Electronic Supplementary Information

Amino Acid/Crown Ether Hybrid Materials: How Charge Affects Liquid Crystalline Self-Assembly†

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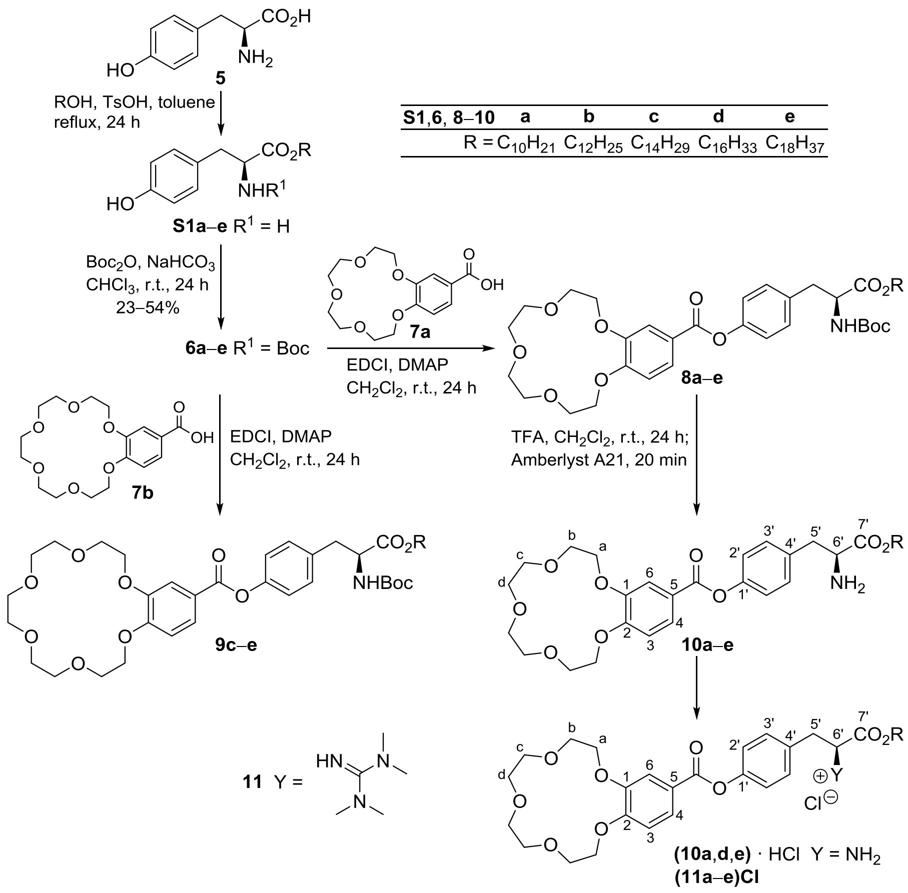
1. Synthesis



Scheme S1. Synthesis of target compounds **8**–**10**. Numbering for NMR assignment.

General Procedure for the Synthesis of Alkyl *N*-(*tert*-butoxycarbonyl)-L-tyrosinates 6a–e (GP 1).[1,2] a) Alkyl L-tyrosinates **S1**:[2] A suspension of **5** (1.0 equiv.), the respective alcohol (1.0 equiv.) and *p*-toluenesulfonic acid monohydrate (1.1 equiv.) in toluene (250 mL) was refluxed for 24 h under Dean-Stark conditions. Then the solvent was removed under vacuum. The residue was dissolved in EtOAc (250 mL) and washed with a 10% solution of Na_2CO_3 (3 × 250 mL), H_2O (250 mL) and brine (250 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was used without further purification.

b) To a solution of the appropriate **S1** (1.0 equiv.) and $NaHCO_3$ (3.0 equiv.) in $CHCl_3$ (120 mL) was added dropwise at 0 °C a solution of di-*tert*-butyldicarbonate (1.1 equiv.) in $CHCl_3$ (20 mL). The reaction mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in EtOAc (150 mL) and washed successively with 2M HCl (3 × 150 mL), a 10% solution of $NaHCO_3$ (3 × 150 mL), H_2O (150 mL) and brine (150 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on SiO_2 (*n*-hexanes/EtOAc 20 : 1→5 : 1) to give products **6** as colorless solids.

Decyl *N*-(*tert*-butoxycarbonyl)-L-tyrosinate (6a). Yield: 5.69 g, 13.50 mmol, 56%.; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.24-1.33 (m, 14H, CH_2), 1.42 (s, 9H, OC(CH_3)$_3$), 1.56-1.65 (m, 2H, OCH_2CH_2), 2.92-3.07 (m, 2H, 5-H), 4.09 (m$_c$, 2H, OCH_2), 4.48-4.56 (m, 1H, 6-H), 5.01 (br s, 1H, N*H*), 6.72 (m$_c$, 2H, 2-H), 6.97 (m$_c$, 2H, 3-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H_3), 22.7, 25.8, 28.3, 28.5, 29.2, 29.3, 29.49, 29.54, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.6 (C-5), 54.6 (C-6), 65.7 (O*C*H_2), 80.1 (O*C*(CH_3)$_3$), 115.4 (C-2), 127.6 (C-4), 130.4 (C-3), 155.1 (C-1), 155.3 (HN*C*=O), 172.3 (C-7) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3369 (w), 2925 (s), 2855 (m), 1716 (s), 1688 (s), 1615 (w), 1596 (w), 1516 (s), 1454 (m), 1393 (s), 1366 (s), 1221 (s), 1165 (vs), 1103 (w), 1058 (m), 1024 (w), 828 (w), 779 (w), 731 (w), 540 (w), 494 (w), 464 (w) cm^{-1}; MS (ESI): *m/z* = 444 $[M + Na]^+$, 388, 344; HRMS (ESI): *m/z* calc. for $C_{24}H_{39}NO_5Na^+$: 444.2720 $[M + Na]^+$, found.: 444.2722.

Dodecyl *N*-(*tert*-butoxycarbonyl)-L-tyrosinate (6b). Yield: 4.72 g, 10.50 mmol, 35%; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.22-1.33 (m, 18H, CH_2), 1.42 (s, 9H, OC(CH_3)$_3$), 1.56-1.66 (m, 2H, OCH_2CH_2), 2.92-3.07 (m, 2H, 5-H), 4.09 (m$_c$, 2H, OCH_2), 4.48-4.56 (m, 1H, 6-H), 4.97-5.05 (m, 1H, N*H*), 6.72 (d, $J_{2,3}$ = 7.8 Hz, 2H, 2-H), 6.97 (d, $J_{2,3}$ = 7.8 Hz, 2H, 3-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.3, 28.5, 29.2, 29.3, 29.5, 29.58, 29.63, 29.7, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.6 (C-5), 54.6 (C-6), 65.7 (O*C*H_2), 80.1 (O*C*(CH_3)$_3$), 115.4 (C-2), 127.6 (C-4), 130.4 (C-3), 155.1 (C-1), 155.3 (HN*C*=O), 172.3 (C-7) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3369 (w), 2924 (s), 2854 (m), 1716 (m), 1688 (s), 1615 (w), 1596 (w), 1516 (s), 1454 (m), 1392 (m), 1366 (m), 1220 (s), 1164 (vs), 1103 (w), 1058 (m), 1024 (w), 828 (w), 778 (w), 726 (w), 539 (w), 494 (w) cm^{-1}; MS (ESI): *m/z* = 472 $[M + Na]^+$, 416, 394, 372, 350, 182, 165, 136, 121, 107; HRMS (ESI): *m/z* calc. for $C_{26}H_{43}NO_5Na^+$: 472.3033 $[M + Na]^+$, found: 472.3008.

Hexadecyl *N*-(*tert*-butoxycarbonyl)-L-tyrosinate (6d). Yield: 3.25 g, 6.43 mmol, 31%; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.22-1.34 (m, 26H, CH_2), 1.42 (s, 9H, OC(CH_3)$_3$), 1.56-1.65 (m, 2H, OCH_2CH_2), 2.93-3.08 (m, 2H, 5-H), 4.09 (m$_c$, 2H, OCH_2), 4.48-4.56 (m, 1H, 6-H), 4.97-5.04 (m, 1H, N*H*), 6.72 (d, $J_{2,3}$ = 7.9 Hz, 2H, 2-H), 6.97 (d, $J_{2,3}$ = 7.9 Hz, 2H, 3-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.69, 29.70, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.6 (C-5), 54.6 (C-6), 65.7 (O*C*H_2), 80.0 (O*C*(CH_3)$_3$), 115.4 (C-2), 127.7 (C-4), 130.4 (C-3), 155.0 (C-1), 155.3 (HN*C*=O), 172.2 (C-7) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3369 (w), 2923 (vs), 2853 (s), 1717 (s), 1689 (s), 1615 (m), 1596 (w), 1516 (s), 1455 (m), 1393 (m), 1366 (s), 1222 (s), 1167 (vs), 1103 (w), 1059 (m), 1025 (w), 828 (w), 778 (w), 722 (w), 541 (w), 498 (w), 436 (w) cm^{-1}; MS (ESI): *m/z* = 528 $[M + Na]^+$, 472, 428, 406; HRMS (ESI): *m/z* calc. for $C_{30}H_{51}NO_5Na^+$: 528.3659 $[M + Na]^+$, found: 528.3644.

General Procedure for the Steglich esterification (GP 2).[3] A solution of the appropriate **7a**,**b**[4,5] (1.0 equiv.), **6** (1.1.equiv.), EDCI (1.2 equiv.) and DMAP (0.1 equiv.) in abs. CH_2Cl_2 under nitrogen atmosphere was stirred for 24 h at room temperature. Then the reaction mixture was washed with H_2O (3 × 130 mL), dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on SiO_2 with CH_2Cl_2/EtOAc (10:1) to give products **8** or **9** as colorless solids.

Benzo[15]crown-5 decyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (8a). From **7a** (1.00 g, 3.20 mmol), **6a** (1.50 g, 3.56 mmol), EDCI (750 mg, 3.91 mmol), DMAP (44 mg, 0.36 mmol), abs. CH_2Cl_2 (120 mL); yield: 1.63 g, 2.28 mmol, 71%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.21-1.33 (m, 14H, C*H*$_2$), 1.43 (s, 9H, OC(C*H*$_3$)$_3$), 1.56-1.65 (m, 2H, OCH$_2$C*H*$_2$), 3.05-3.16 (m, 2H, 5'-H), 3.75-3.81 (m, 8H, c-H, d-H), 3.90-3.97 (m, 4H, b-H), 4.05-4.14 (m, 2H, OC*H*$_2$), 4.19-4.24 (m, 4H, a-H), 4.53-4.61 (m, 1H, 6'-H), 4.97-5.05 (m, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.82 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.3, 28.5, 29.2, 29.3, 29.48, 29.53, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (O*C*H$_2$), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 79.9 (O*C*(CH$_3$)$_3$), 112.1 (C-3), 115.0 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.8 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HN*C*=O), 164.8 (Ar*C*=O), 172.3 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3357 (w), 2925 (m), 2855 (m), 1717 (s), 1599 (w), 1509 (s), 1452 (m), 1429 (m), 1391 (w), 1366 (m), 1347 (m), 1273 (s), 1250 (m), 1194 (vs), 1165 (s), 1133 (vs), 1053 (s), 1018 (m), 982 (m), 960 (m), 870 (w), 784 (w), 756 (m), 729 (m), 648 (w), 542 (w) cm^{-1}; MS (ESI): *m/z* = 738 $[M + Na]^+$, 703, 682, 635, 567, 499, 431, 363; HRMS (ESI): *m/z* calc. for $C_{39}H_{57}NO_{11}Na^+$: 738.3824 $[M + Na]^+$, found: 738.3840; anal. calcd. for $C_{39}H_{57}NO_{11}$: C 65.43 H 8.03 N 1.96, found C 65.48 H 7.78 N 1.87; DSC: Cr 55 °C [-13.0 kJ/mol] Col_r 90 °C [-25.7 kJ/mol] I.

Benzo[15]crown-5 dodecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (8b). From **7a** (1.00 g, 3.20 mmol), **6b** (1.60 g, 3.56 mmol), EDCI (752 mg, 3.92 mmol), DMAP (44 mg, 0.36 mmol), abs. CH_2Cl_2 (120 mL), yield: 1.85 g, 2.49 mmol, 78%. ^{1}H-NMR ($CDCl_3$, 500

MHz) δ = 0.87 (t, J = 6.8 Hz, 3H, CH_3), 1.21-1.34 (m, 18H, CH_2), 1.43 (s, 9H, OC(CH_3)$_3$), 1.58-1.64 (m, 2H, OCH$_2$CH_2), 3.04-3.18 (m, 2H, 5'-H), 3.75-3.81 (m, 8H, c-H, d-H), 3.90-3.97 (m, 4H, b-H), 4.07-4.13 (m, 2H, OCH_2), 4.18-4.25 (m, 4H, a-H), 4.54-4.61 (m, 1H, 6'-H), 4.97-5.05 (m, 1H, NH), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2,3'}$ = 8.3 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 3'-H), 7.63-7.66 (m, 1H, 6-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (CH$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.3, 29.5, 29.58, 29.63, 29.65, 31.9 (CH$_2$, OC(CH$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (OCH$_2$), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 79.9 (OC(CH$_3$)$_3$), 112.1 (C-3), 115.0 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.8 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HNC=O), 164.8 (ArC=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3342 (w), 2924 (m), 2854 (m), 1718 (s), 1599 (w), 1510 (s), 1453 (w), 1429 (m), 1391 (w), 1365 (m), 1347 (m), 1273 (s), 1250 (m), 1195 (vs), 1165 (s), 1135 (s), 1054 (m), 1018 (m), 983 (w), 960 (m), 869 (w), 784 (w), 756 (m), 728 (m), 647 (w), 515 (w) cm^{-1}; MS (ESI): m/z = 766 [M + Na]$^+$, 710; HRMS (ESI): m/z calc. for $C_{41}H_{61}NO_{11}Na^+$: 766.4137 [M + Na]$^+$, found: 766.4167; anal. calc. for $C_{41}H_{61}NO_{11}$: C 66.20 H 8.27 N 1.88, found C 66.21 H: 8.12 N 1.76; DSC: I 61 °C [28.7 kJ/mol] Col$_r$ 91 °C [-47.7 kJ/mol] I.

Benzo[15]crown-5 tetradecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (8c). From **7a** (600 mg, 1.92 mmol), **6c** (1.02 g, 2.13 mmol), EDCI (449 mg, 2.34 mmol), DMAP (26 mg, 0.21 mmol), abs. CH_2Cl_2 (100 mL), yield: 1.28 g, 1.66 mmol, 86%. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.21-1.33 (m, 22H, CH_2), 1.43 (s, 9H, OC(CH_3)$_3$), 1.58-1.64 (m, 2H, OCH$_2$CH_2), 3.04-3.18 (m, 2H, 5'-H), 3.75-3.81 (m, 8H, c-H, d-H), 3.90-3.97 (m, 4H, b-H), 4.07-4.13 (m, 2H, OCH_2), 4.18-4.25 (m, 4H, a-H), 4.54-4.61 (m, 1H, 6'-H), 4.97-5.05 (m, 1H, NH), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 3'-H), 7.63-7.66 (m, 1H, 6-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (CH$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.65, 29.67, 31.9 (CH$_2$, OC(CH$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (OCH$_2$), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 79.9 (OC(CH$_3$)$_3$), 112.1 (C-3), 115.0 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.8 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HNC=O), 164.8 (ArC=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3357 (w), 2923 (m), 2853 (m), 1717 (s), 1599 (w), 1509 (s), 1454 (w), 1429 (m), 1391 (w), 1365 (m), 1347 (m), 1273 (s), 1250 (m), 1194 (vs), 1165 (s), 1134 (vs), 1054 (s), 1018 (m), 982 (m), 960 (m), 915 (m), 869 (w), 783 (w), 756 (m), 730 (m), 648 (w), 515 (w), 464 (w) cm^{-1}; MS (ESI): m/z = 794 [M + Na]$^+$, 738; HRMS (ESI): m/z calc. for $C_{43}H_{65}NO_{11}Na^+$: 794.4450 [M + Na]$^+$, found

794.4453; anal. calc. for $C_{43}H_{65}NO_{11}$: C 66.90 H 8.49 N 1.81, found C 66.81 H 8.36 N 1.64; DSC: I 39 °C [25.6 kJ/mol] Cr 58 °C [12.8 kJ/mol] Cr_1 91 °C [-53.4 kJ/mol] I.

Benzo[15]crown-5 hexadecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (8d). From **7a** (1.00 g, 3.20 mmol), **6d** (1.80 g, 3.56 mmol), EDCI (752 mg, 3.92 mmol), DMAP (44 mg, 0.36 mmol), abs. CH_2Cl_2 (120 mL), yield: 1.74 g, 2.18 mmol, 68%. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.20-1.34 (m, 26H, CH_2), 1.43 (s, 9H, OC(CH_3)$_3$), 1.57-1.64 (m, 2H, OCH$_2$CH_2), 3.04-3.18 (m, 2H, 5'-H), 3.75-3.82 (m, 8H, c-H, d-H), 3.90-3.97 (m, 4H, b-H), 4.07-4.13 (m, 2H, OCH_2), 4.18-4.25 (m, 4H, a-H), 4.54-4.61 (m, 1H, 6'-H), 4.97-5.05 (m, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 3'-H), 7.63-7.66 (m, 1H, 6-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (O*C*H$_2$), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 79.9 (O*C*(CH$_3$)$_3$), 112.1 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HN*C*=O), 164.8 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3345 (w), 2923 (m), 2853 (m), 1718 (s), 1599 (w), 1510 (m), 1454 (w), 1429 (m), 1391 (w), 1365 (m), 1347 (m), 1273 (s), 1250 (m), 1194 (vs), 1165 (s), 1135 (s), 1055 (m), 1019 (m), 982 (w), 960 (m), 869 (w), 784 (w), 756 (m), 726 (w), 649 (w), 517 (w) cm^{-1}; MS (ESI): *m/z* = 822 $[M + Na]^+$; HRMS (ESI): *m/z* calc. for $C_{45}H_{69}NO_{11}Na^+$: 822.4763 $[M + Na]^+$, found: 822.4779; anal. calc. for $C_{45}H_{69}NO_{11}$: C 67.56 H 8.69 N 1.75, found C 67.41 H: 8.55 N 1.67; DSC: Cr 50 °C [-10.2 kJ/mol] Col_r 76 °C [-20.3 kJ/mol] I.

Benzo[15]crown-5 octadecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (8e). From **7a** (600 mg, 1.92 mmol), **6e** (1.14 g, 2.13 mmol), EDCI (449 mg, 2.34 mmol), DMAP (26 mg, 0.21 mmol), abs. CH_2Cl_2 (100 mL), yield: 1.14 g, 1.38 mmol, 72%. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.21-1.33 (m, 30H, CH_2), 1.43 (s, 9H, OC(CH_3)$_3$), 1.56-1.64 (m, 2H, OCH$_2$CH_2), 3.04-3.17 (m, 2H, 5'-H), 3.75-3.81 (m, 8H, c-H, d-H), 3.90-3.97 (m, 4H, b-H), 4.05-4.14 (m, 2H, OCH_2), 4.19-4.24 (m, 4H, a-H), 4.53-4.61 (m, 1H, 6'-H), 4.97-5.04 (m, 1H, N*H*), 6.91 (m_c, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 2'-H), 7.18 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 3'-H), 7.63-7.66 (m, 1H, 6-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (O*C*H$_2$), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 79.9 (O*C*(CH$_3$)$_3$), 112.1 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HN*C*=O), 164.8 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3361 (w), 2922 (s), 2853 (m), 1718 (s), 1599 (w), 1509 (s), 1453 (m), 1429 (m), 1391 (w), 1365 (m), 1347 (m), 1273 (s), 1250 (m), 1194 (vs), 1165 (s), 1133 (vs), 1054 (s), 1018 (m), 982 (m), 960 (m), 870 (w), 783 (w), 756 (m), 729 (m), 648 (w), 514 (w) cm^{-1}; MS (ESI): *m/z* = 850 $[M + Na]^+$, 846, 741, 728; HRMS (ESI): *m/z* calc. for $C_{47}H_{73}NO_{11}Na^+$: 850.5076 $[M + Na]^+$, found 850.5100; anal. calc. for $C_{47}H_{73}NO_{11}$: C 68.17 H 8.89 N 1.69, found C 67.92 H 8.73 N 1.67; DSC: Cr 67 °C [-10.6 kJ/mol] Col_r 78 °C [-16.1 kJ/mol] I.

Benzo[18]crown-6 tetradecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (9c). From **7b** (300 mg, 0.84 mmol), **6c** (447 mg, 0.94 mmol), EDCI (198 mg, 1.03 mmol), DMAP (12 mg, 0.09 mmol), abs. CH_2Cl_2 (50 mL), yield: 70 mg, 0.09 mmol, 10%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.20-1.35 (m, 22H, CH_2), 1.43 (s, 9H, $OC(CH_3)_3$), 1.56-1.66 (m, 2H, OCH_2CH_2), 3.04-3.18 (m, 2H, 5'-H), 3.70 (br s, 4H, e-H), 3.71-3.76 (m, 4H, d-H), 3.77-3.82 (m, 4H, c-H), 3.92-4.00 (m, 4H, b-H), 4.07-4.13 (m, 2H, OCH_2), 4.21-4.27 (m, 4H, a-H), 4.54-4.61 (m, 1H, 6'-H), 4.97-5.05 (m, 1H, N*H*), 6.93 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.66 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.82 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (CH_3), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.65, 29.68, 29.69, 31.9 (CH_2, $OC(CH_3)_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (OCH_2), 69.0, 69.2 (C-a), 69.4, 69.5 (C-b), 70.67, 70.73 (C-c), 70.8, 70.9, 71.0 (C-d, C-e), 79.9 ($OC(CH_3)_3$), 112.2 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.5 (C-1), 150.1 (C-1'), 153.6 (C-2), 155.1 (HN*C*=O), 164.8 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3340 (w), 2923 (s), 2854 (m), 1720 (s), 1599 (w), 1510 (s), 1454 (m), 1428 (m), 1391 (w), 1365 (m), 1347 (m), 1272 (s), 1250 (m), 1196 (vs), 1166 (s), 1132 (vs), 1057 (m), 1019 (m), 962 (m), 869 (w), 785 (w), 756 (w), 723 (w), 647 (w), 519 (w) cm^{-1}; MS (ESI): *m/z* = 838 $[M + Na]^+$; HRMS (ESI): *m/z* calc. for $C_{45}H_{69}NO_{12}Na^+$: 838.4712 $[M + Na]^+$, found 838.4705; anal. calc. for $C_{45}H_{69}NO_{12}$: C 66.23 H 8.52 N 1.72, found C 66.02 H 8.77 N 1.77; DSC: Cr 51 °C [-3.0 kJ/mol] Col_r 66°C [-15.5 kJ/mol] I.

Benzo[18]crown-6 hexadecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (9d). From **7b** (300 mg, 0.84 mmol), **6d** (473 mg, 0.94 mmol), EDCI (198 mg, 1.03 mmol), DMAP (12 mg, 0.09 mmol), abs. CH_2Cl_2 (70 mL), yield: 85 mg, 0.10 mmol, 12%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.20-1.35 (m, 26H, CH_2), 1.43 (s, 9H, $OC(CH_3)_3$), 1.56-1.66 (m, 2H, OCH_2CH_2), 3.04-3.19 (m, 2H, 5'-H), 3.70 (br s, 4H, e-H), 3.71-3.76 (m, 4H, d-H), 3.77-3.82 (m, 4H, c-H), 3.92-4.00 (m, 4H, b-H), 4.07-4.13 (m, 2H, OCH_2), 4.21-4.27 (m, 4H, a-H), 4.54-4.61 (m, 1H, 6'-H), 4.97-5.04 (m, 1H, N*H*), 6.93 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 3'-H), 7.66 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.82 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.69, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.7 (C-5'), 54.4 (C-6'), 65.6 (O*C*H_2), 69.0, 69.2 (C-a), 69.4, 69.5 (C-b), 70.67, 70.73 (C-c), 70.76, 70.84, 71.0 (C-d, C-e), 79.9 (O*C*(CH_3)$_3$), 112.2 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.5 (C-1), 150.0 (C-1'), 153.6 (C-2), 155.1 (HN*C*=O), 164.8 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3339 (w), 2923 (m), 2854 (m), 1719 (m), 1599 (w), 1510 (m), 1454 (w), 1428 (w), 1391 (w), 1366 (w), 1347 (w), 1272 (s), 1250 (m), 1196 (vs), 1166 (s), 1133 (vs), 1019 (w), 962 (w), 869 (w), 786 (w), 756 (w), 648 (w), 519 (w) cm^{-1}; MS (ESI): *m/z* = 867 $[M + Na]^+$, 437; HRMS (ESI): *m/z* calc. for $C_{47}H_{73}NO_{12}Na^+$: 866.5025 $[M + Na]^+$, found 866.5050; anal. calc. for $C_{47}H_{73}NO_{12}$: C 66.88 H 8.72 N 1.66, found C 65.76 H 9.10 N 1.54; DSC: Cr 46°C [-8.3 kJ/mol] Col_r 73°C [-15.8 kJ/mol] I.

Benzo[18]crown-6 octadecyl (*tert*-butoxycarbonyl)-*L*-tyrosinate (9e). From **7b** (300 mg, 0.84 mmol), **6e** (496 mg, 0.93 mmol), EDCI (196 mg, 1.02 mmol), DMAP (11 mg, 0.09 mmol), abs. CH_2Cl_2 (50 mL), yield: 225 mg, 0.26 mmol, 31%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.21-1.36 (m, 30H, C*H*$_2$), 1.43 (s, 9H, OC(C*H*$_3$)$_3$), 1.56-1.65 (m, 2H, OCH$_2$C*H*$_2$), 3.04-3.18 (m, 2H, 5'-H), 3.70 (br s, 4H, e-H), 3.71-3.76 (m, 4H, d-H), 3.77-3.82 (m, 4H, c-H), 3.92-4.00 (m, 4H, b-H), 4.07-4.13 (m, 2H, OC*H*$_2$), 4.21-4.27 (m, 4H, a-H), 4.54-4.61 (m, 1H, 6'-H), 4.97-5.04 (m, 1H, N*H*), 6.93 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.66 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.82 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.65, 29.70, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.6 (O*C*H_2), 68.9, 69.2 (C-a), 69.3, 69.5 (C-b), 70.66, 70.72 (C-c), 70.76, 70.84, 70.99, 71.02 (C-d, C-e), 79.9 (O*C*(CH_3)$_3$), 112.2 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.3 (C-3') 133.6 (C-4'), 148.5 (C-1), 150.1 (C-1'), 153.6 (C-2), 155.1 (HN*C*=O), 164.8 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3353 (w), 2919 (s), 2850 (m), 1731 (s), 1687 (s), 1599 (w), 1516 (s), 1467 (w), 1429 (m), 1391 (w), 1366 (m), 1346 (w), 1274 (s), 1250 (m), 1196 (vs), 1167 (s), 1133 (vs), 1086 (m), 1053 (s), 1020 (m), 993 (w), 962 (m), 945 (w), 918 (w), 895 (w), 870 (w), 786 (w), 755 (m), 723 (w), 647 (w), 538 (w), 510 (w), 432 (w) cm^{-1}; MS (ESI): = 895 $[M + Na]^+$, 429; HRMS (ESI): *m/z* calc. for $C_{49}H_{77}NO_{12}Na^+$: 894.5338 $[M + Na]^+$, found 894.5322; anal. calc. for $C_{49}H_{77}NO_{12}$: C 67.48 H 8.90 N 1.61, found C 67.45 H 8.78 N 1.54; DSC: Cr 48°C [-7.2 kJ/mol] Col_r 79°C [-30.9 kJ/mol] I.

General Procedure for the Deprotection of 8a–e to Amines 10a–e (GP 3).[6] To a solution of the respective **8a–e** (1.0 equiv.) in abs. CH_2Cl_2 (50 mL) under nitrogen atmosphere at 0 °C was added dropwise a solution of trifluoroacetic acid (10.0 equiv.) in abs. CH_2Cl_2 (2 mL), and the reaction mixture was stirred for 24 h at room temperature. The reaction was then quenched with Amberlyst A21 resin and the mixture stirred for 20 min at room temperature. After filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on SiO_2 with CH_2Cl_2/MeOH (20:1) to give products **10** as colorless solids.

Benzo[15]crown-5 decyl *L*-tyrosinate (10a). From **8a** (200 mg, 0.28 mmol), TFA (0.22 mL, 320 mg, 2.80 mmol), abs. CH_2Cl_2 (50 mL), yield: 130 mg, 0.21 mmol, 75%, yellow wax-like solid. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.87 (t, J = 6.8 Hz, 3H, CH_3), 1.21-1.35 (m, 14H, CH_2), 1.58-1.66 (m, 2H, OCH$_2$CH_2), 2.91 (dd, $J_{5a',6'}$ = 8.0 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5a'-H), 3.11 (dd, $J_{5b',6'}$ = 5.1 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.74-3.82 (m, 9H, c-H, d-H 6'-H), 3.91-3.99 (m, 4H, b-H), 4.11 (t, J = 6.8 Hz, 2H, OCH_2), 4.19-4.26 (m, 4H, a-H), 6.92 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 2'-H), 7.26 (m$_c$, 2H, 3'-H), 7.65 (br s, 1H, 6-H), 7.83 (m$_c$, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (CH$_3$), 22.7, 25.9, 28.6, 29.2, 29.3, 29.50, 29.53, 31.9 (CH$_2$), 40.6 (C-5'), 55.8 (C-6'), 65.2 (OCH$_2$), 68.6, 69.0 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.8 (C-4), 130.3 (C-3') 134.8 (C-4'), 148.6 (C-1), 149.9 (C-1'), 153.7 (C-2), 164.9 (ArC=O), 175.0 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3375 (w), 2923 (m), 2854 (m), 1728 (s), 1599 (w), 1509 (m), 1453 (w), 1429 (m), 1346 (w), 1273 (s), 1193 (vs), 1167 (s), 1132 (s), 1084 (m), 1053 (m), 1019 (w), 960 (m), 940 (w), 875 (w), 847 (w), 786 (w), 756 (m), 728 (w), 649 (w), 523 (w) cm^{-1}; MS (ESI): m/z = 638 [M + Na]$^+$, 616 [M + H]$^+$, 512, 490, 416, 349, 295; HRMS (ESI): calc for $C_{34}H_{49}NO_9Na^+$: 638.3300 [M + Na]$^+$, found 638.3315; anal. calc. for $C_{34}H_{49}NO_9$: C 66.32 H 8.02 N 2.27, found C 66.02 H 7.99 N 2.20; DSC: I 18°C [11.2 kJ/mol] Cr.

Benzo[15]crown-5 dodecyl *L*-tyrosinate (10b). From **8b** (850 mg, 1.14 mmol), TFA (1.31 mL, 1.95 g, 17.1 mmol), abs. CH_2Cl_2 (100 mL), yield: 390 mg, 0.61 mmol, 54%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.21-1.35 (m, 18H, CH_2), 1.52-1.70 (m, 4H, OCH$_2$CH_2, NH_2), 2.88 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5a'-H), 3.11 (dd, $J_{5b',6'}$ = 5.3 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.73 (dd, $J_{5b',6'}$ = 5.3 Hz, $J_{5a',6'}$ = 7.9 Hz, 1H, 6'-H), 3.76-3.81 (m, 8H, c-H, d-H), 3.91-3.97 (m, 4H, b-H), 4.11 (t, J = 6.8 Hz, 2H, OCH_2), 4.19-4.24 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.26 (m$_c$, 2H, 3'-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.83 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.6, 29.2, 29.3, 29.5, 29.58, 29.63, 31.9 (*C*H_2), 40.6 (C-5'), 55.8 (C-6'), 65.2 (O*C*H_2), 68.6, 69.0 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.8 (C-4), 130.3 (C-3') 134.8 (C-4'), 148.6 (C-1), 149.9 (C-1'), 153.7 (C-2), 164.9 (Ar*C*=O), 175.0 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2853 (m), 1729 (s), 1599 (m), 1510 (m), 1453 (w), 1429 (m), 1346 (w), 1274 (s), 1194 (vs), 1167 (m), 1134 (s), 1085 (m), 1019 (w), 982 (m), 960 (w), 876 (w), 847 (w), 787 (w), 756 (m), 726 (w), 649 (w), 517 (w), 426 (w) cm^{-1}; MS (ESI): *m/z* = 666 $[M + Na]^+$, 644 $[M + H]^+$, 547, 503, 459, 415, 385, 334; HRMS (ESI): calc. for $C_{36}H_{53}NO_9Na^+$: 666.3613 $[M + Na]^+$, found 666.3625; anal. calc. for $C_{36}H_{53}NO_9$: C 67.16 H 8.30 N 2.18, found C 66.86 H 8.18 N 2.09; DSC: Cr 40°C [-42.9 kJ/mol] I.

Benzo[15]crown-5 tetradecyl *L*-tyrosinate (10c). From **8c** (1.60 g, 2.07 mmol), TFA (2.38 mL, 3.54 g, 31.05 mmol) abs. CH_2Cl_2 (100 mL), yield: 1.34 g, 1.99 mmol, 96%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.20-1.37 (m, 22H, CH_2), 1.46-1.69 (m, 4H, OCH$_2$CH_2, NH_2), 2.88 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5a'-H), 3.11 (dd, $J_{5b',6'}$ = 5.3 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.73 (dd, $J_{5b',6'}$ = 5.3 Hz, $J_{5a',6'}$ = 7.9 Hz, 1H, 6'-H), 3.76-3.82 (m, 8H, c-H, d-H), 3.90-3.98 (m, 4H, b-H), 4.11 (t, J = 6.8 Hz, 2H, OCH_2), 4.18-4.25 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.26 (m_c, 2H, 3'-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.82 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.6, 29.2, 29.4, 29.5, 29.6, 29.66, 29.68, 31.9 (*C*H_2), 40.6 (C-5'), 55.8 (C-6'), 65.2 (O*C*H_2), 68.6, 69.0 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.3 (C-3') 134.9 (C-4'), 148.6 (C-1), 149.9 (C-1'), 153.7 (C-2), 164.9 (Ar*C*=O), 175.0 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2853 (m), 1729 (s), 1599 (w), 1510 (m), 1453 (w), 1428 (m), 1346 (w), 1273 (s), 1192 (vs), 1166 (s), 1132 (s), 1084 (m), 1053 (m), 1019 (w), 982 (m), 960 (w), 876 (w), 847 (w), 786 (w), 756 (m), 726 (w), 649 (w), 518 (w) cm^{-1}; MS (ESI): *m/z* = 694 $[M + Na]^+$, 672 $[M + H]^+$; HRMS (ESI): calc. for $C_{38}H_{57}NO_9Na^+$: 694.3926 $[M + Na]^+$, found 694.3946; anal. calc. for $C_{38}H_{57}NO_9$: C 67.93 H 8.55 N 2.08, found C 67.91 H 8.48 N 2.01; DSC: Cr 45°C [-56.4 kJ/mol] I.

Benzo[15]crown-5 hexadecyl-*L*-tyrosinate (10d). From **8d** (800 mg, 1.00 mmol), TFA (1.49 mL, 1.71 g, 15.0 mmol) abs. CH_2Cl_2 (75 mL), yield: 605 mg, 0.86 mmol, 86%. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.20-1.34 (m, 26H, CH_2), 1.52-1.70 (m, 4H, OCH$_2$CH_2, NH_2), 2.88 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5a'-H), 3.11 (dd, $J_{5b',6'}$ = 5.3 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.73 (m_c, 1H, 6'-H), 3.76-3.80 (m, 8H, c-H, d-H), 3.91-3.97 (m, 4H, b-H), 4.11 (t, J = 6.8 Hz, 2H, OCH_2), 4.19-4.24 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ =

8.4 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 2'-H), 7.26 (m_c, 2H, 3'-H), 7.65 (m_c, 1H, 6-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.6, 29.2, 29.4, 29.5, 29.6, 29.66, 29.69, 31.9 (*C*H_2), 40.6 (C-5'), 55.9 (C-6'), 65.2 (O*C*H_2), 68.6, 69.1 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.0 (C-5), 124.8 (C-4), 130.3 (C-3') 134.9 (C-4'), 148.6 (C-1), 149.9 (C-1'), 153.8 (C-2), 164.9 (Ar*C*=O), 175.0 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 1730 (s), 1599 (m), 1510 (m), 1454 (w), 1429 (m), 1346 (w), 1274 (s), 1195 (vs), 1167 (m), 1136 (s), 1085 (m), 1054 (m), 1019 (w), 981 (m), 960 (w), 940 (w), 875 (w), 849 (w), 786 (w), 756 (m), 725 (w), 650 (w), 520 (w) cm^{-1}; MS (ESI): *m/z* = 722 $[M + Na]^+$, 700 $[M + H]^+$, 580; HRMS (ESI): calc. for $C_{40}H_{61}NO_9Na^+$: 722.4239 $[M + Na]^+$, found 722.4241; anal. calc. for $C_{40}H_{61}NO_9$: C 68.64 H 8.78 N 2.00, found C 68.57 H 8.62 N 1.97; DSC: Cr 18°C [-26.2 kJ/mol] Cr_1 32°C [-28.5 kJ/mol] I.

Benzo[15]crown-5 octadecyl *L*-tyrosinate (10e). From **8e** (900 mg, 1.09 mmol), TFA (0.84 mL, 1.24 g, 10.9 mmol), abs. CH_2Cl_2 (50 mL), yield: 735 mg, 1.01 mmol, 93%. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.20-1.35 (m, 30H, C*H*$_2$), 1.53-1.66 (m, 4H, OCH_2C*H*$_2$, N*H*$_2$), 2.88 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5a'-H), 3.11 (dd, $J_{5b',6'}$ = 5.3 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.73 (m_c, 1H, 6'-H), 3.76-3.80 (m, 8H, c-H, d-H), 3.91-3.97 (m, 4H, b-H), 4.11 (t, *J* = 6.7 Hz, 2H, OC*H*$_2$), 4.19-4.24 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 2'-H), 7.26 (m_c, 2H, 3'-H), 7.65 (m_c, 1H, 6-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (*C*H_3), 22.7, 25.9, 28.6, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H_2), 40.6 (C-5'), 55.9 (C-6'), 65.2 (O*C*H_2), 68.6, 69.1 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.8 (C-2'), 122.1 (C-5), 124.8 (C-4), 130.3 (C-3') 134.9 (C-4'), 148.6 (C-1), 149.9 (C-1'), 153.8 (C-2), 164.9 (Ar*C*=O), 175.0 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2919 (vs), 2851 (s), 1730 (s), 1599 (w), 1510 (m), 1467 (w), 1429 (m), 1346 (w), 1275 (s), 1195 (vs), 1167 (m), 1136 (s), 1085 (m), 1019 (w), 960 (m), 756 (m), 726 (w), 650 (w), 519 (w) cm^{-1}; MS (ESI): *m/z* = 750 $[M + Na]^+$, 728 $[M + H]^+$; HRMS (ESI): calc. for $C_{42}H_{65}NO_9Na^+$: 750.4552 $[M + Na]^+$, found 750.4572; anal. calc. for $C_{42}H_{65}NO_9$: C 69.30 H 9.00 N 1.92, found C 69.03 H 9.12 N 2.02; DSC: Cr 30°C [-13.3 kJ/mol] Col_r 41°C [-3.6 kJ/mol] I.

General Procedure for the Synthesis of Z- and Fmoc-Protected Benzo[15]crown-5 Alkyl *L*-tyrosinates 12 and 13 (GP 4).[1,7] To a solution of the appropriate **10** (1.0 equiv.) and $KHCO_3$ (3.0 equiv.) in abs. CH_2Cl_2 (30 mL) under nitrogen atmosphere was added slowly at 0 °C benzyl chloroformate (Z-Cl) or 9-fluorenylmethyl chloroformate (Fmoc-Cl) (1.0 equiv.) and the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was then washed with H_2O (30 mL), dried ($MgSO_4$) and the solvent was removed under reduced pressure The residue was purified by flash chromatography on SiO_2 with CH_2Cl_2/MeOH (30:1) to give products **12** or **13** as colorless solids.

Benzo[15]crown-5 dodecyl-((benzyloxy)carbonyl)-*L*-tyrosinate (12b). From **10b** (50 mg, 78 µmol), Z-Cl (0.01 mL, 13 mg, 78 µmol), $KHCO_3$ (23 mg, 233 µmol), abs. CH_2Cl_2 (30 mL), yield: 60 mg, 78 µmol, quant. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, J = 6.9 Hz, 3H, CH_3), 1.19-1.34 (m, 18H, CH_2), 1.55-1.66 (m, 2H, OCH_2CH_2), 3.13 (m$_c$, 2H, 5'-H), 3.74-3.81 (m, 8H, c-H, d-H), 3.89-3.97 (m, 4H, b-H), 4.05-4.14 (m, 2H, OCH_2), 4.17-4.25 (m, 4H, a-H), 4.54-4.71 (m, 1H, 6'-H), 5.04-5.19 (m, 2H, 5''-H), 5.26 (br s, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.11 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 2'-H), 7.15 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 3'-H), 7.29-7.41 (m, 5H, 1''-H, 2''-H, 3''-H), 7.65 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.83 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.69, 29.63, 29.7, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.7 (C-5'), 54.8 (C-6'), 65.8 (O*C*H_2), 67.0 (C-5''), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.9 (C-2'), 122.0 (C-5), 124.7 (C-4), 128.1, 128.2, 128.3, 128.5, 128.6, 128.8, 128.9, 129.4 (C-1'', C-2'', C-3'') 130.3 (C-3') 133.3 (C-4'), 136.3 (C-4''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3326 (w), 2923 (m), 2853 (m), 2539 (w), 1777 (w), 1724 (s), 1599 (w), 1509 (s), 1454 (m), 1429 (m), 1395 (w), 1345 (m), 1272 (s), 1194 (vs), 1166 (s), 1132 (vs), 1052 (s), 1018 (m), 982 (m), 959 (m), 913 (m), 847 (w), 788 (w), 755 (m), 732 (m), 697 (m), 647 (w), 509 (w) cm^{-1}; MS (ESI): *m/z* = 800 [M + Na]$^+$, 778 [M + H]$^+$, 734; HRMS (ESI): calc. for $C_{44}H_{59}NO_{11}Na^+$: 800.3980 [M + Na]$^+$, found 800.3982; anal. calc. for $C_{44}H_{59}NO_{11}$: C 67.93 H 7.64 N 1.80, found C 67.82 H 7.43 N 1.65; DSC: I 33°C [34.2 kJ/mol] Cr 98°C [-46.8 kJ/mol] I.

Benzo[15]crown-5 tetradecyl ((benzyloxy)carbonyl)-*L*-tyrosinate (12c). From **10c** (70 mg, 104 µmol), Z-Cl (0.02 mL, 18 mg, 104 µmol), $KHCO_3$ (31 mg, 312 µmol), abs. CH_2Cl_2 (30 mL), yield: 80 mg, 99 µmol, 95%. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.19-1.34 (m, 22H, CH_2), 1.55-1.66 (m, 2H, OCH_2CH_2), 3.13 (m$_c$, 2H, 5'-H), 3.74-3.82 (m, 8H, c-H, d-H), 3.89-3.98 (m, 4H, b-H), 4.05-4.14 (m, 2H, OCH_2), 4.18-4.25 (m, 4H, a-H), 4.65 (m$_c$, 1H, 6'-H), 5.11 (m$_c$, 2H, 5''-H), 5.26 (m$_c$, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.4 Hz, 1H, 3-H), 7.11 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.15 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.28-7.39 (m, 5H, 1''-H, 2''-H, 3''-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.83 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.4 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.65, 29.69, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.7 (C-5'), 54.8 (C-6'), 65.8 (O*C*H_2), 67.0 (C-5''), 68.7, 69.1 (C-a), 69.3, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 115.0 (C-6), 121.9

(C-2'), 122.0 (C-5), 124.8 (C-4), 128.1, 128.2, 128.5 (C-1'', C-2'', C-3'') 130.3 (C-3') 133.3 (C-4'), 136.3 (C-4''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3324 (w), 2923 (m), 2853 (w), 1724 (s), 1599 (w), 1509 (m), 1454 (m), 1429 (w), 1345 (w), 1273 (s), 1193 (vs), 1167 (s), 1132 (s), 1052 (s), 1019 (m), 982 (w), 960 (m), 877 (w), 776 (w), 755 (m), 731 (w), 698 (w), 648 (w), 517 (w) cm^{-1}; MS (ESI): *m/z* = 828 $[M + Na]^+$, 580; HRMS (ESI): calc. for $C_{46}H_{63}NO_{11}Na^+$: 828.4293 $[M + Na]^+$, found: 828.4297; anal. calc. for $C_{46}H_{63}NO_{11}$: C 68.55 H 7.88 N 1.74, found C 68.34 H 8.03 N 1.75; DSC: I 35°C [33.0 kJ/mol] Cr_1 68°C [6.6 kJ/mol] Cr_2 105°C [-61.6 kJ/mol] I.

Benzo[15]crown-5 hexadecyl ((benzyloxy)carbonyl)-*L*-tyrosinate (12d). From **10d** (70 mg, 100 µmol), Z-Cl (0.02 mL, 17 mg, 100 µmol), $KHCO_3$ (30 mg, 300 µmol), abs. CH_2Cl_2 (30 mL), yield: 83 mg, 100 µmol, quant. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.19-1.35 (m, 26H, CH_2), 1.54-1.66 (m, 2H, OCH_2CH_2), 3.13 (m_c, 2H, 5'-H), 3.74-3.82 (m, 8H, c-H, d-H), 3.89-3.98 (m, 4H, b-H), 4.05-4.16 (m, 2H, OCH_2), 4.18-4.25 (m, 4H, a-H), 4.62-4.72 (m, 1H, 6'-H), 5.11 (m_c, 2H, 5''-H), 5.26 (m_c, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.11 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.15 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.28-7.39 (m, 5H, 1''-H, 2''-H, 3''-H), 7.65 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.83 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 14.1 (CH_3), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (CH_2, $OC(CH_3)_3$), 37.7 (C-5'), 54.8 (C-6'), 65.8 (OCH_2), 67.0 (C-5''), 68.6, 69.0 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.9 (C-6), 121.9 (C-2'), 122.0 (C-5), 124.8 (C-4), 128.1, 128.2, 128.5 (C-1'', C-2'', C-3'') 130.3 (C-3') 133.3 (C-4'), 136.2 (C-4''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3323 (w), 2923 (m), 2853 (m), 1727 (s), 1599 (w), 1510 (m), 1454 (w), 1429 (w), 1346 (w), 1274 (s), 1196 (vs), 1167 (m), 1136 (s), 1055 (m), 1019 (w), 982 (w), 960 (w), 877 (w), 777 (w), 756 (m), 698 (w), 648 (w), 517 (w) cm^{-1}; MS (ESI): *m/z* = 856 $[M + Na]^+$; HRMS (ESI): calc. for $C_{48}H_{67}NO_{11}Na^+$: 856.4606 $[M + Na]^+$, found 856.4597; anal. calc. for $C_{48}H_{67}NO_{11}$: C 69.12 H 8.10 N 1.68, found C 69.21 H 7.88 N 1.65; DSC: I 31°C [29.9 kJ/mol] Cr_1 52°C [14.6 kJ/mol] Cr_2 106°C [-60.6 kJ/mol] I.

Benzo[15]crown-5 octadecyl ((benzyloxy)carbonyl)-*L*-tyrosinate (12e). From **10e** (70 mg, 96 µmol), Z-Cl (0.01 mL, 16 mg, 96 µmol), $KHCO_3$ (29 mg, 289 µmol), abs. CH_2Cl_2 (30 mL), yield: 75 mg, 87 µmol, 90%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.19-1.35 (m, 30H, CH_2), 1.54-1.67 (m, 2H, OCH_2CH_2), 3.13 (m_c, 2H, 5'-H), 3.74-3.83 (m, 8H, c-H, d-H), 3.89-3.98 (m, 4H, b-H), 4.05-4.17 (m, 2H, OCH_2), 4.18-4.26 (m, 4H, a-H), 4.61-4.71 (m, 1H, 6'-H), 5.11 (m_c, 2H, 5''-H), 5.26 (m_c, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.11 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.15 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.28-7.39 (m, 5H, 1''-H, 2''-H, 3''-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.83 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.7 (C-5'), 54.8 (C-6'), 65.8 (O*C*H_2), 67.0 (C-5''), 68.6, 69.0 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.9 (C-6), 121.9 (C-2'), 122.0 (C-5), 124.8 (C-4), 128.1, 128.2, 128.5 (C-1'', C-2'', C-3'') 130.3 (C-3') 133.3 (C-4'), 136.2 (C-4''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3334 (w), 2923 (s), 2853 (m), 1727 (s), 1599 (w), 1510 (m), 1454 (m), 1429 (m), 1395 (w), 1345 (m), 1274 (s), 1196 (vs), 1167 (m), 1136 (s), 1055 (m), 1019 (m), 982 (w), 960 (m), 878 (w), 777 (w), 756 (m), 698 (w), 649 (w), 515 (w) cm^{-1}; MS (ESI): *m/z* = 885 $[M + Na]^+$; HRMS (ESI): calc. for $C_{50}H_{71}NO_{11}Na^+$: 884.4919 $[M + Na]^+$, found 884.4906; anal. calc. for $C_{50}H_{71}NO_{11}$: C 69.66 H 8.30 N 1.62, found C 69.62 H 8.20 N 1.53; DSC: I 33°C [36.2 kJ/mol] Cr_1 52°C [18.9 kJ/mol] Cr_2 106°C [-64.3 kJ/mol] I.

Benzo[15]crown-5 dodecyl [(9*H*-fluoren-9-ylmethoxy)carbonyl]-*L*-tyrosinate (13b). From **10b** (70 mg, 109 µmol), Fmoc-Cl (28 mg, 109 µmol), $KHCO_3$ (33 mg, 327 µmol), abs. CH_2Cl_2 (30 mL), yield: 94 mg, 109 µmol, quant. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, *J* = 6.9 Hz, 3H, C*H_3*), 1.19-1.35 (m, 18H, C*H_2*), 1.55-1.66 (m, 2H, OCH_2C*H_2*), 3.06-3.19 (m, 2H, 5'-H), 3.74-3.81 (m, 8H, c-H, d-H), 3.90-3.97 (m, 4H, b-H), 4.07-4.16 (m, 2H, OC*H_2*), 4.18-4.26 (m, 5H, a-H, 7''-H), 4.34-4.40 (m, 1H, 8''-H), 4.41-4.48 (m, 1H, 8''-H), 4.64-4.71 (m, 1H, 6'-H), 5.27-5.33 (m, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.08-7.20 (m, 4H, 2'-H, 3'-H), 7.29-7.35 (m, 2H, 4''-H), 7.37-7.44 (m, 2H, 3''-H), 7.55-7.62 (m, 2H, 5''-H), 7.65 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.77 (m_c, 2H, 2''-H), 7.82 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 14.1 (*C*H_3), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H_2, OC(*C*H_3)$_3$), 37.7 (C-5'), 47.2 (C-7''), 54.8 (C-6'), 65.9 (O*C*H_2), 67.0 (C-8''), 68.6, 69.0 (C-a), 69.2, 69.3 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.8 (C-6), 120.0 (C-2''), 121.9 (C-2'), 122.0 (C-5), 124.7 (C-4), 125.07, 125.14 (C-5''), 127.1 (C-4''), 127.7 (C-3'') 130.4 (C-3') 133.3 (C-4'), 141.3 (C-6''), 143.7, 143.9 (C-1''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.4 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3332 (w), 2923 (w), 2853 (w), 1723 (m), 1599 (w), 1509 (m), 1450 (w), 1429 (w), 1396 (w), 1345 (w), 1273 (s), 1193 (vs), 1166 (m), 1132 (s), 1052 (m), 1019 (m), 982 (w), 959 (w), 910 (m), 825 (w), 757 (m), 730 (s), 647 (w), 621 (w), 538 (w) cm^{-1}; MS (ESI): *m/z* = 888 $[M + Na]^+$, 456; HRMS (ESI): calc. for $C_{51}H_{63}NO_{11}Na^+$: 888.4293 $[M + Na]^+$, found 888.4313; anal. calc. for $C_{51}H_{63}NO_{11}$: C 70.73 H 7.33 N 1.62, found C 70.28 H 7.56 N 1.65; DSC: Cr 69°C [-31.1 kJ/mol] I.

Benzo[15]crown-5 tetradecyl-[(9*H*-fluoren-9-ylmethoxy)carbonyl]-*L*-tyrosinate (13c). From **10c** (70 mg, 104 µmol), Fmoc-Cl (27 mg, 104 µmol), $KHCO_3$ (31 mg, 312 µmol), abs. CH_2Cl_2 (30 mL), yield: 93 mg, 104 µmol, quant. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.87 (t, *J* = 6.8 Hz, 3H, CH_3), 1.19-1.36 (m, 22H, CH_2), 1.54-1.67 (m, 2H, OCH$_2$CH_2), 3.06-3.20 (m, 2H, 5'-H), 3.73-3.82 (m, 8H, c-H, d-H), 3.90-3.98 (m, 4H, b-H), 4.05-4.17 (m, 2H, OCH_2), 4.17-4.26 (m, 5H, a-H, 7''-H), 4.28-4.40 (m, 1H, 8''-H), 4.41-4.50 (m, 1H, 8''-H), 4.63-4.71 (m, 1H, 6'-H), 5.27-5.34 (m, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.07-7.20 (m, 4H, 2'-H, 3'-H), 7.29-7.36 (m, 2H, 4''-H), 7.36-7.47 (m, 2H, 3''-H), 7.55-7.62 (m, 2H, 5''-H), 7.62-7.67 (m, 1H, 6-H), 7.74-7.79 (m, 2H, 2''-H), 7.82 (m_c, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.65, 29.68, 29.69, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.7 (C-5'), 47.2 (C-7''), 54.8 (C-6'), 65.9 (O*C*H$_2$), 67.0 (C-8''), 68.6, 69.0 (C-a), 69.2, 69.3 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.8 (C-6), 120.0, 120.3 (C-2''), 121.9 (C-2'), 122.0 (C-5), 124.8 (C-4), 125.07, 125.14 (C-5''), 127.1, 127.4 (C-4''), 127.7, 128.2 (C-3'') 130.4 (C-3') 133.3 (C-4'), 141.3, 142.4 (C-6''), 143.7, 143.9 (C-1''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.4 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3327 (w), 2922 (m), 2853 (m), 1724 (s), 1599 (w), 1509 (m), 1450 (m), 1429 (w), 1396 (w), 1345 (w), 1273 (s), 1193 (vs), 1166 (m), 1052 (m), 1019 (w), 982 (w), 960 (w), 876 (w), 825 (w), 782 (w), 757 (m), 740 (s), 687 (w), 648 (w), 621 (w), 589 (w), 539 (w) cm^{-1}; MS (ESI): *m/z* = 916 $[M + Na]^+$, 790; HRMS (ESI): calc. for $C_{53}H_{67}NO_{11}Na^+$: 916.4606 $[M + Na]^+$, found 916.4605; anal. calc. for $C_{53}H_{67}NO_{11}$: C 71.20 H 7.55 N 1.57, found C 71.04 H 7.25 N 1.34; DSC: Cr 61°C [-35.7 kJ/mol] I.

Benzo[15]crown-5 hexadecyl-[(9*H*-fluoren-9-ylmethoxy)carbonyl]-*L*-tyrosinate (13d). From **10d** (70 mg, 100 µmol), Fmoc-Cl (26 mg, 100 µmol), $KHCO_3$ (30 mg, 300 µmol), abs. CH_2Cl_2 (30 mL), yield: 92 mg, 100 µmol, quant. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.18-1.36 (m, 26H, CH_2), 1.54-1.66 (m, 2H, OCH$_2$CH_2), 3.07-3.20 (m, 2H, 5'-H), 3.73-3.83 (m, 8H, c-H, d-H), 3.90-3.98 (m, 4H, b-H), 4.05-4.17 (m, 2H, OCH_2), 4.18-4.26 (m, 5H, a-H, 7''-H), 4.33-4.40 (m, 1H, 8''-H), 4.41-4.48 (m, 1H, 8''-H), 4.63-4.71 (m, 1H, 6'-H), 5.27-5.34 (m, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.08-7.20 (m, 4H, 2'-H, 3'-H), 7.29-7.36 (m, 2H, 4''-H), 7.37-7.43 (m, 2H, 3''-H), 7.55-7.61 (m, 2H, 5''-H), 7.65 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.77 (m_c, 2H, 2''-H), 7.82 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.7 (C-5'), 47.2 (C-7''), 54.8 (C-6'), 65.9 (O*C*H$_2$), 67.0 (C-8''), 68.6, 69.0 (C-a), 69.2, 69.3 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.8 (C-6), 120.0 (C-2''), 121.9 (C-2'), 122.0 (C-5), 124.7 (C-4), 125.07, 125.14 (C-5''), 127.1 (C-4''), 127.7 (C-

3'') 130.4 (C-3') 133.3 (C-4'), 141.3 (C-6''), 143.7, 143.9 (C-1''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.4 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3324 (w), 2922 (m), 2852 (m), 1725 (s), 1599 (w), 1510 (m), 1450 (w), 1429 (w), 1395 (w), 1345 (w), 1273 (s), 1193 (vs), 1167 (m), 1133 (s), 1105 (m), 1052 (m), 1019 (w), 982 (w), 960 (w), 875 (w), 757 (m), 740 (m), 648 (w), 621 (w), 537 (w) cm^{-1}; MS (ESI): *m/z* = 944 $[M + Na]^+$, 851; HRMS (ESI): calc. for $C_{55}H_{71}NO_{11}Na^+$: 944.4919 $[M + Na]^+$, found 944.4947; anal. calc. for $C_{55}H_{71}NO_{11}$: C 71.64 H 7.76 N 1.52, found C 71.36 H 7.72 N 1.46; DSC: Cr_1 89°C [-2.9 kJ/mol] Cr_2 96°C [-1.9 kJ/mol] I.

Benzo[15]crown-5 octadecyl-[(9*H*-fluoren-9-ylmethoxy)carbonyl]-*L*-tyrosinate (13e). From **10e** (70 mg, 96 µmol), Fmoc-Cl (25 mg, 96 µmol), $KHCO_3$ (29 mg, 389 µmol), abs. CH_2Cl_2 (30 mL), yield: 91 mg, 96 µmol, quant. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.17-1.36 (m, 30H, C*H*$_2$), 1.54-1.67 (m, 2H, OCH$_2$C*H*$_2$), 3.07-3.20 (m, 2H, 5'-H), 3.72-3.83 (m, 8H, c-H, d-H), 3.90-3.98 (m, 4H, b-H), 4.04-4.17 (m, 2H, OC*H*$_2$), 4.18-4.26 (m, 5H, a-H, 7''-H), 4.30-4.40 (m, 1H, 8''-H), 4.41-4.49 (m, 1H, 8''-H), 4.63-4.72 (m, 1H, 6'-H), 5.27-5.34 (m, 1H, N*H*), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.08-7.19 (m, 4H, 2'-H, 3'-H), 7.29-7.36 (m, 2H, 4''-H), 7.37-7.45 (m, 2H, 3''-H), 7.55-7.61 (m, 2H, 5''-H), 7.65 (d, $J_{4,6}$ = 1.8 Hz, 1H, 6-H), 7.77 (m_c, 2H, 2''-H), 7.82 (dd, $J_{4,6}$ = 1.8 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.7 (C-5'), 47.2 (C-7''), 54.8 (C-6'), 65.9 (O*C*H$_2$), 67.0 (C-8''), 68.6, 69.0 (C-a), 69.2, 69.3 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.0 (C-3), 114.8 (C-6), 120.0, 120.3 (C-2''), 121.9 (C-2'), 122.0 (C-5), 124.7 (C-4), 125.07, 125.14 (C-5''), 127.1 (C-4''), 127.4, 127.7 (C-3'') 130.4 (C-3') 133.3 (C-4'), 141.3 (C-6''), 143.7, 143.9 (C-1''), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.6 (HN*C*=O), 164.8 (Ar*C*=O), 171.4 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3329 (w), 2922 (m), 2852 (m), 1725 (s), 1599 (w), 1510 (m), 1450 (w), 1429 (w), 1396 (w), 1345 (w), 1273 (s), 1249 (m), 1194 (vs), 1167 (m), 1134 (s), 1105 (m), 1053 (m), 1019 (w), 982 (w), 960 (w), 875 (w), 825 (w), 757 (m), 740 (m), 648 (w), 621 (w), 538 (w) cm^{-1}; MS (ESI): *m/z* = 973 $[M + Na]^+$, 851; HRMS (ESI): calc. for $C_{57}H_{75}NO_{11}Na^+$: 972.5232 $[M + Na]^+$, found 972.5255; anal. calc. for $C_{57}H_{75}NO_{11}$: C 72.05 H 7.96 N 1.47, found C 71.96 H 7.80 N 1.45; DSC: Cr 65°C [-54.1 kJ/mol] I.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-dodecyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium chloride (11b)Cl. According to ref.,[8] to a solution of **10b** (200 mg, 311 µmol) and $KHCO_3$ (311 mg, 3.11 mmol) in abs. CH_2Cl_2 (30 mL) under nitrogen atmosphere was added dropwise chloroformamidinium chloride[8-10](1.78 mL, 783 µmol, 0.44 M in CH_2Cl_2). The reation mixture was stirred at room temperature until complete conversion. After addition of H_2O (56 mL, 3.11 mmol), the mixture was stirred for a further 15 min. The solvent was removed under reduced pressure and the residue was dissolved in Et_2O (30 mL). Then HCl·Et_2O was added (pH = 1) and the mixture stirred for 15 min. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on SiO_2, which was stirred in 6 M HCl for 30 min, then filtered, washed with H_2O and acetone and finally dried under vacuum prior to use. The column was flushed with pure EtOAc followed by CH_2Cl_2/MeOH (20:1) to give (**11b**)**Cl** (190 mg, 244 µmol, 79 %) as a colorless solid. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.20-1.34 (m, 18H, CH_2), 1.57-1.68 (m, 2H, OCH_2CH_2), 2.38-3.58 (m, 13H, N(CH_3)$_2$, 5b'-H), 3.75-3.81 (m, 8H, c-H, d-H), 3.84-3.97 (m, 5H, 5a'-H, b-H), 4.06-4.14 (m, 3H, OCH_2, 6'-H), 4.18-4.24 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.12 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 2'-H), 7.61 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 3'-H), 7.63 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.81 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 10.23 (br s, 1H, NH) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.8, 28.4, 29.2, 29.3, 29.5, 29.58, 29.62, 31.9 (CH_2), 36.0 (C-5'), 39.6 (N(CH_3)$_2$), 60.6 (C-6'), 66.5 (OCH_2), 68.6, 69.1 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.1 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 122.0 (C-2', C-5), 124.7 (C-4), 130.9 (C-3') 134.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 162.3 (CN(CH_3)$_2$) 165.0 (ArC=O), 170.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3389 (w), 2922 (m), 2853 (m), 1729 (m), 1622 (m), 1599 (m), 1571 (m), 1511 (m), 1454 (w), 1429 (m), 1404 (w), 1346 (w), 1274 (s), 1195 (vs), 1168 (m), 1134 (s), 1068 (m), 981 (w), 960 (w), 912 (w), 787 (w), 757 (w), 756 (w), 727 (w), 649 (w), 546 (w) cm^{-1}; MS (ESI): m/z = 742 [M]$^+$, 501, 448; HRMS (ESI): calc. for $C_{41}H_{64}N_3O_9^+$: 742.4637 [M]$^+$, found 742.4633; anal. calc. for $C_{41}H_{64}ClN_3O_9$: C 63.26 H 8.29 N 5.40, found C 63.05 H 8.59 N 5.47; POM: Cr 44°C I.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-hexadecyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium chloride (11d)Cl. As described above for (**11b**)**Cl**, however, K_2CO_3 as a base; from **10d** (240 mg, 0.34 mmol), chloroformamidinium chloride (1.56 mL, 0.68 mmol, 0.44 M in CH_2Cl_2), K_2CO_3 (474 mg, 3.43 mmol), abs. CH_2Cl_2 (50 mL), yield: 80 mg, 96 µmol, 28%, colorless solid. ^{1}H-NMR ($CDCl_3$, 700 MHz) δ = 0.88 (m$_c$, 3H, CH_3), 1.21-1.36 (m, 26H, CH_2), 1.55-1.65 (m, 2H, OCH_2CH_2), 2.41-3.46 (m, 13H, N(CH_3)$_2$, 5b'-H), 3.64 (m$_c$, 1H, 6'-H), 3.75-3.81 (m, 8H, c-H, d-H), 3.81-3.88 (m, 1H, 5a'-H), 3.90-3.98 (m, 4H, b-H), 4.08-4.16 (m, 2H, OCH_2), 4.18-4.26 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.3 Hz, 1H, 3-H), 7.12 (m$_c$, 2H, 2'-H), 7.55-7.65 (m, 3H, 3'-H, 6-H), 7.81 (m$_c$, 1H, 4-H), 9.92 (br s, 1H, NH) ppm; ^{13}C-NMR ($CDCl_3$, 175 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.7, 25.8, 28.4, 29.2, 29.35, 29.43, 29.5, 29.59, 29.61, 29.64, 29.7, 31.9 (CH_2), 36.1 (C-5'), 39.8 (N(CH_3)$_2$), 60.6 (C-6'), 66.5 (OCH_2), 68.5, 69.0 (C-a), 69.2, 69.3 (C-b), 70.2, 70.3, 71.1 (C-c, C-d), 112.0 (C-3), 114.8 (C-6), 121.9 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.9 (C-3') 134.5 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 162.2 ($CN(CH_3)_2$) 165.0 (Ar*C*=O), 170.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2853 (m), 1729 (m), 1621 (m), 1600 (m), 1569 (m), 1510 (m), 1454 (w), 1429 (m), 1404 (w), 1346 (w), 1274 (s), 1195 (vs), 1167 (m), 1134 (s), 1065 (m), 960 (m), 910 (m), 788 (w), 756 (w), 727 (vs), 644 (w), 543 (w) cm^{-1}; MS (ESI): *m/z* = 799 $[M]^+$, 666, 588, 504, 411; HRMS (ESI): calc. for $C_{45}H_{72}N_3O_9^+$: 798.5263 $[M]^+$, found 798.5245; anal. calc. for $C_{45}H_{72}ClN_3O_9$: C 64.77 H 8.70 N 5.04, found C 61.72 H 8.92 N 4.95; DSC: Cr 42°C [-9.8 kJ/mol] I.

General Procedure for the Synthesis of (11)Cl Using NEt_3 as a Base. Chloroformamidinium chloride (900 µmol, 0.44 M in CH_2Cl_2) was added dropwise to a solution of the appropriate **10** (450 µmol) and NEt_3 (4.50 mmol) in abs. CH_2Cl_2 (30 mL). The reaction mixture was refluxed for 1 h and then washed with H_2O (2 × 30 mL). The residue was dissolved in Et_2O (30 mL), $HCl·Et_2O$ was added (pH = 1) and the mixture stirred for 15 min. The solvent was removed under reduced pressure to give products (**11)Cl** as colorless solids.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-decyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium chloride (11a)Cl. From **10a** (150 mg, 244 µmol), chloroformamidinium chloride (1.11 mL, 487 µmol, 0.44 M in CH_2Cl_2), NEt_3 (0.34 mL, 247 mg, 2.44 mmol), abs. CH_2Cl_2 (30 mL), yield: 130 mg, 173 µmol, 71%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 0.87 (t, *J* = 6.7 Hz, 3H, CH_3), 1.19-1.36 (m, 14H, CH_2), 1.56-1.69 (m, 2H, OCH_2CH_2), 2.49-3.35 (m, 12H, $N(CH_3)_2$), 3.40 (dd, $J_{5b',6'}$ = 4.7 Hz, $J_{5a',5b'}$ = 14.0 Hz, 1H, 5b'-H), 3.73-3.82 (m, 8H, c-H, d-H), 3.82-3.90 (m, 1H, 5a'-H), 3.90-3.98 (m, 4H, b-H), 4.11 (m_c, 3H, OCH_2, 6'-H), 4.18-4.25 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.12 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.60 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.63 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 10.19 (br s, 1H, N*H*) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.8, 28.4, 29.2, 29.3, 29.49, 29.52, 31.9 (CH_2), 36.0 (C-5'), 39.6 ($N(CH_3)_2$), 60.6 (C-6'), 66.5 (OCH_2), 68.6, 69.1 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 122.0 (C-2', C-5), 124.7 (C-4), 130.9 (C-3') 134.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 162.3 ($CN(CH_3)_2$) 164.9 (Ar*C*=O), 170.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3391 (w), 2923 (m), 2854 (m), 1729 (m), 1625 (m), 1599 (m), 1572 (m), 1511 (m), 1454 (w), 1429 (m), 1405 (w), 1347 (w), 1274 (s), 1196 (vs), 1168 (m), 1135 (s), 1067 (m), 960 (w), 912 (w), 785 (w), 757 (w), 756 (w), 727 (w), 649 (w), 548 (w) cm^{-1}; MS (ESI): *m/z* = 714 $[M]^+$, 551, 425, 396, 369; HRMS (ESI): calc. for $C_{39}H_{60}N_3O_9^+$: 714.4324

[M]$^+$, found 714.4318; anal. calc. for $C_{39}H_{60}ClN_3O_9$: C 62.43 H 8.06 N 5.60, found C 59.73 H 8.18 N 5.21; POM: Cr 42°C I.

(*S*)-*N*-(Bis(dimethylamino)methylen)-1-tetradecyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium chloride (11c)Cl. From **10c** (300 mg, 0.45 mmol), chloroformamidinium chloride (2.05 mL, 0.90 mmol, 0.44 M in CH_2Cl_2), NEt_3 (0.62 mL, 455 mg, 4.50 mmol), abs. CH_2Cl_2 (30 mL), yield: 295 mg, 0.37 mmol, 82%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.19-1.37 (m, 22H, CH_2), 1.56-1.69 (m, 2H, OCH_2CH_2), 2.50-3.45 (m, 13H, N(CH_3)$_2$, 5b'-H), 3.71-3.81 (m, 8H, c-H, d-H), 3.81-3.89 (m, 1H, 5a'-H), 3.89-3.98 (m, 4H, b-H), 4.11 (m_c, 3H, OCH_2, 6'-H), 4.17-4.26 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.12 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.60 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.63 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 10.24 (br s, 1H, N*H*) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.8, 28.4, 29.2, 29.3, 29.5, 29.58, 29.64, 29.7, 31.9 (CH_2), 36.0 (C-5'), 39.6 (N(CH_3)$_2$), 60.6 (C-6'), 66.5 (OCH_2), 68.6, 69.1 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.2 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.9 (C-2', C-5), 124.7 (C-4), 130.9 (C-3') 134.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 162.3 (*C*N(CH_3)$_2$) 164.9 (Ar*C*=O), 170.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3390 (w), 2923 (s), 2853 (m), 1731 (s), 1625 (m), 1599 (m), 1572 (m), 1511 (m), 1455 (w), 1429 (m), 1405 (w), 1347 (w), 1275 (s), 1197 (vs), 1168 (m), 1136 (s), 1068 (m), 960 (w), 757 (w), 727 (w), 649 (w) cm^{-1}; MS (ESI): *m/z* = 770 [M]$^+$, 425, 397, 369; HRMS (ESI): calc. for $C_{43}H_{68}N_3O_9^+$: 770.4950 [M]$^+$, found 770.4936; anal. calc. for $C_{43}H_{68}ClN_3O_9$: C 64.04 H 8.50 N 5.21, found C 61.63 H 8.34 N 4.84; DSC: Cr 34°C [-5.7 kJ/mol] I.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-octadecyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium chloride (11e)Cl. From **10e** (100 mg, 137 µmol), chloroformamidinium chloride **35** (0.62 mL, 274 µmol, 0.44 M in CH_2Cl_2), NEt_3 (0.20 mL, 139 mg, 1.37 mmol), abs. CH_2Cl_2 (30 mL), yield: 109 mg, 126 µmol, 92%. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.18-1.34 (m, 30H, CH_2), 1.57-1.67 (m, 2H, OCH_2CH_2), 2.42-3.36 (m, 12H, N(CH_3)$_2$), 3.40 (dd, $J_{5b'-6'}$ = 4.5 Hz, $J_{5a',5b'}$ = 14.1 Hz, 1H, 5b'-H), 3.73-3.81 (m, 8H, c-H, d-H), 3.86 (dd, $J_{5a',6'}$ = 9.4 Hz, $J_{5a',5b'}$ = 14.1 Hz, 1H, 5a'-H), 3.90-3.97 (m, 4H, b-H), 4.11 (m_c, 3H, OCH_2, 6'-H), 4.18-4.24 (m, 4H, a-H), 6.91 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.12 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 2'-H), 7.60 (d, $J_{2',3'}$ = 8.3 Hz, 2H, 3'-H), 7.63 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 10.05-10.12 (m, 1H, N*H*) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.9, 28.4, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (CH_2), 36.0 (C-5'), 39.6 (N(CH_3)$_2$), 60.6 (C-6'), 66.5 (OCH_2), 68.6, 69.1 (C-a), 69.2, 69.4 (C-b), 70.3, 70.4, 71.1 (C-c, C-d), 112.1 (C-3), 114.9 (C-6), 121.9 (C-2'), 122.0 (C-5), 124.7 (C-4), 130.9 (C-3') 134.6 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 162.2 ($CN(CH_3)_2$) 165.0 (Ar*C*=O), 170.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3394 (w), 2922 (s), 2852 (s), 1730 (s), 1624 (m), 1599 (m), 1571 (m), 1511 (m), 1466 (w), 1429 (m), 1405 (w), 1347 (w), 1274 (s), 1196 (vs), 1168 (m), 1136 (s), 1067 (m), 960 (w), 788 (w), 757 (w), 724 (w), 649 (w), 542 (w) cm^{-1}; MS (ESI): *m/z* = 826 $[M]^+$, 425; HRMS (ESI): calc. for $C_{47}H_{76}N_3O_9^+$: 826.5621 $[M]^+$, found 826.5617; anal. calc. for $C_{47}H_{76}ClN_3O_9$: C 65.44 H 8.88 N 4.87, found C 63.79 H 8.64 N 4.59; DSC: Cr 34°C [-10.4 kJ/mol] I.

Table S1. Optimization experiments for the synthesis of guanidinium salts **11**.

11	R	Base	Equiv.	Temperature	Time	Yield
(11b)Cl	$C_{12}H_{25}$	$KHCO_3$	10	r.t.	24 h	79%
(11e)Cl	$C_{18}H_{37}$	$KHCO_3$	10	r.t.	3 d	-
(11d)Cl	$C_{16}H_{33}$	$KHCO_3$	10	r.t.	5 d	-
(11d)Cl	$C_{16}H_{33}$	$KHCO_3$	10	reflux	16 h	-
(11c)Cl	$C_{14}H_{29}$	$KHCO_3$	10	reflux	2 d	-
(11e)Cl	$C_{18}H_{37}$	$KHCO_3$ / K_2CO_3	10 / 10	reflux	24 h	65%
(11d)Cl	$C_{16}H_{33}$	K_2CO_3	20	reflux	2 d	28%
(11c)Cl	$C_{14}H_{29}$	K_2CO_3	20	microwave, 40°C	6 h	-
(11c)Cl	$C_{14}H_{29}$	$CsCO_3$	20	reflux	12 h	-
(11a)Cl	$C_{10}H_{21}$	Net_3	10	reflux	2 h	71%
(11c)Cl	$C_{14}H_{29}$	Net_3	10	reflux	2 h	82%
(11e)Cl	$C_{18}H_{37}$	Net_3	10	reflux	2 h	92%

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-dodecyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium iodide (11b)I. According to ref.,[8] a suspension of guanidinium chloride **(11b)Cl** (60 mg, 77 µmol) and caesium iodide (30 mg, 116µmol) in acetonitrile (10 mL) was heated at reflux for 5 min. Then the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (10 mL) and filtered through a syringe filter (0.20 µm). The filtrate was concentrated under reduced pressure to give (**11b**)**I** (67 mg, 77 µmol, quant.) as a yellow solid. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.17-1.38 (m, 18H, CH_2), 1.65 (m_c, 2H, OCH_2CH_2), 2.49-3.36 (m, 12H, $N(CH_3)_2$), 3.43 (dd, $J_{5b',6'}$ = 4.9 Hz, $J_{5a',5b'}$ = 14.2 Hz, 1H, 5b'-H) 3.69-3.88 (m, 9H, c-H, d-H, 5a'-H), 3.89-3.99 (m, 4H, b-H), 4.15 (t, *J* = 6.9 Hz, 2H, OCH_2), 4.18-4.30 (m, 5H, a-H, 6'-H), 6.92 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.56 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.61 (m_c, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 7.94 (m_c, 1H, N*H*) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.8, 28.4, 29.2, 29.3, 29.58, 29.62, 31.9 (CH_2), 36.3 (C-5'), 40.0 ($N(CH_3)_2$), 60.1 (C-6'), 66.7 (OCH_2), 68.5, 69.0 (C-a), 69.2, (C-b), 70.0, 70.2, 70.9 (C-c, C-d), 112.2 (C-3), 114.9 (C-6), 121.9 (C-2'), 122.2 (C-5), 124.8 (C-4), 130.8 (C-3') 133.7 (C-4'), 148.5 (C-1), 150.3 (C-1'), 153.7 (C-2), 161.7 (*C*N(CH_3)$_2$) 164.9 (Ar*C*=O), 170.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2854 (m), 1730 (s), 1621 (m), 1599 (m), 1568 (m), 1511 (m), 1454 (w), 1429 (m), 1403 (m), 1346 (w), 1274 (s), 1195 (vs), 1167 (m), 1134 (s), 1069 (m), 960 (w), 789 (w), 757 (w), 727 (w), 649 (w), 515 (w) cm^{-1}; MS (ESI): *m/z* = 764 $[M + Na]^+$, 742 $[M]^+$, 551, 383, 299, 127 $[I]^-$; HRMS (ESI): calc. for $C_{41}H_{64}N_3O_9]^+$: 742.4637 $[M]^+$, found 742.4643; anal. calc. for $C_{41}H_{64}IN_3O_9$: C 56.61 H 7.42 N 4.83, found C 55.21 H 7.30 N 4.41; POM: Cr 70°C I.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-octadecyloxy-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium iodide (11e)I. As described above for (**11b**)**I**, from **(11e)Cl** (70 mg, 81 µmol) and caesium iodide (32 mg, 122 µmol), yield: 77 mg, 81 µmol, quant., yellow solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.17-1.36 (m, 30H, CH_2), 1.65 (m_c, 2H, OCH_2CH_2), 2.53-3.38 (m, 12H, N(CH_3)$_2$), 3.43 (dd, $J_{5b',6'}$ = 4.9 Hz, $J_{5a',5b'}$ = 14.2 Hz, 1H, 5b'-H) 3.72-3.86 (m, 9H, c-H, d-H, 5a'-H), 3.89-3.98 (m, 4H, b-H), 4.15 (t, *J* = 6.9 Hz, 2H, OCH_2), 4.18-4.28 (m, 5H, a-H, 6'-H), 6.92 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.56 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.61 (m_c, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 7.93 (m_c, 1H, N*H*) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.8, 28.4, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (CH_2), 36.3 (C-5'), 40.1 (N(CH_3)$_2$), 60.0 (C-6'), 66.7 (OCH_2), 68.6, 69.1 (C-a), 69.1, 69.3 (C-b), 70.2, 70.3, 71.0 (C-c, C-d), 112.2 (C-3), 114.9 (C-6), 121.9 (C-2'), 122.2 (C-5), 124.8 (C-4), 130.8 (C-3') 133.7 (C-4'), 148.6 (C-1), 150.3 (C-1'), 153.8 (C-2), 161.7 (*C*N(CH_3)$_2$) 164.9 (Ar*C*=O), 170.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (m), 2852 (m), 1729 (m), 1621 (m), 1599 (m), 1568 (m), 1510 (m), 1455 (w), 1429 (m), 1403 (m), 1346 (w), 1273 (s), 1193 (vs), 1167 (m), 1132 (s), 1067 (m), 960 (m), 936 (w), 915 (w), 877 (w), 846 (w), 789 (w), 756 (m), 726 (w), 648 (w), 546 (w) cm^{-1}; MS (ESI): *m/z* = 826 $[M]^+$, 425, 127 $[I]^-$; HRMS (ESI): calc. for $C_{47}H_{76}N_3O_9^+$: 826.5576 $[M]^+$, found 826.5576; anal. calc. for $C_{47}H_{76}IN_3O_9$: C 59.17 H 8.03 N 4.40, found C 58.47 H 8.00 N 4.00; POM: Cr 55°C I.

General Procedure for the Complexation of Crown Ethers 8, 10 and 11 (GP 6).[11] To a solution of the respective **8** or **10** (1.0 equiv.) in CH_2Cl_2 (5 mL) was added a solution of sodium iodide (1.5 equiv.) in MeOH (5 mL), and the reaction mixture was stirred for 18 h at room temperature. Then the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (5 mL) and filtered through a syringe filter (0.20 µm). The filtrate was concentrated under reduced pressure to give the crown ether complexes [**NaI · 8a**,**d**,**e**], [**NaI · 10a**,**d**,**e**] or [**NaI · (11b**,**e)I**] as colorless solids in quantitative yield.

Benzo[15]crown-5 decyl-(*tert*-butoxycarbonyl)-*L*-tyrosinate sodium iodide complex [NaI·8a]. From **8a** (50 mg, 69.8 µmol) and NaI (16 mg, 105 µmol), yield: 60 mg, 69.8 µmol. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 0.87 (t, *J* = 6.7 Hz, 3H, CH_3), 1.21-1.36 (m, 14H, CH_2), 1.43 (s, 9H, OC(CH_3)$_3$), 1.55-1.68 (m, 2H, OCH$_2$CH_2), 3.01-3.21 (m, 2H, 5'-H), 3.74-3.84 (m, 4H, d-H), 3.88-3.97 (m. 4H, c-H), 4.06-4.19 (m, 6H, b-H, OCH_2), 4.31-4.42 (m, 4H, a-H), 4.53-4.64 (m, 1H, 6'-H), 4.97-5.06 (m, 1H, N*H*), 7.01 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.20 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.68 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.89 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.3, 28.5, 29.2, 29.3, 29.48, 29.53, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.7 (O*C*H$_2$), 67.3, 67.4 (C-a), 67.6, 67.7 (C-b), 69.1, 69.2 (C-c, C-d), 80.0 (O*C*(CH$_3$)$_3$), 111.9 (C-3), 113.7 (C-6), 121.7 (C-2'), 123.4 (C-5), 125.4 (C-4), 130.4 (C-3') 133.9 (C-4'), 146.5 (C-1), 149.8 (C-1'), 150.9 (C-2), 155.1 (HN*C*=O), 164.2 (Ar*C*=O), 171.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3435 (w), 2924 (m), 2855 (w), 1716 (s), 1602 (w), 1510 (m), 1455 (w), 1431 (m), 1391 (w), 1365 (m), 1345 (m), 1270 (s), 1248 (m), 1193 (vs), 1166 (s), 1129 (s), 1102 (s), 1050 (m), 1020 (m), 961 (m), 942 (m), 919 (w), 855 (w), 831 (w), 786 (w), 756 (m), 728 (w), 651 (w), 545 (w) cm^{-1}; MS (ESI): *m/z* = 738 [M]$^+$, 710, 682, 616, 127 [I]$^-$; HRMS (ESI): calc. for $C_{39}H_{57}NO_{11}^{+}$: 738.3824 [M]$^+$, found 738.3810; anal. calc. for $C_{39}H_{57}$ INNaO$_{11}$: C 53.34 H 6.45 N 1.83, found C 46.72 H 6.28 N 1.58; POM: Cr 78°C I.

Benzo[15]crown-5 hexadecyl-(*tert*-butoxycarbonyl)-*L*-tyrosinate sodium iodide complex [NaI·8d]. From **8d** (40 mg, 50 µmol) and NaI (11 mg, 75 µmol), yield: 48 mg, 50 µmol. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.21-1.36 (m, 26H, CH_2), 1.43 (s, 9H, OC(CH_3)$_3$), 1.56-1.67 (m, 2H, OCH$_2$CH_2), 3.12 (m$_c$, 2H, 5'-H), 3.75-3.83 (m, 4H, d-H), 3.89-3.97 (m. 4H, c-H), 4.06-4.19 (m, 6H, b-H, OCH_2), 4.32-4.42 (m, 4H, a-H), 4.53-4.64 (m, 1H, 6'-H), 4.97-5.07 (m, 1H, N*H*), 7.01 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.20 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.68 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.89 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29, 69, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.7 (O*C*H$_2$), 67.3, 67.4 (C-a), 67.6, 67.7 (C-b), 69.1, 69.2 (C-c, C-d), 80.0 (O*C*(CH$_3$)$_3$), 111.9 (C-3), 113.7 (C-6), 121.7 (C-2'), 123.4 (C-5), 125.4 (C-4), 130.4 (C-3') 133.9 (C-4'), 146.5 (C-1), 149.8 (C-1'), 150.9 (C-2), 155.1 (HN*C*=O), 164.2 (Ar*C*=O), 171.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3435 (w), 2921 (s), 2853 (m), 1718 (s), 1602 (w), 1510 (s), 1456 (w), 1432 (m), 1391 (w), 1365 (w), 1345 (m), 1271 (s), 1248 (m), 1195 (vs), 1167 (s), 1130 (s), 1103 (s), 1051 (m), 1020 (w), 961 (m), 942 (m), 919 (w), 855 (w), 786 (w), 756 (m), 723 (w), 652 (w), 547 (w) cm^{-1}; MS (ESI): *m/z* = 822 [M]$^+$, 127 [I]$^-$; HRMS (ESI): calc. for

$C_{45}H_{69}NO_{11}Na^+$: 822.4763 [M]$^+$, found 822.4752; anal. calc. for $C_{45}H_{69}INNaO_{11}$: C 56.90 H 7.32 N 1.47, found C 57.42 H 7.63 N 1.32; POM: Cr 40°C SmA 120°C I.

Benzo[15]crown-5 octadecyl-(*tert*-butoxycarbonyl)-*L*-tyrosinate sodium iodide complex [NaI·8e]. From **8e** (40 mg, 48 µmol) and NaI (11 mg, 73 µmol), yield: 47 mg, 48 µmol. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.20-1.36 (m, 30H, C*H*$_2$), 1.43 (s, 9H, OC(C*H*$_3$)$_3$), 1.57-1.67 (m, 2H, OCH$_2$C*H*$_2$), 3.12 (m$_c$, 2H, 5'-H), 3.75-3.83 (m, 4H, d-H), 3.89-3.97 (m. 4H, c-H), 4.06-4.19 (m, 6H, b-H, OC*H*$_2$), 4.33-4.42 (m, 4H, a-H), 4.54-4.64 (m, 1H, 6'-H), 4.97-5.06 (m, 1H, N*H*), 7.01 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.20 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.68 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.89 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.8, 28.3, 28.5, 29.2, 29.4, 29.5, 29.6, 29.66, 29, 70, 31.9 (*C*H$_2$, OC(*C*H$_3$)$_3$), 37.8 (C-5'), 54.4 (C-6'), 65.7 (O*C*H$_2$), 67.3, 67.4 (C-a), 67.6, 67.7 (C-b), 69.1, 69.2 (C-c, C-d), 80.0 (O*C*(CH$_3$)$_3$), 111.9 (C-3), 113.7 (C-6), 121.7 (C-2'), 123.4 (C-5), 125.4 (C-4), 130.4 (C-3') 133.9 (C-4'), 146.5 (C-1), 149.8 (C-1'), 150.9 (C-2), 155.1 (HN*C*=O), 164.2 (Ar*C*=O), 171.8 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3439 (w), 2922 (s), 2853 (m), 1718 (s), 1602 (w), 1510 (m), 1456 (w), 1432 (m), 1391 (w), 1365 (w), 1345 (w), 1271 (s), 1248 (m), 1195 (vs), 1167 (s), 1130 (s), 1103 (m), 1051 (m), 1020 (w), 961 (m), 942 (m), 855 (w), 786 (w), 756 (w), 722 (w), 652 (w), 525 (w) cm^{-1}; MS (ESI): *m/z* = 851 [M]$^+$, 127 [I]$^-$; HRMS (ESI): calc. for $C_{47}H_{73}NO_{11}Na^+$: 850.5076 [M]$^+$, found 850.5085; anal. calc. for $C_{47}H_{73}INNaO_{11}$: C 57.72 H 7.52 N 1.43, found C 56.74 H 7.48 N 1.31; POM: Cr 44°C [10.0 kJ/mol] SmA 111°C [-0.3 kJ/mol] I.

Benzo[15]crown-5 decyl-*L*-tyrosinate sodium iodide complex [NaI·10a]. From **10a** (50 mg, 81 µmol) and NaI (18 mg, 121 µmol), yield: 62 mg, 81 µmol. ^{1}H-NMR (CD_3OD, 400 MHz) δ = 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.20-1.36 (m, 14H, C*H*$_2$), 1.52-1.62 (m, 2H, OCH$_2$C*H*$_2$), 3.03 (m$_c$, 2H, 5'-H), 3.71-3.83 (m, 9H, c-H, d-H, 6'-H), 3.89-3.97 (m, 4H, b-H) 4.70 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.25-4.31 (m, 2H, a-H), 4.31-4.37 (m, 2H, a-H), 7.16 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 2'-H), 7.22 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.29 ($J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.77 (d, $J_{4,6}$ = 1.8 Hz, 1H, 6-H), 7.83 (dd, $J_{4,6}$ = 1.8 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR (CD_3OD, 100 MHz) δ = 14.5 (*C*H$_3$), 23.8, 27.0, 29.6, 30.4, 30.5, 30.67, 30.73, 33.1 (*C*H$_2$), 40.9 (C-5'), 56.7 (C-6'), 66.4 (O*C*H$_2$), 68.7, 68.9 (C-a), 69.1, 69.3 (C-b), 69.6, 69.7, 70.0, 70.1 (C-c, C-d), 113.9 (C-3), 116.2 (C-6), 123.0 (C-2'), 124.1 (C-5), 126.6 (C-4), 131.5 (C-3') 135.9 (C-4'), 148.8 (C-1), 151.4 (C-1'), 154.0 (C-2), 166.0 (Ar*C*=O), 175.3 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3431 (w), 2923 (m), 2854 (m), 2539 (w), 1726 (s), 1601 (m), 1510 (m), 1455 (w), 1431 (m), 1345 (w), 1271 (s), 1249 (m), 1194 (vs), 1167 (m), 1128 (s), 1104 (m), 1085 (m), 1050 (m), 1019 (w), 961 (m), 940 (m), 875 (w), 854 (w), 829 (w), 787 (w), 756 (w), 724 (w), 653 (w), 516 (w) cm^{-1}; MS (ESI): *m/z* = 638 $[M^+]$, 616 $[M - Na]^+$, 555, 498, 453, 320, 295, 127 $[I]^-$; HRMS (ESI): calc. for $C_{34}H_{49}NNaO_9^+$: 638.3300 $[M]^+$, found 638.3282; anal. calc. for $C_{34}H_{49}INNaO_9$: C 53.34 H 6.45 N 1.83, found C 46.72 H 6.28 N 1.58; POM: Cr 78°C I.

Benzo[15]crown-5 hexadecyl-*L*-tyrosinate sodium iodide complex [NaI·10d]. From **10d** (40 mg, 57 µmol) and NaI (13 mg, 86 µmol), yield: 48 mg, 57 µmol. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.21-1.37 (m, 26H, C*H*$_2$), 1.58-1.70 (m, 2H, OCH_2CH_2), 2.89 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5a',5b'}$ = 13.8 Hz, 1H, 5a'-H), 3.12 (dd, $J_{5b',6'}$ = 5.1 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.75 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5b',6'}$ = 5.1 Hz, 1H, 6'-H), 3.77-3.83 (m, 4H, d-H), 3.89-3.97 (m, 4H, c-H), 4.07-4.18 (m, 6H, OC*H*$_2$, b-H), 4.32-4.41 (m, 2H, a-H), 7.01 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.27 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.68 (d, $J_{4,6}$ = 1.8 Hz, 1H, 6-H), 7.89 (dd, $J_{4,6}$ = 1.8 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.2, 29.4, 29.5, 29.6, 29.66, 29.69, 31.9 (*C*H$_2$), 40.4 (C-5'), 55.7 (C-6'), 65.3 (O*C*H$_2$), 67.3, 67.4 (C-a), 67.6, 67.7 (C-b), 69.1, 69.2 (C-c, C-d), 111.9 (C-3), 113.7 (C-6), 121.8 (C-2'), 123.4 (C-5), 125.4 (C-4), 130.4 (C-3') 135.1 (C-4'), 146.5 (C-1), 149.7 (C-1'), 150.9 (C-2), 164.3 (Ar*C*=O), 175.0 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3436 (w), 2922 (s), 2853 (m), 1728 (s), 1602 (w), 1510 (m), 1457 (w), 1431 (w), 1344 (w), 1272 (s), 1249 (m), 1195 (vs), 1167 (m), 1129 (s), 1103 (m), 1051 (m), 1019 (w), 961 (m), 942 (m), 890 (w), 830 (w), 787 (w), 756 (w), 723 (w), 653 (w), 515 (w) cm^{-1}; MS (ESI): *m/z* = 722 $[M]^+$, 700 $[M - Na]^+$, 498, 361, 295, 127 $[I]^-$; HRMS (ESI): calc. for $C_{40}H_{61}NNaO_9^+$: 722.4239 $[M]^+$, found 722.4226; anal. calc. for $C_{40}H_{61}INNaO_9$: C 56.53 H 7.24 N 1.65, found C 56.05 H 7.19 N 1.56; POM: Cr 28°C SmA 75°C I.

Benzo[15]crown-5 octadecyl-*L*-tyrosinate sodium iodide complex [NaI·10e]. From **10e** (40 mg, 55 µmol) and NaI (12 mg, 83 µmol), yield: 48 mg, 55 µmol. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.19-1.36 (m, 30H, C*H*$_2$), 1.55-1.71 (m, 2H, OCH_2CH_2), 2.89 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5a',5b'}$ = 13.8 Hz, 1H, 5a'-H), 3.12 (dd, $J_{5b',6'}$ = 5.1 Hz, $J_{5a',5b'}$ = 13.7 Hz, 1H, 5b'-H), 3.75 (dd, $J_{5a',6'}$ = 7.9 Hz, $J_{5b',6'}$ = 5.1 Hz, 1H, 6'-H), 3.77-3.83 (m, 4H, d-H), 3.89-3.97 (m, 4H, c-H) 4.06-4.18 (m, 6H, OC*H*$_2$, b-H), 4.32-4.41 (m, 2H, a-H), 7.01 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.14 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.27 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.68 (d, $J_{4,6}$ = 1.9 Hz, 1H, 6-H), 7.90 (dd, $J_{4,6}$ = 1.9 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (*C*H$_3$), 22.7, 25.9, 28.6, 29.2, 29.4, 29.5, 29.6, 29.66, 29.70, 31.9 (*C*H$_2$), 40.5 (C-5'), 55.8 (C-6'), 65.3 (O*C*H$_2$), 67.3, 67.4 (C-a), 67.6, 67.7 (C-b), 69.1, 69.2 (C-c, C-d), 111.9 (C-3), 113.7 (C-6), 121.8 (C-2'), 123.4 (C-5), 125.4 (C-4), 130.4 (C-3') 135.1 (C-4'), 146.5 (C-1), 149.7 (C-1'), 150.9 (C-2), 164.3 (Ar*C*=O), 175.0 (C-7') ppm;

FT-IR (ATR): $\tilde{\nu}$ = 3436 (w), 2922 (s), 2853 (m), 1718 (s), 1602 (w), 1510 (m), 1457 (w), 1431 (m), 1344 (w), 1272 (s), 1248 (m), 1195 (vs), 1167 (m), 1129 (s), 1103 (m), 1051 (m), 1019 (w), 961 (m), 942 (m), 890 (w), 830 (w), 787 (w), 756 (w), 723 (w), 653 (w), 515 (w) cm^{-1}; MS (ESI): *m/z* = 750 $[M]^+$, 728 $[M - Na]^+$, 127 $[I]^-$; HRMS (ESI): calc. for $C_{42}H_{65}NNaO_9^+$: 750.4517 $[M]^+$, found 750.4513; anal. calc. for $C_{42}H_{65}INNaO_9$: C 57.46 H 7.46 N 1.60, found C 56.84 H 7.52 N 1.59; POM: Cr 38°C SmA 115°C I.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-(dodecyloxy)-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium iodide sodium iodide complex [NaI·(11b)I]. From **(11b)I** (25 mg, 29 µmol) and NaI (6 mg, 43 µmol), yield: 29 mg, 29 µmol, yellow solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.17-1.35 (m, 18H, C*H*$_2$), 1.66 (m$_c$, 2H, OCH$_2$C*H*$_2$), 2.57-3.35 (m, 12H, N(C*H*$_3$)$_2$), 3.38-3.47 (m, 1H, 5b'-H), 3.74-3.83 (m, 5H, 5a'-H, d-H), 3.86-3.95 (m, 4H, c-H), 4.05-4.13 (m, 4H, b-H), 4.15 (t, *J* = 6.9 Hz, 2H, OC*H*$_2$), 4.25-4.36 (m, 3H, a-H, 6'-H), 4.36-4.43 (m, 2H, a-H), 7.04 (d, $J_{3,4}$ = 8.6 Hz, 1H, 3-H), 7.12 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 2'-H), 7.57 (d, $J_{2',3'}$ = 8.4 Hz, 2H, 3'-H), 7.63 (br s, 1H, 6-H), 7.71-7.77 (m, 1H, N*H*), 7.84 (dd, $J_{4,6}$ = 1.8 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1 (CH$_2$*C*H$_3$), 22.7, 25.8, 28.4, 29.2, 29.3, 29.5, 29.60, 29.64, 31.9 (*C*H$_2$), 36.2 (C-5'), 40.2 (N(*C*H$_3$)$_2$), 60.0 (C-6'), 66.8 (O*C*H$_2$), 67.56, 67.62 (C-a), 67.8, 67.9 (C-b), 69.1, 69.3 (C-c, C-d), 112.2 (C-3), 113.9 (C-6), 122.1 (C-2'), 123.0 (C-5), 125.4 (C-4), 130.9 (C-3') 133.9 (C-4'), 146.6 (C-1), 150.1 (C-1'), 151.3 (C-2), 161.7 (*C*N(CH$_3$)$_2$) 164.4 (Ar*C*=O), 170.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3438 (w), 2923 (m), 2853 (m), 1730 (s), 1621 (m), 1604 (m), 1567 (m), 1510 (m), 1457 (m), 1431 (m), 1403 (m), 1343 (w), 1270 (s), 1193 (vs), 1167 (s), 1129 (s), 1103 (s), 1036 (m), 961 (m), 942 (m), 918 (m), 829 (w), 795 (w), 756 (m), 727 (m), 643 (w), 511 (w), 411 (w) cm^{-1}; MS (ESI): *m/z* = 743 $[M–Na]^+$, 383 $[M]^{2+}$, 127 $[I]^–$; HRMS (ESI): calcd. for $C_{41}H_{64}N_3NaO_9^{2+}$: 382.7265 $[M]^{2+}$, found 382.7276; anal. calc. for $C_{41}H_{64}I_2N_3NaO_9$: C 48.29 H 6.33 N 4.12, found C 48.20 H 6.67 N 4.25; POM: Cr 97°C I.

(*S*)-*N*-(Bis(dimethylamino)methylene)-1-(octadecyloxy)-3-((carboxybenzo[15]crown-5)-phenyl)-1-oxopropan-2-aminium iodide sodium iodide complex [NaI·(11e)I]. From **(11e)I** (30 mg, 32 µmol) and NaI (7 mg, 47 µmol), yield: 35 mg, 32 µmol, yellow solid. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.19-1.36 (m, 30H, C*H*$_2$), 1.66 (m$_c$, 2H, OCH$_2$C*H*$_2$), 2.62-3.32 (m, 12H, N(C*H*$_3$)$_2$), 3.42 (dd, $J_{5b',6'}$ = 4.5 Hz, $J_{5a',5b'}$ = 14.3 Hz, 1H, 5b'-H), 3.76-3.82 (m, 5H, 5a'-H, d-H), 3.86-3.95 (m, 4H, c-H), 4.06-4.19 (m, 6H, OC*H*$_2$, b-H), 4.26-4.32 (m, 1H, 6'-H), 4.32-4.37 (m, 2H, a-H), 4.37-4.43 (m, 2H, a-H), 7.05 (d, $J_{3,4}$ = 8.6 Hz, 1H, 3-H), 7.12 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 2'-H), 7.57 (d, $J_{2',3'}$ = 8.5 Hz, 2H, 3'-H), 7.63-7.66 (m, 1H, 6-H), 7.70-7.76 (m, 1H, N*H*), 7.84 (m$_c$, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 125

MHz) δ = 14.1 (CH_2CH_3), 22.7, 25.9, 28.5, 29.2, 29.4, 29.55, 29.63, 29.66, 29.71, 31.9 (CH_2), 36.2 (C-5'), 40.2 ($N(CH_3)_2$), 60.0 (C-6'), 66.8 (OCH_2), 67.4, 67.6 (C-a), 67.7, 67.8 (C-b), 69.0, 69.2 (C-c, C-d), 112.2 (C-3), 113.9 (C-6), 122.1 (C-2'), 123.1 (C-5), 125.5 (C-4), 130.9 (C-3') 133.9 (C-4'), 146.5 (C-1), 150.1 (C-1'), 151.1 (C-2), 161.7 ($CN(CH_3)_2$) 164.4 (Ar*C*=O), 170.5 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (m), 1729 (m), 1620 (m), 1604 (m), 1567 (m), 1510 (m), 1457 (m), 1431 (m), 1403 (m), 1343 (w), 1270 (s), 1247 (m), 1193 (vs), 1127 (s), 1102 (s), 1036 (m), 961 (m), 942 (m), 918 (m), 855 (w), 828 (w), 796 (w), 756 (m), 726 (m), 643 (w), 546 (w), 514 (w) cm^{-1}; MS (ESI): *m/z* = 424 $[M]^{2+}$, 127 $[I]^-$; HRMS (ESI): calcd. for $C_{47}H_{76}N_3NaO_9^{2+}$: 424.7734 $[M]^{2+}$, found 424.7738; anal. calc. for $C_{47}H_{76}I_2N_3NaO_9$: C 51.14 H 6.94 N 3.81, found C 49.63 H 7.14 N 3.71; POM: Cr 137°C [-0.5 kJ/mol] I.

Dodecyloxy *O*-[3,4-bis(dodecyloxy)benzoyl]-*N*-(*tert*-butoxycarbonyl)-L-tyrosinate (15a). According to GP 2, from 3,4-bis(dodecyloxy)benzoic acid **14**[12] (501 mg, 1.02 mmol), **6b** (510 mg, 1.13 mmol), EDCI (238 mg, 1.24 mmol), DMAP (13 mg, 0.11 mmol), abs. CH_2Cl_2 (60 mL), flash chromatography on SiO_2 with hexanes/EtOAc (15:1), yield: 640 mg, 0.69 mmol, 68%, colorless solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.84-0.92 (m, 9H, CH_2CH_3), 1.20-1.40 (m, 50H, CH_2), 1.44 (s, 9H, $OC(CH_3)_3$), 1.46-1.54 (m, 4H, $OCH_2CH_2CH_2$), 1.56-1.65 (m, 2H, $(C=O)OCH_2CH_2$), 1.80-1.91 (m, 4H, OCH_2CH_2), 3.05-3.18 (m, 2H, 5'-H), 4.02-4.15 (m, 6H, OCH_2, $(C=O)OCH_2$), 4.54-4.62 (m, 1H, 6'-H), 4.97-5.05 (m, 1H, N*H*), 6.92 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1, 14.2 (CH_3), 22.7 25.9, 25.97, 26.01, 28.3, 28.5, 29.0, 29.17, 29.23, 29.38, 29.42, 29.5, 29.61, 29.64, 29.67, 29.70, 31.9 (CH_2), 37.8 (C-5'), 54.4 (C-6'), 60.4, 65.6 ($(C=O)OCH_2$), 69.0, 69.3 (OCH_2CH_2), 79.9 ($OC(CH_3)_3$), 111.9 (C-3), 114.5 (C-6), 121.5 (C-2'), 121.8 (C-5), 124.3 (C-4), 130.3 (C-3'), 133.5 (C-4'), 148.6 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HN*C*=O), 165.0 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3351 (w), 2918 (s), 2850 (m), 1727 (m), 1687 (s), 1598 (w), 1518 (m), 1467 (m), 1429 (m), 1391 (w), 1366 (w), 1346 (w), 1290 (m), 1273 (s), 1248 (m), 1198 (vs), 1166 (s), 1141 (m), 1086 (m), 1058 (w), 1019 (m), 966 (w), 943 (w), 876 (w), 817 (w), 785 (w), 755 (m), 722 (w), 654 (w), 615 (w), 545 (w), 517 (w) cm^{-1}; MS (ESI): *m/z* = 945 $[M + Na]^+$, 823, 547, 503, 381, 353, 301; HRMS (ESI): calc. for $C_{57}H_{95}NO_8Na^+$: 944.6950 $[M + Na]^+$, found 944.6921; anal. calc. for $C_{57}H_{95}NO_8$: C 74.22 H 10.38 N 1.52, found C 74.42 H 10.19 N 1.47; DSC: Cr 47°C [-49.5 kJ/mol] I.

Tetradecyloxy *O*-[3,4-bis(dodecyloxy)benzoyl]-*N*-(*tert*-butoxycarbonyl)-L-tyrosinate (15b). According to GP 2, from 3,4-bis(dodecyloxy)benzoic acid **14** (600 mg, 1.22 mmol), **6b**

(650 mg, 60 mL), EDCI (288 mg, 1.50 mmol), DMAP (17 mg, 0.14 mmol), abs. CH_2Cl_2 (60 mL), flash chromatography on SiO_2 with hexanes/EtOAc (15:1), yield: 810 mg, 0.85 mmol, 70%, colorless solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.84-0.92 (m, 9H, CH_2CH_3), 1.19-1.41 (m, 58H, CH_2), 1.44 (s, 9H, $OC(CH_3)_3$), 1.46-1.54 (m, 4H, $OCH_2CH_2CH_2$), 1.57-1.66 (m, 2H, (C=O)OCH_2CH_2), 1.80-1.91 (m, 4H, OCH_2CH_2), 3.05-3.18 (m, 2H, 5'-H), 4.02-4.15 (m, 6H, OCH_2, (C=O)OCH_2), 4.54-4.62 (m, 1H, 6'-H), 4.96-5.05 (m, 1H, N*H*), 6.92 (d, $J_{3,4}$ = 8.5 Hz, 1H, 3-H), 7.13 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 2'-H), 7.19 (d, $J_{2',3'}$ = 8.6 Hz, 2H, 3'-H), 7.65 (d, $J_{4,6}$ = 2.0 Hz, 1H, 6-H), 7.80 (dd, $J_{4,6}$ = 2.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 14.1, 14.1 (CH_3), 22.7 25.9, 25.97, 26.01, 28.3, 28.5, 29.0, 29.17, 29.23, 29.38, 29.42, 29.5, 29.61, 29.63, 29.67, 29.70, 31.7 (CH_2), 37.8 (C-5'), 54.4 (C-6'), 60.4, 65.6 ((C=O)OCH_2), 69.0, 69.3 (OCH_2CH_2), 79.9 ($OC(CH_3)_3$), 111.9 (C-3), 114.5 (C-6), 121.5 (C-2'), 121.8 (C-5), 124.3 (C-4), 130.3 (C-3'), 133.5 (C-4'), 148.5 (C-1), 150.1 (C-1'), 153.8 (C-2), 155.1 (HN*C*=O), 165.0 (Ar*C*=O), 171.9 (C-7') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3352 (w), 2918 (s), 2850 (m), 1727 (m), 1687 (s), 1598 (w), 1518 (m), 1467 (m), 1429 (m), 1391 (w), 1366 (w), 1346 (w), 1290 (m), 1273 (s), 1249 (m), 1199 (vs), 1167 (s), 1142 (m), 1087 (m), 1059 (w), 1019 (m), 966 (w), 944 (w), 876 (w), 817 (w), 785 (w), 755 (m), 722 (w), 654 (w), 545 (w) cm^{-1}; MS (ESI): *m/z* = 973 $[M + Na]^+$, 851; HRMS (ESI): calc. for $C_{59}H_{99}NO_8Na^+$: 972.7263 $[M + Na]^+$, found 972.7240; anal. calc. for $C_{59}H_{99}NO_8$: C 74.56 H 10.50 N 1.47, found C 74.52 H 10.28 N 1.45; DSC: Cr 50°C [-56.7 kJ/mol] I.

2. References

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3. Chemical shift by NaI complexation

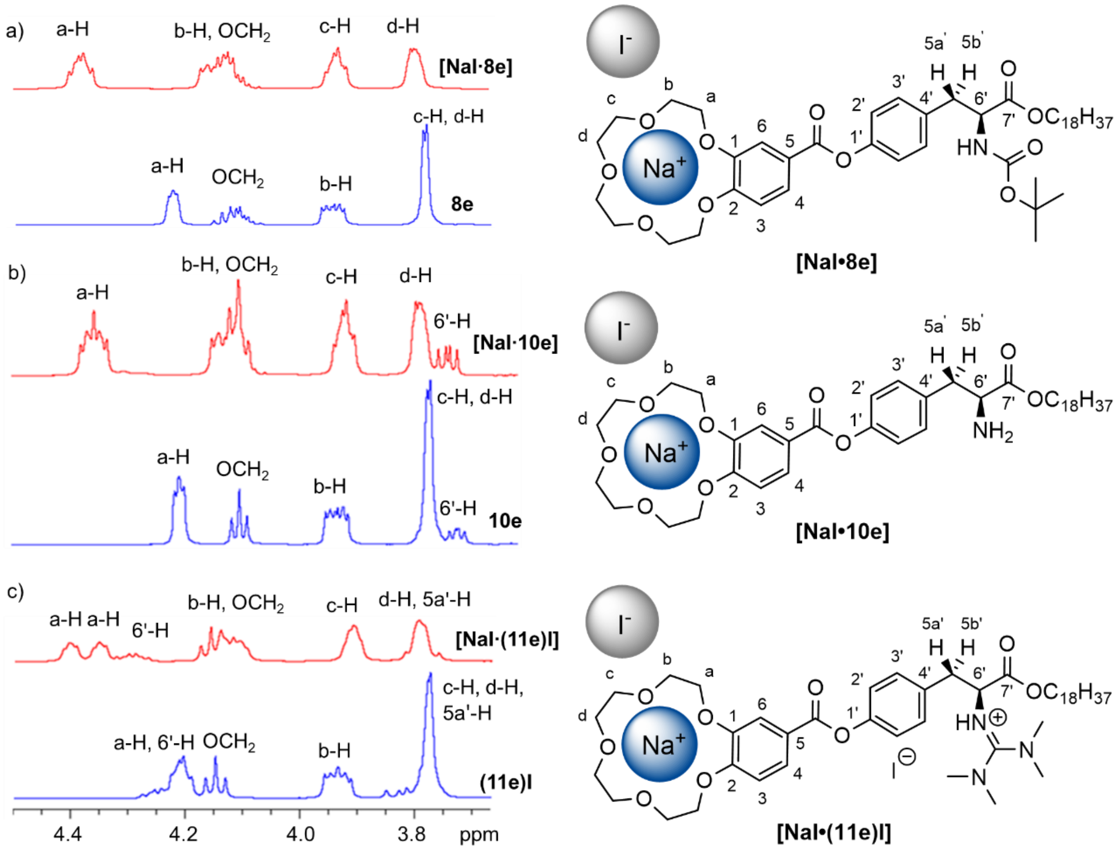


Figure S1. ^{1}H-NMR spectra of neat (blue line) and complexed crown ether derivatives (red line) **8e** (a), **10e** (b) and (**11e**)**I** (c) at room temperature (400 MHz, $CDCl_3$).

4. Differential Scanning Calorimetry (DSC)

Table S2. Phase transition temperatures *T* (°C) and enthalpies Δ*H* (kJ mol^{-1}) of derivatives **8** and **9** determined by DSC (cooling rate 10 K min^{-1})

Compd	n	Cr_1	*T* (Δ*H*) [a]	Col_r	*T* (Δ*H*) [a]	I	Cycle
8a	10	●	55 (–13.0)	●	90 (–25.7)	●	1st heating
	10	–		–		●	1st cooling
8b	12	–		● [b]	91 (–47.7)	●	3rd heating
	12	–		–		●	3rd cooling
8c	14	● [c]	91 (–53.4)	–		●	3rd heating
	14	–		–		●	3rd cooling
8d	16	● [d]	50 (–10.2)	●	76 (–20.3)	●	3rd heating
	16	–		–		●	3rd cooling
8e	18	●	67 (–10.6)	●	78 (–16.1)	●	3rd heating
	18	●	8 (0.5)	●	60 (44.3)	●	3rd cooling
9c	14	● [e]	51 (–3.0)	●	66 (–15.5)	●	3rd heating
	14	–		–		●	3rd cooling
9d	16	● [f]	46 (–8.3)	●	73 (–15.8)	●	3rd heating
	16	–		–		●	3rd cooling
9e	18	● [g]	48 (–7.2)	●	79 (–30.9)	●	3rd heating
	18	–		–		●	3rd cooling

Crystalline (Cr), isotropic liquid (I), phase observed (●), not observed (–). [a] Phase transitions were determined from the onset temperatures of the DSC curves. [b] I – Col_r transition at 61°C, 28.7 kJ mol^{-1}. [c] Spontaneous recrystallization at 39°C, 25.6 kJ mol^{-1}, Cr – Cr_1 transition at 58°C, 12.8 kJ mol^{-1}. [d] Spontaneous recrystallization at 33°C, 35.3 kJ mol^{-1}. [e] Spontaneous recrystallization at 24°C, 27.6 kJ mol^{-1}. [f] Spontaneous recrystallization at 14°C, 13.5 kJ mol^{-1}. [g] Spontaneous recrystallization at 24°C, 35.2 kJ mol^{-1}.

Table S3. Phase transition temperatures T (°C) and enthalpies ΔH (kJ mol^{-1}) of derivatives **10**, **10·HCl** and **11** determined by DSC (cooling rate 10 K min^{-1}) or POM (cooling rate 1 K min^{-1})

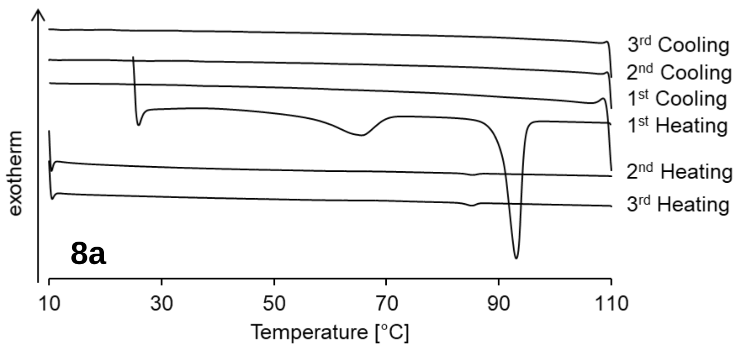
Compd	n	Cr_1	T (ΔH) [a]	Col_r	T (ΔH) [a]	I	Cycle	
10a	10	–		–		●	1st heating	DSC
	10	●	18 (11.2)	–		●	1st cooling	DSC
10b	12	●	40 (–42.9)	–		●	1st heating	DSC
	12	–		–		●	1st cooling	DSC
10c	14	●	45 (–56.4)	–		●	1st heating	DSC
	14	–		–		●	1st cooling	DSC
10d	16	● [b]	32 (–28.5)	–		●	3rd heating	DSC
	16	●	15 (24.6)	–		●	3rd cooling	DSC
10e	18	●	30 (–13.3)	●	41 (–3.6)	●	3rd heating	DSC
	18	●	34 (13.7)	–		●	3rd cooling	DSC
10c·HCl	14	●	134 (–28.5)	–		●	1st heating	DSC
	14	●	113 (28.2)	–		●	1st cooling	DSC
10d·HCl	16	●	133 (–26.1)	–		●	1st heating	DSC
	16	●	114 (24.7)	–		●	1st cooling	DSC
10e·HCl	18	●	136 (–29.9)	–		●	1st heating	DSC
	18	●	114 (28.7)	–		●	1st cooling	DSC
(11a)Cl	10	●	42	–		●	1st heating	POM
	10	●	29	–		●	1st cooling	POM
(11b)Cl	12	●	44	–		●	1st heating	POM
	12	●	32	–		●	1st cooling	POM
(11c)Cl	14	●	34 (–5.7)	–		●	1st heating	DSC
	14	–		–		●	1st cooling	DSC
(11d)Cl	16	●	42 (–9.8)	–		●	3rd heating	DSC
	16	●	41 (9.9)	–		●	3rd cooling	DSC
(11e)Cl	18	●	34 (–10.4)	–		●	1st heating	DSC
	18	–		–		●	1st cooling	DSC
(11b)I	12	●	70	–		●	1st heating	POM
	12	●	52	–		●	1st cooling	POM
(11e)I	18	●	55	–		●	1st heating	POM
	18	●	39	–		●	1st cooling	POM

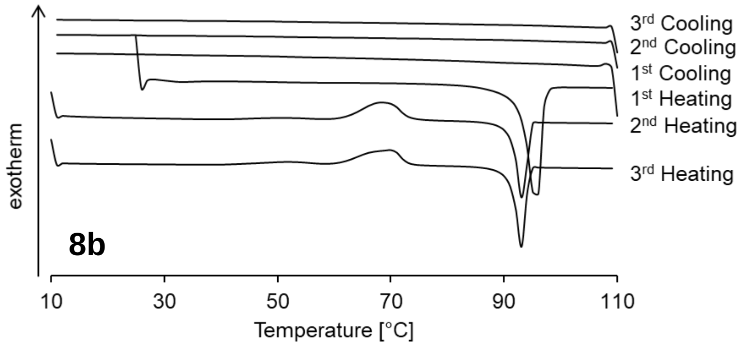
Crystalline (Cr), isotropic liquid (I), phase observed (●), not observed (–). [a] Phase transitions were determined from the onset temperatures of the DSC curves. [b] Additional Cr to Cr_1 transition at 18°C (–26.2 kJ mol^{-1}).

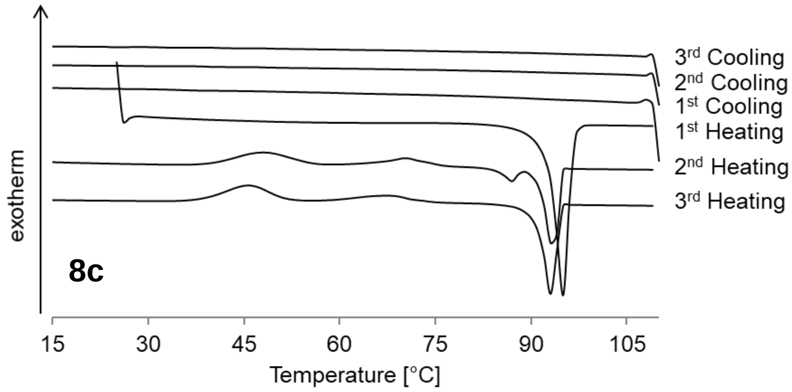
Table S4. Phase transition temperatures T [°C] and enthalpies ΔH [kJ mol^{-1}] of derivatives **12**, **13** and **15** determined by DSC (cooling rate 10 K min^{-1}).

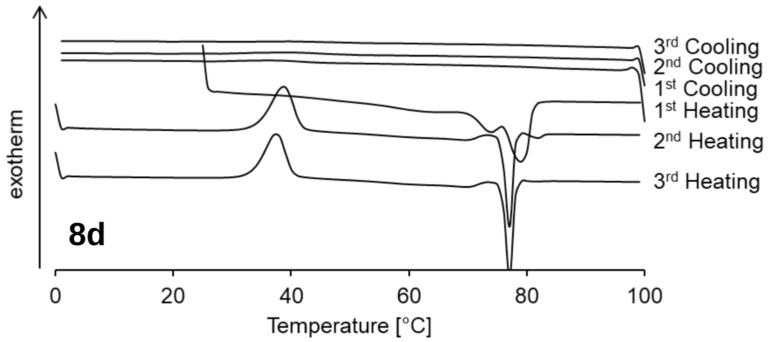
Compd	n	Cr_1	T (ΔH) [a]	Cr_2	T (ΔH)	I	Cycle
12b	12	● [b]		–	98 (–46.8)	●	3rd heating
	12	–		–		●	3rd cooling
12c	14	● [c]	68 (8.6)	●	105 (–61.6)	●	3rd heating
	14	–		–		●	3rd cooling
12d	16	● [d]	52 (14.6)	●	106 (-60.6)	●	3rd heating
	16	–		–		●	3rd cooling
12e	18	● [e]	52 (18.9)	●	106 (–64.3)	●	3rd heating
	18	–		–		●	3rd cooling
13b	12	●		–	69 (-31.1)	●	1st heating
	12	–		–		●	1st cooling
13c	14	●		–	61 (-35.7)	●	1st heating
	14	–		–		●	1st cooling
13d	16	● [f]	89 (-2.9)	●	96 (-1.9)	●	3rd heating
	16	–		–		●	3rd cooling
13e	18	●		–	65 (-54.1)	●	1st heating
	18	–		–		●	1st cooling
15a	12	●		–	47 (-49.5)	●	3rd heating
	12	●		–	33 (52.0)	●	3rd cooling
15b	14	●		–	50 (-56.7)	●	3rd heating
	14	●		–	37 (58.5)	●	3rd cooling

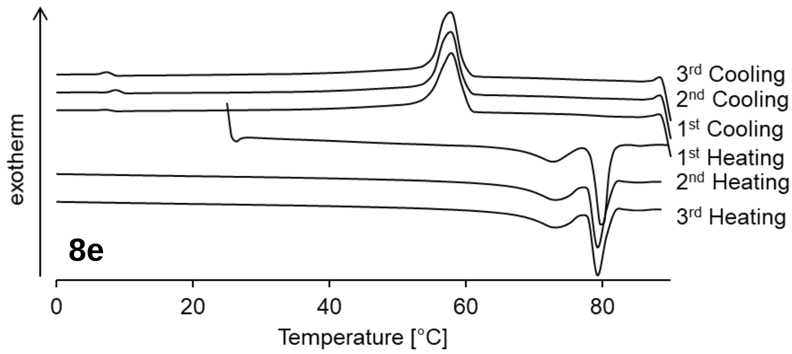
Cr = crystalline, I = isotropic liquid, ● phase observed, – phase not observed. [a] Phase transitions were determined from the onset temperatures of the DSC curves. [b] Spontaneous recrystallization at 33°C (34.2 kJ mol^{-1}). [c] Spontaneous recrystallization at 35°C (33.0 kJ mol^{-1}). [d] Spontaneous recrystallization at 31°C (29.9 kJ mol^{-1}). [e] Spontaneous recrystallization at 33°C (36.2 kJ mol^{-1}). [f] Spontaneous recrystallization at 67°C (8.2 kJ mol^{-1}).

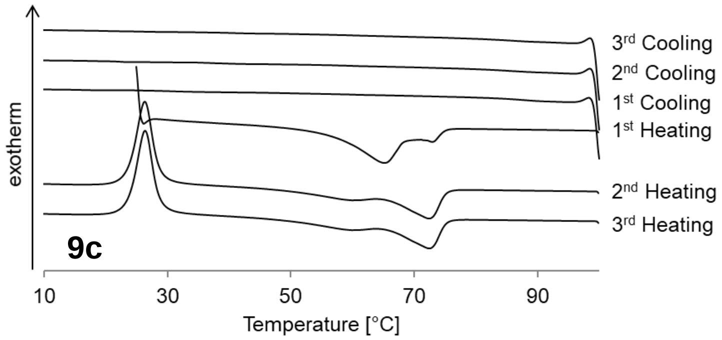


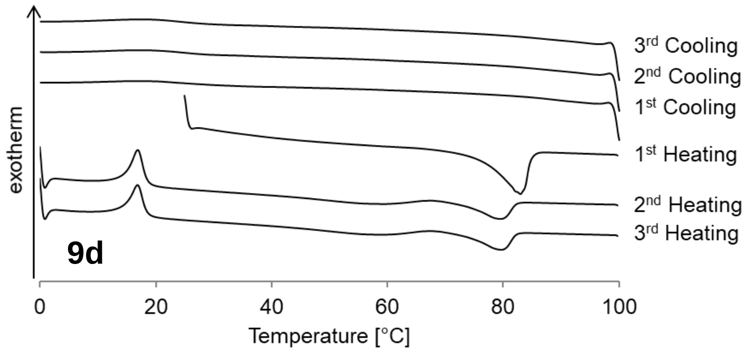

3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
8b
10
30
50
70
90
110
Temperature [°C]


3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
8c
15
30
45
60
75
90
105
Temperature [°C]


3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
8d
0
20
40
60
80
100
Temperature [°C]


3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
8e
0
20
40
60
80
Temperature [°C]





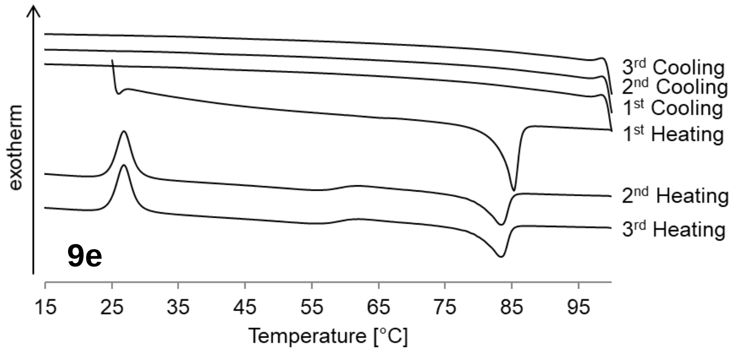
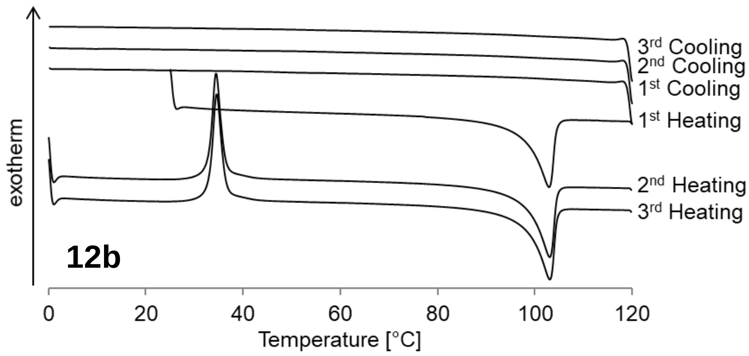
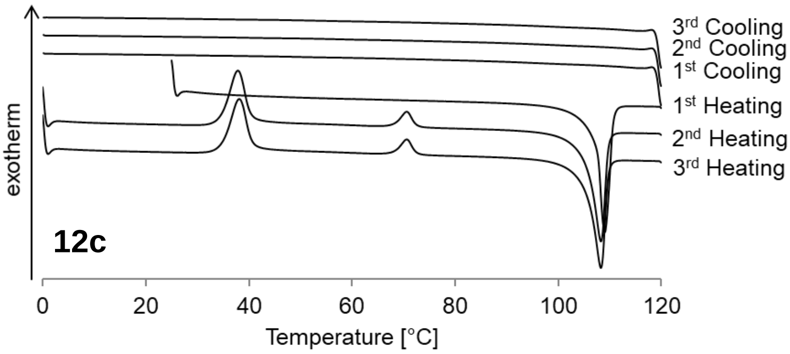
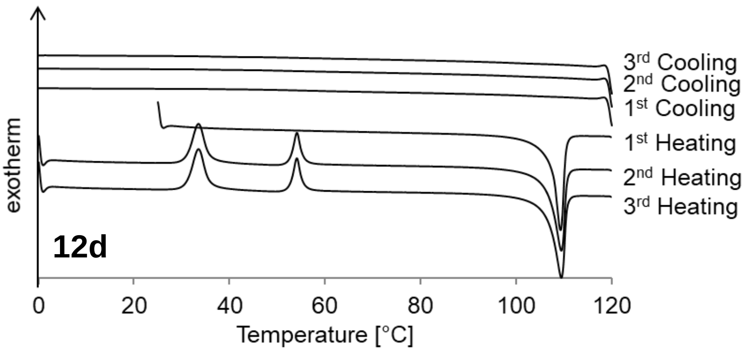
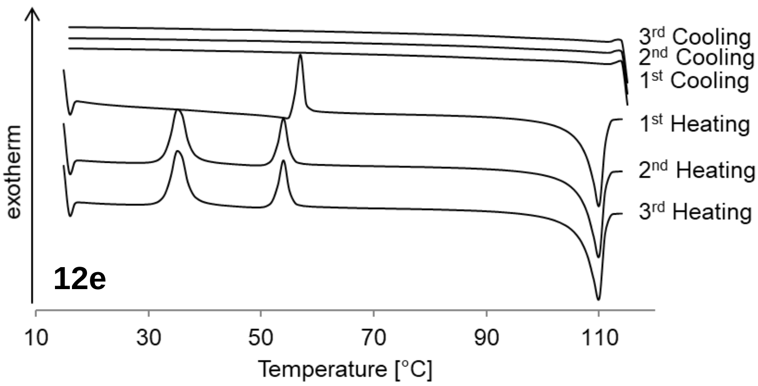


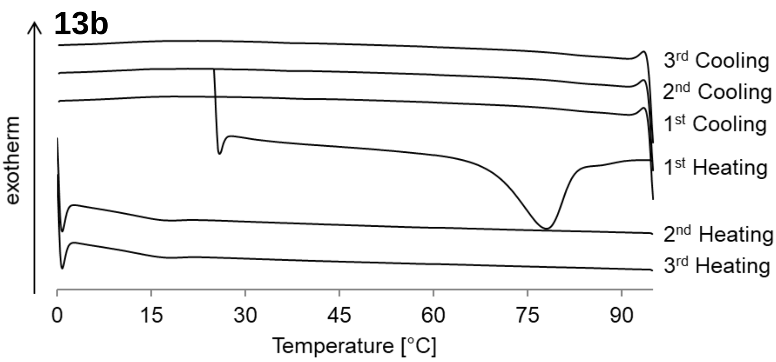
Figure S2. DSC curves of N-Boc protected [15]crown-5 derivatives **8a**–**e** and [18]crown-6 derivatives **9c**–**e** (heating/cooling rate 10 K min^{-1}).

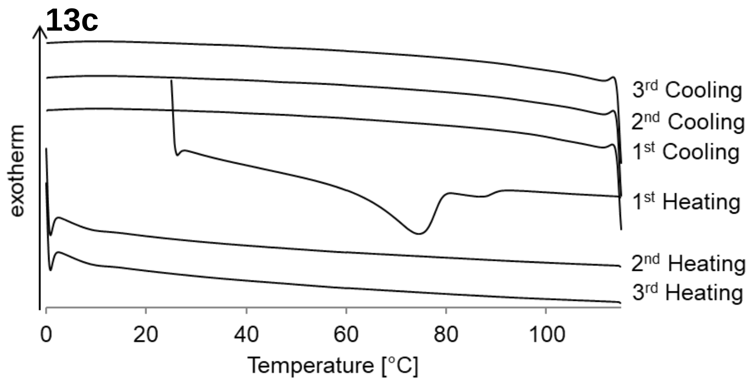


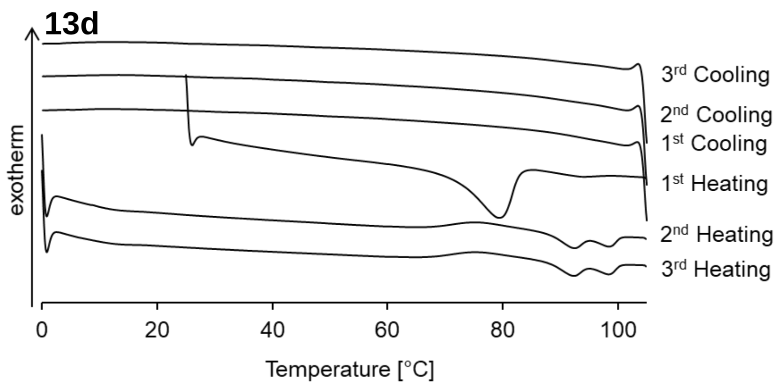

3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
12c
0
20
40
60
80
100
120
Temperature [°C]


3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
12d
0
20
40
60
80
100
120
Temperature [°C]


3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
12e
10
30
50
70
90
110
Temperature [°C]


13b
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
0
15
30
45
60
75
90
Temperature [°C]





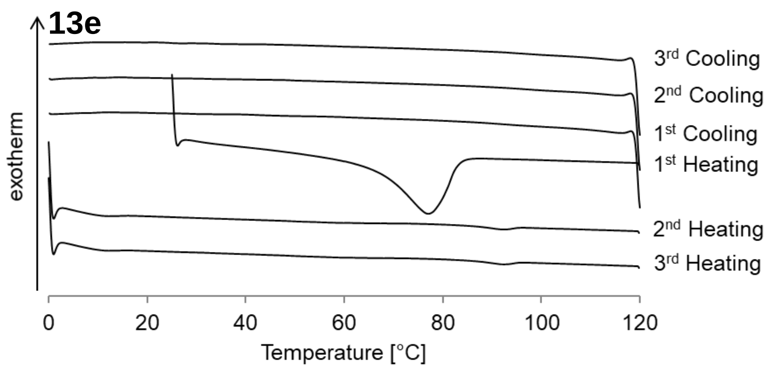
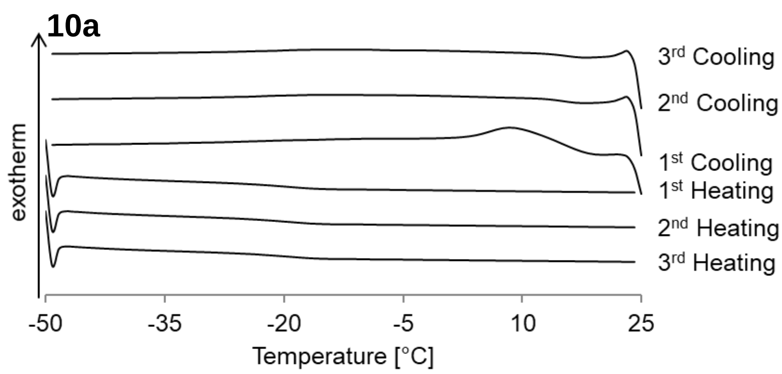
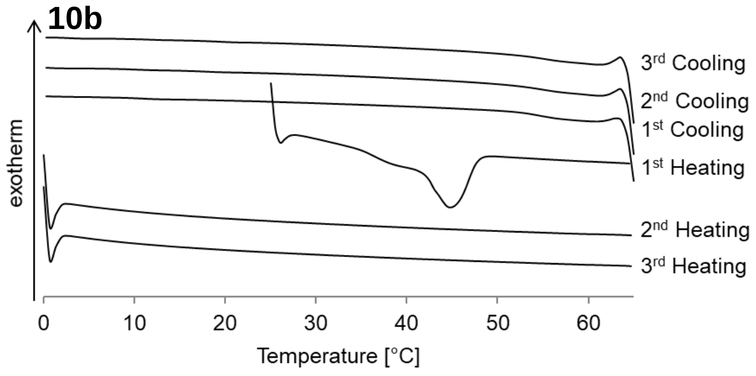
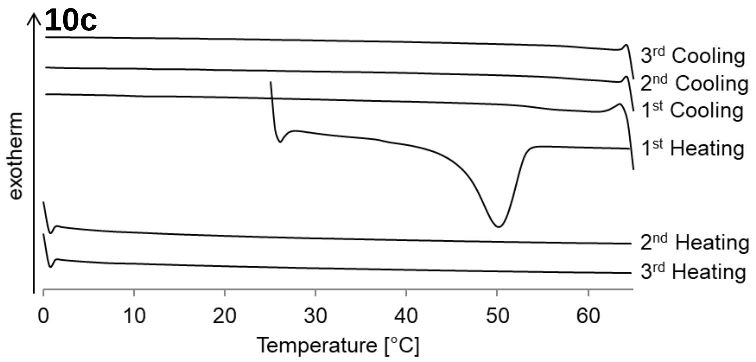
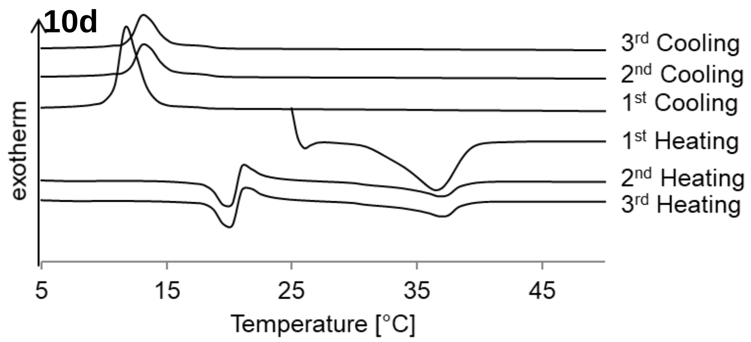


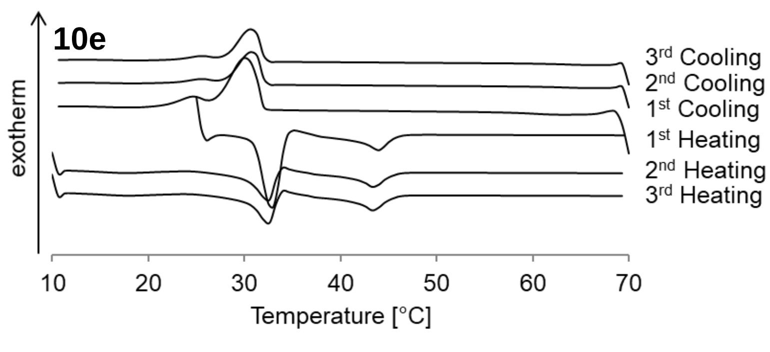
Figure S3. DSC curves of *N*-Z and *N*-Fmoc protected [15]crown-5 derivatives **12b**–**e** and **13b**–**e** (heating/cooling rate 10 K min^{-1}).




10b
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
0
10
20
30
40
50
60
Temperature [°C]


10c
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
0
10
20
30
40
50
60
Temperature [°C]


10d
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
5
15
25
35
45
Temperature [°C]


10e
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
10
20
30
40
50
60
70
Temperature [°C]

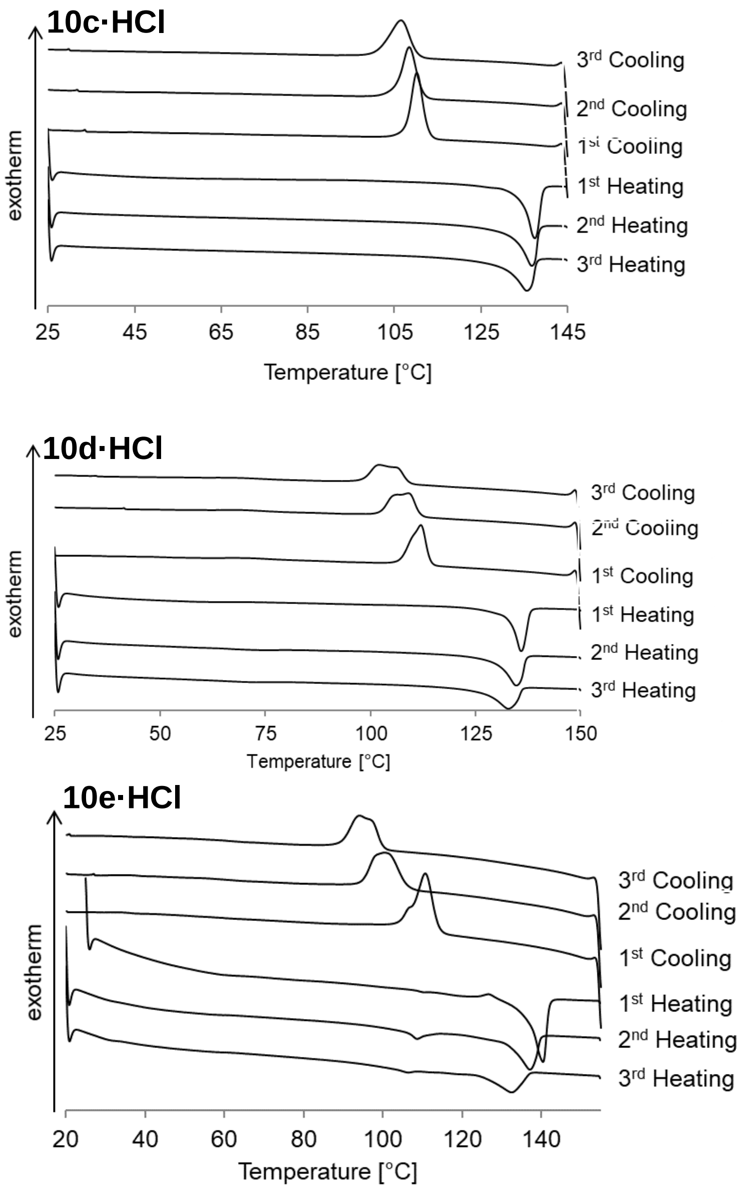
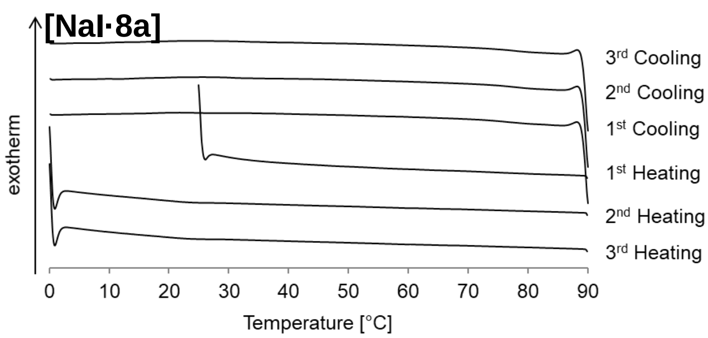


Figure S4. DSC curves of unprotected [15]crown-5 derivatives **10a**–**e** and the hydrochlorides of **10·HCl** (heating/cooling rate 10 K min^{-1}).



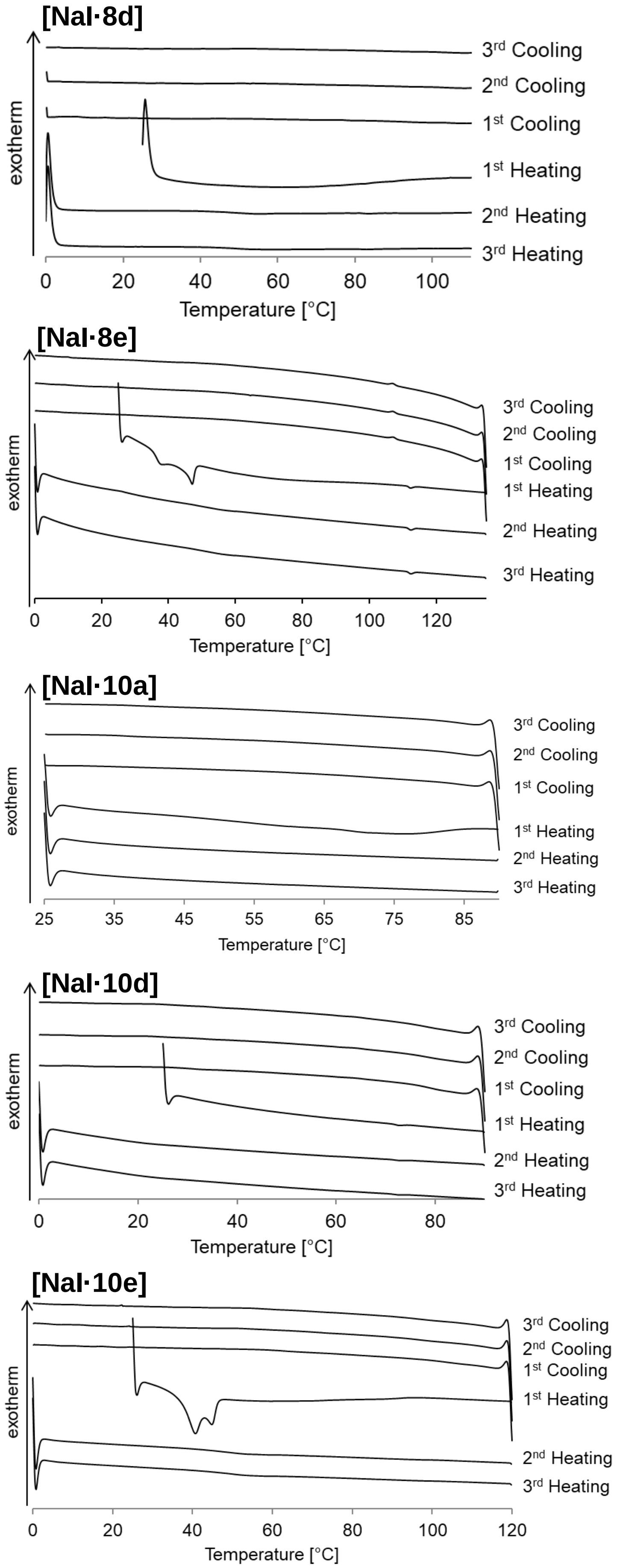
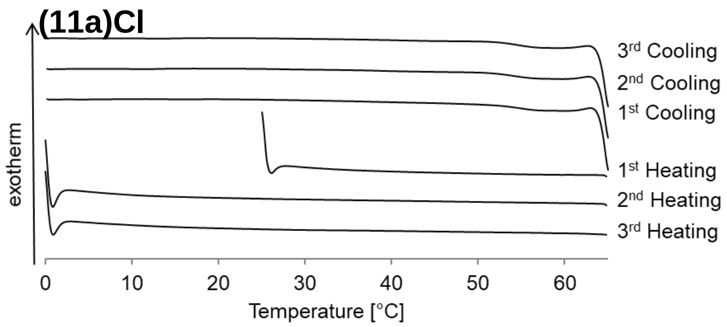
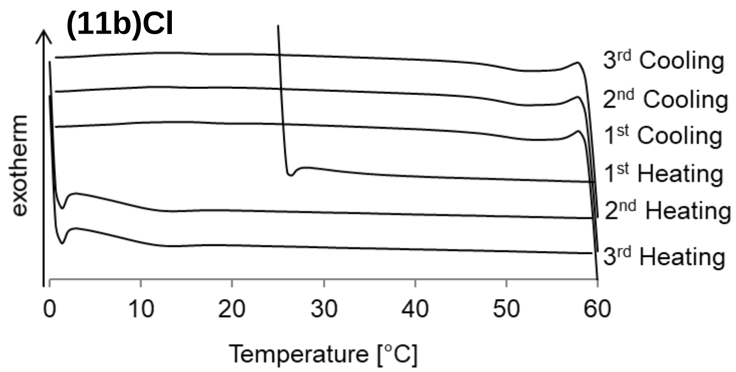
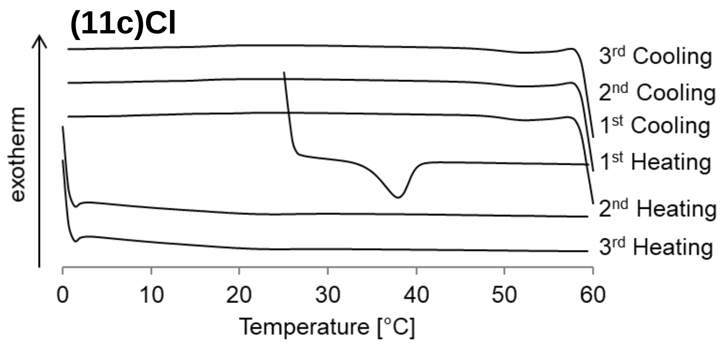
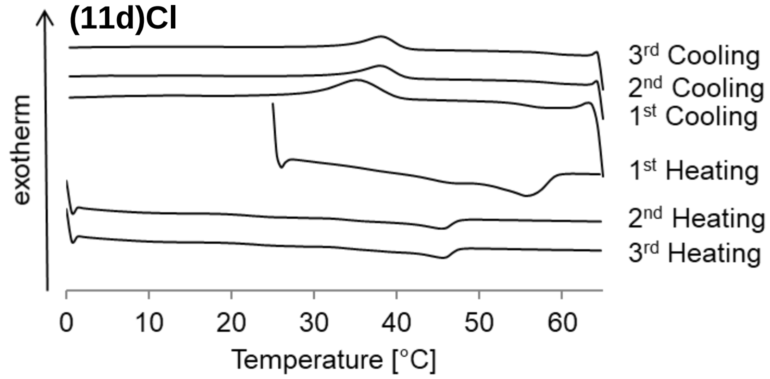


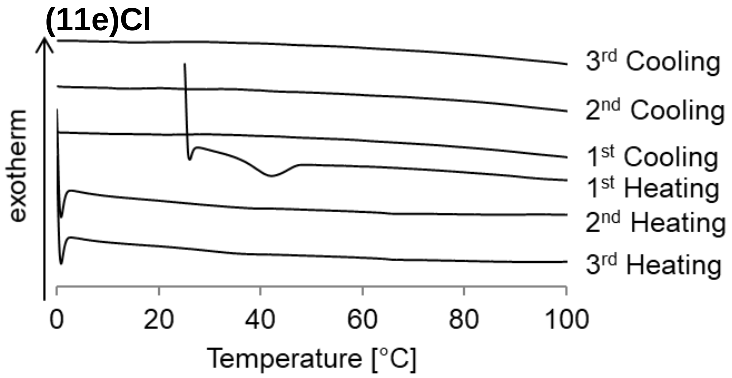
Figure S5. DSC curves of the NaI complexes of [15]crown-5 derivatives **8a**,**d**,**e** and **10a**,**d**,**e** (heating/cooling rate 10 K min^{-1}).

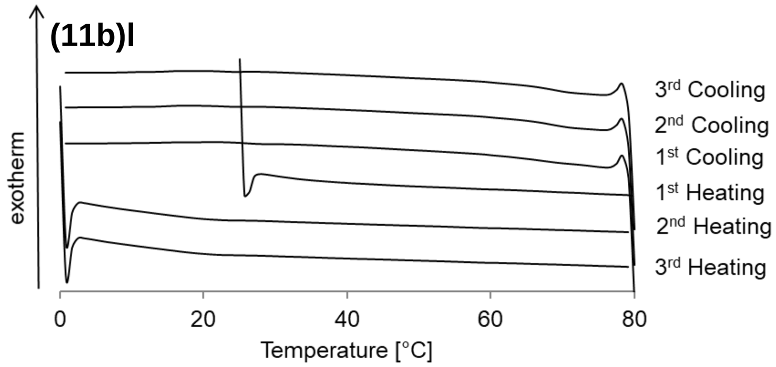

(11a)Cl
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
0 10 20 30 40 50 60
Temperature [°C]

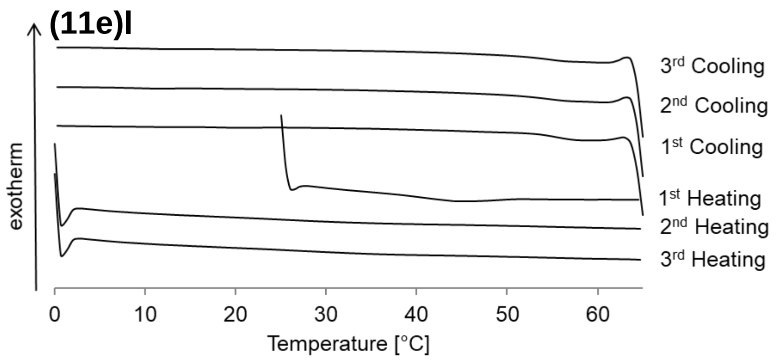

(11b)Cl
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
0 10 20 30 40 50 60
Temperature [°C]

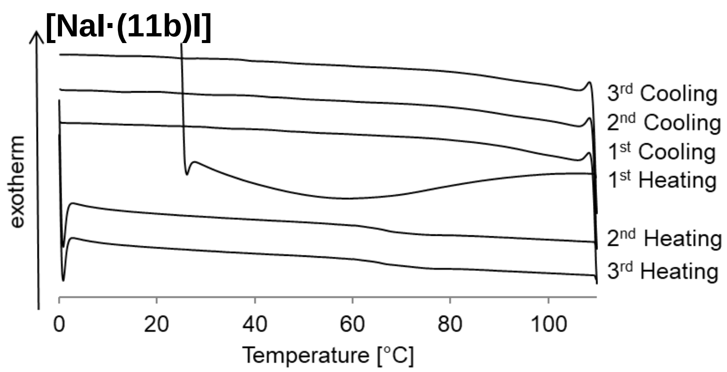

(11c)Cl
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
0 10 20 30 40 50 60
Temperature [°C]


(11d)Cl
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
exotherm
0 10 20 30 40 50 60
Temperature [°C]


(11e)Cl
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
0
20
40
60
80
100
Temperature [°C]


(11b)I
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
0
20
40
60
80
Temperature [°C]


(11e)I
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
0
10
20
30
40
50
60
Temperature [°C]


[NaI·(11b)I]
exotherm
3rd Cooling
2nd Cooling
1st Cooling
1st Heating
2nd Heating
3rd Heating
0
20
40
60
80
100
Temperature [°C]

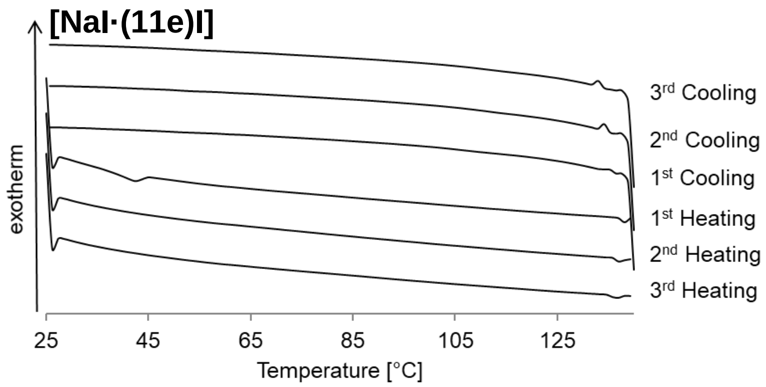
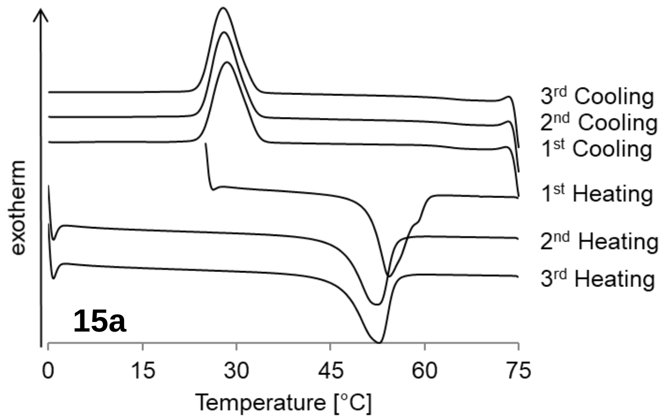


Figure S6. DSC curves of [15]crown-5 guanidinium salts (heating/cooling rate 10 K min^{-1}).



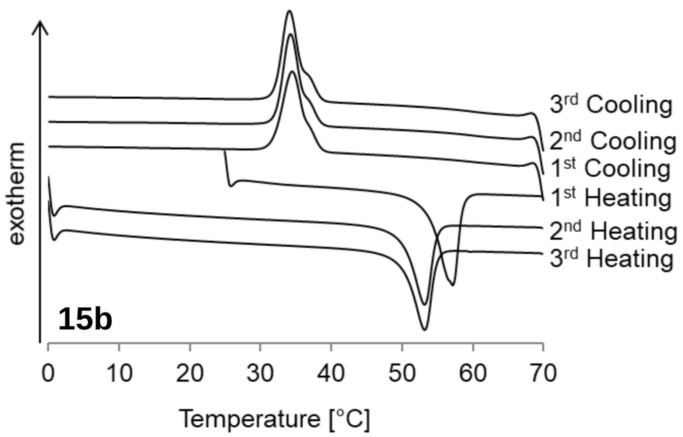


Figure S7. DSC curves of tyrosinates **15a**,**b** (heating/cooling rate 10 K min^{-1}).

5. Polarizing Optical Microscopy (POM)

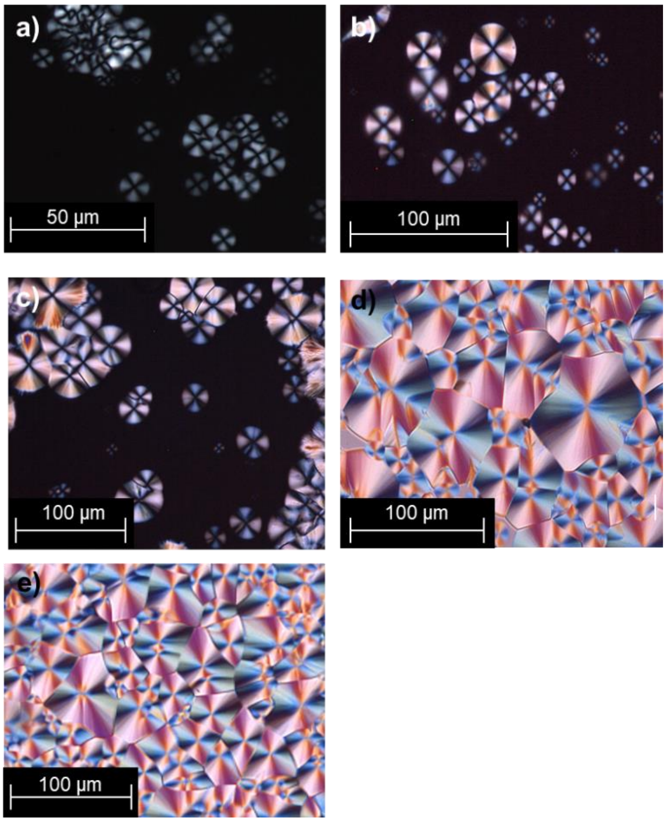


Figure S8. Textures of **8a–e** as seen between crossed polarizers upon cooling from the isotropic liquid (cooling rate 10 K min^{-1}). a) **8a** at 30°C (magnification ×200), b) **8b** at 25°C (magnification ×200), c) **8c** at 43°C (magnification ×200), d) **8d** at 35°C (magnification ×200), and e) **8e** at 21°C (magnification ×100).

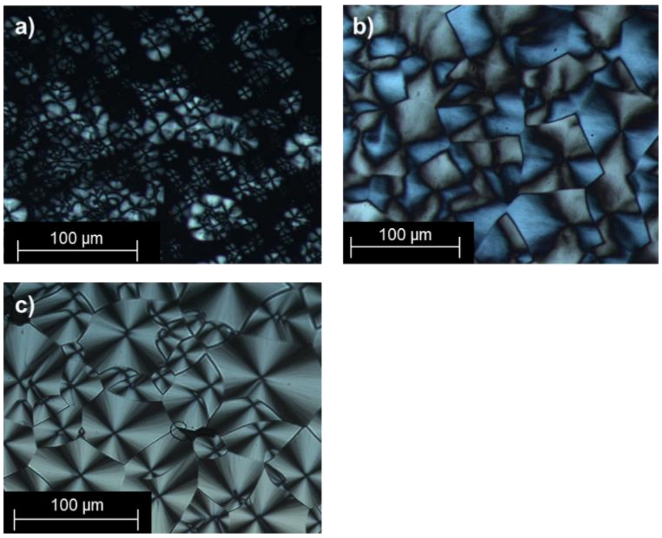


Figure S9. Textures of **9c–e** upon cooling from the isotropic liquid. a) **9c** at 37°C (magnification ×100, cooling rate 30 K min^{-1}), b) **9d** at 47°C (magnification ×100, cooling rate 30 K min^{-1}), c) **9e** at 44°C (magnification ×200, cooling rate 5 K min^{-1}).

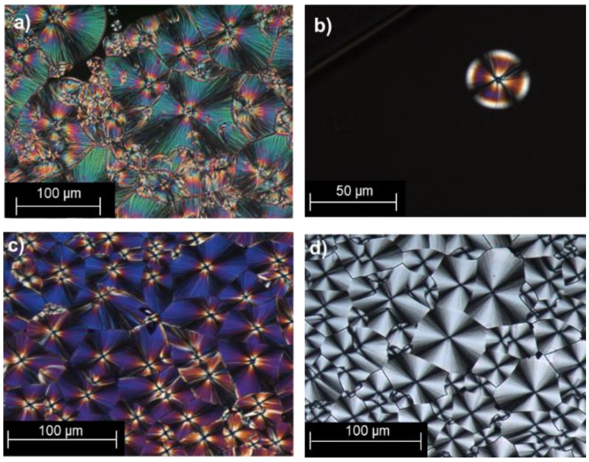


Figure S10. Textures of **12b–e** upon cooling from the isotropic liquid: a) **12b** at 96 °C (cooling rate 5 K min^{-1}, magnification ×200), b) **12c** at 30 °C (cooling rate 5 K min^{-1}, magnification ×200), c) **12d** at 45 °C (cooling rate 20 K min^{-1}, magnification ×100), d) **12e** at 44 °C (cooling rate 20 K min^{-1}, magnification ×100).

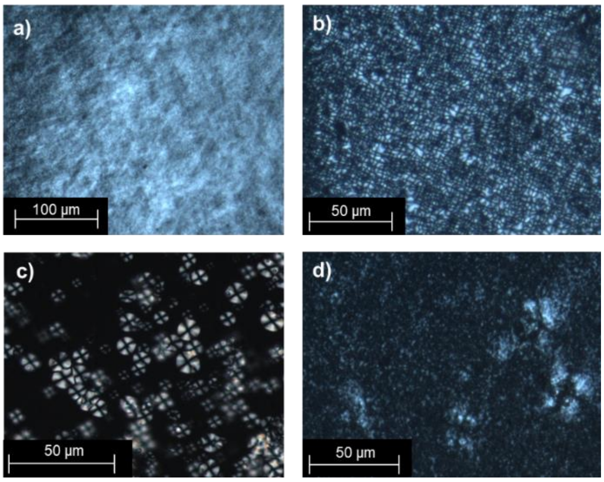


Figure S11. Textures of **13b-e** upon cooling from the isotropic liquid: a) **13b** at 35 °C (cooling rate 5 K min^{-1}, magnification ×100), b) **13c** at 30 °C (cooling rate 5 K min^{-1}, magnification ×100), c) **13d** at 54 °C (cooling rate 30 K min^{-1}, magnification ×200), d) **13e** at 41 °C, (cooling rate 20 K min^{-1}, magnification ×100).

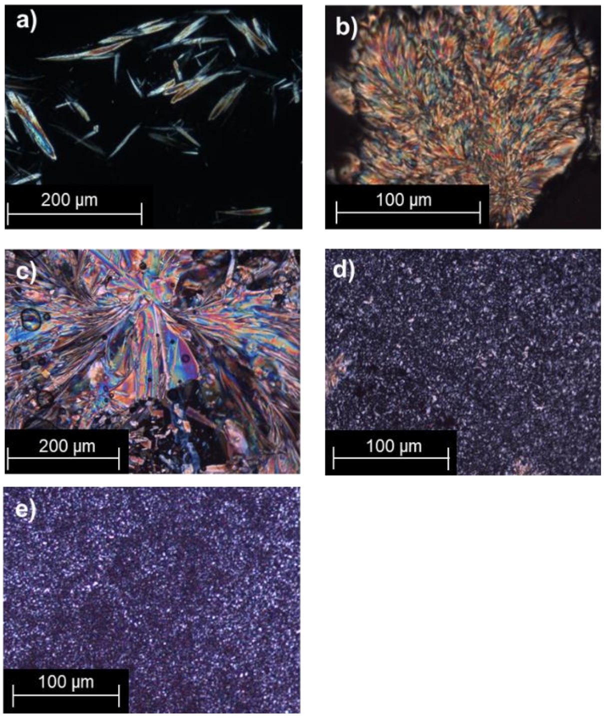


Figure S12. Textures of **10a**–**e** upon cooling from the isotropic liquid (cooling rate 5 K min^{-1}). a) **10a** at 23°C (magnification ×100), b) **10b** at 25°C (magnification ×200), c) **10c** at 25°C (magnification ×100), d) **10d** at 18°C (magnification ×200), e) **10e** at 30°C (magnification ×100).

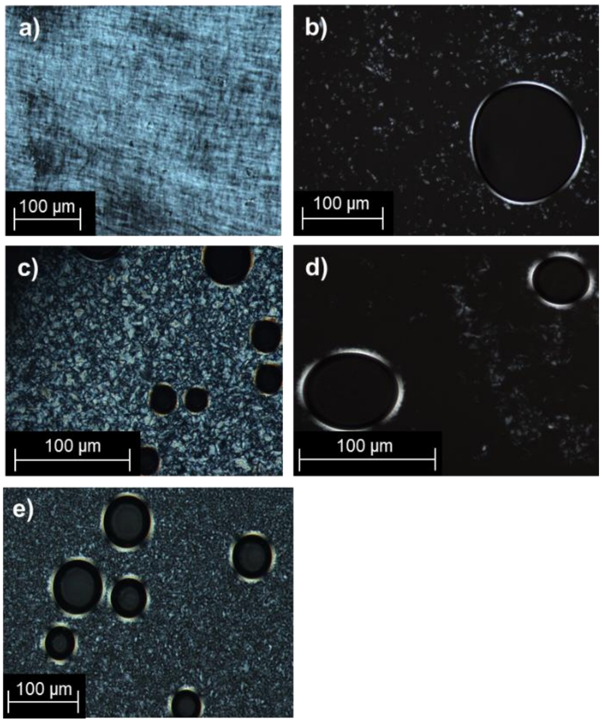


Figure S13. Textures of complexes upon cooling from the isotropic liquid (cooling rate 5 K min^{-1}). a) [**NaI·8a**] at 30°C (magnification ×100), b) [**NaI·8d**] at 99°C (magnification ×100), c) [**NaI·8d**] at 114°C on silylated glass slides (magnification ×200), d) [**NaI·8e**] at 110°C (magnification ×200), e) [**NaI·8e**] at 100°C on silylated glass slides (magnification ×100).

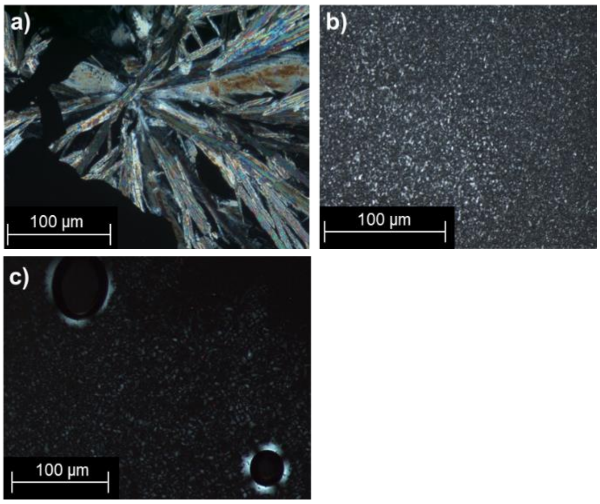


Figure S14. Textures of complexes upon cooling from the isotropic liquid. a) [**NaI·10a**] at 35°C (cooling rate 20 K min^{-1}, magnification ×200), b) [**NaI·10d**] at 55°C (cooling rate 20 K min^{-1}, magnification ×200), c) [**NaI·10e**] at 88°C (cooling rate 5 K min^{-1}, magnification ×100).

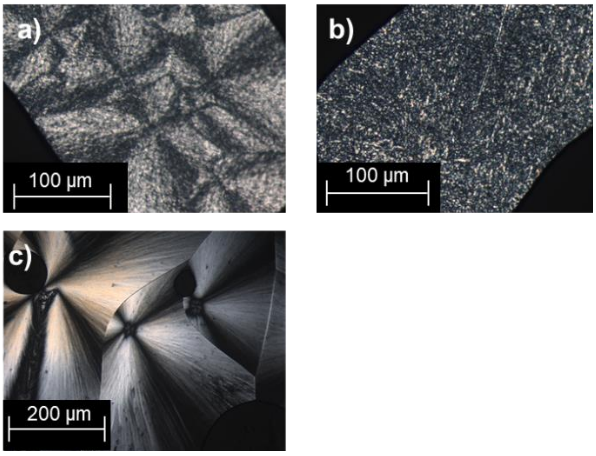


Figure S15. Textures of hydrochlorides of **10** upon cooling from the isotropic liquid (cooling rate 5 K min^{-1}, magnification ×100). a) **10c·HCl** at 116°C, b) **10d·HCl** at 120°C, c) **10e·HCl** at 117°C.

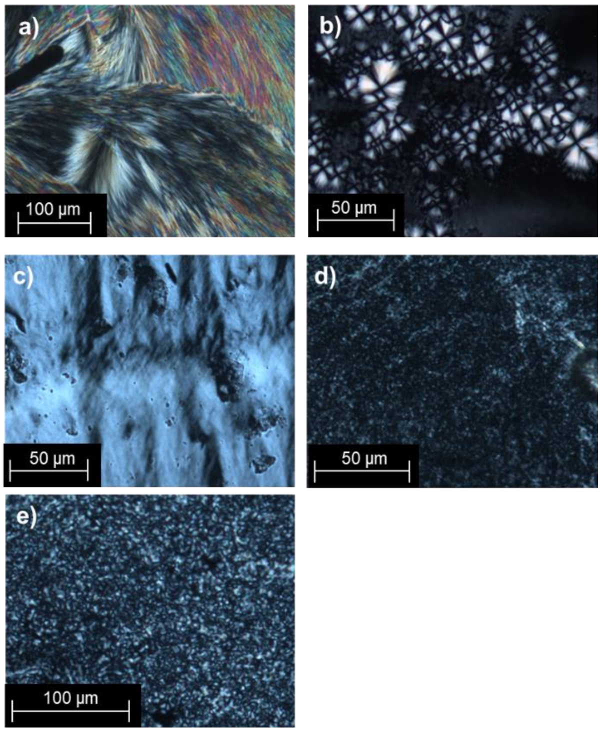


Figure S16. Textures of guanidinium chlorides (**11a**–**e**)**Cl** upon cooling from the isotropic liquid (cooling rate 5 K min^{-1}). a) (**11a**)**Cl** at 23°C (magnification ×100), b) (**11b**)**Cl** at 25°C (magnification ×100), c) (**11c**)**Cl** at 30°C (magnification ×200), d) (**11d**)**Cl** at 18°C (magnification ×200), e) (**11e**)**Cl** at 21°C (magnification ×100).

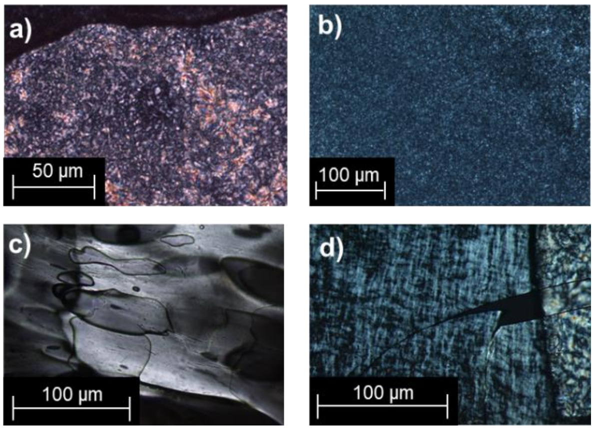


Figure S17. Textures of guanidinium iodides and their NaI complexes upon cooling from the isotropic liquid (cooling rate 5 K min^{-1}). a) (**11b**)**I** at 23°C (magnification ×200), b) (**11e**)**I** at 20°C (magnification ×100), c) [**NaI·(11b)I**] at 30°C (magnification ×200), d) [**NaI·(11e)I**] at 18°C (magnification ×200).

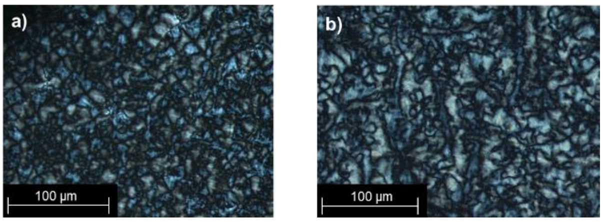


Figure S18. Textures of **15a**,**b** upon cooling from the isotropic liquid (cooling rate 5 K min^{-1}, magnification ×200**)**: a) **15a** at 33 °C, b) **15b** at 39 °C.

6. X-ray diffraction (XRD)

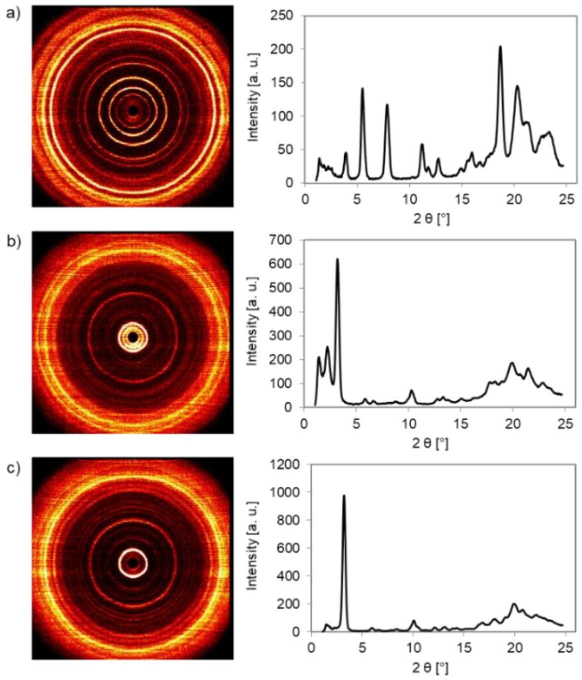


Figure S19. Left: WAXS diffraction patterns of the soft crystalline phases of a) **8a** at 22°C, b) **8d** at 22°C, c) **8e** at 22°C, right: the corresponding X-ray scattering profiles.

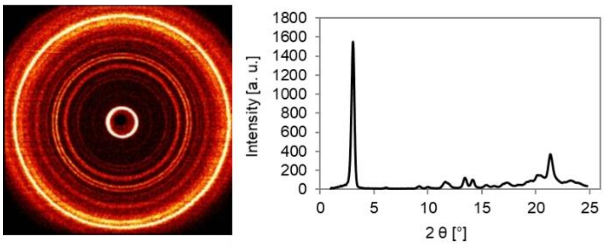


Figure S20. Left: WAXS diffraction pattern of amine **10d** at 31°C, right: the corresponding X-ray scattering profile.

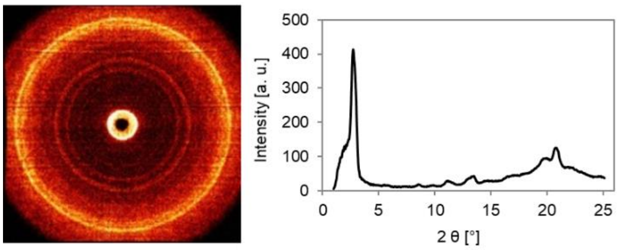


Figure S21. Left: WAXS diffraction pattern of *N*-Z protected amine **12e** at 45°C, right: the corresponding X-ray scattering profile.

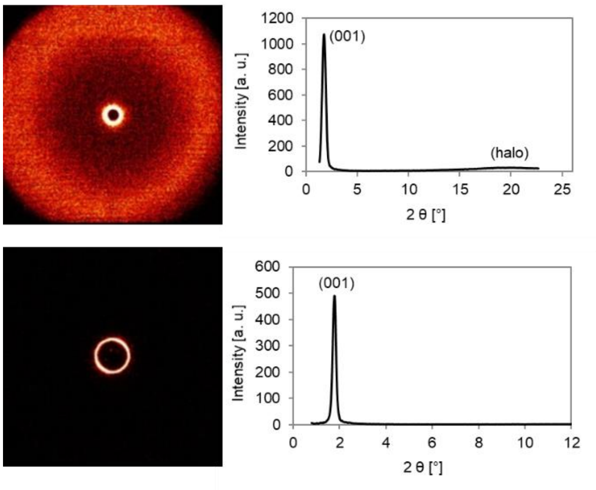


Figure S22. Left: WAXS diffraction pattern of the LC phase of **[NaI · 8d]** (above) and SAXS diffraction pattern (below) at 64°C, right: the corresponding X-ray scattering profiles.

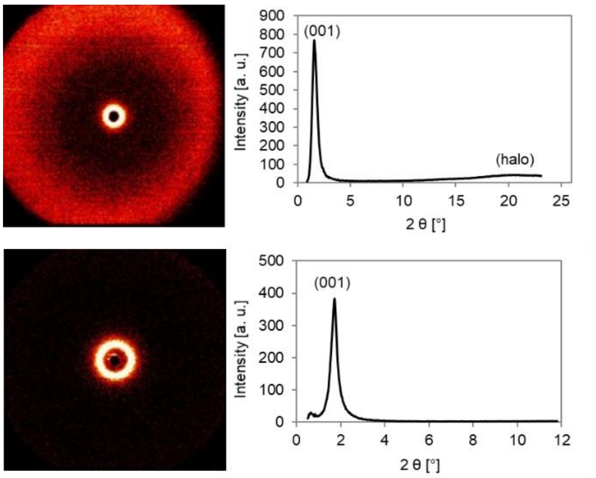


Figure S23. Left: WAXS diffraction pattern of the LC phase of **[NaI · 10d]** (above) and SAXS diffraction pattern (below) at 50°C, right: the corresponding X-ray scattering profiles.

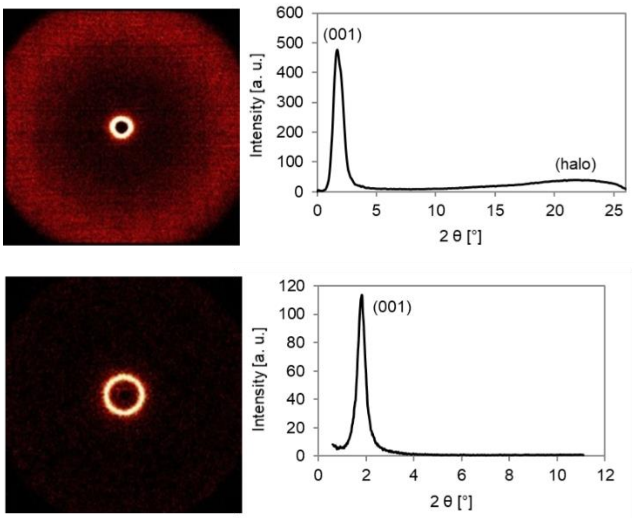
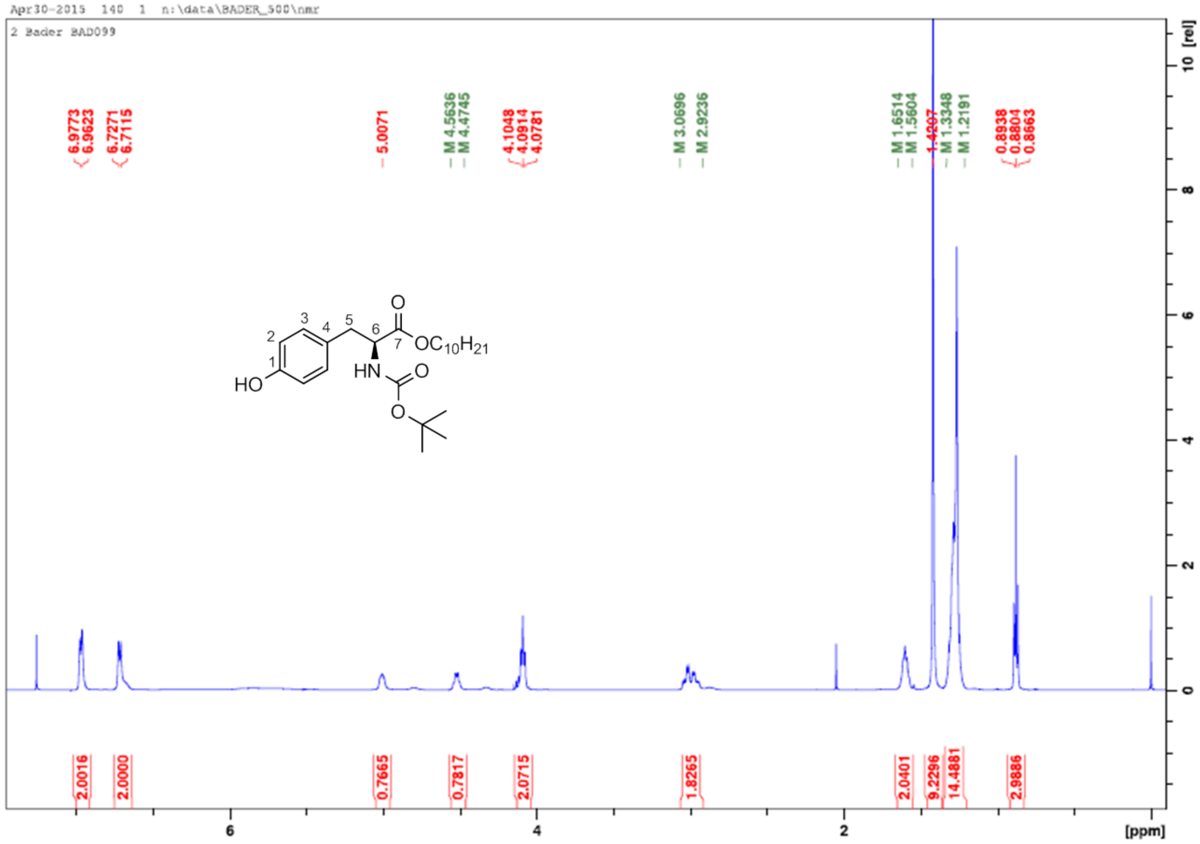
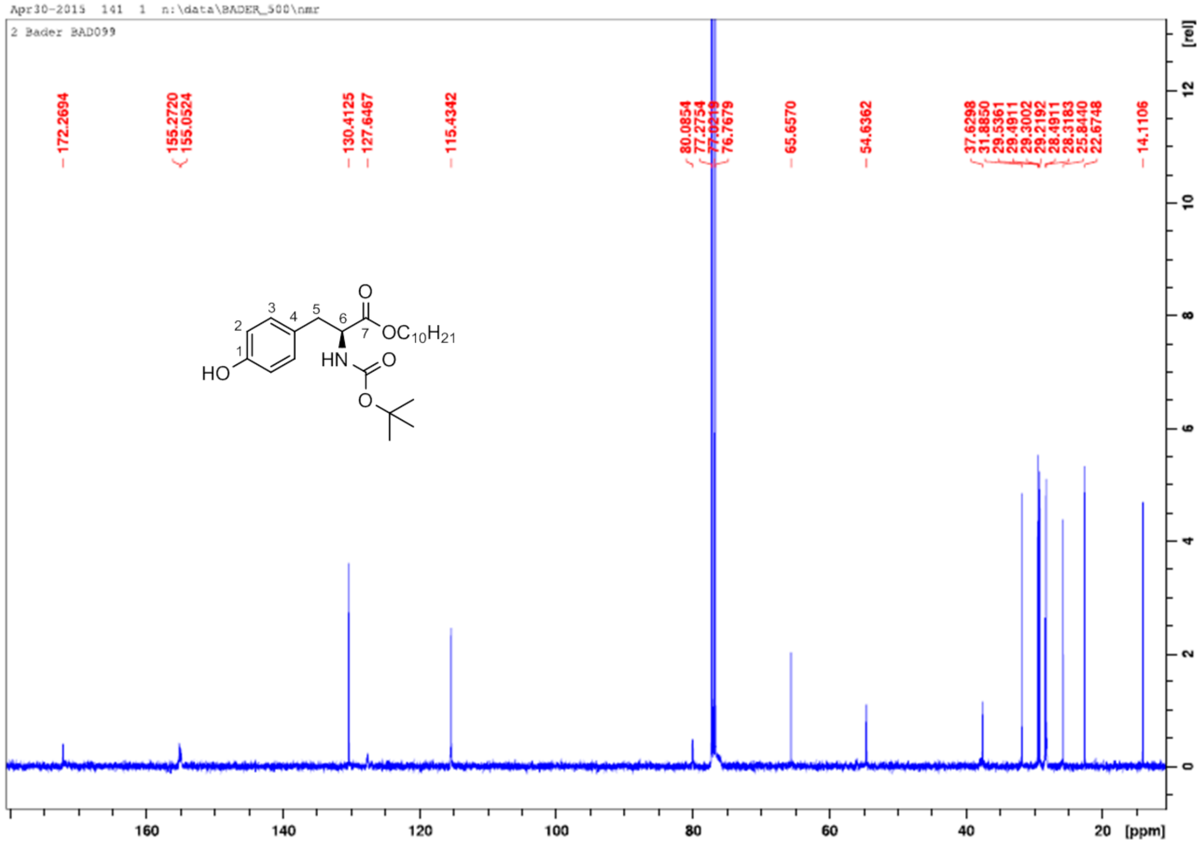
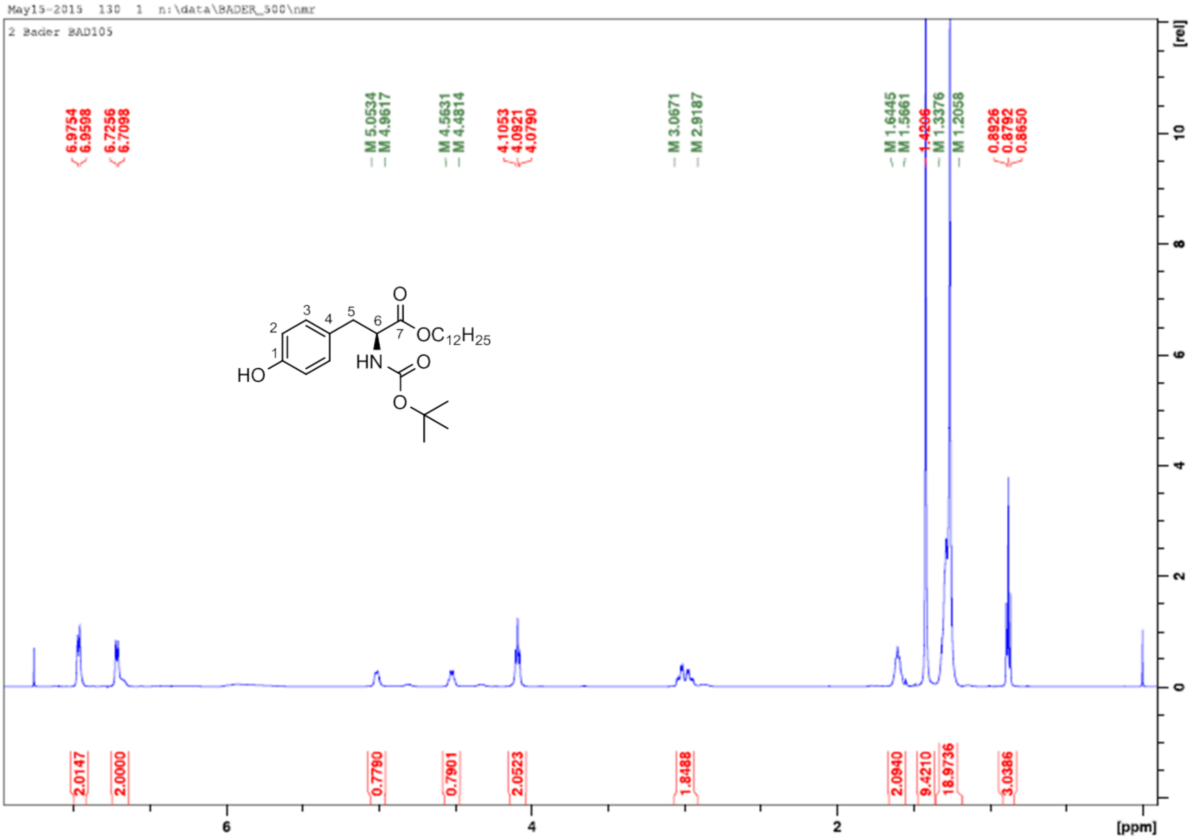


Figure S24. Left: WAXS diffraction pattern of the LC phase of **[NaI · 10e]** at 80°C (above) and SAXS diffraction pattern at 83°C (below), right: the corresponding X-ray scattering profiles.

7. NMR data of all new compounds



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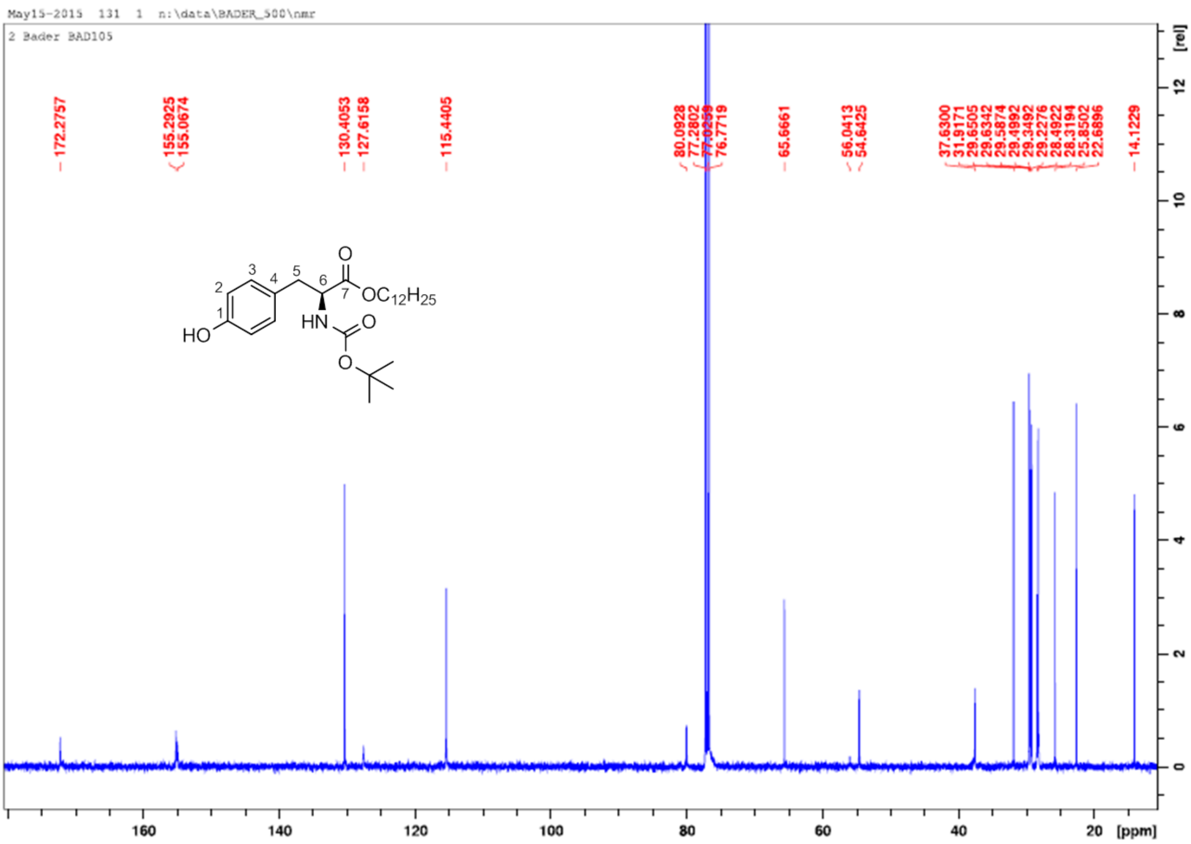
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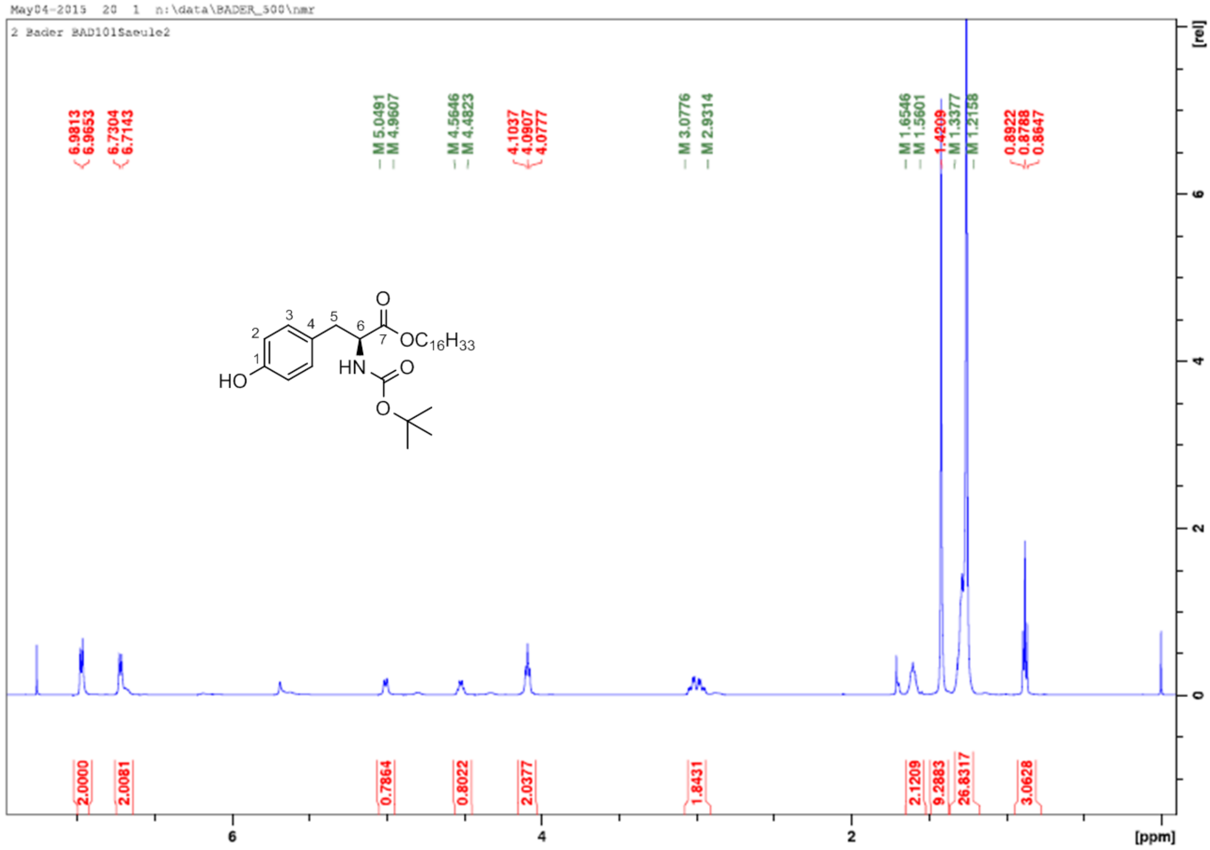
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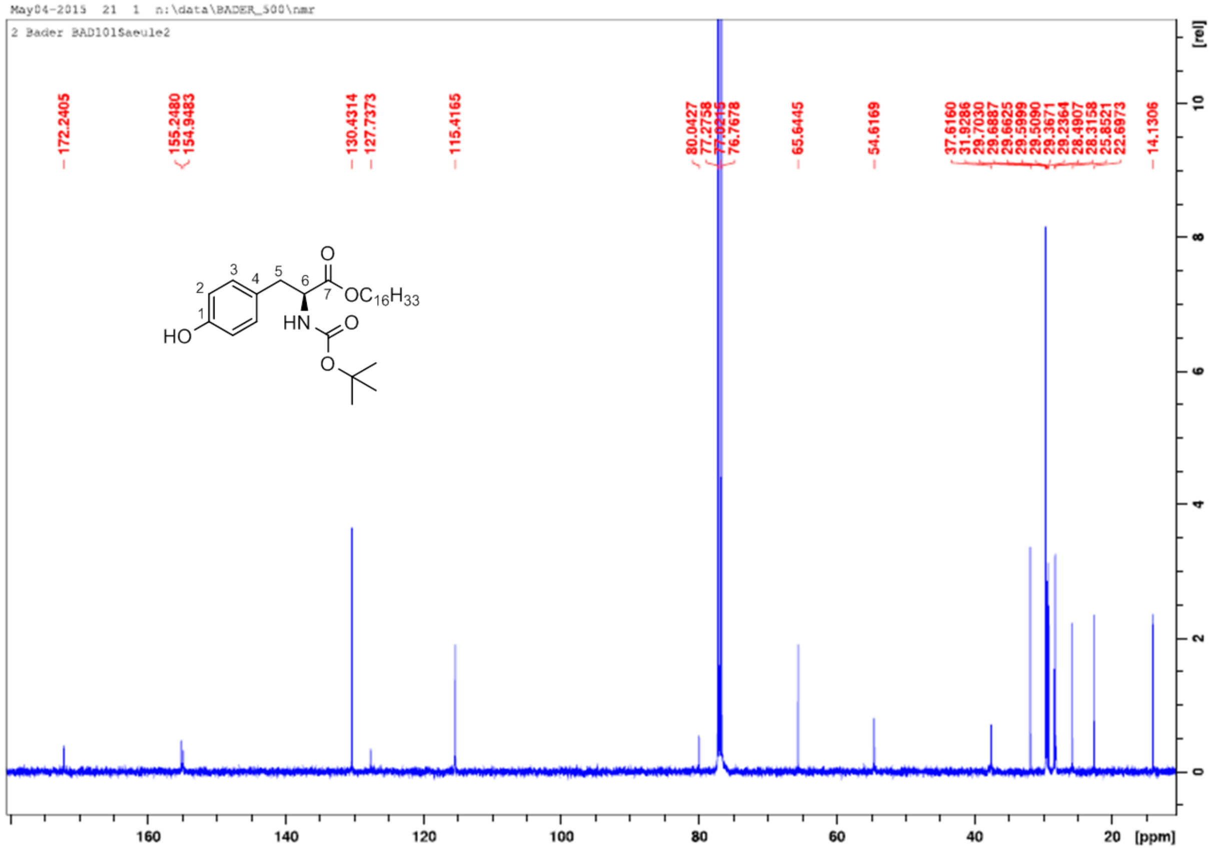
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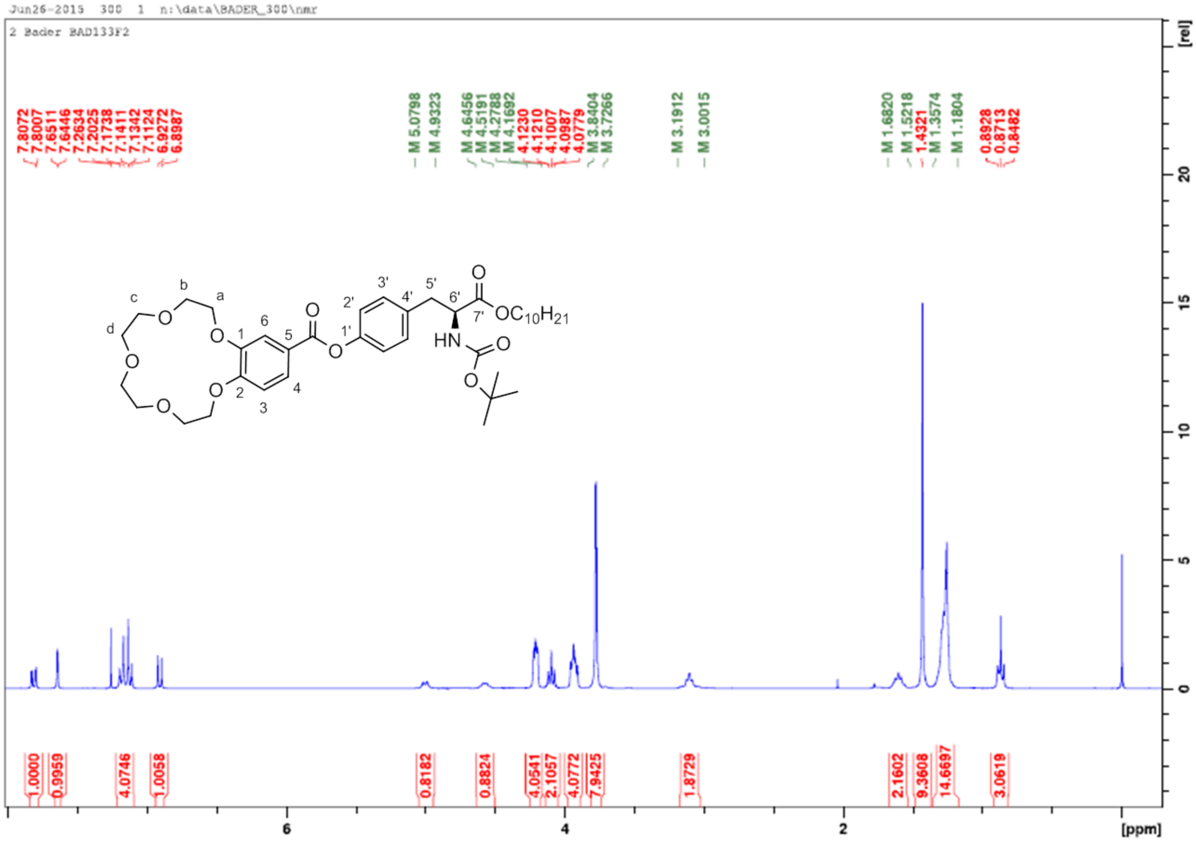
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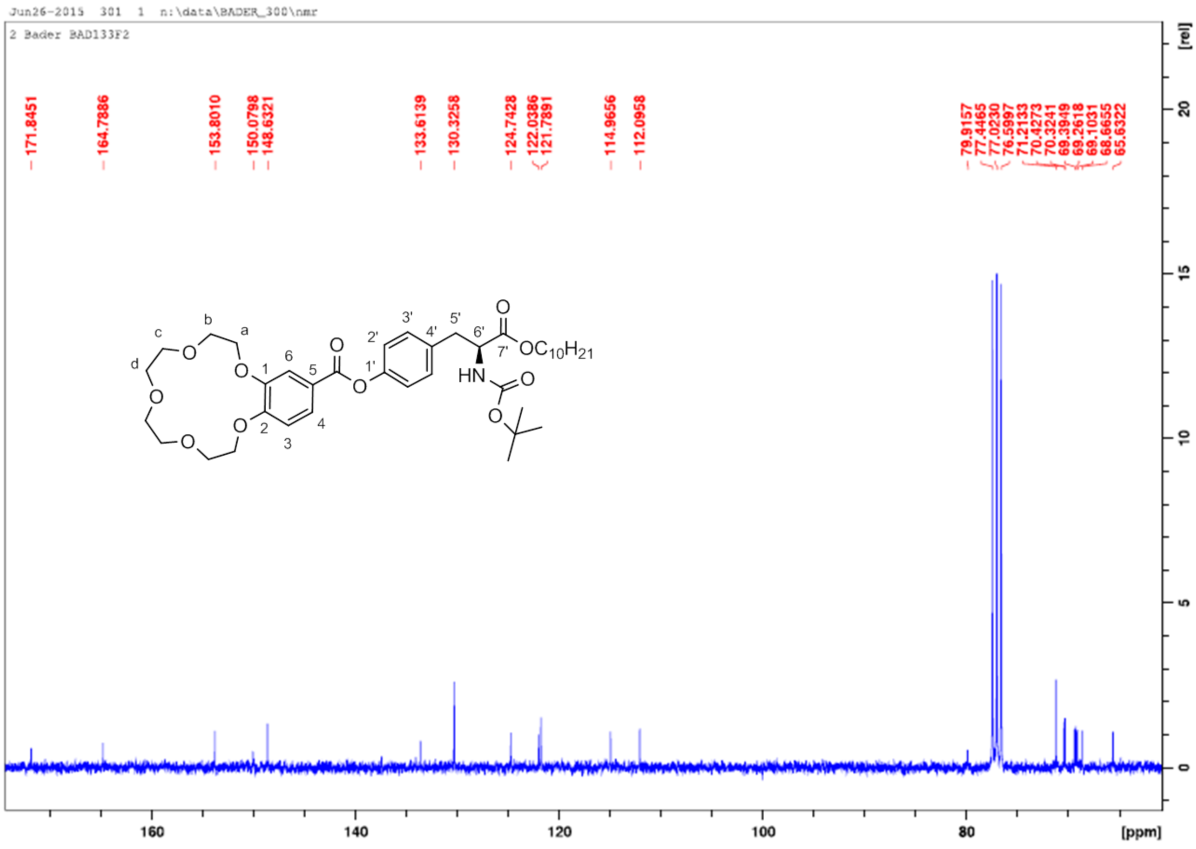
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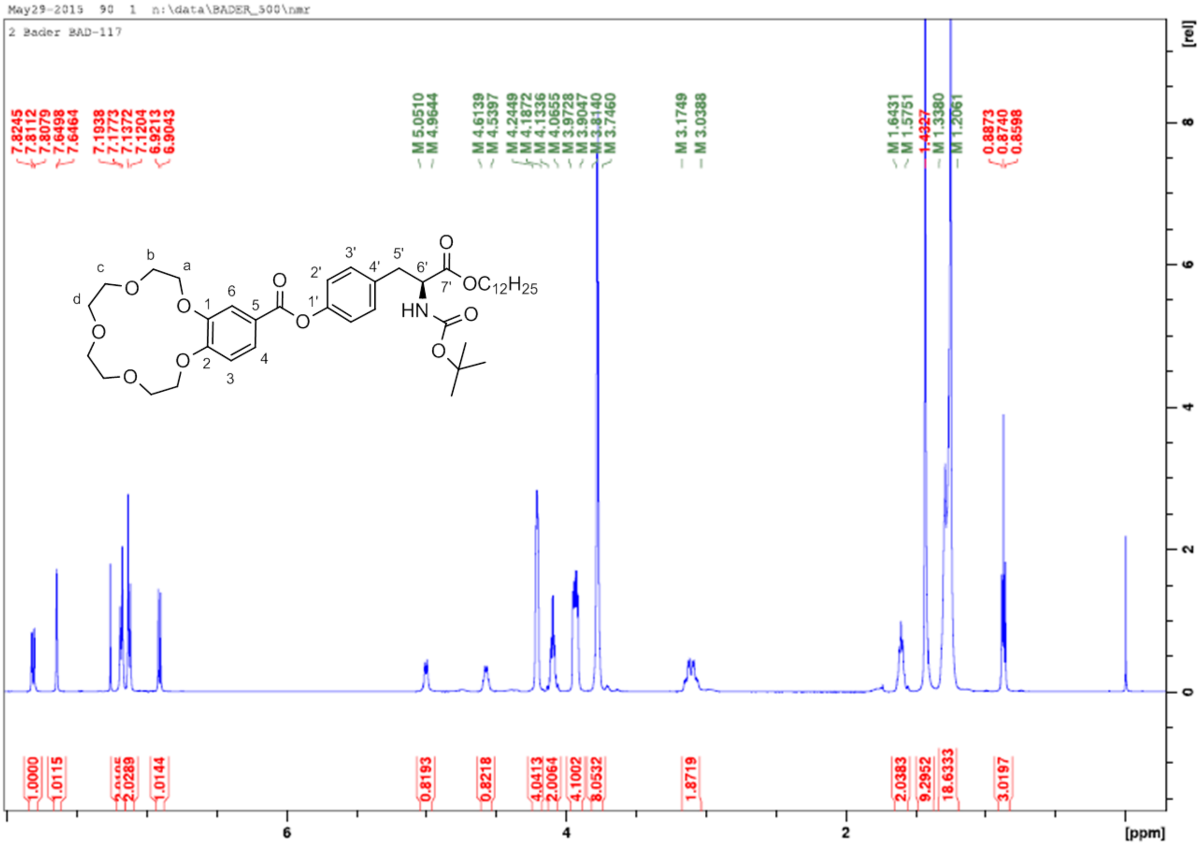
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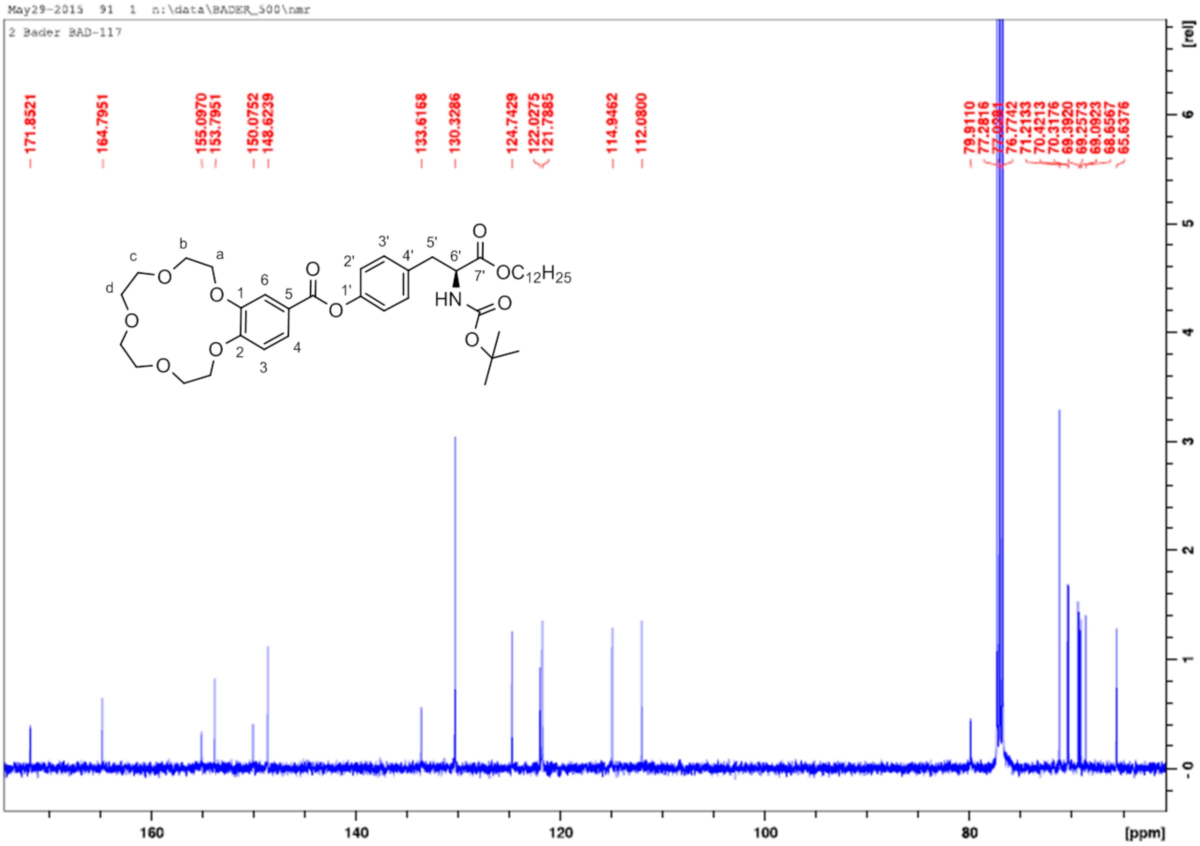
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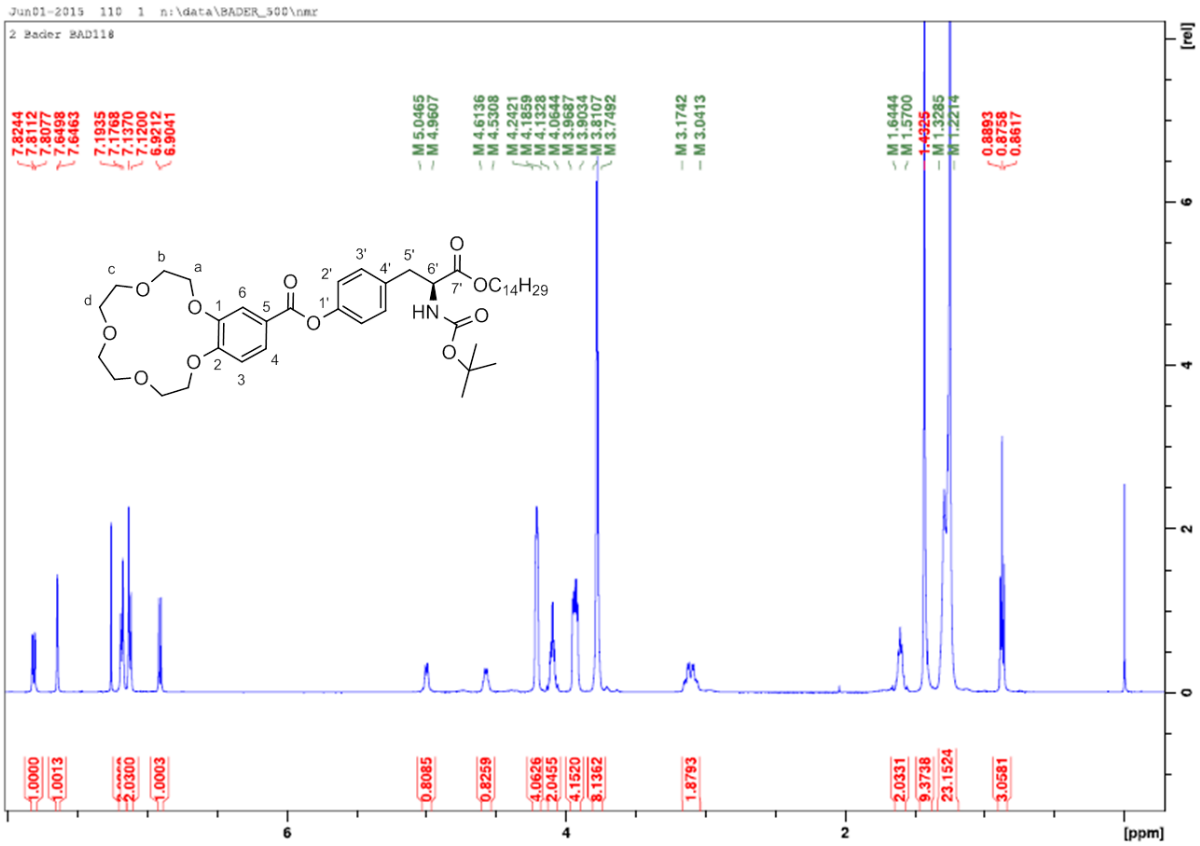

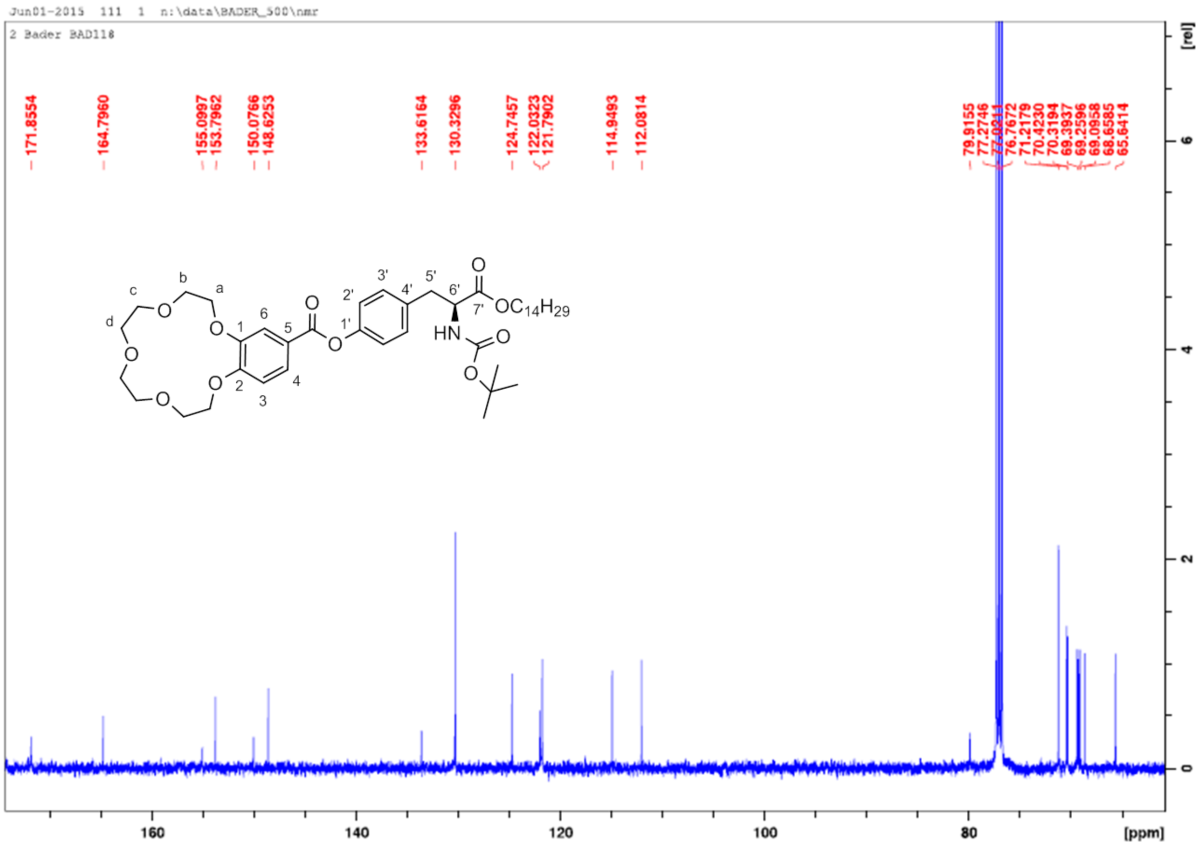

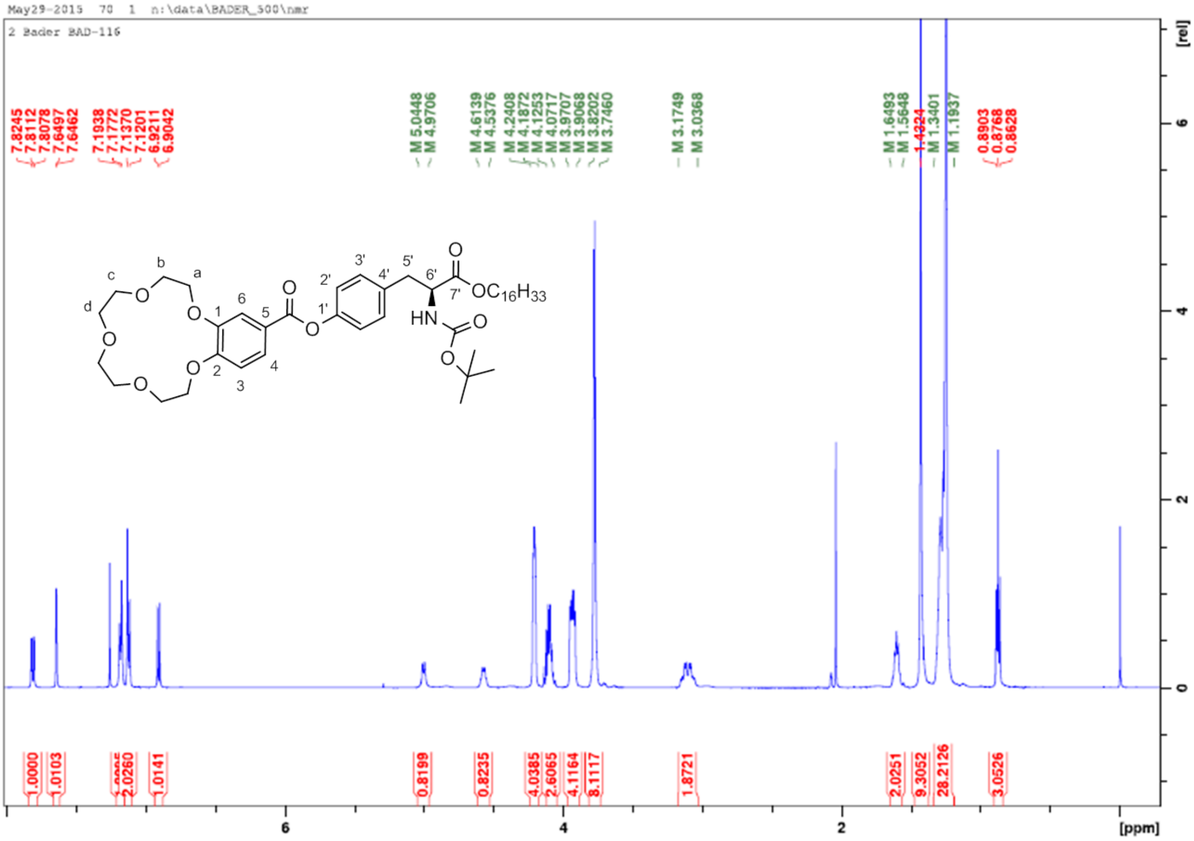

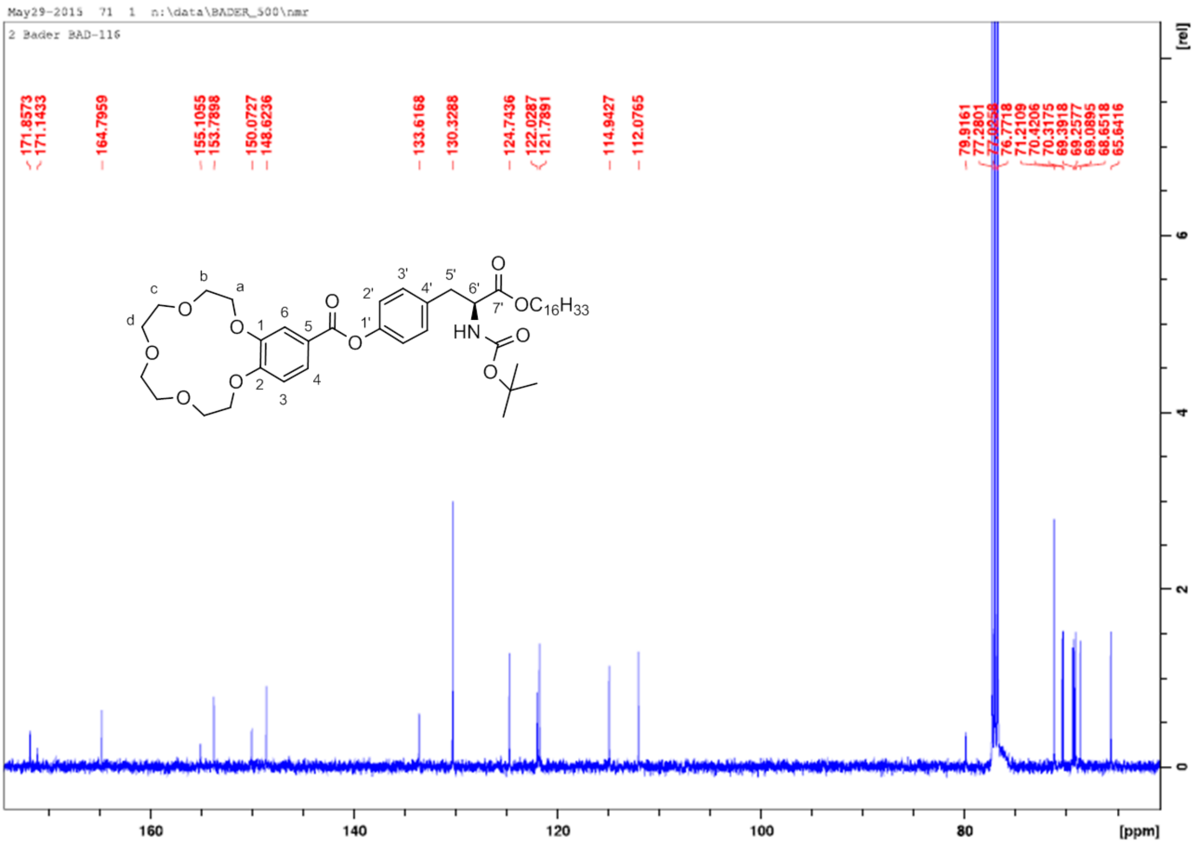

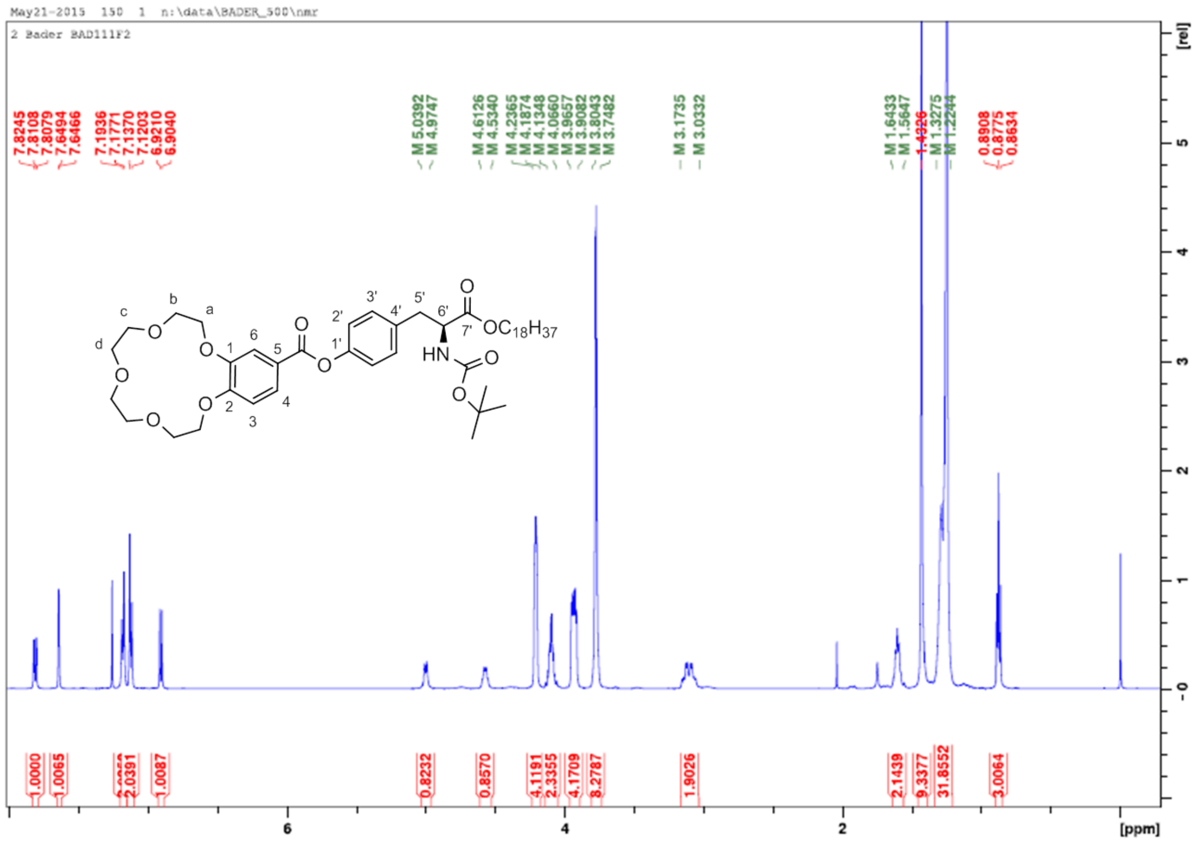

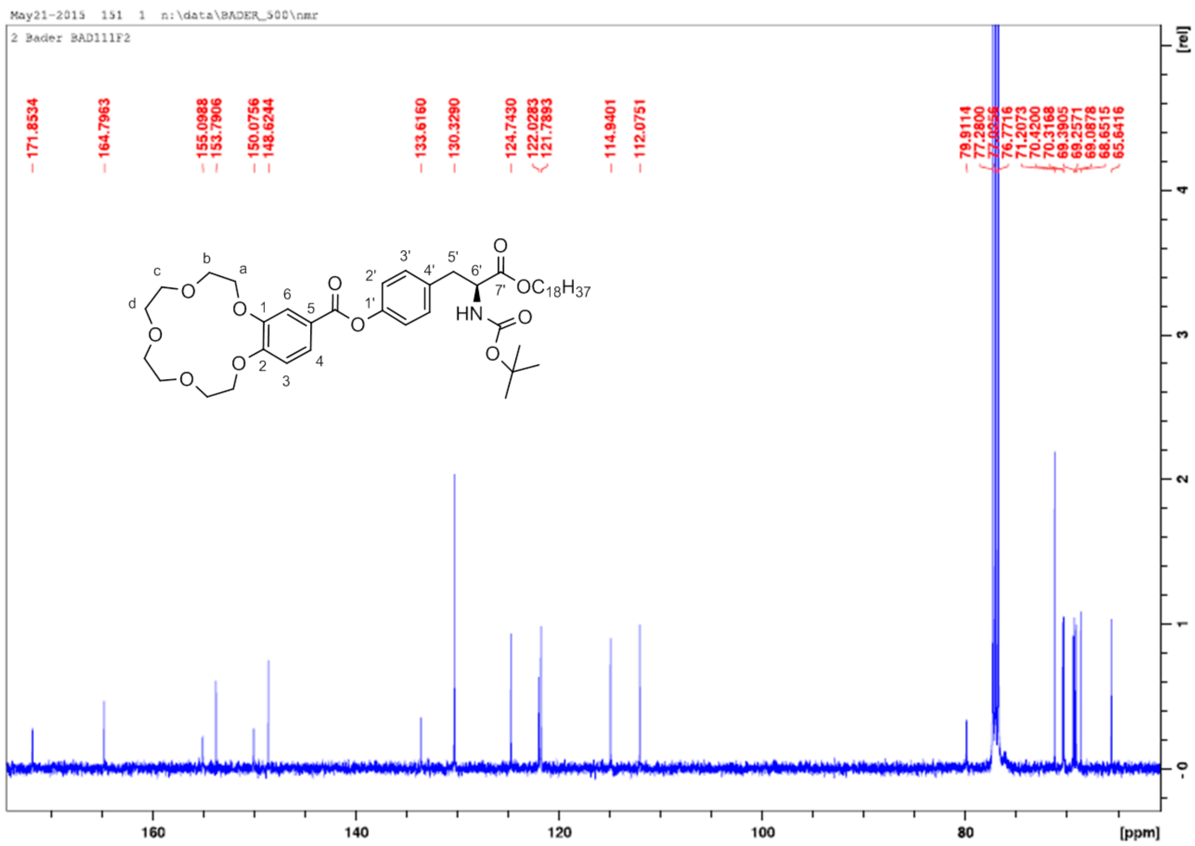

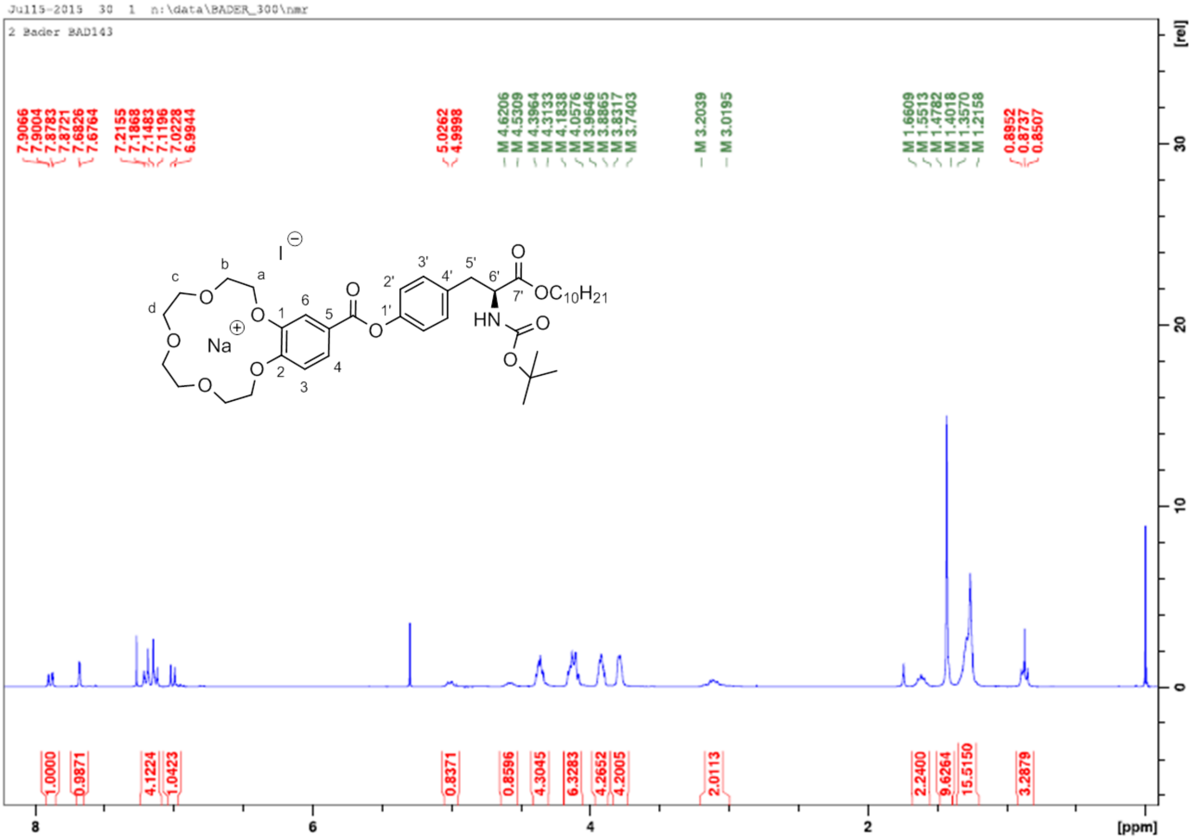

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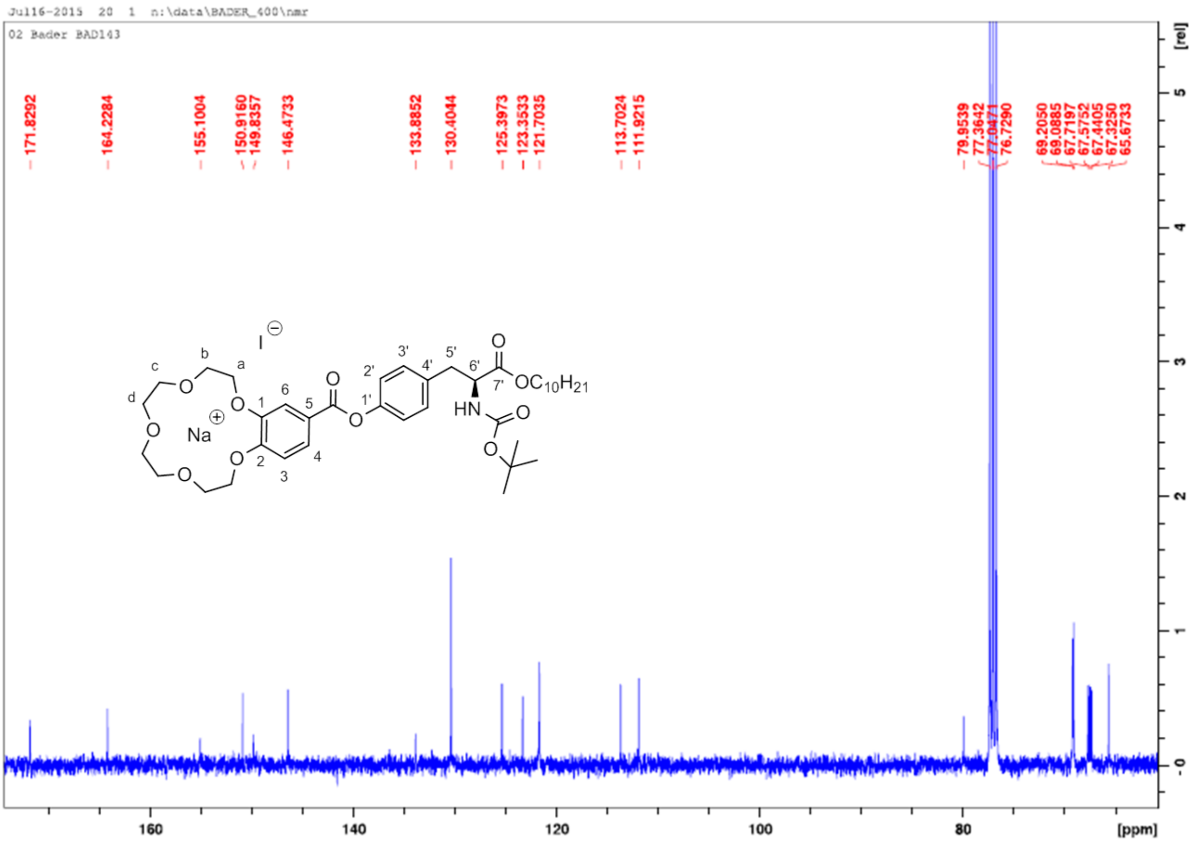

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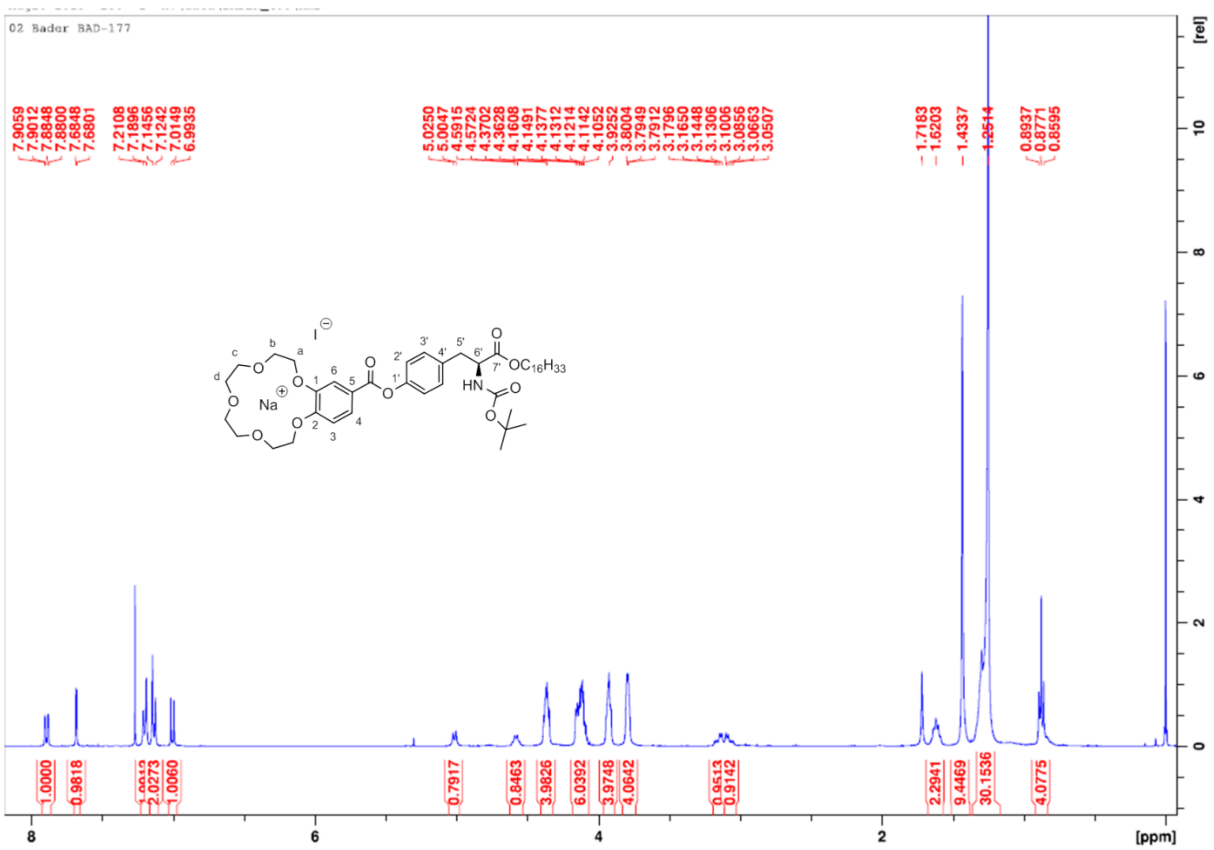
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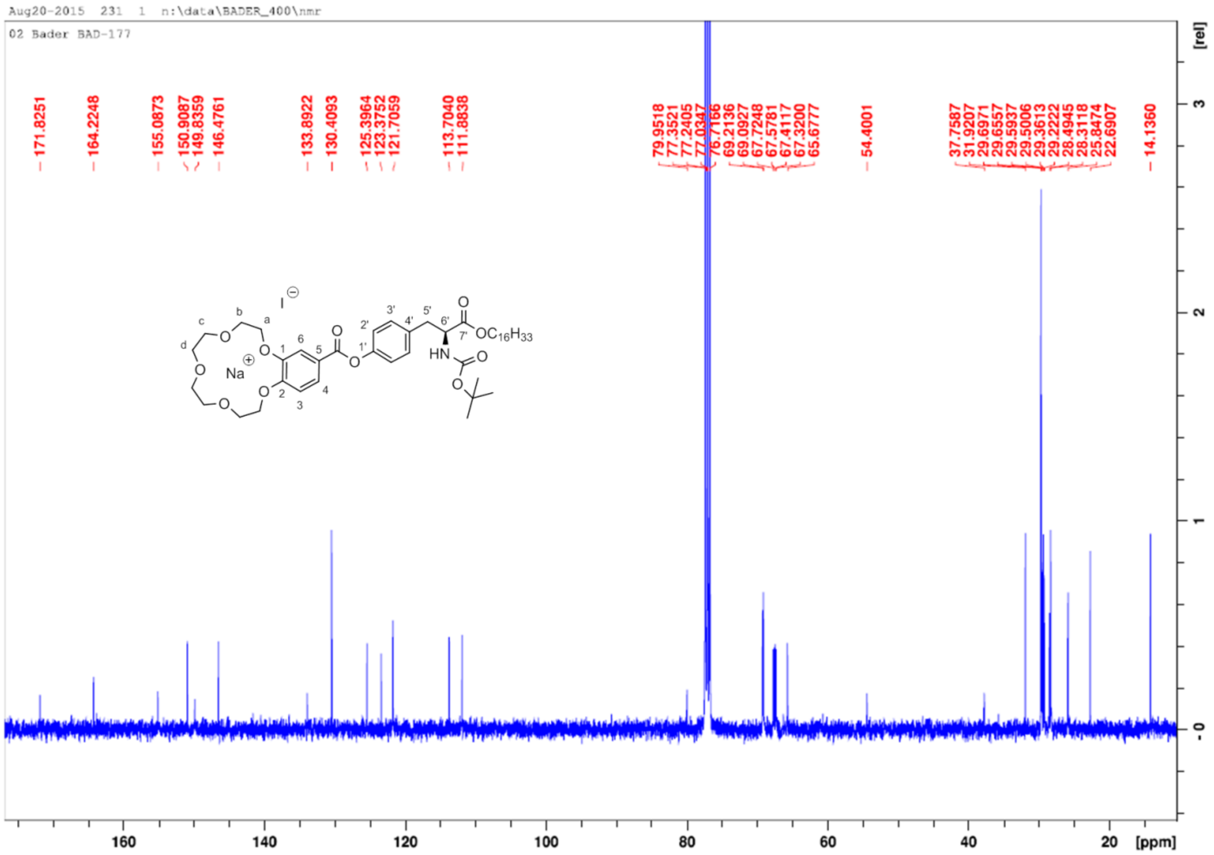
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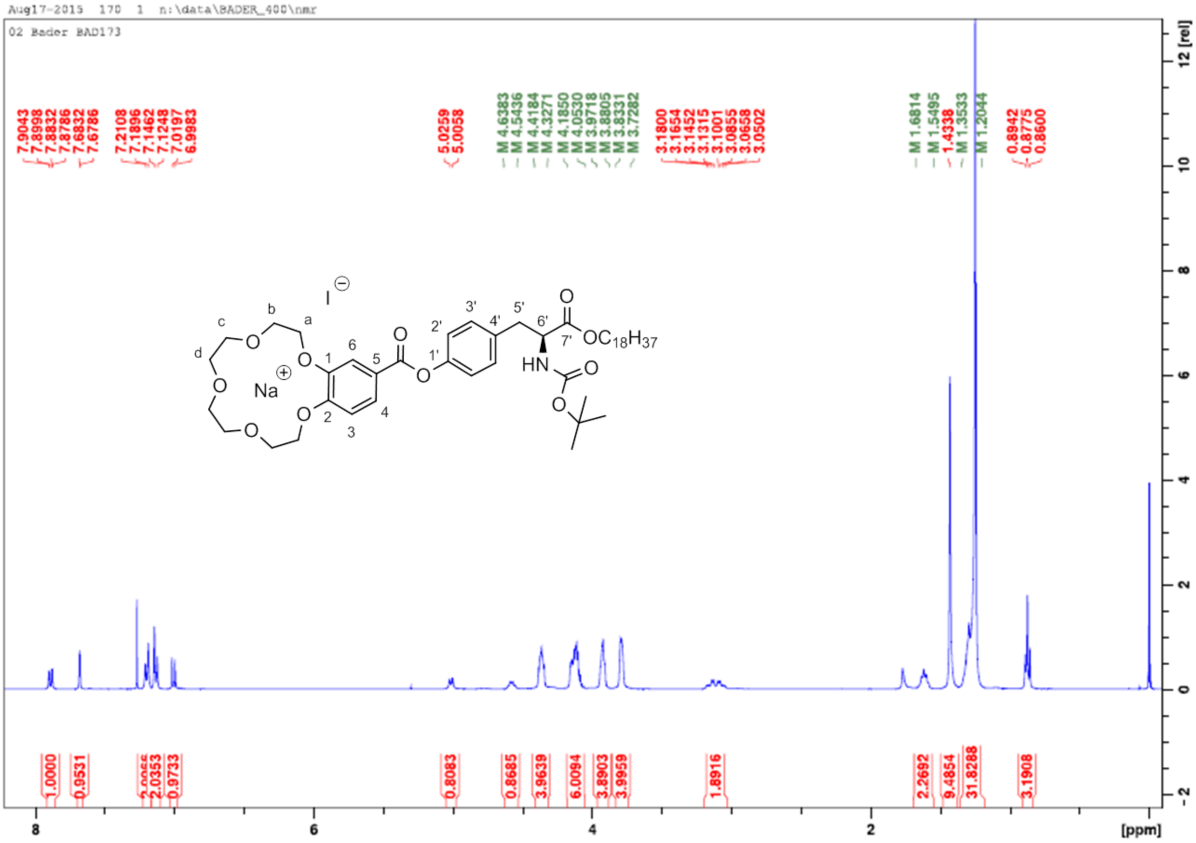
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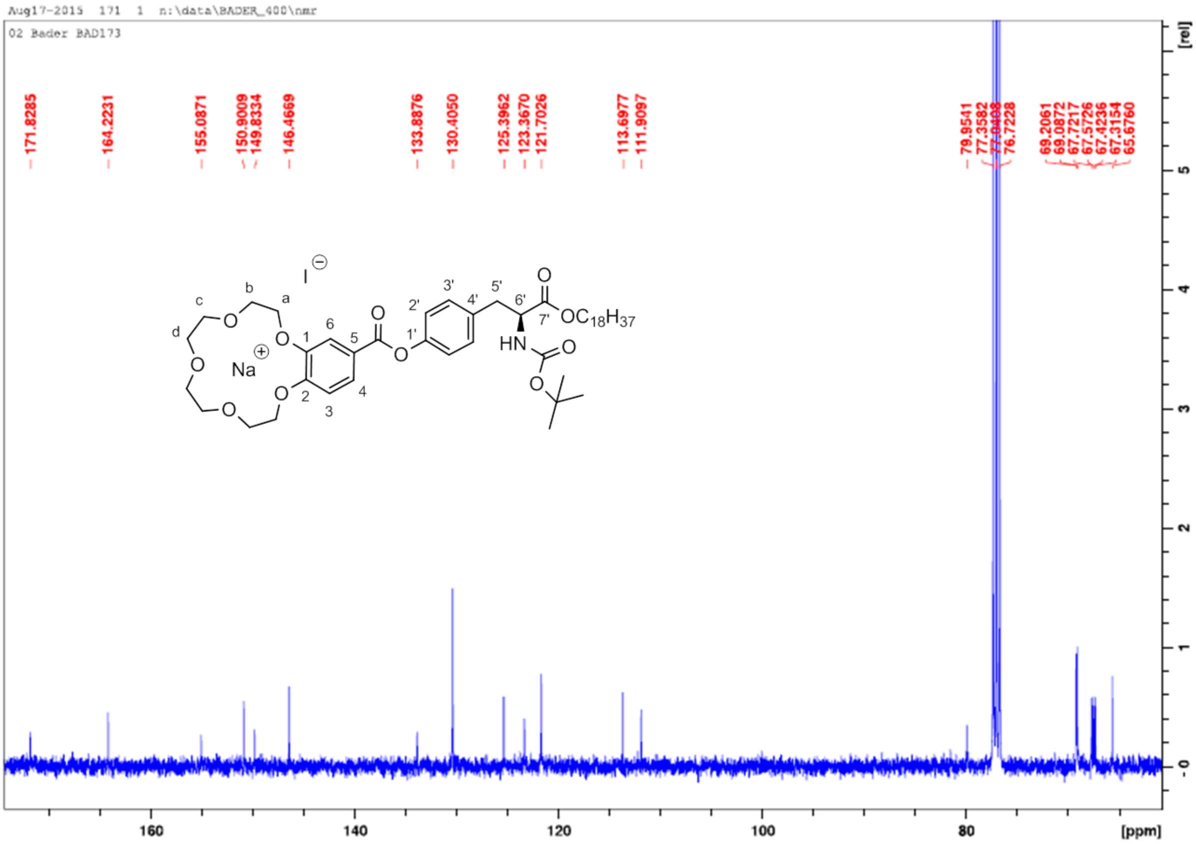
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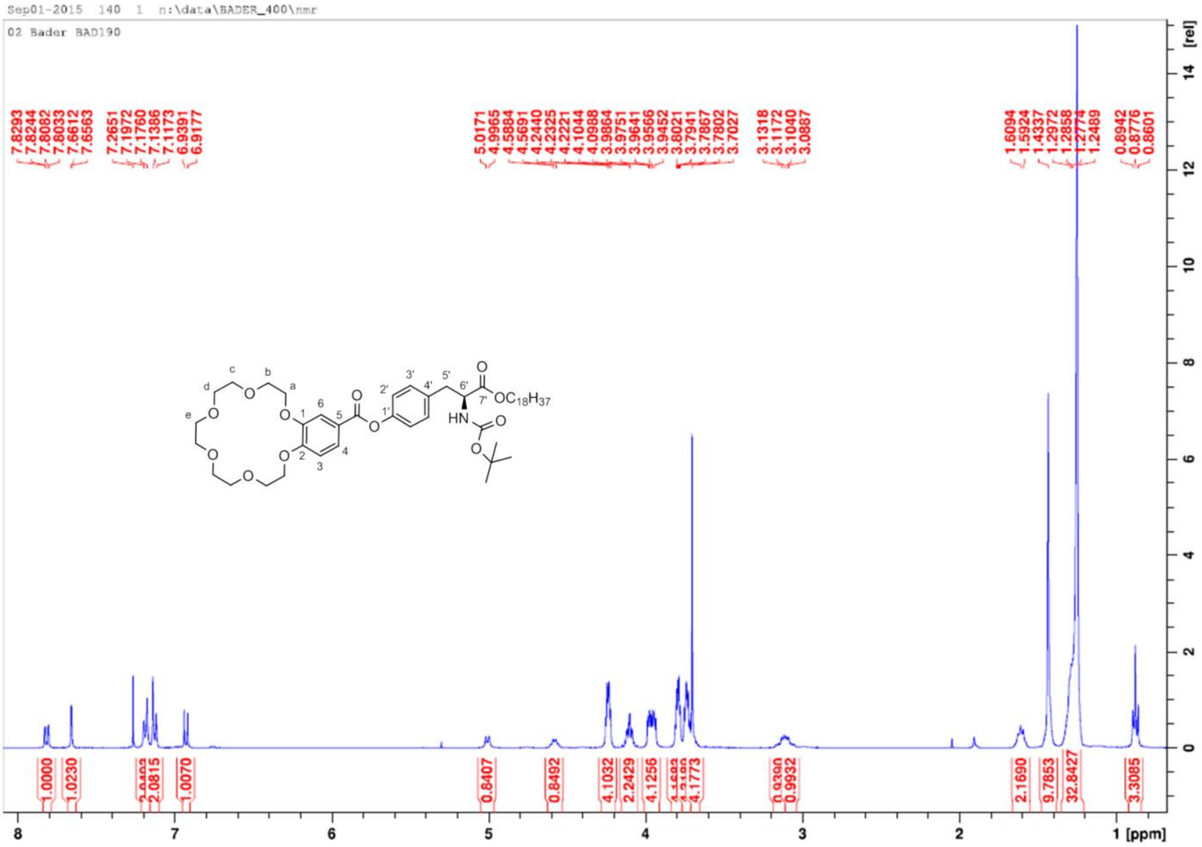

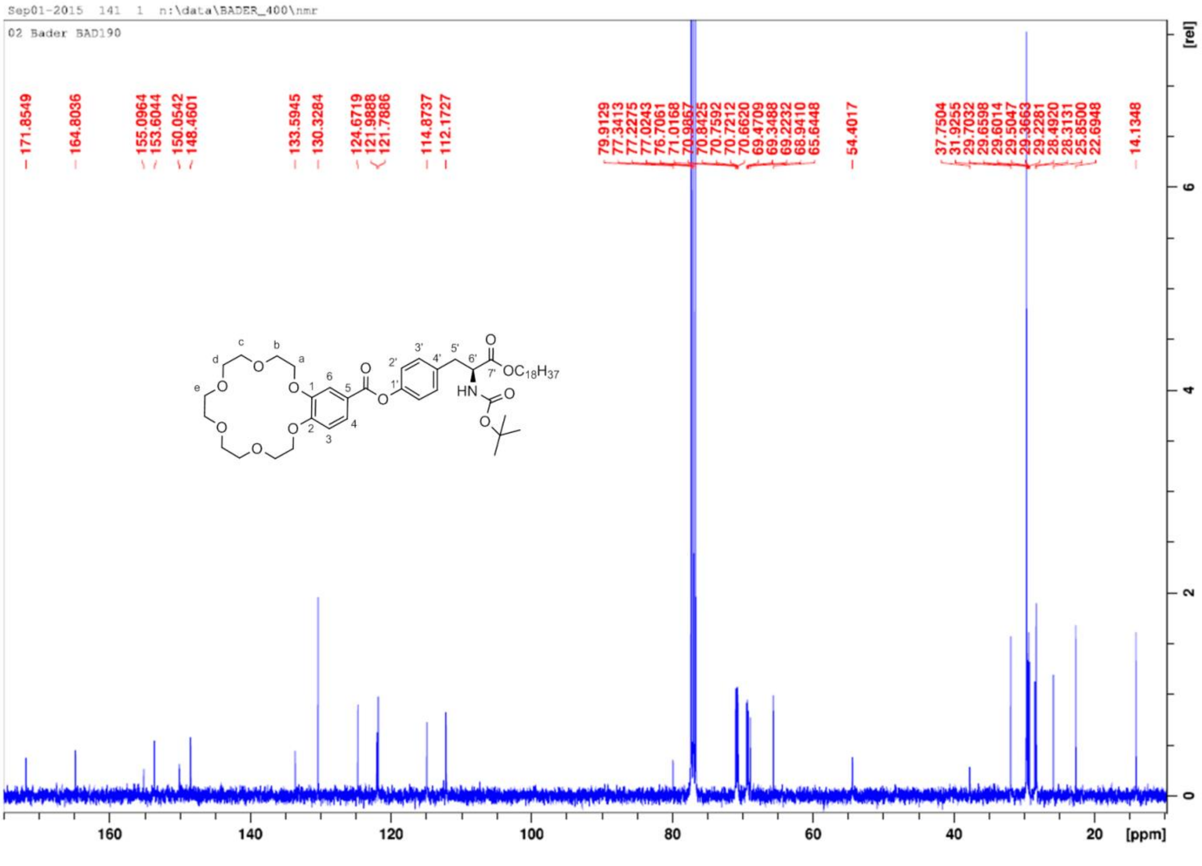

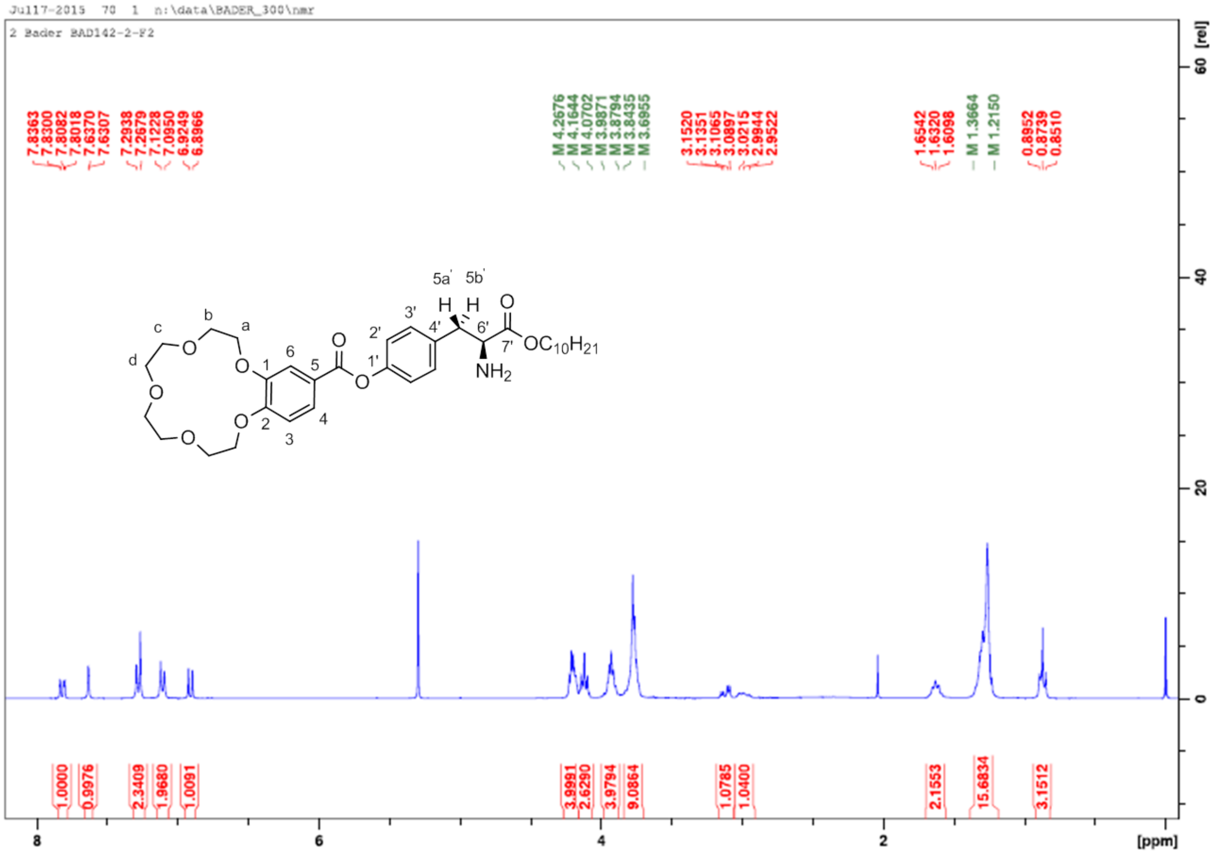

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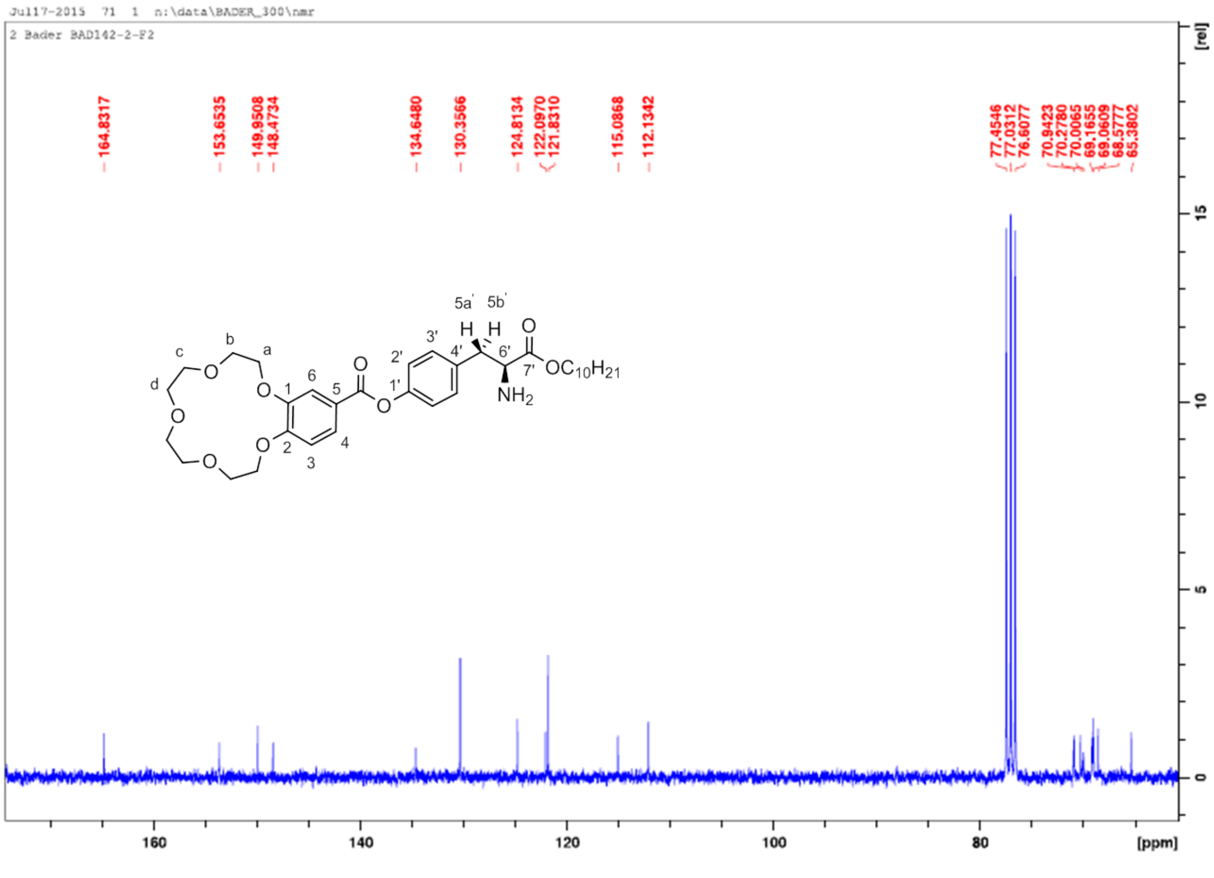

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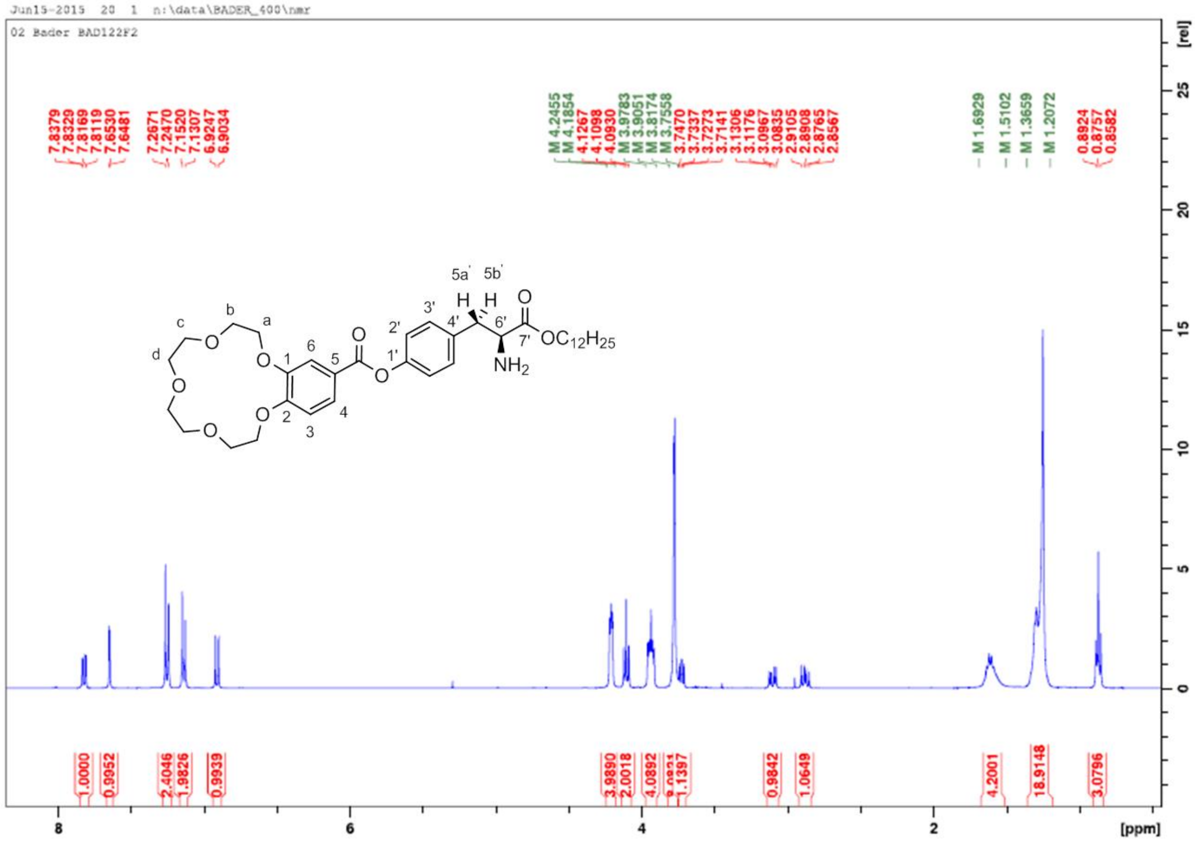

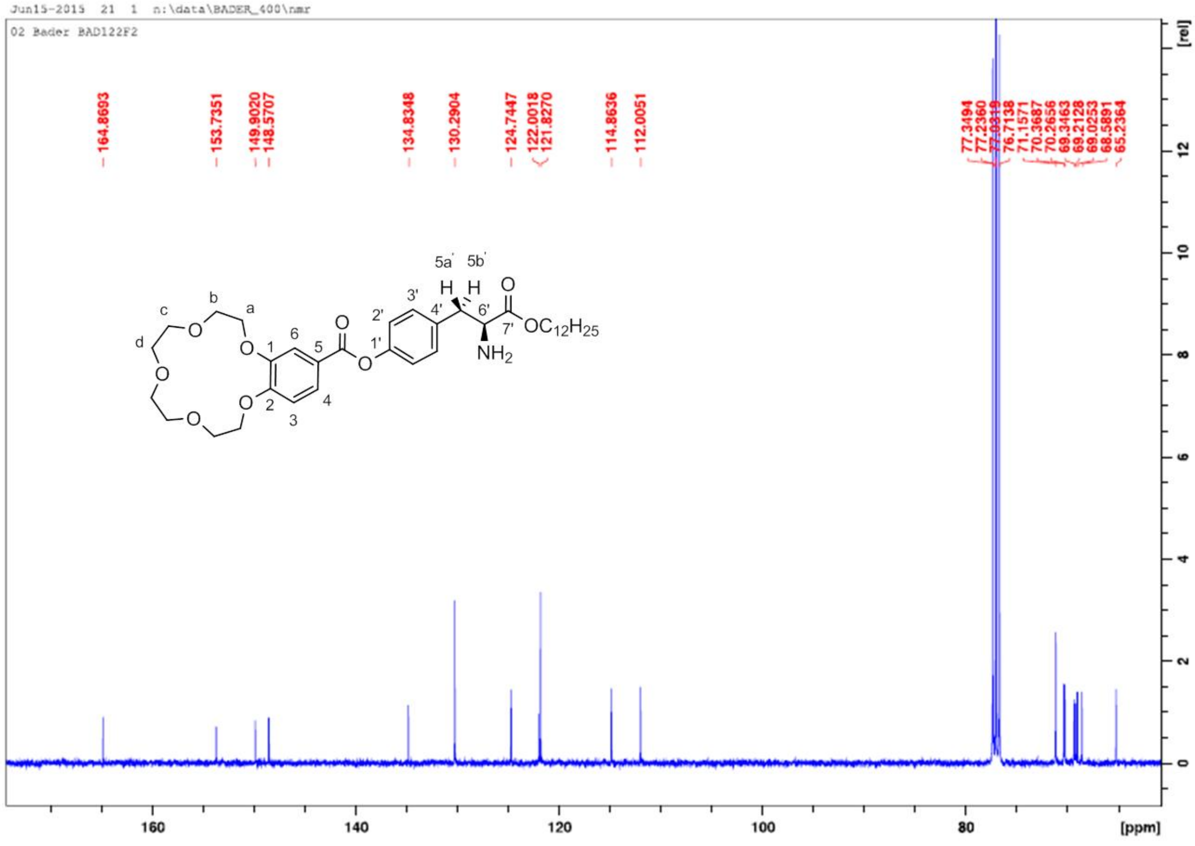

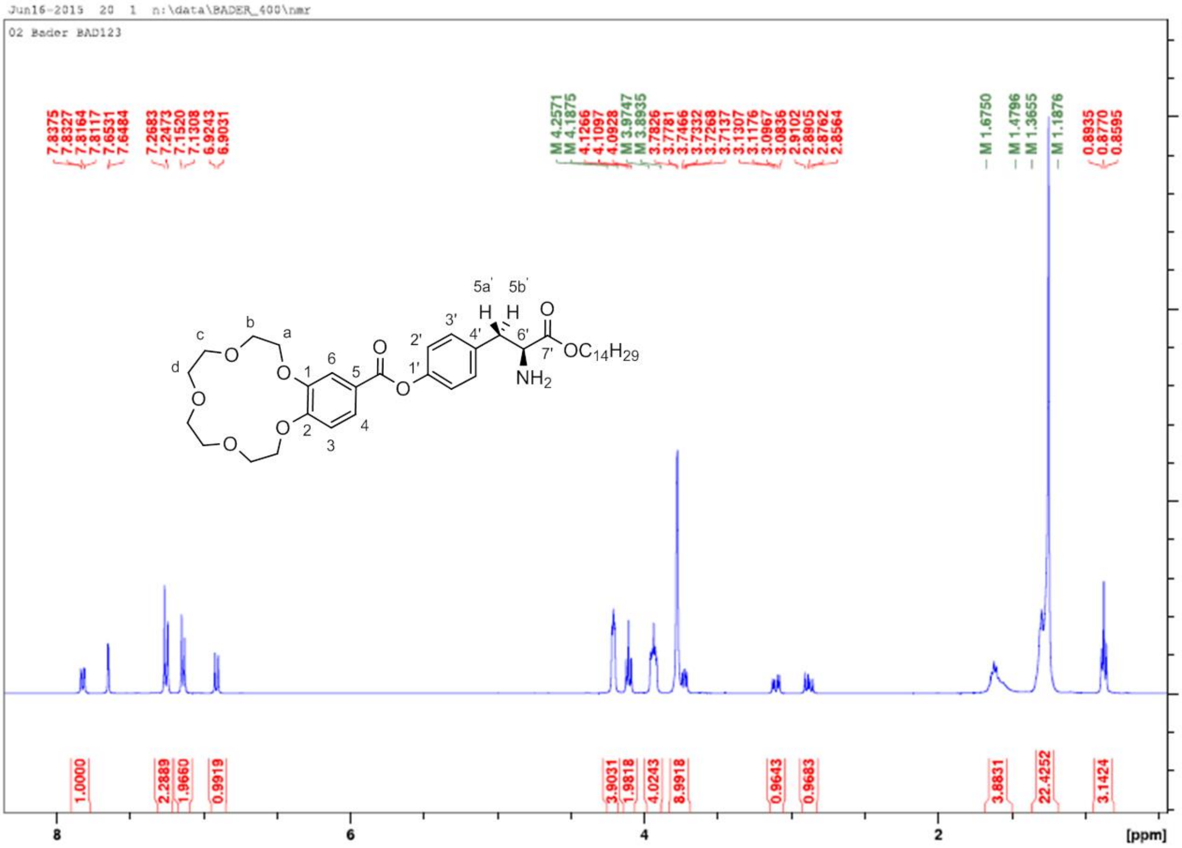

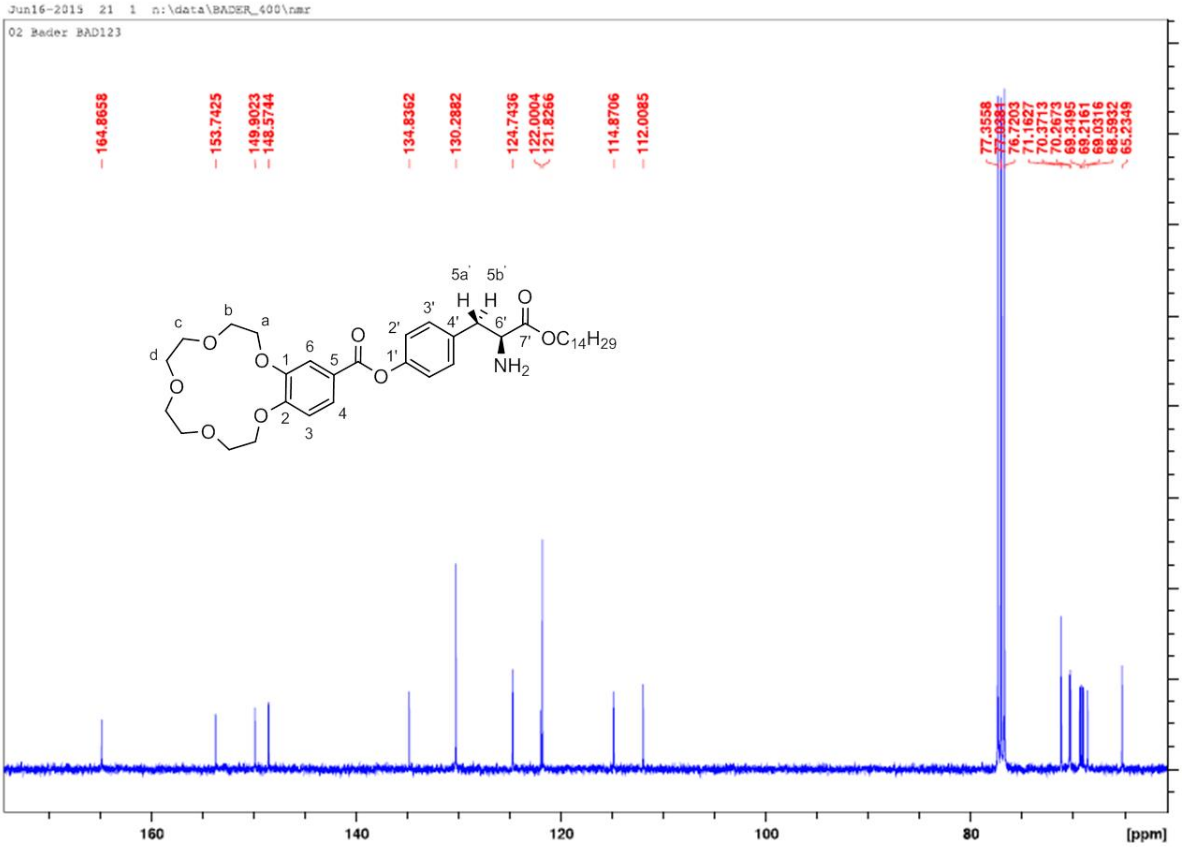

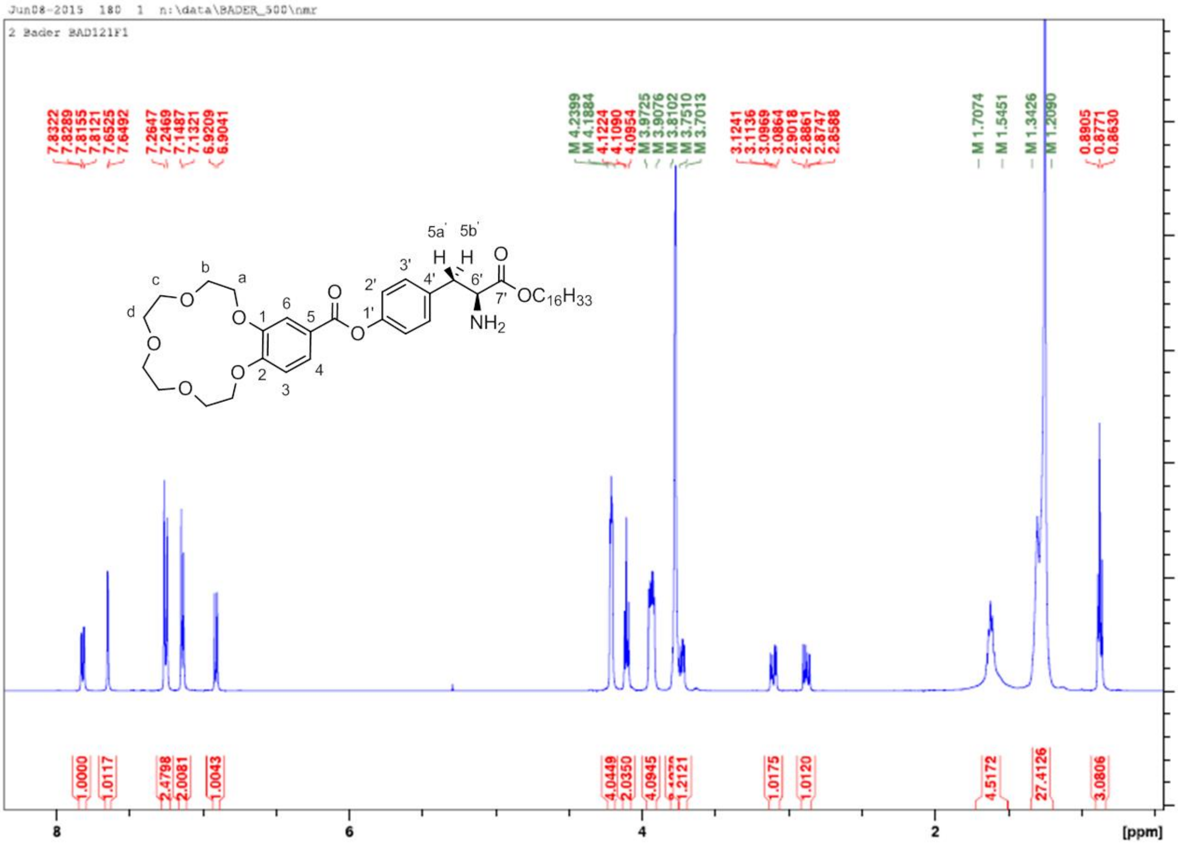
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2.0350
4.0945
1.2121
1.0175
1.0120
4.5172
27.4126
3.0806
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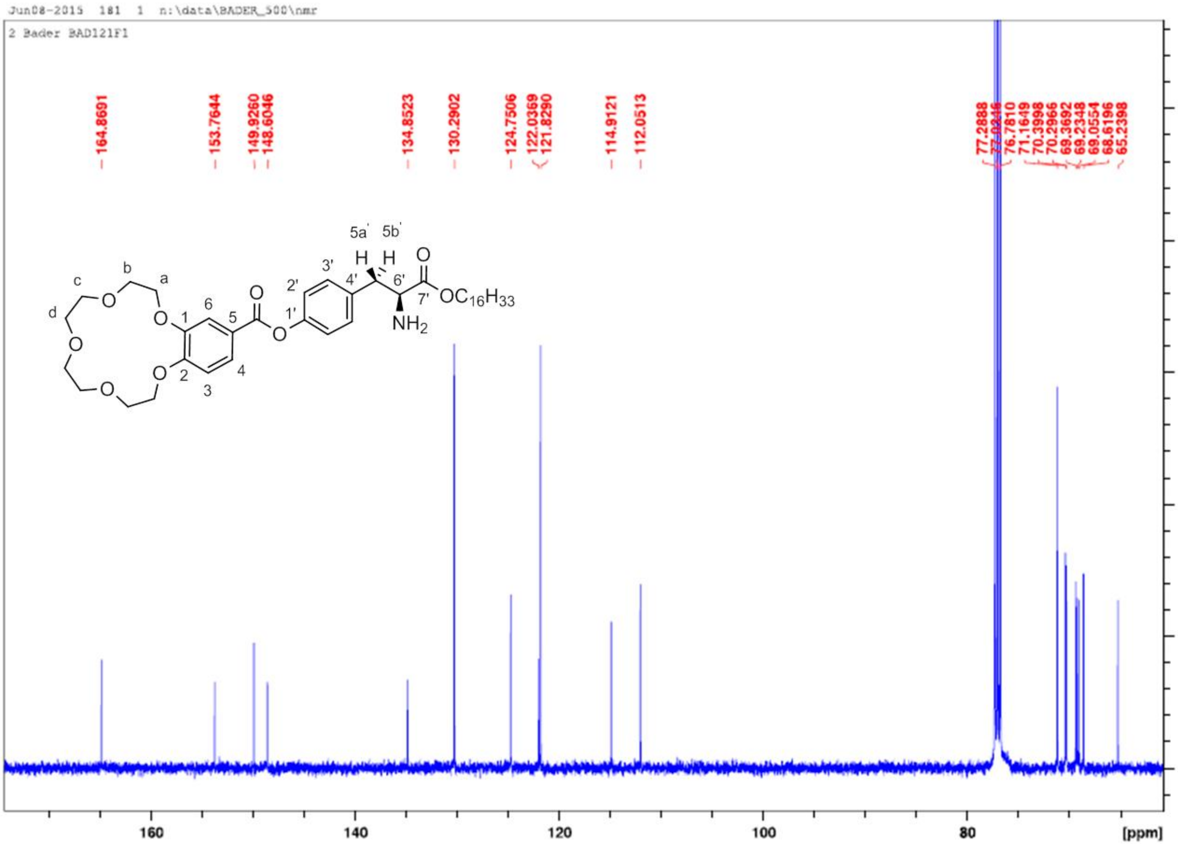
Jun08-2015 181 1 n:\data\BADER_500\nmr
2 Bader BAD121F1
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153.7644
149.9260
148.6046
134.8523
130.2902
124.7506
122.0369
121.8290
114.9121
112.0513
77.2888
76.7810
71.1649
70.3998
70.2966
69.3692
69.2348
69.0554
68.6196
65.2398
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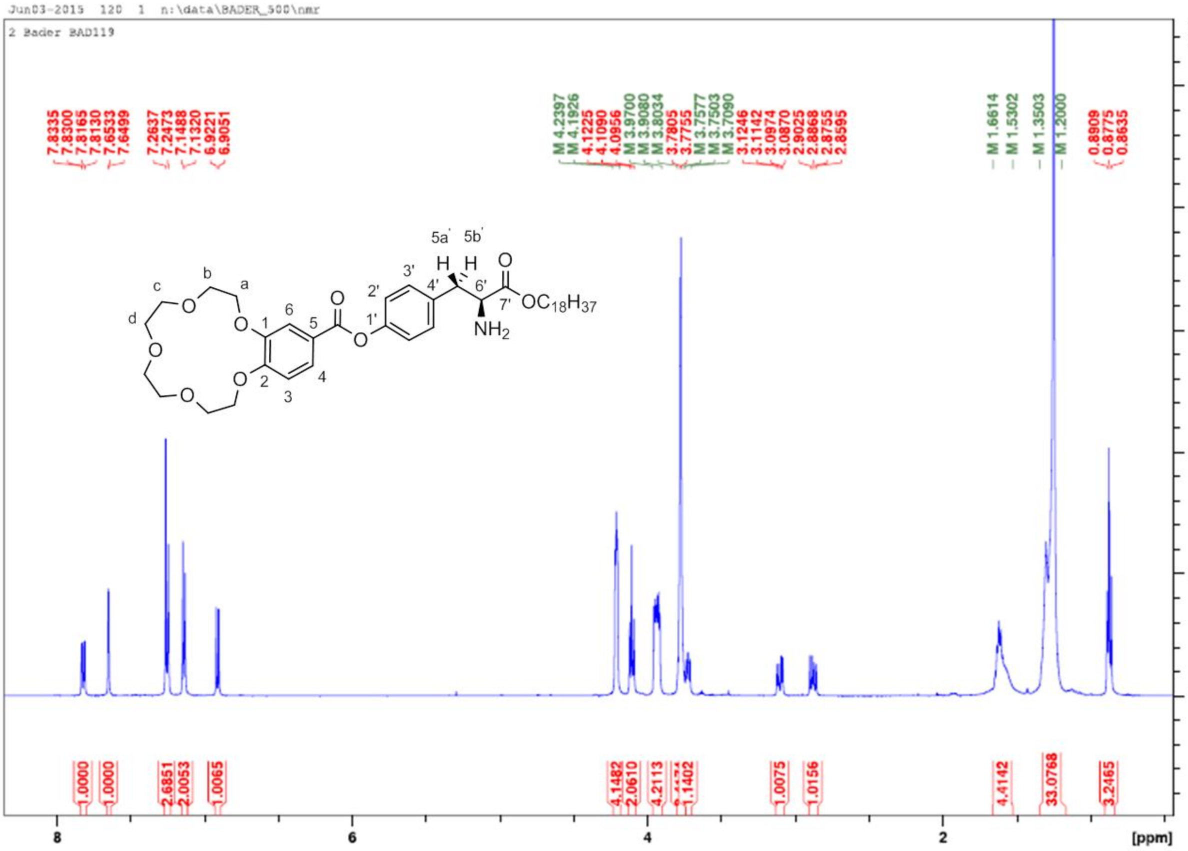
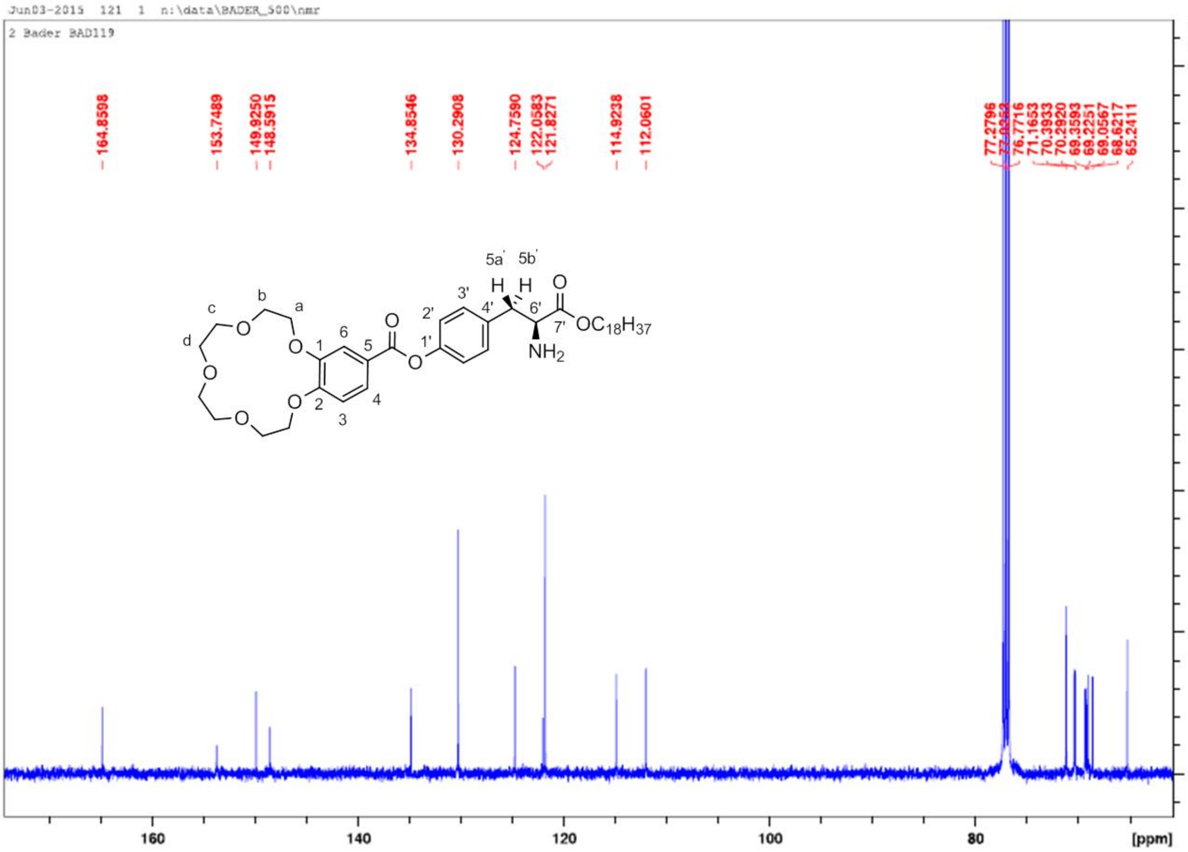


Jun03-2015 120 1 n:\data\BADER_500\nmr
2 Bader BAD119
5a' 5b'
OC18H37
NH2
[ppm]
[rel]



Jun03-2015 121 1 n:\data\BADER_500\nmr
2 Bader BAD119
164.8598
153.7489
149.9250
148.5915
134.8546
130.2908
124.7590
122.0583
121.8271
114.9238
112.0601
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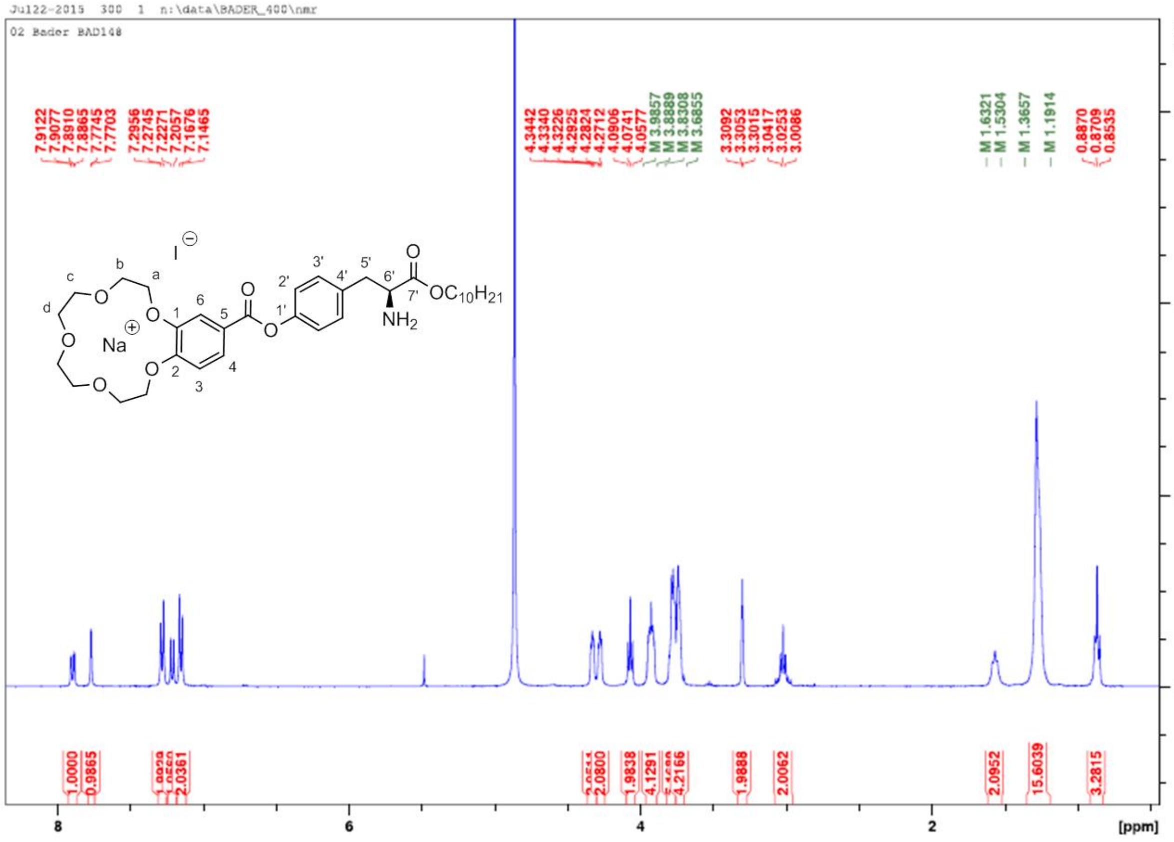
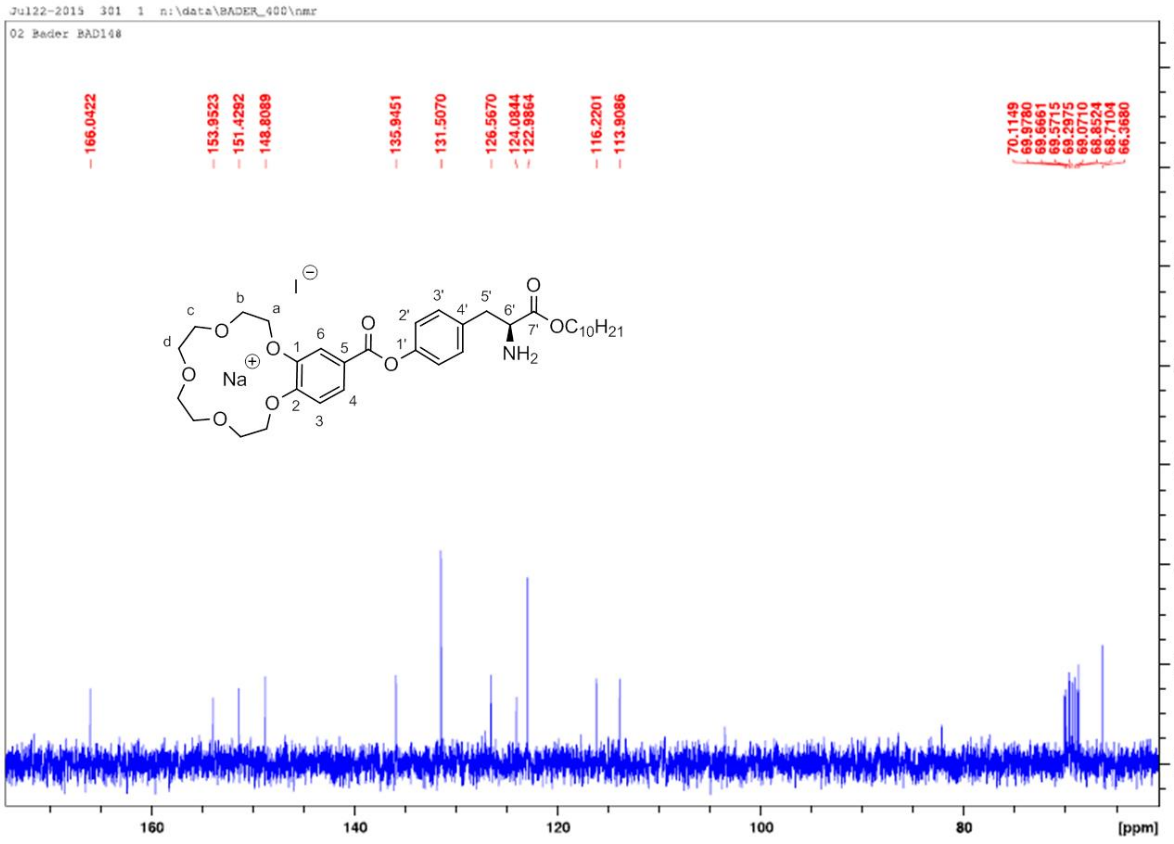

Jul22-2015 300 1 n:\data\BADER_400\nmr
02 Bader BAD148
7.9122 7.9077 7.8910 7.8865 7.7745 7.7703 7.2956 7.2745 7.2271 7.2057 7.1676 7.1465
4.3442 4.3340 4.3226 4.2825 4.2824 4.2712 4.0906 4.0741 4.0577
M 3.9857 M 3.8889 M 3.8308 M 3.6855
3.3092 3.3053 3.3015 3.0417 3.0253 3.0086
M 1.6321 M 1.5304 M 1.3657 M 1.1914
0.8870 0.8709 0.8535
1.0000 0.9865 2.0361 2.0800 1.9838 4.1291 4.2166 1.9888 2.0062 2.0952 15.6039 3.2815
[rel] [ppm]


Jul22-2015 301 1 n:\data\BADER_400\nmr
02 Bader BAD148
166.0422 153.9523 151.4292 148.8089 135.9451 131.5070 126.5670 124.0844 122.9864 116.2201 113.9086
70.1149 69.9780 69.6661 69.5715 69.2975 69.0710 68.8524 68.7104 66.3680
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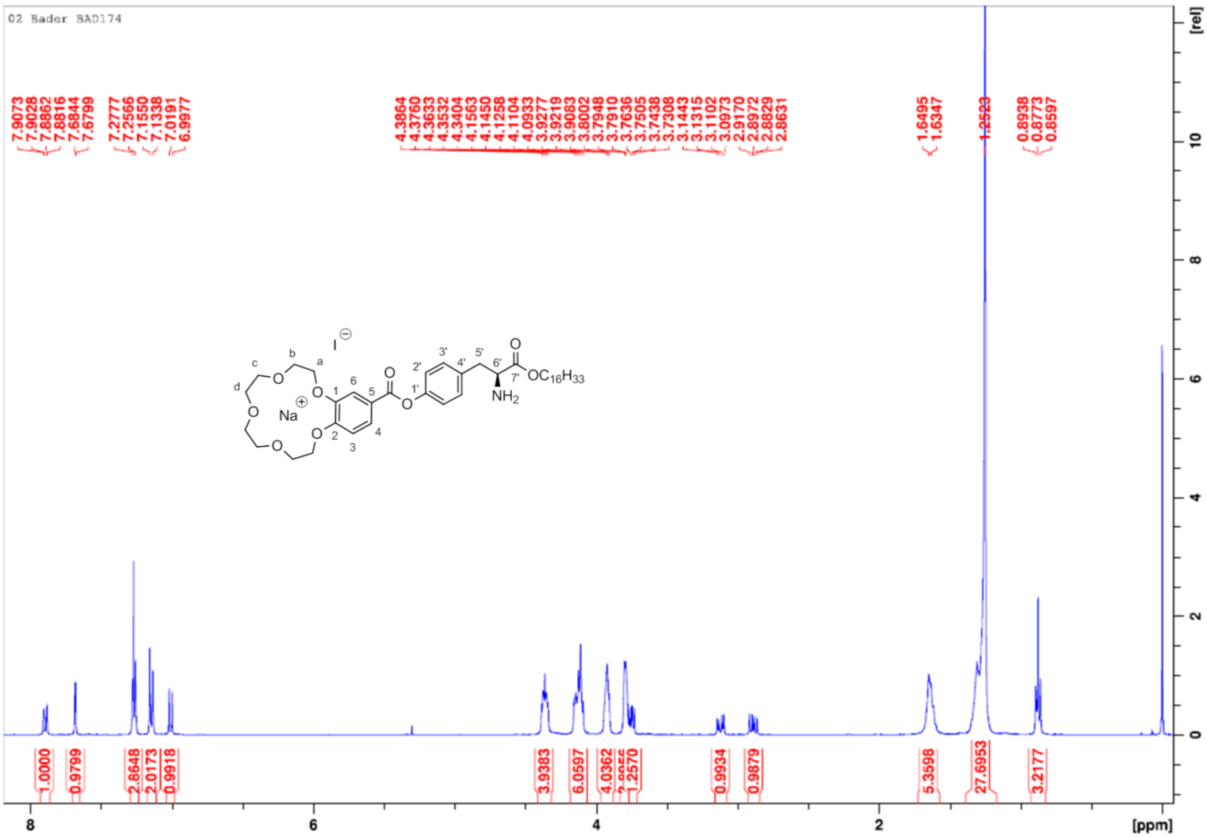
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NH2
OC16H33
Na
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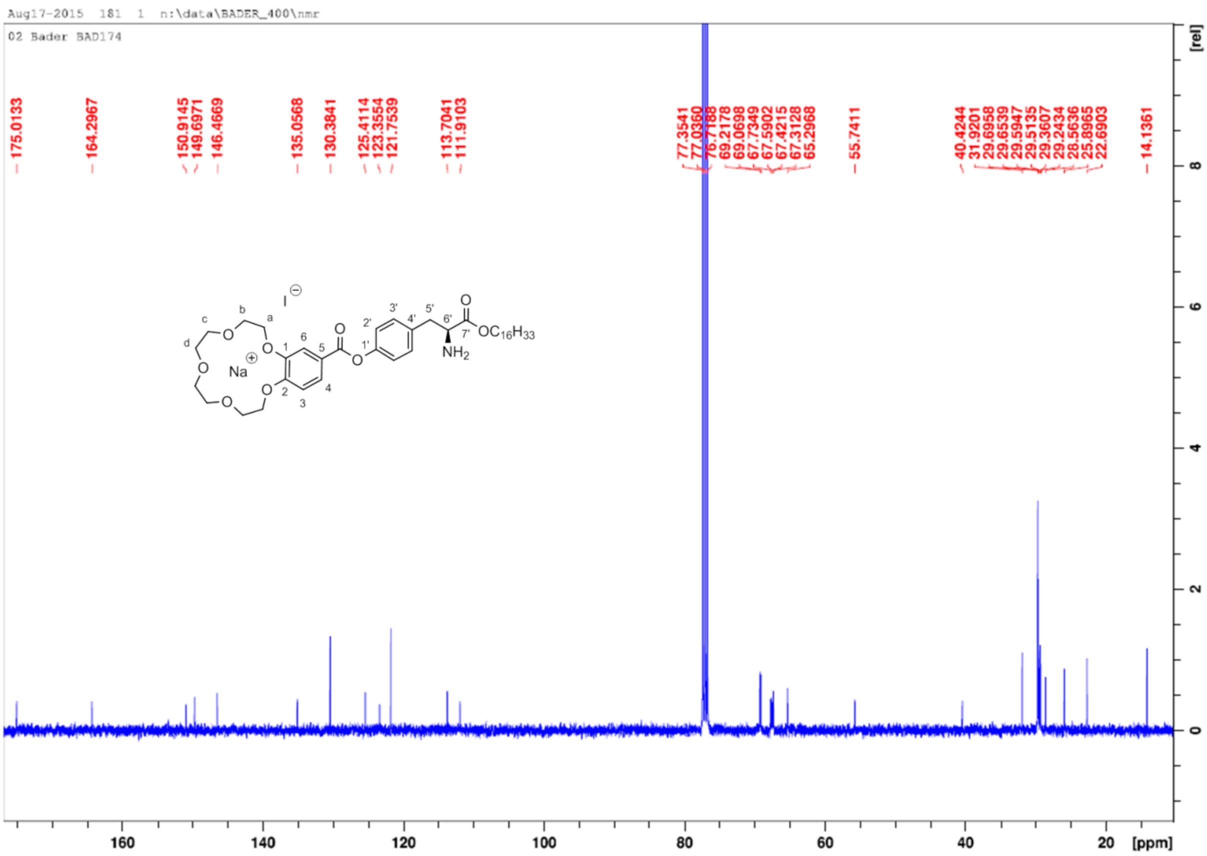
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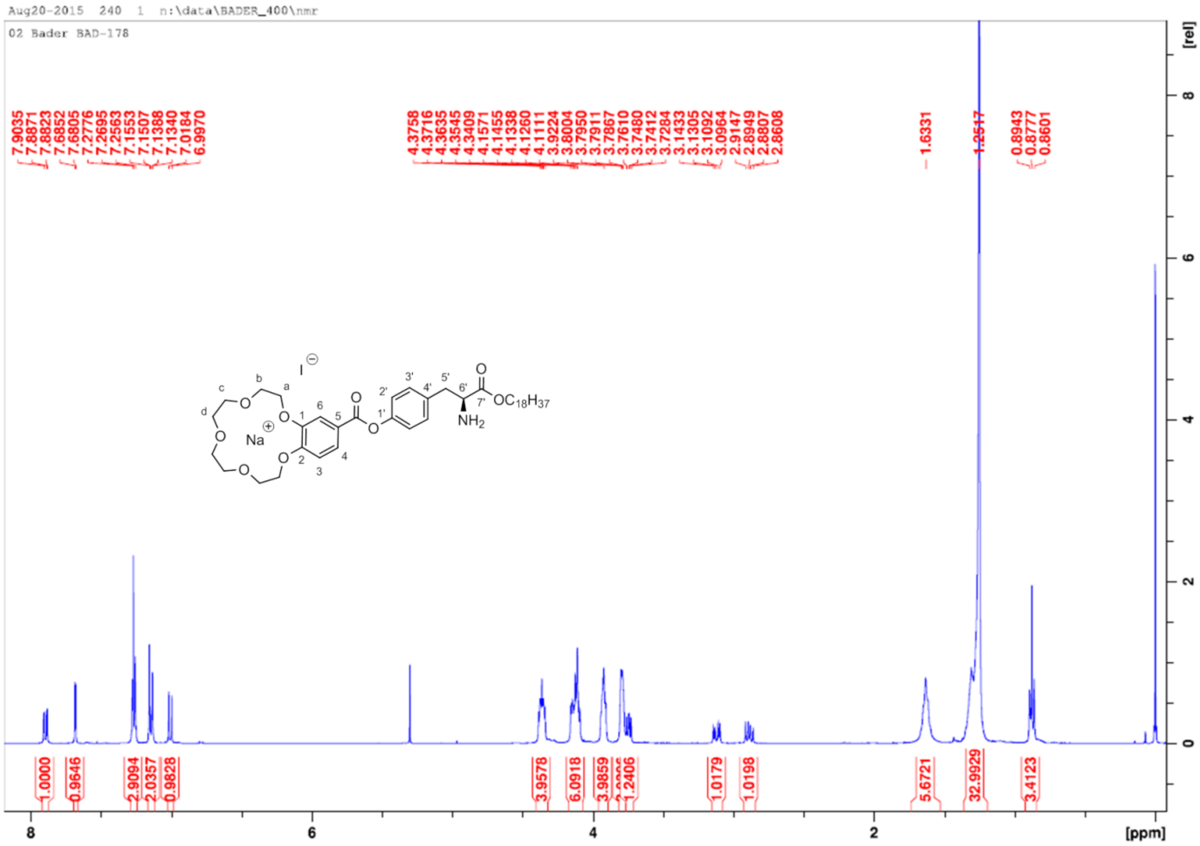
Aug20-2015 240 1 n:\data\BADER_400\nmr
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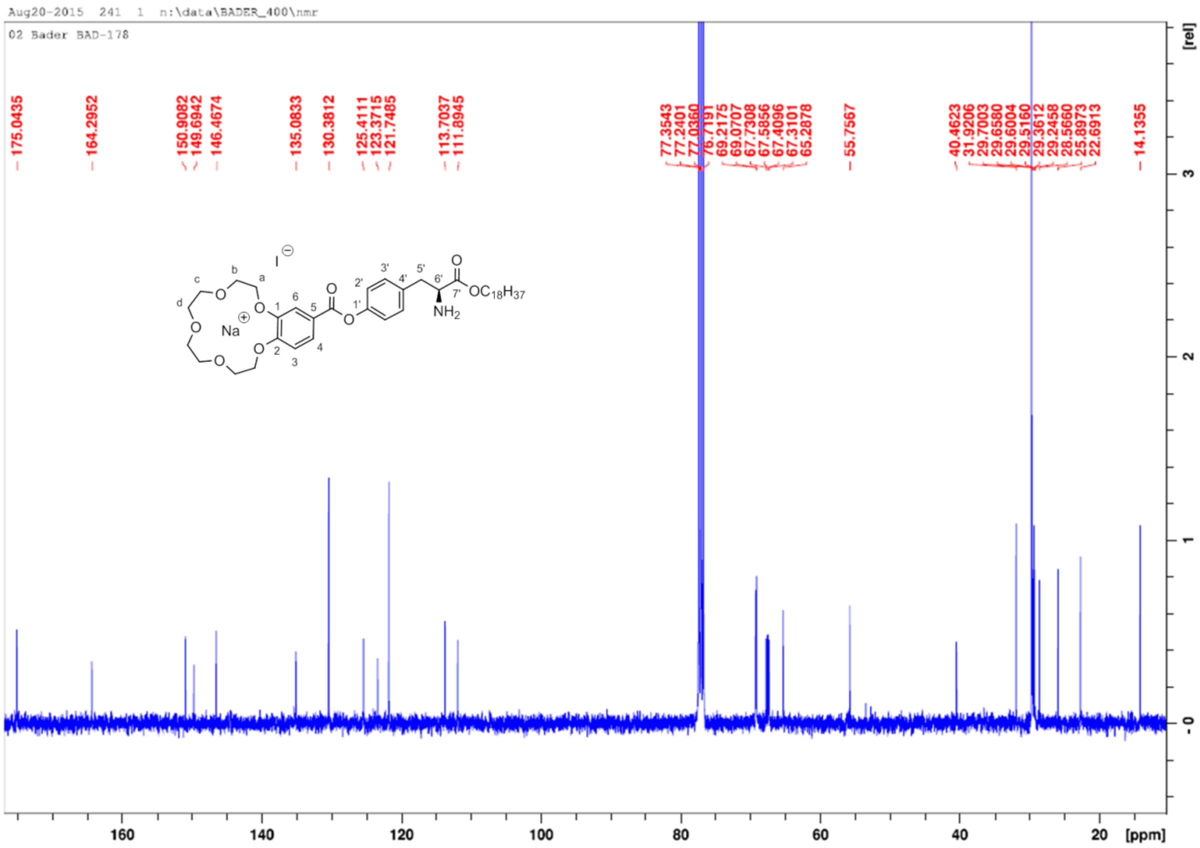
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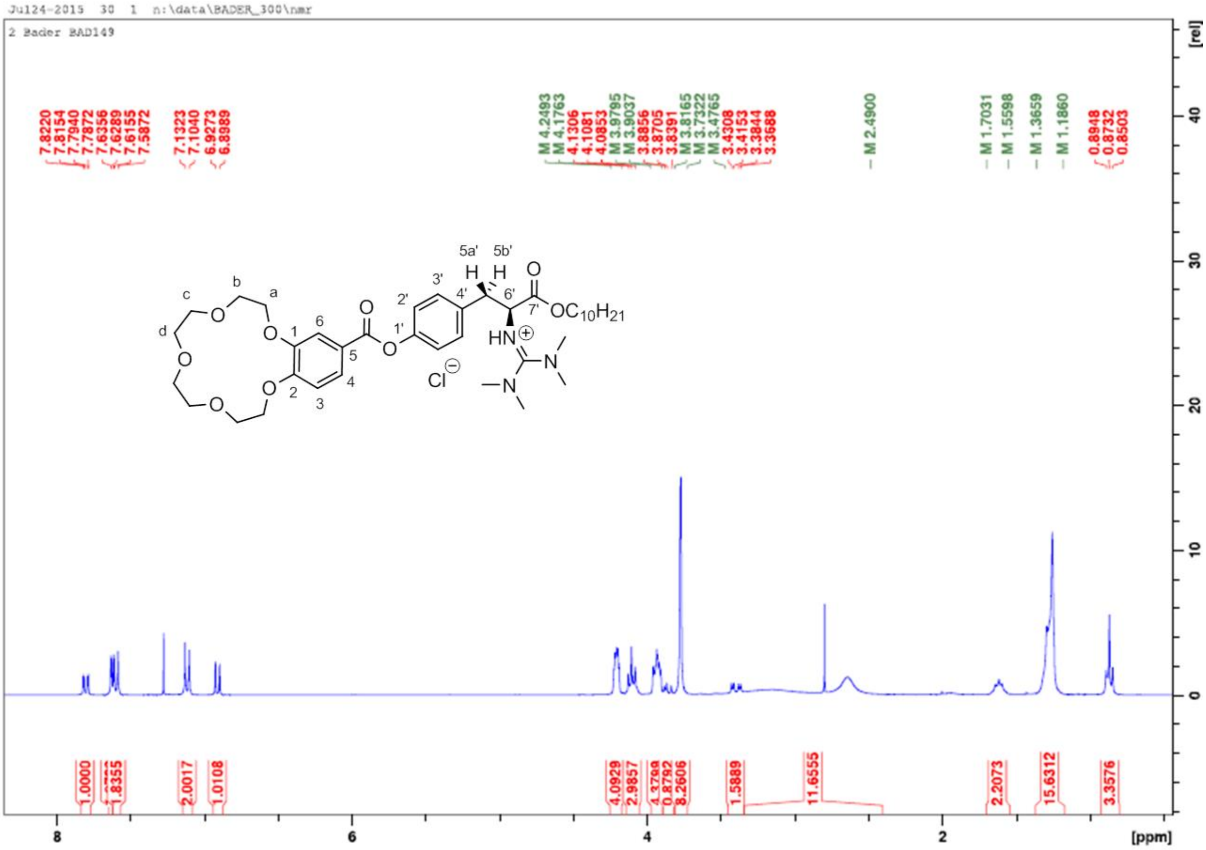

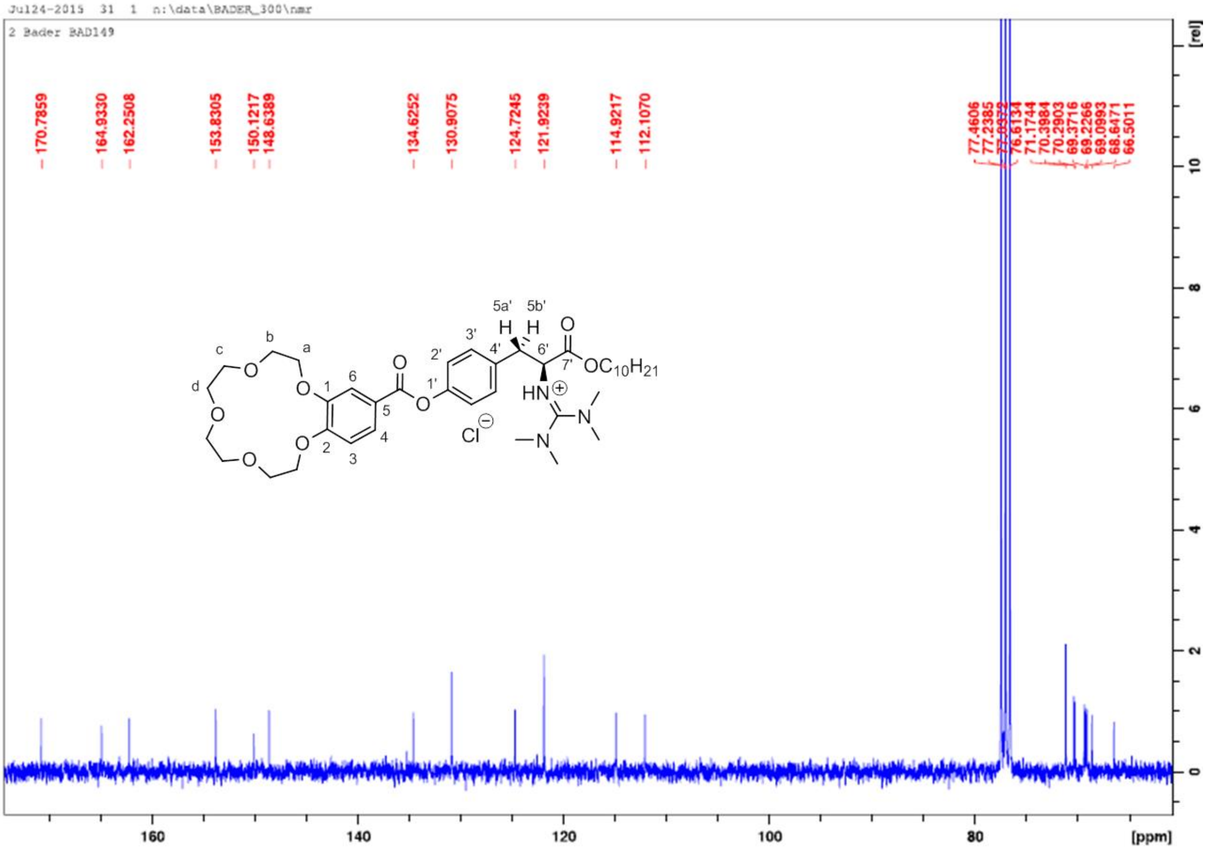

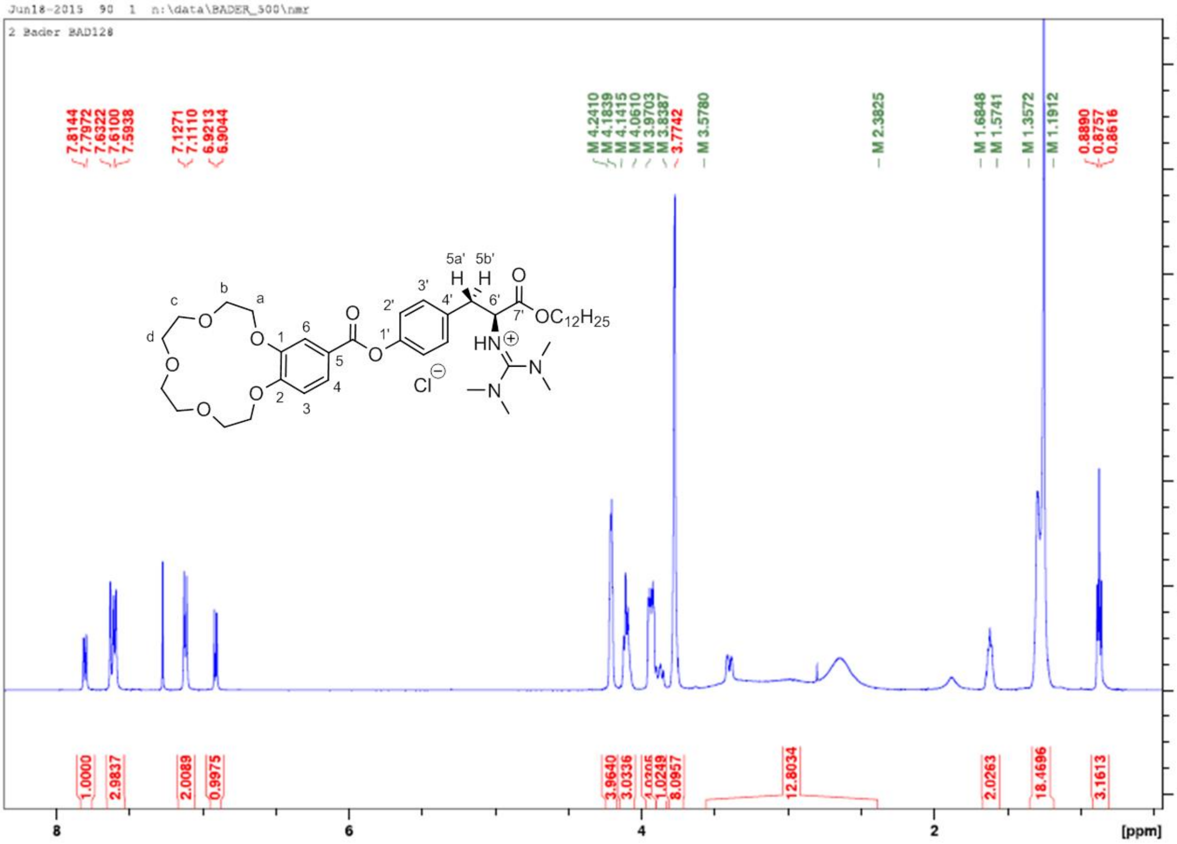
Jun18-2015 90 1 n:\data\BADER_500\nmr
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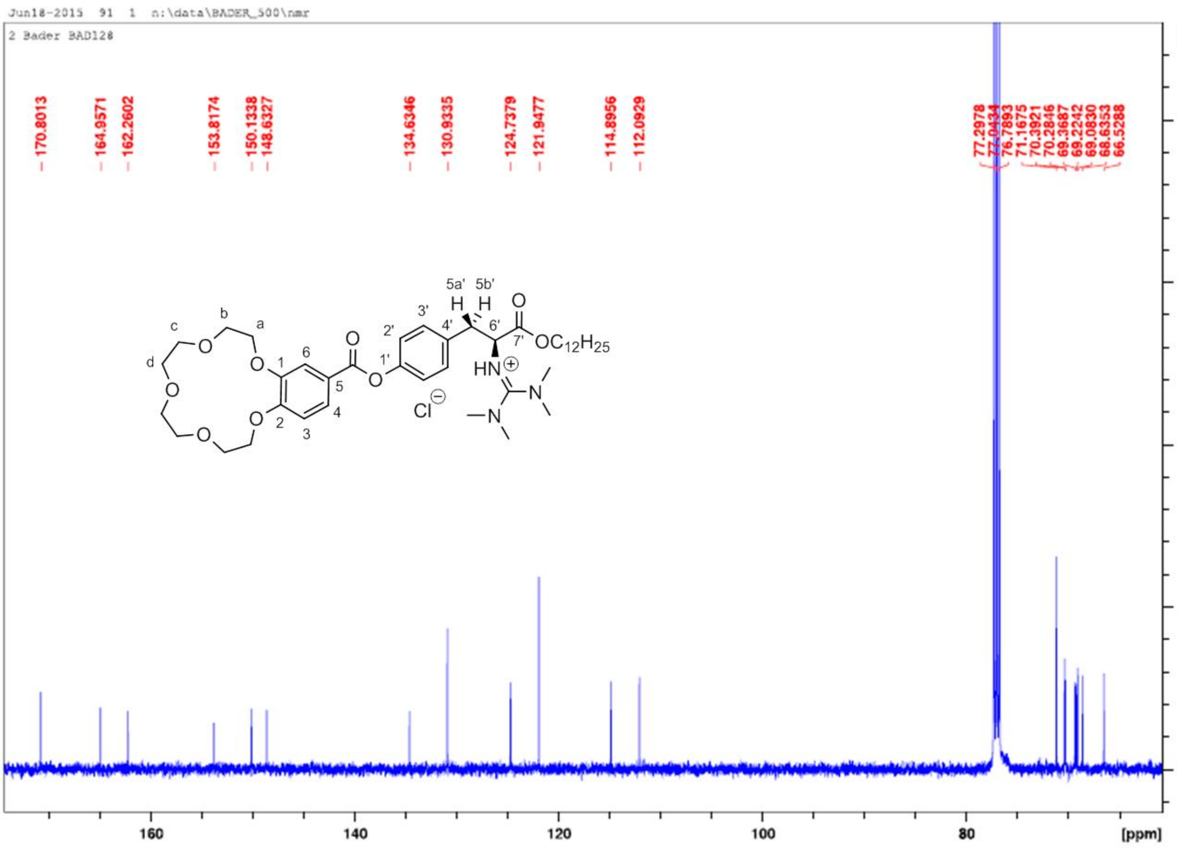
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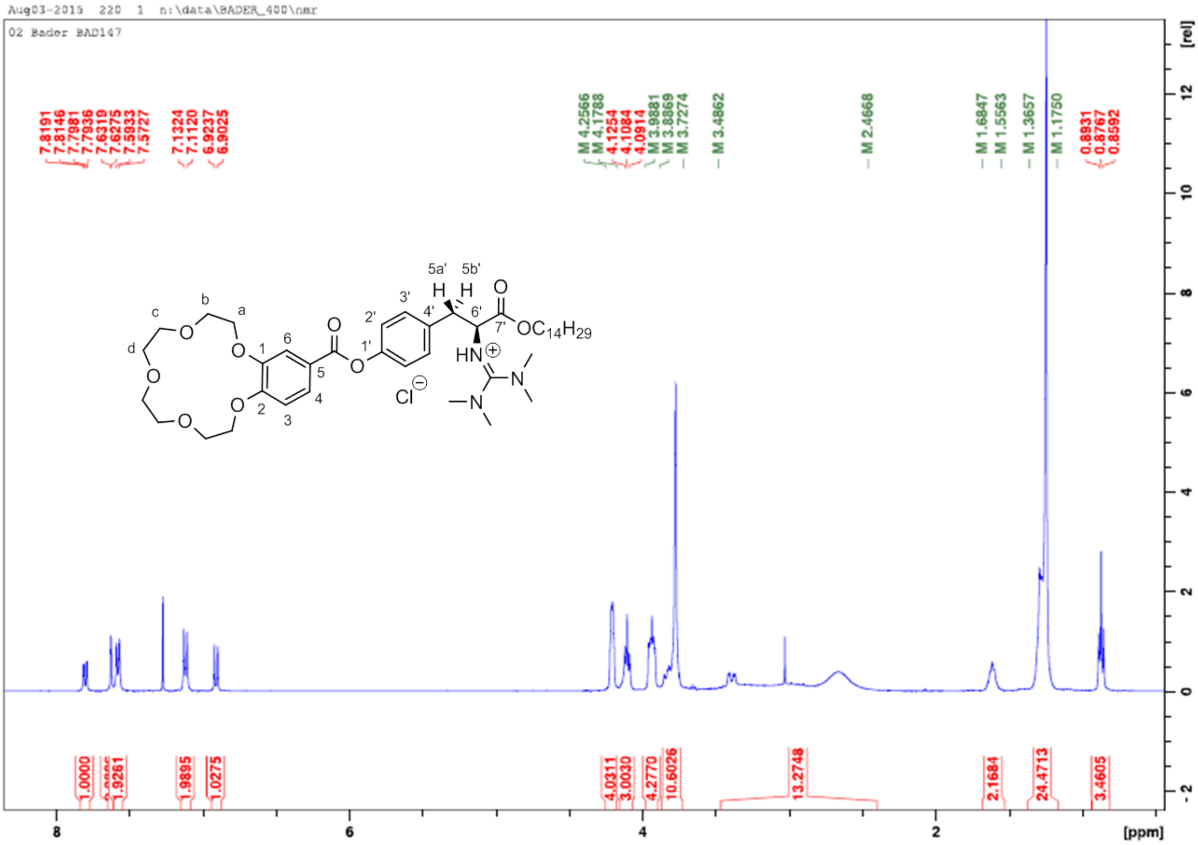
Aug03-2015 220 1 n:\data\BADER_400\nmr
02 Bader BAD147
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7.8146
7.7981
7.7936
7.6319
7.6275
7.5933
7.5727
7.1324
7.1120
6.9237
6.9025
M 4.2566
M 4.1788
4.1254
4.1084
4.0914
M 3.9881
M 3.8869
M 3.7274
M 3.4862
M 2.4668
M 1.6847
M 1.5563
M 1.3657
M 1.1750
0.8931
0.8767
0.8592
1.0000
1.9261
1.9895
1.0275
4.0311
3.0030
4.2770
10.6026
13.2748
2.1684
24.4713
3.4605
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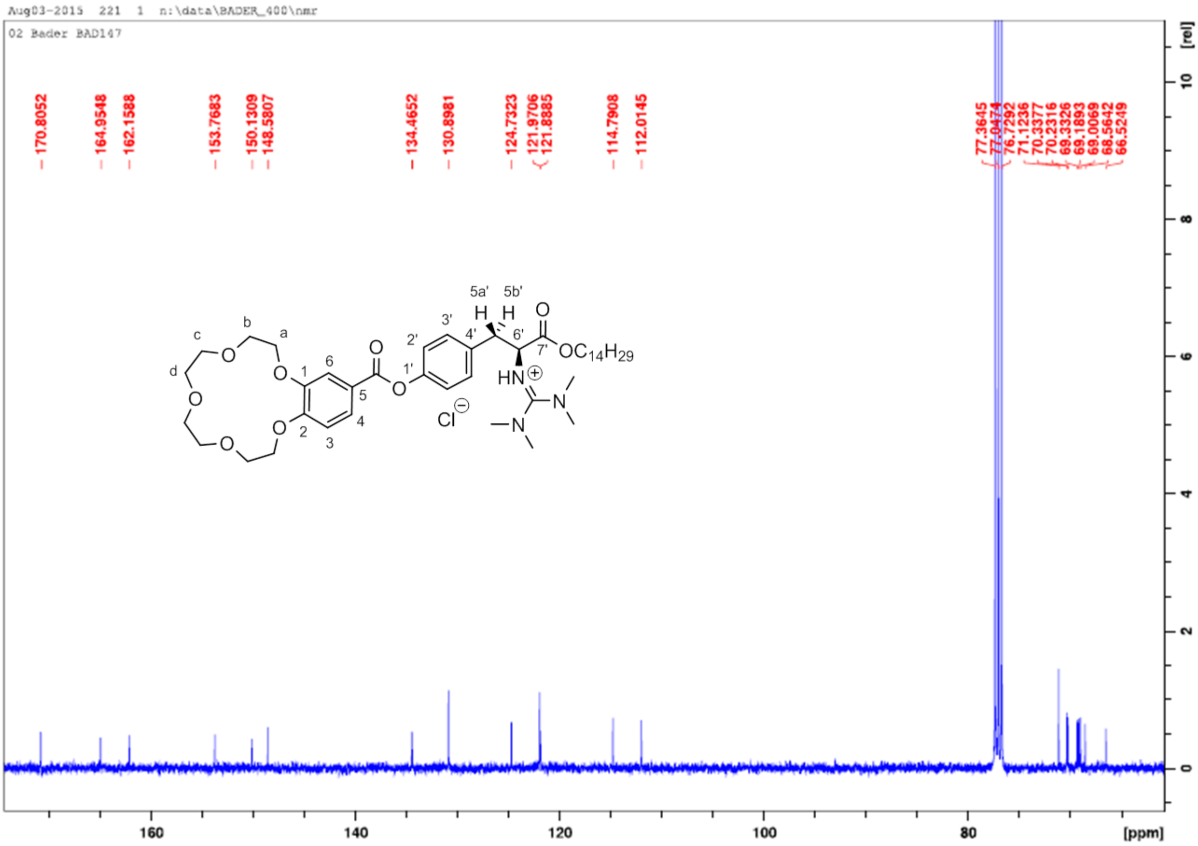
[rel]


Aug03-2015 221 1 n:\data\BADER_400\nmr
02 Bader BAD147
170.8052
164.9548
162.1588
153.7683
150.1309
148.5807
134.4652
130.8981
124.7323
121.9706
121.8885
114.7908
112.0145
77.3645
76.7292
71.1236
70.3377
70.2316
69.3326
69.1893
69.0069
68.5642
66.5249
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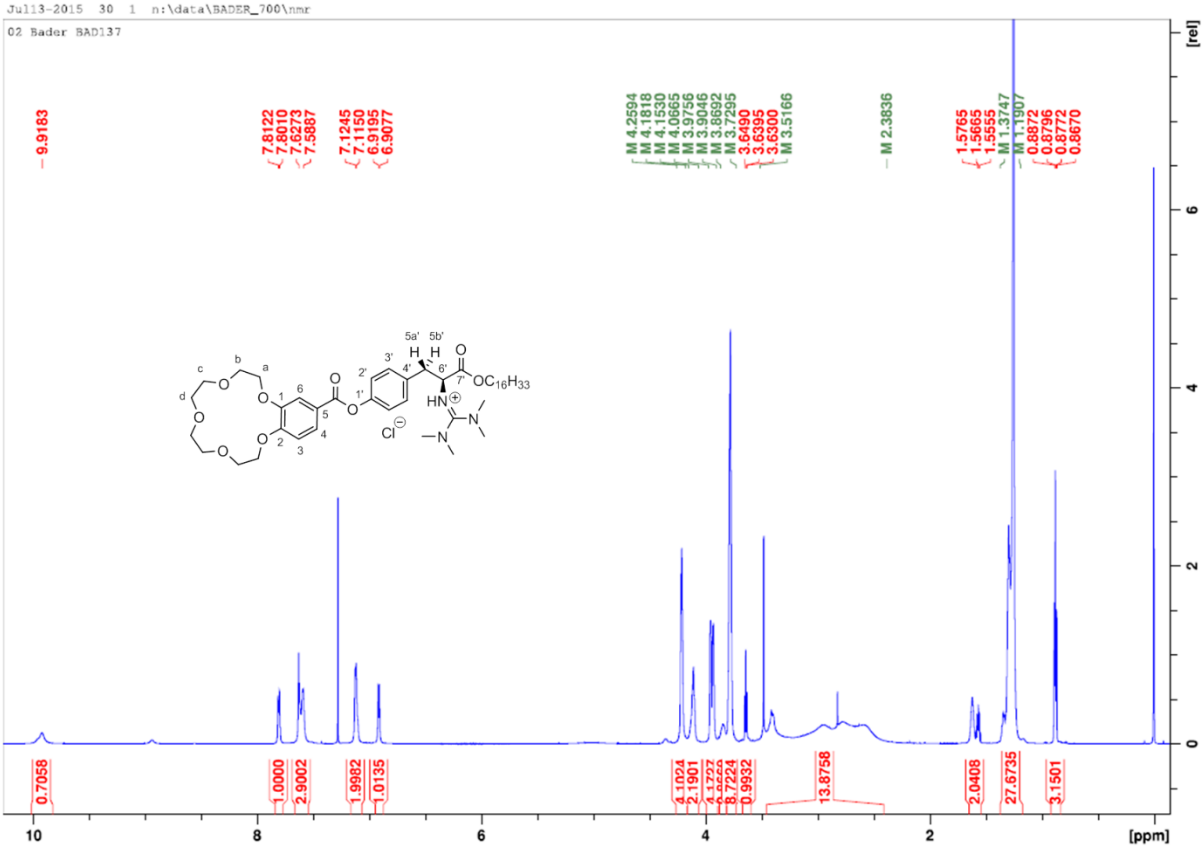
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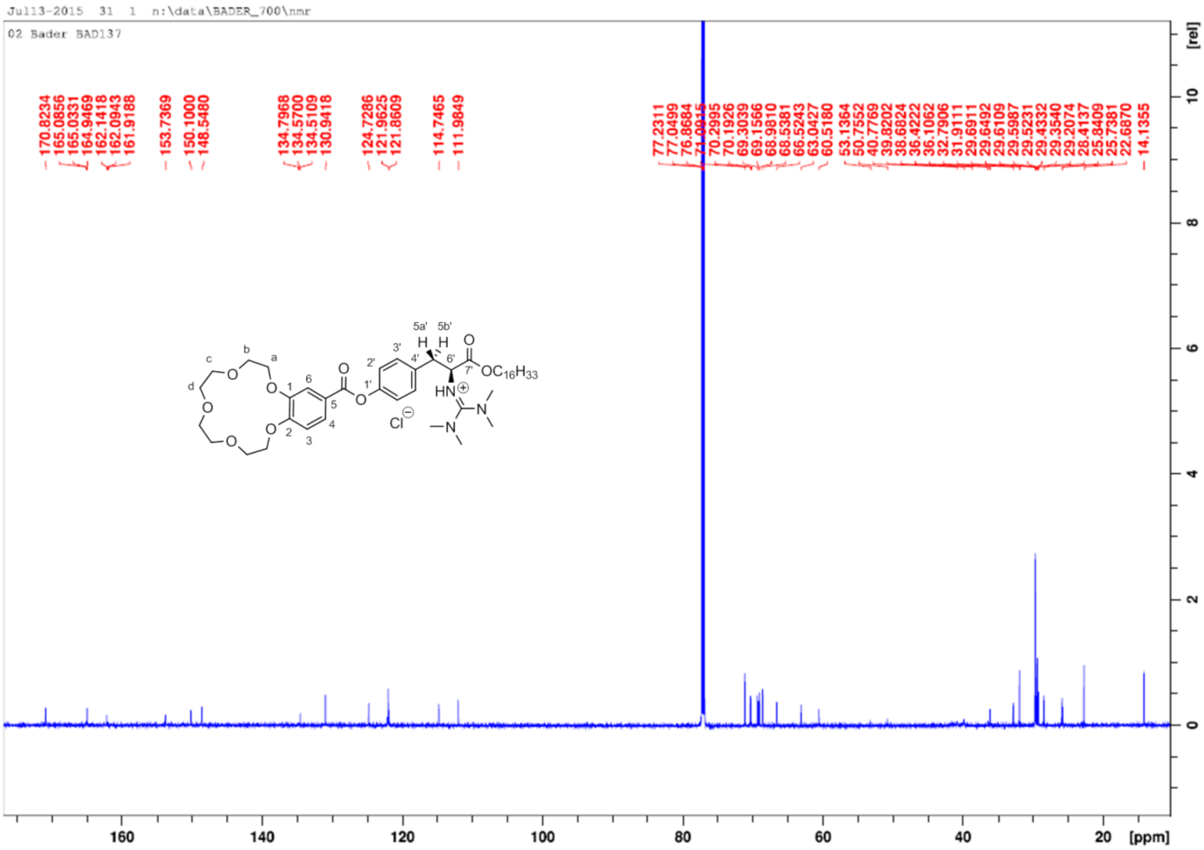
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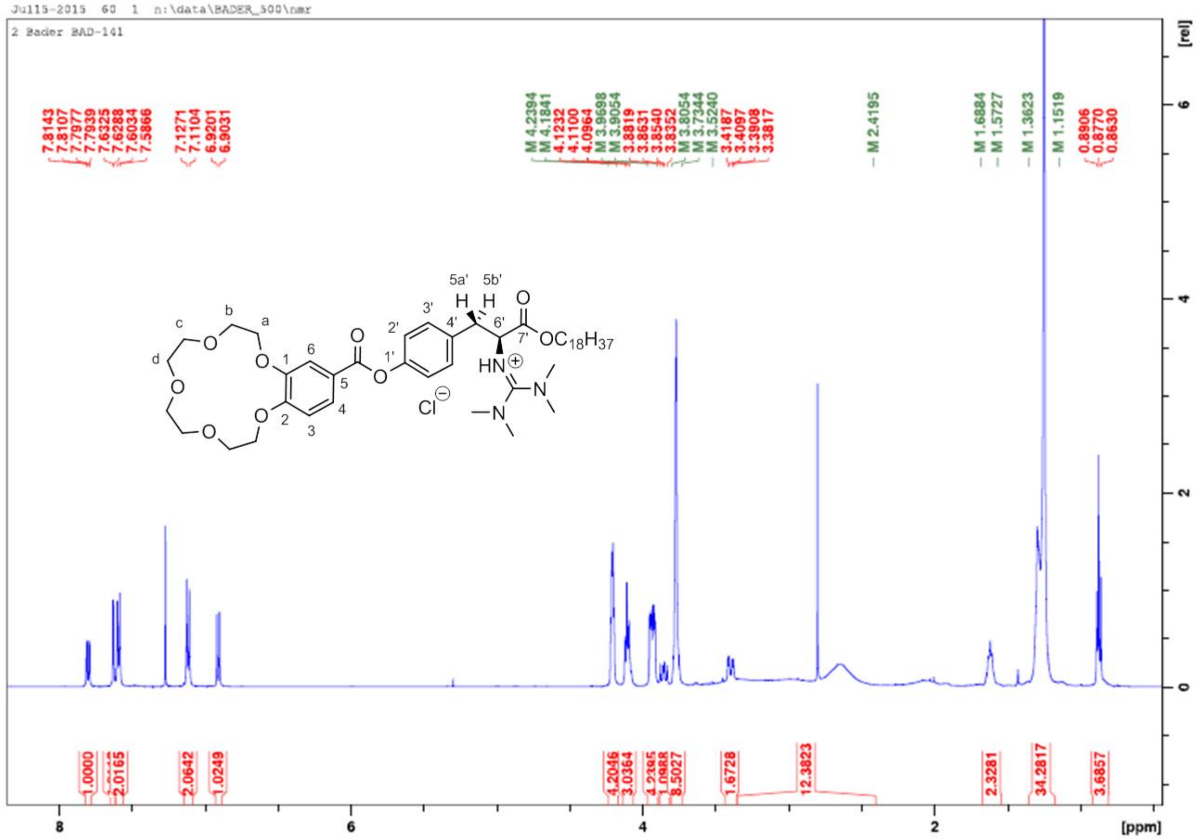

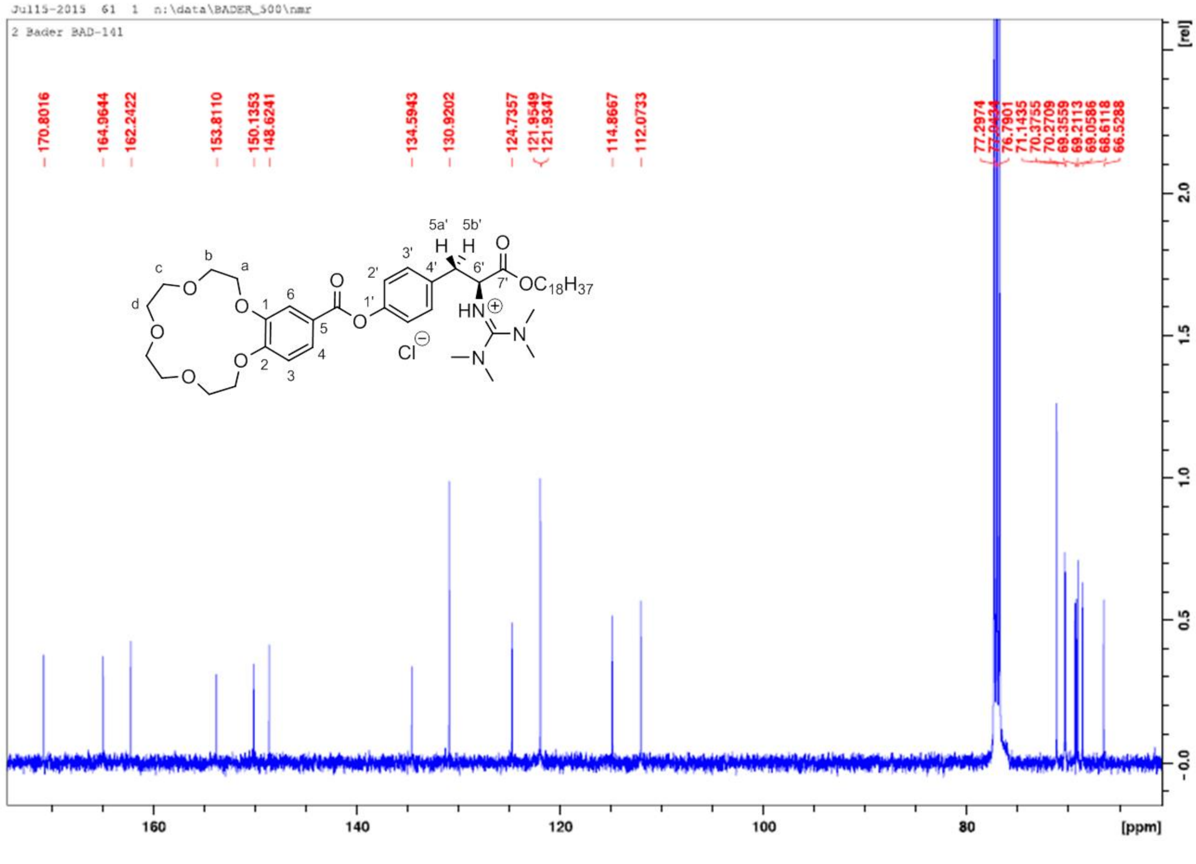

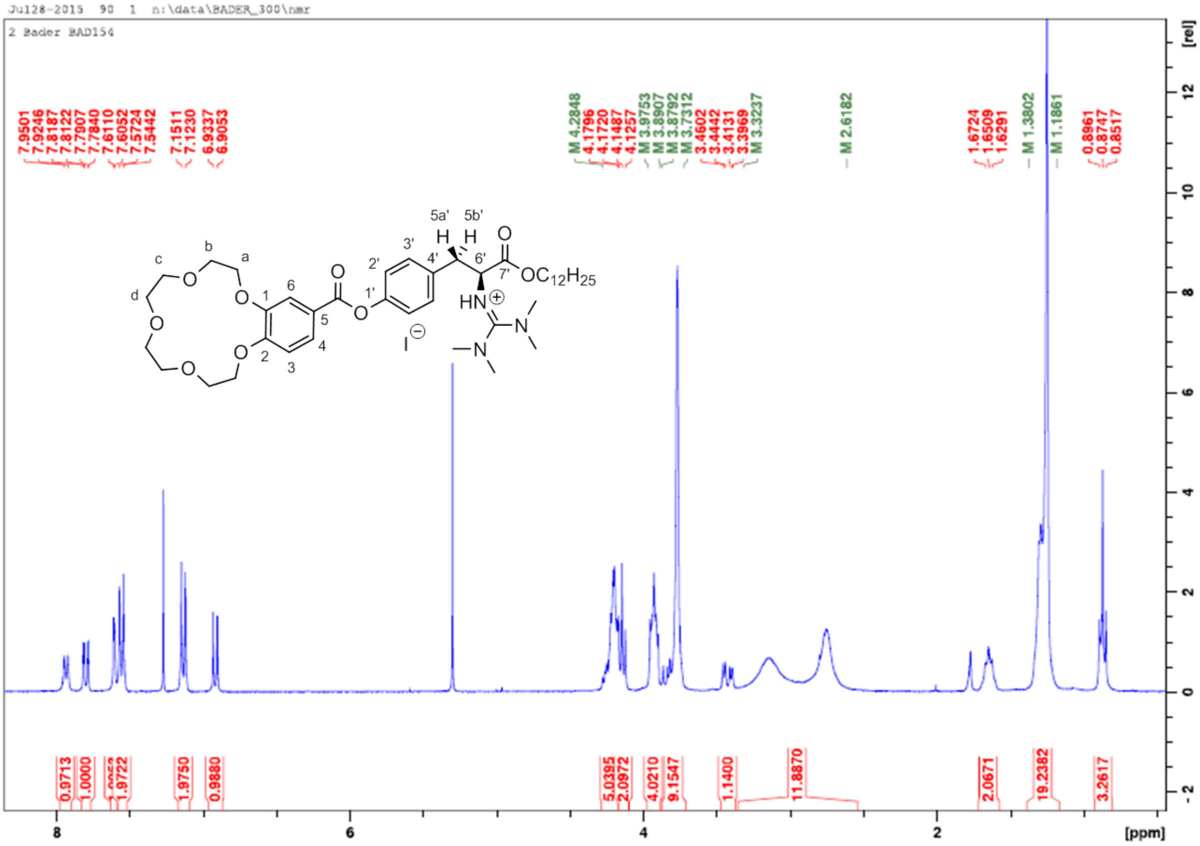
Jul28-2015 90 1 n:\data\BADER_300\nmr
2 Bader BAD154
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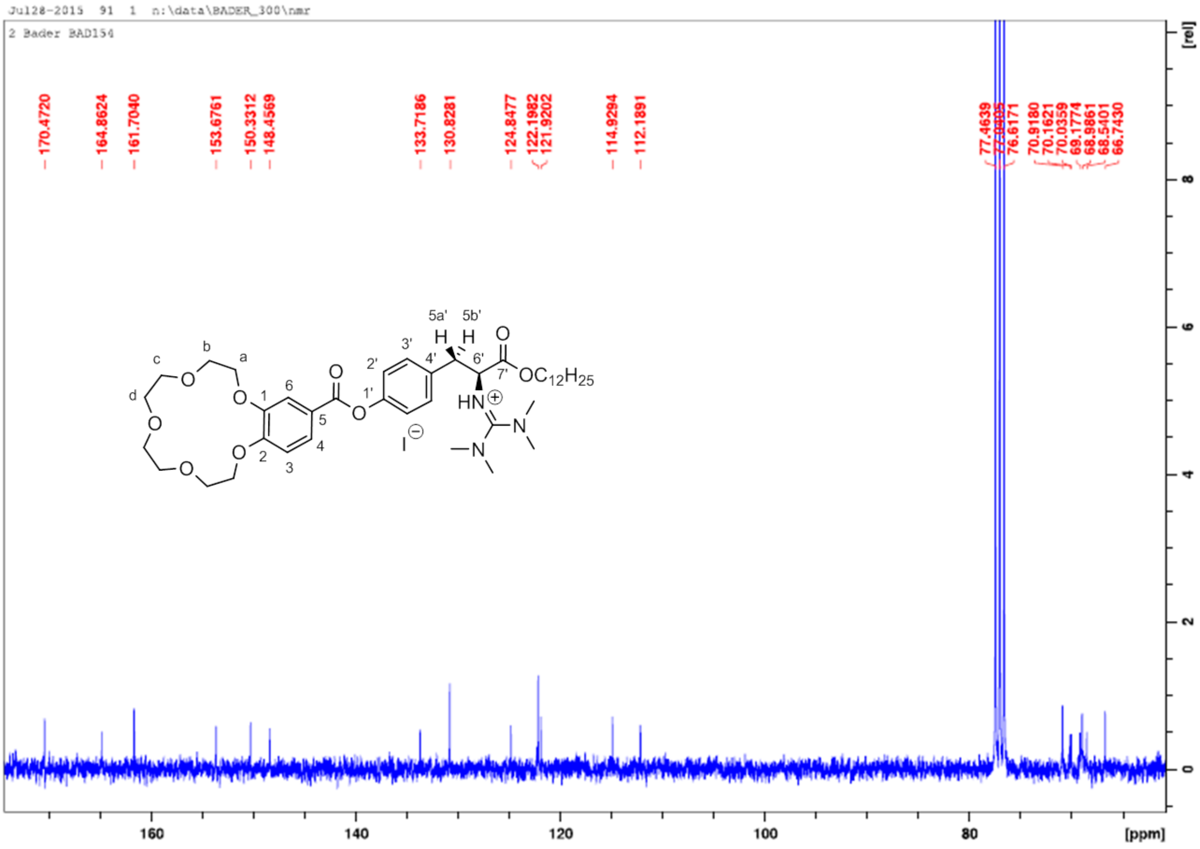
Jul28-2015 91 1 n:\data\BADER_300\nmr
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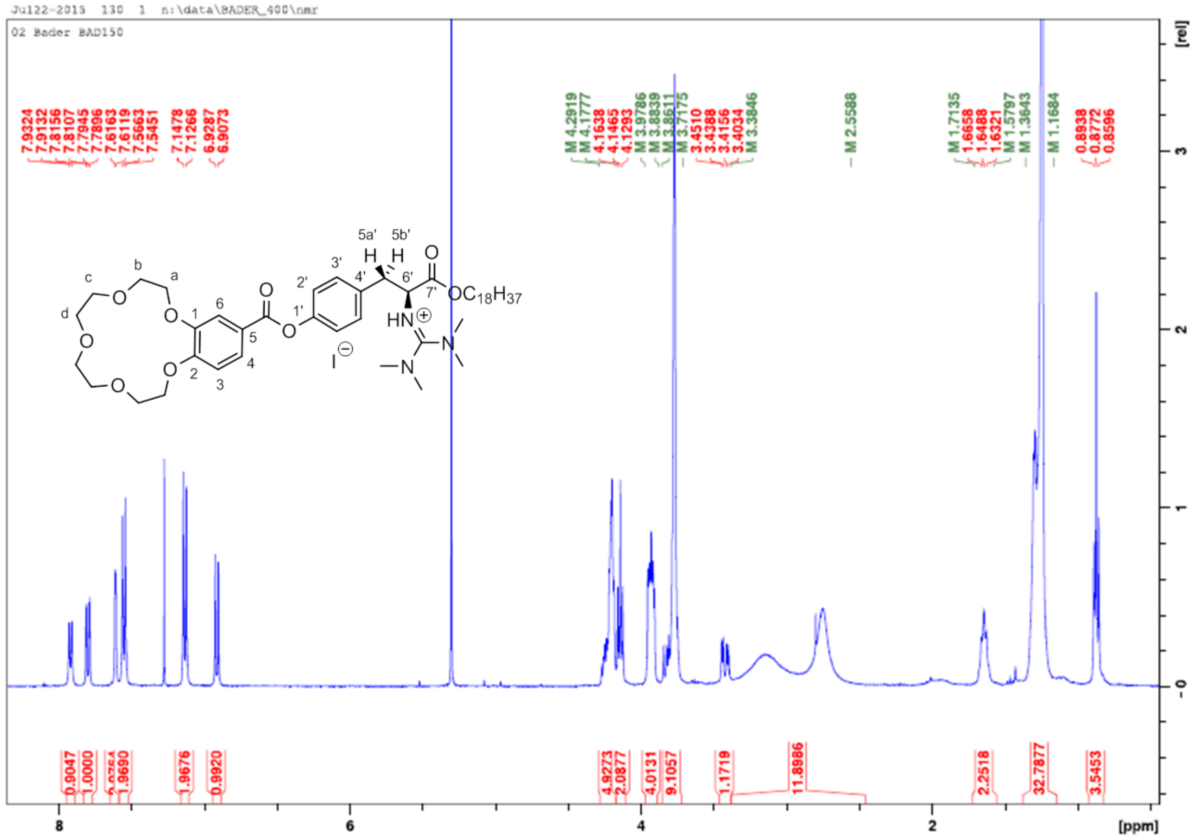
Jul22-2015 130 1 n:\data\BADER_400\nmr
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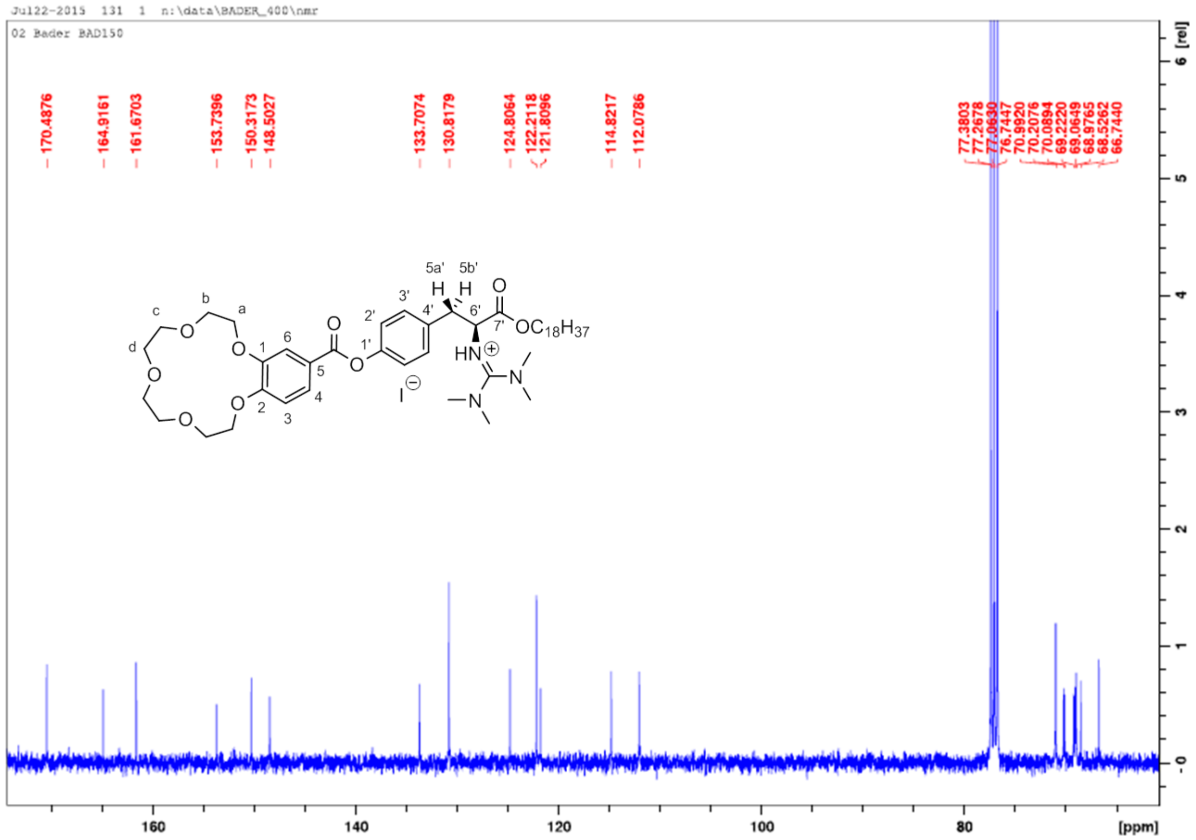
Jul22-2015 131 1 n:\data\BADER_400\nmr
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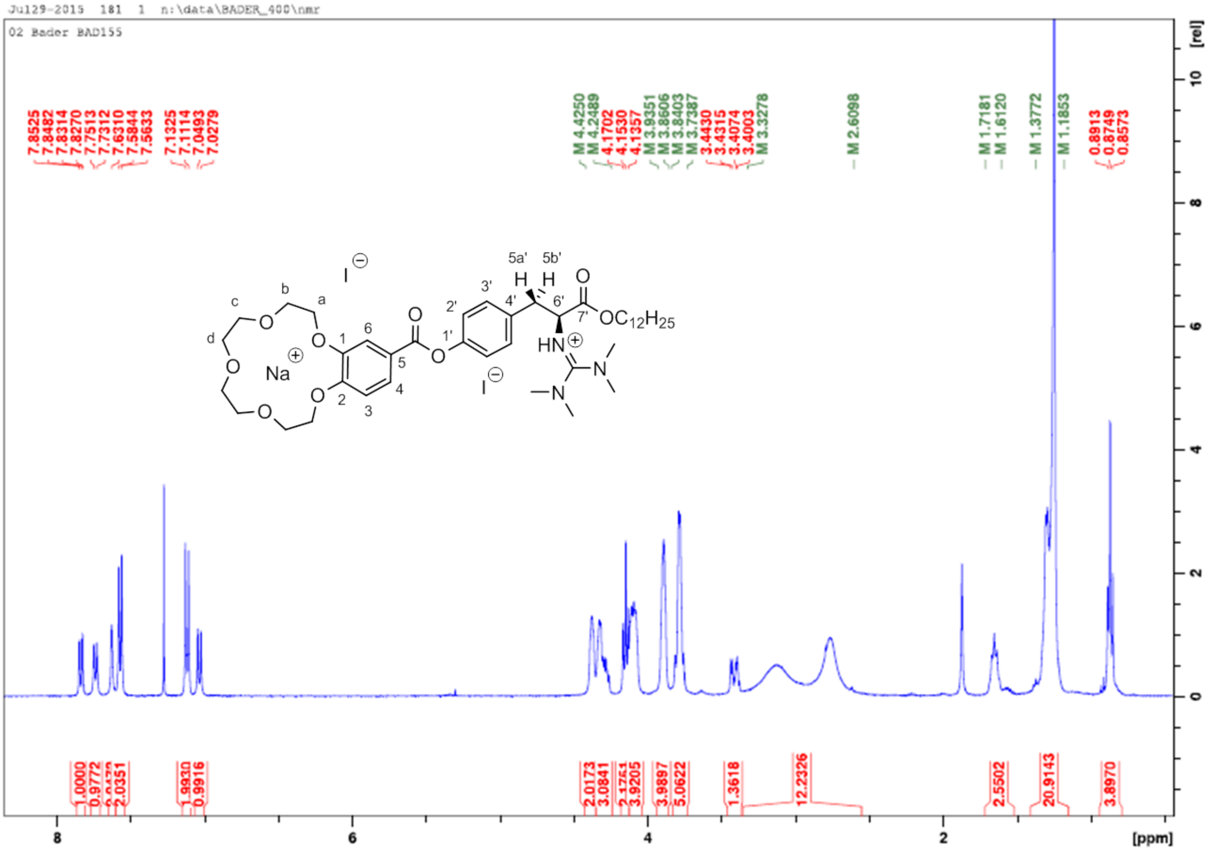

Jul29-2015 181 1 n:\data\BADER_400\nmr
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7.8314
7.8270
7.7513
7.7312
7.6310
7.5844
7.5633
7.1325
7.1114
7.0493
7.0279
M 4.4250
M 4.2489
4.1702
4.1530
4.1357
M 3.9351
M 3.8606
M 3.8403
M 3.7387
3.4430
3.4315
3.4074
3.4003
M 3.3278
M 2.6098
M 1.7181
M 1.6120
M 1.3772
M 1.1853
0.8913
0.8749
0.8573
1.0000
0.9772
2.0351
1.9930
0.9916
2.0173
3.0841
3.9205
3.9897
5.0622
1.3618
12.2326
2.5502
20.9143
3.8970
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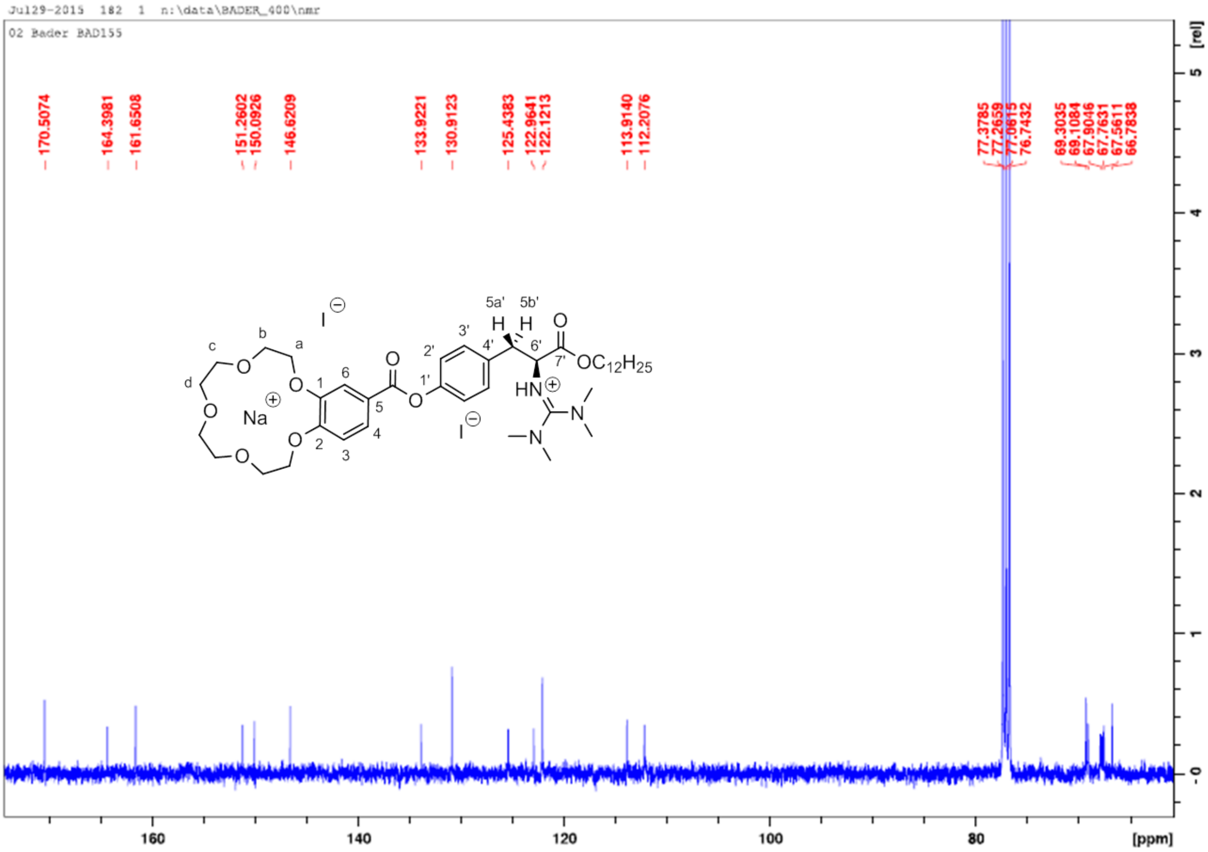

Jul29-2015 182 1 n:\data\BADER_400\nmr
02 Bader BAD155
170.5074
164.3981
161.6508
151.2602
150.0926
146.6209
133.9221
130.9123
125.4383
122.9641
122.1213
113.9140
112.2076
77.3785
76.7432
69.3035
69.1084
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67.5611
66.7838
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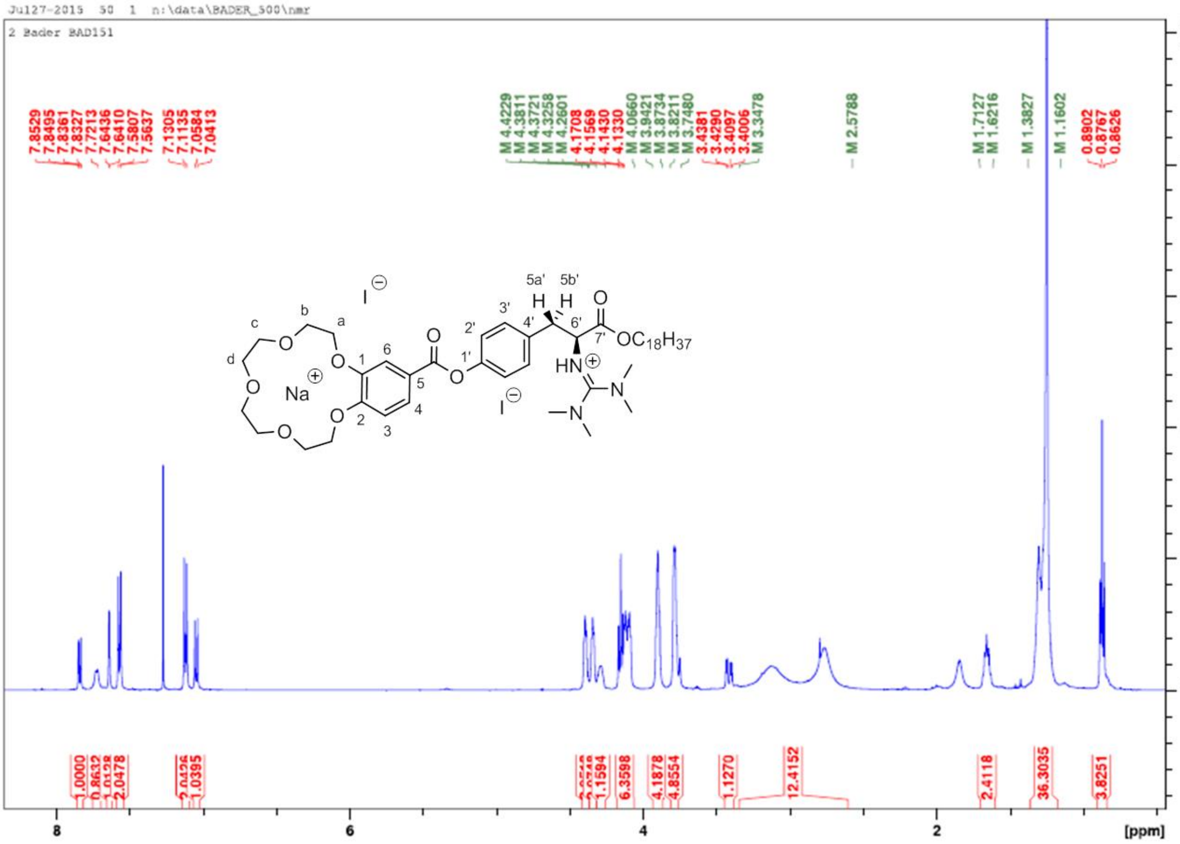
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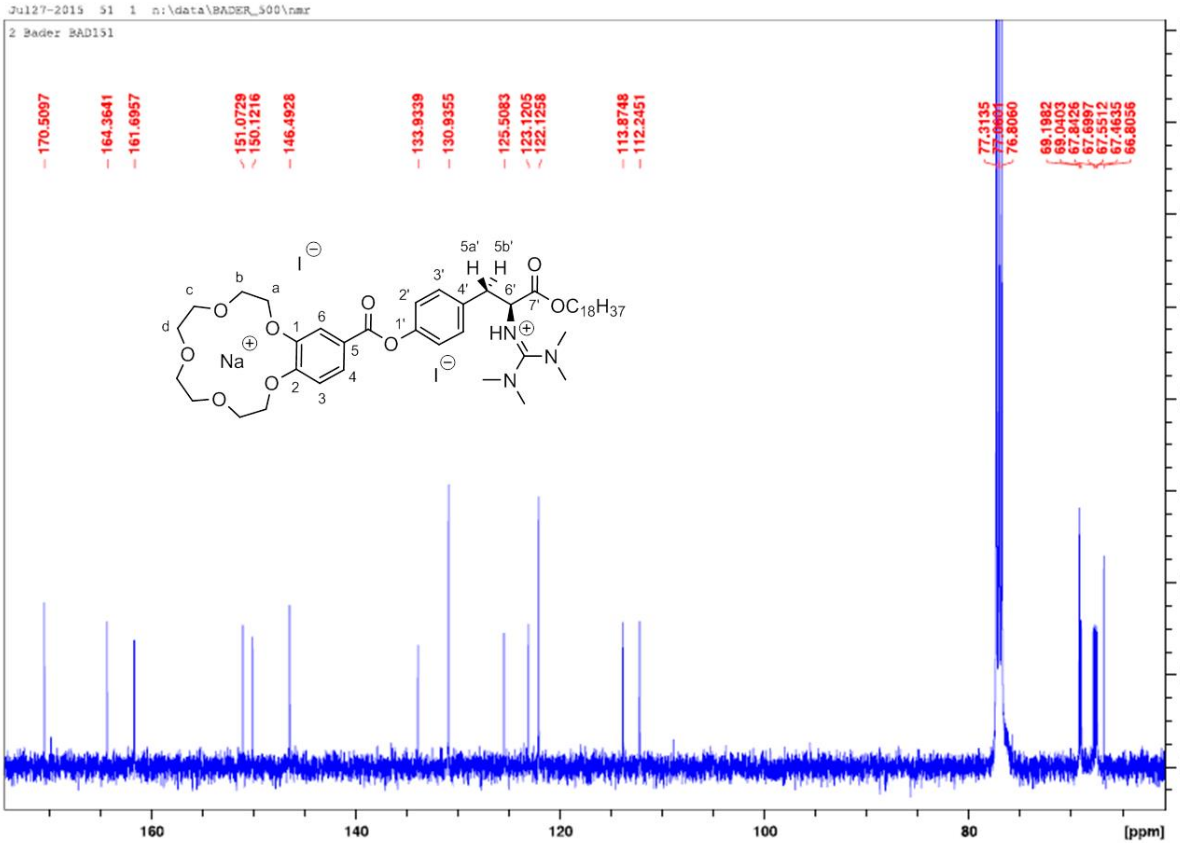
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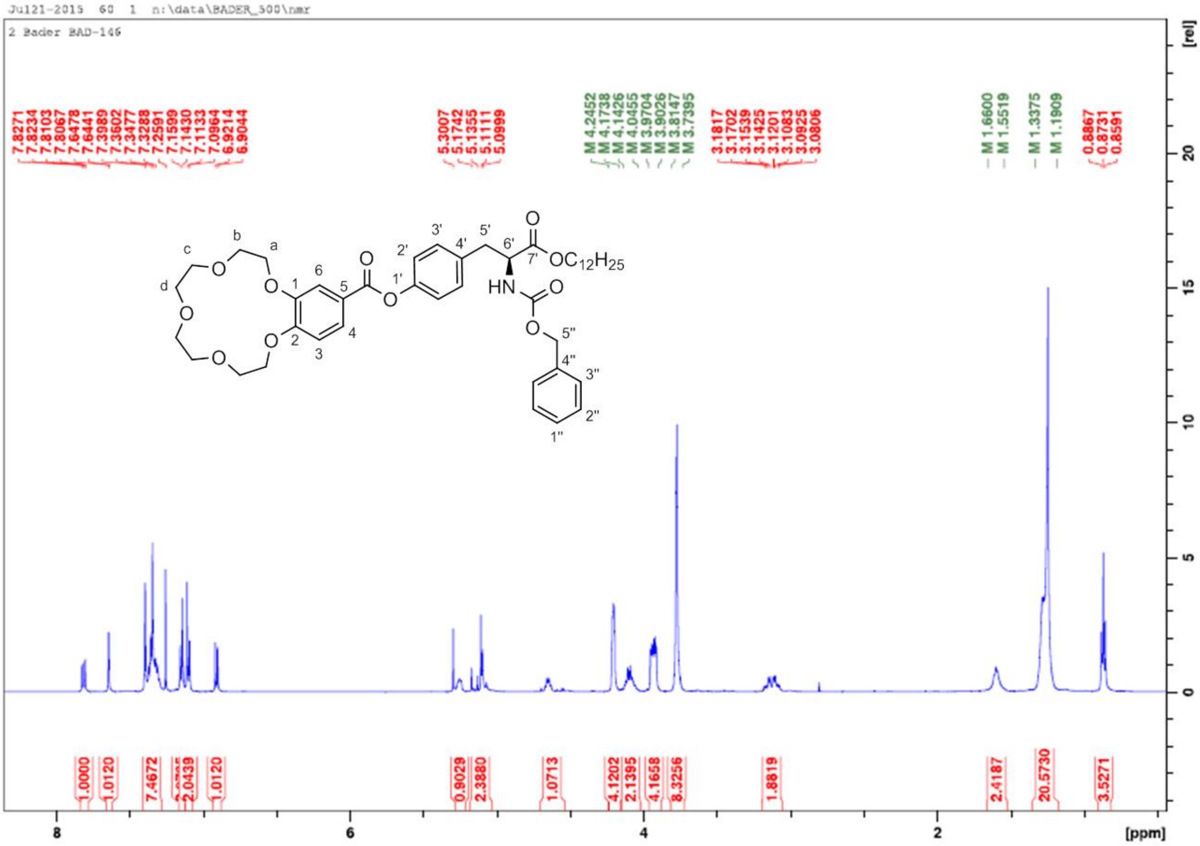
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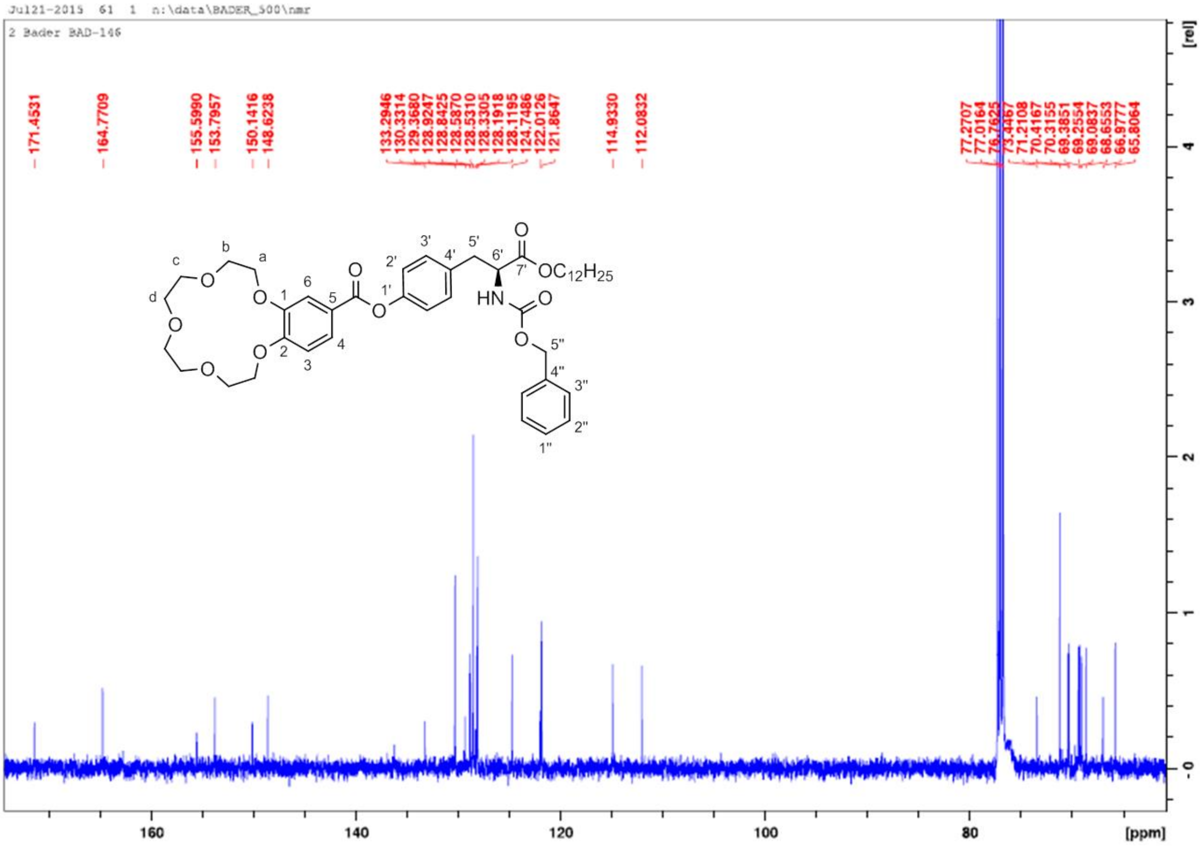
HN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2 Bader BAD-146
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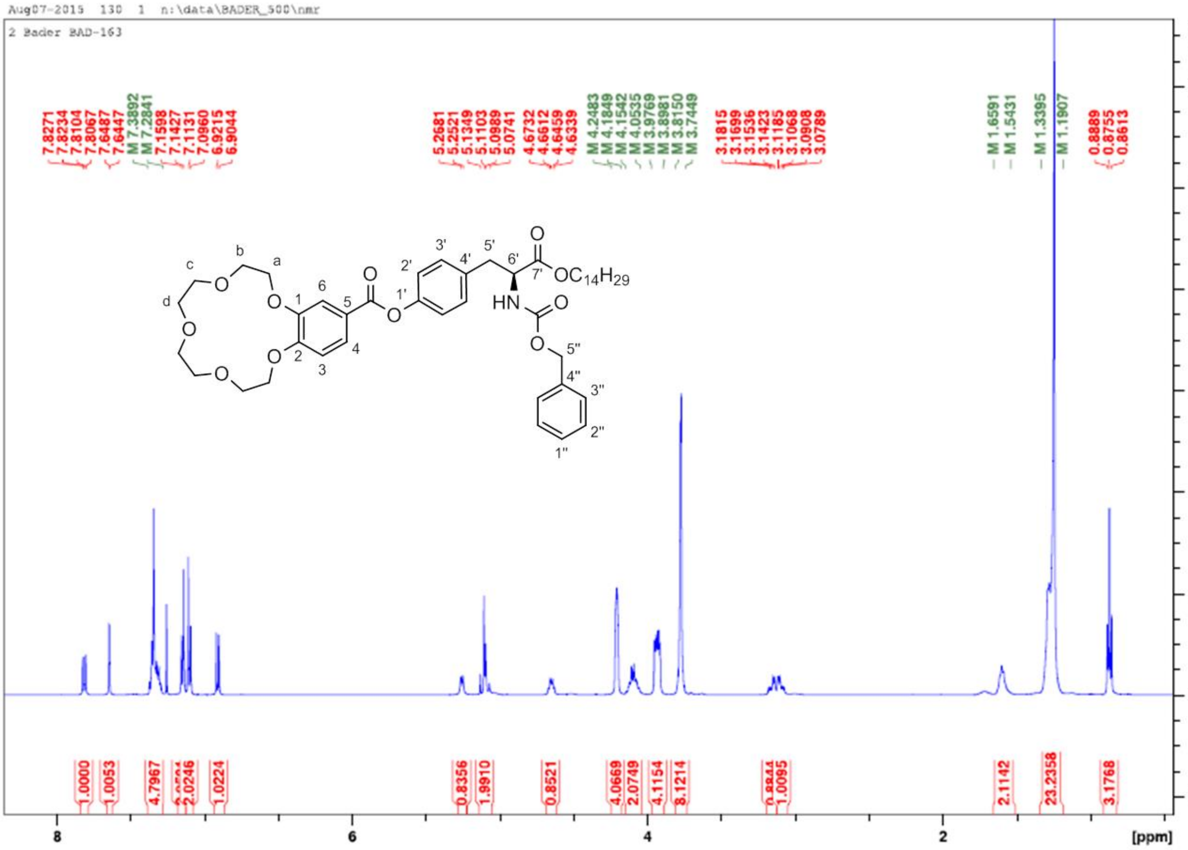
Aug07-2015 130 1 n:\data\BADER_500\nmr
2 Bader BAD-163
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5.2681 5.2521 5.1349 5.1103 5.0989 5.0741 4.6732 4.6612 4.6459 4.6339
M 4.2483 M 4.1849 M 4.1542 M 4.0535 M 3.9769 M 3.8981 M 3.8150 M 3.7449
3.1815 3.1699 3.1536 3.1423 3.1185 3.1068 3.0908 3.0789
M 1.6591 M 1.5431 M 1.3395 M 1.1907 0.8889 0.8755 0.8613
1.0000 1.0053 4.7967 2.0246 1.0224 0.8356 1.9910 0.8521 4.0669 2.0749 4.1154 8.1214 1.0095 2.1142 23.2358 3.1768
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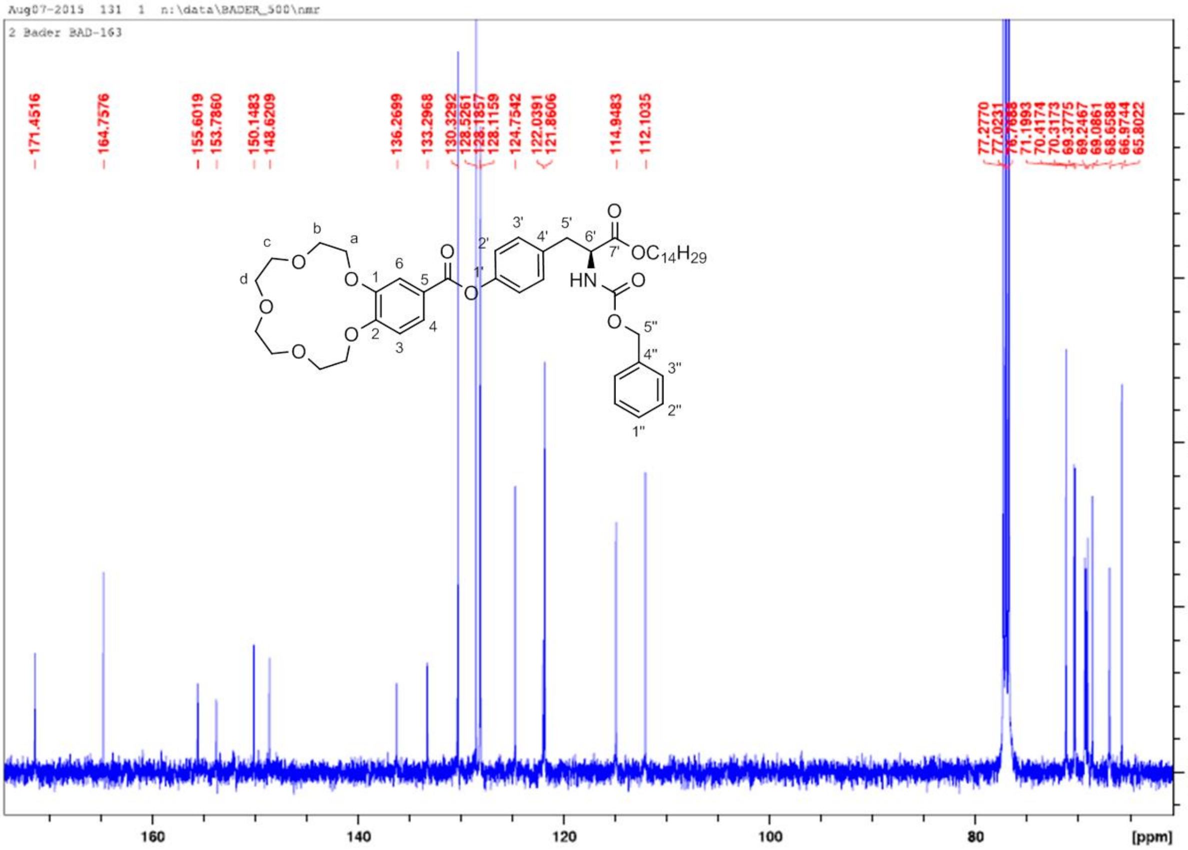
Aug07-2015 131 1 n:\data\BADER_500\nmr
2 Bader BAD-163
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77.2770 77.0231 71.1993 70.4174 70.3173 69.3775 69.2467 69.0861 68.6588 66.9744 65.8022
OC14H29
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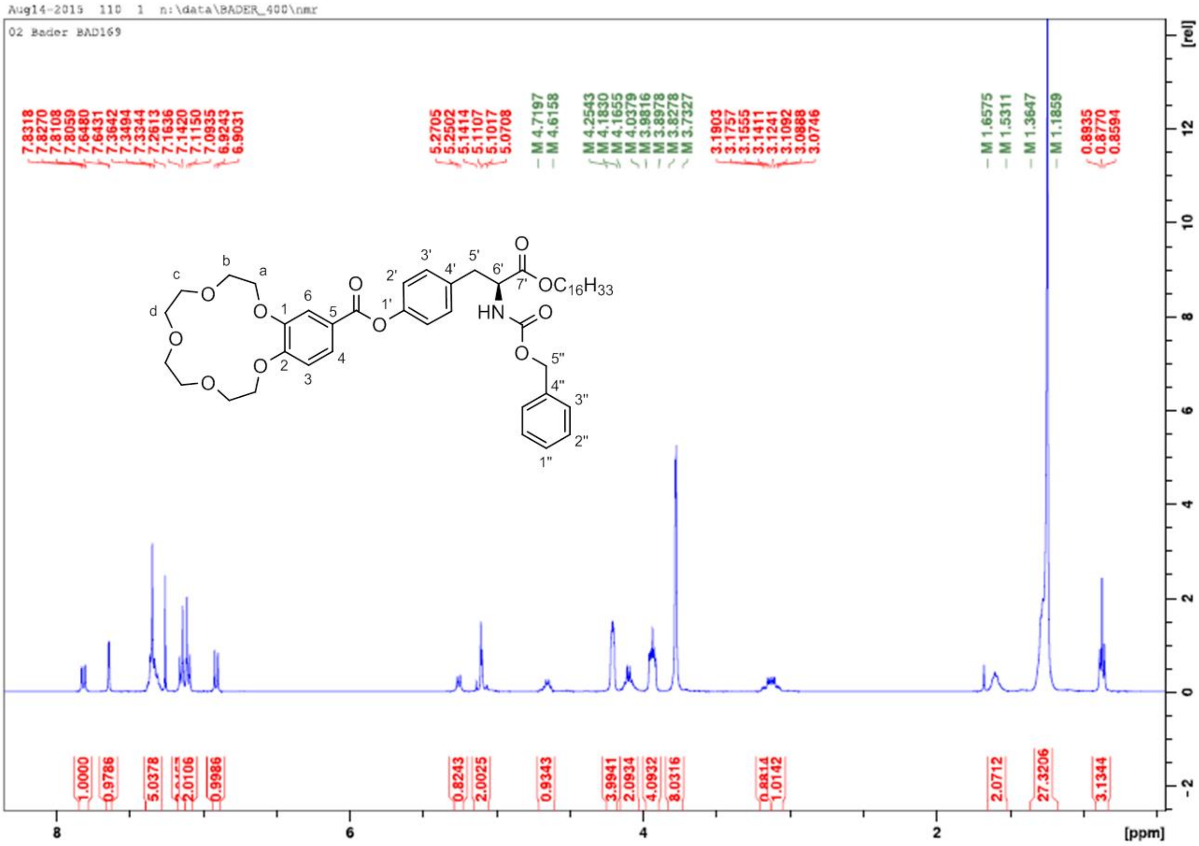

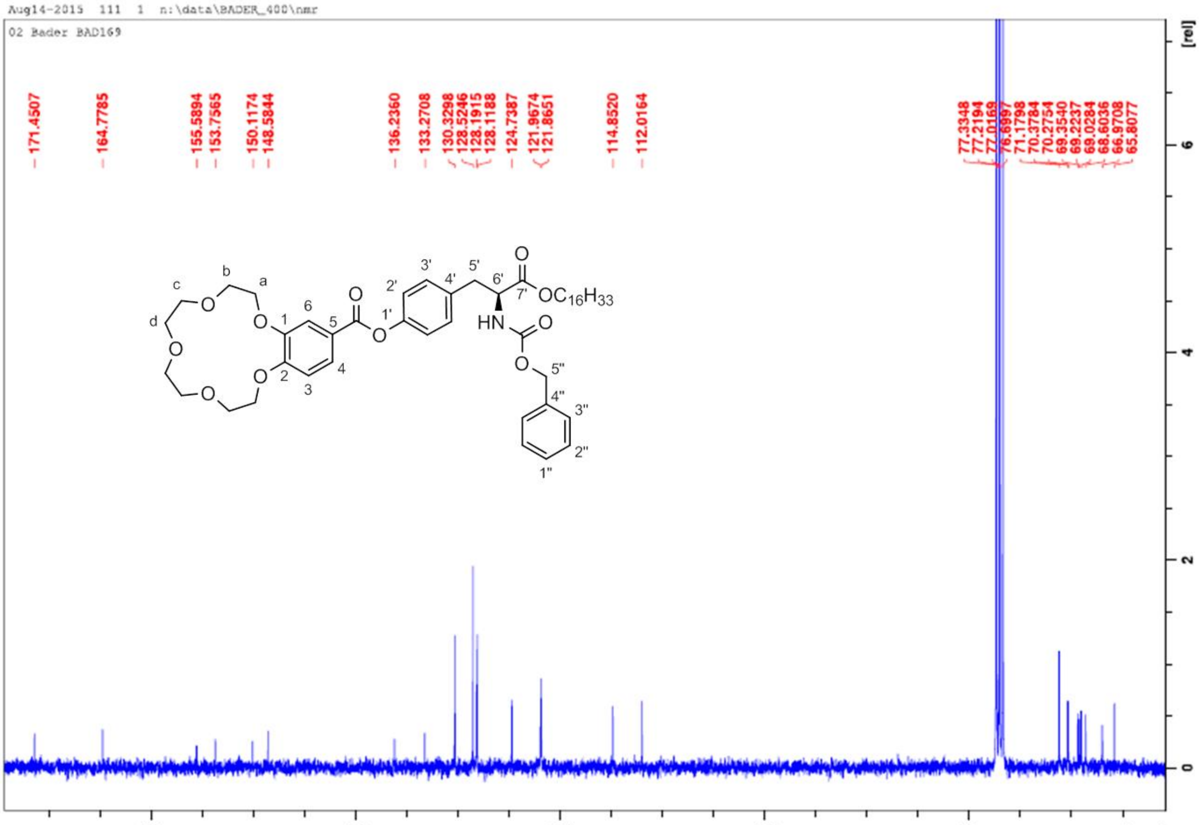

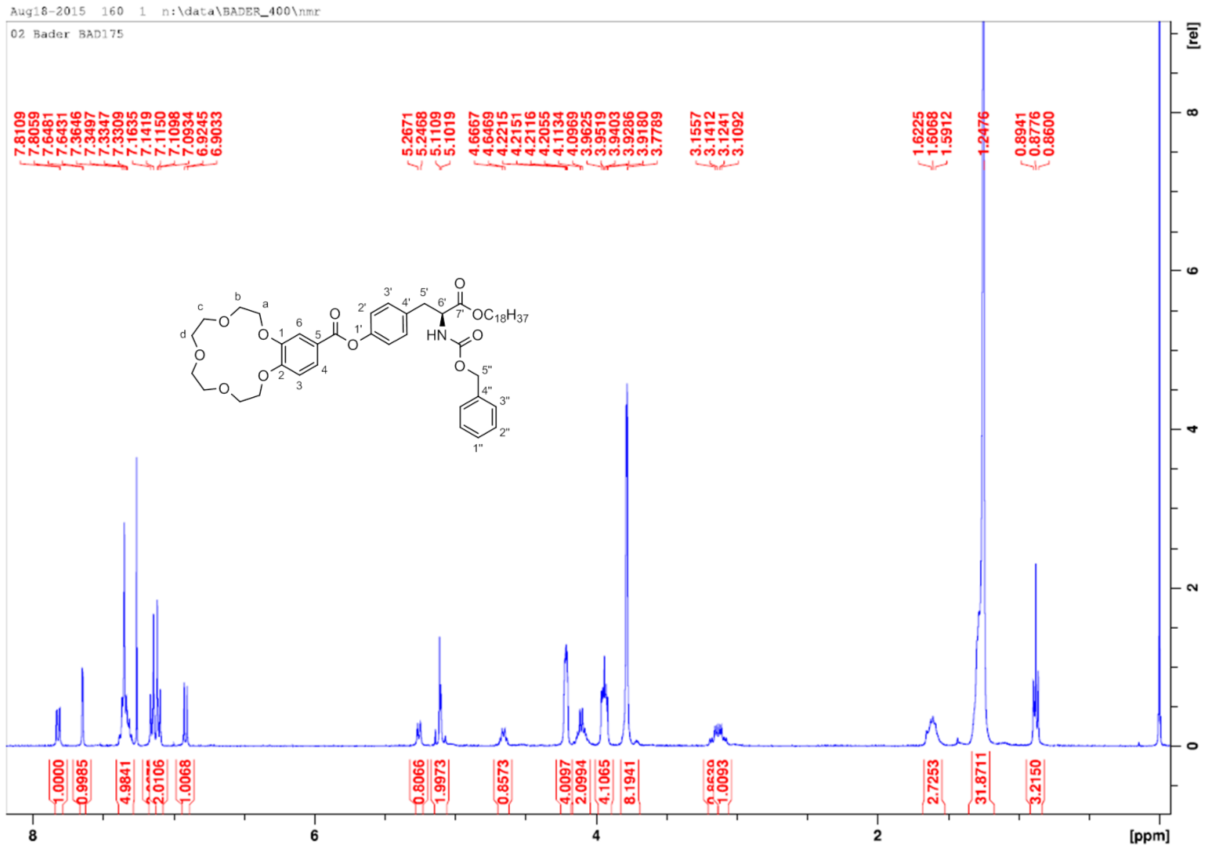

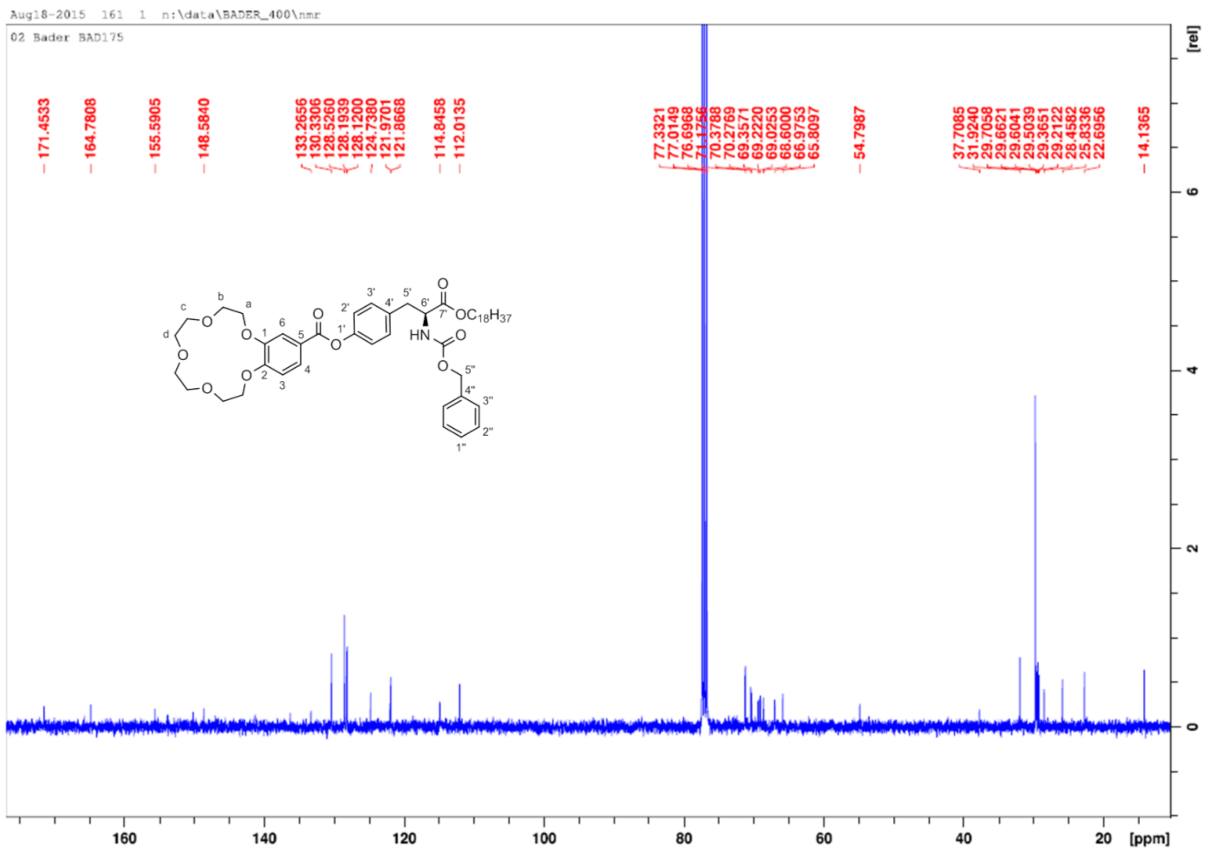

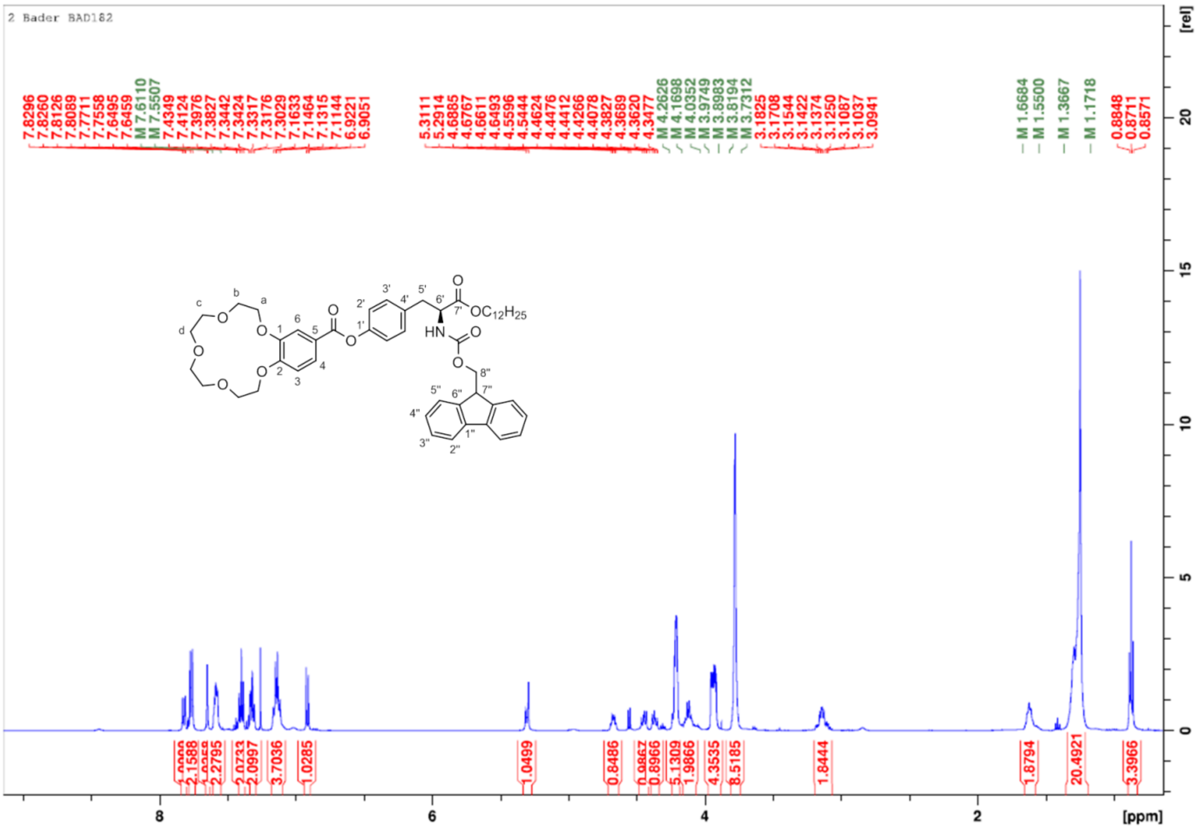

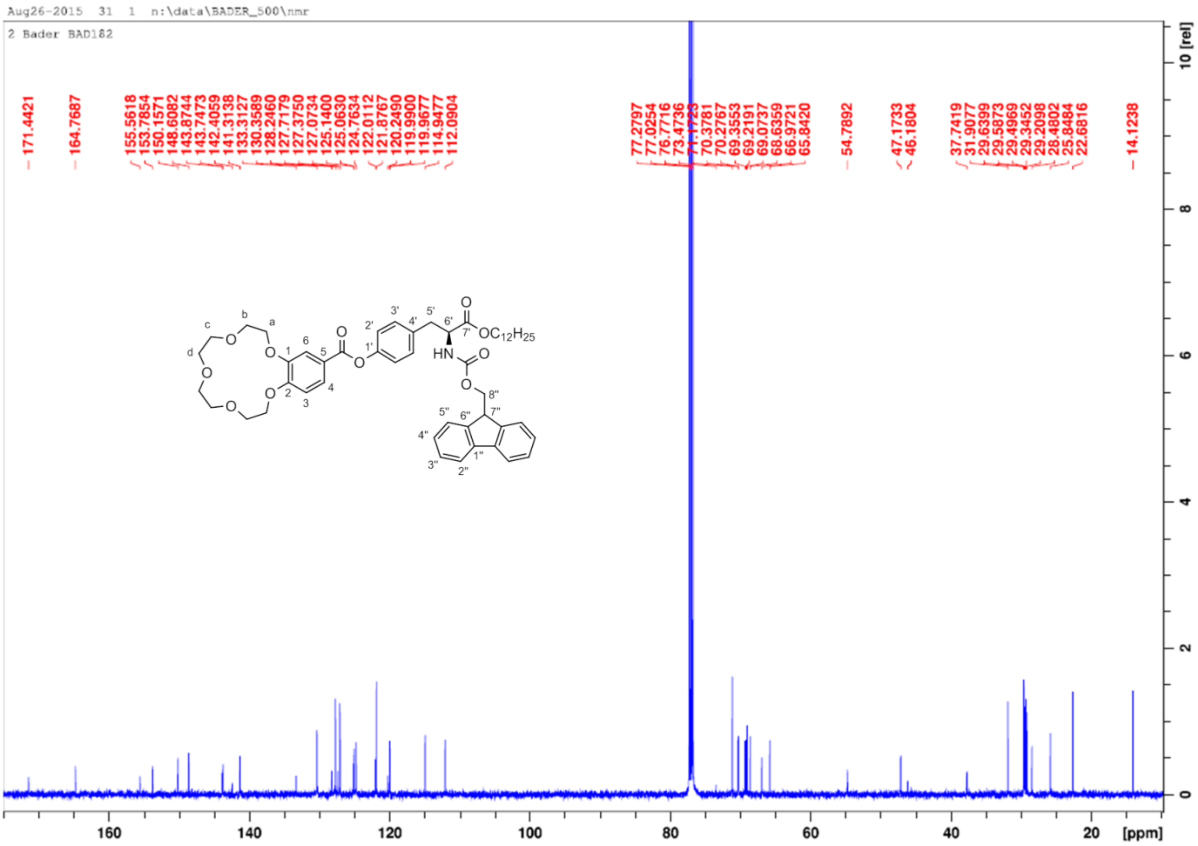

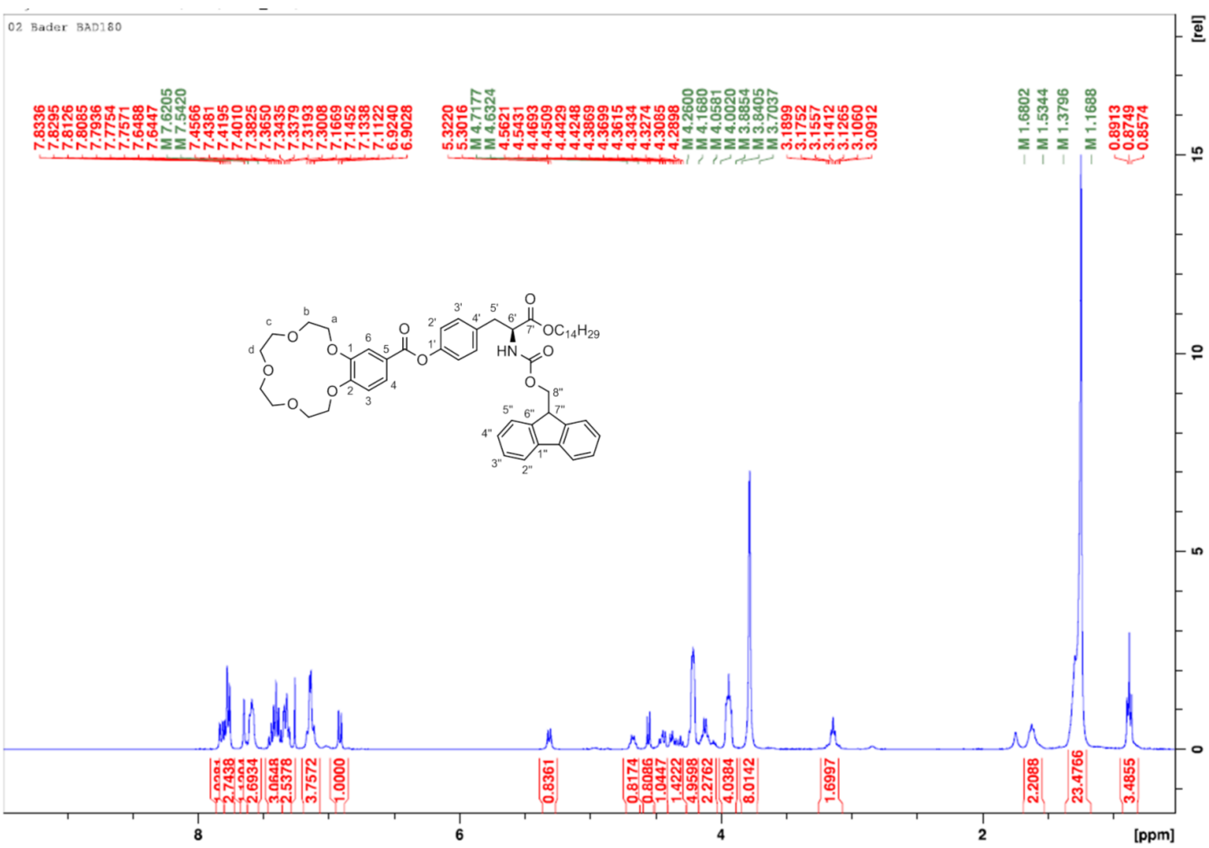
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7.7571
7.6488
7.6447
M 7.6205
M 7.5420
7.4566
7.4381
7.4195
7.4010
7.3825
7.3650
7.3435
7.3379
7.3193
7.3008
7.1669
7.1452
7.1338
7.1122
6.9240
6.9028
5.3220
5.3016
M 4.7177
M 4.6324
4.5621
4.5431
4.4693
4.4509
4.4429
4.4248
4.3869
4.3699
4.3615
4.3434
4.3274
4.3085
4.2898
M 4.2600
M 4.1680
M 4.0581
M 4.0020
M 3.8854
M 3.8405
M 3.7037
3.1899
3.1752
3.1557
3.1412
3.1265
3.1060
3.0912
M 1.6802
M 1.5344
M 1.3796
M 1.1688
0.8913
0.8749
0.8574
2.7438
3.0648
2.5378
3.7572
1.0000
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0.8174
0.8086
1.0447
1.4222
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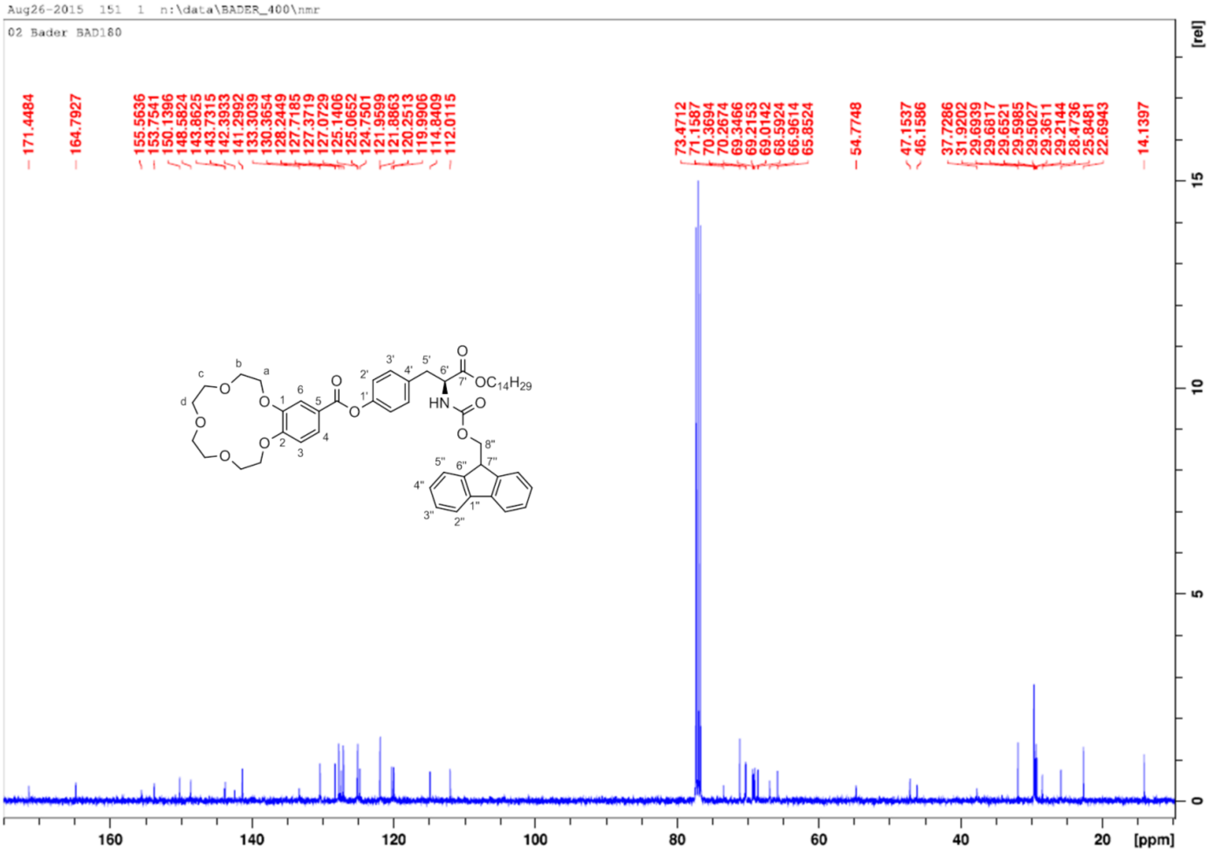
2.2762
4.0384
8.0142
1.6997
2.2088
23.4766
3.4855
[ppm]
[rel]
a
b
c
d
1
2
3
4
5
6
1'
2'
3'
4'
5'
6'
7'
1''
2''
3''
4''
5''
6''
7''
8''
O
HN
OC14H29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143.7315
142.3933
141.2992
133.3039
130.3654
128.2449
127.7185
127.3719
127.0729
125.1406
125.0652
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120.2513
119.9906
114.8409
112.0115
73.4712
71.1587
70.3694
70.2674
69.3466
69.2153
69.0142
68.5924
66.9614
65.8524
54.7748
47.1537
46.1586
37.7286
31.9202
29.6939
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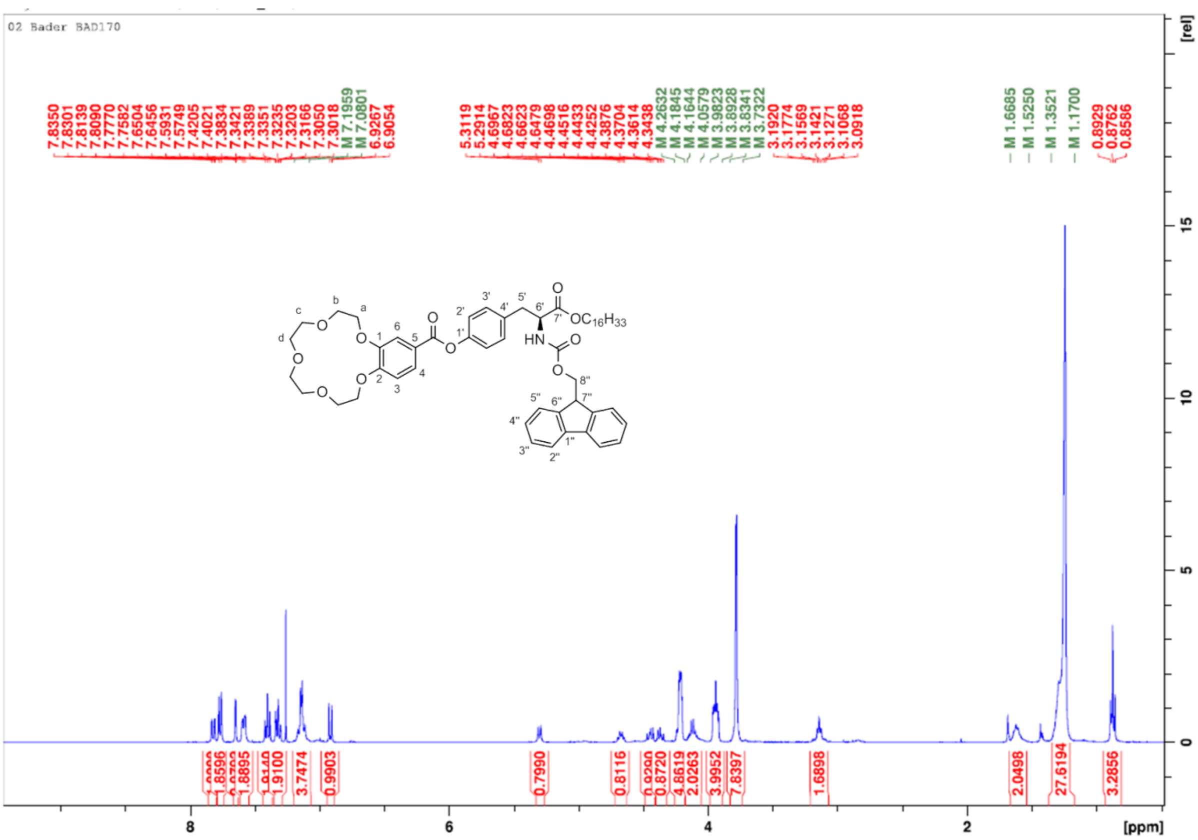
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7.6456
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7.5749
7.4205
7.4021
7.3834
7.3421
7.3389
7.3351
7.3235
7.3203
7.3166
7.3050
7.3018
M 7.1959
M 7.0801
6.9267
6.9054
5.3119
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4.6823
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4.6479
4.4698
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4.4433
4.4252
4.3876
4.3704
4.3614
4.3438
M 4.2632
M 4.1845
M 4.1644
M 4.0579
M 3.9823
M 3.8928
M 3.8341
M 3.7322
3.1920
3.1774
3.1569
3.1421
3.1271
3.1068
3.0918
M 1.6685
M 1.5250
M 1.3521
M 1.1700
0.8929
0.8762
0.8586
$OC_{16}H_{33}$
HN
1.8596
1.8895
1.9100
3.7474
0.9903
0.7990
0.8116
0.8720
4.8619
2.0263
3.9952
7.8397
1.6898
2.0498
27.6194
3.2856
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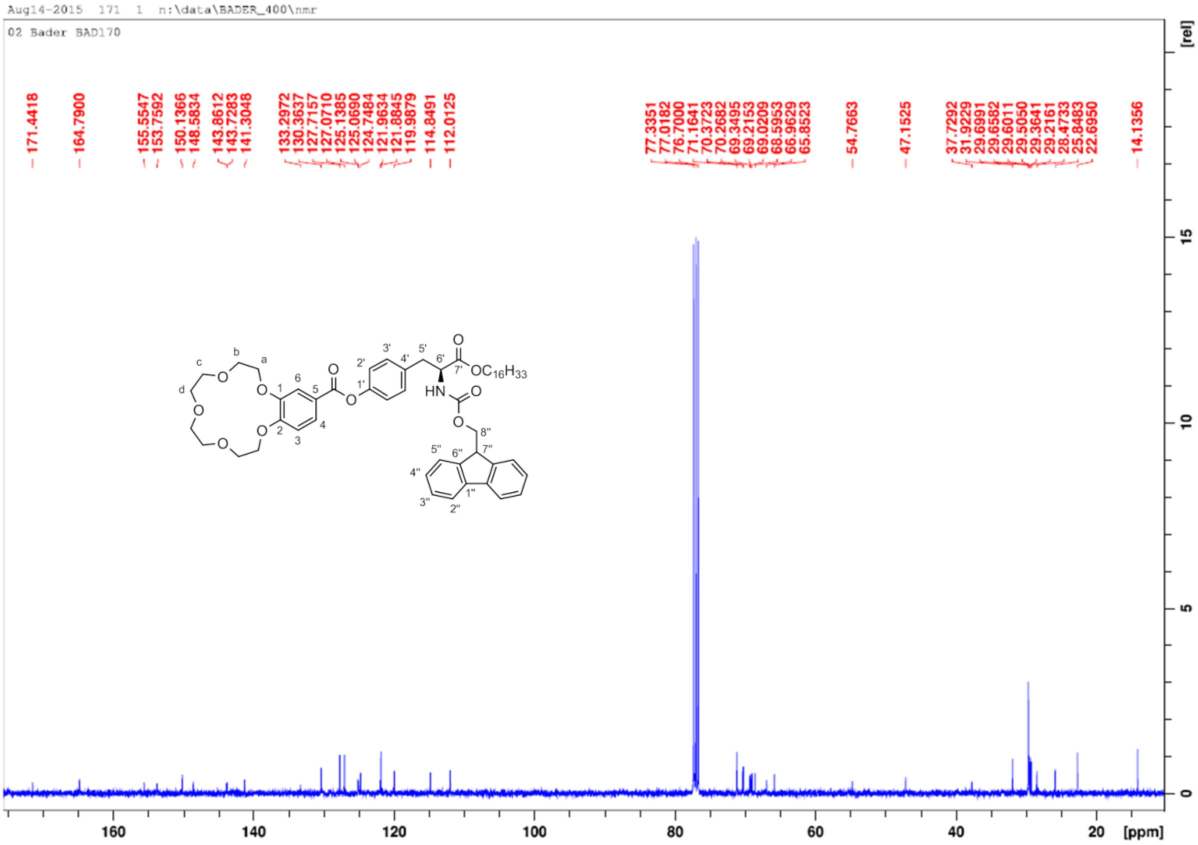
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150.1366
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143.8612
143.7283
141.3048
133.2972
130.3637
127.7157
127.0710
125.1385
125.0690
124.7484
121.9634
121.8845
119.9879
114.8491
112.0125
77.3351
77.0182
76.7000
71.1641
70.3723
70.2682
69.3495
69.2153
69.0209
68.5953
66.9629
65.8523
54.7663
47.1525
37.7292
31.9229
29.6991
29.6582
29.6011
29.5050
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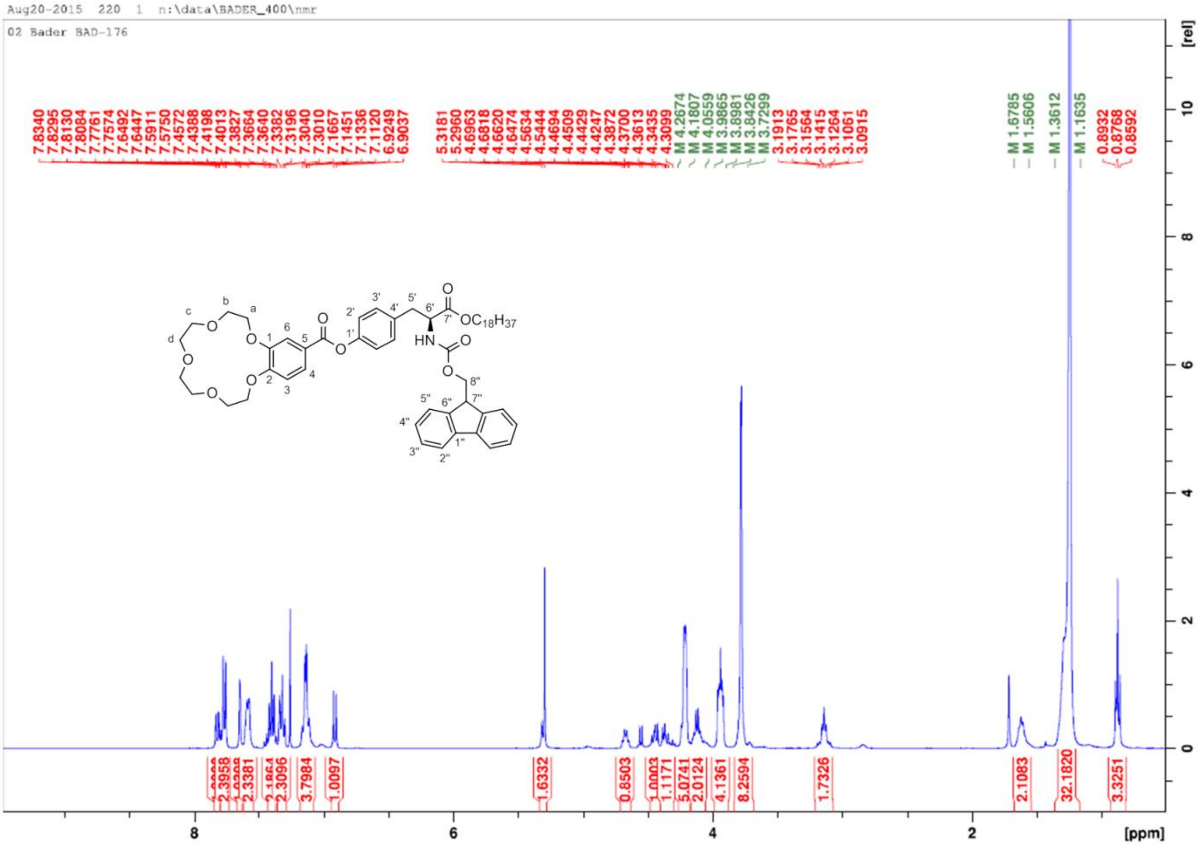
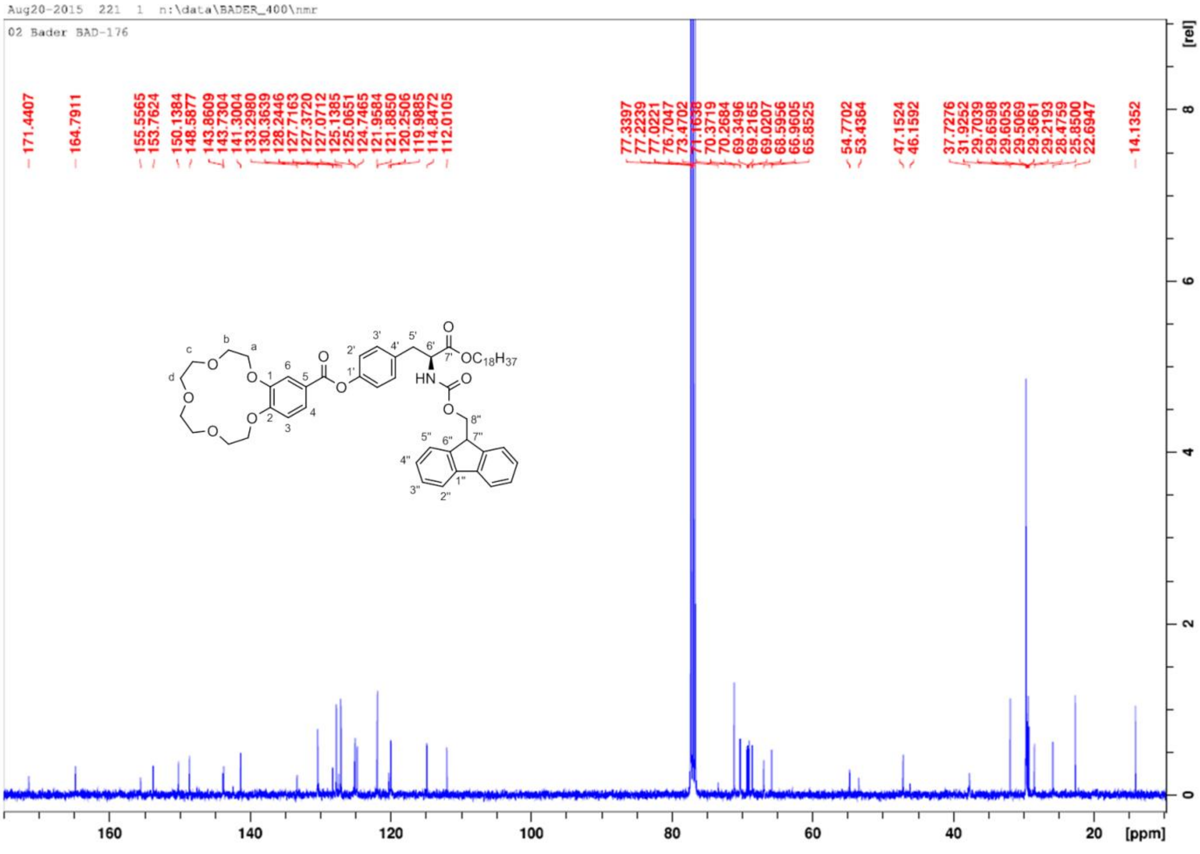
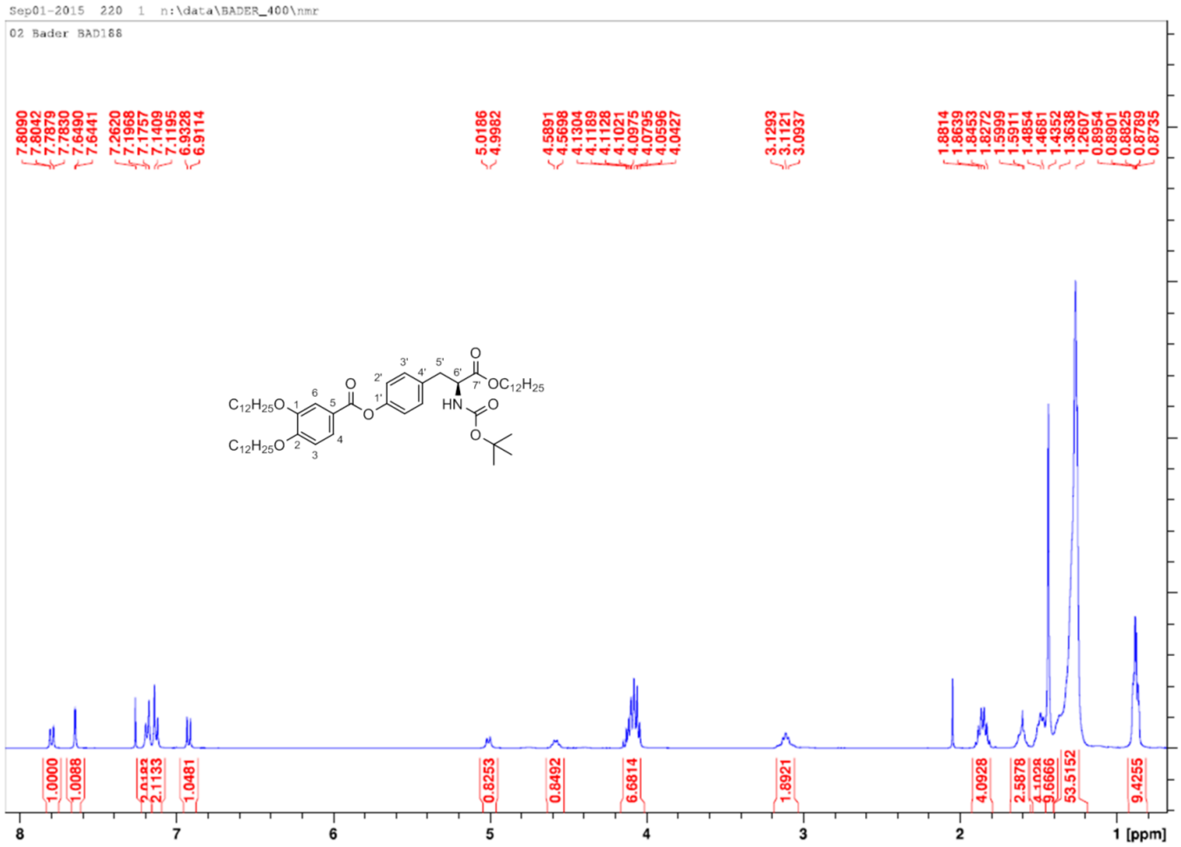
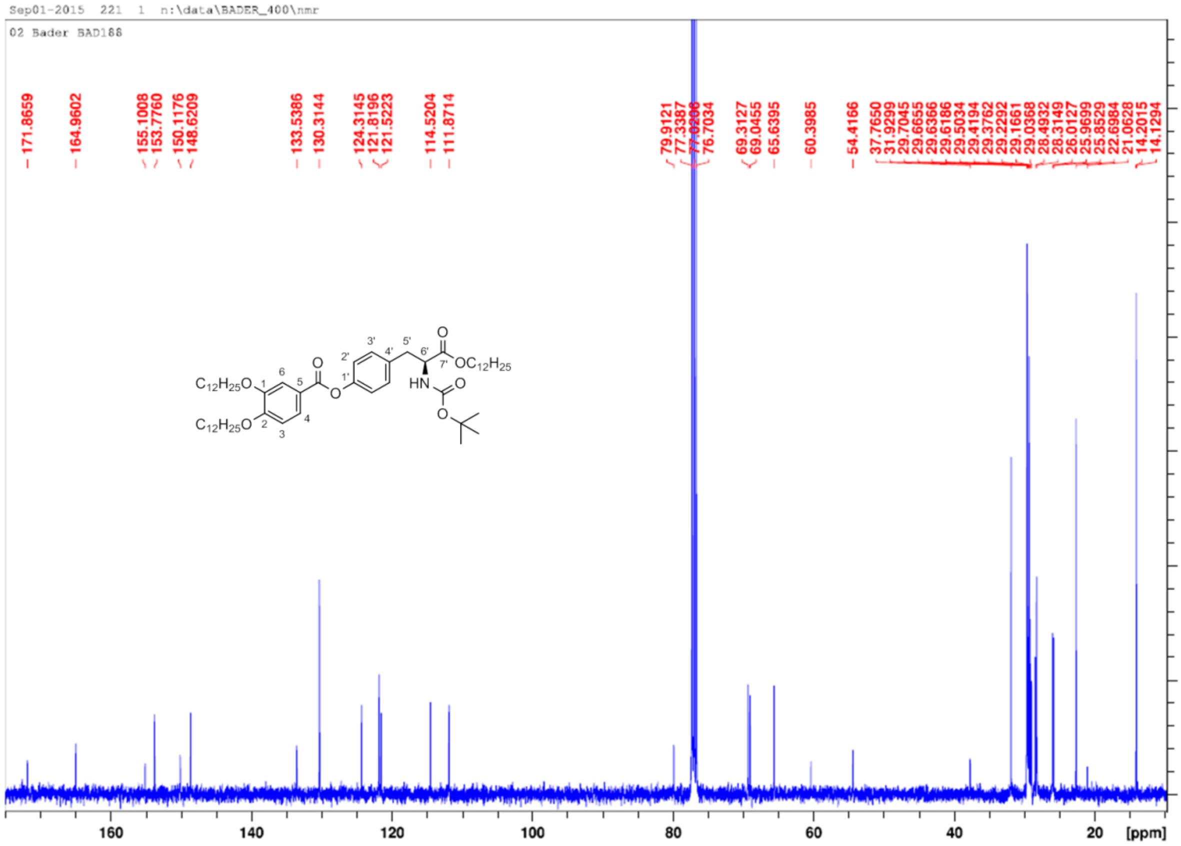
25.8483
22.6950
14.1356
$OC_{16}H_{33}$
HN
[rel]
[ppm]







Sep01-2015 220 1 n:\data\BADER_400\nmr
02 Bader BAD188
C12H25O
C12H25O
1
2
3
4
5
6
O
O
1'
2'
3'
4'
5'
6'
7'
O
OC12H25
HN
O
O



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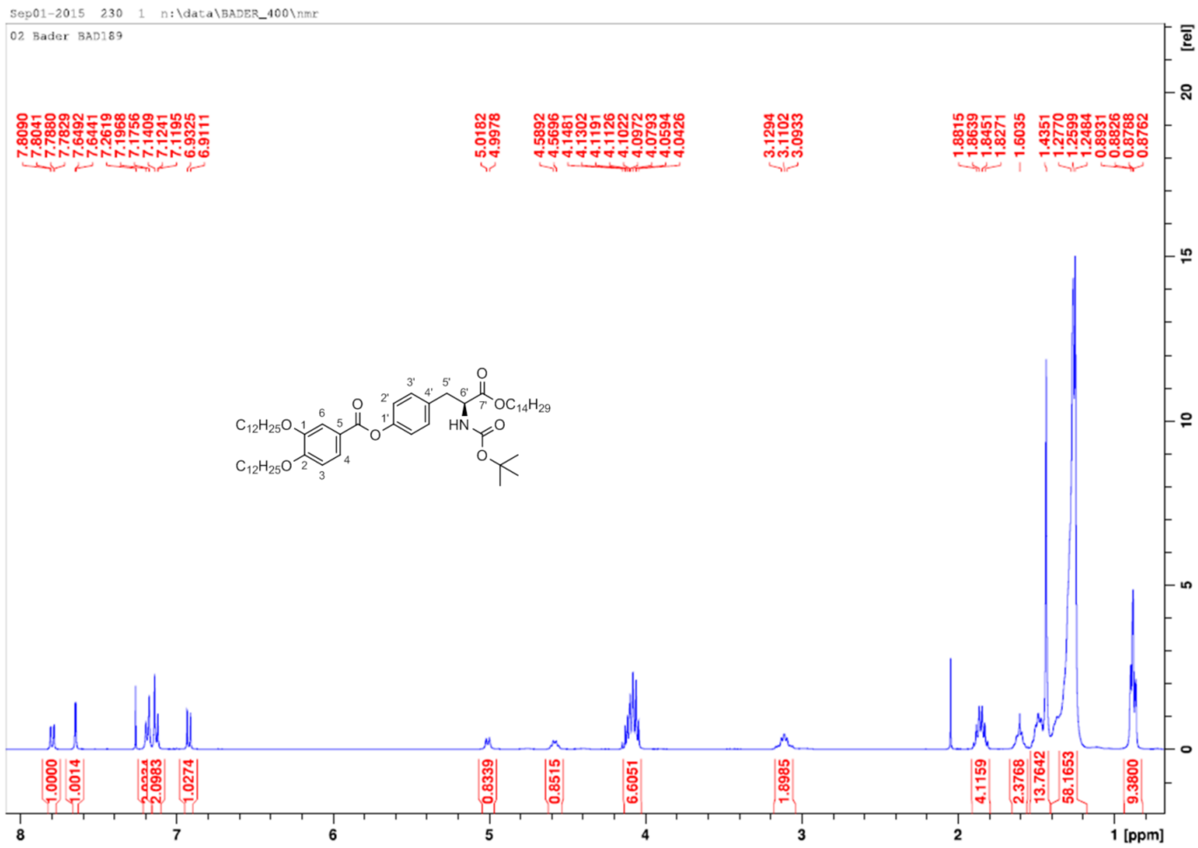
02 Bader BAD188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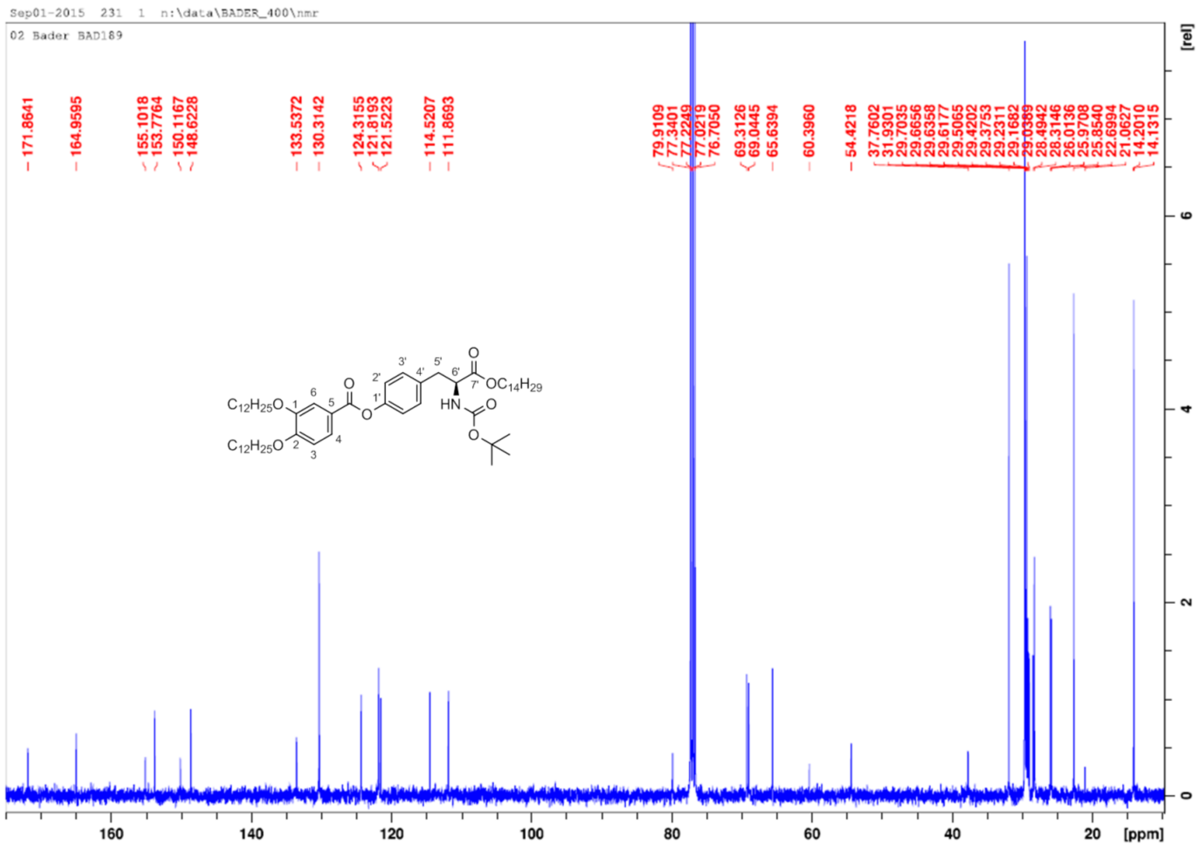
5.0182 4.9978
4.5892 4.5696 4.1481 4.1302 4.1191 4.1126 4.1022 4.0972 4.0793 4.0594 4.0426
3.1294 3.1102 3.0933
1.8815 1.8639 1.8451 1.8271 1.6035 1.4351 1.2770 1.2599 1.2484 0.8931 0.8826 0.8788 0.8762
C12H25O
C12H25O
OC14H29
HN
1.0000 1.0014 2.0983 1.0274 0.8339 0.8515 6.6051 1.8985 4.1159 2.3768 13.7642 58.1653 9.3800
[rel]
ppm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79.9109 77.3401 77.2249 77.0219 76.7050 69.3126 69.0445 65.6394 60.3960 54.4218
37.7602 31.9301 29.7035 29.6656 29.6358 29.6177 29.5065 29.4202 29.3753 29.2311 29.1682 29.0389 28.4942 28.3146 26.0136 25.9708 25.8540 22.6994 21.0627 14.2010 14.1315
C12H25O
C12H25O
OC14H29
HN
[rel]
ppm