Electronic Supplementary Information for:

New amphiphilic materials showing the lyotropic analogue to the thermotropic smectic C* liquid crystal phase

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Experimental Part

Synthesis of JP003. The amphiphile was synthesised in a straight forward approach, shown in Figure 1. The etherification of the phenol **1** with 2-(2-bromoethoxy)ethanol[1] (**2**) gave the alcohol **3**, which then was etherified with (R)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate[2] (**4**). The resultant acetal **5** was cleaved after purification affording the diol **JP003**.

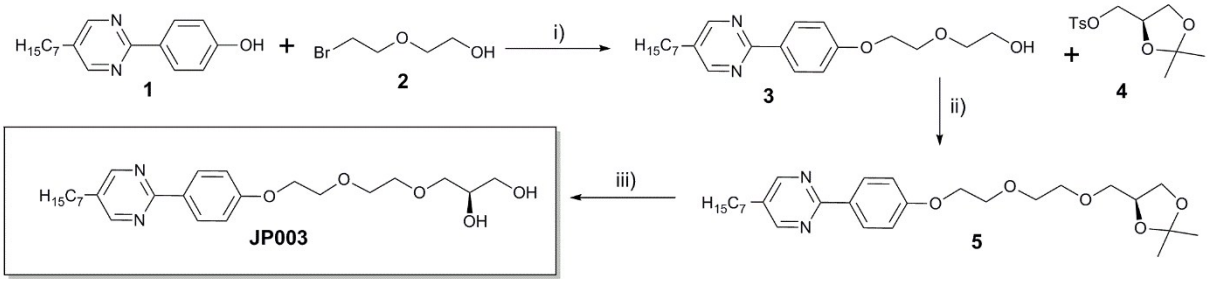

Figure 1: i) Cs_2CO_3, DMF, 80 °C, 10 h, 96%, ii) 1. NaH, DMF, 0 °C, 1 h, 2. (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate[2] (**4**), DMF, 80 °C, 12 h, 66%; iii) HCl (1M, aq.), MeOH, 50 °C, 1 h, 89 %.

To a solution of 4´-(5-heptylpyrimidin-2-yl)phenol (**1**, 1.893 g, 7.00 mmol) and caesium carbonate (2.925 g, 9 mmol) in 30 mL dry DMF freshly distilled 2-(2-bromoethoxy)ethanol[1] (**2**, 1.521 g, 9 mmol) was given. The reaction mixture was stirred for 10 h under argon at 80 °C. After cooling to room temperature 20 mL 1N HCl, 100 mL water and 100 mL ethyl acetate were added and the organic phase was washed 5 times with 100 mL water and once with 100 mL brine, before drying over $MgSO_4$. The crude product was purified chromatographically on silica with ethyl acetate as eluent affording 2.403 g (6.70 mmol, 96 %) **3** as a colourless solid.

To a stirred, ice cooled solution **3** (1.935 g, 5.40 mmol) in 20 mL dry DMF NaH (0.360 g, 8.80 mmol) was added within 5 minutes under nitrogen atmosphere. After addition, the solution was allowed to warm to room temperature and stirred for an additional hour. (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate[2] (**4**, 2.004 g, 7.00 mmol) was added in one portion and the reaction solution was heated to 80 °C for 12 hours. When cooled to room temperature. 50 mL ether and 100 mL water were added and the organic phase was washed two times with 50 mL water and once with 50 mL brine. After drying over $MgSO_4$, the solvent was removed and the crude product was purified chromatographically on silica with ethyl acetate/*n*-hexane 1:1 as eluent yielding 1.687 g (3.57 mmol, 66 %) **5** as a colourless solid. To a solution of **5** (1.652 g, 3.57 mmol) in 40 mL MeOH 1 mL of a 1M aqueous HCl solution was added and the solution was heated to 50 °C for 1 hour (TLC control). After full conversion the solvent was removed under vacuum and the crude product was purified chromatographically on silica using ethyl acetate/methanol 9:1 as eluent. The product was solved in chloroform and filtered through a PTFE syringe filter (0.2 µm) and precipitated by addition of methanol, yielding 1.377 g (3.18 mmol, 89 %) **JP003** as a colourless solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.57 (s, 2H), 8.34 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.24 - 4.17 (m, 2H), 3.92 - 3.82 (m, 3H), 3.77 - 3.65 (m, 5H), 3.64 - 3.59 (m, 2H), 3.56 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.04 (s, broad 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.47 (s, broad, 1H), 1.64 (p, *J* = 7.2 Hz, 2H), 1.41 – 1.20 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ = 162.50 (s), 160.79 (s), 157.09 (d), 132.36 (s), 130.75 (s), 129.55 (d), 114.70 (d), 73.14 (t), 70.93 (t), 70.87 (t), 70.65 (d), 69.87 (t), 67.54 (t), 64.08 (t), 31.86 (t), 30.94 (t), 30.27 (t), 29.14 (t), 29.12 (t), 22.74 (t), 14.20 (q); **HR-MS** (ESI, 70 eV, positive) m/z: calc. for $C_{24}H_{36}N_2O_5Na$ [M+Na$^+$]: 455.2516, found: 455.2520; **EA** (%) calc. for $C_{24}H_{36}N_2O_5$: C 66.64, H 8.39, N 6.48, found: C 66.53, H 8.19, N 6.42.

Synthesis of QL38-n and QL41-6.

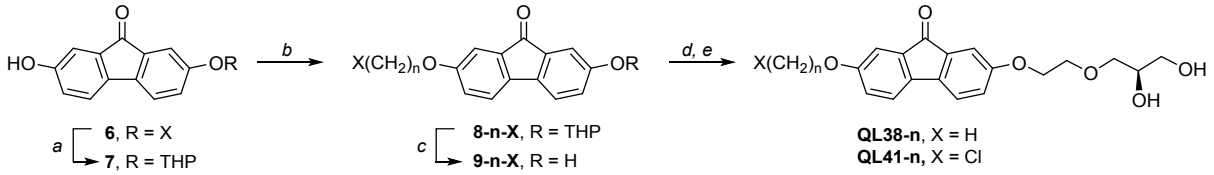

Figure 2: (a) 3,4- dihydropyran, pyridinium *p*-toluenesulphonate, THF; (b) $X(CH_2)_nOH$, PPh_3, DIAD, THF; (c) TsOH, 1:1 DCM/EtOH; (d) 2-[[(4S)-2,2-dimethyl-1,3-dioxolane-4-yl]methoxy]ethanol, PPh_3, DIAD, THF; (e) TFA, 4:1 MeOH/H_2O, 60 °C.

2-[[(4S)-2,2-dimethyl-1,3-dioxolane-4-yl]methoxy]ethanol. Sodium metal (0.60 g, 26.19 mmol) was added to anhydrous ethylene glycol (50 mL) under argon at ambient temperature. The mixture was heated to 40 °C until complete dissolution of the sodium before cooling to 0 °C. (*R*)-(-)-2,2-Dimethyl-1,3-dioxolan-4-ylmethyl *p*-toluenesulphonate (5.00 g, 17.46 mmol) was added in portions before heating the solution to 100 °C for 16 hours. The mixture was cooled and quenched with sat. aq. NH_4Cl (40 mL) before extracting with DCM (3x20 mL). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure to afford the title compound as a colourless oil (2.57 g, 83 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21-4.26 (m, 1H), 3.99 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.63-3.70 (m, 3H), 3.54-3.57 (m, 2H), 3.46-3.53 (m, 4H), 2.11 (t, *J* = 6.2 Hz, 1H), 1.37 (s, 3H), 1.30 (s, 3H).

2-Hydroxy-7-tetrahydropyran-2-yloxyfluoren-9-one (7)*.* To a solution of 2,7-dihydroxy-9-fluorenone (2.01 g, 9.47 mmol) in anhydrous 4:1 DCM/THF (50 mL) was added dihydropyran (0.79 g, 9.47 mmol) and pyridinium *p*-toluenesulphonate (0.24 g, 0.95 mmol). The mixture was stirred at ambient temperature for 16 hours before the solvent was removed under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded **7** as an orange crystalline solid (0.55 g, 20 %).

2-Butyloxy-7-hydroxyfluoren-9-one (9-4-H). A mixture of **7** (0.55 g, 1.86 mmol), 2-bromobutane (0.51 g, 3.72 mmol) and K_2CO_3 (0.77 g, 5.57 mmol in acetone (30 mL) was heated to reflux for 24 hours. The mixture was filtered and the solvent removed under reduced pressure. The crude product was dissolved in ethyl acetate and washed with 1M HCl (20 mL), brine (20 mL), dried ($MgSO_4$), the solvent removed under reduced pressure and purified by silica gel column chromatography (Hexane/Ethyl Acetate 3:1). The resulting **8-4-H** was dissolved in 1:1 DCM/EtOH (20 mL) and *p*-toluenesulphonic acid (0.035 g, 0.19 mmol) was

added. The mixture was stirred at ambient temperature for 16 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 2:1) afforded **9-4-H** as a dark purple solid (0.40 g, 80 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.4 Hz, 1H), 7.25 (d, J = 7.4 Hz, 1H), 7.16 (d, J = 2.1 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 6.94 (d, J = 7.4, 2.1 Hz, 1H), 6.89 (d, J = 7.4, 2.1 Hz, 1H), 4.00 (t, J = 6.6 Hz, 2H), 1.73-1.83 (m, 2H), 1.44-1.56 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H).

2-Pentyloxy-7-hydroxyfluoren-9-one (9-5-H). 2,7-Dihydroxyfluoren-9-one (128 g, 6.03 mmol), 1-pentanol (0.53 g, 6.03 mmol) and triphenylphosphine (2.37 g, 9.05 mmol) were dissolved in anhydrous THF (50 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (1.22 g, 6.03 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded **9-5-H** as a dark purple solid (0.55 g, 32%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.30 (m, 2H), 7.16 (d, J = 2.1 Hz, 1H), 7.08 (d, J = 2.6 Hz, 1H), 6.94 (dd, J = 8.2, 2.1 Hz, 1H), 6.88 (dd, J = 7.9, 2.6 Hz, 1H), 4.93 (s, 1H), 3.99 (t, J = 6.6 Hz, 2H), 1.75-1.85 (m, 2H), 1.39-1.47 (m, 4H), 0.95 (t, J = 6.9 Hz, 3H).

2-Hexyloxy-7-hydroxyfluoren-9-one (9-6-H). 2,7-Dihydroxyfluoren-9-one (1.06 g, 4.99 mmol), 1-hexanol (0.46 g, 4.49 mmol) and triphenylphosphine (1.96 g, 7.49 mmol) were dissolved in anhydrous THF (50 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (0.91 g, 4.49 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded **9-6-H** as a red solid (0.39 g, 27%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 8.2 Hz,1H), 7.25 (s, 1H) 7.16 (d, J = 2.5 Hz, 1H) 7.09 (d, J = 2.5 Hz, 1H), 6.95 (dd, J = 8.2, 2.4 Hz, 1H), 6.89 (dd, J = 8.2, 2.4 Hz, 1H), 4.93 (s, 1H), 3.99 (t, J = 6.6 Hz, 2H), 1.75-1.83 (m, 2H), 1.43-1.50 (m, 2H), 1.33-1.38 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H).

2-(6-Chlorohexyloxy)-7-hydroxyfluoren-9-one (9-6-Cl). 2,7-Dihydroxyfluoren-9-one (1.11 g, 5.23 mmol), 6-chlorohexanol (0.71 g, 5.23 mmol) and triphenylphosphine (2.06 g, 7.85 mmol) were dissolved in anhydrous THF (50 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (1.06 g, 5.23 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under

reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 3:1) afforded **9-6-Cl** as an dark orange solid (0.66 g, 38%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.31 (m, 2H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.89 (dd, *J* = 7.9, 2.1 Hz, 1H), 4.91 (s, 1H), 4.00 (t, *J* = 6.4 Hz, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 1.77-1.87 (m, 4H), 1.49-1.57 (m, 4H).

2-[2-[(2R)-2,3-Dihydroxypropoxy]ethoxy]-7-butyloxyfluoren-9-one (QL38-4). Compound **9-4-H** (0.35 g, 1.30 mmol), 2-[[(4*R*)-2,2-dimethyl-1,3-dioxolane-4-yl]ethanol] (0.34 g, 1.96 mmol) and triphenylphosphine (0.68 g, 2.60 mmol) were dissolved in anhydrous THF (20 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (0.53 g, 2.60 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded a dark orange solid (0.46 g, 84%). The product was dissolved in 4:1 MeOH/H_2O (20 mL), 5mol% TFA was added and the mixture was heated to 60 °C for 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography afforded **QL38-4** as an orange solid which was further purified by recrystallisation from ethyl acetate/hexane (0.34 g, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H); 7.15 (dd, *J* = 8.7, 1.9 Hz, 2H), 6.94 (dt, *J* = 8.7, 1.9 Hz, 2H), 4.15 (t, *J* = 4.5 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.84-3.93 (m, 3H), 3.57-3.71 (m, 4H), 2.02-2.09 (m, 1H), 1.71-1.80 (m, 2H), 1.42-1.53 (m, 2H), 1.25 (d, *J* = 6.4 Hz, 1H); 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 159.7, 159.0, 138.1, 137.2, 136.0, 136.0, 121.1, 121.0, 120.7, 120.6, 110.3, 73.2, 70.6, 70.0, 68.3, 67.8, 64.0, 31.3, 19.3, 13.9; HRMS (ESI) *m/z* calcd for $C_{22}H_{27}O_6$ 387.1802 found 387.1801. Anal. calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78; found C, 67.91; H, 6.81.

2-[2-[(2R)-2,3-Dihydroxypropoxy]ethoxy]-7-pentyloxyfluoren-9-one (QL38-5). Compound **9-5-H** (0.30 g, 1.06 mmol), 2-[[(4*R*)-2,2-dimethyl-1,3-dioxolane-4-yl]ethanol] (0.28 g, 1.59 mmol) and triphenylphosphine (0.56 g, 2.12 mmol) were dissolved in anhydrous THF (20 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (0.43 g, 2.12 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded a dark orange solid (0.35 g, 74%). The product was dissolved in 4:1 MeOH/H_2O (20 mL), 5mol% TFA was added

and the mixture was heated to 60 °C for 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography afforded **QL38-5** as an orange solid which was further purified by recrystallisation from ethyl acetate/hexane (0.23 g, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.2, 2.5 Hz, 2H), 7.17 (dd, *J* = 8.2, 2.5 Hz, 2H), 6.97 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.94 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.17 (t, *J* = 4.5 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.87-3.94 (m, 3H), 3.63-3.70 (m, 4H), 2.67 (d, *J* = 4.8 Hz, 1H); 2.10 (dd, *J* = 6.8, 5.3 Hz, 1H), 1.75-1.82 (m, 2H), 1.43-1.51 (m, 2H), 1.25-1.36 (m, 2H), 0.92 (t, *J* = 6.6 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 159.6, 158.8, 137.9, 137.1, 135.9, 135.8, 121.0, 120.8, 120.6, 120.5, 110.2, 73.1, 70.5, 69.9, 68.5, 67.7, 63.9, 31.5, 29.1, 25.6, 14.0; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}O_6$ 401.1958 found 401.1959. Anal. calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05; found C, 68.81; H, 7.00.

2-[2-[(2R)-2,3-Dihydroxypropoxy]ethoxy]-7-hexyloxyfluoren-9-one (QL38-6). Compound **9-6-H** (1.25 g, 4.22 mmol), 2-[[(4*R*)-2,2-dimethyl-1,3-dioxolane-4-yl]ethanol] (1.11 g, 6.33 mmol) and triphenylphosphine (2.21 g, 8.44 mmol) were dissolved in anhydrous THF (80 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (1.71 g, 8.44 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded a dark orange solid (1.70 g, 89%). The product was dissolved in 4:1 MeOH/H_2O (75 mL), 5mol% TFA was added and the mixture was heated to 60 °C for 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography afforded **QL38-6** as an orange solid which was further purified by recrystallisation from ethyl acetate/hexane (0.76 g, 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.2, 2.5 Hz, 2H), 7.17 (dd, *J* = 8.2, 2.5 Hz, 2H), 6.97 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.94 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.17 (t, *J* = 4.5 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.87-3.94 (m, 3H), 3.63-3.70 (m, 4H), 2.67 (d, *J* = 4.8 Hz, 1H); 2.10 (dd, *J* = 6.8, 5.2 Hz, 1H), 1.76-1.84 (m, 2H), 1.43-1.50 (m, 2H), 1.25-1.37 (m, 4H), 0.92 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 159.6, 158.8, 137.9, 137.1, 135.9, 135.8, 121.0, 120.8, 120.6, 120.5, 110.2, 73.1, 70.5, 69.9, 68.5, 67.7, 63.9, 31.5, 29.1, 25.6, 22.6, 14.0; LRMS. (EI) *m/z* 414 (M^+, 64), 212 (100); HRMS (EI) *m/z* calcd for $C_{24}H_{30}O_6$ 414.2043 found 414.2050. Anal. calcd for $C_{24}H_{30}O_6$: C, 69.54; H, 7.30; found C, 69.10; H, 7.31.

2-[2-[(2R)-2,3-Dihydroxypropoxy]ethoxy]-7-(6-chlorohexyloxy)fluoren-9-one (QL41-6). Compound **9-6-Cl** (0.29 g, 0.88 mmol), 2-[[(4*R*)-2,2-dimethyl-1,3-dioxolane-4-yl]ethanol] (0.23 g, 1.31 mmol) and triphenylphosphine (0.46 g, 1.76 mmol) were dissolved in anhydrous THF (20 mL) under an inert atmosphere. The solution was cooled to 0 °C and DIAD (0.36 g, 1.76 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature over 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography (Hexane/Ethyl Acetate 4:1) afforded a dark orange solid (0.38 g, 89%). The product was dissolved in 4:1 MeOH/H_2O (20 mL), 5mol% TFA was added and the mixture was heated to 60 °C for 12 hours before removing the solvent under reduced pressure. Purification by silica gel column chromatography afforded **QL41-6** as an orange solid which was further purified by recrystallisation from ethyl acetate/hexane (0.27 g, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.2, 2.5 Hz, 2H), 7.17 (dd, *J* = 8.2, 2.5 Hz, 2H), 6.97 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.94 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.16 (t, *J* = 4.5 Hz, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.87-3.94 (m, 3H), 3.61-3.69 (m, 4H), 3.59 (d, *J* = 6.6 Hz, 2H), 2.67 (d, *J* = 4.8 Hz, 1H); 2.10 (dd, *J* = 6.8, 5.3 Hz, 1H), 1.75-1.83 (m, 2H), 1.45-1.52 (m, 2H), 1.24-1.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.4, 193.7, 159.5, 158.9, 137.9, 137.2, 135.9, 121.0, 120.8, 120.6, 120.5, 110.2, 110.2, 73.1, 70.5, 69.9, 68.2, 67.7, 63.9, 45.0, 32.5, 29.0, 26.6, 25.3; HRMS (ESI) *m/z* calcd for $C_{24}H_{30}O_6Cl$ 449.1725 found 449.1726. Anal. calcd for $C_{24}H_{29}O_6Cl$: C, 64.21; H, 6.51; found C, 64.41; H, 6.79.

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