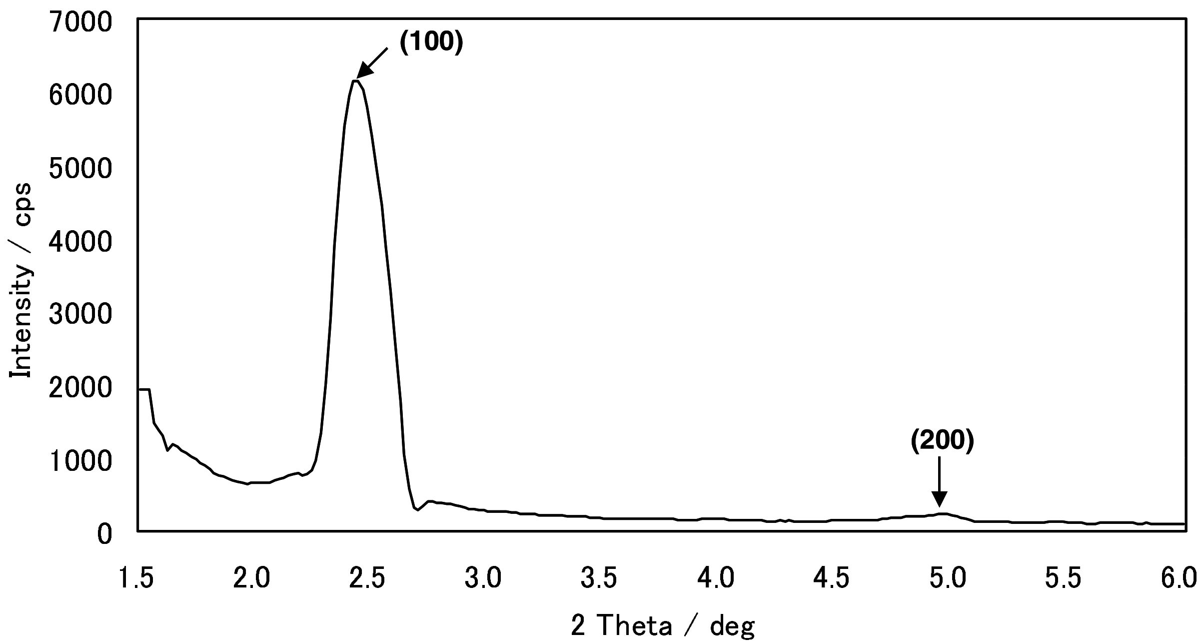
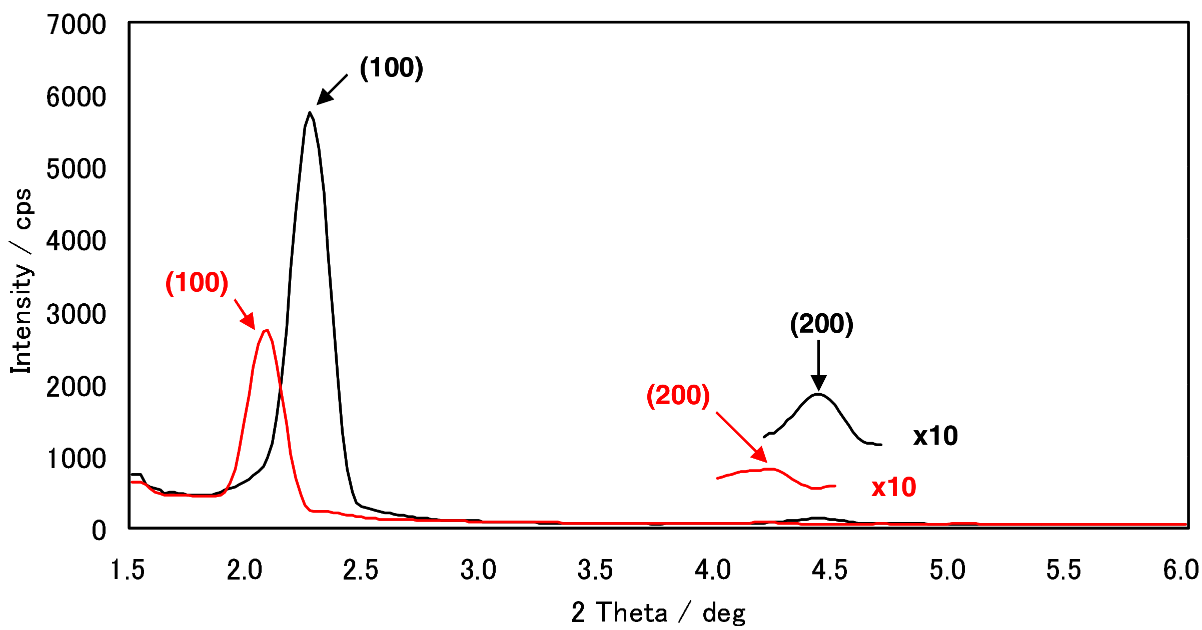
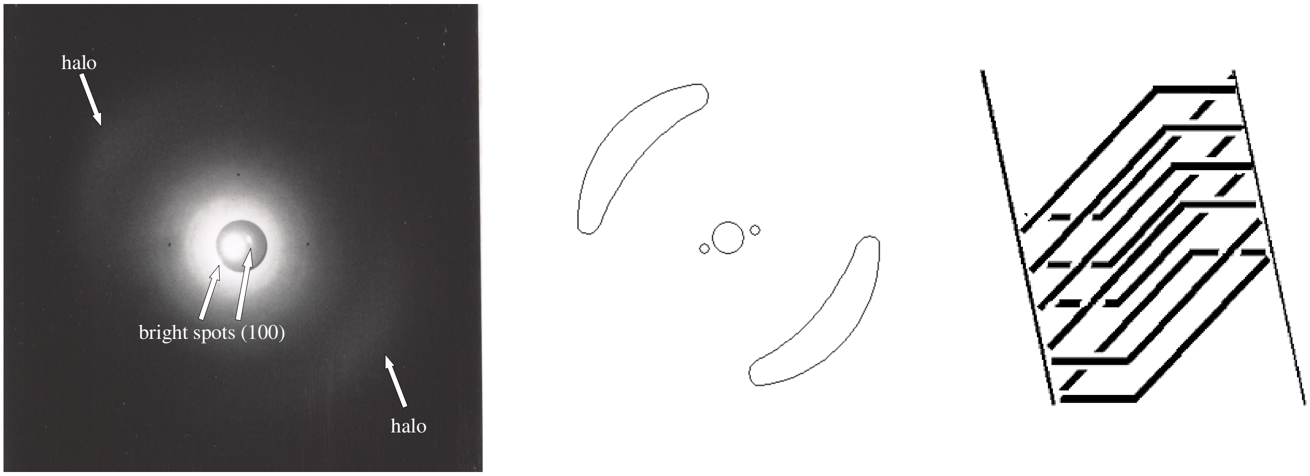


1D-XRD of 1a (190 ℃, SmA)



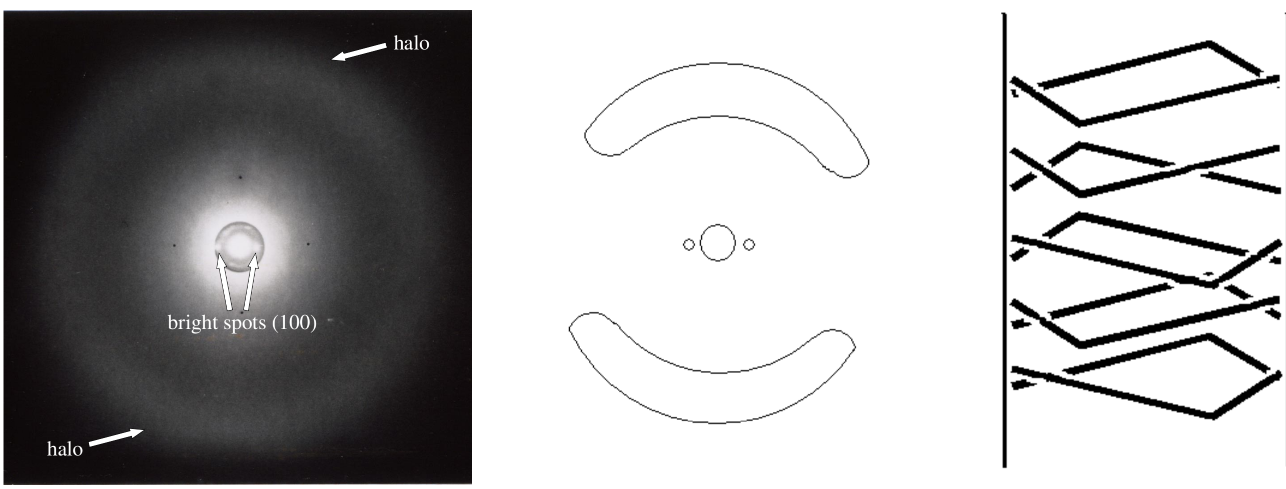
1D-XRD of 1b (black line: 180 ℃ (SmC), red line: 205 ℃ (SmA))

(a)



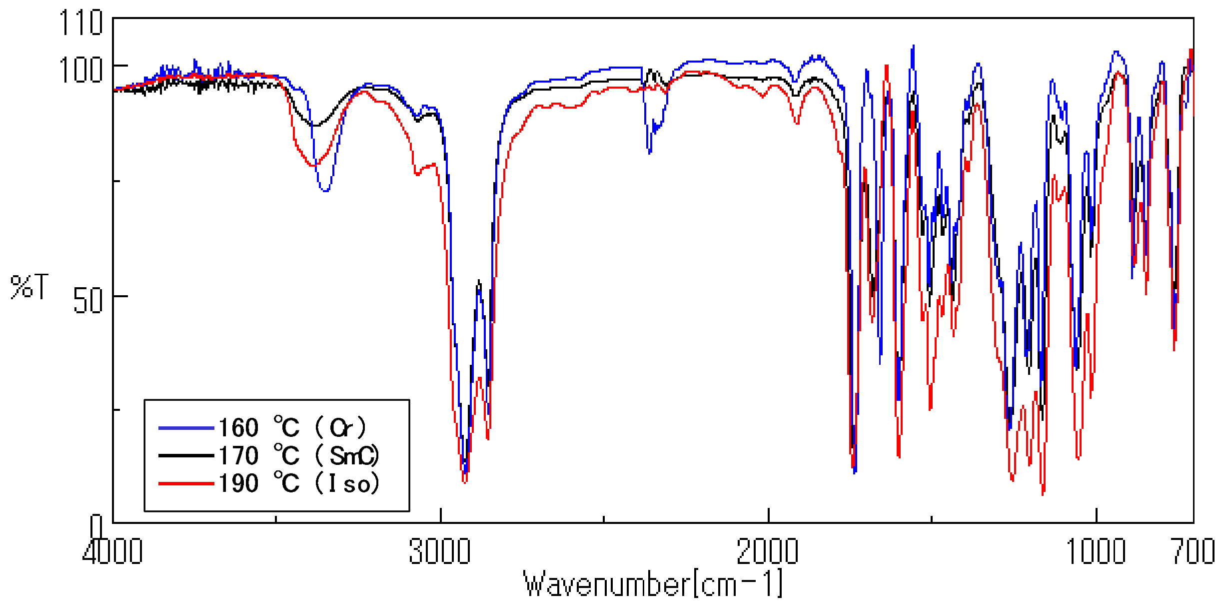
The molecules are well aligned in the layer, and the rods are stacked rigidly.

(b)

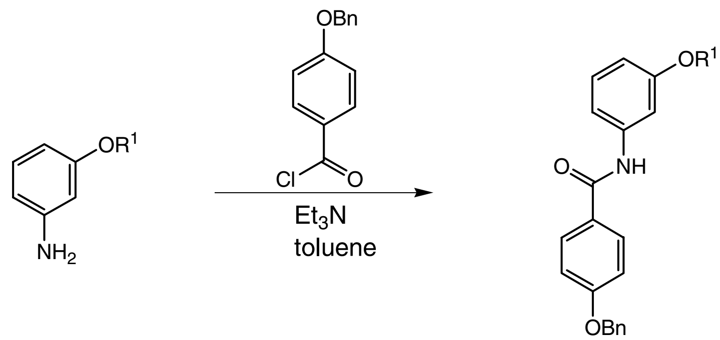


The molecules are well aligned. However, the rod directions are slightly disordered.

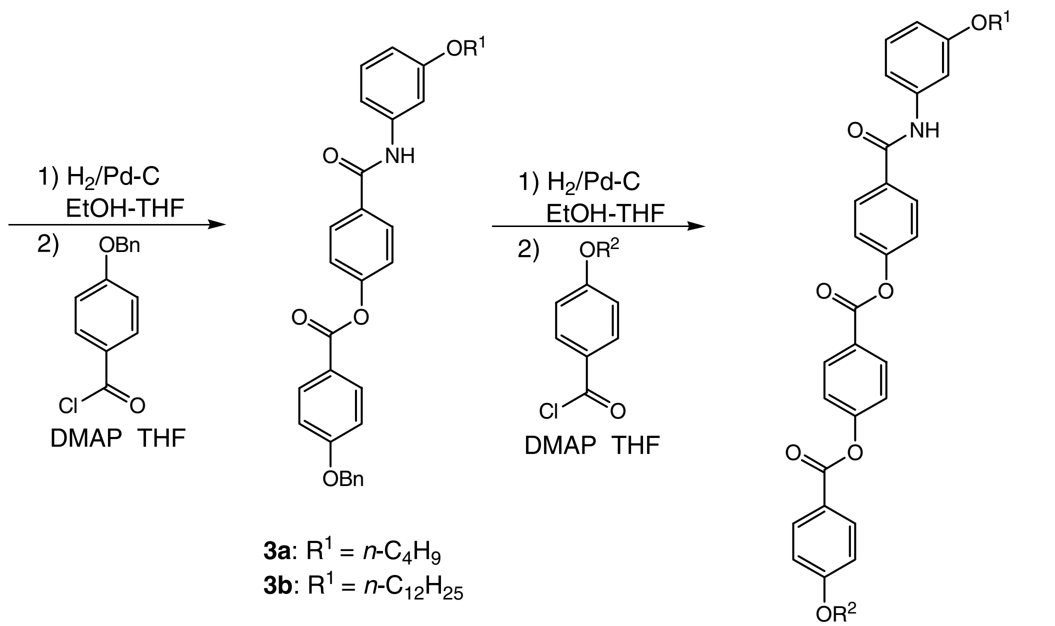
2D-XRD of 1b, their diffraction patterns, and the schematic layer structures. (a: 175℃ (SmC), b: 205℃ (SmA))



Temperature-variable FT-IR spectra of 1d



2a: $R^1 = n\text{-}C_4H_9$
2b: $R^1 = n\text{-}C_{12}H_{25}$



3a: $R^1 = n\text{-}C_4H_9$
3b: $R^1 = n\text{-}C_{12}H_{25}$

1a: $R^1 = R^2 = n\text{-}C_4H_9$
1b: $R^1 = n\text{-}C_4H_9$, $R^2 = n\text{-}C_{12}H_{25}$
1c: $R^1 = n\text{-}C_{12}H_{25}$, $R^2 = n\text{-}C_4H_9$
1d: $R^1 = R^2 = n\text{-}C_{12}H_{25}$

Synthetic Route of 1a-1d

An example for preparation of 2. To a 300 mL-round-bottom flask were added 4-benzyloxybenzoyl chloride (9.47 g, 38.4 mmol), 3-butoxyaniline (4.23 g, 25.6 mmol), triethylamine (21.4 mL, 153.6 mmol), and toluene (100 mL). The mixture was then stirred at reflux for 1.5 h. After cooling, the solution was washed with *1N* HCl (200 mL), and aqueous solution of $NaHCO_3$ (300 mL), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and a yellow solid was obtained as the residue. The crude product was purified by silica gel chromatography eluting with chloroform to give **2a** as a white solid (8.79 g, 91.4 %).

2a: yield 91.4 %; white solid; mp 116.7-117.1 ℃ (methanol-ethyl acetate); IR (KBr) 2952, 2869, 1648, 1606, 1507, 1437, 1249, 1173, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, 3H, *J* = 7.4Hz), 1.48 (q, 2H, *J* = 7.4Hz), 1.76 (t, 2H, *J* = 7.5Hz), 3.98 (t, 2H, *J* = 6.8Hz), 5.13 (s, 2H), 6.68 (d, 1H, *J* = 7.6Hz), 7.04 (d, 3H, *J* = 8.9Hz), 7.22 (t, 1H, *J* = 8.3Hz), 7.35 (d, 1H, *J* = 7.8Hz), 7.40 (d, 2H, *J* = 7.7Hz), 7.41 (d, 2H, *J* = 7.7Hz), 7.43 (t, 1H, *J* = 7.7Hz), 7.72 (s, 1H), 7.82 (d, 2H, *J* = 8.6Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 13.87, 19.25, 31.32, 67.79, 70.18, 106.31, 110.98, 111.97, 114.90, 127.44, 127.50, 128.25, 128.72, 128.90, 129.67, 136.28, 139.29, 159.86, 161.65, 165.15 ; Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.77, H, 6.71, N, 3.73, Found: C, 76.46, H, 6.62, N, 3.61

2b: yield 63.9 %; white solid; mp 104.6-104.9 ℃ (methanol-ethyl acetate); IR (KBr) 2915, 2847, 1644, 1600, 1508, 1467, 1249, 1173, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.0Hz), 1.26-1.38 (m, 16H), 1.43 (t, 2H, *J* = 7.3Hz), 1.78 (t, 2H, *J* = 7.0Hz), 3.98 (t, 2H, *J* = 6.7Hz), 5.14 (s, 2H), 6.68 (d, 1H, *J* = 8.0Hz), 7.04 (d, 3H, *J* = 8.9Hz), 7.23 (t, 1H, *J* = 8.1Hz), 7.35 (d, 1H, *J* = 7.0Hz), 7.40 (d, 2H, *J* = 7.6Hz), 7.41 (d, 2H, *J* = 7.6Hz), 7.43 (t, 1H, *J* = 7.7Hz), 7.71 (s, 1H), 7.83 (d, 2H, *J* = 8.8Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 14.12, 22.70, 26.06, 29.28, 29.37, 29.42, 29.60, 29.62, 29.65, 29.69, 31.93, 68.12, 70.20, 106.31, 110.98, 111.95, 114.93, 127.46, 127.50, 128.25, 128.72, 128.89, 129.68, 136.29, 139.28, 159.87, 161.67, 165.12 ; Anal. Calcd for $C_{32}H_{41}NO_3$: C, 78.81, H, 8.47, N, 2.87, Found: C, 78.69, H, 8.69, N, 2.78

A typical procedure for synthesis of 3. To a 500 mL-flask were added **2a** (8.50 g, 22.6 mmol), ethanol (100 mL), THF (100 mL), and 10% palladium-activated carbon (1.50 g). The mixture was stirred at room temperature for 2 h under an atmosphere of hydrogen. After filtrating off by celite, the solution was concentrated in vacuo to give a white solid (6.45 g). The solid was added to a 300 mL-roun-bottom flask, and 4-benzyloxybenzoyl chloride (8.36 g, 33.9 mmol), 4-(*N*,*N*-dimethlamino)pyridine (2.00 g, 16.4 mmol), and THF (150 mL) were added. The mixture was stirred at room temperature for 20 h. To the solution was added ethyl acetate (100 mL), and the solution was washed with aqueous solution of $NaHCO_3$ (300 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and a white solid was obtained as the residue. The crude product was purified by silica gel chromatography (chloroform) to give **3a** as a white solid (9.35 g, 83.5 %)

3a: yield 83.5 %; white solid; mp 159.3-159.8 ℃ (methanol-ethyl acetate); IR (KBr) 2957, 2871, 1656, 1606, 1510, 1454, 1274, 1170, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, 3H, *J* = 7.4Hz), 1.49 (q, 2H, *J* = 7.7Hz), 1.78 (t, 2H, *J* = 7.6Hz), 4.00 (t, 2H, *J* = 6.8Hz), 5.18 (s, 2H), 6.71 (d, 1H, *J* = 8.3Hz), 7.08 (d, 3H, *J* = 8.7Hz), 7.25 (t, 1H, *J* = 8.2Hz), 7.33 (d, 2H, *J* = 8.6Hz), 7.36 (d, 1H, *J* = 8.6Hz), 7.39 (d, 2H, *J* = 8.5Hz), 7.43 (t, 1H, *J* = 7.1Hz), 7.44 (d, 2H, *J* = 8.5Hz), 7.81 (s, 1H), 7.94 (d, 2H, *J* = 8.5Hz), 8.18 (d, 2H, *J* = 8.9Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 13.85, 19.23, 31.29, 67.80, 70.24, 106.37, 111.23, 112.03, 114.85, 121.50, 122.26, 127.50, 128.34, 128.56, 128.74, 129.73, 132.45, 132.48, 136.02, 139.01, 153.78, 159.86, 163.30, 164.08, 164.85 ; Anal. Calcd for $C_{31}H_{29}NO_5$: C, 75.13, H, 5.90, N, 2.83, Found: C, 75.17, H, 5.61, N, 2.86

3b: yield 66.2 %; white solid; mp 132.4-132.9 ℃ (methanol-ethyl acetate); IR (KBr) 2920, 2852, 1732, 1655, 1606, 1511, 1473, 1271, 1171, 777 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.1Hz), 1.26-1.37 (m, 16H), 1.44 (t, 2H, J = 7.7Hz), 1.77 (t, 2H, J = 8.0Hz), 3.96 (t, 2H, J = 6.8Hz), 5.16 (s, 2H), 6.70 (d, 1H, J = 8.1Hz), 7.07 (d, 3H, J = 8.9Hz), 7.23 (t, 1H, J = 8.0Hz), 7.27 (d, 2H, J = 8.9Hz), 7.36 (d, 1H, J = 7.5Hz), 7.40 (d, 2H, J = 7.7Hz), 7.43 (t, 1H, J = 7.2Hz), 7.44 (d, 2H, J = 8.6Hz), 7.88 (d, 2H, J = 8.9Hz), 7.95 (s, 1H), 8.15 (d, 2H, J = 9.2Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 14.13, 22.70, 26.04, 29.27, 29.37, 29.43, 29.60, 29.63, 29.65, 29.69, 31.93, 68.11, 70.24, 106.34, 111.18, 112.08, 114.83, 121.50, 122.18, 127.51, 128.34, 128.53, 128.75, 129.69, 132.47, 132.52, 136.03, 139.12, 153.73, 159.82, 163.32, 164.55, 165.04 ; Anal. Calcd for $C_{39}H_{45}NO_5$: C, 77.07, H, 7.46, N, 2.30, Found: C, 76.78, H, 7.58, N, 2.19

An example for synthesis of 1. To a 100 mL-flask were added **3a** (1.10 g, 2.22 mmol), ethanol (30 mL), THF (30 mL), and 10% palladium-activated carbon (300 mg). The mixture was stirred at room temperature for 2 h under an atmosphere of hydrogen. After filtrating off by celite, the solution was concentrated in vacuo to give a white solid (0.90 g). The solid was added to a 100 mL-roun-bottom flask, and 4-butoxybenzoyl chloride (0.71 g, 3.33 mmol), 4-(N,N-dimethlamino)pyridine (0.50 g, 4.09 mmol), and THF (50 mL) were added. The mixture was stirred at room temperature for 20 h. To the solution was added ethyl acetate (50 mL), and the solution was washed with aqueous solution of $NaHCO_3$ (200 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and a white solid was obtained as the residue. The crude product was purified by silica gel chromatography (chloroform) to give **1a** as a white solid (0.94 g, 73%)

1a: yield 72.8 %; white solid (methanol-ethyl acetate); IR (KBr) 2956, 2871, 1733, 1657, 1604, 1510, 1474, 1271, 1163, 762 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, 3H, J = 7.3Hz), 1.00 (t, 3H, J = 7.4Hz), 1.51 (q, 2H, J = 7.7Hz), 1.52 (q, 2H, J = 7.6Hz), 1.79 (t, 2H, J = 7.3Hz), 1.81 (t, 2H, J =

7.4Hz), 4.00 (t, 2H, J = 6.6Hz), 4.07 (t, 2H, J = 6.6Hz), 6.71 (d, 1H, J = 8.3Hz), 6.99 (d, 2H, J = 9.2Hz), 7.08 (d, 1H, J = 7.9Hz), 7.25 (t, 1H, J = 8.3Hz), 7.35 (d, 2H, J = 8.9Hz), 7.39 (d, 2H, J = 8.5Hz), 7.43 (t, 1H, J = 7.8Hz), 7.84 (s, 1H), 7.94 (d, 2H, J = 8.6Hz), 8.15 (d, 2H, J = 9.2Hz), 8.28 (d, 2H, J = 8.9Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 13.83, 13.87, 19.21, 19.26, 31.13, 31.32, 67.83, 68.11, 106.43, 111.26, 112.09, 114.48, 120.90, 122.20, 122.27, 126.40, 128.59, 129.75, 131.93, 132.47, 132.77, 139.05, 153.63, 155.68, 159.89, 163.92, 164.13, 164.35, 164.90 ; Anal. Calcd for $C_{35}H_{35}NO_7$: C, 72.27, H, 6.06, N, 2.41, Found: C, 72.00, H, 6.04, N, 2.22

1b: yield 70.1 %; white solid (methanol-ethyl acetate); IR (KBr) 2956, 2871, 1733, 1657, 1604, 1510, 1474, 1271, 1163, 762 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 7.1Hz), 0.98 (t, 3H, J = 7.5Hz), 1.27-1.38 (m, 16H), 1.45-1.52 (m, 4H), 1.78 (t, 2H, J = 7.9Hz), 1.83 (t, 2H, J = 7.6Hz), 4.00 (t, 2H, J = 6.6Hz), 4.06 (t, 2H, J = 6.6Hz), 6.71 (d, 1H, J = 8.6Hz), 6.99 (d, 2H, J = 9.2Hz), 7.08 (d, 1H, J = 9.2Hz), 7.25 (t, 1H, J = 8.2Hz), 7.35 (d, 2H, J = 8.9Hz), 7.39 (d, 2H, J = 8.9Hz), 7.43 (t, 1H, J = 7.0Hz), 7.82 (s, 1H), 7.94 (d, 2H, J = 8.9Hz), 8.15 (d, 2H, J = 8.9Hz), 8.28 (d, 2H, J = 8.9Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 13.88, 14.13, 19.26, 22.70, 25.99, 29.10, 29.37, 29.57, 29.60, 29.65, 29.67, 31.33, 31.93, 67.84, 68.44, 106.42, 111.26, 112.07, 114.48, 120.91, 122.22, 122.26, 126.40, 128.58, 129.75, 131.93, 132.47, 132.79, 139.04, 153.64, 155.62, 159.90, 163.92, 164.13, 164.32, 164.85 ; Anal. Calcd for $C_{43}H_{51}NO_7$: C, 74.43, H, 7.41, N, 2.02, Found: C, 74.18, H, 7.31, N, 1.85

1c: yield 45.1 %; white solid (methanol-ethyl acetate); IR (KBr) 2921, 2852, 1656, 1604, 1510, 1473, 1267, 1164, 780 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.4Hz), 1.00 (t, 3H, J = 7.3Hz), 1.27-1.37 (m, 16H), 1.46 (t, 2H, J = 8.0Hz), 1.52 (q, 2H, J = 7.7Hz), 1.81 (t, 4H, J = 6.6Hz), 3.99 (t, 2H, J = 6.4Hz), 4.07 (t, 2H, J = 6.4Hz), 6.71 (d, 1H, J = 8.3Hz), 6.99 (d, 2H, J = 9.2Hz), 7.08 (d, 1H, J = 8.0Hz), 7.25 (t, 1H, J = 8.3Hz), 7.37 (d, 2H, J = 8.9Hz), 7.40 (d, 2H, J = 8.9Hz), 7.43 (t, 1H, J = 7.0Hz), 7.83 (s, 1H), 7.95 (d, 2H, J = 8.6Hz), 8.15 (d, 2H, J = 8.9Hz), 8.29 (d, 2H, J = 8.9Hz) ; ^{13}C

NMR (125.65 MHz, $CDCl_3$) δ 13.80, 14.11, 19.18, 22.68, 26.03, 29.26, 29.34, 29.41, 29.59, 29.60, 29.63, 29.66, 31.11, 31.92, 68.08, 68.13, 106.38, 111.21, 112.00, 114.45, 120.85, 122.11, 122.24, 126.36, 128.56, 129.72, 131.91, 132.44, 132.75, 138.99, 153.60, 155.62, 159.80, 163.90, 164.11, 164.32, 164.85 ; Anal. Calcd for $C_{43}H_{51}NO_7$: C, 74.43, H, 7.41, N, 2.02, Found: C, 74.26, H, 7.50, N, 1.92

1d: yield 40.7 %; white solid (methanol-ethyl acetate); IR (KBr) 2921, 2851, 1736, 1656, 1604, 1510, 1469, 1264, 1165, 761 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.0Hz), 0.89 (t, 3H, J = 7.1Hz), 1.27-1.38 (m, 32H), 1.46 (t, 4H, J = 7.7Hz), 1.81 (t, 4H, J = 7.0Hz), 3.99 (t, 2H, J = 6.6Hz), 4.06 (t, 2H, J = 6.7Hz), 6.71 (d, 1H, J = 8.3Hz), 6.99 (d, 2H, J = 8.9Hz), 7.08 (d, 1H, J = 8.0Hz), 7.24 (t, 1H, J = 8.0Hz), 7.35 (d, 2H, J = 8.9Hz), 7.39 (d, 2H, J = 8.6Hz), 7.43 (t, 1H, J = 6.7Hz), 7.83 (s, 1H), 7.94 (d, 2H, J = 8.6Hz), 8.15 (d, 2H, J = 8.9Hz), 8.28 (d, 2H, J = 8.6Hz) ; ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 14.12, 22.70, 25.99, 26.06, 29.09, 29.28, 29.37, 29.42, 29.56, 29.60, 29.62, 29.65, 29.69, 31.93, 68.15, 68.43, 106.41, 111.25, 112.07, 114.47, 120.88, 122.21, 122.26, 126.39, 128.58, 129.74, 131.93, 132.46, 132.76, 139.02, 153.62, 155.67, 159.88, 163.91, 164.11, 164.34, 164.87 ; Anal. Calcd for $C_{51}H_{67}NO_7$: C, 75.99, H, 8.38, N, 1.74, Found: C, 76.00, H, 8.47, N, 1.65