Fluorine containing nonsymmetrical five-ring achiral banana-shaped compounds with columnar and synclinic antiferroelectric layered phases

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Experimental

Synthetic and molecular structural characterization details

The procedure for the synthesis of 2,3-difluoro1-decyloxybenzene (4)

A solution of 2,3-difluorobenzene (1 g, 7.6 m.mol, 1 equiv.), 1-bromodecane (1.2 g, 9.12 m.mol, 1.2 equiv.), potassium carbonate (4.1 g, 30.4 m.mol, 4 equiv.) was taken in dry DMF (20 ml) solvent. The resulting mixture was stirred for 16 h under dry nitrogen atmosphere at 80 °C. The reaction was quenched by adding ice water (300 ml) and the crude product was extracted with dichloromethane (2 × 200 ml). The combined organic extracts was washed with water (200 ml) followed by brine and dried over anhydrous Na₂SO₄. Evaporation of solvent furnished the crude product, which was further purified by column chromatography using silica gel (100-200 mesh). The column was initially eluted with hexanes to remove the unreacted 1-bromodecane and then with 5% EtOAchexanes to get the pure product. Yield: 90%. A colourless liquid; $R_f = 0.55$ (10% EtOAchexanes); IR (neat) v_{max} in cm⁻¹ 2928, 2857, 1727, 1514, 1289 and 1074; ¹H NMR (400MHz, CDCl₃): δ 6.99-6.84 (m, 1H, Ar), 6.77-6.69 (m, 2H, Ar), 4.02 (t, *J* = 6.6 Hz, 2H, 1 × OCH₂), 1.98-1.71 (m, 2H, 1 × CH₂), 1.69-1.00 (m, 14H, 7 × CH₂) and 0.88 (t, *J* = 6.88 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 71.08 (71.08) ; H 8.95 (8.46) for C₁₆H₂₄F₂O.

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The procedure for the synthesis of 2,3-difluoro-4-decyloxybenzoic acid (3)

n-Butyllithium (0.28 ml, 0.44 m.mol, 1.2 equiv. in hexanes) was added dropwise to a stirred, cooled (-40 °C) solution of 2,3-difluoro1-decyloxybenzene (4) (100 mg, 0.37 m.mol, 1.0 equiv.) in dry tetrahydrofuran (10 ml) under nitrogen atmosphere. The resulting solution was kept at *ca*. -40 °C for 2 h before being poured onto stirred slurry of crushed solid CO₂ and dry tetrahydrofuran (5 ml) and the reaction mixture was allowed to warm up to room temperature. The solution was acidified with 3N hydrochloric acid. The product was extracted with dichloromethane $(2 \times 25 \text{ ml})$, the combined organic extracts was washed with water $(2 \times 25 \text{ ml})$, brine $(2 \times 25 \text{ ml})$ and dried over anhydrous Na₂SO₄. The crude compound was purified by repeated recrystallizations with a mixture of dichloromethane-hexanes (1:10) to obtain a constant isotropic temperature. Yield: 95%. A white solid; $R_f = 0.12$ (20% EtOAc-hexanes); m.p. 111-112 °C; (KBr Pellet) v_{max} in cm⁻¹ 2918, 2848, 1690, 1621, 1305 and 1092; ¹H NMR (400MHz, CDCl₃): δ 7.81-7.71 (m, 1H, Ar), 6.82-6.74 (m, 1H, Ar), 4.11 (t, J = 6.6 Hz, 2H, $1 \times OCH_2$), 1.88-1.78 (m, 2H, 1 × CH₂), 1.47-1.27 (m, 14H, 7 × CH₂) and 0.88 (t, J = 6.6 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 64.95 (65.07) ; H 7.69 (7.64) for $C_{17}H_{24}F_2O_3$.

The procedure for the synthesis of 4-formyl-3-hydroxyphenyl 4-(decyloxy)-2,3difluorobenzoate (1a)

2,4-dihydroxybenzaldehyde (0.28 mg, 0.73 m.mol, 1 equiv.) and 2,3-difluoro-4decyloxybenzoic acid (**3**) (1 g, 0.8 m.mol, 1.1 equiv.) were dissolved in dry dichloromethane (20 ml). To this DCC (0.47 mg, 0.73 m.mol, 1.1 equiv.) and a catalytic amount of DMAP was added and the mixture was stirred at room temperature for about 2 h. The precipitate dicyclohexylurea was filtered off and washed thoroughly with dichloromethane. The combined filtrate was washed with water, brine and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography using

silica gel (100-200 mesh) and 10% EtOAc-hexanes elution afforded the product. Yield: 80%. A white solid; $R_f = 0.30$ (10% EtOAc-hexanes); m.p. 101-102 °C; (KBr Pellet) v_{max} in cm⁻¹ 2915, 2849, 1736, 1475, 1275 and 1084; ¹H NMR (400MHz, CDCl₃): δ 11.25 (s, 1H, 1 × OH), 9.89 (s, 1H, 1x CHO), 7.87-7.78 (m, 1H, Ar), 7.62 (d, *J* = 8.0 Hz, 1H, Ar), 6.95-6.79 (m, 3H, Ar), 4.14 (t, *J* = 6.6 Hz, 2H, 1 × OCH₂), 1.91-1.80 (m, 2H, 1 × CH₂), 1.50-1.28 (m, 14H, 7 × CH₂) and 0.89 (t, *J* = 6.0 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 67.25 (67.15); H 6.32 (6.29) for C₂₄H₂₈F₂O₅.

The preparation of 4-formylphenyl 4-(decyloxy)-2,3-difluorobenzoate (1b)

4-hydroxybenzaldehyde (0.25 g, 2.09 m.mol, 1 equiv.) and 2,3-difluoro-4decyloxybenzoic acid (**3**) (1g, 2.30 m.mol, 1.1 equiv.) were dissolved in dry dichloromethane (20 ml). To this DCC (0.47 mg, 2.3 m.mol, 1.1 equiv.) and a catalytic amount of DMAP was added and the mixture was stirred at room temperature for about 2 h. The precipitate dicyclohexylurea was filtered off and washed thoroughly with dichloromethane. The combined filtrate was washed with water, brine and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography using silica gel (100-200 mesh) and 10% EtOAc-hexanes elution afforded the product. Yield: 80%. A white solid; $R_f = 0.30$ (10% EtOAc-hexanes); m.p. 65-66 °C; (KBr Pellet) v_{max} in cm⁻¹ 2917, 2851, 1732, 1625, 1476, 1293 and 1086; ¹H NMR (200MHz, CDCl₃): δ 10.03 (s, 1H, 1 × CHO), 7.97 (d, *J* = 8.5 Hz, 2H, Ar), 7.89-7.80 (m, 1H, Ar), 7.42 (d, *J* = 8.5 Hz, 2H, Ar), 6.87-6.80 (m, 1H, Ar), 4.14 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.9-1.8 (m, 2H, 1 × CH₂), 1.49-1.28 (m, 14H, 7 × CH₂) and 0.89 (t, *J* = 6.0 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 68.88(69.02) ; H 6.74 (6.49) for C₂₄H₂₈F₂O₅.

The General preparation of 4-((3-(4-(alkoxy)benzoyloxy)benzoyloxy)phenyl imino) methyl)-3-hydroxyphenyl 4-(decyloxy)-2,3-difluorobenzoate (**I-6 to I-10**)

A mixture of 4-(decyloxy)-2,3-difluorophenyl 4-formyl–3-hydroxybenzoate (1**a**) (0.18 m.mol, 1.0 equiv.), 4-((3-aminophenoxy)carbonyl)phenyl 4-(alkoxy)benzoate (2**a-h**) (0.18 m.mol, 1.0 equiv.), absolute ethanol (10 ml) and catalytic amount of acetic acid was refluxed until the yellow solid precipitated out (2 h). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was purified by repeated recrystallization with a mixture of absolute ethanol-dichloromethane (9:1) to get constant isotropic phase transition temperature. Yield: 85-91%.

I-6: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2927, 2856, 1728, 1611, 1477 and 1085; ¹H NMR (400MHz, CDCl₃): δ 13.36 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, *J* = 8.7 Hz, 2H, Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 7.86-7.82 (m, 1H, Ar), 7.49 (t, *J* = 8.1 Hz, 1H, Ar), 7.45 (d, *J* = 8.5 Hz, 1H, Ar), 7.38 (d, *J* = 8.7 Hz, 2H, Ar), 7.23- 7.16 (m, 3H, Ar), 6.99 (d, *J* = 8.9 Hz, 2H, Ar), 6.91 (d, *J* = 2.2 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.06 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.22 (m, 20H, 10 × CH₂) and 0.88 (t, *J* = 7.0 Hz, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₀H₅₃F₂NO₉, Calculated: 849.3, Found: 851.3; Elemental analysis: Calculated (Found)%: C 70.66 (70.93) ; H 6.29 (6.20) ; N 1.65 (1.68).

I-7: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2924, 2856, 1732, 1607, 1475 and 1084; ¹H NMR (400MHz, CDCl₃): δ 13.36 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, *J* = 8.8 Hz, 2H, Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, *J* = 8.0 Hz, 1H, Ar), 7.45 (d, *J* = 8.5 Hz, 1H, Ar), 7.39 (d, *J* = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, *J* = 8.9 Hz, 2H, Ar), 6.91 (d, *J* = 2.2 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.06 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.88-1.79 (m, 4H, 2 × CH₂), 1.48-1.22 (m, 22H, 11 × CH₂) and 0.88 (t, *J* = 7.0 Hz, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₁H₅₅F₂NO₉, Calculated: 863.4, Found: 865.4; Elemental analysis: Calculated (Found)%: C 70.90 (71.05) ; H 6.42 (6.05) ; N 1.62 (2.00).

I-8: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2922, 2854, 1733, 1603, 1475 and 1082; ¹H NMR (400MHz, CDCl₃): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, *J* = 8.8 Hz, 2H, Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, *J* = 8.0 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22- 7.16 (m, 3H, Ar), 6.99 (d, J = 9.0 Hz, 2H, Ar), 6.91 (d, J = 2.2 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, $1 \times \text{OCH}_2$), 4.06 (t, J = 6.5 Hz, 2H, $1 \times \text{OCH}_2$), 1.88-1.79 (m, 4H, $2 \times \text{CH}_2$), 1.48-1.24 (m, 24H, $12 \times \text{CH}_2$) and 0.88 (t, J = 7.0 Hz, 6H, $2 \times \text{CH}_3$); MS (FAB⁺): m/z for C₅₂H₅₇F₂NO₉, Calculated: 877.4, Found: 879.4; Elemental analysis: Calculated (Found)%: C 71.13 (71.20) ; H 6.54 (6.35) ; N 1.60 (1.63).

I-9: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2922, 2854, 1733, 1603, 1472 and 1082; ¹H NMR (400MHz, CDCl₃): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, *J* = 8.8 Hz, 2H, Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, *J* = 8.6 Hz, 1H, Ar), 7.45 (d, *J* = 8.5 Hz, 1H, Ar), 7.39 (d, *J* = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, *J* = 9 Hz, 2H, Ar), 6.91 (d, *J* = 2.6 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.24 (m, 26H, 13 × CH₂) and 0.88 (t, *J* = 7.0 Hz, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₃H₅₉F₂NO₉, Calculated: 891.4, Found: 893.5; Elemental analysis: Calculated (Found)%: C 71.36 (71.70) ; H 6.67 (6.31) ; N 1.57 (1.99).

I-10: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2920, 2852, 1731, 1604, 1473, and 1080; ¹H NMR (400MHz, CDCl₃): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, *J* = 8.8 Hz, 2H, Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 7.86-7.82 (m, 1H, Ar), 7.49 (t, *J* = 8.4 Hz, 1H, Ar), 7.45 (d, *J* = 8.5 Hz, 1H, Ar), 7.39 (d, *J* = 8.8 Hz, 2H, Ar), 7.22- 7.16 (m, 3H, Ar), 6.99 (d, *J* = 8.9 Hz, 2H, Ar), 6.91 (d, *J* = 2.1 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.24 (m, 28H, 14 × CH₂) and 0.88 (t, *J* = 6.7 Hz, 6H, 2 × CH₃); ¹³C NMR (100MHz, CDCl₃): 164.26, 164.25, 163.86, 162.60, 161.29, 155.55, 154.50, 153.27, 153.26, 153.25, 151.76, 150.53, 149.58, 140.40, 133.38, 132.38, 131.79, 130.19, 127.02, 126.64, 122.11, 120.97, 120.11, 119.08, 117.16, 114.44, 112.98, 111.04, 110.55, 108.55, 70.03, 68.40, 31.84, 29.47, 29.24, 29.06, 28.91, 25.94, 25.76, 22.62 and 14.03; MS (FAB⁺): m/z for C₅₄H₆₁F₂NO₉, Calculated: 905.4, Found: 907.2; Elemental analysis: Calculated (Found)%: C 71.58 (71.36) ; H 6.79 (6.87) ; N 1.55 (1.66).

I-12: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2920, 2852, 1731, 1605, 1473, 1275, 1165 and 1079; ¹H NMR (400MHz, CDCl₃): δ 13.36 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.8 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J = 8.0 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22- 7.16 (m, 3H, Ar), 6.99 (d, J = 8.9 Hz, 2H, Ar), 6.91 (d, J = 2.1 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.24 (m, 32H, 16 × CH₂) and 0.88 (t, J = 6.9 Hz, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₆H₆₅F₂NO₉, Calculated: 933.5, Found: 935.5; Elemental analysis: Calculated (Found)%: C 72.00 (71.71) ; H 7.01 (6.60) ; N 1.50 (1.52).

I-20: A yellow solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2918, 2849, 1732, 1604, 1473, 1272, 1161 and 1071; ¹H NMR (400MHz, CDCl₃): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.7 Hz, 2H, Ar), 8.16 (d, J = 8.8 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J = 8.0 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22- 7.16 (m, 3H, Ar), 6.99 (d, J = 8.9 Hz, 2H, Ar), 6.91 (d, J = 2.1 Hz, 1H, Ar), 6.86- 6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.24 (m, 48H, 24 × CH₂) and 0.88 (t, J = 6.9 Hz, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₆₄H₈₁F₂NO₉, Calculated: 1045.6, Found: 1047.5; Elemental analysis: Calculated (Found)%: C 73.47(73.42) ; H 7.80 (7.59) ; N 1.34 (1.41).

<u>General procedure for 4-((3-(4-(alkoxy)benzoyloxy)benzoyloxy)phenylimino)</u> <u>methyl)phenyl4-(decyloxy)-2,3-difluorobenzoate (II-6 to II-10)</u>

A mixture of 4-(decyloxy)-2,3-difluorophenyl 4-formylbenzoate (**1b**) (0.2 m.mol, 1.0 equiv.), 4-((3-aminophenoxy)carbonyl)phenyl 4-(alkoxy)benzoate (**2a-h**) (0.2 m.mol, 1.0 equiv.), absolute ethanol (10 ml) and catalytic amount of acetic acid was refluxed until the white solid precipitated out (2 h). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was purified by repeated recrystallization with a mixture of absolute ethanol-dichloromethane (9:1) to get constant isotropic phase transition temperature. Yield: 85-91%.

II-6: A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2923, 1731, 1612, 1515, 1476, 1273, 1168 and 1072; ¹H NMR (400MHz, CDCl₃): δ 8.49 (s, 1H, CH=N), 8.29 (d, *J* = 8.7 Hz, 2H, Ar), 8.15 (d, *J* = 8.6 Hz, 2H, Ar), 7.98 (d, *J* = 8.6 Hz, 2H, Ar), 7.87-7.83 (m, 1H, Ar), 7.45 (t, *J* = 8.3 Hz, 1H, Ar), 7.38 (t, *J* = 6.2 Hz, 4H, Ar), 7.12- 7.10 (m, 3H, Ar), 6.97 (d, *J* = 8.9 Hz, 2H, Ar), 6.85- 6.80 (m, 1H, Ar), 4.13 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.86-1.83 (m, 4H, 2 × CH₂), 1.48-1.28 (m, 20H, 10 × CH₂) and 0.93-0.87 (m, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₀H₅₃ F₂NO₈, Calculated: 833.4, Found: 834.5; Elemental analysis: Calculated (Found)%: C 72.01 (72.38) ; H 6.41 (5.89) ; N 1.68 (1.62).

II-7: A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2919, 1729, 1603, 1475, 1293, 1130, and 1061; ¹H NMR (400MHz, CDCl₃): δ 8.50 (s, 1H, CH=N), 8.29 (d, *J* = 8.6 Hz, 2H, Ar), 8.16(d, *J* = 8.8 Hz, 2H, Ar), 7.98 (d, *J* = 8.64 Hz, 2H, Ar), 7.88-7.83 (m, 1H, Ar), 7.46 (t, *J* = 8.3 Hz, 1H, Ar), 7.37 (t, *J* = 8.0 Hz, 4H, Ar), 7.16- 7.10 (m, 3H, Ar), 6.97 (d, *J* = 8.76 Hz, 2H, Ar), 6.85- 6.81 (m, 1H, Ar), 4.14 (t, *J* = 6.6 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.6 Hz, 2H, 1 × OCH₂), 1.89-1.83 (m, 4H, 2 × CH₂), 1.48-1.28 (m, 22H, 11 × CH₂) and 0.92-0.87 (m, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₁H₅₅ F₂NO₈, Calculated: 847.4, Found: 848.6; Elemental analysis: Calculated (Found)%: C 72.24 (72.38) ; H 6.54 (6.14) ; N 1.65 (1.68).

II-8: A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2922, 1730, 1603, 1476, 1293, 1130, and 1060; ¹H NMR (400MHz, CDCl₃): δ 8.50 (s, 1H, CH=N), 8.29 (d, *J* = 8.68 Hz, 2H, Ar), 8.16(d, *J* = 8.9 Hz, 2H, Ar), 7.96 (d, *J* = 8.7 Hz, 2H, Ar), 7.87-7.83 (m, 1H, Ar), 7.47 (t, *J* = 8.3 Hz, 1H, Ar), 7.37 (t, *J* = 8.2 Hz, 4H, Ar), 7.16- 7.12 (m, 3H, Ar), 6.99 (d, *J* = 8.92 Hz, 2H, Ar), 6.85- 6.81 (m, 1H, Ar), 4.14 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.6 Hz, 2H, 1 × OCH₂), 1.85-1.83 (m, 4H, 2 × CH₂), 1.48-1.28 (m, 24H, 12 × CH₂) and 0.91-0.87 (m, 6H, 2 × CH₃); ¹³C NMR (100MHz, CDCl₃): 164.34, 164.26, 163.84, 161.56, 159.75, 155.45, 153.20, 153.12, 151.58, 133.88, 132.37, 131.76, 130.13, 129.87, 127.00, 126.86, 122.08, 121.01, 119.06, 118.78, 114.43, 114.11, 111.13, 111.05, 108.57, 70.04, 68.40, 31.83, 31.75, 29.46, 29.23, 29.16, 29.06, 28.92, 25.94, 25.75, 22.60 and 14.01; MS

 (FAB^+) : m/z for C₅₂H₅₇ F₂NO₈, Calculated: 861.4, Found: 862.6; Elemental analysis: Calculated (Found)%: C 72.45 (72.76); H 6.66 (6.44); N 1.62 (1.64).

II-9: A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2921, 1731, 1603, 1475, 1295, 1129, and 1061; ¹H NMR (400MHz, CDCl₃): δ 8.50 (s, 1H, CH=N), 8.29 (d, *J* = 8.76 Hz, 2H, Ar), 8.16(d, *J* = 8.9 Hz, 2H, Ar), 7.98 (d, *J* = 8.6 Hz, 2H, Ar), 7.88-7.83 (m, 1H, Ar), 7.46 (t, *J* = 8.3 Hz, 1H, Ar), 7.36 (t, *J* = 9 Hz, 4H, Ar), 7.16- 7.10 (m, 3H, Ar), 6.98 (d, *J* = 8.96 Hz, 2H, Ar), 6.85- 6.81 (m, 1H, Ar), 4.14 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.48-1.28 (m, 4H, 2 × CH₂), 1.90-1.79 (m, 26H, 13 × CH₂), and 0.90-0.87 (m, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₃H₅₉ F₂NO₈, Calculated: 875.4, Found: 877; Elemental analysis: Calculated (Found)%: C 72.66 (72.90) ; H 6.79 (6.59) ; N 1.60 (1.65).

II-10: A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2923, 1731, 1612, 1476, 1273, 1168 and 1072; ¹H NMR (400MHz, CDCl₃): δ 8.50 (s, 1H, CH=N), 8.29 (d, *J* = 8.6 Hz, 2H, Ar), 8.15 (d, *J* = 8.8 Hz, 2H, Ar), 7.98 (d, *J* = 8.6 Hz, 2H, Ar), 7.88-7.83 (m, 1H, Ar), 7.48 (t, *J* = 8.4 Hz, 1H, Ar), 7.37 (t, *J* = 8.0 Hz, 4H, Ar), 7.17- 7.10 (m, 3H, Ar), 6.98 (d, *J* = 8.8 Hz, 2H, Ar), 6.83- 6.79 (m, 1H, Ar), 4.14 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.94-1.76 (m, 4H, 2 × CH₂), 1.47-1.28 (m, 28H, 14 × CH₂), and 0.90-0.87 (m, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₄H₆₁ F₂NO₈, Calculated: 889.4, Found: 890.8; Elemental analysis: Calculated (Found)%: C 72.87 (72.97) ; H 6.91 (6.8) ; N 1.57 (1.63).

II-12: A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2923, 1731, 1612, 1476, 1273, 1168 and 1072; ¹H NMR (400MHz, CDCl₃): δ 8.50 (s, 1H, CH=N), 8.29 (d, *J* = 8.8 Hz, 2H, Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 7.98 (d, *J* = 8.7 Hz, 2H, Ar), 7.96-7.83 (m, 1H, Ar), 7.46 (t, *J* = 8.6 Hz, 1H, Ar), 7.36 (t, *J* = 9.0 Hz, 4H, Ar), 7.16- 7.10 (m, 3H, Ar), 6.99 (d, *J* = 8.9 Hz, 2H, Ar), 6.85- 6.80 (m, 1H, Ar), 4.14 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.94-1.76 (m, 4H, 2 × CH₂), 1.47-1.28 (m, 32H, 16 × CH₂), and 0.90-0.87 (m, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₆H₆₅ F₂NO₈, Calculated: 917.5,

Found: 918.9; Elemental analysis: Calculated (Found)%: C 73.26 (73.59); H 7.14 (6.74); N 1.53 (1.57).

II-20:

A white solid; IR (KBr Pellet) v_{max} in cm⁻¹ 2923, 1731, 1612, 1476, 1273, 1168 and 1072; ¹H NMR (400MHz, CDCl₃): δ 8.50 (s, 1H, CH=N), 8.29 (d, *J* = 8.7 Hz, 2H, Ar), 8.16 (d, *J* = 8.8 Hz, 2H, Ar), 7.98 (d, *J* = 8.6 Hz, 2H, Ar), 7.87-7.86 (m, 1H, Ar), 7.46 (t, *J* = 8.5 Hz, 1H, Ar), 7.36 (t, *J* = 9.0 Hz, 4H, Ar), 7.16- 7.10 (m, 3H, Ar), 6.98 (d, *J* = 8.9 Hz, 2H, Ar), 6.85- 6.83 (m, 1H, Ar), 4.14 (t, *J* = 6.6 Hz, 2H, 1 × OCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, 1 × OCH₂), 1.89-1.79 (m, 4H, 2 × CH₂), 1.48-1.25 (m, 48H, 24 × CH₂), and 0.88-0.87 (m, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₆₄H₈₁ F₂NO₈, Calculated: 1029.5, Found: 1030.6; Elemental analysis: Calculated (Found)%: C 74.61 (74.67) ; H 7.92 (7.74); N 1.36 (1.42).