"Columnar Self-assembly, Gelation and Electrochemical behavior of Cone-shaped Luminescent Supramolecular Calix[4]arene LCs based on Oxadiazole and Thiadiazole derivatives"

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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. 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. Cyclic voltammetry (CV) experiments were performed on a CH Instruments electrochemical workstation.

2. Synthesis and characterization

2.1 Preparation of 4-methyl benzohydrazide (2)

4-nitro benzohydrazide (2) was synthesized by reaction of 4-methyl benzoyl chloride (1 equiv.) with hydrazine hydrate (1 equiv.) at room temperature in dry acetone [1]. Yield 81 %, FT-IR (KBr) in cm^{-1}: 3227, 2890, 1684, 1241. ^{1}H NMR $CDCl_3$ (400 MHz): 2.41 (s, 3H, $-CH_3$), 4.31 (s, 2H, $-NH_2$), 7.67-8.23 (d, 4H, Ar), 9.71 (s, 1H, -CONH), ^{13}C NMR: 153.4, 139.3, 129.6, 124.1 (Ar-C), 163.2 (-C=O).

2.2 4-methoxy-N'-(4-methylbenzoyl) benzohydrazide (3)

4-methoxy-N'-(4-methylbenzoyl) benzohydrazide (3) is synthesised from the mixture of 4-methyl benzohydrazide (1 equiv.) in dry pyridine, later, the solution of 4-methoxy benzoyl chloride (1 equiv.) in THF was added in it[1]. 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: 74%; FT-IR (KBr pellet) in cm-1: 3103, 2940, 1630, 1507, 1430, 1234, 713, 681, 563;^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.24 (s, 1H, -CONH), 9.62 (s, 1H, -CONH), 8.08 (d, 2H, Ar), 7.48 (d, 2H, *J* = 8Hz, Ar), 7.74 (d, 2H, *J* = 8Hz, Ar), 7.02 (d, 2H, Ar), 3.81 (s, 3H,-OCH_3), 2.58 (s, 3H, -CH_3); ^{13}C NMR: 164.80, 164.31, 141.82, 133.51, 129.10, 128.50, 127.45, 114.40, 77.44, 77.02, 76.59, 55.82, 21.36.

2.3 2-(4-methoxyphenyl)-5-(p-tolyl)-1,3,4-oxadiazole (4a)

Compound (**4a**) was prepared by the reported method in literature[2]. 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 7.29 (d, 2H, *J* = 6 Hz, Ar), 7.42 (d, 2H, J = 8Hz, Ar), 7.71 (s, 3H, Ar), 3.82 (s, 3H, -OCH_3), 2.51 (s, 3H, -CH_3).^{13}C NMR: 164.51, 160.61, 142.22, 131.71, 129.01, 127.43, 126.32, 115.90, 114.81, 77.46, 77.04, 76.61, 55.52, 21.34.

2.4 2-(4-methoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (4b)

Compound (**4b**) was prepared by reported method in literature[2]. Yield: 69 %; IR (KBr pellet) in cm^{-1}: 3101, 2940, 1606, 1554, 1457, 1341, 1321, 1212, 869. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (d, 2H, *J* = 6 Hz, Ar), 7.48 (d, 2H, J = 8Hz, Ar), 7.72 (s, 3H, Ar), 3.81 (s, 3H, -OCH_3), 2.51 (s, 3H, -CH_3).^{13}C NMR: 174.12, 160.63, 131.72, 130.51, 129.51, 128.54, 127.41, 125.80, 114.81, 77.44, 77.01, 76.59, 55.57, 21.32.

2.5 2-(4-hydroxy phenyl)-5-(p-tolyl)-1,3,4-oxadiazole (5a)

Compound (**5a**) was prepared by reported method in literature[2]. Yield: 76 %; IR (KBr pellet) in cm^{-1}: 3321, 1640, 1540, 1441, 1243, 787, 641; ^{1}H NMR (DMSO, 400 MHz): δ 3.73 (s, 1H, -OH), 7.51 (d, 3H, Ar), 6.62 (d, 2H, Ar), 7.41 (s, 2H, Ar). ^{13}C NMR: 164.58, 158.52, 142.40, 131.71, 129.27, 127.44, 126.30, 116.39, 77.44, 77.02, 76.59, 21.32.

2.6 2-(4-hydroxy phenyl)-5-(p-tolyl)-1,3,4-thiadiazole (5b)

Compound (**5b**) was prepared by reported method in literature[2]. Yield: 71 %; IR (KBr pellet) in cm^{-1}: 3321, 1640, 1540, 1441, 1243, 787, 641; ^{1}H NMR (DMSO, 400 MHz): δ 3.73 (s, 1H, -OH), 7.51 (d, 3H, Ar), 6.62 (d, 2H, Ar), 7.41 (s, 2H, Ar).^{13}C NMR: 174.12, 158.51, 131.73, 130.51, 129.49, 128.92, 127.49, 125.14, 116.40, 77.47, 77.04, 76.62, 21.34.

2.7 4-(5-(4-hydroxy phenyl)-1,3,4-oxadiazole-2-yl) benzoic acid (6a)

Compound (**6b**) was prepared by reported method in literature[2]. Compound **(6a):** yield: 69 %; IR (KBr pellet) cm^{-1}: 3468, 2930, 2849, 1590, 1551, 1520, 1493, 1440, 1436, 1330, 1226, 1021; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, 2H, *J*= 8.8 Hz, Ar), 7.61 (d, 2H, *J*= 8.6 Hz, Ar), 7.42 (d, 2H, Ar), 3.42 (s, 1H, -OH), 13.82 (s, 1H, -COOH). ^{13}C NMR: 169.43, 164.48,158.56,131.36, 130.29, 129.27, 127.51, 127.14, 116.70, 77.44, 77.01, 76.59, 21.34.

2.8 4-(5-(4-hydroxy phenyl)-1,3,4-thiadiazole-2-yl) benzoic acid (6b)

Compound (**6b**) was prepared by reported method in literature[2]. Compound **(6b):** yield: 62 %; IR (KBr pellet) cm^{-1}: 3460, 2960, 2849, 1520, 1551, 1523, 1493, 1468, 1436, 1338, 1120, 1022, 861, 721, 703; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, 2H, *J*= 8.8 Hz, Ar), 7.61 (d, 2H, *J*= 8.6 Hz, Ar), 7.42 (d, 2H, Ar), 3.43 (s, 1H, -OH), 13.84 (s, 1H, -COOH).; ^{13}C NMR: 174.18, 169.29,158.52,138.84, 130.22, 128.89, 127.56, 126.17, 116.06, 77.45, 77.03, 76.61, 21.34.

2.9 4-(5-(4-butyloxy phenyl)-1,3,4-oxadiazole-2-yl) benzoic acid (7a)

A mixture of compound **6a** (1equiv.), butyl bromide (1 equiv.), anhydrous K_2CO_3 (1.5 equiv.), dry acetone (30 ml) was heated at 60 ^oC for 4 h. Then the reaction mixture was extracted by using ethyl acetate[3]. The combined organic layer was washed with water, brine. Evaporation of the solvent by using rota evaporator and purification of the residue by using column chromatography followed by ethyl acetate-hexanes system (3:2). Yield: 61%; IR (KBr pellet) in cm^{-1}: 2930, 2848, 1610, 1495, 1448, 1390, 1331, 1122, 986, 835, 721; ^1H NMR ($CDCl_3$, 400MHz): δ 13.87 (s, 1H, -COOH), 8.42 (d, 2H, *J*= 8.2 Hz ,Ar), 7.98 (d, 2H, Ar), 7.58 (d, 2H, *J*= 7.8 Hz, Ar), 7.14 (d, 2H, Ar), 4.08 (t, 2H, $-OC_4H_9$), 0.90 (t, 3H, $-OC_4H_9$), 1.52 (sext, 2H, $-OC_4H_9$), 1.75 (t, 2H, $-OC_4H_9$); ^{13}C NMR: 169.31, 164.51, 159.41, 131.30, 130.22, 128.35, 127.51, 127.46, 115.53, 114.93, 77.51, 77.09, 76.67, 68.42, 31.85, 19.04, 14.10.

3.0 4-(5-(4-octyloxy phenyl)-1,3,4-oxadiazole-2-yl) benzoic acid (7b)

A mixture of compound **6a** (1equiv.), octyl bromide (1 equiv.), anhydrous K_2CO_3 (1.5 equiv.), dry acetone (30 ml) was heated at 60 ^oC for 4 h. Then the reaction mixture was extracted by using ethyl acetate[3]. The combined organic layer was washed with water, brine. Evaporation of the solvent by using rota evaporator and purification of the residue by using column chromatography followed by ethyl acetate-hexanes system (3:2). Yield: 67%; IR (KBr pellet) in cm^{-1}: 2930, 2848, 1610, 1495, 1448, 1390, 1331, 1122, 986, 835, 721; ^1H NMR ($CDCl_3$, 400MHz): δ 13.87 (s, 1H, -COOH), 8.48 (d, 2H, *J*= 8.2 Hz ,Ar), 7.98 (d, 2H, Ar), 7.48 (d, 2H, *J*= 7.8 Hz, Ar), 7.12 (d, 2H, Ar), 4.08 (t, 6H, $-OC_8H_{17}$), 0.90 (t, 3H, $-OC_8H_{17}$), 1.24-1.26 (m, 8H, $-OC_8H_{17}$), 1.56 (sext, 2H, $-OC_8H_{17}$), 1.78 (t, 2H, $-OC_8H_{17}$), 4.08 (t, 2H, $-OC_8H_{17}$); ^{13}C NMR: 169.39, 164.52, 159.41, 131.38, 130.20, 128.31, 127.59, 127.46, 115.51, 114.81, 77.45, 77.03, 76.61, 68.71, 31.94, 29.61, 29.31, 25.92, 22.74, 14.10.

3.1 4-(5-(4-butyloxy phenyl)-1,3,4-thiadiazole-2-yl) benzoic acid (7c)

A mixture of compound **6b** (1equiv.), butyl bromide (1 equiv.), anhydrous K_2CO_3 (1.5 equiv.), dry acetone (30 ml) was heated at 60 ^oC for 4 h. Then the reaction mixture was extracted by using ethyl acetate[3]. The combined organic layer was washed with water, brine. Evaporation of the solvent by using rota evaporator and purification of the residue by using column chromatography followed by ethyl acetate-hexanes system (3:2). Yield: 64%; IR (KBr pellet) in cm^{-1}: 2930, 2848, 1610, 1495, 1448, 1390, 1331, 1122, 986, 835, 721; ^1H NMR ($CDCl_3$, 400MHz): δ 13.84 (s, 1H, -COOH), 8.42 (d, 2H, *J*= 8.2 Hz ,Ar), 7.98 (d, 2H, Ar), 7.48 (d, 2H, *J*= 7.8 Hz, Ar), 7.14 (d, 2H, Ar), 4.08 (t, 2H, $-OC_4H_9$), 0.90 (t, 3H, $-OC_4H_9$), 1.54 (sext, 2H, $-OC_4H_9$), 1.75 (t, 2H, $-OC_4H_9$); ^{13}C NMR: 174.14, 169.31, 159.41, 138.75, 130.24, 128.11, 127.43, 127.15, 125.04, 114.91, 77.44, 77.01, 76.59, 68.49, 31.82, 19.07, 14.12.

3.2 4-(5-(4-octyloxy phenyl)-1,3,4-thiadiazole-2-yl) benzoic acid (7d)

A mixture of compound **6b** (1equiv.), octyl bromide (1 equiv.), anhydrous K_2CO_3 (1.5 equiv.), dry acetone (30 ml) was heated at 60 ^oC for 4 h. Then the reaction mixture was extracted by using ethyl acetate[3] The combined organic layer was washed with water, brine. Evaporation of the solvent by using rota evaporator and purification of the residue by using column chromatography followed by ethyl acetate-hexanes system (3:2). Yield: 64%; IR (KBr pellet) in cm^{-1}: 2930, 2848, 1610, 1495, 1448, 1390, 1331, 1122, 986, 835, 721; ^1H NMR ($CDCl_3$, 400MHz): 13.87 (s, 1H, -COOH), 8.48 (d, 2H, *J*= 8.2 Hz ,Ar), 7.98 (d, 2H, Ar), 7.48 (d, 2H, *J*= 7.8 Hz, Ar), 7.12 (d, 2H, Ar), 4.08 (t, 6H, $-OC_8H_{17}$), 0.90 (t, 3H, $-OC_8H_{17}$), 1.26-1.28 (m, 8H, $-OC_8H_{17}$), 1.56 (sext, 2H, $-OC_8H_{17}$), 1.78 (t, 2H, $-OC_8H_{17}$), 4.08 (t, 2H, $-OC_8H_{17}$); ^{13}C NMR: 174.10, 169.33, 159.41, 138.70, 138.64, 130.24, 128.14, 127.50, 127.41, 125.14, 114.91, 77.48, 77.05, 76.63, 68.71, 31.93, 29.61, 29.35, 25.93, 22.76, 14.14.

3.3 Preparation of *p-tert*-butyl calix[4]arene (9)

p-tert-butyl calix[4]arene (9) was synthesized by reported in the literature[4], 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.

3.4 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra n-butyloxy phenyl oxadiazole phenyl ester calix[4]arene (10a)

The compound has been prepared by esterification of the appropriate compound (9) (0.0015 mol.) and compound (7) (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].

(10a): Yield 76 %, Elemental analysis: $C_{120}H_{120}N_8O_{16}$: Calcu: C, 74.67; H, 6.27; N, 5.81; O, 13.26 %; Found: C, 73.41; H, 6.19; N, 5.76; O, 13.16 %. FT-IR (KBr) in cm^{-1}: 2990, 1750, 1640, 1441, 1320, 1140, 1120, 981, 886. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.23 (s, 36H, t-butyl group), 0.88 (t, 12H, -OC_4H_9), 1.48 (sext, 8H, -OC_4H_9), 1.74 (p, 8H, -OC_4H_9), 3.61 (d, J = 18.0 Hz, 4H, -ArCH_2Ar-), 4.14 (d, J = 18.0 Hz, 4H, -ArCH_2Ar-), 4.02 (t, 8H, -OC_4H_9), 7.12 (s, 8H, Ar), 7.26 (d, 8H, Ar), 7.51 (d, 8H, Ar), 8.08 (d, 8H, Ar), 7.74 (d, 8H, Ar). ^{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, 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 10a (M+1) Calculated: 1928.2760 Found 1929.314.

3.5 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra n-octyloxy phenyl oxadiazole phenyl ester calix[4]arene (10b)

(10b): Yield 78 %, Elemental analysis: $C_{136}H_{152}N_8O_{16}$: Calcu: C, 75.81; H, 7.11; N, 5.20; O, 11.88 %; Found: C, 74.73; H, 7.04; N, 5.14; O, 11.76 %. FT-IR (KBr) in cm^{-1}: 2990, 1730, 1640, 1441, 1410, 1236, 1121, 886, 630. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 1.21 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, $-OC_8H_{17}$), 1.26-1.28 (m, 32 H, $-OC_8H_{17}$), 1.48 (sext, 8H, $-OC_8H_{17}$), 1.75 (p, 8H, $-OC_8H_{17}$), 3.61 (d, J = 18.0 Hz, 4H, $-ArCH_2Ar-$), 4.12 (d, J = 18.0 Hz, 4H, $-ArCH_2Ar-$), 4.04 (t, 8H, $-OC_8H_{17}$), 7.12 (s, 8H, Ar), 7.26 (d, 8H, Ar), 7.51 (d, 8H, Ar), 8.08 (d, 8H, Ar), 7.74 (d, 8H, Ar). ^{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, 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 10b (M+1) Calculated: 2153.6990 Found 2154.158.

3.6 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra n-butyloxy phenyl thiadiazole phenyl ester calix[4]arene (10c)

(10c): Yield 71 %, Elemental analysis: $C_{120}H_{120}N_8O_{12}S_4$: Calcu: C, 73.61; H, 6.90; N, 5.05; O, 8.65 %; S, 5.78%. Found: C, 73.54; H, 6.86; N, 4.98; O, 8.55 %. FT-IR (KBr) in cm^{-1}: 2930, 1750, 1630, 1410, 1340, 1214, 1148, 886, 741. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 1.24 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, $-OC_4H_9$), 1.51 (sext, 8H, $-OC_4H_9$), 1.74 (p, 8H, $-OC_4H_9$), 3.62 (d, J = 18.0 Hz, 4H, $-ArCH_2Ar-$), 4.12 (d, J = 18.0 Hz, 4H, $-ArCH_2Ar-$), 4.01 (t, 8H, $-OC_4H_9$), 7.14 (s, 4H, Ar), 7.26 (d, 8H, Ar), 7.03 (d, 7H, Ar), 7.91 (d, 7H, Ar), 8.04 (d, 8H, Ar). ^{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, 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 10c (M+1) Calculated: 2217.1760 Found 1994.582.

3.7 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra n-octyloxy phenyl thiadiazole phenyl ester calix[4]arene (10d)

(10d): Yield 73 %, Elemental analysis: $C_{136}H_{152}N_8O_{12}S_4$: Calcu: C, 73.61; H, 6.90; N, 5.05; O, 8.65 %; S, 5.78 %. Found: C, 73.56; H, 6.85; N, 4.93; O, 8.54 %. FT-IR (KBr) in cm^{-1}: 2896, 1750, 1630, 1440, 1415, 1361, 1230, 1120, 1121, 886, 742, 640. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): 1.31 (s, 36H, t-butyl group), 0.88 (t, 12H, -OC_8H_{17}), 1.28-1.30 (m, 32H, -OC_8H_{17}), 1.51 (sext, 8H, -OC_8H_{17}), 1.74 (p, 8H, -OC_8H_{17}), 3.62 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 4.12 (d, *J* = 18.0 Hz, 4H, -$ArCH_2Ar$-), 4.01 (t, 8H, -OC_8H_{17}), 7.12 (s, 8H, Ar), 7.26 (d, 8H, Ar), 7.08 (d, 4H, Ar), 7.91 (d, 8H, Ar), 8.04 (d, 8H, Ar). ^{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, 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 10d (M+1) Calculated: 2217.9624 Found 2218.853.

Table S_1: Gelation behaviour of compound 10b and 10d

Sr.No.	Solvent	Comp.10b		Comp.10d	
		Properties	CGC (wt %)	Properties	CGC (wt %)
1	Decane	G(O)	1.8 wt %	G(O)	2.1 wt %
2	Dodecane	G(O)	1.4 wt %	G(O)	1.9 wt %
3	Toluene	S	-	S	-
4	Benzene	S	-	S	-
5	DCM	S	-	S	-
6	THF	S	-	S	-
7	Chloroform	S	-	S	-
8	Ethanol	P	-	P	-
9	Butanol	P	-	P	-

G = stable gel; P = precipitate; O = opaque; S = the critical gelation concentration (wt %) is the minimum concentration necessary for gelation.

Table S_2: Results of (hkl) indexation of XRD profiles of the compound 10b in xerogel state at room temperature.

Compound (D/Å)	Phase (T/°C)	dobs (Å)	Miller indices	Lattice Parameters (Å)
10b	Colr (RT)	30.23	200	
		18.84	110	
		8.77	320	a = 61.22
		5.67	240	b = 27.26
		4.46	440	
		4.16	520	

		3.80	640	
		3.39	500	

Table S_3: Results of (hkl) indexation of XRD profiles of the compound 10d in xerogel state at room temperature.

Compound (D/Å)	**Phase (T/°C)**	**dobs (Å)**	**Miller indices**	**Lattice Parameters (Å)**
10d	Colr (RT)	30.02	200	
		19.05	110	
		10.19	320	a = 60.04
		7.20	240	b = 27.24
		7.06	420	
		5.58	520	
		5.02	640	
		3.72	500	

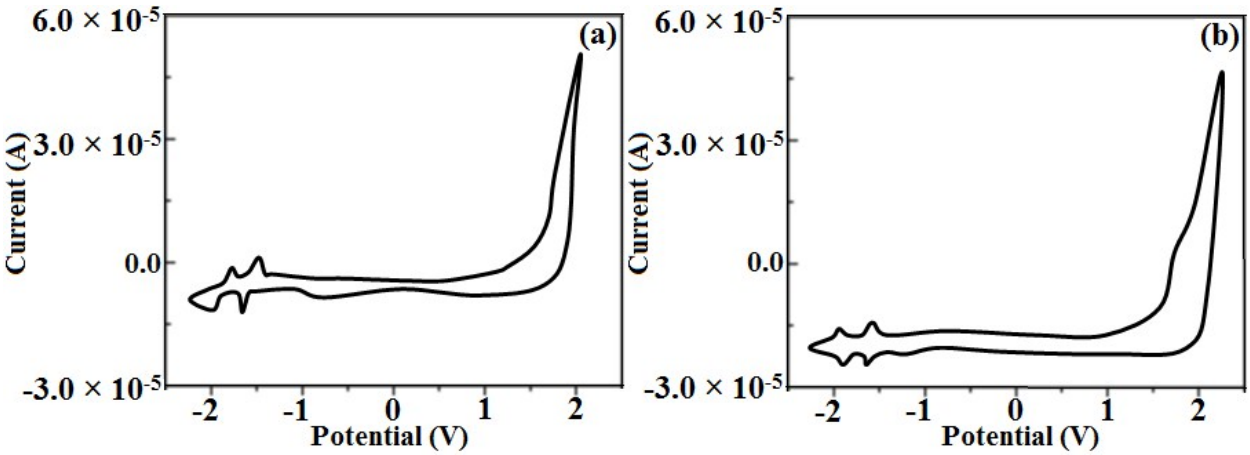

Figure S_1: Cyclic voltammogram of compound 10a (a); compound 10b (b) in anhydrous THF solution of TBAP (0.1 M) at a scanning rate of 0.5 mV/s.

The x,y,z direction of the dipole moment of present synthesised supramolecules (**10a-10d**) is given in below Table S_4.

Table S_4: Dipole moment (field-independent basis, Debye):

Compounds	X	Y	Z	Total (D)
10a	-11.9630	4.0024	8.2059	15.0489
10b	-13.1561	4.0707	7.5826	15.7210
10c	-4.9296	13.1138	6.9189	15.6251
10d	-13.1561	14.3883	5.2062	16.5646

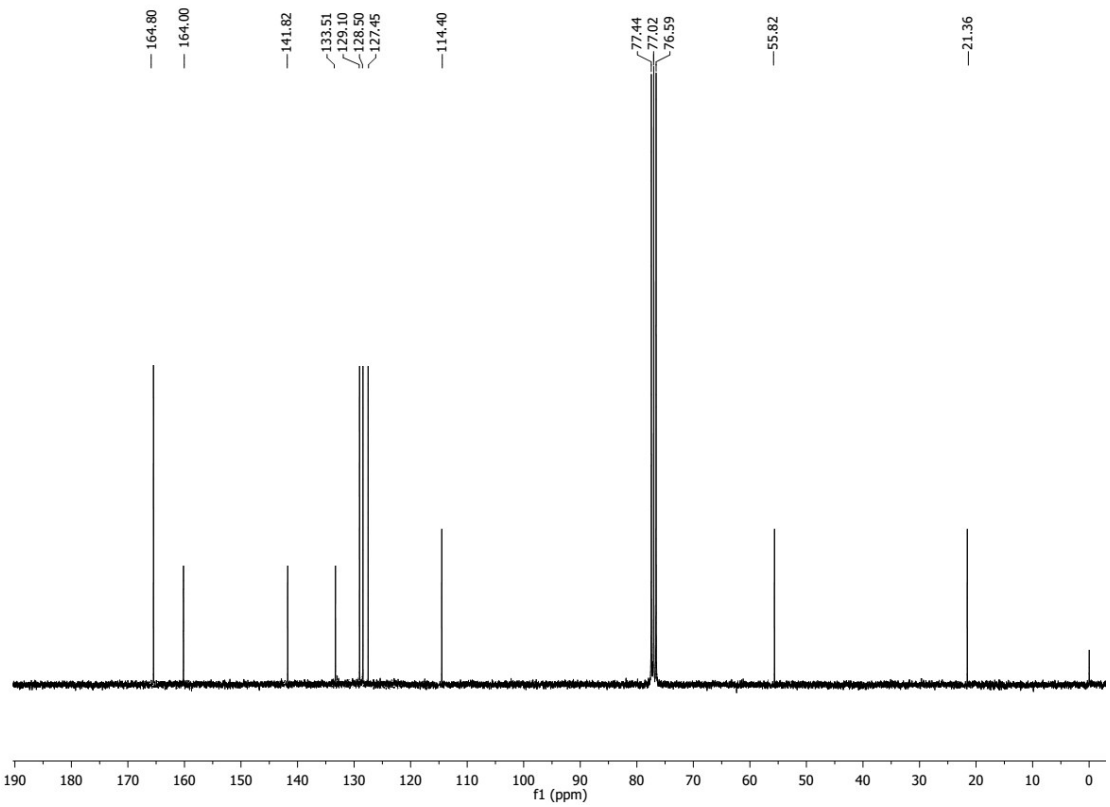

Figure S_2: ^{13}C NMR of compound **3**

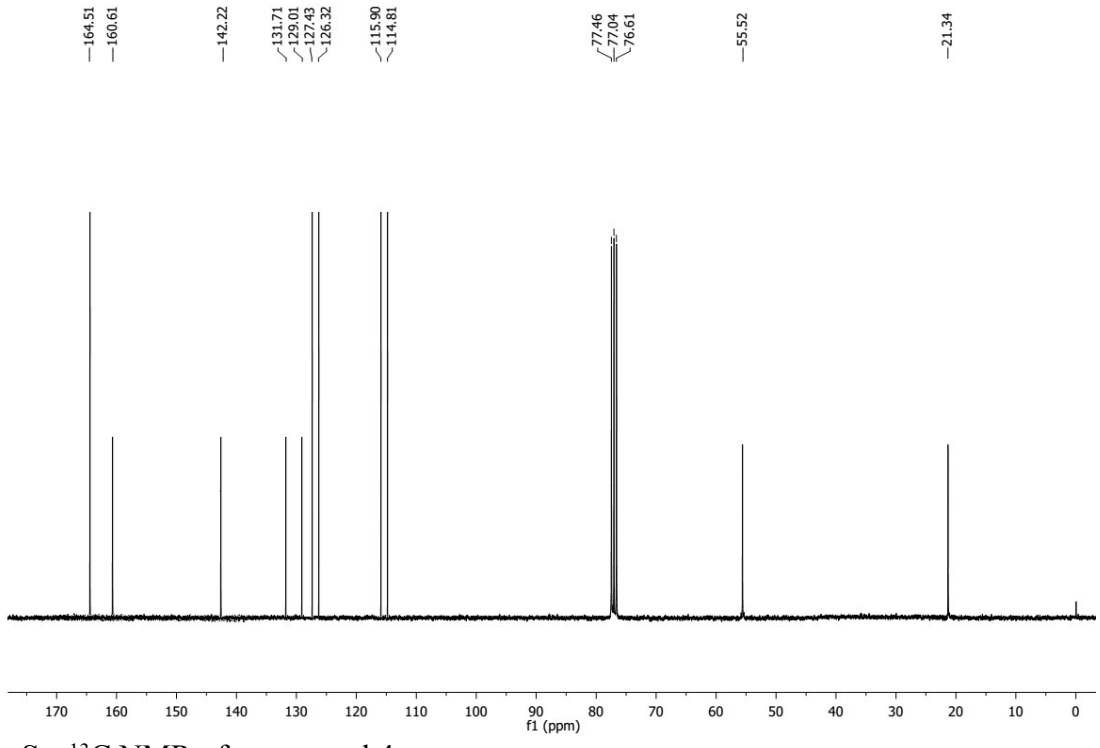

Figure S_3: ^{13}C NMR of compound **4a**

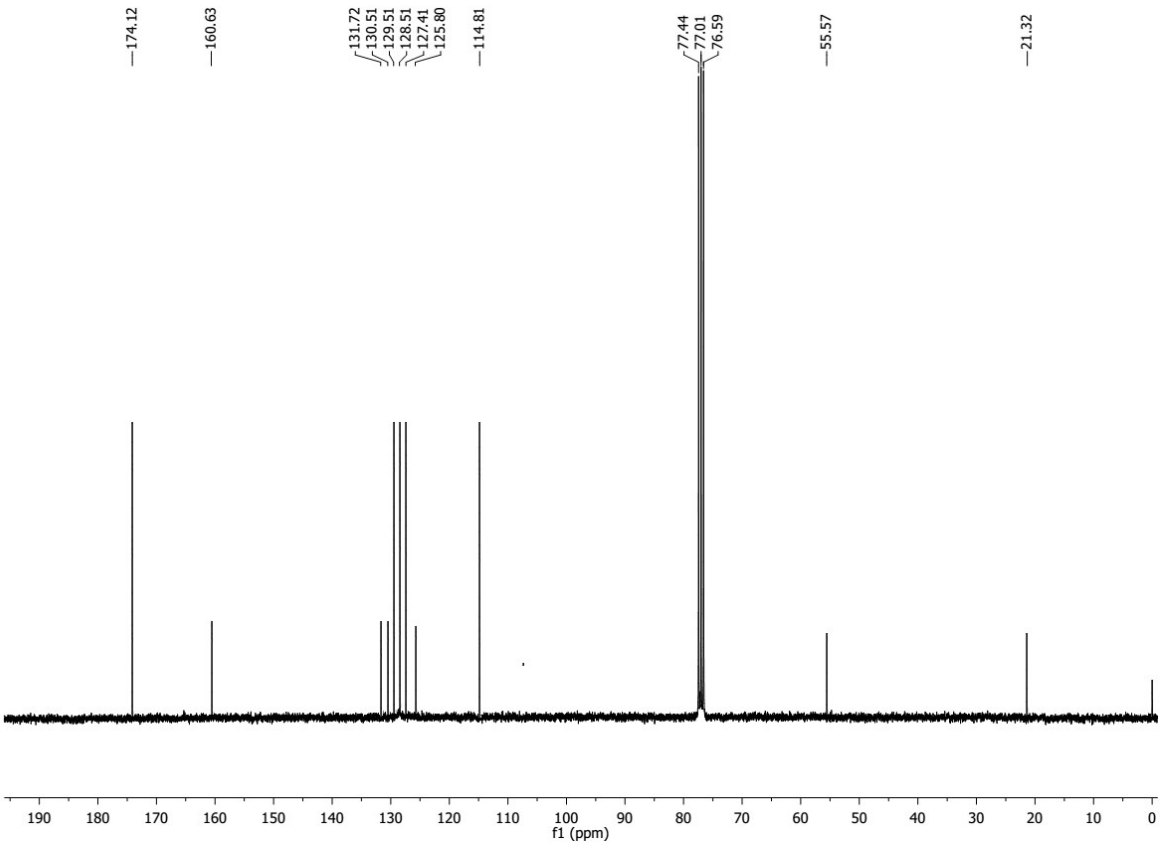

Figure S$_4$: ^{13}C NMR of compound **4b**

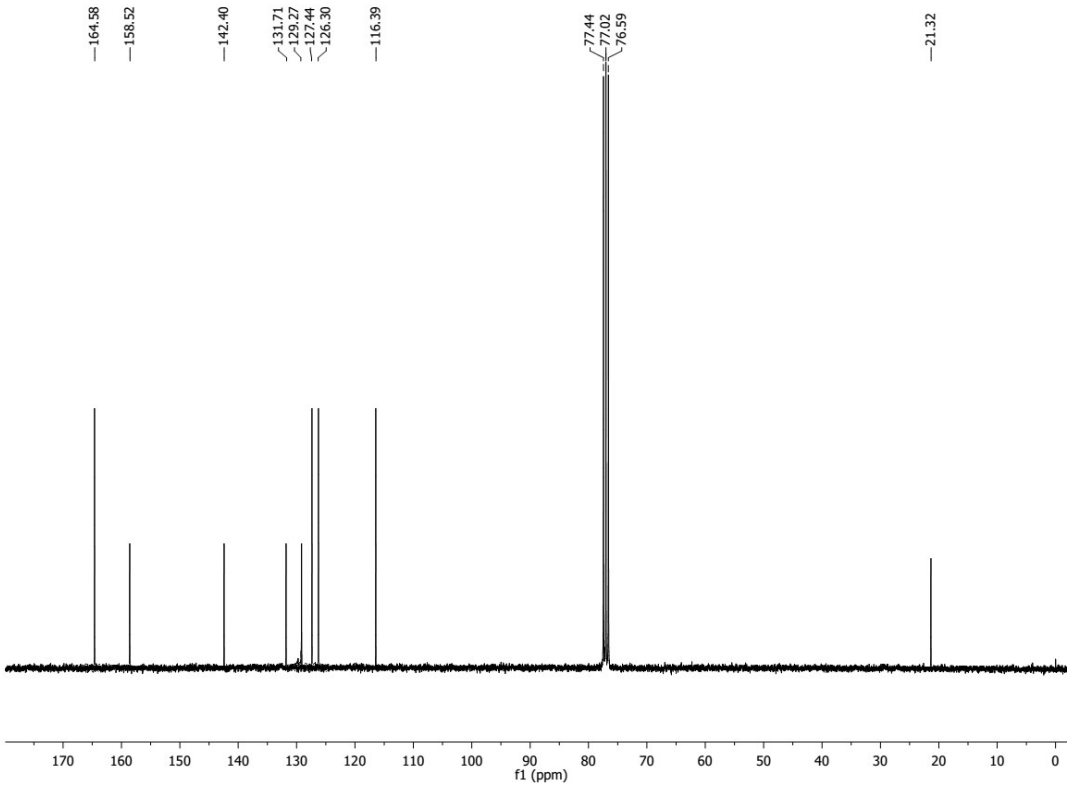

Figure S_5: ^{13}C NMR of compound **5a**

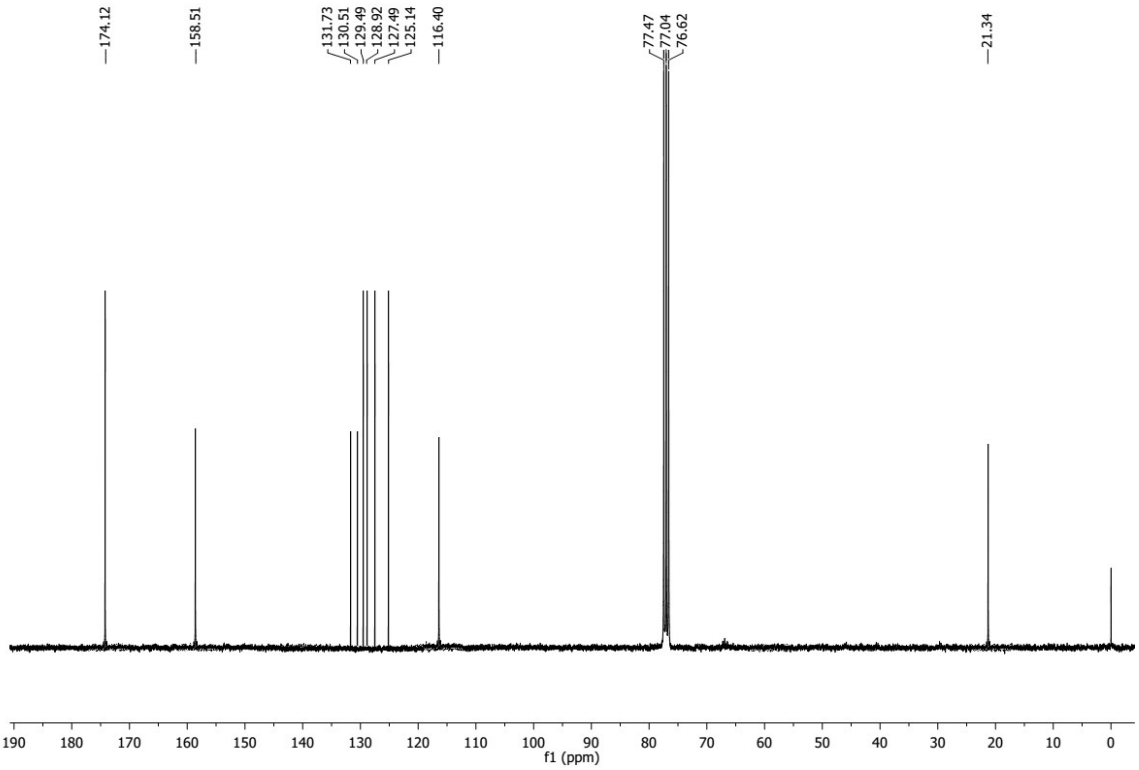

Figure S_6: ^{13}C NMR of compound **5b**

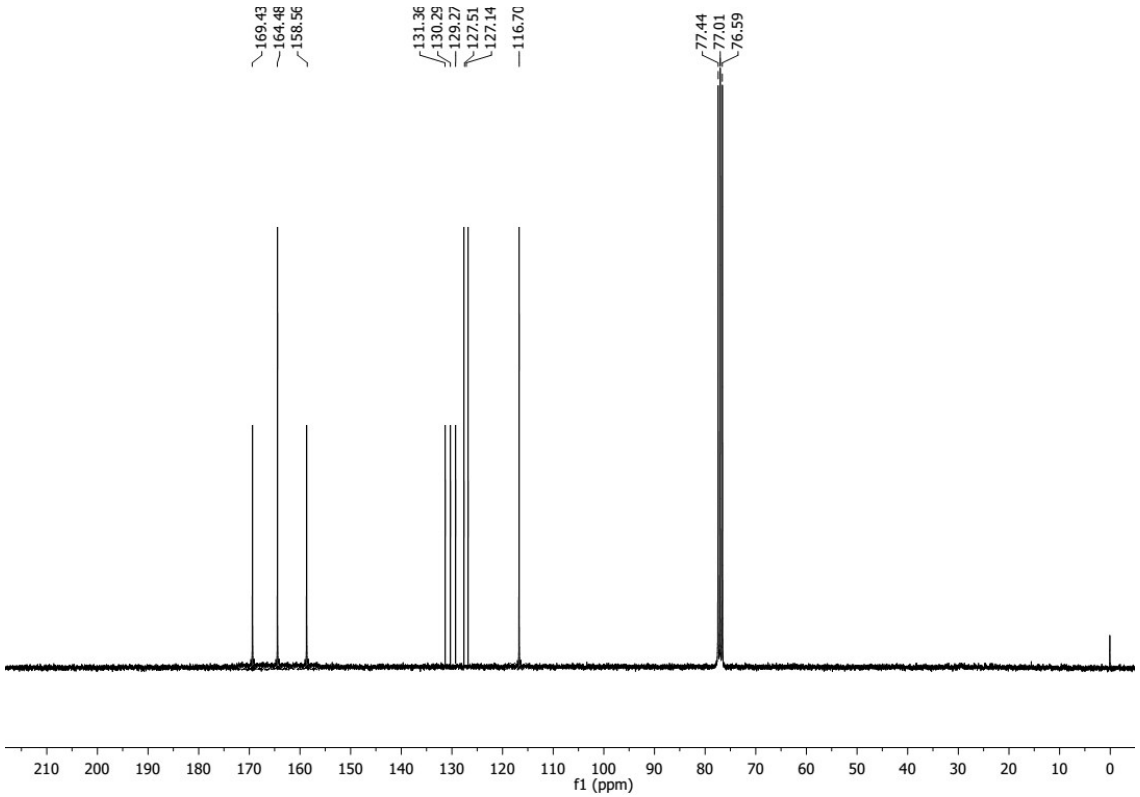

Figure S_7: ^{13}C NMR of compound **6a**

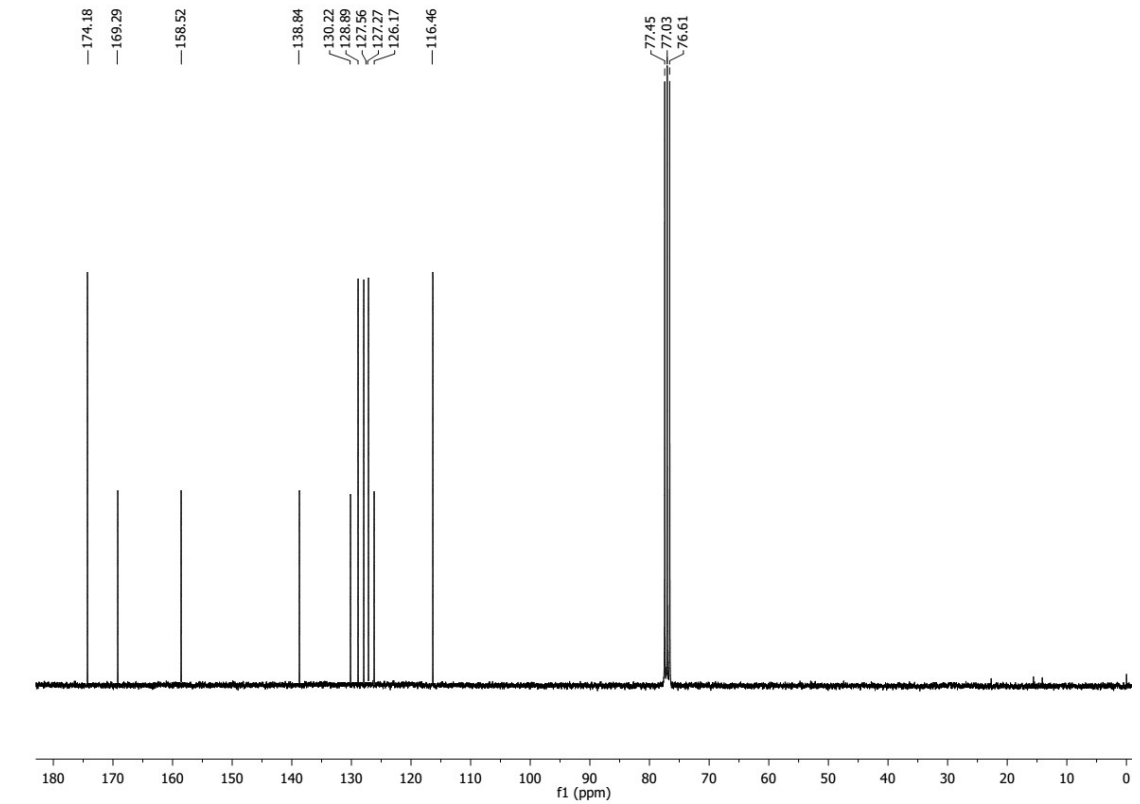

Figure S_8: ^{13}C NMR of compound **6b**

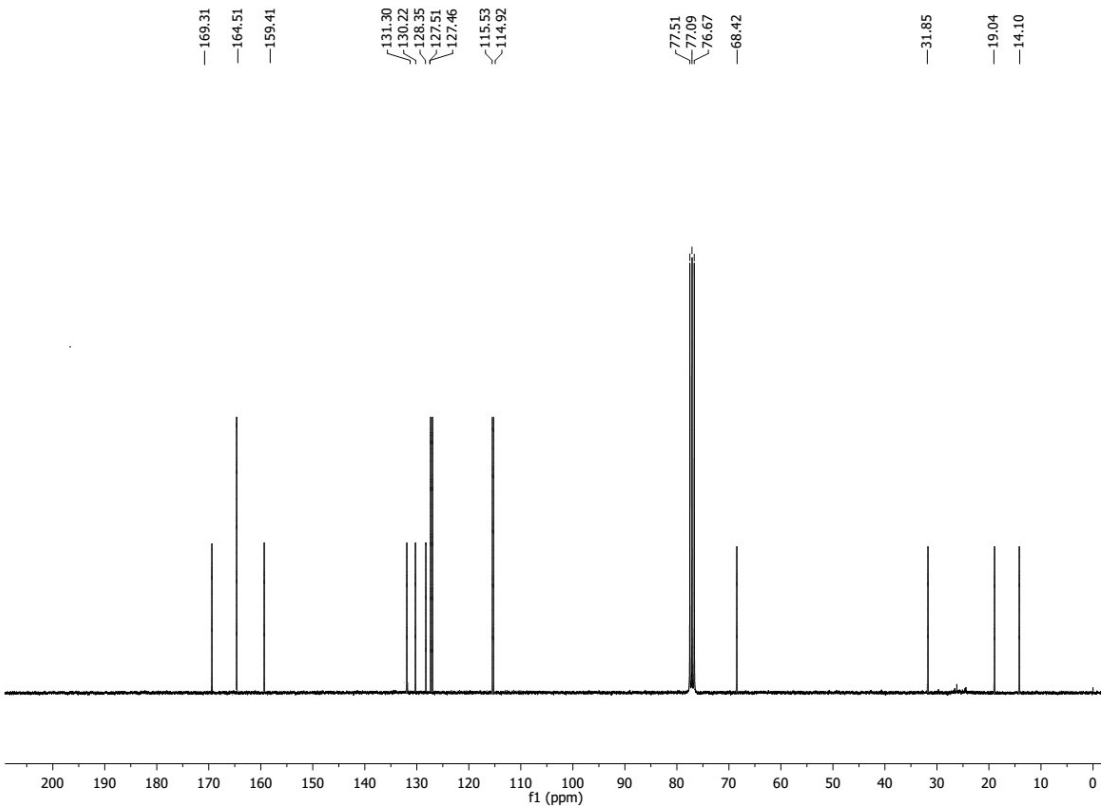

Figure S_9: ^{13}C NMR of compound **7a**

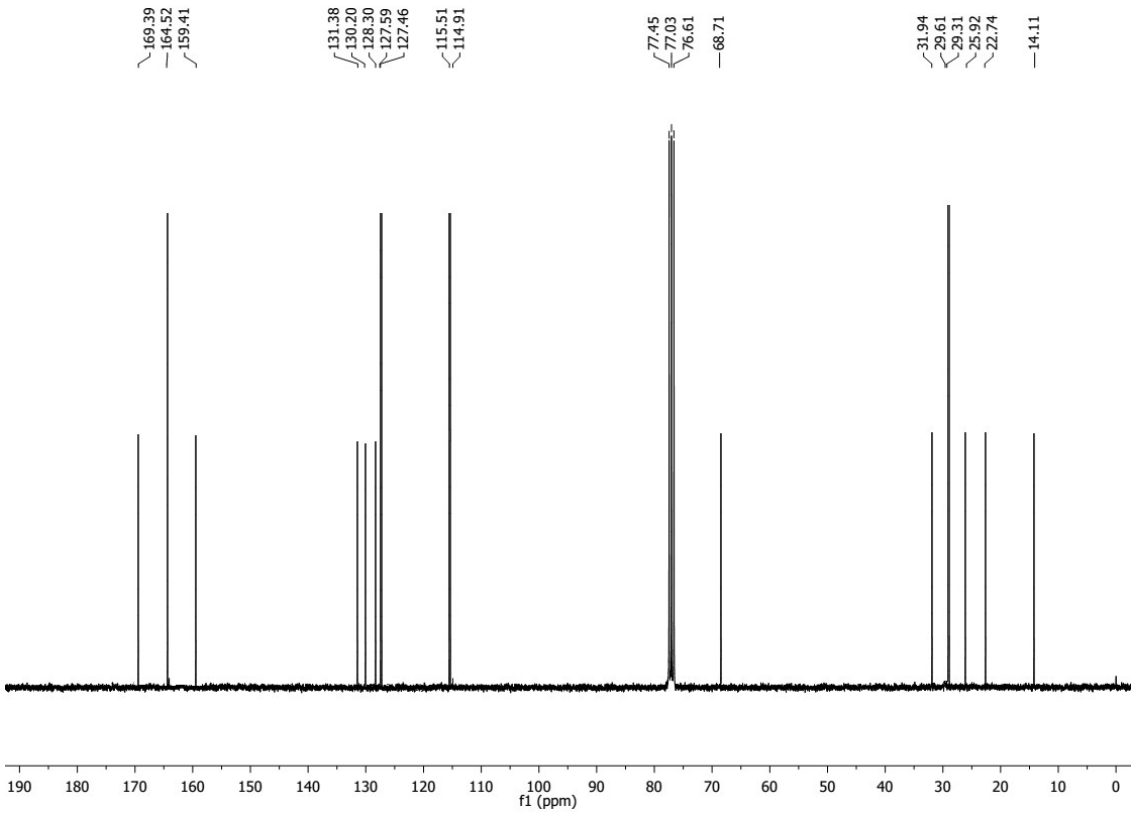

Figure S_{10}: ^{13}C NMR of compound **7b**

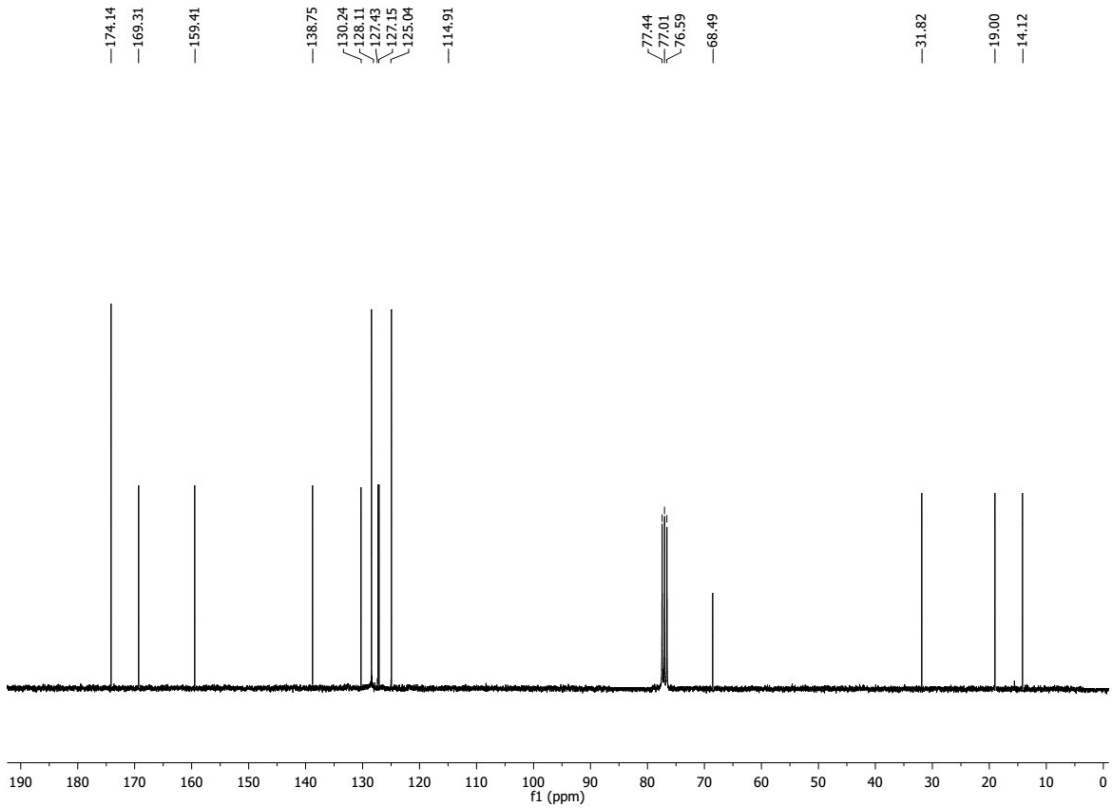

Figure S_{11}: ^{13}C NMR of compound **7c**

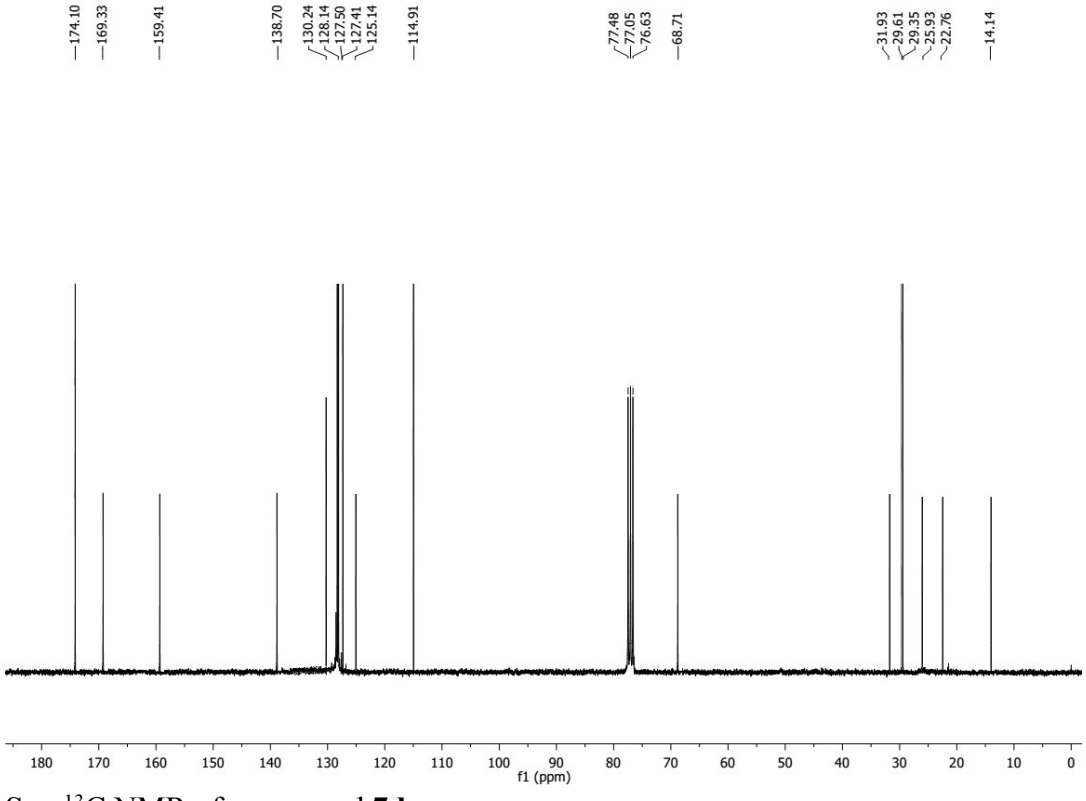

Figure S_{12}: ^{13}C NMR of compound **7d**

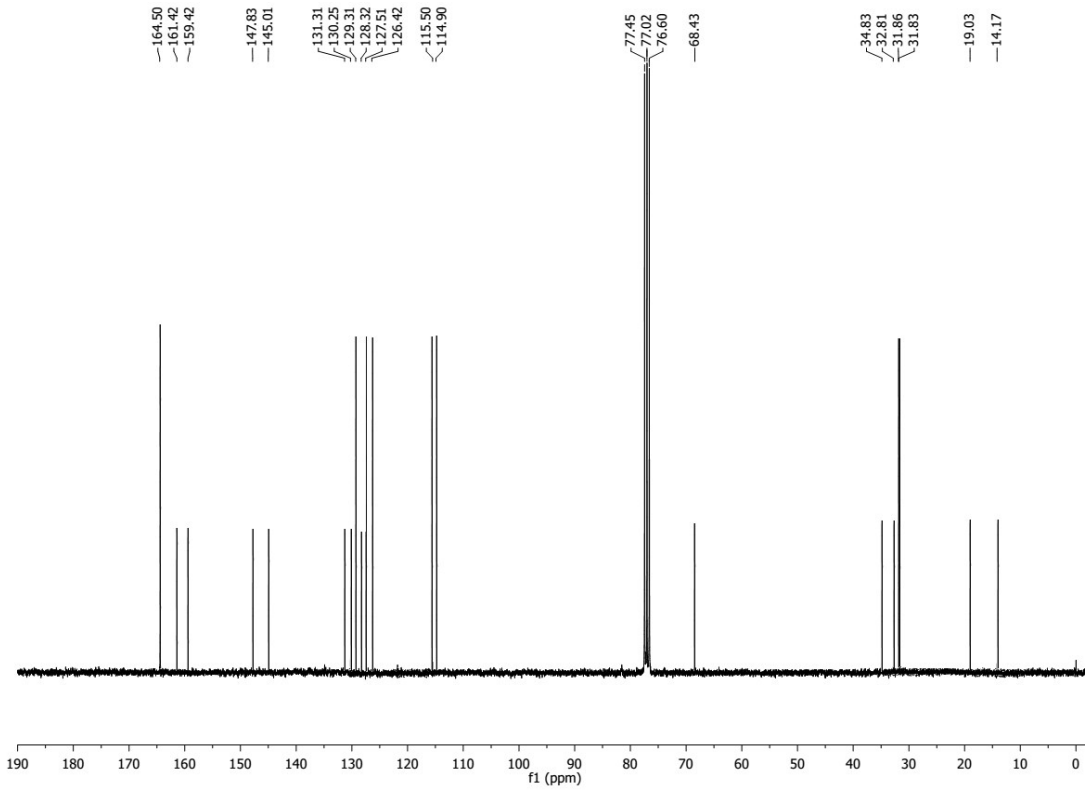

Figure S_{13}: ^{13}C NMR of compound **10a**

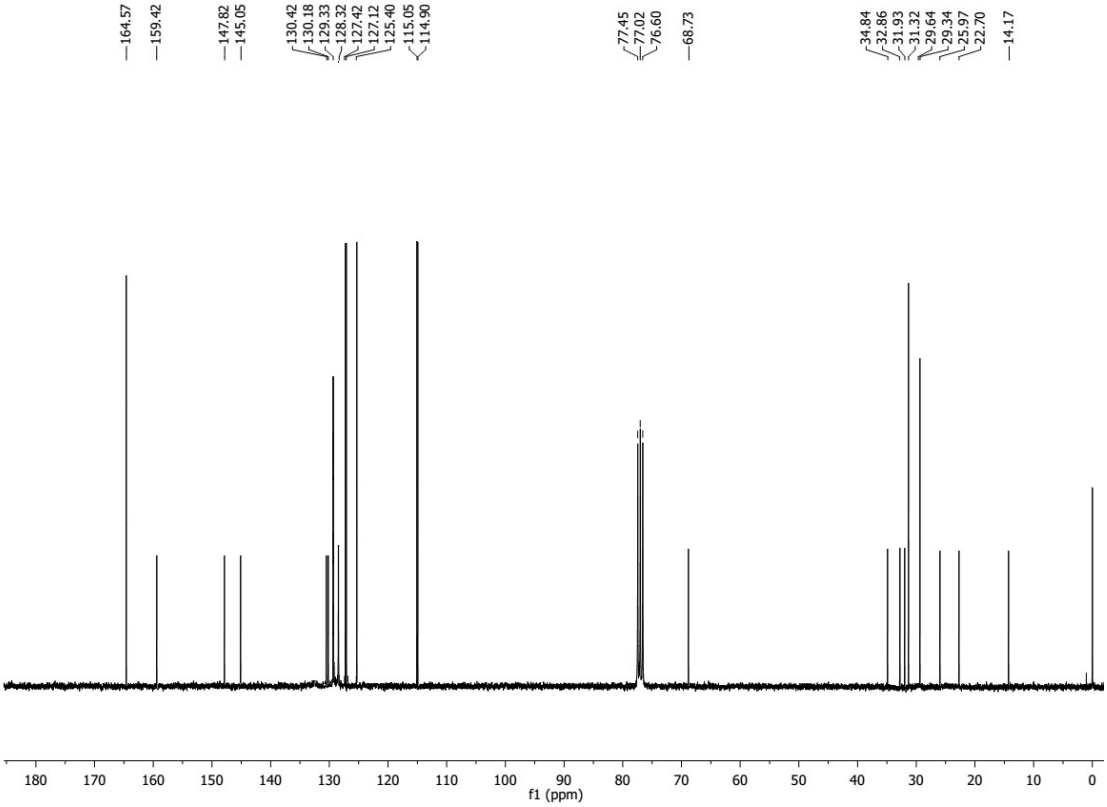

Figure S_{14}: ^{13}C NMR of compound **10b**

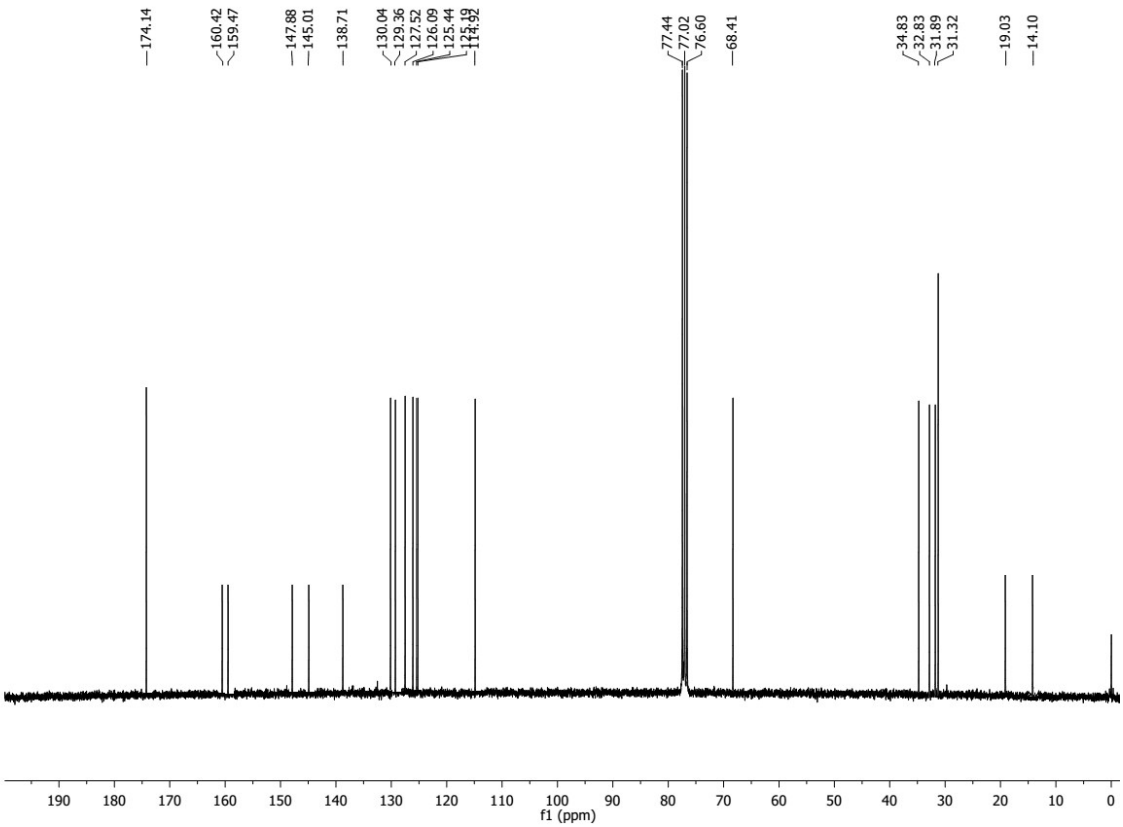

Figure S_{15}: ^{13}C NMR of compound **10c**

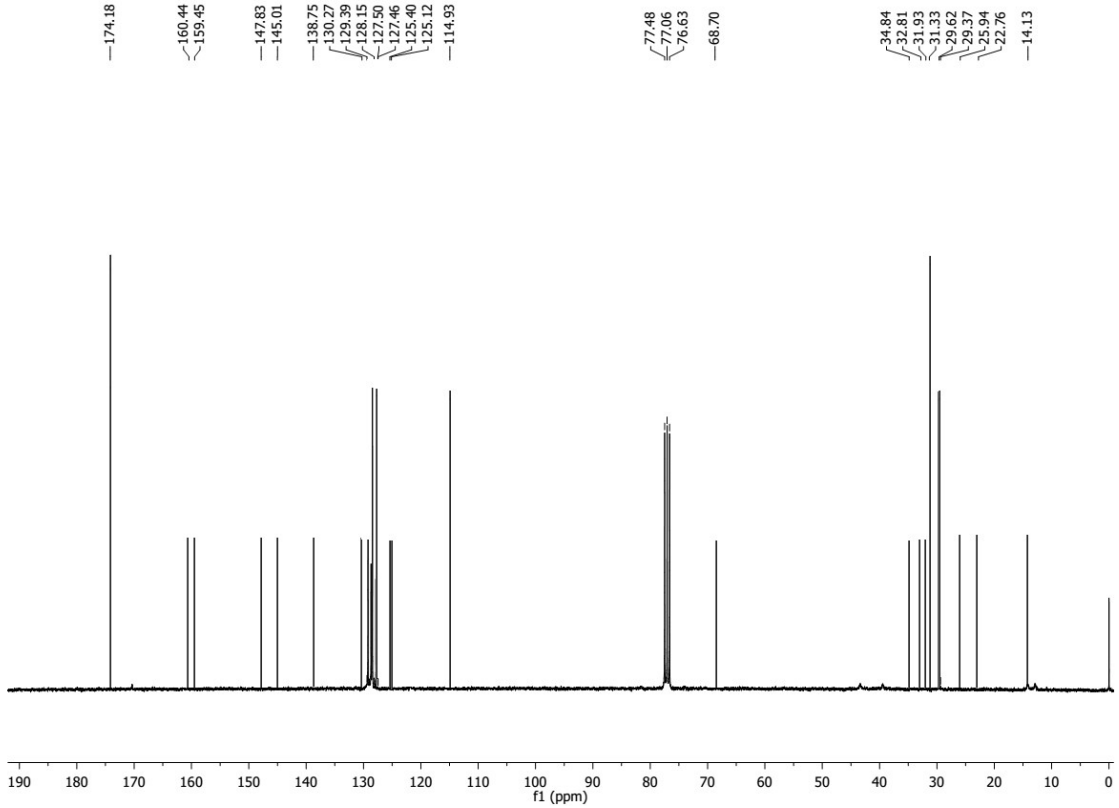

Figure S_{16}: ^{13}C NMR of compound **10d**

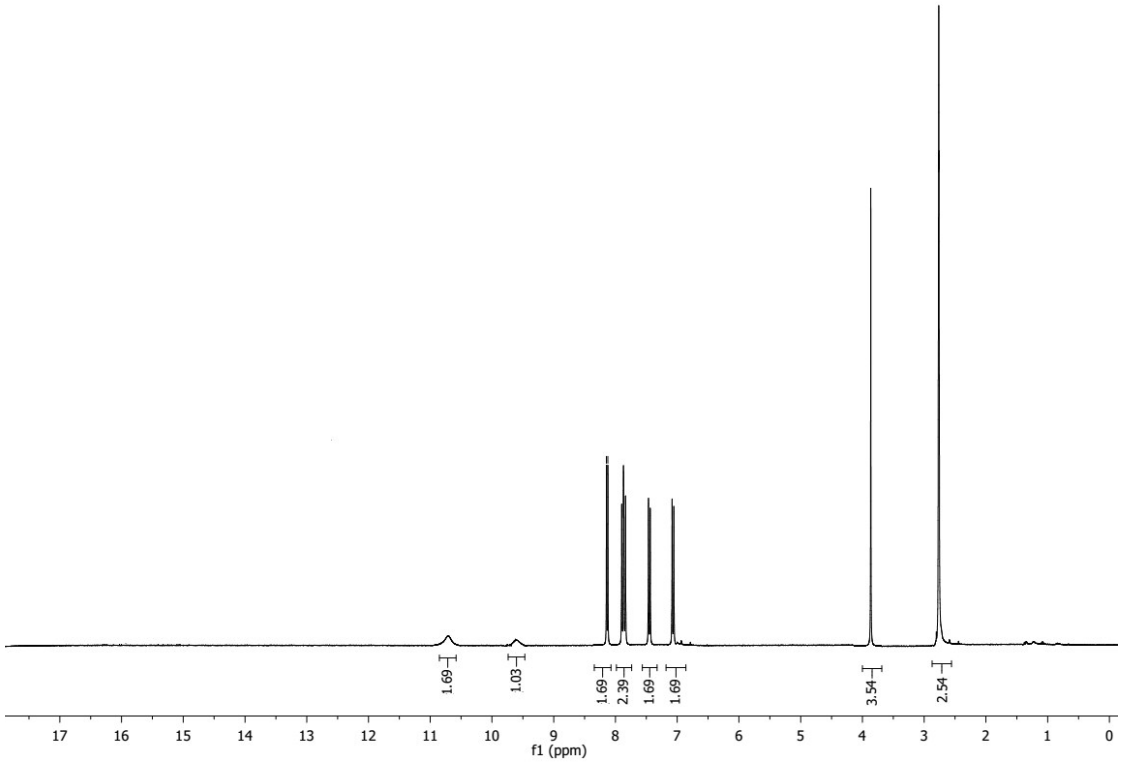

Figure S_{17}: ^{1}H NMR of compound **3**

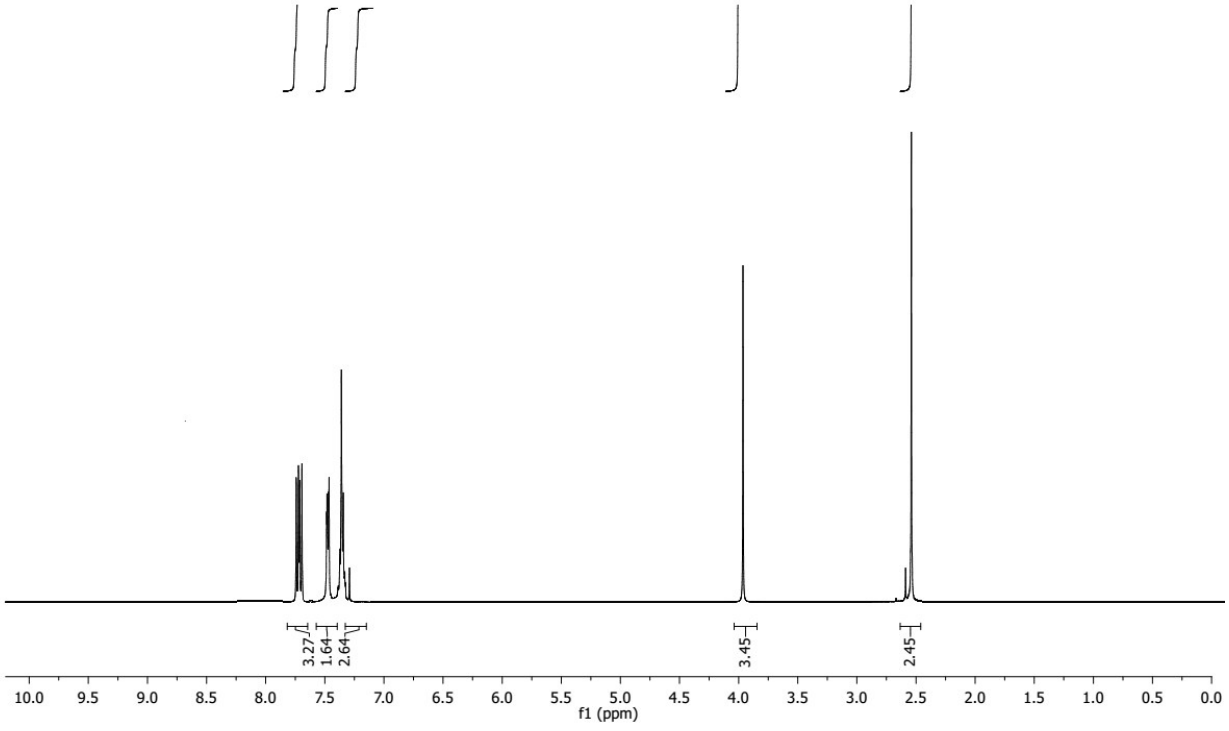

Figure S_{18}: ^{1}H NMR of compound **4a**

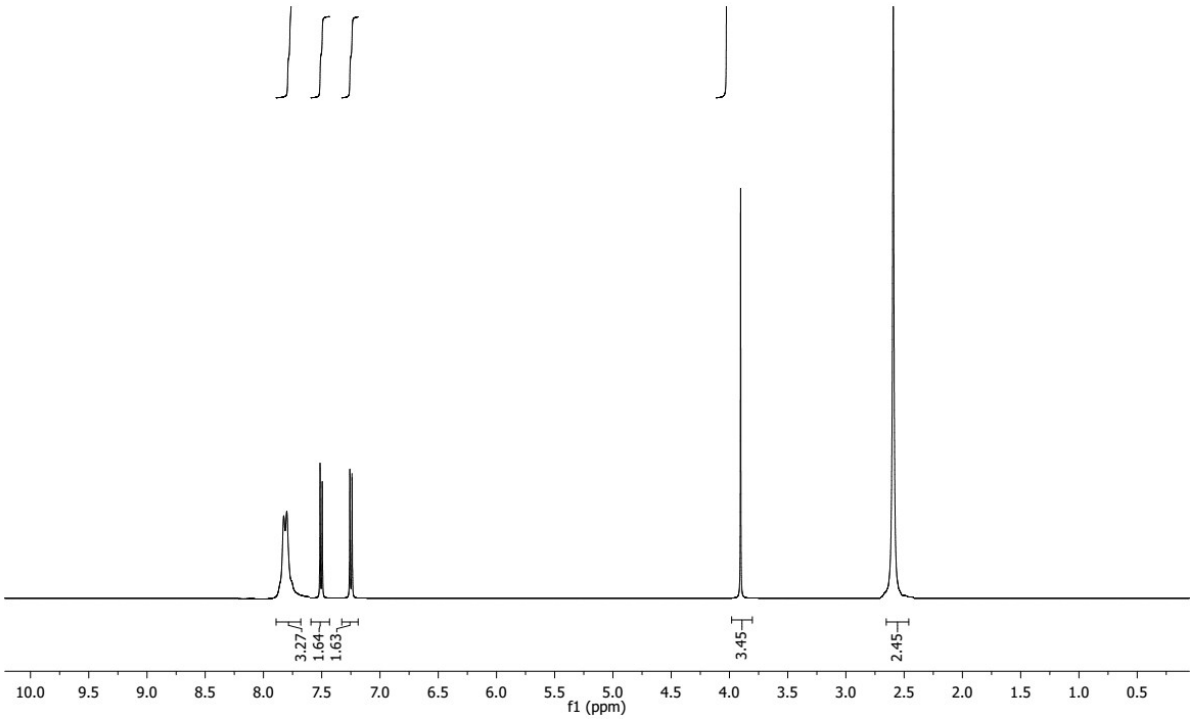

Figure S_{19}: ^{1}H NMR of compound **4b**

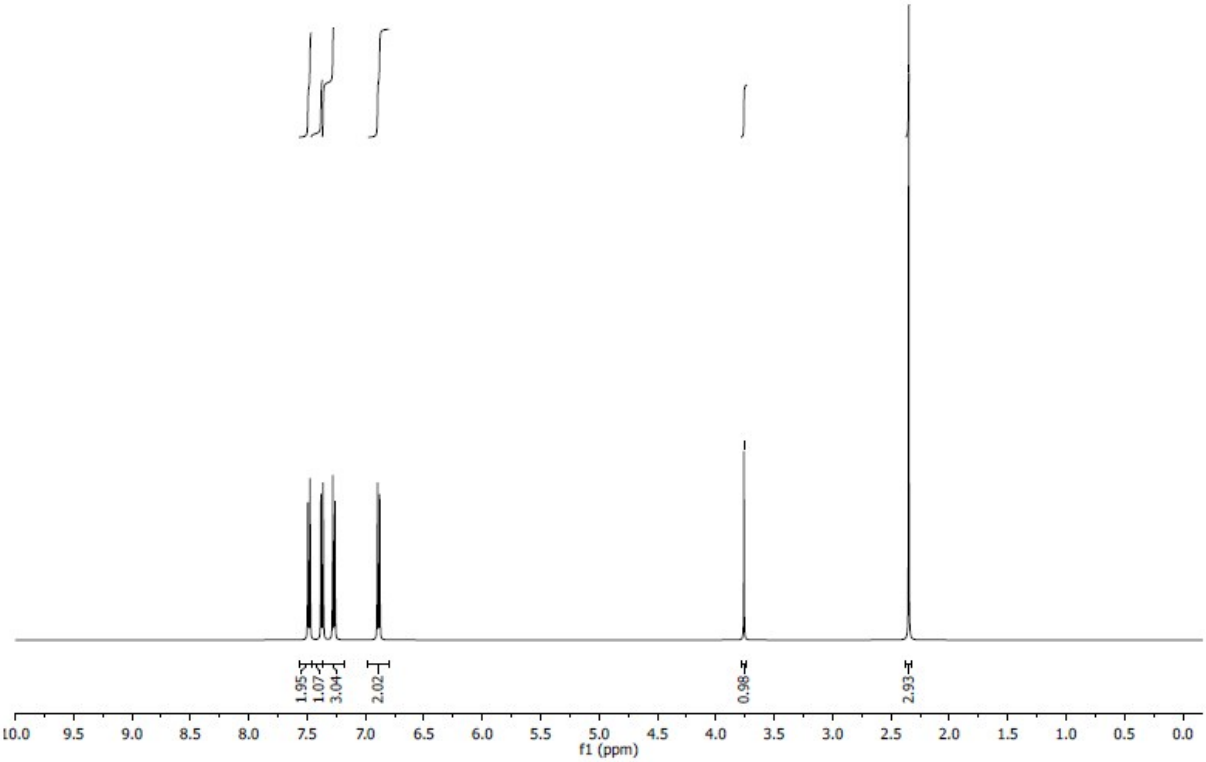

Figure S_{20}: ^{1}H NMR of compound **5a**

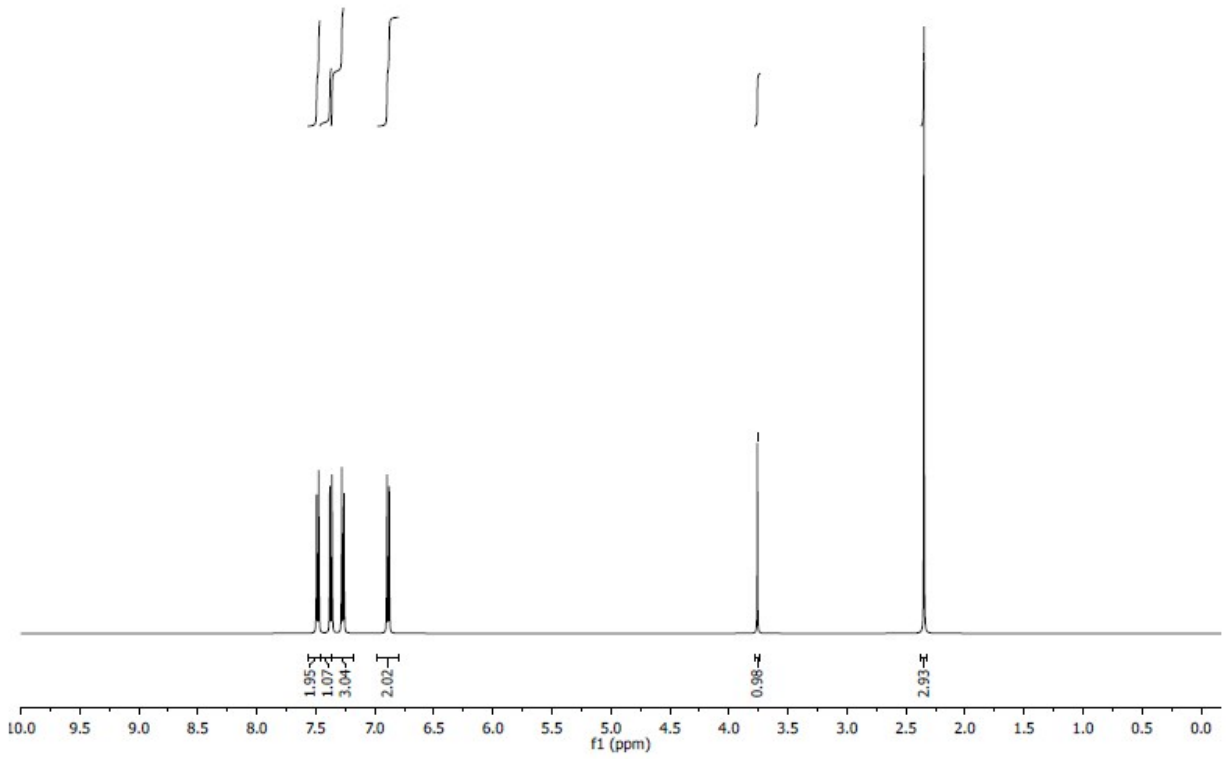

Figure S_{21}: ^{1}H NMR of compound **5b**

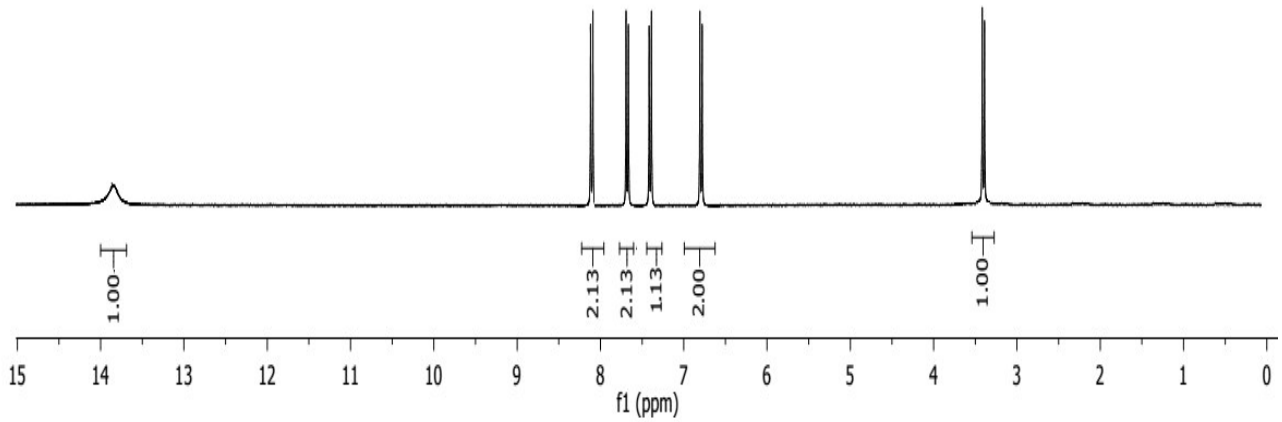

Figure S_{22}: ^{1}H NMR of compound **6a**

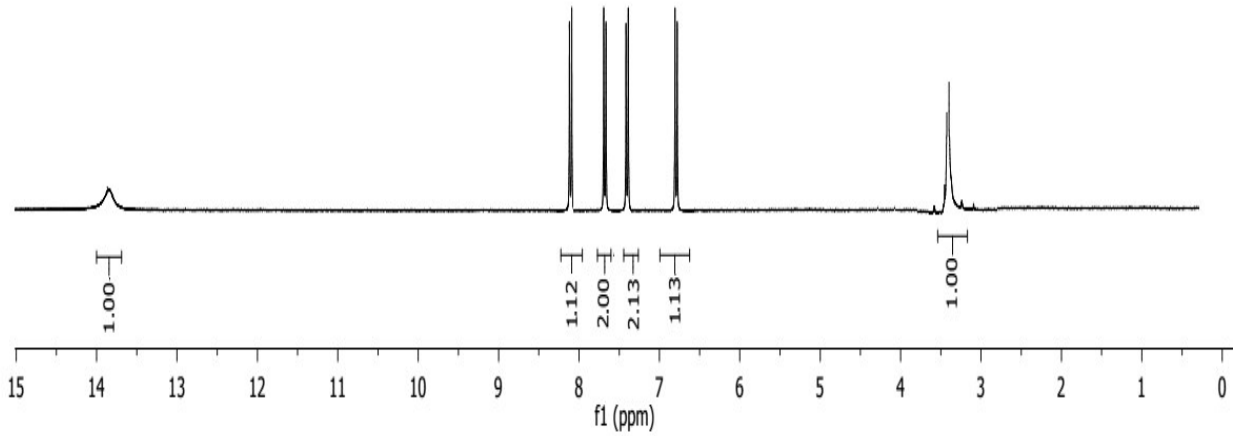

Figure S_{23}: ^{1}H NMR of compound **6b**

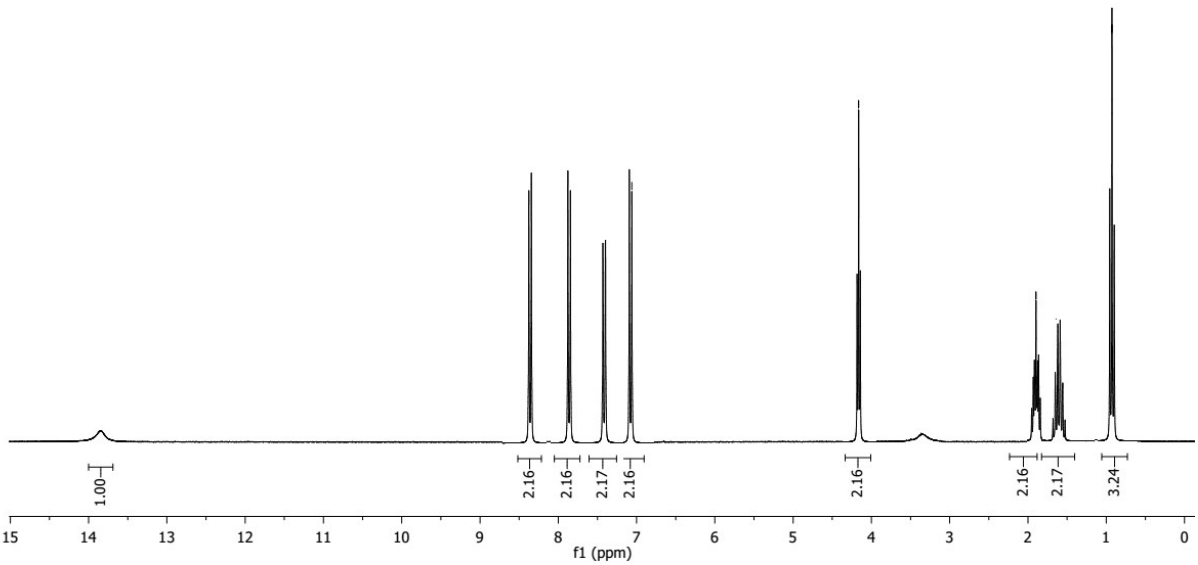

Figure S_{24}: ^{1}H NMR of compound **7a**

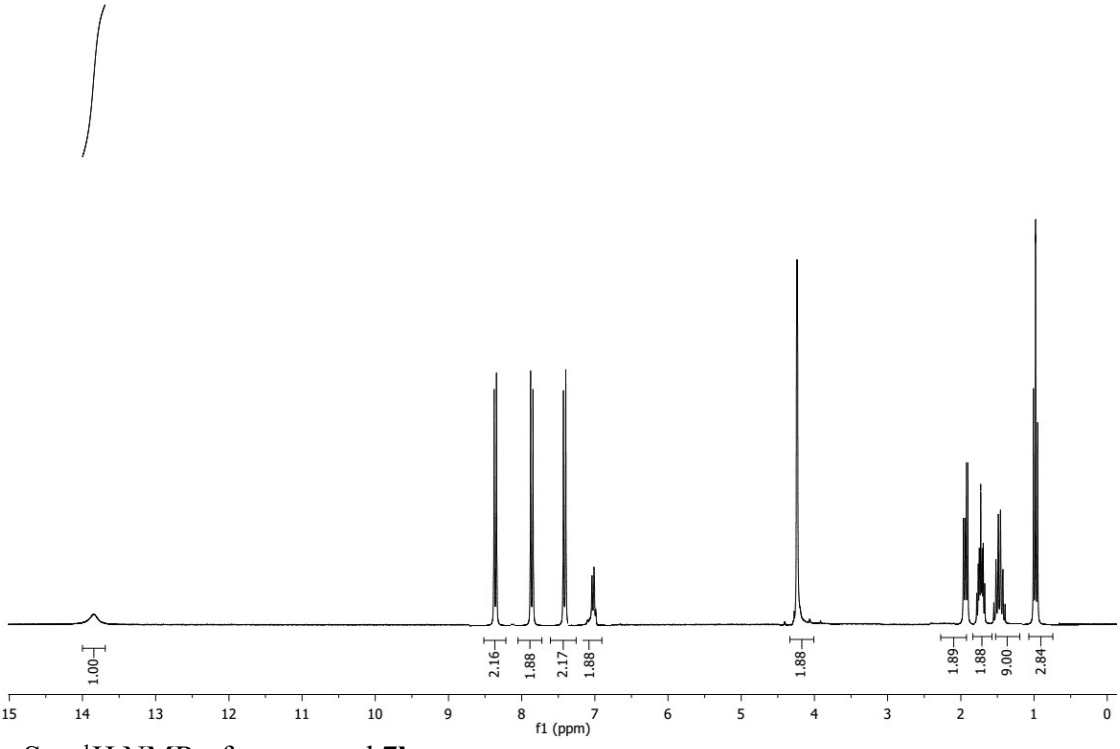

Figure S_{25}: ^{1}H NMR of compound **7b**

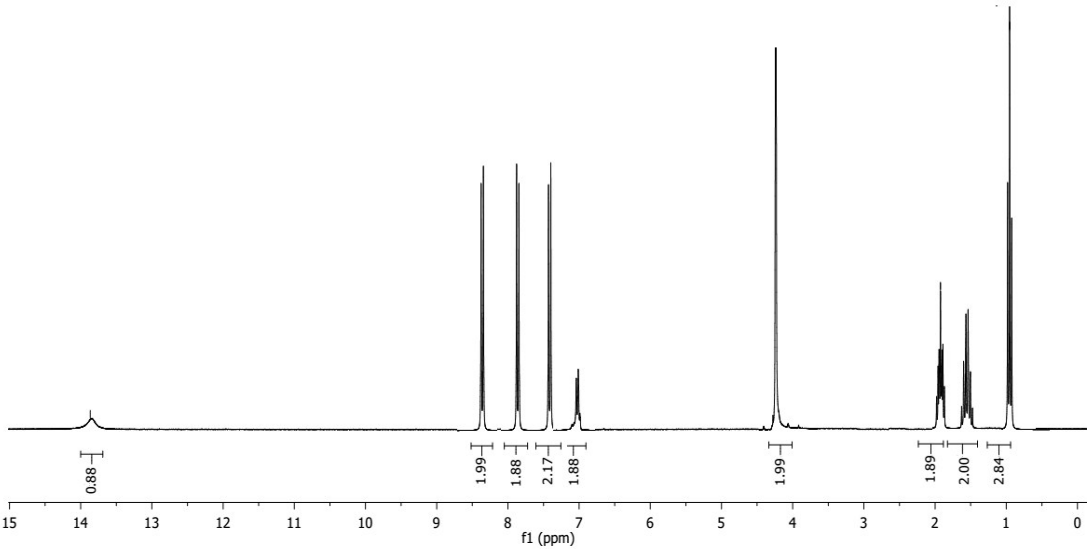

Figure S_{26}: ^{1}H NMR of compound **7c**

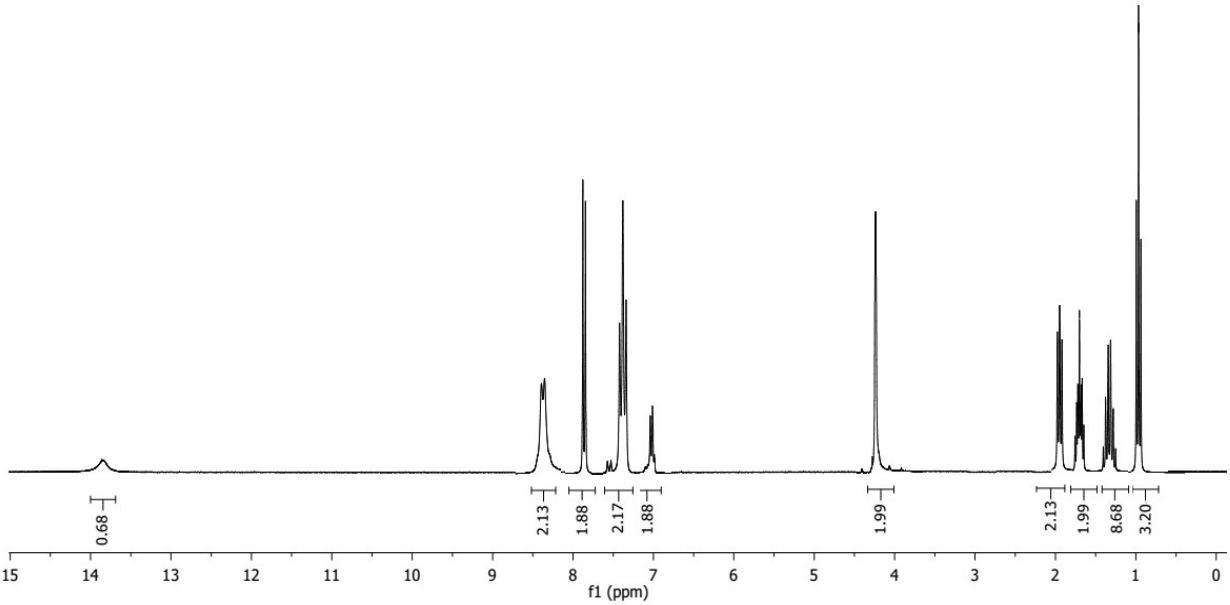

Figure S_{27}: ^{1}H NMR of compound **7d**

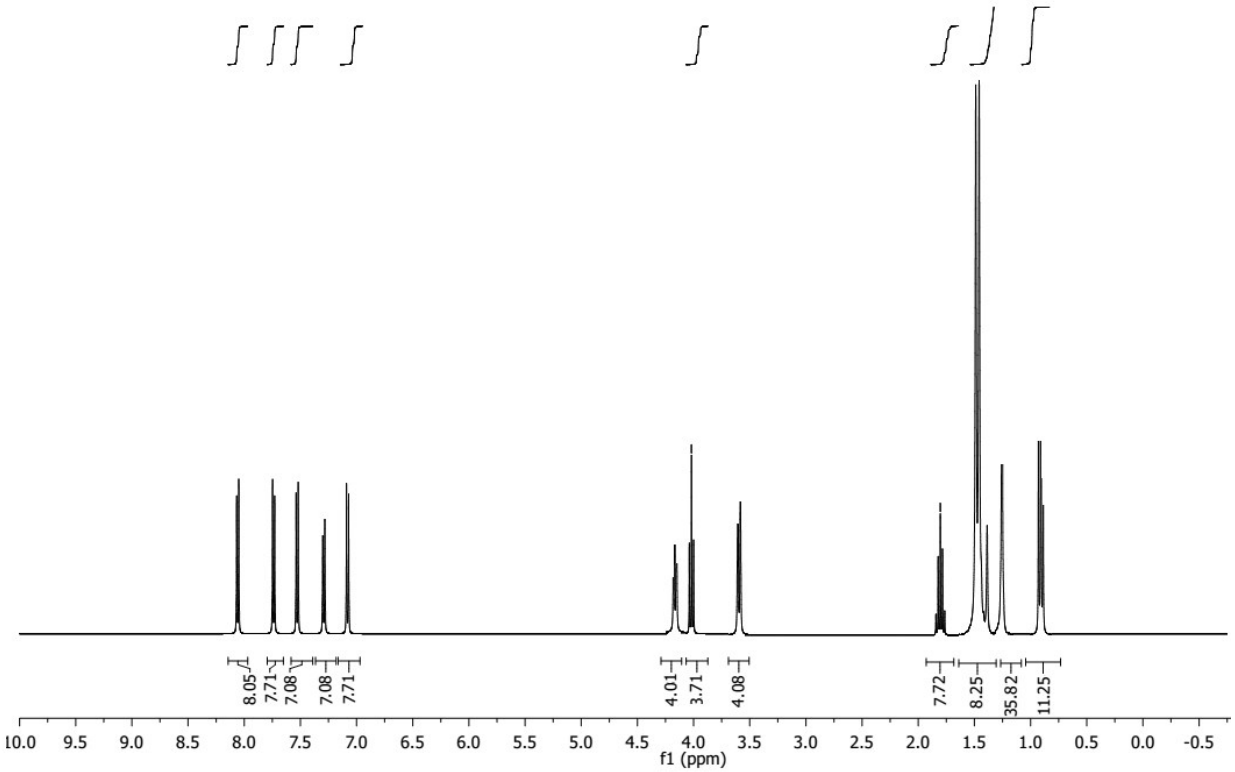

Figure S_{28}: ^{1}H NMR of compound **10a**

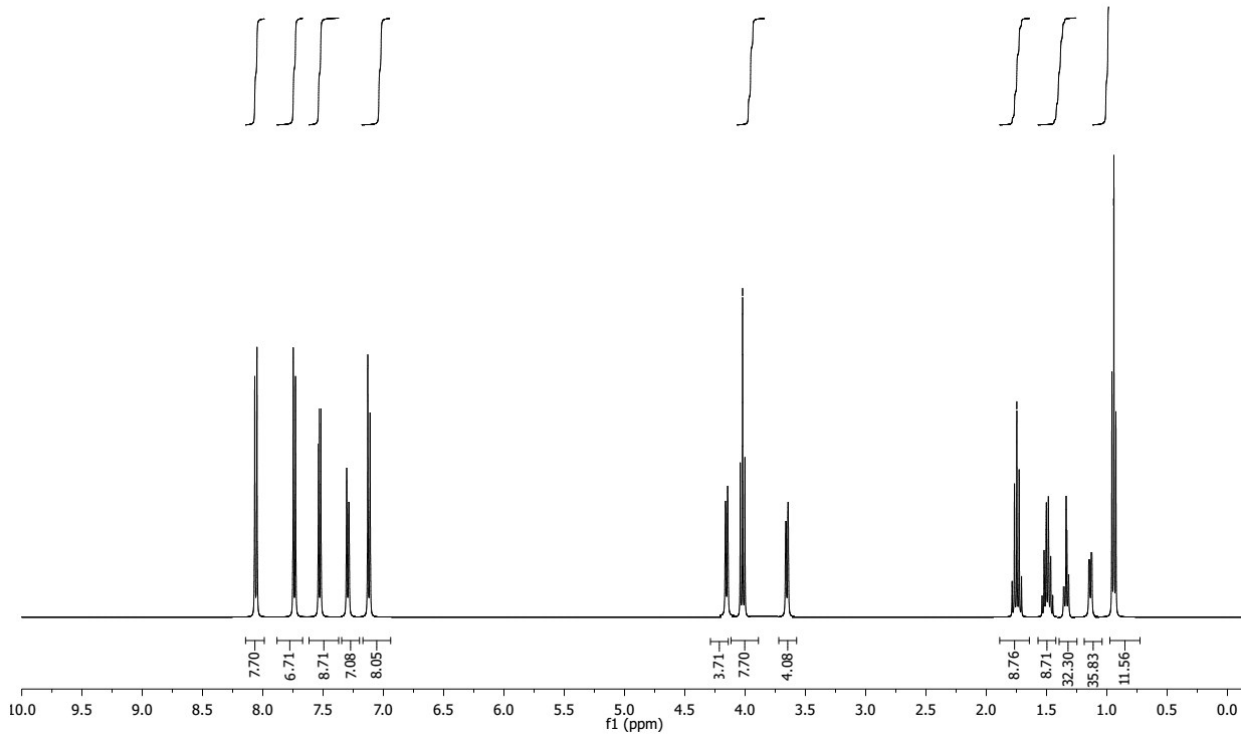

Figure S_{29}: ^{1}H NMR of compound **10b**

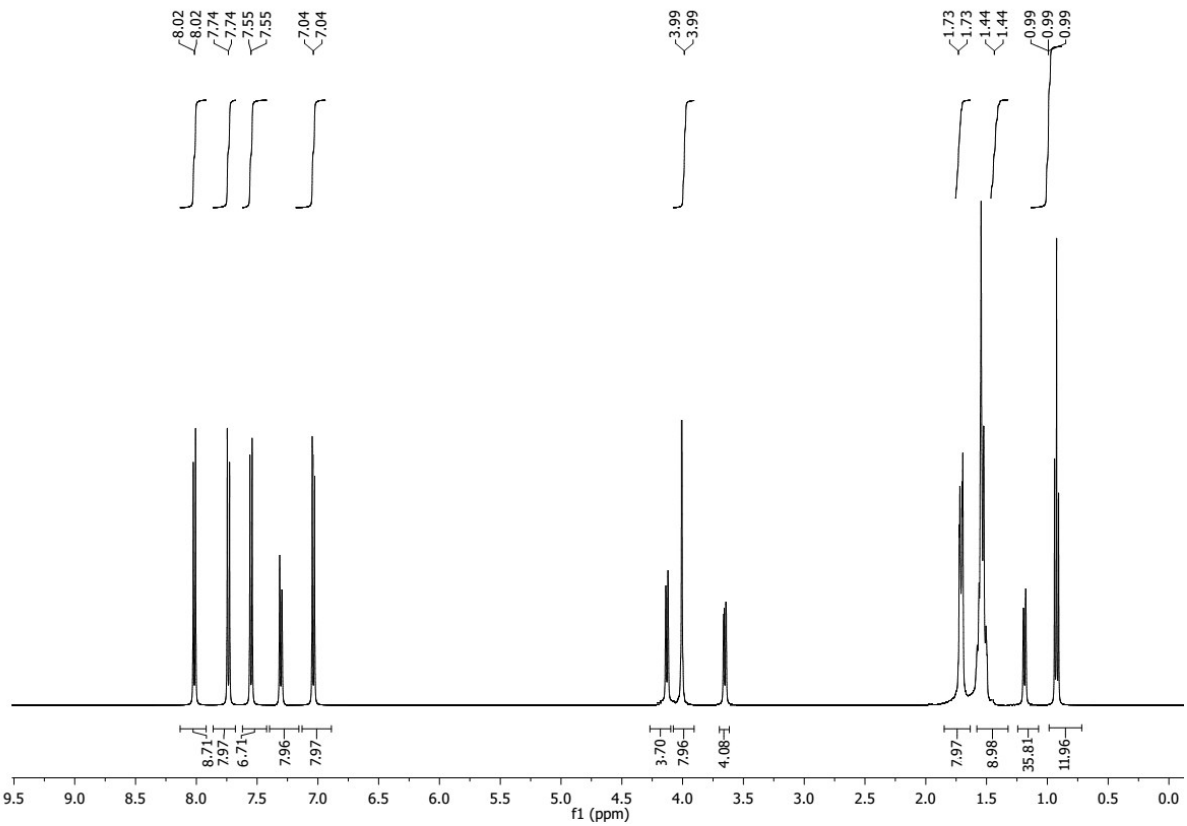

Figure S_{30}: ^{1}H NMR of compound **10c**

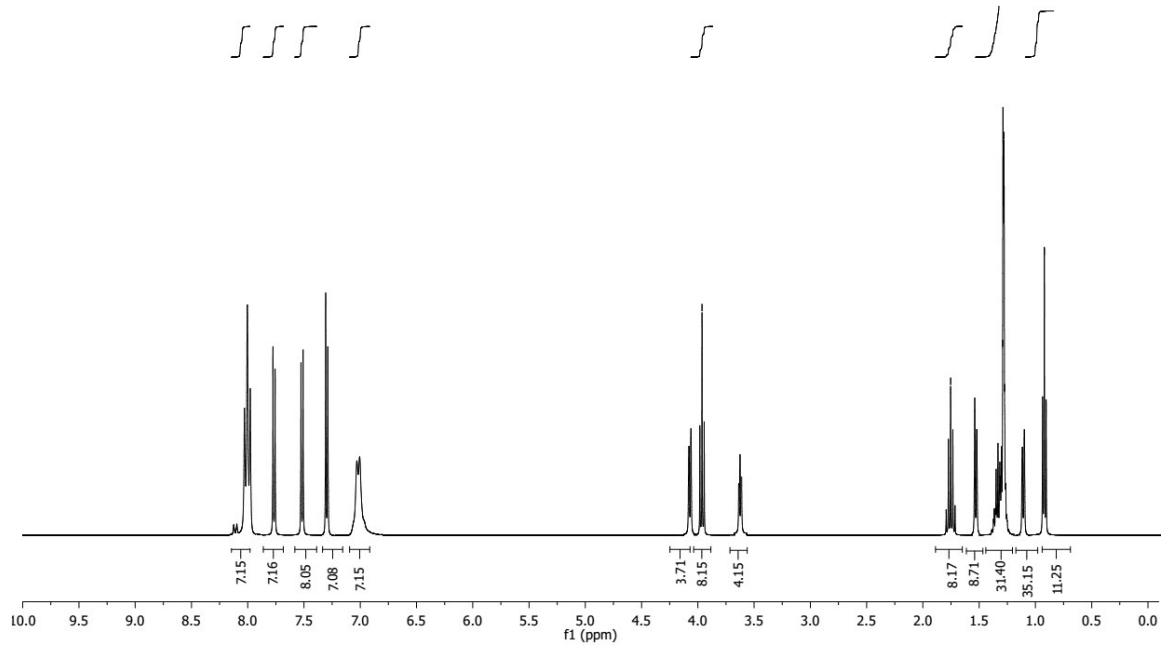

Figure S_{31}: ^{1}H NMR of compound **10**

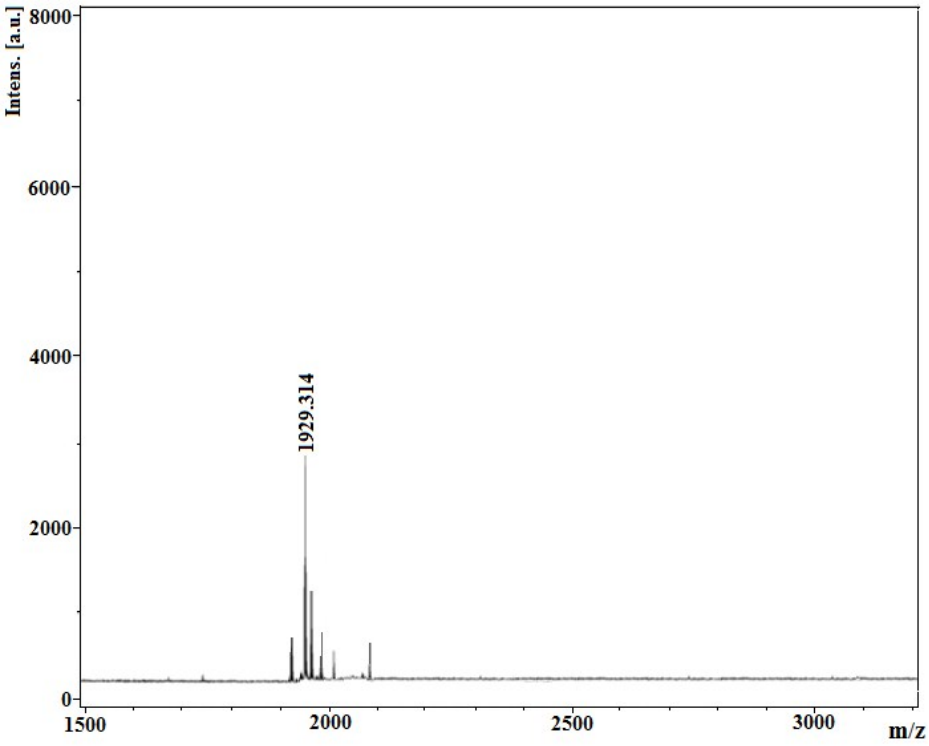

Figure S_{32}: MALDI-TOF mass spectra of compound 10a.

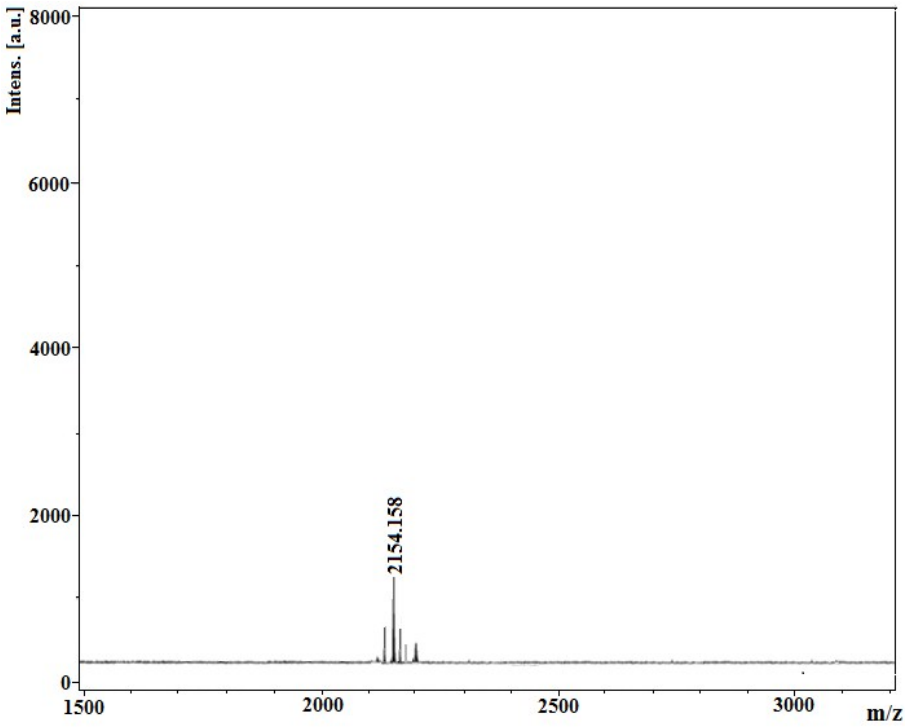

Figure S_{33}: MALDI-TOF mass spectra of compound 10b.

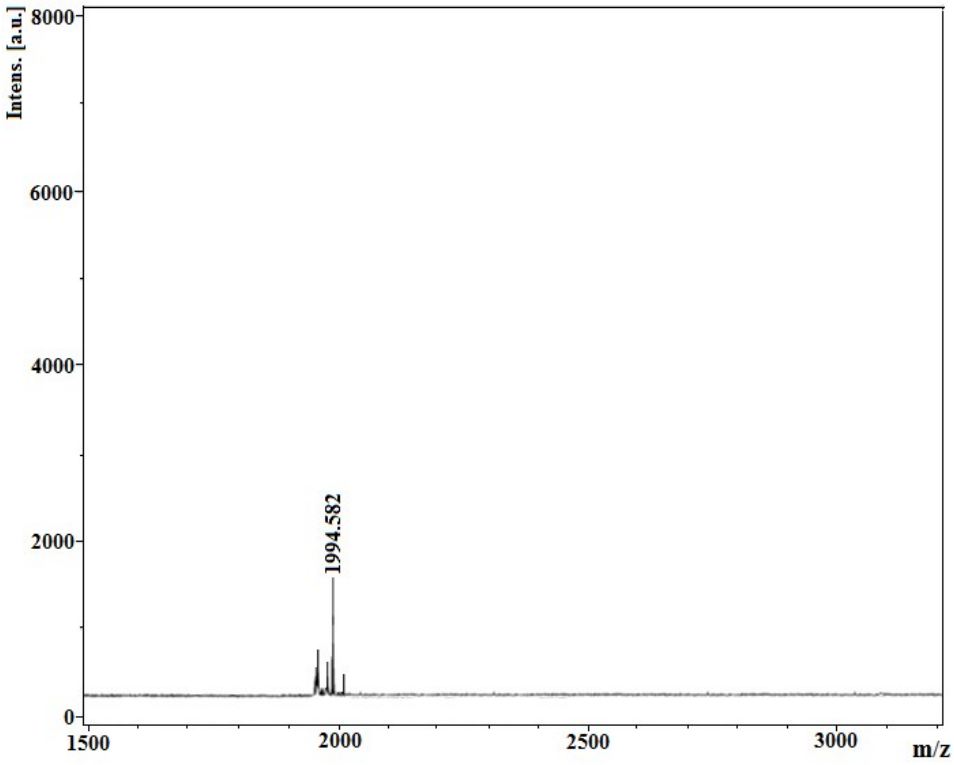

Figure S_{34}: MALDI-TOF mass spectra of compound 10c.

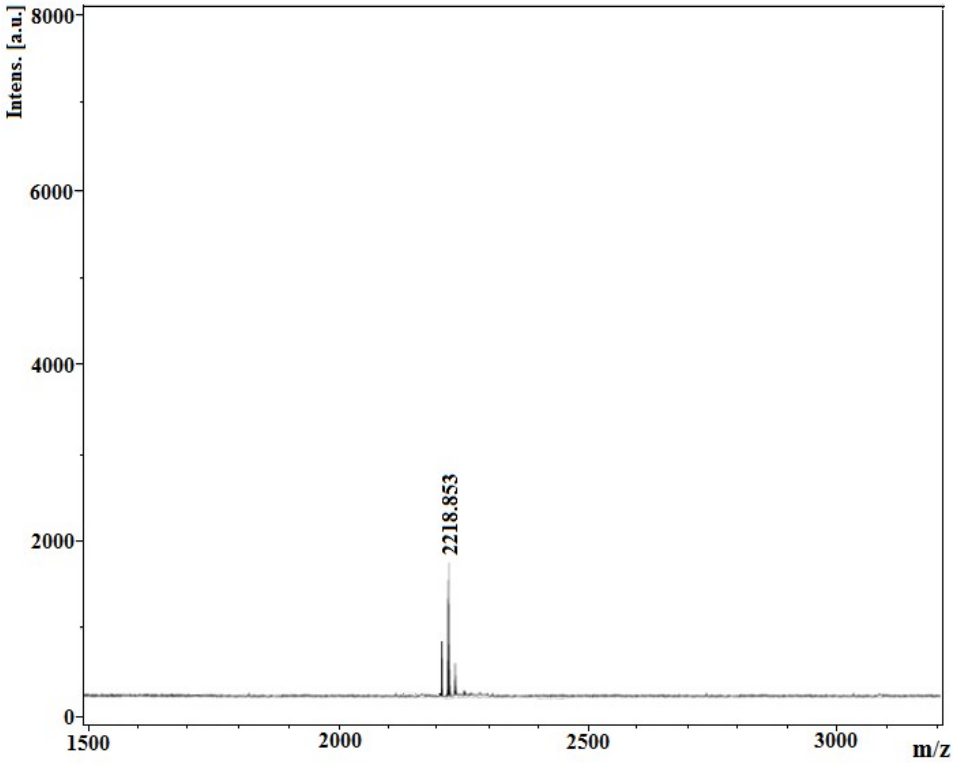

Figure S_{35}: MALDI-TOF mass spectra of compound 10d.

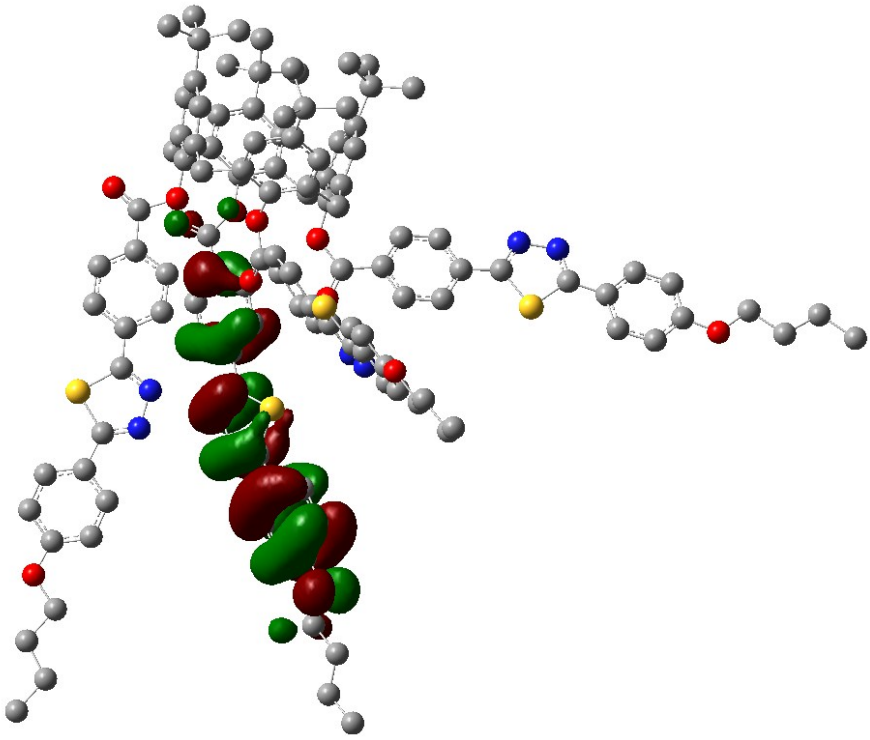

Figure S_{36}: The HOMO energy levels of compound **10c** obtained from DFT calculation at the B3LYP/3-21G* level. Hydrogen atoms were omitted for clarity.

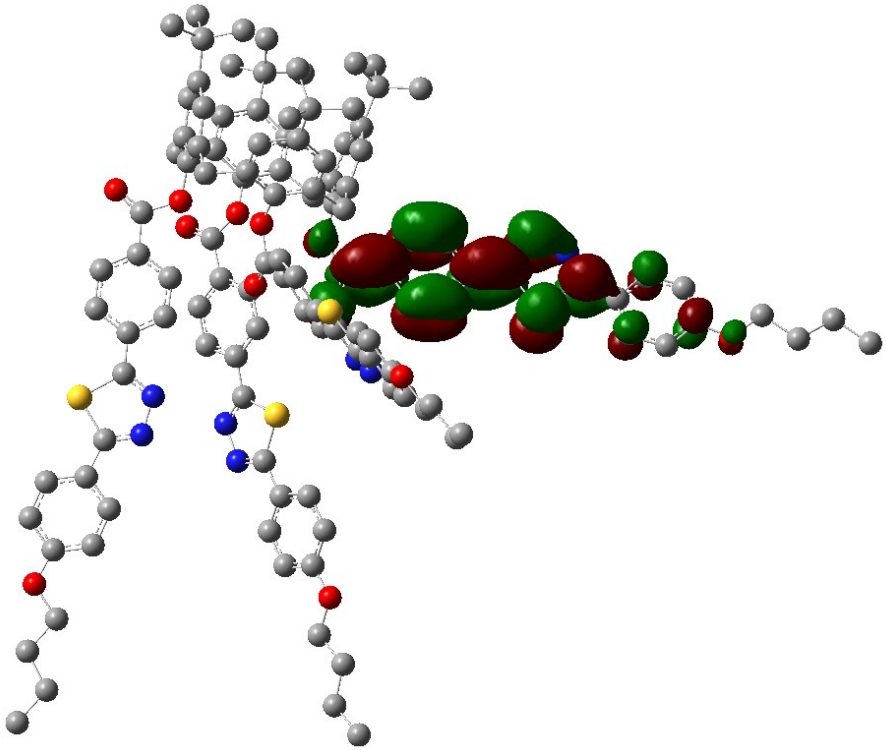

Figure S_{37}: The LUMO energy levels of compound **10c** obtained from DFT calculation at the B3LYP/3-21G* level. Hydrogen atoms were omitted for clarity.

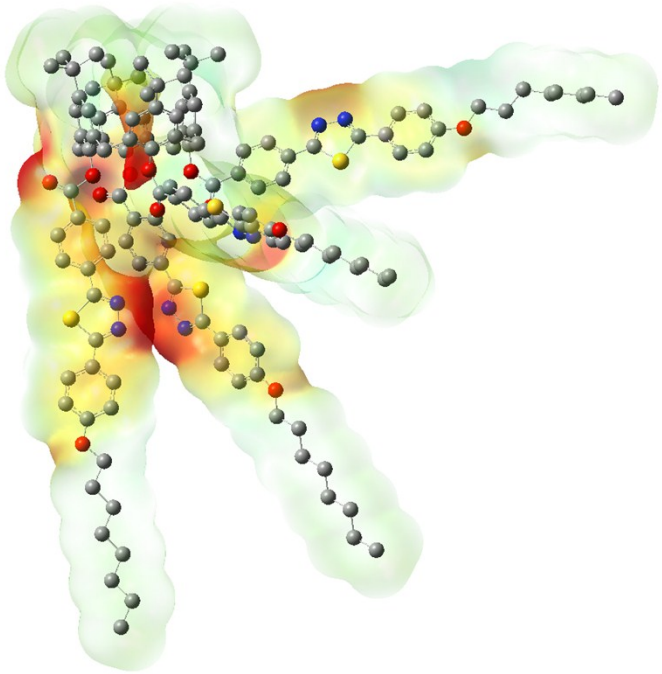

Figure S_{38}: Molecular electrostatic potential (MEP) diagram of compound 10c.

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