Electronic Supplementary Information

Self-assembly and biological activities of ionic liquid crystals derived from aromatic amino acids

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Contents

1) General Procedures

General Procedure 1 (GP1)

Following a procedure of Van,[1] a suspension of the respective amino acid **1** (113 mmol), *p*-toluenesulfonic acid (23.6 g, 124 mmol) and the appropriate alcohol (118 mmol) in toluene (450 mL) was heated to reflux under Dean-Stark conditions for 24 h. The resulting clear solution was concentrated under vaccum and the residue was taken up in chloroform. Insoluble impurities were filtered off. The filtrate was successively washed with a 10%ic Na_2CO_3 solution (3 × 150 mL), H_2O (2 × 100 mL), and brine (1 × 100 mL) and dried ($MgSO_4$). The solvent was removed to give the amino acid esters **2**, **3**, **4a**–**c** as colorless solids.

General Procedure 2 (GP2)

Following a procedure of Butschies,[2] to a solution of **2a**–**e**, **8a**–**d**, **9a**–**d**, **10a**–**e** and **11a**–**e** (1.09 mmol) under inert gas atmosphere in abs. CH_2Cl_2 (10 mL) was added anhydrous $NaHCO_3$ (914 mg, 10.9 mmol) followed by dropwise addition of a solution of **6** (1.41 mmol) in abs. CH_2Cl_2, and the reaction mixture was then heated to reflux for 1 h. The inorganic solid was filtered off, H_2O was added to the filtrate and stirred for 5 min. The solvent was removed under vacuum and the residue was taken up in Et_2O and acidified to pH 1 with HCl in Et_2O. After concentration, the residue was dissolved in CH_2Cl_2 and purified by chromatography on SiO_2, which was treated with HCl and washed with CH_2Cl_2, with EtOAc as solvent followed by CH_2Cl_2/MeOH (10 : 1) to give products **Phe(m)**, **Tyr(m,n)** and **Dopa(m,n,n)**. After recrystallization from EtOAc, the products were obtained as colorless solids.

General Procedure 3 (GP3)

In analogy to a patent,[3] to a solution of the respective **3**, **4a**–**c** (110 mmol) and $NaHCO_3$ (27.8 g, 331 mmol) in acetone/H_2O (1 : 1, 500 mL) was added dropwise di-*tert*-butyldicarbonate (26.5 g, 121 mmol), and the reaction mixture was stirred for 16 h at room temperature. After addition of EtOAc (200 mL), the mixture was successively washed with H_2O (2 × 200mL), 1 M HCl (2 × 200mL) and H_2O (2 × 200mL) and dried ($MgSO_4$). The solvent was removed under vacuum to give products **6**, and **7a**–**c** as colorless solids.

General Procedure 4 (GP4)

In analogy to a procedure of von Azefu,[4] a solution the respective **7a**–**c** (11.4 mmol), K_2CO_3 (3.94 g, 28.5 mmol), NaI (171 mg, 1.14 mmol) and the appropriate 1-bromoalkane (25.1 mmol) in MeCN (150 mL) was heated to reflux for 24 h. Then the solvent was removed under vacuum and the residue was taken up in CH_2Cl_2. The insoluble salts were filtered off and washed with CH_2Cl_2. The combined filtrates were evaporated under vacuum and the residue purified by chromatography on SiO_2 with *n*-hexanes/EtOAc (15 : 1) to give the products as colorless solids.

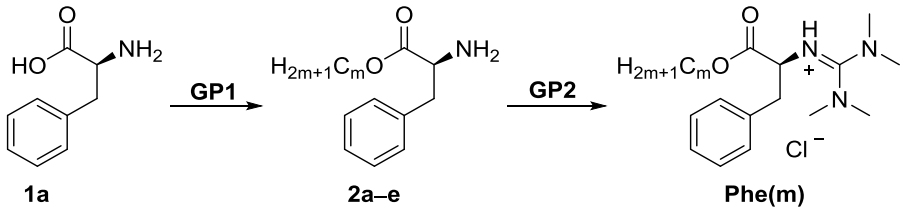
General Procedure 5 (GP 5)

In analogy to a procedure of Srinivasan,[5] to a solution of the respective **S1a**–**d**, **S2a**–**e** and **S3a**–**e** (1.32 mmol) in CH_2Cl_2 (15 mL) at 0 °C was slowly added trifluoroacetic acid (1.01 mL, 1.51 g, 13.2 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Then Amberlyst®A21 was added to neutralize the reaction mixture. Amberlyst was filtered off and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on SiO_2 with *n*-hexanes/EtOAc (3 : 1) to give products **9a**–**d**, **10a**–**e** and **11a**–**e** as colorless solids.

General Procedure 6 (GP6)

A solution of amino acid ester **6** (7.12 mmol), K_2CO_3 (9.83 g, 71.2 mmol), NaI (107 mg, 712 µmol) and the appropriate 1-bromoalkane (7.83 mmol) in MeCN (75 mL) was heated under reflux for 24 h. After being cooled to room temperature, the reaction mixture was poured onto H_2O, extracted with EtOAc (3 × 100mL), washed with brine (1 × 50mL) and dried ($MgSO_4$). The solvent was removed and the residue taken up in CH_2Cl_2 (100 mL). At 0 °C, trifluoroacetic acid (51.5 mmol) was slowly added, the reaction mixture was allowed to warm to room temperature and was stirred for 24 h. After neutralization with Amberlyst®A21 and removal of the solvent under vacuum, the residue was purified by flash chromatography on SiO_2 with *n*-hexanes/EtOAc (3 : 1) to give products **8a**–**d** as colorless solids.[4,5]

2) Synthesis of phenylalanine guanidinium chlorides Phe(m)



1a **2a–e** **Phe(m)**

Scheme S1

Decyl L-phenylalaninate (2a). According to GP1, yield: 500 mg, 1.64 mmol, 23%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, C*H*$_3$), 1.20-1.35 (m, 12H, C*H*$_2$), 1.47 (bs, 2H, C*H*$_2$), 1.60 (p, J = 7.0 Hz, 2H, C*H*$_2$), 2.87 (dd, J = 13.5 Hz, 7.8 Hz, 1H, ArC*H*$_2$), 3.08 (dd, J = 13.5 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.72 (dd, J = 7.8 Hz, 5.4 Hz, 1H, HNC*H*), 4.09 (t, J = 6.7 Hz, 2H CO_2C*H*$_2$), 7.18-7.21 (m, 2H, 3-H), 7.21-7.25 (m, 1H, 4-H), 7.27-7.33 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.2, 29.3, 29.5, 31.9 (*C*H$_2$), 41.2 (Ar*C*H2), 55.9 (*C*HNH$_2$), 65.1 (CO_2*C*H$_2$), 126.8 (C-4), 128.5 (C-2), 129.3 (C-3), 137.3 (C-1), 175.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3343 (w), 2955 (m), 2924 (s), 2854 (m), 1739 (w), 1676 (w), 1465 (w), 1378 (w), 1260 (w), 1120 (w), 1057 (w), 877 (w), 795 (w), 721 (w), 699 (w), 673 (w), 314 (w) cm^{-1}; MS (ESI): *m/z*: 328 $[M + Na]^+$, 306 $[M + H]^+$; HRMS (ESI): *m/z* calcd.

for $C_{19}H_{31}NO_2Na$: 328.2247 $[M + Na]^+$, found: 328.2258, *m/z* calcd. for $C_{19}H_{31}NO_2H$: 306.2428 $[M + H]^+$, found: 306.2445.

Dodecyl L-phenylalaninate (2b). According to GP1, yield: 701 mg, 2.10 mmol, 98%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, J = 6.9 Hz, 3H, CH_3), 1.16-1.20 (m, 16H, CH_2), 1.43 (bs, 2H, CH_2), 1.46-1.52 (m, 2H, CH_2), 2.77 (dd, J = 13.5 Hz, 7.7 Hz, 1H, ArCH_2), 2.96 (dd, J = 13.5 Hz, 5.4 Hz, 1H, ArCH_2), 3.60 (dd, J = 7.7 Hz, 5.4 Hz, 1H, HNC*H*), 3.99 (t, J = 6.7 Hz, 2H CO_2CH_2), 7.06-7.14 (m, 3H, 3-H, 4-H), 7.15-7.22 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.1 (*C*H_3), 21.7, 24.9, 27.6, 28.2, 28.4, 28.5, 28.6, 28.7, 30.9 (*C*H_2), 40.2 (Ar*C*H_2), 54.9 (*C*HNH_2), 64.0 (CO_2*C*H_2), 125.7 (C-4), 127.4 (C-2), 128.3 (C-3), 136.3 (C-1), 174.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3030 (w), 2923 (s), 2853 (m), 1733 (m), 1604 (w), 1496 (w), 1455 (w), 1377 (w), 1179 (m), 1112 (w), 1076 (w), 1030 (w), 1001 (mw), 908 (m), 844 (w), 730 (s), 699 (s), 646 (w), 595 (w), 486 (w) cm^{-1}; MS (ESI): *m/z*: 378 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{21}H_{35}NO_2H$: 334.2741 $[M + H]^+$, found: 334.2757.

Tetradecyl L-phenylalaninate (2c). According to GP1, yield: 2.94 g, 8.1 mmol, 67%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.19-1.42 (m, 22H, CH_2), 1.52-1.67 (m, 2H, CH_2), 2.98 (dd, J = 13.5 Hz, 5.5 Hz, 1H, ArCH_2), 3.72 (dd, J = 13.5 Hz, 7.7 Hz, 1H, Ar CH_2), 3.60 (dd, J = 7.7 Hz, 5.4 Hz, 1H, HNC*H*), 3.99 (t, J = 6.7 Hz, 2H CO2C*H2*), 7.06-7.14 (m, 3H, 3-H, 4-H), 7.15-7.22 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.1 (*C*H_3), 21.7, 24.9, 27.6, 28.2, 28.4, 28.5, 28.6, 28.7, 30.9 (*C*H_2), 40.2 (Ar*C*H_2), 54.9 (*C*HNH_2), 64.0 (CO2*C*H2), 125.7 (C-4), 127.4 (C-2), 128.3 (C-3), 136.3 (C-1), 174.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3386 (w), 3028 (w), 2921 (s), 2851 (s), 1736 (m), 1604 (w), 1496 (w), 1466 (s), 1179 (m), 1112 (w), 1075 (w), 1030 (w), 840 (w), 741 (m), 699 (m), 503 (w) cm^{-1}; MS (ESI): *m/z*: 362 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{23}H_{39}NO_2H$: 362.3059 $[M + H]^+$, found: 362.3054.

Hexadecyl L-phenylalaninate (2d). According to GP1, yield: 402 mg, 1.03 mmol, 85%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.20-1.34 (m, 24H, CH_2), 1.48 (bs, 2H, CH_2), 1.55-1.64 (m, 2H, CH_2), 2.87 (dd, J = 13.5 Hz, 7.8 Hz, 1H, ArCH_2), 3.08 (dd, J = 13.5 Hz, 5.4 Hz, 1H, ArCH_2), 3.72 (dd, J = 7.8 Hz, 5.4 Hz, 1H, HNCH), 4.09 (t, J = 6.7 Hz, 2H CO_2CH_2), 7.18-7.25 (m, 3H, 3-H, 4-H), 7.27-7.35 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 41.2 ($ArCH_2$), 55.9 ($CHNH_2$), 65.2 (CO_2CH_2), 126.8 (C-4), 128.5 (C-2), 129.3 (C-3), 137.3 (C-1), 175.2 (C=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3386 (w), 3029 (w), 2921 (s), 2852 (s), 1735 (s), 1604 (w), 1496 (w), 1466 (m), 1455 (m), 1377 (w), 1176 (s), 1112 (w), 1076 (w), 1030 (w), 1000 (w), 838 (m), 743 (m), 699 (s), 596 (w), 485 (w), 422 (w) cm^{-1}; MS (ESI): *m/z*: 378 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{25}H_{43}NO_2H$: 390.3367 $[M + H]^+$, found: 390.3357.

Octadecyl L-phenylalaninate (2e). According to GP1, yield: 3.67 mg, 8.79 mmol, 77%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, C*H*$_3$), 1.20-1.34 (m, 24H, C*H*$_2$), 1.48 (bs, 2H, C*H*$_2$), 1.55-1.64 (m, 2H, C*H*$_2$), 2.87 (dd, J = 13.5 Hz, 7.8 Hz, 1H, ArC*H*$_2$), 3.08 (dd, J = 13.5 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.72 (dd, J = 7.8 Hz, 5.4 Hz, 1H, HNC*H*), 4.09 (t, J = 6.7 Hz, 2H CO_2CH_2), 7.18-7.25 (m, 3H, 3-H, 4-H), 7.27-7.35 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 41.2 (Ar*C*H$_2$), 55.9 (*C*HNH$_2$), 65.2 (CO_2CH_2), 126.8 (C-4), 128.5 (C-2), 129.3 (C-3), 137.3 (C-1), 175.2 (*C*=O) ppm ; FT-IR (ATR): $\tilde{\nu}$ = 3363 (w), 2921 (s), 2852 (s), 1737 (m), 1603 (w), 1496 (w), 1465 (s), 1377 (w), 1182 (m), 1057 (m), 742 (m), 721 (m), 699 (m), 513 (w) cm^{-1}; MS (ESI): *m/z*: 418 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{27}H_{47}NO_2H$: 418.3685 [M + H]$^+$, found: 418.3680.

Decyl *N*-[bis(dimethylamino)methylene]-L-phenylalaninate chloride (Phe(10)). According to GP2, yield: 530 mg, 1.20 mmol, 79%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.1 Hz, 3H, C*H*$_3$), 1.19-1.34 (m, 12H, C*H*$_2$), 1.51-1.49 (m, 2H, C*H*$_2$), 1.71-1.87 (m, 2H, C*H*$_2$), 2.34-3.59 (m, 13H, $ArCH_2$, N(C*H*$_3$)$_2$), 3.77-3.86 (m, 1H, ArC*H*$_2$), 4.05 (t, J = 6.8 Hz, 2H CO_2CH_2), 4.10-4.18 (m, 1H, HNC*H*), 7.19-7.24 (m, 1H, 4-H), 7.28-7.31 (m, 2H, 3-H), 7.45-7.50 (m, 2H, 2-H), 10.04 (bs, 1H, NH) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.2, 29.3, 29.5, 31.9 (*C*H$_2$), 36.9 (Ar*C*H$_2$), 39.5 (N(*C*H$_3$)$_2$), 60.4 (HN*C*H), 66.4 (CO_2CH_2), 127.1 (C-4), 128.5 (C-3), 129.8 (C-2), 136.7 (C-1), 162.1 (HN=C) 171.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3384 (w), 3061 (w), 2923 (s), 2854 (m), 1736 (m), 1623 (s), 1569 (s), 1497 (w), 1456 (m), 1433 (w), 1404 (m), 1363 (w), 1315 (w), 1199 (m), 1175 (s), 1116 (w), 1031 (m), 978 (w), 899 (w), 743 (s), 7001 (s), 584 (m), 549 (m), 507 (m) cm^{-1}; MS (ESI): *m/z*: 404 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{24}H_{42}N_3O_2^{+}$: 404.3303 [M$^+$], found: 404.3267.

Dodecyl *N*-[bis(dimethylamino)methylene]-L-phenylalaninate chloride (Phe(12)). According to GP2, yield: 871 mg, 1.86 mmol, 93%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3H, C*H*$_3$), 1.17-1.35 (m, 18H, C*H*$_2$), 1.50-1.59 (m, 2H, C*H*$_2$), 2.46-3.85 (m, 13H, $ArCH_2$, N(C*H*$_3$)$_2$), 3.77-3.86 (m, 1H, ArC*H*$_2$), 4.05 (t, J = 6.8 Hz, 2H CO_2CH_2), 4.09-4.18 (m, 1H, HNC*H*), 7.18-7.25 (m, 1H, 4-H), 7.25-7.32 (m, 2H, 3-H), 7.43-7.53 (m, 2H, 2-H), 9.95 (d, J = 6.5 Hz, 1H, NH) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.4, 29.2, 29.3, 29.5, 29.6 (*C*H$_2$), 36.9 (Ar*C*H$_2$), 39.6 (N(*C*H$_3$)$_2$), 60.4 (HN*C*H), 66.3 (CO_2CH_2), 127.1 (C-4), 128.5 (C-3), 129.7 (C-2), 136.7 (C-1), 162.1 (HN=C) 171.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3399 (w), 2923 (s), 2853 (m), 2183 (w), 1737 (m), 1620 (s), 1568 (s), 1498 (w), 1456 (m), 1432 (m), 1404 (m), 1315 (w), 1177 (m), 1115 (w), 1066 (w), 1031 (m), 925 (m), 907 (m), 726 (s), 701 (s), 639 (m), 583 (w), 548 (w), 504 (w) cm^{-1}; MS (ESI): *m/z*: 432 [M$^+$]; HRMS

(ESI): *m/z* calcd. for $C_{26}H_{46}N_3O_2^+$: 432.3585 [M^+], found: 432.3587; DSC: Cr 26 °C * SmA_2 57 °C [0.6 kJ mol^{-1}] I. (2. cooling) *determined by POM

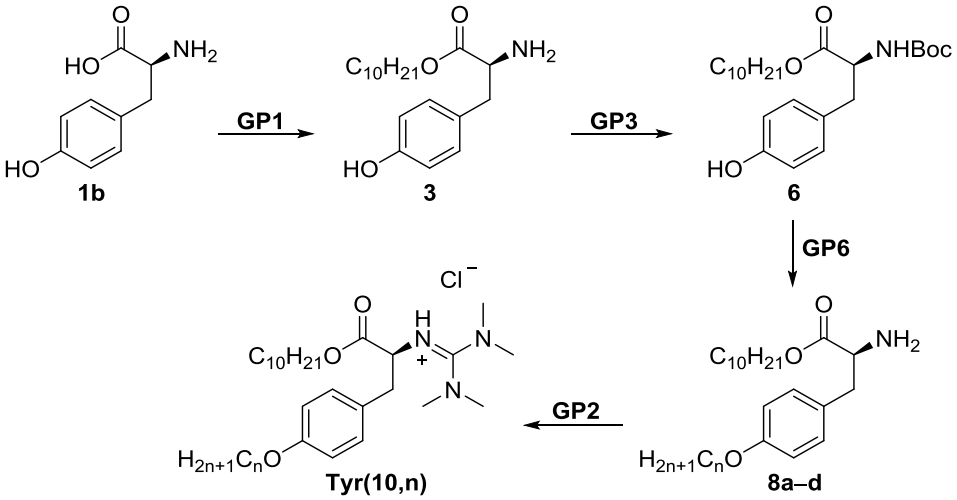
Tetradecyl *N*-[bis(dimethylamino)methylene]-L-phenylalaninate chloride (Phe(14)). According to GP2, yield: 185 mg, 0.37 mmol, 68%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, C*H*$_3$), 1.26 (bs, 22H, C*H*$_2$), 2.42-3.53 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.85 (dd, J = 14.0 Hz, 8.6 Hz, 1H, ArC*H*$_2$), 4.05 (t, J = 6.8 Hz, 2H CO_2CH_2), 4.09-4.16 (m, 1H, HNCH), 7.21 (t, J = 7.4 Hz, 1H, 4-H), 7.29 (t, J = 7.5 Hz, 2H, 3-H), 7.48 (t, J = 7.8 Hz, 2H, 2-H), 10.24 (d, J = 6.4 Hz, 1H, NH) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.4, 29.2, 29.3, 29.5, 29.6, 31.9 (*C*H_2), 37.0 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.2 (HN*C*H), 66.3 (CO_2*C*H_2), 127.1 (C-4), 128.5 (C-3), 129.7 (C-2), 136.5 (C-1), 162.0 (HN=C) 171.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3404 (w), 2923 (s), 2853 (s), 2258 (w), 2224 (w), 2201 (w), 2178 (w), 2159 (w), 2138 (w), 2026 (w), 2009 (w), 1972 (w), 1736 (m), 1625 (s), 1571 (m), 1497 (w), 1456 (w), 1405 (w), 1315 (w), 1201 (w), 1176 (w), 1113 (w), 1067 (w), 1030 (w), 899 (w), 742 (w), 701 (w), 583 (w), 560 (w) cm^{-1}; MS (ESI): *m/z*: 460 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{28}H_{50}N_3O_2^+$: 460.3898 [M^+], found: 460.3887; DSC: G 20 °C SmA_2 52 °C I. (POM)

Hexadecyl *N*-[bis(dimethylamino)methylene]-L-phenylalaninate chloride (Phe(16)). According to GP2, yield: 401 mg, 0.77 mmol, 75%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 3H, C*H*$_3$), 1.16-1.34 (m, 26H, C*H*$_2$), 1.48-1.62 (m, 2H, C*H*$_2$), 2.48-3.52 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.82 (dd, J = 13.9 Hz, 8.6 Hz, 1H, ArC*H*$_2$), 4.05 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 4.09-4.17 (m, 1H, HNC*H*), 7.17-7.24 (m, 1H, 4-H), 7.25-7.33 (m, 2H, 3-H), 7.44-7.52 (m, 2H, 2-H), 10.04 (d, J = 6.5 Hz, 1H, NH) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.8 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.4 (HN*C*H), 66.4 (CO_2*C*H_2), 127.1 (C-4), 128.5 (C-3), 129.7 (C-2), 136.7 (C-1), 162.1 (HN=C) 171.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3382 (w), 3061 (w), 2921 (s), 2852 (s), 1736 (m), 1625 (s), 1569 (s), 1497 (w), 1456 (m), 1405 (m), 1364 (m), 1314 (w), 1200 (m), 1175 (s), 1116 (w), 1066 (w), 1031 (m), 900 (w), 741 (m), 700 (s), 640 (w), 583 (w), 506 (w), 416 (w) cm^{-1}; MS (ESI): *m/z*: 488 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{30}H_{54}N_3O_2^+$: 488.42 [M^+], found: 488.43; DSC: Cr 26 °C [8:1 kJ mol^{-1}] SmA_2 72 °C [0:4 kJ mol^{-1}] I. (2. cooling)

Octadecyl *N*-[bis(dimethylamino)methylene]-L-phenylalaninate chloride (Phe(18)). According to GP2, yield: 405 mg, 0.73 mmol, 75%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, C*H*$_3$), 1.17-1.33 (m, 30H, C*H*$_2$), 1.52-1.59 (m, 2H, C*H*$_2$), 2.42-3.56 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.84 (dd, J = 14.0 Hz, 8.6 Hz, 1H, ArC*H*$_2$), 4.05 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 4.10-4.16 (m, 1H, HNCH), 7.21 (t, J = 7.4 Hz 1H, 4-H), 7.29 (t, J = 7.5 Hz, 2H, 3-H), 7.49 (d, J = 7.2 Hz,2H, 2-H), 10.22 (d, J = 6.3 Hz, 1H, NH) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.8 (Ar*C*H_2), 39.5 (N(*C*H_3)$_2$), 60.5 (HN*C*H), 66.4 (CO_2*C*H_2), 127.0 (C-4), 128.5 (C-3), 129.8 (C-2), 136.8 (C-1),

162.2 (HN=C) 171.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3389 (w), 2921 (s), 2851 (s), 1736 (m), 1625 (s), 1571 (m), 1497 (m), 1466 (m), 1456 (m), 1405 (w), 1364 (w), 1314 (w), 1200 (m), 1176 (m), 1115 (w), 1066 (m), 1031 (w), 899 (w), 742 (m), 720 (w), 700 (m), 582 (w), 507 (w) cm^{-1}; MS (ESI): *m/z*: 516 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{32}H_{58}N_3O_2^+$: 516.4524 [M^+], found: 516.4515; DSC: Cr 28 °C [20:0 kJ mol^{-1}] SmA_2 81 °C [0:6 kJ mol^{-1}] I. (2nd cooling)

3) Synthesis of tyrosine derivatives Tyr(10,n)



Scheme S2

Decyl L-tyrosinate (3). According to GP1, yield: 35.6 g, 111 mmol, 98%. ^{1}H-NMR (500 MHz, MeOD): δ = 0.88 (t, J = 6.8 Hz, 3H, C*H*$_3$), 1.18-1.38 (m, 14H, C*H*$_2$), 1.59-1.68 (m, 2H, C*H*$_2$), 2.74-2.85 (m, 1H, ArC*H*$_2$), 2.97-3.10 (m, 1H, ArC*H*$_2$), 3.69-3.74 (m, 1H, HNC*H*), 4.11 (t, J = 6.8 Hz, 2H CO_2CH_2), 6.67 (d, J = 5.5 Hz, 2H, 3-H), 7.00 (d, J = 5.7 Hz, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, MeOD): δ = 14.1 (*C*H$_3$), 22.7, 25.7, 25.9, 28.6, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 39.8 (Ar*C*H$_2$), 55.6 (*C*HNH$_2$), 63.1 (CO_2CH_2), 115.7 (C-3), 128.2 (C-1), 130.3 (C-2), 155.5 (C-4), 175.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2928 (w), 2856 (w), 2254 (w), 2169 (w), 2012 (w), 1731 (w), 1614 (w), 1515 (w), 1467 (w), 1379 (w), 1192 (w), 1105 (w), 903 (s), 723 (s), 649 (m), 541 (w) cm^{-1}; MS (ESI): *m/z*: 322 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{19}H_{31}NO_3H$: 322.2377 [M + H]$^+$, found: 322.2397.

Decyl *N*-(*tert*-butoxycarbonyl)-L-tyrosinate (6): According to GP3, yield: 33.7 g, 80.0 mmol, 72%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.20-1.35 (m, 14H, C*H*$_2$), 1.42 (s, 9H, t-Bu-C*H*$_3$), 1.55-1.65 (m, 2H, C*H*$_2$), 2.96 (dd, J = 14.1 Hz, 6.2 Hz, 1H, ArC*H*$_2$), 3.02 (dd, J = 14.0 Hz, 5.8 Hz, 1H, ArC*H*$_2$), 4.09 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.48-4.57 (m, 1H, HNC*H*), 5.14 (d, J = 8.4 Hz, 1H, N*H*), 6.74 (d, J = 8.0 Hz, 2H, 3-H), 6.95 (d, J = 8.1 Hz, 2H, 2-H), 7.33 (s, 1H, OH) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.2 (*C*H2), 28.3 (t-Bu-*C*H$_3$), 28.5, 29.2, 29.3, 29.5, 31.9 (*C*H$_2$), 37.5 (Ar*C*H$_2$), 54.7 (HN*C*H), 65.7 (CO_2CH_2), 80.3 (t-Bu-*C*), 115.6 (C-3), 127.0 (C-1), 130.3 (C-2), 155.6 (N*C*=O),

172.5 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3376 (w), 2926 (m), 2855 (w), 2254 (w), 1689 (m), 1615 (w), 1960 (w), 1515 (m), 1454 (w), 1393 (m), 1367 (m), 1219 (m), 1163 (s), 1103 (w), 1025 (w), 907 (s), 828 (w), 779 (w), 729 (s), 648 (m), 540 (w) cm^{-1}; MS (ESI): *m/z*: 444 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{24}H_{39}NO_5Na$: 444.2720 $[M + Na]^+$, found: 444.2712.

Decyl *O*-octyl-L-tyrosinate (8a). According to GP6, yield: 2.13 g, 4.91 mmol, 69%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.85-0.92 (m, 6H, C*H*$_3$), 1.21-1.38 (m, 22H, C*H*$_2$), 1.40-1.46 (m, 2H, C*H*$_2$) 1.56-1.65 (m, 2H, C*H*$_2$), 1.71-1.80 (m, 2H, C*H*$_2$), 2.81 (dd, J = 13.7 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.01 (dd, J = 13.7 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.67 (dd, J = 7.6 Hz, 5.4 Hz, 1H, H_2NC*H*), 3.92 (t, J = 6.6 Hz, 2H, OC*H*$_2$), 4.09 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 6.79-6.86 (m, 2H, 3-H), 7.04-7.13 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 31.9 (*C*H_2), 40.3 (Ar*C*H_2), 56.0 (NH_2*C*H), 65.1 (CO_2*C*H_2), 68.0 (O*C*H_2), 114.5 (C-3), 129.0 (C-1), 130.2 (C-2), 158.1 (C-4), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\upsilon}$ = 2923 (s), 2854 (m), 1735 (s), 1612 (w), 1582 (w), 1511 (s), 1468 (m), 1378 (w), 1298 (w), 1244 (s), 1175 (s), 1113 (w), 1031 (w), 820 (m), 723 (w), 588 (w), 530 (w), 423 (w) cm^{-1}; MS (ESI): *m/z*: 434 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{27}H_{47}NO_3^+$: 434.3629 $[M + H]^+$, found: 434.3639.

Decyl *O*-tetradecyl-L-tyrosinate (8b). According to GP6, yield: 2.80 g, 5.41 mmol, 87%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H, C*H*$_3$), 1.23-1.33 (m, 34H, C*H*$_2$), 1.39-1.47 (m, 2H, C*H*$_2$) 1.57-1.64 (m, 2H, C*H*$_2$), 1.74-1.79 (m, 2H, C*H*$_2$), 2.82 (dd, J = 13.7 Hz, 7.7 Hz, ArC*H*$_2$), 3.01 (dd, J = 13.7 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.3 Hz, 1H, H_2NC*H*), 3.92 (t, J = 6.6 Hz, 2H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.80-6.85 (m, 2H, 3-H), 7.06-7.11 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 40.2 (Ar*C*H_2), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H_2), 68.0 (O*C*H_2), 114.6 (C-3), 128.9 (C-1), 130.2 (C-2), 158.1 (C-4), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1735 (m), 1612 (w), 1582 (w), 1511 (m), 1467 (m), 1378 (w), 1244 (s), 1175 (s), 1113 (w), 1030 (w), 821 (m), 722 (w), 590 (w), 527 (w) cm^{-1}; MS (ESI): *m/z*: 518 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{33}H_{59}NO_3^+$: 518.4574 $[M + H]^+$, found: 518.4568.

Decyl *O*-hexadecyl-L-tyrosinate (8c). According to GP6, yield: 2.65 g, 5.83 mmol, 82%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H, C*H*$_3$), 1.26-1.32 (m, 38H, C*H*$_2$), 1.40-1.47 (m, 2H, C*H*$_2$), 1.56-1.64 (m, 2H, C*H*$_2$), 1.72-1.79 (m, 2H, C*H*$_2$), 2.81 (dd, J = 13.7 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.01 (dd, J = 13.6 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.67 (dd, J = 7.7 Hz, 5.4 Hz, 1H, H_2NC*H*), 3.92 (t, J = 6.6 Hz, 2H, OC*H*$_2$), 4.09 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 6.80-6.84 (m, 2H, 3-H), 7.06-7.11 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 40.3 (Ar*C*H_2), 56.0 (H_2N*C*H), 65.1 (CO_2*C*H_2), 68.0 (O*C*H_2), 114.5 (C-3), 129.0 (C-1), 130.2 (C-2), 158.1 (C-4), 175.2 (*C*=O)

ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2853 (w), 1733 (w), 1612 (w), 1582 (w), 1511 (w), 1466 (w), 1378 (w), 1244 (w), 1176 (w), 1113 (w), 1030 (w), 906 (m), 822 (w), 800 (w), 729 (s), 648 (w), 530 (w) cm^{-1}; MS (ESI): *m/z*: 546 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{35}H_{63}NO_3^+$: 546.4880 $[M + H]^+$, found: 546.4881.

Decyl *O*-octadecyl-L-tyrosinate (8d). According to GP6, yield: 3.01 g, 5.25 mmol, 74%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.1 Hz, 6H, C*H*$_3$), 1.22-1.31 (m, 42H, C*H*$_2$), 1.39-1.46 (m, 2H, C*H*$_2$) 1.54-1.65 (m, 2H, C*H*$_2$), 1.70-1.81 (m, 2H, C*H*$_2$), 2.81 (dd, J = 13.7 Hz, 7.6 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.7 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.66 (dd, J = 7.6 Hz, 5.4 Hz, 1H, H_2NC*H*), 3.91 (t, J = 6.6 Hz, 2H, OC*H*$_2$), 4.09 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 6.78-6.87 (m, 2H, 3-H), 7.03-7.14 (m, 2H, 2-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 32.0 (*C*H$_2$), 40.3 (Ar*C*H$_2$), 56.0 (NH_2*C*H), 65.1 (CO_2*C*H$_2$), 68.0 (O*C*H$_2$), 114.5 (C-3), 129.0 (C-1), 130.2 (C-2), 158.1 (C-4), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2915 (s), 2849 (s), 1716 (m), 1612 (w), 1583 (w), 1512 (m), 1468 (m), 1395 (w), 1378 (m), 1285 (w), 1248 (m), 1176 (s), 1111 (w), 1038 (w), 1022 (w), 1009 (w), 968 (w), 909 (w), 888 (w), 814 (m), 721 (m), 580 (w), 563 (w), 519 (w), 420 (w) cm^{-1}; MS (ESI): *m/z*: 575 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{37}H_{67}NO_3H$: 574.5196 $[M + H]^+$, found: 574.5194.

Decyl *N*-[bis(dimethylamino)methylene]-*O*-octyl-L-tyrosinate chloride (Tyr(10,8)). According to GP2, yield: 400 mg, 0.70 mmol, 95%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.84-0.92 (m, 6H, C*H*$_3$), 1.21-1.38 (m, 22H, C*H*$_2$), 1.38-1.48 (m, 2H, C*H*$_2$), 1.52-1.61 (m, 2H, C*H*$_2$), 1.71-1.78 (m, 2H, C*H*$_2$), 2.50-3.53 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.68-3.74 (m, 1H, ArC*H*$_2$), 3.90 (t, J = 6.6 Hz, 2H, OC*H*$_2$), 4.05 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.08-4.16 (m, 1H, HNC*H*), 6.81 (d, J = 7.5 Hz, 2H, 3-H), 7.38 (d, J = 7.8 Hz, 2H, 2-H), 9.75 (s, 1H, N*H*) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 36.3 (Ar*C*H$_2$), 39.8 (N(*C*H$_3$)$_2$), 60.3 (HN*C*H), 66.3 (CO_2*C*H$_2$), 68.1 (O*C*H$_2$), 114.5 (C-3), 128.2 (C-1), 130.8 (C-2), 158.2 (C-4), 162.0 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (s), 2854 (m), 1735 (m), 1622 (s), 1569 (s), 1512 (s), 1467 (m), 1404 (m), 1300 (w), 1244 (s), 1201 (m), 1176 (m), 1117 (w), 1065 (m), 1031 (m), 924 (m), 906 (m), 829 (w), 728 (s), 641 (m), 582 (m), 534 (m) cm^{-1}; MS (ESI): *m/z*: 532 $[M^+]$; HRMS (ESI): *m/z* calcd. for $C_{32}H_{58}N_3O_3^+$: 532.4473 $[M^+]$, found: 532.4481; DSC: G -34°C [0.2 kJ mol^{-1}] SmA_2 8 °C [0.3 kJ mol^{-1} I.

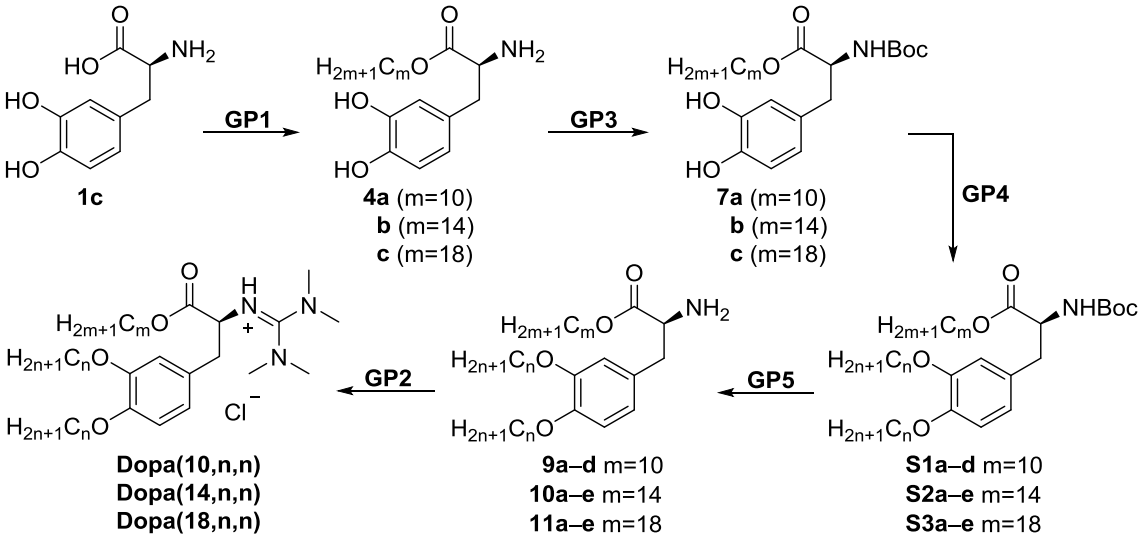
Decyl *N*-[bis(dimethylamino)methylene]-*O*-tetradecyl-L-tyrosinate chloride (Tyr(10,14)). According to GP2, yield: 280 mg, 0.43 mmol, 92%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H, C*H*$_3$), 1.21-1.31 (m, 34H, C*H*$_2$), 1.38- 1.47 (m, 2H, C*H*$_2$), 1.51-1.61 (m, 2H, C*H*$_2$), 1.70-1.79 (m, 2H, C*H*$_2$), 2.59-3.72 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.89 (t, J = 6.6 Hz, 2H, OC*H*$_2$), 4.05 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.09-4.17 (m, 1H, HNC*H*), 6.81 (d, J = 7.4 Hz, 2H,

3-H), 7.33-7.46 (m, 2H, 2-H), 9.60 (bs, 1H, NH) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.0 (Ar*C*H_2), 39.8 (N(*C*H_3)$_2$), 60.4 (HN*C*H), 66.3 (CO_2*C*H_2), 68.0 (O*C*H_2), 114.5 (C-3), 128.2 (C-1), 130.8 (C-2), 158.2 (C-4), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s) 2853 (s), 1736 (m), 1623 (s), 1571 (m), 1512 (s), 1467 (m), 1401 (m), 1300 (w), 1243 (s), 1200 (m) 1176 (s), 1117 (w), 1031 (m), 926 (w), 902 (w), 828 (w), 725 (m), 639 (w), 583 (w), 533 (w) cm^{-1}; MS (ESI): *m/z*: 617 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{38}H_{70}N_3O_3^+$: 616.5412 [M$^+$], found: 616.5422; DSC: G 28 °C [0.8 kJ mol^{-1}] SmA_2 82 °C [0.4 kJ mol^{-1}] I.

Decyl N-[bis(dimethylamino)methylene]-O-hexadecyl-L-tyrosinate chloride (Tyr(10,16)). According to GP2, yield: 240 mg, 0.35 mmol, 64%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 6H, C*H*$_3$), 1.19-1.32 (m, 38H, C*H*$_2$), 1.38- 1.47 (m, 2H, C*H*$_2$), 1.51-1.62 (m, 2H, C*H*$_2$), 1.70-1.80 (m, 2H, C*H*$_2$), 2.33-3.65 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.68-3.78 (m, 1H, ArC*H*$_2$), 3.90 (t, J = 6.7 Hz, 2H, OC*H*$_2$), 4.01 – 4.15 (m, 3H, CO_2C*H*$_2$; HNC*H*), 6.81 (d, J = 7.1 Hz, 2H, 3-H), 7.39 (d, J = 7.7 Hz, 2H, 2-H), 10.01 (bs, 1H, N*H*) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.1 (Ar*C*H_2), 39.7 (N(*C*H_3)$_2$), 60.6 (HN*C*H), 66.3 (CO_2*C*H_2), 68.0 (O*C*H_2), 114.5 (C-3), 128.4 (C-1), 130.9 (C-2), 158.2 (C-4), 162.2 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1736 (m), 1621 (m), 1570 (m), 1512 (s), 1466 (m), 1404 (m), 1300 (w), 1244 (s), 1198 (m), 1176 (m), 1117 (w), 1066 (w), 1031 (m), 978 (w), 928 (w), 905 (w), 826 (w), 726 (s), 639 (w), 583 (w), 534 (w) cm^{-1}; MS (ESI): *m/z*: 645 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{40}H_{74}N_3O_3^+$: 644.5725 [M$^+$], found: 644.5725; DSC: G 41 °C [5.9 J mol^{-1}] SmA_2 77 °C [0.4 kJ mol^{-1}] I.

Decyl *N*-[bis(dimethylamino)methylene]-*O*-octadecyl-L-tyrosinate chloride (Tyr(10,18)). According to GP2, yield: 231 mg, 0.33 mmol, 91%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 6H, C*H*$_3$), 1.19-1.32 (m, 42H, C*H*$_2$), 1.38- 1.48 (m, 2H, C*H*$_2$), 1.51-1.61 (m, 2H, C*H*$_2$), 1.69-1.80 (m, 2H, C*H*$_2$), 2.48-3.61 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.67-3.77 (m, 1H, ArC*H*$_2$), 3.90 (t, J = 6.5 Hz, 2H, OC*H*$_2$), 4.01-4.15 (m, 3H, CO_2C*H*$_2$, HNC*H*), 6.81 (d, J = 6.8 Hz, 2H, 3-H), 7.39 (d, J = 7.6 Hz, 2H, 2-H), 9.91 (bs, 1H, NH) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.1 (Ar*C*H_2), 39.9 (N(*C*H_3)$_2$), 60.6 (HN*C*H), 66.3 (CO_2*C*H_2), 68.0 (O*C*H_2), 114.5 (C-3), 128.4 (C-1), 130.8 (C-2), 158.2 (C-4), 162.2 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2924 (s), 2853 (s), 2152 (w), 2035 (w), 2015 (w), 1992 (w), 1737 (w), 1603 (w), 1512 (w), 1466 (w), 1250 (m), 1176 (w), 1028 (w), 800 (w), 723 (w), 565 (w) cm^{-1}; MS (ESI): *m/z*: 673 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{42}H_{78}N_3O_3^+$: 672.6044 [M+], found: 672.6049; DSC: Cr 14 °C [1.7 kJ mol^{-1}] SmA_2 79 °C [1.4 kJ mol^{-1}] I.

4) Synthesis of 3,4-dihydroxyphenylalanine derivatives Dopa(m,n,n)



Scheme S3

Decyl L-DOPA (4a). According to GP1, yield: 6.80 g, 20.1 mmol, 74%. ^{1}H-NMR (500 MHz, MeOD): δ = 0.89 (t, J = 6.8 Hz, 3H, C*H*$_3$), 1.27-1.31 (m, 14H, C*H*$_2$), 1.53-1.62 (m, 2H, C*H*$_2$), 2.73-2.89 (m, 2H, ArC*H*$_2$), 3.61 (t, J = 6.6 Hz, 1H, H_2NC*H*), 4.06 (t, J = 6.6 Hz, 2H, CO_2C*H*$_2$), 6.48 (dd, J = 8.0 Hz, 2.1 Hz, 1H, 2-H), 6.60 (d, J = 2.1 Hz, 1H, 6-H), 6.68 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, MeOD): δ = 14.5 (*C*H$_3$), 23.8, 27.0, 29.7, 30.4, 30.5, 30.7, 33.1 (*C*H$_2$), 41.3 (Ar*C*H$_2$), 56.8 (*C*HNH$_2$), 66.1 (CO_2*C*H$_2$), 116.4 (C-3), 117.3 (C-6), 121.6 (C-2), 129.5 (C-1), 145.4 (C-4), 146.4 (C-5), 176.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3424 (w), 3336 (w), 3304 (w), 2953 (w), 2919 (s), 2851 (m), 2537 (w), 2491 (w), 2072 (w), 2031 (w), 1980 (w), 1731 (s), 1603 (w), 1520 (w), 1467 (w), 1402 (w), 1369 (w), 1326 (w), 1285 (s), 1208 (w), 1116 (w), 1085 (w), 1054 (w), 975 (w), 887 (w), 872 (w), 795 (w), 721 (w), 626 (w) cm^{-1}; MS (ESI): *m/z*: 338 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{19}H_{31}NO_4H$: 338.2326 [M + H]$^+$, found: 338.2335.

Tetradecyl L-DOPA (4b). According to GP1, yield: 4.21 g, 11.5 mmol, 77%. ^{1}H-NMR (400 MHz, MeOD): δ = 0.89 (t, J = 6.9 Hz, 3H, C*H*$_3$), 1.21-1.39 (m, 22H, C*H*$_2$), 1.51-1.64 (m, 2H, C*H*$_2$), 2.73-2.88 (m, 2H, ArC*H*$_2$), 3.61 (t, J = 6.5 Hz, 1H, H_2NC*H*), 4.06 (t, J = 6.6 Hz, 2H, CO_2C*H*$_2$), 6.48 (dd, J = 8.1 Hz, 2.1 Hz, 1H, 2-H), 6.60 (d, J = 2.0 Hz, 1H, 6-H), 6.68 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (101 MHz, MeOD): δ = 13.1 (*C*H$_3$), 22.4, 25.6, 28.3, 29.0, 29.1, 29.2, 29.3, 29.4, 29.4, 31.7 (*C*H$_2$), 39.2 (Ar*C*H$_2$), 55.4 (*C*HNH$_2$), 64.7 (CO_2*C*H$_2$), 114.0 (C-3), 115.9 (C-6), 120.2 (C-2), 128.0 (C-1), 144.0 (C-4), 145.0 (C-5), 174.7 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3422 (m), 3335 (w), 3287 (w), 2917 (s), 2849 (s), 1732 (s), 1605 (m), 1530 (w), 1463 (m), 1407 (w), 1378 (w), 1286 (m), 1259 (s), 1211 (s), 1162 (m), 1109 (m), 1054 (m), 1020 (m), 887 (w), 859 (w), 796 (s), 720 (w), 629 (w), 481 (w) cm^{-1}; MS (ESI): *m/z*: 394 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{23}H_{29}NO_4H$: 394.2952 [M + H]$^+$, found: 394.2950.

Octadecyl L-DOPA (4c). According to GP1, yield: 11.0 g, 24.5 mmol, 96%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, C*H*$_3$), 1.08-1.34 (m, 30H, C*H*$_2$), 1.34-1.50 (m, 2H, C*H*$_2$), 2.74-3.04 (m, 2H, ArC*H*$_2$), 3.77-3.98 (m, 2H, CO_2C*H*$_2$), 4.11-4.27 (m, 1H, H_2NC*H*), 6.23-6.40 (m, 1H, 2-H), 6.61-6.72 (m, 1H, 6-H), 6.73-6.87 (m, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 21.3, 22.7, 25.7, 28.2, 29.3, 29.4, 29.6, 29.7, 29.8, 31.9 (*C*H_2), 35.2 (Ar*C*H_2), 54.4 (*C*HNH_2), 66.8 (CO_2*C*H_2), 116.0 (C-3), 116.9 (C-6), 121.3 (C-2), 129.0 (C-1), 140.7 (C-4), 144.2 (C-5), 169.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\upsilon}$ = 3459 (w), 2924 (w), 2853 (w), 1731 (w), 1609 (w), 1529 (w), 1454 (w), 1404 (w), 1352 (w), 1286 (w), 1197 (w), 1172 (m), 1124 (w), 1081 (w), 1012 (w), 905 (s), 816 (w), 777 (w), 728 (s), 685 (m), 649 (w), 618 (w), 577 (w), 565 (w), 548 (w) cm^{-1}; MS (ESI): *m/z*: 450 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{27}H_{47}NO_4H$: 450.3578 $[M + H]^+$, found: 450.3575.

Decyl *N*-(*tert*-butoxycarbonyl)-L-DOPA (7a). According to GP3, yield: 8.50 g, 19.4 mmol, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, C*H*$_3$), 1.17-1.37 (m, 14H, C*H*$_2$), 1.40 (s, 9H, t-Bu-C*H*$_3$), 1.50-1.70 (m, 2H, C*H*$_2$), 2.89 (dd, J = 14.0 Hz, 6.6 Hz, 1H, ArC*H*$_2$), 2.97 (dd, J = 14.0 Hz, 5.7 Hz, 1H, ArC*H*$_2$), 4.09 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.43-4.57 (m, 1H, HNC*H*), 5.06-5.24 (m, 1H, N*H*), 6.42-6.76 (m, 2H, 2-H, 3-H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 27.6, 28.2 (*C*H_2), 28,3 (t-Bu-*C*H_3), 28.5, 29.2, 29.3, 29.5, 31.9 (*C*H_2), 37.8 (Ar*C*H_2), 54.7 (*C*HNH_2), 65.8 (CO_2*C*H_2), 80.5 (t-Bu-*C*), 115.3 (C-3), 116.1 (C-6), 121.3 (C-2), 128.0 (C-1), 143.2 (C-4), 144.0 (C-5), 155.6 (N*C*=O), 172.5 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3359 (w), 2925 (m), 2855 (w), 1686 (m), 1608 (w), 1517 (m), 1447 (m), 1393 (m), 1367 (m), 1282 (m), 1253 (m), 1162 (s), 1113 (m), 1058 (m), 1023 (m), 909 (m), 857 (w), 803 (w), 779 (m), 731 (s), 647 (m), 622 (m), 588 (m), 436 (m) cm^{-1}; MS (ESI): *m/z*: 460 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{24}H_{39}NO_6Na$: 460.2670 $[M + Na]^+$, found: 460.2653.

Tetradecyl *N*-(*tert*-butoxycarbonyl)-L-DOPA (7b). According to GP3, yield: 4.81 g, 9.74 mmol, 89%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, C*H*$_3$), 1.17-1.35 (m, 22H, C*H*$_2$), 1.42 (s, 9H, t-Bu-C*H*$_3$), 1.57-1.68 (m, 2H, C*H*$_2$), 2.85-3.01 (m, 2H, ArC*H*$_2$), 4.03-4.16 (m, 2H, CO_2C*H*$_2$), 4.42- 4.53 (m, 1H, HNC*H*), 5.05-5.18 (m, 1H, N*H*), 6.43-6.55 (m, 2H, 2-H, 6-H), 6.67-6.77 (m, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.8, 27.6, 28.2 (*C*H_2), 28.3 (t-Bu-*C*H_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 37.9 (Ar*C*H_2), 54.8 (*C*HNH_2), 65.8 (CO_2*C*H_2), 80.4 (t-Bu-*C*), 115.2 (C-3), 116.2 (C-6), 121.4 (C-2), 128.1 (C-1), 143.2 (C-4), 144.0 (C-5), 155.6 (N*C*=O), 172.5 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3359(w), 2923 (s), 2853 (m), 1686 (s), 1608 (w), 1517 (m), 1447 (m), 1393 (m), 1284 (s), 1253 (s), 1162 (s), 1113 (m), 1058 (m), 1023 (m), 909 (m), 857 (w), 803 (w), 779 (m), 732 (s), 647 (w), 588 (m), 457 (m), 436 (m) cm^{-1}; MS (ESI): *m/z*: 516 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{28}H_{47}NO_6Na$: 516.3296 $[M + Na]^+$, found: 516.3293.

Octadecyl *N*-(*tert*-butoxycarbonyl)-L-DOPA (7c). According to GP3, yield: 8.50 g, 15.5 mmol, 63%. ^{1}H-NMR (500 MHz, MeOD): δ = 0.89 (t, J = 6.8 Hz, 3H, C*H*$_3$), 1.18-1.34 (m, 30H, C*H*$_2$), 1.40 (s, 9H, t-Bu-C*H*$_3$), 1.53-1.65 (m, 2H, C*H*$_2$), 2.73-2.98 (m, 2H, ArC*H*$_2$), 4.02-4.16 (m, 2H, CO_2C*H*$_2$), 4.15-4.32 (m, 1H, HNC*H*), 6.48-6.53 (m, 1H, 2-H), 6.60-6.72 (m, 2H, 6-H, 3-H) ppm; ^{13}C-NMR (126 MHz, MeOD): δ = 14.5 (*C*H$_3$), 23.7, 27.0 (*C*H$_2$), 28.5 (t-Bu-*C*H$_3$), 28.7, 29.6, 29.7, 30.4, 30.5, 30.6, 30.7, 30.8 (*C*H$_2$), 33.1 (Ar*C*H$_2$), 56.3 (*C*HNH), 66.6 (CO_2*C*H$_2$), 116.2 (C-3), 117.3 (C-6), 121.6 (C-2), 129.5 (C-1), 145.2 (C-4), 146.2 (C-5), 157.7 (N*C*=O), 174.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3357 (w), 2919 (s), 2851 (s), 2488 (w), 2072 (w), 1731 (m), 1688 (m), 1604 (w), 1519 (m), 1467 (w), 1393 (w), 1367 (m), 1284 (m), 1166 (m), 1118 (m), 1059 (w), 976 (m), 872 (w), 777 (w), 720 (w), 459 (w) cm^{-1}; MS (ESI): *m/z*: 572 [M + Na]$^+$; HRMS (ESI): *m/z* calcd. for $C_{32}H_{55}NO_6Na$: 572.3922 [M + Na]$^+$, found: 572.3910.

Decyl *N*-(*tert*-butoxycarbonyl)-*O*-bishexyl-L-DOPA (S1a). According to GP4, yield: 0.81 g, 1.34 mmol, 54%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.84–0.94 (m, 9H, C*H*$_3$), 1.21–1.37 (m, 22H, C*H*$_2$), 1.38–1.50 (m, 13H, t-Bu-CH$_3$, C*H*$_2$), 1.55–1.63 (m, 2H, C*H*$_2$), 1.75–1.84 (m, 4H, C*H*$_2$), 2.95–3.06 (m, 2H, ArC*H*$_2$), 3.95 (t, J = 6.7 Hz, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.47–4.55 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.60–6.66 (m, 2H, 2-H, 6-H), 6.76–6.80 (m, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.0, 14.1 (*C*H$_3$), 22.6, 22.7, 25.7, 25.7, 25.9 (*C*H$_2$), 28.3 (t-Bu-*C*H$_3$), 28.5, 29.3, 29.5, 29.6, 31.6, 31.9 (*C*H$_2$), 37.8 (Ar*C*H$_2$), 54.5 (HN*C*H), 65.5 (CO_2*C*H$_2$), 69.2, 69.3 (O*C*H$_2$), 79.8 (t-Bu-*C*), 113.8 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.0 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3440 (w), 3369 (w), 2954 (w), 2925 (m), 2856 (w), 2153 (w), 1994 (w), 1716 (m), 1607 (w), 1589 (w), 1510 (m), 1468 (m), 1429 (w), 1391 (w),1365 (m), 1351 (w), 1259 (s), 12235 (m), 1164 (s), 1140 (m), 1058 (m), 1018 (w), 938 (w), 862 (w), 797 (w), 778 (w), 724 (w), 592 (w) cm^{-1}; MS (ESI): *m/z*: 628 [M + Na]$^+$; HRMS (ESI): *m/z* calcd. for $C_{36}H_{63}NO_6Na$: 628.4548 [M + Na]$^+$, found: 628.4537.

Decyl *N*-(*tert*-butoxycarbonyl)-*O*-bisdecyl-L-DOPA (S1b). According to GP4, yield: 1.02 g, 1.42 mmol, 61%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6,8 Hz, 9H, C*H*$_3$), 1.17–1.39 (m, 38H, C*H*$_2$), 1.39–1.50 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.54–1.64 (m, 2H, C*H*$_2$), 1.73–1.87 (m, 4H, C*H*$_2$), 2.93–3.04 (m, 2H, ArC*H*$_2$), 3.89-3.98 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.47–4.56 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.60–6.65 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8,3 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1 (*C*H$_2$), 28.3 (t-Bu-*C*H$_3$), 28.5, 29.3, 29,4, 29.5, 29.6, 29,7, 31.9 (*C*H$_2$), 37.9 (Ar*C*H$_2$), 54.5 (HN*C*H), 65.5 (CO_2*C*H$_2$), 69.2, 69.3 (O*C*H$_2$), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3442 (w), 2922 (s), 2853 (s), 1717 (s), 1589 (w), 1510 (s), 1467 (m), 1391 (m), 1365

(m), 1261 (s), 1234 (s), 1165 (s), 1140 (s), 1057 (m), 1018 (m), 863 (w), 798 (w), 777 (w), 722 (w), 598 (w) cm^{-1}; MS (ESI): *m/z*: 741 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{44}H_{79}NO_6Na$: 740.5800 $[M + Na]^+$, found: 740.5802.

Decyl *N*-(*tert*-butoxycarbonyl)-*O*-bistetradecyl-L-DOPA (S1c). According to GP4, yield: 1.42 g, 1.71 mmol, 72%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, CH_3), 1.24–1.36 (m, 54H, CH_2), 1.39–1.49 (m, 13H, t-Bu-CH_3, CH_2), 1.52–1.63 (m, 2H, CH_2), 1.73–1.85 (m, 4H, CH_2), 2.93–3.08 (m, 2H, ArCH_2), 3.88-4,01 (m, 4H, OCH_2), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.45–4.59 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.59–6.65 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1 (CH_2), 28.3 (t-Bu-CH_3), 28.5, 29.3, 29,4, 29.5, 29.6, 29,7, 31.9 (CH_2), 37.9 (ArCH_2), 54.5 (HN*C*H), 65.5 (CO_2CH_2), 69.2, 69.3 (OCH_2), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\upsilon}$ = 3342 (w), 2954 (m), 2917 (s), 2849 (s), 1733 (m), 1691 (s), 1588 (w), 1529 (m), 1517 (m), 1467 (m), 1428 (w), 1389 (w), 1367 (w), 1345 (w), 1290 (m), 1260 (s), 1232 (m), 1168 (s), 1138 (m), 1058 (m), 1058 (m), 1011 (w), 899 (w), 892 (w), 821 (w), 795 (m), 675 (w), 621 (w), 594 (w) cm^{-1}; MS (ESI): *m/z*: 741 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{52}H_{95}NO_6Na$: 852.7052 $[M + Na]^+$, found: 852.7050.

Decyl *N*-(*tert*-butoxycarbonyl)-*O*-bisoctadecyl-L-DOPA (S1d). According to GP4, yield: 1.87 g, 1.98 mmol, 87%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, CH_3), 1.20–1.38 (m, 70H, CH_2), 1.39–1.50 (m, 13H, t-Bu-CH_3, CH_2), 1.56–1.63 (m, 2H, CH_2), 1.73–1.84 (m, 4H, CH_2), 2.96–3.05 (m, 2H, ArCH_2), 3.91-3.98 (m, 4H, OCH_2), 4.05-4.11 (m, 2H, CO_2CH_2), 4.48–4.55 (m, 1H, HNC*H*), 4.95 (d, J = 8.4 Hz, 1H, N*H*), 6.58–6.66 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1 (CH_2), 28.3 (t-Bu-CH_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 37.9 (ArCH_2), 54.5 (HN*C*H), 65.5 (CO_2CH_2), 69.2, 69.3 (OCH_2), 79.8 (t-Bu-*C*), 113.9 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.0 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3338 (w), 2916 (s), 2849 (s), 1734 (m), 1691 (s), 1589 (w), 1532 (m), 1517 (m), 1467 (m), 1427 (w), 1388 (w), 1367 (w), 1344 (w), 1290 (m), 1260 (s), 1233 (m), 1168 (s), 1137 (m), 1060 (m), 849 (w), 795 (m), 721 (m), 674 (w) cm^{-1}; MS (ESI): *m/z*: 965 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{60}H_{111}NO_6Na$: 964.8304 $[M + Na]^+$, found: 964.8317.

Tetradecyl *N*-(*tert*-butoxycarbonyl)-*O*-bisdecyl-L-DOPA (S2a). According to GP4, yield: 1.20 g, 1.57 mmol, 92%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.19–1.38 (m, 46H, CH_2), 1.38–1.50 (m, 13H, t-Bu-CH_3, CH_2), 1.53–1.63 (m, 2H, CH_2), 1.74–1.85 (m, 4H, CH_2), 2.95–3.05 (m, 2H, ArCH_2), 3.98-4.00 (m, 4H, OCH_2), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.47–4.56 (m, 1H, HNC*H*), 4.96 (d, J = 8.4 Hz, 1H, N*H*), 6.59–6.67 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7,

25.9, 26.1 (*C*H_2), 28.3 (t-Bu-*C*H_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 37.9 (Ar*C*H_2), 54.5 (HN*C*H), 65.5 (CO_2*C*H_2), 69.2, 69.3 (O*C*H_2), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3437 (w), 2923 (s), 2853 (m), 1715 (m), 1589 (w), 1509 (m), 1467 (m), 1391 (w), 1366 (m), 1165 (s), 1139 (m), 1058 (m), 1019 (m), 908 (s), 862 (w), 798 (w), 778 (w), 731 (vs), 648 (w), 462 (w) cm^{-1}; MS (ESI): *m/z*: 797 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{48}H_{87}NO_6Na$: 796.6426 $[M + Na]^+$, found: 796.6400.

Tetradecyl *N*-(*tert*-butoxycarbonyl)-*O*-bisdodecyl-L-DOPA (S2b). According to GP4, yield: 1.14 g, 1.74 mmol, 78%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.37 (m, 54H, C*H*$_2$), 1.38–1.49 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.53–1.63 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.95–3.05 (m, 2H, ArC*H*$_2$), 3.89-3.99 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.47–4.58 (m, 1H, HNC*H*), 4.96 (d, J = 8.3 Hz, 1H, N*H*), 6.60–6.66 (m, 2H, 2-H, 6-H), 6.77 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.1, 26.9 (*C*H_2), 28.3 (t-Bu-*C*H_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0 (*C*H_2), 37.9 (Ar*C*H_2), 54.5 (HN*C*H), 65.5 (CO_2*C*H_2), 69.3 (O*C*H_2), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6), 121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3440 (w), 3369 (w), 2852 (s), 2321 (s), 1717 (m), 1607 (w), 1589 (w), 1510 (w), 1467 (m), 1429 (m), 1391 (w), 1365 (m), 1351 (m), 1261 (s), 1234 (m), 1165 (s), 1139 (m), 1058 (m), 1019 (m), 909 (w), 862 (w), 798 (w), 778 (m), 732 (w), 647 (w), 592 (w), 464 (w) cm^{-1}; MS (ESI): *m/z*: 853 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{52}H_{95}NO_6Na$: 852.7052 $[M + Na]^+$, found: 852.7045.

Tetradecyl *N*-(*tert*-butoxycarbonyl)-*O*-bistetradecyl-L-DOPA (S2c). According to GP4, yield: 1.81 g, 2.04 mmol, 88%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.38 (m, 62H, C*H*$_2$), 1.37–1.49 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.54–1.66 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.95–3.05 (m, 2H, ArC*H*$_2$), 3.90-3.99 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2C*H*$_2$), 4.47–4.57 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.59–6.68 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.1 (*C*H_2), 28.3 (t-Bu-*C*H_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 37.9 (Ar*C*H_2), 54.5 (HN*C*H), 65.5 (CO_2*C*H_2), 69.3 (O*C*H_2), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6), 121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3445 (w), 2954 (w), 2917 (s), 2849 (s), 1734 (m), 1691 (s), 1589 (w), 1530 (m), 1517 (m), 1467 (m), 1428 (w), 1389 (w), 1367 (w), 1344 (w), 1290 (m), 1261 (s), 1233 (m), 1168 (s), 1138 (m), 1057 (m), 988 (w), 890 (w), 849 (w), 796 (w), 721 (w), 674 (w), 621 (w), 594 (w), 467 (w), 437 (w) cm^{-1}; MS (ESI): *m/z*: 886 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{56}H_{103}NO_6Na$: 908.7678 $[M + Na]^+$, found: 908.7680.

Tetradecyl *N*-(*tert*-butoxycarbonyl)-*O*-bishexadecyl-L-DOPA (S2d). According to GP4, yield: 0.85 g, 0.91 mmol, 53%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.38 (m, 70H, C*H*$_2$), 1.37–1.49 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.53–1.64 (m, 2H, C*H*$_2$), 1.73–1.83 (m, 4H, C*H*$_2$), 2.96–3.04 (m, 2H, ArC*H*$_2$), 3.90-3.99 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.46–4.56 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.58–6.66 (m, 2H, 2-H, 6-H), 6.77 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1 (*C*H$_2$), 28.3 (t-Bu-*C*H$_3$), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0 (*C*H$_2$), 37.9 (Ar*C*H$_2$), 54.5 (HN*C*H), 65.5 (CO_2*C*H$_2$), 69.3 (O*C*H$_2$), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6), 121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3343 (w), 2955 (w), 2916 (s), 2849 (s), 1733 (m), 1692 (s), 1589 (w), 1532 (m), 1518 (m), 1467 (m), 1427 (w), 1389 (w), 1368 (w), 1341 (w), 1259 (s), 1234 (m), 1168 (m), 1137 (m), 1060 (w), 1037 (w), 1016 (w), 993 (w), 893 (w), 849 (w), 795 (w), 721 (w), 673 (w), 616 (w), 593 (w), 466 (w), 419 (w) cm^{-1}; MS (ESI): *m/z*: 965 [M + Na]$^+$; HRMS (ESI): *m/z* calcd. for $C_{60}H_{111}NO_6Na$: 964.8304 [M + Na]$^+$, found: 964.8324.

Tetradecyl *N*-(*tert*-butoxycarbonyl)-*O*-bisoctadecyl-L-DOPA (S2e). According to GP4, yield: 1.31 g, 1.31 mmol, 76%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.21–1.38 (m, 78H, C*H*$_2$), 1.42 (s, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.54–1.62 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.94–3.05 (m, 2H, ArC*H*$_2$), 3.90-4.00 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.8 Hz, 2H, CO_2CH_2), 4.47–4.57 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.59–6.66 (m, 2H, 2-H, 6-H), 6.77 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1 (*C*H$_2$), 28.3 (t-Bu-*C*H$_3$), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0 (*C*H$_2$), 37.9 (Ar*C*H$_2$), 54.5 (HN*C*H), 65.5 (CO_2*C*H$_2$), 69.3 (O*C*H$_2$), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6), 121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3344 (w), 2916 (s), 2849 (s), 1733 (m), 1692 (s), 1589 (w), 1532 (m), 1518 (w), 1467 (w), 1428 (w), 1389 (w), 1368 (w), 1342 (w), 1260 (s), 1234 (m), 1168 (m), 1138 (m), 1060 (w), 998 (w), 892 (w), 849 (w), 796 (w), 721 (w), 674 (w), 617 (w), 594 (w), 466 (w) cm^{-1}; MS (ESI): *m/z*: 1021 [M + Na]$^+$; HRMS (ESI): *m/z* calcd. for $C_{64}H_{119}NO_6Na$: 1020.8930 [M + Na]$^+$, found: 1020.8953.

Octadecyl *N*-(*tert*-butoxycarbonyl)-*O*-bisdecyl-L-DOPA (S3a). According to GP4, yield: 1.12 g, 1.35 mmol, 62%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, C*H*$_3$), 1.19–1.38 (m, 54H, C*H*$_2$), 1.38-1.49 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.52–1.66 (m, 2H, C*H*$_2$), 1.73–1.83 (m, 4H, C*H*$_2$), 2.95–3.05 (m, 2H, ArC*H*$_2$), 3.90-4.00 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.8 Hz, 2H, CO_2CH_2), 4.47–4.56 (m, 1H, HNC*H*), 4.95 (d, J = 8.2 Hz, 1H, N*H*), 6.58–6.67 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*CH*$_3$), 22.7, 25.9, 26.1 (*C*H$_2$), 28.3 (t-Bu-*C*H$_3$), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 37.9 ($ArCH_2$), 54.5 (HN*C*H), 65.5 (CO_2CH_2), 69.3 (OCH_2), 79.8 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6),

121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3378 (w), 2955 (w), 2917 (s), 2851 (s), 1751 (m), 1679 (s), 1588 (w), 1510 (m), 1472 (m), 1441 (w), 1394 (w), 1366 (w), 1329 (w), 1274 (m), 1218 (m), 1169 (s), 1140 (s), 1069 (w), 1046 (m), 1023 (w), 890 (w), 851 (w), 798 (w), 784 (w), 761 (w), 718 (w), 622 (w), 593 (w), 542 (w), 466 (w), 425 (w) cm^{-1}; MS (ESI): *m/z*: 853 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{52}H_{95}NO_6Na$: 852.7053 $[M + Na]^+$, found: 852.7055.

Octadecyl *N*-(*tert*-butoxycarbonyl)-*O*-bisdodecyl-L-DOPA (S3b). According to GP4, yield: 1.42 g, 1.60 mmol, 73%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.18–1.39 (m, 62H, C*H*$_2$), 1.38-1.50 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.53–1.64 (m, 2H, C*H*$_2$), 1.73–1.85 (m, 4H, C*H*$_2$), 2.93–3.05 (m, 2H, ArC*H*$_2$), 3.90-3.99 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.48–4.56 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.59–6.66 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1 (CH_2), 28.3 (t-Bu-CH_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0 (CH_2), 37.9 (ArCH_2), 54.5 (HN*C*H), 65.5 (CO_2CH_2), 69.3 (OCH_2), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6), 121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3344 (w), 2953 (w), 2919 (s), 2849 (s), 1734 (m), 1691 (s), 1589 (w), 1529 (m), 1467 (m), 1467 (m), 1428 (w), 1389 (w), 1347 (w), 1291 (m), 1262 (m), 1233 (m), 1169 (m), 1139 (m), 1057 (w), 998 (w), 889 (w), 848 (w), 798 (w), 122 (w), 675 (w), 622 (w), 594 (w), 465 (w) cm^{-1}; MS (ESI): *m/z*: 909 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{56}H_{103}NO_6Na$: 908.7678 $[M + Na]^+$, found: 908.7673.

Octadecyl *N*-(*tert*-butoxycarbonyl)-*O*-bistetradecyl-L-DOPA (S3c). According to GP4, yield: 0.20 g, 0.21 mmol, 23%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.17–1.39 (m, 70H, C*H*$_2$), 1.38-1.50 (m, 13H, t-Bu-C*H*$_3$, C*H*$_2$), 1.54–1.64 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.94–3.05 (m, 2H, ArC*H*$_2$), 3.90-3.99 (m, 4H, OC*H*$_2$), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.48–4.56 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.59–6.66 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H3), 22.7, 25.9, 26.1 (*C*H2), 28.3 (t-Bu-*C*H3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H2), 37.9 (Ar*C*H2), 54.5 (HN*C*H), 65.5 (CO2*C*H2), 69.3 (O*C*H2), 79.8 (t-Bu-*C*), 113.9 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.0 (C-5), 155.0 (N*C*=O), 172.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3336 (w), 2954 (w), 2917 (s), 2848 (s), 1733 (m), 1691 (s), 1588 (w), 1530 (m), 1517 (m), 1467 (m),1389 (w), 1367 (w), 1347 (w)m 1291 (m), 1261 (m), 1232 (m), 1168 (m), 1138 (m), 1057 (w), 1017 (w), 990 (w), 888 (w), 848 (w), 821 (w), 797 (w), 764 (w), 722 (w), 676 (w), 622 (w), 593 (w), 549 (w), 465 (w), 420 (w) cm^{-1}; MS (ESI): *m/z*: 965 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{60}H_{111}NO_6Na$: 964.8304 $[M + Na]^+$, found: 964.8292.

Octadecyl *N*-(*tert*-butoxycarbonyl)-*O*-bishexadecyl-L-DOPA (S3d). According to GP4, yield: 0.23 g, 0.23 mmol, 30%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$),

1.19–1.38 (m, 78H, CH_2), 1.38-1.49 (m, 13H, t-Bu-CH_3, CH_2), 1.53–1.64 (m, 2H, CH_2), 1.74–1.84 (m, 4H, CH_2), 2.94–3.05 (m, 2H, ArCH_2), 3.89-3.99 (m, 4H, OCH_2), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.47–4.56 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.58–6.67 (m, 2H, 2-H, 6-H), 6.77 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.7, 25.9, 26.1 (*C*H_2), 28.3 (t-Bu-*C*H_3), 28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 37.9 (Ar*C*H_2), 54.5 (HN*C*H), 65.5 (CO_2*C*H_2), 69.3 (O*C*H_2), 79.7 (t-Bu-*C*), 113.9 (C-3), 115.0 (C-6), 121.6 (C-2), 128.5 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 1711 (m), 1589 (w), 1510 (m), 1467 (m), 1392 (w), 1366 (w), 1261 (m), 1166 (m), 1139 (w), 1060 (w), 1022 (w), 907 (s), 730 (vs), 648 (w), 467 (w) cm^{-1}; MS (ESI): *m/z*: 1021 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{64}H_{119}NO_6Na$: 1020.8930 $[M + Na]^+$, found: 1020.8920.

Octadecyl *N*-(*tert*-butoxycarbonyl)-*O*-bisoctadecyl-L-DOPA (S3e). According to GP4, yield: 1.65 g, 1.56 mmol, 82%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, CH_3), 1.18–1.38 (m, 86H, CH_2), 1.39-1.50 (m, 13H, t-Bu-CH_3, CH_2), 1.53–1.63 (m, 2H, CH_2), 1.75–1.84 (m, 4H, CH_2), 2.96–3.04 (m, 2H, ArCH_2), 3.90-3.98 (m, 4H, OCH_2), 4.08 (t, J = 6.7 Hz, 2H, CO_2CH_2), 4.48–4.55 (m, 1H, HNC*H*), 4.95 (d, J = 8.3 Hz, 1H, N*H*), 6.59–6.67 (m, 2H, 2-H, 6-H), 6.77 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1, 14.2 (*C*H_3), 22.7, 25.9, 26.1, 26.9 (*C*H_2), 28.3 (t-Bu-*C*H_3),28.5, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0 (*C*H_2), 37.9 (Ar*C*H_2), 54.5 (HN*C*H), 65.5 (CO_2*C*H_2), 69.3 (O*C*H_2), 79.8 (t-Bu-*C*), 113.9 (C-3), 115.1 (C-6), 121.6 (C-2), 128.6 (C-1), 148.2 (C-4), 149.1 (C-5), 155.1 (N*C*=O), 172.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2853 (m), 1710 (w), 1509 (w), 1467 (w), 1367 (w), 1261 (w), 1166 (w), 1060 (w), 1022 (w), 906 (s), 729 (vs), 649 (m), 466 (w) cm^{-1}; MS (ESI): *m/z*: 1077 $[M + Na]^+$; HRMS (ESI): *m/z* calcd. for $C_{68}H_{127}NO_6Na$: 1076.9556 $[M + Na]^+$, found: 1076.9543.

Decyl *O*-bishexyl-L-DOPA (9a). According to GP5, yield: 650 mg, 1.29 mmol, 97%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.84–0.94 (m, 9H, CH_3), 1.21–1.38 (m, 20H, CH_2), 1.42–1.50 (m, 4H, CH_2), 1.50–1.57 (m, 2H, CH_2), 1.58-1.66 (m, 2H, CH_2), 1.74–1.85 (m, 4H, CH_2), 2.79 (dd, J = 13.6 Hz, 7.8 Hz, 1H, ArCH_2), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, ArCH_2), 3.68 (dd, J = 7.7 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.92–4.00 (m, 4H, OCH_2), 4.10 (t, J = 6.8 Hz, 2H, CO_2CH_2), 6.67–6.74 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.0, 14.1 (*C*H_3), 22.6, 22.7, 25.7, 25.9, 28.6, 29.3, 29.5, 29.6, 31.6, 31.9 (*C*H_2), 40.7 (Ar*C*H_2), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H_2), 69.3, 69.4 (O*C*H_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3376 (w), 2954 (m), 2924 (s), 2855 (s), 1735 (s), 1606 (w), 1588 (w), 1511 (s), 1467 (m), 1427 (w), 1379 (w), 1260 (s), 1233 (s), 1170 (s), 1138 (s), 1017 (m), 936 (w), 799 (w), 724 (w), 648 (w), 599 (w), 461 (w)

cm^{-1}; MS (ESI): *m/z*: 528 [M + Na]$^+$; HRMS (ESI): *m/z* calcd. for $C_{31}H_{55}NO_4Na$: 528.4023 [M + Na]$^+$, found: 528.4028.

Decyl *O*-bisdecyl-L-DOPA (9b). According to GP5, yield: 841 mg, 1:36 mmol, 98%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.19–1.39 (m, 36H, C*H*$_2$), 1.40–1.54(m, 6H, C*H*$_2$), 1.56-1.65 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.79 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.8 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.96 (t, J = 6.6 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.67–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 40.7 (Ar*C*H$_2$), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H$_2$), 69.3, 69.4 (O*C*H$_2$), 114.1 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3363 (w), 3253 (w), 2955 (m), 2917 (s), 2873 (m), 2849 (s), 1744 (s), 1591 (w), 1519 (m), 1468 (m), 1426 (w), 1396 (w), 1378 (w), 1332 (w), 1271 (s), 1233 (m), 1189 (m), 1138 (s), 1110 (w), 1068 (w), 1047 (w), 1021 (w), 987 (w), 951 (w), 892 (w), 865 (w), 852 (w), 811 (w), 722 (w), 629 (w), 589 (w), 427 (w) cm^{-1}; MS (ESI): *m/z*: 619 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{39}H_{71}NO_4H$: 618.5456 [M + H]$^+$, found: 618.5449.

Decyl *O*-bistetradecyl-L-DOPA (9c). According to GP5, yield: 1.00 g, 1.37 mmol, 88%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.39 (m, 52H, C*H*$_2$), 1.40–1.55 (m, 6H, C*H*$_2$), 1.57-1.65 (m, 2H, C*H*$_2$), 1.74–1.83 (m, 4H, C*H*$_2$), 2.79 (dd, J = 13.6 Hz, 7.8 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.8 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.96 (t, J = 6.7 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.67–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 40.7 (Ar*C*H$_2$), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H$_2$), 69.3, 69.4 (O*C*H$_2$), 114.1 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1736 (m), 1588 (w), 1512 (m), 1467 (m), 1428 (w), 1378 (w), 1261 (m), 1233 (m), 1173 (m), 1138 (m), 1025 (w), 908 (w), 800 (w), 732 (m), 647 (w), 461 (w), 409 (w) cm^{-1}; MS (ESI): *m/z*: 753 [M + Na]$^+$, 731 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{47}H_{87}NO_4H$: 730.6708 [M + H]$^+$, found: 730.6737.

Decyl *O*-bisoctadecyl-L-DOPA (9d). According to GP5, yield: 1.24 g, 1.47 mmol, 93%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.19–1.39 (m, 52H, C*H*$_2$), 1.41–1.51 (m, 6H, C*H*$_2$), 1.57-1.65 (m, 2H, C*H*$_2$), 1.75–1.84 (m, 4H, C*H*$_2$), 2.79 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.3 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.3 Hz, 1H, H_2NC*H*), 3.95 (t, J = 6.6 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.67–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 40.7 (Ar*C*H$_2$), 55.9

(H_2NCH), 65.1 (CO_2CH_2), 69.3, 69.4 (OCH_2), 114.1 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2916 (s), 2849 (s), 1743 (w), 1673 (m), 1608 (w), 1517 (m), 1467 (m), 1432 (w), 1379 (w), 1267 (m), 1237 (s), 1139 (s), 1068 (w), 908 (w), 838 (w), 799 (w), 722 (m), 649 (w), 598 (w), 519 (w), 436 (w) cm^{-1}; MS (ESI): *m/z*: 843 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{55}H_{103}NO_4H$: 842.7960 $[M + H]^+$, found: 842.7962.

Tetradecyl *O*-bisdecyl-L-DOPA (10a). According to GP5, yield: 1.02 g, 1.51 mmol, 87%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, C*H*$_3$), 1.19–1.40 (m, 46H, C*H*$_2$), 1.40–1.51 (m, 4H, C*H*$_2$), 1.57-1.66 (m, 2H, C*H*$_2$), 1.73–1.86 (m, 4H, C*H*$_2$), 2.80 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.3 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.3 Hz, 1H, H_2NCH), 3.96 (t, J = 6.7 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2CH_2), 6.67–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 40.7 (ArCH_2), 55.9 (H_2NCH), 65.1 (CO_2CH_2), 69.3 (OCH_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.7 (C-1), 148.1 (C-4), 149.1 (C-5), 175.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1736 (m), 1588 (w), 1511 (m), 1468 (m), 1428 (w), 1378 (w), 1262 (s), 1233 (m), 1177 (m), 1138 (w), 1017 (m), 908 (m), 800 (w), 732 (s), 647 (w), 458 (w), 420 (w) cm^{-1}; MS (ESI): *m/z*: 675 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{43}H_{79}NO_4H$: 674.6082 $[M + H]^+$, found: 974.6069.

Tetradecyl *O*-bisdodecyl-L-DOPA (10b). According to GP5, yield: 0.87 g, 1.19 mmol, 87%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, C*H*$_3$), 1.19–1.39 (m, 52H, C*H*$_2$), 1.39–1.52 (m, 6H, C*H*$_2$), 1.56-1.67 (m, 2H, C*H*$_2$), 1.72–1.87 (m, 4H, C*H*$_2$), 2.80 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.2 Hz, 1H, H_2NCH), 3.96 (t, J = 6.5 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.7 Hz, 2H, CO_2CH_2), 6.67–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0 (CH_2), 40.7 (ArCH_2), 55.9 (H_2NCH), 65.1 (CO_2CH_2), 69.3 (OCH_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.1 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3363 (w), 3259 (w), 2955 (w), 2915 (s), 2848 (s), 1745 (m), 1590 (w), 1519 (m), 1468 (m), 1426 (w), 1395 (w), 1378 (w), 1332 (w), 1272 (m), 1234 (m), 1186 (m), 1138 (s), 1112 (w), 1069 (w), 1031 (w), 1012 (w), 957 (w), 889 (w), 867 (w), 580 (w), 810 (w), 721 (w), 628 (w), 590 (w), 475 (w) cm^{-1}; MS (ESI): *m/z*: 731 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{47}H_{87}NO_4H$: 730.6708 $[M + H]^+$, found: 730.6726.

Tetradecyl *O*-bistetradecyl-L-DOPA (10c). According to GP5, yield: 1.34 g, 1.70 mmol, 88%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.5 Hz, 9H, C*H*$_3$), 1.20–1.41 (m, 60H, C*H*$_2$), 1.42–1.55 (m, 6H, C*H*$_2$), 1.56-1.65 (m, 2H, C*H*$_2$), 1.73–1.84 (m, 4H, C*H*$_2$), 2.80 (dd, J = 13.6 Hz, 7.5 Hz, 1H, ArC*H*$_2$), 2.98 (dd, J = 13.6 Hz, 5.4 Hz, 1H, ArC*H*$_2$), 3.67 (dd, J = 7.5 Hz, 5.4

Hz, 1H, H_2NCH), 3.90-3.99 (m, 4H, OCH_2), 4.04-4.15 (m, 2H, CO_2CH_2), 6.65–6.73 (m, 2H, 2-H, 6-H), 6.78 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.8, 26.0, 26.2, 28.7, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0 (CH_2), 40.7 ($ArCH_2$), 56.0 (H_2NCH), 65.0 (CO_2CH_2), 69.2, 69.3 (OCH_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.1 (C=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3361 (w), 2954 (m), 2917 (s), 2849 (s), 1738 (m), 1590 (w), 1518 (m), 1468 (m),1427 (w), 1394 (w), 1377 (w), 1334 (w), 1264 (m), 1187 (m), 1139 (m), 1113 (m), 1012 (w), 948 (m), 907 (w), 868 (w), 852 (w), 801 (w), 729 (s), 648 (w), 629 (w), 591 (w), 474 (w), 450 (w) cm^{-1}; MS (ESI): *m/z*: 787 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{51}H_{95}NO_4H$: 786.7334 $[M + H]^+$, found: 786.7338.

Tetradecyl *O*-bishexadecyl-L-DOPA (10d). According to GP5, yield: 0.71 g, 0.84 mmol, 93%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.21–1.39 (m, 68H, CH_2), 1.40–1.52 (m, 6H, CH_2), 1.57-1.66 (m, 2H, CH_2), 1.74–1.86 (m, 4H, CH_2), 2.80 (dd, J = 13.6 Hz, 7.7 Hz, 1H, $ArCH_2$), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, $ArCH_2$), 3.68 (dd, J = 7.6 Hz, 5.2 Hz, 1H, H_2NCH), 3.91-4.00 (m, 4H, OCH_2), 4.09 (t, J = 6.7 Hz, 2H, CO_2CH_2), 6.66–6.74 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1, 28.6,29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0 (CH_2), 40.7 ($ArCH_2$), 55.9 (H_2NCH), 65.1 (CO_2CH_2), 69.3 (OCH_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.1 (C-5), 175.2 (C=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2852 (m), 1734 (w), 1589 (w), 1512 (w), 1467 (w), 1378 (w), 1261 (w), 1233 (w), 1184 (w), 1138 (w), 1019 (w), 907 (s), 802 (w), 730 (vs), 648 (w) cm^{-1}; MS (ESI): *m/z*: 843 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{55}H_{103}NO_4H$: 842.7960 $[M + H]^+$, found: 842.7962.

Tetradecyl *O*-bisoctadecyl-L-DOPA (10e). According to GP5, yield: 0.97 g, 1.08 mmol, 90%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, CH_3), 1.19–1.38 (m, 78H, CH_2), 1.40-1.49 (m, 4H, CH_2), 1.55-1.67 (m, 2H, CH_2), 1.72–1.85 (m, 4H, CH_2), 2.80 (dd, J = 13.6 Hz, 7.7 Hz, 1H, $ArCH_2$), 3.00 (dd, J = 13.6 Hz, 5.3 Hz, 1H, $ArCH_2$), 3.68 (dd, J = 7.6 Hz, 5.3 Hz, 1H, H_2NCH), 3.91-3.99 (m, 4H, OCH_2), 4.09 (t, J = 6.7 Hz, 2H, CO_2CH_2), 6.66–6.73 (m, 2H, 2-H, 6-H), 6.79 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0 (CH_2), 40.7 ($ArCH_2$), 55.9 (H_2NCH), 65.1 (CO_2CH_2), 69.2, 69.3 (OCH_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.1 (C-5), 175.2 (C=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 1733 (w), 1589 (w), 1512 (w), 1467 (w), 1378 (w), 1261 (m), 1232 (w), 1184 (w), 1138 (w), 1022 (w), 906 (s), 802 (w), 730 (vs), 648 (w) cm^{-1}; MS (ESI): *m/z*: 899 $[M + H]^+$; HRMS (ESI): *m/z* calcd. for $C_{59}H_{111}NO_4H$: 898.8586 $[M + H]^+$, found: 898.8552.

Octadecyl *O*-bisdecyl-L-DOPA (11a). According to GP5, yield: 0.75 g, 1.03 mmol, 85%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 9H, CH_3), 1.20–1.39 (m, 52H, CH_2), 1.40–1.54 (m, 6H, CH_2), 1.57–1.65 (m, 2H, CH_2), 1.74–1.83 (m, 4H, CH_2), 2.80 (dd, J = 13.6 Hz, 7.7 Hz,

1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.3 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.96 (dt, J = 6.7 Hz, 2.0 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.67–6.73 (m, 2H, 2-H, 6-H), 66.80 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 40.7 (Ar*C*H$_2$), 55.9 (HN*C*H), 65.1 (CO_2*C*H$_2$), 69.3, 69.4 (O*C*H$_2$), 114.1 (C-3), 115.1 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3362 (w), 3273 (w), 2954 (w), 2917 (s). 2849 (s), 1787 (w), 1743 (m), 1736(m), 1642 (w), 1589 (w), 1551 (w), 1517 (m), 1467 (m), 1426 (w), 1396 (m), 1378 (w), 1332 (w), 1268 (m), 1233 (m), 1186 (m), 1138 (s), 111 (w), 1067 (w), 1021 (w), 988 (w), 951 (w), 907 (w), 864 (w), 851 (w), 805 (w), 758 (w), 722 (m), 629 (w),589 (w), 449 (w) cm^{-1}; MS (ESI): *m/z*: 731 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{47}H_{87}NO_4H$: 730.6708 [M + H]$^+$, found: 730.6717.

Octadecyl *O*-bisdodecyl-L-DOPA (11b). According to GP5, yield: 0.89 g, 1.13 mmol, 84%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.21–1.38 (m, 60H, C*H*$_2$), 1.41-1.53 (m, 6H, C*H*$_2$), 1.57-1.65 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.79 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.96 (t, J = 6.6 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.66–6.74 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9 (*C*H$_2$), 40.7 (Ar*C*H$_2$), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H$_2$), 69.3, 69.4 (O*C*H$_2$), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2920 (s), 2851 (s), 1737 (w), 1589 (w), 1513 (w), 1467 (w), 1427 (w), 1378 (w), 1262 (m), 1233 (w), 1182 (w), 1138 (w), 1014 (w), 908 (w), 848 (w), 801 (w), 732 (s), 647 (w), 460 (w) cm^{-1}; MS (ESI): *m/z*: 809 [M + Na]$^+$, 787 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{51}H_{95}NO_4H$: 786.7334 [M + H]+, found: 786.7303.

Octadecyl *O*-bistetradecyl-L-DOPA (11c). According to GP5, yield: 111 mg, 0.13 mmol, 84%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 9H, C*H*$_3$), 1.20–1.39 (m, 70H, C*H*$_2$), 1.41-1.48 (m, 4H, C*H*$_2$), 1.57-1.65 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.79 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.3 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.91-3.99 (m, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.66–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H$_2$), 40.7 (Ar*C*H$_2$), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H$_2$), 69.3, 69.4 (O*C*H$_2$),114.1 (C-3), 115.1 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR(ATR): $\tilde{\nu}$ = 3362 (w), 3259 (w), 2955 (w), 2915 (s), 2849(s), 1737 (w), 1590 (w), 1518 (w), 1468 (m), 1427 W8), 1393 (w), 1378 (w), 1333 (w), 1265 (m), 1234 (m), 1187 (m), 1165 (w), 1139 (w), 1112 (m), 1071 (w), 1053 (w), 1011 (w), 947 (w), 908 (w), 879 (w), 867 (w), 852 (w), 810 (w), 801 (w), 767 (w), 734 (m),

722 (m), 647 (w), 629 (w), 611 (w), 590 (w), 561 (w), 492 (w) cm^{-1}; MS (ESI): *m/z*: 843 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{55}H_{103}NO_4H$: 842.7886 [M + H]$^+$, found: 842.7913.

Octadecyl *O*-bishexadecyl-L-DOPA (11d). According to GP5, yield: 123 mg, 0.14 mmol, 90%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 9H, C*H*$_3$), 1.20–1.38 (m, 78H, C*H*$_2$), 1.43-1.50 (m, 4H, C*H*$_2$), 1.58-1.65 (m, 2H, C*H*$_2$), 1.75–1.83 (m, 4H, C*H*$_2$), 2.80 (dd, J = 13.6 Hz, 7.7 Hz, 1H,ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.3 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.3 Hz, 1H, H_2NC*H*), 3.92-3.99 (m, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.67–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1, 14.2 (*C*H_3), 22.7, 25.9, 26.1, 28.6,29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 40.7 (Ar*C*H_2), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H_2), 69.3, 69.4(O*C*H_2), 114.1 (C-3), 115.1 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2853 (m), 1734 (w), 1588 (w), 1512 (w), 1467 (w), 1376 (w), 1261 (w), 1235 (w), 1184 (w), 1138 (w), 1025 (w), 906 (s), 803 (w), 729 (s), 648 (w), 548 (w) cm^{-1}; MS (ESI): *m/z*: 899 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{59}H_{111}NO_4H$: 898.8586 [M + H]$^+$, found: 898.8574.

Octadecyl *O*-bisoctadecyl-L-DOPA (11e). According to GP5, yield: 321 mg, 0.34 mmol, 93%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 9H, C*H*$_3$), 1.19–1.39 (m, 84H, C*H*$_2$), 1.41-1.54 (m, 6H, C*H*$_2$), 1.57-1.65 (m, 2H, C*H*$_2$), 1.74–1.84 (m, 4H, C*H*$_2$), 2.79 (dd, J = 13.6 Hz, 7.7 Hz, 1H, ArC*H*$_2$), 3.00 (dd, J = 13.6 Hz, 5.2 Hz, 1H, ArC*H*$_2$), 3.68 (dd, J = 7.7 Hz, 5.2 Hz, 1H, H_2NC*H*), 3.95 (t, J = 6.7 Hz, 4H, OC*H*$_2$), 4.09 (t, J = 6.8 Hz, 2H, CO_2C*H*$_2$), 6.66–6.73 (m, 2H, 2-H, 6-H), 6.80 (d, J = 8.0 Hz, 1H, 3-H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.9, 26.1, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 40.7 (Ar*C*H_2), 55.9 (H_2N*C*H), 65.1 (CO_2*C*H_2), 69.3, 69.4 (O*C*H_2), 114.0 (C-3), 115.0 (C-6), 121.6 (C-2), 129.8 (C-1), 148.1 (C-4), 149.2 (C-5), 175.2 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2853 (m), 1732 (w), 1589 (w), 1512 (w), 1467 (w), 1378 (w), 1261 (w), 1232 (w), 1186 (w), 1138 (w), 1018 (w), 906 (s), 803 (w), 728 (s), 649 (m) cm^{-1}; MS (ESI): *m/z*: 955 [M + H]$^+$; HRMS (ESI): *m/z* calcd. for $C_{63}H_{119}NO_4H$: 954.9212 [M + H]$^+$, found: 954.9226.

Decyl *N*-[bis(dimethylamino)methylene]-*O*-bishexyl-L-DOPA chloride (Dopa(10,6,6)). According to GP2, yield: 62.0 mg, 96.8 µmol, 61%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.83-0.96 (m, 9H, C*H*$_3$), 1.20–1.39 (m, 22H, C*H*$_2$), 1.39-1.52 (m,4H, C*H*$_2$), 1.53-1.63 (m, 2H, C*H*$_2$), 1.73–1.85 (m, 4H, C*H*$_2$), 2.39-3.52 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.70 (dd, J = 14.0 Hz, 8.5 Hz, 1H, ArC*H*$_2$), 3.89-4.15 (m, 7H, OC*H*$_2$, CO_2C*H*$_2$, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.98 (dd, J = 8.2 Hz, 1.9 Hz, 1H, 3-H), 7.07 (d, J = 1.9 Hz, 1H, 6-H), 9.98 (bs, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.0, 14.1, (*C*H_3), 22.6, 22.7, 25.7, 25.8, 28.4, 29.2, 29.3, 29.5, 31.6, 31.7, 31.9 (*C*H_2), 36.4 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.4 (HN*C*H), 66.3 (CO_2*C*H_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.3 (C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3394 (w), 2955 (m), 2924 (s), 2855 (m),

1735 (m), 1626 (m), 1572 (m), 1515 (m), 1468 (m), 1430 (w), 1405 (w), 1262 (m), 1234 (m), 1202 (w), 1172 (w), 1142 (w), 1065 (w), 1025 (w), 900 (w), 802 (w), 724 (w), 635 (w), 594 (w), 421 (w) cm^{-1}; MS (ESI): *m/z*: 605 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{36}H_{66}N_3O_4^+$: 604.5048 [M^+], found: 604.5021; POM: Cr 18 °C Col_h 95 °C I. (2nd cooling)

Decyl *N*-[bis(dimethylamino)methylene]-*O*-bisdecyl-L-DOPA chloride (Dopa(10,10,10)). According to GP2, yield: 62.1 mg, 82.4 µmol, 70%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, CH_3), 1.20–1.39 (m, 36H, CH_2), 1.39- 1.51 (m, 4H, CH_2), 1.54-1.63 (m, 2H, CH_2), 1.67–1.86 (m, 6H, CH_2), 2.48-3.47 (m, 13H, ArCH_2,N(CH_3)$_2$), 3.62-3.75 (m, 1H, ArCH_2), 3.90-4.09 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.80 (d, J = 7.8Hz, 1H, 2-H), 6.98 (d, J = 7.4 Hz, 1H, 3-H), 7.07 (s, 1H, 6-H), 9.84 (bs, 1H, NH) ppm; ^{13}C-NMR (101MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9(*C*H_2), 36.5 (Ar*C*H_2), 39.7 (N(*C*H_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2*C*H_2), 69.4, 69.5 (O*C*H_2), 113.9 (C-3), 115.7 (C-6), 122.1 (C-2), 129.2 (C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2853 (s), 1736 (w), 1623 (m), 1571 (m), 1513 (m), 1467 (m), 1430 (w), 1404 (w), 1313 (w), 1261 (w), 1233 (s), 1167 (m), 1141 (m), 1065 (m), 1031 (w), 901 (w), 802 (w), 723 (w), 639 (w), 594 (w), 465 (w) cm^{-1}; MS (ESI): *m/z*: 717 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{44}H_{82}N_3O_4^+$: 716.6300 [M^+], found: 716.6314; DSC: Cr 21 °C [1.2 kJ mol^{-1}] Col_h 46 °C [0.8 kJ mol^{-1}] I. (2nd cooling)

Decyl *N*-[bis(dimethylamino)methylene]-*O*-bistetradecyl-L-DOPA chloride (Dopa(10,14,14)). According to GP2, yield: 54.3 mg, 62.8 µmol, 85%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, CH_3), 1.19–1.39 (m, 54H, CH_2), 1.39- 1.51 (m, 4H, CH_2), 1.51-1.63 (m, 2H, CH_2), 1.71–1.81 (m, 4H, CH_2), 2.47-3.51 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.68 (dd, J = 14.1 Hz, 8.5 Hz, 1H, ArCH_2), 3.90-4.15 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.94 – 7.01 (m, 1H, 3-H), 7.07 (d, J = 2.0 Hz, 1H, 6-H), 9.88 (d, J = 6.3 Hz, 1H, NH) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.5 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2*C*H_2),69.4, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.2 (C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3385 (w), 2955 (w), 2920 (s), 2851 (s), 1735 (w), 1627 (m), 1572 (m), 1514 (m), 1467 (m), 1431 (w), 1405 (w), 1263 (m), 1233 (m), 1202 (w), 1173 (w), 1142 (w), 1066 (w), 1024 (w), 900 (w), 721 (w), 635 (w), 596 (w) cm^{-1}; MS (ESI): *m/z*: 829 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{52}H_{98}N_3O_4^+$: 828.7552 [M^+], found: 828.7567; DSC: Cr 29 °C [9.3 kJ mol^{-1}] Col_h 46 °C [0.8 kJ mol^{-1}] I. (2nd cooling)

Decyl *N*-[bis(dimethylamino)methylene]-*O*-bisoctadecyl-L-DOPA chloride (Dopa(10,18,18)). According to GP2, yield: 87.6 mg, 87.9 µmol, 78%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.1 Hz, 9H, CH_3), 1.18–1.38 (m, 70H, CH_2), 1.40- 1.50 (m, 4H, CH_2), 1.52-1.61 (m, 2H, CH_2), 1.72–1.83 (m, 4H, CH_2), 2.48-3.48 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.60-

3.73 (m, 1H, ArCH_2), 3.90-4.09 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.78 (d, J = 8.1 Hz, 1H, 2-H), 6.97 (d, J = 8.0 Hz, 1H, 3-H), 7.07 (bs, 1H, 6-H), 9.85 (bs, 1H, N*H*) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.1, (CH_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 36.5 (ArCH_2), 39.7 (N(CH_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2CH_2), 69.4, 69.5 (OCH_2), 114.0 (C-3), 115.7 (C-6), 122.1 (C-2), 129.3 (C-1), 148.2 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 1738 (w), 1621 (w), 1570 (w), 1512 (w), 1467 (w), 1430 (w), 1404 (w), 1261 (w), 1234 (w), 1164 (w), 1140 (w), 1065 (w), 1030 (w), 907 (w), 805 (w), 727 (vs), 641 (w) cm^{-1}; MS (ESI): *m/z*: 941 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{60}H_{114}N_3O_4^+$: 940.8804 [M$^+$], found: 940.8841; DSC: Cr 45 °C [42.6 kJ mol^{-1}] Col_h 50 °C [0.6 kJ mol^{-1}] I. (2nd cooling, monotropic!)

Tetradecyl *N*-[bis(dimethylamino)methylene]-*O*-bisdecyl-L-DOPA chloride (Dopa(14,10,10)). According to GP2, yield: 341 mg, 0.42 mmol, 91%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.18–1.39 (m, 46H, CH_2), 1.39- 1.51 (m, 4H, CH_2), 1.52-1.62 (m, 2H, CH_2), 1.73–1.85 (m, 4H, CH_2), 2.45-3.45 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.69 (dd, J = 14.0 Hz, 8.4 Hz, 1H, ArCH_2), 3.88-4.17 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.98 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.07 (d, J = 1.9 Hz, 1H, 6-H), 9.86 (d, J = 6.0 Hz, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (CH_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 36.5 (ArCH_2), 39.7 (N(CH_3)$_2$), 60.5 (HN*C*H), 66.3(CO_2CH_2), 69.4, 69.5 (OCH_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.2 (C-1), 148.1 (C-4), 149.1 (C-5), 162.0 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3390 (w), 2956 (w), 2919 (s), 2850 (s), 1734 (w), 1626 (m), 1571 (m), 1515 (m), 1468 (m), 1431 (w), 1405 (w), 1264 (m), 1232 (m), 1205 (w), 1172 (w), 1141 (w), 1067 (w), 1024 (w), 901 (w), 722 (w), 640 (w), 595 (w) cm^{-1}; MS (ESI): *m/z*: 773 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{48}H_{90}N_3O_4^+$: 772.6926 [M$^+$], found: 772.6936; DSC: Cr 28 °C [1.9 kJ mol^{-1}] Col_h 54 °C [1.1 kJ mol^{-1}] I (2nd cooling).

Tetradecyl *N*-[bis(dimethylamino)methylene]-*O*-bisdodecyl-L-DOPA chloride (Dopa(14,12,12)). According to GP2, yield: 346 mg, 0.40 mmol, 87%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.81-0.94 (m, 9H, CH_3), 1.17–1.39 (m, 54H, CH_2), 1.39-1.51 (m, 4H, CH_2), 1.52-1.63 (m, 2H, CH_2), 1.76–1.84 (m, 4H, CH_2), 2.43-3.46 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.70 (dd, J = 14.0 Hz, 8.5 Hz, 1H, ArCH_2), 3.88-4.16 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.79 (d, J = 8.2 Hz, 1H, 2-H), 6.98 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.08 (d, J = 1.9 Hz, 1H, 6-H), 9.97 (d, J = 6.2 Hz, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (CH_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 36.5 (ArCH_2), 39.7 (N(CH_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2CH_2), 69.3, 69.5 (OCH_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.3 (C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 1737 (w), 1623 (m), 1571 (w), 1512 (w), 1467 (m), 1430 (w), 1404 (w), 1261 (m), 1233 (w),

1167 (w), 1140 (w), 1030 (w), 907 (m), 728 (vs), 641 (w) cm^{-1}; MS (ESI): *m/z*: 829 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{52}H_{98}N_3O_4^+$: 828.7552 [M^+], found: 828.7548; DSC: Cr 52 °C [46.7 kJ mol^{-1}] Col_h 119 °C [1.5 kJ mol^{-1}] I. (2nd cooling)

Tetradecyl *N*-[bis(dimethylamino)methylene]-*O*-bistetradecyl-L-DOPA chloride (Dopa(14,14,14)). According to GP2, yield: 327 mg, 0.36 mmol, 90%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.84-0.93 (m, 9H, C*H*$_3$), 1.16–1.39 (m, 62H, C*H*$_2$), 1.39-1.51 (m, 4H, C*H*$_2$), 1.52-1.62 (m, 2H, C*H*$_2$), 1.73–1.84 (m, 4H, C*H*$_2$), 2.45-3.51 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.68 (dd, J = 14.0 Hz, 8.5 Hz, 1H, ArC*H*$_2$), 3.90-4.08 (m, 6H, OC*H*$_2$, CO_2C*H*$_2$), 4.08-4.15 (m, 1H, HNC*H*), 6.78 (d, J = 8.2 Hz, 1H, 2-H), 6.97 (dd, J = 8.2 Hz, 2.0 Hz, 1H, 3-H), 7.07 (d, J = 2.0 Hz, 1H,6-H), 9.85 (d, J = 6.3 Hz, 1H), N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8,26.0, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.5 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.4 (HN*C*H),66.3 (CO_2*C*H_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.0 (C-2), 129.2 (C-1), 148.1 (C-4),149.1 (C-5), 162.0 (HN=*C*), 171.0 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3380(w), 2956 (w), 2916 (s), 2873 (w), 2849 (s), 1734 (w), 1627 (m), 1570 (m), 1515 (m), 1467 (m), 1341 (w), 1405 (w), 1365 (w), 1265 (m), 1233 (w), 1206 (w), 1171 (w), 1141 (w), 1066 (w), 1021 (w), 928 (w), 900 (w), 853 (w), 818 (w), 786 (w), 767 (w), 721 (m), 682 (w), 640 (w), 596 (w), 467 (w), 438 (w) cm^{-1}; MS (ESI): *m/z*: 885 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{56}H_{106}N_3O_4^+$: 884.8178 [M^+], found: 884.8189; DSC: Cr 61 °C [52.6 kJ mol^{-1}] Col_h 134 °C [1.6 kJ mol^{-1}] I. (2nd cooling)

Tetradecyl *N*-[bis(dimethylamino)methylene]-*O*-bishexadecyl-L-DOPA chloride (Dopa(14,16,16)). According to GP2, yield: 289 mg, 0.30 mmol, 96%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.6 Hz, 9H, C*H*$_3$), 1.15–1.38 (m, 70H, C*H*$_2$), 1.39- 1.51 (m, 4H, C*H*$_2$), 1.52-1.64 (m, 2H, C*H*$_2$), 1.72–1.83 (m, 4H, C*H*$_2$), 2.46-3.46 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.69 (dd, J = 14.1 Hz, 8.5 Hz, 1H, ArC*H*$_2$), 3.89-4.16 (m, 7H, OC*H*$_2$, CO_2C*H*$_2$, HNC*H*), 6.79 (d, J = 8.2 Hz, 1H, 2-H), 6.97 (dd, J = 8.2 Hz, 1.9 Hz, 1H, 3-H), 7.07 (d, J = 2.0 Hz, 1H, 6-H), 9.90 (d, J = 6.2 Hz, 1H), N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.5 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2*C*H_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.2 (C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 1738 (w), 1621 (w), 1571 (w), 1512 (w), 1467 (w), 1404 (w), 1261 (w), 1234 (w), 1165 (w), 1140 (w), 1030 (w), 907 (s), 728 (vs), 641 (w) cm^{-1}; MS (ESI): *m/z*: 941 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{60}H_{114}N_3O_4^+$: 940.8804 [M^+], found: 940.8823; DSC: Cr 60 °C [52.3 kJ mol^{-1}] Col_h 118 °C [1.0 kJ mol^{-1}] I. (2nd cooling)

Tetradecyl *N*-[bis(dimethylamino)methylene]-*O*-bisoctadecyl-L-DOPA chloride (Dopa(14,18,18)). According to GP2, yield: 326 mg, 0.32 mmol, 92%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, C*H*$_3$), 1.19–1.38 (m, 76H, C*H*$_2$), 1.39- 1.51 (m, 4H, C*H*$_2$),

1.56-1.66 (m, 2H, CH_2), 1.76–1.85 (m, 6H, CH_2), 2.49-3.45 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.70 (dd, J = 14.1 Hz, 8.5 Hz, 1H, ArCH_2), 3.90-4.14 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.79 (d, J = 8.2 Hz, 1H, 2-H), 6.98 (dd, J = 8.2 Hz, 1.9 Hz, 1H, 3-H), 7.08 (d, J = 2.0 Hz, 1H, 6-H), 10.00 (d, J = 6.3 Hz, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.4 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.6 (HN*C*H), 66.3 (CO_2CH_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.7 (C-6), 122.1 (C-2), 129.3 (C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2918 (s), 2850 (s), 1737 (w), 1620 (m), 1571 (w), 1513 (w), 1467 (m), 1430 (w), 1404 (w), 1262 (m), 1165 (w), 1141 (w), 1066 (w), 1031 (w), 907 (s), 727 (vs), 641 (w) cm^{-1}; MS (ESI): *m/z*: 997 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{64}H_{122}N_3O_4^+$: 996.9430 [M$^+$], found: 996.9440; DSC: Cr 59 °C [60.8 kJ mol^{-1}] Col_h 126 °C [1.6 kJ mol^{-1}] I. (2nd cooling)

Octadecyl *N*-[bis(dimethylamino)methylene]-*O*-bisdecyl-L-DOPA chloride (Dopa(18,10,10)). According to GP2, yield: 149 mg, 0.17 mmol, 70%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.16–1.39 (m, 52H, CH_2), 1.39-1.51 (m, 4H, CH_2), 1.52-1.67 (m, 2H, CH_2), 1.73–1.84 (m, 4H, CH_2), 1.91–2.05 (m, 2H, CH_2), 2.47-3.57 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.68 (dd, J = 14.1 Hz, 8.5 Hz, 1H, ArCH_2), 3.89-4.16 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.97 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.07 (d, J = 2.0 Hz, 1H, 6-H), 9.84 (d, J = 6.4 Hz, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.5 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2CH_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.2(C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1736 (w), 1623 (m), 1572 (m), 1513 (m), 1467 (m), 1430 (w), 1404 (w), 1378 (w), 1261 (m), 1234 (m), 1168 (m), 1141 (w), 1066 (w), 1030 (w), 927 (w), 907 (w), 803 (w), 728 (s), 639 (w), 595 (w), 471 (w), 419 (w) cm^{-1}; MS (ESI): *m/z*: 829 [M$^+$]; HRMS (ESI): *m/z* calcd. for $C_{52}H_{98}N_3O_4^+$: 828.7552 [M$^+$], found: 828.7543; DSC: Cr 38 °C [25.2 kJ mol^{-1}] Col_h 112 °C [1.0 kJ mol^{-1}] I. (2nd cooling)

Octadecyl *N*-[bis(dimethylamino)methylen]-*O*-bisdodecyl-L-DOPA chloride (Dopa(18,12,12)). According to GP2, yield: 132 mg, 0.14 mmol, 84%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.18–1.38 (m, 60H, CH_2), 1.40-1.50 (m, 4H, CH_2), 1.52-1.63 (m, 2H, CH_2), 1.72–1.83 (m, 4H, CH_2), 1.83–2.00 (m, 2H, CH_2), 2.51-3.49 (m, 13H, ArCH_2, N(CH_3)$_2$), 3.66 (dd, J = 14.0 Hz, 8.4 Hz, 1H, ArCH_2), 3.89-4.16 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.96 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.06 (d, J = 1.9 Hz, 1H, 6-H), 9.77 (d, J = 6.3 Hz, 1H), N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.5 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.4 (HN*C*H), 66.3 (CO_2CH_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.2(C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR

(ATR): $\tilde{\nu}$ = 2922 (s), 2852 (s), 1737 (w), 1621 (w), 1571 (w), 1513 (w), 1466 (m), 1430 (w), 1404 (w), 1261 (m), 1235 (w), 1165 (w), 1140 (w), 1065 (w), 907 (s), 804 (w), 728 (vs), 641 (w) cm^{-1}; MS (ESI): *m/z*: 885 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{56}H_{106}N_3O_4^+$: 884.8178 [M+], found: 884.8175; DSC: Cr 35 °C [19.4 kJ mol^{-1}] Col_h 113 °C [2.3 kJ mol^{-1}] I. (2nd cooling)

Octadecyl *N*-[bis(dimethylamino)methylene]-*O*-bistetradecyl-L-DOPA chloride (Dopa(18,14,14)). According to GP2, yield: 41.3 mg, 42.3 µmol, 71%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, C*H*$_3$), 1.15–1.39 (m, 68H, C*H*$_2$), 1.38-1.50 (m, 4H, C*H*$_2$), 1.52-1.64 (m, 2H, C*H*$_2$), 1.72–1.83 (m, 4H, C*H*$_2$), 1.83–1.98 (m, 2H, C*H*$_2$), 2.52-3.51 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.70 (dd, J = 14.1 Hz, 8.5 Hz, 1H, ArC*H*$_2$), 3.89-4.15 (m, 7H, OC*H*$_2$, CO_2C*H*$_2$, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.98 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.08 (d, J = 1.9 Hz, 1H, 6-H), 9.95 (d, J = 6.2 Hz, 1H), N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.4 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.5 (HN*C*H), 66.3 (CO_2*C*H_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.6 (C-6), 122.1 (C-2), 129.3(C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (s), 2853 (m), 1739 (w), 1620 (m), 1570 (w), 1512 (w), 1467 (m), 1430 (w), 1404 (w), 1261 (m), 1234 (w), 1164 (w), 1140 (w), 1065 (w), 1030 (w), 906 (s), 727 (vs), 641 (m) cm^{-1}; MS (ESI): *m/z*: 941 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{60}H_{114}N_3O_4^+$: 940.8804 [M^+], found: 940.8790; POM: Cr 50 °C Col_h 110 °C I. (2nd cooling)

Octadecyl *N*-[bis(dimethylamino)methylene]-*O*-bishexadecyl-L-DOPA chloride (Dopa(18,16,16)). According to GP2, yield: 112 mg, 108 µmol, 81%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 9H, C*H*$_3$), 1.20–1.37 (m, 76H, C*H*$_2$), 1.10- 1.51 (m, 4H, C*H*$_2$), 1.54-1.61 (m, 2H, C*H*$_2$), 1.73–1.83 (m, 6H, C*H*$_2$), 2.56-3.50 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.71 (dd, J = 14.1 Hz, 8.5 Hz, 1H, ArC*H*$_2$), 3.89-4.15 (m, 7H, OC*H*$_2$, CO_2C*H*$_2$, HNC*H*), 6.79 (d, J = 8.1 Hz, 1H, 2-H), 6.98 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.08 (d, J = 2.0 Hz, 1H, 6-H), 10.03 (d, J = 6.3 Hz, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.4 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.6 (HN*C*H), 66.3 (CO_2*C*H_2), 69.3, 69.5 (O*C*H_2), 113.9 (C-3), 115.7 (C-6), 122.1 (C-2), 129.3(C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ =2924 (m), 2853 (m), 1739 (w), 1620 (w), 1570 (w), 1513 (w), 1467 (w), 1404 (w), 1261 (w), 1163 (w), 1140 (w), 1030 (w), 906 (s), 727 (vs), 642 (m) cm^{-1}; MS (ESI): *m/z*: 997 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{64}H_{122}N_3O_4^+$: 996.9430 [M^+], found: 996.9425; DSC: Cr 70 °C [62.2 kJ mol^{-1}] Col_h 112 °C [1.2 kJ mol^{-1}] I. (2nd cooling)

Octadecyl *N*-[bis(dimethylamino)methylene]-*O*-bisoctadecyl-L-DOPA chloride (Dopa(18,18,18)). According to GP2, yield: 88.2 mg, 81.0 µmol, 93%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 9H, C*H*$_3$), 1.15–1.39 (m, 84H, C*H*$_2$), 1.38- 1.51 (m, 4H, C*H*$_2$), 1.52-1.64 (m, 2H, C*H*$_2$), 1.68–1.87 (m, 6H, C*H*$_2$), 2.51-3.54 (m, 13H, ArC*H*$_2$, N(C*H*$_3$)$_2$), 3.71

(dd, J = 14.1 Hz, 8.5 Hz, 1H, ArCH_2), 3.88-4.17 (m, 7H, OCH_2, CO_2CH_2, HNC*H*), 6.78 (d, J = 8.1 Hz, 1H, 2-H), 6.98 (dd, J = 8.1 Hz, 1.9 Hz, 1H, 3-H), 7.09 (d, J = 2.0 Hz, 1H, 6-H), 10.04 (d, J = 6.3 Hz, 1H, N*H*) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.1, (*C*H_3), 22.7, 25.8, 26.1, 28.4, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9 (*C*H_2), 36.4 (Ar*C*H_2), 39.6 (N(*C*H_3)$_2$), 60.6 (HN*C*H), 66.3 (CO_2*C*H_2), 69.4, 69.5 (O*C*H_2), 113.9 (C-3), 115.7 (C-6), 122.1 (C-2), 129.3(C-1), 148.1 (C-4), 149.1 (C-5), 162.1 (HN=*C*), 171.1 (*C*=O) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3392 (w), 2956 (w), 2917 (s), 2849 (s), 1735 (w), 1627 (m), 1572 (w), 1514 (w), 1467 (m), 1431 (w), 1405 (w), 1266 (m), 1233 (w), 1202 (w), 1173 (w), 1141 (w), 1067 (w), 1024 (w), 906 (m), 723 (s), 641 (w), 597 (w), 550 (w), 516 (w), 501 (w), 480 (w), 467 (w) cm^{-1}; MS (ESI): *m/z*: 1053 [M^+]; HRMS (ESI): *m/z* calcd. for $C_{68}H_{130}N_3O_4^+$: 1053.0056 [M^+], found: 1053.0065; DSC: Cr 75 °C [81.5 kJ mol^{-1}] Col_h 120 °C[1.2 kJ mol^{-1}] I. (2nd cooling)

5) Biological investigations

Evaluation of cytotoxicity of compounds using the WST-assay

L-929 is a murine fibroblast cell line (can be obtained from Sigma). Cell cultures were routinely kept in Dulbecco´s modified eagle medium (DMEM) with serum (10%) and phenolred as indicator.

For cytotoxicity studies the medium was removed from the cell culture flask and the cell detachment solution accutase™ (Sigma) was added and incubated for approximately 45 min. Detached cells were resuspended and transferred to a Falcon® tube and centrifuged. The cell pellet was suspended in colorless DMEM. Cell density was adjusted to 1.56×10^4 cells/ mL with DMEM supplemented with serum (10%), without phenolred. 30 µL of this cell suspension were seeded in each well of a 384 well microtiter plate (Corning 3701, polystyrene, flat bottom, cell-culture treated, sterile, with lid). Cells were allowed to adhere to the bottom of the plates overnight in an incubator at 37°C, with 10% CO_2 atmosphere. On the next day from a compound plate 0.5 µl of the compound solutions were added to each well using the semi-automatic 96-fold pipettor CyBio® Selma (Analytik Jena AG), and the compounds were allowed to incubate with the cells for 3 days. 2.5 µL of a ready-to-use WST-1 solution were added, allowed to incubate for 45 min at 37°C, and the optical density was determined at 450 nm using the microtiterplate reader µQuant together with the Gen5 software (BioTek). The compound plate was prepared from compound stock solutions in DMSO. If the IC_{50} was determined a compound plate was prepared comprising serially diluted compound solutions, usually with dilution factors 2 or 3 and 10 dilution steps within the dilution series. Maximum compound concentrations in the compound plate were 5 mg/mL or 1 mg/mL, depending on compound solubility and availability. From the resulting data IC_{50} values were calculated using the non-linear regression module of GraphPad Prism 5.

Table S1 Dependence of antiproliferative activity on the L-929 cell line of amino acid-based ILCs **Phe(m)**, **Tyr(m,n)** and **Dopa(18,n,n)** on the length of the alkyl chain

Compd	m/n	IC_{50} (µM)	Compd	m/n	IC_{50} (µM)
Phe(10)[a]	10	2.05 ± 0.68	**Tyr(10,8)**	8	4.89 ± 1.3
Phe(12)	12	1.55 ± 1.2	**Tyr(10,10)**	10	2.85 ± 1.01
Phe(14)	14	2.89 ± 1.4	***cycl*-Tyr(10,10)**	10	3.7 ± 1.68
Phe(16)	16	2.74 ± 0.66	**Tyr(10,14)**	14	50.66 ± 12.5
Phe(18)	18	4.58 ± 2.1	**Tyr(10,16)**	16	58.85 ± 14.2
Phe(18)[b]	18	2.2 ± 0.199	**Tyr(10,18)**	18	68.73 ± 24.3
Tyr(14,8)	8	90.04 ± 25.5	**Dopa(18,10,10)**	10	3.43 ± 0.84
Tyr(14,10)	10	45.14 ± 13.8	**Dopa(18,12,12)**	12	8.96 ± 0.14
Tyr(14,12)	12	47.98 ± 12.3	**Dopa(18,14,14)**	14	61.72 ± 14.74
Tyr(14,14)	14	9.13 ± 6.3	**Dopa(18,16,16)**	16	120 ± 10
***cycl*-Tyr(14,14)**	14	3.68 ± 3.1	**Dopa(18,18,18)**	18	21.94 ± 12.52
Tyr(14,16)	16	120[c]			
Tyr(14,18)	18	120[c]			

[a] Non-mesomorphic. [b] Derivative from D-phenyl-alanine. [c] No standard deviation because IC_{50} values higher than the highest used concentration.

Microbial growth inhibition assays

Test organisms were *Staphylococcus aureus* DSM 346, *Escherichia coli* K12 and D21f2. The latter is an *E. coli* mutant strain with defects in biosynthesis of lipopolysaccharides (LPS) resulting in an outer cell membrane with higher permeability. Strains were cultivated in a complex medium based on tryptic broth. All cultivations were done at 37°C, and overnight cultures and precultures were done in cultivation flasks with shaking. Assay plates were either 96 well half area plates (Costar 3697) or 384 well plates (Corning 3701). The working volume was 45 µl for 384 well plates and 90 µl for the 96 well plates. Optical densities were determined at 600 nm using the microtiter plate reader µQuant (BioTek). Overnight cultures were used to inoculate a preculture, which was incubated for approximately 3 h, until exponential growth of the culture could be observed. This culture was diluted again with fresh medium so that the starting OD in the microtiter plate was 0.1. Compound solutions were added from a compound plate with the semi-automatic 96-fold pipettor CyBio® Selma (Analytik Jena AG). The volumes were chosen so that the final DMSO concentration in the test plate was not above 1%. Growth of the bacteria was followed by determination of OD600 in regular intervals for the first 4–5 h and then again after 21 h and eventually after 24 h. From the resulting data IC_{50} values were calculated using the non-linear regression module of GraphPad Prism 5.

Table S2 Antibacterial activity on Staphylococcus aureus of amino acid-based ILCs **Phe(m)** and **Tyr(10,n)** depending on the length of the alkyl chain

Compd	m/n	IC_{50} (µM)
Phe(10)[a]	10	21.1 ± 6.8
Phe(12)	12	8.1 ± 4.3
Phe(14)	14	4.2 ± 2.0
Phe(16)	16	12.6 ± 6.9
Phe(18)	18	14.6 ± 5.4
Tyr(10,8)	8	52.1 ± 25.3
Tyr(10,10)	10	14.5 ± 5.0
***cycl*-Tyr(10,10)**	10	13.5 ± 5.0
Tyr(10,14)	14	inactive
Tyr(10,16)	16	inactive
Tyr(10,18)	18	inactive

[a] Non-mesomorphic.

Determination of the influx of Ca^{2+}-ions

The assay was performed with the human monocytic cell line U937 (suspension cells). The cell culture was routinely kept in RPMI medium supplemented with serum (10%) and glutamine. Ca^{2+}-ions were determined with the Fluo-4 NW Calcium assay kit (Life Technologies) according to the instructions given by the manufacturer. On the day of the assay cells were harvested and resuspended in buffer C from the assay kit resulting in 2.4 x 10^6 cells/mL. Assay plates were 96 well plates (Costar 3697: half area, cell-culture treated, flat bottom). In each well 25 µl of the cell suspension were seeded (60.000 cells/well) and 25 µl of the indicator solution (mixture of Fluo-4, probenenecid, buffer C, according to the recipe of the manufacturer) were added. The plates were incubated at 37°C for 30 min and at room temperature for another 30 min. 20 µl of the compound solutions were added and incubated at room temperature. After 1 h, fluorescence was determined (microtiterplate reader Synergy 4, BioTek; excitation: 485 nm; emission: 528 nm) first, and then again after 3 h and after 4 h. Compound solutions were prepared such that the final DMSO concentration in the well was not higher than 1%. From the resulting data IC_{50} values were calculated using the non-linear regression module of GraphPad Prism 5.

6) DSC data of Tyr(10,n) derivatives

Table S3 Phase transition temperature (°C) and enthalpies ΔH (kJ mol^{-1}) of tyrosine ILCs **Tyr(10,n)** as determined by DSC[a]

Compd	Phase	T (ΔH)	SmA	T (ΔH)	I
Tyr(10,8)[b]	G	20	●	61	●
Tyr(10,10)[c]	G	30 (0.8)	●	79 (1.5)	●
Tyr(10,14)	G	28 (0.8)	●	82 (0.4)	●
Tyr(10,16)	G	41 (5.9)	●	77 (0.4)	●
Tyr(10,18)	Cr	14 (1.7)	●	79 (1.4)	●

[a] Phases observed: G (glass), Cr (crystalline), SmA (smectic A), I (isotropic liquid). [b] Determined by POM. [c] Taken from ref.[22]

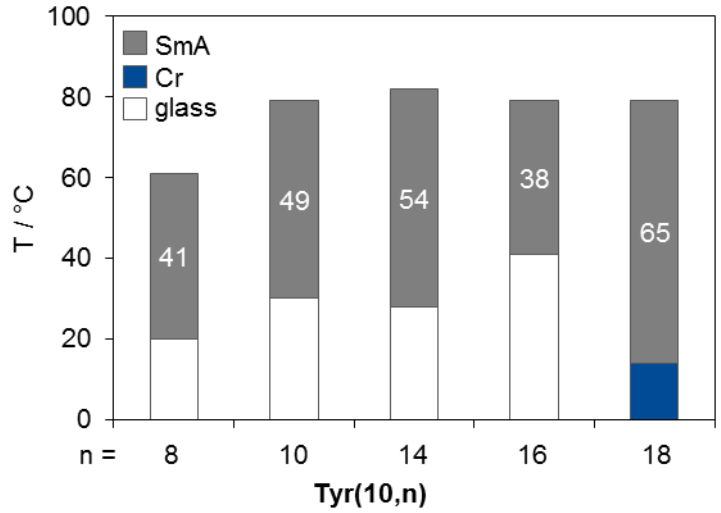


Fig. S1 Mesophase ranges (given in K).

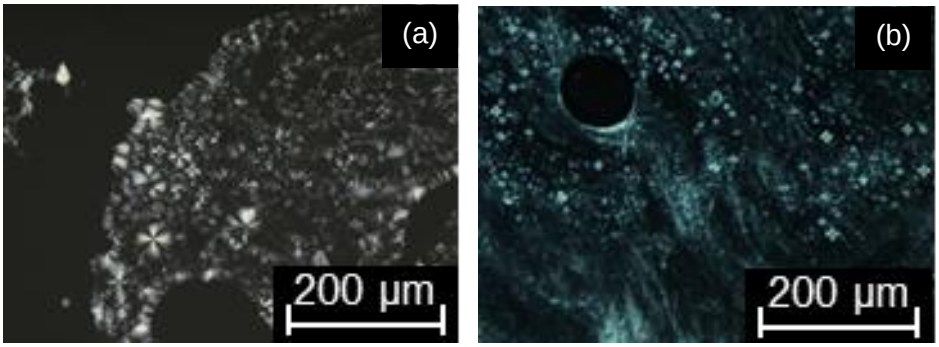


Fig. S2 Comparison of POM textures with the known **Tyr(14,n)** indicated smectic A phases for **Tyr(10,n)**. For example, Maltese cross textures were observed between crossed polarizers upon cooling from the isotropic liquid for both **Tyr(10,18)** at 90°C (a) and **Tyr(14,16)** at 110°C (b).[6]

7) Comparison of mesophase ranges of Dopa(m,n,n) derivatives

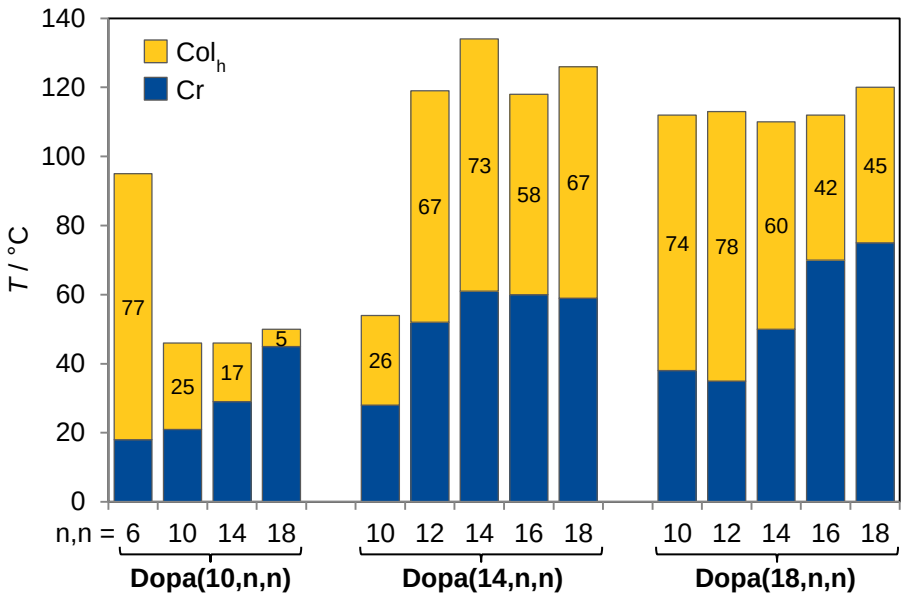


Fig. S3 Mesophase ranges of ILCs **Dopa(m,n,n)** were obtained by DSC upon second cooling or POM (m = 10, n = 6 and m = 18, n = 14) and are given in K. Mesophase widths.

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8) Differential scanning calorimetry (DSC)

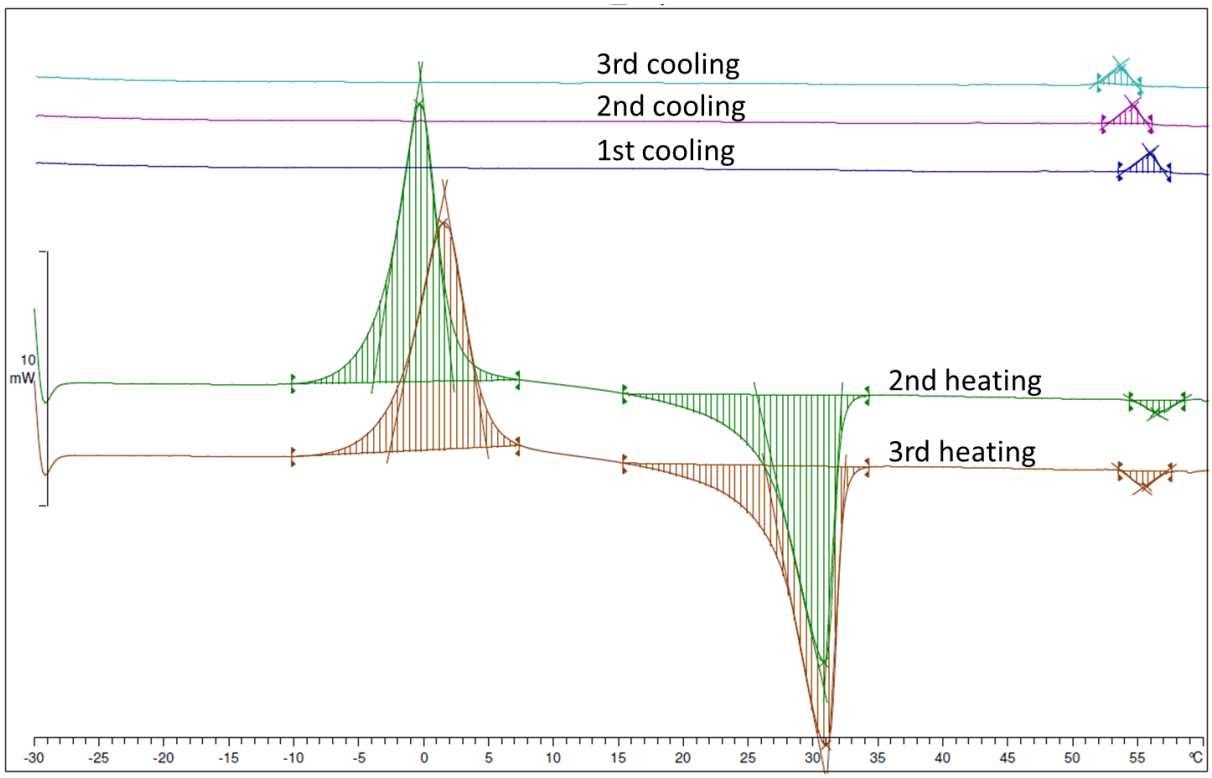


Fig. S4 DSC curves (onset) of **Phe(12)**.

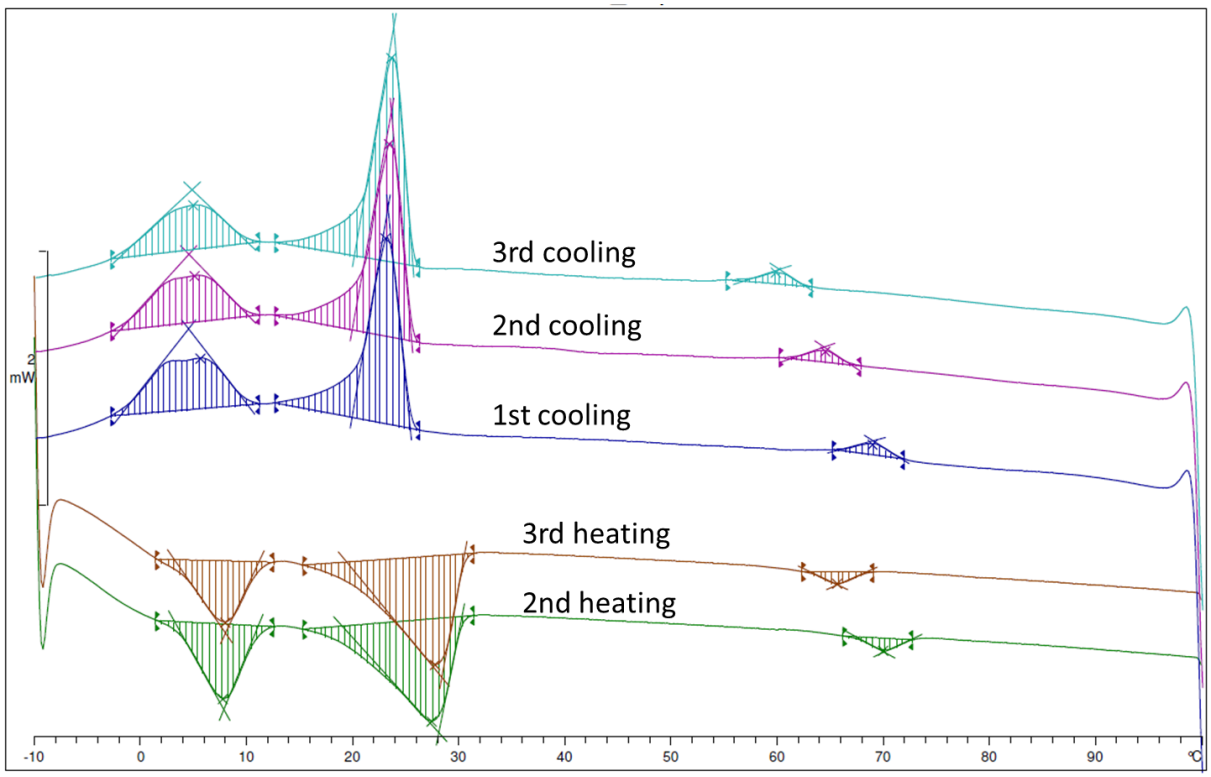


Fig. S5 DSC curves (onset) of **Phe(16).**

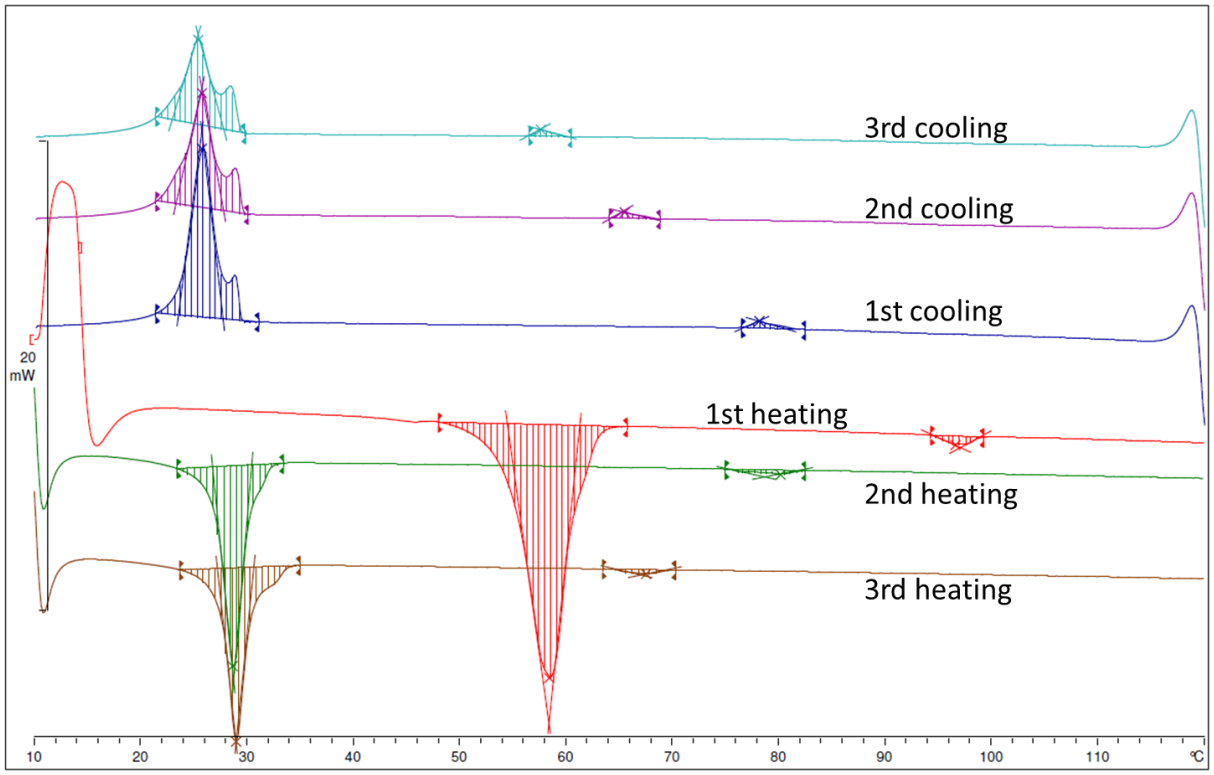


Fig. S6 DSC curves (onset) of **Phe(18).**

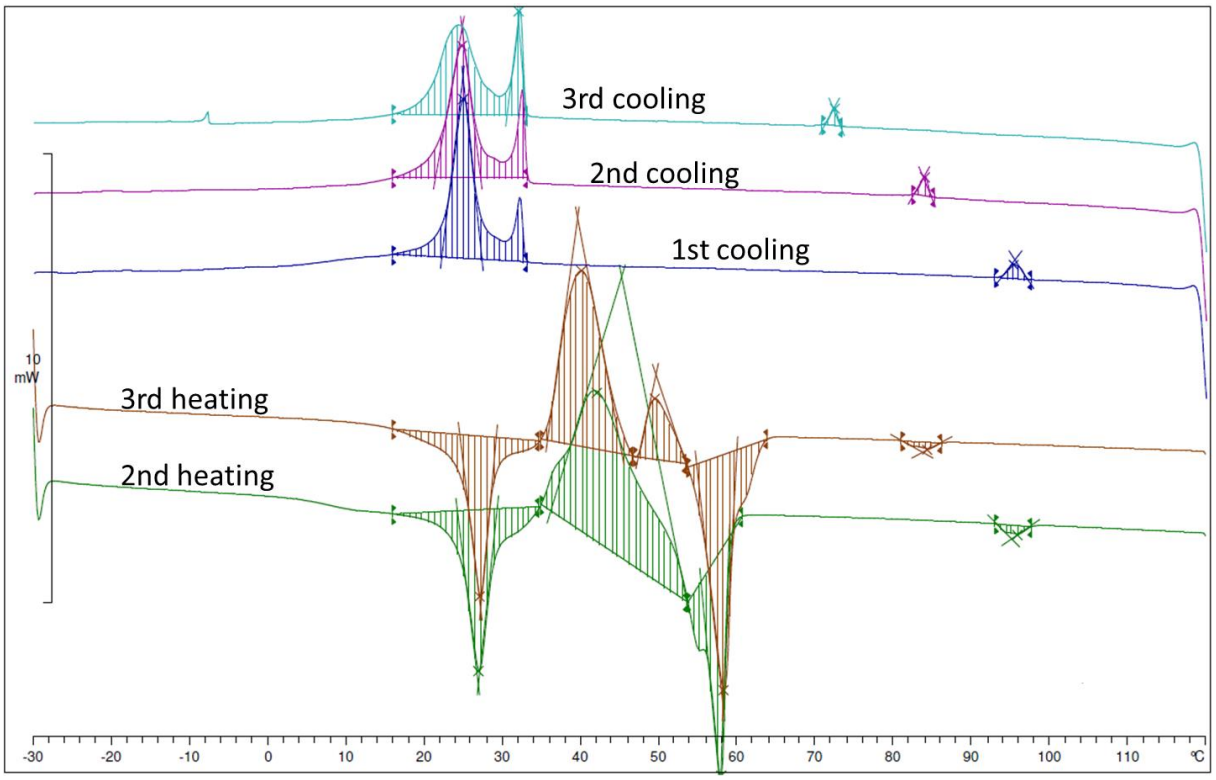


Fig. S7 DSC curves (onset) of **D-Phe(18).**

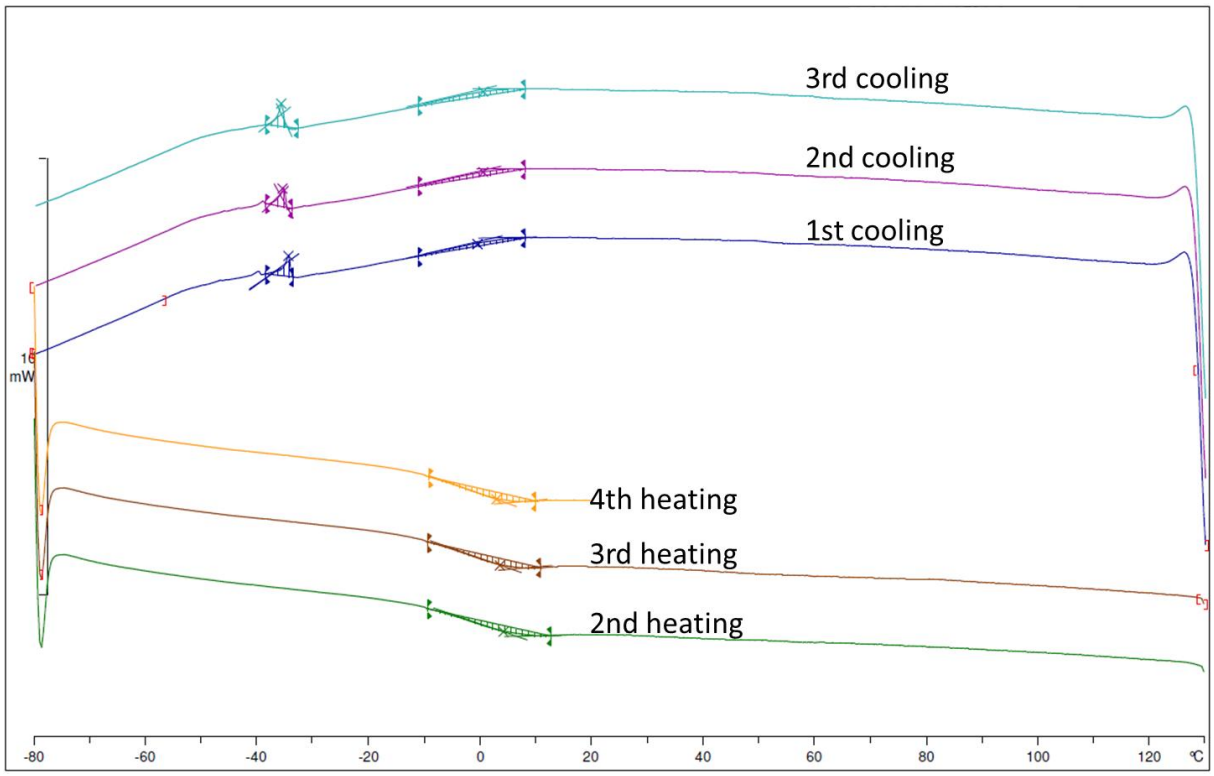


Fig. S8 DSC curves (onset) of **Tyr(10,8).**

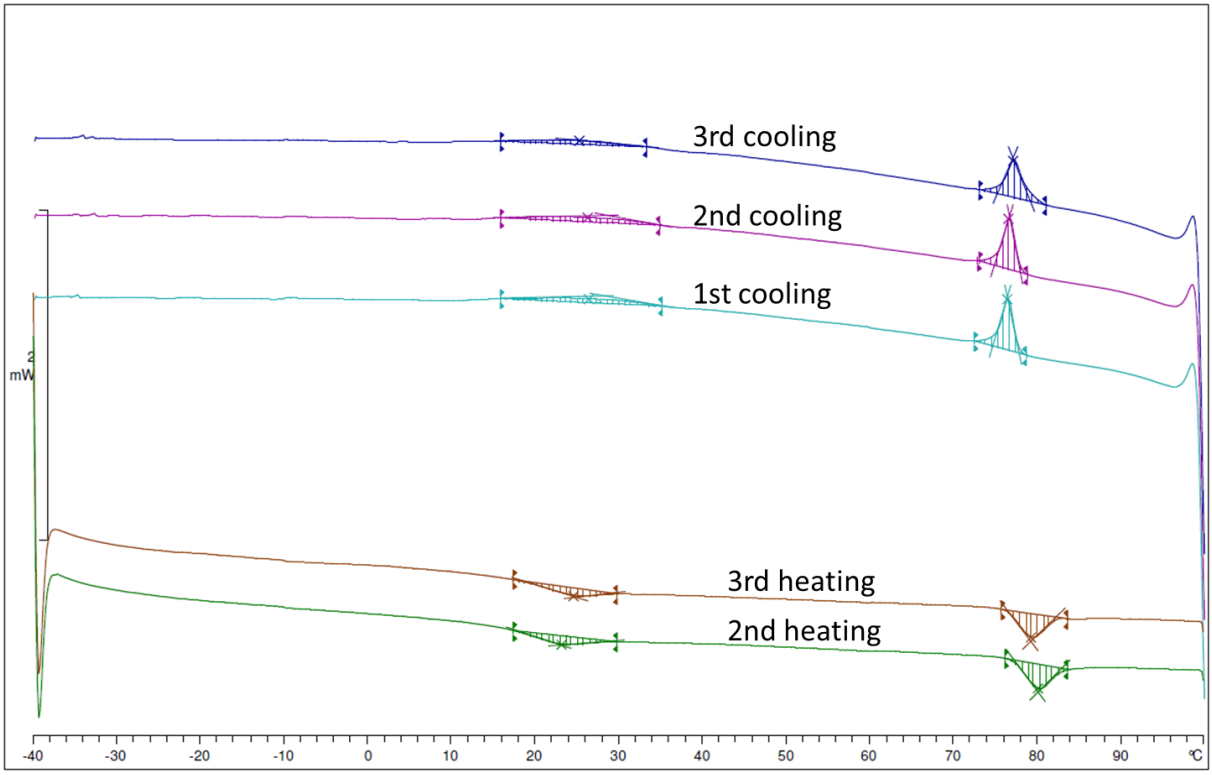


Fig. S9 DSC curves (onset) of **Tyr(10,10).**

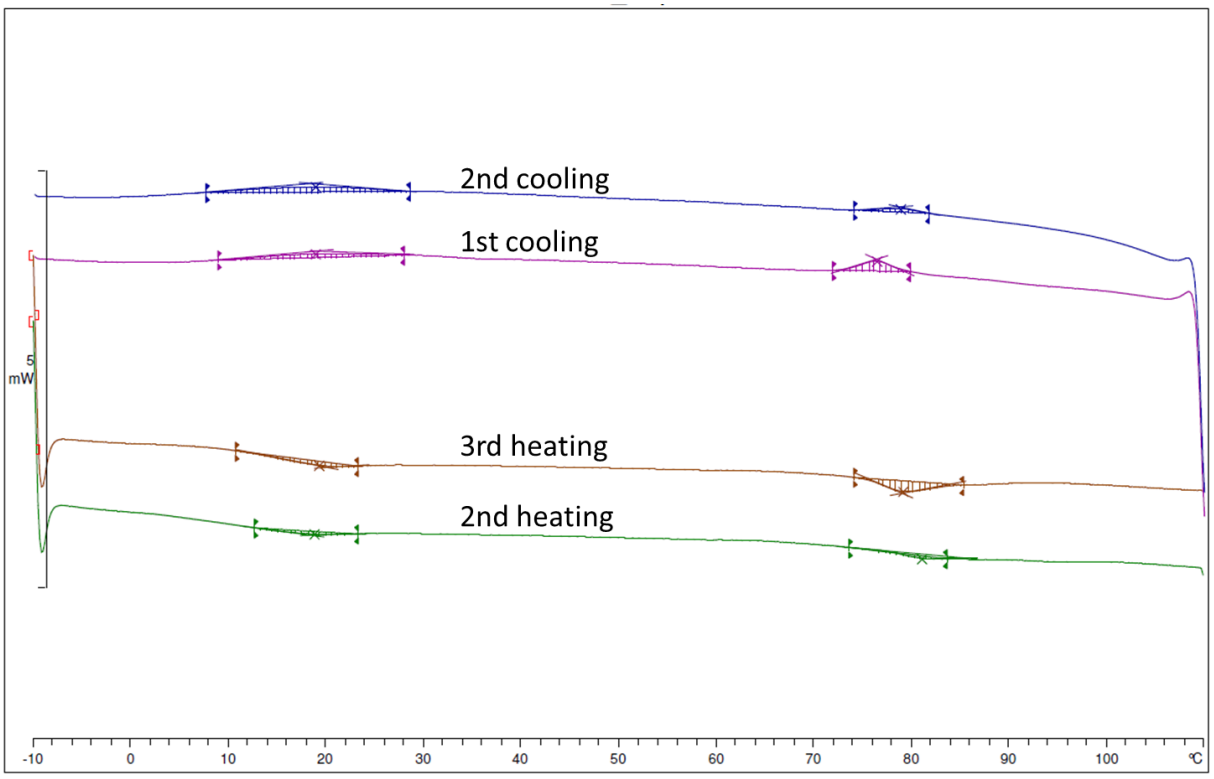


Fig. S10 DSC curves (onset) of **Tyr(10,14).**

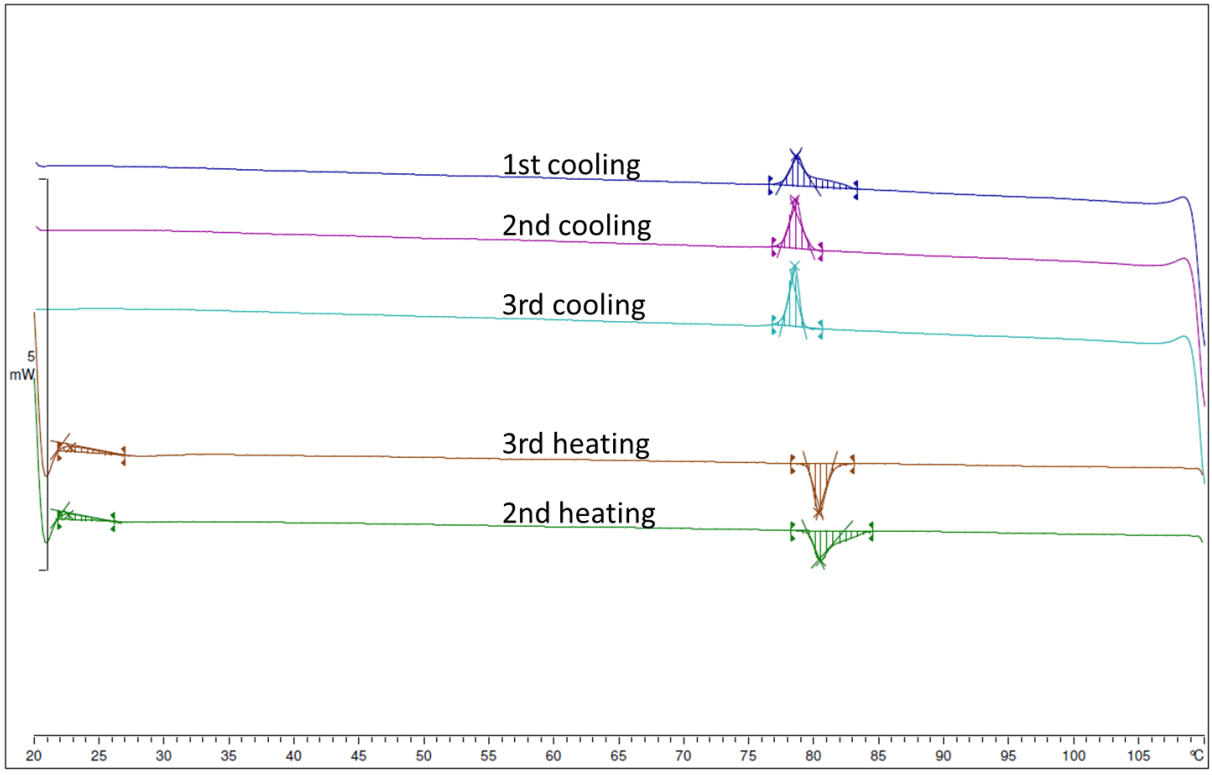


Fig. S11 DSC curves (onset) of **Tyr(10,18).**

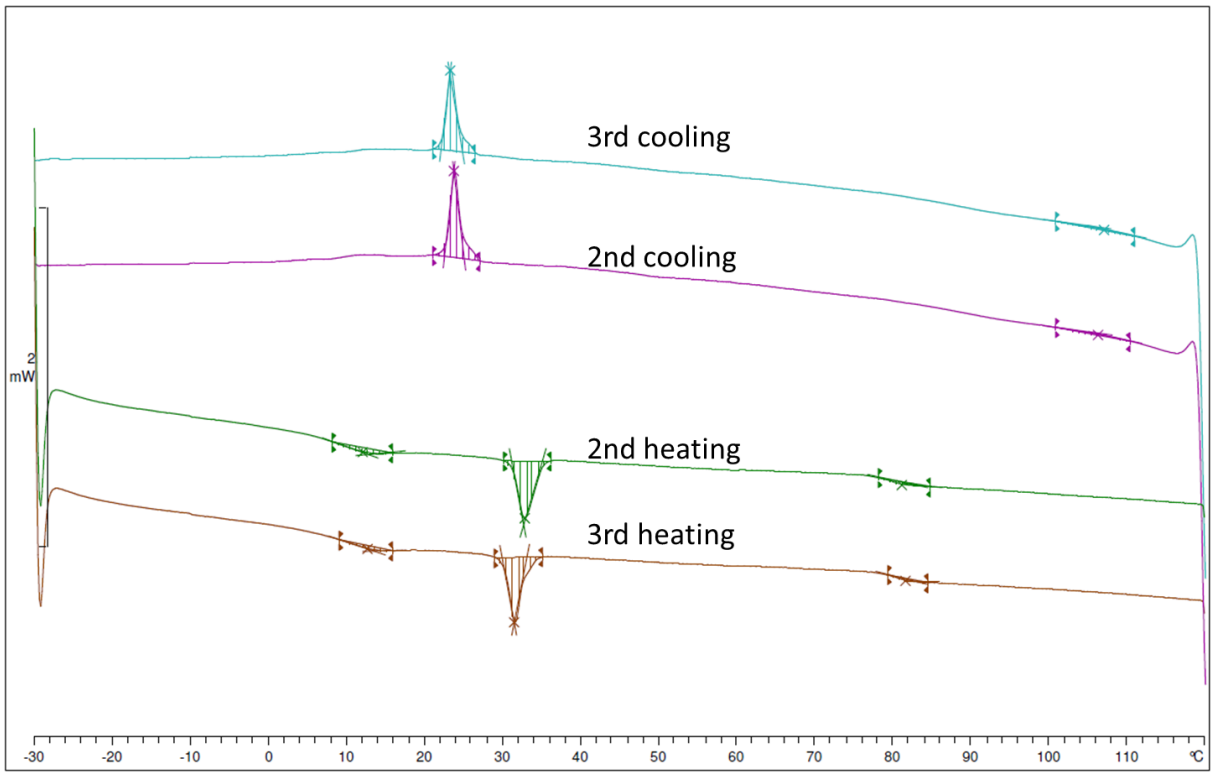


Fig. S12 DSC curves (onset) of **Dopa(10,6,6).**

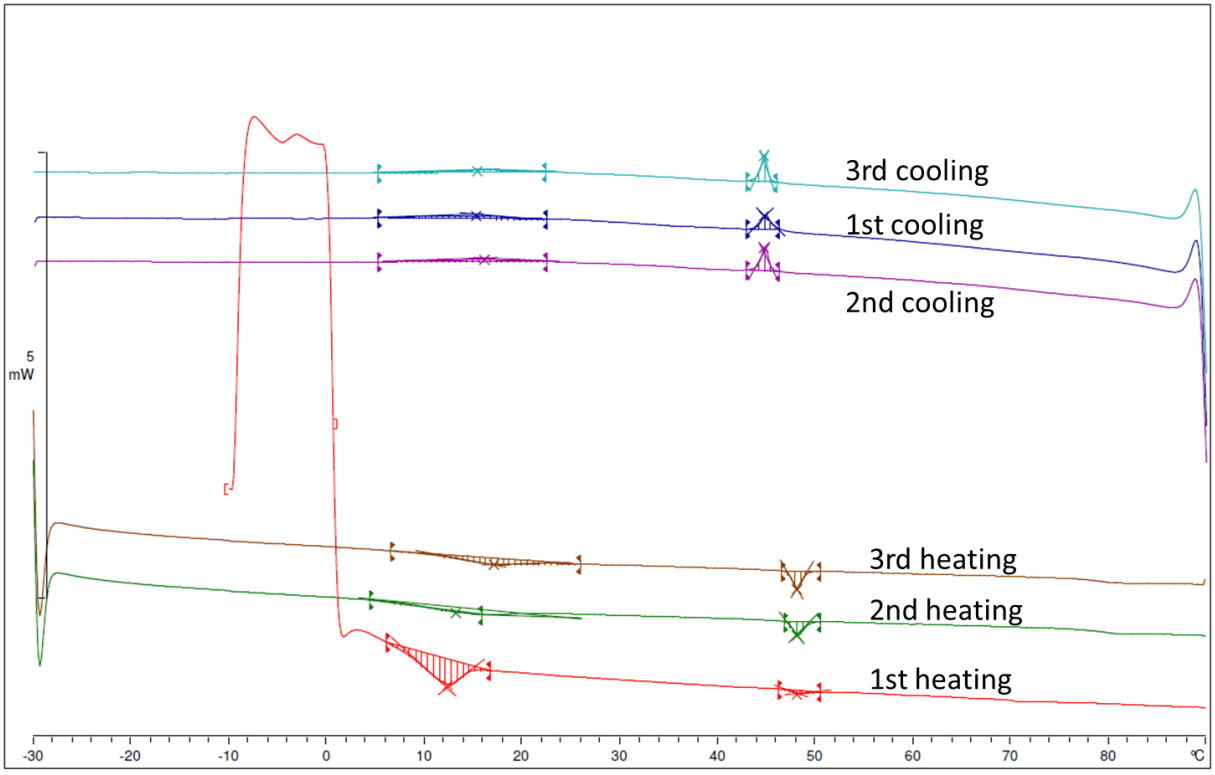


Fig. S13 DSC curves (onset) of **Dopa(10,10,10).**

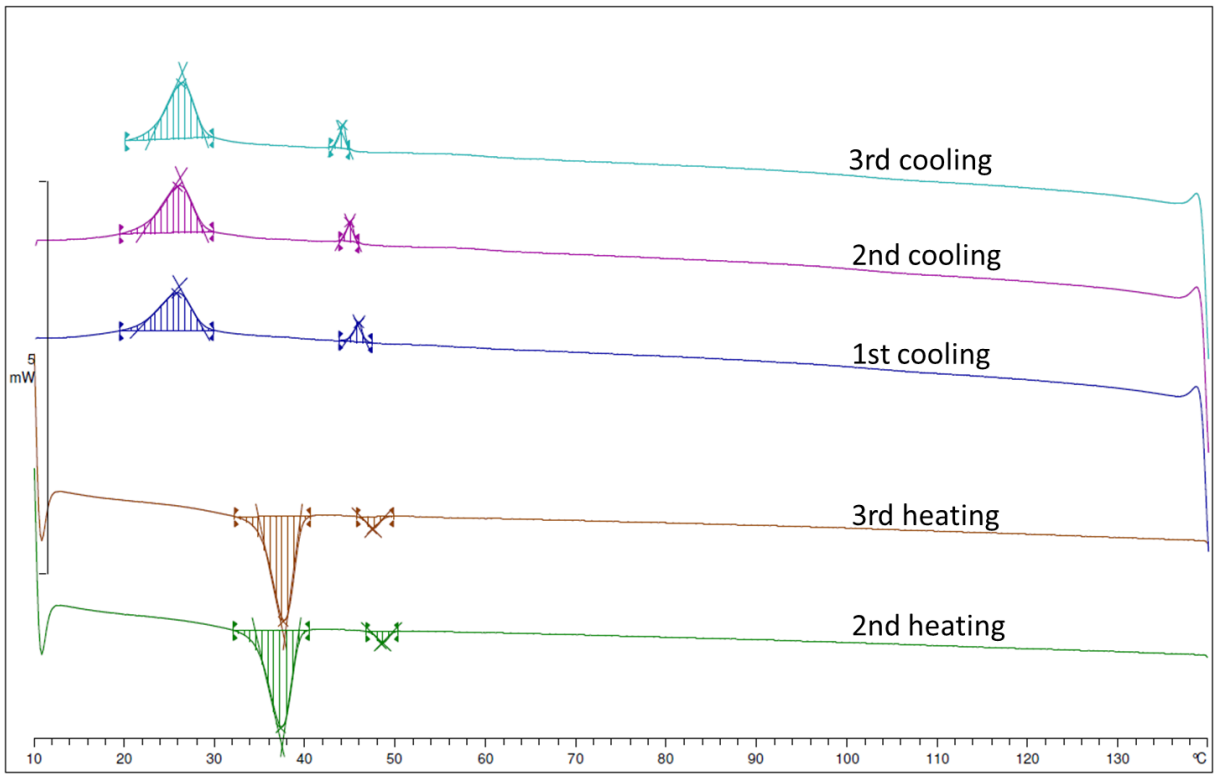


Fig. S14 DSC curves (onset) of **Dopa(10,14,14).**

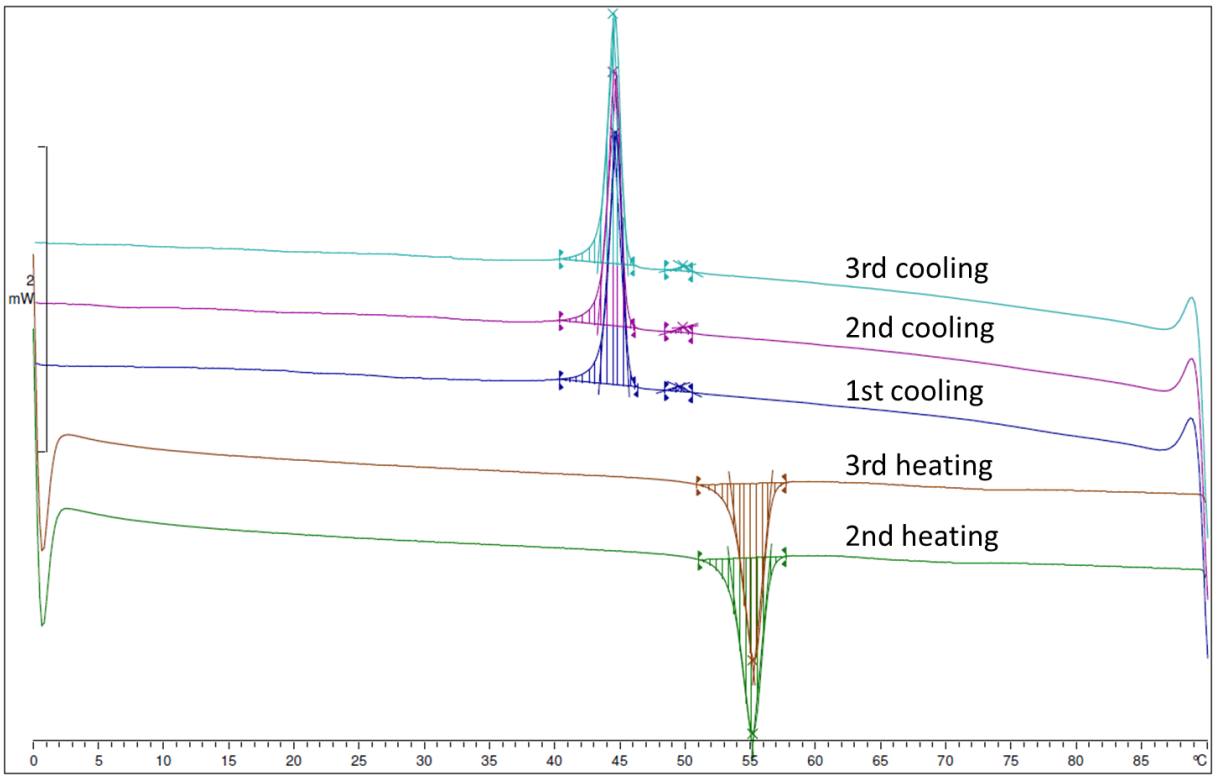


Fig. S15 DSC curves (onset) of **Dopa(10,18,18).**

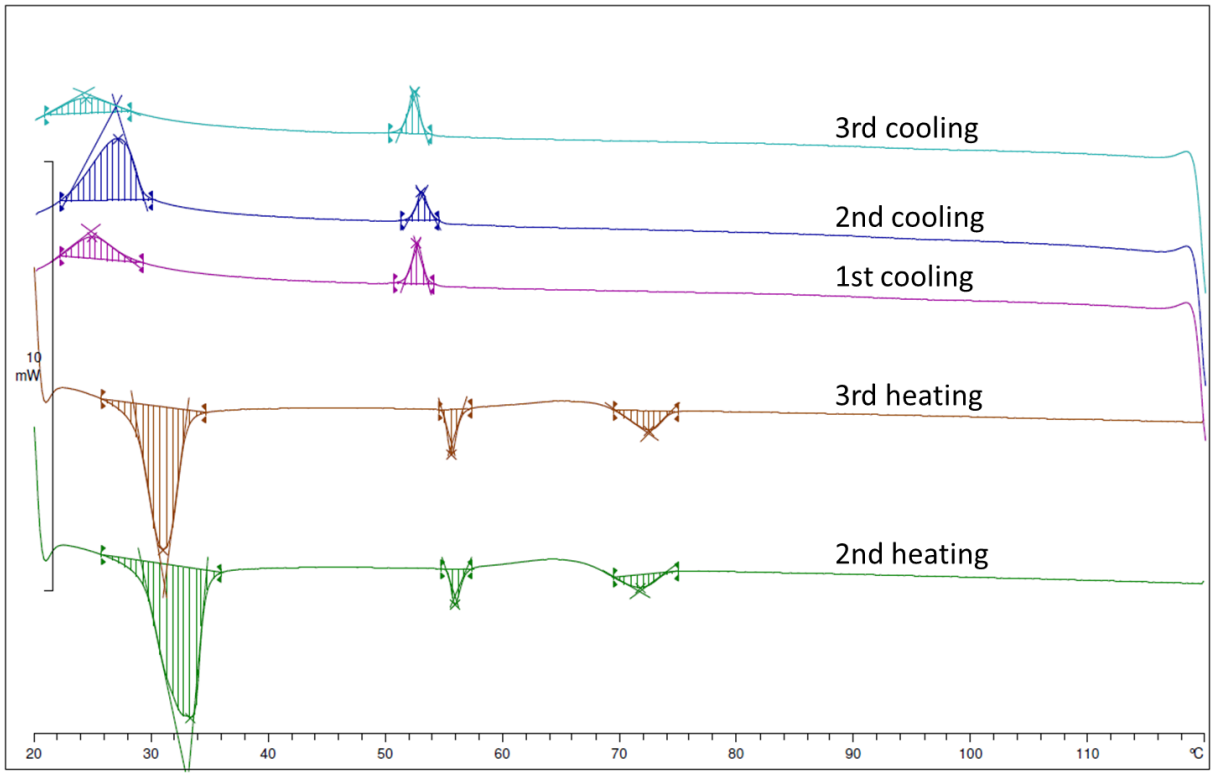


Fig. S16 DSC curves (onset) of **Dopa(14,10,10).**

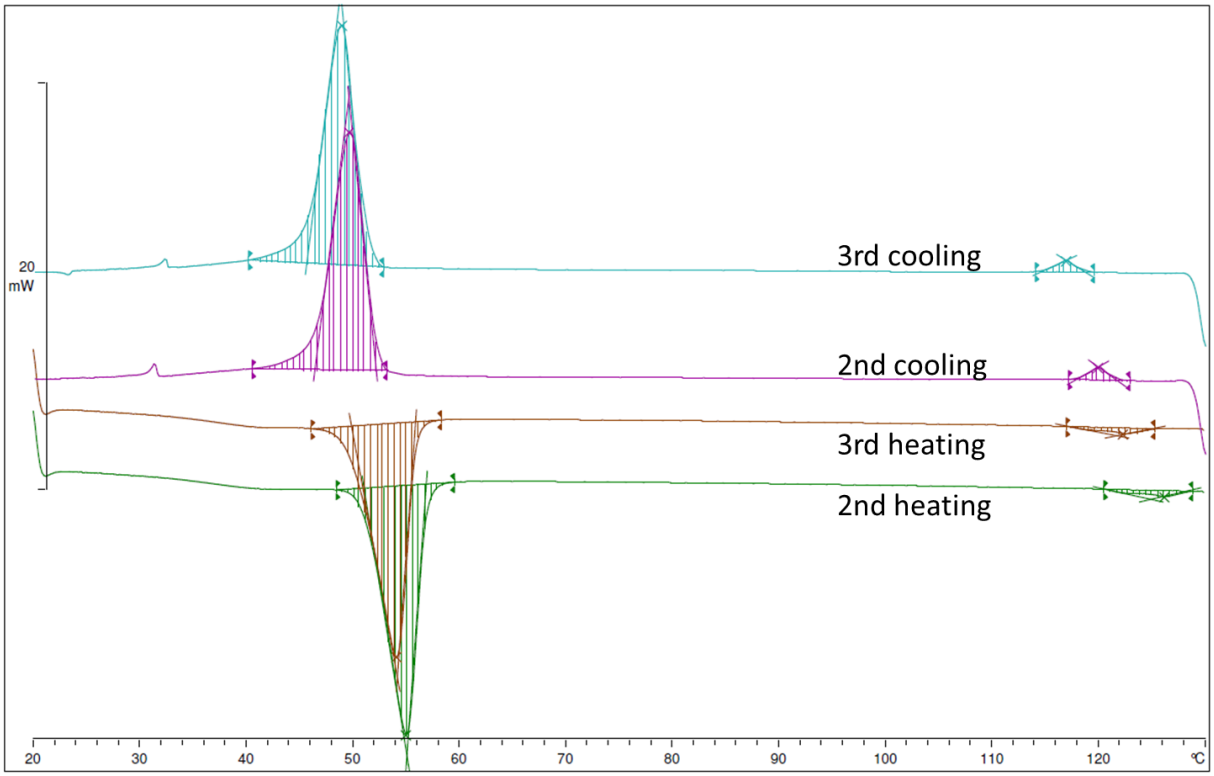


Fig. S17 DSC curves (onset) of **Dopa(14,12,12).**

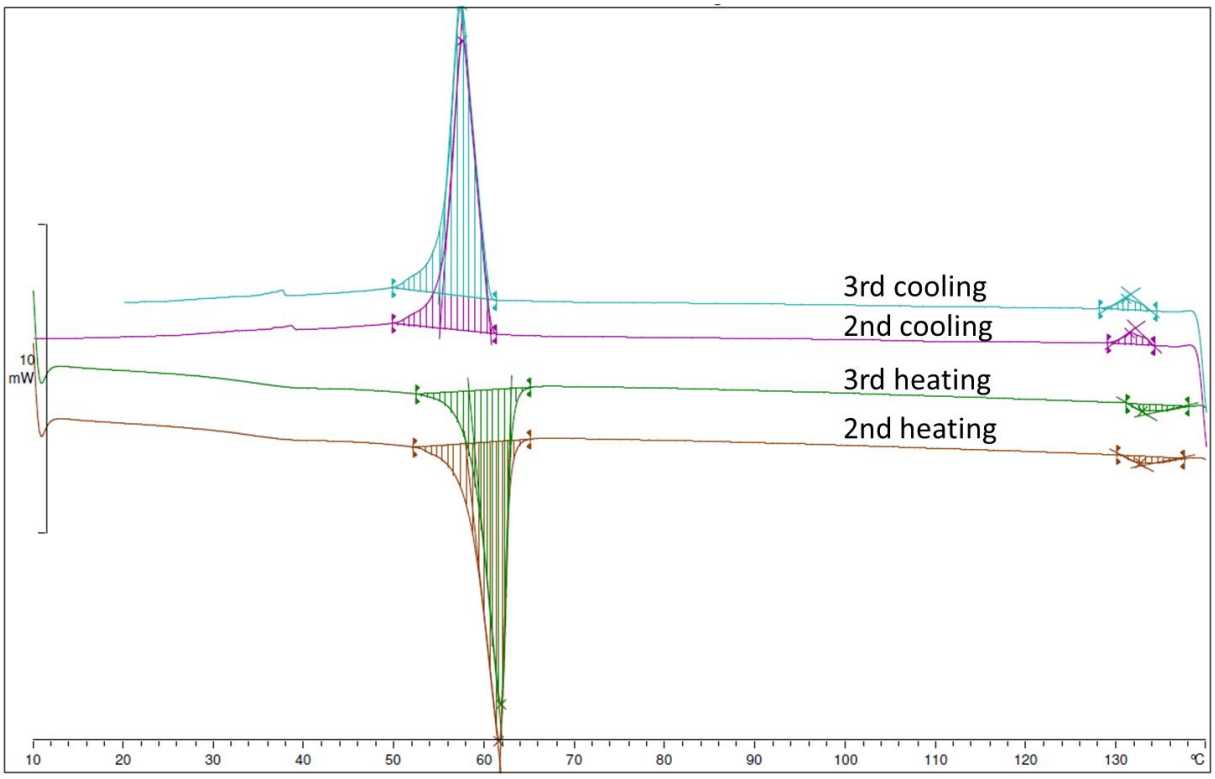


Fig. S18 DSC curves (onset) of **Dopa(14,14,14).**

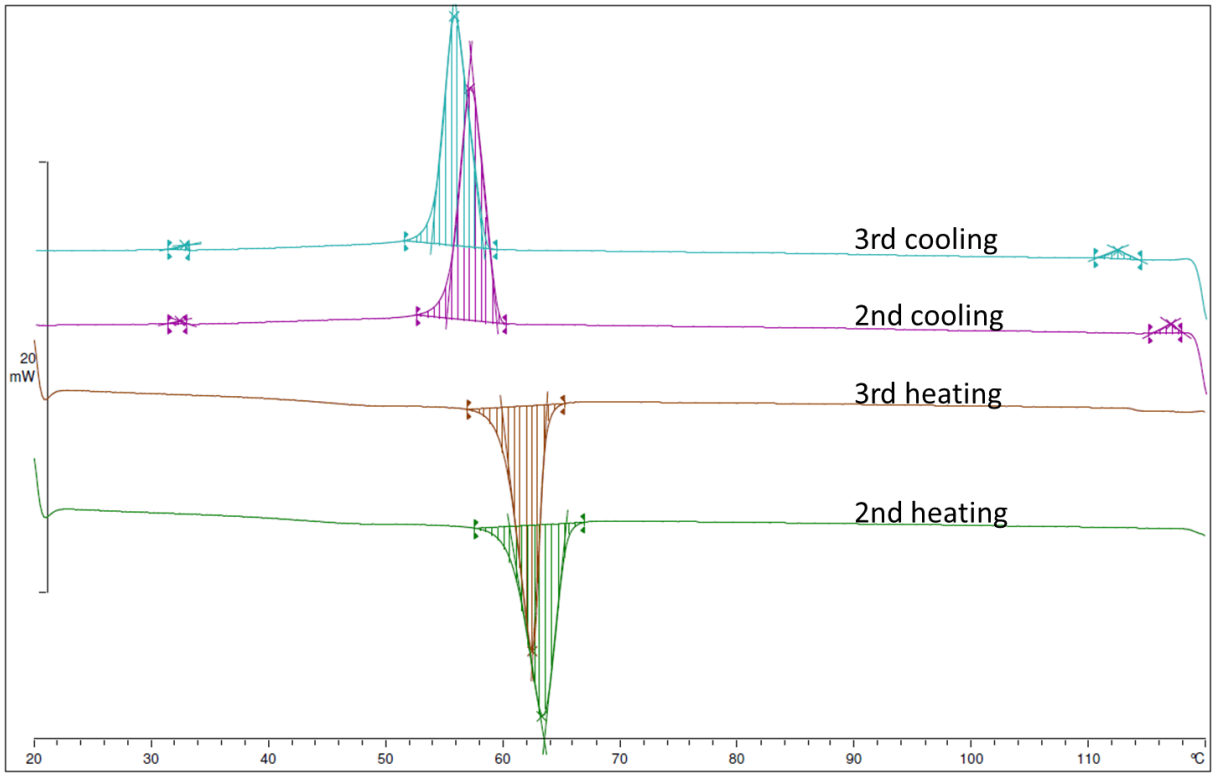


Fig. S19 DSC curves (onset) of **Dopa(14,16,16).**

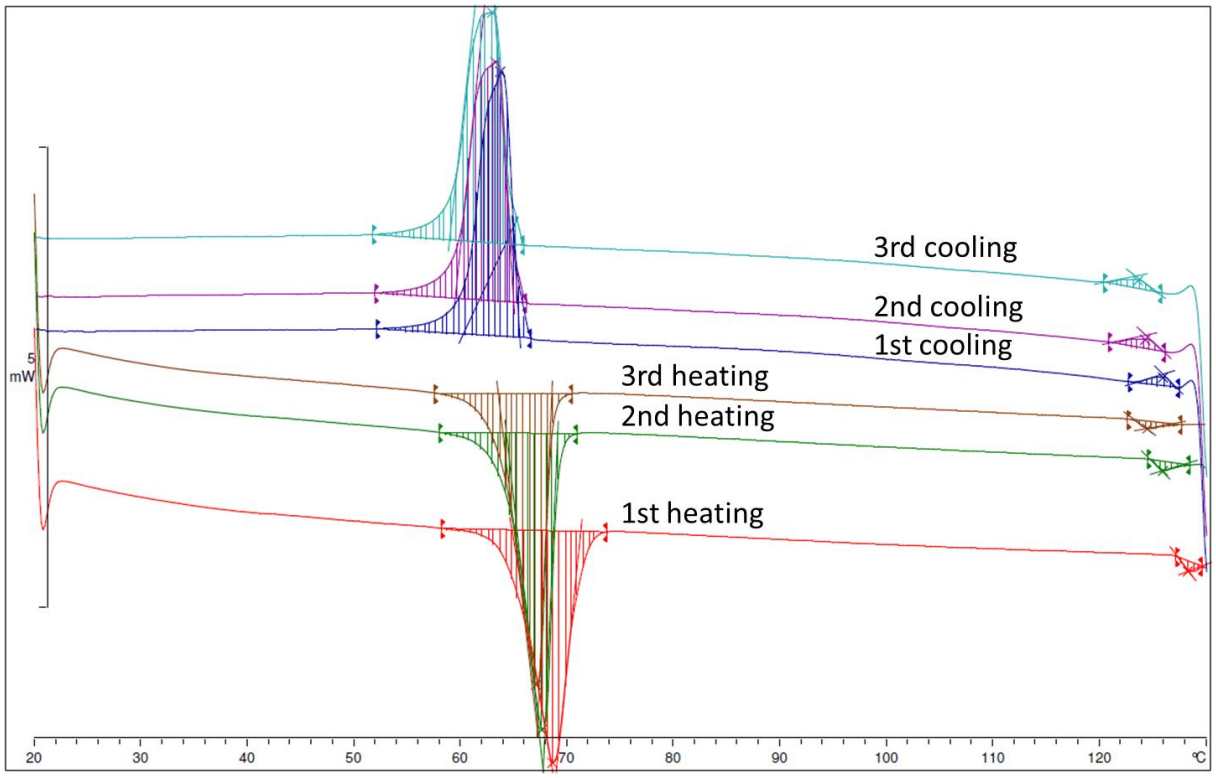


Fig. S20 DSC curves (onset) of **Dopa(14,18,18).**

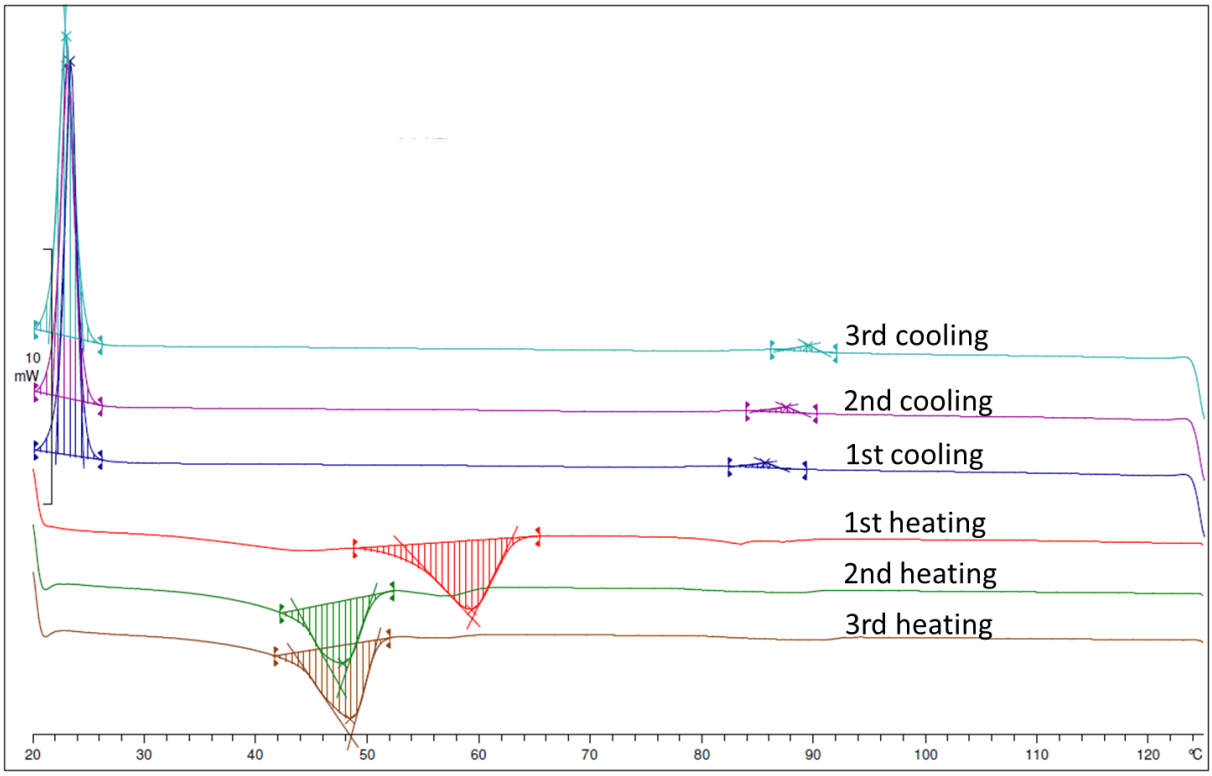


Fig. S21 DSC curves (onset) of **Dopa(18,10,10).**

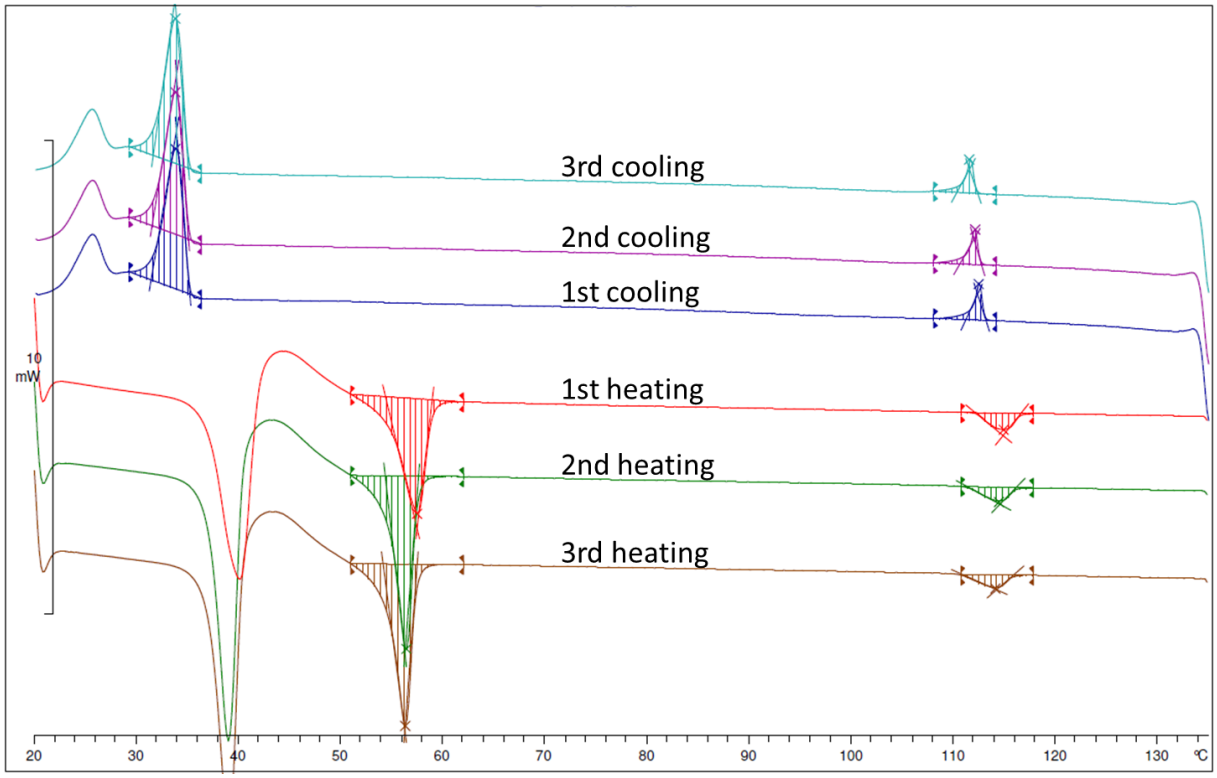


Fig. S22 DSC curves (onset) of **Dopa(18,12,12).**

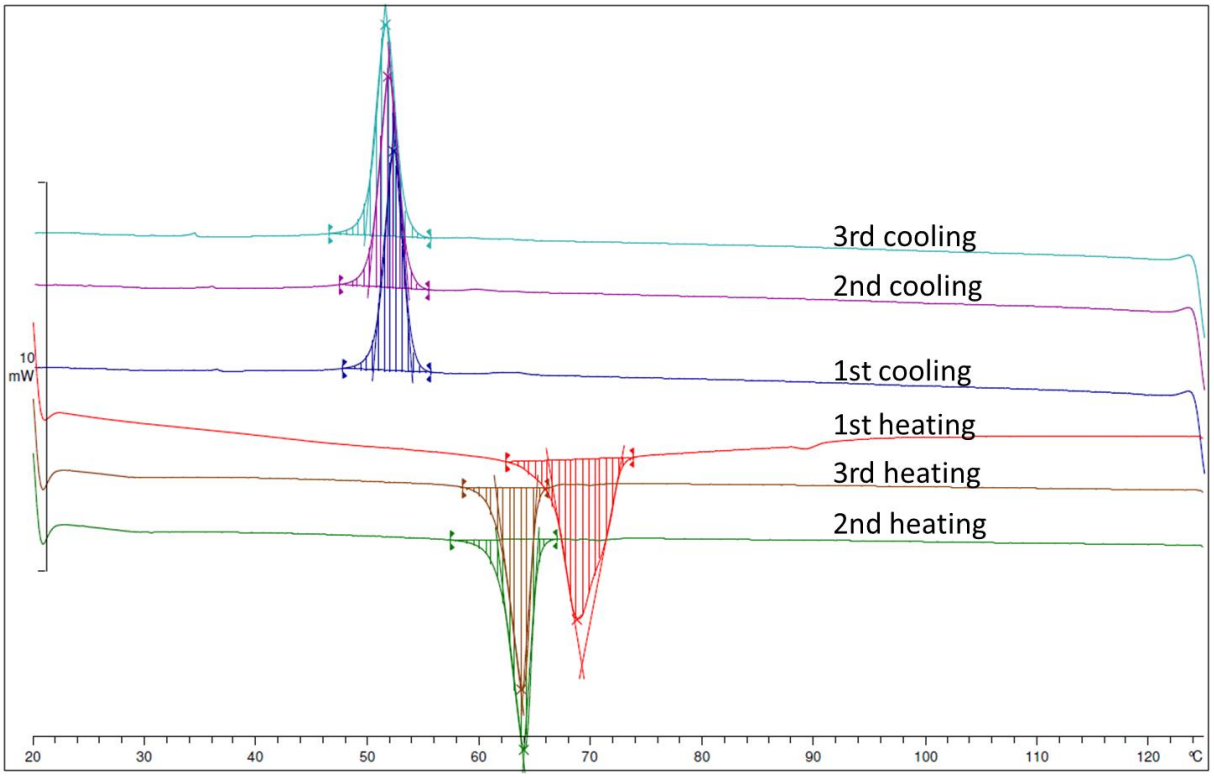


Fig. S23 DSC curves (onset) of **Dopa(18,14,14).**

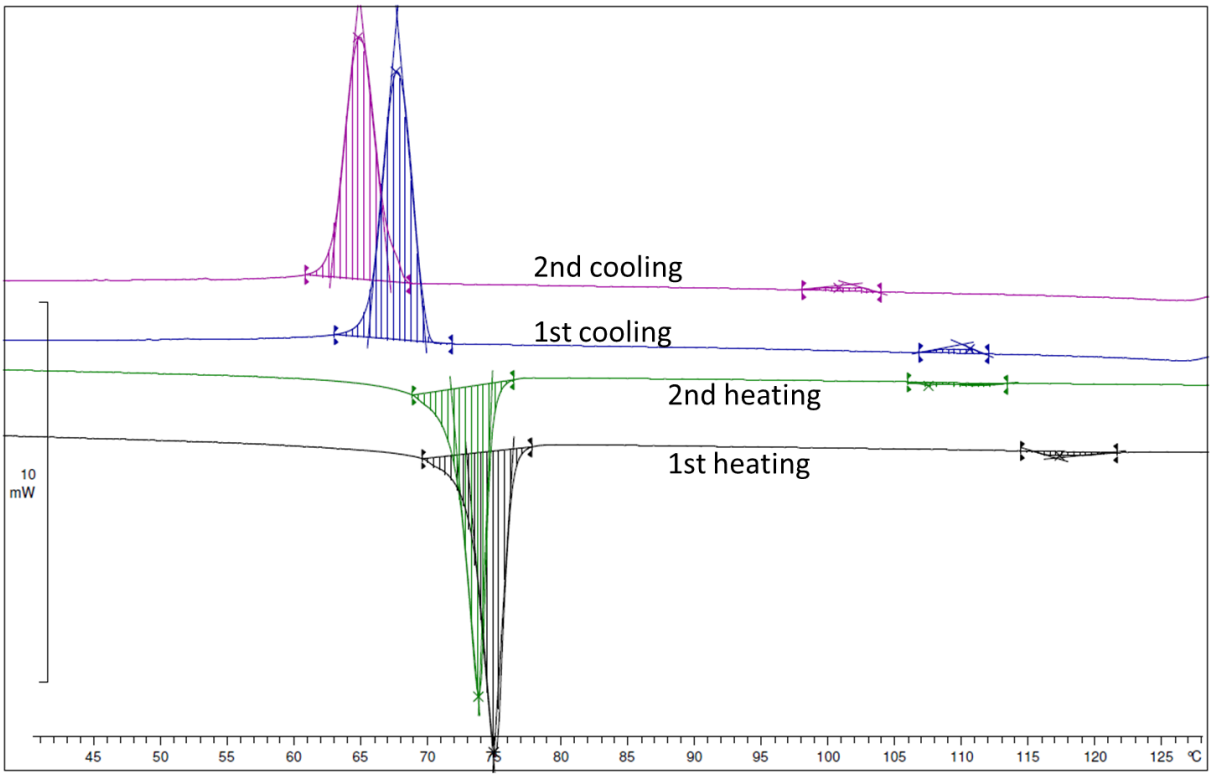


Fig. S24 DSC curves (onset) of **Dopa(18,16,16).**

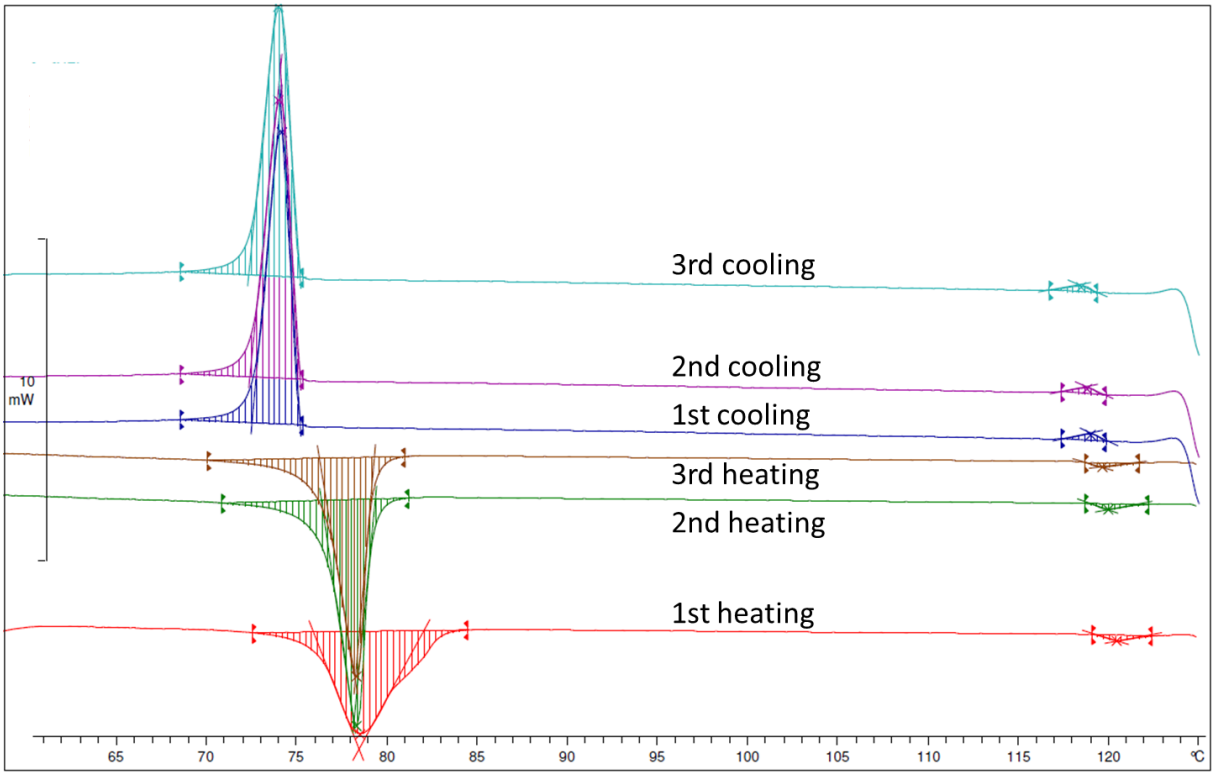
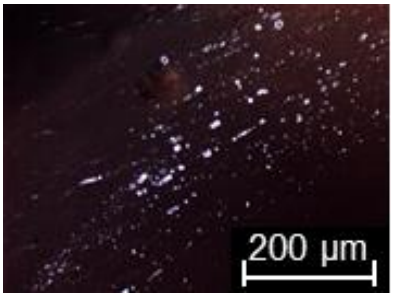
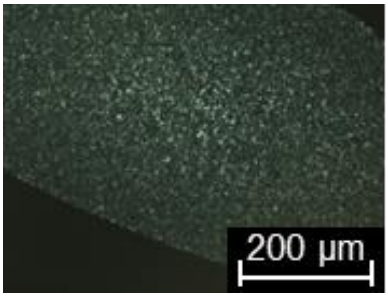


Fig. S25 DSC curves (onset) of **Dopa(18,18,18).**

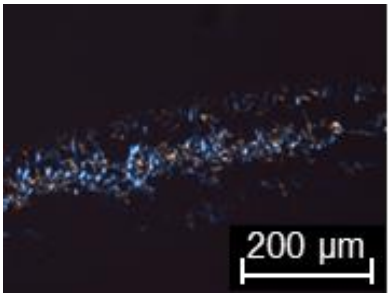
9) Polarizing optical microscopy (POM)



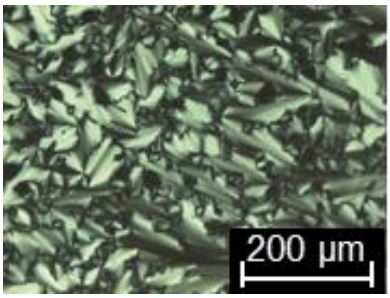
Phe(12) 38°C



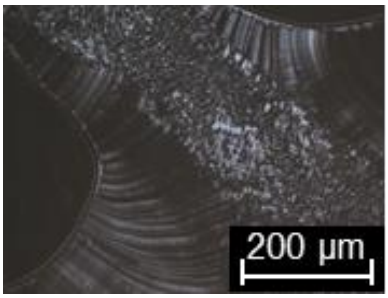
Phe(14) 33°C



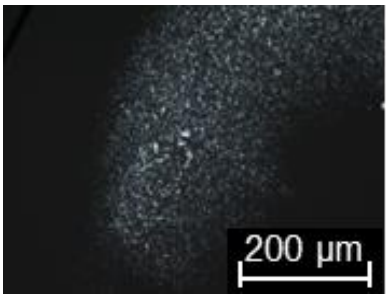
Phe(16) 65°C



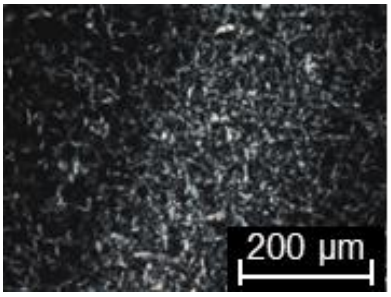
Phe(18) 97°C



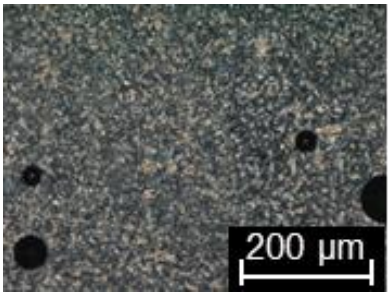
D-Phe(18) 100°C



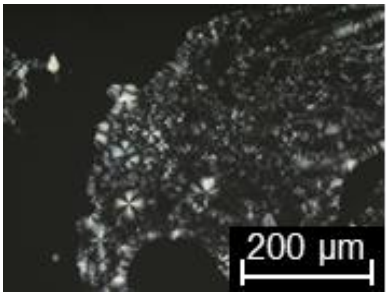
Tyr(10,8) 55°C



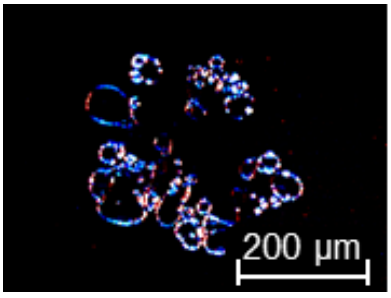
Tyr(10,14) 75°C



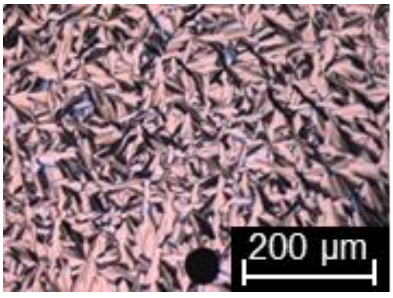
Tyr(10,16) 80°C



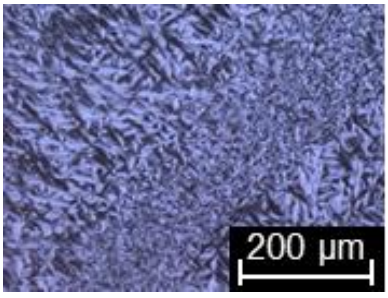
Tyr(10,18) 90°C



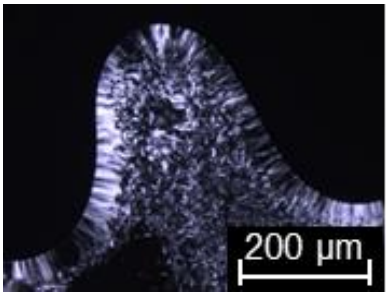
Dopa(10,6,6) 50°C



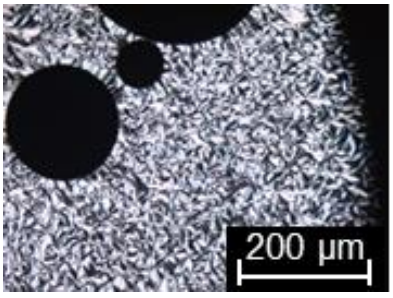
Dopa(10,10,10) 85°C



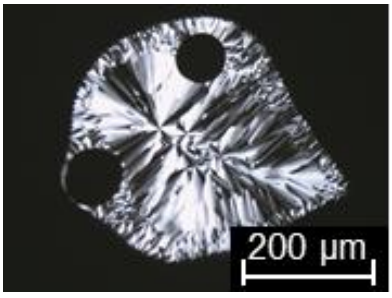
Dopa(10,14,14) 115°C



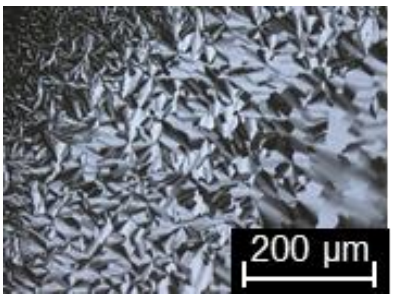
Dopa(10,18,18) 69°C



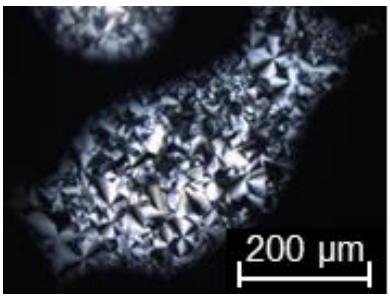
Dopa(14,10,10) 87°C



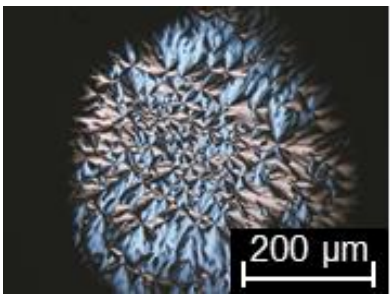
Dopa(14,12,12) 100°C



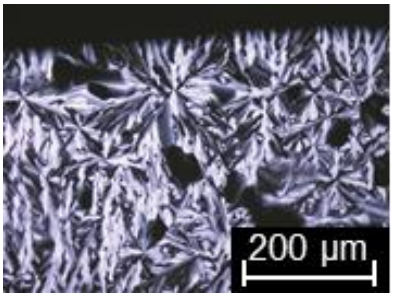
Dopa(14,14,14) 110°C



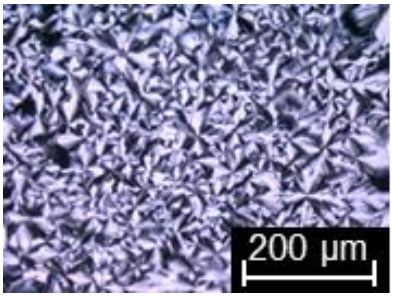
Dopa(14,16,16) 87°C



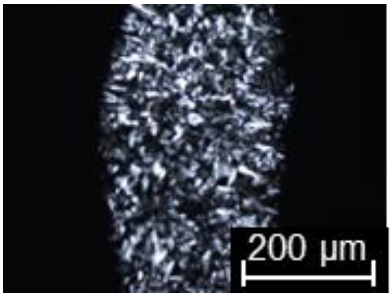
Dopa(14,18,18) 100°C



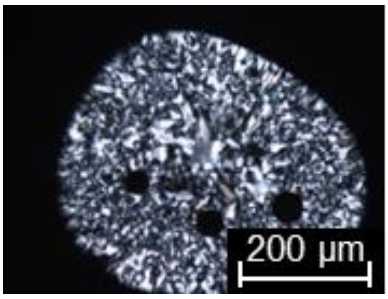
Dopa(18,10,10) 110°C



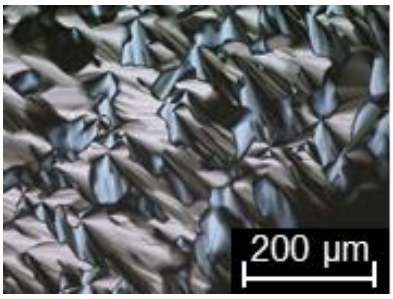
Dopa(18,12,12) 115°C



Dopa(18,14,14) 95°C



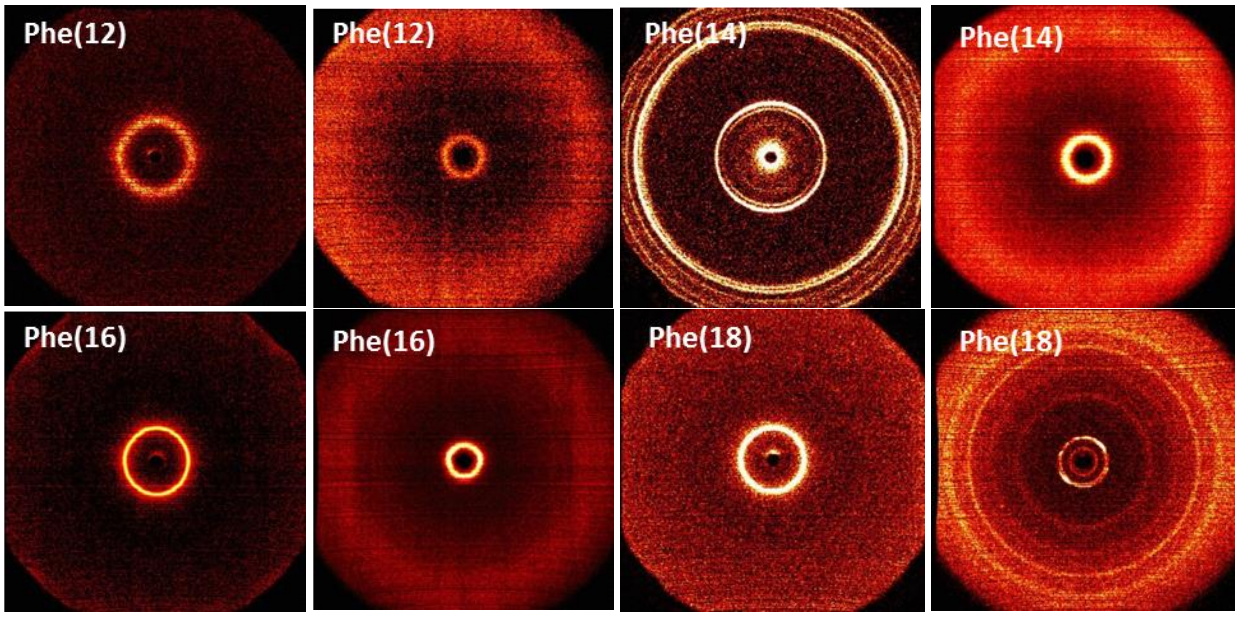
Dopa(18,16,16) 95°C

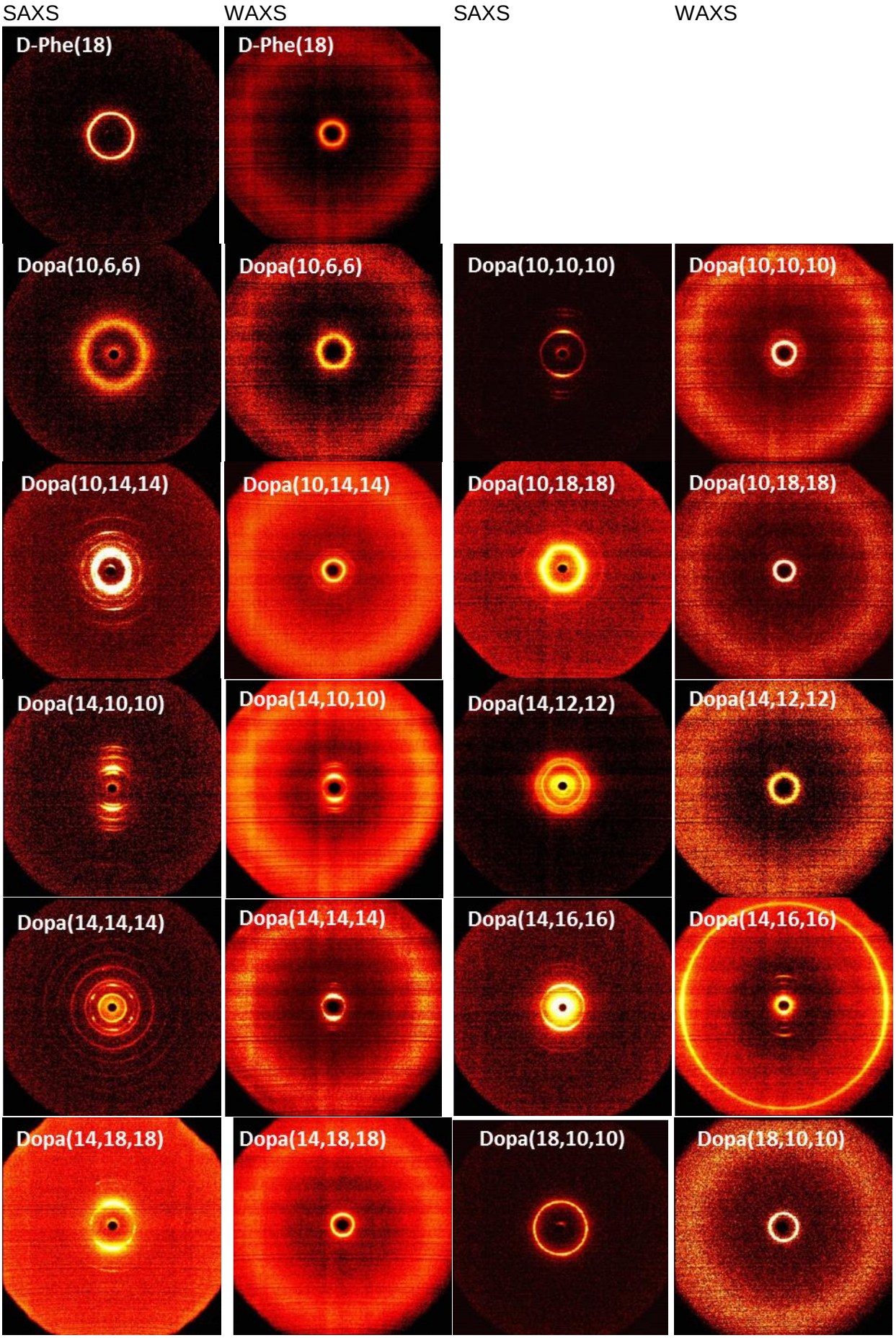


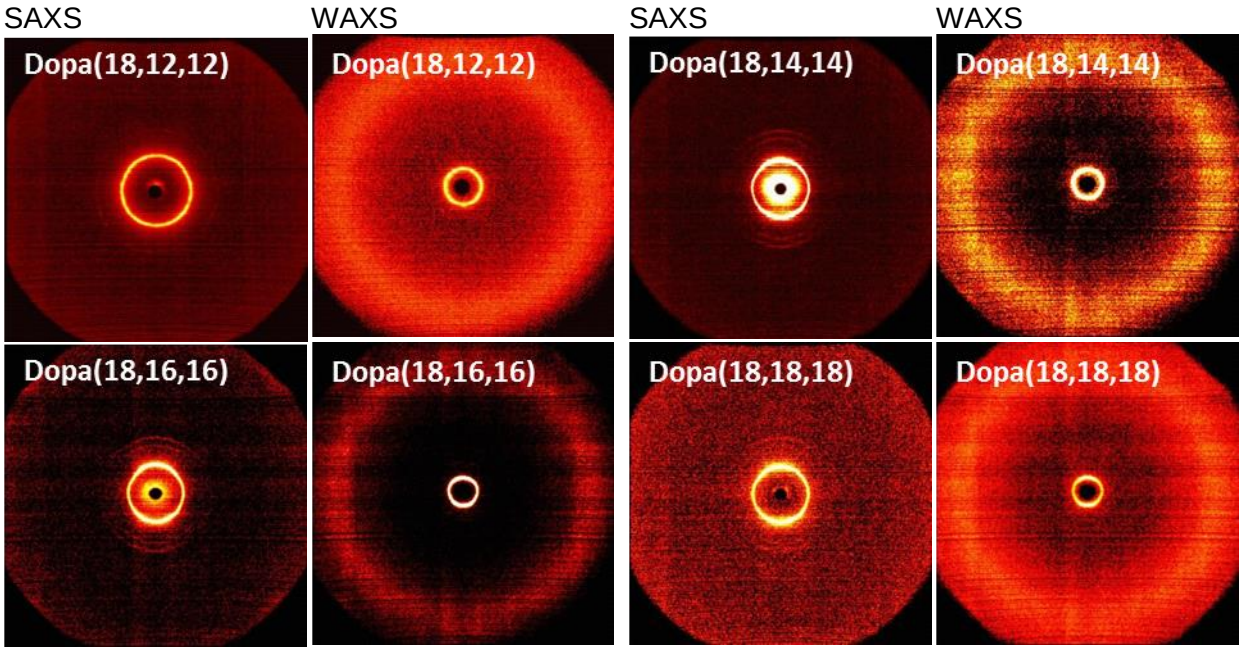
Dopa(18,18,18) 108°C

10) X-ray diffraction images (SAXS and WAXS)

SAXS WAXS SAXS WAXS

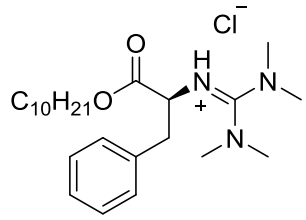



SAXS
WAXS
SAXS
WAXS
D-Phe(18)
D-Phe(18)
Dopa(10,6,6)
Dopa(10,6,6)
Dopa(10,10,10)
Dopa(10,10,10)
Dopa(10,14,14)
Dopa(10,14,14)
Dopa(10,18,18)
Dopa(10,18,18)
Dopa(14,10,10)
Dopa(14,10,10)
Dopa(14,12,12)
Dopa(14,12,12)
Dopa(14,14,14)
Dopa(14,14,14)
Dopa(14,16,16)
Dopa(14,16,16)
Dopa(14,18,18)
Dopa(14,18,18)
Dopa(18,10,10)
Dopa(18,10,10)

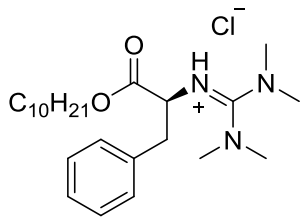

SAXS
WAXS
SAXS
WAXS
Dopa(18,12,12)
Dopa(18,12,12)
Dopa(18,14,14)
Dopa(18,14,14)
Dopa(18,16,16)
Dopa(18,16,16)
Dopa(18,18,18)
Dopa(18,18,18)

11) NMR (^{1}H, ^{13}C) spectra of all new compounds

Phe(10)

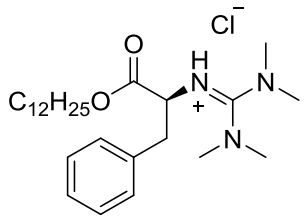


Phe(10)


Cl⁻
O
H
N
+
N
N
C10H21O

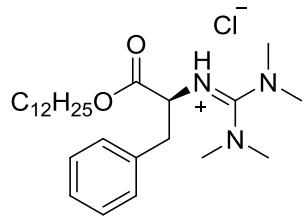
66.37
60.44
39.53
36.89
31.88
29.52
29.48
29.29
29.18
25.80
22.67
14.12
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-15
δ / ppm

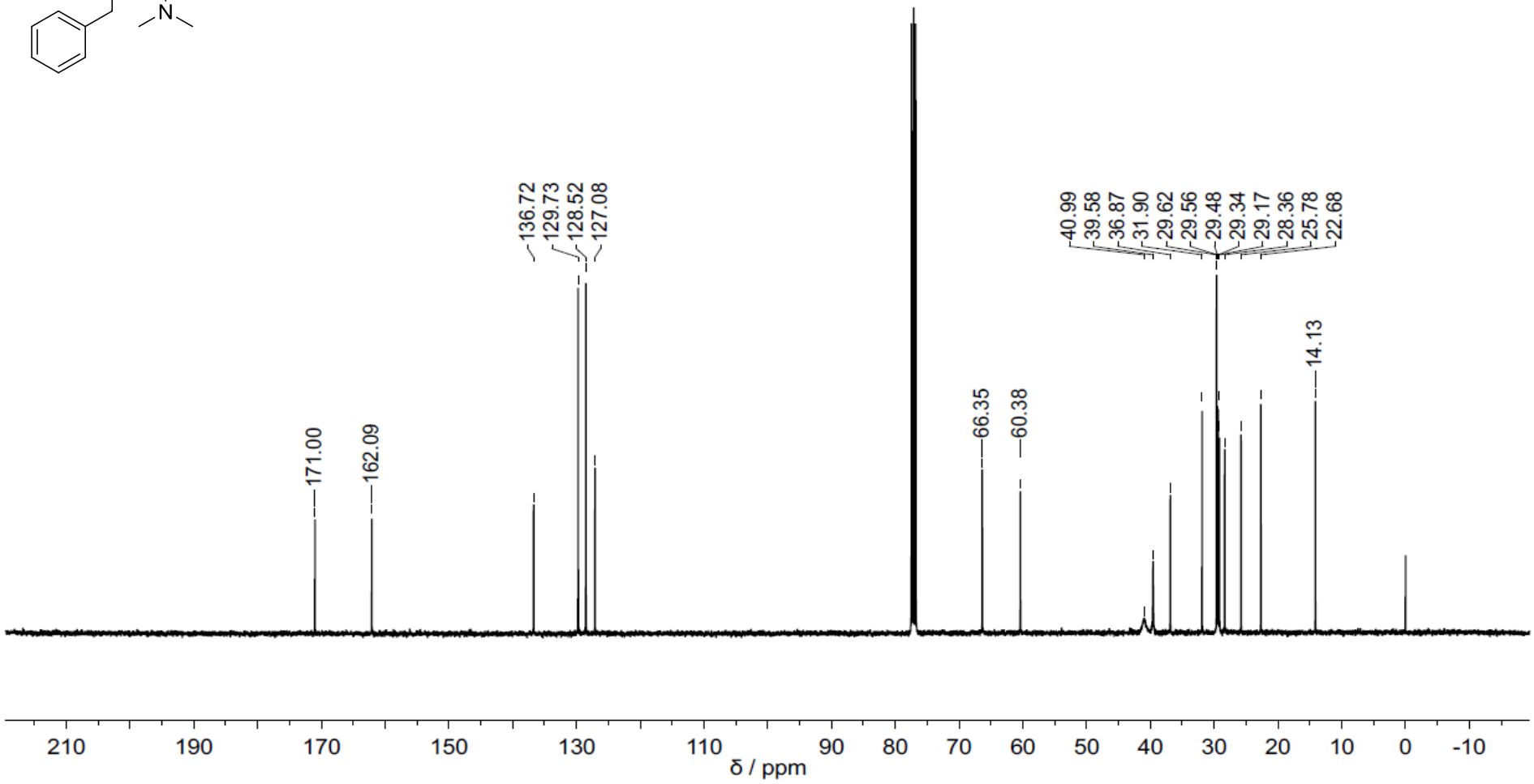
Phe(12)


Cl⁻
O
H
N
+
N
N
C12H25O

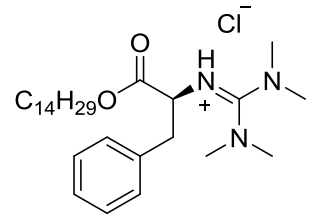
1.58
1.56
1.55
1.53
1.32
1.30
1.26
0.90
0.88
0.86
9.95
9.94
7.49
7.47
7.30
7.29
7.27
7.23
7.21
7.20
4.16
4.15
4.14
4.13
4.13
4.11
4.07
4.05
4.03
3.83
3.81
3.80
3.78
3.37
3.36
3.34
3.32
2.97
2.67
0.98
2.00
2.06
0.99
1.00
1.99
1.00
13.01
2.03
18.05
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ / ppm

Phe(12)


Cl⁻
O
H
N
+
N
N
C12H25O

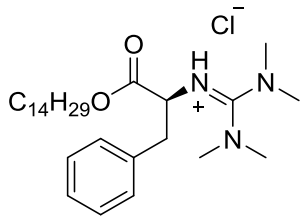

136.72
129.73
128.52
127.08
40.99
39.58
36.87
31.90
29.62
29.56
29.48
29.34
29.17
28.36
25.78
22.68
14.13
66.35
60.38
171.00
162.09
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Phe(14)


Cl⁻
O
H
N
+
N
N
C14H29O

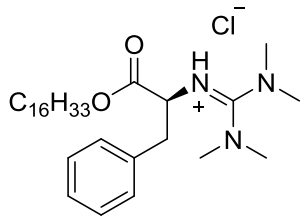
7.50
7.48
7.30
7.29
7.27
7.26
7.23
7.21
10.25
10.23
4.15
4.13
4.12
4.11
4.06
4.05
4.04
3.87
3.85
3.84
3.83
3.38
3.37
2.95
2.64
1.55
1.28
1.26
0.89
0.88
0.87
1.01
2.00
2.05
0.99
1.08
1.95
1.09
13.17
22.19
3.14
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Phe(14)


Cl⁻
O
H
N
+
N
C14H29O
N

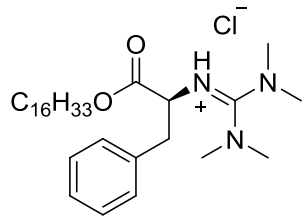
171.01
162.01
136.55
129.69
128.55
127.14
66.35
60.56
60.23
39.60
37.03
31.90
29.63
29.57
29.48
29.34
29.18
28.36
25.78
22.68
14.13
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Phe(16)


Cl⁻
O
H
N
+
N
N
C16H33O

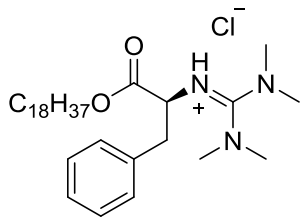
1.56
1.55
1.53
1.32
1.30
1.26
10.05
10.03
7.49
7.47
7.30
7.29
7.27
7.23
7.21
7.19
4.14
4.12
4.06
4.05
4.03
3.85
3.83
3.81
3.79
3.38
3.36
2.97
2.67
0.89
0.88
0.86
0.96
2.00
2.22
0.99
1.00
1.99
1.00
13.07
2.00
26.08
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Phe(16)


Cl⁻
O
H
N
+
N
N
C16H33O

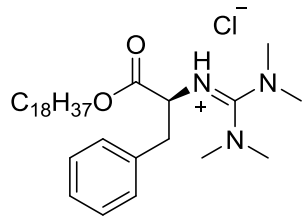
39.56
36.84
31.92
29.69
29.65
29.58
29.50
29.36
29.19
28.36
25.79
22.69
136.75
129.76
128.52
127.07
171.01
162.12
66.36
60.44
14.14
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Phe(18)


Cl⁻
O
H
N
+
N
N
C18H37O

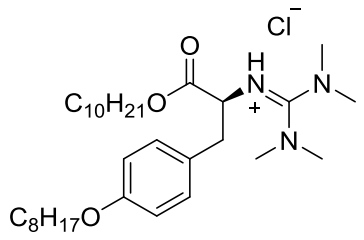
10.22
10.21
7.50
7.48
7.30
7.29
7.27
7.26
7.23
7.21
7.20
4.14
4.12
4.06
4.05
4.04
3.87
3.85
3.84
3.82
3.38
3.37
2.95
2.65
1.61
1.56
1.55
1.54
1.31
1.30
1.28
1.26
0.89
0.88
0.87
0.92
2.00
1.94
0.99
1.02
1.94
1.01
13.03
2.00
30.12
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Phe(18)


Cl⁻
O
H
N
+
N
N
C18H37O

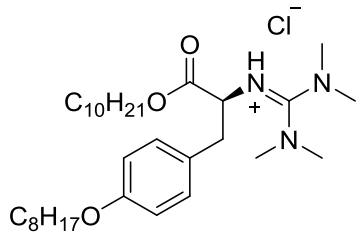
171.06
162.20
136.78
129.81
128.52
127.06
66.38
60.52
31.93
29.71
29.67
29.59
29.51
29.37
22.70
14.13
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
δ / ppm

Tyr(10,8)


Cl⁻
O
H
N
+
N
N
C10H21O
C8H17O

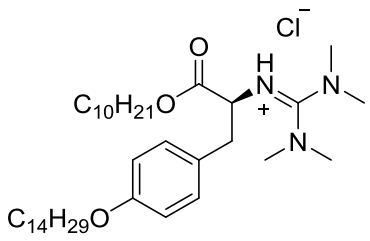
171.11
162.13
158.24
130.82
128.30
114.52
68.03
66.32
60.51
36.15
31.89
31.82
29.55
29.50
29.40
29.30
29.24
29.21
28.43
26.06
25.84
22.68
22.66
14.11
14.11
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
δ / ppm

Tyr(10,8)


Cl⁻
O
H
N
+
N
N
C10H21O
C8H17O

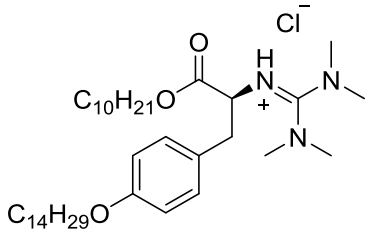
1.78
1.76
1.75
1.74
1.72
1.59
1.57
1.56
1.45
1.43
1.42
1.40
1.33
1.32
1.31
1.30
1.28
1.26
4.11
4.07
4.05
4.04
3.91
3.90
3.89
3.73
3.70
3.69
3.68
3.66
3.65
3.63
3.48
3.34
3.30
3.28
3.02
2.70
0.90
0.89
0.89
0.88
0.87
0.87
7.38
7.37
7.28
6.82
6.80
0.79
1.96
2.00
0.95
1.85
2.11
1.04
13.19
2.12
2.02
2.22
22.17
6.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Tyr(10,14)


Cl⁻
O
H
N
+
N
N
C10H21O
C14H29O

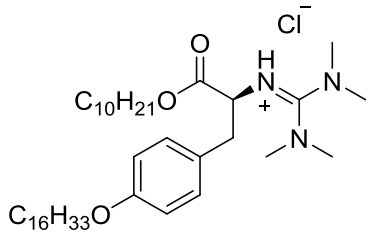
171.10
162.12
158.25
130.80
128.27
114.52
68.03
66.32
60.49
31.93
31.89
29.70
29.68
29.66
29.62
29.60
29.55
29.46
29.36
29.31
29.30
22.69
22.68
14.13
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
δ / ppm

Tyr(10,14)


Cl⁻
O
H
N
+
N
N
C10H21O
C14H29O

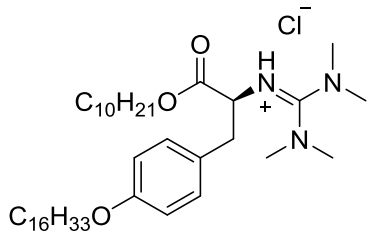
1.78
1.76
1.75
1.73
1.72
1.59
1.57
1.56
1.55
1.44
1.43
1.42
1.40
1.31
1.30
1.26
4.12
4.11
4.07
4.05
4.04
3.91
3.90
3.88
3.73
3.68
3.66
3.65
3.64
3.48
3.36
3.34
3.30
3.28
3.02
2.70
0.89
0.88
0.87
9.71
7.38
7.37
7.29
6.82
6.80
0.76
2.00
2.11
0.89
1.78
2.12
1.07
13.19
2.09
2.02
2.08
34.18
6.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Tyr(10,16)


Cl⁻
O
H
N
+
N
N
C10H21O
C16H33O

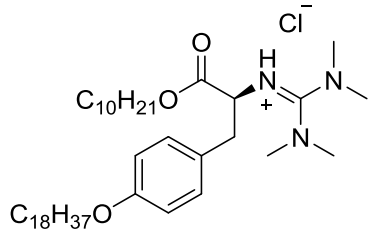
1.76
1.75
1.73
1.72
1.56
1.43
1.41
1.40
1.30
1.26
0.89
0.88
0.87
10.01
7.40
7.39
7.27
6.82
6.80
4.10
4.07
4.05
4.04
3.91
3.90
3.89
3.73
3.31
3.29
3.02
2.68
0.84
2.00
2.12
3.16
2.15
0.99
13.23
2.18
2.14
2.30
38.14
6.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Tyr(10,16)


Cl⁻
O
H
N
+
N
N
C10H21O
C16H33O

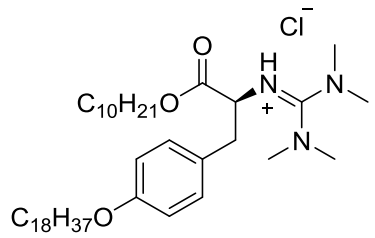
39.71
36.06
31.93
31.89
29.70
29.66
29.63
29.60
29.55
29.50
29.46
29.36
29.32
29.30
29.21
28.43
26.07
25.84
22.70
22.68
171.13
162.20
158.22
130.86
128.42
114.50
68.03
66.33
60.63
14.12
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
δ / ppm

Tyr(10,18)


Cl⁻
O
H
N
+
N
N
C10H21O
C18H37O

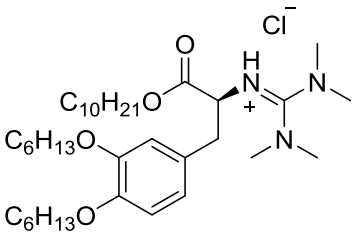
1.76
1.75
1.74
1.56
1.43
1.42
1.40
1.30
1.26
0.89
0.88
0.87
9.91
7.39
7.38
7.30
6.81
6.80
4.10
4.05
3.91
3.90
3.89
3.72
3.31
3.28
3.03
2.70
2.62
0.73
2.00
2.15
3.17
2.25
0.99
13.12
2.14
2.16
2.29
42.17
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Tyr(10,18)


Cl⁻
O
H
N
+
N
N
C10H21O
C18H37O

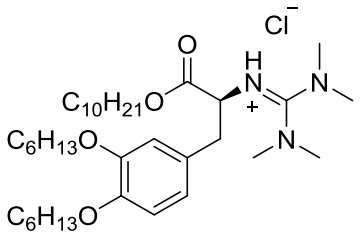
39.87
36.09
31.93
31.89
29.70
29.66
29.63
29.61
29.55
29.50
29.47
29.36
29.32
29.30
29.21
28.44
26.08
25.84
22.69
22.68
171.10
162.17
158.22
130.84
128.40
114.50
68.03
66.34
60.61
14.12
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
δ / ppm

Dopa(10,6,6)


Cl⁻
O
H
N
+
N
N
C10H21O
C6H13O
C6H13O

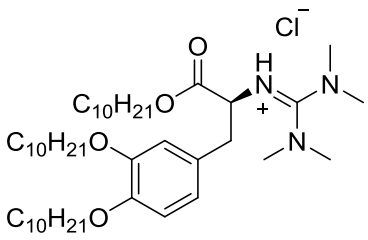
1.81
1.80
1.79
1.77
1.76
1.60
1.58
1.56
1.49
1.47
1.45
1.44
1.34
1.34
1.33
1.32
1.31
1.30
1.26
0.92
0.91
0.90
0.88
0.86
4.10
4.08
4.06
4.05
4.03
4.03
4.01
4.01
3.99
3.98
3.97
3.97
3.96
3.94
3.92
3.73
3.71
3.70
3.68
7.09
7.09
6.99
6.99
6.97
6.97
6.80
6.78
3.31
3.30
3.27
3.26
3.00
2.67
9.98
0.90
1.00
1.01
1.02
7.15
1.03
13.08
4.30
2.12
4.30
22.17
9.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(10,6,6)


Cl⁻
O
H
N
+
N
N
C10H21O
C6H13O
C6H13O

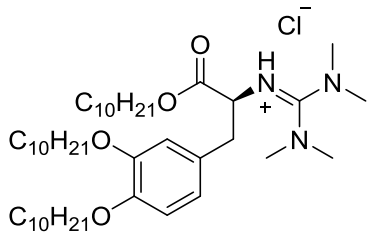
171.09
162.14
149.08
148.10
129.30
122.08
115.64
113.88
69.48
69.33
66.32
60.55
36.40
31.89
31.67
31.63
29.55
29.51
29.35
29.30
29.21
28.42
25.83
25.77
25.71
22.68
22.62
14.12
14.06
14.04
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(10,10,10)


Cl⁻
O
H
N
+
N
N
C10H21O
C10H21O
C10H21O

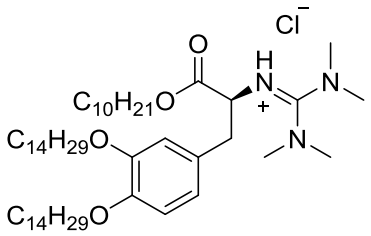
1.80
1.78
1.77
1.58
1.46
1.45
1.30
1.26
0.90
0.88
0.86
9.84
7.07
6.98
6.97
6.80
6.78
4.13
4.11
4.08
4.06
4.05
4.02
4.00
3.99
3.97
3.95
3.94
3.92
3.68
3.30
3.27
2.68
1.06
1.00
0.94
1.14
7.23
1.15
13.15
6.20
2.10
4.14
36.09
9.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(10,10,10)


Cl⁻
O
H
N
+
N
N
C10H21O
C10H21O
C10H21O

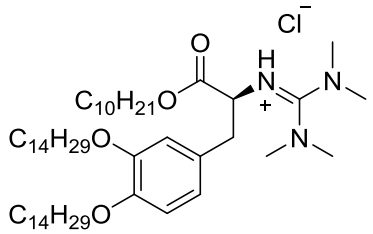
171.12
162.11
149.10
148.14
129.22
122.13
115.68
113.93
69.55
69.36
66.34
60.51
31.92
29.67
29.65
29.62
29.60
29.52
29.36
22.70
14.13
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(10,14,14)


Cl⁻
O
H
N
+
N
N
C10H21O
C14H29O
C14H29O

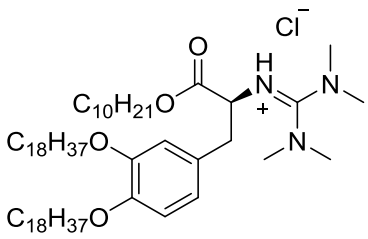
1.85
1.80
1.78
1.77
1.58
1.46
1.45
1.43
1.30
1.26
0.90
0.88
0.86
9.89
9.88
7.07
6.98
6.96
6.80
6.78
4.10
4.08
4.06
4.05
4.02
4.00
3.98
3.96
3.95
3.93
3.92
3.31
3.29
3.27
3.26
3.00
2.68
0.97
1.00
1.02
1.05
7.35
1.07
13.05
4.15
2.14
4.12
54.00
9.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(10,14,14)


Cl⁻
O
H
N
+
N
N
C10H21O
C14H29O
C14H29O

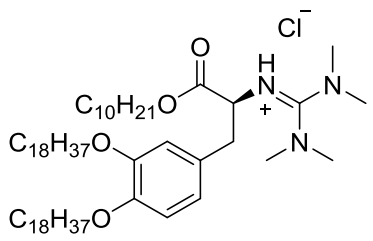
39.59
36.46
31.89
29.73
29.69
29.56
29.52
29.50
29.38
29.31
29.21
28.43
26.13
26.06
25.84
22.70
22.68
14.14
171.10
162.12
149.10
148.13
129.24
122.09
115.64
113.92
69.52
69.36
66.33
60.50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(10,18,18)


Cl⁻
O
H
N
+
N
N
C10H21O
C18H37O
C18H37O

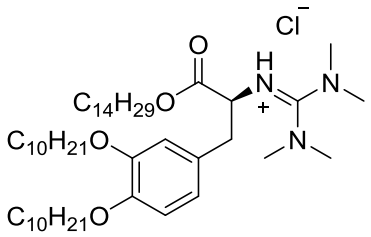
1.78
1.77
1.57
1.46
1.45
1.43
1.26
0.89
0.88
0.86
9.86
7.07
6.98
6.96
6.79
6.78
4.12
4.07
4.06
4.05
4.02
3.98
3.97
3.95
3.93
3.92
3.68
3.29
3.26
3.02
2.69
0.80
1.00
0.98
1.05
7.07
0.95
13.14
4.18
2.08
4.16
70.15
9.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(10,18,18)


Cl⁻
O
H
N
+
N
N
C10H21O
C18H37O
C18H37O

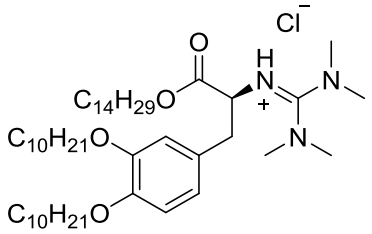
39.65
36.51
31.94
31.90
29.73
29.70
29.68
29.56
29.52
29.44
29.38
29.30
29.22
28.44
26.14
26.08
25.84
22.70
22.68
14.13
171.07
162.11
149.14
148.18
129.27
122.11
115.71
113.99
69.54
69.39
66.31
60.49
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
δ / ppm

Dopa(14,10,10)


Cl⁻
O
H
N
+
N
N
C14H29O
C10H21O
C10H21O

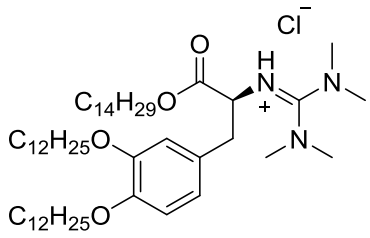
1.80
1.78
1.77
1.59
1.57
1.56
1.48
1.46
1.45
1.43
1.33
1.30
1.26
0.90
0.88
0.86
9.85
7.31
7.06
6.99
6.97
6.80
6.78
4.07
4.06
4.04
4.02
4.00
3.98
3.96
3.95
3.93
3.92
3.46
3.30
3.29
3.27
3.25
2.69
0.89
1.00
1.01
1.03
7.15
1.06
13.10
4.21
2.16
4.29
46.14
9.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(14,10,10)


Cl⁻
O
H
N
+
N
N
C14H29O
C10H21O
C10H21O

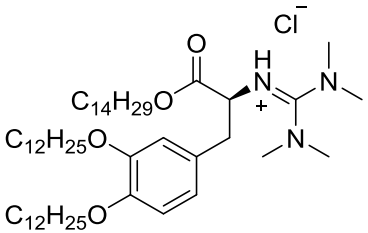
39.62
36.46
31.90
29.68
29.64
29.60
29.58
29.51
29.46
29.39
29.34
29.20
28.40
26.10
26.04
25.82
22.67
14.11
171.05
162.06
149.06
148.11
129.22
122.07
115.59
113.87
69.47
69.31
66.28
60.46
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(14,12,12)


Cl⁻
O
H
N
+
N
N
C14H29O
C12H25O
C12H25O

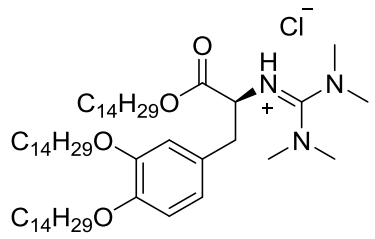
1.80
1.78
1.77
1.59
1.57
1.56
1.48
1.46
1.45
1.43
1.30
1.26
0.90
0.88
0.86
9.98
9.97
7.08
7.08
6.99
6.99
6.97
6.97
6.80
6.78
4.11
4.10
4.08
4.06
4.04
4.03
4.02
4.00
3.98
3.98
3.97
3.96
3.95
3.93
3.92
3.71
3.70
3.68
3.47
3.31
3.29
3.27
3.26
3.01
2.68
2.63
0.96
1.00
1.00
1.02
7.11
1.02
13.02
4.18
2.04
4.10
54.05
9.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(14,12,12)


Cl⁻
O
H
N
+
N
N
C14H29O
C12H25O
C12H25O

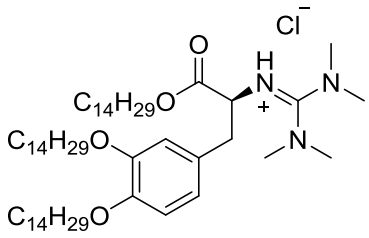
39.59
36.42
31.93
29.73
29.67
29.66
29.61
29.53
29.49
29.41
29.37
29.22
28.42
26.12
26.06
25.84
22.69
14.13
171.08
162.12
149.08
148.11
129.29
122.09
115.64
113.90
69.49
69.34
66.31
60.54
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(14,14,14)


Cl⁻
O
H
N
+
N
N
C14H29O
C14H29O
C14H29O

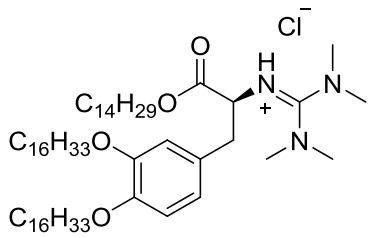
1.80
1.78
1.77
1.59
1.57
1.55
1.48
1.46
1.45
1.43
1.30
1.26
0.90
0.88
0.86
9.86
9.84
7.07
7.06
6.99
6.98
6.96
6.96
6.80
6.77
4.13
4.11
4.07
4.06
4.04
4.02
4.02
4.00
3.98
3.98
3.97
3.96
3.95
3.93
3.92
3.71
3.69
3.68
3.66
3.46
3.30
3.29
3.26
3.25
3.01
2.69
0.96
1.00
0.99
0.99
7.05
1.02
13.09
4.21
2.02
4.10
62.06
9.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(14,14,14)


Cl⁻
O
H
N
+
N
N
C14H29O
C14H29O
C14H29O

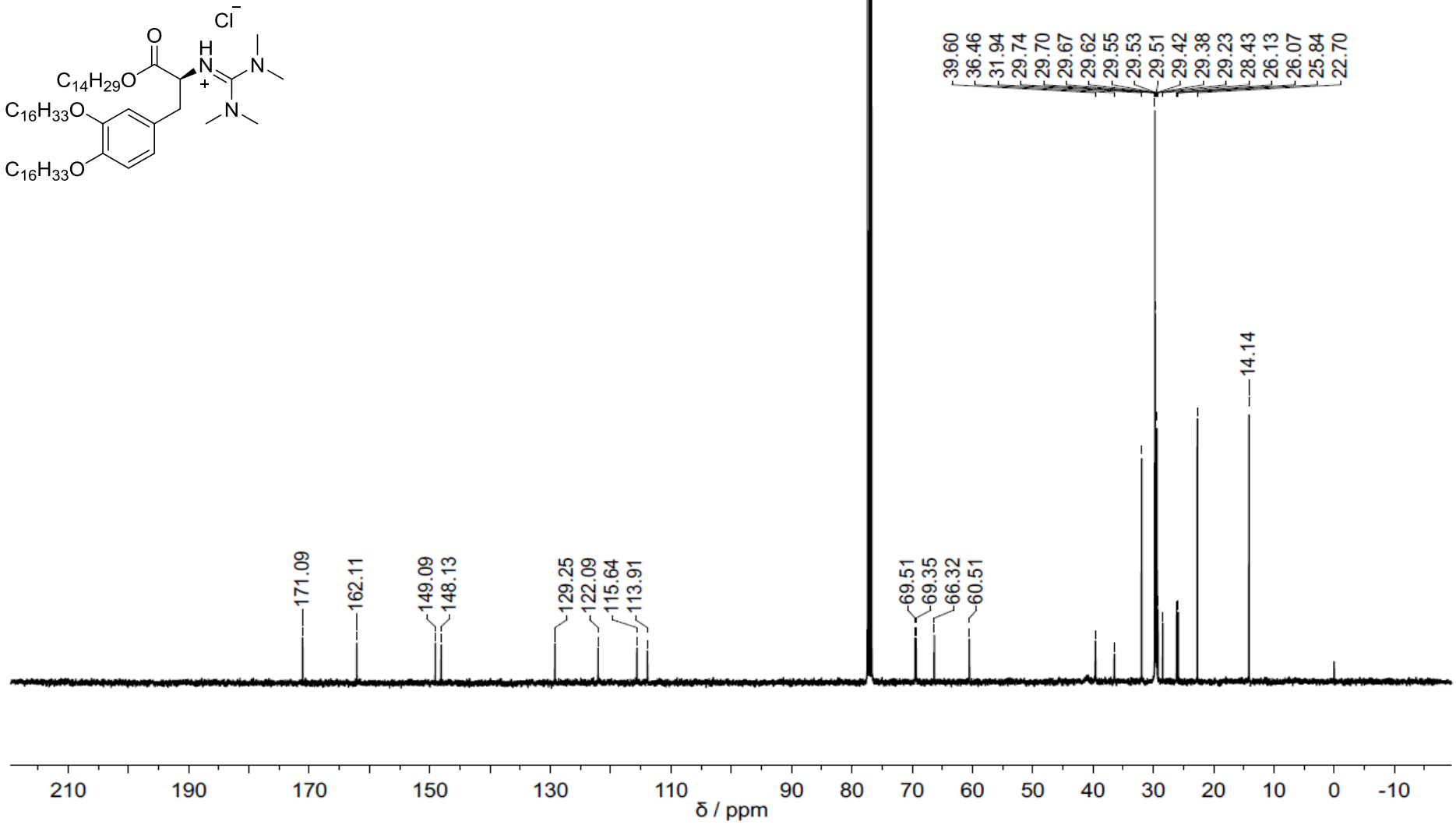
39.60
36.47
31.91
29.72
29.71
29.69
29.67
29.65
29.60
29.52
29.51
29.48
29.40
29.36
29.20
28.40
26.11
26.05
25.82
22.68
14.11
171.05
162.06
149.07
148.11
129.21
122.06
115.59
113.87
69.47
69.32
66.28
60.45
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(14,16,16)

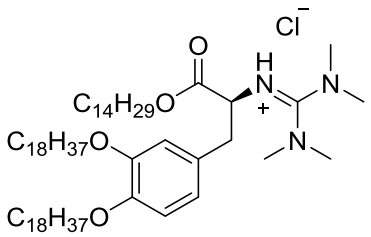

Cl⁻
O
H
N
+
N
N
C14H29O
C16H33O
C16H33O

1.82
1.80
1.78
1.77
1.75
1.75
1.59
1.57
1.56
1.46
1.45
1.43
1.41
1.30
1.26
0.90
0.88
0.86
9.91
9.89
7.07
7.07
6.99
6.98
6.97
6.96
6.80
6.78
4.10
4.08
4.06
4.04
4.02
4.00
3.98
3.97
3.96
3.95
3.93
3.92
3.30
3.29
3.27
3.26
3.00
2.81
2.68
2.62
0.98
1.00
0.99
1.01
7.12
1.00
13.07
4.07
1.92
4.12
70.15
9.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(14,16,16)

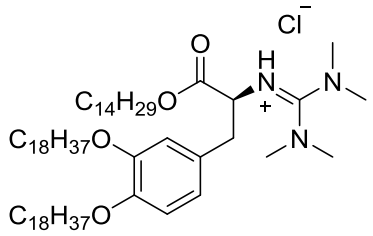

Cl⁻
O
H
N
+
N
N
C14H29O
C16H33O
C16H33O
39.60
36.46
31.94
29.74
29.70
29.67
29.62
29.55
29.53
29.51
29.42
29.38
29.23
28.43
26.13
26.07
25.84
22.70
14.14
171.09
162.11
149.09
148.13
129.25
122.09
115.64
113.91
69.51
69.35
66.32
60.51
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(14,18,18)


Cl⁻
O
H
N
+
N
N
C14H29O
C18H37O
C18H37O

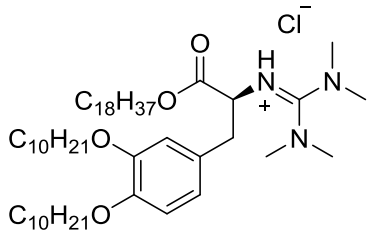
1.80
1.78
1.77
1.75
1.75
1.59
1.58
1.56
1.46
1.44
1.43
1.41
1.30
1.26
0.90
0.88
0.86
10.01
9.99
7.09
7.08
6.99
6.99
6.97
6.97
6.80
6.78
4.13
4.11
4.09
4.08
4.06
4.05
4.02
4.01
4.00
3.99
3.97
3.96
3.95
3.93
3.92
3.73
3.71
3.70
3.68
3.49
3.31
3.30
3.27
3.26
2.99
2.67
2.62
1.04
1.00
0.99
1.02
7.19
1.02
13.09
6.17
2.11
4.26
76.15
9.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(14,18,18)


Cl⁻
O
H
N
+
N
N
C14H29O
C18H37O
C18H37O

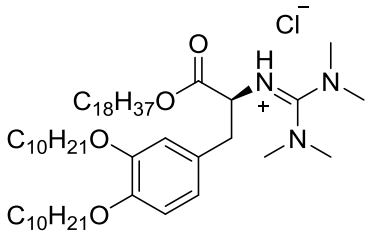
39.57
36.41
31.93
29.74
29.70
29.68
29.62
29.53
29.51
29.42
29.38
29.22
28.43
26.13
26.07
25.84
22.70
14.14
171.10
162.14
149.09
148.12
129.30
122.10
115.66
113.91
69.51
69.36
66.33
60.56
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(18,10,10)


Cl⁻
O
H
N
+
N
N
C18H37O
C10H21O
C10H21O

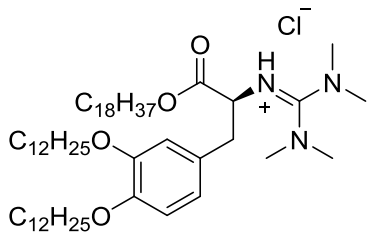
1.99
1.80
1.78
1.77
1.58
1.46
1.45
1.43
1.30
1.25
0.90
0.88
0.86
9.85
7.07
6.98
6.96
6.80
6.78
4.10
4.08
4.06
4.04
4.02
4.00
3.98
3.97
3.96
3.95
3.93
3.92
3.30
3.29
3.27
2.68
0.95
1.00
1.00
1.02
7.14
1.05
13.05
4.03
2.09
4.10
52.12
9.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(18,10,10)


Cl⁻
O
H
N
+
N
N
C18H37O
C10H21O
C10H21O

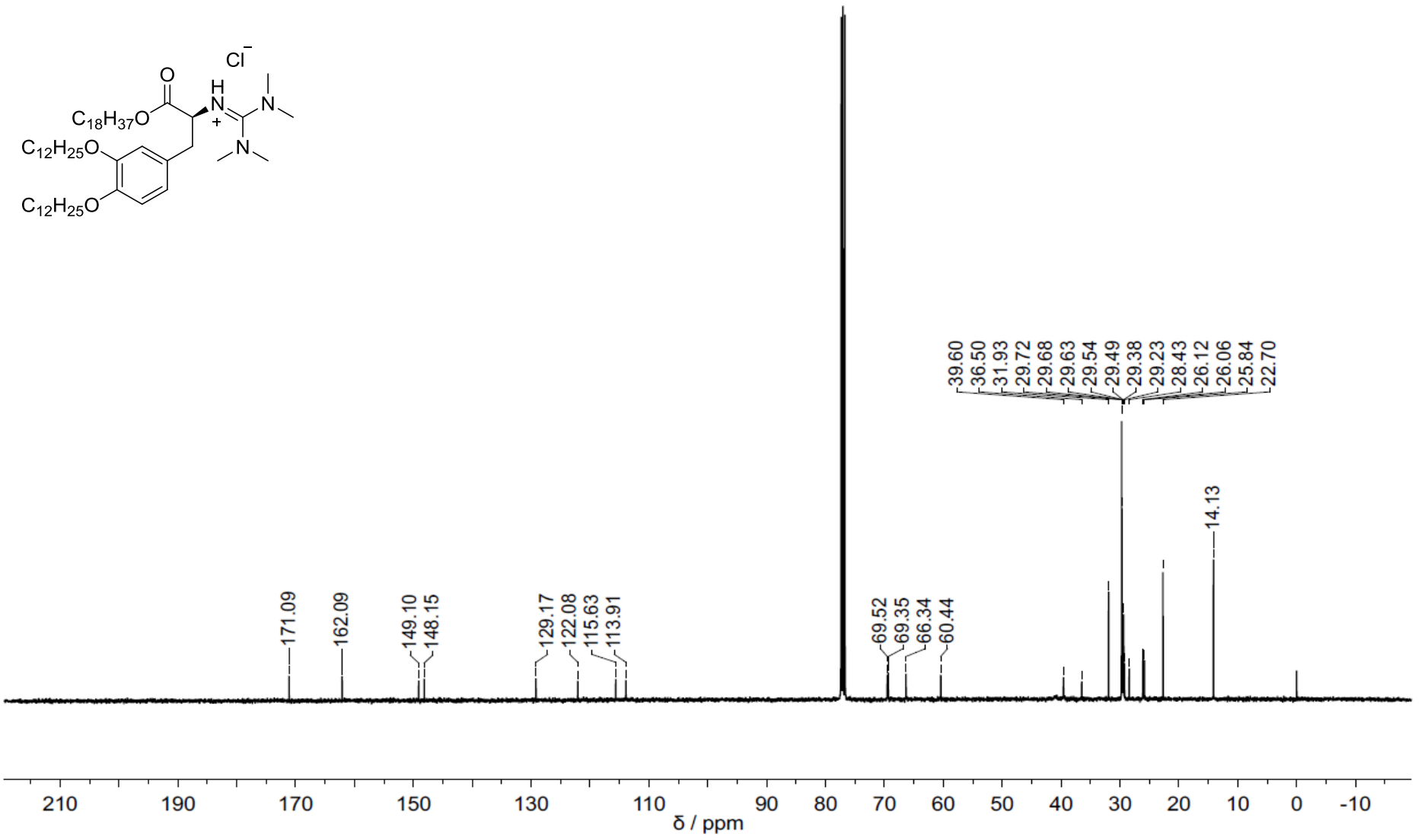
39.59
36.47
31.93
29.72
29.67
29.63
29.61
29.53
29.48
29.41
29.37
29.23
28.43
26.12
26.06
25.84
22.70
14.13
171.09
162.10
149.09
148.14
129.22
122.09
115.64
113.90
69.51
69.35
66.33
60.47
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(18,12,12)

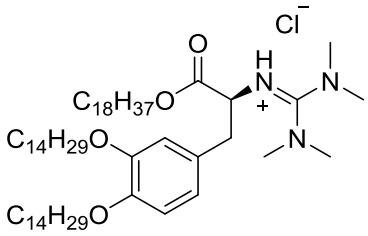

Cl⁻
O
H
N
+
N
N
C18H37O
C12H25O
C12H25O

1.90
1.82
1.80
1.78
1.77
1.59
1.58
1.46
1.45
1.43
1.30
1.25
0.90
0.88
0.86
9.78
9.76
7.06
6.98
6.96
6.80
6.78
4.08
4.06
4.05
4.02
4.00
3.98
3.97
3.96
3.95
3.93
3.92
3.65
3.30
3.29
3.27
2.68
0.99
1.00
1.01
1.03
7.04
1.08
13.11
4.03
2.16
4.19
60.22
9.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(18,12,12)

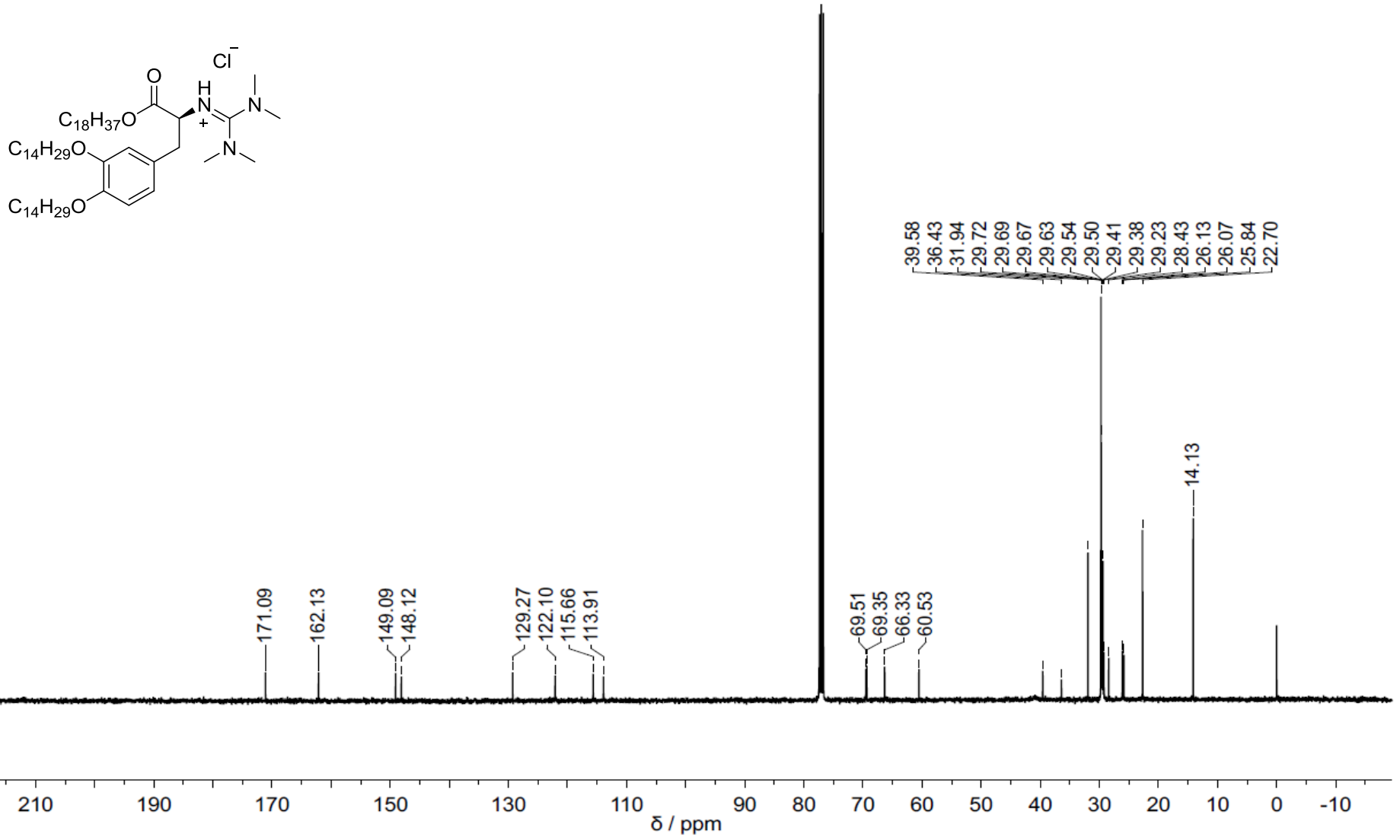

Cl⁻
O
H
N
+
N
N
C18H37O
C12H25O
C12H25O
39.60
36.50
31.93
29.72
29.68
29.63
29.54
29.49
29.38
29.23
28.43
26.12
26.06
25.84
22.70
14.13
171.09
162.09
149.10
148.15
129.17
122.08
115.63
113.91
69.52
69.35
66.34
60.44
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(18,14,14)

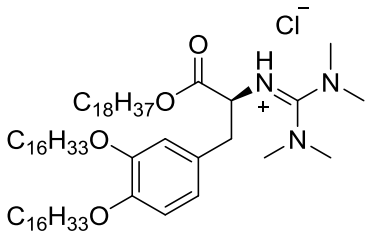

Cl⁻
O
H
N
+
N
N
C18H37O
C14H29O
C14H29O

1.89
1.82
1.80
1.78
1.77
1.75
1.59
1.58
1.56
1.46
1.45
1.43
1.41
1.30
1.25
0.90
0.88
0.86
9.96
9.95
7.08
6.99
6.97
6.80
6.78
4.09
4.08
4.06
4.04
4.02
4.00
3.99
3.96
3.95
3.93
3.92
3.31
3.29
3.27
3.26
2.98
2.67
0.98
1.00
1.02
1.02
7.12
1.05
13.15
4.16
2.11
4.19
68.25
9.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(18,14,14)

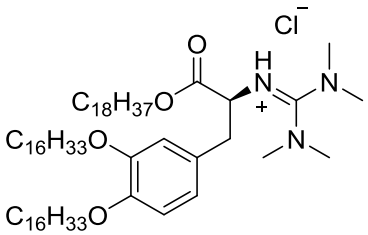

Cl⁻
O
H
N
+
N
N
C18H37O
C14H29O
C14H29O
39.58
36.43
31.94
29.72
29.69
29.67
29.63
29.54
29.50
29.41
29.38
29.23
28.43
26.13
26.07
25.84
22.70
14.13
171.09
162.13
149.09
148.12
129.27
122.10
115.66
113.91
69.51
69.35
66.33
60.53
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(18,16,16)


Cl⁻
O
H
N
+
N
N
C18H37O
C16H33O
C16H33O

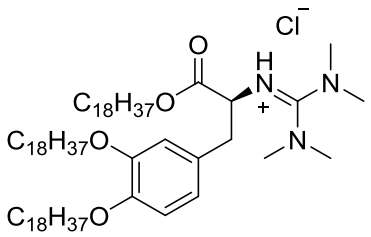
1.80
1.78
1.77
1.59
1.58
1.46
1.45
1.43
1.41
1.30
1.25
0.89
0.88
0.86
10.03
10.02
7.08
6.99
6.97
6.80
6.77
4.09
4.08
4.06
4.04
4.02
4.00
3.99
3.96
3.95
3.93
3.92
3.31
3.30
3.27
3.26
2.67
1.00
1.00
1.01
1.03
7.00
1.06
13.06
6.02
2.09
4.17
76.33
9.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(18,16,16)


Cl⁻
O
H
N
+
N
N
C18H37O
C16H33O
C16H33O

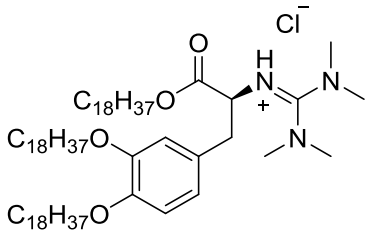
39.58
36.41
31.94
29.73
29.68
29.63
29.54
29.50
29.42
29.38
29.23
28.43
26.13
26.07
25.84
22.70
14.14
171.10
162.14
149.09
148.11
129.31
122.10
115.67
113.91
69.51
69.35
66.32
60.57
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm

Dopa(18,18,18)


Cl⁻
O
H
N
+
N
N
C18H37O
C18H37O
C18H37O

1.80
1.78
1.77
1.59
1.58
1.46
1.44
1.43
1.41
1.30
1.25
0.89
0.88
0.86
10.05
10.03
7.08
6.99
6.97
6.80
6.77
4.11
4.09
4.08
4.06
4.04
4.02
4.00
3.99
3.97
3.96
3.95
3.93
3.92
3.71
3.68
3.49
3.31
3.30
3.27
3.26
2.67
0.97
1.00
1.02
1.02
7.28
1.02
13.09
5.94
2.07
4.15
84.04
9.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

Dopa(18,18,18)


Cl⁻
O
H
N
+
N
N
C18H37O
C18H37O
C18H37O

39.58
36.41
31.94
29.73
29.68
29.63
29.54
29.51
29.42
29.38
29.23
28.43
26.13
26.07
25.85
22.70
14.14
171.10
162.14
149.09
148.11
129.31
122.10
115.66
113.91
69.51
69.36
66.32
60.57
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ / ppm