"A New Class of Supramolecular LCs derived from Azo Calix[4]arene Functionalized 1,3,4-thiadiazole 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. Thermo gravimetric analysis (TGA) was performed using a Perkin Elmer-STA 6000 apparatus under high purity nitrogen. Mass Spectrometry was carried out using High Resolution Mass Spectrometer. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10°C min^{-1}. 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. Mass spectrometry was carried out by using MALDI-TOF mass spectrometer. The absorption spectra were studied by using Jasco V-570 UV-Vis recording spectrophotometer with a variable wavelength between 200 and 800 nm. The fluorescence spectra were recorded on a Jasco FP-6500 spectrofluorometer. The mixtures in square quartz cuvettes were excited at 320 nm, and the emission spectra were collected from 320 to 600 nm.

2. Synthesis and characterization

2.1 Preparation of *p-tert*-butyl calix[4]arene

p-tert-butyl calix[4]arene 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: (400 MHz, $CDCl_3$): 1.18 (s, 36H, t-butyl), 3.61 (d, J = 12.0Hz, 4H,

Ar-CH_2-Ar), 4.16 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 7.08 (s, 8H, Ar-H), 9.78 (s, 4H, Ar-OH); ^{13}C NMR: 149.1, 126.2, 126.1, 34.2, 31.4, 32.6.

2.2 Preparation of calix[4]arene (1)

calix[4]arene (**1**) was synthesized by deterbutylation reactions reported in the literature[1], white precipitates, yield 71%. Elemental analysis: $C_{28}H_{24}O_4$: Calcu: C, 79.23; H, 5.70; O, 15.08 %, Found: C, 78.97; H, 5.66; O, 14.89 %. ^{1}H NMR: (400 MHz, $CDCl_3$): 3.61 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 4.16 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 7.08 (s, 4H, Ar-H), 6.91 (d, 4H, Ar-H), 6.07 (d, 4H, Ar-H), 9.78 (s, 4H, Ar-OH); ^{13}C NMR: 152.1, 128.2, 126.1, 34.2, 31.48.

2.3.1 Preparation of 4-propyloxy azo calix[4]arene (2a)

4-propyloxy azo calix[4]arene (**2a**) was synthesized by reported in the literature[2], orange precipitates, yield 71%. Elemental analysis: $C_{65}H_{68}N_8O_8$: Calcu: C, 71.67; H, 6.29; N, 10.29 %, Found: C, 71.63; H, 6.21; N, 10.23 %. ^{1}H NMR: (400 MHz, $CDCl_3$): 0.88-0.90 (t, 12H, -OC_3H_7), 1.71 (p, 8H, -OC_3H_7), 4.08 (t, 8H, -OC_3H_7), 3.63 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 4.12 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 7.08 (d, 8H, Ar-H), 6.91 (d, 4H, Ar-H), 6.07 (d, 4H, Ar-H), 7.51 (s, 8H, Ar-H), 9.04 (s, 4H, Ar-OH); ^{13}C NMR: 161.3, 146.3, 144.1, 128.2, 126.1, 123.6, 114.2, 34.2, 31.48, 22.8.

2.3.2 Preparation of 4-octyloxy azo calix[4]arene (2b)

4-octyloxy azo calix[4]arene (**2b**) was synthesized by reported in the literature[2], orange precipitates, yield 71%. Elemental analysis: $C_{84}H_{104}N_8O_8$: Calcu: C, 74.33; H, 7.74; N, 8.28 %, Found: C, 74.29; H, 7.71; N, 8.19 %. ^{1}H NMR: (400 MHz, $CDCl_3$): 0.88-0.90 (t, 12H, -OC_8H_{17}), 1.26-1.28 (m, 32H, -OC_8H_{17}), 1.71 (p, 8H, -OC_8H_{17}), 1.42 (sext, 8H, -OC_8H_{17}), 4.08 (t, 8H, -OC_8H_{17}), 3.63 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 4.12 (d, *J* = 12.0Hz, 4H, Ar-CH_2-Ar), 7.08

(d, 8H, Ar-H), 6.91 (d, 4H, Ar-H), 6.07 (d, 4H, Ar-H), 7.51 (s, 8H, Ar-H), 9.04 (s, 4H, Ar-OH); ^{13}C NMR: 161.3, 146.3, 144.1, 128.2, 126.1, 123.6, 122.6, 114.2, 34.2, 31.48, 22.8.

2.4.1 Preparation of 3,4,5-tributyloxy benzohydrazide (4a)

3,4,5-tributyloxy benzohydrazide (**4a**) was synthesized by the refluxing the reaction mixture of methyl 3,4,5-tributyloxy benzoate (**3**) (1 equiv.) with hydrazine hydrate (1 equiv.) in n-butanol at 24 hr[3]. Yield 79 %, FT-IR (KBr) in cm^{-1}: 3227, 2890, 1684, and 1245. ^{1}H NMR $CDCl_3$ (400 MHz): 4.41 (s, 2H, -NH_2), 7.12 (s, 2H, Ar-H), 9.71 (s, 1H, -CONH), 0.88 (t, 9H, -OC_3H_7), 1.71 (p, 6H, -OC_3H_7), 4.06 (t, 6H, -OC_3H_7). ^{13}C NMR: 153.4, 139.3, 129.6, 124.1, 164.2, 34.8.

2.4.2 Preparation of 3,4,5-trihexyloxy benzohydrazide (4b)

3,4,5-trihexyloxy benzohydrazide (**4b**) was synthesized by the refluxing the reaction mixture of methyl 3,4,5-trihexoloxy benzoate (**3**) (1 equiv.) with hydrazine hydrate (1 equiv.) in n-butanol at 24 hr[3]. Yield 76 %, FT-IR (KBr) in cm^{-1}: 3127, 2891, 1654, 1240, 1130 and 791. ^{1}H NMR $CDCl_3$ (400 MHz): 4.41 (s, 2H, -NH_2), 7.14 (s, 2H, Ar), 9.71 (s, 1H, -CONH), 0.88 (t, 9H, -OC_6H_{13}), 1.71 (p, 6H, -OC_6H_{13}), 1.41 (t, 6H, -OC_6H_{13}), 1.26-1.28 (m, 12H, -OC_6H_{13}). ^{13}C NMR: 153.4, 139.3, 129.6, 124.1, 123.6, 164.2, 34.8, 31.8, 22.6.

2.4.3 Preparation of 3,4,5-trioctyloxy benzohydrazide (4c)

3,4,5-trioctyloxy benzohydrazide (**4c**) was synthesized by the refluxing the reaction mixture of methyl 3,4,5-trioctoloxy benzoate (**3**) (1 equiv.) with hydrazine hydrate (1 equiv.) in n-butanol at 24 hr[3]. Yield 81 %, FT-IR (KBr) in cm^{-1}: 3227, 2890, 1684, 1240, 1130, 730, 610. ^{1}H NMR $CDCl_3$ (400 MHz): 4.41 (s, 2H, -NH_2), 7.14 (s, 2H, Ar), 9.71 (s, 1H, -CONH), 0.88 (t, 9H, -OC_8H_{17}), 1.71 (p, 6H, -OC_8H_{17}), 1.41 (t, 6H, -OC_8H_{17}), 1.26-1.28 (m, 24H, -OC_8H_{17}). ^{13}C NMR: 153.4, 139.3, 129.6, 124.1, 123.6, 164.2, 122.6, 31.8, 22.6.

2.5.1 Preparation of 3,4,5-tributyloxy-N'-(4-nitrobenzoyl) benzohydrazide (5a)

3,4,5-tributyloxy-N'-(4-nitrobenzoyl) benzohydrazide (**5a**) is synthesised from the mixture of 3,4,5-tributyloxy benzohydrazide (**4a**) (1 equiv.) in dry pyridine, later, the solution of 4-nitro benzoyl chloride (1 equiv.) in THF was added in it[3]. The reaction mixture was stirred at room temperature for 10 h and then poured into cold water. The obtained solid residue was further recrystallized in hot ethanol[1].Yield: 76%; FT-IR (KBr pellet) in cm-1: 3103, 2940, 1640, 1521, 1433, 1234, 803, 604;^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.24 (s, 1H, -CONH), 9.62 (s, 1H, -CONH), 8.21 (d, 2H, *J* = 8Hz, Ar), 8.07 (d, 2H, *J* = 8Hz, Ar), 7.01 (s, 2H, Ar), 3.83 (s, 9H,-OC_3H_7), 1.71 (p, 6H, -OC_3H_7), 1.46 (sext, 6H, -OC_3H_7), 4.04 (t, 6H, -OC_3H_7); ^{13}C NMR: 167.8, 161.3, 153.3, 151.7, 142.6, 138.1, 129.9, 124.6, 123.8, 108.4, 61.4, 55.4.

2.5.2 Preparation of 3,4,5-trihexyloxy-N'-(4-nitrobenzoyl) benzohydrazide (5b)

3,4,5-trihexyloxy-N'-(4-nitrobenzoyl) benzohydrazide (**5b**) is synthesised from the mixture of 3,4,5-trihexyloxy benzohydrazide (**4b**) (1 equiv.) in dry pyridine, later, the solution of 4-nitro benzoyl chloride (1 equiv.) in THF was added in it[3]. The reaction mixture was stirred at room temperature for 10 h and then poured into cold water. The obtained solid residue was further recrystallized in hot ethanol[1].Yield: 69%; FT-IR (KBr pellet) in cm-1: 3103, 2940, 1650, 1520, 1310, 1234, 808, 731;^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.24 (s, 1H, -CONH), 9.62 (s, 1H, -CONH), 8.21 (d, 2H, *J* = 8Hz, Ar), 8.07 (d, 2H, *J* = 8Hz, Ar), 7.01 (s, 2H, Ar), 3.83 (s, 9H,-OC_6H_{13}), 1.71 (t, 6H, -OC_6H_{13}), 1.43 (t, 6H, -OC_6H_{13}), 1.26-1.28 (m, 12H, -OC_6H_{13}); ^{13}C NMR: 167.8, 161.3, 153.3, 151.7, 142.6, 138.1, 129.9, 124.6, 123.8, 108.4, 61.4, 55.4.

2.5.3 Preparation of 3,4,5-trioctyloxy-N'-(4-nitrobenzoyl) benzohydrazide (5c)

3,4,5-trioctyloxy-N'-(4-nitrobenzoyl) benzohydrazide (**5c**) is synthesised from the mixture of 3,4,5-trioctyloxy benzohydrazide (**4c**) (1 equiv.) in dry pyridine, later, the solution of 4-nitro benzoyl chloride (1 equiv.) in THF was added in it[3]. The reaction mixture was stirred at room temperature for 10 h and then poured into cold water. The obtained solid residue was further recrystallized in hot ethanol[1].Yield: 76%; FT-IR (KBr pellet) in cm-1: 3103, 2940, 1630, 1540, 1410, 1210, 803, 730;^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.24 (s, 1H, -CONH), 9.62 (s, 1H, -CONH), 8.21 (d, 2H, *J* = 8Hz, Ar), 8.07 (d, 2H, *J* = 8Hz, Ar), 7.01 (s, 2H, Ar), 3.83 (s, 9H,-OC_8H_{17}), 1.26-1.28 (m, 32H, -OC_6H_{13}), 1.42 (sext, 6H, -OC_8H_{17}), 1.71 (p, 6H, -OC_8H_{17}); ^{13}C NMR: 167.8, 161.3, 153.3, 151.7, 142.6, 138.1, 129.9, 124.6, 123.8, 108.4, 61.4, 55.4, 31.8, 22.8.

2.6.1 Preparation of 2-(4-nitrophenyl)-5-(3,4,5-tributyloxy phenyl)-1, 3, 4-thiadiazole (6a)

The solution of compound **5a** (1 equiv.) in THF (20 ml) was added to P_2S_5 (3.6 equiv.) at 0˚C under inert atmosphere and refluxed for 48 hr. The reaction mixture was poured on to ice water and extracted by using chloroform. The yellow residue obtained by extraction using chloroform solvent. Evaporation of solvent and recrystallization with ethanol furnished the desire product[4]. Yield: 67 %; IR (KBr pellet) in cm^{-1}: 3101, 2940, 1606, 1554, 1457, 1341, 1321, 1212, 869. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, 2H, *J* = 6Hz, Ar), 7.83 (d, 2H, J = 8Hz, Ar), 6.87 (s, 2H, Ar), 0.88 (t, 9H, -OC_4H_9), 1.71 (t, 6H, -OC_4H_9), 4.04 (t, 6H, -OC_4H_9).^{13}C NMR: 161.5, 153.3, 151.7, 142.6, 129.6, 124.6, 124.55, 108.4, 61.9, 55.4.

2.6.2 Preparation of 2-(4-nitrophenyl)-5-(3,4,5-trihexyloxy phenyl)-1, 3, 4-thiadiazole (6b)

The solution of compound **5b** (1 equiv.) in THF (20 ml) was added to P_2S_5 (3.6 equiv.) at 0˚C under inert atmosphere and refluxed for 48 hr. The reaction mixture was poured on to ice water

and extracted by using chloroform. The yellow residue obtained by extraction using chloroform solvent. Evaporation of solvent and recrystallization with ethanol furnished the desire product[4]. Yield: 67 %; IR (KBr pellet) in cm^{-1}: 3101, 2940, 1606, 1554, 1457, 1341, 1321, 1212, 869. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, 2H, *J* = 6Hz, Ar), 7.83 (d, 2H, J = 8Hz, Ar), 6.87 (s, 2H, Ar), 0.88 (t, 9H, $-OC_6H_{13}$), 1.71 (t, 6H, $-OC_6H_{13}$), 1.26-1.28 (m, 12H, $-OC_6H_{13}$), 4.04 (t, 6H, $-OC_6H_{13}$). ^{13}C NMR: 161.5, 153.3, 151.7, 142.6, 129.6, 124.6, 124.55, 108.4, 61.9, 55.4.

2.6.3 Preparation of 2-(4-nitrophenyl)-5-(3,4, 5-trioctyloxy phenyl)-1, 3,4-thiadiazole (6c)

The solution of compound **5c** (1 equiv.) in THF (20 ml) was added to P_2S_5 (3.6 equiv.) at 0˚C under inert atmosphere and refluxed for 48 hr. The reaction mixture was poured on to ice water and extracted by using chloroform. The yellowish residue obtained by extraction using chloroform solvent. Evaporation of solvent and recrystallization with ethanol furnished the desire product[4]. Yield: 67 %; IR (KBr pellet) in cm^{-1}: 3101, 2940, 1606, 1554, 1457, 1341, 1321, 1212, 869. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, 2H, *J* = 6 Hz, Ar), 7.83 (d, 2H, J = 8Hz, Ar), 6.87 (s, 2H, Ar), 0.88 (t, 9H, $-OC_8H_{17}$), 1.26-1.28 (m, 32H, $-OC_8H_{17}$), 1.42 (sext, 6H, $-OC_8H_{17}$), 1.72 (p, 6H, $-OC_8H_{17}$).^{13}C NMR: 161.5, 153.3, 151.7, 142.6, 129.6, 124.6, 124.55, 108.4, 61.9, 55.4.

2.7.1 Preparation of 4-(5-3, 4, 5-tributyloxy phenyl)-1,3,4-thiadiazol-2-yl) aniline (7a)

The solution of nitro compound **6a** (1 equiv.) in dry THF was added 10 % Pd-C and stirred under hydrogen atmosphere (balloon) for 10h. The reaction mixture was filtered and further purification of the residue by column chromatography using ethylacetate-hexane (3:2) system[3]. Yield: 67%; IR (KBr pellet) in cm^{-1}: 2931, 2858, 2810, 1610, 1491, 1448, 1390, 1331, 1122, 986, 835; ^1H NMR ($CDCl_3$, 400MHz): δ 7.37 (d, 2H, *J*= 8.2 Hz ,Ar), 6.88 (s, 2H, Ar), 6.72 (d, 2H, *J*= 7.8 Hz, Ar), 5.31 (s, 2H, $-NH_2$), 4.06 (t, 6H, $-OC_4H_9$), 0.90 (t, 9H, $-OC_4H_9$), 1.47 (sext,

6H, -OC_4H_9), 1.76 (p, 6H, -OC_4H_9); ^{13}C NMR: 164.13, 147.88, 145.53, 138.64, 128.29, 118.91, 116.38, 103.61, 77.01, 68.82, 31.88, 19.07, 14.16.

2.7.2 Preparation of 4-(5-3, 4, 5-trihexyloxy phenyl)-1,3,4-thiadiazol-2-yl) aniline (7b)

The solution of nitro compound **6b** (1 equiv.) in dry THF was added 10 % Pd-C and stirred under hydrogen atmosphere (balloon) for 10h. The reaction mixture was filtered and further purification of the residue by column chromatography using ethylacetate-hexane (3:2) system[3].

Yield: 71%; IR (KBr pellet) in cm^{-1}: 2930, 2848, 1640, 1495, 1458, 1390, 1310, 1120, 986, 835, 721; ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.37 (d, 2H, *J*= 8.2 Hz ,Ar), 6.88 (s, 2H, Ar), 6.72 (d, 2H, *J*= 7.8 Hz, Ar), 5.33 (s, 2H, -NH_2), 4.06 (t, 6H, -OC_6H_{13}), 0.88-0.90 (t, 9H, -OC_6H_{13}), 1.47 (sext, 6H, -OC_6H_{13}), 1.76 (t, 6H, -OC_6H_{13}), 1.26-1.28 (m, 12H, -OC_6H_{13}); ^{13}C NMR: 164.13, 147.88, 145.53, 138.64, 128.29, 118.91, 116.38, 103.61, 77.01, 68.82, 31.88, 19.07, 14.16.

2.7.3 Preparation of 4-(5-3, 4, 5-trioctyloxy phenyl)-1,3,4-thiadiazol-2-yl) aniline (7c)

The solution of nitro compound **6c** (1 equiv.) in dry THF was added 10 % Pd-C and stirred under hydrogen atmosphere (balloon) for 10h. The reaction mixture was filtered and further purification of the residue by column chromatography using ethylacetate-hexane (3:2) system[3].

Yield: 74%; IR (KBr pellet) in cm^{-1}: 2930, 2848, 1610, 1491, 1448, 1390, 1331, 1120, 986, 835, 721; ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.37 (d, 2H, *J*= 8.2 Hz ,Ar), 6.88 (s, 2H, Ar), 6.72 (d, 2H, *J*= 7.8 Hz, Ar), 5.33 (s, 2H, -NH_2), 4.06 (t, 6H, -OC_8H_{17}), 0.88-0.90 (t, 9H, -OC_8H_{17}), 1.47 (sext, 6H, -OC_8H_{17}), 1.71(t, 6H, -OC_8H_{17}), 1.26-1.28 (m, 32H, -OC_8H_{17}) ; ^{13}C NMR: 164.13, 147.88, 145.53, 138.64, 128.29, 118.91, 116.38, 103.61, 77.01, 68.82, 31.88, 19.07, 14.16.

2.8.1 4-(((4-(5-(3,4,5-tris(butyloxy) phenyl)-1,3,4-thiadiazol-2-yl) phenyl) imino) methyl) benzoic acid (8a)

Compound (**8a**) is synthesised from the reaction of compound **7a** (1 equiv.) with 4-formyl benzoic acid (1 equiv.) in ethanol (20 ml) with presence of few drops of glacial acetic acid for 1

hr. The obtained yellowish orange colour residue is washed with ethanol and further purified by column chromatography using ethaylacetate: hexane (3:2) systems[4]. Yield: 79%; IR (KBr pellet) in cm^{-1}: 3450, 2930, 2848, 1610, 1495, 1440, 1415, 1390, 1331, 1296, 1210, 1122, 986, 835, 721, 629; ^{1}H NMR ($CDCl_3$, 400MHz): δ 13.87 (s, 1H, -COOH), 8.58 (s, 1H, -CH=N), 7.61 (d, 2H, *J*= 8.4 Hz ,Ar), 7.43 (d, 2H, *J*= 8.2 Hz, Ar), 7.08 (d, 2H, *J*= 7.8 Hz, Ar), 6.71 (d, 2H, Ar), 6.72 (d, 2H, *J* = 7.8 Hz, Ar), 4.08 (t, 6H, $-OC_3H_7$), 0.99 (t, 9H, $-OC_3H_7$), 1.48 (sext, 6H, $-OC_3H_7$), 1.71 (p, 6H, $-OC_3H_7$); ^{13}C NMR: 164.48, 160.65, 152.31, 149.52, 147.04,138.72, 131.35, 129.25, 124.74, 122.27, 118.81, 116.72, 101.09, 77.43, 69.23, 31.53, 29.29, 25.89, 22.44, 14.03.

2.8.2 4-(((4-(5-(3,4,5-tris(hexyloxy) phenyl)-1,3,4-thiadiazol-2-yl) phenyl) imino) methyl) benzoic acid (8b)

Compound (**8b**) is synthesised from the reaction of compound **7b** (1 equiv.) with 4-formyl benzoic acid (1 equiv.) in ethanol (20 ml) with presence of few drops of glacial acetic acid for 1 hr. The obtained yellow colour residue is washed with ethanol and further purified by column chromatography using ethaylacetate: hexane (3:2) systems[4]. Yield: 81%; IR (KBr pellet) in cm^{-1}: 3450, 2930, 2848, 1610, 1495, 1440, 1415, 1390, 1331, 1122, 986, 835, 721, 629; ^{1}H NMR ($CDCl_3$, 400MHz): δ 13.87 (s, 1H, -COOH), 8.58 (s, 1H, -CH=N), 7.61 (d, 2H, *J*= 8.4 Hz ,Ar), 7.40 (d, 2H, *J*= 8.2 Hz, Ar), 7.05 (d, 2H, *J*= 7.8 Hz, Ar), 6.79 (d, 2H, Ar), 6.72 (d, 2H, *J* = 7.8 Hz, Ar), 4.08 (t, 6H, $-OC_6H_{13}$), 0.88-0.99 (t, 9H, $-OC_6H_{13}$), 1.26-1.28 (m, 12H, $-OC_6H_{13}$), 1.47 (sext, 6H, $-OC_6H_{13}$), 1.71 (p, 6H, $-OC_6H_{13}$); ^{13}C NMR: 164.48, 160.65, 152.31, 149.54, 147.04,138.72, 131.35, 129.25, 124.71, 122.27, 118.81, 116.72, 101.09, 77.41, 69.23, 31.53, 29.29, 25.79, 22.47, 14.10, 14.03.

2.8.3 4-(((4-(5-(3,4,5-tris(octyloxy) phenyl)-1,3,4-thiadiazol-2-yl) phenyl) imino) methyl) benzoic acid (8c)

Compound (**8c**) is synthesised from the reaction of compound **7c** (1 equiv.) with 4-formyl benzoic acid (1 equiv.) in ethanol (20 ml) with presence of few drops of glacial acetic acid for 1 hr. The obtained yellow colour residue is washed with ethanol and further purified by column chromatography using ethaylacetate: hexane (3:2) systems[4]. Yield: 81%; IR (KBr pellet) in cm^{-1}: 3450, 2930, 2848, 1610, 1491, 1440, 1415, 1380, 1341, 1122, 981, 835, 810, 720, 701, 629, 621; ^{1}H NMR ($CDCl_3$, 400MHz): δ 13.84 (s, 1H, -COOH), 8.58 (s, 1H, -CH=N), 7.61 (d, 2H, *J*= 8.4 Hz ,Ar), 7.40 (d, 2H, *J*= 8.2 Hz, Ar), 7.05 (d, 2H, *J*= 7.8 Hz, Ar), 6.79 (d, 2H, Ar), 6.72 (d, 2H, *J* = 7.8 Hz, Ar), 4.08 (t, 6H, $-OC_8H_{17}$), 0.88-0.90 (t, 6H, $-OC_8H_{17}$), 1.26-1.28 (m, 32H, $-OC_8H_{17}$), 1.47 (sext, 6H, $-OC_8H_{17}$), 1.71 (p, 6H, $-OC_8H_{17}$); ^{13}C NMR: 164.48, 160.65, 152.31, 149.54, 147.04,138.71, 131.34, 129.29, 124.71, 122.27, 118.81, 116.72, 101.34, 77.48, 69.23, 31.53, 29.29, 25.83, 22.44, 14.10, 14.03.

3.4 Preparation of 5, 11, 17, 23-tetra-alkoxy azocalix-25, 26, 27, 28 tetra n-alkoxy phenyl thiadiazole phenyl schiff base-ester (9a-9f)

The compound has been prepared by esterification of the appropriate compound (**2a-2b**) (0.0015 mol.) and compound (**8a-8c**) (0.0060 mol.), dicyclohexyl carbodiimide (DCC) (0.0060 mol.) and dimethylaminopyridine (DMAP) in catalytic amount (0.0030 mmol) in dry CH_2Cl_2 (DCM) (40 ml) was stirred at room temperature for 24 h. The slightly yellowish precipitate of DCU is obtained which was isolated by filtration and remove, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4)[5].

(9a): Yield 71 %, Elemental analysis: $C_{200}H_{210}N_{20}O_{24}S_4$: Calcu: C, 70.52; H, 6.21; N, 8.22; O, 11.27 %; S, 3.76 %. Found: C, 71.56; H, 5.85; N, 8.12; O, 11.17 %. FT-IR (KBr) in cm^{-1}: 2990, 1750, 1640, 1441, 1320, 1140, 1120, 981, 886. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88 (t, 48H, -OC_4H_9 & -OC_3H_7), 1.48 (sext, 24H, -OC_4H_9), 1.74 (p, 32H, -OC_4H_9 & -OC_3H_7), 3.61 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-), 4.02 (t, 32H, -OC_4H_9 & -OC_3H_7), 4.14 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-), 6.74 (s, 8H, *J* = 8 Hz, Ar), 6.98 (d, 8H, *J* = 8.8 Hz, Ar), 7.12 (d, 8H, Ar), 7.26 (d, 4H, *J* =6.9 Hz, Ar), 7.58 (d, 8H, Ar), 8.28 (s, 4H, -CH=N). ^{13}C NMR: 164.50, 161.42, 159.42, 147.83, 145.01, 131.31, 130.25, 129.31, 128.32, 127.51, 126.42, 115.50, 114.90, 103.58, 77.45, 77.02, 76.60, 68.43, 34.83, 32.81, 31.86, 31.83, 19.03, 14.17. MALDI Tof MS for compound **9a** (M+1) Calculated: 3403.4782 Found 3404.586.

(9b): Yield 74 %, Elemental analysis: $C_{224}H_{258}N_{20}O_{24}S_4$: Calcu: C, 71.88; H, 6.95; N, 7.48; O, 10.26 %; S, 3.43 %. Found: C, 71.76; H, 6.84; N, 7.41; O, 10.16 %. FT-IR (KBr) in cm^{-1}: 2890, 1730, 1660, 1446, 1410, 1236, 1121, 886, 730, 704, 630. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88-0.90 (t, 48H, -OC_6H_{13} & -OC_3H_7), 1.26-1.28 (m, 24 H, -OC_6H_{13}), 1.48 (sext, 24H, -OC_6H_{13}), 1.75 (p, 32H, -OC_6H_{13} & -OC_3H_7), 3.61 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-),

4.04 (t, 32H, -OC_6H_{13} & -OC_3H_7), 4.12 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 6.74 (d, 8H, *J* = 8 Hz, Ar), 6.98 (d, 8H, *J* = 8.8 Hz, Ar), 7.12 (s, 8H, Ar), 7.26 (d, 8H, J = 6.9 Hz, Ar), 7.58 (d, 8H, Ar), 8.42 (s, 4H, -CH=N). ^{13}C NMR: 164.57, 159.42, 147.82, 145.05, 130.42, 130.18, 129.37, 128.32, 127.42, 127.12, 125.40, 115.05, 114.90, 103.58, 77.45, 77.02, 76.60, 68.73, 34.84, 32.86, 31.93, 31.32, 29.64, 29.34, 25.97, 22.70, 14.17. MALDI Tof MS for compound **9b** (M+1) Calculated: 3742.8872 Found 3743.698.

(9c): Yield 78 %, Elemental analysis: $C_{248}H_{306}N_{20}O_{24}S_4$: Calcu: C, 73.02; H, 7.56; N, 6.87; O, 9.41 %; S, 3.14 %. Found: C, 72.86; H, 7.47; N, 6.79; O, 8.17 %. FT-IR (KBr) in cm^{-1}: 2980, 1760, 1610, 1440, 1340, 1214, 1148, 886, 821, 741, 689. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88-0.90 (t, 48H, -OC_8H_{17} & -OC_3H_7), 1.49 (sext, 32H, -OC_8H_{17}), 1.26-1.28 (m, 92H, -OC_8H_{17}), 1.74 (p, 32H, -OC_8H_{17} & -OC_3H_7), 3.62 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 4.01 (t, 32H, -OC_8H_{17} & -OC_3H_7), 4.12 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 6.94 (d, 8H, *J* = 8 Hz, Ar), 7.03 (d, 7H, Ar), 7.14 (s, 4H, Ar), 7.91 (d, 7H, *J* = 8.8 Hz, Ar), 8.04 (d, 8H, *J* = 7.6 Hz, Ar), 8.51 (s, 4H, -CH=N). ^{13}C NMR: 174.14, 160.42, 159.47, 147.88, 146.01, 138.71, 130.04, 129.36, 127.52, 126.09, 125.44, 125.19, 114.92, 103.58, 77.44, 77.02, 76.60, 68.41, 34.83, 32.83, 31.89, 31.32, 19.03, 14.10. MALDI Tof MS for compound **9c** (M+1) Calculated: 4076.2298 Found 4077.452.

(9d): Yield 70 %, Elemental analysis: $C_{220}H_{250}N_{20}O_{24}S_4$: Calcu: C, 71.67; H, 6.84; N, 7.60; O, 10.41 %; S, 3.48 %. Found: C, 70.96; H, 6.81; N, 7.43; O, 10.19 %. FT-IR (KBr) in cm^{-1}: 2896, 1750, 1630, 1441, 1415, 1361, 1240, 1120, 1121, 881, 741, 648. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88-0.90 (t, 48H, -OC_4H_9 & -OC_8H_{17}), 1.28-1.30 (m, 32H, -OC_8H_{17}), 1.51 (sext, 32H, -OC_4H_9 & -OC_8H_{17}), 1.74 (p, 32H, -OC_4H_9 & -OC_8H_{17}), 3.62 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 4.08 (t, 32H, -OC_4H_9 & -OC_8H_{17}), 4.12 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 6.56 (d, 8H, *J* = 8 Hz, Ar),

6.91 (d, 8H, Ar), 7.08 (d, 4H, *J* = 8.8 Hz, Ar), 7.12 (s, 8H, Ar), 7.26 (d, 8H, *J* = 8Hz, Ar), 8.51 (s, 4H, -CH=N). ^{13}C NMR: 174.18, 160.44, 159.45, 147.83, 145.01, 138.75, 130.47, 129.39, 128.15, 127.46, 125.40, 125.12, 114.63, 103.58, 77.48, 77.05, 76.63, 68.70, 34.84, 32.81, 31.93, 31.33, 29.62, 29.37, 25.37, 22.76, 14.13. MALDI Tof MS for compound **9d** (M+1) Calculated: 3683.7841 Found 3684.478.

(9e): Yield 63 %, Elemental analysis: $C_{244}H_{298}N_{20}O_{24}S_4$: Calcu: C, 72.84; H, 7.47; N, 6.96; O, 9.54 %; S, 3.19 %. Found: C, 72.06; H, 7.81; N, 6.98; O, 9.71 %. FT-IR (KBr) in cm^{-1}: 2891, 1730, 1630, 1440, 1417, 1361, 1289, 1230, 1120, 1121, 886, 741, 640. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88-0.90 (t, 48H, -OC_6H_{13} & -OC_8H_{17}), 1.28-1.30 (m, 72H, -OC_6H_{13} & -OC_8H_{17}), 1.51 (sext, 32H, -OC_6H_{13} & -OC_8H_{17}), 1.74 (p, 32H, -OC_6H_{13} & -OC_8H_{17}), 3.62 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-), 4.06 (t, 32H, -OC_6H_{13} & -OC_8H_{17}), 4.12 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-), 6.26 (d, 8H, *J* = 8 Hz, Ar), 6.91 (d, 8H, Ar), 7.08 (d, 4H, *J* = 8.8 Hz, Ar), 7.12 (s, 8H, Ar), 8.04 (d, 8H, *J* = 6Hz, Ar), 8.51 (s, 4H, -CH=N). ^{13}C NMR: 174.18, 160.44, 159.45, 147.83, 145.01, 138.75, 130.47, 129.39, 128.15, 127.46, 125.40, 125.12, 114.63, 103.58, 77.48, 77.05, 76.63, 68.70, 34.84, 32.81, 31.93, 31.33, 29.62, 29.37, 25.37, 22.76, 14.13. MALDI Tof MS for compound **9e** (M+1) Calculated: 4020.1624 Found 4021.342.

(9f): Yield 68 %, Elemental analysis: $C_{268}H_{346}N_{20}O_{24}S_4$: Calcu: C, 73.83; H, 8.02; N, 6.43; O, 8.81 %; S, 2.94 %. Found: C, 73.76; H, 7.91; N, 6.58; O, 9.01 %. FT-IR (KBr) in cm^{-1}: 2896, 1760, 1640, 1440, 1418, 1361, 1230, 1120, 1121, 876, 742, 641. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88-0.90 (t, 48H, -OC_8H_{17} & -OC_8H_{17}), 1.28-1.30 (m, 118H, -OC_8H_{17} & -OC_8H_{17}), 1.51 (sext, 32H, -OC_8H_{17} & -OC_8H_{17}), 1.74 (p, 32H, -OC_8H_{17} & -OC_8H_{17}), 3.62 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-), 4.06 (t, 32H, -OC_8H_{17} & -OC_8H_{17}), 4.12 (d, *J* = 18.0 Hz, 4H, -ArCH_2Ar-), 6.91 (d, 8H, *J* = 8 Hz, Ar), 7.08 (d, 4H, Ar), 7.12 (s, 8H, Ar), 7.26 (d, 8H, *J* =

8.8 Hz, Ar), 8.04 (d, 8H, J = 6 Hz, Ar), 8.51(s, 4H, -CH=N). ^{13}C NMR: 174.18, 160.44, 159.45, 147.83, 145.01, 138.75, 130.47, 129.39, 128.15, 127.46, 125.40, 125.12, 114.63, 103.58, 77.48, 77.05, 76.63, 68.70, 34.84, 32.81, 31.93, 31.33, 29.62, 29.37, 25.37, 22.76, 14.13. MALDI Tof MS for compound **9f** (M+1) Calculated: 4356.5472 Found 4357.467.

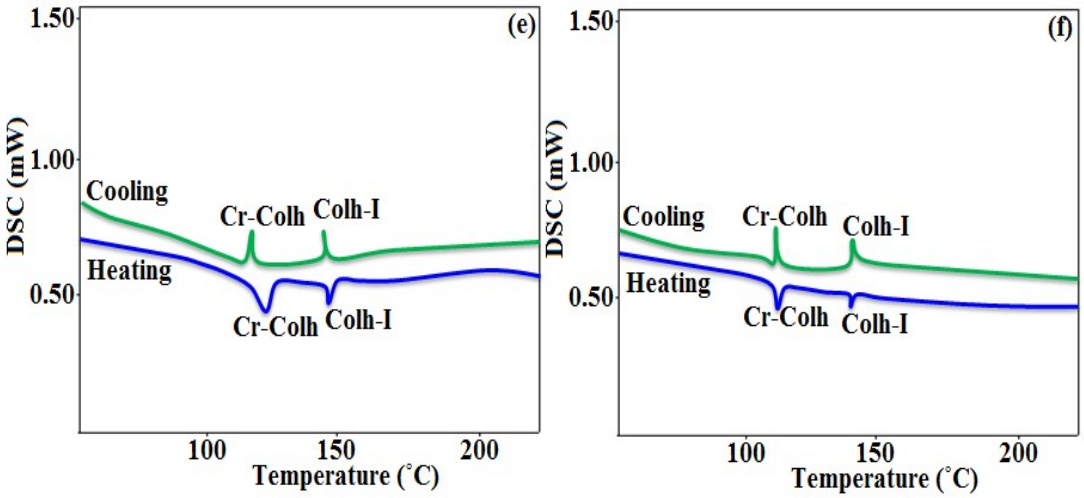

Figure S_1: The DSC traces of compounds **9e** (e) and **9f** (f) on second heating and cooling (scan rate 10˚C/min).

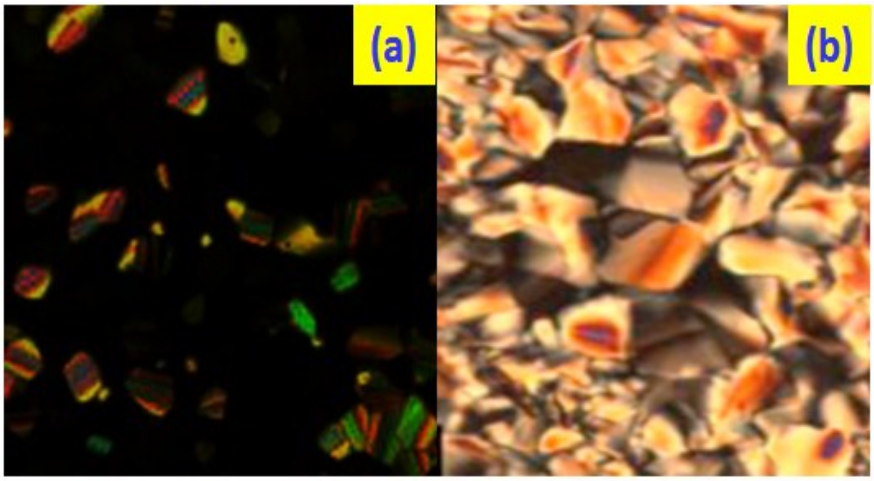

Figure S_2: POM texture image of compound **9b** at 139.1 ˚C (a) compound **9d** at 129.8 ˚C (b) on heating condition from solid crystalline state as seen under cross polarizers.

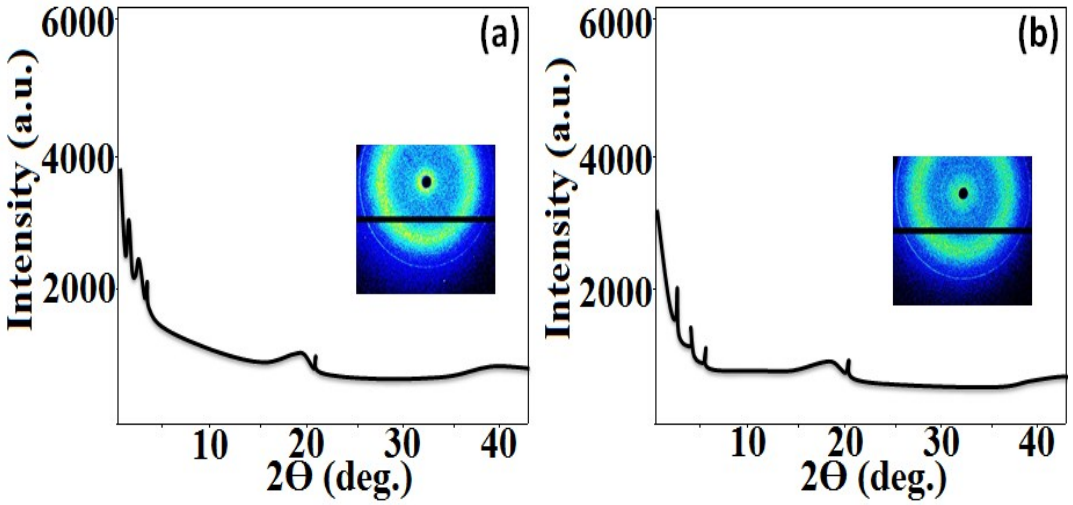

Figure S_3: XRD profiles depicting the intensity against the 2Θ obtained for the Colh phase of compound **9f** at 114.0 ˚C (a); Colh phase of compound **9c** at 133.0 ˚C on cooling from isotropic temperature; the insert shows the image pattern obtained.

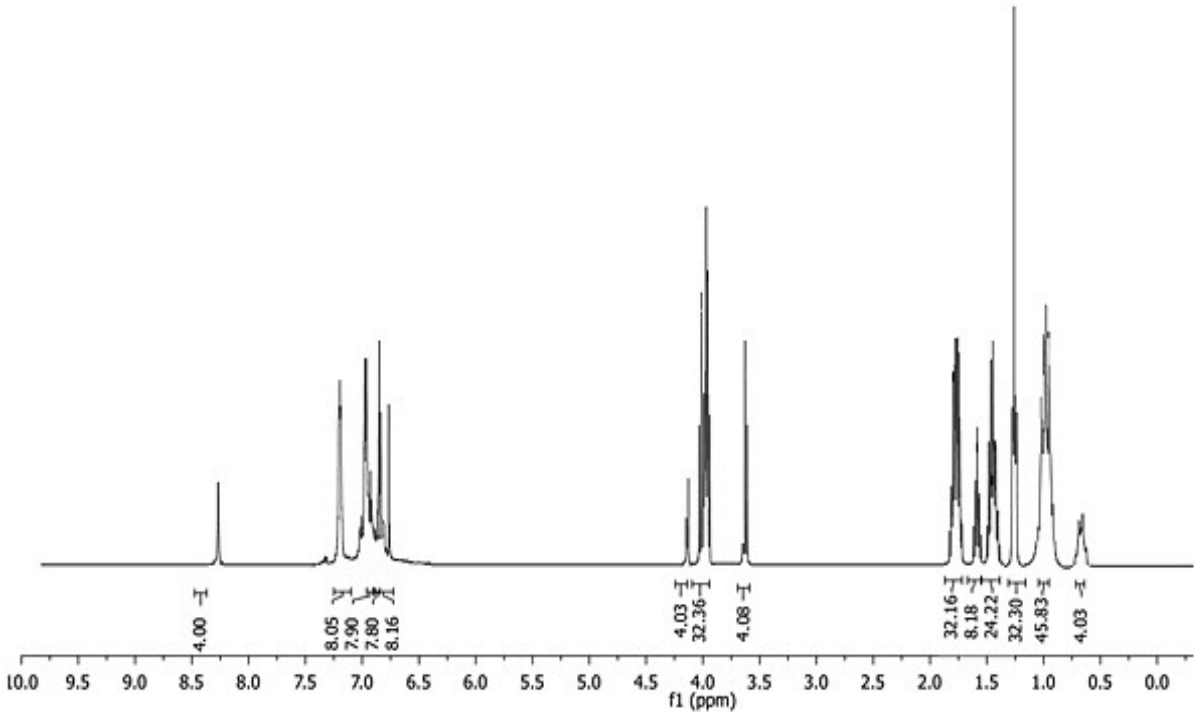

Figure S_4: ^{1}H NMR of compound **9a**.

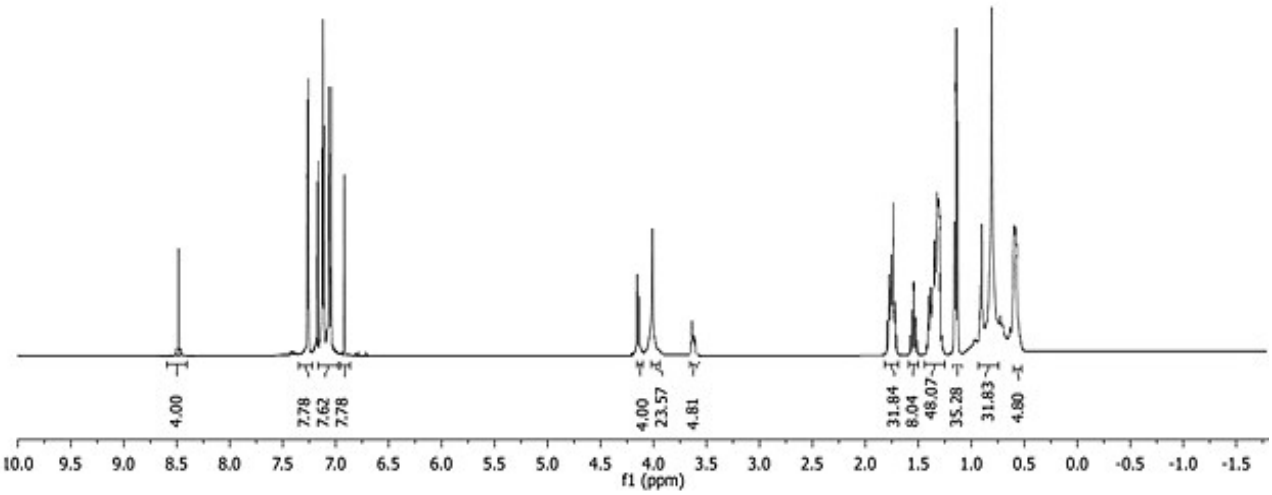

Figure S_5: ^{1}H NMR of compound **9b**.

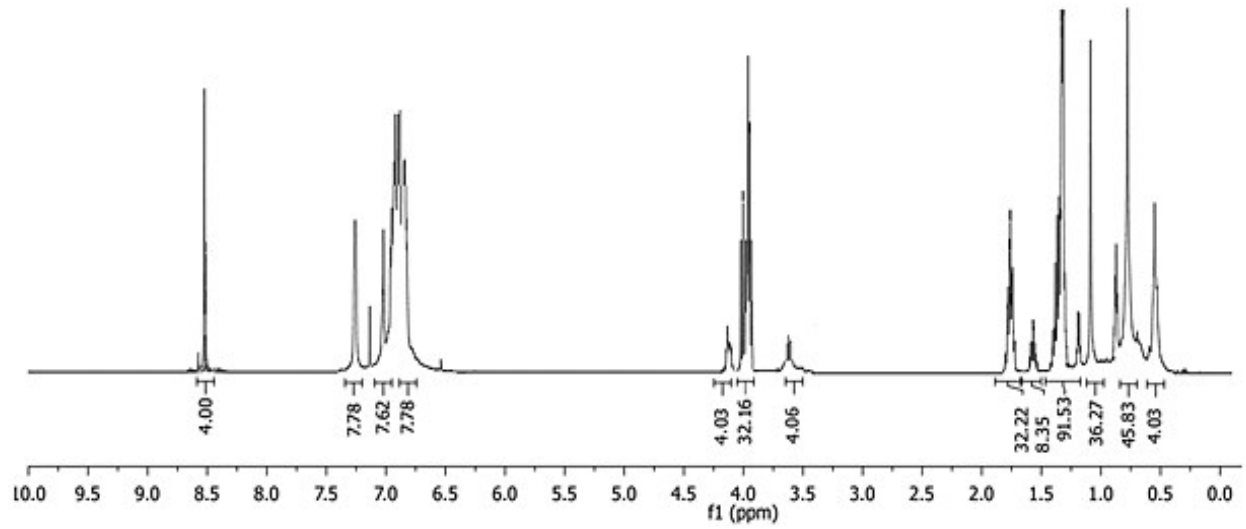

Figure S_6: ^{1}H NMR of compound **9c**.

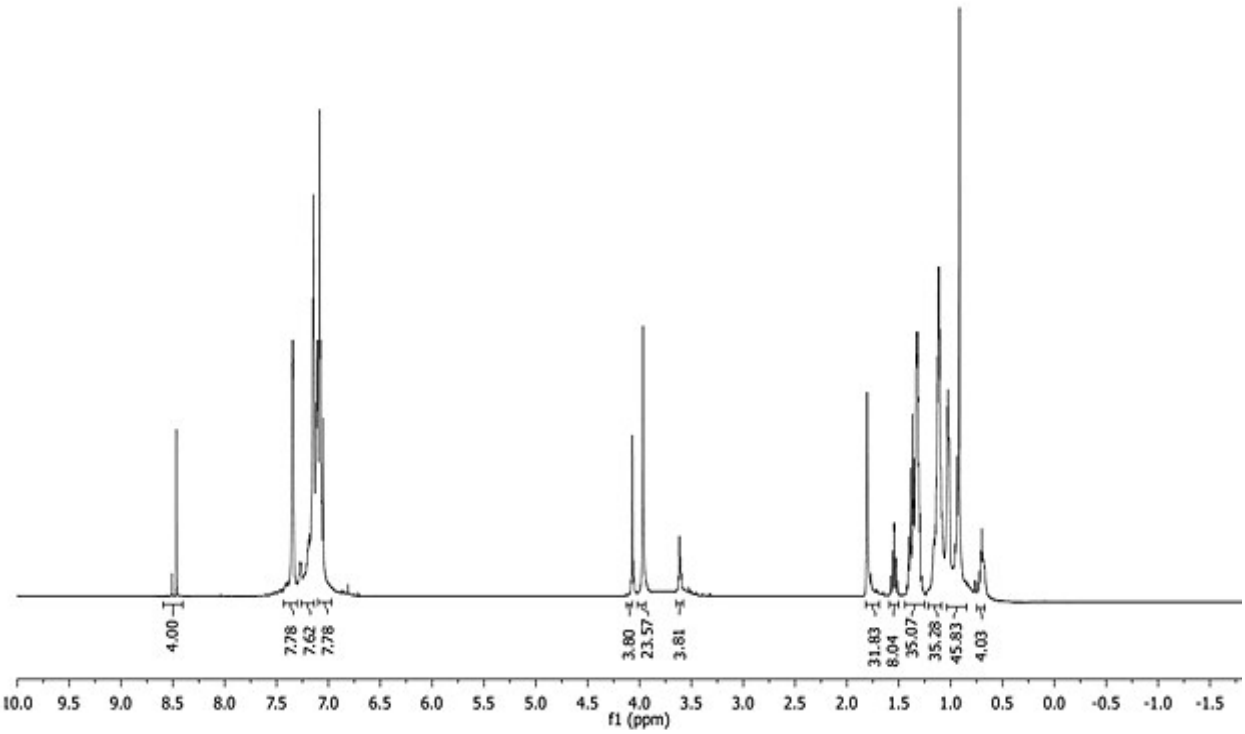

Figure S_7: ^{1}H NMR of compound **9d**.

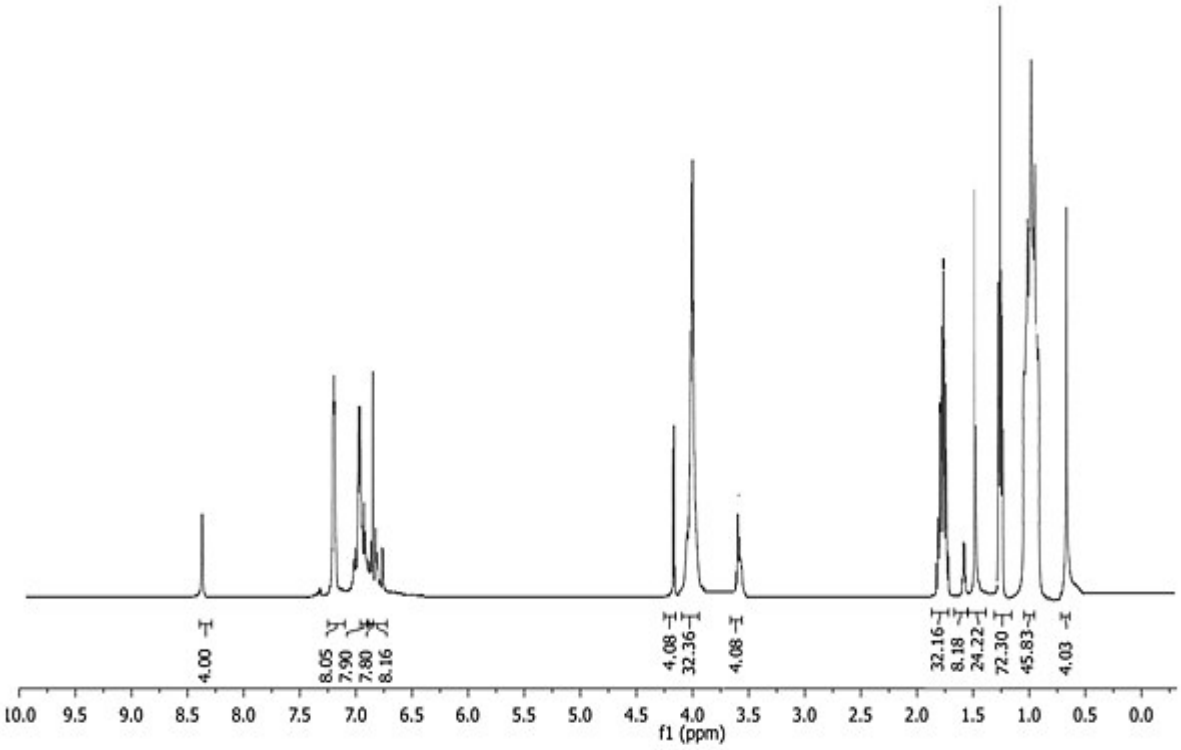

Figure S_8: ^{1}H NMR of compound **9e**.

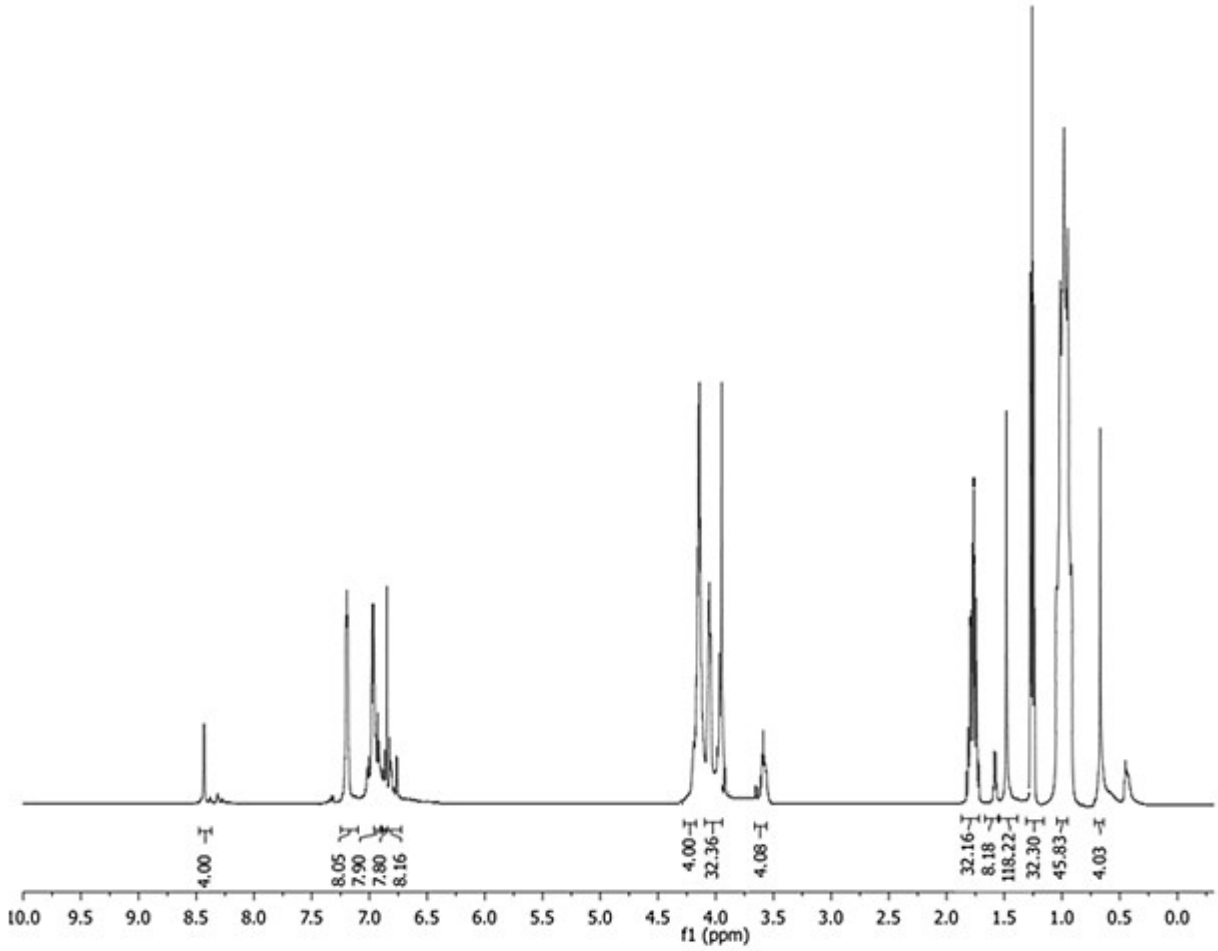

Figure S_9: ^{1}H NMR of compound **9f**.

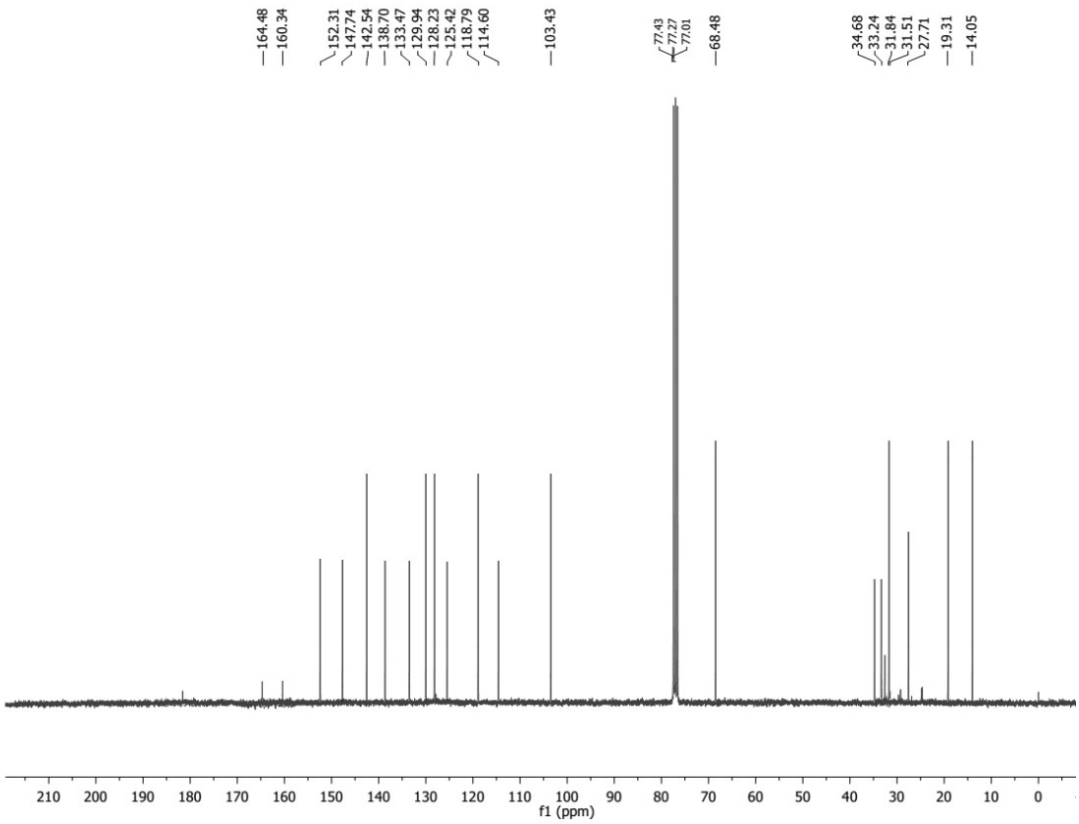

Figure S_{10}: ^{13}C NMR of compound **9a**.

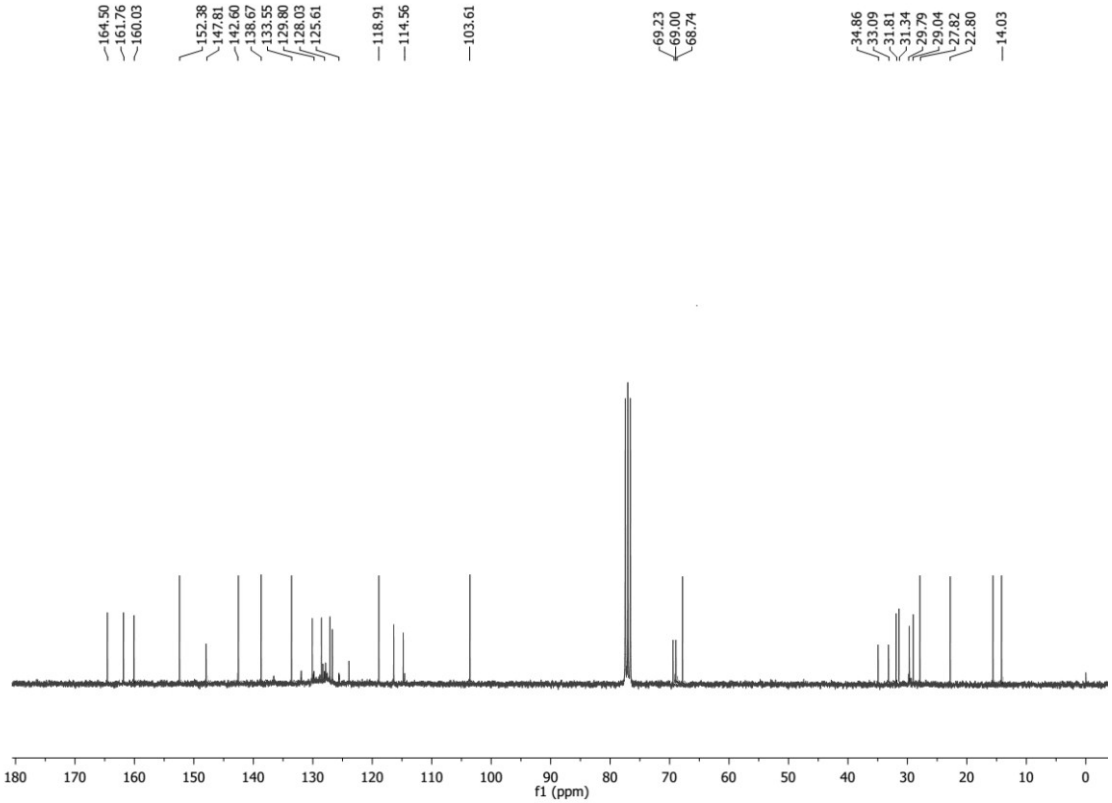

Figure S_{11}: ^{1}H NMR of compound **9b**.

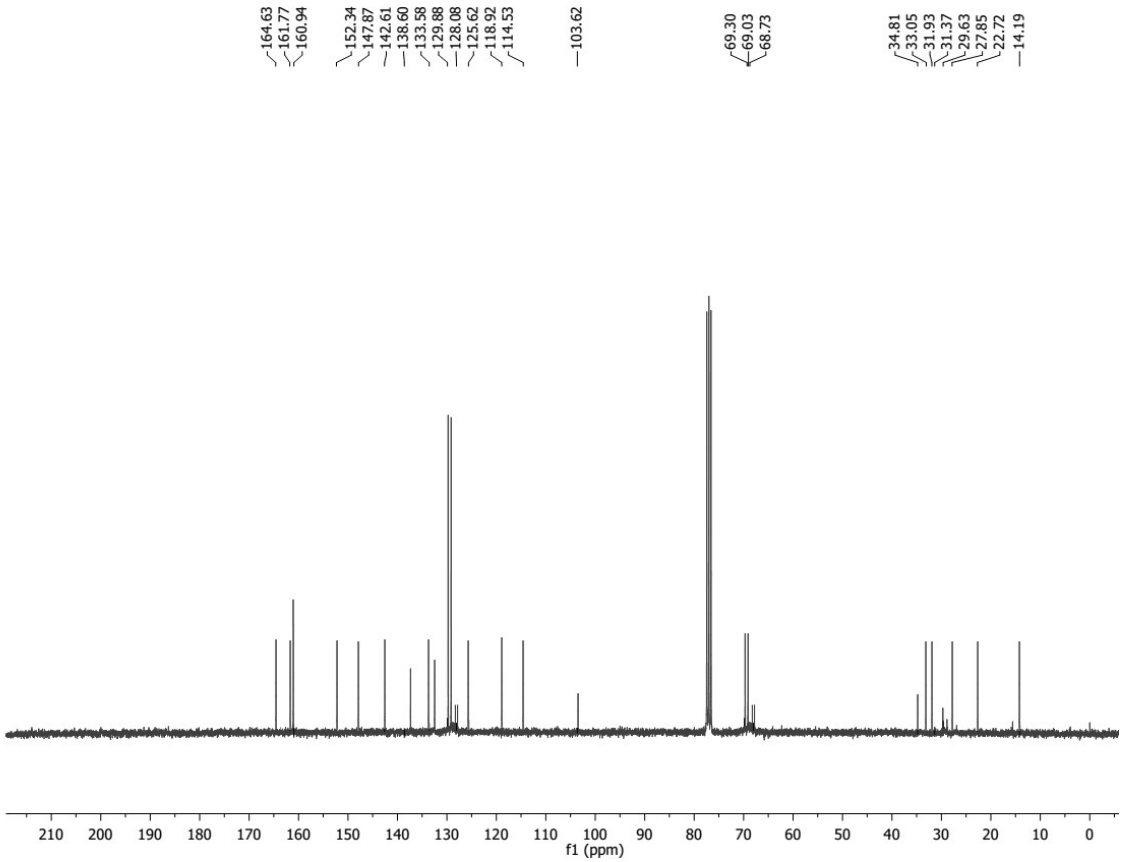

Figure S_{12}: ^{1}H NMR of compound **9c**.

Figure S_{13}: ^{1}H NMR of compound **9d**.

Figure S_{14}: ^{1}H NMR of compound **9e**.

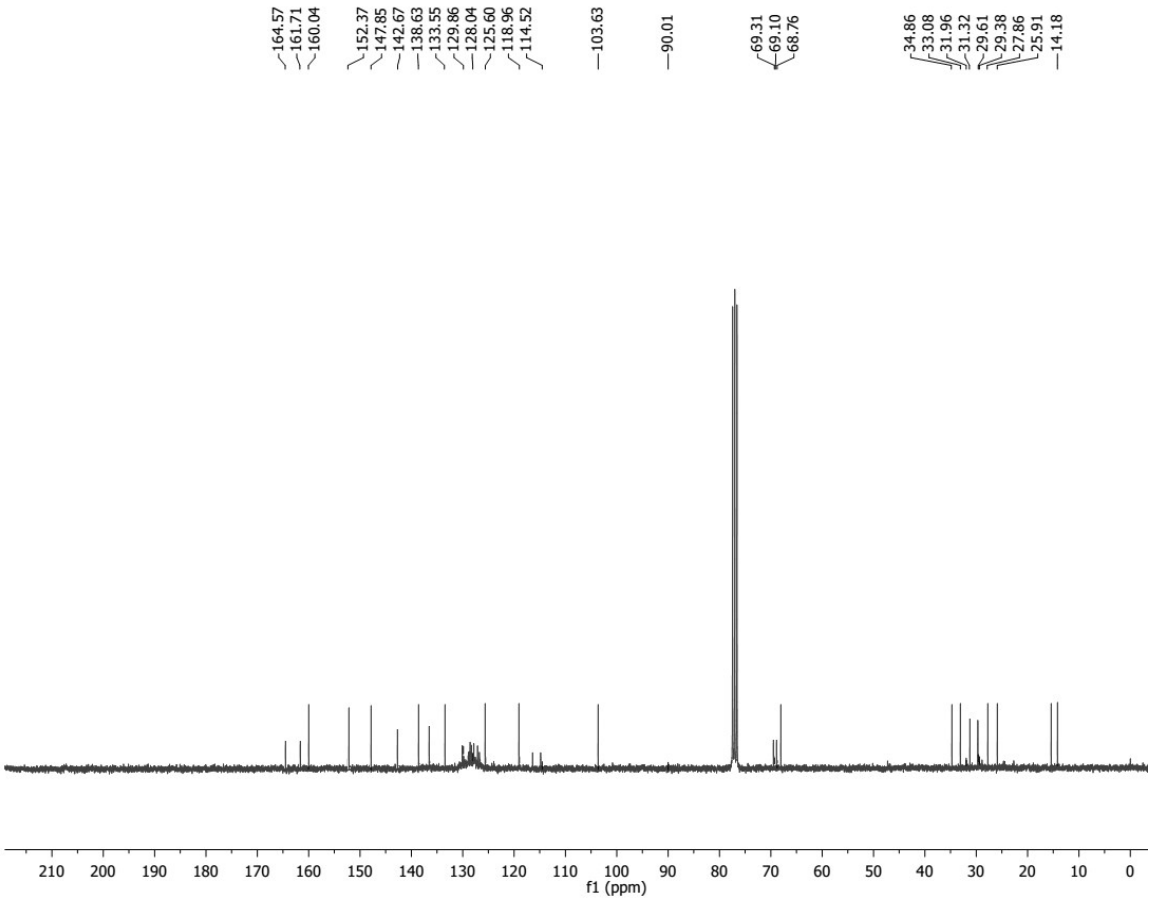

Figure S_{15}: ^{1}H NMR of compound 9f.

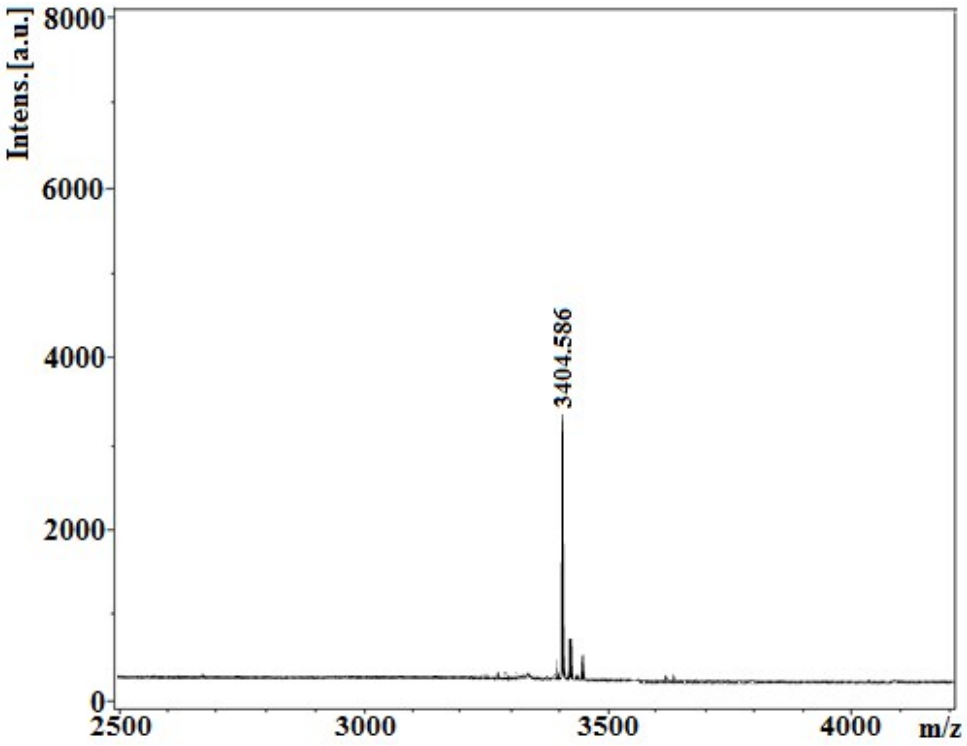

Figure S_{16}: MALDI-TOF mass spectra of compound **9a**.

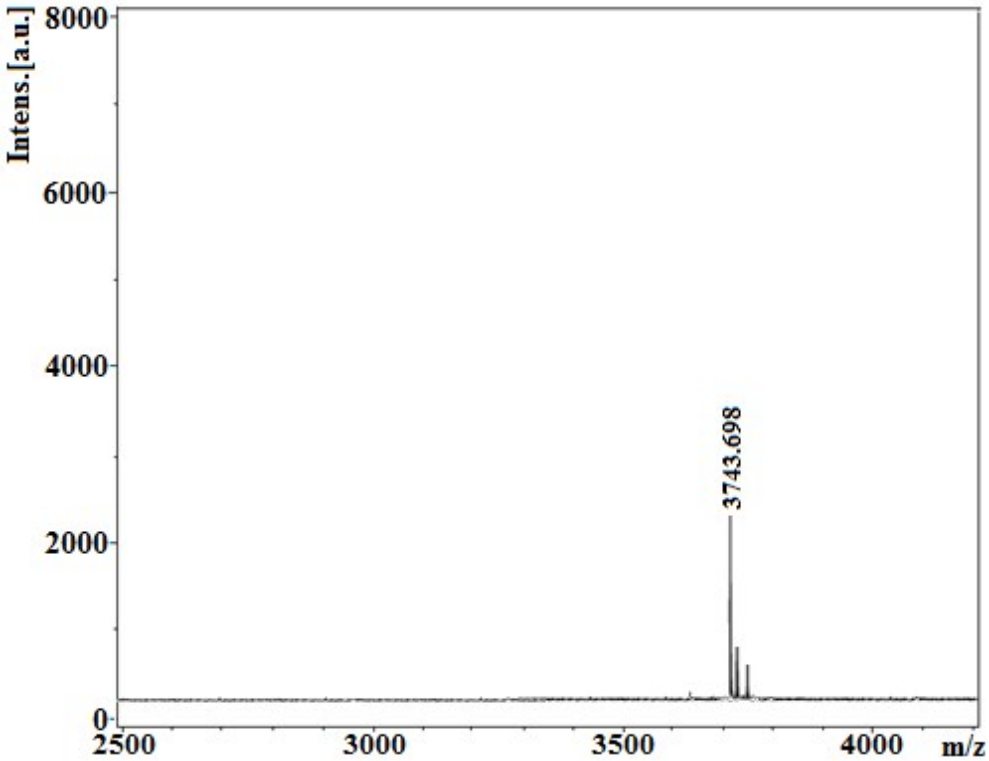

Figure S_{17}: MALDI-TOF mass spectra of compound **9b**.

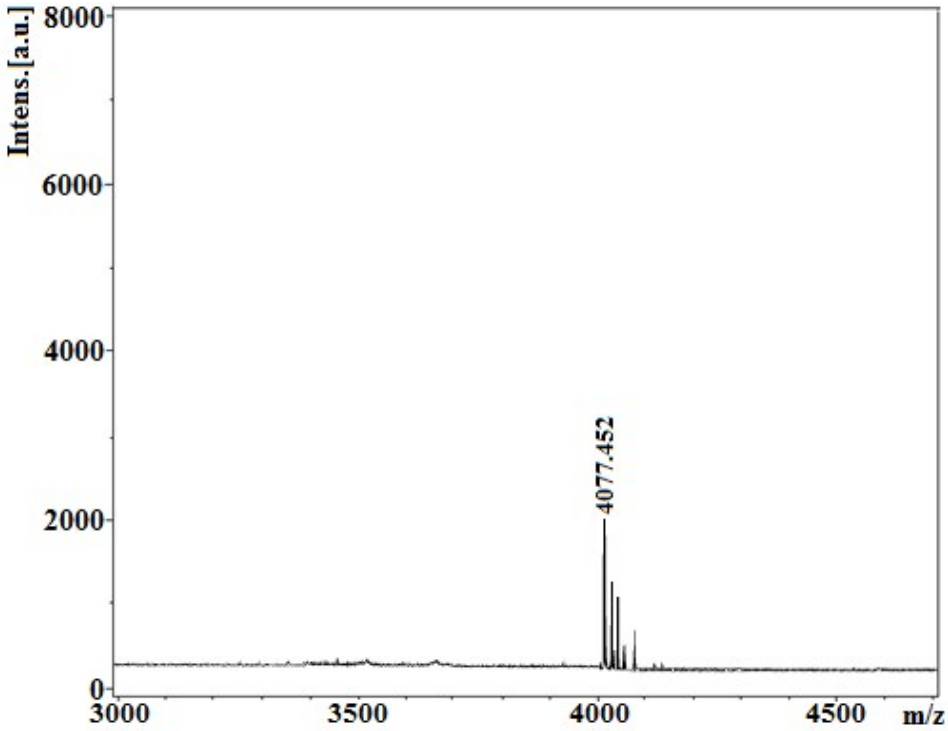

Figure S_{18}: MALDI-TOF mass spectra of compound **9c**.

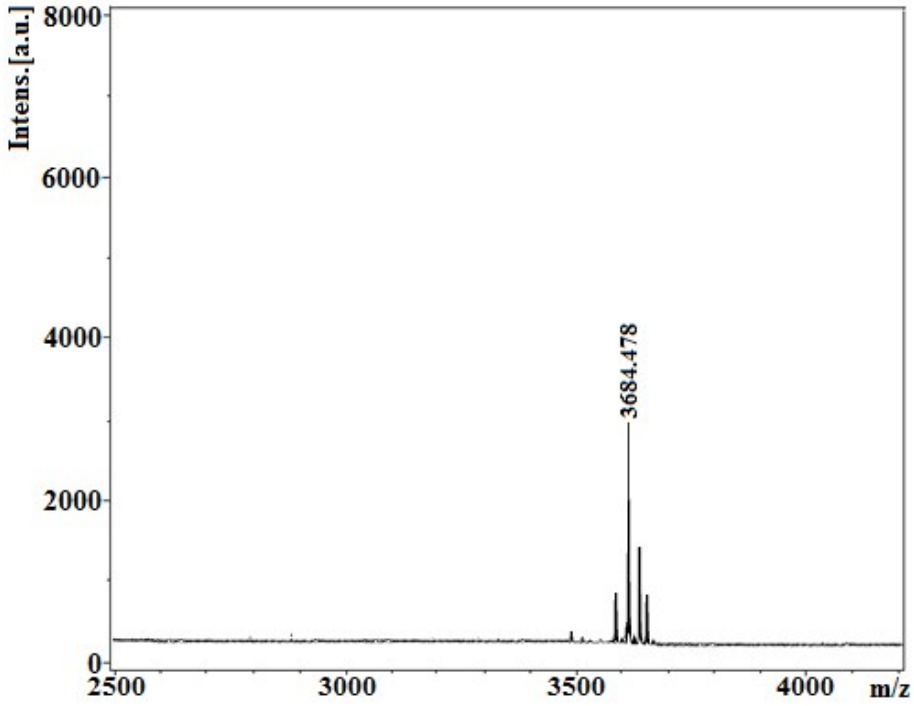

Figure S_{18}: MALDI-TOF mass spectra of compound **9d**.

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