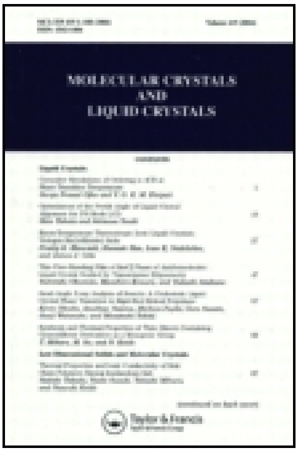

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Synthesis and Anisotropic Properties of Novel Asymmetric Diones Fused With 1,3-Oxazepine and Oxazepane Rings

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Synthesis and Anisotropic Properties of Novel Asymmetric Diones Fused With 1,3-Oxazepine and Oxazepane Rings

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Novel synthesis of heterocyclic liquid crystal compounds containing seven-membered 1,3-oxazepine-4,7-diones, 5,6-dihydro-1,3-oxazepane-4,7-diones, and 5,6-benzo[e][1,3]oxazepine-4,7-diones rings at para position has been carried out from the reaction of maleic, succinic, and phthalic anhydrides with N-(4-(tetradecyloxy)benzylidene) alkylamine. The various lengths of the even-parity alkyl chains C_nH_{2n+1}, *in which n ranges from 6 to 18, were employed in the present study. The molecular structures of these compounds were substantiated by Fourier transformed infrared and nuclear magnetic resonance along with elemental analysis. The correlation between the structures and the mesomorphic behaviors of N-(4-(tetradecyloxy)benzylidene)alkylamines and their derivatives was investigated. Present work shows that the formation of mesophases is strongly dependent on the type of core moiety. Although the imines possessing the alkyl chain* C_nH_{2n+1} ($n = 6$–14) *exhibit smectic A (SmA) phases, the nematogenic properties can only be observed in the series of 3,4-dihydrobenzo[e][1,3]oxazepine-1,5-diones.*

Keywords 5,6-Benzo[e][1,3]oxazepine-4,7-diones; 5,6-dihydro-1,3-oxazepane-4,7-diones; liquid crystal; N-(4-(tetradecyloxy)benzylidene)alkylamine; nematic; 1,3-oxazepine-4,7-diones; smectic A; synthesis

1. Introduction

It has well been claimed that the liquid crystalline behavior of an organic compound is dependent on its molecular architecture in which a slight change in its molecular geometry gives rise to a considerable change in its mesomorphic properties [1–5]. In general, the mesomorphic behavior of an organic compound can be varied by changing the linking, terminal, and central core systems [6]. In recent years, interest in mesogenic structures containing heterocyclic rings has increased remarkably owing to their abilities to exhibit mesogenic behavior either similar to or superior to the linear phenyl analogs [7–15].

The heterocyclic compounds are of great importance as core units in thermotropic liquid crystals due to their abilities to impart lateral and/or longitudinal dipoles. Moreover, the presence of heteroatoms (O, S, and N) could lead to significant changes in

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*Address correspondence to Guan-Yeow Yeap, Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia. Fax: 60-4-6574854. E-mail: gyyeap@usm.my; gyyeap_liqcryst_usm@yahoo.com the corresponding liquid crystalline phases and/or in the physical properties of the observed phases. Since most of the heteroatoms thus introduced are claimed to be more polarizable than carbon, therefore, a large dipole may eventually be introduced into a liquid crystal structure in comparison with the analogous phenyl-based mesogens [16–18]. The direction of the dipole moments of the core parts of the liquid crystal molecules is known to be important especially in determining the molecular alignment in mesophase [19]. This information propels us to consider the 1,3-oxazepine-diones, which possess seven-membered heterocyclic ring system. Since the modification of oxazepine core as liquid crystalline compounds was not well documented, therefore, we report the novel compounds of 3-alkyl-2-(4-(tetradecyloxy)phenyl)-1,3-oxazepine-4,7-dione, 3-alkyl-2-(4-(tetradecyloxy)phenyl)-5,6-dihydro-1,3-oxazepane-4,7-diones, and 3-alkyl-2-(4-(tetradecyloxy)phenyl)-5,6-benzo[e][1,3]oxazepine-4,7-diones. The physical properties of the title compounds were studied by Fourier transformed infrared (FT-IR) and high-resolution nuclear magnetic resonance (NMR) (^{1}H and ^{13}C NMR). The phase transition temperatures and enthalpy values of the title compounds were measured by differential scanning calorimetry (DSC) and the textures of the mesophases were studied by using a polarizing optical microscope (POM).

2. Experimental

2.1. Synthesis

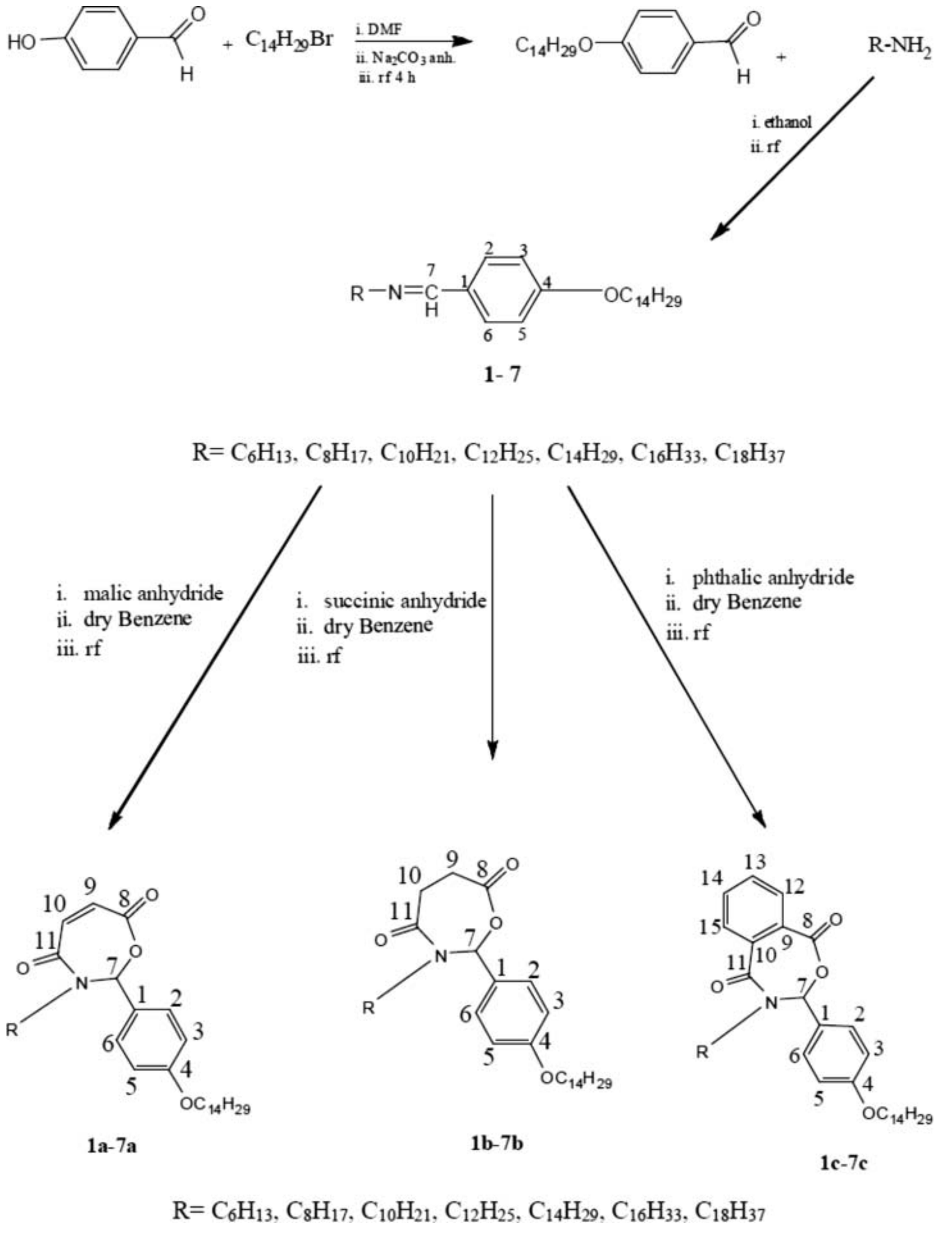
The synthetic routes toward formation of all the title compounds are depicted in Scheme 1. The synthesis of each compound in all the series was identical.

2.1.1. Synthesis of 4-(Tetradecyloxy)benzaldehyde. A mixture containing 0.1 mol of 4-hydroxybenzeldehyde, 0.25 mol anhydrous sodium carbonate, and 0.1 mol 1-bromotetradecane in 50 mL of DMF was allowed to heat for 4 h at 150°C under continuous stirring as documented by Catanescu et al. [20]. The resulting mixture was then poured into an ice water bath (approximately 5°C) whereupon a precipitate formed. The precipitate was filtered and washed once with KOH and water, dried, and finally recrystallized from ethanol.

*2.1.2. General Procedure for the Synthesis of N-(4-(Tetradecyloxy)-Benzylidene) alkylamine (**1–7**).* The imines were synthesized by the same method. The synthetic method will be described on the basis of compound **1**.

A mixture containing equimolar amounts of hexylamine and 4-(tetradecyloxy) benzaldehyde in absolute ethanol was refluxed for 14 h. The reaction mixture was allowed to cool to 0°C overnight. It was filtered and washed with 2% HCl and cold water before being dried at room temperature. The solid thus obtained was recrystallized twice from absolute ethanol. The analytical data, FT-IR, and ^{1}H and ^{13}C NMR for compounds **1–7** are summarized as follows.

1: Yield 81% m.p. 60°C–61°C. Anal.: found for $C_{27}H_{47}NO$ (%): C 80.69, H 11.67, N 3.58. Calc. (%) C 80.74, H 11.79, N 3.49. IR: υ_{max}(KBr) (cm^{-1}) 3060, 2991, 2960, 1638, 1600, 1593, 1250; ^{1}H NMR δ ($CDCl_3$): 8.02 (s, H7), 7.54 (d, J = 8.8 Hz, H2 and H6), 6.93 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C_4-OCH_2), 3.58 (t, N-CH_2), 1.85–1.23 (m, $OCH_2{-}((CH_2)_2{-}CH_2)_{13}$) and $NCH_2{-}(CH_2{-}CH_n)$, 0.91 (t, CH_3); ^{13}C NMR δ ($CDCl_3$): 162.07 (C=N), 158.11 (Ar—C—O), 132.05–116.11 (Ar-C), 71.03 (O—CH_2),



Scheme 1. The reaction scheme for intermediates and title compounds with numbering atom.

60.83 ($N{-}CH_2$), 32.88–21.56 ($OCH_2{-}((CH_2)_2{-}CH_2)_{13}$) and $NCH_2{-}(CH_2{-}CH_n)$, 14.93 (CH_3).

2: Yield 79% m.p. 64°C–65°C. Anal.: found for $C_{29}H_{51}NO$ (%): C 81.08, H 11.84, N, 3.15. Calc. (%) C 81.05, H 11.96, N 3.26. IR: υ_{max}(KBr) (cm^{-1}): 3044, 2990, 2958, 1640, 1598, 1581, 1258; ^1H NMR δ ($CDCl_3$): 8.02 (s, H7), 7.53 (d, $J = 8.8$ Hz, H2 and H6), 6.94 (d, $J = 8.6$ Hz, H3 and H5), 4.03 (t, $C_4{-}OCH_2$), 3.60 (t, $N{-}CH_2$), 1.86–1.22 (m, $OCH_2{-}((CH_2)_2{-}CH_2)_{13}$) and $NCH_2{-}(CH_2{-}CH_n)$, 0.90 (t, CH_3); ^{13}C NMR δ ($CDCl_3$): 162.02 (C=N), 158.15 (Ar—C—O), 132.04–116.13 (Ar—C), 71.07 (O—CH_2), 60.75 (N—CH_2), 32.85–21.57 (OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 14.92 (CH_3).

3: Yield 77% m.p. 68°C–69°C. Anal.: found for $C_{31}H_{55}NO$ (%): C 81.29, H 12.07, N 3.04. Calc. (%) C 81.34, H 12.11, N 3.06. IR: υ_{max}(KBr) (cm^{-1}): 3010, 2986, 2938, 1629, 1581, 1510, 1249; ^{1}H NMR δ ($CDCl_3$): 8.04 (s, H7), 7.55 (d, J = 8.9 Hz, H2 and H6), 6.94 (d, J = 8.7 Hz, H3 and H5), 4.05 (t, C_4—OCH_2), 3.57 (t, N—CH_2), 1.86–1.21 (m, OCH_2—((CH_2)$_2$-CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 0.88 (t, CH_3); ^{13}C NMR δ ($CDCl_3$): 161.95 (C=N), 158.20 (Ar—C—O), 132.09–116.15 (Ar—C), 71.09 (O—CH_2), 61.01 (N—CH_2), 32.86–21.60 (OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 14.93 (CH_3).

4: Yield 69% m.p. 74°C–75°C. Anal.: found for $C_{33}H_{59}NO$ (%): C 81.69, H 12.17, N 2.81. Calc. (%) C 81.58, H 12.24, N 2.88. IR: υ_{max}(KBr) (cm^{-1}): 3030, 2992, 2951, 1640, 1594, 1522, 1250; ^{1}H NMR δ (ppm) ($CDCl_3$): 8.03 (s, H7), 7.54 (d, J = 8.8 Hz, H2 and H6), 6.93 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C_4—OCH_2), 3.58 (t, N—CH_2), 1.87–1.23 (m, OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 0.89 (t, CH_3); ^{13}C NMR (ppm) δ ($CDCl_3$): 161.87 (C=N), 158.28 (Ar—C—O), 132.11–116.20 (Ar—C), 71.12 (O—CH_2), 60.92 (N—$CH_{2),}$ 32.85–21.58 (OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 14.93 (CH_3).

5: Yield 61% m.p. 78°C–79°C. Anal.: found for $C_{35}H_{63}NO$ (%): C 81.91, H 12.46, N 2.61. Calc (%) C 81.80, H 12.36, N 2.73. IR: υ_{max}(KBr) (cm^{-1}): 3061, 2988, 2960, 1635, 1600, 1582, 1255; ^{1}HNMR δ (ppm) ($CDCl_3$): 8.06 (s, H7), 7.54 (d, J = 8.8 Hz, H2 and H6), 6.95 (d, J = 8.6 Hz, H3 and H5), 4.05 (t, C_4—OCH_2), 3.61 (t, N—CH_2), 1.88–1.25 (m, OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 0.91 (t, CH_3); ^{13}C NMR δ (ppm) ($CDCl_3$): 161.95 (C=N), 158.29 (Ar—C—O), 132.05–116.14 (Ar—C), 71.04 (O—CH_2), 61.21 (N—CH_2), 32.86–21.60 (OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 14.95 (CH_3).

6: Yield 58% m.p. 77°C–78°C. Anal.: found for $C_{37}H_{67}NO$ (%): C 82.03, H 12.48, N 2.60. Calc (%) C 82.00, H 12.46, N 2.58. IR: υ_{max}(KBr) (cm^{-1}): 3056, 2985, 2953, 1631, 1588, 1542, 1248; ^{1}H NMR δ (ppm) ($CDCl_3$): 8.05 (s, H7), 7.52 (d, J = 8.8 Hz, H2 and H6), 6.94 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C_4—OCH_2), 3.60 (t, N—CH_2), 1.89–1.25 (m, OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 0.90 (t, CH_3); ^{13}C NMR δ (ppm) ($CDCl_3$): 162.11 (C=N), 158.28 (Ar—C—O), 132.04–116.15 (Ar-C), 71.03 (O—CH_2), 61.16 (N—CH_2), 32.12–21.60 (OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 14.93 (CH_3).

7: Yield 61% m.p. 82°C–83°C. Anal.: found for $C_{39}H_{71}NO$ (%): C 82.23, H 12.50, N 2.54. Calc (%) C 82.18, H, 12.56, N 2.46. IR: υ_{max}(KBr) (cm^{-1}): 3017, 2990, 2959, 1638, 1591, 1572, 1250. ^{1}HNMR δ (ppm) ($CDCl_3$): 8.06 (s, H7), 7.55 (d, J = 8.8 Hz, H2 and H6), 6.95 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C_4—OCH_2), 3.61 (t, N—CH_2), 1.88–1.24 (m, OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 0.91 (t, CH_3); ^{13}C NMR δ (ppm) ($CDCl_3$): 162.05 (C=N), 158.29 (Ar—C—O), 132.05–116.18 (Ar-C), 71.08 (O—CH_2), 61.76 (N—CH_2), 31.98–21.59 (OCH_2—((CH_2)$_2$—CH_2)$_{13}$) and NCH_2—(CH_2—CH_n), 14.93 (CH_3).

2.1.3. Synthesis of Compounds ***1a–7a, 1b–7b,*** *and* ***1c–7c***. The title compounds were synthesized by the same method. The synthetic method will be described on the basis of compound **1a**.

A solution containing maleic anhydride (0.01 mol) in dry benzene (10 mL) was added dropwise to a hot dry benzene solution (20 mL) containing compound **1** (0.01 mol) in a round bottom flask equipped with a double-surface condenser fitted with calcium chloride guard tube. The reaction mixture was refluxed for 4 h. The reaction was monitored by thin layer chromatography (TLC) and the solvent was distilled off in vacuo. The solid product thus obtained was filtered and washed with distilled cool water. Resulting solid was recrystallized twice from 1,4-dioxane. The analytical data, FT-IR, and ^{1}H and ^{13}C NMR for compounds **1a–7b**, **1b–7b**, and **1c–7c** are summarized as follows.

1a: Yield 61% m.p. 78°C–79°C. Anal.: found for $C_{31}H_{49}NO_4$ (%): C 74.61, H 9.85, N 2.74. Calc. (%) C 74.51, H 9.88, N 2.80. IR: υ_{max}(KBr) (cm^{-1}): 2960, 2928, 2864, 2830, 1730, 1600, 1570, 1246. ^{1}HNMR δ (ppm) [dimethyl sulfoxide (DMSO)]: 9.85 (s, H7), 7.83 (d, $J = 8.1$ Hz, H2 and H6), 7.11 (d, $J = 8.3$ Hz, H3 and H5), 6.41 (d, $J = 12.6$ Hz, H10), 6.22 (d, $J = 12.4$ Hz, H9), 4.05 (t, $C_4{-}OCH_2$), 3.15 (t, $N{-}CH_2$), 1.75–1.24 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}$* and $NCH_2{-}$ $(CH_2{-}CH_n)^+$), 0.87 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.29 (C11), 166.05 (C8), 164.37 (C4), 132.62 (C9), 132.57 (C2 and C6), 130.87 (C10), 115.80 (C3 and C5), 90.06 (C7), 68.89 ($O{-}CH_2$), 39.70 ($N{-}CH_2$), 14.66 (CH_3).

2a: Yield 62% m.p. 81°C–82°C. Anal.: found for $C_{33}H_{53}NO_4$ (%): C 75.07, H 10.37, N 2.71. Calc. (%) C 75.10, H 10.12, N 2.65. IR: υ_{max}(KBr) (cm^{-1}): 2958, 2924, 2859, 2807, 1728, 1604, 1582, 1244. ^{1}HNMR δ (ppm) (DMSO): 9.85 (s, H7), 7.82 (d, $J = 8.1$ Hz, H2 and H6), 7.10 (d, $J = 8.3$ Hz, H3 and H5), 6.40 (d, $J = 12.5$ Hz, H10), 6.23 (d, $J = 12.5$, Hz H9), 4.04 (t, $C_4{-}OCH_2$), 3.15 (t, $N{-}CH_2$), 1.74–1.23 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}$* and $NCH_2{-}$ $(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.24 (C11), 166.04 (C8), 164.37 (C4), 132.62 (C9), 132.56 (C2 and C6), 130.90 (C10), 115.79 (C3 and C5), 90.12 (C7), 68.90 ($O{-}CH_2$), 39.70 ($N{-}CH_2$), 14.61 (CH_3).

3a: Yield 66% m.p. 84°C–85°C. Anal.: found for $C_{35}H_{57}NO_4$ (%): C 75.72, H 10.59, N 2.62. Calc. (%) C 75.63, H 10.34, N 2.52. IR: υ_{max}(KBr) (cm^{-1}): 2960, 2935, 2863, 2809, 1698, 1597, 1581, 1250. ^{1}H NMR δ (ppm) (DMSO): 9.87 (s, H7), 7.85 (d, $J = 8.2$ Hz, H2 and H6), 7.12 (d, $J = 8.3$ Hz, H3 and H5) 6.40 (d, $J = 12.5$ Hz, H10), 6.26 (d, $J = 12.5$ Hz, H9), 4.04 (t, $C_4{-}OCH_2$), 3.16 (t, $N{-}CH_2$), 1.76–1.23 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}$* and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.22 (C11), 166.06 (C8), 164.50 (C4), 132.64 (C9), 132.59 (C2 and C6), 130.88 (C10), 115.71 (C3 and C5), 90.06 (C7), 68.88 (O-CH_2), 39.74 (N-CH_2), 14.62 (CH_3).

4a: Yield 64% m.p. 90°C–91°C. Anal.: found for $C_{37}H_{61}NO_4$ (%): C 76.15, H 10.51, N, 2.60. Calc. (%) C 76.11, H 10.53, N 2.40. IR: υ_{max}(KBr) (cm^{-1}): 2950, 2919, 2854, 2810, 1685, 1604, 1582, 1252. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.82 (d, $J = 8.1$ Hz, H2 and H6), 7.11 (d, $J = 8.3$ Hz, H3 and H5), 6.42 (d, $J = 12.5$ Hz, H10), 6.21 (d, $J = 12.4$ Hz, H9), 4.03 (t, C_4-OCH_2), 3.14 (t, $N{-}CH_2$), 1.75–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}$* and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.85 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.25 (C11), 166.05 (C8), 164.32 (C4), 132.64 (C9), 132.57 (C2 and C6), 130.89 (C10), 115.90 (C3 and C5), 90.05 (C7), 68.89 ($O{-}CH_2$), 39.73 ($N{-}CH_2$), 14.59 (CH_3).

5a: Yield 63% m.p. 98°C–99°C. Anal.: found for $C_{39}H_{65}NO_4$ (%): C 76.62, H 10.72, N 2.47. Calc. (%) C 76.55, H 10.71, N 2.29. IR: υ_{max}(KBr) (cm^{-1}): 2958, 2917, 2849, 2798, 1709, 1602, 1583, 1250. ^{1}HNMR δ (ppm) (DMSO): 9.84 (s, H7), 7.81 (d, $J = 8.1$ Hz, H2 and H6), 7.12 (d, $J = 8.4$ Hz, H3 and H5), 6.39 (d, $J = 12.5$ Hz, H10), 6.20 (d, $J = 12.3$ Hz, H9), 4.04 (t, $C_4{-}OCH_2$), 3.15 (t, $N{-}CH_2$), 1.73–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}$* and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.23 (C11), 166.09 (C8), 164.61 (C4), 132.65 (C9), 132.55 (C2 and C6), 130.88 (C10), 116.05 (C3 and C5), 90.00 (C7), 68.90 (O-CH_2), 39.73 ($N{-}CH_2$), 14.65 (CH_3).

6a: Yield 58% m.p. 114°C–115°C. Anal.: found for $C_{41}H_{69}NO_4$ (%): C 76.84, H 10.82, N 2.13. Calc. (%) C 76.94, H 10.87, N 2.19. IR: υ_{max}(KBr) (cm^{-1}): 2952, 2916, 2860, 2829, 1710, 1601, 1581, 1254. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.80 (d, $J = 8.1$ Hz, H2 and H6), 7.10 (d, $J = 8.3$ Hz, H3 and H5), 6.40 (d, $J = 12.5$ Hz, H10), 6.23 (d, $J = 12.4$ Hz, H9), 4.05 (t, C_4-OCH_2), 3.15 (t, N-CH_2), 1.72–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}$ $(CH_2{-}CH_n)^+$), 0.85 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.24 (C11), 166.10 (C8), 164.41 (C4), 132.66 (C9), 132.56 (C2 and C6), 130.90 (C10), 116.09 (C3 and C5), 90.05 (C7), 68.92 (O$-$$CH_2$), 39.74 (N$-$$CH_2$), 14.68 ($CH_3$).

7a: Yield 51% m.p. 119°C–120°C. Anal: found for $C_{43}H_{73}NO_4$ (%): C 77.24, H 11.10, N 2.18. Calc (%) C 77.31, H, 11.01, N 2.10. IR: υ_{max}(KBr) (cm^{-1}): 2956, 2917, 2864, 2831, 1732, 1600, 1582, 1251. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.85 (d, $J = 8.1$ Hz, H2 and H6), 7.43 (d, $J = 8.5$ Hz, H3 and H5), 6.41 (d, $J = 12.6$ Hz, H10), 6.24 (d, $J = 12.5$ Hz, H9), 4.05 (t, $C_4{-}OCH_2$), 3.16 (t, N$-$$CH_2$), 1.71–1.21 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}$ $(CH_2{-}CH_n)^+$), 0.85 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 166.25 (C11), 166.11 (C8), 164.61 (C4), 132.64 (C9), 132.57 (C2 and C6), 130.89 (C10), 115.84 (C3 and C5), 90.06 (C7), 68.90 (O$-$$CH_2$), 39.73 (N$-$$CH_2$), 14.68 ($CH_3$).

1b: Yield 64% m.p. 85°C–86°C. Anal.: found for $C_{31}H_{51}NO_4$ (%): C 74.17, H 10.22, N 2.81. Calc. (%) C 74.21, H 10.25, N 2.79. IR: υ_{max}(KBr) (cm^{-1}): 2959, 2914, 2860, 2829, 1718, 1603, 1580, 1249. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.86 (d, $J = 8.6$ Hz, H2 and H6), 7.12 (d, $J = 8.6$ Hz, H3 and H5), 4.06 (t, $C_4{-}OCH_2$), 3.01 (t, N$-$$CH_2$), 2.41 (t, $J = 7.1$ Hz, H10), 2.27 (t, $J = 7.0$ Hz, H9), 1.70–1.21 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}$ $(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.52 (C11), 171.12 (C8), 164.32 (C4), 132.76 (C2 and C6), 115.72 (C3 and C5), 90.10 (C7), 68.88 (O$-$$CH_2$), 39.35 (N$-$$CH_2$), 29.33 (C9), 27.81 (C10), 14.70 (CH_3).

2b: Yield 67% m.p. 91°C–92°C. Anal.: found for $C_{33}H_{55}NO_4$ (%): C 74.90, H 10.59, N 2.72. Calc. (%) C 74.81, H 10.46, N 2.64. IR: υ_{max}(KBr) (cm^{-1}): 2965, 2925, 2849, 2801, 1720, 1605, 1583, 1250. ^{1}H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.87 (d, $J = 8.6$ Hz, H2 and H6), 7.13 (d, $J = 8.6$ Hz, H3 and H5), 4.07 (t, $C_4{-}OCH_2$), 3.01 (t, N$-$$CH_2$), 2.40 (t, $J = 7.1$ Hz, H10), 2.27 (t, $J = 7.0$ Hz, H9), 1.71–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.87 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.50 (C11), 171.11 (C8), 164.33 (C4), 132.77 (C2 and C6), 115.71 (C3 and C5), 90.11 (C7), 68.89 (O$-$$CH_2$), 39.33 (N$-$$CH_2$), 29.32 (C9), 27.82 (C10), 14.72 (CH_3).

3b: Yield 63% m.p. 110°C–111°C. Anal.: found for $C_{35}H_{59}NO_4$ (%): C 75.28, H 10.50, N 2.48. Calc. (%) C 75.36, H 10.66, N 2.51. IR: υ_{max}(KBr) (cm^{-1}): 2979, 2934, 2862, 2830, 1721, 1603, 1580, 1255. ^{1}H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.86 (d, $J = 8.6$ Hz, H2 and H6), 7.11 (d, $J = 8.6$ Hz, H3 and H5), 4.07 (t, $C_4{-}OCH_2$), 3.02 (t, N$-$$CH_2$), 1.71–1.23 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 2.40 (t, $J = 7.1$ Hz, H10), 2.28 (t, $J = 7.0$ Hz, H9), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.52 (C11), 171.12 (C8), 164.34 (C4), 132.75 (C2 and C6), 115.70 (C3 and C5), 90.10 (C7), 68.90 (O$-$$CH_2$), 39.36 (N$-$$CH_2$), 29.32 (C9), 27.80 (C10), 14.72 (CH_3).

4b: Yield 56% m.p. 114°C–115°C. Anal.: found for $C_{37}H_{63}NO_4$ (%): C 75.90, H 10.80, N 2.30. Calc. (%) C 75.85, H 10.84, N 2.39. IR: υ_{max}(KBr) (cm^{-1}): 2959, 2914, 2860, 2829, 1718, 1601, 1587, 1250. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.88 (d, $J = 8.6$ Hz, H2 and H6), 7.12 (d, $J = 8.6$ Hz, H3 and H5), 4.06 (t, $C_4{-}OCH_2$), 3.01 (t, N$-$$CH_2$), 2.41 (t, $J = 7.1$ Hz, H10), 2.27 (t, $J = 7.0$ Hz, H9), 1.72–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.51 (C11), 171.11 (C8), 164.32 (C4), 115.72 (C3 and C5), 132.77 (C2 and C6), 90.12 (C7), 68.91 (O$-$$CH_2$), 39.33 (N$-$$CH_2$), 29.31 (C9), 27.82 (C10), 14.73 (CH_3).

5b: Yield 55% m.p. 120°C–121°C. Anal.: found for $C_{39}H_{67}NO_4$ (%): C 76.28, H 11.15, N 2.19. Calc. (%) C 76.30, H 11.00, N 2.28. IR: υ_{max}(KBr) (cm^{-1}): 2959, 2914, 2860, 2829, 1725, 1600, 1582, 1252. ^{1}H NMR δ (ppm) (DMSO): 9.84 (s, H7), 7.85 (d, J = 8.6 Hz, H2 and H6), 7.10 (d, J = 8.6 Hz, H3 and H5), 4.06 (t, $C_4{-}OCH_2$), 3.02 (t, $N{-}CH_2$), 2.42 (t, J = 7.1 Hz, H10), 2.26 (t, J = 7.0 Hz, H9), 1.71–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}$ $(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.50 (C11), 171.13 (C8), 164.33 (C4), 132.76 (C2 and C6), 115.71 (C3 and C5), 90.11 (C7), 68.92 ($O{-}CH_2$), 39.37 ($N{-}CH_2$), 29.33 (C9), 27.82 (C10), 14.75 (CH_3).

6b: Yield 55% m.p. 123°C–124°C. Anal.: found for $C_{41}H_{71}NO_4$ (%): C 76.66, H 11.19, N 2.30. Calc. (%) C 76.70, H 11.15, N 2.18. IR: υ_{max}(KBr) (cm^{-1}): 2961, 2922, 2852, 2817, 1730, 1603, 1584, 1252. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.86 (d, J = 8.6 Hz, H2 and H6), 7.11 (d, J = 8.6 Hz, H3 and H5), 4.05 (t, $C_4{-}OCH_2$), 3.00 (t, $N{-}CH_2$), 2.41 (t, J = 7.1 Hz H10), 2.25 (t, J = 7.0 Hz, H9), 1.72–1.23 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.52 (C11), 171.12 (C8), 164.34 (C4), 132.76 (C2 and C6), 115.72 (C3 and C5), 90.12 (C7), 68.90 ($O{-}CH_2$), 39.36 ($N{-}CH_2$), 29.33 (C9), 27.80 (C10), 14.78 (CH_3).

7b: Yield 48% m.p. 130°C–131°C. Anal.: found for $C_{43}H_{75}NO_4$ (%): C 77.36, H 11.07, N 2.38. Calc. (%) C 77.08, H 11.28, N 2.09. IR: υ_{max}(KBr) (cm^{-1}): 2953, 2915, 2859, 2824, 1719, 1602, 1579, 1254. ^{1}H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.88 (d, J = 8.6 Hz, H2 and H6), 7.13 (d, J = 8.6 Hz, H3 and H5 4.06 (t, $C_4{-}OCH_2$), 3.01 (t, $N{-}CH_2$),), 2.41 (t, J = 7.1 Hz, H10), 2.26 (t, J = 7.0 Hz, H9), 1.71–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.85 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 174.52 (C11), 171.11 (C8), 164.34 (C4), 132.77 (C2 and C6), 115.72 (C3 and C5), 90.12 (C7), 68.90 ($O{-}CH_2$), 39.36 ($N{-}CH_2$), 29.34 (C9), 27.81 (C10), 14.79 (CH_3).

1c: Yield 51% m.p. 85°C–86°C. Anal.: found for $C_{35}H_{51}NO_4$ (%): C 76.52, H 9.28, N 2.60. Calc. (%) C 76.46, H 9.35, N, 2.55. IR: υ_{max}(KBr) (cm^{-1}): 2961, 2930, 2853, 2802, 1704, 1607, 1582, 1262. ^{1}H NMR δ (ppm) (DMSO): 9.84 (s, H7), 7.84 (d, J = 7.5 Hz, H12), 7.74 (d, J = 7.7 Hz, H15), 7.51 (t, J = 7.2 Hz, H13), 7.47 (t, J = 7.4 Hz, H14), 7.35 (d, J = 8.3 Hz, H2 and H6), 7.09 (d, J = 8.2 Hz, H3 and H5), 4.06 (t, $C_4{-}OCH_2$), 3.14 (t, $N{-}CH_2$), 1.74–1.22 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.85 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 168.84 (C11), 167.45 (C8), 164.14 (C4), 135.22 (C14), 129.97 (C12), 128.41 (C13), 125.45 (C2 and C6), 122.35 (C15), 115.00 (C3 and C5), 89.98 (C7), 68.03 ($O{-}CH_2$), 39.03 ($N{-}CH_2$), 14.56 (CH_3).

2c: Yield 50% m.p. 126°C–127°C. Anal.: found for $C_{37}H_{55}NO_4$ (%): C 77.98, H 9.48, N 2.34. Calc. (%) C 77.91, H 9.59, N 2.42. IR: υ_{max}(KBr) (cm^{-1}): 2948, 2924, 2854, 2831, 1700, 1605, 1580, 1261. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.85 (d, J = 7.5 Hz, H12), 7.74 (d, J = 7.7 Hz, H15), 7.50 (t, J = 7.2 Hz, H13), 7.48 (t, J = 7.4 Hz, H14), 7.36 (d, J = 8.3 Hz, H2 and H6), 7.10 (d, J = 8.2 Hz, H3 and H5), 4.06 (t, $C_4{-}OCH_2$), 3.15 (t, $N{-}CH_2$), 1.74–1.21 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.86 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 168.85 (C11), 167.44 (C8), 163.12 (C4), 135.23 (C14), 129.97 (C12), 128.40 (C13), 125.44 (C2 and C6), 122.34 (C15), 115.01 (C3 and C5), 89.97 (C7), 68.05 ($O{-}CH_2$), 39.05 ($N{-}CH_2$), 14.55 (CH_3).

3c: Yield 43% m.p. 125°C–126°C. Anal.: found for $C_{39}H_{59}NO_4$ (%): C 77.40, H 9.71, N 2.22. Calc. (%) C 77.31, H 9.82, N 2.31. IR: υ_{max}(KBr) (cm^{-1}): 2950, 2918, 2857, 2821, 1706, 1600, 1577, 1259. ^{1}H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.86 (d, J = 7.6 Hz, H12), 7.75 (d, J = 7.7 Hz, H15), 7.52 (t, J = 7.2 Hz, H13), 7.49 (t, J = 7.4 Hz, H14), 7.39 (d, J = 8.3 Hz, H2 and H6), 7.11 (d, J = 8.2 Hz, H3 and H5), 4.07 (t, $C_4{-}OCH_2$), 3.15 (t, $N{-}CH_2$), 1.73–1.23 ($OCH_2{-}(CH_2)_2{-}(CH_2)_{13}{}^*$ and $NCH_2{-}(CH_2{-}CH_n)^+$), 0.85 (t, CH_3); ^{13}C NMR δ (ppm) (DMSO): 168.85 (C11), 167.45 (C8), 163.22 (C4), 135.22

(C14), 129.98 (C12), 128.44 (C13), 125.46 (C2 and C6), 122.32 (C15), 115.04 (C3 and C5), 89.98 (C7), 68.05 (O—CH$_2$), 39.04 (N—CH$_2$), 14.55 (CH$_3$).

4c: Yield 47% m.p. 132°C–133°C. Anal.: found for $C_{41}H_{63}NO_4$ (%): C 77.60, H 10.12, N 2.30. Calc. (%) C 77.68, H 10.02, N 2.21. IR: υ_{max}(KBr) (cm^{-1}): 2952, 2922, 2864, 2811, 1727, 1601, 1583, 1260. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.85 (d, J = 7.5 Hz, H12), 7.74 (d, J = 7.7 Hz, H15), 7.52 (t, J = 7.2 Hz, H13), 7.48 (t, J = 7.4 Hz, H14), 7.39 (d, J = 8.3 Hz, H2 and H6), 7.11 (d, J = 8.2 Hz, H3 and H5), 4.08 (t, C$_4$—OCH$_2$), 3.15 (t, N—CH$_2$), 1.72–1.22 (OCH$_2$—(CH$_2$)$_2$—(CH$_2$)$_{13}$* and NCH$_2$—(CH$_2$—CH$_n$)$^+$), 0.87 (t, CH$_3$); ^{13}C NMR δ (ppm) (DMSO): 168.84 (C11), 167.43 (C8), 163.13 (C4), 135.24 (C14), 129.99 (C12), 128.43 (C13), 125.45 (C2 and C6), 122.36 (C15), 115.03 (C3 and C5), 89.99 (C7), 68.08 (O—CH$_2$), 39.04 (N—CH$_2$), 14.56 (CH$_3$).

5c: Yield 44% m.p. 128°C–129°C. Anal.: found for $C_{43}H_{67}NO_4$ (%): C 78.14, H 10.25, N 2.08. Calc. (%) C 78.02, H 10.20, N 2.12. IR: υ_{max}(KBr) (cm^{-1}): 2956, 2925, 2848, 2804, 1725, 1604, 1579, 1258. ^{1}H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.88 (d, J = 7.6 Hz H12), 7.74 (d, J = 7.7 Hz, H15), 7.52 (t, J = 7.2 Hz, H13), 7.49 (t, J = 7.4 Hz, H14), 7.40 (d, J = 8.4 Hz, H2 and H6), 7.14 (d, J = 8.2 Hz, H3 and H5), 4.09 (t, C$_4$—OCH$_2$), 3.17 (t, N—CH$_2$), 1.74–1.23 (OCH$_2$—(CH$_2$)$_2$—(CH$_2$)$_{13}$* and NCH$_2$—(CH$_2$—CH$_n$)$^+$), 0.88 (t, CH$_3$); ^{13}C NMR δ (ppm) (DMSO): 168.84 (C11), 167.44 (C8), 163.12 (C4), 135.23 (C14), 129.98 (C12), 128.44 (C13), 125.44 (C2 and C6), 122.36 (C15), 115.07 (C3 and C5), 90.08 (C7), 68.08 (O—CH$_2$), 39.05 (N—CH$_2$), 14.57 (CH$_3$).

6c: Yield 57% m.p. 129°C–130°C. Anal.: found for $C_{45}H_{71}NO_4$ (%): C 78.58, H 10.63, N 2.29. Calc. (%) C 78.33, H 10.37, N 2.03. IR: υ_{max}(KBr) (cm^{-1}): 2957, 2921, 2855, 2813, 1728, 1600, 1581, 1260. ^{1}H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.86 (d, J = 7.6 Hz, H12), 7.73 (d, J = 7.7 Hz, H15), 7.53 (t, J = 7.2 Hz, H13), 7.48 (t, J = 7.4 Hz, H14), 7.38 (d, J = 8.3 Hz, H2 and H6), 7.11 (d, J = 8.2 Hz, H3 and H5), 4.08 (t, C$_4$—OCH$_2$), 3.16 (t, N—CH$_2$), 1.73–1.23 (OCH$_2$—(CH$_2$)$_2$—(CH$_2$)$_{13}$* and NCH$_2$—(CH$_2$—CH$_n$)$^+$), 0.86 (t, CH$_3$); ^{13}C NMR δ (ppm) (DMSO): 168.95 (C11), 167.45 (C8), 163.11 (C4), 135.22 (C14), 129.98 (C12), 128.45 (C13), 125.46 (C2 and C6), 123.37 (C15), 115.07 (C3 and C5), 90.08 (C7), 68.06 (O—CH$_2$), 39.08 (N—CH$_2$), 14.56 (CH$_3$).

7c: Yield 51% m.p. 148°C–149°C. Anal.: found for $C_{47}H_{75}NO_4$ (%): C 78.56, H 10.60, N 1.98. Calc. (%) C 78.61, H 10.53, N 1.95. IR: υ_{max}(KBr) (cm^{-1}): 2961, 2929, 2849, 2816, 1710, 1603, 1580, 1261. ^{1}H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.87 (d, J = 7.5 Hz, H12), 7.75 (d, J = 7.7 Hz, H15), 7.50 (t, J = 7.2 Hz, H13), 7.49 (t, J = 7.4 Hz, H14), 7.40 (d, J = 8.3 Hz, H2 and H6), 7.15 (d, J = 8.2 Hz, H3 and H5), 4.08 (t, C$_4$—OCH$_2$), 3.16 (t, N—CH$_2$), 1.73–1.24 (OCH$_2$—(CH$_2$)$_2$—(CH$_2$)$_{13}$* and NCH$_2$—(CH$_2$—CH$_n$)$^+$), 0.87 (t, CH$_3$); ^{13}C NMR δ (ppm) (DMSO): 169.16 (C11), 167.44 (C8), 163.12 (C4), 135.24 (C14), 129.97 (C12), 128.45 (C13), 125.45 (C2 and C6), 123.37 (C15), 115.08 (C3 and C5), 90.07 (C7), 68.07 (O—CH$_2$), 39.11 (N—CH$_2$), 14.57 (CH$_3$).

2.2. Reagents and Techniques

Hexylamine, octylamine, decylamine, dodecylamine, 4-hydroxybenzeldehyde, and anhydrides (maleic, succinic, and phthalic) were obtained from Aldrich. While tetradecylamine, hexadecylamine, and octadecylamine were purchased from Acros, 1-bromotetradecane was obtained from Merck. They were used without further purification.

The elemental (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. Melting points were recorded by Gallenkamp digital melting point. The measurements were carried out through the scanning at room temperature. FT-IR measurements on intermediates and title compounds were performed on samples in the

KBr pellets and the spectra were recorded in the range of 4000–400 cm^{-1} using a Perkin Elmer 2000-FT-IR spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (for **1–7**) and DMSO (for **1a–7b**, **1b–7b**, and **1c–7c**) at 298 K on a Bruker 400 MHz Ultrashied FT-NMR spectrometer equipped with a 5-mm BBI inverse gradient probe. Chemicals shifts were referenced to internal tetramethylsilane (TMS). The concentration of solute molecules was 50 mg in 1.0 mL DMSO. Standard Bruker pulse programs [21] were used throughout the entire experiment.

The phase transition temperatures and enthalpy values were measured by Perkin Elmer Pyris 1 DSC at heating and cooling rates of 5°C min^{-1}, respectively.

The textures were observed using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Mettler FP5 hot stage and TMS94 temperature controller. The samples studied by optical microscopy were prepared in thin film sandwiched between glass slide and cover.

3. Results and Discussion

3.1. Mesomorphic Properties of Intermediates 1–7 and Title Compounds 1a–7a, 1b–7b, and 1c–7c

The textures illustrated by intermediates **1–7** and title compounds **1a–7a, 1b–7b,** and **1c–7c** under POM have been ascertained by comparing them with relevant photomicrograph from literature [22, 23]. The transition temperatures and associated enthalpies for **1–7***,* **1a–7a**, **1b–7b**, and **1c–7c** upon heating and cooling are listed in Table 1. It can be inferred from Table 1 that the imines **1–5** exhibit monotropic behaviors. In addition, the temperatures with respect to the crystal-isotropic (Cr-Iso) transition upon heating run in these compounds are found to be higher than the temperature associated with the isotropic-mesophase (Iso-M) transition in which the compounds undergo supercooling [24]. The observation under polarized light within the mesomorphic region shows the presence of fan-shaped texture characteristic of the smectic A (SmA) phase upon cooling from the isotropic liquid (Fig. 1). The mesomorphic temperature ranges for compounds **1–5** are 9.92°C, 7.64°C, 9.24°C, 7.47°C, and 7.90°C, respectively. However, only isotropization and crystallization are observed upon heating (at 77.14°C and 82.54°C, respectively) and cooling (at 42°C and 61.71°C, respectively) runs in compounds **6** and **7**.

In compounds **1a–7a**, it is noteworthy that liquid crystal phases were not observed in **1a**, **2a**, and **3a**, but they exhibit the Cr-Iso transition on heating at 78.32°C, 81.00°C, and 84.11°C, respectively. A reverse process of Iso-Cr was observed on cooling at respective temperatures of 67.34°C, 74.45°C, and 77.27°C. Moreover, the **4a**, **5a**, **6a**, and **7a** are not mesogenic and inclined to the Cr_1-Cr_2-Iso transition upon heating run. Moreover, the Iso-Cr_2-Cr_1 transition is also observed on cooling run. The texture observed under POM is indicative of the presence of subphases within the crystal phase (Cr_1-Cr_2), which resembled the phenomena reported in literature [2, 25].

For the series of compounds **1b–7b**, the DSC and POM analyses reveal that the new compounds thus synthesized are not mesogenic and exhibit only Cr_1-Cr_2-Iso and Iso-Cr_2-Cr_1 transitions upon heating and cooling runs. This can be substantiated by the DSC, as shown for compound **6b** (Fig. 2). The high values of the enthalpy of the phase transition obtained from DSC substantiate the crystallization and the Cr_1-Cr_2 transition. The changes in crystalline structure for **6a**, as observed under polarized light, show a transition from the texture consisting huge number of slender threads (Cr_1) to colored plates (Cr_2) when the

Table 1. Phase transition temperatures (°C) and the corresponding enthalpies (J g^{-1}) of intermediates **1–7** and title compounds **1a–7a**, **1b–7b**, and **1c–7c**

Compounds	Transition temperature (°C) (corresponding enthalpy changes in KJ mol^{-1}) heating/cooling
1	Cr 60.43 (23.16) I
	Cr 43.20 (−19.82) SmA 53.12 (−3.51) I
2	Cr 64.16 (36.05) I
	Cr 51.41 (−33.72) SmA 59.05(−2.94) I
3	Cr 68.31 (47.55) I
	Cr 53.07 (−64.32) SmA 62.31(−0.91) I
4	Cr 74.11 (29.64) I
	Cr 56.95 (−49.23) SmA 64.42 (−8.54) I
5	Cr 78.00 (26.54) I
	Cr 60.71 (−19.62) SmA 68.61 (−2.64) I
6	Cr 77.14 (45.31) I
	Cr 57.42 (−28.41) I
7	Cr 82.54 (33.89) I
	Cr 61.71 (−19.65) I
1a	Cr 78.32 (58.12) I
	Cr 67.34 (−38.46) I
2a	Cr 81.00 (64.75) I
	Cr 74.45 (−42.87) I
3a	Cr 84.11 (81.23) I
	Cr 77.27 (−37.79) I
4a	Cr_1 60.19(4.56) Cr_2 90.54 (75.70) I
	Cr_1 48.55(−14.81) Cr_2 59.68 (−49.51) I
5a	Cr_1 68.31(33.61) Cr_2 98.67 (65.31) I
	Cr_1 52.61(−29.84) Cr_2 70.41 (−41.35) I
6a	Cr_1 88.28(48.27) Cr_2 114.23 (19.75) I
	Cr_1 48.81(−11.13) Cr_2 86.31 (−37.66) I
7a	Cr_1 63.49(25.51) Cr_2 119.14 (8.26) I
	Cr_1 40.59(−21.62) Cr_2 84.03 (−26.45) I
1b	Cr_1 41.35(38.69) Cr_2 85.14 (70.31) I
	Cr_1 37.56(−25.62) Cr_2 64.42 (−44.52) I
2b	Cr_1 58.47(39.78) Cr_2 91.23 (56.29) I
	Cr_1 43.67(−21.56) Cr_2 61.54 (−39.42) I
3b	Cr_1 63.45(28.46) Cr_2 109.32 (63.26) I
	Cr_1 38.79(−29.83) Cr_2 65.65 (−33.45) I
4b	Cr_1 88.28(48.27) Cr_2 114.23 (19.75) I
	Cr_1 48.81(−11.13) Cr_2 86.31 (−37.66) I
5b	Cr_1 79.32(42.51) Cr_2 119.62 (57.81) I
	Cr_1 68.43(−39.76) Cr_2 79.44 (−17.31) I
6b	Cr_1 87.51(51.42) Cr_2 123 (45.61) I
	Cr_1 50.43(−28.43) Cr_2 91.64 (−42.86) I
7b	Cr_1 96.14(18.26) Cr_2 129.16 (33.89) I
	Cr_1 60.59(−21.62) Cr_2 84.03 (−26.45) I

Table 1. Phase transition temperatures (°C) and the corresponding enthalpies (J g^{-1}) of intermediates **1–7** and title compounds **1a–7a**, **1b–7b**, and **1c–7c** *(Continued)*

Compounds	Transition temperature (°C) (corresponding enthalpy changes in KJ mol^{-1}) heating/cooling
1c	Cr_1 74.39(26.23) Cr_2 130.01 (37.87) I
	Cr_1 58.35(−30.46) Cr_2 117.57 (−40.34) N 126.21 (0.72) I
2c	Cr_1 77.46(22.67) Cr_2 126.61 (28.56) I
	Cr_1 51.74(−32.89) Cr_2 112.92 (−25.22) N 122.45 (0.82) I
3c	Cr_1 78.41(18.65) Cr_2 125.41 (22.34) I
	Cr_1 60.26(−37.56) $Cr_2$113.67 (−19.78) N 121.44 (1.53) I
4c	Cr_1 76.33(7.57) Cr_2 132.92(17.24) I
	Cr_1 58.57(−39.43) Cr_2 117.12 (−3.83) N 125.67 (5.42) I
5c	Cr_1 81.41(14.32) Cr_2 128.12 (21.31) I
	Cr_1 69.62(−30.82) Cr_2 114.32 (−25.31) N 121.23 (0.91) I
6c	Cr_1 82.30(60.83) Cr_2 129.36 (15.41) I
	Cr_1 72.32(−5.95) Cr_2 120.45 (−10.64) N 125.36 (1.34) I
7c	Cr_1 86.98(13.09) Cr_2 148.35 (18.67) I
	Cr_1 68.35(−18.17) Cr_2 132.45 (−53.54) N 142.45 (1.02) I

temperature was increased from 94°C to 110°C. This phenomenon can be rationalized by the minor change of molecular rearrangement within the crystal phase.

All compounds from the series of **1c–7c** upon cooling exhibit a nematic (N) phase. On cooling from the isotropic liquid, the presence of Schlieren texture characteristics of N phase was observed. The photomicrograph for compound **7c** is shown as an example in Fig. 1. Inspection from the DSC data further suggests that the temperature ranges of mesophase upon cooling are found to be relatively narrow (8.6°C, 9.5°C, 7.8°C, 8.5°C, 6.9°C, 4.9°C, and 10.0°C for **1c**, **2c**, **3c**, **4c**, **5c**, **6c**, and **7c**, respectively). The narrow ranges of mesomorphic temperatures indicate that the molecules **1c–7c** are not kinetically stable within this anisotropic region [26]. A thermogram associated with the thermal properties of compound **7c** is shown in Fig. 2.

3.2. Structure–Mesomorphic Property Relationship

From Fig. 3(a), it is apparent that the temperatures associated with the Cr-I and SmA-I transitions for the intermediates are dependent on the carbon number. These temperatures increase when the length of the terminal alkyl chain is increased from 6 to 18. A drastic change is observed when the carbon number varied from 12 to 14 upon the cooling run.

All the compounds **1a–7a** and **1b–7b** are not mesogenic despite knowing that upon heating and cooling, the transitions of Cr_1-Cr_2 and its reverse process occurred within the crystalline state. Figure 3(b) shows that the isotropization (Cr_2-I) temperatures for **4a–7a** ascended from 90.54°C (**4a**) to 119.14°C (**7a**). The opposite trend was observed when these compounds were cooled down from isotropic liquid.

The thermal behavior as observed in compounds **1a–7a** was not found in **1b–7b** (Fig. 3(c)) and this can be explained in terms of the saturation of the seven-membered ring. Compounds **1a–7a** with a C=C double bond in the seven-membered ring led to a more ordered arrangement within the lattice system in comparison to compounds **1b–7b**.

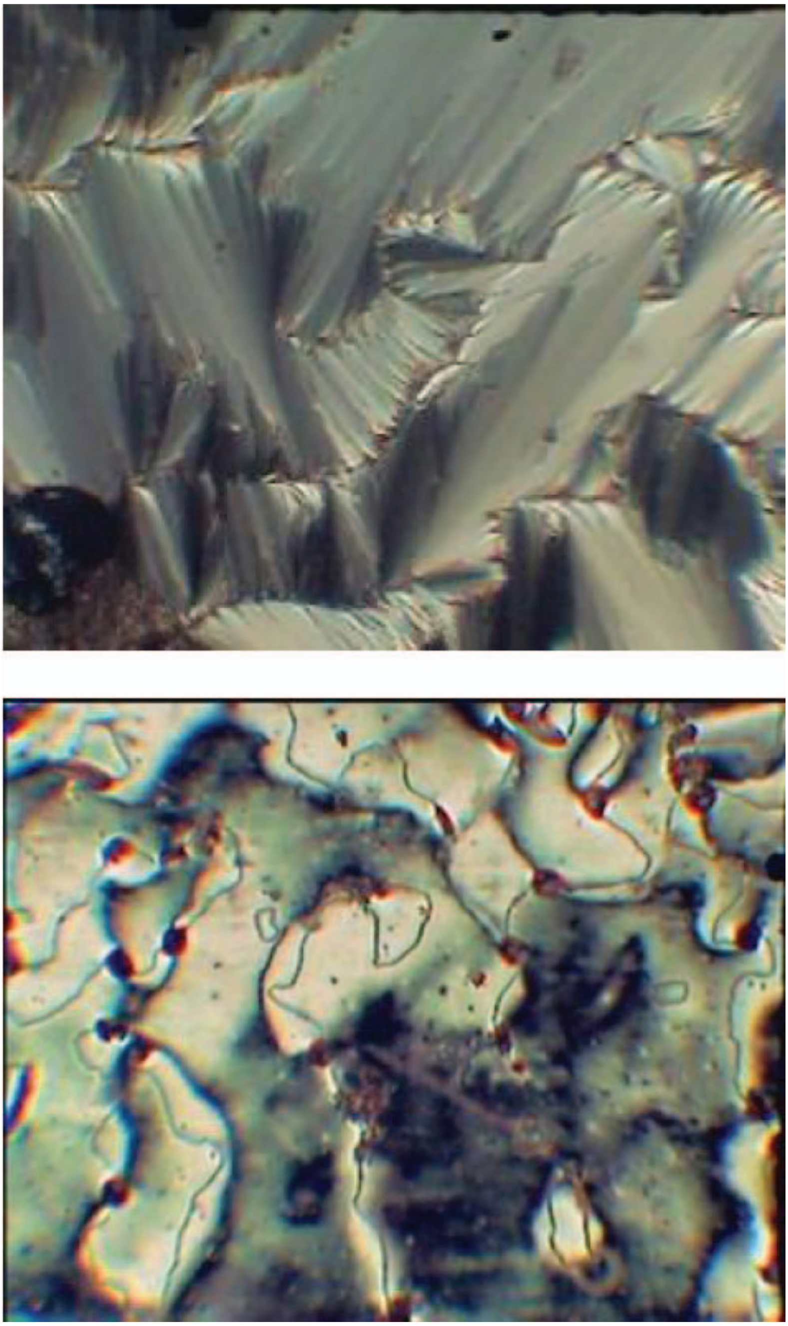


Figure 1. Optical texture of SmA phase at 64.52°C (top plate) observed in compound **5** and N phase at 137.23°C (bottom plate) observed in compound **7c**.

A remarkable feature can be inferred from Fig. 3(d) in which the monotropic **1c**--**7c** upon cooling exhibited well-distinguished transition temperatures associated with I-N, N-Cr_1, and Cr_1-Cr_2. The transition temperatures for each of the compounds **1c**--**7c** differ in

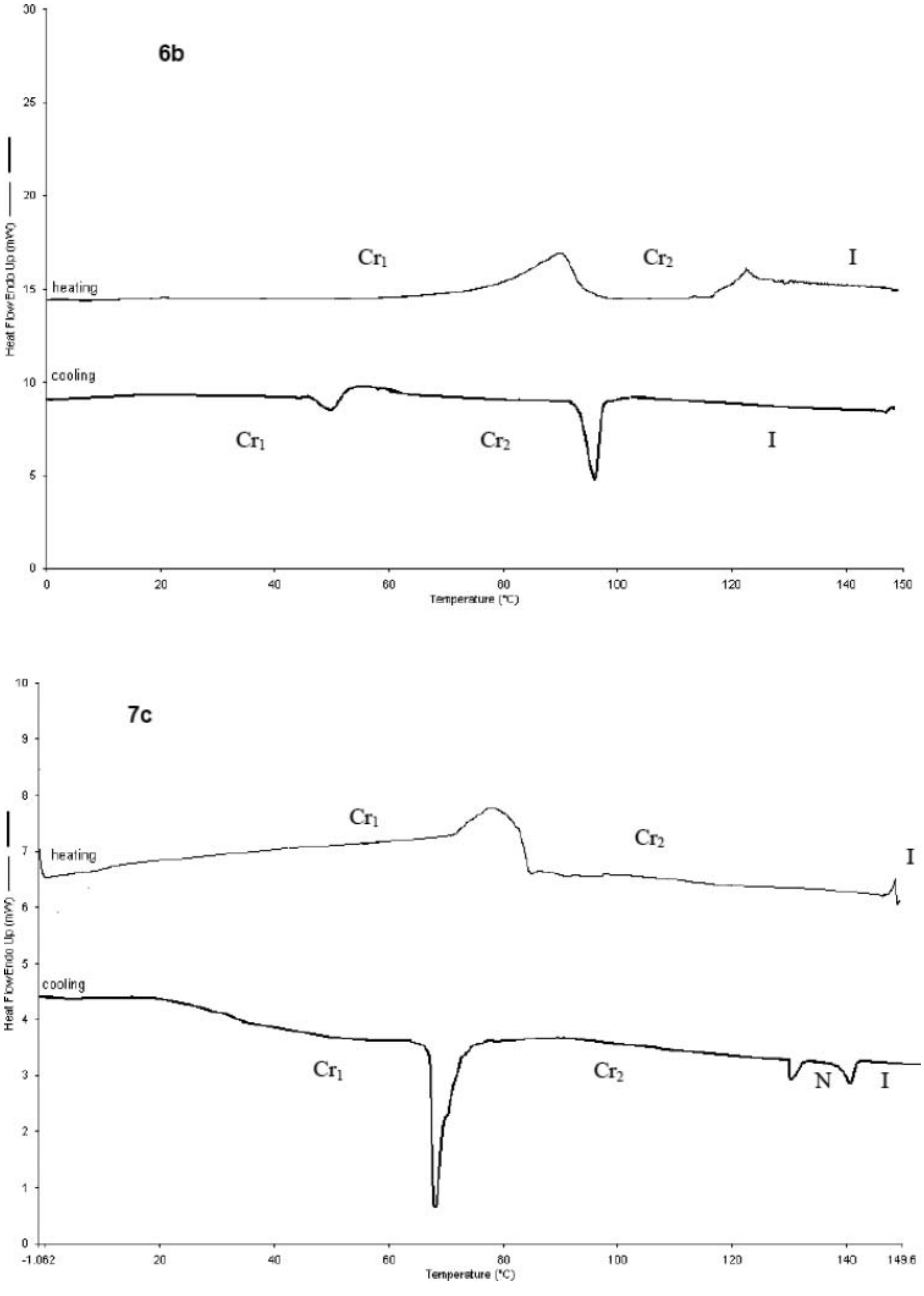


Figure 2. DSC thermograms of compounds **6b** and **7c**.

the following order:

$$\mathrm{I} - \mathrm{N} > \mathrm{N} - \mathrm{Cr}_1 > \mathrm{Cr}_1 - \mathrm{Cr}_2.$$

The ability of compounds **1c–7c** to exhibit nematogenic properties can probably be attributed to the presence of the additional aromatic ring fused with the seven-membered ring resulting in a more rigid core system in comparison to compounds **1a--7a** and **1b--7b**.

3.3. FT-IR, ^{1}H NMR, and ^{13}C NMR Spectral Studies

The infrared spectra of the title compounds **1a–7a**, **1b–7b**, and **1c–7c** show a strong band at the range of 1685–1732 cm$^{-1,}$ which can be assigned to the stretching vibration of carbonyl group C=O in the seven-membered rings. The absorption bands observed in the frequency range of 1244–1262 cm^{-1} can be assigned to the stretching of the C_4—O of the ether linkage [27]. The presence of the diagnostic bands at the range of 1597–1607 cm^{-1} and 1570–1587

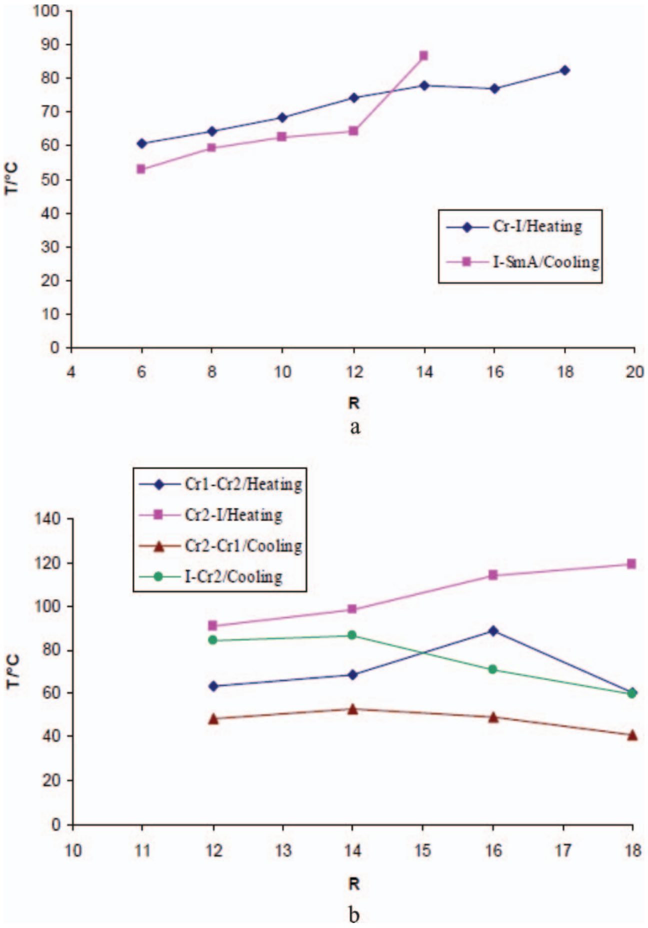


Figure 3. The dependence of phase transition temperatures T on the number of methylene in the terminal alkyl chain of (a) compounds **1–7**, (b) compounds **4a–7a**, (c) compounds **1b–7b**, and (d) compounds **1c–7c**.

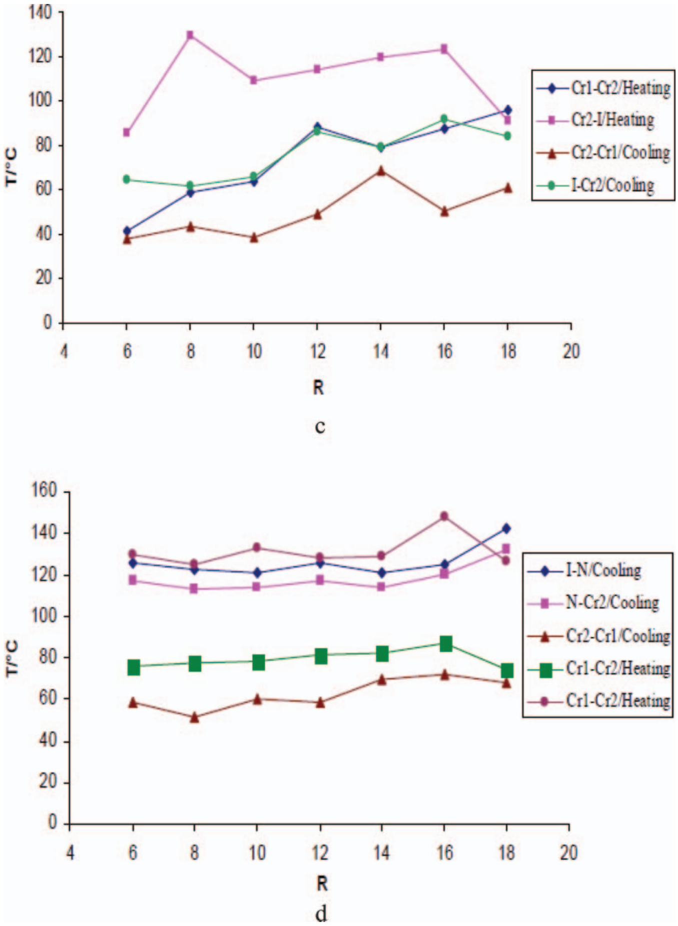


Figure 3. (Continued)

cm^{-1} is attributable to the C=C stretching of the aromatic ring [28]. Other major bands observed at 2914–2979 cm^{-1} and 2798–2864 cm^{-1} indicate the presence of carbon chains in the respective compounds in which the hydrogen atoms are attached to sp^3 carbons [29].

A complete ^{1}H NMR assignment for the title compounds can be described on the basis of respective compounds, as shown in Scheme 1, in which three types of compounds have been differentiated by **a**, **b**, and **c**. The ^{1}H NMR spectra of title compounds **1a–7a**, **1b–7b**, and **1c–7c** showed a singlet that integrates as one hydrogen at the chemical shift δ = 9.84–9.87 ppm that corresponds to the proton attached to the carbon C7 in heterocyclic ring. The presence of two doublets in the downfield region of δ = 6.21–6.26 ppm and δ = 6.39–6.41 ppm for compounds **1a–7a** can be attributed to H9 and H10 of heterocyclic ring. However, the ^{1}H NMR spectra of compounds **1b–7b** indicate that the H9 and H10 protons from the heterocyclic ring appear as two triplets at the range of δ = 2.25–2.28 ppm and δ = 2.40–2.42 ppm, respectively. Moreover, the resonances for the C_6H_5— appear as two doublets in downfield region of δ = 7.80–7.85 ppm and δ = 7.10–7.43 ppm corresponding to the respective phenyl protons H2 (or H6) and H3 (or H5) in compounds **1a–7a**. The phenyl protons H2 (or H6) and H3 (or H5) from compounds **1b–7b** appear as doublet at the ranges of $\delta = 7.85$–7.88 ppm and 7.10–7.13 ppm, respectively. The ^{1}H NMR data for compounds **1c–7c** show diagnostic signals within the range of $\delta = 7.10$–7.88 ppm assignable to the aromatic protons. As for ^{1}H NMR spectra of compounds **1a–7a, 1b–7b**, and **1c–7c**, there are three triplet signals due to the presence of methylene protons, $C_4{-}OCH_2$ of the ether linking group, methylene protons, and $N{-}CH_2$, and CH_3 protons in both chains at the respective chemical shift ranges of $\delta = 4.03$–4.09 ppm, 3.00–3.17 ppm, and 0.85–0.88 ppm. Two sets of multiplets at $\delta = 1.21$–1.76 ppm can be assigned to protons $OCH_2{-}((CH_2)_2{-}CH_2)_{13}$ and $NCH_2{-}(CH_2{-}CH_n)$.

The structures of the title compounds are further substantiated by the ^{13}C NMR data. The resonances due to the carbonyl group (C8 and C11) of heterocyclic rings in the title compounds **1a–7a**, **1b–7b**, and **1c–7c** are located in the downfield ($\delta = 166.04$–166.29 ppm, 171.11–174.52 ppm, and 167.43–168.95 ppm, respectively). The signal that appears within the range of $\delta = 89.97$–90.12 ppm can be attributed to the C7 in the heterocyclic rings. The ^{13}C NMR spectra of compounds **1a–7a**, **1b–7b**, and **1c–7c** indicate that the aromatic carbons give rise to different signals within the frequency range of $\delta = 115.00$–164.61 ppm. Signals at $\delta = 132.62$–132.66 ppm and $\delta = 130.87$–130.90 ppm indicate the presence of C9 and C10 in heterocyclic ring in compounds **1a–7a**. However, the resonance due to the C9 and C10 in compounds **1b–7b** can be located at the respective chemical shift of $\delta = 29.31$–29.34 ppm and 27.80–27.82 ppm.

The ^{13}C NMR spectra of title compounds confirm that the signal at $\delta = 68.03$–68.92 ppm attributed to the presence of $C_4O\text{-}CH_2$ group from the ether linkage. Similarly, the presence of $N{-}CH_2$ can be confirmed by the signal observable at the range of $\delta = 39.03$–39.74 ppm. Signals ascribed to the methylene carbons of the terminal alkyloxy chain $(CH_2)_2{-}(CH_2)_{13}$ and alkyl group $NCH_2{-}(CH_2{-}CH_n)$ can be assigned within the range of $\delta = 22.90$–32.39 ppm. At a high field, a signal at $\delta = 14.55$–14.79 ppm can be assigned to methyl carbons.

4. Conclusion

Three series of heterocyclic-based liquid crystalline compounds with the heterocyclic ring at the core position have been synthesized using new methodology and their mesomorphic properties were analyzed with respect to phase transition temperature and chemical structure. The intermediate compounds were found to exhibit SmA upon cooling. However, the types of compounds from **a** and **b** series were not mesogenic and only exhibit Cr_1-Cr_2 upon cooling and heating. The compounds in **c** series were found to show monotropic N phase upon cooling.

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