Bowl-shaped Fluorescent Liquid Crystals derived from 4-*tert* butyl calix[4]arene and trans cinnamic acid derivatives

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Contents:

1. Experimental

Melting points were taken on Opti-Melt (Automated melting point system). The FT-IR spectra were recorded as KBr pellet on Shimadzu in the range of 3800-600 cm^{-1}. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyser. The texture images were studied on a trinocular optical polarising microscope (POM) equipped with a heating stage. ^{1}H NMR spectra and ^{13}C NMR was recorded on a 400 MHz in Bruker Advance 400 in the range of 0.5 ppm-16 ppm using $CDCl_3$ solvent. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10°C min^{-1}. Texture image of nematic phase were determined by miscibility method. Thermo gravimetric analysis (TGA) was performed using a Perkin Elmer-STA 6000 apparatus under high purity nitrogen. The samples were heated from room temperature to 550˚C at 10˚C/min. X-ray diffraction (XRD) measurements were performed on a Rigaku-Ultima IV powder diffractometer equipped with a Cu kα source (λ = 1.5418 A˚ and 1.6 kW, X-ray tube with applied voltage and current values as 40 kV and 30 mA power) and also Philips X'PERT MPD.

2. Synthesis and characterization

2.1 Preparation of *p-tert*-butyl calix[4]arene (1c)

p-tert-Butylcalix[4]arene (1c) was synthesized by reported in the literature [1], white precipitates, yield 87%. Elemental analysis: $C_{44}H_{56}O_4$: Calcu: C, 80.44; H, 8.70; O, 9.80 %, Found: C, 80.14; H, 8.62; O, 9.72 %. ^{1}H NMR: (300 MHz, $CDCl_3$): 1.18 (s, 36H, t-butyl), 3.48 (d, *J = 12.0Hz*, 4H, Ar-CH_2-Ar), 4.21 (d, *J = 12.0Hz*, 4H, -ArCH_2Ar-), 7.08 (s, 8H, Ar-H), 9.78 (s, 4H, Ar-OH); ^{13}C NMR: 149.1, 126.2, 126.1 (Ar-C), 34.2 (t-butyl), 31.4 (t-butyl), 32.6 (Ar-CH_2-Ar).

2.2 Preparation of 4-n-alkoxy benzaldehyde (1a)

4-n-alkoxy benzaldehyde (1a) was synthesized by refluxing the mixture of 4-hydroxy benzaldehyde (1 equiv.) with corresponding n-alkyl bromide (R-Br) (1 equiv.) in presence of anhydrous K_2CO_3 (1 equiv.) in dry acetone as a solvent.[2]

2.3 Preparation of *Trans* 4-n-alkoxy cinnamic acid (1b)

Trans 4-n-alkoxy cinnamic acids are prepared by reported method in literature.[3]

2.4 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra n-alkoxy cinnamate calix[4]arene (Series-1):

The compound has been prepared by esterification of the appropriate compound (1b) (0.0015 mol.) and compound (1c) (0.0060 mol.), dicyclohexyl carbodiimide (DCC) (0.0060 mol.) and dimethylaminopyridine (DMAP) in catalytic amount (0.0030 mmol) in dry CH_2Cl_2 (DCM) (30 ml) was stirred at room temperature for 48 h. The white precipitate of DCU is obtained which was isolated by filtration. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4).[4]

2.4.1 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra decyloxy cinnamate calix[4]arene ($1d_{10}$-I) (Series-1): Yield 72%, Elemental analysis: $C_{120}H_{160}O_{12}$: Calcu: C, 80.31; H, 8.99; O, 10.70 %. Found: C, 81.68; H, 9.08; O, 10.64 %. FT-IR (KBr) in cm^{-1}: 3030 (-C-H-Str in aromatic), 1365 and 1240 (-C-O str), 1750 (-COO- group), 960 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.25 (s, 36H, t-butyl group), 0.88 (t, 12H, -$OC_{10}H_{21}$), 1.28 (m, 40H, -$OC_{10}H_{21}$), 1.47 (p, 8H, -$OC_{10}H_{21}$), 3.21 (d, J = 18.0Hz, 4H, -ArCH_2Ar-), 4.14 (d, J = 18.0 Hz, 4H, -ArCH_2Ar-), 3.98 (t, 8H, -$OC_{10}H_{21}$), 6.34 (d, J= 15.5 Hz, 4H, -CH=CH-), 7.42 (d, J = 15.5 Hz, 4H, -CH=CH-), 7.21 (d, 8H, Ar-H), 7.67 (s, 8H, Ar-H), 6.86 (s, 8H, Ar-H), 7.68 (d, 2H, Ar-H), 8.01 (d, 4H, Ar-H). ^{13}C NMR: 161.18, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91,

127.6, 125.3, 121.75, 115.80, 114.8, 34.62, 32.51, 31.92, 14.17, 25.56, 29.30, 29.65. ESI-MS for compound $1d_{10}$-1 (M+1) Calculated: 1794.19; Found 1795.43.

2.4.2 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra dodecyloxy cinnamate calix[4]arene ($1d_{12}$-I) (Series-1): Yield 71%, Elemental analysis: $C_{128}H_{176}O_{12}$: Calcu: C, 80.63; H, 9.30; O, 10.07 %;. Found: C, 81.32; H, 9.45; O, 10.12 %. FT-IR (KBr) in cm^{-1}: 3031 (-C-H-Str in aromatic), 1365 and 1236 (-C-O str), 1740 (-COO- group), 963 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.88 (t, 12H, $-OC_{12}H_{25}$), 1.28 (m, 43H, $-OC_{12}H_{25}$), 1.47 (p, 8H, $-OC_{12}H_{25}$), 3.51 (d, J = 18.0Hz, 4H, $-ArCH_2Ar-$), 4.14 (d, J = 18.0, 4H, $-ArCH_2Ar-$), 3.98 (t, 8H, $-OC_{12}H_{25}$), 6.34 (d, J = 15.5 Hz, 4H, -CH=CH-), 7.42 (d, J = 15.5 Hz, 4H, -CH=CH-), 8.01 (d, 4H, Ar-H), 7.68 (d, 2H, Ar-H), 7.54 (d, 4H, Ar-H), 7.24 (d, 8H, Ar-H), 6.98 (d, 8H, Ar-H). ^{13}C NMR: 161.18, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 14.1, 22.63, 29.61, 25.96. ESI-MS for compound $1d_{12}$-1 (M+1) Calculated: 1906.32; Found 1907.53.

2.4.3 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra octyloxy cinnamate calix[4]arene ($1d_8$-I) (Series-1): Yield 69%, Elemental analysis: $C_{112}H_{144}O_{12}$: Calcu: C, 79.96; H, 8.63; O, 11.41 %. Found: C, 79.57; H, 9.02; O, 11.37 %. FT-IR (KBr) in cm^{-1}: 3029 (-C-H-Str in aromatic), 1361 and 1240 (-C-O str), 1760 (-COO- group), 941 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.86 (t, 12H, $-OC_8H_{17}$), 1.28 (m, 24H, $-OC_8H_{17}$), 1.46 (p, 8H, $-OC_8H_{17}$), 3.51 (d, J = 18.0Hz, 4H, $-ArCH_2Ar-$), 4.14 (d, J = 18.0, 4H, $-ArCH_2Ar-$),3.98 (t, 8H, $-OC_8H_{17}$), 6.34 (d, J = 15.5 Hz, 4H, -CH=CH-), 8.01 (d, 4H, Ar-H), 7.68 (d, 2H, Ar-H), 7.42 (d, J = 15.5 Hz, 4H, -CH=CH-), 7.84 (d, 4H, Ar-H), 7.24 (d, 8H, Ar-H), 7.01 (s, 4H, Ar-H), 6.98 (d, 8H, Ar-H). ^{13}C NMR: 161.18, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91,

131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 31.32, 14.41, 22.61, 25.56, 29.61, 27.62, 25.96. ESI-MS for compound $1d_8$-1 (M+1) Calculated: 1682.07; Found 1683.12.

2.4.4 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra pentyloxy cinnamate calix[4]arene ($1d_5$-I) (Series-1): Yield 74%, Elemental analysis: $C_{100}H_{120}O_{12}$: Calcu: C, 79.33; H, 7.99; O, 12.68 %. Found: C, 79.26; H, 7.83; O, 12.59 %. FT-IR (KBr) in cm^{-1}: 3020 (-C-H-Str in aromatic), 1361 and 1246 (-C-O str), 1760 (-COO- group), 961 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.86 (t, 12H, $-OC_5H_{11}$), 1.28 (m, 13H, $-OC_5H_{11}$), 1.47 (p, 8H, $-OC_5H_{11}$), 3.51 (d, J = 18.0Hz, 4H, $-ArCH_2Ar-$), 4.14 (d, J = 18.0, 4H, $-ArCH_2Ar-$), 3.98 (t, 8H, $-OC_5H_{11}$), 6.24 (d, J = 15.5 Hz, 4H, -CH=CH-), 7.43 (d, J = 15.5 Hz, 4H, -CH=CH-), 8.01 (d, 4H, Ar-H), 7,78 (d, 2H, Ar-H), 7.24 (d, 8H, Ar-H), 7.01 (s, 4H, Ar-H), 6.98 (d, 8H, Ar-H). ^{13}C NMR: 161.12, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 14.14, 22.13, 29.61, 27.72, 25.16. ESI-MS for compound $1d_5$-1 (M+1) Calculated: 1513.88; Found 1514.13.

2.4.5 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra butyloxy cinnamate calix[4]arene ($1d_4$-I) (Series-1): Yield 74%, Elemental analysis: $C_{96}H_{112}O_{12}$: Calcu: C, 79.09; H, 7.74; O, 13.17 %. Found: C, 78.86; H, 7.87; O, 13.34 %. FT-IR (KBr) in cm^{-1}: 3020 (-C-H-Str in aromatic), 1361 and 1246 (-C-O str), 1760 (-COO- group), 948 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.86 (t, 12H, $-OC_4H_9$), 1.75 (sext, 8H, $-OC_4H_9$), 1.47 (p, 8H, $-OC_4H_9$), 3.51 (d, J = 18.0Hz, 4H, $-ArCH_2Ar-$), 4.14 (d, J = 18.0, 4H, $-ArCH_2Ar-$), 3.98 (t, 8H, $-OC_4H_9$), 6.24 (d, J = 15.5 Hz, 4H, -CH=CH-), 7.42 (d, J = 15.5 Hz, 4H, -CH=CH-), 8.01 (d, 4H, Ar-H), 7.84 (d, 8H, Ar-H), 7.01 (d, 4H, Ar-H), 6.87 (d, 8H, Ar-H), 7.32 (d, 4H, Ar-H). ^{13}C NMR: 161.18, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72,

121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 29.61, 29.30, 27.72, 25.96, 14.13. ESI-MS for compound $1d_4$-1 (M+1) Calculated: 1457.82; Found 1458.63.

2.5 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 28 di-n-alkoxy cinnamate calix[4]arene (Series-2):

The compound has been prepared by esterification of the appropriate compound (1a) (0.0015 mol.) and compound (1c) (0.0030 mol.), dicyclohexyl carbodiimide (DCC) (0.0030 mol.) and dimethylaminopyridine (DMAP) in catalytic amount (0.0015 mmol) in dry CH_2Cl_2 (DCM) (30 ml) was stirred at room temperature for 48 h. The white precipitate of DCU is obtained which was isolated by filtration. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4) [4].

2.5.1 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 28 di-decyloxy cinnamate calix[4]arene ($1d_{10}$-II) (Series-2): Yield 72 %, Elemental analysis: $C_{82}H_{108}O_8$: Calcu: C, 80.61; H, 8.91; O, 10.48 %. Found: C, 80.84; H, 9.15; O, 10.34 %. FT-IR (KBr) in cm^{-1}: 2950 (-C-H- Str in aromatic), 3450 (-OH), 1361 and 1240 (-C-O str), 1760 (-COO- group), 961 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.88 (t, 6H, $-OC_{10}H_{21}$), 1.28 (m, 20H, $-OC_{10}H_{21}$), 1.46 (p, 4H, $-OC_{10}H_{21}$), 3.56 (d, *J = 15.0Hz*, 4H, $-ArCH_2Ar-$), 4.14 (d, *J = 15.0 Hz*, 4H, $-ArCH_2Ar-$), 3.98 (t, 4H, $-OC_{10}H_{21}$), 6.29 (d, *J = 15.5 Hz*, 4H, $-OC_{10}H_{21}$), 7.52 (d, *J = 15.5 Hz*), 9.02 (s, 2H, Ar-OH), 8.04 (d, 4H, Ar-H), 7.56 (s, 2H, Ar-H), 7.31 (s, 2H, Ar-H), 7.4 (s, 4H, Ar-H), 6.94 (d, 2H, Ar-H), 6.83 (d, 2H, Ar-H). ^{13}C NMR: 161.12, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 22.13, 29.61, 27.72, 25.16, 14.08. ESI-MS for compound $1d_{10}$-1l (M+1) Calculated: 1220.80; Found 1221.04.

2.5.2 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 28 di-dodecyloxy cinnamate calix[4]arene ($1d_{12}$-II) (Series-2): Yield 69 %, Elemental analysis: $C_{86}H_{116}O_8$: Calcu: C, 80.83; H, 9.15; O, 10.02 %. Found: C, 80.98; H, 9.23; O, 10.14 %. FT-IR (KBr) in cm^{-1}: 2941 (-C-H- Str in aromatic), 3450 (-OH), 1361 and 1260 (-C-O str), 1750 (-COO- group), 953 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.86 (t, 6H, $-OC_{12}H_{25}$), 1.28 (m, 18H, $-OC_{12}H_{25}$), 1.47 (p, 4H, $-OC_{12}H_{25}$), 3.56 (d, *J = 15.0Hz*, 4H, $-ArCH_2Ar-$), 4.14 (d, *J = 15.0 Hz*, 4H, $-ArCH_2Ar-$), 3.98 (t, 4H, $-OC_{12}H_{25}$), 6.27 (d, *J = 15.5 Hz*, 2H, -CH=CH-), 7.52 (d, *J = 15.5 Hz, 2H,* -CH=CH-), 9.04 (s, 2H, Ar-OH), 8.01 (d, 4H, Ar-H), 7.56 (s, 2H, Ar-H), 7.03 (s, 4H, Ar-H), 6.98 (d, 2H, Ar-H), 6.83 (d, 2H, Ar-H), 7.31 (s, 2H, Ar-H). ^{13}C NMR: 161.12, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 14.14, 22.13, 29.61, 27.72, 25.16. ESI-MS for compound $1d_{12}$-1l (M+1) Calculated: 1276.87; Found 1277.21.

2.5.2 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 28 di-octyloxy cinnamate calix[4]arene ($1d_8$-II) (Series-2): Yield 64 %, Elemental analysis: $C_{78}H_{100}O_8$: Calcu: C, 80.37; H, 8.65; O, 10.98 %. Found: C, 80.46; H, 8.61; O, 11.09 %. FT-IR (KBr) in cm^{-1}: 2947 (-C-H- Str in aromatic), 3451 (-OH), 1343 and 1250 (-C-O str), 1760 (-COO- group), 947 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.88 (t, 6H, $-OC_8H_{17}$), 1.28 (m, 12H, $-OC_8H_{17}$), 1.47 (p, 4H, $-OC_8H_{17}$), 3.51 (d, *J = 15.0Hz*, 4H, $-ArCH_2Ar-$), 4.14 (d, *J = 15.0 Hz*, 4H, $-ArCH_2Ar-$), 3.98 (t, 4H, $-OC_8H_{17}$), 6.41 (d, *J = 15.5 Hz*, 4H, $-OC_8H_{17}$), 7.53 (d, *J = 15.5 Hz*), 9.01 (s, 2H, Ar-OH),8.02 (d, 4H, Ar-H), 7.49 (s, 4H, Ar-H), 7.26 (s, 2H, Ar-H), 7.01 (d, 4H, Ar-H), 6.72 (s, 2H, Ar-H). ^{13}C NMR: 161.12, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.14, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 14.14, 22.13, 29.63, 27.72, 25.16. ESI-MS for compound $1d_8$-1l (M+1) Calculated: 1164.74; Found 1165.56.

2.5.2 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 28 di-pentyloxy cinnamate calix[4]arene (1d$_5$-II) (Series-2): Yield 67 %, Elemental analysis: $C_{72}H_{88}O_8$: Calcu: C, 79.96; H, 8.04; O, 12.15 %. Found: C, 79.91; H, 7.94; O, 12.09 %. FT-IR (KBr) in cm^{-1}: 2940 (-C-H- Str in aromatic), 3456 (-OH), 1343 and 1240 (-C-O str), 1760 (-COO- group), 961 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.88 (t, 6H, -OC$_6$H$_{13}$), 1.28 (m, 8H, -OC$_5$H$_{11}$), 1.47 (p, 4H, -OC$_5$H$_{11}$), 3.54 (d, *J = 15.0Hz*, 4H, -ArCH$_2$Ar-), 4.14 (d, *J = 15.0 Hz*, 4H, -ArCH$_2$Ar-), 3.97 (t, 4H, -OC$_5$H$_{11}$), 6.27 (d, *J = 15.5 Hz*, 4H, -CH=CH-), 7.52 (d, *J = 15.5 Hz,*-CH=CH-), 9.03 (s, 2H, Ar-OH), 8.03 (d, 4H, Ar-H), 7.25 (d, 4H, Ar-H), 7.18 (s, 2H, Ar-H), 6.81 (s, 4H, Ar-H). ^{13}C NMR: 161.18, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 22.13, 29.61, 27.72, 25.06, 14.13. ESI-MS for compound 1d$_5$-1l (M+1) Calculated: 1080.65; Found 1081.17.

2.5.3 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 28 di-butyloxy cinnamate calix[4]arene (1d$_4$-II) (Series-2): Yield 67 %, Elemental analysis: $C_{70}H_{84}O_8$: Calcu: C, 79.81; H, 8.04; O, 12.15 %. Found: C, 79.76; H, 7.95; O, 12.21 %. FT-IR (KBr) in cm^{-1}: 2940 (-C-H- Str in aromatic), 3456 (-OH), 1343 and 1240 (-C-O str), 1760 (-COO- group), 961 (-CH=CH- str, trans alkene). ^{1}H NMR: 1.24 (s, 36H, t-butyl group), 0.88 (t, 6H, -OC$_4$H$_9$), 1.75 (sext, 4H, -OC$_4$H$_9$), 1.47 (p, 4H, -OC$_4$H$_9$), 3.52 (d, *J = 15.0Hz*, 4H, -ArCH$_2$Ar-), 4.14 (d, *J = 15.0 Hz*, 4H, -ArCH$_2$Ar-), 3.98 (t, 4H, -OC$_4$H$_9$), 6.49 (d, *J = 15.5 Hz*, 4H, -CH=CH-), 7.51 (d, *J = 15.5 Hz*, -CH=CH-), 9.03 (s, 2H, Ar-OH),8.03 (d, 4H, Ar-H), 7.58 (s, 2H, Ar-H), 7.21 (d, 4H, Ar-H), 6.73 (s, 4H, Ar-H). ^{13}C NMR: 161.12, 160.01, 157.90, 147.51, 145.08, 142.06, 132.91, 131.82, 129.94, 128.72, 121.75, 115.82, 114.80, 34.62, 32.51, 31.92, 22.13, 29.61, 27.72, 25.16, 14.14. ESI-MS for compound 1d$_4$-ll (M+1) Calculated: 1052.62; Found 1053.64.

Table S_1:- Transition Temperature in °C by POM (**1dn-l**, Series-1)

Sr.no	R= n-alkyl group	Transition temperatures in ^{0}C			
		SmC	SmA	N	I
1	**$1d_4$-l**	112.0	146.0	-	168.0
2	**$1d_5$-l**	103.0	134.0	-	158.0
3	**$1d_8$-l**	107.0	116.0	-	131.0
4	**$1d_{10}$-l**	96.0	-	110.0	128.0
5	**$1d_{12}$-l**	84.0	-	104.0	121.0
6	**$1d_{14}$-l**	-	-	81.0	116.4

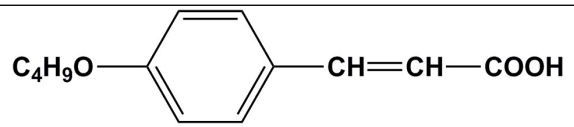
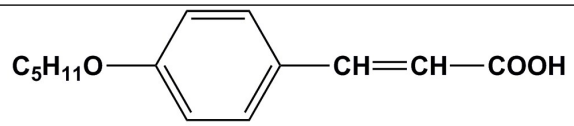
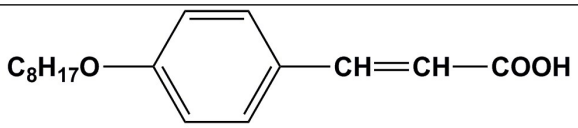
(Cr = solid crystal; Sm C = smectic C phase; SmA = smectic A phase; N = nematic phase; I = isotropic phase).

Table S_2:- Transition Temperature in °C by POM (**1dn-ll**, Series-2)

Sr.no	R= n-alkyl group	Transition temperatures in ^{0}C			
		SmC	SmA	N	I
1	**$1d_4$-ll**	123.0	-	-	168.0
2	**$1d_5$-ll**	121.0	152.0	-	162.0
3	**$1d_8$-ll**	115.0	130.0	-	133.0
4	**$1d_{10}$-ll**	109.0	127.0	-	143.0
5	**$1d_{12}$-ll**	101.0	-	116.0	131.0
6	**$1d_{14}$-ll**	96.0	-	114.0	129.0

(Cr = solid crystal; Sm C = smectic C phase; SmA = smectic A phase; N = nematic phase; I = isotropic phase).

Table S_3:- Transition Temperature in °C by POM (**$1b_4$-$1b_{14}$**)

Comp.	Structure	Transition temperature in ˚C		
		Sm	N	I
$1b_4$		-	156.0	189.0
$1b_5$		-	144.0	180.0
$1b_8$		-	145.0	172.0

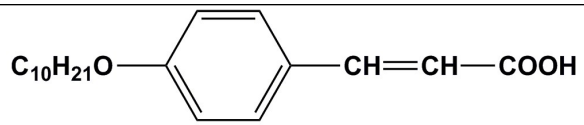
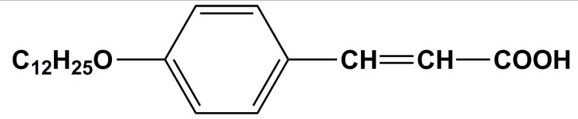
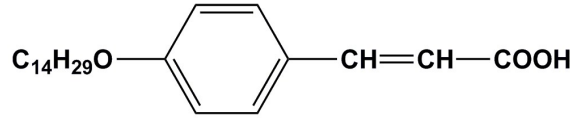
$1b_{10}$		136.0	150.0	169.0
$1b_{12}$		132.0	157.0	164.0
$1b_{14}$		127.0	-	160.0

Figure S_1: The DSC traces of compounds **$1d_{14}$-l** (a), **$1d_4$-l** (b) on first heating and cooling (scan rate 10˚C/min).

Figure S_2: The DSC traces of compounds **$1d_5$-ll** (a), **$1d_8$-ll** (b) on first heating and cooling (scan rate 10˚C/min).

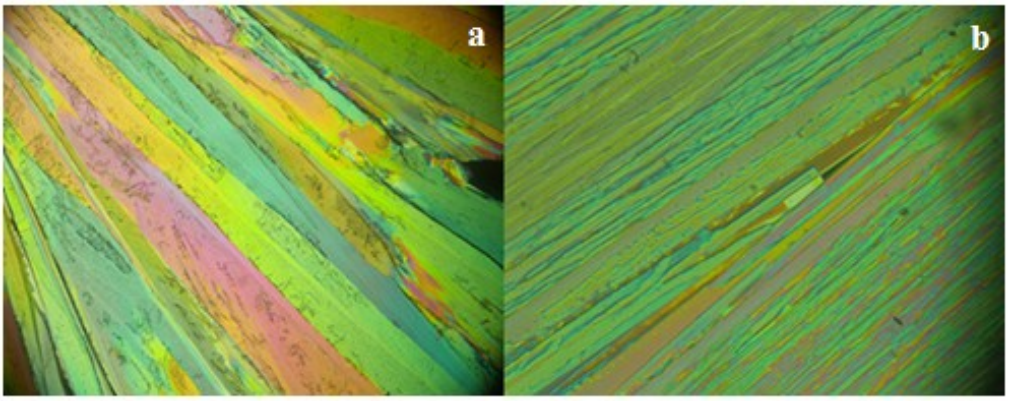


Figure S_3: Photomicrographs of the texture obtained for series-1 and series-2: (a) fan type texture image of SmA phase at 134 °C for comp. **$1d_5$-l**; (b) threaded line type texture image of SmA phase at 130 °C for comp. **$1d_8$-ll**.

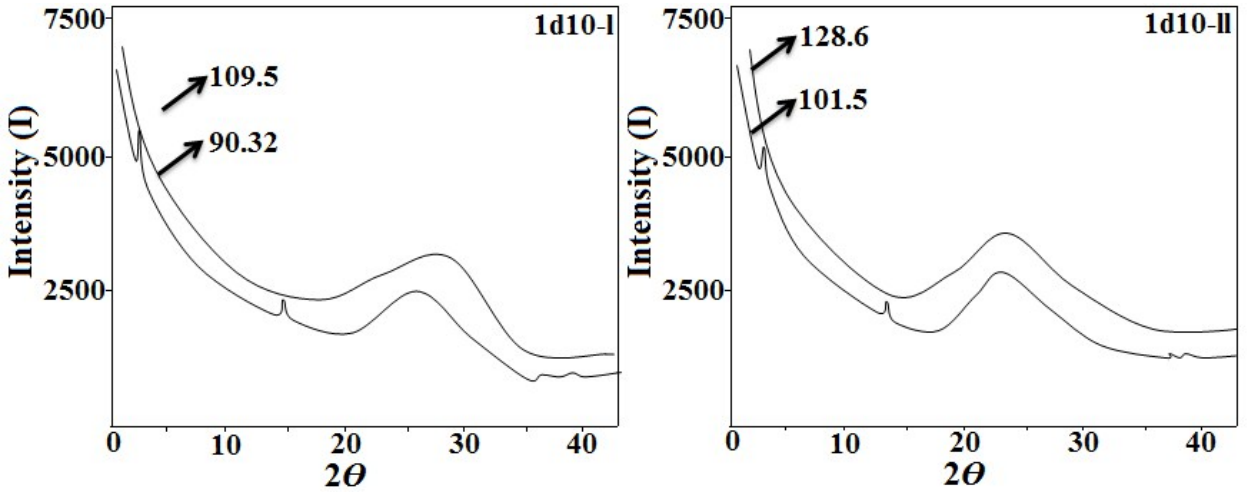


Figure S_4: XRD patterns of (a) Compound **$1d_{10}$-I** (series-1) at 109.5 °C and 90.32 °C; (b) Compound **$1d_{10}$-II** (series-2) at 128.6 °C and 101.5 °C.

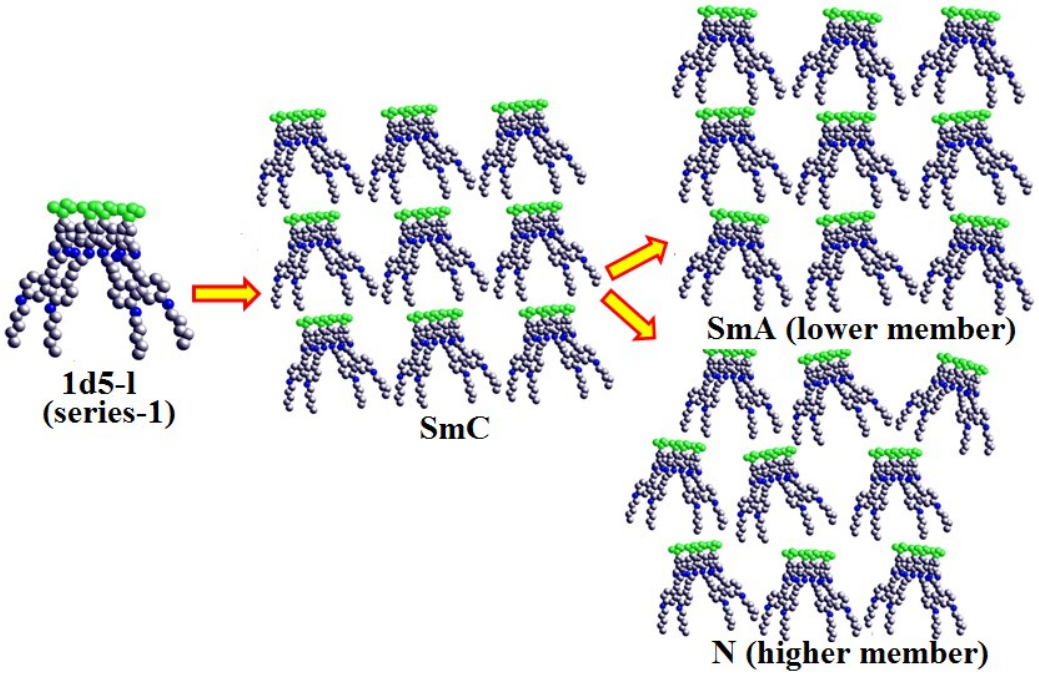


Figure S_5: Schematic representation of liquid crystal molecule self-assembled in the mesophase arrangement in Series-1 (1dn-1).

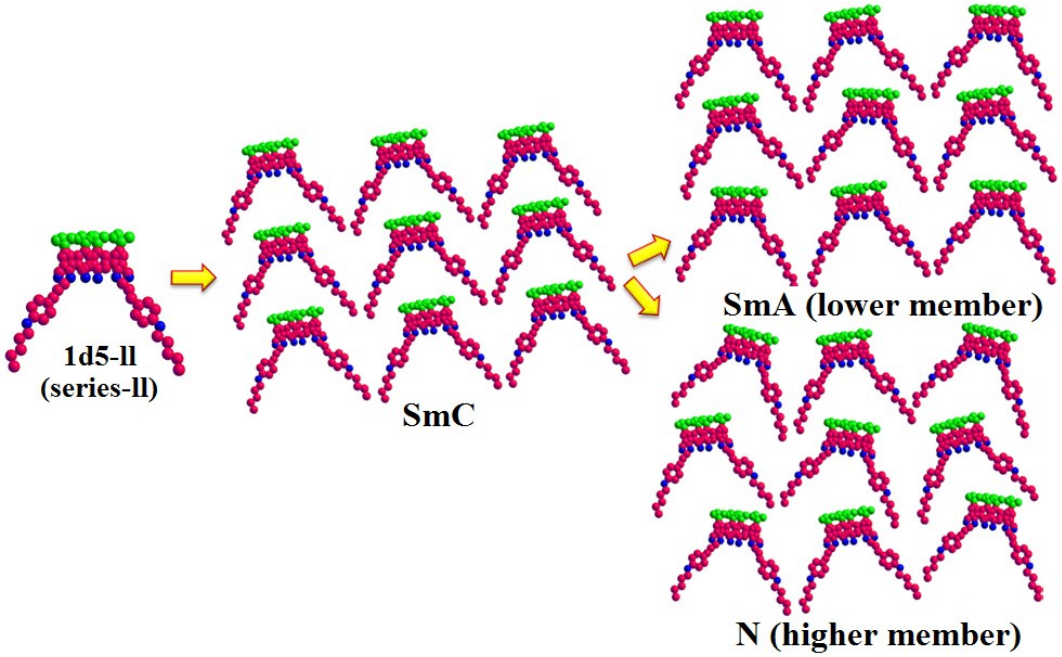


Figure S_6: Schematic representation of liquid crystal molecule self-assembled in the mesophase arrangement in Series-2 (1dn-ll).

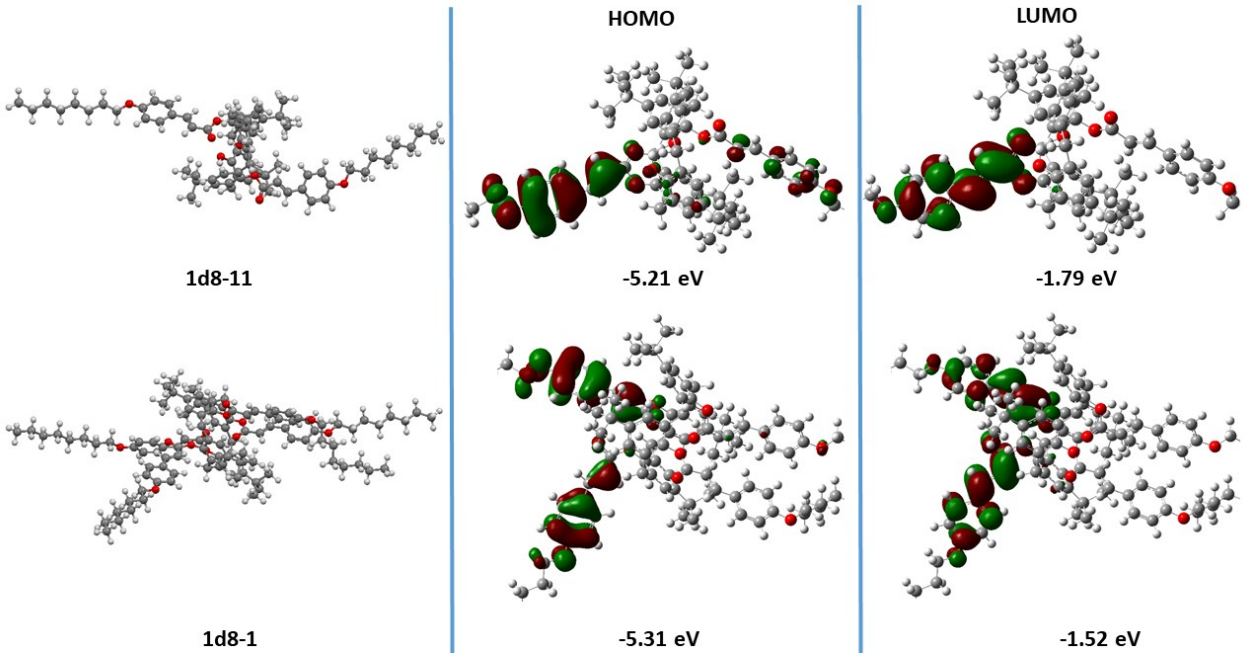
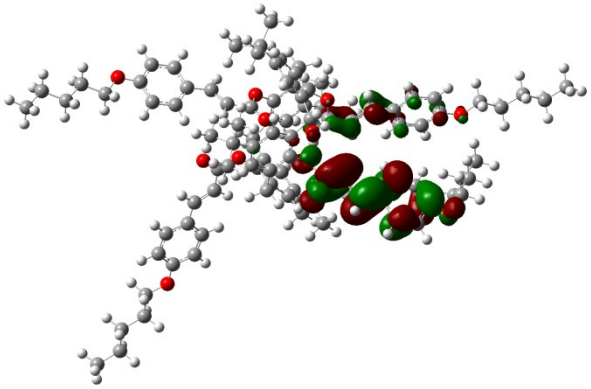
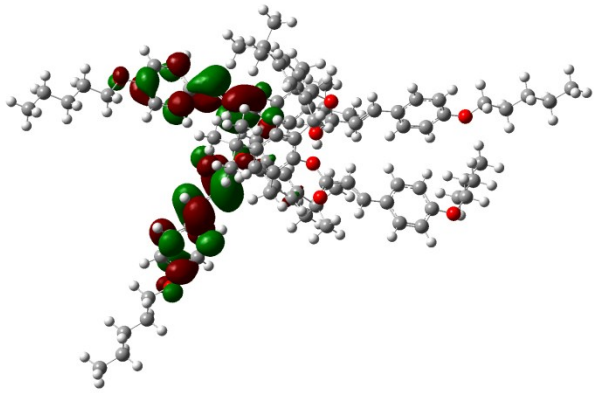
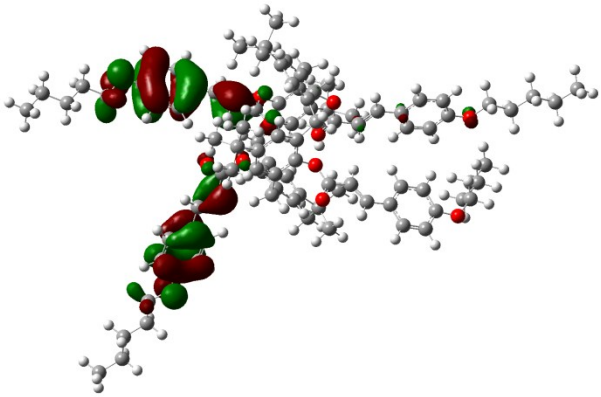
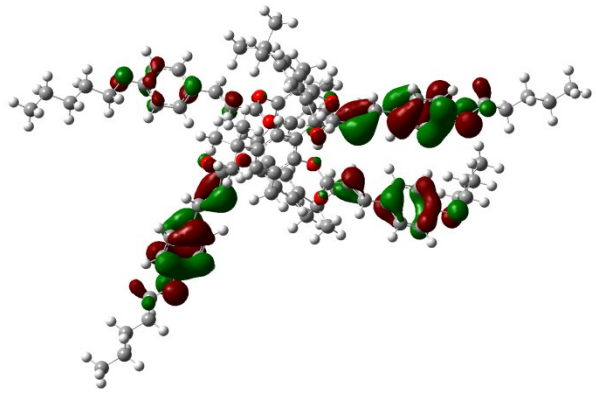
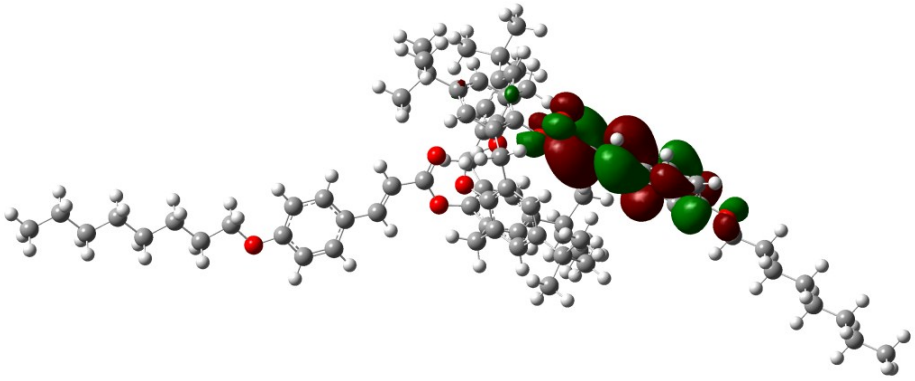
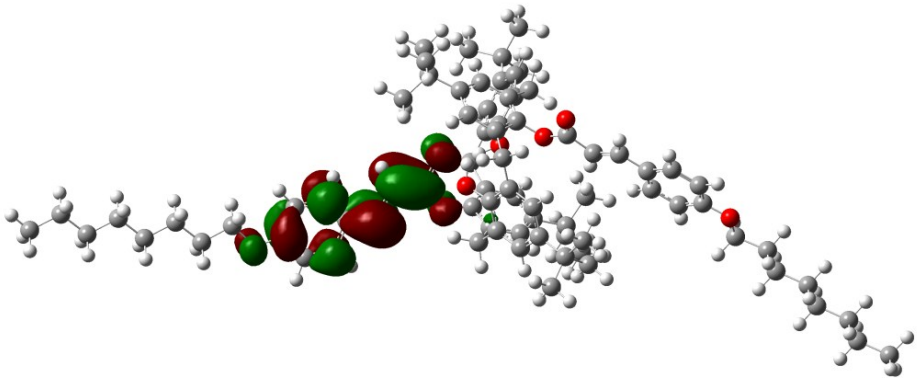


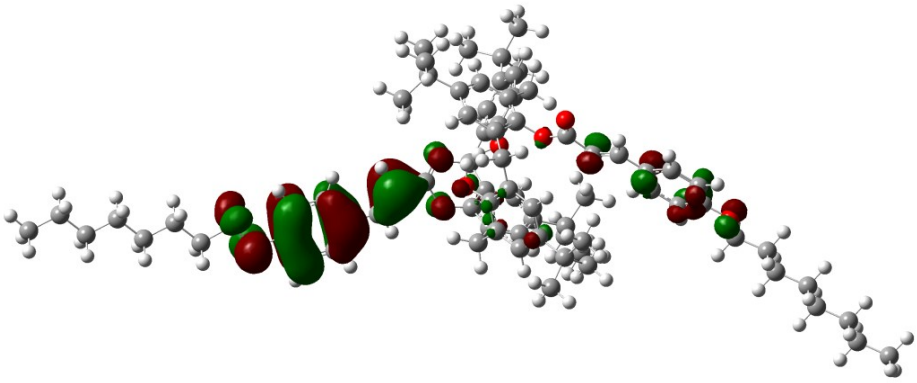
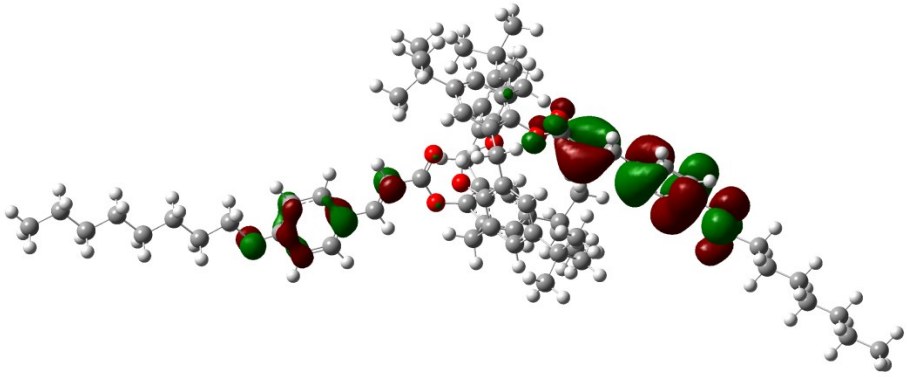
Figure S_7: Optimized geometry and HOMO and LUMO frontier molecular orbitals of the compounds **$1d_8$-l** and **$1d_8$-1l** at the B3LYP/6-31G (dp) level (some part of alkyl chain is omitted for clear view in HOMO and LUMO orbitals).

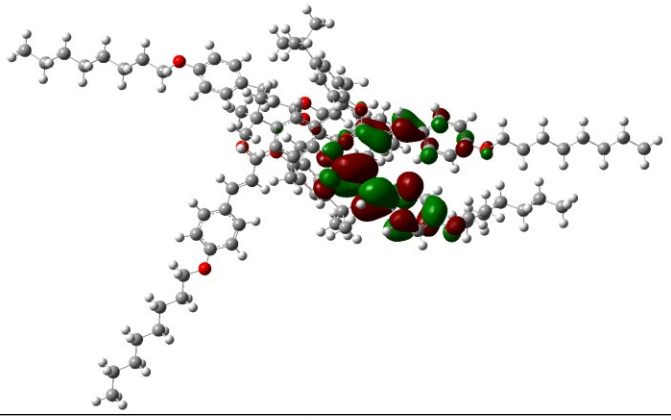
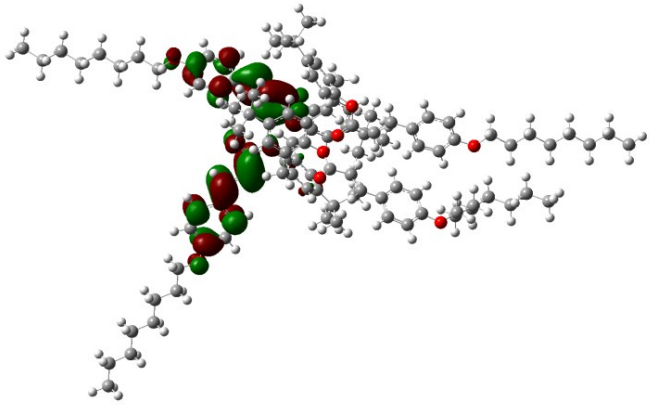
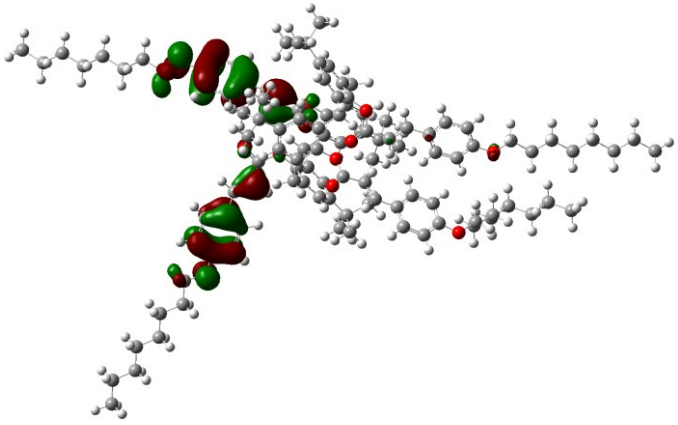
Table S_4: Frontier molecular orbitals of comp.**$1d_5$-l**, **$1d_5$-ll**, **$1d_8$-l** and **$1d_8$-ll** at the B3LYP/6-31G (dp) level.

$1d_5$-l	**Orbital Energy**	**Orbital diagram**
LUMO+1	-1.49 eV	
LUMO	-1.52 eV	
HOMO	-5.32 eV	

HOMO-1	-5.42 eV	

1d_8-ll	**Orbital Energy**	**Orbital diagram**
LUMO+1	-1.46 eV	
LUMO	-1.79 eV	

HOMO	-5.21 eV	
HOMO-1	-5.28 eV	

$1d_8$-l	Orbital Energy	Orbital diagram
LUMO+1	-1.48 eV	
LUMO	-1.52 eV	
HOMO	-5.31 eV	

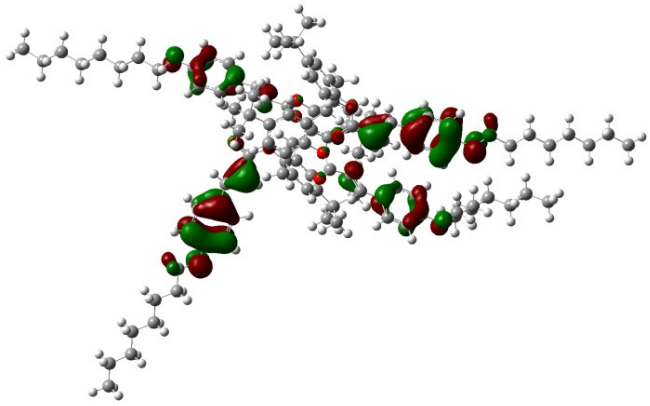
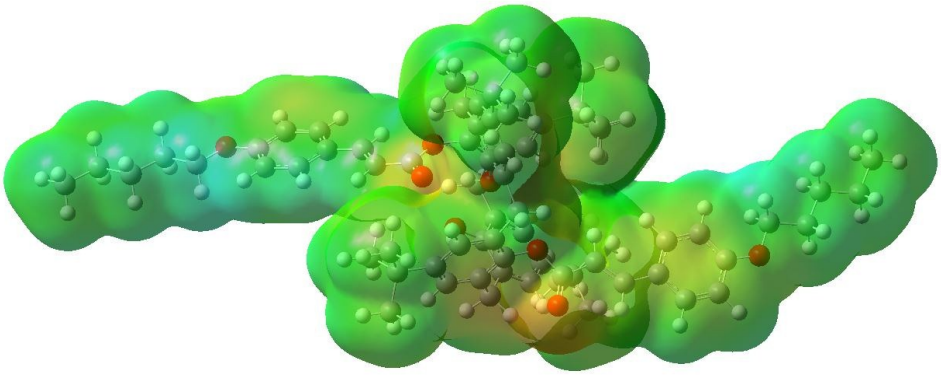
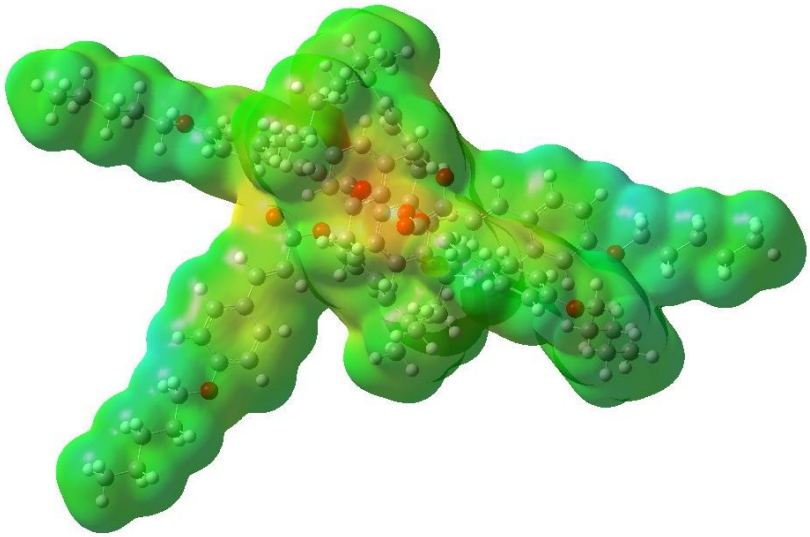
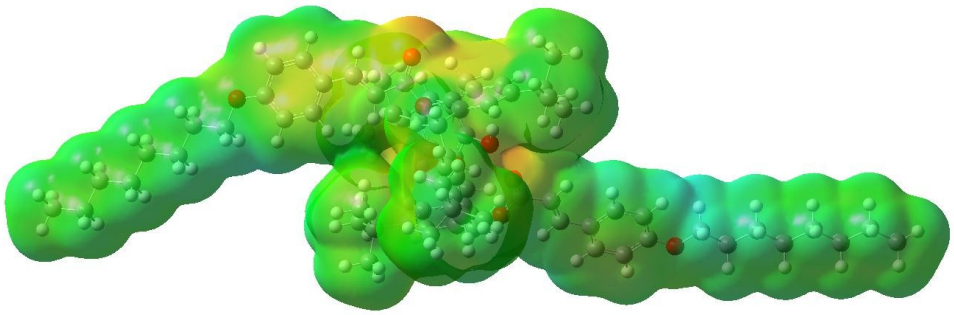
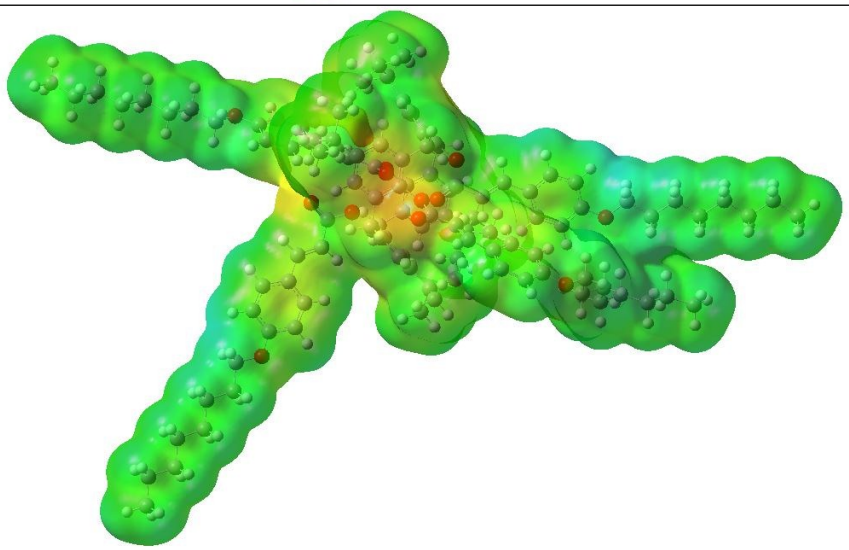
HOMO-1	-5.42 eV	

Table S_5: Molecular electrostatic potential (MEP) diagram of comp.**$1d_5$-ll**, **$1d_8$-ll** (series-2) and comp.**$1d_5$-l**,**$1d_8$-l** (series-1).

$1d_5$-ll	
$1d_5$-l	

$1d_8$-ll	
$1d_8$-l	

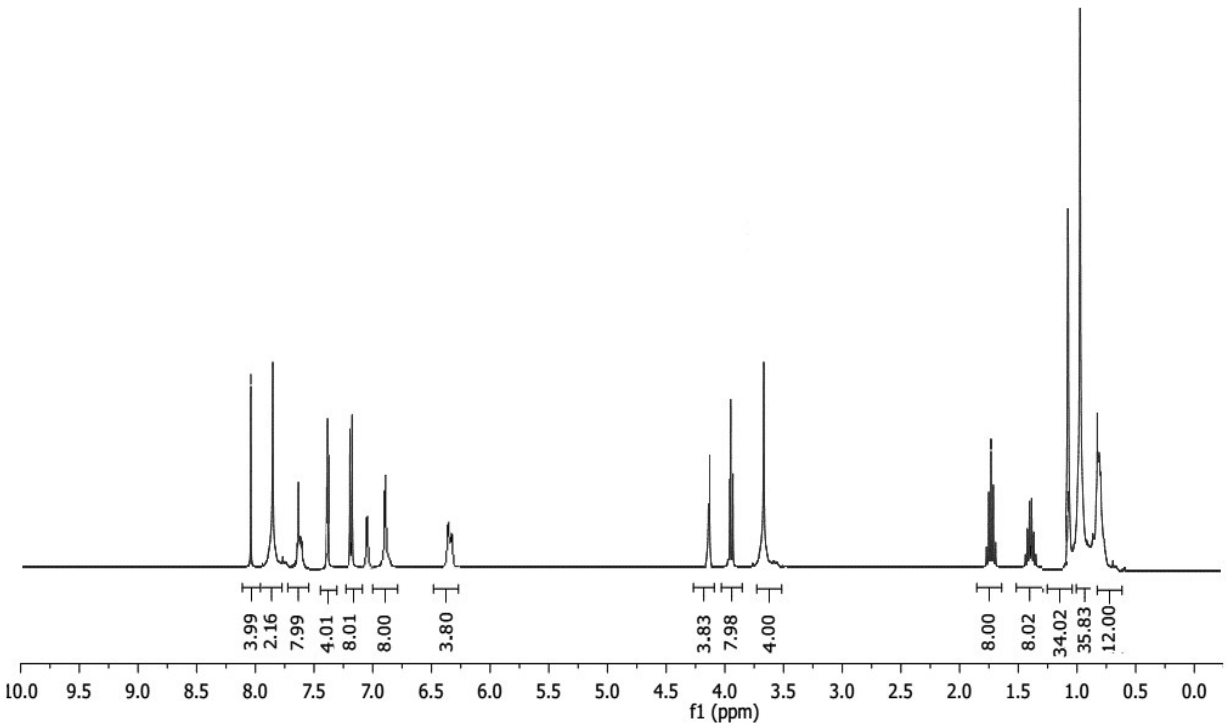


Figure S_8: ^{1}H NMR of compound 1d_{10}-l (series-1)

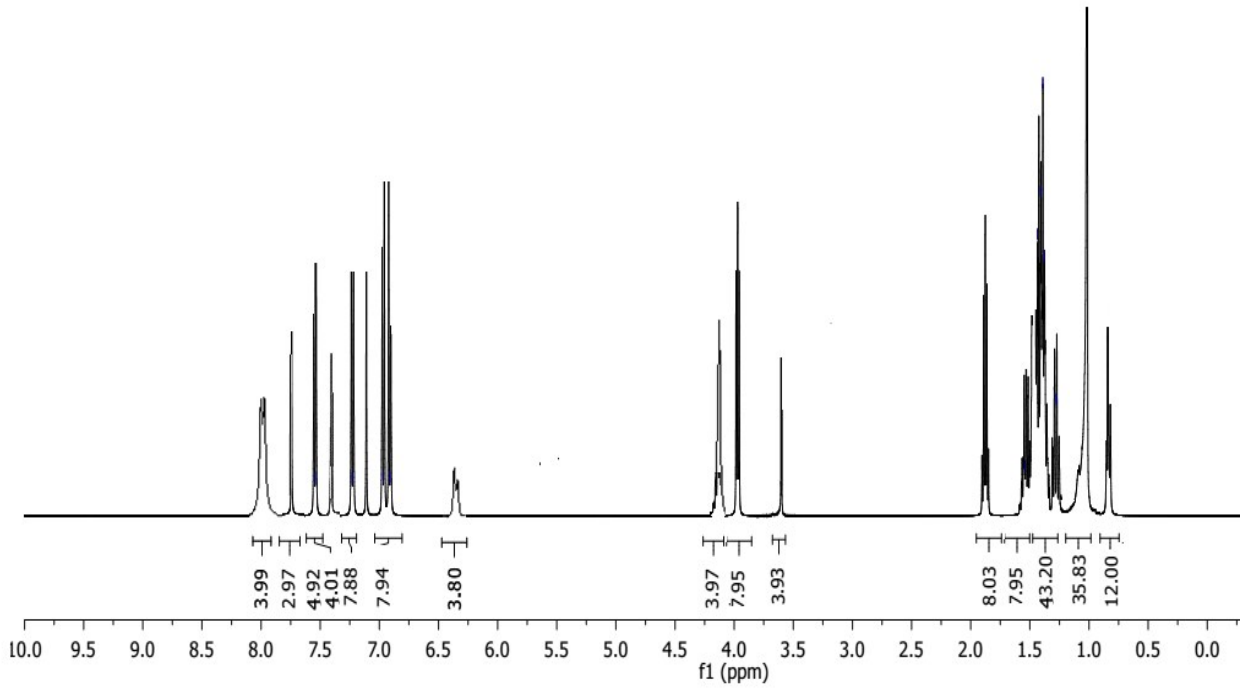


Figure S_9: ^{1}H NMR of compound 1d_{12}-l (series-1)

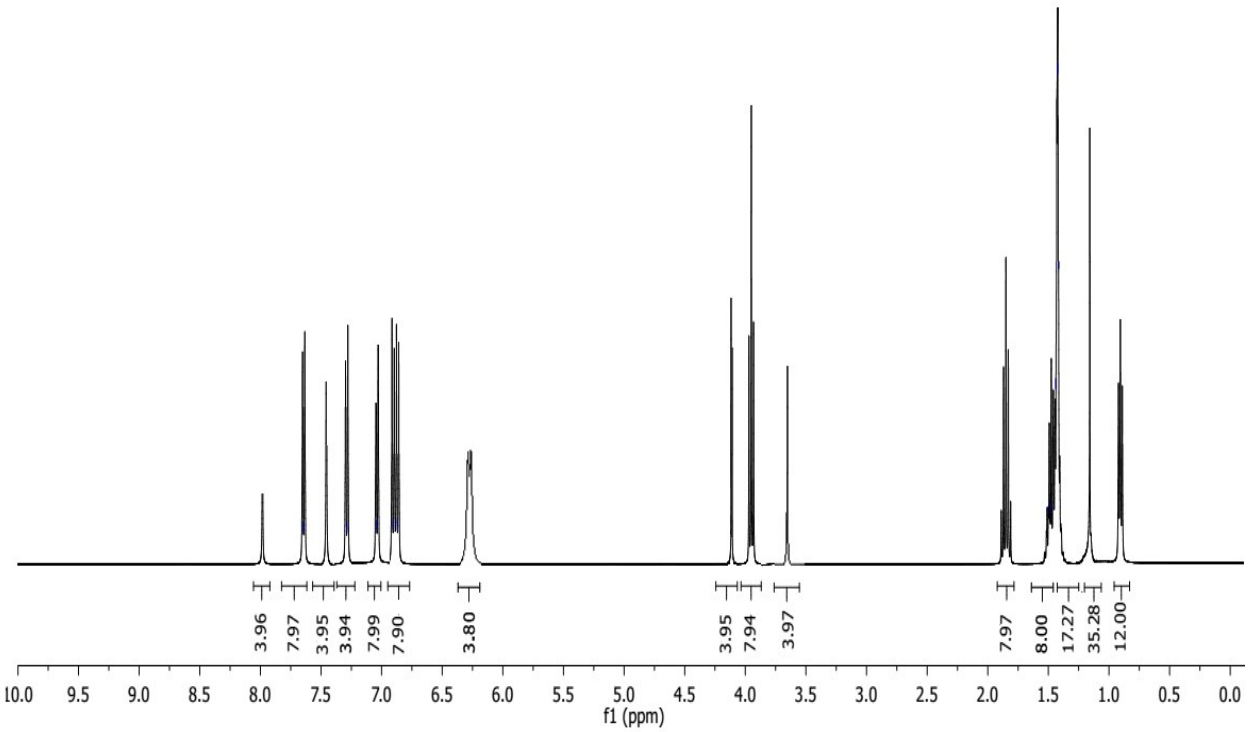


Figure S_{10}: ^{1}H NMR of compound $1d_8$-l (series-1)

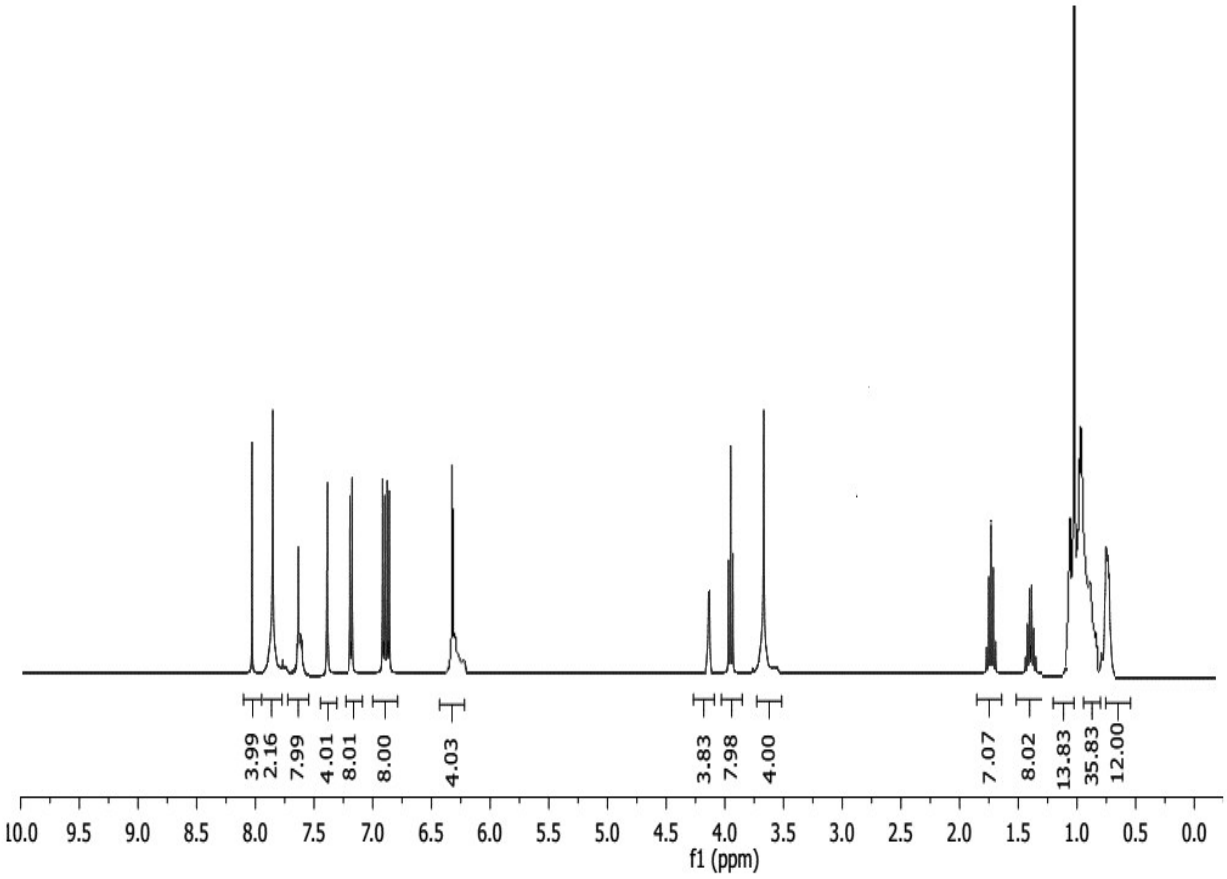


Figure S_{11}: ^{1}H NMR of compound $1d_5$-l (series-1)

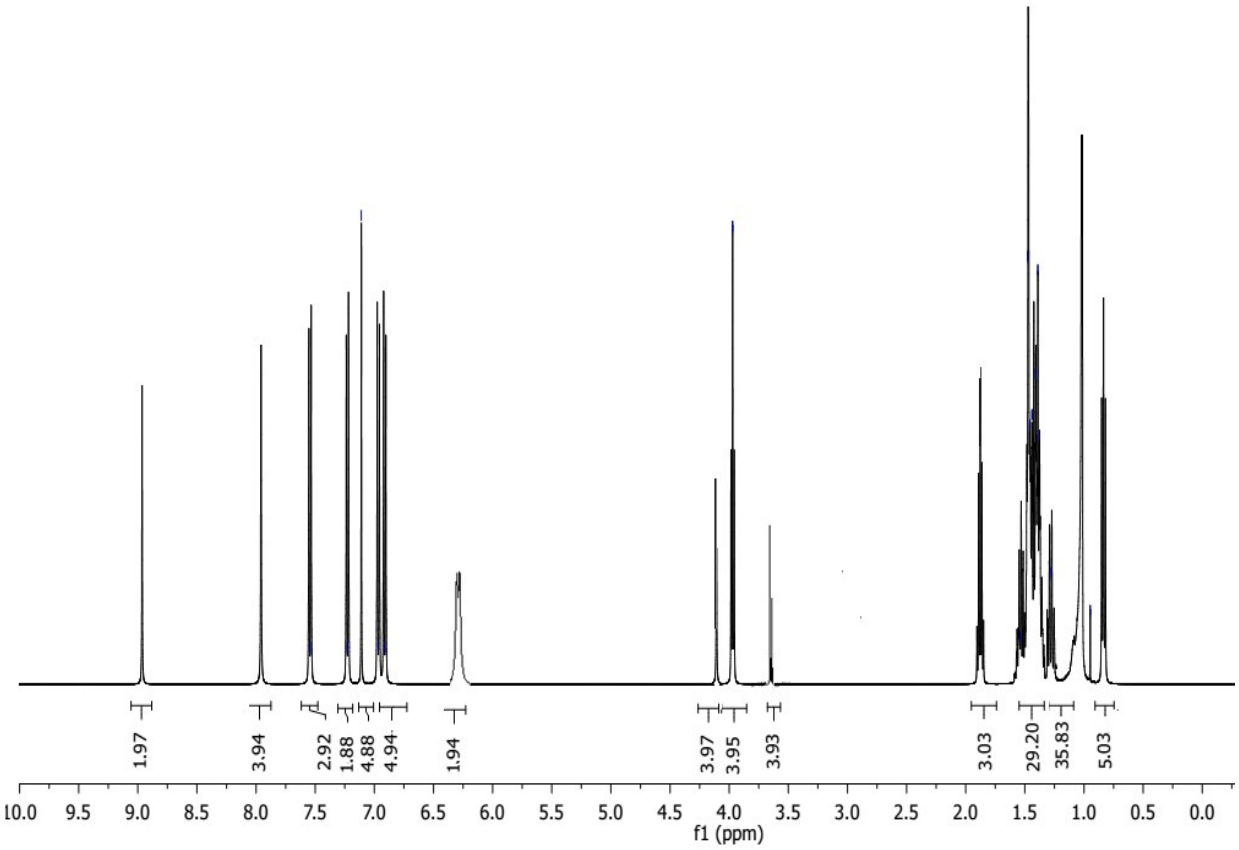


Figure S_{12}: ^{1}H NMR of compound $1d_{12}$-ll (series-2)

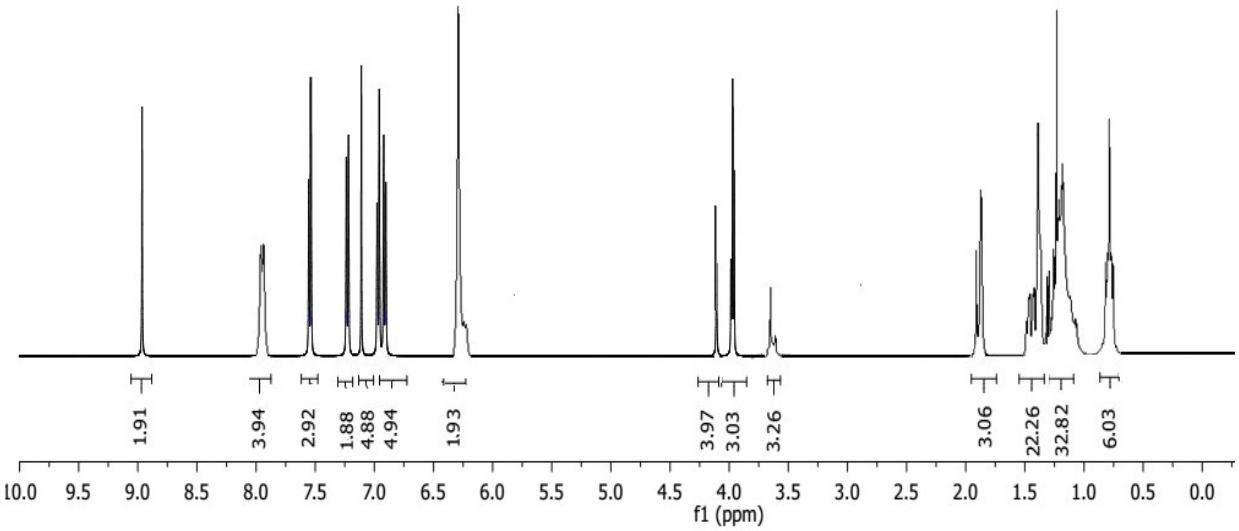


Figure S_{13}: ^{1}H NMR of compound $1d_{10}$-ll (series-2)

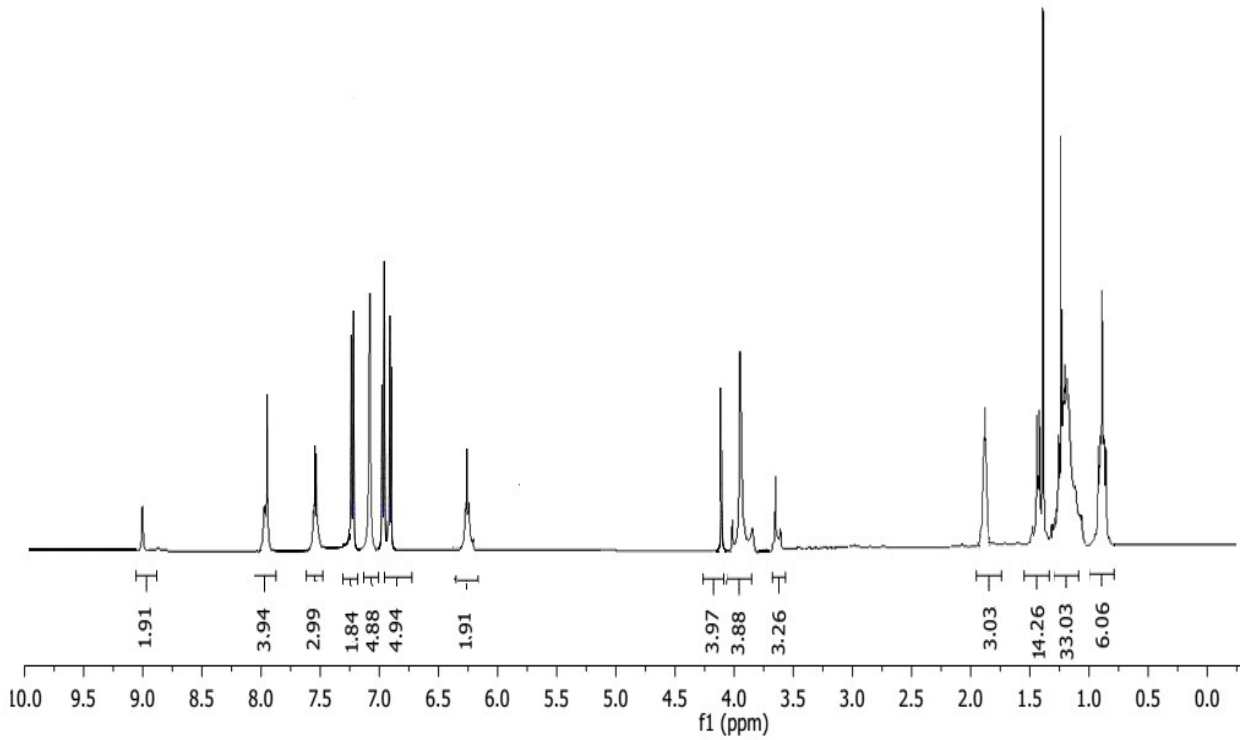


Figure S_{14}: ^{1}H NMR of compound $1d_8$-ll (series-2)

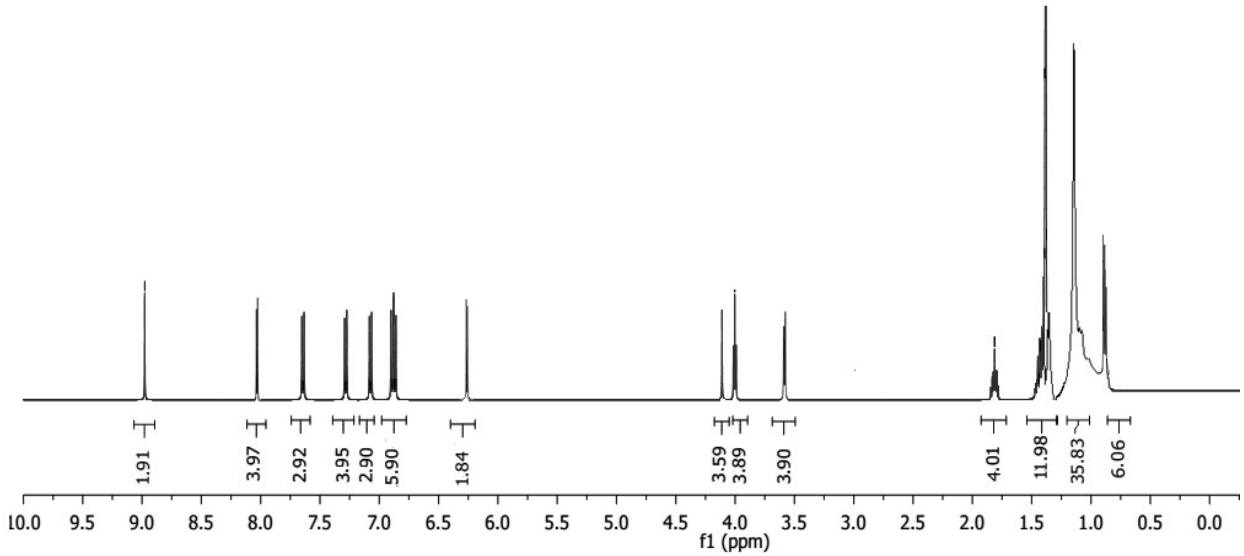


Figure S_{15}: ^{1}H NMR of compound $1d_5$-ll (series-2)

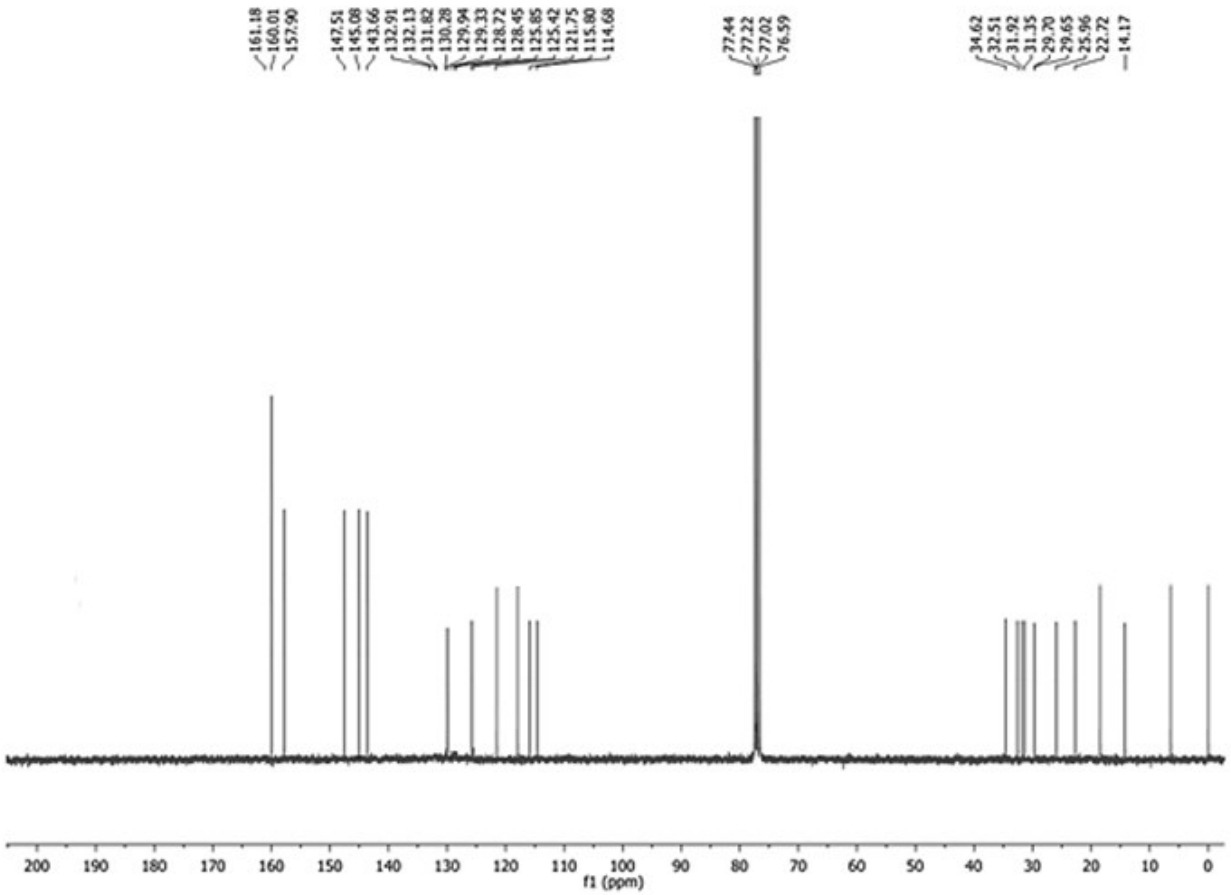


Figure S_{16}: ^{13}C NMR of compound $1d_{12}$-l (series-1)

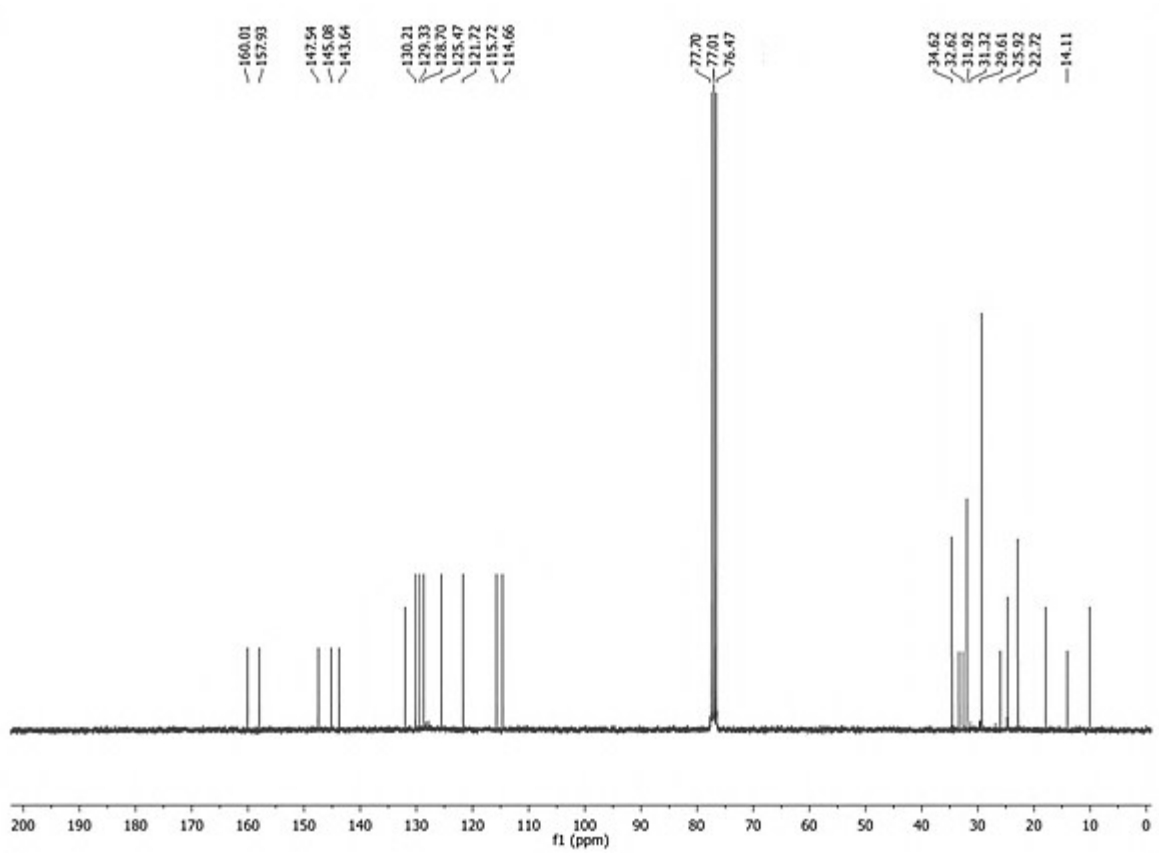


Figure S_{17}: ^{13}C NMR of compound $1d_{10}$-l (series-1)

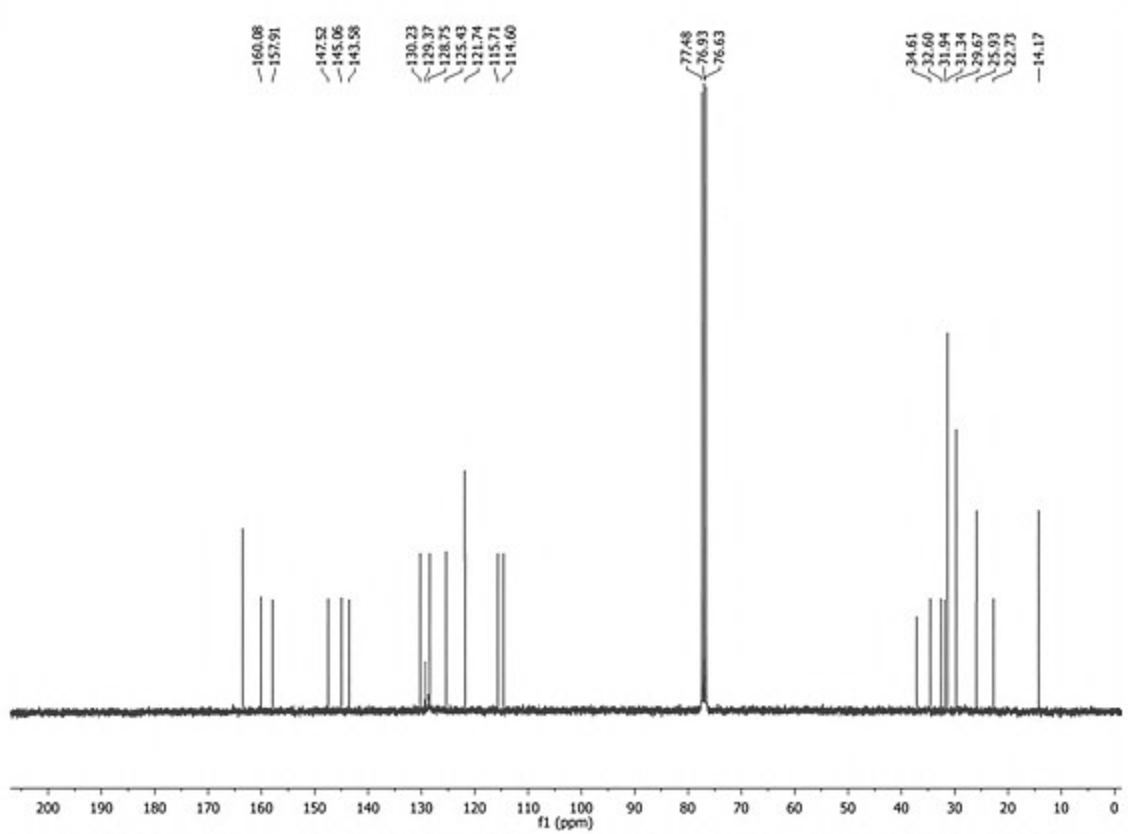


Figure S_{18}: ^{13}C NMR of compound $1d_8$-l (series-1)

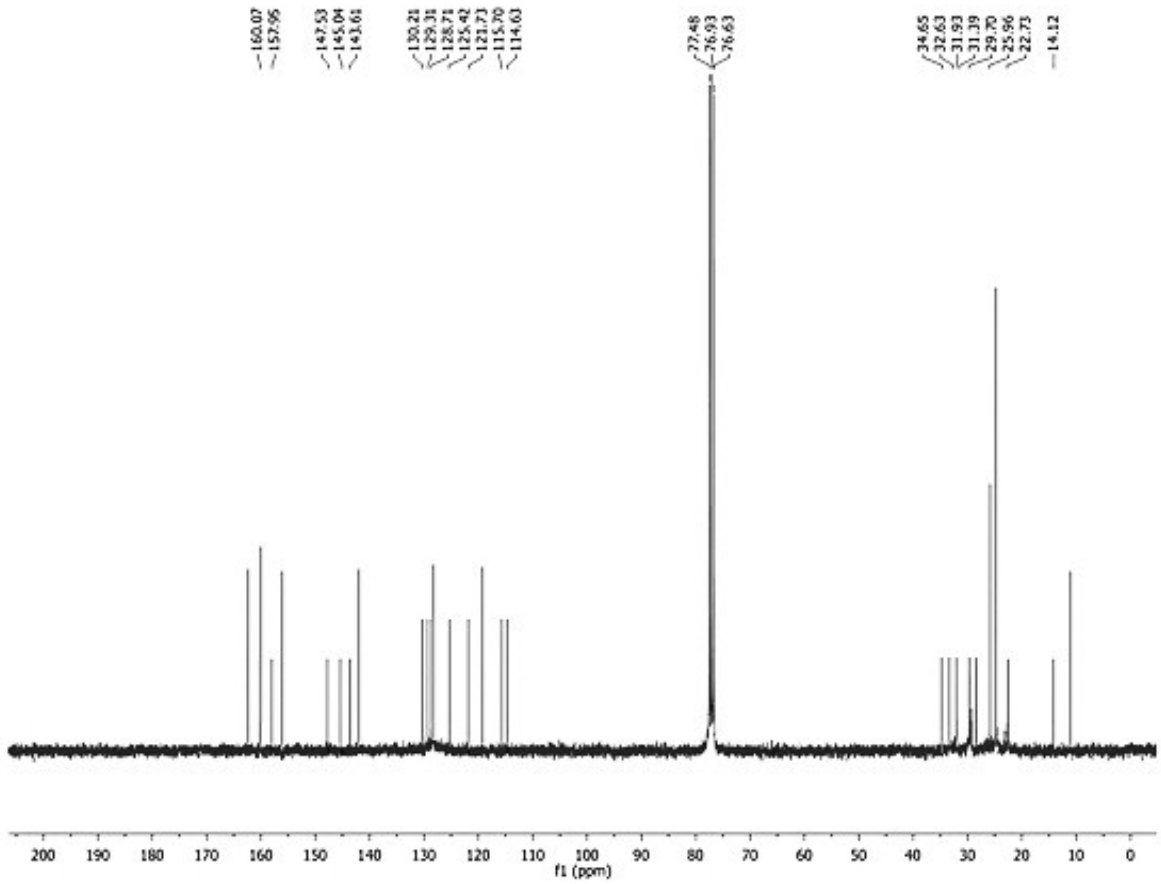


Figure S_{19}: ^{13}C NMR of compound $1d_{12}$-ll (series-2)

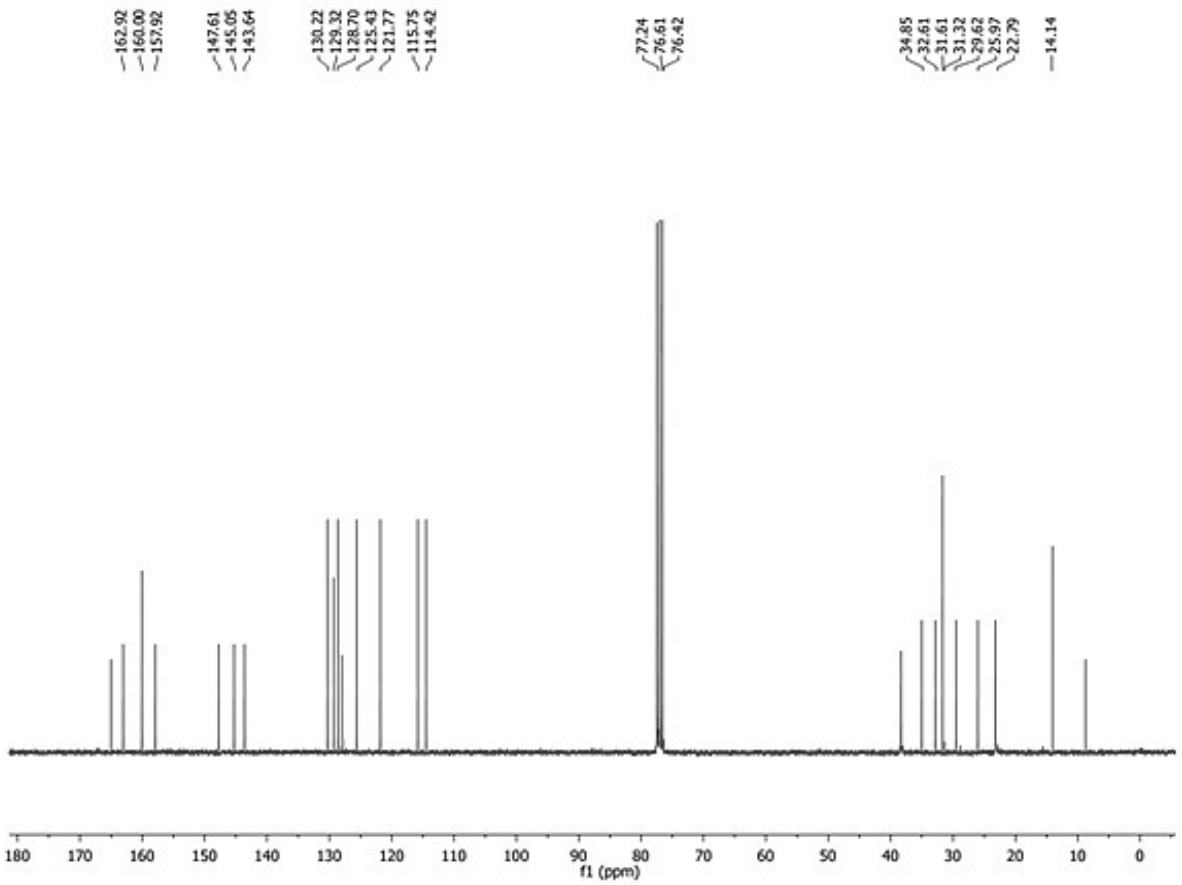


Figure S_{20}: ^{13}C NMR of compound $1d_{10}$-ll (series-2)

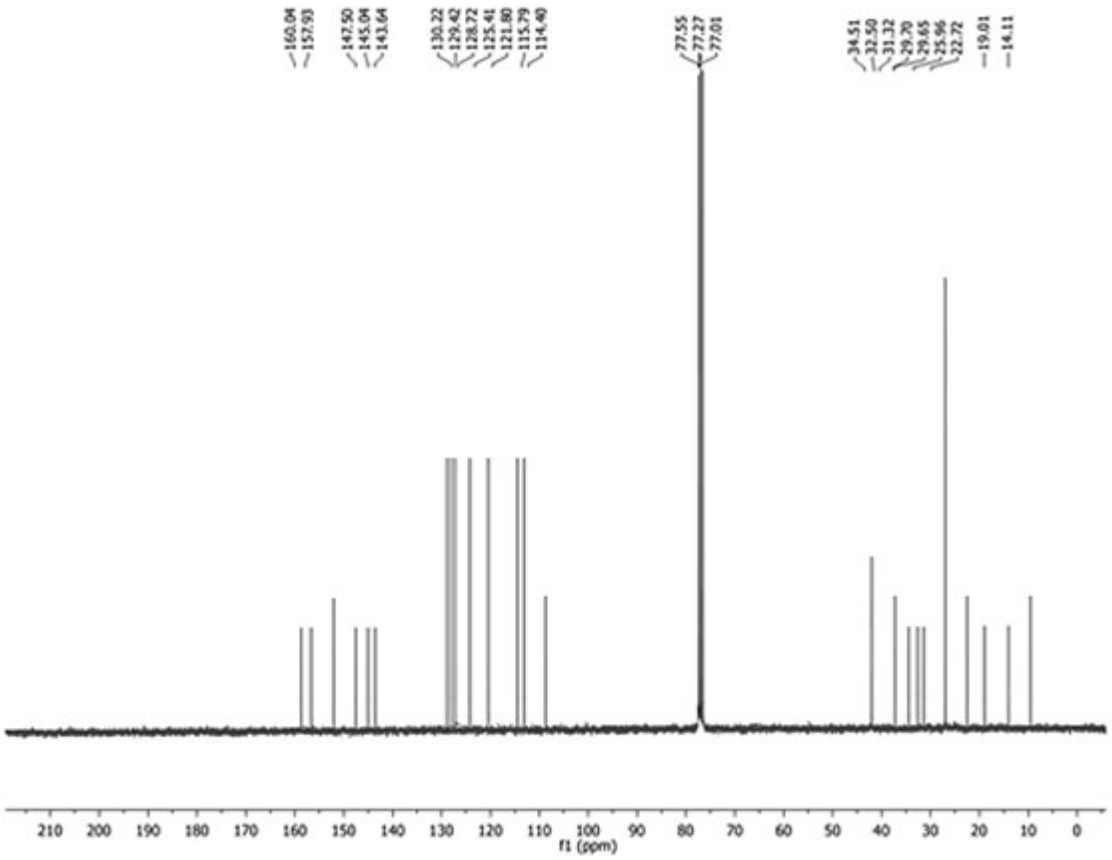


Figure S_{21}: ^{13}C NMR of compound $1d_8$-ll (series-2)

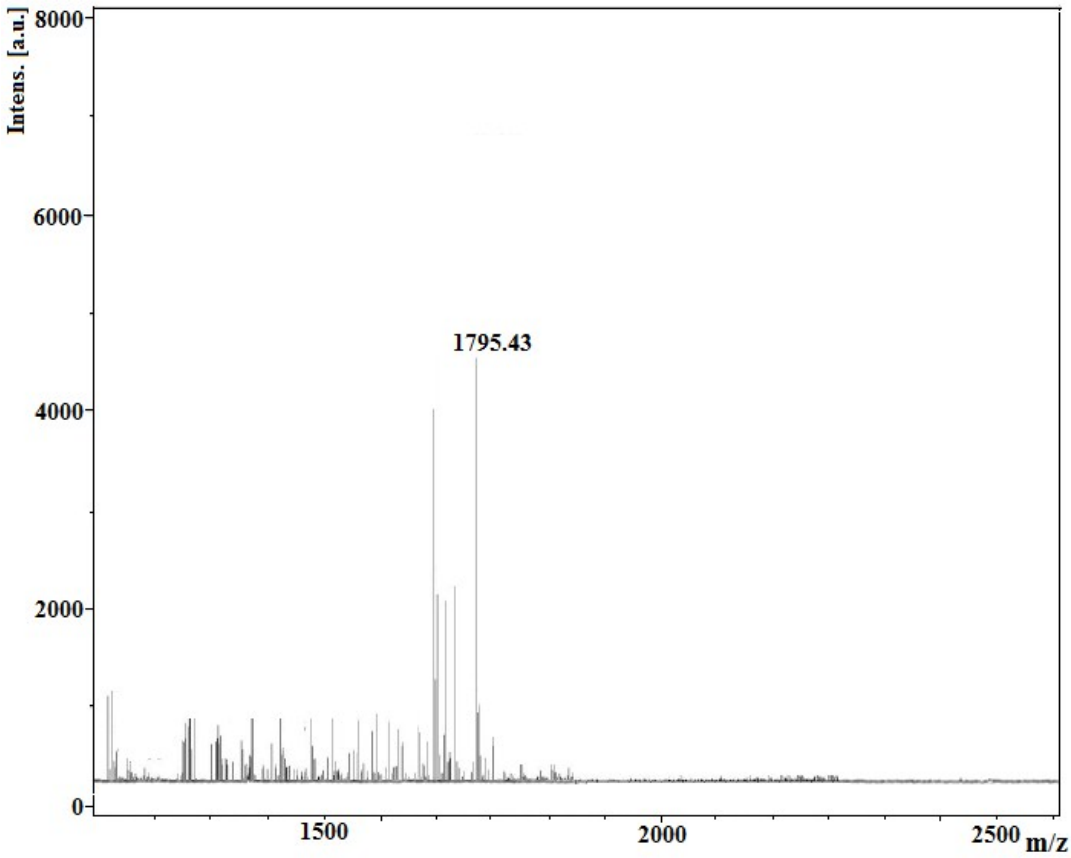


Figure S_{22}: ESI Mass of compound $^{1}d_{10}$-l (series-1)

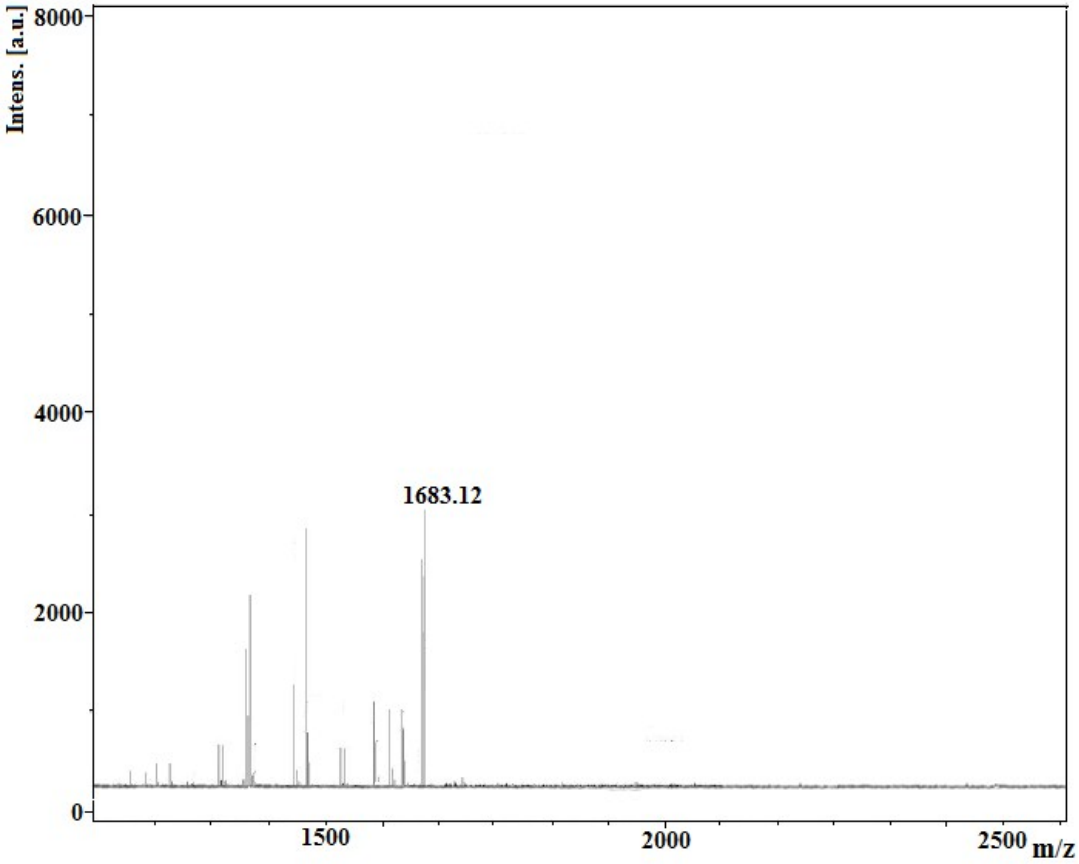


Figure S_{23}: ESI Mass of compound $^{1}d_{8}$-l (series-1)

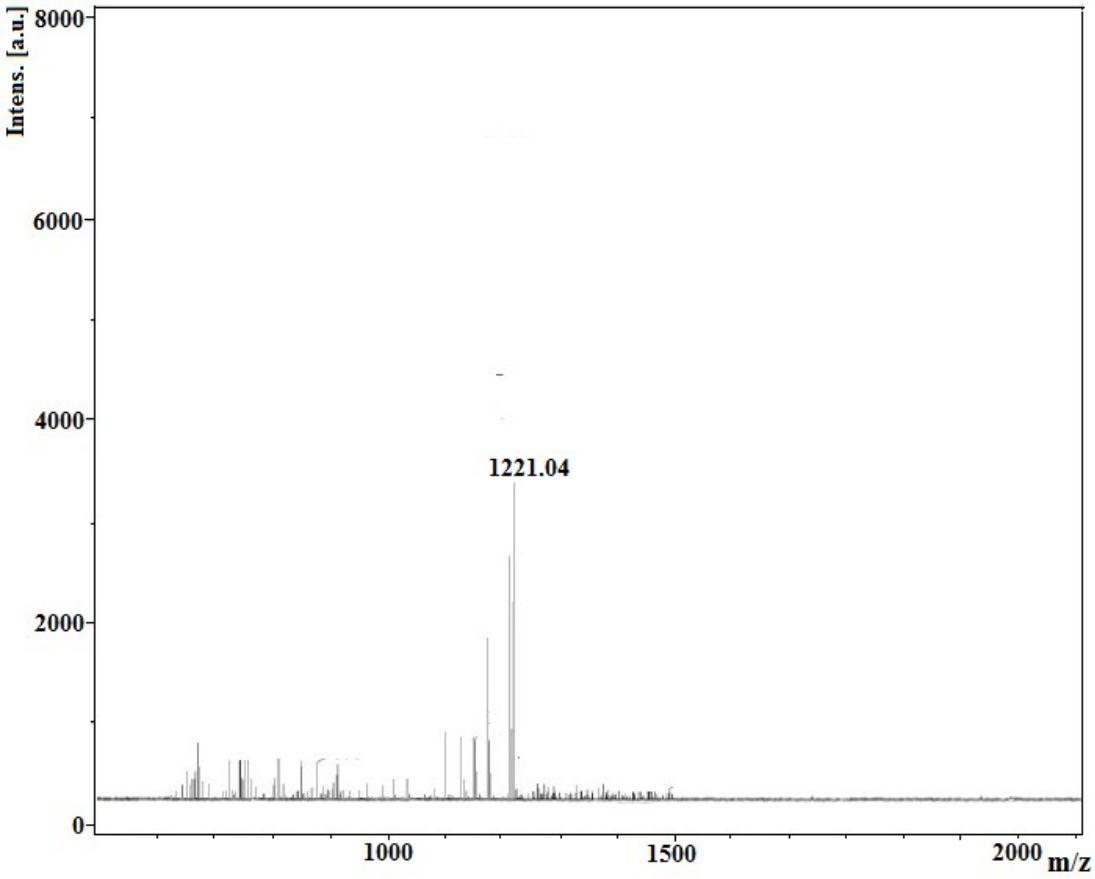


Figure S_{24}: ESI Mass of compound $^{1}d_{10}$-ll (series-2)

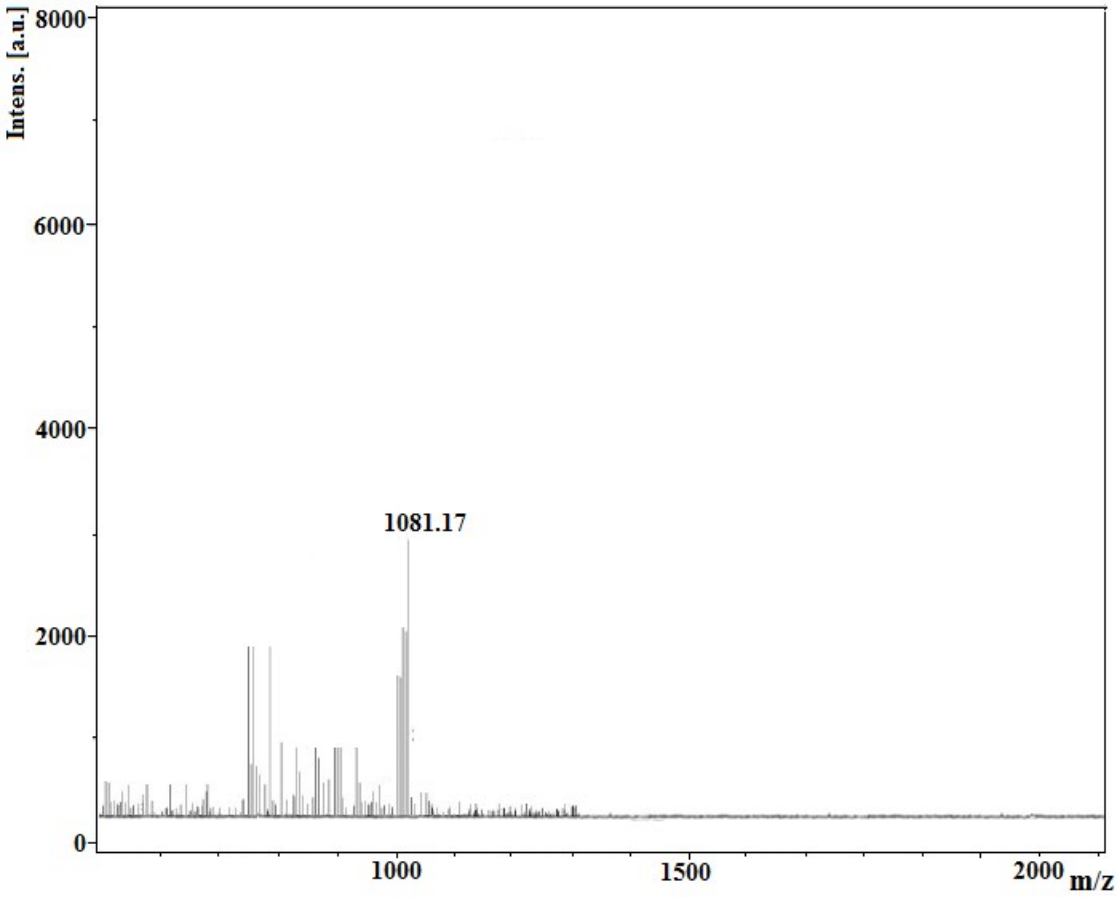


Figure S_{25}: ESI Mass of compound $^{1}d_5$-ll (series-2)

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