

Supporting Information

Bile Acid Amphiphiles with Tunable Head Groups as Highly Selective Antitubercular Agents

Sandhya Bansal,^{a,†} Manish Singh,^{a,†} Saqib Kidwai,^{b,†} Priyanshu Bhargava,^a Ashima Singh,^a Vedagopuram Sreekanth,^a Ramandeep Singh,^{b,*} and Avinash Bajaj^{a,*}

^aThe Laboratory of Nanotechnology and Chemical Biology, Regional Centre for Biotechnology, 180 Udyog Vihar, Phase 1, Gurgaon-122016, Haryana, India. ^bVaccine and Infectious Disease Research Centre, Translational Health Science and Technology Institute, 496 Udyog Vihar Phase III, Gurgaon-122016, Haryana, India.

[†]These Authors contributed equally.

*Corresponding Author:

Ramandeep Singh: Email: ramandeep@thsti.res.in, +91-124-2876501.

Avinash Bajaj: Email: bajaj@rcb.res.in, Ph: +91-124-2848831, Fax: +91-124-4038117

Table S1: Topological parameters of *E. coli* and *M. bovis* BCG probed by AFM showing the selective membrane perturbations of *E. coli* by CA-AMM₃ and of *M. bovis* BCG by CA-DMAP₃.

<i>E. coli</i>	Length (μm)	Width (μm)	Height (nm)	Corrugation (nm)
Control	2.57 ± 0.19	1.06 ± 0.01	180.66 ± 9.70	6.42 ± 0.79
CA-AMM₃	2.61 ± 0.25	1.01 ± 0.01	157.67 ± 3.81	40.96 ± 4.40
CA-DMAP₃	2.78 ± 0.29	1.15 ± 0.05	176.80 ± 11.09	10.93 ± 1.62
<i>M. bovis</i> (BCG)	Length (μm)	Width (μm)	Height (nm)	Corrugation (nm)
Control	4.14 ± 0.39	0.61 ± 0.02	207.60 ± 1.48	18.77 ± 1.57
CA-AMM₃	4.27 ± 0.02	0.67 ± 0.01	184.95 ± 13.31	18.77 ± 1.28
CA-DMAP₃	2.84 ± 0.37	0.69 ± 0.05	145.0 ± 11.31	48.24 ± 2.70

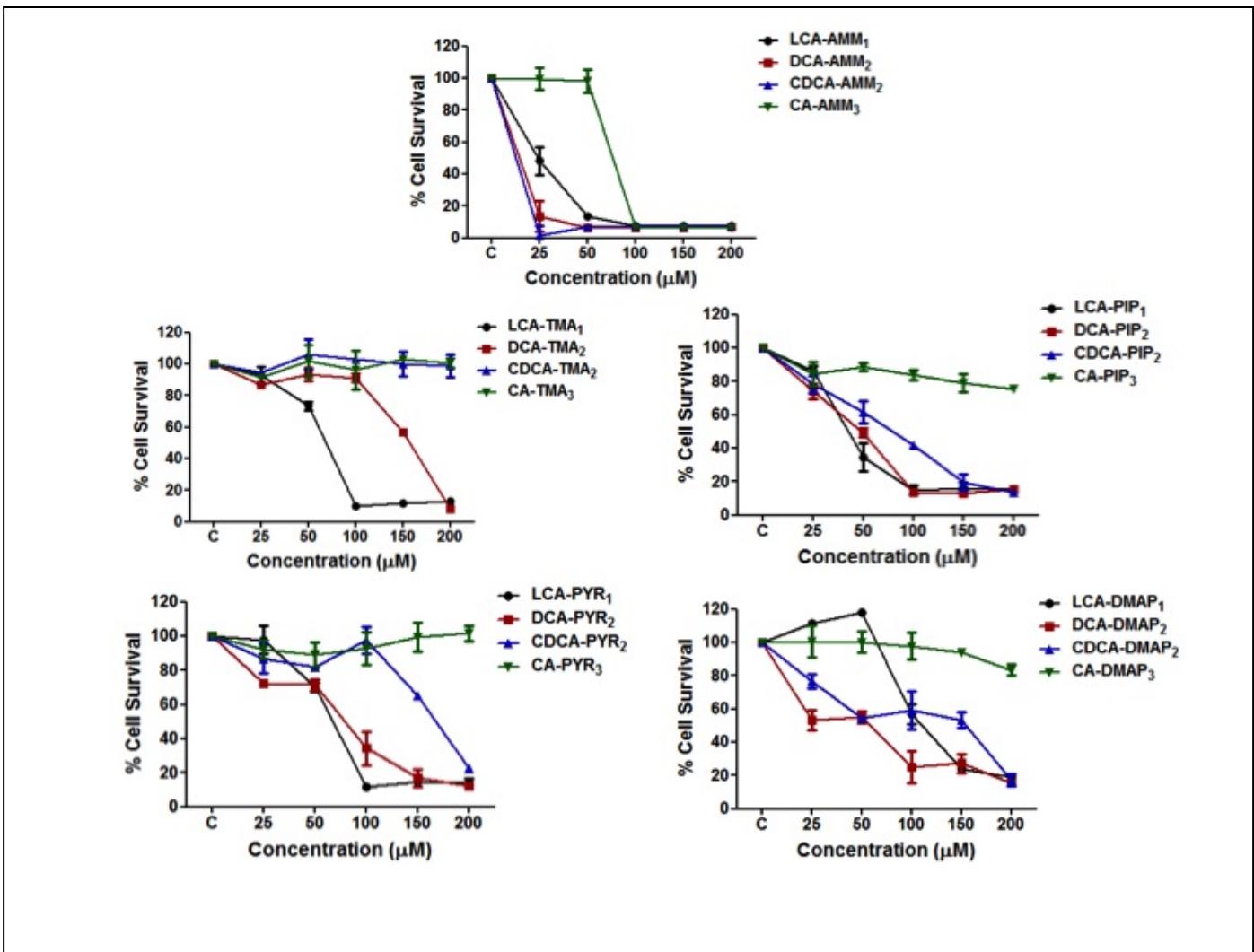


Fig. S1. Cytotoxic activities of bile acid facial amphiphiles at different concentrations against lung epithelial A549 cells.

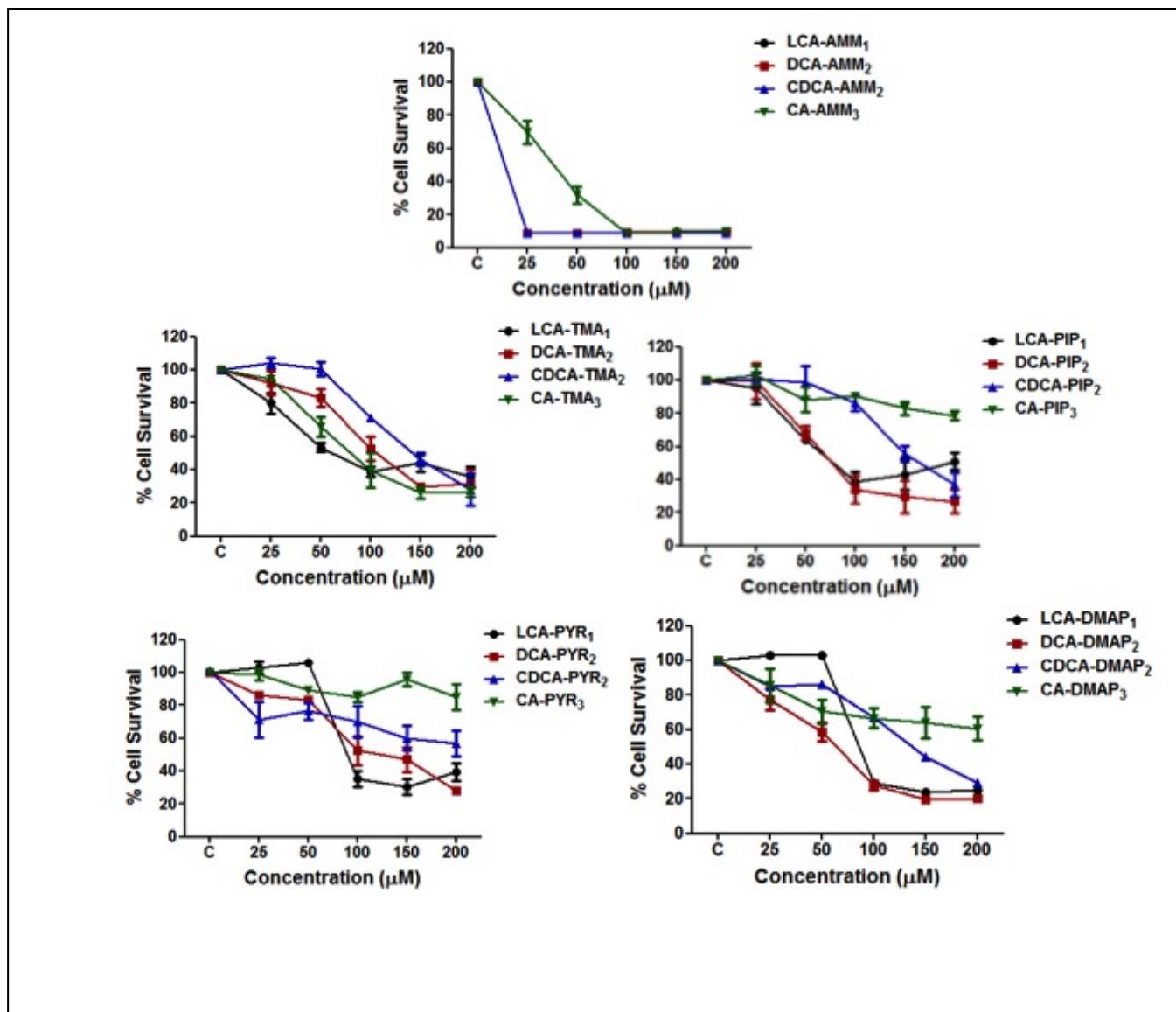


Fig. S2. Cytotoxic activities of bile acid facial amphiphiles at different concentrations against macrophage THP-1 cells.

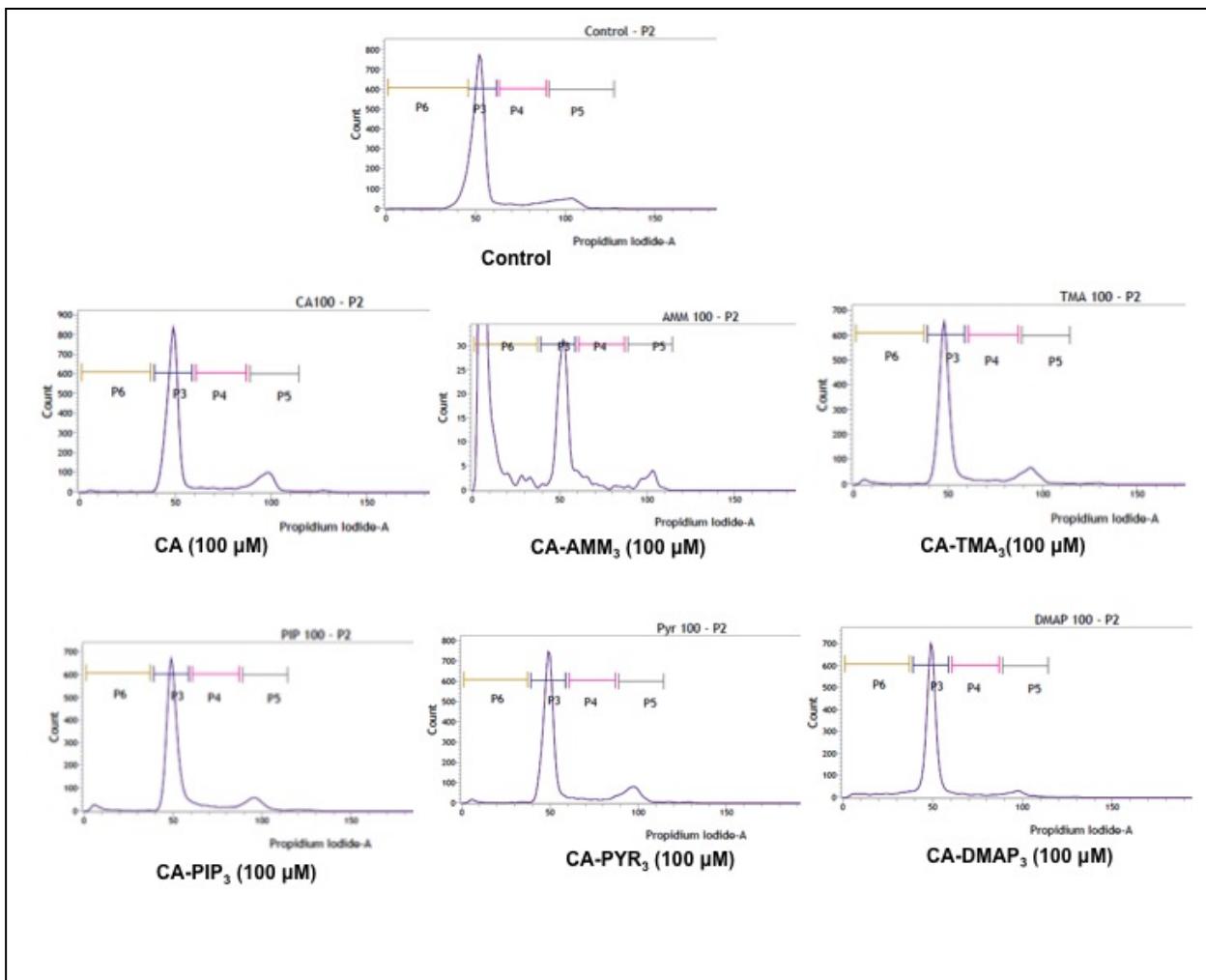


Fig. S3: Cell cycle analysis of cholic acid based amphiphiles against A549 cells showing no change in cell cycle phase of cells up at 100 μM concentration of hard-charged amphiphiles.

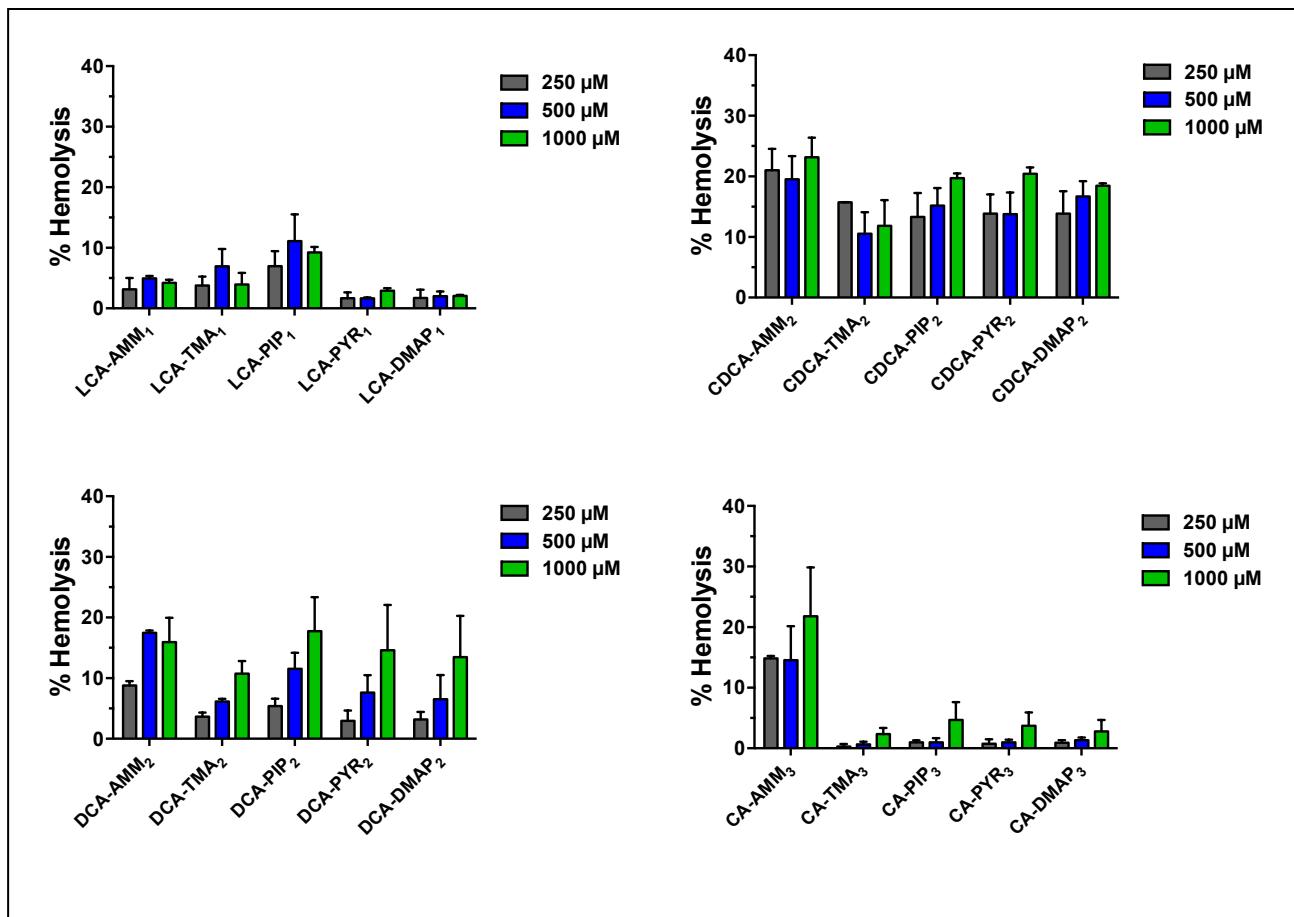


Fig. S4: Hemolytic activities of bile acid amphiphiles showing percentage of hemolysis at 250, 500 and 1000 μM concentrations of bile acid amphiphiles.

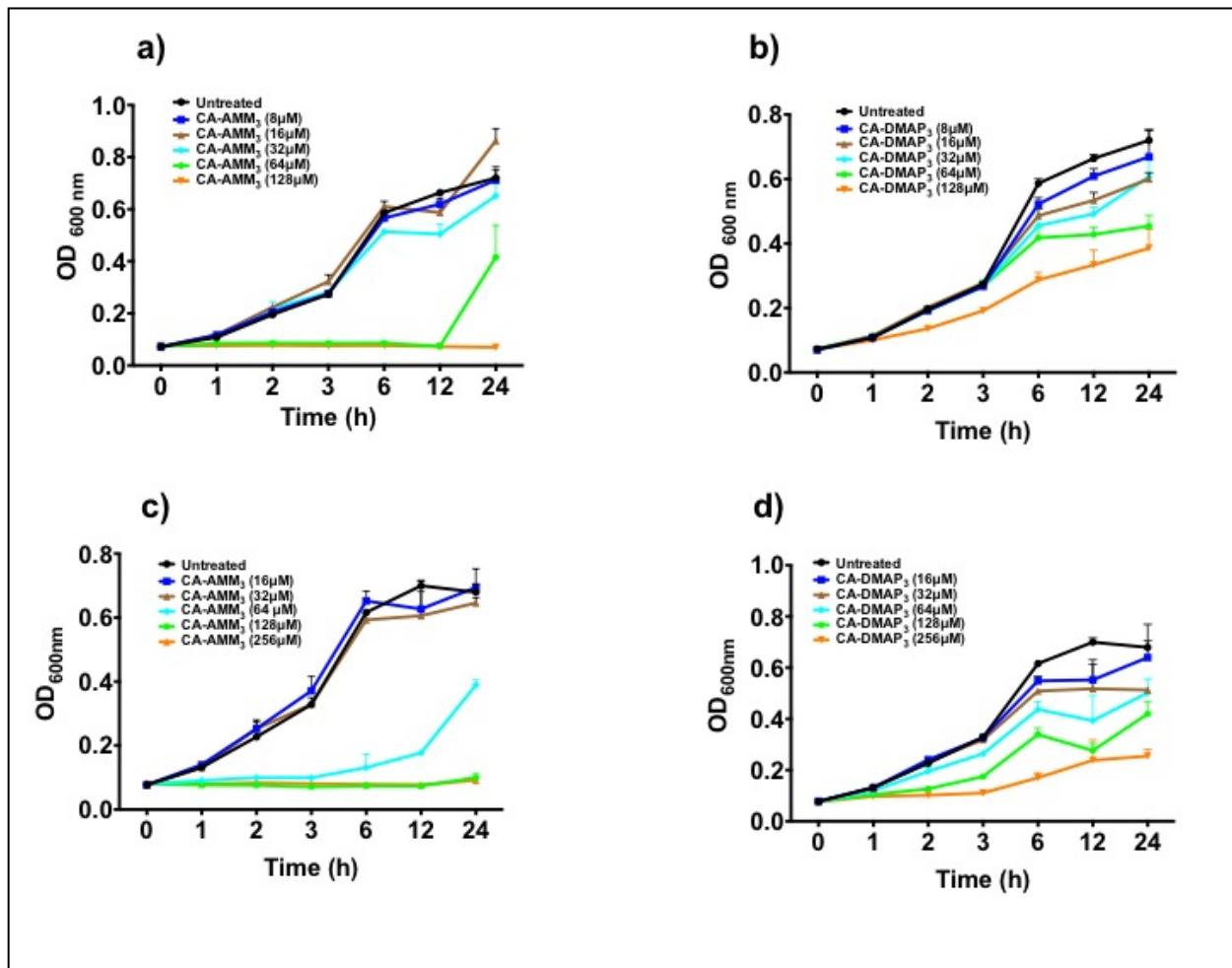
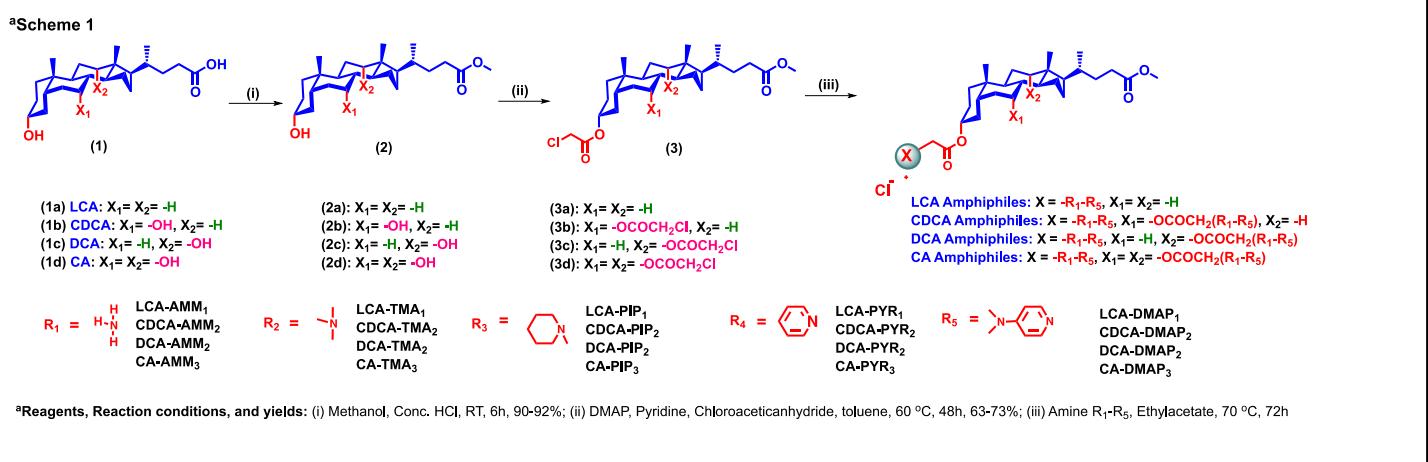


Fig. S5. Concentration and time dependent activities of CA-AMM₃ (a, c) and CA-DMAP₃ (b, d) against *E. coli* (a, b) and *S. aureus* (c, d) bacteria showing their selective killing by soft-charged amphiphile CA-AMM₃.



Synthesis of bile acid facial amphiphiles:

Synthesis of Bile Acid Amphiphiles

Chloroactetyl derivatives of bile acid methyl esters (**3a-3d**) was synthesized as described earlier (Biochim. Biophys. Acta Biomembr. 2013, 1828, 1926). Bile Acid amphiphiles were synthesized by quaternization of corresponding chloroactetyl derivatives of bile acid methyl esters in ethyl acetate (5 mL) in seal tube with corresponding amine derivative. The reaction mixture was heated at 70 °C for 48h-72h. After completion of reaction, solvent was removed and repeated washing with ethyl acetate or acetone give purified product.

LCA-AMM₁: ¹H NMR (CDCl₃, 400 MHz) δ: 0.64 (s, 3H, -CH₃), 0.91 (s, 6H, -2 x CH₃), 1.02-2.35 (steroid), 3.66 (s, 3H, -CO-OCH₃), 3.90 (m, 2H, -CO-CH₂-N-), 4.82 (s, 1H, -O-CH), 8.49 (bs, 2H, -NH₂). ¹³C-NMR (DMSO, 100 MHz) δ: 12.30, 18.56, 20.84, 23.22, 24.27, 26.40, 26.54, 27.00, 28.15, 30.82, 31.06, 32.13, 34.59, 34.74, 35.25, 35.73, 41.47, 42.72, 51.69, 55.91, 56.37, 76.09, 167.58, 174.26. HRMS (ESI-MS): m/z (C₂₇H₄₆NO₄)⁺ calculated 448.3427; found (M)⁺ 448.3431.

LCA-TMA₁: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.63 (s, 3H, -CH₃), 0.91 (s, 6H, -2 x CH₃), 1.02-2.35 (steroid), 3.64(s, 9H, -N-(CH₃)₃; 3H, -CO-OCH₃), 4.78 (m, 1H, -O-CH), 4.84 (m, 2H, -CO-CH₂-N-). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.05, 18.28, 20.25, 23.22, 24.17, 26.21, 26.40, 26.94, 28.18, 31.01,

31.08, 31.98, 34.55, 34.86, 35.37, 35.76, 39.98, 40.37, 41.94, 42.73, 51.51, 54.28, 55.89, 56.28, 63.34, 77.24, 77.96, 164.24, 174.83. HRMS (ESI-MS): m/z ($C_{30}H_{52}NO_4$)⁺ calculated (M)⁺ 490.3896; found (M)⁺ 490.3897.

LCA-PIP₁: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.61 (s, 3H, -CH₃), 0.88 (s, 3H, -CH₃), 0.90 (s, 3H, -CH₃), 1.02-2.35 (steroid), 3.59 (s, 3H, -N-CH₃), 3.63 (s, 3H, -CO-OCH₃), 3.91 (m, 2H, -N-CH₂), 4.12 (m, 2H, -N-CH₂), 4.91 (m, 3H, -O-CH, -CO-CH₂-N-). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.04, 18.27, 20.25, 20.83, 23.22, 24.16, 26.22, 26.41, 26.93, 28.17, 31.00, 31.07, 31.98, 34.55, 34.86, 35.36, 35.76, 40.00, 40.39, 41.92, 42.72, 47.89, 51.49, 55.91, 56.33, 61.06, 61.42, 77.25, 77.73, 164.27, 174.79. HRMS (ESI-MS): m/z ($C_{33}H_{56}NO_4$)⁺ calculated 530.4179; found (M)⁺ 530.4193.

LCA-PYR₁: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.62 (s, 3H, -CH₃), 0.90 (s, 6H, -2 x CH₃), 0.98-2.34 (steroid), 3.65 (s, 3H, -CO-OCH₃), 4.78 (m, 1H, -O-CH), 6.26 (s, 2H, -CO-CH₂-N-), 8.05 (s, 2H, ArH), 8.46-8.47 (m, 1H, ArH), 9.40 (s, 2H, ArH). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.05, 18.28, 20.86, 23.24, 24.18, 26.25, 26.48, 26.95, 28.18, 31.08, 32.01, 34.55, 34.88, 35.38, 35.77, 40.01, 40.39, 41.94, 42.73, 51.50, 55.91, 56.34, 61.27, 78.53, 127.55, 139.52, 145.94, 165.55, 174.83. HRMS (ESI-MS): m/z ($C_{32}H_{48}NO_4$)⁺ calculated (M)⁺ 510.3583; found (M)⁺ 510.3592.

LCA-DMAP₁: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.63 (s, 3H, -CH₃), 0.89 (s, 3H, -CH₃), 0.90 (s, 3H, -CH₃) 0.98-2.34 (steroid), 3.26 (s, 6H, -N(CH₃)₂), 3.65 (s, 3H, -CO-OCH₃), 4.76 (m, 1H, -O-CH), 4.84 (m, 2H, -CO-CH₂-N-), 6.89 (d, *J* = 7.2 Hz, 2H, ArH), 8.48 (d, *J* = 6.8 Hz, 2H, ArH). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.04, 18.27, 20.84, 23.25, 24.17, 26.24, 26.48, 26.97, 28.16, 31.01, 31.07, 32.05, 34.55, 34.92, 35.35, 35.78, 40.02, 40.38, 40.42, 41.95, 42.73, 51.47, 55.90, 56.32, 57.82, 77.23, 77.70, 107.57, 143.98, 156.54, 166.74, 174.79. HRMS (ESI-MS) : m/z ($C_{34}H_{53}N_2O_4$)⁺ calculated (M)⁺ 553.3993; found (M)⁺ 553.3994.

CDCA-AMM₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.64 (s, 3H, -CH₃), 0.92 (s, 6H, -2 x CH₃), 1.06-2.34 (steroid), 3.65 (s, 3H, -CO-OCH₃), 3.41-4.2 (m, 4H, (-CO-CH₂-N-)₂), 4.62 (s, 1H, -O-CH), 4.90 (s, 1H, -O-CH). ¹³C-NMR (DMSO, 100 MHz) δ: 11.96, 18.55, 20.65, 22.93, 23.70, 26.76, 28.03, 30.76, 31.01, 31.28, 34.00, 34.56, 34.78, 35.17, 37.53, 41.51, 41.67, 42.73, 50.17, 51.69, 55.63, 72.74, 75.23, 169.53, 169.91, 174.24. HRMS (ESI-MS): m/z (C₂₉H₄₉N₂O₆)⁺ calculated 521.3591; found (M)⁺ 521.3648.

CDCA-TMA₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.64 (s, 3H, -CH₃), 0.92 (d, J=6.4, 3H, -CH₃), 0.93 (s, 3H, -CH₃), 1.08-2.36 (steroid), 3.60(m, 9H, -N-(CH₃)₃), 3.63(s, 3H, -CO-OCH₃), 3.65(s, 9H, -N-(CH₃)₃), 4.68 (m, 2H, -CO-CH₂-N-), 4.80 (m, 1H, -CO-CH₂-N-; 1H, -O-CH), 5.04 (s, 1H, -O-CH), 5.46 (m, 1H, -CO-CH₂-N-), 5.66 (m, 1H, -CO-CH₂-N-). ¹³C-NMR (CDCl₃, 100 MHz) δ: 11.70, 18.23, 20.57, 22.53, 23.75, 26.37, 28.07, 29.70, 31.02, 31.08, 31.31, 34.00, 34.64, 34.73, 35.35, 37.92, 39.21, 40.58, 42.79, 50.07, 51.49, 53.99, 54.10, 55.41, 62.74, 63.10, 74.43, 75.38, 77.23, 164.64, 164.82, 174.75. HRMS (ESI-MS): m/z (C₃₅H₆₂N₂O₆)⁺² calculated 303.2303; found (M)⁺²/2 303.2308, M⁺²Cl⁻ calculated 641.4296; found M⁺²Cl⁻ 641.4279.

CDCA-PIP₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.63 (s, 3H, -CH₃), 0.91 (s, 6H, 2 x -CH₃), 1.04-2.36 (steroid), 3.55 (s, 6H, -N-(CH₃)₂), 3.63 (s, 3H, -CO-OCH₃), 3.82-4.13 (m, 8H, 2 × -CH₂-N-CH₂-), 4.55 (m, 1H, -CO-CH₂-N-), 4.82 (m, 1H, -CO-CH₂-N-; 1H, -O-CH), 5.02 (s, 1H, -O-CH), 5.59 (m, 2H, -CO-CH₂-N-). ¹³C-NMR (DMSO, 100 MHz) δ: 11.71, 18.21, 20.16, 20.24, 20.56, 20.84, 20.89, 22.47, 23.79, 26.35, 28.07, 29.69, 30.97, 31.11, 31.22, 34.11, 34.59, 34.63, 34.71, 35.37, 37.86, 39.25, 42.81, 46.55, 50.26, 51.48, 55.47, 80.52, 61.10, 61.56, 61.90, 62.41, 65.84, 74.39, 75.08, 164.48, 164.73, 174.76. HRMS (ESI-MS): m/z (C₄₁H₇₀N₂O₆)²⁺ calculated 343.2616; found (M)²⁺/2 343.2615, M²⁺Cl⁻ calculated 721.4922; found M²⁺Cl⁻ 721.4911.

CDCA-PYR₂: ¹H NMR (MeOH, 400 MHz) δ: 0.72 (s, 3H, -CH₃), 0.98 (s, 6H, -2 x CH₃), 1.02-2.35 (steroid), 3.68 (s, 3H, -CO-OCH₃), 4.82 (m, 1H, -O-CH), 5.11 (s, 1H, -O-CH), 5.65-5.98 (m, 4H, -CO-

CH₂-N-, -CO-CH₂-N-), 8.21 (t, 2H, J = 6.8Hz, ArH), 8.28 (t, 2H, J = 6.8Hz, ArH), 9.19 (m, 1H, ArH).

¹³C-NMR (DMSO, 100 MHz) δ: 10.65, 17.30, 20.24, 21.51, 23.14, 26.33, 27.64, 30.41, 30.74, 30.80, 34.04, 34.29, 34.41, 34.50, 35.25, 37.75, 39.39, 40.67, 42.59, 50.31, 50.63, 55.79, 60.70, 75.21, 77.18, 127.70, 128.01, 146.28, 146.61, 146.80, 164.89, 165.64, 175.01. HRMS (ESI-MS): m/z (C₃₉H₅₄N₂O₆)²⁺ calculated 323.1990; found (M)²⁺/2 323.1989, M²⁺Cl⁻ calculated 681.3670; found M²⁺Cl⁻ 681.3663.

CDCA-DMAP₂: ¹H NMR (CDCl₃, 400 MHz) δ: 0.61 (s, 3H, -CH₃), 0.98 (s, 6H, -2 x CH₃), 1.03-2.35 (steroid), 3.24 (s, 6H, -N(CH₃)₂), 3.30 (s, 6H, -N(CH₃)₂), 3.65 (s, 3H, -CO-OCH₃), 4.72 (m, 1H, -O-CH), 4.93 (m, 1H, -O-CH), 5.29-5.56 (m, 2H, -CO-CH₂-N-), 5.58-6.03 (m, 2H, -CO-CH₂-N-), 6.93 (d, J = 6.4 Hz, 2H, ArH), 7.00 (d, J = 6.4 Hz, 2H, ArH), 8.56 (d, J = 6Hz, 2H, ArH), 8.79 (s, 2H, ArH).

¹³C-NMR (DMSO, 100 MHz) δ: 11.65, 18.32, 20.53, 22.50, 23.60, 28.02, 29.70, 31.00, 31.09, 34.08, 34.61, 34.71, 35.29, 37.85, 39.44, 40.44, 40.55, 40.67, 42.77, 50.21, 51.57, 55.94, 57.64, 70, 57.76, 74.56, 77.26, 107.55, 107.73, 143.98, 144.26, 156.50, 156.52, 166.49, 167.22, 174.74. HRMS (ESI-MS): m/z (C₄₃H₆₄N₄O₆)²⁺ calculated 366.2412; found (M)²⁺/2 366.2414, M²⁺Cl⁻ calculated 767.4514; found M²⁺Cl⁻ 767.4512.

DCA-AMM₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.73 (s, 3H, -CH₃), 0.83 (s, 3H, -CH₃), 0.99 (s, 3H, -CH₃), 1.06-2.34 (steroid), 3.64 (s, 3H, -CO-OCH₃), 3.46-4.19 (m, 4H, (-CO-CH₂-N-)₂), 4.74 (s, 1H, -O-CH), 5.16 (s, 1H, -O-CH). ¹³C-NMR (DMSO, 100 MHz) δ: 11.27, 16.64, 20.65, 21.99, 23.05, 25.37, 25.69, 26.22, 26.58, 27.00, 30.40, 30.52, 31.76, 33.82, 34.28, 34.35, 34.72, 35.56, 40.30, 41.78, 44.96, 49.40, 50.63, 76.34, 78.02, 167.61, 168.00, 174.99, HRMS (ESI-MS): m/z (C₂₉H₄₉N₂O₆)⁺ calculated 521.3591; found (M)⁺ 521.3590.

DCA-TMA₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.75 (s, 3H, -CH₃), 0.84 (d, J = 12, 3H, -CH₃), 0.92 (s, 3H, -CH₃), 1.03-2.36 (steroid), 3.55 (m, 9H, -N-(CH₃)₃), 3.60 (s, 4H, -N-(CH₃)₃), 3.66 (s, 3H, -CO-OCH₃), 3.68 (s, 5H, -N-(CH₃)₃), 4.63 (d, J = 17.6 Hz, 1H, -CO-CH₂-N-), 4.80 (m, 1H, -O-CH), 5.16 (d,

$J=16.8$, 1H, -CO-CH₂-N-), 5.28 (s, 1H, -O-CH), 5.53 (d, $J = 17.2$ Hz, 1H, -CO-CH₂-N-), 5.62 (d, $J = 17.2$ Hz, 1H, -CO-CH₂-N-). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.27, 17.68, 22.53, 23.35, 25.84, 26.46, 27.32, 30.51, 31.03, 33.81, 33.95, 34.38, 34.64, 35.31, 41.32, 45.13, 49.30, 51.57, 54.04, 55.98, 63.12, 77.23, 78.99, 164.64, 164.82, 174.93. HRMS (ESI-MS): m/z (C₃₅H₆₂N₂O₆)²⁺ calculated 303.2303; found (M)²⁺/2 303.2308, M²⁺Cl⁻ calculated 641.4296; found M²⁺Cl⁻ 641.4279.

DCA-PIP₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.78 (s, 3H, -CH₃), 0.83 (d, $J = 6.4$, 3H, -CH₃), 0.97 (s, 3H, -CH₃), 1.04-2.34 (steroid), 3.50 (s, 3H, -N-CH₃), 3.62 (s, 3H, -N-CH₃), 3.64 (s, 3H, -CO-OCH₃), 3.79-4.17 (m, 8H, 2 × -CH₂-N-CH₂-), 4.58 (m, 1H, -CO-CH₂-N-), 4.78 (s, 1H, -O-CH), 5.09 (m, 1H, -CO-CH₂-N-, 5.23 (s, 1H, -O-CH), -), 5.27 (m, 2H, -CO-CH₂-N-), 5.42 (m, 2H, -CO-CH₂-N-), ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.27, 17.73, 20.15, 20.36, 20.80, 20.85, 22.50, 23.37, 25.25, 25.82, 25.99, 26.44, 27.39, 30.57, 31.04, 31.10, 33.79, 34.44, 34.73, 35.32, 41.30, 45.11, 49.19, 51.60, 60.38, 61.04, 61.43, 62.68, 75.88, 77.24, 79.02, 164.32, 164.80, 174.81. HRMS (ESI-MS): m/z (C₄₁H₇₀N₂O₆)²⁺ calculated 343.2616; found (M)²⁺/2 343.2611, M²⁺Cl⁻ calculated 721.4922; found M²⁺Cl⁻ 721.4910.

DCA-PYR₂: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.71 (s, 3H, -CH₃), 0.85 (d, $J = 6.4$, 3H, -CH₃), 0.88 (s, 3H, -CH₃), 1.02-2.41 (steroid), 3.67 (s, 3H, -CO-OCH₃), 4.82 (m, 1H, -O-CH), 5.29 (m, 1H, -O-CH), 6.25 (d, $J = 17.2$ Hz, 2H, -CO-CH₂-N-), 6.44 (d, $J = 15.6$ Hz, 2H, -CO-CH₂-N-), 8.05 (t, 2H, $J = 6.8$ Hz, ArH), 8.26 (t, $J = 6.8$ Hz, 2H, ArH), 8.48 (t, $J = 7.2$ Hz, 1H, ArH), 8.70 (t, $J = 7.2$ Hz, 2H, ArH), 9.58 (m, 4H, ArH). ¹³C-NMR (MeOH, 100 MHz) δ: 11.24, 16.76, 21.92, 23.07, 25.36, 25.80, 26.32, 26.57, 27.02, 30.45, 30.58, 31.76, 33.87, 34.23, 34.39, 34.83, 35.46, 41.72, 45.12, 47.10, 48.12, 49.11, 50.71, 60.72, 77.56, 79.11, 128.75, 128.21, 146.26, 146.63, 146.96, 164.58, 165.71, 175.19. HRMS (ESI-MS): m/z (C₃₉H₅₄N₂O₆)²⁺ calculated 323.1990; found (M)²⁺/2 323.1992, M²⁺Cl⁻ calculated 681.3670; found M²⁺Cl⁻ 681.3671.

DCA-DMAP₂: ¹H NMR (CDCl₃, 400 MHz) δ: 0.70 (s, 3H, -CH₃), 0.82 (s, 3H, -CH₃), 0.86 (s, 3H, -CH₃), 1.03-2.33 (steroid), 3.23 (s, 6H, -N(CH₃)₂), 3.33 (s, 6H, -N(CH₃)₂), 3.66 (s, 3H, -CO-OCH₃), 4.78 (s, 1H, -O-CH), 5.20 (s, 1H, -O-CH), 5.52-5.72 (m, 2H, -CO-CH₂-N-), 5.82-6.14 (m, 2H, -CO-CH₂-N-), 6.85 (s, 2H, ArH), 7.07 (s, 2H, ArH), 8.56 (s, 2H, ArH), 8.83 (s, 2H, ArH). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.24, 17.77, 22.48, 23.35, 25.27, 25.96, 26.26, 26.45, 27.37, 30.71, 31.16, 31.30, 33.72, 33.85, 24.51, 34.77, 35.24, 40.32, 40.83, 41.34, 45.16, 47.24, 49.46, 51.59, 57.66, 57.82, 76.49, 77.35, 78.60, 107.37, 107.89, 143.93, 144.42, 156.49, 156.57, 165.94, 167.35, 174.89. HRMS (ESI-MS): m/z (C₄₃H₆₄N₄O₆)⁺² calculated 366.2412; found (M)⁺²/2 366.2415, M⁺²Cl⁻ calculated 767.4514; found M⁺²Cl⁻ 767.4509.

CA-AMM₃: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.74 (s, 6H, -2CH₃), 0.94 (d, J = 12.8 Hz, 3H, -CH₃), 1.08-2.33 (steroid), 3.65 (s, 3H, -CO-OCH₃), 3.46-4.19 (m, 4H, (-CO-CH₂-N-)₂), 4.70 (s, 1H, -O-CH), 5.16 (s, 1H, -O-CH), 5.24 (s, 1H, -O-CH). ¹³C-NMR (DMSO, 100 MHz) δ: 12.26, 17.63, 21.58, 22.53, 22.66, 22.72, 22.96, 25.65, 30.78, 34.42, 34.48, 34.68, 37.34, 39.41, 39.62, 39.83, 40.03, 40.24, 40.45, 40.66, 41.68, 43.09, 45.18, 45.21, 47.16, 51.65, 72.22, 75.34, 76.35, 169.77, 170.00, 171.90, 174.20. HRMS (ESI-MS): m/z (C₃₁H₅₂N₃O₈)⁺ calculated 594.3754; found (M)⁺ 594.3773.

CA-TMA₃: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.74 (s, 3H, -CH₃), 0.84 (s, 3H, -CH₃), 0.94 (s, 3H, -CH₃), 1.07-2.36 (steroid), 3.52 (s, 9H, -N-(CH₃)₃), 3.61 (s, 12H, -N-(CH₃)₃; -CO-OCH₃), 3.65 (s, 9H, -N-(CH₃)₃), 4.80 (s, 1H, -O-CH), 5.12 (s, 1H, -O-CH), 5.18 (d, J = 16.0 Hz, 1H, -CO-CH₂-N-), 5.29 (s, 1H, -O-CH), 5.36 (d, J = 15.6, 2H, -CO-CH₂-N-), 5.57 (d, J = 15.6, 1H, -CO-CH₂-N-), 5.36 (s, 1H, -CO-CH₂-N-), 5.76 (d, J = 17.6, 2H, -CO-CH₂-N-). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.01, 17.88, 21.77, 23.36, 24.87, 26.07, 27.26, 27.83, 30.64, 30.80, 31.28, 34.04, 34.41, 34.76, 37.95, 39.97, 41.83, 45.37, 46.55, 51.48, 53.93, 54.16, 54.28, 60.40, 62.14, 64.06, 73.10, 74.71, 77.23, 164.29, 164.92, 174.63.

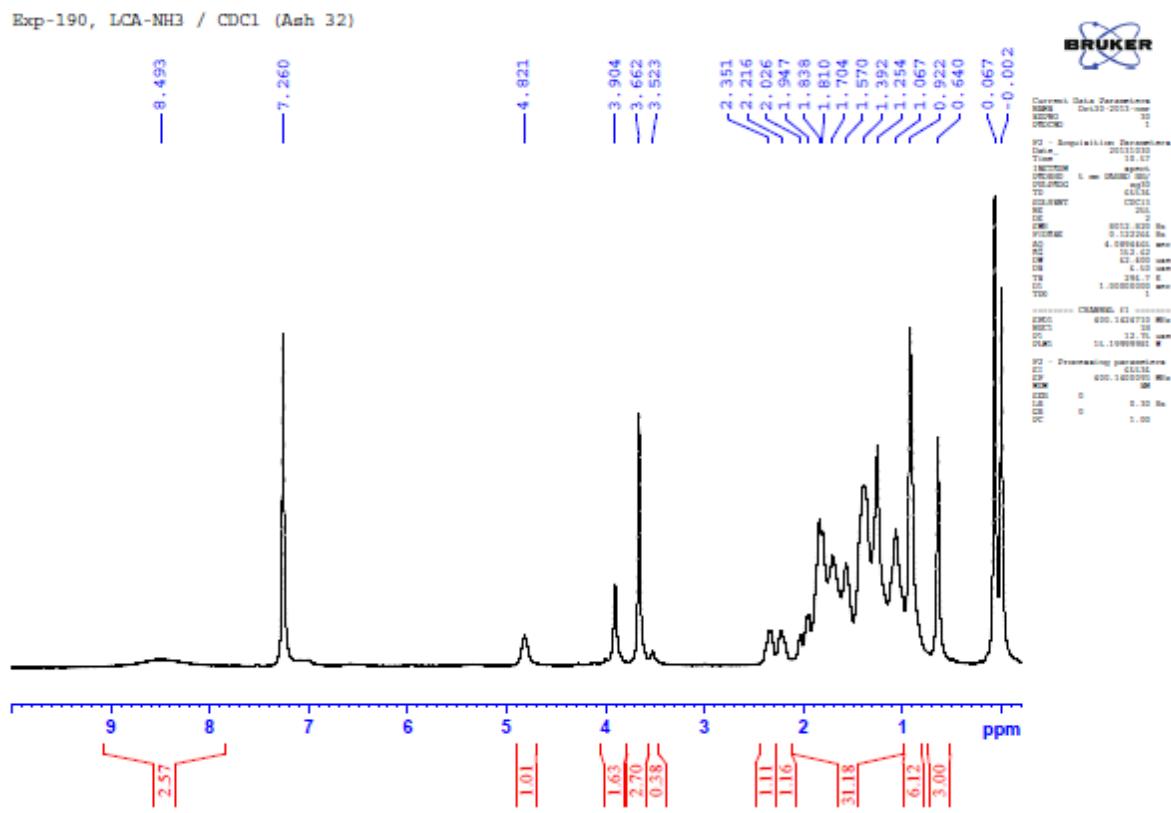
HRMS (ESI-MS): m/z ($C_{40}H_{72}N_3O_8$)³⁺ calculated 240.8439; found (M)^{3+/3} 240.8429, $M^{3+}Cl^-/2$ calculated 378.7504; found $M^{3+}Cl^-/2$ 378.7507, $M^{3+}Cl^{2-}$ calculated 792.4696; found $M^{3+}Cl^{2-}$ 792.4687.

CA-PIP₃: ¹H-NMR ($CDCl_3$, 400 MHz) δ: 0.73 (s, 3H, - CH_3), 0.83 (d, $J = 5.2$, 3H, - CH_3), 0.93 (s, 3H, - CH_3), 1.03-2.41 (steroid), 3.46 (s, 3H, - $N-CH_3$), 3.50 (s, 3H, - $N-CH_3$), 3.53 (s, 3H, - $N-CH_3$), 3.61 (s, 3H, - $CO-OCH_3$), 3.68-4.13 (m, 12H, 3 × - CH_2-N-CH_2-), 4.79 (m, 1H, - $CO-CH_2-N-$), 4.95 (d, $J = 7.2$ Hz, 2H, - $O-CH$), 5.53 (d, $J = 17.2$ Hz, 1H, - $CO-CH_2-N-$), 5.09 (s, 3H, - $CO-OCH_3$), 5.29 (s, 3H, 1H, - $O-CH$; - $CO-CH_2-N-$), 5.32 (d, $J = 7.2$ Hz, 1H, - $CO-CH_2-N-$), 5.53 (d, $J = 17.2$ Hz, 1H, - $CO-CH_2-N-$), 5.70 (d, $J = 17.2$ Hz, 1H, - $CO-CH_2-N-$), 5.77 (d, $J = 17.2$ Hz, 1H, - $CO-CH_2-N-$). ¹³C-NMR ($CDCl_3$, 100 MHz) δ: 12.03, 17.89, 21.11, 21.30, 21.35, 21.42, 21.69, 21.79, 23.39, 24.97, 26.11, 27.31, 27.77, 30.61, 30.78, 31.36, 34.07, 34.47, 34.77, 37.98, 40.83, 45.34, 46.52, 47.65, 48.91, 51.48, 62.69, 62.90, 64.54, 64.97, 65.37, 65.50, 72.95, 74.19, 77.24, 77.62, 164.82, 165.39, 165.39, 174.67. HRMS (ESI-MS): m/z ($C_{49}H_{84}N_3O_8$)³⁺ calculated 280.8752; found (M)^{3+/3} 280.8750, $M^{3+}Cl^-/2$ calculated 438.7973; found $M^{3+}Cl^-/2$ 438.7971.

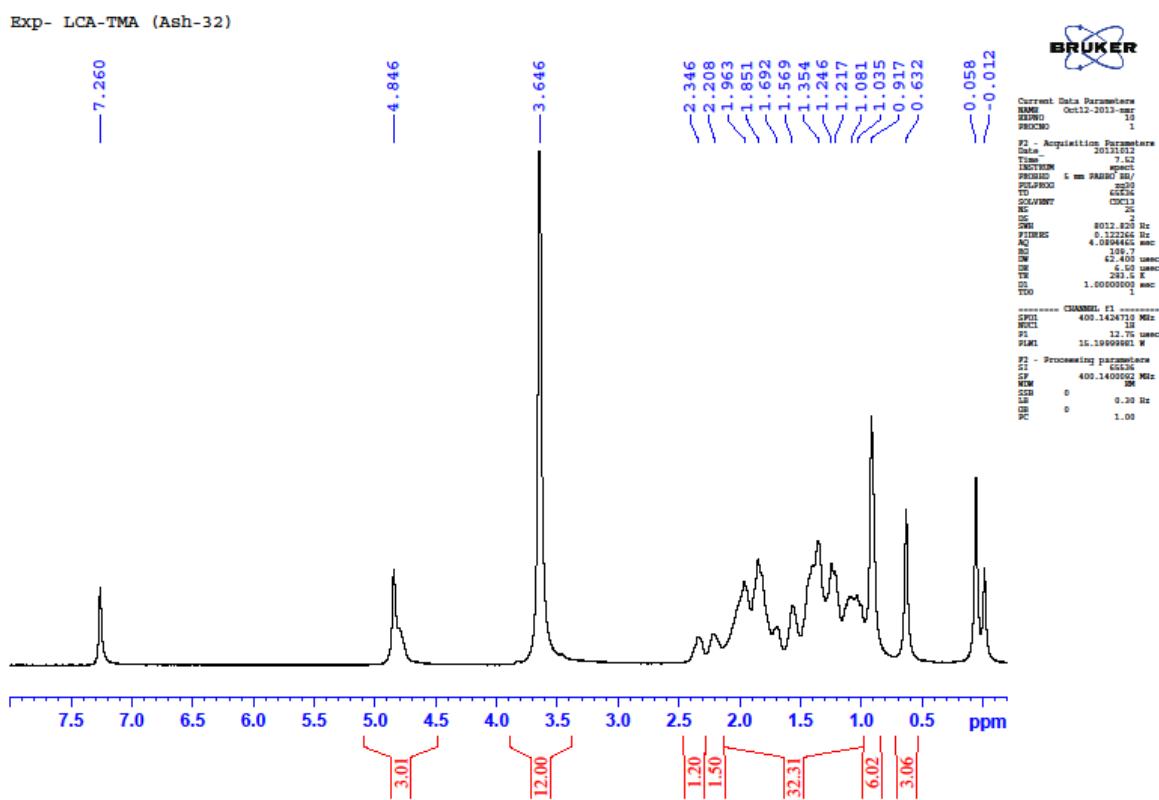
CA-PYR₃: ¹H-NMR ($CDCl_3$, 400 MHz) δ: 0.72 (s, 3H, - CH_3), 0.90 (s, 6H, 2 X - CH_3), 1.02-2.41 (steroid), 3.64 (s, 3H, - $CO-OCH_3$), 4.66 (m, 1H, - $O-CH$), 5.05 (m, 1H, - $O-CH$), 6.29-6.39 (m, 2H, - $CO-CH_2-N-$), 6.51-6.70 (m, 2H, - $CO-CH_2-N-$), 6.77-6.88 (m, 2H, - $CO-CH_2-N-$), 8.01 (m, 2H, ArH), 8.16 (m, 2H, ArH), 8.43 (m, 2H, ArH), 8.44 (m, H, ArH), 8.62 (m, 1H, ArH), 8.93 (m, 1H, ArH), 9.52 (s, 3H, ArH), 8.61 (s, 3H, ArH). ¹³C-NMR ($CDCl_3$, 100 MHz) δ: 12.25, 17.76, 21.99, 23.12, 25.53, 26.19, 26.44, 27.11, 28.49, 29.67, 30.49, 31.15, 31.34, 34.04, 34.17, 34.40, 34.76, 37.73, 40.30, 42.116, 42.53, 45.45, 46.81, 51.54, 60.70, 61.16, 74.12, 77.26, 78.24, 127.61, 127.81, 128.77, 145.47, 145.87, 146.36, 146.71, 146.92, 147.02, 164.80, 165.81, 165.99, 175.08. HRMS (ESI-MS): m/z ($C_{46}H_{60}N_3O_8$)³⁺ calculated 260.8126; found (M)^{3+/3} 260.8132, $M^{3+}Cl^-/2$ calculated 408.7034; found $M^{3+}Cl^-/2$ 408.7029.

CA-DMAP₃: ¹H NMR (CDCl₃, 400 MHz) δ: 0.72 (s, 3H, -CH₃), 0.82 (d, *J*=5.2 Hz, 3H, -CH₃), δ: 0.90 (s, 3H, -CH₃) 1.04-2.35 (steroid), 3.19 (s, 6H, -N(CH₃)₂), 3.25 (s, 6H, -N(CH₃)₂), 3.31 (s, 6H, -N(CH₃)₂), 3.63 (s, 3H, -CO-OCH₃), 4.66 (m, 1H, -O-CH), 5.04 (s, 1H, -O-CH), 5.23 (s, 1H, -O-CH), 5.55 (m, H, -CO-CH₂-N-), 5.88 (m, 3H, -CO-CH₂-N-; -CO-CH₂-N-), 6.84 (d, *J*=7.2 Hz, 2H, ArH), 6.94 (d, *J*=6.8 Hz, 2H, ArH), 7.20 (d, *J*=7.2 Hz, 2H, ArH), 8.56 (d, *J*=7.2 Hz, 2H, ArH), 8.87 (s, 2H, ArH), 8.87 (s, 2H, ArH). ¹³C-NMR (CDCl₃, 100 MHz) δ: 12.09, 17.679, 22.09, 23.12, 25.06, 26.21, 27.25, 28.14, 29.68, 30.53, 31.20, 34.00, 34.22, 34.675, 34.88, 37.97, 40.36, 40.47, 40.63, 42.35, 45.29, 46.91, 51.52, 57.67, 63.03, 73.389, 77.27, 107.42, 107.60, 108.06, 143.64, 144.06, 144.17, 156.33, 156.44, 156.513, 167.13, 167.43, 167.58, 174.81. HRMS (ESI-MS): m/z (C₅₂H₇₅N₆O₈)³⁺ calculated 303.8548; found (M)³⁺/3 303.8537, M³⁺Cl⁻/2 calculated 473.2667; found M³⁺Cl⁻/2 473.2650.

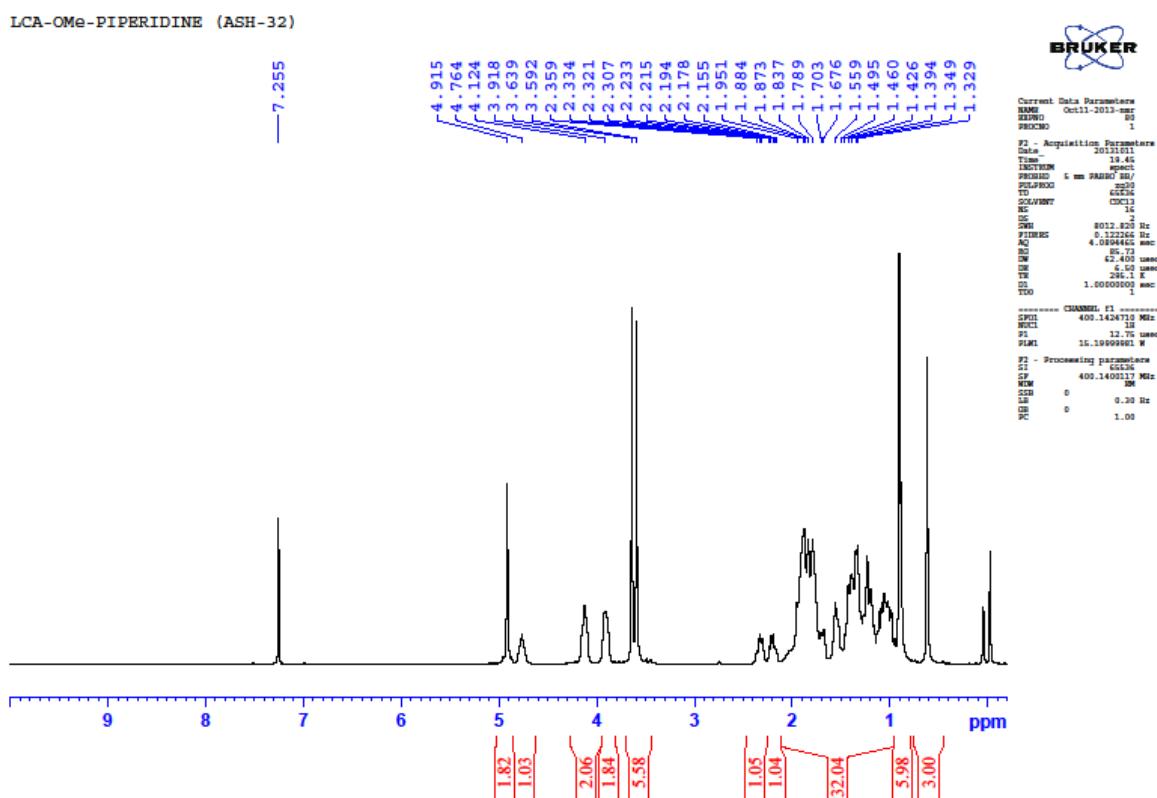
¹H, LCA-AMM₁



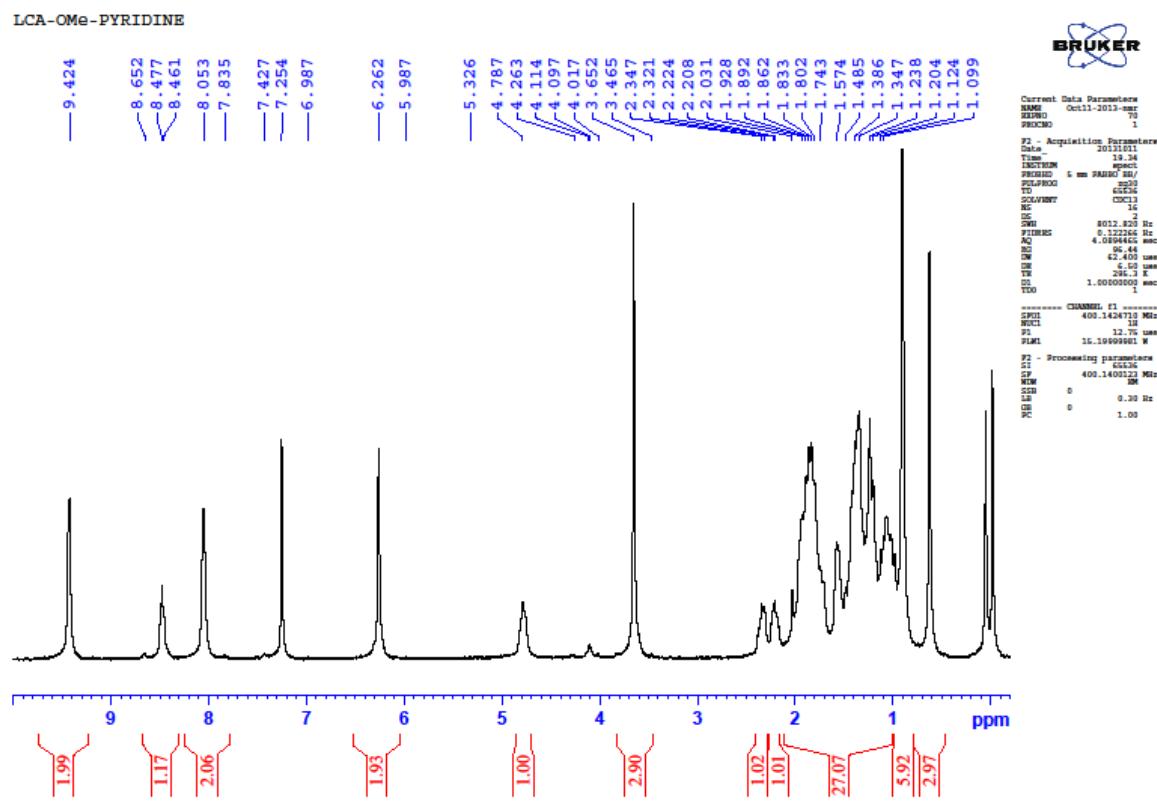
¹H, LCA-TMA₁



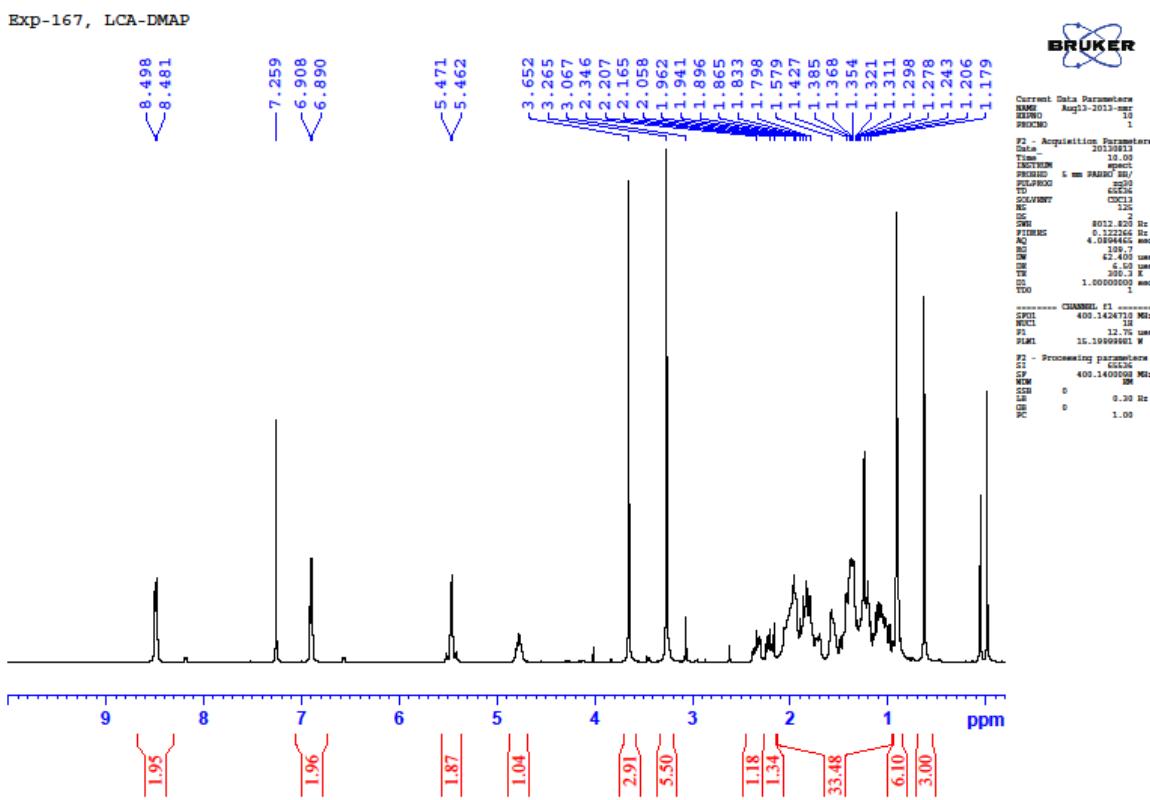
¹H, LCA-PIP₁



¹H, LCA-PYR₁



¹H, LCA-DMAP₁



¹H, CDCA-AMM₂

Exp-192, DCA_NH3 /CDC13 (Ash-32)

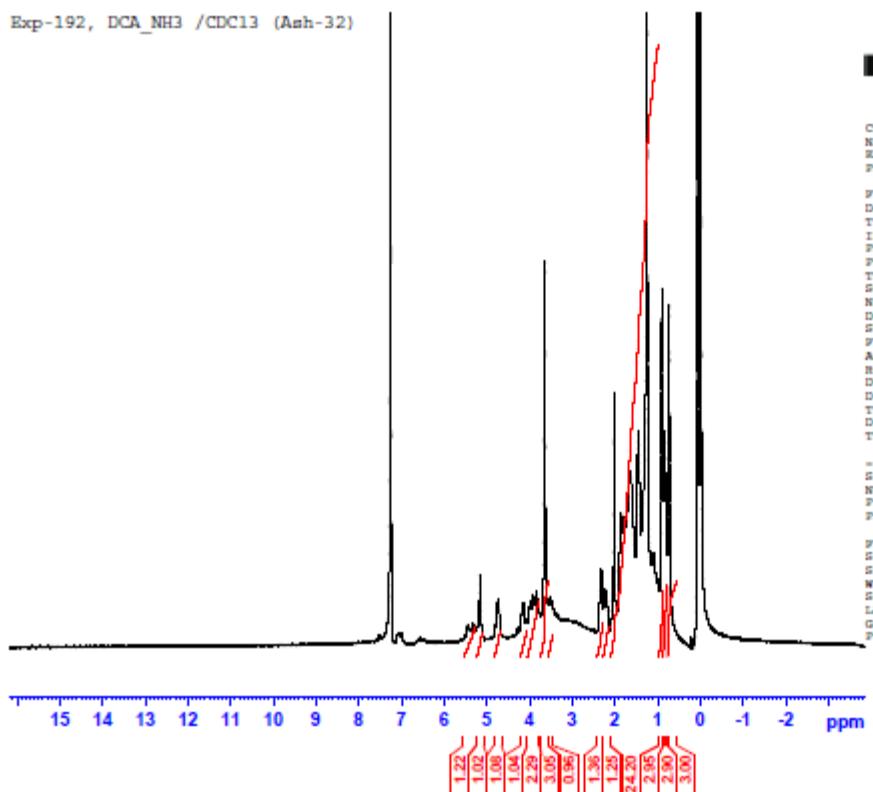


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PROCNO 1

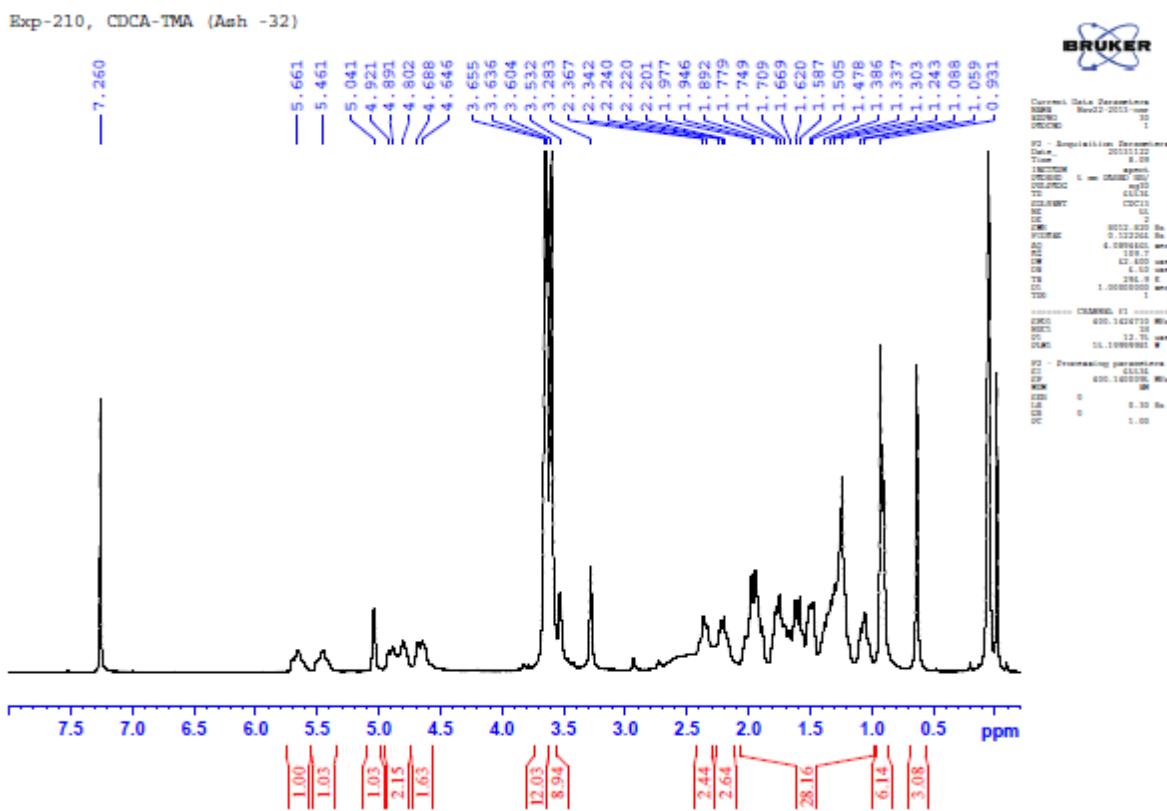
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FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 152.62
DW 62.400 usec
DE 6.50 usec
TE 295.7 K
D1 1.0000000 sec
TDD 1

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NUC1 1H
P1 12.75 usec
PLW1 15.19999981 W

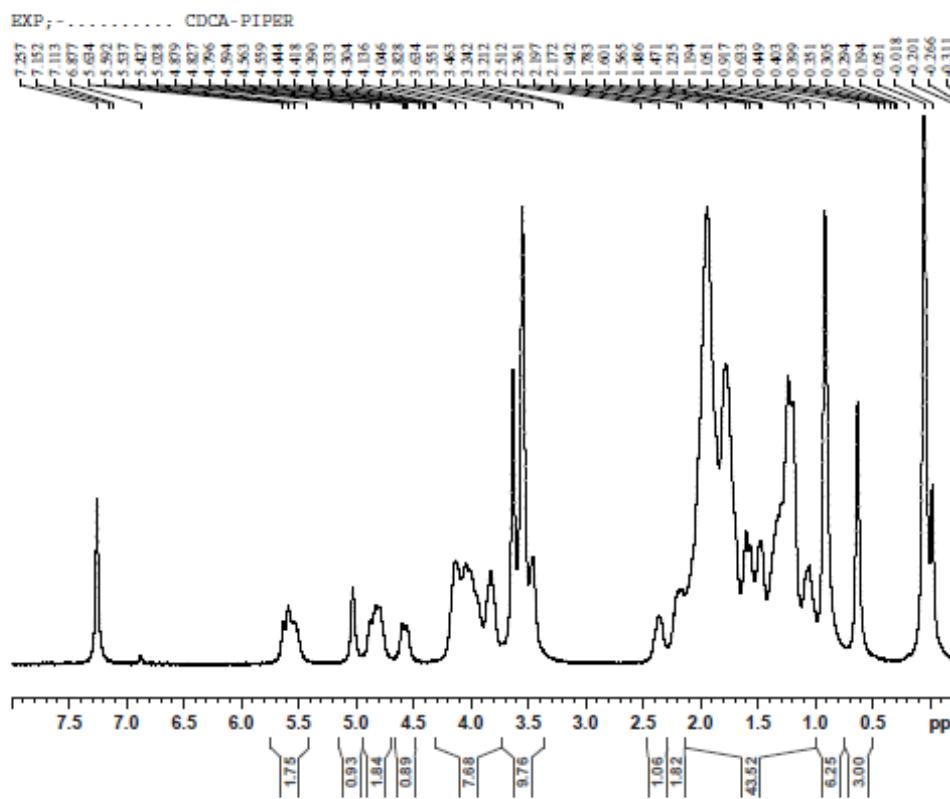
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¹H, CDCA-TMA₂



¹H, CDCA-PIP₂



BRUKER

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current data parameters
date NOV14-2013-001
REFID 20
PROGNO 1

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INSTRUM_N 0 Mhz
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THERM 14
TIE 3
TRIG 8012.820 MHz
PULSEFORM 0.1250000 MHz
RSC 4.0000000 MHz
TM 109.7
TM 1.0000000 MHz
TR 287.0 K
THI 1.0000000 MHz
TDO 1

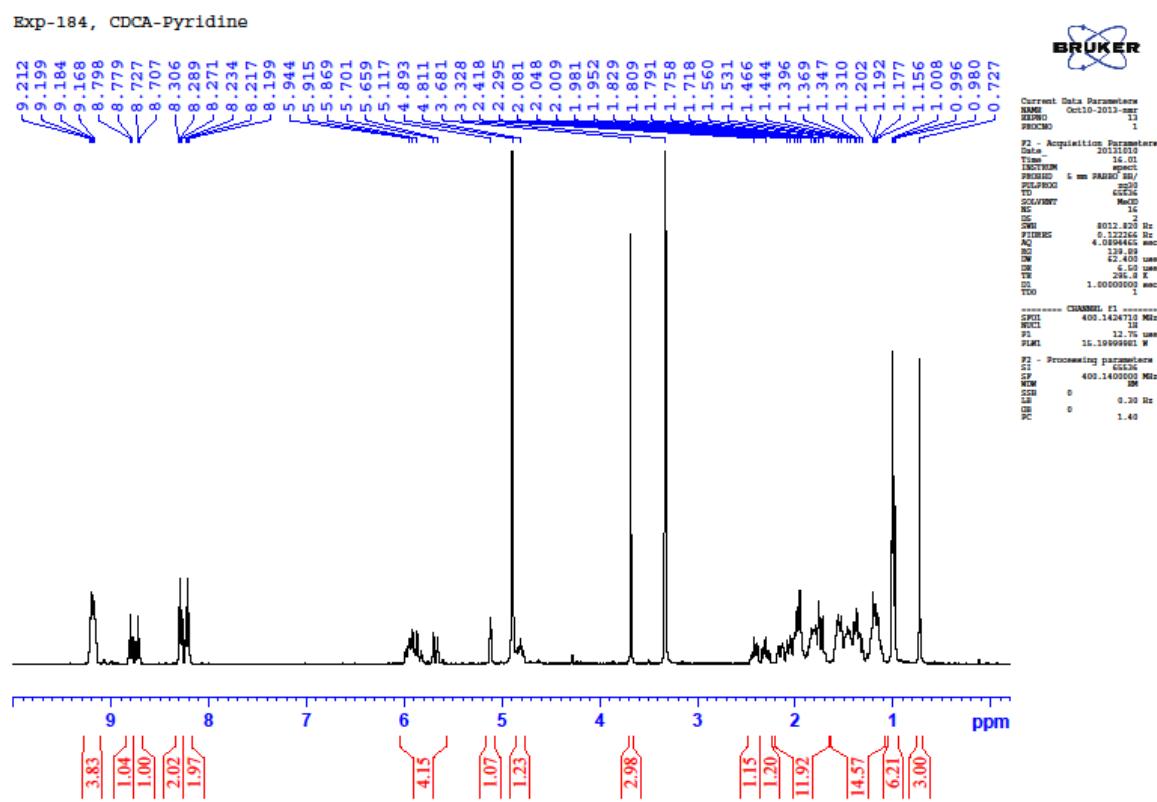
***** CHANNELS E1 *****

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MECI1 3W
PSI 12.72 W
PLATE 10.1888888 W

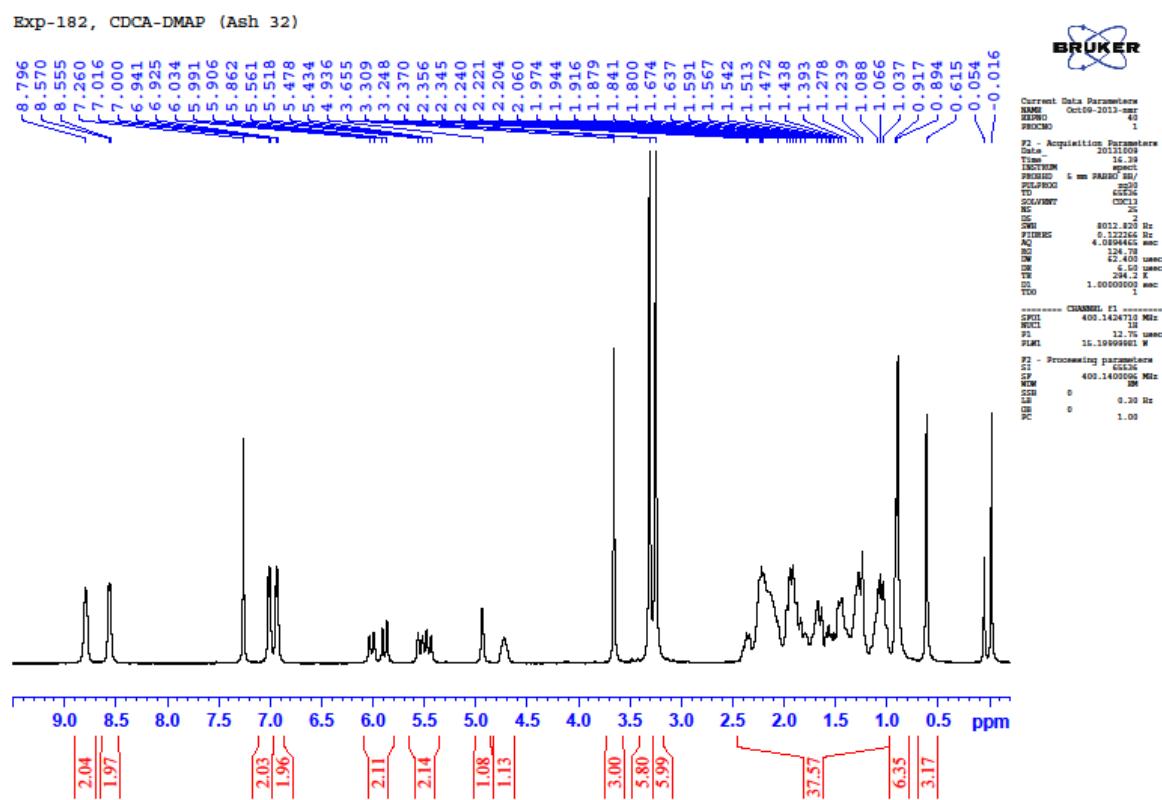
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KERN 0
LAM 12.72 W
PC 0.1000000 W
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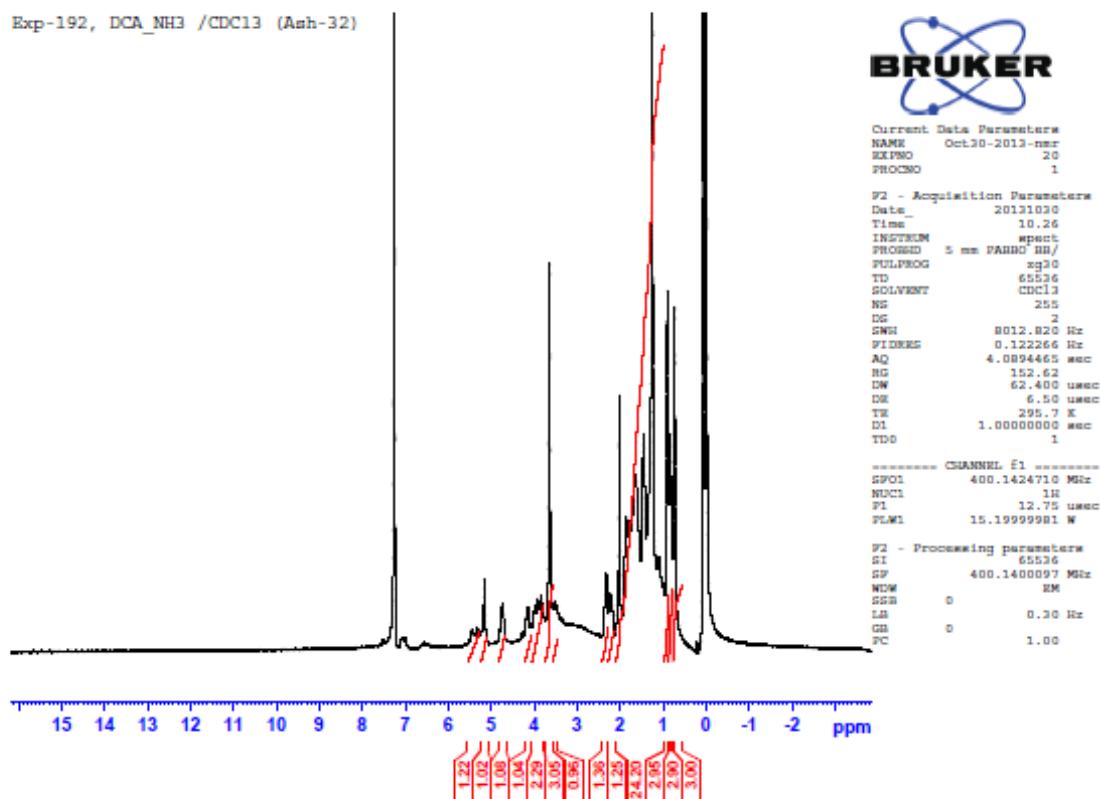
¹H, CDCA-PYR₂



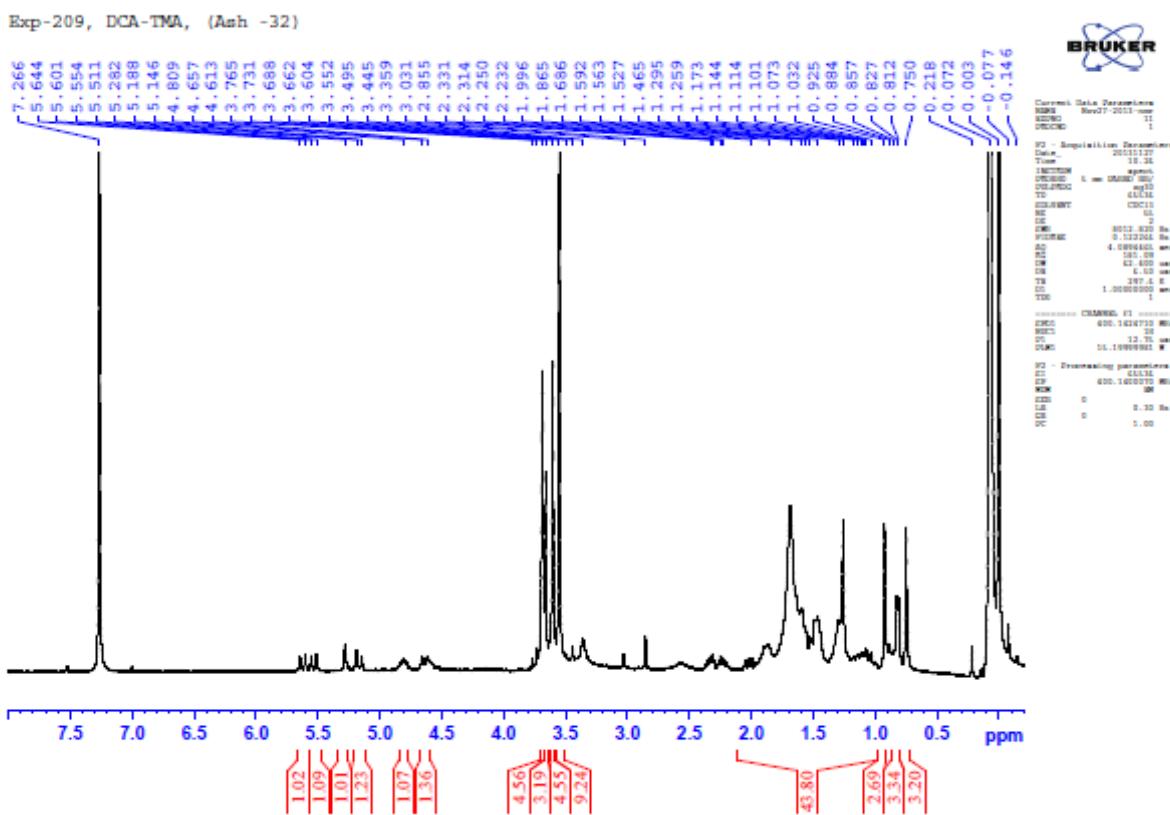
¹H, CDCA-DMAP₂



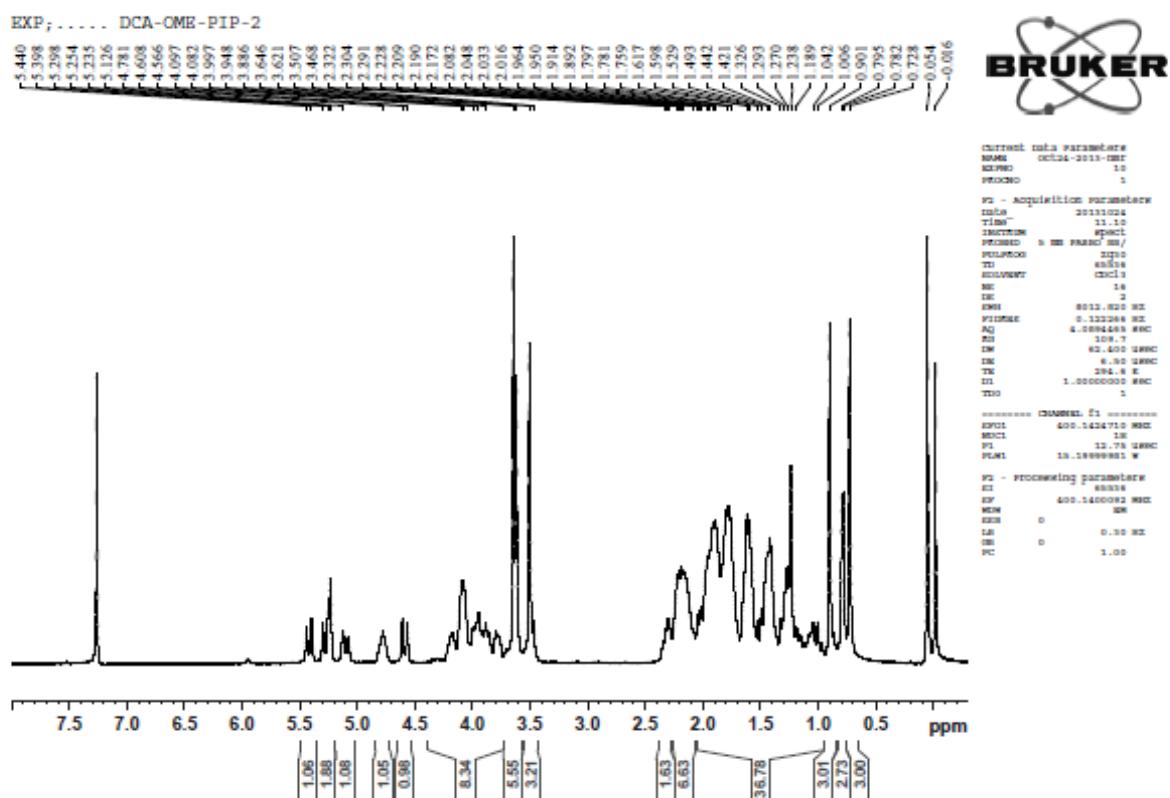
¹H, DCA-AMM₂



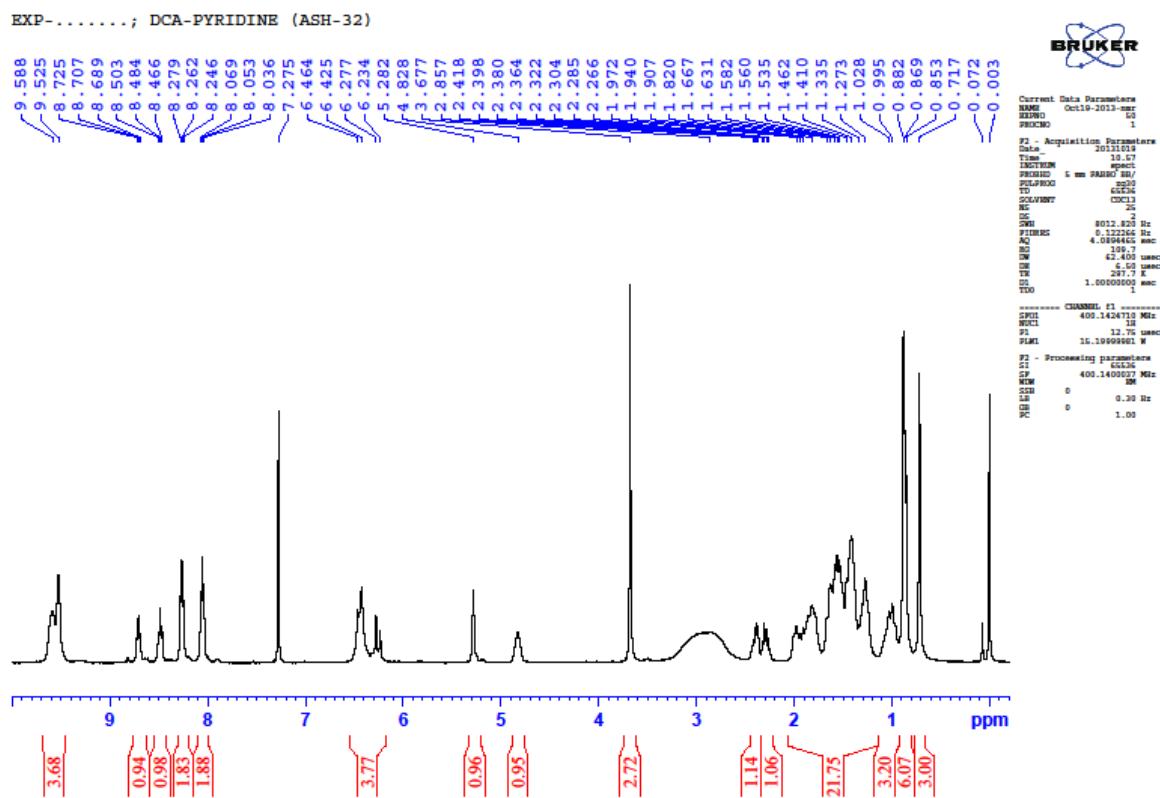
¹H, DCA-TMA₂



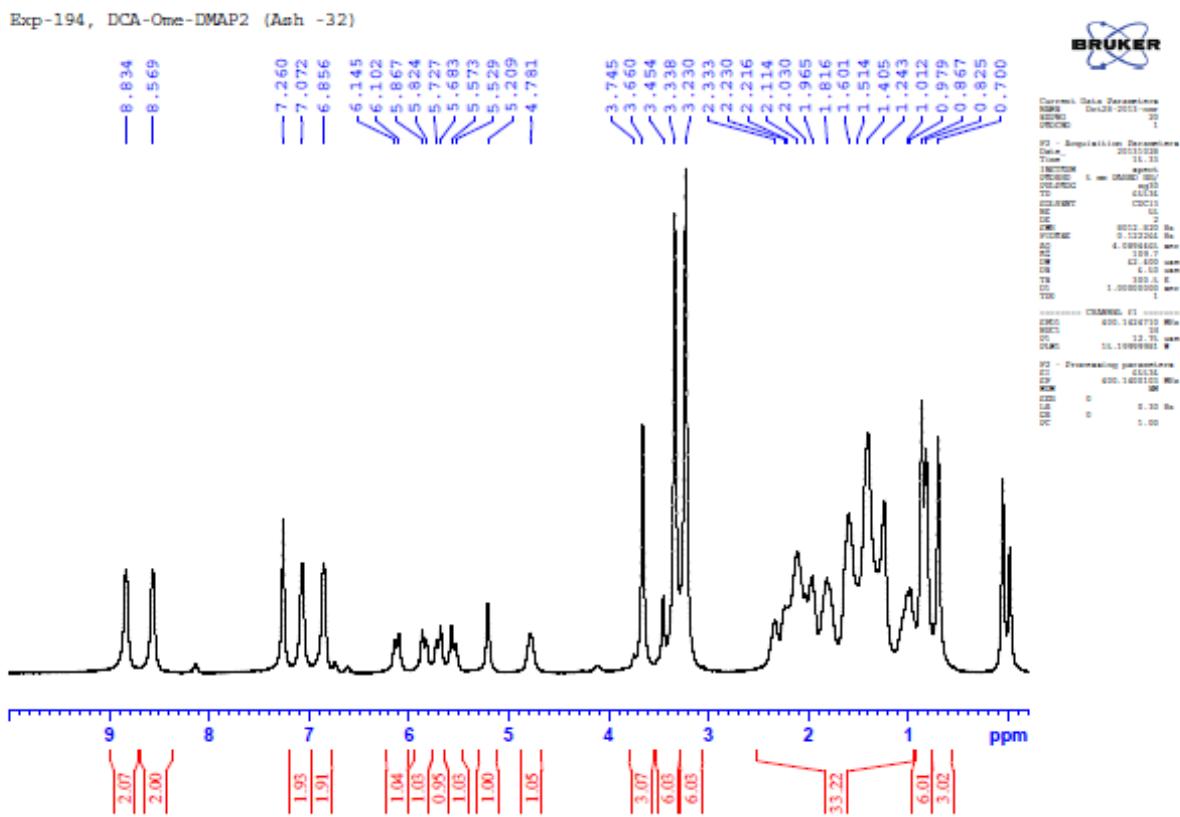
¹H, DCA-PIP₂



¹H, DCA-PYR₂

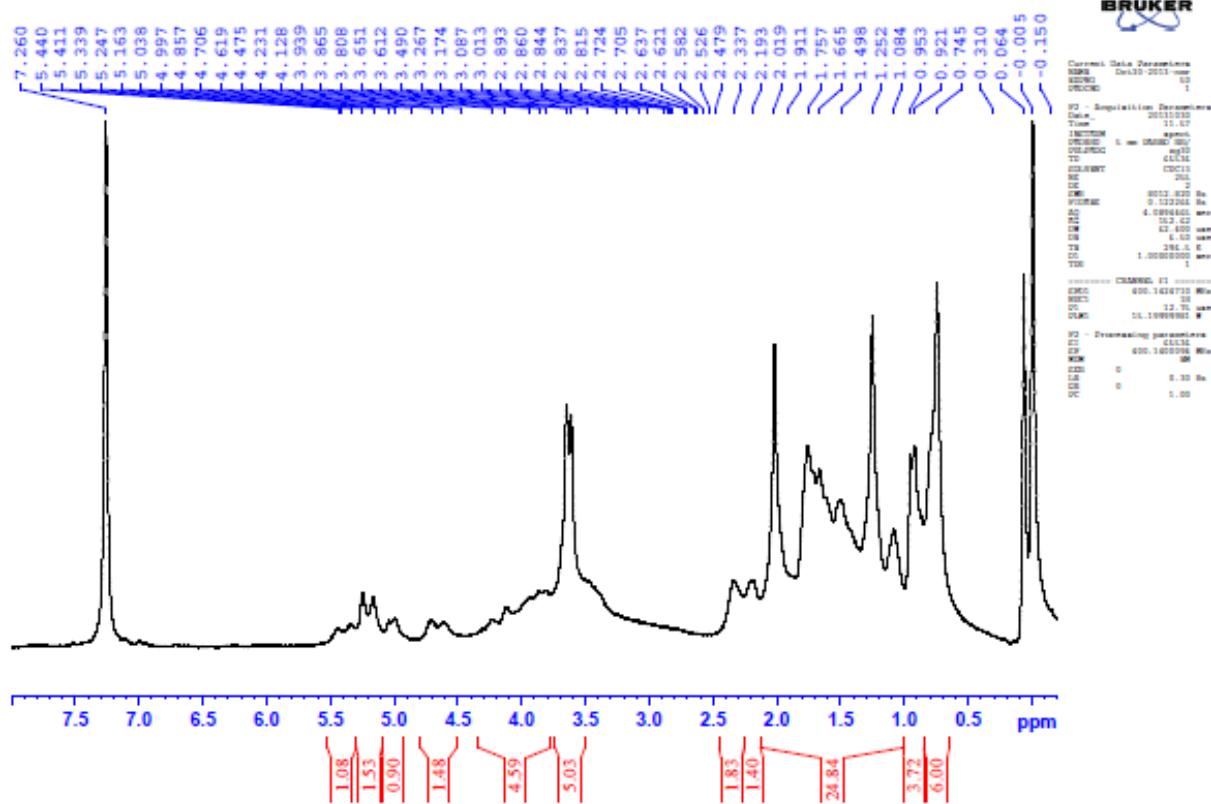


¹H, DCA-DMAP₂

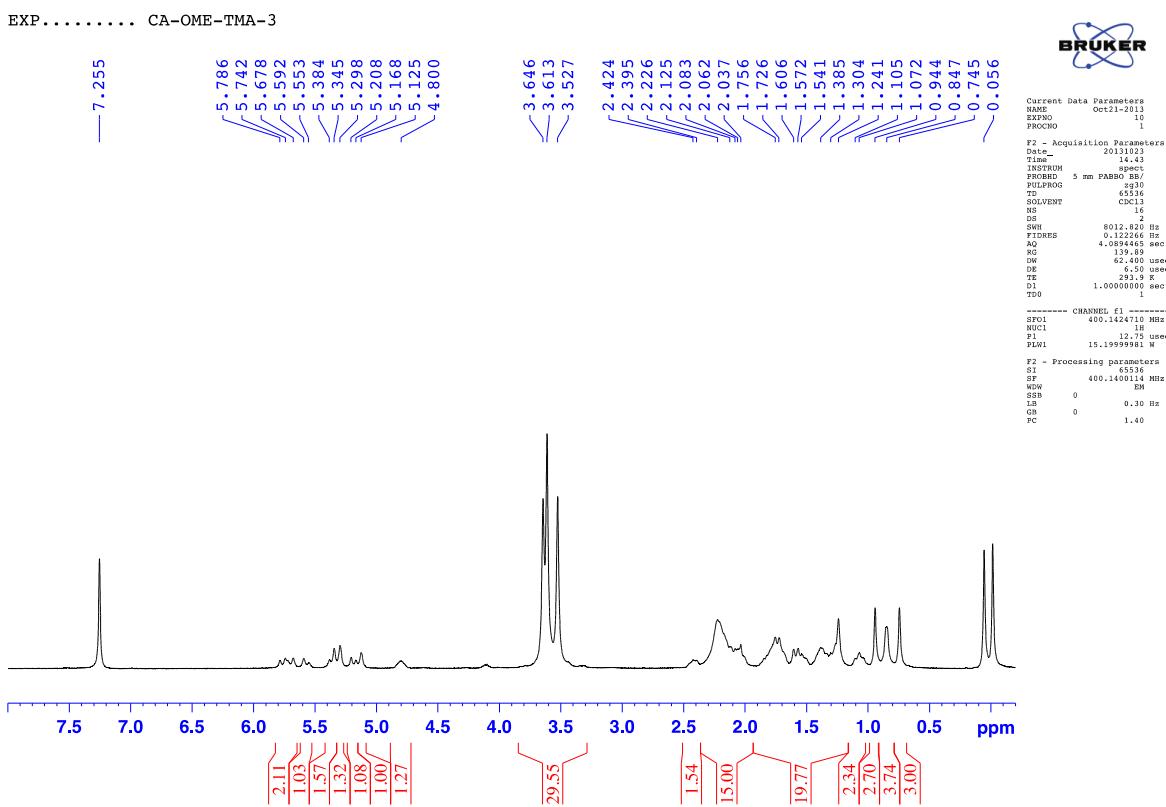


¹H, CA-AMM₃

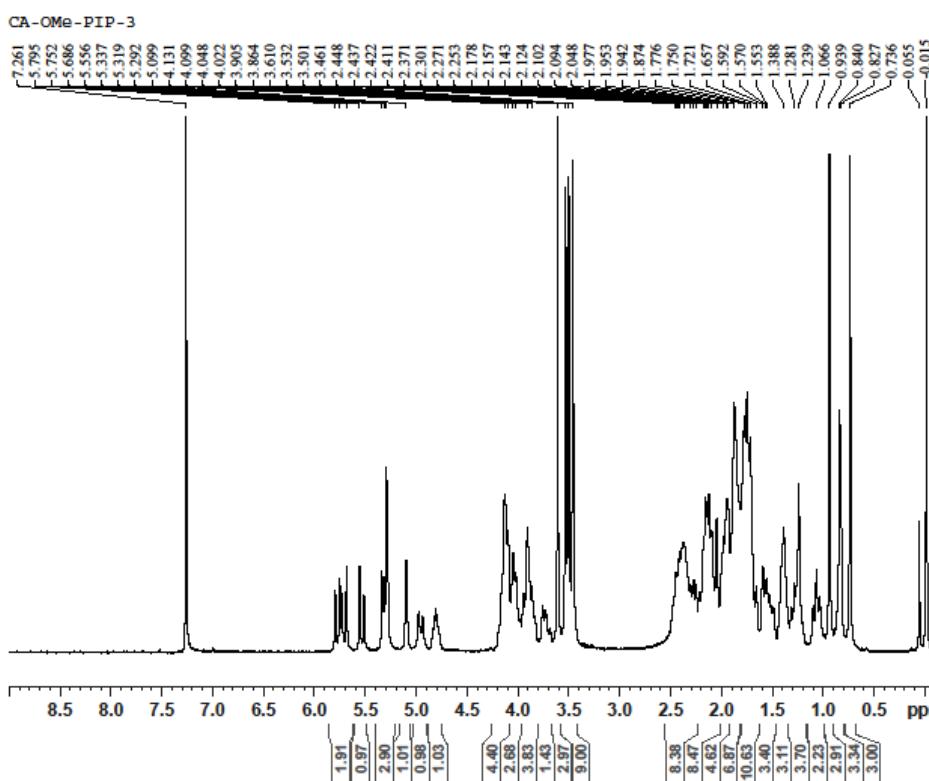
Exp-193, CA-NH3 / CDCl₃ (Ash-32)



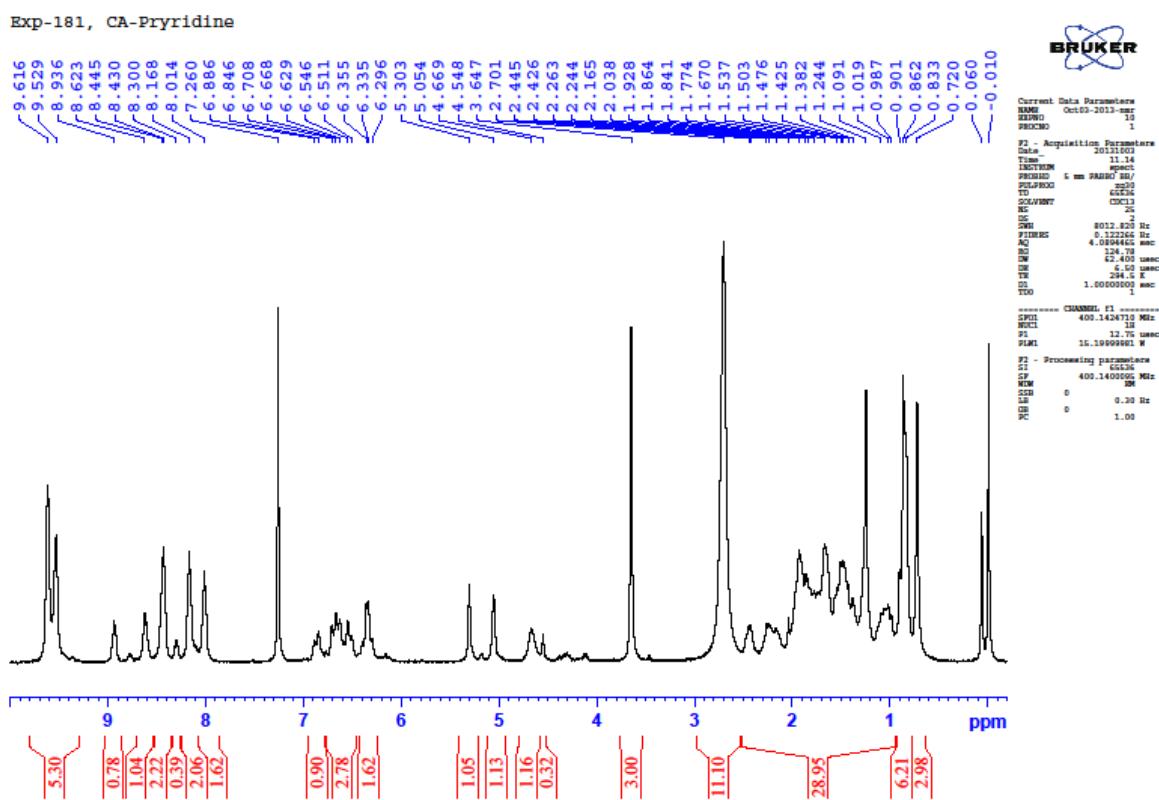
¹H, CA-TMA₃



¹H, CA-PIP₃



¹H, CA-PYR₃



¹H, CA-DMAP₃

