 2 H), 7.81-7.75 (m, 12 H), 7.57-7.55 (m, 12 H), 7.33 (d, *J* = 7.8 Hz, 2 H), 7.25-7.19 (m, 20 H), 3.85 (br, 12 H), 3.77 (s, 3 H), 1.48(br, 12 H), 1.19 (br, 60 H), 0.83-0.81 (m, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 166.4, 164.9, 144.8, 144.5, 142.1, 132.6, 130.7, 130.1, 129.4, 127.9, 127.4, 126.9, 124.1, 123.5, 119.9, 119.3, 52.3, 52.2, 50.8, 50.7, 31.9, 31.8, 29.8, 29.4, 29.4, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.2, 28.0, 27.1, 27.0, 26.9, 26.5, 26.4, 22.8, 22.8, 22.6, 14.3, 14.2. HRMS (ESI+) m/z calcd for $C_{133}H_{158}N_{12}NaO_{15}$ $[M+Na]^+$ 2186.1867 , found 2186.1862.

Synthesis of Compound **II-3f**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (12.7 mg, 2.4 eq.) and *N*,*N*-dimethyl-4-aminopyridine (9.0 mg, 2.7 eq.) were added to a solution of **II-22f** (43.6 mg, 0.027 mmol) and **II-15f** (29.5 mg, 1.3 eq.) in DMF (2 mL). The resulting mixture was stirred for 3 days at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo.* The residue was purified by preparative-TLC (ethyl acetate / methanol = 8 / 1) to give **II-3f** (15.9 mg, 6.5 μmol, 24%) as a pale yellow solid; ^{1}H NMR(400 MHz, DMSO-d_6) δ 10.24 (s, 5 H), 8.07 (br, 2 H), 7.79-7.74 (m, 12 H), 7.58-7.40 (m, 10 H), 7.40 (br, 4 H), 7.34 (m, 10 H), 7.33-7.20 (m, 10 H), 3.99 (m, 6 H), 3.78 (s, 3 H), 3.70-3.68 (m, 14 H), 3.56 (m, 6 H), 3.46-3.31 (m, 36 H), 3.31-3.17 (m, 18 H), 1.10 (s, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 164.8, 144.1, 141.6, 132.6, 130.4, 129.9, 129.2, 129.0, 127.2, 123.3, 119.8, 71.9, 71.6, 70.8, 70.6、70.5, 70.4, 68.2, 59.2, 59.1, 59.0, 59.0, 56.7, 52.1, 29.7, 16.9. HRMS (ESI+) m/z calcd for $C_{133}H_{158}N_{12}NaO_{33}$ $[M+Na]^+$ 2474.0946 , found 2474.0897.

Synthesis of Compound **II-22d**: LiI (33.5 mg, 0.25 mmol) was added to a solution of **II-2d** (79.0 mg, 0.05 mmol) in pyridine (2 mL) and the resulting mixture was stirred for 6 days at 115°C. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane and washed with 2 M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-22d** (71.9 mg, 88%) as a brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 9.00 (br, 2 H), 8.83 (br, 1 H), 8.00 (m, 2 H), 7.78 (m, 6 H), 7.50 (m, 8 H), 7.18 (m, 16 H), 4.12 (m, 8H), 3.95 (m, 8 H), 3.70-3.50 (m, 36 H), 3.33-3.26 (m, 12 H), 1.20-1.10 (m, 12 H).

Synthesis of Compound **II-4d**: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (51.3 mg, 2.5 eq.) and *N*,*N*-dimethyl-4-aminopyridine (34.6 mg, 2.5 eq.) were added to a solution of **II-21d** (181 mg, 1.1 eq.) and **II-22d** (163 mg, 0.11 mmol) in DMF (2 mL). The resulting mixture was stirred for 2 day at rt. After removal of the solvent *in vacuo*, the residue was extracted with dichloromethane. The organic layer was washed successively with 2 M HCl, sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue (31.7 mg) was purified by preparative-TLC (ethyl acetate / *n*-hexane / methanol = 40 / 40 / 1) to give **II-4d** (16.1 mg, 5.6 μmol, 58%) as a pale yellow solid; ^{1}H NMR(400 MHz, DMSO-d_6) δ 10.26 (s, 7 H), 8.06 (d, *J* = 7.8 Hz, 2 H), 7.80 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 7.8 Hz, 14 H), 7.57-7.55 (m, 16 H), 7.32 (d, *J* = 7.2 Hz, 2 H), 7.23-7.19 (m, 28 H), 3.84 (s, 16 H), 3.76 (s, 3 H), 1.47 (s, 16 H), 1.18 (s, 80 H), 0.82-0.79 (m, 24 H); ^{13}C NMR(150 MHz, $CDCl_3$) δ 172.9, 172.2, 170.3,

168.1, 166.4, 164.9, 148.3, 144.8, 144.5, 142.1, 132.6, 130.7, 130.2, 129.4, 127.9, 127.4, 126.9, 124.1, 123.5, 119.9, 119.3, 52.3, 52.2, 50.8, 50.7, 31.9, 31.8, 29.8, 29.4, 29.4, 29.4, 29.3, 29.2, 29.1, 28.9, 28.7, 28.2, 28.0, 27.1, 27.0 ,26.9, 26.5, 26.4, 22.8, 22.8, 22.6, 14.3, 14.2.

Synthesis of Compound **II-23**[98)]: Methyl *p*-iodobenzoate (205.4 mg, 0.78 mmol), $Pd(PPh_3)_2Cl_2$ (26.8 mg, 5% mmol), triphenylphosphine (20.3 mg, 10% mmol), CuI (15.7 mg, 10% mmol) and DMF (8 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (0.3 mL, 2.8 eq.) and (trimethylsilyl)acetylene (0.14 mL, 1.3 eq.), and the mixture was stirred at room temperature for 3 h. Then saturated aqueous ammonium chloride was added, and the mixture was extracted with Et_2O. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (CH_2Cl_2/hexane = 1/2) to give **II-23** as a pale yellow solid (200.4 mg, quant.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2 H), 3.91 (s, 3 H), 0.26 (s, 9 H).

Synthesis of Compound **II-24**[98)]: A 1.0 M solution of tetrabutylammonium fluoride in THF (1 mL, 77 mmol) was added to a stirred solution of **II-23** (182.1 mg, 0.78 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with AcOEt, washed with water three times and brine, and dried over anhydrous Na_2SO_4. Purification with silica gel column chromatography (AcOEt/hexane = 1/2) afforded **II-24** as a colorless solid (96.4 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2 H), 3.92 (s, 3 H), 3.23 (s, 1 H).

Synthesis of Compound **II-25**: Sonogashira coupling reaction of **II-24** with *p*-iodoaniline was carried out in a manner similar to the synthesis of **II-23** by addition of Et_3N (0.23 mL, 2.8 eq.) and *p*-iodoaniline (171.3 mg, 1.3 eq.) to a degassed stirred mixture of **II-24** (96.4 mg, 0.60 mmol), $Pd(PPh_3)_2Cl_2$ (20.9 mg, 5 mol%), triphenylphosphine (15.6 mg, 10 mol%) and CuI (12.0 mg, 10 mol%) in DMF (7 mL) at room temperature, followed by stirring at that temperature for 3 h. Then saturated aqueous ammonium chloride was added, and the mixture was extracted with Et_2O. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (AcOEt/hexane = 1/4) to give **II-25** as a yellow solid (107.8 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 6.64 (d, *J* = 8.2 Hz, 2 H), 3.92 (s, 3 H), 3.87 (br, 2 H).

Synthesis of Compound **II-26**: Triethylamine (0.07 mL, 1.2 eq.) was added to a solution of **II-25** (107.8 mg, 0.43 mmol) in dichloromethane (5 mL), and the mixture was stirred at 0 °C. Benzoyl chloride (0.05 mL, 1.0 eq) was added to the cold amine solution and the mixture was stirred at room temperature for 4 h. The white precipitates were collected and dried to give **II-26** (132.3 mg, 87%) as white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2 H), 7.88 (br, 3 H), 7.68 (m, 2 H), 7.59 (m, 5 H), 7.53 (m, 2 H), 3.93 (s, 3 H).

Synthesis of Compound **II-27**: **II-26** (107.6 mg, 0.30 mmol) and $LiOH \cdot H_2O$ (23.5 mg, 7 eq.) was dissolved in THF (10

mL), methanol (4 mL) and water (4 mL). The mixture was stirred for 3 h at room temperature, acidified with 2 M HCl and extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-27** (85.0 mg, 82%) as a white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 3 H), 7.97 (d, *J* = 8.2 Hz, 2 H), 7.96 (d, *J* = 7.3 Hz, 2 H), 7.89 (d, *J* = 8.7 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.62-7.53 (m, 5 H). ^{13}C NMR (600 MHz, DMSO-d_6) δ 166.8, 165.9, 140.2, 134.8, 132.3, 131.9, 131.5, 129.7, 128.6, 127.8, 126.9, 120.2, 116.5, 92.4, 88.2. HRMS (ESI+) m/z calcd for $C_{22}H_{16}NO_3$ $[M+H]^+$ 342.1125, found 342.1121.

Synthesis of Compound **II-28**: 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (97.5 mg, 2.0 eq.) and *N,N*-dimethyl-4-aminopyridine (61.9 mg, 2.0 eq.) was added to a solution of **II-27** (85.0 mg, 0.25 mmol) and aniline (0.03 mL, 1.3 eq.) in DMF (3.5 mL). The resulting mixture was stirred for 18 h at room temperature. After removal of the solvent *in vacuo*, 2 M HCl was added and the white precipitates were collected and dried to give **II-28** (96.8 mg, 93%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1 H), 10.34 (s, 1 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.96 (d, *J* = 7.2 Hz, 2 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 7.8 Hz, 2 H), 7.70 (d, *J* = 7.8 Hz, 2 H), 7.63-7.58 (m, 3 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 7.36 (t, *J* = 8.4 Hz, 2 H), 7.11 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (600 MHz, DMSO-d_6) δ 165.8, 164.7, 140.0, 139.0, 134.7, 134.4, 132.1, 131.7, 131.2, 128.6, 128.4, 128.0, 127.7, 125.6, 123.8, 91.8, 88.2. HRMS (ESI+) m/z calcd for $C_{28}H_{21}N_2O_2$ $[M+H]^+$ 417.1598, found 417.1592.

Synthesis of Compound **II-5a**: A solution of **II-28** (120.7 mg, 0.29 mmol) in DMF (3.5 mL) was added at 0 °C to a suspension of NaH (60 %, 38.4 mg, 3.3 eq, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min. 1-iodomethane (0.05 mL, 2.8 eq.) was added at 0 °C. The resulting solution was stirred at room temperature for 2.5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 1/1) to give **II-5a** (96.0 mg, 74%) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2 H), 7.30-7.27 (m, 6 H), 7.25-7.22 (m, 3 H), 7.19-7.14 (m, 3 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 3.50 (s ,6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 145.1, 144.8, 135.9, 135.7, 132.5, 131.0, 130.0, 129.4, 129.0, 128.9, 128.0, 127.0, 126.8, 126.8, 124.3, 121.0, 90.0, 89.6, 38.5, 38.3. HRMS (ESI+) m/z calcd for $C_{30}H_{25}N_2O_2$ $[M+H]^+$ 445.1911, found 455.1904.

Synthesis of Compound **II-29**: A solution of **II-26** (200 mg, 0.56 mmol) in DMF (8 mL) was added at 0 °C to a suspension of NaH (60 %, 27.1 mg, 1.2 eq, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min. 1-iodomethane (0.05 mL, 1.4 eq.) was added at 0 °C. The resulting solution was stirred at room temperature for 1.5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 1/1) to give **II-29** (191 mg, 91%) as a pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 6.0 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 6.7 Hz, 2 H), 7.38 (d, J = 8.6 Hz, 2 H), 7.29 (d, J = 7.0 Hz, 2 H), 7.27 (t, J = 8.0 Hz, 1 H), 7.19 (t, J = 7.7 Hz, 2 H), 7.01 (d, J = 8.5 Hz, 2 H), 3.92 (s, 3 H), 3.51 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 166.6, 145.3, 135.7, 132.6, 131.6, 130.1, 129.7, 128.9, 128.1, 127.7, 126.8, 120.7, 119.9, 91.5, 89.4, 52.4, 38.3. HRMS (ESI+) m/z calcd for

$C_{24}H_{20}NO_3$ $[M+H]^+$ 370.1438, found 370.1434.

Synthesis of Compound **II-30**: **II-29** (829 mg, 2.2 mmol) and LiOH·H_2O (567 mg, 6 eq.) was dissolved in THF (60 mL), methanol (24 mL) and water (24 mL). The mixture was stirred for 3 h at room temperature, acidified with 2 M HCl and extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-30** (757 mg, 95%) as a pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.30 (m, 3 H), 7.20 (t, J = 7.2 Hz, 2 H), 7.03 (d, J = 8.4 Hz, 2 H), 3.53 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 169.8, 145.4, 135.7, 132.7, 131.7, 130.3, 130.1, 128.9, 128.6, 128.1, 126.9, 120.6, 92.0, 89.4, 38.3. HRMS (ESI+) m/z calcd for $C_{23}H_{18}NO_3$ $[M+H]^+$ 356.1281, found 356.1272.

Synthesis of Compound **II-31**: 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (61.6 mg, 1.9 eq.) and *N,N*-dimethyl-4-aminopyridine (1.4 mg, 5 mol%) was added to a solution of **II-30** (61.3 mg, 0.17 mmol) and **II-25** (43.4 mg, 1.0 eq.) in DMF (2 mL). The resulting mixture was stirred for 2 day at room temperature. After removal of the solvent *in vacuo*, 2 M HCl was added and the white precipitates were collected and dried to give **II-31** (67.0 mg, 66%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2 H), 7.86 (d, J = 6.0 Hz, 3 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.61 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 9.0 Hz, 2 H), 7.41 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 6.6 Hz, 2 H), 7.28 (t, J = 7.2 Hz, 1 H), 7.21 (m, 3 H), 7.03 (d, J = 8.4 Hz, 2 H), 3.93 (s, 3 H), 3.53 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 166.7, 164.9, 145.4, 138.4, 135.8, 134.2, 132.9, 132.7, 132.1, 131.7, 131.6, 130.1, 129.7, 129.6, 128.9, 128.2, 128.1, 127.3, 127.1, 126.9, 120.7, 120.0, 118.9, 92.2, 91.5, 89.2, 88.8, 52.4, 38.3. HRMS (ESI+) m/z calcd for $C_{39}H_{29}N_2O_4$ $[M+H]^+$ 589.2122, found 589.2107.

Synthesis of Compound **II-32**: A solution of **II-31** (124 mg, 0.21 mmol) in DMF (3 mL) was added at 0 °C to a suspension of NaH (60 %, 22.4 mg, 2.6 eq, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min. 1-iodomethane (123.1 mg, 4.1 eq.) was added at 0 °C. The resulting solution was stirred at room temperature for 1.5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 1/1) to give **II-32** (54.7 mg, 43%) as a yellow solid; ^{1}H NMR (600 MHz, CD_3OD) δ 8.00 (d, J = 8.4 Hz, 2 H), 7.60 (d, J = 6.6 Hz, 2 H), 7.46 (d, J = 9.0 Hz, 2 H), 7.37 (m, 4 H), 7.30 (m, 5 H), 7.23 (t, J = 7.2 Hz, 2 H), 7.19 (d, J = 9.0 Hz, 2 H), 7.14 (d, J = 9.0 Hz, 2 H), 3.92 (s, 3 H), 3.50 (s, 3 H), 3.47 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 166.6, 145.1, 144.9, 135.7, 135.4, 132.7, 132.5, 131.6, 131.2, 139.0, 129.8, 129.7, 129.0, 128.9, 128.0, 127.7, 126.8, 126.8, 124.7, 121.0, 120.8, 91.3, 90.3, 89.6, 89.4, 52.4, 38.3. HRMS (ESI+) m/z calcd for $C_{40}H_{31}N_2O_4$ $[M+H]^+$ 603.2278, found 603.2264.

Synthesis of Compound **II-33**: **II-32** (44.6 mg, 0.07 mmol) and LiOH · H_2O (20.5 mg, 7 eq.) was dissolved in THF (2.5 mL), methanol (1 mL) and water (1 mL). The mixture was stirred for 7 h at room temperature, acidified with 2 M HCl and the yellow precipitates were collected and dried to give **II-33** (39.2 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 6.8 Hz, 2 H), 7.57 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 7.33- 7.16 (m, 11 H), 7.03 (m, 2 H), 6.98 (d, J = 8.4 Hz, 2 H), 3.52 (s, 3 H), 3.50 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 170.1, 170.0, 145.1, 145.0, 135.6,

135.4, 132.8, 132.7, 132.5, 131.7, 131.2, 130.3, 130.1, 130.1, 129.0, 128.9, 128.9, 128.5, 128.1, 128.1, 126.9, 126.8, 124.7, 121.0, 120.9, 91.8, 90.3, 89.6, 89.5, 38.3, 38.3. HRMS (ESI+) m/z calcd for $C_{39}H_{29}N_2O_4$ $[M+H]^+$ 589.2122, found 589.2108.

Synthesis of Compound **II-34**: 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (63.8 mg, 1.9 eq.) and *N,N*-dimethyl-4-aminopyridine (1.1 mg, 5 mol%) was added to a solution of **II-33** (99.0 mg, 0.17 mmol) and aniline (41.3 mg, 2.6 eq.) in DMF (2 mL). The resulting mixture was stirred overnight at room temperature. After removal of the solvent *in vacuo*, 2 M HCl was added and the pale yellow precipitates were collected and dried to give **II-34** (87.2 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1 H), 7.85 (d, *J* = 6.6 Hz, 2 H), 7.64 (d, *J* = 7.9 Hz, 2 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.38 (m, 4 H), 7.37-7.24 (m, 9 H), 7.17 (m, 3 H), 7.02 (m, 2 H), 6.99 (d, *J* = 8.5 Hz, 2 H), 3.52 (s, 3 H), 3.49 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 165.0, 145.1, 144.9, 137.8, 135.6, 135.4, 134.6, 132.7, 132.6, 132.5, 132.0, 132.0, 131.2, 130.1, 130.0, 129.3, 129.0, 128.9, 128.9, 128.1, 128.0, 127.3, 126.9, 126.8, 126.7, 126.7, 124.9, 124.7, 121.0, 120.9, 120.7, 120.3, 91.1, 90.3, 89.5, 89.4, 38.3. HRMS (ESI+) m/z calcd for $C_{45}H_{34}N_3O_3$ $[M+H]^+$ 664.2595, found 664.2580.

Synthesis of Compound **II-6a**: A solution of **II-34** (84.4 mg, 0.13 mmol) in DMF (3 mL) was added at 0 °C to a suspension of NaH (60 %, 17.3 mg, 3.3 eq, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min. 1-iodomethane (55.8 mg, 3.0 eq.) was added at 0 °C. The resulting solution was stirred at room temperature for 1 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 2/1) to give **II-6a** (50.4 mg, 58%) as a yellow solid; ^{1}H NMR (600 MHz, CD_3OD) δ 7.39-7.34 (m, 6 H), 7.31-7.26 (m, 11 H), 7.24-8.18 (m, 3 H), 7.13 (m, 6 H), 3.43 (m, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 145.1, 144.8, 144.8, 135.9, 135.7, 135.5, 132.6, 132.5, 131.2, 131.0, 130.0, 129.4, 129.0, 128.9, 128.0, 127.0, 126.8, 124.7, 124.2, 121.3, 120.9, 90.3, 89.9, 89.8, 89.5, 38.5, 38.3, 38.3. HRMS (ESI+) m/z calcd for $C_{46}H_{36}N_3O_3$ $[M+H]^+$ 678.2751, found 678.2734.

Synthesis of Compound **II-35**: 2-Nitrobenzenesulfonyl chloride (20.2 g, 91.2 mmol) was added to a solution of 4-Iodoaniline (20.0 g, 91.3 mmol) in dry pyridine (55 mL) at 0°C, and the reaction mixture was stirred for 2 h at room temperature. After the solvent was removed *in vacuo*, the residue was poured into 2 M hydrochloric acid, and extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated to give **II-35** (31.4 g, 77.7 mmol, 85%) as a brown solid; ^{1}H NMR(400 MHz, DMSO-d_6) δ 10.87 (s, 1 H), 8.07-7.95 (m, 2 H), 7.87-7.81 (m, 2 H), 7.62 (d, *J* = 8.9 Hz, 2 H), 6.94 (d, *J* = 8.6 Hz, 2 H).

Synthesis of Compound **II-36a**: A solution of **II-35** (5 g, 12.4 mmol) in DMF (10 mL) was added to a suspension of NaH (60 %, 544 mg, 1.1 eq., washed with *n*-hexane twice) in DMF (10 mL) at 0°C. The solution was stirred at r.t. for 5 min. MeI (0.8 mL, 1.0 eq.) was added to the mixture at 0°C. The resulting solution was stirred at rt overnight. After removal of the solvent *in vacuo*, the residue was extracted with ethyl acetate and washed with water. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was

purified by silica gel column chromatography (ethyl acetate /*n*-hexane = 1:3) to give **II-36a** (4.4 g, 85%) as orange oil; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.69-7.64 (m, 3 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 7.55 (m, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 3.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 138.6, 134.1, 131.7, 131.3, 130.9, 129.3, 125.0, 124.0, 93.5, 39.3.

Synthesis of Compound **II-36c**: A solution of **II-35** (4.28 g, 10.6 mmol) in DMF (10 mL) was added at 0°C to a suspension of NaH (60 %, 636 mg, 1.5 eq., washed with *n*-hexane twice) in DMF (10 mL). The solution was stirred at rt for 5 min. 1-iodo-2-methylpropane (1.8 mL, 1.5 eq.) was added at 0°C. The resulting solution was stirred overnight at 50°C. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo.* The residue was purified by silica gel column chromatography (silica gel, chloroform / *n*-hexane = 3 / 1) to give **II-36c** (2.93 g, 60%) as a pale yellow solid; ^{1}H NMR(600 MHz,$CDCl_3$) δ 7.64 (m, 3 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 7.48 (m, 2 H), 6.98 (d, *J* = 7.8 Hz, 2 H), 3.56 (d, *J* = 7.2 Hz, 2H), 1.59 (nonuplet, 1 H), 0.94 (s, 3 H), 0.93 (s, 3 H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 138.7, 138.2, 133.8, 132.1, 131.8, 131.3, 131.1, 123.9, 93.9, 59.5, 27.2, 19.8.

Synthesis of Compound **II-36e**: Diisopropyl azodicarboxylate (10.03 g, 49.6 mmol) in dry tetrahydrofuran (20 mL) was added to a mixture of **II-35** (9.96 g, 24.6 mmol), triethylene glycol monomethyl ether (4.1 g, 25.2 mmol), and triphenylphosphine (12.89 g, 49.1 mmol) in dry tetrahydrofuran (130 mL) under an argon atmosphere at 0°C. The reaction mixture was stirred for 8 h at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1/2) to give **II-36e** (9.91 g, 18.0 mmol, 73%) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.58 (m, 5 H), 7.52 (t, *J* = 6.6 Hz, 1 H), 7.00 (d, *J* = 6.6 Hz, 2 H), 3.94 (t, *J* = 5.4 Hz, 2 H), 3.61-3.52 (m ,10 H), 3.38 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 138.7, 138.2, 133.8, 132.1, 132.1, 131.8, 131.4, 124.1, 94.3, 72.0, 70.7, 70.6, 70.4, 68.9, 59.2, 51.7. HRMS (ESI+) m/z calcd for $C_{19}H_{23}IN_2NaO_7S$ $[M+Na]^+$ 573.0163, found 573.0157. HRMS (ESI+) m/z calcd for $C_{19}H_{23}IN_2NaO_7S$ $[M+Na]^+$ 573.0163, found 573.0157.

Synthesis of Compound **II-36g**: Diisopropyl azodicarboxylate (208 mg, 1.0 mmol) in dry tetrahydrofuran (4 mL) was added to a mixture of **II-35** (200 mg, 0.49 mmol), (*S*)-2-(methoxyethoxyethoxy)propanol (110 mg, 0.62 mmol), and triphenylphosphine (260 mg, 1.0 mmol) in dry tetrahydrofuran (3 mL) under an argon atmosphere at 0°C. The reaction mixture was stirred for 1 h at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 / 1) to give **II-36g** (233 mg, 0.41 mmol, 83%) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65-7.60 (m, 4 H), 7.53 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.49 (dt, *J* = 7.2, 1.2 Hz, 1 H), 7.03 (d, *J* = 7.2 Hz, 2 H), 3.81 (dd, *J* = 16.2, 7.2 Hz, 1 H), 3.76 (dd, *J* = 13.8, 4.8 Hz, 1 H), 3.64-3.48 (m, 8 H), 3.43-3.39 (m, 1 H), 3.38 (s, 3 H), 1.17 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.0, 139.0, 138.5, 133.7, 132.1, 131.8, 131.3, 131.3, 123.9, 93.8, 74.6, 71.9, 70.6, 68.1, 59.1, 57.0, 17.3. HRMS (ESI+) m/z calcd for $C_{20}H_{25}IN_2NaO_7S$ $[M+Na]^+$ 587.0319, found 587.0312.

Synthesis of Compound **II-37a**: **II-36a** (4.38 g, 10.5 mmol), $Pd(PPh_3)_2Cl_2$ (368 mg, 5 mol%), triphenylphosphine (271 mg, 10 mol%), CuI (206 mg, 10 mol%) and acetonitrile (25 mL) were placed in a two-neck round bottom flask.

Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (2.9 mL, 2.1 eq.) and (trimethylsilyl)acetylene (1.7 mL, 10.5 mmol) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate /*n*-hexane = 1:3) to give **II-37a** (4.07 g, quant.) as a white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ7.65 (m, 1 H), 7.59 (d, *J* = 7.2 Hz, 1 H), 7.49 (d, *J* = 5.4 Hz, 2 H), 7.41 (dd, *J* = 6.6, 2.4 Hz, 2 H), 7.19 (dd, *J* = 6.6, 1.8 Hz, 2 H), 3.38 (s, 3 H), 0.24 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ148.5, 140.4, 133.9, 133.0, 131.8, 131.2, 131.0, 127.1, 124.0, 123.0, 104.0, 96.0, 39.2, 0.0.

Synthesis of Compound **II-37c**: **II-36c** (2.90 g, 6.30 mmol), $Pd(PPh_3)_2Cl_2$ (222 mg, 5% mmol), triphenylphosphine (162 mg, 10% mmol), CuI (124 mg, 10% mmol) and DMF (40 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (1.75 mL, 2.0 eq.) and (trimethylsilyl) acetylene (1 mL, 1.3 eq.), and the mixture was stirred at room temperature for 4 h. Then saturated aqueous ammonium chloride was added, and the mixture was extracted with Et_2O. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. The crude product was purified by recrystallization (chloroform) to give **II-37c** (2.85 g, quant.) as a orange solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (m, 2 H), 7.43 (d, *J* = 6.0 Hz, 2 H), 7.40 (d, *J* = 6.6 Hz, 2 H), 7.19 (d, *J* = 6.6 Hz, 2 H), 3.60 (d, *J* = 7.2 Hz, 2 H), 1.59 (nonuplet, *J* = 7.2 Hz, 1 H), 0.94 (s, 3 H), 0.93 (s, 3 H), 0.24 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 138.4, 133.6, 133.1, 132.2, 131.9, 131.1, 128.9, 123.9, 123.9, 123.1, 103.9, 96.1, 59.5, 27.3, 19.8, 0.0.

Synthesis of Compound **II-37e**: **II-36e** (11.4 g, 20.8 mmol), $Pd(PPh_3)_2Cl_2$ (650 mg, 4 mol%), triphenylphosphine (600 mg, 11 mol%), CuI (360 mg, 9 mol%) and acetonitrile (90 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (8.3 mL, 2.8 eq.) and (trimethylsilyl)acetylene (3.4 mL, 1.2 eq.), and the mixture was stirred at room temperature for 3 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **II-37e** (8.13 g, 75%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2 H), 7.52 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.46 (dt, *J* = 7.2, 1.8 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 3.97 (t, *J* = 6.6 Hz, 2 H), 3.61-3.52 (m, 10 H), 3.38 (s, 3 H), 0.24 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 138.3, 133.7, 133.0, 132.2, 131.3, 129.6, 124.0, 123.5, 103.9, 96.2, 72.1, 70.7, 70.7, 70.4, 69.0, 59.2, 52.7, -0.01. HRMS (ESI+) m/z calcd for $C_{24}H_{32}N_2NaO_7SSi$ $[M+Na]^+$ 543.1592, found 543.1581.

Synthesis of Compound **II-37g**: **II-36g** (300 mg, 0.53 mmol), $Pd(PPh_3)_2Cl_2$ (19.0 mg, 5 mol%), triphenylphosphine (16.7 mg, 12 mol%), CuI (10.5 mg, 10 mol%) and acetonitrile (7 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (0.22 mL, 3.0 eq.) and (trimethylsilyl)acetylene (0.09 mL, 1.2 eq.), and the mixture was stirred at room temperature for 2 h. Then the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1 / 2) to give **II-37g** as yellow oil (283 mg, quant.);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2 H), 7.47 (d, *J* = 6.9 Hz, 1 H), 7.43 (dt, *J* = 7.2, 1.8 Hz, 1 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 3.85 (dd, *J* = 14.4, 7.2 Hz, 1 H), 3.78 (dd, *J* = 14.4, 4.8 Hz, 1 H), 3.60-3.48 (m, 8 H), 3.42-3.38 (m, 1 H), 3.37 (s, 3 H), 1.17 (d, *J* = 6.6 Hz, 3 H), 0.23 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.9, 139.0, 133.6, 132.9, 132.1, 131.8, 131.2, 129.1, 123.9, 123.0, 103.8, 95.9, 74.7, 71.9, 70.6, 70.6, 68.2, 59.1, 56.9, 17.4. HRMS (ESI+) m/z calcd for $C_{25}H_{34}N_2NaO_7SSi$ $[M+Na]^+$ 557.1748, found 557.1732.

Synthesis of Compound **II-38a**: A solution of **II-37a** (4.50 g, 11.6 mmol) in dry acetonitrile (50 mL) and cesium carbonate (4.81 g, 14.7 mmol) was added to a solution of benzenethiol (1.75 mL, 17.1 mmol). The mixture was stirred for 2 h at 60°C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, dichloromethane/*n*-hexane = 1 / 2) to give **II-38a** (1.61 g, 7.93 mmol, 68%) as orange oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 9.0 Hz, 2 H), 6.49 (d, *J* = 9.0 Hz, 2 H), 3.87 (br, 1 H), 2.83 (s, 3 H), 0.22 (s, 9 H).^{13}C NMR (150 MHz, $CDCl_3$) δ149.5, 133.5, 111.9, 111.0, 106.6, 91.2, 30.5, 0.3.

Synthesis of Compound **II-38c**: A solution of **II-37c** (2.85 g, 6.30 mmol) in dry acetonitrile (60 mL) and cesium carbonate (2.79 g, 1.3 eq.) was added to a solution of benzenethiol (1 mL, 1.5 eq.) in acetonitrile (5 mL). The mixture was stirred for 1 h at 45°C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1 / 4) to give **II-38c** (1.45 g, 89%) as a pale yellow solid; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2 H), 6.47 (d, *J* = 8.4 Hz, 2 H), 3.87 (br, 1 H), 2.92 (d, *J* = 6.6 Hz, 2 H), 1.87 (nonuplet, *J* = 6.6 Hz, 2 H), 0.98 (s, 3 H), 0.97 (s, 3 H), 0.22 (s, 9 H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 133.5, 112.2, 110.7, 106.6, 91.1, 51.5, 28.2, 20.6. 0.4.

Synthesis of Compound **II-38e**: A solution of **II-37e** (8.10 g, 15.6 mmol) in dry acetonitrile (100 mL) and cesium carbonate (5.69 g, 17.5 mmol) was added to a solution of benzenethiol (2.2 mL, 0.82 mmol). The mixture was stirred for 7 h at 45^{o}C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1/1) to give **II-38e** (3.57 g, 68%) as a yellow oil; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2 H), 6.50 (d, *J* = 8.4 Hz, 2 H), 4.39 (br, 1 H), 3.69 (t, *J* = 5.4 Hz, 2 H), 3.65-3.64 (m, 6 H), 3.56-3.55 (m, 2 H), 3.38 (s, 3 H), 3.29 (t, *J* = 5.4 Hz, 2 H), 0.22 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.5, 133.4, 112.5, 111.1, 106.5, 91.2, 72.0, 70.7, 70.4, 69.5, 59.2, 43.2, 0.31. HRMS (ESI+) m/z calcd for $C_{18}H_{30}NO_3Si$ $[M+H]^+$ 336.1989, found 336.1982.

Synthesis of Compound **II-38g**: A solution of **II-37g** (280 mg, 0.52 mmol) in dry acetonitrile (6 mL) and cesium carbonate (211 mg, 0.64 mmol) was added to a solution of benzenethiol (91 mg, 0.82 mmol) in acetonitrile (1 mL). The mixture was stirred for 2 h at 45°C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 / 2) to give **II-38g** (158 mg, 0.45 mmol, 86%) as yellow oil;

^{1}H NMR(600 MHz, $CDCl_3$) δ 7.27 (d, *J* = Hz, 2 H), 6.51 (d, *J* = Hz, 2 H), 4.55 (br, 1 H), 3.76-3.70 (m, 2 H), 3.66-3.62 (m, 4 H), 3.57-3.54 (m, 3 H), 3.38 (s, 3 H), 3.21 (m, 1 H), 3.02 (dd, *J* = Hz, 1 H), 1.21 (d, *J* = Hz, 3 H), 0.22 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 133.4, 112.5, 110.9, 106.6, 91.1, 74.4, 72.1, 70.9, 70.6, 68.1, 59.2, 48.8, 17.9. HRMS (ESI+) m/z calcd for $C_{19}H_{31}NNaO_3Si$ $[M+Na]^+$ 372.1965, found 372.1962.

Synthesis of Compound **II-39a**: Triethylamine (2.4 mL, 17.2 mmol) was added to a solution of **II-38a** (1.20 g, 5.92 mmol) in dichloromethane (4 mL), and the mixture was stirred at 0°C. 4-iodobenzoyl chloride (1.58 g, 5.92 mmol) in dichloromethane (2 mL) was added to the cold amine solution and the mixture was stirred for 1 h at room temperature. *n*-hexane was added to the reaction solution and precipitant was removed by filtration. The filtrate was washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated to give **II-39a** as a yellow solid (2.31 g, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.4, 1.8 Hz, 2 H), 7.33 (dd, *J* = 9.0, 2.4 Hz, 2 H), 7.00 (dd, *J* = 8.4, 1.8 Hz, 2 H), 6.93 (dd, *J* = 9.0, 2.4 Hz, 2 H), 3.46 (s, 3 H), 0.23 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ169.7, 144.7, 137.2, 135.2, 133.1, 130.6, 126.6, 121.6, 104.0, 96.7, 95.6, 38.4, 0.0.

Synthesis of Compound **II-39c**: Triethylamine (1.1 mL, 2.0 eq.) was added to a solution of **II-38c** (966 mg, 3.9 mmol) in dichloromethane (5 mL), and the mixture was stirred at 0°C. A solution of 4-iodobenzoyl chloride (1.05 g, 1.1 eq.) in dichloromethane (5 mL) was added to the cold amine solution and the mixture was stirred at rt overnight. The mixuture was washed successively with 2 M hydrochloric acid, 2 M NaOH and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **II-39c** (1.69 g, 90%) as pale yellow amorphous; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.6 Hz, 2 H), 7.31 (d, *J* = 6.6 Hz, 2 H), 6.97 (d, *J* = 6.6 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 3.76 (d, *J* = 7.2 Hz, 2 H), 1.88 (nonuplet, *J* = 7.2 Hz, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H), 0.22 (s, 9 H). ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 137.2, 135.8, 133.0, 130.4, 127.3, 121.5, 104.0, 96.3, 95.6, 57.0, 27.1, 20.3, 0.0.

Synthesis of Compound **II-39e**: Triethylamine (1.25 mL, 8.97 mmol) was added to a solution of **II-38e** (1.50 g, 4.47 mmol) in dichloromethane (32 mL), and the mixture was stirred at 0°C. 4-iodobenzoyl chloride (1.19 g, 4.46 mmol) in dichloromethane (6 mL) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated to give **II-39e** as yellow oil (2.49 g, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 9.0 Hz, 2 H), 7.04 (d, *J* = 9.0 Hz, 2 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 4.05 (t, *J* = 6.0 Hz, 2 H), 3.74 (t, *J* = 5.4 Hz, 2 H), 3.60 (m, 6 H), 3.54-3.52 (m, 2 H), 3.37 (s, 3 H), 0.21 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 137.1, 135.3, 132.8, 130.5, 127.5, 121.4, 104.0, 96.6, 95.3, 71.9, 70.6, 70.6, 70.3, 68.1, 59.1, 50.5, -0.1. HRMS (ESI+) m/z calcd for $C_{25}H_{32}INNaO_4Si$ $[M+Na]^+$ 588.1037, found 588.1036.

Synthesis of Compound **II-39g**: Triethylamine (53.4 mg, 0.53 mmol) was added to a solution of **II-38g** (80.0 mg, 0.23 mmol) in dichloromethane (4 mL), and the mixture was stirred at 0°C. 4-iodobenzoyl chloride (67.3 mg, 0.25 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over

anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **II-39g** as yellow oil (113.6 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 9.0 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 4.05 (dd, *J* = 13.8 Hz, 3.0 Hz, 1 H), 3.91 (m, 1 H), 3.71-3.61 (m, 2 H), 3.60-3.56 (m, 4 H), 3.51-3.50 (m, 3 H), 3.36 (s, 3 H), 1.18 (d, *J* = 6.0 Hz, 3 H), 0.21 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 137.2, 135.7, 132.8, 130.6, 127.6, 121.4, 104.3, 96.6, 95.3, 73.8, 72.1, 70.9, 70.6, 68.4, 59.2, 56.6, 17.7, 0.0. HRMS (ESI+) m/z calcd for $C_{26}H_{34}INNaO_4Si$ $[M+Na]^+$ 602.1194, found 602.1184.

Synthesis of Compound **II-40a**: Triethylamine (0.7 mL, 5.02 mmol) was added to a solution of **II-38a** (408 mg, 2.00 mmol) in dichloromethane (4 mL), and the mixture was stirred at 0^{o}C. Benzoyl chloride (281 mg, 2.00 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. *n*-hexane was added to the reaction solution and precipitant was removed by filtration. The filtrate was washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to give **II-40a** as a yellow solid (617 mg, quant.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.7, 2.3 Hz, 2 H), 7.27 (m, 2 H), 7.25 (tt, *J* = 7.2, 1.8 Hz, 1 H), 7.17 (dt, *J* = 7.2, 1.8 Hz, 2 H), 6.95 (dd, *J* = 8.7, 2.3 Hz, 2 H), 3.48 (s, 3 H), 0.22 (s, 9 H).^{13}C NMR (150 MHz, $CDCl_3$) δ170.7, 145.1, 135.8, 132.9, 130.0, 128.9, 128.0, 126.7, 121.2, 104.2, 95.2, 38.3, 0.0.

Synthesis of Compound **II-40c**: Triethylamine (0.55 mL, 2.0 eq.) was added to a solution of **II-38c** (485 mg, 1.97 mmol) in dichloromethane (15 mL), and the mixture was stirred at 0°C. A solution of benzoyl chloride (0.25 mL, 1.3 eq.) was added to the cold amine solution and the mixture was stirred at rt overnight. The mixuture was washed successively with 2 M hydrochloric acid, 2 M NaOH and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to give **II-40c** (676 mg, 98%). ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 3.76 (d, *J* = 7.2 Hz, 2 H), 1.88 (m, 1 H), 0.92 (d, *J* = 6.6 Hz, 6 H), 0.22 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.7, 144.0, 136.4, 132.8, 129.7, 128.7, 128.0, 127.4, 121.1, 104.2, 95.2, 56.9, 27.2, 20.3, 0.0.

Synthesis of Compound **II-40e**: Triethylamine (0.83 mL, 5.95 mmol) was added to a solution of **II-38e** (1.00 g, 2.98 mmol) in dichloromethane (25 mL), and the mixture was stirred at 0^{o}C. Benzoyl chloride (0.35 mL, 3.01 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **II-40e** as yellow oil (1.34 mg, quant.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27-7.25 (m, 4 H), 7.22 (tt, *J* = 6.6, 1.2 Hz, 1 H), 7.14 (t, *J* = 7.2 Hz, 2 H), 4.06 (t, *J* = 5.4 Hz, 2 H), 3.75 (t, *J* = 5.4 Hz, 2 H), 3.61-3.60 (m, 6 H), 3.53-3.51 (m, 2 H), 3.36 (s, 3 H), 0.20 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 144.4, 135.9, 132.7, 129.9, 128.9, 128.0, 127.6, 121.1, 104.3, 95.0, 72.0, 70.7, 70.7, 70.4, 68.3, 59.2, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{25}H_{33}NNaO_4Si$ $[M+Na]^+$ 462.2071, found 462.2063.

Synthesis of Compound **II-40g**: Triethylamine (50.4 mg, 0.50 mmol) was added to a solution of **II-38g** (70.0 mg, 0.20 mmol) in dichloromethane (4 mL), and the mixture was stirred at 0°C. Benzoyl chloride (35.6 mg, 0.25 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **II-40g** as yellow oil (88.4 mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (m, 3 H), 7.23 (t, *J* =7.8 Hz, 2 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 4.08 (dd, *J* = 13.8, 3.6 Hz, 1 H), 3.93 (m, 1 H), 3.72-3.65 (m, 2 H), 3.60-3.57 (m, 4 H), 3.52-3.51 (m, 3 H), 3.36 (s, 3 H), 1.19 (d, *J* = 6.6 Hz, 3 H), 0.22 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 136.2, 132.6, 129.9, 128.9, 128.0, 127.6, 121.0, 104.5, 95.0, 73.8, 72.1, 71.0, 70.6, 68.5, 59.2, 56.6, 17.7, 0.0. HRMS (ESI+) m/z calcd for $C_{26}H_{35}NNaO_4Si$ $[M+Na]^+$ 476.2228, found 476.2224.

Synthesis of Compound **II-41a**: A 1.0 M solution of tetrabutylammonium fluoride in THF (2 mL, 2 mmol) was added to a stirred solution of **II-40a** (620 mg, 2.0 mmol) in THF (12 mL) at room temperature. After stirred at room temperature for 30 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **II-41a** as a white solid (439 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.4, 1.8 Hz, 2 H), 7.28 (m, 3 H), 7.19 (dt, *J* = 7.8, 1.8 Hz, 2 H), 6.98 (dd, *J* = 8.4, 1.8 Hz, 2 H), 3,49 (s, 3 H), 3.06 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.7, 145.4, 135.7, 133.1, 130.0, 128.9, 128.0, 126.7, 120.2, 82.8, 78.0, 38.3.

Synthesis of Compound **II-41c**: A 1.0 M solution of tetrabutylammonium fluoride in THF (2 mL, 2 mmol) was added to a stirred solution of **II-40c** (665 mg, 1.90 mmol) in THF (18 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to give **II-41c** as a white solid (504 mg, 95%); ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2 H), 7.24 (m, 3 H), 7.17 (t, *J* = 7.8 Hz, 2 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 3.81 (d, *J* = 7.2 Hz, 2 H), 3.05 (s, 1 H), 1.91 (m, 1 H), 0.95 (d, *J* = 7.2 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.7, 144.2, 136.3, 133.0, 129.8, 128.0, 127.5, 120.1, 82.9, 78.0, 56.8, 27.1, 20.3.

Synthesis of Compound **II-41e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (3 mL, 3 mmol) was added to a stirred solution of **II-40e** (1.32 g, 3.0 mmol) in THF (25 mL) at room temperature. After stirred at room temperature for 1 h, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **II-41e** as yellow oil (990 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 7.2 Hz, 2 H), 7.24 (d, *J* = 7.8 Hz, 1 H), 7.17 (t, *J* = 7.8 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 4.08 (t, *J* = 6.0 Hz, 2 H), 3.77 (t, *J* = 5.4 Hz, 2 H), 3.62-3.61 (m, 6 H), 3.54-3.52 (m, 2 H), 3.37 (s, 3 H), 3.05 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 144.8, 135.9, 132.9, 130.0, 128.9, 128.0, 127.8, 120.1, 83.0, 77.9, 72.1, 70.7, 70.7, 70.5, 68.4, 59.2, 50.6. HRMS (ESI+) m/z calcd for $C_{22}H_{25}NNaO_4$ $[M+Na]^+$ 390.1676, found 390.1686.

Synthesis of Compound **II-41g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (1.84 mL, 1.84 mmol) was added to a stirred solution of **II-40g** (700 mg, 1.54 mmol) in THF (10 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **II-41g** as yellow oil (555 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.28 (m, 4 H), 7.23 (tt, *J* =7.2, 1.2 Hz, 1 H), 7.17 (t, *J* = 7.8 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 4.10 (m, 1 H), 3.95 (m, 1 H), 3.74-3.71 (m, 1 H), 3.68-3.64 (m, 1 H), 3.61-3.56 (m, 4 H), 3.53-3.51 (m, 3 H), 3.36 (s, 3 H), 3.04 (s, 1 H), 1.20 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 145.3, 136.0, 132.8, 130.0, 128.9, 128.0, 127.7, 119.9, 83.1, 77.8, 73.8, 72.0, 70.9, 70.6, 68.4, 59.2, 56.6, 17.7. HRMS (ESI+) m/z calcd for $C_{23}H_{27}NNaO_4$ $[M+Na]^+$ 404.1832, found 404.1831.

Synthesis of Compound **II-42**: 2-Nitrobenzenesulfonyl chloride (755 mg, 3.41 mmol) in dry dichloromethane (8 mL) was added to a solution of aniline (320 mg, 3.43 mmol) and pyridine (350 mg, 4.44 mmol) in dry dichloromethane (2 mL) at 0°C, and the reaction mixture was stirred for 1 h 30 min at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq.,dried over $MgSO_4$, filtered, and evaporated to give **II-42** as a red solid (912 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.82 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.69 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.57 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.27 (t, *J* = 8.4 Hz, 2 H), 7.25 (br, 1 H), 7.20-7.18 (m, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.3, 135.6, 134.1, 132.7, 132.3, 132.0, 129.6, 126.8, 125.5, 123.4.

Synthesis of Compound **II-43e**: Diisopropyl azodicarboxylate (724 mg, 3.58 mmol) in dry tetrahydrofuran (5 mL) was added to a mixture of **II-42** (504 mg, 1.81 mmol), triethylene glycol monomethyl ether (325 mg, 1.98 mmol), and triphenylphosphine (947 mg, 3.61 mmol) in dry tetrahydrofuran (10 mL) under an argon atmosphere at 0°C. The reaction mixture was stirred overnight at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=2/1) to give **II-43e** (770 mg, quant.) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 2 H), 7.52 (dd, *J* = 7.8, 1.2 Hz, 1 H),7.45 (dt, *J* = 7.2, 1.2 Hz, 1 H), 7.30 (m, 3 H), 7.23 (m, 2 H), 3.97 (t, *J* = 6.0 Hz, 2 H), 3.63-3.53 (m, 10 H), 3.37 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 138.2, 133.6, 132.3, 132.1, 131.2, 129.9, 129.5, 128.7, 123.9, 72.0, 70.7, 70.6, 70.3, 68.8, 59.2, 51.7. HRMS (ESI+) m/z calcd for $C_{19}H_{24}N_2NaO_7S$ $[M+Na]^+$ 447.1196, found 447.1191.

Synthesis of Compound **II-43g**: Diisopropyl azodicarboxylate (364 mg, 1.80 mmol) in dry tetrahydrofuran (5 mL) was added to a mixture of **II-42** (250 mg, 0.90 mmol), TEG (170 mg, 0.94 mmol), and triphenylphosphine (470 mg, 1.80 mmol) in dry tetrahydrofuran (5 mL) under an argon atmosphere at 0°C. The reaction mixture was stirred for 3 h at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=2/1) to give **II-43g** (455 mg, quant.) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2 H), 7.48 (dd, *J* = 7.8, 1.2 Hz, 1 H),7.42 (t, *J* = 7.2 Hz, 1 H), 7.30-7.25 (m, 5 H), 3.88 (dd, *J* = 14.4, 7.2 Hz, 1 H), 3.77 (dd, *J* = 15.0, 5.4 Hz, 1 H), 3.62-3.41 (m, 9 H), 3.37 (s, 3 H), 1.19 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 139.0, 133.6, 132.2, 132.1, 131.1, 129.5, 129.4, 128.4, 123.8, 74.5, 72.0, 70.7, 70.6, 68.2, 59.2, 57.0, 17.5. HRMS (ESI+) m/z calcd for $C_{20}H_{27}N_2O_7S$ $[M+H]^+$ 439.1533, found 439.1521.

Synthesis of Compound **II-44e**: A solution of **II-43e** (740 mg, 1.74 mmol) in dry acetonitrile (12 mL) and cesium carbonate (681 mg, 2.09 mmol) was added to a solution of benzenethiol (0.27 mL, 2.64 mmol) in dry acetonitrile (2 mL). The mixture was stirred for 4 h at 45°C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1/1) to give **II-44e** (271 mg, 65%) as yellow oil; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.17 (dt, *J* =7.8, 1.2 Hz, 2 H), 6.70 (tt, *J* = 7.2, 1.2 Hz, 1 H), 6.63 (dt, *J* = 7.8, 1.2 Hz, 2 H), 3.71 (t, *J* = 4.8 Hz, 2 H), 3.66 (m, 6 H), 3.56 (m, 2 H), 3.39 (s, 3 H), 3.30 (t, *J* = 5.4 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.4, 129.3, 117.6, 113.2, 72.1, 70.7, 70.4, 69.7, 59.2, 43.6. HRMS (ESI+) m/z calcd for $C_{13}H_{21}NNaO_3$ $[M+Na]^+$ 262.1414, found 262.1418.

Synthesis of Compound **II-44g**: A solution of **II-43g** (425 mg, 0.97 mmol) in dry acetonitrile (6 mL) and cesium carbonate (353 mg, 1.09 mmol) was added to a solution of benzenethiol (151.2 mg, 1.37 mmol) in dry acetonitrile (4 mL). The mixture was stirred for 9 h at 45°C, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1/1) to give **II-44g** (154 mg, 63%) as yellow oil; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.16 (dt, *J* =7.8, 1.2 Hz, 2 H), 6.69 (tt, *J* = 7.2, 1.2 Hz, 1 H), 6.62 (dt, *J* =7.8, 1.2 Hz, 2 H), 4.28 (br, 1 H), 3.75-3.56 (m, 9 H), 3.39 (s, 3 H), 3.22 (dd, *J* = 12.6, 3.6 Hz, 1 H), 3.04 (dd, *J* =12.6, 7.8 Hz, 1 H), 1.22 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 129.3, 117.4, 113.2, 74.5, 72.1, 70.9, 70.7, 68.1, 59.2, 49.3, 18.0. HRMS (ESI+) m/z calcd for $C_{14}H_{23}NNaO_3$ $[M+Na]^+$ 276.1570, found 276.1564.

Synthesis of Compound **II-45a**: Triethylamine (0.2 mL, 1.43 mmol) was added to a solution of *N*-methylaniline (80 mg, 0.74 mmol) in dichloromethane (2 mL), and the mixture was stirred at 0°C. 4-iodobenzoyl chloride (209 mg, 3.01 mmol) was added to the cold amine solution and the mixture was stirred for 2 h at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated to give **II-45a** as a yellow solid (245 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.2, 1.2 Hz, 2 H), 7.25 (m, 2 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 4 H).

Synthesis of Compound **II-45e**: Triethylamine (0.3 mL, 2.15 mmol) was added to a solution of **II-44e** (271 mg, 1.13 mmol) in dichloromethane (5 mL), and the mixture was stirred at 0°C. 4-iodobenzoyl chloride (290 mg, 1.09 mmol) in dichloromethane (5 mL) was added to the cold amine solution and the mixture was stirred for 6 h at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated to give **II-45e** as a yellow oil (463 mg, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2 H), 7.21 (t, *J* = 7.8 Hz, 2 H), 7.15 (t, *J* = 7.2 Hz, 1 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 4.07 (t, *J* = 5.4 Hz, 2 H), 3.74 (t, *J* = 5.4 Hz, 2 H), 3.61 (m, 6 H), 3.52 (m, 2 H), 3.36 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 137.0, 135.7, 130.6, 129.3, 128.0, 126.9, 96.3, 72.1, 70.7, 70.7, 70.4, 68.1, 59.2, 50.5. HRMS (ESI+) m/z calcd for $C_{20}H_{24}INNaO_4$ $[M+Na]^+$ 492.0642, found 492.0640.

Synthesis of Compound **II-45g**: Triethylamine (114 mg, 1.12 mmol) was added to a solution of **II-44g** (140 mg, 0.55

mmol) in dichloromethane (2 mL), and the mixture was stirred at 0°C. 4-iodobenzoyl chloride (150 mg, 0.56 mmol) in dichloromethane (6 mL) was added to the cold amine solution and the mixture was stirred for 5 h at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq. and brine, and dried over $MgSO_4$, filtered, and evaporated to give **II-45g** as yellow oil (265 mg, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2 H), 7.20 (m, 2 H), 7.14 (m, 3 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 4.04 (br, 1 H), 3.92 (br, 1 H), 3.73- 3.50 (m, 9 H), 3.36 (s, 3 H), 1.19 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 137.0, 135.9, 130.6, 129.2, 127.9, 126.7, 96.3, 73.6, 72.1, 70.9, 70.6, 68.3, 59.2, 56.6, 17.7. HRMS (ESI+) m/z calcd for $C_{21}H_{26}INNaO_4$ $[M+Na]^+$ 506.0799, found 506.0788.

Synthesis of Compound **II-5e**: **II-45e** (49.3 mg, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 5 mol%), triphenylphosphine (2.6 mg, 10 mol%), CuI (1.9 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (29.8 mg, 2.9 eq.) and **II-41e** (38.0 mg, 0.10 mmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **II-5e** (60.0 mg, 82%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.08 (m, 18 H), 4.08 (m, 4 H), 3.76 (m, 4 H), 3.62 (m, 12 H), 3.53 (m, 4 H), 3.36 (s, 3 H), 3.36 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.0, 144.4, 143.8, 136.0, 135.9, 133.2, 132.3, 130.9, 130.1, 130.0, 129.2, 128.9, 128.9, 128.0, 128.0, 127.8, 126.8, 124.2, 120.9, 90.1, 89.5, 72.0, 70.7, 70.6, 70.6, 70.4, 70.4, 68.3, 68.1, 59.2, 50.5, 50.4. HRMS (ESI+) m/z calcd for $C_{42}H_{48}N_2NaO_8$ $[M+Na]^+$ 731.3303, found 731.3282.

Synthesis of Compound **II-5g**: **II-45g** (25.7 mg, 53 μmol), $Pd(PPh_3)_2Cl_2$ (2.0 mg, 5 mol%), triphenylphosphine (1.4 mg, 10 mol%), CuI (1.0 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (12.4 mg, 2.3 eq.) and **II-41g** (20.2 mg, 1.0 eq.) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature for 9 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 10/1to methanol 10%) to give **II-5g** (31.8 mg, 82%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.27 (m, 5 H), 7.25-7.23 (m, 4 H), 7.19-7.11 (m, 9 H), 4.12-4.06 (m, 2 H), 3.94 (br, 2 H), 3.75-3.50 (m, 18 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 1.20 (d, *J* =5.4 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.1, 145.0, 136.2, 136.1, 133.1, 132.2, 130.9, 129.9, 129.1, 128.9, 128.0, 128.0, 127.9, 127.7, 126.6, 124.2, 120.6, 90.2, 89.4, 73.8, 73.6, 72.0, 70.9, 70.6, 68.4, 68.3, 59.2, 59.2, 56.6, 56.5, 17.7, 17.7, 17.6. HRMS (ESI+) m/z calcd for $C_{44}H_{52}N_2NaO_8$ $[M+Na]^+$ 759.3616, found 759.3616.

Synthesis of Compound **II-46a**: **II-39a** (780 mg, 1.80 mmol), $Pd(PPh_3)_2Cl_2$ (64 mg, 5 mol%), triphenylphosphine (48 mg, 10 mol%), CuI (35 mg, 10 mol%) and *N*,*N*-dimethylformamide (12 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.5 mL, 2.0 eq.) and **II-41a** (430 mg, 1.83 mmol) in *N*,*N*-dimethylformamide (8 mL) was added, and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. The

residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2 to chloroform/ethyl acetate = 5/1) to give **II-46a** (895 mg, 92%) as a yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.6 Hz, 2 H), 7.33 (d, *J* = 5.4 Hz, 2 H), 7.29 (m, 4 H), 7.25 (t, *J* = 8.4 Hz, 3 H), 7.18 (t, *J* = 7.8 Hz, 2 H), 6.99 (d, *J* = 9.0 Hz, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 3.50 (s, 3 H), 3.49 (s, 3 H), 0.22 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.7, 135.7, 135.5, 133.0, 132.5, 131.1, 130.0, 128.9, 128.9, 128.0, 126.8, 126.6, 124.6, 121.5, 120.9, 104.0, 95.5, 90.3, 89.5, 38.3, 38.3, 0.0.

Synthesis of Compound **II-46c**: **II-39c** (836 mg, 1.76 mmol), $Pd(PPh_3)_2Cl_2$ (58 mg, 5 mol%), triphenylphosphine (48 mg, 10 mol%), CuI (32 mg, 10 mol%) and *N*,*N*-dimethylformamide (7 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.5 mL, 2.0 eq.) and **II-41c** (490 mg, 1.77 mmol) in *N*,*N*-dimethylformamide (10 mL) was added, and the mixture was stirred for 5 h at room temperature. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to give **II-46c** (967 mg, 88%) as a yellow oil; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.31 (m, 4 H), 7.26 (m, 4 H), 7.22 (m, 3 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 3.81 (d, *J* = 7.8 Hz, 2 H), 3.79 (d, *J* = 7.2 Hz, 2 H), 1.90 (m, 2 H), 0.95 (d, *J* = 6.6 Hz, 6 H), 0.94 (d, *J* = 6.6 Hz, 6 H), 0.22 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.8, 169.9, 143.9, 143.6, 136.4, 136.1, 132.9, 132.4, 131.1, 129.7, 128.8, 128.7, 128.0, 127.6, 127.4, 124.3, 121.4, 120.9, 104.0, 95.5, 90.1, 89.5, 56.8, 27.2, 20.3, 0.0.

Synthesis of Compound **II-46e**: **II-39e** (707 mg, 1.25 mmol), $Pd(PPh_3)_2Cl_2$ (43.7 mg, 5 mol%), triphenylphosphine (37.1 mg, 10 mol%), CuI (23.6 mg, 10 mol%) and acetonitrile (6 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.3 mL, 1.7 eq.) and **II-41e** (463 mg, 1.26 mmol) in acetonitrile (4 mL) was added, and the mixture was stirred at room temperature for 7 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-46e** (1.25 g, quant.) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.23 (m, 11 H), 7.17 (quart., *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 4.08 (m, 4 H), 3.76 (m, 4 H), 3.61 (m, 12 H), 3.53 (m, 4 H), 3.37 (m, 6 H), 0.22 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.0, 135.9, 135.8, 135.7, 133.2, 133.1, 132.8, 132.3, 131.1, 130.1, 130.0, 129.0, 128.9, 128.9, 128.0, 128.0, 127.8, 127.6, 124.5, 121.4, 120.9, 119.5, 104.2, 95.3, 90.4, 89.4, 72.0, 70.7, 70.7, 70.5, 70.4, 68.4, 68.3, 68.2, 59.2, 50.6, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{47}H_{56}N_2NaO_8Si$ $[M+Na]^+$ 827.3698, found 827.3714.

Synthesis of Compound **II-46g**: **II-39g** (70.2 mg, 0.12 mmol), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 5 mol%), triphenylphosphine (2.6 mg, 10 mol%), CuI (1.9 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (35.6 mg, 3.5 eq.) and **II-41g** (38.4 mg, 0.12 mmol) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give

II-46g (70.5 mg, 84%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.28 (m, 6 H), 7.25-7.24 (m, 4 H), 7.18-7.13 (m, 5 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 4.10 (m, 2 H), 3.94 (m, 2 H), 3.73-3.51 (m, 18 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 1.20 (t, *J* = 6.6 Hz, 6 H), 0.22 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 145.1, 144.7, 136.1, 135.8, 133.1, 132.7, 132.3, 132.2, 132.1, 131.1, 130.0, 129.0, 128.9, 128.7, 128.6, 128.1, 128.0, 127.7, 127.6, 124.6, 121.2, 120.6, 104.3, 95.2, 90.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.9, 70.6, 68.5, 68.4, 60.6, 59.2, 56.7, 56.5, 21.2, 17.7, 17.7, 14.3, 0.0. HRMS (ESI+) m/z calcd for $C_{49}H_{60}N_2NaO_8Si$ $[M+Na]^+$ 855.4011, found 855.4005.

Synthesis of Compound **II-47a**: A 1.0 M solution of tetrabutylammonium fluoride in THF (1.2 mL, 1.2 mmol) was added to a stirred solution of **II-46a** (640 mg, 1.2 mmol) in THF (2 mL) at room temperature. After stirred at room temperature for 5 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **II-47a** as white solid (516 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.29 (m, 4 H), 7.24 (m, 3 H), 7.19 (t, *J* = 7.8 Hz, 2 H), 6.99 (d, *J* = 9.0 Hz, 2 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 3.50 (s, 3 H), 3.49 (s, 3 H), 3.07 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7,169.9, 145.1, 145.1, 135.7, 135.4, 133.2, 132.5, 131.2, 130.0, 129.0, 128.9, 128.0, 126.8, 126.7, 124.7, 120.9, 120.5, 90.3, 89.5, 82.7, 78.3, 38.3. HRMS (ESI+) m/z calcd for $C_{32}H_{25}N_2O_2$ $[M+H]^+$ 469.1911, found 469.1906.

Synthesis of Compound **II-47c**: A 1.0 M solution of tetrabutylammonium fluoride in THF (1.6 mL, 1.6 mmol) was added to a stirred solution of **II-46c** (735 mg, 1.18 mmol) in THF (12 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **II-47c** as a white solid (580 mg, 89%); ^{1}H NMR(600 MHz, $CDCl_3$) δ7.32 (t, *J* = 8.4 Hz, 4 H), 7.29-7.25 (m, 5 H), 7.21 (d, *J* = 6.6 Hz, 2 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 6.97 (m, 4 H), 3.80 (t, *J* = 7.2 Hz, 4 H), 3.07 (s, 1 H), 1.91 (m, 2 H), 0.95 (m, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.7, 169.9, 143.9, 143.9, 136.3, 136.1, 133.1, 132.4, 131.1, 129.7, 128.8, 128.7, 128.0, 127.5, 127.4, 124.3, 120.8, 120.4, 90.2, 89.5, 82.7, 78.3, 56.8, 27.2, 27.1, 20.3, 20.3.

Synthesis of Compound **II-47e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (1.5 mL, 1.5 mmol) was added to a stirred solution of **II-46e** (1.15 g, 1.43 mmol) in THF (10 mL) at room temperature. After stirred at room temperature for 45 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 20/5/1) to give **II-47e** as yellow oil (728 mg, 69%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.28 (m, 9 H), 7.25-7.24 (m, 2 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.10-7.08 (m, 4 H), 4.08 (m, 4 H), 3.77 (m ,4 H), 3.62 (m, 12 H), 3.53 (m, 4 H), 3.37 (s, 3 H), 3.37 (s, 3 H), 3.06 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.7, 144.4, 135.9, 135.6, 133.2, 132.9, 132.3, 131.0, 129.9, 128.9, 128.8, 127.9, 127.8, 127.7, 124.6, 120.8, 120.4, 90.4, 89.4, 82.8, 78.1, 72.0, 70.6, 70.6, 70.4, 68.3, 68.2, 59.1, 50.6, 50.5. HRMS (ESI+) m/z calcd for $C_{44}H_{48}N_2NaO_8$ $[M+Na]^+$ 755.3303, found 755.3299.

Synthesis of Compound **II-47g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (1.34 mL, 1.34 mmol) was added to a stirred solution of **II-46g** (945 mg, 1.13 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 1 h, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 2/1) to give **II-47g** as yellow oil (860 mg, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.23 (m, 11 H), 7.18-7.12 (m, 6 H), 4.11 (m, 2 H), 3.95 (br, 2 H), 3.74-3.51 (m, 18 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 3.05 (s, 1 H), 1.20 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 145.1, 136.1, 135.8, 132.9, 132.3, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.7, 124.7, 120.6, 120.2, 90.5, 89.3, 83.0, 78.0, 73.8, 73.7, 72.1, 70.9, 70.9, 70.6, 68.5, 68.4, 59.2, 56.6, 17.7, 17.6. HRMS (ESI+) m/z calcd for $C_{46}H_{52}N_2NaO_8$ $[M+Na]^+$ 783.3616, found 783.3639.

Synthesis of Compound **II-6e**: **II-45e** (47.5 mg, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 5 mol%), triphenylphosphine (2.6 mg, 10 mol%), CuI (1.9 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (29.9 mg, 3.0 eq.) and **II-47e** (73.3 mg, 0.10 mmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **II-6e** (82.1 mg, 76%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 8 H), 7.25-7.08 (m, 18 H), 4.08 (m, 6 H), 3.77 (m, 6 H), 3.62-3.60 (m, 18 H), 3.53 (m, 6 H), 3.36 (s, 3 H), 3.36 (s, 3 H), 3.36 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.9, 169.8, 144.5, 144.1, 136.0, 135.9, 135.6, 132.4, 132.3, 131.1, 131.0, 130.0, 129.2, 129.0, 129.0, 128.9, 128.0, 127.8, 126.8, 124.6, 124.2, 121.2, 120.8, 90.4, 90.0, 89.7, 89.4, 72.0, 70.7, 70.7, 70.5, 70.4, 68.3, 68.3, 68.1, 59.2, 50.6, 50.4. HRMS (ESI+) m/z calcd for $C_{64}H_{71}N_3NaO_{12}$ $[M+Na]^+$ 1096.4930, found 1096.4932.

Synthesis of Compound **II-6g**: **II-45g** (41.0 mg, 85 μmol), $Pd(PPh_3)_2Cl_2$ (2.9 mg, 5 mol%), triphenylphosphine (2.2 mg, 10 mol%), CuI (1.6 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (20.5 mg, 2.4 eq.) and **II-47g** (62.1 mg, 82 μmol) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature for 9 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform = 1/1) to give **II-6g** (74.3 mg, 82%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 13 H), 7.25-7.24 (m, 2 H), 7.18-7.12 (m, 11 H), 4.11 (m, 3 H), 3.95 (br, 3 H), 3.73-3.50 (m, 27 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 3.35 (s, 3 H), 1.20 (d, *J* = 6.0 Hz, 9 H); ^{13}C NMR (150 MHz, CD_3OD) δ 173.0, 172.1, 137.6, 137.4, 137.3, 134.2, 134.0, 133.3, 133.2, 132.0, 131.9, 131.0, 130.2, 129.9, 129.8, 129.6, 129.6, 129.5, 129.4, 129.0, 128.1, 125.9, 125.6, 122.6, 122.3, 91.1, 90.9, 90.1, 90.0, 70.5, 74.8, 74.7, 74.6, 73.0, 71.9, 71.4, 69.3, 69.3, 61.5, 59.1, 57.0, 20.9, 17.7, 17.6, 17.6, 14.5. HRMS (ESI+) m/z calcd for $C_{67}H_{77}N_3NaO_{12}$ $[M+Na]^+$ 1138.5399, found 1138.5391.

Synthesis of Compound **II-48a**: **II-39a** (416 mg, 0.96 mmol), $Pd(PPh_3)_2Cl_2$ (33 mg, 5 mol%), triphenylphosphine (25 mg, 10 mol%), CuI (18 mg, 10 mol%) and *N*,*N*-dimethylformamide (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room

temperature Et_3N (0.5 mL, 3.7 eq.) and **II-47a** (450 mg, 0.96 mmol) in *N*,*N*-dimethylformamide (3 mL) was added, and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1 to chloroform only) to give **II-48a** (562 mg, 76%) as a orange-white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.25 (m, 17 H), 7.18 (t, *J* = 7.8 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 4 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 3.50 (s, 3 H), 3.50 (s, 3 H), 3.49 (s, 3 H), 0.22 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.8, 169.8, 145.0, 144.7, 144.7, 135.6, 135.5, 135.4, 133.0, 132.6, 132.5, 131.1, 130.0, 128.9, 128.9, 128.8, 128.0, 126.8, 126.6, 124.6, 124.5, 121.4, 121.2, 120.8, 104.0, 95.4, 90.3, 90.1, 89.6, 89.4, 38.3, 0.0.

Synthesis of Compound **II-48c**: **II-39c** (475 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 5 mol%), triphenylphosphine (26 mg, 10 mol%), CuI (19 mg, 10 mol%) and *N*,*N*-dimethylformamide (5 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.3 mL, 2.0 eq.) and **II-47c** (550 mg, 1 mmol) in *N*,*N*-dimethylformamide (5 mL) was added, and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **II-48c** (870 mg, 97%) as a yellow solid; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.33- 7.20 (m, 17 H), 7.15 (t, *J* = 7.8 Hz, 2 H), 6.97 (dd, *J* = 8.4, 1.8 Hz, 4 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 3.79 (m, 6 H), 1.90 (m, 3 H), 0.94 (m, 18 H), 0.21 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.7, 169.9, 169.9, 144.0, 143.6, 136.4, 136.2, 136.1, 135.3, 132.9, 132.5, 132.4, 131.1, 129.7, 128.8, 128.7, 128.0, 127.5, 127.5, 127.4, 124.3, 124.3, 121.4, 121.2, 120.9, 104.1, 95.5, 90.2, 90.0, 89.7, 89.5, 56.9, 27.2, 20.3, 0.0.

Synthesis of Compound **II-48e**: **II-39e** (501 mg, 0.89 mmol), $Pd(PPh_3)_2Cl_2$ (31.8 mg, 5 mol%), triphenylphosphine (23.8 mg, 10 mol%), CuI (20.3 mg, 10 mol%) and acetonitrile (2.5 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.25 mL 2.0 eq.) and **II-47e** (650 mg, 1.0 eq.) in acetonitrile (5.5 mL) was added, and the mixture was stirred at room temperature for 8 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-48e** (916 mg, 88%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.22 (m, 17 H), 7.15 (t, *J* = 7.8 Hz, 2 H), 7.09 (m, 4 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 4.08 (m, 6 H), 3.76 (m, 6 H), 3.63-3.60 (m, 18 H), 3.52 (m, 6 H), 3.36 (s, 3 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 0.21 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.1, 144.1, 135.9, 135.7, 135.6, 133.1, 132.8, 1322.4, 132.3, 131.1, 130.0, 129.0, 128.9, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.2, 89.6, 89.4, 72.0, 70.7, 70.7, 70.4, 70.4, 68.3, 68.2, 59.2, 50.6, 50.6, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{69}H_{79}N_3NaO_{12}Si$ $[M+Na]^+$ 1192.5325, found 1192.5299.

Synthesis of Compound **II-48g**: **II-39g** (582 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (35.7 mg, 5 mol%), triphenylphosphine (28.9 mg, 10 mol%), CuI (20.0 mg, 10 mol%) and acetonitrile (5 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.3 mL 2.1 eq.) and **II-47g** (765 mg, 1.0 eq.) in acetonitrile (6 mL) was added, and the mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform = 2/1) to give **II-48g** (1.05

mg, 86%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.22 (m, 17 H), 7.17-7.07 (m, 8 H), 4.07 (m, 3 H), 3.92 (br, 3 H), 3.73-3.49 (m, 27 H), 3.35 (s, 3 H), 3.34 (s, 3 H), 3.34 (s, 3 H), 1.19 (m, 9 H), 0.20 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 144.7, 136.1, 135.9, 135.8, 132.7, 132.3, 132.2, 131.1, 129.9, 129.0, 128.9, 128.9, 128.0, 127.7, 127.6, 124.6, 124.5, 121.2, 120.9, 120.6, 104.3, 95.1, 90.5, 90.3, 89.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.4, 59.1, 56.6, 56.5, 17.7, 17.7, 17.6, 0.0. HRMS (ESI+) m/z calcd for $C_{72}H_{85}N_3NaO_{12}Si$ $[M+Na]^+$ 1234.5795, found 1234.5762.

Synthesis of Compound **II-49a**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.7 mL, 0.7 mmol) was added to a stirred solution of **II-48a** (545 mg, 0.7 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 5 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform = 1/1) to give **II-49a** as a white solid (494 mg, quant.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.24 (m, 17 H), 7.18 (t, *J* = 7.8 Hz, 2 H), 6.98 (m, 6 H), 3.50 (m, 9 H), 3.49 (s, 3 H), 3.06 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 145.0 144.8, 135.7, 135.4, 135.4, 133.2, 132.6, 132.5, 131.2, 131.1, 130.0, 129.0, 128.9, 128.0, 126.8, 126.7, 124.6, 124.6, 121.2, 120.9, 120.4, 90.3, 90.1, 89.6, 89.4, 82.7, 78.3, 38.3, 38.3, 38.3.

Synthesis of Compound **II-49c**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.9 mL, 0.9 mmol) was added to a stirred solution of **II-48c** (860 mg, 0.96 mmol) in THF (10 mL) at room temperature. After stirred at room temperature for 5 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **II-49c** as a yellow solid (453 mg, 57%); ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.34-7.22 (m, 17 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 6.98 (m, 6 H), 3.80 (m, 6 H), 3.05 (s, 1 H), 1.91 (m, 3 H), 0.95 (m, 18 H).

Synthesis of Compound **II-49e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.8 mL, 0.8 mmol) was added to a stirred solution of **II-48e** (875 mg, 0.75 mmol) in THF (8 mL) at room temperature. After stirred at room temperature for 30 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-49e** as yellow oil (723 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.26 (m, 17 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.10-7.08 (m, 6 H), 4.08 (m, 6 H), 3.76 (m, 6 H), 3.63-3.61 (m, 18 H), 3.53 (m, 6 H), 3.37 (s, 3 H), 3.36 (s, 3 H), 3.36 (s, 3 H), 3.06 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.2, 135.9, 135.7, 135.6, 133.1, 133.0, 132.4, 132.3, 131.1, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.7, 124.6, 124.6, 121.1, 120.8, 120.4, 90.4, 90.3, 89.6, 89.4, 82.8, 78.2, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.6, 50.6, 50.6. HRMS (ESI+) m/z calcd for $C_{66}H_{71}IN_3NaO_{12}$ $[M+Na]^+$ 1120.4930, found 1120.4896.

Synthesis of Compound **II-49g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.83 mL, 0.83 mmol) was added to a stirred solution of **II-48g** (1.01 g, 0.83 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 30 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/methanol =

20/1) to give **II-49g** as yellow oil (888 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.26 (m, 17 H), 7.17-7.11 (m, 8 H), 4.10 (br, 3 H), 3.94 (br, 3 H), 3.73-3.49 (m, 27 H), 3.35 (s, 3 H), 3.34 (s, 3 H), 3.34 (s, 3 H), 3.05 (s, 1 H), 1.19 (m, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.0, 144.8, 136.1, 135.8, 132.8, 132.3, 132.2, 131.1, 131.1, 129.9, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.6, 120.9, 120.6, 120.2, 90.5, 90.3, 89.5, 89.3, 82.9, 78.0, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.6, 17,7, 17,6, 17.6. HRMS (ESI+) m/z calcd for $C_{69}H_{77}N_3NaO_{12}$ $[M+Na]^+$ 1162.5399, found 1162.5396.

Synthesis of Compound **II-7a**: **II-45a** (36.3 mg, 1.08 mmol), $Pd(PPh_3)_2Cl_2$ (4.7 mg, 5 mol%), triphenylphosphine (3.5 mg, 10 mol%), CuI (2.4 mg, 10 mol%) and *N*, *N*-dimethylformamide (0.1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (22.8 mg, 2.3 eq.) and **II-49a** (70 mg, 0.10 mmol) in *N*, *N*-dimethylformamide (0.9 mL) was added, and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform = 1/1 to chloroform/methanol = 10/1) and GPC to give **II-7a** (45.8 mg, 51%) as a white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.13 (m, 26 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 6.98 (m, 6 H), 3.49 (s, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 169.8, 169.7, 145.0, 144.7, 144.7, 135.8, 135.7, 135.4, 135.4, 132.6, 132.5, 132.4, 131.1, 131.1, 130.9, 129.9, 129.3, 128.9, 128.9, 128.8, 128.0, 126.9, 126.7, 126.7, 126.7, 124.6, 124.5, 124.1, 121.2, 121.1, 120.8, 90.3, 90.1, 89.8, 89.7, 89.6, 89.4, 38.4, 38.2.

Synthesis of Compound **II-7e**: **II-45e** (31.9 mg, 68 μmol), $Pd(PPh_3)_2Cl_2$ (2.1 mg, 5 mol%), triphenylphosphine (1.6 mg, 10 mol%), CuI (1.1 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (17.5 mg, 2.7 eq.) and **II-49e** (69.5 mg, 63 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give **II-7e** (53.0 mg, 58%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.08 (m, 34 H), 4.07 (m, 8 H), 3.76 (m, 8 H), 3.61 (m, 24 H), 3.52 (m, 8 H), 3.35 (m, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.9, 169.8, 169.7, 144.4, 144.1, 143.8, 136.0, 135.9, 135.6, 135.6, 133.1, 132.4, 132.4, 132.3, 131.1, 130.9, 130.8, 130.0, 129.2, 129.0, 128.9, 128.9, 127.9, 127.8, 126.8, 124.6, 124.5, 124.1, 121.1, 121.1, 120.8, 90.4, 90.2, 90.0, 89.7, 89.5, 89.4, 72.4, 72.0, 70.7, 70.6, 70.4, 70.4, 68.3, 68.2, 68.1, 61.9, 59.2, 50.6, 50.5, 50.4. HRMS (ESI+) m/z calcd for $C_{86}H_{94}N_4NaO_{16}$ $[M+Na]^+$ 1461.6557, found 1461.6559.

Synthesis of Compound **II-7g**: **II-45g** (39.1 mg, 81 μmol), $Pd(PPh_3)_2Cl_2$ (3.2 mg, 5 mol%), triphenylphosphine (2.2 mg, 10 mol%), CuI (1.6 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (18.3 mg, 2.1 eq.) in acetonitrile (1 mL) and **II-49g** (95.4 mg, 84 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give

II-7g (69.4 mg, 57%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.12 (m, 34 H), 4.11 (br, 4 H), 3.94 (br, 4 H), 3.73-3.49 (m, 36 H), 3.34 (m, 12 H), 1.19 (d, *J* = 6.6 Hz, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.9, 145.0, 144.7, 144.5, 136.2, 136.0, 135.8, 135.7, 132.3, 132.3, 132.2, 131.1, 130.9, 129.9, 129.0, 128.9, 128.9, 127.9, 127.9, 127.7, 126.6, 124.6, 124.5, 124.1, 120.9, 120.8, 120.5, 90.4, 90.3, 90.0, 89.6, 89.4, 89.3, 73.7, 73.6, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.1, 56.6, 56.6, 56.5, 17.7, 17.6, 17.6. HRMS (ESI+) m/z calcd for $C_{90}H_{102}N_4NaO_{16}$ $[M+Na]^+$ 1517.7183, found 1517.7152.

Synthesis of Compound **II-50c**: **II-39c** (275 mg, 0.58 mmol), $Pd(PPh_3)_2Cl_2$ (20.3 mg, 5 mol%), triphenylphosphine (15.4 mg, 10 mol%), CuI (11.2 mg, 10 mol%) and *N*,*N*-dimethylformamide (10 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.17 mL, 2.2 eq.) and **II-49c** (480 mg, 0.58 mmol) in *N*,*N*-dimethylformamide (10 mL) was added, and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **II-50c** (283 mg, 41%) as yellow oil; ^{1}H NMR(600 MHz, $CDCl_3$) δ 7.33-7.20 (m, 23 H), 7.14 (t, *J* = 7.8 Hz, 2 H), 6.97 (m, 6 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 3.79 (m, 8 H), 1.91 (m, 4 H), 0.94 (m, 24 H), 0.20 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 169.9, 144.0, 143.6, 143.6, 136.4, 136.2, 136.2, 136.1, 132.9, 132.5, 132.5, 132.4, 131.1, 131.1, 129.7, 128.8, 128.7, 128.0, 127.6, 127.5, 127.4, 124.4, 124.3, 124.2, 121.4, 121.2, 120.9, 104.1, 95.5, 90.2, 90.0, 89.7, 89.5, 56.9, 27.2, 20.3, 0.0.

Synthesis of Compound **II-50e**: **II-39e** (329 mg, 0.58 mmol), $Pd(PPh_3)_2Cl_2$ (20.3 mg, 5 mol%), triphenylphosphine (15.2 mg, 10 mol%), CuI (11.2 mg, 10 mol%) and acetonitrile (3 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (117.4 mg, 2.0 eq.) in acetonitrile (1 mL) and **II-49e** (639 mg, 1.0 eq.) in acetonitrile (3 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-50e** (606 mg, 68%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.22 (m, 23 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.09 (m, 6 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 4.07 (m, 8 H), 3.75 (m, 8 H), 3.61 (m, 24 H), 3.53 (m, 8 H), 3.36 (m, 12 H), 0.21 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.1, 144.0, 135.9, 135.7, 135.6, 135.6, 132.8, 132.5, 132.4, 132.3, 131.1, 131.1, 130.0, 129.0, 129.0, 129.0, 128.9, 128.0, 127.8, 127.8, 127.6, 124.6, 124.6, 124.5, 121.4, 121.1, 121.1, 120.8, 104.2, 95.3, 90.4, 90.2, 90.2, 89.6, 89.6, 89.4, 72.0, 70.7, 70.7, 70.4, 70.4, 68.3, 68.2, 59.2, 50.7, 50.6, 50.6, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{91}H_{102}N_4NaO_{16}Si$ $[M+Na]^+$ 1557.6952, found 1557.6995.

Synthesis of Compound **II-50g**: **II-39g** (380 mg, 0.65 mmol), $Pd(PPh_3)_2Cl_2$ (23.3 mg, 5 mol%), triphenylphosphine (17.0 mg, 10 mol%), CuI (12.4 mg, 10 mol%) and acetonitrile (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.20 mL, 2.0 eq.) and **II-49g** (740 mg, 1.0 eq.) in acetonitrile (6 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in*

vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-50g** (776 mg, 75%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.23 (m, 22 H), 7.16-7.08 (m, 11 H), 4.10 (br, 4 H), 3.92 (br, 4 H), 3.73-3.50 (m, 36 H), 3.35 (m, 12 H), 1.20 (m, 12 H), 0.21 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 144.7, 144.7, 136.1, 135.9, 135.8, 132.7, 132.4, 132.3, 132.2, 132.1, 131.1, 131.1, 130.0, 129,0, 129.0, 129.0, 128.9, 128.7, 128.6, 128.0, 127.7, 127.6, 124.7, 124.5, 121.2, 120.9, 120.6, 104.3, 90.5, 90.3, 90.3, 89.5, 89.3, 73.8, 73.7, 72.1, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.5, 17.7, 17.7, 0.0. HRMS (ESI+) m/z calcd for $C_{95}H_{110}N_4NaO_{16}Si$ $[M+Na]^+$ 1613.7578, found 1613.7577.

Synthesis of Compound **II-51e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.4 mL, 0.4 mmol) was added to a stirred solution of **II-50e** (592 mg, 0.39 mmol) in THF (4 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-51e** as yellow oil (503 mg, 89%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.24 (m, 22 H), 7.15 (t, *J* = 7.8 Hz, 2 H), 7.10-7.08 (m, 8 H), 4.08 (m, 8 H), 3.77 (m, 8 H), 3.61 (m, 24 H), 3.53 (m, 8 H), 3.36 (m, 12 H), 3.06 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.2, 135.9, 135.7, 135.6, 133.1, 133.0, 132.5, 132.3, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.7, 124.6, 124.6, 124.6, 121.1, 120.8, 120.4, 90.4, 90.3, 90.2, 89.6, 89.4, 82.9, 78.2, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.6, 50.6. HRMS (ESI+) m/z calcd for $C_{88}H_{94}N_4NaO_{16}$ $[M+Na]^+$ 1485.6563, found 1485.6546.

Synthesis of Compound **II-51g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.5 mL, 0.5 mmol) was added to a stirred solution of **II-50g** (767.7 g, 0.48 mmol) in THF (5 mL) at room temperature. After stirred at room temperature for 2 h, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-51g** as yellow oil (625.6 mg, 85%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.22 (m, 23 H), 7.17-7.12 (m, 10 H), 4.11 (br, 4 H), 3.95 (br, 4 H), 3.73-3.50 (m, 36 H), 3.35 (m, 12 H), 3.05 (s, 1 H), 1.20 (m, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.8, 135.8, 132,9, 132.4, 132.3, 131.1, 130.0, 129.0, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.6, 124.6, 120.9, 120.6, 120.1, 90.5, 90.3, 89.5, 89.5, 89.3, 82.9, 78.1, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.4, 59.2, 56.7, 56.6, 17.7, 17.7. HRMS (ESI+) m/z calcd for $C_{92}H_{102}N_4NaO_{16}$ $[M+Na]^+$ 1541.7183, found 1541.7136.

Synthesis of Compound **II-8e**: **II-45e** (24.4 mg, 50 μmol), $Pd(PPh_3)_2Cl_2$ (1.8 mg, 5 mol%), triphenylphosphine (1.3 mg, 10 mol%), CuI (1.0 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (10.1 mg, 2.0 eq.) in acetonitrile (1 mL) and **II-51e** (73.2 mg, 50 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **II-8e** (61.9 mg, 69%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.08 (m, 42 H), 4.08 (br, 10 H), 3.75 (br, 10 H), 3.60 (br, 30 H), 3.53 (m, 10 H), 3.56 (m, 15 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.8,

144.3, 144.0, 143.7, 136.0, 135.8, 135.6, 135.6, 132.4, 132.4, 131.1, 131.0, 130.0, 129.3, 129.0, 128.9, 128.9, 128.0, 127.8, 126.9, 124.6, 124.6, 124,2, 124.2, 121.1, 120.9, 90.4, 90.2, 90.0, 89.7, 89.6, 89.4, 72.0, 70.6, 70.6, 70.6, 70.4, 70.3, 68.3, 68.2, 68.1, 59.2, 50.6, 50.6, 50.5, 50.4. HRMS (ESI+) m/z calcd for $C_{108}H_{117}N_5NaO_{20}$ $[M+Na]^+$ 1826.8184, found 1826.8201.

Synthesis of Compound **II-8g**: **II-45g** (33.6 mg, 70 μmol), $Pd(PPh_3)_2Cl_2$ (2.5 mg, 5 mol%), triphenylphosphine (1.8 mg, 10 mol%), CuI (1.3 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (16.2 mg, 2.3 eq.) in acetonitrile (1 mL) and **II-51g** (106.4 mg, 70 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give **II-8g** (87.5 mg, 67%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.22 (m, 27 H), 7.16-7.11 (m, 15 H), 4.10 (br, 5 H), 3.94 (br, 5 H), 3.73-3.49 (m, 45 H), 3.34 (m, 15 H), 1.19 (d, *J* = 6.6 Hz, 15 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.9, 145.1, 144.8, 136.2, 136.1, 135.8, 135.8, 132.3, 132.2, 131.1, 131.0, 129.9, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.6, 124.2, 120.9, 120.8, 120.6, 90.5, 90.3, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2, 56.7, 56.7, 56.6, 56.6, 56.5, 17.7, 17.7, 17.6. HRMS (ESI+) m/z calcd for $C_{113}H_{127}N_5NaO_{20}$ $[M+Na]^+$ 1896.8967, found 1896.8966.

Synthesis of Compound **II-52e**: **II-39e** (160.5 mg, 0.28 mmol), $Pd(PPh_3)_2Cl_2$ (10.2 mg, 5 mol%), triphenylphosphine (7.6 mg, 10 mol%), CuI (5.5 mg, 10 mol%) and acetonitrile (3 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (59.3 mg, 2.1 eq.) in acetonitrile (1 mL) and **II-51e** (415.3 mg, 1.0 eq.) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-52e** (435.2 mg, 81%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.25 (m, 29 H), 7.16 (t, *J* = 7.2 Hz, 2 H), 7.11 (m, 8 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 4.08 (m , 10 H), 3.76 (m, 10 H), 3.61 (m, 30 H), 3.53 (m, 10 H), 3.37 (m, 15 H), 0.21 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.2, 135.9, 135.7, 135.7, 133.1, 132.8, 132.5, 132.3, 131.1, 131.1, 131.0, 130.0, 129.0, 120.0, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.2, 89.6, 89.6, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.7, 50.6, 50.6, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{113}H_{125}N_5NaO_{20}Si$ $[M+Na]^+$ 1922.8579, found 1922.8529.

Synthesis of Compound **II-52g**: **II-39g** (191.2 mg, 0.33 mmol), $Pd(PPh_3)_2Cl_2$ (11.6 mg, 5 mol%), triphenylphosphine (8.7 mg, 10 mol%), CuI (6.3 mg, 10 mol%) and acetonitrile (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (67.5 mg, 2.0 eq.) in acetonitrile (1 mL) and **II-51g** (494.0 mg, 1.0 eq.) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl

acetate/chloroform/methanol = 10/10/1) to give **II-52g** (496.1 mg, 77%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.23 (m, 28 H), 7.14-7.05 (m, 13 H), 4.09 (br, 5 H), 3.92 (br, 5 H), 3.71-3.48 (m, 45 H), 3.33 (m, 15 H), 1.18 (m, 15 H), 0.19 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.7, 136.1, 135.8, 135.8, 135.8, 133.2, 132.7, 132.3, 132.2, 131.1, 131.1, 129.9, 129.0, 129.0, 128.9, 128.0, 127.7, 127.5, 124.6, 124.6, 124.5, 121.1, 130.9, 120.8, 120.5, 104.3, 95.3, 90.5, 90.3, 90.3, 90.3, 89.5, 89.5, 89.4, 89.3, 73.8, 73.7, 73.6, 72.0, 70.9, 70.6, 68.4, 68.4, 68.4, 59.2, 56.7, 56.7, 56.6, 56.5, 17.7, 17.6, 0.0. HRMS (ESI+) m/z calcd for $C_{118}H_{135}N_5NaO_{20}Si$ $[M+Na]^+$ 1992.9362, found 1992.9314.

Synthesis of Compound **II-53e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.25 mL, 0.25 mmol) was added to a stirred solution of **II-52e** (425 mg, 0.22 mmol) in THF (4 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **II-53e** as yellow oil (216 mg, 53%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.21 (m, 29 H), 7.14 (t, *J* = 7.8 Hz, 2 H), 7.09-7.07 (m, 10 H), 4.07 (m, 10 H), 3.75 (m, 10 H), 3.61 (m, 30 H), 3.52 (m, 10 H), 3.35 (m, 15 H), 3.06 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.7, 144.3, 144.0, 135.8, 135.6, 133.0, 132.9, 132.4, 132.2, 131.0, 130.6, 129.9, 128.9, 128.9, 128.8, 127.9, 127.7, 127.7, 124.5, 124.5, 124.4, 121.0, 120.7, 120.3, 90.3, 90.2, 89.5, 89.3, 82.7, 78.1, 71.9, 70.6, 70.6, 70.3, 68.2, 68.2, 59.1, 50.5, 50.4. HRMS (ESI+) m/z calcd for $C_{110}H_{117}N_5NaO_{20}$ $[M+Na]^+$ 1850.8184, found 1850.8207.

Synthesis of Compound **II-53g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.3 mL, 0.3 mmol) was added to a stirred solution of **II-52g** (483.1 g, 0.25 mmol) in THF (3 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **II-53g** as yellow oil (356.0 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.21 (m, 29 H), 7.16-7.12 (m, 12 H), 4.10 (br, 5 H), 3.94 (br, 5 H), 3.73-3.56 (m, 45 H), 3.34 (m, 15 H), 3.05 (s, 1 H), 1.19 (m, 15 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 145.0, 144.7, 136.0, 135.7, 133.1, 132.8, 132.3, 132.2, 131.0, 129.9, 128.9, 128.8, 127.9, 127.6, 127.6, 124.7, 124.5, 124.5, 124.5, 120.8, 120.5, 120.0, 90.4, 90.3, 89.4, 89.4, 89.2, 82.8, 78.0, 73.7, 73.6, 71.9, 70.8, 80.5, 68.3, 68.3, 68.3, 59.1, 56.6, 56.6, 56.5, 17.6, 17.6. HRMS (ESI+) m/z calcd for $C_{115}H_{127}N_5NaO_{20}$ $[M+Na]^+$ 1920.8967, found 1920.8920.

Synthesis of Compound **II-9e**: **II-45e** (9.4 mg, 20 μmol), $Pd(PPh_3)_2Cl_2$ (0.7 mg, 5 mol%), triphenylphosphine (0.5 mg, 10 mol%), CuI (0.4 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (7.2 mg, 3.5 eq.) in acetonitrile (1 mL) and **II-53e** (36.6 mg, 20 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature for 9 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give **II-9e** (17.0 mg, 39%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.07 (m, 50 H), 4.08 (m, 12 H), 3.75 (m, 12 H), 3.61 (m, 36 H), 3.53 (m, 12 H), 3.36 (m, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.8, 144.3, 144.0,

136.0, 135.8, 135.6, 133.1, 132.5, 132.4, 131.1, 131.0, 130.0, 129.2, 129.0, 128.9, 128.9, 128.0, 127.8, 126.9, 124.6, 124.2, 121.2, 121.1, 120.9, 90.4, 90.3, 90.0, 89.7, 89.6, 89.4, 72.0, 70.6, 70.6, 70.6, 70.4, 70.3, 68.3, 68.3, 68.1, 59.2, 50.6, 50.6, 50.5, 50.4. HRMS (ESI+) m/z calcd for $C_{130}H_{140}N_6NaO_{24}$ $[M+Na]^+$ 2191.9811, found 2191.9821.

Synthesis of Compound **II-9g**: **II-45g** (14.5 mg, 30 μmol), $Pd(PPh_3)_2Cl_2$ (1.1 mg, 5 mol%), triphenylphosphine (0.8 mg, 10 mol%), CuI (0.6 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (6.5 mg, 2.1 eq.) in acetonitrile (1 mL) and **II-53g** (57.9 mg, 30 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by recycle-GPC to give **II-9g** (42.0 mg, 61%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.21 (m, 32 H), 7.17-7.11 (m, 18 H), 4.09 (br, 6 H), 3.94 (br, 6 H), 3.75-3.49 (m, 54 H), 3.34 (m, 18 H), 1.19 (d, *J* = 5.4 Hz, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 145.1, 144.7, 136.2, 136.1, 135.8, 132.3, 132.2, 131.1, 131.0, 129.9, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.6, 124.2, 120.9, 120.8, 120.6, 90.5, 90.3, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 74.6, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2, 56.7, 56.6, 56.6, 56.5, 17.7, 17.6. HRMS (ESI+) m/z calcd for $C_{136}H_{152}N_6NaO_{24}$ $[M+Na]^+$ 2276.0750, found 2276.0744.

Synthesis of Compound **II-54e**: **II-39e** (54.3 mg, 98 μmol), $Pd(PPh_3)_2Cl_2$ (3.4 mg, 5 mol%), triphenylphosphine (2.5 mg, 10 mol%), CuI (1.8 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (19.5 mg, 2.0 eq.) in acetonitrile (1 mL) and **II-53e** (174.8 mg, 1.0 eq.) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-54e** (159.7 mg, 74%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.23 (m, 35 H), 7.14 (t, *J* = 7.8 Hz, 2 H), 7.08 (m, 10 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 4.06 (m, 12 H), 3.75 (m, 12 H), 3.60 (m, 36 H), 3.52 (m, 12 H), 3.35 (m, 18 H), 0.20 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.1, 135.9, 135.7, 135.7, 132.8, 132.5, 132.4, 132.1, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.3, 90.2, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.7, 50.6, 50.6, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{135}H_{148}N_6NaO_{24}Si$ $[M+Na]^+$ 2288.0206, found 2288.0178.

Synthesis of Compound **II-54g**: **II-39g** (86.9mg, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (5.3 mg, 5 mol%), triphenylphosphine (3.9 mg, 10 mol%), CuI (2.8 mg, 10 mol%) and acetonitrile (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (30.4 mg, 2.0 eq.) in acetonitrile (1 mL) and **II-53g** (286.6 mg, 1.0 eq.) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-54g** (275.1 mg, 78%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.25 (m, 34 H), 7.15-7.07 (m, 15 H), 4.10 (br, 6 H), 3.92 (br, 6 H), 3.74-3.49 (m, 54 H), 3.34 (m, 18 H), 1.19 (m, 18 H), 0.20 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.9, 135.8, 133.2, 132.7,

132.4, 132.2, 131.1, 131.1, 130.0, 129.0, 129.0, 128.0, 127.7, 127.5, 124.6, 124.5, 121.1, 120.9, 120.6, 104.3, 95.1, 90.5, 90.3, 90.3, 89.5, 89.3, 73.8, 73.7, 73.7, 72.0, 80.9, 80.6, 68.4, 68.4, 68.4, 59.2, 56.7, 56.7, 56.6, 56.5, 17.7, 17.6, 0.0.HRMS (ESI+) m/z calcd for $C_{141}H_{160}N_6NaO_{24}Si$ $[M+Na]^+$ 2372.1145, found 2372.1126.

Synthesis of Compound **II-55e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.1 mL, 0.1 mmol) was added to a stirred solution of **II-54e** (153.1 mg, 68 μmol) in THF (1.5 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by recycle-GPC (chloroform) to give **II-55e** as yellow oil (105.5 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.21 (m, 35 H), 7.15 (t, *J* = 7.8 Hz, 2 H), 7.10-7.07 (m, 12 H), 4.07 (m, 12 H), 3.75 (m, 12 H), 3.61 (m, 36 H), 3.52 (m, 12 H), 3.35 (m, 18 H), 3.06 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.7, 144.4, 144.1, 135.9, 135.6, 132.9, 132.4, 132.3, 131.1, 130.0, 129.0, 128.9, 128.9, 128.0, 127.8, 127.7, 124.6, 124.5, 124.5, 121.1, 120.8, 120.4, 90.4, 90.2, 89.6, 89.4, 82.8, 78.2, 72.0, 70.7, 70.6, 70.4, 68.3, 68.2, 59.2, 50.6, 50.6, 50.5. HRMS (ESI+) m/z calcd for $C_{132}H_{140}N_6NaO_{24}$ $[M+Na]^+$ 2215.9811, found 2215.9751.

Synthesis of Compound **II-55g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.15 mL, 0.15 mmol) was added to a stirred solution of **II-54g** (265.1 mg, 0.11 mmol) in THF (3 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-55g** as yellow oil (195.0 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.21 (m, 34 H), 7.17-7.12 (m, 15 H), 4.11 (br, 6 H), 3.94 (br, 6 H), 3.74-3.49 (m, 54 H), 3.34 (m, 18 H), 3.05 (s, 1 H), 1.19 (m, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.8, 132.9, 132.4, 132.2, 131.1, 129.9, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.5, 120.9, 120.6, 120.1, 90.5, 90.4, 89.5, 89.3, 82.9, 78.1, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.6, 17.7, 17.6. HRMS (ESI+) m/z calcd for $C_{138}H_{152}N_6NaO_{24}$ $[M+Na]^+$ 2300.0750, found 2300.0700.

Synthesis of Compound **II-10e**: **II-45e** (8.0 mg, 17 μmol), $Pd(PPh_3)_2Cl_2$ (0.6 mg, 5 mol%), triphenylphosphine (0.5 mg, 10 mol%), CuI (0.4 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (9.8 mg, 6 eq.) in acetonitrile (1 mL) and **II-55e** (34.6 mg, 16 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give **II-10e** (18.1 mg, 45%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.07 (m, 58 H), 4.07 (m, 14 H), 3.76 (m, 14 H), 3.62 (m, 42 H), 3.52 (m, 14 H), 3.35 (m, 21 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.9, 169.8, 144.5, 144.2, 136.1, 136.0, 135.7, 135.7, 132.5, 132.4, 131.1, 131.0, 130.0, 129.2, 129.0, 128.9, 128.9, 128.0, 128.0, 127.8, 126.9, 124.6, 124.6, 124.2, 124.2, 121.2, 121.2, 120.9, 90.4, 90.3, 90.0, 89.8, 89.6, 89.4, 72.1, 70.7, 70.7, 70.5, 70.4, 68.4, 68.3, 68.2, 59.2, 50.7, 50.7, 50.6, 50.5. HRMS (ESI+) m/z calcd for $C_{152}H_{163}N_7NaO_{28}$ $[M+Na]^+$ 2557.1438, found 2557.1429.

Synthesis of Compound **II-10g**: **II-45g** (14.7 mg, 30 μmol), $Pd(PPh_3)_2Cl_2$ (1.1 mg, 5 mol%), triphenylphosphine (0.8 mg, 10 mol%), CuI (0.6 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (9.3 mg, 3.1 eq.) in acetonitrile (1 mL) and **II-55g** (68.3 mg, 30 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give **II-10g** (32.8 mg, 42%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.21 (m, 39 H), 7.18-7.10 (m, 19 H), 4.10 (br, 7 H), 3.94 (br, 7 H), 3.75-3.49 (m, 63 H), 3.34 (m, 21 H), 1.19 (m, 21 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.2, 136.1, 135.8, 132.4, 132.2, 131.1, 131.0, 130.0, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.2, 120.9, 120.9, 120.6, 90.5, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2, 56.7, 56.6, 56.5, 17.6. HRMS (ESI+) m/z calcd for $C_{159}H_{177}N_7NaO_{28}$ $[M+Na]^+$ 2655.2534, found 2655.2526.

Synthesis of Compound **II-56e**: **II-39e** (15.0 mg, 0.27 mmol), $Pd(PPh_3)_2Cl_2$ (0.9 mg, 5 mol%), triphenylphosphine (0.7 mg, 10 mol%), CuI (0.5 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (5.2 mL 2.0 eq.) in acetonitrile (1 mL) and **II-55e** (58.0 mg, 1.0 eq.) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-56e** (39.7 mg, 57%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.23 (m, 39 H), 7.15 (t, *J* = 7.2 Hz, 4 H), 7.09 (m, 12 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 4.08 (m, 14 H), 3.76 (m, 14 H), 3.62 (m, 42 H), 3.52 (m, 14 H), 3.36 (m,21 H), 0.21 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.7, 144.5, 144.1, 136.0, 135.8, 135.7, 132.8, 132.4, 132.3, 131.1, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.3, 90.2, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 68.4, 68.3, 59.2, 50.7, 50.6, 50.5, 0.0. HRMS (ESI+) m/z calcd for $C_{157}H_{171}N_7NaO_{28}Si$ $[M+Na]^+$ 2653.1834, found 2653.1801.

Synthesis of Compound **II-56g**: **II-39g** (34.8 mg, 0.06 mmol), $Pd(PPh_3)_2Cl_2$ (2.1 mg, 5 mol%), triphenylphosphine (1.6 mg, 10 mol%), CuI (1.1 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (12.1 mg 2.0 eq.) in acetonitrile (1 mL) and **II-55g** (137.7 mg, 1.0 eq.) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-56g** (135.9 mg, 82%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.23 (m, 40 H), 7.17-7.08 (m, 17 H), 4.11 (br, 7 H), 3.92 (br, 7 H), 3.74-3.50 (m, 63 H), 3.34 (m, 21 H), 1.19 (m, 21 H), 0.21 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.9, 135.8, 133.2, 132.7, 132.4, 132.2, 131.1, 131.1, 130.0, 129.0, 129.0, 128.9, 128.0, 127.7, 127.6, 123.6, 124.5, 121.2, 120.9, 120.6, 104.3, 95.1, 90.5, 90.3, 90.3, 89.5, 89.3, 73.8, 73.7, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.5, 17.7, 17.6, 0.0. HRMS (ESI+) m/z calcd for $C_{164}H_{185}N_7NaO_{28}Si$ $[M+Na]^+$ 2751.2929, found 2751.2900.

Synthesis of Compound **II-57e**: A 1.0 M solution of tetrabutylammonium fluoride in THF (14.5 mg, 0.016 mmol) was added to a stirred solution of **II-56e** (37.7 mg, 0.014 mmol) in THF (1.5 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **II-57e** as yellow oil (28.9 mg, 79%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.21 (m, 41 H), 7.14 (t, *J* = 7.8 Hz, 2 H), 7.07 (m, 14 H), 4.07 (m, 14 H), 3.75 (m, 14 H), 3.60 (m, 42 H), 3.52 (m, 14 H), 3.35 (m, 21 H), 3.05 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.1, 135.9, 135.7, 133.4, 133.0, 132.5, 132.3, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.8, 124.6, 121.1, 120.8, 120.4, 90.4, 90.3, 89.6, 89.4, 82.8, 78.2, 72.0, 70.7, 70.7, 70.4, 68.3, 68.3, 59.2, 50.7, 50.6, 50.6. HRMS (ESI+) m/z calcd for $C_{154}H_{163}N_7NaO_{28}$ $[M+Na]^+$ 2581.1438, found 2581.1402.

Synthesis of Compound **II-57g**: A 1.0 M solution of tetrabutylammonium fluoride in THF (0.1 mL, 0.1 mmol) was added to a stirred solution of **II-56g** (129.5 mg, 0.047 mmol) in THF (1.5 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **II-57g** as yellow oil (61.2 mg, 49%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.21 (m, 41 H), 7.16-7.11 (m, 16 H), 4.10 (br, 7 H), 3.92 (br, 7 H), 3.73-3.49 (m, 63 H), 3.33 (m, 21 H), 3.05 (s, 1 H), 1.18 (m, 21 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.0, 144.7, 136.0, 135.8, 133.2, 132.8, 132.3, 132.2, 131.1, 129.9, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.5, 120.8, 120.6, 120.1, 90.5, 90.3, 89.5, 89.3, 82.9, 78.1, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.6, 17.7, 17.6. HRMS (ESI+) m/z calcd for $C_{161}H_{177}N_7NaO_{28}$ $[M+Na]^+$ 2679.2534, found 2679.2560.

Synthesis of Compound **II-11e**: **II-45e** (5.4 mg, 12 μmol), $Pd(PPh_3)_2Cl_2$ (0.4 mg, 5 mol%), triphenylphosphine (0.3 mg, 10 mol%), CuI (0.3 mg, 15 mol%) and acetonitrile (3 drops) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (5.8 mg, 5.2 eq.) in acetonitrile (0.5 mL) and **II-57e** (28.9 mg, 11 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by recycle-GPC (chloroform) to give **II-11e** (8.1 mg, 25%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.07 (m, 66 H), 4.07 (m, 16 H), 3.76 (m, 16 H), 3.60 (m, 48 H), 3.52 (m, 16 H), 3.35 (m, 24 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 144.2, 136.1, 135.9, 135.7, 132.5, 132.3, 131.1, 131.0, 130.0, 129.2, 129.0, 128.9, 128.9, 128.7, 128.6, 128.0, 127.8, 126.9, 124.6, 124.2, 121.1, 120.8, 90.4, 90.3, 90.0, 89.7, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 70.4, 68.3, 68.3, 68.1, 59.2, 50.7, 50.6, 50.4. HRMS (ESI+) m/z calcd for $C_{174}H_{186}N_8NaO_{32}$ $[M+Na]^+$ 2922.3065, found 2922.3048.

Synthesis of Compound **II-11g**: **II-45g** (10.2 mg, 21 μmol), $Pd(PPh_3)_2Cl_2$ (0.7 mg, 5 mol%), triphenylphosphine (0.6 mg, 10 mol%), CuI (0.4 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature

Et_3N (9.3 mg, 4.4 eq.) in acetonitrile (1 mL) and **II-57g** (55.9 mg, 21 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative-TLC (silica gel, ethyl acetate/methanol = 10/1) to give **II-11g** (22.1 mg, 35%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.11 (m, 66 H), 4.10 (br, 8 H), 3.93 (br, 8 H), 3.72-3.49 (m, 72 H), 3.34 (m, 24 H), 1.19 (m, 24 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.7, 136.2, 136.1, 135.8, 135.8, 132.4, 132.2, 132.2, 131.1, 131.0, 10.0, 129.1, 129.0, 128.9, 128.7, 128.6, 128.0, 127.9, 127.7, 126.6, 124.6, 124.2, 120.9, 120.9, 120.6, 90.5, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 73.7, 72.1, 70.9, 70.6, 68.4, 68.3, 59.2, 56.7, 56.6, 56.5, 17.6. HRMS (ESI+) m/z calcd for $C_{182}H_{202}N_8NaO_{32}$ $[M+Na]^+$ 3034.4317, found 3034.4345.

Synthesis of Compound **III-1**: To a solution of **III-22** (207 mg, 0.24 mmol) in dry dichloromethane (2.5 mL), DBU (37 mg, 1.0 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 15 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-1** as a yellow solid (106 mg, 69%).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 1 H), 7.18 (d, *J* = 7.9 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 2 H), 7.32 (m, 3 H), 7.10 (t, *J* = 7.1 Hz, 1 H), 6.60 (d, *J* = 6.2 Hz, 1 H), 6.40 (d, *J* = 7.8 Hz, 1 H), 6.17 (s, 1 H), 5.26 (d, *J* = 4.8 Hz, 2 H), 3.93 (m, 4 H), 3.73 (s, 3 H), 3.31 (s, 3 H), 2.17 (m, 2 H), 1.07 (m, 12 H).

Synthesis of Compound **III-2**: To a solution of **III-26** (314 mg, 0.23 mmol) in dry dichloromethane (3 mL), DBU (0.04 mL, 1.0 eq.) was added. The mixture was stirred for 30 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-2** as a yellow solid (152 mg, 58%).^{1}H NMR (300 MHz, $CDCl_3$) δ 12.62 (s, 1 H), 11.10 (s, 1 H), 9.25 (d, *J* = 6.8 Hz, 1 H), 8.64 (d, *J* = 6.7 Hz, 1 H), 8.16 (dd, *J* = 1.0, 8.4 Hz, 1 H), 7.92 (s, 1 H), 7.84 (t, *J* = 8.0 Hz, 1 H), 7.78 (s, 1 H), 7.71 (dd, *J* = 1.1, 8.4 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 1 H), 7.51 - 7.38 (m, 4 H), 7.05 (t, *J* = 7.7 Hz, 1 H), 6.93 (s, 1 H), 6.75 (s, 1 H), 6.20 (dd, *J* = 2.3, 8.4 Hz, 1 H), 5.92 (d, *J* = 7.8 Hz, 1 H), 5.86 (d, *J* = 8.0 Hz, 1 H), 5.70 (d, *J* = 2.3 Hz, 1 H), 5.03 (d, *J* = 13.7 Hz, 1 H), 4.37 (d, *J* = 13.6 Hz, 1 H), 4.34 (t, *J* = 8.6 Hz, 1 H), 4.24 (d, *J* = 6.5 Hz, 2 H), 4.18 (t, *J* = 7.7 Hz, 1 H), 3.79 - 3.68 (m, 6 H), 3.58 (s, 3 H), 2.68 (s, 3 H), 2.44 (m, 2 H), 2.17 (m, 1 H), 2.06 (m, 1 H), 1.23 (m, 12 H), 1.09 (t, *J* = 6.4 Hz, 6 H), 0.94 (d, *J* = 6.5 Hz, 6 H).

Synthesis of Compound **III-3**: To a solution of **III-29** (120 mg, 0.088 mmol) in dry dichloromethane (0.5 mL), DBU (19 mg, 1.4 eq.) was added. The mixture was stirred for 1 h. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-3** as a yellow solid (87 mg, 87%).^{1}H NMR (300 MHz, $CDCl_3$) δ 11.98 (s, 1 H), 11.54 (s, 1 H), 9.04 (d, *J* = 7.5 Hz, 1 H), 8.89 (d, *J* = 7.4 Hz, 1 H), 8.07 (d, *J* = 7.9 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 7.85 (s, 1 H), 7.82 (s, 1 H), 7.65 (m, 2 H), 7.54 (t, *J* = 7.9 Hz, 1 H), 7.30 (d, *J* = 8.6 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 7.00 (m, 2 H), 6.77 (s, 1 H), 6,75 (s, 2 H), 6.68 (d, *J* = 7.0 Hz, 1 H), 6.44 (d, *J* = 7.1 Hz, 1 H), 6.20 (d, *J* = 7.7 Hz, 1 H), 5.95 (d, *J* = 2.0 Hz, 1 H), 5.46 (d, *J* = 14.4 Hz, 1 H), 4.60 (d, *J* = 14.7 Hz, 1 H), 4.14 (m, 5 H), 3.67 (s, 3 H), 3.54 (m, 1 H), 3.45 (m, 1 H), 2.96 (s, 3 H), 2.30 (m, 4 H), 2.11 (m, 4 H), 1.15 (d, *J* = 6.6 Hz, 12 H), 1.11-0.99 (m,

12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 163.6, 163.1, 159.9, 158.2, 145.4, 143.9, 143.7, 139.7, 135.0, 134.2, 131.6, 128.1, 128.0, 127.6, 127.0, 126.2, 123.1, 122.7, 121.9, 120.6, 120.2, 118.9, 118.3, 116.9, 116.5, 109.7, 109.3, 103.7, 100.8, 100.0, 99.1, 98.6, 97.7, 75.5, 75.5, 74.9, 74.3, 55.3, 54.5, 28.3, 28.3, 28.2, 19.4, 19.3.

Synthesis of Compound **III-4**: To a solution of **III-32** (157 mg, 0.098 mmol) in dry dichloromethane (0.5 mL), DBU (20 mg, 1.3 eq.) was added. The mixture was stirred for 1 h. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-4** as a yellow solid (90 mg, 68%).^{1}H NMR (300 MHz, $CDCl_3$) δ 12.75 (s, 1 H), 11.64 (s, 1 H), 10.66 (s, 1 H), 9.24 (d, *J* = 7.1 Hz, 1 H), 8.16 (d, *J* = 7.8 Hz, 1 H), 6.09 (t, *J* = 6.7 Hz, 2 H), 8.02 (s, 1 H), 7.99 (d, *J* = 8.2 Hz, 1 H), 7.88 (t, *J* = 7.9 Hz, 1 H), 7.73 (d, *J* = 7.7 Hz, 1 H), 7.51-7.43 (m, 3 H), 7.37-7.28 (m, 4 H), 7.18 (s, 1 H), 7.01 (t, *J* = 7.8 Hz, 1 H), 6.97 (s, 1 H), 6.84 (s, 1 H), 6.21 (dd, *J* = 2.2, 8.4 Hz, 1 H), 5.96 (d, *J* = 7.1 Hz, 1 H), 5.81 (t, *J* = 8.0 Hz, 1 H), 5.67 (d, *J* = 2.1 Hz, 1 H), 5.13 (d, *J* = 13.6 Hz, 1 H), 4.47 (dd, *J* = 6.0, 8.9 Hz, 1 H), 4.38 (d, *J* = 13.7 Hz, 1 H), 4.29 (d, *J* = 8.1 Hz, 1 H), 4.19 (dd, *J* = 6.3, 9.0 Hz, 1 H), 4.40-3.90 (m, 4 H), 3.82-3.69 (m, 4 H), 3.60 (d, *J* = 6.4 Hz, 2 H), 3.57 (s, 3 H), 2.65 (s, 3 H), 2.57 (m, 1 H), 2.39 (m, 2 H), 2.21 (m, 1 H), 1.96 (m, 1 H), 1.42 (s, 3 H), 1.30-1.24 (m, 15 H), 1.21-1.11 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 165.0, 164.1, 163.9, 163.3, 163.2, 162.9, 161.6, 160.7, 160.2, 158.4, 151.2, 150.1, 149.8, 148.9, 145.1, 143.3, 142.7, 141.9, 139.0, 138.2, 134.7, 133.7, 133.4, 132.9, 128.9, 127.9, 127.2, 127.0, 126.7, 126.3, 123.4, 123.1, 122.2, 122.1, 120.5, 119.5, 117.6, 117.2, 116.8, 116.7, 116.4, 116.3, 115.9, 110.1, 109.6, 103.6, 100.3, 99.0, 98.6, 97.7, 75.9, 75.5, 75.2, 55.3, 54.3, 48.6, 28.4, 28.3, 28.2, 27.9, 27.0, 19.7, 19.5, 19.5, 19.3, 19.2, 19.1.

Synthesis of compound **III-5**: To a solution of **III-39** (655 mg, 0.37 mmol) in dry dichloromethane (2 mL), DBU (68.2 mg, 1.2 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-5** as a yellow solid (500 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$, 273 K) δ 12.39 (s, 1 H), 10.84 (s, 1 H), 9.25 (d, *J* = 7.7 Hz, 1 H), 8.53 (d, *J* = 6.7 Hz, 1 H), 8.18 (m, 1 H), 8.12 (d, *J* = 7.2 Hz, 1 H), 8.03 (dd, *J* = 8.3, 1.0 Hz, 1 H), 7.81 (s, 1 H), 7.78 (m, 2 H), 7.71 (t, *J* = 8.0 Hz, 1 H), 7.60 (s, 1 H), 7.58 (m, 1 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.43 (m, 2 H), 7.30 (m, 1 H), 7.19 (s, 1 H), 7.13 (d, *J* = 7.3 Hz, 1 H), 7.08 (t, *J* = 7.9 Hz, 1 H), 6.95 (s, 1 H), 6.92 (d, *J* = 8.3 Hz, 1 H), 6.64 (s, 1 H), 6.43 (d, *J* = 7.6 Hz, 1 H), 6.20 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.17 (d, *J* = 6.8 Hz, 1 H), 6.04 (m, 3 H), 5.71 (d, *J* = 2.3 Hz, 1 H), 5.42 (t, *J* = 7.9 Hz, 1 H), 5.22 (d, *J* = 14.3 Hz, 1 H), 5.06 (d, *J* = 13.9 Hz, 1 H), 4.70 (d, *J* = 13.7 Hz, 1 H), 4.29 (m, 2 H), 4.23 (m, 2 H), 4.12 (m, 6 H), 3.84-3.45 (m, 31 H), 3.24 (s, 3 H), 3.14 (br, 1 H), 2.99 (br, 1 H), 2.72 (s, 1 H), 2.44 (m, 1 H), 2.33 (m, 1 H), 2.24 (m, 1 H), 1.22 (s, 3 H), 2.04 (m, 1 H), 1.90 (m, 1 H), 1.27-1.10 (m, 36 H). minor peak: (major : minor = 3 : 2) δ 12.72 (br, 1 H), 12.41 (s, 1 H), 11.09 (s, 1 H), 9.34 (d, *J* = 7.5 Hz, 1 H), 9.23 (d, *J* = 7.7 Hz, 1 H), 8.75 (d, *J* = 7.7 Hz, 1 H), 8.67 (d, *J* = 7.5 Hz, 1 H), 8.03 (m, 1 H), 7.93 (br, 1 H), 7.89 (br, 1 H), 7.72-7.67 (br, 5 H), 7.62 (m, 2 H), 7.30 (m, 2 H), 7.13 (m, 2 H), 7.08 (br, 2 H), 6.89 (br, 1 H), 6.68 (br, 1 H), 6.39 (d, *J* = 9.1 Hz, 1 H), 6.31 (d, *J* = 6.4 Hz, 1 H), 6.22 (d, *J* = 7.7 Hz, 1 H), 6.1 (s, 1 H), 5.94-5.77 (br, 5 H), 5.67-5.52 (br, 2 H), 5.23-5.05 (br, 3 H), 4.72 (br, 2 H), 4.58 (br, 2 H), 4.05 (t, *J* = 7.0 Hz, 2 H), 3.99 (br, 3 H), 3.19 (s, 2 H), 2.84 (br, 2 H), 0.99-0.57 (m, 36 H). ^{13}C NMR (150 MHz, $CDCl_3$, 273 K) δ169.0, 164.1, 163.9, 163.8, 163.7, 163.6, 163.5, 161.5, 161.1, 160.3, 159.8, 158.5, 158.5, 158.3, 154.4, 153.7,

151.4, 148.5, 143.5, 142.9, 142.5, 140.5, 140.2, 138.6, 138.4, 137.4, 137.0, 134.8, 134.7, 133.8, 131.6, 131.2, 128.8, 128.2, 127.8, 127.6, 127.4, 126.2, 124.1, 123.2, 122.9 ,122.5, 122.4, 122.3, 122.2, 120.8, 120.7, 120.5, 120.4, 119.2, 117.7, 117.4, 117.2, 116.5, 116.3, 110.4, 110.2, 109.9, 103.8, 103.7, 103.5, 101.4, 99.7, 99.3, 98.6, 98.3, 98.1, 98.0, 97.7, 75.5, 75.4, 75.4, 75.2, 74.9, 74.8, 74.5, 55.5, 55.4, 55.3, 55.2, 55.0, 54.9, 54.1, 53.8, 48.9, 47.4, 28.3, 28.3, 28.2, 28.1, 28.1, 28.0, 27.9, 18.6, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 19.1, 19.1, 19.0. HRMS (ESI+) m/z calcd for $C_{88}H_{93}N_{10}O_{15}$ $[M+H]^+$ 1529.6816, found 1539.6805.

Synthesis of Compound **III-6**: To a solution of **III-45** (129 mg, 0.07 mmol) in dry dichloromethane (1 mL), DBU (13.6 mg, 1.3 eq.) was added. The mixture was stirred for 1 h. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-6** as a yellow solid (128 mg, 93%).^{1}H NMR (600 MHz, $CDCl_3$) δ 12.24 (s, 1 H), 11.74 (s, 1 H), 11.68 (s, 1 H), 10.57 (s, 1 H), 8.76 (dd, *J* = 7.4, 1.0 Hz, 1 H), 8.23 (dd, *J* = 8.3, 1.2 Hz, 1 H), 8.21 (dd, *J* = 7.5, 1.1 Hz, 1 H), 8.09 (dd, *J* = 8.4, 1.2 Hz, 1 H), 8.06 (dd, *J* = 7.5, 1.1 Hz, 1 H), 8.00 (dd, *J* = 7.4, 1.1 Hz, 1 H), 7.93 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.83 (t, *J* = 7.9 Hz, 1 H), 7.74 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.56 (dd, *J* = 8.1, 1.1 Hz, 1 H), 7.37 (m, 2 H), 7.35 (s, 1 H), 7.27 (m, 2 H), 7.21 (m, 2 H), 7.19 (s, 1 H), 7.11 (s, 1 H), 7.04 (t, *J* = 7.9 Hz, 1 H), 6.87 (s, 1 H), 6.78 (s, 1 H), 6.54 (s, 1 H), 6.11 (dd, *J* = 8.4, 2.3 Hz, 1 H), 5.91 (dd, *J* = 7.4, 1.0 Hz, 1 H), 5.62 (dd, *J* = 8.6, 7.4 Hz, 1 H), 5.55 (d, *J* = 2.3 Hz, 1 H), 4.80 (d, *J* = 13.9 Hz, 1 H), 4.32 (dd, *J* = 8.4, 6.1 Hz, 1 H), 4.28 (dd, *J* = 8.4, 6.2 Hz, 1 H), 4.20 (dd, *J* = 8.6, 5.5 Hz, 1 H), 4.13-3.97 (m, 5 H), 3.93 (t, *J* = 8.4 Hz, 1 H), 3.72 (dd, *J* = 8.6, 6.8 Hz, 1 H), 3.65 (dd, *J* = 8.5, 6.5 Hz, 1 H), 3.56 (m, 2 H), 3.52 (s, 3 H), 3.49 (br, 2 H), 2.52-2.35 (m, 4 H), 2.47 (s, 3 H), 2.18 (m, 1 H), 1.94 (m, 1 H), 1.32 (d, *J* = 6.7 Hz, 6 H), 1.26 (m, 18 H), 1.13 (d, *J* = 6.7 Hz, 3 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 0.84 (d, *J* =6.7 Hz, 3 H), 0.84 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 164.2, 164.1, 163.4, 163.2, 163.1, 163.0, 161.7, 161.7, 161.6, 161.5, 160.8, 160.0, 158.2, 151.3, 150.3, 149.2, 149.0, 148.6, 144.8, 143.3, 142.5, 141.7, 138.4, 138.2, 137.7, 137.0, 136.4, 133.7, 133.5, 133.4, 133.3, 132.9, 128.7, 127.6, 127.2, 126.9, 126.8, 126.6, 126.1, 123.0, 122.8, 122.3, 122.1, 121.8, 120.4, 119.4, 118.3, 117.3, 117.0, 116.6, 116.4, 116.4, 115.9, 115.7, 115.2, 110.0, 109.9, 103.3, 100.1, 99.6, 98.7, 98.3, 98.1, 97.6, 97.4, 75.7, 75.6, 75.4, 75.3, 75.1, 75.1, 55.3, 54.1, 48.4, 28.4, 28.4, 28.3, 28.3, 28.1, 27.9, 19.8, 19.7, 19.6, 19.6, 19.5, 19.5, 19.4, 19.3, 19.1, 19.1. HRMS (ESI+) m/z calcd for $C_{93}H_{97}N_{12}O_{15}$ $[M+H]^+$ 1621.7191, found 1691.7192.

Synthesis of Compound **III-7**: To a solution of **III-47** (60.1 mg, 0.03 mmol) in dry dichloromethane (1 mL), DBU (20.1 mg, 1.0 eq.) was added. The mixture was stirred for 10 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-7** as a yellow solid (43.7 mg, 82%).^{1}H NMR (300 MHz, $CDCl_3$) (Major : Minor 1 : Minor 2) = (10 : 3 : 1) (Major) δ 12.51 (s, 1 H), 11.59 (s, 1 H), 10.62 (s, 1 H), 9.23 (d, *J* = 7.5 Hz, 1 H), 8.08 (d, *J* = 7.2 Hz, 1 H), 8.04 (m, 2 H), 7.92 (m, 2 H), 7.85 (s, 1 H), 7.76 (m, 3 H), 7.59 (d, *J* = 8.6 Hz, 1 H), 7.48 (m, 2 H), 7.29 (m, 2 H), 7.18 (s, 1 H), 7.14 (s, 1 H), 7.06 (d, *J* = 8.2 Hz, 1 H), 7.03 (t, *J* = 8.0 Hz, 1 H), 6.96 (m, 3 H), 6.80 (s, 1 H), 6.72 (s, 1 H), 6.48 (dd, *J* = 2.2, 8.5 Hz, 1 H), 6.43 (s, 1 H), 6.27 (dd, *J* = 2.3, 8.2 Hz, 1 H), 6.07 (m, 2 H), 5.90 (d, *J* = 7.3 Hz, 1 H), 5.54 (d, *J* = 2.2 Hz, 1 H), 5.39 (t, *J* = 7.9 Hz, 1 H), 5.17 (d, *J* = 14.5 Hz, 1 H), 5.03 (d, *J* = 14.5 Hz, 1 H), 4.51 (m, 2 H), 4.27 (t, *J* = 8.2 Hz, 1 H), 4.14 (m, 1 H), 3.96 (m, 1 H), 3.76 (s, 3 H), 3.61 (s, 3 H), 3.25 (s,

3 H), 2.40 (m, 1 H), 2.28 (m, 3 H), 2.01 (m, 1 H), 1.80 (m, 1 H), 1.35 (m, 6 H), 1.18 (m, 27 H), 1.09 (d, *J* = 6.6 Hz, 3 H), 0.90 (d, *J* = 6.6 Hz, 6 H), 0.88 (d, *J* = 6.6 Hz, 3 H), 0.77 (m, 6 H). (Minor 1) δ 12.82 (s, 1 H), 11.71 (s, 1 H), 10.66 (s, 1 H), 9.27 (d. *J* = 7.5 Hz, 1 H), 6.16 (d, *J* = 2.2 Hz, 1 H). (Minor 2) δ 12.81 (s, 1 H), 12.57 (s, 1 H), 11.61 (s, 1 H), 9.21 (d, *J* = 7.6 Hz, 1 H). (Minor not assignable) δ 8.20 (d, *J* = 9.1 Hz), 8.17 (d, *J* = 8.3 Hz), 7.98 (m), 7.86 (m), 7.39 (m), 6.56 (s), 6.59 (m), 5.86 (m), 3.98 (br), 3.87 (m), 3.80 (m), 3.66 (m), 3.53-3.45 (m), 3.08 (s), 2.98 (s), 2.62 (m), 1.28 (m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 168.8, 164.7, 164.6, 164.4, 163.6, 162.9, 162.6, 161.4, 161.1, 160.7, 160.4, 160.2, 159.7, 158.7, 158.7, 158.2, 153.9, 152.2, 150.1, 150.0, 148.7, 145.4, 143.0, 142.8, 142.5, 140.5, 139.8, 138.4, 137.9, 136.7, 136.1, 134.6, 134.5, 133.4, 133.0, 132.7, 132.2, 131.5, 131.2, 128.7, 128.6, 127.7, 127.3, 126.9, 126.9, 126.7, 125.6, 123.9, 122.9, 122.7, 122.4, 121.9, 121.7, 120.7, 120.2, 118.9, 117.6, 117.2, 117.1, 116.7, 116.6, 116.5, 116.3, 116.2, 115.8, 115.6, 109.9, 109.5, 109.4, 103.7, 103.3, 101.0, 99.2, 98.8, 98.7, 98.2, 98.0, 97.8, 97.5, 75.7, 75.4, 75.2, 75.1, 74.8, 74.6, 74.2, 55.4, 55.4, 55.2, 55.2, 55.0, 54.8, 54.4, 54.0, 53.4, 48.9, 47.1, 28.3, 28.3, 28.2, 28.1, 28.0, 27.9, 27.7, 19.8, 19.6, 19.6, 19.5, 19.5, 19.4, 19.3, 19.2, 19.1, 19.0.

Synthesis of Compound **III-8:** To a solution of **III-49** (43.4 mg, 0.022 mmol) in dry dichloromethane (0.5 mL), DBU (13.2 mg, 3.9 eq.) in dry dichloromethane (0.5 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by GPC to give **III-8** as a yellow solid (29.8 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) (Major : Minor = 10 : 1) (Major) δ 12.38 (s, 1 H), 11.56 (s, 1 H), 10.85 (s, 1 H), 9.27 (d, *J* = 7.6 Hz, 1 H), 9.08 (d, *J* = 6.8 Hz, 1 H), 8.43 (d, *J* = 6.6 Hz, 1 H), 8.05 (d. *J* = 8.3 Hz, 1 H), 8.00 (d, *J* = 8.3 Hz, 1 H), 7.82 (s, 1 H), 7.79 (d, *J* = 7.4 Hz, 1 H), 7.74 (m, 2 H), 7.71 (s, 1 H), 7.68 (m, 2 H), 7.62 (t, *J* = 8.0 Hz, 2 H), 7.57 (s, 1 H), 7.54 (d, *J* = 8.2 Hz, 1 H), 7.51 (s, 1 H), 7.33-7.26 (m, 4 H), 7.07 (m, 3 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 6.72 (s, 1 H), 6.38 (d, *J* = 2.2 Hz, 1 H), 6.34 (dd, *J* = 2.3, 8.4 Hz, 1 H), 6.14 (m, 2 H), 6.02 (dd, *J* = 1.1, 7.5 Hz, 1 H), 5.71 (m, 2 H), 5.48 (t, *J* = 8.1 Hz, 1 H), 4.89 (d, *J* = 14.3 Hz, 1 H), 4.73 (d, *J* = 13.4 Hz, 1 H), 4.32 (dd, *J* = 6.4, 8.8 Hz, 1 H), 4.16 (m, 1 H), 4.10 (m, 5 H), 3.90 (dd, *J* = 6.3, 8.9 Hz, 1 H), 3.84 (d, *J* = 6.6 Hz, 2 H), 3.82 (m, 1 H), 3.76 (s, 6 H), 3.69 (m, 2 H), 3.67 (s, 3 H), 3.60 (d, *J* = 13.7 Hz, 1 H), 3.05 (m, 1 H), 2.99 (m, 1 H), 2.45 (m, 1 H), 2.31 (m, 3 H), 2.14 (s, 3 H), 2.08 (m, 1 H), 1.72 (m, 1 H), 1.25 (d, *J* = 6.6 Hz, 6 H), 1.17 (m, 12 H), 1.13 (d, *J* = 6.6 Hz, 6 H), 0.96 (m, 6 H).0.68 (d, *J* = 6.6 Hz, 3 H), 0.61 (d, *J* = 6.6 Hz, 3 H). (Minor) δ 12.43 (s, 1 H), 11.52 (s, 1 H), 11.48 (s, 1 H), 9.22 (d, *J* = 7.6 Hz, 1 H), 8.98 (d, *J* = 6.6 Hz, 1 H), 8.80 (d, *J* = 7.5 Hz, 1 H), 8.13 (d, *J* = 8.3 Hz, 1 H), 7.43 (m, 5 H), 7.36 (m, 3 H), 6.26 (m, 6 H), 5.98 (d, *J* = 2.3 Hz, 1 H), 5.79 (d, *J* = 14.5 Hz, 1 H), 5.68 (s, 3 H), 5.60 (d, *J* = 7.1 Hz, 1 H), 5.37 (d, *J* = 14.3 Hz, 1 H), 3.43 (s, 3 H), 2.94 (s, 3 H), 1.07 (m, 12 H), 0.89 (d, *J* = 6.6 Hz, 6 H), 0.85 (d, *J* = 6.6 Hz, 6 H), 0.70 (d, *J* = 6.6 Hz, 3 H), 0.53 (m, 6 H);^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 169.4, 167.2, 164.2, 163.7, 163.7, 163.5, 163.4, 163.3, 161.5, 160.9, 160.7, 159.9, 158.9, 158.6, 154.2, 151.5, 150.1, 149.5, 148.6, 143.6, 143.2, 142.6, 140.7, 140.0, 139.3, 138.4, 137.3, 137.1, 135.0, 134.6, 133.8, 131.7, 131.5, 130.0, 127.9, 127.8, 127.8, 127.7, 127.4, 126.0, 124.4, 123.3, 123.1, 122.3, 122.2, 120.7, 120.6, 120.5, 119.8, 119.0, 117.7, 117.4, 117.4, 116.7, 116.3, 116.2, 110.3, 109.9, 103.9, 103.6, 101.7, 101.4, 99.9, 99.3, 98.6, 98.4, 97.8, 75.5, 75.5, 75.2, 74.9, 74.0, 55.6, 55.4, 55.3, 53.8, 49.9, 47.7, 28.4, 28.3, 28.3, 28.2, 28.1, 27.8, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.2, 19.2, 19.1. HRMS (ESI+) m/z calcd for $C_{102}H_{107}N_{12}O_{17}$ $[M+H]^+$ 1771.7872, found 1771.7914.

Synthesis of Compound **III-9**: To a solution of **III-54** (108.4 mg, 0.054 mmol) in dry dichloromethane (0.5 mL), DBU

(15.6 mg, 3.9 eq.) in dry dichloromethane (0.5 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by GPC to give **III-9** as a yellow solid (80.7 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.08 (s, 1 H), 11.11 (s, 1 H), 10.92 (s, 1 H), 9.26 (d, *J* = 6.7 Hz, 1 H), 8.97 (d, *J* = 7.7 Hz, 1 H), 8.40 (d, *J* = 6.7 Hz, 1 H), 8.23 (d, *J* = 8.3 Hz, 1 H), 8.10 (d, *J* = 8.3 Hz, 1 H), 8.00 (d, *J* = 8.5 Hz, 1 H), 7.95 (s, 1 H), 7.83 (m, 2 H), 7.75 (s, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 8.6 Hz, 1 H), 7.35-7.28 (m, 3 H), 7.20 (s, 1 H), 7.17 (d, *J* = 8.2 Hz, 1 H), 7.15 (s, 1 H), 7.07-7.01 (m, 4 H), 6.80 (m, 2 H), 6.76 (d, *J* = 7.2 Hz, 1 H), 6.53 (d, *J* = 6.5 Hz, 1 H), 6.06 (dd, *J* = 2.3, 8.3 Hz, 1 H), 5.84 (dd, *J* = 2.3, 8.5 Hz, 1 H), 5.79 (d, *J* = 2.3 Hz, 1 H), 5.69 (d, *J* = 2.3 Hz, 1 H), 5.63 (t, *J* = 8.2 Hz, 1 H), 5.50 (d, *J* = 14.5 Hz, 1 H), 5.30 (d, *J* = 14.2 Hz, 1 H), 4.97 (d, *J* = 14.4 Hz, 1 H), 4.41 (m, 1 H), 4.24 (d, *J* = 6.4 Hz, 1 H), 4.17 (m, 1 H), 4.13 (d, *J* = 6.5 Hz, 2 H), 3.77 (d, *J* = 14.1 Hz, 1 H), 3.73 (d, *J* = 6.4 Hz, 2 H), 3.64 (s, 3 H), 3.45 (s, 3 H), 3.18 (m, 2 H), 3.04 (m, 1 H), 3.02 (s, 3 H), 2.79 (s, 3 H), 2.41-2.32 (m, 3 H), 2.05 (m, 1 H), 1.96 (m, 1 H), 1.78 (m, 1 H), 1.23 (d, *J* = 6.6 Hz, 6 H), 1.18 (m, 12 H), 0.95-0.90 (m, 12 H), 0.66 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 164.1, 163.8, 163.4, 163.3, 163.2, 163.1, 162.6, 161.4, 161.1, 160.0, 159.5, 158.6, 157.9, 152.2, 152.1, 151.9, 151.0, 150.2, 149.0, 143.9, 143.8, 142.7, 142.3, 140.6, 139.6, 139.4, 137.3, 136.7, 135.0, 134.7, 134.0, 132.3, 132.1, 128.8, 127.8, 127.7, 127.5, 126.8, 125.9, 125.3, 123.2, 123.1, 122.7, 121.7, 121.3, 120.9, 120.5, 120.4, 119.8, 119.4, 118.2, 117.5, 117.4, 117.2, 116.3, 115.3, 110.1, 109.4, 103.1, 101.9, 101.0, 100.6, 100.0, 98.8, 98.1, 97.7, 97.4, 75.6, 75.5, 75.4, 75.0, 74.3, 74.2, 55.2, 55.1, 54.6, 54.1, 48.5, 47.8, 28.4, 28.3, 28.1, 28.0, 27.8, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 18.9, 18.9. HRMS (ESI+) m/z calcd for $C_{102}H_{107}N_{12}O_{17}$ $[M+H]^+$ 1771,7872, found 1771.7828.

Synthesis of Compound **III-10**: To a solution of **III-57** (92.0 mg, 0.044 mmol) in dry dichloromethane (0.5 mL), DBU (14.2 mg, 3.9 eq.) in dry dichloromethane (0.5 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by GPC to give **III-10** as a yellow solid (68.2 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) (Major : Minor = 10 : 3) (Major) δ 12.43 (s, 1 H), 11.69 (s, 1 H), 11.57 (s, 1 H), 10.89 (s, 1 H), 10.34 (s, 1 H), 8.97 (d, *J* = 7.6 Hz, 1 H), 8.87 (d, *J* = 7.4 Hz, 1 H), 8.80 (d, *J* = 7.4 Hz, 1 H), 8.05 (m, 3 H), 7.98 (m, 1 H), 7.93 (t, *J* = 7.6 Hz, 1 H), 7.90 (s, 1 H), 7.87 (d, *J* = 7.4 Hz, 1 H), 7.76 (m, 2 H), 7.70 (m, 2 H), 7.63 (m, 4 H), 7.43 (m, 1 H), 7.04 (d, *J* = 8.2 Hz, 2 H), 7.30 (s, 1 H), 7.27 (m, 1 H), 7.24 (s, 1 H), 7.06 (t, *J* = 7.0 Hz, 1 H), 6.95 (m, 3 H), 6.70 (s, 1 H), 6.31 (d, *J* = 6.7 Hz, 1 H), 5.95 (m, 3 H), 5.05 (d, *J* = 2.3 Hz, 1 H), 4.67 (d, *J* = 12.2 Hz, 1 H), 4.45 (d, *J* = 13.2 Hz, 1 H), 4.04 (m, 1 H), 4.15 (m, 8 H), 4.06 (m, 2 H), 3.80 (m, 2 H), 3.68-3.60 (m, 4 H), 3.50 (t, *J* = 6.7 Hz, 1 H), 3.40 (m, 1 H), 3.34-3.29 (m, 2 H), 2.89 (s, 3 H), 2.83 (t, *J* = 8.1 Hz, 1 H), 2.53 (m, 1 H), 2.42 (m, 1 H), 2.36 (m, 3 H), 1.87 (m, 1 H), 1.82 (t, *J* = 6/7 Hz, 1 H), 1.70 (m, 1 H), 1.33-1.20 (m, 27 H), 1.16 (m, 9 H), 1.00 (d, *J* = 6.6 Hz, 3 H), 0.92 (d, *J* = 6.6 Hz, 3 H), 0.86 (m, 12 H), 0.70 (m, 6 H). (Minor) δ 11.44 (s, 1 H), 11.10 (s, 1 H), 10.59 (s, 1 H), 9.02 (d, *J* = 6.8 Hz, 1 H), 8.65 (d, *J* = 7.4 Hz, 1 H), 8.45 (d, *J* = 7.3 Hz, 1 H), 8.14 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 8.3 Hz, 1 H), 7.49 (t, *J* = 7.9 Hz, 1 H), 7.20 (s, 1 H), 7.10 (br, 1 H), 7.08 (br, 1 H), 7.03 (d, *J* = 8.2 Hz, 1 H), 7.01 (d, *J* = 8.1 Hz, 1 H), 6.80 (s, 1 H), 6.18 (s, 1 H), 5.90 (d, *J* = 6.7 Hz, 1 H), 5.57 (d, *J* = 2.3 Hz, 1 H), 3.98 (m, 1 H), 3.93 (m, 1 H), 3.44 (m, 1 H), 3.18 (m, 1 H), 2.11 (m, 1 H), 1.16 (m, 9 H), 0.88 (m, 18 H).^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 168.2, 164.8, 164.4, 164.0, 163.9, 163.8, 163.8, 163.7, 163.6, 163.4, 163.3, 163.2, 162.9, 162.9, 162.8, 161.7, 161.6, 161.6, 161.1, 160.7, 160.5, 160.1, 159.9, 159.0, 158.2, 157.0, 152.4, 151.4, 151.2, 150.8, 150.2, 150.1, 150.1, 149.9, 149.7, 149.2, 149.1, 148.9, 145.8, 145.1, 144.2, 143.3, 143.2, 140.3,

139.3, 138.9, 138.9, 138.6, 138.5, 138.5, 137.8, 137.7, 137.6, 136.9, 136.5, 136.3, 135.1, 134.9, 134.8, 134.7, 133.9, 133.5, 133.3, 133.2, 131.9, 131.0, 130.4, 129.7, 128.1, 128.0, 127.6, 127.3, 127.0, 126.8, 126.7, 126.2, 125.9, 124.7, 123.7, 123.0, 122.9, 122.9, 122.6, 122.5, 122.4, 121.9, 121.7, 121.3, 121.1, 121.0, 120.5, 120.3, 119.7, 119.5, 119.0, 117.7, 117.2, 116.9, 116.7, 116.5, 116.4, 116.2, 115.8, 115.5, 115.2, 110.2, 109.8, 109.5, 103.6, 101.8, 100.7, 99.5, 99.3, 99.2, 99.1, 98.8, 98.2, 98.1, 97.9, 97.2, 97.1, 75.7, 75.5, 75.4, 74.2, 75.1, 74.9, 74.7, 74.5, 74.1, 55.3, 54.3, 53.7, 53.3, 47.7, 28.4, 28.4, 28.2, 28.1, 28.0, 27.9, 27.8, 27.5, 19.7, 19.6, 19.5, 19.5, 19.3, 19.3, 19.3, 19.2, 19.2, 19.1, 19.1, 18.9, 18.8, 18.7. HRMS (ESI+) m/z calcd for $C_{107}H_{111}N_{14}O_{17}$ $[M+H]^+$ 1863.8246, found 1863.8230.

Synthesis of Compound **III-11**: To a solution of **III-62** (113 mg, 0.05 mmol) in dry dichloromethane (1 mL), DBU (7.5 mg, 1.0 eq.) was added. The mixture was stirred for 10 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-11** as a yellow solid (85.5 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major and three kinds of minor) (Major) δ 12.76 (s, 1 H), 12.37 (s, 1 H), 11.62 (s, 1 H), 11.06 (s, 1 H), 9.43 (d, *J* = 7.8 Hz, 1 H), 9.10 (d, *J* = 8.0 Hz, 1 H), 9.05 (d, *J* = 6.8 Hz, 1 H), 8.99 (t, *J* = 7.6 Hz, 1 H), 8.72 (d, *J* = 8.0 Hz, 1 H), 8.67 (m, 2 H), 8.64 (m, 2 H), 8.33 (m, 2 H), 8.01 - 7.95 (m, 8 H), 7.90 (s, 1 H), 7.87 - 7.27 (m, 40 H), 7.02 (m, 2 H), 6.97 - 6.92 (m, 3 H), 6.87 (m, 2 H), 6.79 (m, 2 H), 6.74 (s, 1 H), 6.71 (t, *J* = 7.4 Hz, 1 H), 6.66 (m, 1 H), 6.57 - 6.48 (m, 6 H), 6.08 (d, *J* = 1.2 Hz, 1 H), 6.06 (dd, *J* = 7.0, 1.2 Hz, 1 H), 5.98 (d, *J* = 1.2 Hz, 1 H), 5.79 (d, *J* = 14.0 Hz, 1 H), 5.39 (m, 2 H), 4.88 (m, 3 H), 4.63 (br, 3 H), 4.44 (br, 1 H), 4.32 (m, 4 H), 4.24 - 4.08 (m, 18 H), 3.90 (m, 10 H), 3.81 - 3.76 (m, 6 H), 3.62 (m, 3 H), 3.53 (s, 5 H), 3.11 (s, 3 H), 3.03 (s, 3 H), 2.74 (m, 3 H), 2.58 (t, *J* = 6.4 Hz, 2 H), 2.55 (s, 1 H), 2.48 (m, 1 H), 2.38 - 2.27 (m, 13 H), 2.17 - 1.52 (m, 15 H), 1.29 - 1.09 (m, 74 H), 1.05 - 0.78 (m, 40 H), 0.68 (m, 8 H), 0.57 (m, 9 H), 0.52 (d, *J* = 6.7 Hz, 3 H). (Minor) δ 11.91 (s, 1 H), 11.82 (s, 1 H), 11.80 (s, 1 H), 11.59 (s, 1 H), 11.55 (s, 1 H), 11.48 (s, 1 H), 11.40 (s, 1 H), 11.32 (s, 1 H), 11.28 (s, 1 H), 11.08 (s, 1 H), 10.63 (br, 1 H), 9.16 (br, 1 H), 8.89 (d, *J* = 7.8 Hz, 1 H), 8.58 (d, *J* = 7.8 Hz, 1 H), 8.54 (d, *J* = 7.8 Hz, 1 H), 8.46 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 7.6 Hz, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 7.13 (s, 1 H), 6.33 (d, *J* = 6.8 Hz, 1 H), 6.29 (d, *J* = 1.2 Hz, 1 H), 6.22 (dd, *J* = 7.4, 1.2 Hz, 1 H), 5.99 (d, *J* = 7.4 Hz, 1 H), 5.90 (d, *J* = 1.2 Hz, 1 H), 5.67 (d, *J* = 1.2 Hz, 1 H), 5.1 (dd, *J* = 6.8, 1.2 Hz, 1 H), 5.57 (d, *J* = 13.0 Hz, 1 H), 5.44 (d, *J* = 1.2 Hz, 1 H), 5.42 (s, 1 H), 5.32 (d, *J* = 13.8 Hz, 1 H), 5.23 (br, 1 H), 5.04 (d, *J* = 14.2 Hz, 1 H), 4.97 (d, *J* = 14.8 Hz, 1 H), 3.50 (t, *J* = 6.4 Hz, 1 H), 3.47 (s, 3 H), 3.28 (s, 3 H), 3.27 (s, 3 H), 3.18 (s, 3 H), 0.48 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.4, 169.1, 168.7, 166.4, 165.3, 164.5, 164.2, 164.1, 163.8, 163.7, 163.6, 163.5, 163.5, 163.4, 163.3, 163.3, 163.2, 163.1, 163.0, 162.9, 162.7, 162.6, 162.4, 162.2, 161.9, 161.7, 161.3, 160.9, 160.9, 159.8, 159.7, 159.5, 159.3, 159.3, 158.5, 157.3, 157.2, 156.1, 155.8, 155.3, 152.8, 151.6, 150.6, 148.9, 148.2, 148.2, 146.3, 145.0, 145.0, 144.8, 143.6, 143.0, 141.7, 140.2, 140.2, 140.0, 140.0, 139.9, 139.3, 138.9, 138.8, 138.5, 138.3, 137.2, 136.9, 136.8, 135.4, 135.4, 135.2, 134.9, 134.7, 134.4, 134.3, 134.2, 134.1, 133.5, 133.2, 133.1, 128.4, 128.1, 128.0, 127.6, 127.4, 127.3, 126.9, 126.7, 126.5, 126.4, 126.3, 126.2, 126.1, 125.9, 123.9, 123.2, 123.1, 123.0, 122.9, 122.8, 122.6, 122.5, 122.3, 122.2, 122.1, 122.0, 121.8, 121.7, 121.5, 121.3, 120.9, 120.9, 120.7, 120.5, 120.3, 120.2, 120.0, 119.2, 119.0, 118.6, 118.5, 118.4, 118.3, 118.2, 117.9, 117.7, 117.5, 117.1, 117.0, 116.5, 116.4, 116.2, 116.0, 115.9, 115.8, 115.5, 115.1, 110.6, 110.4, 109.9, 109.3, 109.1, 108.7, 108.6, 104.2, 104.0, 103.4, 103.2, 102.6, 102.2, 102.0, 101.3, 101.2, 100.9, 100.8, 100.3, 99.8, 99.6, 99.6, 98.9, 98.8, 98.6, 98.6, 98.4, 98.3, 98.2, 98.0, 97.5, 97.3, 97.2, 97.1, 96.3, 77.4, 77.2, 77.0, 75.6, 75.4, 75.3, 75.1, 74.9, 74.8, 74.5,

74.4, 74.0, 73.6, 70.7, 55.6, 55.5, 55.3, 55.2, 55.2, 55.1, 55.0, 54.9, 54.8, 54.7, 54.2, 53.8, 53.6, 53.5, 50.5, 49.5, 28.4, 28.3, 28.3, 28.1, 28.1, 27.7, 27.6, 19.5, 19.5, 19.5, 19.4, 19.4. 19.3, 19.3, 19.2, 19.2, 19.1, 19.1, 19.0, 18.9, 18.8, 18.7, 18.6. HRMS (ESI+) m/z calcd for $C_{116}H_{121}N_{14}O_{19}$ $[M+H]^+$ 2013.8927, found 2013.8982.

Synthesis of Compound **III-12**: To a solution of **III-67** (68.9 mg, 0.029 mmol) in dry dichloromethane (1 mL), DBU (6.2 mg, 1.0 eq.) was added. The mixture was stirred for 10 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **III-12** as a yellow solid (56 mg, 90%). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 174.7, 170.9, 169.1, 168.8, 167.2, 167.1, 164.3, 163.1, 163.9, 163.7, 163.5, 163.3, 163.0, 162.9, 161.3, 161.2, 160.9, 160.8, 160.7, 160.6, 159.7, 159.5, 158.8, 158.8, 158.6, 158.5, 158.4, 158.0, 154.2, 153.8, 153.0, 152.1, 151.0, 150.1, 149.5, 144.3, 144.2, 144.1, 143.9, 143.3, 142.5, 142.5, 142.0, 140.5, 140.1, 139.3, 139.2, 137.3, 136.6, 135.9, 135.3, 134.6, 133.5, 133.0, 132.4, 131.7, 131.7 ,13.15, 131.3, 129.9, 129.7, 129.4, 129.1, 128.6, 127.8, 127.6, 127.2, 126.7, 126.2, 125.9, 125.8, 124.9, 124.3, 124.1, 123.1, 123.0, 123.0, 122.3, 122.3, 122.3, 122.2, 121.3, 120.8, 120.7, 120.7, 120.4, 120.2, 119.8, 119.4, 119.4, 119.3, 118.8, 118.3, 118.0, 117.9, 117.6m 117.4, 117.4, 117.3, 116.9, 116.8, 116.5, 116.1, 115.9, 111.0, 110.0, 109.4, 109.0, 104.5, 104.2, 104.0, 104.0, 103.5, 103.2, 101.7, 101.1, 101.0, 100.8, 100.6, 100.3, 100.1, 100.1, 98.7, 98.6, 98.4, 98.2, 98.1, 97.9, 97.5, 97.0, 75.5, 75.4, 75.4, 75.3, 74.7, 74.1, 74.0, 55.5, 55.5, 55.4, 55.4, 55.2, 55.1, 54.3, 54.3, 54.2, 53.9, 49.7, 48.2, 47.4, 28.4, 28.3, 28.3, 28.3, 28.2, 28.2, 28.0, 27.8, 27.8, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 19.2, 19.1, 19.1, 19.1.

Synthesis of Compound **III-13**: See the reference 118.

Synthesis of Compound **III-14**: 10% Pd / C (204 mg) was added to a solution of **III-13** (2.002 g, 6.58 mmol) in ethyl acetate (45 mL) and stirred for 16 h at rt under hydrogen atmosphere. The reaction mixture was filtered through celite and concentrated to give **III-14** as a yellow solid (1.746 g, 96%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.48 (s, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 6.93 (dd, *J* = 7.5, 1.3 Hz, 1 H), 5.09 (br, 2 H), 4.02 (s, 3 H), 4.01 (d, *J* = 6.3 Hz, 2 H), 2.27 (m, *J* = 6.6 Hz, 1 H), 1.13 (d, *J* = 6.7 Hz, 6 H).

Synthesis of compound **III-15**: **III-14** (990 mg, 3.61 mmol) and 2,4-dimethoxybenzaldehyde (484 mg, 2.91 mmol) were mixed in 1,2-dichloroethane (15 mL) and then sodium triacetoxyborohydride (1.16 g, 5.47 mmol) was added. The mixture was stirred at r.t. under a N_2 atmosphere for 18 h. The reaction mixture was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with ethyl acetate. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 5) to give **III-15** as a yellow solid (1.265 g, 96%.). ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1 H), 7.37 (m, 2 H), 7.22 (d, *J* = 8.3 Hz, 1 H), 6.74 (t, *J* = 6.1 Hz, 1 H), 6.65 (dd, *J* = 6.9, 2.0 Hz, 1 H), 6.49 (d, *J* = 2.4 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.4 Hz, 1 H), 4.51 (d, *J* = 6.2 Hz, 2 H), 4.01 (s, 3 H), 4.00 (d, *J* = 6.4 Hz, 2 H), 3.87 (s, 3 H), 3.78 (s, 3 H), 2.26 (m, *J* = 6.7 Hz, 1 H), 1.12 (d, *J* = 6.7Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 162.7, 160.1, 158.4, 145.7, 145.3, 138.4, 129.2, 128.9, 123.0, 119.5, 107.3, 106.2, 104.0, 101.1, 98.7, 75.0, 55.5, 52.8, 42.1, 28.4, 19.4. HRMS (ESI+) m/z calcd for $C_{24}H_{29}N_2O_5$ $[M+H]^+$ 425.2071, found

425.2065.

Synthesis of Compound **III-16**: Potassium hydroxide (925 mg, 16.49 mmol) was added to a solution of **III-13** (2.001 g, 6.58 mmol) in 1,4-dioxane / water (80 mL / 80 mL) and stirred for 20 h at room temperature. The reaction mixture was quenched with 5% citric acid aq. and 1,4-dioxane was removed *in vacuo*. The residue was extracted with dichloromethane. The organic layer was washed with water, brine and dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-16** as a pale yellow solid (1.664 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.5, 1.3 Hz, 1 H), 8.22 (dd, *J* = 7.5, 1.3 Hz, 1 H), 7.72 (t, *J* = 8.2 Hz, 1 H), 7.26 (s, 1 H), 4.13 (d, *J* = 6.5 Hz, 2 H), 2.32 (m, *J* = 6.7 Hz, 1 H), 1.15 (d, *J* = 6.7 Hz, 6 H).

Synthesis of Compound **III-17**: A solution of **III-16** (504 mg, 1.74 mmol) in dry $CHCl_3$ (5 mL) was cooled to 0^{o}C. Oxalyl chloride (0.45 mL, 3 eq.) were added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. The resulting acid chloride was dissolved in dry $CHCl_3$ (9 mL) and added to a solution of **III-15** (667 mg, 0.9 eq.) and dry DIPEA (1.5 mL, 5 eq.) in dry $CHCl_3$ (3 mL). The mixture was stirred for 18h. The organic layer was washed with water, sat. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 3) to give **III-17** as a pale yellow solid (1.124 g, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.64 (t, *J* = 8.3 Hz, 3 H), 7.47 (m, 2 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.27 (s, 1 H), 6.39 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.30 (s, 1 H), 5.61 (d, *J* = 14.9 Hz, 1 H), 4.89 (d, *J* = 15.9 Hz, 1 H), 4.06 (s, 3 H), 4.00 (t, *J* = 8.6 Hz, 1 H), 3.88 (d, *J* = 6.5 Hz, 2 H), 3.79 (s, 1 H), 3.76 (s, 3 H), 3.54 (s, 3 H), 2.18 (m, 2 H), 1.06 (m, 12 H).

Synthesis of Compound **III-18**: The mixture of **III-17** (100 mg, 0.14 mmol) and LiI (96 mg, 5.1 eq.) in degassed ethyl acetate (1.4 mL) was heated to 80°C for 5 h. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-18** as a white solid (107 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.53 (dd, *J* = 7.4, 1.3 Hz, 1 H), 3.39-3.31 (m, 4 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 6.61 (d, *J* = 7.5 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.29 (d, *J* = 2.4 Hz, 1 H), 5.65 (d, *J* = 15.9 Hz, 1 H), 5.03 (d, *J* = 15.3 Hz, 1 H), 4.11 (br, 1 H), 4.04 (s, 3 H), 3.91 (d, *J* = 6.5 Hz, 3 H), 3.75 (s, 3 H), 3.69 (br, 1 H), 3.51 (s, 3 H), 2.18 (m, 2 H), 1.06 (m, 12 H).

Synthesis of Compound **III-19**: To a solution of **III-21** (427 mg, 0.48 mmol) in dichloromethane (4 mL), DBU (0.07 mL, 1 eq.) was added. The mixture was stirred for 15 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-19** as a yellow solid (330 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.53 (dd, *J* = 7.4, 1.3 Hz, 1 H), 3.39-3.31 (m, 4 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 6.61 (d, *J* = 7.5 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.29 (d, *J* = 2.4 Hz, 1 H), 5.65 (d, *J* = 15.9 Hz, 1 H), 5.03 (d, *J* = 15.3 Hz, 1 H), 4.11 (br, 1 H), 4.04 (s, 3 H), 3.91 (d, *J* = 6.5 Hz, 3 H), 3.75 (s, 3 H), 3.69 (br, 1 H), 3.51 (s, 3 H), 2.18 (m, 2 H), 1.06 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ166.6, 162.6, 161.6, 160.1, 158.5,

152.7, 148.3, 144.5, 144.1, 131.1, 127.8, 126.9, 126.8, 123.0, 121.7, 120.3, 118.6, 110.2, 109.5, 104.1, 101.4, 100.7, 98.1, 75.1, 74.7, 55.4, 55.1, 52.9, 28.2, 28.2, 19.3, 19.3. HRMS (ESI+) m/z calcd for $C_{38}H_{43}N_4O_7$ $[M+H]^+$ 667.3126, found 667.3111.

Synthesis of Compound **III-20**: See the reference 118.

Synthesis of Compound **III-21**: A solution of acid **III-20** (188 mg, 0.39 mmol) in dry $CHCl_3$ (3 mL) was cooled to 0°C. Oxalyl chloride (0.1 mL, 3 eq.) were added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. The resulting acid chloride was dissolved in dry $CHCl_3$ (4 mL) and added to a solution of **III-15** (150 mg, 0.9 eq.) and dry DIPEA (0.34 mL, 5 eq.) in dry $CHCl_3$ (1.5 mL). The mixture was stirred for 17h. The organic layer was washed with water, sat. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 3) to give **III-21** as a pale yellow solid (341 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (br, 2 H), 7.82 (d, *J* = 7.0 Hz, 3 H), 7.70 (t, *J* = 5.7 Hz, 3 H), 7.57 (t, *J* = 7.6 Hz, 2 H), 7.47-7.30 (m, 5 H), 7.21 (s, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 6.40 (dd, *J* = 8.5, 2.2 Hz, 1 H), 6.33 (d, *J* = 2.2 Hz, 1 H), 5.63 (d, *J* = 15.3 Hz, 1 H), 4.99 (d, *J* = 15.1 Hz, 1 H), 4.65 (m, 1 H), 4.54 (m, 1 H), 4.38 (t, *J* = 6.6 Hz, 1 H), 4.01 (s, 3 H), 3.99 (m, 1 H), 3.83 (t, *J* = 6.5 Hz, 2 H), 3.72 (s, 3 H), 3.56 (s, 3 H), 2.16 (m, 2 H), 1.05 (t, *J* = 6.8 Hz, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 166.2, 162.4, 161.6, 160.1, 158.3, 154.1, 153.2, 147.9, 144.0, 143.9, 143.2, 141.5, 141.4, 136.4, 134.4, 130.8, 127.9, 127.3, 126.9, 126.6, 125.1, 122.8, 120.8, 120.2, 120.1, 118.3, 114.8, 114.5, 104.2, 101.9, 100.7, 98.2, 75.0, 74.9, 66.8, 55.3, 55.2, 52.8, 49.2, 47.3, 28.1, 19.3. HRMS (ESI+) m/z calcd for $C_{53}H_{53}N_4O_9$ $[M+H]^+$ 889.3807, found 889.3785.

Synthesis of compound **III-22**: The mixture of **III-21** (1.5 g, 1.69 mmol) and LiI (1.16 g, 5 eq.) in degassed ethyl acetate (12 mL) was heated to 80°C for 12 h. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-22** as a white solid (1.44 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$, 273 K) δ 8.13 (d, *J* = 7.7 Hz, 1 H), 7.87 (m, 3 H), 7.81 (d, *J* = 8.2 Hz, 1 H), 7.76 (d, *J* = 7.1 Hz, 1 H), 7.73 (d, *J* = 7.3 Hz, 1 H), 7.67 (d, *J* = 7.1 Hz, 1 H), 7.59 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 1 H), 7.49 (t, *J* = 7.3 Hz, 2 H), 7.44 (t, *J* = 7.3 Hz, 1 H), 7.38 (t, *J* = 7.1 Hz, 1 H), 7.35 (s, 1 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.21 (s, 1 H), 7.04 (t, *J* = 8.1 Hz, 1 H), 6.43 (dd, *J* = 8.3, 2.1 Hz, 1 H), 6.14 (d, *J* = 2.2 Hz, 1 H), 5.29 (d, *J* = 14.5 Hz, 1 H), 5.21 (d, *J* = 14.3 Hz, 1 H), 4.78 (dd, *J* = 10.7, 6.1 Hz, 1 H), 4.60 (dd, *J* = 10.3, 6.2 Hz, 1 H), 4.41 (t, *J* = 6.1 Hz, 1 H), 3.96 (dd, *J* = 8.9, 6.8 Hz, 1 H), 3.85 (m, 2 H), 3.79 (dd, *J* = 8.7, 6.5 Hz, 1 H), 3.74 (s, 3 H), 3.27 (s, 3 H), 2.17 (m, 2 H), 1.04 (m, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$, 273 K) δ 169.5, 164.4, 163.7, 162.4, 160.3, 158.5, 153.1, 152.3, 145.9, 143.9, 143.8, 142.6, 142.3, 141.6, 141.4, 136.3, 134.3, 131.9, 128.1, 128.1, 128.0, 127.4, 127.1, 125.0, 122.9, 120.8, 120.5, 120.3, 117.4, 115.0, 114.6, 103.8, 100.8, 98.6, 98.2, 75.5, 75.0, 66.4, 55.5, 55.0, 53.7, 49.3, 47.3.28.1, 28.0, 19.3, 19.3, 19.3. HRMS (ESI+) m/z calcd for $C_{52}H_{51}N_4O_9$ $[M+H]^+$ 875.3651, found 875.3625.

Synthesis of Compound **III-23**: A solution of acid **III-20** (1.130 g, 2.34 mmol) in dry $CHCl_3$ (7 mL) was cooled to 0°C. Oxalyl chloride (0.6 mL, 3 eq.) were added. The solution was stirred at rt for 2 h. The solvent was removed under

high-vacuum line. The resulting acid chloride was dissolved in dry $CHCl_3$ (15 mL) and added to a solution of **III-14** (585 mg, 0.9 eq.) and dry DIPEA (2.0 mL, 5 eq.) in dry $CHCl_3$ (2 mL). The mixture was stirred for 17h. The organic layer was washed with water, sat. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 10) to give **III-23** as a yellow solid (1.481 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.52 (s, 1 H), 9.36 (s, 1 H), 8.95 (dd, *J* = 1.2, 7.6 Hz, 1 H), 8.44 (d, *J* = 7.2 Hz, 1 H), 8.01 (dd, *J* = 1,2, 8.5 Hz, 1 H), 7.96 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.81 (s, 1 H), 7.72 (t, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 7.7 Hz, 2 H), 7.58 (d, *J* = 8.1 Hz, 1 H), 7.44 (m, 3 H), 7.21 (t, *J* = 7.4 Hz, 2 H), 6.81 (dt, *J* = 1.0, 7.5 Hz, 2 H), 4.49 (d, *J* = 7.6 Hz, 2 H), 4.16 (m, 3 H), 3.97 (d, *J* = 6.0 Hz, 2 H), 3.96 (s, 3 H), 2.30 (m, 2 H), 1.17 (d, *J* = 6.7 Hz, 6 H), 1.12 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 163.9, 163.2, 162.9, 153.8, 150.4, 147.6, 143.7, 141.2, 134.9, 134.8, 128.5, 127.7, 127.6, 126.9, 125.2, 122.5, 119.9, 117.6, 117.3, 116.3, 115.8, 101.7, 99.1, 75.5, 75.4, 67.5, 53.0, 47.1, 28.3, 28.3, 27.0, 19.4, 19.3.

Synthesis of compound **III-24**: To a solution of **III-37** (1.00 g, 1.32 mmol) in dry dichloromethane (10 mL), phenylsilane (0.27 mL, 1.7 eq.) and tetrakis(triphenylphosphine)palladium(0) (29.6 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate) to give **III-24** as a yellow solid (950 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$, 273 K) δ 11.95 (br, 1 H), 9.06 (br, 1 H), 8.87 (br, 1 H), 8.41 (br, 1 H), 7.92 (br, 1 H), 7.85 (d, *J* = 8.2 Hz, 1 H), 7.64 (m, 7 H), 7.41 (br, 1 H), 6.96 (br, 2 H), 4.56 (br, 2 H), 4.26 (br, 1 H), 3.97 (d, *J* = 6.6 Hz, 2 H), 3.95 (d, *J* = 6.5 Hz, 2 H), 2.28 (m, 2 H), 1.14 (d, *J* = 6.8 Hz, 6 H), 1.13 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$, 273 K) δ165.8, 163.2, 162.6, 153.5, 149.5, 146.5, 143.8, 141.2, 138.2, 127.3, 134.2, 133.8, 128.0, 127.5, 126.9, 125.3, 121.9, 119.9, 117.8, 116.2, 115.2, 100.3, 98.7, 75.4, 75.0, 67.5, 46.8, 28.2, 19.3. HRMS (ESI+) m/z calcd for $C_{43}H_{41}N_4O_7$ $[M+H]^+$ 725.2970, found 725.2967.

Synthesis of Compound **III-25:** A solution of acid **III-24** (362 mg, 0.50 mmol) in dry $CHCl_3$ (2 mL) was cooled to 0^{o}C. Oxalyl chloride (0.1 mL, 2.3 eq.) were added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. The resulting acid chloride was dissolved in dry $CHCl_3$ (3 mL) and added to a solution of **III-19** (291 mg, 0.9 eq.) and dry DIPEA (0.4 mL, 4.6 eq.) in dry $CHCl_3$ (0.5 mL). The mixture was stirred for 15h. The organic layer was washed with water, sat. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 10) to give **III-25** as a yellow solid (579 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.8 (s, 1 H), 11.0 (s, 1 H), 9.30 (dd, *J* = 1.2, 7.7 Hz, 1 H), 8.67 (dd, *J* = 1.1, 7.6 Hz, 1 H), 8.58 (s, 1 H), 8.17 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.98 (s, 1 H), 7.92 (dd, *J* = 1.0, 8.3 Hz, 1 H), 7.87 (t, *J* = 8.1 Hz, 1 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.65-7.14 (m, 12 H), 6.91-6.78 (m, 4 H), 6.07 (dd, *J* = 2.4, 8.5 Hz, 1 H), 5.95 (d, *J* = 2.3 Hz, 1 H), 5.79 (t, *J* = 8.1 Hz, 1 H), 5.03 (d, *J* = 15.0 Hz, 1 H), 4.57 (d, *J* = 14.9 Hz, 1 H), 4.37 (dd, *J* = 5.8, 8.9 Hz, 1 H), 4.22-3.99 (m, 6 H), 3.82 (s, 3 H), 3.80-3.60 (m, 4 H), 3.58 (s, 3 H), 3.25 (s, 3 H), 2.50-1.97 (m, 4 H), 1.21-1.10 (m, 18 H), 0.91 (d, *J* = 6.7 Hz, 6 H).

Synthesis of Compound **III-26**: The mixture of **III-25** (50 mg, 0.036 mmol) and LiI (25 mg, 5.3 eq.) in degassed ethyl acetate (1 mL) was heated to 80°C for 20 h. After quenching the reaction mixture with water, the solution was

washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-26** as a white solid (34 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.8 (s, 1 H), 11.1 (s, 1 H), 9.26 (dd, *J* = 1.0, 7.7 Hz, 1 H), 8.70 (dd, *J* = 1.2, 7.7 Hz, 1 H), 8.57 (s, 1 H), 8.20 (dd, *J* = 1.2, 8.4 Hz, 1 H), 8.01 (s, 1 H), 7.98 (dd, *J* = 1.1, 8.3 Hz, 1 H), 7.89 (t, *J* = 7.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 164.9, 164.1, 164.0, 163.3, 163.3, 163.1, 161.9, 160.2, 158.4, 151.6, 151.6, 151.5, 149.4, 145.3, 144.2, 143.9, 142.8, 142.0, 141.3, 141.1, 138.7, 137.2, 137.1, 134.4, 134.3, 133.5, 132.9, 128.6, 128.3, 127.4, 127.0, 126.8, 126.7, 126.7, 126.6, 125.2, 125.1, 123.2, 122.6, 122.2, 120.6, 119.8, 119.8, 119.6, 118.3, 117.1, 116.8, 116.4, 115.9, 115.4, 114.6, 103.6, 100.3, 99.8, 98.9, 97.9, 97.7, 75.9, 75.6, 75.4, 75.2, 67.2, 55.3, 54.4, 48.6, 46.8, 28.4, 28.3, 28.1, 27.9, 27.0, 19.7, 19.4, 19.4, 19.3, 19.3, 19.2, 19.1.

Synthesis of Compound **III-27**: To a solution of **III-23** (100 mg, 0.14 mmol) in dichloromethane (1.5 mL), DBU (0.02 mL, 1 eq.) was added. The mixture was stirred for 15 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-27** as a yellow solid (74 mg, quant.).^{1}H NMR (300 MHz, $CDCl_3$) δ 12.69 (s, 1 H), 9.05 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.76 (s, 1 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.56 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.56 (s, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.00 (dd, *J* = 7.5, 1.2 Hz, 1 H), 5.52 (br, 2 H), 4.10 (s, 3 H), 4.10 (d, *J* = 6.5 Hz, 2 H), 4.06 (d, *J* = 6.5 Hz, 2 H), 2.31 (m, 2 H), 1.17 (d, *J* = 5.2 Hz, 6 H), 1.14 (d, *J* = 5.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 163.2, 163.1, 162.9, 148.2, 146.7, 144.8, 139.5, 137.4, 135.2, 128.4, 128.1, 123.0, 122.1, 117.1, 115.6, 110.9, 109.5, 101.3, 98.2, 75.1, 75.0, 52.9, 28.3, 19.4, 19.3.

Synthesis of Compound **III-28**: A solution of acid **III-22** (300 mg, 0.34 mmol) in dry $CHCl_3$ (3 mL) was cooled to 0°C. 1-Chloro-*N*, *N*, 2-trimethyl-1-propenylamine (80 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1.5 mL) and added to a solution of **III-27** (170 mg, 0.9 eq.) and dry DIPEA (0.44 mL, 5 eq.) in dry $CHCl_3$ (1.5 mL). The mixture was stirred for 15 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-28** as a white solid (329 g, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.12 (s, 1 H), 11.94 (s, 1 H), 8.98 (t, *J* = 7.3 Hz, 2 H), 8.08 (d, *J* = 7.4 Hz, 1 H), 7.90 (s, 1 H), 7.83 (br, 1 H), 7.74 (m, 4 H), 7.69 (d, *J* = 8.3 Hz, 1 H), 7.65 (t, *J* = 8.0 Hz, 1 H), 7.58-7.47 (m, 6 H), 7.38 (m, 2 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 7.5 Hz, 1 H), 7.00 (s, 1 H), 6.93 (m, 2 H), 6.83 (br, 1 H), 6.81 (s, 1 H), 6.20 (dd, *J* = 2.3, 8.4 Hz, 1 H), 6.09 (m, 1 H), 5.31 (d, *J* = 14.9 Hz, 1 H), 4.55 (dd, *J* = 6.9, 10.4 Hz, 1 H), 4.37 (br, 1 H), 4.29 (t, *J* = 6.8 Hz, 1 H), 4.18 (m, 2 H), 3.97 (m, 1 H), 3.92 (m, 1 H), 3.81 (br, 1 H), 3.76 (br, 1 H). 3.71 (s, 3 H), 3.61 (s, 3 H), 3.34 (t, *J* = 7.3 Hz, 1 H), 3.20 (s, 3 H), 2.37 (m, 1 H), 2.21 (m, 2 H), 1.93 (m, 1 H), 1.17 (m, 6 H), 1.16-1.07 (m, 12 H), 0.90 (d, *J* = 6.6 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3, 163.7, 163.6, 163.5, 163.1, 162.4, 161.7, 160.0, 158.0, 153.2, 151.8, 150.8, 146.2, 144.0, 143.9, 142.7, 142.6, 141.5, 141.4, 139.5, 139.4, 136.2, 135.1, 135.0, 128.2, 127.9, 127.8, 127.5, 127.3, 1227.2, 126.5, 125.2, 125.1, 122.7, 121.9, 120.6, 120.2, 120.1, 119.4, 118.4, 118.2, 118.1, 117.0, 115.8, 114.7, 114.6, 193.6, 100.8, 100.5, 99.9, 98.2, 97.8, 75.5, 75.3, 74.9, 74.3, 68.9, 55.3, 54.6, 52.9, 48.5, 47.2, 28.3, 28.3, 28.0, 19.4, 19.4, 19.4, 19.3, 19.1.

Synthesis of Compound **III-29:** The mixture of **III-28** (50 mg, 0.036 mmol) and LiI (25 mg, 5.3 eq.) in degassed ethyl acetate (1 mL) was heated to 80°C for 20 h. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-29** as a white solid (55 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.63 (s, 1 H), 11.57 (s, 1 H), 8.94 (d, *J* = 7.4 Hz, 1 H), 8.75 (d, *J* = 7.5 Hz, 1 H), 8.11 (m, 2 H), 7.89-7.48 (m, 14 H), 7.36 (m, 3 H), 7.10 (m, 4 H), 6.94 (m, 3 H), 6.20 (d, *J* = 7.5 Hz, 1 H), 6.03 (s, 1 H), 5.30 (s, 2 H), 4.53 (m, 1 H), 4.40 (m, 1 H), 4.27 (m, 1 H), 4.13 (m, 2 H), 3.85 (m, 5 H), 2.37-1.93 (m, 4 H), 1.28-1.02 (m, 18 H), 0.87 (m, 6 H).

Synthesis of Compound **III-30**: To a solution of **III-25** (300 mg, 0.22 mmol) in dichloromethane (5 mL), DBU (30 μL, 1 eq.) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-30** as a yellow solid (177 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.12 (s, 1 H), 10.54 (s, 1 H), 8.84 (d, *J* = 7.6 Hz, 1 H), 8.15 (d, *J* = 7.8 Jz, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H), 7.43 (s, 1 H), 7.34 (t, *J* = 8.2 Hz, 1 H), 7.10 (d, *J* = 7.8 Hz, 1 H), 7.95 (m, 3 H), 6.82 (m, 1 H), 6.57 (t, *J* = 8.0 Hz, 1 H), 6.47 (s, 1 H), 6.43 (s, 3 H), 5.60 (d, *J* = 6.7 Hz, 1 H), 5.50 (m, 2 H), 5.29 (t, *J* = 7.2 Hz, 1 H), 4.45 (d, *J* = 14.5 Hz, 1 H), 4.15 (d, *J* = 13.6 Hz, 1 H), 3.76 (d, *J* = 7.3 Hz, 2 H), 3.66 (t, *J* = 7.8 Hz, 1 H), 3.40 (s, 3 H), 3.20 (m, 3 H), 3.21 (s, 3 H), 2.79 (s, 3 H), 0.66 (m, 18 H), 0.48 (d, *J* = 6.6 Hz, 6 H).

Synthesis of Compound **III-31**: A solution of acid **III-20** (70 mg, 0.15 mmol) in dry $CHCl_3$ (2 mL) was cooled to 0^{o}C. Oxalyl chloride (36 μL, 2.3 eq.) were added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **III-30** (150 mg, 0.9 eq.) and dry DIPEA (0.12 mL, 4.6 eq.) in dry $CHCl_3$ (0.5 mL). The mixture was stirred for 2 h. The organic layer was washed with water, sat. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 10) to give **III-31** as a yellow solid (191 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.69 (s, 1 H), 11.80 (s, 1 H), 10.62 (s, 1 H), 9.38 (d, *J* = 7.5 Hz, 1 H), 8.63 (s, 1 H), 8.15 (m, 2 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 7.97 (d, *J* = 7.8 Hz, 1 H), 7.90 (d, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.76 (s, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 6.7 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.31 (m, 4 H), 7.17 (m, 4 H), 6.85 (s, 1 H), 6.74 (d, *J* = 7.5 Hz, 2 H), 6.03 (dd, *J* = 2.3, 7.9 Hz, 1 H), 5.91 (d, *J* = 2.3 Hz, 1 H), 5.64 (t, *J* = 8.0 Hz, 1 H), 4.98 (d, *J* = 13.5 Hz, 1 H), 4.52 (d, *J* = 12.8 Hz, 1 H), 4.26 (m, 6 H), 4.10-3.83 (m, 8 H), 3.80 (s, 3 H), 3.69 (m, 2 H), 3.54 (s, 3 H), 3.20 (s, 3 H), 2.38 (m, 4 H), 1.93 (m, 1 H), 1.22 (m, 24 H), 0.85 (d, *J* = 6.6 Hz, 6 H).

Synthesis of Compound **III-32**: The mixture of **III-31** (50 mg, 0.031 mmol) and LiI (20 mg, 5.0 eq.) in degassed ethyl acetate (1 mL) was heated to 80°C for 22 h. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give

III-32 as a white solid (71 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.75 (s, 1 H), 11.80 (s, 1 H), 10.69 (s, 1 H), 9.36 (d, *J* = 7.5 Hz, 1 H), 8.64 (s, 1 H), 8.19 (d, *J* = 8.0 Hz, 2 H), 8.11 (d, *J* = 8.2 Hz, 1 H), 8.00-7.74 (m, 7 H), 7.66 (m, 2 H), 7.54-7.28 (m, 10 H), 7.21 (m, 2 H), 6.91 (s, 1 H), 6.84 (s, 1 H), 6.64 (s, 1 H), 6.21 (dd, *J* = 2.3, 7,8 Hz, 1 H), 5.79 (t, *J* = 8.0 Hz, 1 H), 5.66 (d, *J* = 2.3 Hz, 1 H), 5.07 (d, *J* = 13.6 Hz, 1 H), 4.38-3.69 (m, 18 H), 3.61 (d, *J* = 6.7 Hz, 2 H), 3.56 (s, 3 H), 2.63 (s, 3 H), 2.45 (m, 4 H), 2.22 (m, 1 H), 2.00 (m, 1 H), 1.17 (m, 24 H), 0.88 (d, *J* = 6.6 Hz, 6 H).

Synthesis of compound **III-33**: **III-14** (7.06 g, 25.7 mmol), allyl alcohol (45 mL) and triethylamine (18 mL) were mixed and stirred at 70°C for 4 days. The solvent was removed *in vacuo*, the residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 4) to give **III-33** as a yellow solid (6.30 g, 81%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.48 (s, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 6.93 (dd, *J* = 7.5, 1.3 Hz, 1 H), 6.11 (m, 1 H), 5.48 (dq, *J* = 17.2, 1.5 Hz, 1 H), 5.33 (dq, *J* = 10.4, 1.3 Hz, 1 H), 5.10 (br, 1 H), 4.93 (dt, *J* = 5.7, 1.4 Hz, 2 H), 4.01 (d, *J* = 6.5 Hz, 2 H), 2.27 (m, 1 H), 1.13 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 162.7, 146.0, 145.0, 138.5, 132.2, 128.7, 123.1, 118.9, 110.9, 109.7, 100.9, 75.0, 66.5, 28.4, 19.4. HRMS (ESI+) m/z calcd for $C_{17}H_{21}N_2O_3$ $[M+H]^+$ 301.1547, found 301.1548.

Synthesis of compound **III-34**: **III-33** (1.01 g, 3.38 mmol) and 2,4-dimethoxybenzaldehyde (546 mg, 3.28 mmol) were mixed in 1,2-dichloroethane (17 mL) and then sodium triacetoxyborohydride (1.07 g, 5.03 mmol) was added. The mixture was stirred at rt under N_2 atmosphere for 3 h. The reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 10) to give **III-34** as a yellow solid (1.33 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ7.48 (s, 1 H), 7.37 (m, 2 H), 7.22 (d, *J* = 8.3 Hz, 1 H), 6.78 (br, 1 H), 6.65 (dd, *J* = 6.6, 2.4 Hz, 1 H), 6.49 (d, *J* = 2.3 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.4 Hz, 1 H), 6.11 (m, 1 H), 5.46 (dq, *J* = 17.2, 1.5 Hz, 1 H), 5.31 (dq, *J* = 10.4, 1.3 Hz, 1 H), 4.92 (dt, *J* = 5.6, 1.4 Hz, 2 H), 4.50 (d, *J* = 5.0 Hz, 2 H), 3.99 (d, *J* = 6.5 Hz, 2 H), 3.87 (s, 3 H), 3.78 (s, 3 H), 2.26 (m, 1 H), 1.12 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ165.8, 162.6, 160.1, 158.4, 145.7, 145.3, 138.4, 132.3, 129.2, 128.8, 122.9, 119.5, 118.7, 107.3, 106.1, 103.9, 101.1, 98.6, 74.9, 66.4, 55.5, 55.5, 42.1, 28.3, 19.4. HRMS (ESI+) m/z calcd for $C_{26}H_{31}N_2O_5$ $[M+H]^+$ 451.2227, found 451.2240.

Synthesis of compound **III-35**: A solution of acid **III-22** (1.10 g, 1.26 mmol) in dry $CHCl_3$ (7 mL) was cooled to 0°C. 1-Chloro-*N*, *N*,2-trimethyl-1-propenylamine (0.3 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (3 mL) and added to a solution of **III-34** (495 mg, 0.9 eq.) and dry DIPEA (0.44 mL, 5 eq.) in dry $CHCl_3$ (4 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-35** as a white solid (1.43 g, 91%.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.29 (br, 1 H), 8.20 (d, *J* = 7.3 Hz, 1 H), 8.12 (br, 1 H), 8.03 (d, *J* = 8.3 Hz, 1 H), 7.90 (d, *J* = 8.2 Hz, 1 H), 7.76 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 7.6 H, 1 H), 7.66 (d, *J* = 7.3 Hz, 1 H), 7.62 (d, *J* = 9.1 Hz, 1 H), 7.59 (t, *J* = 7.9 Hz, 1 H), 7.54 (d, *J* = 8.1 Hz, 1 H), 7.38 (t, *J* = 7.4 Hz, 2 H), 7.34 (s, 1 H), 7.31-7.27 (m, 3 H), 7.20 (t, *J* = 7.4 Hz, 1 H), 7.16 (d, *J* = 8.3 Hz, 1 H), 7.12 (s, 1 H), 7.08 (d, *J*

= 6.6 Hz, 1 H), 6.78 (m, 1 H), 6.57 (dd, *J* = 8.4, 2.2 Hz, 1 H), 6.42 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.36 (d, *J* = 2.2 Hz, 1 H), 6.34 (d, *J* = 2.1 Hz, 1 H), 6.16 (m, 1 H), 5.70 (d, *J* = 16.4 Hz, 1 H), 5.64 (d, *J* = 15.7 Hz, 1 H), 5.60 (d, *J* = 15.0 Hz, 1 H), 5.41 (d, *J* = 6.4 Hz, 1 H), 4.95 (m, 3 H), 4.62 (dd, *J* = 10.7, 6.7 Hz, 1 H), 4.45 (br, 1 H), 4.32 (d, *J* = 6.6 Hz, 1 H), 3.87 (m, 3 H), 3.76 (s, 3 H), 3.74 (m, 1 H), 3.74 (s, 3 H), 3.71 (m, 1 H), 3.66 (s, 3 H), 3.46 (m, 2 H), 3.38 (s, 3 H), 2.15 (m, 2 H), 2.02 (m, 1 H), 1.03 (m, 10 H), 0.96 (m, 6 H), 0.84 (m, 2 H), minor peaks δ 7.79 (d, *J* = 7.6 Hz, 3 H), 7.66 (m, 4 H), 7.47 (br, 2 H), 7.42 (m, 3 H), 6.39 (m, 2 H), 6.28 (d, *J* = 2.1 Hz, 1 H), 6.24 (d, *J* = 2.0 Hz, 1 H), 5.77 (d, *J* = 15.0 Hz, 1 H), 4.57 (m, 1 H), 4.38 (t, *J* = 6.8 Hz, 1 H), 3.36 (s, 3 H), 0.99 (d, *J* = 6.7 Hz, 6 H), 0.84 (m, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 170.2, 165.6, 162.4, 162.0, 160.8, 160.3, 160.0, 158.6, 158.1, 156.6, 154.1, 153.3, 147.6, 144.0, 144.0, 143.9, 142.4, 142.1, 141.8, 141.5, 141.4, 136.5, 134.2, 132.1, 131.5, 131.5, 130.6, 130.0, 128.7, 128.2, 127.9, 127.8, 127.3, 126.4, 125.4, 125.1, 125.0, 122.6, 121.5, 120.8, 120.8, 120.2, 120.1, 120.1, 120.1, 118.7, 118.5, 118.4, 114.9, 114.7, 104.1, 104.0, 101.6, 101.5, 100.6, 98.4, 98.1, 98.1, 75.0, 75.0, 74.5, 66.8, 66.4, 66.3, 55.4, 55.4, 55.3, 55.2, 55.1, 55.0, 54.9, 49.4, 48.6, 47.3, 47.1, 28.2, 28.1, 19.3, 19.3, 19.1. HRMS (ESI+) m/z calcd for $C_{78}H_{79}N_6O_{13}$ $[M+H]^+$ 1307.5700, found 1307.5670.

Synthesis of compound **III-36**: To a solution of **III-35** (850 mg, 0.65 mmol) in dichloromethane (7 mL), DBU (0.1 mL, 1 eq.) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-36** as a yellow solid (703 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (m, 3 H), 7.66 (s, 1 H), 7.40 (m, 2 H), 7.28 (d, *J* = 9.3 Hz, 1 H), 7.24 (d, *J* = 1.1 Hz, 1 H), 7.21 (dd, *J* = 8.3, 1.1 Hz, 1 H), 7.06 (m, 2 H), 6.74 (dd, *J* = 8.2, 7.6 Hz, 1 H), 6.71 (s, 1 H), 6.37 (m, 4 H), 6.32 (d, *J* = 2.3 Hz, 1 H), 5.75 (dd, *J* = 17.2, 1.4 Hz, 1 H), 5.64 (d, *J* = 15.8 Hz, 1 H), 5.54 (d, *J* = 14.5 Hz, 1 H), 5.47 (dd, *J* = 10.6, 1.3 Hz, 1 H), 5.43 (t, *J* = 10.3 Hz, 1 H), 5.02-4.87 (m, 6 H), 4.10 (br, 1 H), 4.05 (dd, *J* = 9.2, 7.0 Hz, 1 H), 3.92 (dd, *J* = 9.2, 6.5 Hz, 1 H), 3.87-3.78 (m, 2 H), 3.76-3.60 (m, 18 H), 3.20 (s, 3 H), 2.59 (dd, *J* = 8.7, 5.7 Hz, 1 H), 2.34 (br, 2 H), 2.25 (m, 1 H), 2.12 (m, 2 H), 1.10 (m, 6 H), 1.03 (m, 6 H), 0.75 (m, 6 H). minor peaks: (ma*J*or: minor = 2:1) 8.07 (d, *J* = 7.4 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 1 H), 7.68 (m, 1 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 7.20 (m, 1 H), 7.17 (s, 1 H), 7.06 (m, 1 H), 6.92 (t, *J* = 7.6 Hz, 1 H), 6.86 (d, *J* = 7.2 Hz, 1 H), 6.58 (dd, *J* = 7.4, 1.0 Hz, 1 H), 6.42 (dd, *J* = 8.5, 2.3 Hz, 1 H), 6.37 (m, 1 H), 6.30 (m, 1 H), 6.25-6.16 (m, 3 H), 5.72 (m, 1 H), 5.65 (d, *J* = 15.8 Hz, 1 H), 3.83 (m, 1 H), 3.46 (d, *J* = 14.7 Hz, 1 H), 3.16 (m, 2 H), 3.10 (s, 3 H), 2.12 (m, 1 H), 1.60 (m, 2 H), 1.25 (br, 1 H), 1.03 (m, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.9, 169.6, 166.4, 166.0, 165.5, 161.7, 161.5, 161.2, 159.9, 159.8, 158.7, 158.0, 154.9, 152.4, 160.9, 160.0, 159.8, 158.4, 156.6, 149.6, 147.5, 144.1, 144.0, 143.8, 143.5, 143.4, 143.3, 142.7, 142.5, 141.4, 141.0, 136.9, 135.9, 131.8, 131.7, 131.5, 131.1, 130.0, 130.0, 128.9, 128.3, 128.0, 128.0, 127.9, 127.0, 126.7, 126.6, 125.4, 124.9, 122.6, 121.6, 121.5, 121.4, 121.2, 120.1, 119.9, 119.4, 118.5, 118.4, 118.3, 110.0, 109.3, 108.7, 103.9, 103.8, 101.8, 101.7, 101.5, 100.8, 100.4, 99.7, 98.0, 97.9, 97.9, 74.9, 74.8, 74.5, 73.9, 66.2, 65.9, 55.2, 55.1, 55.1, 54.7, 54.5, 50.6, 49.5, 47.8, 47.1, 28.1, 28.1, 28.1, 28.0, 27.6, 19.3, 19.2, 19.2, 19.2, 19.1, 19.1, 19.1, 19.0, 19.6. HRMS (ESI+) m/z calcd for $C_{63}H_{69}N_6O_{11}$ $[M+H]^+$ 1085.5019, found 1085.4996.

Synthesis of compound **III-37**: A solution of acid **III-20** (2.00 g, 4.15 mmol) in dry $CHCl_3$ (10 mL) was cooled to 0°C. Oxalyl chloride (1 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under

high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (10 mL) and added to a solution of **III-33** (1.18 g, 0.9 eq.) and dry DIPEA (3.6 mL, 5 eq.) in dry $CHCl_3$ (20 mL). The mixture was stirred for 15 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 4) to give **III-37** as a white solid (2.59 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.35 (s, 1 H), 8.94 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.43 (d, *J* = 7.6 Hz, 1 H), 8.00 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.96 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.79 (s, 1 H), 7.72 (t, *J* = 7.9 Hz, 1 H), 7.65 (d, *J* = 7.6 Hz, 2 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.40 (s, 1 H), 7.21 (t, *J* = 7.4 Hz, 2 H), 6.81 (t, *J* = 7.5 Hz, 2 H), 5.90 (m, 1 H), 5.29 (dq, *J* = 17.2, 1.5 Hz, 1 H), 5.04 (dq, *J* = 10.4, 1.2 Hz, 1 H), 4.84 (dt, *J* = 5.9, 1.3 Hz, 2 H), 4.46 (d, *J* = 7.6 Hz, 2 H), 4.15 (d, *J* = 6.5 Hz, 2 H), 3.95 (d, *J* = 6.4 Hz, 2 H), 3.95 (d, *J* = 6.4 Hz, 2 H), 2.34 (m, 1 H), 2.26 (m, 1 H), 1.17 (d, *J* = 6.7 Hz, 6 H), 1.13 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 163.9, 163.2, 163.0, 153.7, 150.5, 147.8, 143.8, 141.3, 139.8, 138.2, 135.1, 134.9, 131.6, 128.5, 127.8, 127.6, 126.9, 125.2, 122.5, 122.5, 119.9, 118.9, 117.5, 117.1, 116.2, 115.6, 101.8, 99.1, 76.7, 75.4, 67.5, 66.9, 47.2, 28.3, 28.3, 19.4, 19.4. HRMS (ESI+) m/z calcd for $C_{46}H_{45}N_4O_7$ $[M+H]^+$ 765.3283, found 765.3261.

Synthesis of compound **III-38**: A solution of acid **III-24** (504 mg, 0.70 mmol) in dry $CHCl_3$ (5 mL) was cooled to 0°C. Oxalyl chloride (0.17 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **III-36** (680 mg, 0.9 eq.) and dry DIPEA (0.59 mL, 5 eq.) in dry $CHCl_3$ (2 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-38** as a white solid (1.01 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$, 273 K) δ 12.6 (s, 1 H), 11.1 (s, 1 H), 9.26 (d, *J* = 7.6 Hz, 1 H), 8.59 (s, 1 H), 8.58 (d, *J* = 7.9 Hz, 1 H), 8.06 (d , *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 8.3 Hz, 1 H), 7.94 (d, *J* = 8.5 Hz, 1 H), 7.91 (m, 2 H), 7.78 (t, *J* = 7.9 Hz, 1 H), 7.73 (t, *J* = 8.5 Hz, 2 H), 7.63 (d, *J* = 7.5 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.45 (s, 1 H), 7.38 (m, 4 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.23-7.15 (m, 7 H), 7.12 (d, *J* = 8.2 Hz, 1 H), 7.09 (dd, *J* = 8.3, 1.1 Hz, 1 H), 6.87 (t, *J* = 7.5 Hz, 1 H), 6.80 (s, 1 H), 6.76 (t, *J* = 7.9 Hz, 1 H), 6.72 (s, 1 H), 6.59 (dd, *J* = 8.5, 2.2 Hz, 1 H), 6.30 (d, *J* = 2.3 Hz, 1 H), 6.29 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.20 (d, *J* = 7.3 Hz ,1 H), 6.10 (m, 1 H), 5.64 (dq, *J* = 17.2, 1.2 Hz, 1 H), 5.58 (d, *J* = 2.3 Hz, 1 H), 5.53 (t, *J* = 8.2 Hz, 1 H), 5.45 (d, *J* = 16.1 Hz, 1 H), 5.35 (dq, *J* = 10.6, 1.1 Hz, 1 H), 4.93-4.79 (m, 4 H), 4.56 (d, *J* = 13.1 Hz, 1 H), 4.51 (dd, *J* = 8.8, 5.9 Hz, 1 H), 4.25 (t, *J* = 8.4 Hz, 1 H), 4.16-3.96 (m, 8 H), 3.86 (s, 3 H), 3.79 (m, 2 H), 3.67 (m, 4 H), 3.64 (s, 3 H), 3.61 (s, 3 H), 3.51 (t, *J* = 8.6 Hz, 1 H), 3.11 (dd, *J* = 8.8, 6.5 Hz. 1 H), 2.60 (m, 1 H), 2.28 (m, 1 H), 2.18 (m, 1 H), 2.04 (m, 1 H), 1.85 (m, 1 H), 1.79 (m, 3 H), 1.13 (m, 12 H), 1.05 (d, *J* = 6.7 Hz, 3 H), 0.94 (d, *J* = 6.7 Hz, 3 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 0.84 (d, *J* = 6.7 Hz, 3 H), 0.81 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, 273 K) δ 170.1, 168.7, 165.7, 164.7, 163.9, 163.6, 163.0, 162.3, 161.3, 160.2, 159.6, 158.8, 157.8, 155.7, 152.5, 151.6, 151.5, 149.8, 147.2, 144.2, 143.8, 142.8, 141.9, 141.2, 141.0, 140.1, 138.2, 137.0, 136.9, 134.5, 133.8, 133.3, 132.4, 131.2, 129.8, 128.9, 128.3, 128.0, 127.7, 127.3, 126.7, 126.6, 125.8, 125.3, 125.2, 123.5, 122.8, 122.4, 122.2, 120.4, 120.4, 120.3, 119.8, 119.7, 119.0, 118.8, 118.3, 117.3, 117.2, 116.8, 116.5, 115.1, 115.0, 114.3, 103.7, 103.1, 101.3, 100.5, 100.3, 99.5, 98.7, 97.7, 97.4, 75.7, 75.4, 74.9, 74.8, 74.0, 67.0, 66.4, 55.4, 55.2, 55.1, 53.5, 49.3, 47.2, 46.6, 28.3, 28.2, 28.0, 28.0, 27.9, 19.8, 19.5, 19.5, 19.4, 19.4, 19.3, 19.2, 19.2. HRMS (ESI+) m/z calcd for $C_{106}H_{107}N_{10}O_{17}$ $[M+H]^+$ 1791.7810, found 1791.7817.

Synthesis of compound **III-39**: To a solution of **III-38** (1.00 g, 0.56 mmol) in dry dichloromethane (6 mL), phenylsilane (0.16 mL, 2.3 eq.) and tetrakis(triphenylphosphine)palladium(0) (15.0 mg, 2 mol%) were added. The mixture was stirred for 1.5 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **III-39** as a yellow solid (970 mg, quant.) ^{1}H NMR (600 MHz, $CDCl_3$, 273 K) δ 12.62 (s, 1 H), 11.04 (s, 1 H), 9.25 (d, *J* = 7.4 Hz, 1 H), 8.73 (d, *J* = 7.4 Hz, 1 H), 8.59 (m, 2 H), 8.20 (d, *J* = 8.1 Hz, 1 H), 8.07 (m, 2 H), 7.98 (d, *J* = 8.1 Hz, 1 H), 7.91 (m, 1 H), 7.88 (t, *J* = 8.0 Hz, 1 H), 7.78 (m, 4 H), 7.67-7.54 (m, 10 H), 7.50-7.38 (m, 12 H), 7.20 (m, 8 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 8.2 Hz, 1 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 6.76 (m, 2 H), 6.50 (s, 1 H), 6.46 (dd, *J* = 8.5, 2.0 Hz, 1 H),6.26 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.16 (d, *J* = 6.6 Hz, 1 H), 6.06 (d, *J* = 2.0 Hz, 1 H), 5.60 (d, *J* = 2.2 Hz, 1 H), 5.54 (t, *J* = 7.9 Hz, 1 H), 5.20 (d, *J* = 14.8 Hz, 1 H), 5.01 (d, *J* = 14.4 Hz, 1 H), 4.54 (d, *J* = 13.1 Hz, 1 H), 4.50 (m, 1 H), 4.26 (t, *J* = 8.3 Hz, 2 H), 4.15-3.95 (m, 14 H), 3.83-3.61 (m, 18 H), 3.54 (m, 4 H), 3,29 (m, 1 H), 3.24 (s, 3 H), 3.10 (br, 1 H), 2.99 (br, 1 H), 2.68 (br, 2 H), 2.60 (m, 1 H), 2.35 (m, 1 H), 2.26 (m, 3 H), 2.09-1.85 (m, 5 H), 1.83 (s, 3 H), 1.32-1.09 (m, 36 H). minor peaks: (ma*J*or: minor = 3 : 2) δ 12.89 (s, 1 H), 11.11 (br, 1 H), 9.31 (m, 1 H), 9.22 (m, 1 H), 8.69 (m, 1 H), 8.63 (d, *J* = 7.4 Hz, 1 H), 8.59 (m, 1 H), 8.03 (br, 1 H), 7.88 (br, 1 H), 7.67-7.54 (m, 1 H), 7.50-7.38 (m, 1 H), 6.87-6.73 (br, 3 H), 6.62 (br, 1 H), 6.55 (br, 1 H), 6.16 (s, 1 H), 6.01 (m, 1 H), 5.87-5.73 (br, 5 H), 5.53 (br, 1 H), 5.07 (br, 1 H), 4.91 (br, 1 H), 4.74 (br, 1 H), 4.58-4.46 (br, 3 H), 3.40-3.34 (br, 3 H), 3.18 (s, 1 H), 2.57 (br, 2 H), 2.42 (br, 1 H), 0.98-0.62 (m, 36 H). ^{13}C NMR (150 MHz, $CDCl_3$, 273 K) δ170.7, 168.7, 164.7, 164.4, 163.9, 163.7, 163.6, 163.3, 162.9, 161.3, 160.9, 160.2, 159.8, 158.7, 158.3, 154.1, 152.6, 151.8, 151.6, 151.5, 149.8, 149.4, 145.6, 144.2, 143.8, 142.9, 142.7, 141.2, 141.0, 140.5, 140.1, 138.5, 138.2, 137.0, 136.9, 134.5, 133.8, 133.3, 133.1, 132.2, 132.1, 131.9, 131.6, 131.4, 128.8, 128.7, 128.6, 128.3, 127.7, 127.3, 126.7, 126.6, 126.0, 125.3, 125.2, 123.9, 122.8, 122.5, 122.2, 120.8, 120.4, 120.4, 119.8, 119.0, 117.6, 117.2, 117.1, 116.8, 116.6, 116.5, 115.3, 115.0, 114.4, 103.7, 103.5, 101.0, 99.6, 99.4, 98.8, 98.0, 97.5, 75.7, 75.4, 75.4, 74.9, 74.7, 74.4, 67.1, 55.5, 55.2, 55.0, 54.1, 53.5, 48.9, 47.2, 46.6, 28.3, 28.2, 28.2, 28.1, 28.0, 27.8, 19.7, 19.6, 19.5, 19.4, 19.4, 19.3, 19.1, 19.1. HRMS (ESI+) m/z calcd for $C_{103}H_{103}N_{10}O_{17}$ $[M+H]^+$ 1751.7497, found 1751.7479.

Synthesis of Compound **III-40**: A solution of acid **III-20** (508 mg, 1.05 mmol) in dry $CHCl_3$ (3 mL) was cooled to 0°C. Oxalyl chloride (0.27 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **III-27** (461 mg, 0.9 eq.) and dry DIPEA (0.92 mL, 5 eq.) in dry $CHCl_3$ (2 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-40** as a white solid (808 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ12.53 (s, 1 H), 12.44 (s, 1 H), 9.04 (d, *J* = 7.6 Hz, 1 H), 9.02 (d, *J* = 7.6 Hz, 1 H), 8.73 (s, 1 H), 8.05 (dd, *J* = 8.3, 1.1 Hz, 1 H), 7.98 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 8.2 Hz, 1 H), 7.76 (s, 1 H), 7.73 (m, 2 H), 7.66 (d, *J* = 7.5 Hz, 2 H), 7.58 (s, 1 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.41 (br, 2 H), 7.24 (br, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 6.91 (br, 2 H), 6.68 (s, 1 H), 4.20 (m, 5 H), 4.02 (d, *J* = 6.0 Hz, 2 H), 3.80 (d, *J* = 6.2 Hz, 2 H), 3.53 (s, 3 H), 2.41 (m, 1 H), 2.28 (m, 2 H), 1.21 (d, *J* = 6.7 Hz, 6 H), 1.18 (d, *J* = 6.7 Hz, 6 H), 1.13 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2, 164.0, 163.8, 163.4, 163.3, 162.6, 151.7, 151.2, 150.5, 145.7, 141.3, 139.3, 138.9, 136.9, 135.1, 134.6, 133.8, 128.2, 128.0, 127.5, 127.1, 126.9, 125.3, 122.5, 122.0, 121.9, 119.9, 117.3, 116.6,

116.5, 114.7, 114.6, 100.5, 99.5, 98.6, 75.7, 75.5, 75.1, 67.4, 52.6, 46.8, 28.4, 28.3, 28.3, 19.5, 19.5, 19.4. HRMS (ESI+) m/z calcd for $C_{58}H_{57}N_6O_9$ $[M+H]^+$ 981.4182, found 981.4172.

Synthesis of Compound **III-41**: The mixture of **III-40** (240 mg, 0.25 mmol) and LiI (230 mg, 6.9 eq.) in degassed ethyl acetate (3 mL) was heated to 80°C for 3 day. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-41** as a white solid (174 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ12.35 (s, 1 H), 11.89 (s, 1 H), 9.10 (d, *J* = 7.6 Hz, 1 H), 9.01 (d, *J* = 7.4 Hz, 1 H), 8.67 (s, 1 H), 8.03 (d, *J* = 8.3 Hz, 2 H), 7.83 (m, 2 H), 7.77 (t, *J* = 7.9 Hz, 1 H), 7.73 (t, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 7.5 Hz, 2 H), 7.58 (s, 1 H), 7.53 (d, *J* = 7.3 Hz, 1 H), 7.39 (br, 2 H), 7.24 (m, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 6.92 (br, 2 H), 6.75 (s, 1 H), 4.22 (br, 2 H), 4.15 (br, 3 H), 4.01 (d, *J* = 6.4 Hz, 2 H), 3.86 (d, *J* = 6.4 Hz, 2 H), 2.39 (m, 1 H), 2.29 (m, 2 H), 1.20 (d, *J* = 6.7 Hz, 6 H), 1.18 (d, *J* = 6.7 Hz, 6 H), 1.13 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 164.2, 163.9, 163.1, 162.7, 162.4, 151.6, 151.1, 150.7, 144.7, 143.9, 141.3, 138.7, 137.8, 136.6, 134.4, 134.0, 133.5, 128.5, 128.3, 127.6, 126.9, 126.9, 125.2, 122.6, 122.3, 120.0, 117.8, 177.6, 117.2, 116.6, 115.3, 114.4, 99.6, 99.5, 98.7, 75.8, 75.7, 75.6, 67.4, 46.9, 28.3, 28.3, 28.2, 19.4, 19.4. HRMS (ESI+) m/z calcd for $C_{57}H_{55}N_6O_9$ $[M+H]^+$ 967.4025, found 967.4011.

Synthesis of Compound **III-42**: A solution of acid **III-20** (219 mg, 0.45 mmol) in dry $CHCl_3$ (2 mL) was cooled to 0°C. Oxalyl chloride (0.12 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **III-19** (303 mg, 0.9 eq.) and dry DIPEA (0.40 mL, 5 eq.) in dry $CHCl_3$ (0.5 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-42** as a white solid (560 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.39 (s, 1 H), 9.52 (s, 1 H), 8.72 (d, *J* = 7.0 Hz, 1 H), 8.60 (d, *J* = 7.1 Hz, 1 H), 8.04 (d, *J* = 7.7 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.77 (s, 1 H), 7.71 (m, 3 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.52 (d, 8.5 Hz, 1 H), 7.43 (m, 2 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.34 (s, 1 H), 7.27 (t, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 7.03 (s, 1 H), 6.77 (t, *J* = 7.4 Hz, 1 H), 6.20 (dd, *J* = 8.5, 2.3 Hz, 1 H), 6.15 (t, *J* = 7.9 Hz, 1 H), 6.08 (d, *J* = 2.3 Hz, 1 H), 5.62 (d, *J* = 15 Hz, 1 H), 5.13 (d, *J* = 15 Hz, 1H), 4.75 (m, 1 H), 4.54 (m, 2 H), 4.19 (d, *J* = 6.5 Hz, 2 H), 4.00 (s, 3 H), 3.90 (m, 1 H), 3.71 (dd, *J* = 6.4, 2.2 Hz, 2 H), 3.68 (m, 1 H), 3.65 (s, 3 H), 3.32 (s, 3 H), 2.38 (m, 1 H), 2.15 (m ,1 H), 2.08 (m, 1 H), 1.21 (d, *J* = 6.5 Hz, 6 H), 1.04 (d, *J* = 6.6 Hz, 3 H), 1.03 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ170.2, 166.3, 163.8, 162.6, 162.0, 161.4, 159.8, 158.2, 155.0, 153.8, 150.6, 147.2, 144.7, 143.9, 143.8, 142.3, 141.4, 141.2, 137.5, 137.3, 134.8, 133.9, 131.6, 128.1, 127.6, 127.5, 127.3, 126.9, 126.7, 126.5, 126.1, 125.7, 125.4, 122.4, 122.3, 120.8, 119.9, 119.9, 119.8, 117.5, 116.6, 116.5, 116.0, 115.5, 103.7, 102.7, 100.3, 99.3, 97.6, 75.6, 74.9, 74.8, 68.1, 55.3, 55.0, 52.8, 48.3, 46.8, 28.4, 28.2, 28.1, 19.5, 19.4, 19.4, 19.3, 19.3. HRMS (ESI+) m/z calcd for $C_{67}H_{67}N_6O_{11}$ $[M+H]^+$ 1131.4862, found 1131.4842.

Synthesis of Compound **III-43**: To a solution of **III-42** (260 mg, 0.23 mmol) in dichloromethane (3 mL), DBU (0.03

mL, 1 eq.) was added. The mixture was stirred for 50 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-43** as a yellow solid (186 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.33 (s, 1 H), 8.72 (d, *J* = 7.5 Hz, 1 H), 7.81 (t, *J* = 8.1 Hz, 2 H), 7.70 (s, 1 H), 7.65 (d, *J* = 7.4 Hz, 1 H), 7.62 (d, *J* = 8.3 Hz, 1 H), 7.56 (d, *J* = 8.2 Hz, 1 H), 7.41 (m, 2 H), 7.35 (s, 1 H), 6.98 (s, 1 H), 6.92 (d, *J* = 7.4 Hz, 1 H), 6.80 (t, *J* = 7.9 Hz, 1 H), 6.46 (d, *J* = 7.0 Hz, 1 H), 6.31 (s, 1 H), 5.62 (d, *J* = 14.5 Hz, 1 H), 5.09 (m, 3 H), 4.10 (m, 6 H), 3.92 (t, *J* = 8.3 Hz, 1 H), 3.88 (t, *J* = 8.7 Hz, 1 H), 3.80 (s, 3 H), 3.69 (t, *J* = 7.3 Hz, 1 H), 3.35 (s, 3 H), 3.15 (t, *J* = 7.3 Hz, 1 H), 2.32 (m, 1 H), 2.18 (m, 1 H), 1.98 (m, 1 H), 1.16 (d, *J* = 6.7 Hz, 6 H), 1.05 (d, *J* = 6.7 Hz, 6 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.92 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 166.5, 163.3, 163.0, 162.6, 161.3, 160.3, 158.8, 154.9, 148.5, 148.4, 144.8, 144.4, 141.3, 138.6, 137.2, 134.4, 132.7, 131.2, 128.3, 127.0, 126.7, 123.0, 122.7, 121.3, 120.7, 118.4, 116.4, 115.4, 110.6, 109.4, 103.8, 101.3, 100.8, 98.3, 98.1, 75.2, 74.6, 55.5, 55.0, 53.2, 48.7, 28.3, 28.2, 27.9, 19.5, 19.4, 19.2, 14.3. HRMS (ESI+) m/z calcd for $C_{52}H_{57}N_6O_9$ $[M+H]^+$ 909.4182, found 909.4162.

Synthesis of Compound **III-44**: A solution of acid **III-41** (128 mg, 0.13 mmol) in dry $CHCl_3$ (1 mL) was cooled to 0°C. Oxalyl chloride (53.8 mg, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **III-43** (120 mg, 0.9 eq.) and dry DIPEA (0.1 mL, 5 eq.) in dry $CHCl_3$ (0.5 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-44** as a white solid (194 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.26 (s, 1 H), 11.85 (s, 1 H), 11.75 (s, 1 H), 10.53 (s, 1 H), 8.91 (d, *J* = 6.5 Hz, 1 H), 8.33 (s, 1 H), 8.25 (dd, *J* = 8.3, 1.2 Hz, 1 H), 8.08 (m, 3 H), 7.98 (m, 2 H), 7.94 (d, *J* = 8.2 Hz, 1 H), 7.86 (t, *J* = 7.8 Hz, 1 H), 7.68 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.52 (t, *J* = 6.2 Hz, 3 H), 7.48 (s, 1 H), 7.35 (m, 3 H), 7.25 (m, 3 H), 7.09 (m, 5 H), 7.02 (d, *J* = 7.5 Hz, 2 H), 7.00 (m, 2 H), 6.86 (s, 1 H), 6.70 (t, *J* = 7.4 Hz, 1 H), 6.68 (s, 1 H), 6.64 (s, 1 H), 6.57 (t, *J* = 7.5 Hz, 1 H), 5.92 (dd, *J* = 8.7, 2.4 Hz, 1 H), 5.80 (d, *J* = 2.4 Hz, 1 H), 5.48 (dd, *J* = 8.5, 7.4 Hz, 1 H), 4.72 (d, *J* = 15.2 Hz, 1 H), 4.45 (dd, *J* = 8.3, 6.1 Hz, 1 H), 4.22-4.11 (m, 6 H), 4.07-3.97 (m, 5 H), 3.90-3.85 (m, 4 H), 3.77 (dd, *J* = 8.5, 6.7 Hz, 1 H), 3.75 (s, 3 H), 3.68 (dd, *J* = 10.2, 7.8 Hz, 1 H), 3.60 (dd, *J* = 8.5, 6.7 Hz, 1 H), 3.51-3.46 (m, 2 H), 3.49 (s, 3 H), 3.08 (s, 3 H), 2.56 (m, 1 H), 2.40 (m, 3 H), 2.20 (m, 1 H), 1.89 (m, 1 H), 1.33-1.28 (m, 18 H), 1.20 (m, 6 H), 1.13 (d, *J* = 6.8 Hz, 3 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 0.81 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4,166.2, 164.1, 163.7, 163.4, 163.1, 161.8, 161.4, 161.4, 161.2, 160.8, 160.7, 159.2, 157.8, 152.6, 151.4, 150.9, 149.8, 149.5, 148.6, 146.4, 143.8, 143.8, 143.5, 142.2, 141.1, 138.2, 138.1, 137.7, 136.7, 136.6, 133.8, 133.6, 133.5, 133.2, 131.6, 127.5, 127.2, 127.1, 126.9, 126.7, 126.5, 126.4, 126.3, 125.7, 125.5, 125.1, 122.9, 122.5, 122.4, 122.1, 121.6, 120.3, 119.6, 119.6, 118.6, 117.8, 117.3, 117.1, 116.9, 116.3, 116.2, 115.4, 115.0, 114.9, 114.4, 103.3, 101.5, 100.2, 99.6, 99.4, 98.3, 97.9, 97.0, 75.7, 75.5, 75.4, 75.4, 74.8, 74.5, 66.7, 55.1, 54.8, 52.5, 47.4, 46.6, 28.4, 28.4, 28.2, 28.2, 28.1, 27.9, 19.8, 19.7, 19.6, 19.5, 19.5, 19.5, 19.4, 19.4, 19.2, 19.1. HRMS (ESI+) m/z calcd for $C_{109}H_{109}N_{12}O_{17}$ $[M+H]^+$ 1857.8028, found 1857.8030.

Synthesis of Compound **III-45**: The mixture of **III-44** (157 mg, 0.084 mmol) and LiI (60.1 mg, 5.4 eq.) in degassed ethyl acetate (1 mL) was heated to 80°C for 8 day. After quenching the reaction mixture with water, the solution

was washed with 5% $NaHSO_3$ aq. and acidified with a 5% citric acid aqueous solution. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give **III-45** as a white solid (141 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.31 (s, 1 H), 11.87 (s, 1 H), 11.75 (s, 1 H), 10.60 (s, 1 H), 8.87 (d, *J* = 7.4 Hz, 1 H), 8.34 (s, 1 H), 8.27 (dd, *J* = 8.3, 1.0 Hz, 1 H), 8.15 (d, *J* = 6.6 Hz, 1 H), 8.12 (d, *J* = 8.3 Hz, 1 H), 8.08 (d, *J* = 7.5 Hz, 1 H), 7.99 (m, 2 H), 7.93 (d, *J* = 8.2 Hz, 1 H), 7.88 (t, *J* = 7.9 Hz, 1 H), 7.69 (dd, *J* = 8.2, 1.1 Hz, 1 H), 7.53 (m, 3 H), 7.49 (s, 1 H), 7.37 (m, 2 H), 7.30 (m, 2 H), 7.23 (m, 3 H), 7.10 (m, 3 H), 7.03 (m, 3 H), 6.89 (s, 1 H), 6.78 (s, 1 H), 6.70 (t, *J* = 7.4 Hz, 1 H), 6.58 (t, *J* = 7.4 Hz, 1 H), 6.53 (s, 1 H), 6.11 (dd, *J* = 8.6, 2.4 Hz, 1 H), 5.63 (t, *J* = 8.6, 7.5 Hz, 1 H), 5.57 (d, *J* = 2.3 Hz, 1 H), 4.78 (d, *J* = 14.0 Hz, 1 H), 4.44 (dd, *J* = 8.3, 6.1 Hz, 1 H), 4.20 (m, 3 H), 4.03 (m, 4 H), 3.91 (m, 3 H), 3.72 (m, 2 H), 3.65 (dd, *J* = 8.4, 6.5 Hz, 1 H), 3.56 (m, 2 H), 3.52 (s, 3 H), 2.56 (m, 2 H), 2.50 (s, 3 H), 2.42 (m, 2 H), 2.18 (m, 1 H), 1.94 (m, 1 H), 1.32 (m, 15 H), 1.27 (d, *J* = 6.7 Hz, 3 H), 1.21 (d, *J* = 6.7 Hz 6 H), 1.12 (d, *J* = 6.7 Hz, 3 H), 1.09 (d, *J* = 6.7 Hz, 3 H), 0.84 (d, *J* = 6.7 Hz, 3 H), 0.84 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 164.3, 164.1, 163.8, 163.5, 163.2, 163.0, 161.7, 161.6, 161.4, 161.2, 160.8, 160.0, 158.2, 151.4, 151.3, 150.8, 149.9, 149.4, 148.5, 144.9, 143.9, 143.8, 142.5, 141.7, 141.1, 138.2, 138.0, 137.7, 137.0, 136.7, 133.6, 133.5, 133.5, 133.4, 133.3, 132.9, 128.6, 127.6, 127.2, 127.1, 127.0, 126.8, 126.7, 126.6, 126.5, 126.5, 126.1, 125.1, 123.0, 122.5, 122.4, 122.1, 121.8, 120.4, 119.7, 119.6, 119.4, 118.2, 117.4, 117.0, 116.9, 116.6, 116.4, 116.3, 115.5, 115.0, 115.0, 114.4, 103.3, 100.2, 100.1, 99.4, 98.3, 97.8, 97.7, 97.5, 75.7, 75.7, 75.5, 75.5, 75.2, 75.1, 66.7, 55.3, 54.1, 48.3, 46.7, 28.4, 28.4, 28.3, 28.2, 28.1, 27.9, 19.9, 19.7, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.1, 19.1. HRMS (ESI+) m/z calcd for $C_{108}H_{107}N_{12}O_{17}$ $[M+H]^+$ 1843.7872, found 1843.7917.

Synthesis of Compound **III-46**: A solution of acid **III-41** (179 mg, 0.18 mmol) in dry $CHCl_3$ (1.5 mL) was cooled to 0°C. Oxalyl chloride (40 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **III-36** (165 mg, 0.9 eq.) and dry DIPEA (140 μL, 5 eq.) in dry $CHCl_3$ (0.5 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-46** as a white solid (188 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.53 (s, 1 H), 11.77 (s, 1 H), 10.72 (s, 1 H), 9.32 (d, *J* = 7.4 Hz, 1 H), 8.61 (s, 1 H), 8.11 (d, *J* = 8.2 Hz, 1 H), 8.05 (m, 2 H), 7.95 (d, *J* = 7.5 Hz, 1 H), 7.87 (d, *J* = 8.6 Hz, 1 H), 7.83 (m, 3 H), 7.76 (d, *J* = 8.3 Hz, 1 H), 7.70 (m, 3 H), 7.64 (d, *J* = 7.4 Hz, 1 H), 7.48 (m, 2 H), 7.32 (m, 4 H), 7.26 (m, 2 H), 7.17 (m, 4 H), 7.09 (d, *J* = 8.2 Hz, 1 H), 6.94 (d, *J* = 8.3 Hz, 1 H), 6.85 (m, 2 H), 6.77 (s, 1 H), 6.76 (s, 1 H), 6.60 (m, 2 H), 6.30 (d, *J* = 1.9 Hz, 1 H), 6.25 (dd, *J* = 8.2, 2.0 Hz, 1 H), 6.18 (d, *J* = 7.2 Hz, 1 H), 6.08 (m, 1 H), 5.58 (d, *J* = 17.3 Hz, 1 H), 5.55 (d, *J* = 1.7 Hz, 1 H), 5.45 (d, *J* = 15.9 Hz, 1 H), 5.41 (t, *J* = 7.9 Hz, 1 H), 5.33 (d, *J* = 10.6 Hz, 1 H), 4.83 (m, 3 H), 4.55 (d, *J* = 13.0 Hz, 1 H), 4.42 (m, 1 H), 4.42 (m, 5 H), 4.14 (m, 1 H), 4.09 (m, 1 H), 3.98 (m, 2 H), 3.87 (s, 3 H), 3.80-3.66 (m, 7 H), 3.59 (s, 6 H), 3.44 (t, *J* = 8.2 Hz, 1 H), 3.11 (d, *J* = 9.5 Hz, 1 H), 3.05 (t, *J* = 8.2 Hz, 1 H), 2.54 (m, 1 H), 2.44 (m, 1 H), 2.31 (m, 1 H), 2.23 (m, 1 H), 2.02 (m, 1 H), 1.80 (s, 3 H), 1.17 (m, 1 H), 1.30 (d, *J* = 6.7 Hz, 3 H), 1.27 (d, *J* = 6.7 Hz, 3 H), 1.22 (m, 12 H), 1.17 (d, *J* = 6.5 Hz, 3 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 0.91 (m, 6 H), 0.76 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 168.8, 165.6, 164.9, 163.6, 163.4, 162.3, 161.2, 161.1, 160.6, 160.1, 159.8, 159.7, 158.8, 157.9, 155.6, 152.6, 151.7, 150.8, 150.2, 149.7, 147.4, 144.2, 144.0, 142.8, 141.9, 141.3, 141.2, 140.0, 138.2, 138.1, 136.9, 136.6, 134.9, 133.5, 133.4, 132.8, 132.4, 131.4, 130.2, 129.2, 128.6, 127.9, 127.4,

127.4, 126.8, 126.5, 125.4, 125.3, 125.3, 123.5, 123.2, 122.5, 122.2, 121.9, 120.4, 120.4, 120.2, 119.9, 119.8, 118.9, 118.8, 118.5, 117.6, 116.9, 116.7, 116.5, 116.2, 116.0, 115.6, 115.1, 114.1, 104.1, 103.4, 101.7, 100.4, 100.2, 99.7, 99.4, 98.0, 97.9, 97.5, 75.7, 75.5, 75.3, 74.9, 74.9, 74.1, 67.3, 66.4, 55.5, 55.2, 53.5, 49.1, 47.2, 46.9, 28.3, 28.3, 28.3, 28.1, 28.1, 27.9, 19.7, 19.6, 19.5, 19.5, 19.5, 19.4, 19.3, 19.2, 19.2.

Synthesis of Compound **III-47**: To a solution of **III-46** (73.5 mg, 0.036 mmol) in dry dichloromethane (1 mL), phenylsilane (10 μL, 2.3 eq.) and tetrakis(triphenylphosphine)palladium(0) (1.1 mg, 2 mol%) were added. The mixture was stirred for 30 min. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give **III-47** as a yellow solid (60.1 mg, 83%) ^{13}C NMR (150 MHz, $CDCl_3$, 273 K) δ 170.7, 168.7, 164.7, 164.4, 164.3, 163.6, 163.3, 163.0, 161.1, 161.0, 160.7, 160.4, 160.2, 159.7, 158.6, 158.2, 153.9, 152.4, 151.6, 150.6, 150.0, 149.4, 145.4, 144.0, 143.9, 142.8, 142.6, 141.1, 140.1, 140.4, 139.7, 138.0, 137.9, 136.6, 136.3, 134.6, 133.2, 133.2, 132.7, 132.3, 131.6, 131.3, 128.7, 128.5, 127.4, 127.3, 127.3, 126.9, 126.8, 126.8, 126.5, 125.5, 125.2, 123.9, 123.0, 122.4, 122.0, 121.7, 120.8, 120.2, 120.1, 119.8, 118.8, 117.5, 116.9, 116.8, 116.7, 116.4, 116.1, 115.5, 115.0, 114.0, 103.6, 103.3, 101.1, 99.6, 99.2, 99.1, 98.0, 97.9, 97.4, 75.7, 75.4, 75.3, 75.2, 74.8, 74.2, 67.2, 55.4, 55.1, 55.0, 54.0, 53.3, 48.8, 47.1, 46.7, 28.2, 28.2, 27.9, 27.9, 27.7, 19.7, 19.6, 19.6, 19.5, 19.4, 19.4, 19.3, 19.2, 19.2, 19.1, 19.0.

Synthesis of Compound **III-48**: A solution of acid **III-39** (200 mg, 0.11 mmol) in dry chloroform (1 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (26 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-33** (30 mg, 0.9 eq.) and dry DIPEA (37 μL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-48** as a yellow solid (58.0 mg, 78%).^1H NMR (600 MHz, $CDCl_3$) δ 12.61 (s, 1 H), 11.43 (s, 1 H), 11.21 (s, 1 H), 9.26 (d, *J* = 7.6 Hz, 1 H), 8.87 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.57 (s, 1 H), 8.51 (d, *J* = 7.6 Hz, 1 H), 8.05 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.98 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.97 (d, *J* = 7.2 Hz, 1 H), 7.91 (s, 1 H), 7.76 (m, 4 H), 7.66-7.56 (m, 6 H), 7.48 (s, 1 H), 7.46 (br, 1 H), 7.44 (s, 1 H), 7.39 (m, 3 H), 7.32 (t, *J* = 7.0 Hz, 1 H), 7.25-7.13 (m, 9 H), 7.07 (dd, *J* = 7.2, 1.2 Hz, 1 H), 6.85 (t, *J* = 7.0 Hz, 1 H), 6.80 (s, 1 H), 6.74 (t, *J* = 7.2 Hz, 1 H), 6.73 (s, 1 H), 6.44 (dd, *J* = 8.3, 1.2 Hz, 1 H), 6.32 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.24 (d, *J* = 1.3 Hz, 1 H), 6.22 (d, *J* = 7.3 Hz, 1 H), 5.66 (m, 2 H), 5.58 (d, *J* = 15.4 Hz, 1 H), 5.30 (m, 1 H), 4.85 (d, *J* = 15.2 Hz, 1 H), 4.77 (dd, *J* = 13.3, 5.4 Hz, 1 H), 4.63 (d, *J* = 13.1 Hz, 1 H), 4.62 (d, *J* = 10.3 Hz, 1 H), 4.50 (dd, *J* = 8.8, 6.0 Hz, 1 H), 4.43 (d, *J* = 17.2 Hz, 1 H), 4.27 (t, *J* = 8.4 Hz, 1 H), 4.14-3.98 (m, 12 H), 3.90 (dd, *J* = 9.1, 6.2 Hz, 1 H), 3.79 (dd, *J* = 9.0, 6.2 Hz, 1 H), 3.74 (s, 3 H), 3.74-3.62 (m, 4 H), 3.65 (s, 3 H), 3.44 (s, 3 H), 3.12 (dd, *J* = 9.1, 7.1 Hz, 1 H), 2.87 (dd, *J* = 9.0, 6.8 Hz, 1 H), 2.57 (m, 1 H), 2.28 (m, 2 H), 2.18 (m, 1 H), 2.08 (m, 1 H), 1.94 (s, 3 H), 1.58 (m, 1 H), 1.32 (d, *J* = 6.7 Hz, 3 H), 1.29 (d, *J* = 6.7 Hz, 3 H), 1.13 (m, 15 H), 1.04 (d, *J* = 6.7 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 0.51 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 169.0, 165.9, 164.8, 164.0, 163.7, 163.4, 162.9, 162.9, 162.6, 161.2, 160.2, 159.9, 159.8, 158.9, 158.2, 155.9, 153.0, 151.6, 151.5, 150.6, 149.9, 149.6, 144.3, 143.9, 143.6, 143.0, 141.4, 141.2, 141.1, 140.2, 140.1, 138.4, 137.2, 137.0, 134.9, 134.7, 133.9, 133.4, 132.5, 132.0, 131.5, 130.9, 129.8, 128.6, 127.7, 127.5, 127.3, 126.7, 126.6, 125.9, 125.3, 125.2, 123.5, 123.0, 122.4,

122.3, 120.7, 120.3, 119.8, 119.7, 119.2, 119.1, 119.0, 118.1, 117.7, 117.3, 116.9, 116.6, 116.4, 115.2, 115.0, 114.4, 104.0, 103.5, 101.9, 101.6, 101.4, 100.7, 99.5, 98.9, 98.4, 97.9, 97.8, 75.8, 75.4, 75.2, 75.1, 74.9, 73.9, 67.1, 66.0, 55.4, 55.3, 55.2, 54.9, 54.7, 53.7, 48.7, 47.2, 46.7, 28.4, 28.3, 28.1, 28.0, 27.6, 19.7, 19.6, 19.5, 19.4, 19.2 19.1, 18.9. HRMS (ESI+) m/z calcd for $C_{120}H_{121}N_{12}O_{19}$ $[M+H]^+$ 2033.8865, found 2033.8871.

Synthesis of Compound **III-49**: To a solution of **III-48** (49.5 mg, 0.024 mmol) in dry dichloromethane (0.5 mL), phenylsilane (10 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (2.8 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **III-49** as a yellow solid (48.6 mg, quant.). ^1H NMR (600 MHz, $CDCl_3$) δ 12.63 (s, 1 H), 11.56 (s, 1 H), 11.15 (s, 1 H), 9.28 (d, *J* = 7.5 Hz, 1 H), 9.08 (d, *J* = 7.6 Hz, 1 H), 8.56 (s, 1 H), 8.48 (d, *J* = 7.4 Hz, 1 H), 8.05 (d, *J* = 8.3 Hz, 2 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 7.92 (s, 1 H), 7.78 (m, 2 H), 7.74 (d, *J* = 8.6 Hz, 1 H), 7.70 (s, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 7.1 Hz, 1 H), 7.51 (s, 1 H), 7.43 (s, 1 H), 7.38 (m, 3 H), 7.32 (m, 3 H), 7.24 (m, 1 H), 7.21 (m, 1 H), 7.20 (m, 2 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 7.04 (d, *J* = 7.3 Hz, 2 H), 6.84 (s, 1 H), 6.84 (t, *J* = 8.0 Hz, 1 H), 6.76 (t, *J* = 7.3 Hz, 1 H), 6.62 (s, 1 H), 6.46 (d, *J* = 2.2 Hz, 1 H), 6.41 (d, *J* = 8.3 Hz, 1 H), 6.20 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.06 (d, *J* = 7.0 Hz, 1 H), 5.73 (d, *J* = 14.4 Hz, 1 H), 5.62 (t, *J* = 7.9 Hz, 1 H), 5.59 (d, *J* = 2.3 Hz, 1 H), 4.83 (d, *J* = 14.5 Hz, 1 H), 4.58 (d, *J* = 13.0 Hz, 1 H), 4.53 (dd, *J* = 8.8, 6.2 Hz, 1 H), 4.30 (t, *J* = 7.7 Hz, 1 H), 4.10 (m, 3 H), 4.03-3.96 (m, 4 H), 3.91 (m, 1 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.81 (m, 3 H), 3.75 (m, 2 H), 3.64 (s, 3 H), 3.01 (t, *J* = 8.6 Hz, 1 H), 2.96 (t, *J* = 8.6 Hz, 1 H), 2.60 (m, 1 H), 2.33-2.23 (m, 3 H), 2.09 (m, 1 H), 1.80 (s, 3 H), 1.70 (m, 1 H), 1.36 (d, *J* = 6.7 Hz, 3 H), 1.35 (d, *J* = 6.7 Hz, 3 H), 1.20 (d, *J* = 6.5 Hz, 3 H), 1.19 (d, *J* = 6.5 Hz, 3 H), 1.13 (m, 12 H), 0.97 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H), 0.66 (d, *J* = 6.7 Hz, 3 H), 0.60 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 169.1, 167.2, 164.8, 164.0, 163.7, 163.4, 163.2, 162.8, 161.3, 160.7, 160.6, 158.8, 158.8, 154.0, 153.0, 151.6, 151.5, 150.1, 149.9, 149.6, 144.3, 143.9, 143.2, 142.8, 141.2, 141.1, 140.4, 140.1, 139.4, 138.3, 137.1, 136.9, 134.7, 134.5, 134.2, 133.7, 133.4, 132.3, 131.6, 130.0, 128.2, 127.9, 127.7, 127.6, 127.3, 126.7, 126.6, 125.8, 125.3, 125.2, 124.2, 123.1, 122.9, 122.3, 122.2, 120.6, 120.5, 120.3, 119.8, 119.7, 118.8, 117.4, 117.3, 117.2, 116.9, 116.8, 116.4, 115.1, 114.9, 114.5, 104.0, 103.5, 101.7, 101.0, 99.7, 99.5, 99.0, 98.6, 98.4, 97.5, 75.7, 75.5, 75.4, 74.2, 74.8, 73.9, 67.1, 55.7, 55.4, 55.2, 53.4, 50.0, 47.5, 46.7, 28.5, 28.3, 28.2, 28.2, 28.1, 27.8, 19.7, 19.6, 19.5, 19.4, 19.3, 19.3, 19.2, 19.2, 19.1, 19.0. HRMS (ESI+) m/z calcd for $C_{117}H_{117}N_{12}O_{19}$ $[M+H]^+$ 1993.8552, found 1993.8567.

Synthesis of Compound **III-50**: A solution of acid **III-22** (457.8 mg, 0.52 mmol) in dry chloroform (4 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (0.12 mL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-33** (153.0 mg, 0.9 eq.) and dry DIPEA (0.46 mL, 5 eq.) in dry chloroform (4 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-22** as a yellow solid (455.8 mg, 77%.). ^1H NMR (600 MHz, $CDCl_3$) δ 11.84 (s, 1 H), 8.92 (dd, *J* = 7.7, 1.1 Hz, 1 H), 8.12 (br, 1 H), 8.06 (s, 1 H), 8.02 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.87 (d, *J* = 7.7 Hz, 1 H),

7.81 (t, *J* = 8.2 Hz, 2 H), 7.71 (d, *J* = 7.3 Hz, 1 H), 7.65 (m, 3 H), 7.57 (d, *J* = 7.2 Hz, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.49 (s, 1 H), 7.47 (s, 1 H), 7.43 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.26 (m, 2 H), 7.08 (br, 1 H), 6.99 (s, 1 H), 6.43 (m, 2 H), 6.00 (m, 2 H), 5.26 (dd, *J* = 17.2, 1.5 Hz, 1 H), 5.11 (dd, *J* = 10.3, 1.3 Hz, 1 H), 4.92 (m, 2 H), 4.85 (dd, *J* = 13.0, 6.0 Hz, 1 H), 4.65 (dd, *J* = 10.6, 6.7 Hz, 1 H), 4.48 (br, 1 H), 4.36 (t, *J* = 6.8 Hz, 1 H), 4.08 (d, *J* = 6.3 Hz, 2 H), 3.92 (d, *J* = 6.7 Hz, 2 H), 3.73 (s, 3 H), 3.62 (s, 3 H), 3.32 (dd, *J* = 8.8, 6.5 Hz, 1 H), 2.92 (dd, *J* = 8.8, 6.8 Hz, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 1.86 (m, 1 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.07 (d, *J* = 6.7 Hz, 3 H), 1.06 (d, *J* = 6.7 Hz, 3 H), 0.78 (d, *J* = 6.7 Hz, 3 H), 0.76 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 165.8, 163.4, 163.0, 162.8, 161.7, 160.2, 158.5, 153.9, 153.3, 150.8, 149.6, 144.1, 143.9, 143.1, 141.6, 141.4, 140.1, 136.3, 135.2, 132.4, 131.0, 128.0, 127.9, 127.8, 127.3, 127.3, 127.0, 126.5, 125.2, 125.1, 122.9, 122.3, 120.7, 120.2, 119.0, 118.7, 118.5, 116.6, 114.8, 114.7, 104.2, 101.6, 101.1, 98.6, 98.3, 75.3, 75.2, 74.2, 66.8, 55.4, 55.2, 49.3, 47.4, 28.4, 28.2, 27.9, 19.4, 19.4, 19.1, 19.0. HRMS (ESI+) m/z calcd for $C_{69}H_{69}N_6O_{11}$ $[M+H]^+$ 1157.5019, found 1157.5007.

Synthesis of Compound **III-51**: To a solution of **III-50** (180.0 mg, 0.16 mmol) in dry dichloromethane (1.5 mL), phenylsilane (44 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (7.4 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **III-51** as a yellow solid (164.7 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.44 (s, 1 H), 9.03 (d, *J* = 7.6 Hz, 1 H), 8.14 (br, 2 H), 8.11 (d, *J* = 8.2 Hz, 1 H), 7.83 (d, *J* = 7.3 Hz, 2 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.78 (s, 1 H), 7.68 (m, 2 H), 7.60 (d, *J* = 7.4 Hz, 1 H), 7.53 (d, *J* = 8.3 Hz, 1 H), 7.51 (s, 1 H), 7.45 (m, 4 H), 7.38 (t, *J* = 7.1 Hz, 1 H), 7.34 (s, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.28 (br, 1 H), 7.01 (br, 1 H), 6.34 (m, 2 H), 5.79 (d, *J* = 14.6 Hz, 1 H), 4.95 (d, *J* = 14.6 Hz, 1 H), 4.66 (dd, *J* = 10.5, 6.3 Hz, 1 H), 4.46 (br, 1 H), 4.25 (t, *J* = 6.5 Hz, 1 H), 4.12 (m, 2 H), 3,93 (t, *J* = 6.6 Hz, 1 H), 3.90 (t, *J* = 6.5 Hz, 1 H), 3.71 (s, 3 H), 3.52 (s, 3 H), 3.37 (t, *J* = 6.8 Hz, 1 H), 3.17 (t, *J* = 7.2 Hz, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 1.88 (m, 1 H), 1.15 (d, *J* = 6.7 Hz, 6 H), 1.07 (d, *J* = 6.7 Hz, 3 H), 1.06 (d, *J* = 6.7 Hz, 3 H), 0.77 (d, *J* = 6.7 Hz, 3 H), 0.74 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 167.1, 163.3, 163.2, 163.1, 161.9, 160.6, 158.8, 153.1, 152.3, 150.1, 149.3, 143.9, 143.7, 142.8, 142.3, 141.5, 141.3, 139.5, 136.5, 134.7, 134.5, 131.6, 127.9, 127.8, 127.2, 127.1, 126.3, 124.9, 124.9, 123.0, 122.7, 120.9, 120.3, 120.2, 120.2, 120.1, 117.4, 117.2, 115.0, 114.5, 104.0, 101.5, 101.2, 98.9, 98.3, 75.4, 75.2, 74.4, 66.6, 55.2, 55.2, 49.7, 47.1, 28.1, 28.1, 27.7, 19.2, 19.0, 18.9. HRMS (ESI+) m/z calcd for $C_{66}H_{65}N_6O_{11}$ $[M+H]^+$ 1117.4706, found 1117.4687.

Synthesis of Compound **III-52:** To a solution of **III-50** (180.0 mg, 0.16 mmol) in dry dichloromethane (0.5 mL), DBU (27.8 mg, 3.9 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **III-52** as a yellow solid (141.0 mg, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.81 (s, 1 H), 8.93 (d, *J* = 7.6 Hz, 1 H), 8.02 (d, *J* = 7.1 Hz, 1 H), 8.00 (d, *J* = 7.2 Hz, 1 H), 7.68 (d, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 8.1 Hz, 1 H), 7.57 (s, 1 H), 7.48 (s, 1 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 7.35 (t, *J* = 8.1 Hz, 1 H), 7.19 (d, *J* = 7.4 Hz, 1 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 6.96 (s, 1 H), 6.57 (d, *J* = 7.4 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.34 (d, *J* = 2.3 Hz, 1 H), 5.97 (d, *J* = 15.1 Hz, 1 H), 5.95 (m, 1 H), 5.23 (dd, *J* = 17.2, 1.3 Hz, 1 H), 5.09 (d, *J* = 10.4 Hz, 1 H), 4.99 (d, *J* = 15.2 Hz, 1 H), 4.85 (dd, *J* = 13.1, 5.9 Hz, 1 H), 4.75 (dd, *J* =

13.1, 6.0 Hz, 1 H), 4.07 (d, *J* = 5.2 Hz, 2 H), 3.99 (d, *J* = 6.5 Hz, 4 H), 3.74 (s, 3 H), 3.53 (s, 3 H), 3.39 (dd, *J* = 8.8, 6.5 Hz, 1 H), 3.01 (dd, *J* = 8.8, 6.8 Hz, 1 H), 2.32 (m, 1 H), 2.23 (m, 1 H), 1.88 (m, 1 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 1.09 (d, *J* = 6.7 Hz, 3 H), 0.81 (d, *J* = 6.7 Hz, 3 H), 0.80 (d, *J* = 6.7 Hz ,3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 165.6, 163.4, 163.0, 162.6, 161.4, 159.9, 158.4, 152.3, 151.0, 149.2, 143.9, 143.7, 143.2, 140.1, 136.5, 135.1, 132.3, 131.2, 127.7, 125.6, 126.3, 122.9, 122.2, 121.3, 120.2, 119.1, 118.6, 118.5, 116.5, 110.1, 109.4, 103.9, 101.4, 100.6, 98.6, 98.0, 75.1, 75.1, 74.0, 66.7, 55.2, 55.0, 49.1, 28.2, 28.1, 27.8, 19.3, 19.2, 19.2, 19.1, 18.9. HRMS (ESI+) m/z calcd for $C_{54}H_{59}N_6O_9$ $[M+H]^+$ 935.4338, found 935.4319.

Synthesis of Compound **III-53**: A solution of acid **III-52** (150.0 mg, 0.13 mmol) in dry chloroform (1 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (30 μL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-52** (112.0 mg, 0.9 eq.) and dry DIPEA (0.1 mL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-53** as a yellow solid (166.4 mg, 68%.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.05 (s, 1 H), 10.98 (s, 1 H), 10.82 (s, 1 H), 9.17 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.87 (dd, *J* = 7.7, 1.1 Hz, 1 H), 8.52 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.23 (dd, *J* = 8.3, 1.2 Hz, 1 H), 8.00 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.87 (s, 1 H), 7.85 (d, *J* = 7.9 Hz, 1 H), 7.79 (t, *J* = 8.0 Hz. 1 H), 7.74 (s, 1 H), 7.72 (d, *J* = 8.6 Hz, 1 H), 7.71 (d, *J* = 8.6 Hz, 1 H), 7.61-7.54 (m, 4 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.48 (d, *J* = 7.6 Hz, 1 H), 7.39 (m, 2 H), 7.35 (m, 4 H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 7.18 (s, 1 H), 7.13 (m, 2 H), 7.04 (t, *J* = 7.9 Hz, 1 H), 6.98 (d, *J* = 7.0 Hz, 1 H), 6.78 (s, 1 H), 6.51 (d, *J* = 8.3 Hz, 1 H), 6.06 (dd, *J* = 8.4, 2.3 Hz, 1 H), 5.97 (d, *J* = 2.3 Hz, 1 H), 5.82 (d, *J* = 2.3 Hz, 1 H), 5.69 (m, 2 H), 5.58 (dd, *J* = 8.3, 7.4 Hz, 1 H), 5.29 (d, *J* = 14.6 Hz, 1 H), 5.26 (d, *J* = 14.3 Hz, 1 H), 4.98 (d, *J* = 9.4 Hz, 1 H), 4.94 (dd, *J* = 17.2, 1.5 Hz, 1 H), 4.89 (d, *J* = 14.2 Hz, 1 H), 4.62 (m, 2 H), 4.36 (d, *J* = 5.9 Hz, 1 H), 4.35 (d, *J* = 6.1 Hz, 1 H), 4.29-4.23 (m, 4 H), 4.16 (dd, *J* = 8.8, 6.5 Hz, 1 H), 4.12-4.02 (m, 4 H), 3.75 (d, *J* = 6.5 Hz, 2 H), 3.64 (s, 3 H), 3.40 (d, *J* = 14.5 Hz, 1 H), 3.30 (s, 3 H), 3.28 (m, 2 H), 3.12 (s, 3 H), 2.94 (s, 3 H), 2.85 (dd, *J* = 8.6, 6.8 Hz, 1 H), 2.45 (m, 1 H), 2.32 (m, 2 H), 2.10 (m, 1 H), 1.90 (m, 1 H), 1.71 (m, 1 H), 1.25 (m, 6 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.25 (d, *J* = 6.5 Hz, 3 H), 1.11 (d, *J* = 6.5 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.7 Hz, 3 H), 0.60 (d, *J* = 6.7 Hz, 3 H), 0.52 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 168.3, 166.4, 163.8, 163.6, 163.5, 163.4, 163.2, 162.5, 162.4, 161.6, 161.0, 159.8, 159.6, 158.5, 158.0, 154.1, 153.5, 153.2, 152.7, 150.5, 150.3, 149.8, 144.0, 143.8, 143.5, 143.1, 142.4, 141.7, 141.5, 141.3, 140.1, 139.4, 137.2, 136.3, 135.0, 135.0, 134.3, 133.9, 132.6, 132.4, 131.5, 128.7, 127.9, 127.8, 127.5, 127.5, 127.2, 126.6, 126.5, 126.0, 125.4, 125.1, 125.0, 123.1, 122.6, 122.2, 121.9, 120.6, 120.4, 120.1, 120.1, 119.7, 119.4, 118.9, 118.3, 118.0, 118.0, 117.4, 117.1, 116.7, 115.6, 114.7, 114.5, 103.4, 103.3, 101.9, 101.3, 100.8, 100.4, 98.9, 98.2, 97.6, 97.3, 75.6, 75.3, 75.3, 74.9, 74.2, 74.1, 66.7, 66.3, 55.2, 54.9, 54.7, 54.5, 48.2, 47.7 47.2, 28.4, 28.3, 28.3, 28.1, 28.0, 27.7, 19.5, 19.5, 19.5, 19.4, 19.4, 19.4, 19.4, 19.3, 19.3, 19.1, 18.8, 18.8. HRMS (ESI+) m/z calcd for $C_{120}H_{121}N_{12}O_{19}$ $[M+H]^+$ 2033.8865, found 2033.8883.

Synthesis of Compound **III-54**: To a solution of **III-53** (137.9 mg, 0.068 mmol) in dry dichloromethane (1 mL),

phenylsilane (19 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (3.1 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **III-54** as a yellow solid (118.4 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.11 (s, 1 H), 11.18 (s, 1 H), 10.96 (s, 1 H), 9.26 (d, *J* = 7.6 Hz, 1 H), 9.00 (d, *J* = 7.7 Hz, 1 H), 8.54 (d, *J* = 7.6 Hz, 1 H), 8.25 (d, *J* = 8.3 Hz, 1 H), 8.10 (d, *J* = 7.3 Hz, 1 H), 8.10 (br, 1 H), 7.95 (s, 1 H), 7.88 (s, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 7.82 (m, 2 H), 7.74 (s, 1 H), 7.71 (t, *J* = 7.9 Hz, 2 H), 7.67 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.4 Hz, 1 H), 7.54 (d, *J* = 7.4 Hz, 1 H), 7.50 (d, *J* = 8.3 Hz, 1 H), 7.45 (d, *J* = 8.5 Hz, 1 H), 7.38-7.30 (m, 5 H), 7.26 (m, 1 H), 7.23 (s, 2 H), 7.22 (br, 1 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 7.10 (s, 2 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 6.9 Hz, 1 H), 6.80 (s, 1 H), 6.78 (br, 1 H), 6.55 (d, *J* = 8.3 Hz, 1 H), 6.08 (dd, *J* = 8.3, 2.2 Hz, 1 H), 5.91 (d, *J* = 2.2 Hz, 1 H), 5.89 (dd, *J* = 8.5, 2.3 Hz, 1 H), 5.81 (d, *J* = 2.3 Hz, 1 H), 5.65 (t, *J* = 8.0 Hz, 1 H), 5.45 (d, *J* = 14.5 Hz, 1 H), 5.29 (d, *J* = 14.2 Hz, 1 H), 4,98 (d, *J* = 14.5 Hz, 1 H), 4.58 (dd, *J* = 10.6, 6.7 Hz, 1 H), 4.40 (br, 1 H), 4.33 (dd, *J* = 8.6, 6.7 Hz, 1 H), 4.27 (m, 4 H), 4.12 (m, 3 H), 4.05 (dd, *J* = 8.6, 6.8 Hz, 1 H), 3.74 (d, *J* = 6.4 Hz, 2 H), 3.66 (s, 3 H), 3.47 (s, 3 H), 3.35 (m, 2 H), 3.19 (dd, *J* = 8.6, 6.8 Hz, 1 H), 3.05 (s, 3 H), 3.01 (s, 3 H), 2.44 (m, 1 H), 2.32 (m, 2 H), 2.07 (m, 1 H), 1.94 (m, 1 H), 1.80 (m, 1 H), 1.25 (m, 6 H), 1.17 (m, 6 H), 1.14 (d, *J* = 6.7 Hz, 3 H), 1.12 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 6 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.68 (d, *J* = 6.7 Hz, 6 H).^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 168.6, 167.1, 164.0, 163.7, 163.5, 163.4, 163.2, 163.2, 162.7, 161.6, 161.2, 159.9, 159.8, 158.5, 158.1, 153.5, 153.2, 152.3, 152.2, 150.7, 150.1, 149.0, 144.0, 143.8, 143.1, 142.7, 141.8, 141.4, 141.3, 149.5, 139.5, 139.2, 137.3, 136.4, 135.0, 134.7, 134.3, 134.1, 132.2, 131.8, 128.1, 127.8, 127.8, 127.7, 127.7, 127.4, 127.2, 127.2, 126.8, 126.5, 126.3, 125.2, 125.1, 125.0, 123.0, 122.7, 121.7, 120.7, 120.6, 120.5, 120.3, 120.1, 120.1, 119.8, 119.0, 117.9, 117.6, 117.3, 117.2, 116.2, 115.5, 114.8, 114.5, 103.3, 103.2, 101.8, 100.9, 100.8, 100.2, 98.8, 98.2, 97.7, 97.6, 75.6, 75.5, 75.3, 75.9, 74.2, 74.2, 66.8, 55.2, 55.1, 54.6, 54.5, 48.2, 47.7, 47.2, 28.4, 28.3, 28.3, 28.1, 28.0, 27.8, 19.5, 19.4, 19.4, 19.3, 19.3, 19.3, 19.1, 19.0, 18.9. HRMS (ESI+) m/z calcd for $C_{117}H_{117}N_{12}O_{19}$ $[M+H]^+$ 1993.8552, found 1993.8558.

Synthesis of Compound **III-55**: To a solution of **III-28** (196.8 mg, 0.14 mmol) in dry dichloromethane (1 mL), DBU (35.6 mg, 3.9 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **III-55** as a yellow solid (139.9 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.14 (s, 1 H), 12.00 (s, 1 H), 9.06 (d, *J* = 7.5 Hz, 1 H), 8.94 (d, *J* = 8.0 Hz, 1 H), 8.06 (d, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.85 (s, 1 H), 7.76 (s, 1 H), 7.66 (t, *J* = 7.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 6.7 Hz, 1 H), 7.14 (m, 2 H), 6.99 (m, 2 H), 6.83 (s, 1 H), 6.75 (s, 1 H), 6.65 (d, *J* = 7.8 Hz, 1 H), 6.45 (d, *J* = 7.8 Hz, 1 H), 6.16 (d, *J* = 6.7 Hz, 1 H), 5.94 (d, *J* = 2.3 Hz, 1 H), 5.40 (d, *J* = 12.6 Hz, 1 H), 4.20 (br, 1 H), 4.13 (dd, *J* = 6.5, 8.2 Hz, 4 H), 3.68 (m, 6 H), 3.64 (m, 1 H), 3.51 (m, 2 H), 3.38 (m, 1 H), 2.98 (s, 3 H), 2.32 (m, 2 H), 2.15 (m, 1 H), 2.04 (m, 1 H), 1.16 (m, 12 H), 1.08 (m, 6 H), 1.00 (d, *J* = 6.6 Hz, 3 H), 0.97 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 165.8, 163.9, 163.6, 163.5, 163.3, 162.0, 161.2, 159.7, 158.0, 151.9, 150.9, 146.0, 143.8, 143.8, 142.8, 139.6, 139.1, 136.1, 135.1, 135.0, 131.7, 127.9, 127.4, 126.7, 126.2, 122.8, 122.6, 121.4, 121.1, 119.7, 118.9, 118.5, 118.0, 116.8, 115.7, 109.8, 109.4, 103.5, 100.7, 100.4, 99.8, 98.2, 97.5, 75.4, 75.4, 74.6, 74.3, 55.2, 54.3, 52.9, 48.0, 28.3, 28.2, 28.1, 19.4, 19.4, 19.2. HRMS (ESI+) m/z calcd for $C_{66}H_{71}N_8O_{11}$ $[M+H]^+$ 1151.5237,

found 1151.5232.

Synthesis of Compound **III-56**: A solution of acid **III-41** (111.2 mg, 0.11 mmol) in dry chloroform (1 mL) was cooled to 0°C. Oxalyl chloride (24 μL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-55** (120.0 mg, 0.9 eq.) and dry DIPEA (85 μL, 5 eq.) in dry chloroform (1 mL). The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-56** as a yellow solid (153.6 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major : Minor = 10 : 3) (Major) δ 12.44 (s, 1 H), 11.86 (s, 1 H), 11.65 (s, 1 H), 11.12 (s, 1 H), 10.69 (s, 1 H), 9.05 (d, *J* = 8.0 Hz, 1 H), 8.99 (d, *J* = 7.8 Hz, 1 H), 8.92 (d, *J* = 8.2 Hz, 1 H), 8.63 (s, 1 H), 8.10-7.96 (m, 8 H), 7.88 (d, *J* = 8.2 Hz, 1 H), 7.87 (s, 1 H), 7.73 (m, 2 H), 7.68 (d, *J* = 8.2 Hz, 1 H), 7.63-7.54 (m, 6 H), 7.52 (s, 1 H), 7.43 (s, 1 H), 7.37 (d, *J* = 6.7 Hz, 2 H), 7.30 (m, 2 H), 7.20 (m, 6 H), 7.11 (m, 4 H), 7.02 (t, *J* = 8.2 Hz, 1 H), 7.91 (m, 2 H), 6.79 (t, *J* = 6.8 Hz, 1 H), 6.71 (m, 2 H), 6.63 (s, 1 H), 6.26 (d, *J* = 6.8 Hz, 1 H), 5.99 (s, 1 H), 5.90 (d, *J* = 7.6 Hz, 1 H), 5.04 (d, *J* = 2.3 Hz, 1 H), 4.51 (m, 2 H), 4.26 (m, 2 H), 4.19-4.04 (m. 12 H), 3.45 (s, 3 H), 2.88 (s, 3 H), 2.61 (m, 1 H), 2.46-2.28 (m, 3 H), 1.89 (s, 3 H), 1.86 (m, 2 H), 1.72 (m, 1 H), 1.37 (d, *J* = 6.6 Hz, 3 H), 1.35 (d, *J* = 6.6 Hz, 3 H), 1.31-1.20 (m, 12 H), 1.13 (m, 6 H), 0.95 (m, 3 H), 0.85 (m, 6 H), 0.81 (d, *J* = 6.6 Hz, 3 H), 0.70 (d, *J* = 6.6 Hz, 3 H), 0.66 (d, *J* = 6.6 Hz, 3 H). (Minor) δ 12.30 (s, 1 H), 11.62 (s, 1 H), 11.57 (s, 1 H), 11.23 (s, 1 H), 10.56 (s, 1 H), 9.07 (d, *J* = 8.0 Hz, 1 H), 8.84 (d, *J* = 7.8 Hz, 1 H), 8.68 (d, *J* = 8.0 Hz, 1 H), 8.45 (s, 1 H), 7.79 (m, 2 H), 6.38 (d, *J* = 7.0 Hz, 1 H), 6.23 (m, 1 H), 6.07 (s, 1 H), 5.47 (br, 1 H), 5.34 (t, *J* = 7.8 Hz, 1 H), 4.42 (m, 2 H), 3.95 (m, 1 H), 3.90 (m, 1 H), 3.83 (m, 1 H), 3.70 (m, 3 H), 3,36 (d, *J* = 7.8 Hz, 1 H), 3.30 (m, 1 H), 3.24 (m, 1 H), 0.91 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 165.8, 164.7, 164.3, 163.9, 163.6, 163.5, 163.4, 162.7, 161.8, 161.8, 161.1, 160.8, 160.5, 158.9, 157.0, 152.8, 151.6, 150.9, 150.7, 150.4, 149.9, 149.4, 145.9, 144.4, 144.1, 143.7, 141.2, 141.1, 139.3,139.1, 138.8, 138.5, 137.9, 136.7, 135.1, 135.0, 133.6, 133.6, 133.1, 133.1, 131.0, 130.4, 128.0, 127.4, 127.3, 126.8, 126.7, 126.6, 126.1, 126.1, 124.2, 125.0, 123.8, 122.8, 122.5, 122.3, 121.8, 121.3, 121.0, 120.8, 119.8, 119.7, 119.1, 118.9, 118.6, 117.9, 116.9, 116.8, 116.6, 116.3, 115.7, 115.3, 115.1, 114.2, 101.9, 100.5, 99.9, 99.8, 99.7. 99.6, 98.6, 98.0, 97.0, 75.7, 75.7, 75.5, 75.4, 75.1, 74.6, 74.3, 67.2, 54.3, 53.4, 52.7, 47.7, 46.8, 28.5, 28.4, 28.4, 28.2, 28.1, 27.8, 27.5, 19.8, 19.6, 19.6, 19.5, 19.4, 19.4, 19.4, 19.4, 19.3, 19.3, 19.2, 19.0, 18.8, 18.7. HRMS (ESI+) m/z calcd for $C_{123}H_{123}N_{14}O_{19}$ $[M+H]^+$ 2099.9083, found 2099.9084.

Synthesis of Compound **III-57**: The mixture of **III-56** (128.4 mg, 0.061 mmol) and LiI (40.8 mg, 4.9 eq.) in degassed ethyl acetate (1.5 mL) was heated to 80°C overnight. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with 5% citric acid aq. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3 / 7) to give **III-57** as a yellow solid (107.5 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major : Minor = 10 : 4)(Major) δ 12.46 (s, 1 H), 11.87 (s, 1 H), 11.67 (s, 1 H), 10.89 (s, 1 H), 10.33 (s, 1 H), 9.00 (d, *J* = 8.0 Hz, 1 H), 8.98 (d, *J* = 7.8 Hz, 1 H), 8.90 (d, *J* = 8.0 Hz, 1 H), 8.64 (s, 1 H), 8.10 (d, *J* = 8.2 Hz, 1 H), 8.02 (m, 6 H), 7.89 (m, 2 H), 7.83 (m, 3 H), 7.68-7.56 (m, 9 H), 7.51 (s, 1 H), 7.47 (m, 1 H), 7.41 (s, 1 H), 7.39 (m, 2 H), 7.30 (m, 2 H), 7.23-7.07 (m, 10 H), 7.02 (t, *J* = 8.2 Hz, 1 H), 6.93 (m, 2

H), 6.79 (m, 2 H), 6.72 (m, 2 H), 6.27 (d, *J* = 8.2 Hz, 1 H), 6.18 (m, 1 H), 5.97 (s, 1 H), 5.92 (d, *J* = 8.2 Hz, 1 H), 5.03 (d, *J* = 2.3 Hz, 1 H), 4.66 (d, *J* = 12.1 Hz, 1 H), 4.50 (m, 1 H), 4.38 (m, 1 H), 4.28 (m, 2 H), 4.28-4.04 (m, 14 H), 3.64 (s, 3 H), 3.51 (t, *J* = 6.8 Hz, 1 H), 3.47 (t, *J* = 7.8 Hz, 1 H), 3.35 (m, 2 H), 3.25 (m, 1 H), 2.92 (s, 3 H), 2.84 (t, *J* = 8.2 Hz, 1 H), 2.60 (m, 1 H), 2.40 (m, 5 H), 1.91 (s, 3 H), 1.86 (m, 3 H), 1,72 (m, 1 H), 1.38 (d, *J* = 6.6 Hz, 3 H), 1.34 (d, *J* = 6.6 Hz, 3 H), 1.31-1.20 (m, 12 H), 1.12 (m, 6 H), 1.00 (d, *J* = 6.6 Hz, 3 H), 0.95 (d, *J* = 6.6 Hz, 3 H), 0.86 (m, 3 H), 0.80 (d, *J* = 6.6 Hz, 3 H), 0.72 (d, *J* = 6.7 Hz, 3 H), 0.67 (d, *J* = 6.6 Hz, 3 H). (Minor) δ 12.46 (s, 1 H), 11.61 (s, 1 H), 11.07 (s, 1 H), 10.60 (s, 2 H), 9.12 (d, *J* = 8.0 Hz, 1 H), 8.66 (d, *J* = 7.8 Hz, 1 H), 8.50 (br, 1 H), 8.49 (s, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 6.62 (d, *J* = 8.5 Hz, 1 H), 5.48 (br, 1 H), 5.42 (t, *J* = 7.8 Hz, 1 H), 3.99 (m, 1 H), 3.93 (m, 1 H), 3.84 (m, 1 H), 3.78 (m, 1 H), 3.17 (m, 1 H), 2.77 (m, 1 H), 2.26 (s, 3 H), 0.89 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 168.2, 164.7, 163.9, 163.8, 163.6, 163.5, 163.4, 163.4, 163.2, 162.9, 162.7, 161.8, 161.0, 160.8, 160.6, 160.2, 159.8, 159.0, 157.0, 152.6, 151.6, 150.8, 150.4, 150.1, 149.8, 149.3, 145.1, 144.1, 144.1, 143.7, 141.2, 141.1, 140.1, 139.0, 138.8, 138.7, 138.5, 138.0, 137.9, 137.6, 136.9, 136.7, 135.1, 134.9, 134.7, 133.6, 133.1, 133.1, 131.9, 130.9, 130.3, 128.0, 127.6, 127.4, 127.3, 127.1, 126.8, 126.8, 126.7, 126.5, 126.1, 125.8, 125.2, 125.0, 123.7, 123.0, 122.9, 122.7, 122.5, 122.4, 122.3, 122.2, 121.8, 121.7, 121.3, 121.2, 121.0, 120.2, 119.8, 119.7, 119.6, 118.7, 117.8, 116.9, 116.8, 116.6, 116.5, 116.3, 116.3, 116.2, 116.0, 115.3, 115.2, 115.1, 114.2, 101.8, 100.6, 100.2, 99.9, 99.6, 99.5, 99.3, 98.0, 97.9, 97.1, 75.7, 75.7, 75.5, 75.5, 75.4, 75.2, 74.9, 74.6, 67.2, 60.5, 55.2, 54.4, 53.6, 53.3, 47.7, 46.7, 28.5, 28.4, 28.3, 28.3, 28.3, 28.2, 28.2, 28.1, 28.0, 27.9, 27.8, 27.5, 19.7, 19.6, 19.6, 19.5, 19.5, 19.5, 19.4, 19.4, 19.4, 19.3, 19.3, 19.2, 19.2, 19.2, 19.1, 19.1, 19.0, 18.8, 18.7.

Synthesis of Compound **III-58**: A solution of acid **III-51** (200 mg, 0.18 mmol) in dry chloroform (1.5 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (40 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-33** (51.2 mg, 0.9 eq.) and dry DIPEA (0.15 mL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **III-58** as a yellow solid (178 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.01 (s, 1 H), 11.90 (s, 1 H), 8.99 (m, 2 H), 8.08 (d, *J* = 8.1 Hz, 1 H), 7.88 (s, 1 H), 7.76 (m, 3 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.2 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 8.2 Hz, 1 H), 7.49 (s, 1 H), 7.47 (d, *J* = 8.3 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.28 (br, 1 H), 7.24 (m, 1 H). 7.20 (br, 1 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 6.98 (m, 2 H), 6.94 (d, *J* = 8.2 Hz, 1 H), 6.87 (br, 1 H), 6.82 (s, 1 H), 6.20 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.10 (d, *J* = 2.1 Hz, 1 H), 5.67 (m, 1 H), 5.28 (d, *J* = 14.9 Hz, 1 H), 5.17 (dd, *J* = 17.2, 1.4 Hz, 1 H), 4.88 (d, *J* = 10.4 Hz, 1 H), 4.53 (m, 2 H), 4.41 (dd, *J* = 13.4, 5.7 Hz, 1 H), 4.37 (br, 1 H), 4.29 (t, *J* = 7.0 Hz, 1 H), 4.18 (m, 2 H), 3.96 (t, *J* = 8.6 Hz, 1 H), 3.93 (t, *J* = 6.5 Hz, 1 H), 3.82 (t, *J* = 6.4 Hz, 1 H), 3.77 (t, *J* = 6.5 Hz, 1 H), 3.70 (s, 3 H), 3.42 (br, 1 H), 3.33 (br, 1 H), 3.27 (s, 3 H), 3.30 (br, 1 H), 2.36 (br, 1 H), 2.20 (m, 2 H), 1.92 (m, 1 H), 1.19 (m, 6 H), 1.10 (m, 12 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.3, 163.8, 163.6, 163.4, 163.0, 162.3, 161.7, 159.9, 158.0, 153.2, 151.9, 151.0, 146.2, 144.0, 143.9, 142.7, 141.4, 141.4, 139.4, 139.4, 136.2, 135.2, 135.1, 134.2, 131.3, 130.6, 128.2, 127.9, 127.8, 127.3, 127.2, 126.5, 125.2, 125.1, 122.7, 122.6, 121.8, 120.6, 120.2, 120.1, 119.3, 118.5, 118.4, 118.3, 118.1, 116.8, 115.8, 114.7, 114.6, 103.6, 100.8, 100.5, 100.0, 98.3, 97.8, 77.4, 77.2, 76.9, 75.5, 75.2, 74.9, 74.3, 66.9, 66.2, 55.3, 54.7,

48.6, 47.2, 28.3, 28.3, 28.2, 28.0, 19.4, 19.4, 19.4, 19.3, 19.1. HRMS (ESI+) m/z calcd for $C_{83}H_{82}N_8NaO_{13}$ $[M+Na]^+$ 1421.5894, found 1421.5854.

Synthesis of Compound **III-59**: To a solution of **III-58** (170 mg, 0.12 mmol) in dry dichloromethane (1 mL), DBU (19.2 mg, 3.9 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **III-59** as a yellow solid (155 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.07 (s, 1 H), 11.87 (s, 1 H), 9.06 (d, *J* = 7.4 Hz, 1 H), 8.94 (d, *J* = 7.2 Hz, 1 H), 8.06 (d, *J* = 8.3, 0.9 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 7.83 (s, 1 H), 7.71 (s, 1 H), 7.67 (t, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 7.9 Hz, 1 H), 7.16 (d, *J* = 8.3 Hz, 1 H), 7.11 (d, *J* = 7.9 Hz, 1 H), 6.98 (m, 2 H), 6.83 (s, 1 H), 6.74 (s, 1 H), 6.70 (d, *J* = 7.1 Hz, 1 H), 6.44 (d, *J* = 7.1 Hz, 1 H), 6.15 (dd, *J* = 8.3, 2.2 Hz, 1 H), 5.95 (d, *J* = 2.1 Hz, 1 H), 5.73 (m, 1 H), 5.37 (d, *J* = 14.6 Hz, 1 H), 5.23 (d, *J* = 15.8 Hz, 1 H), 4.95 (d, *J* = 9.6 Hz, 1 H), 4.54 (m, 2 H), 4.14 (d, *J* = 6.4 Hz, 2 H), 4.08 (d, *J* = 6.6 Hz, 2 H), 3.68 (m, 1 H), 3.67 (s, 3 H), 3.59 (br, 2 H), 3.49 (dd, *J* = 8.8, 6.6 Hz, 1 H), 3.35 (t, *J* = 7.2 Hz, 1 H), 3.05 (s, 3 H), 2.31 (m, 2 H), 2.15 (m, 1 H), 2.02 (m. 1 H), 1.15 (m, 12 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 1.09 (d, *J* = 6.7 Hz, 1 H). 0.98 (d, *J* = 6.7 Hz, 3 H), 0.95 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 164.7, 163.9, 163.8, 163.4, 163.2, 162.0, 161.3, 159.7, 158.1, 152.0, 151.1, 151.0, 146.2, 143.8, 143.8, 142.9, 139.5, 139.2, 136.2, 135.3, 135.1, 131.6, 127.9, 127.6, 127.4, 126.7, 126.1, 122.8, 122.6, 121.4, 121.1, 119.6, 118.8, 118.6, 118.6, 118.0, 116.7, 115.7, 109.8, 109.4, 103.6, 100.7, 100.4, 99.9, 98.3, 97.6, 75.4, 75.3, 74.6, 74.3, 66.2, 55.2, 54.4, 48.2, 28.3, 28.3, 28.3, 28.1, 19.4, 19.4, 19.2. HRMS (ESI+) m/z calcd for $C_{68}H_{73}N_8O_{11}$ $[M+H]^+$ 1177.5393, found 1177.5368.

Synthesis of Compound **III-60**: The mixture of **III-42** (232 mg, 0.20 mmol) and LiI (140 mg, 4.9 eq.) in degassed ethyl acetate (3 mL) was heated to 80°C overnight. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with 5% citric acid aq. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3 / 7) to give **III-60** as a yellow solid (291 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.38 (s, 1 H), 9.55 (s, 1 H), 8.72 (s, 1 H), 8.61 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.06 (d, *J* = 7.4 Hz, 1 H), 7.78 (s, 1 H), 7.74-7.67 (m, 6 H), 7.61 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.54 (d, *J* = 8.5 Hz, 1 H), 7.49 (d, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.22 (s, 1 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.07 (s, 1 H), 6.99 (t, *J* = 6.9 Hz, 1 H), 6.87 (t, *J* = 7.4 Hz, 1 H), 6.28 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.24 (dd, *J* = 8.3, 7.6 Hz, 1 H), 5.89 (d, *J* = 2.3 Hz, 1 H), 5.80 (d, *J* = 13.9 Hz, 1 H), 4.82 (d, *J* = 13.9 Hz, 1 H), 4.76 (m, 2 H), 4.53 (t, *J* = 7.7 Hz, 1 H), 4.19 (t, *J* = 6.0 Hz, 2 H), 3.88 (dd, *J* = 8.9, 6.7 Hz, 1 H), 3.79 (dd, *J* = 8.8, 6.4 Hz, 1 H), 3.76 (dd, *J* = 6.7, 2.9 Hz, 2 H), 3.64 (s, 3 H), 2.95 (s, 3 H), 2.39 (m, 1 H), 2.12 (m, 2 H), 1.23 (d, *J* = 6.7 Hz, 3 H), 1.22 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 6.7 Hz, 3 H), 1.04 (d, *J* = 6.7 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 164.2, 163.9, 163.5, 162.4, 162.3, 160.4, 158.6, 153.7, 153.7, 150.5, 145.6, 144.5, 143.7, 142.8, 141.5, 141.4, 141.3, 137.4, 137.4, 134.7, 133.9, 132.8, 129.3, 128.2, 127.5, 127.5, 127.0, 126.9, 126.8, 126.8, 125.5, 125.4, 122.4, 122.4, 120.8, 120.4, 119.9, 119.9, 117.2, 116.7, 116.0, 115.6, 103.8, 101.4, 99.2, 98.2, 98.1, 75.6, 75.4, 75.2, 68.2, 55.4, 54.8, 48.7, 47.0, 28.4, 28.1, 28.0, 19.4, 19.3, 19.2, 19.2. HRMS (ESI+) m/z calcd for $C_{66}H_{65}N_6O_{11}$ $[M+H]^+$

1117.4706, found 1117.4679.

Synthesis of Compound **III-61**: A solution of acid **III-60** (76.6 mg, 0.069 mmol) in dry chloroform (1 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (15 μL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-59** (72.6 mg, 0.9 eq.) and dry DIPEA (22 μL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-61** as a yellow solid (90.9 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major/Minor 1/ Minor 2 = 10/ 5/ 1) Major δ 11.87 (s, 1 H), 11.40 (s, 1 H), 11.20 (s, 1 H), 10.98 (s, 1 H), 9.54 (s, 1 H), 9.18 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.81 (d, *J* = 7.6 Hz, 1 H), 8.68 (dd, *J* = 7.8, 1.2 Hz, 1 H), 8.65 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.52 (dd, *J* = 7.2, 1.2 Hz, 1 H), 8.09 (m, 2 H), 7.97 - 7.54 (m, 23 H), 7.51 - 7.27 (m, 14 H), 7.16 (s, 1 H), 7.16 (br, 1 H), 7.10 (m, 2 H), 7.05 (s, 1 H), 7.04 - 6.99 (m, 4 H), 6.78 (s, 1 H), 6.69 (t, *J* = 7.4 Hz, 1 H), 6.63 (s, 1 H), 6.57 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.06 (d, *J* = 1.2 Hz, 1 H), 6.02 (br, 1 H), 5.94 (m, 1 H), 5.52 (m, 2 H), 5.27 (m, 2 H), 4.99 (m, 3 H), 4.90 (d, *J* = 7.8 Hz, 1 H), 4.29-4.06 (m, 18 H), 3.95 (m, 1 H), 3.82-3.68 (m, 13 H), 3.21 (m, 2 H), 3.43 (s, 3 H), 2,90 (m, 1 H), 2.70 (br, 1 H), 2.65 (m, 1 H), 2.42 -2.04 (m, 6 H), 1.66 (m, 1 H), 1.22 -1.17 (m, 28 H), 1.16-1.12 (m, 22 H), 0.98 (d, *J* = 6.7 Hz, 6 H), 0.76 (d, *J* = 6.7 Hz, 3 H), 0.72 (d, *J* = 6.7 Hz, 1 H), 0.63 (d, *J* = 6.7 Hz, 3 H), 0.52 (d, *J* = 6.7 Hz, 3 H). Minor 1 δ 11.50 (s, 1 H), 11.36 (s. 1 H), 11.06 (s, 1 H), 10.80 (s, 1 H), 9.31 (s, 1 H), 9.08 (s, 1 H), 9.01 (d, *J* = 7.4 Hz, 1 H), 8.55 (m, 2 H), 8.45 (br, 1 H), 8.16 (d, *J* = 7.4 Hz, 1 H), 8.12 (br, 1 H), 6.71 (s, 1 H), 6.49 (d, *J* = 6.4 Hz, 1 H), 6.28 - 6.11 (m, 8 H), 5.13 (m, 3 H), 4.82 (d, *J* = 7.4 Hz, 1 H), 4.76 (m, 2 H), 4.67 (m, 2 H), 4.54 (m, 2 H), 3.16 (s, 3 H). Minor 2 δ 11.81 (s, 1 H), 11.48 (s, 1 H), 11.22 (s, 1 H), 10.74 (s, 1 H), 9.16 (d, *J* = 8.0 Hz, 1 H), 8.73 (m, 2 H), 8.35 (d, *J* = 6.4 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.04 (d, *J* = 8.4 Hz, 2 H), 6.97-6.89 (m, 16 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.7, 168.1, 164.9, 164.0, 163.8, 163.7, 163.6, 163.5, 163.2, 162.8, 162.5, 162.3, 162.2, 161.4, 160.7, 159.6, 159.3, 157.8, 157.5, 156.2, 154.9, 153.5, 152.7, 151.4. 150.6, 150.2, 146.2, 144.8, 144.6, 143.7, 143.2, 141.2, 141.0, 140.8, 140.1, 139.6, 139.3, 137.4, 136.9, 135.1, 134.9, 134.8, 134.3, 134.2, 133.8, 133.3, 132.7, 131.5, 131.4, 127.9, 127.7, 127.5, 127.3, 127.2, 127.0, 126.8, 126.6, 126.6, 126.4, 126.2, 126.0, 125.7, 125.6, 125.4, 125.3, 124.9, 122.9, 122.7, 122.4, 122.3, 122.2, 122.1, 121.4, 121.1, 120.9, 120.7, 120.6, 120.0, 119.9, 119.5, 119.4, 119.4, 119.2, 119.1, 118.4, 118.2, 117.3, 117.0, 116.9, 116.8, 116.5, 116.4, 116.2, 116.1, 116.1, 115.8, 115.6, 115.0, 105.0, 104.1, 102.5, 102.0, 101.7, 100.9,100.3, 100.2, 100.1, 99.3, 99.1, 98.5, 98.2, 98.0, 97.0, 75.6, 75.4, 75.4, 74.8, 74.7, 74.2, 73.8, 67.6, 66.9, 66.1, 66.0, 55.6, 55.4, 55.0, 55.0, 54.7, 54.1, 53.6, 53.2, 47.5, 46.5, 45.8, 45.0, 29.8, 28.4, 28.4, 28.3, 28.2, 28.2, 28.2, 28.1, 27.7, 27.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 19.2.HRMS (ESI+) m/z calcd for $C_{134}H_{134}N_{14}NaO_{21}$ $[M+Na]^+$ 2297.9740, found 2297.9738.

Synthesis of Compound **III-62**: To a solution of **III-61** (125 mg, 0.055 mmol) in dry dichloromethane (1 mL), phenylsilane (16 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (1.3 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **III-62** as a yellow solid (113 mg, 92%).^{1}H NMR (600 MHz, $CDCl_3$) (Major and three

kinds of minor) Major δ 11.59 (s, 1 H), 11.89 (s, 1 H), 11.34 (s, 1 H), 11.00 (s, 1 H), 9.53 (s, 1 H), 9.08 (d, *J* = 7.0 Hz, 1 H), 8.80 (d, *J* = 7.4 Hz, 1 H), 8.73 (d, *J* = 7.8 Hz, 1 H), 8.68 (dd, *J* = 7.4, 1.2 Hz, 1 H), 8.52 (dd, *J* = 7.2, 1.2 Hz, 1 H), 8.10 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.08 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.03 (s, 1 H), 7.94 (m, 2 H), 7.82 - 7.32 (m, 36 H), 7.14 (m, 6 H), 7.02 (m, 5 H), 6.78 (s, 1 H), 6.64 (s, 1 H), 6.51 (dd, *J* = 6.8, 1.2 Hz, 1 H), 6.29 - 6.11 (m, 5 H), 6.03 (d, *J* = 1.2 Hz, 1 H), 5.93 (dd, *J* = 6.8, 8.0 Hz, 1 H), 5.40 (d, *J* = 14.4 Hz, 1 H), 5.23 (s, 1 H), 5.06 (d, *J* = 13.6 Hz, 1 H), 4.93 (d, *J* = 13.6 Hz, 1 H), 4.83 (m, 2 H), 4.33 (m, 1 H), 4.24 - 3.95 (m, 18 H), 3.89 - 3.67 (m, 12 H), 3.84 (s, 3 H), 3.73 (s, 3 H), 3.40 (s, 3 H), 2.46 - 1.64 (m, 7 H), 1.26 - 1.10 (m, 54 H), 1.03 (m, 5 H), 0.99 (d, *J* = 6.7 Hz, 9 H), 0.90 (m, 7 H), 0.77 (m, 10 H), 0.65 (d, *J* = 6.7 Jz, 5 H), 0.54 (d, *J* = 6.7 Hz, 3 H). Minor δ 11.79 (s, 1 H), 11.55 (s, 1 H), 11.34 (s, 2 H), 11.26 (m, 3 H), 11.17 (s, 1 H), 11.03 (s, 1 H), 10.90 (s, 1 H), 10.80 (s, 1 H), 10.62 (s, 1 H), 10.53 (s, 1 H), 9.33 (s, 1 H), 9.27 (d, *J* = 6.8 Hz, 1 H), 9.15 (br, 1 H), 9.00 (d, *J* = 6.8 Hz, 1 H), 8.90 (d, *J* = 6.6 Hz, 1 H), 8.64 (m, 2 H), 8.53 (t, *J* = 6.6 Hz, 1 H), 8.44 (br, 1 H), 8.41 (d, *J* = 6.4 Hz, 1 H), 8.18 (d, *J* = 7.0 Hz, 1 H), 5.74 (d, *J* = 13.1 Hz, 1 H), 5.66 (m, 2 H), 5.59 (d, *J* = 13.1 Hz, 1 H), 5.22 (d, *J* = 1.2 Hz, 1 H), 5.16 (br, 1 H), 3.60 (s, 3 H), 3.45 (s, 3 H), 3.29 (s, 3 H), 3.25 (s, 3 H), 3.19 (m, 1 H), 3.15 (s, 1 H), 2.92 (m, 1 H), 2.67 (m, 1 H), 0.35 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.6, 168.4, 164.0, 163.9, 163.8, 163.7, 163.6, 163.5, 163.4, 163.4, 163.2, 163.2, 163.1, 162.8, 162.6, 162.5, 162.2, 161.4, 160.9, 159.5, 159.4, 157.7, 157.2, 156.0, 154.8, 154.4, 153.4, 151.6, 151.5, 150.5, 150.1, 145.3, 144.8, 144.5, 144.3, 143.5, 143.1, 141.3, 141.1, 140.9, 140.7, 140.2, 139.7, 139.0, 137.9, 137.3, 136.9, 134.9, 134.7, 134.6, 134.3, 134.1, 133.7, 133.3, 133.0, 132.5, 128.1, 127.9, 127.5, 127.5, 127.3, 127.2, 127.0, 126.8, 126.6, 126.6, 126.5, 126.2, 126.0, 125.6, 125.6, 125.4, 125.2, 124.8, 122.9, 122.6, 122.3, 122.1, 122.0, 121.9, 121.2, 120.7, 120.7, 120.0, 119.8, 119.6, 119.5, 119.4, 119.3, 119.2, 118.2, 117.4, 116.9, 116.6, 116.4, 116.4, 116.2, 116.2, 116.0, 115.6, 104.9, 102.5, 101.6, 100.8, 99.8, 99.3, 99.2, 98.5, 98.2, 97.9, 97.4, 97.1, 75.6, 75.5, 75.4, 75.4, 74.3, 74.8, 74.6, 74.3, 73.7, 66.7, 55.5, 55.5, 55.4, 55.2, 55.2, 55.0, 55.0, 54.8, 54.8, 54.7, 54.5, 54.1, 53.5, 53.3, 53.2, 47.7, 46.5, 45.8, 44.8, 28.4, 28.3, 28.2, 28.0, 27.6, 27.5, 19.5, 19.4, 19.4, 19.4, 19.4, 19.3, 19.3, 19.3, 19.3, 19.2, 19.2, 19.1, 19.1, 18.9, 18.7. HRMS (ESI+) m/z calcd for $C_{131}H_{131}N_{14}O_{21}$ $[M+H]^+$ 2235.9608, found 2235.9597.

Synthesis of Compound **III-63**: To a solution of **III-35** (223 mg, 0.17 mmol) in dry dichloromethane (2 mL), phenylsilane (47 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (6.1 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **III-63** as a yellow solid (67.4 mg, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 6.5 Hz, 1 H), 8.19 (br, 1 H), 7.96 (d, *J* = 7.5 Hz, 1 H), 7.80-7.73 (m, 4 H), 7.68-7.53 (m, 8 H), 7.47-7.30 (m, 8 H), 7.19 (m, 1 H), 7.09 (d, *J* = 7.4 Hz, 1 H), 7.08 (s, 1 H), 6.96 (s, 1 H), 6.79 (br, 1 H), 6.48 (d, *J* = 6.8 Hz, 1 H), 6.43 (m, 1 H), 6.37 (s, 1 H), 6.33 (m, 1 H), 6.18 (s, 1 H), 6.15 (s, 1 H), 5.57 (d, *J* = 15.6 Hz, 2 H), 5.42 (d, *J* = 13.6 Hz, 1 H), 5.14 (d, *J* = 13.6 Hz, 1 H), 4.60 (m, 1 H), 4.44 (br, 1 H), 4.31 (m, 1 H), 3.94 (m, 2 H), 3.85 (m, 2 H), 3.74 (m, 8 H), 3.64 (m, 1 H), 3.41 (s, 3 H), 3.36 (s, 3 H), 2.21-2.02 (m, 3 H), 1.10 (d, *J* = 6.6 Hz, 6 H), 1.03 (m, 6 H), 0.96 (m, 6 H). HRMS (ESI+) m/z calcd for $C_{75}H_{75}N_6O_{13}$ $[M+H]^+$ 1267.5387, found 1267.5360.

Synthesis of Compound **III-64**: A solution of acid **III-63** (191 mg, 0.15 mmol) in dry chloroform (1.5 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (33 μL, 3 eq.) was added. The solution was stirred at rt for 1 h.

The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-33** (41.2 mg, 0.9 eq.) and dry DIPEA (0.12 mL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-64** as a yellow solid (107 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.67 (s, 1 H), 8.95 (d, *J* = 8.0 Hz, 1 H), 8.28 (s, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 7.95 (d, *J* = 7.5 Hz, 1 H), 7.93 (d, *J* = 7.8 Hz, 1 H), 7.75 (d, *J* = 8.2 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.61 (m, 3 H), 7.55 (m, 2 H), 7.52 (s, 1 H), 7.46 (s, 1 H), 7.36 (m, 2 H), 7.19 (m, 2 H), 7.08 (d, 1 H), 7.01 (s, 3 H), 6.98 (d, *J* = 7.0 Hz, 1 H), 6.68 (br, 1 H), 6.54 (dd, *J* = 2.3, 7.8 Hz, 1 H), 6.40 (dd, *J* = 2.2, 7.8 Hz, 1 H), 6.35 (dd, *J* = 2.3, 8.0 Hz, 2 H), 5.92 (d, *J* = 15.6 Hz, 2 H), 5.60 (m, 3 H), 4.92 (d, *J* = 15.6 Hz, 2 H), 4.81 (m, 1 H), 4.76 (m, 2 H), 4.59 (m, 2 H), 4.43 (m, 2 H), 4.29 (m, 1 H), 4.05 (d, *J* = 6.4 Hz, 2 H), 3.95 (m, 2 H), 3.73 (s, 3 H), 3.69 (s, 3 H), 3.63 (s, 3 H), 3.32 (s, 3 H), 2.32 (m, 1 H), 2.17 (m, 1 H), 2.09 (m, 1 H), 1.73 (m, 1 H), 1.16 (d, *J* = 6.6 Hz, 6 H), 1.05 (m, 6 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.67 (d, *J* = 6.6 Hz, 3 H), 0.63 (d, *J* = 6.6 Hz, 3 H).HRMS (ESI+) m/z calcd for $C_{92}H_{92}N_8NaO_{15}$ $[M+Na]^+$ 1571.6574, found 1571.6547.

Synthesis of Compound **III-65**: To a solution of **III-64** (108 mg, 0.07 mmol) in dry dichloromethane (1 mL), DBU (13.7 mg, 1.3 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **III-65** as a yellow solid (78 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major : Minor = 10 : 4.5)(Major) δ 11.88 (s, 1 H), 9.00 (dd, *J* = 2.3, 8.2 Hz, 1 H), 8.05 (d, *J* = 2.3, 8.0 Hz, 1 H), 7.78 (dd, *J* = 2.3, 8.2 Hz, 1 H), 7.73 (d, *J* = 8.5 Hz, 1 H), 7.69 (m, 2 H), 7.52 (s, 1 H), 7.40 (m, 1 H), 7.35 (d, *J* = 7.8 Hz, 1 H), 7.28 (m, 2 H), 7.14 (m, 3 H), 7.03 (s, 1 H), 6.92 (s, 1 H), 6.68 (m, 1 H), 6.56 (dd, *J* = 2.0, 7.0 Hz, 1 H), 6.4 (m, 2 H), 6.33 (m, 3 H), 6.15 (d, *J* = 2.3 Hz, 1 H), 6.03 (m, 1 H), 5.53 (d, *J* = 13.6 Hz, 1 H), 5.27 (s, 1 H), 5.11 (dd, *J* = 1.9, 8.5 Hz, 1 H), 5.00 (m, 1 H), 4.91 (m, 1 H), 4.89 (m, 1 H), 4.75 (d, *J* = 13.4 Hz, 1 H), 4.09 (m, 3 H), 3.79 (m, 2 H), 3.75 (s, 3 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 3.16 (s, 3 H), 2.73 (m, 1 H), 2.50 (m, 1 H), 2.33 (m, 1 H), 2.15 (m, 1 H), 1.84 (m, 1 H), 1.60 (m, 1 H), 1.18 (m, 6 H), 1.08 (d, *J* = 6.6 Hz, 3 H), 1.05 (d, *J* = 6.6 Hz, 3 H), 0.77 (m, 12 H). (Minor) δ 11.85 (d, 1 H), 9.00 (dd, *J* = 2.3, 8.2 Hz, 1 H), 8.03 (dd, *J* = 2.3, 8.5 Hz, 1 H), 7.98 (dd, *J* = 2.2, 7.8 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.86 (dd, *J* = 2.1, 8.2 Hz, 1 H), 7.65 (t, *J* = 8.5 Hz, 1 H), 7.60 (dd, *J* = 2.2, 7.8 Hz, 1 H), 7.53 (s, 1 H), 7.50 (d, *J* = 8.2 Hz, 1 H), 7.48 (s, 1 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 7.07 (s, 1 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 6.86 (t, *J* = 7.8 Hz, 1 H), 6.75 (dd, *J* = 1.9, 6.7 Hz, 1 H), 6.50 (dd, *J* = 1.9, 6.9 Hz, 1 H), 6.36 (dd, *J* = 2.2, 8.2 Hz, 1 H), 6.30 (dd, *J* = 2.3, 7.6 Hz, 1 H), 6.17 (d, *J* = 2.2 Hz, 1 H), 6.11 (s, 1 H), 6.08 (s, 1 H), 5.81 (m, 1 H), 5.37 (d, *J* = 13.6 Hz, 1 H), 5.30 (m, 1 H), 5.03 (m, 1 H), 4.94 (m, 1 H), 4.70 (m, 1 H), 3.95 (m, 1 H), 3.88 (m, 1 H), 3,64 (s, 3 H), 3.59 (s, 3 H), 3.32 (m, 2 H), 3.23 (m, 2 H), 3.01 (s, 3 H), 1.01 (m, 6 H), 0.96 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 166.3, 165.9, 165.7, 164.3, 163.7, 162.7, 162.4, 161.6, 161.4, 161.0, 161.0, 160.1, 160.0, 159.9, 158.8, 158.7, 158.2, 156.7, 154.9, 150.4, 149.8, 149.5, 144.4, 144.1, 143.5, 143.3, 142.5, 142.4, 141.1, 140.1, 135.9, 135.5, 132.6, 132.2, 131.8, 131.6, 130.1, 129.8, 129.0, 128.6, 127.8, 127.6, 127.5, 127.2, 126.7, 126.1, 125.3, 122.8, 122.3, 121.6, 121.3, 120.3, 120.2, 119.9, 119.5, 119.2, 119.1, 118.7, 118.6, 118.6, 118.3, 118.1, 116.5, 109.9, 109.3, 108.7, 103.1, 103.0, 103.9, 101.9, 101.5, 101.2, 100.9, 100.5, 98.3, 98.0, 75.3, 73.7, 74.0, 74.0, 68.8, 55.4, 55.3, 55.3, 55.2, 55.1, 54.8, 54.6, 50.7, 47.2, 28.3, 28.3, 28.3, 28.1, 27.8, 27.7, 19.4, 19.4, 19.3, 19.3, 19.2, 19.1, 19.0,

18.9, 18.7. HRMS (ESI+) m/z calcd for $C_{77}H_{83}N_8O_{13}$ $[M+H]^+$ 1327.6074, found 1327.6040.

Synthesis of Compound **III-66**: A solution of acid **III-51** (69.3 mg, 0.062 mmol) in dry chloroform (0.8 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (14 μL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **III-65** (75.3 mg, 0.9 eq.) and dry DIPEA (50 μL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **III-66** as a yellow solid (118 mg, 86%).^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.1, 169.4, 165.9, 164.1, 164.0, 163.5, 163.4, 163.0, 163.0, 162.7, 161.5, 161.1, 160.4, 160.0, 159.9, 159.8, 158.6, 158.3, 158.2, 156.1, 153.9, 153.7, 153.2, 153.2, 150.7, 149.6, 144.0, 143.8, 143.6, 143.4, 142.7, 141.7, 141.5, 141.4, 141.3, 140.2, 140.1, 139.1, 137.4, 136.3, 135.2, 134.9, 133.7, 131.7, 131.4, 131.4, 130.9, 129.7, 128.8, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 126.3, 125.8, 125.1, 125.0, 123.6, 122.9, 122.5, 122.4, 122.3, 130.6, 120.5, 120.3, 120.2, 120.1, 119.6, 119.1, 118.9, 118.5, 118.2, 118.1, 117.9, 117.8, 117.7, 116.0, 115.9, 114.6, 114.5, 104.0, 103.8, 103.4, 101.7, 101.6, 100.9, 100.3, 98.6, 98.5, 98.0, 97.9, 97.3, 75.5, 75.2, 75.2, 75.1, 74.7, 74.3, 74.0, 66.7, 66.6, 66.1, 55.5, 55.4, 55.3, 55.2, 55.0, 54.8, 54.5, 54.2, 54.1, 48.7, 47.9, 47.7, 47.2, 28.3, 28.2, 28.1, 28.0, 27.6, 19.5, 19.4, 19.4, 19.4, 19.3, 19.2, 19.1, 19.1, 19.0, 18.9, 18.9. HRMS (ESI+) m/z calcd for $C_{143}H_{144}N_{14}NaO_{23}$ $[M+Na]^+$ 2448.0421, found 2448.0421.

Synthesis of Compound **III-67**: To a solution of **III-66** (102 mg, 0.042 mmol) in dry dichloromethane (1 mL), phenylsilane (12 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (1.5 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **III-67** as a yellow solid (69 mg, 69%). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 170.8, 169.4, 167.1, 164.1, 164.0, 163.4, 163.3, 163.3, 162.9, 161.5, 161.2, 160.9, 160.6, 160.0, 159.8, 158.8, 158.5, 158.1, 154.3, 153.8, 153.7, 153.2, 150.7, 150.1, 149.5, 144.0, 143.8, 143.4, 143.3, 142.4, 141.7, 141.5, 141.3, 140.6, 140.1, 139.3, 139.1, 137.2, 136.3, 135.2, 134.5, 134.3, 133.6, 131.6, 131.2, 129.9, 128.5, 127.9, 127.8, 127.6, 127.2, 126.4, 125.8, 125.1, 125.0, 124.3, 123.1, 122.9, 122.3, 122.2, 120.8, 120.6, 120.5, 120.3, 120.2, 120.1, 119.8, 119.4, 118.1, 117.9, 117.6, 117.4, 117.3, 116.8, 116.7, 116.1, 114.6, 114.5, 104.0, 103.3, 101.7, 101.0, 100.9, 100.3, 100.1, 98.7, 98.6, 98.4, 97.9, 97.3, 75.5, 75.4, 75.2, 75.2, 74.7, 74.0, 66.7, 55.4, 55.4, 55.2, 54.5, 54.0, 49.7, 48.2, 47.6, 47.2, 28.3, 28.3, 28.2, 28.2, 28.1, 17.9, 17.8, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 19.2, 19.2, 19.1, 19.0, 18.9.

Synthesis of compound **C4-DMB: 3** (30 mg, 0.026 mmol) and triphenylphosphine (28 mg, 4 eq.) were mixed in dry chloroform (1.5 mL) and then trichloroacetonitrile (11 μL, 4 eq.) and dry DIPEA (28 μL, 6 eq.) were added. The mixture was stirred at rt for 15 h. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **C4-DMB** as a white solid (11 mg, 36%).^{1}H NMR (300 MHz, $CDCl_3$) δ 11.26 (s, 1 H), 11.00 (s, 1 H), 9.49 (s, 1

H), 8.75 (d, *J* = 6.8 Hz, 1 H), 8.57 (d, *J* = 6.5 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H), 8.00 (m, 3 H), 7.86 (s, 1 H), 7.83 (d, *J* = 9.0 Hz, 1 H), 7.78 (s, 1 H), 7.70 (s, 1 H), 7.64 (t, *J* = 8.0 Hz, 2 H), 7.50 (s, 1 H), 7.36 (d, *J* = 7.3 Hz, 1 H), 7.34 (s, 1 H), 7.21 (m, 2 H), 6.75 (d, *J* = 6.1 Hz, 1 H), 5.82 (d, *J* = 13.6 Hz, 1 H), 5.57 (dd, *J* = 2.2, 8.4 Hz, 1 H), 5.11 (d, *J* = 2.3 Hz, 1 H), 4.15 (d, *J* = 6.5 Hz, 2 H), 5.37 (m, 8 H), 3.46 (s, 3 H), 2.58 (s, 3 H), 2.26 (m, 4 H), 1.16 (m, 12 H), 1.02 (m, 12 H).

Synthesis of compound **C5-2DMB**: **5** (462 mg, 0.30 mmol) and triphenylphosphine (317 mg, 4 eq.) were mixed in dry chloroform (20 mL) and then trichloroacetonitrile (0.12 mL, 4 eq.) and dry DIPEA (0.30 mL, 6 eq.) were added. The mixture was stirred at rt for 4.5 h. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) and GPC to give **C5-2DMB** as a white solid (208 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.73 (s, 1 H), 11.67 (br, 1 H), 9.71 (s, 1 H), 9.10 (d, *J* = 6.9 Hz, 1 H), 8.68 (br, 1 H), 8.35 (br, 1 H), 8.08 (dd, *J* = 8.3, 1.3 Hz, 2 H), 7.85-7.73 (m, 4 H), 7.60 (m, 3 H), 7.53 (m, 2 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.29 (t, *J* = 7.9 Hz, 1 H), 6.96-6.82 (m, 5 H), 6.71 (s, 1 H), 6.37 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.32 (d, *J* = 2.3 Hz, 1 H), 6.22 (s, 1 H), 5.94 (d, *J* = 2.3 Hz, 1 H), 5.59 (d, *J* = 14.3 Hz, 1 H), 5.41 (br, 1 H), 4.14 (dd, *J* = 9.1, 6.5 Hz, 1 H), 4.05 (dd, *J* = 9.1, 6.5 Hz, 1 H), 3.98-3.84 (m, 8 H), 3.79 (s, 3 H), 3.57 (dd, *J* = 9.1, 6.8 Hz, 1 H), 3.47 (d, *J* = 14.6 Hz, 1 H), 3.27 (m, 7 H), 2.99 (d, *J* = 5.6 Hz, 2 H), 2.31 (m, 2 H), 2.17 (m, 1 H), 1.95 (m, 1 H), 1.71 (m, 1 H), 1.25 (d, *J* = 6.6 Hz, 3 H), 1.20 (d, *J* = 6.7 Hz, 3 H), 1.13 (d, *J* = 6.7 Hz, 3 H), 1.13 (d, *J* = 6.7 Hz, 3 H), 1.04 (d, *J* = 6.7 Hz, 3 H), 1.03 (d, *J* = 6.7 Hz, 3 H), 0.93 (d, *J* = 6.7 Hz, 3 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 0.79 (d, *J* = 6.7 Hz, 3 H), 0.71 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 170.8, 168.4, 167.1, 163.6, 163.1, 162.7, 161.9, 160.5, 160.4, 159.9, 159.4, 159.0, 155.8, 155.8, 150.4, 142.7, 141.5, 140.3, 139.4, 134.9, 134.8, 134.5, 131.5, 130.9, 128.2, 127.8, 126.9, 126.5, 125.8, 125.5, 124.5, 122.9, 122.7, 122.4, 121.6, 121.1, 120.0, 118.9, 118.7, 118.6, 117.3, 104.0, 103.9, 102.3, 101.7, 100.5, 98.8, 98.4, 98.4, 97.5, 75.2, 75.1, 74.4, 73.7, 55.4, 54.9, 54.8, 48.4, 47.5, 28.4, 28.2, 28.1, 28.0, 19.5, 19.5, 19.5, 19.5, 19.4, 19.3, 19.3, 19.3, 19.3, 19.2, 19.2, 19.2, 19.1, 19.1. HRMS (ESI+) m/z calcd for $C_{88}H_{91}N_{10}O_{14}$ $[M+H]^+$ 1511.6711, found 1511.6720.

Synthesis of compound **C5**: Trifluoroacetic acid (5 mL) was added to **C5-2DMB** (80.0 mg, 0.05 mmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC to give **C5** as a yellow solid (62.8 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$, 263 K) δ 11.91 (s, 1 H), 11.87 (s, 1 H), 10.85 (s, 1 H), 9.43 (d, *J* = 7.6 Hz, 1 H), 9.33 (d, *J* = 7.4 Hz, 1 H), 8.95 (s, 1 H), 8.82 (s, 1 H), 8.44 (d, *J* = 7.2 Hz, 1 H), 8.20 (d, *J* = 8.1 Hz, 1 H), 8.14 (d, *J* = 7.9 Hz, 1 H), 7.93 (d, *J* = 8.6 Hz, 1 H), 7.93 (s, 1 H), 7.73 (m, 2 H), 7.64 (m, 2 H), 7.60 (t, *J* = 7.8 Hz, 1 H), 7.45 (s, 1 H), 7.43 (d, *J* = 8.7 Hz, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 6.94 (s, 1 H), 6.80 (s, 1 H), 6.77 (s, 1 H), 6.72 (t, *J* = 7.8 Hz, 1 H), 6.38 (d, *J* = 7.4 Hz, 1 H), 4.15 (m, 3 H), 3.99 (m, 2 H), 3.94 (t, *J* = 6.2 Hz, 1 H), 3.74 (t, *J* = 6.4 Hz, 1 H), 3.60 (t, *J* = 8.0 Hz, 1 H), 3.23 (t, *J* = 7.8 Hz, 1 H), 2.34 (m, 3 H), 2.15 (t, *J* = 6.2 Hz, 1 H), 2.07 (m, 1 H), 1.69 (m, 1 H), 1.25 (d, *J* = 6.5 Hz, 3 H), 1.21 (d, *J* = 7.0 Hz, 3 H), 1.16 (m, 12 H), 1.06 (d, *J* = 6.4 Hz, 3 H), 1.01 (d, *J* = 6.4 Hz, 3 H), 0.81 (d, *J* = 6.4 Hz, 3 H), 0.75 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, 263 K) δ 168.0, 165.5, 164.0, 163.4, 163.2, 162.8, 162.2, 162.1, 161.9, 161.6, 152.0, 151.3, 150.2, 149.4, 147.3, 141.6, 139.0, 138.7, 137.8, 137.6, 135.7, 135.6, 134.9, 134.6, 133.9, 129.0, 127.8, 127.7, 127.6, 127.1, 125.1,

123.2, 122.7, 122.5, 121.9, 121.3, 121.1, 118.7, 118.4, 117.1, 116.4, 116.0, 115.7, 101.2, 100.1, 99.2, 97.7, 97.6, 75.4, 75.4, 75.3, 74.7, 74.0, 28.3, 28.2, 28.2, 28.1, 27.9, 19.5, 19.4, 19.3, 19.2, 19.1, 18.8. HRMS (ESI+) m/z calcd for $C_{70}H_{71}N_{10}O_{10}$ $[M+H]^+$ 1211.5349, found 1211.5314.

Synthesis of Compound **C6-*o*-2DMB**: **8** (26 mg, 0.015 mmol) and triphenylphosphine (14.8 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (5.6 μL, 4 eq.) and dry DIPEA (14 μL, 6 eq.) were added. The mixture was stirred at rt for 4.5 h. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) and GPC to give **C6-*o*-2DMB** as a white solid (33.1 mg, 26%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.20 (s, 1 H), 11.86 (s, 1 H), 11.56 (s, 1 H), 9.20 (d, *J* = 6.8 Hz, 1 H), 9.01 (s, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.26 (d, *J* = 7.4 Hz, 1 H), 8.13 (m, 2 H), 8.05 (d, *J* = 8.1 Hz, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 7.97 (m, 2 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.81 (t, *J* = 8.1 Hz, 1 H), 7.65 (m, 6 H), 7.53 (m, 2 H), 7.48 (t, *J* = 7.9 Hz, 2 H), 7.43 (m, 2 H), 7.34 (d, *J* = 6.8 Hz, 1 H), 7.23 (m, 3 H), 7.11 (d, *J* = 8.2 Hz, 1 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 6.83 (s, 1 H), 6.73 (m, 5 H), 6.30 (d, *J* = 7.1 Hz, 1 H), 6.29 (s, 1 H), 6.23 (m, 1 H), 6.15 (d, *J* = 2.3 Hz, 1 H), 6.12 (dd, *J* = 8.4, 2.3 Hz, 1 H), 6.04 (dd, *J* = 8.3, 2.3 Hz, 1 H), 5.97 (d, *J* = 2.3 Hz, 1 H), 5.47 (m, 3 H), 4.36 (m, 2 H), 4.21-4.12 (m, 6 H), 4.07-4.00 (m, 5 H), 3.91 (m, 2 H), 3.82 (m, 2 H), 3.64 (s, 3 H), 3.64 (s, 3 H), 3.39 (s, 3 H), 2.75 (s, 3 H), 2.37-2.25 (m, 3 H), 2.08 (m, 2 H), 1.96 (m, 1 H), 1.17 (m, 18 H), 0.95 (m, 12 H), 0.84 (d, *J* = 6.7 Hz, 3 H), 0.75 (d, *J* = 6.7 Hz, 3 H). minor peaks: (major: minor = 2:1) 11.71 (s, 1 H), 11.64 (s, 1 H), 9.90 (s, 1 H), 9.47 (s, 1 H), 9.37 (d, *J* = 6.8 Hz, 1 H), 8.68 (d, *J* = 7.2 Hz, 1 H), 8.52 (d, *J* = 7.6 Hz, 1 H), 8.32 (d, *J* = 6.9 Hz, 1 H), 8.20 (t, *J* = 7.6 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 1 H), 7.78-7.68 (m, 6 H), 7.20 (t, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.5 Hz, 1 H), 6.89 (s, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 6.52 (s, 1 H), 6.19 (d, *J* = 2.3 Hz, 1 H), 5.82 (d, *J* = 13.8 Hz, 2 H), 5.37 (d, *J* = 17.9 Hz, 2 H), 4.83 (d, *J* = 17.8 Hz, 2 H), 3.70 (m, 4 H), 3.65 (s, 3 H), 3.64 (s, 3 H), 3.41 (s, 3 H), 2.74 (s, 3 H), 2.31 (m, 3 H), 2.15 (m, 1 H), 1.85 (m, 3 H), 1.58 (m, 1 H), 1.17 (m, 18 H), 1.04 (m, 6 H), 1.00 (d, *J* = 6.7 Hz, 3 H), 0.95 (m, 6 H), 0.87 (m, 3 H), 0.82 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 170.2, 169.9, 167.2, 166.5, 165.6, 165.3, 165.1, 164.3, 164.1, 163.9, 163.4, 163.4, 163.3, 163.0, 162.9, 162.8, 162.6, 162.6, 162.1, 162.0, 161.9, 160.9, 160.0, 159.8, 159.3, 158.4, 158.1, 157.5, 155.8, 155.6, 155.3, 154.0, 153.2, 153.0, 152.4, 151.9, 151.5, 151.0, 150.9, 150.4, 145.6, 143.9, 143.1, 143.1, 142.2, 141.9, 141.3, 140.9, 140.4, 140.3, 140.0, 139.9, 139.7, 137.9, 137.1, 136.5, 135.8, 135.7, 135.1, 135.0, 134.7, 134.4, 134.4, 134.1, 133.1, 131.6, 130.7, 130.3, 129.5, 128.0, 127.8, 127.6, 127.3, 127.2, 126.7, 126.6, 126.5, 126.4, 126.0, 126.0, 125.6, 125.5, 125.3, 124.9, 123.7, 123.5, 122.9, 122.7, 122.5, 122.4, 122.4, 122.3, 122.1, 122.0, 122.0, 121.9, 121.8, 121.7, 120.7, 120.5, 120.3, 120.0, 119.4, 118.7, 118.6, 118.5, 118.5, 118.3, 118.2, 118.1, 118.0, 117.7, 117.1, 116.9, 116.3, 115.1, 103.5, 103.0, 102.8, 101.3, 100.5, 100.3, 100.2, 99.0, 98.6, 98.6, 98.5, 98.5, 98.1, 97.6, 97.3, 75.5, 75.4, 75.3, 75.1, 75.1, 74.9, 74.7, 74.7, 74.6, 73.9, 55.3, 55.3, 55.3, 55.2, 55.0, 54.0, 52.8. 52.3, 50.5, 49.8, 48.7, 29.8, 28.4, 28.4, 28.4, 28.3, 28.3, 28.2, 28.1, 28.1, 28.0, 27.9, 19.5, 19.4, 19.4, 19.4, 19.3, 19.3, 19.3, 19.2, 19.2, 19.2, 19.1, 19.1, 18.8. HRMS (ESI+) m/z calcd for $C_{102}H_{105}N_{12}O_{16}$ $[M+H]^+$ 1753.7766, found 1753.7774.

Synthesis of Compound **C6-*p*-2DMB**: **III-9** (30.4 mg, 0.017 mmol) and triphenylphosphine (17.9 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (6.8 μL, 4 eq.) and dry DIPEA (17 μL, 6 eq.) were

added. The mixture was stirred at rt overnight. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC and PLC to give **C6-*p*-2DMB** as a yellow solid (10.7 mg, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.31 (s, 1 H), 10.13 (s, 1 H), 9.02 (br, 1 H), 7.96 (d, *J* = 7.3 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 7.59 (s, 1 H), 7.45 (d, *J* = 8.2 Hz, 1 H), 7.15 (d, *J* = 8.3 Hz, 1 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 6.88 (t, *J* = 7.7 Hz, 1 H), 6.84 (br, 1 H), 6.65 (br, 1 H), 6.34 (s, 1 H), 5.87 (d, *J* = 8.2 Hz, 1 H), 5.86 (s, 1 H), 5.17 (d, *J* = 14.3 Hz, 1 H), 4.81 (d, *J* = 14.3 Hz, 1 H), 4.38 (t, *J* = 8.4 Hz, 1 H), 4.08 (dd, *J* = 8.8, 6.3 Hz, 1 H), 3.77 (m, 2 H), 3.64 (br, 1 H), 3.57 (dd, *J* = 8.9, 6.4 Hz, 1 H), 3.52 (s, 3 H), 2.84 (s, 3 H), 2.36 (m, 1 H), 2.17 (m, 1 H), 2.07 (m, 1 H), 1.26 (d, *J* = 6.7 Hz, 3 H), 1.25 (d, *J* = 6.7 Hz, 3 H), 1.14 (d, *J* = 6.7 Hz, 3 H), 1.11 (d, *J* = 6.7 Hz, 3 H), 1.10 (d, *J* = 6.8 Hz, 3 H), 0.99 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 162.1, 160.8, 159.9, 158.5, 153.7, 151.8, 151.7, 143.5, 141.4, 140.9, 139.0, 136.0, 133.9, 132.4, 128.7, 128.1, 126.9, 125.5, 125.2, 122.6, 122.1, 120.6, 120.0, 118.2, 118.0, 117.9, 116.3, 103.4, 101.4, 100.7, 98.9, 97.5, 74.9, 74.5, 55.2, 54.4, 47.2, 28.6, 28.2, 28.2, 19.7, 19.6, 19.5, 19.4, 19.2. HRMS (ESI+) m/z calcd for $C_{102}H_{105}N_{12}O_{16}$ $[M+H]^+$ 1753.7766, found 1753.7798.

Synthesis of Compound **C6**: Trifluoroacetic acid (0.5 mL) was added to **C6-*p*-2DMB** (11.1 mg, 6.3 μmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC to give **C6** as a yellow solid (6.1 mg, 52%).^{1}H NMR (600 MHz, $CDCl_3$) δ 12.49 (s, 4 H), 9.83 (s, 2 H), 8.60 (d, *J* = 7.5 Hz, 2 H), 8.28 (d, *J* = 7.5 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.59 (t, *J* = 8.0 Hz, 2 H), 7.57 (s, 2 H), 7.44 (t, *J* = 7.9 Hz, 2 H), 7.37 (s, 2 H), 7.27 (t, *J* = 7.7 Hz, 2 H), 7.19 (d, *J* = 7.3 Hz, 2 H), 6.55 (s, 2 H), 4.07 (t, *J* = 8.9 Hz, 2 H), 4.02 (t, *J* = 6.8 Hz, 2 H), 4.01 (t, *J* = 6.6 Hz, 2 H), 3.81 (t, *J* = 5.8 Hz, 2 H), 3.77 (t, *J* = 7.0 Hz, 2 H), 3.62 (t, *J* = 8.1 Hz, 2 H), 2.64 (t, *J* = 6.7 Hz, 2 H), 2.26 (m, 4 H), 1.95 (m, 2 H), 1.21 (d, *J* = 6.7 Hz, 6 H), 1.16 (d, *J* = 6.7 Hz, 6 H), 1.07 (m, 12 H), 0.99 (m, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 165.8, 164.3, 163.3, 162.9, 162.3, 154.5, 152.1, 150.1, 142.4, 141.2, 138.5, 135.1, 134.7, 134.4, 127.6, 127.3, 127.1, 126.9, 126.5, 123.1, 122.6, 121.8, 121.2, 118.9, 116.5, 116.2, 110.9, 99.5, 97.8, 75.5, 74.8, 70.7, 29.8, 28.3, 28.2, 19.6, 19.4, 19.3, 19.2.HRMS (ESI+) m/z calcd for $C_{84}H_{85}N_{12}O_{12}$ $[M+H]^+$ 1453.6404, found 1453.6393.

Synthesis of Compound **C7-2DMB**: **II-11** (30.0 mg, 0.015 mmol) and triphenylphosphine (15.6 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (6.4 μL, 4 eq.) and dry DIPEA (15 μL, 6 eq.) were added. The mixture was stirred at rt overnight. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC and PLC to give **C7-2DMB** as a yellow solid (23.9 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major : Minor = 5 : 3) (Major)δ 11.70 (s, 1 H), 11.27 (s, 1 H), 10.34 (s, 1 H), 10.29 (s, 1 H), 9.44 (d, *J* = 8.2 Hz, 1 H), 9.18 (s, 1 H), 8.30 (dd, *J* = 1.9, 8.2 Hz, 1 H), 8.24 (dd, *J* = 1.0, 7.8 Hz, 1 H), 8.19 (m, 2 H), 8.09 (m, 1 H), 8.00 (dd, *J* = 2.2, 8.4 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 1 H), 7.82-7.63 (m, 10 H), 7.57-7.50 (m, 3 H), 7.42 (m, 4 H), 7.37 (d, *J* = 2.2 Hz, 2 H), 7.21 (m, 2 H), 7.15 (dd, *J* = 2.0, 8.0

Hz, 1 H), 7.11 (dd. *J* = 2.0, 8.0 Hz, 1 H), 7.07 (m, 2 H), 6.98 (dd, *J* = 6.8, 7.8 Hz, 1 H), 6.92 (d, *J* = 7.2 Hz, 1 H), 6.72 (s, 1 H), 6.57 (s, 1 H), 6.48 (s, 1 H), 6.21 (m, 2 H), 6.14 (d, *J* = 2.3 Hz, 1 H), 6.08 (s, 1 H), 6.01 (m, 2 H), 5.98 (d, *J* = 2.0 Hz, 1 H), 5.79 (m, 2 H), 5.70 (d, *J* = 13.6 Hz, 1 H), 5.53 (m, 2 H), 4.38 (m, 1 H), 4.33 (m, 1 H), 4.24-4.06 (m, 10 H), 4.02 (m, 1 H), 3.96 (m, 1 H), 3.90 (m, 1 H), 3.84 (m, 3 H), 3.76 (m, 1 H), 3.59 (s, 3 H), 3.52 (m, 6 H), 3.17 (s, 3 H), 2.48-2.32 (m, 7 H), 1.32 (d, *J* = 6.6 Hz, 3 H), 1.23 (m, 24 H), 1.10 (d, *J* = 6.6 Hz, 3 H), 1.03 (d, *J* = 6.6 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H), 0.80 (d, *J* = 6.6 Hz, 3 H). (Minor) δ 12.22 (s, 1 H), 11.89 (s, 1 H), 11.70 (s, 1 H), 10.86 (s, 1 H), 10.82 (s, 1 H), 9.37 (d, *J* = 8.2 Hz, 1 H), 8.67 (d, *J* = 7.8 Hz, 1 H), 8.63 (d, *J* = 7.8 Hz, 1 H), 8.55 (d, *J* = 7.8 Hz, 1 H), 8.36 (br, 1 H), 8.09 (m, 1 H), 7.33 (d, *J* = 8.4 Hz, 1 H), 6.77 (t, *J* = 7.4 Hz, 1 H), 6.69 (t, *J* = 7.0 Hz, 1 H), 6.37 (d, *J* = 7.8 Hz, 1 H), 6.09 (d, *J* = 7.8 Hz, 1 H), 5.91 (s, 1 H), 5.86 (d, *J* = 2.3 Hz, 1 H), 5.38 (d, *J* = 12.6 Hz, 1 H), 5.24 (d, *J* = 13.0 Hz, 1 H), 4.75 (d, *J* = 12.8 Hz, 1 H), 3.43 (s, 3 H), 3.42 (s, 3 H), 2.82 (s, 3 H), 2.37 (s, 3 H), 1.25 (m, 30 H), 0.89 (m, 6 H), 0.73 (d, *J* = 6.6 Hz, 3 H), 0.70 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 167.7, 167.4, 167.0, 165.3, 164.9, 163.9, 163.5, 163.4, 163.3, 163.0, 162.8, 162.7, 162.6, 162.1, 162.1, 162.0, 161.9, 161.6, 161.2, 161.1, 160.9, 160.8, 160.6, 160.0, 160.0, 159.8, 159.6, 158.9, 158.8, 158.5, 158.3, 157.7, 155.0, 154.3, 152.5, 151.7, 151.0, 150.9, 150.7, 150.6, 150.1, 149.7, 147.3, 145.3, 144.6, 144.3, 144.2, 142.4, 141.5, 141.2, 139.1, 138.5, 138.5, 138.1, 137.9, 137.9, 137.4, 136.8, 136.1, 135.3, 134.6, 134.4, 134.1, 134.0, 133.8, 133.4, 133.3, 133.0, 132.7, 132.3, 131.6, 130.8, 130.7, 130.5, 130.1, 129.7, 129.0, 128.6, 126.7, 126.6, 126.5, 126.4, 126.3, 126.1, 125.9, 125.7, 125.6, 123.4, 123.0, 122.8, 122.7, 122.6, 122.6, 122.5, 122.5, 122.4, 122.4, 122.0, 121.9, 121.0, 120.9, 120.8, 120.7, 120.7, 120.6, 120.0, 119.3, 118.8, 118.7, 118.5, 118.0, 117.9, 117.7, 117.4, 117.0, 116.8, 116.6, 116.3, 116.1, 116.1, 116.0, 115.7, 104.1, 103.8, 103.4, 103.2, 102.7, 102.6, 101.7, 101.4, 100.9, 99.8, 99.8, 99.3, 98.5, 98.0, 98.0, 97.8, 97.8, 97.7, 97.7, 96.9, 96.9, 75.8, 75.6, 75.4, 75.3, 75.2, 75.1, 75.1, 75.0, 74.4, 73.9, 73.8, 73.4, 70.6, 55.2, 55.1, 55.1, 54.8, 54.3, 53.8, 47.8, 47.6, 47.5, 46.8, 29.8, 28.6, 28.4, 28.4, 28.3, 28.3, 28.2, 28.0, 27.6, 27.5, 27.4, 19.8, 19.8, 19.6, 19.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.3, 19.2, 19.1, 19.1, 19.0, 18.9, 18.9, 18.5, 18.5, 19.3, 18.1. HRMS (ESI+) m/z calcd for $C_{116}H_{119}N_{14}O_{18}$ $[M+H]^+$ 1995.8821, found 1995.8845.

Synthesis of Compound **C7-3DMB**: **II-12** (30.0mg, 0.014 mmol) and triphenylphosphine (14.5 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (6 μL, 4 eq.) and dry DIPEA (14 μL, 6 eq.) were added. The mixture was stirred at rt overnight. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC and PLC to give **C7-3DMB** as a yellow solid (1.8 mg, 6%).^{1}H NMR (600 MHz, $CDCl_3$) δ 12.11 (br, 1 H), 11.60 (s, 1 H), 10.95 (s, 1 H), 10.70 (s, 1 H), 9.50 (d, *J* = 7.0 Hz, 1 H), 9.00 (d, *J* = 7.0 Hz, 1 H), 8.22 (d, *J* = 6.9 Hz, 1 H), 8.15 (d, *J* = 7.1 Hz, 1 H), 8.10 (d, 7.3 Hz, 1 H), 7.88 (br, 1 H), 7.80 (d, *J* = 8.3 Hz, 1 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.71 (s, 1 H), 7.69 (t, *J* = 7.9 Hz, 1 H), 7.64 (d, *J* = 7.9 Hz, 1 H), 7.57 (s, 1 H), 7.52 (br, 1 H), 7.46 (s, 1 H), 7.41 (m, 3 H), 7.36 (br, 1 H), 7.31 (br, 1 H), 7.28 (s, 3 H), 7.06 (s, 1 H), 6.90 (m, 3 H), 6.79 (d, *J* = 6.1 Hz, 1 H), 6.62 (d, *J* = 6.2 Hz, 1 H), 6.50 (br, 1 H), 6.41 (br, 1 H), 6.20 (dd, *J* = 2.3, 8.5 Hz, 1 H), 6.14 (d, *J* = 2.3 Hz, 1 H), 6.10 (d, *J* = 13.9 Hz, 1 H), 5.93 (d, *J* = 2.3 Hz, 1 H), 5.73 (dd, *J* = 2.3, 8.5 Hz, 1 H), 5.79 (d, *J* = 13.9 Hz, 1 H), 5.63 (br, 1 H), 5.49 (d, *J* = 2.3 Hz, 1 H), 4.59 (m, 1 H), 4.21-4.09 (m, 5 H), 4.03 (m, 2 H), 3.94 (m, 2 H), 3.87 (m, 3 H), 3.76 (br, 1 H), 3.67 (s, 3 H), 3.48 (s, 3 H), 3.45 (s, 3 H), 3.33 (s, 3 H), 3.11 (s, 3 H), 2.87 (s, 3 H), 2.35 (m, 3 H), 2.11 (m, 4 H), 1.43 (d, *J* = 6.6 Hz, 3 H), 1.39 (d, *J* = 6.6 Hz, 3 H), 1.19-1.16 (m, 9 H), 1.04-1.00 (m,

12 H), 0.44 (d, *J* = 6.6 Hz, 3 H), 0.10 (d, *J* = 6.6 Hz, 3 H).

Synthesis of Compound **C7**: Trifluoroacetic acid (1 mL) was added to **C7-2DMB** (10.0 mg, 5 μmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC to give **C7** as a yellow solid (5.8 mg, 68%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.26 (s, 1 H), 11.64 (s, 1 H), 10.98 (s, 1 H), 10.72 (s, 1 H), 10.51 (s, 1 H), 9.81 (s, 1 H), 9.23 (d, *J* = 7.3 Hz, 1 H), 8.89 (d, *J* = 7.7 Hz, 1 H), 8.69 (s, 1 H), 8.38 (d, *J* = 7.4 Hz, 1 H), 8.13 (d, *J* = 8.3 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 7.94 (m, 3 H), 7.87 (t, *J* = 8.0 Hz, 1 H), 7.84 (s, 1 H), 7.73 (m, 2 H), 7.64 (s, 1 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.58 (m, 3 H), 7.51 (d, *J* = 7.4 Hz, 1 H), 7.42 (s, 1 H), 7.29 (m, 2 H), 7.15 (m, 4 H), 6.72 (s, 1 H), 5.63 (t, *J* = 7.8 Hz, 1 H), 4.88 (s, 1 H), 4.35 (m, 4 H), 4.25 (t, *J* = 7.2 Hz, 1 H), 4.21 (t, *J* = 8.1 Hz, 1 H), 4.13 (t, *J* = 6.7 Hz, 1 H), 4.05 (m, 2 H), 3.94 (t, *J* = 6.8 Hz, 1 H), 3.37 (m, 2 H), 3.14 (t, *J* = 6.9 Hz, 1 H), 2.71 (t, *J* = 7.0 Hz, 1 H), 2.38 (m, 3 H), 2.25 (m, 3 H), 2.05 (m, 1 H), 1.28 (d, *J* = 6.6 Hz, 3 H), 1.24 (d, *J* = 6.6 Hz, 3 H), 1.22 (d, *J* = 6.6 Hz, 6 H), 1.14 (m, 18 H), 1.08 (d, *J* = 6.6 Hz, 3 H), 1.07 (d, *J* = 6.6 Hz, 3 H), 0.34 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 165.2, 164.5, 164.5, 164.3, 164.2, 164.2, 163.6, 163.3, 163.2, 163.0, 162.8, 162.6, 162.5, 162.4, 162.2, 162.1, 161.9, 161.6, 161.5, 161.2, 156.1, 153.1, 152.9, 152.5, 151.4, 151.4, 151.2, 150.7, 150.6, 150.4. 150.1, 149.2, 148.8, 142.5, 141.3, 140.7, 140.2, 139.9, 139.3, 139.1, 138.9, 138.7, 138.0, 137.5, 137.4, 137.0, 136.1, 135.9, 135.6, 135.4, 135.2, 134.9, 134.6, 134.4, 134.0, 133.8, 133.3, 132.5, 132.3, 132.2, 131.2, 127.9, 127.8, 127.6, 128.3, 126.7, 126.3, 126.1, 124.0, 122.6, 122.5, 122.1, 121.9, 121.8, 121.6, 121.5, 121.3, 120.6, 119.5, 119.3, 119.1, 118.6, 118.2, 117.4, 117.2, 117.0, 116.9, 116.7, 116.6, 116.5, 116.4, 116.3, 116.0, 115.7, 103.4, 102.3, 101.5, 100.2, 100.0, 99.7, 99.6, 99.3, 99.2, 98.6, 98.5, 97.8, 96.9, 75.7, 75.6, 75.5, 75.1, 75.0, 74.7, 74.5, 74.4, 74.3, 73.9, 70.6, 29.8, 28.4, 28.3, 28.2, 28.1, 27.9, 27.6, 19.6, 19.5, 19.4, 19.4, 19.3, 19.2, 19.1, 19.0, 18.8, 18.7, 18.4. HRMS (ESI+) m/z calcd for $C_{98}H_{99}N_{14}O_{14}$ $[M+H]^+$ 1695.7460, found 1695.7437.