Supporting Information

(Revised)

Title: Supramolecular Liquid Crystalline π-Conjugates: The Role of Aromatic π-stacking and van der Waals Forces on the Molecular Self-assembly of Oligo-Phenylenevinylenes

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Synthesis of compounds

Synthesis of 1, 4-bis (1, 8-tricyclodecanemethyleneoxy) benzene (2): Hydroquinone (4.40 g, 0.04 mol) and NaOH (3.2 g, 0.08 mol) were dissolved in mixture of water (4.8 mL) and ethanol (40 mL). TCD- tosylate (26.88 g, 0.08 mol) was added and the reaction mixture was refluxed for 24 hours. The reaction mixture was then poured into 100 mL of water, extracted in DCM, washed with 5% NaOH solution, dried over brine and anhydrous sodium sulphate. It was filtered, rotaevaporated and the product was obtained as brown coloured solid. It was purified by passing though silica gel column using 0.5% ethyl acetate in hexane as eluent. Yield: 7.4 g (45 %). Mp: 125-126 °C. ^{1}H NMR δ: ($CDCl_3$, 400MHz): 6.7 (s, 4H, Ar-H); 3.6 (m, 4H, -OCH_2); 2.5-0.88 (cyclic H, 30 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 153.2, 115.4 (Ar-C), 72.8 (Ar-OCH_2), 45.5, 45.2, 43.7, 41.2, 40.1, 34.5, 28.9, 28.0, 26.9, 26.4 (cyclic-C). FT-IR (KBr, cm^{-1}): 2946.4, 2866.8, 2357, 1643, 1508.3, 1466.4, 1390.7, 1282, 1283.9, 1109.5, 1028.5 and 824.5.

Synthesis of 1, 4-bis (bromomethyl)-2, 5-di-(1, 8-tricyclodecanemethyleneoxy) benzene (3): 1,4-bis(1,8-tricyclodecanemethyleneoxy)benzene (3.0 g, 7.39 mmol) and *p*-HCHO (0.88 g, 29.3 mmol) were taken in 100 ml of glacial acetic acid and HBr in glacial acetic acid (5.5ml, 20.35mmol) was added to it using a pressure equalizing funnel . The reaction mixture was then refluxed for 8 hours, cooled to room temperature and poured into large amount of water. The product precipitated as a white solid, which was repeatedly washed with cold water to remove any acidic impurities. This white solid was filtered and recrystallised to obtain pure product. Yield: 4.1 g, 95 %. M.p. =135-136 °C. ^{1}H NMR ($CDCl_3$, 400Hz) δ: 6.8 (s, 2H, aromatic), 4.5 (s, 4H, -CH_2Br), 3.7 (m, 4H, -OCH_2), 2.5-1 (m, 30H, cyclic H and aliphatic H). ^{13}C NMR δ: ($CDCl_3$, 100 MHz): 150.6, 127.5, 114.7 (Ar-C), 72.9 (Ar-OCH_2), 45.6, 45.2, 43.8, 41.3, 40.3, 34.6, 29.0, 28.7, 27.9, 27.0, 26.5 (cyclic-C). FT-IR (KBr, cm^{-1}): 2946.0, 2863.4, 1510.05, 1442.9, 1405.9, 1313.6, 1225.8, 1028.6 and 688.

Synthesis of 1, 4-bis (tricyclodecanemethyleneoxy)-2, 5-Xylenetetraethyldiphosphonate(4): 1,4-bis(bromomethyl)-2,5-di-(1,8-tricyclodecanemethyleneoxy)benzene(2.9 g, 5mmoL) and triethyl phosphite (1.66 g, 10 mmol) were refluxed at 150 °C and excess triethyl phosphite was

removed by applying high vacuum. The product separated as thick yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.8 (s, 2H, Ar-H), 3.9 (m, 8H, -PO-OCH_2), 3.6 (m, 4H, Ar-OCH_2), 3.2 (m, 4H, Ar-CH_2P), 2.5-0.8 (m, 42H, aliphatic). ^{13}C-NMR ($CDCl_3$, 100 MHz): 150.3, 119.4, 115 (Ar-C), 72.9 (Ar-OCH_2), 61.9(P-O-C), 45.6, 45.2, 43.8, 41.3, 40.3, 34.6, 29.0, 28.7, 27.9, 27.0, 26.5 ppm(cyclic-C and aliphatic carbon). FT-IR (cm^{-1}): 2944.8, 1515.9, 1472.1, 1395.8, 1247.2, 1219.2, 1032.8, 957.5, 900.05, 831.9, 646.3 and 533.4

Synthesis of OPVs: All the OPVs were prepared by Wittig reaction of compound-4 with corresponding 4- alkoxybenzaldehydes as described for OPV-10. OPVs were also purified by passing though silica gel column using 1 % ethyl acetate in hexane as eluent.

OPV-0: Compound 4 (1.10 g, 1.6 mmol) and benzaldehyde (0.41 g, 3.9 mmol). Yield = 0.22 g (36 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.53-6.97 (m, 16H, Ar-H and vinylic H), 3.80-3.67(m, 4H, Ar-OCH_2), 2.41-0.98 (m, 30H,cyclic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 151.3, 138.1, 129.1, 128.7, 127.7, 126.8, 126.5, 123.8, 111.3 (Ar-C), 73.7 (Ar-OCH_2-TCD) 45.7, 45.3,44.1,41.4, 34.8, 32, 29.7, 29.5, 29.4, 29.17, 28.1, 26.6. FT-IR (KBr, cm^{-1}): 2930.2, 2862.1, 1493.9, 1420.2, 1258.79, 1188.9, 1095.01, 804.1 and 688.2. MALDI-TOF-TOF-MS (MW=610.349): m/z = 610.38

OPV-1: Compound 4 (0.47 g, 66.0 mmol) and 4-methoxybenzaldehyde (0.18 g, 132 mmol). Yield = 0.30 g (67 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.46 (d, 4H, Ar-H), 7.27 (d, 2H, CH=CH), 7.14 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.90 (d, 4H, Ar-H), 3.99 (s, 6H, Ar-O**H$_3$**), 3.82-3.75 (m, 4H, Ar-O**H**$_2$-TCD), 2.5-0.88 (m, 30H, cyclic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 159.1, 151.1, 130.8, 128.3, 127.7, 126.6, 121.6, 114.1, 111.0 (Ar-C), 73.6 (Ar-OCH_3), 55.3(Ar-OCH_2-TCD) 45.6, 45.2, 43.9, 41.2, 34.7, 29.05,27.9, 27.0 and 26.5. FT-IR (KBr, cm^{-1}): 2924.45, 2862.1, 1605.02, 1510.87, 1493.9, 1420.2, 1188.64, 1095.43, 971.82, 849.72, and 816.88. . MALDI-TOF-TOF-MS (MW= 670.92): m/z = 670.380

OPV-2: Compound 4 (0.47 g, 66.0 mmol) and 4-ethoxybenzaldehyde (0.20 g, 132 mmol). Yield = 0.29 g (62 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.29 (d, 2H, CH=CH), 7.13 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 4.06 (t, 4H, Ar-O**H**$_2$-alkyl), 3.82-3.75

(m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 36H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.5, 151.2, 130.8, 128.5, 127.7, 126.8, 121.7, 114.8, 111.1 (Ar-C), 73.7 (Ar-OCH_2-alkyl), 68.2 (Ar-OCH_2-TCD) 45.8, 45.3,44.1, 41.4, 34.8, 29.2, 28.1, 27.1, 26.6, and 14.9. FT-IR (KBr, cm^{-1}): 2994.45, 2867.1, 1604.02, 1510.87, 1493.9, 1420.2, 1188.64, 1095.43, 971.82, 849.72, and 816.88. . MALDI-TOF-TOF-MS (MW=698.97): m/z = 698.400

OPV-3: Compound 4 (0.47 g, 66.0 mmol) and 4-propoxybenzaldehyde (0.22 g, 132 mmol). Yield = 0.33 g (67%). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.44 (d, 4H, Ar-H), 7.27 (d, 2H, CH=CH), 7.13 (d, 2H, CH=CH), 7.04 (s, 2H, Ar-H), 6.88 (d, 4H, Ar-H), 3.94 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.81-3.74 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 40H, cyclic-H and aliphatic-H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 158.7, 151.2, 130.8, 128.5, 127.7, 126.8, 121.6, 114.8, 111.1 (Ar-C), 73.7 (Ar-OCH_2-), 68.6 (Ar-OCH_2-TCD) 45.8, 45.3, 44.1, 40.4, 34.8, 29.1, 28.1, 27.1, 26.6, 22.7, and 10.6. FT-IR (KBr, cm^{-1}): 2924.45, 2862.1, 1605.0, 1510.8, 1493.9, 1420.2, 1188.6, 1095.43, 971.82, 849.72, and 816.88. MALDI-TOF-TOF-MS (MW=727.02): m/z = 726.490

OPV-4: Compound 4 (0.47 g, 66.0 mmol) and 4-butoxybenzaldehyde (0.24 g, 132 mmol). Yield = 0.30 g (60 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.29 (d, 2H, CH=CH), 7.14 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.99 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 44H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 130.8, 128.5, 127.7, 126.7, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2-D), 68.2 (Ar-OCH_2-TCD) 45.8, 45.4,44.1, 34.8,32, 29.7,29.5, 29.4, 29.17, 28.1, 26.6, 26.1, 22.4, and 14.1. FT-IR (KBr, cm^{-1}): 2944.0, 2867.1, 1604.0, 1510.6, 1493.9, 1420.2, 1188.6, 1095.4, 971.8, 849.7, and 816.8. MALDI-TOF-TOF-MS (MW =755.08): m/z = 754.470

OPV-5: Compound 4 (0.47 g, 66.0 mmol) and 4-(pentyloxy)benzaldehyde (0.25 g, 132 mmol). Yield = 0.35g (67 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.37 (d, 4H, Ar-H), 7.22 (d, 2H, CH=CH), 7.07 (d, 2H, CH=CH), 6.98 (s, 2H, Ar-H), 6.82 (d, 4H, Ar-H), 3.90 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.68-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 48H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 130.8, 128.3, 127.5, 126.6, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2), 67.7 (Ar-OCH_2-TCD) 45.6, 45.2,43.9, 41.3, 40.3, 34.7, 32, 29.7,29.1, 27.9, 27.01, 26.5, 19.2 and 13.8. FT-IR (KBr, cm^{-1}): 2935.4, 2863.6, 2363.9, 1605.0, 1510.8, 1467.8,

1384.1, 1245.8, 1174.2, 1021.6, 971.8, 847.7, and 809.2.MALDI-TOF-TOF-MS (MW= 783.13): m/z = 782.520

OPV-6: Compound 4 (0.47 g, 66.0 mmol) and 4-(hexyloxy)benzaldehyde (0.27 g, 132 mmol). Yield = 0.34 g (63 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.28 (d, 2H, CH=CH), 7.14 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.98 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 52H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 130.8, 128.4, 127.6, 126.6, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2-), 68.2 (Ar-OCH_2-TCD) 45.6, 45.3,43.9, 41.3, 34.8, 31.6, 29.2, 29.1, 27.9, 27.01, 26.5, 25.7, 22.6, and 14.04. FT-IR (KBr, cm^{-1}): 2943.4, 2864.7, 2363.9, 1604.8, 1511.1, 1467.8, 1384.1, 1246.8, 1174.8, 1026.1, 971.8, 847.7, and 809.2. MALDI-TOF-TOF-MS (MW=811.18): m/z = 810.550

OPV-7: Compound 4 (0.47 g, 66.0 mmol) and 4-(heptyloxy)benzaldehyde (0.29 g, 132 mmol). Yield = 0.37 g (66%). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.29 (d, 2H, CH=CH), 7.13 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.98 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 56H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 130.6, 128.3, 127.5, 126.6, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2-), 68.2 (Ar-OCH_2-TCD), 45.6, 45.2, 43.9, 34.2, 31.6, 29.2, 29.05, 27.98, 27.01, 26.5, 25.7, 22.6 and 14.1. FT-IR (KBr, cm^{-1}): 2930.7, 2859.9, 2363.9, 1604.8, 1510.1, 1467.8, 1384.1, 1244.8, 1174.8, 1026.1, 971.8, 847.7, and 809.2. MALDI-TOF-TOF-MS (MW=839.24): m/z = 838.578

OPV-8: Compound 4 (0.47 g, 66.0 mmol) and 4-(octyloxy)benzaldehyde (0.31 g, 132 mmol). Yield = 0.34g (58 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.26 (d, 2H, CH=CH), 7.13 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.97 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 60H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 130.8, 128.4, 127.6, 126.6, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2-), 68.2 (Ar-OCH_2-TCD), 45.6, 45.2, 43.9, 41.3, 31.8, 29.3, 29.2, 29.1, 27.9, 27.1, 26.03, 22.6,and 14.1. FT-IR (KBr, cm^{-1}): 2926.3, 2857.3, 2360.9, 1604.4, 1510.3, 1467.6,

1422.4, 1384.1, 1246.8, 1174.8, 1026.1, 971.8, 847.7, and 809.2. MALDI-TOF-TOF-MS (MW=867.29): m/z = 866.640

OPV-9: Compound 4 (0.47 g, 66.0 mmol) and 4-(nonyloxy)benzaldehyde (0.33 g, 132 mmol). Yield = 0.46g (77 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.44 (d, 4H, Ar-H), 7.30 (d, 2H, CH=CH), 7.14 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.88 (d, 4H, Ar-H), 3.97 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 64H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 130.8, 128.4, 127.6, 126.6, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2-), 68.2 (Ar-OCH_2-TCD),45.7, 44.1, 41.4, 34.9, 31.9, 29.7, 29.5, 29.3, 29.1, 26.6, 26.1, 22.8 and 14.2. FT-IR (KBr, cm^{-1}): 2925.7, 2856.6, 2363.9, 1604.8, 1510.8, 1467.8, 1384.1, 1245.8, 1174.8, 1026.1, 971.8, 847.7, and 809.1. MALDI-TOF-TOF-MS (MW=895.34): m/z = 894.630

OPV-10: Compound 4 (0.47 g, 66.0 mmol) and 4-(decyloxy)benzaldehyde (0.34 g, 132 mmol). Yield = 0.22 g (36 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.29 (d, 2H, CH=CH), 7.13 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.97 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 68H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.8, 151.2, 130.8, 128.5, 127.7, 126.8, 121.6, 114.8, 111.1 (Ar-C), 73.7 (Ar-OCH_2-), 68.2 (Ar-OCH_2-TCD) 45.8, 45.4,44.1, 34.8,32, 29.7,29.5, 29.4, 29.17, 28.1, 26.6, 26.1, 22.8, and 14.2. FT-IR (KBr, cm^{1}): 2924.45, 2855.64, 1605.02, 1510.87, 1469.77, 1245.62, 1178.64, 1018.43, 971.82, 849.72, and 816.88. MALDI-TOF-TOF-MS (MW=923.40) : m/z = 922.677

OPV-11: Compound 4 (0.47 g, 66.0 mmol) and 4-undecyloxybenzaldehyde (0.36 g, 132 mmol). Yield = 0.44 g (69 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.30 (d, 2H, CH=CH), 7.14 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.98 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 72H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.8, 151.0, 130.8, 128.4, 127.6, 126.6, 121.4, 114.6, 110.9 (Ar-C), 73.6 (Ar-OCH_2-), 68.2 (Ar-OCH_2-TCD),45.7,45.3, 34.9, 32.0, 29.7, 29.5, 29.4, 29.1, 28.1, 27.1, 26.1, 22.8 and 14.2. FT-IR (KBr, cm^{-1}): 2922.8, 2853.9, 2360.6, 1605.1, 1510.2, 1468.3, 1384.1,

1246.8, 1174.8, 1026.1, 971.8, 847.7, and 808. MALDI-TOF-TOF-MS (MW=951.45): m/z = 950.708

OPV-12: Compound 4 (0.53 g, 75.0 mmol) and 4-propoxybenzaldehyde (0.55 g, 190 mmol). Yield = 0.73 g (90 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.22 (d, 2H, CH=CH), 7.14 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.97 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 76H, cyclic-H and aliphatic-H). ^{13}C-NMR($CDCl_3$, 100 MHz) δ: 158.6, 151.0, 128.5, 127.8, 121.6, 114.6, 110.9 (Ar-C), 73.7 (Ar-OCH_2-), 68.1 (Ar-OCH_2-TCD),45.7,45.7, 45.3, 44.09, 41.4, 32.0, 29.9, 29.7, 29.5, 29.4, 29.1, 14.2 and 14.1. FT-IR (KBr, cm^{-1}): 2921.8, 2853.3, 2363.9, 1604.8, 1510.1, 1467.8, 1384.1, 1244.8, 1174.8, 1026.1, 971.8, 847.7, and 809.3. MALDI-TOF-TOF-MS (MW=979.5): m/z = 978.717

OPV-16: Compound 4 (0.47 g, 66.0 mmol) and 4-(hexadecyloxy)benzaldehyde (0.36 g, 132 mmol). Yield = 0.50 g (68 %). ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 7.45 (d, 4H, Ar-H), 7.3 (d, 2H, CH=CH), 7.11 (d, 2H, CH=CH), 7.05 (s, 2H, Ar-H), 6.89 (d, 4H, Ar-H), 3.99 (t, 4H, Ar-OC**H**$_2$-alkyl), 3.82-3.75 (m, 4H, Ar-OC**H**$_2$-TCD), 2.5-0.88 (m, 92H, cyclic-H and aliphatic-H). FT-IR (KBr, cm^{-1}): 2919.4, 2851.7, 2363.9, 1604.8, 1511.1, 1467.8, 1384.1, 1244.7, 1174.8, 1026.1, 971.8, 847.6, and 800. MALDI-TOF-TOF-MS (MW=1091.72): m/z = 1090.997

Table 1. DSC Thermal data of OPVs at 10°/min heating cooling cycle.

OPV-n	**ΔH_m ($kJmol^{-1}$)**	**T_m(K)**	**ΔS_m ($kJmol^{-1}K^{-1}$)**	**$\Delta H_{i\text{-}c/l.c}$ ($kJmol^{-1}$)**	**$T_{ic/l.c}$(K)**	**$\Delta S_{i\text{-}c/l.c}$ ($kJmol^{-1}K^{-1}$)**
OPV-0	28.4	489.7	0.058	-23.3	435.1	-0.054
OPV-1	44.8	505.1	0.089	-34.5	421	-0.082
OPV-2	43.6	506.9	0.086	-37.4	419.1	-0.089
OPV-3	47.5	505.5	0.094	-44.8	466.6	-0.096
OPV-4	127.4	503.01	0.25	-120.3	446.6	-0.27
OPV-5	45.4	478.7	0.095	-44.6	447.9	-0.0996
OPV-6	52.2	467.2	0.11	-43.5	407.9	-0.106
OPV-7	40.2	447.5	0.090	-36.3	385.9	-0.094
OPV-8	91.3	451.7	0.20	-54.7	398.3	-0.137
OPV-9	51.4	444.9	0.115	-44.5	388.3	-0.114
OPV-10	75.6	440.9	0.17	-66	381.0	-0.173
OPV-11	57.0	436.8	0.13	-47.4	380.4	-0.12
OPV-12	120.2	435.6	0.28	-107.4	387.9	-0.28
OPV-16	97.6	413.6	0.24	-100.8	358.1	-0.28

Table 2. Fluorescence decay life time data of OPVs

OPV-n	**τ_1(ns)**	**τ_2(ns)**	**χ^2**
2	0.30	1.19	1.003
3	0.26	1.26	1.010
4	1.19	2.34	1.001
5	0.39	1.36	1.140
6	0.40	1.48	1.001
7	0.27	1.21	1.001
8	0.41	1.95	1.001
9	0.39	1.60	1.056
10	0.33	1.47	1.005
11	0.40	1.62	1.054
12	0.36	1.77	1.020

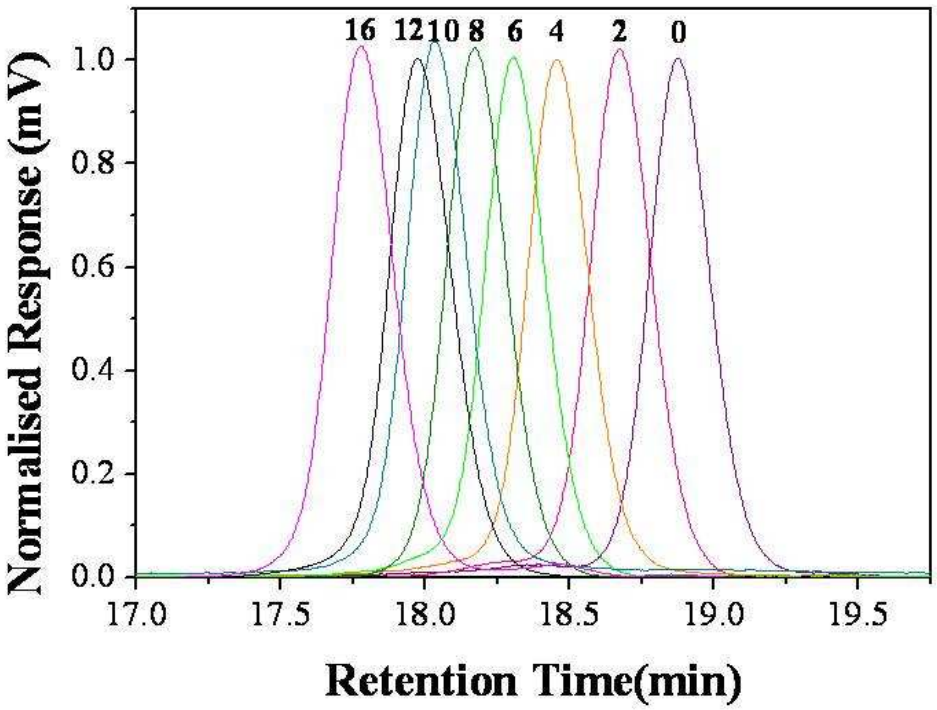


Figure 1. GPC Chromatograms of OPVs in tetrahydrofuran at 25 °C.

Note: GPC Chromatograms of all the OPVs were recorded to check their purity All the chromatograms showed a single peak confirming high purity of these samples. In GPC, higher molecular weight OPVs elute faster than lower molecular weight OPVs and this is beautifully reflected in the above chromatogram showing highest molecular weight OPV-16 to extreme left and lowest molecular weight OPV-0 to the extreme right. All other OPVs fall in between these two extremes and follow the similar trend.

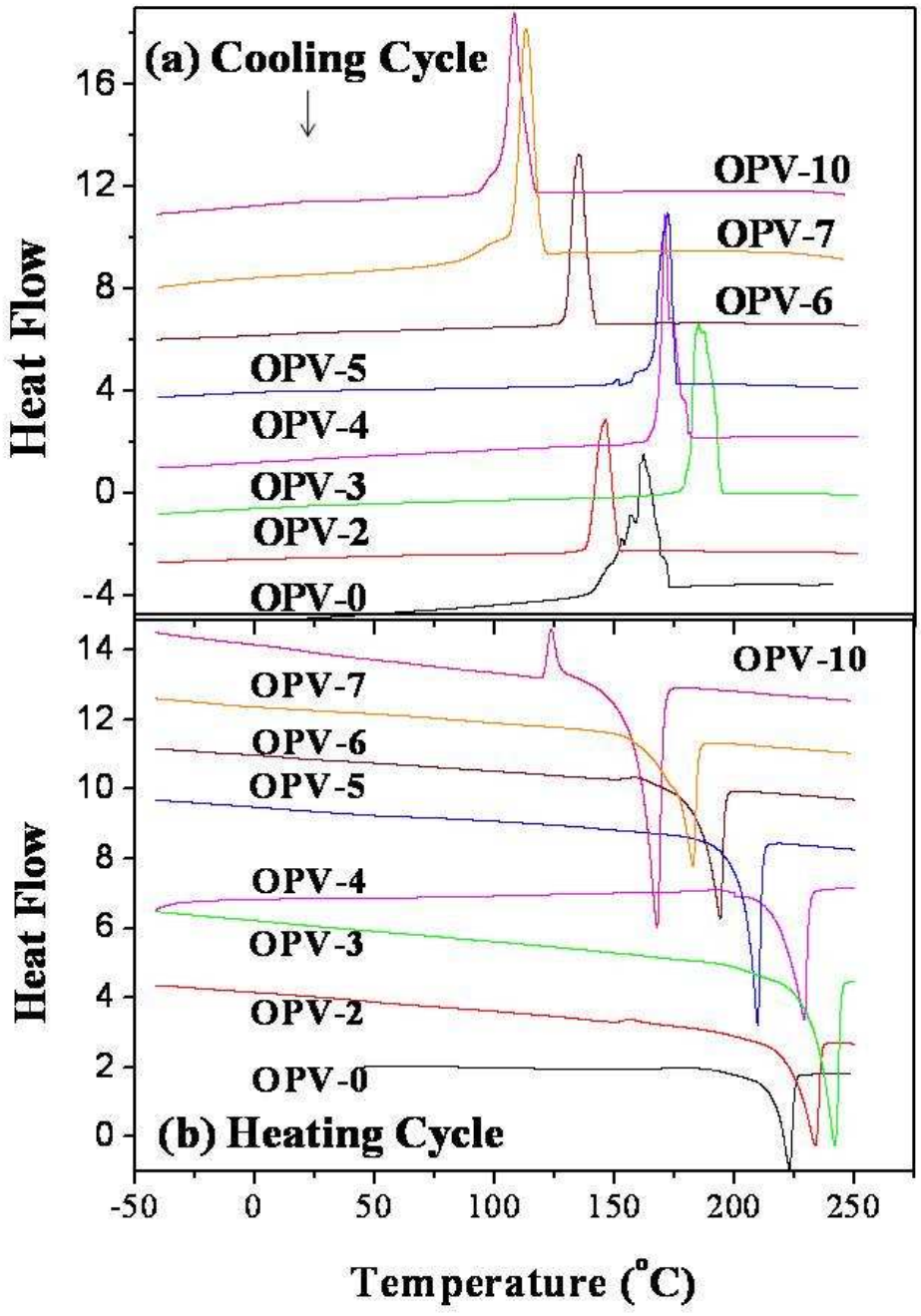


Figure 2. DSC thermograms of OPVs

Note: figure (a) shows the DSC profiles of OPVs in the cooling cycles and the peaks correspond to the temperatures at which OPVs undergo crystalline or LC transitions from their respective isotropic states. OPV-10 shows two peaks at 108 °C and 24 °C which are assigned to LC and Crystalline phase changes. Similar trend is seen in OPV-0, but the LC window is too narrow to effectively resolve the two peaks. Figure (b) shows the DSC profiles of OPVs in the heating cycles and the peaks correspond to the temperatures at which OPVs undergo melting transitions. The melting temperature continuously increases from OPV-7 to OPV-3 but starts to decrease in case of OPV-2 and OPV-0.

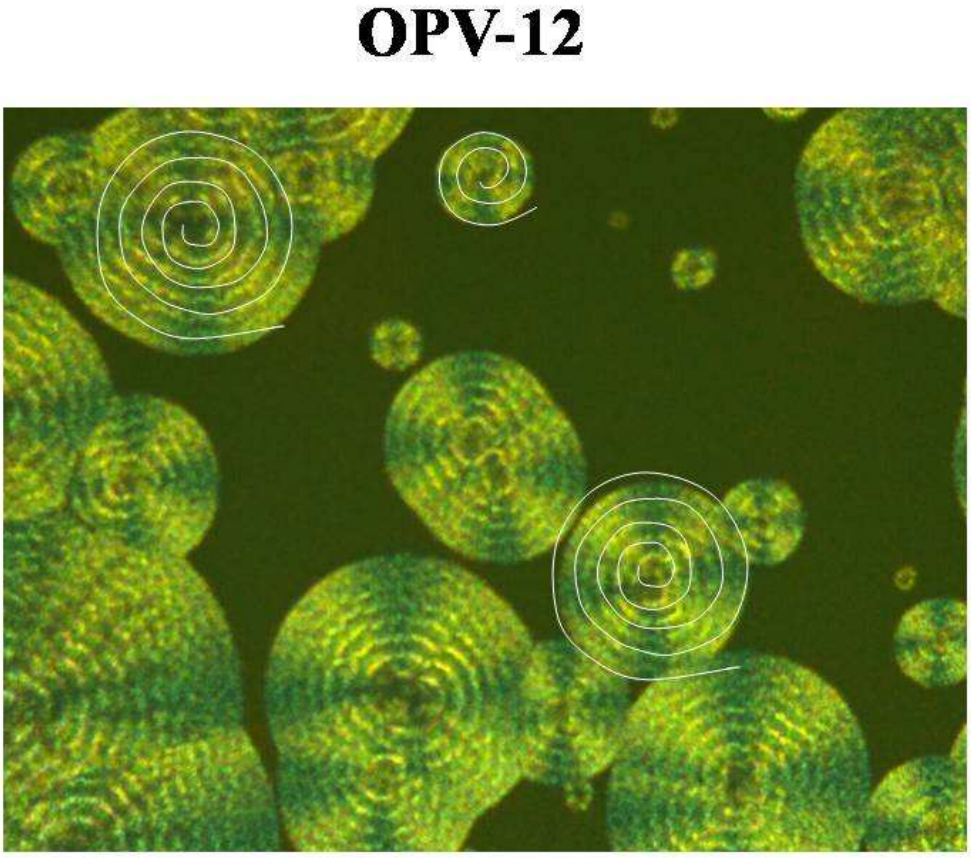


Figure 3. Expanded PLM image of OPV-12 and the lines showed the formation of left-handed helical ring bands.

Note: This PLM image shows the ring banded textures formed when OPV-12 was cooled from its melt at 10°/min on glass cover slips and observed through crossed polarizer's. The lines are drawn on the bright bands, which indicate the left-handed rotation.

OPV-11

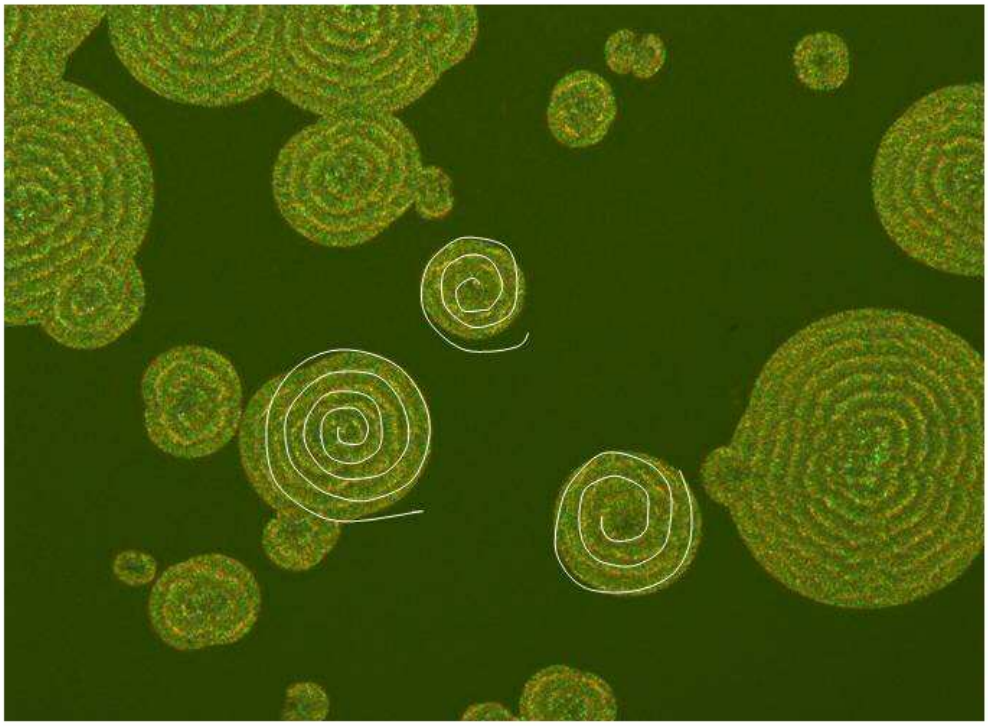


Figure 4. Expanded PLM image of OPV-11 and the lines showed the formation of left-handed helical ring bands.

Note: This PLM image shows the ring banded textures formed when OPV-11 was cooled from its melt at 10°/min on glass coverslips and observed through crossed polarisers. The lines are drawn on the bright bands, which indicate the left-handed rotation.

OPV-10

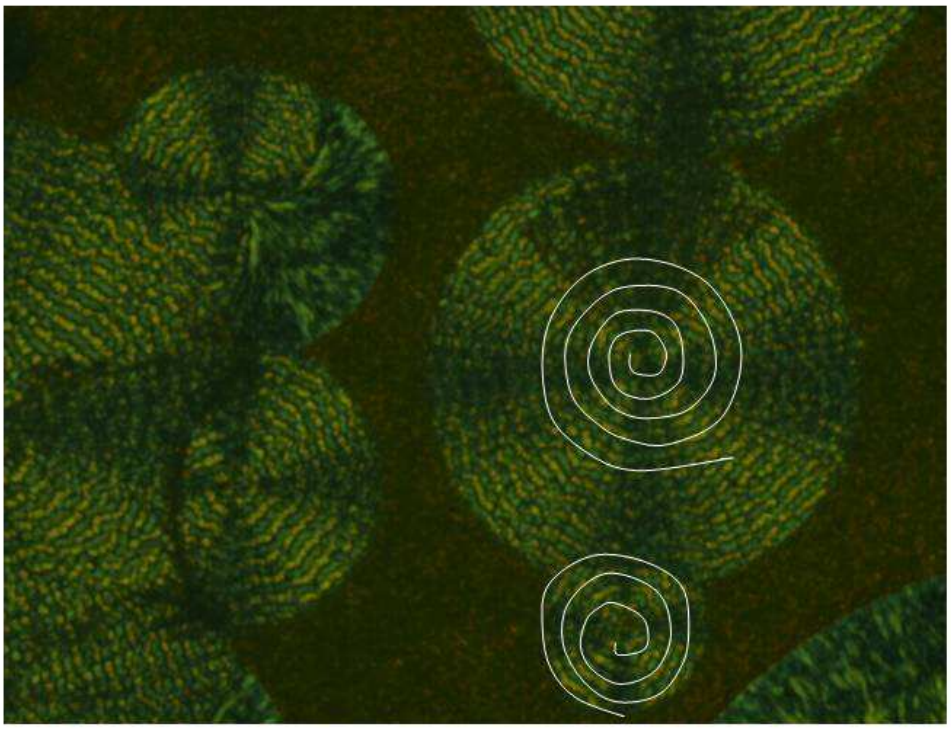


Figure5. Expanded PLM image of OPV-11 and the lines showed the formation of left-handed helical ring bands

Note: This PLM image shows the ring banded textures formed when OPV-10 was cooled from its melt at 10°/min on glass cover slips and observed through crossed polarisers. The lines are drawn on the bright bands, which indicate the left-handed rotation.

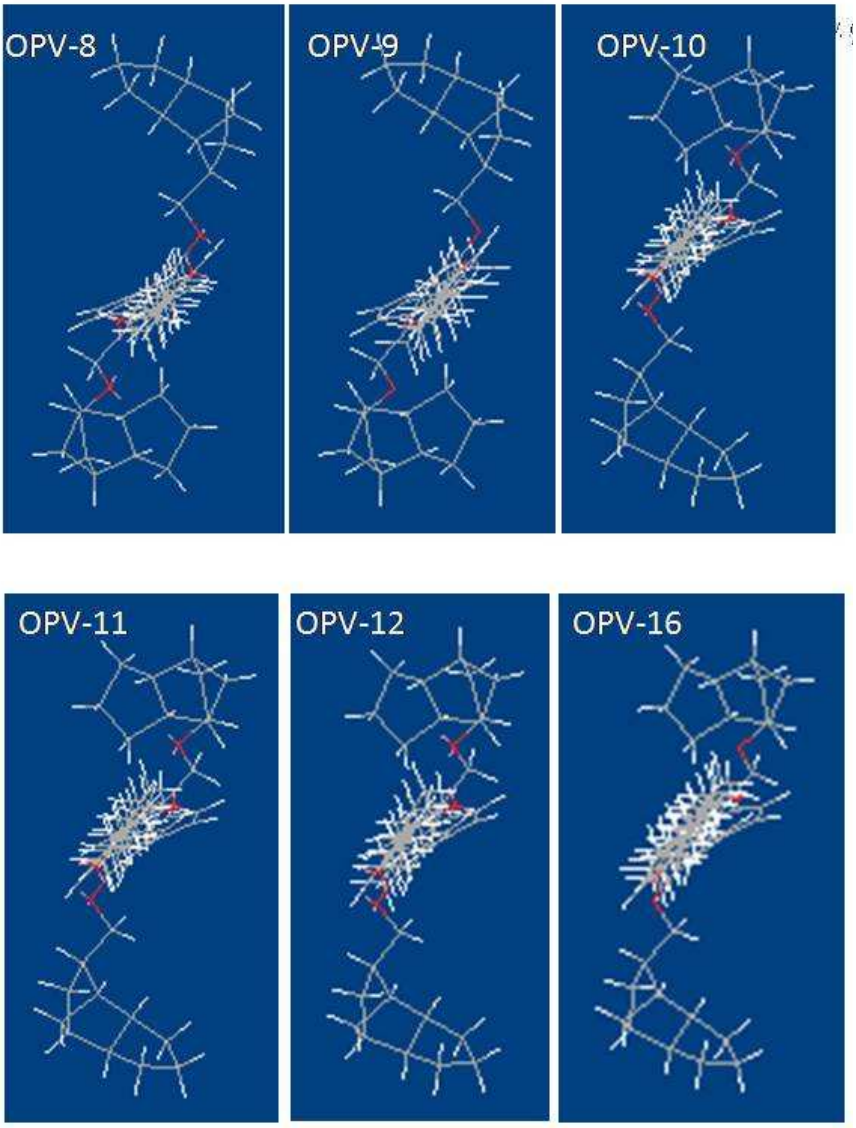


Figure 6. Energy minimized structures of OPVs using chem. Draw 8.0 MM2 energy minimization.

Note: Energy minimized structures of OPV-8,9,10,11,12 and OPV-16 .These structures indicate that the two TCD-bulky groups attached in the aromatic rings project away in opposite directions from the plane of aromatic backbone. The long alkyl chains are extended along the axis of the molecule and stay in the plane of aromatic back bone (longitudinally).

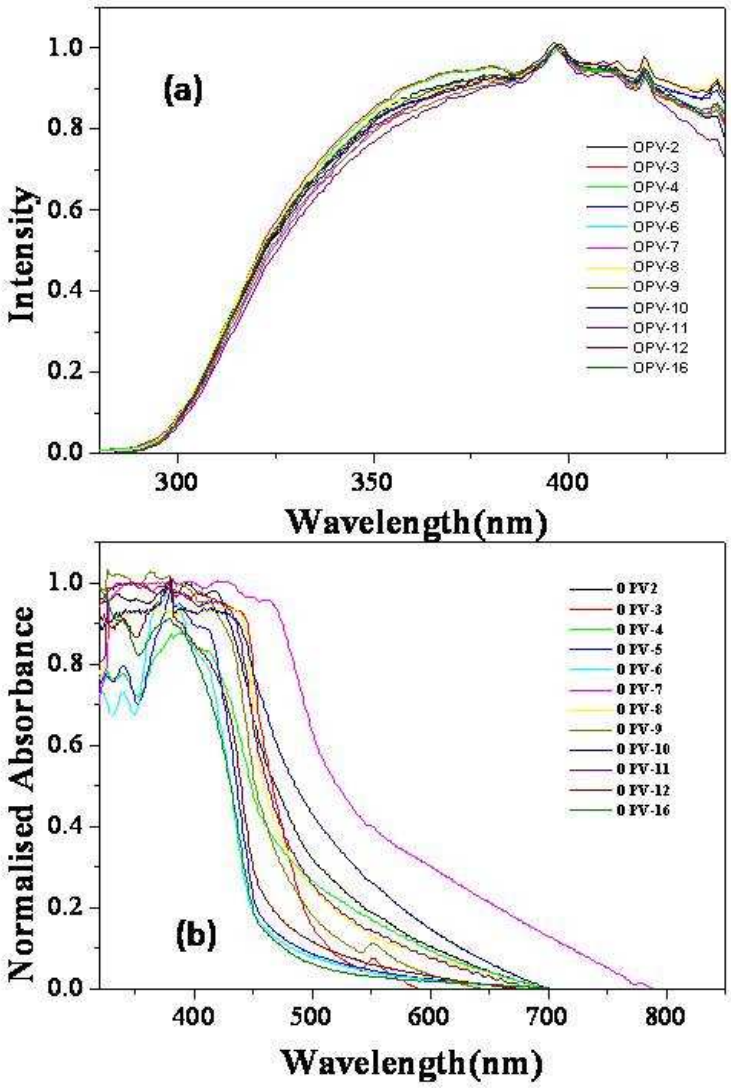


Figure 7. Excitation (a) and absorbance spectra of OPVs in the LC frozen phase.

Note: Figure (a) shows the excitation spectrums and figure (b) shows the absorption spectrums of OPV2-OPV16. These spectrums were recorded in solid state. Samples were prepared by heating all the OPVs to melt and then cooling them to freeze in to their respective LC states on glass coverslips. These thin, transparent films were put under polarized light microscope to confirm the formation of LC textures and then used for recording the spectra.

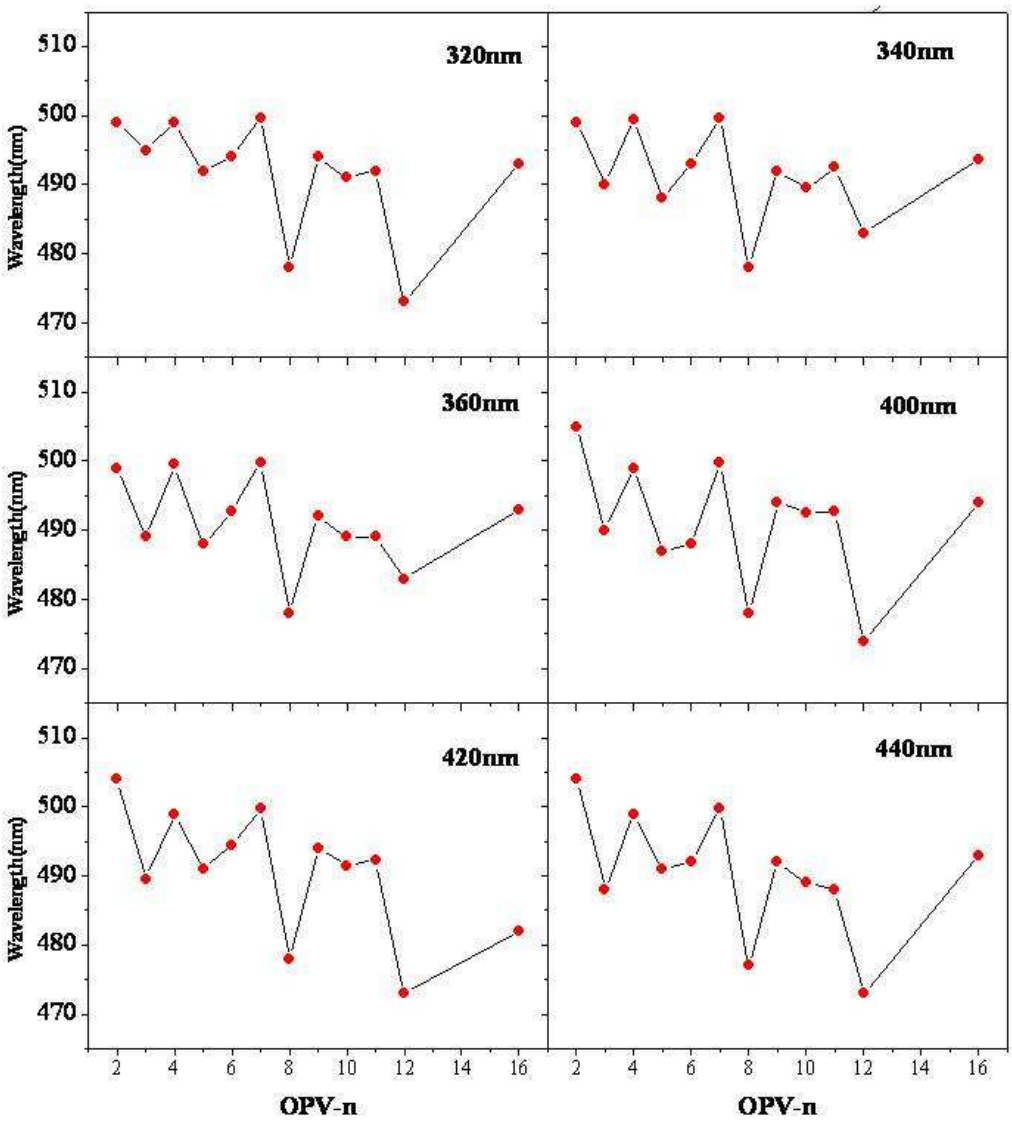


Figure 8. Odd-even oscillation of OPVs in the PL emission spectar at various excitation wavelengths.

Note: The above plot shows the odd- even oscillation observed in the emission wavelength at PL Intensity (0.8) with respect to number of carbon atoms in the alkyl chains. All the OPVs were excited at variable wavelengths (320, 340, 360, 380, 400, 420, 440 nm) to confirm the even –odd oscillation with respect to excitation wavelength.

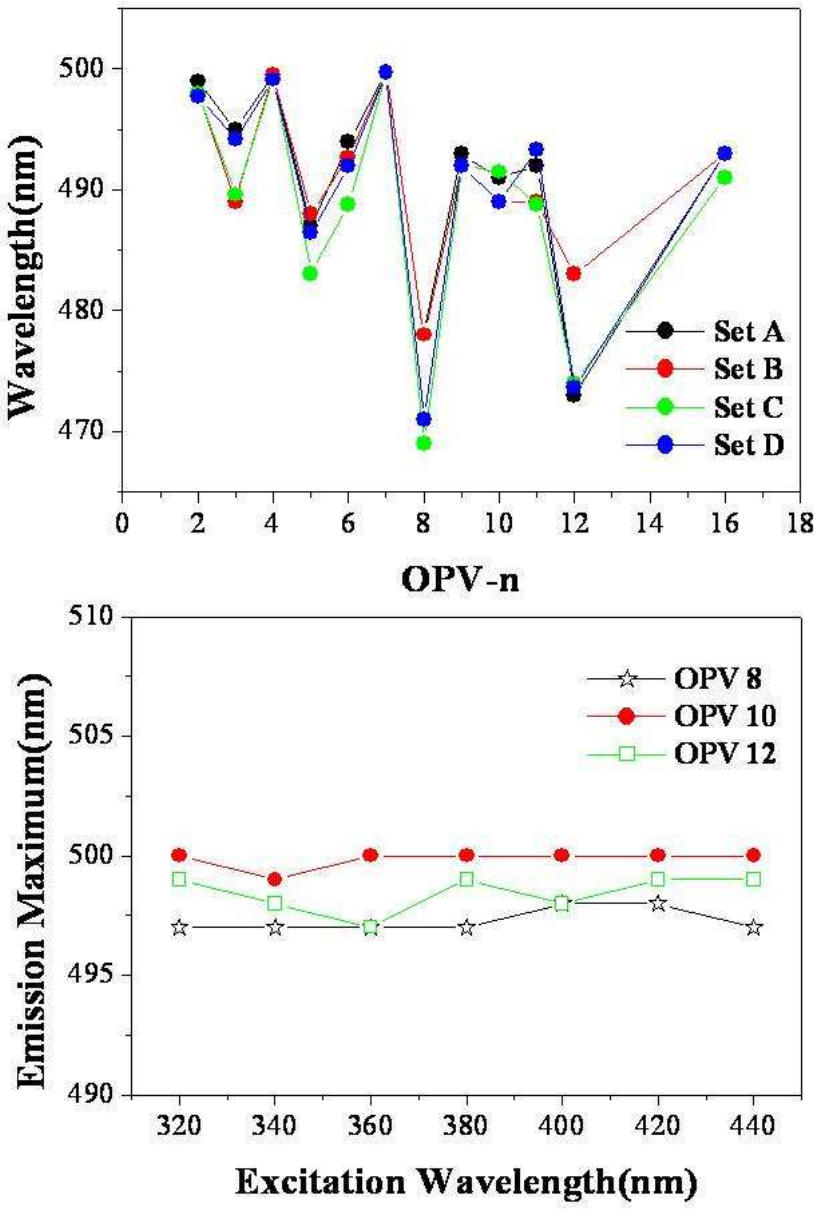


Figure 9. Odd-even oscillation (above) of four different sets of new LC frozen texture created for each OPV samples (A, B. C and D indicates each set). Pl intensity of OPVs at emission max for various excitation wavelength.

Note: Plot (above) shows the odd-even oscillation for four different sets of each OPV. The samples were excited at 380 nm and their emission maxima were plotted against the number of carbon atoms in the alkyl chains. This was done to confirm that odd-even oscillation is inherent property for the entire series of these OPVs and is independent of sample preparation. Similar trends are observed at all other wavelengths for all the four sets. Plot (below) shows emission maxima for OPV 8,10 and 12 when excited at seven different wavelengths. The emission maximum is found to be almost independent of excitation wavelength.

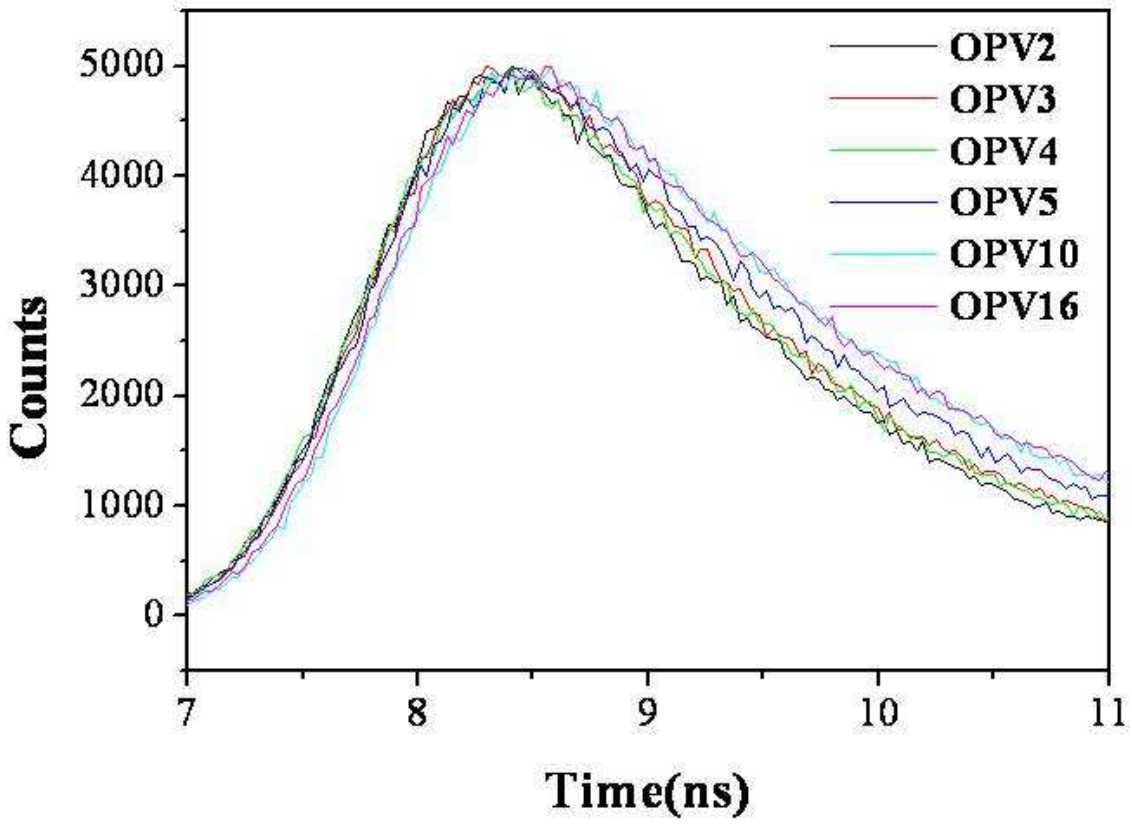


Figure 10. Time resolved Fluorescence decay profiles of OPVs.

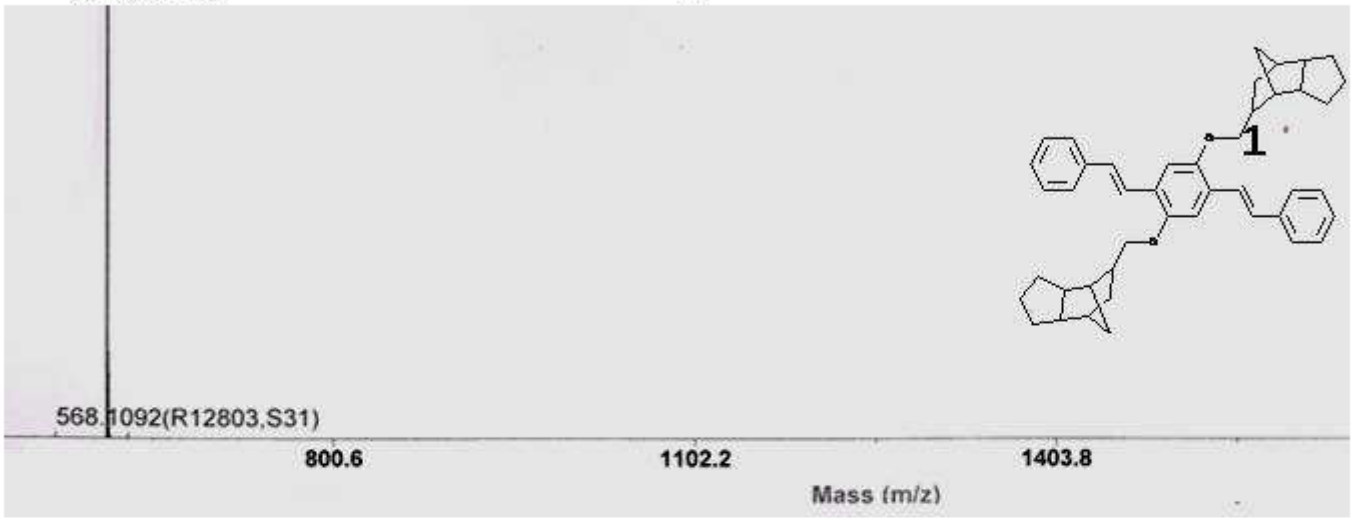
Note: the above plot shows the decay profiles for OPV2, 3, 4, 5, 10 and 16. All the samples were excited at 371nm using a Nano LED source and the spectrums were recorded at 500nm collection wavelengths. The life time values are given in table -2.

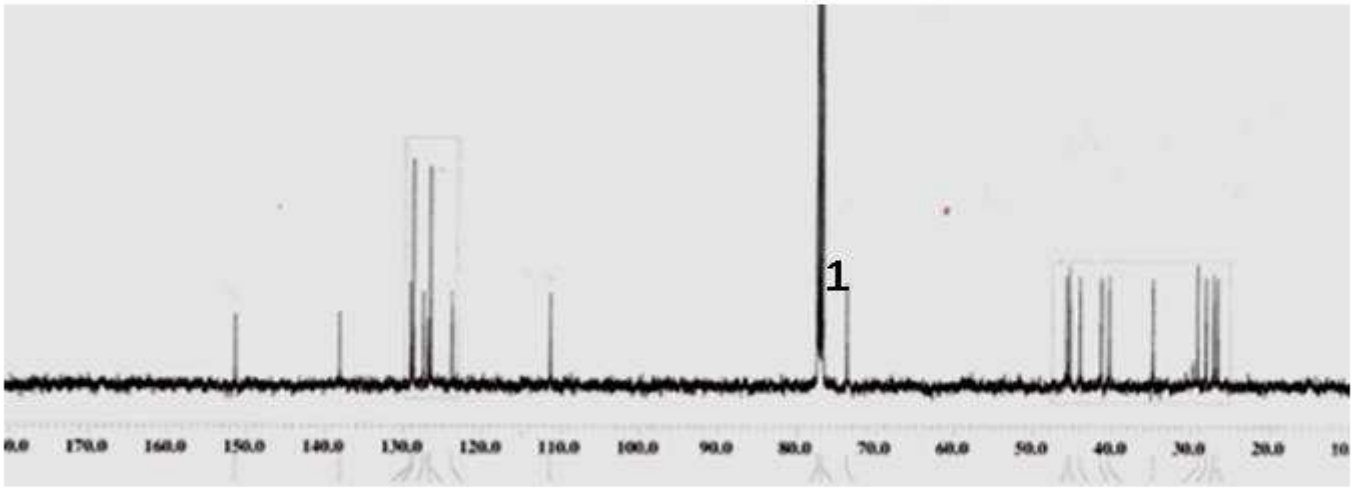
1H-NMR, 13C-NMR and MALDI-TOF-TOF data of OPVs

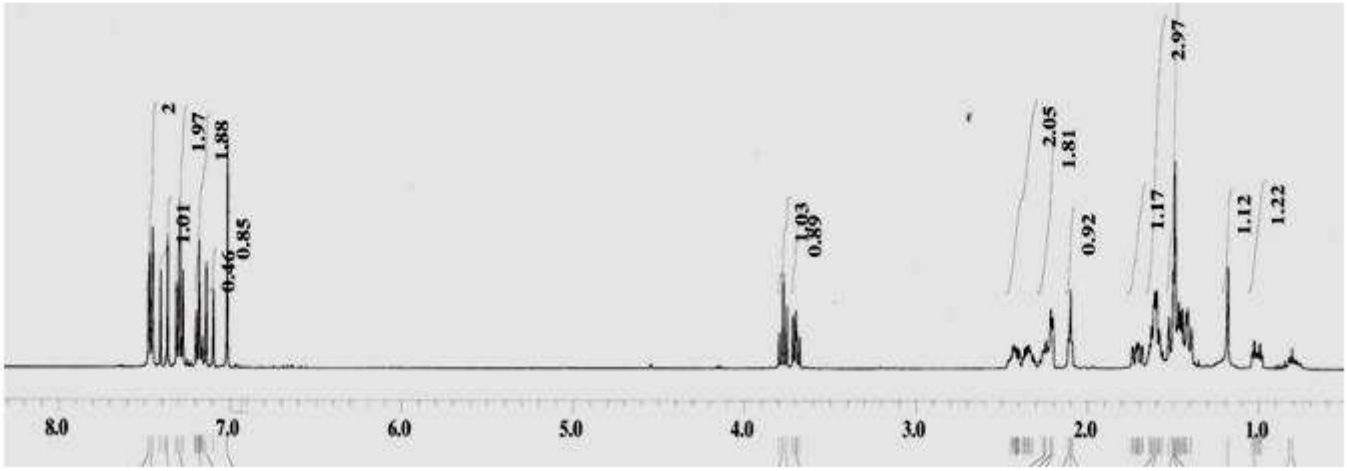
OPV-0

Molecular Formula = $C_{44}H_{50}O_2$

Molecular Weight = 610.87



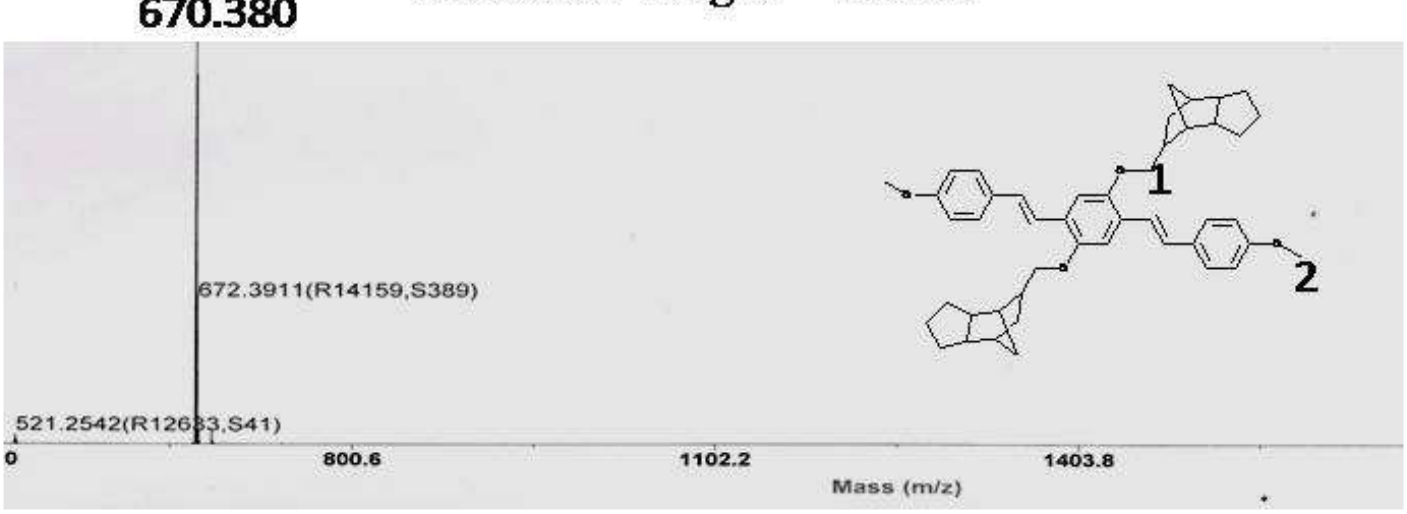


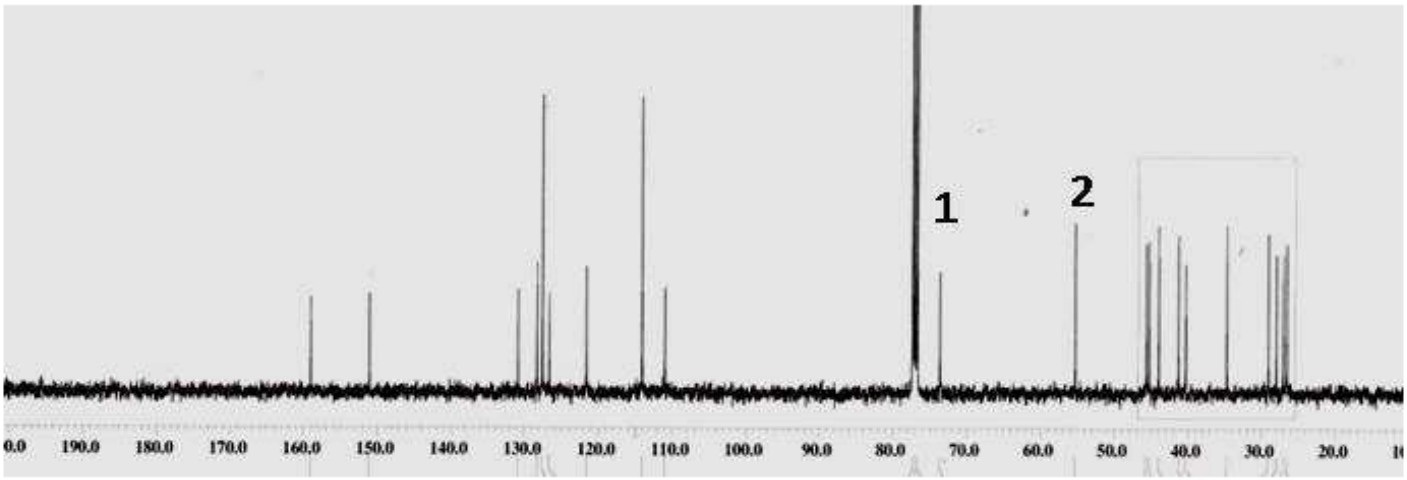


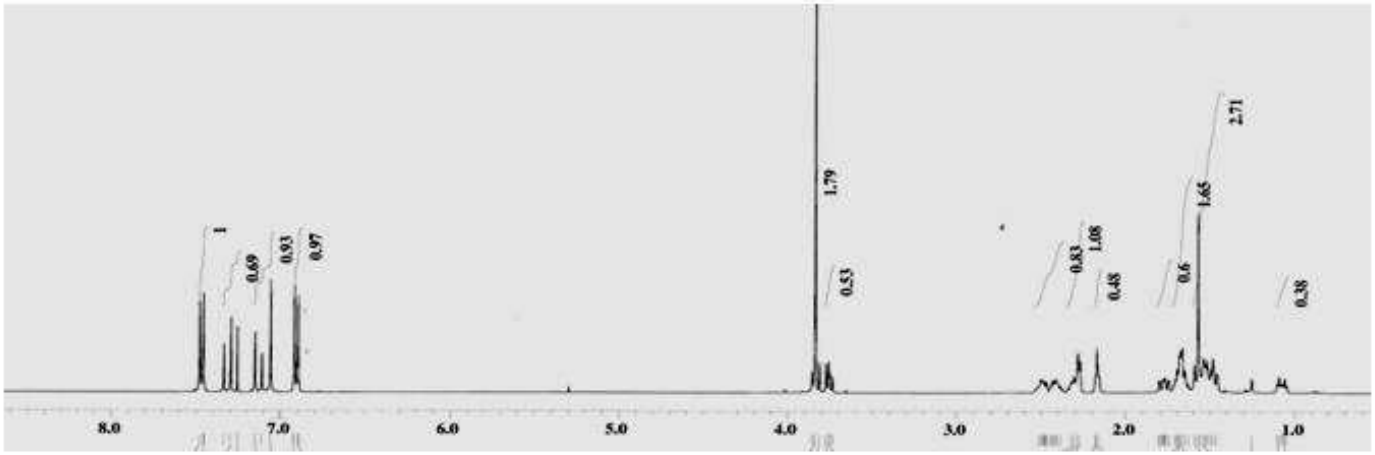
OPV-1

Molecular Formula = $C_{46}H_{54}O_4$

Molecular Weight = 670.92



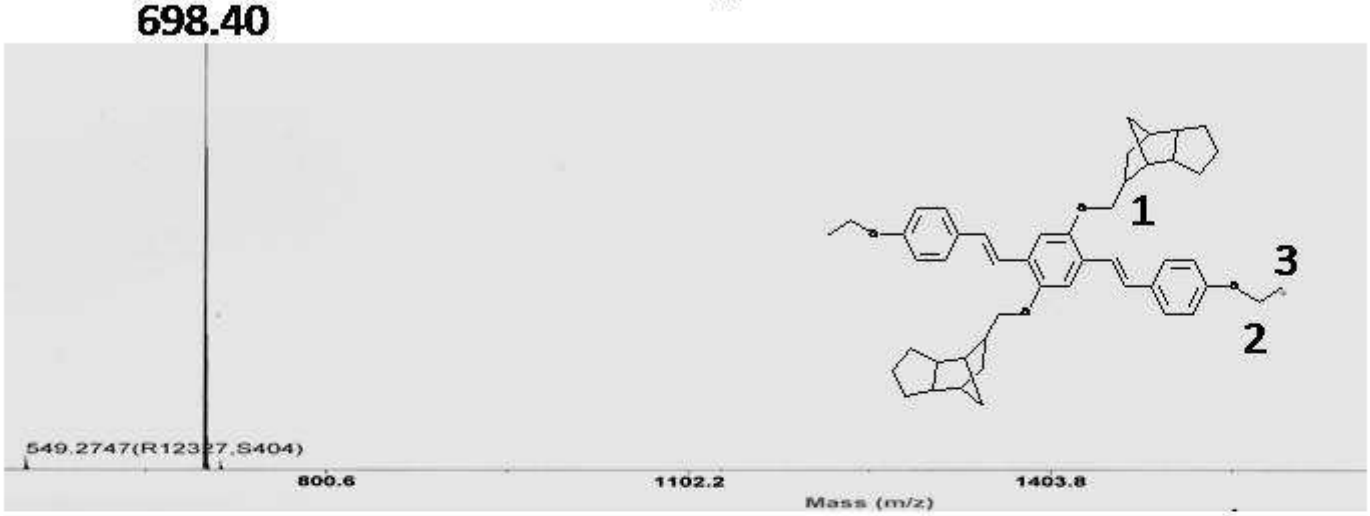


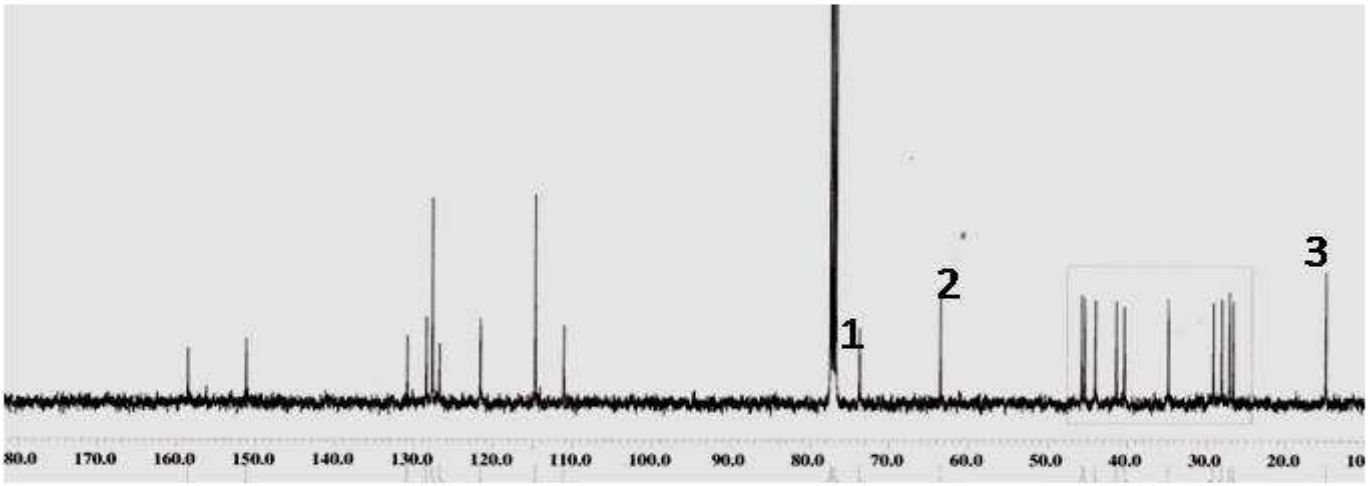


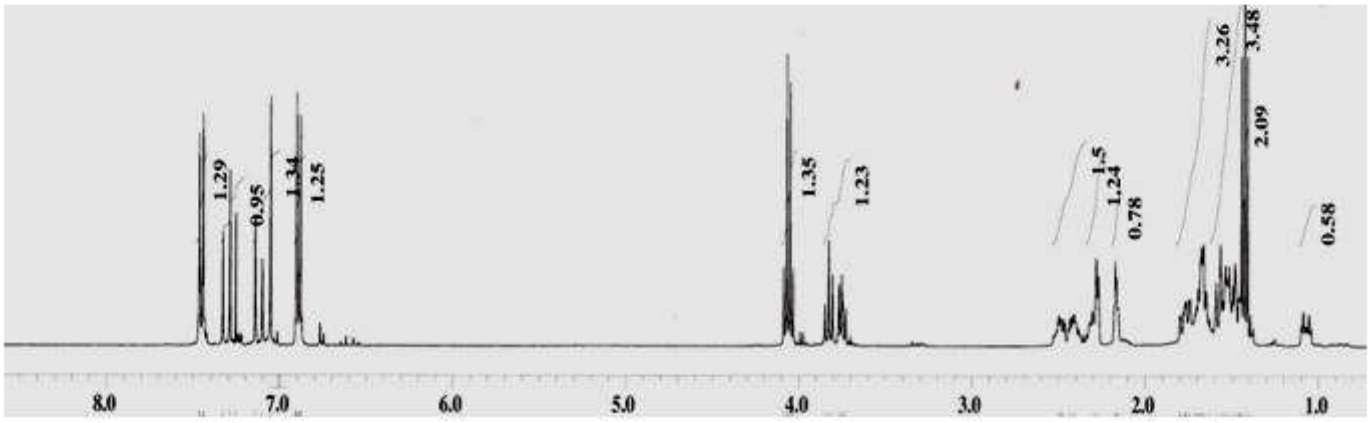
OPV-2

Molecular Formula = $C_{48}H_{58}O_4$

Molecular Weight = 698.97



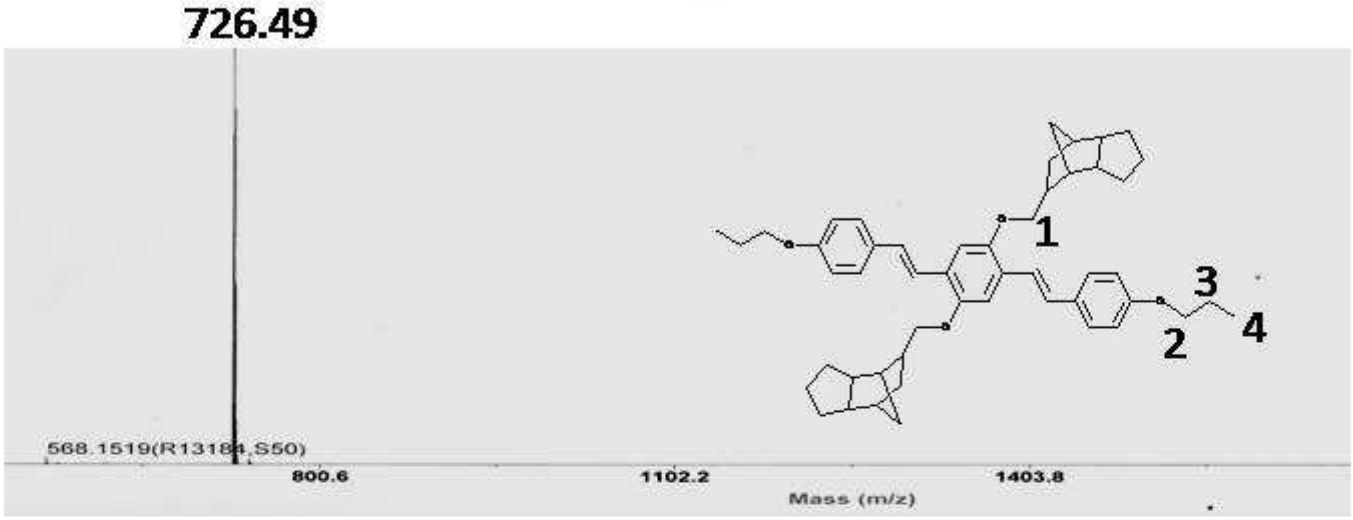


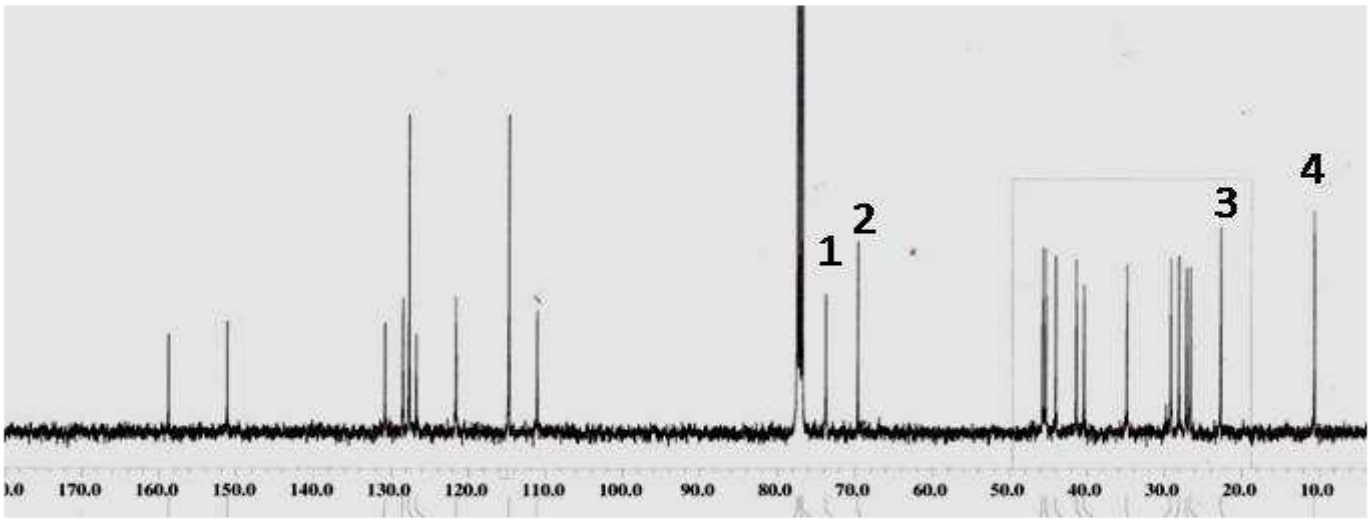


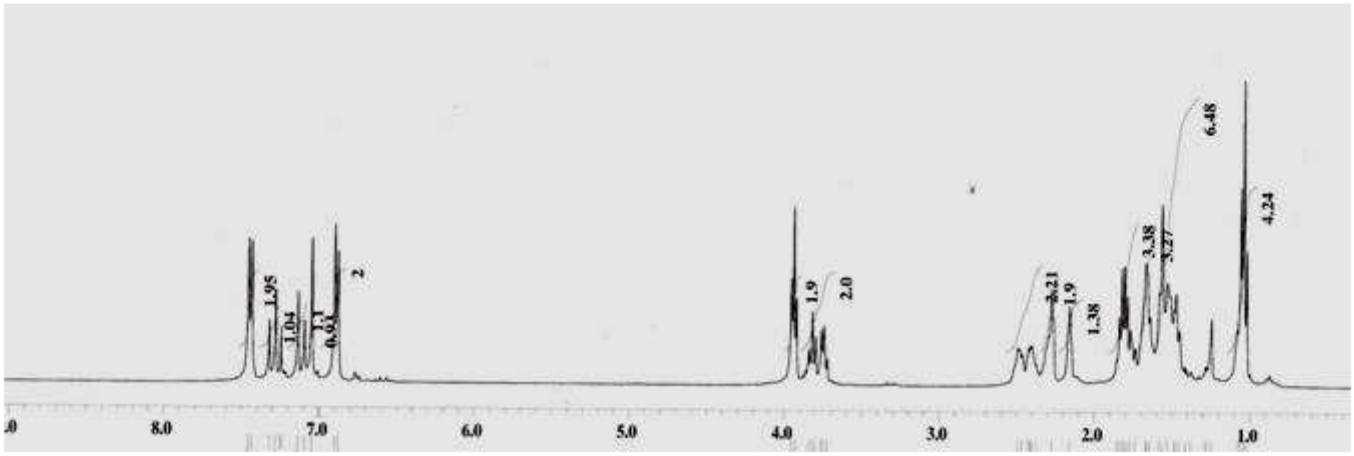
OPV-3

Molecular Formula = $C_{50}H_{62}O_4$

Molecular Weight = 727.02





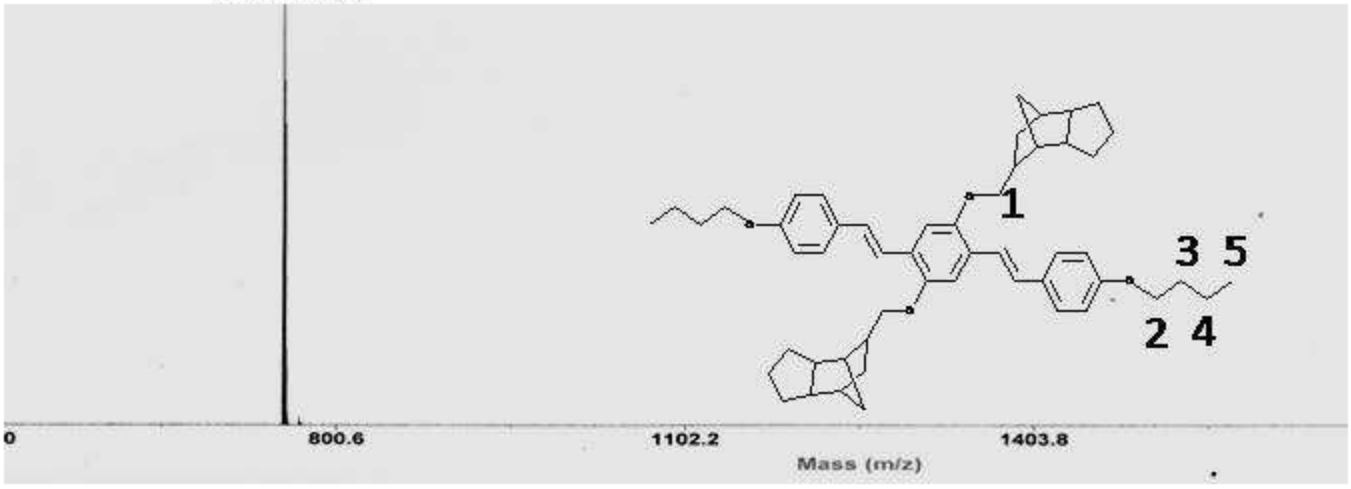


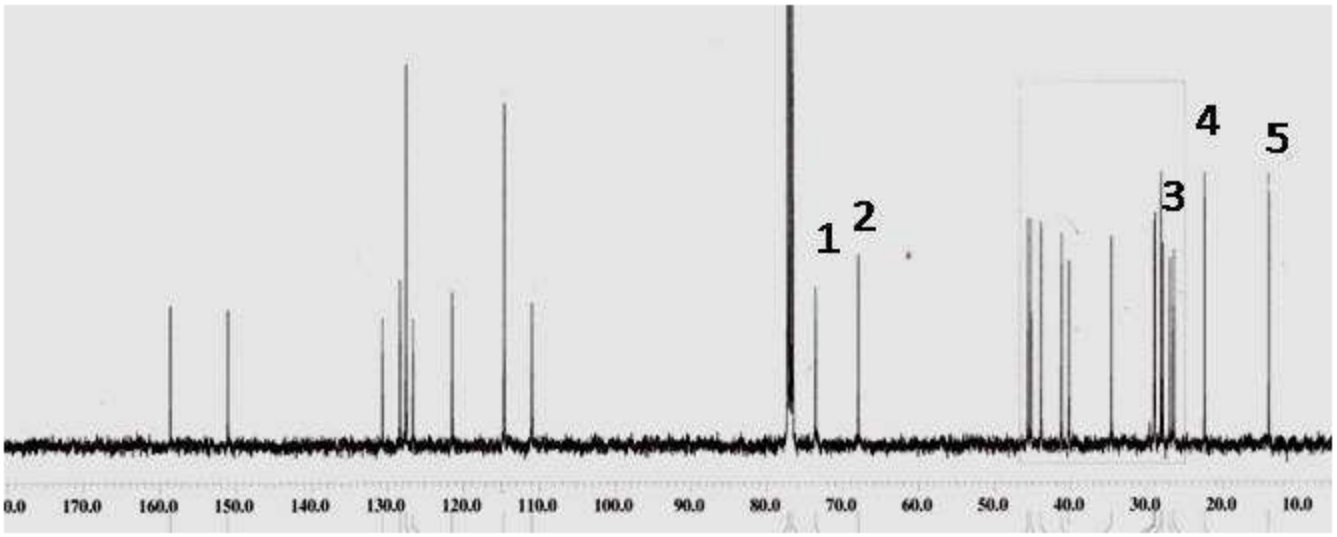
OPV-4

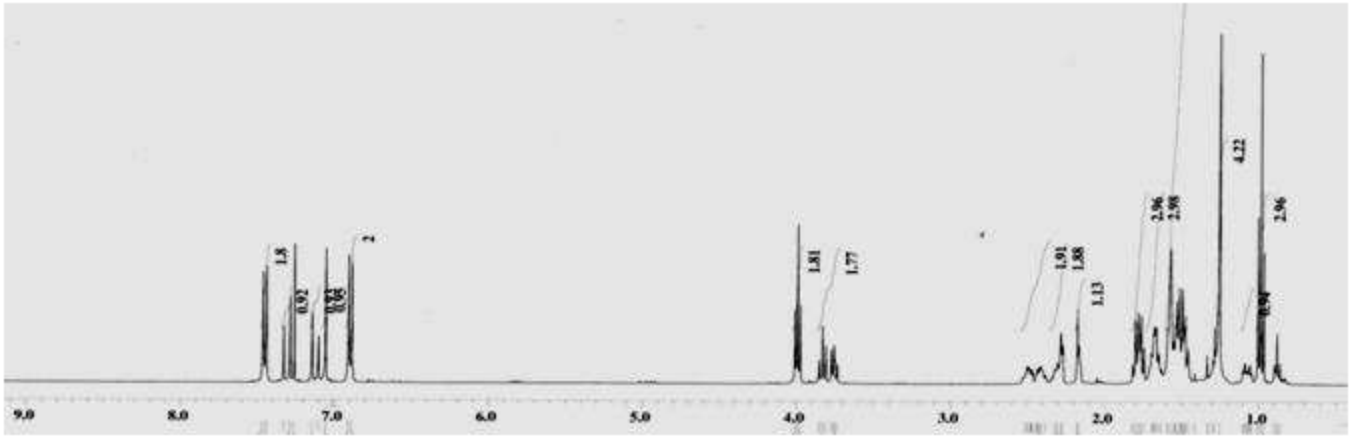
Molecular Formula = $C_{52}H_{66}O_4$

Molecular Weight = 755.08

754.470



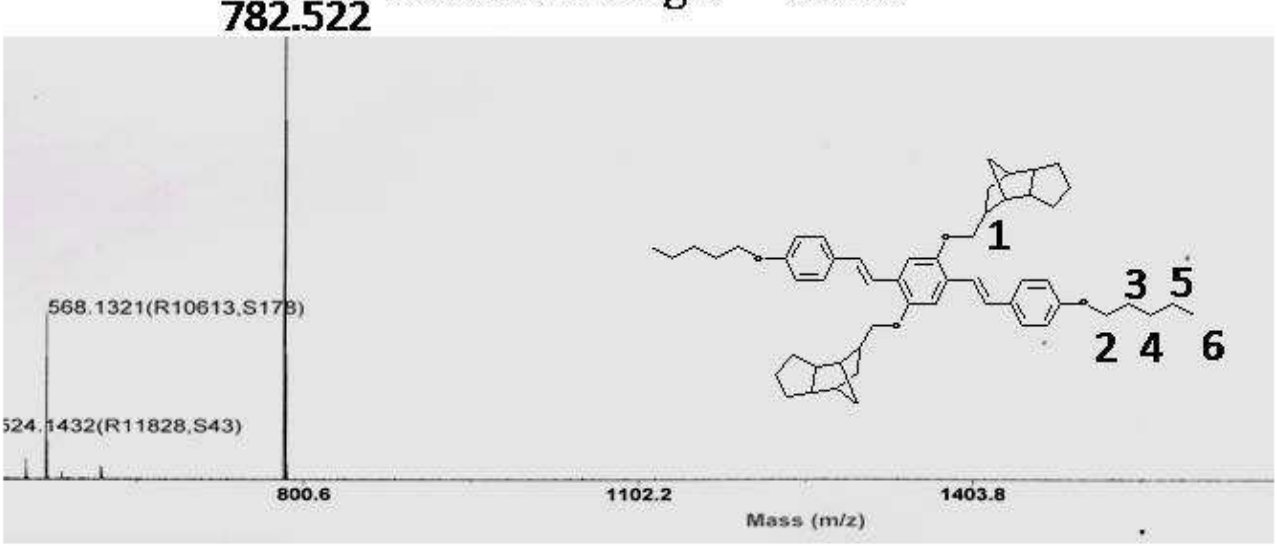


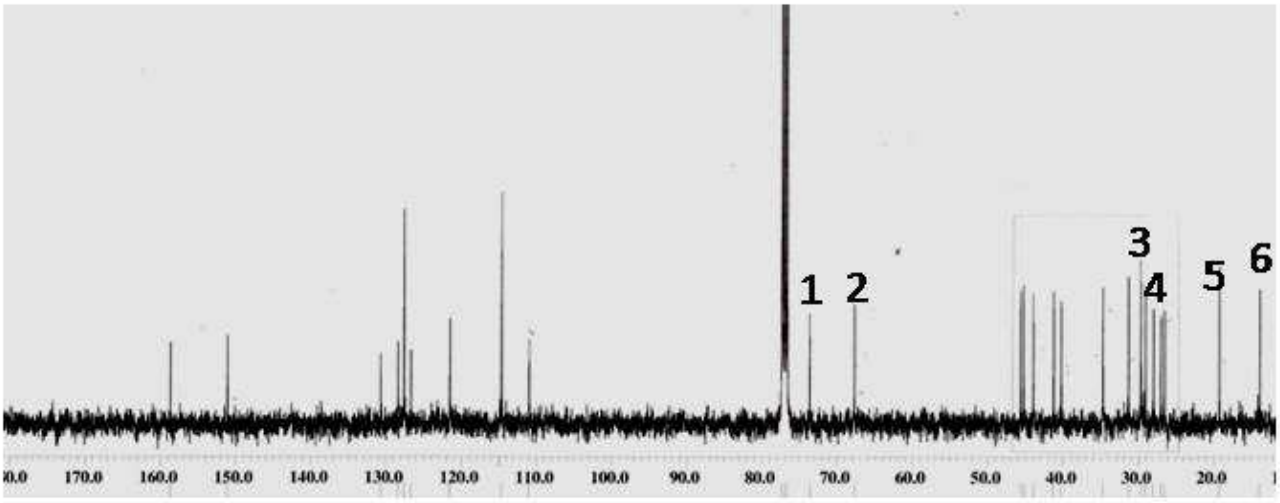


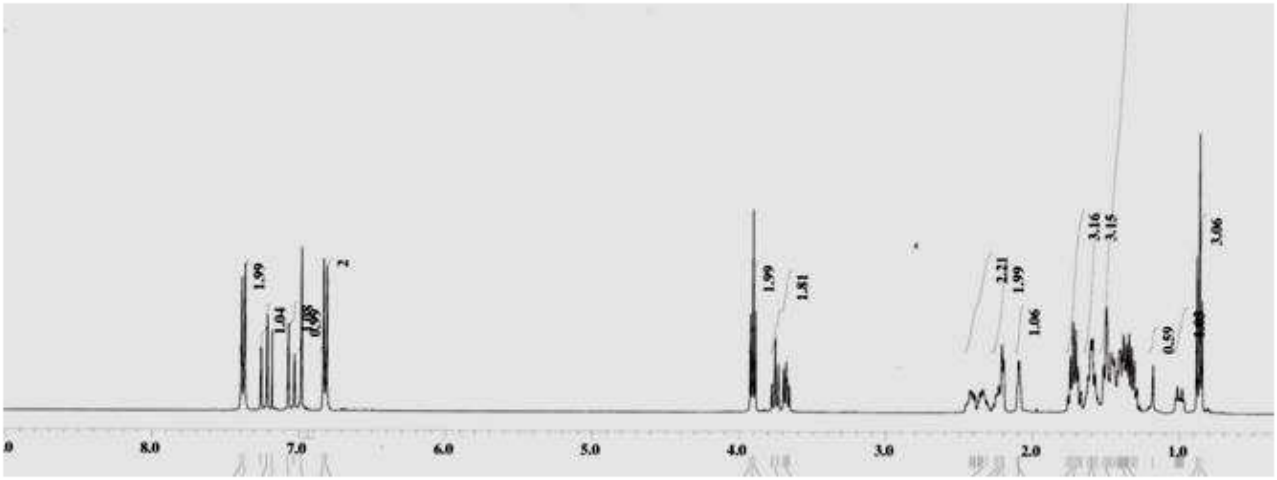
OPV-5

Molecular Formula = $C_{54}H_{70}O_4$

Molecular Weight = 783.13





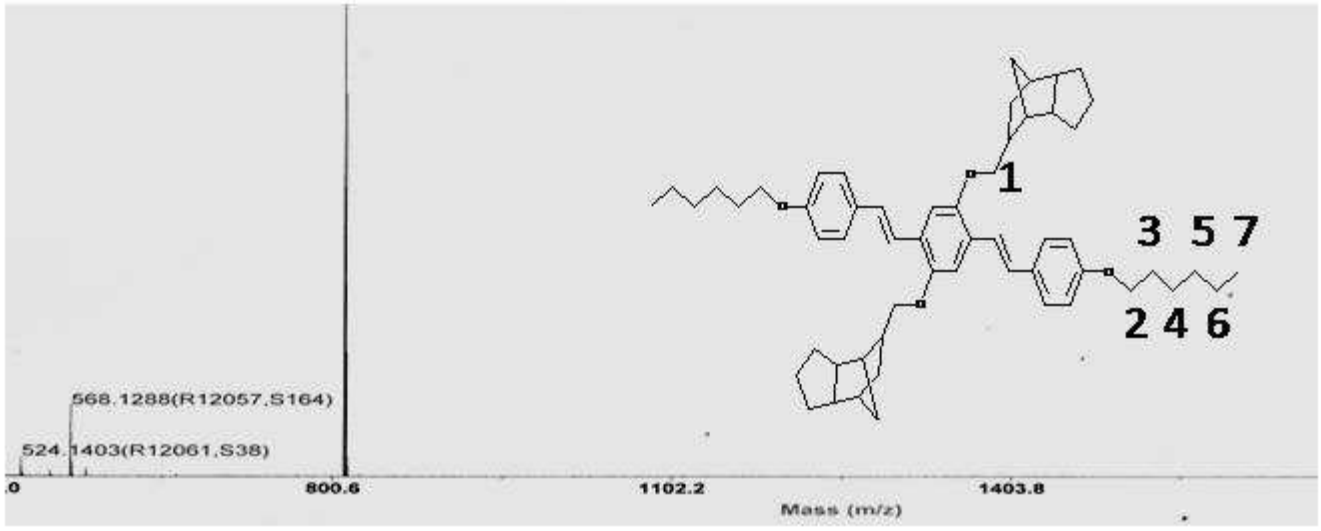


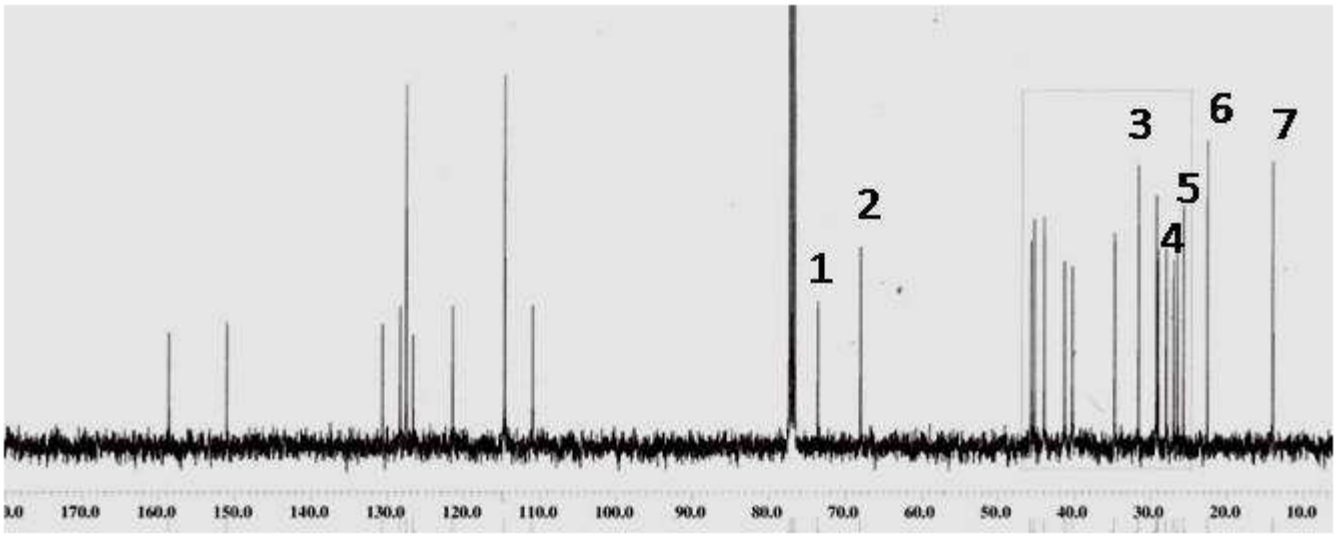
OPV-6

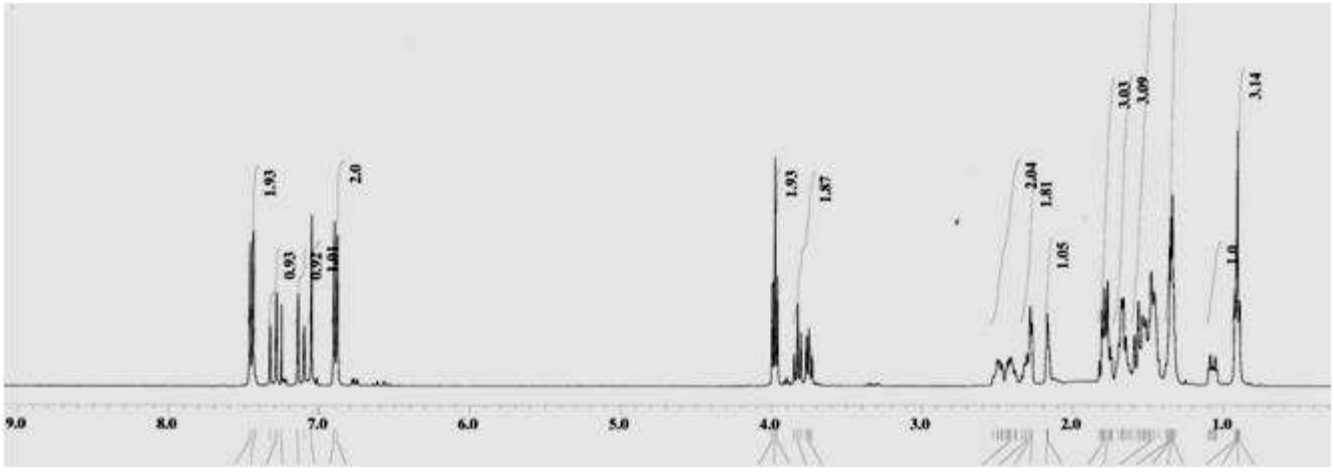
Molecular Formula = $C_{56}H_{74}O_4$

Molecular Weight = 811.18

810.553





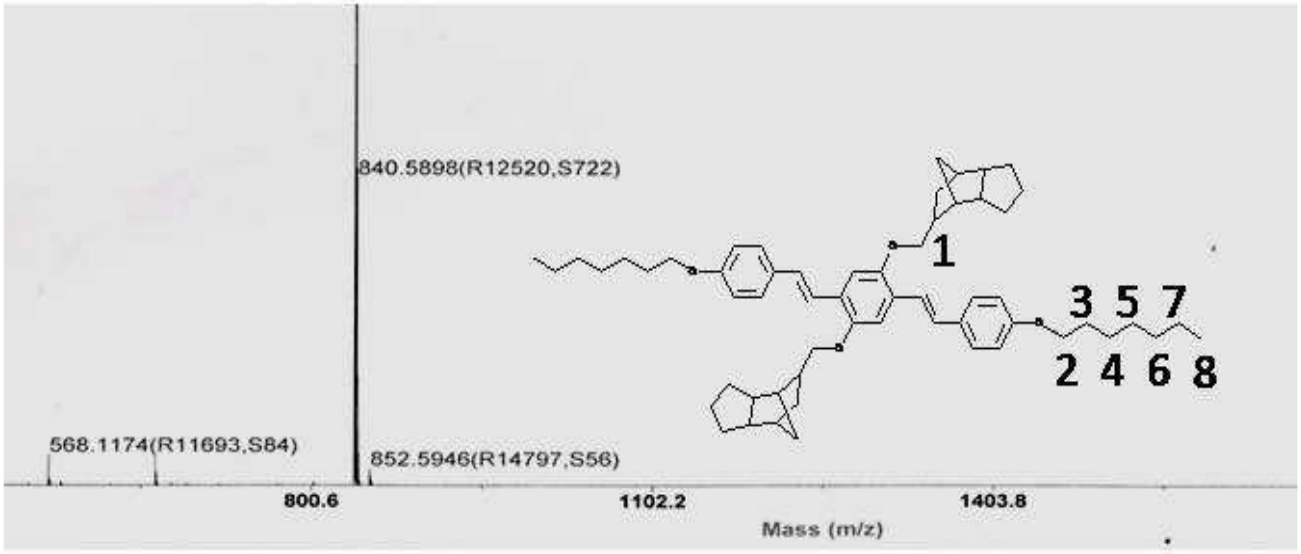


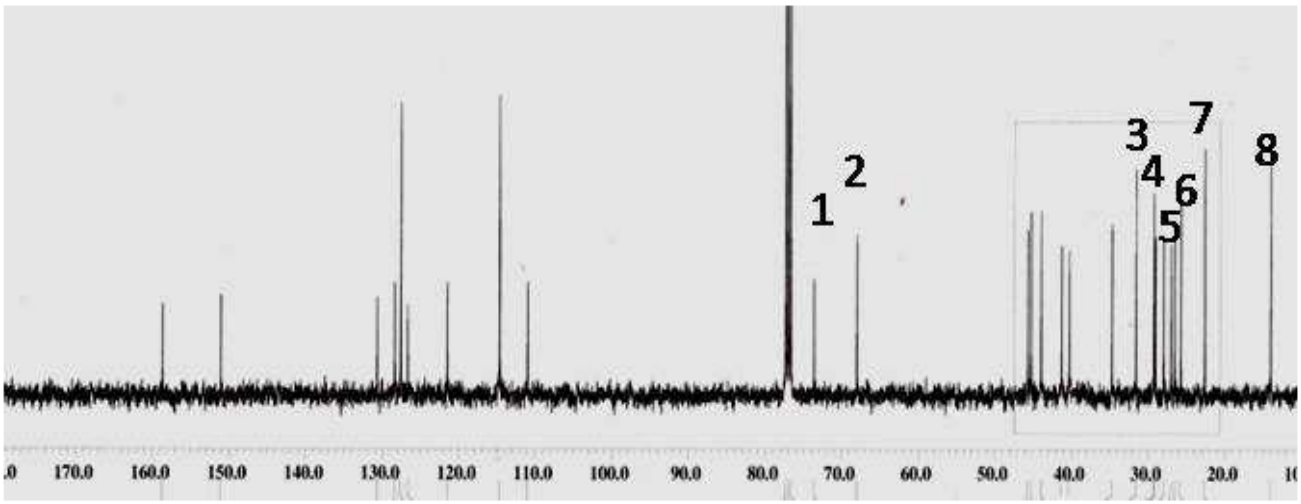
OPV-7

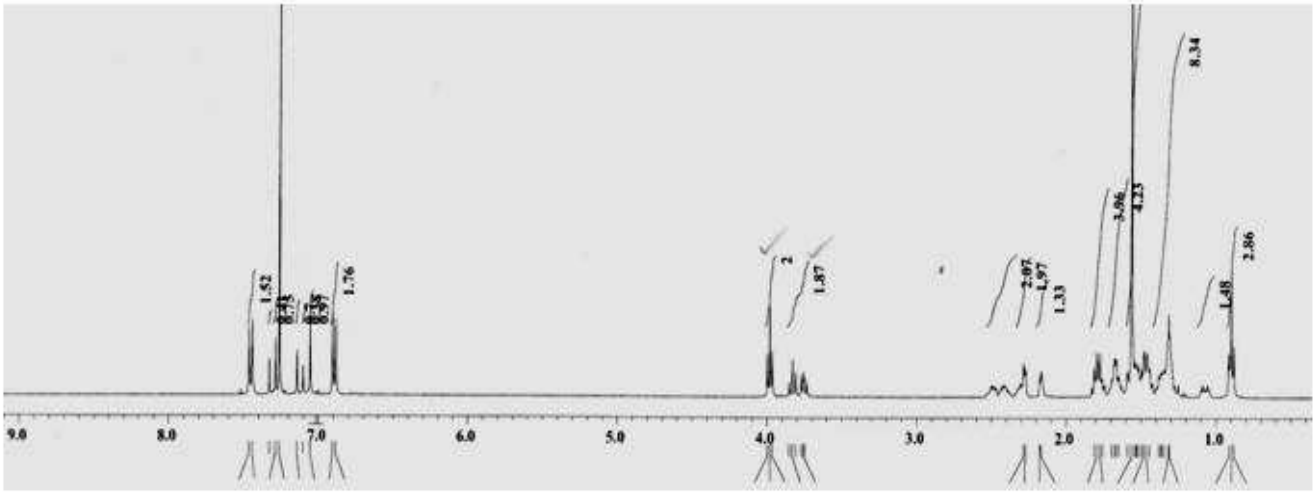
Molecular Formula = $C_{58}H_{78}O_4$

Molecular Weight = 839.24

838.578



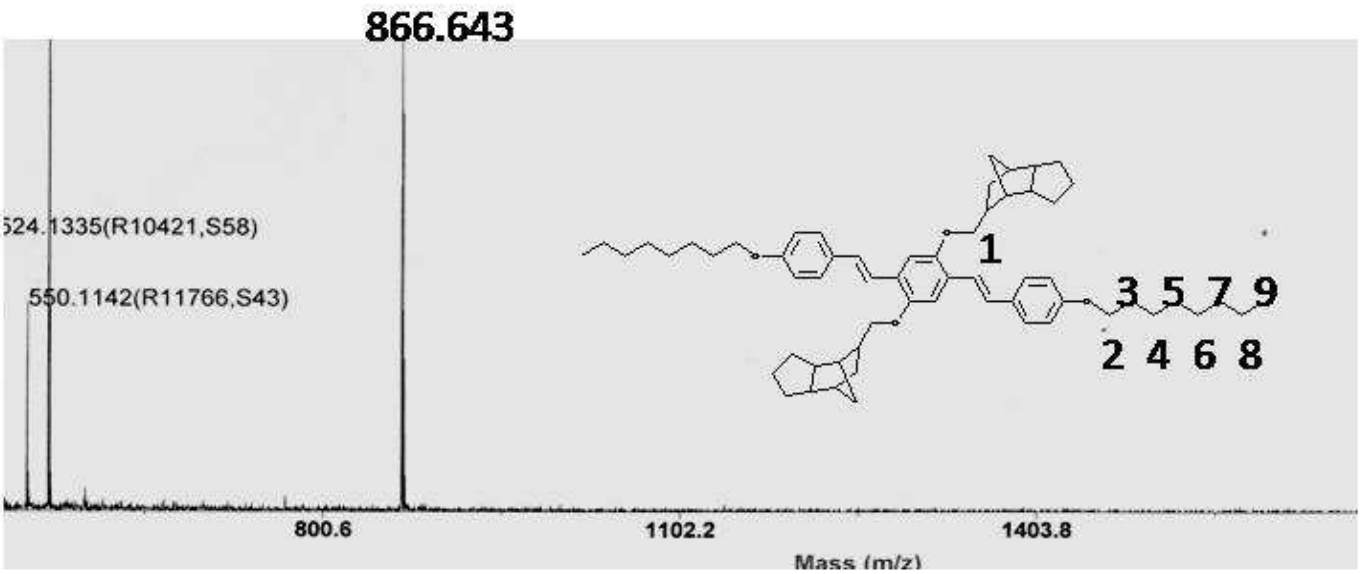


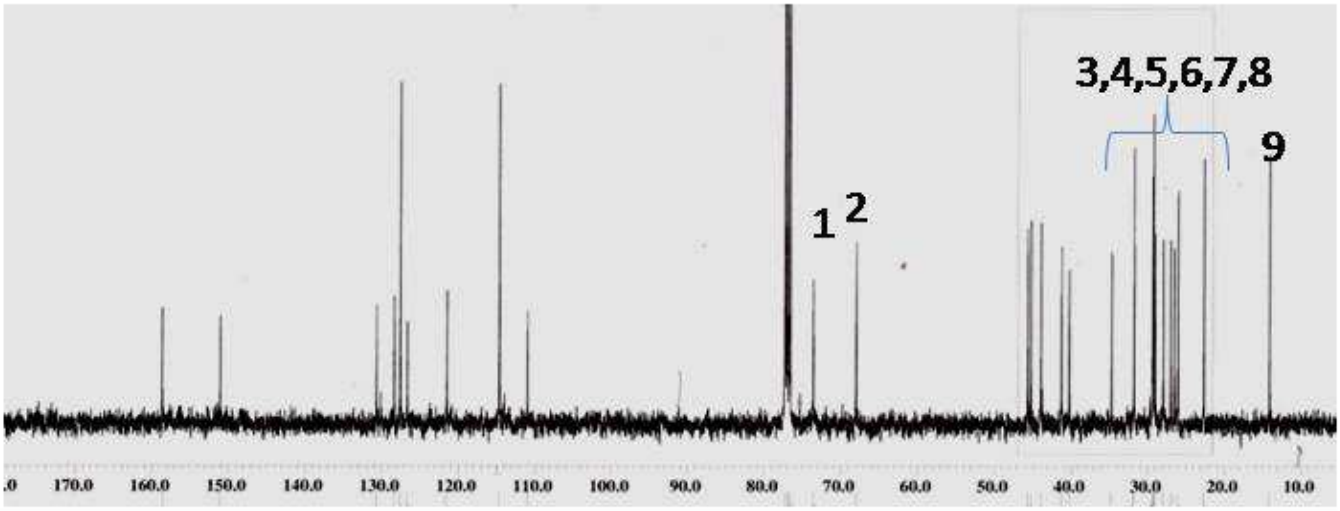


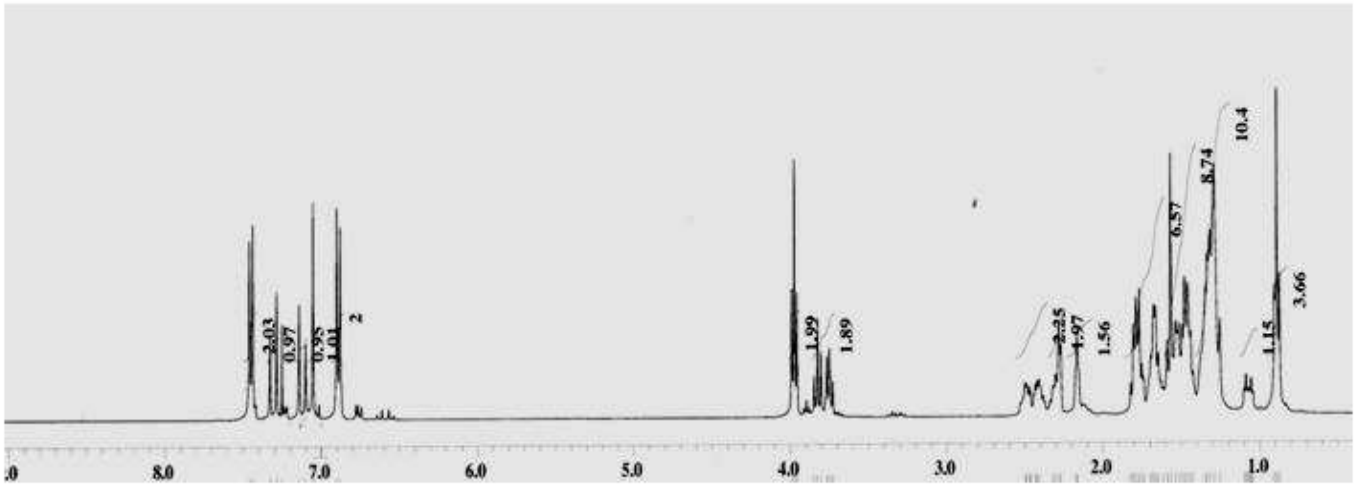
OPV-8

Molecular Formula = $C_{60}H_{82}O_4$

Molecular Weight = 867.29



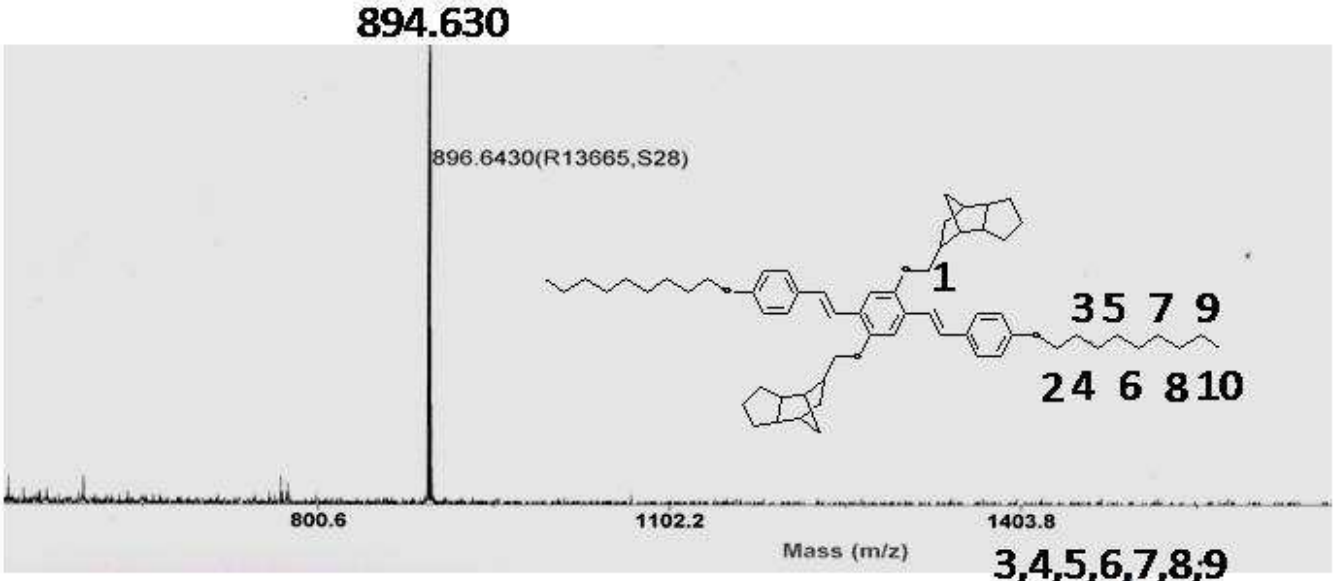


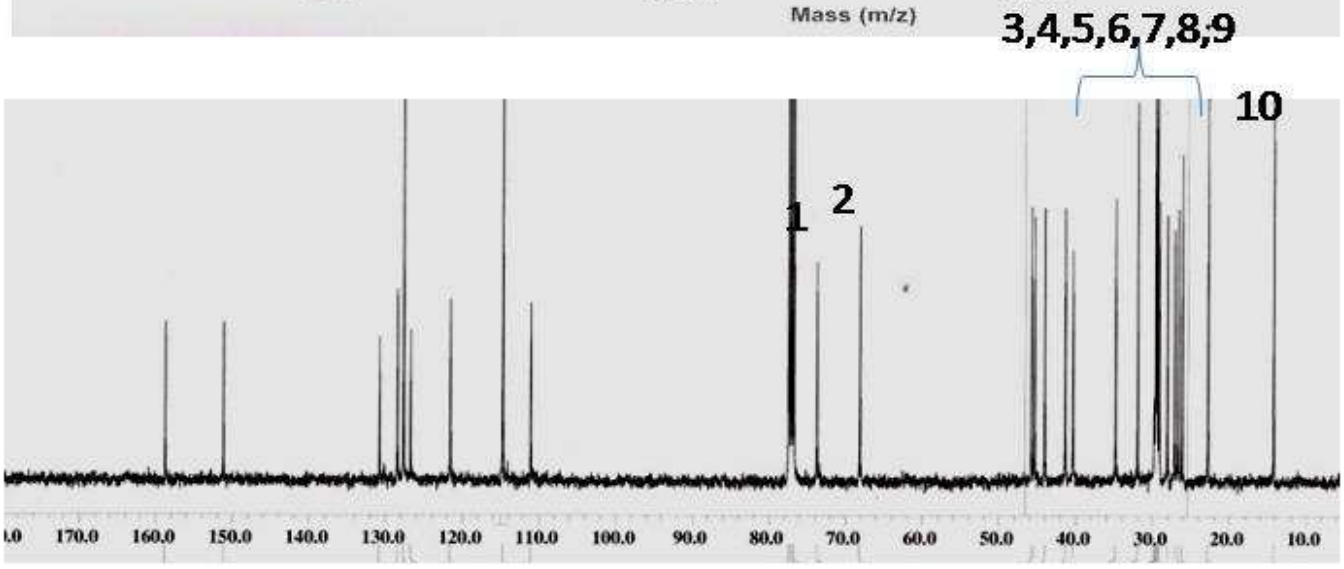


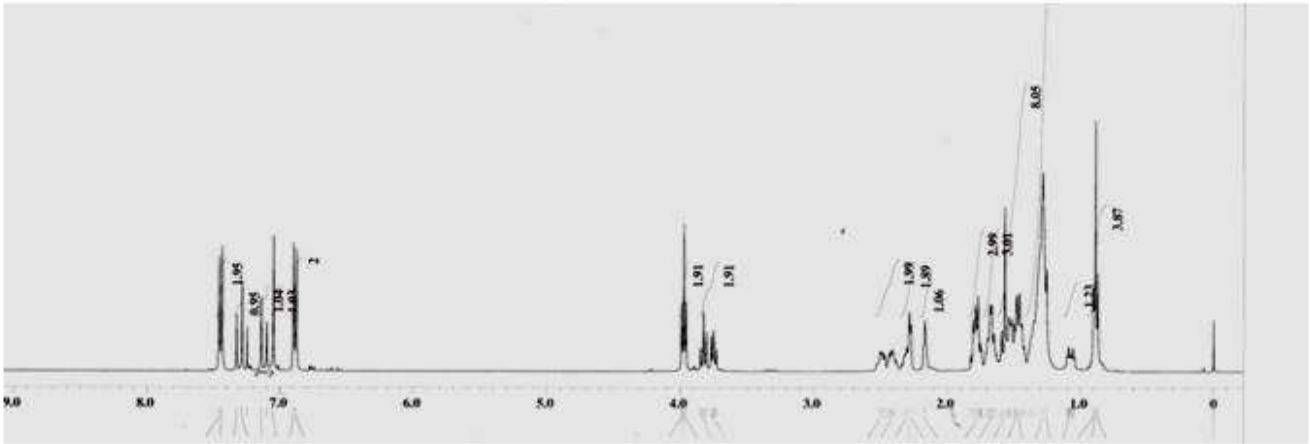
OPV-9

Molecular Formula = $C_{62}H_{86}O_4$

Molecular Weight = 895.34



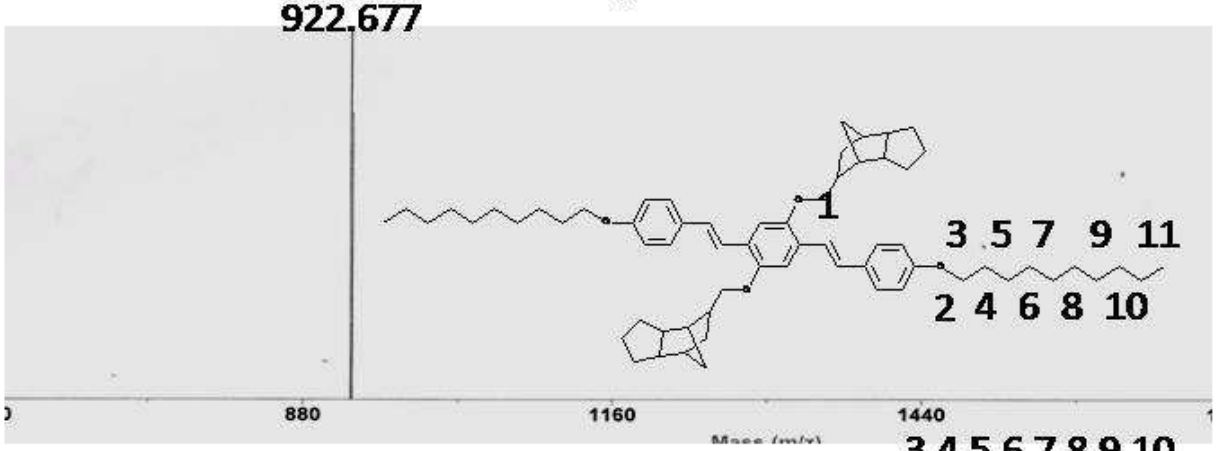


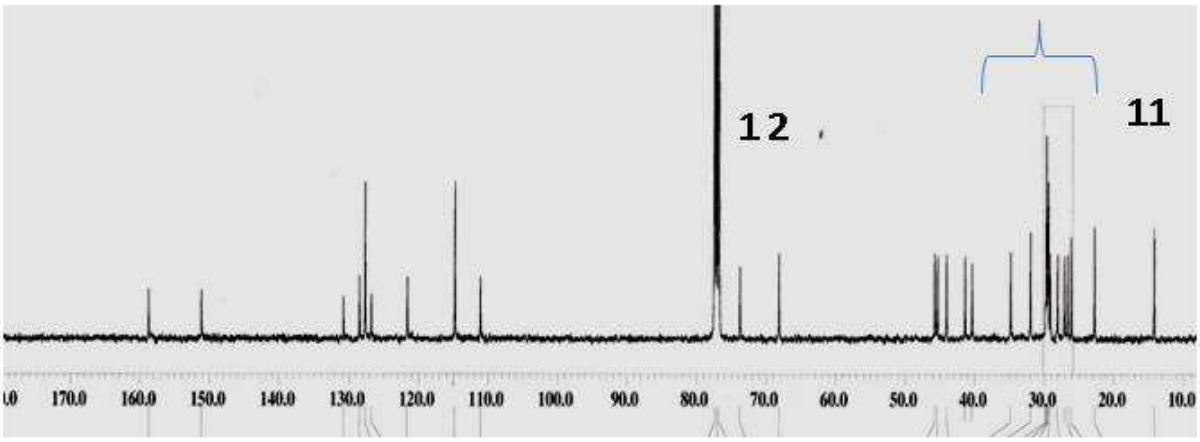


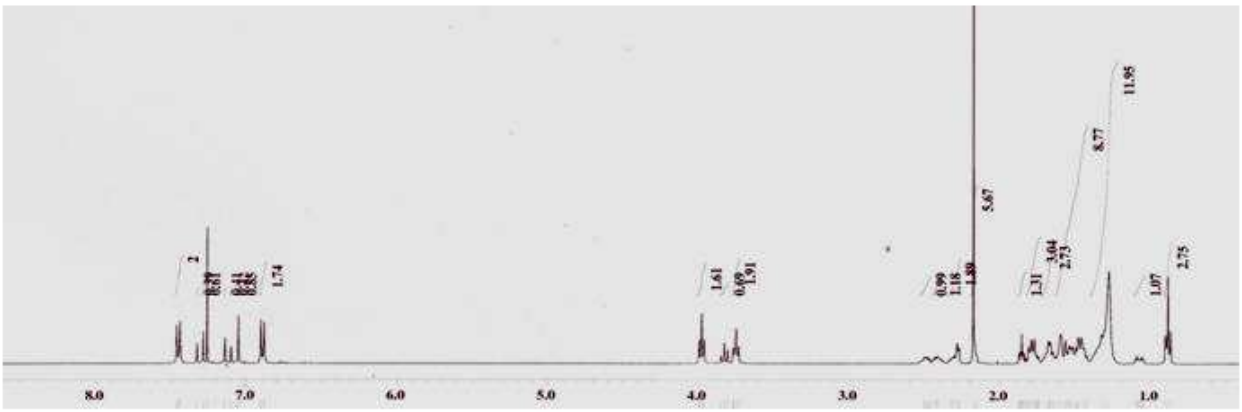
OPV-10

Molecular Formula = $C_{64}H_{90}O_4$

Molecular Weight = 923.40



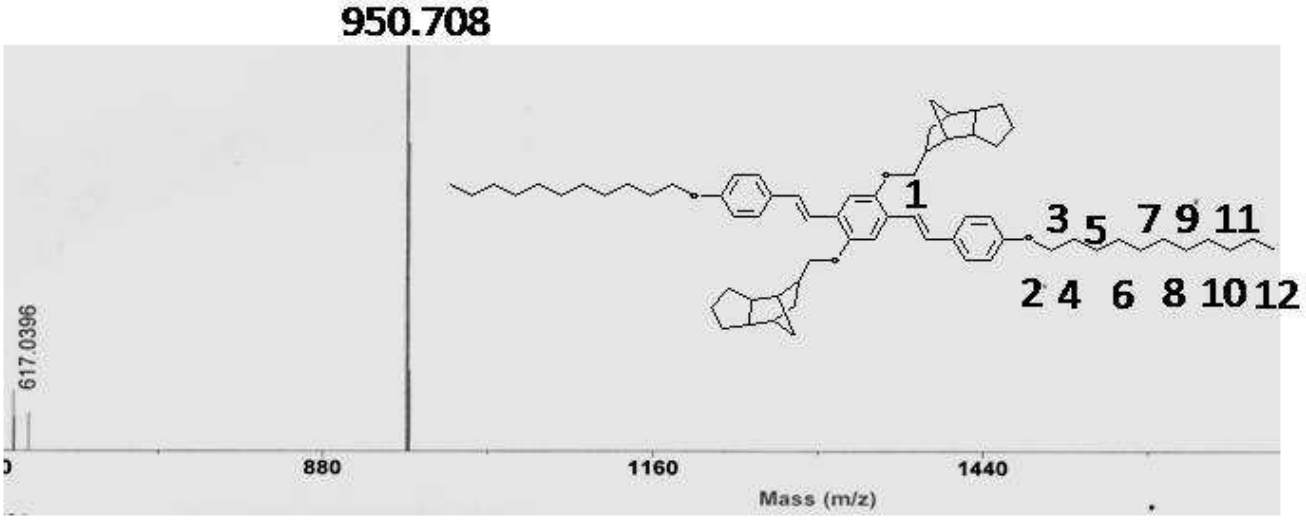


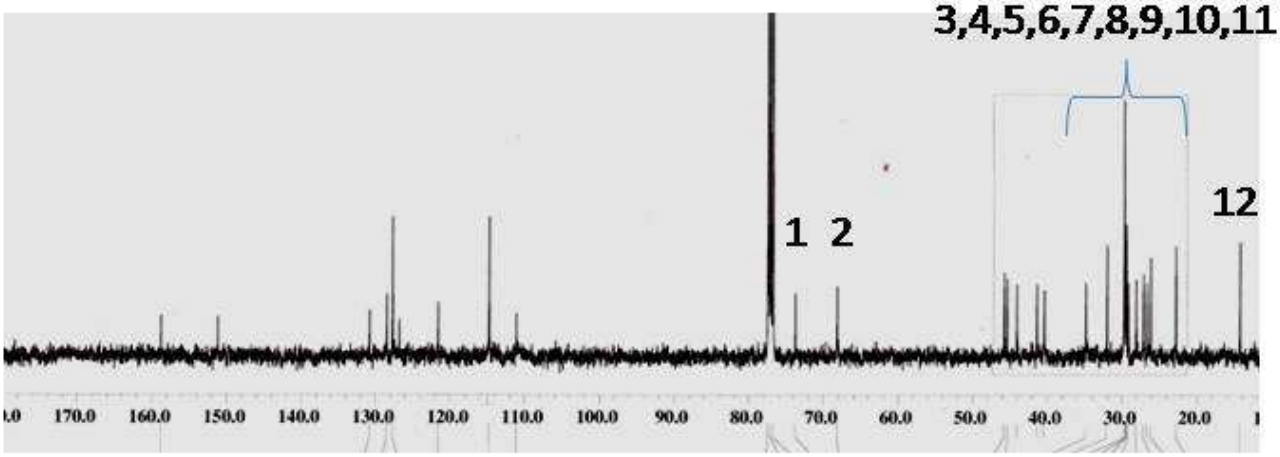


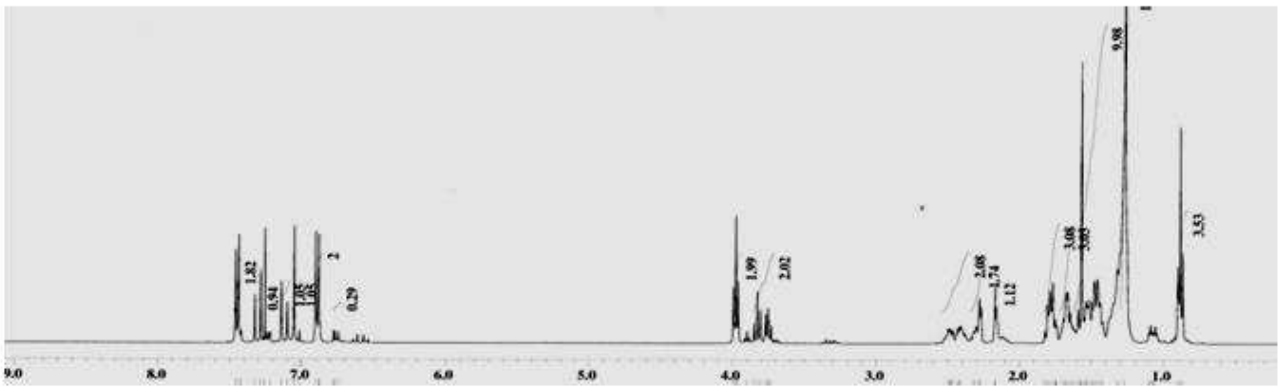
OPV-11

Molecular Formula = $C_{66}H_{94}O_4$

Molecular Weight = 951.45



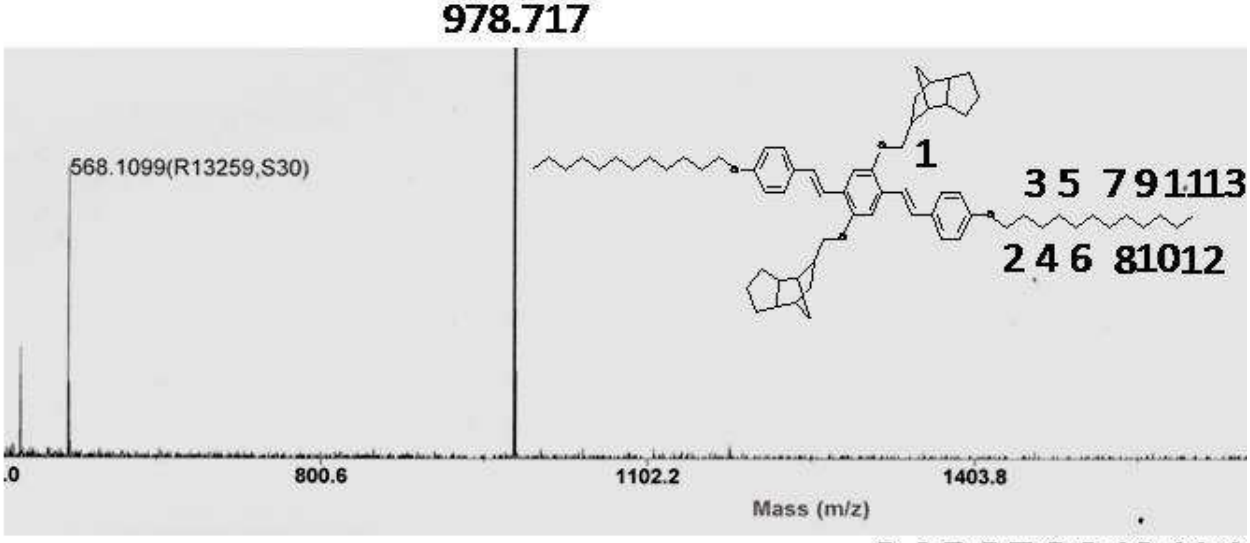


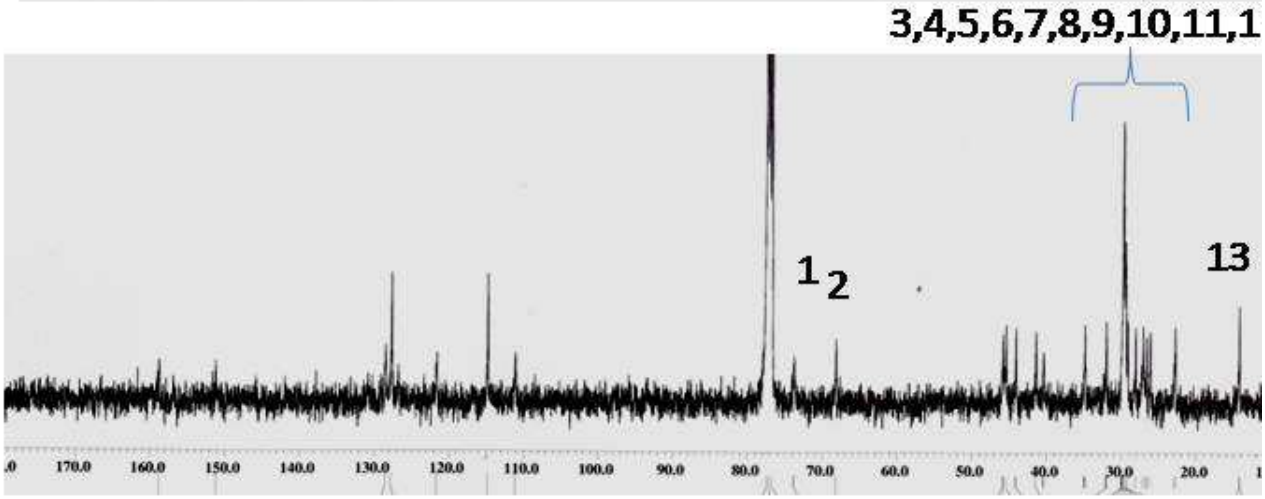


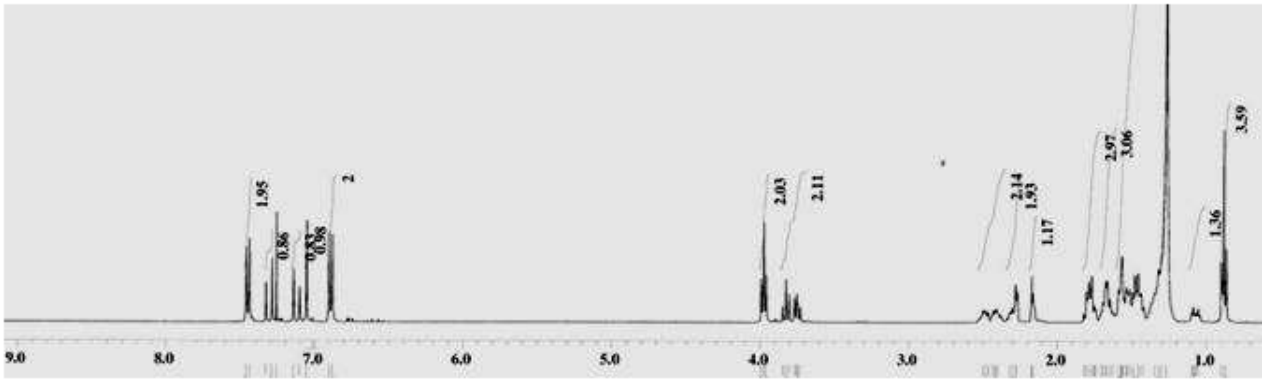
OPV-12

Molecular Formula = $C_{68}H_{98}O_4$

Molecular Weight = 979.5



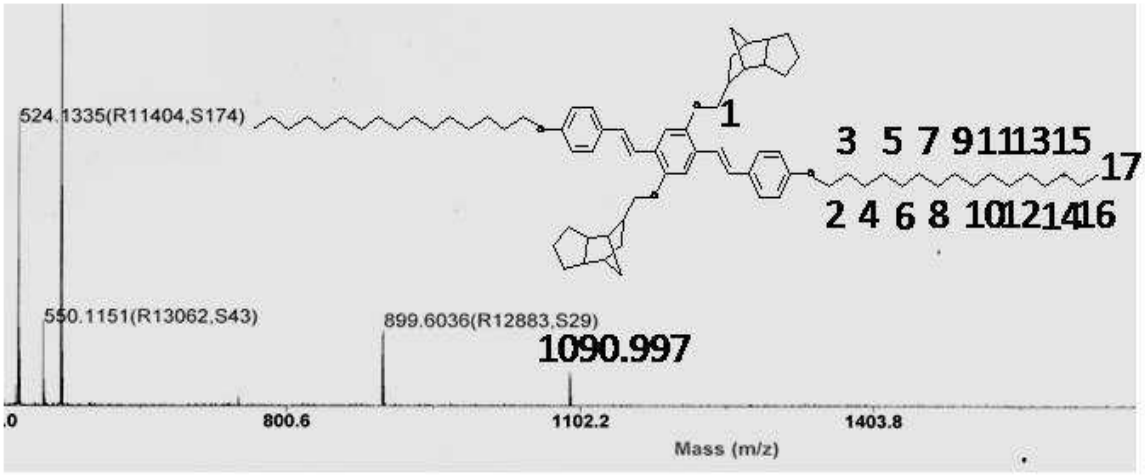


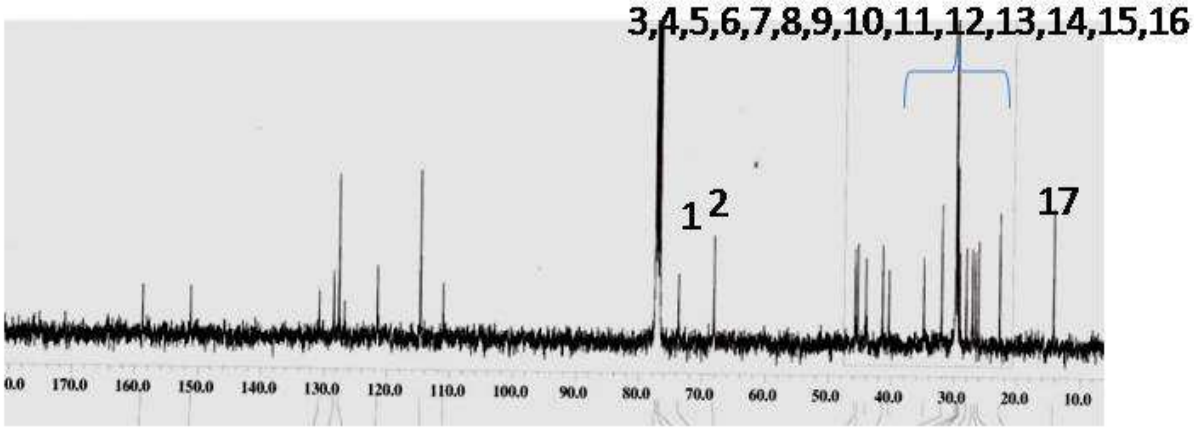


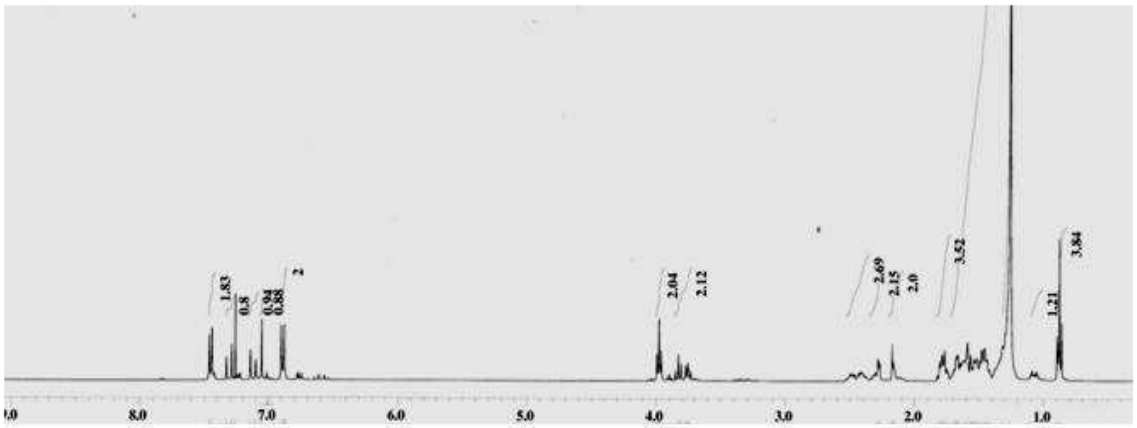
OPV-16

Molecular Formula = $C_{76}H_{114}O_4$

Molecular Weight = 1091.72



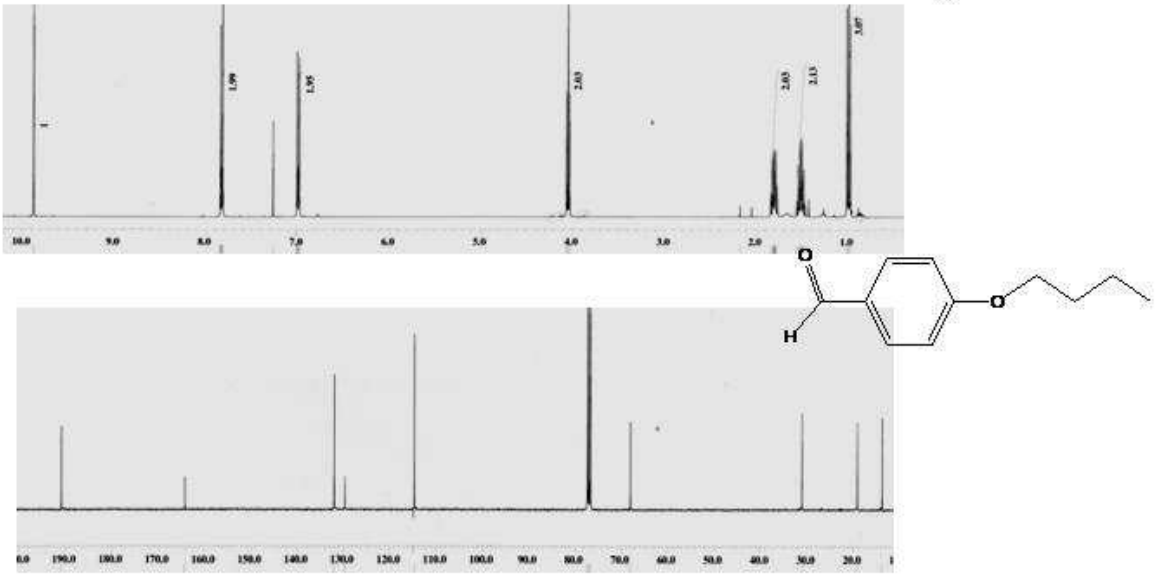




4-butoxybenzaldehyde

Molecular Formula = $C_{11}H_{14}O_2$

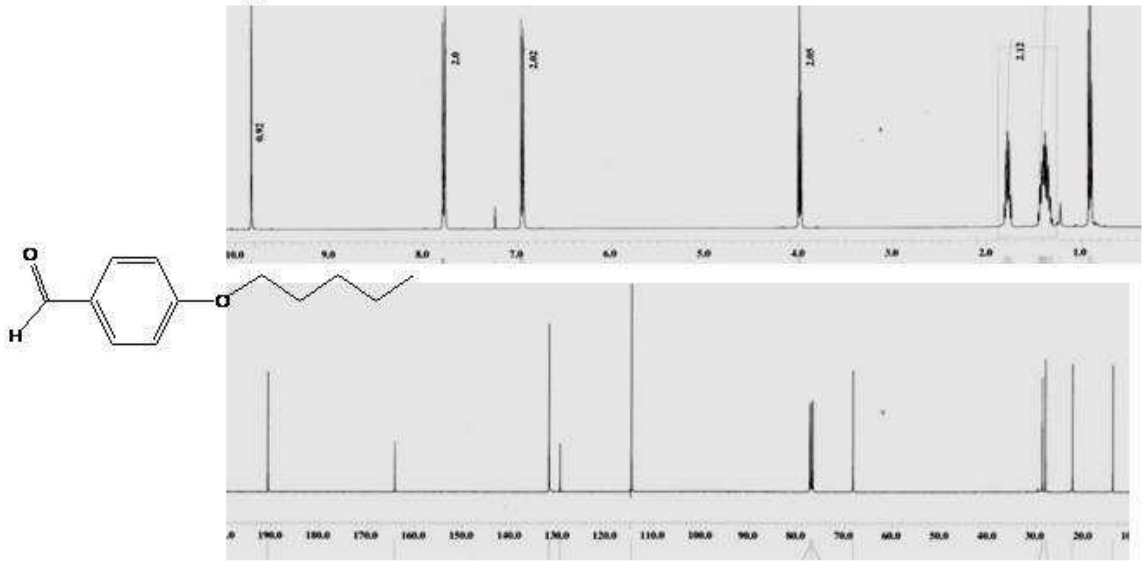
Molecular Weight = 178.23



4-(pentyloxy)benzaldehyde

Molecular Formula = $C_{12}H_{16}O_2$

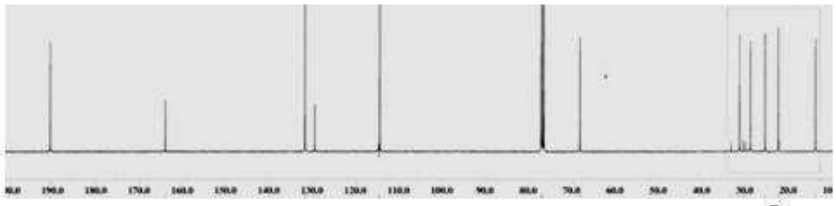
Molecular Weight = 192.25

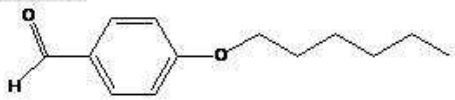


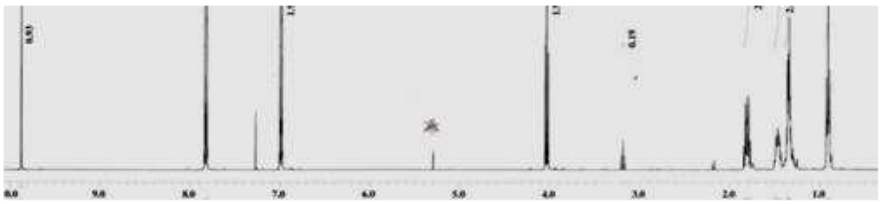
4-(hexyloxy)benzaldehyde

Molecular Formula = $C_{13}H_{18}O_2$

Molecular Weight = 206.28



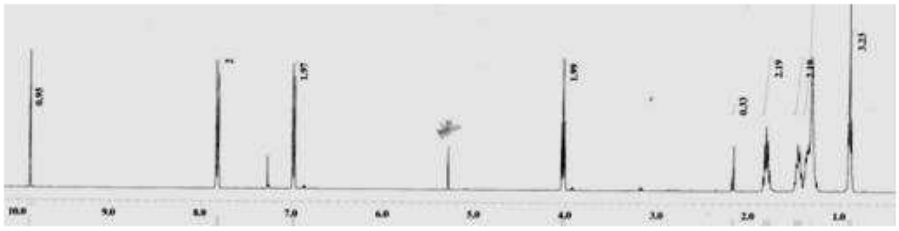


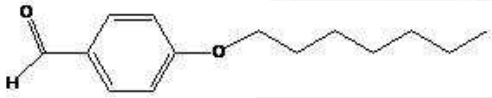


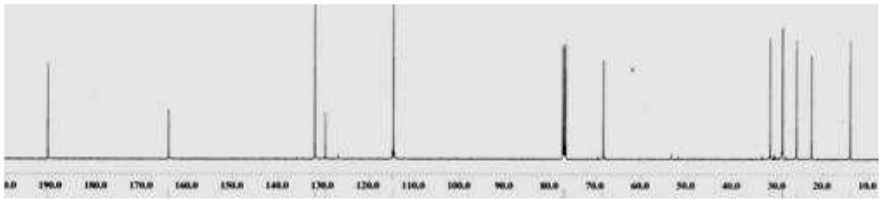
4-(heptyloxy)benzaldehyde

Molecular Formula = $C_{14}H_{20}O_2$

Molecular Weight = 220.31



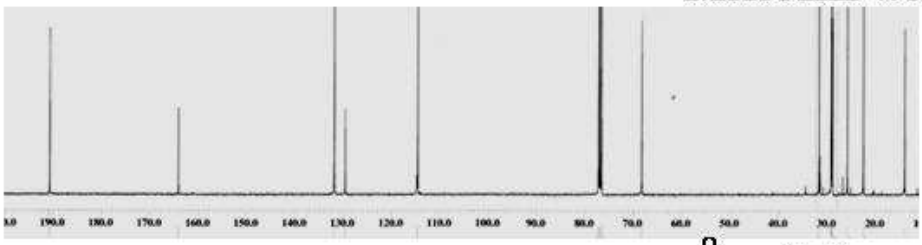


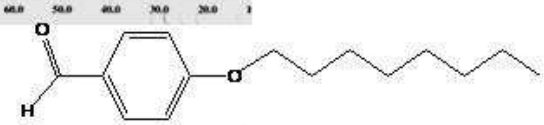


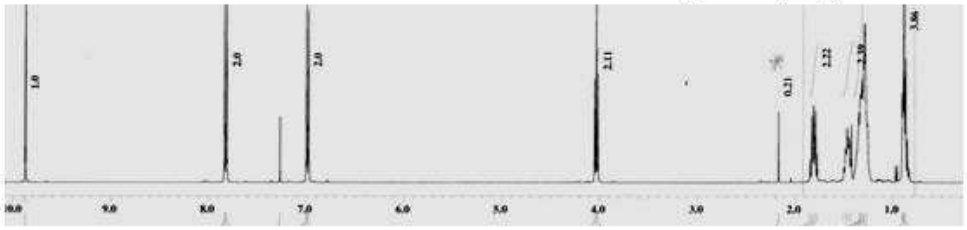
4-(octyloxy)benzaldehyde

Molecular Formula = $C_{15}H_{22}O_2$

Molecular Weight =234.33



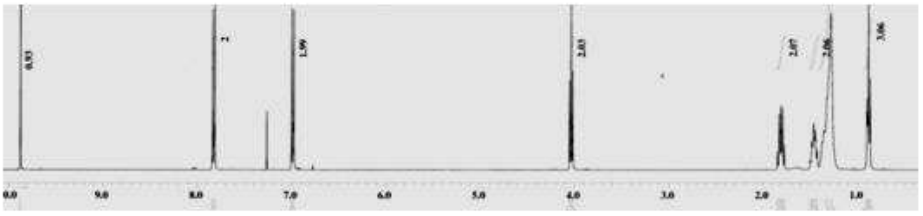


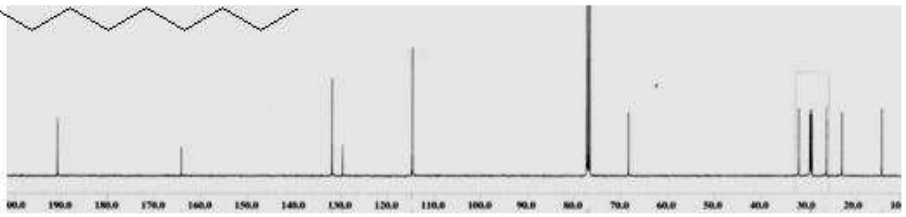


4-(nonyloxy)benzaldehyde

Molecular Formula = $C_{16}H_{24}O_2$

Molecular Weight = 248.36

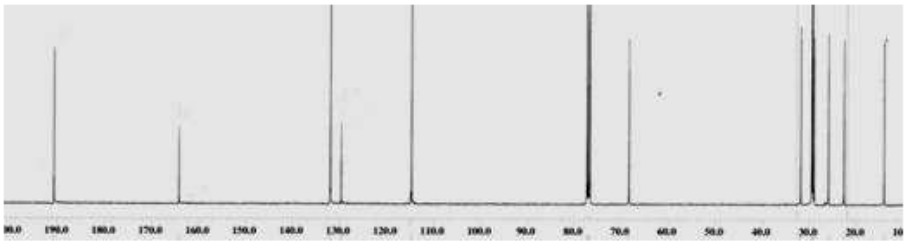




4-(decyloxy)benzaldehyde

Molecular Formula = $C_{17}H_{26}O_2$

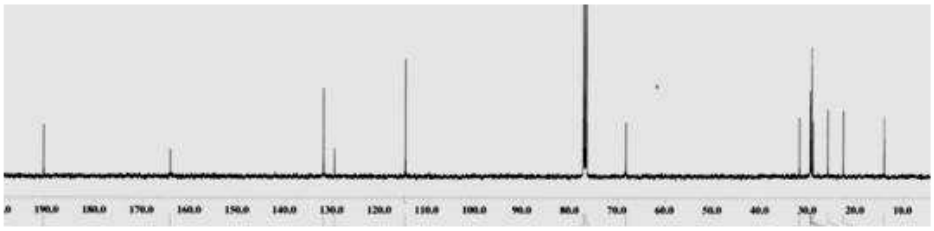
Molecular Weight = 262.39.



4-(undecyloxy)benzaldehyde

Molecular Formula = $C_{18}H_{28}O_2$

Molecular Weight = 276.41



4-(dodecyloxy)benzaldehyde

Molecular Formula = $C_{19}H_{30}O_2$

Molecular Weight = 290.44