Supporting Information

Does thermotropic liquid crystalline self-assembly control biological activity in amphiphilic amino acids? – Tyrosine ILCs as a case study

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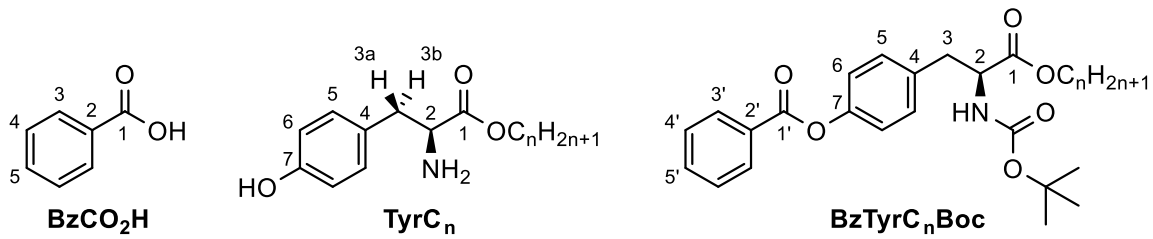
Content

1 Materials and Equipment

All chemicals were obtained from the supplier and used without further purification. Anhydrous tetrahydrofuran (THF) was prepared by distillation over potassium under a nitrogen atmosphere. Anhydrous dichloromethane was prepared by distillation over $CaCl_2$ under a nitrogen atmosphere. The eluents for chromatography hexanes (low boiling), ethyl acetate (EtOAc) and dichloromethane were distilled prior to use. When water was needed for reaction or work-up, demineralized water was always used. The degassed solvents acetonitrile (MeCN) and ethanol were prepared by channeling the respective gas (nitrogen or hydrogen) through the solvent.

For thin-layer chromatography, TLC SiO_2 60 F_{254} glass plates (layer thickness of 0.20 mm on aluminum, pore size 60 Å, fluorescence at 254 nm) from the company Merck were used. The identification of compounds with activity in the UV range was carried out by light irradiation of wavelengths 254 nm and 366 nm. In the case of UV-inactive compounds, staining reagents were used ($KMnO_4$, Seebach's reagent and phosphomolybdic acid). Column chromatography was either carried out with silica gel (SiO_2, particle diameter of 40–63 µm) from the company Macherey-Nagel. The silica gel used for the purification of ionic compounds was prepared by stirring SiO_2 with 6.0 M HCl for 30 min at room temperature, followed by filtration and washing with water as well as acetone until it was colourless.

^{1}H NMR (and ^{13}C NMR) spectra were recorded using Bruker spectrometers Avance 300, Ascend 400, Avance 500 and Ascend 700 at 300 MHz (75 MHz), 400 MHz (101 MHz), 500 MHz (126 MHz) and 700 MHz (176 MHz), respectively. ^{19}F NMR spectra were recorded at 376 MHz. Deuterated chloroform ($CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.2±0.1 ppm) was used as solvent with tetramethyl silane (TMS, δ_H = 0.00 ppm, δ_C = 0.0 ppm) as reference for the chemical shift δ in ppm (parts per million). In some cases, deuterated dimethyl sulfoxide (DMSO-d6, δ_H = 2.50 ppm, δ_C = 39.5±0.1 ppm) was used instead. Coupling constants *J* were reported in Hertz (Hz) and signal multiplicities were abbreviated as follows: s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublets), dt (doublet of triplets), t (triplet), q (quartet), m (multiplet). Atom numbering can differ from the IUPAC nomenclature due to a better comparison of several compounds. ^{1}H- and ^{13}C NMR spectra, COSY, HSQC and HMBC experiments were carried out to assign the NMR signals. The uniformity of the numbering is illustrated by the examples in Scheme S1. By numbering the COO groups, the signals can be compared more easily due to the continuous numbering already from the building blocks (left and center).



Scheme S1

FT-IR spectra were recorded on a Bruker Vektor 22, equipped with a MKII Golden Gate Single Reflection Diamond ATR system. The intensity maxima were rounded to whole wave numbers (cm^{-1}) and the relative absorption bands were indicated using the following abbreviations: w (weak), m (medium), s (strong), vs (very strong).

Mass spectra (MS) as well as high resolution mass spectra (HRMS) were recorded by electrospray ionisation (ESI) with a Bruker MicrOTOF-Q spectrometer, and electron ionisation (EI) with a Bruker Varian MAT 711 spectrometer.

An Elemental Analyzer Model 1106 from the company Carlo Erba Strumentazione was used for quantitative determination of the elements carbon, hydrogen and nitrogen. In addition, the water content could be determined via this method. Furthermore, a Karl Fischer titration (KFT) was performed for **3,4,5-C$_{14}$TyrC$_{14}$Cl** on a C10S/C20S/C30S coulometric KF titrator with DO308 drying oven from Mettler Toledo.

The rotational values α of new, ionic substances were measured at a wavelength of 589 nm and a temperature of 20 °C using a 241 polarimeter from Perkin Elmer. For the measurement, the substances were dissolved in chloroform and placed in a measuring cuvette. With the aid of the measured rotation values α, the specific angle of rotation could be determined via the Biot law

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{c \cdot l} \tag{1}$$

at T = 20 °C and λ = 589 nm with the concentration c of the specimen [$g \cdot mL^{-1}$] and the cuvette thickness l (l = 1 dm). The specific rotation $[\alpha]_{D}^{20}$ [$° \cdot mL \cdot g^{-1} \cdot mL^{-1}$] was reported without dimensions for a better overview.

Optical investigations were carried out with a polarising optical microscope Olympus BX 50, which could be heated via the hot plate LTS 350 from Linkam. Temperature was regulated with the control units TP93 and LNP from the company Linkam (ΔT = ±1 K). Recorded images to capture occurring mesophase textures were taken over the digital camera Axiocam 105 Color from ZEISS, processed and archived using the software ZenCore v3 from ZEISS.

Differential scanning calorimetry was performed on a DSC822e from the company Mettler Toledo. Therefore, sealed aluminum crucibles with heating and cooling rates of 5 K min^{-1} were used. The phase transition temperatures of the extrapolated onset values were determined using

the software STAR^{e} 14.0. A transition marked with '[–]' was observed at the appropriate temperature in the POM, but could not be reproduced in the DSC thermogram.

Melting points (M.p.) were determined either by investigation using the polarising optical microscope (heating rate 2–3 K) or by DSC measurements. The melting point was determined as the temperature at which the sample began to melt (liquid crystals) or was completely melted (for substances without mesophase).

X-ray diffractograms in the small (SAXS) and wide angle (WAXS) range were recorded on an AXS Nanostar C from Bruker. X-rays (nickel-filtered, monochromatic Cu-Kα radiation, wavelength λ: 1.5406 Å) were generated in a Siemens X-ray tube with a power of 1500 W. Calibration was performed with silver behenate at 298 K. For the measurement of a sample to be examined, it was extruded, melted in a pith tube of the company Hilgenberg GmbH (outer diameter: 0.7 mm) and transferred into a heatable sample holder. Diffraction patterns were recorded using a HI-STAR detector from Bruker. The analysis of the measurement data was carried out with the software SAXS (version 4.1.51) of the company Bruker, that of the X-ray diffractograms with the programs Datasqueeze (version 2.2.8) and OriginPro 2021 (version 9.8.0.200) from OriginLab®.

The investigations of lyotropic liquid crystalline behavior were carried out at the Institute of Physical Chemistry at the University of Stuttgart in the working groups of Prof. Dr. Frank Giesselmann, Prof. Dr. Cosima Stubenrauch and Prof. Dr. Thomas Sottmann. The optical investigations were performed on a Leica DMC2900 polarizing microscope from Leica Microsystems GmbH. The temperature could be controlled by the program WinTemp and a mK1000 High Precision temperature controller from Instec Inc. The surface tension was measured on a Tensiometer STA-1 from Sinterface with an integrated balance CP64 from Sartorius. The monitoring of the measurement and data output was carried out by the software supplied with the tensiometer (version 1.0.0.28). The evaluation of the data was carried out by the program IsoFit.

2 Synthesis

The synthesis of the respective crown ether based derivatives **CrCO$_2$Et**, **CrCO$_2$H**, **CrTyrC$_n$Boc**, **CrTyrC$_n$NH$_2$** and **CrTyrC$_n$Cl** (n = 10, 12, 14) was carried out according to previous work.[1] Comparable yields and purities could be achieved and their synthesis will not be discussed any further.

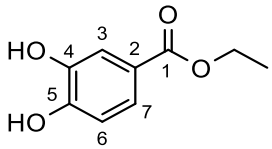
2.1 Preparation of Substituted Benzoic Acid Building Blocks

General Procedure GP1: Fischer esterification of dihydroxy benzoic acids[2]

The respective dihydroxybenzoic acid **3,4-CO$_2$H** or **3,5-CO$_2$H** (5.00 g, 32.4 mmol) was dissolved in ethanol or methanol (55 mL). Conc. sulfuric acid (0.4 mL) was added and the solution was heated for 24 h under reflux. After cooling to room temperature, excess solvent was removed under reduced pressure. The remaining residue was dissolved in ether (100 mL) and washed with conc. sodium bicarbonate solution (4 × 50 mL). Subsequently, the combined organic phases were dried over magnesium sulphate and the solvent was removed under reduced pressure.

3,4-Dihydroxybenzoic acid ethyl ester (3,4-CO$_2$Et)

According to GP1: Protocatechuic acid **3,4-CO$_2$H** (5.00 g, 32.4 mmol), conc. H_2SO_4 (0.4 mL), EtOH (55 mL).

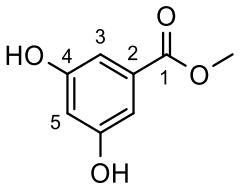


3,4-CO$_2$Et
$C_9H_{10}O_4$
(182.18)

Colourless solid (96%, 5.66 g, 31.1 mmol, purity >95%); ^{1}H NMR (500 MHz, DMSO-d6): δ = 1.27 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 4.22 (q, *J* = 7.1 Hz, 2H, C*H*$_2$), 6.83 (d, *J* = 8.2 Hz, 1H, 6-H), 7.33 (dd, *J* = 8.3 Hz, 2.1 Hz, 1H, 7-H), 7.39 (d, *J* = 2.1 Hz, 1H, 3-H), 9.37 (s, 2H, OH) ppm; ^{13}C NMR (126 MHz, DMSO-d6): δ = 14.2 (*C*H$_3$), 60.0 (*C*H$_2$), 115.3 (C-6), 116.2 (C-3), 120.8 (C-2), 121.7 (C-7), 145.0 (C-4), 150.3 (C-5), 165.7 (C=O) ppm; MS (ESI): *m*/*z* = 183.07 $[M + H]^+$, 205.05 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_9H_{10}O_4$) calcd.: 205.0471 $[M + Na]^+$, found: 205.0472. The spectroscopic data were in accordance with the literature.[3]

3,5-Dihydroxybenzoic acid methyl ester (3,5-CO$_2$Me)

According to GP1: α-Resorcylic acid **3,5-CO$_2$H** (5.00 g, 32.4 mmol), conc. H_2SO_4 (0.4 mL), MeOH (55 mL).



3,5-CO_2Me
$C_8H_8O_4$
(168.15)

Beige solid (91%, 4.95 g, 29.4 mmol, purity >92%); ^{1}H NMR (500 MHz, DMSO-d6): δ = 3.79 (s, 3H, C*H*$_3$), 6.47 (d, *J* = 2.3 Hz, 1H, 5-H), 6.84 (d, *J* = 2.3 Hz, 2H, 3-H), 9.64 (s, 2H, OH) ppm; ^{13}C NMR (126 MHz, DMSO-d6): δ = 51.9 (*C*H$_3$), 107.1 (C-3), 107.2 (C-5), 131.3 (C-2), 158.5 (C-4), 166.2 (C=O) ppm; MS (ESI): *m*/*z* = 191.03 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_8H_8O_4$) calcd.: 191.0315 [M + Na]$^+$, found: 191.0313. The spectroscopic data were in accordance with the literature.[4,5]

General Procedure GP2: Williamson ether synthesis of benzoic acid esters with hydroxy groups

Method A: Monohydroxybenzoic acid esters[6]

4-Hydroxybenzoic acid methyl ester **4-CO_2Me** (1.92 g, 12.6 mmol) and potassium carbonate (5.22 g, 37.8 mmol) were suspended in degassed acetonitrile (55 mL) under a nitrogen atmosphere. The respective 1-bromoalkane (12.0 mmol) was added and the mixture was heated for 24 h under reflux. After cooling to room temperature, the mixture was poured into a sodium hydroxide solution (100 mL, 1.0 M in H_2O). The aqueous phase was extracted successively hexanes (8 × 50 mL) and the combined organic phases were dried over magnesium sulphate. Subsequently, the solvent was removed under reduced pressure.

Method B: Dihydroxybenzoic acid esters[7]

Potassium carbonate (8.29 g, 60.0 mmol) and the respective dihydroxybenzoic acid ester **3,4-CO_2Et** or **3,5-CO_2Me** (12.0 mmol) were suspended in degassed acetonitrile (55 mL) under a nitrogen atmosphere. The corresponding 1-bromoalkane (26.4 mmol) was added and the mixture was heated for 24 h under reflux. After cooling to room temperature, the mixture was poured into water (100 mL). Precipitated solid was dissolved in hexanes (100 mL). The aqueous phase was extracted successively hexanes (8 × 50 mL) and the combined organic phases were dried over magnesium sulphate. Subsequently, the solvent was removed under reduced pressure and the residue was recrystallised from ethanol.

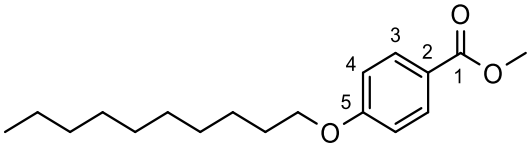
Method C: Trihydroxybenzoic acid esters[8,9]

Potassium carbonate (13.3 g, 96.2 mmol), sodium iodide (180 mg, 1.20 mmol) and 3,4,5-trihydroxybenzoic acid ethyl ester **3,4,5-CO_2Et** (2.38 g, 12.0 mmol) were suspended in

degassed acetonitrile (55 mL). The corresponding 1-bromoalkane (39.6 mmol) was added and the mixture was heated for 48 h under reflux. After cooling to room temperature, the mixture was poured into water (100 mL). Precipitated solid was dissolved in hexanes (100 mL). The aqueous phase was extracted successively hexanes (8 × 50 mL) and the combined organic phases were dried over magnesium sulphate. Subsequently, the solvent was removed under reduced pressure and the residue was recrystallised from ethanol.

4-Decyloxybenzoic acid methyl ester [4-$C_{10}CO_2Me$]

According to GP2, method A: 4-Hydroxybenzoic acid methyl ester **4-CO_2Me** (1.92 g, 12.6 mmol), 1-bromodecane (2.5 mL, 12.1 mmol), potassium carbonate (5.50 g, 39.8 mmol), MeCN (70 mL).

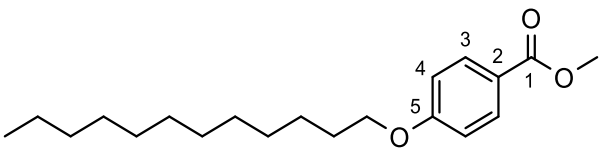


4-$C_{10}CO_2Me$
$C_{18}H_{28}O_3$
(292.42)

Colourless solid (89%, 3.15 g, 10.8 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.18–1.40 (m, 12H, C*H*$_2$), 1.40–1.52 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.72–1.86 (m, 2H, OCH$_2$C*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 3.99 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 6.89 (d, *J* = 8.9 Hz, 2H, 4-H), 7.97 (d, *J* = 8.9 Hz, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.1, 29.3, 29.4, 29.56, 29.58, 31.9 (*C*H$_2$), 51.8 (O*C*H$_3$), 68.2 (O*C*H$_2$), 114.1 (C-3), 122.4 (C-2), 131.6 (C-4), 163.0 (C-5), 166.9 (C=O) ppm; MS (ESI): *m*/*z* = 293.21 [M + H]$^+$, 315.19 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{18}H_{28}O_3$) calcd.: 315.1931 [M + Na]$^+$, found: 315.1932. The spectroscopic data were in accordance with the literature.[10]

4-Dodecyloxybenzoic acid methyl ester [4-$C_{12}CO_2Me$]

According to GP2, method A: 4-Hydroxybenzoic acid methyl ester **4-CO_2Me** (1.93 g, 12.7 mmol), 1-bromodecane (2.9 mL, 12.1 mmol), potassium carbonate (5.32 g, 38.5 mmol), MeCN (70 mL).



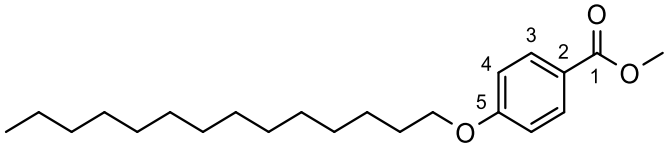
4-$C_{12}CO_2Me$
$C_{20}H_{32}O_3$
(320.47)

Colourless solid (93%, 3.59 g, 11.2 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.15–1.39 (m, 16H, C*H*$_2$), 1.40–1.52 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.67–2.30 (m, 2H, OCH$_2$C*H*$_2$), 3.88 (s, 3H, OC*H*$_3$), 4.00 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 6.90 (d,

J = 8.9 Hz, 2H, 4-H), 7.97 (d, J = 8.9 Hz, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.0, 29.1, 29.36, 29.38, 29.57, 29.60, 29.65, 29.7, 31.9 (CH_2), 51.8 (OCH_3), 68.2 (OCH_2), 114.1 (C-3), 122.4 (C-2), 131.6 (C-4), 163.0 (C-5), 166.9 (C=O) ppm; MS (ESI): m/z = 321.24 $[M + H]^+$, 343.22 $[M + Na]^+$; HRMS (ESI): m/z ($C_{20}H_{32}O_3$) calcd.: 343.2244 $[M + Na]^+$, found: 343.2244. The spectroscopic data were in accordance with the literature.[10]

4-Tetradecyloxybenzoic acid methyl ester [4-$C_{14}CO_2Me$]

According to GP2, method A: 4-Hydroxybenzoic acid methyl ester **4-CO_2Me** (1.94 g, 12.8 mmol), 1-bromotetradecane (3.3 mL, 12.1 mmol), potassium carbonate (5.30 g, 38.4 mmol), MeCN (70 mL).

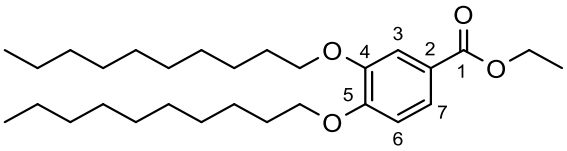


4-$C_{14}CO_2Me$
$C_{22}H_{36}O_3$
(348.53)

Colourless solid (90%, 3.82 g, 11.0 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.21–1.39 (m, 20H, CH_2), 1.40–1.53 (m, 2H, $OCH_2CH_2CH_2$), 1.71–1.90 (m, 2H, OCH_2CH_2), 3.88 (s, 3H, OCH_3), 4.00 (t, J = 6.5 Hz, 2H, OCH_2), 6.90 (d, J = 8.9 Hz, 2H, 4-H), 7.97 (d, J = 8.9 Hz, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.0, 29.1, 29.4, 29.57, 29.60, 29.67, 29.69, 29.71, 31.9 (CH_2), 51.8 (OCH_3), 68.2 (OCH_2), 114.1 (C-3), 122.4 (C-2), 131.6 (C-4), 163.0 (C-5), 166.9 (C=O) ppm; MS (ESI): m/z = 349.27 $[M + H]^+$, 371.26 $[M + Na]^+$; HRMS (ESI): m/z ($C_{22}H_{36}O_3$) calcd.: 371.2557 $[M + Na]^+$, found: 371.2557. The spectroscopic data were in accordance with the literature.[11]

3,4-Bis(decyloxy)benzoic acid ethyl ester [3,4-$C_{10}CO_2Et$]

According to GP2, method B: 3,4-Dihydroxybenzoic acid ethyl ester **3,4-CO_2Et** (2.19 g, 12.0 mmol), 1-bromodecane (5.6 mL, 27.1 mmol), potassium carbonate (8.50 g, 61.5 mmol), MeCN (70 mL).



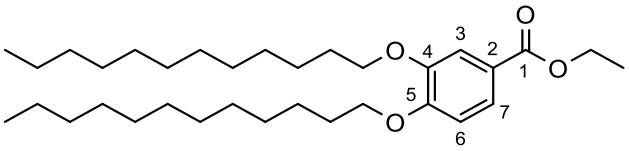
3,4-$C_{10}CO_2Et$
$C_{29}H_{50}O_4$
(462.72)

Colourless solid (96%, 5.32 g, 11.5 mmol, purity >94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.18–1.53 (m, 31H, CH_2, OCH_2CH_3), 1.75–1.91 (m, 4H, OCH_2CH_2), 4.04 (t, J = 6.7 Hz, 4H, OCH_2), 4.34 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 6.86 (d, J = 8.4 Hz, 1H,

6-H), 7.54 (d, *J* = 2.0 Hz, 1H, 3-H), 7.64 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, 7-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.4 (*C*H_3), 22.71, 26.00, 26.04, 29.1, 29.2, 29.3, 29.37, 29.41, 29.44, 29.47, 29.53, 29.59, 29.60, 29.63, 29.65, 31.9, 31.9 (*C*H_2), 60.7 (O*C*H_2CH$_3$), 69.1, 69.3 (O*C*H_2CH$_2$), 112.0 (C-6), 114.4 (C-3), 122.8 (C-2), 123.5 (C-7), 148.6 (C-4), 153.2 (C-5), 166.5 (C=O) ppm; MS (ESI): *m*/*z* = 463.38 $[M + H]^+$, 485.36 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{29}H_{50}O_4$) calcd.: 463.3782 $[M + H]^+$, found: 463.3784. The spectroscopic data were in accordance with the literature.[12]

3,4-Bis(dodecyloxy)benzoic acid ethyl ester [3,4-C$_{12}$CO$_2$Et]

According to GP2, method B: 3,4-Dihydroxybenzoic acid ethyl ester **3,4-CO$_2$Et** (2.19 g, 12.0 mmol), 1-bromododecane (6.3 mL, 26.3 mmol), potassium carbonate (8.42 g, 60.9 mmol), MeCN (70 mL).

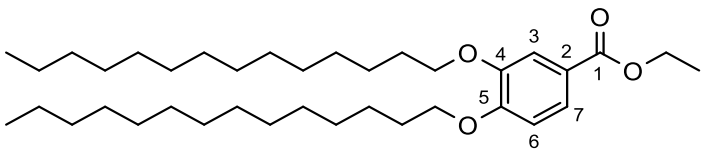


3,4-C$_{12}$CO$_2$Et
$C_{33}H_{58}O_4$
(518.82)

Colourless solid (90%, 5.60 g, 10.8 mmol, purity >94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6H, C*H*$_3$), 1.14–1.56 (m, 39H, C*H*$_2$, OCH$_2$C*H*$_3$), 1.72–1.95 (m, 4H, OCH$_2$C*H*$_2$), 4.04 (t, *J* = 6.6 Hz, 4H, OC*H*$_2$CH$_2$), 4.34 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 6.86 (d, *J* = 8.4 Hz, 1H, 6-H), 7.54 (d, *J* = 2.0 Hz, 1H, 3-H), 7.64 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, 7-H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.4 (*C*H_3), 22.7, 26.0, 29.09, 29.12, 29.2, 29.36, 29.39, 29.41, 29.44, 29.47, 29.55, 29.57, 29.59, 29.63, 29.65, 29.69, 29.73, 31.93, 31.95 (*C*H_2), 60.7 (O*C*H_2CH$_3$), 69.1, 69.3 (O*C*H_2CH$_2$), 112.0 (C-6), 114.4 (C-3), 122.8 (C-2), 123.5 (C-7), 148.6 (C-4), 153.2 (C-5), 166.5 (C=O) ppm; MS (ESI): *m*/*z* = 519.44 $[M + H]^+$, 536.47 $[M + NH_4]^+$, 541.42 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{33}H_{58}O_4$) calcd.: 519.4408 $[M + H]^+$, found: 519.4404. The spectroscopic data were in accordance with the literature.[13]

3,4-Bis(tetradecyloxy)benzoic acid ethyl ester [3,4-C$_{14}$CO$_2$Et]

According to GP2, method B: 3,4-Dihydroxybenzoic acid ethyl ester **3,4-CO$_2$Et** (2.19 g, 12.0 mmol), 1-bromotetradecane (7.2 mL, 26.5 mmol), potassium carbonate (8.44 g, 61.1 mmol), MeCN (70 mL).

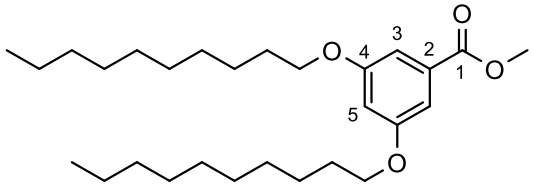


3,4-C$_{14}$CO$_2$Et
$C_{37}H_{66}O_4$
(574.93)

Colourless solid (93%, 6.43 g, 11.2 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6H, C*H*$_3$), 1.12–1.42 (m, 43H, C*H*$_2$, OCH$_2$C*H*$_3$), 1.41–1.54 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.77–1.92 (m, 4H, OCH$_2$C*H*$_2$), 4.04 (t, *J* = 6.7 Hz, 4H, OC*H*$_2$), 4.34 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 6.86 (d, *J* = 8.5 Hz, 1H, 6-H), 7.54 (d, *J* = 2.0 Hz, 1H, 3-H), 7.64 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, 7-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.4 (*C*H$_3$), 22.7, 26.0, 29.1, 29.2, 29.39, 29.41, 29.44, 29.63, 29.65, 29.69, 29.73, 32.0 (*C*H$_2$), 60.7 (O*C*H$_2$CH$_3$), 69.1, 69.3 (O*C*H$_2$CH$_2$), 112.0 (C-6), 114.4 (C-3), 122.8 (C-2), 123.5 (C-7), 148.6 (C-4), 153.2 (C-5), 166.6 (C=O) ppm; MS (ESI): *m*/*z* = 575.50 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{37}H_{66}O_4$) calcd.: 575.5034 [M + H]$^+$, found: 575.5033. The spectroscopic data were in accordance with the literature.[11]

3,5-Bis(decyloxy)benzoic acid methyl ester [3,5-$C_{10}CO_2Me$]

According to GP2, method B: 3,5-Dihydroxybenzoic acid methyl ester **3,5-CO_2Me** (2.02 g, 12.0 mmol), 1-bromodecane (5.5 mL, 26.6 mmol), potassium carbonate (8.31 g, 60.1 mmol), MeCN (70 mL).

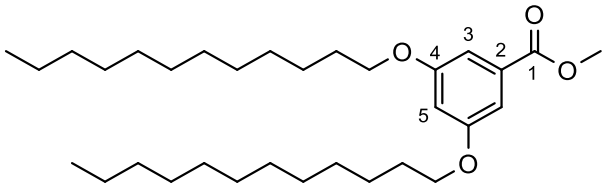


3,5-$C_{10}CO_2Me$
$C_{28}H_{48}O_4$
(448.69)

Colourless solid (94%, 5.07 g, 11.3 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 6H, C*H*$_3$), 1.22–1.38 (m, 24H, C*H*$_2$), 1.39–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.71–1.82 (m, 4H, OCH$_2$C*H*$_2$), 3.89 (s, 3H, OC*H*$_3$), 3.96 (t, *J* = 6.6 Hz, 4H, OC*H*$_2$), 6.63 (t, *J* = 2.4 Hz, 1H, 5-H), 7.16 (d, *J* = 2.4 Hz, 2H, 3-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.2, 29.34, 29.38, 29.57, 29.59, 31.9 (*C*H$_2$), 52.18 (O*C*H$_3$), 68.3 (O*C*H$_2$), 106.6 (C-5), 107.6 (C-3), 131.8 (C-2), 160.2 (C-4), 167.0 (C=O) ppm; MS (ESI): *m*/*z* = 449.36 [M + H]$^+$, 471.34 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{28}H_{48}O_4$) calcd.: 449.3625 [M + H]$^+$, found: 449.3626. The spectroscopic data were in accordance with the literature.[14]

3,5-Bis(dodecyloxy)benzoic acid methyl ester [3,5-$C_{12}CO_2Me$]

According to GP2, method B: 3,5-Dihydroxybenzoic acid methyl ester **3,5-CO_2Me** (2.02 g, 12.0 mmol), 1-bromododecane (6.4 mL, 26.7 mmol), potassium carbonate (8.38 g, 60.6 mmol), MeCN (70 mL).

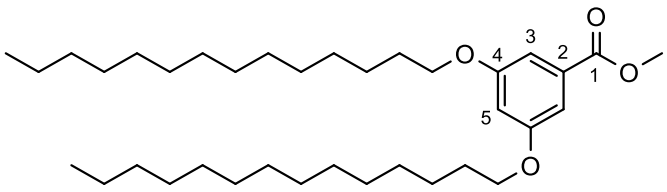


3,5-$C_{12}CO_2Me$
$C_{32}H_{56}O_4$
(504.80)

Colourless solid (91%, 5.50 g, 10.9 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 6H, C*H*$_3$)), 1.03–1.39 (m, 32H, C*H*$_2$), 1.38–1.59 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.66–1.84 (m, 4H, OCH$_2$C*H*$_2$), 3.89 (s, 3H, OC*H*$_3$), 3.96 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 6.63 (t, *J* = 2.3 Hz, 1H, 5-H), 7.16 (d, *J* = 2.3 Hz, 2H, 3-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.2, 29.36, 29.38, 29.58, 29.61, 29.65, 29.67, 31.9 (*C*H$_2$), 52.2 (O*C*H$_3$), 68.3 (O*C*H$_2$), 106.6 (C-5), 107.6 (C-3), 131.8 (C-2), 160.2 (C-4), 167.0 (C=O) ppm; MS (ESI): *m*/*z* = 505.43 [M + H]$^+$, 527.41 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{32}H_{56}O_4$) calcd.: 505.4251 [M + H]$^+$, found: 505.4251. The spectroscopic data were in accordance with the literature.[15]

3,5-Bis(tetradecyloxy)benzoic acid methyl ester [3,5-$C_{14}CO_2Me$]

According to GP2, method B: 3,5-Dihydroxybenzoic acid methyl ester **3,5-CO_2Me** (2.020 g, 12.0 mmol), 1-bromotetradecane (7.2 mL, 26.5 mmol), potassium carbonate (8.30 g, 60.1 mmol), MeCN (70 mL).

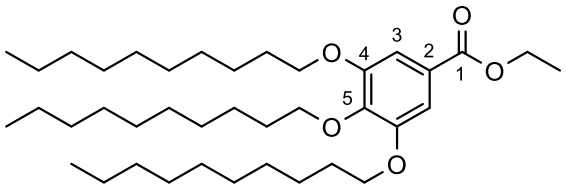


3,5-$C_{14}CO_2Me$
$C_{36}H_{64}O_4$
(560.90)

Colourless solid (quant., 6.72 g, 12.0 mmol, purity >93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6H, C*H*$_3$), 1.13–1.39 (m, 40H, C*H*$_2$), 1.39–1.54 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.64–2.00 (m, 4H, OCH$_2$C*H*$_2$), 3.89 (s, 3H, OC*H*$_3$), 3.96 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 6.63 (t, *J* = 2.4 Hz, 1H, 5-H), 7.15 (d, *J* = 2.4 Hz, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.2, 29.4, 29.60, 29.62, 29.68, 29.70, 29.72, 32.0 (*C*H$_2$), 52.2 (O*C*H$_3$), 68.4 (O*C*H$_2$), 106.6 (C-5), 107.7 (C-3), 131.8(C-2), 160.2 (C-4), 167.0 (C=O) ppm; MS (ESI): *m*/*z* = 561.49 [M + H]$^+$, 583.47 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{36}H_{64}O_4$) calcd.: 561.4877 [M + H]$^+$, found: 561.4871. The spectroscopic data were in accordance with the literature.[16]

3,4,5-Tris(decyloxy)benzoic acid ethyl ester [3,4,5-$C_{10}CO_2Et$]

According to GP2, method C: 3,4,5-Trihydroxybenzoic acid ethyl ester **3,4,5-CO_2Et** (2.38 g, 12.0 mmol), 1-bromodecane (8.2 mL, 39.7 mmol), potassium carbonate (13.4 g, 97.0 mmol), sodium iodide (0.20 g, 1.33 mmol), MeCN (70 mL).

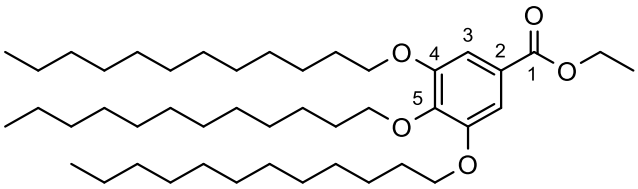


3,4,5-$C_{10}CO_2Et$
$C_{39}H_{70}O_5$
(618.98)

Colourless solid (quant., 7.43 g, 12.0 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 9H, C*H*$_3$), 1.14–1.57 (m, 45H, C*H*$_2$, OCH$_2$C*H*$_3$), 1.54–2.14 (m, 6H, OCH$_2$C*H*$_2$), 4.01 (t, *J* = 6.5 Hz, 6H, OC*H*$_2$), 4.35 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 7.26 (s, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.4 (*C*H$_3$), 22.7, 22.7, 26.09, 26.12, 29.38, 29.43, 29.60, 29.61, 29.66, 29.70, 29.75, 30.4, 31.94, 31.97 (*C*H$_2$), 61.0 (O*C*H$_2$CH$_3$), 69.2, 73.5 (O*C*H$_2$CH$_2$), 108.1 (C-3), 125.1 (C-2), 142.4 (C-5), 152.8 (C-4), 166.5 (C=O) ppm; MS (ESI): *m*/*z* = 619.53 $[M + H]^+$, 641.51 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{39}H_{70}O_5$) calcd.: 619.5296 $[M + H]^+$, found: 619.5298. The spectroscopic data were in accordance with the literature.[17]

3,4,5-Tris(dodecyloxy)benzoic acid ethyl ester [3,4,5-$C_{12}CO_2Et$]

According to GP2, method C: 3,4,5-Trihydroxybenzoic acid ethyl ester **3,4,5-CO_2Et** (2.38 g, 12.0 mmol), 1-bromododecane (9.5 mL, 39.6 mmol), potassium carbonate (13.5 g, 97.7 mmol), sodium iodide (0.20 g, 1.33 mmol), MeCN (70 mL).

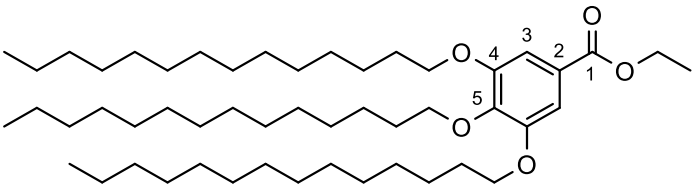


3,4,5-$C_{12}CO_2Et$
$C_{45}H_{82}O_5$
(703.15)

Colourless solid (91%, 7.68 g, 10.9 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 9H, C*H*$_3$), 1.13–1.57 (m, 57H, C*H*$_2$, OCH$_2$C*H*$_3$), 1.64–1.93 (m, 6H, OCH$_2$C*H*$_2$), 4.01 (t, *J* = 6.5 Hz, 6H, OC*H*$_2$), 4.35 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 7.26 (s, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.4 (*C*H$_3$), 22.7, 26.08, 26.10, 29.35, 29.38, 29.41, 29.45, 29.56, 29.58, 29.65, 29.67, 29.71, 29.74, 29.76, 30.4, 31.92, 31.94, 31.95 (*C*H$_2$), 60.9 (O*C*H$_2$CH$_3$), 69.2, 73.5 (O*C*H$_2$CH$_2$), 108.1 (C-3), 125.1 (C-2), 142.4 (C-5), 152.8 (C-4), 166.4 (C=O) ppm; MS (ESI): *m*/*z* = 703.62 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{45}H_{82}O_5$) calcd.: 703.6235 $[M + H]^+$, found: 703.6239. The spectroscopic data were in accordance with the literature.[17]

3,4,5-Tris(tetradecyloxy)benzoic acid ethyl ester [3,4,5-$C_{14}CO_2Et$]

According to GP2, method C: 3,4,5-Trihydroxybenzoic acid ethyl ester **3,4,5-CO_2Et** (2.38 g, 12.0 mmol), 1-bromotetradecane (10.8 mL, 39.7 mmol), potassium carbonate (13.5 g, 97.7 mmol), sodium iodide (0.20 g, 1.33 mmol), MeCN (70 mL).



3,4,5-$C_{14}CO_2Et$
$C_{51}H_{94}O_5$
(787.31)

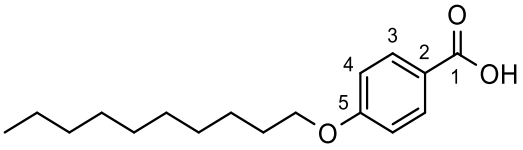
Colourless solid (99%, 9.33 g, 11.8 mmol, purity >94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 9H, C*H*$_3$), 1.03–1.43 (m, 63H, C*H*$_2$, OCH$_2$C*H*$_3$), 1.48 (dd, *J* = 10.9 Hz, 5.0 Hz, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.65–2.21 (m, 6H, OCH$_2$C*H*$_2$), 4.01 (t, *J* = 6.5 Hz, 6H, OC*H*$_2$), 4.35 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 7.26 (s, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.4 (*C*H$_3$), 22.7, 26.10, 26.13, 29.37, 29.41, 29.44, 29.58, 29.61, 29.67, 29.70, 29.72, 29.74, 29.78, 30.4, 32.0 (*C*H$_2$), 61.0 (O*C*H$_2$CH$_3$), 69.2, 73.5 (O*C*H$_2$CH$_2$), 108.1 (C-3), 125.1 (C-2), 142.4 (C-5), 152.8 (C-4), 166.5 (C=O) ppm; MS (ESI): *m*/*z* = 787.72 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{51}H_{94}O_5$) calcd.: 787.7174 $[M + H]^+$, found: 787.7176. The spectroscopic data were in accordance with the literature.[17]

General Procedure GP3: Saponification of benzoic acid esters[9]

Potassium hydroxide (1.23 g, 22.0 mmol) and the respective etherified benzoic acid ester **Ar(C_m)CO_2R** (10.0 mmol) were suspended in a mixture of ethanol (67 mL) and water (14 mL). The mixture was heated for 24 h under reflux. After cooling to room temperature, the mixture was poured into water (100 mL) and ethyl acetate (200 mL) was added. Subsequently, the mixture was acidified (pH < 3) with diluted HCl (50 mL, 2.0 M in H_2O) and the phases were separated. The organic phase was washed with water (3 × 50 mL) and brine (2 × 50 mL). Afterwards, the organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure.

4-Decyloxybenzoic acid [4-$C_{10}CO_2H$]

According to GP3: 4-Decyloxybenzoic acid methyl ester **4-$C_{10}CO_2Me$** (2.92 g, 10.0 mmol), potassium hydroxide (1.30 g, 23.2 mmol), H_2O (15 mL), EtOH (70 mL).

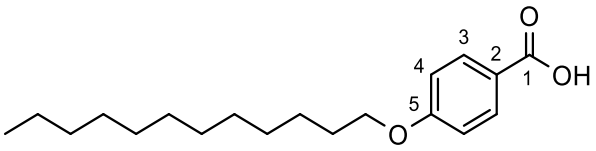


4-$C_{10}CO_2H$
$C_{17}H_{26}O_3$
(278.39)

Colourless solid (quant., 2.78 g, 10.0 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.21–1.42 (m, 12H, C*H*$_2$), 1.42–1.51 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.73–1.85 (m, 2H, OCH$_2$C*H*$_2$), 4.02 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 6.93 (d, *J* = 8.9 Hz, 2H, 4-H), 8.06 (d, *J* = 8.9 Hz, 2H, 3-H), 12.67 (br. s, 1H, COOH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.1, 29.32, 29.37, 29.6, 31.9 (*C*H$_2$), 68.3 (O*C*H$_2$), 114.2 (C-3), 121.4 (C-2), 132.4 (C-4), 163.7 (C-5), 172.1 (C=O) ppm; MS (ESI): *m*/*z* = 279.20 [M + H]$^+$, 301.18 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{17}H_{26}O_3$) calcd.: 301.1774 [M + Na]$^+$, found: 301.1775. The spectroscopic data were in accordance with the literature.[10]

4-Dodecyloxybenzoic acid [4-C$_{12}$CO$_2$H]

According to GP3: 4-Dodecyloxybenzoic acid methyl ester **4-C$_{12}$CO$_2$Me** (3.21 g, 10.0 mmol), potassium hydroxide (1.25 g, 22.3 mmol), H_2O (15 mL), EtOH (70 mL).

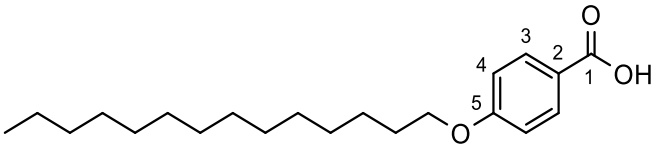


4-C$_{12}$CO$_2$H
$C_{19}H_{30}O_3$
(306.45)

Colourless solid (98%, 2.99 g, 9.76 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.21–1.40 (m, 16H, C*H*$_2$), 1.41–1.52 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.66–1.89 (m, 2H, OCH$_2$C*H*$_2$), 4.02 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 6.93 (d, *J* = 8.8 Hz, 2H, 4-H), 8.05 (d, *J* = 8.8 Hz, 2H, 3-H), 11.93 (br. s, 1H, COOH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.1, 29.4, 29.56, 29.59, 29.64, 29.66, 31.9 (*C*H$_2$), 68.3 (O*C*H$_2$), 114.2 (C-3), 121.3 (C-2), 132.3 (C-4), 163.7 (C-5), 171.5 (C=O) ppm; MS (ESI): *m*/*z* = 307.23 [M + H]$^+$, 329.21 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{19}H_{30}O_3$) calcd.: 329.2087 [M + Na]$^+$, found: 329.2089. The spectroscopic data were in accordance with the literature.[10]

4-Tetradecyloxybenzoic acid [4-C$_{14}$CO$_2$H]

According to GP3: 4-Tetradecyloxybenzoic acid methyl ester **4-C$_{14}$CO$_2$Me** (3.49 g, 10.0 mmol), potassium hydroxide (1.23 g, 21.9 mmol), H_2O (15 mL), EtOH (70 mL).



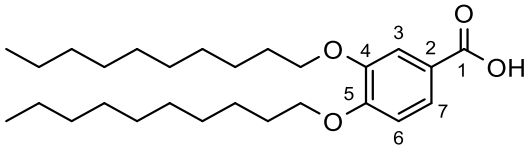
4-C$_{14}$CO$_2$H
$C_{21}H_{34}O_3$
(334.50)

Colourless solid (94%, 3.15 g, 9.42 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.14–1.41 (m, 20H, C*H*$_2$), 1.41–1.57 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.61–1.96 (m, 2H, OCH$_2$C*H*$_2$), 4.02 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 6.93 (d, *J* = 8.8 Hz, 2H, 4-H), 8.05 (d, *J* = 8.8 Hz, 2H, 3-H), 11.75 (br. s, 1H, COOH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$):

δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.1, 29.4, 29.56, 29.60, 29.66, 29.68, 29.70, 31.9(*C*H$_2$), 68.3 (O*C*H$_2$), 114.2 (C-3), 121.3 (C-2), 132.4 (C-4), 163.7 (C-5), 171.3 (C=O) ppm; MS (ESI): *m*/*z* = 335.26 [M + H]$^+$, 357.24 [M + Na]$^+$; HRMS (ESI): *m*/*z* (C$_{21}$H$_{34}$O$_3$) calcd.: 357.2400 [M + Na]$^+$, found: 357.2400. The spectroscopic data were in accordance with the literature.[18]

3,4-Bis(decyloxy)benzoic acid [3,4-C$_{10}$CO$_2$H]

According to GP3: 3,4-Bis(decyloxy)benzoic acid ethyl ester **3,4-C$_{10}$CO$_2$Et** (4.63 g, 10.0 mmol), potassium hydroxide (1.40 g, 25.0 mmol), H$_2$O (15 mL), EtOH (70 mL).

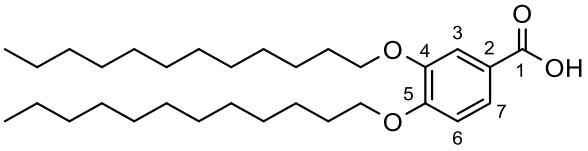


3,4-C$_{10}$CO$_2$H
C$_{27}$H$_{46}$O$_4$
(434.66)

Colourless solid (92%, 4.00 g, 9.21 mmol, purity >95%); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.88 (t, *J* = 6.6 Hz, 6H, C*H*$_3$), 1.22–1.42 (m, 24H, C*H*$_2$), 1.42–1.61 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.72–1.97 (m, 4H, OCH$_2$C*H*$_2$), 4.06 (q, *J* = 6.6 Hz, 4H, OC*H*$_2$), 6.89 (d, *J* = 8.5 Hz, 1H, 6-H), 7.59 (d, *J* = 2.0 Hz, 1H, 3-H), 7.73 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7-H), 11.85 (br. s, 1H, COOH) ppm; ^{13}C NMR (101 MHz, CDCl$_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 26.0, 29.06, 29.17, 29.36, 29.39, 29.42, 29.57, 29.59, 29.61, 29.64, 31.9 (*C*H$_2$), 69.1, 69.3 (O*C*H$_2$), 111.9 (C-6), 114.6 (C-3), 121.3 (C-2), 124.5 (C-7), 148.6 (C-4), 154.0 (C-5), 171.4 (C=O) ppm; MS (ESI): *m*/*z* = 435.35 [M + H]$^+$, 457.33 [M + Na]$^+$; HRMS (ESI): *m*/*z* (C$_{27}$H$_{46}$O$_4$) calcd.: 457.3288 [M + Na]$^+$, found: 457.3285. The spectroscopic data were in accordance with the literature.[19]

3,4-Bis(dodecyloxy)benzoic acid [3,4-C$_{12}$CO$_2$H]

According to GP3: 3,4-Bis(dodecyloxy)benzoic acid ethyl ester **3,4-C$_{12}$CO$_2$Et** (5.19 g, 10.0 mmol), potassium hydroxide (1.34 g, 23.9 mmol), H$_2$O (15 mL), EtOH (70 mL).



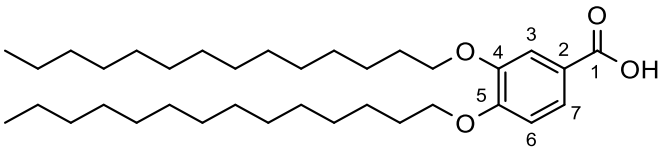
3,4-C$_{12}$CO$_2$H
C$_{31}$H$_{54}$O$_4$
(490.77)

Colourless solid (91%, 4.47 g, 9.10 mmol, purity >90%); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6H, C*H*$_3$), 1.21–1.41 (m, 32H, C*H*$_2$), 1.41–1.53 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.78–1.90 (m, 4H, OCH$_2$C*H*$_2$), 4.06 (q, *J* = 6.6 Hz, 4H, OC*H*$_2$), 6.89 (d, *J* = 8.5 Hz, 1H, 6-H), 7.58 (d, *J* = 2.0 Hz, 1H, 3-H), 7.72 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7-H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.98, 26.02, 29.06, 29.18, 29.38, 29.42, 29.62, 29.64, 29.68, 29.71, 31.9 (*C*H$_2$), 69.1, 69.3 (O*C*H$_2$), 111.9 (C-6), 114.6 (C-3), 121.3 (C-2), 124.5 (C-7), 148.6 (C-4), 154.0 (C-5), 170.9 (C=O) ppm; MS (ESI): *m*/*z* = 491.41 [M + H]$^+$, 513.39 [M + Na]$^+$;

HRMS (ESI): *m*/*z* ($C_{31}H_{54}O_4$) calcd.: 513.3914 $[M + Na]^+$, found: 513.3915. The spectroscopic data were in accordance with the literature.[19]

3,4-Bis(tetradecyloxy)benzoic acid [3,4-$C_{14}CO_2H$]

According to GP3: 3,4-Bis(tetradecyloxy)benzoic acid ethyl ester **3,4-$C_{14}CO_2Et$** (5.75 g, 10.0 mmol), potassium hydroxide (1.38 g, 24.6 mmol), H_2O (15 mL), EtOH (70 mL).

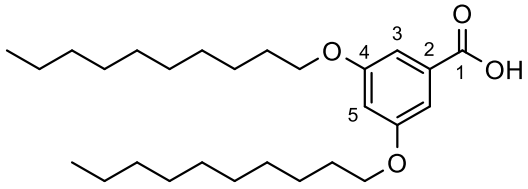


3,4-$C_{14}CO_2H$
$C_{35}H_{62}O_4$
(546.88)

Colourless solid (97%, 5.32 g, 9.72 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H, C*H*$_3$), 1.21–1.41 (m, 40H, C*H*$_2$), 1.47 (q, *J* = 7.8 Hz, 7.3 Hz, 4H, $OCH_2CH_2CH_2$), 1.76–1.88 (m, 4H, OCH_2CH_2), 4.00–4.10 (m, 4H, OC*H*$_2$), 6.88 (d, *J* = 8.5 Hz, 1H, 6-H), 7.59 (d, *J* = 2.0 Hz, 1H, 3-H), 7.71 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.06, 26.11, 29.2, 29.34, 29.39, 29.43, 29.46, 29.65, 29.68, 29.71, 29.73, 29.75, 32.0 (*C*H$_2$), 69.3, 69.6 (O*C*H$_2$), 112.5 (C-6), 115.4 (C-3), 121.7 (C-2), 124.64 (C-7), 148.9 (C-4), 154.3 (C-5), 171.2 (C=O) ppm; MS (ESI): *m*/*z* = 547.47 $[M + H]^+$, 569.45 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{62}O_4$) calcd.: 569.4540 $[M + Na]^+$, found: 569.4546. The spectroscopic data were in accordance with the literature.[16]

3,5-Bis(decyloxy)benzoic acid [3,5-$C_{10}CO_2H$]

According to GP3: 3,5-Bis(decyloxy)benzoic acid methyl ester **3,5-$C_{10}CO_2Me$** (4.49 g, 10.0 mmol), potassium hydroxide (1.32 g, 23.5 mmol), H_2O (15 mL), EtOH (70 mL).

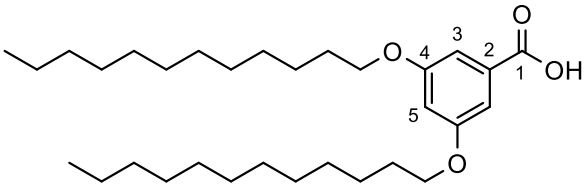


3,5-$C_{10}CO_2H$
$C_{27}H_{46}O_4$
(434.66)

Colourless solid (98%, 4.27 g, 9.81 mmol, purity >93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H, C*H*$_3$), 1.23–1.40 (m, 24H, C*H*$_2$), 1.45 (q, *J* = 7.1 Hz, 4H, $OCH_2CH_2CH_2$), 1.72–1.83 (m, 4H, OCH_2CH_2), 3.98 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 6.69 (t, *J* = 2.1 Hz, 1H, 5-H), 7.23 (d, *J* = 2.1 Hz, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 26.0, 26.2, 29.2, 29.34, 29.39, 29.53, 29.58, 29.59, 29.63, 31.9 (*C*H$_2$), 68.4 (O*C*H$_2$), 107.5 (C-5), 108.2 (C-3), 131.0 (C-2), 160.3 (C-4), 172.1 (C=O) ppm; MS (ESI): *m*/*z* = 435.35 $[M + H]^+$, 457.33 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{27}H_{46}O_4$) calcd.: 435.3469 $[M + H]^+$, found: 435.3464. The spectroscopic data were in accordance with the literature.[20]

3,5-Bis(dodecyloxy)benzoic acid [3,5-$C_{12}CO_2H$]

According to GP3: 3,5-Bis(dodecyloxy)benzoic acid methyl ester **3,5-$C_{12}CO_2Me$** (5.05 g, 10.0 mmol), potassium hydroxide (1.35 g, 24.1 mmol), H_2O (15 mL), EtOH (70 mL).

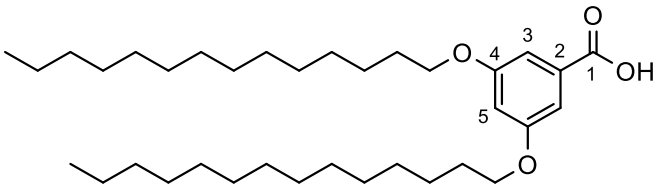


3,5-$C_{12}CO_2H$
$C_{31}H_{54}O_4$
(490.77)

Colourless solid (98%, 4.79 g, 9.76 mmol, purity >95%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 6H, C*H*$_3$), 1.17–1.56 (m, 36H, C*H*$_2$), 1.64–1.89 (m, 4H, OCH$_2$C*H*$_2$), 3.98 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 6.69 (t, *J* = 2.2 Hz, 1H, 5-H), 7.23 (d, *J* = 2.2 Hz, 2H, 3-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.0, 29.2, 29.4, 29.52, 29.58, 29.61, 29.65, 29.68, 31.9 (*C*H$_2$), 68.4 (O*C*H$_2$), 107.5 (C-5), 108.2 (C-3), 130.9 (C-2), 160.2 (C-4), 172.2 (C=O) ppm; MS (ESI): *m*/*z* = 491.41 [M + H]$^+$, 513.39 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{31}H_{54}O_4$) calcd.: 491.4095 [M + H]$^+$, found: 491.4097. The spectroscopic data were in accordance with the literature.[7]

3,5-Bis(tetradecyloxy)benzoic acid [3,5-$C_{14}CO_2H$]

According to GP3: 3,5-Bis(tetradecyloxy)benzoic acid methyl ester **3,5-$C_{14}CO_2Me$** (5.61 g, 10.0 mmol), potassium hydroxide (1.41 g, 25.1 mmol), H_2O (15 mL), EtOH (70 mL).

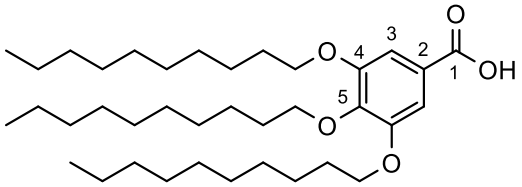


3,5-$C_{14}CO_2H$
$C_{35}H_{62}O_4$
(546.88)

Colourless solid (99%, 5.42 g, 9.91 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 6H, C*H*$_3$), 1.06–1.38 (m, 40H, C*H*$_2$), 1.37–1.60 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.94 (m, 4H, OCH$_2$C*H*$_2$), 3.95 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 6.65 (t, *J* = 2.3 Hz, 1H, 5-H), 7.19 (d, *J* = 2.3 Hz, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.1, 29.2, 29.40, 29.45, 29.63, 29.66, 29.70, 29.72, 29.74, 32.0 (*C*H$_2$), 68.3 (O*C*H$_2$), 107.2 (C-5), 108.0 (C-3), 131.7 (C-2), 160.2 (C-4), 171.9 (C=O) ppm; MS (ESI): *m*/*z* = 547.47 [M + H]$^+$, 569.46 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{62}O_4$) calcd.: 547.4721 [M + H]$^+$, found: 547.4724. The spectroscopic data were in accordance with the literature.[16]

3,4,5-Tris(decyloxy)benzoic acid [3,4,5-$C_{10}CO_2H$]

According to GP3: 3,4,5-Tris(decyloxy)benzoic acid ethyl ester **3,4,5-$C_{10}CO_2Et$** (6.19 g, 10.0 mmol), potassium hydroxide (1.43 g, 25.5 mmol), H_2O (15 mL), EtOH (70 mL).

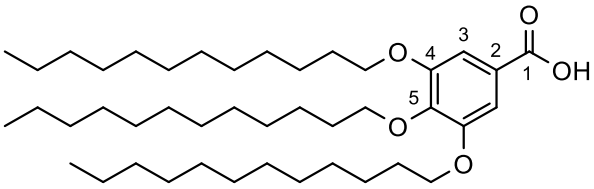


3,4,5-$C_{10}CO_2H$
$C_{37}H_{66}O_5$
(590.93)

Colourless solid (93%, 5.48 g, 9.28 mmol, purity >94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.42 (m, 36H, C*H*$_2$), 1.42–1.56 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.68–1.89 (m, 6H, OCH$_2$C*H*$_2$), 3.96–4.11 (m, 6H, OC*H*$_2$), 7.32 (s, 2H, 3-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.08, 26.12, 29.32, 29.36, 29.40, 29.44, 29.60, 29.63, 29.68, 29.71, 29.77, 30.4, 31.93, 31.95, 31.98 (*C*H$_2$), 69.2, 73.6 (O*C*H$_2$CH$_2$), 108.5 (C-3), 123.9 (C-2), 143.1 (C-5), 152.9 (C-4), 172.1 (C=O) ppm; MS (ESI): *m*/*z* = 591.50 $[M + H]^+$, 613.48 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{37}H_{66}O_5$) calcd.: 613.4802 $[M + Na]^+$, found: 613.4804. The spectroscopic data were in accordance with the literature.[17]

3,4,5-Tris(dodecyloxy)benzoic acid [3,4,5-$C_{12}CO_2H$]

According to GP3: 3,4,5-Tris(dodecyloxy)benzoic acid ethyl ester **3,4,5-$C_{12}CO_2Et$** (7.03 g, 10.0 mmol), potassium hydroxide (1.42 g, 25.3 mmol), (15 mL), EtOH (70 mL).

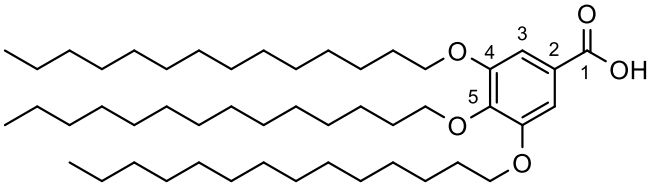


3,4,5-$C_{12}CO_2H$
$C_{43}H_{78}O_5$
(675.09)

Colourless solid (98%, 6.59 g, 9.77 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 9H, C*H*$_3$), 1.11–1.50 (m, 54H, C*H*$_2$), 1.49–1.76 (m, 6H, OCH$_2$C*H*$_2$), 3.67–3.91 (m, 6H, OC*H*$_2$), 7.03 (s, 2H, 3-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.07, 14.10 (*C*H$_3$), 22.70, 22.73, 26.25, 26.28, 26.40, 26.44, 29.43, 29.47, 29.50, 29.54, 29.67, 29.76, 29.82, 29.85, 29.89, 30.6, 31.98, 32.01 (*C*H$_2$), 69.1, 73.3 (O*C*H$_2$), 107.7 (C-3), 130.7 (C-2), 140.9 (C-5), 152.5 (C-4), 173.0 (C=O) ppm; MS (ESI): *m*/*z* = 675.59 $[M + H]^+$, 697.57 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{43}H_{78}O_5$) calcd.: 697.5741 $[M + Na]^+$, found: 697.5747. The spectroscopic data were in accordance with the literature.[17] Because of an impurity (s, 1.5H, δ_H = 5.21 ppm), the obtained signals are shifted by up to $\delta_H \approx \pm 0.30$ ppm and $\delta_C \approx \pm 3.0$ ppm.

3,4,5-Tris(tetradecyloxy)benzoic acid [3,4,5-$C_{14}CO_2H$]

According to GP3: 3,4,5-Tris(tetradecyloxy)benzoic acid ethyl ester **3,4,5-$C_{14}CO_2Et$** (7.87 g, 10.0 mmol), potassium hydroxide (1.38 g, 24.6 mmol), H_2O (15 mL), EtOH (70 mL).



3,4,5-$C_{14}CO_2H$
$C_{49}H_{90}O_5$
(759.25)

Colourless solid (quant., 7.59 g, 10.0 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.18–1.40 (m, 60H, C*H*$_2$), 1.41–1.54 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.67–1.96 (m, 6H, OCH$_2$C*H*$_2$), 3.91–4.13 (m, 6H, OC*H*$_2$), 7.32 (s, 2H, 3-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 26.08, 26.13, 29.3, 29.41, 29.42, 29.45, 29.60, 29.68, 29.70, 29.72, 29.75, 29.78, 30.4, 32.0 (*C*H$_2$), 69.2, 73.6 (O*C*H$_2$), 108.5 (C-3), 124.0 (C-2), 143.0 (C-5), 152.8 (C-4), 171.9 (C=O) ppm; MS (ESI): *m*/*z* = 759.69 $[M + H]^+$, 781.67 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{49}H_{90}O_5$) calcd.: 781.6680 $[M + Na]^+$, found: 781.6681. The spectroscopic data were in accordance with the literature.[17]

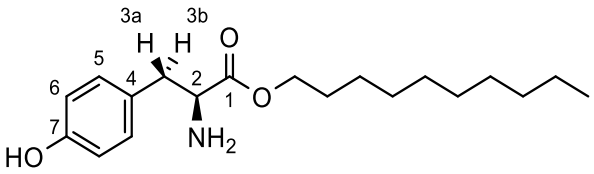
2.2 Synthesis of L-Tyrosine Based Guanidinium Chlorides and Salts

General Procedure GP4: Fischer esterification of L-tyrosine[1,21]

The amino acid L-tyrosine **Tyr** (10.1 g, 55.9 mmol), the respective alcohol ($C_{10}H_{21}OH$ and $C_{12}H_{25}OH$: 1.1 eq.; $C_{14}H_{29}OH$: 0.9 eq.) and *para*-toluenesulfonic acid (TsOH, 15.4 g, 81.0 mmol) were suspended in toluene (500 mL) and were heated for 48 h under reflux. Water was removed azeotropically with a Dean–Stark apparatus. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (600 mL), washed with sodium carbonate solution (3 × 100 mL, 10 wt% in H_2O), water (100 mL) and brine (2 × 100 mL). The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. Esterified L-tyrosinate **$TyrC_{14}$** was used without further purification. The crude products **$TyrC_{10}$** and **$TyrC_{12}$** were purified using column chromatography (SiO_2, gradient hexanes/EtOAc, 3 : 1 to pure EtOAc).

Decyl-L-tyrosinate [$TyrC_{10}$]

According to GP4: L-Tyrosine **Tyr** (10.1 g, 55.9 mmol), decanol (10.3 g, 64.8 mmol), TsOH (15.1 g, 79.5 mmol), toluene (500 mL); R_f = 0.18 – 0.48 (EtOAc, $KMnO_4$).

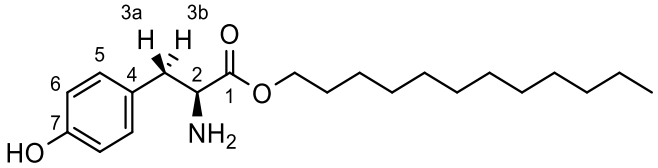


TyrC$_{10}$
$C_{19}H_{31}NO_3$
(321.46)

Colourless solid (66%, 11.9 g, 36.9 mmol, purity >89%); H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.16–1.46 (m, 14H, C*H*$_2$), 1.63 (t, *J* = 7.0 Hz, 2H, OCH$_2$C*H*$_2$), 2.81 (dd, *J* = 13.8 Hz, 7.7 Hz, 1H, 3a-H), 3.04 (dd, *J* = 13.8 Hz, 5.1 Hz, 1H, 3b-H), 3.71 (dd, *J* = 7.7 Hz, 5.1 Hz, 1H, H$_2$NC*H*), 4.12 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 6.66 (d, *J* = 8.2 Hz, 2H, 6-H), 6.99 (d, *J* = 8.2 Hz, 2H, 5-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.2, 29.3, 29.51, 29.54, 31.9 (*C*H$_2$), 39.8 (C-3), 55.6 (H$_2$N*C*H), 65.5 (O*C*H$_2$), 115.8 (C-6), 127.9 (C-4), 130.4 (C-5), 155.5 (C-7), 175.0 (C=O) ppm; MS (ESI): *m*/*z* = 322.24 $[M + H]^+$, 344.22 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{19}H_{31}NO_3$) calcd.: 322.2377 $[M + H]^+$, found: 322.2377. The compound was used without further purification.

Dodecyl-L-tyrosinate [TyrC$_{12}$]

According to GP4: L-Tyrosine **Tyr** (12.0 g, 66.5 mmol), dodecanol (13.0 g, 69.8 mmol), TsOH (15.0 g, 78.9 mmol), toluene (500 mL); R_f = 0.18 – 0.48 (EtOAc, $KMnO_4$).

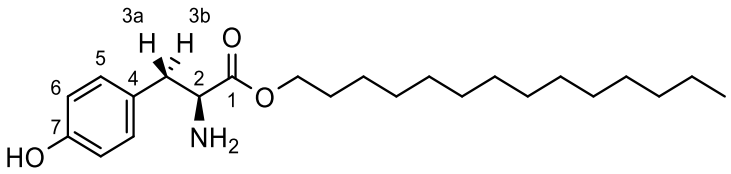


TyrC$_{12}$
$C_{21}H_{35}NO_3$
(349.52)

Colourless solid (88%, 20.5 g, 58.6 mmol, purity >91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.08–1.40 (m, 18H, C*H*$_2$), 1.56–1.76 (m, 2H, OCH$_2$C*H*$_2$), 2.82 (dd, *J* = 13.8 Hz, 7.7 Hz, 1H, 3a-H), 3.04 (dd, *J* = 13.8 Hz, 5.0 Hz, 1H, 3b-H), 3.72 (dd, *J* = 7.7 Hz, 5.0 Hz, 1H, H$_2$NC*H*), 4.12 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 6.69 (d, *J* = 8.4 Hz, 2H, 6-H), 6.99 (d, *J* = 8.4 Hz, 2H, 5-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.3, 29.4, 29.52, 29.59, 29.64, 29.66, 31.9 (*C*H$_2$), 39.8 (C-3), 55.6 (H$_2$N*C*H), 65.5 (O*C*H$_2$), 115.8 (C-6), 127.9 (C-4), 130.4 (C-5), 155.4 (C-7), 174.9 (C=O) ppm; MS (ESI): *m*/*z* = 350.27 $[M + H]^+$, 372.25 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{21}H_{35}NO_3$) calcd.: 350.2690 $[M + H]^+$, found: 350.2693. The compound was used without further purification.

Tetradecyl-L-tyrosinate [TyrC$_{14}$]

According to GP4: L-Tyrosine **Tyr** (10.3 g, 56.8 mmol), tetradecanol (11.0 g, 51.4 mmol), TsOH (15.3 g, 80.6 mmol), toluene (500 mL);



TyrC$_{14}$
$C_{23}H_{39}NO_3$
(377.57)

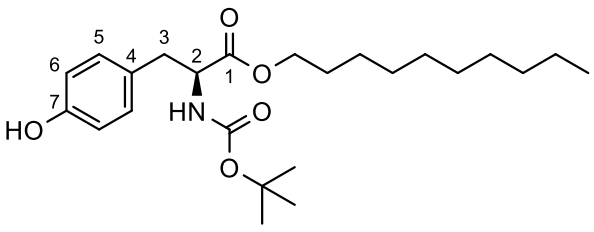
Colourless solid (93%, 18.0 g, 47.7 mmol, purity >93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.11–1.45 (m, 22H, C*H*$_2$), 1.50–1.83 (m, 2H, OCH$_2$C*H*$_2$), 2.81 (dd, *J* = 13.8 Hz, 7.7 Hz, 1H, 3a-H), 3.04 (dd, *J* = 13.8 Hz, 5.1 Hz, 1H, 3b-H), 3.71 (dd, *J* = 7.7 Hz, 5.1 Hz, 1H, H$_2$NC*H*), 4.12 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 6.67 (d, *J* = 8.1 Hz, 2H, 6-H), 7.00 (d, *J* = 8.1 Hz, 2H, 5-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.3, 29.4, 29.5, 29.60, 29.66, 29.69, 29.70, 31.9 (*C*H$_2$), 39.8 (C-3), 55.7 (H$_2$N*C*H), 65.4 (O*C*H$_2$), 115.7 (C-6), 127.9 (C-4), 130.4 (C-5), 155.2 (C-7), 175.0 (C=O) ppm; MS (ESI): *m*/*z* = 378.30 $[M + H]^+$, 400.28 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{23}H_{39}NO_3$) calcd.: 378.3003 $[M + H]^+$, found: 378.3009. The compound was used without further purification.

General Procedure GP5: *N*-Boc protection of L-tyrosinates[1,21,22]

The respective esterified L-tyrosinate **TyrC$_n$** (36.9 mmol) was dissolved in a mixture of acetone (120 mL) and water (60 mL) and a solution of sodium bicarbonate (9.66 g, 115 mmol) in water (60 mL) was added. Afterwards, di-*tert*-butyl dicarbonate (8.88 g, 40.6 mmol) was added and the mixture was stirred for 24 h at room temperature. Acetone was removed under reduced pressure and ethyl acetate (200 mL) was added. The organic phase was washed with diluted HCl (2 × 100 mL, 2.0 M in H_2O), H_2O (2 × 100 mL) and brine (100 mL). Subsequently, the organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. The crude products were purified by column chromatography (SiO_2, gradient hexanes/EtOAc, 20 : 1 → 5 : 1), followed by recrystallisation from hexanes.

Decyl-(*tert*-butoxycarbonyl)-L-tyrosinate [TyrC$_{10}$Boc]

According to GP5: Decyl-L-tyrosinate **TyrC$_{10}$** (11.5 g, 35.8 mmol), di-*tert*-butyl dicarbonate (8.88 g, 40.7 mmol), sodium bicarbonate (9.66 g, 115 mmol), acetone (120 mL), H_2O (120 mL); R_f = 0.30 (hexanes/EtOAc = 5 : 1, $KMnO_4$).

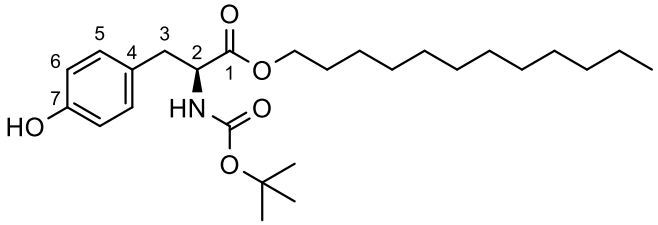


TyrC$_{10}$Boc
$C_{24}H_{39}NO_5$
(421.58)

Colourless solid (96%, 14.4 g, 34.2 mmol, purity >94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.27 (d, *J* = 7.4 Hz, 14H, C*H*$_2$), 1.42 (s, 9H, OC(C*H*$_3$)$_3$), 1.56–1.65 (m, 2H, OCH$_2$C*H*$_2$), 2.78–3.20 (m, 2H, 3-H), 3.93–4.18 (m, 2H, OC*H*$_2$), 4.38–4.66 (m, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 6.72 (d, *J* = 8.0 Hz, 2H, 6-H), 6.96 (d, *J* = 8.0 Hz, 2H, 5-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 27.4, 28.3, 28.5, 29.2, 29.3, 29.50, 29.54, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.7 (C-3), 54.7 (C-2), 65.7 (O*C*H$_2$), 80.1 (O*C*(CH$_3$)$_3$), 115.5 (C-6), 127.6 (C-4), 130.4 (C-5), 155.2 (C-7), 155.3 (HNC=O), 172.3 (C-1) ppm; MS (ESI): *m*/*z* = 422.29 [M + H]$^+$, 444.27 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{24}H_{39}NO_5$) calcd.: 444.2720 [M + Na]$^+$, found: 444.2720. The spectroscopic data were in accordance with the literature.[1]

Dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate [TyrC$_{12}$Boc]

According to GP5: Dodecyl-L-tyrosinate **TyrC$_{12}$** (20.5 g, 58.7 mmol), di-*tert*-butyl dicarbonate (14.3 g, 65.5 mmol), sodium bicarbonate (15.0 g, 179 mmol), acetone (150 mL), H_2O (150 mL); R_f = 0.30 (hexanes/EtOAc = 5 : 1, $KMnO_4$).

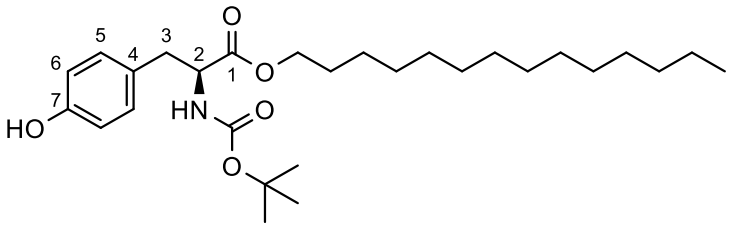


TyrC$_{12}$Boc
$C_{26}H_{43}NO_5$
(449.63)

Colourless solid (91%, 24.0 g, 53.4 mmol, purity >92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74–1.08 (m, 3H, C*H*$_3$), 1.06–1.33 (m, 18H, C*H*$_2$), 1.42 (s, 9H, OC(C*H*$_3$)$_3$), 1.53–1.79 (m, 2H, OCH$_2$C*H*$_2$), 2.80–3.32 (m, 2H, 3-H), 4.09 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 4.41–4.61 (m, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 6.72 (d, *J* = 8.0 Hz, 2H, 6-H), 6.96 (d, *J* = 8.0 Hz, 2H, 5-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.35, 29.49, 29.58, 29.63, 29.65, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.6 (C-3), 54.7 (C-2), 65.7 (O*C*H$_2$), 80.1 (O*C*(CH$_3$)$_3$), 115.5 (C-6), 127.6 (C-4), 130.4 (C-5), 155.1 (C-7), 155.3 (HNC=O), 172.3 (C-1) ppm; MS (ESI): *m*/*z* = 450.32 [M + H]$^+$, 472.30 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{26}H_{43}NO_5$) calcd.: 472.3033 [M + Na]$^+$, found: 472.3034. The spectroscopic data were in accordance with the literature.[1]

Tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate [TyrC$_{14}$Boc]

According to GP5: Tetradecyl-L-tyrosinate **TyrC$_{14}$** (17.9 g, 47.4 mmol), di-*tert*-butyl dicarbonate (11.8 g, 54.1 mmol), sodium bicarbonate (12.0 g, 143 mmol), acetone (150 mL), H_2O (150 mL); R_f = 0.30 (hexanes/EtOAc = 5 : 1, $KMnO_4$).



TyrC$_{14}$Boc
$C_{28}H_{47}NO_5$
(477.69)

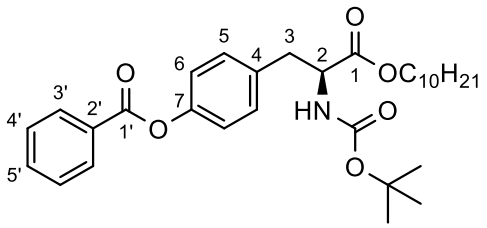
Colourless solid (88%, 19.8 g, 41.5 mmol, purity >95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.12–1.33 (m, 22H, C*H*$_2$), 1.42 (s, 9H, OC(C*H*$_3$)$_3$), 1.51–1.77 (m, 2H, OCH$_2$C*H*$_2$), 2.77–3.27 (m, 2H, 3-H), 4.09 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 4.52 (d, *J* = 7.2 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 6.71 (d, *J* = 8.0 Hz, 2H, 6-H), 6.96 (d, *J* = 8.0 Hz, 2H, 5-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.60, 29.66, 29.69, 29.70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.7 (C-3), 54.7 (C-2), 65.7 (O*C*H$_2$), 80.2 (O*C*(CH$_3$)$_3$), 115.5 (C-6), 127.5 (C-4), 130.4 (C-5), 155.1 (C-7), 155.3 (HNC=O), 172.3 (C-1) ppm; MS (ESI): *m*/*z* = 478.35 $[M + H]^+$, 500.33 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{28}H_{47}NO_5$) calcd.: 500.3346 $[M + Na]^+$, found: 500.3345. The spectroscopic data were in accordance with the literature.[1]

General Procedure GP6: Steglich esterification of L-tyrosinates and benzoic acid derivatives[1,23]

The respective etherified benzoic acid **Ar(C$_m$)CO$_2$H** (2.00 mmol), the respective alkyl-(*tert*-butoxy-carbonyl)-L-tyrosinate **TyrC$_n$Boc** (2.00 mmol) and 4-dimehtylaminopyridine (DMAP, 48.8 mg, 0.40 mmol) were dissolved in dry CH_2Cl_2 (100 mL) under a nitrogen atmosphere. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI, 767 mg, 4.00 mmol) was added and the mixture was stirred for 24 – 72 h at room temperature. Afterwards, the mixture was washed with water (3 × 50 mL) and brine (3 × 50 mL). The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. The crude products were purified by column chromatography (SiO_2, gradient hexanes/EtOAc).

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl benzoate [BzTyrC$_{10}$Boc]

According to GP6: Benzoic acid **BzCO$_2$H** (320 mg, 2.62 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{10}$Boc** (1.11 g, 2.63 mmol), EDCI (1.05 g, 5.48 mmol), DMAP (72.0 mg, 0.59 mmol), dry CH_2Cl_2 (70 mL); reaction time: 24 h; column gradient 15 : 1 → 11 : 1; R_f = 0.38 (PE/EtOAc = 10 : 1).

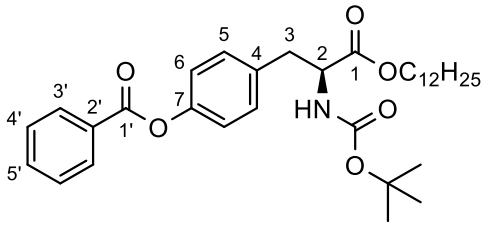


BzTyrC$_{10}$Boc
$C_{31}H_{43}NO_6$
(525.69)

Colourless oil (92%, 1.27 g, 2.42 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.23–1.31 (m, 14H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.58–1.64 (m, 2H, OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.06–4.14 (m, 2H, OC*H*$_2$), 4.59 (q, *J* = 6.6 Hz, 1H, 2-H), 5.03 (d, *J* = 8.2 Hz, 1H, NH), 7.15 (d, *J* = 8.5 Hz, 2H, 6-H), 7.20 (d, *J* = 8.5 Hz, 2H, 5-H), 7.51 (t, *J* = 8.4 Hz, 2H, 4'-H), 7.62–7.65 (m, 1H, 5'-H), 8.19 (d, *J* = 8.4 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.3, 29.50, 29.55, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 121.7 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.2 (C-3'), 130.4 (C-5), 133.6 (C-5'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 165.1 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3382 (w), 2925 (m), 2855 (m), 1737 (s), 1714 (s), 1601 (w), 1507 (s), 1452 (m), 1392 (w), 1365 (m), 1262 (vs), 1198 (vs), 1164 (vs), 1103 (w), 1080 (m), 1060 (vs), 1023 (s), 939 (w), 862 (w), 797 (w), 780 (w), 733 (w), 706 (vs), 685 (w), 672 (w), 553 (w), 520 (w), 461 (w) cm^{-1}; MS (ESI): *m*/*z* = 543.34 [M + NH$_4$]$^+$, 548.30 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{31}H_{43}NO_6$) calcd.: 543.3429 [M + NH$_4$]$^+$, found: 543.3429.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl benzoate [BzTyrC$_{12}$Boc]

According to GP6: Benzoic acid **BzCO$_2$H** (290 mg, 2.38 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{12}$Boc** (1.07 g, 2.38 mmol), EDCI (965 mg, 5.03 mmol), DMAP (68.0 mg, 0.56 mmol), dry CH_2Cl_2 (70 mL); reaction time: 24 h; column gradient 14 : 1 → 11 : 1; R_f = 0.38 (PE/EtOAc = 10 : 1).



BzTyrC$_{12}$Boc

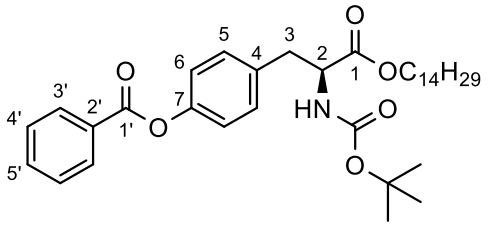
$C_{33}H_{47}NO_6$

(553.74)

Colourless solid (90%, 1.19 g, 2.14 mmol, purity >95%); M.p. 66.4 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.25–1.31 (m, 18H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.58–1.63 (m, 2H, OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.06–4.14 (m, 2H, OC*H*$_2$), 4.59 (q, *J* = 6.3 Hz, 1H, 2-H), 5.02 (d, *J* = 8.3 Hz, 1H, NH), 7.15 (d, *J* = 8.5 Hz, 2H, 6-H), 7.20 (d, *J* = 8.5 Hz, 2H, 5-H), 7.51 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.62–7.65 (m, 1H, 5'-H), 8.19 (d, *J* = 7.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.61, 29.63, 29.65, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 121.7 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.2 (C-3'), 130.4 (C-5), 133.6 (C-5'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 165.1 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3372 (w), 2924 (m), 2854 (m), 1738 (s), 1714 (s), 1601 (w), 1507 (m), 1452 (m), 1391 (w), 1365 (m), 1262 (vs), 1198 (vs), 1164 (vs), 1103 (w), 1080 (m), 1060 (vs), 1023 (s), 874 (w), 798 (w), 780 (w), 706 (vs), 685 (w), 673 (w), 522 (w), 463 (w) cm^{-1}; MS (ESI): *m*/*z* = 571.37 [M + NH$_4$]$^+$, 576.33 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{33}H_{47}NO_6$) calcd.: 571.3742 [M + NH$_4$]$^+$, found: 571.3741.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl benzoate [BzTyrC$_{14}$Boc]

According to GP6: Benzoic acid **BzCO$_2$H** (308 mg, 2.52 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (1.21 g, 2.52 mmol), EDCI (1.04 g, 5.43 mmol), DMAP (81.0 mg, 0.66 mmol), dry CH_2Cl_2 (70 mL); reaction time: 24 h; column gradient 14 : 1 → 11 : 1; R_f = 0.38 (PE/EtOAc = 10 : 1).



BzTyrC$_{14}$Boc

$C_{35}H_{51}NO_6$

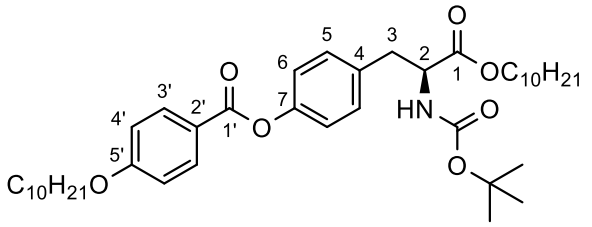
(581.79)

Colourless solid (90%, 1.32 g, 2.26 mmol, purity >95%); M.p. 60.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.25–1.31 (m, 22H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.56–1.66 (m, 2H, OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.06–4.14 (m, 2H, OC*H*$_2$), 4.59 (q, *J* = 6.7 Hz, 1H, 2-H), 5.03 (d, *J* = 8.2 Hz, 1H, NH), 7.15 (d, *J* = 8.5 Hz, 2H, 6-H), 7.20

(d, J = 8.5 Hz, 2H, 5-H), 7.51 (t, J = 7.8 Hz, 2H, 4'-H), 7.62–7.65 (m, 1H, 5'-H), 8.19 (d, J = 7.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.61, 29.66, 29.69, 31.9 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (OCH_2), 79.9 ($OC(CH_3)_3$), 121.7 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.2 (C-3'), 130.4 (C-5), 133.6 (C-5'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 165.1 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3376 (w), 2923 (s), 2853 (m), 1739 (s), 1715 (s), 1601 (w), 1507 (s), 1452 (m), 1391 (w), 1365 (m), 1262 (vs), 1198 (vs), 1164 (vs), 1103 (w), 1080 (m), 1060 (vs), 1023 (s), 873 (w), 798 (w), 706 (vs), 685 (w), 673 (w), 521 (w), 464 (w) cm^{-1}; MS (ESI): m/z = 599.41 $[M + NH_4]^+$, 604.36 $[M + Na]^+$; HRMS (ESI): m/z ($C_{35}H_{51}NO_6$) calcd.: 599.4055 $[M + NH_4]^+$, found: 599.4054.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 4-(decyloxy)benzoate [4-C$_{10}$TyrC$_{10}$Boc]

According to GP6: 4-Decyloxy-benzoic acid **4-C$_{10}$CO$_2$H** (690 mg, 2.48 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{10}$Boc** (1032 mg, 2.45 mmol), EDCI (950 mg, 4.96 mmol), DMAP (80.0 mg, 0.65 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.



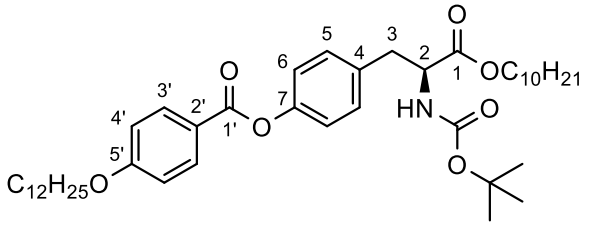
4-C$_{10}$TyrC$_{10}$Boc
$C_{41}H_{63}NO_7$
(681.96)

Colourless solid (84%, 1.40 g, 2.06 mmol); M.p. 60.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 6H, CH_3), 1.27 (d, 26H, J = 11.7 Hz, CH_2), 1.44–1.52 (m, 11H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.57–1.63 (m, 2H, $COOCH_2CH_2$), 1.79–1.84 (m, 2H, OCH_2CH_2), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, J = 6.6 Hz, 2H, OCH_2), 4.06–4.13 (m, 2H, $COOCH_2$), 4.58 (q, J = 6.5 Hz, 1H, 2-H), 5.03 (d, J = 8.2 Hz, 1H, NH), 6.96 (d, J = 8.9 Hz, 2H, 4'-H), 7.13 (d, J = 8.5 Hz, 2H, 6-H), 7.18 (d, J = 8.2 Hz, 2H, 5-H), 8.12 (d, J = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.3, 29.4, 29.51, 29.56, 31.90 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.5 (C-2), 65.6 ($COOCH_2$), 68.3 (OCH_2), 79.9 ($OC(CH_3)_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 520 (w), 631 (w), 651 (w), 692 (w), 722 (w). 763 (m), 845 (m), 1008 (m), 1018 (m), 1065 (s), 1104 (w), 1161 (vs), 1200 (s), 1252 (vs), 1365 (m), 1391 (w), 1422 (w), 1467 (m), 1510 (s), 1580 (w),

1605 (m), 1715 (s), 1733 (s), 2854 (m), 2923 (m), 3374 (w) cm^{-1}; MS (ESI): *m*/*z* = 699.49 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{41}H_{63}NO_7$) calcd.: 699.4943 $[M + NH_4]^+$, found: 699.4935.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 4-(dodecyloxy)benzoate [4-C_{12}TyrC_{10}Boc]

According to GP6: 4-Dodecyloxy-benzoic acid **4-$C_{12}CO_2H$** (743 mg, 2.42 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (984 mg, 2.33 mmol), EDCI (886 mg, 4.62 mmol), DMAP (75.0 mg, 0.61 mmol), CH_2Cl_2 (100 mL); reaction time: 48 h.

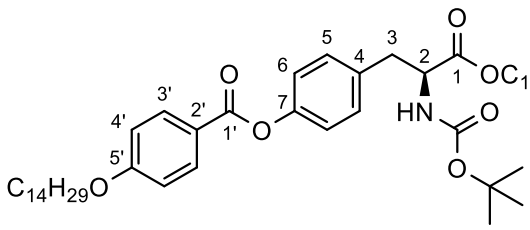


4-C_{12}TyrC_{10}Boc
$C_{43}H_{67}NO_7$
(710.01)

Colourless solid (84%, 1.40 g, 1.97 mmol); M.p. 66.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.91 (m, 6H, C*H*$_3$), 1.27 (d, 30H, C*H*$_2$), 1.44–1.52 (m, 11H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.55–1.63 (m, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.05–4.14 (m, 2H, $COOCH_2$), 4.58 (q, *J* = 6.6 Hz, 1H, 2-H), 5.02 (d, *J* = 8.3 Hz, 1H, NH), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.18 (d, *J* = 8.2 Hz, 2H, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.3, 29.4, 29.51, 29.56, 29.59, 29.64, 29.66, 31.90, 31.93 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.5 (C-2), 65.6 ($COOCH_2$), 68.3 (OCH_2), 79.9 ($OC(CH_3)_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 522 (w), 632 (w), 651 (w), 692 (w), 722 (w), 763 (m), 845 (m), 1008 (m), 1018 (m), 1065 (s), 1104 (w), 1161 (vs), 1200 (s), 1252 (vs), 1313 (w), 1365 (m), 1391 (w), 1422 (w), 1467 (m), 1510 (s), 1580 (w), 1605 (m), 1716 (s), 1733 (s), 2853 (m), 2923 (m), 3374 (w) cm^{-1}; MS (ESI): *m*/*z* = 727.52 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{43}H_{67}NO_7$) calcd.: 727.5256 $[M + NH_4]^+$, found: 727.5246.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 4-(tetradecyloxy)benzoate [4-C_{14}TyrC_{10}Boc]

According to GP6: 4-Tetradecyloxy-benzoic acid **4-$C_{14}CO_2H$** (781 mg, 2.33 mmol), decyl-(*tert*- butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (980 mg, 2.32 mmol), EDCI (863 mg, 4.50 mmol), DMAP (89.0 mg, 0.73 mmol), CH_2Cl_2 (100 mL); reaction time: 48 h.



4-C$_{14}$TyrC$_{10}$Boc

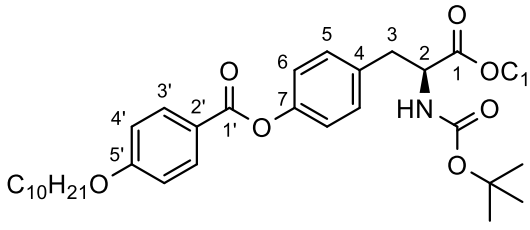
$C_{45}H_{71}NO_7$

(738.06)

Colourless solid (78%, 1.34 g, 1.82 mmol); M.p. 60.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 6H, C*H*$_3$), 1.27 (d,, *J* = 10.2 Hz, 34H, C*H*$_2$), 1.44–1.52 (m, 11H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.05–4.15 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.6 Hz, 1H, 2-H), 5.01 (d, *J* = 8.3 Hz, 1H, NH), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.18 (d, *J* = 8.2 Hz, 2H, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.3, 29.4, 29.51, 29.56, 29.60, 29.66, 29.68, 29.70, 31.90, 31.93 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 522 (w), 650 (w), 692 (w), 722 (w), 763 (w), 846 (w), 1019 (m), 1068 (m), 1104 (w), 1164 (vs), 1201 (s), 1254 (vs), 1313 (w), 1366 (m), 1391 (w), 1422 (w), 1467 (w), 1511 (m), 1580 (w), 1606 (m), 1735 (s), 2853 (m), 2923 (s), 3369 (w) cm^{-1}; MS (ESI): *m*/*z* = 755.55 [M + NH$_4$]$^+$; HRMS (ESI): *m*/*z* ($C_{45}H_{71}NO_7$) calcd.: 755.5569 [M + NH$_4$]$^+$, found: 755.5558.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 4-(decyloxy)benzoate [4-C$_{10}$TyrC$_{12}$Boc]

According to GP6: 4-Decyloxy-benzoic acid **4-C$_{10}$CO$_2$H** (606 mg, 2.18 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{12}$Boc** (956 mg, 2.13 mmol), EDCI (825 mg, 4.30 mmol), DMAP (53.0 mg, 0.43 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.



4-C$_{10}$TyrC$_{12}$Boc

$C_{43}H_{67}NO_7$

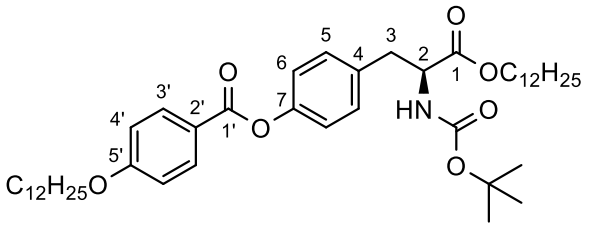
(710.01)

Colourless solid (79%, 1.20 g, 1.69 mmol); M.p. 68.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 6H, C*H*$_3$), 1.27 (d, 30H, C*H*$_2$), 1.44–1.52 (m, 11H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, *J* = 14.7 Hz, 6.7 Hz, 2H, OCH$_2$C*H*$_2$), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.05–4.15 (m, 2H,

COOC*H*$_2$), 4.58 (q, *J* = 6.7 Hz, 1H, 2-H), 5.01 (d, *J* = 8.1 Hz, 1H, NH), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.18 (d, *J* = 8.3 Hz, 2H, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.3, 29.4, 29.51, 29.55, 29.61, 29.65, 29.66, 31.90, 31.92 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 412 (w), 429 (w), 455 (w), 526 (m), 577 (w), 630 (w), 652 (m), 692 (m), 724 (m), 763 (m), 788 (m), 820 (w), 846 (m), 863 (w), 881 (w), 899 (w), 943 (w), 987 (m), 1018 (s), 1040 (m), 1064 (s), 1107 (w), 1165 (vs), 1200 (vs), 1264 (vs), 1366 (m), 1390 (w), 1422 (w), 1470 (m), 1510 (vs), 1579 (w), 1605 (m), 1700 (s), 1726 (s), 1742 (s), 2851 (m), 2919 (s), 3371 (w) cm^{-1}; MS (ESI): *m*/*z* = 727.53 [M + NH$_4$]$^+$; HRMS (ESI): *m*/*z* ($C_{43}H_{67}NO_7$) calcd.: 727.5256 [M + NH$_4$]$^+$, found: 727.5252.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 4-(dodecyloxy)benzoate [4-C$_{12}$TyrC$_{12}$Boc]

According to GP6: 4-Dodecyloxy-benzoic acid **4-C$_{12}$CO$_2$H** (678 mg, 2.21 mmol), dodecyl-(*tert*- butoxycarbonyl)-L-tyrosinate **TyrC$_{12}$Boc** (973 mg, 2.16 mmol), EDCI (844 mg, 4.40 mmol), DMAP (53.0 mg, 0.43 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.



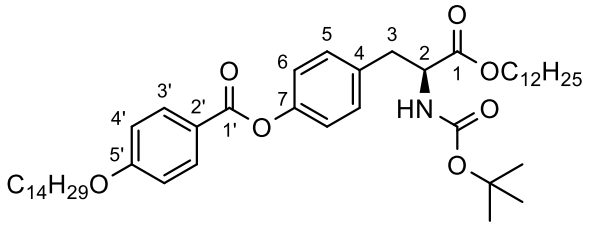
4-C$_{12}$TyrC$_{12}$Boc
$C_{45}H_{71}NO_7$
(738.06)

Colourless solid (77%, 1.22 g, 1.66 mmol); M.p. 52.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 6H, C*H*$_3$), 1.26 (d, *J* = 9.3 Hz, 34H, C*H*$_2$), 1.44–1.52 (m, 11H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.05–4.15 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.6 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 6.96 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.18 (d, *J* = 8.3 Hz, 2H, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.4, 29.51, 29.57, 29.60, 29.62, 29.65, 29.67, 31.93 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.5 (C-2), 65.6 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 518 (w), 631 (w), 651 (w), 692 (w), 722 (w), 763 (m), 845 (m), 1008

(m), 1018 (m), 1065 (s), 1103 (w), 1162 (vs), 1200 (s), 1252 (vs), 1365 (m), 1391 (w), 1422 (w), 1467 (m), 1510 (m), 1580 (w), 1605 (m), 1716 (s), 1734 (s), 2853 (m), 2922 (s), 3382 (w) cm^{-1}; MS (ESI): *m*/*z* = 755.56 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{45}H_{71}NO_7$) calcd.: 755.5569 $[M + NH_4]^+$, found: 755.5568.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 4-(tetradecyloxy)benzoate [4-C_{14}TyrC_{12}Boc]

According to GP6: 4-Tetradecyloxy-benzoic acid **4-$C_{14}CO_2H$** (768 mg, 2.23 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (1003 mg, 2.23 mmol), EDCI (859 mg, 4.48 mmol), DMAP (58.0 mg, 0.50 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.

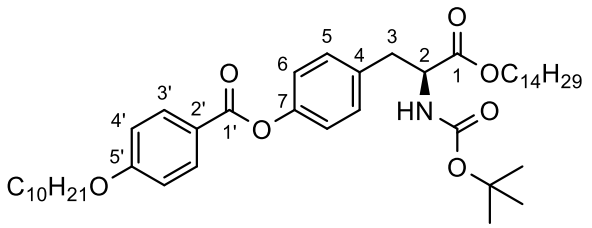


4-C_{14}TyrC_{12}Boc
$C_{47}H_{75}NO_7$
(766.12)

Colourless solid (76%, 1.30 g, 1.70 mmol); M.p. 59.9 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 6H, C*H*$_3$), 1.26 (d,, *J* = 7.4 Hz, 38H, C*H*$_2$), 1.44–1.52 (m, 11H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.57–1.63 (m, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.5 Hz, 2H, OCH_2), 4.05–4.14 (m, 2H, $COOCH_2$), 4.58 (q, *J* = 6.5Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.96 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.18 (d, *J* = 8.2 Hz, 2H, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.4, 29.51, 29.57, 29.60, 29.62, 29.65, 29.66, 29.68, 29.70, 31.93 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.6 ($COOCH_2$), 68.3 (OCH_2), 79.9 ($OC(CH_3)_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 428 (w), 526 (w), 631 (w), 651 (w), 692 (w), 722 (w), 762 (m), 845 (m), 1009 (m), 1018 (m), 1068 (s), 1104 (w), 1162 (vs), 1199 (s), 1252 (vs), 1366 (m), 1391 (w), 1421 (w), 1467 (m), 1510 (s), 1580 (w), 1606 (m), 1693 (m), 1733 (s), 2852 (m), 2921 (s), 3372 (w) cm^{-1}; MS (ESI): *m*/*z* = 783.59 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{47}H_{75}NO_7$) calcd.: 783.5882 $[M + NH_4]^+$, found: 783.5880.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 4-(decyloxy)benzoate [4-C_{10}TyrC$_{14}$Boc]

According to GP6: 4-Decyloxy-benzoic acid **4-$C_{10}CO_2H$** (558 mg, 2.00 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (958 mg, 2.01 mmol), EDCI (774 mg, 4.04 mmol), DMAP (54.0 mg, 0.44 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.

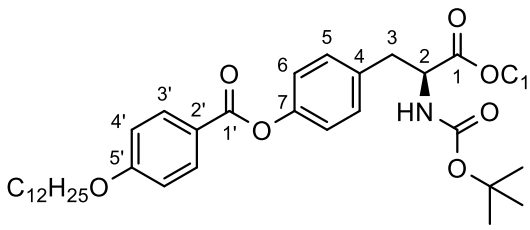


4-C_{10}TyrC$_{14}$Boc
$C_{45}H_{71}NO_7$
(738.06)

Colourless solid (81%, 1.21 g, 1.63 mmol); M.p. 65.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.92(m, 6H, C*H*$_3$), 1.26 (d, *J* = 16.2 Hz, 34H, C*H*$_2$), 1.44–1.52 (m, 11H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 11.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 3.04–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 4.05–4.14 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 7.1 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.18 (d, *J* = 8.6 Hz, 2H, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.3, 29.4, 29.51, 29.55, 29.57, 29.62, 29.67, 29.70, 31.90, 31.93 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.5 (C-2), 65.6 (COO*C*H$_2$), 68.3 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 523 (w), 568 (w), 632 (w), 651 (w), 692 (w), 722 (w), 763 (m), 784 (w), 847 (w), 879 (w), 1019 (m), 1072 (m), 1106 (w), 1166 (vs), 1200 (s), 1255 (vs), 1366 (w), 1392 (w), 1422 (w), 1469 (m), 1512 (s), 1580 (w), 1607 (m), 1691 (s), 1727 (s), 2851 (s), 2919 (vs), 3377 (w) cm^{-1}; MS (ESI): *m*/*z* = 755.56 $[M + NH_4]^+$, 1493.11 $[2M + NH_4]^{2+}$; HRMS (ESI): *m*/*z* ($C_{45}H_{71}NO_7$) calcd.: 755.5569 $[M + NH_4]^+$, found: 755.5565.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 4-(dodecyloxy)benzoate [4-C_{12}TyrC$_{14}$Boc]

According to GP6: 4-Dodecyloxy-benzoic acid **4-$C_{12}CO_2H$** (620 mg, 2.02 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (965 mg, 2.02 mmol), EDCI (740 mg, 3.86 mmol), DMAP (69.0 mg, 0.56 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.

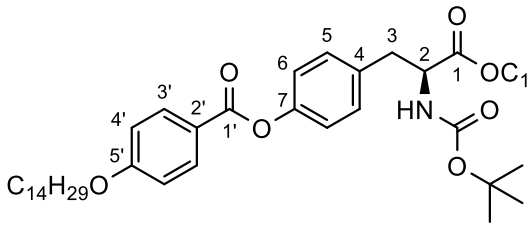


4-C$_{12}$TyrC$_{14}$Boc
$C_{47}H_{75}NO_7$
(766.12)

Colourless solid (77%, 1.19 g, 1.56 mmol); M.p. 64.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.91 (m, 6H, C*H*$_3$), 1.32 (d, *J* = 10.1 Hz, 38H, C*H*$_2$), 1.44–1.52 (m, 11H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.55–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.84 (m, 2H, OCH$_2$C*H*$_2$), 3.04–3.17 (m, 2H, 3-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.05–4.15 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 7.1 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.18 (d, *J* = 8.3 Hz, 2H, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.36, 29.37, 29.51, 29.57, 29.60, 29.62, 29.64, 29.67, 29.70, 31.93 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.5 (C-2), 65.6 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 420 (w), 431 (w), 464 (w), 511 (w), 529 (w), 567 (w), 631 (w), 650 (w), 691 (w), 722 (w), 762 (m), 783 (w), 846 (m), 879 (w), 1019 (m), 1070 (s), 1105 (w), 1163 (vs), 1199 (s), 1253 (vs), 1366 (m), 1392 (w), 1421 (w), 1468 (m), 1510 (s), 1580 (w), 1606 (m), 1692 (m), 1726 (s), 2851 (m), 2919 (s), 3375 (w) cm^{-1}; MS (ESI): *m*/*z* = 783.59 $[M + NH_4]^+$, 788.54 $[M + Na]^+$, 1550.13 $[2M + H + NH_4]^{2+}$; HRMS (ESI): *m*/*z* ($C_{47}H_{75}NO_7$) calcd.: 783.5882 $[M + NH_4]^+$, found: 783.5882.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 4-(tetradecyloxy)benzoate [4-C$_{14}$TyrC$_{14}$Boc]

According to GP6: 4-Tetradecyloxy-benzoic acid **4-C$_{14}$CO$_2$H** (676.0 mg, 2.02 mmol), tetradecyl-*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (962 mg, 2.01 mmol), EDCI (741 mg, 3.87 mmol), DMAP (56.0 mg, 0.46 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h.



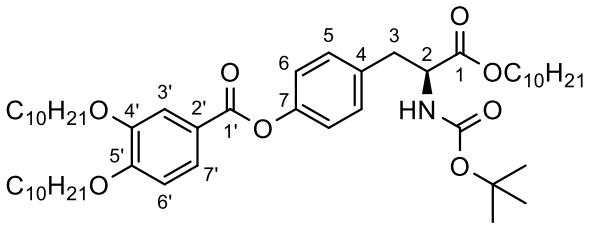
4-C$_{14}$TyrC$_{14}$Boc
$C_{49}H_{79}NO_7$
(794.17)

Colourless solid (75%, 1.20 g, 1.51 mmol); M.p. 78.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 6H, C*H*$_3$), 1.26 (d, *J* = 8.2 Hz, 42H, C*H*$_2$), 1.40–1.51 (m, 11H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.55–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, *J* = 6.7 Hz, 2H,

OCH_2CH_2), 3.05–3.17 (m, 2H, 3-H), 4.04 (t, J = 6.5 Hz, 2H, OCH_2), 4.07–4.13 (m, 2H, $COOCH_2$), 4.58 (q, J = 5.8 Hz, 1H, 2-H), 5.01 (d, J = 7.9 Hz, 1H, NH), 6.96 (d, J = 8.8 Hz, 2H, 4'-H), 7.13 (d, J = 8.5 Hz, 2H, 6-H), 7.18 (d, J = 8.4 Hz, 2H, 5-H), 8.12 (d, J = 9.0 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.1, 29.2, 29.4, 29.51, 29.57, 29.60, 29.62, 29.67, 29.70, 31.93 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.5 (C-2), 65.6 ($COOCH_2$), 68.3 (OCH_2), 79.9 ($OC(CH_3)_3$), 114.3 (C-4'), 121.5 (C-2'), 121.8 (C-6), 130.3 (C-5), 132.2 (C-3'), 133.5 (C-4), 150.1 (C-7), 155.1 (HNC=O), 163.5 (C-5'), 164.8 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 430 (w), 528 (w), 631 (w) 648 (w), 692 (w), 732 (s), 763 (m), 846 (m), 879 (w), 908 (m), 1009 (m), 1019 (m), 1068 (s), 1104 (w), 1163 (vs), 1200 (s), 1253 (vs), 1366 (w), 1392 (w), 1422 (w), 1467 (m), 1511 (s), 1580 (w), 1606 (m), 1723 (m), 2852 (m), 2921 (s), 3374 (w) cm^{-1}; MS (ESI): m/z = 811.62 $[M + NH_4]^+$, 816.57 $[M + Na]^+$; HRMS (ESI): m/z ($C_{49}H_{79}NO_7$) calcd.: 811.6195 $[M + NH_4]^+$, found: 811.6193, calcd.: 816.5749 $[M + Na]^+$, found: 816.5747.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,4-bis(decyloxy)-benzoate [3,4-C_{10}TyrC_{10}Boc]

According to GP6: 3,4-Bis(decyloxy)benzoic acid **3,4-$C_{10}CO_2H$** (988 mg, 2.27 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (957 mg, 2.27 mmol), EDCI (886 mg, 4.62 mmol), DMAP (70.0 mg, 0.57 mmol), dry CH_2Cl_2 (100 mL); reaction time: 24 h; column gradient 15 : 1 → 11 : 1; R_f = 0.36 (PE/EtOAc = 10 : 1).



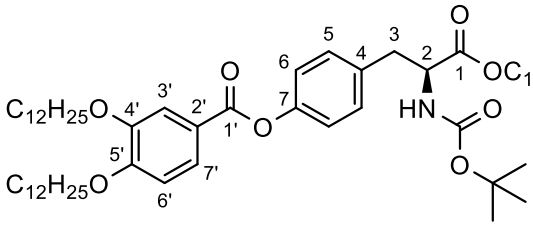
3,4-C_{10}TyrC_{10}Boc
$C_{51}H_{83}NO_8$
(838.22)

Colourless solid (86%, 1.64 g, 1.96 mmol, purity >95%); M.p. 66.8 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, CH_3), 1.23–1.39 (m, 38H, CH_2), 1.41–1.51 (m, 13H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.61 (dt, J = 14.3 Hz, 6.9 Hz, 2H, $COOCH_2CH_2$), 1.82–1.88 (m, 4H, OCH_2CH_2), 3.07–3.15 (m, 2H, 3-H), 4.04–4.13 (m, 6H, OCH_2), 4.58 (q, J = 6.6 Hz, 1H, 2-H), 5.01 (d, J = 8.2 Hz, 1H, NH), 6.92 (d, J = 8.5 Hz, 1H, 6'-H), 7.13 (d, J = 8.1 Hz, 2H, 6-H), 7.18 (d, J = 8.1 Hz, 2H, 5-H), 7.65 (d, J = 2.0 Hz, 1H, 3'-H), 7.79 (dd, J = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.11, 14.13 (CH_3), 22.64, 22.69, 22.70, 25.86, 25.98, 26.02, 28.3, 28.5, 29.06, 29.18, 29.23, 29.32, 29.36, 29.39, 29.42, 29.51, 29.56, 29.58, 29.59, 29.62, 29.64, 31.89, 31.93 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.6 ($COOCH_2$),

69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3378 (w), 2923 (s), 2853 (m), 1718 (s), 1599 (m), 1509 (s), 1467 (m), 1428 (m), 1391 (m), 1366 (m), 1347 (m), 1270 (vs), 1194 (vs), 1132 (s), 1103 (w), 1064 (m), 1018 (m), 959 (w), 911 (w), 870 (w), 817 (w), 779 (w), 756 (m), 731 (m), 647 (w), 517 (w) cm^{-1}; MS (ESI): *m*/*z* = 855.65 [M + NH$_4$]$^+$; HRMS (ESI): *m*/*z* (C$_{51}$H$_{83}$NO$_8$) calcd.: 855.6457 [M + NH$_4$]$^+$, found: 855.6458.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,4-bis(dodecyloxy)benzoate [3,4-C$_{12}$TyrC$_{10}$Boc]

According to GP6: 3,4-Bis(dodecyloxy)benzoic acid **3,4-C$_{12}$CO$_2$H** (1.08 g, 2.20 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{10}$Boc** (927 mg, 2.20 mmol), EDCI (851 mg, 4.44 mmol), DMAP (75.0 mg, 0.61 mmol), dry CH$_2$Cl$_2$ (100 mL); reaction time: 24 h; column gradient 15 : 1 → 11 : 1; R$_f$ = 0.36 (PE/EtOAc = 10 : 1).



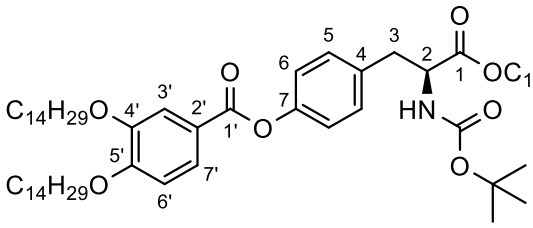
3,4-C$_{12}$TyrC$_{10}$Boc
C$_{55}$H$_{91}$NO$_8$
(894.33)

Colourless solid (83%, 1.64 g, 1.83 mmol, purity >95%); M.p. 56.2 °C (POM); ^{1}H NMR (700 MHz, CDCl$_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.24–1.38 (m, 46H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.51 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.5 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.82–1.88 (m, 4H, OCH$_2$C*H*$_2$), 3.07–3.15 (m, 2H, 3-H), 4.05–4.13 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.1 Hz, 2H, 6-H), 7.18 (d, *J* = 8.1 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (176 MHz, CDCl$_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.69, 22.71, 25.86, 25.98, 26.03, 28.3, 28.5, 29.06, 29.19, 29.23, 29.32, 29.38, 29.40, 29.43, 29.51, 29.56, 29.63, 29.64, 29.68, 29.71, 29.72, 31.90, 31.94 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3349 (w), 2954 (m), 2919 (vs), 2850 (s), 1728 (s), 1687 (vs), 1598 (m), 1519 (s), 1467 (m), 1429 (s), 1391 (m), 1367 (m), 1345 (w), 1290 (s), 1274 (vs), 1248 (s), 1199 (vs), 1167 (vs), 1141 (s), 1087 (m), 1058 (m), 1019 (m), 967 (w), 941 (w), 876 (w), 817 (w),

787 (w), 755 (m), 722 (w), 654 (w), 546 (w) cm^{-1}; MS (ESI): *m*/*z* = 911.71 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{91}NO_8$) calcd.: 911.7083 $[M + NH_4]^+$, found: 911.7059.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,4-bis(tetradecyloxy)benzoate [3,4-C_{14}TyrC_{10}Boc]

According to GP6: 3,4-Bis(tetradecyloxy)benzoic acid **3,4-$C_{14}CO_2H$** (1.21 g, 2.22 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (936 mg, 2.22 mmol), EDCI (867 mg, 4.52 mmol), DMAP (67.0 mg, 0.55 mmol), dry CH_2Cl_2 (100 mL); reaction time: 24 h; column gradient 15 : 1 → 11 : 1; R_f = 0.36 (PE/EtOAc = 10 : 1).

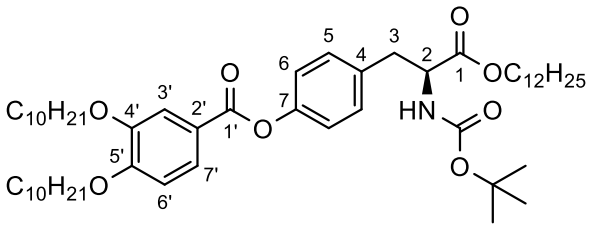


3,4-C_{14}TyrC_{10}Boc
$C_{59}H_{99}NO_8$
(950.44)

Colourless solid (83%, 1.75 g, 1.84 mmol, purity >95%); M.p. 75.8 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.23–1.39 (m, 54H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.51 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.5 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.82–1.88 (m, 4H, OCH$_2$C*H*$_2$), 3.07–3.15 (m, 2H, 3-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.5 Hz, 1H, 2-H), 5.01 (d, *J* = 8.3 Hz, 1H, NH), 6.92 (d, *J* = 8.4 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.1 Hz, 2H, 6-H), 7.18 (d, *J* = 8.1 Hz, 2H, 5-H), 7.65 (d, *J* = 2.1 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H, 7'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.10, 14.12, 14.13 (*C*H$_3$), 22.69, 22.71, 25.86, 25.99, 26.03, 28.3, 28.5, 29.06, 29.19, 29.23, 29.31, 29.32, 29.39, 29.40, 29.43, 29.51, 29.56, 29.61, 29.63, 29.63, 29.65, 29.68, 29.71, 29.72, 29.73, 31.90, 31.94 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3347 (w), 2955 (m), 2917 (vs), 2850 (vs), 1729 (s), 1687 (vs), 1598 (m), 1518 (s), 1468 (m), 1429 (m), 1390 (m), 1367 (m), 1344 (w), 1289 (s), 1275 (vs), 1248 (s), 1199 (vs), 1167 (vs), 1139 (s), 1087 (m), 1054 (m), 1018 (m), 986 (w), 954 (w), 927 (w), 874 (w), 819 (w), 790 (w), 755 (m), 722 (w), 654 (w), 545 (w) cm^{-1}; MS (ESI): *m*/*z* = 967.77 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{59}H_{99}NO_8$) calcd.: 967.7709 $[M + NH_4]^+$, found: 967.7690.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4-bis(decyloxy)benzoate [3,4-C_{10}TyrC_{12}Boc]

According to GP6: 3,4-Bis(decyloxy)benzoic acid **3,4-$C_{10}CO_2H$** (939 mg, 2.16 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (971 mg, 2.16 mmol), EDCI (849 mg, 4.43 mmol), DMAP (73.0 mg, 0.60 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 11 : 1; R_f = 0.38 (PE/EtOAc = 10 : 1).



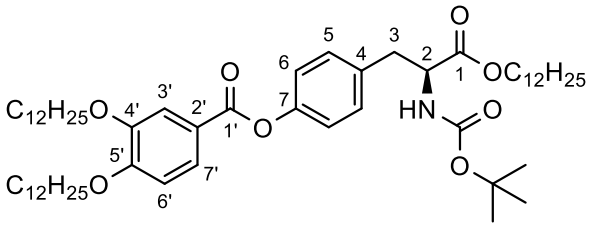
3,4-C_{10}TyrC_{12}Boc
$C_{53}H_{87}NO_8$
(866.28)

Colourless solid (86%, 1.60 g, 1.85 mmol, purity >95%); M.p. 68.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.22–1.39 (m, 42H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.52 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.85 (dt, *J* = 15.3 Hz, 8.8 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.2 Hz, 2H, 6-H), 7.19 (d, *J* = 8.2 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.86, 25.97, 26.01, 28.3, 28.5, 29.05, 29.18, 29.23, 29.36, 29.39, 29.42, 29.48, 29.51, 29.58, 29.61, 29.64, 29.66, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.6 (C-4'), 150.1 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3359 (w), 2919 (vs), 2851 (s), 1725 (s), 1689 (s), 1598 (m), 1512 (s), 1467 (m), 1430 (m), 1391 (m), 1366 (m), 1289 (s), 1273 (vs), 1249 (s), 1199 (vs), 1141 (vs), 1086 (m), 1060 (m), 1019 (m), 990 (m), 955 (m), 921 (w), 875 (m), 815 (w), 780 (w), 756 (s), 723 (m), 654 (w), 597 (w), 544 (w), 517 (w), 434 (w) cm^{-1}; MS (ESI): *m*/*z* = 883.67 [M + NH$_4$]$^+$, 888.63 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{53}H_{87}NO_8$) calcd.: 888.6324 [M + Na]$^+$, found: 888.6321.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4-bis(dodecyloxy)benzoate [3,4-C_{12}TyrC_{12}Boc]

According to GP6: 3,4-Bis(dodecyloxy)benzoic acid **3,4-$C_{12}CO_2H$** (1.05 g, 2.13 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (958 mg, 2.13 mmol), EDCI (829 mg,

4.32 mmol), DMAP (69.0 mg, 0.57 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 11 : 1; R_f = 0.38 (PE/EtOAc = 10 : 1).

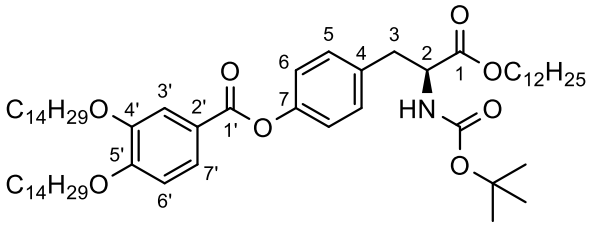


3,4-C_{12}TyrC$_{12}$Boc
$C_{57}H_{95}NO_8$
(922.39)

Colourless solid (82%, 1.62 g, 1.75 mmol, purity >95%); M.p. 58.1 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.25–1.39 (m, 50H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.52 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.85 (dt, *J* = 15.4 Hz, 8.6 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.3 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.86, 25.98, 26.02, 28.3, 28.5, 29.05, 29.18, 29.24, 29.36, 29.38, 29.40, 29.43, 29.51, 29.61, 29.62, 29.64, 29.67, 29.71, 31.92, 31.94 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.6 (C-4'), 150.1 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3352 (w), 2920 (s), 2851 (s), 1733 (m), 1707 (m), 1687 (m), 1597 (w), 1511 (m), 1467 (m), 1430 (m), 1391 (w), 1366 (w), 1347 (w), 1271 (s), 1250 (m), 1196 (vs), 1166 (s), 1141 (m), 1087 (w), 1055 (m), 1018 (m), 967 (w), 908 (s), 873 (w), 812 (w), 756 (m), 729 (vs), 648 (m), 539 (w), 518 (w), 464 (w), 432 (w) cm^{-1}; MS (ESI): *m*/*z* = 939.74 [M + NH$_4$]$^+$; HRMS (ESI): *m*/*z* ($C_{57}H_{95}NO_8$) calcd.: 944.6950 [M + Na]$^+$, found: 944.6956.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4-bis(tetradecyloxy)benzoate [3,4-C_{14}TyrC$_{12}$Boc]

According to GP6: 3,4-Bis(tetradecyloxy)benzoic acid **3,4-$C_{14}CO_2H$** (1.18 g, 2.16 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{12}$Boc** (969 mg, 2.16 mmol), EDCI (845 mg, 4.41 mmol), DMAP (76.0 mg, 0.62 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 11 : 1; R_f = 0.38 (PE/EtOAc = 10 : 1).



3,4-C_{14}TyrC_{12}Boc

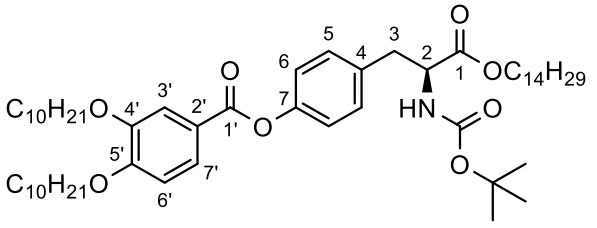
$C_{61}H_{103}NO_8$

(978.49)

Colourless solid (83%, 1.75 g, 1.79 mmol, purity >95%); M.p. 65.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.25–1.39 (m, 58H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.51 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.85 (dt, *J* = 15.3 Hz, 8.5 Hz, 6.8 Hz, 4H, OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.3 Hz, 2H, 6-H), 7.19 (d, *J* = 8.3 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.86, 25.98, 26.03, 28.3, 28.5, 29.05, 29.18, 29.24, 29.36, 29.39, 29.40, 29.43, 29.47, 29.51, 29.61, 29.63, 29.65, 29.67, 29.68, 29.73, 31.92, 31.94 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.6 (C-4'), 150.1 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3357 (w), 2917 (vs), 2849 (vs), 1734 (s), 1707 (m), 1687 (vs), 1596 (w), 1516 (s), 1467 (m), 1430 (m), 1389 (w), 1365 (w), 1275 (s), 1249 (s), 1211 (s), 1197 (vs), 1166 (s), 1141 (s), 1088 (m), 1053 (m), 1016 (m), 974 (w), 953 (w), 919 (w), 872 (w), 854 (w), 811 (w), 754 (w), 737 (w), 722 (m), 649 (w), 615 (w), 539 (w), 432 (w) cm^{-1}; MS (ESI): *m*/*z* = 995.80 [M + NH$_4$]$^+$; HRMS (ESI): *m*/*z* ($C_{61}H_{103}NO_8$) calcd.: 995.8022 [M + NH$_4$]$^+$, found: 995.8024.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4-bis(decyloxy)benzoate [3,4-C_{10}TyrC_{14}Boc]

According to GP6: 3,4-Bis(decyloxy)benzoic acid **3,4-$C_{10}CO_2H$** (873 mg, 2.01 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{14}Boc** (960 mg, 2.01 mmol), EDCI (780 mg, 4.07 mmol), DMAP (77.0 mg, 0.63 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 11 : 1; R_f = 0.40 (PE/EtOAc = 10 : 1).



3,4-C_{10}TyrC_{14}Boc

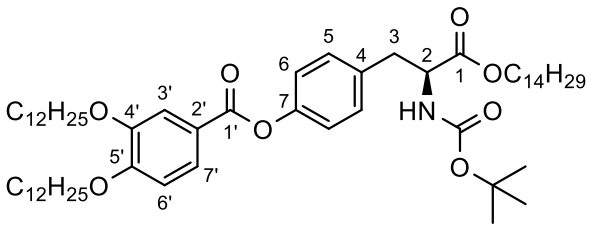
$C_{55}H_{91}NO_8$

(894.33)

Colourless solid (84%, 1.50 g, 1.68 mmol, purity >95%); M.p. 60.1 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.22–1.39 (m, 46H, C*H*$_2$), 1.43 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.85 (dt, *J* = 15.2 Hz, 7.6 Hz, 4H, OCH$_2$C*H*$_2$), 3.06–3.16 (m, 2H, 3-H), 4.05–4.14 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.5 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.3 Hz, 2H, 6-H), 7.19 (d, *J* = 8.3 Hz, 2H, 5-H), 7.65 (d, *J* = 2.1 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.88, 25.99, 26.03, 28.3, 28.5, 29.07, 29.19, 29.25, 29.38, 29.41, 29.43, 29.46, 29.53, 29.60, 29.63, 29.65, 29.68, 29.71, 29.72, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.5 (C-2), 65.7 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3354 (w), 2919 (vs), 2850 (s), 1727 (s), 1686 (s), 1598 (m), 1517 (s), 1467 (m), 1429 (s), 1391 (m), 1366 (m), 1346 (w), 1290 (s), 1272 (vs), 1249 (s), 1198 (vs), 1166 (vs), 1143 (s), 1086 (m), 1065 (m), 1019 (m), 988 (m), 955 (m), 922 (w), 877 (m), 817 (w), 785 (w), 755 (s), 723 (m), 653 (w), 592 (w), 546 (w), 517 (w), 465 (w), 432 (w) cm^{-1}; MS (ESI): *m*/*z* = 911.70 [M + NH$_4$]$^+$, 916.66 [M + Na]$^+$;
HRMS (ESI): *m*/*z* ($C_{55}H_{91}NO_8$) calcd.: 911.7083 [M + NH$_4$]$^+$, found: 911.7080.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4-bis(dodecyloxy)benzoate [3,4-C$_{12}$TyrC$_{14}$Boc]

According to GP6: 3,4-Bis(dodecyloxy)benzoic acid **3,4-C$_{12}$CO$_2$H** (992 mg, 2.02 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (966 mg, 2.02 mmol), EDCI (789 mg, 4.12 mmol), DMAP (85.0 mg, 0.70 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 11 : 1; R_f = 0.40 (PE/EtOAc = 10 : 1).



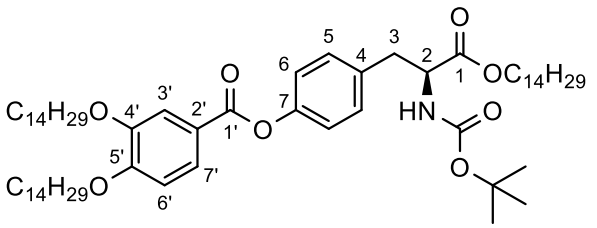
3,4-C$_{12}$TyrC$_{14}$Boc
$C_{59}H_{99}NO_8$
(950.44)

Colourless solid (81%, 1.55 g, 1.63 mmol, purity >95%); M.p. 55.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.21–1.39 (m, 54H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.82–1.89 (m, 4H, OCH$_2$C*H*$_2$), 3.06–3.16 (m, 2H, 3-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.3 Hz, 2H,

6-H), 7.19 (d, *J* = 8.3 Hz, 2H, 5-H), 7.65 (d, *J* = 2.1 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.86, 25.98, 26.02, 28.3, 28.5, 29.05, 29.18, 29.24, 29.38, 29.40, 29.43, 29.51, 29.62, 29.64, 29.67, 29.69, 29.71, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H_2), 69.1 (C-5'-O*C*H_2), 69.3 (C-4'-O*C*H_2), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.8 (C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.1 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: ṽ = 3352 (w), 2918 (vs), 2850 (s), 1728 (s), 1706 (m), 1687 (s), 1597 (m), 1516 (s), 1467 (m), 1429 (m), 1390 (m), 1366 (m), 1349 (m), 1289 (s), 1273 (vs), 1249 (s), 1197 (vs), 1141 (s), 1087 (m), 1056 (m), 1018 (m), 966 (m), 939 (m), 908 (m), 875 (m), 813 (w), 784 (w), 755 (m), 726 (s), 684 (w), 650 (w), 615 (w), 542 (w), 518 (w), 468 (w), 431 (w) cm^{-1}; MS (ESI): *m*/*z* = 967.77 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{59}H_{99}NO_8$) calcd.: 967.7709 $[M + NH_4]^+$, found: 967.7709.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4-bis-(tetradecyloxy)benzoate [3,4-C$_{14}$TyrC$_{14}$Boc]

According to GP6: 3,4-Bis(tetradecyloxy)benzoic acid **3,4-C$_{14}$CO$_2$H** (1.10 g, 2.01 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (960 mg, 2.01 mmol), EDCI (780 mg, 4.07 mmol), DMAP (69.0 mg, 0.57 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 11 : 1; R_f = 0.40 (PE/EtOAc = 10 : 1).



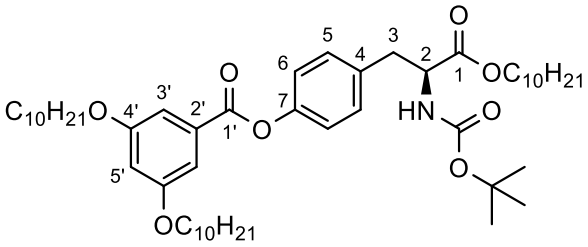
3,4-C$_{14}$TyrC$_{14}$Boc
C$_{63}$H$_{107}$NO$_8$
(1006.55)

Colourless solid (79%, 1.59 g, 1.58 mmol, purity >95%); M.p. 73.2 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.89 (m, 9H, C*H*$_3$), 1.20–1.39 (m, 62H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.51 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.59–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.82–1.88 (m, 4H, OCH$_2$C*H*$_2$), 3.07–3.15 (m, 2H, 3-H), 4.05–4.13 (m, 6H, OC*H*$_2$), 4.58 (q, *J* = 6.1 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.3 Hz, 2H, 6-H), 7.18 (d, *J* = 8.3 Hz, 2H, 5-H), 7.65 (d, *J* = 2.1 Hz, 1H, 3'-H), 7.79 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.87, 25.99, 26.03, 28.3, 28.5, 29.06, 29.19, 29.24, 29.38, 29.39, 29.41, 29.44, 29.51, 29.62, 29.63, 29.65, 29.67, 29.69, 29.70, 29.71, 29.72, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H_2), 69.1 (C-5'-O*C*H_2), 69.4 (C-4'-O*C*H_2), 79.9 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.8

(C-6), 124.3 (C-7'), 130.3 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 155.1 (HNC=O), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3345 (w), 2954 (m), 2917 (vs), 2850 (vs), 1727 (s), 1687 (vs), 1598 (m), 1518 (s), 1467 (m), 1429 (m), 1390 (m), 1366 (m), 1346 (w), 1290 (s), 1273 (vs), 1248 (s), 1198 (vs), 1166 (vs), 1140 (s), 1087 (m), 1055 (m), 1018 (m), 985 (m), 953 (w), 927 (w), 875 (w), 818 (w), 786 (w), 755 (m), 721 (m), 654 (w), 545 (w), 519 (w), 431 (w) cm^{-1}; MS (ESI): *m*/*z* = 1023.83 $[M + NH_4]^+$, 1028.78 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{107}NO_8$) calcd.: 1023.8335 $[M + NH_4]^+$, found: 1023.8332.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,5-bis(decyloxy)-benzoate [3,5-C_{10}TyrC_{10}Boc]

According to GP6: 3,5-Bis(decyloxy)benzoic acid **3,5-$C_{10}CO_2H$** (1.00 g, 2.30 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (964 mg, 2.29 mmol), EDCI (886 mg, 4.62 mmol), DMAP (80.0 mg, 0.66 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 20 : 1 → 11 : 1; R_f = 0.51 (PE/EtOAc = 10 : 1).

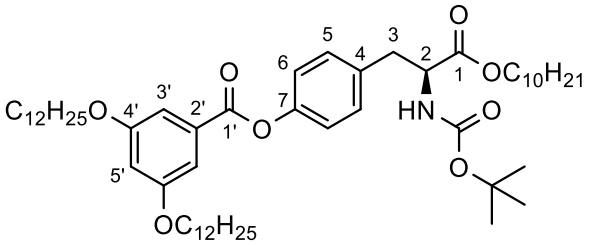


3,5-C_{10}TyrC_{10}Boc
$C_{51}H_{83}NO_8$
(838.22)

Colourless wax (85%, 1.63 g, 1.95 mmol, purity >95%); M.p. 41.4 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.37 (m, 38H, C*H*$_2$), 1.41–1.49 (m, 13H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.6 Hz, 6.6 Hz, 4H, OCH$_2$C*H*$_2$), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.06–4.14 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.5 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.3 Hz, 2H, 6-H), 7.19 (d, *J* = 8.3 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.18, 29.22, 29.31, 29.33, 29.37, 29.50, 29.54, 29.56, 29.58, 31.89, 31.90 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COO*C*H$_2$), 68.4 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3438 (w), 3380 (w), 2924 (vs), 2854 (s), 1740 (s), 1718 (s), 1595 (m), 1508 (m), 1448 (m), 1391 (m), 1350 (m), 1327 (m), 1299 (m), 1250 (m), 1212 (s), 1197 (vs), 1166 (vs), 1057 (m), 1019 (m), 951 (w), 931 (w), 860 (w), 778 (w), 758 (w), 722 (w), 676 (w), 542 (w), 510 (w) cm^{-1}; MS (ESI): *m*/*z* = 860.60 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{51}H_{83}NO_8$) calcd.: 860.6011 $[M + Na]^+$, found: 860.5999.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,5-bis(dodecyloxy)benzoate [3,5-C_{12}TyrC$_{10}$Boc]

According to GP6: 3,5-Bis(dodecyloxy)benzoic acid **3,5-$C_{12}CO_2H$** (1.09 g, 2.23 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{10}$Boc** (935 mg, 2.22 mmol), EDCI (900 mg, 4.70 mmol), DMAP (81.0 mg, 0.66 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 20 : 1 → 11 : 1; R_f = 0.51 (PE/EtOAc = 10 : 1).

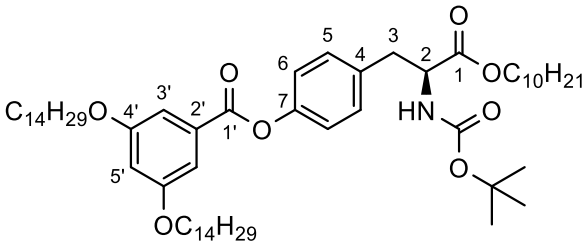


3,5-C_{12}TyrC$_{10}$Boc
$C_{55}H_{91}NO_8$
(894.33)

Colourless wax (86%, 1.71 g, 1.91 mmol, purity >95%); M.p. 38.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.38 (m, 46H, C*H*$_2$), 1.43–1.49 (m, 13H, $OCH_2CH_2CH_2$, OC(C*H*$_3$)$_3$), 1.57–1.62 (m, 2H, $COOCH_2CH_2$), 1.78 (dt, *J* = 13.9 Hz, 6.7 Hz, 4H, OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.06–4.14 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.6 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.68, 22.70, 25.9, 26.0, 28.3, 28.5, 29.19, 29.22, 29.31, 29.36, 29.38, 29.50, 29.55, 29.58, 29.61, 29.64, 29.67, 31.89, 31.92 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COO*C*H$_2$), 68.4 (C-4'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.2 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3372 (w), 2922 (s), 2853 (m), 1739 (m), 1717 (s), 1594 (m), 1507 (m), 1447 (m), 1390 (m), 1349 (m), 1326 (m), 1298 (m), 1249 (m), 1196 (vs), 1163 (vs), 1101 (w), 1056 (s), 1019 (m), 948 (w), 859 (w), 777 (w), 757 (m), 722 (w), 676 (w), 500 (w) cm^{-1}; MS (ESI): *m*/*z* = 916.60 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{91}NO_8$) calcd.: 916.6637 [M + Na]$^+$, found: 916.6627.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,5-bis(tetradecyloxy)benzoate [3,5-C_{14}TyrC$_{10}$Boc]

According to GP6: 3,5-Bis(tetradecyloxy)benzoic acid **3,5-$C_{14}CO_2H$** (1.22 g, 2.23 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{10}$Boc** (932 mg, 2.21 mmol), EDCI (870 mg, 4.54 mmol), DMAP (87.0 mg, 0.71 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 20 : 1 → 11 : 1; R_f = 0.51 (PE/EtOAc = 10 : 1).



3,5-C_{14}TyrC_{10}Boc

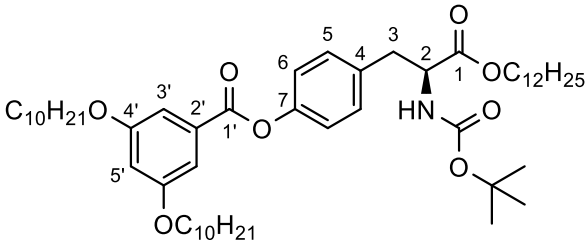
$C_{59}H_{99}NO_8$

(950.44)

Colourless wax (83%, 1.74 g, 1.83 mmol, purity >95%); M.p. 61.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 9H, C*H*$_3$), 1.23–1.37 (m, 54H, C*H*$_2$), 1.40–1.49 (m, 13H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.58–1.62 (m, 2H, $COOCH_2CH_2$), 1.80 (dt, *J* = 13.9 Hz, 6.5 Hz, 4H, OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.06–4.14 (m, 2H, $COOCH_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (CH_3), 22.68, 22.70, 25.9, 26.0, 28.3, 28.5, 29.19, 29.22, 29.31, 29.37, 29.39, 29.50, 29.55, 29.59, 29.61, 29.67, 29.68, 29.70, 31.89, 31.93 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.7 ($COOCH_2$), 68.4 (C-4'-OCH_2), 79.9 ($OC(CH_3)_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3439 (w), 2922 (s), 2852 (s), 1740 (m), 1717 (s), 1594 (m), 1507 (m), 1447 (m), 1390 (m), 1350 (m), 1326 (m), 1298 (m), 1249 (m), 1196 (s), 1163 (vs), 1102 (w), 1056 (s), 1019 (m), 933 (w), 859 (w), 778 (w), 757 (m), 722 (w), 676 (w), 512 (w) cm^{-1}; MS (ESI): *m*/*z* = 967.80 $[M + NH_4]^+$; HRMS (ESI): *m*/*z* ($C_{59}H_{99}NO_8$) calcd.: 967.7709 $[M + NH_4]^+$, found: 967.7708.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,5-bis(decyloxy)benzoate [3,5-C_{10}TyrC_{12}Boc]

According to GP6: 3,5-Bis(decyloxy)benzoic acid **3,5-$C_{10}CO_2H$** (926 mg, 2.13 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (958 mg, 2.13 mmol), EDCI (824 mg, 4.30 mmol), DMAP (73.0 mg, 0.60 mmol), dry CH_2Cl_2 (100 mL); reaction time: 72 h; column gradient 16 : 1 → 12 : 1; R_f = 0.54 (PE/EtOAc = 10 : 1).



3,5-C_{10}TyrC_{12}Boc

$C_{53}H_{87}NO_8$

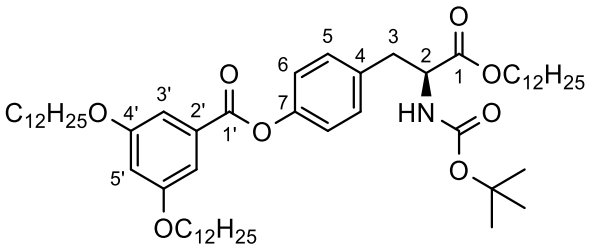
(866.28)

Colourless wax (78%, 1.44 g, 1.66 mmol, purity >95%); M.p. 33.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.37 (m, 42H, C*H*$_2$), 1.38–1.49 (m, 13H,

$OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.61 (q, *J* = 6.9 Hz, 2H, $COOCH_2CH_2$), 1.78 (dt, *J* = 13.7 Hz, 6.6 Hz, 4H, OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.08–4.13 (m, 2H, $COOCH_2$), 4.58 (q, *J* = 6.7 Hz, 1H, 2-H), 5.01 (d, *J* = 8.3 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.19 (d, *J* = 8.6 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.18, 29.23, 29.33, 29.36, 29.38, 29.51, 29.56, 29.58, 29.60, 29.64, 29.66, 31.90, 31.92 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.7 ($COOCH_2$), 68.4 (C-4'-OCH_2), 79.9 ($OC(CH_3)_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3366 (w), 2922 (s), 2853 (m), 1739 (s), 1717 (s), 1594 (m), 1507 (m), 1447 (m), 1390 (w), 1349 (m), 1326 (m), 1298 (m), 1250 (m), 1196 (vs), 1163 (vs), 1101 (w), 1056 (s), 1019 (m), 950 (w), 859 (w), 778 (w), 757 (m), 723 (w), 676 (w), 508 (w) cm^{-1}; MS (ESI): *m*/*z* = 888.363 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{53}H_{87}NO_8$) calcd.: 888.6324 $[M + Na]^+$, found: 888.6326.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,5-bis(dodecyloxy)benzoate [3,5-C_{12}TyrC$_{12}$Boc]

According to GP6: 3,5-Bis(dodecyloxy)benzoic acid **3,5-$C_{12}CO_2H$** (1.05 g, 2.14 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{12}$Boc** (956 mg, 2.13 mmol), EDCI (830 mg, 4.33 mmol), DMAP (75.0 mg, 0.61 mmol), dry CH_2Cl_2 (100 mL); reaction time: 72 h; column gradient 16 : 1 → 12 : 1; R_f = 0.54 (PE/EtOAc = 10 : 1).



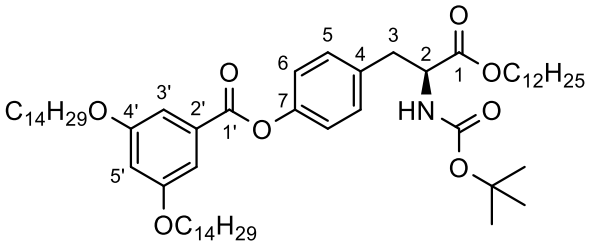
3,5-C_{12}TyrC$_{12}$Boc
$C_{57}H_{95}NO_8$
(922.39)

Colourless wax (86%, 1.69 g, 1.83 mmol, purity >95%); M.p. 34.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, CH_3), 1.25–1.37 (m, 50H, CH_2), 1.38–1.49 (m, 13H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.58–1.62 (m, 2H, $COOCH_2CH_2$), 1.79 (dt, *J* = 13.8 Hz, 6.6 Hz, 4H, OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.08–4.12 (m, 2H, $COOCH_2$), 4.58 (d, *J* = 7.0 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.19 (d, *J* = 8.6 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.18, 29.23, 29.36, 29.38, 29.50, 29.58, 29.60, 29.64, 29.67, 31.9 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.7 ($COOCH_2$), 68.4 (C-4'-OCH_2), 79.9 ($OC(CH_3)_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7

(C-6), 130.4 (C-5), 131.1 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3434 (w), 2922 (s), 2853 (s), 1739 (m), 1717 (s), 1594 (m), 1507 (m), 1447 (m), 1390 (w), 1349 (m), 1326 (m), 1298 (m), 1249 (m), 1196 (vs), 1163 (vs), 1101 (w), 1056 (s), 1019 (m), 948 (w), 860 (w), 778 (w), 757 (m), 722 (w), 676 (w), 509 (w) cm^{-1}; MS (ESI): *m*/*z* = 944.69 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{57}H_{95}NO_8$) calcd.: 944.6950 $[M + Na]^+$, found: 944.6950.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,5-bis(tetradecyloxy)benzoate [3,5-C_{14}TyrC_{12}Boc]

According to GP6: 3,5-Bis(tetradecyloxy)benzoic acid **3,5-$C_{14}CO_2H$** (1.17 g, 2.14 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (963 mg, 2.14 mmol), EDCI (840 mg, 4.38 mmol), DMAP (73.0 mg, 0.60 mmol), dry CH_2Cl_2 (100 mL); reaction time: 72 h; column gradient 16 : 1 → 12 : 1; R_f = 0.54 (PE/EtOAc = 10 : 1).

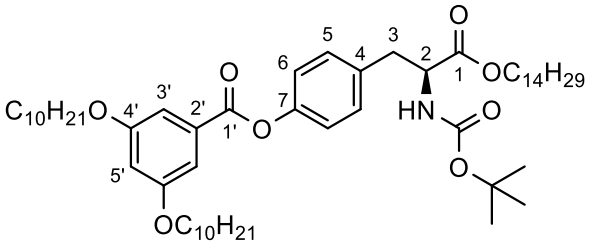


3,5-C_{14}TyrC_{12}Boc
$C_{61}H_{103}NO_8$
(978.49)

Colourless wax (87%, 1.83 g, 1.87 mmol, purity >95%); M.p. 52.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.37 (m, 58H, C*H*$_2$), 1.40–1.47 (m, 13H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.8 Hz, 6.6 Hz, 4H, OCH$_2$C*H*$_2$), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.08–4.13 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.3 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (*C*H$_3$), 22.72, 25.9, 26.0, 28.3, 28.5, 29.21, 29.25, 29.37, 29.39, 29.40, 29.52, 29.60, 29.63, 29.66, 29.68, 29.70, 29.72, 32.0 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COO*C*H$_2$), 68.4 (C-4'-O*C*H$_2$), 80.0 (O*C*(CH$_3$)$_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3441 (w), 2921 (vs), 2852 (s), 1740 (m), 1717 (s), 1595 (m), 1507 (m), 1447 (m), 1390 (w), 1350 (m), 1326 (m), 1298 (m), 1249 (m), 1196 (vs), 1164 (vs), 1101 (m), 1056 (s), 1019 (m), 949 (w), 859 (w), 779 (w), 757 (m), 722 (w), 676 (w), 507 (w) cm^{-1}; MS (ESI): *m*/*z* = 1000.76 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{61}H_{103}NO_8$) calcd.: 1000.7576 $[M + Na]^+$, found: 1000.7568.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,5-bis(decyloxy)benzoate [3,5-C_{10}TyrC_{14}Boc]

According to GP6: 3,5-Bis(decyloxy)benzoic acid **3,5-$C_{10}CO_2H$** (866 mg, 1.99 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{14}Boc** (949 mg, 1.99 mmol), EDCI (795 mg, 4.15 mmol), DMAP (68.0 mg, 0.56 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 15 : 1 → 12 : 1; R_f = 0.51 (PE/EtOAc = 10 : 1).

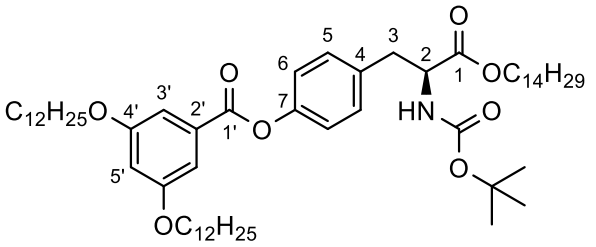


3,5-C_{10}TyrC_{14}Boc
$C_{55}H_{91}NO_8$
(894.33)

Colourless wax (90%, 1.60 g, 1.79 mmol, purity >95%); M.p. 30.4 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.37 (m, 46H, C*H*$_2$), 1.38–1.49 (m, 13H, $OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.58–1.62 (m, 2H, $COOCH_2CH_2$), 1.79 (dt, *J* = 13.9 Hz, 6.5 Hz, 4H, OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.08–4.12 (m, 2H, $COOCH_2$), 4.58 (q, *J* = 6.6 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.18 (d, *J* = 8.6 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 26.9, 28.3, 28.5, 29.20, 29.25, 29.34, 29.39, 29.53, 29.58, 29.60, 29.62, 29.68, 29.71, 31.92, 31.95 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.7 ($COOCH_2$), 68.4 (C-4'-OCH_2), 80.0 ($OC(CH_3)_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3436 (w), 2922 (s), 2853 (m), 1739 (m), 1717 (s), 1594 (m), 1507 (m), 1447 (m), 1390 (w), 1349 (m), 1326 (m), 1298 (m), 1250 (m), 1196 (vs), 1163 (vs), 1101 (w), 1056 (s), 1019 (m), 860 (w), 778 (w), 757 (m), 722 (w), 676 (w), 505 (w) cm^{-1}; MS (ESI): *m*/*z* = 916.66 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{91}NO_8$) calcd.: 916.6637 $[M + Na]^+$, found: 916.6614.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,5-bis(dodecyloxy)benzoate [3,5-C_{12}TyrC_{14}Boc]

According to GP6: 3,5-Bis(dodecyloxy)benzoic acid **3,5-$C_{12}CO_2H$** (991 mg, 2.02 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{14}Boc** (956 mg, 2.00 mmol), EDCI (810 mg, 4.23 mmol), DMAP (84.0 mg, 0.69 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 16 : 1 → 12 : 1; R_f = 0.54 (PE/EtOAc = 10 : 1).



3,5-C_{12}TyrC$_{14}$Boc

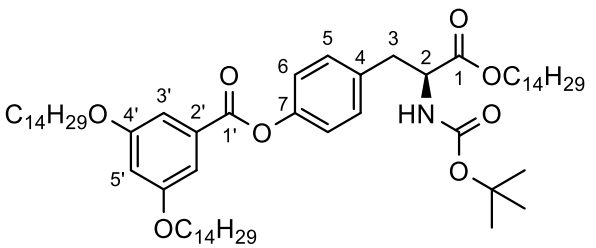
$C_{59}H_{99}NO_8$

(950.44)

Colourless wax (89%, 1.69 g, 1.78 mmol, purity >95%); M.p. 34.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.37 (m, 54H, C*H*$_2$), 1.43–1.49 (m, 13H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.57–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.78 (dt, *J* = 13.9 Hz, 6.5 Hz, 4H, OCH$_2$C*H*$_2$), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.07–4.12 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.5 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.3, 28.5, 29.21, 29.25, 29.38, 29.40, 29.53, 29.60, 29.62, 29.66, 29.68, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COO*C*H$_2$), 68.4 (C-4'-O*C*H$_2$), 80.0 (O*C*(CH$_3$)$_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.4 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3438 (w), 2922 (s), 2852 (s), 1739 (m), 1717 (m), 1594 (m), 1507 (m), 1447 (m), 1390 (w), 1350 (m), 1326 (m), 1298 (m), 1249 (m), 1196 (vs), 1163 (vs), 1101 (w), 1056 (s), 1019 (m), 947 (w), 859 (w), 757 (m), 721 (w), 676 (w), 516 (w) cm^{-1}; MS (ESI): *m*/*z* = 972.73 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{59}H_{99}NO_8$) calcd.: 972.7263 [M + Na]$^+$, found: 972.7262.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,5-bis-(tetradecyloxy)benzoate [3,5-C$_{14}$TyrC$_{14}$Boc]

According to GP6: 3,5-Bis(tetradecyloxy)benzoic acid **3,5-$C_{14}CO_2H$** (1.10 g, 2.02 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (961 mg, 2.01 mmol), EDCI (840 mg, 4.38 mmol), DMAP (79.0 mg, 0.65 mmol), dry CH_2Cl_2 (100 mL); reaction time: 48 h; column gradient 17 : 1 → 13 : 1; R_f = 0.56 (PE/EtOAc = 10 : 1).



3,5-C_{14}TyrC$_{14}$Boc

$C_{63}H_{107}NO_8$

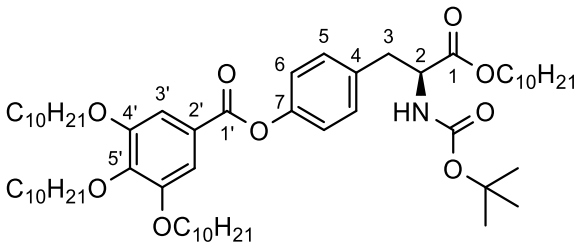
(1006.55)

Colourless wax (83%, 1.69 g, 1.68 mmol, purity >95%); M.p. 35.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.37 (m, 62H, C*H*$_2$), 1.39–1.49 (m, 13H,

$OCH_2CH_2CH_2$, $OC(CH_3)_3$), 1.57–1.62 (m, 2H, $COOCH_2CH_2$), 1.79 (dt, *J* = 13.9 Hz, 6.6 Hz, 4H, OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.07–4.12 (m, 2H, $COOCH_2$), 4.58 (q, *J* = 6.7 Hz, 1H, 2-H), 5.01 (d, *J* = 8.3 Hz, 1H, NH), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.19 (d, *J* = 8.6 Hz, 2H, 5-H), 7.29 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 25.9, 26.0, 28.3, 28.5, 29.21, 29.25, 29.38, 29.40, 29.52, 29.60, 29.63, 29.68, 29.70, 29.72, 32.0 (CH_2, $OC(CH_3)_3$), 37.8 (C-3), 54.4 (C-2), 65.7 ($COOCH_2$), 68.4 (C-4'-OCH_2), 80.0 ($OC(CH_3)_3$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.4 (C-5), 131.2 (C-2'), 133.8 (C-4), 150.0 (C-7), 155.1 (HNC=O), 160.3 (C-4'), 165.0 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3435 (w), 2921 (vs), 2852 (s), 1740 (m), 1717 (m), 1594 (m), 1507 (m), 1447 (m), 1390 (w), 1350 (m), 1326 (m), 1298 (m), 1249 (m), 1196 (vs), 1164 (vs), 1101 (w), 1056 (s), 1019 (m), 933 (w), 859 (w), 778 (w), 757 (m), 722 (w), 676 (w), 509 (w) cm^{-1}; MS (ESI): *m*/*z* = 1028.79 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{107}NO_8$) calcd.: 1028.7889 $[M + Na]^+$, found: 1028.7870.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,4,5-tris(decyloxy)benzoate [3,4,5-C_{10}TyrC_{10}Boc]

According to GP6: 3,4,5-Tris(decyloxy)benzoic acid **3,4,5-$C_{10}CO_2H$** (1.41 g, 2.39 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (854 mg, 2.03 mmol), EDCI (808 mg, 4.22 mmol), DMAP (76.0 mg, 0.62 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 40 : 1 → 25 : 1; R_f = 0.45 (PE/EtOAc = 10 : 1).



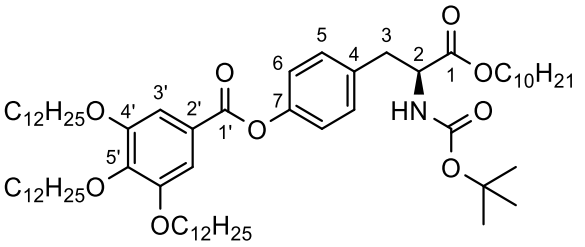
3,4,5-C_{10}TyrC_{10}Boc
$C_{61}H_{103}NO_9$
(994.49)

Colourless solid (87%, 1.74 g, 1.75 mmol, purity >95%); M.p. 45.4 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 12H, CH_3), 1.23–1.38 (m, 50H, CH_2), 1.43 (s, 9H, $OC(CH_3)_3$), 1.45–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.61 (dt, *J* = 13.7 Hz, 7.0 Hz, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 14.8 Hz, 6.6 Hz, 2H, C-5'-OCH_2CH_2), 1.83 (dt, *J* = 13.8 Hz, 6.6 Hz, 4H, C-4'-OCH_2CH_2), 3.06–3.16 (m, 2H, 3-H), 4.02–4.13 (m, 8H, OCH_2), 4.58 (q, *J* = 6.3 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 7.12 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.69, 22.70, 22.72, 25.9, 26.08, 26.10, 28.3, 28.5, 29.22, 29.27, 29.32, 29.37, 29.41, 29.50, 29.55, 29.58, 29.60, 29.65, 29.69, 29.75, 30.4, 31.90, 31.93, 31.96 (CH_2, $OC(CH_3)_3$), 37.8

(C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3440 (w), 2923 (s), 2854 (m), 1733 (m), 1586 (w), 1499 (m), 1466 (m), 1430 (m), 1391 (m), 1366 (m), 1335 (m), 1188 (vs), 1166 (vs), 1114 (s), 1060 (m), 1019 (m), 954 (w), 908 (s), 862 (w), 731 (vs), 648 (w), 524 (w), 427 (w) cm^{-1}; MS (ESI): *m*/*z* = 1016.80 [M + Na]$^+$; HRMS (ESI): *m*/*z* (C$_{61}$H$_{103}$NO$_9$) calcd.: 1016.7525 [M + Na]$^+$, found: 1016.7516.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,4,5-tris(dodecyloxy)benzoate [3,4,5-C$_{12}$TyrC$_{10}$Boc]

According to GP6: 3,4,5-Tris(dodecyloxy)benzoic acid **3,4,5-C$_{12}$CO$_2$H** (1.58 g, 2.34 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{10}$Boc** (860 mg, 2.04 mmol), EDCI (806 mg, 4.20 mmol), DMAP (79.0 mg, 0.65 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 40 : 1 → 20 : 1; R_f = 0.45 (PE/EtOAc = 10 : 1).



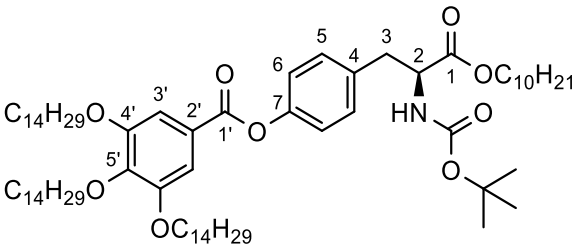
3,4,5-C$_{12}$TyrC$_{10}$Boc
C$_{67}$H$_{115}$NO$_9$
(1078.66)

Colourless solid (56%, 1.24 g, 1.15 mmol, purity >95%); M.p. 47.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 12H, C*H*$_3$), 1.23–1.38 (m, 62H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.7 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 14.3 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 13.4 Hz, 6.6 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 3.07–3.17 (m, 2H, 3-H), 4.03–4.13 (m, 8H, OC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.69, 22.71, 25.9, 26.08, 26.10, 28.3, 28.5, 29.22, 29.32, 29.39, 29.42, 29.46, 29.50, 29.55, 29.59, 29.66, 29.68, 29.72, 29.75, 29.78, 30.4, 31.90, 31.94, 31.96 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.2 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3438 (w), 2922 (vs), 2853 (s), 1732 (s), 1586 (w), 1499 (m), 1466 (m), 1430 (m), 1391 (m), 1366 (m), 1335 (m), 1188 (vs), 1166 (vs), 1115 (s), 1059 (m), 1019 (m), 952 (w), 908 (s), 862 (w),

778 (w), 754 (m), 732 (vs), 648 (w), 522 (w), 428 (w), 416 (w) cm^{-1}; MS (ESI): *m*/*z* = 1100.85 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{67}H_{115}NO_9$) calcd.: 1100.8464 $[M + Na]^+$, found: 1100.8451.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(decyloxy)-3-oxopropyl)phenyl 3,4,5-tris(tetradecyloxy)benzoate [3,4,5-C_{14}TyrC_{10}Boc]

According to GP6: 3,4,5-Tris(tetradecyloxy)benzoic acid **3,4,5-$C_{14}CO_2H$** (1.54 g, 2.03 mmol), decyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{10}Boc** (852 mg, 2.02 mmol), EDCI (806 mg, 4.20 mmol), DMAP (60.0 mg, 0.49 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 15 : 1 → 11 : 1; R_f = 0.48 (PE/EtOAc = 10 : 1).

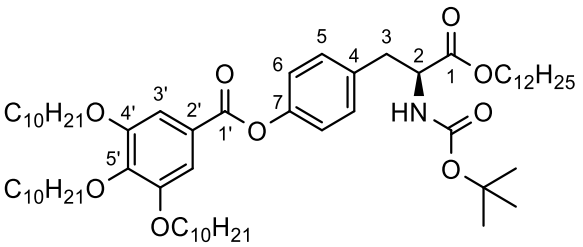


3,4,5-C_{14}TyrC_{10}Boc
$C_{73}H_{127}NO_9$
(1162.82)

Colourless solid (89%, 2.09 g, 1.80 mmol, purity >95%); M.p. 59.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 12H, C*H*$_3$), 1.23–1.38 (m, 74H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.45–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.9 Hz, 6.9 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 14.3 Hz, 6.6 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 13.5 Hz, 6.6 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 3.07–3.17 (m, 2H, 3-H), 4.02–4.12 (m, 8H, OC*H*$_2$), 4.58 (q, *J* = 6.2 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.19 (d, *J* = 8.6 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.14 (*C*H$_3$), 22.69, 22.72, 25.9, 26.09, 26.11, 28.3, 28.5, 29.23, 29.32, 29.39, 29.42, 29.51, 29.56, 29.60, 29.66, 29.69, 29.73, 29.77, 30.4, 31.90, 31.95 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3438 (w), 2921 (vs), 2852 (s), 1734 (s), 1718 (s), 1586 (m), 1499 (m), 1466 (m), 1430 (m), 1390 (m), 1366 (m), 1334 (s), 1188 (vs), 1166 (vs), 1116 (vs), 1059 (m), 1019 (m), 952 (w), 862 (w), 778 (w), 754 (m), 721 (m), 668 (w), 520 (w) cm^{-1}; MS (ESI): *m*/*z* = 1179.98 $[M + NH_4]^+$, 1184.94 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{73}H_{127}NO_9$) calcd.: 1179.9849 $[M + NH_4]^+$, found: 1179.9852 calcd.: 1184.9403 $[M + Na]^+$, found: 1184.9399.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(decyloxy)benzoate [3,4,5-C_{10}TyrC_{12}Boc]

According to GP6: 3,4,5-Tris(decyloxy)benzoic acid **3,4,5-$C_{10}CO_2H$** (1.240 g, 2.10 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (916 mg, 2.04 mmol), EDCI (800 mg, 4.17 mmol), DMAP (79.0 mg, 0.65 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 30 : 1 → 25 : 1; R_f = 0.43 (PE/EtOAc = 10 : 1).

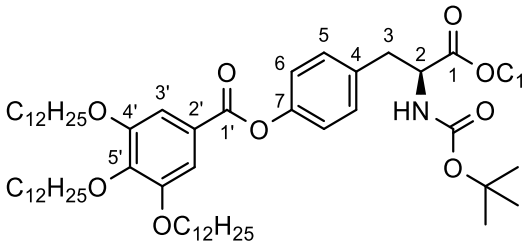


3,4,5-C_{10}TyrC_{12}Boc
$C_{63}H_{107}NO_9$
(1022.55)

Colourless solid (59%, 1.23 g, 1.21 mmol, purity >95%); M.p. 49.2 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 12H, C*H*$_3$), 1.21–1.38 (m, 54H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.4 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.73–1.86 (m, 6H, OCH$_2$C*H*$_2$), 3.07–3.17 (m, 2H, 3-H), 4.03–4.13 (m, 8H, OC*H*$_2$), 4.58 (q, *J* = 6.2 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 7.13 (d, *J* = 8.6 Hz, 2H, 6-H), 7.19 (d, *J* = 8.6 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 26.1, 28.3, 28.5, 29.23, 29.32, 29.37, 29.41, 29.51, 29.58, 29.60, 29.65, 29.67, 29.69, 29.75, 30.4, 31.93, 31.96 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.2 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3438 (w), 2922 (vs), 2853 (s), 1734 (s), 1718 (s), 1586 (m), 1499 (m), 1466 (m), 1430 (m), 1390 (m), 1365 (m), 1334 (s), 1187 (vs), 1115 (vs), 1059 (m), 1018 (m), 953 (w), 862 (w), 777 (w), 754 (m), 722 (w), 670 (w), 526 (w), 413 (w) cm^{-1}; MS (ESI): *m*/*z* = 1044.78 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{107}NO_9$) calcd.: 1044.7838 [M + Na]$^+$, found: 1044.7837.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(dodecyloxy)benzoate [3,4,5-C_{12}TyrC_{12}Boc]

According to GP6: 3,4,5-Tris(dodecyloxy)benzoic acid **3,4,5-$C_{12}CO_2H$** (1.38 g, 2.04 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{12}Boc** (901 mg, 2.00 mmol), EDCI (794 mg, 4.14 mmol), DMAP (60.0 mg, 0.49 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 35 : 1 → 25 : 1; R_f = 0.46 (PE/EtOAc = 10 : 1).



3,4,5-C$_{12}$TyrC$_{12}$Boc

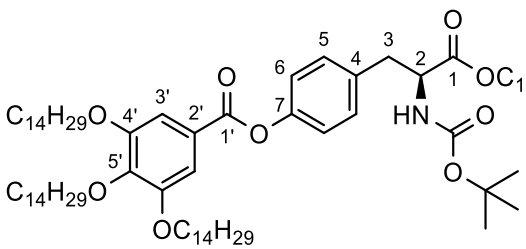
$C_{69}H_{119}NO_9$

(1106.71)

Colourless solid (68%, 1.50 g, 1.36 mmol, purity >95%); M.p. 54.9 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 12H, C*H*$_3$), 1.22–1.39 (m, 66H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.52 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.5 Hz, 6.7 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 13.9 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 12.8 Hz, 6.9 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 3.07–3.17 (m, 2H, 3-H), 4.03–4.12 (m, 8H, OC*H*$_2$), 4.58 (q, *J* = 6.6 Hz, 1H, 2-H), 5.02 (d, *J* = 8.2 Hz, 1H, NH), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.09, 26.11, 28.3, 28.5, 29.23, 29.32, 29.37, 29.39, 29.42, 29.51, 29.60, 29.66, 29.68, 29.72, 29.76, 29.78, 30.4, 31.93, 31.95, 31.97 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.6 (COO*C*H$_2$), 69.2 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3437 (w), 2921 (vs), 2852 (s), 1734 (s), 1586 (w), 1499 (m), 1466 (m), 1430 (m), 1390 (m), 1366 (m), 1334 (s), 1188 (vs), 1166 (vs), 1115 (s), 1059 (m), 1019 (m), 952 (w), 909 (w), 862 (w), 777 (w), 754 (m), 733 (m), 647 (w), 518 (w), 418 (w) cm^{-1}; MS (ESI): *m*/*z* = 1123.92 [M + NH$_4$]$^+$, 1128.88 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{69}H_{119}NO_9$) calcd.: 1128.8777 [M + Na]$^+$, found: 1128.8777.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4,5-tris-(tetradecyloxy)benzoate [3,4,5-C$_{14}$TyrC$_{12}$Boc]

According to GP6: 3,4,5-Tris(tetradecyloxy)benzoic acid **3,4,5-C$_{14}$CO$_2$H** (1.547 g, 2.04 mmol), dodecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{12}$Boc** (902 mg, 2.01 mmol), EDCI (800 mg, 4.17 mmol), DMAP (64.0 mg, 0.52 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 35 : 1 → 20 : 1; R_f = 0.50 (PE/EtOAc = 10 : 1).



3,4,5-C$_{14}$TyrC$_{12}$Boc

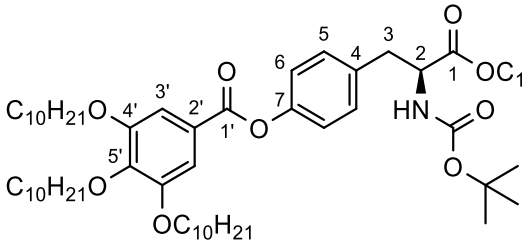
$C_{75}H_{131}NO_9$

(1190.87)

Colourless solid (84%, 2.00 g, 1.68 mmol, purity >95%); M.p. 55.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.22–1.38 (m, 78H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.52 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.8 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 14.1 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 13.7 Hz, 6.6 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 3.07–3.17 (m, 2H, 3-H), 4.02–4.13 (m, 8H, OC*H*$_2$), 4.58 (q, *J* = 6.5 Hz, 1H, 2-H), 5.02 (d, *J* = 8.3 Hz, 1H, NH), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.19 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.09, 26.11, 28.3, 28.5, 29.24, 29.33, 29.37, 29.40, 29.42, 29.51, 29.61, 29.66, 29.70, 29.73, 29.77, 30.4, 31.93, 31.96 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3381 (w), 2921 (vs), 2852 (vs), 1734 (s), 1586 (w), 1499 (m), 1466 (m), 1430 (m), 1390 (m), 1366 (m), 1335 (s), 1189 (vs), 1166 (vs), 1116 (s), 1059 (m), 1019 (m), 952 (w), 908 (w), 862 (w), 777 (w), 754 (w), 732 (s), 648 (w), 518 (w), 425 (w) cm^{-1}; MS (ESI): *m*/*z* = 1208.02 [M + NH$_4$]$^+$, 1212.97 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{75}H_{131}NO_9$) calcd.: 1212.9716 [M + Na]$^+$, found: 1212.9711.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4,5-tris-(decyloxy)benzoate [3,4,5-C$_{10}$TyrC$_{14}$Boc]

According to GP6: 3,4,5-Tris(decyloxy)benzoic acid **3,4,5-C$_{10}$CO$_2$H** (1.24 g, 2.11 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (960 mg, 2.01 mmol), EDCI (827 mg, 4.31 mmol), DMAP (48.0 mg, 0.39 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 20 : 1 → 15 : 1; R_f = 0.48 (PE/EtOAc = 10 : 1).



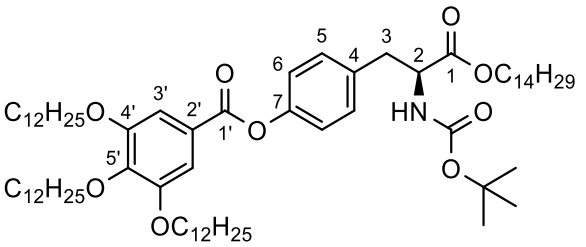
3,4,5-C$_{10}$TyrC$_{14}$Boc
C$_{65}$H$_{111}$NO$_9$
(1050.60)

Colourless solid (81%, 1.71 g, 1.63 mmol, purity >95%); M.p. 56.7 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.90 (m, 12H, C*H*$_3$), 1.23–1.38 (m, 58H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 13.2 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 13.2 Hz, 6.9 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 14.5 Hz, 6.8 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.03–4.07 (m, 6H, OC*H*$_2$), 4.08–4.12 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.4 Hz, 1H, 2-H), 5.01 (d, *J* = 8.2 Hz, 1H, NH), 7.13 (d, *J* = 8.1 Hz,

2H, 6-H), 7.19 (d, J = 8.1 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.12, 14.13 (CH_3), 22.70, 22.72, 25.9, 26.07, 26.10, 28.3, 28.5, 29.23, 29.32, 29.37, 29.38, 29.41, 29.51, 29.56, 29.58, 29.60, 29.65, 29.67, 29.69, 29.71, 29.75, 30.4, 31.93, 31.94, 31.96 (CH_2, OC(CH_3)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COOCH_2), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 79.9 (OC(CH_3)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3360 (w), 2922 (vs), 2853 (s), 1734 (s), 1718 (s), 1586 (m), 1499 (m), 1466 (m), 1430 (m), 1390 (m), 1366 (m), 1334 (s), 1188 (vs), 1115 (vs), 1059 (m), 1018 (m), 953 (w), 934 (w), 909 (w), 862 (w), 777 (w), 754 (m), 733 (m), 647 (w), 516 (w) cm^{-1}; MS (ESI): m/z = 1067.86 [M + NH_4]$^+$, 1072.82 [M + Na]$^+$; HRMS (ESI): m/z ($C_{65}H_{111}NO_9$) calcd.: 1072.8151 [M + Na]$^+$, found: 1072.8151.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4,5-tris-(dodecyloxy)benzoate [3,4,5-C$_{12}$TyrC$_{14}$Boc]

According to GP6: 3,4,5-Tris(dodecyloxy)benzoic acid **3,4,5-C$_{12}$CO$_2$H** (1.35 g, 2.00 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC$_{14}$Boc** (962 mg, 2.01 mmol), EDCI (793 mg, 4.14 mmol), DMAP (68.0 mg, 0.56 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 25 : 1 → 20 : 1; R_f = 0.49 (PE/EtOAc = 10 : 1).



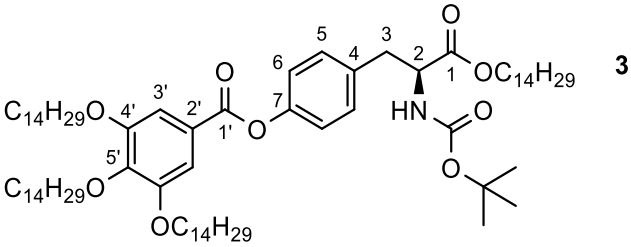
3,4,5-C$_{12}$TyrC$_{14}$Boc
$C_{71}H_{123}NO_9$
(1134.76)

Colourless solid (71%, 1.60 g, 1.41 mmol, purity >95%); M.p. 50.7 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.89 (m, 12H, CH_3), 1.22–1.38 (m, 70H, CH_2), 1.44 (s, 9H, OC(CH_3)$_3$), 1.46–1.51 (m, 6H, OCH$_2$CH$_2$CH_2), 1.61 (dt, J = 14.1 Hz, 6.9 Hz, 2H, COOCH$_2$CH_2), 1.76 (dt, J = 14.1 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$CH_2), 1.83 (dt, J = 13.5 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$CH_2), 3.07–3.16 (m, 2H, 3-H), 4.03–4.07 (m, 6H, OCH_2), 4.08–4.13 (m, 2H, COOCH_2), 4.58 (q, J = 6.3 Hz, 1H, 2-H), 5.02 (d, J = 8.2 Hz, 1H, NH), 7.13 (d, J = 8.4 Hz, 2H, 6-H), 7.19 (d, J = 8.4 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.09, 26.11, 28.3, 28.5, 29.24, 29.33, 29.38, 29.39, 29.42, 29.52, 29.60, 29.61, 29.66, 29.68, 29.68, 29.70, 29.72, 29.72, 29.75, 29.77, 29.78, 30.37, 31.95, 31.97 (CH_2, OC(CH_3)$_3$), 37.8 (C-3), 54.4 (C-2), 65.7 (COOCH_2), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 79.9 (OC(CH_3)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4),

143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3368 (w), 2921 (vs), 2852 (s), 1734 (s), 1718 (s), 1586 (w), 1499 (m), 1466 (m), 1430 (m), 1390 (m), 1365 (m), 1334 (s), 1188 (vs), 1166 (vs), 1115 (vs), 1059 (m), 1019 (m), 952 (w), 862 (w), 778 (w), 754 (m), 721 (w), 669 (w), 523 (w) cm^{-1}; MS (ESI): *m*/*z* = 1151.95 $[M + NH_4]^+$, 1156.91$[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{71}H_{123}NO_9$) calcd.: 1156.9090 $[M + Na]^+$, found: 1156.9093.

(*S*)-4-(2-((*tert*-Butoxycarbonyl)amino)-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4,5-tris-(tetradecyloxy)benzoate [3,4,5-C_{14}TyrC_{14}Boc]

According to GP6: 3,4,5-Tris(tetradecyloxy)benzoic acid **3,4,5-$C_{14}CO_2H$** (1.52 g, 2.00 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-tyrosinate **TyrC_{14}Boc** (962 mg, 2.01 mmol), EDCI (796 mg, 4.15 mmol), DMAP (71.0 mg, 0.58 mmol), dry CH_2Cl_2 (150 mL); reaction time: 72 h; column gradient 25 : 1 → 20 : 1; R_f = 0.50 (PE/EtOAc = 10 : 1).



3,4,5-C_{14}TyrC_{14}Boc

$C_{77}H_{135}NO_9$

(1218.93)

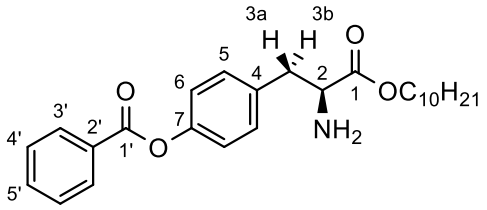
Colourless solid (78%, 1.91 g, 1.57 mmol, purity >95%); M.p. 53.3 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.89 (m, 12H, C*H*$_3$), 1.23–1.38 (m, 82H, C*H*$_2$), 1.44 (s, 9H, OC(C*H*$_3$)$_3$), 1.46–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (dt, *J* = 14.0 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 13.5 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 13.7 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 3.07–3.16 (m, 2H, 3-H), 4.03–4.07 (m, 6H, OC*H*$_2$), 4.08–4.12 (m, 2H, COOC*H*$_2$), 4.58 (q, *J* = 6.3 Hz, 1H, 2-H), 5.01 (d, *J* = 8.1 Hz, 1H, NH), 7.13 (d, *J* = 8.2 Hz, 2H, 6-H), 7.19 (d, *J* = 8.2 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.09, 26.11, 28.3, 28.5, 29.24, 29.33, 29.38, 29.40, 29.41, 29.43, 29.46, 29.48, 29.52, 29.57, 29.60, 29.61, 29.67, 29.68, 29.70, 29.72, 29.73, 29.76, 29.78, 29.79, 30.4, 31.95, 31.97 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-3), 54.5 (C-2), 65.7 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 79.9 (O*C*(CH$_3$)$_3$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.4 (C-5), 133.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 155.1 (HNC=O), 164.9 (C-1'), 171.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2924 (m), 2854 (m), 1729 (w), 1587 (w), 1499 (w), 1467 (w), 1431 (w), 1367 (w), 1335 (w), 1190 (m), 1166 (m), 1116 (w), 1061 (w), 1019 (w), 905 (vs), 728 (vs), 649 (m), 501 (w) cm^{-1}; MS (ESI): *m*/*z* = 1236.05 $[M + NH_4]^+$, 1241.00 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{77}H_{135}NO_9$) calcd.: 1241.0029 $[M + Na]^+$, found: 1241.0027.

General Procedure GP7: Boc deprotection[1,24]

The respective protected amino acid ester **Ar(C$_m$)TyrC$_n$Boc** (0.80 mmol) was dissolved in dry CH_2Cl_2 (50 mL) under a nitrogen atmosphere and cooled to 0 °C while stirring. Afterwards, trifluoroacetic acid (1.3 mL, 16.4 mmol) was added slowly and the mixture was stirred for 24 – 72 h at room temperature. After complete conversion, the ion exchange resin Amberlyst® A21 (free base) was added until a neutral pH value was obtained, and the mixture was stirred for additional 20 min. Subsequently, the ion exchange resin was filtered off and the solvent was removed under reduced pressure. The crude products were used without further purification. Differences from this procedure can be found at the respective compound.

(*S*)-4-(2-Amino-3-(decyloxy)-3-oxopropyl)phenyl benzoate [BzTyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **BzTyrC$_{10}$Boc** (860 mg, 1.64 mmol), TFA (1.9 mL, 24.7 mmol), dry CH_2Cl_2 (40 mL); reaction time: 24 h.

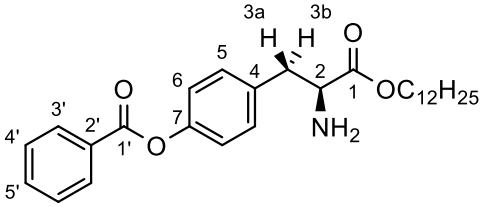


BzTyrC$_{10}$NH$_2$
$C_{26}H_{35}NO_4$
(425.57)

Light-yellow oil (99%, 688 mg, 1.62 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.22–1.33 (m, 14H, C*H*$_2$), 1.59–1.65 (m, 2H, OCH$_2$C*H*$_2$), 2.90 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H, 2-H), 4.11 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 7.16 (d, *J* = 8.5 Hz, 2H, 6-H), 7.27 (d, *J* = 8.5 Hz, 2H, 5-H), 7.51 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.62–7.65 (m, 1H, 5'-H), 8.20 (dd, *J* = 7.8 Hz, 1.4 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.25, 29.31, 29.51, 29.55, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (O*C*H$_2$), 121.8 (C-6), 128.6 (C-4'), 129.6 (C-2'), 130.2 (C-3'), 130.3 (C-5), 133.6 (C-5'), 135.0 (C-4), 149.8 (C-7), 165.1 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3382 (w), 2924 (m), 2854 (m), 1732 (vs), 1601 (w), 1507 (m), 1452 (m), 1377 (w), 1314 (w), 1262 (vs), 1196 (vs), 1109 (m), 1080 (s), 1061 (vs), 1023 (s), 1002 (m), 937 (w), 876 (m), 799 (m), 705 (vs), 685 (m), 673 (m), 618 (w), 581 (w), 519 (w), 449 (w) cm^{-1}; MS (ESI): *m*/*z* = 426.26 [M + H]$^+$, 448.24 [M + Na]$^+$, 464.22 [M + K]$^+$; HRMS (ESI): *m*/*z* ($C_{26}H_{35}NO_4$) calcd.: 426.2639 [M + H]$^+$, found: 426.2642.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl benzoate [BzTyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **BzTyrC$_{12}$Boc** (820 mg, 1.48 mmol), TFA (1.7 mL, 22.1 mmol), dry CH_2Cl_2 (40 mL); reaction time: 24 h.

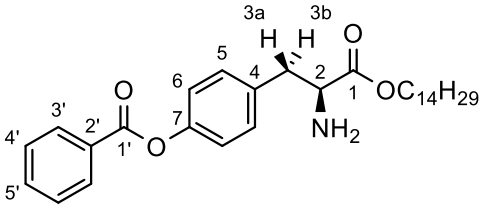


BzTyrC$_{12}$NH$_2$
$C_{28}H_{39}NO_4$
(453.62)

Yellow oil (99%, 665 mg, 1.47 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.21–1.33 (m, 18H, C*H*$_2$), 1.59–1.65 (m, 2H, OCH$_2$C*H*$_2$), 2.90 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H, 2-H), 4.11 (t, *J* = 6.8 Hz, 2H, OC*H*$_2$), 7.16 (d, *J* = 8.5 Hz, 2H, 6-H), 7.27 (d, *J* = 8.5 Hz, 2H, 5-H), 7.51 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.62–7.65 (m, 1H, 5'-H), 8.10–8.23 (m, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.25, 29.35, 29.52, 29.60, 29.64, 29.66, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (O*C*H$_2$), 121.8 (C-6), 128.6 (C-4'), 129.6 (C-2'), 130.2 (C-3'), 130.3 (C-5), 133.6 (C-5'), 135.0 (C-4), 149.8 (C-7), 165.1 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3389 (w), 2923 (s), 2853 (m), 1732 (vs), 1601 (w), 1507 (m), 1466 (w), 1452 (m), 1377 (w), 1314 (w), 1262 (vs), 1197 (vs), 1109 (w), 1080 (s), 1061 (vs), 1023 (s), 1002 (m), 878 (m), 849 (m), 799 (m), 705 (vs), 685 (w), 673 (m), 617 (w), 580 (w), 520 (w), 451 (w) cm^{-1}. MS (ESI): *m*/*z* = 454.30 $[M + H]^+$, 476.28 $[M + Na]^+$, 492.25 $[M + K]^+$. HRMS (ESI): *m*/*z* ($C_{28}H_{39}NO_4$) calcd.: 454.2952 $[M + H]^+$, found: 454.2950.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl benzoate [BzTyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **BzTyrC$_{14}$Boc** (811 mg, 1.39 mmol), TFA (1.6 mL, 20.8 mmol), dry CH_2Cl_2 (40 mL); reaction time: 24 h.



BzTyrC$_{14}$NH$_2$
$C_{30}H_{43}NO_4$
(481.68)

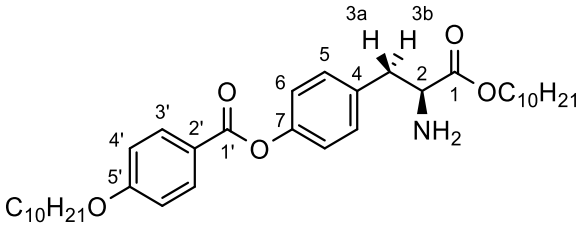
Yellow oil (quant., 668 mg, 1.39 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.21–1.33 (m, 22H, C*H*$_2$), 1.59–1.65 (m, 2H, OCH$_2$C*H*$_2$), 2.90 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H, 2-H), 4.11 (t, *J* = 6.8 Hz, 2H, OC*H*$_2$), 7.16 (d, *J* = 8.5 Hz, 2H, 6-H), 7.27 (d, *J* = 8.5 Hz, 2H, 5-H), 7.51 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.63 (t, *J* = 7.8 Hz, 1H, 5'-H), 8.20 (dd, *J* = 7.8 Hz, 1.4 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.26, 29.36, 29.52, 29.61, 29.66, 29.69, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (O*C*H$_2$), 121.8 (C-6), 128.6 (C-4'), 129.6 (C-2'), 130.2 (C-3'), 130.3 (C-5), 133.6 (C-5'), 135.0 (C-4),

149.8 (C-7), 165.1 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3381 (w), 2922 (s), 2852 (m), 1733 (vs), 1601 (w), 1507 (m), 1466 (w), 1452 (m), 1377 (w), 1314 (w), 1263 (vs), 1197 (vs), 1103 (w), 1080 (s), 1061 (vs), 1024 (s), 936 (w), 878 (m), 848 (m), 799 (m), 705 (vs), 685 (w), 673 (w), 617 (w), 580 (w), 519 (w), 443 (w), 417 (w) cm^{-1}; MS (ESI): *m*/*z* = 482.33 $[M + H]^+$, 504.31 $[M + Na]^+$, 520.28 $[M + K]^+$; HRMS (ESI): *m*/*z* ($C_{30}H_{43}NO_4$) calcd.: 482.3265 $[M + H]^+$, found: 482.3271.

(*S*)-4-(2-Amino-3-(decyloxy)-3-oxopropyl)phenyl 4-(decyloxy)benzoate

[4-C$_{10}$TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{10}$TyrC$_{10}$Boc** (810 mg, 1.19 mmol), TFA (1.4 mL, 18.17 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



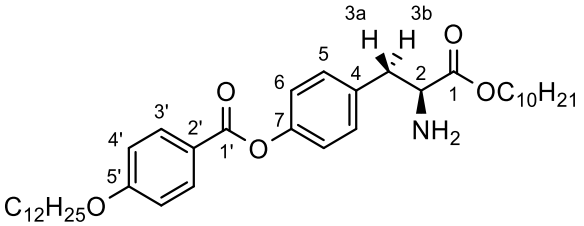
4-C$_{10}$TyrC$_{10}$NH$_2$
$C_{36}H_{55}NO_5$
(581.84)

Light-yellow solid (75%, 520 mg, 0.89 mmol); M.p. 62.2 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.92 (m, 6H, C*H*$_3$), 1.18–1.42 (m, 28H, C*H*$_2$), 1.42–1.52 (m, 2H, $OCH_2CH_2CH_2$), 1.61 (q, *J* = 6.9 Hz, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.3 Hz, 7.8 Hz, 1H, 2-H), 4.04 (t, *J* = 6.5 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.1 Hz, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.6, 29.1, 29.25, 29.32, 29.37, 29.52, 29.56, 31.90 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.3 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.8 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 433 (w), 484 (w), 516 (w), 567 (w), 647 (w), 691 (w), 721 (w), 762 (m), 793 (m), 846 (m), 886 (m), 1007 (m), 1016 (m), 1074 (m), 1107 (m), 1127 (m), 1167 (vs), 1197 (s), 1258 (vs), 1315 (m), 1379 (w), 1420 (w), 1469 (m), 1510 (m), 1606 (s), 1724 (vs), 2850 (s), 2918 (s), 2954 (m), 3379 (w) cm^{-1}; MS (ESI): *m*/*z* = 582.42 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{36}H_{55}NO_5$) calcd.: 582.4153 $[M + H]^+$, found: 582.4158.

(*S*)-4-(2-Amino-3-(decyloxy)-3-oxopropyl)phenyl 4-(dodecyloxy)benzoate

[4-C$_{12}$TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{12}$TyrC$_{10}$Boc** (800 mg, 1.13 mmol), TFA (1.3 mL, 16.87 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



4-C$_{12}$TyrC$_{10}$NH$_2$

$C_{38}H_{59}NO_5$

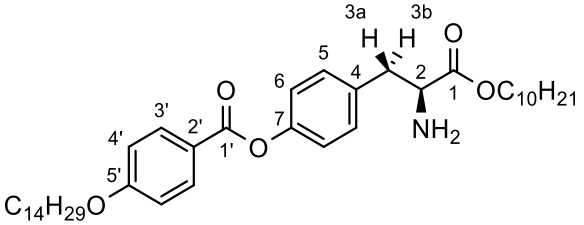
(609.89)

Colourless solid (99%, 681 mg, 1.12 mmol); M.p. 65.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.91(m, 6H, C*H*$_3$), 1.20–1.42 (m, 30H, C*H*$_2$), 1.43–1.49 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.62 (q, *J* = 7.0 Hz, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 2.88 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.4 Hz, 7.8 Hz, 1H, 2-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.11 (t, *J* = 6.8 Hz, 2H, COOC*H*$_2$), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.68, 22.70, 25.91, 25.99, 28.58, 29.10, 29.25, 29.32, 29.36, 29.52, 29.56, 29.60, 29.64, 29.66, 31.90, 31.93 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.8 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 432 (w), 516 (m), 572 (w), 646 (m), 691 (m), 721 (w), 761 (m), 792 (m), 846 (m), 886 (m), 949 (w), 1007 (s), 1017 (s), 1074 (vs), 1107 (m), 1126 (w), 1166 (vs), 1197 (s), 1258 (vs), 1315 (m), 1378 (w), 1420 (w), 1469 (m), 1510 (m), 1606 (s), 1725 (vs), 2850 (s), 2918 (vs), 2955 (m), 3306 (w), 3379 (w) cm^{-1}; MS (ESI): *m*/*z* = 610.45 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{38}H_{59}NO_5$) calcd.: 610.4466 [M + H]$^+$, found: 610.4462.

(*S*)-4-(2-Amino-3-(decyloxy)-3-oxopropyl)phenyl 4-(tetradecyloxy)benzoate

[4-C$_{14}$TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{14}$TyrC$_{10}$Boc** (803 mg, 1.09 mmol), TFA (1.2 mL, 15.58 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



4-C$_{14}$TyrC$_{10}$NH$_2$

$C_{40}H_{63}NO_5$

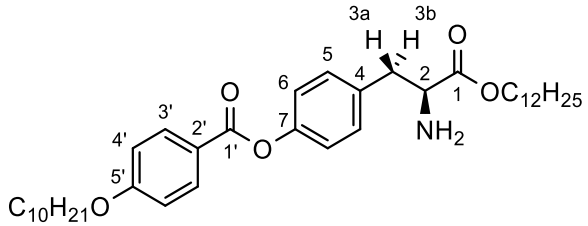
(637.95)

Colourless solid (quant. (693 mg, 1.09 mmol); M.p. 67.1 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.91(m, 6H, C*H*$_3$), 1.20–1.40 (m, 34H, C*H*$_2$), 1.41–1.48 (m, 2H, $OCH_2CH_2CH_2$), 1.62 (q, *J* = 7.0 Hz, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.4 Hz, 7.9 Hz, 1H, 2-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 9.0 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.3 Hz, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.68, 22.70, 25.91, 25.99, 28.58, 29.10, 29.26, 29.32, 29.37, 29.52, 29.56, 29.60, 29.66, 29.68, 29.70, 31.90, 31.93 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.8 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 443 (w), 518 (w), 567 (w), 653 (w), 691 (w), 720 (m), 761 (m), 798 (w), 844 (m), 891 (w), 940 (w), 1018 (m), 1040 (w), 1078 (m), 1107 (w), 1173 (s), 1195 (s), 1218 (m), 1254 (s), 1288 /s), 1380 (w), 1420 (w), 1470 (m), 1510 (m), 1584 (w), 1608 (m), 1726 (s), 2849 (s), 2873 (m), 2916 (vs), 2955 (m) cm^{-1}; MS (ESI): *m*/*z* = 638.48 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{40}H_{63}NO_5$) calcd.: 638.4779 $[M + H]^+$, found: 638.4781.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 4-(decyloxy)benzoate

[4-C$_{10}$TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{10}$TyrC$_{12}$Boc** (800 mg, 1.13 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



4-C$_{10}$TyrC$_{12}$NH$_2$

$C_{38}H_{59}NO_5$

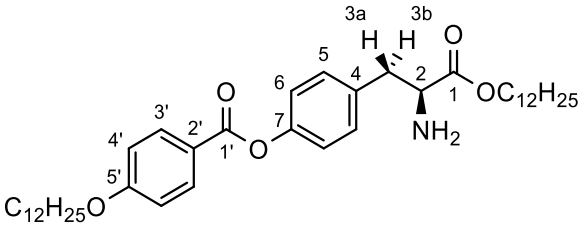
(609.89)

Colourless solid (93%, 637 mg, 1.04 mmol); M.p. 69.1 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.93 (m, 6H, C*H*$_3$), 1.19–1.41 (m, 30H, C*H*$_2$), 1.41–1.51 (m, 2H, $OCH_2CH_2CH_2$), 1.62 (q, *J* = 7.0 Hz, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.3 Hz, 7.8 Hz, 1H, 2-H), 4.04 (t, *J* = 6.5 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.6 Hz, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.6, 29.1, 29.26, 29.32, 29.36, 29.52, 29.56, 29.61, 29.65, 29.66, 31.90, 31.92 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9

(C-6), 130.3 (C-5), 132.3 (C-3'), 134.8 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 433 (w), 484 (w), 516 (w), 568 (w), 646 (m), 691 (m), 721 (m), 761 (m), 792 (m), 812 (m), 846 (m), 886 (m), 1007 (m), 1017 (m), 1073 (s), 1107 (m), 1126 (m), 1167 (vs), 1196 (vs), 1257 (vs), 1315 (m), 1378 (w), 1420 (w), 1469 (m), 1510 (m), 1606 (s), 1725 (vs), 2850 (s), 2918 (vs), 2955 (m), 3379 (w) cm^{-1}; MS (ESI): *m*/*z* = 610.45 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{38}H_{59}NO_5$) calcd.: 610.4466 $[M + H]^+$, found: 610.4465.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 4-(dodecyloxy)benzoate [4-C$_{12}$TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{12}$TyrC$_{12}$Boc** (806 mg, 1.10 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.

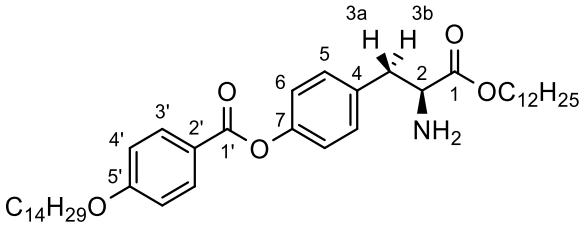


4-C$_{12}$TyrC$_{12}$NH$_2$
$C_{40}H_{63}NO_5$
(637.95)

Colourless solid (95%, 660 mg, 1.04 mmol); M.p. 67.2 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.91 (m, 6H, C*H*$_3$), 1.18–1.41 (m, 34H, C*H*$_2$), 1.42–1.52 (m, 2H, $OCH_2CH_2CH_2$), 1.61 (q, *J* = 6.8 Hz, 2H, $COOCH_2CH_2$), 1.79–1.84 (m, 2H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.4 Hz, 7.8 Hz, 1H, 2-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.25 (d, *J* = 8.7 Hz, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.6, 29.1, 29.26, 29.36, 29.52, 29.56, 29.60, 29.61, 29.65, 29.67, 31.92 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.8 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 433 (w), 517 (w), 572 (w), 647 (m), 691 (m), 721 (m), 762 (m), 793 (m), 846 (m), 886 (m), 956 (w), 1007 (m), 1018 (m), 1073 (s), 1108 (m), 1126 (m), 1167 (vs), 1197 (vs), 1258 (vs), 1315 (m), 1378 (w), 1420 (w), 1469 (m), 1511 (m), 1606 (s), 1725 (vs), 2850 (s), 2917 (vs), 2955 (m), 3380 (w) cm^{-1}; MS (ESI): *m*/*z* = 638.48 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{40}H_{63}NO_5$) calcd.: 638.4779 $[M + H]^+$, found: 638.4780.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 4-(tetradecyloxy)benzoate [4-C$_{14}$TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{14}$TyrC$_{12}$Boc** (800 mg, 1.04 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.

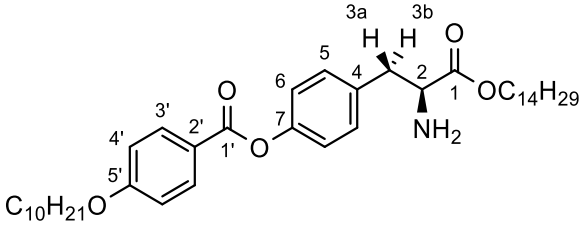


4-C$_{14}$TyrC$_{12}$NH$_2$
$C_{42}H_{67}NO_5$
(666.00)

Light-yellow solid (97%, 673 mg, 1.01 mmol); M.p. 70.1 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.91 (m, 6H, C*H*$_3$), 1.19–1.41 (m, 38H, C*H*$_2$), 1.41–1.51 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.61 (t, *J* = 6.9 Hz, 2H, COOCH$_2$C*H*$_2$), 1.79–1.84 (m, 2H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.3 Hz, 7.8 Hz, 1H, 2-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.11 (t, *J* = 6.8 Hz, 2H, COOC*H*$_2$), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.6 Hz, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.6, 29.1, 29.26, 29.37, 29.52, 29.57, 29.60, 29.61, 29.65, 29.66, 29.68, 29.70, 31.93 (*C*H$_2$), 40.5 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.7 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 432 (w), 517 (m), 572 (w), 646 (m), 691 (m), 721 (m), 761 (m), 792 (m), 804 (m), 847 (m), 885 (m), 1008 (m), 1016 (m), 1074 (s), 1107 (m), 1125 (w), 1168 (vs), 1197 (s), 1257 (vs), 1315 (m), 1378 (w), 1420 (w), 1469 (m), 1511 (m), 1606 (s), 1726 (vs), 2849 (vs), 2917 (vs), 2955 (m), 3380 (w) cm^{-1}; MS (ESI): *m*/*z* = 666.51 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{42}H_{67}NO_5$) calcd.: 666.5092 $[M + H]^+$, found: 666.5096.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 4-(decyloxy)benzoate [4-C$_{10}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{10}$TyrC$_{14}$Boc** (805 mg, 1.10 mmol), TFA (1.3 mL, 16.4 mmol), dry CH_2Cl_2 (35 mL); reaction time: 48 h.

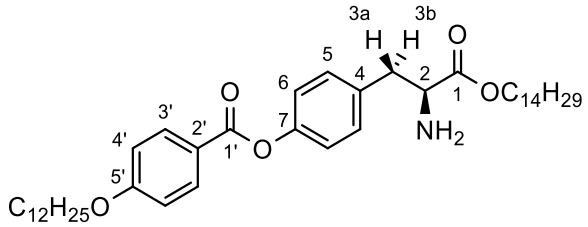


4-C$_{10}$TyrC$_{14}$NH$_2$
$C_{40}H_{63}NO_5$
(637.95)

Light-yellow solid (98%, 680 mg, 1.07 mmol); M.p. 69.2 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.92 (m, 6H, C*H*$_3$), 1.23–1.40 (m, 34H, C*H*$_2$), 1.42–1.52 (m, 2H, $OCH_2CH_2CH_2$), 1.61 (q, *J* = 6.8 Hz, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.7 Hz, 5.4 Hz, 1H, 3b-H), 3.73 (dd, *J* = 5.4 Hz, 7.8 Hz, 1H, 2-H), 4.04 (t, *J* = 6.5 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 9.0 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.25 (d, *J* = 8.7 Hz, 2H, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.6, 29.1, 29.26, 29.32, 29.37, 29.52, 29.56, 29.61, 29.66, 29.70, 31.90, 31.93 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.8 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 432 (w), 484 (w), 517 (m), 571 (w), 632 (w), 647 (m), 691 (m), 721 (m), 762 (s), 792 (m), 846 (s), 886 (m), 949 (w), 1008 (m), 1017 (m), 1073 (s), 1107 (m), 1126 (m), 1167 (vs), 1196 (vs), 1257 (vs), 1315 (m), 1378 (w), 1420 (w), 1469 (m), 1510 (m), 1606 (s), 1725 (vs), 1922 (w), 2850 (s), 2917 (vs), 2955 (m) 3378 (w) cm^{-1}; MS (ESI): *m*/*z* = 638.48 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{40}H_{63}NO_5$) calcd.: 638.4779 $[M + H]^+$, found: 638.4761.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 4-(dodecyloxy)benzoate [4-C$_{12}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{12}$TyrC$_{14}$Boc** (766 mg, 1.00 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



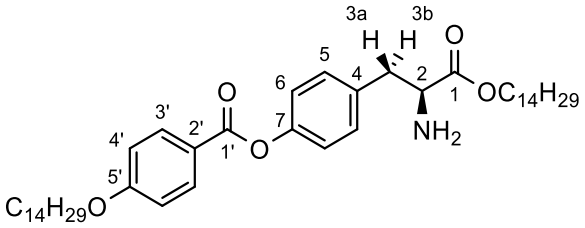
4-C$_{12}$TyrC$_{14}$NH$_2$
$C_{42}H_{67}NO_5$
(666.00)

Colourless solid (87%, 582 mg, 0.87 mmol); M.p. 72.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 6H, C*H*$_3$), 1.19–1.41 (m, 38H, C*H*$_2$), 1.42–1.52 (m, 2H, $OCH_2CH_2CH_2$), 1.62 (q, *J* = 7.0 Hz, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.74 (dd, *J* = 5.3 Hz, 7.9 Hz, 1H, 2-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 9.0 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.25 (d, 5-H), 8.12 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.6, 29.1, 29.26, 29.36, 29.37, 29.53, 29.57, 29.60, 29.62, 29.64, 29.67, 29.70, 31.93 (CH_2), 40.5 (C-3), 55.8 (C-2), 65.3 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3

(C-5), 132.3 (C-3'), 134.7 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 433 (w), 518 (w), 571 (w), 647 (w), 691 (m), 721 (m), 762 (m), 793 (m), 846 (m), 886 (m), 955 (w), 1007 (m), 1017 (m), 1074 (s), 1107 (m), 1126 (w), 1168 (vs), 1197 (vs), 1258 (vs), 1315 (m), 1378 (w), 1420 (w), 1469 (m), 1511 (m), 1606 (s), 1726 (vs), 2849 (vs), 2917 (vs), 2955 (m), 3379 (w) cm^{-1}; MS (ESI): *m*/*z* = 666.51 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{42}H_{67}NO_5$) calcd.: 666.5092 $[M + H]^+$, found: 666.5098.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 4-(tetradecyloxy)benzoate [4-C$_{14}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **4-C$_{14}$TyrC$_{14}$Boc** (794 mg, 1.00 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.

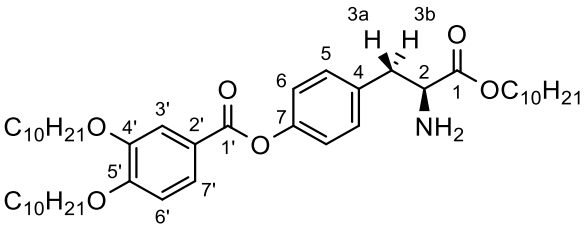


4-C$_{14}$TyrC$_{14}$NH$_2$
$C_{44}H_{71}NO_5$
(694.05)

Colourless solid (93%, 642 mg, 0.93 mmol); M.p. 66.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.92 (m, 6H, C*H*$_3$), 1.18–1.42 (m, 42H, C*H*$_2$), 1.42–1.51 (m, 2H, $OCH_2CH_2CH_2$), 1.61 (q, *J* = 6.9 Hz, 2H, $COOCH_2CH_2$), 1.82 (q, 2H, OCH_2CH_2), 2.91 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.4 Hz, 1H, 3b-H), 3.74 (dd, *J* = 5.3 Hz, 7.9 Hz, 1H, 2-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.25 (d, *J* = 8.2 Hz, 5-H), 8.12 (d, *J* = 8.9 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.6, 29.1, 29.26, 29.37, 29.53, 29.57, 29.60, 29.62, 29.67, 29.68, 29.70, 31.93 (CH_2), 40.4 (C-3), 55.8 (C-2), 65.3 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 121.9 (C-6), 130.3 (C-5), 132.3 (C-3'), 134.7 (C-4), 150.0 (C-7), 163.5 (C-5'), 164.9 (C-1'), 174.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 419 (w), 446 (w), 519 (w), 546 (w), 567 (w), 631 (w), 653 (m), 691 (m), 719 (m), 760 (s), 798 (m), 843 (s), 893 (m), 940 (w), 969 (m), 1018 (m), 1040 (m), 1083 (s), 1106 (m), 1174 (vs), 1216 (s), 1253 (vs), 1288 (vs), 1396 (w), 1420 (w), 1469 (s), 1510 (s), 1583 (w), 1607 (m), 1713 (s), 1725 (s), 2848 (vs), 2914 (vs), 2954 (w) cm^{-1}; MS (ESI): *m*/*z* = 694.54 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{44}H_{71}NO_5$) calcd.: 694.5405 $[M + H]^+$, found: 694.5409.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,4-bis(decyloxy)benzoate [3,4-C_{10}Tyr$C_{10}$$NH_2$]

According to GP7: Boc protected amine **3,4-C_{10}TyrC_{10}Boc** (937 mg, 1.12 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (50 mL); reaction time: 48 h.

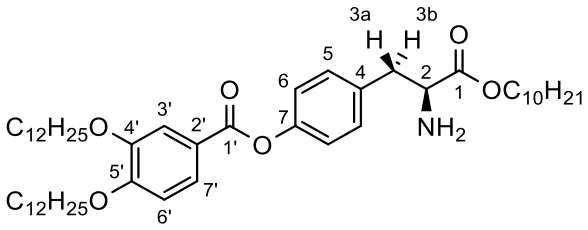


3,4-C_{10}Tyr$C_{10}$$NH_2$
$C_{46}H_{75}NO_6$
(738.11)

Colourless solid (99%, 816 mg, 1.11 mmol, purity >95%); M.p. 52.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.23–1.40 (m, 38H, C*H*$_2$), 1.45–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.82–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.0 Hz, 2H, 6-H), 7.25 (d, *J* = 8.0 Hz, 2H, 5-H), 7.65 (d, *J* = 2.1 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.68, 22.70, 25.91, 25.98, 26.02, 28.59, 29.06, 29.18, 29.25, 29.31, 29.36, 29.39, 29.42, 29.52, 29.56, 29.58, 29.62, 29.63, 31.90, 31.92 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3389 (w), 2955 (m), 2917 (vs), 2872 (m), 2849 (vs), 1722 (vs), 1597 (m), 1512 (s), 1467 (m), 1429 (s), 1394 (w), 1344 (w), 1294 (s), 1274 (vs), 1210 (vs), 1199 (vs), 1167 (s), 1143 (s), 1091 (s), 1068 (m), 1046 (m), 1019 (m), 987 (m), 954 (m), 921 (w), 879 (m), 822 (m), 793 (m), 756 (s), 723 (m), 653 (w), 615 (w), 546 (w), 515 (w), 502 (w), 467 (w) cm^{-1}; MS (ESI): *m*/*z* = 738.57 $[M + H]^+$, 760.55 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{46}H_{75}NO_6$) calcd.: 738.5667 $[M + H]^+$, found: 738.5673.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,4-bis(dodecyloxy)benzoate [3,4-C_{12}Tyr$C_{10}$$NH_2$]

According to GP7: Boc protected amine **3,4-C_{12}TyrC_{10}Boc** (897 mg, 1.00 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



3,4-C$_{12}$TyrC$_{10}$NH$_2$

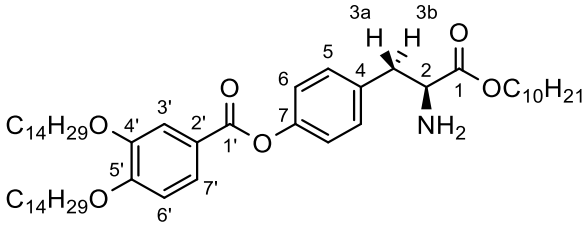
$C_{50}H_{83}NO_6$

(794.22)

Colourless solid (quant., 796 mg, 1.00 mmol, purity >95%); M.p. 59.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.23–1.40 (m, 46H, C*H*$_2$), 1.45–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.81–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.68, 22.70, 25.91, 25.98, 26.02, 28.58, 29.06, 29.18, 29.25, 29.31, 29.38, 29.40, 29.42, 29.52, 29.56, 29.62, 29.64, 29.67, 29.71, 31.90, 31.94 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3382 (w), 2955 (m), 2916 (vs), 2849 (vs), 1722 (s), 1597 (m), 1514 (m), 1468 (m), 1430 (m), 1393 (w), 1346 (w), 1293 (s), 1276 (vs), 1251 (m), 1211 (vs), 1169 (m), 1141 (m), 1089 (m), 1070 (w), 1042 (w), 1018 (w), 998 (w), 966 (w), 940 (w), 906 (w), 874 (w), 823 (w), 794 (w), 756 (m), 722 (w), 654 (w), 516 (w), 422 (w) cm^{-1}; MS (ESI): *m*/*z* = 794.63 [M + H]$^+$, 816.61 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{50}H_{83}NO_6$) calcd.: 794.6293 [M + H]$^+$, found: 794.6293.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,4-bis(tetradecyloxy)benzoate [3,4-C$_{14}$TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **3,4-C$_{14}$TyrC$_{10}$Boc** (883 mg, 0.93 mmol), TFA (1.1 mL, 14.3 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



3,4-C$_{14}$TyrC$_{10}$NH$_2$

$C_{54}H_{91}NO_6$

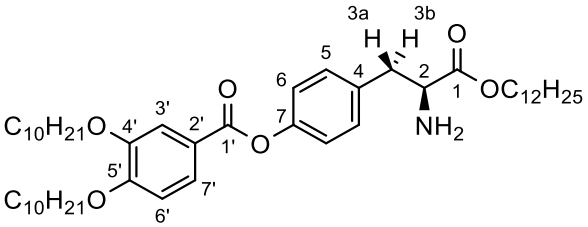
(850.32)

Colourless solid (quant., 787 mg, 0.93 mmol, purity >95%); M.p. 55.4 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.39 (m, 54H, C*H*$_2$), 1.45–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.81–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.89 (dd,

J = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.1 Hz, 2H, 6-H), 7.25 (d, *J* = 8.1 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.68, 22.71, 25.91, 25.99, 26.03, 28.59, 29.06, 29.19, 29.25, 29.32, 29.38, 29.40, 29.43, 29.52, 29.56, 29.63, 29.64, 29.68, 29.72, 31.90, 31.94 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (s), 2852 (s), 1730 (s), 1599 (w), 1510 (m), 1467 (m), 1429 (m), 1378 (w), 1345 (w), 1270 (s), 1194 (vs), 1167 (s), 1132 (s), 1071 (m), 1018 (m), 908 (s), 872 (w), 819 (w), 756 (m), 730 (vs), 648 (w), 517 (w), 420 (w) cm^{-1}; MS (ESI): *m*/*z* = 850.69 [M + H]$^+$, 872.67 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{54}H_{91}NO_6$) calcd.: 850.6919 [M + H]$^+$, found: 850.6912.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4-bis(decyloxy)benzoate [3,4-C$_{10}$TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **3,4-C$_{10}$TyrC$_{12}$Boc** (900 mg, 1.04 mmol), TFA (1.6 mL, 20.8 mmol), dry CH_2Cl_2 (65 mL); reaction time: 48 h; column gradient 80 : 1 → 30 : 1; R_f = 0.38 (CH_2Cl_2/MeOH = 40 : 1).



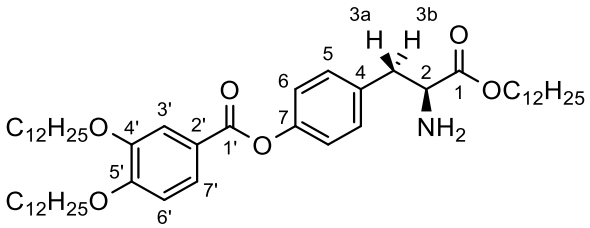
3,4-C$_{10}$TyrC$_{12}$NH$_2$
$C_{48}H_{79}NO_6$
(766.16)

Colourless solid (96%, 760 mg, 0.99 mmol, purity >95%); M.p. 50.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.21–1.40 (m, 42H, C*H*$_2$), 1.45–1.52 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.62 (dt, *J* = 13.5 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.82–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.92, 25.98, 26.02, 28.59, 29.07, 29.19, 29.26, 29.36, 29.40, 29.42, 29.52, 29.59, 29.61, 29.64, 29.65, 29.67, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'),

130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (s), 2852 (s), 1729 (s), 1598 (m), 1510 (m), 1467 (m), 1428 (m), 1393 (w), 1344 (w), 1271 (vs), 1193 (vs), 1167 (s), 1134 (s), 1086 (m), 1070 (m), 1018 (m), 989 (m), 953 (w), 908 (m), 877 (w), 819 (w), 756 (m), 730 (vs), 648 (w), 516 (w), 423 (w) cm^{-1}; MS (ESI): *m*/*z* = 766.60 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{48}H_{79}NO_6$) calcd.: 766.5980 $[M + H]^+$, found: 766.5975.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4-bis(dodecyloxy)benzoate [3,4-C_{12}Tyr$C_{12}$$NH_2$]

According to GP7: Boc protected amine **3,4-C_{12}TyrC_{12}Boc** (909 mg, 0.99 mmol), TFA (1.5 mL, 19.5 mmol), dry CH_2Cl_2 (60 mL); reaction time: 48 h.

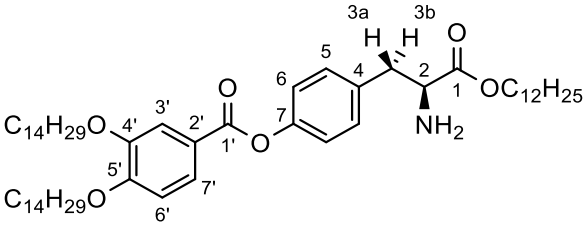


3,4-C_{12}Tyr$C_{12}$$NH_2$
$C_{52}H_{87}NO_6$
(822.27)

Colourless solid (94%, 762 mg, 0.93 mmol, purity >95%); M.p. 63.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.20–1.39 (m, 50H, C*H*$_2$), 1.45–1.52 (m, 4H, $OCH_2CH_2CH_2$), 1.59–1.65 (m, 2H, $COOCH_2CH_2$), 1.82–1.89 (m, 4H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OCH_2), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.1 Hz, 2H, 6-H), 7.25 (d, *J* = 8.1 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.92, 25.99, 26.03, 28.59, 29.06, 29.19, 29.26, 29.36, 29.38, 29.40, 29.43, 29.46, 29.52, 29.56, 29.61, 29.63, 29.65, 29.68, 29.71, 31.93, 31.94 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 69.1 (C-5'-OCH_2), 69.4 (C-4'-OCH_2), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2920 (s), 2850 (s), 1730 (m), 1598 (w), 1510 (m), 1467 (m), 1429 (m), 1394 (w), 1344 (w), 1271 (s), 1195 (vs), 1167 (m), 1141 (m), 1090 (m), 1018 (m), 965 (w), 907 (s), 878 (w), 822 (w), 756 (m), 730 (vs), 648 (w), 506 (w) cm^{-1}; MS (ESI): *m*/*z* = 822.66 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{52}H_{78}NO_6$) calcd.: 822.6606 $[M + H]^+$, found: 822.6604.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4-bis(tetradecyloxy)benzoate [3,4-C_{14}Tyr$C_{12}$$NH_2$]

According to GP7: Boc protected amine **3,4-C_{14}TyrC_{12}Boc** (1.24 g, 1.27 mmol), TFA (1.5 mL, 19.5 mmol), dry CH_2Cl_2 (50 mL); reaction time: 48 h.

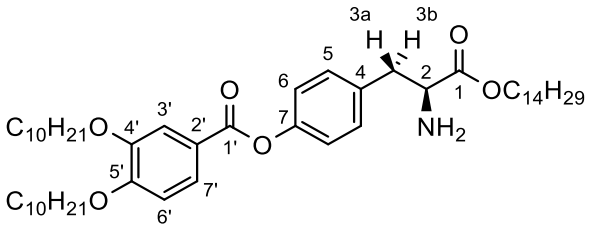


3,4-C_{14}Tyr$C_{12}$$NH_2$
$C_{56}H_{95}NO_6$
(878.38)

Colourless solid (99%, 1.10 g, 1.25 mmol, purity >95%); M.p. 77.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.23–1.39 (m, 58H, C*H*$_3$), 1.45–1.50 (m, 4H, $OCH_2CH_2CH_2$), 1.60–1.65 (m, 2H, $COOCH_2CH_2$), 1.81–1.89 (m, 4H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OCH_2), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.91, 25.98, 26.03, 28.58, 29.06, 29.19, 29.26, 29.36, 29.39, 29.40, 29.43, 29.52, 29.61, 29.63, 29.65, 29.66, 29.68, 29.72, 31.92, 31.94 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 69.1 (C-5'-OCH_2), 69.3 (C-4'-OCH_2), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3390 (w), 2918 (vs), 2850 (vs), 1729 (s), 1598 (m), 1510 (m), 1467 (m), 1429 (m), 1392 (w), 1345 (w), 1272 (vs), 1195 (vs), 1167 (s), 1135 (s), 1089 (m), 1071 (m), 1018 (m), 953 (w), 908 (s), 874 (w), 821 (w), 756 (m), 732 (vs), 648 (w), 519 (w), 436 (w) cm^{-1}; MS (ESI): *m*/*z* = 878.72 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{56}H_{95}NO_6$) calcd.: 878.7232 $[M + H]^+$, found: 878.7237.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4-bis(decyloxy)benzoate [3,4-C_{10}Tyr$C_{14}$$NH_2$]

According to GP7: Boc protected amine **3,4-C_{10}TyrC_{14}Boc** (1.01 g, 1.13 mmol), TFA (1.8 mL, 23.4 mmol), dry CH_2Cl_2 (50 mL); reaction time: 72 h; column gradient 70 : 1 → 40 : 1; R_f = 0.34 (CH_2Cl_2/MeOH = 40 : 1).



3,4-C$_{10}$TyrC$_{14}$NH$_2$

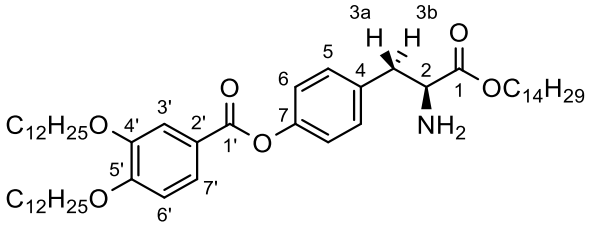
$C_{50}H_{83}NO_6$

(794.22)

Colourless powder (95%, 856 mg, 1.08 mmol, purity >95%); M.p. 53.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.23–1.40 (m, 46H, C*H*$_2$), 1.46–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.62 (dt, *J* = 13.9 Hz, 6.9 Hz, 2H, COOCH$_2$C*H*$_2$), 1.82–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.7 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.4 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.91, 25.98, 26.02, 28.6, 29.05, 29.18, 29.26, 29.36, 29.39, 29.42, 29.52, 29.58, 29.61, 29.63, 29.67, 29.70, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.6 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2955 (m), 2918 (vs), 2849 (vs), 1723 (s), 1597 (m), 1513 (m), 1468 (m), 1429 (m), 1394 (w), 1344 (w), 1296 (s), 1274 (vs), 1212 (vs), 1169 (m), 1145 (m), 1092 (m), 1068 (w), 1020 (m), 988 (w), 954 (w), 877 (w), 823 (w), 786 (w), 757 (m), 722 (w), 654 (w), 501 (w) cm^{-1}; MS (ESI): *m*/*z* = 794.63 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{50}H_{83}NO_6$) calcd.: 794.6293 [M + H]$^+$, found: 794.6291.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4-bis(dodecyloxy)benzoate [3,4-C$_{12}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **3,4-C$_{12}$TyrC$_{14}$Boc** (1.01 g, 1.06 mmol), TFA (1.7 mL, 22.1 mmol), dry CH_2Cl_2 (50 mL); reaction time: 72 h; column gradient 70 : 1 → 40 : 1; R_f = 0.34 (CH_2Cl_2/MeOH = 40 : 1).



3,4-C$_{12}$TyrC$_{14}$NH$_2$

$C_{54}H_{91}NO_6$

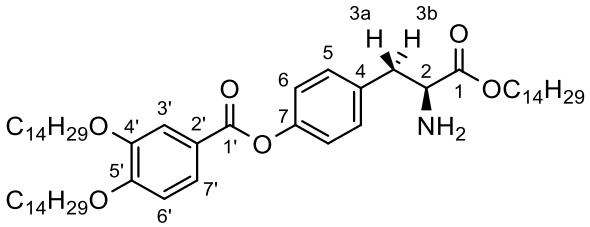
(850.32)

Light-yellow powder (93%, 837 mg, 0.98 mmol, purity >95%); M.p. 60.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.22–1.39 (m, 54H, C*H*$_2$), 1.45–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.82–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.89 (dd,

J = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.91, 25.98, 26.02, 28.59, 29.06, 29.18, 29.26, 29.38, 29.40, 29.43, 29.52, 29.61, 29.62, 29.64, 29.67, 29.71, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5), 134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3375 (w), 2955 (m), 2916 (vs), 2848 (vs), 1722 (s), 1597 (m), 1512 (m), 1467 (m), 1429 (m), 1395 (w), 1344 (w), 1295 (s), 1275 (vs), 1211 (vs), 1169 (m), 1145 (m), 1091 (m), 1070 (w), 1019 (w), 996 (w), 964 (w), 939 (w), 906 (w), 879 (w), 823 (w), 757 (m), 722 (m), 654 (w), 546 (w), 506 (w), 416 (w) cm^{-1}; MS (ESI): *m*/*z* = 850.69 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{54}H_{91}NO_6$) calcd.: 850.6919 [M + H]$^+$, found: 850.6919.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4-bis(tetradecyloxy)benzoate [3,4-C$_{14}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **3,4-C$_{14}$TyrC$_{14}$Boc** (1.02 g, 1.02 mmol), TFA (1.6 mL, 20.8 mmol), dry CH_2Cl_2 (50 mL); reaction time: 72 h; column gradient 70 : 1 → 40 : 1; R_f = 0.34 (CH_2Cl_2/MeOH = 40 : 1).



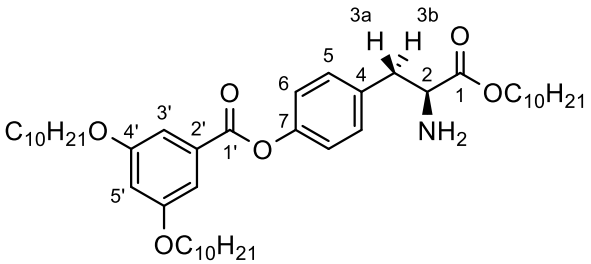
3,4-C$_{14}$TyrC$_{14}$NH$_2$
$C_{58}H_{99}NO_6$
(906.43)

Colourless solid (82%, 756 mg, 0.834 mmol, purity >95%); M.p. 70.9 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.25–1.38 (m, 62H, C*H*$_2$), 1.45–1.50 (m, 4H, $OCH_2CH_2CH_2$), 1.60–1.65 (m, 2H, $COOCH_2CH_2$), 1.81–1.89 (m, 4H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.4 Hz, 1H, 2-H), 4.05–4.12 (m, 6H, OC*H*$_2$), 6.92 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.25 (d, *J* = 8.4 Hz, 2H, 5-H), 7.65 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.80 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.91, 25.98, 26.03, 28.6, 29.06, 29.19, 29.26, 29.37, 29.38, 29.40, 29.43, 29.52, 29.61, 29.63, 29.65, 29.67, 29.69, 29.72, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.6 (C-2'), 121.9 (C-6), 124.3 (C-7'), 130.3 (C-5),

134.8 (C-4), 148.7 (C-4'), 150.0 (C-7), 153.8 (C-5'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2955 (m), 2915 (vs), 2873 (m), 2848 (vs), 1722 (s), 1597 (w), 1513 (m), 1467 (m), 1430 (m), 1394 (w), 1345 (w), 1294 (m), 1276 (s), 1211 (s), 1169 (m), 1143 (m), 1090 (m), 1019 (w), 975 (w), 953 (w), 877 (w), 822 (w), 792 (m), 756 (w), 722 (w), 654 (w) cm^{-1}; MS (ESI): *m*/*z* = 906.75 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{58}H_{99}NO_6$) calcd.: 906.7545 $[M + H]^+$, found: 906.7546.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,5-bis(decyloxy)benzoate [3,5-C_{10}Tyr$C_{10}$$NH_2$]

According to GP7: Boc protected amine **3,5-C_{10}TyrC_{10}Boc** (969 mg, 1.16 mmol), TFA (1.4 mL, 18.2 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.

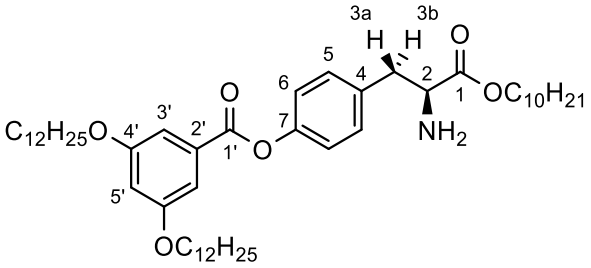


3,5-C_{10}Tyr$C_{10}$$NH_2$
$C_{46}H_{75}NO_6$
(738.11)

Yellow oil (98%, 838 mg, 1.14 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.38 (m, 38H, C*H*$_2$), 1.43–1.49 (m, 4H, $OCH_2CH_2CH_2$), 1.62 (dt, *J* = 13.4 Hz, 6.8 Hz, 2H, $COOCH_2CH_2$), 1.79 (dt, *J* = 14.1 Hz, 7.3 Hz, 4H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, $COOCH_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.91, 26.03, 28.59, 29.19, 29.25, 29.31, 29.33, 29.38, 29.51, 29.56, 29.58, 31.9 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 68.4 (OCH_2), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3382 (w), 2922 (vs), 2853 (s), 1737 (s), 1594 (m), 1508 (m), 1447 (m), 1387 (w), 1350 (m), 1326 (m), 1299 (m), 1212 (vs), 1195 (vs), 1166 (vs), 1094 (w), 1057 (m), 1019 (m), 931 (w), 845 (w), 757 (m), 722 (w), 676 (w), 525 (w) cm^{-1}; MS (ESI): *m*/*z* = 738.57 $[M + H]^+$, 760.54 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{46}H_{75}NO_6$) calcd.: 738.5667 $[M + H]^+$, found: 738.5662.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,5-bis(dodecyloxy)benzoate [3,5-C_{12}TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **3,5-C_{12}TyrC$_{10}$Boc** (983 mg, 1.10 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.

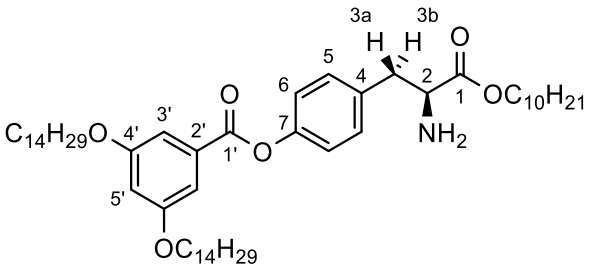


3,5-C_{12}TyrC$_{10}$NH$_2$
$C_{50}H_{83}NO_6$
(794.22)

Yellow oil (99%, 862 mg, 1.09 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.38 (m, 46H, C*H*$_2$), 1.43–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.9 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.11 (t, *J* = 6.7 Hz, 2H, COOC*H*$_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.68, 22.70, 25.90, 26.02, 28.6, 29.19, 29.24, 29.31, 29.36, 29.38, 29.51, 29.55, 29.58, 29.61, 29.64, 29.67, 31.90, 31.93 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3380 (w), 2922 (vs), 2853 (s), 1737 (s), 1594 (m), 1508 (m), 1447 (m), 1386 (w), 1350 (m), 1326 (m), 1299 (m), 1212 (vs), 1195 (vs), 1166 (vs), 1093 (w), 1056 (m), 1019 (m), 948 (w), 845 (w), 757 (m), 722 (w), 676 (w), 516 (w), 421 (w) cm^{-1}; MS (ESI): *m*/*z* = 794.63 [M + H]$^+$, 816.61 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{50}H_{83}NO_6$) calcd.: 794.6293 [M + H]$^+$, found: 794.6292.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,5-bis(tetradecyloxy)benzoate [3,5-C_{14}TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **3,5-C_{14}TyrC$_{10}$Boc** (976 mg, 1.03 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.



3,5-C$_{14}$TyrC$_{10}$NH$_2$

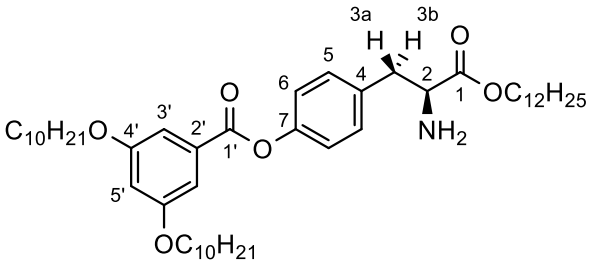
$C_{54}H_{91}NO_6$

(850.32)

Yellow oil (99%, 866 mg, 1.02 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.37 (m, 54H, C*H*$_2$), 1.43–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 14.4 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.11 (t, *J* = 6.8 Hz, 2H, COOC*H*$_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.68, 22.70, 25.91, 26.03, 28.6, 29.19, 29.25, 29.31, 29.37, 29.39, 29.52, 29.55, 29.59, 29.61, 29.67, 29.69, 29.70, 31.90, 31.94 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1736 (s), 1594 (m), 1508 (m), 1447 (m), 1386 (w), 1350 (m), 1325 (m), 1299 (m), 1212 (s), 1195 (vs), 1165 (vs), 1093 (w), 1055 (m), 1019 (m), 931 (w), 845 (m), 757 (m), 722 (m), 676 (w), 515 (w) cm^{-1}; MS (ESI): *m*/*z* = 850.69 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{54}H_{91}NO_6$) calcd.: 850.6919 [M + H]$^+$, found: 850.6914.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,5-bis(decyloxy)benzoate [3,5-C$_{10}$TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **3,5-C$_{10}$TyrC$_{12}$Boc** (965 mg, 1.11 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (50 mL); reaction time: 48 h.



3,5-C$_{10}$TyrC$_{12}$NH$_2$

$C_{48}H_{79}NO_6$

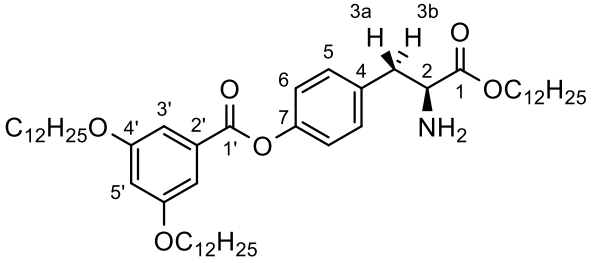
(766.16)

Yellow oil (96%, 815 mg, 1.06 mmol, purity >95%): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 9H, C*H*$_3$), 1.21–1.38 (m, 42H, C*H*$_2$), 1.43–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.59–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.7 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.89 (dd,

J = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, COOCH_2), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.0, 28.6, 29.19, 29.25, 29.33, 29.36, 29.38, 29.52, 29.56, 29.58, 29.60, 29.65, 29.66, 31.91, 31.92 (*C*H_2), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H_2), 68.4 (O*C*H_2), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: ṽ = 2922 (s), 2853 (s), 1736 (s), 1594 (m), 1508 (m), 1447 (m), 1386 (w), 1350 (m), 1325 (m), 1299 (m), 1212 (s), 1194 (vs), 1164 (vs), 1093 (m), 1055 (m), 1018 (m), 949 (w), 844 (m), 757 (m), 722 (w), 676 (w), 516 (w) cm^{-1}; MS (ESI): *m*/*z* = 766.60 $[M + H]^+$, 788.59 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{48}H_{79}NO_6$) calcd.: 766.5980 $[M + H]^+$, found: 766.5978.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,5-bis(dodecyloxy)benzoate [3,5-C_{12}Tyr$C_{12}$$NH_2$]

According to GP7: Boc protected amine **3,5-C_{12}TyrC_{12}Boc** (962 mg, 1.04 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (50 mL); reaction time: 48 h.



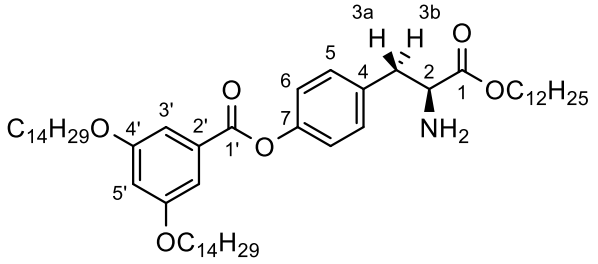
3,5-C_{12}Tyr$C_{12}$$NH_2$
$C_{52}H_{87}NO_6$
(822.27)

Yellow oil (96%, 826 mg, 1.01 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.38 (m, 50H, C*H*$_2$), 1.43–1.49 (m, 4H, $OCH_2CH_2CH_2$), 1.60–1.65 (m, 2H, $COOCH_2CH_2$), 1.79 (dt, *J* = 13.7 Hz, 6.7 Hz, 4H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.11 (t, *J* = 6.7 Hz, 2H, COOC*H*$_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.91, 26.03, 28.59, 29.19, 29.25, 29.36, 29.38, 29.52, 29.58, 29.61, 29.65, 29.67, 31.9 (*C*H_2), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H_2), 68.4 (O*C*H_2), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: ṽ = 2922 (vs), 2853 (s), 1737 (s), 1595 (m), 1508 (w), 1447 (m), 1386 (w), 1350 (m), 1326 (m), 1299 (m), 1213 (s), 1196 (vs), 1167 (vs), 1094 (w), 1057 (m), 1019 (w), 948 (w), 845 (w), 757

(w), 722 (w), 676 (w), 512 (w) cm^{-1}; MS (ESI): *m*/*z* = 822.66 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{52}H_{87}NO_6$) calcd.: 822.6606 $[M + H]^+$, found: 822.6592.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,5-bis(tetradecyloxy)benzoate [3,5-C_{14}Tyr$C_{12}$$NH_2$]

According to GP7: Boc protected amine **3,5-C_{14}TyrC_{12}Boc** (962 mg, 0.98 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (40 mL); reaction time: 48 h.

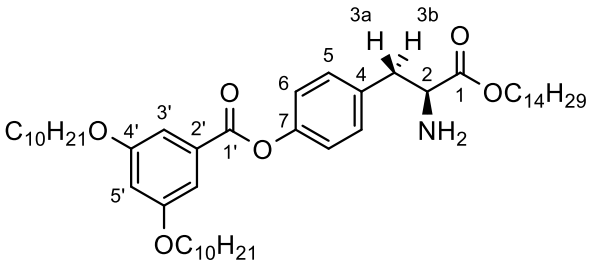


3,5-C_{14}Tyr$C_{12}$$NH_2$
$C_{56}H_{95}NO_6$
(878.38)

Yellow oil (98%, 848 mg, 0.97 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.22–1.38 (m, 58H, C*H*$_2$), 1.43–1.49 (m, 4H, $OCH_2CH_2CH_2$), 1.59–1.65 (m, 2H, $COOCH_2CH_2$), 1.79 (dt, *J* = 13.9 Hz, 6.7 Hz, 4H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, $COOCH_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.91, 26.03, 28.6, 29.20, 29.25, 29.36, 29.37, 29.39, 29.52, 29.59, 29.61, 29.64, 29.66, 29.69, 29.70, 31.9 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.3 ($COOCH_2$), 68.4 (OCH_2), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (vs), 2853 (s), 1737 (s), 1595 (m), 1508 (w), 1447 (m), 1379 (w), 1350 (m), 1326 (m), 1299 (m), 1213 (s), 1196 (s), 1167 (vs), 1094 (w), 1056 (m), 1019 (w), 949 (w), 847 (w), 757 (w), 722 (w), 676 (w), 519 (w) cm^{-1}; MS (ESI): *m*/*z* = 878.72 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{56}H_{95}NO_6$) calcd.: 878.7232 $[M + H]^+$, found: 878.7231.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,5-bis(decyloxy)benzoate [3,5-C_{10}Tyr$C_{14}$$NH_2$]

According to GP7: Boc protected amine **3,5-C_{10}TyrC_{14}Boc** (956 mg, 1.07 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (60 mL); reaction time: 48 h.



3,5-C$_{10}$TyrC$_{14}$NH$_2$

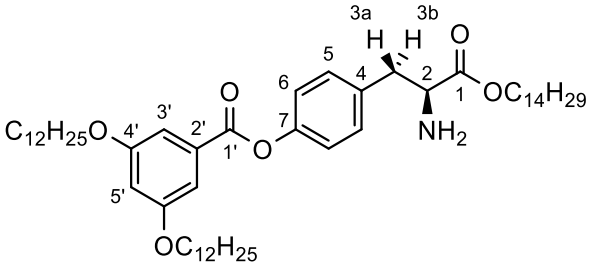
$C_{50}H_{83}NO_6$

(794.22)

Yellow oil (99%, 843 mg, 1.06 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.38 (m, 46H, C*H*$_2$), 1.43–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.62 (dt, *J* = 13.6 Hz, 6.8 Hz, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.7 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.11 (t, *J* = 6.8 Hz, 2H, COOC*H*$_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.69, 22.70, 25.91, 26.03, 28.6, 29.19, 29.25, 29.33, 29.38, 29.52, 29.56, 29.58, 29.61, 29.66, 29.69, 29.70, 31.90, 31.93 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (vs), 2853 (s), 1736 (s), 1594 (m), 1508 (m), 1447 (m), 1386 (w), 1350 (m), 1325 (m), 1299 (m), 1212 (s), 1195 (vs), 1165 (vs), 1094 (m), 1055 (m), 1018 (m), 909 (m), 845 (m), 757 (m), 732 (s), 676 (w), 647 (w), 518 (w) cm^{-1}; MS (ESI): *m*/*z* = 794.63 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{50}H_{83}NO_6$) calcd.: 794.6293 [M + H]$^+$, found: 794.6284.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,5-bis(dodecyloxy)benzoate [3,5-C$_{12}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **3,5-C$_{12}$TyrC$_{14}$Boc** (958 mg, 1.01 mmol), TFA (1.2 mL, 15.6 mmol), dry CH_2Cl_2 (60 mL); reaction time: 48 h.



3,5-C$_{12}$TyrC$_{14}$NH$_2$

$C_{54}H_{91}NO_6$

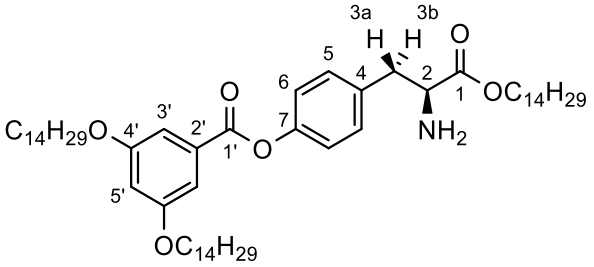
(850.32)

Yellow oil (99%, 852 mg, 1.00 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 9H, C*H*$_3$), 1.21–1.38 (m, 54H, C*H*$_2$), 1.43–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.62 (dt, *J* = 13.7 Hz, 6.9 Hz, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.7 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.89

(dd, *J* = 13.7 Hz, 7.9 Hz, 1H, 3a-H), 3.10 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.11 (t, *J* = 6.7 Hz, 2H, COOC*H*$_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.91, 26.03, 28.6, 29.19, 29.25, 29.36, 29.38, 29.52, 29.58, 29.61, 29.64, 29.67, 29.70, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: ṽ = 2921 (vs), 2852 (s), 1736 (s), 1594 (m), 1508 (m), 1447 (m), 1386 (w), 1350 (m), 1325 (m), 1299 (m), 1212 (s), 1195 (vs), 1165 (vs), 1094 (w), 1056 (m), 1019 (m), 948 (w), 845 (m), 757 (m), 722 (w), 676 (w), 515 (w) cm^{-1}; MS (ESI): *m*/*z* = 850.69 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{54}H_{91}NO_6$) calcd.: 850.6919 [M + H]$^+$, found: 850.6911.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,5-bis(tetradecyloxy)benzoate [3,5-C$_{14}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **3,5-C$_{14}$TyrC$_{14}$Boc** (918 mg, 0.91 mmol), TFA (1.0 mL, 13.0 mmol), dry CH_2Cl_2 (50 mL); reaction time: 48 h.



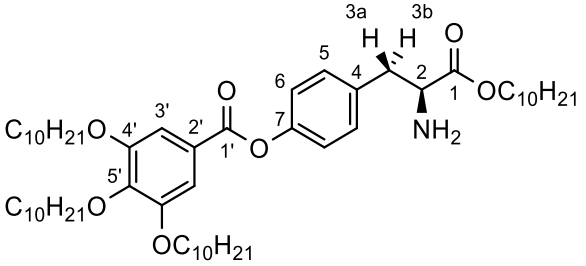
3,5-C$_{14}$TyrC$_{14}$NH$_2$
$C_{58}H_{99}NO_6$
(906.43)

Yellow oil (99%, 814 mg, 0.90 mmol, purity >95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 9H, C*H*$_3$), 1.21–1.38 (m, 62H, C*H*$_2$), 1.43–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.61–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.11 (t, *J* = 6.8 Hz, 2H, COOC*H*$_2$), 6.70 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.30 (d, *J* = 2.3 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.91, 26.03, 28.6, 29.20, 29.26, 29.37, 29.39, 29.52, 29.59, 29.61, 29.67, 29.69, 29.70, 31.9 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.2 (C-3'), 121.7 (C-6), 130.3 (C-5), 131.2 (C-2'), 135.0 (C-4), 149.9 (C-7), 160.3 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: ṽ = 2921 (vs), 2852 (s), 1737 (s), 1594 (m), 1508 (m), 1447 (m), 1386 (w), 1350 (m), 1325 (m), 1299 (m), 1212 (s), 1195 (vs), 1165 (vs), 1093 (w), 1056 (m), 1019 (m), 931 (w), 845 (m), 757 (m),

721 (m), 676 (w), 518 (w) cm^{-1}; MS (ESI): *m*/*z* = 906.75 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{58}H_{99}NO_6$) calcd.: 906.7545 $[M + H]^+$, found: 906.7544.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,4,5-tris(decyloxy)benzoate [3,4,5-C_{10}Tyr$C_{10}$$NH_2$]

According to GP7: Boc protected amine **3,4,5-C_{10}TyrC_{10}Boc** (1.02 g, 1.03 mmol), TFA (1.6 mL, 20.8 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).

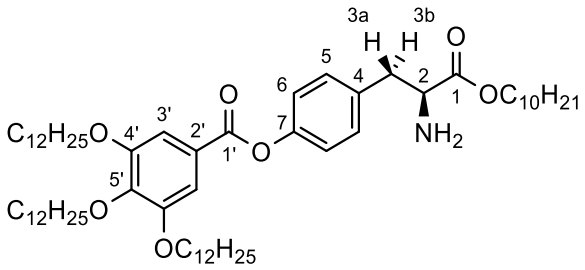


3,4,5-C_{10}Tyr$C_{10}$$NH_2$
$C_{56}H_{95}NO_7$
(894.38)

Colourless solid (63%, 580 mg, 0.65 mmol, purity >95%); M.p. 31.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 12H, C*H*$_3$), 1.22–1.39 (m, 50H, C*H*$_2$), 1.45–1.52 (m, 6H, $OCH_2CH_2CH_2$), 1.60–1.66 (m, 2H, $COOCH_2CH_2$), 1.73–1.86 (m, 6H, OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.03–4.07 (m, 6H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, $COOCH_2$), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.68, 22.69, 22.72, 25.90, 26.07, 26.09, 28.58, 29.24, 29.31, 29.36, 29.41, 29.51, 29.55, 29.58, 29.59, 29.64, 29.69, 29.74, 30.4, 31.90, 31.92, 31.95 (*C*H$_2$), 40.5 (C-3), 55.9 (C-2), 65.2 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (vs), 2853 (s), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1335 (s), 1189 (vs), 1115 (s), 1019 (w), 952 (w), 862 (w), 755 (w), 722 (w), 516 (w) cm^{-1}; MS (ESI): *m*/*z* = 894.72 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{56}H_{95}NO_7$) calcd.: 894.7181 $[M + H]^+$, found: 894.7187.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,4,5-tris(dodecyloxy)benzoate [3,4,5-C_{12}Tyr$C_{10}$$NH_2$]

According to GP7: Boc protected amine **3,4,5-C_{12}TyrC_{10}Boc** (934 mg, 0.87 mmol), TFA (1.4 mL, 18.2 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).

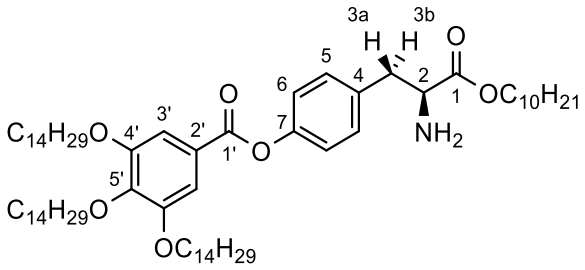


3,4,5-C$_{12}$TyrC$_{10}$NH$_2$
$C_{62}H_{107}NO_7$
(978.54)

Colourless solid (65%, 550 mg, 0.56 mmol, purity >95%); M.p. 34.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 12H, C*H*$_3$), 1.22–1.39 (m, 62H, C*H*$_2$), 1.45–1.52 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.59–1.66 (m, 2H, COOCH$_2$C*H*$_2$), 1.73–1.86 (m, 6H, OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.7 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 4.03–4.07 (m, 6H, OC*H*$_2$), 4.11 (t, *J* = 6.7 Hz, 2H, COOC*H*$_2$), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.68, 22.71, 25.90, 26.07, 26.10, 28.6, 29.24, 29.31, 29.38, 29.41, 29.45, 29.51, 29.55, 29.59, 29.65, 29.67, 29.71, 29.75, 29.77, 30.4, 31.90, 31.94, 31.96 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H$_2$), 69.2 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1334 (s), 1188 (vs), 1115 (vs), 1018 (m), 952 (m), 861 (w), 754 (m), 721 (w), 520 (w) cm^{-1}; MS (ESI): *m*/*z* = 978.81 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{62}H_{107}NO_7$) calcd.: 978.8120 [M + H]$^+$, found: 978.8128.

(*S*)-4-(2-Amino-(decyloxy)-3-oxopropyl)phenyl 3,4,5-tris(tetradecyloxy)benzoate [3,4,5-C$_{14}$TyrC$_{10}$NH$_2$]

According to GP7: Boc protected amine **3,4,5-C$_{14}$TyrC$_{10}$Boc** (1.01 g, 0.87 mmol), TFA (1.4 mL, 18.2 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).



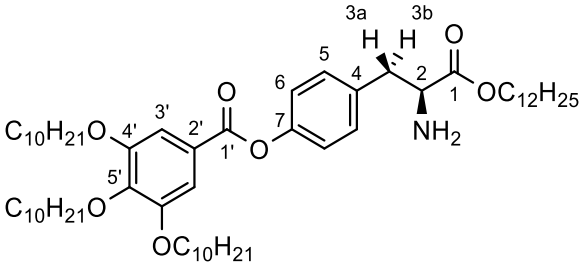
3,4,5-C$_{14}$TyrC$_{10}$NH$_2$
$C_{68}H_{119}NO_7$
(1062.70)

Colourless solid (90%, 826 mg, 0.78 mmol, purity >95%); M.p. 44.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.22–1.38 (m, 74H, C*H*$_2$), 1.45–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.59–1.66 (m, 2H, COOCH$_2$C*H*$_2$), 1.73–1.85 (m, 6H, OCH$_2$C*H*$_2$), 2.89 (dd,

J = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.02–4.07 (m, 6H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, COOCH_2), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H_3), 22.69, 22.71, 25.91, 26.08, 26.10, 28.6, 29.24, 29.31, 29.39, 29.41, 29.51, 29.55, 29.59, 29.65, 29.68, 29.72, 29.76, 30.4, 31.90, 31.95 (*C*H_2), 40.6 (C-3), 55.9 (C-2), 65.2 (COO*C*H_2), 69.3 (C-4'-O*C*H_2), 73.6 (C-5'-O*C*H_2), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2920 (vs), 2852 (s), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1334 (s), 1188 (vs), 1115 (vs), 1019 (m), 952 (w), 861 (w), 754 (m), 721 (m), 520 (w) cm^{-1}; MS (ESI): *m*/*z* = 1062.90 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{68}H_{119}NO_7$) calcd.: 1062.9059 $[M + H]^+$, found: 1062.9059.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(decyloxy)benzoate [3,4,5-C$_{10}$TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **3,4,5-C$_{10}$TyrC$_{12}$Boc** (916 mg, 0.90 mmol), TFA (1.4 mL, 18.2 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).



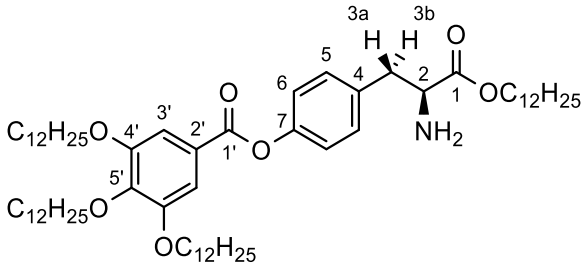
3,4,5-C$_{10}$TyrC$_{12}$NH$_2$
$C_{58}H_{99}NO_7$
(922.43)

Colourless solid (89%, 733 mg, 0.80 mmol, purity >95%); M.p. 43.3 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, CH_3), 1.23–1.38 (m, 54H, CH_2), 1.46–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.63 (dt, *J* = 13.8 Hz, 6.9 Hz, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 15.0 Hz, 6.7 Hz, 2H, C-5'-OCH_2CH_2), 1.83 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, C-4'-OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05 (dt, *J* = 12.7 Hz, 6.5 Hz, 6H, OCH_2), 4.11 (t, *J* = 6.8 Hz, 2H, COOCH_2), 7.13 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.10, 14.12, 14.13 (*C*H_3), 22.66, 22.67, 22.68, 22.70, 22.72, 25.91, 26.07, 26.10, 28.6, 29.23, 29.25, 29.30, 29.31, 29.37, 29.41, 29.45, 29.50, 29.52, 29.56, 29.58, 29.60, 29.65, 29.66, 29.69, 29.71, 29.75, 30.4, 31.92, 31.93, 31.96 (*C*H_2), 40.5 (C-3), 55.9 (C-2), 65.3 (COO*C*H_2), 69.3 (C-4'-O*C*H_2), 73.6 (C-5'-O*C*H_2), 108.6 (C-3'), 121.8 (C-6), 123.9

(C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2853 (s), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1334 (s), 1188 (vs), 1114 (vs), 1018 (m), 953 (w), 861 (m), 754 (m), 722 (w), 522 (w) cm^{-1}; MS (ESI): *m*/*z* = 922.75 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{58}H_{99}NO_7$) calcd.: 922.7494 $[M + H]^+$, found: 922.7496.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(dodecyloxy)benzoate [3,4,5-C_{12}Tyr$C_{12}NH_2$]

According to GP7: Boc protected amine **3,4,5-C_{12}TyrC_{12}Boc** (969 mg, 0.88 mmol), TFA (1.4 mL, 18.2 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).

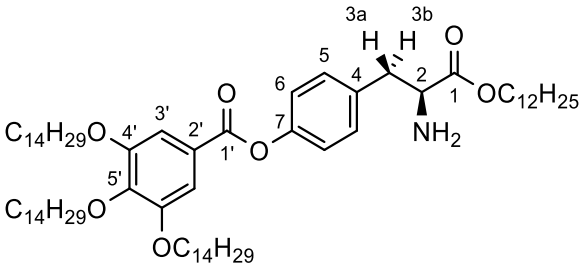


3,4,5-C_{12}Tyr$C_{12}NH_2$
$C_{64}H_{111}NO_7$
(1006.59)

Colourless solid (82%, 719 mg, 0.71 mmol, purity >95%); M.p. 44.1 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.24–1.38 (m, 66H, C*H*$_2$), 1.46–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.63 (dt, *J* = 14.0 Hz, 7.0 Hz, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 14.3 Hz, 6.8 Hz, 2H, C-5'-OCH_2CH_2), 1.83 (dt, *J* = 14.0 Hz, 6.8 Hz, 4H, C-4'-OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05 (dt, *J* = 12.6 Hz, 6.5 Hz, 6H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 7.14 (d, *J* = 8.3 Hz, 2H, 6-H), 7.26 (d, *J* = 8.3 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.70, 22.71, 22.72, 25.91, 26.08, 26.10, 28.6, 29.25, 29.32, 29.36, 29.38, 29.42, 29.52, 29.59, 29.60, 29.65, 29.67, 29.68, 29.72, 29.75, 29.76, 29.77, 30.4, 31.93, 31.94, 31.96 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.6 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1334 (s), 1188 (vs), 1115 (s), 1018 (w), 952 (w), 861 (w), 754 (m), 721 (w), 519 (w) cm^{-1}; MS (ESI): *m*/*z* = 1006.84 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{64}H_{111}NO_7$) calcd.: 1006.8433 $[M + H]^+$, found: 1006.8432.

(*S*)-4-(2-Amino-3-(dodecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(tetradecyloxy)benzoate [3,4,5-C_{14}TyrC$_{12}$NH$_2$]

According to GP7: Boc protected amine **3,4,5-C_{14}TyrC$_{12}$Boc** (1.04 g, 0.87 mmol), TFA (1.4 mL, 18.2 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).

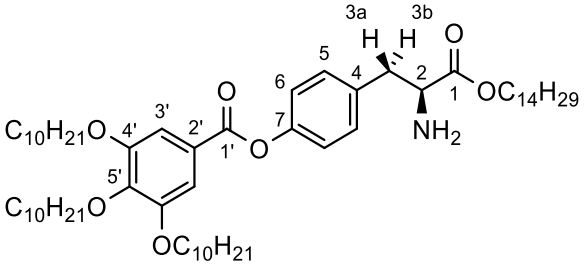


3,4,5-C_{14}TyrC$_{12}$NH$_2$
$C_{70}H_{123}NO_7$
(1090.75)

Colourless solid (94%, 895 mg, 0.82 mmol, purity >95%); M.p. 47.9 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.23–1.38 (m, 78H, C*H*$_2$), 1.46–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.63 (dt, *J* = 14.2 Hz, 7.0 Hz, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 14.2 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 13.5 Hz, 6.8 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.89 (dd, *J* = 13.6 Hz, 7.9 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05 (dt, *J* = 12.6 Hz, 6.5 Hz, 6H, OC*H*$_2$), 4.11 (t, *J* = 6.7 Hz, 2H, COOC*H*$_2$), 7.14 (d, *J* = 8.4 Hz, 2H, 6-H), 7.26 (d, *J* = 8.4 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.70, 22.71, 25.91, 26.08, 26.11, 28.6, 29.25, 29.32, 29.37, 29.39, 29.41, 29.42, 29.52, 29.60, 29.60, 29.66, 29.69, 29.71, 29.73, 29.73, 29.76, 29.77, 29.78, 30.4, 31.93, 31.95, 31.96 (*C*H$_2$), 40.6 (C-3), 55.9 (C-2), 65.3 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (vs), 2852 (s), 1733 (m), 1586 (w), 1507 (w), 1466 (m), 1430 (m), 1379 (w), 1335 (m), 1188 (vs), 1115 (s), 1019 (w), 952 (w), 907 (s), 861 (w), 731 (vs), 648 (w), 521 (w) cm^{-1}; MS (ESI): *m*/*z* = 1090.94 [M + H]$^+$; HRMS (ESI): *m*/*z* ($C_{70}H_{123}NO_7$) calcd.: 1090.9372 [M + H]$^+$, found: 1090.9358.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(decyloxy)benzoate [3,4,5-C_{10}TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **3,4,5-C_{10}TyrC$_{14}$Boc** (859 mg, 0.82 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).



3,4,5-C$_{10}$TyrC$_{14}$NH$_2$

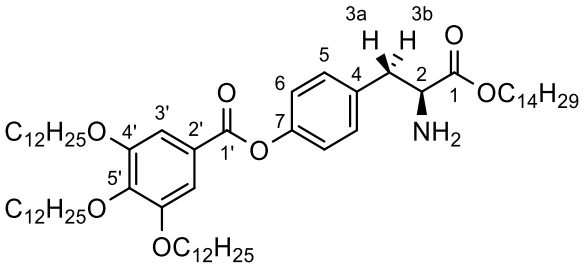
$C_{60}H_{103}NO_7$

(950.48)

Colourless solid (94%, 728 mg, 0.77 mmol, purity >95%); M.p. 37.3 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.90 (m, 12H, C*H*$_3$), 1.22–1.38 (m, 58H, C*H*$_3$), 1.46–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.63 (dt, *J* = 14.1 Hz, 6.9 Hz, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 13.9 Hz, 6.8 Hz, 2H, C-5'-OCH_2CH_2), 1.83 (dt, *J* = 13.9 Hz, 6.8 Hz, 4H, C-4'-OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.8 Hz, 5.3 Hz, 1H, 2-H), 4.05 (dt, *J* = 12.7 Hz, 6.5 Hz, 6H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.12, 14.13 (CH_3), 22.70, 22.72, 25.91, 26.08, 26.10, 28.6, 29.26, 29.32, 29.37, 29.38, 29.41, 29.47, 29.52, 29.59, 29.60, 29.65, 29.67, 29.69, 29.71, 29.75, 30.4, 31.93, 31.94, 31.96 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.3 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.6 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 150.0 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1335 (s), 1189 (vs), 1115 (s), 1018 (w), 1000 (w), 954 (w), 934 (w), 862 (w), 754 (w), 722 (w), 527 (w) cm^{-1}; MS (ESI): *m*/*z* = 950.78 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{60}H_{103}NO_7$) calcd.: 950.7807 $[M + H]^+$, found: 950.7809.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(dodecyloxy)benzoate [3,4,5-C$_{12}$TyrC$_{14}$NH$_2$]

According to GP7: Boc protected amine **3,4,5-C$_{12}$TyrC$_{14}$Boc** (824 mg, 0.73 mmol), TFA (1.1 mL, 14.3 mmol), dry CH_2Cl_2 (40 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).



3,4,5-C$_{12}$TyrC$_{14}$NH$_2$

$C_{66}H_{115}NO_7$

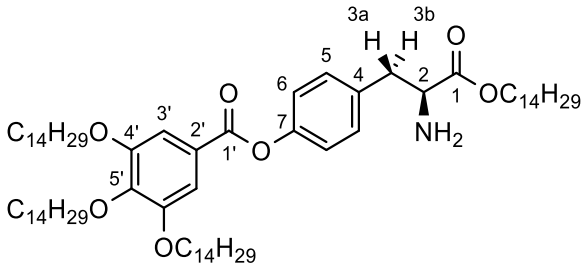
(1034.65)

Colourless solid (93%, 701 mg, 0.68 mmol, purity >95%); M.p. 43.6 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.89 (m, 12H, C*H*$_3$), 1.24–1.38 (m, 70H, C*H*$_2$), 1.46–1.50 (m, 6H,

$OCH_2CH_2CH_2$), 1.63 (dt, *J* = 14.3 Hz, 6.9 Hz, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 14.3 Hz, 6.8 Hz, 2H, C-5'-OCH_2CH_2), 1.83 (dt, *J* = 14.3 Hz, 6.7 Hz, 4H, C-4'-OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.73 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H, 2-H), 4.05 (dt, *J* = 12.6 Hz, 6.5 Hz, 6H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 7.14 (d, *J* = 8.3 Hz, 2H, 6-H), 7.26 (d, *J* = 8.3 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.71, 22.72, 25.91, 26.08, 26.11, 28.6, 29.26, 29.32, 29.38, 29.39, 29.42, 29.45, 29.52, 29.59, 29.61, 29.66, 29.67, 29.68, 29.70, 29.71, 29.72, 29.75, 29.76, 29.78, 30.4, 31.94, 31.96 (CH_2), 40.6 (C-3), 55.9 (C-2), 65.3 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.6 (C-3'), 121.8 (C-6), 123.9 (C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (vs), 1734 (s), 1586 (m), 1507 (m), 1466 (m), 1430 (m), 1379 (w), 1335 (s), 1190 (vs), 1116 (s), 1018 (w), 952 (w), 861 (w), 754 (w), 722 (w), 516 (w) cm^{-1}; MS (ESI): *m*/*z* = 1034.87 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{66}H_{115}NO_7$) calcd.: 1034.8746 $[M + H]^+$, found: 1034.8743.

(*S*)-4-(2-Amino-3-(tetradecyloxy)-3-oxopropyl)phenyl 3,4,5-tris(tetradecyloxy)benzoate [3,4,5-C_{14}Tyr$C_{14}NH_2$]

According to GP7: Boc protected amine **3,4,5-C_{14}TyrC_{14}Boc** (992 mg, 0.81 mmol), TFA (1.3 mL, 16.9 mmol), dry CH_2Cl_2 (50 mL); reaction time: 72 h; column gradient 80 : 1 → 30 : 1; R_f = 0.43 (CH_2Cl_2/MeOH = 40 : 1).



3,4,5-C_{14}Tyr$C_{14}NH_2$
$C_{72}H_{127}NO_7$
(1118.81)

Colourless solid (77%, 700 mg, 0.63 mmol, purity >95%); M.p. 43.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 12H, CH_3), 1.25–1.39 (m, 82H, CH_2), 1.45–1.52 (m, 6H, $OCH_2CH_2CH_2$), 1.60–1.66 (m, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 14.2 Hz, 6.7 Hz, 2H, C-5'-OCH_2CH_2), 1.83 (dt, *J* = 14.4 Hz, 13.7 Hz, 6.6 Hz, 4H, C-4'-OCH_2CH_2), 2.89 (dd, *J* = 13.6 Hz, 7.8 Hz, 1H, 3a-H), 3.11 (dd, *J* = 13.6 Hz, 5.3 Hz, 1H, 3b-H), 3.74 (dd, *J* = 7.8 Hz, 5.2 Hz, 1H, 2-H), 4.02–4.07 (m, 6H, OCH_2), 4.11 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.26 (d, *J* = 8.5 Hz, 2H, 5-H), 7.39 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.91, 26.08, 26.10, 28.6, 29.25, 29.31, 29.37, 29.39, 29.42, 29.52, 29.60, 29.66, 29.68, 29.71, 29.72, 29.76, 30.4, 31.94 (CH_2), 40.5 (C-3), 55.8 (C-2), 65.3 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.5 (C-3'), 121.8 (C-6), 123.9

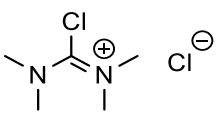
(C-2'), 130.3 (C-5), 134.9 (C-4), 143.0 (C-5'), 149.9 (C-7), 153.0 (C-4'), 165.0 (C-1'), 175.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1735 (m), 1587 (w), 1507 (w), 1466 (m), 1430 (m), 1379 (w), 1335 (m), 1191 (s), 1117 (m), 1019 (w), 953 (w), 862 (w), 754 (w), 721 (w), 527 (w) cm^{-1}; MS (ESI): *m*/*z* = 1118.97 $[M + H]^+$; HRMS (ESI): *m*/*z* ($C_{72}H_{127}NO_7$) calcd.: 1118.9685 $[M + H]^+$, found: 1118.9677.

General Procedure GP8: Functionalization of free amines to guanidinium chlorides[1,25]

The respective free amine **Ar(C$_m$)TyrC$_n$NH$_2$** (1.00 mmol) and dried sodium bicarbonate (1.26 g, 15.0 mmol) were suspended in dry CH_2Cl_2 (30 mL) under a nitrogen atmosphere and *N*,*N*,*N*',*N*'-tetramethylchloroformamidinium chloride **GuaCl** (1.5 mL, 1.50 mmol, 1.0 M in dry CH_2Cl_2) was added. The solution was stirred at room temperature. Near the end of the specified reaction time, additional equivalents of **GuaCl** (0.5 mL, 0.50 mmol, 1.0 M in dry CH_2Cl_2) and base (5.00 mmol) had to be added every 1 h and 30 min to achieve complete conversion of the starting material. The number of additions can be found at the respective compound. Afterwards, excess base was filtered off, water (180 µL, 10.0 mmol) was added and the mixture was stirred for additional 15 min. The solvents were removed under reduced pressure and the remaining residue was dissolved in ether (30 mL). Subsequently, the solution was acidified (pH ≈ 1) with $HCl \cdot Et_2O$ and stirred for additional 15 min. The solvent was removed under reduced pressure and the residue was purified by were purified by column chromatography (SiO_2 treated with 6.0 M HCl). At first, the column was flushed with pure EtOAc and EtOAc/MeOH (10 : 1), followed by a gradient of CH_2Cl_2/MeOH (25 : 1 → 15 : 1). Differences from this procedure can be found at the respective compound.

***N*,*N*,*N*',*N*'-Tetramethylchloroformamidinium chloride (GuaCl)[26–29]**

Tetramethylurea (6.93 g, 59.7 mmol) was dissolved in dry THF (75 mL) under a nitrogen atmosphere, cooled to 0 °C and oxalyl chloride (10.1 mL, 118 mmol) was added dropwise. The light-yellow solution was stirred for 5 d at room temperature. Subsequently, the precipitated solid was filtered, washed with ice cold dry THF (100 mL) until it was colourless and dried under reduced pressure.



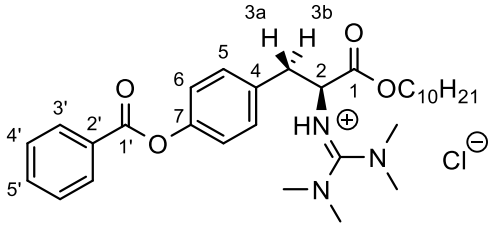
GuaCl
$C_5H_{12}Cl_2N_2$
(171.07)

The colourless powder **GuaCl** (93%, 9.51 g, 55.6 mmol) was dissolved in dry CH_2Cl_2 (55.6 mL; 1.0 M solution) under a nitrogen atmosphere and stored in the refrigerator for longer

storage. Further solutions with different concentrations were prepared. The reagent was used without further characterisation.

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(decyloxy)propan-2-aminium chloride [BzTyrC$_{10}$Cl]

According to GP8: Free amine **BzTyrC$_{10}$NH$_2$** (411 mg, 0.97 mmol), sodium bicarbonate (1.35 g, 16.1 mmol), **GuaCl** (1.6 mL, 1.61 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 1.2 mL, 1.21 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 69 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



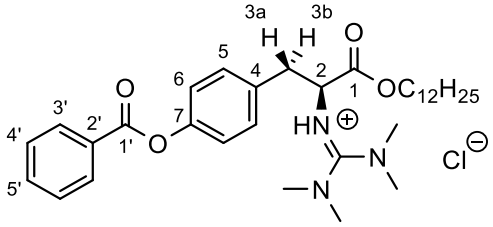
BzTyrC$_{10}$Cl
$C_{31}H_{46}ClN_3O_4$
(560.18)

Colourless glass (84%, 452 mg, 0.81 mmol, purity >99%); M.p. 33.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.19–1.27 (m, 14H, C*H*$_2$), 1.57 (t, *J* = 6.9 Hz, 2H, OCH$_2$C*H*$_2$), 2.40–3.47 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.85 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.03–4.10 (m, 3H, OC*H*$_2$, 2-H), 7.10 (d, *J* = 8.5 Hz, 2H, 6-H), 7.47 (t, *J* = 8.0 Hz, 2H, 4'-H), 7.57–7.62 (m, 3H, 5-H, 5'-H), 8.14 (dd, *J* = 8.0 Hz, 1.4 Hz, 2H, 3'-H), 10.07 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.19, 29.28, 29.50, 29.54, 31.9 (*C*H$_2$), 36.0 (C-3), 39.7 (N(*C*H$_3$)$_2$), 60.5 (C-2), 66.5 (O*C*H$_2$), 121.9 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.1 (C-3'), 131.0 (C-5), 133.6 (C-5'), 134.8 (C-4), 150.0 (C-7), 162.2 (N=C), 165.2 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3366 (w), 3035 (w), 2924 (s), 2854 (m), 1733 (vs), 1621 (s), 1569 (s), 1508 (m), 1467 (m), 1452 (m), 1404 (m), 1314 (m), 1263 (vs), 1198 (vs), 1168 (vs), 1116 (w), 1081 (m), 1062 (vs), 1025 (s), 979 (w), 928 (w), 902 (w), 874 (w), 801 (w), 708 (s), 686 (w), 674 (w), 639 (w), 584 (w), 549 (w), 521 (w) cm^{-1}; MS (ESI): *m*/*z* = 524.35 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{31}H_{46}ClN_3O_4$) calcd.: 524.3483 [M – Cl]$^+$, found: 524.3480; CHN ($C_{31}H_{46}ClN_3O_4 \cdot 0.9\ H_2O$) calcd.: C 64.60 H 8.36 N 7.29, found: C 64.52 H 8.31 N 7.12; $[\alpha]_D^{20}$: +166 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(dodecyloxy)propan-2-aminium chloride [BzTyrC$_{12}$Cl]

According to GP8: Free amine **BzTyrC$_{12}$NH$_2$** (411 mg, 0.91 mmol), sodium bicarbonate (1.15 g, 13.6 mmol), **GuaCl** (1.6 mL, 1.61 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL);

addition of 3 × **GuaCl** (total of 1.2 mL, 1.21 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 69 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

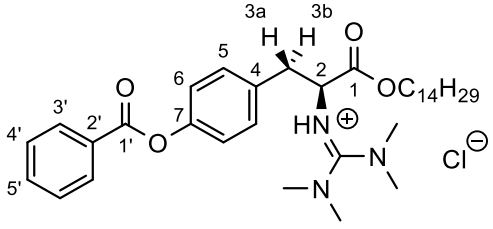


BzTyrC$_{12}$Cl
$C_{33}H_{50}ClN_3O_4$
(588.23)

Colourless glass (92%, 490 mg, 0.83 mmol, purity >99%); M.p. 49.6 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.20–1.28 (m, 18H, C*H*$_2$), 1.56–1.62 (m, 2H, OCH$_2$C*H*$_2$), 2.44–3.46 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.06–4.11 (m, 3H, OC*H*$_2$, 2-H), 7.12 (d, *J* = 8.5 Hz, 2H, 6-H), 7.49 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.58–7.63 (m, 3H, 5-H, 5'-H), 8.15 (d, *J* = 7.8 Hz, 2H, 3'-H), 10.14 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.21, 29.34, 29.52, 29.60, 29.64, 31.9 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (O*C*H$_2$), 121.9 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.1 (C-3'), 131.0 (C-5), 133.6 (C-5'), 134.8 (C-4), 150.0 (C-7), 162.2 (N=C), 165.2 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3383 (w), 3198 (w), 3039 (w), 2923 (vs), 2853 (s), 1735 (vs), 1623 (s), 1571 (s), 1509 (m), 1467 (m), 1452 (m), 1405 (m), 1314 (m), 1265 (vs), 1199 (vs), 1168 (vs), 1116 (w), 1081 (m), 1063 (s), 1025 (m), 900 (w), 801 (w), 707 (s), 674 (w), 586 (w), 524 (w) cm^{-1}; MS (ESI): *m*/*z* = 552.38 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{33}H_{50}ClN_3O_4$) calcd.: 552.3796 [M – Cl]$^+$, found: 552.3800. CHN ($C_{33}H_{50}ClN_3O_4 \cdot 0.7\ H_2O$) calcd.: C 65.97 H 8.62 N 6.99, found: C 65.88 H 8.70 N 6.87; $[\alpha]_D^{20}$: +157 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 37.1 °C [28.4 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(tetradecyl-oxy)propan-2-aminium chloride [BzTyrC$_{14}$Cl]

According to GP8: Free amine **BzTyrC$_{14}$NH$_2$** (416 mg, 0.86 mmol), sodium bicarbonate (1.10 g, 13.1 mmol), **GuaCl** (1.5 mL, 1.51 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 1.2 mL, 1.21 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 69 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

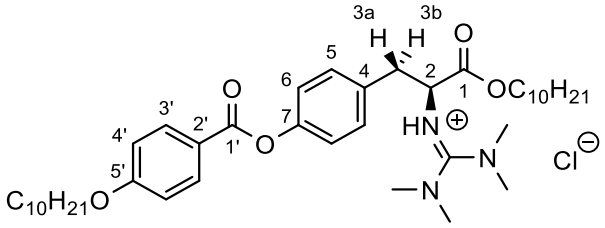


BzTyrC$_{14}$Cl
$C_{35}H_{54}ClN_3O_4$
(616.28)

Colourless glass (88%, 469 mg, 0.76 mmol, purity >99%); M.p. 54.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.19–1.30 (m, 22H, C*H*$_2$), 1.58 (t, *J* = 6.9 Hz, 2H, OCH$_2$C*H*$_2$), 2.36–3.51 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.85 (dd, *J* = 13.9 Hz, 9.3 Hz, 1H, 3a-H), 4.05–4.11 (m, 3H, OC*H*$_2$, 2-H), 7.11 (d, *J* = 8.5 Hz, 2H, 6-H), 7.48 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.58–7.63 (m, 3H, 5-H, 5'-H), 8.14–8.16 (m, 2H, 3'-H), 10.09 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.21, 29.35, 29.52, 29.61, 29.65, 29.69, 31.9 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.5 (C-2), 66.5 (O*C*H$_2$), 121.9 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.1 (C-3'), 131.0 (C-5), 133.6 (C-5'), 134.7 (C-4), 150.0 (C-7), 162.2 (N=C), 165.2 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3351 (w), 2922 (s), 2852 (s), 1733 (vs), 1621 (s), 1569 (s), 1508 (m), 1466 (m), 1452 (m), 1404 (m), 1314 (w), 1263 (vs), 1197 (vs), 1116 (w), 1081 (m), 1062 (vs), 1024 (s), 929 (w), 903 (w), 800 (w), 706 (vs), 686 (w), 674 (w), 639 (w), 585 (w), 522 (w) cm^{-1}; MS (ESI): *m*/*z* = 580.41 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{54}ClN_3O_4$) calcd.: 580.4109 [M – Cl]$^+$, found: 580.4102; CHN ($C_{35}H_{54}ClN_3O_4 \cdot 0.7\ H_2O$) calcd.: C 66.85 H 8.88 N 6.68, found: C 66.78 H 8.94 N 6.52; $[\alpha]_D^{20}$: +158 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-decyloxybenzoyl)oxy)phenyl)-1-(decyloxy)propan-2-aminium chloride [4-C$_{10}$TyrC$_{10}$Cl]

According to GP8: Free amine **4-C$_{10}$TyrC$_{10}$NH$_2$** (450 mg, 0.77 mmol), sodium bicarbonate (1.98 g, 23.5 mmol), **GuaCl** (1.1 mL, 1.10 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 5 × **GuaCl** (total of 1.6 mL, 1.60 mmol, 1.0 M in CH_2Cl_2); reaction time: 32 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



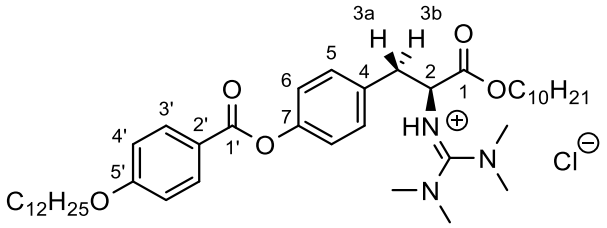
4-C$_{10}$TyrC$_{10}$Cl
$C_{41}H_{66}ClN_3O_5$
(716.45)

Colourless solid (70%, 386 mg, 0.54 mmol); M.p. 55 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.77–0.90 (m, 6H, C*H*$_3$), 1.13–1.39 (m, 26H, C*H*$_2$), 1.41–1.47 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.51–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.76–1.82 (m, 2H, OCH$_2$C*H*$_2$), 2.38–3.46 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, *J* = 13.9 Hz, 8.9 Hz, 1H, 3a-H), 4.01 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 4.04–4.12 (m, 3H, COOC*H*$_2$, 2-H), 6.93 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.09 (d, *J* = 7.8 Hz, 2H, 6-H), 7.56 (d, *J* = 8.0 Hz, 2H, 5-H), 8.08 (d, *J* = 9.0 Hz, 2H, 3'-H), 10.08 (s, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.8, 26.0, 28.4, 29.1, 29.21, 29.29, 29.31,

29.36, 29.52, 29.55, 31.89 (*C*H_2), 36.0 (C-3), 39.7 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 68.3 (O*C*H_2), 114.3 (C-4'), 121.4 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.5 (C-4), 150.2 (C-7), 162.2 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 522 (w), 585 (w), 651 (w), 692 (w), 725 (m), 763 (m), 813 (w), 844 (m), 901 (w), 929 (w), 1009 (m), 1020 (m), 1069 (s), 1117 (w), 1163 (vs), 1199 (vs), 1252 (vs), 1314 (m), 1404 (m), 1420 (w), 1467 (m), 1510 (s), 1572 (m), 1605 (s), 1731 (s), 2853 (m), 2922 (s), 3039 (w), 3385 (w) cm^{-1}; MS (ESI): *m*/*z* = 680.50 [M – Cl]$^+$. HRMS (ESI): *m*/*z* ($C_{41}H_{66}N_3O_5$) calcd.: 680.4997 [M – Cl]$^+$, found: 680.4999. CHN ($C_{41}H_{66}ClN_3O_5$) calcd.: C 68.74 H 9.29 N 5.87, found: C 68.49 H 9.36 N 5.78; $[\alpha]_D^{20}$: +124 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-dodecyloxybenzoyl)oxy)phenyl)-1-(decyloxy)propan-2-aminium chloride [4-C_{12}TyrC$_{10}$Cl]

According to GP8: Free amine **4-C_{12}TyrC$_{10}$NH$_2$** (450 mg, 0.74 mmol), sodium bicarbonate (990 mg, 1.8 mmol), **GuaCl** (1.1 mL, 1.10 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 1 × **GuaCl** (0.4 mL, 0.40 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (448 mg, 5.33 mmol); reaction time: 50 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



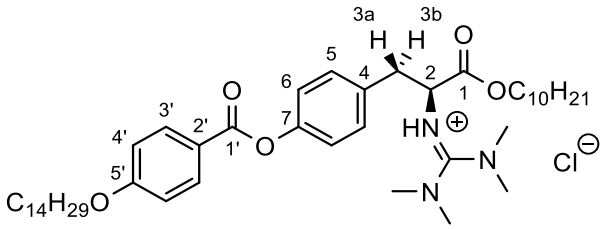
4-C_{12}TyrC$_{10}$Cl
$C_{43}H_{70}ClN_3O_5$
(744.50)

Colourless solid (82%, 449 mg, 0.60 mmol, purity >99%); M.p. 75 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.83–0.92 (m, 6H, C*H*$_3$), 1.17–1.42 (m, 30H, C*H*$_2$), 1.44–1.50 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.66 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 2.43–3.47 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 4.06–4.15 (m, 3H, COOC*H*$_2$, 2-H), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.2 Hz, 2H, 6-H), 7.60 (d, *J* = 8.2 Hz, 2H, 5-H), 8.11 (d, *J* = 8.9 Hz, 2H, 3'-H), 10.21 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.68, 22.70, 25.9, 26.0, 28.4, 29.1, 29.2, 29.3, 29.4, 29.52, 29.56, 29.59, 29.64, 29.66, 31.89, 31.92 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 114.3 (C-4'), 121.4 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 520 (w), 589 (w), 631 (w), 657 (w), 691 (w), 722 (w), 762 (m), 821 (w), 843 (m), 878 (w), 901 (w), 1021 (m), 1076 (s), 1101 (w), 1117 (w), 1201 (vs), 1257 (vs), 1312 (w), 1375 (w), 1394 (m), 1407 (m), 1420 (m), 1468 (m), 1511 (s), 1569 (s), 1607 (s),

1639 (s), 1728 (vs), 2851 (s), 2917 (vs), 3067 (w), 3356 (w) cm^{-1}; MS (ESI): *m*/*z* = 708.53 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{43}H_{70}N_3O_5$) calcd.: 708.5310 $[M - Cl]^+$, found: 708.5302; CHN ($C_{43}H_{70}ClN_3O_5 \cdot 0.4\ H_2O$) calcd.: C 68.71 H 9.49 N 5.59, found: C 68.70 H 9.49 N 5.56; $[\alpha]_D^{20}$: +125 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 64 °C [52.38 kJ · mol^{-1}] SmA_d 71 °C [1.69 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-tetradecyloxybenzoyl)oxy)phenyl)-1-(decyloxy)propan-2-aminium chloride [4-C_{14}TyrC_{10}Cl]

According to GP8: Free amine **4-C_{14}Tyr$C_{10}NH_2$** (455 mg, 0.71 mmol), sodium bicarbonate (990 mg, 11.8 mmol), **GuaCl** (1.1 mL, 1.10 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 1 × **GuaCl** (0.4 mL, 0.40 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (436 mg, 5.19 mmol); reaction time: 50 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

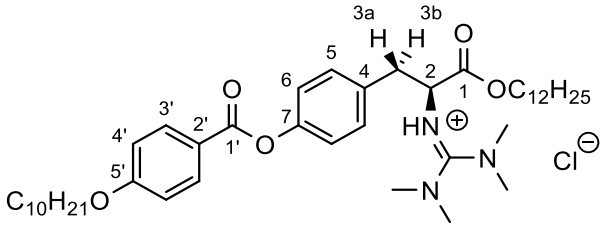


4-C_{14}TyrC_{10}Cl
$C_{45}H_{74}ClN_3O_5$
(772.55)

Colourless solid (79%, 436 mg, 0.56 mmol, purity >99%); M.p. 80 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 6H, C*H*$_3$), 1.19–1.41 (m, 34H, C*H*$_2$), 1.44–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.56–1.66 (m, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.38–3.49 (m, 13H, $N(CH_3)_2$, 3b-H), 3.89 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.06–4.15 (m, 3H, $COOCH_2$, 2-H), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.5 Hz, 2H, 6-H), 7.60 (d, *J* = 8.4 Hz, 2H, 5-H), 8.11 (d, *J* = 8.9 Hz, 2H, 3'-H), 10.23 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.67, 22.70, 25.9, 26.0, 28.4, 29.1, 29.2, 29.3, 29.4, 29.52, 29.56, 29.59, 29.66, 29.68, 29.69, 31.89, 31.93 (CH_2), 36.0 (C-3), 39.6 ($N(CH_3)_2$), 60.7 (C-2), 66.5 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 523 (w), 589 (w), 658 (w), 691 (w), 721 (w), 762 (m), 822 (w), 843 (w), 876 (w), 901 (w), 978 (w), 1021 (w), 1039 (w), 1075 (m), 1102 (w), 1172 (s), 1204 (s), 1259 (vs), 1312 (w), 1394 (m), 1405 (m), 1418 (m), 1469 (m), 1513 (s), 1567 (m), 1608 (s), 1638 (s), 1728 (vs), 2851 (s), 2917 (vs), 3368 (w) cm^{-1}; MS (ESI): *m*/*z* = 736.56 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{45}H_{74}N_3O_5$) calcd.: 736.5623 $[M - Cl]^+$, found: 736.5613; CHN ($C_{45}H_{74}ClN_3O_5 \cdot 0.3\ H_2O$) calcd.: C 69.48 H 9.67 N 5.40, found: C 69.48 H 9.71 N 5.40; $[\alpha]_D^{20}$: +117 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 55 °C [0.97 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-decyloxybenzoyl)oxy)phenyl)-1-(dodecyloxy)propan-2-aminium chloride [4-C$_{10}$TyrC$_{12}$Cl]

According to GP8: Free amine **4-C$_{10}$TyrC$_{12}$NH$_2$** (463.0 mg, 0.76 mmol), sodium bicarbonate (1.26 g, 15.0 mmol), **GuaCl** (1.2 mL, 1.20 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 1 × **GuaCl** (0.3 mL, 0.30 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (491 mg, 5.85 mmol); reaction time: 24 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



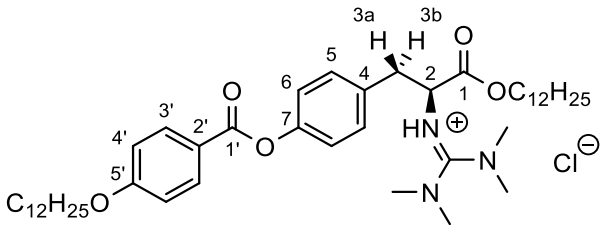
4-C$_{10}$TyrC$_{12}$Cl
$C_{43}H_{70}ClN_3O_5$
(744.50)

Colourless solid (87%, 493.0 mg, 0.66 mmol, purity >99%); M.p. 60 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.83–0.93 (m, 6H, C*H*$_3$), 1.18–1.41 (m, 30H, C*H*$_2$), 1.44–1.50 (m, OCH$_2$CH$_2$C*H*$_2$), 1.55–1.66 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 2.41–3.50 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.06–4.15 (m, 3H, COOC*H*$_2$, 2-H), 6.96 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.4 Hz, 2H, 6-H), 7.59 (d, *J* = 8.4 Hz, 2H, 5-H), 8.11 (d, *J* = 8.9 Hz, 2H, 3'-H), 10.19 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.4, 29.1, 29.2, 29.3, 29.4, 29.53, 29.56, 29.61, 29.65, 31.90, 31.92 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.3 (O*C*H$_2$), 114.3 (C-4'), 121.4 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.2 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 523 (w), 586 (w), 653 (w), 692 (m), 725 (m), 763 (m), 810 (w), 844 (m), 877 (w), 904 (w), 928 (w), 1021 (s), 1073 (S), 1117 (w), 1166 (vs), 1200 (vs), 1254 (vs), 1313 (m), 1405 (m), 1420 (m), 1467 (m), 1511 (s), 1571 (s), 1606 (s), 1631 (s), 1730 (vs), 2853 (s), 2922 (vs), 3363 (w) cm^{-1}; MS (ESI): *m*/*z* = 708.53 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{43}H_{70}N_3O_5$) calcd.: 708.5310 [M – Cl]$^+$, found: 708.5308; CHN ($C_{43}H_{70}ClN_3O_5 \cdot 0.6\ H_2O$) calcd.: C 68.38 H 9.50 N 5.56, found: C 68.30 H 9.51 N 5.56; $[\alpha]_D^{20}$: +120 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 44 °C [6.39 · 10^{-2} kJ · mol^{-1}] SmA$_d$ 74 °C [1.78 kJ · mol^{-1}]I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-dodecyloxybenzoyl)oxy)phenyl)-1-(dodecyloxy)propan-2-aminium chloride [4-C$_{12}$TyrC$_{12}$Cl]

According to GP8: Free amine **4-C$_{12}$TyrC$_{12}$NH$_2$** (450 mg, 0.71 mmol), sodium bicarbonate (1.10 g, 13.1 mmol), **GuaCl** (1.1 mL, 1.10 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL);

addition of 1 × **GuaCl** (0.3 mL, 0.30 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (422 mg, 5.02 mmol); reaction time: 24 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

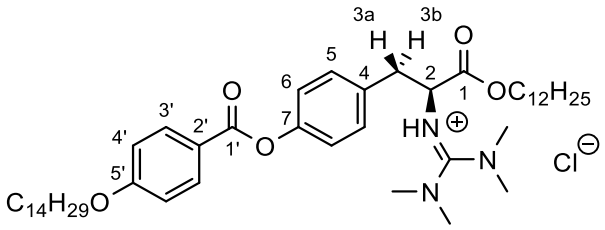


4-C12TyrC12Cl
$C_{45}H_{74}ClN_3O_5$
(772.55)

Colourless solid (77%, 422 mg, 0.55 mmol, purity >99%); M.p. 66.0 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.82–0.92 (m, 6H, C*H*$_3$), 1.15–1.41 (m, 34H, C*H*$_2$), 1.44–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.55–1.67 (m, 2H, $COOCH_2CH_2$), 1.79–1.85 (m, 2H, OCH_2CH_2), 2.40–3.48 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 14.0 Hz, 9.2 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.06–4.15 (m, 3H, $COOCH_2$, 2-H), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.1 Hz, 2H, 6-H), 7.60 (d, *J* = 8.2 Hz, 2H, 5-H), 8.11 (d, *J* = 8.9 Hz, 2H, 3'-H), 10.21 (d, *J* = 6.9 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7, 25.9, 26.0, 28.4, 29.1, 29.2, 29.35, 29.37, 29.53, 29.56, 29.59, 29.61, 29.65, 31.92 (CH_2), 36.0 (C-3), 39.6 (N(CH_3)$_2$), 60.6 (C-2), 66.5 ($COOCH_2$), 68.3 (OCH_2), 114.3 (C-4'), 121.4 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 479 (w), 525 (w), 587 (w), 656 (w), 691 (w), 722 (w), 762 (m), 843 (m), 878 (w), 899 (w), 1021 (m), 1075 (s), 1102 (w), 1170 (s), 1203 (s), 1258 (vs), 1313 (w), 1376 (w), 1406 (m), 1419 (m), 1468 (m), 1512 (s), 1570 (s), 1607 (s), 1638 (s), 1730 (vs), 2852 (s), 2921 (vs), 3062 (w), 3186 (w), 3358 (w) cm^{-1}; MS (ESI): *m*/*z* = 736.56 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{45}H_{74}N_3O_5$) calcd.: 736.5623 [M – Cl]$^+$, found: 736.5629; CHN ($C_{45}H_{74}ClN_3O_5 \cdot 0.6\ H_2O$) calcd.: C 69.00 H 9.68 N 5.36, found: C 69.04 H 9.65 N 5.36; $[\alpha]_D^{20}$: +124 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 35 °C [0.86 kJ · mol^{-1}] SmA_d 81 °C [1.70 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-tetradecyloxybenzoyl)oxy)phenyl)-1-(dodecyloxy)propan-2-aminium chloride [4-C14TyrC12Cl]

According to GP8: Free amine **4-C14TyrC12NH2** (455 mg, 0.68 mmol), sodium bicarbonate (1.87 g, 22.3 mmol), **GuaCl** (1.1 mL, 1.10 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 5 × **GuaCl** (total of 1.6 mL, 1.60 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (486 mg, 5.79 mmol); reaction time: 32 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

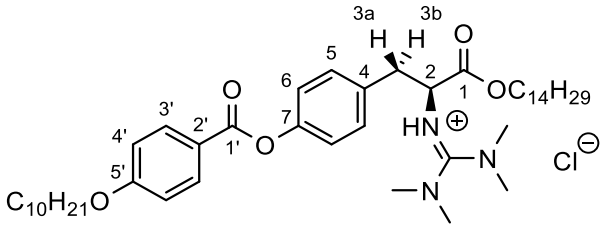


4-C$_{14}$TyrC$_{12}$Cl
$C_{47}H_{78}ClN_3O_5$
(800.61)

Colourless solid (89%, 486 mg, 0.61 mmol, purity >99%); M.p. 67.0 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.82–0.92 (m, 6H, C*H*$_3$), 1.16–1.42 (m, 38H, C*H*$_2$), 1.45–1.49 (m, $OCH_2CH_2CH_2$), 1.56–1.65 (m, 2H, $COOCH_2CH_2$), 1.80–1.84 (m, OCH_2CH_2), 2.39–3.51 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 14.0 Hz, 9.2 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.07–4.14 (m, 3H, COOC*H*$_2$, 2-H), 6.96 (d, *J* = 8.5 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.0 Hz, 2H, 6-H), 7.59 (d, *J* = 8.0 Hz, 2H, 5-H), 8.10 (d, *J* = 8.5 Hz, 2H, 3'-H), 10.16 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.4, 29.1, 29.2, 29.35, 29.37, 29.53, 29.56, 29.59, 29.62, 29.64, 29.66, 29.70, 31.93 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 114.3 (C-4'), 121.5 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 523 (w), 538 (w), 590 (w), 656 (w), 691 (w), 721 (w), 762 (w), 843 (w), 878 (w), 1021 (w), 1076 (m), 1102 (w), 1171 (m), 1205 (m), 1259 (s), 1312 (w), 1406 (w), 1418 (w), 1468 (m), 1513 (m), 1569 (m), 1608 (m), 1639 (m), 1729 (vs), 2851 (s), 2920 (vs), 3362 (w) cm^{-1}; MS (ESI): *m*/*z* = 764.59 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{47}H_{78}N_3O_5$) calcd.: 764.5936 $[M - Cl]^+$, found: 764.5935; CHN ($C_{47}H_{78}ClN_3O_5 \cdot 0.5\ H_2O$) calcd.: C 69.73 H 9.84 N 5.19, found: C 69.72 H 9.83 N 5.16; $[\alpha]_D^{20}$: +117 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 37 °C [0.92 kJ · mol^{-1}] SmA_d 83 °C [1.60 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-decyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [4-C$_{10}$TyrC$_{14}$Cl]

According to GP8: Free amine **4-C$_{10}$TyrC$_{14}$NH$_2$** (457 mg, 0.72 mmol), sodium bicarbonate (990 mg, 11.8 mmol), **GuaCl** (1.4 mL, 0.72 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (30 mL); addition of 2 × **GuaCl** (total of 1.4 mL, 0.72 mmol, 0.5 M in CH_2Cl_2); reaction time: 26 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

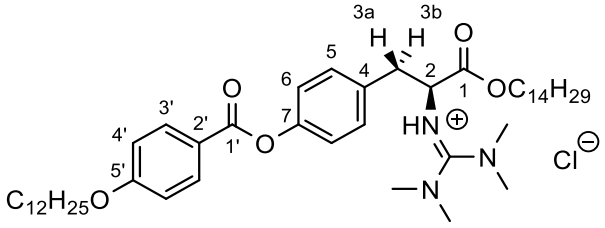


4-C$_{10}$TyrC$_{14}$Cl
$C_{45}H_{74}ClN_3O_5$
(772.55)

Colourless solid (84%, 467 mg, 0.60 mmol, purity >99%); M.p. 84 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 6H, C*H*$_3$), 1.18–1.42 (m, 34H, C*H*$_2$), 1.45–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.56–1.65 (m, 2H, $COOCH_2CH_2$), 1.80–1.87 (m, 2H, OCH_2CH_2), 2.33–3.58 (m, 13H, $N(CH_3)_2$, 3b-H), 3.87 (dd, *J* = 14.0 Hz, 9.2 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.07–4.14 (m, 3H, $COOCH_2$, 2-H), 6.96 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.3 Hz, 2H, 6-H), 7.59 (d, *J* = 8.3 Hz, 2H, 5-H), 8.11 (d, *J* = 8.8 Hz, 2H, 3'-H), 10.16 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.69, 22.70, 25.85, 25.98, 28.4, 29.1, 29.2, 29.3, 29.4, 29.53, 29.55, 29.56, 29.62, 29.66, 29.70, 31.90, 31.93 (CH_2), 36.0 (C-3), 39.6 ($N(CH_3)_2$), 60.6 (C-2), 66.5 ($COOCH_2$), 68.4 (OCH_2), 114.3 (C-4'), 121.5 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 527 (w), 589 (w), 632 (w), 656 (w), 691 (m), 724 (m), 763 (m), 844 (m), 878 (w), 901 (w), 928 (w), 949 (w), 1021 (m), 1076 (s), 1102 (w), 1118 (w), 1168 (vs), 1202 (vs), 1257 (vs), 1313 (m), 1376 (w), 1406 (m), 1420 (m), 1469 (m), 1512 (s), 1571 (s), 1607 (s), 1637 (s), 1727 (vs), 2850 (S), 2919 (vs), 2066 (w), 2188 (w), 3375 (w) cm^{-1}; MS (ESI): *m*/*z* = 736.56 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{45}H_{74}N_3O_5$) calcd.: 736.5623 $[M - Cl]^+$, found: 736.5621; CHN ($C_{45}H_{74}ClN_3O_5 \cdot 0.5\ H_2O$) calcd.: C 69.16 H 9.67 N 5.38, found: C 69.15 H 9.63 N 5.38; $[\alpha]_D^{20}$: +126 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 51 °C [8.69 kJ · mol^{-1}] SmA_d 93 °C [2.05 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-dodecyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [4-C$_{12}$TyrC$_{14}$Cl]

According to GP8: Free amine **4-C$_{12}$TyrC$_{14}$NH$_2$** (450 mg, 0.68 mmol), sodium bicarbonate (1.61 g, 19.1 mmol), **GuaCl** (1.0 mL, 1.00 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 1 × **GuaCl** (0.8 mL, 0.8 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (358 g, 4.26 mmol); reaction time: 24 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



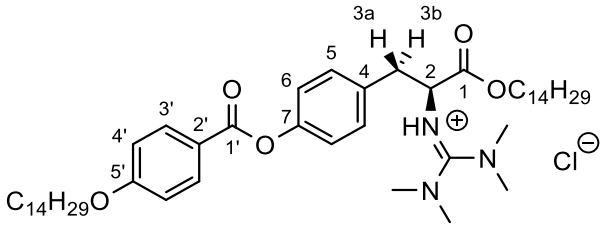
4-C$_{12}$TyrC$_{14}$Cl
$C_{47}H_{78}ClN_3O_5$
(800.61)

Colourless solid (66%, 358 mg, 0.45 mmol, purity >99%); M.p. 76 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.84–0.91 (m, 6H, C*H*$_3$), 1.19–1.41 (m, 38H, C*H*$_2$), 1.44–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.56–1.65 (m, 2H, $COOCH_2CH_2$), 1.76–1.85 (m, 2H, OCH_2CH_2), 2.43–3.52 (m, 13H, $N(CH_3)_2$, 3b-H), 3.88 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H,

OCH_2), 4.06–4.15 (m, 3H, COOCH_2, 2-H), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.1 Hz, 2H, 6-H), 7.60 (d, *J* = 8.3 Hz, 2H, 5-H), 8.11 (d, *J* = 8.9 Hz, 2H, 3'-H), 10.20 (d, *J* = 6.9 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (*C*H_3), 22.7, 25.9, 26.0, 28.4, 29.1, 29.2, 29.35, 29.37, 29.53, 29.56, 29.59, 29.61, 29.64, 29.66, 29.70, 31.92 (*C*H_2), 36.0 (C-3), 39.6 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 68.3 (O*C*H_2), 114.3 (C-4'), 121.4 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 527 (w), 591 (w), 657 (w), 691 (w), 722 (w), 763 (m), 843 (m), 878 (w), 901 (w), 1022 (w), 1077 (m), 1102 (w), 1170 (vs), 1203 (s), 1258 (vs), 1313 (w), 1375 (w), 1407 (m), 1419 (m), 1469 (m), 1512 (m), 1572 (s), 1607 (s), 1639 (s), 1729 (vs), 2851 (s), 2920 (vs), 3076 (w), 3206 (w), 3361 (w) cm^{-1}; MS (ESI): *m*/*z* = 764.59 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{47}H_{78}N_3O_5$) calcd.: 764.5936 [M – Cl]$^+$, found: 764.5939. CHN ($C_{45}H_{74}ClN_3O_5 \cdot 0.8\ H_2O$) calcd.: C 69.26 H 9.84 N 5.16, found: C 69.25 H 9.80 N 5.14; $[\alpha]_D^{20}$: +118 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G °C [2.50 kJ · mol^{-1}] SmA_d 101 °C [1.96 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-teradecyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [4-C$_{14}$TyrC$_{14}$Cl]

According to GP8: Free amine **4-C$_{14}$TyrC$_{14}$NH$_2$** (455 mg, 0.66 mmol), sodium bicarbonate (1.61 g, 19.2 mmol), **GuaCl** (1.8 mL, 0.93 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 2 × **GuaCl** (total of 0.8 mL, 0.80 mmol, 1.0 M in CH_2Cl_2), 1 × sodium bicarbonate (430 mg, 5.12 mmol); reaction time: 26 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



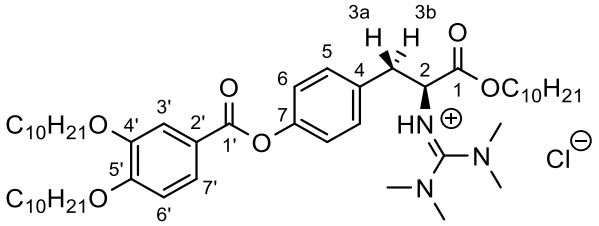
4-C$_{14}$TyrC$_{14}$Cl
$C_{49}H_{82}ClN_3O_5$
(828.66)

Colourless solid (79%, 430 mg, 0.52 mmol, purity >99%); M.p. 68 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.83–0.93 (m, 6H, C*H*$_3$), 1.14–1.41 (m, 42H, C*H*$_2$), 1.44–1.50 (m, OCH$_2$CH$_2$C*H*$_2$), 1.54–1.67 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.85 (m, 2H, OCH$_2$C*H*$_2$), 2.39–3.56 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 14.0 Hz, 9.1 Hz, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.06–4.15 (m, 3H, COOC*H*$_2$, 2-H), 6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.12 (d, *J* = 7.6 Hz, 2H, 6-H), 7.59 (d, *J* = 7.8 Hz, 2H, 5-H), 8.11 (d, *J* = 8.8 Hz, 2H, 3'-H), 10.20 (s, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1 (*C*H_3), 22.7, 25.9, 26.0, 28.4, 29.1, 29.2, 29.4, 29.53, 29.56, 29.59, 29.61, 29.66, 29.68, 29.70, 31.93 (*C*H_2), 36.0 (C-3), 39.7 (N(*C*H_3)$_2$), 60.6 (C-2),

66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 114.3 (C-4'), 121.4 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 527 (w), 632 (w), 657 (w), 691 (w), 722 (w), 763 (w), 843 (w), 878 (w), 901 (w), 1021 (w), 1078 (m), 1102 (w), 1171 (s), 1203 (s), 1258 (S), 1312 (w), 1375 (w), 1407 (w), 1419 (w), 1469 (m), 1512 (m), 1571 (m), 1608 (m), 1639 (m), 1728 (s), 2851 (S), 2920 (vs), 3078 (w), 3192 (w), 3368 (w) cm^{-1}; MS (ESI): *m*/*z* = 792.63 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{49}H_{82}N_3O_5$) calcd.: 792.6249 [M – Cl]$^+$, found: 792.6251. CHN ($C_{45}H_{74}ClN_3O_5 \cdot 1.3\ H_2O$) calcd.: C 69.07 H 10.01 N 4.93, found: C 69.06 H 9.96 N 4.90; $[\alpha]_D^{20}$: +111 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 4 °C [6.73 · 10^{-2} kJ · mol^{-1}] Cr_2 58 °C [5.25 kJ · mol^{-1}] SmA_d 111 °C [2.09 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(decyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,4-C$_{10}$TyrC$_{10}$Cl]

According to GP8: Free amine **3,4-C$_{10}$TyrC$_{10}$NH$_2$** (443 mg, 0.60 mmol), sodium bicarbonate (870 mg, 10.4 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.30 g, 15.5 mmol); reaction time: 75 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



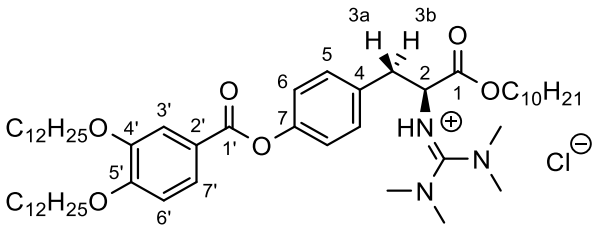
3,4-C$_{10}$TyrC$_{10}$Cl
$C_{51}H_{86}ClN_3O_6$
(872.71)

Colourless solid (91%, 474 mg, 0.54 mmol, purity >99%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.86 (m, 9H, C*H*$_3$), 1.17–1.36 (m, 38H, C*H*$_2$), 1.42–1.48 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.55–1.61 (m, 2H, COOCH$_2$C*H*$_2$), 1.78–1.85 (m, 4H, OCH$_2$C*H*$_2$), 2.35–3.54 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.01–4.09 (m, 7H, OC*H*$_2$, 2-H), 6.89 (d, *J* = 8.6 Hz, 1H, 6'-H), 7.08 (d, *J* = 8.2 Hz, 2H, 6-H), 7.56 (d, *J* = 8.2 Hz, 2H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.75 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H, 7'-H), 10.08 (d, *J* = 7.2 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.66, 22.68, 25.83, 25.96, 26.00, 28.4, 29.04, 29.18, 29.28, 29.34, 29.37, 29.40, 29.50, 29.53, 29.56, 29.59, 29.61, 31.87, 31.90 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 112.0 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.9 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3381 (w), 2922 (s), 2853 (s), 1731 (s), 1626 (m), 1599 (m), 1572 (m),

1510 (s), 1467 (m), 1428 (m), 1405 (m), 1343 (w), 1269 (vs), 1194 (vs), 1167 (s), 1133 (s), 1069 (m), 1018 (m), 958 (w), 926 (w), 902 (w), 815 (w), 756 (m), 724 (m), 647 (w), 585 (w), 537 (w) cm^{-1}; MS (ESI): *m*/*z* = 836.65 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{51}H_{86}ClN_3O_6$) calcd.: 836.6511 $[M - Cl]^+$, found: 836.6511; CHN ($C_{51}H_{86}ClN_3O_6 \cdot 1.4\ H_2O$) calcd.: C 68.22 H 9.97 N 4.68, found: C 68.15 H 9.92 N 4.66; $[\alpha]_D^{20}$: +105 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 25.0 °C [–] SmA_d 85.3 °C [1.64 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(dodecyloxy)benzoyl)oxy)phenyl)-1-(decyloxy)propan-2-aminium chloride [3,4-C_{12}TyrC$_{10}$Cl]

According to GP8: Free amine **3,4-C_{12}TyrC$_{10}$NH$_2$** (445 mg, 0.56 mmol), sodium bicarbonate (808 mg, 9.62 mmol), **GuaCl** (1.0 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.30 g, 15.5 mmol); reaction time: 75 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



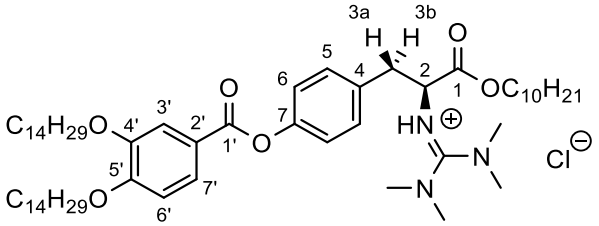
3,4-C_{12}TyrC$_{10}$Cl
$C_{55}H_{94}ClN_3O_6$
(928.82)

Colourless solid (86%, 448 mg, 0.48 mmol, purity >99%); M.p. 40.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.20–1.38 (m, 46H, C*H*$_2$), 1.43–1.49 (m, 4H, $OCH_2CH_2CH_2$), 1.57–1.62 (m, 2H, $COOCH_2CH_2$), 1.79–1.86 (m, 4H, OCH_2CH_2), 2.44–3.52 (m, 13H, $N(CH_3)_2$, 3b-H), 3.85 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.02–4.11 (m, 7H, OCH_2, 2-H), 6.90 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.09 (d, *J* = 8.2 Hz, 2H, 6-H), 7.58 (d, *J* = 8.2 Hz, 2H, 5-H), 7.61 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.76 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H), 10.14 (d, *J* = 7.2 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.67, 22.69, 25.84, 25.97, 26.02, 28.4, 29.05, 29.19, 29.29, 29.37, 29.38, 29.42, 29.51, 29.54, 29.61, 29.63, 29.66, 29.70, 31.88, 31.93 (CH_2), 36.0 (C-3), 39.6 ($N(CH_3)_2$), 60.6 (C-2), 66.5 ($COOCH_2$), 69.1 (C-5'-OCH_2), 69.4 (C-4'-OCH_2), 112.0 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.9 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3391 (w), 2921 (vs), 2852 (s), 1731 (s), 1627 (s), 1599 (m), 1572 (m), 1510 (s), 1467 (m), 1428 (m), 1406 (m), 1343 (w), 1269 (vs), 1195 (vs), 1167 (s), 1141 (s), 1069 (m), 1019 (m), 971 (w), 941 (w), 901 (w), 873 (w), 756 (m), 722 (m), 651 (w), 589 (w), 534 (w) cm^{-1}; MS (ESI): *m*/*z* = 892.71 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{94}ClN_3O_6$) calcd.: 892.7137 $[M - Cl]^+$, found: 892.7138; CHN ($C_{55}H_{94}ClN_3O_6 \cdot 0.8\ H_2O$) calcd.: C 70.04

H 10.22 N 4.46, found: C 70.00 H 10.30 N 4.42; $[\alpha]_D^{20}$: +98 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 17.9 °C [1.75 kJ · mol^{-1}] SmA_d 93.1 °C [1.45 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,4-C$_{14}$TyrC$_{10}$Cl]

According to GP8: Free amine **3,4-C$_{14}$TyrC$_{10}$NH$_2$** (477 mg, 0.56 mmol), sodium bicarbonate (904 mg, 10.8 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.30 g, 15.5 mmol); reaction time: 75 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

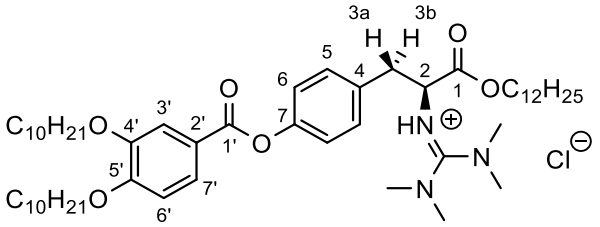


3,4-C$_{14}$TyrC$_{10}$Cl
$C_{59}H_{102}ClN_3O_6$
(984.93)

Colourless solid (83%, 460 mg, 0.47 mmol, purity >99%); M.p. 42.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.86 (m, 9H, C*H*$_3$), 1.19–1.36 (m, 54H, C*H*$_2$), 1.42–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.61 (m, 2H, COOCH$_2$C*H*$_2$), 1.78–1.86 (m, 4H, OCH$_2$C*H*$_2$), 2.34–3.44 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, J = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.01–4.10 (m, 7H, OC*H*$_2$, 2-H), 6.89 (d, J = 8.5 Hz, 1H, 6'-H), 7.09 (d, J = 8.3 Hz, 2H, 6-H), 7.57 (d, J = 8.3 Hz, 2H, 5-H), 7.60 (d, J = 2.0 Hz, 1H, 3'-H), 7.75 (dd, J = 8.5 Hz, 2.0 Hz, 1H, 7'-H), 10.10 (d, J = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.67, 22.70, 25.84, 25.98, 26.03, 28.4, 29.06, 29.20, 29.29, 29.37, 29.39, 29.43, 29.51, 29.55, 29.62, 29.64, 29.67, 29.71, 31.89, 31.93 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 112.0 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.9 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (s), 2853 (m), 2186 (m), 1731 (m), 1621 (m), 1599 (m), 1570 (m), 1510 (m), 1467 (m), 1429 (m), 1404 (w), 1344 (w), 1270 (s), 1194 (vs), 1167 (m), 1132 (m), 1068 (m), 1030 (m), 925 (m), 908 (s), 871 (w), 815 (w), 756 (m), 726 (vs), 640 (m), 584 (w), 546 (w), 432 (w) cm^{-1}; MS (ESI): m/z = 948.78 $[M - Cl]^+$; HRMS (ESI): m/z ($C_{59}H_{102}ClN_3O_6$) calcd.: 948.7763 $[M - Cl]^+$, found: 948.7756; CHN ($C_{59}H_{102}ClN_3O_6 \cdot 1.0\ H_2O$) calcd.: C 70.66 H 10.45 N 4.19, found: C 70.57 H 10.34 N 4.16; $[\alpha]_D^{20}$: +82 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 9.50 °C [0.44 kJ · mol^{-1}] Cr_2 22.0 °C [33.4 kJ · mol^{-1}] SmA_d 100.8 °C [1.01 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(decyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,4-C_{10}TyrC_{12}Cl]

According to GP8: Free amine **3,4-C_{10}Tyr$C_{12}$$NH_2$** (477 mg, 0.62 mmol), sodium bicarbonate (1.09 g, 12.9 mmol), **GuaCl** (2.4 mL, 1.23 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 4 × **GuaCl** (total of 2.4 mL, 1.23 mmol, 0.5 M in CH_2Cl_2), 4 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 71 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



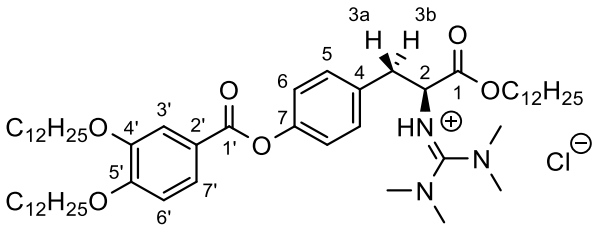
3,4-C_{10}TyrC_{12}Cl
$C_{53}H_{90}ClN_3O_6$
(900.77)

Colourless solid (90%, 503 mg, 0.56 mmol, purity >99%); M.p. 55.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.18–1.37 (m, 42H, C*H*$_2$), 1.42–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.86 (m, 4H, OCH$_2$C*H*$_2$), 2.37–3.49 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.85 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.01–4.10 (m, 7H, OC*H*$_2$, 2-H), 6.89 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.09 (d, *J* = 8.0 Hz, 2H, 6-H), 7.57 (d, *J* = 8.0 Hz, 2H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.76 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H), 10.10 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 25.97, 26.02, 28.4, 29.05, 29.18, 29.21, 29.35, 29.38, 29.41, 29.52, 29.57, 29.60, 29.63, 29.65, 31.9 (*C*H), 36.0 (C-3), 39.7 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.5 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (s), 2853 (s), 1730 (s), 1622 (m), 1599 (m), 1572 (m), 1510 (s), 1467 (m), 1428 (m), 1404 (m), 1344 (w), 1269 (vs), 1193 (vs), 1167 (s), 1132 (s), 1069 (m), 1019 (m), 958 (w), 927 (m), 908 (m), 869 (w), 801 (w), 756 (m), 726 (vs), 641 (w), 583 (w), 546 (w) cm^{-1}; MS (ESI): *m*/*z* = 864.68 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{53}H_{90}ClN_3O_6$) calcd.: 864.6824 [M – Cl]$^+$, found: 864.6819; CHN ($C_{53}H_{90}ClN_3O_6 \cdot 1.0\ H_2O$) calcd.: C 69.29 H 10.09 N 4.57, found: C 69.22 H 10.05 N 4.51; $[\alpha]_D^{20}$: +100 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 40.0 °C [–] SmA_d 90.6 °C [1.54 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(dodecyloxy)benzoyl)oxy)phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,4-C_{12}TyrC_{12}Cl]

According to GP8: Free amine **3,4-C_{12}Tyr$C_{12}$$NH_2$** (456 mg, 0.56 mmol), sodium bicarbonate (974 mg, 11.6 mmol), **GuaCl** (2.2 mL, 1.13 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL);

addition of 4 × **GuaCl** (total of 2.4 mL, 1.23 mmol, 0.5 M in CH_2Cl_2), 4 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 71 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

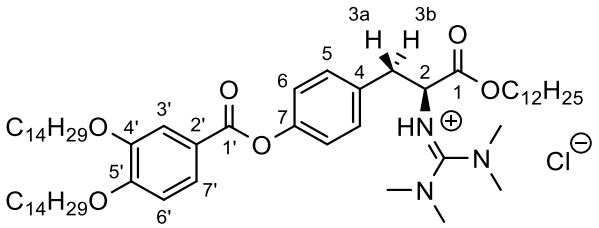


3,4-C_{12}TyrC$_{12}$Cl
$C_{57}H_{98}ClN_3O_6$
(956.88)

Colourless solid (93%, 494 mg, 0.52 mmol, purity >99%); M.p. 50.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.87 (m, 9H, C*H*$_3$), 1.23–1.38 (m, 50H, C*H*$_2$), 1.43–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.87 (m, 4H, OCH$_2$C*H*$_2$), 2.41–3.56 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.02–4.11 (m, 7H, OC*H*$_2$, 2-H), 6.90 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.10 (d, *J* = 8.3 Hz, 2H, 6-H), 7.57 (d, *J* = 8.3 Hz, 2H, 5-H), 7.61 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.76 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H), 10.08 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 25.98, 26.03, 28.4, 29.05, 29.19, 29.21, 29.35, 29.38, 29.39, 29.42, 29.52, 29.60, 29.62, 29.64, 29.67, 29.70, 31.91, 31.93 (*C*H$_2$), 36.01 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.5 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.5 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3371 (w), 2921 (vs), 2852 (s), 1731 (s), 1625 (m), 1599 (m), 1572 (m), 1510 (s), 1467 (m), 1428 (m), 1405 (m), 1344 (w), 1269 (vs), 1194 (vs), 1167 (s), 1133 (s), 1070 (m), 1019 (m), 941 (w), 905 (w), 870 (w), 815 (w), 756 (m), 724 (m), 647 (w), 589 (w), 541 (w), 437 (w) cm^{-1}; MS (ESI): *m*/*z* = 920.75 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{57}H_{98}ClN_3O_6$) calcd.: 920.7450 [M – Cl]$^+$, found: 920.7459; CHN ($C_{57}H_{98}ClN_3O_6 \cdot 1.7\ H_2O$) calcd.: C 69.33 H 10.35 N 4.26, found: C 69.36 H 10.40 N 4.20; $[\alpha]_D^{20}$: +94 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 38.8 °C [4.15 kJ · mol^{-1}] SmA_d 93.7 °C [1.67 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,4-C_{14}TyrC$_{12}$Cl]

According to GP8: Free amine **3,4-C_{14}TyrC$_{12}$NH$_2$** (468 mg, 0.53 mmol), sodium bicarbonate (466 mg, 5.547 mmol), **GuaCl** (1.1 mL, 1.10 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 2 × **GuaCl** (total of 1.2 mL, 1.20 mmol, 1.0 M in CH_2Cl_2), 2 × sodium bicarbonate (total of 800 mg, 9.52 mmol); reaction time: 71 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

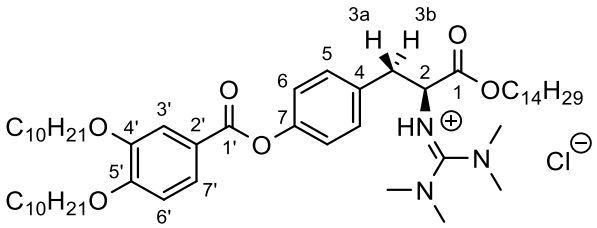


3,4-C_{14}TyrC_{12}Cl
$C_{61}H_{106}ClN_3O_6$
(1012.98)

Colourless solid (81%, 435 mg, 0.43 mmol, purity >99%); M.p. 38.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.18–1.37 (m, 58H, C*H*$_2$), 1.42–1.49 (m, 4H, $OCH_2CH_2CH_2$), 1.56–1.62 (m, 2H, $COOCH_2CH_2$), 1.78–1.86 (m, 4H, OCH_2CH_2), 2.36–3.65 (m, 13H, $N(CH_3)_2$, 3b-H), 3.85 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.01–4.10 (m, 7H, OCH_2, 2-H), 6.89 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.09 (d, *J* = 8.3 Hz, 2H, 6-H), 7.57 (d, *J* = 8.3 Hz, 2H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.75 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H), 10.11 (d, *J* = 7.2 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.85, 25.99, 26.03, 28.4, 29.06, 29.21, 29.35, 29.38, 29.40, 29.43, 29.52, 29.55, 29.60, 29.62, 29.64, 29.68, 29.72, 31.92, 31.94 (CH_2), 36.0 (C-3), 39.6 ($N(CH_3)_2$), 60.6 (C-2), 66.5 ($COOCH_2$), 69.1 (C-5'-OCH_2), 69.4 (C-4'-OCH_2), 112.0 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.9 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3377 (w), 2921 (vs), 2852 (s), 1731 (s), 1626 (m), 1599 (m), 1572 (m), 1510 (s), 1467 (m), 1428 (m), 1405 (m), 1344 (w), 1270 (vs), 1195 (vs), 1167 (s), 1140 (s), 1070 (m), 1019 (m), 956 (w), 929 (w), 902 (w), 871 (w), 815 (w), 756 (m), 723 (m), 648 (w), 587 (w), 536 (w), 519 (w) cm^{-1}; MS (ESI): *m*/*z* = 976.81 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{61}H_{106}ClN_3O_6$) calcd.: 976.8076 $[M - Cl]^+$, found: 976.8083; CHN ($C_{61}H_{106}ClN_3O_6$) calcd.: C 72.33 H 10.55 N 4.15, found: C 72.08H 10.76N 4.08; $[\alpha]_D^{20}$: +95 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 32.9 °C [6.06 kJ · mol^{-1}] SmA_d 94.8 °C [1.10 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(decyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,4-C_{10}TyrC_{14}Cl]

According to GP8: Free amine **3,4-C_{10}Tyr$C_{14}NH_2$** (525 mg, 0.66 mmol), sodium bicarbonate (591 mg, 7.04 mmol), **GuaCl** (2.6 mL, 1.34 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 2 × **GuaCl** (total of 1.3 mL, 0.67 mmol, 0.5 M in CH_2Cl_2), 2 × potassium carbonate (total of 620 mg, 4.49 mmol); reaction time: 26 h 30 min; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 35 : 1 → 10 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

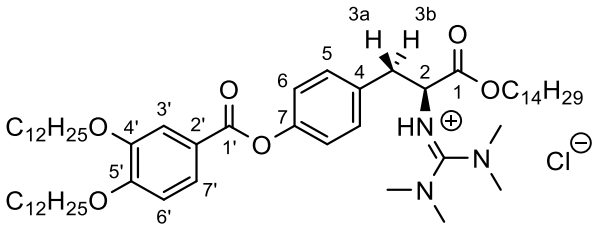


3,4-C_{10}TyrC$_{14}$Cl
$C_{55}H_{94}ClN_3O_6$
(928.82)

Colourless solid (61%, 376 mg, 0.41 mmol, purity >99%); M.p. 108.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.18–1.37 (m, 46H, C*H*$_2$), 1.42–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.61 (m, 2H, COOCH$_2$C*H*$_2$), 1.78–1.86 (m, 4H, OCH$_2$C*H*$_2$), 2.43–3.61 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.01–4.10 (m, 7H, OC*H*$_2$, 2-H), 6.89 (d, *J* = 8.6 Hz, 1H, 6'-H), 7.09 (d, *J* = 8.3 Hz, 2H, 6-H), 7.57 (d, *J* = 8.3 Hz, 2H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.75 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H, 7'-H), 10.08 (d, *J* = 7.3 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 25.97, 26.02, 28.4, 29.05, 29.19, 29.21, 29.35, 29.39, 29.41, 29.53, 29.57, 29.61, 29.63, 29.66, 29.70, 31.9 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.5 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2923 (s), 2853 (m), 2193 (w), 1731 (m), 1621 (m), 1599 (m), 1570 (m), 1510 (m), 1467 (m), 1429 (m), 1404 (w), 1344 (w), 1270 (s), 1194 (vs), 1167 (m), 1132 (m), 1068 (m), 1019 (w), 907 (s), 816 (w), 756 (w) 726 (vs), 641 (m), 584 (w), 547 (w) cm^{-1}; MS (ESI): *m*/*z* = 892.71 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{94}ClN_3O_6$) calcd.: 892.7137 [M – Cl]$^+$, found: 892.7139; CHN ($C_{55}H_{94}ClN_3O_6 \cdot 0.9\ H_2O$) calcd.: C 69.90 H 10.22 N 4.45. found: C 69.74 H 10.34 N 4.53; $[\alpha]_D^{20}$: +102 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 46.0 °C [–] SmA_d 95.4 °C [1.50 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(dodecyloxy)benzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,4-C_{12}TyrC$_{14}$Cl]

According to GP8: Free amine **3,4-C_{12}TyrC$_{14}$NH$_2$** (606 mg, 0.71 mmol), potassium carbonate (1.08 g, 7.81 mmol), **GuaCl** (2.1 mL, 1.08 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (30 mL); addition of 3 × **GuaCl** (total of 1.8 mL, 0.93 mmol, 0.5 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 664 mg, 7.90 mmol); reaction time: 98 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

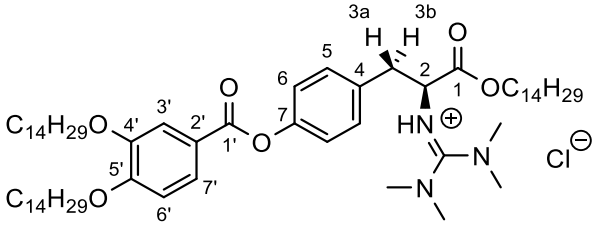


3,4-C_{12}TyrC$_{14}$Cl
$C_{59}H_{102}ClN_3O_6$
(984.93)

Colourless solid (89%, 625 mg, 0.64 mmol, purity >99%); M.p. 50.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.18–1.37 (m, 54H, C*H*$_2$), 1.42–1.49 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.61 (m, 2H, COOCH$_2$C*H*$_2$), 1.78–1.86 (m, 4H, OCH$_2$C*H*$_2$), 2.34–3.67 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.01–4.10 (m, 7H, OC*H*$_2$, 2-H), 6.89 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.09 (d, *J* = 8.3 Hz, 2H, 6-H), 7.57 (d, *J* = 8.3 Hz, 2H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.75 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H), 10.09 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 25.98, 26.03, 28.4, 29.05, 29.19, 29.21, 29.37, 29.40, 29.42, 29.53, 29.57, 29.62, 29.64, 29.66, 29.70, 31.9 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 111.9 (C-6'), 114.5 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.9 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3386 (w), 2921 (vs), 2852 (s), 1731 (s), 1624 (m), 1599 (m), 1572 (m), 1510 (s), 1467 (m), 1428 (m), 1404 (m), 1344 (w), 1269 (vs), 1194 (vs), 1167 (s), 1132 (s), 1069 (m), 1019 (m), 972 (w), 928 (m), 907 (m), 870 (w), 815 (w), 756 (m), 725 (s), 642 (w), 587 (w), 535 (w), 426 (w) cm^{-1}. MS (ESI): *m*/*z* = 948.78 [M – Cl]$^+$. HRMS (ESI): *m*/*z* ($C_{59}H_{102}ClN_3O_6$) calcd.: 948.7763 [M – Cl]$^+$, found: 948.7779. CHN ($C_{59}H_{102}ClN_3O_6 \cdot 1.0\ H_2O$) calcd.: C 70.66 H 10.45 N 4.19, found: C 70.60 H 10.49 N 4.15; $[\alpha]_D^{20}$: +94 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 29.7 °C [7.08 kJ · mol^{-1}] SmA_d 95.2 °C [1.04 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,4-C$_{14}$TyrC$_{14}$Cl]

According to GP8: Free amine **3,4-C$_{14}$TyrC$_{14}$NH$_2$** (563 mg, 0.62 mmol), potassium carbonate (922 mg, 6.67 mmol), **GuaCl** (1.9 mL, 0.98 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 1.8 mL, 0.93 mmol, 0.5 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 664 mg, 7.90 mmol); reaction time: 98 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



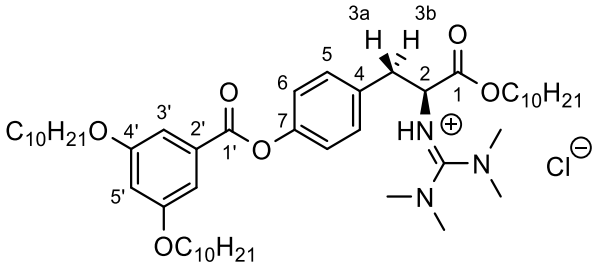
3,4-C$_{14}$TyrC$_{14}$Cl
$C_{63}H_{110}ClN_3O_6$
(1041.04)

Colourless solid (85%, 551 mg, 0.53 mmol, purity >99%); M.p. 52.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.87 (m, 9H, C*H*$_3$), 1.18–1.38 (m, 62H, C*H*$_2$), 1.43–1.50 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.87 (m, 4H, OCH$_2$C*H*$_2$), 2.30–3.66 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.86 (dd, *J* = 13.9 Hz, 9.5 Hz, 1H, 3a-H), 4.02–4.10 (m, 7H, OC*H*$_2$,

2-H), 6.90 (d, J = 8.4 Hz, 1H, 6'-H), 7.10 (d, J = 8.5 Hz, 2H, 6-H), 7.58 (d, J = 8.5 Hz, 2H, 5-H), 7.61 (d, J = 2.0 Hz, 1H, 3'-H), 7.76 (dd, J = 8.4 Hz, 2.0 Hz, 1H, 7'-H), 10.15 (d, J = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.85, 25.98, 26.03, 28.4, 29.05, 29.20, 29.21, 29.38, 29.40, 29.43, 29.53, 29.61, 29.62, 29.64, 29.66, 29.68, 29.70, 29.72, 31.93, 31.93 (CH_2), 36.0 (C-3), 39.6 (N(CH_3)$_2$), 60.6 (C-2), 66.5 (COOCH_2), 69.1 (C-5'-OCH_2), 69.4 (C-4'-OCH_2), 111.9 (C-6'), 114.5 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4), 148.7 (C-4'), 150.2 (C-7), 153.8 (C-5'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 2191 (w), 1731 (s), 1623 (m), 1599 (m), 1571 (m), 1510 (s), 1467 (m), 1428 (m), 1404 (m), 1344 (w), 1270 (vs), 1194 (vs), 1167 (s), 1132 (s), 1069 (m), 1019 (m), 927 (m), 907 (m), 870 (w), 814 (w), 756 (m), 726 (vs), 641 (w), 586 (w), 537 (w), 422 (w) cm^{-1}; MS (ESI): m/z = 1004.84 [M – Cl]$^+$; HRMS (ESI): m/z ($C_{63}H_{110}ClN_3O_6$) calcd.: 1004.8389 [M – Cl]$^+$, found: 1004.8381; CHN ($C_{63}H_{110}ClN_3O_6 \cdot 0.9\ H_2O$) calcd.: C 71.57 H 10.66 N 3.97, found: C 71.56 H 10.76 N 3.86; $[\alpha]_D^{20}$: +98 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 9.97 °C [0.11 kJ · mol^{-1}] Cr_2 31.4 °C [15.3 kJ · mol^{-1}] SmA_d 94.6 °C [0.90 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(decyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,5-C$_{10}$TyrC$_{10}$Cl]

According to GP8: Free amine **3,5-C$_{10}$TyrC$_{10}$NH$_2$** (468 mg, 0.63 mmol), sodium bicarbonate (814 mg, 9.69 mmol), **GuaCl** (1.0 mL, 1.00 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 2 × **GuaCl** (total of 0.6 mL, 0.60 mmol, 1.0 M in CH_2Cl_2), 2 × sodium bicarbonate (total of 532 mg, 6.33 mmol); reaction time: 75 h 30 min; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



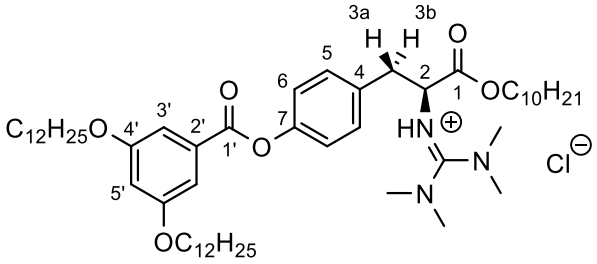
3,5-C$_{10}$TyrC$_{10}$Cl
$C_{51}H_{86}ClN_3O_6$
(872.71)

Colourless glass (90%, 498 mg, 0.57 mmol, purity >99%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 9H, CH_3), 1.20–1.37 (m, 38H, CH_2), 1.41–1.47 (m, 4H, OCH$_2$CH$_2$CH_2), 1.58–1.63 (m, 2H, COOCH$_2$CH_2), 1.77 (dt, J = 13.7 Hz, 7.0 Hz, 4H, OCH$_2$CH_2), 2.46–3.48 (m, 13H, N(CH_3)$_2$, 3b-H), 3.87 (dd, J = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 3.98 (t, J = 6.5 Hz, 4H, OCH_2), 4.05–4.11 (m, 3H, COOCH_2, 2-H), 6.69 (t, J = 2.3 Hz, 1H, 5'-H), 7.10 (d, J = 8.1 Hz, 2H, 6-H), 7.26 (d, J = 2.3 Hz, 2H, 3'-H), 7.60 (d, J = 8.1 Hz, 2H, 5-H),

10.20 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.84, 26.02, 28.41, 29.18, 29.20, 29.29, 29.32, 29.37, 29.51, 29.55, 29.57, 31.88, 31.89 (*C*H_2), 35.9 (C-3), 39.6 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 68.4 (O*C*H_2), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3378 (w), 2922 (s), 2853 (s), 1736 (s), 1593 (s), 1508 (m), 1446 (m), 1404 (m), 1349 (m), 1324 (m), 1299 (m), 1214 (s), 1196 (vs), 1165 (vs), 1119 (w), 1056 (m), 901 (w), 860 (w), 757 (m), 722 (w), 676 (w), 586 (w), 540 (w), 430 (w) cm^{-1}; MS (ESI): *m*/*z* = 836.65 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{51}H_{86}ClN_3O_6$) calcd.: 836.6511 $[M - Cl]^+$, found: 836.6495; CHN ($_{51}H_{86}ClN_3O_6$) calcd.: C 70.19 H 9.93 N 4.81, found: C 69.89 H 10.07 N 4.81; $[\alpha]_D^{20}$: +115 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(dodecyloxy)benzoyl)oxy)phenyl)-1-(decyloxy)propan-2-aminium chloride [3,5-C$_{12}$TyrC$_{10}$Cl]

According to GP8: Free amine **3,5-C$_{12}$TyrC$_{10}$NH$_2$** (459 mg, 0.58 mmol), sodium bicarbonate (736 mg, 8.76 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 2 × **GuaCl** (total of 0.6 mL, 0.60 mmol, 1.0 M in CH_2Cl_2), 2 × sodium bicarbonate (total of 485 mg, 5.77 mmol); reaction time: 74 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



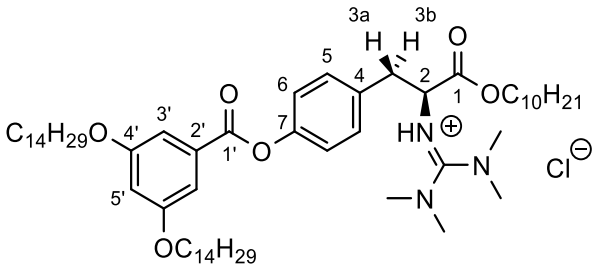
3,5-C$_{12}$TyrC$_{10}$Cl
$C_{55}H_{94}ClN_3O_6$
(928.82)

Colourless glass (90%, 484 mg, 0.52 mmol, purity >99%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.20–1.35 (m, 46H, C*H*$_2$), 1.40–1.46 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.57–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.34–3.47 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.86 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 3.97 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.07–4.10 (m, 3H, COOC*H*$_2$, 2-H), 6.68 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.10 (d, *J* = 8.1 Hz, 2H, 6-H), 7.25 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.59 (d, *J* = 8.1 Hz, 2H, 5-H), 10.14 (d, *J* = 6.9 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H_3), 22.67, 22.69, 25.84, 26.02, 28.4, 29.18, 29.20, 29.29, 29.35, 29.37, 29.51, 29.54, 29.58, 29.60, 29.64, 29.67, 31.88, 31.92 (*C*H_2), 36.0 (C-3), 39.7 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 68.4 (O*C*H_2), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (vs), 2852 (s), 1736 (s), 1593 (s), 1508 (m), 1446 (m), 1404 (m), 1350 (m), 1324 (m), 1299 (m), 1214 (s),

1195 (vs), 1165 (vs), 1117 (w), 1055 (m), 1033 (m), 930 (w), 906 (w), 860 (w), 845 (w), 757 (m), 725 (m), 676 (w), 639 (w), 586 (w), 544 (w), 417 (w) cm^{-1}; MS (ESI): *m*/*z* = 892.71 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{94}ClN_3O_6$) calcd.: 892.7137 $[M - Cl]^+$, found: 892.7121; CHN ($C_{55}H_{94}ClN_3O_6$) calcd.: C 71.12 H 10.20 N 4.52, found: C 71.00 H 10.32 N 4.49; $[\alpha]_D^{20}$: +110 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,5-C_{14}TyrC_{10}Cl]

According to GP8: Free amine **3,5-C_{14}Tyr$C_{10}NH_2$** (474 mg, 0.56 mmol), sodium bicarbonate (710 mg, 8.45 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 2 × **GuaCl** (total of 0.6 mL, 0.60 mmol, 1.0 M in CH_2Cl_2), 2 × sodium bicarbonate (total of 485 mg, 5.77 mmol); reaction time: 74 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



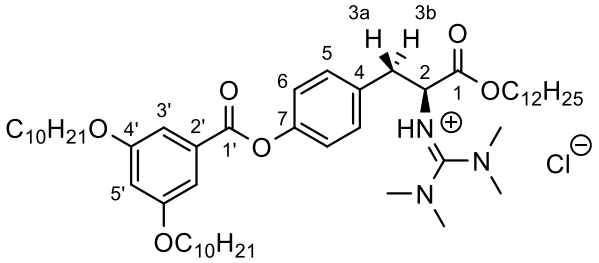
3,5-C_{14}TyrC_{10}Cl
$C_{59}H_{102}ClN_3O_6$
(984.93)

Colourless glass (87%, 478 mg, 0.49 mmol, purity >99%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 9H, C*H*$_3$), 1.19–1.36 (m, 54H, C*H*$_2$), 1.41–1.47 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.77 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.43–3.59 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 13.9 Hz, 9.2 Hz, 1H, 3a-H), 3.98 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.08–4.10 (m, 3H, COOC*H*$_2$, 2-H), 6.69 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.11 (d, *J* = 8.2 Hz, 2H, 6-H), 7.26 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.60 (d, *J* = 8.2 Hz, 2H, 5-H), 10.19 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H$_3$), 22.67, 22.70, 25.85, 26.02, 28.4, 29.19, 29.29, 29.36, 29.38, 29.51, 29.54, 29.58, 29.61, 29.66, 29.68, 29.70, 31.88, 31.93 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3375 (w), 2921 (vs), 2852 (s), 1736 (s), 1594 (s), 1508 (m), 1446 (s), 1404 (m), 1350 (m), 1324 (m), 1299 (m), 1214 (s), 1196 (vs), 1165 (vs), 1118 (w), 1056 (m), 934 (w), 902 (w), 861 (w), 845 (w), 758 (m), 676 (w), 585 (w), 537 (w) cm^{-1}; MS (ESI): *m*/*z* = 948.78 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{59}H_{102}ClN_3O_6$) calcd.: 948.7763 $[M - Cl]^+$, found: 948.7754; CHN ($C_{59}H_{102}ClN_3O_6$) calcd.:

C 71.95 H 10.44 N 4.27, found: C 71.81 H 10.61 N 4.29; $[\alpha]_D^{20}$: +100 (c = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(decyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,5-C_{10}TyrC$_{12}$Cl]

According to GP8: Free amine **3,5-C_{10}TyrC$_{12}$NH$_2$** (463 mg, 0.60 mmol), sodium bicarbonate (780 mg, 9.29 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 762 mg, 9.07 mmol); reaction time: 74 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

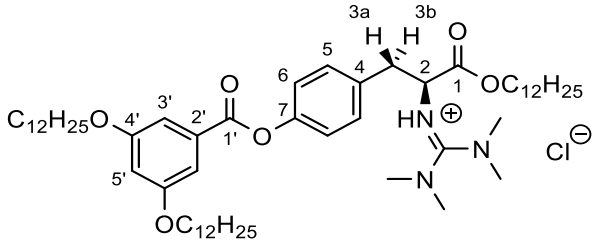


3,5-C_{10}TyrC$_{12}$Cl
$C_{53}H_{90}ClN_3O_6$
(900.77)

Colourless glass (84%, 458 mg, 0.51 mmol, purity >99%); M.p. 33.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 9H, CH_3), 1.20–1.37 (m, 42H, CH_2), 1.41–1.47 (m, 4H, OCH$_2$CH$_2$CH_2), 1.57–1.63 (m, 2H, COOCH$_2$CH_2), 1.77 (dt, J = 13.8 Hz, 6.7 Hz, 4H, OCH$_2$CH_2), 2.43–3.58 (m, 13H, N(CH_3)$_2$, 3b-H), 3.87 (dd, J = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 3.97 (t, J = 6.5 Hz, 4H, OCH_2), 4.07–4.10 (m, 3H, COOCH_2, 2-H), 6.68 (t, J = 2.3 Hz, 1H, 5'-H), 7.10 (d, J = 8.5 Hz, 2H, 6-H), 7.26 (d, J = 2.3 Hz, 2H, 3'-H), 7.59 (d, J = 8.5 Hz, 2H, 5-H), 10.17 (d, J = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.02, 28.4, 29.18, 29.21, 29.32, 29.35, 29.37, 29.52, 29.56, 29.57, 29.60, 29.64, 31.89, 31.91 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3395 (w), 3039 (vs), 2922 (s), 2853 (s), 1736 (s), 1625 (s), 1594 (s), 1572 (m), 1509 (m), 1446 (m), 1405 (m), 1350 (m), 1325 (m), 1299 (m), 1215 (vs), 1197 (vs), 1166 (vs), 1118 (w), 1098 (w), 1056 (m), 954 (w), 900 (w), 860 (w), 845 (w), 758 (m), 722 (w), 676 (w), 638 (w), 584 (w), 537 (w) cm^{-1}; MS (ESI): m/z = 864.68 [M – Cl]$^+$; HRMS (ESI): m/z ($C_{53}H_{90}ClN_3O_6$) calcd.: 864.6824 [M – Cl]$^+$, found: 864.6831; CHN ($C_{53}H_{90}ClN_3O_6 \cdot 0.2\ H_2O$) calcd.: C 70.39 H 10.08 N 4.65, found: C 70.15 H 10.23 N 4.67; $[\alpha]_D^{20}$: +102 (c = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(dodecyloxy)benzoyl)oxy)phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,5-C_{12}TyrC$_{12}$Cl]

According to GP8: Free amine **3,5-C_{12}TyrC$_{12}$NH$_2$** (461 mg, 0.56 mmol), sodium bicarbonate (714 mg, 8.50 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 707 mg, 8.41 mmol); reaction time: 52 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



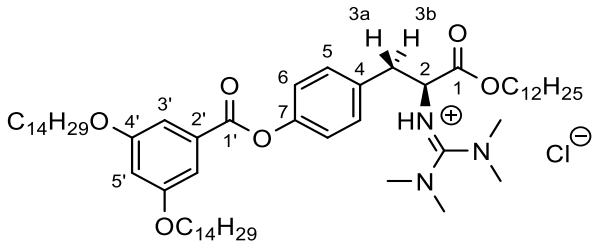
3,5-C_{12}TyrC$_{12}$Cl
$C_{57}H_{98}ClN_3O_6$
(956.88)

Colourless wax (88%, 472 mg, 0.49 mmol, purity >99%); M.p. 35.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 9H, C*H*$_3$), 1.18–1.35 (m, 50H, C*H*$_2$), 1.40–1.46 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, OCH$_2$C*H*$_2$), 2.36–3.54 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.86 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 3.96 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.06–4.10 (m, 3H, COOC*H*$_2$, 2-H), 6.67 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.09 (d, *J* = 8.1 Hz, 2H, 6-H), 7.25 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.58 (d, *J* = 8.1 Hz, 2H, 5-H), 10.13 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.02, 28.4, 29.18, 29.21, 29.35, 29.38, 29.52, 29.58, 29.60, 29.64, 29.66, 31.9 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3375 (w), 2921 (vs), 2852 (s), 1736 (s), 1624 (m), 1594 (s), 1572 (m), 1508 (m), 1446 (m), 1404 (m), 1350 (m), 1324 (m), 1299 (m), 1214 (s), 1196 (vs), 1165 (vs), 1117 (w), 1098 (w), 1055 (m), 932 (w), 901 (w), 860 (w), 845 (w), 757 (m), 723 (m), 676 (w), 639 (w), 587 (w), 536 (w) cm^{-1}; MS (ESI): *m*/*z* = 920.75 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{57}H_{98}ClN_3O_6$) calcd.: 920.7450 [M – Cl]$^+$, found: 920.7455; CHN ($C_{57}H_{98}ClN_3O_6$) calcd.: C 71.55 H 10.32 N 4.39, found: C 71.67 H 10.45 N 4.34; $[\alpha]_D^{20}$: +97 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,5-C_{14}TyrC$_{12}$Cl]

According to GP8: Free amine **3,5-C_{14}TyrC$_{12}$NH$_2$** (465 mg, 0.53 mmol), sodium bicarbonate (676 mg, 8.05 mmol), **GuaCl** (0.8 mL, 0.80 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL);

addition of 2 × **GuaCl** (total of 0.6 mL, 0.60 mmol, 1.0 M in CH_2Cl_2), 2 × sodium bicarbonate (total of 532 mg, 6.33 mmol); reaction time: 75 h 30 min; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

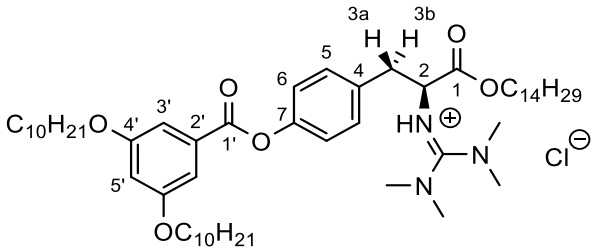


3,5-C_{14}TyrC$_{12}$Cl
$C_{61}H_{106}ClN_3O_6$
(1012.98)

Colourless wax (93%, 496 mg, 0.49 mmol, purity >99%); M.p. 40.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.87 (m, 9H, C*H*$_3$), 1.19–1.36 (m, 58H, C*H*$_2$), 1.41–1.47 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.77 (dt, *J* = 13.8 Hz, 6.8 Hz, 4H, OCH$_2$C*H*$_2$), 2.37–3.66 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 3.97 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.07–4.10 (m, 3H, COOC*H*$_2$, 2-H), 6.68 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.10 (d, *J* = 8.3 Hz, 2H, 6-H), 7.26 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.59 (d, *J* = 8.3 Hz, 2H, 5-H), 10.18 (d, *J* = 7.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.02, 28.4, 29.19, 29.21, 29.35, 29.36, 29.38, 29.52, 29.59, 29.61, 29.64, 29.66, 29.68, 29.70, 31.91, 31.93 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1736 (s), 1594 (s), 1570 (m), 1508 (m), 1446 (m), 1404 (m), 1349 (m), 1324 (m), 1299 (m), 1214 (s), 1195 (vs), 1165 (vs), 1119 (w), 1055 (m), 932 (w), 903 (w), 860 (w), 845 (w), 757 (m), 722 (m), 676 (w), 637 (w), 584 (w), 538 (w), 427 (w) cm^{-1}; MS (ESI): *m*/*z* = 976.81 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{61}H_{106}ClN_3O_6$) calcd.: 976.8076 [M – Cl]$^+$, found: 976.8072; CHN ($C_{61}H_{106}ClN_3O_6 \cdot 0.3\ H_2O$) calcd.: C 71.94 H 10.55 N 4.13, found: C 71.73 H 10.69 N 4.12; $[\alpha]_D^{20}$: +93 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(decyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,5-C_{10}TyrC$_{14}$Cl]

According to GP8: Free amine **3,5-C_{10}TyrC$_{14}$NH$_2$** (456 mg, 0.57 mmol), sodium bicarbonate (780 mg, 9.29 mmol), **GuaCl** (0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 76 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

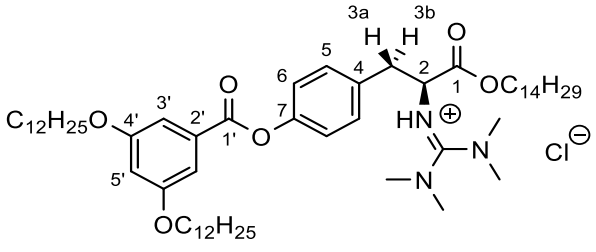


3,5-C_{10}TyrC$_{14}$Cl
$C_{55}H_{94}ClN_3O_6$
(928.82)

Colourless wax (87%, 463 mg, 0.50 mmol, purity >99%); M.p. 37.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.87 (m, 9H, C*H*$_3$), 1.19–1.36 (m, 46H, C*H*$_2$), 1.41–1.46 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.57–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.77 (dt, *J* = 13.8 Hz, 6.8 Hz, 4H, OCH$_2$C*H*$_2$), 2.36–3.59 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.86 (dd, *J* = 13.8 Hz, 9.3 Hz, 1H, 3a-H), 3.97 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.07–4.10 (m, 3H, COOC*H*$_2$, 2-H), 6.67–6.68 (m, 1H, 5'-H), 7.10 (d, *J* = 8.0 Hz, 2H, 6-H), 7.26 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.59 (d, *J* = 8.0 Hz, 2H, 5-H), 10.14 (d, *J* = 15.0 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.68, 22.70, 25.85, 26.02, 28.4, 29.18, 29.21, 29.32, 29.37, 29.53, 29.56, 29.58, 29.61, 29.66, 29.70, 31.90, 31.93 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.9 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 2359 (w), 2159 (w), 2027 (w), 1966 (w), 1845 (w), 1736 (s), 1593 (s), 1575 (m), 1508 (m), 1446 (m), 1404 (m), 1349 (m), 1324 (m), 1299 (m), 1196 (vs), 1164 (vs), 1055 (m), 901 (w), 860 (w), 757 (m), 721 (m), 675 (w), 539 (w) cm^{-1}; MS (ESI): *m*/*z* = 892.71 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{55}H_{94}ClN_3O_6$) calcd.: 892.7137 [M – Cl]$^+$, found: 892.7139; CHN ($_{55}H_{94}ClN_3O_6 \cdot 0.5\ H_2O$) calcd.: C 70.44 H 10.21 N 4.48, found: C 70.26 H 10.33 N 4.43; $[\alpha]_D^{20}$: +111 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(dodecyloxy)benzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,5-C_{12}TyrC$_{14}$Cl]

According to GP8: Free amine **3,5-C_{12}TyrC$_{14}$NH$_2$** (447 mg, 0.53 mmol), sodium bicarbonate (800 mg, 9.52 mmol), **GuaCl** (0.8 mL, 0.80 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 1.20 g, 14.3 mmol); reaction time: 76 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

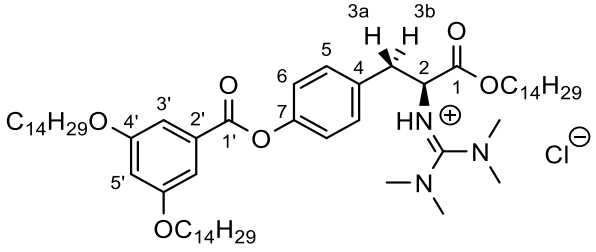


3,5-C_{12}TyrC$_{14}$Cl
$C_{59}H_{102}ClN_3O_6$
(984.93)

Colourless wax (84%, 434 mg, 0.44 mmol, purity >99%); M.p. 45.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.37 (m, 54H, C*H*$_2$), 1.41–1.47 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.77 (dt, *J* = 13.9 Hz, 6.8 Hz, 4H, OCH$_2$C*H*$_2$), 2.37–3.60 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 13.9 Hz, 9.3 Hz, 1H, 3a-H), 3.98 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.06–4.11 (m, 3H, COOC*H*$_2$, 2-H), 6.69 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.10 (d, *J* = 8.3 Hz, 2H, 6-H), 7.26 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.59 (d, *J* = 8.3 Hz, 2H, 5-H), 10.18 (t, *J* = 6.7 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.02, 28.4, 29.19, 29.21, 29.35, 29.38, 29.53, 29.58, 29.60, 29.64, 29.66, 29.69, 31.9 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.8 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3372 (w), 2921 (vs), 2852 (m), 1736 (s), 1625 (s), 1594 (s), 1572 (m), 1508 (m), 1446 (m), 1405 (m), 1350 (m), 1324 (m), 1299 (m), 1214 (s), 1196 (vs), 1165 (vs), 1099 (w), 1056 (m), 1020 (m), 934 (w), 901 (w), 860 (w), 845 (w), 757 (m), 721 (w), 676 (w), 589 (w), 537 (w) cm^{-1}; MS (ESI): *m*/*z* = 948.78 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{59}H_{102}ClN_3O_6$) calcd.: 948.7763 [M – Cl]$^+$, found: 948.7771; CHN ($C_{59}H_{102}ClN_3O_6$) calcd.: C 71.95 H 10.44 N 4.27, found: C 71.72 H 10.56 N 4.27; $[\alpha]_D^{20}$: +97 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,5-C$_{14}$TyrC$_{14}$Cl]

According to GP8: Free amine **3,5-C$_{14}$TyrC$_{14}$NH$_2$** (454 mg, 0.50 mmol), sodium bicarbonate (637 mg, 7.58 mmol), **GuaCl** (0.8 mL, 0.80 mmol, 1.0 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 0.9 mL, 0.90 mmol, 1.0 M in CH_2Cl_2), 3 × sodium bicarbonate (total of 762 mg, 9.07 mmol); reaction time: 75 h; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



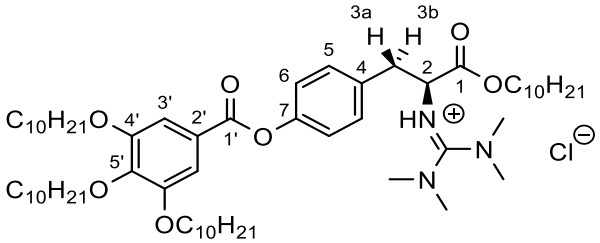
3,5-C$_{14}$TyrC$_{14}$Cl
C$_{63}$H$_{110}$ClN$_3$O$_6$
(1041.04)

Colourless wax (78%, 406 mg, 0.39 mmol, purity >99%); M.p. 47.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.36 (m, 62H, C*H*$_2$), 1.41–1.47 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.77 (dt, *J* = 13.9 Hz, 6.8 Hz, 4H, OCH$_2$C*H*$_2$), 2.38–3.66 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 13.8 Hz, 7.4 Hz, 1H, 3a-H), 3.97 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.06–4.10 (m, 3H, COOC*H*$_2$, 2-H), 6.69 (t, *J* = 2.3 Hz, 1H, 5'-H),

7.10 (d, *J* = 8.1 Hz, 2H, 6-H), 7.26 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.59 (d, *J* = 8.1 Hz, 2H, 5-H), 10.15–10.18 (m, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.85, 26.03, 28.4, 29.19, 29.21, 29.37, 29.39, 29.53, 29.58, 29.61, 29.66, 29.68, 29.70, 31.9 (*C*H_2), 36.0 (C-3), 39.6 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 68.4 (O*C*H_2), 107.1 (C-5'), 108.1 (C-3'), 121.9 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.0 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3398 (w), 2921 (vs), 2852 (s), 1736 (s), 1625 (m), 1594 (s), 1572 (m), 1508 (m), 1465 (m), 1446 (m), 1405 (m), 1350 (m), 1324 (m), 1299 (m), 1214 (d), 1196 (vs), 1165 (vs), 1100 (w), 1055 (m), 932 (w), 900 (w), 860 (w), 845 (w), 757 (m), 721 (m), 676 (w), 637 (w), 584 (w), 543 (w) cm^{-1}; MS (ESI): *m*/*z* = 1004.84 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}ClN_3O_6$) calcd.: 1004.8389 [M – Cl]$^+$, found: 1004.8386; CHN ($C_{63}H_{110}ClN_3O_6 \cdot 0.3\ H_2O$) calcd.: C 72.31 H 10.65 N 4.02, found: C 72.08 H 10.78 N 4.05; $[\alpha]_D^{20}$: +102 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G_1 –13.1 °C [1.61 kJ · mol^{-1}] G_2 34.7 °C [9.76 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(decyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,4,5-C$_{10}$TyrC$_{10}$Cl]

According to GP8: Free amine **3,4,5-C$_{10}$TyrC$_{10}$NH$_2$** (482 mg, 0.54 mmol), sodium bicarbonate (723 mg, 8.61 mmol), **GuaCl** (2.1 mL, 1.08 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 1.7 mL, 0.88 mmol, 0.5 M in CH_2Cl_2) after 24 h, 28 h and 45 h; reaction time: 47 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 30 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



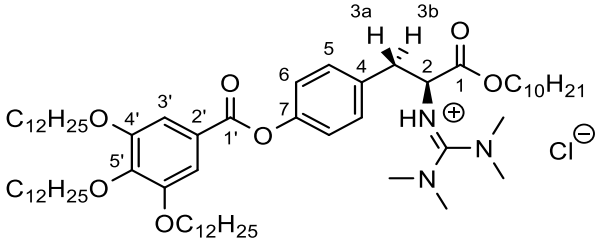
3,4,5-C$_{10}$TyrC$_{10}$Cl
$C_{61}H_{106}ClN_3O_7$
(1028.98)

Colourless wax (57%, 378 mg, 0.31 mmol, purity >99%); M.p. 40.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 12H, C*H*$_3$), 1.21–1.37 (m, 50H, C*H*$_2$), 1.43–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.71–1.77 (m, 2H, C-5'-OCH$_2$C*H*$_2$), 1.78–1.84 (m, 4H, C-4'-OCH$_2$C*H*$_2$), 2.36–3.56 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.86 (dd, *J* = 14.0 Hz, 9.3 Hz, 1H, 3a-H), 4.00–4.05 (m, 6H, OC*H*$_2$), 4.06–4.11 (m, 3H, COOC*H*$_2$, 2-H), 7.09 (d, *J* = 8.3 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.60 (d, *J* = 8.3 Hz, 2H, 5-H), 10.14 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.67, 22.69, 22.71, 25.84, 26.06, 26.10, 28.4, 29.20, 29.30, 29.31, 29.36, 29.40, 29.48, 29.51, 29.54, 29.57, 29.59, 29.64, 29.68,

29.74, 30.4, 31.89, 31.92, 31.95 (*C*H_2), 35.9 (C-3), 39.6 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 69.3 (C-4'-O*C*H_2), 73.6 (C-5'-O*C*H_2), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3374 (w), 2921 (vs), 2853 (s), 1732 (s), 1627 (m), 1582 (m), 1507 (m), 1466 (m), 1429 (s), 1405 (m), 1335 (s), 1190 (vs), 1115 (s), 1067 (w), 1019 (w), 900 (w), 862 (w), 755 (m), 721 (w), 585 (w) cm^{-1}; MS (ESI): *m*/*z* = 992.80 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{61}H_{106}ClN_3O_7$) calcd.: 992.8025 [M – Cl]$^+$, found: 992.8014; CHN ($C_{61}H_{106}ClN_3O_7 \cdot 1.0\ H_2O$) calcd.: C 69.98 H 10.40 N 4.01, found: C 69.97 H 10.44 N 3.94; $[\alpha]_D^{20}$: +90 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 47.3 °C [14.3 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,4,5-C$_{12}$TyrC$_{10}$Cl]

According to GP8: Free amine **3,4,5-C$_{12}$TyrC$_{10}$NH$_2$** (457 mg, 0.47 mmol), sodium bicarbonate (652 mg, 7.76 mmol), **GuaCl** (1.8 mL, 0.93 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (20 mL); addition of 3 × **GuaCl** (total of 1.7 mL, 0.88 mmol, 0.5 M in CH_2Cl_2) after 24 h, 28 h and 45 h. reaction time: 47 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 35 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



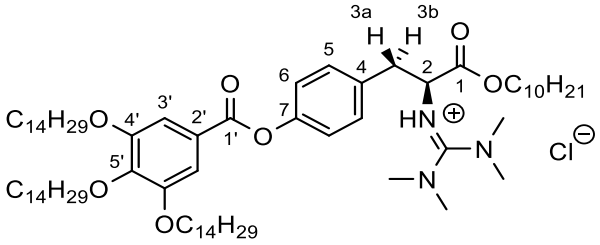
3,4,5-C$_{12}$TyrC$_{10}$Cl
$C_{67}H_{118}ClN_3O_7$
(1113.15)

Colourless wax (82%, 427 mg, 0.38 mmol, purity >99%); M.p. 80.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.88 (m, 12H, C*H*$_3$), 1.21–1.37 (m, 62H, C*H*$_2$), 1.44–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.59–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.75 (dt, *J* = 14.6 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.9 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.25–3.60 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 13.9 Hz, 9.4 Hz, 1H, 3a-H), 4.01–4.05 (m, 6H, OC*H*$_2$), 4.07–4.11 (m, 3H, COOC*H*$_2$, 2-H), 7.10 (d, *J* = 8.1 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.61 (d, *J* = 8.1 Hz, 2H, 5-H), 10.19 (d, *J* = 7.3 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.12, 14.13 (*C*H_3), 22.67, 22.70, 25.84, 26.07, 26.10, 28.4, 29.20, 29.30, 29.31, 29.37, 29.41, 29.51, 29.54, 29.58, 29.64, 29.67, 29.71, 29.75, 29.76, 30.4, 31.88, 31.93, 31.95 (*C*H_2), 35.9 (C-3), 39.6 (N(*C*H_3)$_2$), 60.6 (C-2), 66.5 (COO*C*H_2), 69.3 (C-4'-O*C*H_2), 73.6 (C-5'-O*C*H_2), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3394 (w), 2921 (vs), 2852 (s), 1733 (s), 1627 (m),

1582 (m), 1507 (m), 1466 (m), 1430 (s), 1405 (m), 1335 (s), 1191 (vs), 1168 (s), 1115 (vs), 1067 (w), 1019 (w), 952 (w), 901 (w), 862 (w), 754 (m), 721 (w), 581 (w), 543 (w) cm^{-1}; MS (ESI): *m*/*z* = 1076.90 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{67}H_{118}ClN_3O_7$) calcd.: 1076.8964 $[M - Cl]^+$, found: 1076.8953; CHN ($C_{67}H_{118}ClN_3O_7 \cdot 1.0\ H_2O$) calcd.: C 71.14 H 10.69 N 3.71, found: C 71.21 H 10.66 N 3.67; $[\alpha]_D^{20}$: +89 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 53.6 °C [11.5 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(decyloxy)propan-2-aminium chloride [3,4,5-C_{14}TyrC$_{10}$Cl]

According to GP8: Free amine **3,4,5-C_{14}TyrC$_{10}$NH$_2$** (693 mg, 0.65 mmol), sodium bicarbonate (903 mg, 10.8 mmol), **GuaCl** (2.5 mL, 1.29 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 3 × **GuaCl** (total of 1.7 mL, 0.88 mmol, 0.5 M in CH_2Cl_2) after 24 h, 28 h and 45 h; reaction time: 47 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 35 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



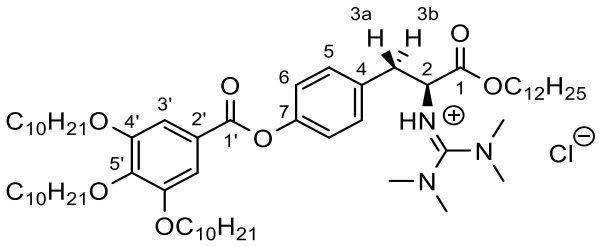
3,4,5-C_{14}TyrC$_{10}$Cl
$C_{73}H_{130}ClN_3O_7$
(1197.31)

Colourless wax (81%, 630 mg, 0.53 mmol, purity >99%); M.p. 55.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 12H, C*H*$_3$), 1.20–1.37 (m, 74H, C*H*$_2$), 1.43–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.74 (dt, *J* = 13.8 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.8 Hz, 6.6 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.36–3.58 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.00–4.05 (m, 6H, OC*H*$_2$), 4.07–4.12 (m, 3H, COOC*H*$_2$, 2-H), 7.09 (d, *J* = 8.1 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.60 (d, *J* = 8.1 Hz, 2H, 5-H), 10.16 (d, *J* = 6.8 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.11, 14.13 (*C*H$_3$), 22.67, 22.70, 25.84, 26.07, 26.10, 28.4, 29.20, 29.30, 29.32, 29.38, 29.40, 29.41, 29.51, 29.54, 29.58, 29.65, 29.68, 29.72, 29.76, 30.4, 31.88, 31.94 (*C*H$_2$), 35.9 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3373 (w), 2916 (vs), 2849 (vs), 1732 (s), 1628 (m), 1573 (m), 1508 (m), 1468 (m), 1430 (s), 1405 (m), 1385 (w), 1338 (s), 1195 (vs), 1170 (s), 1121 (vs), 1067 (w), 1020 (w), 993 (w), 959 (w), 929 (w), 901 (w), 858 (w), 745 (m), 720 (m), 583 (w), 546 (w) cm^{-1}; MS (ESI): *m*/*z* = 1160.99 $[M - Cl]^+$; HRMS (ESI): *m*/*z* ($C_{73}H_{130}ClN_3O_7$) calcd.:

1160.9903 $[M - Cl]^+$, found: 1160.9892; CHN ($C_{73}H_{130}ClN_3O_7 \cdot 0.7\ H_2O$) calcd.: C 72.47 H 10.95 N 3.47, found: C 72.44 H 10.97 N 3.40; $[\alpha]_D^{20}$: +79 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G_1 –4.03 °C [7.53 kJ · mol^{-1}] G_2 45.0 °C [–] Col_h 96.0 °C [–] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(decyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,4,5-C$_{10}$TyrC$_{12}$Cl]

According to GP8: Free amine **3,4,5-C$_{10}$TyrC$_{12}$NH$_2$** (613 mg, 0.67 mmol), sodium bicarbonate (998 mg, 11.9 mmol), **GuaCl** (2.6 mL, 1.34 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 1 × **GuaCl** (1.0 mL, 0.51 mmol, 0.5 M in CH_2Cl_2); reaction time: 26 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 17 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

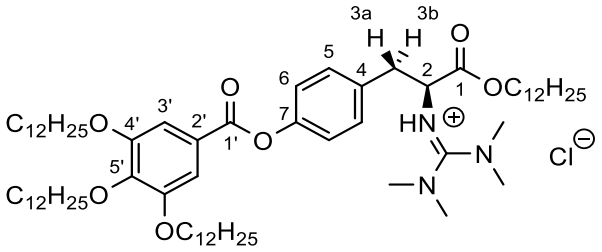


3,4,5-C$_{10}$TyrC$_{12}$Cl
$C_{63}H_{110}ClN_3O_7$
(1057.04)

Colourless wax (66%, 460 mg, 0.44 mmol, purity >99%); M.p. 65.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 12H, C*H*$_3$), 1.18–1.36 (m, 54H, C*H*$_2$), 1.42–1.49 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.56–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.70–1.76 (m, 2H, C-5'-OCH$_2$C*H*$_2$), 1.79 (dt, J = 13.8 Hz, 5.9 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.35–3.56 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.85 (dd, J = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 3.99–4.04 (m, 6H, OC*H*$_2$), 4.05–4.09 (m, 3H, COOC*H*$_2$, 2-H), 7.08 (d, J = 8.3 Hz, 2H, 6-H), 7.35 (s, 2H, 3'-H), 7.58 (d, J = 8.3 Hz, 2H, 5-H), 10.08 (d, J = 7.2 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.69, 22.71, 25.85, 26.06, 26.10, 28.4, 29.20, 29.31, 29.35, 29.40, 29.52, 29.57, 29.59, 29.64, 29.68, 29.74, 30.4, 31.91, 31.95 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3398 (w), 2921 (vs), 2852 (s), 1733 (s), 1625 (m), 1583 (m), 1507 (m), 1466 (m), 1430 (m), 1404 (m), 1334 (s), 1190 (vs), 1168 (s), 1114 (vs), 1067 (w), 1033 (w), 1020 (w), 959 (w), 901 (w), 862 (w), 754 (m), 722 (m), 637 (w), 583 (w), 532 (w) cm^{-1}; MS (ESI): m/z = 1020.83 $[M - Cl]^+$; HRMS (ESI): m/z ($C_{63}H_{110}ClN_3O_7$) calcd.: 1020.8338 $[M - Cl]^+$, found: 1020.8339; CHN ($C_{63}H_{110}ClN_3O_7 \cdot 0.3\ H_2O$) calcd.: C 71.22 H 10.49 N 3.96, found: C 71.18 H 10.49 N 3.82; $[\alpha]_D^{20}$: +92 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 41.3 °C [4.48 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(dodecyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,4,5-C_{12}TyrC_{12}Cl]

According to GP8: Free amine **3,4,5-C_{12}Tyr$C_{12}$$NH_2$** (616 mg, 0.61 mmol), sodium bicarbonate (841 mg, 10.0 mmol), **GuaCl** (2.4 mL, 1.23 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 1 × **GuaCl** (1.0 mL, 0.51 mmol, 0.5 M in CH_2Cl_2); reaction time: 26 h. eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 20 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

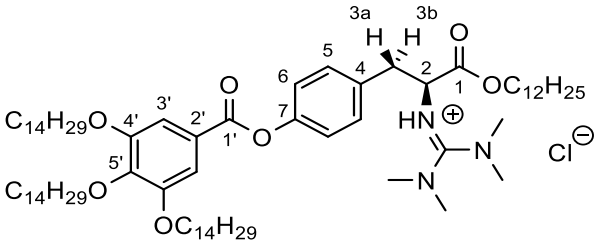


3,4,5-C_{12}TyrC_{12}Cl
$C_{69}H_{122}ClN_3O_7$
(1141.20)

Colourless wax (62%, 434 mg, 0.38 mmol, purity >99%); M.p. 62.4 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.88 (m, 12H, C*H*$_3$), 1.24–1.37 (m, 66H, C*H*$_2$), 1.44–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.59–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.75 (dt, *J* = 13.8 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.44–3.61 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.88 (dd, *J* = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.01–4.05 (m, 6H, OC*H*$_2$), 4.07–4.11 (m, 3H, COOC*H*$_2$, 2-H), 7.10 (d, *J* = 8.4 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.61 (d, *J* = 8.4 Hz, 2H, 5-H), 10.20 (d, *J* = 13.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.07, 26.10, 28.4, 29.21, 29.31, 29.35, 29.37, 29.41, 29.52, 29.58, 29.60, 29.64, 29.67, 29.71, 29.75, 29.76, 30.35, 31.91, 31.93, 31.95 (*C*H$_2$), 35.9 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.8 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3372 (w), 2921 (vs), 2852 (s), 1733 (s), 1626 (m), 1582 (m), 1507 (m), 1466 (m), 1429 (s), 1405 (m), 1335 (s), 1190 (vs), 1168 (s), 1115 (vs), 1067 (w), 1020 (w), 952 (w), 901 (w), 862 (w), 754 (m), 721 (m), 583 (w), 545 (w) cm^{-1}; MS (ESI): *m*/*z* = 1104.93 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{69}H_{122}ClN_3O_7$) calcd.: 1104.9277 [M – Cl]$^+$, found: 1104.9274; CHN ($C_{69}H_{122}ClN_3O_7 \cdot 1.0\ H_2O$) calcd.: C 71.49 H 10.78 N 3.62, found: C 71.37 H 10.77 N 3.61; $[\alpha]_D^{20}$: +62 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 32.0 °C [2.57 kJ · mol^{-1}] Col$_h$ 86.6 °C [–] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(dodecyloxy)propan-2-aminium chloride [3,4,5-C_{14}TyrC$_{12}$Cl]

According to GP8: Free amine **3,4,5-C_{14}TyrC$_{12}$NH$_2$** (670 mg, 0.61 mmol), sodium bicarbonate (778 mg, 9.26 mmol), **GuaCl** (2.4 mL, 1.23 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (25 mL); addition of 1 × **GuaCl** (0.6 mL, 0.31 mmol, 0.5 M in CH_2Cl_2); reaction time: 26 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 30 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

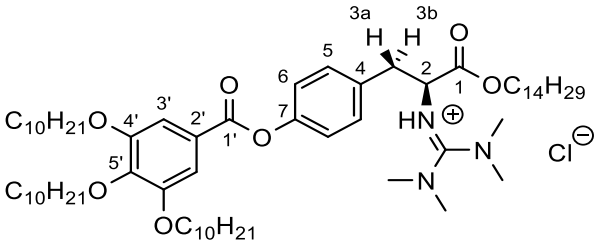


3,4,5-C_{14}TyrC$_{12}$Cl
$C_{75}H_{134}ClN_3O_7$
(1225.36)

Colourless wax (77%, 580 mg, 0.47 mmol, purity >99%); M.p. 80.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 12H, C*H*$_3$), 1.20–1.37 (m, 78H, C*H*$_2$), 1.43–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.74 (dt, *J* = 13.9 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.38–3.62 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.86 (dd, *J* = 14.1 Hz, 9.4 Hz, 1H, 3a-H), 4.00–4.05 (m, 6H, OC*H*$_2$), 4.07–4.11 (m, 3H, COOC*H*$_2$, 2-H), 7.09 (d, *J* = 8.2 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.60 (d, *J* = 8.2 Hz, 2H, 5-H), 10.12 (d, *J* = 15.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.69, 22.70, 25.85, 26.07, 26.11, 28.4, 29.21, 29.32, 29.35, 29.38, 29.40, 29.42, 29.52, 29.59, 29.65, 29.68, 29.72, 29.76, 30.4, 31.92, 31.94 (*C*H$_2$), 35.9 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (vs), 1733 (s), 1623 (m), 1583 (m), 1508 (m), 1466 (m), 1430 (s), 1404 (m), 1335 (s), 1190 (vs), 1167 (s), 1116 (s), 1067 (w), 1031 (m), 929 (m), 908 (m), 862 (w), 754 (m), 727 (s), 639 (w), 582 (w), 548 (w), 430 (w) cm^{-1}; MS (ESI): *m*/*z* = 1189.02 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{75}H_{134}ClN_3O_7$) calcd.: 1189.0216 [M – Cl]$^+$, found: 1189.0216; CHN ($C_{75}H_{134}ClN_3O_7 \cdot 2.1\ H_2O$) calcd.: C 71.31 H 11.03 N 3.33, found: C 71.34 H 10.95 N 3.28; $[\alpha]_D^{20}$: +75 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr$_1$ –11.0 °C [0.40 kJ · mol^{-1}] Cr$_2$ 13.8 °C [39.4 kJ · mol^{-1}] Col$_h$ 115.0 °C [–] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(decyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,4,5-C_{10}TyrC_{14}Cl]

According to GP8: Free amine **3,4,5-C_{10}Tyr$C_{14}NH_2$** (605 mg, 0.64 mmol), sodium bicarbonate (740 mg, 8.81 mmol), **GuaCl** (3.0 mL, 1.54 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (40 mL); addition of 3 × **GuaCl** (total of 2.0 mL, 1.03 mmol, 0.5 M in CH_2Cl_2) after 2 h, 4 h and 6 h; reaction time: 10 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).

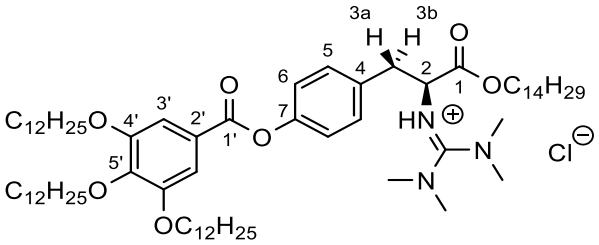


3,4,5-C_{10}TyrC_{14}Cl
$C_{65}H_{114}ClN_3O_7$
(1085.09)

Colourless wax (74%, 509 mg, 0.47 mmol, purity >99%); M.p. 70.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.86 (m, 12H, C*H*$_3$), 1.16–1.35 (m, 58H, C*H*$_2$), 1.42–1.49 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.57–1.62 (m, 2H, COOCH$_2$C*H*$_2$), 1.70–1.75 (m, 2H, C-5'-OCH$_2$C*H*$_2$), 1.79 (dt, *J* = 13.8 Hz, 6.5 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.43–3.60 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.84 (dd, *J* = 14.3 Hz, 8.6 Hz, 1H, 3a-H), 3.99–4.04 (m, 6H, OC*H*$_2$), 4.06–4.10 (m, 3H, COOC*H*$_2$, 2-H), 7.08 (d, *J* = 7.9 Hz, 2H, 6-H), 7.35 (s, 2H, 3'-H), 7.58 (d, *J* = 7.9 Hz, 2H, 5-H), 10.04 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.69, 22.71, 25.85, 26.06, 26.10, 28.4, 29.21, 29.31, 29.36, 29.40, 29.53, 29.57, 29.59, 29.61, 29.64, 29.66, 29.68, 29.70, 29.74, 30.4, 31.92, 31.95 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.5 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.0 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1732 (s), 1623 (m), 1583 (m), 1508 (m), 1466 (m), 1430 (s), 1404 (m), 1334 (s), 1189 (vs), 1168 (s), 1115 (s), 1067 (w), 1032 (w), 961 (w), 928 (m), 907 (w), 862 (w), 754 (m), 726 (s), 640 (w), 583 (w), 546 (w), 427 (w) cm^{-1}; MS (ESI): *m*/*z* = 1048.87 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{65}H_{114}ClN_3O_7$) calcd.: 1048.8651 [M – Cl]$^+$, found: 1048.8651; CHN ($C_{65}H_{114}ClNO_7 \cdot 0.7\ H_2O$) calcd.: C 71.12 H 10.60 N 3.83, found: C 71.13 H 10.66 N 3.77; $[\alpha]_D^{20}$: +97 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 56.6 °C [7.51 kJ · mol^{-1}] Col$_h$ 105.0 °C [–] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(dodecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,4,5-C_{12}TyrC_{14}Cl]

According to GP8: Free amine **3,4,5-C_{12}Tyr$C_{14}$$NH_2$** (603 mg, 0.58 mmol), sodium bicarbonate (822 mg, 9.79 mmol), **GuaCl** (2.8 mL, 1.44 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (40 mL); addition of 3 × **GuaCl** (total of 2.0 mL, 1.03 mmol, 0.5 M in CH_2Cl_2) after 2 h, 4 h and 6 h; reaction time: 10 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 30 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



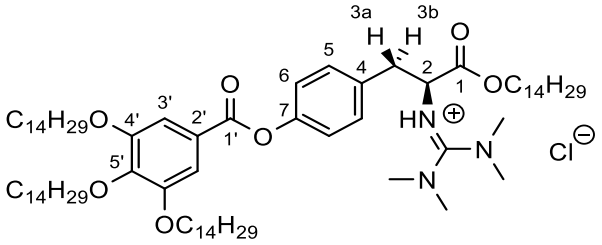
3,4,5-C_{12}TyrC_{14}Cl
$C_{71}H_{126}ClN_3O_7$
(1169.25)

Colourless wax (79%, 540 mg, 0.46 mmol, purity >99%); M.p. 66.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 12H, C*H*$_3$), 1.21–1.38 (m, 70H, C*H*$_2$), 1.45–1.52 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.65 (m, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 14.1 Hz, 7.0 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.83 (dt, *J* = 14.1 Hz, 6.8 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.33–3.59 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 13.9 Hz, 9.5 Hz, 1H, 3a-H), 4.02–4.07 (m, 6H, OC*H*$_2$), 4.08–4.12 (m, 3H, COOC*H*$_2$, 2-H), 7.11 (d, *J* = 7.9 Hz, 2H, 6-H), 7.37 (s, 2H, 3'-H), 7.61 (d, *J* = 7.9 Hz, 2H, 5-H), 10.10 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.07, 26.10, 28.4, 29.21, 29.32, 29.37, 29.41, 29.53, 29.58, 29.61, 29.65, 29.67, 29.71, 29.75, 29.76, 30.4, 31.93, 31.95 (*C*H$_2$), 36.0 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.0 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.2 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2922 (s), 2853 (s), 2189 (w), 1733 (m), 1621 (m), 1583 (m), 1508 (w), 1466 (m), 1430 (m), 1404 (w), 1335 (m), 1189 (vs), 1167 (m), 1115 (s), 1067 (w), 1031 (w), 925 (m), 907 (s), 862 (w), 728 (vs), 640 (w), 583 (w), 546 (w), 433 (w) cm^{-1}; MS (ESI): *m*/*z* = 1132.96 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{71}H_{126}ClN_3O_7$) calcd.: 1132.9590 [M – Cl]$^+$, found: 1132.9591; CHN ($C_{71}H_{126}ClN_3O_7 \cdot 0.5\ H_2O$) calcd.: C 72.38 H 10.86 N 3.57, found: C 72.38 H 10.86 N 3.50; $[\alpha]_D^{20}$: +86 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 81.4 °C [0.66 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium chloride [3,4,5-C_{14}TyrC_{14}Cl]

According to GP8: Free amine **3,4,5-C_{14}Tyr$C_{14}$$NH_2$** (318 mg, 0.28 mmol), sodium bicarbonate (241 mg, 2.87 mmol), **GuaCl** (1.1 mL, 0.57 mmol, 0.5 M in CH_2Cl_2), dry CH_2Cl_2 (40 mL);

addition of 3 × **GuaCl** (total of 1.2 mL, 0.62 mmol, 0.5 M in CH_2Cl_2) after 4 h, and 24 h; reaction time: 26 h; eluent for chromatography: EtOAc followed by CH_2Cl_2/MeOH gradient = 20 : 1 → 15 : 1; R_f = 0.30 (CH_2Cl_2/MeOH = 15 : 1).



3,4,5-C_{14}TyrC$_{14}$Cl
$C_{77}H_{138}ClN_3O_7$
(1253.42)

Colourless wax (59%, 211 mg, 0.17 mmol, purity >99%); M.p. 83.5 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.88 (m, 12H, C*H*$_3$), 1.20–1.37 (m, 82H, C*H*$_2$), 1.43–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.58–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.74 (dt, *J* = 14.5 Hz, 6.6 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.81 (dt, *J* = 14.5 Hz, 6.6 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.27–3.54 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 13.9 Hz, 9.5 Hz, 1H, 3a-H), 4.00–4.06 (m, 6H, OC*H*$_2$), 4.06–4.12 (m, 3H, COOC*H*$_2$, 2-H), 7.09 (d, *J* = 8.5 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.60 (d, *J* = 8.5 Hz, 2H, 5-H), 10.18 (d, *J* = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.07, 26.11, 28.4, 29.21, 29.32, 29.37, 29.38, 29.40, 29.42, 29.53, 29.59, 29.60, 29.65, 29.68, 29.70, 29.72, 29.76, 30.4, 31.9 (*C*H$_2$), 35.9 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3396 (w), 2920 (vs), 2851 (vs), 1733 (s), 1626 (m), 1583 (m), 1507 (m), 1466 (m), 1430 (s), 1405 (m), 1379 (w), 1335 (s), 1191 (vs), 1168 (s), 1116 (s), 1067 (w), 1020 (w), 959 (w), 900 (w), 862 (w), 754 (m), 721 (m), 583 (w), 539 (w), 443 (w) cm^{-1}; MS (ESI): *m*/*z* = 1217.05 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{77}H_{138}ClN_3O_7$) calcd.: 1217.0529 [M – Cl]$^+$, found: 1217.0517; CHN ($C_{77}H_{138}ClN_3O_7 \cdot 0.8\ H_2O$) calcd.: C 72.95 H 11.10 N 3.31, found: C 72.92 H 11.06 N 3.20; KFT: 0.70% (6988.1 ppm) water content (3.59 mg H_2O for 514 mg sample); $[\alpha]_D^{20}$: +77 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 10.3 °C [19.4 kJ · mol^{-1}] Col$_h$ 92.4 °C [0.85 kJ · mol^{-1}] I (2nd cool).

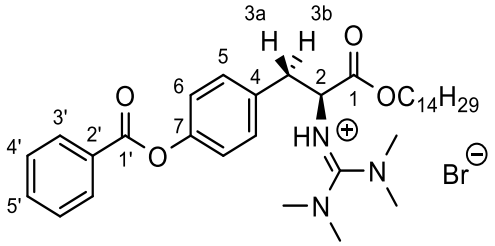
General Procedure GP9: Anion exchange of guanidinium chlorides[1,25]

The respective guanidinium chloride **Ar(C$_m$)TyrC$_n$Cl** (0.10 mmol) and the respective sodium or potassium salt (0.30 mmol) were suspended in a mixture of acetonitrile (9 mL) and CH_2Cl_2 (1 mL). The mixture was heated for 30 min under reflux. After cooling to room temperature, the solvents were removed under reduced pressure and the remaining residue was suspended in

CH_2Cl_2 (25 mL) and filtered through Celite®. Subsequently, the solvent was removed under reduced pressure. Differences from this procedure can be found at the respective compound.

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(tetradecyloxy)-propan-2-aminium bromide [BzTyrC$_{14}$Br]

According to GP9: Guanidinium chloride **BzTyrC$_{14}$Cl** (142 mg, 0.23 mmol), potassium bromide (100 mg, 0.84 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

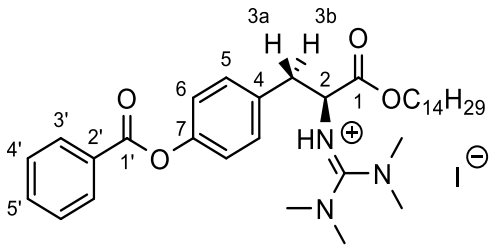


BzTyrC$_{14}$Br
$C_{35}H_{54}BrN_3O_4$
(660.74)

Colourless glass (87%, 132 mg, 0.20 mmol, purity >99%); M.p. 61.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.22–1.32 (m, 22H, C*H*$_2$), 1.63 (dt, *J* = 13.7 Hz, 7.1 Hz, 2H, OCH$_2$C*H*$_2$), 2.48–3.56 (m, 13H, N(C*H*$_3$)$_2$, 3b-H), 3.87 (dd, *J* = 13.9 Hz, 9.4 Hz, 1H, 3a-H), 4.08–4.15 (m, 3H, OC*H*$_2$, 2-H), 7.15 (d, *J* = 8.2 Hz, 2H, 6-H), 7.52 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.61–7.67 (m, 3H, 5-H, 5'-H), 8.19 (d, *J* = 7.8 Hz, 2H, 3'-H), 9.99 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.2, 29.52, 29.60, 29.65, 29.68, 31.9 (*C*H$_2$), 36.1 (C-3), 39.7 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (O*C*H$_2$), 121.9 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.1 (C-3'), 131.0 (C-5), 133.65 (C-5'), 134.74 (C-4), 150.1 (C-7), 162.2 (N=C), 165.2 (C-1'), 170.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3218 (m), 3066 (w), 2922 (vs), 2851 (s), 1733 (vs), 1637 (s), 1601 (m), 1573 (s), 1508 (m), 1452 (m), 1429 (w), 1417 (w), 1405 (m), 1368 (w), 1313 (w), 1266 (vs), 1199 (vs), 1178 (s), 1101 (w), 1082 (m), 1064 (s), 1024 (m), 900 (w), 877 (w), 813 (w), 748 (w), 703 (vs), 684 (m), 587 (w), 539 (w), 520 (w) cm^{-1}; MS (ESI): *m*/*z* = 78.92 [Br]$^-$, 580.41 [M – Br]$^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{54}BrN_3O_4$) calcd.: 580.4109 [M – Br]$^+$, found: 580.4107, calcd.: 78.9189 [Br]$^-$, found: 78.9172; CHN ($C_{35}H_{54}BrN_3O_4$) calcd.: C 63.62 H 8.24 N 6.36, found: C 63.75 H 8.01 N 6.13; $[\alpha]_D^{20}$: +135 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 14.5 °C [2.84 kJ · mol^{-1}] I (1st cool).

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(tetradecyloxy)-propan-2-aminium iodide [BzTyrC$_{14}$I]

According to GP9: Guanidinium chloride **BzTyrC$_{14}$Cl** (129 mg, 0.21 mmol), potassium iodide (110 mg, 0.66 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



BzTyrC$_{14}$I

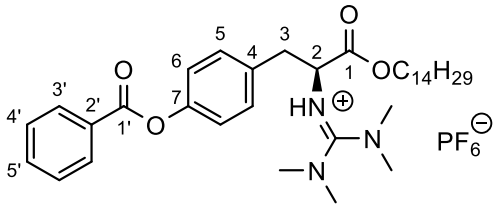
$C_{35}H_{54}IN_3O_4$

(707.74)

Colourless glass (quant., 149 mg, 0.21 mmol, purity >99%); M.p. 76.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.16–1.29 (m, 22H, C*H*$_2$), 1.62 (dt, *J* = 13.9 Hz, 6.9 Hz, 2H, OCH$_2$C*H*$_2$), 2.60–3.30 (m, 12H, N(*C*H$_3$)$_2$), 3.41 (dd, *J* = 14.1 Hz, 5.2 Hz, 1H, 3b-H), 3.80 (dd, *J* = 14.1 Hz, 8.5 Hz, 1H, 3a-H), 4.12 (t, *J* = 6.9 Hz, 2H, OC*H*$_2$), 4.25 (dd, *J* = 8.5 Hz, 5.2 Hz, 1H, 2-H), 7.14 (d, *J* = 8.8 Hz, 2H, 6-H), 7.50 (t, *J* = 7.7 Hz, 2H, 4'-H), 7.55 (d, *J* = 8.8 Hz, 2H, 5-H), 7.63 (t, *J* = 7.5 Hz, 1H, 5'-H), 7.90 (br. s, 1H, NH), 8.16 (d, *J* = 7.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.2, 29.4, 29.53, 29.61, 29.65, 29.69, 31.9 (*C*H$_2$), 36.5 (C-3), 40.0 (N(*C*H$_3$)$_2$), 60.0 (C-2), 66.8 (O*C*H$_2$), 122.1 (C-6), 128.6 (C-4'), 129.4 (C-2'), 130.1 (C-3'), 130.9 (C-5), 133.7 (C-5'), 133.8 (C-4), 150.3 (C-7), 161.7 (N=C), 165.2 (C-1'), 170.6 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3436 (w), 3195 (w), 3060 (w), 2922 (vs), 2852 (s), 1733 (vs), 1621 (s), 1566 (s), 1508 (m), 1465 (m), 1451 (m), 1403 (m), 1313 (w), 1263 (s), 1198 (s), 1167 (s), 1113 (w), 1080 (m), 1061 (s), 1024 (m), 908 (w), 800 (w), 706 (s), 685 (w), 673 (w), 641 (w), 582 (w), 519 (w) cm^{-1}; MS (ESI): *m*/*z* = 126.91 [I]$^-$, 580.41 [M – I]$^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{54}IN_3O_4$) calcd.: 580.4109 [M – I]$^+$, found: 580.4105, calcd.: 126.9050 [I]$^-$, found: 126.9051; CHN ($C_{35}H_{54}IN_3O_4 \cdot 0.6\ H_2O$) calcd.: C 58.50 H 7.74 N 5.85, found: C 58.53 H 7.86 N 5.70; $[\alpha]_D^{20}$: +115 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 1.52 °C [3.35 kJ · mol^{-1}] I (1st cool).

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(tetradecyloxy)-propan-2-aminium hexafluorophosphate [BzTyrC$_{14}$PF$_6$]

According to GP9: Guanidinium chloride **BzTyrC$_{14}$Cl** (142 mg, 0.23 mmol), potassium hexafluorophosphate (140 mg, 0.76 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



BzTyrC$_{14}$PF$_6$

$C_{35}H_{54}F_6N_3O_4P$

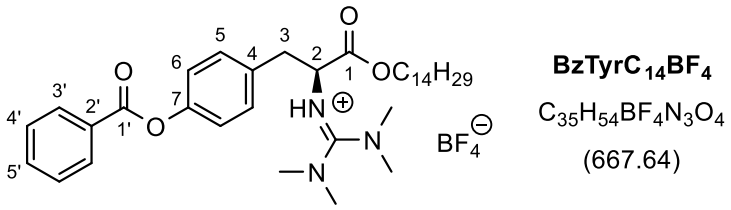
(725.80)

Colourless glass (78%, 131 mg, 0.18 mmol, purity >99%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.15–1.25 (m, 22H, C*H*$_2$), 1.58 (dt, *J* = 14.1 Hz, 7.0 Hz, 2H, OCH$_2$C*H*$_2$), 2.83 (br. s, 6H, N(C*H*$_3$)$_2$), 2.95 (br. s, 6H, N(C*H*$_3$)$_2$), 3.25

(d, *J* = 6.3 Hz, 2H, 3-H), 4.09 (t, *J* = 6.9 Hz, 1H, OC*H*$_2$), 4.23 (t, *J* = 6.3 Hz, 1H, 2-H), 5.61 (br. s, 1H, NH), 7.12 (d, *J* = 8.3 Hz, 2H, 6-H), 7.26 (d, *J* = 8.3 Hz, 2H, 5-H), 7.45 (t, *J* = 7.6 Hz, 2H, 4'-H), 7.58 (t, *J* = 7.6 Hz, 1H, 5'-H), 8.10 (d, *J* = 7.6 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.69, 25.8, 28.4, 29.21, 29.36, 29.52, 29.62, 29.65, 29.69, 31.9 (*C*H$_2$), 37.1 (C-3), 39.8 (N(*C*H$_3$)$_2$), 58.6 (C-2), 66.9 (O*C*H$_2$), 122.5 (C-6), 128.7 (C-4'), 129.3 (C-2'), 130.2 (C-3'), 130.5 (C-5), 132.6 (C-4), 133.8 (C-5'), 150.6 (C-7), 161.6 (N=C), 165.2 (C-1'), 170.4 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.4 (s, PF_6), –71.5 (s, PF_6) ppm; FT-IR: $\tilde{\nu}$ = 3378 (w), 2923 (m), 2853 (w), 1737 (m), 1627 (m), 1568 (m), 1509 (w), 1453 (w), 1406 (w), 1265 (m), 1202 (m), 1169 (w), 1081 (w), 1063 (w), 1024 (w), 840 (vs), 708 (w), 557 (m) cm^{-1}; MS (ESI): *m*/*z* = 144.97 $[PF_6]^-$, 580.41 $[M - PF_6]^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{54}F_6N_3O_4P$) calcd.: 580.4109 $[M - PF_6]^+$, found: 580.4108, calcd.: 144.9647 $[PF_6]^-$, found: 144.9651; CHN ($C_{35}H_{54}F_6N_3O_4P$) calcd.: C 57.92 H 7.50 N 5.79, found: C 58.00 H 7.51 N 5.67; $[\alpha]_D^{20}$: +84 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G_1 –44.8 °C [0.49 kJ · mol^{-1}] G_2 6.35 °C [1.19 kJ · mol^{-1}] I (1st cool).

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(tetradecyloxy)-propan-2-aminium tetrafluoroborate [BzTyrC$_{14}$BF$_4$]

According to GP9: Guanidinium chloride **BzTyrC$_{14}$Cl** (160 mg, 0.26 mmol), sodium tetrafluoroborate (90.0 mg, 0.82 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

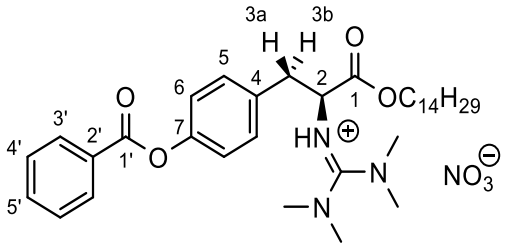


Colourless glass (88%, 154 mg, 0.23 mmol, purity >99%); M.p. 35.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.18–1.33 (m, 22H, C*H*$_2$), 1.63 (dt, *J* = 14.1 Hz, 7.1 Hz, 2H, OCH$_2$C*H*$_2$), 2.78 (br. s, 6H, N(*C*H$_3$)$_2$), 3.00 (br. s, 6H, N(C*H*$_3$)$_2$), 3.35 (d, *J* = 6.9 Hz, 2H, 3-H), 4.13 (t, *J* = 6.9 Hz, 2H, OC*H*$_2$), 4.24 (t, *J* = 6.9 Hz, 1H, 2-H), 6.56 (s, 1H, NH), 7.16 (d, *J* = 8.2 Hz, 2H, 6-H), 7.38 (d, *J* = 8.2 Hz, 2H, 5-H), 7.50 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.63 (t, *J* = 7.8 Hz, 1H, 5'-H), 8.16 (d, *J* = 7.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.21, 29.36, 29.53, 29.61, 29.65, 29.69, 31.9 (*C*H$_2$), 36.9 (C-3), 39.8 (N(*C*H$_3$)$_2$), 59.2 (C-2), 66.7 (O*C*H$_2$), 122.3 (C-6), 128.6 (C-4'), 129.4 (C-2'), 130.2 (C-3'), 130.6 (C-5), 133.3 (C-5'), 133.7 (C-4), 150.4 (C-7), 161.9 (N=C), 165.2 (C-1'), 170.5 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –151.2 (d, *J* = 19.7 Hz, BF_4) ppm; FT-IR: $\tilde{\nu}$ = 3332 (w), 2922 (s), 2852 (s), 1734 (s), 1625 (s), 1568 (m), 1508 (m),

1452 (m), 1405 (m), 1313 (w), 1263 (s), 1199 (s), 1168 (s), 1057 (vs), 905 (w), 801 (w), 706 (vs), 685 (w), 673 (w), 583 (w), 520 (m) cm^{-1}; MS (ESI): *m*/*z* = 87.00 $[BF_4]^-$, 580.41 $[M - BF_4]^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{54}BF_4N_3O_4$) calcd.: 580.4109 $[M - BF_4]^+$, found: 580.4110, calcd.: 87.0035 $[BF_4]^-$, found: 87.0023; CHN ($C_{35}H_{54}BF_4N_3O_4 \cdot 0.6\ H_2O$) calcd.: C 61.96 H 8.20 N 6.19, found: C 61.88 H 7.97 N 6.12; $[\alpha]_D^{20}$: +104 (*c* = 1.0 $mg \cdot mL^{-1}$ in $CHCl_3$); DSC: G 5.24 °C [3.59 $kJ \cdot mol^{-1}$] I (1st cool).

(*S*)-3-(4-(Benzoyloxy)phenyl)-*N*-(bis(dimethylamino)methylene)-1-oxo-1-(tetradecyloxy)-propan-2-aminium nitrate [BzTyrC$_{14}$NO$_3$]

According to GP9: Guanidinium chloride **BzTyrC$_{14}$Cl** (142 mg, 0.23 mmol), sodium nitrate (57.8 mg, 0.68 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

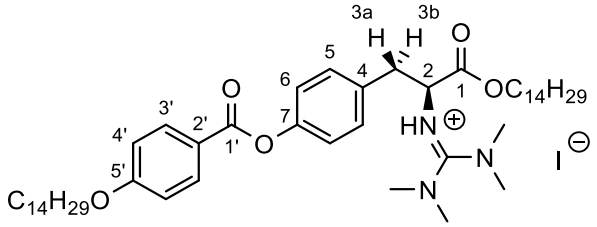


BzTyrC$_{14}$NO$_3$
$C_{35}H_{54}N_4O_7$
(642.84)

Colourless glass (96%, 141 mg, 0.22 mmol, purity >95%); M.p. 50.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.19–1.29 (m, 22H, C*H*$_2$), 1.55–1.62 (m, 2H, OCH$_2$C*H*$_2$), 2.48–3.23 (m, 12H, N(*C*H$_3$)$_2$), 3.38 (dd, *J* = 14.1 Hz, 4.8 Hz, 1H, 3b-H), 3.76 (dd, *J* = 14.1 Hz, 9.2 Hz, 1H, 3a-H), 4.05–4.12 (m, 3H, OC*H*$_2$, 2-H), 7.12 (d, *J* = 8.2 Hz, 2H, 6-H), 7.49 (t, *J* = 7.7 Hz, 2H, 4'-H), 7.55 (d, *J* = 8.2 Hz, 2H, 5-H), 7.62 (t, *J* = 7.7 Hz, 1H, 5'-H), 8.15 (d, *J* = 7.7 Hz, 2H, 3'-H), 9.92 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.21, 29.35, 29.53, 29.61, 29.65, 29.69, 31.9 (*C*H$_2$), 36.2 (C-3), 39.7 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (O*C*H$_2$), 121.9 (C-6), 128.6 (C-4'), 129.5 (C-2'), 130.1 (C-3'), 130.9 (C-5), 133.7 (C-5'), 134.8 (C-4), 150.0 (C-7), 162.3 (N=C), 165.2 (C-1'), 170.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3213 (w), 3062 (w), 2921 (s), 2851 (m), 1732 (vs), 1636 (s), 1601 (m), 1572 (s), 1508 (m), 1452 (m), 1429 (w), 1416 (m), 1405 (m), 1367 (w), 1313 (m), 1265 (vs), 1198 (vs), 1178 (s), 1169 (s), 1101 (w), 1082 (m), 1063 (s), 1023 (m), 900 (w), 877 (w), 831 (w), 748 (w), 702 (vs), 684 (m), 587 (w), 539 (w), 520 (w) cm^{-1}; MS (ESI): *m*/*z* = 61.99 $[NO_3]^-$, 580.41 $[M - NO_3]^+$; HRMS (ESI): *m*/*z* ($C_{35}H_{54}N_4O_7$) calcd.: 580.4109 $[M - NO_3]^+$, found: 580.4105, calcd.: 61.9884 $[NO_3]^-$, found: 61.9906; CHN ($C_{35}H_{54}N_4O_7$) calcd.: C 65.39 H 8.47 N 8.72, found: C 64.82 H 8.94 N 6.65; $[\alpha]_D^{20}$: +134 (*c* = 1.0 $mg \cdot mL^{-1}$ in $CHCl_3$); DSC: G_1 –46.3 °C [0.23 $kJ \cdot mol^{-1}$] G_2 21.3 °C [2.02 $kJ \cdot mol^{-1}$] I (1st cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-tetradecyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium iodide [4-C$_{14}$TyrC$_{14}$I]

According to GP9: Guanidinium chloride **4-C$_{14}$TyrC$_{14}$Cl** (133 mg, 0.16 mmol), potassium iodide (100 mg, 0.60 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL); reaction at 50 °C.

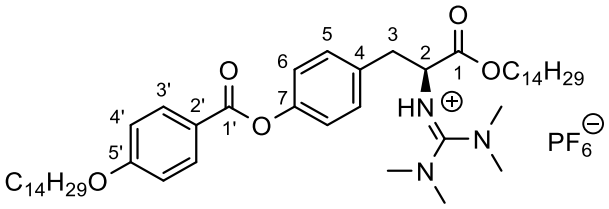


4-C$_{14}$TyrC$_{14}$I
$C_{49}H_{82}IN_3O_5$
(920.12)

Colourless solid (quant., 147 mg, 0.16 mmol, purity >99%); M.p. 114.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.88 (m, 6H, C*H*$_3$), 1.19–1.38 (m, 42H, C*H*$_2$), 1.46 (dt, *J* = 14.7 Hz, 7.3 Hz, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.63 (dt, *J* = 13.2 Hz, 6.9 Hz, 2H, COOCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.7 Hz, 6.9 Hz, 2H, OCH$_2$C*H*$_2$), 2.59–3.30 (m, 12H, N(*C*H$_3$)$_2$), 3.41 (dd, *J* = 14.4 Hz, 5.1 Hz, 1H, 3b-H), 3.81 (dd, *J* = 14.4 Hz, 8.7 Hz, 1H, 3a-H), 4.03 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.13 (t, *J* = 6.9 Hz, 2H, COOC*H*$_2$), 4.24 (dd, *J* = 8.7 Hz, 5.1 Hz, 1H, 2-H), 6.95 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.13 (d, *J* = 8.0 Hz, 2H, 6-H), 7.53 (d, *J* = 8.0 Hz, 2H, 5-H), 7.89 (s, 1H, NH), 8.09 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.0, 28.4, 29.10, 29.21, 29.36, 29.53, 29.56, 29.59, 29.62, 29.66, 29.70, 31.9 (*C*H$_2$), 36.4 (C-3), 40.0 (N(*C*H$_3$)$_2$), 60.1 (C-2), 66.7 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 114.3 (C-4'), 121.3 (C-2'), 122.2 (C-6), 130.8 (C-5), 132.2 (C-3'), 133.6 (C-4), 150.4 (C-7), 161.7 (N=C), 163.7 (C-5'), 165.0 (C-1'), 170.5 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3394 (w), 3213 (w), 2919 (vs), 2850 (s), 1727 (s), 1635 (s), 1605 (s), 1570 (m), 1511 (s), 1467 (m), 1419 (m), 1404 (m), 1374 (w), 1311 (w), 1255 (s), 1200 (s), 1166 (vs), 1117 (w), 1103 (w), 1074 (s), 1021 (m), 898 (w), 878 (w), 843 (m), 763 (m), 721 (w), 690 (w), 654 (w), 631 (w), 585 (w), 525 (w) cm^{-1}; MS (ESI): *m*/*z* = 126.91 [I]$^-$, 792.62 [M – I]$^+$; HRMS (ESI): *m*/*z* ($C_{49}H_{82}IN_3O_5$) calcd.: 792.6249 [M – I]$^+$, found: 792.6247, calcd.: 126.9050 [I]$^-$, found: 126.9069; CHN ($C_{49}H_{82}IN_3O_5 \cdot 0.5\ H_2O$) calcd.: C 63.34 H 9.00 N 4.52, found: C 63.10 H 8.97 N 4.45; $[\alpha]_D^{20}$: +76 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 43.8 °C [1.62 kJ · mol^{-1}] SmA_d 101.0 °C [1.60 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-tetradecyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium hexafluorophosphate [4-C$_{14}$TyrC$_{14}$PF$_6$]

According to GP9: Guanidinium chloride **4-C$_{14}$TyrC$_{14}$Cl** (141 mg, 0.17 mmol), potassium hexafluorophosphate (93.9 mg, 0.51 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL); reaction at 50 °C.

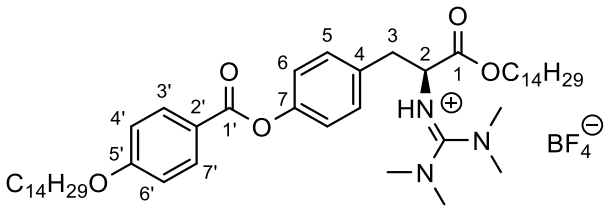


4-C$_{14}$TyrC$_{14}$PF$_6$
$C_{49}H_{82}F_6N_3O_5P$
(938.18)

Colourless solid (quant., 159 mg, 0.17 mmol, purity >99%); M.p. 63.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 6H, C*H*$_3$), 1.17–1.39 (m, 42H, C*H*$_2$), 1.47 (dt, *J* = 14.1 Hz, 7.6 Hz, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.64 (dt, *J* = 14.0 Hz, 7.0 Hz, 2H, COOCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.9 Hz, 6.6 Hz, 2H, OCH$_2$C*H*$_2$), 2.82 (br. s, 6H, N(C*H*$_3$)$_2$), 2.84 (br. s, 6H, N(C*H*$_3$)$_2$), 3.30 (d, *J* = 6.3 Hz, 2H, 3-H), 4.03 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 4.15 (t, *J* = 6.9 Hz, 2H, COOC*H*$_2$), 4.28 (t, *J* = 6.3 Hz, 1H, 2-H), 5.65 (br. s, 1H, NH), 6.96 (d, *J* = 8.4 Hz, 2H, 4'-H), 7.16 (d, *J* = 8.2 Hz, 2H, 6-H), 7.30 (d, *J* = 8.2 Hz, 2H, 5-H), 8.09 (d, *J* = 8.4 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 26.0, 28.4, 29.11, 29.22, 29.37, 29.44, 29.53, 29.57, 29.66, 29.71, 31.9 (*C*H$_2$), 37.1 (C-3), 39.8 (N(*C*H$_3$)$_2$), 58.6 (C-2), 66.9 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 114.4 (C-4'), 121.2 (C-2'), 122.6 (C-6), 130.4 (C-5), 132.3 (C-3'), 132.4 (C-4), 150.7 (C-7), 161.5 (N=C), 163.7 (C-5'), 165.0 (C-1), 170.4 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.4 (s, PF_6), –71.5 (s, PF_6) ppm; FT-IR: $\tilde{\nu}$ = 3381 (w), 2921 (m), 2852 (m), 1732 (m), 1628 (m), 1604 (m), 1569 (m), 1510 (m), 1466 (w), 1420 (w), 1406 (w), 1312 (w), 1252 (s), 1200 (s), 1163 (s), 1116 (w), 1068 (m), 1018 (w), 834 (vs), 763 (m), 738 (w), 721 (w), 692 (w), 650 (w), 631 (w), 556 (s) cm^{-1}; MS (ESI): *m*/*z* = 144.97 $[PF_6]^-$, 792.62 $[M - PF_6]^+$; HRMS (ESI): *m*/*z* ($C_{49}H_{82}F_6N_3O_5P$) calcd.: 792.6249 $[M - PF_6]^+$, found: 792.6246, calcd.: 144.9647 $[PF_6]^-$, found: 144.9642; CHN ($C_{49}H_{82}F_6N_3O_5P \cdot 0.4\ H_2O$) calcd.: C 62.25 H 8.83 N 4.44, found: C 62.27 H 8.74 N 4.25; $[\alpha]_D^{20}$: +55 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 29.9 °C [1.78 kJ · mol^{-1}] SmA_d 84.0 °C [1.57 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-tetradecyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium tetrafluoroborate [4-C$_{14}$TyrC$_{14}$BF$_4$]

According to GP9: Guanidinium chloride **4-C$_{14}$TyrC$_{14}$Cl** (133 mg, 0.16 mmol), sodium tetrafluoroborate (60.4 mg, 0.55 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL); reaction at 50 °C.

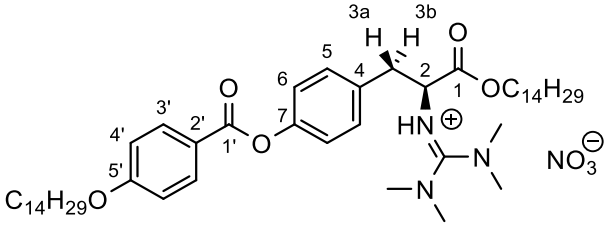


4-C$_{14}$TyrC$_{14}$BF$_4$
$C_{49}H_{82}BF_4N_3O_5$
(880.01)

Colourless solid (quant., 141 mg, 0.16 mmol, purity >99%); M.p. 72.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 6H, C*H*$_3$), 1.19–1.39 (m, 42H, C*H*$_2$), 1.47 (dt, *J* = 14.4 Hz, 7.8 Hz, 7.1 Hz, 2H, $OCH_2CH_2CH_2$), 1.63 (dt, *J* = 14.2 Hz, 7.1 Hz, 2H, $COOCH_2CH_2$), 1.81 (dt, *J* = 14.1 Hz, 6.7 Hz, 2H, OCH_2CH_2), 2.77 (br. s, 6H, $N(CH_3)_2$), 3.00 (br. s, 6H, $N(CH_3)_2$), 3.34 (d, *J* = 6.7 Hz, 2H, 3-H), 4.03 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.13 (t, *J* = 6.9 Hz, 2H, $COOCH_2$), 4.23 (t, *J* = 6.7 Hz, 1H, 2-H), 6.57 (br. s, 1H, NH), 6.95 (d, *J* = 8.7 Hz, 2H, 4'-H), 7.14 (d, *J* = 8.3 Hz, 2H, 6-H), 7.36 (d, *J* = 8.3 Hz, 2H, 5-H), 8.09 (d, *J* = 8.7 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.8, 26.0, 28.4, 29.10, 29.21, 29.30, 29.36, 29.53, 29.56, 29.60, 29.62, 29.66, 29.70, 31.9 (CH_2), 36.9 (C-3), 39.8 ($N(CH_3)_2$), 59.2 (C-2), 66.7 ($COOCH_2$), 68.4 (OCH_2), 114.3 (C-4'), 121.3 (C-2'), 122.4 (C-6), 130.5 (C-5), 132.2 (C-3'), 133.0 (C-4), 150.5 (C-7), 161.9 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.5 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –151.3 (d, *J* = 19.8 Hz, BF_4) ppm; FT-IR: $\tilde{\nu}$ = 3620 (w), 3344 (w), 2921 (vs), 2852 (s), 1732 (s), 1630 (s), 1605 (s), 1573 (s), 1510 (s), 1467 (m), 1420 (w), 1407 (m), 1312 (m), 1252 (vs), 1201 (vs), 1165 (vs), 1066 (vs), 899 (w), 845 (w), 763 (m), 733 (w), 691 (w), 651 (w), 631 (w), 586 (w), 521 (w)521 (w) cm^{-1}; MS (ESI): *m*/*z* = 87.00 $[BF_4]^-$, 792.62 $[M - BF_4]^+$; HRMS (ESI): *m*/*z* ($C_{49}H_{82}BF_4N_3O_5$) calcd.: 792.6249 $[M - BF_4]^+$, found: 792.6249; CHN ($C_{49}H_{82}BF_4N_3O_5$) calcd.: C 66.88 H 9.39 N 4.78, found: C 66.79 H 9.19 N 4.69; $[\alpha]_D^{20}$: +71 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 39.8 °C [5.86 kJ · mol^{-1}] SmA_d 97.3 °C [1.94 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((4-tetradecyloxybenzoyl)oxy)phenyl)-1-(tetradecyloxy)propan-2-aminium nitrate [4-C$_{14}$TyrC$_{14}$NO$_3$]

According to GP9: Guanidinium chloride **4-C$_{14}$TyrC$_{14}$Cl** (141 mg, 0.17 mmol), sodium nitrate (57.8 mg, 0.68 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL); reaction at 50 °C.



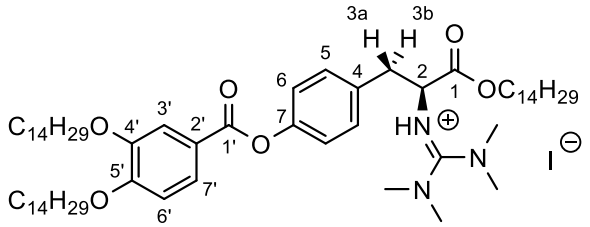
4-C$_{14}$TyrC$_{14}$NO$_3$
$C_{49}H_{82}N_4O_8$
(855.22)

Colourless solid (88%, 128 mg, 0.15 mmol, purity >95%); M.p. 68.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 6H, C*H*$_3$), 1.21–1.39 (m, 42H, C*H*$_2$), 1.44–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.62 (dt, *J* = 13.5 Hz, 6.6 Hz, 2H, $COOCH_2CH_2$), 1.82 (dt, *J* = 13.6 Hz, 6.7 Hz, 2H, OCH_2CH_2), 2.45–3.25 (m, 12H, $N(CH_3)_2$), 3.39 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H, 3b-H), 3.78–3.86 (m, 1H, 3a-H), 4.04 (t, *J* = 6.6 Hz, 2H, OCH_2), 07–4.14 (m, 3H, $COOCH_2$, 2-H),

6.96 (d, *J* = 8.9 Hz, 2H, 4'-H), 7.12 (d, *J* = 8.0 Hz, 2H, 6-H), 7.57 (d, *J* = 8.0 Hz, 2H, 5-H), 8.10 (d, *J* = 8.9 Hz, 2H, 3'-H), 10.12 (s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.85, 25.98, 28.4, 29.10, 29.21, 29.36, 29.53, 29.56, 29.61, 29.65, 29.67, 29.69, 31.9 (C-3), 39.6 (N(*C*H_3)$_2$), 60.7 (C-2), 66.5 (COO*C*H_2), 68.4 (O*C*H_2), 114.3 (C-4'), 121.5 (C-2'), 122.0 (C-6), 130.9 (C-5), 132.2 (C-3'), 134.6 (C-4), 150.2 (C-7), 162.3 (N=C), 163.6 (C-5'), 165.0 (C-1'), 170.7 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3220 (br, w), 2919 (vs), 2851 (vs), 1728 (vs), 1637 (s), 1607 (s), 1573 (s), 1511 (s), 1468 (m), 1418 (m), 1405 (m), 1374 (w), 1312 (m), 1256 (vs), 1202 (vs), 1168 (vs), 1102 (w), 1076 (s), 1020 (w)901 (w), 878 (w), 843 (m), 762 (m), 721 (m), 690 (m), 656 (w), 631 (w), 588 (w), 526 (w) cm^{-1}; MS (ESI): *m*/*z* = 61.99 $[NO_3]^-$, 792.62 $[M - NO_3]^+$; HRMS (ESI): *m*/*z* ($C_{49}H_{82}N_4O_8$) calcd.: 792.6249 $[M - NO_3]^+$, found: 792.6247, calcd.: 61.9884 $[NO_3]^-$, found: 61.9885; CHN ($C_{49}H_{82}N_4O_8$) calcd.: C 68.82 H 9.66 N 6.55, found: C 68.98 H 10.21 N 4.90; $[\alpha]_D^{20}$: +110 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 45.0 °C [8.25 kJ · mol^{-1}] SmA_d 99.7 °C [1.94 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium iodide [3,4-C_{14}TyrC_{14}I]

According to GP9: Guanidinium chloride **3,4-C_{14}TyrC_{14}Cl** (135 mg, 0.13 mmol), potassium iodide (89.6 mg, 0.54 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



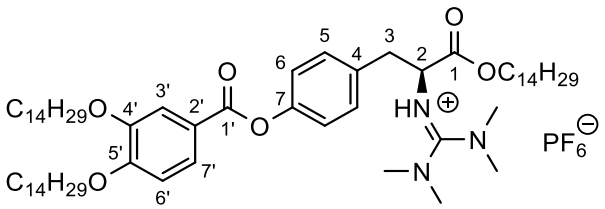
3,4-C_{14}TyrC_{14}I
$C_{63}H_{110}IN_3O_6$
(1132.49)

Colourless solid (77%, 113 mg, 0.10 mmol, purity >95%); M.p. 108.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.21–1.39 (m, 62, C*H*$_2$), 1.44–1.51 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.61–1.67 (m, 2H, COOCH$_2$C*H*$_2$), 1.80–1.88 (m, 4H, OCH$_2$C*H*$_2$), 2.58–3.35 (m, 12H, N(*C*H$_3$)$_2$), 3.42 (dd, *J* = 14.0 Hz, 5.1 Hz, 1H, 3b-H), 3.82 (dd, *J* = 14.0 Hz, 8.7 Hz, 1H, 3a-H), 4.06 (dt, *J* = 12.5 Hz, 6.6 Hz, 4H, OC*H*$_2$), 4.14 (t, *J* = 6.9 Hz, 2H, COOC*H*$_2$), 4.24 (dd, *J* = 8.7 Hz, 5.1 Hz, 1H, 2-H), 6.91 (d, *J* = 8.8 Hz, 1H, 6'-H), 7.13 (d, *J* = 8.0 Hz, 2H, 6-H), 7.54 (d, *J* = 8.0 Hz, 2H, 5-H), 7.61 (s, 1H, 3'-H), 7.77 (d, *J* = 8.8 Hz, 1H, 7'-H), 7.91 (s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 25.98, 26.03, 28.4, 29.06, 29.21, 29.38, 29.4, 29.5, 29.6, 29.65, 29.67, 29.72, 31.9 (*C*H$_2$), 36.4 (C-3), 40.0 (N(*C*H$_3$)$_2$), 60.1 (C-2), 66.8 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 112.0 (C-6'), 114.5 (C-'), 121.3 (C-2'), 122.3 (C-6), 124.4 (C-7'), 130.8 (C-5), 133.6 (C-4), 148.7 (C-4'), 150.5

(C-7), 153.9 (C-5'), 161.7 (N=C), 165.2 (C-1'), 170.5 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3440 (w), 3196 (w), 2955 (m), 2919 (vs), 2850 (s), 1730 (s), 1624 (m), 1598 (m), 1568 (m), 1511 (m), 1467 (m), 1429 (m), 1403 (m), 1345 (w), 1273 (s), 1197 (vs), 1168 (m), 1132 (m), 1068 (m), 1018 (w), 922 (w), 868 (w), 816 (w), 755 (w), 722 (w) cm^{-1}; MS (ESI): *m*/*z* = 126.91 $[I]^-$, 1004.84 $[M - I]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}IN_3O_6$) calcd.: 1004.8389 $[M - I]^+$, found: 1004.8388, calcd.: 126.9050 $[I]^-$, found: 126.9057; CHN ($C_{63}H_{110}IN_3O_6$) calcd.: C 66.82 H 9.79 N 3.71, found: C 67.20 H 9.87 N 3.59; $[\alpha]_D^{20}$: +76 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 51.5 °C [5.20 kJ · mol^{-1}] SmA_d 104.0 °C [1.19 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium hexafluorophosphate [3,4-C_{14}Tyr$C_{14}$$PF_6$]

According to GP9: Guanidinium chloride **3,4-C_{14}TyrC_{14}Cl** (135 mg, 0.13 mmol), potassium hexafluorophosphate (71.8 mg, 0.39 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



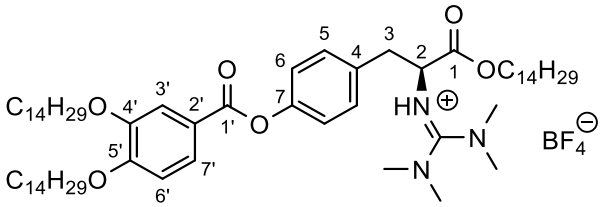
3,4-C_{14}Tyr$C_{14}$$PF_6$
$C_{63}H_{110}F_6N_3O_6P$
(1150.55)

Colourless solid (77%, 115 mg, 0.10 mmol, purity >99%); M.p. 79.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.41 (m, 62H, C*H*$_2$), 1.45–1.51 (m, 4H, $OCH_2CH_2CH_2$), 1.65 (dt, *J* = 13.5 Hz, 6.9 Hz, 2H, $COOCH_2CH_2$), 1.81–1.89 (m, 4H, OCH_2CH_2), 2.83 (br. s, 6H, $N(CH_3)_2$), 2.94 (br. s, 6H, $N(CH_3)_2$), 3.31 (d, *J* = 6.3 Hz, 2H, 3-H), 4.04–4.09 (m, 4H, OCH_2), 4.16 (t, *J* = 6.9 Hz, 2H, $COOCH_2$), 4.29 (t, *J* = 6.3 Hz, 1H, 2-H), 5.64 (s, 1H, NH), 6.92 (d, *J* = 8.4 Hz, 1H, 6'-H), 7.16 (d, *J* = 8.1 Hz, 2H, 6-H), 7.30 (d, *J* = 8.4 Hz, 2H, 5-H), 7.62 (s, 1H, 3'-H), 7.77 (d, *J* = 8.4 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.8, 25.99, 26.05, 28.4, 29.07, 29.16, 29.21, 29.37, 29.41, 29.45, 29.49, 29.53, 29.6, 29.66, 29.71, 31.9 (CH_2), 37.1 (C-3), 39.8 ($N(CH_3)_2$), 58.6 (C-2), 66.9 ($COOCH_2$), 69.1 (C-5'-OCH_2), 69.4 (C-4'-OCH_2), 112.0 (C-6'), 114.6 (C-3'), 121.3 (C-2'), 122.6 (C-6), 124.4 (C-7'), 130.4 (C-5), 132.3 (C-4), 148.7 (C-4'), 150.8 (C-7), 154.0 (C-5'), 161.6 (N=C), 165.1 (C-1'), 170.4 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.4 (s, PF_6), –71.5 (s, PF_6) ppm; FT-IR: $\tilde{\nu}$ = 3387 (w), 2919 (s), 2850 (s), 1731 (m), 1629 (m), 1598 (w), 1569 (m), 1511 (m), 1467 (m), 1429 (w), 1406 (w), 1346 (w), 1273 (s), 1198 (s), 1168 (m), 1133 (m), 1068 (w), 1018 (w), 839 (vs), 756 (w), 721 (w), 647 (w), 557 (m) cm^{-1}; MS (ESI): *m*/*z* = 144.97 $[PF_6]^-$, 1004.84 $[M - PF_6]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}F_6N_3O_6P$) calcd.: 1004.8389 $[M - PF_6]^+$, found: 1004.8388, calcd.: 144.9647 $[PF_6]^-$, found: 144.9653; CHN

($C_{63}H_{110}F_6N_3O_6P$) calcd.: C 65.77 H 9.64 N 3.65, found: C 65.78 H 9.65 N 3.61; $[\alpha]_D^{20}$: +53 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G 28.7 °C [10.9 kJ · mol^{-1}] SmA_d 94.6 °C [1.02 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium tetrafluoroborate [3,4-C_{14}Tyr$C_{14}$$BF_4$]

According to GP9: Guanidinium chloride **3,4-C_{14}TyrC_{14}Cl** (146 mg, 0.14 mmol), sodium tetrafluoroborate (60.4 mg, 0.55 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

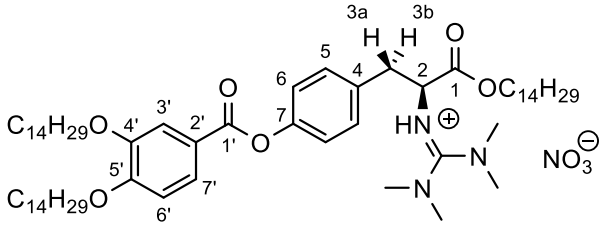


3,4-C_{14}Tyr$C_{14}$$BF_4$
$C_{63}H_{110}BF_4N_3O_6$
(1092.39)

Colourless solid (quant., 175 mg, 0.16 mmol, purity >99%); M.p. 89.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 9H, C*H*$_3$), 1.21–1.40 (m, 62H, C*H*$_2$), 1.45–1.51 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.64 (dt, J = 13.9 Hz, 7.1 Hz, 2H, COOCH$_2$C*H*$_2$), 1.81–1.89 (m, 4H, OCH$_2$C*H*$_2$), 2.77 (br. s, 6H, N(C*H*$_3$)$_2$), 3.00 (br. s, 6H, N(C*H*$_3$)$_2$), 3.35 (d, J = 6.5 Hz, 2H, 3-H), 4.04–○4.09 (m, 4H, OC*H*$_2$), 4.15 (t, J = 6.9 Hz, 2H, COOC*H*$_2$), 4.23 (t, J = 6.6 Hz, 1H, 2-H), 6.55 (br. s, 1H, NH), 6.92 (d, J = 8.2 Hz, 1H, 6'-H), 7.15 (d, J = 8.2 Hz, 2H, 6-H), 7.36 (d, J = 8.4 Hz, 2H, 5-H), 7.62 (d, J = 2.3 Hz, 1H, 3'-H), 7.77 (d, J = 8.4 Hz, 2.3 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.82, 25.99, 26.04, 28.4, 29.06, 29.21, 29.37, 29.40, 29.44, 29.53, 29.63, 29.65, 29.68, 29.72, 31.9 (*C*H$_2$), 36.9 (C-3), 39.8 (N(*C*H$_3$)$_2$), 59.2 (C-2), 66.7 (OO*C*H$_2$), 69.1 (O*C*H$_2$), 69.4 (O*C*H$_2$), 111.9 (C-6'), 114.6 (C-3'), 121.3 (C-2'), 122.4 (C-6), 124.4 (C-7'), 130.5 (C-5), 133.0 (C-4), 148.7 (C-4'), 150.6 (C-7), 153.9 (C-5'), 161.9 (N=C), 165.1 (C-1'), 170.5 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –151.4 (d, J = 20.1 Hz, BF_4) ppm; FT-IR: ṽ = 3344 (w), 2955 (m), 2918 (vs), 2850 (vs), 1730 (s), 1628 (s), 1598 (m), 1571 (m), 1512 (s), 1467 (s), 1429 (m), 1406 (m), 1346 (w), 1273 (vs), 1197 (vs), 1168 (s), 1132 (m), 1068 (vs), 907 (w), 869 (w), 819 (w), 756 (m), 723 (m), 647 (w), 585 (w), 520 (w) cm^{-1}; MS (ESI): m/z = 87.00 $[BF_4]^-$, 1004.84 $[M - BF_4]^+$; HRMS (ESI): m/z ($C_{63}H_{110}BF_4N_3O_6$) calcd.: 1004.8389 $[M - BF_4]^+$, found: 1004.8393; CHN ($C_{63}H_{110}BF_4N_3O_6$) calcd.: C 69.27 H 10.15 N 3.85, found: C 69.08 H 10.07 N 3.77; $[\alpha]_D^{20}$: +64 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 30.5 °C [15.4 kJ · mol^{-1}] SmA_d 96.6 °C [0.95 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium nitrate [3,4-C_{14}Tyr$C_{14}NO_3$]

According to GP9: Guanidinium chloride **3,4-C_{14}TyrC_{14}Cl** (135 mg, 0.13 mmol), sodium nitrate (33.1 mg, 0.39 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

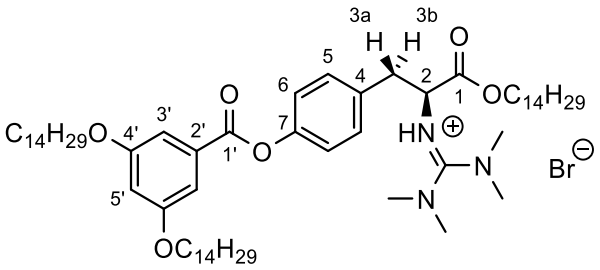


3,4-C_{14}Tyr$C_{14}NO_3$
$C_{63}H_{110}N_4O_9$
(1067.59)

Colourless solid (85%, 117 mg, 0.11 mmol, purity >95%); M.p. 83 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.11–1.38 (m, 62H, C*H*$_2$), 1.44–1.50 (m, 4H, C*H*$_2$), 1.61 (dt, *J* = 13.9 Hz, 6.8 Hz, 2H, C*H*$_2$), 1.80–1.88 (m, 4H, C*H*$_2$), 2.43–3.27 (m, 12H, N(*C*H$_3$)$_2$), 3.38 (dd, *J* = 14.1 Hz, 4.7 Hz, 1H, 3b-H), 3.74–3.81 (m, 1H, 3a-H), 4.03–4.12 (m, 7H, 2-H, COOC*H*$_2$, OC*H*$_2$), 6.91 (d, *J* = 8.4 Hz, 1H, 6'-H), 7.10 (d, *J* = 8.2 Hz, 2H, 6-H), 7.55 (d, *J* = 8.2 Hz, 2H, 5-H), 7.62 (s, 1H, 3'-H), 7.77 (d, *J* = 8.4 Hz, 1H, 7'-H), 10.04 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 25.98, 26.03, 28.4, 29.06, 29.21, 29.37, 29.40, 29.43, 29.5, 29.6, 29.66, 29.67, 29.71, 31.9 (*C*H$_2$), 39.1, 39.6 (N(*C*H$_3$)$_2$), 40.9 (C-2), 60.7 (C-13), 66.5 (COO*C*H$_2$), 69.1 (C-5'-O*C*H$_2$), 69.4 (C-4'-O*C*H$_2$), 112.0 (C-6'), 114.6 (C-3'), 121.5 (C-2'), 122.0 (C-6), 124.3 (C-7'), 130.9 (C-5), 134.6 (C-4) 148.7 (C-4'), 150.2 (C-7), 153.9 (C-5'), 162.3 (N=C), 165.2 (C-1') ppm (two signals (C-1 and C-3) in the ^{13}C NMR spectrum could not be observed, this is probably because of insufficient intensity of the signals); FT-IR: $\tilde{\nu}$ = 3407 (w), 2920 (vs), 2851 (s), 1730 (s), 1625 (m), 1598 (m), 1572 (m), 1510 (s), 1466 (m), 1428 (m), 1404 (m), 1343 (m), 1269 (vs), 1194 (vs), 1167 (s), 1132 (m), 1069 (m), 1019 (m), 926 (m), 907 (m), 870 (w), 814 (w), 756 (m), 728 (s), 644 (w), 584 (w), 539 (w) cm^{-1}; MS (ESI): *m*/*z* = 61.99 $[NO_3]^-$, 1004.84 $[M - NO_3]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}N_4O_9$) calcd.: 1004.8389 $[M - NO_3]^+$, found: 1004.8381 calcd.: 61.9884 $[NO_3]^-$, found: 61.9882; CHN ($C_{63}H_{110}N_4O_9$) calcd.: C 70.88 H 10.39 N 5.25, found: C 71.00 H 10.70 N 4.03; $[\alpha]_D^{20}$: +78 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 11.0 °C [0.17 kJ · mol^{-1}] Cr_2 31.6 °C [20.2 kJ · mol^{-1}] SmA_d 88.4 °C [0.85 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium bromide [3,5-C_{14}TyrC_{14}Br]

According to GP9: Guanidinium chloride **3,5-C_{14}TyrC_{14}Cl** (135 mg, 0.13 mmol), potassium bromide (70.2 mg, 0.59 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

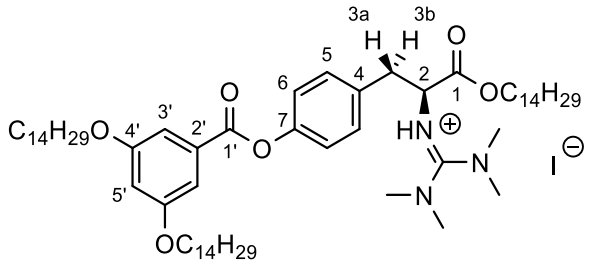


3,5-C_{14}TyrC$_{14}$Br
$C_{63}H_{110}BrN_3O_6$
(1085.49)

Colourless glass (92%, 130 mg, 0.12 mmol, purity >95%); M.p. 50.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.7 Hz, 9H, C*H*$_3$), 1.19–1.37 (m, 62H, C*H*$_2$), 1.44 (dt, *J* = 14.4 Hz, 7.3 Hz, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.60 (dt, *J* = 13.7 Hz, 6.8 Hz, 6.3 Hz, 2H, COOCH$_2$C*H*$_2$), 1.77 (dt, *J* = 13.7 Hz, 6.9 Hz, 4H, OCH$_2$C*H*$_2$), 2.42–3.27 (m, 12H, N(*C*H$_3$)$_2$), 3.38 (dd, *J* = 14.0 Hz, 4.9 Hz, 1H, 3b-H), 3.81–3.86 (m, 1H, 3a-H), 3.98 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.05–4.13 (m, 3H, 2-H, COOC*H*$_2$), 6.68–6.69 (m, 1H, 5'-H), 7.10 (d, *J* = 8.0 Hz, 2H, 6-H), 7.26 (s, 2H, 3'-H), 7.58 (d, *J* = 8.0 Hz, 2H, 5-H), 10.06 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.86, 26.02, 28.4, 29.19, 29.22, 29.36, 29.39, 29.5, 29.58, 29.61, 29.67, 29.69, 31.9 (*C*H$_2$), 36.1 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.7 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.2 (C-3'), 121.9 (C-6), 131.0 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.1 (C-7), 160.3 (C-4'), 162.2 (N=C), 165.2 (C-1'), 170.1 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3383 (br, w), 2920 (vs), 2851 (s), 1736 (s), 1626 (s), 1594 (s), 1572 (m), 1508 (m), 1464 (m), 1446 (m), 1405 (m), 1350 (m), 1324 (m), 1298 (m), 1214 (s), 1196 (vs), 1165 (vs), 1100 (w), 1055 (m), 1020 (m), 932 (w), 899 (w), 859 (w), 844 (w), 757 (m), 720 (m), 675 (w), 585 (w), 538 (w) cm^{-1}; MS (ESI): *m*/*z* = 78.92 [Br]$^-$, 1004.84 [M – Br]$^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}BrN_3O_6$) calcd.: 1004.8389 [M – Br]$^+$, found: 1004.8386, calcd.: 78.9189 [Br]$^-$, found: 78.9185; CHN ($C_{63}H_{110}BrN_3O_6$) calcd.: C 69.71 H 10.21 N 3.87, found: C 70.62 H 10.78 N 3.82; $[\alpha]_D^{20}$: +83 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr –8.98 °C [22.5 kJ · mol^{-1}] I (1st cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium iodide [3,5-C_{14}TyrC$_{14}$I]

According to GP9: Guanidinium chloride **3,5-C_{14}TyrC$_{14}$Cl** (146 mg, 0.14 mmol), potassium iodide (71.4 mg, 0.43 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

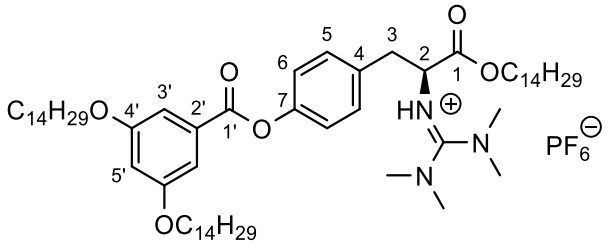


3,5-C_{14}TyrC$_{14}$I
$C_{63}H_{110}IN_3O_6$
(1132.49)

Colourless glass (86%, 136 mg, 0.12 mmol, purity >99%); M.p. 40.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.21–1.37 (m, 62H, C*H*$_2$), 1.45 (dt, *J* = 14.3 Hz, 7.2 Hz, 4H, $OCH_2CH_2CH_2$), 1.63 (dt, *J* = 14.2 Hz, 7.0 Hz, 2H, $COOCH_2CH_2$), 1.78 (dt, *J* = 13.9 Hz, 6.7 Hz, 4H, OCH_2CH_2), 2.56–3.34 (m, 12H, N(*C*H$_3$)$_2$), 3.42 (dd, *J* = 14.2 Hz, 5.1 Hz, 1H, 3b-H), 3.81 (dd, *J* = 14.2 Hz, 8.6 Hz, 1H, 3a-H), 3.98 (t, *J* = 6.6 Hz, 4H, OCH_2), 4.13 (t, *J* = 6.9 Hz, 2H, $COOCH_2$), 4.25 (dd, *J* = 8.6 Hz, 5.1 Hz, 1H, 2-H), 6.69 (t, *J* = 2.3 Hz, 1H, 5'-H), 7.13 (d, *J* = 8.3 Hz, 2H, 6-H), 7.27 (d, *J* = 2.3 Hz, 2H, 3'-H), 7.55 (d, *J* = 8.3 Hz, 2H, 5-H), 7.90 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.03, 28.4, 29.20, 29.36, 29.39, 29.53, 29.58, 29.61, 29.66, 29.69, 32.0 (*C*H$_2$), 36.5 (C-3), 40.0 (N(*C*H$_3$)$_2$), 60.0 (C-2), 66.7 ($COOCH_2$), 68.4 (OCH_2), 107.2 (C-5'), 108.2 (C-3'), 122.1 (C-6), 130.9 (C-5), 131.0 (C-2'), 133.8 (C-4), 150.3 (C-7), 160.3 (C-4'), 161.7 (N=C), 165.2 (C-1'), 170.5 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3438 (w), 3200 (w), 2920 (vs), 2851 (s), 1735 (s), 1624 (s), 1608 (s), 1594 (s), 1568 (m), 1508 (w), 1446 (m), 1403 (m), 1349 (m), 1324 (m), 1299 (m), 1213 (s), 1196 (vs), 1165 (vs), 1100 (w), 1055 (m), 933 (w), 898 (w), 860 (w), 757 (m), 721 (w), 675 (w), 536 (w) cm^{-1}; MS (ESI): *m*/*z* = 126.91 [I]$^-$, 1004.84 [M – I]$^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}IN_3O_6$) calcd.: 1004.8389 [M – I]$^+$, found: 1004.8379; CHN ($C_{63}H_{110}IN_3O_6 \cdot 0.5\ H_2O$) calcd.: C 66.29 H 9.80 N 3.68, found: C 66.31 H 9.85 N 3.64; $[\alpha]_D^{20}$: +50 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G –21.6 °C [5.32 kJ · mol^{-1}] I (1st cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium hexafluorophosphate [3,5-C_{14}Tyr$C_{14}$$PF_6$]

According to GP9: Guanidinium chloride **3,5-C_{14}TyrC_{14}Cl** (135 mg, 0.13 mmol), potassium hexafluorophosphate (79.1 mg, 0.43 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



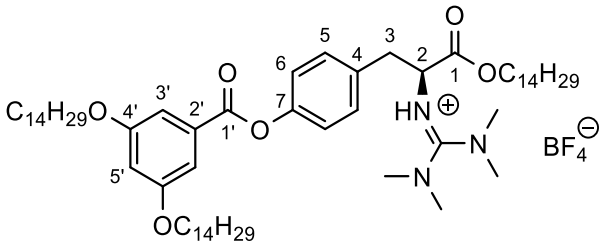
3,5-C_{14}Tyr$C_{14}$$PF_6$
$C_{63}H_{110}F_6N_3O_6P$
(1150.55)

Colourless glass (92%, 138 mg, 0.12 mmol, purity >95%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 9H, C*H*$_3$), 1.12–1.38 (m, 62H, C*H*$_2$), 1.45 (dt, *J* = 14.2 Hz, 7.4 Hz, 4H, $OCH_2CH_2CH_2$), 1.65 (dt, *J* = 14.2 Hz, 6.9 Hz, 2H, $COOCH_2CH_2$), 1.78 (dt, *J* = 13.9 Hz, 6.6 Hz, 4H, OCH_2CH_2), 2.83 (br. s, 6H, N(C*H*$_3$)$_2$), 2.95 (br. s, 6H, N(C*H*$_3$)$_2$),3.31 (d, *J* = 6.2 Hz, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.16 (t, *J* = 6.8 Hz, 2H, $COOCH_2$), 4.29 (t, *J* = 6.2 Hz, 1H, 2-H), 5.68 (br. s, 1H, NH), 6.70 (t, *J* = 2.4 Hz, 1H, 5'-H),

7.16 (d, *J* = 8.2 Hz, 2H, 6-H), 7.27 (d, *J* = 2.4 Hz, 2H, 3'-H), 7.31 (d, *J* = 8.2 Hz, 2H, 5-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.82, 26.04, 28.4, 29.20, 29.37, 29.40, 29.53, 29.59, 29.62, 29.66, 29.70, 31.9 (*C*H$_2$), 37.1 (C-3), 39.8 (N(*C*H$_3$)$_2$), 58.6 (C-2), 66.9 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.2 (C-5'), 108.2 (C-3'), 122.5 (C-6), 130.5 (C-5), 130.9 (C-2'), 132.6 (C-4), 150.6 (C-7), 160.4 (C-4'), 161.6 (N=C), 165.1 (C-1'), 170.4 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.4 (s, PF_6), –71.5 (s, PF_6) ppm; FT-IR: $\tilde{\nu}$ = 3381 (w), 2921 (s), 2852 (m), 1736 (m), 1628 (m), 1593 (m), 1569 (m), 1508 (w), 1446 (m), 1406 (w), 1350 (w), 1325 (w), 1299 (m), 1197 (s), 1166 (s), 1056 (w), 933 (w), 835 (vs), 757 (w), 739 (w), 721 (w), 675 (w), 557 (s) cm^{-1}; MS (ESI): *m*/*z* = 144.97 $[PF_6]^-$, 1004.84 $[M - PF_6]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}F_6N_3O_6P$) calcd.: 1004.8389 $[M - PF_6]^+$, found: 1004.8390, calcd.: 144.9647 $[PF_6]^-$, found: 144.9651; CHN ($C_{63}H_{110}F_6N_3O_6P$) calcd.: C 65.77 H 9.64 N 3.65, found: C 63.36 H 9.63 N 3.66; $[\alpha]_D^{20}$: +50 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G –12.4 °C [6.90 kJ · mol^{-1}] I (1st cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium tetrafluoroborate [3,5-C$_{14}$TyrC$_{14}$BF$_4$]

According to GP9: Guanidinium chloride **3,5-C$_{14}$TyrC$_{14}$Cl** (146 mg, 0.14 mmol), sodium tetrafluoroborate (60.4 mg, 0.55 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



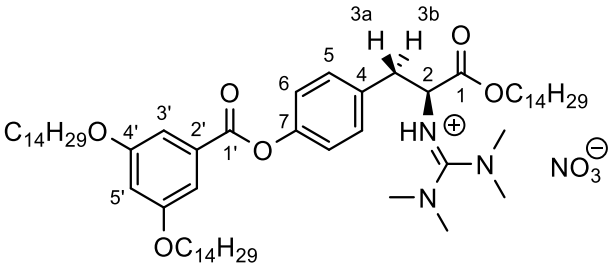
3,5-C$_{14}$TyrC$_{14}$BF$_4$
$C_{63}H_{110}BF_4N_3O_6$
(1092.39)

Colourless glass (93%, 142 mg, 0.13 mmol, purity >99%); M.p. 25.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 9H, C*H*$_3$), 1.18–1.38 (m, 62H, C*H*$_2$), 1.45 (dt, *J* = 14.3 Hz, 7.4 Hz, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.64 (dt, *J* = 14.0 Hz, 7.1 Hz, 2H, COOCH$_2$C*H*$_2$), 1.78 (dt, *J* = 13.9 Hz, 6.9 Hz, 4H, OCH$_2$C*H*$_2$), 2.77 (br. s, 6H, N(C*H*$_3$)$_2$), 3.00 (br. s, 6H, N(C*H*$_3$)$_2$), 3.35 (d, *J* = 6.7 Hz, 2H, 3-H), 3.99 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.14 (t, *J* = 6.9 Hz, 2H, COOC*H*$_2$), 4.23 (t, *J* = 6.6 Hz, 1H, 2-H), 6.54 (br. s, 1H, NH), 6.70 (t, *J* = 2.6 Hz, 1H, 5'-H), 7.15 (d, *J* = 8.2 Hz, 2H, 6-H), 7.26–7.27 (m, 2H, 3'-H), 7.37 (d, *J* = 8.2 Hz, 2H, 5-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.82, 26.03, 28.4, 29.20, 29.36, 29.39, 29.53, 29.59, 29.61, 29.66, 29.70, 31.9 (*C*H$_2$), 36.9 (C-3), 39.8 (N(*C*H$_3$)$_2$), 59.2 (C-2), 66.7 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.2 (C-5'), 108.2 (C-3'), 122.3 (C-6), 130.6 (C-5), 131.0 (C-2'), 133.2 (C-4), 150.4 (C-7), 160.4 (C-4'), 161.9 (N=C), 165.1 (C-1'), 170.5 (C-1) ppm; ^{19}F NMR

(376 MHz, $CDCl_3$): δ = –151.5 (d, *J* = 19.7 Hz, BF_4) ppm; FT-IR: ṽ = 3614 (w), 3343 (w), 2921 (vs), 2852 (s), 1737 (s), 1629 (s), 1594 (m), 1571 (m), 1508 (w), 1446 (m), 1447 (m), 1406 (w), 1350 (m), 1325 (m), 1299 (m), 1214 (s), 1198 (s), 1167 (vs), 1056 (vs), 898 (w), 860 (w), 758 (w), 721 (w), 676 (w), 520 (w), 441 (w) cm^{-1}; MS (ESI): *m*/*z* = 87.00 $[BF_4]^-$, 1004.84 $[M – BF_4]^+$; HRMS (ESI): *m*/*z* ($C_{63}H_{110}BF_4N_3O_6$) calcd.: 1004.8389 $[M – BF_4]^+$, found: 1004.8382, calcd.: 87.0035 $[BF_4]^-$, found: 87.0032; CHN ($C_{63}H_{110}BF_4N_3O_6$) calcd.: C 69.27 H 10.15 N 3.85, found: C 69.14 H 9.96 N 3.79; $[\alpha]_D^{20}$: +55 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 –52.3 °C [0.06 kJ · mol^{-1}] Cr_2 –11.5 °C [11.7 kJ · mol^{-1}] I (1st cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,5-bis(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium nitrate [3,5-C_{14}Tyr$C_{14}NO_3$]

According to GP9: Guanidinium chloride **3,5-C_{14}TyrC_{14}Cl** (146 mg, 0.14 mmol), sodium nitrate (35.7 mg, 0.42 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



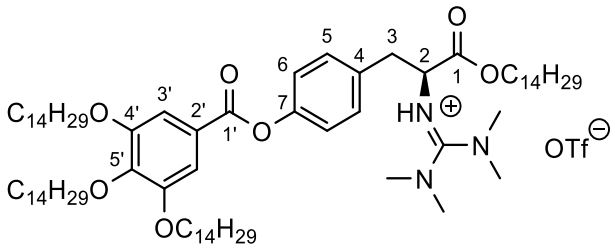
3,5-C_{14}Tyr$C_{14}NO_3$
$C_{63}H_{110}N_4O_9$
(1067.59)

Colourless glass (quant., 149 mg, 0.14 mmol, purity >95%); M.p. 40.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 9H, C*H*$_2$), 1.12–1.37 (m, 62H, C*H*$_2$), 1.44 (dt, *J* = 14.5 Hz, 7.4 Hz, 4H, C*H*$_2$), 1.61 (dt, *J* = 14.1 Hz, 6.8 Hz, 2H, C*H*$_2$), 1.78 (dt, *J* = 14.1 Hz, 6.8 Hz, 4H, C*H*$_2$), 2.40–3.25 (m, 12H, N(*C*H$_3$)$_2$), 3.39 (dd, *J* = 13.9 Hz, 4.8 Hz, 1H, 3b-H), 3.77–3.83 (m, 1H, 3a-H), 3.98 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 4.06–4.13 (m, 3H, 2-H, COOC*H*$_2$), 6.69 (t, *J* = 2.4 Hz, 1H, 5'-H), 7.11 (d, *J* = 8.1 Hz, 2H, 6-H), 7.26–7.27 (m, 2H, 3'-H), 7.56 (d, *J* = 8.1 Hz, 2H, 5-H), 10.04 (br. s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.03, 28.4, 29.19, 29.21, 29.36, 29.39, 29.52, 29.58, 29.60, 29.66, 29.69, 31.9 (*C*H$_2$), 36.10 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.6 (C-2), 66.5 (COO*C*H$_2$), 68.4 (O*C*H$_2$), 107.1 (C-5'), 108.1 (C-3'), 121.9 (C-6), 130.9 (C-5), 131.1 (C-2'), 134.8 (C-4), 150.1 (C-7), 160.3 (C-4'), 162.3 (N=C), 165.2 (C-1'), 170.8 (C-1) ppm; FT-IR: ṽ = 3400 (br, w), 2920 (vs), 2851 (vs), 1736 (s), 1626 (s), 1594 (s), 1572 (m), 1508 (m), 1464 (m), 1446 (s), 1405 (m), 1349 (m), 1324 (m), 1298 (s), 1214 (vs), 1197 (vs), 1166 (vs), 1100 (w), 1055 (m), 933 (w), 900 (w), 859 (w), 757 (m), 721 (w), 675 (w), 536 (w) cm^{-1}; MS (ESI): *m*/*z* = 61.99 $[NO_3]^-$, 1004.84 $[M – NO_3]^+$;

HRMS (ESI): *m*/*z* ($C_{63}H_{110}N_4O_9$) calcd.: 1004.8389 $[M - NO_3]^+$, found: 1004.8381; CHN ($C_{63}H_{110}N_4O_9$) calcd.: C 70.88 H 10.39 N 5.25, found: C 70.75 H 10.67 N 3.85; $[\alpha]_D^{20}$: +73 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: G_1 –43.5 °C [0.34 kJ · mol^{-1}] G_2 –1.40 °C [11.7 kJ · mol^{-1}] G_3 33.1 °C [5.94 kJ · mol^{-1}] I (1st cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium triflate [3,4,5-C_{14}TyrC_{14}OTf]

According to GP9: Guanidinium chloride **3,4,5-C_{14}TyrC_{14}Cl** (160 mg, 0.13 mmol), sodium trifluoromethanesulfonate (60.0 mg, 0.35 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



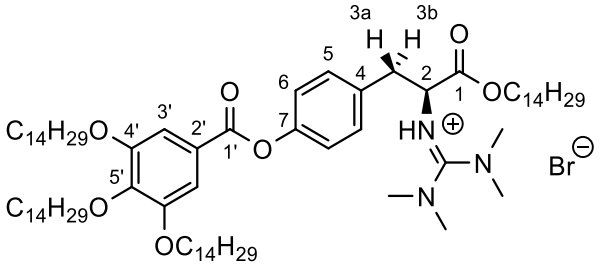
3,4,5-C_{14}TyrC_{14}OTf
$C_{78}H_{138}F_3N_3O_{10}S$
(1367.03)

Colourless solid (98%, 171 mg, 0.13 mmol, purity >99%); M.p. 38 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.21–1.37 (m, 82H, C*H*$_2$), 1.46–1.51 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.63–1.66 (m, 2H, COOCH$_2$C*H*$_2$), 1.76 (dt, *J* = 13.8 Hz, 6.7 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.82 (dt, *J* = 14.2 Hz, 6.6 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.62–3.19 (m, 12H, N(C*H*$_3$)$_2$), 3.35–3.41 (m, 2H, 3-H), 4.02–4.06 (m, 6H, OC*H*$_2$), 4.15 (t, *J* = 6.9 Hz, 2H, COOC*H*$_2$), 4.18–4.21 (m, 1H, 2-H), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.37 (s, 2H, 3'-H), 7.39 (d, *J* = 8.5 Hz, 2H, 5-H), 7.43 (d, *J* = 7.2 Hz, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.82, 26.08, 26.12, 28.4, 29.20, 29.33, 29.37, 29.39, 29.40, 29.43, 29.52, 29.60, 29.66, 29.68, 29.71, 29.72, 29.77, 30.4, 31.9 (*C*H$_2$), 36.7 (C-3), 39.8 (N(*C*H$_3$)$_2$), 59.5 (C-2), 66.7 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.3 (C-6), 123.7 (C-2'), 130.6 (C-5), 133.4 (C-4), 143.1 (C-5'), 150.5 (C-7), 153.0 (C-4'), 162.0 (N=C), 165.1 (C-1'), 170.4 (C-1) ppm (the ^{13}C NMR signal for the triflate anion could not be observed, but some satellite signals around 120.6 ppm indicated its presence. The anion could be detected by mass spectrometry and was confirmed by elemental analysis); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –78.3 (s, CF_3SO_3) ppm; FT-IR: $\tilde{\nu}$ = 3270 (w), 2921 (vs), 2852 (s), 1734 (m), 1627 (m), 1582 (m), 1509 (m), 1466 (m), 1430 (m), 1406 (m), 1379 (w), 1335 (s), 1278 (s), 1249 (vs), 1224 (s), 1190 (vs), 1166 (vs), 1116 (s), 1067 (w), 1031 (vs), 902 (w), 862 (w), 755 (m), 721 (w), 638 (s), 573 (w), 517 (w) cm^{-1}; MS (ESI): *m*/*z* = 148.95 $[CF_3SO_3]^-$, 1217.05 $[M - CF_3SO_3]^+$; HRMS (ESI): *m*/*z* ($C_{78}H_{138}F_3N_3O_{10}S$) calcd.: 1217.0529 $[M - CF_3SO_3]^+$, found: 1217.0521, calcd.: 148.9526 $[CF_3SO_3]^-$, found: 148.9522; CHN ($C_{78}H_{138}F_3N_3O_{10}S$) calcd.: C 68.53 H 10.18

N 3.11 S 2.35, found: C 68.65 H 10.30 N 3.11 S 2.12; $[\alpha]_D^{20}$: +58 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 –4.54 °C [0.68 kJ · mol^{-1}] Cr_2 23.1 °C [45.8 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium bromide [3,4,5-C$_{14}$TyrC$_{14}$Br]

According to GP9: Guanidinium chloride **3,4,5-C$_{14}$TyrC$_{14}$Cl** (140 mg, 0.11 mmol), potassium bromide (51.0 mg, 0.43 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).

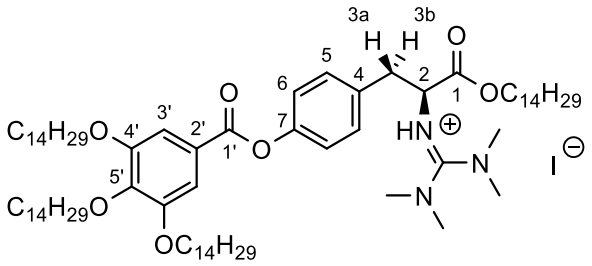


3,4,5-C$_{14}$TyrC$_{14}$Br
$C_{77}H_{138}BrN_3O_7$
(1297.87)

Colourless wax (88%, 128 mg, 0.10 mmol, purity >95%); M.p. 82.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.8 Hz, 12H, CH_3), 1.20–1.37 (m, 82H, CH_2), 1.43–1.50 (m, 6H, $OCH_2CH_2CH_2$), 1.58–1.64 (m, 2H, $COOCH_2CH_2$), 1.71–1.85 (m, 6H, OCH_2CH_2), 2.36–3.29 (m, 12H, $N(CH_3)_2$), 3.39 (dd, J = 14.0 Hz, 4.7 Hz, 1H, 3b-H), 3.86 (dd, J = 14.0 Hz, 9.4 Hz, 1H, 3a-H), 4.00–4.05 (m, 6H, OCH_2), 4.07–4.11 (m, 3H, $COOCH_2$, 2-H), 7.09 (d, J = 8.3 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.60 (d, J = 8.3 Hz, 2H, 5-H), 10.13 (d, J = 7.1 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.85, 26.07, 26.11, 28.4, 29.21, 29.32, 29.37, 29.38, 29.40, 29.42, 29.53, 29.59, 29.60, 29.65, 29.68, 29.70, 29.72, 29.76, 29.77, 30.4, 31.9 (CH_2), 35.9 (C-3), 39.6 ($N(CH_3)_2$), 60.6 (C-2), 66.5 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.5 (C-3'), 121.9 (C-6), 123.8 (C-2'), 131.0 (C-5), 134.7 (C-4), 143.0 (C-5'), 150.1 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.1 (C-1'), 170.8 (C-1) ppm; FT-IR: ṽ = 3388 (w), 2921 (vs), 2852 (vs), 1733 (m), 1627 (m), 1583 (m), 1508 (w), 1467 (m), 1430 (m), 1405 (w), 1336 (s), 1193 (vs), 1117 (m), 1020 (w), 900 (w), 862 (w), 755 (w), 721 (w), 584 (w) cm^{-1}; MS (ESI): m/z = 1217.05 [M – Br]$^+$; HRMS (ESI): m/z ($C_{77}H_{138}BrN_3O_7$) calcd.: 1217.0529 [M – I]$^+$, found: 1217.0523; CHN ($C_{77}H_{138}BrN_3O_7$) calcd.: C 71.26 H 10.72 N 3.24, found: C 72.31 H 11.18 N 3.25; $[\alpha]_D^{20}$: +83 (c = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 16.2 °C [39.6 kJ · mol^{-1}] Col_h 104.8 °C [1.09 kJ · mol^{-1}] I (1st cool, decomposition).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium iodide [3,4,5-C$_{14}$TyrC$_{14}$I]

According to GP9: Guanidinium chloride **3,4,5-C$_{14}$TyrC$_{14}$Cl** (141 mg, 0.11 mmol), potassium iodide (80.0 mg, 0.48 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



3,4,5-C_{14}TyrC$_{14}$I

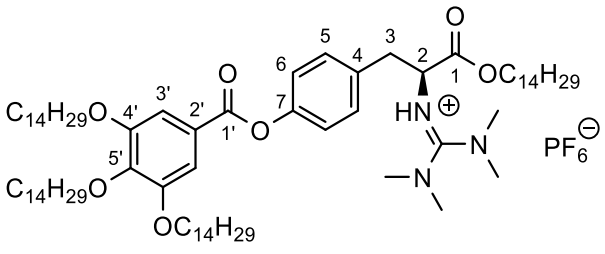
$C_{77}H_{138}IN_3O_7$

(1344.87)

Light-yellow wax (91%, 138 mg, 0.10 mmol, purity >99%); M.p. 37 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 12H, C*H*$_3$), 1.18–1.39 (m, 82H, C*H*$_2$), 1.43–1.52 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.66 (m, 2H, COOCH$_2$C*H*$_2$), 1.75 (dt, *J* = 13.8 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.82 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.56–3.39 (m, 12H, N(C*H*$_3$)$_2$), 3.43 (dd, *J* = 14.2 Hz, 5.0 Hz, 1H, 3b-H), 3.82 (dd, *J* = 14.2 Hz, 8.6 Hz, 1H, 3a-H), 4.00–4.06 (m, 6H, OC*H*$_2$), 4.14 (t, *J* = 6.9 Hz, 2H, COOC*H*$_2$), 4.18–4.27 (m, 1H, 2-H), 7.12 (d, *J* = 8.5 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.53–7.57 (m, 2H, 5-H), 7.94 (d, *J* = 7.5 Hz, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.07, 26.11, 28.4, 29.21, 29.32, 29.38, 29.40, 29.42, 29.53, 29.59, 29.61, 29.65, 29.68, 29.70, 29.72, 29.76, 30.4, 31.9 (*C*H$_2$), 36.4 (C-3), 40.0 (N(*C*H$_3$)$_2$), 60.1 (C-2), 66.8 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.2 (C-6), 123.7 (C-2'), 130.9 (C-5), 133.7 (C-4), 143.1 (C-5'), 150.4 (C-7), 153.0 (C-4'), 161.7 (N=C), 165.1 (C-1'), 170.5 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1733 (m), 1626 (m), 1583 (m), 1508 (w), 1467 (m), 1430 (m), 1404 (w), 1335 (s), 1192 (vs), 1168 (m), 1117 (m), 1019 (w), 900 (w), 862 (w), 755 (w), 722 (w), 583 (w) cm^{-1}; MS (ESI): *m*/*z* = 1217.05 [M – I]$^+$; HRMS (ESI): *m*/*z* ($C_{77}H_{138}IN_3O_7$) calcd.: 1217.0529 [M – I]$^+$, found: 1217.0523; CHN ($C_{77}H_{138}IN_3O_7$) calcd.: C 68.77 H 10.34 N 3.12, found: C 68.47 H 10.32 N 3.01; $[\alpha]_D^{20}$: +66 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 12.4 °C [22.0 kJ · mol^{-1}] Col$_h$ 90.6 °C [0.69 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium hexafluorophosphate [3,4,5-C_{14}TyrC$_{14}$PF$_6$]

According to GP9: Guanidinium chloride **3,4,5-C_{14}TyrC$_{14}$Cl** (148 mg, 0.12 mmol), potassium hexafluorophosphate (90.0 mg, 0.49 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



3,4,5-C_{14}TyrC$_{14}$PF$_6$

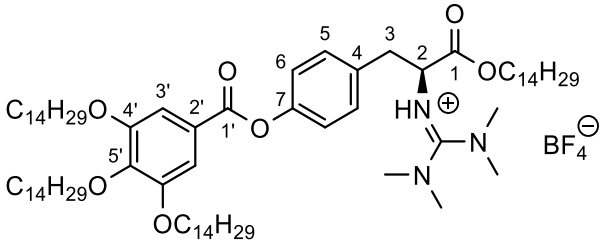
$C_{77}H_{138}F_6N_3O_7P$

(1362.93)

Colourless solid (quant., 161 mg, 0.12 mmol, purity >99%); M.p. 41.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.21–1.38 (m, 82H, C*H*$_2$), 1.45–1.52 (m, 6H, $OCH_2CH_2CH_2$), 1.63–1.69 (m, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 14.5 Hz, 6.7 Hz, 2H, C-5'-OCH_2CH_2), 1.82 (dt, *J* = 13.8 Hz, 6.6 Hz, 4H, C-4'-OCH_2CH_2), 2.82 (br. s, 6H, $N(CH_3)_2$), 2.95 (br. s, 6H, $N(CH_3)_2$), 3.33 (d, *J* = 6.6 Hz, 2H, 3-H), 4.02–4.07 (m, 6H, OCH_2), 4.17 (t, *J* = 6.9 Hz, 2H, $COOCH_2$), 4.28 (q, *J* = 6.6 Hz, 1H, 2-H), 5.76 (d, *J* = 7.7 Hz, 1H, NH), 7.15–7.17 (m, 2H, 6-H), 7.32 (d, *J* = 8.5 Hz, 2H, 5-H), 7.36 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.82, 26.08, 26.13, 28.4, 29.20, 29.33, 29.37, 29.38, 29.40, 29.43, 29.52, 29.60, 29.61, 29.66, 29.68, 29.70, 29.73, 29.76, 29.78, 30.4, 31.9 (CH_2), 37.0 (C-3), 39.8 ($N(CH_3)_2$), 58.6 (C-2), 66.9 ($COOCH_2$), 69.3 (C-4'-OCH_2), 73.6 (C-5'-OCH_2), 108.5 (C-3'), 122.6 (C-6), 123.6 (C-2'), 130.5 (C-5), 132.5 (C-4), 143.1 (C-5'), 150.7 (C-7), 153.0 (C-4'), 161.6 (N=C), 165.1 (C-1'), 170.4 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.4 (s, PF_6), –71.5 (s, PF_6) ppm; FT-IR: $\tilde{\nu}$ = 3384 (w), 2921 (vs), 2852 (s), 1735 (m), 1630 (m), 1582 (m), 1508 (w), 1467 (m), 1431 (m), 1407 (w), 1336 (m), 1193 (s), 1169 (m), 1117 (m), 1068 (w), 1019 (w), 842 (vs), 756 (w), 721 (w), 558 (m) cm^{-1}; MS (ESI): *m*/*z* = 144.96 $[BF_4]^-$, 1217.05 $[M - PF_6]^+$; HRMS (ESI): *m*/*z* ($C_{78}H_{138}F_6N_3O_7P$) calcd.: 1217.0529 $[M - PF_6]^+$, found: 1217.0526; CHN ($C_{78}H_{138}F_6N_3O_7P$) calcd.: C 67.86 H 10.21 N 3.08, found: C 67.98 H 10.23 N 3.07; $[\alpha]_D^{20}$: +55 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 13.6 °C [38.9 kJ · mol^{-1}] Col_h 85.8 °C [0.63 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium tetrafluoroborate [3,4,5-C$_{14}$TyrC$_{14}$BF$_4$]

According to GP9: Guanidinium chloride **3,4,5-C$_{14}$TyrC$_{14}$Cl** (143 mg, 0.11 mmol), sodium tetrafluoroborate (100 mg, 0.91 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



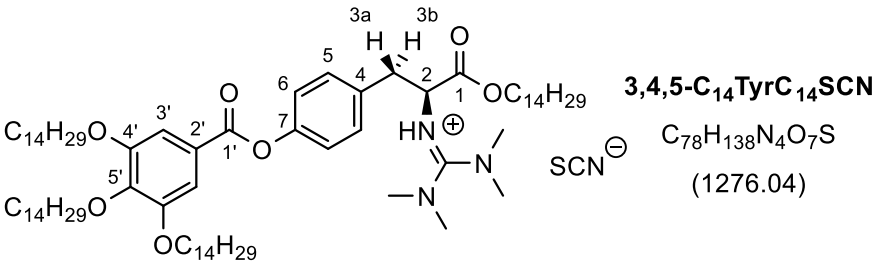
3,4,5-C$_{14}$TyrC$_{14}$BF$_4$
$C_{77}H_{138}BF_4N_3O_7$
(1304.77)

Colourless solid (quant., 150 mg, 0.12 mmol, purity >99%); M.p. 40.0 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.89 (m, 12H, C*H*$_3$), 1.22–1.38 (m, 82H, C*H*$_2$), 1.45–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.62–1.65 (m, 2H, $COOCH_2CH_2$), 1.76 (dt, *J* = 14.5 Hz, 6.7 Hz, 2H, C-5'-OCH_2CH_2), 1.82 (dt, *J* = 13.8 Hz, 6.6 Hz, 4H, C-4'-OCH_2CH_2), 2.77 (br. s, 6H, $N(CH_3)_2$), 3.00 (br. s, 6H, $N(CH_3)_2$), 3.35 (d, *J* = 6.6 Hz, 2H, 3-H), 4.02–4.06 (m, 6H, OCH_2), 4.15 (t,

J = 6.9 Hz, 2H, COOC*H*$_2$), 4.23 (q, *J* = 6.6 Hz, 1H, 2-H), 6.55 (d, *J* = 7.4 Hz, 1H, NH), 7.14 (d, *J* = 8.5 Hz, 2H, 6-H), 7.37 (d, *J* = 8.5 Hz, 4H, 5-H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.82, 26.08, 26.12, 28.4, 29.20, 29.33, 29.37, 29.38, 29.40, 29.43, 29.53, 29.59, 29.61, 29.66, 29.68, 29.70, 29.72, 29.76, 29.78, 30.4, 31.9 (*C*H$_2$), 36.8 (C-3), 39.8 (N(*C*H$_3$)$_2$), 59.1 (C-2), 66.7 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.4 (C-6), 123.7 (C-2'), 130.6 (C-5), 133.1 (C-4), 143.1 (C-5'), 150.5 (C-7), 153.0 (C-4'), 161.9 (N=C), 165.1 (C-1'), 170.4 (C-1) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –151.3 (d, *J* = 20.0 Hz, BF_4) ppm; FT-IR: ṽ = 3336 (w), 2921 (vs), 2852 (s), 1735 (m), 1631 (m), 1582 (m), 1508 (w), 1467 (m), 1431 (m), 1407 (w), 1379 (w), 1336 (m), 1193 (s), 1169 (m), 1117 (s), 1070 (s), 899 (w), 863 (w), 755 (w), 721 (w), 522 (w) cm^{-1}; MS (ESI): *m*/*z* = 87.00 $[BF_4]^-$, 1217.05 $[M – BF_4]^+$; HRMS (ESI): *m*/*z* ($C_{77}H_{138}BF_4N_3O_7$) calcd.: 1217.0529 $[M – BF_4]^+$, found: 1217.0520; CHN ($C_{77}H_{138}BF_4N_3O_7$) calcd.: C 70.88 H 10.66 N 3.22, found: C 70.71 H 10.80 N 3.21; $[\alpha]_D^{20}$: +62 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 15.3 °C [43.3 kJ · mol^{-1}] Col$_h$ 100.2 °C [0.74 kJ · mol^{-1}] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium thiocyanate [3,4,5-C$_{14}$TyrC$_{14}$SCN]

According to GP9: Guanidinium chloride **3,4,5-C$_{14}$TyrC$_{14}$Cl** (147 mg, 0.12 mmol), potassium thiocyanate (50.0 mg, 0.52 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



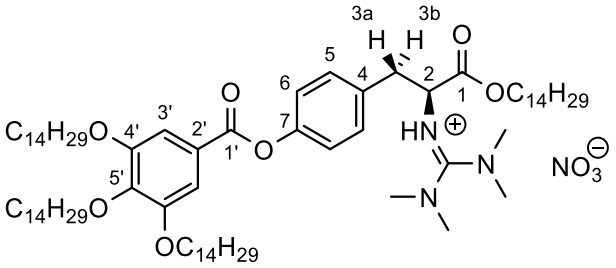
3,4,5-C$_{14}$TyrC$_{14}$SCN
$C_{78}H_{138}N_4O_7S$
(1276.04)

Colourless solid (quant., 150 mg, 0.12 mmol, purity >99%); M.p. 36.0 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 12H, C*H*$_3$), 1.22–1.37 (m, 82H, C*H*$_2$), 1.45–1.50 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.63–1.67 (m, 2H, COOCH$_2$C*H*$_2$), 1.75 (dt, *J* = 13.8 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.82 (dt, *J* = 13.8 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.49–3.25 (m, 12H, N(C*H*$_3$)$_2$), 3.37 (dd, *J* = 14.2 Hz, 4.8 Hz, 1H, 3b-H), 3.47 (dd, *J* = 14.2 Hz, 9.2 Hz, 1H, 3a-H), 4.02–4.05 (m, 6H, OC*H*$_2$), 4.14–4.16 (m, 3H, COOC*H*$_2$, 2-H), 7.13 (d, *J* = 8.2 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.45 (d, *J* = 8.2 Hz, 2H, 5-H), 8.67 (s, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.84, 26.08, 26.12, 28.5, 29.22, 29.33, 29.37, 29.38, 29.40, 29.43, 29.54, 29.59, 29.62, 29.66, 29.67, 29.68, 29.71, 29.72, 29.75, 29.76, 29.78, 30.4, 31.93, 31.94, 31.95 (*C*H$_2$), 36.5 (C-3), 39.8, 40.6 (N(*C*H$_3$)$_2$), 60.0 (C-2), 66.7 (COO*C*H$_2$), 69.3

(C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.3 (C-6), 123.7 (C-2'), 130.7 (C-5), 132.8 (SCN), 133.9 (C-4), 143.1 (C-5'), 150.3 (C-7), 153.0 (C-4'), 162.0 (N=C), 165.1 (C-1'), 170.5 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2921 (vs), 2852 (vs), 2052 (m), 1733 (m), 1625 (m), 1583 (m), 1508 (m), 1466 (m), 1430 (s), 1404 (m), 1335 (s), 1189 (vs), 1167 (s), 1116 (s), 1067 (w), 1032 (w), 908 (m), 862 (w), 754 (m), 732 (s), 645 (w), 581 (w), 547 (w) cm^{-1}; MS (ESI): *m*/*z* = 1217.05 [M – SCN]$^+$; HRMS (ESI): *m*/*z* ($C_{78}H_{138}N_4O_7S$) calcd.: 1217.0529 [M – SCN]$^+$, found: 1217.0526; CHN ($C_{78}H_{138}N_4O_7S \cdot 0.2\ H_2O$) calcd.: C 73.21 H 10.90 N 4.38 S 2.51, found: C 72.94 H 10.93 N 4.32 S 2.27; $[\alpha]_D^{20}$: +49 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr_1 –1.48 °C [0.40 kJ · mol^{-1}] Cr_2 18.3 °C [45.3 kJ · mol^{-1}] Col_h 50.0 °C [–] I (2nd cool).

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-oxo-3-(4-((3,4,5-tris(tetradecyloxy)benzoyl)oxy)-phenyl)-1-(tetradecyloxy)propan-2-aminium nitrate [3,4,5-C$_{14}$TyrC$_{14}$NO$_3$]

According to GP9: Guanidinium chloride **3,4,5-C$_{14}$TyrC$_{14}$Cl** (156 mg, 0.13 mmol), sodium nitrate (170 mg, 2.00 mmol), MeCN (9 mL), CH_2Cl_2 (1 mL).



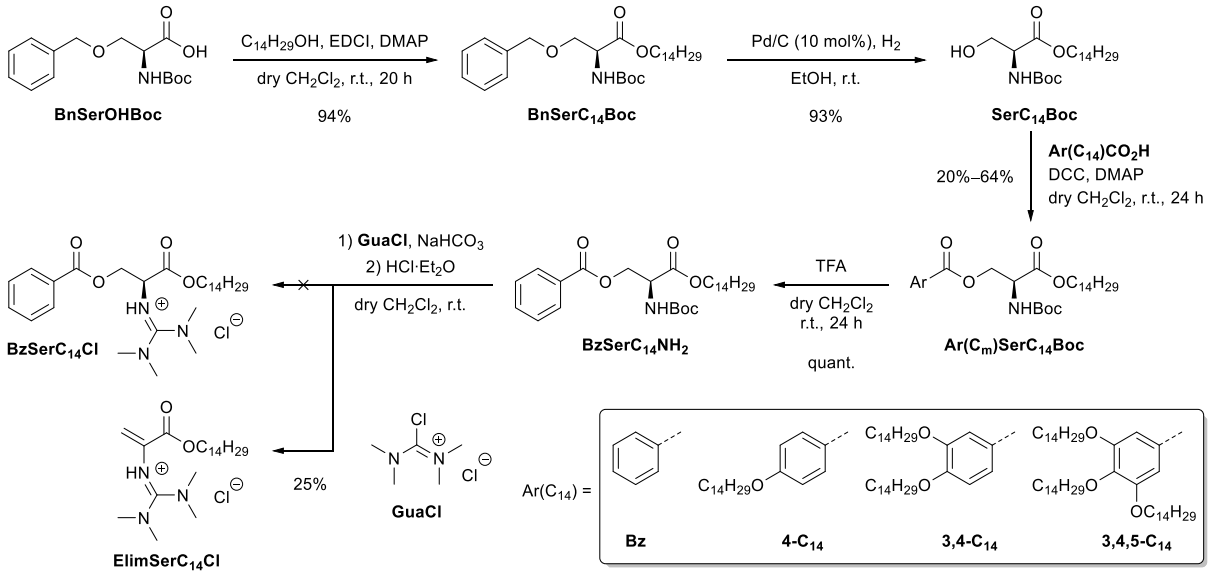
3,4,5-C$_{14}$TyrC$_{14}$NO$_3$
$C_{77}H_{138}N_4O_{10}$
(1279.97)

Colourless wax (quant., 159 mg, 0.12 mmol, purity >95%); M.p. 40.0 °C (POM); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.0 Hz, 12H, C*H*$_3$), 1.21–1.36 (m, 82H, C*H*$_2$), 1.44–1.49 (m, 6H, OCH$_2$CH$_2$C*H*$_2$), 1.60–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.74 (dt, *J* = 14.1 Hz, 6.8 Hz, 2H, C-5'-OCH$_2$C*H*$_2$), 1.81 (dt, *J* = 13.9 Hz, 6.7 Hz, 4H, C-4'-OCH$_2$C*H*$_2$), 2.37–3.31 (m, 12H, N(C*H*$_3$)$_2$), 3.39 (dd, *J* = 14.0 Hz, 4.7 Hz, 1H, 3b-H), 3.74 (dd, *J* = 14.0 Hz, 9.5 Hz, 1H, 3a-H), 4.01–4.05 (m, 6H, OC*H*$_2$), 4.08–4.12 (m, 3H, COOC*H*$_2$, 2-H), 7.10 (d, *J* = 8.0 Hz, 2H, 6-H), 7.36 (s, 2H, 3'-H), 7.54 (d, *J* = 8.0 Hz, 2H, 5-H), 9.87 (br. s, 1H, NH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.85, 26.08, 26.11, 28.4, 29.21, 29.33, 29.37, 29.38, 29.40, 29.42, 29.46, 29.53, 29.59, 29.61, 29.66, 29.67, 29.68, 29.70, 29.71, 29.72, 29.75, 29.76, 29.78, 30.4, 31.93, 31.94, 31.95 (*C*H$_2$), 36.1 (C-3), 39.6 (N(*C*H$_3$)$_2$), 60.5 (C-2), 66.6 (COO*C*H$_2$), 69.3 (C-4'-O*C*H$_2$), 73.6 (C-5'-O*C*H$_2$), 108.5 (C-3'), 122.0 (C-6), 123.8 (C-2'), 130.9 (C-5), 134.6 (C-4), 143.0 (C-5'), 150.2 (C-7), 153.0 (C-4'), 162.3 (N=C), 165.2 (C-1'), 170.8 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2920 (vs), 2852 (vs), 1733 (s), 1625 (m), 1583 (m), 1508 (m), 1466 (m), 1430 (s), 1404 (m), 1378 (m), 1334 (s), 1190 (vs), 1168 (s), 1116 (s), 1068 (w), 1032 (w), 932 (w), 907 (w),

861 (w), 754 (m), 723 (m), 640 (w), 583 (w), 547 (w) cm^{-1}; MS (ESI): *m*/*z* = 1217.05 $[M - NO_3]^+$; HRMS (ESI): *m*/*z* ($C_{77}H_{138}N_4O_{10}$) calcd.: 1217.0529 $[M - NO_3]^+$, found: 1217.0544; CHN ($C_{77}H_{138}N_4O_{10}$) calcd.: C 72.26 H 10.87 N 4.38, found: C 72.17 H 11.34 N 3.71; $[\alpha]_D^{20}$: +74 (*c* = 1.0 mg · mL^{-1} in $CHCl_3$); DSC: Cr 15.7 °C [38.0 kJ · mol^{-1}] Col_h 96.2 °C [0.92 kJ · mol^{-1}] I (2^{nd} cool).

2.3 Synthesis Approach of L-Serine Based Guanidinium Chlorides

As outlined in Scheme S2, L-serinat **BnOSerOHBoc** was treated with tetradecanol in the presence of EDCI and DMAP in CH_2Cl_2 to give the ester **BnOSerOC$_{14}$Boc** in 94%.[30] Subsequent benzyl deprotection with palladium on coal (10 mol%) under a hydrogen atmosphere in degassed ethanol yielded the free hydroxide **SerC$_{14}$Boc** in 93%,[30] which was esterified with the alkoxybenzoates **Ar(C$_{14}$)CO$_2$H** in the presence of DCC and DMAP in CH_2Cl_2 to give the hybrids **Ar(C$_{14}$)SerC$_{14}$Boc** in 20– 64%.[1,23] Removal of the Boc group of **BzSerC$_{14}$Boc** was accomplished with TFA according to Vallakati yielding the corresponding amine **BzSerC$_{14}$NH$_2$** in quant. yield,[1,24] which was reacted with tetramethylchloro-formamidinium chloride **GuaCl**.[1,25] However, the desired amphiphilic guanidinium chloride **BzSerC$_{14}$Cl** could not be obtained, since the product immediately eliminated to the vinyl species **ElimSerC$_{14}$Cl**. This by-product could be isolated in 25% yield. Since elimination already occurred with the unsubstituted benzoate under mild conditions, further approaches with respect to L-serine were dismissed.

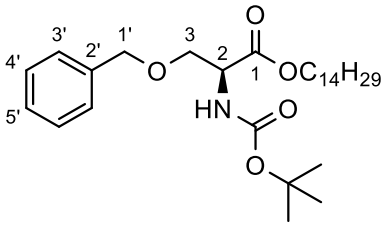


Scheme S2

Tetradecyl (*S*)-3-benzyloxy-2-((*tert*-butoxycarbonyl)amino)propanoate (BnSerC$_{14}$Boc)[30]

N-*tert*-Boc-*O*-Benzyl-L-serine **BnSerOHBoc** (2.00 g, 6.79 mmol), tetradecanol (1.46 g, 6.81 mmol) and DMAP (89.0 mg, 0.73 mmol) were dissolved in dry CH_2Cl_2 (40 mL) under a nitrogen atmosphere, cooled to 0 °C and EDCI (1.47 g, 7.67 mmol) was added. The solution was stirred for 20 h at room temperature. After complete conversion, the solvent was removed under reduced pressure and the remaining residue was dissolved in ether (100 mL). The organic phase was washed with water (3 × 50 mL), dried over magnesium sulphate and the solvent was

removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, gradient hexanes/EtOAc, 15 : 1 → 12 : 1) to give the product as colourless solid (94%, 3.13 g, 6.36 mmol, purity >94%). R_f = 0.38 (hexanes/EtOAc = 15 : 1, phosphomolybdic acid).

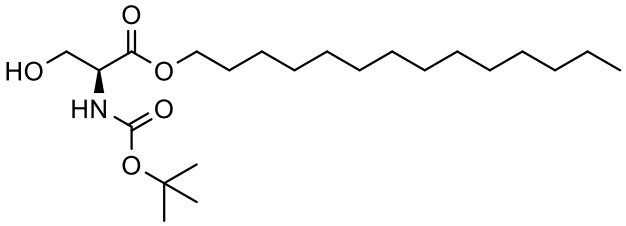


BnSerC$_{14}$Boc
$C_{29}H_{49}NO_5$
(491.71)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.21–1.33 (m, 22H, C*H*$_2$), 1.45 (s, 9H, OC(C*H*$_3$)$_3$), 1.57–1.64 (m, 2H, OCH$_2$C*H*$_2$), 3.69 (dd, *J* = 9.4 Hz, 3.3 Hz, 1H, 3-H), 3.88 (dd, *J* = 9.4 Hz, 3.2 Hz, 1H, 3-H), 4.08–4.19 (m, 2H, OC*H*$_2$), 4.41–4.56 (m, 3H, 1'-H, 2-H), 5.39 (d, *J* = 8.8 Hz, 1H, NH), 7.25–7.36 (m, 5H, 3'-H, 4'-H, 5'-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.3, 28.6, 29.2, 29.4, 29.52, 29.60, 29.66, 29.68, 29.70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 54.1 (C-2), 65.7 (O*C*H$_2$), 70.2 (C-3), 73.3 (C-5), 79.9 (O*C*(CH$_3$)$_3$), 127.6, 127.8, 128.4 (C-1', C-2', C-3'), 137.6 (C-4), 155.5 (HNC=O), 170.7 (C=O) ppm; MS (ESI): *m*/*z* = 492.37 [M + H]$^+$, 514.35 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{29}H_{49}NO_5$) calcd.: 514.3503 [M + Na]$^+$, found: 514.3500. The spectroscopic data were in accordance with the literature.[30]

Tetradecyl (*tert*-butoxycarbonyl)-L-serinate [SerC$_{14}$Boc][30]

Benzyl protected tetradecyl (*tert*-butoxycarbonyl)-L-serinate **BnSerC$_{14}$Boc** (2.58 g, 5.24 mmol) and Pd/C catalyst (10 mol%, 300 mg) were suspended in degassed EtOH (105 mL) under a hydrogen atmosphere and the mixture was stirred for 48 h at room temperature. After complete conversion, the suspension was filtered through Celite® and the solvent was removed under reduced pressure to give the product as colourless, transparent needles (93%, 1.96 g, 4.88 mmol, purity >95%).



SerC$_{14}$Boc
$C_{22}H_{43}NO_5$
(401.59)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3H, C*H*$_3$), 1.23–1.36 (m, 22H, C*H*$_2$), 1.46 (s, 9H, OC(C*H*$_3$)$_3$), 1.62–1.69 (m, 2H, OCH$_2$C*H*$_2$), 2.22–2.42 (m, 1H, OH), 3.89–3.97 (m, 2H, C*H*$_2$OH), 4.17 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 4.36 (s, 1H, HNC*H*), 5.43 (s, 1H, NH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.3, 28.5, 29.2, 29.4, 29.50, 29.58, 29.65,

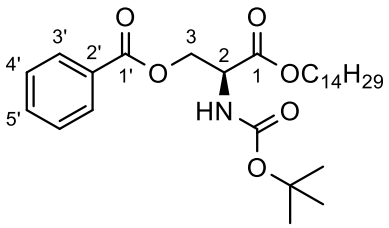
29.67, 29.70, 31.9 (CH_2, OC(CH_3)$_3$), 55.9 (HN*C*H), 63.9 (CH_2OH), 66.0 (OCH_2), 80.3 (OC(CH_3)$_3$), 154.1 (HNC=O), 170.8 (C=O) ppm; MS (ESI): *m*/*z* = 402.32 $[M + H]^+$, 424.30 $[M + Na]^+$; HRMS (ESI): *m*/*z* ($C_{22}H_{43}NO_5$) calcd.: 424.3033 $[M + Na]^+$, found: 424.3034. The spectroscopic data were in accordance with the literature.[30]

General Procedure GP10: Steglich esterification of L-serinates and benzoic acids derivatives[1,23]

The respective etherified benzoic acid **Ar(C$_{14}$)CO$_2$H** (0.45 mmol), tetradecyl (*tert*-butoxycarbonyl)-L-serinate **SerC$_{14}$Boc** (205 mg, 0.51 mmol) and DMAP (10.0 mg, 0.08 mmol) were dissolved in dry CH_2Cl_2 (100 mL) under a nitrogen atmosphere, and *N*,*N*'-dicyclohexylcarbodiimide (DCC, 105 mg, 0.50 mmol) was added. The mixture was stirred for 24 h at room temperature and was eventually filtered through Celite®. The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. The crude products were purified by column chromatography (SiO_2, gradient hexanes/EtOAc).

(*S*)-2-((*t*ert-Butoxycarbonyl)amino)-3-oxo-3-(tetradecyloxy)propyl benzoate [BzSerC$_{14}$Boc]

According to GP10: Benzoic acid **BzCO$_2$H** (55.0 mg, 0.45 mmol), tetradecyl (*tert*-butoxycarbonyl)-L-serinate **SerC$_{14}$Boc** (199 mg, 0.50 mmol), DCC (118 mg, 0.57 mmol), DMAP (10.0 mg, 81.9 μmol), dry CH_2Cl_2 (30 mL); column gradient 25 : 1 → 10 : 1; R_f = 0.41 (hexanes/EtOAc = 15 : 1).



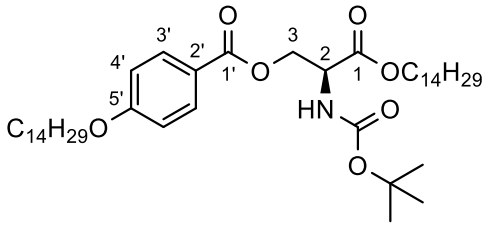
BzSerC$_{14}$Boc
$C_{29}H_{47}NO_6$
(505.70)

Colourless solid (64%, 145 mg, 287 μmol, purity >95%); M.p. 102.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.16–1.32 (m, 22H, CH_2), 1.45 (s, 9H, OC(CH_3)$_3$), 1.57–1.64 (m, 2H, OCH$_2$CH_2), 4.11–4.24 (m, 2H, OCH_2), 4.58–4.72 (m, 3H, 3-H, 2-H), 5.39 (d, *J* = 8.3 Hz, 1H, NH), 7.43 (t, *J* = 7.8 Hz, 2H, 4'-H), 7.57 (t, *J* = 7.8 Hz, 1H, 5'-H), 8.00 (dd, *J* = 7.8 Hz, 1.4 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.8, 28.3, 28.6, 29.2, 29.37, 29.44, 29.56, 29.62, 29.66, 29.70, 31.9 (CH_2, OC(CH_3)$_3$), 53.1 (C-2), 65.2 (C-3), 66.2 (OCH_2CH$_2$), 80.3 (OC(CH_3)$_3$), 128.5 (C-4'), 129.5, 129.7 (C-3', C-2'), 133.3 (C-5'), 155.2 (HNC=O), 166.0 (C-1'), 169.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3340 (w), 2919 (s), 2851 (s), 1743 (s), 1703 (vs), 1603 (w), 1585 (w), 1521 (m), 1469 (m), 1454 (m), 1392 (m),

1367 (m), 1338 (m), 1267 (vs), 1250 (vs), 1203 (s), 1161 (vs), 1117 (s), 1059 (s), 1028 (s), 923 (w), 875 (w), 855 (w), 779 (w), 763 (w), 710 (vs), 686 (w), 618 (w), 577 (w), 548 (w), 479 (w) cm^{-1}. MS (EI): *m*/*z* = 504.3 $[M]^+$.

(*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-oxo-3-(tetradecyloxy)propyl 4-tetradecyloxybenzoate [4-C_{14}SerC_{14}Boc]

According to GP10: 4-Tetradecyloxybenzoic acid **4-$C_{14}CO_2H$** (155 mg, 0.46 mmol), tetradecyl (*tert*-butoxycarbonyl)-L-serinate **SerC_{14}Boc** (205 mg, 0.51 mmol), DCC (107 mg, 0.52 mmol), DMAP (10.0 mg, 81.9 µmol), dry CH_2Cl_2 (30 mL); column gradient 25 : 1 → 20 : 1; R_f = 0.41 (hexanes/EtOAc = 15 : 1).

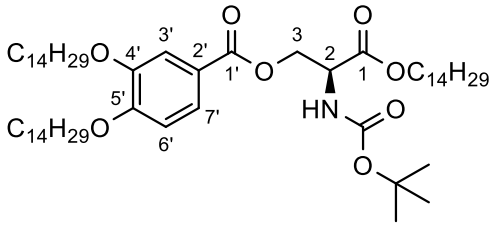


4-C_{14}SerC_{14}Boc
$C_{43}H_{75}NO_7$
(718.07)

Colourless solid (45%, 148 mg, 206 µmol, purity >95%); M.p. 56.8 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 6H, C*H*$_3$), 1.18–1.37 (m, 44H, C*H*$_2$), 1.45 (s, 9H, OC(C*H*$_3$)$_3$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.77–1.82 (m, 2H, OCH$_2$C*H*$_2$), 4.00 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.11–4.23 (m, 2H, OC*H*$_2$), 4.53–4.69 (m, 3H, 3-H, 2-H), 5.39 (d, *J* = 8.3 Hz, 1H, NH), 6.89 (d, *J* = 8.8 Hz, 2H, 4'-H), 7.92 (d, *J* = 8.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 26.0, 28.3, 28.6, 29.1, 29.2, 29.37, 29.38, 29.46, 29.57, 29.59, 29.61, 29.64, 29.67, 29.68, 29.71, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 53.2 (C-2), 64.9 (C-3), 66.1, 68.3 (O*C*H$_2$CH$_2$), 80.3 (O*C*(CH$_3$)$_3$), 114.2 (C-4'), 121.6 (C-2'), 131.8 (C-3'), 155.2 (HNC=O), 163.3 (C-5'), 165.8 (C-1'), 170.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3372 (w), 2922 (s), 2852 (s), 1719 (vs), 1606 (m), 1580 (w), 1510 (m), 1466 (m), 1422 (w), 1391 (w), 1367 (m), 1343 (m), 1250 (vs), 1204 (m), 1164 (vs), 1102 (s), 1058 (m), 1027 (m), 847 (m), 769 (m), 722 (w), 696 (w), 649 (w), 511 (w), 462 (w) cm^{-1}. MS (EI): *m*/*z* = 717.6 $[M]^+$.

(*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-oxo-3-(tetradecyloxy)propyl 3,4-bis(tetradecyloxy)-benzoate [3,4-C_{14}SerC_{14}Boc]

According to GP10: 3,4-Bis(tetradecyloxy)benzoic acid **3,4-$C_{14}CO_2H$** (200 mg, 0.37 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-serinate **SerC_{14}Boc** (162 mg, 0.40 mmol), DCC (95.0 mg, 0.46 mmol), DMAP (20.0 mg, 0.16 mmol), dry CH_2Cl_2 (30 mL); column gradient 25 : 1 → 10 : 1; R_f = 0.46 (hexanes/EtOAc = 15 : 1).

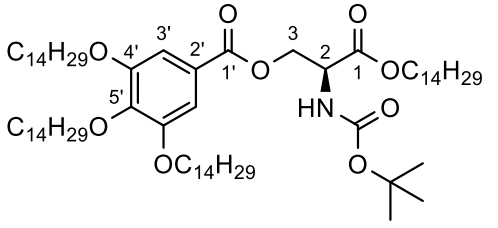


3,4-C$_{14}$SerC$_{14}$Boc
$C_{57}H_{103}NO_8$
(930.45)

Colourless solid (40%, 135 mg, 0.15 mmol, purity >87%); M.p. 59.3 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 9H, C*H*$_3$), 1.20–1.37 (m, 60H, C*H*$_2$), 1.41–1.49 (m, 15H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.57–1.63 (m, 2H, COOCH$_2$C*H*$_2$), 1.79–1.86 (m, 4H, OCH$_2$C*H*$_2$), 4.00–4.05 (m, 4H, OC*H*$_2$), 4.11–4.22 (m, 2H, OC*H*$_2$), 4.54–4.60 (m, 2H, 3-H), 4.66–4.69 (m, 1H, 2-H), 5.38 (d, *J* = 8.3 Hz, 1H, NH), 6.84 (d, *J* = 8.5 Hz, 1H, 6'-H), 7.49 (d, *J* = 2.0 Hz, 1H, 3'-H), 7.57 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, 7'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 26.00, 26.06, 28.3, 28.6, 29.1, 29.2, 29.38, 29.42, 29.46, 29.48, 29.60, 29.64, 29.66, 29.69, 29.72, 29.74, 32.0 (*C*H$_2$, OC(*C*H$_3$)$_3$), 53.2 (C-2), 64.9 (C-3), 66.1, 69.1, 69.4 (O*C*H$_2$CH$_2$), 80.2 (O*C*(CH$_3$)$_3$), 111.9 (C-6'), 114.4 (C-3'), 121.6 (C-2'), 123.8 (C-7'), 148.7 (C-4'), 153.6 (C-5'), 155.2 (HNC=O), 165.9 (C-1'), 170.0 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3374 (w), 2921 (vs), 2852 (s), 1719 (vs), 1600 (w), 1511 (m), 1466 (m), 1430 (m), 1391 (w), 1367 (m), 1343 (m), 1266 (vs), 1208 (s), 1164 (s), 1131 (s), 1101 (s), 1057 (s), 1016 (vs), 910 (w), 874 (w), 795 (vs), 762 (s), 724 (m), 661 (w), 462 (w) cm^{-1}; MS (EI): *m*/*z* = 929.7 [M]$^+$.

(*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-oxo-3-(tetradecyloxy)propyl 3,4,5-tris(tetradecyloxy)benzoate [3,4,5-C$_{14}$SerC$_{14}$Boc]

According to GP10: 3,4,5-Tris(tetradecyloxy)benzoic acid **3,4,5-C$_{14}$CO$_2$H** (377 mg, 0.50 mmol), tetradecyl-(*tert*-butoxycarbonyl)-L-serinate **SerC$_{14}$Boc** (201 mg, 0.50 mmol), DCC (250 mg, 1.21 mmol), DMAP (34.0 mg, 0.28 mmol), dry CH_2Cl_2 (25 mL); column gradient 25 : 1 → 15 : 1; R_f = 0.45 (hexanes/EtOAc = 15 : 1).



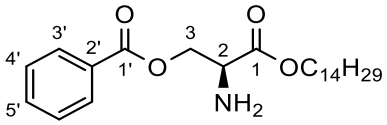
3,4,5-C$_{14}$SerC$_{14}$Boc
$C_{71}H_{131}NO_9$
(1142.83)

Colourless solid (20%, 115 mg, 0.10 mmol, purity >95%); M.p. 51.7 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 12H, C*H*$_3$), 1.21–1.37 (m, 80H, C*H*$_2$), 1.43–1.50 (m, 17H, OCH$_2$CH$_2$C*H*$_2$, OC(C*H*$_3$)$_3$), 1.58–1.64 (m, 2H, COOCH$_2$C*H*$_2$), 1.71–1.76 (m, 2H, OCH$_2$C*H*$_2$), 1.78–1.83 (m, 4H, OCH$_2$C*H*$_2$), 3.98–4.02 (m, 6H, OC*H*$_2$), 4.11–4.22 (m, 2H, OC*H*$_2$), 4.57 (t, *J* = 3.9 Hz, 2H, 3-H), 4.67–4.70 (m, 1H, 2-H), 5.37 (d, *J* = 8.2 Hz, 1H, NH),

7.20 (s, 2H, 3'-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 26.09, 26.14, 28.31, 28.36, 28.6, 29.2, 29.36, 29.39, 29.45, 29.50, 29.60, 29.68, 29.69, 29.71, 29.74, 29.77, 30.4, 32.0 (*C*H_2, OC(*C*H_3)$_3$), 53.2 (C-2), 65.1 (C-3), 66.1, 69.3, 73.6 (O*C*H_2CH_2), 80.3 (O*C*(CH_3)$_3$), 108.3 (C-3'), 123.9 (C-2'), 142.9 (C-5'), 152.9 (C-4'), 155.2 (HNC=O), 165.9 (C-1'), 169.9 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3363 (w), 2921 (vs), 2852 (vs), 1721 (s), 1587 (w), 1499 (m), 1466 (m), 1431 (m), 1390 (m), 1367 (s), 1333 (s), 1207 (s), 1164 (s), 1114 (s), 1059 (m), 1026 (m), 863 (w), 763 (m), 721 (w), 465 (w) cm^{-1}; MS (ESI): *m*/*z* = 1164.97 [M + Na]$^+$. HRMS (ESI): *m*/*z* ($C_{71}H_{131}NO_9$) calcd.: 1164.9716 [M + Na]$^+$, found: 1164.9710.

(*S*)-2-Amino-3-oxo-3-(tetradecyloxy)propylbenzoate [BzSerC$_{14}$NH$_2$][1,24]

Boc-protected amine **BzSerC$_{14}$Boc** (81.0 mg, 0.16 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under a nitrogen atmosphere and cooled to 0 °C while stirring. Afterwards, trifluoroacetic acid (0.2 mL, 2.60 mmol) was added slowly and the mixture was stirred for 24 h at room temperature. After complete conversion, the ion exchange resin Amberlyst® A21 (free base) was added until a neutral pH value was obtained, and the mixture was stirred for additional 20 min. Subsequently, the ion exchange resin was filtered off and the solvent was removed under reduced pressure. The crude product was obtained as light-yellow oil (quant., 65.0 mg, 0.16 mmol, purity >92%) and was used without further purification.

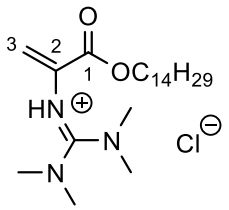


BzSerC$_{14}$NH$_2$
$C_{24}H_{39}NO_4$
(405.58)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$), 1.16–1.36 (m, 22H, C*H*$_2$), 1.61 (dt, *J* = 13.7 Hz, 7.0 Hz, 2H, OCH$_2$C*H*$_2$), 3.85 (t, *J* = 4.6 Hz, 1H, 2-H), 4.07–4.24 (m, 2H, OC*H*$_2$), 4.51–4.60 (m, 2H, 3-H), 7.43 (t, *J* = 7.6 Hz, 2H, 4'-H), 7.56 (t, *J* = 7.6 Hz, 1H, 5'-H), 8.01 (d, *J* = 7.8 Hz, 2H, 3'-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.60, 29.20, 29.36, 29.45, 29.56, 29.62, 29.65, 29.69, 31.9 (*C*H_2), 53.9 (C-2), 65.7 (C-3), 66.9 (O*C*H_2CH_2), 128.4 (C-4'), 129.7 (C-3', C-2'), 133.2 (C-5'), 166.1 (C-1'), 173.1 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 2924 (vs), 2854 (s), 1731 (m), 1459 (m), 1378 (m), 1271 (m), 711 (m) cm^{-1}; MS (ESI): *m*/*z* = 406.29 [M + H]$^+$, 428.28 [M + Na]$^+$; HRMS (ESI): *m*/*z* ($C_{24}H_{39}NO_4$) calcd.: 406.2952 [M + H]$^+$, found: 406.2940.

***N*-(Bis(dimethylamino)methylene)-3-oxo-3-(tetradecyloxy)prop-1-ene-2-aminium chloride [ElimSerC$_{14}$Cl]^{1,25}**

Free amine **BzSerC$_{14}$NH$_2$** (47.0 mg, 0.12 mmol) and dried sodium bicarbonate (235 mg, 2.80 mmol) were suspended in dry CH_2Cl_2 (5 mL) under a nitrogen atmosphere and *N*,*N*,*N*',*N*'-tetramethylchloroformamidinium chloride **GuaCl** (0.2 mL, 0.20 mmol, 1.0 M in dry CH_2Cl_2) was added. The solution was stirred for 21 h at room temperature. After 17 h and 19 h, additional **GuaCl** (each 0.1 mL, 0.10 mmol, 1.0 M in dry CH_2Cl_2) had to be added to achieve complete conversion of the starting material. Afterwards, excess base was filtered off, water (180 µL, 10.0 mmol) was added and the mixture was stirred for additional 15 min. The solvents were removed under reduced pressure and the remaining residue was dissolved in ether (30 mL). Subsequently, the solution was acidified (pH ≈ 1) with HCl · Et_2O and stirred for additional 15 min. The solvent was removed under reduced pressure and the residue was purified by were purified by column chromatography (SiO_2 treated with 6.0 M HCl). At first, the column was flushed with pure EtOAc and EtOAc/MeOH (10 : 1), followed by a gradient of CH_2Cl_2/MeOH (15 : 1 → 9 : 1) to give the product as colourless solid (25%, 10.0 mg, 23.9 µmol, purity >95%). R_f = 0.18 (CH_2Cl_2/MeOH = 15 : 1, phosphomolybdic acid).



ElimSerC$_{14}$Cl
$C_{22}H_{44}ClN_3O_2$
(418.06)

No M.p., decomposition >250 °C (POM); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.19–1.37 (m, 22H, C*H*$_2$), 1.65 (dt, *J* = 13.5 Hz, 6.3 Hz, 2H, OCH$_2$C*H*$_2$), 2.97 (br. s, 12H, N(C*H*$_3$)$_2$), 4.15 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 6.01 (s, 1H, 3-H), 6.11 (s, 1H, 3-H), 11.85 (s, 1H, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.2, 29.4, 29.51, 29.57, 29.63, 29.65, 29.66, 29.69, 31.9 (*C*H$_2$), 40.4 (N(*C*H$_3$)$_2$), 66.4 (O*C*H$_2$), 117.6 (C-3), 133.8 (C-2), 160.3 (N=C), 163.6 (C-1) ppm; FT-IR: $\tilde{\nu}$ = 3390 (w), 2920 (vs), 2851 (s), 2685 (w), 1718 (s), 1632 (vs), 1563 (s), 1468 (m), 1427 (m), 1408 (s), 1342 (m), 1308 (m), 1232 (m), 1193 (s), 1069 (w), 1055 (w), 973 (w), 899 (w), 816 (w), 772 (w), 720 (w), 612 (w) cm^{-1}; MS (ESI): *m*/*z* = 382.34 [M – Cl]$^+$; HRMS (ESI): *m*/*z* ($C_{22}H_{44}ClN_3O_2$) calcd.: 382.3428 [M – Cl]$^+$, found: 382.3428; CHN ($C_{22}H_{44}ClN_3O_2 \cdot 0.3\ H_2O$) calcd.: C 62.40 H 10.62 N 9.92, found: C 62.34 H 10.65 N 9.69.

3 Polarising Optical Microscopy (POM)

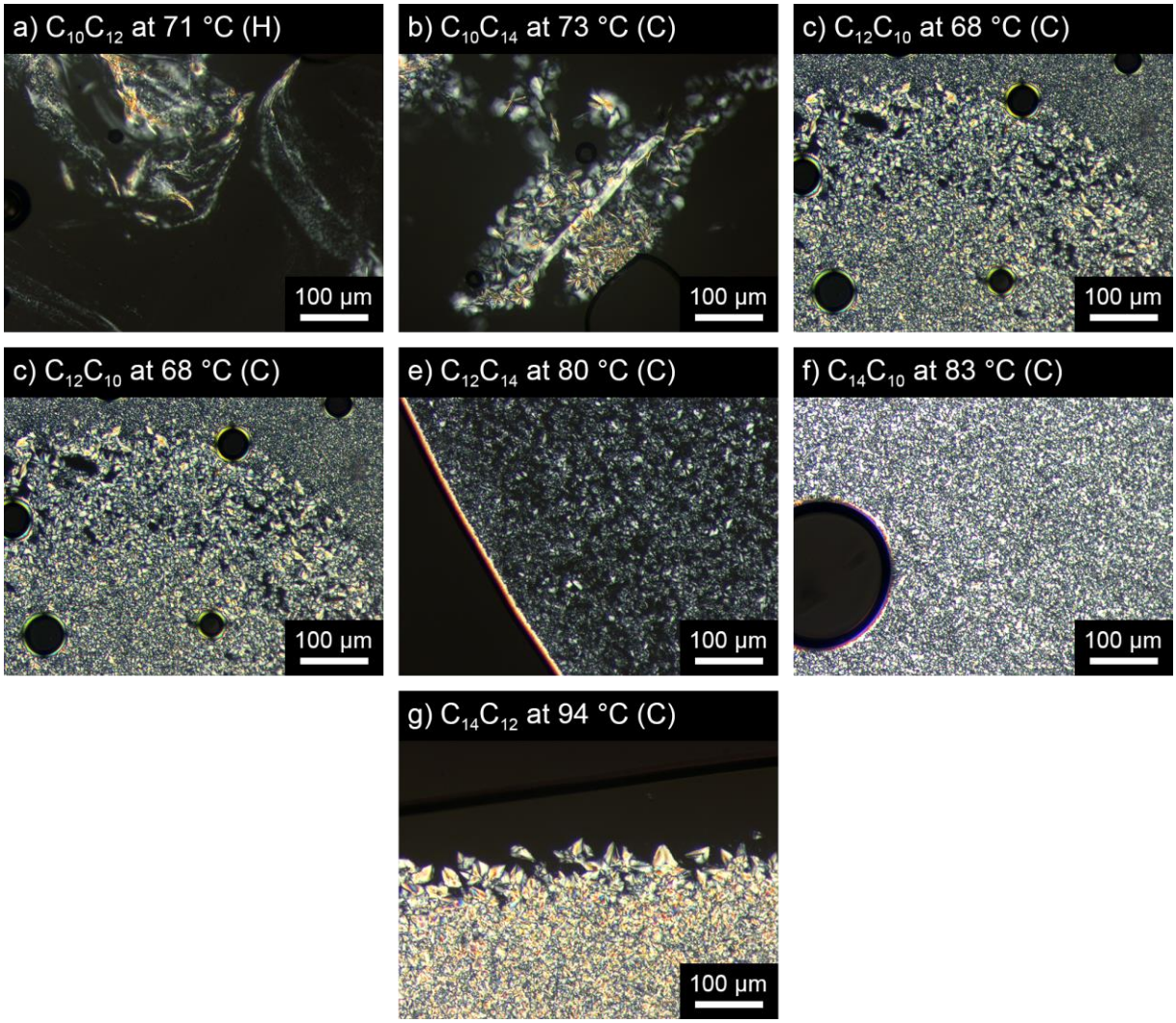


Figure S1. POM images of **4-C_mTyrC_nCl**. H/C: heating/cooling in/from isotropic phase. Rate of 1 or 5 $K \cdot min^{-1}$.

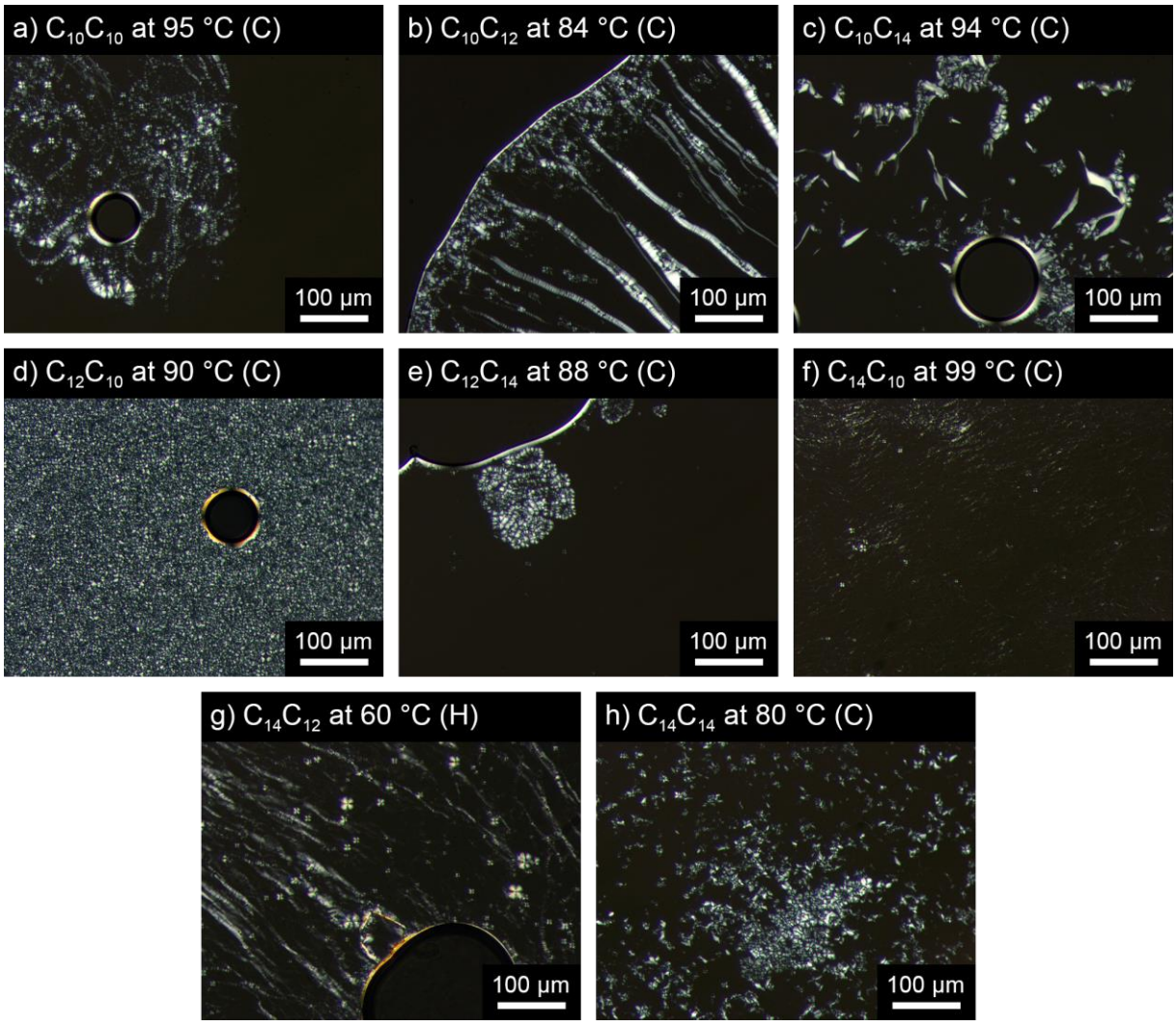


Figure S2. POM images of **3,4-C_mTyrC$_n$Cl**. H/C: heating/cooling in/from isotropic phase. Rate of 1 or 5 K · min^{-1}.

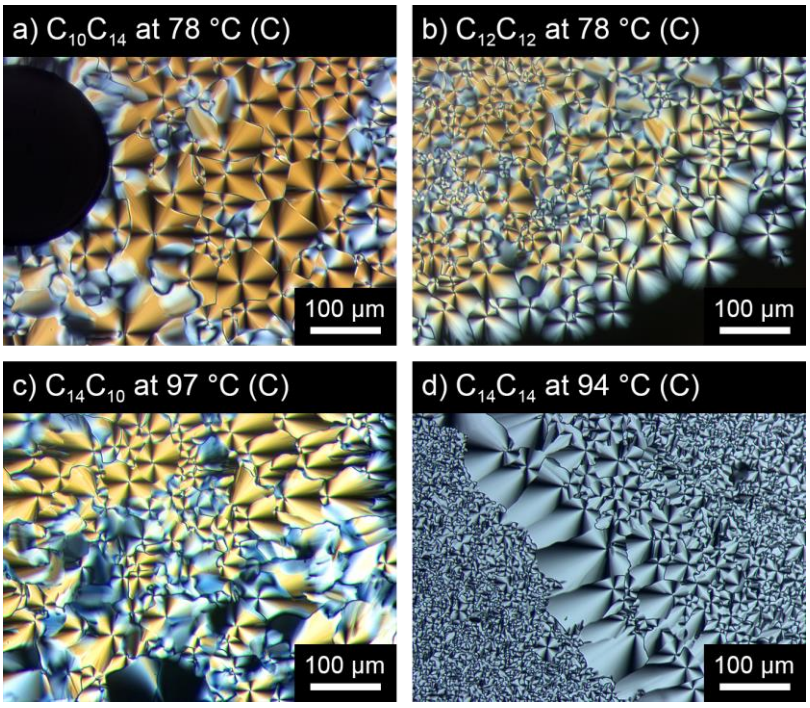


Figure S3. POM images of **3,4,5-C_mTyrC$_n$Cl**. H/C: heating/cooling in/from isotropic phase. Rate of 1 or 5 K · min^{-1}.

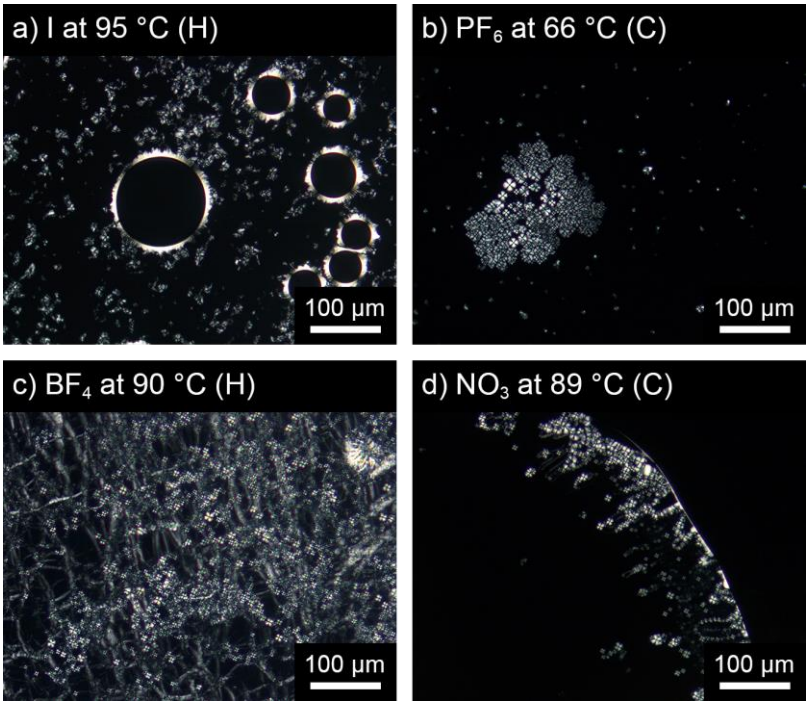


Figure S4. POM images of **4-C_{14}TyrC$_{14}$X**. H/C: heating/cooling in/from isotropic phase. Rate of 1 or 5 K · min^{-1}.

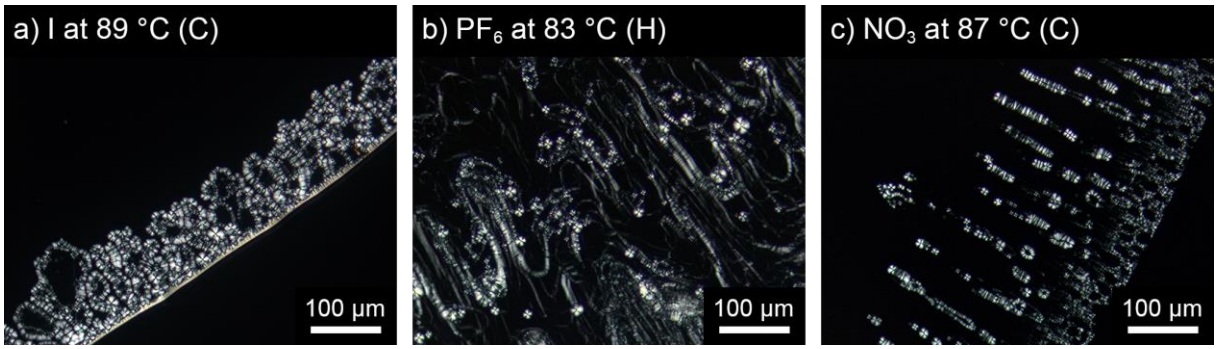


Figure S5. POM images of **3,4-C$_{14}$TyrC$_{14}$X**. H/C: heating/cooling in/from isotropic phase. Rate of 1 or 5 K · min^{-1}.

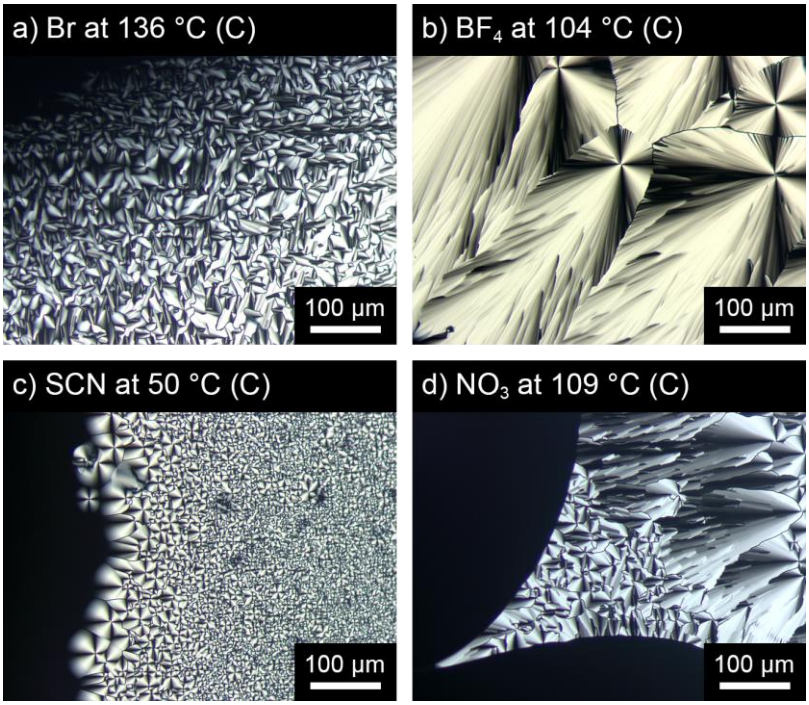


Figure S6. POM images of **3,4,5-C$_{14}$TyrC$_{14}$X**. H/C: heating/cooling in/from isotropic phase. Rate of 1 or 5 K · min^{-1}.

4 Differential Scanning Calorimetry (DSC)

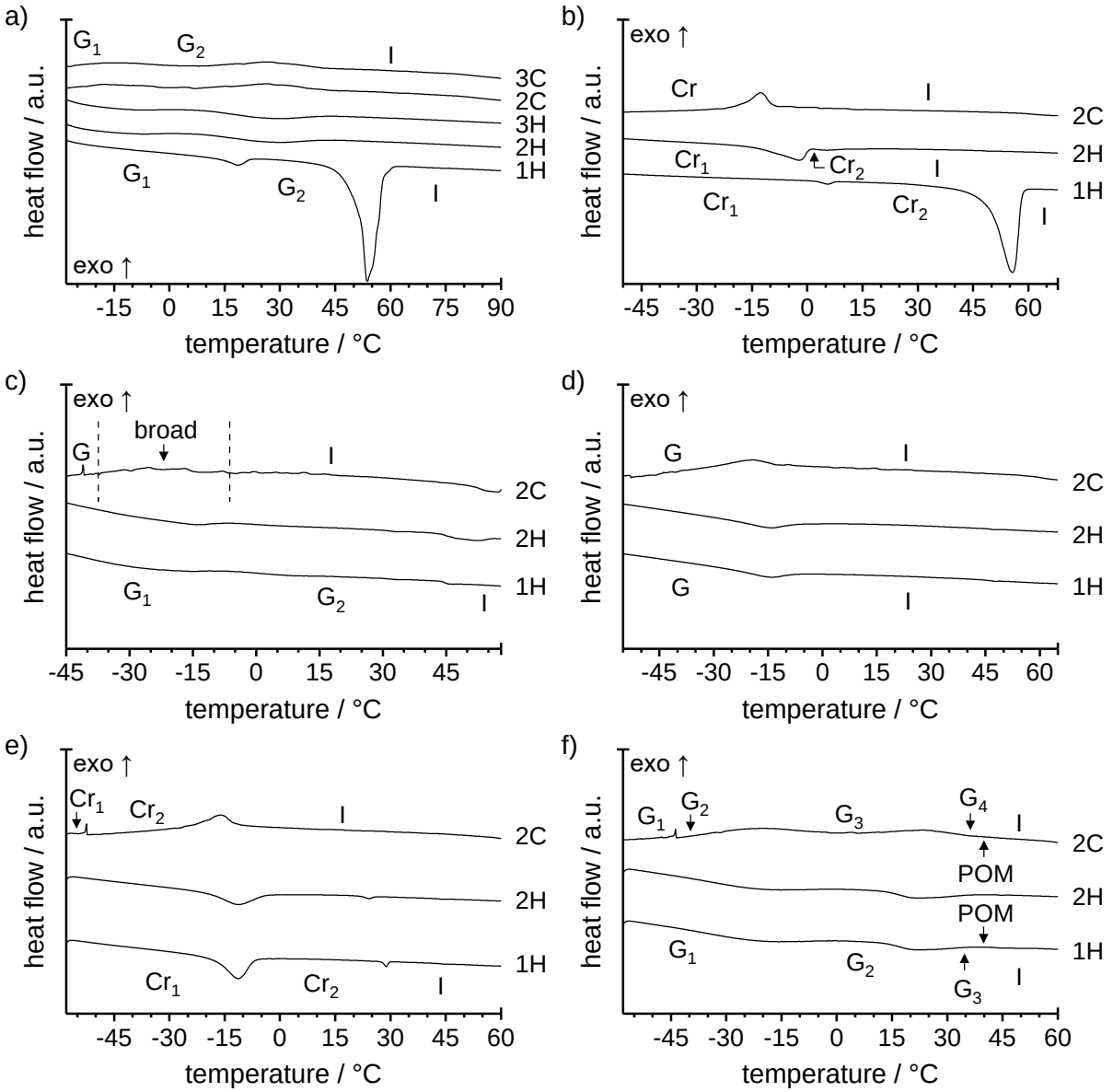


Figure S7. DSC curves of a) **3,5-C$_{14}$TyrC$_{14}$Cl**, b) **3,5-C$_{14}$TyrC$_{14}$Br**, c) **3,5-C$_{14}$TyrC$_{14}$I**, d) **3,5-C$_{14}$TyrC$_{14}$PF$_6$**, e) **3,5-C$_{14}$TyrC$_{14}$BF$_4$** and f) **3,5-C$_{14}$TyrC$_{14}$NO$_4$**; Cr: crystalline; G: glass-like; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min^{-1}).

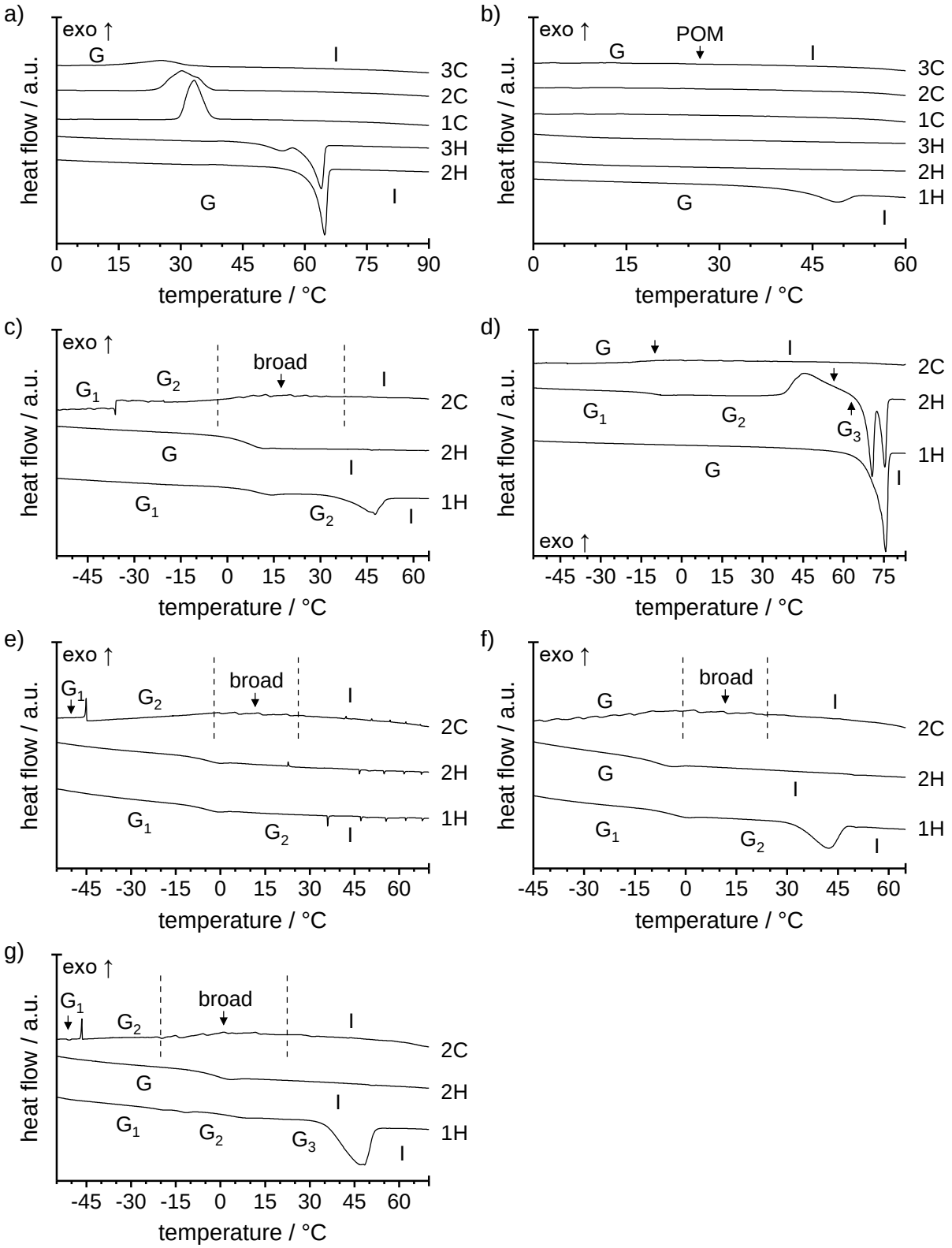


Figure S8. DSC curves of a) **BzTyrC$_{12}$Cl**, b) **BzTyrC$_{14}$Cl**, c) **BzTyrC$_{14}$Br**, d) **BzTyrC$_{14}$I**, e) **BzTyrC$_{14}$PF$_6$**, f) **BzTyrC$_{14}$BF$_4$** and g) **BzTyrC$_{14}$NO$_4$**; G: glass-like; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min^{-1}).

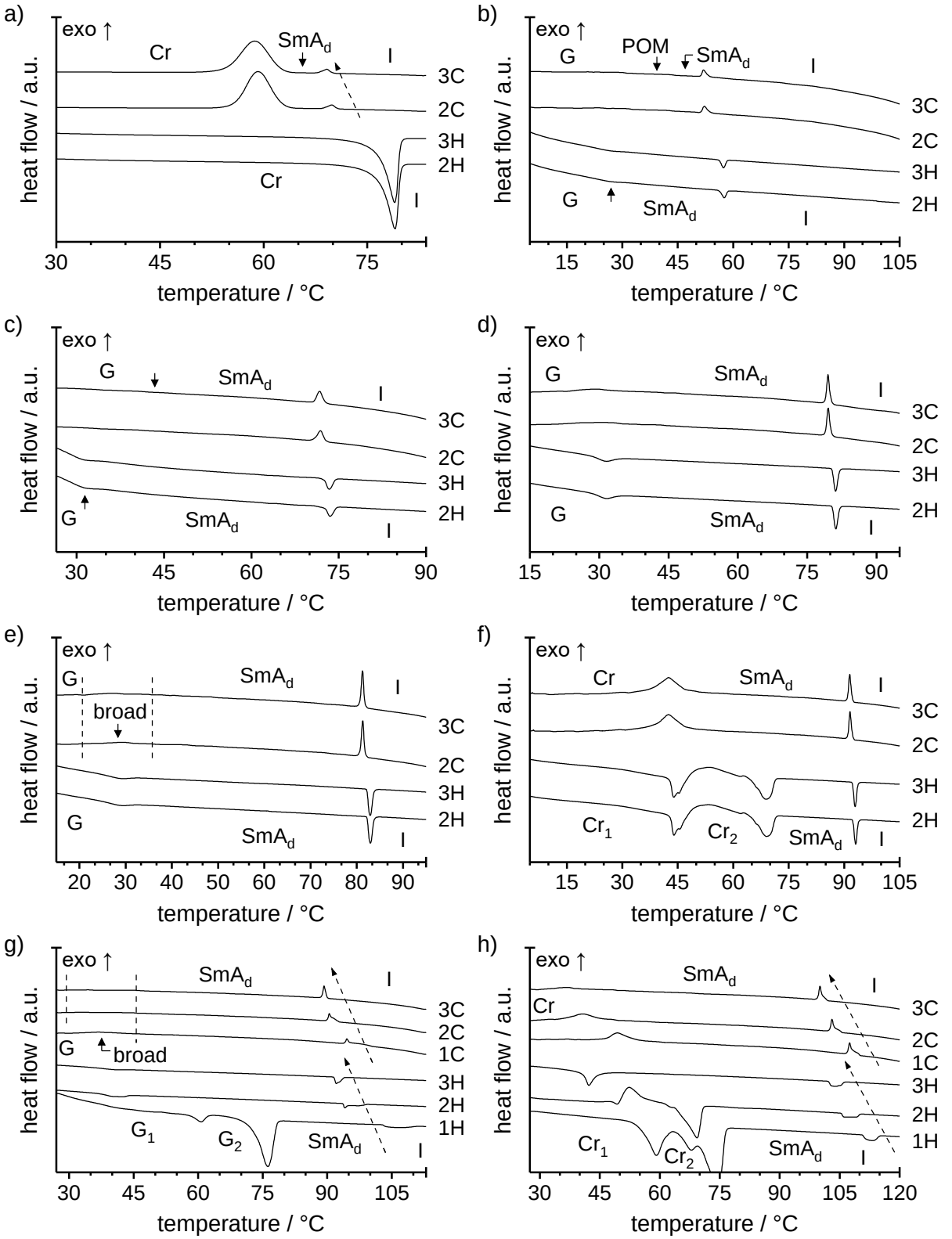


Figure S9. DSC curves of a) **4-C$_{10}$TyrC$_{10}$Cl**, b) **4-C$_{12}$TyrC$_{10}$Cl**, c) **4-C$_{14}$TyrC$_{10}$Cl**, d) **4-C$_{10}$TyrC$_{12}$Cl**, e) **4-C$_{12}$TyrC$_{12}$Cl**, f) **4-C$_{14}$TyrC$_{12}$Cl**, g) **4-C$_{12}$TyrC$_{14}$Cl** and h) **4-C$_{14}$TyrC$_{14}$Cl**; Cr: crystalline; G: glass-like; SmA$_d$: smectic A$_d$; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min^{-1}).

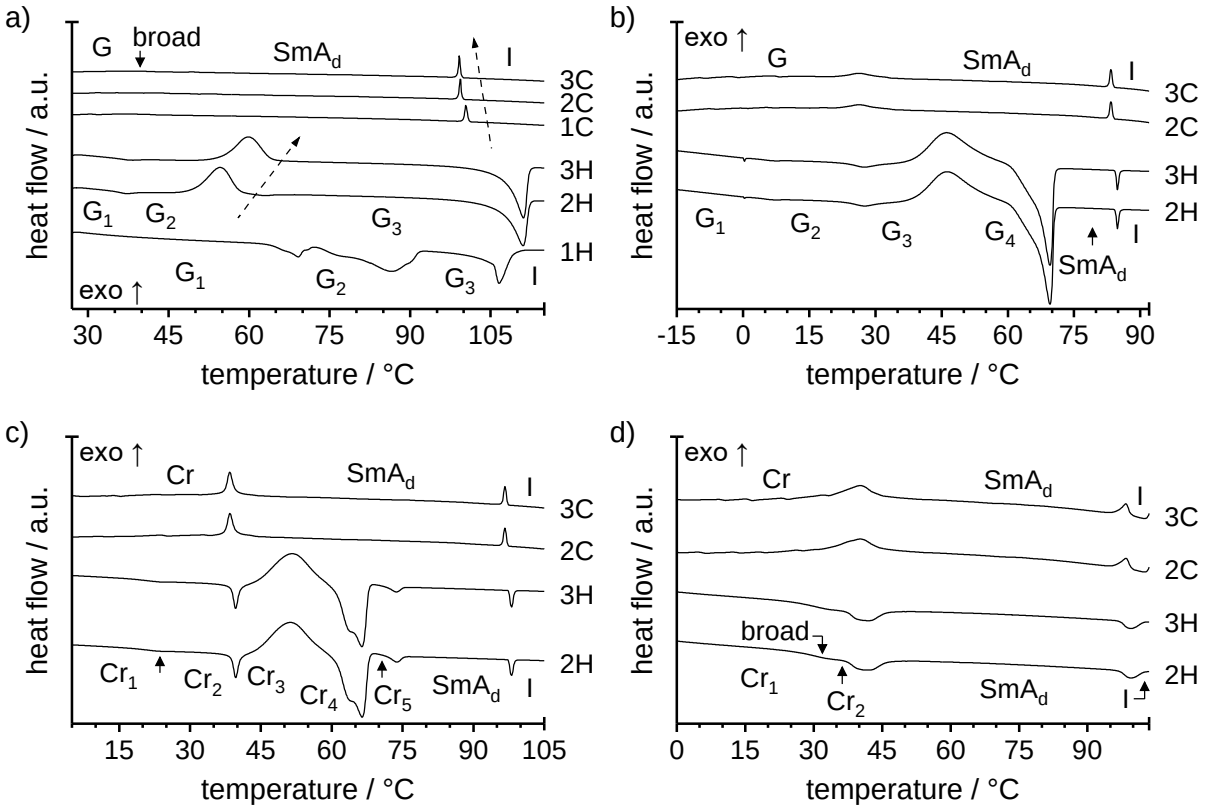


Figure S10. DSC curves of **4-C$_{14}$TyrC$_{14}$X** with X a) I, b) PF_6, c) BF_4 and d) NO_4; Cr: crystalline; G: glass-like; SmA_d: smectic A_d; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K · min^{-1}). Dashed arrows correspond to decomposition.

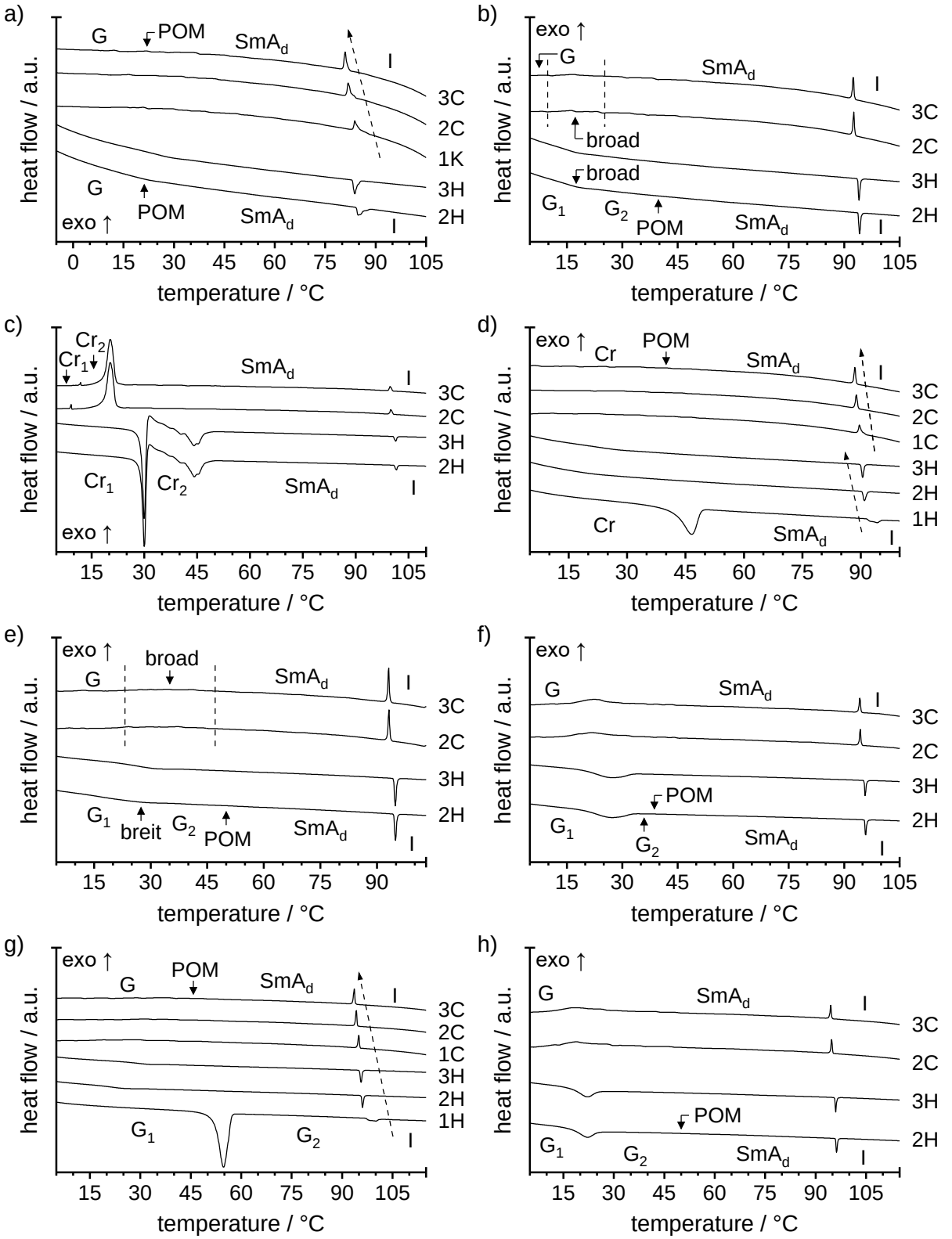


Figure S11. Part one: DSC curves of a) **3,4-C$_{10}$TyrC$_{10}$Cl**, b) **3,4-C$_{12}$TyrC$_{10}$Cl**, c) **3,4-C$_{14}$TyrC$_{10}$Cl**, d) **3,4-C$_{10}$TyrC$_{12}$Cl**, e) **3,4-C$_{12}$TyrC$_{12}$Cl**, f) **3,4-C$_{14}$TyrC$_{12}$Cl**, g) **3,4-C$_{10}$TyrC$_{14}$Cl** and h) **3,4-C$_{12}$TyrC$_{14}$Cl**; Cr: crystalline; G: glass-like; SmA$_d$: smectic A$_d$; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min^{-1}).

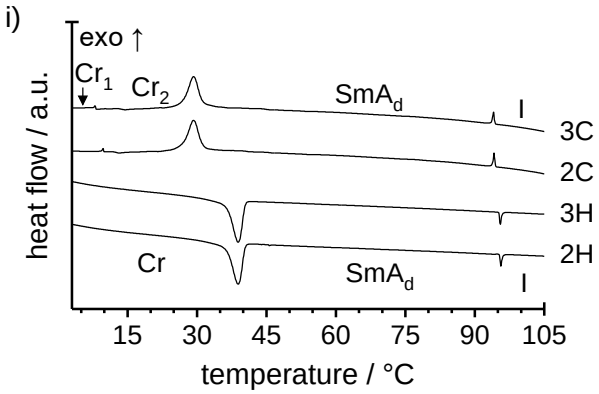


Figure S11. Part two: DSC curves of i) **3,4-C$_{14}$TyrC$_{14}$Cl**.

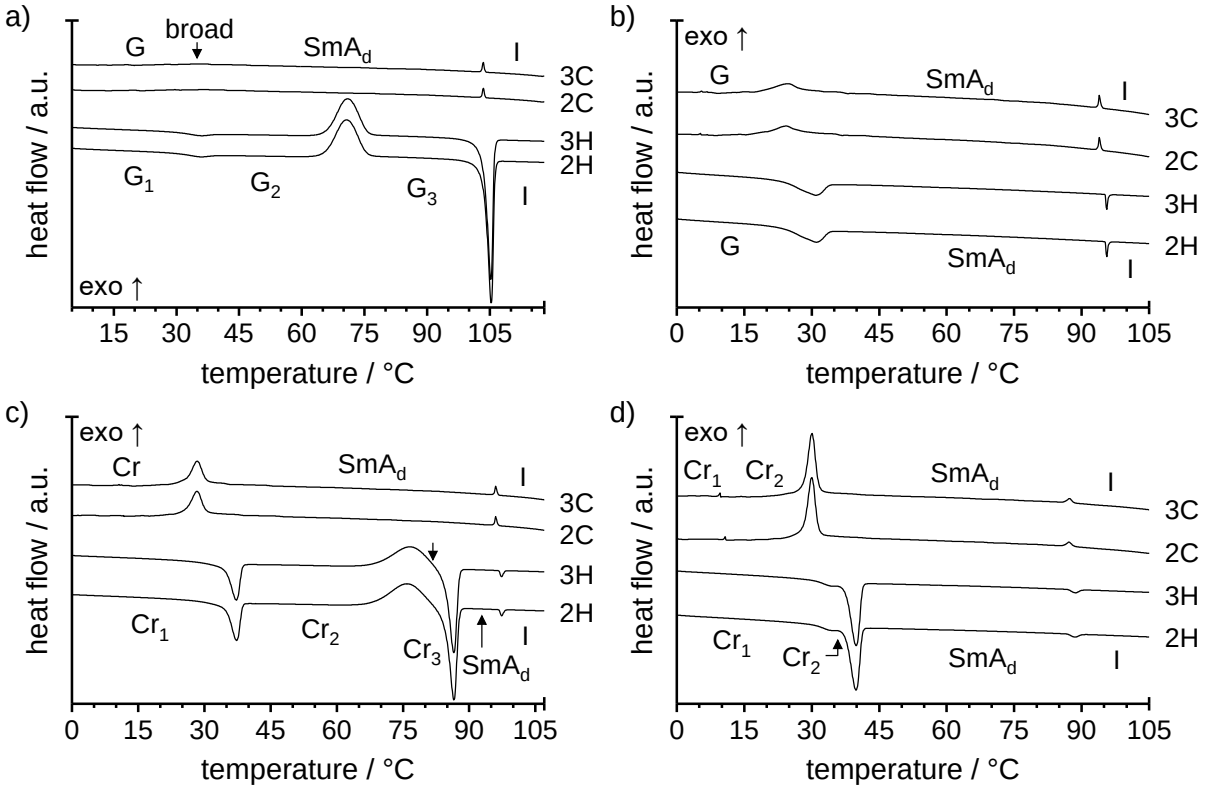


Figure S12. DSC curves of **3,4-C$_{14}$TyrC$_{14}$X** with X a) I, b) PF_6, c) BF_4 and d) NO_4; Cr: crystalline; G: glass-like; SmA_d: smectic A_d; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K · min^{-1}). Dashed arrows correspond to decomposition.

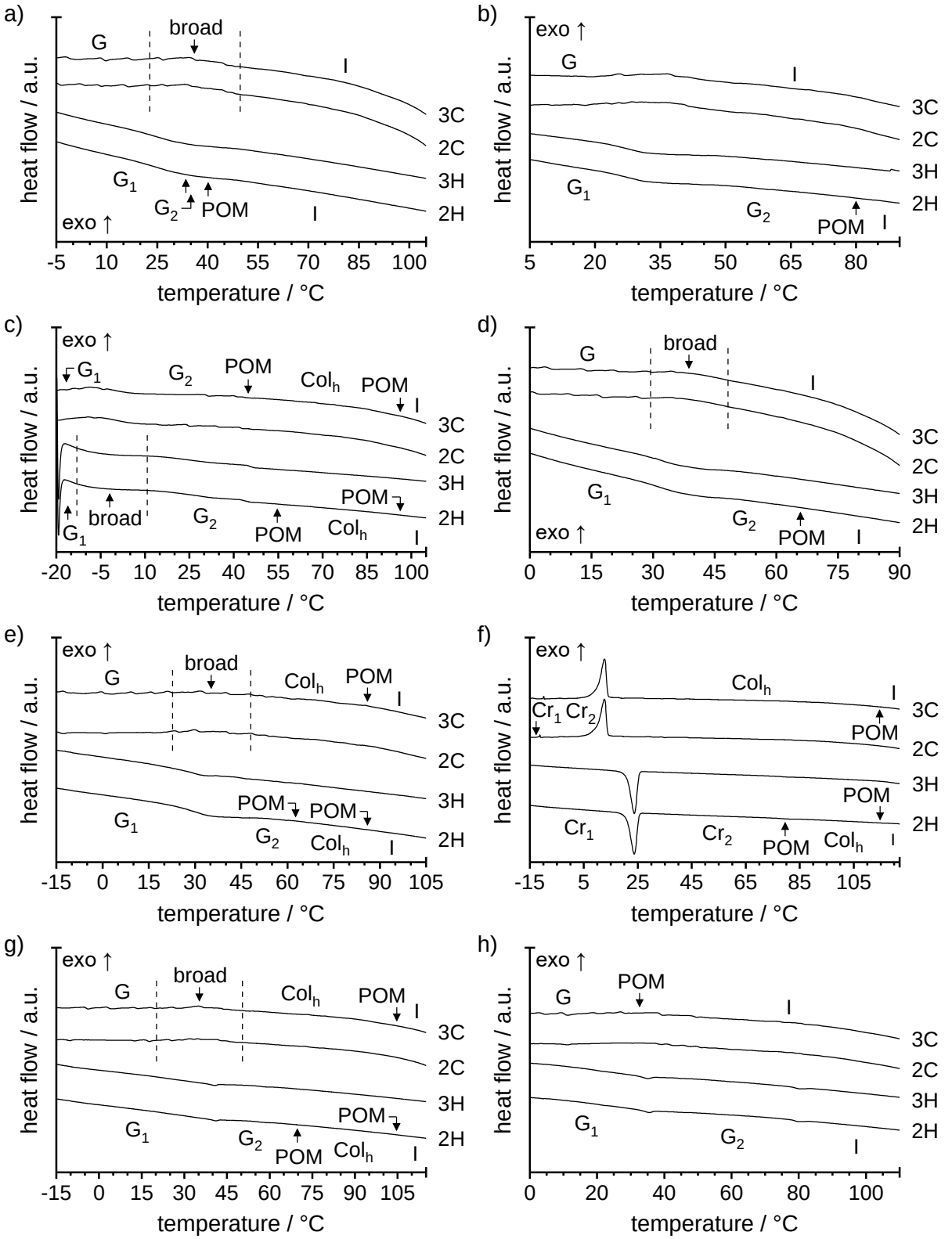


Figure S13. Part one: DSC curves of a) **3,4,5-C$_{10}$TyrC$_{10}$Cl**, b) **3,4,5-C$_{12}$TyrC$_{10}$Cl**, c) **3,4,5-C$_{14}$TyrC$_{10}$Cl**, d) **3,4,5-C$_{10}$TyrC$_{12}$Cl**, e) **3,4,5-C$_{12}$TyrC$_{12}$Cl**, f) **3,4,5-C$_{14}$TyrC$_{12}$Cl**, g) **3,4,5-C$_{10}$TyrC$_{14}$Cl** and h) **3,4,5-C$_{12}$TyrC$_{14}$Cl**; Cr: crystalline; G: glass-like; Col$_h$: columnar hexagonal; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min^{-1}).

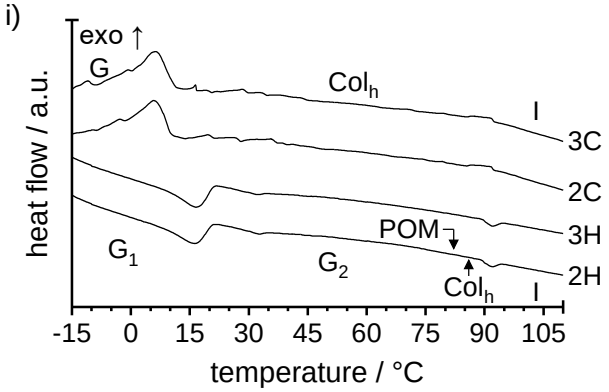


Figure S13. Part two: DSC curves of i) **3,4,5-C$_{14}$TyrC$_{14}$Cl**.

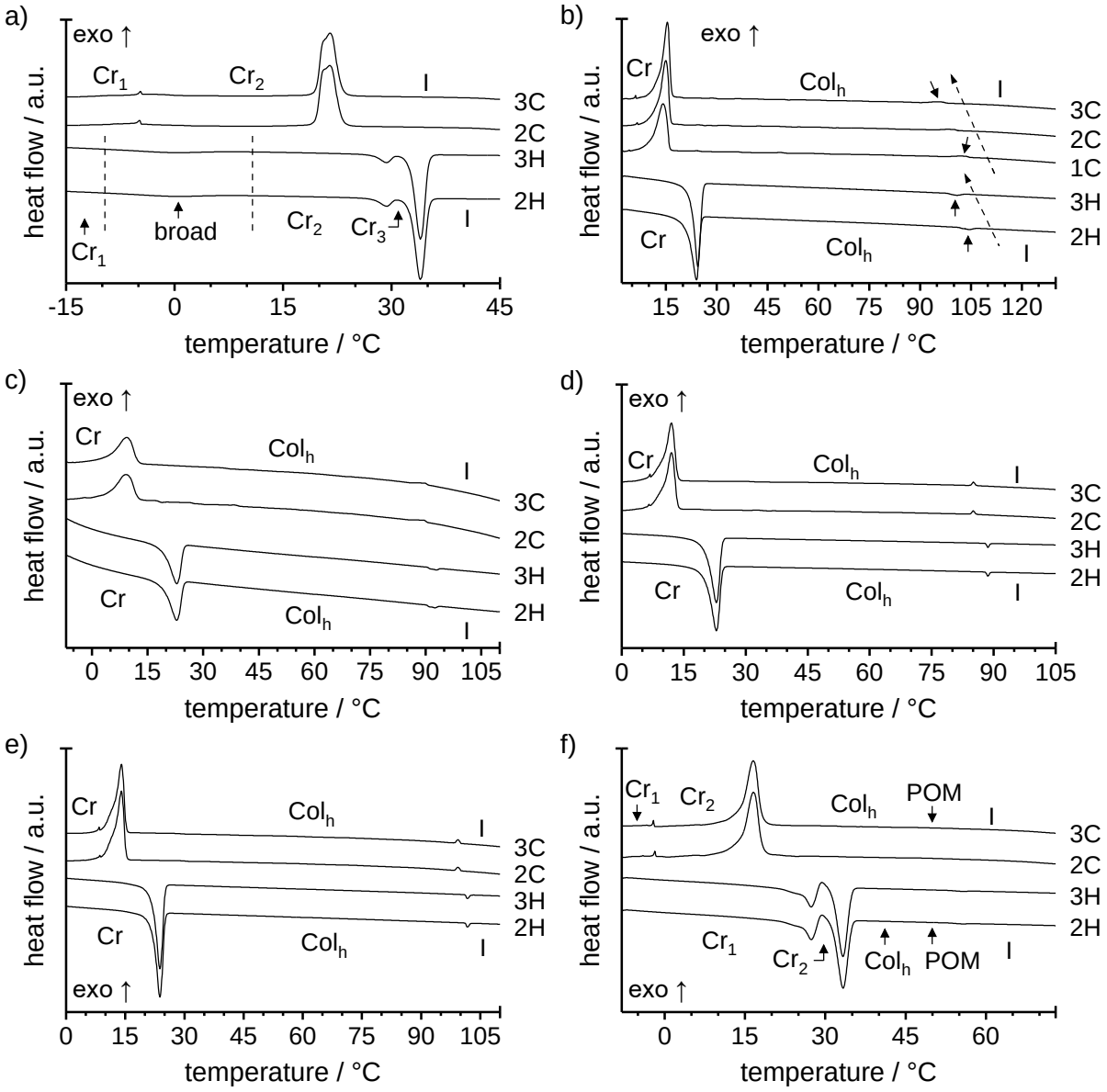


Figure S14. Part one: DSC curves of **3,4-C$_{14}$TyrC$_{14}$X** with X a) OTf, b) Br, c) I, d) PF_6, e) BF_4 and f) SCN; Cr: crystalline; Col$_h$: columnar hexagonal; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K · min^{-1}). Dashed arrows correspond to decomposition.

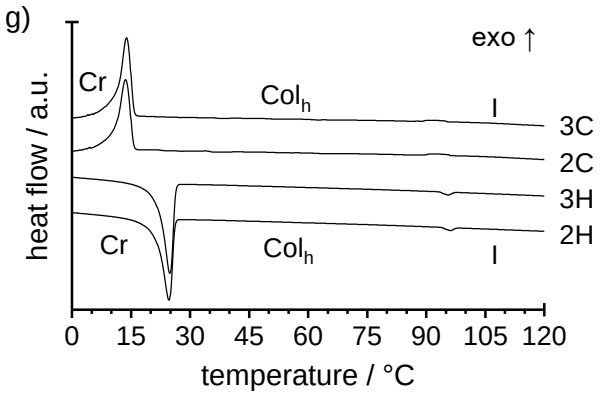


Figure S14. Part two: DSC curves of g) **3,4,5-C_{14}Tyr$C_{14}$$NO_3$**.

5 Phase Temperature Ranges

Table S1. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium salts **BzTyrC$_n$Cl** and **BzTyrC$_{14}$X**. G: Glass-like; I: isotropic liquid; • observed in DSC; ⁕ observed in POM; – not observed. Values from DSC with cooling/heating rates of 5 K · min^{-1}.

n	X	G_1			G_2			G_3			I	
10	Cl	⁕	33.0		–			–			⁕	H
		⁕	25.0		–			–			⁕	C
12	Cl	•	64.0	(–42.1)	–			–			•[a]	1st H
		•[b]	37.1	(48.2)	–			–			•[a]	1st C
14	Cl	•	43.4	(–6.13)	–			–			•	1st H
		⁕	27.0		–			–			⁕	1st C
	Br	•	6.63	(–0.75)	•	42.7	(–4.65)	–			•	1st H
		•	–35.9	(–0.16)	•	14.5	(2.84)	–			•	1st C
	I	•	72.4	(–46.0)	–			–			•	1st H
		•	1.52	(3.35)	–			–			•	1st C
	PF_6	•	–8.05	(–1.13)	•	35.6	(–0.16)	–			•	1st H
		•	–44.8	(0.49)	•	6.35	(1.19)	–			•	1st C
	BF_4	•	–6.46	(–0.45)	•	32.8	(–6.83)	–			•	1st H
		•	5.24	(3.59)	–			–			•	1st C
	NO_3	•	–14.6	(–0.18)	•	0.13	(–0.78)	•	35.4	(–13.6)	•	1st H
		•	–46.3	(0.23)	•	21.3	(2.02)	–			•	1st C

[a] decomposition. [b] supercooled.

Table S2. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium salts **3,5-C$_m$TyrC$_n$Cl** and **3,5-C$_{14}$TyrC$_{14}$X**. G: Glass-like; I: isotropic liquid; • observed in DSC; ⁕ observed in POM; – not observed. Values from DSC with cooling/heating rates of 5 K · min^{-1}.

n	m	X	G_1			G_2			G_3			I	
14	14	Cl	•	13.5	(–3.54)	•	50.9	(–58.9)	–			•	1st H
			•[a]	1.33	(1.99)	•[b]	18.2	(–3.92)	–			•	2nd H
			•	–13.1	(1.61)	•[b]	34.7	(9.75)	–			•	2nd C
		Br	•[c]	2.61	(–1.15)	•[c]	48.9	(–82.9)	–			•	1st H
			•[c]	–8.98	(22.5)	–			–			•	1st C
		I	•	44.1	(–1.67)	–			–			•	1st H
			•	–21.6	(5.32)	–			–			•	1st C
		PF_6	•	46.3	(–0.07)	•	46.3	(–0.07)	–			•	1st H
			•	–12.4	(6.90)	–			–			•	1st C
		BF_4	•[c]	–18.1	(–15.4)	•[c]	27.6	(–0.61)	–			•	1st H
			•[c]	–52.3	(0.06)	•[c]	–11.5	(11.7)	–			•	1st C
		NO_3	•	–34.3	(–6.72)	•	13.5	(–5.84)	⁕	40.0		⁕	1st H
			•	–43.5	(0.34)	•	–1.40	(11.7)	•	33.1	(5.94)	•	1st C

[a] cold crystalisation. [b] supercooled. [c] crystalline (Cr).

Table S3. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium chlorides **4-C$_m$TyrC$_n$Cl**. Cr: Crystalline; G: glass-like; SmA$_d$: smectic A$_d$; I: isotropic liquid; • observed in DSC; ⁎ observed in POM; – not observed. Values from DSC (2nd cycle) with cooling/heating rates of 5 K · min^{-1}.

n	m	Cr_1			Cr_2			SmA_d			I	
10	10	⁎	55.0		–			–			⁎	no
		⁎[a]	35.0		–			–			⁎	no
	12	•	76.7	(–51.9)	–			–			•[b]	1st H
		•[a]	63.0	(53.0)	–			•	71.5	(1.71)	•[b]	1st C
	14	•[c]	16.8	(–1.69)	–			•	56.1	(–0.97)	•	2nd H
		⁎[c]	39.0		–			•	53.8	(0.97)	•	2nd C
12	10	•[c,d]	32.1	(0.36)	•	60.3	(–)	•	72.5	(–1.66)	•	2nd H
		•[c]	43.1	(0.01)	–			•	72.9	(1.78)	•	2nd C
	12	•[c]	27.8	(–1.50)	–			•	80.4	(–1.67)	•	2nd H
		•[c]	35.3	(0.86)	–			•	80.3	(1.70)	•	2nd C
	14	•[c]	24.7	(–0.70)	–			•	82.2	(–1.57)	•	2nd H
		•[c]	33.2	(0.92)	–			•	81.9	(1.60)	•	2nd C
14	10	•	42.9	(–6.46)	•	65.5	(–7.71)	•	92.3	(–2.03)	•	2nd H
		•	47.6	(8.69)	–			•	92.4	(2.05)	•	2nd C
	12	•[c]	58.0	(–3.48)	•	72.6	(–35.7)	•	102.8	(–2.47)	•[b]	1st H
		•[a,c]	43.0	(2.50)	–			•	95.5	(1.96)	•[b]	1st C
	14	•	55.4	(–16.2)	•	70.7	(–45.2)	•	110.6	(–2.33)	•[b]	1st H
		•	54.1	(5.25)	–			•	108.5	(2.09)	•[b]	1st C

[a] supercooled. [b] decomposition (G). [c] glass transition (G). [d] cold crystallisation.

Table S4. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium chlorides **3,4-C$_m$TyrC$_n$Cl**. Cr: Crystalline; G: glass-like; SmA$_d$: smectic A$_d$; I: isotropic liquid; • observed in DSC; ⁎ observed in POM; – not observed. Values from DSC (2nd cycle) with cooling/heating rates of 5 K · min^{-1}.

n	m	Cr$_1$			Cr$_2$			SmA$_d$			I	
10	10	•[a]	31.5	(–11.3)	–			•	88.6	(–1.66)	•[b]	1st H
		⁎[a]	27.0		–			•	85.3	(1.64)	•[b]	1st C
	12	•[a]	12.6	(–2.14)	–			•	93.6	(–1.48)	•	2nd H
		•[a]	17.9	(1.75)	–			•	93.1	(1.45)	•	2nd C
	14	•[c]	28.7	(–42.3)	•	41.8	(–14.6)	•	100.8	(–1.02)	•	2nd H
		•[c]	9.50	(0.44)	•	22.0	(33.3)	•	100.8	(1.01)	•	2nd C
12	10	•	41.7	(–27.6)	–			•	91.5	(–1.59)	•[b]	1st H
		⁎	40.0		–			•	90.6	(1.54)	•[b]	1st C
	12	•[a]	19.6	(–1.53)	–			•	94.3	(–1.56)	•	2nd H
		•[a]	38.8	(4.15)	–			•	93.7	(1.67)	•	2nd C
	14	•[a]	19.3	(–8.23)	–			•	95.4	(–1.08)	•	2nd H
		•[a]	32.9	(6.06)	–			•	94.8	(1.10)	•	2nd C
14	10	•[a]	51.9	(–41.8)	•	97.0	(–1.43)	–			•[b]	1st H
		⁎[a]	46.0		–			•	95.4	(1.50)	•[b]	1st C
	12	•[a]	17.3	(–5.97)	–			•	95.8	(–1.04)	•	2nd H
		•[a]	29.7	(7.08)	–			•	95.2	(1.04)	•	2nd C
	14	•	36.3	(–18.2)	–			•	95.2	(–0.80)	•	2nd H
		•[c]	9.97	(0.12)	•	31.4	(15.3)	•	94.6	(0.90)	•	2nd C

[a] glass transition (G). [b] decomposition. [c] supercooled.

Table S5. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium salts **4-C$_{14}$TyrC$_{14}$X** and **3,4-C$_{14}$TyrC$_{14}$X**. Cr: Crystalline; G: glass-like; SmA_d: smectic A_d; I: isotropic liquid; • observed in DSC; ⁕ observed in POM; – not observed. Values from DSC (2nd cycle) with cooling/heating rates of 5 K · min^{-1}.

	X	Cr_1			Cr_2			Cr_3			SmA_d			I	
4	I	•[a]	65.8	(–5.51)	•	77.3	(–33.4)	•	105.0	(–20.0)	–			•[b]	1st H
		•[a,c]	43.8	(1.62)	–			–			•	101.0	(1.60)	•[b]	1st C
	PF_6	•[a,d]	23.0	(–2.42)	•[e]	38.7	(-35.8)	•	65.5	(–50.3)	•	84.2	(–1.58)	•	2nd H
		•[a,c]	29.9	(1.78)	–			–			•	84.0	(1.57)	•	2nd C
	BF_4	•[a,f]	43.9	(35.6)	•	60.9	(–34.6)	•	71.2	(–2.10)	•	97.3	(–1.72)	•	2nd H
		•[c]	39.8	(5.86)	–			–			•	97.3	(1.72)	•	2nd C
	NO_3	•	26.4	(–0.27)	•	37.4	(–4.21)	–			•	97.0	(–2.01)	•	2nd H
		•	45.0	(8.25)	–			–			•	99.7	(1.94)	•	2nd C
3,4	I	•[a]	–30.3	(–3.47)	•[e]	65.6	(50.7)	•	103.3	(–61.3)	–			•	2nd H
		•[a,c]	51.5	(5.20)	–			–			•	104.0	(1.19)	•	2nd C
	PF_6	•[a]	23.5	(–12.7)	–			–			•	95.1	(–1.01)	•	2nd H
		•[a]	28.7	(10.9)	–			–			•	94.6	(1.02)	•	2nd C
	BF_4	•	34.7	(–19.4)	•[e]	67.6	(46.0)	•	84.4	(–33.5)	•	96.6	(–0.94)	•	2nd H
		•	30.5	(15.4)	–			–			•	96.6	(0.95)	⁕	2nd C
	NO_3	•[e]	26.4	(0.27)	•[a]	37.4	(–19.1)	–			•	86.8	(–0.81)	•	2nd H
		•	11.0	(0.17)	•[a]	31.6	(20.2)	–			•	88.4	(0.85)	•	2nd C

[a] glass transition (G). [b] decomposition. [c] supercooled. [d] additional G–G transition at 0.00 °C (–0.08). [e] cold crystallisation.
[f] additional G–G transition at 38.6 °C (–5.30).

Table S6. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium chlorides **3,4,5-C$_m$TyrC$_n$Cl**. Cr: Crystalline; G: glass-like; Col$_h$: columnar hexagonal; I: isotropic liquid; • observed in DSC; ⁕ observed in POM; – not observed. Values from DSC (2nd cycle) with cooling/heating rates of 5 K · min^{-1}.

n	m	Cr$_1$			Cr$_2$			Col$_h$			I	
10	10	•[a]	10.4	(–11.4)				–			•	2nd H
		•[a]	47.3	(14.3)				–			•	2nd C
	12	•[a]	20.9	(–14.1)				–			•	2nd H
		•[a,b]	53.6	(11.5)				–			•	2nd C
	14	•[a]	–16.5	(–11.2)				⁕	100.0		⁕	2nd H
		•[c]	–4.03	(7.53)	⁕[a,b]	(45.0)		⁕	96.0		⁕	2nd C
12	10	•[a]	25.2	(–5.76)				–			•	2nd H
		•[a,b]	41.3	(4.48)				–			•	2nd C
	12	•[a]	25.9	(–6.87)				⁕	86.6		⁕	2nd H
		•[a]	32.1	(2.57)				⁕	86.6		⁕	2nd C
	14	•	20.9	(–43.8)				⁕	115.0		⁕	2nd H
		•	–11.0	(0.40)	•[d]	13.8	(39.4)	⁕	115.0		⁕	2nd C
14	10	•[a]	34.1	(–6.66)				⁕	105.0		⁕	2nd H
		•[a,b]	56.6	(7.51)				⁕	105.0		⁕	2nd C
	12	•	32.1	(–1.12)	•	77.9	(–0.41)	–			•	2nd H
		•[a]	81.4	(0.66)				–			•	2nd C
	14	•[a]	6.62	(–10.2)				•	89.6	(–0.79)	•	2nd H
		•[a]	10.3	(19.4)				•	92.4	(0.85)	•	2nd C

[a] glass transition (G). [b] M.p. of 1st heating. [c] cold crystallisation. [d] supercooled.

Table S7. Phase transition temperatures T in °C (-enthalpies ΔH in kJ · mol^{-1}, if available) of guanidinium salts **3,4,5-C$_{14}$TyrC$_{14}$X**. Cr: Crystalline; G: glass-like; Col$_h$: columnar hexagonal; I: isotropic liquid; • observed in DSC; ⁎ observed in POM; – not observed. Values from DSC (2nd cycle) with cooling/heating rates of 5 K · min^{-1}.

X	Cr$_1$			Cr$_2$			Cr$_3$			Col$_h$			I	
OTf	•	–9.39	(–5.07)	•	29.2	(–3.57)	•	32.4	(–40.9)	–			•	2nd H
	•[a]	–4.54	(0.68)	•	23.1	(45.8)	–			–			•	2nd C
Br	•	–16.8	(–6.52)	•	28.7	(–39.6)	–			•	105.7	(–1.87)	•[b]	1st H
	•[a]	16.2	(39.6)	–			–			•	104.8	(1.09)	•[b]	1st C
I	•	18.9	(–24.4)	–			–			•	90.1	(–0.71)	•	2nd H
	•[a]	12.4	(22.0)	–			–			•	90.6	(0.79)	•	2nd C
PF$_6$	•	20.1	(–42.3)	–			–			•	87.9	(–0.65)	•	2nd H
	•[a]	13.6	(38.9)	–			–			•	85.8	(0.63)	•	2nd C
BF$_4$	•	21.7	(–46.7)	–			–			•	101.1	(–0.78)	•	2nd H
	•[a]	15.3	(43.3)	–			–			•	100.2	(0.74)	•	2nd C
SCN	•	24.9	(–21.2)	•	31.2	(–37.7)	–			•	53.2	(–0.35)	•	2nd H
	•[a]	–1.48	(0.40)	•	18.3	(45.3)	–			⁎	50.0		⁎	2nd C
NO$_3$	•	21.3	(–38.5)	–			–			•	93.8	(–0.86)	•	2nd H
	•[a]	15.7	(38.0)	–			–			•	96.2	(0.92)	•	2nd C

[a] supercooled. [b] decomposition.

6 X-Ray Scatterings and Diffraction Profiles (SAXS/WAXS)

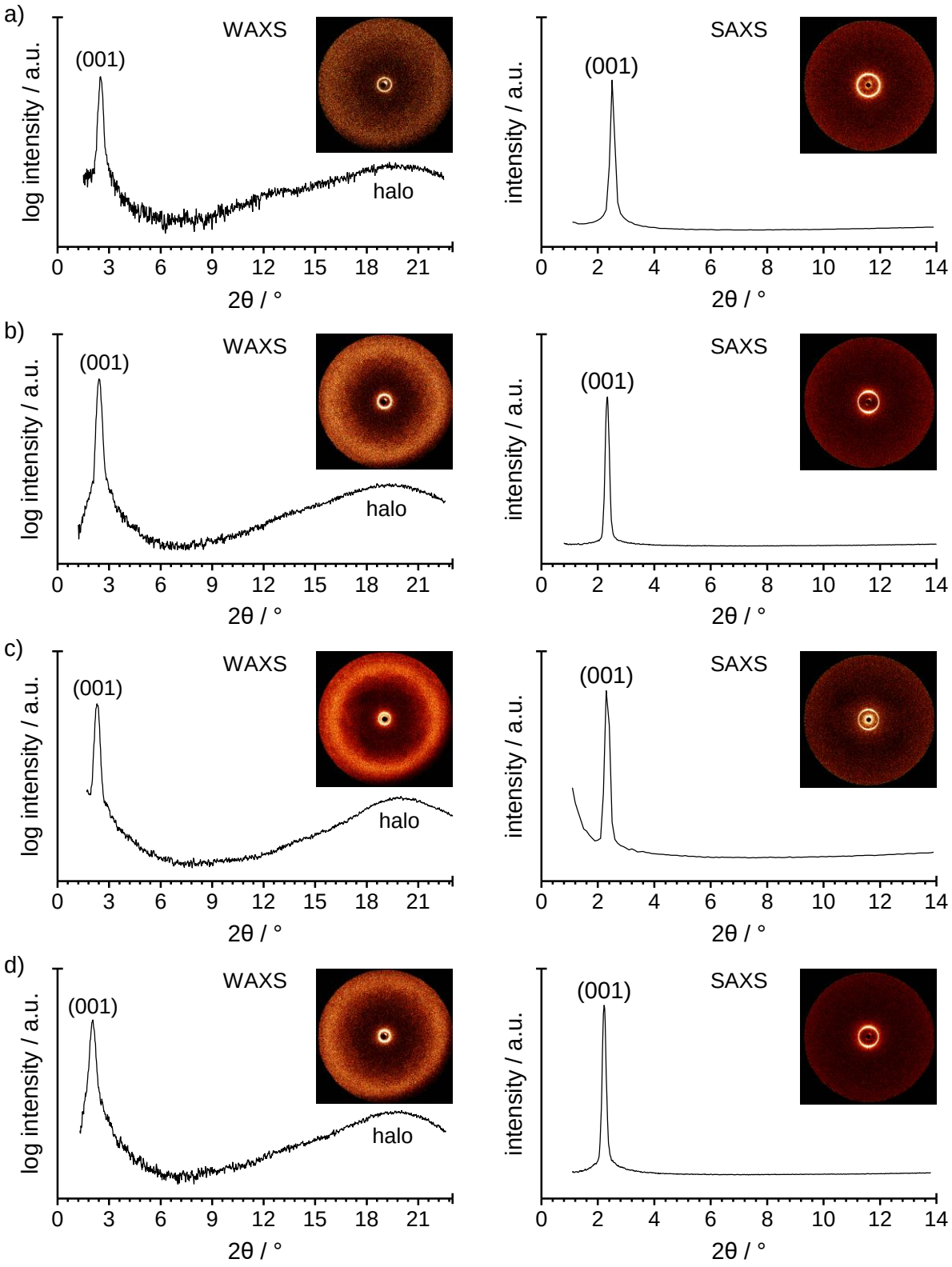


Figure S15. X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of a) **4-C_{14}TyrC_{10}Cl** at 45 °C, b) **4-C_{14}TyrC_{14}Cl** at 98 °C, c) **3,4-C_{12}TyrC_{12}Cl** at 69 °C and d) **3,4-C_{14}TyrC_{14}Cl** at 74 °C.

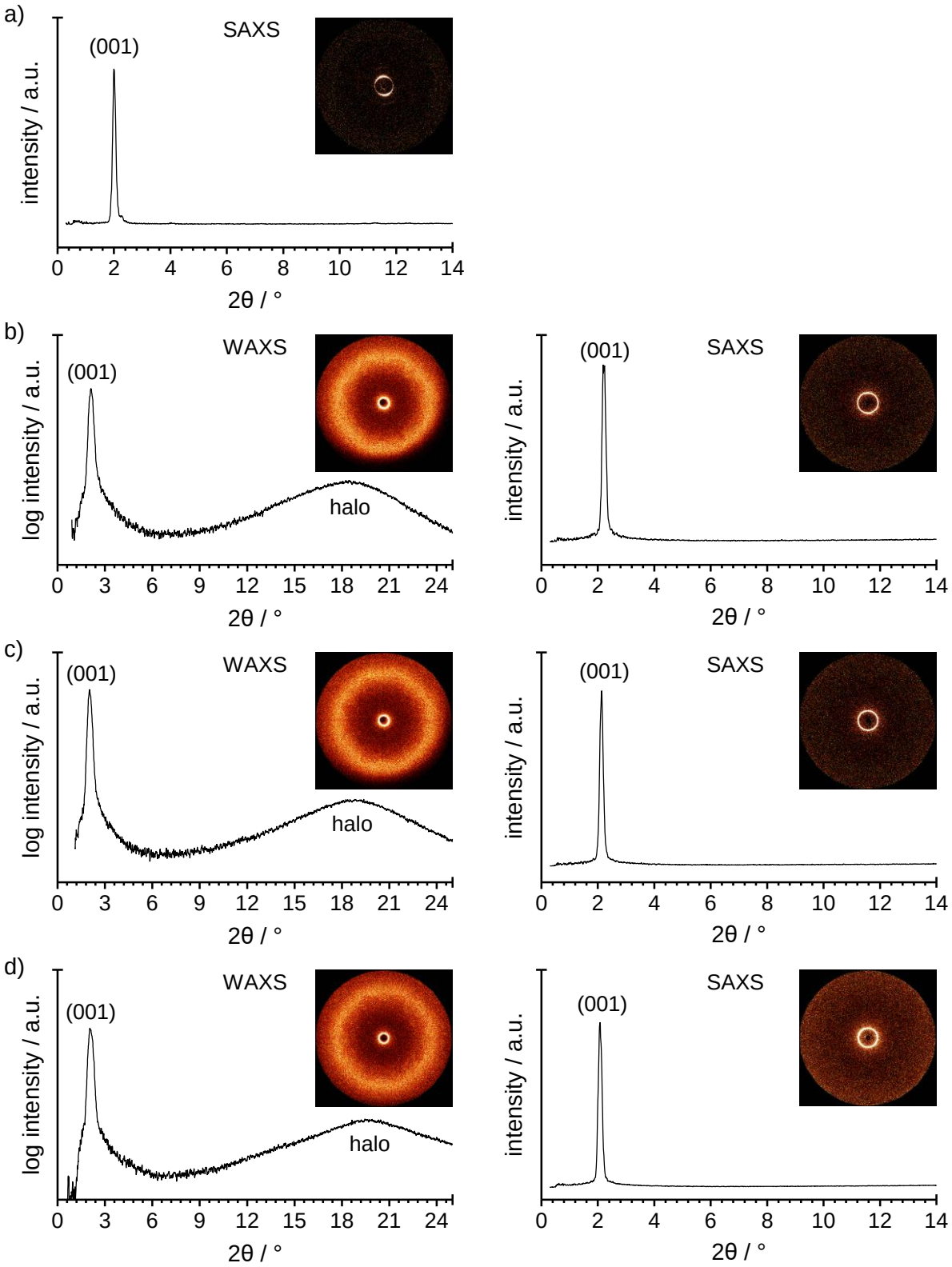


Figure S16. X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of a) **4-C$_{14}$TyrC$_{14}$I** at 95 °C, b) **4-C$_{14}$TyrC$_{14}$PF$_6$** at 70 °C, c) **4-C$_{14}$TyrC$_{14}$BF$_4$** at 61 °C and d) **4-C$_{14}$TyrC$_{14}$NO$_3$** at 70 °C.

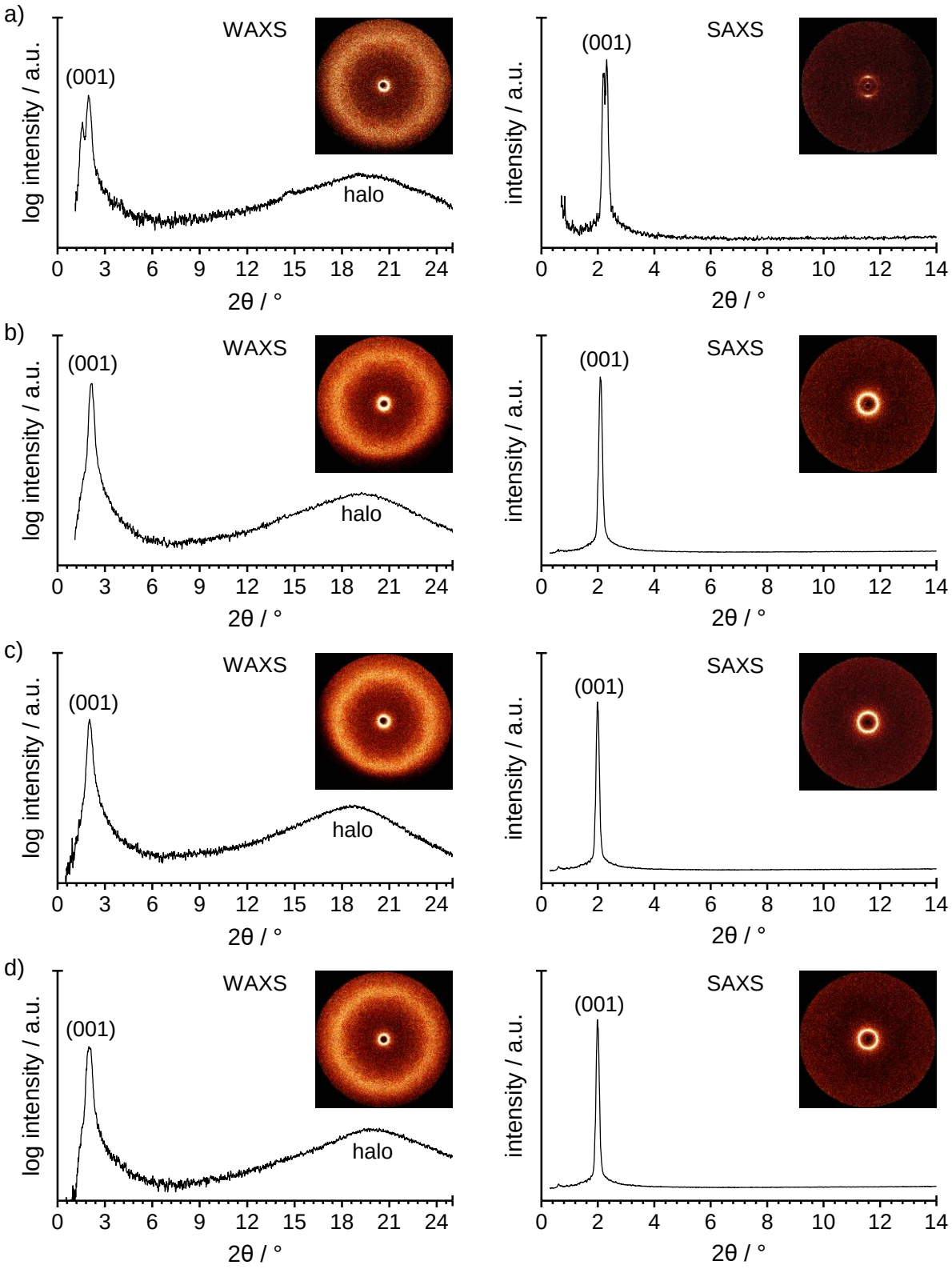


Figure S17. X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of a) **3,4-C$_{14}$TyrC$_{14}$I** at 70 °C, b) **3,4-C$_{14}$TyrC$_{14}$PF$_6$** at 90 °C, c) **3,4-C$_{14}$TyrC$_{14}$BF$_4$** at 80 °C and d) **3,4-C$_{14}$TyrC$_{14}$NO$_3$** at 61 °C.

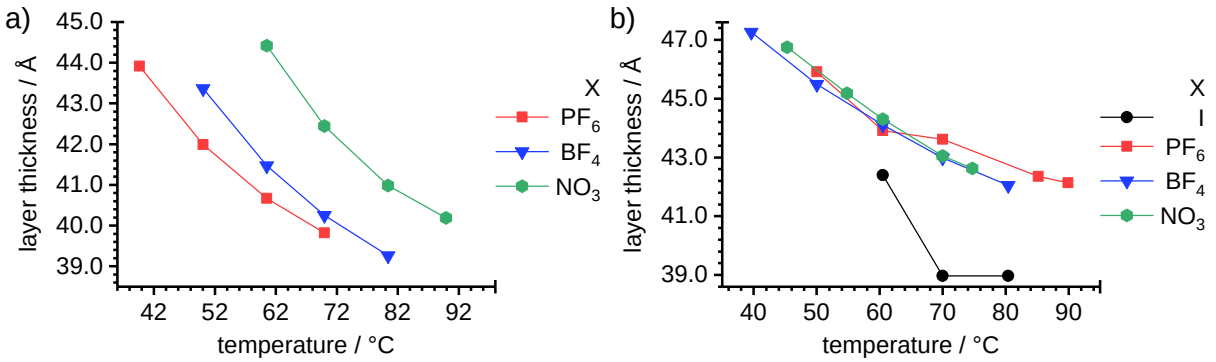


Figure S18. Determined layer distances d_{001} of a) **4-C$_{14}$TyrC$_{14}$X** and b) **3,4-C$_{14}$TyrC$_{14}$X** as a function of temperature.

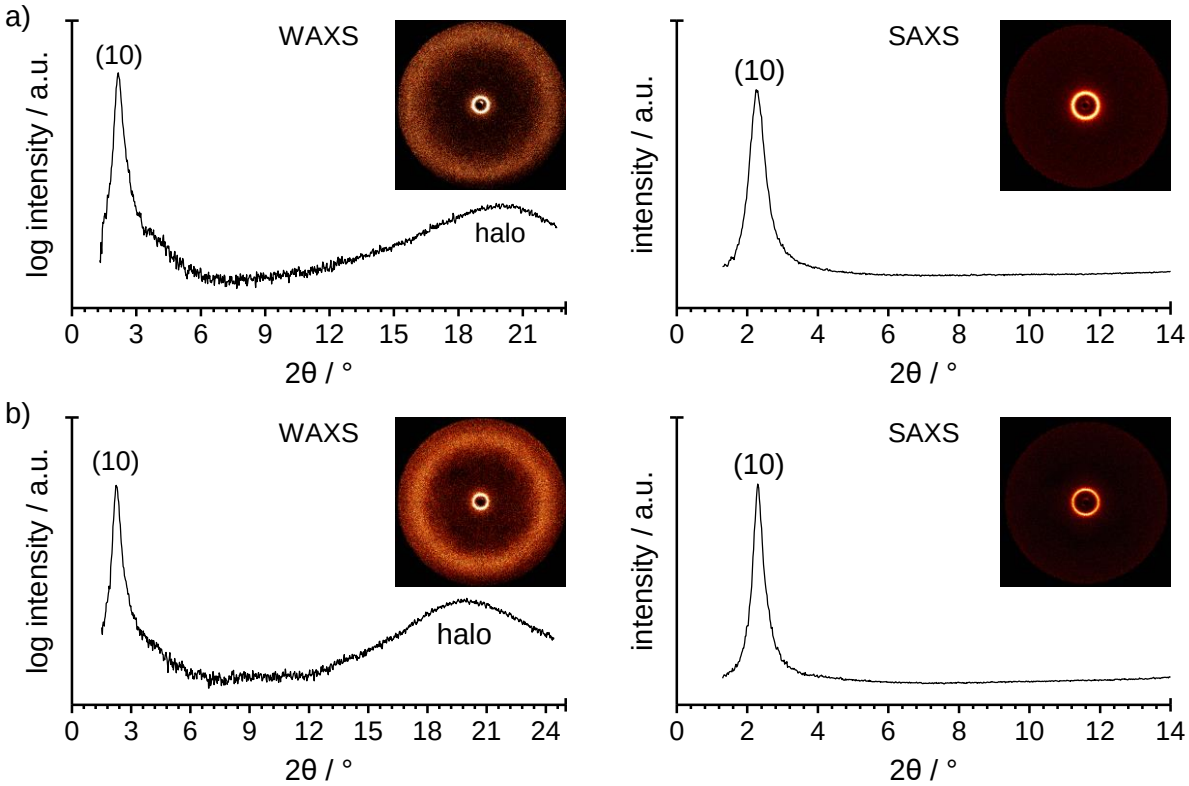


Figure S19. X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of a) **3,4,5-C$_{14}$TyrC$_{10}$Cl** at 45 °C and b) **3,4,5-C$_{14}$TyrC$_{14}$Cl** at 98 °C.

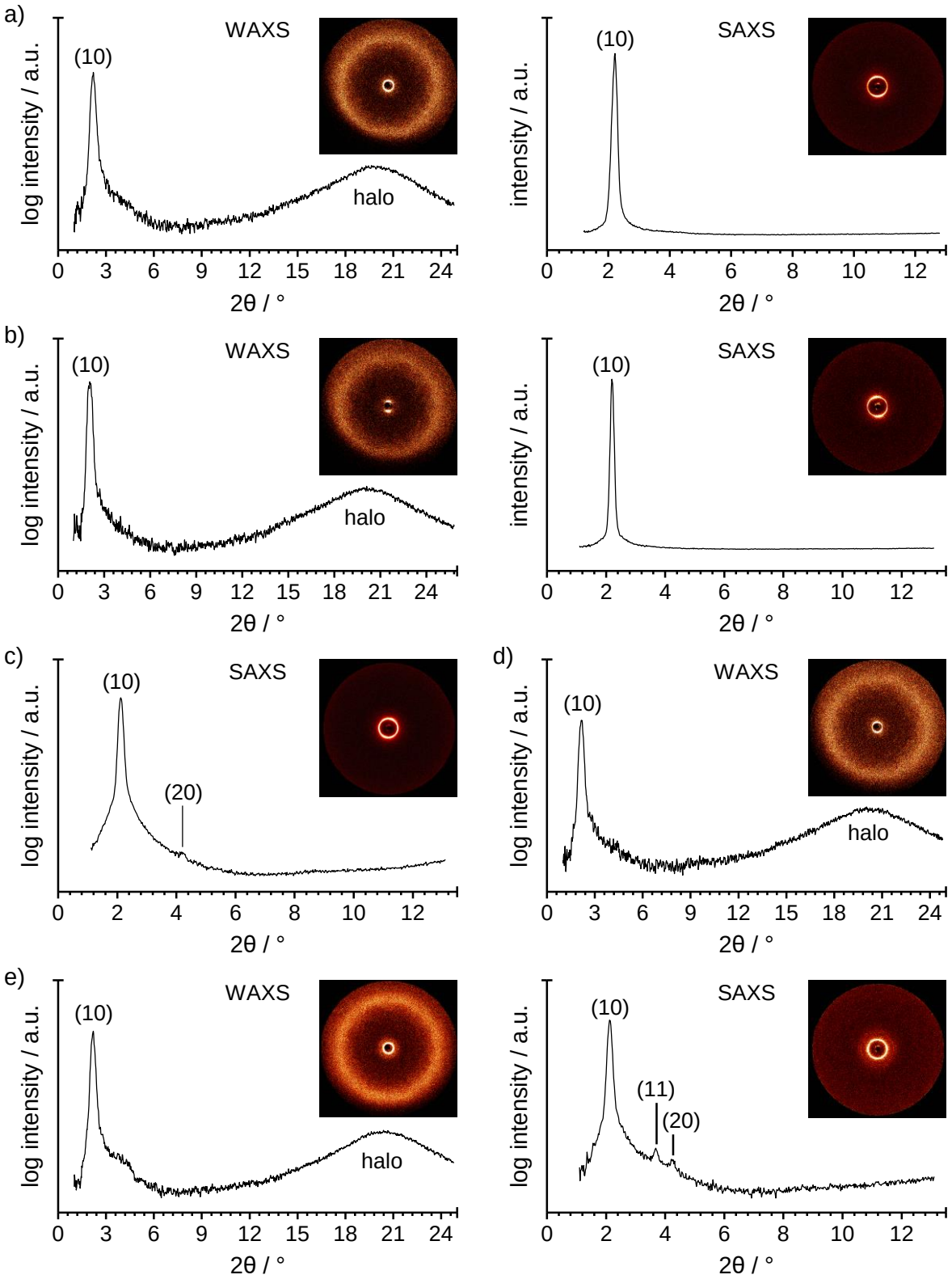


Figure S20. Part one: X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of a) **3,4,5-C$_{14}$TyrC$_{14}$Br** at 55 °C, b) **3,4,5-C$_{14}$TyrC$_{14}$I** at 55 °C, c) **3,4,5-C$_{14}$TyrC$_{14}$PF$_6$**, at 55 °C, d) **3,4,5-C$_{14}$TyrC$_{14}$BF$_4$** at 55 °C and e) **3,4,5-C$_{14}$TyrC$_{14}$SCN** at 41 °C.

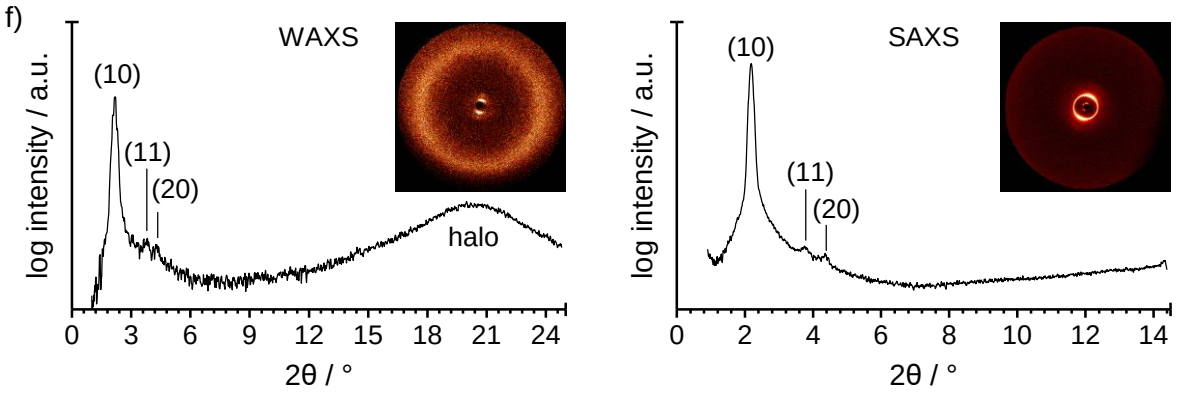


Figure S20. Part two: X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of f) **3,4,5-C_{14}Tyr$C_{14}NO_3$** at 55 °C.

7 Proposed Packing Models

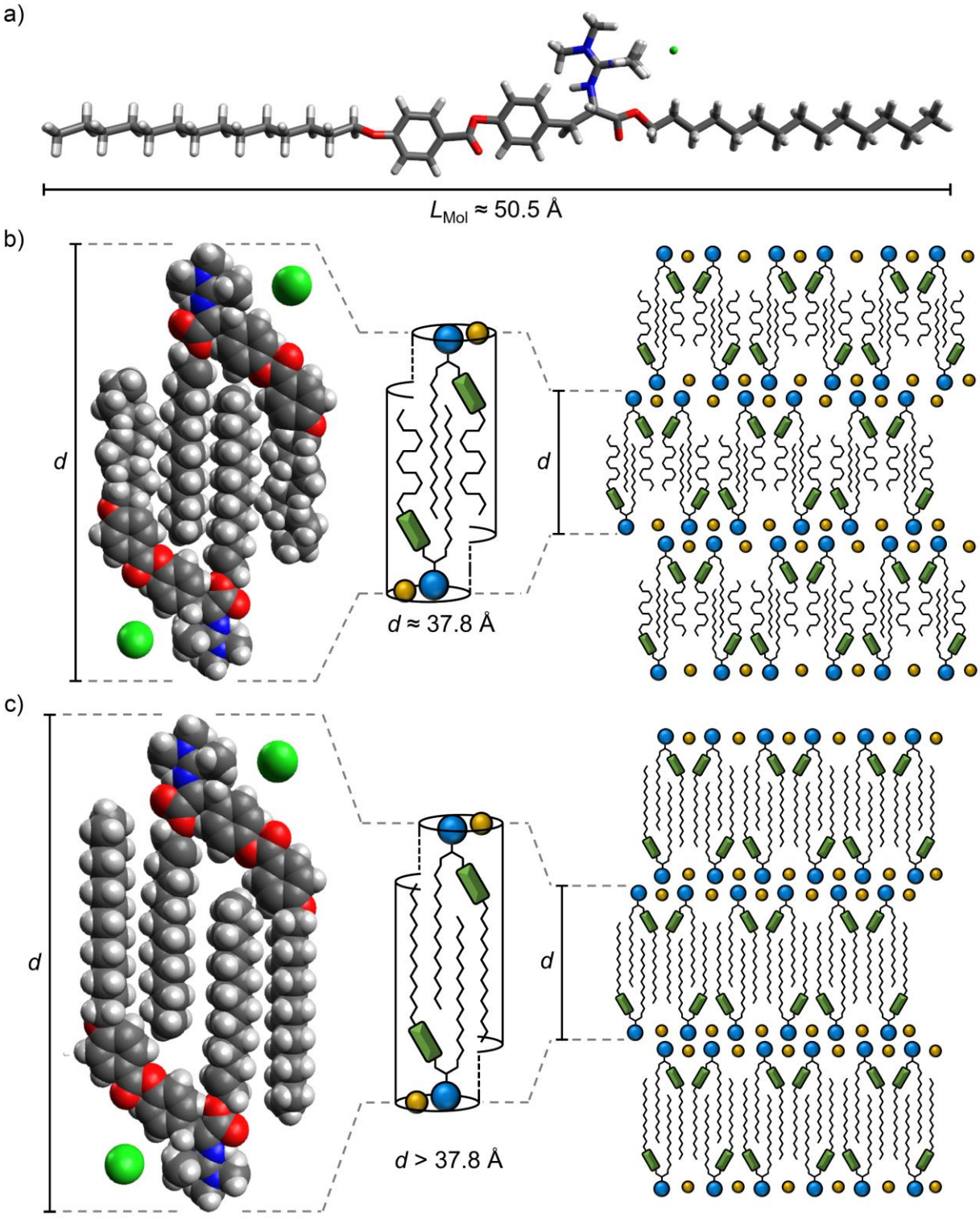


Figure S21. a) Structure of guanidinium chloride **4-C_{14}TyrC_{14}Cl** in extended form: C (gray), H (white), O (red), N (blue), Cl (light green). b) Tangled and c) stretched form of the alkoxy chain; Proposed packing models (left) of **4-C_{14}TyrC_{14}Cl**: C (gray), H (white), O (red), N (blue), Cl (light green); Schematic representation of two anion-cation pairs with indicated cylindrical structure (center) and resulting liquid crystalline bilayer (right): cationic head group (blue), chloride anion (yellow), aromatic system (green).

In order to rationalize the experimentally observed XRD data for 4- and 3,4-substituted tyrosine benzoates **4-C$_m$TyrC$_n$X**, **3,4-C$_m$TyrC$_n$X** molecular modeling of compounds **4-C$_{14}$TyrC$_{14}$Cl** and **3,4-C$_{14}$TyrC$_{14}$Cl** as monomeric and dimeric structures via Avogadro[31] was performed. In the extended *all-trans* conformation ILCs **4-C$_{14}$TyrC$_{14}$Cl** (Figure S21a) and **3,4-C$_{14}$TyrC$_{14}$Cl** (Figure S23a) have the same molecular lengths L_{mol} = 50.5 Å. Despite these identical values for L_{mol}, the experimental SmA layer thickness for **3,4-C$_{14}$TyrC$_{14}$Cl** is significantly larger (d = 39.7 Å) as compared to the layer thickness for **4-C$_{14}$TyrC$_{14}$Cl** is (d = 36.1 Å).

This might be explained by a smectic bilayer arrangement for **4-C$_{14}$TyrC$_{14}$Cl** in a folded *cis*-conformation, consisting of alternating polar sublayers and non-polar layers with aryl-aryl contacts enabling π–π interactions and interdigitating alkyl side chains (Figure S21b and c). The interdigitating alkyl chain might be undulated in a similar fashion as was previously proposed by Goossens (Figure S21b).[32] Such packing should be favoured by strong electrostatic interactions in the ionic sublayer and relatively weak π–π interactions (because the phenyl units are not coplanar oriented). On the other hand, this packing should be disfavoured by larger voids and decreased van der Waals interactions due to the undulated alkyl chains.

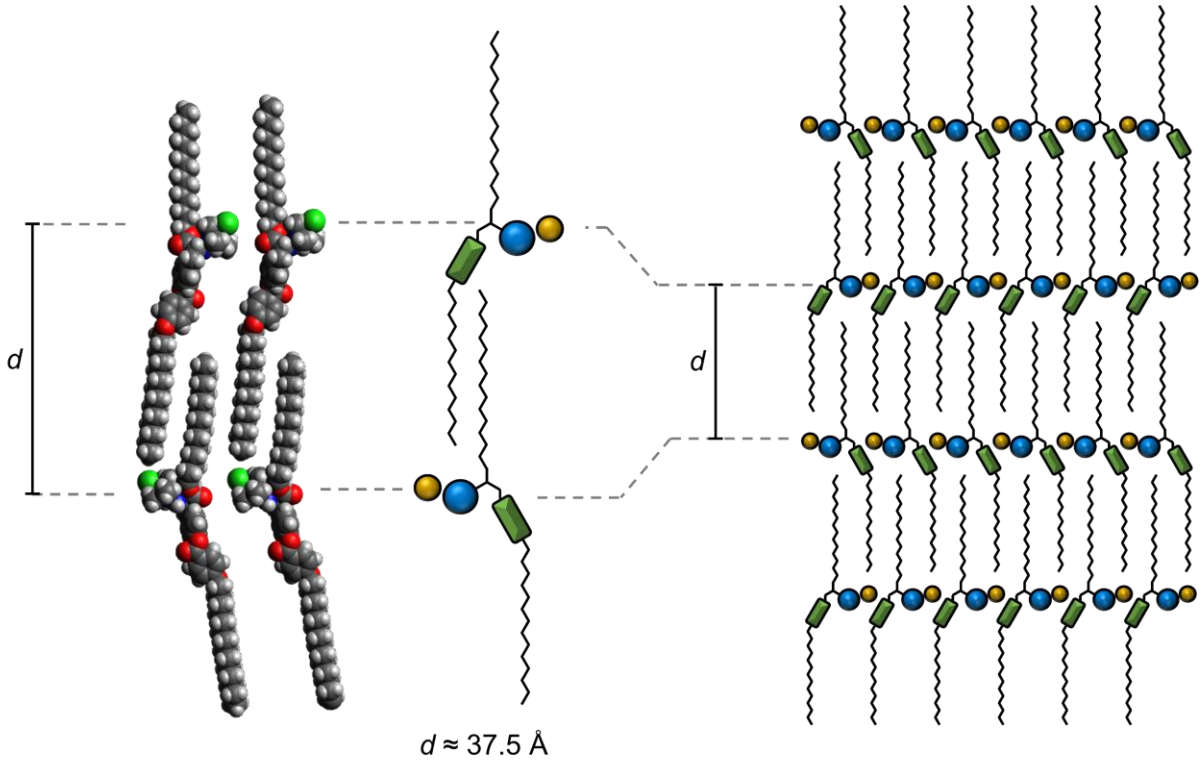


Figure S22. Proposed packing model of **4-C$_{14}$TyrC$_{14}$Cl** in bilayers visualised in a space-filling model (left): C (gray); H (white); O (red); N (blue); Cl (green); Schematic representaition of a molecule pair (center) and resulting liquid crystalline bilayer (right): cationic head group (blue), chloride anion (yellow), aromatic system (green).

In an alternative packing model with **4-C$_{14}$TyrC$_{14}$Cl** in a folded *cis*-conformation, the side chains are fully extended (Figure S21c), enabling strong van der Waals interaction by a high

degree of interdigitation. This model should be further favoured by the reduced free volume as compared to the above discussed packing model. Strong electrostatic interactions and weak aryl-aryl contacts further support this packing model. However, with the chain stretched out, the layer distances would be greater than those actually obtained.

A third packing model consists of a bilayers of tyrosine benzoates in the extended *all-trans* conformation, resulting in alternating polar sublayers, aromatic sublayers, and alkyl sublayers (Figure S22). This model should be favoured by strong van der Waals interactions of the interdigitated side chains and π–π interactions of the coplanar oriented aryl units. However, as the guanidinium groups are partially sandwiched between alkyl ester chains, the Couloumb interaction should be reduced as compared to the above discussed models. As the XRD data support the first (Figure S21b) and third (Figure S22) model, we still prefer the first model with strong Coulomb interaction and strong van der Waals interactions.

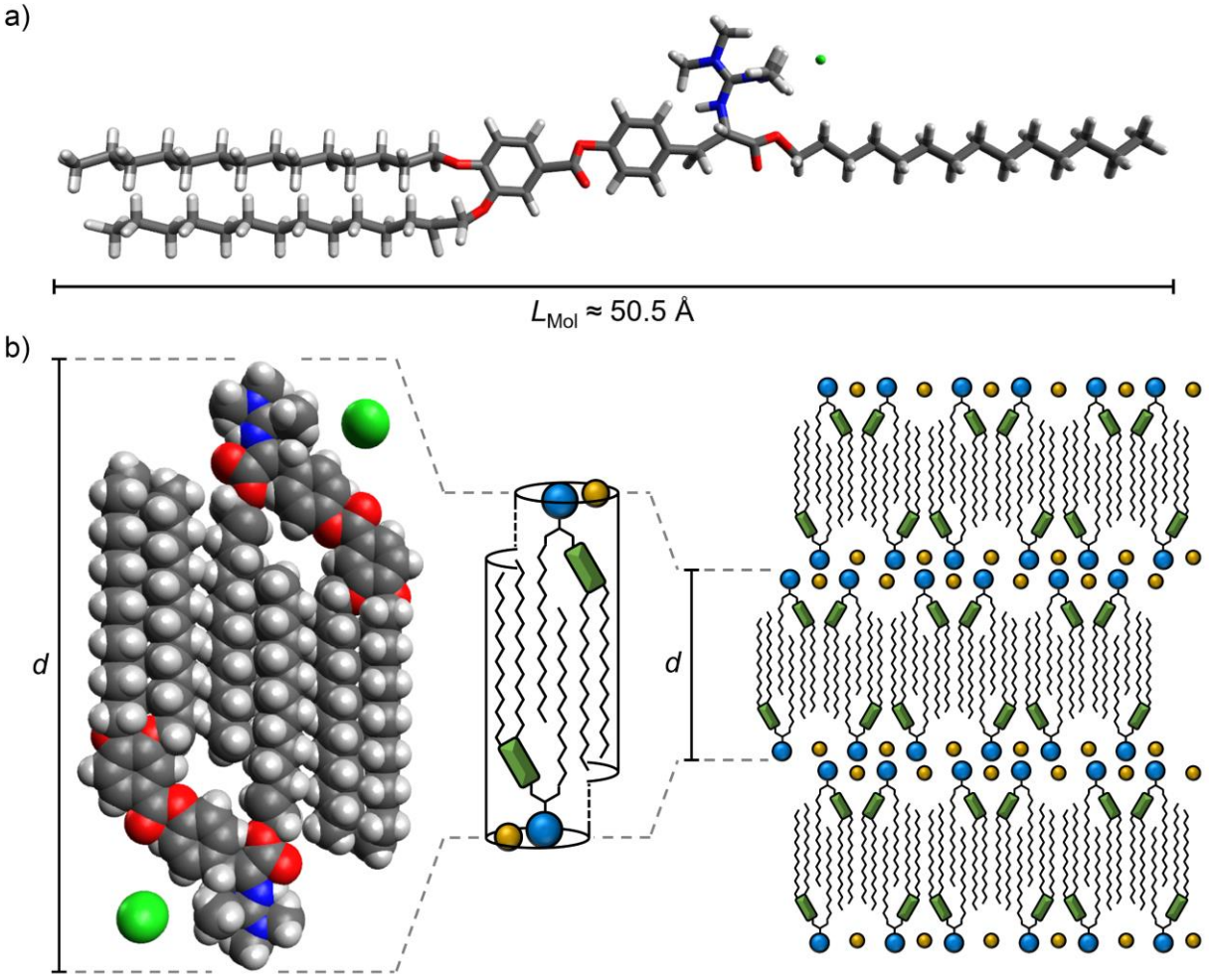


Figure S23. a) Structure of guanidinium chloride **3,4-C$_{14}$TyrC$_{14}$Cl** in extended form: C (gray), H (white), O (red), N (blue), Cl (light green). Proposed packing models (left) of **3,4-C$_{14}$TyrC$_{14}$Cl**: C (gray), H (white), O (red), N (blue), Cl (light green); Schematic representation of two anion-cation pairs with indicated cylindrical structure (center) and resulting liquid crystalline bilayer (right): cationic head group (blue), chloride anion (yellow), aromatic system (green).

In a similar fashion two related packing models were proposed for the 3,4-disubstituted compounds, e.g. **3,4-C$_{14}$TyrC$_{14}$Cl** (Figure S23 – S24). It should be noted that the first model of **4-C$_{14}$TyrC$_{14}$Cl** (Figure S21b) with undulating side chains is highly unlikely in this case for steric reasons. In contrast, the second model offers both strong Coulomb interactions as well as van der Waals interactions and optimum space filling. Based on the XRD data which support the models shown in Figure S2323b and Figure **S24**24 respectively, we prefer the model in Figure S4b with strong Coulomb interaction and strong van der Waals interactions.

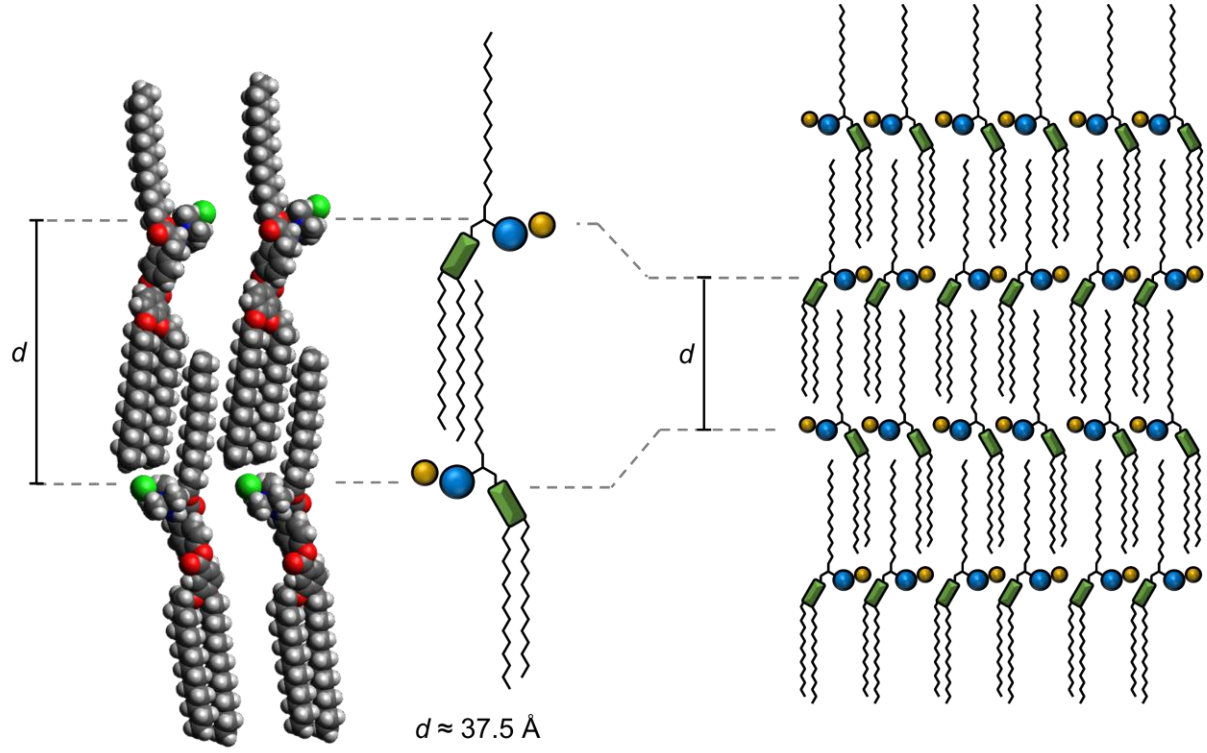


Figure S24. Proposed packing model of **3,4-C$_{14}$TyrC$_{14}$Cl** in bilayers visualised in a space-filling model (left): C (gray); H (white); O (red); N (blue); Cl (green); Schematic representation of a molecule pair (center) and resulting liquid crystalline bilayer (right): cationic head group (blue), chloride anion (yellow), aromatic system (green).

Additionally, the models with bent molecules (Figure S21b and S23b) are consistent with the models postulated by Neidhardt[21,33] and correspond to the lipid bilayers of cell membranes which served as inspiration for the molecule design of this work.

8 Experimental Dipole Moment Determination

Ionic liquid crystal solutions of different concentrations were prepared by dissolving in toluene. To avoid dipole orientation correlations between the molecules, solutions with dilute concentrations were used for the measurements.

Dielectric measurements on the solutions were performed using a high-resolution ALPHA analyzer (Novocontrol, Montabaur, Germany) interfaced to a sample holder with an active sample head. The three-electrode cylindrical liquid sample cell BDS 1307, which avoids errors related to thermal expansion of the measured liquid.[34] prevents evaporation and protects the sample from leakage, was used for measuring the permittivity of the three solutions. The measurements were carried out in a cylindrical geometry by mounting the BDS 1307 cell between the electrodes of the active sample head. An alternating voltage was applied between the electrodes and the complex dielectric permittivity $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ was recorded at a frequency f = 1000 Hz at room temperature. Here ε' and ε'' represent the real and imaginary part of the complex permittivity. $i = \sqrt{-1}$ is the imaginary unit. Prior to the measurement, the liquid cell 1307 was calibrated using toluene.

9 Biological Investigations

The biological investigations of the guanidinium chlorides **Ar(C$_m$)TyrC$_n$Cl** were carried out by the working group of Prof. Dr. Ursula Bilitewski at the Helmholtz Centre for Infection Research (HZI) in Braunschweig. Compounds **CrTyrC$_n$Cl** were investigated independently by Luca Altevogt at the HZI in a similar way as **Ar(C$_m$)TyrC$_n$Cl**. The experiments were designed to examine the inhibitory potential of the compounds towards the growth of selected bacterial strains as well as the cell viability of the cell line L929 (mouse fibroblasts). The Gram-positive bacterium *Staphylococcus aureus* (*S. aureus*, strain SH1000) and the Gram-negative bacterium *Escherichia coli* K12 (*E. coli* K12) and its deletion mutant *E. coli* ΔTolC were used as test organisms. The protein TolC is a component of an efflux pump, which transports non-cellular substances out of the cell, but it is missing in the deletion mutant. As a result, the pump becomes inactive and substances foreign to the cell cannot be transported further out of the cell.

To investigate the biological activity of the guanidinium chlorides **Ar(C$_m$)TyrC$_n$Cl**, 10 mM stock solutions of the substances were prepared in DMSO. Some of the higher substituted derivatives could not be dissolved completely or only after incubation for 16 h at 37 °C. In initial tests, the compounds were analysed in concentrations of 100 µM and subsequently 20 µM (bacteria) and 10 µM (L929). Optical densities OD_{600} were measured at a wavelength of λ = 600 nm. The results are presented in so-called heat maps in Figure S25 (bacterial growth after 0–24 h) and Figure S26 (bacterial growth after 24 h and cell viability).

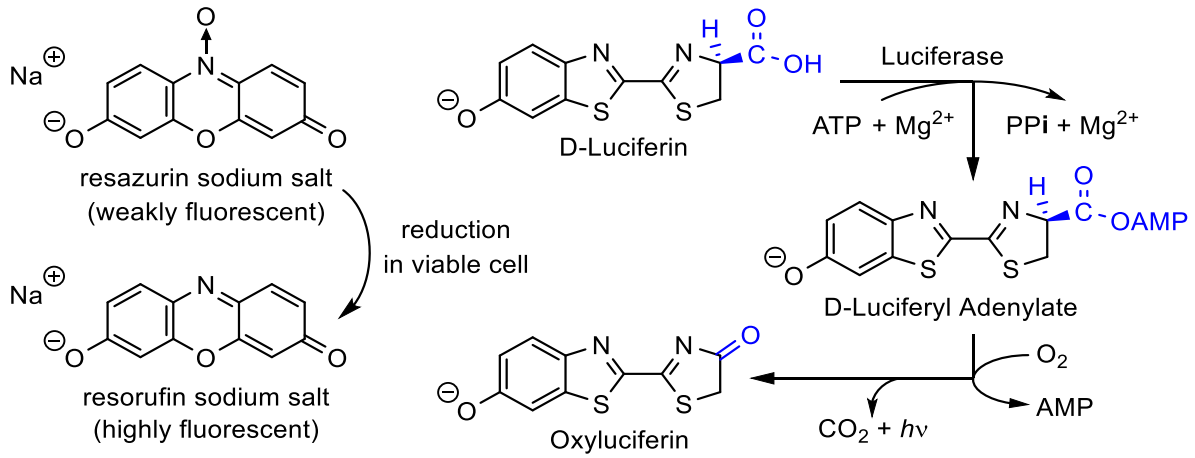
9.1 Tests for Antibacterial Effect

For preparation, the bacterial strains previously stored on agar plates and in the refrigerator were used as inoculation in the respective medium (tryptic soy broth medium for *S. aureus* and lysogeny broth medium for *E. coli*). The inoculated media were incubated for 16 h at 37 °C to propagate the strains and then the OD_{600} optical density was measured as a measure of the number of bacteria. The suspensions were diluted to an $OD_{600} \approx 0.1$ and placed on microtiter plates. There, they were mixed with the stock solutions to the substance concentrations indicated above (100 µM). The microtiter plates were incubated for a total of 24 h at 37 °C and the optical density was measured at defined time intervals. For evaluation, the background (medium and microtiter plates; ~0.05) was subtracted from the measured optical densities and the measured value for pure solvent was set as reference. Substances that resulted in bacterial growth below 50% were considered active. For these substances, the experiment was repeated at a substance concentration of 20 µM. If growth below 50% was again observed, a dilution

series of 6–8 concentration levels below 10 µM was examined. From the values obtained, the respective IC_{50} value could be calculated by non-linear regression (4-parameter equation) with the program GraphPad Prism.

9.2 Tests for Cytotoxicity

Cytotoxicity assays were performed using *AlamarBlue*™ as well as *CellTiter-Glo*® assays and were performed with cell line L929. The cells were incubated and cultured in Dulbecco's modified Eagle Medium containing 10% fetal bovine serum at 37 °C in an atmosphere containing 10% CO_2. For the *AlamarBlue*™ assay,[35] the medium was incubated with defined number of cells and a substance concentration of 100 µM for 72 h at 37 °C, the blue fluorescent reagent resazurin was added, and after up to 4 h reaction time, the fluorescence was measured at $\lambda_{excitation}$ = 540 nm and $\lambda_{emmision}$ = 600 nm. Due to the metabolism taking place, resazurin is reduced to red resofurin in the vicinity of a viable cell (Scheme S3).[36] The measured fluorescence intensity is proportional to the number of living cells. The repetition (10 µM) and evaluation of the experiments was carried out analogously to the tests for antimicrobial effect.



Scheme S3

Cell viability could be determined by the *CellTiter-Glo*® assay, since healthy cells generally have more ATP than damaged cells. By adding the reagent containing Luciferase and D-Luciferin, the reaction shown in Scheme S3 is initiated,[37,38] in which the reactants are converted to Oxyluciferin as well as AMP and light ($h\upsilon$) is emitted (stoichiometric). After 24 h of incubation, the medium was mixed with defined number of cells with substance (100 µM), and after another 24 h with the reagent. After mixing the samples and 10 min reaction time, the luminescence was determined.

9.3 Results of Biological Investigations

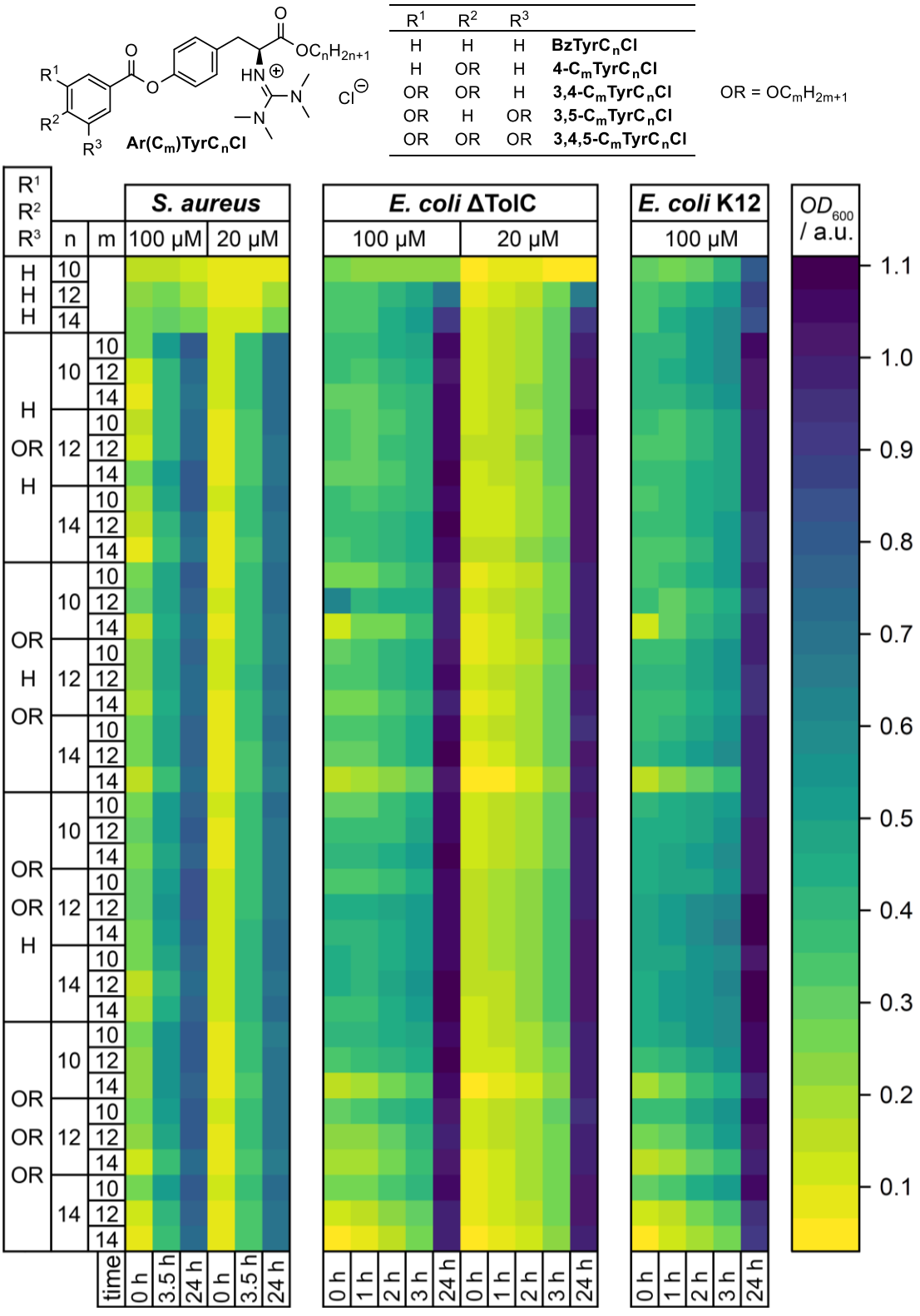


Figure S25. Results (heatmap) of the primary screening tests of guanidinium chlorides **Ar(C$_m$)TyrC$_n$Cl** in terms of inhibition potential against the growth of bacterial strains *S. aureus* and *E. coli* (ΔTolC- and K12). Dependence of optical density OD_{600} (λ = 600 nm) on concentration (100 µM and 20 µM) and incubation time (0–24 h).

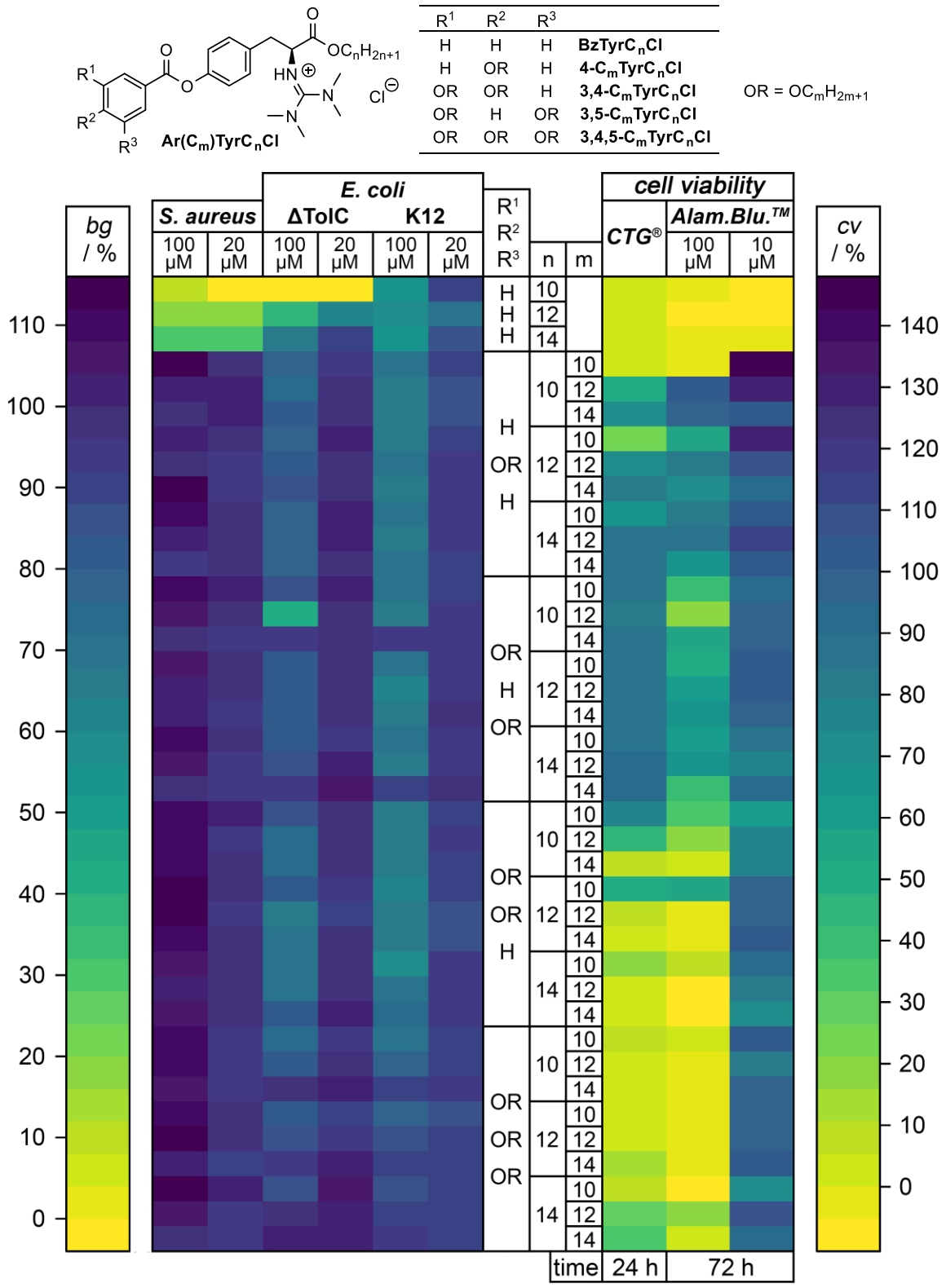


Figure S26. Inhibition potential of guanidinium chlorides **Ar(C$_m$)TyrC$_n$Cl** against the bacterial growth *bg* (via OD_{600}) of *S. aureus* and *E. coli* (ΔTolC and K12) and cell viability *cv* of the L929 mouse fibroblasts (via fluorescence measurements). Fluorescence measurements by *CellTiter-Glo*® (*CTG*®) as well as *AlamarBlue*™ (*Alam.Blu*™) assay. Dependence on concentration (100 µM and 20 or 10 µM) and incubation time (24 h or 24 and 72 h).

The **CrTyrC$_n$Cl** series was measured separately, but in the same way as the series **Ar(C$_m$)TyrC$_n$Cl**. Because of the small number of compounds, the screening results were not displayed in a heatmap. However, compounds **CrTyrC$_n$Cl** (n = 10, 12) showed a comparable inhibitory effect as series **BzTyrC$_n$Cl** and were accordingly investigated in a dilution series (Figure S27). The IC$_{50}$ values were determined analogously to **BzTyrC$_n$Cl**.

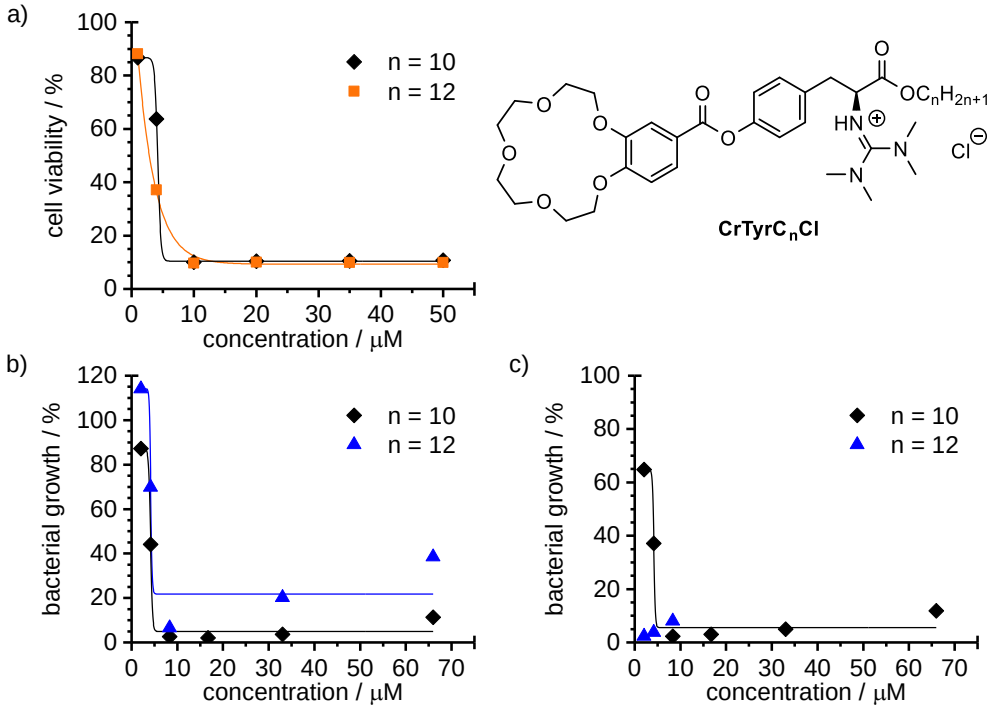


Figure S27. Graph of the inhibition by **CrTyrC$_n$Cl** against a) the cell viability of L929 and the bacterial growth of b) *E. coli* ΔTolC as well as c) *S. aureus* as a function of the concentration.

Table S8. Bioactivity as IC$_{50}$ values of guanidinium chlorides **BzTyrC$_n$Cl** and **CrTyrC$_n$Cl** against L929, *S. aureus* and *E. coli* ΔTolC. – Compound was inactive.

	n	IC$_{50,L929}$ / µM	IC$_{50,S.aureus}$ / µM	IC$_{50,E.coli\ \Delta TolC}$ / µM
BzTyrC$_n$Cl	10	5.1 ± 1.6	~0.9[b]	1.3 ± 0.2
	12	4.0 ± 1.7	0.6 ± 0.2	–
	14	5.6[a]	0.25[a]	–
CrTyrC$_n$Cl	10	4.7 ± 1.1	2.9 ± 0.2	3.8 ± 0.2
	12	3.0 ± 1.1	< 2.0	4.8 ± 1.1
	14	–	–	–

[a] Because of missing plateaus, error limits could not be determined mathematically.
[b] Estimated value (could not be determined mathematically).

10 Temperature-dependent ^{1}H NMR studies

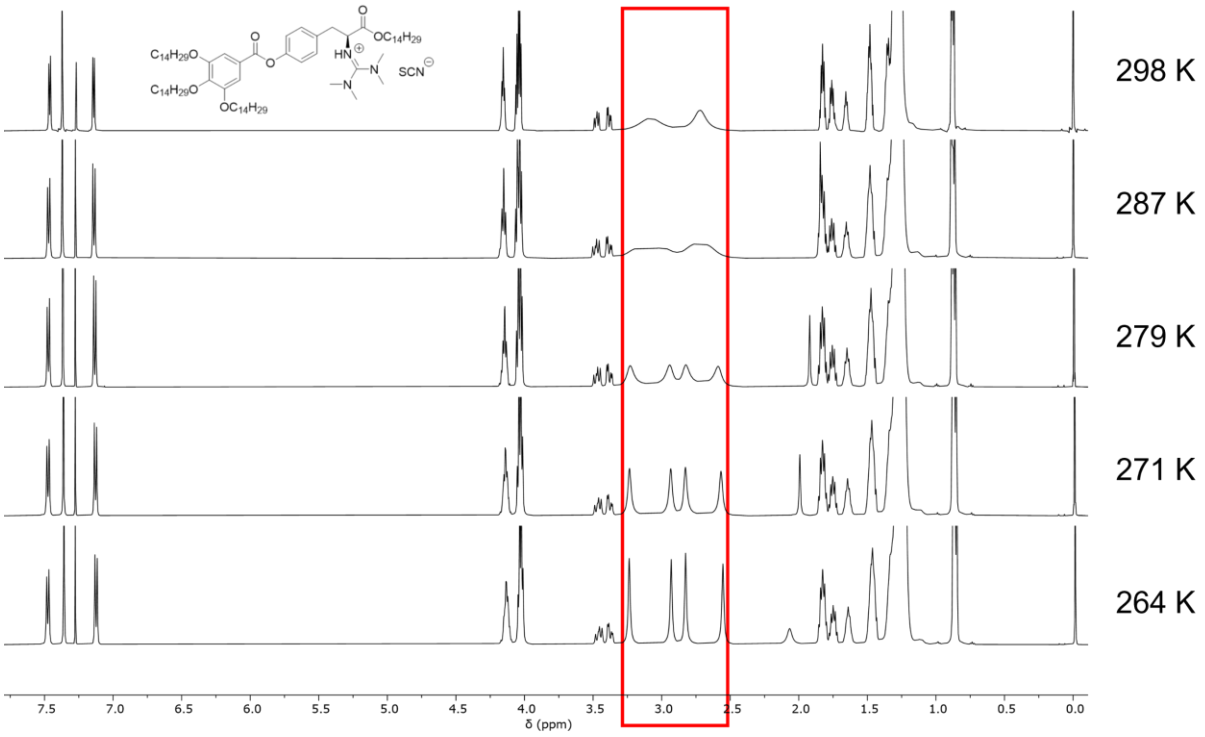


Figure S28. Temperature-dependent ^{1}H NMR spectra of guanidinium salts **3,4,5-C$_{14}$TyrC$_{14}$SCN** (500 or 700 MHz, $CDCl_3$). The respective hydrogen atoms in the methyl groups of the guanidinium moiety are highlighted by the red box. Interpretations of the important sections are found in the main manuscript (Figure 3).

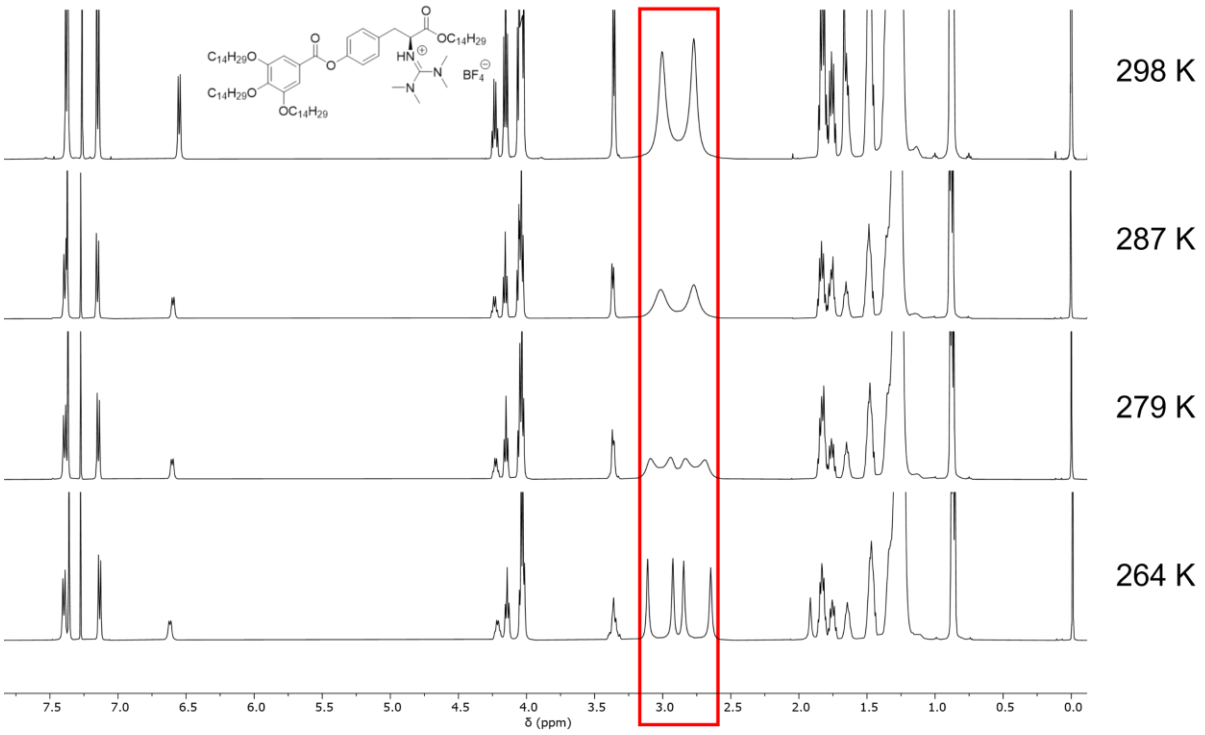


Figure S29. Temperature-dependent ^{1}H NMR spectra of guanidinium salts **3,4,5-C$_{14}$TyrC$_{14}$BF$_4$** (500 or 700 MHz, $CDCl_3$). The respective hydrogen atoms in the methyl groups of the guanidinium moiety are highlighted by the red box. Interpretations of the important sections are found in the main manuscript (Figure 3).

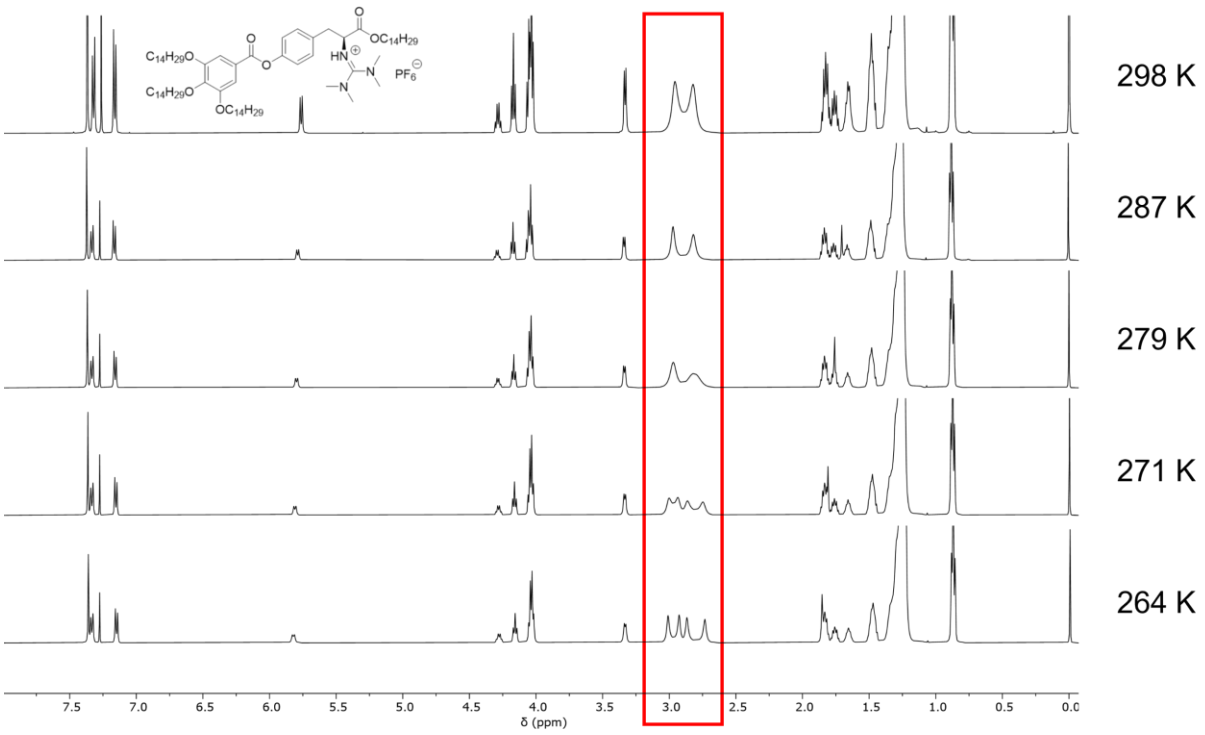


Figure S30. Temperature-dependent ^{1}H NMR spectra of guanidinium salts **3,4,5-C$_{14}$TyrC$_{14}$PF$_6$** (500 or 700 MHz, $CDCl_3$). The respective hydrogen atoms in the methyl groups of the guanidinium moiety are highlighted by the red box. Interpretations of the important sections are found in the main manuscript (Figure 3).

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